Photoswitchable phosphines for light-modulated metal catalysts

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Synopsis

Photoswitchable catalysis has gained increased attention in recent years, driven by the potential to dynamically alter the catalytic behavior of a system between distinct states *in situ*. As a result, it enables precise and reversible light-control over catalytic reactions with spatiotemporal resolution. Existing examples of organo- and metal-based photoswitchable catalysts show the great potential of this approach. While phosphine ligands play a crucial role in the design of transition metal-catalyzed systems due to their ability to complex various metals and modulate the catalytic activity, the utilization of phosphine-based photoswitchable ligands in catalysis remains limited.

Aiming to tackle this challenge, two approaches to obtain photoswitchable phosphine-based catalysts were explored in this doctoral project. On the one hand, the electronic properties of phosphine ligands should be altered through the photoswitching of appended light-responsive dithienylethene (DTE) scaffolds. In particular, electron density modulation on the phosphorus atom of the ligands was pursued by exploiting the intrinsic change in conjugation occurring in the DTE structure upon ring-closing and ring-opening reactions, which should allow switching the communication with the introduced electron-withdrawing groups on and off. On the other hand, it was also attempted to modulate the coordination mode of phosphine ligands to metals through the geometrical changes induced by *Z*/*E* photoisomerization of tethered diazocine photoswitches.

First, the synthesis of DTE- and diazocine-based phosphine ligands was conducted. For the latter, computational calculations were performed to identify the best candidate to accomplish interconversion between mono- to bidentate complexation with bisphosphines anchored to a central diazocine core. Unfortunately, the target compound could not be prepared even though several synthetic routes were considered and new insights in the derivatization of diazocine photoswitches were achieved. In contrast, successful results were obtained for DTE-based ligands, as four different phosphines attached to one or two DTE units could be synthesized. These compounds exhibited a range of interesting features. First, all of them preserved the capacity to photoisomerize between the ring-open and ring-closed states under irradiation, which in the case of the bisDTE ligand resulted in the light-induced conversion between three different possible isomers. Second, a decrease in phosphorus σ-donating ability upon DTE photocyclization was

observed experimentally, while several calculated computational descriptors, including ligand-metal binding energy, confirmed the effect that was amplified for the ligand anchored to two DTE units.

These findings prompted further complexation studies of the obtained ligands, for which the monoDTE phosphines were used to form *trans*-coordinated palladium(II) complexes and the bisDTE ligand was complexed with gold(I). Despite the fact that metal complexation introduced certain hindrance to DTE photoizomerization, reversible light-induced conversion of the prepared metal complexes between ring-open and ring-closed states was demonstrated. Furthermore, the prepared palladium(II) complexes were tested as pre-catalysts for the Stille coupling reaction, revealing higher catalytic performance for the ring-closed state of the complexes - i.e., for the state with decreased σ-electron density at the phosphorus atom of the ligands. In addition, the catalytic enhancement was dependent on the strength of the electron-withdrawing substituent introduced to the DTE photoswitches as a modulating group. Finally, this behavior was rationalized by elucidating the catalytic cycle of the reaction through DFT calculations, revealing lower energy barriers for species containing ring-closed ligands.

Overall, this work contributes to the rapidly advancing field of photoswitchable homogeneous catalysis, presenting new strategies for catalyst light-modulation and providing insights into the molecular design, photochemical behavior, and catalytic performance of such systems.

Zusammenfassung

Die photoschaltbare Katalyse hat in den letzten Jahren zunehmend an Aufmerksamkeit gewonnen, da sie die Möglichkeit bietet, das Verhalten eines katalytischen Systems *in situ* dynamisch zwischen verschiedenen Zuständen zu verändern. Dadurch ist eine präzise und reversible Lichtsteuerung katalytischer Reaktionen in hoher räumlicher und zeitlicher Auflösung möglich. Eine Vielzahl von Publikation über photoschaltbare Katalysatoren auf Organo- und Metallbasis sind ein Beweis für das große Potenzial, das dieser Ansatz bietet. Während Phosphanliganden aufgrund ihrer Fähigkeit, verschiedene Metalle zu komplexieren und deren katalytische Aktivität zu modulieren, eine entscheidende Rolle bei der Entwicklung von übergangsmetallkatalysierten Systemen spielen, ist ihr Einsatz im Bereich photoschaltbarer Liganden noch begrenzt.

Im Rahmen des Promotionsforschungsprojektes wurden daher zwei Ansätze zur Gewinnung photoschaltbarer Katalysatoren auf Phosphanbasis untersucht. Dabei sollten zunächst die elektronischen Eigenschaften von Phosphanliganden durch die Photoschaltung von integrierten lichtempfindlichen Dithienylethen (DTE)-Gerüsten verändert werden. Insbesondere wurde eine Modulation der Elektronendichte am Phosphoratom der Liganden durch eine Veränderung der Konjugation, die in der DTE-Struktur bei Ringschluss- und Ringöffnungsreaktionen auftritt, angestrebt, welche das Ein- und Ausschalten der Kommunikation mit den eingeführten elektronenziehenden Gruppen ermöglichen sollte. Weiterhin sollte die Modulation des

Koordinationsmodus von Phosphanliganden an Metalle durch geometrische Veränderungen, die durch die *Z*/*E*-Photoisomerisierung von Diazocin-Photoschaltern als Rückgrat hervorgerufen wird, untersucht werden.

Zu Beginn des Projektes wurden die Synthesen von Diazocin- und DTE-basierten Phosphanliganden ausgeführt. Um den am besten geeigneten Kandidaten für die Umwandlung von ein- in zweizähnige Bisphosphankomplexe, die an einen zentralen Diazocinkern gebunden sind, zu identifizieren, wurden zunächst Dichtefunktionaltheorieberechnungen (DFT) durchgeführt. Im Labor konnte die gewünschte Diazocin-Zielverbindung jedoch nicht hergestellt werden, obwohl mehrere Synthesewege in Betracht gezogen wurden. Dabei konnten jedoch neue Erkenntnisse über die Derivatisierung von Diazocin-Photoschaltern gewonnen werden. Im Gegensatz dazu wurden erfolgreiche Ergebnisse für DTE-basierte Liganden erzielt. Vier verschiedene Phosphane, die an eine oder zwei DTE-Einheiten gebunden sind, konnten synthetisiert und charakterisiert werden. Diese Verbindungen wiesen eine Reihe interessanter Eigenschaften auf. Unter Lichtbestrahlung behielten sie die Fähigkeit zwischen ringoffenen und ringgeschlossenen Zuständen zu photoisomerisieren, was im Falle des bisDTE-Liganden zu einer lichtinduzierten Umwandlung zwischen drei verschiedenen möglichen Isomeren führte. Weiterhin wurde experimentell eine Abnahme der σ-Donorstärke der Phosphoratome bei der DTE-Photocyclisierung beobachtet. Die DFT-Berechnungen bestätigten diesen Effekt, welcher für den an zwei DTE-Einheiten verankerten Liganden noch verstärkt wurde.

Diesen Ergebnissen folgten weitere Komplexierungsstudien. Die monoDTE-Phosphanliganden konnten zur Bildung von *trans*-koordinierten Palladium(II)-Komplexen verwendet werden. Die bisDTE-Liganden komplexierten erfolgreich Gold(I)-Verbindungen. Obwohl die Metallkomplexierung ein gewisses Hindernis für die DTE-Photoisomerisierung darstellte, konnte eine reversible lichtinduzierte Umwandlung der hergestellten Metallkomplexe zwischen einem ringgeöffneten und einem ringgeschlossenen Zustand nachgewiesen werden. Darüber hinaus wurden die hergestellten Palladium(II)-Komplexe als Präkatalysatoren für eine Stille-Kupplungsreaktion getestet. Dabei zeigte sich eine höhere katalytische Leistung für den ringgeschlossenen Zustand der Komplexe, d. h. für den Zustand mit verringerter σ-Elektronendichte am Phosphoratom der Liganden. Darüber hinaus war die Verbesserung der katalytischen Leistung abhängig von der Stärke des elektronenziehenden Substituenten, der als modulierende Gruppe in die DTE-Photoschalter eingeführt wurde. Schließlich wurde dieses Verhalten durch die Aufklärung des katalytischen Zyklus der Reaktion mit Hilfe von DFT-Berechnungen rationalisiert, wobei niedrigere Energiebarrieren für Spezies mit ringgeschlossenen Liganden festgestellt wurden.

Insgesamt leistet diese Arbeit einen Beitrag zu dem sich rasch entwickelnden Gebiet der photoschaltbaren homogenen Katalyse, indem sie neue Strategien für die Lichtmodulation von Katalysatoren vorstellt und Einblicke in das molekulare Design, das photochemische Verhalten und die katalytische Leistung solcher Systeme gewährt.

Resumen

La catálisis fotoconmutable ha ganado una mayor atención en los últimos años, impulsada por la posibilidad de alterar de forma dinámica e *in situ* el comportamiento catalítico de un sistema entre distintos estados. Como resultado, ésta permite un control preciso y reversible de la luz sobre las reacciones catalíticas con resolución espaciotemporal. Los ejemplos existentes tanto orgánicos como metálicos de catalizadores fotoconmutables demuestran el gran potencial de este enfoque. Los ligandos fosfina desempeñan un papel crucial en el diseño de sistemas catalizados por metales de transición debido a su capacidad para formar complejos con diversos metales y modular la actividad catalítica. Aun así, la utilización de ligandos fotosensibles de tipo fosfina en catálisis sigue siendo limitada.

Con el fin de abordar este reto, en esta tesis se han explorado dos estrategias diferentes para obtener catalizadores fotoconmutables basados en fosfinas. Por un lado, se propuso alterar las propiedades electrónicas de ligandos tipo fosfina mediante su unión a unidades de ditienileteno (DTE), las cuales interconvierten entre un isómero abierto y otro cerrado en respuesta a estímulos lumínicos. En concreto, se planeó llevar a cabo la modulación de la densidad electrónica en el átomo de fósforo de esos ligandos mediante el cambio en la conjugación que se produce en la estructura de los DTE mediante sus reacciones de cierre y apertura de anillo. Esto permitiría activar y desactivar la comunicación de la fosfina con grupos atractores de electrones introducidos en dicha estructura. Por otro lado, también se ha intentado modular el modo de coordinación de los ligandos fosfina a metales, a través de la inducción de un cambio en la geometría de esos ligandos cuando se hallan unidos a fotointerruptores de tipo diazocina capaces de experimentar una fotoisomerización de tipo Z/E.

En primer lugar, se llevó a cabo la síntesis de ligandos de fosfina basados en DTE y diazocina. Para este último caso, se realizaron previamente cálculos computacionales para identificar el mejor candidato para lograr una interconversión en la complejación de metales, pasando de una forma mono a bidentada con bisfosfinas ancladas a un núcleo central de diazocina. Desafortunadamente, el compuesto deseado no se pudo preparar a pesar de que se estudiaron varias rutas sintéticas. Por otro lado, se obtuvieron resultados satisfactorios con los ligandos basados en DTE, ya que se pudieron sintetizar cuatro fosfinas diferentes unidas a una o dos unidades de DTE. Estos compuestos presentaron una serie de características interesantes. En primer lugar, todos ellos conservaron la capacidad de fotoisomerizar bajo irradiación entre sus estados abierto y cerrado, lo que en el caso del ligando bisDTE dio lugar a la conversión inducida por luz entre tres posibles isómeros diferentes. En segundo lugar, se observó experimentalmente una disminución de la capacidad σ-donadora del átomo de fósforo de la fosfina tras la fotociclización del DTE, mientras que varios descriptores computacionales calculados (incluida la energía de unión ligando-metal) confirmaron ese efecto, que se amplificó para el ligando anclado a dos unidades DTE.

Estos resultados dieron lugar a nuevos estudios de complejación de los ligandos obtenidos, donde se utilizaron las fosfinas monoDTE para formar complejos *trans* de paladio(II), y el ligando bisDTE para preparar complejos de oro(I). A pesar de que la complejación a los precursores metálicos disminuyó la eficiencia de fotoizomerización de las unidades de DTE, se pudo demostrar la conversión reversible de los complejos preparados entre los estados de abierto y cerrado del sistema mediante el uso de luz. Además, los complejos de paladio(II) preparados fueron probados como pre-catalizadores para la reacción de acoplamiento de Stille, observándose un mayor rendimiento catalítico para el estado cerrado de los complejos; es decir, para el estado con menor densidad electrónica σ en el átomo de fósforo de los ligandos. Además, la mejora catalítica demostró ser dependiente de la naturaleza del sustituyente aceptor de electrones introducido en los DTE como grupo modulador. Finalmente, este comportamiento se pudo racionalizar mediante la elucidación del ciclo catalítico de la reacción a través de cálculos DFT, determinando barreras energéticas más bajas para las especies que contienen ligandos DTE en su estado cerrado.

En conjunto, este trabajo ha contribuido al avance del conocimiento en el campo de la catálisis homogénea fotoconmutable, desarrollándose nuevas estrategias para la modulación reversible de catalizadores mediante la aplicación de luz y proporcionando información valiosa sobre el diseño molecular, el comportamiento fotoquímico y el rendimiento catalítico de dichos sistemas.

Resum

La catàlisi fotocommutable ha guanyat més atenció en els darrers anys, impulsada per la possibilitat d'alterar de manera dinàmica i in situ el comportament catalític d'un sistema entre diferents estats. Com a resultat, aquesta permet un control precís i reversible de la llum sobre les reaccions catalítiques amb resolució espaciotemporal. Els exemples existents tant orgànics com a metàl·lics de catalitzadors fotocommutables demostren el gran potencial d'aquest enfocament. Els lligands fosfina exerceixen un paper crucial en el disseny de sistemes catalitzats per metalls de transició degut a la seva capacitat per formar complexos amb diversos metalls i modular l'activitat catalítica. Tot i així, la utilització de lligands fotosensibles de tipus fosfina en catàlisi continua sent limitada.

Per abordar aquest repte, en aquesta tesi s'han explorat dues estratègies diferents per obtenir catalitzadors fotocommutables basats en fosfines. D'una banda, es va proposar alterar les propietats electròniques de lligands tipus fosfina mitjançant la seva unió a unitats de ditieniletè (DTE), les quals interconverteixen entre un isòmer obert i un altre tancat en resposta a estímuls lumínics. En concret, es va planejar dur a terme la modulació de la densitat electrònica a l'àtom de fòsfor d'aquests lligands mitjançant el canvi en la conjugació que es produeix a l'estructura dels DTE mitjançant les seves reaccions de tancament i obertura d'anell. Això permetria activar i desactivar la comunicació de la fosfina amb grups atractors delectrons introduïts en aquesta estructura. D'altra banda, també

s'ha intentat modular la manera de coordinació dels lligands fosfina a metalls, a través de la inducció d'un canvi en la geometria dels lligands quan estan units a fotointerruptors de tipus diazocina capaços d'experimentar una fotoisomerització de tipus Z/E.

En primer lloc, es va dur a terme la síntesi de lligands de fosfina basats en DTE i diazocina. Per a aquest últim cas, es van realitzar prèviament càlculs computacionals per identificar el millor candidat per aconseguir una interconversió en la complexació de metalls, passant d'una forma mono a bidentada amb bisfosfines ancorades a un nucli central de diazocina. Desafortunadament, el compost desitjat no es va poder preparar tot i que es van estudiar diverses rutes sintètiques. D'altra banda, es van obtenir resultats satisfactoris amb els lligands basats en DTE, ja que es van poder sintetitzar quatre fosfines diferents unides a una o dues unitats de DTE. Aquests compostos van presentar una sèrie de característiques interessants. En primer lloc, tots ells van conservar la capacitat de fotoisomeritzar sota irradiació entre els seus estats obert i tancat, cosa que en el cas del lligand bisDTE va donar lloc a la conversió induïda per llum entre tres possibles isòmers diferents. En segon lloc, es va observar experimentalment una disminució de la capacitat σ-donadora de l'àtom de fòsfor de la fosfina després de la fotociclització del DTE, mentre que diversos descriptors computacionals calculats (inclosa l'energia d'unió lligant-metall) van confirmar aquest efecte, que va amplificar per al lligand ancorat a dues unitats DTE.

Aquests resultats van donar lloc a nous estudis de complexació dels lligands obtinguts, on es van utilitzar les fosfines monoDTE per formar complexos trans de pal·ladi(II) i el lligand bisDTE per preparar complexos d'or(I). Tot i que la complexació als precursors metàl·lics va disminuir l'eficiència de fotoizomerització de les unitats de DTE, es va poder demostrar la conversió reversible dels complexos preparats entre els estats d'obert i tancat del sistema mitjançant l'ús de llum. A més, els complexos de pal·ladi(II) preparats van ser provats com a pre-catalitzadors per a la reacció d'acoblament de Stille, observant-se un major rendiment catalític per a l'estat tancat dels complexos; és a dir, per a l'estat amb menys densitat electrònica σ a l'àtom de fòsfor dels lligands. A més, la millora catalítica va demostrar ser depenent de la naturalesa del substituent acceptor d'electrons introduït als DTE com a grup modulador. Finalment, aquest comportament es va poder racionalitzar mitjançant l'elucidació del cicle catalític de la reacció a través de càlculs DFT, determinant barreres energètiques més baixes per a les espècies que contenen lligands DTE al seu estat tancat.

En conjunt, aquest treball ha contribuït a l'avenç del coneixement en el camp de la catàlisi homogènia fotocommutable, desenvolupant noves estratègies per a la modulació reversible de catalitzadors mitjançant l'aplicació de llum i proporcionant informació valuosa sobre el disseny molecular, el comportament fotoquímic i el rendiment catalític d'aquests sistemes.

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Chapter 1

Introduction

1. 1. Switchable catalysis

The last century has witnessed enormous progress in the field of homogeneous catalysis, which has led to the development of a large variety of catalytic systems to enhance the reactivity and selectivity of chemical reactions. Switchable catalysis is a new emerging topic in this area that paves the way to reach even higher levels of control of catalytic reactions. Inspired by nature, where enzymatic processes in cells involve sophisticated feedback loops and trigger-induced effects for spatial and temporal control,[1] switchable catalysis aims to provide a bio-like level of control over chemical transformations through the response to tunable external stimuli, such as light, pH, metal coordination, redox switching or mechanical forces.[2,3]

In order to obtain switchable catalysts, stimuli-responsive features are incorporated into their structure, whose changes upon application of external triggers lead to the adjustment of the reaction rates and/or selectivity of the catalytic process on demand. Thus, photoswitchable catalysis requires the presence of photoswitchable moieties in the system – e.g., azobenzene,[4] stilbene[3] or diarylethene (DAE)[5] photoswitches –, which upon light absorption undergo isomerization and, consequently, induce changes in the electronic and/or geometrical properties of the catalyst that modulate its activity. In a similar fashion, pH-responsive moieties must be introduced into pH-switchable catalysts. Known examples of this behavior include the electronic changes occurring in *N*-heterocyclic carbenes (NHC)[6] upon protonation and the pH-induced translocation of a catalytic rotaxane macrocycle.[7] Alternatively, catalysis can also be modulated by tuning metal coordination, which is achieved by adding or removing external ligands that can complex with a metal ion in the catalyst, or adding or removing metal ions that can coordinate with binding motifs in the catalytic system's structure.[8] As for redox modulation in catalysis, it is frequently accomplished by regulating the oxidation state of redox-active ligands, such as ferrocene or cobaltocene groups, in the catalyst.[9] Mechanical forces, applied through ultrasound fields, offer another avenue for externally manipulating catalysis, which often requires catalyst structures with sufficiently long polymer chains.[10] Finally, catalysis can also be modulated by changes in reaction conditions, such as switching the reaction atmosphere or solvent, a strategy that demands the presence of chemical groups in the catalyst that are sensitive to these effects.[11]

Among all these external stimuli to accomplish switchable catalysis, light stands out because of a series of advantageous properties: it is non-invasive, cheap, ubiquitous, environmentally friendly, easily tunable in terms of wavelength, power and polarization, and even more importantly, provides

precise temporal and spatial control – i.e., light doses can be administered locally (using lenses) and for very short lapses of time (using pulsed illumination sources) with high degree of precision. The usage of light as an external stimulus for chemical transformations was recognized as early as in 1912, when Giacomo Ciamician – the father of photochemistry – wrote "…I believe that industry will do well in using from this very day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?".[12] Since then, light has been profusely implemented to promote and control chemical reactivity through the photoactivation of substrates,[13] catalysts[14] or products, giving rise to very successful applications such as photopolymerization,[15] organic photocycloadditions[16] and artificial photosynthesis.[17] When considering the use of light to control catalyst activity, three main approaches have been developed: photoredox catalysis, photocaged catalysis and photoswitchable catalysis. The latter is the field of study of this work.

1. 2. Photoswitchable catalysis

Photoswitchable catalysis allows to reversibly toggle a catalytic system between two or more distinct states upon irradiation, each of them exhibiting different catalytic activity, selectivity, solubility, or sensitivity to the substrate (Figure 1-1). This light-controlled approach is especially useful in the fields where chemical reactions are to be conducted with high spatial - e.g., bioconjugation[18] and surface patterning[19] – and/or temporal precision – e.g., (co-)polymer synthesis.[20] As mentioned earlier, it is the light-induced isomerization of the photoswitchable moieties within the catalyst structure what leads to geometrical and/or electronic changes that alter its catalytic properties, a strategy that has been exploited to control both organo-[21,22] and metal-based catalysts.[22]

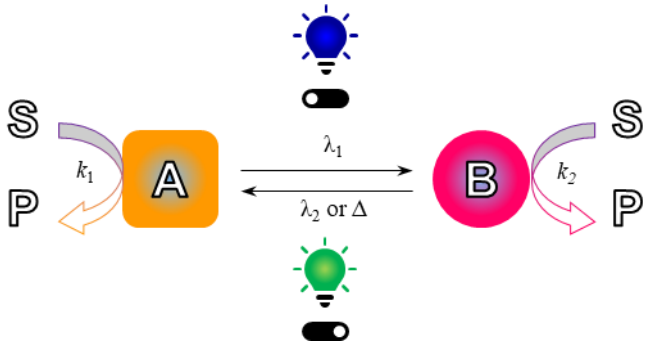
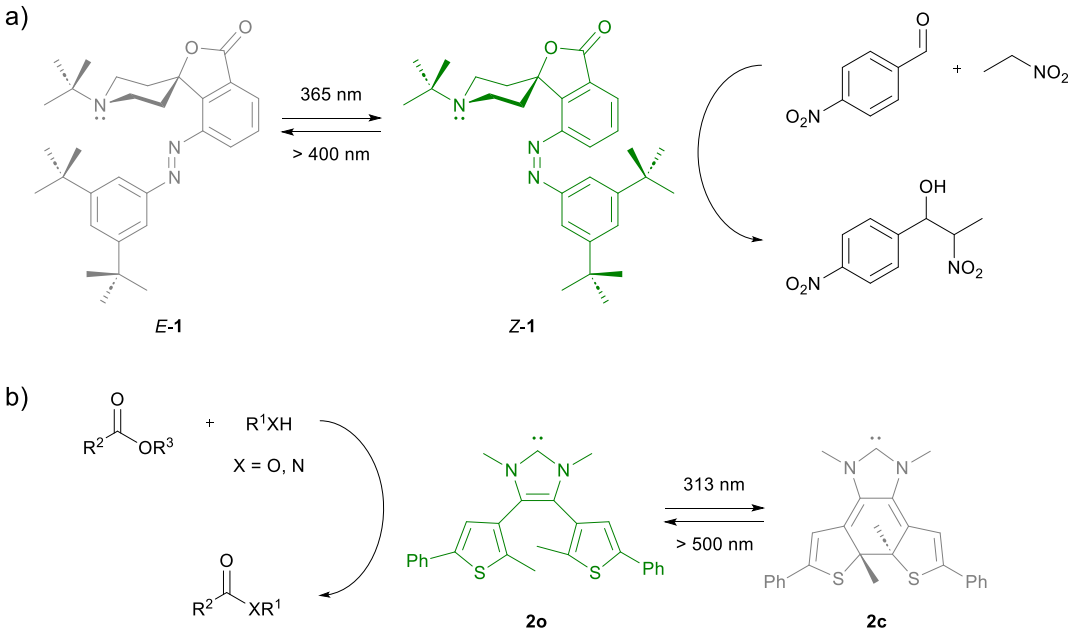


Figure 1-1 – The general concept of photoswitchable catalysis, where a catalyst presents two different states with distinct catalytic properties (A and B) that can be mutually interconverted through light absorption.

In the case of photoswitchable organocatalysis, there are several examples worth mentioning to illustrate the main strategies used to accomplish reversible light control. On the one hand, photoinduced geometrical changes can be used to sterically shield and deshield the active sites of a catalyst. For instance, as demonstrated by Hecht's group,[23] the nitrogen atom lone pair of the *N*-

alkylated piperidine base **1** can undergo reversible shielding and deshielding through the *E*/*Z* photoisomerization of a rigidly connected azobenzene. This results in changes in basicity that can be exploited to reach photocontrol over the conversion of a base-catalyzed nitroaldol (Henry) reaction (Scheme 1-1a). On the other hand, electronic effects can also be exploited in photoswitchable catalysis; for example, when a NHC group was introduced to the central ring of the DAE photoswitch **2**, as described by Bielawski and Neilson (Scheme 1-1b).[24] Because of the variation of the conjugation in the system that occurs upon photoisomerization, the electron density on the NHC group in **2** decreases upon photocyclization, which makes the ring-open form **2o** a better catalyst to activate alcohol and amine nucleophiles in transesterification and amidation reactions, respectively. In all these examples, authors have shown that the modulation in reaction rates can be reversibly switched several times under sequential irradiation with different light sources to interconvert between the active and inactive states of the catalysts.

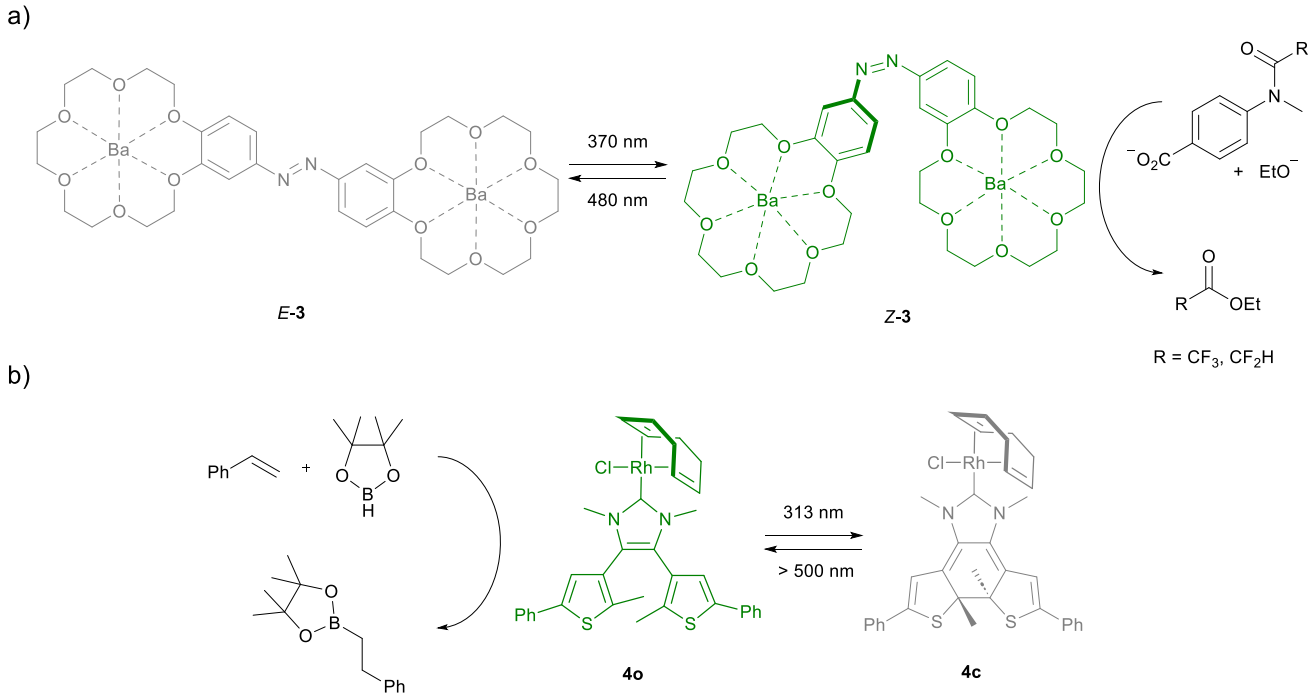
It is worth mentioning that these two examples do not exclude in any way other possibilities to influence the catalytic performance of photoswitchable organocatalysts. For example, the use of photoisomerization reactions to modify catalyst solubility[25] or regulate the cooperative action of two separated catalytic sites are well represented in the literature.[26]



Scheme 1-1 – Examples of photoswitchable organocatalysis. The active form of the catalyst is presented in green. a) Control over the catalytic activity of a piperidine base through shielding and deshielding of the amine lone pair using azobenzene *E*/*Z* photoisomerization. The more basic deshielded state of the catalyst is capable of catalyzing a model Henry reaction. b) Control over the electronic properties of a NHC moiety through photoisomerization between the ring-open and ring-closed states of a DAE photoswitch. The more electron-rich NHC group in the ring-open isomer is capable of better activating alcohols and amines to promote transesterification and amidation reactions.

As metal catalysis remains one of the most versatile tools in the arsenal of synthetic chemists, the development of photoswitchable transition metal catalysts has also been explored.[3] As in the case of organocatalysis, the modulation of catalytic activity is mainly achieved through the exploitation of geometrical and/or electronic effects. However, in this case, the alteration in properties is aimed to modify the catalytic properties of a metal center to which photoswitchable ligands are bound.

Among all the available photoswitches, the azobenzene scaffold has been used in the preparation of a wide variety of transition metal complexes to accomplish photoswitchable catalysis through geometrical effects. One of the first examples of this type of systems was presented by Cacciapaglia's group, where two barium-coordinated crown ethers were integrated into a central azobenzene photoswitch (Scheme 1-2a).[27] In this case, catalyst activity could be modulated depending on the proximity of the two barium centers. In its more stable elongated configuration *E*-**3**, this system has shown low catalytic activity towards the basic ethanolysis of tertiary amides. In contrast, cooperative catalytic effects were found to occur in the *Z*-**3** isomer where the two barium centers are arranged at shorter distances. For this configuration, catalysis is assisted through the coordination of the carboxylate group of the anilide substrate to one of the barium ions, while a nucleophilic ethoxide ion is bound to the second barium ion.



Scheme 1-2 – Examples of photoswitchable metal catalysis. The active form of the catalyst is presented in green. a) Control over the proximity of two coordinated Ba^{2+} ions governed through azobenzene *E*/*Z* photoisomerization. Cooperative action of the two metal centers in close proximity is required to catalyze the ethanolysis of tertiary anilides. b) Control over the electronic properties of a Rh(I) catalytic center through photoisomerization of a ligated NHC moiety. The electron-richer Rh(I) species in the ring-open state is capable of catalyzing the hydroboration of arenes faster than its more electron-deficient ring-closed isomer.

To prepare photoswitchable metal catalysts based on electronic effects, diarylethenes are often the photoswitches of choice. For instance, by complexing DAE-based NHC **2o** with Rh(I), Bielawski and Neilson obtained complex **4o** also exhibiting photoswitchable catalytic performance (Scheme 1-2b).[24] In particular, the authors observed that the reductive elimination step of the hydroboration reaction of various alkenes was affected by the change in Rh(I) electronic density when **4** was employed as a catalyst. As a result, the reaction proceeded faster when the ring-open state complex **4o** was used, due to higher donating ability of the NHC ligand in this isomer form.

As mentioned above, a key component of any of these photoswitchable metal catalysts are the coordinating photoisomerizable ligands, which are the ultimate responsible of catalytic activity modulation. In this work attention has been especially focused on photoswitchable phosphine ligands.

1. 2. 1. Photoswitchable phosphine ligands

The success of the molecular design of a photoswitchable metal catalyst depends on two main structural features: the photoisomerizable scaffold and the binding group chosen to complex the metal. The choice of the former is essentially determined by the change in the metal properties required to accomplish catalysis modulation – i.e., whether it will be achieved by altering the electron density on the metal center or the geometry around it. In many instances, both of these parameters are important, and the final selection should take into account all the electronic and steric factors that can affect the catalytic properties of the metal center. As for the selection of the binding group, it is mainly dependent on the nature of the metal that would be active in the catalysis. Existing examples include not only NHCs and crown ethers but also pyridine,[28,29] salen,[30] oxazoline,[31] cyano[32] and phosphine[33] groups.

Phosphines play a crucial role in the advancement of modern catalysis due to their particular electronic and steric properties, which make them very versatile ligands for metal complexation (Figure 1-2a).[34] Thus, phosphines are known for their capacity to bind a variety of metals in both high and low oxidation states thanks to their adjustable electronic features.[35] When acting as σ-donors, they bind metals through electronic density donation from the lone pair of electrons of their phosphorus atom to the empty orbitals of the metal. At the same time, these ligands can act as π-acceptors, receiving electron density from filled metal *d* orbitals into phosphorus antibonding σ* orbitals.[36] The contribution of these two types of electronic interactions and, therefore, the nature of the metal-phosphine bond is influenced by the substituents incorporated at the phosphorus atom.[37] Phosphines containing electron-withdrawing groups exhibit reduced electron density on phosphorus, resulting in a diminished σ-donor capacity; this effect is accompanied by the lowering of phosphorus σ* orbital energy, thus increasing their tendency to act as π-acceptors. In contrast, the introduction of electron-donating groups to phosphines enhances their σ-donor character at the

expense of their π-acceptor properties. Therefore, the modulation of phosphine electronic features could significantly change the nature of its bonding to a metal center and, eventually, affect its catalytic activity.

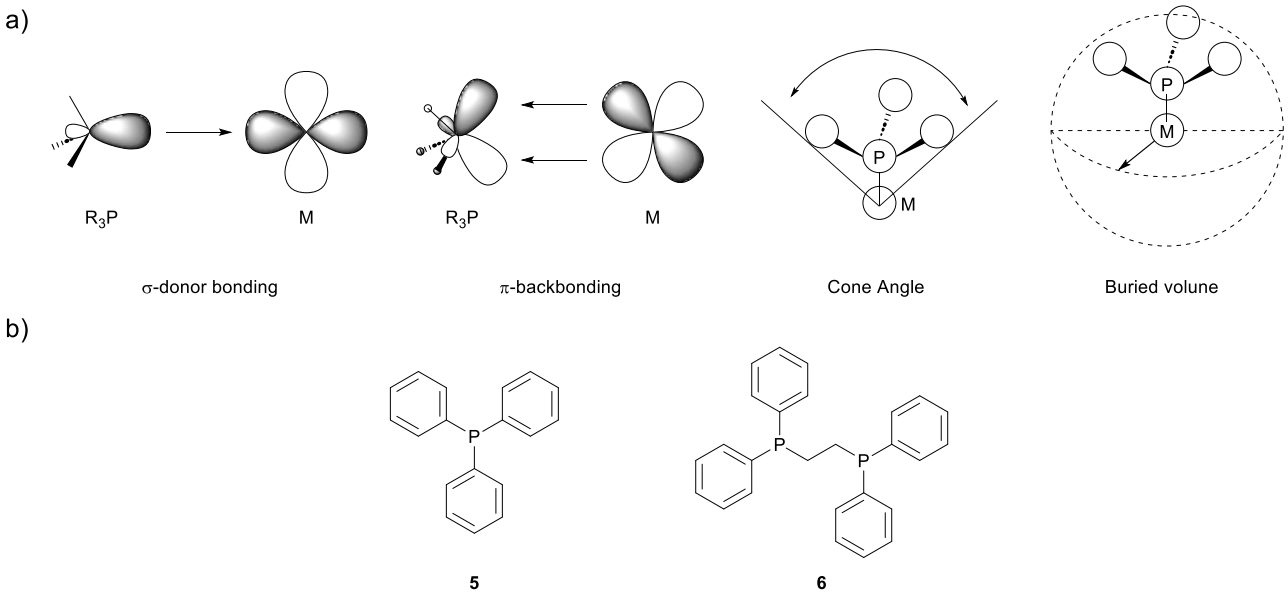
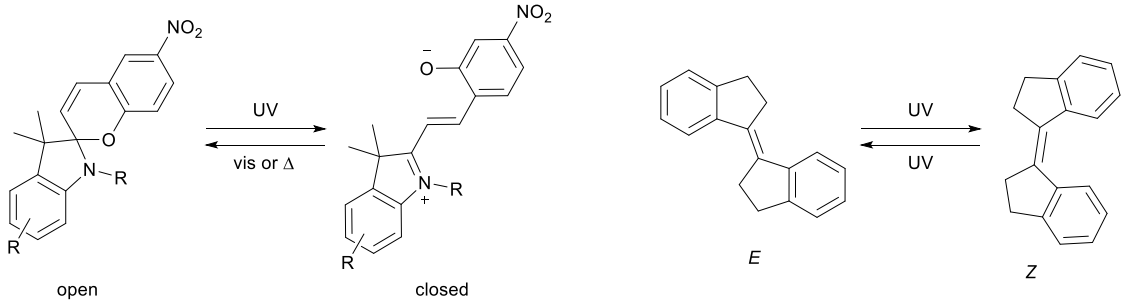


Figure 1-2 – a) Electronic and structural properties of tertiary phosphine ligands in metal complexes. b) Example of monodentate triphenylphosphine ligand **5** and bidentate 1,2-bis(diphenylphosphino)ethane **6**.

Steric effects imparted by tertiary phosphines also play a very significant role in the catalytic activity of coordinated metals.[34,38] To rationalize this behavior, phosphine ligands can be described through Tolman cone angle and percent buried volume. Tolman defined the cone angle as the "apex angle of a cylindrical cone, centered at 2.28 Å from the center of the P atom, which touches the van der Waals radii of the outmost atoms of the model".[39] As for the buried volume,[40] it is defined as the percentage of a sphere (r = 3.5 Å) around the metal center that is occupied by a given ligand. These steric descriptors of phosphines should be considered during the design of photoswitchable catalysts, as the size of the ligand affects the reactivity of the attached metal center.[41] In addition, ligands containing more than one phosphine group in their structure can act as bidentate or even tridentate ligands (Figure 1-2b), thus opening a different way to alter their influence on catalytic metal centers by varying their coordination mode or the steric and electronic properties of the linker.

The light-responsive scaffolds used in photoswitchable catalysis also exhibit a variety of tunable characteristic features.[42] Generally, existing molecular photoswitches can be divided into two main groups depending on the type of isomerization process induced by light. The first group is formed by the photoswitches that undergo ring-cyclization and ring-opening reactions; for example, this is the case of the diarylethenes shown in Schemes 1-1b and 1-2b as well as of the spiropyran in Scheme 1-3. The second group of photoswitches are characterized by a light-triggered *E*/*Z* isomerization around a double bond. This is the case of the azobenzenes in Schemes 1-1a and 1-2a

and of the 1,1'-biindane in Scheme 1-3, an illustrative example of the stiff stilbene photoswitches used for the preparation of molecular rotors and for which Ben Feringa was awarded with the Nobel Prize in Chemistry in 2016.[43] Additionally, photoswitches are also divided depending on the stimuli required for their back-isomerization. Those that are thermally unstable in their photoinduced state and isomerize back to their most stable configuration with time in the dark are called thermally reversible type or T-type (e. g., azobenzenes and spiropyrans). On the other hand, photoswitches that only undergo back-isomerization under light irradiation are classified as photochemically reversible type or P-type (e. g., DAEs and 1,1'-biindane).



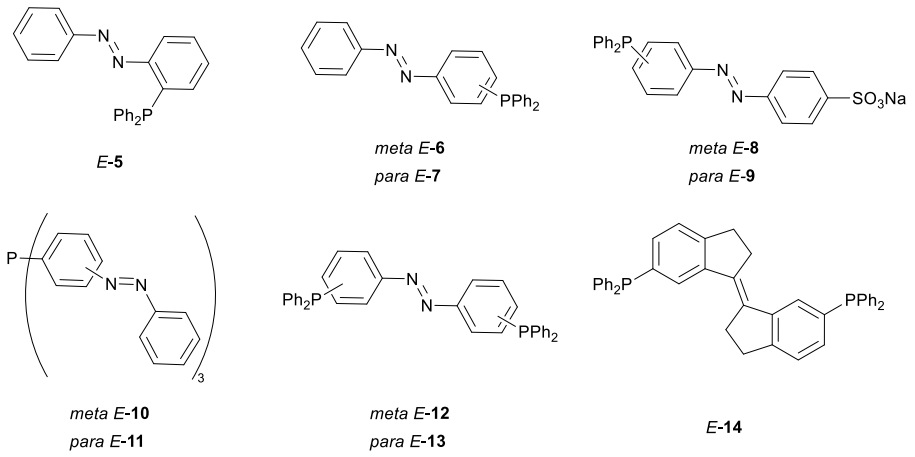
Scheme 1-3 – Examples of different types of photoswitches. Left: a spiropyran photoswitch undergoing ring-closing and ring-opening reactions upon light irradiation; in this case, reversed back-isomerization is also possible through thermal relaxation in the dark (T-type). Right: 1,1'-biindane photoswitch undergoing *E*/*Z* photoisomerization only upon light irradiation (P-type).

Various parameters are utilized to assess the light-induced efficacy of molecular photoswitches. Firstly, photoisomerization quantum yields (Φ_i) serve as a metric for the efficiency of the process in the excited state - i.e., they quantify the number of molecules undergoing the isomerization reaction per photon absorbed, excluding those that revert back to the initial ground state without isomerizing through alternative processes such as luminescence emission or internal conversion.[44] Secondly, the composition of the photostationary states (PSS)[45] defines the extent of the photoreaction - i.e., the composition of the final equilibrium mixtures of the two interconverting isomers that are achieved under continuous irradiation when the rates of the photoisomerization process and the back-reaction become equal. The composition of PSSs depends on factors such as the absorbance of the two isomers at the irradiation wavelength, their respective photoisomerization quantum yields, and, in the case of T-type photochromes, the thermal lifetime of the photoinduced isomer along with the irradiation intensity. Thirdly, fatigue resistance[46] characterizes the decline in performance of the molecular photoswitch over repetitive photoisomerization cycles, a phenomenon attributed to photodegradation.

Typically, photoisomerization is accompanied by alteration in the geometrical and electronic properties of the photoswitch, which in turn leads to ample variation of their physicochemical properties (e.g., polarity, light absorbance and redox potentials). The extent of these changes

depends on the specific scaffold, providing a high degree of flexibility in selecting desired outcomes. This is demonstrated by existing examples of photoswitchable phosphine ligands, where different photoisomerizable units have been introduced to promote a range of property changes.

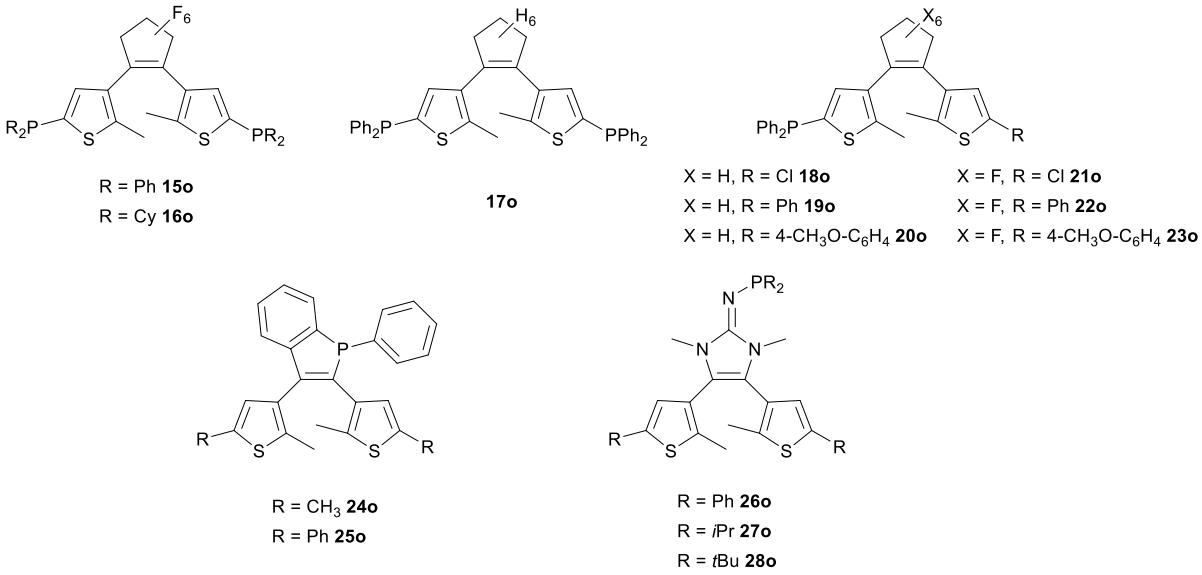
Probably, the most employed scaffold for photoswitchable phosphine ligand preparation is azobenzene (Scheme 1-4). In 2005 Kawashima et al. reported the first functionalized azobenzene bearing one diphenylphosphanyl group in the *ortho* position to the N=N double bond (*E*-**5**).[47] Later on, they expanded the library of this type of compounds, obtaining monophosphine ligands attached to the positions *meta* (*E*-**6**) and *para* (*E*-**7**) of the azobenzene core. Additionally, with the aim of modulating their solubility, azobenzenes *E*-**8** and *E*-**9** also bearing a sodium sulfonate group in their structure were prepared in Monflier's group.[48] Feringa's group further advanced the research in this field by introducing more than one azobenzene unit to the central phosphorus atom of the phosphine (*E*-**10** and *E*-**11**).[49] And more recently, Marinetti's group reported bifunctionalized azobenzenes *E*-**12** and *E*-**13** where diphenyphosphanyl groups were introduced to both arenes.[50] In contrast, the use of other *E*/*Z* photoisomerizable switches such as 1,1'-biindane for the preparation of light-responsive phosphines has been less explored. One example is the 1,1'-biindane derivative *E*-**14** with two phosphines directly anchored described by Feringa's group in 2020 (Scheme 1-4).[51] Other similar ligands were previously reported where phosphines were attached to the stiff stilbene scaffold through various linkers, exploiting a distant change in the switch geometry. [52]



Scheme 1-4 – Examples of phosphine ligands based on photoswitches undergoing *E*/*Z* photoisomerization: azobenzene derivatives *E*-**5** – *E*-**13** and 1,1' biindane-based bisphosphine *E*-**14**.

Another class of photoswitchable units employed for the preparation of light-responsive phosphine ligands are dithyenilethenes (DTE), the most common type of DAE switches that also operate upon ring-cyclization and ring-opening reactions (Scheme 1-5).[5] In this case, symmetrically substituted DTE-based phosphines were first synthesized, and only later on examples of asymmetric structures were reported. The pioneering work in this area was developed in Branda's group,[53] who reported DTE-based ligand **15o** bearing two diphenylphosphanyl substituents in both thiophene

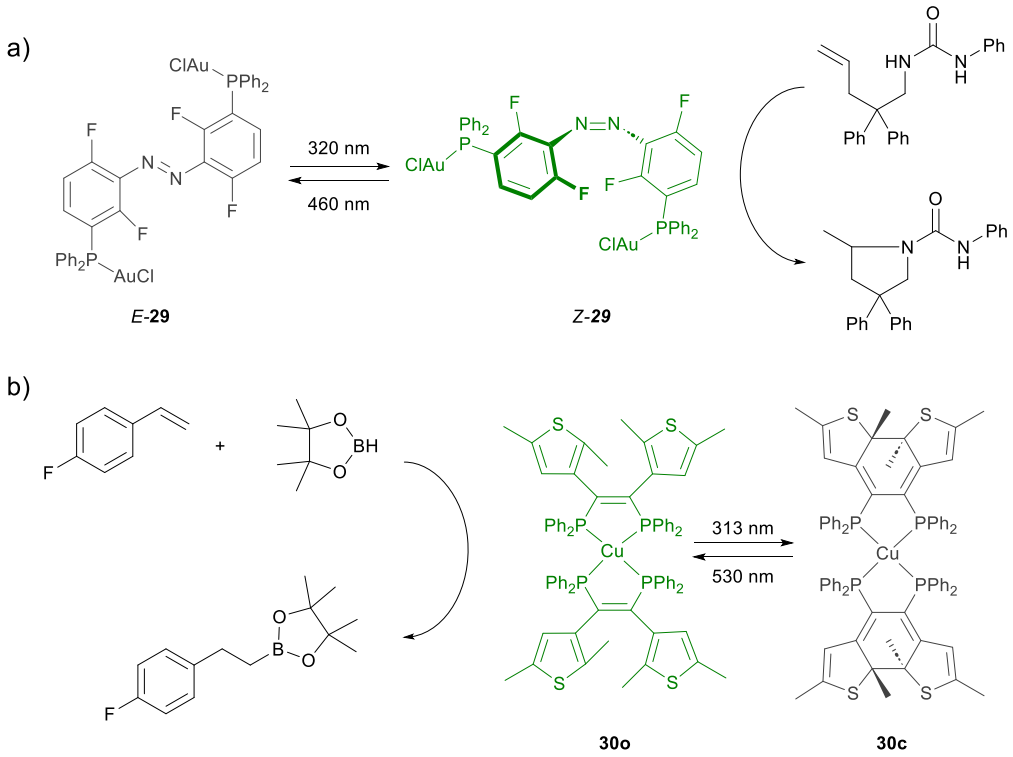
rings and a central perfluorinated cyclopentene unit. A few years later, Liu's group expanded this concept to derive ligands **16o** and **17o** by changing the bridging cyclopentene ring of the DTE core and the nature of the substituents at the phosphorus atom.[54] As for asymmetrically substituted DTE-based phosphines, a library of this type of compounds was derived by Scarco et al. (**18o** – **23o**).[55] In this way, they could study the effect of two different factors on the modulation of the electronic properties of the phosphine group upon photoisomerization: the nature of the substituents installed in the other thiophene ring of the DTE core and of the central bridging cyclopentene unit. Finally, other examples of DTE-based phosphorus(III) ligands have been reported where the binding group was introduced to the cyclopentene moiety of the photoswitch. This is the case of compounds **24o** – **25o** synthesized by Yam et al., which allowed exploring the electron density change occurring on the phosphole group upon ring closing.[56] As for ligands **26o** – **28o** described very recently by Glorius and Dielmann et al., an electron-rich phosphine was attached to an NHC imine installed in the DTE scaffold to achieve significant modulation of phosphorus electron density upon photoisomerization.[57]



Scheme 1-5 – Open-state structures of DTE-based phosphorus(III) ligands.

Despite all these examples of photoswitchable phosphine ligands, photoswitchable complexes based on them capable of undergoing photoisomerization and showing modulation of catalytic activity are scarce. Two major factors account for this situation. On the one hand, complexation of transition metals very often hinders ligand photoisomerization due to competitive light-induced charge transfer processes or steric restrictions.[55,58] On top of that, a noticeable change in the in situ photoswitched catalytic activity is rare due to the inability to achieve true active and inactive states upon catalysts photoisomerization.

One of the few successful examples of azobenezene-based photoswitchable catalysis with phosphines was reported by Marinetti et al., who exploited the geometrical changes occurring upon photoisomerization to modulate cooperative catalytic effects (Scheme 1-6a).[59] To this goal, they prepared complex **29**, where two diphenylphosphanyl groups were attached to a central azobenzene core and coordinated to two gold(I) centers. For this compound they demonstrated that intramolecular hydroamination proceeds 1.3 times faster when the *Z* state of the catalyst is used due to the closer proximity of the two gold(I) centers in the structure. However, this result was obtained by testing independently the catalytic activity of the *E* and *Z* isomers of **29** prepared beforehand, as the reactivity modulation observed in situ upon irradiation was even more moderate. As for DTE-based phosphines, to our knowledge their use in metal complexes to achieve light-induced catalysis modulation has only been reported by Wolf's group (Scheme 1-6b).[60] For this they developed copper(I) dimer **30** where metal binding phosphanyl groups were introduced to the central bridging unit of the DTE core. When using the ring-open and ring-closed isomers of this compound separately prepared as pre-catalysts of the hydroboration of 4-fluorostyrene with pinacolborane, lower yields were observed for **30c** that were attributed to decreased electron density on the metal (from 62% yield for **30o** to 44% yield for **30c**). In this case, no attempts to conduct in situ modulation of catalysis were reported.



Scheme 1-6 – Examples of transition metal-catalyzed reactions using photoswitchable catalysts. a) Modulation of the cooperative effect between two gold(I) centers by altering their separation distance with a photoisomerizable azobenzene-based bisphosphine ligand, leading to an enhancement of catalytic activity towards intramolecular hydroamination for the *Z* isomer. b) Use of the electron density change on a copper(I)

metal center as a result of ring-cyclization in DTE-based phosphine ligands, which leads to lower yields in the hydroboration of 4-fluorostyrene.

Only a small number of other examples demonstrating catalytically active photoswitchable complexes are known, especially for those made of phosphine ligands. To broaden up the range of existing catalysts of this type, this work has focused on creating new photoswitchable complexes based on photoisomerizable phosphines. With this aim, two different photoswitchable scaffolds have been utilized whose photochemical properties are explained in detail below: (i) DTEs, with which the modulation of the electronic properties of phosphines under light irradiation was attempted; and (ii) diazocines, whose geometrical changes occurring upon photoisomerization have been explored to control the coordination mode of phosphines.

1. 2. 2. Dithienylethenes

DTEs are a well-known class of molecular photoswitches which, in their more thermodynamically stable open isomer, consist of two thiophene moieties connected through a *Z*-ethene bridge (Figure 1-3a).[61] This is a particular case of the broader family of DAE photoswitches, wherein the thiophene rings may be substituted with other aryl groups. Due to the occurrence of free rotation between the ethene linker and the thiophene rings, the structure of the open-state DTE is non-planar. Consequently, electronic communication between the two aryl groups is absent, resulting in strong absorption primarily in the UV, and occasionally violet, regions (Figure 1-3b).[62]

Upon exposure to UV light, the open state of DTEs undergoes a 6π electrocyclization reaction to produce the corresponding closed isomer, which displays an absorption band in the visible region due to its extended conjugation path (Figure 1-3b). The closed state of DTEs typically exhibits thermal stability, precluding spontaneous back-isomerization in the absence of external stimuli over time in the dark. The recovery of the open isomer therefore necessitates exposure to visible light, inducing an electrocyclic ring-opening reaction.[62]

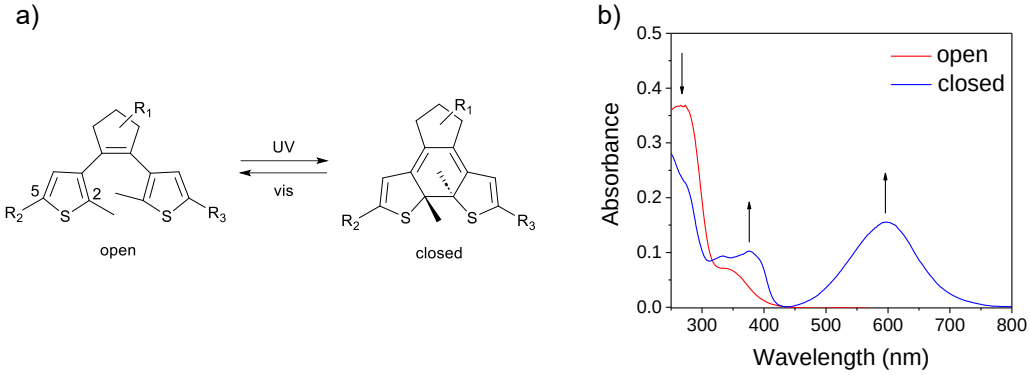
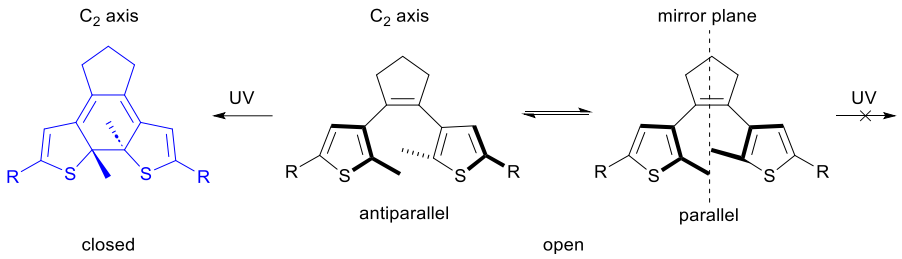


Figure 1-3 – a) Ring-closing and ring-opening photochemical reactions of DTEs. b) Typical UV-vis absorption spectra of the open and closed forms of DTEs (R_1 = H, R_2 = R_3 = $COCF_3$).

A number of structural features in the DTE scaffold have a significant influence on its photochemical behavior. Firstly, cyclic *Z*-ethene bridges, often in the form of a central ring, are typically employed.[63] This strategic choice serves to hinder light-induced *cis-trans* ethene photoisomerization in the open isomer, a process that could potentially compete with the desired ring-closing reaction. Cyclopentene groups, frequently perfluorinated (R_1 = F) to enhance the molecular switch performance, are commonly selected for this purpose. Secondly, internal substituents are routinely introduced at the 2 and 2' positions of the thiophene moieties.[64] This serves the purpose of preventing further oxidation during the ring-closing process driven by rearomatization, as typically observed for *cis*-stilbenes. Additionally, external substituents are typically tethered to the 5 and 5' positions of the thiophene groups. This practice aims to impart additional functionality and/or modify the photochemical properties of DTEs.

The non-planar flexible structure of the open form of DTEs plays an essential role in their photocyclization reaction, as it can exist in two main interconverting conformations: (i) a parallel conformation with both thiophenes arranged symmetrically; and (ii) an antiparallel conformation, endowing the molecule with a C_2 axis of symmetry (Scheme 1-7).[65] According to the Woodward-Hoffman rules, the light-induced 6π-electrocyclization reaction of DTEs must be conrotatory - i.e., with rings turning in the same direction. For this reason, only the open antiparallel conformation of DTEs can undergo photoconversion into the closed isomer. This rule is illustrated by the relative stereochemistry of the internal substituents of the closed-state DTE generated, where they always undertake a *trans* configuration. Conversely, the parallel conformation of the open state DTE could potentially undergo a thermal disrotatory ring-cyclization reaction - i.e., with rings turning in different directions. However, this outcome is predominantly avoided by the steric hindrance imposed by the internal substituents.



Scheme 1-7 – Photochemical behavior of open-state DTEs in parallel and antiparallel conformations.

Consequently, photocyclization quantum yields ($\Phi_{o\text{-}c}$) in DTEs are impacted by the thermal equilibrium between the parallel and antiparallel conformations of the open state. Generally, open isomers exist in a 1:1 ratio between these conformers, restricting $\Phi_{o\text{-}c}$ values to 0.5, as only half of the absorbing molecules can undergo the photochemical reaction.[66] To enhance the efficiency of the cyclization reaction, a higher population of the antiparallel conformer is desirable. This advantageous situation can be accomplished through the stabilization of the antiparallel conformation via intramolecular interactions[67] or the introduction of bulky substituents[68] in the internal positions.

Solvent properties are an additional factor influencing the efficiency of the ring-closing reaction. Many DTEs exhibit a significant decrease in $\Phi_{o\text{-}c}$ with increasing solvent polarity.[69] This phenomenon is attributed to intramolecular charge transfer processes that compete with cyclization upon photoexcitation, which are particularly prone to occur when electron-rich and electron-poor groups are present in the molecule.

As for photocycloreversion quantum yields ($\Phi_{c\text{-}o}$) in DTEs, they are generally lower than $\Phi_{o\text{-}c}$ values. This is typically attributed to the occurrence of a non-negligible energy barrier in the excited potential energy surface through which cycloreversion takes place, which makes $\Phi_{c\text{-}o}$ values more sensitive to temperature changes.[70] Unlike the photocyclization process, photocycloreversion efficiency is almost unaffected by solvent polarity and is not influenced by any conformational equilibrium involving the closed state of DTEs. In contrast, the substitution pattern of the thienyl groups significantly influences $\Phi_{c\text{-}o}$; for instance, the introduction of electron-donating groups or π-conjugated groups in specific positions decreases the photocycloreversion quantum yields.[61]

UV irradiation of open-state DTEs seldom leads to complete transformation into their closed isomer, as it also absorbs in this spectral region (Figure 1-3b) and, therefore, suffers simultaneous back-photoisomerization. Consequently, the photostationary state achieved during the photocyclization process with UV light is a mixture of both isomers. The molar fraction of each isomer in this mixture depends on their extinction coefficients at the irradiation wavelength and the quantum yields of the ring-closing and ring-opening processes. Thus, high absorbance and $\Phi_{o\text{-}c}$ values for the open isomer at the irradiation wavelength are desirable, while low extinction

coefficients and low quantum yields are preferred for the closed state, especially in the UV and violet region. Notably, the modest $\Phi_{c\text{-}o}$ values exhibited by most closed-state DTEs favor the formation of closed state-enriched photostationary state mixtures. In contrast, visible light irradiation of the closed isomer results in quantitative ring-opening, as the open state does not absorb in that region of the spectrum, thus enabling selective excitation and phototransformation of the closed state.

As shown in section §1.2.1, a number of photoswitchable DTE-based phosphines are already known. There are several well-known synthetic strategies that can be used for their preparation, which vary depending on the desired symmetric or asymmetric structure and on the nature of the central bridging ring. However, as described above, only one example of metal catalysis modulation accomplished with DTE-based phosphines has been reported so far, where the electronic effects occurring on the central ring of the DTE scaffold are exploited. To our knowledge, the electronic changes occurring at other positions of the DTE unit are yet to be exploited in photoswitchable metal catalysis. For instance, this is the case of the variation of electronic communication upon ring-closing between the substituents at positions 5 and 5' of the thiophene rings of DTE, which is intended to be capitalized on in this work.

1. 2. 3. Diazocines

Diazocines, also known as C_2-bridged azobenzenes, are a particular type of azobenzene photoswitches wherein the diazene unit is incorporated within an eight-membered ring (Figure 1-4a). The discovery of diazocines dates back to 1910,[71] as reported by Duval. Subsequent advancements in their synthesis were achieved by Paudler and Zeiler in 1969[72] and further refined by Tauer and Machinek in 1996.[73] However, the molecular photoswitching properties of diazocines were not elucidated until 2009 by Temps, Herges et al., who demonstrated that they preserve the T-type photoswitching behavior azobenzenes - i.e., they can undergo *E*/*Z* photoisomerization and can also relax thermally to the initial state in the dark.[74]

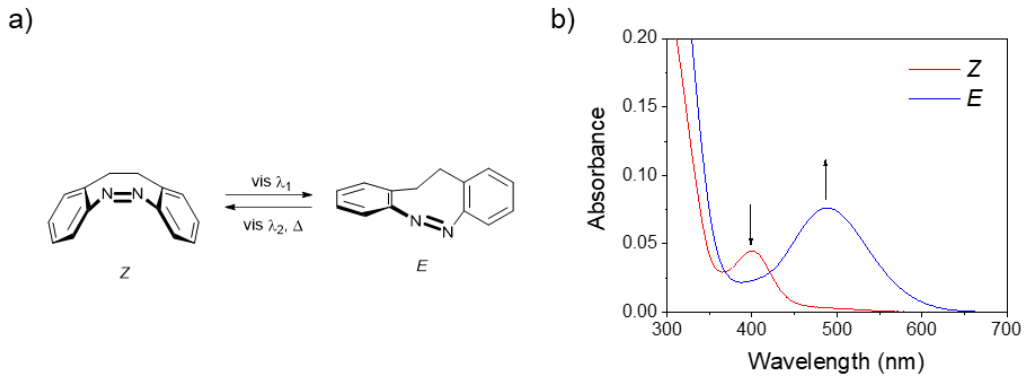


Figure 1-4 – a) *Z*/*E* isomerization of diazocines. b) Typical UV-vis absorption spectra of the *Z* and *E* diazocine isomers.

However, diazocines present some unique photoswitching properties compared to regular azobenzenes. First, due to ring strain, the most stable configuration of diazocines is the *Z* isomer.

Second, because of the non-planar structure of the *Z* and *E* diazocine isomers deriving from the short C_2 bridge, they exhibit stronger n→π* absorption bands in the visible region of the spectrum that are fairly separated, which can therefore be used to promote all-visible reversible photoisomerization (Figure 1-4b). Thus, *Z*-to-*E* photoisomerization takes place by irradiation with violet-blue light (370-400 nm) with high efficiencies.[74] In a similar fashion to DTEs, the achieved PSS mainly depends on the extinction coefficients of the two isomers at the excitation wavelength and their respective photoisomerization quantum yields, though the thermal lifetime of the photoinduced *E* isomer can also play a role in this case. Generally, high PSS for *Z*-to-*E* photoisomerization has been reported for this photoswitch, though they vary with the substitution pattern and the solvent used. As for the reverse *E*-to-*Z* photoconversion, it can be triggered selectively by irradiation with green light, which thus ensures quantitative back-isomerization, or by thermal relaxation in the dark. The thermal lifetime of the photoinduced *E* isomer at room temperature is usually long, though it is also dependent on substituents and solvent. In addition, the photoswitching properties of diazocines (and others such as solubility) can be further modulated through the introduction of hetero atoms (O, N, S) into the C_2 bridge.[75]

Since their discovery as molecular photoswitches, diazocines have gained a lot of attention and have been mainly applied in photopharmacology and for the design of photoresponsive materials.[28,29,76,77] However, their broader use as photoswitches has been somewhat hampered, especially because of their difficult synthesis. Up until 2019, diazocines were mainly synthesized through a reductive approach with medium to low yields.[78] In this reductive pathway, the formation of the cyclic 8-membered ring involves the reduction of dinitroaromatic derivatives using Zn or Pb, resulting in the generation of a cyclic hydrazine that is subsequently oxidized to afford the diazo bond. This reductive ring closure process has also been successfully accomplished in an aqueous glucose solution under basic conditions. In 2019 Trauner's group achieved high yields for diazocine synthesis by directly oxidizing a bisaniline precursor using *meta*-chloroperoxybenzoic acid, thereby generating a diverse library of differently substituted diazocine compounds (yields up to 86%).[79] Additionally, Staubitz's group employed a cascade coupling strategy, involving consecutive C-N cross-couplings starting from 2-bromobenzylbromide derivatives, to introduce the diazo unit.[80] Compared to oxidative coupling, this approach yields lower conversions but appears to be more effective for some substrates. Finally, Herges' group reported the synthesis of heteroatom-bridged diazocines through intramolecular azocondensation following the Baeyer-Mills reaction, resulting in diazocines ring closure.[75]

Aside from diazocine core synthesis, their late-stage functionalization may also be a challenging task due to the intrinsic features of the scaffold. For instance, the electrophilicity of the N=N bond precludes the usage of many organometallic reagents,[81] while the high ring-strain of diazocines can easily result in degradation at harsh reaction conditions. Consequently, despite reported synthesis of brominated diazocines, there are limited examples of their further functionalization.[28,77,81,82] This

is a challenge that has been faced in this work to pioneer the preparation of diazocine-based phosphine ligands for photoswitchable catalysis.

1. 3. Objectives of the project

As established in section §1.2, photoswichable catalysis presents great opportunities for the precise spatiotemporal control of catalytic reactions. However, existing examples of photoswitchable phosphine ligands to accomplish this goal are scarce and present ample space for further development, as discussed in section §1.2.1. Aiming to obtain novel photoswitchable ligands for the preparation of light-responsive transition metal catalysts, two strategies have been investigated in this work.

The first objective of this thesis was to modulate the electron density on the phosphorus atom of phosphine ligands by exploiting the photoisomerization of DTE switches (Figure 1-5). To pursue this objective, an approach not yet described for the development of photoswitchable catalysts was explored herein: the introduction of a diphenylphosphanyl group and an electron-withdrawing substituent (EWG) at positions 5 and 5' of the thiophenes rings of the DTE core. In the open state where the two thiophene rings are fully isolated, no electronic communication should occur between these two groups and, consequently, the phosphine ligand must have a strong σ-donor character. However, conjugation between the phosphanyl and EWG groups should occur upon photocyclization, thus decreasing the σ-donating ability of the phosphine. To further amplify this effect, two DTE moieties were devised to be introduced to the same phosphorus atom, whose electronic properties could then be modulated by electronic communication to two EWGs simultaneously. For all these ligands, it was planned to investigate the effects of metal complexation (Pd^{II}, Au^{I}) on the photocyclization reaction and eventually test them for modulating metal-catalyzed reactions with light. The results obtained in these studies are described in chapters 2 and 3 of this thesis.

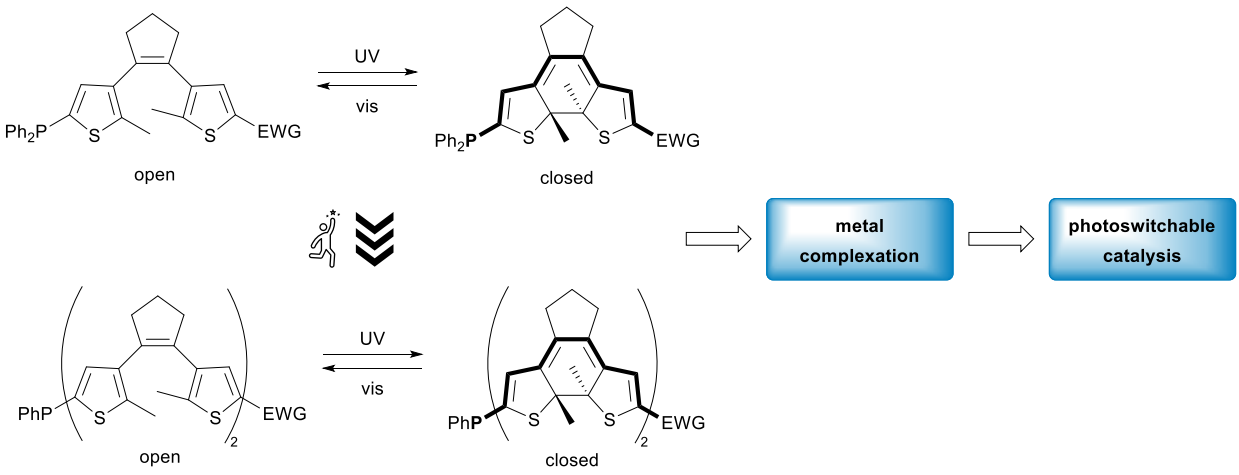


Figure 1-5 – Electron density modulation of phosphines explored in this work through the preparation of mono- (top) and bisDTE (bottom) phosphanyl ligands.

The second objective of this work was to modulate the coordination mode of bisphosphine ligands exploiting the geometrical changes occurring upon the photoisomerization of diazocines (Figure 1-6). In particular, the targeted ligands were devised to photoswitch between mono- and bidentate complexation behavior while toggling between the elongated *E* and compact *Z* geometries of the diazocine scaffold. A major challenge to reach this goal would be to find a suitable synthetic route for the preparation of diazocine-based phosphines. As mentioned above, only a limited number of diazocine derivatives have been reported so far, and the chemistry of this type of photoswitches remains rather underexplored. With these ligands in hand, their complexation with palladium(II) would be studied as well as the photoswitching performance of the resulting metal complexes. In the case of positive results, further implementation of these metal complexes in photoswitchable catalysis was envisioned.

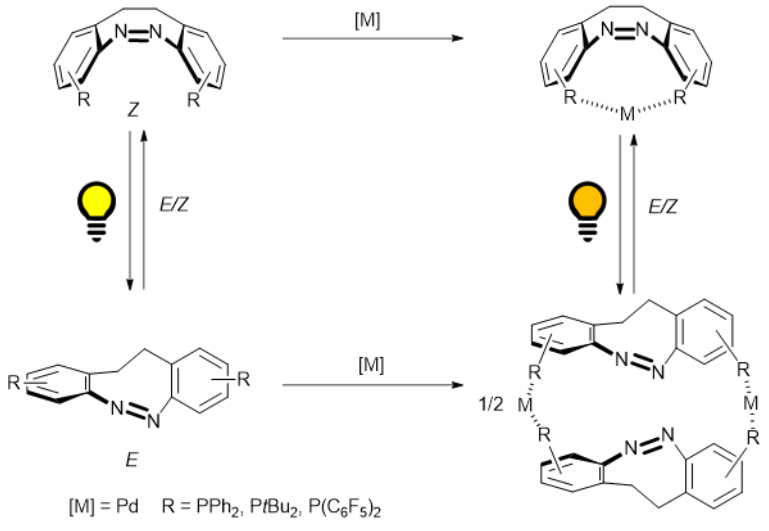


Figure 1-6 – Photoisomerization-driven changes in the coordination mode of diazocine-based phosphine ligands.

1. 4. References

1 T. Traut, *Encyclopedia of Life Sciences*, John Wiley & Sons, Ltd, 2014.

2 a) J. Choudhury, *Tetrahedron Lett.*, 2018, **59**, 487–495; b) V. Blanco, D. A. Leigh and V. Marcos, *Chem. Soc. Rev.*, 2015, **44**, 5341–5370.

3 G. C. Thaggard, J. Haimerl, R. A. Fischer, K. C. Park and N. B. Shustova, *Angew. Chem. Int. Ed.,* 2023, e202302859.

4 R. Dorel and B. L. Feringa, *Chem. Comm.,* 2019, **55**, 6477–6486.

5 D. Majee and S. Presolski, *ACS Catal.*, 2021, **11**, 2244–2252.

6 a) S. L. Balof, S. J. P'Pool, N. J. Berger, E. J. Valente, A. M. Shiller and H.-J. Schanz, *Dalton Trans.,* 2008, 5791–5799; b) S. L. Balof, B. Yu, A. B. Lowe, Y. Ling, Y. Zhang and H.-J. Schanz, *Eur. J. Inorg. Chem.*, 2009, **2009**, 1717–1722; c) L. H. Peeck, S. Leuthäusser and H. Plenio, *Organometallics*, 2010, **29**, 4339–4345.

7 a) D. A. Leigh, V. Marcos and M. R. Wilson, *ACS Catal.*, 2014, **4**, 4490–4497; b) V. Blanco, A. Carlone, K. D. Hänni, D. A. Leigh and B. Lewandowski, *Angew. Chem. Int. Ed.*, 2012, **51**, 5166–5169.

8 M. J. Wiester, P. A. Ulmann and C. A. Mirkin, *Angew. Chem. Int. Ed.*, 2011, **50**, 114–137.

9 N. I. Regenauer, J. S. Doll and D.-A. Roșca. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd, 2022, pp. 1–21.

10 R. Groote, R. T. M. Jakobs and R. P. Sijbesma, *Polym. Chem.*, 2013, **4**, 4846–4859.

11 Z. Dai, J. Lee and W. Zhang, *Molecules,* 2012, **17**, 1247–1277.

12 G. Ciamician, *Science,* 1912, **36**, 385–394.

13 a) S. Lazzaroni, D. Ravelli, S. Protti, M. Fagnoni and A. Albini, *C. R. Chim.*, 2017, **20**, 261–271. b) Q.-Q. Zhou, Y.-Q. Zou, L.-Q. Lu and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2019, **58**, 1586–1604.

14 L. Marzo, S. K. Pagire, O. Reiser and B. König, *Angew. Chem. Int. Ed.*, 2018, **57**, 10034–10072.

15 A. Bagheri and J. Jin, *ACS Appl. Polym. Mater.*, 2019, **1**, 593–611.

16 A. G. Griesbeck, *Beilstein J. Org. Chem.*, 2011, **7**, 111–112.

17 A. Machín, M. Cotto, J. Ducongé and F. Márquez, *Biomimetics*, 2023, **8**, 298–342.

18 W. Szymański, J. M. Beierle, H. A. V. Kistemaker, W. A. Velema and B. L. Feringa, *Chem. Rev.*, 2013, **113**, 6114–6178.

19 H. J. Meteling, F. Bosse, L. Schlichter, B. J. Tyler, H. F. Arlinghaus and B. J. Ravoo, *Small*, 2022, **18**, 2203245–2203251.

20 S. P. Ihrig, F. Eisenreich and S. Hecht, *Chem. Comm.,* 2019, **55**, 4290–4298.

21 V. Blanco, D. A. Leigh, U. Lewandowska, B. Lewandowski and V. Marcos, *J. Am. Chem. Soc.*, 2014, **136**, 15775–15780.

22 U. Lüning, *Angew. Chem. Int. Ed.*, 2012, **51**, 8163–8165.

23 M. V. Peters, R. S. Stoll, A. Kühn and S. Hecht, *Angew. Chem. Int. Ed.*, 2008, **47**, 5968–5972.

24 B. M. Neilson and C. W. Bielawski, *J. Am. Chem. Soc.*, 2012, **134**, 12693–12699.

25 A. Nojiri, N. Kumagai and M. Shibasaki, *Chem. Commun.*, 2013, **49**, 4628–4630.

26 T. Imahori, R. Yamaguchi and S. Kurihara, *Chem. Eur. J.*, 2012, **18**, 10802–10807.

27 R. Cacciapaglia, S. Di Stefano and L. Mandolini, *J. Am. Chem. Soc.*, 2003, **125**, 2224–2227.

28 D. Hugenbusch, M. Lehr, J.-S. von Glasenapp, A. J. McConnell and R. Herges, *Angew. Chem. Int. Ed.*, 2023, **62**, e202212571.

29 H. Lee, J. Tessarolo, D. Langbehn, A. Baksi, R. Herges and G. H. Clever, *J. Am. Chem. Soc.*, 2022, **144**, 3099–3105.

30 A. Kumar, R. Pandey, R. K. Gupta, V. Mishra, S. M. Mobin and D. S. Pandey, *Dalton Trans.*, 2014, **43**, 6365–6376.

31 a) D. Sud, T. B. Norsten and N. R. Branda, *Angew. Chem. Int. Ed.*, 2005, **44**, 2019–2021; b) H.-Z. Wei, Y. Wei and M. Shi, *Chem. Asian J.,* 2023, **18**, e202300633.

32 B. Kaur, R. Raza, M. J. Stashick and N. R. Branda, *Org. Chem. Front.*, 2019, **6**, 1253–1256.

33 F. Medici, N. Goual, V. Delattre, a. voituriez and A. Marinetti, *ChemCatChem*, 2020, **12**, 5573–5589.

34 P. C. J. Kamer and P. W. N. M. Leeuwen. *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, John Wiley & Sons, Ltd, 2012.

35 H. A. Mayer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239–1272.

36 A. G. Orpen and N. G. Connelly, *Organometallics*, 1990, **9**, 1206–1210.

37 C. H. Suresh and N. Koga, *Inorg. Chem.*, 2002, **41**, 1573–1578.

38 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313–348.

39 a) C. A. Tolman, W. C. Seidel and L. W. Gosser, *J. Am. Chem. Soc.*, 1974, **96**, 53–60; b) C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956–2965.

40 H. Clavier and S. P. Nolan, *Chem. Comm.*, 2010, **46**, 841–861.

41 Zoraida Freixa and Piet W. N. M. van Leeuwen. *Dalton Trans*., 2003, 1890-1901.

42 M.-M. Russew and S. Hecht, *Adv. Mater.*, 2010, **22**, 3348–3360.

43 B. L. Feringa, *Angew. Chem. Int. Ed.,* 2017, **56**, 11060–11078.

44 E. Stadler, A. Eibel, D. Fast, H. Freißmuth, C. Holly, M. Wiech, N. Moszner and G. Gescheidt, *Photochem. Photobiol. Sci.*, 2018, **17**, 660–669.

45 J. W. Verhoeven, *Pure Appl. Chem.,* 1996, **68**, 2223–2286.

46 S. E. Braslavsky. *Pure Appl. Chem.,* 2007, **79**, 293–465.

47 M. Yamamura, N. Kano and T. Kawashima, *J. Am. Chem. Soc.*, 2005, **127**, 11954–11955.

48 H. Bricout, E. Banaszak, C. Len, F. Hapiot and E. Monflier, *Chem. Comm.*, 2010, **46**, 7813–7815.

49 M. D. Segarra-Maset, P. W. N. M. van Leeuwen and Z. Freixa, *Eur. J. Inorg. Chem.*, 2010, **2010**, 2075–2078.

50 C. Cazorla, L. Casimiro, T. Arif, C. Deo, N. Goual, P. Retailleau, R. Métivier, J. Xie, A. Voituriez, A. Marinetti and N. Bogliotti, *Dalton Trans.,* 2021, **50**, 7284–7292.

51 R. Costil, S. Crespi, L. Pfeifer and B. L. Feringa, *Chem. Eur. J.,* 2020, **26**, 7783–7787.

52 a) Z. S. Kean, S. Akbulatov, Y. Tian, R. A. Widenhoefer, R. Boulatov and S. L. Craig, *Angew. Chem. Int. Ed.*, 2014, **53**, 14508–14511; b) D. Zhao, T. M. Neubauer and B. L. Feringa, *Nat. Commun.,* 2015, **6**, 6652–6658.
53 D. Sud, R. McDonald and N. R. Branda, *Inorg. Chem.*, 2005, **44**, 5960–5962.
54 J. Yin, Y. Lin, X. Cao, G.-A. Yu, H. Tu and S. H. Liu, *Dyes Pigms*, 2009, **81**, 152–155.
55 G. Bianchini, G. Strukul, D. F. Wass and A. Scarso, *RSC Adv.*, 2015, **5**, 10795–10798.
56 N. M.-W. Wu, M. Ng and V. W.-W. Yam, *Nat. Commun.*, 2022, **13**, 33–43.
57 F. Buß, M. Das, D. Janssen-Müller, A. Sietmann, A. Das, L. F. B. Wilm, M. Freitag, M. Seidl, F. Glorius and F. Dielmann, *Chem. Comm.,* 2023, **59**, 12019–12022.
58 J. Liang, J. Yin, Z. Li, C. Zhang, Di Wu and S. H. Liu, *Dyes Pigm.*, 2011, **91**, 364–369.
59 T. Arif, C. Cazorla, N. Bogliotti, N. Saleh, F. Blanchard, V. Gandon, R. Métivier, J. Xie, A. Voituriez and A. Marinetti, *Catal. Sci. Technol.*, 2018, **8**, 710–715.
60 Z. Xu, Y. Cao, B. O. Patrick and M. O. Wolf, *Chem. Eur. J.,* 2018, **24**, 10315–10319.
61 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.,* 2014, **114**, 12174–12277.
62 M. Irie, *Chem. Rev.,* 2000, **100**, 1685–1716.
63 P. R. Hania, A. Pugzlys, L. N. Lucas, J. J. D. de Jong, B. L. Feringa, J. H. van Esch, H. T. Jonkman and K. Duppen, *J. Phys. Chem. A*, 2005, **109**, 9437–9442.
64 D. H. Waldeck, *Chem. Rev.,* 1991, **91**, 415–436.
65 S. Nakamura and M. Irie, *J. Org. Chem.*, 1988, **53**, 6136–6138.
66 M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305–8309.
67 S. Fukumoto, T. Nakashima and T. Kawai, *Angew. Chem. Int. Ed.*, 2011, **50**, 1565–1568.
68 a) K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura and M. Irie, *Chem. Lett.*, 1999, **28**, 63–64; b) T. Yamaguchi and M. Irie, *J. Photochem. Photobiol. A,* 2006, **178**, 162–169.
69 M. Irie and K. Sayo, *J. Phys. Chem.*, 1992, **96**, 7671–7674.
70 M. Cipolloni, F. Ortica, L. Bougdid, C. Moustrou, U. Mazzucato and G. Favaro, *J. Phys. Chem.*, 2008, **112**, 4765–4771.
71 H. Duval, *Bull. Soc. Chim. Fr.*, 1910, **7**, 727–732.
72 W. W. Paudler, A. G. Zeiler, *J. Org. Chem.*, 1969, **34**, 3237–3239.
73 E. Tauer and R. Machinek, *Liebigs Ann. Chem.*, 1996, **1996**, 1213–1216.
74 R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Näther, F. Renth and F. Temps, *J. Am. Chem. Soc.,* 2009, **131**, 15594–15595.
75 M. Hammerich, C. Schütt, C. Stähler, P. Lentes, F. Röhricht, R. Höppner and R. Herges, *J. Am. Chem. Soc.,* 2016, **138**, 13111–13114.
76 a) Y. Wang, M. Li, C. Yan, N. Ma and Y. Chen, *CCS Chem*, 2022, **4**, 704–712; b) A. Mukherjee, M. D. Seyfried and B. J. Ravoo, *Angew. Chem. Int. Ed.,* 2023, **62**, e202304437; c) G. Cabré, A. Garrido-Charles, À. González-Lafont, W. Moormann, D. Langbehn, D. Egea, J. M. Lluch, R. Herges, R. Alibés, F. Busqué, P. Gorostiza and J. Hernando, *Org. Lett.,* 2019, **21**, 3780–3784.

77 M. Reynders, A. Chaikuad, B.-T. Berger, K. Bauer, P. Koch, S. Laufer, S. Knapp and D. Trauner, *Angew. Chem. Int. Ed.,* 2021, **60**, 20178–20183.

78 a) W. Moormann, D. Langbehn and R. Herges, *Synthesis*, 2017, **49**, 3471–3475; b) D. K. Joshi, M. J. Mitchell, D. Bruce, A. J. Lough and H. Yan, *Tetrahedron*, 2012, **68**, 8670–8676.

79 M. S. Maier, K. Hüll, M. Reynders, B. S. Matsuura, P. Leippe, T. Ko, L. Schäffer and D. Trauner, *J. Am. Chem. Soc.,* 2019, **141**, 17295–17304.

80 S. Li, N. Eleya and A. Staubitz, *Org. Lett.*, 2020, **22**, 1624–1627.

81 H. Gilman and R. M. Pickens, *J. Am. Chem. Soc.*, 1925, **47**, 2406–2416.

82 O. Galangau, L. Norel and S. Rigaut, *Dalton Trans.,* 2021, **50**, 17879–17891.

Preface to Chapter 2

As laid out in the introduction, dithienylethene photoswitches can be used for the preparation of photoswitchable phosphine ligands to control metal catalytic activity. The following chapter describes how the dithienylethene scaffold was employed to reach this objective by preparing a library of ligands bearing a diphenylphosphanyl moiety in one of the thiophene rings of the photoswitch, and various electron-withdrawing groups in the other. As a result of photoinduced dithienylethene ring-cyclization, these groups become electronically connected to each other, leading to the modulation of phosphine σ-donating ability that was found to be dependent on the strength of the introduced electron-withdrawing group both experimentally and computationally. The obtained ligands were used to prepare monometallic palladium(II) 1:2 type complexes, which preserved the capacity of their constituting dithienylethene units to photoswitch between ring-open and ring-closed states. The variation of phosphine electronic properties occurring upon photoisomerization was observed to affect the catalytic activity of these palladium(II) complexes in a model Stille coupling reaction, as higher product conversion rates were achieved with their ring-closed isomer. This experimental result could be rationalized through computational calculations, which revealed lower energy barriers for the rate-determining steps of the Stille reaction for the more catalytically active ring-closed complexes.

Chapter 2

Dithienylethene-based Photoswitchable Phosphines for Light-controlled Palladium-catalyzed Stille Coupling Reaction

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Abstract

Homogeneous transition metal catalysis is a constantly developing field of the chemical sciences. A growing interest in this area is photoswitchable catalysis, which pursues *in-situ* modulation of catalyst activity through non-invasive light irradiation. Phosphorus ligands are excellent targets to accomplish this goal by introducing photoswitchable moieties; however, only a limited number of examples has been reported so far. In this work we have developed a series of palladium complexes capable of catalyzing the Stille coupling reaction that contain photoisomerizable phosphine ligands based on dithienylethene switches. Incorporation of electron-withdrawing substituents into these dithienylethene moieties allows to vary the electron density on the phosphorus atom of the ligands upon light irradiation, which in turn leads to a modulation of the catalytic properties of the formed complexes and their activity in a model Stille coupling reaction. These results are supported by theoretical computations, which show that the energy barriers for the rate-determining steps of the catalytic cycle decrease when the photoswitchable phosphine ligands are converted to their closed state.

The author of this thesis performed the synthesis of the compounds and their characterization, conducted the photochemical experiments and the DFT calculations, did data analysis and wrote the

original text. Agustí Lledós supervised the DFT calculations. Peter Lönnecke performed single crystal X-ray analysis and interpreted the structural data. Jordi Hernando performed data analysis, supervised the project and prepared the original draft. Rosa María Sebastián and Evamarie Hey-Hawkins have supervised and administered the project. The original draft of the manuscript was proof-read by all co-authors and changed according to their suggestions.

2. 1. Introduction

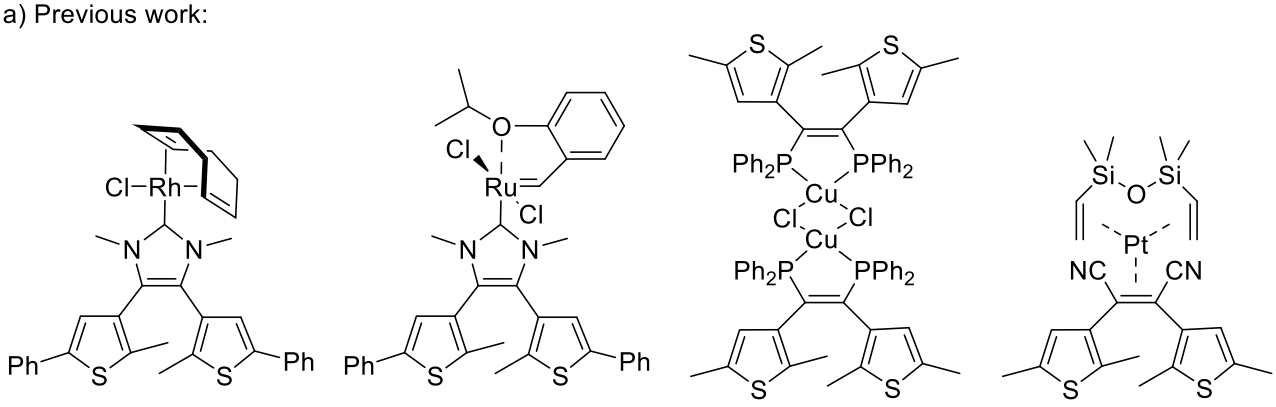
Inspired by the dynamic behavior of enzymes in nature, controlling the operation of artificial molecular catalysts with external stimuli has become an active area of research with potential application in a variety of fields[1–3] (e.g., polymer synthesis,[4,5] bioorthogonal chemistry,[6,7] and additive manufacturing[8]). The use of light to achieve this goal holds great promise, as it opens the way to non-invasive catalyst regulation on-demand with high selectivity and spatiotemporal precision.[9–11] A major strategy toward this purpose is the design of photoswitchable catalysts, whose activity and selectivity can be reversibly modulated with light by installing photochromic units into their structure – i.e., light-responsive moieties such as azobenzenes,[12,13] dithienylethenes[14] and stilbenes[12] that alter the reactivity of nearby catalytic sites by photoisomerizing between two different states.

Because of their fundamental role in modern synthetic chemistry, transition metal complexes are amongst the principal targets of photoswitchable catalysis.[15–17] Reversible light-control of the catalytic activity of these compounds is generally accomplished by introducing photochromic ligands (e.g., photoswitchable phosphines[18]). In most of the cases, the geometrical changes that these ligands undergo upon photoisomerization cause catalyst reactivity modulation;[15–17] for instance, by distorting the structure around the catalytic site[19–21] or varying the separation distance between two cooperative active metal centers.[22,23] However, the actual impact of these effects on catalytic activity and selectivity can be detrimentally affected by catalyst conformational flexibility[24] and be dependent on substrate size and geometry. An alternative, less exploited approach to light-control the performance of transition metal catalysts is to capitalize on the electronic changes that occur upon ligand photoisomerization.[15–17] For this strategy, dithienylethenes (DTE) are the photochromic units of choice[14] because, in contrast to azobenzenes and stilbenes, they undergo a large modification in electronic structure when reversibly toggling between their ring-open (**o**) and ring-closed (**c**) isomers. [25]

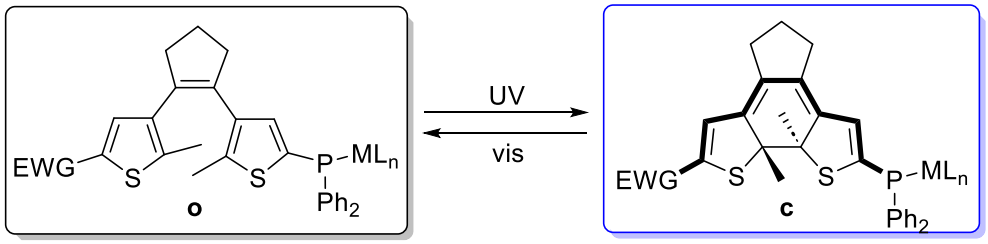
To date, only a reduced number of DTE-based complexes have been described where photomodulation of catalysis is accomplished via electronic effects.[26–29] All these systems share a common design principle: they contain DTE ligands that bind to the metal center through the groups installed in their central ethylene bridging moiety (e.g., carbene,[26,27] phosphines[28]), which are either removed[29] or lose electron density[26–28] upon ring-closing (Scheme 2-1a). In contrast, other electronic

features that accompany DTE photoisomerization are yet to be exploited in metal-based photoswitchable catalysis. In this work we propose to explore one of these additional features: the variation in electronic communication between the external thiophene substituents upon photoconversion, which has already been utilized to control chemical reactivity with light-responsive organocatalysts[30,31] and organic substrates.[32,33] In particular, herein we devised the synthesis of asymmetric DTE derivatives as photoswitchable ligands bearing (i) a metal-binding phosphine group at one thiophene ring, and (ii) an electron-withdrawing substituent at the other (Scheme 2-1b). As these two groups must be electronically insulated in the open state of the system and become selectively conjugated upon ring-closing, our molecular design should allow modulating the electron density of the phosphine ligand with light and, eventually, the catalytic activity of metal centers upon coordination. To validate this hypothesis, we prepared palladium(II) complexes of our DTE ligands and tested them as pre-catalysts in Stille coupling reaction, a widely employed Pd-catalyzed transformation that is sensitive to electronic effects[34–36] and has not been tested yet in photoswitchable catalysis.

a) Previous work:



b) This work:



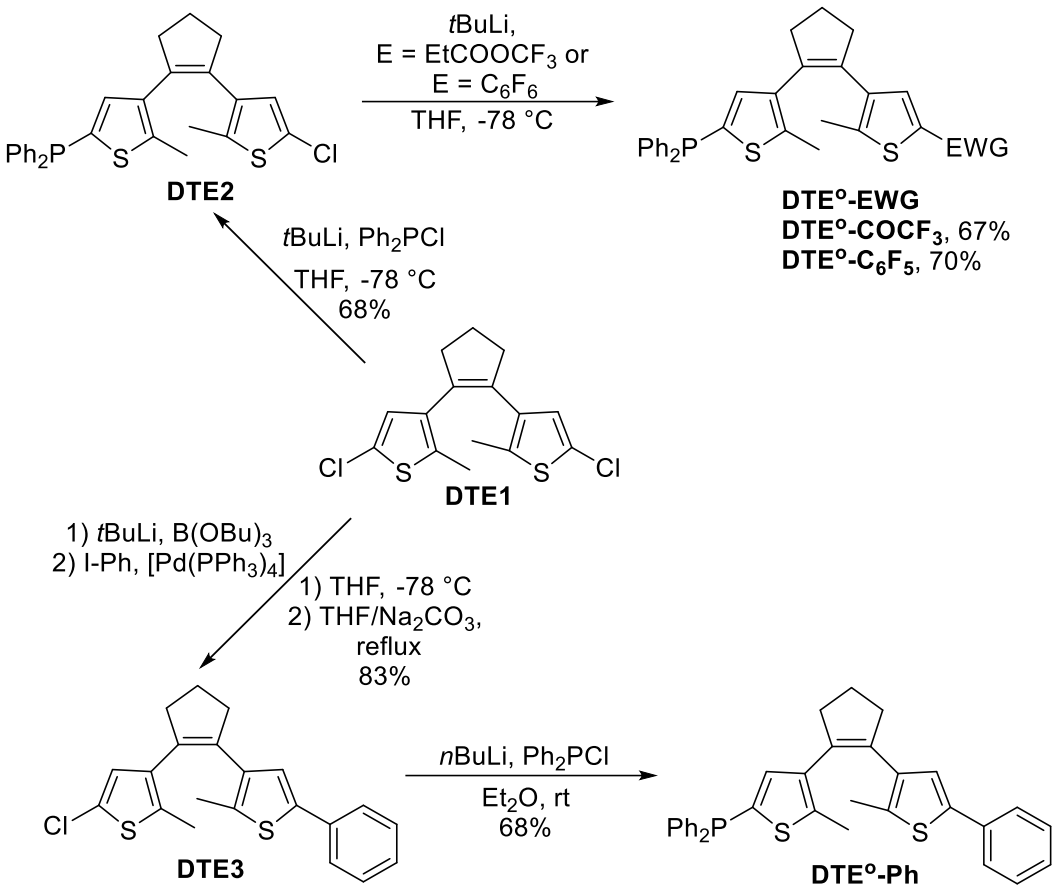
Scheme 2-1 – a) Previously reported transition metal complexes incorporating DTE-based photoswitchable units as ligands. b) DTE-based photoswitchable complexes studied in this work.

2. 2. Results and discussion

2. 2. 1. Synthesis of photoswitchable ligands and monometallic complexes

To explore our approach towards photoswitchable catalysts, two different electron-withdrawing groups (EWG) were introduced in DTE-based phosphine ligands: (i) a trifluoroacetyl group in **DTE-COCF$_3$**, which is a strong EWG according to its Hammett σ-*meta* and σ-*para* substituent constants (σ_m = 0.63, σ_p = 0.80),[37] and (ii) a pentafluorophenyl group in **DTE-C$_6$F$_5$**, which presents a less pronounced electron-withdrawing power (σ_m = 0.26, σ_p = 0.27).[37] As a reference, we also considered the preparation of a DTE-based phosphine ligand bearing a phenyl substituent (**DTE-Ph**), which should impart very minor electronic effects (σ_m = 0.06, σ_p = -0.01).[37]

The ring-open isomer of the DTE-based ligands were synthesized through asymmetrical stepwise functionalization of 1,2-bis(2-chloro-5-methylthien-4-yl)cyclopentene (**DTE1**, Scheme 2-2), which is a common precursor for the preparation of dithienylethene derivatives via lithiation-mediated processes.[38] For **DTE^o-COCF$_3$** and **DTE^o-C$_6$F$_5$**, the sequence to introduce the phosphine and EWG groups in **DTE1** was governed by their sensitivity towards lithium reagents. For this reason, we first conducted lithiation of **DTE1** with *t*-butyllithium (*t*BuLi) followed by quenching with chlorodiphenylphosphine to obtain phosphanyl compound **DTE2** (67% yield); next, additional lithiation with *t*BuLi followed by reaction with ethyl trifluoroacetate (69% yield) or hexafluorobenzene (70% yield) furnished **DTE^o-COCF$_3$** and **DTE^o-C$_6$F$_5$**, respectively. As for **DTE^o-Ph**, we inverted the order in which the external thiophene substituents were introduced to the DTE core according to a previously reported procedure.[39] In particular, its phenyl side group was first installed through consecutive lithiation, borylation and Suzuki coupling steps to produce compound **DTE3** (83% yield), which was then subjected to further lithiation with *n*-butyllithium (*n*BuLi) and subsequent treatment with chlorodiphenylphosphine (68% yield) to introduce the phosphanyl moiety of **DTE^o-Ph**. All synthesized phosphines presented a singlet in the $^{31}P\{^1H\}$ NMR spectra at around $\delta \approx$ -19.6 ppm, a chemical shift value that is similar to those reported for (2-methyl-5-thienyl)diphenylphosphine (δ = -21.9 ppm)[40] and symmetric bis(phosphine) DTE ($\delta \approx$ -20.0 ppm).[41,42] As expected, this result corroborates that the phosphanyl and electron-modulating groups in the non-planar structure of **DTE^o-COCF$_3$**, **DTE^o-C$_6$F$_5$** and **DTE^o-Ph** are not conjugated and, therefore, do not significantly affect each other.



Scheme 2-2 – Synthetic route towards phosphanyl-substituted DTEs.

When two equivalents of the phosphine ligands were used to react with *trans*-[$PdCl_2(PhCN)_2$], monometallic palladium(II) 1:2 type complexes were formed (Figure 2-1a). For all these compounds, an isolated singlet was registered in their $^{31}P\{^1H\}$ NMR spectra that shifted downfield to $\delta \approx 12$ ppm, thereby corroborating metal complexation and the formation of exclusively one isomer (*cis* or *trans*). In addition, negligible differences were found in the chemical shift of this $^{31}P\{^1H\}$ NMR signal for the three Pd complexes prepared, which again demonstrates the lack of electronic communication between the external thiophene substituents in the open isomer of the ligands. Furthermore, complexation to the Pd center could also be verified by the downfield shift of the ^1H NMR resonance of the thiophene ring proton next to the phosphanyl group. Single crystals suitable for X-ray structure determination were obtained for the three complexes, which revealed that formed Pd complexes have a square-planar geometry with *trans* orientation of the phosphine ligands (Figure 2-1b, Figures S1-S3 and Table S1 in the section §2.5). The main difference observed between the crystal structures of these compounds was the conformation of their DTE ligands. In [$PdCl_2$(**DTE^o-Ph**)$_2$] and [$PdCl_2$(**DTE^o-COCF$_3$**)$_2$], the ligands are locked in a distorted parallel open state conformation with a distance of 4.31 Å and 5.19 Å, respectively, between the carbon atoms that should react upon ring-closing photoisomerization ($C_{16} - C_{26}$). As previously described in the literature,[25] this type of conformation cannot undergo the light-induced conrotatory electrocyclization reaction to produce

the corresponding closed isomer and, consequently, no photochromism was observed in the solid state for [$PdCl_2$(**DTE°-Ph**)$_2$] and [$PdCl_2$(**DTE°-COCF$_3$**)$_2$]. Contrarily, in the case of [$PdCl_2$(**DTE°-C$_6$F$_5$**)$_2$], the DTE ligands are present in an antiparallel open state conformation with a shorter distance between the reactive carbons (C_{16} - C_{26}, 3.69 Å), two structural features that are compatible with the photoinduced ring-closing reaction.[43] Indeed, irradiation at 312 nm yielded a color change from yellow to red and the process was reversed with irradiation at 520 nm, thus demonstrating solid state photoswitching for [$PdCl_2$(**DTE°-C$_6$F$_5$**)$_2$] (Figure S4 in the section §2.5).

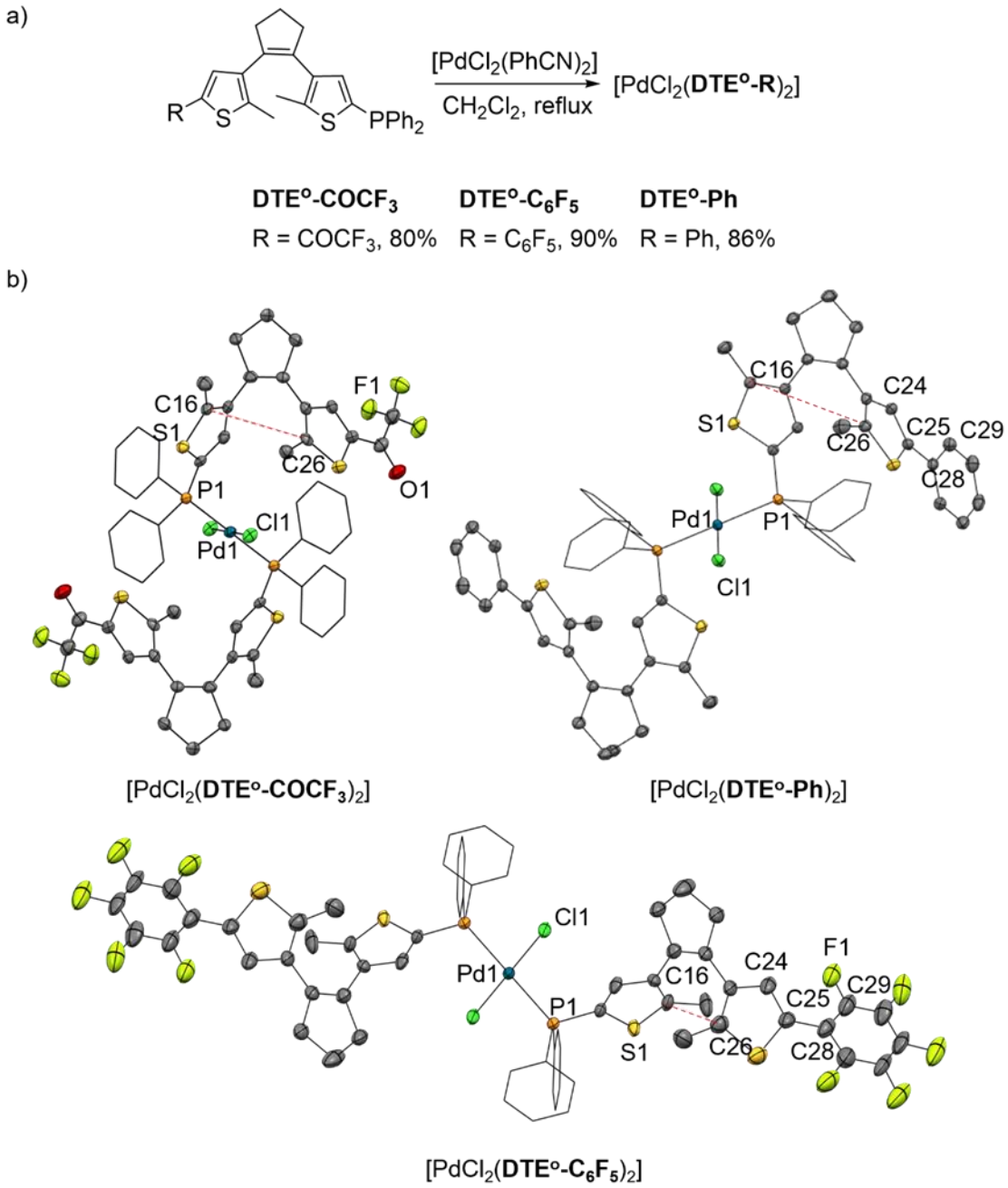
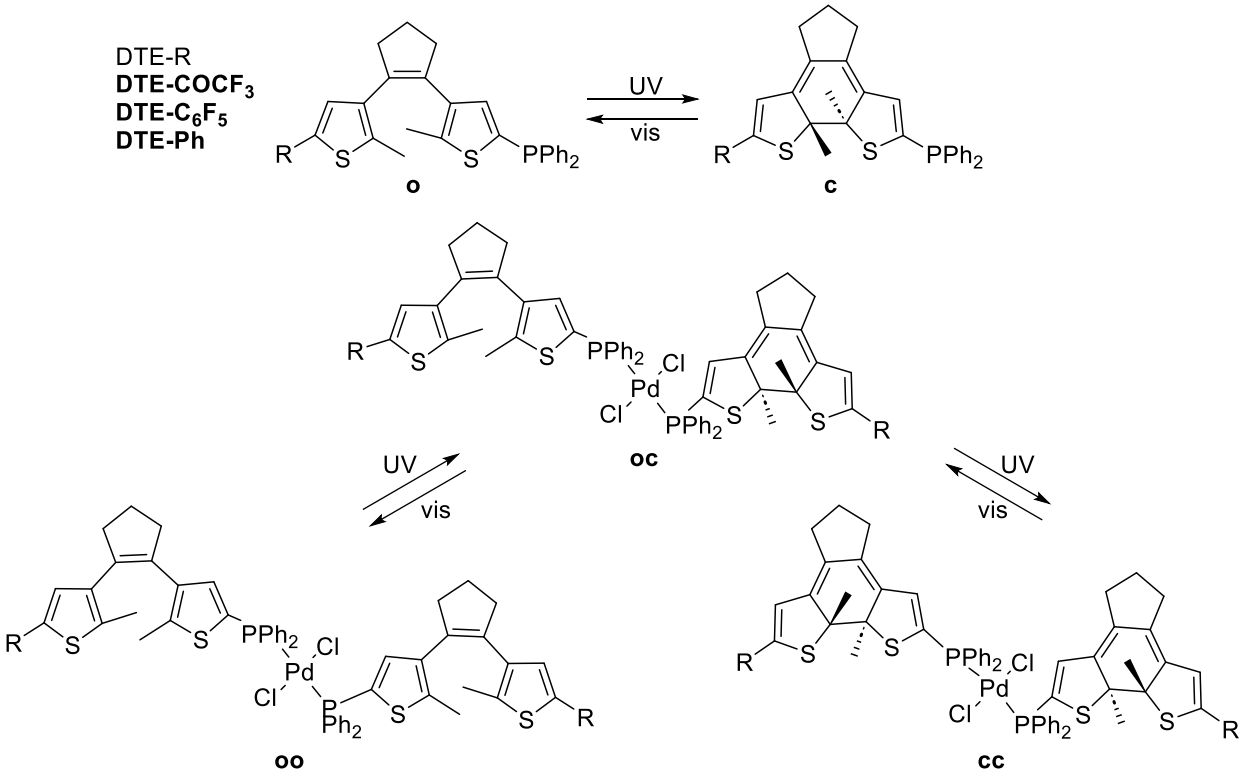


Figure 2-1 – a) Synthesis of [$PdCl_2$(**DTE°-COCF$_3$**)$_2$], [$PdCl_2$(**DTE°-C$_6$F$_5$**)$_2$] and [$PdCl_2$(**DTE°-Ph**)$_2$]. b) Molecular structures of [$PdCl_2$(**DTE°-Ph**)$_2$], [$PdCl_2$(**DTE°-COCF$_3$**)$_2$] and [$PdCl_2$(**DTE°-C$_6$F$_5$**)$_2$]. Thermal ellipsoids set at 50% probability level. For clarity, P-bound phenyl rings are depicted in wireframe style, and co-crystallized solvent

and hydrogen atoms are omitted. Distances between the reactive carbon atoms in DTE photoisomerization are marked with a dashed red line.

2. 2. 2. Photochemical behavior of ligands and complexes

Irrespective of their behavior in the solid state, all DTE-based ligands and complexes prepared should photoisomerize in solution upon irradiation. However, while **DTE-COCF$_3$**, **DTE-C$_6$F$_5$** and **DTE-Ph** should just photoconvert between their ring-open and ring-closed isomers, a more complex situation is expected for their complexes (Scheme 2-3). Because of their 2:1 phosphine:metal stoichiometry, these compounds must toggle between three different states where DTE-based ligands are both ring-open (**oo**), one of them ring-open and the other ring-closed (**oc**), or both ring-closed (**cc**).



Scheme 2-3 – Photoisomerization processes for DTE-based free ligands and their palladium(II) complexes.

To study these photoinduced processes, the UV-vis absorption spectra of the initial ring-open isomer of the synthesized DTE-based ligands and their palladium(II) complexes were first recorded in cyclohexane (Figure 2-2a-b and Figure S5 in the section §2.5). In addition, TD-DFT calculations at the CAM-B3LYP-D3/6,31G(d,p) level were performed to further investigate the electronic excitations of these compounds (Tables S2-S5 in the section §2.5), for which ground state geometries were first computed. For ligands and complexes bearing open state DTE units, we only considered their

photocyclizable antiparallel conformation in our calculations. All open state phosphine ligands were characterized by a strong absorption in the UV region with maxima around $\lambda_{abs} \approx 290$ nm, which was reproduced in computations and could be attributed to π-π^* transitions (HOMO - LUMO+1 or HOMO - LUMO) of their core (Tables S3 and S5, Figures S23 - S25 in the section §2.5). In the case of **DTE-COCF$_3$**, a shallower absorption band ranging up to $\lambda_{abs} \approx 400$ nm was detected due to the lowering of the energy of the LUMO caused by the introduction of a strong EWG (Table S2 in the section §2.5).[44] As for the UV-vis absorption of the open state Pd^{II} complexes, they did not only preserve all the spectral features of their constituting DTE^o ligands, but also exhibited a new red-shifted band with a maximum at $\lambda_{abs} \approx 350$ nm (Table S1). According to our TD-DFT calculations, this additional absorption band can be mainly assigned to a ligand-to-metal charge transfer (LMCT) transition, as the LUMO of all the open state complexes is located on the palladium center (Tables S4, S5 and Figures S26 - S28 in the section §2.5).

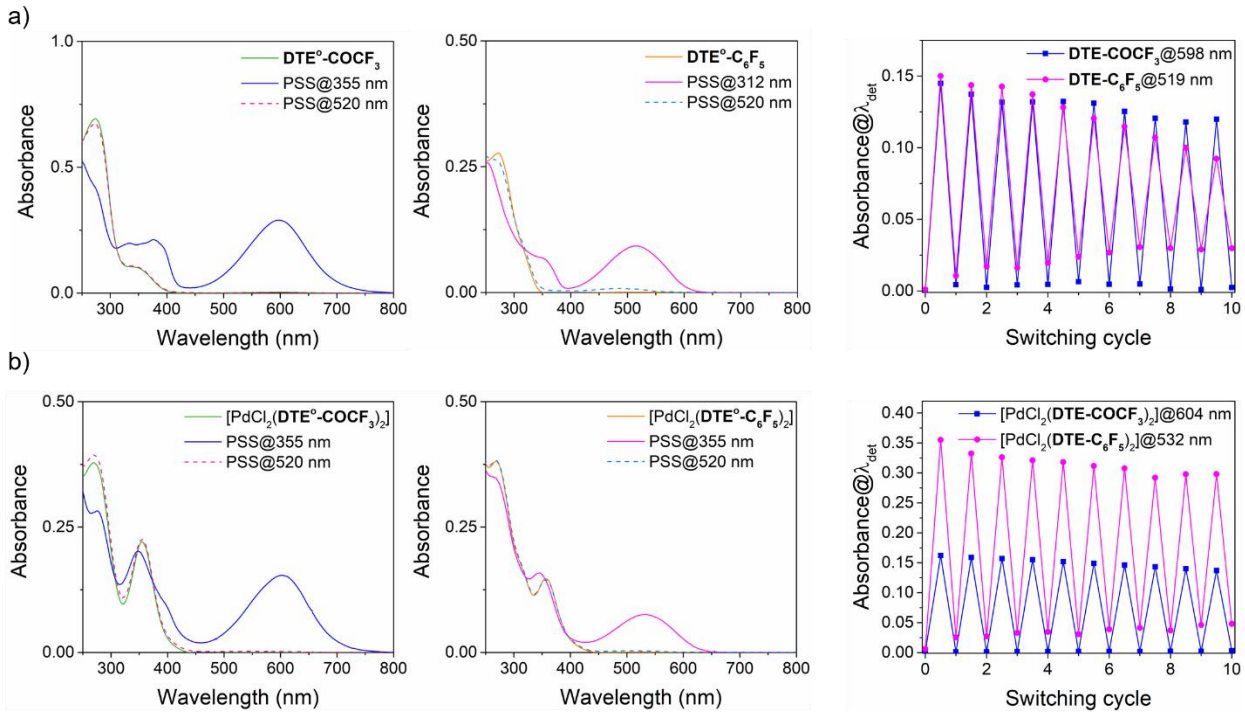


Figure 2-2 – a) Variation of the absorption spectrum of free ligands **DTE^o-COCF$_3$** ($c = 3.0 \cdot 10^{-5}$ M) and **DTE^o-C$_6$F$_5$** ($c = 1.0 \cdot 10^{-5}$ M) in cyclohexane upon sequential irradiation with UV (λ_{exc} = 355 or 312 nm) and green light (λ_{exc} = 520 nm) until the corresponding ring-closing and ring-opening photostationary states (PSSs) are obtained, respectively. The variation of the absorbance at the spectral maximum of the ring-closed isomer of these compounds (λ_{det} = 598 or 519 nm) upon 10 consecutive photoswitching cycles is also given (**DTE^o-COCF$_3$** ($c = 6.0 \cdot 10^{-6}$ M) and **DTE^o-C$_6$F$_5$** ($c = 9.0 \cdot 10^{-6}$ M)). Excitation wavelengths used are: λ_{exc} = 365/312 nm for the ring-closing and λ_{exc} = 520 nm for the ring-opening reactions. b) Variation of the absorption spectrum of the open state complexes [PdCl$_2$(**DTE^o-COCF$_3$**)$_2$] ($c = 1.2 \cdot 10^{-5}$ M) and [PdCl$_2$(**DTE^o-C$_6$F$_5$**)$_2$] ($c = 9.6 \cdot 10^{-6}$ M) in cyclohexane upon sequential irradiation with UV (λ_{exc} = 355 nm) and green light (λ_{exc} = 520 nm) until the corresponding ring-closing and ring-opening PSSs are obtained, respectively. The variation of the absorbance at the spectral maximum of the ring-closed isomer of these compounds (λ_{det} = 604 or 532 nm) upon 10

consecutive photoswitching cycles is also given ([$PdCl_2$(**DTE^o-COCF$_3$**)$_2$] (c = 1.2·10^{-5} M) and [$PdCl_2$(**DTE^o-C$_6$F$_5$**)$_2$] (c = 4.2·10^{-5} M)). Excitation wavelengths used are: λ_{exc} = 365 nm for the ring-closing and λ_{exc} =520 nm for the ring-opening reactions.

Based on the electronic absorption properties of the open state ligands and complexes, their ring-closing photoisomerization was assayed upon irradiation with UV light. For open state ligands, a broad, red-shifted absorption band emerged in the visible part of the spectrum upon UV illumination of their cyclohexane solutions, which changed from colorless to deep blue (λ_{abs} = 598 nm for **DTE^c-COCF$_3$**) or deep pink (λ_{abs} ≈ 518 nm for **DTE^c-C$_6$F$_5$** and **DTE^c-Ph**) (Figure 2-2a, Table 2-1 and Figure S5 in the section §2.5). This behavior is characteristic of closed state DTEs,[45] as confirmed by TD-DFT calculations (Table S5, Figures S23-S25 in the section §2.5) and additional NMR spectroscopic measurements. In particular, we observed the appearance of a new set of signals for the closed isomer in the ^{1}H, ^{31}P (proton-coupled and decoupled) and, when applicable, ^{19}F NMR spectra of the UV-irradiated ligands in toluene-d_8, which were upfield (^{1}H NMR) or downfield shifted (^{31}P, ^{31}P{^{1}H} and ^{19}F NMR) relative to the NMR resonances of the open state (Figures S6-S13 in the section §2.5). Analysis of this NMR data also revealed that the photocyclization reaction of DTE-based ligands was not quantitative. Instead, a photostationary state (PSS) composed of an equilibrium mixture of the ligands' **o** and **c** states was obtained in all the cases, since both isomers absorb at the UV excitation wavelength used and, therefore, should simultaneously undergo ring-closing and ring-opening reactions. Under our illumination conditions in toluene-d_8, better photocyclization conversions were observed for **DTE^o-COCF$_3$** (91% at λ_{exc} = 365 nm) and **DTE^o-C$_6$F$_5$** (81% at λ_{exc} = 312 nm) relative to **DTE^o-Ph** (39% at λ_{exc} = 312 nm) (Table 1). This can be ascribed to the lower ring-closing quantum yield and high photodegradation tendency of **DTE-Ph**, which limited the UV exposure time for photocyclization and led to a lower percentage of closed isomer.

Table 2-1 – Photochemical properties of DTE-based ligands and complexes.

	λ_{abs}^{o} [nm] (ε [M^{-1} cm^{-1}])[a]	λ_{abs}^{c} [nm] (ε [M^{-1} cm^{-1}])[b]	PSS_{o-c} composition [%][c]	Φ_{o-c}[d]	Φ_{c-o}[e]
DTE-$COCF_3$	268 (35 673), 339 (6 431)	598 (12 261)	91:9	0.480	0.012
[$PdCl_2$(**DTE-$COCF_3$**)$_2$]	271 (34 149), 355 (19 065)	604 (18 870)	45:45:10	0.148/ 0.048	0.013/ 0.014
DTE-C_6F_5	272 (28 303)	519 (11 379)	81:19	0.530	0.015
[$PdCl_2$(**DTE-C_6F_5**)$_2$]	268 (40 394), 357 (14 367)	532 (19 391)	25:45:30	0.047/ 0.019	0.015/ 0.018
DTE-Ph	273 (28 117)	518 (13 673)	39:61	0.485	0.011
[$PdCl_2$(**DTE-Ph**)$_2$]	270 (42 700), 359 (15 400)	538 (16 310)	27:44:29	0.060/ 0.023	0.015/ 0.014

[a] Wavelength and molar absorptivity coefficient of the absorption band maxima of the open isomer (for complexes, **oo** state) in cyclohexane. [b] Wavelength and molar absorptivity coefficient of the maximum of the visible absorption band of the closed isomer (for complexes, **cc** state) in cyclohexane. [c] Composition of the PSS reached for the photocyclization process in toluene-d_8 upon irradiation at λ_{exc} = 365 nm (**DTE-$COCF_3$** and all the complexes) or 312 nm (**DTE-C_6F_5** and **DTE-Ph**). DTE^{c}:DTE^{o} and DTE^{cc}:DTE^{oc}:DTE^{oo} concentration ratios are given for free ligands and complexes, respectively. [d] Photocyclization quantum yields measured in cyclohexane at λ_{exc} = 355 nm (**DTE-$COCF_3$** and all the complexes) or 312 nm (**DTE-C_6F_5** and **DTE-Ph**). For the complexes, separate Φ_{o-c} values are given for the **oo** $\rightarrow$ **oc** and **oc** $\rightarrow$ **cc** ring-closing processes. [e] Photocycloreversion quantum yields measured in cyclohexane at λ_{exc} = 532 nm. For the complexes, separate Φ_{c-o} values are given for the **cc** $\rightarrow$ **oc** and **oc** $\rightarrow$ **oo** ring-opening processes.

Similar to free DTE ligands, irradiation of the Pd^{II} complexes in cyclohexane with UV light also caused the appearance of an absorption band in the visible part of the spectrum and a concomitant color change (Figure 2-2b, Table 2-1 and Figure S5 in the section §2.5). In combination with NMR spectroscopic measurements in toluene-d_8 and TD-DFT calculations, it was demonstrated that DTE photocyclization takes place in the complexes, in contrast to some previously reported DTE-based phosphine-metal compounds.[39,46] However, palladium(II) complexation did have a relevant effect on the UV-induced ring-closing process of the phosphine ligands. First, we could use less energetic UV radiation to promote the photocyclization of [$PdCl_2$(**DTE^{o}-C_6F_5**)$_2$] and [$PdCl_2$(**DTE^{o}-Ph**)$_2$] (λ_{exc} = 365 nm) compared to **DTE^{o}-C_6F_5** and **DTE^{o}-Ph** (λ_{exc} = 312 nm). Second, a bathochromic shift of the absorption band of the closed isomer in the visible range was registered relative to the free ligands (λ_{abs} = 604, 532 and 538 nm for [$PdCl_2$(**DTE^{c}-$COCF_3$**)$_2$], [$PdCl_2$(**DTE^{c}-C_6F_5**)$_2$] and [$PdCl_2$(**DTE^{c}-Ph**)$_2$]) (Figure 2-2a-b, Table 2-1 and Figures S26-S28 in the section §2.5). According to

TD-DFT calculations, this effect is due to the stabilization (decrease) of the HOMO-LUMO gap of DTE-based phosphines upon Pd^{II} complexation, which should be especially important for **DTE-C_6F_5** and **DTE-Ph**, as experimentally observed (Table S2 in the section §2.5). On the other hand, the spectral features of the closed DTE absorption band were not influenced by the state of the nearby DTE ligand in the same complex (open or closed) – i.e., it did not evolve when photoconverting from the **oc** species with one open and one closed DTE unit to the fully closed **cc** complex, which was substantiated by TD-DFT calculations (Figures S26-S28 in the section §2.5). As a result, these two different photocyclization products could only be discriminated by NMR spectroscopic experiments, which proved that they were sequentially formed upon UV irradiation and allowed determining the composition of the equilibrium PSS generated in toluene-d_8 (Table 2-1 and Figures S14-S22 in the section §2.5). From this analysis we could conclude that metal complexation detrimentally affected the photocyclization conversion of **DTE^o-$COCF_3$** and **DTE^o-C_6F_5**, as only 66% and 48% of the DTE units in $[PdCl_2$(**DTE^o-$COCF_3$**$)_2]$ and $[PdCl_2$(**DTE^o-C_6F_5**$)_2]$ could be ring-cycled. This result is consistent with the lower photocyclization quantum yields ($\Phi_{o\text{-}c}$) measured for both the **oo** and **oc** states of the complexes relative to the free ligands (Table 2-1), which can be attributed to two main effects: (i) the competition between photoisomerization and ligand-to-metal charge transfer, which, as previously mentioned, gives rise to additional absorption bands in the UV region of the complexes, at which they are excited to promote photocyclization; and (ii) the further reduction of $\Phi_{o\text{-}c}$ for the second ring-closing step in the complexes, a behavior already reported for other DTE dimers,[47] which can be ascribed to intramolecular energy transfer between the open and closed DTE units in the **oc** state upon photoexcitation - i.e., the photocyclization of one of these units severely hinders the ring-closing reaction for the second DTE group.

Once photocyclized with UV light, the closed states of the DTE-based ligands and their palladium(II) complexes were found to be thermally stable in solution and no spontaneous back-isomerization was detected in the dark at room temperature. Accordingly, visible irradiation (λ_{exc} = 520 nm) was applied to promote photoinduced ring-opening of these compounds and to demonstrate the reversibility of their photoswitching behavior in solution. For all of them, complete disappearance of the visible absorption band associated with the closed isomer was registered, which demonstrates quantitative photochemical cycloreversion regardless of metal complexation (Figure 2-2a-b and Figures S5, S14, S17-S19 and S21 in the section §2.5). This is due to the selective photoexcitation of closed-state DTEs with visible light that counterbalances their commonly low ring-opening quantum yields,[25] as we also measured herein for the ligands and the **cc** and **oc** states of the complexes ($\Phi_{c\text{-}o}$ < 0.02, Table 2-1). In spite of this, some residual visible absorption was registered for some of these compounds upon light-induced photocyclization reversion (**DTE-C_6F_5** in Figure 2-2a; **DTE-Ph** and $[PdCl_2$(**DTE-Ph**$)_2]$ in Figure S5 in the section §2.5), which could not be attributed to unreacted closed state species. Instead, it arose from DTE photodegradation, which is normally associated with the UV irradiation of the closed isomer during photocyclization and leads to a characteristic product that absorbs at $\lambda_{abs} \approx 500$ nm.[48] This effect was further proven by an

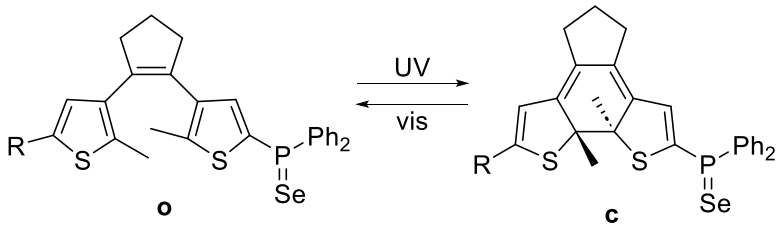
examination of the fatigue resistance of ligands and complexes upon repetitive photoinduced ring-closing and ring-opening cycles in cyclohexane (Figure 2-2a-b and Figure S5 in the section §2.5). Although some deterioration of their photoswitching behavior was eventually observed for all these compounds, the highest photodegradation effects were registered for **DTE-Ph**, **DTE-C_6F_5**, and [$PdCl_2$(**DTE-Ph**)$_2$]. We ascribe these results to two main factors that increase the photostability of the remaining ligands and complexes: (i) the presence of the strong trifluoroacetyl EWG at the external position of the thiophene ring which is known to slow down DTE photodegradation;[48] and (ii) the use of less energetic UV light to photoisomerize the palladium(II) complexes relative to the free ligands. Consequently, the target compounds [$PdCl_2$(**DTE-$COCF_3$**)$_2$] and [$PdCl_2$(**DTE-C_6F_5**)$_2$] showed the highest resistance to photodegradation.

2. 2. 3. Photomodulation of the properties of the phosphine ligand

As anticipated by molecular design and demonstrated by ^{31}P (proton-coupled and decoupled) NMR spectroscopic measurements discussed above, the phosphanyl and electron-modulating groups of the synthesized DTE-based ligands are electronically decoupled in their open state. As a result, these ligands should present similar binding properties to metals, a behavior that we aimed to modulate upon photoisomerization. In fact, UV-induced ligand ring-closing caused a measurable downfield shift of the ^{31}P and ^{31}P{^{1}H} NMR signal of these compounds ($\Delta\delta$ = 9.4, 8.2 and 8.3 ppm for **DTE-$COCF_3$**, **DTE-C_6F_5** and **DTE-Ph**, respectively), thus suggesting a change in the electronic properties of their phosphine groups that might be dependent on the nature of the external substituent present in the other thiophene of the DTE core. In particular, introduction of electron-withdrawing substituents such as trifluoroacetyl and pentafluorophenyl to phosphines is expected to: (i) increase the *s* character of the lone pair of electrons at the phosphorus atom involved in σ bonding to metals, while (ii) stabilizing and enlarging the size of the phosphine's σ* antibonding orbital participating in metal π backbonding.

A well-established method to assess such an effect for phosphines is to measure the spin-spin coupling constant between ^{31}P and ^{77}Se ($^1J_{P,Se}$) for the corresponding selenide derivatives (Scheme 2-4),[39,41] which were prepared by heating the ligands and grey selenium in $CDCl_3$. In these compounds, $^1J_{P,Se}$ values depend on the *s* character of the P=Se bond, which is related to the electronic character and size of the substituents on the phosphorus atom.[49–51] Consequently, they provide an estimate on the σ-donating ability of phosphines, which is lower for higher values of $^1J_{P,Se}$. For the open state selenides of **DTE-$COCF_3$**, **DTE-C_6F_5** and **DTE-Ph**, measured $^1J_{P,Se}$ values are almost identical and match the reported coupling constant for the selenide of (2-methyl-5-thienyl)diphenylphosphine ($^1J_{P,Se}$ = 733 Hz) [40] (Scheme 2-3). Again, this result corroborates that the two thiophenes in DTE structures are electronically isolated and, for that reason, their phosphanyl groups have similar electronic properties. In contrast, as ring-closing extends the conjugation throughout the DTE

moiety, the electron density on the phosphorus atom should decrease and can be affected by the external substituent in the other thiophene ring with which it communicates. This behavior was indeed proven by NMR measurements of the closed selenide isomers: higher $^1J_{P,Se}$ values were detected relative to the open isomers with increments ($\Delta^{c\text{-}o}(^1J_{P,Se})$) that scaled up with the electron-withdrawing nature of the electron-modulating substituents (Scheme 2-3, Table 2-2) - i.e., the studied phosphines became electron-poorer upon photocyclization and introduction of a stronger EWG in the opposite thiophene ring. Thus, the highest value of $\Delta^{c\text{-}o}(^1J_{P,Se})$ was registered for the selenide of **DTE-COCF$_3$** ($\Delta^{c\text{-}o}(^1J_{P,Se})$ = 14 Hz), which equals the best results reported for the DTE-based phosphine ligands[39,41] and mimics the electronic effects caused by substituting one phenyl ring in triphenylphosphine for a *tert*-butyl group.



(Se)**DTE-R**	$^1J_{P,Se}$	(Se)**DTE-R**	$^1J_{P,Se}$
(Se)**DTE-COCF$_3$**	734 Hz	(Se)**DTE-COCF$_3$**	748 Hz
(Se)**DTE-C$_6$F$_5$**	734 Hz	(Se)**DTE-C$_6$F$_5$**	741 Hz
(Se)**DTE-Ph**	733 Hz	(Se)**DTE-Ph**	738 Hz

Scheme 2-4 – Variation of $^1J_{P,Se}$ in the open and closed isomers of the selenides of **DTE-COCF$_3$**, **DTE-C$_6$F$_5$** and **DTE-Ph**.

To further investigate the photomodulation of the electronic features for the prepared DTE-based phosphines, we analyzed a set of properties derived from the DFT calculations of their ground state structures. As a first step, we considered the variation of the Mulliken charges on the phosphorus atom ($\Delta^{c\text{-}o}(q_P^{Mulliken})$) and the percentage of *s* character of the lone pair of electrons at phosphorus ($\Delta^{c\text{-}o}(\%s_P)$) for open anti-parallel and closed conformations of **DTE-COCF$_3$**, **DTE-C$_6$F$_5$** and **DTE-Ph** (Table 2-2). According to the Mulliken charges, photocyclization decreases electron density on phosphorus, while through NBO analysis[52] we can anticipate an increase in *s* orbital participation in the phosphorus lone pair of electrons. More importantly, the variation of these parameters was found to increase with the electron-withdrawing power of the introduced electron-modulating group, thus again validating that **DTE-COCF$_3$** and, to a lesser extent, **DTE-C$_6$F$_5$** suffer the largest change in phosphine's electronic properties upon photoisomerization.

As a second step, the effect of the light-induced modulation of the DTE-based phosphine ligands on the bond energy in their Pd^{II} complexes was investigated computationally. For this, we analyzed the difference in phosphine-Pd^{II} binding energy ($\Delta^{c\text{-}o}(BE_{P\text{-}Pd})$) between the **oo** and **cc** isomers of their 2:1 *trans*-phosphine palladium(II) complexes (Table 2-2). As expected, due to the loss of the

phosphine's σ-donating ability, a varying decrease in $BE_{P\text{-}Pd}$ for the complexes bearing ring-closed DTE ligands is observed, depending on the nature of the introduced electron-modulating group. Thus, weakening of the phosphine-palladium(II) binding upon photocyclization was observed for the ligands bearing the electron-withdrawing pentafluorophenyl and, especially, trifluoroacetyl substituents, as we initially devised.

Table 2-2 – Experimental and computed parameters to estimate the photomodulation of the properties of the phosphine ligands **DTE-COCF$_3$**, **DTE-C$_6$F$_5$** and **DTE-Ph**.

	Free ligands			Pd^{II} complexes[a]
	$\Delta^{c\text{-}o}(^1J_{P,Se})$ [Hz][b]	$\Delta^{c\text{-}o}(q_P^{Mulliken})$[c]	$\Delta^{c\text{-}o}(\%s_P)$[d]	$\Delta^{c\text{-}o}(BE_{P\text{-}Pd})$ [kcal·mol^{-1}][e]
DTE-COCF$_3$	14	0.014	0.79	-1.98
DTE-C$_6$F$_5$	7	0.004	0.42	-0.92
DTE-Ph	5	<0.001	0.34	-0.64

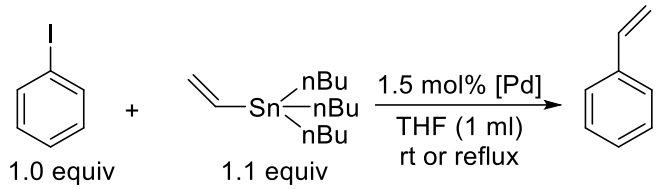
[a] *trans*-[$PdCl_2$(**DTE-COCF$_3$**)$_2$], *trans*-[$PdCl_2$(**DTE-C$_6$F$_5$**)$_2$] and *trans*-[$PdCl_2$(**DTE-Ph**)$_2$]. [b] Difference in $^1J_{P,Se}$ for the corresponding selenides measured in $CDCl_3$. [c] Difference in Mulliken charges in electronic units on the phosphorus atom. [d] Difference in percentage of *s* character of the phosphorus lone pair of electrons. [e] Difference in phosphine-Pd^{II} bond energy (per one bond) between the **oo** and **cc** isomers.

2. 2. 4. Catalytic studies

Among the vast range of Pd-catalyzed reactions, Stille coupling was chosen to evaluate the activity of the open and closed state of the prepared metal complexes. For this reaction, previous mechanistic studies have established that bulky phosphines accelerate the rate of the oxidative addition while electron-poor phosphines are advantageous for the transmetallation step.[36,53,54,55] This makes Stille coupling a suitable benchmark process to validate our model towards photoswitchable catalysis, as we have proven above that the electron density on the DTE-based phosphines developed herein can be modulated upon photoisomerization. With this aim, the palladium(II) complexes were tested as pre-catalysts for the Stille reaction between iodobenzene and tributylvinylstannane in THF-d_8 at two different temperatures (room temperature and 50 °C) (Table 2-3). In all the cases, catalytic experiments were conducted in the dark and separately for the pure **oo** complexes and for **cc**-enriched mixtures of isomers. Because of the moderate efficiency of **oo**-to-**cc** photocyclization in the complexes (see Table 2-1), we maximized the relative amount of **cc** species in such mixtures by first ring-closing the corresponding free ligand and then conducting metal complexation (see Experimental section). In this way, **cc**-enriched pre-catalyst mixtures contained 52, 38 and 49% of the **cc** isomers for [$PdCl_2$(**DTE-COCF$_3$**)$_2$], [$PdCl_2$(**DTE-C$_6$F$_5$**)$_2$] and [$PdCl_2$(**DTE-Ph**)$_2$], respectively (Figures S29-S31 in the section §2.5). To compare the catalytic efficiency of these mixtures with those of their **oo** samples, we monitored the kinetics of the Stille

reaction for 6 h and measured the difference in product formation after this time (entries 1-6 and 8-13 in Table 2-3, Figure S32 in the section §2.5). In addition, equivalent measurements were performed using $[PdCl_2(PPh_3)_2]$ (entries 7 and 14 in Table 2-3) as a non-light responsive reference pre-catalyst, which in most of the cases turned out to be less efficient than our DTE-based complexes.

Table 2-3 – Comparison of the investigated complexes as pre-catalysts in the Stille coupling reaction.



Entry	Pre-catalyst [Pd]	State[a]	T (°C)	Yield (%)[b]	Entry	T (°C)	Yield (%)[b]
1	$[PdCl_2(\mathbf{DTE\text{-}COCF_3})_2]$	**oo**	25	4.5	8	50	36.4
2		**cc**		8.8	9		48.9
3	$[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$	**oo**		21.2	10		42.5
4		**cc**		29.5	11		59.6
5	$[PdCl_2(\mathbf{DTE\text{-}Ph})_2]$	**oo**		13.4	12		53.8
6		**cc**		14.2	13		43.4
7	$[PdCl_2(PPh_3)_2]$			9.8	14		28.0

[a] **cc** state here is a closed state enriched pre-catalyst complex as specified above. [b] The average yields of two repetitions were determined by ^{1}H NMR spectroscopy using 1,3,5,-trimethoxybenzene as a standard.

As shown in Table 2-3, two different behaviors were observed in the catalytic tests. For complexes bearing DTE units with external electron-withdrawing substituents, large increments in yields for the Stille coupling at 6 h were registered for the **cc**-enriched mixtures compared to the **oo** complexes: 94% (relative increment from entry 1 to entry 2) and 34% (relative increment from entry 8 to entry 9) for $[PdCl_2(\mathbf{DTE\text{-}COCF_3})_2]$ at room temperature and 50 °C, respectively, and ~ 40% for $[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$ (relative increments from entries 3 to 4 and 10 to 11) both at room temperature and 50 °C. By contrast, DTE photocyclization did not enhance the Stille coupling efficiency for $[PdCl_2(\mathbf{DTE\text{-}Ph})_2]$ which is lacking the electron-withdrawing substituent on the DTE core. In this case, similar reaction conversions were measured for the **oo** complex and **cc**-enriched mixture at room temperature (entries 5 and 6), while we observed a decrease in reactivity upon ring-closing at 50 °C (entries 12 and 13). Importantly, these results are in agreement with the prediction made to accomplish photoswitchable catalysis by installing external EWGs in DTE-based phosphines. Upon photocyclization, the electron-withdrawing and phosphanyl substituents become selectively

conjugated in these compounds, thus varying the electronic properties of the phosphine ligand and affecting the catalytic behavior of its metal complexes. Unfortunately, the catalytic modulation accomplished in this way is limited by the non-quantitative nature of DTE photocyclization, which prevented us from conducting experiments with pure **cc** pre-catalysts.

To rationalize the modulation of Stille coupling reactivity determined for the open and closed states of [$PdCl_2$(**DTE-COCF$_3$**)$_2$] and [$PdCl_2$(**DTE-C$_6$F$_5$**)$_2$], we conducted additional DFT calculations. For this, we considered the Stille reaction mechanism,[36,56] which requiers reduction of the palladium(II) pre-catalyst to palladium(0) before the catalytic cycle begins. Similar to other palladium-catalyzed couplings, the catalytic cycle consists of three major steps: oxidative addition, transmetallation and reductive elimination,[57] among which the first two are typically the rate-determining steps when aryl halides are used as substrates (Figure 2-3).[35,58] Over the years, various pathways have been proposed for each of these steps. On the one hand, the oxidative addition of the organic electrophile to Pd^0 can occur through a monophosphine pathway, an associative displacement pathway, and a bisphosphine pathway.[59,60] Principally, the presence of bulky ligands should favor oxidative addition *via* a monoligated transition state owing to steric repulsion.[61] Nevertheless, it was recently established that intramolecular dispersion forces can serve to stabilize a bisligated transition state for bulky ligands such as P*t*Bu$_3$,[62] thus demonstrating the importance of incorporating dispersion effects into the analysis. Accordingly, we explored both types of pathways in our computations. As for the transmetallation step, it can also proceed through three different mechanisms: cyclic, open and ionic.[58] In our calculations we only considered the first of these cases, as halides are considered to be good bridging ligands that facilitate the formation of cyclic transitions states; in contrast, open and ionic mechanisms are preferred in the case of poorly coordinating anionic ligands and highly polar solvents. Finally, the reductive elimination step can also proceed through bisligated and monoligated transition states.[58] For simplicity, herein we only explored the second of these options and did not compute the bisligated pathway.

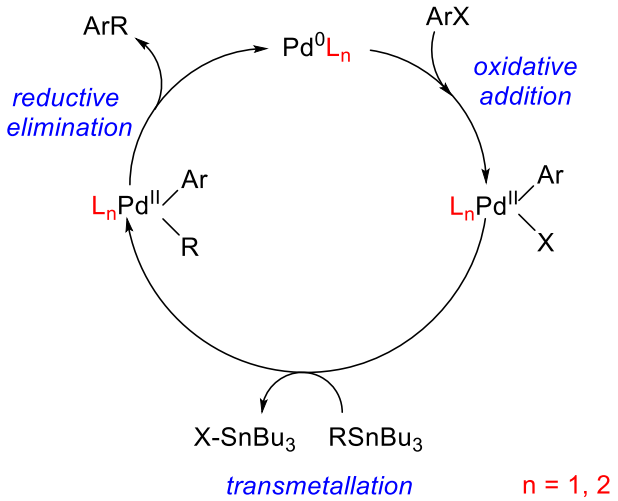


Figure 2-3 – General catalytic cycle for the palladium-catalyzed Stille coupling reaction.

Based on these mechanistic assumptions, we computed the catalytic cycle of the Stille coupling reaction investigated experimentally. Calculations were carried out for complexes formed with the ligand **DTE-COCF$_3$**, as it should impart the strongest electronic effects upon photoisomerization. Three possible states of the **DTE-COCF$_3$**-based Pd^0 catalyst were considered in these calculations: [Pd(**DTE^o-COCF$_3$**)$_2$], [Pd(**DTE^o-COCF$_3$**)(**DTE^c-COCF$_3$**)], and [Pd(**DTE^c-COCF$_3$**)$_2$] (Figure 2-4, Figures S33-S35 and Table S6 in the section §2.5). Reaction intermediates and transition states were computed at the B3LYP-D3 level of theory, with additional computational details provided in the section §2.5. The Gibbs free energies of the species at 298 K are presented relative to the zero point consisting of the corresponding bisligated palladium(0) complex (**0**, Figure 2-4), phenyl iodide and tributylvinyltin. For the oxidative addition step, the monophosphine pathway was found to be disfavored, as phosphine ligand dissociation was computed to have a high energy requirement (> 20 kcal/mol, Figures S34-S35 in the section §2.5). It is worth noting, however, that the energy barrier for the dissociation of the closed-state ligand from the **cc** (23.1 kcal/mol) and **oc** (26.8 kcal/mol) species is lower than for the dissociation of the open ligand from the **oo** (25.8 kcal/mol) and **oc** (27.3 kcal/mol) states of the catalyst, thus, corroborating our predictions on the effect of the **DTE-COCF$_3$** isomerization state on the stability of the phosphine-palladium bond. The bisphosphine oxidative addition pathway was found to be preferred as it proceeds through the less energetic three-center transition state **TS1**, which is accessed through previous intermediate **1** (Figure 2-4). Among the transition states **TS1** computed for three different catalytic systems, the lowest energy values are associated with the **cc** and **oc** states, at 7.4 and 7.8 kcal/mol, respectively, while the **oo** isomer requires 10.6 kcal/mol. As the transition state for the oxidative addition of the bisligated complex leads to the formation of the fully coordinated *cis*-coordinated Pd^{II} species **2**, ligand dissociation is a prerequisite for subsequent steps, which was found to be slightly less energy demanding for the **cc** system (13.2 kcal/mol for **cc** species vs 14.4 kcal/mol for **oo** species). Then, formed intermediate **3** isomerizes through the transition state **TS3** (energy barrier ≈ 2.8-4.7 kcal/mol), and upon stannane coordination, transmetallation takes place with the highest energy barrier among all the steps. In particular, the energy barrier for the cyclic transition state **TS5** involving the closed-state Pd^0 species is 13.5 kcal/mol, which is lower than for the open-state catalytic system (15.4 kcal/mol). Lastly, reductive elimination of the intermediate **6** was observed to take place through the transition state **TS7**, with an energy barrier difference of only 0.3 kcal/mol between the closed- and open-state isomers. In conclusion, our computational analysis revealed that the barriers for the most energy-demanding steps of the investigated Stille coupling reaction, i.e., oxidative addition, ligand dissociation and transmetallation – are lower for the catalytic palladium species bearing closed-state **DTE-COCF$_3$** ligands. This is in agreement with our experimental results, which showed higher catalytic activity for the **cc**-enriched state of the [$PdCl_2$(**DTE-COCF$_3$**)$_2$] pre-catalyst. Nevertheless, the differences in energy barriers computed for the open- and closed-state isomers of the system along the catalytic cycle are moderate (≈ 1-3 kcal/mol), which in combination with incomplete DTE

photocyclization should account for the limited modulation of reactivity accomplished in our experiments.

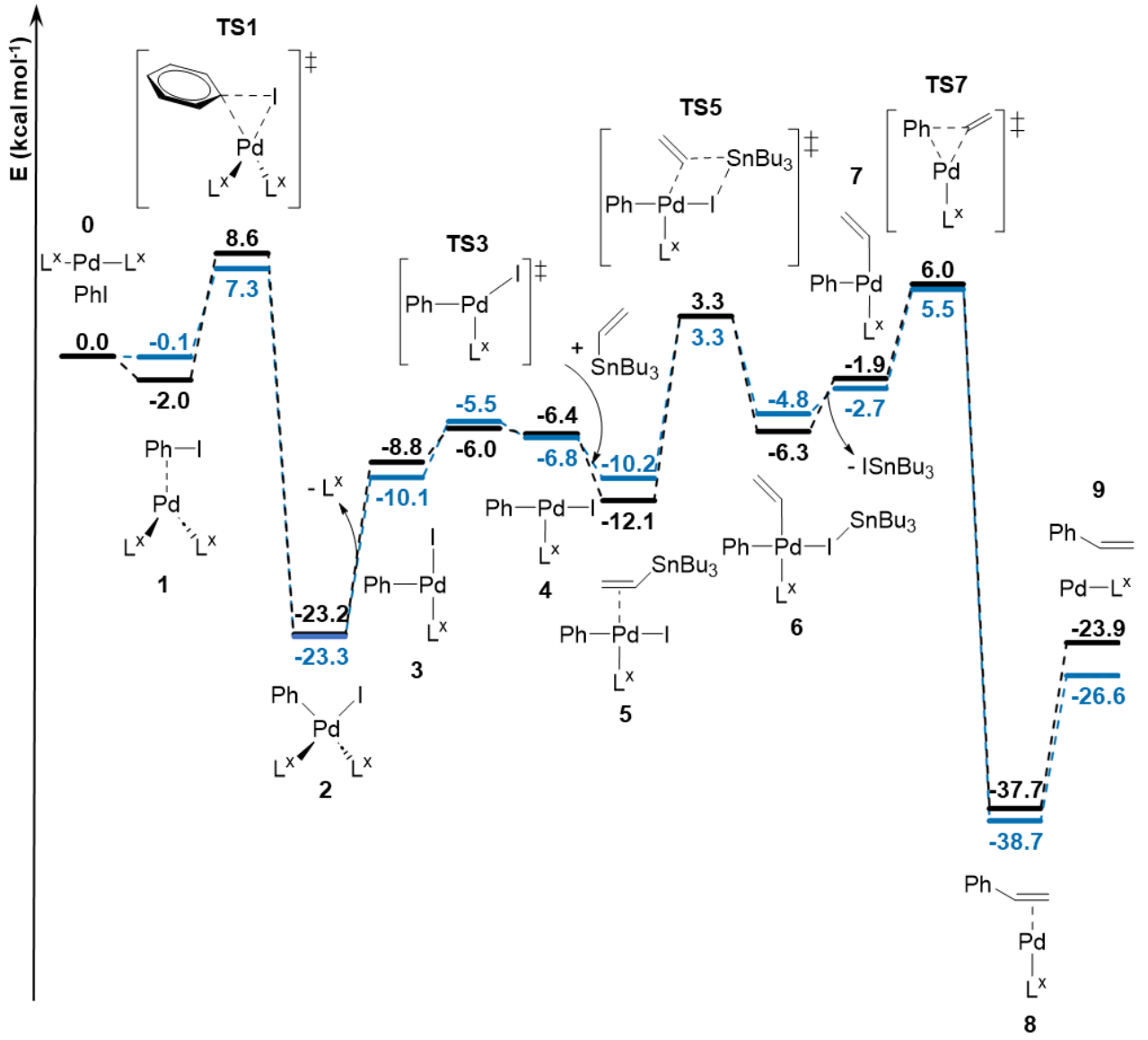


Figure 2-4 – Calculated Gibbs energy profile for the Stille coupling reaction in solution (THF) using [$PdCl_2$(**DTE^o-COCF$_3$**)$_2$] or [$PdCl_2$(**DTE^c-COCF$_3$**)$_2$] as a pre-catalyst, where L^x is **DTE^o-COCF$_3$** (black line) or **DTE^c-COCF$_3$** (blue line).

2. 3. Conclusions

Dithienylethenes were used to prepare the photoisomerizable phosphine ligands **DTE-COCF$_3$** and **DTE-C$_6$F$_5$**, where the electronic communication between the phosphorus atom and electron-withdrawing groups is switched on and off by reversible open- to closed-state conversion. As a result, the σ-donating ability of these phosphines can be efficiently modulated upon light irradiation, in agreement with DFT calculations, improving the behavior observed for the analogous **DTE-Ph** ligand

bearing an EWG-free dithienylethene moiety. Interestingly, when coordinated to palladium(II), the resulting bisphosphine complexes preserve ligand's capacity to undergo ring-cyclization under illumination, albeit resulting in incomplete phototransformation into their dual closed-state isomer. Finally, when testing the synthesized complexes as pre-catalysts in the Stille coupling reaction between phenyl iodide and tributylvinyltin, a clear modulation in reaction rate was observed upon photoisomerization of the compounds bearing **DTE-COCF$_3$** and **DTE-C$_6$F$_5$** ligands. In particular, the catalytic activity of the complexes increased for the closed state of these ligands, which could be rationalized by DFT calculations. Therefore, these results validate our molecular design towards photoswitchable catalysis, which can be extended to other metals and reactions in the future.

2. 4. References

1 Blanco, V.; Leigh, D. A.; Marcos, V. Artificial switchable catalysts. *Chem. Soc. Rev.* **2015**, *44* (15), 5341–5370.

2 Aubert, S.; Bezagu, M.; Spivey, A. C.; Arseniyadis, S. Spatial and temporal control of chemical processes. *Nat. Rev. Chem.* **2019**, *3* (12), 706–722.

3 Thaggard, G. C.; Haimerl, J.; Fischer, R. A.; Park, K. C.; Shustova, N. B. Traffic Lights for Catalysis: Stimuli-Responsive Molecular and Extended Catalytic Systems. *Angew. Chem. Int. Ed.* **2023**, *62* (29), e2023028.

4 Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W. Switchable Polymerization Catalysts. *Chem. Rev.* **2016**, *116* (4), 1969–1992.

5 Ihrig, S. P.; Eisenreich, F.; Hecht, S. Photoswitchable polymerization catalysis: state of the art, challenges, and perspectives. *Chem. Commun.* **2019**, *55* (30), 4290–4298.

6 Wang, F.; Zhang, Y.; Du, Z.; Ren, J.; Qu, X. Designed heterogeneous palladium catalysts for reversible light-controlled bioorthogonal catalysis in living cells. *Nat. Commun.* **2018**, *9* (1), 1209-1217.

7 Jemas, A.; Xie, Y.; Pigga, J. E.; Caplan, J. L.; am Ende, C. W.; Fox, J. M. Catalytic Activation of Bioorthogonal Chemistry with Light (CABL) Enables Rapid, Spatiotemporally Controlled Labeling and No-Wash, Subcellular 3D-Patterning in Live Cells Using Long Wavelength Light. *J. Am. Chem. Soc.* **2022**, *144*, 1647–1662.

8 Ahn, D.; Stevens, L. M.; Zhou, K.; Page, Z. A. Rapid High-Resolution Visible Light 3D Printing. *ACS Cent. Sci.* **2020**, *6* (9), 1555–1563.

9 Neilson, B. M.; Bielawski, C. W. Illuminating Photoswitchable Catalysis. *ACS Catal.* **2013**, *3* (8), 1874–1885.

10 Göstl, R.; Senf, A.; Hecht, S. Remote-controlling chemical reactions by light: towards chemistry with high spatio-temporal resolution. *Chem. Soc. Rev.* **2014**, *43* (6), 1982–1996.

11 Kondo, M.; Nakamura, K.; Krishnan, C. G.; Sasai, H.; Takizawa, S. Photoswitchable Chiral Organocatalysts: Photocontrol of Enantioselective Reactions. *Chem. Rec.* **2023**, *23* (7), e202300040.

12 Dorel, R.; Feringa, B. L. Photoswitchable catalysis based on the isomerisation of double bonds. *Chem. Commun.* **2019**, *55* (46), 6477–6486.

13 Liu R.; Zhang X.; Xia F.; Dai Y. Azobenzene-based photoswitchable catalysts: State of the art and perspectives. *J. Catal.* **2022**, *409*, 33–40.

14 Majee, D.; Presolski, S. Dithienylethene-Based Photoswitchable Catalysts: State of the Art and Future Perspectives. *ACS Catal.* **2021**, *11* (4), 2244–2252.

15 Freixa, Z. Photoswitchable catalysis using organometallic complexes. *Catal. Sci. Technol.* **2020**, *10* (10), 3122–3139.

16 Lunic, D.; Bergamaschi, E.; Teskey, C. J. Using Light to Modify the Selectivity of Transition Metal Catalysed Transformations. *Angew. Chem. Int. Ed.* **2021**, *60* (38), 20594–20605.

17 Galangau, O.; Norel, L.; Rigaut, S. Metal complexes bearing photochromic ligands: photocontrol of functions and processes. *Dalton Trans.* **2021**, *50* (48), 17879–17891.

18 Medici, F.; Goual, N.; Delattre, V.; Voituriez, A.; Marinetti, A. Photoswitchable phosphines in catalysis. *ChemCatChem* **2020**, *12* (22), 5573–5589.

19 Sud, D.; Norsten, T. B.; Branda, N. R. Photoswitching of stereoselectivity in catalysis using a copper dithienylethene complex. *Angew. Chem. Int. Ed.* **2005**, *44* (13), 2019–2021.

20 Kean, Z. S.; Akbulatov, S.; Tian, Y.; Widenhoefer, R. A.; Boulatov, R.; Craig, S. L. Photomechanical Actuation of Ligand Geometry in Enantioselective Catalysis. *Angew. Chem. Int. Ed.* **2014**, *53* (52), 14508–14511.

21 Zhao, D.; Neubauer, T. M.; Feringa, B. L. Dynamic control of chirality in phosphine ligands for enantioselective catalysis. *Nat. Commun.* **2015**, *6* (1), 6652–6658.

22 Cacciapaglia, R.; Di Stefano, S.; Mandolini, L. The Bis-Barium Complex of a Butterfly Crown Ether as a Phototunable Supramolecular Catalyst. *J. Am. Chem. Soc.* **2003**, *125* (8), 2224–2227.

23 Arif, T.; Cazorla, C.; Bogliotti, N.; Saleh, N.; Blanchard, F.; Gandon, V.; Métivier, R.; Xie, J.; Voituriez, A.; Marinetti, A. Bimetallic gold(I) complexes of photoswitchable phosphines: synthesis and uses in cooperative catalysis. *Catal. Sci. Technol.* **2018**, *8* (3), 710–715.

24 Gallarati, S.; Fabregat, R.; Juraskova, V.; Inizan, T. J.; Corminboeuf, C. How Robust Is the Reversible Steric Shielding Strategy for Photoswitchable Organocatalysts? *J. Org. Chem.* **2022**, *87* (14), 8849–8857.

25 Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem. Rev.* **2014**, *114* (24), 12174–12277.

26 Neilson, B. M.; Bielawski, C. W. Photoswitchable Metal-Mediated Catalysis: Remotely Tuned Alkene and Alkyne Hydroborations. *Organometallics* **2013**, *32* (10), 3121–3128.

27 Teator, A. J.; Shao, H.; Lu, G.; Liu, P.; Bielawski, C. W. A Photoswitchable Olefin Metathesis Catalyst. *Organometallics* **2017**, *36* (2), 490–497.

28 Xu, Z.; Cao, Y.; Patrick, B. O.; Wolf, M. O. Photoswitching of Copper(I) Chromophores with Dithienylethene-Based Ligands. *Chem. Eur. J.* **2018**, *24* (41), 10315–10319.

29 Kaur, B.; Raza, R.; Stashick, M. J.; Branda, N. R. Using light to control the inhibition of Karstedt's catalyst. *Org. Chem. Front.* **2019**, *6* (8), 1253–1256.

30 Wilson, D.; Branda, N. R. Turning "on" and "off" a pyridoxal 5'-phosphate mimic using light. *Angew. Chem. Int. Ed.* **2012**, *51* (22), 5431–5434.

31 Majee, D.; Ramanauskaite, G.; Presolski, S. Electronic Influences on the Dynamic Range of Photoswitchable Dithienylethene–Thiourea Organocatalysts. *J. Org. Chem.* **2023**, *88* (7), 4372–4378.

32 Kathan, M.; Kovaříček, P.; Jurissek, C.; Senf, A.; Dallmann, A.; Thünemann, A. F.; Hecht, S. Control of Imine Exchange Kinetics with Photoswitches to Modulate Self-Healing in Polysiloxane Networks by Light Illumination. *Angew. Chem. Int. Ed.* **2016**, *55* (44), 13882–13886

33 Villabona, M.; Wiedbrauk, S.; Feist, F.; Guirado, G.; Hernando, J.; Barner-Kowollik, C. Dual-Wavelength Gated oxo-Diels-Alder Photoligation. *Org. Lett.* **2021**, *23* (7), 2405–2410.

34 Stille, J. K. The Palladium-Catalyzed Cross-Coupling Reactions of Organotin Reagents with Organic Electrophiles [New Synthetic Methods (58)]. *Angew. Chem. Int. Ed.* **1986**, *25* (6), 508–524.

35 Espinet, P.; Echavarren, A. M. The mechanisms of the Stille reaction. *Angew. Chem. Int. Ed.* **2004**, *43* (36), 4704–4734.

36 Cordovilla, C.; Bartolomé, C.; Martínez-Ilarduya, J. M.; Espinet, P. The Stille Reaction, 38 Years Later. *ACS Catal.* **2015**, *5* (5), 3040–3053.

37 Hansch, C.; Leo, A.; Taft, R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* **1991**, *91* (2), 165–195.

38 Sponza, A. D.; Liu D.; Chen, E. P.; Shaw, A.; Diawara, L.; Chiu, M. Synthesis strategies for non-symmetric, photochromic diarylethenes. *Org. Biomol. Chem.* **2020**, *18* (37), 7238–7252.

39 Bianchini, G.; Strukul, G.; Wass, D. F.; Scarso, A. Photomodulable phosphines incorporating diarylethene moieties. *RSC Adv.* **2015**, *5* (14), 10795–10798.

40 Chevykalova, M. N.; Manzhukova, L. F.; Artemova, N. V.; Luzikov, Yu. N.; Nifant´ev, I. E.; Nifant´ev, E. E. Electron-donating ability of triarylphosphines and related compounds studied by ^{31}P NMR spectroscopy. *Russ. Chem. Bull.* **2003**, *52* (1), 78–84.

41 Sud, D.; McDonald, R.; Branda, N. R. Synthesis and coordination chemistry of a photoswitchable bis(phosphine) ligand. *Inorg. Chem.* **2005**, *44* (17), 5960–5962.

42 Yin, J.; Lin, Y.; Cao, X.; Yu, G.-A.; Tu, H.; Liu, S. H. The synthesis and photochromic properties of two bis(phosphine) ligands based on dithienylethene backbone and their oxides, sulfurets and selenides. *Dyes Pigm.* **2009**, *81* (2), 152–155.

43 Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. Single-crystalline photochromism of diarylethenes: reactivity-structure relationship. *Chem. Commun.* **2002** (23), 2804–2805.

44 Herder, M.; Eisenreich, F.; Bonasera, A.; Grafl, A.; Grubert, L.; Pätzel, M.; Schwarz, J.; Hecht, S. Light-Controlled Reversible Modulation of Frontier Molecular Orbital Energy Levels in Trifluoromethylated Diarylethenes. *Chem. Eur. J.* **2017**, *23* (15), 3743–3754.

45 Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. Light-triggered electrical and optical switching devices. *J. Chem. Soc., Chem. Commun.* **1993** (18), 1439–1442.

46 Liang, J.; Yin, J.; Li, Z.; Zhang, C.; Di Wu; Liu, S. H. Synthesis and properties of dithienylethene-based binuclear gold complexes and a palladium chlorine-bridged macrocycle. *Dyes Pigm.* **2011**, *91* (3), 364–369.

47 Lasorne, B.; Fihey, A.; Mendive-Tapia, D.; Jacquemin, D. A curve-crossing model to rationalize and optimize diarylethene dyads. *Chem. Sci.* **2015**, *6* (10), 5695–5702.

48 Herder, M.; Schmidt, B. M.; Grubert, L.; Pätzel, M.; Schwarz, J.; Hecht, S. Improving the fatigue resistance of diarylethene switches. *J. Am. Chem. Soc.* **2015**, *137* (7), 2738–2747.

49 Allen, D. W.; Taylor, B. F. The Chemistry of Heteroarylphosphorus Compounds. Part 15, Phosphorus-31 Nuclear Magnetic Resonance Studies of the Donor Properties of Heteroarylphosphines towards Selenium and Platinum(II). *J. Chem. Soc. Dalton Trans.* **1982** (1), 51–54.

50 Bent, H. A. An Appraisal of Valence-bond Structures and Hybridization in Compounds of the First-row elements. *Chem. Rev.* **1961**, *61* (3), 275–311.

51 Levin, C. C. Qualitative molecular orbital picture of electronegativity effects on XH_3 inversion barriers. *J. Am. Chem. Soc.* **1975**, *97* (20), 5649–5655.

52 Glendening, E. D.; Landis, C. R.; Weinhold, F. Natural bond orbital methods. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2* (1), 1–42.

53 Casado, A. L.; Espinet, P.; Gallego, A. M. Mechanism of the Stille Reaction. 2. Couplings of Aryl Triflates with Vinyltributyltin. Observation of Intermediates. A More Comprehensive Scheme. *J. Am. Chem. Soc.* **2000**, *122* (48), 11771–11782.

54 Casado, A. L.; Espinet, P. Mechanism of the Stille Reaction. 1. The Transmetalation Step. Coupling of R_1I and R_2SnBu_3 Catalyzed by trans-$[PdR_1IL_2]$ (R_1 = $C_6Cl_2F_3$; R_2 = Vinyl, 4-Methoxyphenyl; L = $AsPh_3$). *J. Am. Chem. Soc.* **1998**, *120*, 8978–8985.

55 Meijere, A. de; Diederich, F. *Metal-catalyzed cross-coupling reactions. Second, Completely revised and enlarged edition*; John Wiley & Sons, Ltd, 2004.

56 Nova, A.; Ujaque, G.; Maseras, F.; Lledós, A.; Espinet, P. A critical analysis of the cyclic and open alternatives of the transmetalation step in the stille cross-coupling reaction. *J. Am. Chem. Soc.* **2006**, *128* (45), 14571–14578.

57 García-Melchor, M.; Braga, A. A. C.; Lledós, A.; Ujaque, G.; Maseras, F. Computational perspective on Pd-catalyzed C-C cross-coupling reaction mechanisms. *Acc. Chem. Res.* **2013**, *46* (11), 2626–2634.

58 Echavarren, A. M.; Cárdenas, D. J. Mechanistic Aspects of Metal-Catalyzed C,C- and C,X-Bond-Forming Reactions: 1. In *Metal-Catalyzed Cross-Coupling Reactions*; John Wiley & Sons, Ltd, 2004; pp 1–40.

59 McMullin, C. L.; Fey, N.; Harvey, J. N. Computed ligand effects on the oxidative addition of phenyl halides to phosphine supported palladium(0) catalysts. *Dalton Trans.* **2014**, *43* (36), 13545–13556.

60 McMullin, C. L.; Jover, J.; Harvey, J. N.; Fey, N. Accurate modelling of Pd(0) + PhX oxidative addition kinetics. *Dalton Trans.* **2010**, *39* (45), 10833–10836.

61 Lam, K. C.; Marder, T. B.; Lin, Z. DFT Studies on the Effect of the Nature of the Aryl Halide $Y–C_6H_4–X$ on the Mechanism of Its Oxidative Addition to Pd^0L versus Pd^0L_2. *Organometallics* **2007**, *26* (3), 758–760.

62 Lyngvi, E.; Sanhueza, I. A.; Schoenebeck, F. Dispersion Makes the Difference: Bisligated Transition States Found for the Oxidative Addition of $Pd(PtBu_3)_2$ to Ar-OSO_2R and Dispersion-Controlled Chemoselectivity in Reactions with $Pd[P(iPr)(tBu_2)]_2$. *Organometallics* **2015**, *34* (5), 805–812.

2. 5. Supporting information

2. 5. 1. General procedures

2. 5. 1. 1 Materials and methods

All reactions were carried out under nitrogen atmosphere in the absence of air and water using standard Schlenk line techniques. All solvents (hexanes, CH_2Cl_2, Et_2O, ethyl acetate, *n*-pentane, cyclohexane) were dried and degassed prior to use. THF was distilled over sodium/benzophenone and stored over 4Å activated molecular sieves. $CDCl_3$ and THF-d_8 were degassed by freeze–pump–thaw cycling. Toluene-d_8 was degassed with nitrogen. All starting materials and reagents were commercially purchased and used without further purification. [$Pd(PPh_3)_4$], [$PdCl_2(PPh_3)_2$] and *trans*-[$PdCl_2(PhCN)_2$] were synthesized according to previously reported procedures.[1–3] Flash column chromatography was done using silica gel (230-400 mesh) using a stream of nitrogen.

NMR spectra were recorded on a BRUKER Avance III HD 400 MHz, BRUKER Ascend 300 MHz and BRUKER Ascend 400 MHz at 25 °C. Tetramethylsilane (TMS) was used as an internal reference in ^{1}H and ^{13}C NMR spectra; all other nuclei were referenced to TMS using the Ξ scale.[4] Chemical shifts are reported in parts per million (ppm). Assignment of ^{1}H and ^{13}C NMR signals was carried out using ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR experiments. IR spectra were recorded on FT-IR spectrometers Thermo Scientific Nicolet iS5, BRUKER Tensor 27 Golden Gate and BRUKER Alpha II. Electrospray ionization mass spectrometry was carried out with BRUKER Impact II, BRUKER Esquire 3,000+ and a micrOTOF-Q II BRUKER spectrometer in positive ion mode. UV-vis absorption spectra were recorded on an Agilent HP 8453 spectrophotometer using HPLC quality solvents and 1 cm quartz cuvettes. Photoisomerization studies were carried out using different irradiation sources: 365 nm and 520 nm LEDs (Chanzon), a VL-6.M UV lamp (λ_{exc} = 312 nm, 6 W), and a Nd:YAG pulsed laser (Brilliant, Quantel, λ_{exc} = 355 or 532 nm).

Single crystal X-ray diffraction analysis

The data were collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-Kα radiation and ω-scan rotation. Data reduction was performed with CrysAlisPro[5] including the program SCALE3 ABSPACK for an empirical absorption correction. As a result of the extremely thin crystal, for **8** a numerical absorption correction was applied as well using a multifaceted crystal model based on expressions derived by R.C. Clark and J.S. Reid.[6] All structures were solved by dual space methods with SHELXT[7] and the refinement was performed with SHELXL[7]. Hydrogen atoms were calculated on idealized positions using the riding model. Structure figures were generated with DIAMOND-4[8] and Mercury (version 2022.2.0).[9]

CCDC deposition numbers given in Table S1 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-

summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

Photochemical characterization

Photoswitching was monitored by UV-vis and NMR spectroscopy. The photostationary state PSS^{oc} composition was determined through ^{31}P or ^{19}F NMR spectroscopy from a PSS^{oc} state produced by irradiating a toluene-d_8 solution in an NMR tube with the appropriate wavelength. Spectra of the closed state isomers shown in Figures S23-S28 were estimated from the PSS^{oc} and open state UV-vis spectra. Photoisomerization quantum yields were determined by monitoring the variation of the UV-vis absorption spectra of ligands and complexes in cyclohexane upon irradiation with UV (for photocyclization, λ_{exc} = 312 or 355 nm) or visible light (for photocycloreversion, λ_{exc} = 532 nm). In the case of the free ligands bearing one DTE unit, spectral data was fitted to a simple kinetic model previously reported.[10] For the complexes containing two DTE groups, a more complex kinetic model had to be used to separately determine the photoisomerization quantum yields of their **oo**, **oc** and **cc** isomers.[11] To apply this model, we assumed the UV-vis absorption spectrum of each DTE unit in the complexes to be independent of the isomerization state of the other - i.e., the extinction coefficients of open DTE units are the same in the **oo** and **oc** states, while those of closed DTE groups are equal in the **oc** and **cc** states, as suggested by our TD-DFT calculations and observed in previous works on DTE dimers.[12] In all the cases, the irradiation intensities used in our photoisomerization quantum yield experiments were determined by monitoring the photocyclization and photocycloreversion processes of 1,2-bis(2-methyl-5-trifluoroacetylthien-3-yl)cyclopentene in toluene as a reference (Φ^{oc} = 0.37 and Φ^{co} = 0.031).[13]

Computational methods

DFT calculations were carried out using the Gaussian16 program package.[14] Geometry optimizations were conducted without any constraints using the B3LYP functional[15–17] with Grimme's D3 correction to account for dispersion effects.[18] Optimizations were performed in THF using the solvation model density (SMD) continuum model[19] with basis set 1 (BS1). BS1 included the 6-31G(d,p) basis set for the main group atoms[20,21] (H, C, O, F, P, S) and the Stuttgart-Dresden SDD effective core potential (ECP) and its corresponding double-ζ basis set[22], with a set of *d* polarization functions[23] for I and Sn and *f* polarization functions[24] for Pd. Frequency calculations were performed for all the optimized geometries to determine the stationary points as either minima or transition states. Energies in THF were refined through single-point calculations of the optimized BS1 geometries with an extended basis set (BS2). BS2 consisted of the def2-TZVP for main group atoms, and the quadruple-ζ def2-QZVP basis set for Pd, together with the def2 ECP.[25] Gibbs energies in THF were calculated by adding thermal and entropic correction from BS1 to the BS2 energies in THF. An

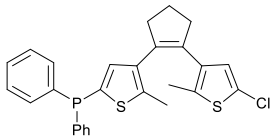
additional correction of 1.9 kcal/mol was applied to all the Gibbs energies to change the standard state from the gas phase (1 atm) to the condensed phase (1 M) at 298.15 K.[26] Frontier molecular orbitals and natural bond orbital (NBO)[27] analysis were calculated at the B3LYP-D3/BS1 level in THF using the SMD continuum model. TD-DFT calculations were carried out using the CAM-B3LYP functional[28] with Grimme's D3 correction to account for dispersion effects.[18] The first 15 electronic transitions were calculated in cyclohexane using the SMD continuum model with the BS1 described above.

2. 5. 1. 2 Synthetic procedures

Synthesis of ligands and complexes

{4-[2-(5-Chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophen-2-yl}diphenylphosphine (**DTE2**)

This compound was synthesized following a modified procedure.[29] A stirred yellow solution of 0.330 g (1.0 mmol, 1.0 eq.) **DTE1**[30] in 20 mL THF was cooled to -78 °C (hexanes/$N_{2(l)}$), and then 0.78 mL (1.41 mol·L^{-1}, 1.1 mmol, 1.1 eq.) *t*BuLi in *n*-pentane were added dropwise. The resultant bright yellow mixture was kept stirring for 50 min at -78 °C, followed by the addition of 0.20 mL (1.1 mmol, 1.1 eq.) of chlorodiphenylphosphine in one swift motion. The reaction mixture was left overnight to warm up to room temperature, and then quenched with a degassed brine solution. Under nitrogen atmosphere, the phases were separated, the aqueous phase was extracted with THF (2 x 5 mL), and the combined organic phases were dried over degassed Na_2SO_4. After canula filtration, the product mixture was absorbed on silica gel and purified through flash column chromatography (hexanes/dichloromethane 85:15). After solvent removal *in vacuo*, a white oil was obtained (0.317 g, 66% yield).



R_f 0.38 (hexanes/dichloromethane 85:15)

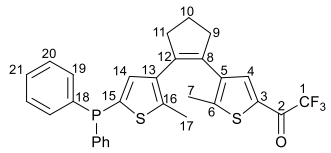
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 – 7.33 (m, 10H), 6.92 (d, *J* = 6.3 Hz, 1H), 6.54 (s, 1H), 2.80 – 2.65 (m, 4H), 2.09 – 1.96 (m, 2H), 2.01 (s, 3H), 1.87 (s, 3H) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 141.9, 138.0 (d, *J* = 8.6 Hz), 137.8 (d, *J* = 26.4 Hz), 136.8 (d, *J* = 7.2 Hz), 135.2, 135.1, 134.1, 133.0 (d, *J* = 19.5 Hz), 131.7 (d, *J* = 10.4 Hz), 128.8, 128.5, 128.4 (d, *J* = 7.0 Hz), 126.9, 125.0, 38.2, 38.2, 22.9, 14.6, 14.1 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): -19.7 (s) ppm.

{4-[2-(5-Trifluoroacetyl-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophen-2-yl}diphenyl-phosphine (**DTE^o-COCF$_3$**)

A stirred solution of 0.385 g (0.8 mmol, 1.0 eq.) **2** in 20 mL THF was cooled to -78 °C (hexane/$N_{2(l)}$), and 0.55 mL (1.6 mol·L^{-1}, 0.9 mmol, 1.1 eq.) *t*BuLi in pentane were added dropwise. The resultant deep red mixture was kept stirring for 45 min at -78 °C, followed by the addition of 0.75 mL (6.4 mmol, 8.0 eq.) of anhydrous ethyl trifluoroacetate in one swift motion. The reaction mixture turned bright yellow and was left to warm up to room temperature over an hour. After quenching with a degassed brine solution, the organic phase was separated, the aqueous phase was extracted with THF (2 x 5 mL), and the combined organic phases were dried over degassed Na_2SO_4. After canula filtration, the product mixture was absorbed on silica gel and purified through flash column chromatography (hexanes/dichloromethane 90:10). After solvent removal *in vacuo*, a yellow oil was obtained (0.298 g, 69% yield). Caution: the product is very sensitive to oxygen nucleophiles (water, alcohols); special care should be taken during the work up to avoid formation of the corresponding hydrate.



R$_f$ 0.17 (hexanes/dichloromethane 90:10)

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 – 7.30 (m, 10H, H18-21), 7.04 (d, $^2J_{H,P}$ = 6.6 Hz, 1H, H14), 6.85 (s, 1H, H4), 2.74 (t, *J* = 7.4 Hz, 4H, H9,11), 2.02 (p, *J* = 7.5 Hz, 2H, H10), 1.95 (s, 3H, H7), 1.88 (s, 3H, H17) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 142.2 (s, C16), 138.2 (d, $^1J_{C,P}$ = 8.4 Hz, C18), 137.9 (d, $^2J_{C,P}$ = 28.6 Hz, C14), 137.1 (d, $^3J_{C,P}$ = 8.4 Hz, C13), 136.1 (s, C6), 135.9 (s, C5), 135.1 (s, C12), 134.6 (s, C8), 133.5 (d, $^1J_{C,P}$ = 26.8 Hz, C15), 133.1 (d, $^2J_{C,P}$ = 19.5 Hz, C19), 128.8 (s, C21), 128.5 (d, $^3J_{C,P}$ = 7.0 Hz, C20), 128.1 (s, C4), 123.1 (q, $^1J_{C,F}$ = 286.0 Hz, C1), 38.5 (s, C9/11), 38.4 (s, C9/11), 23.1 (s, C10), 14.6 (s, C17), 14.3.(s, C7) ppm (not all ^{13}C signals were detected due to coupling to ^{19}F).

^{19}F NMR (376 MHz, $CDCl_3$, δ): -71.9 (s) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): -19.6 (s) ppm.

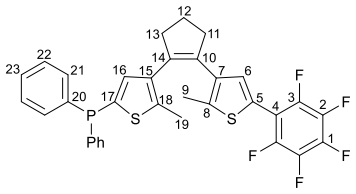
IR (ATR, ṽ): 3053 (w, νC–H), 2918 (w, νC–H), 1681 (s, νC=O), 1585 (w), 1528 (w), 1478 (s), 1373 (w, $νCF_3$), 1220 (s, $νCF_3$), 1167 (s, $νCF_3$), 1069 (m), 1026 (m), 969 (w), 922 (s), 868 (m), 803 (s), 739 (m), 717 (s), 619 (m), 554 (s), 501 (s) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M+H]^+$ 541.1031; found 541.1026.

UV-vis (cyclohexane, $λ_{max}$ (ε)): 268 (35 673), 339 (6 431) nm (M^{-1} cm^{-1}).

{4-[2-(2-Methyl-5-(2,3,4,5,6-pentafluorophenyl)-thiophen-3-yl]cyclopent-1-en-1-yl}-5-methylthiophen-2-yl)diphenylphosphine (**DTE^{o}-C_6F_5**)

A stirred solution of 0.327 g (0.7 mmol, 1.0 eq.) **2** in 9 mL THF was cooled to -78 °C (hexane/$N_{2(l)}$), and 0.85 mL (1.6 mol·L^{-1}, 1.4 mmol, 2.0 eq.) *t*BuLi in pentane were then added dropwise. The resultant deep red mixture was kept stirring for 45 min at -78 °C. In order to avoid complications during the purification step, full lithiation of the substrate was checked by ^{1}H NMR spectroscopy after quenching a reaction aliquot with methanol. After that, 0.55 mL (4.8 mmol, 7.0 eq.) of hexafluorobenzene were added in one swift motion. The reaction mixture turned yellow and was left to warm up to room temperature over an hour. After quenching with a degassed brine solution, the organic phase was separated, the aqueous phase was extracted with THF (2 x 5 mL), and the combined organic phases were dried over degassed Na_2SO_4. After canula filtration, the product mixture was absorbed on silica gel and purified through flash column chromatography (hexanes/dichloromethane gradient from 95:5 to 70:30). After solvent removal *in vacuo*, a colourless oil was obtained (0.290 g, 70% yield).



R$_f$ 0.18 (hexanes/dichloromethane 90:10)

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 – 7.33 (m, 10H, H21-23), 7.16 (s, 1H, H6), 7.01 (d, $^{2}J_{H,P}$ = 6.6 Hz, 1H, H16), 2.82 – 2.78 (m, 4H, H11,13), 2.10 – 2.02 (m, 5H, H12,19), 1.96 (s, 3H, H9) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 142.2 (s, C18), 138.1 (d, $^{1}J_{C,P}$ = 8.5 Hz, C20), 137.8 (d, $^{2}J_{C,P}$ = 27.8 Hz, C16), 136.9 (d, $^{3}J_{C,P}$ = 8.4 Hz, C15), 136.4 (s, C7), 135.5, 134.3, 133.6 (d, $^{1}J_{C,P}$ = 27.7 Hz, C17), 133.2 (d, $^{2}J_{C,P}$ = 19.7 Hz, C21), 133.0 (t, $^{2}J_{C,F}$ = 5.5 Hz, C6), 128.9 (s, C23), 128.6 (d, $^{3}J_{C,P}$ = 6.9 Hz, C22), 128.2, 38.5 (s, C11/13), 38.4 (s, C11/13), 23.1 (s, C12), 14.7 (s, C9), 14.2 (s, C19) ppm (not all ^{13}C signals were detected due to high substitution pattern and coupling to ^{19}F).

^{19}F NMR (376 MHz, $CDCl_3$, δ): -140.2 – 140.3 (m, 2F, F3), -157.1 (t, *J* = 21.1 Hz, 1F, F1), -162.4 – -162.5 (m, 2F, F2) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): -19.5 (s) ppm.

IR (ATR, ṽ): 3052 (w, vC–H), 2921 (w, vC–H), 2846 (w), 1518 (s, vC-F), 1494 (s), 1433 (m), 1413 (w), 1326 (w), 1277 (w), 1239 (w), 1207 (w), 1119 (w), 1053 (m), 1037 (m), 1026 (s), 984 (w), 917 (m), 881 (m), 851 (w), 809 (s), 766 (w), 741 (s), 693 (w), 650 (w), 620 (w), 577 (s), 528 (m), 517 (s), 502 (m) cm^{-1}.

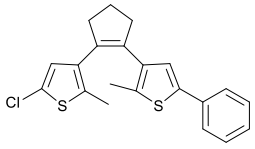
HRMS (ESI-TOF, m/z): calculated for $[M+H]^+$ 611.1050; found 611.1039.

UV-vis (cyclohexane, λ_{max} (ε)): 285 (23 756) nm (M^{-1} cm^{-1}).

5-Chloro-2-methyl-3-[2-(2-methyl-5-phenyl-3-thienyl)-1-cyclopenten-1-yl]thiophene (**DTE3**)

Compound **DTE3** was synthesized following a modified procedure.[29] A stirred solution of 0.532 mg (1.6 mmol, 1.0 eq.) **DTE1**[30] in 10 mL THF was cooled to -78 °C (hexane/$N_{2(l)}$) and 1.16 mL (1.6 mol·L^{-1}, 1.9 mmol, 1.2 eq.) *t*BuLi in pentane were added dropwise. After 15 min, 0.52 mL (1.9 mmol, 1.2 eq.) tri-*n*-butyl borate was added in one swift motion and reaction mixture was left stirring at -78 °C for 30 min more. Once reaching room temperature, crude was added through a canula to a degassed biphasic solution THF/2M Na_2CO_3 (10 mL:10 mL) containing 0.22 mL (1.9 mmol, 1.2 eq.) iodobenzene and 0.075 g (0.06 mmol, 0.04 eq.) [$Pd(PPh_3)_4$]. The reaction mixture was left at reflux for 2 hours, cooled down to room temperature and 10 mL Et_2O were added. The organic phase was separated, the aqueous phase was further extracted with Et_2O (2 x 10mL) and the combined organic phases were dried over anhydrous Na_2SO_4. The solvent was evaporated, and the crude was purified by flash column chromatography (hexanes 100) yielding 0.532 g (83% yield) of a clear oil.

R_f 0.56 (hexanes 100)



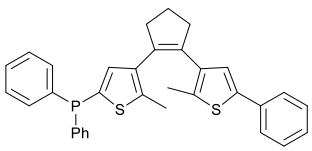
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.46 (m, 2H), 7.29 (m, 2H), 7.17 (m, 1H), 6.97 (s, 1H), 6.60 (s, 1H), 2.80 – 2.68 (m, 4H), 2.02 – 1.96 (m, 5H), 1.85 (s, 3H) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 140.0, 136.5, 135.4, 135.3, 134.6, 134.6, 133.9, 133.4, 129.0, 127.2, 127.0, 125.4, 125.2, 123.9, 38.7, 38.6, 23.1, 14.6, 14.4.

{4-[2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophen-2-yl}diphenylphosphine (**DTE-Ph**)

Compound **DTE-Ph** was synthesized following a modified procedure.[29] **DTE3** was dissolved in 30 mL Et_2O and 0.59 mL (1.6 mol·L^{-1}, 0.9 mmol, 1.1 eq.) *n*BuLi in hexanes were added dropwise at room temperature to a stirred solution. The resultant deep red mixture was kept stirring for 15 min, followed by the addition of 0.18 mL (1.0 mmol, 1.2 eq.) of chlorodiphenylphosphine in one swift motion. The reaction mixture was left overnight at room temperature, and then quenched with a degassed brine solution. Under nitrogen atmosphere, the phases were separated, the aqueous phase was extracted with Et_2O (2 x 10 mL), and the combined organic phases were dried over degassed Na_2SO_4. After canula filtration, the product mixture was absorbed on silica gel and purified through column chromatography (hexanes/dichloromethane 90:10). After solvent removal *in vacuo*, a white oil was obtained (0.305 g, 68% yield).

R_f 0.34 (hexanes/dichloromethane 90:10)



^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 (m, 2H), 7.36 – 7.23 (m, 13H), 7.02 (d, *J* = 6.4 Hz, 1H), 6.97 (s, 1H), 2.87 – 2.75 (m, 4H), 2.09 (p, *J* = 7.5 Hz, 2H), 2.03 (s, 3H), 2.01 (s, 3H) ppm.

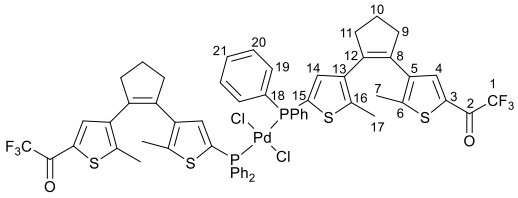
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 142.0, 139.7, 138.1 (d, *J* = 1.9 Hz), 137.9 (d, *J* = 20.0 Hz), 137.1 (d, *J* = 8.0 Hz), 136.6, 135.0, 134.5, 134.3, 133.2, 133.1 (d, *J* = 19.6 Hz), 133.0, 131.7 (d, *J* = 10.3 Hz), 128.7 (d, *J* = 10.7 Hz), 128.4 (d, *J* = 7.0 Hz), 127.0, 125.3, 124.0, 38.3, 38.3, 23.0, 14.6, 14.4 ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): -19.6 (s) ppm.

UV-vis (cyclohexane, λ_{max} (ε)): 273 (28 117) nm (M^{-1} cm^{-1}).

$[PdCl_2$(**DTE^o-COCF$_3$**$)_2]$

0.014 g (0.04 mmol, 0.5 eq.) $[PdCl_2(PhCN)_2]$ and 0.040 g (0.02 mmol, 1.0 eq.) **DTE-COCF$_3$** were dissolved in 2 mL CH_2Cl_2. The reaction mixture was stirred at 50 °C overnight and then cooled down to room temperature. After solvent removal *in vacuo*, the complex was crystallized from CH_2Cl_2/pentane, yielding a yellow solid (0.037 g, 80% yield). Single crystals suitable for X-ray structure analysis were obtained by slow evaporation from CH_2Cl_2/Et_2O.



^1H NMR (300 MHz, $CDCl_3$, δ): 7.65 – 7.52 (m, 10H, H4,19), 7.48 – 7.29 (m, 12H, H20,21), 7.16 (t, $^2J_{H,P}$ = 3.4 Hz, 2H, H14), 2.85 – 2.70 (m, 8H, H9/11), 2.15 – 2.00 (m, 16H, H10, 7, 17) ppm.

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 172.8 (q, $^2J_{C,F}$ = 36.1 Hz, C2), 150.3 (s, C6), 144.2 (s, C16), 140.6 (t, $^2J_{C,P}$ = 4.9 Hz, C14), 138.5 (s, C5), 137.7 (q, $^3J_{C,F}$ = 3.1 Hz, C4), 136.8 (s, C8/12), 136.2 (t, $^3J_{C,P}$ = 5.1 Hz, C13), 134.3 (t, $^2J_{C,P}$ = 6.5 Hz, C19), 133.2 (s, C8/12), 132.1 (s, C3), 130.7 (s, C21), 130.1 (t, $^1J_{C,P}$ = 26.1 Hz, C18), 128.0 (t, $^3J_{C,P}$ = 5.5 Hz, C20), 125.6 (t, $^1J_{C,P}$ = 25.1 Hz, C15), 116.5 (q, $^1J_{C,F}$ = 114.5 Hz, C1), 38.2 (s, C9/11), 38.2 (s, C9/11), 22.9 (s, C10), 15.5 (s, C17), 14.6 (s, C7) ppm (not all ^{13}C signals were detected due to coupling to ^{19}F).

^{19}F NMR (282 MHz, $CDCl_3$, δ): -71.8 (s) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 12.2 (s) ppm.

IR (ATR, $\tilde{\nu}$): 2959 (w, νC–H), 2922 (w, νC–H), 2848 (w, νC–H), 1683 (m, νC=O), 1539 (w), 1478 (w), 1434 (m), 1420 (m), 1373 (w, νCF_3), 1350 (w), 1328 (w), 1305 (w), 1260 (m), 1217 (m, νCF_3), 1184 (m), 1166 (s, νCF_3), 1141 (s), 1094 (s), 1014 (s), 866 (s), 848 (m), 796 (s), 739 (s), 716 (m), 685 (s), 663 (m), 581 (w), 530 (s), 503 (s) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M\text{-}Cl]^+$ 1221.0640, found 1221.0600.

UV-vis (cyclohexane, λ_{max} (ε)): 285 (31 151), 355 (19 065) nm (M^{-1} cm^{-1}).

[$PdCl_2$(**DTE^c-COCF$_3$**)$_2$]

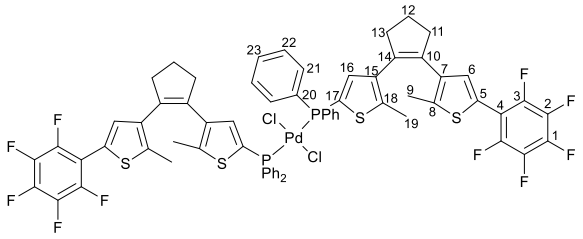
A closed state-enriched mixture of complex [$PdCl_2$(**DTE-COCF$_3$**)$_2$] was prepared by first isomerizing the ligand **DTE^o-COCF$_3$** in cyclohexane solution and then complexing with palladium(II). In the dark, 0.100 g (0.18 mmol, 1.0 eq.) **DTE^o-COCF$_3$** were dissolved in degassed cyclohexane and irradiated with 365 nm until no further change in the PSS composition was observed by ^{19}F NMR spectroscopy. A stock solution of 0.032 g (0.08 mmol, 0.5 eq.) [$PdCl_2$($PhCN)_2$] in 5.7 mL CH_2Cl_2 was added to the ligand and the reaction was kept at 50 °C overnight. After cooling down to room temperature, the solvent was removed *in vacuo* and the product was obtained after flash column chromatography (hexanes/ethyl acetate gradient from 70:30 to 30:70) yielding a deep blue solid – closed state-enriched complex mixture (0.101 g, 87%) with the composition: **cc** 52%, **oc** 40% and **oo** 7%.

^{19}F NMR (377 MHz, $CDCl_3$, δ): -71.7 (s, **cc**), -71.7 (s, **oc**), -72.1 (s, **oc**+**oo**) ppm.

^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$, δ): 18.6 (d, *J* = 582.0 MHz, **oc**), 18.4 (s, **cc**), 12.2 (s, **oo**), 12.1 (d, *J* = 582.0 MHz, **oc**) ppm.

[$PdCl_2$(**DTE^o-C$_6$F$_5$**)$_2$]

Complex [$PdCl_2$(**DTE^o-C$_6$F$_5$**)$_2$] was synthesized following the procedure described for [$PdCl_2$(**DTE^o-COCF$_3$**)$_2$] using 0.087 g (0.14 mmol, 1 eq.) **DTE^o-C$_6$F$_5$** as a ligand and 0.027 g (0.07 mmol, 0.5 eq.) [$PdCl_2$($PhCN)_2$] in 5 mL CH_2Cl_2. After complexation was completed, the solvent was removed *in vacuo* and the product was precipitated from Et_2O/pentane as a yellow solid (0.088 g, 90%). Single crystals suitable for X-ray structure analysis were obtained by slow vapor diffusion of pentane into a CH_2Cl_2 solution.



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.61 (q, $^2J_{H,P}$ = 6.0, 3.5 Hz, 8H, H21), 7.45 – 7.29 (m, 14H, H16, 22, 23), 7.13 (s, 2H, H6), 2.78 (t, *J* = 7.5 Hz, 8H, H11, 13), 2.03 – 1.98 (m, 16H, H12, 9, 19) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 144.2 (s, C18), 141.1 (t, $^2J_{C,P}$ = 4.9 Hz, C16), 138.0 (s, C8), 136.9 (t, $^3J_{C,P}$ = 5.4 Hz, C15), 136.1 (s, C7), 135.0 (s, C10/14), 134.5 (s, C10/14), 134.3 (t, $^2J_{C,P}$ = 6.5 Hz, C21), 131.4 (s, C6), 130.6 (s, C23), 130.5 (t, $^1J_{C,P}$ = 26.3 Hz, C20), 127.9 (t, $^3J_{C,P}$ = 5.4 Hz, C22), 124.8 (t, $^1J_{C,P}$ = 24.6, C17), 122.2 (m, C5), 38.4 (s, C11/13), 22.9 (s, C12), 14.5 (s, C9), 14.2 (s, C19) ppm (not all ^{13}C signals were detected due to high substitution pattern and coupling to ^{19}F).

^{19}F NMR (282 MHz, $CDCl_3$, δ): -140.1 – -140.2 (m, 2F, F3), -156.9 (t, *J* = 21.1 Hz, 1F, F1), -162.2 – -162.4 (m, 2F, F2) ppm.

^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$, δ): 12.1 (s) ppm.

IR (ATR, ṽ): 3070 (w, νC–H), 2961 (w, νC–H), 2838 (w), 1517 (m, νC-F), 1494 (s), 1435 (m), 1344 (w), 1309 (w), 1260 (m), 1211 (w), 1155 (w), 1097 (s), 1062 (m), 1027 (s), 984 (s), 851 (m), 805 (s), 744 (s), 690 (s), 576 (w), 558 (w), 531 (s), 497 (s) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M\text{-}Cl]^+$ 1361.0678, found 1361.0710.

UV-vis (cyclohexane, λ_{max} (ε)): 286 (33 147), 357 (14 367) nm (M^{-1} cm^{-1}).

$[PdCl_2(\mathbf{DTE^c\text{-}C_6F_5})_2]$

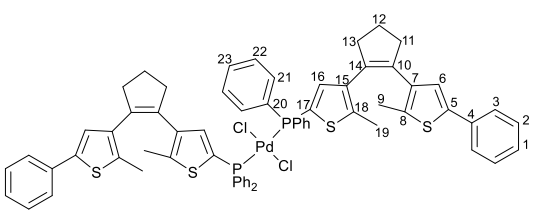
A closed state-enriched mixture of complex $[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$ was synthesized following the procedure described for $[PdCl_2(\mathbf{DTE^c\text{-}COCF_3})_2]$. First, 0.132 g (0.22 mmol, 1 eq.) $\mathbf{DTE^o\text{-}C_6F_5}$ were photoisomerized in cyclohexane using a 312 nm lamp, then a stock solution of 0.041 mg (0.11 mmol, 0.5 eq.) $[PdCl_2(PhCN)_2]$ in 6.6 mL CH_2Cl_2 was added. After stirring overnight at 50 °C and cooling down to room temperature, the solvent was evaporated *in vacuo* and the product was obtained after flash column chromatography (hexanes/ethyl acetate gradient from 70:30 to 30:70) yielding a deep pink solid – closed state-enriched complex with the composition: **cc** 38%, **oc** 48% and **oo** 14%.

^{19}F NMR (282 MHz, $CDCl_3$, δ): -137.94 (dd, *J* = 22.9, 7.1 Hz, **oc**+**cc**), -140.88 (dd, *J* = 22.9, 7.1 Hz, **oc**+**oo**), -154.99 (m, **oc**+**cc**), -157.78 (m, **oc**+**oo**), -162.07 – -162.68 (m, **oc**+**cc**), -162.67 – -163.27 (m, **oc**+**oo**) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 17.9 (d, *J* = 583.6 Hz, **oc**), 17.7 (s, **cc**), 12.1 (s, **oo**), 12.1 (d, *J* = 583.2 Hz, **oc**) ppm.

$[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$

Complex $[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$ was synthesized following the procedure described for $[PdCl_2(\mathbf{DTE^o\text{-}COCF_3})_2]$ using 0.094 g (0.18 mmol, 1 eq.) $\mathbf{DTE^o\text{-}Ph}$ as a ligand and 0.035 g (0.09 mmol, 0.5 eq.) $[PdCl_2(PhCN)_2]$ in 5 mL CH_2Cl_2. After complexation was completed, the solvent was removed *in vacuo* and the product was precipitated from CH_2Cl_2/pentane as a yellow solid (0.093 g, 86%). Single crystals suitable for X-ray structure analysis were obtained by slow evaporation from CH_2Cl_2/Et_2O.



^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.60 (m, 8H, H21), 7.45 (d, *J* = 7.4 Hz, 4H, H3), 7.37 – 7.26 (m, 18H, H2, 16, 22, 23), 7.21 (t, *J* = 7.3 Hz, 2H, H1), 6.91 (s, 2H, H6), 2.77 (t, *J* = 7.5 Hz, 8H, H11, 13), 2.06 – 1.96 (m, 16H, H12, 9, 19) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ): 144.2 (s, C18), 141.2 (t, $^{2}J_{C,P}$ = 4.9 Hz, C16), 139.7 (C5), 137.1 (t, $^{3}J_{C,P}$ = 5.0 Hz, C15), 136.3 (s, C7/8), 135.3 (C10,14), 134.3 (s, C7/8), 134.2 (t, $^{2}J_{C,P}$ = 6.0 Hz, C21), 134.0 (s, C4), 130.4 (t, $^{1}J_{C,P}$ = 26.0 Hz, C20), 130.4 (s, C23), 128.7 (s, C3), 127.8 (t, $^{3}J_{C,P}$ = 5.5 Hz, C22), 126.9 (s, C1), 125.2 (C2), 124.5 (t, $^{1}J_{C,P}$ = 25.4 Hz, C17), 123.8 (s, C6), 38.3 (s, C11/13), 38.1 (s, C11/13), 22.8 (s, C12), 14.5 (s, C9/19), 14.4 (s, C9/19) ppm.

$^{31}P\{^{1}H\}$ NMR (122 MHz, $CDCl_3$, δ): 12.2 (s) ppm.

IR (ATR, ṽ): 3107 (w, νC–H), 3050 (w, νC–H), 2962 (m, νC–H), 2922 (m, νC–H), 2848 (w), 1596 (w), 1498 (w), 1482 (w), 1463 (w), 1435 (m), 1410 (w), 1309 (w), 1261 (m), 1214 (w), 1095 (s), 1026 (m), 861 (w), 845 (w), 802 (m), 760 (m), 751 (w), 739 (w), 707 (w), 694 (m), 687 (m), 658 (w), 526 (m), 513 (m), 495 (m) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M\text{-}Cl]^+$ 1181.1620, found 1181.1617.

UV-vis (cyclohexane, λ_{max} (ε)): 270 (42 700), 359 (15 400) nm (M^{-1} cm^{-1}).

$[PdCl_2(\mathbf{DTE^c\text{-}Ph})_2]$

A closed state-enriched mixture of complex $[PdCl_2(\mathbf{DTE\text{-}Ph})_2]$was synthesized following the procedure described for $[PdCl_2(\mathbf{DTE^c\text{-}COCF_3})_2]$. First 0.058 g (0.11 mmol, 1 eq.) **DTE^o-Ph** were photoisomerized in cyclohexane using a 312 nm lamp, then stock solution of 0.021 mg (0.05 mmol, 0.5 eq.) $[PdCl_2(PhCN)_2]$ in 4.0 mL CH_2Cl_2 was added. After stirring overnight at 50 °C and cooling down to room temperature, the solvent was evaporated *in vacuo* and the product was obtained after flash column chromatography (hexanes/ethyl acetate 70:30) yielding a deep pink solid – closed state-enriched complex with the composition: **cc** 49%, **oc** 39% and **oo** 12%.

$^{31}P\{^{1}H\}$ NMR (122 MHz, $CDCl_3$, δ): 18.2 (d, *J* = 587.5 Hz, **oc**), 17.6 (s, **cc**), 12.2 (s, **oo**), 11.7 (d, *J* = 587.4 Hz, **oc**) ppm.

Preparation of phosphine selenides

Phosphine selenides were prepared by the addition of grey selenium powder to an NMR tube containing the free ligand in $CDCl_3$ and leaving the tube at 30 °C for 30 min. The reaction proceeded with 100% yield. The obtained selenides were not isolated and only studied *in situ*.

General procedure for catalytic studies

In an NMR tube, 0.033 mL iodobenzene (0.30 mmol, 1.0 eq.), 0.097 mL tributylvinyltin (0.33 mmol, 1.1 eq.), 5 mol % [Pd] catalyst and 0.05 g (0.03 mmol, 0.1 eq.) 1,3,5-trimethoxybenzene were dissolved in 1 mL dry, degassed THF-d_8. The reactions were carried out in the dark and monitored every 2 hours by ^{1}H, $^{31}P\{^{1}H\}$ and, when applicable, ^{19}F NMR spectroscopy. The reaction yields are an average of two replicates.

2. 5. 1. 3 Crystallographic data

Table S1 – Fundamental structure parameters

Compound	$[PdCl_2(\mathbf{DTE^o\text{-}COCF_3})_2]$	$[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$	$[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$
Molecular formula	$C_{58}H_{48}Cl_2F_6O_2P_2PdS_4$	$C_{66}H_{48}Cl_2F_{10}P_2PdS_4 \cdot 2\ CH_2Cl_2$	$C_{66}H_{58}Cl_2P_2PdS_4$
Empirical formula	$C_{58}H_{48}Cl_2F_6O_2P_2PdS_4$	$C_{68}H_{52}Cl_6F_{10}P_2PdS_4$	$C_{66}H_{58}Cl_2P_2PdS_4$
Formula weight	1258.44	1568.37	1218.60
Temperature [K]	130(2)	130(2)	130(2)
Wavelength [pm]	71.073	71.073	71.073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\ \bar{1}$	$P\ \bar{1}$	$P2_1/n$
Unit cell dimensions			
a [pm]	939.39(6)	779.12(6)	1132.74(2)
b [pm]	1016.51(6)	1191.26(7)	2230.11(2)
c [pm]	1548.13(9)	1943.0(1)	1192.49(2)
α [deg]	75.581(5)	102.024(5)	90
β [deg]	75.020(5)	99.679(6)	113.502(2)
γ [deg]	73.269(5)	107.099(6)	90
Volume [nm^3]	1.3430(2)	1.6343(2)	2.76250(8)
Z	1	1	2
$\rho_{(calculated)}$ [Mg/m^3]	1.556	1.594	1.465
μ [mm^{-1}]	0.725	0.777	0.685
F(000)	640	792	1256
Crystal size [mm^3]	0.25 · 0.14 · 0.03	0.17 · 0.16 · 0.01	0.44 · 0.21 · 0.10
Θ_{Min} / Θ_{Max} [deg]	2.311 / 27.479	2.766 / 28.166	2.288 / 32.517
Index ranges	-12 ≤ h ≤ 12 -12 ≤ k ≤ 13 -19 ≤ l ≤ 19	-10 ≤ h ≤ 10 -14 ≤ k ≤ 15 -25 ≤ l ≤ 25	-15 ≤ h ≤ 16 -33 ≤ k ≤ 33 -17 ≤ l ≤ 17
Reflections collected	9885	20166	37948
Indp. reflections (R_{int})	9885 (0.0480)	6951 (0.1070)	9263 (0.0384)
Completeness (Θ_{Max})	99.9 % (25.35)	99.9 % (25.35)	100.0 % (30.51)
T_{Max} / T_{Min}	1.00000 / 0.99350	0.992 / 0.895	1.00000 / 0.98121
Restraints / parameters	3 / 350	19 / 446	6 / 346
Gof on F^2	0.799	1.020	1.038
R1 / wR2 (I>2σ(I))	0.0391, 0.0655	0.0766, 0.1201	0.0368, 0.0784
R1 / wR2 (all data)	0.0813, 0.0705	0.1627, 0.1503	0.0516, 0.0856
Residual electron density [$e \cdot Å^{-3}$]	0.763 / -0.603	0.827 / -0.622	0.818 / -0.350
Comments	†[1]	†[2]	†[3]
CCDC No	2310549	2310550	2310551

†[1]: Two-component twin. Twin domain ratio 0.7984(4):0.2016(4). C19, C20 and C21 with envelope disorder (ratio 0.54(2):0.46(2)). †[2]: Disorder detectable for Cl1 (ratio 0.767(5):0.233(5)) and the solvent molecule C34, Cl2, Cl3 (ratio 0.91(1):0.09(1)). †[3]: C20 with envelope disorder (ratio 0.74(2):0.26(2)).

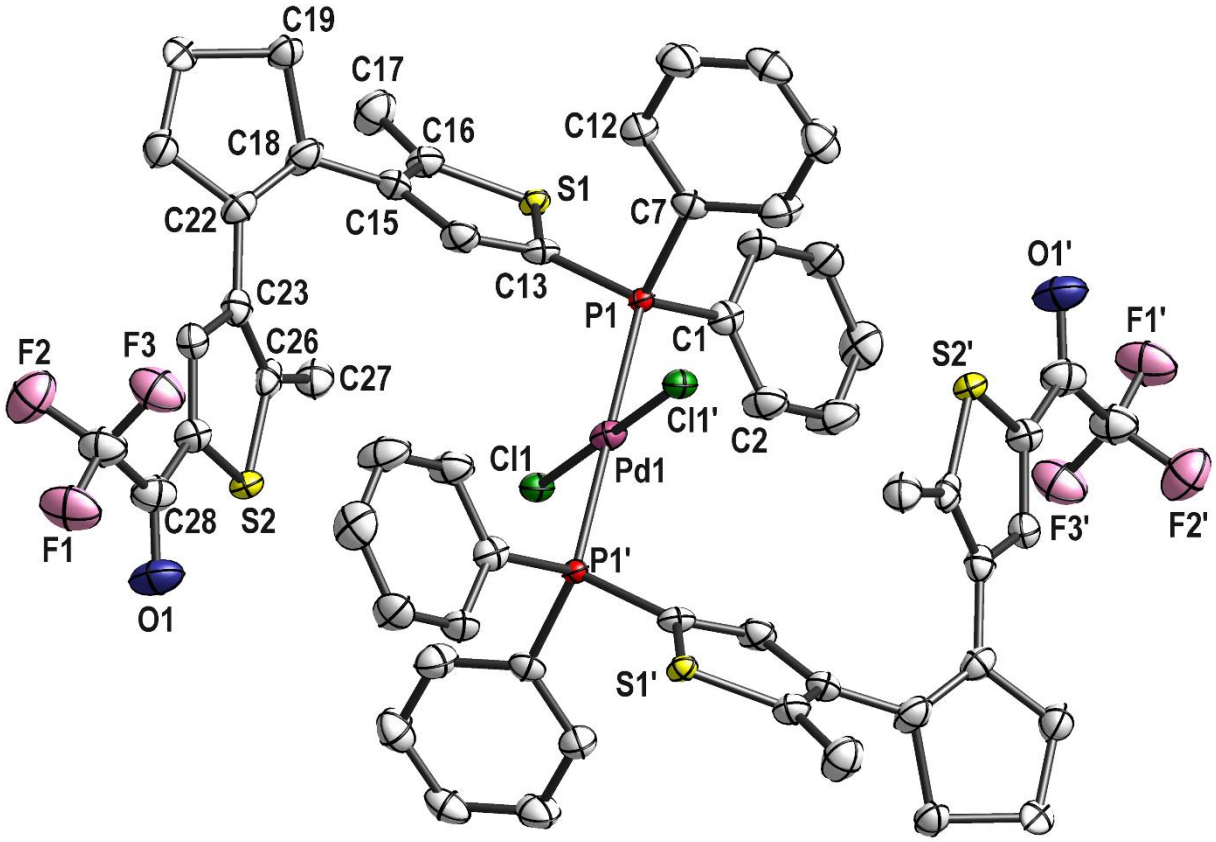


Figure S1 – Molecular structure of $[PdCl_2(\mathbf{DTE^o\text{-}COCF_3})_2]$. Hydrogen atoms and disordered atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level.

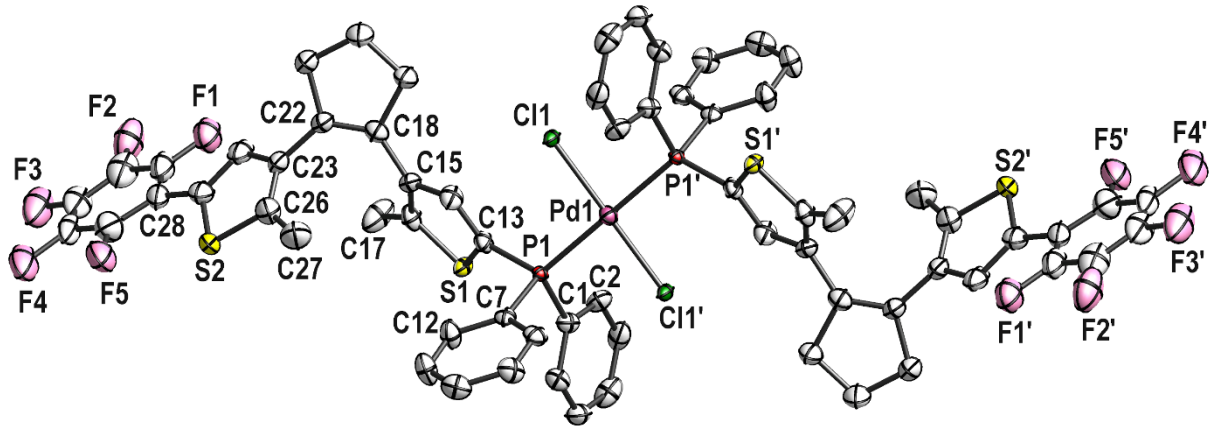


Figure S2 – Molecular structure of $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$. Hydrogen atoms and disordered atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level.

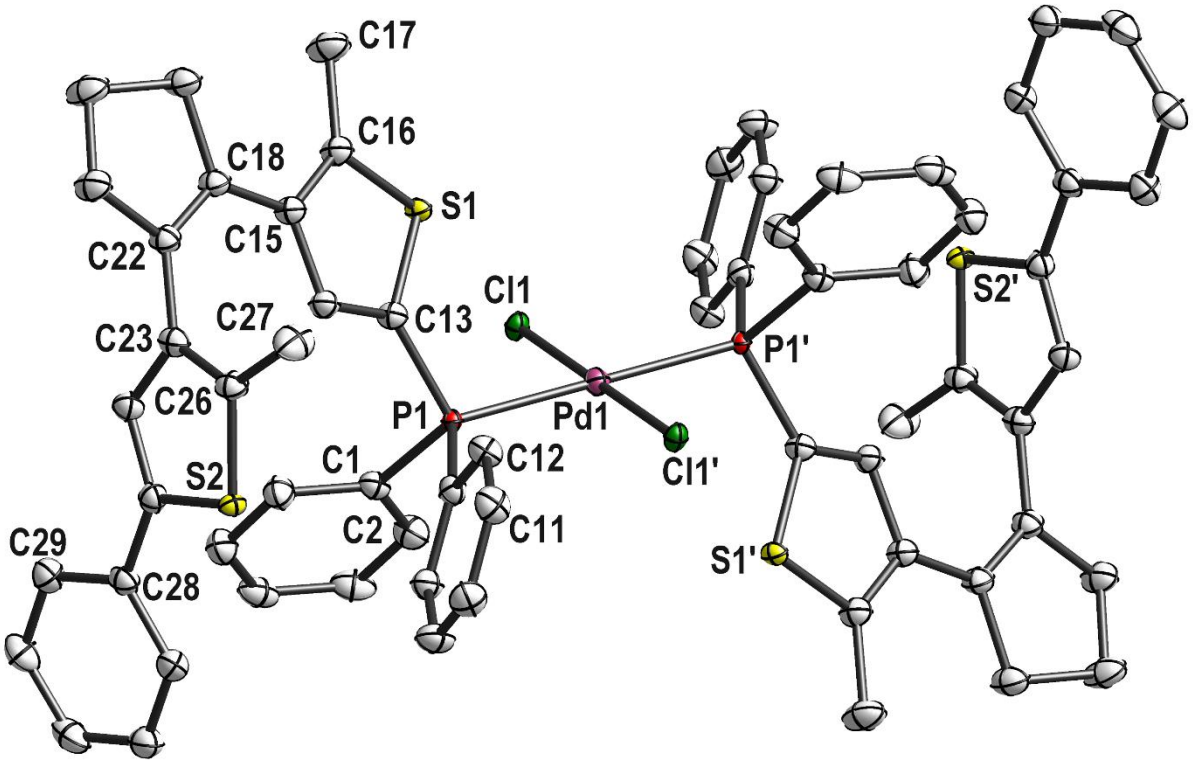


Figure S3 – Molecular structure of [$PdCl_2$(**DTE^o-Ph**)$_2$]. Hydrogen atoms and disordered atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level.

2. 5. 2. Experimental studies of the photochemical behavior of ligands and complexes

2. 5. 2. 1 Solid-state photoisomerization of $[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$

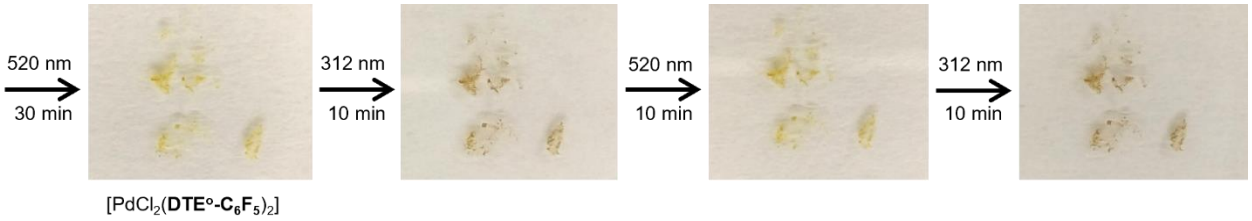


Figure S4 – Illustration of the solid-state photoisomerization of $[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$. Complex crystals were first irradiated with λ_{exc} = 520 nm to ensure that no residual closed state ligand was initially present. Two cycles of subsequent irradiation with λ_{exc} = 312 nm (for photoinduced ring-closing) and λ_{exc} = 520 nm (for photoinduced ring-opening) are presented. Clear changes in color were observed for the crystals in these experiments, which reversibly switched from the characteristic yellow color of the open state $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$ to the reddish color expected upon photocyclization of the DTE ligands. Therefore, these results prove that $[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$ can successfully photoisomerize in the solid state.

2. 5. 2. 2 Study of **DTE-Ph** and $[PdCl_2(\mathbf{DTE\text{-}Ph})_2]$ photoisomerization by UV-vis absorption spectroscopy

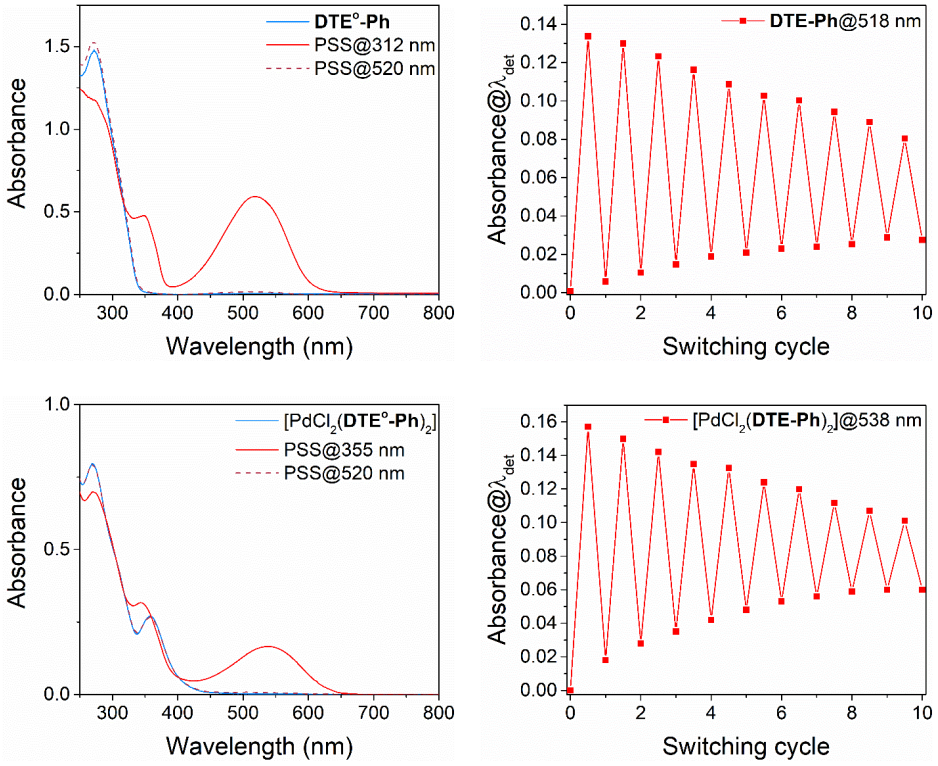


Figure S5 – (Left) Variation of the absorption spectrum of the open state of the free ligand **DTE-Ph** (c = 5.2·10^{-5} M) and of the complex $[PdCl_2(\mathbf{DTE\text{-}Ph})_2]$ (c = 1.7·10^{-5} M) in cyclohexane upon sequential irradiation with UV (λ_{exc} = 312 or 355 nm) and green light (λ_{exc} = 520 nm) until the corresponding ring-closing

and ring-opening PSSs were obtained. (Right) Variation of the absorbance at the spectral maximum of the ring-closed isomer of the ligand **DTE-Ph** (c = 1.3·10^{-5} M) (λ_{det} = 518 nm) and of the complex [$PdCl_2$(**DTE-Ph**)$_2$] (c = 0.7·10^{-6} M) (λ_{det} = 538 nm) in cyclohexane upon 10 consecutive photoswitching cycles. For ring-closing, UV irradiation was conducted at λ_{exc} = 312 (ligand) or 355 (complex) nm, while ring-opening was promoted with green light (λ_{exc} = 520 nm).

2. 5. 2. 3 NMR characterization of the photoisomerization of ligands and complexes

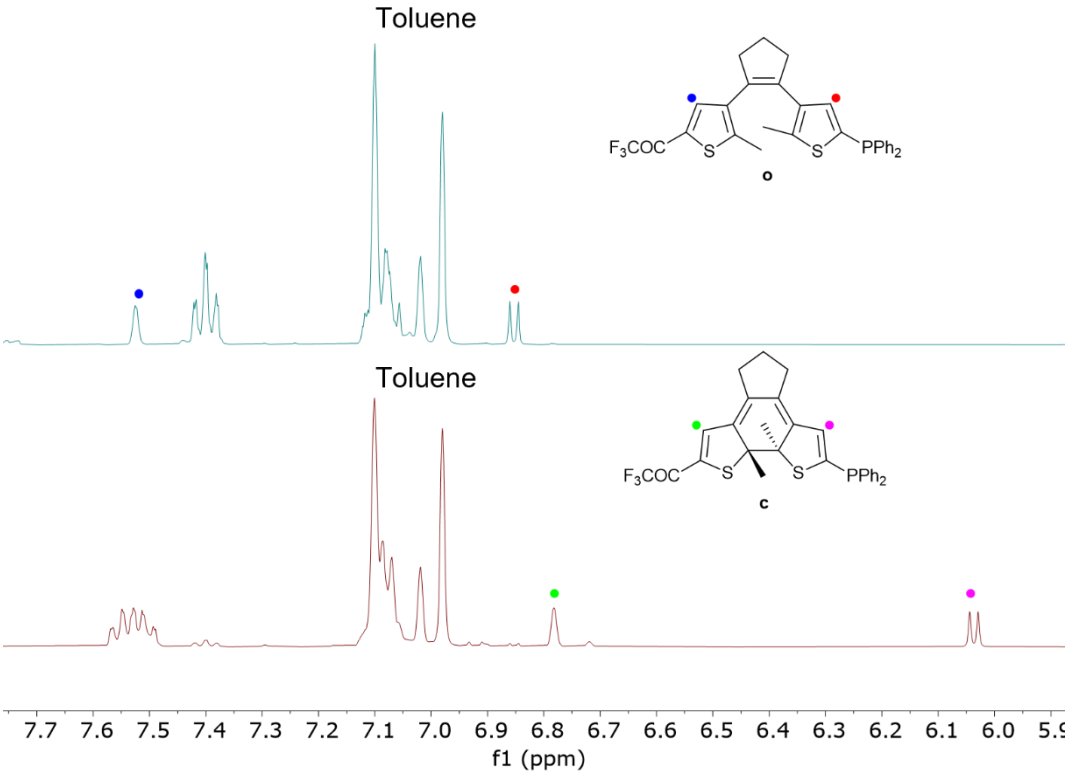


Figure S6 – Changes in the low-field region of the ^{1}H NMR spectrum (toluene-d_8, 400 MHz) of **DTE-COCF$_3$** upon photocyclization: (top) open state ligand (**o**), (bottom) PSS@365 nm, where major conversion to the closed isomer (**c**) is observed. In both cases, the positions of the ^{1}H NMR signals of the sulfur-containing rings are marked.

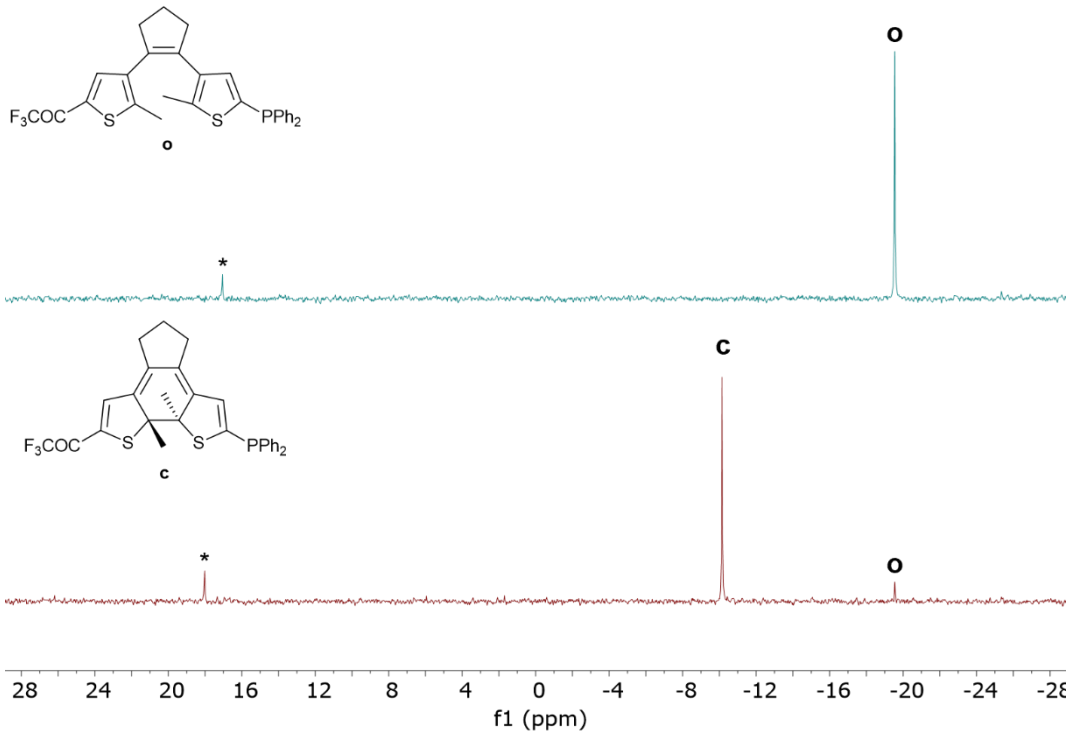


Figure S7 – Changes in the $^{31}P\{^{1}H\}$ NMR spectrum (toluene-d_8, 162 MHz) of **DTE-COCF$_3$** upon photocyclization: (top) open state ligand (**o**), (bottom) PSS@365 nm, where major conversion to the closed isomer (**c**) is observed. Additional low-intensity signals are found for the corresponding oxidized ligands (*).

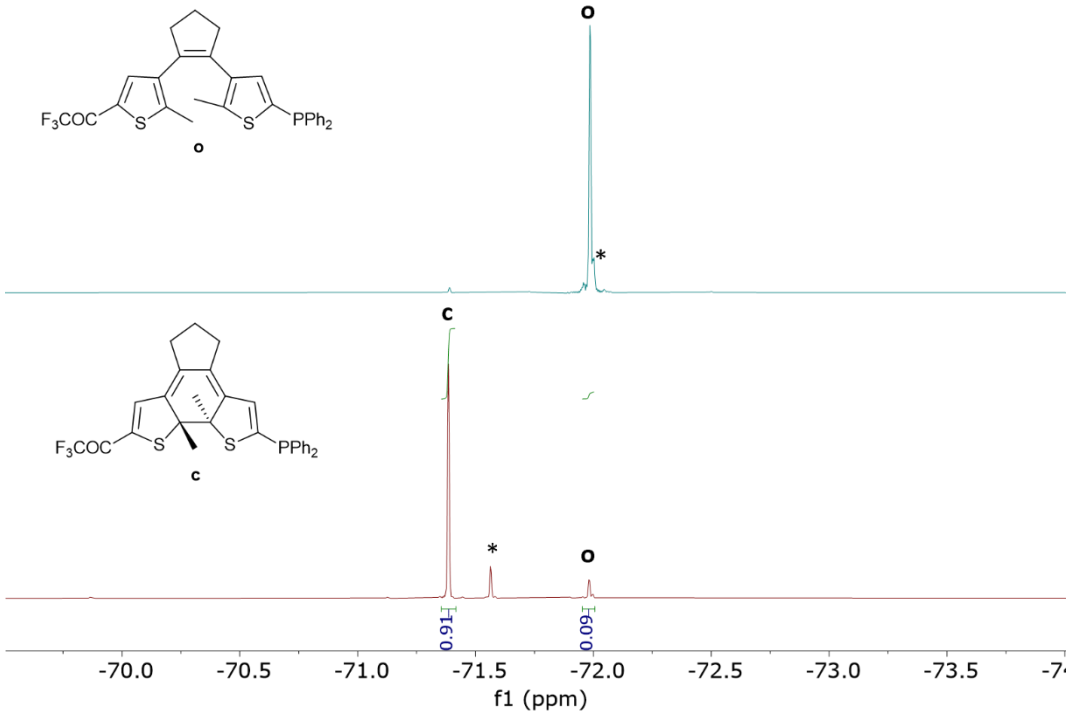


Figure S8 – Changes in the ^{19}F NMR spectra (toluene-d_8, 376 MHz) of **DTE-COCF$_3$** upon photocyclization: (top) open state ligand (**o**), (bottom) PSS@365 nm, where 91% conversion to the closed isomer (**c**) is determined from integrals. Additional low-intensity signals are found for the corresponding oxidized ligands (*).

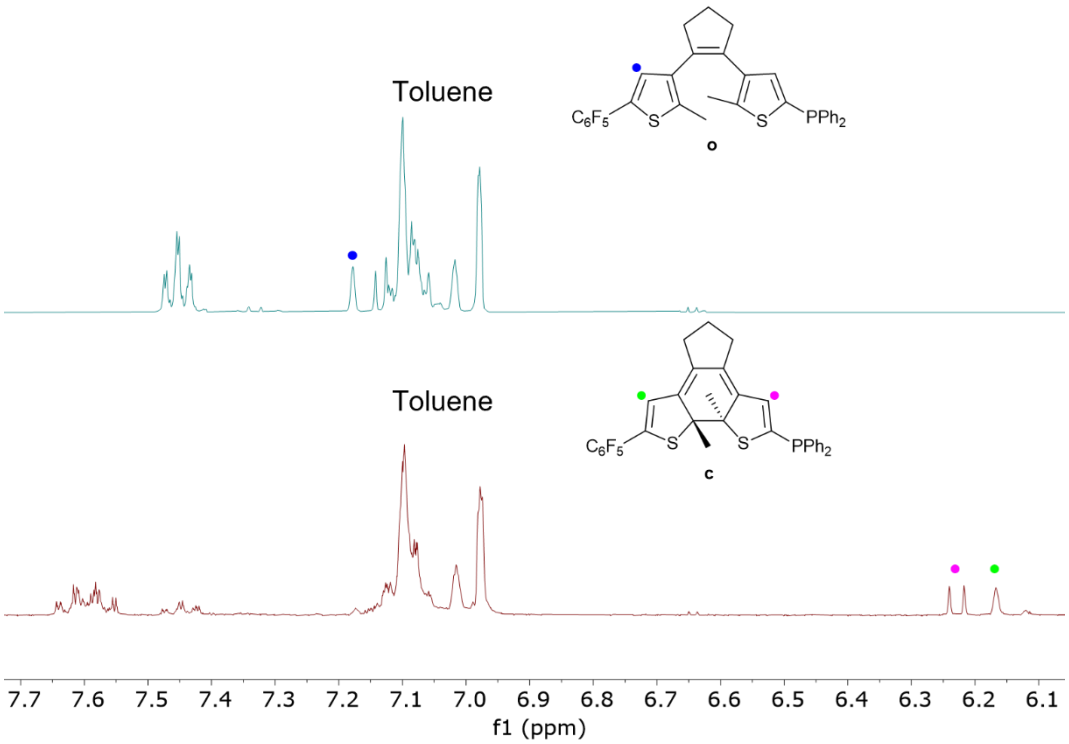


Figure S9 – Changes in the low-field region of the ^{1}H NMR spectrum (toluene-d_8) of **DTE-C$_6$F$_5$** upon photocyclization: (top, 400 MHz) open state ligand (**o**); (bottom, 300 MHz) PSS@312 nm, where major conversion to the closed isomer (**c**) is observed. In both cases, the positions of the ^{1}H NMR signals of the sulfur-containing rings are marked.

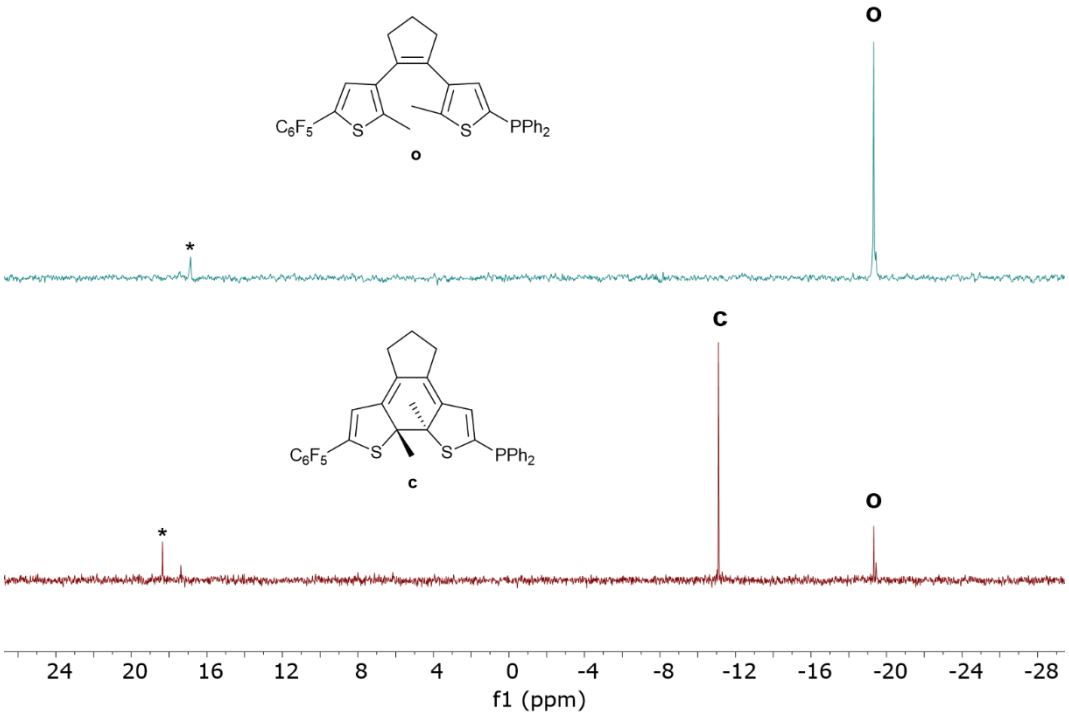


Figure S10 – Changes in the ^{31}P{^{1}H} NMR spectrum (toluene-d_8) of **DTE-C$_6$F$_5$** upon photocyclization: (top, 162 MHz) open state ligand (**o**); (bottom, 121 MHz) PSS@312 nm, where major conversion to the closed isomer (**c**) is observed. Additional low-intensity signals are found for the corresponding oxidized ligands (*).

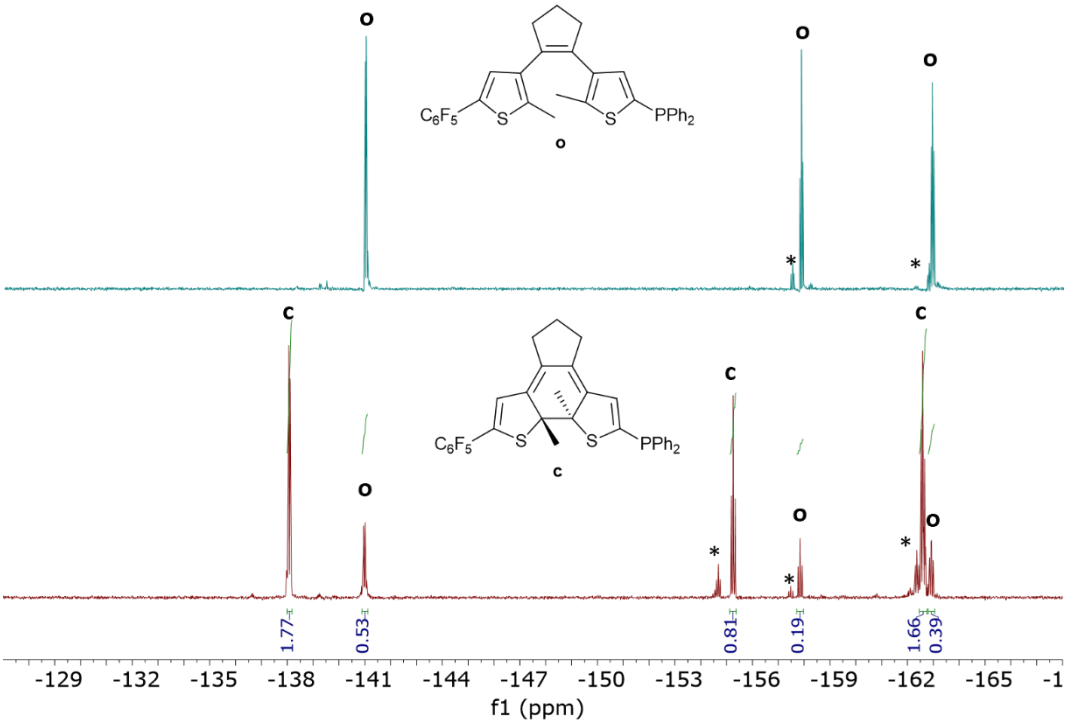


Figure S11 – Changes in the ^{19}F NMR spectrum (toluene-d_8) of **DTE-C$_6$F$_5$** upon photocyclization: (top, 376 MHz) open state ligand (**o**); (bottom, 282 MHz) PSS@312 nm, where 81% conversion to the closed isomer (**c**) is determined from integrals. Additional low-intensity signals are found for the corresponding oxidized ligands (*).

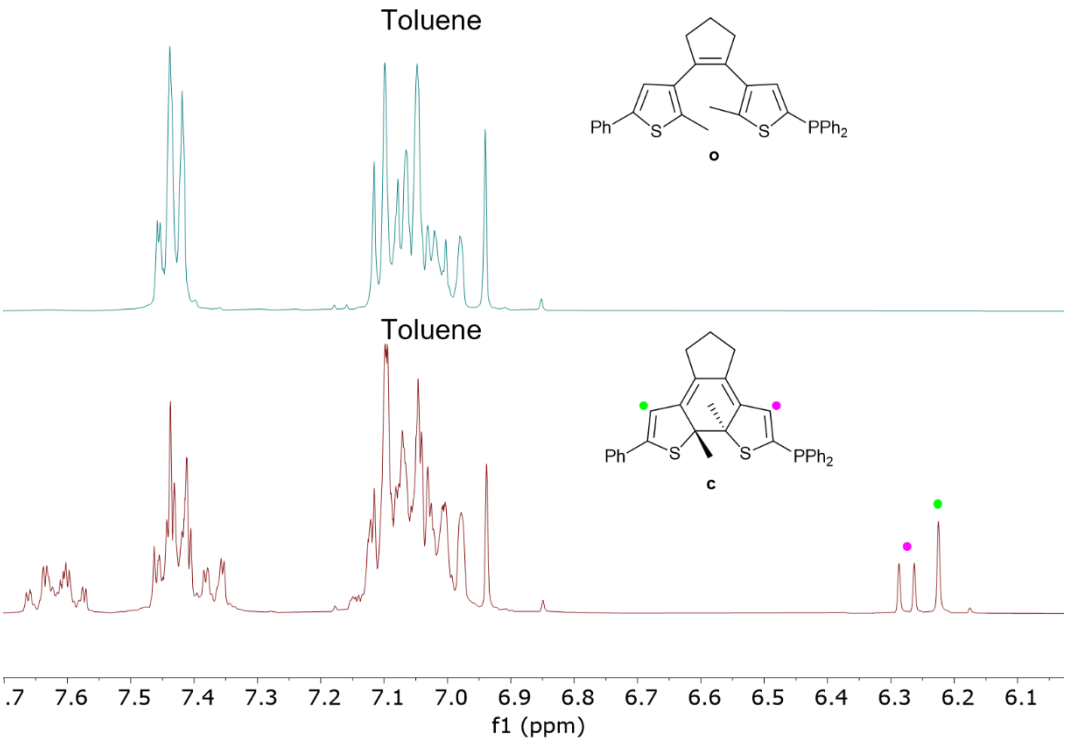


Figure S12 – Changes in the low-field region of the ^{1}H NMR spectrum (toluene-d_8) of **DTE-Ph** upon photocyclization: (top, 400 MHz) open state ligand (**o**); (bottom, 300 MHz) PSS@312 nm, where partial

conversion to the closed state (**c**) is observed. For the PSS@312 nm spectrum, the positions of the ^{1}H NMR signals of the sulfur-containing rings are marked for the closed isomer.

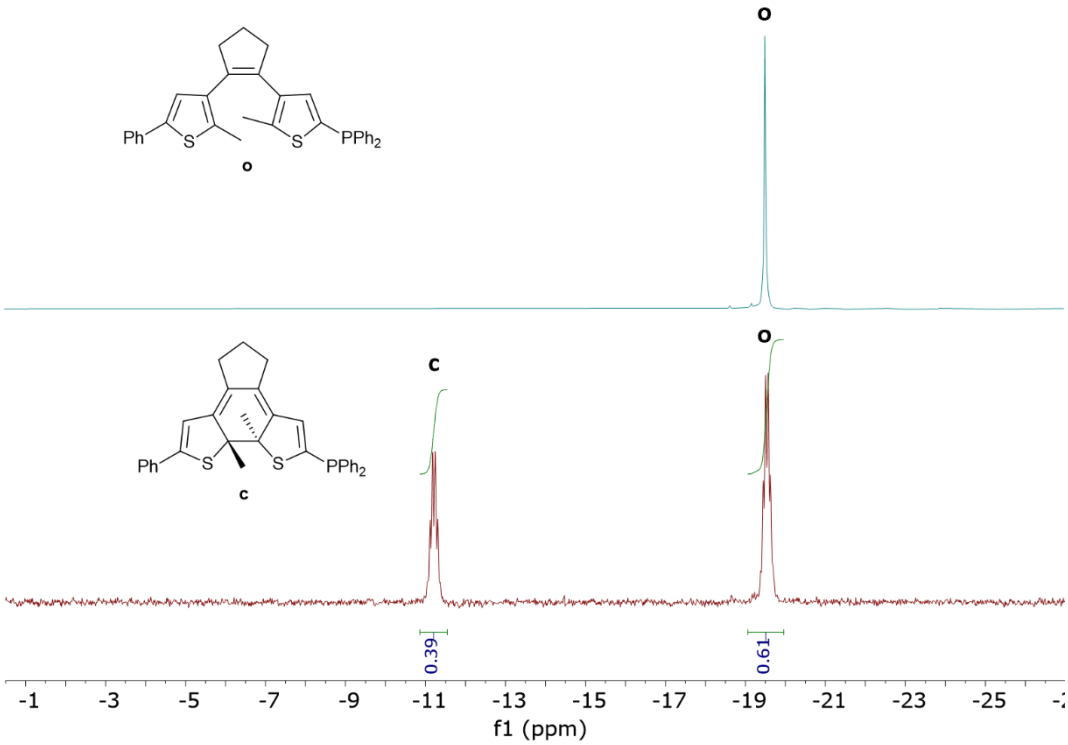


Figure S13 – Changes in the ^{31}P{^{1}H} NMR spectrum (toluene-d_8) of **DTE-Ph** upon photocyclization: (top, 162 MHz) open state ligand (**o**); (bottom, 121 MHz) PSS@312 nm, where 39% open-to-closed conversion is determined from integrals.

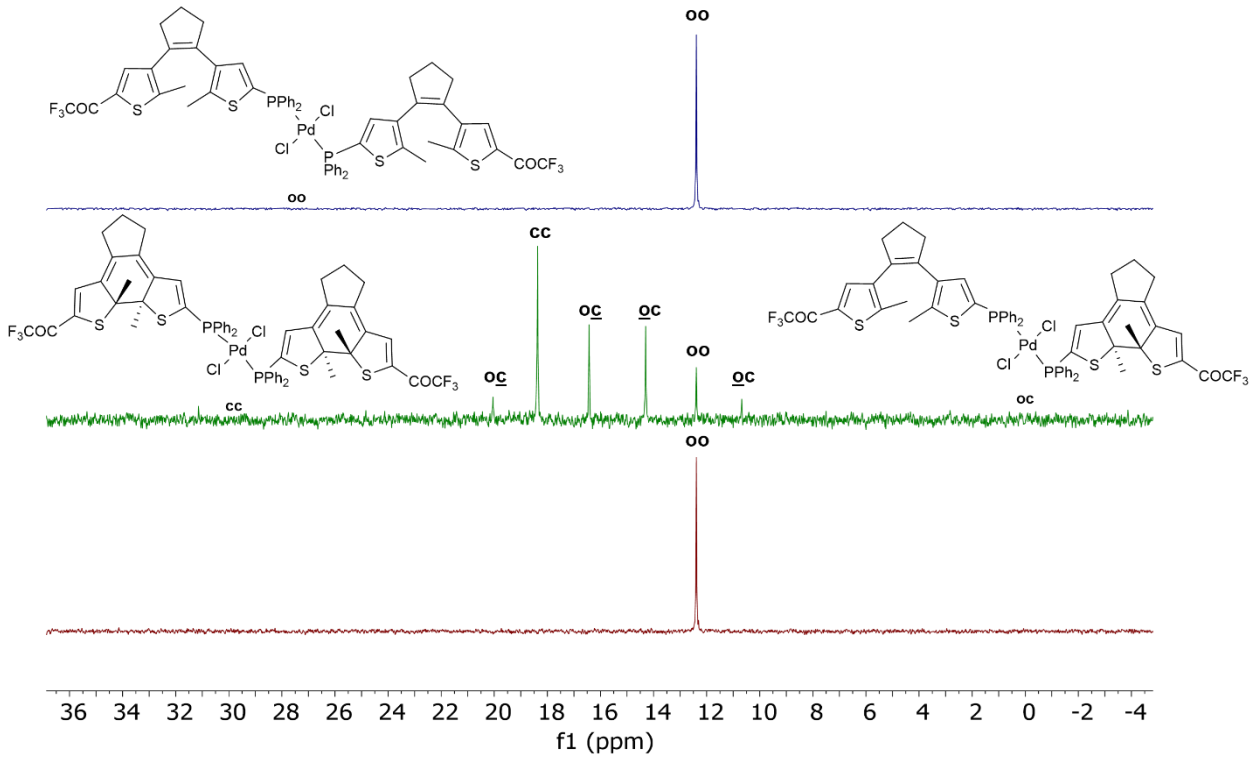


Figure S14 – Changes in the $^{31}P\{^{1}H\}$ NMR spectrum (toluene-d_8, 162 MHz) of $[PdCl_2(\mathbf{DTE\text{-}COCF_3})_2]$ upon photoswitching: (top) initial open state complex (**oo**); (middle) PSS@365 nm, where partial DTE photocyclization produces both **oc** ($^{2}J_{P,P}$ = 581 Hz) and **cc** complexes; (bottom) PSS@520 nm, where full back-photoisomerization to **oo** is observed. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

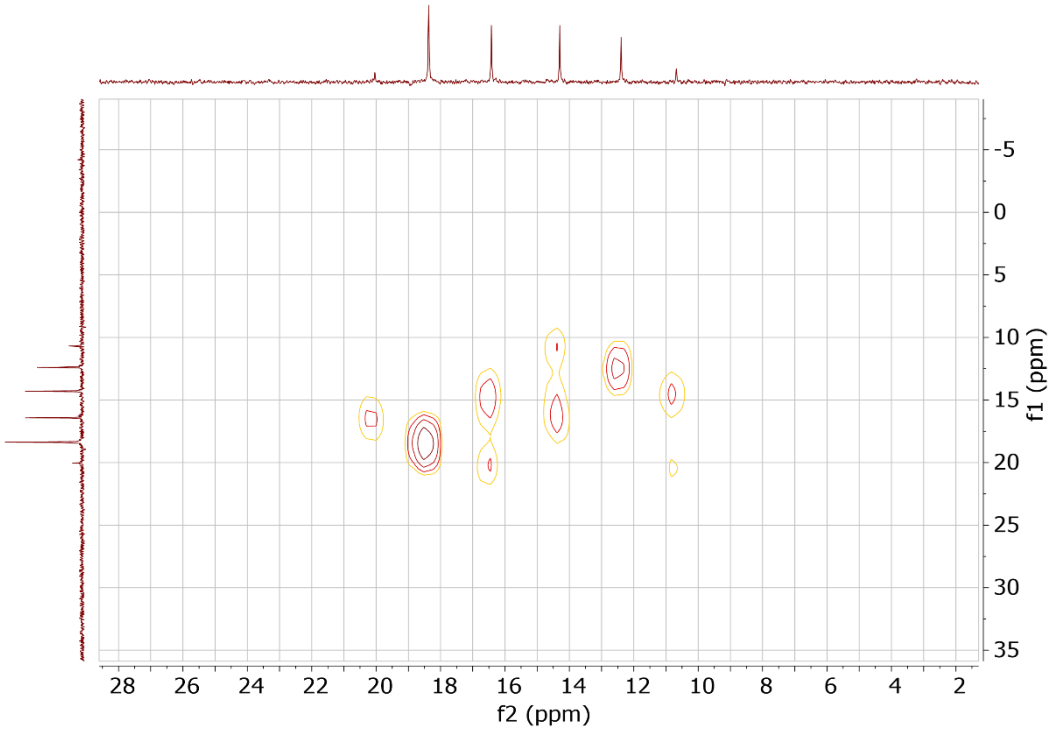


Figure S15 – $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY spectrum (toluene-d_8, 162 MHz) of $[PdCl_2(\textbf{DTE-COCF}_3)_2]$ at PSS@365 nm, where the cross-correlation between the two phosphorus nuclei in the **oc** isomer can be observed.

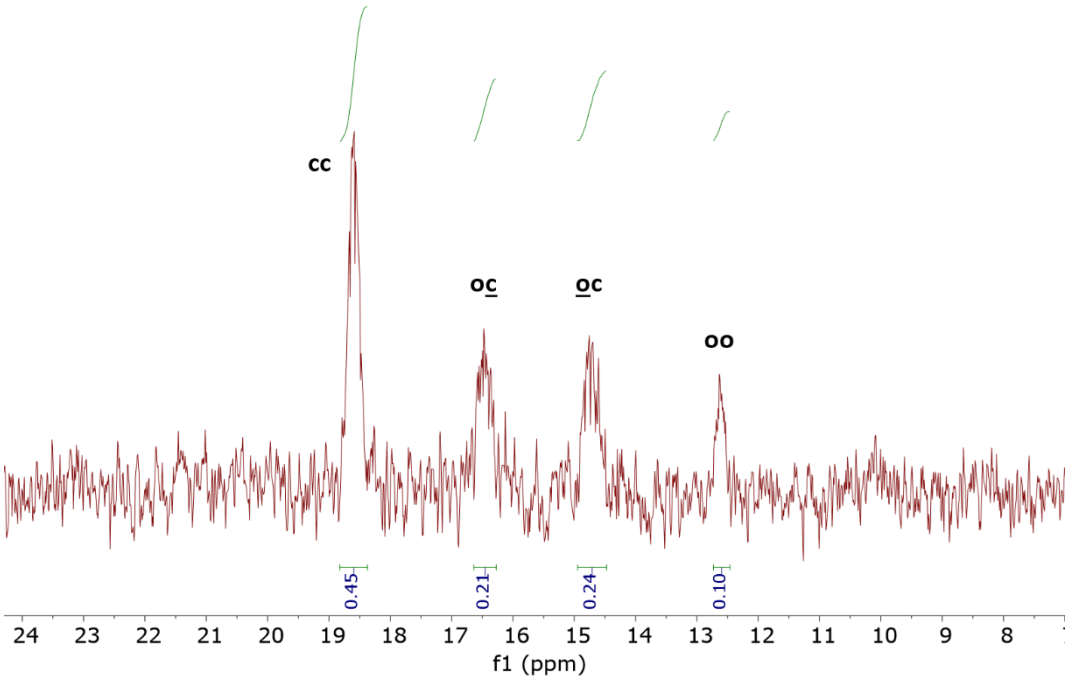


Figure S16 – ^{31}P NMR spectrum (toluene-d_8, 162 MHz) of PSS@365 nm for $[PdCl_2(\textbf{DTE-COCF}_3)_2]$, from which the composition of the photostationary state can be determined: 45:45:10 for **cc**:**oc**:**oo** complexes. Labels **oc** and **oc** are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

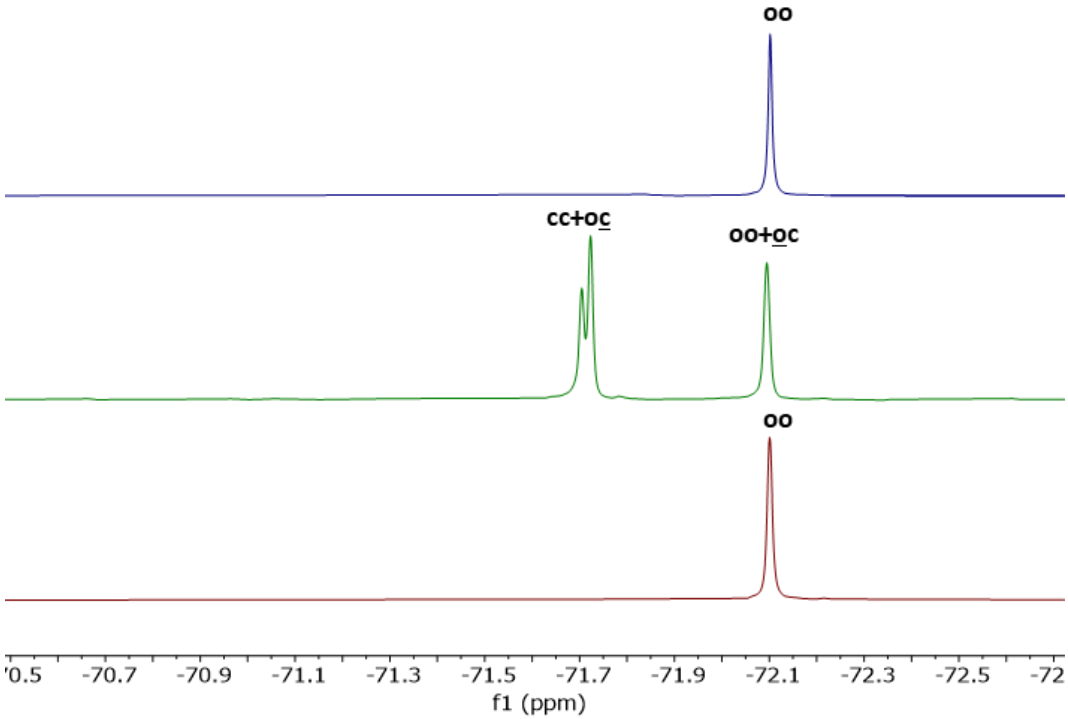


Figure S17 – Changes in the ^{19}F NMR spectrum (toluene-d_8, 376 MHz) of $[PdCl_2(\mathbf{DTE\text{-}COCF_3})_2]$ upon photoswitching: (top) initial open state complex (**oo**); (middle) PSS@365 nm; (bottom) PSS@520 nm, where full back-photoisomerization to **oo** is observed. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the trifluoromethyl ketone group attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

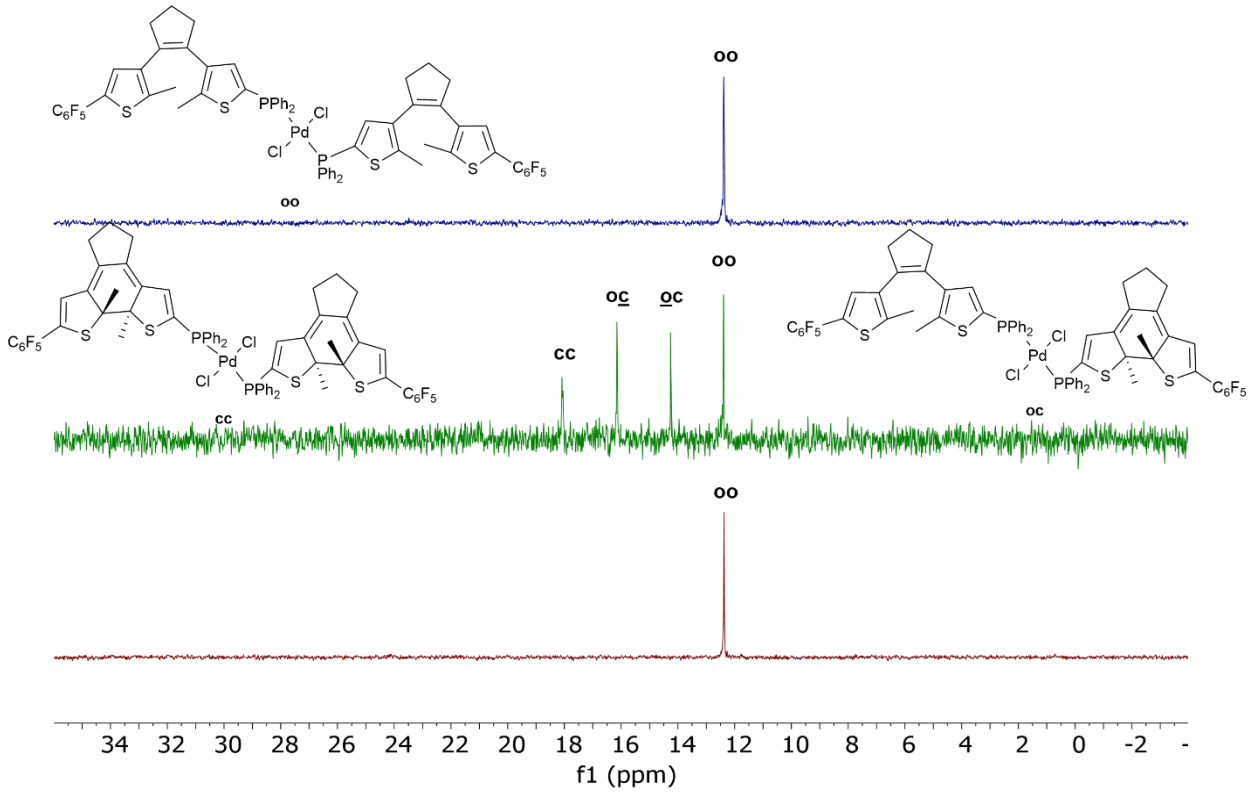


Figure S18 – Changes in the $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8, 121 MHz) of $[PdCl_2(\mathbf{DTE\text{-}C_6F_5})_2]$ upon photoswitching: (top) initial open state complex (**oo**); (middle) PSS@365 nm, where partial DTE

photocyclization produces both **oc** ($^2J_{P,P}$ not determined due to low signal-to-noise ratio) and **cc** complexes; (bottom) PSS@520 nm, where full back-photoisomerization to **oo** is observed.

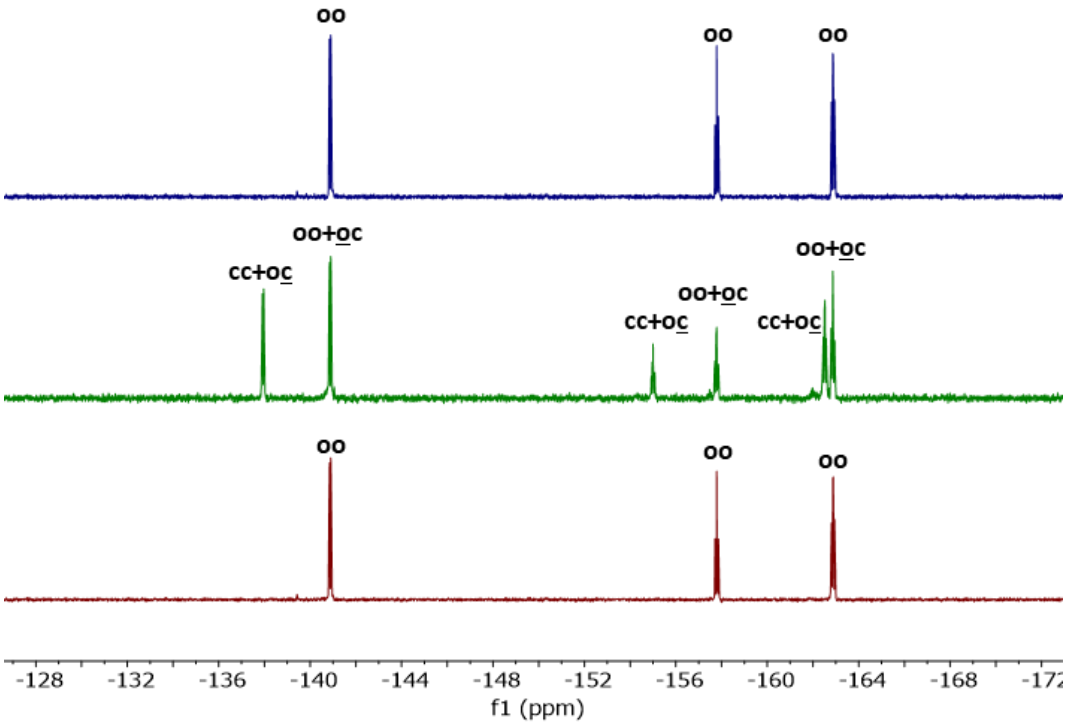


Figure S19 – Changes in the ^{19}F NMR spectrum (toluene-d_8, 282 MHz) of [$PdCl_2$(**DTE-C_6F_5**)$_2$] upon photoswitching: (top) initial open state complex (**oo**); (middle) PSS@365 nm, where partial DTE photocyclization produces both **oc** and **cc** complexes; (bottom) PSS@520 nm, where full back-photoisomerization to **oo** is observed. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the pentafluorophenyl group attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

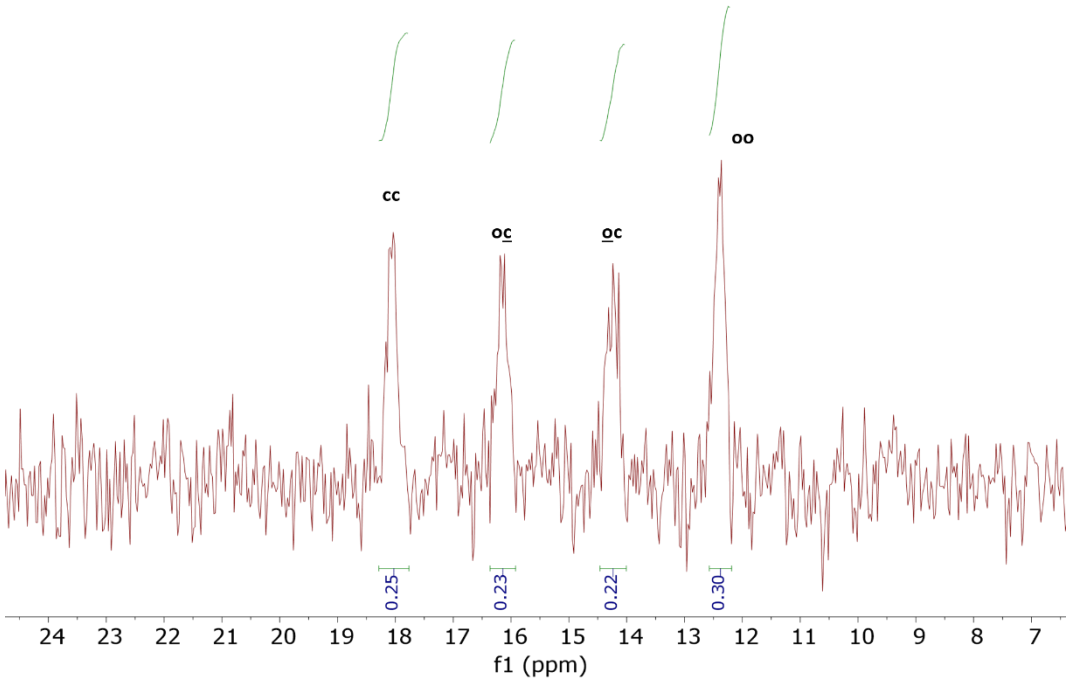


Figure S20 – ^{31}P NMR spectrum (toluene-d_8, 121 MHz) of PSS@365 nm [$PdCl_2$(**DTE-C_6F_5**)$_2$]. From integrals, a 25:45:30 molar ratio can be estimated for the photoequilibrium **cc**:**oc**:**oo** mixture produced. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

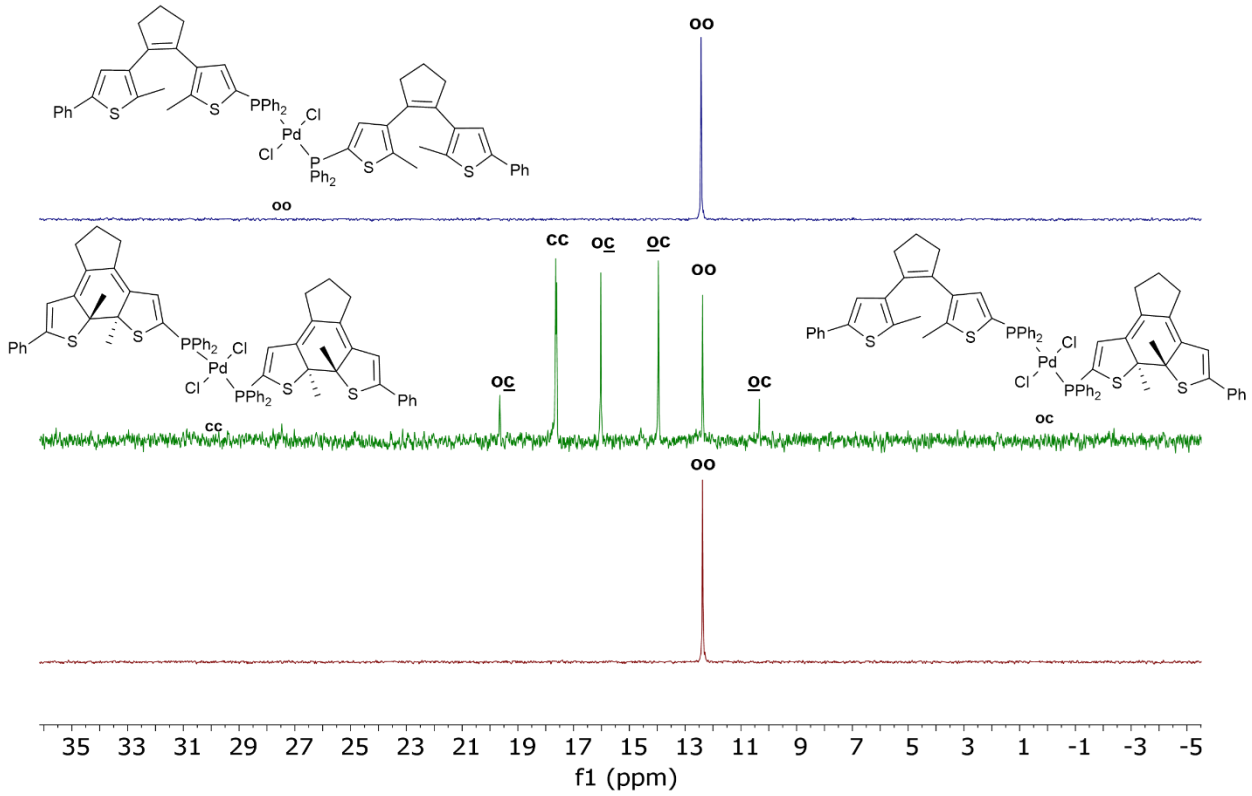


Figure S21 – Changes in the ^{31}P{^{1}H} NMR spectrum (toluene-d_8, 162 MHz) of [$PdCl_2$(**DTE-Ph**)$_2$] upon photoswitching: (top) initial open state complex (**oo**); (middle) PSS@365 nm, where partial DTE

photocyclization produces both **oc** ($^2J_{P,P}$ = 586 Hz) and **cc** complexes; (bottom) PSS@520 nm, where full back-photoisomerization to **oo** is observed. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

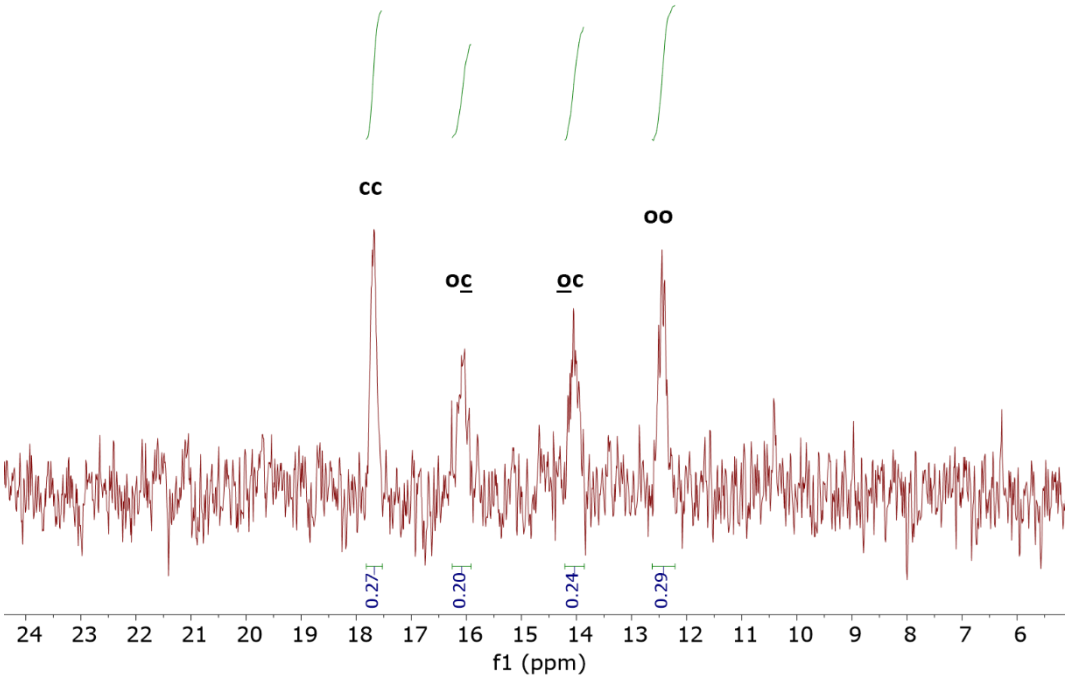


Figure S22 – ^{31}P NMR spectrum (toluene-d_8, 162 MHz) of PSS@365 nm for [$PdCl_2$(**DTE-Ph**)$_2$]. From integrals, a 27:44:29 molar ratio can be estimated for the photoequilibrium **cc**:**oc**:**oo** mixture produced. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

2. 5. 3. DFT calculations of the optical properties of ligands and complexes

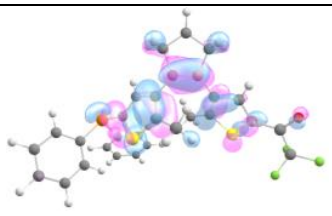
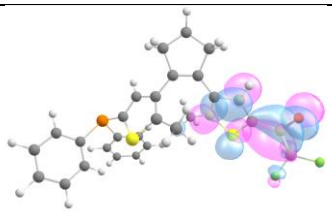
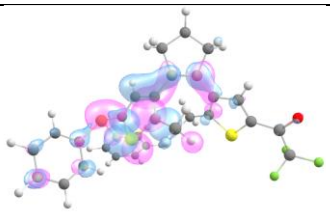
Optimized ligand structures in the ground state show characteristic geometry changes accompanying the isomerization process. For instance, the distance between the reactive carbon atoms changes from 3.49 Å in the open state to 1.54 Å in the closed state, in accordance with previously reported data.[31] However, no significant change in bond lengths or dihedral angles associated with different substituents in one of the thiophene rings was found.

2. 5. 3. 1 Frontier molecular orbitals analysis

Table S2 – Variation of the HOMO-LUMO gap in ligands and their palladium complexes.

State	Parameter	**DTE-$COCF_3$**	**DTE-C_6F_5**	**DTE-Ph**
o	HOMO	-5.63	-5.42	-5.28
	LUMO	-2.15	-1.34	-0.96
	ΔE	**3.48**	**4.09**	**4.32**
c	HOMO	-4.94	-4.69	-4.57
	LUMO	-2.72	-2.09	-1.93
	ΔE	**2.22**	**2.60**	**2.64**
		[$PdCl_2$(**DTE-$COCF_3$**)$_2$]	[$PdCl_2$(**DTE-C_6F_5**)$_2$]	[$PdCl_2$(**DTE-Ph**)$_2$]
oo	HOMO	-5.71	-5.43	-5.29
	LUMO	-2.32	-2.21	-2.20
	ΔE	**3.39**	**3.22**	**3.09**
oc	HOMO	-5.03	-4.72	-4.61
	LUMO	-2.80	-2.29	-2.29
	ΔE	**2.23**	**2.43**	**2.32**
cc	HOMO	-5.01	-4.74	-4.61
	LUMO	-2.80	-2.36	-2.31
	ΔE	**2.21**	**2.38**	**2.31**

Table S3 – Frontier molecular orbitals of the open and closed forms of the ligands.

	HOMO	LUMO	LUMO+1
DTE^o-$COCF_3$			

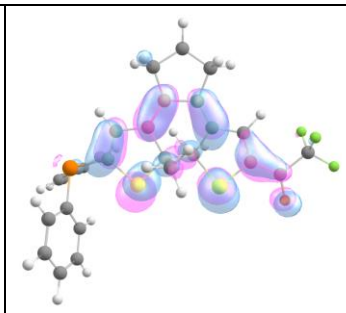
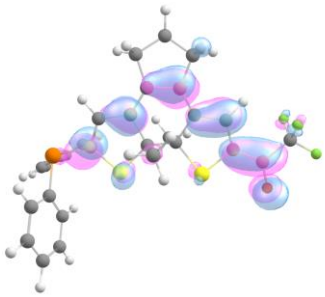
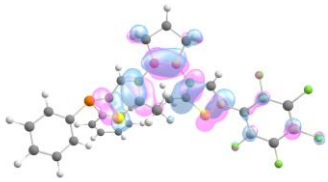
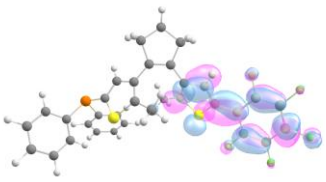
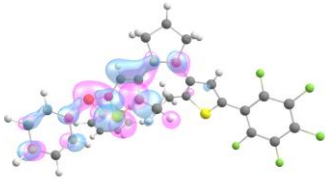
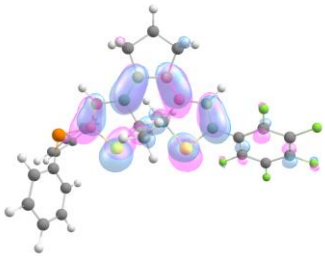
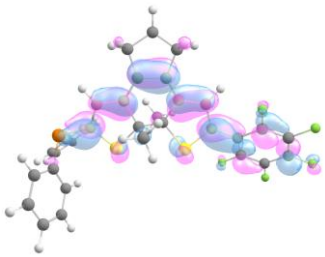
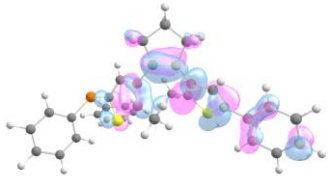
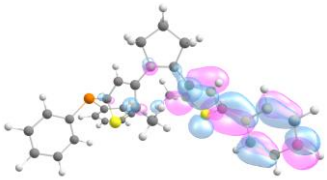
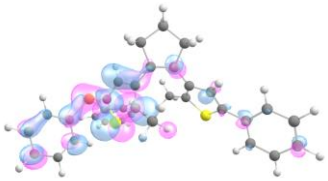
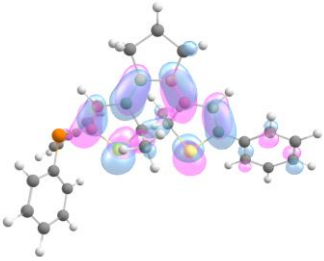
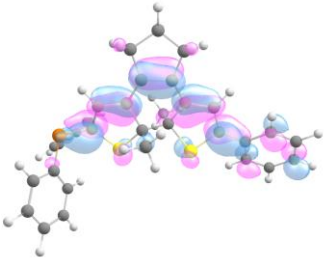
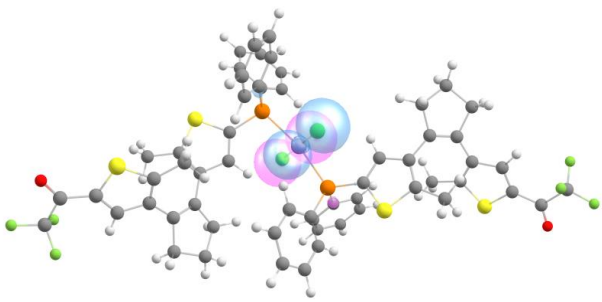
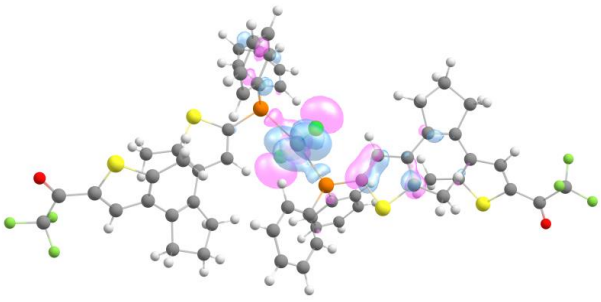
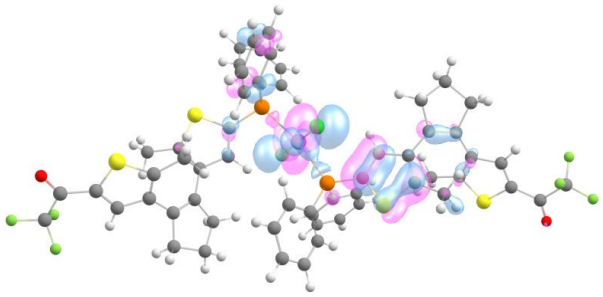
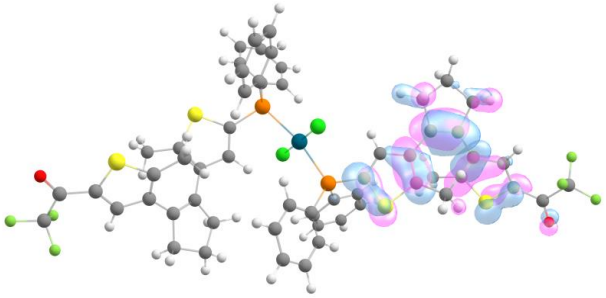
DTE^{c}-COCF$_3$			
DTE^{o}-C$_6$F$_5$			
DTE^{c}-C$_6$F$_5$			
DTE^{o}-Ph			
DTE^{c}-Ph			

Table S4 – Selected frontier molecular orbitals of the **oo**, **oc** and **cc** forms of the complexes

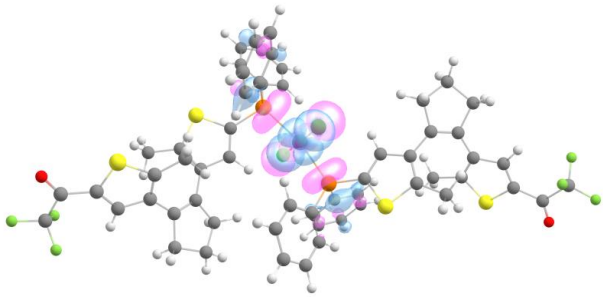
[PdCl$_2$(**DTE^{o}-COCF$_3$**)$_2$]	
	
HOMO-26	HOMO-3



HOMO-2

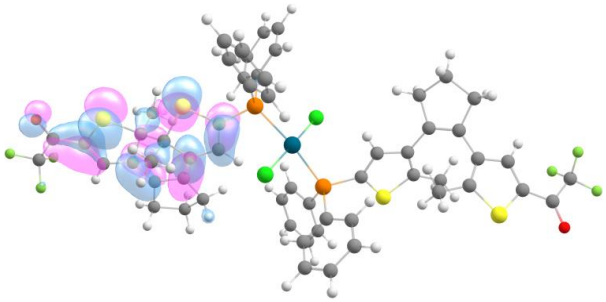


HOMO

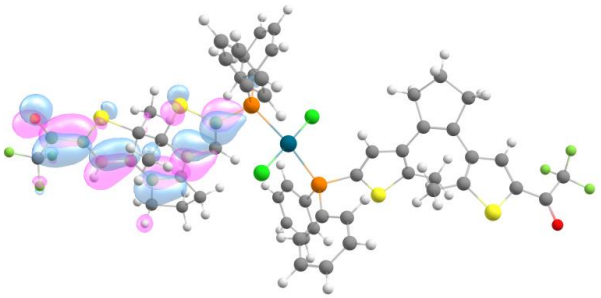


LUMO

$[PdCl_2(\mathbf{DTE^o\text{-}COCF_3})(\mathbf{DTE^c\text{-}COCF_3})]$

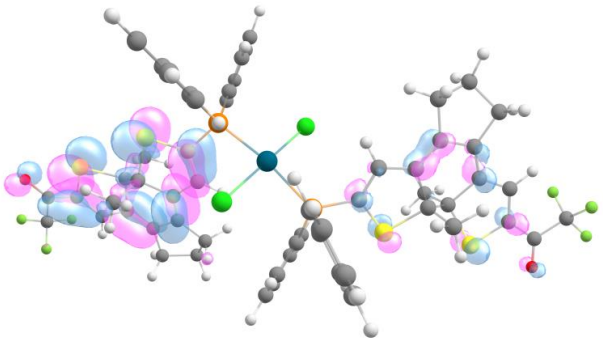


HOMO

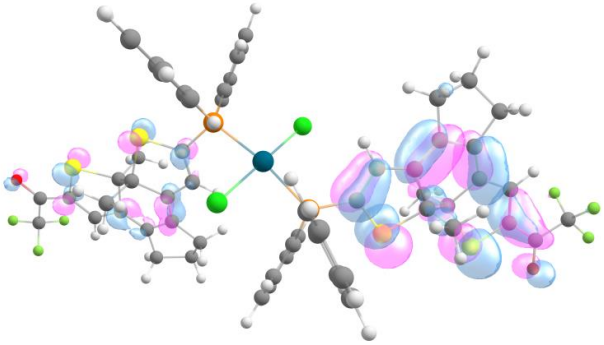


LUMO

$[PdCl_2(\mathbf{DTE^c\text{-}COCF_3})_2]$



HOMO-1



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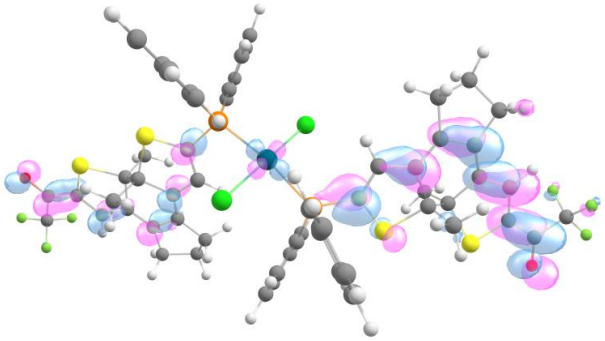
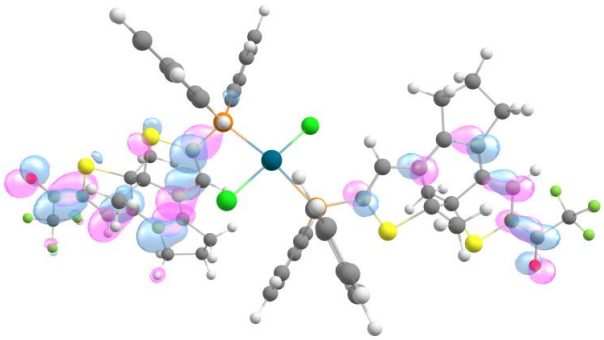
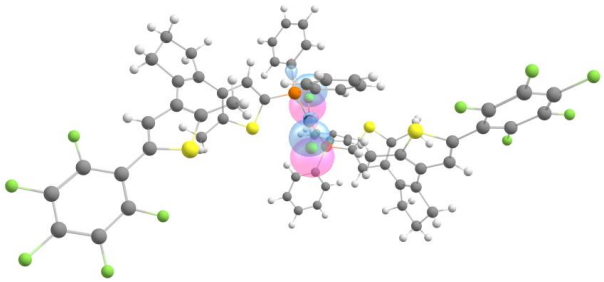


LUMO

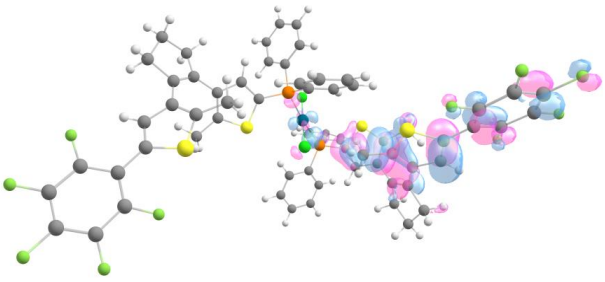


LUMO+1

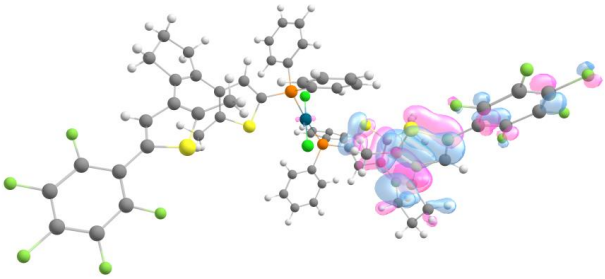
$[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$



HOMO-28



HOMO-2



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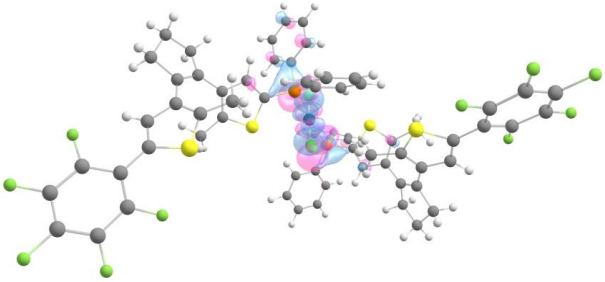
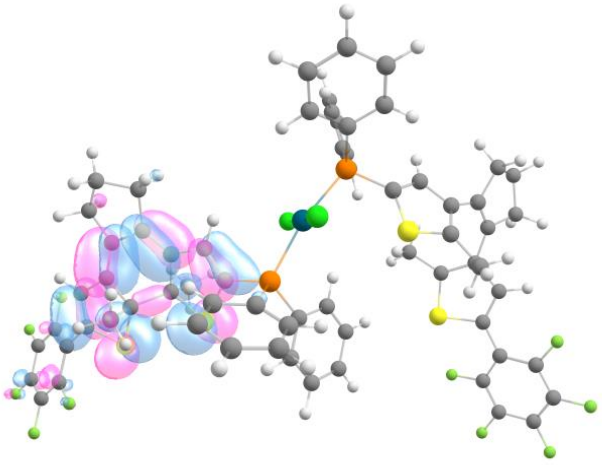


LUMO

$[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})(\mathbf{DTE^c\text{-}C_6F_5})]$



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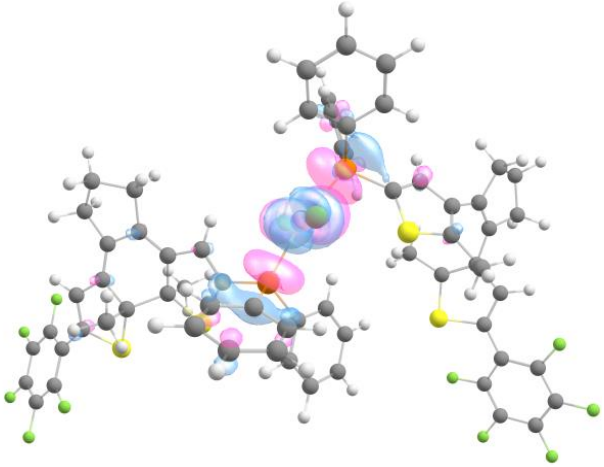

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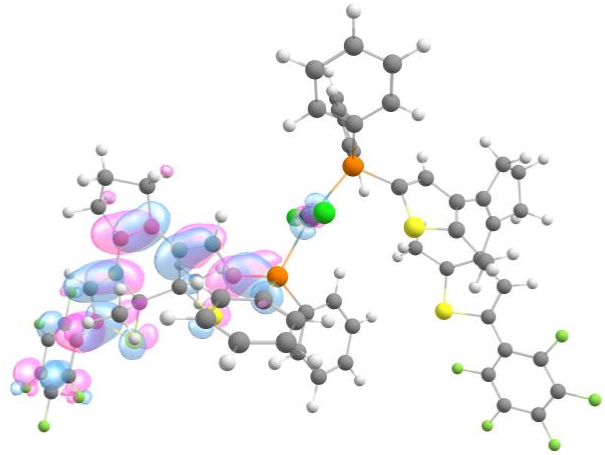
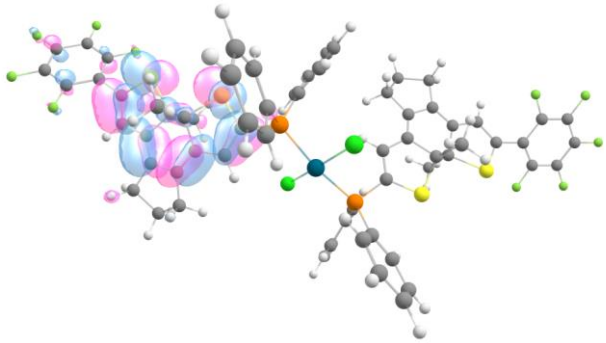
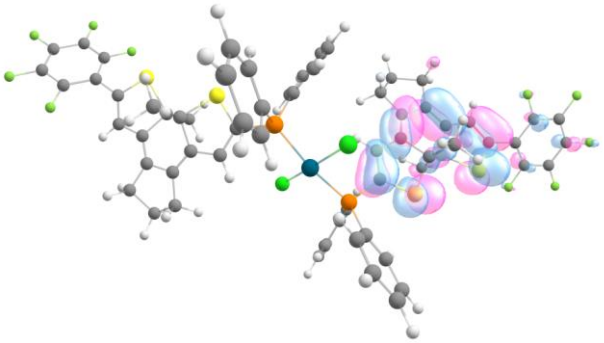


LUMO+1

$[PdCl_2(\mathbf{DT^c\text{-}C_6F_5})_2]$



HOMO-1



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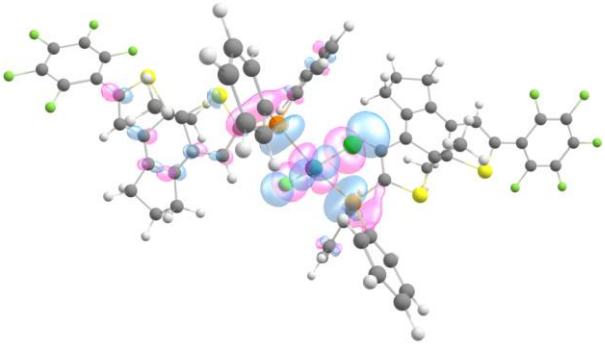

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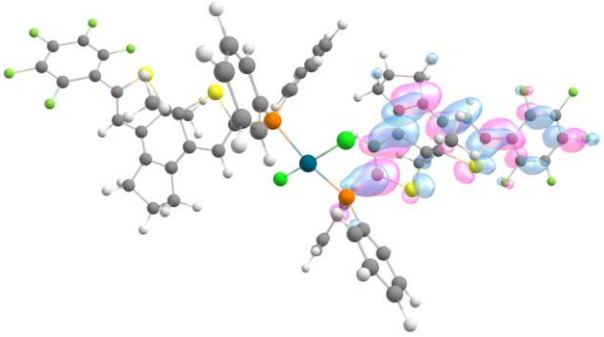
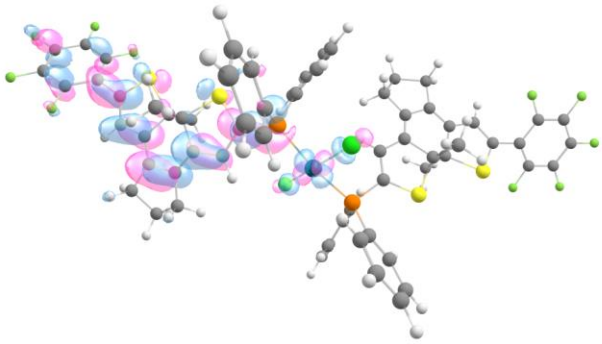
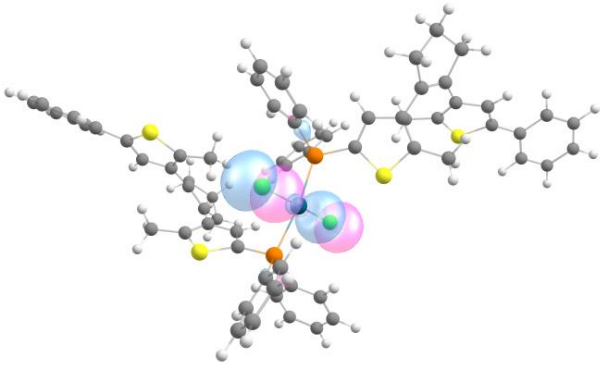


LUMO+1

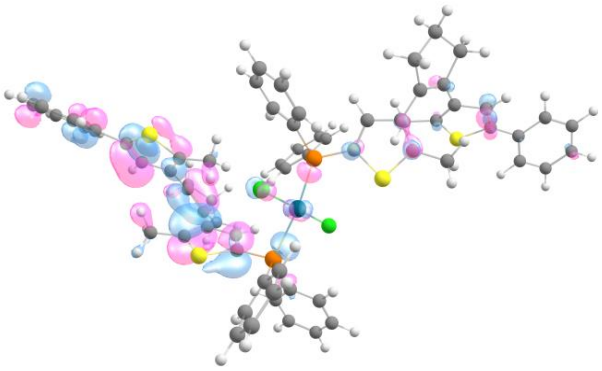


LUMO+2

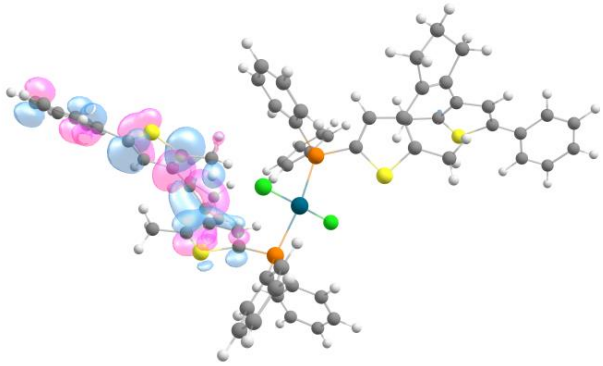
[$PdCl_2$(**DTE°-Ph**)$_2$]



HOMO-28



HOMO-2



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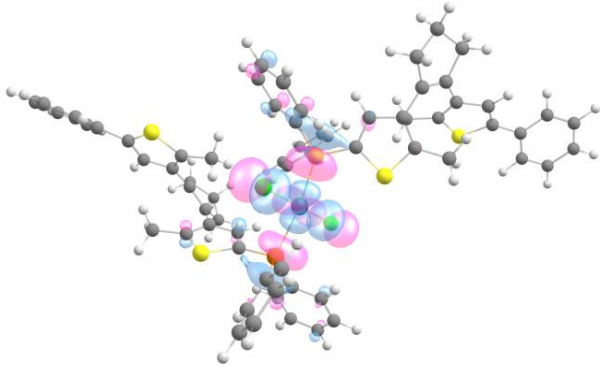
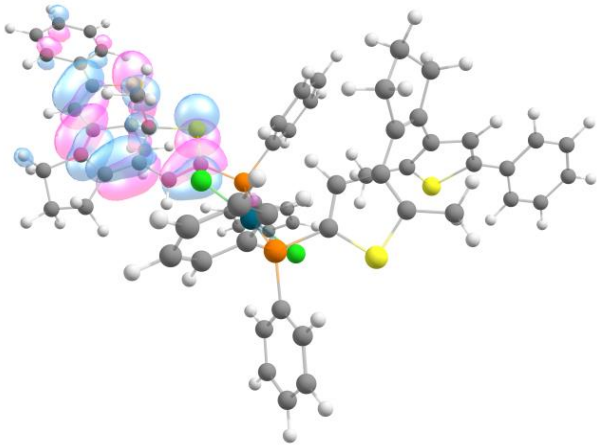


LUMO

[$PdCl_2$(**DTE^o-Ph**)(**DTE^c-Ph**)]



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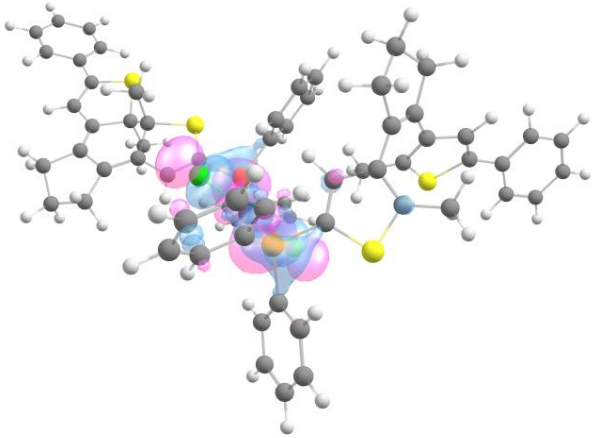
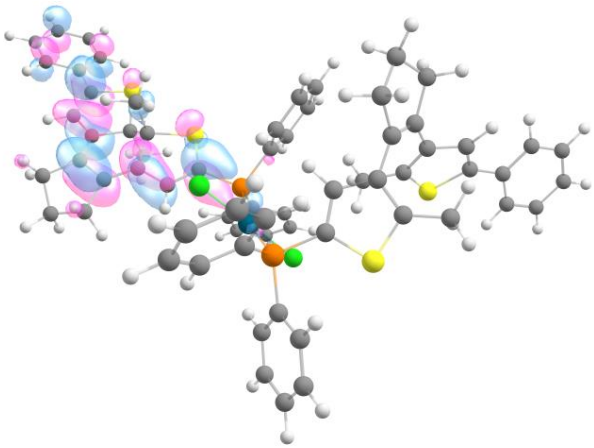
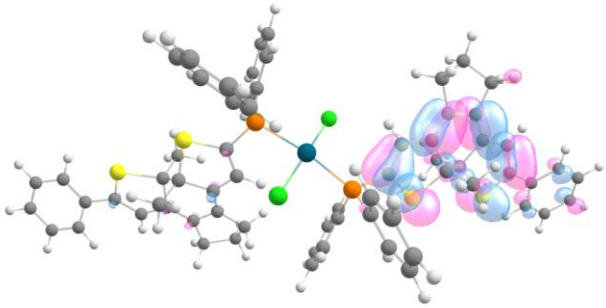


LUMO

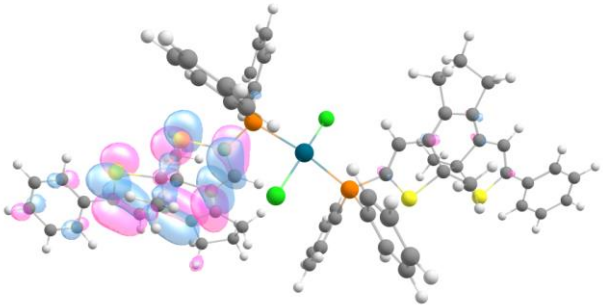


LUMO+1

[$PdCl_2$(**DTE^c-Ph**)$_2$]



HOMO-1



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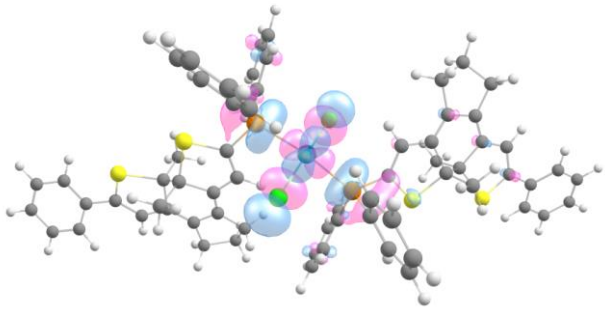
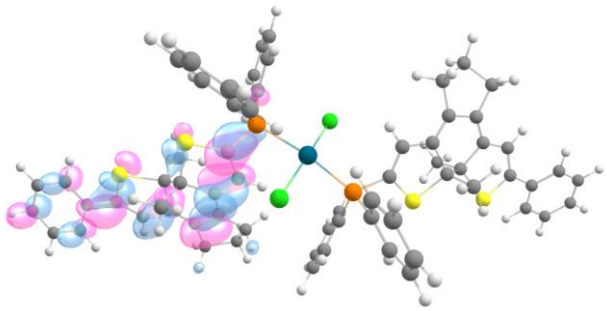
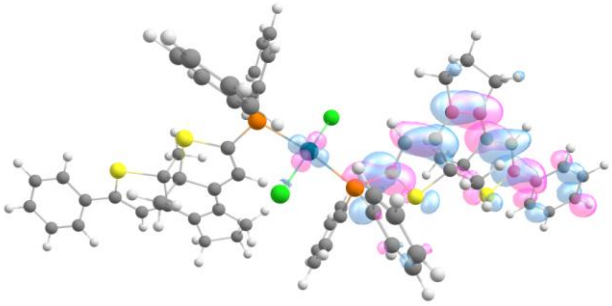


LUMO



LUMO+1



LUMO+2

2. 5. 3. 2 Vertical transitions

Table S5 – Calculated absorption wavelengths (λ), oscillator strengths (*f*) and assigned transitions for singlet state ligands and complexes in toluene within the 250-800 nm range.

	λ (nm)	*f*	Assigned transitions
DTE^{o}-COCF$_3$	319	0.1265	H – L (78.7%)
	272	0.4535	H-4 – L (24.8%); H-3 – L (23.3%); H-2 – L (22.7%); H-5 – L (6.6%); H – L+1 (5.7%)
DTE^{c}-COCF$_3$	576	0.3497	H – L (96.5%)
DTE^{o}-C$_6$F$_5$	292	0.4847	H – L (76.8%)
	268	0.3325	H – L+1 (61.4%)
DTE^{c}-C$_6$F$_5$	500	0.4337	H – L (95.9%)
DTE^{o}-Ph	284	0.4609	H – L (84.5%)
	270	0.3146	H – L+1 (54.7%)
DTE^{c}-Ph	495	0.4667	H – L (96.5%)
[PdCl$_2$(**DTE^{o}-COCF$_3$**)$_2$]	350	0.2612	H-26 – L (33.4%); H-3 – L (22.7%); H-2 – L (19.9%)
[PdCl$_2$(**DTE^{o}-COCF$_3$**)(**DTE^{c}-COCF$_3$**)]	573	0.4026	H – L (96.6%)
[PdCl$_2$(**DTE^{c}-COCF$_3$**)$_2$]	575	0.6814	H-1 – L+1 (31.5%); H – L (27.8%); H – L+1 (27.0%); H-1 – L (9.9%)
	568	0.1539	H-1 – L (53.9%); H – L+1 (37.2%)
[PdCl$_2$(**DTE^{o}-C$_6$F$_5$**)$_2$]	335	0.2618	H-28 – L (34.2%)
	324	0.2353	H-28 – L (37.1%); H-2 – L (20.5%)
[PdCl$_2$(**DTE^{o}-C$_6$F$_5$**)(**DTE^{c}-C$_6$F$_5$**)]	506	0.5280	H – L (70.4%); H – L+1 (25.4%)
[PdCl$_2$(**DTE^{c}-C$_6$F$_5$**)$_2$]	508	0.8420	H – L+1 (61.8%)
	502	0.1962	H-1 – L (44.0%); H – L+1 (26.1%); H-1 – L+2 (23.2%); H-1 – L+1 (2.6%)
[PdCl$_2$(**DTE^{o}-Ph**)$_2$]	348	0.2910	H-28 – L (27.5%)
	324	0.2141	H-28 – L (37.4%); H-2 – L (19.8%)
[PdCl$_2$(**DTE^{o}-Ph**)(**DTE^{c}-Ph**)]	503	0.5810	H – L+1 (87.6%)
[PdCl$_2$(**DTE^{c}-Ph**)$_2$]	506	0.9577	H – L+1 (50.9%); H-1 – L+1 (22.6%)
	500	0.1759	H – L+1 (40.0%); H-1 – L+2 (35.3%); H-1 – L (20.2%)

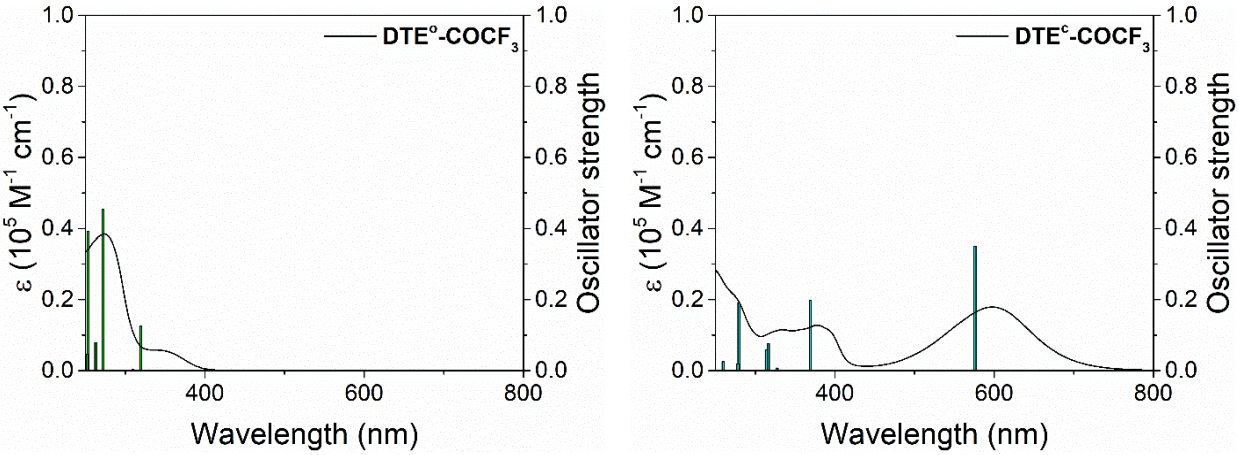


Figure S23 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for **DTE-COCF₃** in toluene: (left) **DTE°-COCF₃**; (right) **DTE^c-COCF₃**.

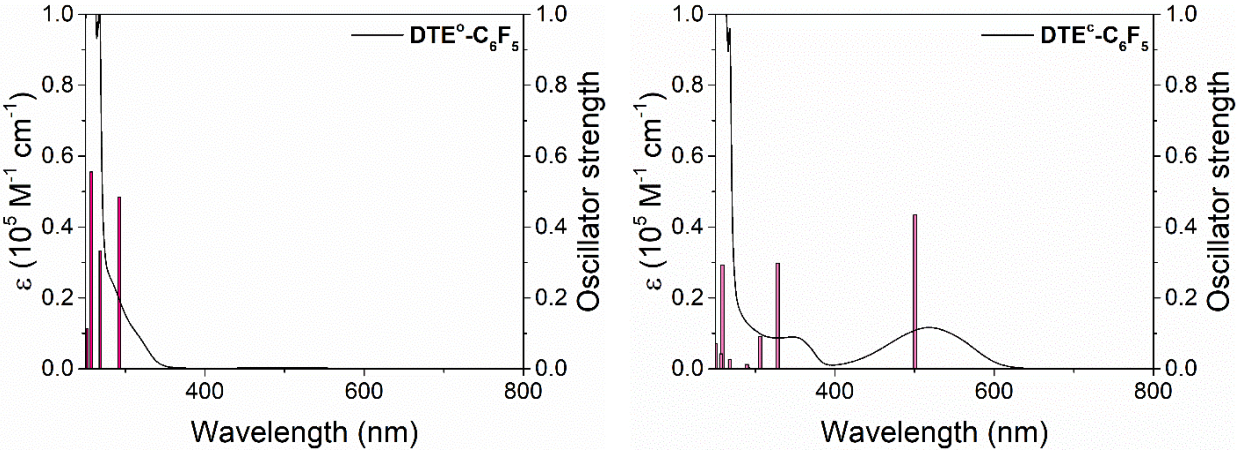


Figure S24 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for **DTE-C₆F₅** in toluene: (left) **DTE°-C₆F₅**; (right) **DTE^c-C₆F₅**.

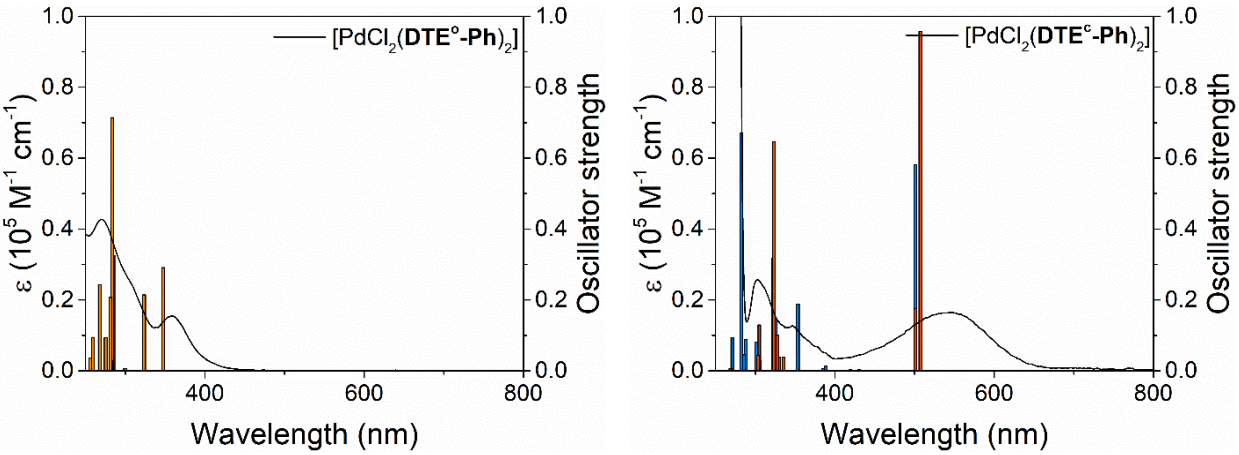


Figure S25 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for **DTE-Ph** in toluene: (left) **DTE°-Ph**; (right) **DTE^c-Ph**.

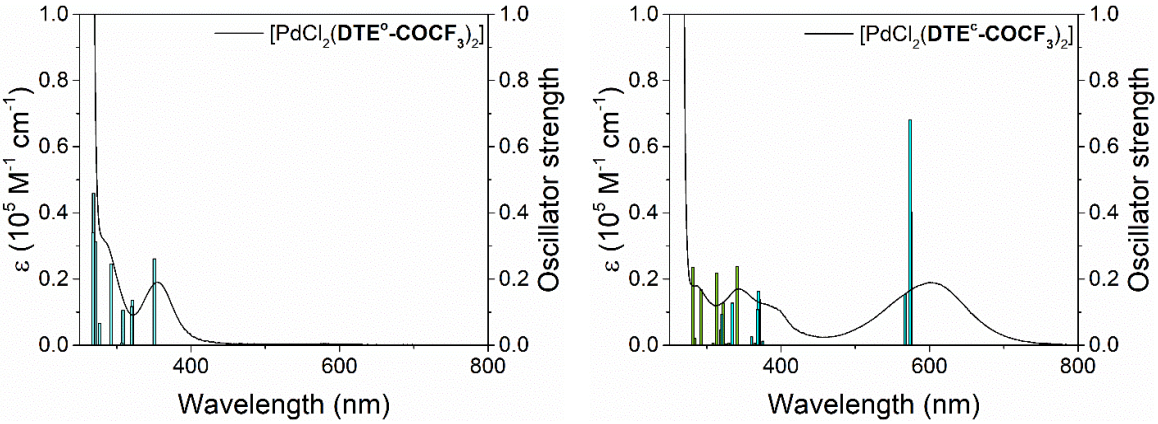


Figure S26 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for [$PdCl_2$(**DTE-$COCF_3$**)$_2$] in toluene: (left) [$PdCl_2$(**DTE°-$COCF_3$**)$_2$]; (right) [$PdCl_2$(**DTE^c-$COCF_3$**)$_2$], for which vertical transitions are shown for both **oc** (green) and **cc** (cyan) isomers.

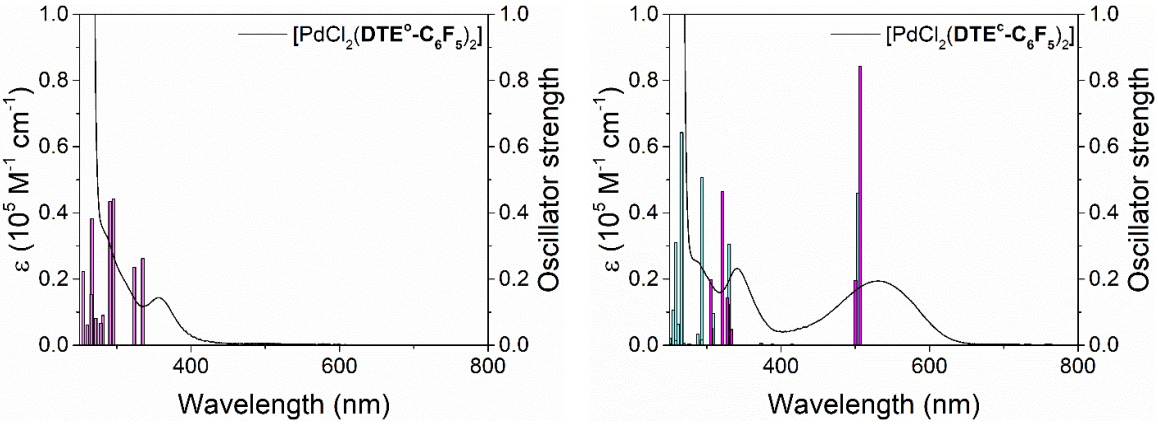


Figure S27 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for [$PdCl_2$(**DTE-C_6F_5**)$_2$] in toluene: (left) [$PdCl_2$(**DTE°-C_6F_5**)$_2$]; (right) [$PdCl_2$(**DTE^c-C_6F_5**)$_2$], for which vertical transitions are shown for both **oc** (light cyan) and **cc** (magenta) isomers.

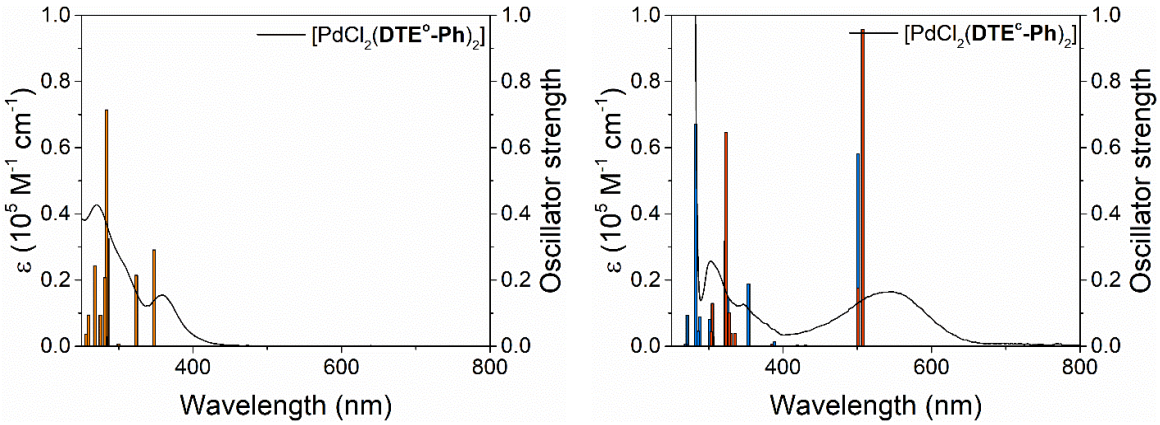


Figure S28 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for [$PdCl_2$(**DTE-Ph**)$_2$] in toluene: (left) [$PdCl_2$(**DTE°-Ph**)$_2$]; (right) [$PdCl_2$(**DTE^c-Ph**)$_2$], for which vertical transitions are shown for both oc (blue) and cc (red) isomers.

2. 5. 4. Catalytic studies

2. 5. 4. 1 NMR characterization of the **cc**-enriched state of the palladium complexes tested

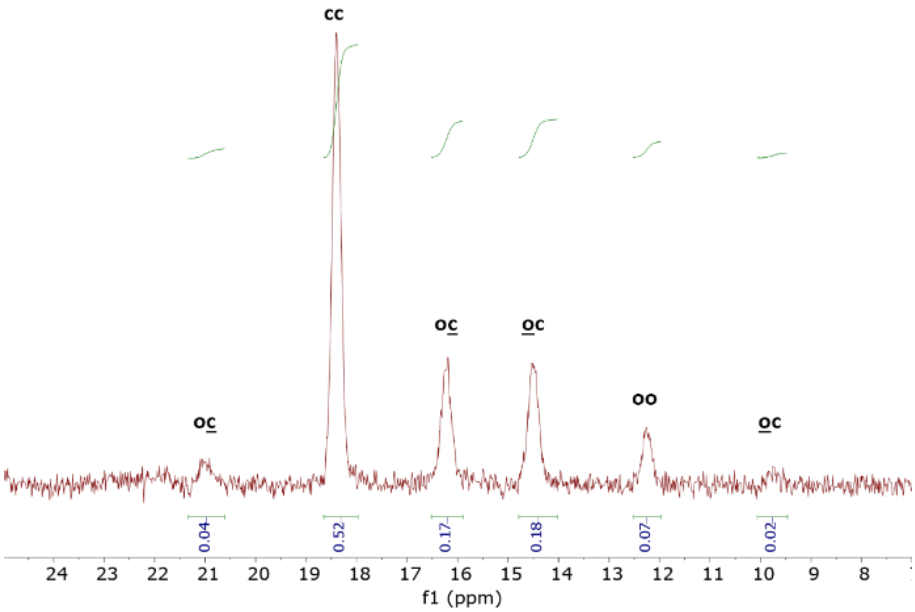


Figure S29 – ^{31}P NMR spectrum ($CDCl_3$, 121 MHz) of the closed state-enriched [$PdCl_2$(**DTE-COCF$_3$**)$_2$] tested in the catalytic reaction. From integrals, a 52:41:7 molar ratio can be assigned to the **cc**, **oc** and **oo** isomers of the complex in this mixture, respectively. Labels **o**c and **o**c are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

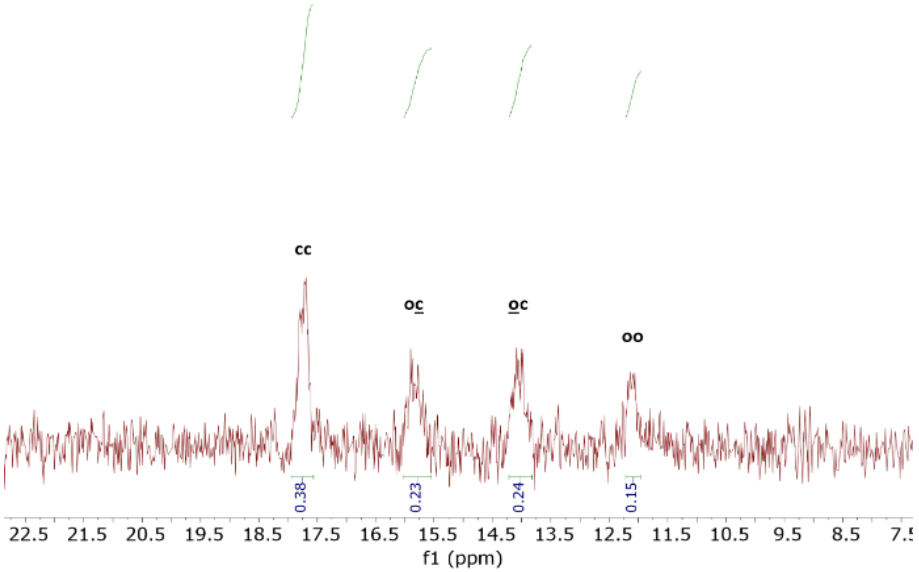


Figure S30 – ^{31}P NMR spectrum ($CDCl_3$, 121 MHz) of the closed state-enriched [$PdCl_2$(**DTE-C$_6$F$_5$**)$_2$] tested in the catalytic reaction. From integrals, a 38:47:15 molar ratio can be assigned to the **cc**, **oc** and **oo** isomers of the complex in this mixture, respectively. Labels **o**c and **o**c are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

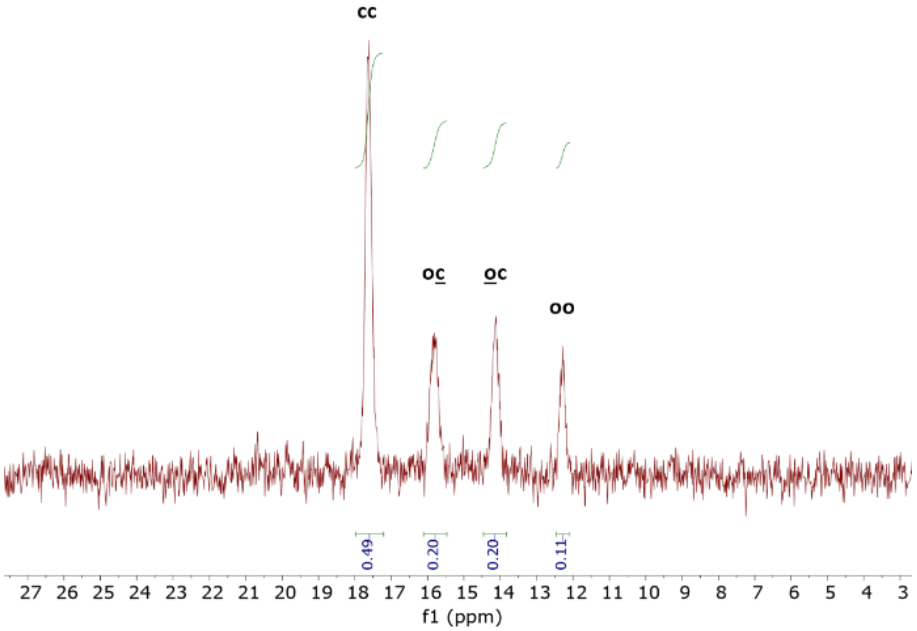


Figure S31 – ^{31}P NMR spectrum ($CDCl_3$, 121 MHz) of the closed state-enriched [$PdCl_2$(**DTE-Ph**)$_2$] tested in the catalytic reaction. From integrals, a 49:40:11 molar ratio can be assigned to the **cc**, **oc** and **oo** isomers of the complex in this mixture, respectively. Labels **o<u>c</u>** and **<u>o</u>c** are used to identify the NMR signals of the phosphorus nucleus attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

2. 5. 4. 2 Catalytic reaction kinetic profiles

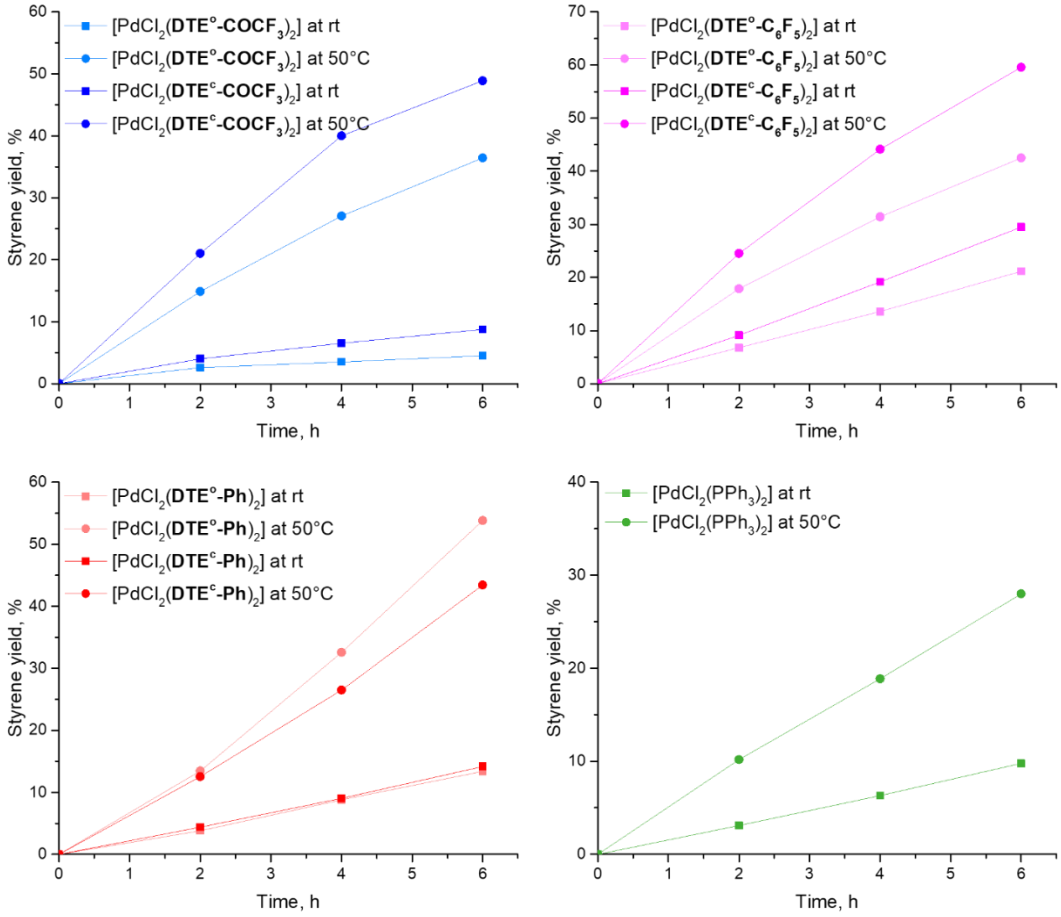


Figure S32 – Yield-over-time graphs for the Stille reaction between iodobenzene and tributylvinyltin (1.5 mol% [Pd], 0.30 mmol iodobenzene, 0.33 mmol tributylvinyltin, 1 mL THF). Data is shown for each of the Pd(II) precatalysts used at rt and 50 °C: the open ([$PdCl_2$(**DTE°-R**)$_2$]) and closed state-enriched mixture ([$PdCl_2$(**DTEc-R**)$_2$]) of the DTE-based complexes, and [$PdCl_2(PPh_3)_2$]. In each case, the average yields of two repetitions were determined by ^{1}H NMR spectroscopy using 1,3,5,-trimethoxybenzene as a standard.

2. 5. 4. 3 Gibbs energy profiles

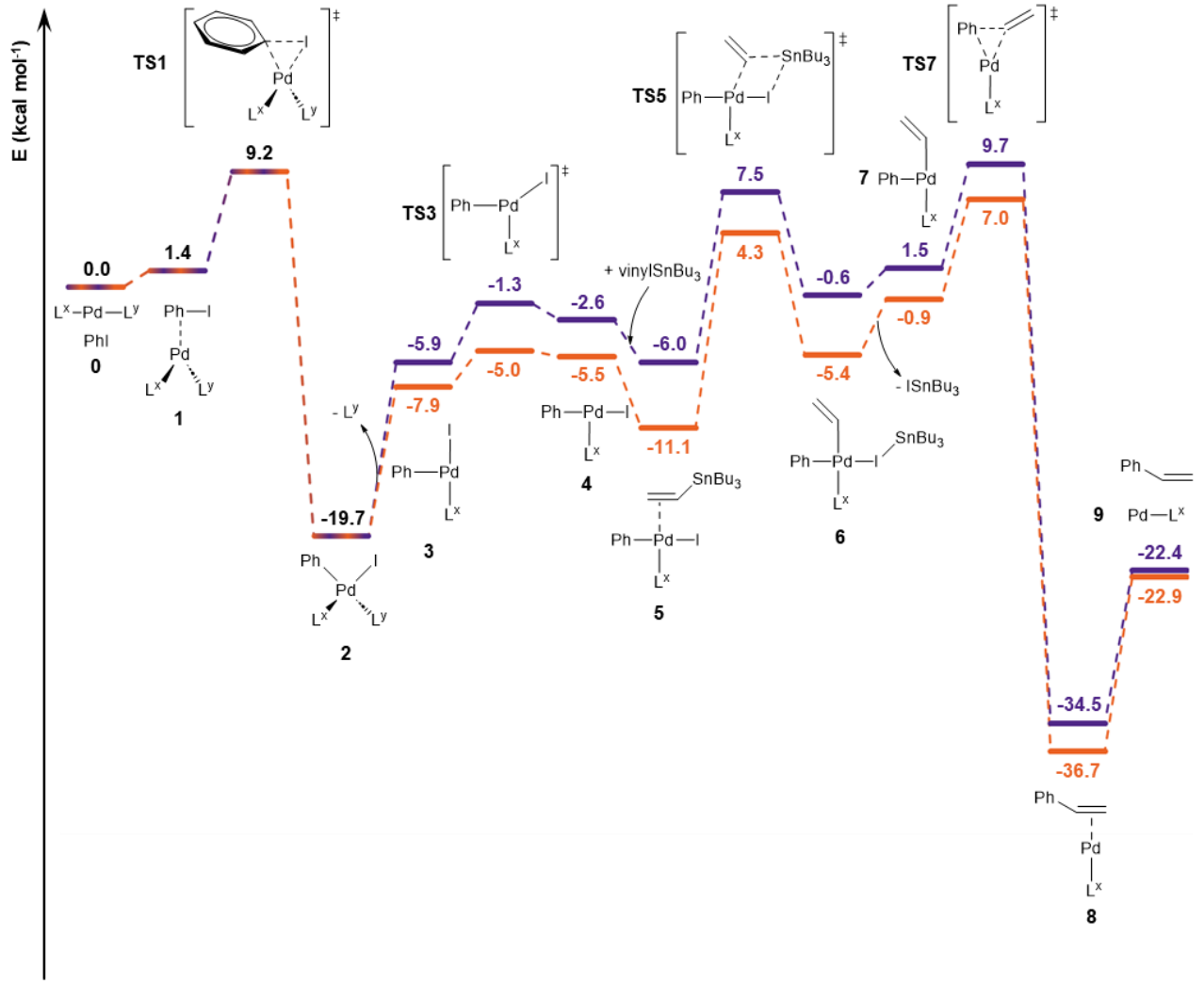


Figure S33 – Calculated Gibbs energy profile for the Stille coupling reaction in solution (THF) using [$PdCl_2$(**DTE^o-COCF$_3$**)(**DTE^c-COCF$_3$**)] as a pre-catalyst, where the orange line corresponds to L^x = **DTE^o-COCF$_3$** and L^y = **DTE^c-COCF$_3$**, and the purple line corresponds to L^x = **DTE^c-COCF$_3$** and L^y = **DTE^o-COCF$_3$**.

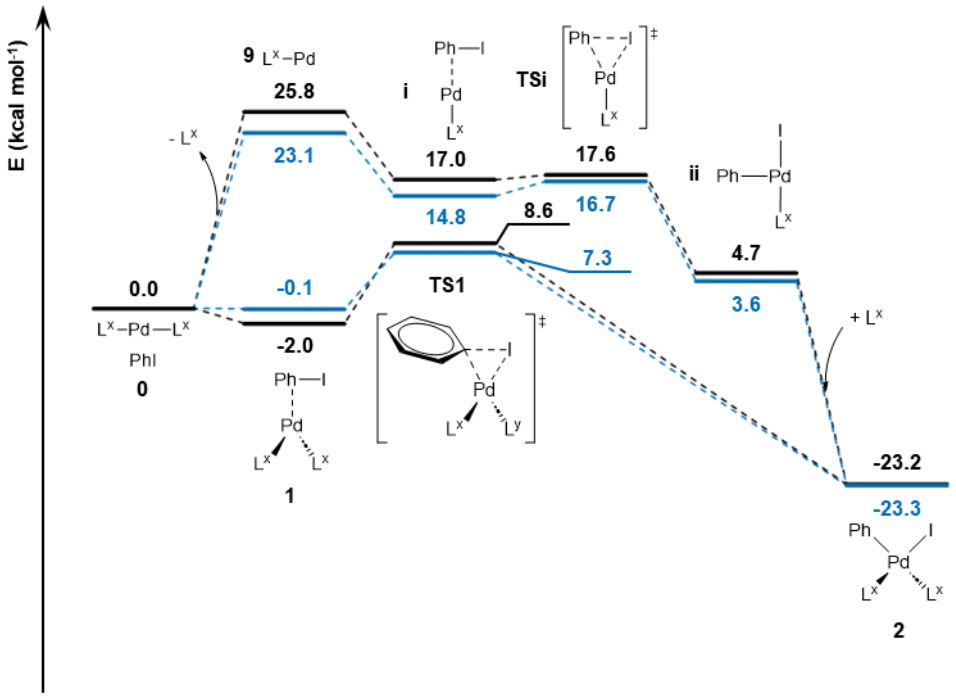


Figure S34 – Comparison of the monoligated and bisligated oxidative addition for the Stille coupling reaction in solution (THF) using [$PdCl_2$(**DTE^o-COCF$_3$**)$_2$] or [$PdCl_2$(**DTE^c-COCF$_3$**)$_2$] as a pre-catalyst, where L^x is **DTE^o-COCF$_3$** (black line) or **DTE^c-COCF$_3$** (blue line).

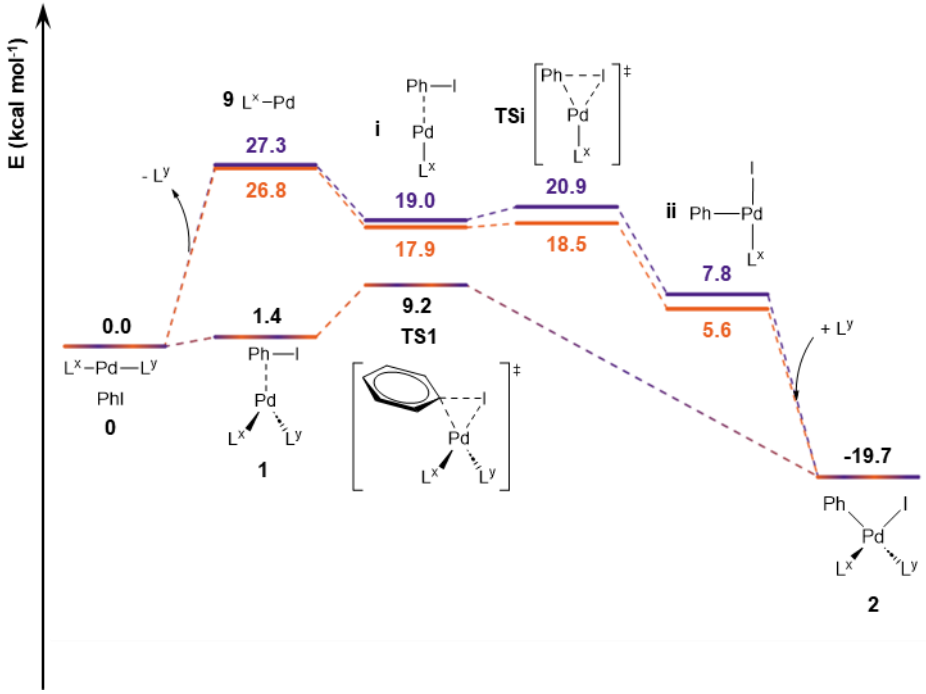


Figure S35 – Comparison of the monoligated and bisligated oxidative addition for the Stille coupling reaction in solution (THF) using [$PdCl_2$(**DTE^o-COCF$_3$**)(**DTE^c-COCF$_3$**)] as a pre-catalyst, where the orange line corresponds to L^x = **DTE^o-COCF$_3$** and L^y = **DTE^c-COCF$_3$**, and the purple line corresponds to L^x = **DTE^c-COCF$_3$** and L^y = **DTE^o-COCF$_3$**.

Table S6 – Absolute energies of the calculated species (a. u.) for the Stille coupling reaction. Gibbs energy profiles are presented in Figures 4, S33-S35.

Structure	Parameter	L_x = **DTE^o-COCF$_3$**	L_x = **DTE^c-COCF$_3$**	L_x = **DTE^o-COCF$_3$**, L_y = **DTE^c-COCF$_3$**	L_x = **DTE^c-COCF$_3$**, L_y = **DTE^o-COCF$_3$**
0	E (BS1)	-5392.239321	-5392.205567	-5392.220537	
	E (BS2)	-5393.608067	-5393.557983	-5393.5821	
	$G_{298.15K}$ (BS2)	-5392.812613	-5392.752535	-5392.786663	
1	E (BS1)	-5635.349282	-5635.313115	-5635.329212	
	E (BS2)	-5923.177619	-5923.124946	-5923.150639	
	$G_{298.15K}$ (BS2)	-5922.302111	-5922.238982	-5922.270821	
TS1	E (BS1)	-5635.33444	-5635.299611	-5635.319281	
	E (BS2)	-5923.163128	-5923.111584	-5923.139066	
	$G_{298.15K}$ (BS2)	-5922.285269	-5922.227193	-5922.258337	
2	E (BS1)	-5635.394044	-5635.358098	-5635.375825	
	E (BS2)	-5923.220121	-5923.167801	-5923.193047	
	$G_{298.15K}$ (BS2)	-5922.335855	-5922.276059	-5922.304301	
3	E (BS1)	-3003.228512	-3003.208841		
	E (BS2)	-3290.39413	-3290.366143		
	$G_{298.15K}$ (BS2)	-3289.930467	-3289.899937		
TS3	E (BS1)	-3003.224764	-3003.204962		
	E (BS2)	-3290.390739	-3290.362707		
	$G_{298.15K}$ (BS2)	-3289.925962	-3289.892501		
4	E (BS1)	-3003.225294	-3003.205886		
	E (BS2)	-3290.391244	-3290.363581		
	$G_{298.15K}$ (BS2)	-3289.926688	-3289.894564		
5	E (BS1)	-3558.264195	-3558.241926		
	E (BS2)	-4056.593907	-4056.563138		
	$G_{298.15K}$ (BS2)	-4055.75176	-4055.716096		
TS5	E (BS1)	-3558.239633	-3558.217603		
	E (BS2)	-4056.570546	-4056.540686		
	$G_{298.15K}$ (BS2)	-4055.727214	-4055.694618		
6	E (BS1)	-3558.248848	-3558.230558		
	E (BS2)	-4056.582015	-4056.555734		
	$G_{298.15K}$ (BS2)	-4055.742589	-4055.707574		
7	E (BS1)	-3069.723993	-3069.704812		
	E (BS2)	-3070.53496	-3070.507582		
	$G_{298.15K}$ (BS2)	-3070.031406	-3070.000007		
TS7	E (BS1)	-3069.712283	-3069.693922		
	E (BS2)	-3070.523049	-3070.496522		
	$G_{298.15K}$ (BS2)	-3070.018803	-3069.986939		
8	E (BS1)	-3069.785511	-3069.76739		
	E (BS2)	-3070.594751	-3070.568412		
	$G_{298.15K}$ (BS2)	-3070.088414	-3070.057437		
9	E (BS1)	-2760.067449	-2760.049102		
	E (BS2)	-2760.773088	-2760.747087		
	$G_{298.15K}$ (BS2)	-2760.388924	-2760.360675		
i	E (BS1)	-3003.183733	-3003.165024		
	E (BS2)	-3290.350084	-3290.323456		
	$G_{298.15K}$ (BS2)	-3289.889373	-3289.860206		

TSi	E (BS1)	-3003.182966	-3003.164299	
	E (BS2)	-3290.349626	-3290.322925	
	$G_{298.15K}$ (BS2)	-3289.888408	-3289.857102	
ii	E (BS1)	-3003.2053	-3003.186745	
	E (BS2)	-3290.370492	-3290.34397	
	$G_{298.15K}$ (BS2)	-3289.909013	-3289.878047	

PhI E (BS1) = -243.0808839

E (BS2) = -529.5483685

$G_{298.15K}$ (BS2) = -529.4893265

DTE^{o}-COCF$_3$ E (BS1) = -2632.101518

E (BS2) = -2632.771651

$G_{298.15K}$ (BS2) = -2632.385516

DTE^{c}-COCF$_3$ E (BS1) = -2632.086005

E (BS2) = -2632.748231

$G_{298.15K}$ (BS2) = -2632.358075

Sn(CH$_2$CH)Bu$_3$ E (BS1) = -554.9948309

E (BS2) = -766.1689977

$G_{298.15K}$ (BS2) = -765.8191377

SnIBu$_3$ E (BS1) = -488.4879923

E (BS2) = -986.0148693

$G_{298.15K}$ (BS2) = -985.7071573

Styrene E (BS1) = -309.6714908

E (BS2) = -309.7830068

$G_{298.15K}$ (BS2) = -309.6805298

2. 5. 5. NMR spectra of the reported compounds

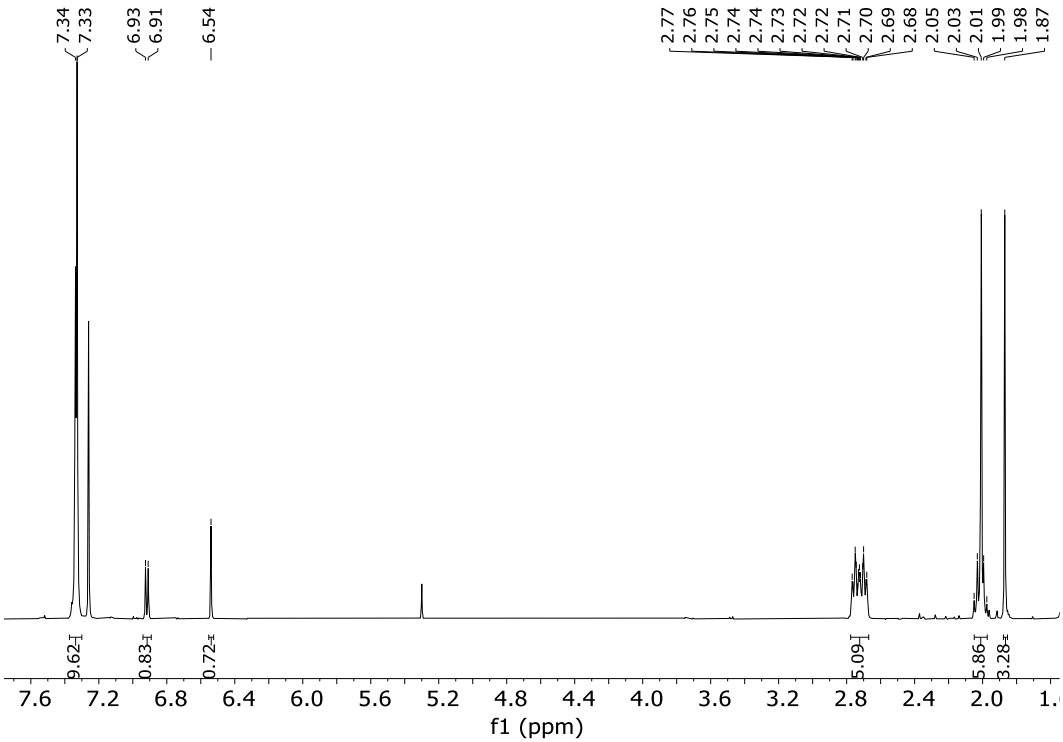


Figure S36 – ^{1}H NMR spectrum (400 MHz) of **DTE2** in $CDCl_3$ recorded at 25 °C.

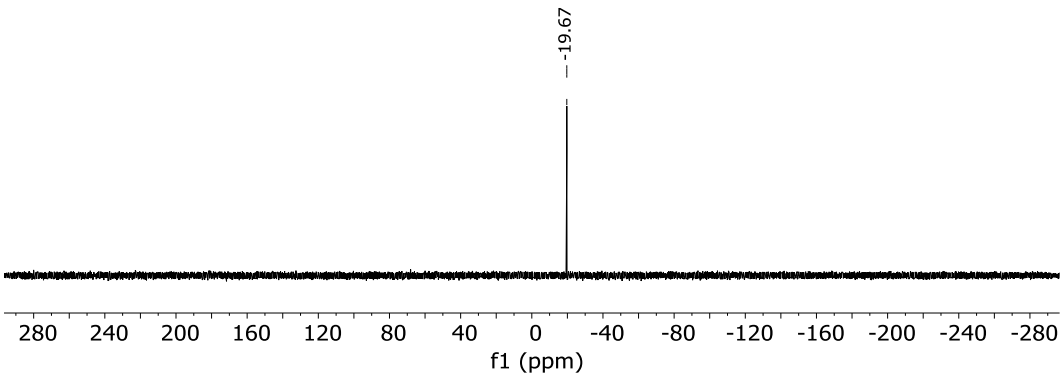


Figure S37 – $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz) of **DTE2** in $CDCl_3$ recorded at 25 °C.

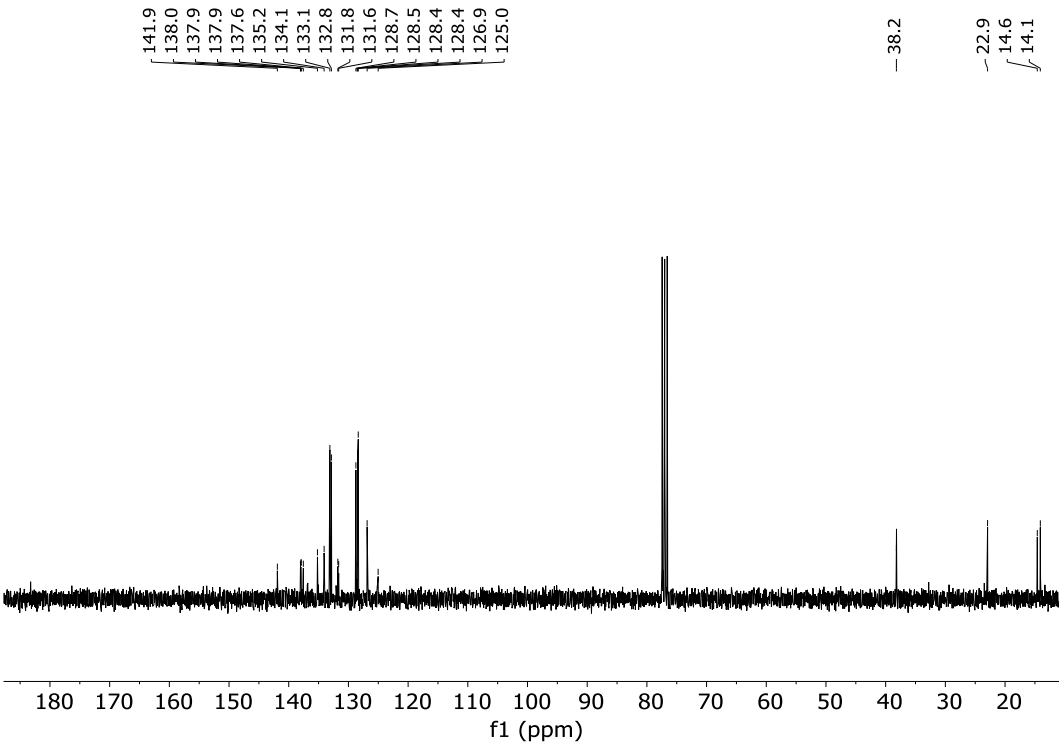


Figure S38 – $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of **DTE2** in $CDCl_3$ recorded at 25 °C.

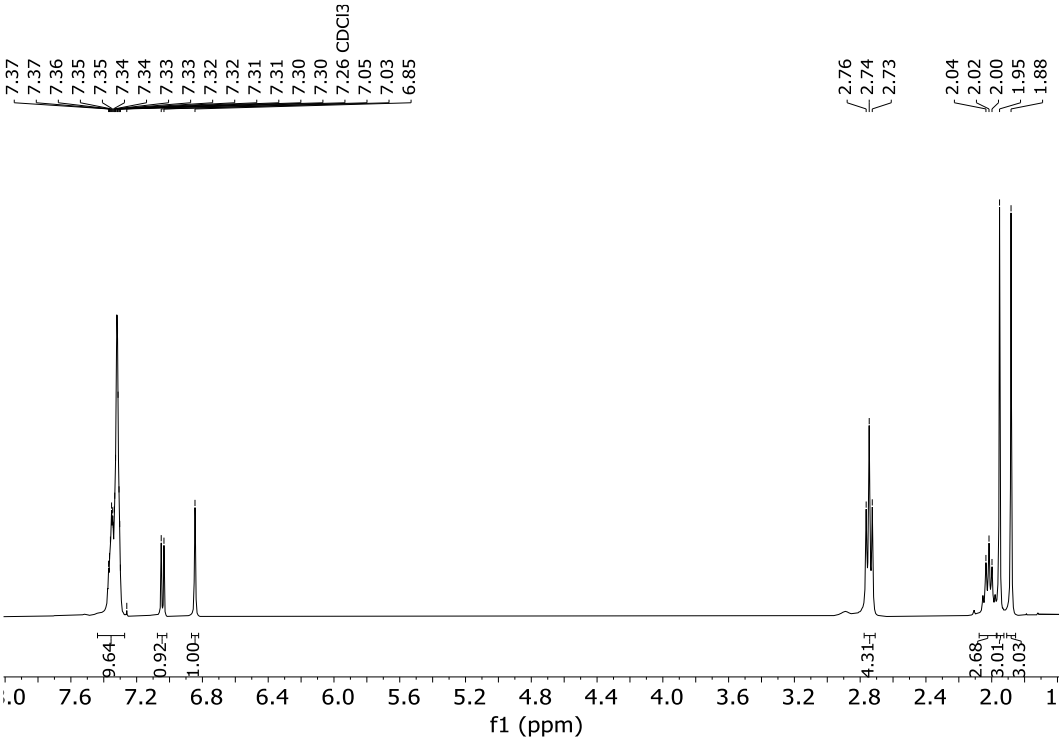


Figure S39 – ^{1}H NMR spectrum (400 MHz) of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

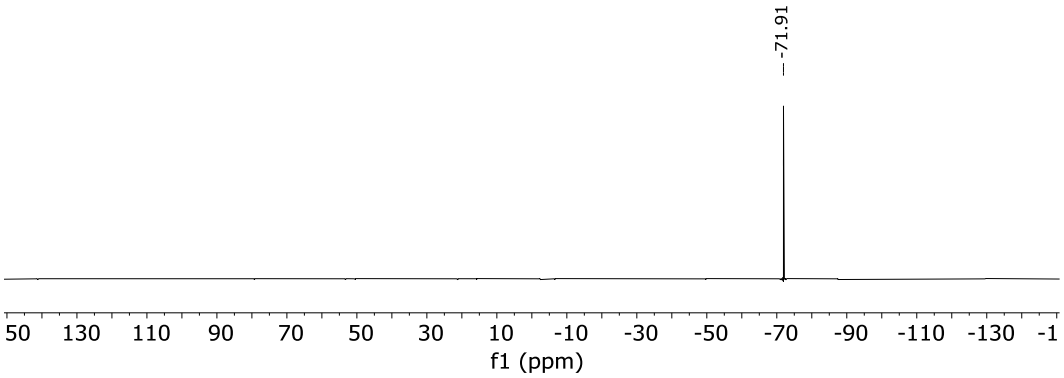


Figure S40 – ^{19}F NMR spectrum (376 MHz) of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

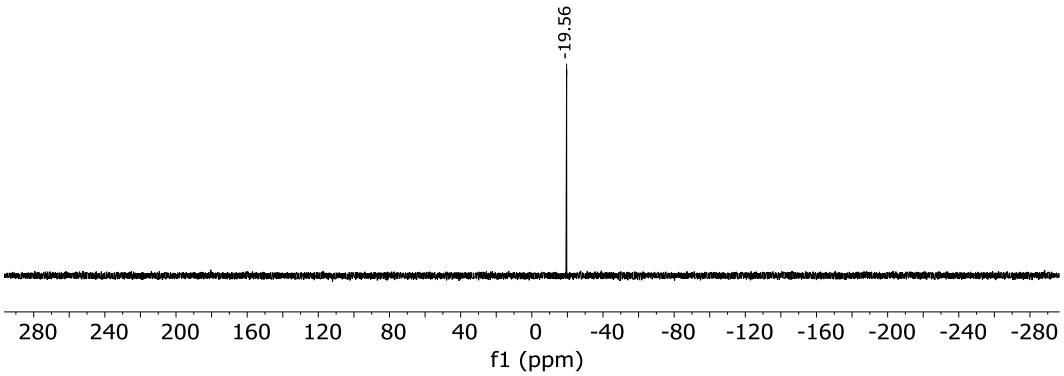


Figure S41 – $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

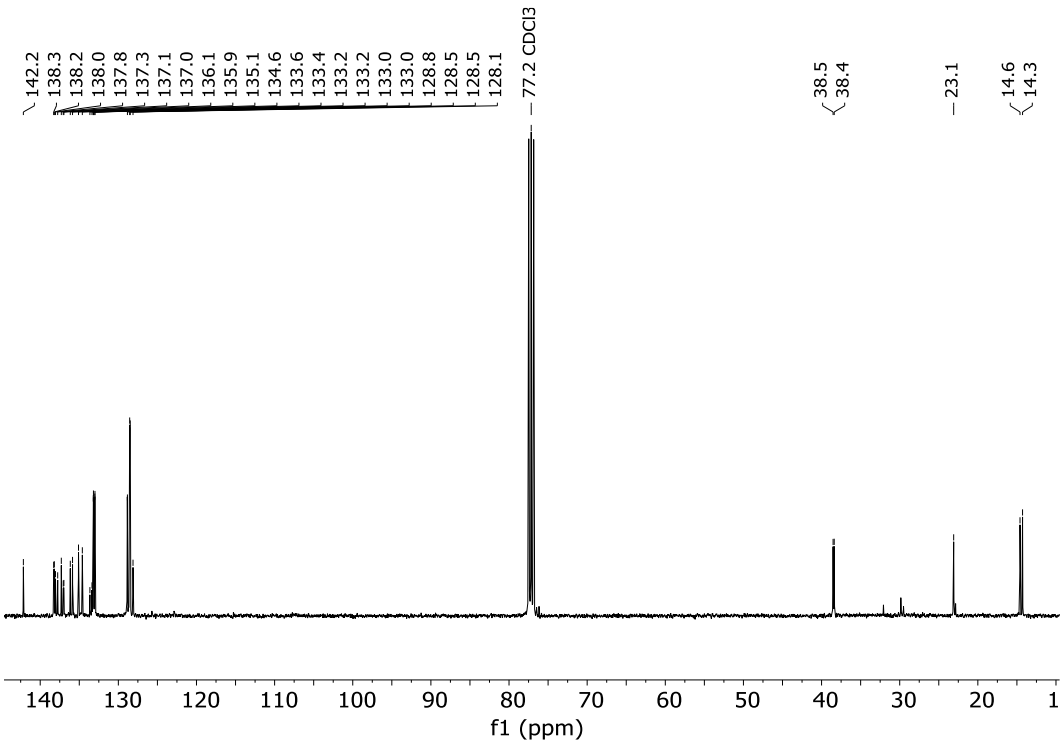


Figure S42 – $^{13}C\{^1H\}$ NMR spectrum (101 MHz) of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

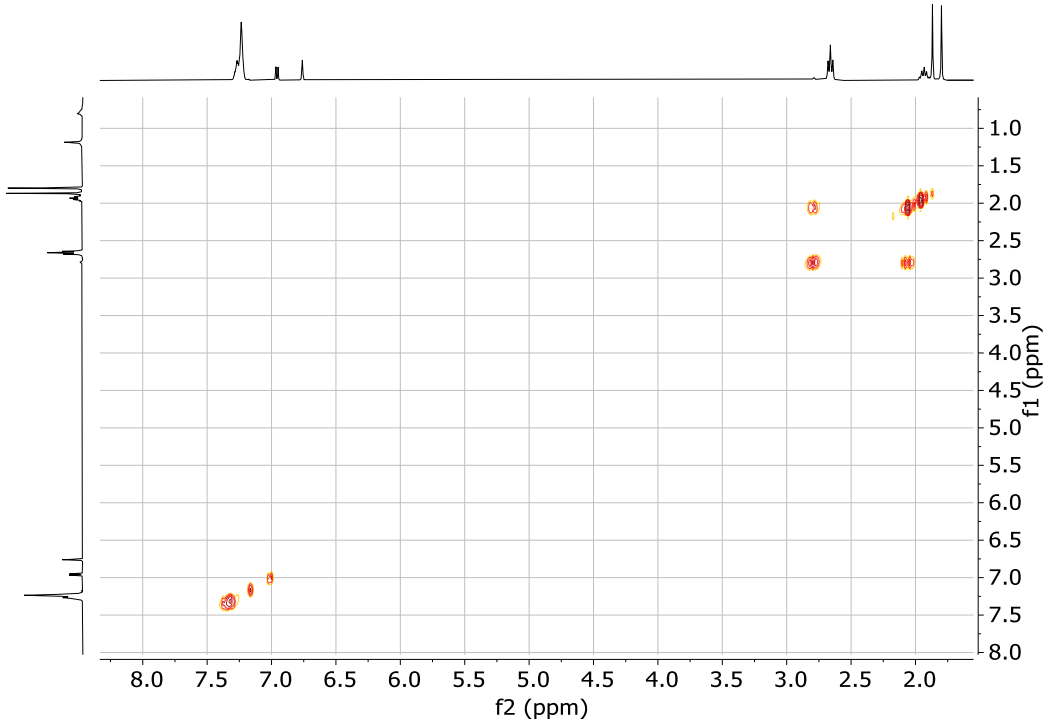


Figure S43 – ^{1}H-^{1}H COSY spectrum of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

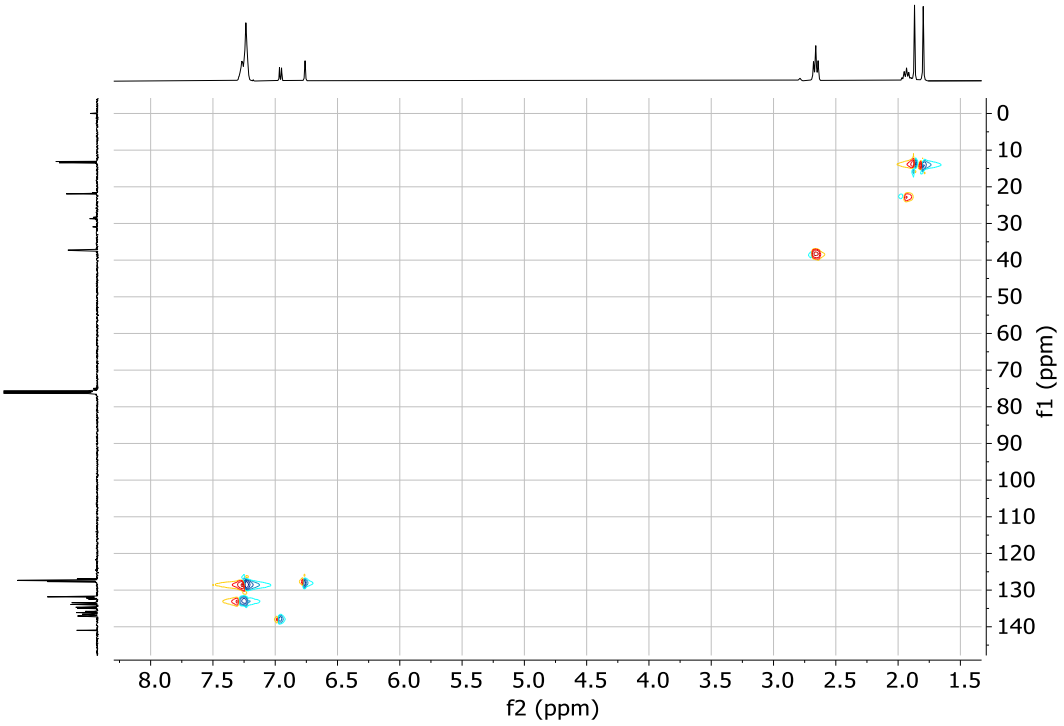


Figure S44 – ^{1}H-^{13}C HSQC spectrum of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

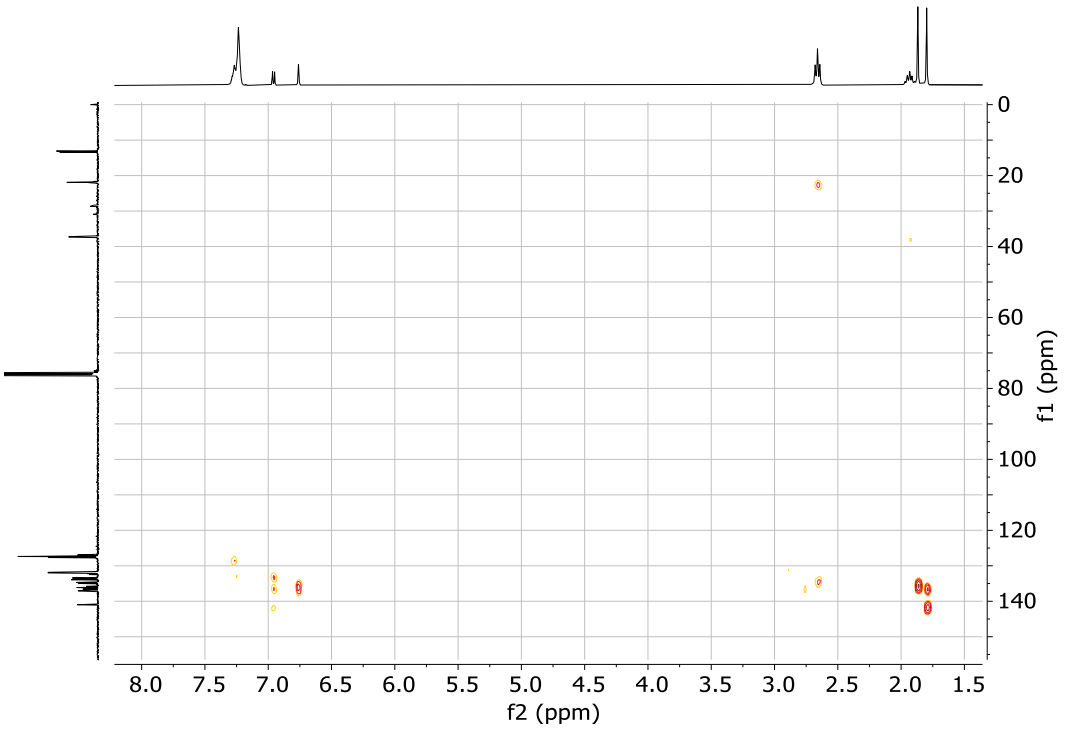


Figure S45 – ^{1}H-^{13}C HMBC spectrum of **DTE-COCF$_3$** in $CDCl_3$ recorded at 25 °C.

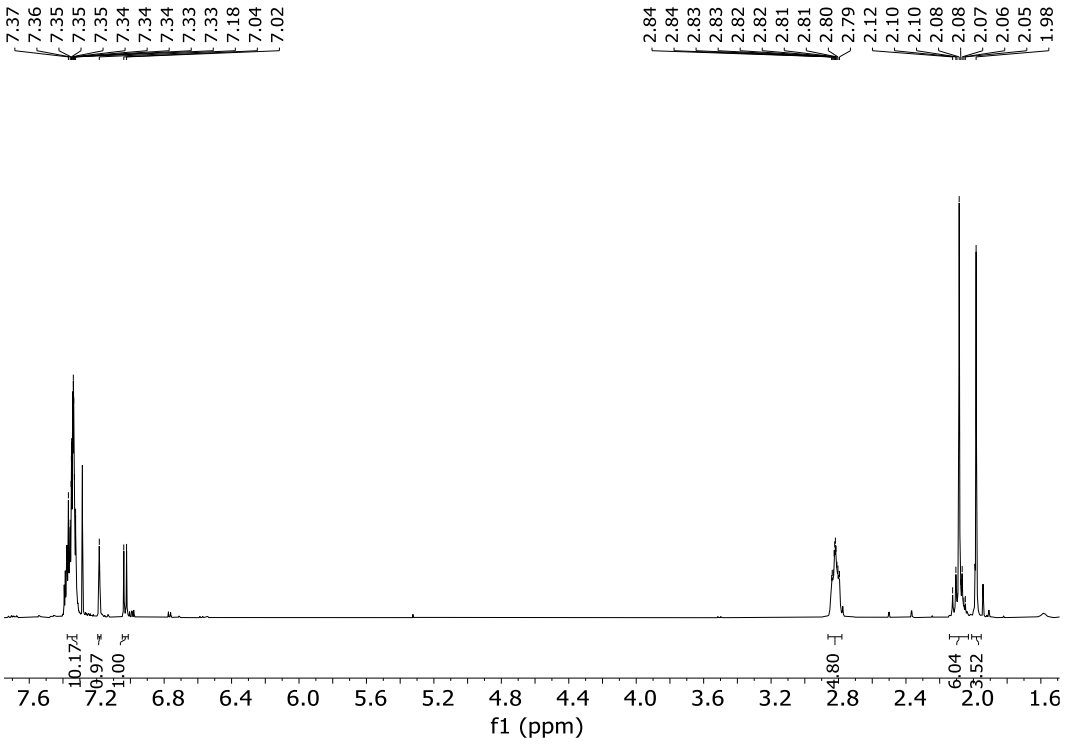


Figure S46 – ^{1}H NMR spectrum (400 MHz) of **DTE-C$_6$F$_5$** in $CDCl_3$ recorded at 25 °C.

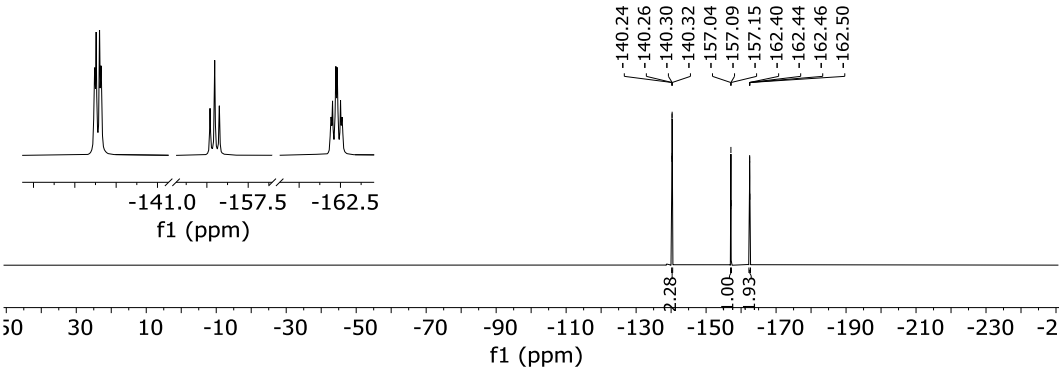


Figure S47 – ^{19}F NMR spectrum (376 MHz) of **DTE-C_6F_5** in $CDCl_3$ recorded at 25 °C.

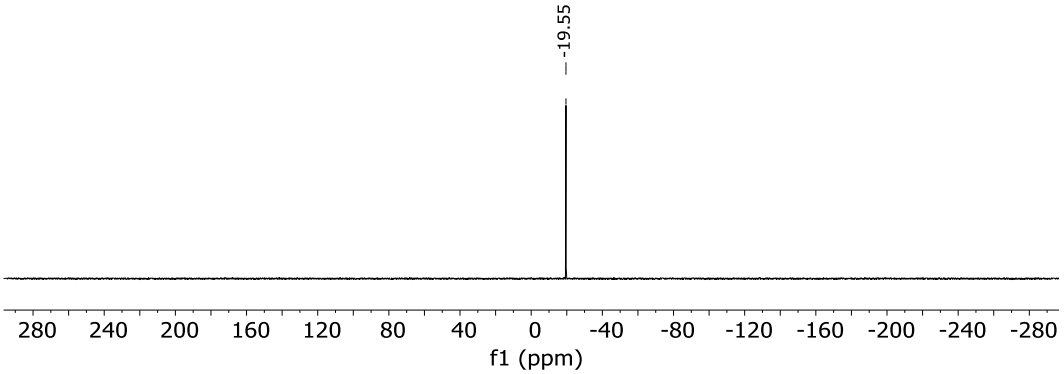


Figure S48 – $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of **DTE-C_6F_5** in $CDCl_3$ recorded at 25 °C.

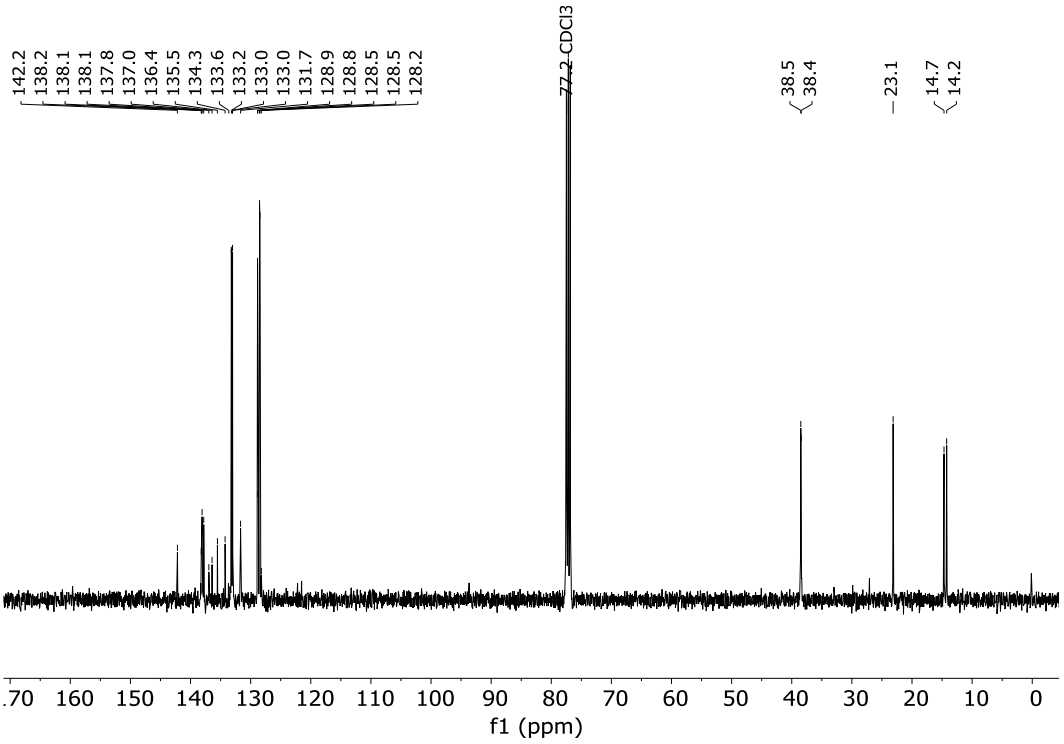


Figure S49 – $^{13}C\{^1H\}$ NMR spectrum (101 MHz) of **DTE-C_6F_5** in $CDCl_3$ recorded at 25 °C.

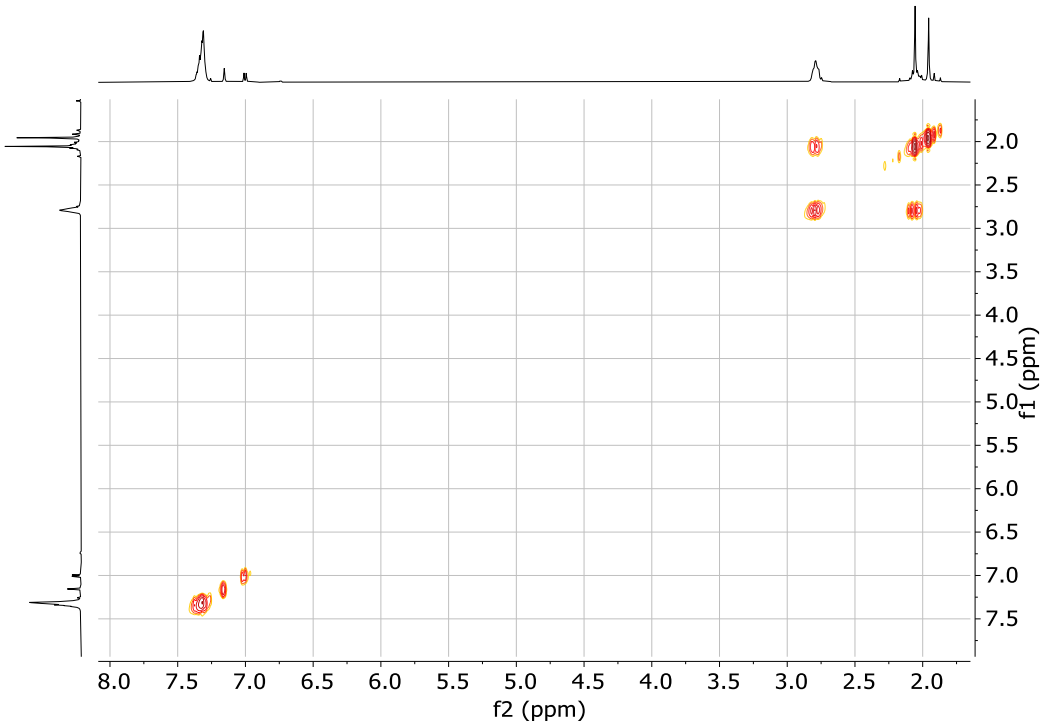


Figure S50 – ^{1}H-^{1}H COSY spectrum of **DTE-C_6F_5** in $CDCl_3$ recorded at 25 °C.

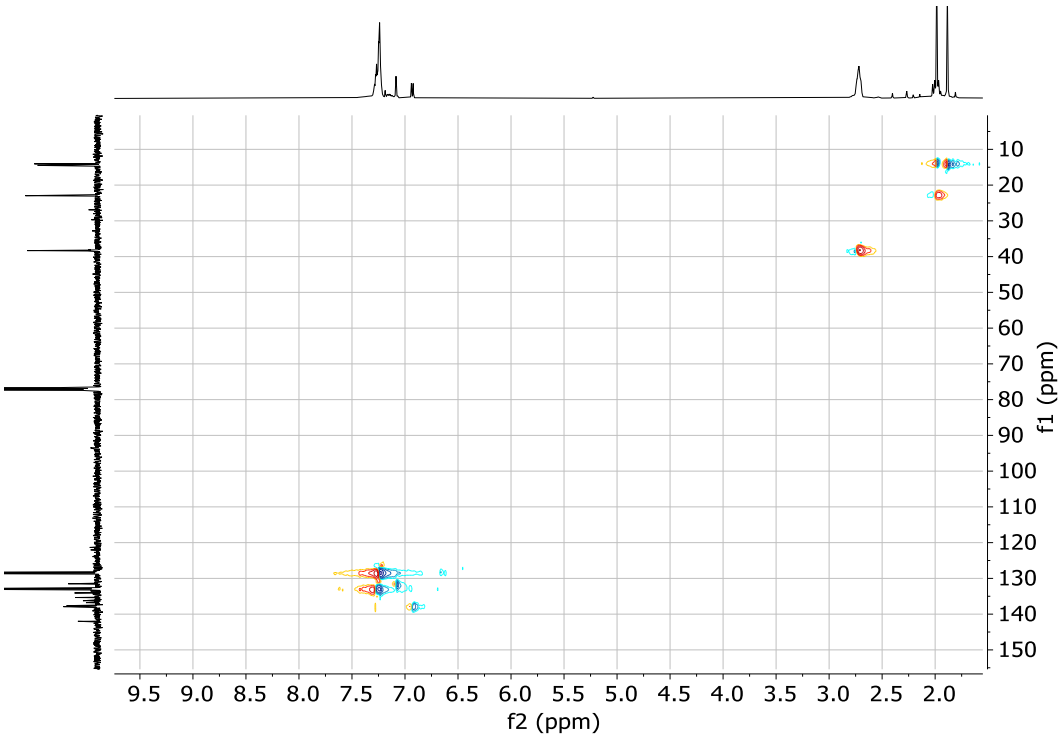


Figure S51 – ^{1}H-^{13}C HSQC spectrum of **DTE-C_6F_5** in $CDCl_3$ recorded at 25 °C.

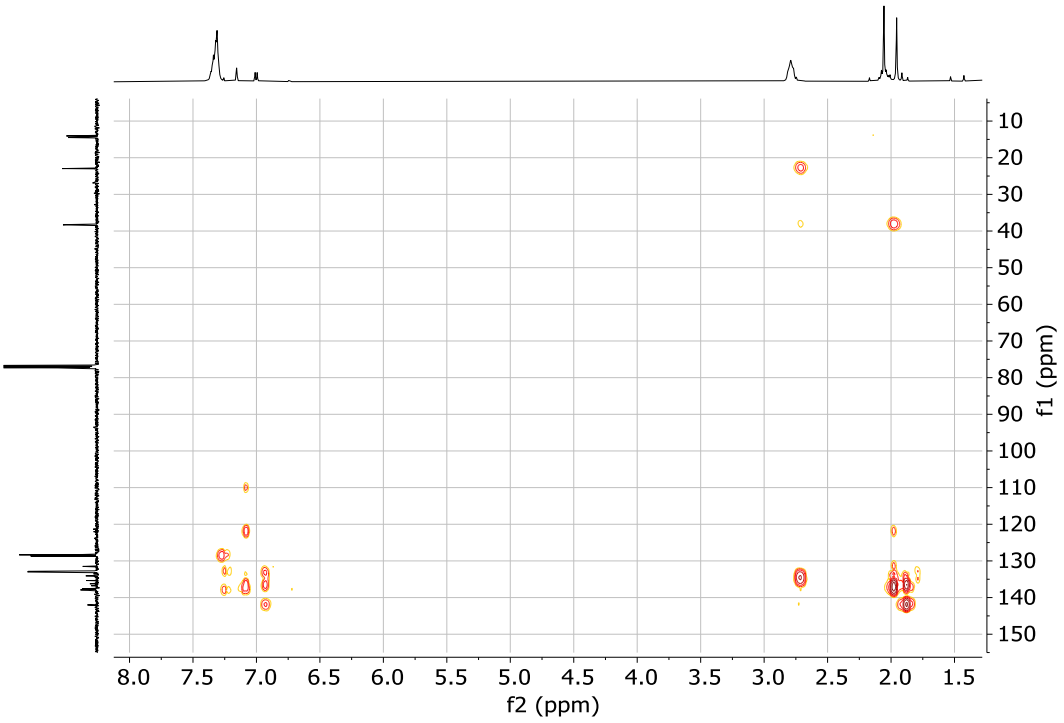


Figure S52 – ^{1}H-^{13}C HMBC spectrum of **DTE-C_6F_5** in $CDCl_3$ recorded at 25 °C.

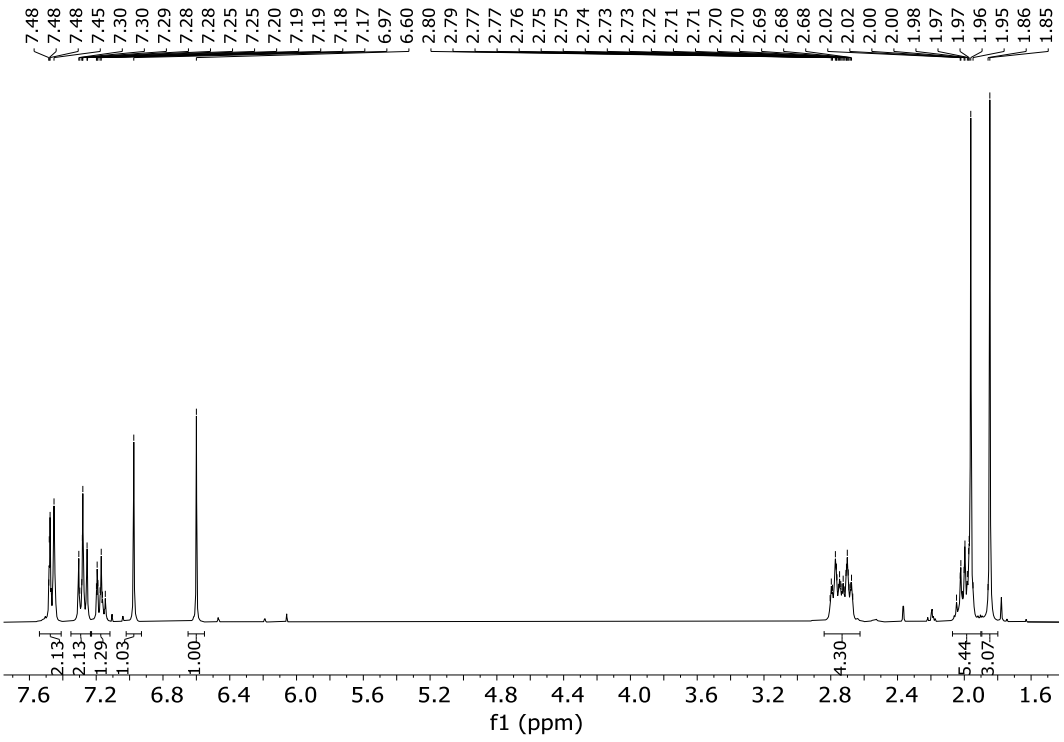


Figure S53 – ^{1}H NMR spectrum (300 MHz) of **DTE3** in $CDCl_3$ recorded at 25 °C.

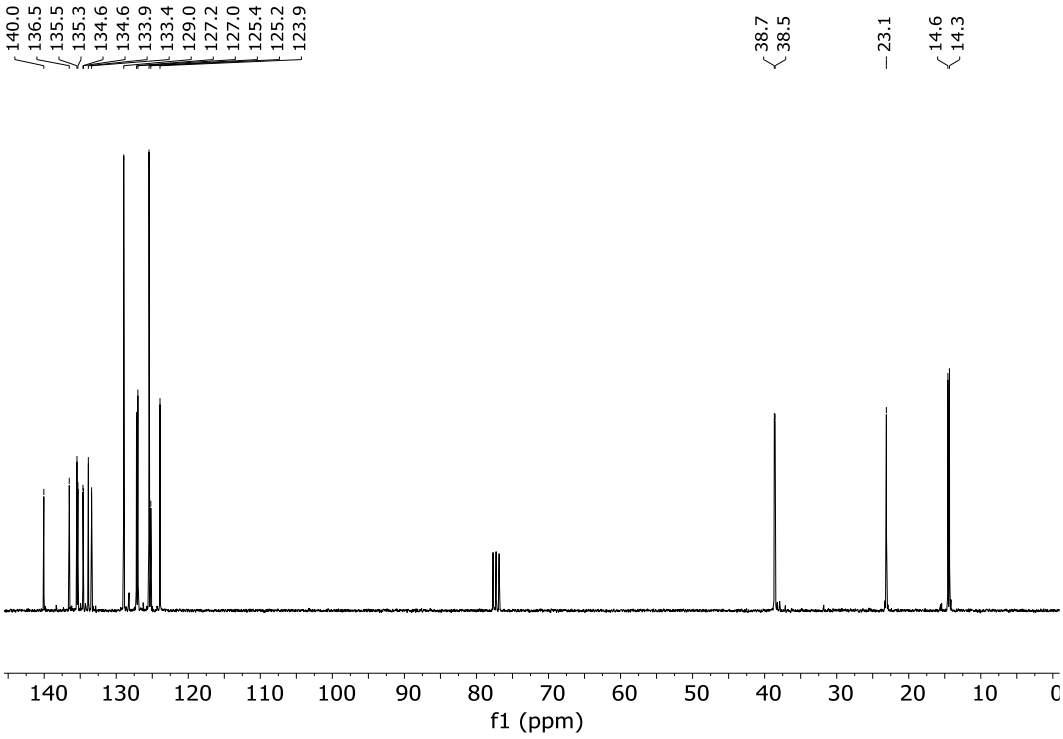


Figure S54 – $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of **DTE3** in $CDCl_3$ recorded at 25 °C.

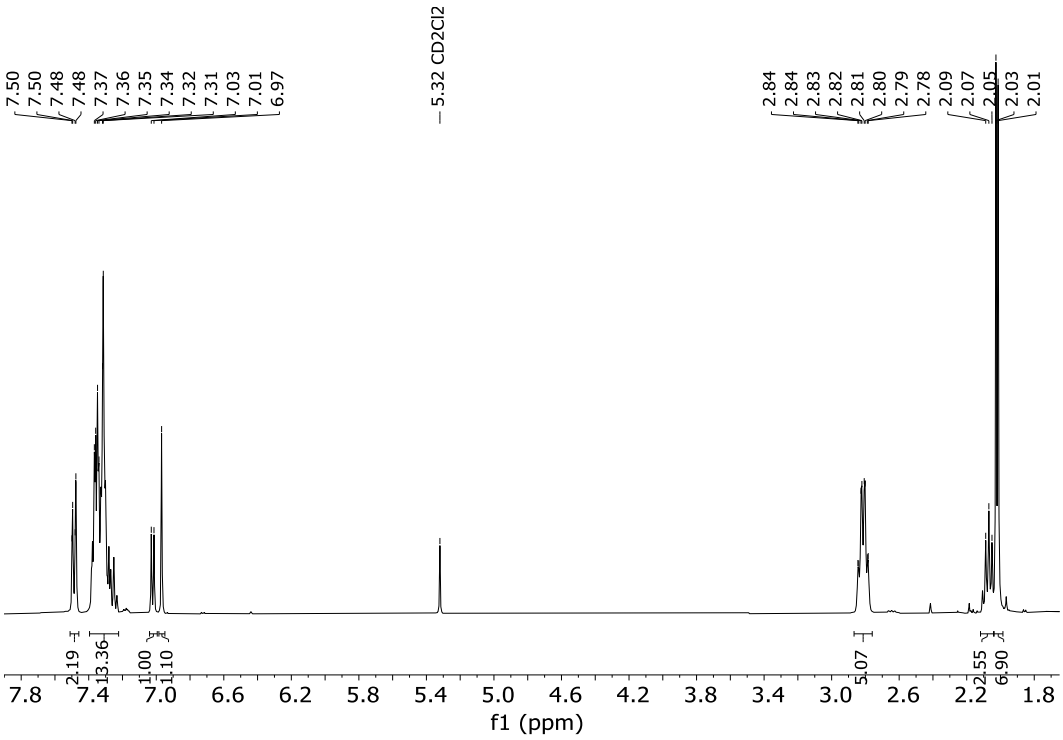


Figure S55 – ^{1}H NMR spectrum (400 MHz) of **DTE-Ph** in $CDCl_3$ recorded at 25 °C.

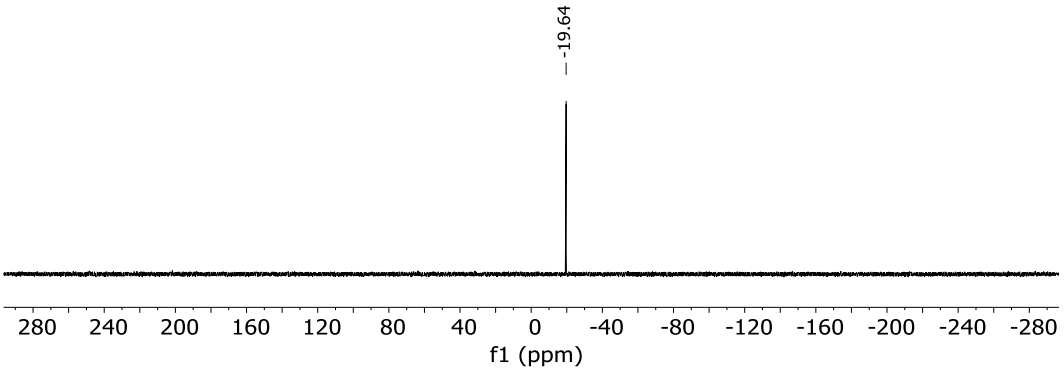


Figure S56 – $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz) of **DTE-Ph** in $CDCl_3$ recorded at 25 °C.

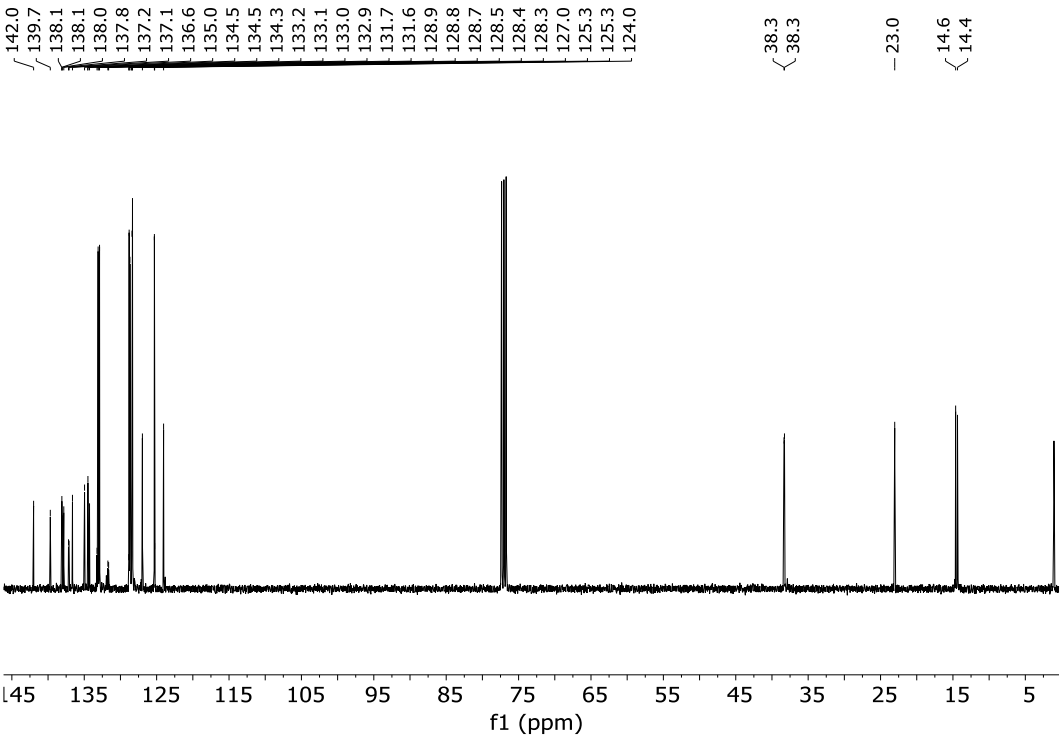


Figure S57 – $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **DTE-Ph** in $CDCl_3$ recorded at 25 °C.

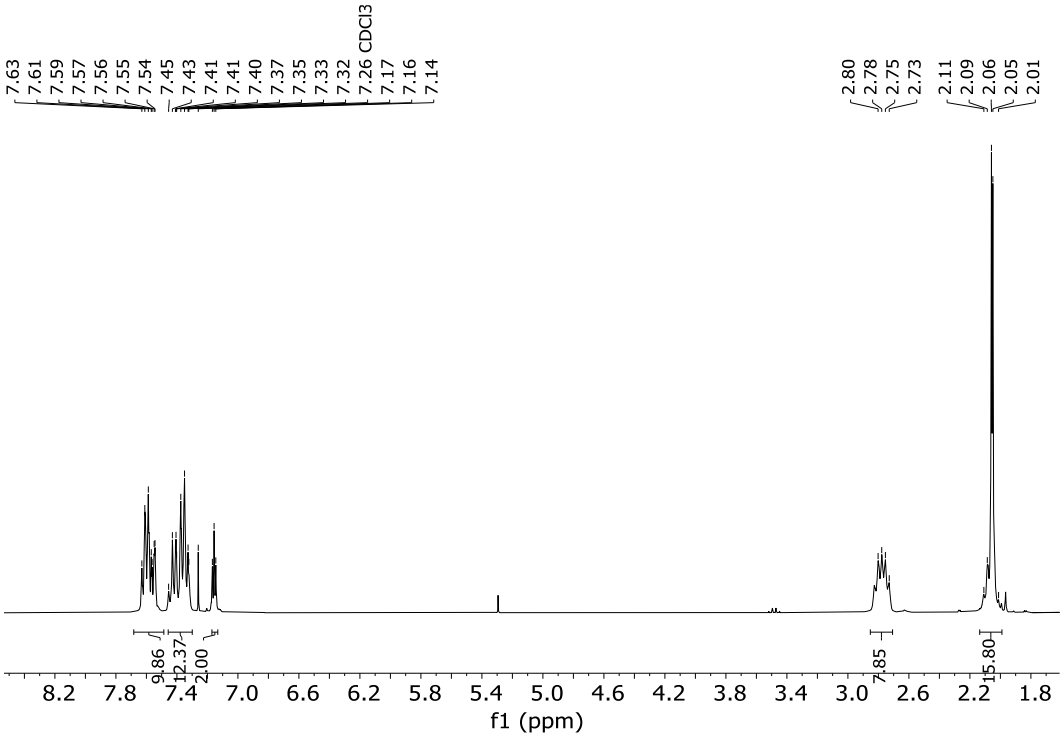


Figure S58 – ^{1}H NMR spectrum (300 MHz) of [$PdCl_2$(**DTE°-COCF$_3$**)$_2$] in $CDCl_3$ recorded at 25 °C.

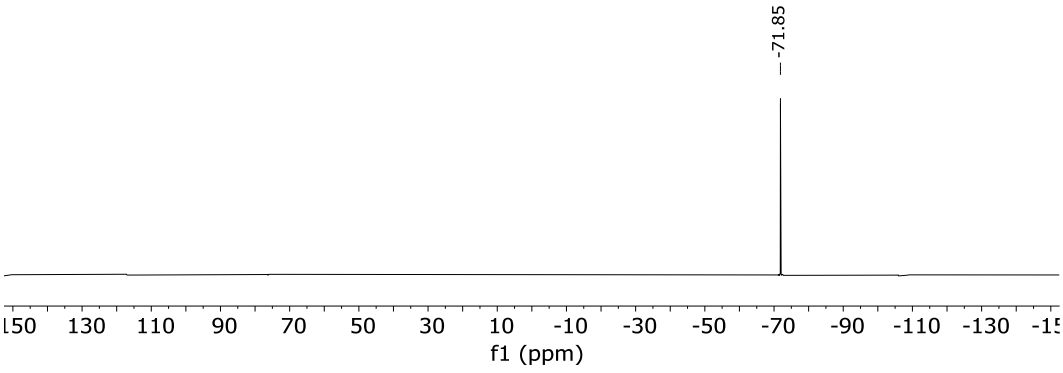


Figure S59 – ^{19}F NMR spectrum (282 MHz) of [$PdCl_2$(**DTE°-COCF$_3$**)$_2$] in $CDCl_3$ recorded at 25 °C.

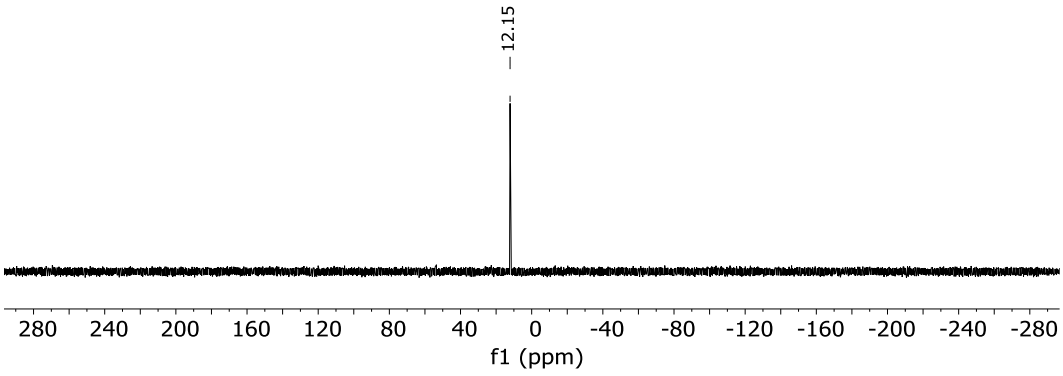


Figure S60 – $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz) of [$PdCl_2$(**DTE°-COCF$_3$**)$_2$] in $CDCl_3$ recorded at 25 °C.

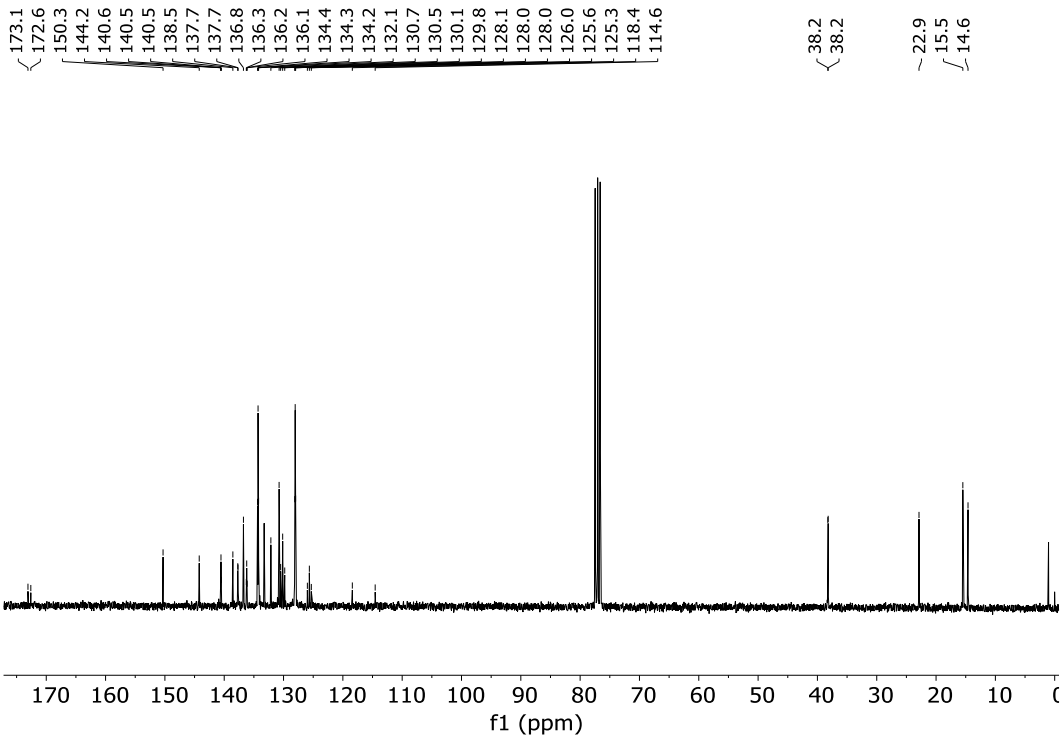


Figure S61 – $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}COCF_3})_2]$ in $CDCl_3$ recorded at 25 °C.

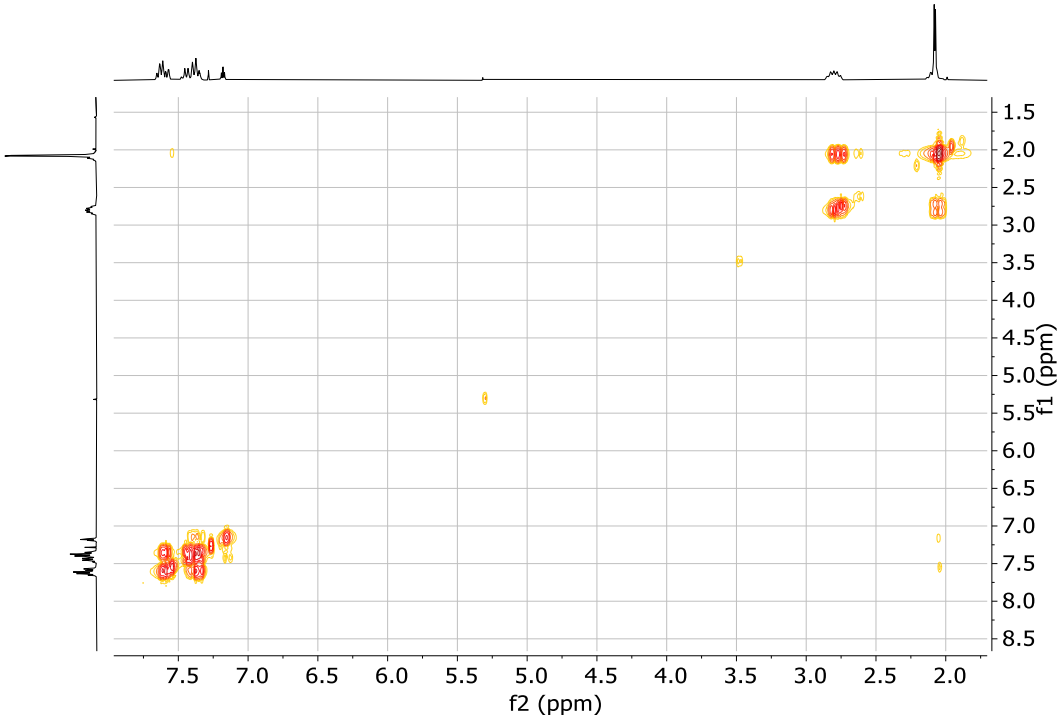


Figure S62 – $^{1}H\text{-}^{1}H$ COSY spectrum of $[PdCl_2(\mathbf{DTE^o\text{-}COCF_3})_2]$ in $CDCl_3$ recorded at 25 °C.

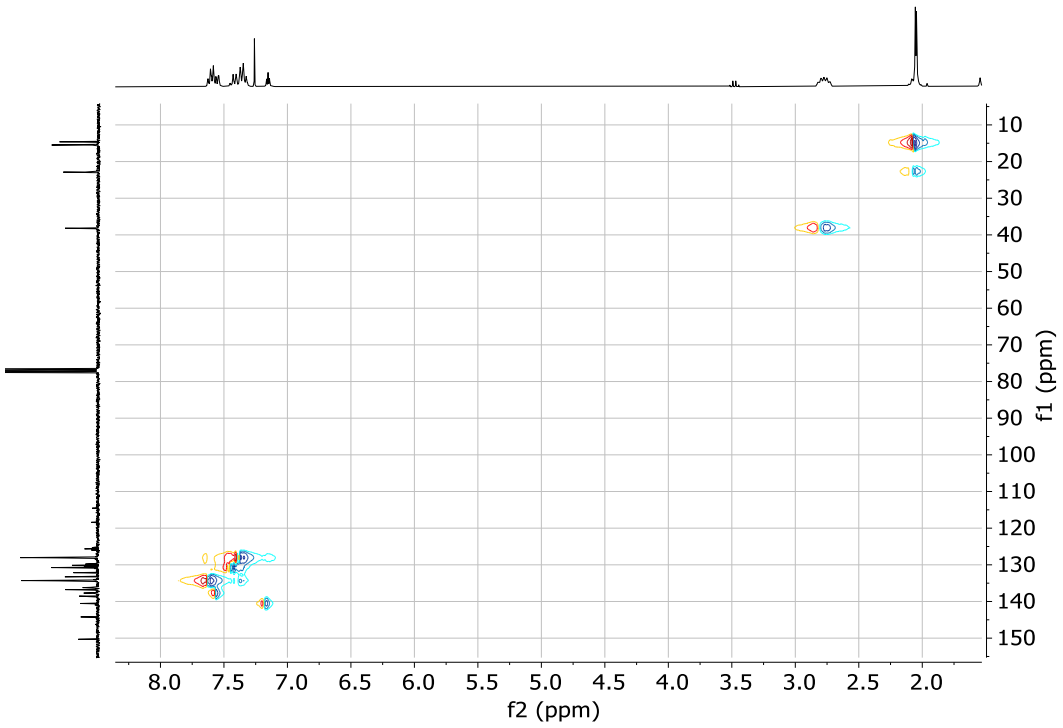


Figure S63 – ^{1}H-^{13}C HSQC spectrum of [$PdCl_2$(**DTE^{o}-COCF$_3$**)$_2$] in $CDCl_3$ recorded at 25 °C.

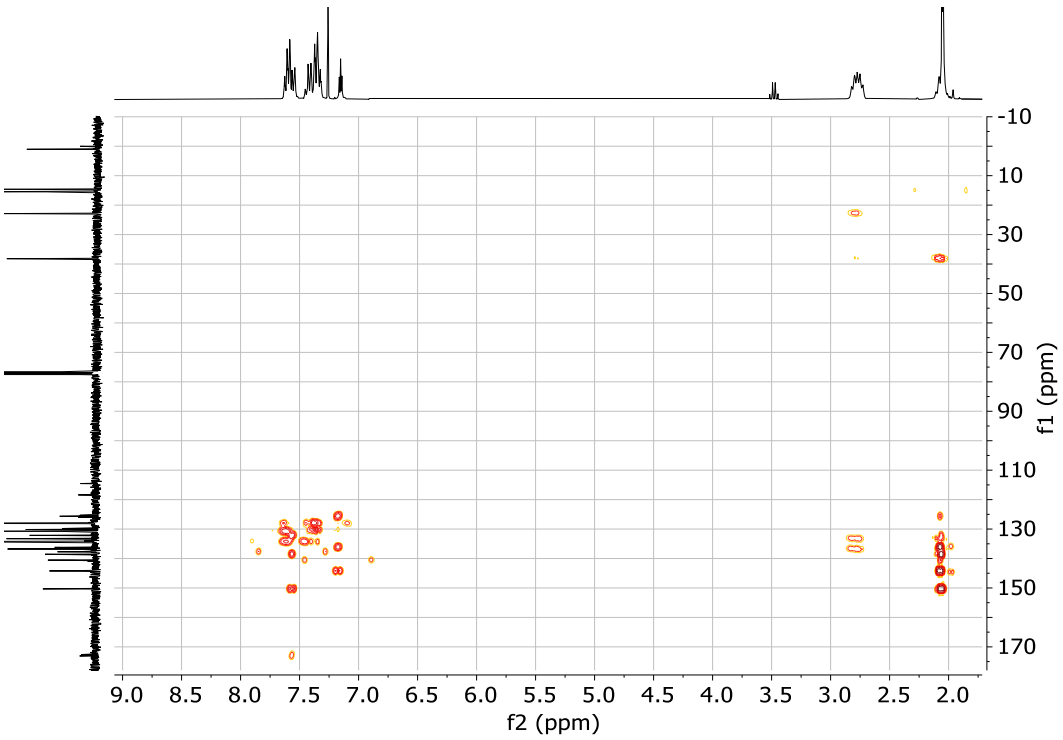


Figure S64 – ^{1}H-^{13}C HMBC spectrum of [$PdCl_2$(**DTE^{o}-COCF$_3$**)$_2$] in $CDCl_3$ recorded at 25 °C.

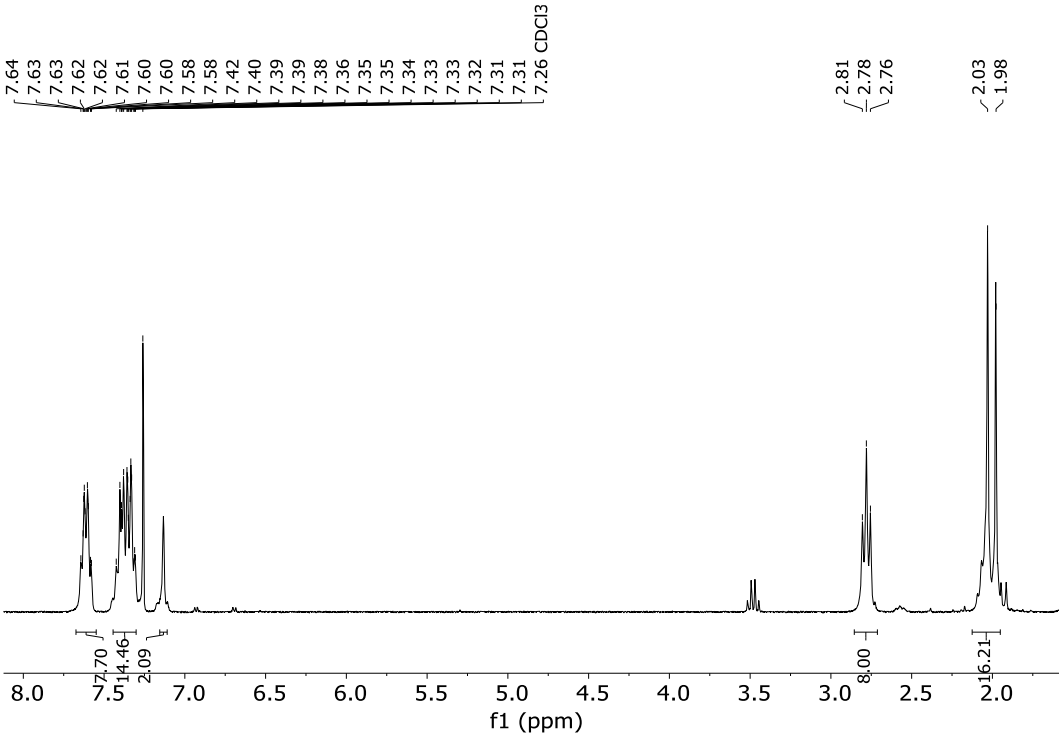


Figure S65 – ^{1}H NMR spectrum (300 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$ in $CDCl_3$ recorded at 25 °C.

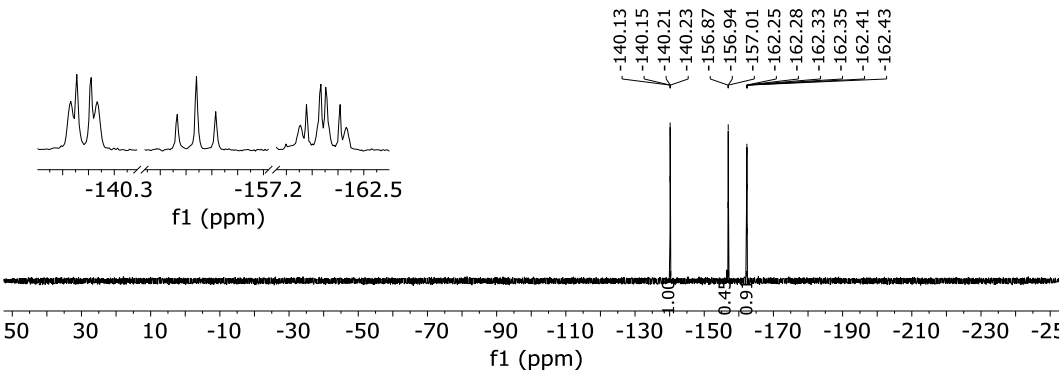


Figure S66 – ^{19}F NMR spectrum (282 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$ in $CDCl_3$ recorded at 25 °C.

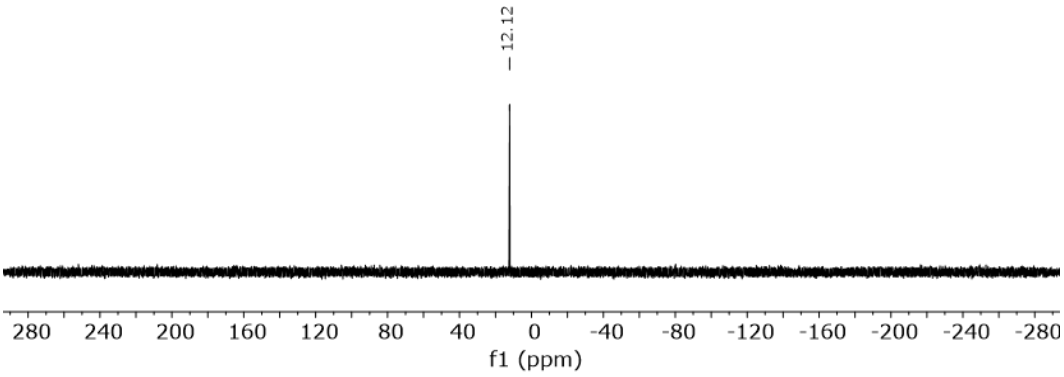


Figure S67 – $^{31}P\{^{1}H\}$ NMR spectrum (122 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$ in $CDCl_3$ recorded at 25 °C.

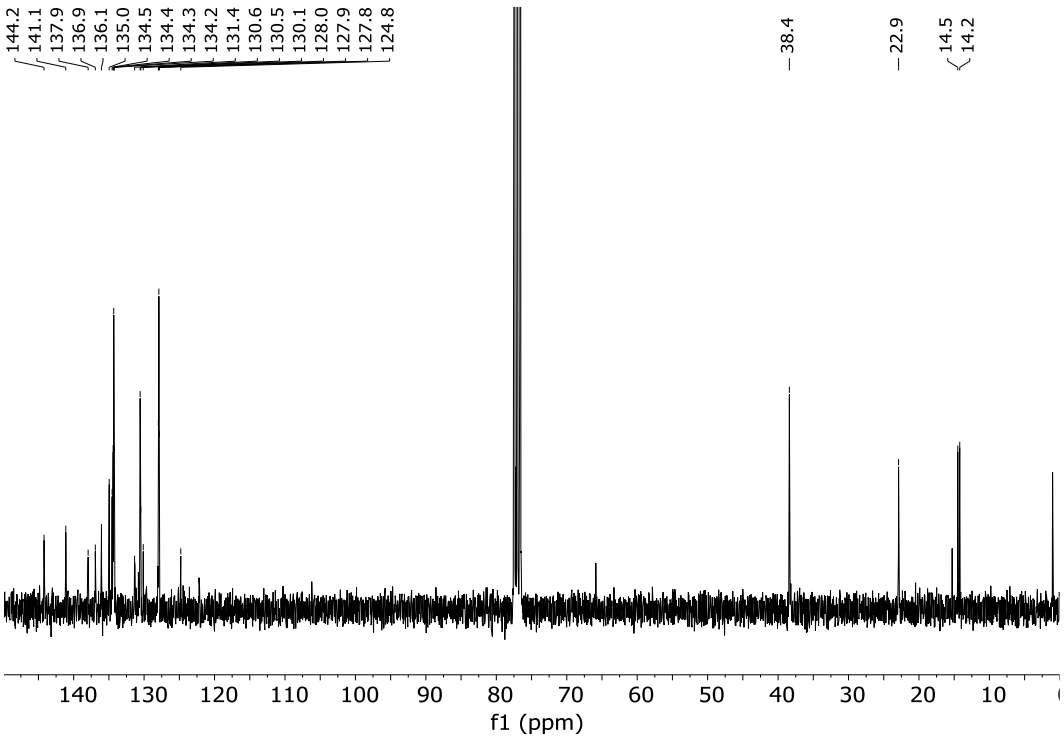


Figure S68 – $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$ in $CDCl_3$ recorded at 25 °C.

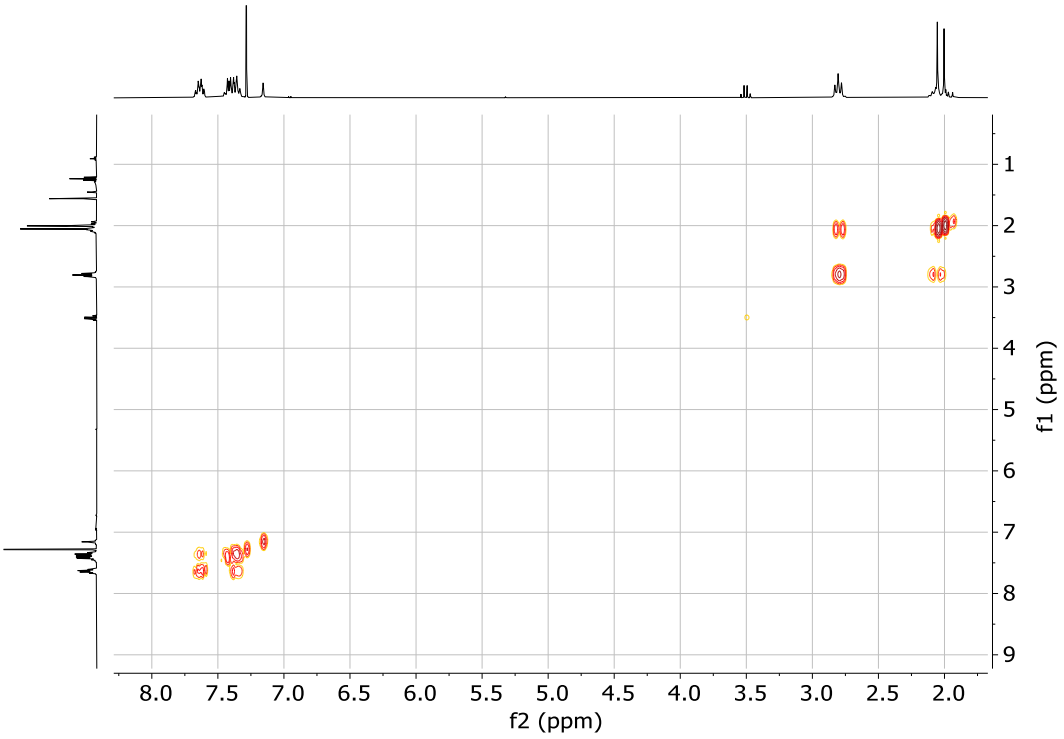


Figure S69 – ^{1}H-^{1}H COSY spectrum of [$PdCl_2$(**DTE°-C_6F_5**)$_2$] in $CDCl_3$ recorded at 25 °C.

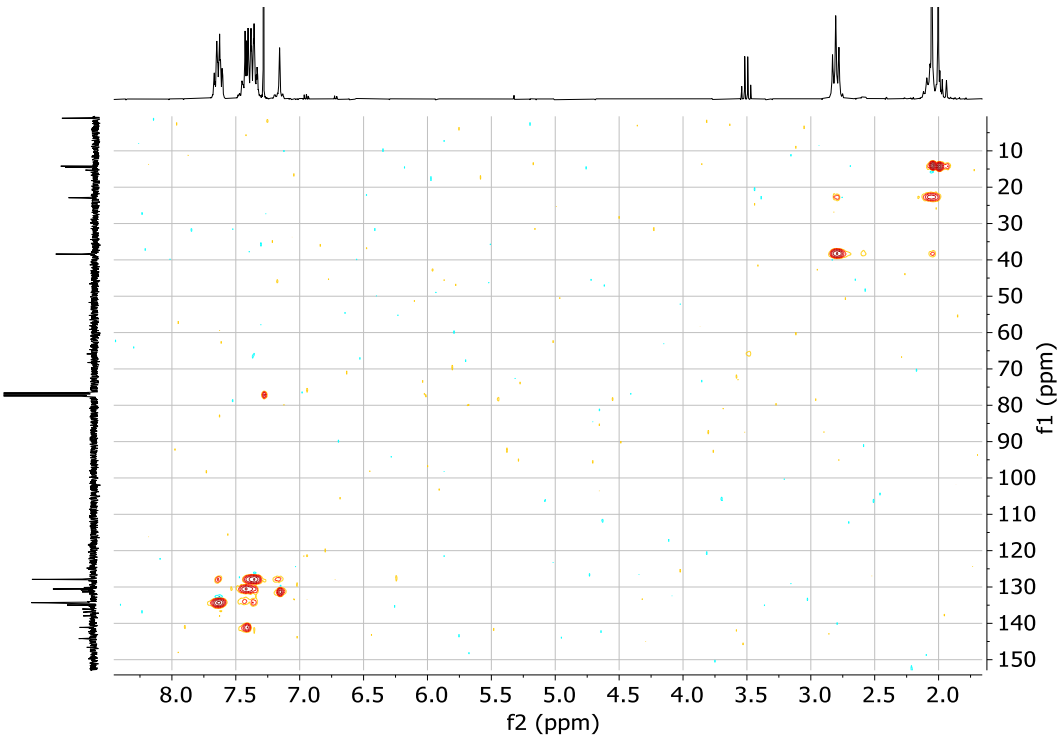


Figure S70 – ^{1}H-^{13}C HSQC spectrum of [$PdCl_2$(**DTE°-C_6F_5**)$_2$] in $CDCl_3$ recorded at 25 °C.

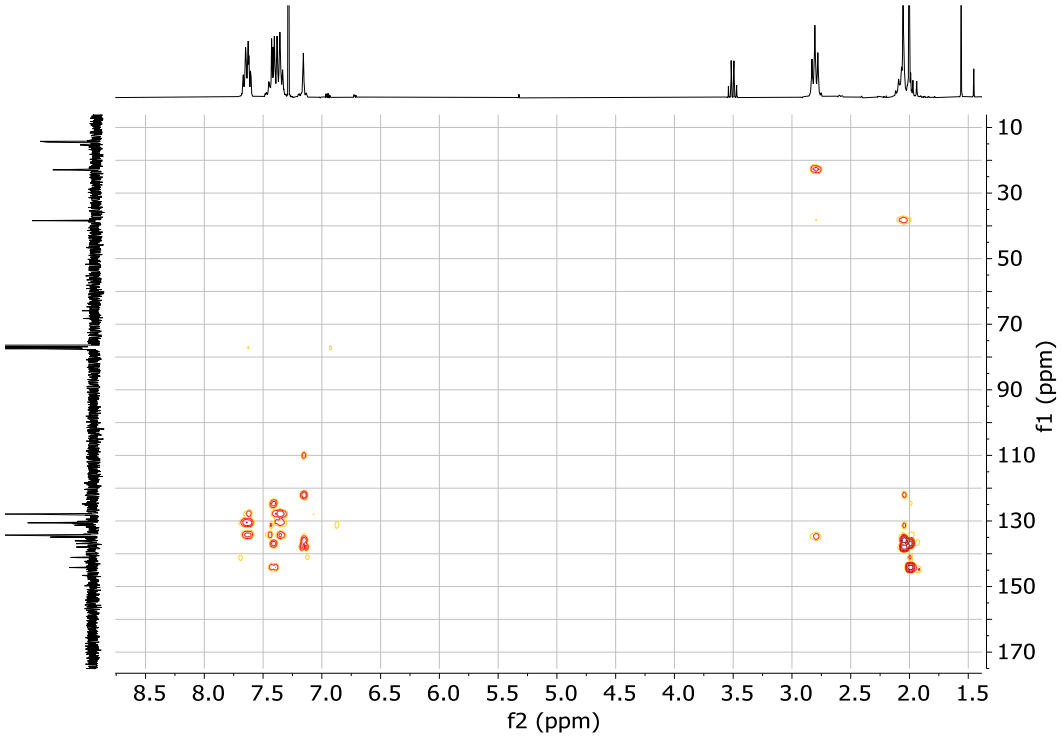


Figure S71 – ^{1}H-^{13}C HMBC spectrum of $[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$ in $CDCl_3$ recorded at 25 °C.

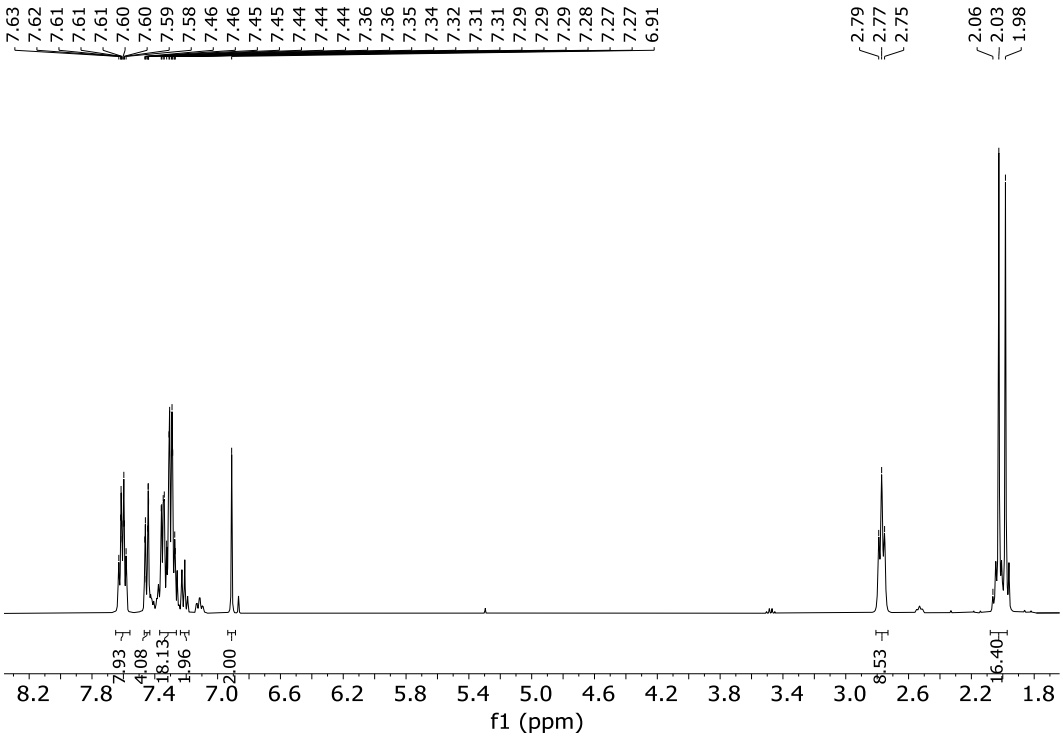


Figure S72 – ^{1}H NMR spectrum (400 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$ in $CDCl_3$ recorded at 25 °C.

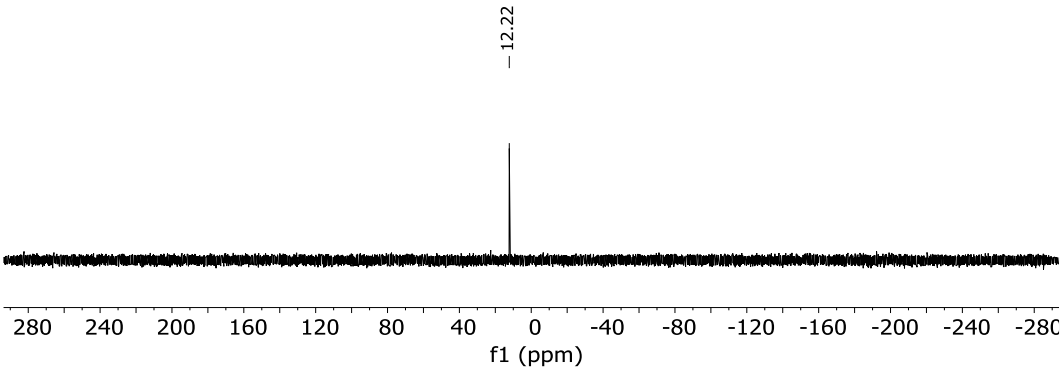


Figure S73 – $^{31}P\{^{1}H\}$ NMR spectrum (122 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$ in $CDCl_3$ recorded at 25 °C.

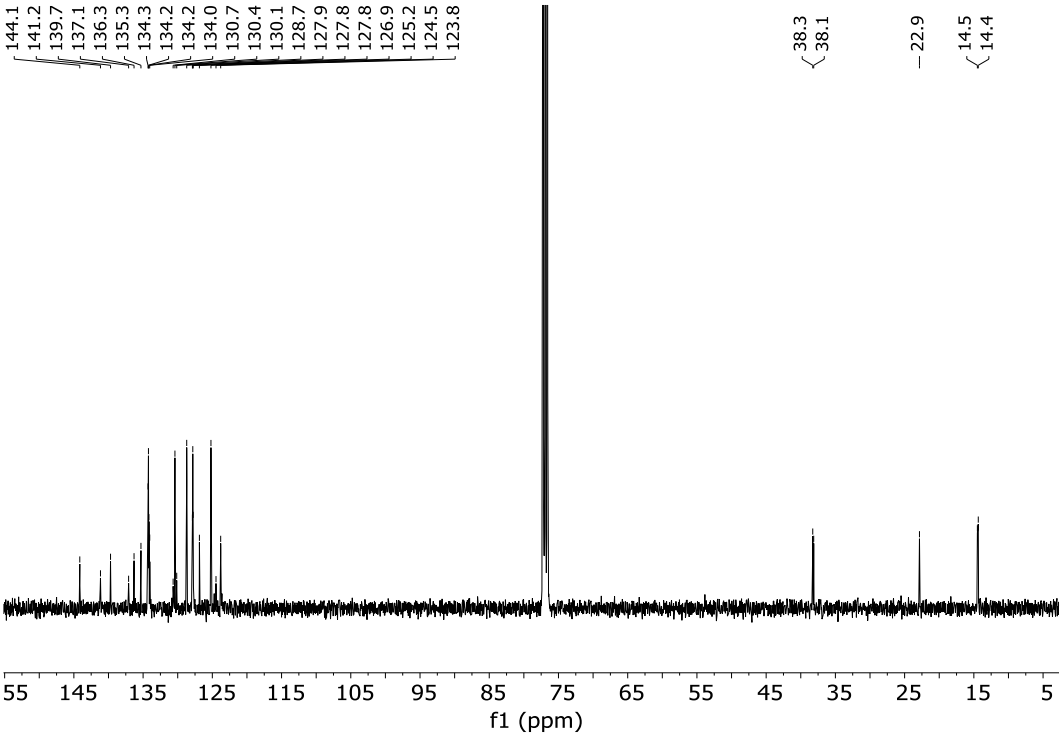


Figure S74 – $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of $[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$ in $CDCl_3$ recorded at 25 °C.

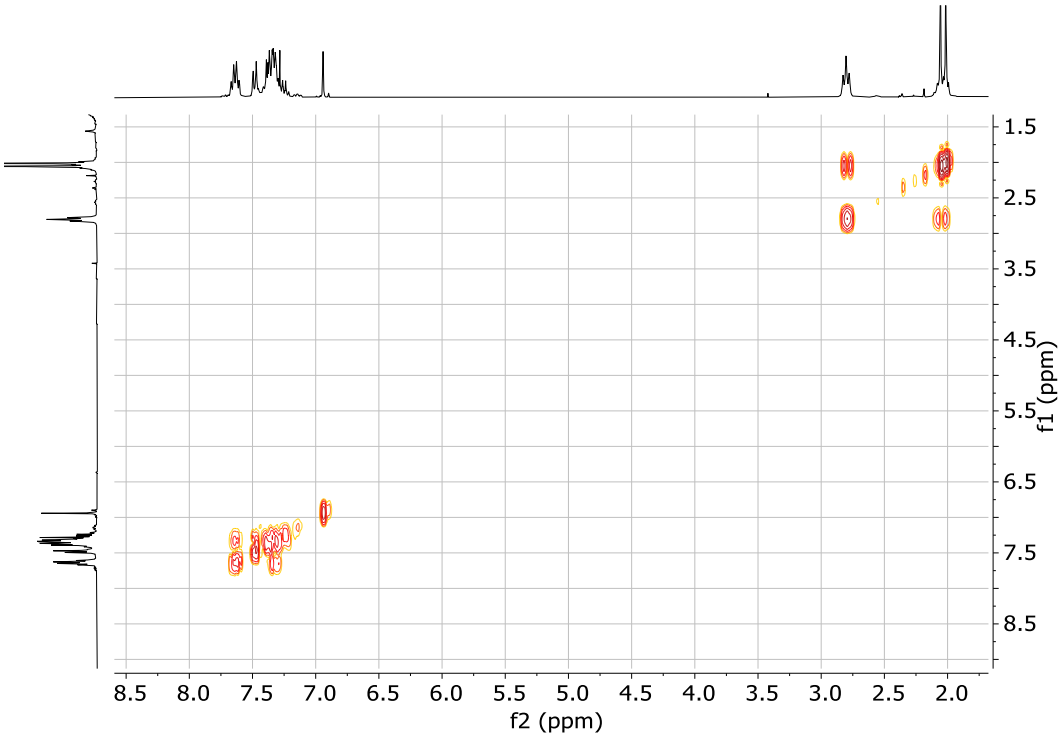


Figure S75 – ^{1}H-^{1}H COSY spectrum of [$PdCl_2$(**DTE^{o}-Ph**)$_2$] in $CDCl_3$ recorded at 25 °C.

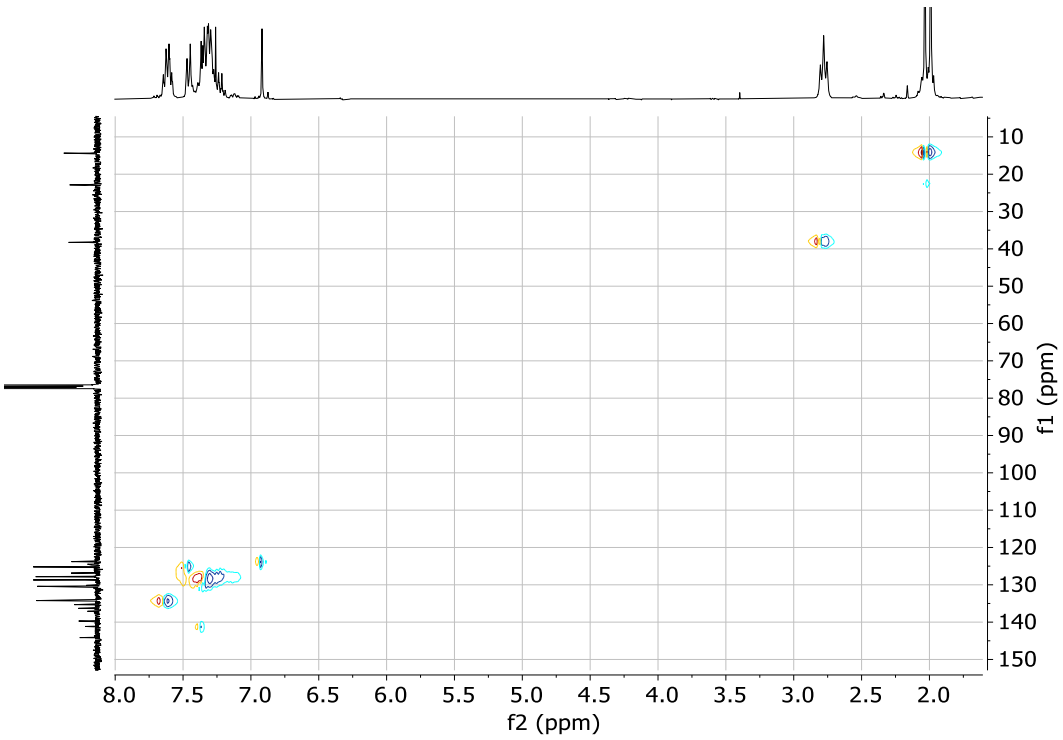


Figure S76 – ^{1}H-^{13}C HSQC spectrum of [$PdCl_2$(**DTE^{o}-Ph**)$_2$] in $CDCl_3$ recorded at 25 °C.

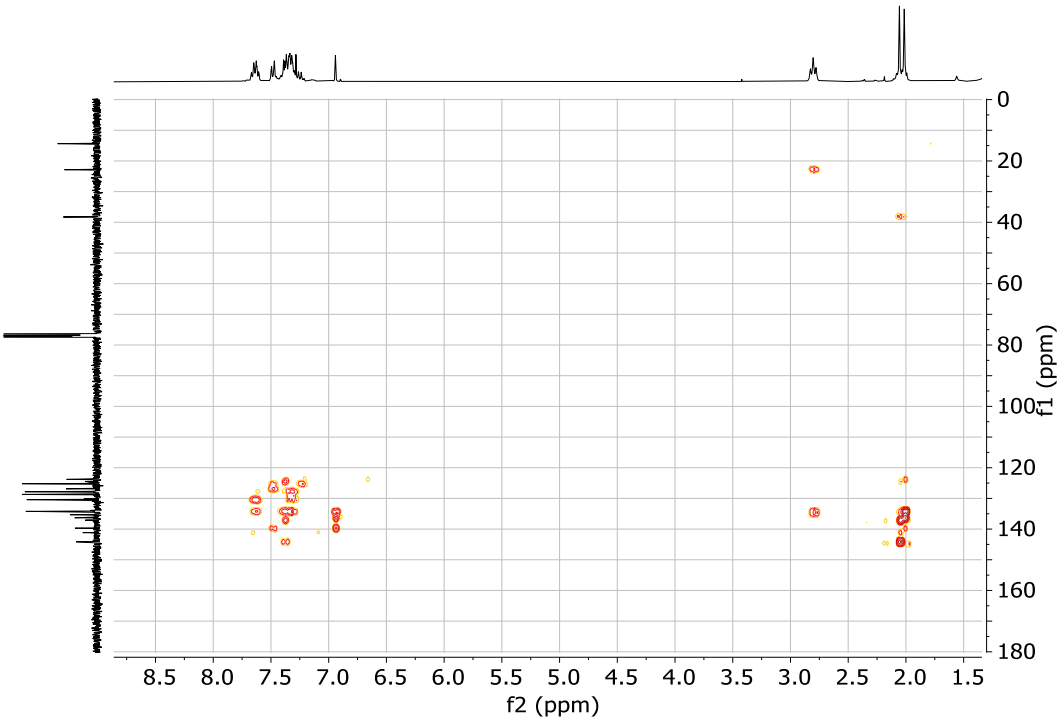


Figure S77 – ^{1}H-^{13}C HMBC spectrum of [$PdCl_2$(**DTE^{o}-Ph**)$_2$] in $CDCl_3$ recorded at 25 °C.

2. 5. 6. References

1 Coulson, D.R., Satek, L.C. and Grim, S.O. (1972). Tetrakis(triphenylphosphine)palladium(0). In *Inorganic Syntheses*, F.A. Cotton (Ed.). John Wiley & Sons, Ltd, 1972; pp 121–124.

2 Negishi, E.; Mohan, S. trans-Dichlorobis(triphenylphosphine)palladium(II). In *Encyclopedia of Reagents for Organic Synthesis (EROS)*; John Wiley & Sons, Ltd, 2008.

3 Tsuji, J.; Guo, H.; Ma, S.; Roman, D. S. Bis(benzonitrile)dichloropalladium(II). In *Encyclopedia of Reagents for Organic Synthesis (EROS)*; John Wiley & Sons, Ltd, 2015; pp 1–27.

4 Harris R. K; Becker E. D.; Cabral de Menezes S. M.; Goodfellow R.; Granger P. NMR Nomenclature: Nuclear Spin Properties and Conventions for Chemical Shifts: IUPAC Recommendations 2001. *Solid State Nucl. Magn. Reson.* **2002**, *22* (4), 458–483.

5 Rigaku Oxford Diffraction, (1995-2023), CrysAlisPro Software system, Rigaku Corporation, Wroclaw, Poland.

6 Clark, R. C.; Reid, J. S. The analytical calculation of absorption in multifaceted crystals. *Acta Crystallogr. A* **1995**, *51* (6), 887–897.

7 Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71* (1), 3–8.

8 DIAMOND 4: K. Brandenburg, Crystal Impact GbR, Bonn, Germany.

9 Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **2008**, *41* (2), 466–470.

10 Lees, A. J. A Photochemical Procedure for Determining Reaction Quantum Efficiencies in Systems with Multicomponent Inner Filter Absorbances. *Anal. Chem.* **1996**, *68* (1), 226–229.

11 Ordronneau, L.; Aubert, V.; Métivier, R.; Ishow, E.; Boixel, J.; Nakatani, K.; Ibersiene, F.; Hammoutène, D.; Boucekkine, A.; Le Bozec, H.; Guerchais, V. Tunable double photochromism of a family of bis-DTE bipyridine ligands and their dipolar Zn complexes. *Phys. Chem. Chem. Phys.* **2012**, *14* (8), 2599–2605.

12 Fihey, A.; Perrier, A.; Browne, W. R.; Jacquemin, D. Multiphotochromic molecular systems. *Chem. Soc. Rev.* **2015**, *44* (11), 3719–3759.

13 Villabona, M.; Wiedbrauk, S.; Feist, F.; Guirado, G.; Hernando, J.; Barner-Kowollik, C. Dual-Wavelength Gated oxo-Diels-Alder Photoligation. *Org. Lett.* **2021**, *23* (7), 2405–2410.

14 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16, Revision B.01*, 2016.

15 Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37* (2), 785–789.

16 Miehlich B.; Savin A.; Stoll H.; Preuss H. Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157* (3), 200–206.

17 Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.

18 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

19 Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113* (18), 6378–6396.

20 Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **2003**, *56* (5), 2257–2261.

21 Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, *77* (7), 3654–3665.

22 Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. Energy-adjusted *ab initio* pseudopotentials for the second and third row transition elements. *Theor. Chem. Acc.* **1990**, *77* (2), 123–141.

23 Höllwarth A.; Böhme M.; Dapprich S.; Ehlers A. W.; Gobbi A.; Jonas V.; Köhler K. F.; Stegmann R.; Veldkamp A.; Frenking G. A set of d-polarization functions for pseudo-potential basis sets of the main group elements Al-Bi and f-type polarization functions for Zn, Cd, Hg. *Chem. Phys. Lett.* **1993**, *208* (3), 237–240.

24 Ehlers A. W.; Böhme M.; Dapprich S.; Gobbi A.; Höllwarth A.; Jonas V.; Köhler K. F.; Stegmann R.; Veldkamp A.; Frenking G. A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc-Cu, Y-Ag and La-Au. *Chem. Phys. Lett.* **1993**, *208* (1), 111–114.

25 Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297–3305.

26 Bryantsev, V. S.; Diallo, M. S.; Goddard III, W. A. Calculation of Solvation Free Energies of Charged Solutes Using Mixed Cluster/Continuum Models. *J. Phys. Chem. B* **2008**, *112* (32), 9709–9719.

27 Glendening E. D.; Reed A. E.; Carpenter J. E.; Weinhold F. *NBO Version 3.1*.

28 Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1), 51–57.

29 Bianchini, G.; Strukul, G.; Wass, D. F.; Scarso, A. Photomodulable phosphines incorporating diarylethene moieties. *RSC Adv.* **2015**, *5* (14), 10795–10798.

30 Sánchez, R. S.; Gras-Charles, R.; Bourdelande, J. L.; Guirado, G.; Hernando, J. Light- and Redox-Controlled Fluorescent Switch Based on a Perylenediimide–Dithienylethene Dyad. *J. Phys. Chem. C* **2012**, *116* (12), 7164–7172.

31 Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. Single-crystalline photochromism of diarylethenes: reactivity-structure relationship. *Chem. Commun.* **2002** (23), 28

Preface to Chapter 3

Despite the positive results obtained for the dithienylethylene-based phosphines presented in Chapter 2, moderate photomodulation of catalytic activity was measured for the resulting palladium(II) complexes. Aiming to improve this effect on metal catalysis by amplifying the light-induced variation of phosphine electronic properties upon dithienylethene photoisomerization, a new strategy was explored that is described in the following chapter. It involves anchoring two dithienylethene units, each featuring electron-withdrawing trifluoroacetyl groups, to the same phenylphosphine. Consequently, this phosphanyl group should experience an additive effect on its σ-donating ability upon double photocyclization. As reported for other multiphotochromic systems, the fully ring-closing reaction of the obtained bis(dithienylethene)phosphine ligand was observed to proceed with low efficiency. Despite this, experimental studies and theoretical calculations showed that the electronic modulation achieved for the fully closed state of the system was indeed higher than in any other reported example of photoswitchable phosphine ligands. Additionally, this behavior could be transferred to metal complexes, as demonstrated by conducting gold(I) complexation and characterizing the resulting coordination compound photochemically.

Chapter 3

Amplified Photomodulation of a Phosphine Ligand with a Dithienylethene Dimer

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Abstract

Phosphine ligands play a crucial role in homogeneous catalysis, allowing to fine-tune the catalytic activity of various metals by modifying their structure. An ultimate challenge in this field is to reach controlled modulation of catalysis *in situ*, for which the development of phosphines capable of photoswitching between states with differential electronic properties has been proposed. To magnify this light-induced behavior, in this work we describe a novel phosphine ligand incorporating two dithienylethene photoswitchable moieties tethered to the same phosphorus atom. Double photoisomerization was observed for this ligand, which remains unhindered upon gold(I) complexation. As a result, the preparation of a fully ring-closed phosphine isomer was accomplished, for which amplified variation of phosphorus electron density was verified both experimentally and by computational calculations. Accordingly, the presented molecular design based on multiphotochromic phosphines could open new ways for preparing enhanced photoswitchable catalytic systems.

The author of this thesis performed the synthesis of the compounds and their characterization, part of the photochemical experiments, conducted DFT calculations, did data analysis and wrote the original text. Marc Villabona performed part of the photochemical experiments. Agustí Lledós

supervised the DFT calculations. Jordi Hernando performed data analysis, supervised the project and prepared the original draft. Rosa María Sebastián and Evamarie Hey-Hawkins have supervised and administered the project. The original draft of the manuscript was proof-read by all co-authors and changed according to their suggestions.

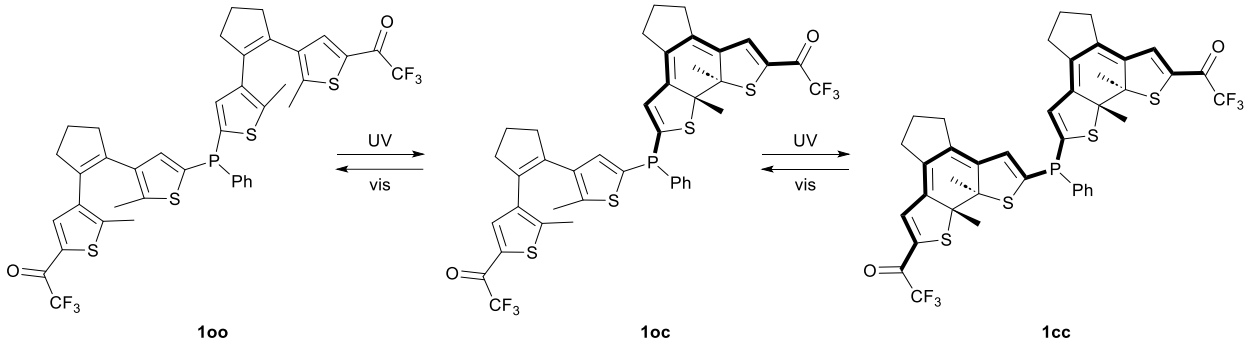
3. 1. Introduction

Diarylethenes (DAEs) are amongst the principal molecular photoswitches used for the development of light-responsive compounds, materials and processes.[1–7] In part, this is due to the excellent photochemical properties that most DAEs exhibit, namely reversible photoisomerization between ring-open (**o**) and ring-closed states (**c**) with high thermal stability, conversion efficiency and fatigue resistance.[1,2] In addition, DAEs undergo large geometrical and electronic changes upon **o**-**c** photoswitching, a feature that is exploited to accomplish light-control in a variety of applications (e.g., information storage and processing,[1,2,8] chemical reactivity and catalysis,[5,9,10] soft matter actuators[4,6] and (bio)imaging[3,11]). In several of these cases, the photoinduced performance of the final system would benefit from the incorporation of multiple DAE units in a single molecular construct;[12–14] for instance, to obtain multistate behavior in molecular switches for larger information storage density, or to amplify the electronic modulation between the two states of a photoswitchable catalyst or reagent.

However, the development of high-performance multiphotochromic molecules based on DAEs is not straightforward. In many of these systems, complete photoisomerization of their DAE units is inhibited by excited state energy transfer between neighboring ring-open and ring-closed units. As a result, only partial photoswitching can be reached where one (or more) of the DAE moieties in the construct remain in their initial open state.[12–14] This detrimental effect is very sensitive to the distance between neighboring DAE photochromes as well as the electronic properties of the linkers through which they are tethered.[12–14] In particular, only very few examples have been reported where full photocyclization was observed for two very close DAE groups separated by short spacers such as silylene,[15] phenylene[16,17] and divinylene bridges.[18] By contrast, the use of much longer linkers favors multiple DAE photoswitching, though at the cost of preventing through-bond electronic communication between nearby photochromic units.[14,19,20]

In this work, we tackled this challenge by directly connecting two dithienylethene (DTE) photochromic units, the most common type of DAE, through a phosphine bridge. Dithienylethene-phosphine tethers have been proposed for the light-control of coordination compounds and catalytic reactions, as the electronic changes occurring upon DTE photoisomerization can modulate the electron-donating ability of phosphane ligands.[5,21] To our knowledge, this goal has only been explored by attaching one DTE unit to phosphines, either through the central[22] or the lateral thiophene[23,24,25,26] rings of the photochromic moiety. Consequently, only limited photomodulation

of phosphine properties can be accomplished in this way. Herein, we hypothesized that this light-promoted effect could be further amplified by introducing additional DTE units to the same ligand, for which we developed bisDTE-substituted phosphine **1** that can present three different isomer states: fully ring-open (**oo**), fully ring-closed (**cc**) and an intermediate form with one ring-open and one ring-closed unit (**oc**) (Scheme 3-1). The structure of compound **1** was designed on the basis of two main principles: (i) two DTE units were connected to the same phosphorus atom, which should be double affected by photochrome isomerization, and (ii) a strong electron-withdrawing trifluoromethyl ketone group was installed in the external thiophene ring of both DTE units, which only communicates with the phosphorus atom on the other thiophene moiety upon light-induced ring-closure. As a result, the effect of DTE photocyclization on the electronic features of the phosphorus atom in **1** should be maximized if full photoisomerization from the initial **oo** isomer to the final **cc** state is accomplished.



Scheme 3-1 – Two-step reversible photoisomerization of the phosphine ligand **1** studied in this work.

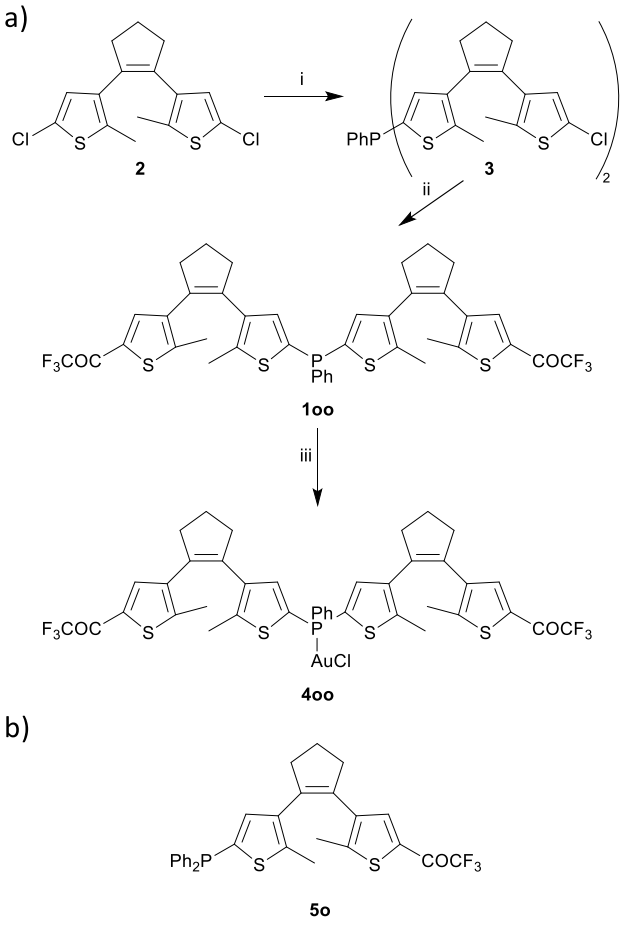
3. 2. Results and discussion

3. 2. 1. Synthesis

Bis(dithienylethenyl)phosphine **1** was synthesized through sequential lithiation-mediated reactions from 1,2-bis(2-chloro-5-methylthien-4-yl)cyclopentene (**2**), a common intermediate for the preparation of DTE derivatives (Scheme 3-2a).[27] At first, the phosphanyl group was introduced by performing chlorine-lithium exchange with *t*-butyllithium (*t*BuLi) and reacting 2 equivalents of the resulting monolithiated substrate with 1 equivalent of $PhPCl_2$ to yield compound **3** (52% yield). In a second step, the remaining chlorine atoms in **3** were substituted for the trifluoroacetyl function through a similar lithiation protocol using ethyl trifluoroacetate as an electrophile source, which finally led to target ligand **1** in its fully ring-open state **oo** (49% yield). In the $^{31}P\{^{1}H\}$ NMR spectrum this compound presents a singlet at δ = -33.4 ppm that very much resembles the reported value for phenyldi-2-thienylphosphine (δ =-33.6 ppm),[28] thereby corroborating the introduction of two DTE units tethered to the central phosphanyl group in **1**. The introduction of the external trifluoromethyl ketones in the final ligand was confirmed by the singlet registered at δ = -71.9 ppm in the ^{19}F NMR

spectrum, which is in agreement with other trifluoroacetyl-functionalized DTEs (δ ca. - 72 ppm)[26,29]. One of these described compounds, mono DTE-substituted phosphine **5o** (Scheme 3-2b),[26] was used herein as a reference in the photochemical and electronic characterization of **1**.

To further investigate the properties of the obtained ligand **1** upon metal binding, the monophosphine gold(I) complex **4** in its ring-open state **oo** (89% yield, Scheme 3-2a) was prepared by reaction with (dimethylsulfide)gold(I) chloride. For this compound, complexation was corroborated through the downfield shift of the singlet in the $^{31}P\{^{1}H\}$ NMR spectrum to δ = 6.1 ppm.



Scheme 3-2 – a) Synthetic route to bisDTE-substituted phosphine **1** and its gold(I) complex **4**. (i) *t*-BuLi/THF, 0.5 eq. $PPhCl_2$, (ii) *t*-BuLi/THF, CF_3COOEt, (iii) $[AuCl(SMe_2)]/CH_2Cl_2$. b) Structure of the monoDTE-substituted phosphine **5** used as a reference in this work.[26]

3. 2. 2. Photochemical characterization

As depicted in Scheme 3-1, DTE-based **1** is expected to undergo photoinduced isomerization between three distinctive states: **oo**, **oc** and **cc**. This photochemical behavior was investigated both experimentally by UV-vis absorption and NMR measurements in organic solvents as well as through TD-DFT calculations at the CAM-B3LYP-D3/6,31-G(d,p) level. First, the UV-vis absorption spectrum of the synthesized **1oo** isomer was recorded in cyclohexane (Figure 3-1a). Similar to other DTE

derivatives,[2] the open-state absorption spectrum of **1** resembles that of substituted thiophenes and features a distinct absorption band with $\lambda_{abs,max}$ = 273 nm corresponding to a dithienylethene $\pi \rightarrow \pi^*$ electronic transition (Table 3-1, Figure S7a and Tables S1-S2 in the section §3.6). Notably, the presence of the electron-withdrawing trifluoroacetyl group results in the observation of an absorption shoulder that extends up to λ_{abs} ~ 400 nm, which should allow irradiation of **1oo** with less energetic UV-A light to promote photoisomerization. Indeed, when a cyclohexane solution of **1oo** was illuminated at λ_{exc} = 355 nm, the emergence of a broad, red-shifted peak at $\lambda_{abs,max}$ = 599 nm was registered, which is characteristic of the lowest-energy $\pi \rightarrow \pi^*$ electronic transition of closed-state DTEs exhibiting higher conjugation pathways (Figure S7b and Tables S1-S2 in the section §3.6).[2] For **1**, this spectral change made the initial colorless solution turn deep blue, a behavior already reported for other trifluoroacetyl-functionalized DTEs upon photocyclization.[26,29] UV-induced photoisomerization of **1** was further confirmed by subsequent irradiation of the sample with visible light (λ_{exc} = 532 nm). The absorption band at $\lambda_{abs,max}$ = 599 nm disappeared entirely while the original spectrum of the initial **1oo** isomer was recovered – i.e., quantitative ring-opening of the previously formed photocyclized species occurred (Figure 3-1b). Indeed, the reversible open-close photoisomerization of **1** could be repeated for ten consecutive cycles of illumination with UV (365 nm) and visible (520 nm) irradiation without observing any spectral sign of photodegradation, thus proving the high fatigue resistance of the bisDTE-substituted phosphine **1** (Figure 3-1c).

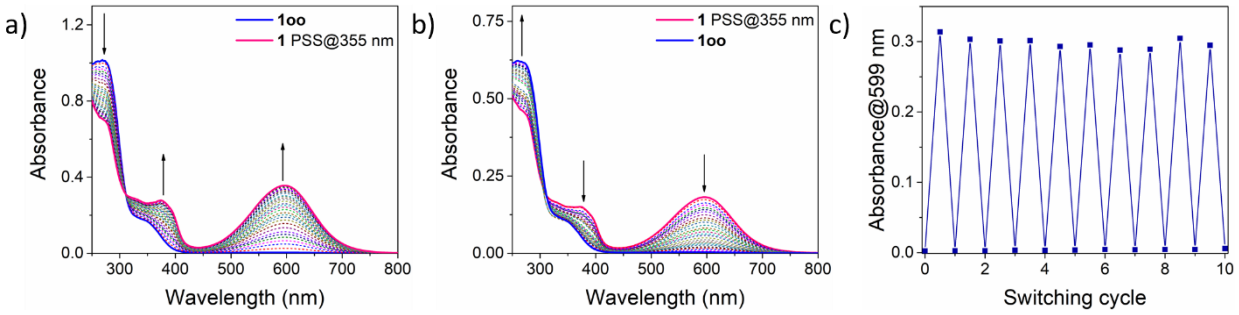


Figure 3-1 – Photochemical properties of **1** in cyclohexane solution. a) Variation of the UV-vis absorption spectrum of **1oo** (c = 3.12·10^{-5} M) upon irradiation at λ_{exc} = 355 nm until a photostationary state is obtained (PSS@355 nm). b) Variation of the UV-vis absorption spectrum of PSS@355 nm for **1** (c = 1.83·10^{-5} M) upon irradiation at λ_{exc} = 532 nm until the initial spectrum of **1oo** is recovered. c) Variation of the ring-closed absorbance of **1** (c = 2.39·10^{-5} M) in the visible region (λ_{abs} = 599 nm) upon 10 consecutive photoswitching cycles with UV and visible light (λ_{exc} = 365 and 520 nm).

As previously described for other systems bearing multiple DTE units,[12–14] a critical parameter of the photoswitching performance of **1** is the extent of its UV-induced photocyclization process, i.e., whether its fully ring-closed isomer **1cc** can be produced. This issue could not be investigated by UV-vis absorption spectroscopy, as no clear spectral shift with the irradiation time was observed for the absorption band in the visible region characteristic of ring-closed DTE species. According to the TD-

DFT calculations, this is to be expected during the formation of **1oc** and **1cc**, because both compounds must present similar spectral maxima for their lowest-energy electronic transitions (Figure S7b and Tables S1-S2 in the section §3.6). For this reason, we analyzed the ring-closing reaction of **1** upon UV irradiation by NMR spectroscopy in toluene-d_8 (Figure 3-2 and Figures S1-S2 in the section §3.6). For this study, we had to consider the particular stereochemistry of DTE photocyclization, which produces a racemic mixture of two ring-closed enantiomers due to its conrotatory nature.[2] As a result, UV-induced photoisomerization of bisDTE-functionalized phosphine **1oo** should generate a diastereomeric mixture of two pairs of enantiomers for the state **oc**, which could give rise to two distinctive sets of NMR signals, and a diastereomeric mixture of two *meso* forms and one pair of enantiomers for the state **cc**, which could produce three separate sets of NMR signals (Scheme S1 in the section §3.6). This behavior was indeed experimentally observed by ^{31}P NMR spectroscopy, where one, two and three different resonances lying at significantly different spectral regions could be identified for **1oo**, **1oc** and **1cc** after UV irradiation, respectively (Figure 3-2 and Figures S1 in the section §3.6). Therefore, this result demonstrates the capacity of **1** to undergo full DTE ring-closing, a quite remarkable feature that has been seldom reported for compounds bearing multiple dithienylethene units separated at short distances.[15–18] However, the efficiency of complete DTE photocyclization was found to be moderate for **1**. Instead, a photostationary state (PSS) mainly enriched in the intermediate **oc** isomer was observed to form upon irradiation at λ_{exc} = 365 nm in toluene-d_8. In particular, the **oo**:**oc**:**cc** molar ratio determined for the PSS mixture produced was 7:84:9, which corresponds to a 52% efficacy in DTE ring-closing (Table 3-1). This is clearly lower than for the reference monoDTE phosphine **5**, which generates 91% of the fully closed isomer under the same irradiation conditions.[26] To rationalize this behavior, the separate **oo**→**oc** and **oc**→**cc** photocyclization quantum yields were determined for **1** ($\Phi_{\mathbf{oo\text{-}oc}}$ = 0.435 and $\Phi_{\mathbf{oc\text{-}cc}}$ = 0.020, Table 3-1). On the one hand, $\Phi_{\mathbf{oo\text{-}oc}}$ closely resembles the photocyclization quantum yield of reference **5** ($\Phi_{\mathbf{o\text{-}c}}$ = 0.480)[26], which indicates that the first ring-closing step in **1** is not significantly affected by the presence of a nearby ring-open DTE unit. By contrast, a 20-fold reduction in Φ was measured for the second ring-closing reaction of **1**, which proceeds notably less effectively when a close-by DTE unit is already in the closed state. As reported for many other multiphotochromic systems,[12–14] energy transfer from the photoexcited open DTE group to the closed DTE unit in **1oc** must account for this situation, which eventually leads to photoconversion back to **1oo** instead of full photocyclization in **1cc**. This behavior was indeed suggested by the TD-DFT calculations, where electronic transitions that transfer electron density from the ring-open to the ring-closed units of **1oc** contribute to the UV absorption of this compound (Table S1-S2 in the section §3.6). Notably, intramolecular DTE interactions did not seem to affect the efficacy of the ring-opening reactions of **1**, as similar $\Phi_{\mathbf{cc\text{-}oc}}$ and $\Phi_{\mathbf{oc\text{-}oo}}$ values were obtained that are of the same order of magnitude as the photocycloreversion quantum yield of reference **5**.[26]

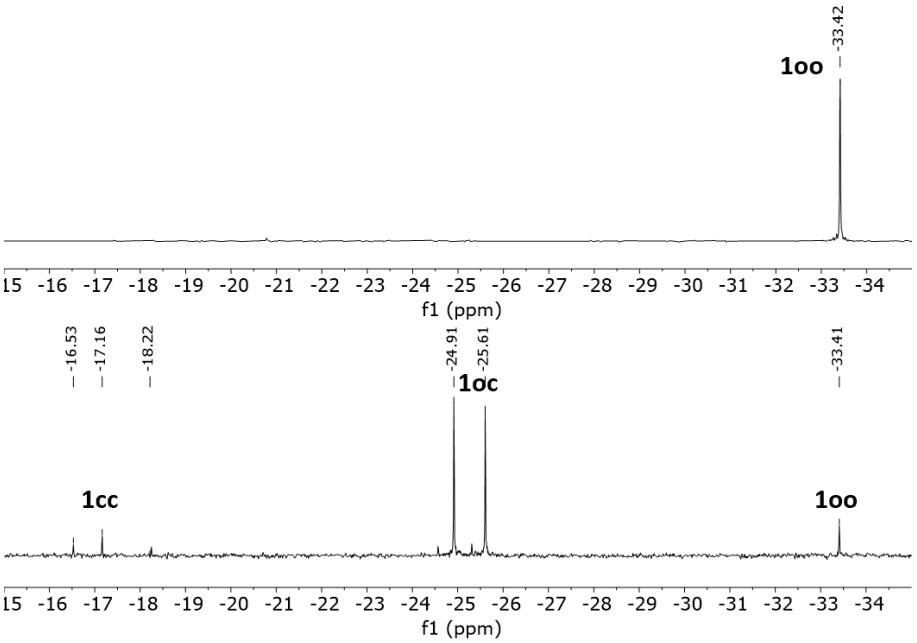


Figure 3-2 – $^{31}P\{^{1}H\}$ NMR spectra (121 MHz, toluene-d_8) of **1oo** (top) and the PSS@365 nm (bottom), where partial DTE photocyclization produces a mixture of **oo**, **oc** and **cc** isomers.

Metal complexation often leads to a change in the photochemical behavior of DTE-based ligands.[20,25,30] For this reason, we evaluated both experimentally and computationally the photochemical properties of gold(I) complex **4** (Scheme 3-2), which can also present three different **oo**, **oc** and **cc** isomers. Resembling free ligand **1**, a solution of the open-state complex **4oo** in cyclohexane exhibited strong absorption in the UV region with an intense peak at $\lambda_{abs,max}$ = 262 nm and an additional shoulder at $\lambda_{abs,max}$ = 336 nm (Table 3-1 and Figure S3 a in the section §3.6). However, it must be noted that, aside from the expected electronic transitions associated with the open state DTE units of **4oo**, other transitions involving metal-to-ligand and ligand-to-metal charge transfers were also found to occur for this compound within the UV region according to the TD-DFT calculations (Figure S8a and Tables S1-S2 in the section §3.6). In spite of this, the expected spectral changes accounting for DTE photoisomerization were observed upon UV irradiation of **4oo** cyclohexane solutions. A new band in the visible part of the spectrum appeared, which was accompanied by a color change of the sample to deep blue, i.e., gold(I) complex **4** also undergoes photocyclization (Table 3-1 and Figure S3a in the section §3.6). Although a 10-nm hypsochromic shift was observed for this band relative to free ligand **1** ($\lambda_{abs,max}$ = 589 nm), the TD-DFT calculations proved that it could also be attributed to $\pi \rightarrow \pi^*$ transitions associated with the closed-state DTE units of the complex, and these transitions present similar spectral maxima for both the **oc** and **cc** isomers of **4** (Figure S8b and Tables S1-S2 in the section §3.6).

As in the case of the free ligand, partial photoconversion of **4oo** under UV irradiation was revealed by NMR spectroscopic analysis. A very similar behavior to **1** was indeed obtained, as an **oo**:**oc**:**cc** molar ratio of 10:77:13 with an overall 52% content in DTE closed units was determined by ^{31}P NMR

spectroscopy for the PSS accomplished at equivalent illuminations conditions (Table 3-1 and Figures S4-S6 in the section §3.6). This result could also be attributed to the change in ring-closing quantum yield values upon partial photocyclization due to excited state energy transfer between neighboring ring-open and ring-closed DTE units in the complex. Thus, a 35-fold decrease in $\Phi_{\mathbf{oc\text{-}cc}}$ was measured relative to $\Phi_{\mathbf{oc\text{-}cc}}$ for **4**, in a similar fashion to free ligand **1** (Table 3-1). Therefore, metal complexation did not cause notable effects on the capacity of the bisDTE-functionalized phosphine to undergo full photocyclization, which allows preparing the double ring-closed isomer **4cc** though with minor efficiency. Photoinduced ring-opening of the bisDTE ligand was not found to be affected either in gold(I) complex **4**, as quantitative photocycloreversion could be promoted through irradiation at λ_{exc}= 532 nm with similar $\Phi_{\mathbf{cc\text{-}oc}}$ and $\Phi_{\mathbf{oc\text{-}oo}}$ values (Table 3-1 and Figure S3b in the section §3.6). As a result, complex **4** demonstrated good fatigue resistance, enduring 10 reversible photoswitching cycles without significant degradation (Figure S3c in the section §3.6).

Table 3-1 – Photochemical properties of DTE-based ligands **1** and **5**, and of gold(I) complex **4**.

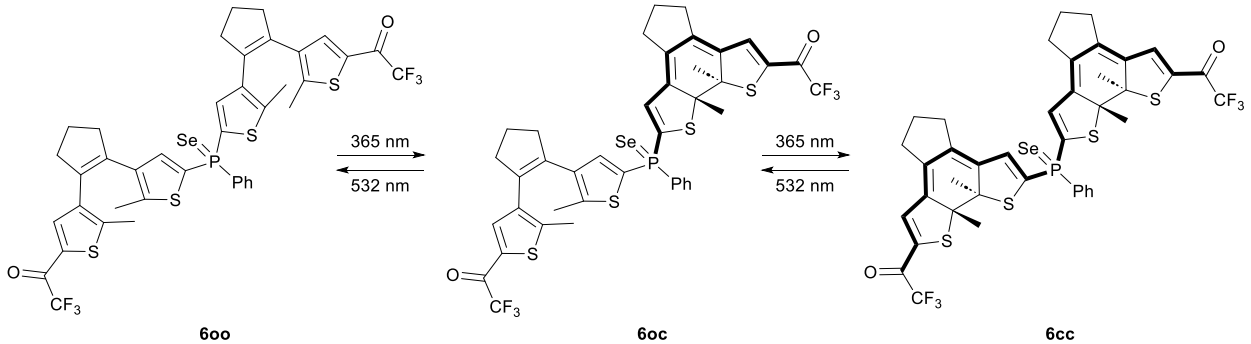
	λ^{o}_{abs} [nm] (ε [M^{-1} cm^{-1}])[a]	λ^{c}_{abs} [nm] (ε [M^{-1} cm^{-1}])[b]	$PSS_{o\text{-}c}$ composition [%][c]	$\Phi_{oo\text{-}oc}$[d]	$\Phi_{oc\text{-}cc}$[d]	$\Phi_{cc\text{-}oc}$[e]	$\Phi_{oc\text{-}oo}$[e]
1	273 (32 423), 336 (5 820)	599 (22 000)	7:84:9	0.435	0.020	0.032	0.022
4	262 (47 527), 336 (7 727)	589 (26 542)	10:77:13	0.246	0.007	0.026	0.023
5[26]	268 (35 673), 339 (6 431)	598 (12 261)	9:91	0.480		0.012	

[a] Wavelength and molar absorptivity coefficient of the absorption band maxima of the open isomer (for **1** and **4**, the **oo** state) in cyclohexane. [b] Wavelength and molar absorptivity coefficient of the maximum of the visible absorption band of the closed isomer (for **1** and **4**, the **cc** state) in cyclohexane. [c] Composition of the PSS reached for the photocyclization process in toluene-d_8 upon irradiation at λ_{exc} = 365 nm. DTE^{oo}:DTE^{oc}:DTE^{cc} (for **1** and **4**) and DTE^{o}:DTE^{c} (for **5**) concentration ratios are given. [d] Photocyclization quantum yields measured in cyclohexane at λ_{exc} = 355 nm. For ligand **5**, a single $\Phi_{o\text{-}c}$ value is given for its **o** → **c** ring-closing process. [e] Photocycloreversion quantum yields measured in cyclohexane at λ_{exc} = 532 nm. For ligand **5**, only $\Phi_{c\text{-}o}$ value is given for its **c** → **o** ring-opening process.

3. 2. 3. Photomodulation of the electronic properties of the phosphine

The introduction of DTE photochromes into phosphine ligands pursues modulating their metal-binding properties upon photoisomerization, eventually aiming to light-control the catalytic activity *in situ* of the resulting complexes.[5,10] For this goal to be accomplished, the phosphorus atom of these compounds should undergo a sufficient change in its electronic properties upon photoswitching of

the DTE units to which it is connected. Due to the nature of the phosphorus-selenium bond,[28,31] a common method to assess the modulation of the phosphorus σ-donating ability upon DTE photoisomerization is through the coupling of ^{77}Se to the ^{31}P nuclei in the corresponding phosphine selenides.[23,25,26] Generally, the rearrangement of the electron density caused by DTE photocyclization results in the retraction of electron density from the substituents at the 5-position in thiophene, resulting in a decrease in phosphorus σ-donating properties for the closed state of the DTE-based phosphines, which can be evidenced by an increase in $^1J_{P,Se}$ for the selenide derivative ($\Delta(^1J_{P,Se}) > 0$ upon ring-closing).[23,25,26] Herein we envisioned to amplify this effect through a two-fold strategy. First, by introduction of the strong electron-withdrawing trifluoroacetyl group at position 5 of the other thiophene ring of the system, which should only become electronically connected to the phosphanyl moiety upon DTE ring-closing. As we have established before for monoDTE-based phosphine **5**,[26] this design leads to a large decrease in $^1J_{P,Se}$ upon photocyclization compared to other DTE-functionalized phosphines ($\Delta(^1J_{P,Se})$ = 14 Hz, Table 3-2). In the bisDTE-based phosphine **1**, a second factor should allow further increasing the photomodulation of electronic properties of the phosphine, namely the additive effect arising from the photoisomerization of the two DTE units linked to the phosphorus atom. This hypothesis was successfully validated by evaluating the variation in ^{31}P–^{77}Se coupling constant upon successive photocyclization of the selenide derivative **6** (Scheme 3-3). Phosphine selenide **6oo** was prepared by reacting **1oo** with grey selenium powder in $CDCl_3$. Irradiation at 365 nm then produced compounds **6oc** and **6cc** that were studied *in situ*. For the fully closed isomer **6cc**, a total change in $^1J_{P,Se}$ of 19 Hz was determined (Table 3-2), the highest modulation measured to date for DTE-based phosphines[23,25,26] also exceeding the variation reported for 2-thienyldiphenylphosphine ($^1J_{P,Se}$ = 743 Hz) to tri-2-thienylphosphine ($^1J_{P,Se}$ = 757 Hz).[28]



Scheme 3-3 – Photoisomerization-induced variation of $^1J_{P,Se}$ in the **oo**, **oc** and **cc** isomers of phosphine selenide **6**.

To corroborate this experimental result, several descriptors commonly used to assess the electronic properties of ground state phosphines were computed using DFT calculations at the B3LYP-D3/6,31G(d,p) level. On the one hand, clear decrements in the Mulliken charge on the phosphorus atom of **1** were predicted upon DTE ring-closing ($\Delta(q_P^{Mulliken})$, Table 3-2). While the first

DTE photocyclization process in **1** should result in a similar $\Delta(q_P^{Mulliken})$ value as for monoDTE-based phosphine **5**, the second ring-closing reaction should lead to further lowering of the electron density on phosphorus. This effect is typically accompanied by changes in composition of the the lone pair at the phosphorus atom with an increased participation of the *s* orbital. Indeed, according to natural bond orbital (NBO) analysis,[32] the photoconversion from the **1oo** to the **1cc** state must lead to a progressive increment of the contribution of the *s* orbital to the lone pair of electrons at phosphorus, eventually reaching twice the variation computed for phosphine **5** (Table 3-2).

Finally, we computationally evaluated how the electron density change on the phosphorus atom in compound **1** and reference **5** upon photoisomerization would affect the ligand-metal bond energies of their respective gold(I) complexes (Table 3-2). As expected, weaker phosphorus-gold(I) bonds were predicted after DTE ring-closing in both ligands. More importantly, double DTE photocyclization in **4** should result in almost a two-fold variation in ligand-metal binding energies compared to the complex with monoDTE-based phosphine **5**. In combination with the experimental and theoretical data disclosed in this section, this result confirms the capacity to accomplish large photomodulation in the electronic properties of phosphines by tethering two photoswitchable DTE units to a central phosphorus atom.

Table 3-2 – Experimental and computed parameters to estimate the photomodulation of properties for phosphines **1** and **5**.

	$\Delta(^1J_{P,Se})$ [Hz]^a		$\Delta(q_P^{Mulliken})^b$		$\Delta(\%s_P)^c$		$\Delta(BE_{P\text{-}Au})$ [kcal·mol^{-1}]^d	
	oo → oc	**oo → cc**	**oo → oc**	**oo → cc**	**oo → oc**	**oo → cc**	**oo → oc**	**oo → cc**
1	11	19	0.011	0.036	0.52	1.58	1.52	2.13
	o → c		**o → c**		**o → c**		**o → c**	
5	14[26]		0.014[26]		0.79[26]		1.23	

^{a} Difference in $^1J_{P,Se}$ for the corresponding selenides measured in $CDCl_3$. ^{b} Difference in Mulliken charges in electronic units on the phosphorus atom. ^{c} Difference in percentage of *s* character of the lone pair of electrons at phosphorus. ^{d} Difference in phosphine-Au bond energy.

3. 3. Conclusions

In this work we reported the synthesis and characterization of a bis(dithienylethenyl)phosphine bearing two photoswitchable moieties connected to the same phosphorus atom. Upon light irradiation, reversible transformation between open-open, open-closed and closed-closed states was accomplished for this compound due to sequential DTE photoisomerization, in contrast to many other multichromophoric systems where several DTE units are arranged at short distances. More importantly, photoconversion allowed switching the communication between the phosphorus atom

and the electron-withdrawing trifluoromethyl ketone substituent of the nearby DTE units on and off. In combination with the additive effect caused by double DTE photoisomerization, this resulted in an unprecedented light-modulation of the electronic properties of the phosphine, as proven experimentally and through computational calculations. As the phosphine's ability to undergo photocyclization remained unhindered upon complexation with gold(I), this study provides valuable insights for the design of novel photoswitchable phosphines with amplified activity for light-controlled catalysis.

3. 4. Experimental section

General procedures

Materials and methods

All reactions were carried out under nitrogen atmosphere in the absence of air and water using standard Schlenk line techniques. All solvents (hexanes, CH_2Cl_2, cyclohexane) were dried and degassed prior to use. THF was distilled over sodium/benzophenone and stored over 4 Å activated molecular sieves. $CDCl_3$ was degassed by freeze–pump–thaw cycling. Toluene-d_8 was degassed with nitrogen. All starting materials and reagents were commercially purchased and used without further purification. Flash column chromatography was done using silica gel (230-400 mesh) using a stream of nitrogen.

NMR spectra were recorded on a BRUKER Avance III HD 400 MHz, BRUKER Ascend 300 MHz and BRUKER Ascend 400 MHz at 25 °C. Tetramethylsilane (TMS) was used as an internal reference in ^{1}H and ^{13}C NMR spectra; all other nuclei were referenced to TMS using Ξ scale.[33] Chemical shifts are reported in parts per million (ppm). Assignment of ^{1}H and ^{13}C NMR signals was carried out using ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR experiments. IR spectra were recorded on FT-IR spectrometers Thermo Scientific Nicolet iS5 and BRUKER Alpha II. Electrospray ionization mass spectrometry was carried out with BRUKER Impact II, BRUKER Esquire 3,000+ and micrOTOF-Q II BRUKER spectrometers in positive ion mode. UV-vis absorption spectra were recorded on an Agilent HP 8453 spectrophotometer using HPLC quality solvents and 1-cm quartz cuvettes. Photoisomerization studies were carried out using different irradiation sources (365 nm and 520 nm LEDs (Chanzon), and a Nd:YAG pulsed laser (Brilliant, Quantel, λ_{exc} = 355 or 532 nm)).

Photochemical characterization

DTE photoswitching in **1** and **4** was monitored by UV-vis and NMR spectroscopy. PSS composition was determined via ^{31}P or ^{19}F NMR spectrascopy from a PSS state produced by irradiating a toluene-d_8 solution in an NMR tube with the appropriate wavelength. UV-vis absorption spectra of the closed-state isomers shown in Figures S7-S8 were estimated from the PSS@365 nm and the corresponding open-state UV-vis spectra. Photoisomerization quantum yields were determined by

monitoring the variation of the UV-vis absorption spectra of **1** and **4** in cyclohexane upon irradiation with UV (for photocyclization, λ_{exc} = 355 nm) or visible light (for photocycloreversion, λ_{exc} = 532 nm). A kinetic model previously reported that accounts for the sequential photoisomerization of DTE units in **1** and **4** was used to separately determine the photoisomerization quantum yields of their **oo**, **oc** and **cc** isomers.[20] To apply this model, we assumed the UV-vis absorption spectrum of each DTE unit to be independent of the isomerization state of the other, i.e., the extinction coefficients of open DTE units are the same in the **oo** and **oc** states, while those of closed DTE groups are equal in the **oc** and **cc** states, as suggested by the TD-DFT calculations and observed in previous work on DTE dimers.[13] In all the cases, the irradiation intensities used in our photoisomerization quantum yield experiments were determined by monitoring the photocyclization and photocycloreversion processes of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane as a reference (Φ_{oc} = 0.59 and Φ_{co} = 0.013).[34]

Computational methods

DFT calculations were carried out using the Gaussian16 program package.[35] Geometry optimizations were conducted without any constraints using the B3LYP functional[36] with Grimme's D3 correction to account for dispersion effects.[37] Geometry optimizations were performed in THF using the solvation model density (SMD) continuum model[38] with basis set 1 (BS1). BS1 included the 6-31G(d,p) basis set for the main group atoms[39] (H, C, O, F, P, S) and the Stuttgart-Dresden SDD effective core potential (ECP) and its corresponding double-ζ basis set[40], with a set of *f* polarization functions[41] for Au. Frequency calculations were performed for all the optimized geometries to determine the stationary points as either minima or transition states. Energies in THF were refined through single-point calculations of the optimized BS1 geometries with an extended basis set (BS2). BS2 consisted of the def2-TZVP for main group atoms, and the quadruple-ζ def2-QZVP basis set for Au, together with the def2 ECP.[42] Frontier molecular orbitals and natural bond orbital (NBO)[43] analysis were calculated at the B3LYP-D3/BS1 level in THF using the SMD continuum model. TD-DFT calculations were carried out using the CAM-B3LYP functional[44] with Grimme's D3 correction to account for dispersion effects.[37] The first 15 electronic transitions were calculated in cyclohexane using the SMD continuum model with the BS1 described above.

Synthetic procedures

Phenyldi-{4-[2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophen-2-yl}phosphine (**3**)

A stirred yellow solution of 0.330 g (1.00 mmol, 1.0 eq.) **2**[45] in 20 mL THF was cooled to -78 °C (hexane/$N_{2(l)}$), and then 0.69 mL (1.6 mol·L^{-1}, 1.10 mmol, 1.1 eq.) *t*BuLi in pentane were added dropwise. The resultant bright yellow mixture was kept stirring for 65 min at -78 °C, followed by the addition of 0.07 mL (0.50 mmol, 0.5 eq.) of dichlorophenylphosphine in one swift motion. The reaction mixture was left overnight to warm up to room temperature, and then quenched with a degassed brine solution. Under nitrogen atmosphere, the phases were separated, the aqueous phase was extracted with THF (2 x 5 mL), and the combined organic phases were dried over degassed anhydrous Na_2SO_4. After canula filtration, the product mixture was absorbed on silica gel and purified through flash column chromatography (hexanes). After solvent removal *in vacuo*, a white oil was obtained (0.182 g, 52% yield).

R_f 0.29 (hexanes)

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.35 – 7.29 (m, 5H), 6.98 (d, *J* = 6.6 Hz, 2H), 6.57 (s, 2H), 2.80 – 2.68 (m, 8H), 2.09 – 1.97 (m, 10H), 1.87 (s, 6H) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 142.0, 139.0 (d, $^1J_{C,P}$ = 6.3 Hz), 137.4 (d, $^2J_{C,P}$ = 27.8 Hz), 136.8 (d, $^3J_{C,P}$ = 8.3 Hz), 135.2, 135.2, 134.2, 133.9 (d, $^1J_{C,P}$ = 23.3 Hz), 133.3, 131.9 (d, $^2J_{C,P}$ = 19.1 Hz), 128.7, 128.4 (d, $^3J_{C,P}$ = 6.7 Hz), 127.0, 125.1, 38.4, 23.1, 14.8, 14.3 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): -33.4 (s) ppm.

IR (ATR, ṽ): 3068 (w), 3050 (w), 2948 (s), 2914 (s), 2841 (s), 2730 (w), 1547 (w), 1456 (m), 1434 (s), 1376 (w), 1307 (w), 1288 (w), 1202 (m), 1162 (m), 1026 (w), 1010 (s), 990 (m), 964 (w), 829 (m), 742 (m), 696 (m), 652 (w), 530 (m), 519 (m), 482 (m), 430 (w) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M+Na]^+$ 717.0472; found 717.0479.

Phenyldi-{4-[2-(5-trifluoroacetyl-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophen-2-yl}-phosphine (**1oo**)

A stirred solution of 0.174 g (0.25 mmol, 1.0 eq.) **3** in 5 mL THF was cooled to -78 °C (hexane/$N_{2(l)}$), and 0.63 mL (1.6 mol·L^{-1}, 1.00 mmol, 4 eq.) *t*BuLi in pentane were added dropwise. The resultant deep red mixture was kept stirring for 60 min at -78 °C, followed by the addition of 0.238 mL (2.00 mmol, 8.0 eq.) of anhydrous ethyl trifluoroacetate in one swift motion. The reaction mixture turned bright yellow and was left to warm up to room temperature over an hour. After quenching with a degassed brine solution, the organic phase was separated, the aqueous phase was extracted

with THF (2 x 5 mL), and the combined organic phases were dried over degassed anhydrous Na_2SO_4. After canula filtration, the product mixture was absorbed on silica gel and purified through flash column chromatography (hexanes/dichloromethane 80:20). After solvent removal *in vacuo*, a yellow oil was obtained (0.100 g, 49% yield). Caution: the product is very sensitive to oxygen nucleophiles (water, alcohols); special care should be taken during the work up to avoid formation of the corresponding hydrate.

R_f 0.18 (hexanes/dichloromethane 80:20)

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.57 (s, 2H), 7.32 – 7.21 (m, 5H), 6.89 (d, *J* = 6.6 Hz, 2H), 2.87 – 2.71 (m, 8H), 2.16 – 2.03 (m, 10H), 1.99 (s, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 173.0 (q, $^2J_{C,F}$ = 36.7 Hz), 150.1, 142.2, 138.9, 138.4 (d, $^1J_{C,P}$ = 6.3 Hz), 138.1 (q, $^4J_{C,F}$ = 3.2 Hz), 137.3, 137.0 (d, $^2J_{C,P}$ = 27.7 Hz), 136.3 (d, $^3J_{C,P}$ = 8.3 Hz), 134.6 (d, $^1J_{C,P}$ = 23.9 Hz), 133.0, 132.2, 131.8 (d, $^2J_{C,P}$ = 19.3 Hz), 128.9, 128.5 (d, $^3J_{C,P}$ = 6.9 Hz), 116.6 (q, $^1J_{C,F}$ = 290.7 Hz), 38.4, 38.3, 23.1, 15.6, 14.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$, δ): -71.9 (s) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): -33.3 (s) ppm.

IR (ATR, ṽ): 2952 (w, νC–H), 2917 (w, νC–H), 2843 (w, νC–H), 1680 (s, νC=O), 1527 (w), 1425 (m), 1331 (w), 1246 (w), 1220 (m), 1194 (m), 1137 (s), 1025 (m), 999 (m), 970 (m), 923 (m), 867 (m), 801 (s), 753 (m), 739 (m), 716 (m), 694 (m), 684 (m), 660 (m), 580 (m), 528 (m), 490 (m), 426 (m) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M+H]^+$ 819.1078; found 819.1095.

UV-vis (cyclohexane, λ_{max} (ε)): 273 (32 423), 336 (5 820) nm (M^{-1} cm^{-1}).

Phenyldi-{4-[2-(5-trifluoroacetyl-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophen-2-yl}-phosphine gold(I) chloride [AuCl(**1**)] (**4oo**)

In the dark, 0.015 g (0.05 mmol, 1.0 eq.) [AuCl(SMe_2)] and 0.042 g (0.05 mmol, 1.0 eq.) **1oo** were dissolved in 3 mL CH_2Cl_2. The reaction mixture was stirred at rt overnight and filtered through a canula. After solvent removal *in vacuo*, the complex was isolated as a white solid (0.046 g, 89%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.52 – 7.43 (m, 5H), 7.43 – 7.37 (m, 2H), 7.11 (d, *J* = 10.0 Hz, 2H), 2.83 – 2.76 (m, 8H), 2.15 – 2.03 (m, 16H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 172.9 (q, $^2J_{C,F}$ = 36.5 Hz), 150.0, 145.5 (d, $^4J_{C,P}$ = 3.1 Hz), 139.6 (d, $^2J_{C,P}$ = 15.3 Hz), 138.4, 137.9 (q, $^4J_{C,F}$ = 3.2 Hz), 137.3 (d, $^3J_{C,P}$ = 12.6 Hz), 136.3, 134.5, 132.6 (d, $^2J_{C,P}$ = 15.3 Hz), 132.3, 132.0, 130.9 (d, $^1J_{C,P}$ = 63.7 Hz), 129.2 (d, $^3J_{C,P}$ = 12.4 Hz), 126.5 (d, $^1J_{C,P}$ = 64.3 Hz), 116.5 (q, $^1J_{C,F}$ = 290.8 Hz), 38.3, 38.1, 23.1, 15.5, 14.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$, δ): -71.9 (s) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 6.1 (s) ppm.

IR (ATR, ṽ): 2955 (m, νC–H), 2922 (m, νC–H), 2850 (m, νC–H), 1680 (s, νC=O), 1527 (w), 1434 (s), 1424 (s), 1332 (w), 1246 (w), 1221 (m), 1194 (s), 1139 (s), 1100 (s), 1061 (m), 1016 (s), 911 (m), 868 (s), 751 (s), 739 (s), 716 (s), 687 (s), 659 (m), 581 (w), 525 (s), 507 (s), 453 (m) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for $[M+Na]^+$ 1073.0252; found 1073.0243.

UV-vis (cyclohexane, λ_{max} (ε)): 262 (47 527), 336 (7 727) nm (M^{-1} cm^{-1}).

Preparation of phosphine selenides

Phosphine selenides were prepared by the addition of grey selenium powder to an NMR tube containing **1** in $CDCl_3$ and leaving the tube at 30 °C for 30 min. The reaction proceeded with 100% yield. The obtained selenides (**6oo**, **6oc**, **6cc**) were not isolated and only studied *in situ*.

3. 5. References

1 M. Irie, *Chem. Rev.*, 2000, **100**, 1685–1716.
2 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174–12277.
3 T. Fukaminato, S. Ishida and R. Métivier, *NPG Asia Mater.*, 2018, **10**, 859–881.
4 J. Boelke and S. Hecht, *Adv. Opt. Mater.*, 2019, **7**, 1900404–19004018
5 D. Majee and S. Presolski, *ACS Catal.*, 2021, **11**, 2244–2252.
6 H.-B. Cheng, S. Zhang, E. Bai, X. Cao, J. Wang, J. Qi, J. Liu, J. Zhao, L. Zhang and J. Yoon, *Adv. Mater.,* 2022, **34**, 2108289–2108356.
7 Z. Li, X. Zeng, C. Gao, J. Song, F. He, T. He, H. Guo and J. Yin, *Coord. Chem. Rev.*, 2023, **497**, 215451–215489.
8 J. Andréasson and U. Pischel, *Chem. Soc. Rev.*, 2015, **44**, 1053–1069.
9 R. Göstl, A. Senf and S. Hecht, *Chem. Soc. Rev.*, 2014, **43**, 1982–1996.
10 G. C. Thaggard, J. Haimerl, R. A. Fischer, K. C. Park and N. B. Shustova, *Angew. Chem. Int. Ed.,* 2023, **62**, e202302859.
11 O. Nevskyi, D. Sysoiev, J. Dreier, S. C. Stein, A. Oppermann, F. Lemken, T. Janke, J. Enderlein, I. Testa, T. Huhn and D. Wöll, *Small* 2018, **14**, 1703333.
12 A. Perrier, F. Maurel and D. Jacquemin, *Acc. Chem. Res.*, 2012, **45**, 1173–1182.
13 A. Fihey, A. Perrier, W. R. Browne and D. Jacquemin, *Chem. Soc. Rev.*, 2015, **44**, 3719–3759.
14 N. M.-W. Wu, M. Ng and V. W.-W. Yam, *Nat. Commun.*, 2022, **13**, 33–43.
15 J. Areephong, W. R. Browne and B. L. Feringa, *Org. Biomol. Chem.*, 2007, **5**, 1170–1174.
16 K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, 2001, **123**, 9896–9897.

17 S. Kobatake and M. Irie, *Tetrahedron*, 2003, **59**, 8359–8364.

18 D. Zhang, C. Fan, C. Zheng and S. Pu, *Dyes Pigm.*, 2017, **136**, 669–677.

19 a) S. Kobatake, S. Kuma and M. Irie, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 945–951; b) R. Arai, S. Uemura, M. Irie and K. Matsuda, *J. Am. Chem. Soc.*, 2008, **130**, 9371–9379; c) J. Areephong, H. Logtenberg, W. R. Browne and B. L. Feringa, *Org. Lett.*, 2010, **12**, 2132–2135; d) B. Li, J.-Y. Wang, H.-M. Wen, L.-X. Shi and Z.-N. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 16059–16067; e) S. Wei, X. Li, C. Fan, G. Liu and S. Pu, *Tetrahedron*, 2017, **73**, 6164–6171. f) T. Biellmann, A. Galanti, J. Boixel, J. A. Wytko, V. Guerchais, P. Samorì and J. Weiss, *Chem. Eur. J.*, 2018, **24**, 1631–1639; g) Y. Wang, Q. Zhou, X. He, Y. Zhang, H. Tan, J. Xu, C. Wang, W. Wang, X. Luo, J. Chen and L. Xu, *Chin. Chem. Lett.*, 2022, **33**, 1613–1618.

20 L. Ordronneau, V. Aubert, R. Métivier, E. Ishow, J. Boixel, K. Nakatani, F. Ibersiene, D. Hammoutène, A. Boucekkine, H. Le Bozec and V. Guerchais, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2599–2605.

21 F. Medici, N. Goual, V. Delattre, A. Voituriez and A. Marinetti, *ChemCatChem*, 2020, **12**, 5573–5589.

22 a) Z. Xu, Y. Cao, B. O. Patrick and M. O. Wolf, *Chem. Eur. J.*, 2018, **24**, 10315–10319; b) F. Buß, M. Das, D. Janssen-Müller, A. Sietmann, A. Das, L. F. B. Wilm, M. Freitag, M. Seidl, F. Glorius and F. Dielmann, *Chem. Commun.*, 2023, **59**, 12019–12022.

23 D. Sud, R. McDonald and N. R. Branda, *Inorg. Chem.*, 2005, **44**, 5960–5962.

24 a) F.-R. Dai, B. Li, L.-X. Shi, L.-Y. Zhang and Z.-N. Chen, *Dalton Trans.,* 2009, 10244–10249; b) J. Yin, Y. Lin, X. Cao, G.-A. Yu, H. Tu and S. H. Liu, *Dyes Pigm.*, 2009, **81**, 152–155; c) J. Liang, J. Yin, Z. Li, C. Zhang, Di Wu and S. H. Liu, *Dyes Pigm.*, 2011, **91**, 364–369; d) H.-M. Wen, J.-Y. Wang, M.-Q. Hu, B. Li, Z.-N. Chen and C.-N. Chen, *Dalton Trans.*, 2012, **41**, 11813–11819; e) B. Li, Y.-H. Wu, H.-M. Wen, L.-X. Shi and Z.-N. Chen, *Inorg. Chem.*, 2012, **51**, 1933–1942.

25 G. Bianchini, G. Strukul, D. F. Wass and A. Scarso, *RSC Adv.*, 2015, **5**, 10795–10798.

26 A. Sherstiuk, A. Lledós, P. Lönnecke, J. Hernando, R. M. Sebastián, E. Hey-Hawkins, *ChemRxiv.*, 2023.

27 A. D. Sponza, Di Liu, E. P. Chen, A. Shaw, L. Diawara and M. Chiu, *Org. Biomol. Chem.*, 2020, **18**, 7238–7252.

28 D. W. Allen, B. F. Taylor, *J. Chem. Soc. Dalton Trans.*, 1982, 51–54.

29 M. Villabona, S. Wiedbrauk, F. Feist, G. Guirado, J. Hernando and C. Barner-Kowollik, *Org. Lett.*, 2021, **23**, 2405–2410.

30 a) M. T. Indelli, S. Carli, M. Ghirotti, C. Chiorboli, M. Ravaglia, M. Garavelli and F. Scandola, *J. Am. Chem. Soc.*, 2008, **130**, 7286–7299; b) V. Aubert, V. Guerchais, E. Ishow, K. Hoang-Thi, I. Ledoux, K. Nakatani and H. Le Bozec, *Angew. Chem. Int. Ed.,* 2008, **47**, 577–580; c) M. N. Roberts, C.-J. Carling, J. K. Nagle, N. R. Branda and M. O. Wolf, *J. Am. Chem. Soc.*, 2009, **131**, 16644–16645; d) M. N. Roberts, J. K. Nagle, M. B. Majewski, J. G. Finden, N. R. Branda and M. O. Wolf, *Inorg. Chem.*, 2011, **50**, 4956–4966; e) J. C.-H. Chan, W. H. Lam, H.-L. Wong, N. Zhu, W.-T. Wong and V. W.-W.

Yam, *J. Am. Chem. Soc.*, 2011, **133**, 12690–12705; f) L. Ordronneau, V. Aubert, R. Métivier, E. Ishow, J. Boixel, K. Nakatani, F. Ibersiene, D. Hammoutène, A. Boucekkine, H. Le Bozec and V. Guerchais, *Phys. Chem. Chem. Phys.,* 2012, **14**, 2599–2605.

31 a) H. A. Bent, *Chem. Rev.*, 1961, **61**, 275–311; b) C. C. Levin, *J. Am. Chem. Soc.*, 1975, **97**, 5649–5655; c) A. Muller, S. Otto and A. Roodt, *Dalton Trans.,* 2008, 650–657.

32 E. D. Glendening, C. R. Landis and F. Weinhold, *Wiley Interdiscip. Rev. Comput. Mol. Sci.,* 2012, **2**, 1–42.

33 R. K Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Solid State Nucl. Magn. Reson.*, 2002, **22**, 458–483.

34 M. Irie, T. Lifka, S. Kobatake and N. Kato, *J. Am. Chem. Soc.*, 2000, **122**, 4871–4876.

35 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16 (Revision B.01), Gaussian Inc., Pittsburgh, PA, 2016.

36 a) C. Lee, W. Yang and R. G. Parr, *J. Phys. Rev. B*, 1988, **37**, 785–789; b) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206; c) A. D. Becke, *Chem. Phys.*, 1993, **98**, 5648–5652.

37 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *Chem. Phys.,* 2010, **132**, 154104.

38 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

39 a) W. J. Hehre, R. Ditchfield and J. A. Pople, *Chem. Phys.,* 2003, **56**, 2257–2261; b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *Chem. Phys.,* 1982, **77**, 3654–3665.

40 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chem. Acc.*, 1990, **77**, 123–141.

41 A.W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111–114.

42 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

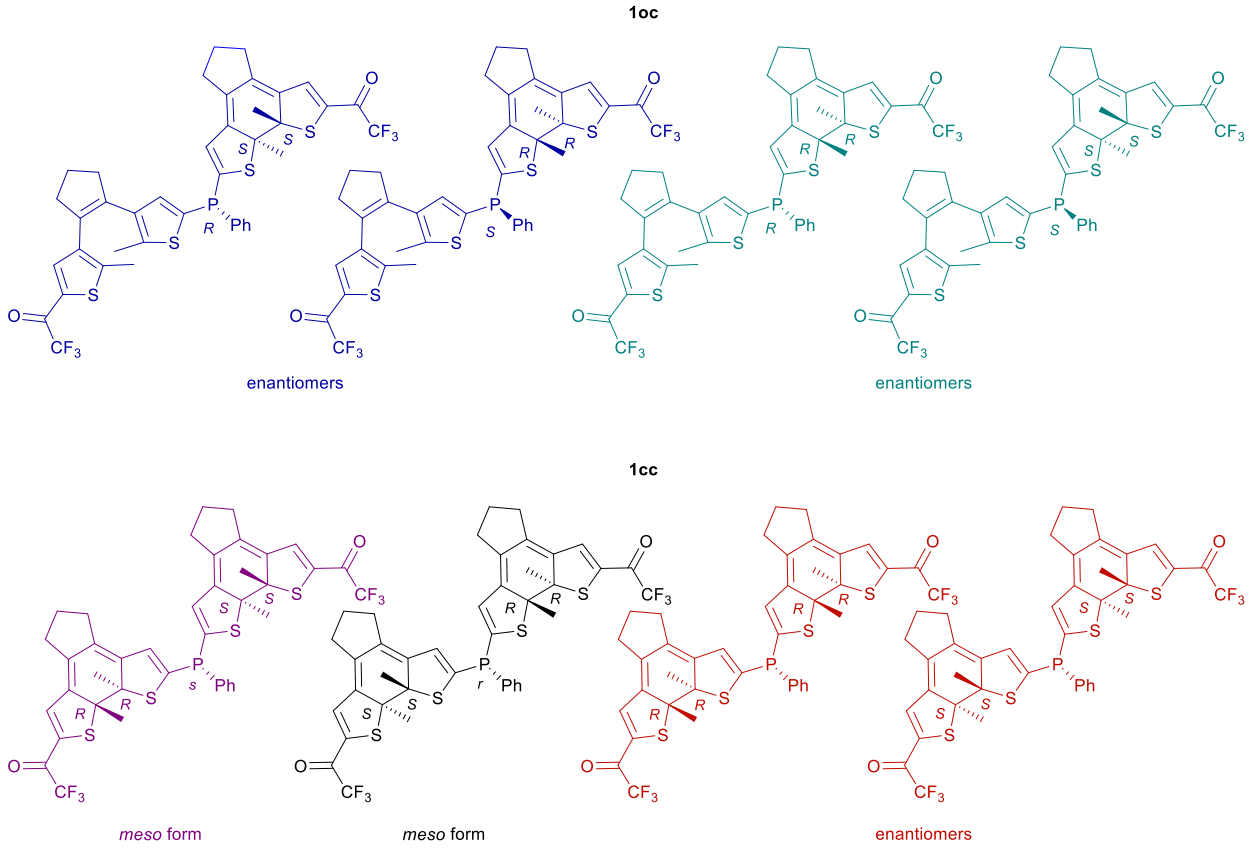
43 E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold, *NBO Version 3.1*.

44 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51–57.

45 R. S. Sánchez, R. Gras-Charles, J. L. Bourdelande, G. Guirado and J. Hernando, *J. Phys. Chem. C*, 2012, **116**, 7164–7172.

3. 6. Supporting information

3. 6. 1. Experimental photochemical properties of ligand 1 and complex 4



Scheme S1 – Possible stereoisomers of ligand **1** in the **oc** and **cc** states.

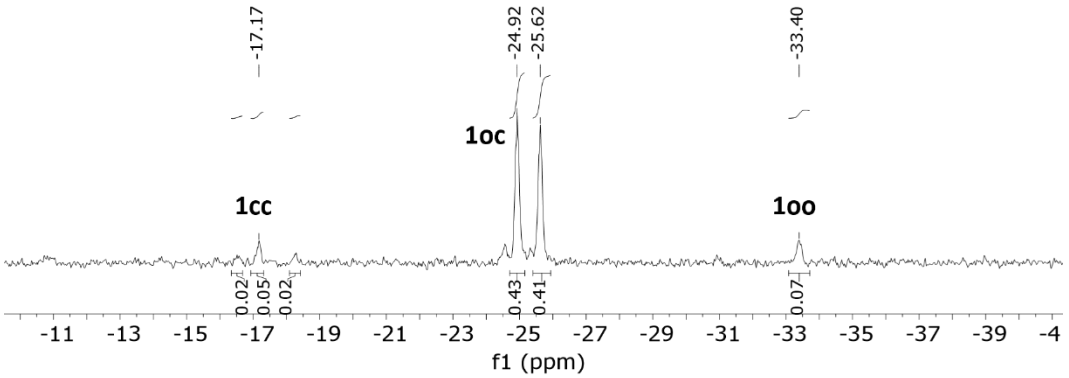


Figure S1 – ^{31}P NMR spectrum (toluene-d_8, 162 MHz) of the PSS@365 nm of **1**, where partial DTE photocyclization produces a mixture of **oo**, **oc** and **cc** isomers. The different signals detected for **oc** and **cc** isomers arise from the stereoisomers shown in Scheme S1.

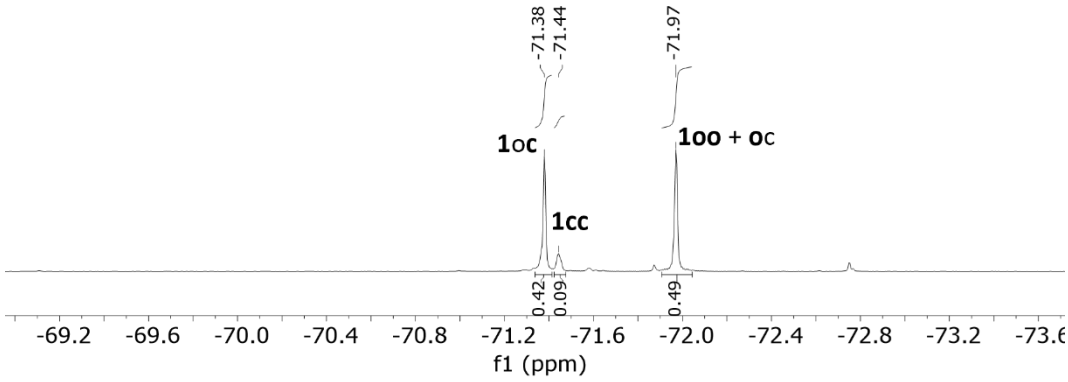


Figure S2 – 19F NMR spectrum (toluene-d_8, 282 MHz) of the PSS@365 nm of **1**, where partial DTE photocyclization produces a mixture of **oo**, **oc** and **cc** isomers. Labels oc and oc are used to identify the 19F NMR signals of the trifluoromethyl ketone group attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

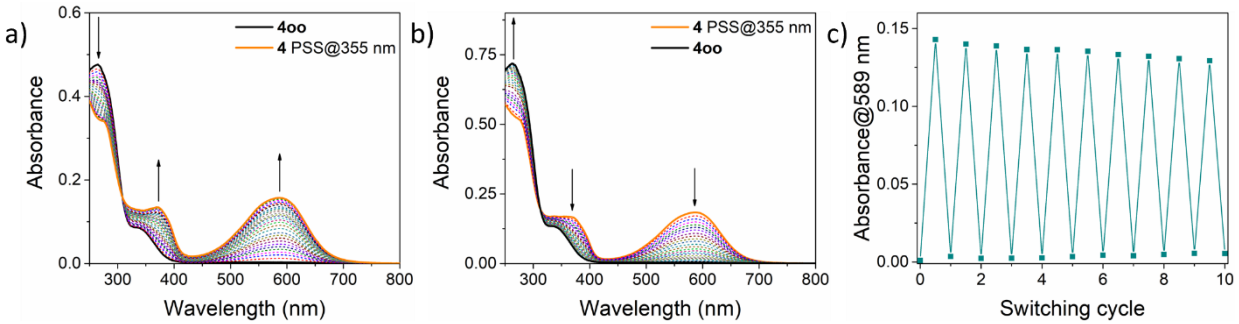


Figure S3 – Photochemical properties of complex **4** in cyclohexane solution. a) Variation of the UV-vis absorption spectrum of **4oo** (c = 1.29·10^{-5} M) upon 355 nm irradiation until a photostationary state is obtained (PSS@355 nm). b) Variation of the UV-vis spectrum of the PSS@355 nm of complex **4** (c = 1.98·10^{-5} M) upon 532 nm irradiation until the initial **4oo** isomer is recovered. c) Variation of the absorbance at the spectral maximum of the ring-closed isomer band of compound **4** (λ_{abs} = 589 nm, c = 2.23·10^{-5} M) upon 10 consecutive photoswitching cycles (λ_{exc} = 365 or 520 nm).

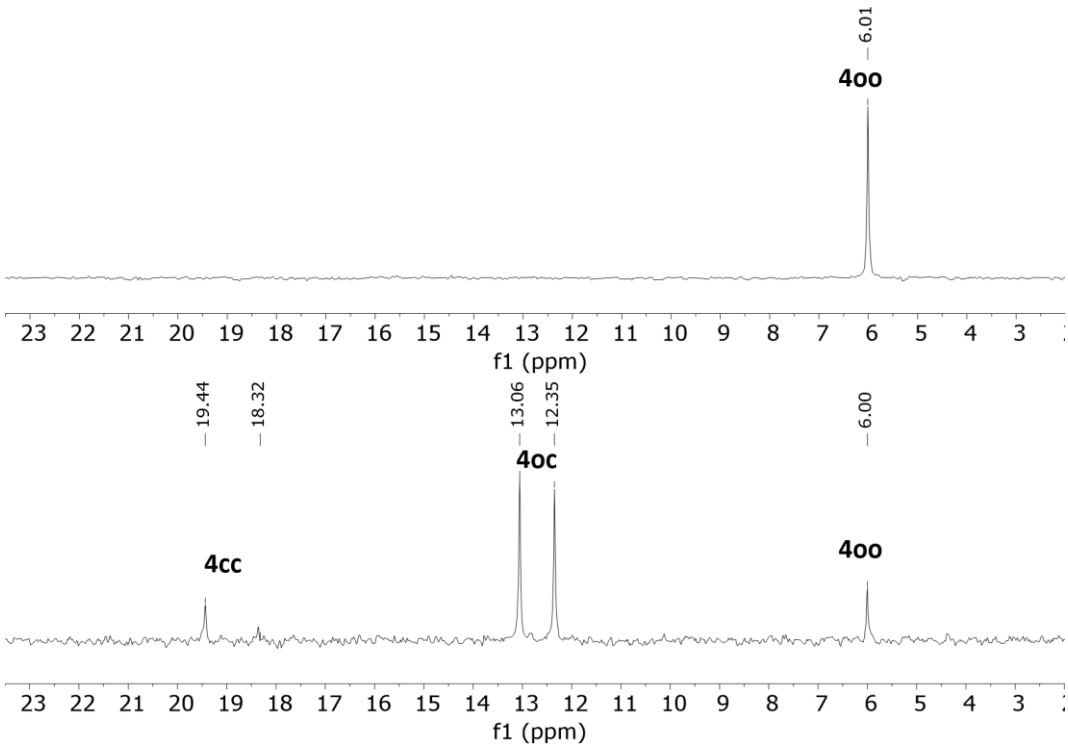


Figure S4 – $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of complex **4oo** (top) and the PSS@365 nm (bottom), where partial DTE photocyclization produces a mixture of **oo**, **oc** and **cc** isomers. The different signals observed for the **oc** and **cc** isomers arise from the distinct stereoisomers produced during photocyclization, which are analogous to those shown for ligand **1** in Scheme S1.

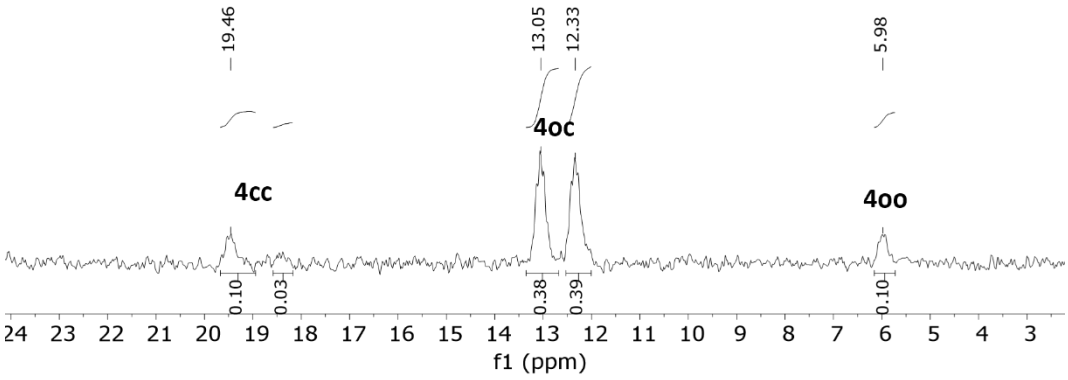


Figure S5 – ^{31}P NMR spectrum (toluene-d_8, 162 MHz) of the PSS@365 nm of complex **4**, where partial DTE photocyclization produces a mixture of **oo**, **oc** and **cc** isomers. The different signals observed for the **oc** and **cc** isomers arise from the distinct stereoisomers produced during photocyclization, which are analogous to those shown for ligand **1** in Scheme S1.

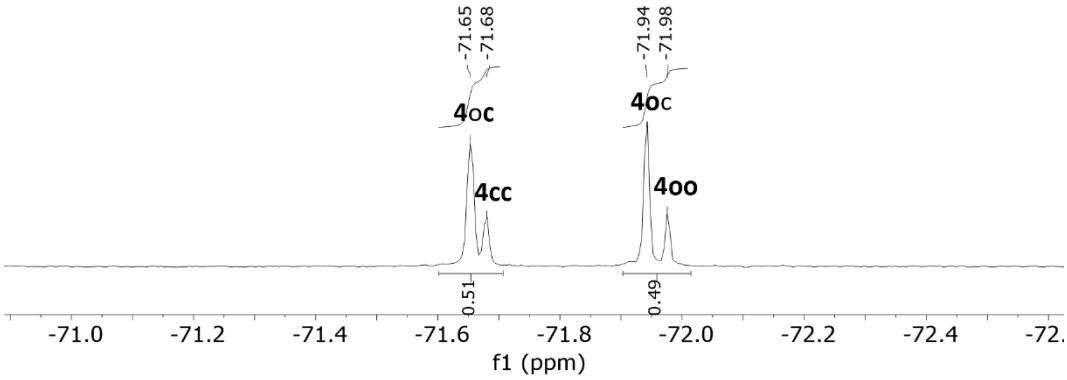


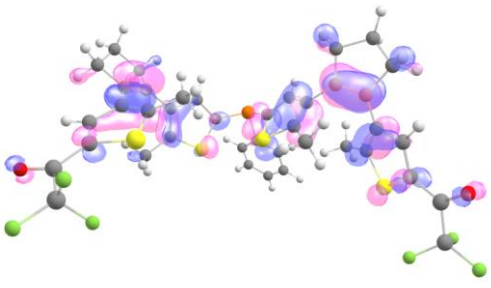
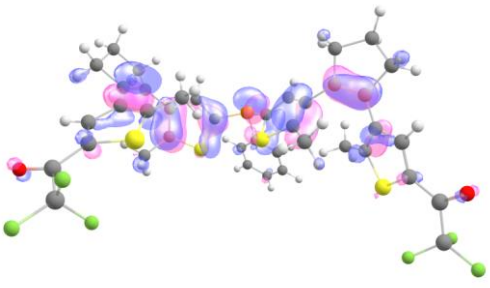
Figure S6 – ^{19}F NMR spectrum (toluene-d_8, 376 MHz) of the PSS@365 nm of complex **4**, where partial DTE photocyclization produces a mixture of **oo**, **oc** and **cc** isomers. Labels **o**c and o**c** are used to identify the ^{19}F NMR signals of the trifluoromethyl ketone group attached to the ring-open and ring-closed units of the **oc** isomer, respectively.

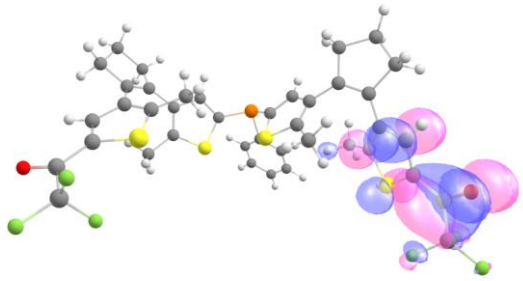
3. 6. 2. DFT calculations of the optical properties of the ligand 1 and complex 4

The optimized structures of ligands in their ground state exhibit distinctive geometric alterations during the isomerization process. Notably, the distance between the reactive carbons changes from 3.48 Å in the open state to 1.54 Å in the closed state, consistent with previously reported findings. For the ring-open state DTEs only photocyclizable antiparallel conformation was considered.

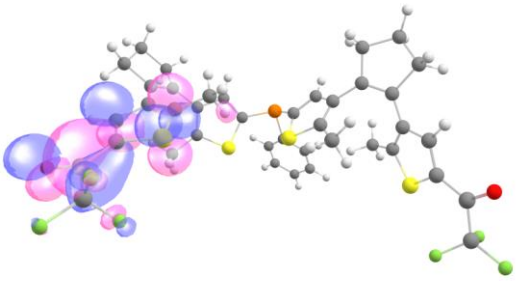
3. 6. 2. 1 Frontier molecular orbitals

Table S1. Selected frontier molecular orbitals of the **oo**, **oc** and **cc** forms of ligand **1** and complex **4**.

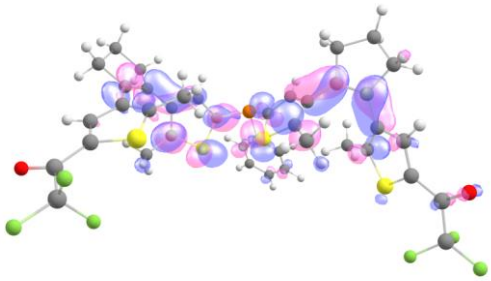
1oo	
	
HOMO-1	HOMO



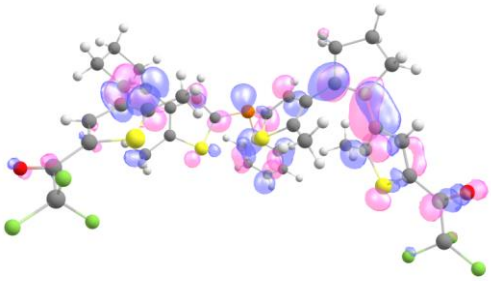
LUMO



LUMO+1

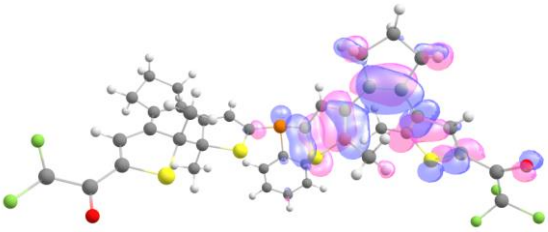


LUMO+3

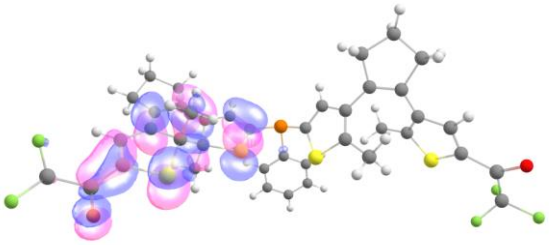


LUMO+4

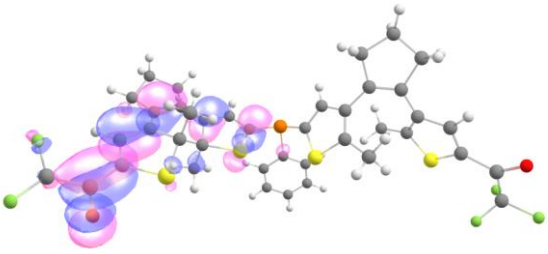
1oc



HOMO-1



HOMO



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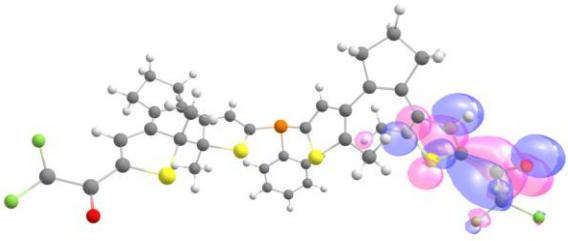

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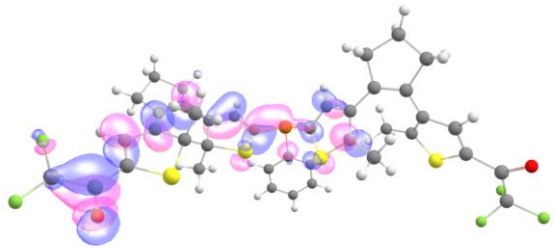

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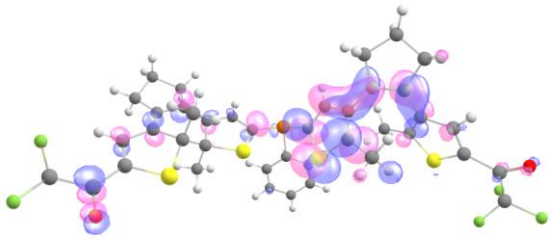
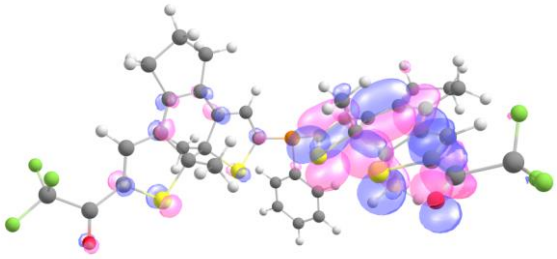


LUMO+3

1cc



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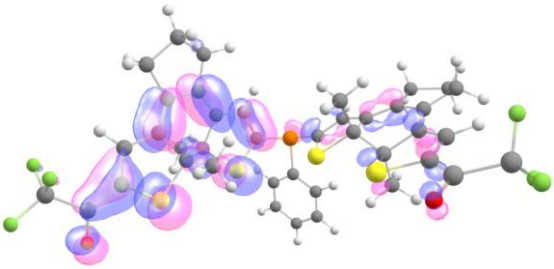

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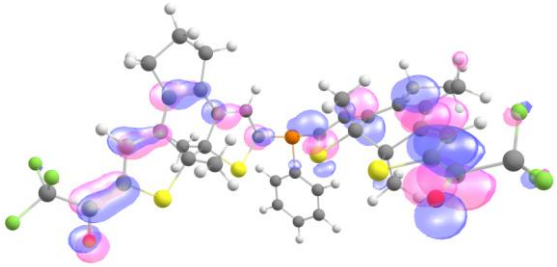

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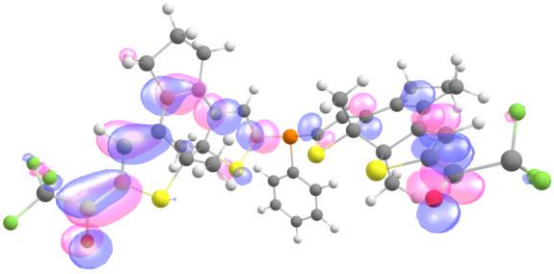

LUMO+1

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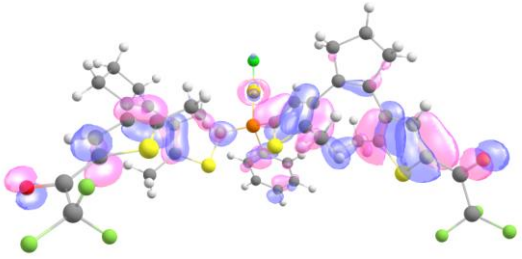

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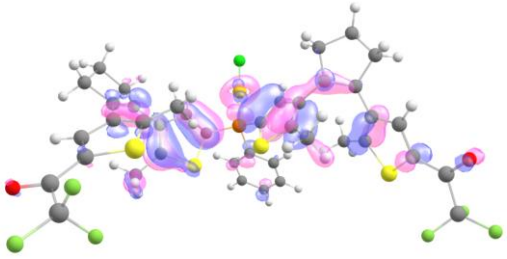

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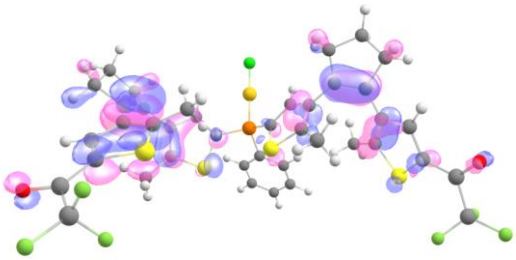

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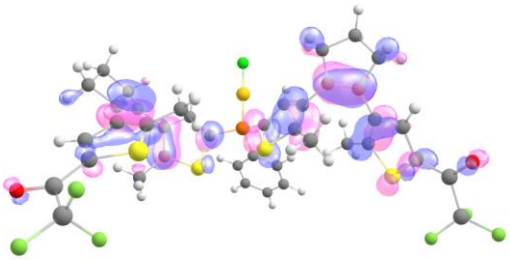

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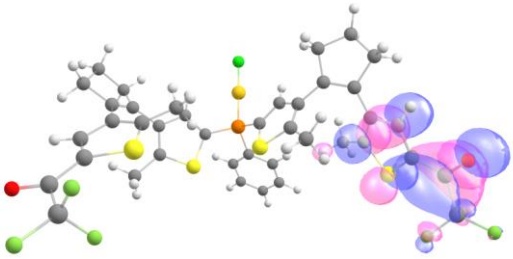

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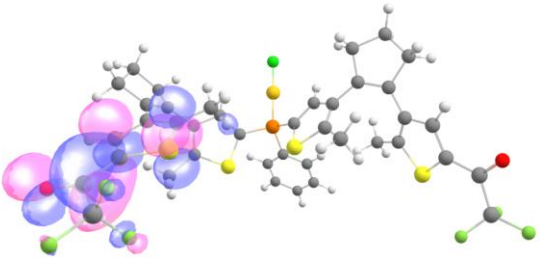

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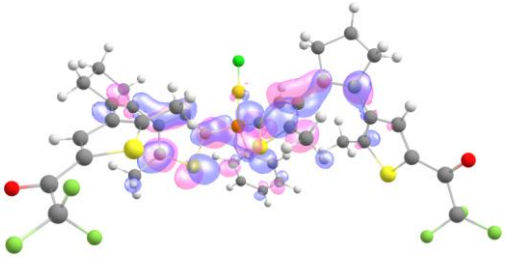

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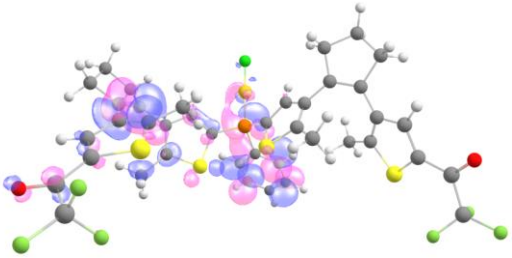

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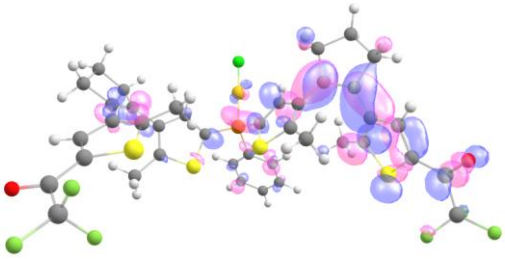

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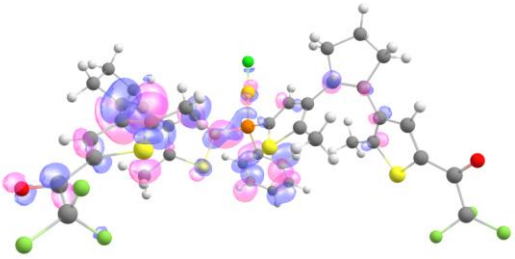

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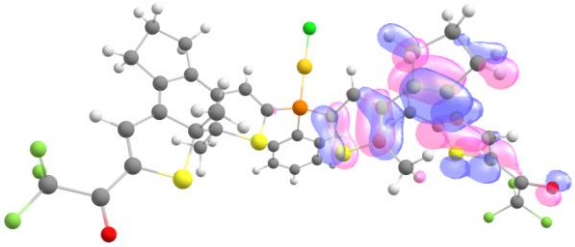
4oc



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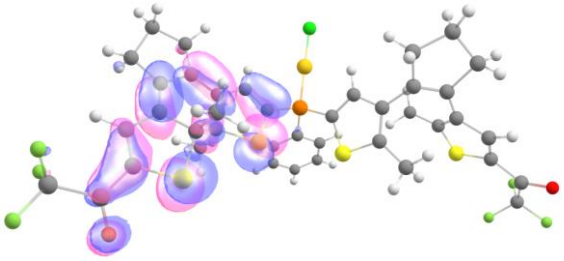

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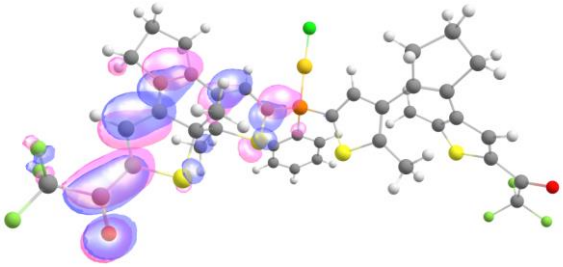

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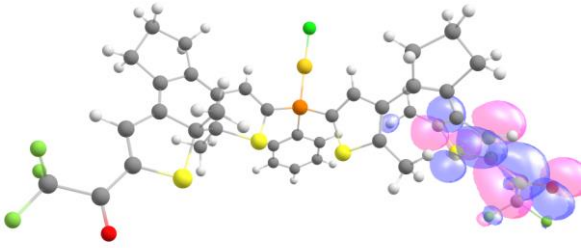

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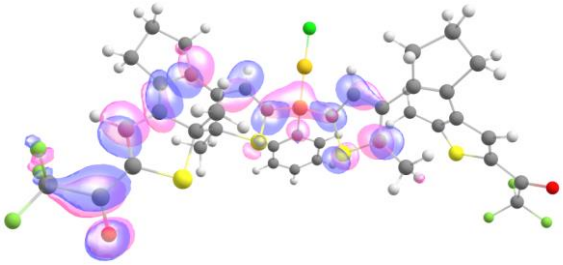

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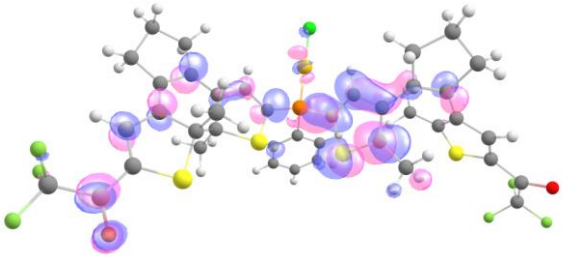
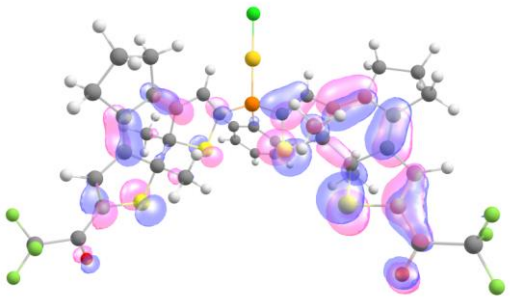


LUMO+3

4cc



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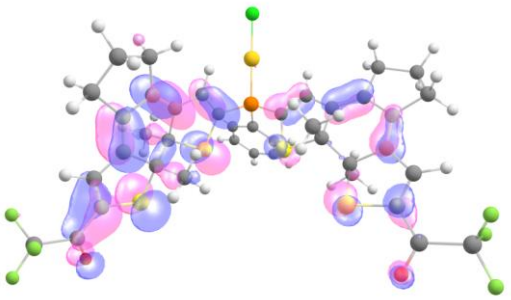

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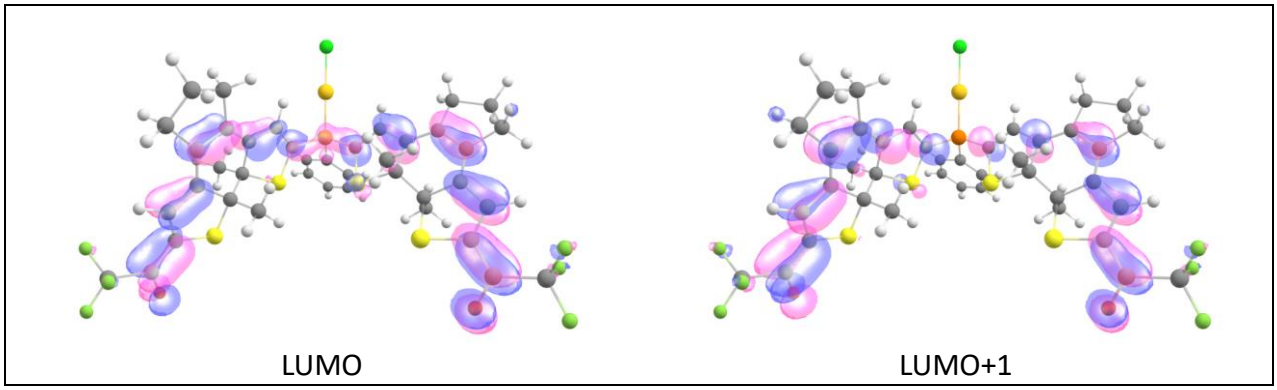

3. 6. 2. 2 Vertical transitions

Table S2. Calculated absorption wavelengths (λ), oscillator strengths (*f*) and assigned transitions for singlet state ligand **1** and complex **4** in toluene within the 250-800 nm range.

	λ (nm)	*f*	Assigned transition
1oo	317	0.1294	H-1 – L (56.5%), H – L (25.4%), H-3 – L (4.5%), H-2 – L (3.5%), H-14 – L (3.3%)
	312	0.1659	H – L+1 (46.4%), H-1 – L+1 (27.4%), H-2 – L+1 (14.2%), H-13 – L+1 (3.3%), H-4 – L+1 (2.7%)
	272	0.2008	H – L+2 (22.1%), H-4 – L+1 (12.9%), H-6 – L (9.8%), H-1 – L+3 (8.4%), H-3 – L (6.5%), H-6 – L+1 (5.8%), H-5 – L+1 (5.7%), H-7 – L (5.3%), H – L+1 (4.6%), H-5 – L (3.4%)
	270	0.5507	H-6 – L (22.1%), H-7 – L (12.6%), H-3 – L (11.7 %), H-4 – L+1 (7.8%), H-5 – L (6.9%), H – L+2 (6.5%), H-9 – L (5.1%), H – L+3 (4.9%), H-6 – L+1 (3.7%), H-5 – L+1 (3.2%), H – L+1 (2.0%)
	253	0.2924	H-2 – L+2 (34.9%), H-1 – L+3 (21.4%), H – L+4 (16.3%), H – L+3 (5.0%), H – L+5 (3.0%), H-1 – L+5 (2.4%)
1oc	568	0.3676	H – L (96.6%)
	368	0.2175	H-2 – L (61.3%), H-3 – L (29.7%), H – L+2 (2.3%)
	316	0.1605	H – L+1 (65.4%), H – L+2 (4.3%), H-1 – L (4.2%), H-3 – L+1 (4.0%), H-2 – L+1 (3.5%), H-3 – L (3.4%), H-12 – L+1 (3.2%), H-2 – L (2.4%)
	270	0.4423	H-5 – L+1 (44.2%), H-6 – L+1 (16.4%), H-4 – L+1 (10.3%), H-1 – L+3 (8.6%), H-7 – L+1 (8.3%), H-1 – L+1 (2.3%), H-3 – L+1 (2.0%)
1cc	597	0.3322	H – L (39.3%), H – L+1 (31.9%), H-1 – L+1 (14.0%), H-1 – L (11.4%)
	559	0.3949	H-1 – L (61.7%), H – L+1 (31.7%), H-1 – L+1 (3.0%)
	368	0.1822	H-3 – L (59.4%), H-2 – L+1 (22.0%), H-3 – L+1 (3.8%), H-4 – L (3.0%), H-4 – L+1 (2.0%)
	312	0.1483	H-1 – L+2 (55.0%), H – L+3 (17.4%), H-1 – L+3 (11.4%), H-4 – L (2.6%)
	281	0.1038	H – L+7 (24.7%), H-7 – L (19.4%), H – L+4 (8.6%), H – L+5 (5.9%), H – L+6 (4.2%), H-1 – L+7 (3.0%), H-6 – L (2.8%), H-7 – L+1 (2.6%), H-3 – L+1 (2.6%), H – L+3 (2.1%)
4oo	309	0.1042	H-15 – L+1 (42.3%), H – L+1 (23.4%), H-1 – L+1 (20.3%)
	269	0.4372	H-1 – L+2 (14.6%), H-5 – L (13.4%), H-3 – L (12.4%), H – L+3 (12.4%), H-4 – L (11.8%), H-4 – L+1 (8.0%), H-3 – L+1 (7.1%), H-2 – L (2.8%)
	264	0.2343	H-1 – L+2 (30.1%), H – L+3 (20.6%), H-4 – L+1 (8.9%), H-3 – L+1 (5.6%), H-5 – L (5.3%), H-3 – L (3.8%), H-4 – L (3.5%)
	560	0.3713	H – L (97%)

4oc	366	0.2097	H-2 – L (90.4%), H – L+2 (2.6%)
	317	0.1234	H – L+2 (75.7%), H – L+3 (11.8%), H-2 – L (2.9%)
	268	0.3919	H-4 – L+1 (49.5%), H-1 – L+3 (13.4%), H-3 – L+1 (10.8%), H-1 – L+2 (7.0%), H-3 – L (3.4%), H-6 – L+1 (2.1%)
4cc	587	0.3089	H – L (53.6%), H-1 – L+1 (23.0%), H – L+1 (15.2%), H-1 – L (5.1%)
	552	0.4254	H-1 – L (57.0%), H – L+1 (37.0%), H-1 – L+1 (2.7%)
	365	0.1805	H-3 – L (58.8%), H-2 – L+1 (24.9%), H-3 – L+1 (5.6%)
	314	0.1157	H-1 – L+2 (45.4%), H – L+3 (24.8%), H-1 – L+3 (14.2%), H-3 – L (2.7%)
	278	0.3306	H-9 – L (39.2%), H-8 – L+1 (20.8%), H-4 – L (5.5%), H-3 – L (5.0%), H-3 – L+2 (4.2%), H-5 – L+1 (2.1%)

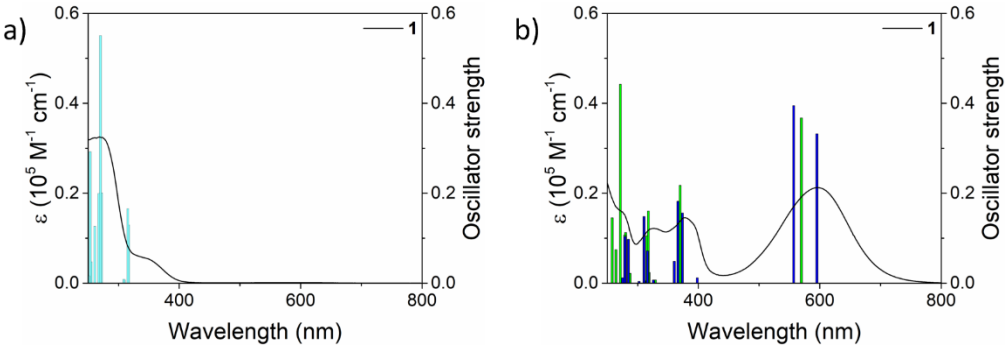

Figure S7 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for **1** in toluene: a) **oo**; b) **oc** (green bars) and **cc** (blue bars).

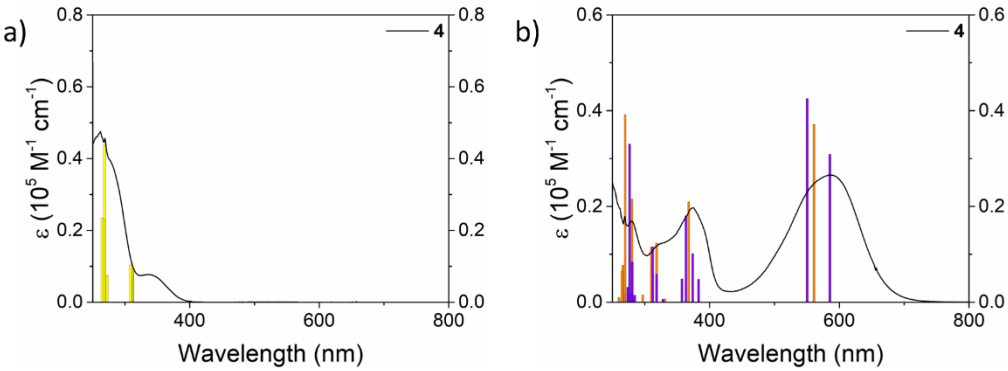

Figure S8 – Experimental absorption spectra (shown as lines) and vertical transitions computed (shown as bars) for **4** in toluene: a) **oo**; b) **oc** (orange bars) and **cc** (violet bars).

3. 6. 3. NMR spectra of the reported compounds

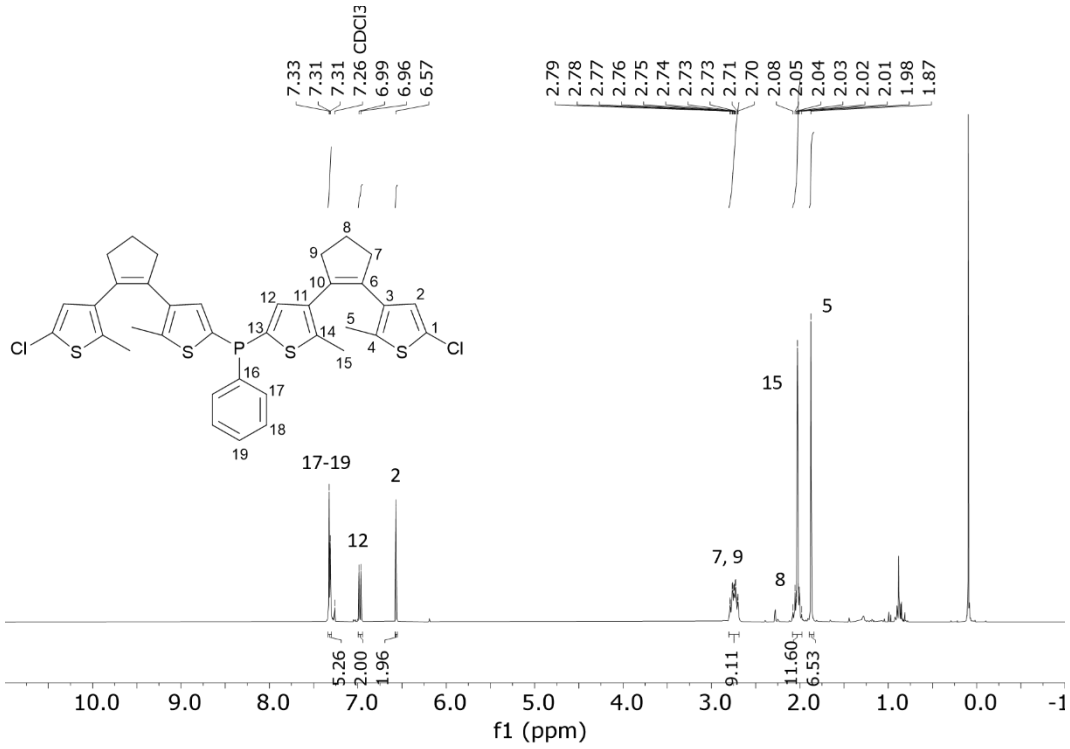

Figure S9 – ^{1}H NMR spectrum (300 MHz) of **3** in $CDCl_3$ recorded at 25 °C.

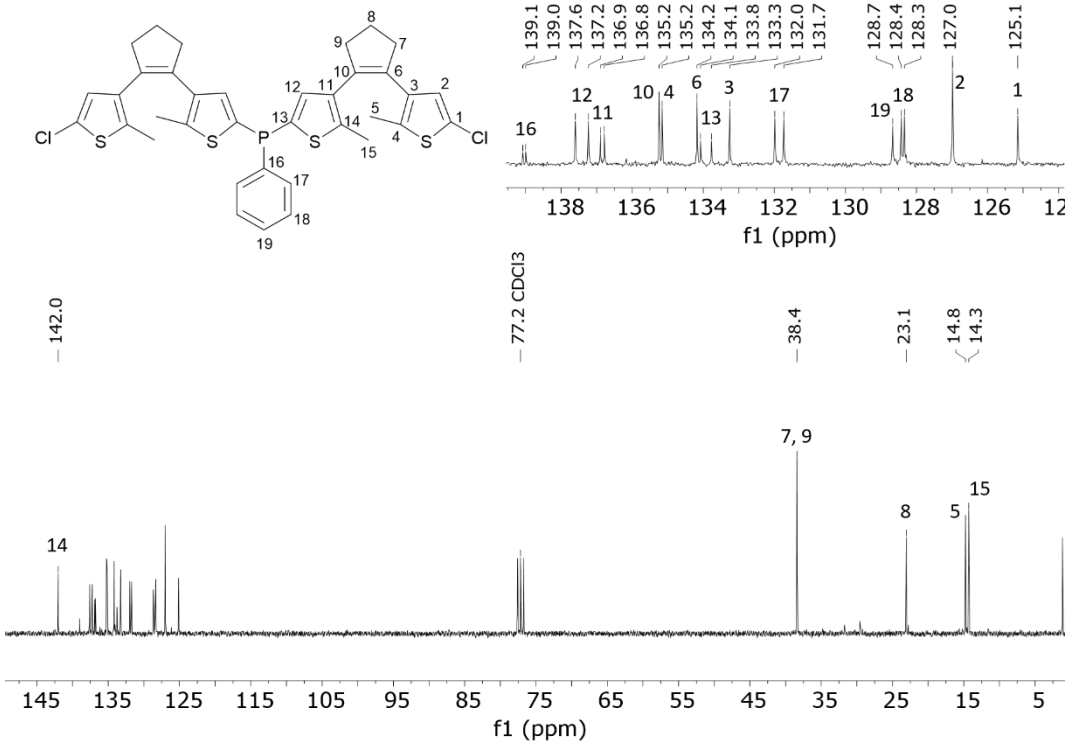

Figure S10 – $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of **3** in $CDCl_3$ recorded at 25 °C.

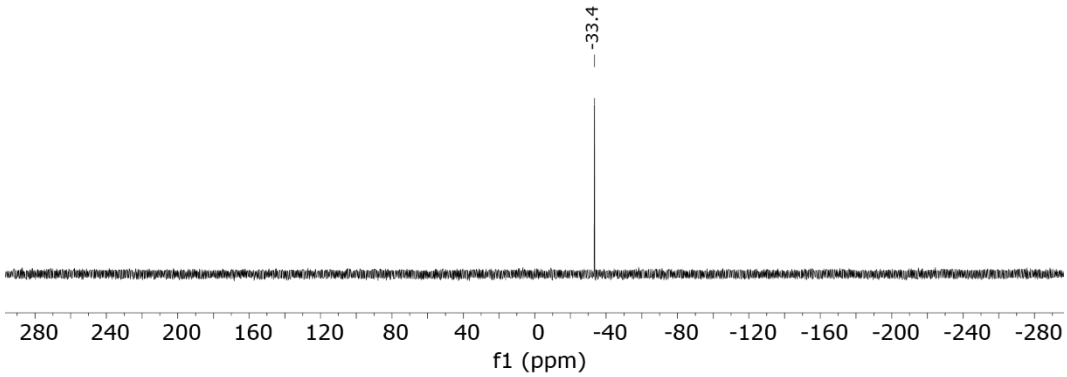

Figure S11 – $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz) of **3** in $CDCl_3$ recorded at 25 °C.

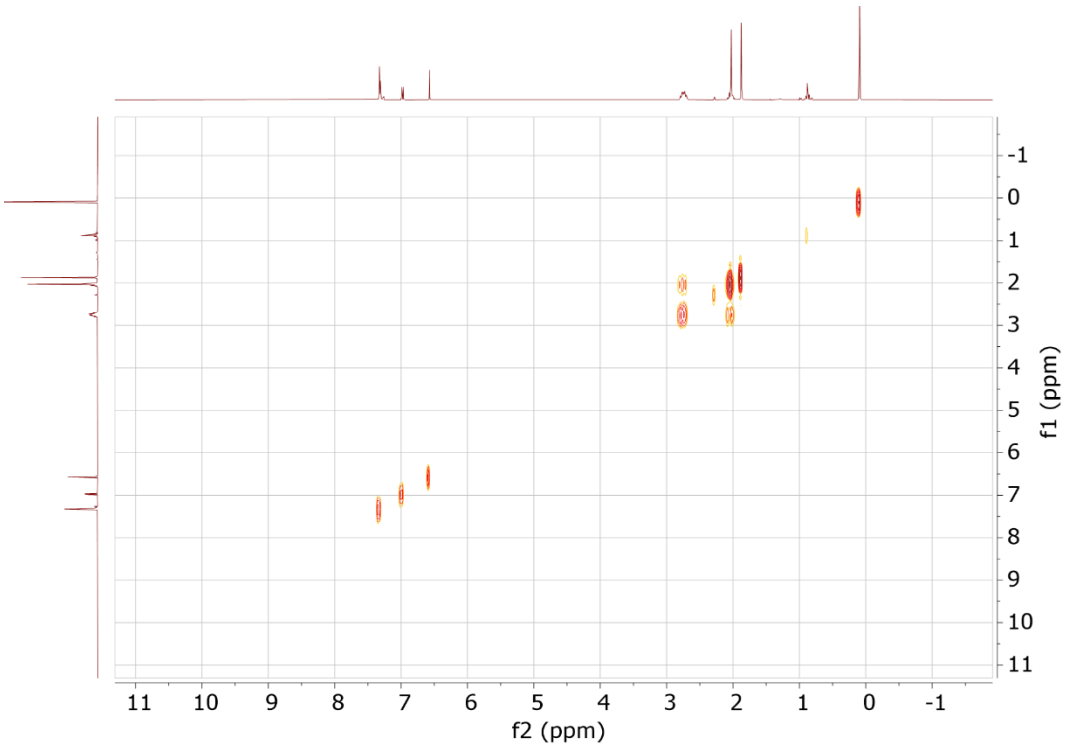

Figure S12 – ^{1}H-^{1}H COSY spectrum of **3** in $CDCl_3$ recorded at 25 °C.

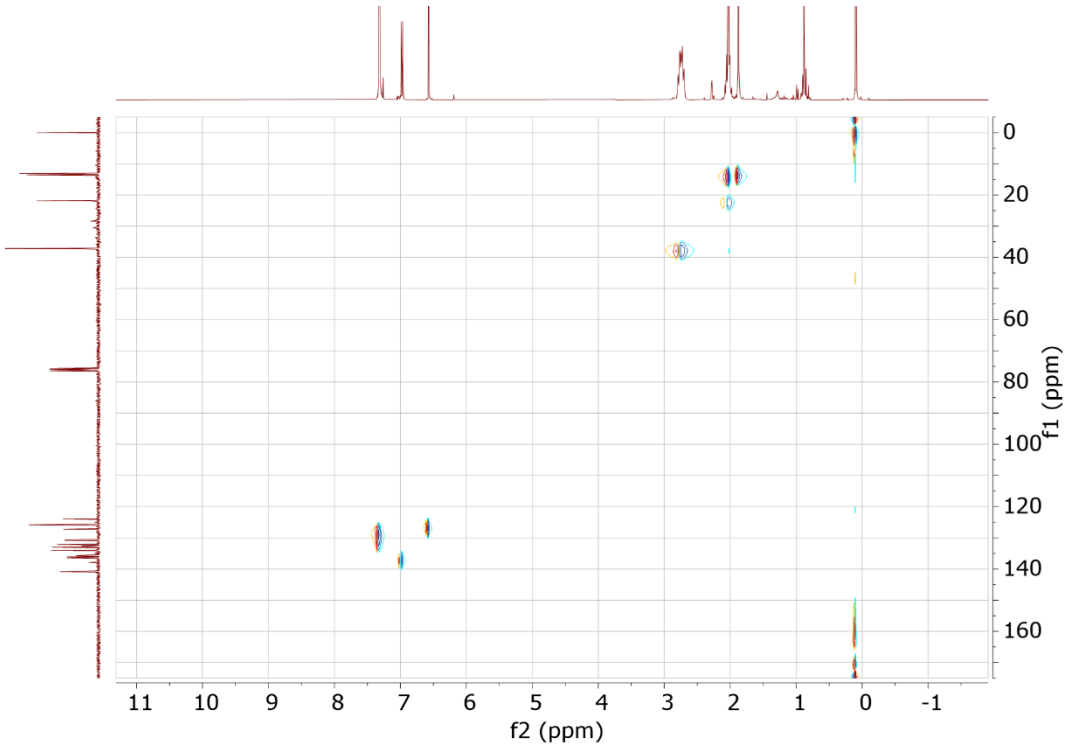

Figure S13 – ^{1}H-^{13}C HSQC spectrum of **3** in $CDCl_3$ recorded at 25 °C.

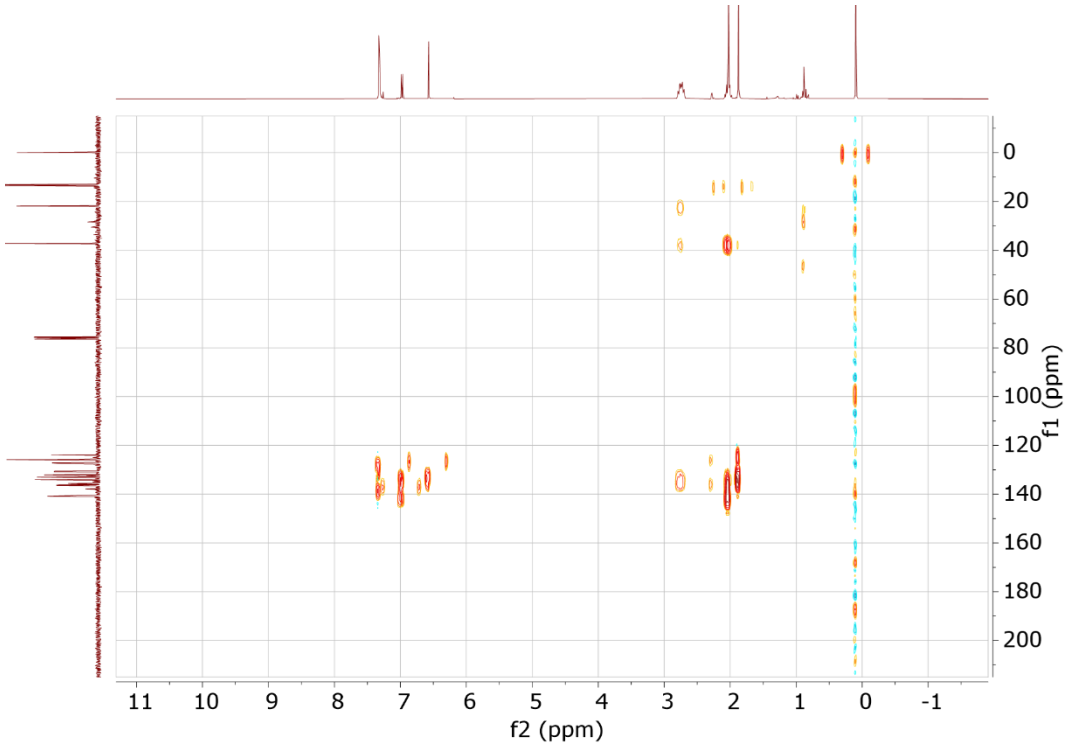

Figure S14 – ^{1}H-^{13}C HMBC spectrum of **3** in $CDCl_3$ recorded at 25 °C.

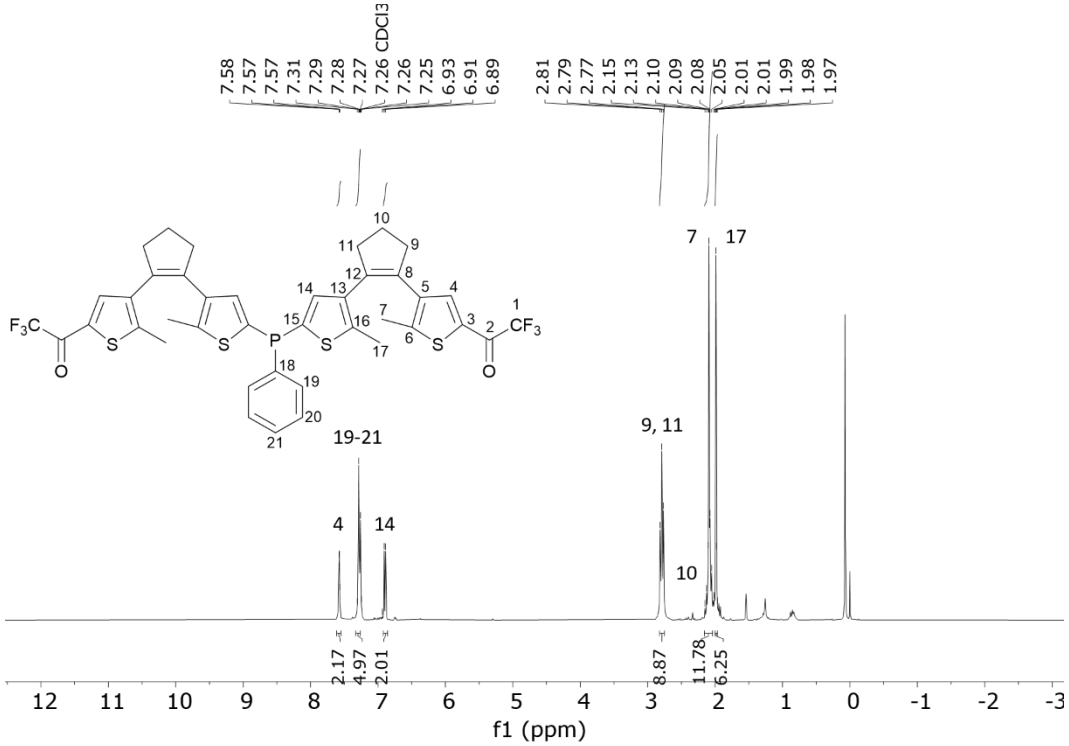

Figure S15 – ^{1}H NMR spectrum (300 MHz) of **1oo** in $CDCl_3$ recorded at 25 °C.

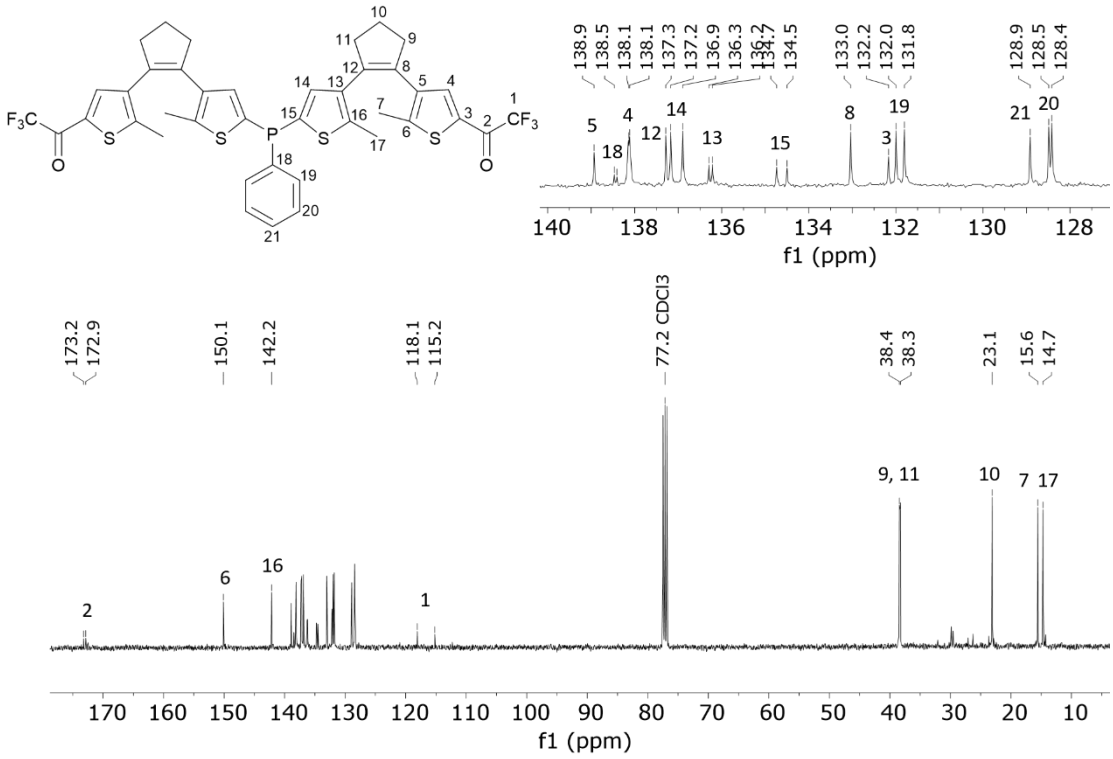

Figure S16 – $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **1oo** in $CDCl_3$ recorded at 25 °C.

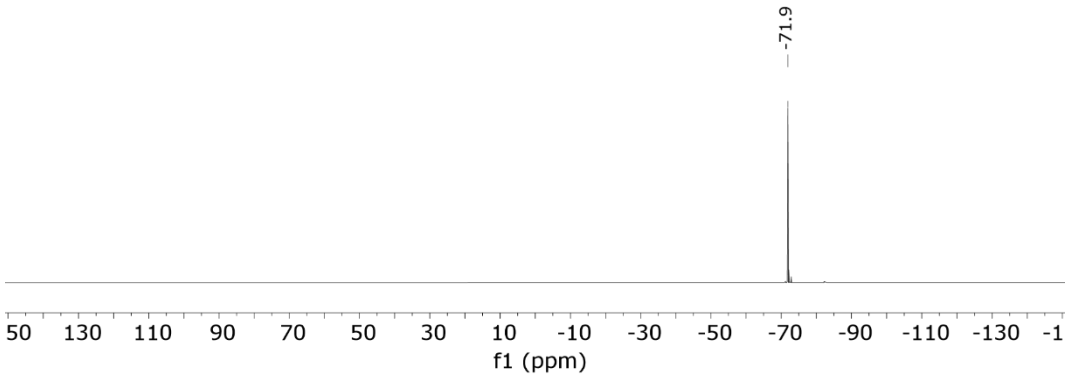

Figure S17 – ^{19}F NMR spectrum (376 MHz) of **1oo** in $CDCl_3$ recorded at 25 °C.

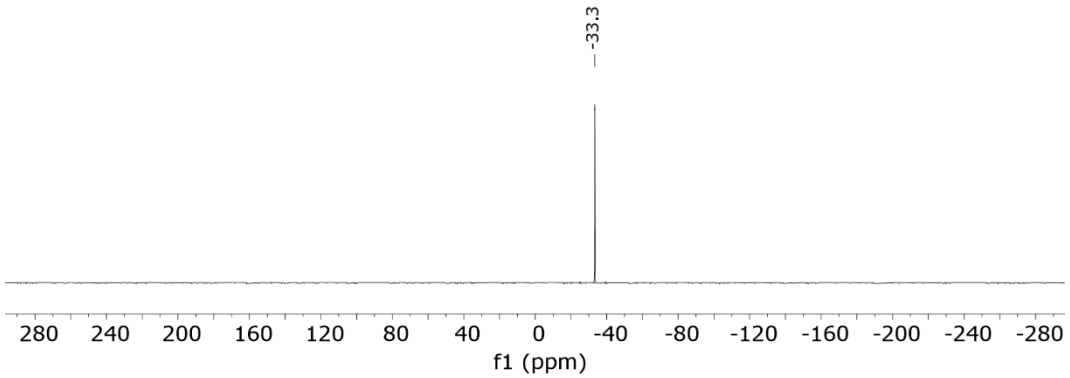

Figure S18 – $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz) of **1oo** in $CDCl_3$ recorded at 25 °C.

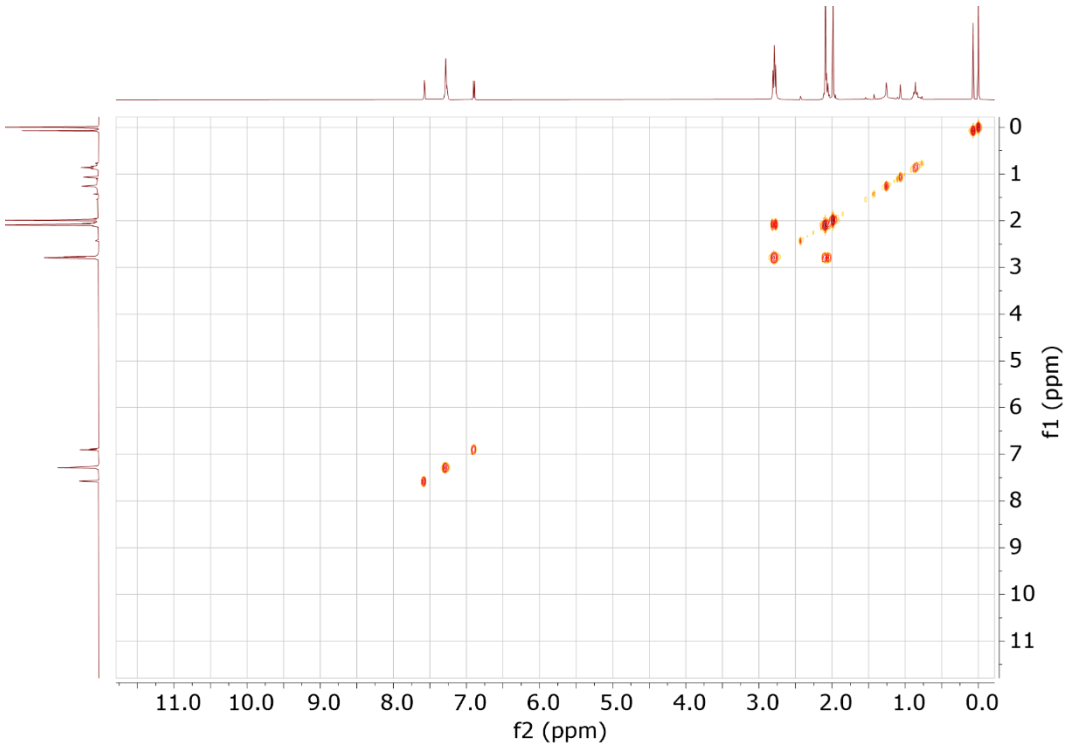

Figure S19 – ^{1}H-^{1}H COSY spectrum of **1oo** in $CDCl_3$ recorded at 25 °C.

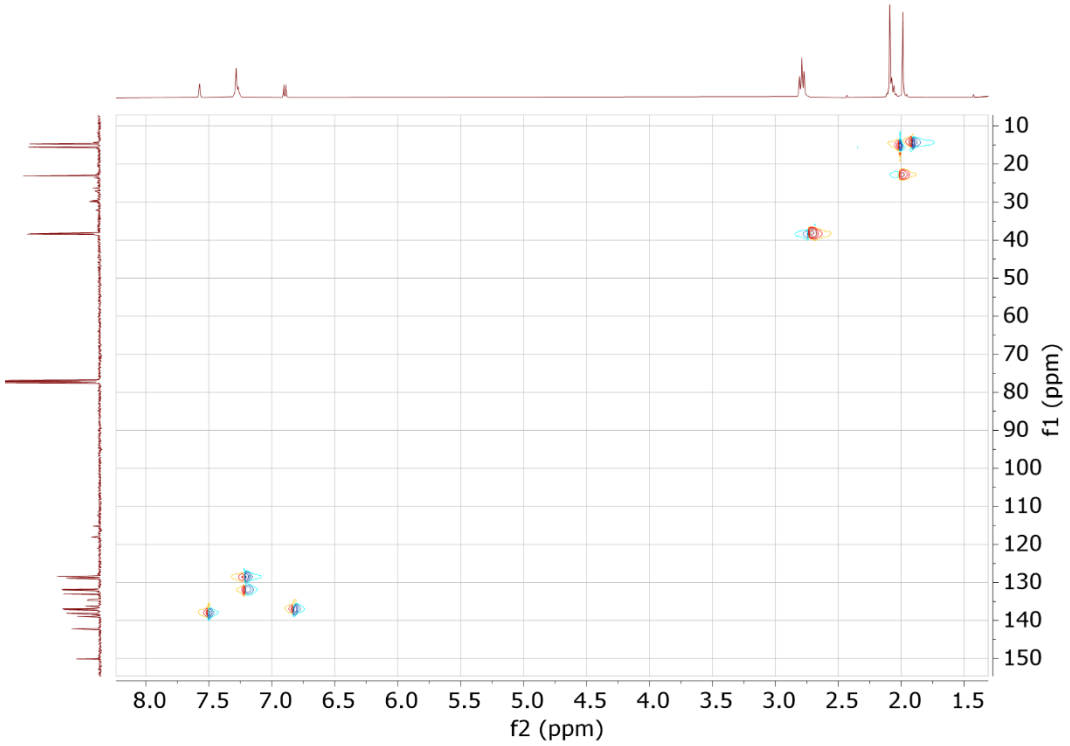

Figure S20 – ^{1}H-^{13}C HSQC spectrum of **1oo** in $CDCl_3$ recorded at 25 °C.

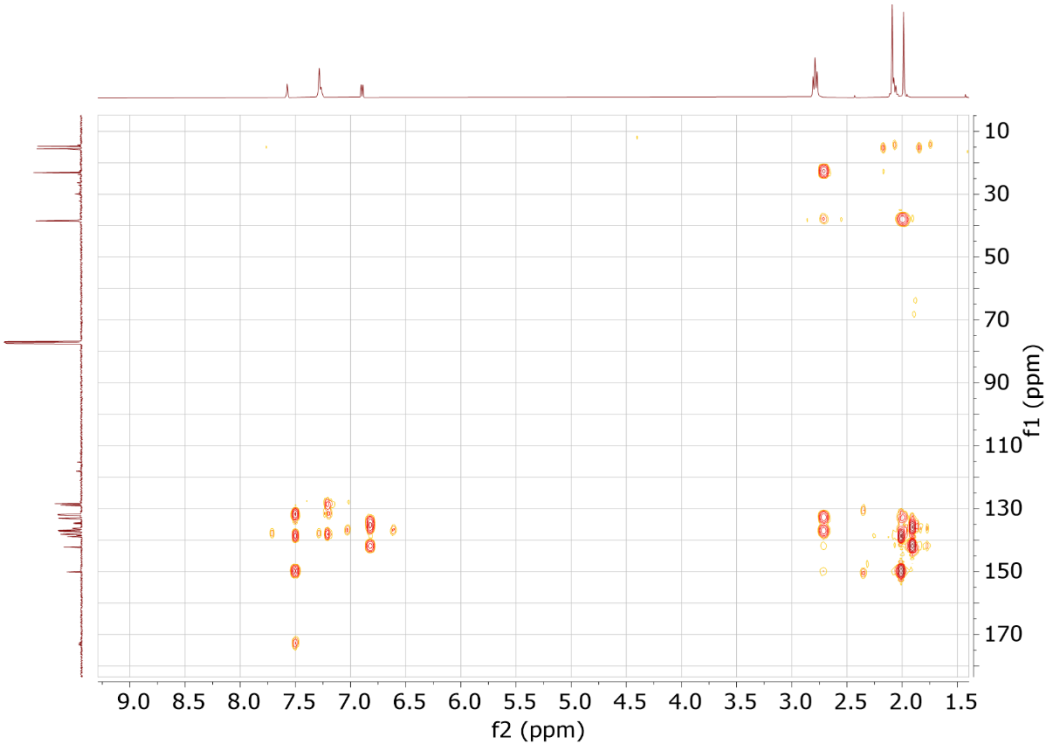

Figure S21 – ^{1}H-^{13}C HMBC spectrum of **1oo** in $CDCl_3$ recorded at 25 °C.

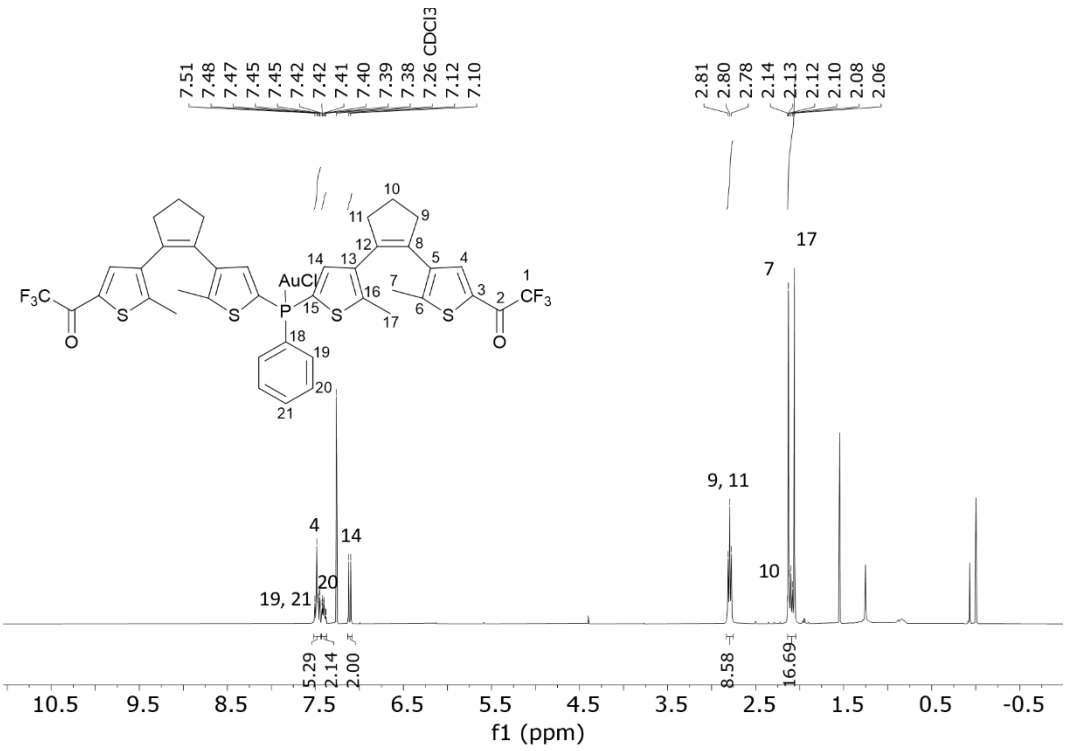

Figure S22 – ^{1}H NMR spectrum (400 MHz) of **4oo** in $CDCl_3$ recorded at 25 °C.

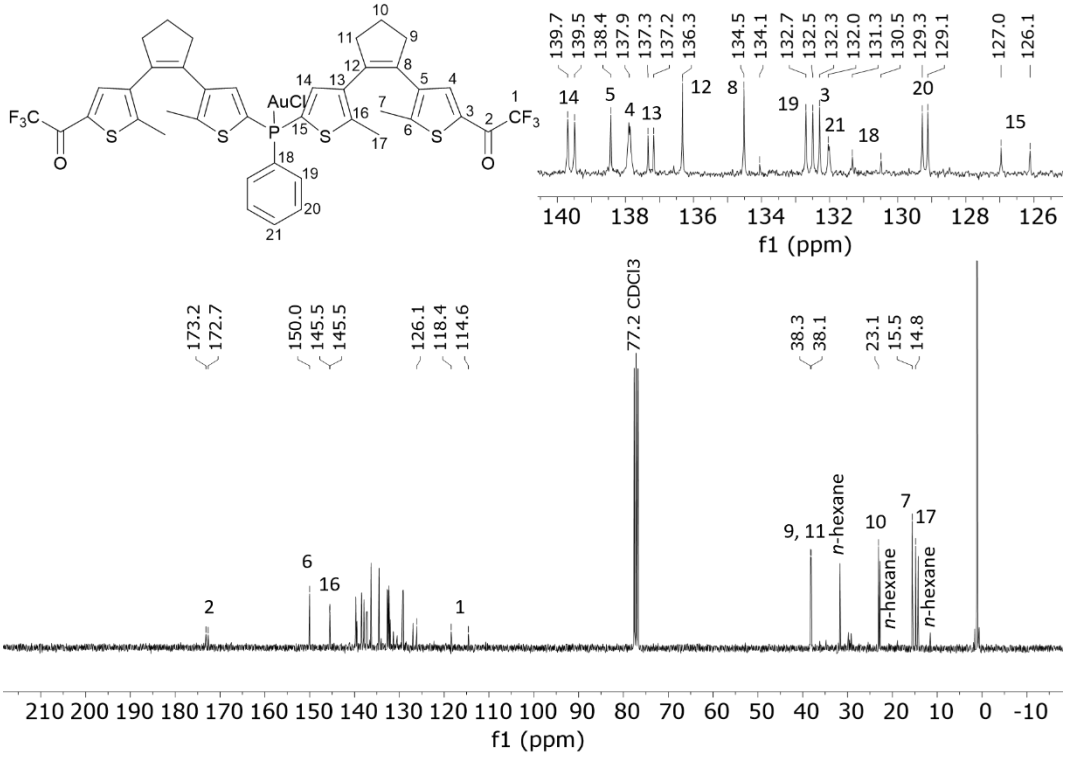

Figure S23 – $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of **4oo** in $CDCl_3$ recorded at 25 °C.

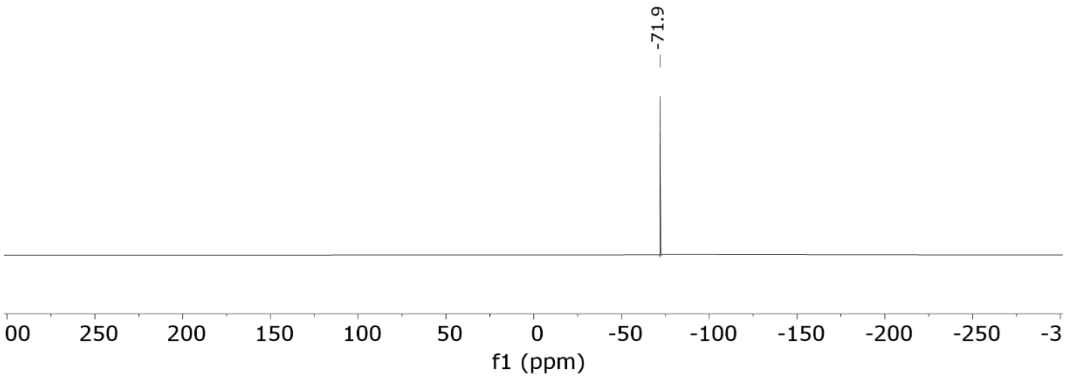

Figure S24 – ^{19}F NMR spectrum (376 MHz) of **4oo** in $CDCl_3$ recorded at 25 °C.

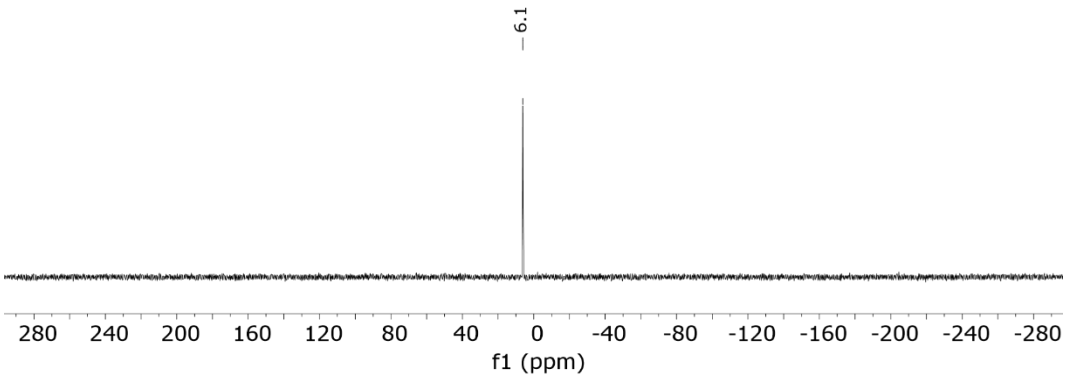

Figure S25 – $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of **4oo** in $CDCl_3$ recorded at 25 °C.

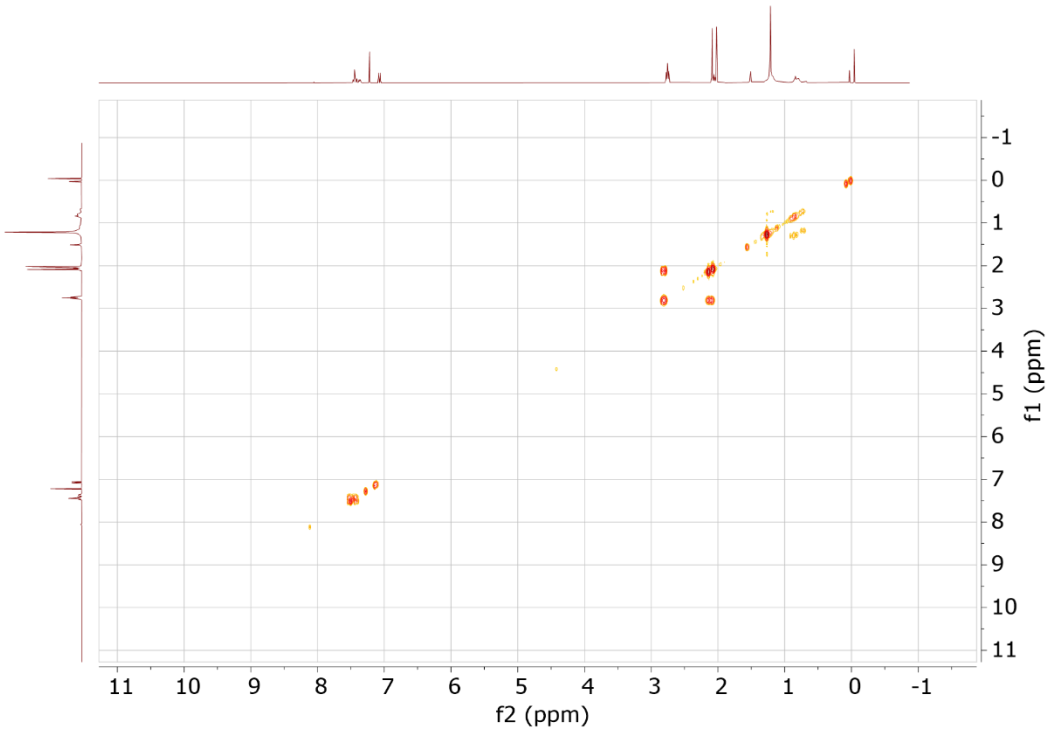

Figure S26 – ^1H-^1H COSY spectrum of **4oo** in $CDCl_3$ recorded at 25 °C.

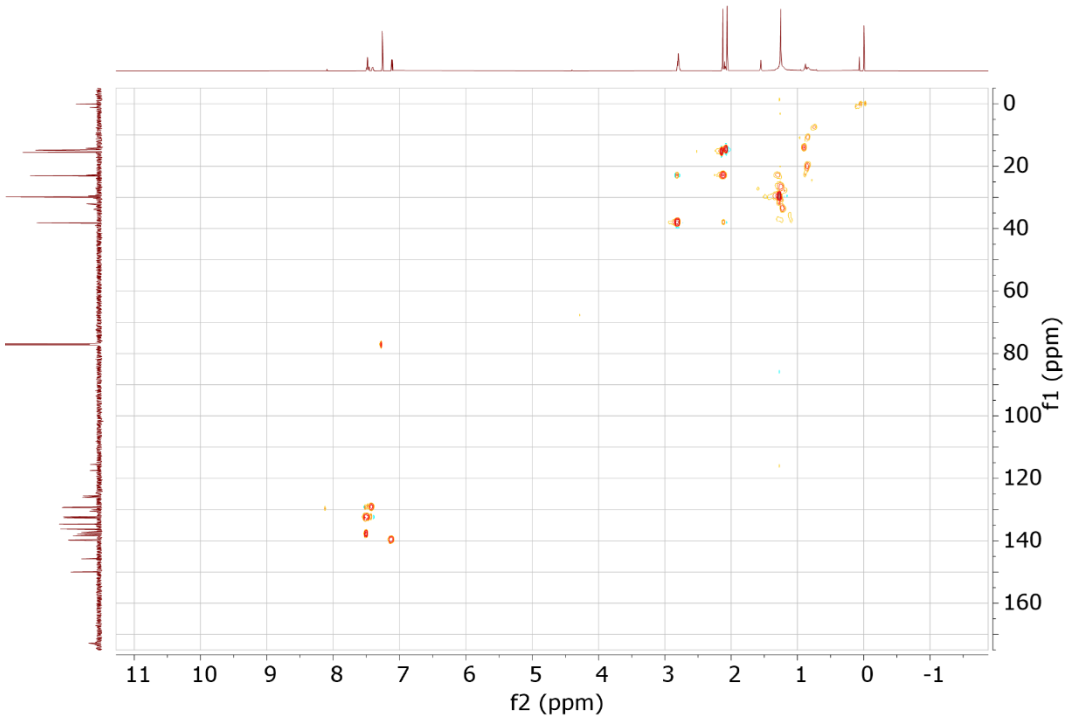

Figure S27 – ^{1}H-^{13}C HSQC spectrum of **4oo** in $CDCl_3$ recorded at 25 °C.

Preface to Chapter 4

Aiming to explore geometrical effects to achieve light-induced modulation of catalytic activity, the use of diazocine-based phosphine ligands was envisioned in Chapter 4. This molecular concept was validated through computational calculations, identifying 1,10-disubstituted diazocine-based bisphosphines as the best candidates to achieve photomodulation of their coordination mode to metals – i.e., switching from mono- to bidentate coordination behavior upon *Z*/*E* photoisomerization of the diazocine core. Although various synthetic strategies were designed and implemented to prepare these diazocine derivatives, unfortunately, no successful results could be obtained. Further functionalization studies conducted on diazocines suggested that steric hindrance effects precluded late-stage derivatization of their positions 1 and 10 to afford the target diazocine-based bisphosphines.

Chapter 4

Exploring Photoswitchable Diazocine-Based Phosphine Ligands for Tailored Catalysis

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Manuscript

Abstract

The field of homogeneous catalysis has witnessed a surge of interest in the development of photoswitchable ligands, driven by the prospect of achieving spatiotemporal control over catalytic activity through light irradiation. To optimize the performance of these systems, herein we pioneered the use of diazocines as light-responsive scaffolds, with which we aimed to create photoswitchable phosphine ligands capable of exhibiting two distinct coordination modes in transition metal complexes upon Z/E photoisomerization. This molecular concept was validated by means of DFT calculations, which revealed that the introduction of phosphanyl groups to positions 1 and 10 of the diazocine core should allow reversible photoconversion from mono- to bidentate-coordination mode in palladium(II) complexes. However, during the synthesis of the computationally designed ligand, formidable challenges were encountered, ascribed to the steric hindrance effects that severely hamper the reactivity of positions 1 and 10 in the diazocine framework. In this work we describe our systematic efforts to synthesize the desired diazocine-based bisphosphine ligand, emphasizing the hurdles encountered, the strategies employed, and the lessons learned.

The author of this thesis designed the synthetic strategies, performed the synthesis of the compounds and their characterization and wrote the original text. Agustí Lledós performed the DFT

calculations. Jordi Hernando, Rosa María Sebastián, and Evamarie Hey-Hawkins have supervised and administered the project. The original draft of the manuscript was proof-read by all co-authors and changed according to their suggestions.

4. 1. Introduction

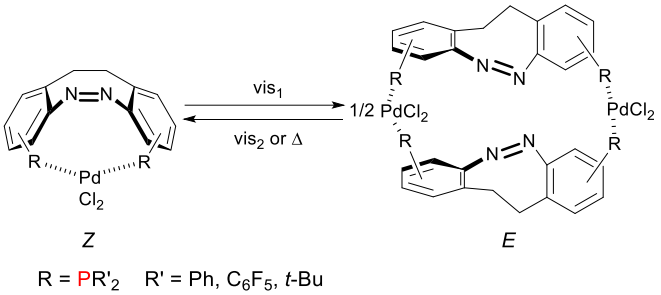
The control of homogeneous catalysis under light irradiation enables the *in situ* manipulation of chemical reactivity with spatiotemporal resolution in a remote and non-invasive manner. This strategy finds application in photocatalysis, photocaged catalysis, and photoswitchable catalysis, with the latter gaining increasing importance due to its capacity to reversibly modulate catalyst activity through photoisomerization between active and inactive states.[1]

In the field of metal catalysis, this goal has been pursued by incorporating azobenzene, stilbene, and diarylethene photoswitching moieties into ligand structure, which allows developing light-responsive catalysts capable of undergoing reversible structural transformations upon irradiation. The accompanying alteration of their stereoelectronic properties upon ligand photoisomerization induces changes in the catalytic activity. Among the different metal-binding ligands to which this approach can be applied, phosphorus ligands have emerged as very promising candidates for optically controlling catalytic activity through photoswitchable motifs.[2,3] This emphasis arises from the widespread use of phosphorus ligands in the creation of transition metal complexes for homogeneous catalysis.[4] However, the performance of photoisomerizable phosphorus ligands in photoswitchable catalysis is currently hampered by a series of limitations[3] – e.g., incomplete ligand photoisomerization efficiency[5] that can be even totally hindered upon metal complexation,[6] and insufficient stereoelectronic changes occurring upon photoswitching,[7] which eventually lead to partial or no light-modulation of the catalytic activity. Therefore, further pursuit of new families of photoswitchable phosphine ligands holds considerable appeal in this area. This is the main objective of this work, where for the first time the use of diazocines as photoswitchable units for the preparation of photoisomerizable phosphines was explored.

Among the variety of molecular photoswitches described in the literature, diazocines stand out due to their specific photochemical properties.[8,9] Although they also operate through the *Z*/*E* photoisomerization of N=N motifs, diazocines exhibit important differences relative to regular azobenzenes that arise from their strained cyclic structure. On the one hand, the most thermally stable configuration of diazocines is the *Z* isomer. As a result, they present a compact bent geometry in the dark where the substituents of both arene rings are in close proximity, which is in striking contrast with the preferred elongated structure of *E*-azobenzenes. On the other hand, because of the rather good separation between the n $\rightarrow$ π* absorption bands of both diazocine isomers, they can be fully photoisomerized with visible light: from the initial *Z* isomer to the *E* state by irradiation with violet-blue light (370 – 400 nm), while reverse photoswitching can be conducted through

illumination with green radiation (480 – 550 nm). These features, combined with their potentially high photoconversion efficiencies, *E* isomer thermal lifetimes, and fatigue resistance,[8] make diazocines very attractive light-responsive building blocks for the construction of photoswitchable phosphines for tailored catalysis.

To exploit the unique photoswitching properties of diazocines, we envisioned the preparation of bisphosphane ligands containing a diazocine core, whose geometrical alteration upon photoisomerization should result in variable binding modes to transition metals and, consequently, to diverse catalytic activities upon irradiation.[4,8–10] In particular, we devised that the two isomers of these phosphines should act as mono- or bidentate ligands forming transition metal complexes with photoswitchable catalytic performance (Scheme 4-1). To reach this ultimate goal, herein we report our progress in the design and synthesis of diazocine-based phosphines.



Scheme 4-1 – General structure of diazocine-based phosphine ligands exhibiting a varying coordination mode in Pd(II) complexes depending on their Z/E configuration.

4. 2. Results and discussion

4. 2. 1. Molecular design through computational calculations

Given the impact of the coordination mode of ligands on catalytic activity,[4,10,11] in this work our aim was to develop a diazocine-based bisphosphine ligand exhibiting variable coordinating capabilities upon irradiation. Because of the particular structures of diazocine isomers, it was anticipated that a bidentate complex could be formed with the *Z* isomer of the ligand, where the phosphanyl groups introduced in the two benzene rings should be in close proximity to each other; in contrast, the elongated geometry of the *E* isomer of the ligand should favor the formation of monodentate complexes (Scheme 4-1).

To test this hypothesis, we conducted DFT calculations on various diazocine structures bearing diphenylphosphanyl substituents at positions 1,10 (**i**, **ii**), 3,8 (**iii**, **iv**), and 4,7 (**v**, **vi**) of the diazocine scaffold (Figure 4-1a). The structural optimization of these compounds was performed using the B3LYP-D3/6,31G(d,p) level of theory in THF as a solvent (see the details in the experimental section). Analysis of the computed free ligand structures revealed that the 3,8-substituted isomer (**iii**, **iv**)

appears incapable of transitioning between different coordination modes upon *Z*/*E* diazocine isomerization (Figure 4-1b). This was attributed to the large distances found between the two phosphorus atoms in both isomers (7.17 Å in the *Z* isomer and 11.26 Å in the *E* isomer), making both of them unsuitable to act as bidentate ligands.[4,10] However, structures with phosphanyl substituents at 4,7 (**v**, **vi**) and 1,10 positions (**i**, **ii**) looked more promising, as the separation distances between these two groups were shorter and varied between 4.0 – 5.4 Å and 5.6 – 6.9 Å upon isomerization, respectively.

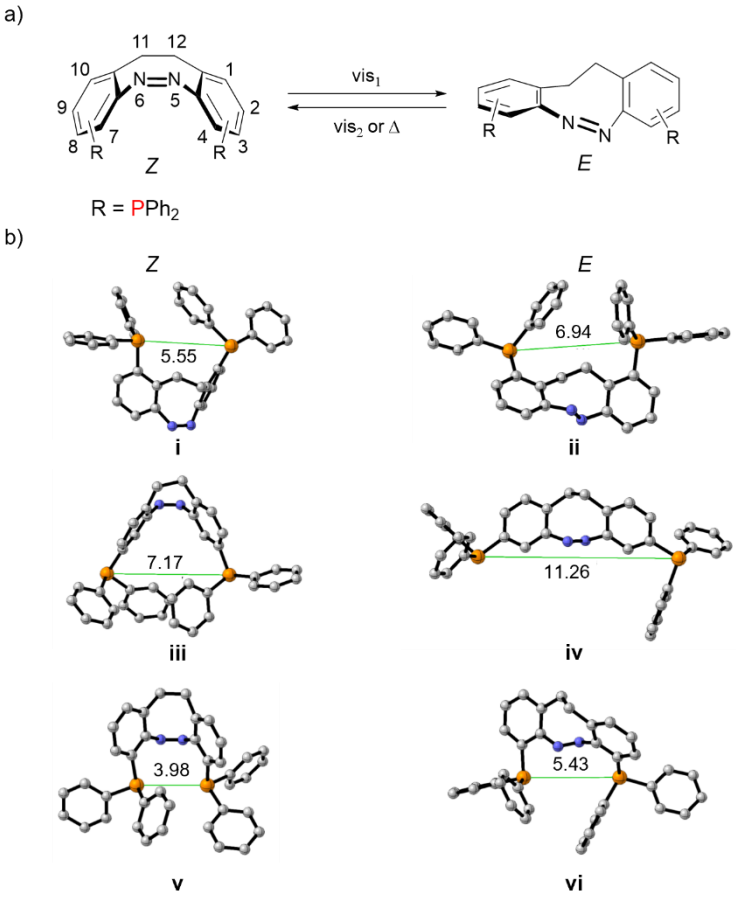


Figure 4-1 – *Z* and *E* configurations of bisphosphanyl-substituted diazocines. a) Diazocine photoisomerization, where the numbering used in the text to refer to the substituent positions is indicated. b) Calculated ligand structures with diphenylphosphanyl substituents at positions 1,10 (**i**, **ii**), 3,8 (**iii**, **iv**), and 4,7 (**v**, **vi**), where P-P distances are marked in green and given in Å.

Accordingly, the structures of the palladium(II) complexes of the 4,7- and 1,10-substituted diazocines were calculated, where the metal coordination sphere was completed with chloride ligands. In the case of the 4,7-substituted diazocine ligand (Figure 4-2a), bidentate coordination is possible in both *Z* and *E* configurations to yield complexes **vii** and **viii**, thereby failing to meet our criterion to achieve light-induced modulation of coordination mode. In contrast, the desired variation from monodentate to bidentate coordination was observed for the computed structures

of the *Z* and *E* complexes **ix** and **x** based on the 1,10-substituted ligand (Figure 4-2b). This prompted us to explore the generalization of this concept to two other types of phosphine ligands. In particular, we considered the introduction of strong electron-withdrawing diperfluorophenyl groups or strong electron-donating di-*tert*-butyl groups to the phosphorus atoms of the 1,10-substituted diazocine, which should allow different catalytic activity upon *Z*/*E* isomerization in a range of catalytic reactions.[4] In both cases, the resulting complexes **xi**, **xii** and **xiii**, **xiv** also showed a clear change in coordination mode upon photoisomerization according to calculations (Figure 4-2b). It must be noted that, for all the bidentate complex structures computed for 1,10-substituted diazocines, the arrangement of the ligands in a *trans* configuration around the metal center was preferred, as shown in Figure 4-2b. However, bidentate complexes formed with bis(diphenylphosphanyl)- and bis(diperfluorophenylphosphanyl)-diazocines in their *Z* configuration can also exist in a *cis* form, though they are less energetically favorable (21.4 and 18.1 kcal·mol^{-1} above the corresponding *trans* complexes, respectively) (**xv** and **xvi** in Figure S1 in the section §4.5). This is not the case for the bis(di-*tert*-butyl-phosphanyl)-substituted diazocine in its *Z* state, which cannot form a *cis* bidentate complex due to steric hindrance (**xvii** in Figure S1 in the section §4.5).

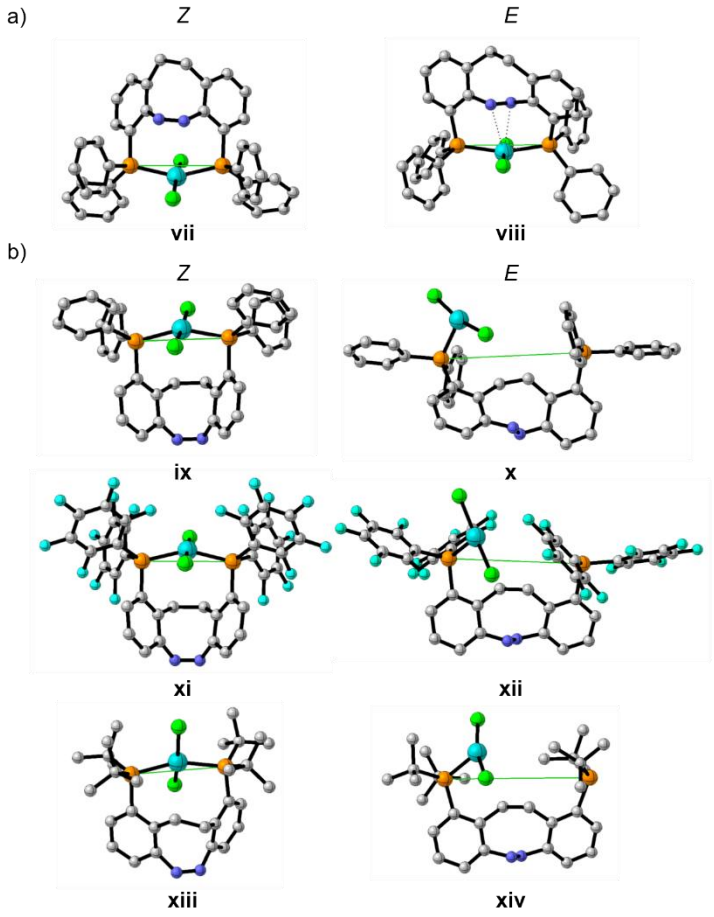


Figure 4-2 – Calculated structures of the palladium(II) *trans* complexes formed by: a) a 4,7-bis(diphenylphosphanyl)diazocine ligand (complexes **vii**-**viii**); and b) 1,10-bis(diphenylphosphanyl)diazocine (complexes **ix** and **x**), 1,10-bis(diperfluorophenylphosphanyl)diazocine (complexes **xi** and **xii**) and 1,10-bis(di-

tert-butyl-phosphanyl)diazocine (complexes **xiii** and **xiv**) ligands. The P-P distance is indicated in each case with a green line.

For the 1,10-substituted diazocine-based palladium(II) complexes, the change of the electron-donating ability of the phosphine ligand caused significant geometrical changes in the predicted structures, especially for the *Z* configuration. While P-Pd bonds remained quite similar, the ligand bite angle (∠P-Pd-P) and P-P distance increased with the increment of electron density on the phosphorus atom and the size enlargement of phosphorus substituents – i.e., from diperfluorophenyl- to diphenyl- and di-*tert*-butyl-substituted phosphines (Table 4-1). To estimate the bond energies of phosphines to palladium ($BE_{P\text{-}Pd}$), we calculated the energies of two additional separate structures: the free ligand and [$PdCl_2$] fragment. The Gibbs free energy was then determined as the difference between the energies of these two fragments and the complex. For the complexes with the diazocine ligand in the *E* configuration, phosphorus-palladium(II) binding energies followed the expected trend,[12] with the more electron-rich di-*tert*-butyl-substituted phosphine in complex **xiv** exhibiting the highest $BE_{P\text{-}Pd}$ value. Notably, this behavior was lost for the bidentate complexes made from *Z* diazocines, where the highest bond energy to palladium(II) was computed for complex **ix** bearing diphenyl-substituted phosphines. This result suggested that sterically bulkier *tert*-butyl groups in complex **xii** are in too close proximity, thereby precluding effective metal binding. In light of this conclusion and the rest of computed data, we identified the 1,10-substituted diazocine ligand **Diazo2P** bearing diphenylphosphanyl groups as the most promising compound to accomplish coordination mode modulation upon *Z*/*E* photoisomerization with light (Figure 4-3).

Table 4-1 – Properties computed for the palladium(II) complexes **ix** – **xiv** formed with 1,10-substituted diazocine ligands.[a]

Z	$BE_{P\text{-}Pd}$ (kcal·mol^{-1})	∠P-Pd^{II}-P (°)	P-Pd^{II} (Å)	P-P (Å)	*E*	$BE_{P\text{-}Pd}$ (kcal·mol^{-1})	P-Pd^{II} (Å)	P-P (Å)
ix	71.1	154.5	2.36	4.61	**x**	49.2	2.24	7.16
xi	59.5	152.8	2.34	4.54	**xii**	34.6	2.23	6.81
xiii	45.8	159.0	2.41	4.75	**xiv**	53.9	2.28	7.42

[a] Computed at the B3LYP-D3/6,31G(d,p) level in THF as a solvent.

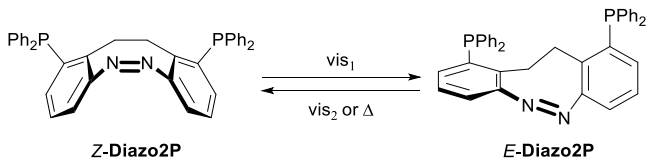


Figure 4-3 – *Z* and *E* configurations of targeted **Diazo2P** ligand.

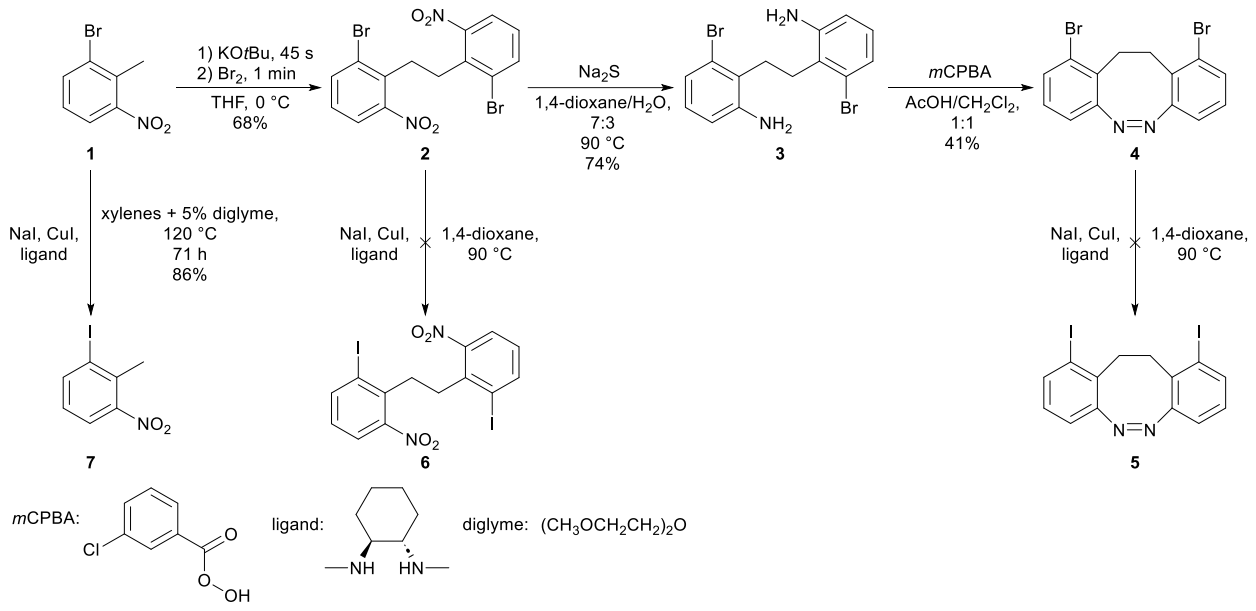
4. 2. 2. Synthetic progress toward diazocine-based bisphosphines

To date, three strategies towards diazocine synthesis have been developed: reductive cyclization, cascade C-N coupling, and oxidative cyclization.[13] Due to the superior yields and adaptability to various functional groups for subsequent late-stage derivatization,[14] the latter approach was selected in the present work to explore the preparation of the target 1,10-substituted diazocine-based bisphosphine **Diazo2P**. It is important to note that existing examples of diazocines with substituents at positions 1 and 10 are rare,[15] and functionalization of these positions generally leads to lower yields. To our knowledge, this is the first work where the introduction of phosphanyl groups to these positions is attempted.

To reach the desired goal, herein we considered two of the most common approaches used to introduce diphenylphosphanyl groups in arenes: the reaction of organometallic (organolithium or organomagnesium) reagents with halogenated phosphines, and transition metal-catalyzed C-P cross-coupling reactions.[16] In the first of these methods, organometallic reagents are generated through halogen-metal exchange reactions employing halogenated substrates, with aryl bromides and iodides exhibiting the fastest reaction rates.[17] As diazocines are bridged azobenzenes, one would anticipate their electronic properties and functional group tolerance to resemble those of azobenzenes, for which the electrophilic nature of the nitrogen-nitrogen double bond (N=N) has been well documented.[18–21] As a result, azobenzenes are susceptible to undergo reduction by the nucleophilic reagents required to promote halogen-metal exchange.[18–21] However, optimized conditions can be found for this type of reaction, as demonstrated by Marinetti's[5,22] and Kawashima's[23,24] groups that reported the preparation of azobenzene-based phosphines with yields up to 85% and 89%, respectively, through halogen-lithium exchange processes. Based on these precedents, the efficacy of halogen-metal exchange reactions on azobenzenes appears to be dependent on two main factors: (i) the use of iodinated azobenzene cores, as C-Br bonds are comparably less electrophilic, thus facilitating competitive N=N bond reduction; and (ii) low reaction temperatures (-95 to -130 °C). Additionally, the Staubitz group also extensively explored and optimized the lithiation process of azobenzenes, reporting yields up to 99% when the halogen atom was exchanged for tin prior to transmetallation with MeLi.[19] As for the introduction of phosphines to azobenzenes via C-P cross-coupling, successful examples have been documented as well. Utilizing iodinated substrates and Pd-assisted phosphination, Freixa's[25] and Monflier's[26,27] groups achieved phosphanyl introduction in one of the azobenzene rings at *para*- and *meta*- positions, with yields reaching up to 77%. According to all these prior reports, we envisioned the preparation of 1,10-diiododiazocine as the key intermediate to obtain target ligand **Diazo2P**.

Due to the commercial availability of 2-bromo-6-nitrotoluene (**1**) and the easier reduction procedures described for brominated substrates, we first explored the synthetic strategy depicted in Scheme 4-2, which should afford the desired diiodinated diazocine **5** through four main steps. Starting from **1**, an oxidative coupling reaction[28] was initially conducted to yield ethylene-bridged

precursor **2**. Upon subsequent reduction of **2** with Na_2S,[29] the corresponding diamine **3** was obtained, which was further transformed into the diazocine core **4** through an intramolecular Baeyer-Mills reaction using the optimized conditions for oxidative cyclization reported by Trauner's group.[14]

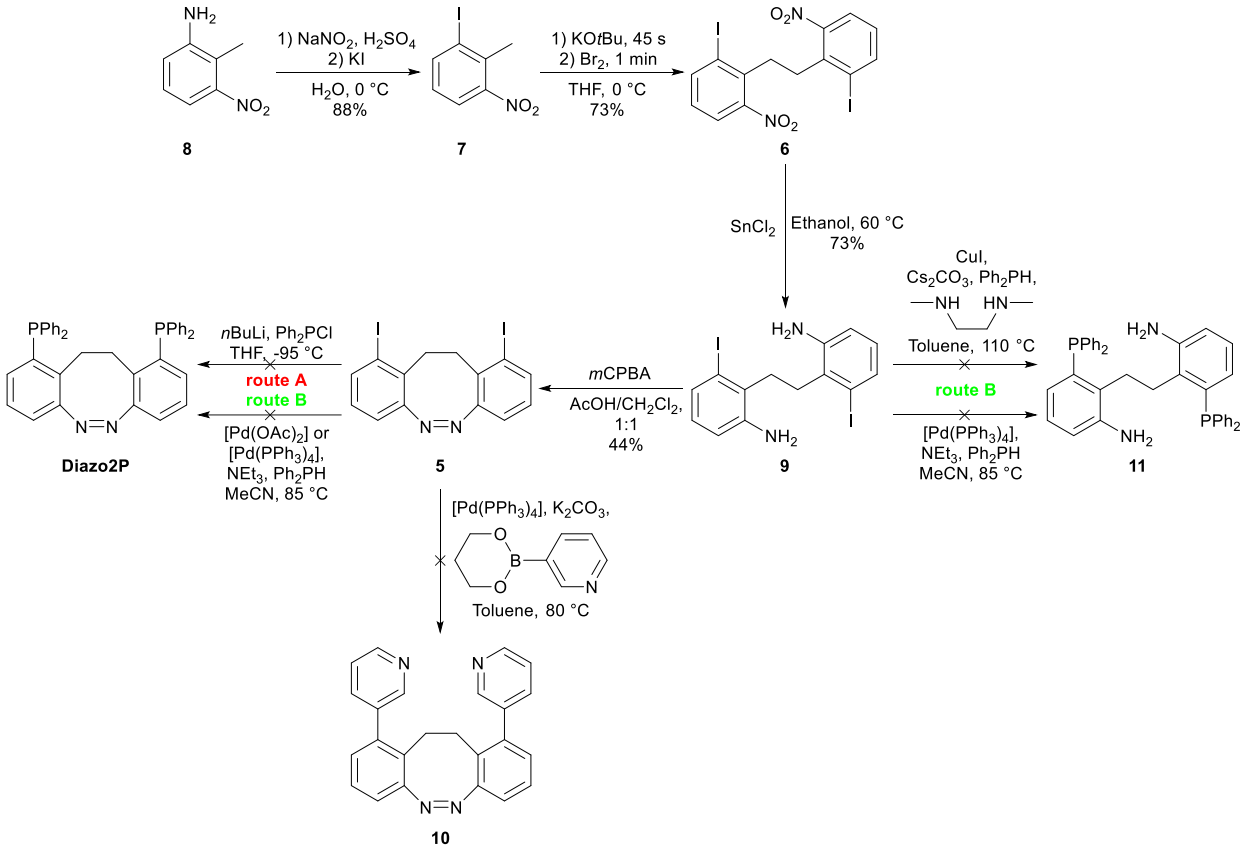


Scheme 4-2 – Synthetic strategy towards 1,10-diiodosubstituted diazocine **5** through oxidative cyclization and consequent bromine-iodine exchange.

With the synthesized 1,10-dibromosubstituted diazocine **4** in hand, we attempted the synthesis of **5** through the aromatic Finkelstein reaction,[30] a well-known protocol to achieve bromine-iodine exchange assisted by Cu(I) salts. However, even with prolonged reaction times (> 130 h), satisfactory yields could not be attained. For this reaction, the resulting mixture of bromo- and iodo substituted diazocines was not separable through flash column chromatography. Similar results were obtained when the bromine-iodine exchange reaction was attempted earlier in the synthetic route – i.e., on compound **2** and even on the starting substrate **1**, where a maximum yield of 86% was accomplished after 3 days. These results were attributed to potential steric effects affecting the reactivity of the C-Br bond in the system, although examples of successful aromatic Finkelstein reactions with sterically hindered substrates are known.[30,31]

In view of these results, an alternative route was devised for the synthesis of key intermediate **5** commencing with commercially available amine **8** (Scheme 4-3). The initial step involved the generation of 2-iodo-6-nitrotoluene (**7**) through a Sandmeyer reaction,[32] which was subsequently subjected to oxidative coupling to obtain 1,2-bis(4-iodo-2-nitrophenyl)ethane (**6**). Given the presence of iodine in this molecule, reduction conditions for the next step of the route had to be carefully chosen to prevent undesired dehalogenation. Replicating the protocol used previously for bromine derivative **2** failed in this case to provide the target diamino derivative **9**, prompting us to

explore alternative conditions. Ultimately, using $SnCl_2$ as a reducing agent, diamine **9** was obtained with 73% yield. Subsequently, **9** was treated with optimized Baeyer-Mills reaction conditions to furnish the novel (*Z*)-1,10-diiodo-11,12-dihydrodibenzo[c,g][1,2]diazocine **5** in 44% yield.



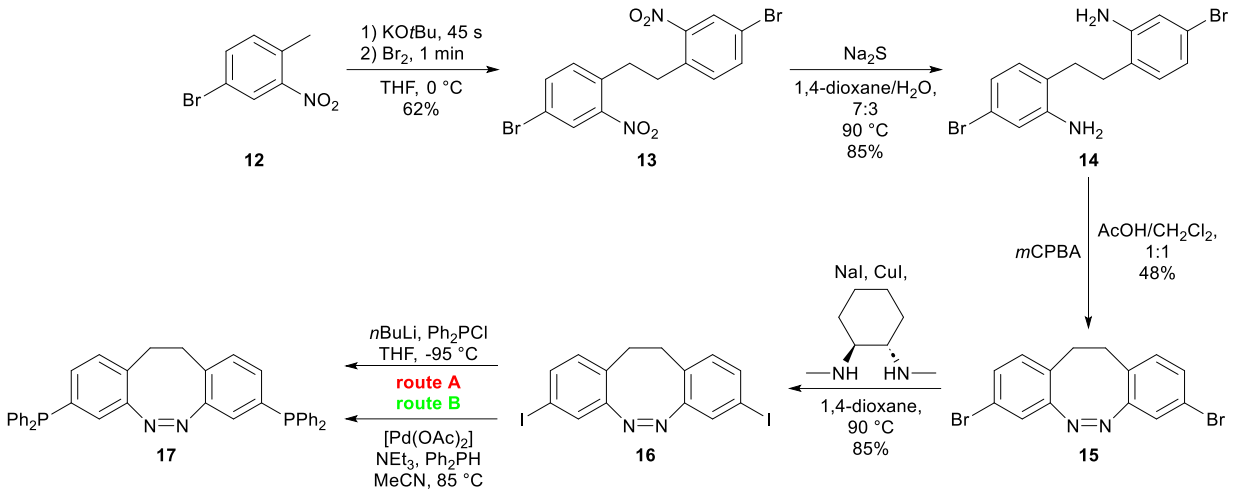
Scheme 4-3 – Synthetic strategies towards the preparation of diazocine **5** through the oxidative cyclization strategy and posterior derivatization for affording 1,10-substituted diazocine-based ligands.

Once key compound **5** was prepared, the synthesis of the desired bisphosphine **Diazo2P** was attempted through the two previously discussed distinct approaches: halogen/lithium exchange followed by electrophile quench (route A), and transition metal-catalyzed C-P cross-coupling (route B). Unfortunately, despite employing a brief lithiation time, vigorous stirring, and low temperatures, all attempts to conduct the lithiation of diazocine **5** and further quenching with Ph_2PCl yielded a complex mixture of products, in which we could not identify the presence of the target compound **Diazo2P** by $^{31}P\{^1H\}$ NMR spectroscopy. In particular, no $^{31}P\{^1H\}$ NMR resonance in the region around $\delta \approx -6$ ppm was found, which is characteristic for azobenzene-based phosphines.[5,22,23,25–27] Additionally, route B was explored using different pre-catalysts and reaction conditions, but once again only side-products were observed. In all the cases, the diazocine core underwent degradation and no traces of the desired product were discernible in the $^{31}P\{^1H\}$ NMR spectra of the crudes. Moreover, it must be noted that equivalent negative results were obtained when the introduction

of phosphanyl groups via routes A and B was explored on the analogous 1,10-dibrominated diazocine **4** (data not shown).

To assess the feasibility of functionalizing diazocine **5** at positions 1 and 10, a Suzuki coupling reaction was attempted to obtain diazocine **10**.[33] Unexpectedly, the reaction resulted in the recovery of 80% of the starting diazocine **5** and no evidences of the product formation were found. These unsuccessful results for the derivatization of diiodinated diazocine **5**, combined with the difficulties encountered with the aromatic Finkelstein reaction attempted on dibrominated substrate **4**, led us to believe that steric hindrance effects dramatically inhibit the reactivity of diazocine positions 1 and 10. As a result, slow side reactions with other functional groups in these molecules eventually take place and become predominant (e.g., N=N reduction). This conclusion was supported by exploring the introduction of phosphanyl groups at an early stage of the synthetic route. In particular, two reported protocols for amine phosphination were conducted on amine **9** involving Cu^{I} and Pd^{II}-catalyzed cross-couplings.[34] Unfortunately, neither of these reactions yielded bisphosphine **11**, which suggests that steric hindrance effects also prevent reactivity at the *ortho* halogenated positions of the ethylene-bridged precursors required for diazocine core formation (see also the bromine-iodine exchange reaction on **2** in Scheme 4-2). Consequently, we could not access the desired ligand **Diazo2P** using our strategy based on the late-stage functionalization of halogenated 1,10-diazocines (or of advanced diazocine precursors).

To further validate our hypothesis regarding the steric influence on diazocine functionalization, we opted to introduce the desired phosphanyl groups to the less sterically hindered positions 3 and 8 of diiododiazocine **16** (Scheme 4-4). To explore this strategy, (*Z*)-3,8-diiodo-11,12-dihydrobenzo[c,g][1,2]diazocine (**16**) had to be first prepared. Employing a previously described[28] three-step sequence, we obtained dibrominated diazocine **15**, which was then subjected to an aromatic Finkelstein reaction furnishing compound **16**. The two above-mentioned synthetic routes A and B were tested on this model diazocine, yielding similarly satisfactory results. The proposed bisphosphinated product **17** was identified in both reaction crudes through $^{31}P\{^{1}H\}$ NMR spectroscopy (Figures S2-S3 in the section §4.5). However, its posterior purification and further characterization was not pursued. In combination with the successful bromine-iodine exchange reaction conducted on **15**, this result reinforces our conclusion that the derivatization of 1,10-diazocines is severely impeded by steric hindrance and still remains an ongoing challenge.



Scheme 4-4 – Synthesis of model 3,8-disubstituted diazocine-based phosphine **17**.

4. 3. Conclusions and outlook

In this work we reported a pioneering attempt to integrate the unique photoswitching properties of diazocines into phosphine ligands for tailored catalysis. In a first step, DFT calculations were employed to validate our vision that reversible *Z*/*E* isomerization in diazocines could be exploited to achieve dynamic control of coordination modes in catalytic metal complexes. In particular, a promising candidate to accomplish this goal could be identified computationally, which was based on a 1,10-bis(phosphanyl)substituted diazocine core capable of transitioning from bi- to monodentate behavior upon photoisomerization. Unfortunately, attempts to synthesize this **Diazo2P** ligand encountered considerable challenges and, despite employing diverse synthetic routes and methodologies, it could not be obtained. The synthetic limitations primarily arose from steric hindrance effects hampering the reactivity at positions 1 and 10 of the diazocine framework, eventually impeding the phosphination of the prepared halogenated diazocine precursor. Thus, attempts to derivatize these precursors via halogen/lithium exchange and transition metal-catalyzed C-P cross-coupling were unsuccessful, resulting in complex mixtures of side products and degradation of the diazocine substrate. Aiming to confirm the impact of steric effects on diazocine functionalization, an analogous ligand was obtained applying the same synthetic strategies to phosphinate the less sterically hindered positions 3 and 8 of the diazocine core.

These findings highlight the complex challenges associated with the functionalization of diazocine structures and underscore the importance of steric considerations in designing synthetic strategies. Future investigations may benefit from exploring alternative routes or modifying reaction conditions to accomplish the synthesis of target ligand **Diazo2P**. Particularly, the slow and incomplete, but feasible, Cu^{I}-catalyzed aromatic Finkelstein reaction proceeding with a 1,10-dibrominated diazocine suggests that the utilization of Cu(I) salts to introduce phosphanyl or phosphoryl groups into diazocines might be a viable strategy. In fact, phosphoryl groups might be potentially more

preferable due to their lower nucleophilicity, thus, slowing down potential side reactions with the electrophilic N=N double bond. At the next step, the exchange of the oxygen atom for sulfur will lead to the corresponding phosphine sulfide,[35] which can be readily reduced to the desired phosphine without affecting the N=N bond.[24]

Another unexplored strategy is metalation through tin-lithium exchange. Very recently, this strategy has been reported to introduce stannane groups into positions 3 and 8, and 2 and 9 of diazocines by Staubitz's group.[36] However, the sensitivity of tin-lithium exchange to steric effects may limit its feasibility for the preparation of the desired ligand **Diazo2P**.

In conclusion, despite our unsuccessful efforts to experimentally demonstrate the viability of the molecular design toward a new family of photoswitchable catalysts, the knowledge gained from this study lays the groundwork for the development of diazocine-based photoswitchable ligands and complexes, as well as contributes to a deeper understanding of the synthetic intricacies involved in the development of this type of complex photoresponsive compounds.

4. 4. References

1 a) B. M. Neilson and C. W. Bielawski, *ACS Catal.*, 2013, **3**, 1874–1885; b) V. Blanco, D. A. Leigh and V. Marcos, *Chem. Soc. Rev.*, 2015, **44**, 5341–5370.

2 a) D. Majee and S. Presolski, *ACS Catal.*, 2021, **11**, 2244–2252; b) S. P. Ihrig, F. Eisenreich and S. Hecht, *Chem. Comm.*, 2019, **55**, 4290–4298; c) G. C. Thaggard, J. Haimerl, R. A. Fischer, K. C. Park and N. B. Shustova, *Angew. Chem. Int. Ed.*, 2023, **62**, e202302859.

3 F. Medici, N. Goual, V. Delattre, A. Voituriez and A. Marinetti, *ChemCatChem*, 2020, **12**, 5573–5589.

4 J. A. Gillespie, E. Zuidema, P. W. N. M. van Leeuwen and P. C. J. Kamer, in *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, John Wiley & Sons, Ltd, 2012, pp. 1–26.

5 T. Arif, C. Cazorla, N. Bogliotti, N. Saleh, F. Blanchard, V. Gandon, R. Métivier, J. Xie, A. Voituriez and A. Marinetti, *Catal. Sci. Technol.*, 2018, **8**, 710–715.

6 a) G. Bianchini, G. Strukul, D. F. Wass and A. Scarso, *RSC Adv.*, 2015, **5**, 10795–10798; b) J. Liang, J. Yin, Z. Li, C. Zhang, Di Wu and S. H. Liu, *Dyes Pigm.*, 2011, **91**, 364–369.

7 a) Z. Xu, Y. Cao, B. O. Patrick and M. O. Wolf, *Chem. Eur. J.*, 2018, **24**, 10315–10319; b) A. Sherstiuk, A. Lledós, P. Lönnecke, J. Hernando, R. M. Sebastián and E. Hey-Hawkins, *ChemRxiv.*, 2023.

8 R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Näther, F. Renth and F. Temps, *J. Am. Chem. Soc.*, 2009, **131**, 15594–15595.

9 a) M. Hammerich, C. Schütt, C. Stähler, P. Lentes, F. Röhricht, R. Höppner and R. Herges, *J. Am. Chem. Soc.*, 2016, **138**, 13111–13114; b) A. Mukherjee, M. D. Seyfried and B. J. Ravoo, *Angew. Chem. Int. Ed.*, 2023, **62**, e202304437.

10 P. W. N. M. van Leeuwen, P. C. J. Kamer and J. N. H. Reek, *Pure Appl. Chem*., 1999, **71**, 1443–1452.

11 a) K. Tsutsumi, T. Yabukami, K. Fujimoto, T. Kawase, T. Morimoto and K. Kakiuchi, *Organometallics*, 2003, **22**, 2996–2999; b) O. Vallcorba, A. Polo and J. Real, *ChemCatChem*, 2017, **9**, 1105–1112.

12 C. L. Daniels, E. Gi, B. A. Atterberry, R. Blome-Fernández, A. J. Rossini and J. Vela, *Inorg. Chem.*, 2022, **61**, 6888–6897.

13 S. Li, N. Eleya and A. Staubitz, *Org. Lett.*, 2020, **22**, 1624–1627.

14 M. S. Maier, K. Hüll, M. Reynders, B. S. Matsuura, P. Leippe, T. Ko, L. Schäffer and D. Trauner, *J. Am. Chem. Soc.*, 2019, **141**, 17295–17304.

15 F. Klockmann, C. Fangmann, E. Zender, T. Schanz, C. Catapano and A. Terfort, *ACS Omega*, 2021, **6**, 18434–18441.

16 a) I. Wauters, W. Debrouwer and C. V. Stevens, *Beilstein J. Org. Chem.,* 2014, **10**, 1064–1096; b) C. Baillie and J. Xiao, *ChemInform*, 2003, **34,** 477-514.

17 L. Degennaro, A. Giovine, L. Carroccia and R. Luisi, in *Lithium Compounds in Organic Synthesis*, John Wiley & Sons, Ltd, 2014, pp. 513–538.

18 A. R. Katritzky, J. Wu and S. V. Verin, *Synthesis* 1995, **1995**, 651–653.

19 J. Strueben, P. J. Gates and A. Staubitz, *J. Org. Chem*., 2014, **79**, 1719–1728.

20 L. A. Carpino, P. H. Terry and P. J. Crowley, *J. Org. Chem*., 1961, **26**, 4336–4340.

21 H. Gilman and R. M. Pickens, *J. Am. Chem. Soc.*, 1925, **47**, 2406–2416.

22 C. Cazorla, L. Casimiro, T. Arif, C. Deo, N. Goual, P. Retailleau, R. Métivier, J. Xie, A. Voituriez, A. Marinetti and N. Bogliotti, *Dalton Trans.*, 2021, **50**, 7284–7292.

23 M. Yamamura, N. Kano and T. Kawashima, *J. Am. Chem. Soc.*, 2005, **127**, 11954–11955.

24 M. Yamamura, N. Kano and T. Kawashima, *Heteroat. Chem.*, 2011, **22**, 301–306.

25 M. D. Segarra-Maset, P. W. N. M. van Leeuwen and Z. Freixa, *Eur. J. Inorg. Chem.*, 2010, **14**, 2075–2078.

26 H. Bricout, E. Banaszak, C. Len, F. Hapiot and E. Monflier, *Chem. Comm.*, 2010, **46**, 7813–7815.

27 A. Telleria, P. W. N. M. van Leeuwen and Z. Freixa, *Dalton Trans.*, 2017, **46**, 3569–3578.

28 G. Cabré, A. Garrido-Charles, À. González-Lafont, W. Moormann, D. Langbehn, D. Egea, J. M. Lluch, R. Herges, R. Alibés, F. Busqué, P. Gorostiza and J. Hernando, *Org. Lett.*, 2019, **21**, 3780–3784.

29 A. Mourot, M. A. Kienzler, M. R. Banghart, T. Fehrentz, F. M. E. Huber, M. Stein, R. H. Kramer and D. Trauner, *ACS Chem. Neurosci.*, 2011, **2**, 536–543.

30 A. Klapars and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 14844–14845.

31 H.-J. Cristau, A. Ouali, J.-F. Spindler and M. Taillefer, *Chem. Eur. J.*, 2005, **11**, 2483–2492.

32 a) C. Bressy, D. Alberico and M. Lautens, *J. Am. Chem. Soc.*, 2005, **127**, 13148–13149; b) M. M. Farah, P. C. B. Page, B. R. Buckley, A. J. Blacker and M. R. Elsegood, *Tetrahedron*, 2013, **69**, 758–769.

33 T. R. Schulte, J. J. Holstein and G. H. Clever, *Angew. Chem. Int. Ed.*, 2019, **58**, 5562–5566.

34 a) D. Gelman, L. Jiang and S. L. Buchwald, *Org. Lett.*, 2003, **5**, 2315–2318; b) O. Herd, A. Heßler, M. Hingst, P. Machnitzki, M. Tepper and O. Stelzer, *Catal. Today*, 1998, **42**, 413–420.
35 M. Yamamura, N. Kano and T. Kawashima, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 110–123.
36 M. Walther, W. Kipke, R. Renken and A. Staubitz, *RSC Adv.*, 2023, **13**, 15805–15809.

4. 5. Supporting information

4. 5. 1. General procedures

Materials and methods

All reactions were carried out under nitrogen atmosphere in the absence of air and water using standard Schlenk line techniques. All solvents (hexanes, CH_2Cl_2, Et_2O, THF, ethyl acetate, MeCN) were dried and degassed prior to use. THF was distilled over sodium/benzophenone and stored over 4Å activated molecular sieves. Anhydrous 1,4-dioxane, xylenes, diglyme, ethanol were commercially purchased and used as received. $CDCl_3$ was degassed by freeze–pump–thaw cycling. All starting materials and reagents were commercially purchased and used without further purification. Flash column chromatography was done using silica gel (230-400 mesh) using a stream of nitrogen.

NMR spectra were recorded on a BRUKER Avance III HD 400 MHz, BRUKER Ascend 300 MHz and BRUKER Ascend 400 MHz at 25 °C. Tetramethylsilane (TMS) was used as an internal reference in ^{1}H and ^{13}C NMR spectra; all other nuclei were referenced to TMS using the Ξ scale.[1] Chemical shifts are reported in parts per million (ppm). Assignment of ^{1}H and ^{13}C NMR signals was carried out using ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR experiments. IR spectra were recorded on FT-IR spectrometers Thermo Scientific Nicolet iS5 and BRUKER Tensor 27 Golden Gate. Electrospray ionization mass spectrometry was carried out with BRUKER Impact II, BRUKER Esquire 3,000+ and a micrOTOF-Q II BRUKER spectrometer in positive ion mode.

Computational methods

DFT calculations were carried out using the Gaussian16 program package.[2] Geometry optimizations were conducted without any constraints using the B3LYP functional[3] with Grimme's D3 correction to account for dispersion effects.[4] Optimizations were performed in THF using the solvation model density (SMD) continuum model[5] with basis set 1 (BS1). BS1 included the 6-31G(d,p) basis set for the main group atoms[6] (H, C, N, P) and the Stuttgart-Dresden SDD effective core potential (ECP) and its corresponding double-ζ basis set[7], with a set of *d* polarization functions[8] for I and *f* polarization functions[9] for Pd. Frequency calculations were performed for all the optimized geometries to determine the stationary points as minima. Energies in THF were refined through single-point calculations of the optimized BS1 geometries with an extended basis set (BS2). BS2 consisted of the def2-TZVP for main group atoms, and the quadruple-ζ def2-QZVP basis set for Pd, together with the def2 ECP.[10]

4. 5. 2. Synthetic procedures

1,2-bis(2-bromo-6-nitrophenyl)ethane (**2**)

This compound was synthesized following a reported procedure for a similar compound.[11] More recently, a slightly different protocol for the preparation of **2** was published.[12] *t*BuOK (3.10 g, 27.7 mmol) was added to an ice-cooled solution of 2-bromo-6-nitrotoluene (**1**) (4.00 g, 18.5 mmol) in anhydrous THF (130 mL) and the solution was stirred for 45 s. Then, Br_2 (1.4 mL, 27.3 mmol) was added, and the mixture was stirred for 1 min. The reaction mixture was let warm up to rt and then was poured into ice. The resulting suspension was filtrated and the solid was washed with acetone to furnish **2** (2.71 g, 68% yield) as a beige solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.66 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 3.42 (s, 4H) ppm.

6,6'-(ethane-1,2-diyl)bis(5-bromoaniline) (**3**)

Compound **3** was synthesized following a modified procedure.[13] Compound **2** (1.0 g, 2.3 mmol) was dissolved in a 7:3 degassed mixture of 1,4-dioxane and water (2.6 mL). The reaction mixture was heated to 90 °C and Na_2S (5.1 g, 21.4 mmol) was added portion-wise over 2 h. The mixture was stirred for 4 h. Then, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL), and the crude product was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with saturated NaOH solution, brine solution, dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum to furnish a crude solid identified as **3** (0.64 g, 1.73 mmol, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.89 (t, *J* = 7.9 Hz, 2H), 6.63 (dd, *J* = 7.9, 1.2 Hz, 2H), 4.04 (s, 4H), 2.92 (s, 4H) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.4, 128.5, 126.0, 124.6, 122.8, 115.1, 29.6 ppm.

IR (ATR, ṽ): 3394 (s), 3309 (m), 3195 (s), 2951 (w), 2878 (w), 1645 (m), 1596 (m), 1571 (s), 1462 (s), 1449 (s), 1306 (w), 1290 (m), 1229 (w), 1162 (w), 1117 (w), 1087 (w), 867 (m), 778 (s), 725 (m), 812 (w), 522 (w), 483 (w) cm^{-1}.

HRMS (ESI-TOF, m/z): calculated for [M+H$^+$] 370.9503, found: 370.9568.

CHN Anal. calcd. for $C_{14}H_{14}Br_2N_2$ C 45.44, H 3.81, N 7.57, found: C 45.20, H 3.48, N 7.49.

Melting point: 171 °C (from CH_2Cl_2).

(*Z*)-1,10-Dibromo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**4**)

Compound **4** was synthesized following a modified procedure.[14] A freshly titrated stock solution of *m*CPBA (621 mg, 3.60 mmol) in acetic acid (0.6 M) was added through a syringe pump over the course of 12 h to a vigorously stirred solution of **3** (570 mg, 1.54 mmol) in a 1:3 mixture of acetic acid:CH_2Cl_2 (38.5 mL). The obtained solution was neutralized with 170 mL of 1M NaOH solution and the product was extracted with ethyl acetate (2 x 200 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The crude was purified by column chromatography (hexanes/CH_2Cl_2, 3:1) to give **4** (232 mg, 0.63 mmol, 41% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.00 (t, *J* = 7.9 Hz, 2H), 6.76 (dd, *J* = 7.8, 1.2 Hz, 2H), 3.58 – 3.17 (m, 2H), 2.96 – 2.63 (m, 2H).

1,10-Diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**5**) through aromatic Finkelstein reaction[15]

Trans-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.018 g, 0.126 mmol), sodium iodide (0.38 g, 2.53 mmol) and copper(I) iodide (0.012 g, 0.063 mmol) were added to a solution of **4** (0.23 g, 0.63 mmol) in 1 mL 1,4-dioxane. The reaction mixture was heated to 110 °C and left overnight. Once cooled down to room temperature, an aliquot was taken and analyzed through ^{1}H NMR. Due to poor conversion the reaction mixture was heated once again. The reaction mixture was left for 40 h; however, the formation of an equilibrium mixture of halogenated products was observed, whose major components where the initial dibrominated substrate and the iodinated product. For this reason, the synthesis was terminated and desired product **5** could not be isolated from the mixture using flash column chromatography.

6,6'-(ethane-1,2-diyl)bis(5-iodoaniline) (**6**) through aromatic Finkelstein reaction[15]

Synthesis was attempted following the protocol above. *Trans*-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.020 g, 0.140 mmol), sodium iodide (0.48 g, 2.79 mmol) and copper(I) iodide (0.013 g, 0.070 mmol) were added to a solution of **2** (0.30 g, 0.70 mmol) in 1 mL 1,4-dioxane. The reaction mixture was heated to 110 °C and left overnight. Once cooled down to room temperature, an aliquot was taken and analyzed through ^{1}H NMR spectroscopy. Around 30% conversion was observed and, due to difficult separation of the bromo and iodo derivatives, the synthesis was terminated and the reaction mixture untreated.

2-iodo-6-nitrotoluene (**7**) through aromatic Finkelstein reaction[15]

Synthesis was attempted following the protocol above with slight modifications. *Trans*-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.033 g, 0.230 mmol), sodium iodide (0.69 g, 4.63 mmol) and copper(I) iodide (0.022 g, 0.115 mmol) were added to a solution of **1** (0.50 g, 2.31 mmol) in 2.5 mL 5% diglyme/xylenes. The reaction mixture was heated to 120 °C and left overnight. Over the course of 3 days, 86% conversion was observed to the desired product **7**. However, due to the difficulties in the separation of the bromo and iodo derivatives, the synthesis was terminated, and the reaction mixture left untreated.

2-iodo-6-nitrotoluene (**7**) through Sandmeyer reaction

This compound was synthesized following a reported procedure.[16] 2-Methyl-3-nitroaniline (**8**) (5.0 g, 0.03 mol) was dissolved in 50 mL water, and 8 mL of concentrated sulfuric acid was added with vigorous stirring. After cooling to 0 °C, sodium nitrite (2.5 g, 0.04 mol) in 5 mL of water was gradually introduced over 30 min, and the reaction mixture was allowed to stand for 1 h. Subsequently, a 20 mL water solution of potassium iodide (8.1 g, 0.05 mol) was slowly added over 1 h. After another hour, the product was extracted with CH_2Cl_2, and the organic phase was washed with $Na_2S_2O_3$, and dried over anhydrous Na_2SO_4. Compound **7** was purified through flash column chromatography (hexanes/CH_2Cl_2, 3:1) yielding 7.6 g (88%) of a light-yellow oil that crystallized over time.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.71 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 2.59 (s, 3H) ppm.

1,2-bis(2-iodo-6-nitrophenyl)ethane (**6**)

Compound **6** was synthesized following the same protocol as for compound **2**.[11] *t*BuOK (3.19 g, 28.4 mmol) was added to an ice-cooled solution of 2-iodo-6-nitrotoluene (**7**) (5.00 g, 19.0 mmol) in anhydrous THF (130 mL), and the solution was stirred for 2 min. Then, Br_2 (1.4 mL, 28.0 mmol) was added, and the mixture was stirred for 1 min. The reaction mixture was let warm up to rt and then was poured into ice. The resulting suspension was filtrated and the solid was washed with acetone to furnish **6** (3.64 g, 73% yield) as a beige solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.66 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 2H), 3.45 (s, 4H) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.8, 144.2, 136.2, 129.1, 124.8, 103.8, 35.4.

IR (ATR, ṽ): 3085 (w), 2951 (w), 2859 (w), 1587 (w), 1558 (w), 1521 (s), 1447 (m), 1351 (s), 1276 (w), 1232 (w), 1208 (w), 1195 (w), 1077 (w), 994 (w), 920 (w), 856 (w), 804 (w), 794 (w), 768 (w), 746 (w), 733 (m), 695 (m) cm^{-1}.

CHN Anal. calcd. for $C_{14}H_{10}I_2N_2O_4$ C 32.09, H 1.92, N 5.35, found: C 32.56, H 1.72, N 5.33.

Melting point: 161 °C (from acetone)

6,6'-(ethane-1,2-diyl)bis(5-iodoaniline) (**9**)

Amine **6** (0.20 g, 0.38 mmol) was dissolved in 8 mL of anhydrous ethanol, and $SnCl_2$ (0.43 g, 2.29 mmol) was added. Then, the reaction mixture was heated to 60 °C. After 2 h the reaction was cooled down to room temperature and poured into 25 mL of saturated $KHCO_3$ solution. The product was extracted with $CHCl_3$ (3 x 7 mL), and the organic phase was additionally washed with saturated KF solution (10 mL) and filtered through Celite™. The solvent was removed, and **9** was obtained as a beige solid in 73% (0.13 g) yield. Due to very poor solubility in deuterated solvents, only ^{1}H and ^{13}C{^{1}H} NMR characterization was possible.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 2H), 6.73 (t, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.15 (s, 4H), 2.91 (s, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.7, 129.9, 129.2, 127.4, 116.2, 102.7, 34.8 ppm.

(*Z*)-1,10-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**5**)

Compound **5** was synthesized following the procedure used for compound **4** with slight modifications due to poor solubility of the starting amine **9**. A freshly titrated stock solution of *m*CPBA (140 mg, 0.81 mmol) in acetic acid (0.3 M) was added through a syringe pump over the course of 14 h to a vigorously stirred solution of **9** (188 mg, 0.40 mmol) in a 1:1 mixture of acetic acid:CH_2Cl_2 (40.5 mL). After concentrating the reaction mixture under vacuum, acetic acid was neutralized with 100 mL of concentrated $NaHCO_3$ solution, and the product was extracted with ethyl acetate (2 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The crude was purified by flash column chromatography (hexanes/ethyl acetate, 9:1) to give **5** (83 mg, 0.18 mmol, 44% yield) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.5 Hz, 2H), 6.82 (t, *J* = 7.7 Hz, 2H), 6.76 (dd, *J* = 7.8, 1.5 Hz, 2H), 3.32 – 3.11 (m, 2H), 3.02 – 2.81 (m, 2H) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.0, 138.3, 130.8, 128.3, 118.8, 101.7, 36.1 ppm.

IR (ATR, ṽ): 3057 (m), 2962 (m), 1577 (w), 1552 (s), 1511 (w), 1454 (w), 1434 (s), 1352 (w), 1261 (w), 1210 (w), 1157 (m), 1084 (s), 976 (w), 929 (w), 812 (m), 778 (s) cm^{-1}.

CHN Anal. calcd. for $C_{14}H_{10}I_2N_2$ C 36.55, H 2.19, N 6.09, found: C 36.43, H 1.87, N 5.98.

Melting point: 191 °C (from ethyl acetate/hexanes).

(*Z*)-1,10-di(diphenylphospanyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**Diazo2P**) through halogen/lithium exchange reaction followed by quench with Ph_2PCl

A stirred bright yellow solution of 0.04 g (0.09 mmol, 1.0 eq.) of **5** in 3 mL THF was cooled to -95 °C (ethanol/$N_{2(l)}$), and then 0.13 mL (1.3 mol·L^{-1}, 0.17 mmol, 2.0 eq.) *n*BuLi in hexanes were added dropwise during 2 min. The resultant dark red mixture was kept stirring for 10 min, followed by the drop-wise addition of 0.04 mL (0.20 mmol, 2.2 eq.) of chlorodiphenylphosphine. The reaction mixture was left overnight to warm up to room temperature, an aliquot was taken and analyzed through $^{31}P\{^1H\}$ NMR spectroscopy (Figure S2 in the section §4.5), and then the crude was quenched with a degassed brine solution. Under nitrogen atmosphere, the phases were separated, the aqueous phase was extracted with THF (2 x 5 mL), and the combined organic phases were dried over degassed Na_2SO_4. After canula filtration, the crude was absorbed on silica gel and purified through flash column chromatography (hexanes/ethyl acetate 95:5). No starting diazocine **5** or target phosphine **Diazo2P** were identified.

(*Z*)-1,10-di(diphenylphospanyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**Diazo2P**) through Pd^{II}-catalyzed cross-coupling reaction

A stock solution of Ph_2PH (0.03 mL, 0.17 mmol) in 3 mL MeCN was added to diazocine **5** (0.04 g, 0.09 mmol) and [$Pd(OAc)_2$] (0.002 g, 0.009 mmol). Once diazocine **5** dissolved, anhydrous NEt_3 (0.02 mL, 0.17 mmol) was introduced into the reaction. The reaction mixture was heated to 85 °C and left overnight. In the $^{31}P\{^1H\}$ NMR spectrum of the crude no peaks attributed to possible product formation were found while Ph_2PH was no longer present. The synthesis was terminated, and the reaction mixture left untreated. In the second trial, [$Pd(PPh_3)_4$] was used as a catalyst keeping reaction conditions the same. However, in the $^{31}P\{^1H\}$ NMR spectrum (Figure S3 in the section §4.5) of an aliquot of the reaction mixture no product was observed accompanied by the disappearance of Ph_2PH peak. The synthesis was terminated, and the reaction mixture left untreated.

(*Z*)-1,10-di(pyridin-3-yl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**10**)

3-(1,3,2-Dioxaborinan-2-yl)-pyridine (0.05 g, 0.28 mmol) was added to 5 mL toluene solution of **5** (0.05 g, 0.11 mmol). Afterwards, K_2CO_3 (0.15 g, 1.09 mmol), [$Pd(PPh_3)_4$] (0.006 g, 0.006 mmol) and a few drops of water were added, and the reaction mixture was heated to 80 °C and left overnight. Once cooled down to room temperature, solvent was evaporated under vacuum and crude was loaded onto silica. Column chromatography (hexanes/ethyl acetate 7:1) yielded the starting compound **5** (0.04 g).

6,6'-(ethane-1,2-diyl)bis(5-diphenylphosphanylaniline) (**11**) through palladium(II)-catalyzed C-P cross-coupling

Amine (**9**) (0.11 g, 0.23 mmol) and [$Pd(PPh_3)_4$] (0.03 g, 0.02 mmol) were added to 3 mL MeCN, where the amine exhibited poor solubility in the solvent. Anhydrous NEt_3 (0.08 mL, 0.57 mmol) and Ph_2PH (0.10 mL, 0.57 mmol) were added, and the reaction mixture was heated to 85 °C and left overnight. Upon cooling down, reaction crude was checked by $^{31}P\{^1H\}$ NMR spectroscopy. No signals of possible product (δ ≈ -6 ppm)[17] were observed, alongside, with the disappearance of the peak of the starting phosphine. The synthesis was terminated, and the reaction mixture left untreated.

6,6'-(ethane-1,2-diyl)bis(5-diphenylphosphanylaniline) (**11**) through copper(I)-catalyzed C-P cross-coupling

Toluene (3mL), Ph_2PH (0.05 mL, 0.26 mmol), copper(I) iodide (0.003 g, 0.013 mmol) and *N*,*N*'-dimethylethylenediamine (0.01 mL, 0.09 mmol) were charged into the Schlenk flask and left stirring for 10 min. Afterwards, Cs_2CO_3 (0.17 g, 0.52 mmol) was added, the reaction mixture was heated to 110 °C and left for 24 h. Upon cooling down, reaction crude was checked by $^{31}P\{^1H\}$ NMR spectroscopy. As some diphenylphosphine was still observed in the reaction, it was once again heated to 110 °C and left for another 24 h. After cooling down to rt, the solvent and volatiles were evaporated, and crude was checked by $^{31}P\{^1H\}$ NMR spectroscopy. No signals of possible product (δ ≈ -6 ppm) were observed. The synthesis was terminated, and the reaction mixture left untreated.

1,2-bis(4-bromo-2-nitrophenyl)ethane (**13**)

This compound was synthesized following a reported procedure.[11] *t*BuOK (3.10 g, 27.7 mmol) was added to an ice-cooled solution of 2-bromo-6-nitrotoluene (**12**) (4.00 g, 18.5 mmol) in anhydrous THF (130 mL) and the solution was stirred for 45 s. Then, Br_2 (1.4 mL, 27.3 mmol) was added, and the mixture was stirred for 1 min. The reaction mixture was let warm up to rt and then was poured into ice. The resulting suspension was filtrated and the solid was washed with acetone to furnish **13** (2.47 g, 62% yield) as a beige solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.1 Hz, 2H), 7.67 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.18 (s, 4H) ppm.

6,6'-(ethane-1,2-diyl)bis(3-bromoaniline) (**14**)

Compound **14** was synthesized following a modified procedure.[13] Compound **13** (0.2 g, 0.5 mmol) was dissolved in a 7:3 degassed mixture of 1,4-dioxane and water (5.2 mL). The reaction mixture was

heated to 90 °C and Na_2S (1.1 g, 4.6 mmol) was added portion-wise over 2 h. The mixture was stirred for 4 h. Then, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL), and the crude product was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with saturated NaOH solution, brine solution, dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum to furnish a crude solid identified as **14** (0.14 g, 0.39 mmol, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.76 (m, 1H), 6.75 – 6.71 (m, 1H), 3.77 – 3.37 (m, 2H), 2.64 (s, 1H) ppm.

(*Z*)-3,8-dibromo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**15**)

Compound **15** was synthesized following the procedure used for compound **4**. A freshly titrated stock solution of *m*CPBA (621 mg, 3.6 mmol) in acetic acid (0.6 M) was added through a syringe pump over the course of 14 h to a vigorously stirred solution of **14** (570 mg, 1.54 mmol) in a 1:1 mixture of acetic acid:CH_2Cl_2 (38.5 mL). Acetic acid was neutralized with 50 mL of 1M NaOH solution and the organic phase was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were additionally washed with 30 mL of concentrated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The crude was purified by flash column chromatography (hexanes/ethyl acetate, 9:1) to give **15** (272 mg, 0.74 mmol, 48% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.01 (d, *J* = 2.0 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 2.97 – 2.83 (m, 2H), 2.81 – 2.67 (m, 2H) ppm.

(*Z*)-3,8-diiodo-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**16**)

Trans-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.005 g, 0.038 mmol), sodium iodide (0.12 g, 0.75 mmol) and copper(I) iodide (0.004 g, 0.019 mmol) were added to a solution of **15** (0.069 g, 0.19 mmol) in 1 mL 1,4-dioxane. The reaction mixture was heated to 110 °C and left overnight. Once cooled down to room temperature, 10 mL of concentrated NH_4Cl solution were added, and the product was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The crude was purified by flash column chromatography (hexanes/ethyl acetate, 9:1) to give a mixture containing 85% of iodo-substituted compound **16**. Further purification was not attempted.

(*Z*)-3,8-di(diphenylphospanyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**17**) through halogen/lithium exchange reaction followed by quench with Ph_2PCl

A stirred bright yellow solution of 0.04 g (0.09 mmol, 1.0 eq.) of **16** in 3 mL THF was cooled to -95 °C (ethanol/$N_{2(l)}$), and then 0.12 mL (1.55 mol·L^{-1}, 0.19 mmol, 2.0 eq.) *n*BuLi in hexanes were added dropwise during 6 min. The resultant ruby red mixture was kept stirring for 10 min, followed by the drop-wise addition of 0.04 mL (0.22 mmol, 2.3 eq.) of chlorodiphenylphosphine. The reaction mixture was left overnight to warm up to room temperature and an aliquot was analyzed through $^{31}P\{^1H\}$ NMR spectroscopy (Figure S2 in the section §4.5). Peaks attributed to possible product formation were found at around δ ≈ -6 ppm, although peaks for side products were also present. The reaction conditions require further modification to obtain better yield of the target compound **17**. The reaction was also attempted in Et_2O at -110 °C with the rest of conditions left the same, but in this case no product **17** was identified.

(*Z*)-3,8-di(diphenylphospanyl)-11,12-dihydrodibenzo[*c*,*g*][1,2]diazocine (**17**) through palladium(II)-catalyzed C-P cross-coupling

A stock solution of Ph_2PH (0.02 mL, 0.13 mmol) in 3 mL MeCN was added to diazocine **16** (0.03 g, 0.06 mmol) and [$Pd(OAc)_2$] (0.003 g, 0.01 mmol). Once diazocine **16** dissolved, NEt_3 (0.02 mL, 0.13 mmol) was introduced into the reaction. The reaction mixture was heated to 85 °C and left for 22 h. The reaction mixture was left overnight to warm up to room temperature and an aliquot was analyzed through $^{31}P\{^1H\}$ NMR spectroscopy (Figure S3 in the section §4.5). In the $^{31}P\{^1H\}$ NMR spectrum of the crude peaks attributed to possible product formation were found, although peaks for side products were also present. The reaction conditions require further modification to obtain better yield of the target compound **17**.

4. 5. 3. Additional computational details

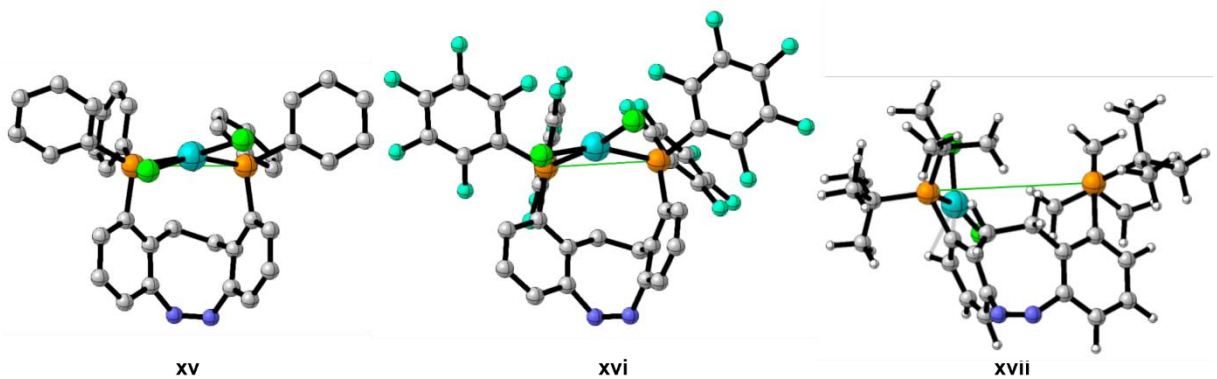


Figure S1 – Calculated structures of the *cis* Pd^{II} complexes formed with the *Z* isomers of 1,10-bis(diphenylphosphanyl)diazocine (complex **xv**) and 1,10-bis(diperfluorophenylphosphanyl)diazocine

(complex **xvi**) ligands. In addition, the calculated structure of the monoligated Pd^{II} complex formed with the *Z* isomer of 1,10-bis(di-*tert*-butyl-phosphanyl)diazocine (complex **xvii**) is also shown. The P-P distance is indicated in each case with a green line.

4. 5. 4. Additional experimental details

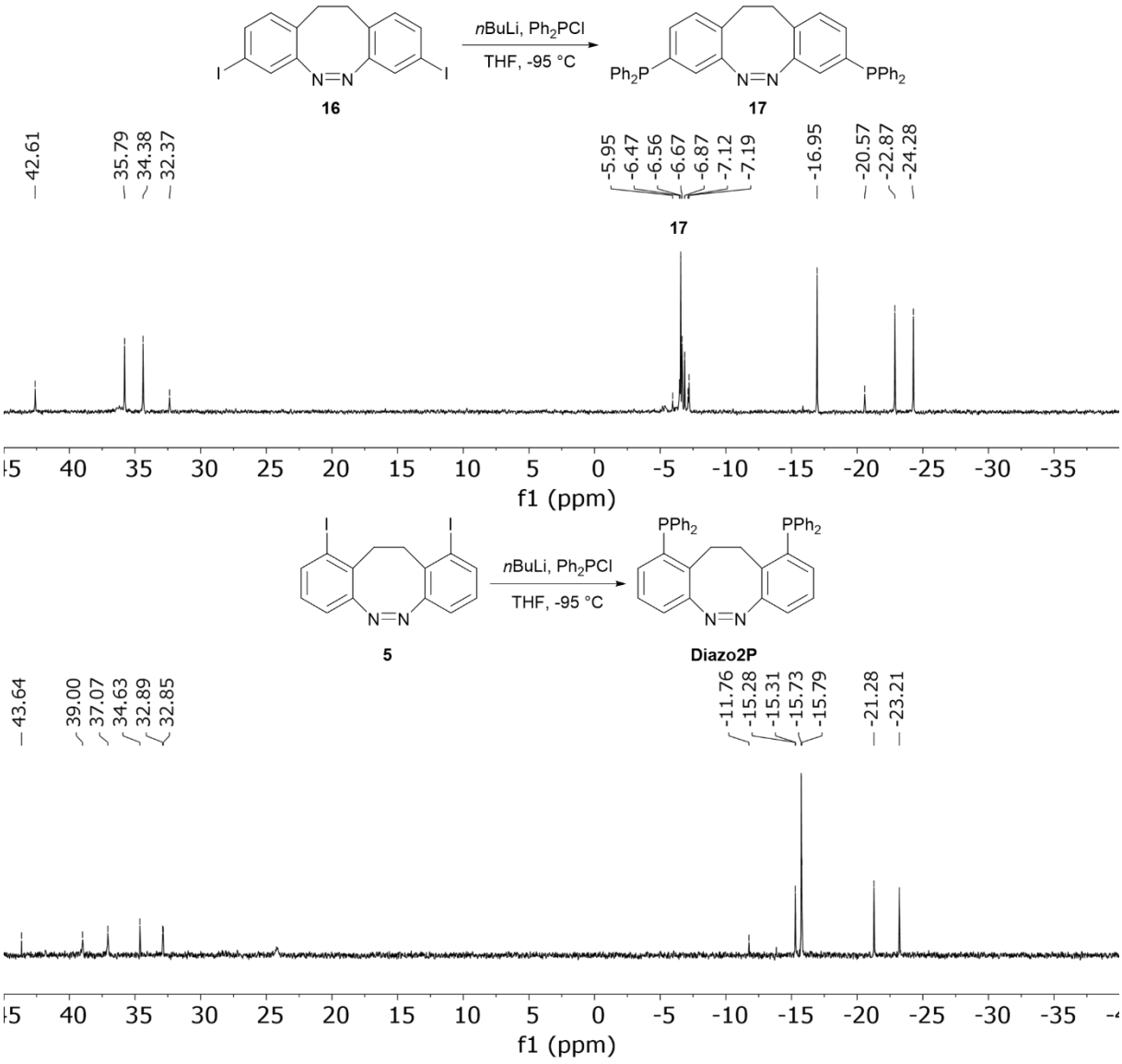


Figure S2 – Comparison of the reaction mixture $^{31}P\{^{1}H\}$ NMR spectra in $CDCl_3$ (top: 162 MHz, bottom: 121 MHz) of the iodide/lithium exchange reaction followed by quench with Ph_2PCl carried out with the substrates **16** and **5**. Peaks attributed to possible product **17** formation were found at around δ ≈ -6 ppm.

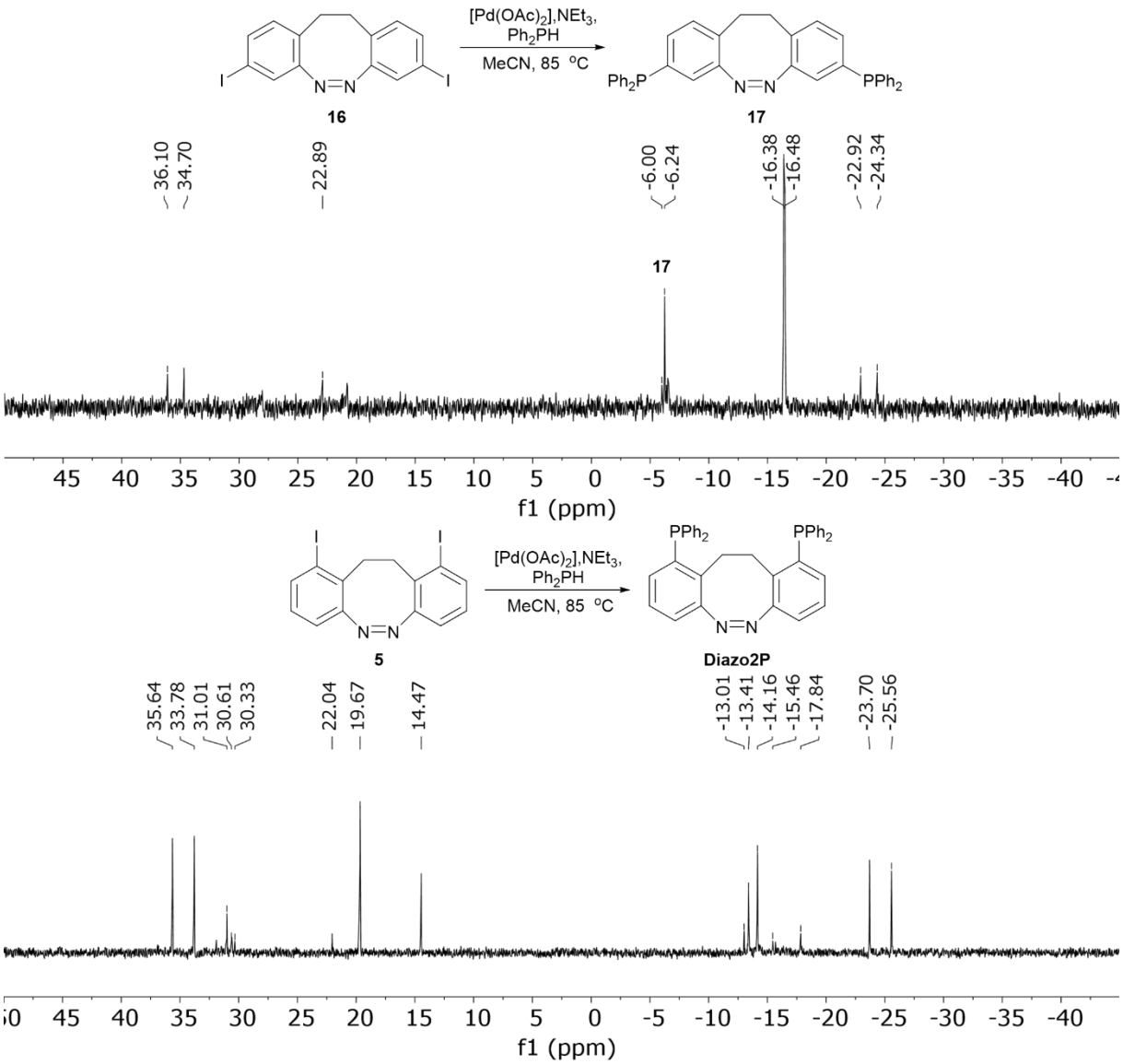


Figure S3 – Comparison of the reaction mixture $^{31}P\{^{1}H\}$ NMR spectra in $CDCl_3$ (top: 162 MHz, bottom: 121 MHz) of the Pd^{II}-catalyzed cross-couplings carried out with diazocines **5** and **16**. Peaks attributed to possible product **17** formation were found at around δ ≈ -6 ppm.

4. 5. 5. NMR Spectra of the reported compounds

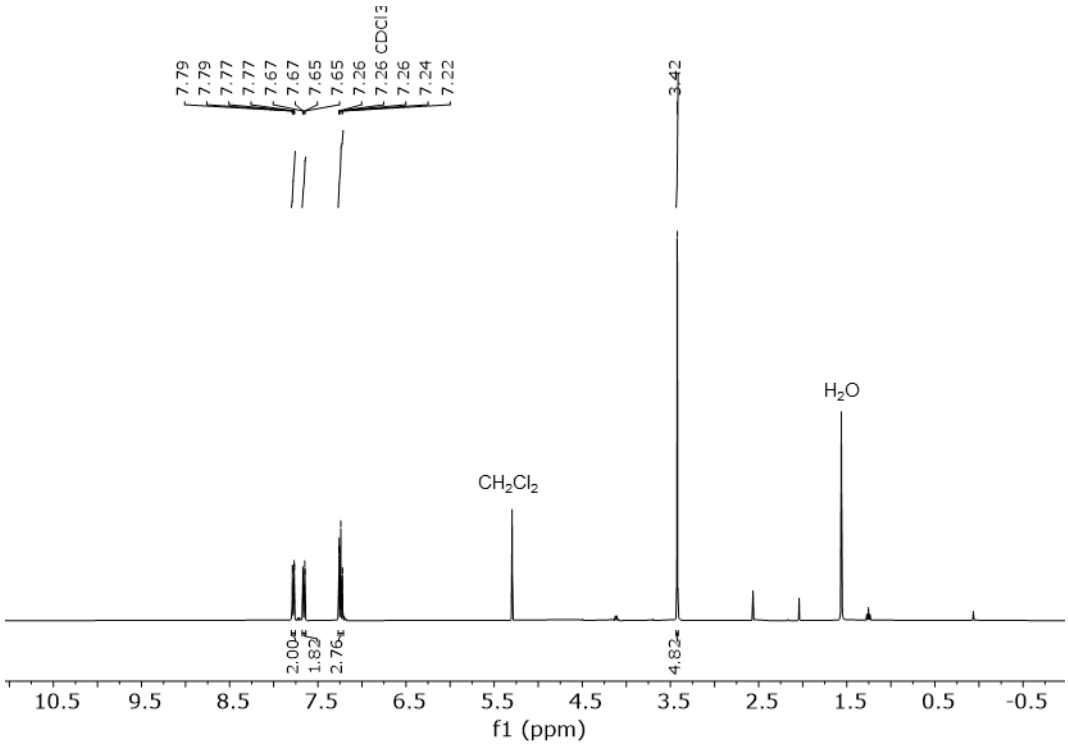


Figure S4 – ^{1}H NMR spectrum (400 MHz) of **2** in $CDCl_3$ recorded at 25 °C.

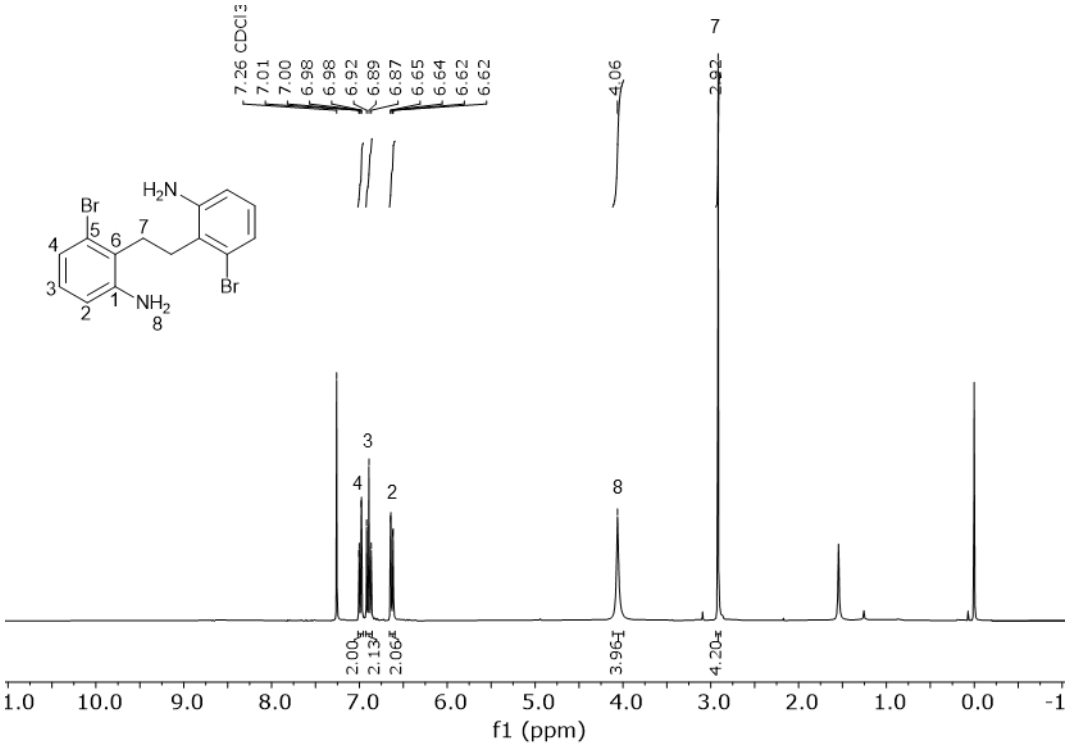


Figure S5 – ^{1}H NMR spectrum (400 MHz) of **3** in $CDCl_3$ recorded at 25 °C.

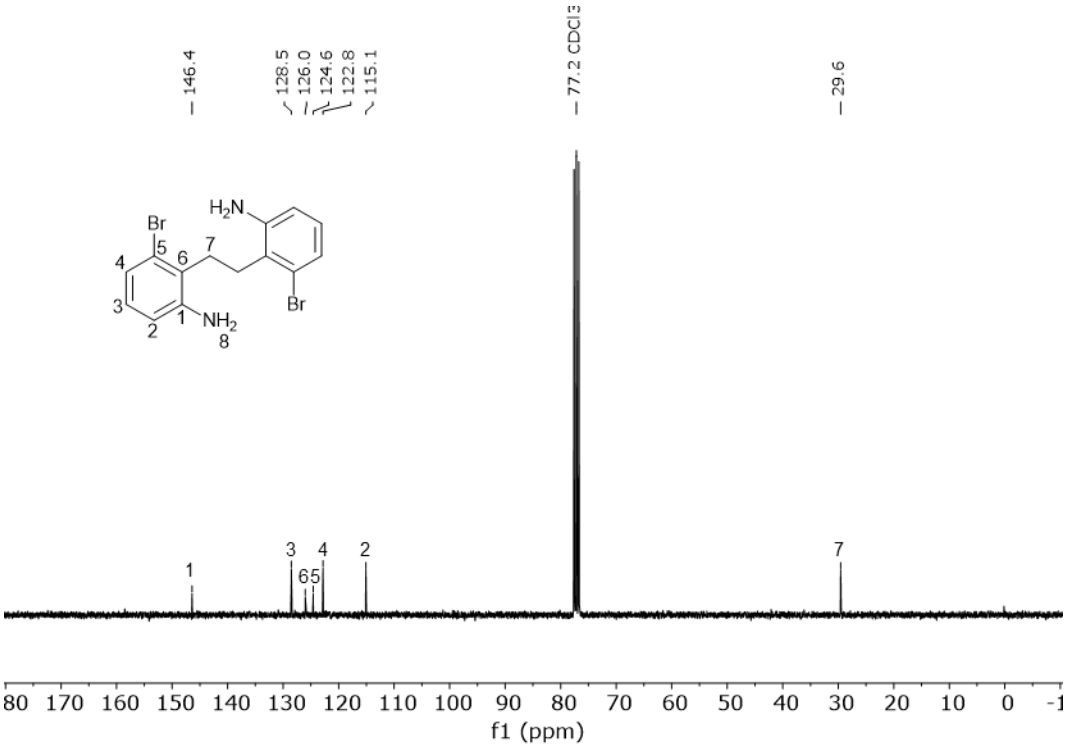


Figure S6 – ^{13}C NMR spectrum (75 MHz) of **3** in $CDCl_3$ recorded at 25 °C.

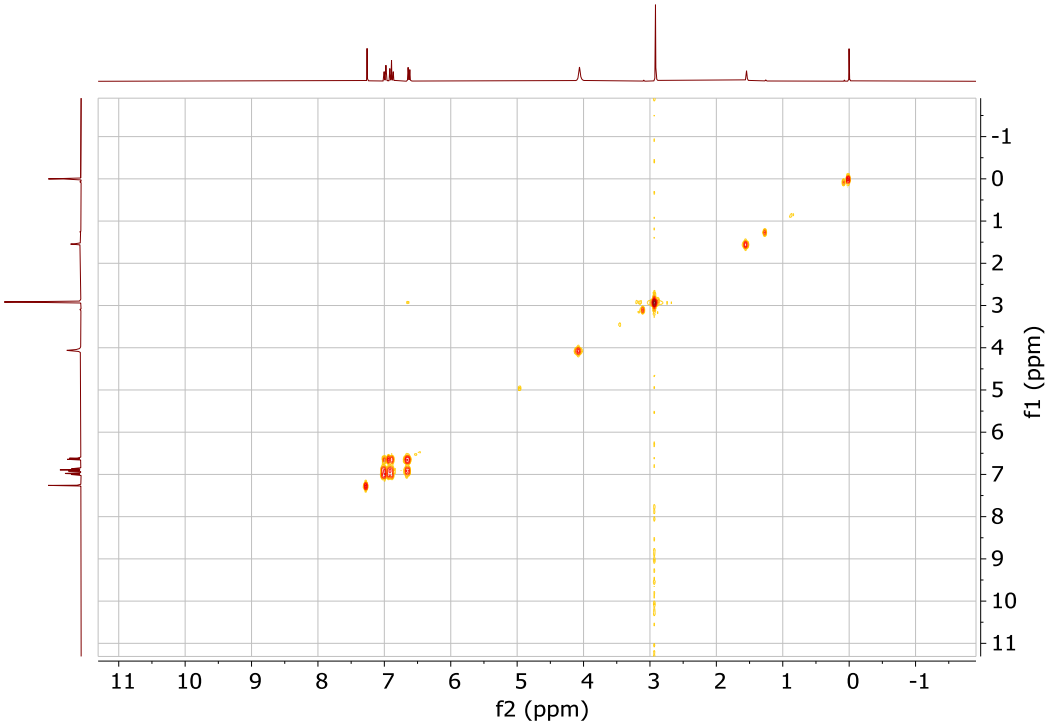


Figure S7 – ^{1}H-^{1}H COSY spectrum of **3** in $CDCl_3$ recorded at 25 °C.

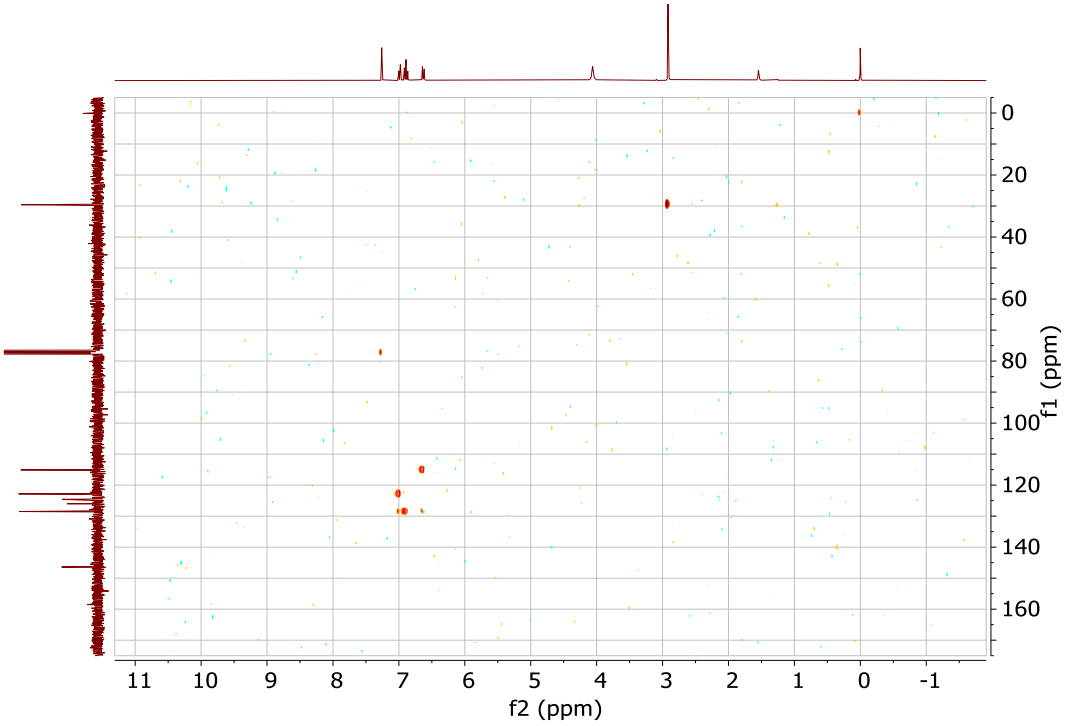


Figure S8 – ^{1}H-^{13}C HSQC spectrum of **3** in $CDCl_3$ recorded at 25 °C.

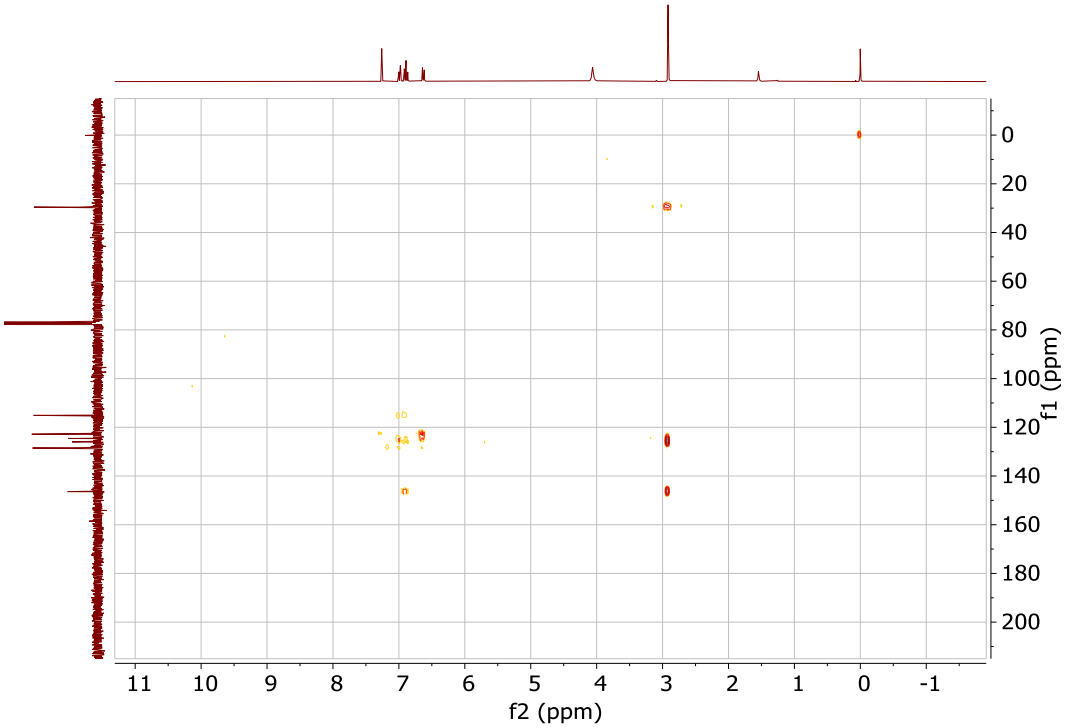


Figure S9 – ^{1}H-^{13}C HMBC spectrum of **3** in $CDCl_3$ recorded at 25 °C.

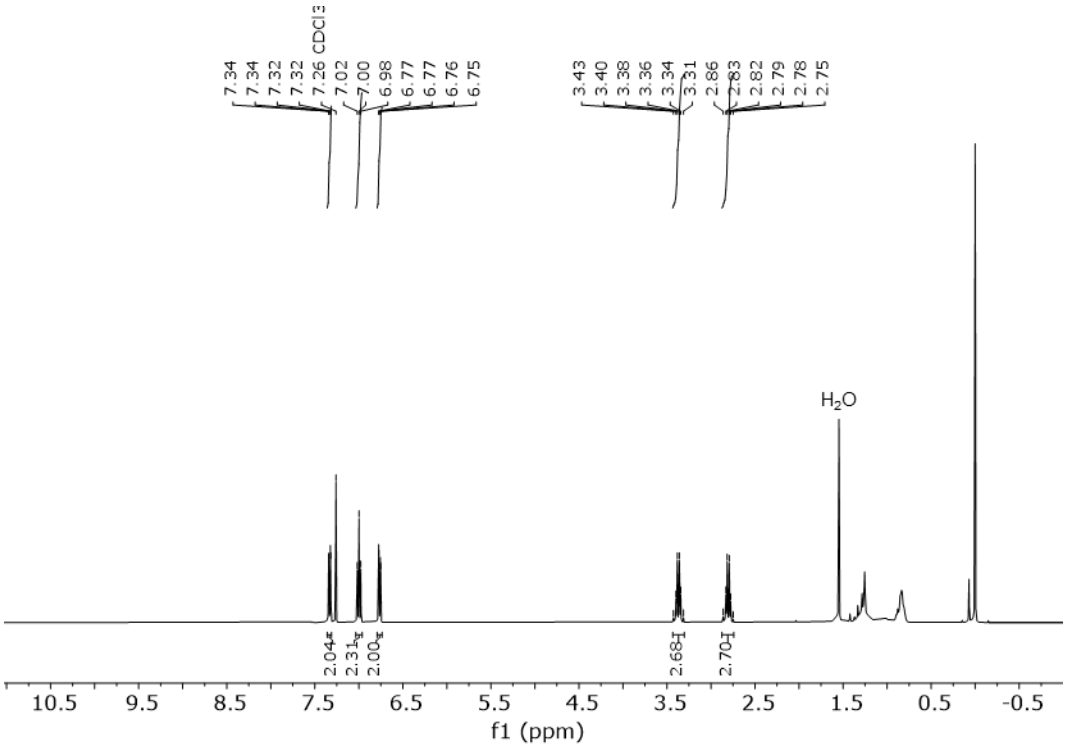


Figure S10 – ^{1}H NMR spectrum (400 MHz) of **4** in $CDCl_3$ recorded at 25 °C.

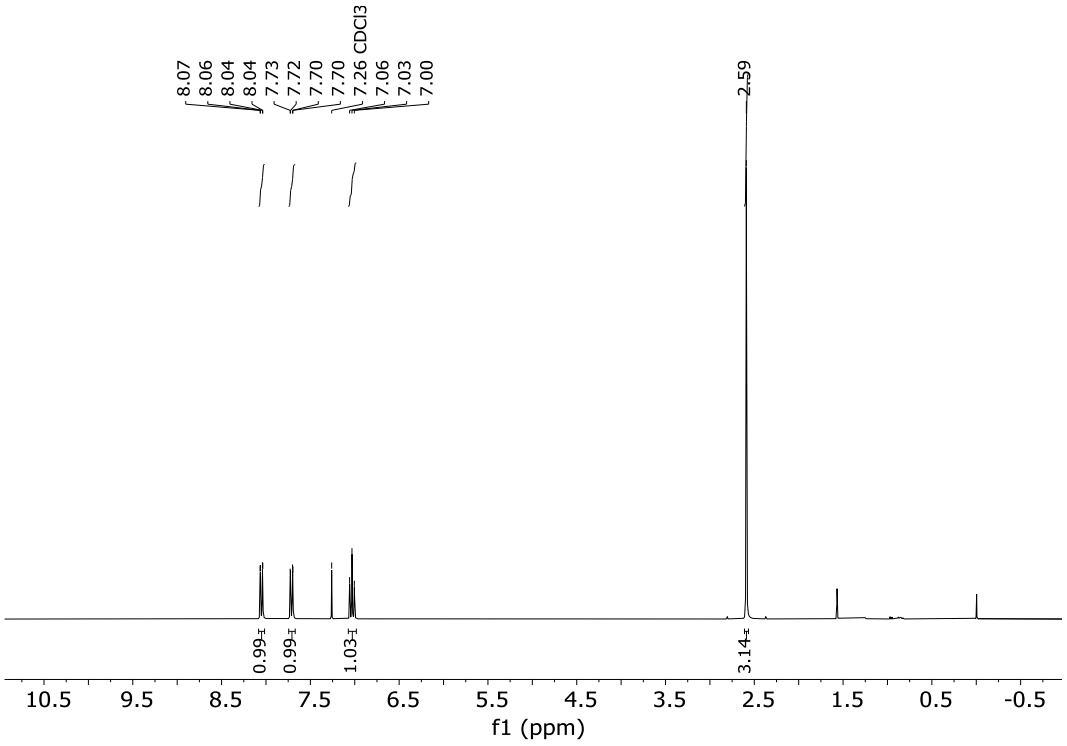


Figure S12– ^{1}H NMR spectrum (300 MHz) of **7** in $CDCl_3$ recorded at 25 °C.

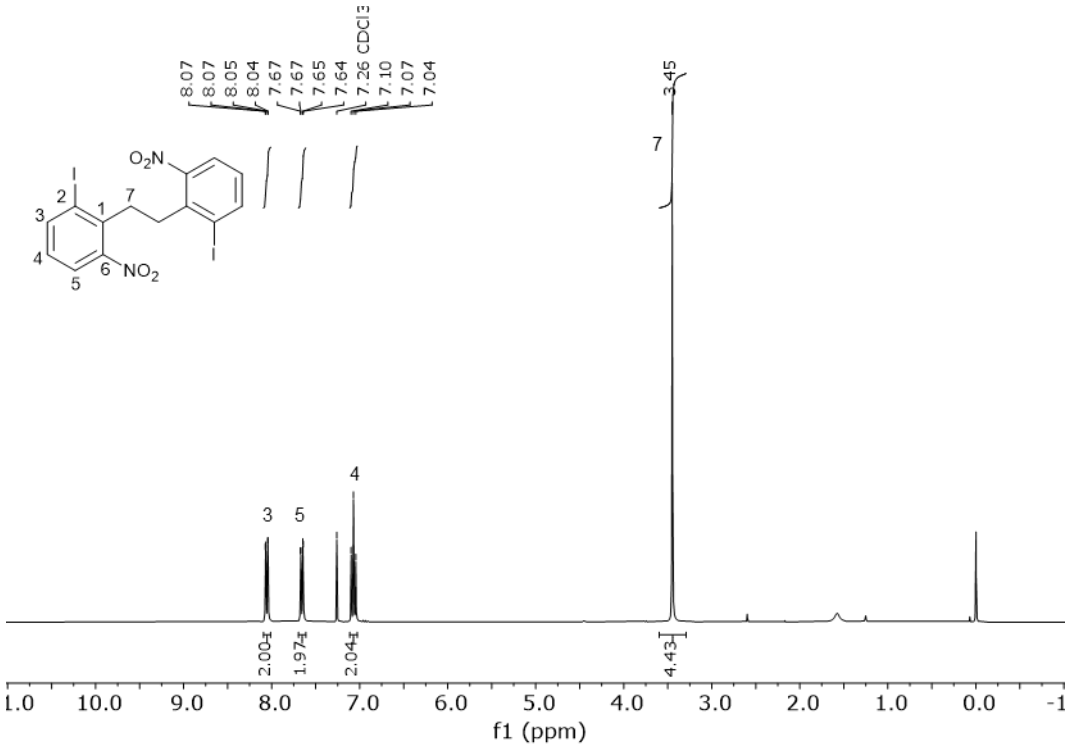


Figure S13 – ^{1}H NMR spectrum (300 MHz) of **6** in $CDCl_3$ recorded at 25 °C.

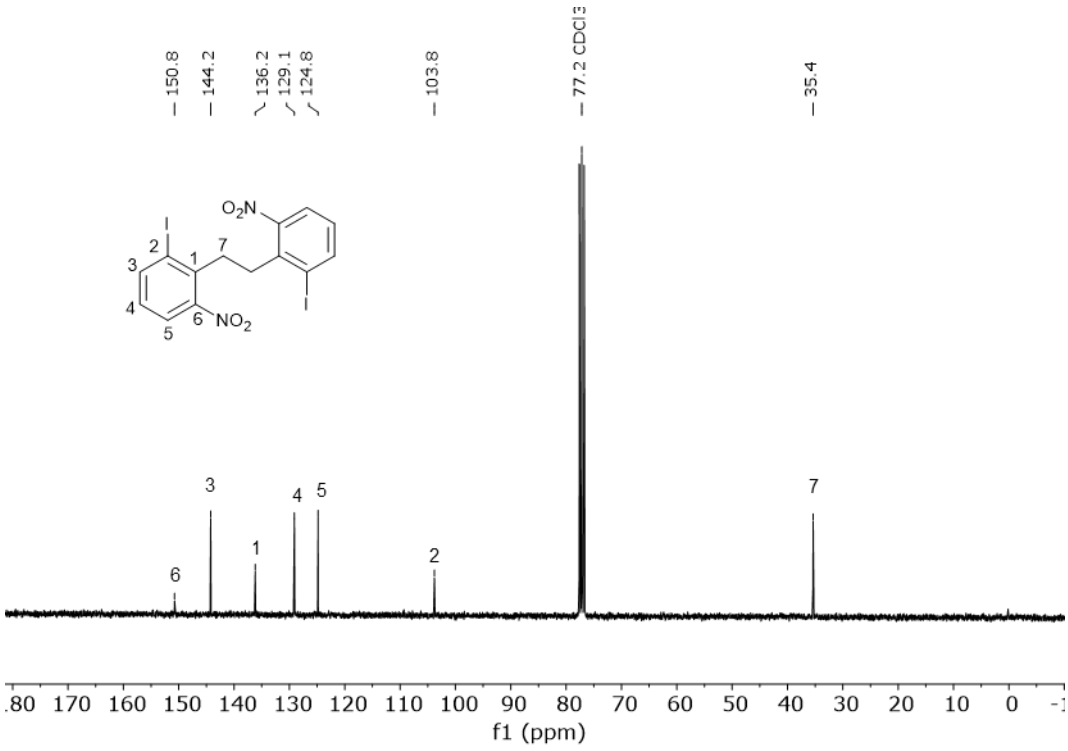


Figure S14 – ^{13}C NMR spectrum (75 MHz) of **6** in $CDCl_3$ recorded at 25 °C.

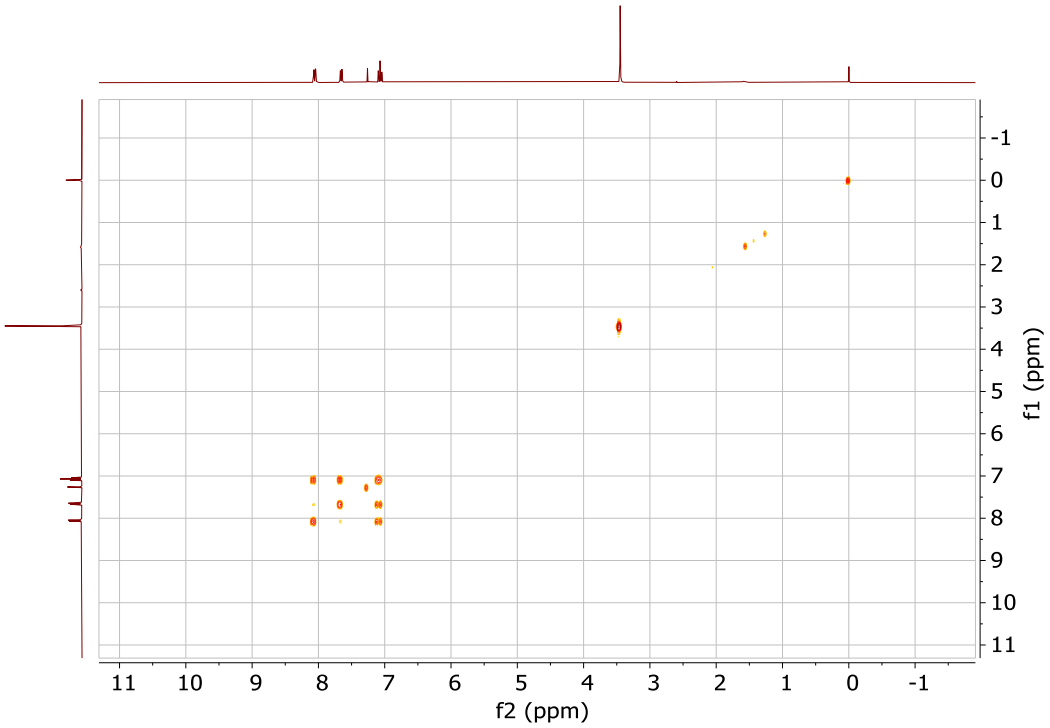


Figure S15 – ^{1}H-^{1}H COSY spectrum of **6** in $CDCl_3$ recorded at 25 °C.

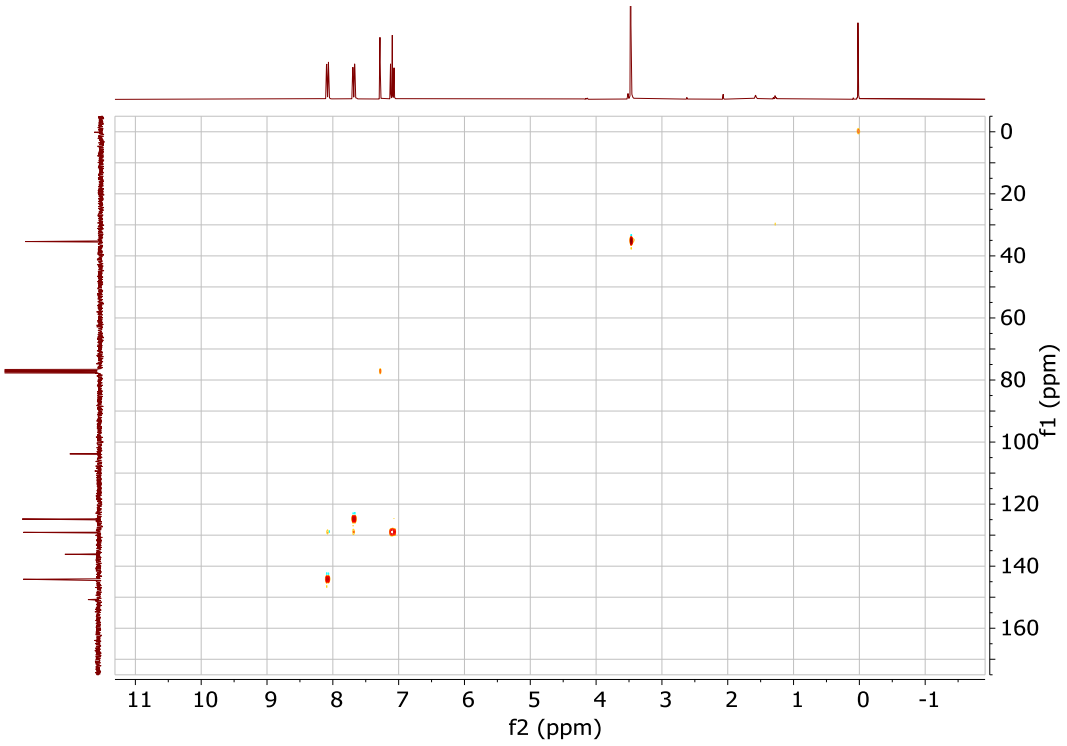


Figure S16 – ^{1}H-^{13}C HSQC spectrum of **6** in $CDCl_3$ recorded at 25 °C.

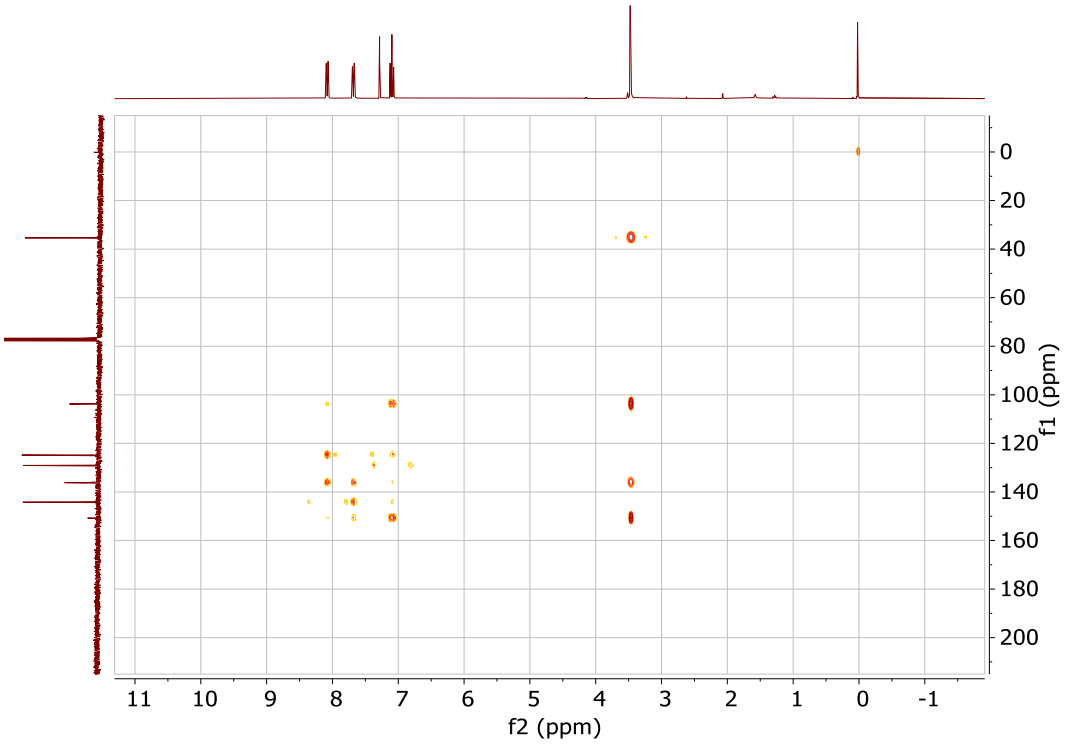


Figure S17 – ^{1}H-^{13}C HMBC spectrum of **6** in $CDCl_3$ recorded at 25 °C.

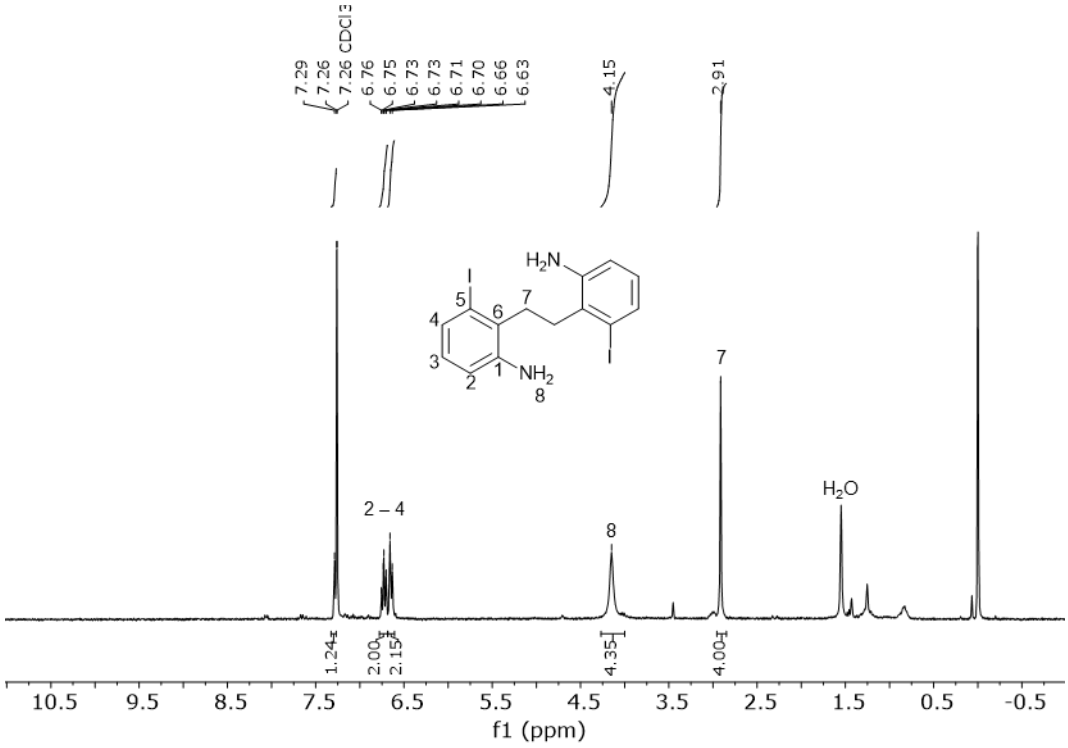


Figure S18 – ^{1}H NMR spectrum (300 MHz) of **9** in $CDCl_3$ recorded at 25 °C.

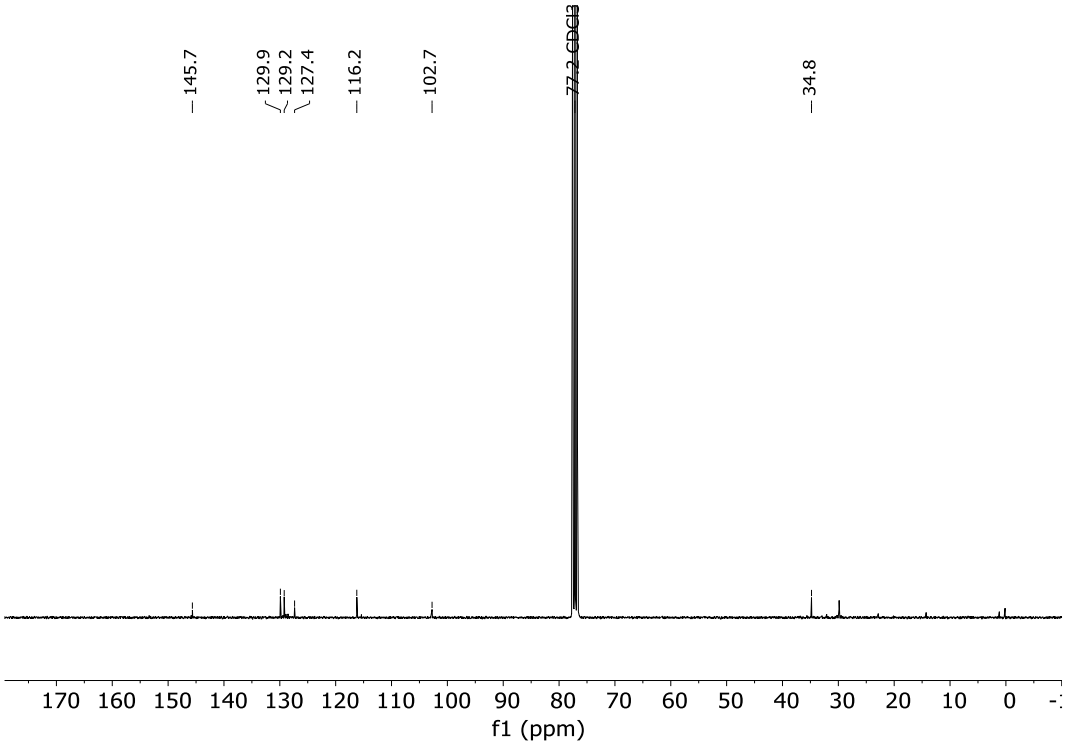


Figure S19 – ^{13}C NMR spectrum (75 MHz) of **9** in $CDCl_3$ recorded at 25 °C.

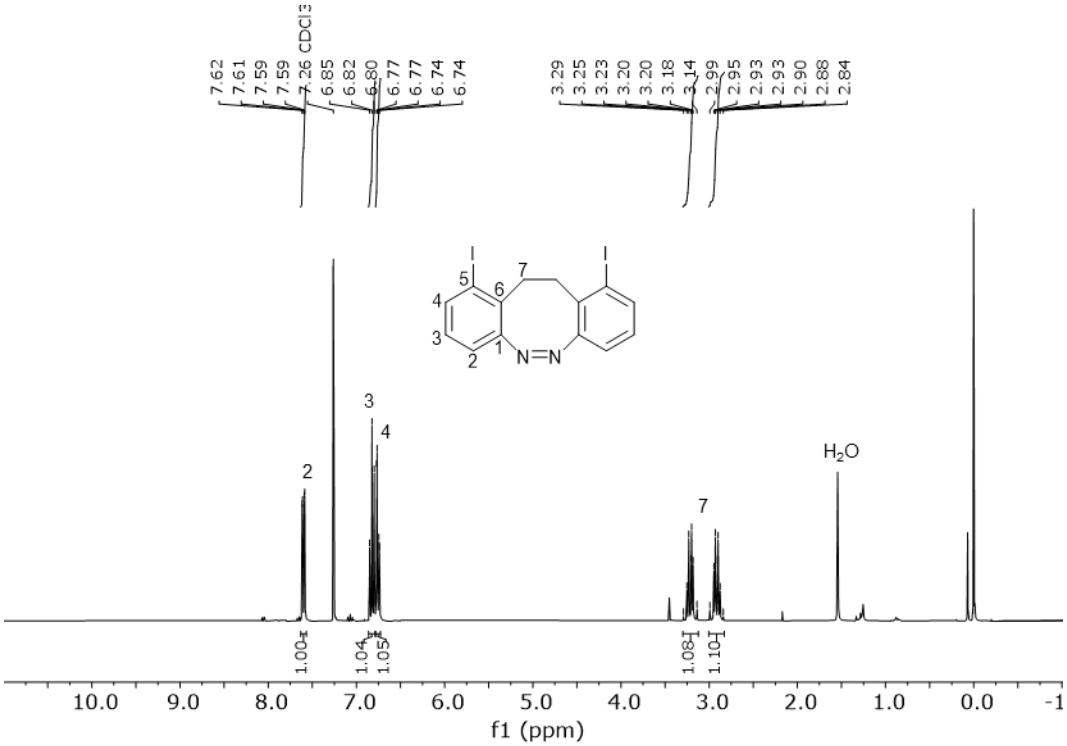


Figure S20 – ^{1}H NMR spectrum (300 MHz) of **5** in $CDCl_3$ recorded at 25 °C.

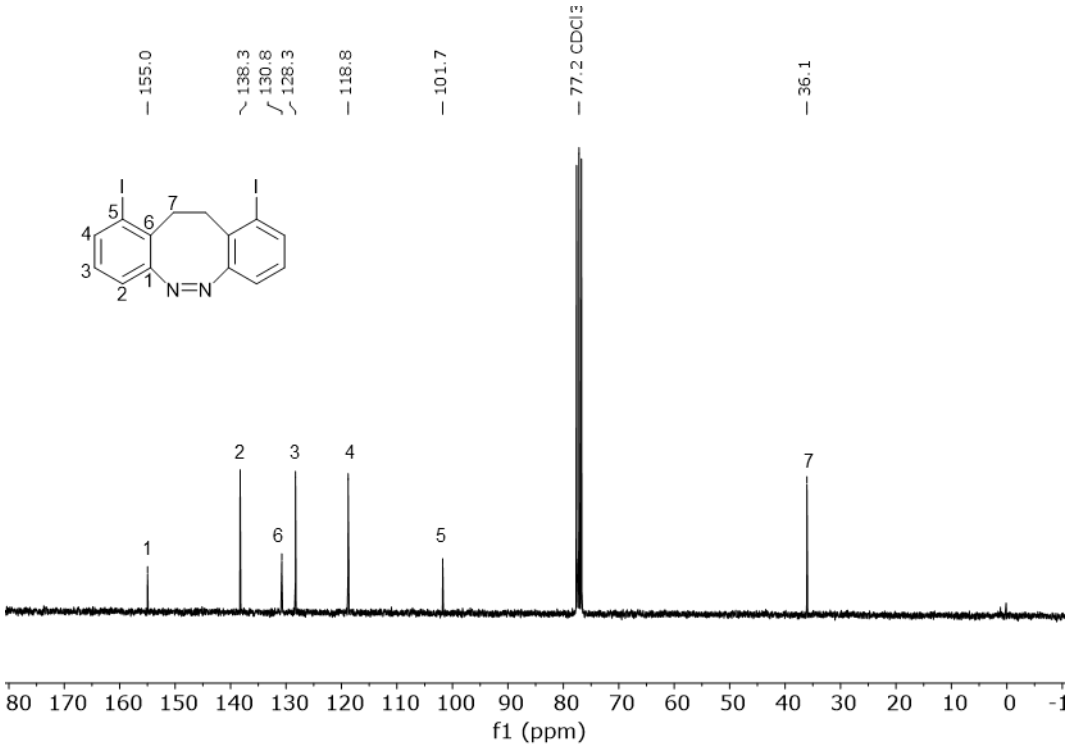


Figure S21 – ^{13}C NMR spectrum (75 MHz) of **5** in $CDCl_3$ recorded at 25 °C.

Figure S22 – ^{1}H-^{1}H COSY spectrum of **5** in $CDCl_3$ recorded at 25 °C.

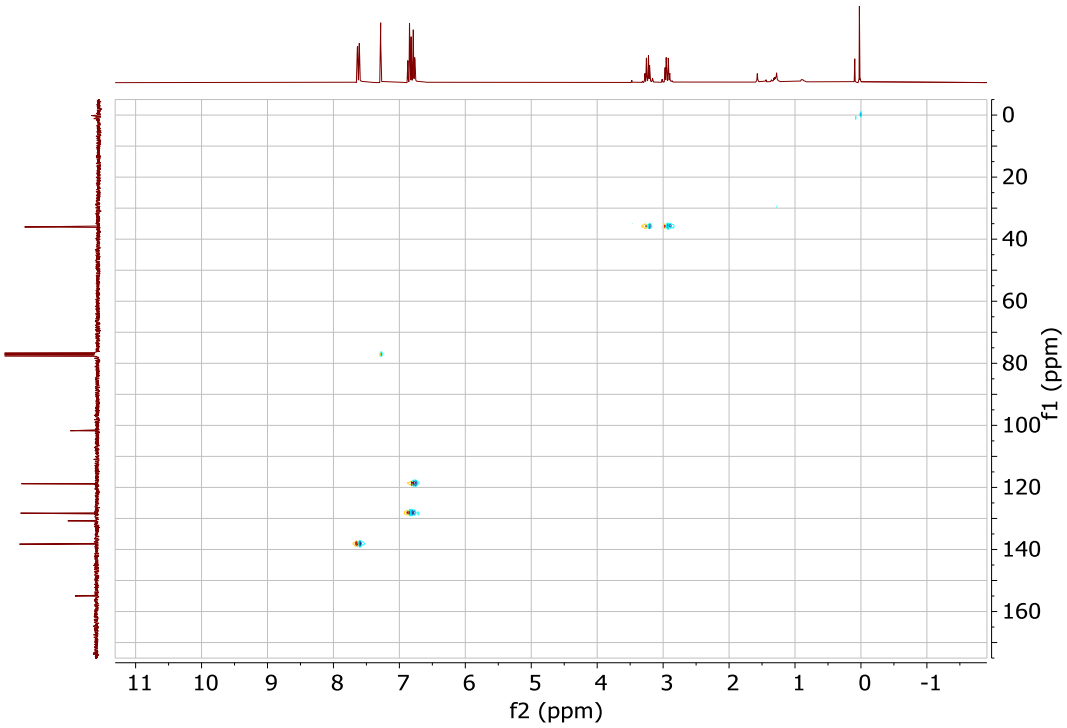


Figure S23 – ^{1}H-^{13}C HSQC spectrum of **5** in $CDCl_3$ recorded at 25 °C.

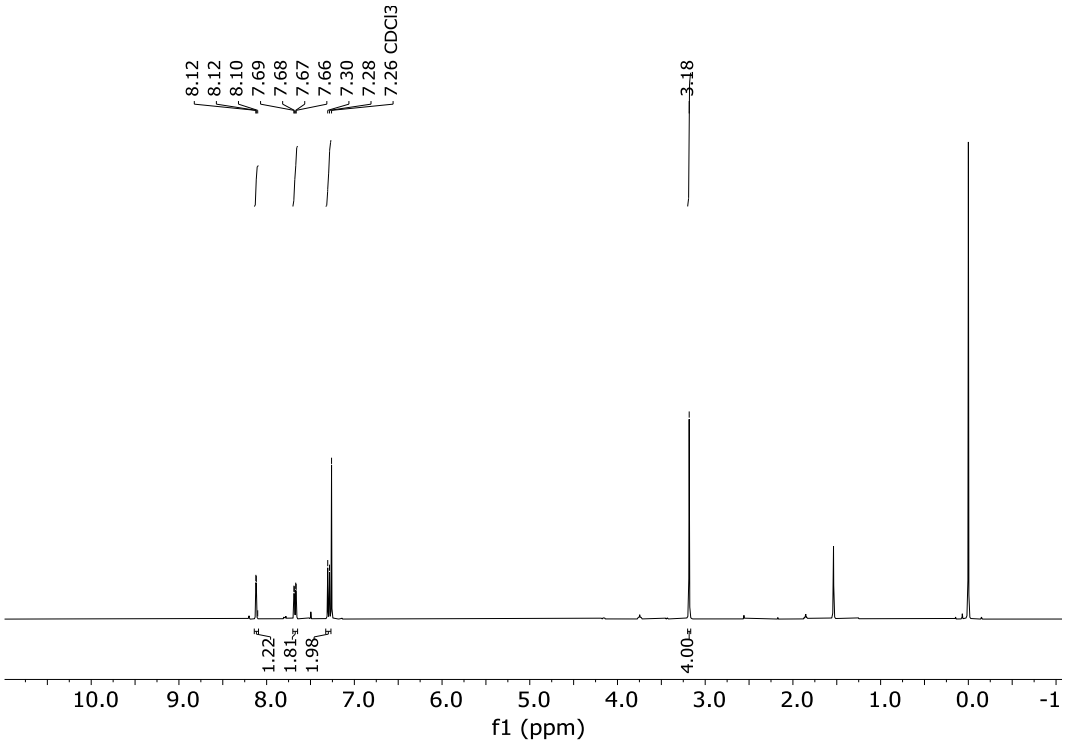


Figure S24 – ^{1}H NMR spectrum (400 MHz) of **13** in $CDCl_3$ recorded at 25 °C.

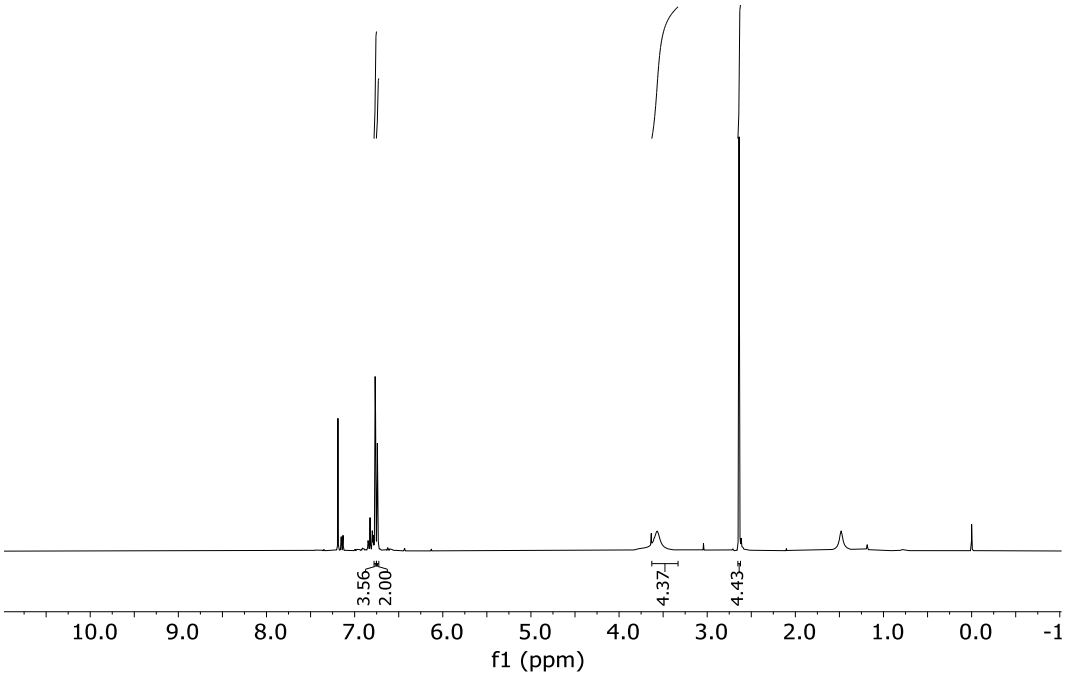


Figure S25 – ^{1}H NMR spectrum (400 MHz) of **14** in $CDCl_3$ recorded at 25 °C.

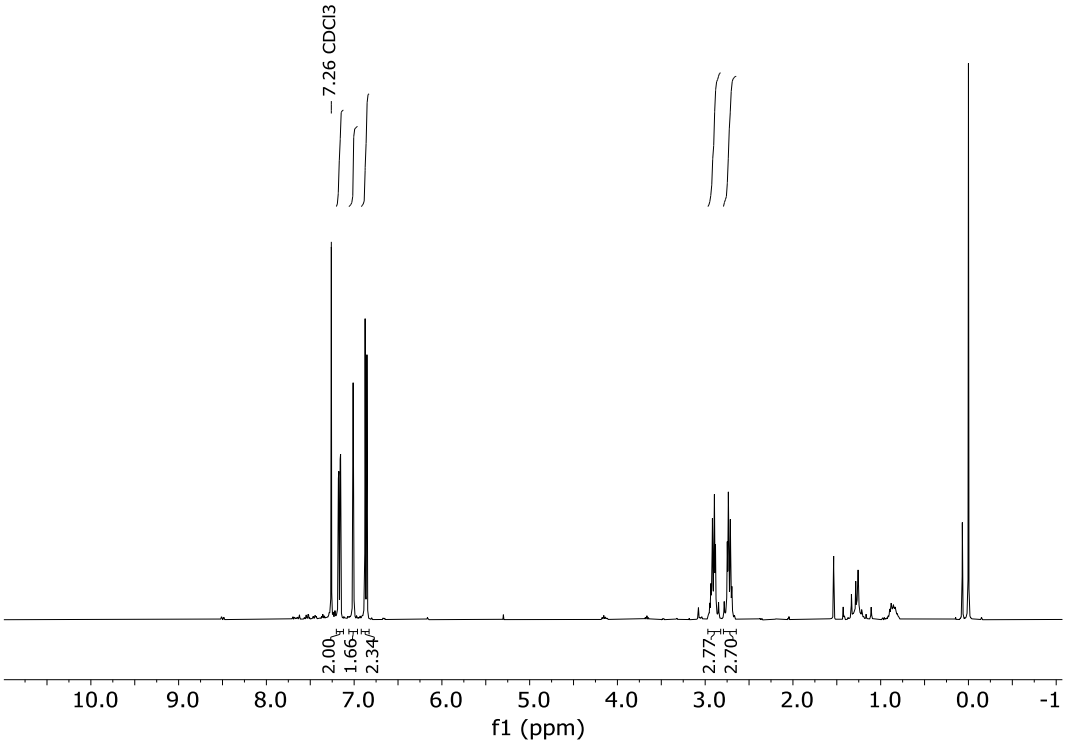


Figure S26 – ^{1}H NMR spectrum (400 MHz) of **15** in $CDCl_3$ recorded at 25 °C.

4. 5. 6. References

1 R. K Harris, E. D Becker, S. M Cabral de Menezes, R. Goodfellow and P. Granger, *Solid State Nucl. Magn. Reason.*, 2002, **22**, 458–483.

2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16 (Revision B.01), Gaussian Inc., Pittsburgh, PA, 2016.

3 a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789; b) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206; c) A. D. Becke, *Chem. Phys*., 1993, **98**, 5648–5652.

4 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *Chem. Phys.*, 2010, **132**, 154104–154123.

5 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

6 a) W. J. Hehre, R. Ditchfield and J. A. Pople, *Chem. Phys.*, 2003, **56**, 2257–2261; b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *Chem. Phys*, 1982, **77**, 3654–3665.

7 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chem. Acc.*, 1990, **77**, 123–141.

8 A. Höllwarth, M. Böhme, S Dapprich, A.W. Ehlers, A. Gobbi, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 237–240.

9 A.W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111–114.

10 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

11 G. Cabré, A. Garrido-Charles, À. González-Lafont, W. Moormann, D. Langbehn, D. Egea, J. M. Lluch, R. Herges, R. Alibés, F. Busqué, P. Gorostiza and J. Hernando, *Org. Lett.*, 2019, **21**, 3780–3784.

12 F. Klockmann, C. Fangmann, E. Zender, T. Schanz, C. Catapano and A. Terfort, *ACS Omega*, 2021, **6**, 18434–18441.

13 A. Mourot, M. A. Kienzler, M. R. Banghart, T. Fehrentz, F. M. E. Huber, M. Stein, R. H. Kramer and D. Trauner, *ACS Chem. Neurosci.*, 2011, **2**, 536–543.

14 M. S. Maier, K. Hüll, M. Reynders, B. S. Matsuura, P. Leippe, T. Ko, L. Schäffer and D. Trauner, *J. Am. Chem. Soc.*, 2019, **141**, 17295–17304.

15 A. Klapars and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 14844–14845.

16 M. M. Farah, P. C. B. Page, B. R. Buckley, A. J. Blacker and M. R. Elsegood, *Tetrahedron*, 2013, **69**, 758–769.

17 O Herd, A Heßler, M Hingst, P Machnitzki, M Tepper and O Stelzer, *Catal. Today*, 1998, **42**, 413–420.

Chapter 5

Summary

This dissertation focused on the development of novel photoswitchable phosphine ligands for their integration into transition metal complexes, eventually aiming to enable light-induced modulation of their catalytic properties. Two different approaches were explored toward this goal, which involved the utilization of two distinct photoswitchable scaffolds: dithienylethenes (DTEs) and diazocines.

5. 1. Dithienylethene-based photoswitchable phosphines

In a first step, the photomodulation of metal catalysts was pursued by exploring the electronic effects achieved on phosphine ligands through the photoisomerization of connected DTE photoswitches. This molecular design capitalizes on the intrinsic change in conjugation that takes place in DTEs upon photocyclization, which makes the substituents at positions 5 and 5' of their thiophene rings become electronically connected only in their ring-closed state. Therefore, by introducing a phosphine group to one of these positions and an electron-withdrawing group (EWG; EWG = trifluoroacetyl and perfluorophenyl) to the other, a decrease in electron density on the phosphorus atom – i.e., on σ-donating ability - should take place upon DTE ring-closing (Figure 5-1).

To validate this concept, the preparation of DTE-based phosphine ligands **DTE-$COCF_3$** and **DTE-C_6F_5**, and of an additional compound containing an electronically neutral substituent (phenyl group, **DTE-Ph**) was first undertaken. The synthesis of all these ligands involved the derivatization of a common dichlorinated DTE substrate promoted through sequential chlorine/lithium exchange reactions. Introduction of the phosphanyl and EWG groups was accomplished by quenching the resulting organolithiated compounds with the required electrophile. As for phenyl ring installation, it was accomplished through subsequent borylation and Suzuki coupling reactions.

The obtained DTE-based ligands underwent successful reversible photoisomerization under UV (for ring-closing) and visible light irradiation (for ring-opening). The best photoswitching performance was observed for ligand **DTE-$COCF_3$**, exhibiting high ring-cyclization quantum yield and conversion as well as good fatigue resistance. These favorable results were attributed to the effect of the strong EWG in its structure.

To estimate the change in electron density on the phosphorus atom of the ligands upon photoisomerization, phosphine selenides were prepared. The nature of the phosphine-selenium bond allowed the estimation of each ligand's σ-donating ability through NMR measurements.

Experimental results demonstrated that electron density modulation depended on the introduced substituent, with **DTE-COCF$_3$** showing the highest modulation. These findings were supported by several calculated phosphine descriptors.

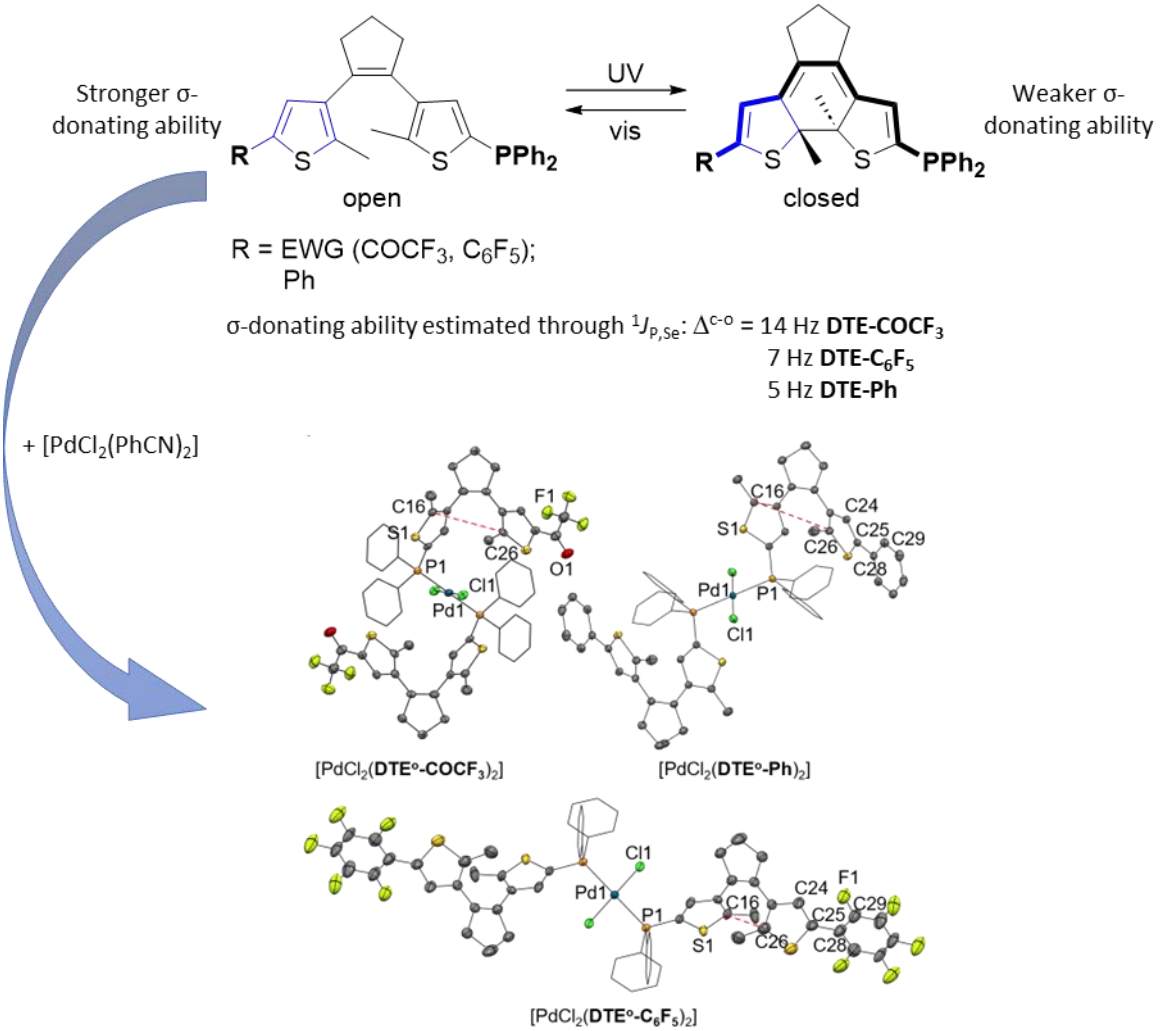


Figure 5-1 – Structure of the DTE-based phosphines prepared, where photoswitching of the dithienylethene backbone caused a change in phosphine electronic properties that was dependent on the introduced EWG substituent. Bisligated Pd^{II} complexes could be obtained from these ligands, which were subsequently tested as pre-catalysts for Stille coupling.

The obtained ligands were complexed with Pd(II) to investigate the impact of metal complexation on the photoswitchable ability of the system. UV-irradiated Pd(II) bisligated complexes exhibited three different isomers featuring two ring-open (**oo**), one ring-open and one ring-closed (**oc**), and two ring-closed (**cc**) DTE units. Complexation detrimentally affected ring-closing quantum yields due to ligand-to-metal charge transfer, resulting in less efficient photochemical reactions. Despite this, photoswitching was not fully hindered by metal complexation, prompting further catalytic studies for the ring-open and ring-closed states of the Pd(II) compounds.

Catalytic tests were conducted for a model Stille coupling reaction, which revealed that higher conversions were achieved when using the ring-closed complexes bearing EWG substituents as pre-catalysts. Therefore, these results verified the initial hypothesis that the presence of these groups would selectively affect phosphine electron properties upon DTE photocyclization, thus ultimately modifying the catalytic performance of their metal complexes. In this case, reaction rate acceleration was expected to take place for the ring-closed state of the metal catalysts due to the lower binding strength of photocyclized DTE-based phosphines to palladium(0) species, a situation that was confirmed by DFT calculations of the catalytic cycle.

As an extension of this strategy toward photoswitchable catalysis, a bisDTE ligand was designed that features two DTE moieties with trifluoroacetyl groups attached to phenylphosphine. To our knowledge, this would represent the first example reported of the introduction of more than one DTE unit to the phosphorus atom of phosphines. The synthesis of the bisDTE ligand **1** was conducted similarly as for **DTE-COCF$_3$**, employing chlorine/lithium exchange reactions and quenching with an appropriate electrophile to install the desired phenylphosphine and trifluoromethyl ketone groups. Photochemical studies in solution revealed that fully open ligand **1oo** can successfully undergo isomerization into ring-closed **1oc** and **1cc** states, though with limited efficacy for the second photocyclization reaction (Figure 5-2). Importantly, the preparation of the corresponding phosphine selenides and their analysis by NMR demonstrated that the fully closed form of the ligand **1cc** experienced the largest modulation of electron density reported to date for photoswitchable phosphines ($\Delta^{cc\text{-}oo}$ ($^1J_{P,Se}$) = 19 Hz). This prompted the preparation of the gold(I) complex of **1**, which was shown to preserve the photoswitching behavior of its constituting bisDTE phosphine ligand.

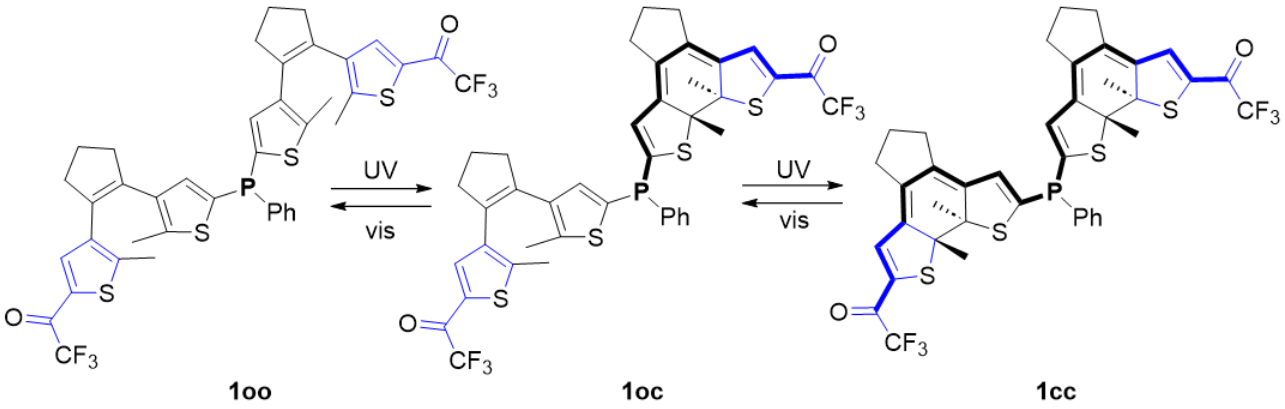


Figure 5-2 – Photoswitching of bisDTE ligand **1**, which strongly modulates the σ-donating ability of the attached phosphanyl group.

5. 2. Diazocine-based photoswitchable phosphine

In an attempt to achieve metal catalyst photomodulation based on geometric effects, the use of diazocine photoswitches was explored in the second part of the thesis. By introducing two phosphanyl groups to this type of photoswitchable scaffold, it was envisioned to modify their coordination mode to metals under irradiation. Through DFT calculations, the preferred substitution pattern of the diazocine core to accomplish this goal was identified: it involved installing the two phosphanyl substituents at positions 1 and 10 of the diazocine (Figure 5-3). For this particular type of ligand structures, variation of the coordination mode was computationally revealed, as their *Z* isomer could act as a bidentate ligand while their *E* isomer could only monocoordinate metal centers due to the increased separation distance between the phosphanyl groups.

Encouraged by these results, several synthetic routes were explored to prepare the desired 1,10-disubstituted diazocine-based bisphosphines. However, functionalization of these positions of the diazocine core with diphenylphosphine groups could not be accomplished, in contrast to what was observed for other positions of the photoswitch scaffold. This indicates that the derivatization of diazocines at the target positions 1 and 10 is severely hampered by steric hindrance effects.

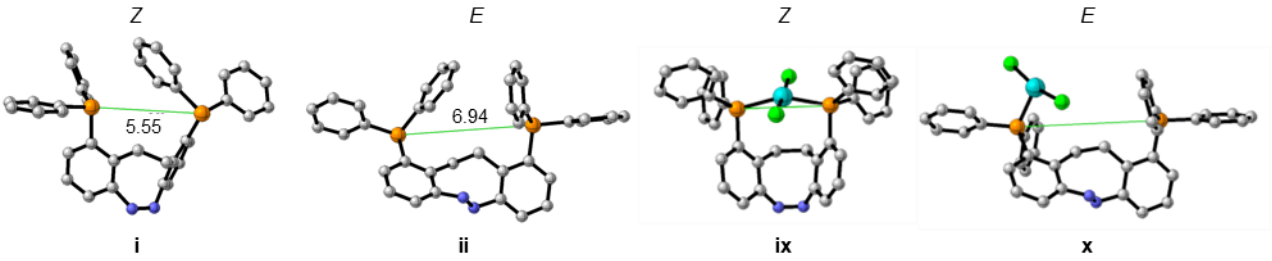


Figure 5-3 – Computed structures of the *Z* and *E* states of the free ligands and palladium(II) complexes of a 1,10-disubstituted diazocine-based bisphosphine. A clear change in separation distance between the two phosphanyl groups occurs upon *Z*-*E* photoisomerization, which leads to a variation of the coordination mode to the metal center.

5. 3. Conclusions and outlook

A library of DTE-substituted ligands was developed in this thesis to validate two new concepts for the modulation of phosphine electron properties upon irradiation: (i) switching the communication between phosphanyl and electron-withdrawing groups installed at the 5 and 5' positions of the thiophene rings of the DTE core; and (ii) connecting two of these DTE photoswitches to the same phosphine. The resulting ligands showed ample variation of phosphine σ-donation ability upon DTE photoisomerization. Aiming to exploit this behavior in photoswitchable catalysis, they were complexed to metal centers and some of them were tested as pre-catalysts for a model Stille coupling reaction, where a change in catalytic activity was finally observed for the different

isomerization states of the system. These results open new ways for the application of DTE-induced electronic changes on ligands in the field of photoswitchable catalysis.

As for the attempt to pioneer the use of diazocines to light-control metal-based catalysis, the synthesis of the target diazocine-based phosphines was not successful. Despite this, valuable knowledge was gained about how to use this type of scaffold for photoswitchable catalysis and what challenges must be faced during their derivatization. To ultimately bring this molecular design to life, further exploration of the synthetic approaches towards diazocine-based ligands is therefore required.

Chapter 6

Appendices

6. 1. Abbreviations

Å	Ångström
BE	binding energy
BS1	basis set
BS2	extended basis set
c	concentration
c	closed state
cc	closed-closed state
CCDC	Cambridge Crystallographic Data Centre
COSY	correlation spectroscopy
δ	chemical shift
d	doublet (NMR)
DAE	diarylethene(s)
DFT	density functional theory
DTE	dithienylethene(s)
ε	(molar decadic) extinction coefficient
e.g.	for example
ECP	effective core potential
EDG	electron-donating group
eq.	equivalents
ESI	electrospray ionization
et al.	*Et alii*
EWG	electron-withdrawing group
Φ	quantum yield
h	hour(s)
HMBC	heteronuclear multiple bond correlation
HOMO	highest occupied molecular orbital
HRMS	high-resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
IR	infrared
$^{n}J_{XY}$	coupling constant of nuclei X and Y over n bonds

λ	wavelength
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
m	multiplet (NMR) / medium strength (IR)
m.p.	melting point
NBO	natural bond orbitals
NHC	*N*-heterocyclic carbenes
nm	nanometer
NMR	nuclear magnetic resonance
o	open state
oc	open-closed state
oo	open-open state
ppm	parts per million
PSS	photostationary state
R	(unspecified) residue
R_f	retention factor
rt	room temperature
s	singlet (NMR) / strong strength (IR)
§	section
SMD	solvent model density
t	triplet (NMR)
TD-DFT	time-dependent density functional theory
THF	tetrahydrofuran
TOF	time-of-flight
TLC	thin layer chromatography
TS	transition state
UV	ultraviolet region of light
Vis	visible region of light
w	weak strength (IR)
XRD	X-ray diffraction

6. 2. Scientific Curriculum Vitae

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EDUCATION

Doctoral Student in Chemistry *October 2020 – Present*

Leipzig University (Leipzig, Germany)
Universitat Autònoma de Barcelona (Bellaterra, Spain)
Supervisors: Prof. Dr. Evamarie Hey-Hawkins and Prof. Dr. Rosa María Sebastián
Title: Photoswitchable phosphines for light-modulated catalysts

Master of Science *September 2018 – June 2020*

ITMO University (Saint Petersburg, Russia)
Nanoengineering for Green chemistry and Advanced Materials
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Supervisor: Dr. Pavel Krivoshapkin
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Bachelor of Science *September 2014 – June 2018*

Saint Petersburg State Technological Institute (Technical University) (Saint Petersburg, Russia)
Chemical technology of organic dyes and phototropic compounds
Graduated with high honors. GPA 4.85 (out of max. 5)
Supervisor: Dr. Andrei Ziminov
Title: Synthesis and study of zinc phthalocyanines with tetrahydrocarbazole- and pyrazole-containing substituents

High-School Diploma *September 2003 – June 2014*
Comprehensive School №106, Saint Petersburg

WORK AND RESEARCH EXPERIENCE

Doctoral Candidate *October 2020 – September 2023*

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INTERNSHIPS AND RESEARCH STAYS

Elkem Silicones France (Lyon, France) *August 2023 –September 2023*

Supervisor: Dr. James Delorme

Universitat Autònoma de Barcelona (Bellaterra, Spain) *February 2022 –April 2022*
Supervisor: Prof. Dr. Agustí Lledós

Leipzig University (Leipzig, Germany) *April 2019 – June 2019*
Supervisor: Prof. Dr. Evamarie Hey-Hawkins

SUMMER SCHOOLS, CONFERENCES and WORKSHOPS

- The VIII scientific and technical conference of students, postgraduates, and young scientists "WEEK OF SCIENCE-2018". 2018. Oral presentation "Synthesis and study of aggregation of tetrasubstituted zinc phthalocyanine containing tetrahydrocarbazole groups".
- The 20th International Sol-Gel Conference. 2019. Poster presentation: "Functionalization of hafnium oxide nanoparticles".
- III International School-Conference "Applied Nanotechnology & Nanotoxicology". 2019. Oral presentation "Hafnium oxide nanoparticles modified with polymer shell"; Diploma for the best oral presentation.
- The BuildMoNa Annual Conference. 2021. Poster presentation "Photo-switchable phosphines for *in situ* modification of catalysts"
- CCIMC 1st International Workshop. *Cutting-Edge Homogeneous Catalysis 1* (CEHC-1) Science Conference (May 4th-6th 2021 in Toulouse, France). Poster presentation "Photoswitchable phosphines for in situ modification of catalysts".
- *Heteroelements and Coordination Chemistry: From Concepts to Applications* (HC3A) International Research Network (20th-21st January 2022 at Universitat de Barcelona). Poster presentation "Synthetic strategies towards diazocine modification".
- The BuildMoNa Annual Conference. 2022. Poster presentation "Dithienylethene-based photoswitchable phosphines for *in situ* modification of catalysts".
- CCIMC 2nd International Workshop. *Cutting-Edge Homogeneous Catalysis 2* (CEHC-2) Science Conference (March 29th-31st 2022 at Universität Leipzig, Leipzig, Germany). Poster presentation "Synthesis of functionalisable photoswitchable diazocines". Award to the best poster".

- International School on Innovations in Homogeneous and Supported Homogeneous Catalysis (ISI-HSHC). Scientific school (25th to 28th April 2023, Bucharest, Romania). Poster presentation "Dithienylethene-based photoswitchable phosphines for in situ modification of catalysts".
- International School on Innovations in Homogeneous and Supported Homogeneous Catalysis (ISI-HSHC). Scientific school (25th to 28th April 2023, Bucharest, Romania). Oral presentation "My thesis in 180 seconds".
- XII Doctoral Workshop, PhD programme in Chemistry UAB, May 29-30 and June 2nd, 2023. Poster presentation "Dithienylethene-based photoswitchable phosphines for in situ modification of catalysts".
- XII Doctoral Workshop, PhD programme in Chemistry UAB, May 29-30 and June 2nd, 2023. Oral presentation "Development of photoswitchable phosphorus ligands".

SCHOLARSHIPS AND AWARDS

- Early-Stage Researcher as part of the CCIMC "Coordination Chemistry Inspires Molecular Catalysis" ITN program, as part of a Horizon 2020 European Union's funded research program. Competitive grant winner for the performance of the doctoral studies in co-tuetelle agreement between Leipzig University and the Universitat Autònoma de Barcelona.

PUBLICATIONS

- Ziminov A.V., Mal'tsev V.K., Sherstiuk A.A., Vikent'eva Yu.A., Seravin N.S., Ramsh S.M. Synthesis and Aggregation of Cationic Zinc and Magnesium Phthalocyanines Containing 4-(3.5-Dimethyl-1H-pyrazol-1-yl)phenoxy Groups, *Russ. J. Gen. Chem.*, **2018**, *88* (8), 1648–1656.
- Shiryaeva E.S., Baranova I.A., Kiselev G.O., Morozov V.N., Belousov A.V., Sherstiuk A.A., Kolyvanova M.A., Krivoshapkin P.V., Feldman V.I. Hafnium Oxide as a Nanoradiosensitizer under X-ray Irradiation of Aqueous Organic Systems: A Model Study Using the Spin-Trapping Technique and Monte Carlo Simulations, *J. Phys. Chem. C.*, **2019**, *123* (45), 27375-27384.
- Sherstiuk A.A., Tsymbal S.A., Fakhardo A.F., Morozov V.N., Krivoshapkina E.F., Hey-Hawkins E., and Krivoshapkin P.V. Hafnium Oxide-Based Nanoplatform for Combined Chemoradiotherapy, *ACS Biomater. Sci. Eng.*, **2021**, *7* (12), 5633-5641.
- Sherstiuk A., Lledós A., Lönnecke P., Hernando J., Sebastián R. M., Hey-Hawkins E., Dithienylethene-based photoswitchable phosphines for light-controlled palladium-catalyzed Stille coupling reaction, *ChemRxiv.*, 2023.
- Sherstiuk A., Villabona M., Lledós A., Hernando J., Sebastián R. M., Hey-Hawkins E., Amplified photomodulation of a bis(dithienylethene)-substituted phosphine, *ChemRxiv.*, 2023.

6. 3. Cartesian coordinates for the structures reported in Chapter 2

DTE^{o}-COCF$_3$

C	2.759474000	1.146499000	-0.626776000
C	2.330436000	-0.124591000	-1.002367000
S	3.456555000	-1.353428000	-0.519939000
C	4.540454000	-0.165924000	0.183190000
C	4.021628000	1.103704000	0.026042000
H	4.541023000	1.980872000	0.393614000
C	1.085029000	-0.516156000	-1.731234000
H	0.302608000	-0.814495000	-1.024929000
H	0.707569000	0.332691000	-2.305344000
H	1.261471000	-1.353653000	-2.413029000
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C	0.467114000	4.150027000	-1.123079000
C	0.749118000	2.712145000	-0.716607000
C	2.059692000	2.413509000	-0.884483000
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C	-0.235588000	1.126519000	1.009245000
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H	1.573392000	1.863586000	1.872605000
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C	-4.912400000	-3.261460000	-2.176732000
C	-2.562801000	-2.838831000	-2.537727000
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H	-1.825520000	-0.944350000	-1.836283000
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O	6.541197000	0.414126000	1.30317100
C	6.229047000	-1.931511000	0.984987000
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F	7.412034000	-2.044746000	1.593510000
F	5.314202000	-2.622947000	1.702546000

DTE^{c}-COCF$_3$

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H	5.302224000	1.792394000	4.720721000
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C	4.485622000	-2.033865000	0.085037000
C	4.807585000	-1.547227000	-2.263833000
C	4.791082000	-3.374334000	-0.154319000
C	5.106598000	-2.890384000	-2.502607000
C	5.099508000	-3.805555000	-1.447767000
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H	-1.963091000	0.663831000	2.261753000
H	-0.330122000	-0.012413000	2.117173000
C	-5.028743000	-1.775774000	0.819537000
O	-4.950382000	-2.932555000	1.215979000
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F	-6.679431000	-0.774979000	-0.603498000
F	-7.392360000	-1.985118000	1.060389000
F	-6.541368000	-0.015711000	1.432909000

DTE^{o}-C_6F_5

C	1.710839000	1.317954000	-0.785383000
C	1.265803000	0.137817000	-1.352811000
S	2.451436000	-1.127434000	-1.186306000
C	3.588114000	-0.057491000	-0.373907000
C	3.036951000	1.196875000	-0.256498000
H	3.550428000	2.021536000	0.218037000
C	-0.035720000	-0.158488000	-2.029869000
H	-0.744688000	-0.621255000	-1.333981000
H	-0.485726000	0.768972000	-2.391153000
H	0.093791000	-0.837300000	-2.878991000
C	0.548035000	4.892410000	-1.276425000
C	-0.647188000	4.301190000	-0.500762000
C	-0.316361000	2.819713000	-0.402592000
C	0.978487000	2.591382000	-0.730579000
C	1.701076000	3.898621000	-1.024120000
H	0.789318000	5.916330000	-0.977137000
H	-1.609600000	4.488514000	-0.990499000
H	-0.729526000	4.722965000	0.512012000
H	2.391446000	3.815318000	-1.870712000
H	2.305837000	4.194723000	-0.153826000
H	0.313791000	4.905891000	-2.346846000
C	-2.672361000	1.859242000	-0.428146000
C	-3.486658000	0.897759000	0.114490000
S	-2.595456000	-0.019137000	1.318825000
C	-1.138937000	0.907982000	1.058747000
C	-1.327063000	1.865658000	0.078349000
H	-3.014216000	2.544527000	-1.196855000
C	0.082755000	0.623054000	1.877452000
H	0.661653000	-0.207816000	1.457491000
H	0.734268000	1.500045000	1.894509000
H	-0.176677000	0.362740000	2.908681000
P	-5.205976000	0.585876000	-0.409737000
C	-5.037497000	-0.948440000	-1.434794000
C	-6.171196000	-1.746741000	-1.668415000
C	-3.838156000	-1.275473000	-2.084611000
C	-6.097598000	-2.855277000	-2.512626000
C	-3.767614000	-2.382478000	-2.933816000
C	-4.894844000	-3.178033000	-3.148286000
H	-7.112254000	-1.511092000	-1.177943000
H	-2.955598000	-0.664146000	-1.927828000
H	-6.980847000	-3.467422000	-2.673938000
H	-2.827620000	-2.623318000	-3.423352000
H	-4.839056000	-4.040970000	-3.805900000
C	-5.966636000	-0.058318000	1.149297000
C	-5.781544000	-1.367550000	1.625294000
C	-6.740077000	0.835785000	1.906221000
C	-6.351072000	-1.766873000	2.835335000
C	-7.305896000	0.436430000	3.119197000
C	-7.112179000	-0.865636000	3.585433000
H	-5.198218000	-2.077875000	1.047518000
H	-6.900565000	1.848855000	1.545710000
H	-6.199691000	-2.781741000	3.192791000
H	-7.901473000	1.139540000	3.694827000
H	-7.555742000	-1.179179000	4.526359000
C	4.924252000	-0.489864000	0.042308000
C	5.989154000	0.421332000	0.173269000
C	5.241504000	-1.827096000	0.336644000
C	7.262783000	0.035641000	0.573873000
C	6.510474000	-2.234928000	0.730177000
C	7.531522000	-1.299817000	0.854356000
F	5.812664000	1.725977000	-0.100529000
F	8.238389000	0.948414000	0.678735000
F	8.755813000	-1.678721000	1.236308000
F	6.748535000	-3.525844000	0.998352000
F	4.298602000	-2.783037000	0.240021000

DTE^{c}-C_6F_5

C	-1.594303000	1.803909000	0.135557000
C	-0.660430000	0.599183000	0.354182000
S	-1.737173000	-0.890394000	-0.017770000
C	-3.221817000	0.098229000	0.137904000

C	-2.976222000	1.438448000	0.192792000
H	-3.768162000	2.175637000	0.239872000
C	-0.557329000	5.326493000	0.456245000
C	0.741465000	4.672671000	-0.076251000
C	0.396871000	3.200244000	-0.141143000
C	-1.042566000	3.036984000	-0.018754000
C	-1.696402000	4.398630000	-0.033804000
H	-0.679183000	6.360388000	0.122235000
H	1.615420000	4.882162000	0.548629000
H	0.973688000	5.040561000	-1.085252000
H	-2.597175000	4.453618000	0.584467000
H	-1.986925000	4.663460000	-1.060458000
H	-0.541141000	5.328111000	1.552131000
C	2.642224000	2.071869000	-0.369369000
C	3.178756000	0.821199000	-0.320122000
S	1.954808000	-0.475059000	-0.219957000
C	0.568172000	0.745170000	-0.570350000
C	1.207927000	2.125075000	-0.322584000
H	3.256325000	2.966501000	-0.398661000
P	4.987948000	0.533344000	-0.299825000
C	5.219765000	-0.265126000	1.354698000
C	6.340385000	-1.084657000	1.576027000
C	4.375712000	0.029976000	2.437082000
C	6.596567000	-1.611466000	2.842615000
C	4.636353000	-0.496031000	3.704470000
C	5.744517000	-1.320169000	3.911563000
H	7.008953000	-1.324312000	0.753377000
H	3.508146000	0.666685000	2.292194000
H	7.462134000	-2.250889000	2.993384000
H	3.967480000	-0.264016000	4.528883000
H	5.943703000	-1.731587000	4.897079000
C	5.159843000	-0.889261000	-1.470074000
C	4.824998000	-2.216242000	-1.151531000
C	5.620554000	-0.597575000	-2.763340000
C	4.944790000	-3.224398000	-2.108443000
C	5.735018000	-1.606765000	-3.722847000
C	5.397720000	-2.921602000	-3.396231000
H	4.478408000	-2.465021000	-0.153409000
H	5.891726000	0.423130000	-3.021695000
H	4.682114000	-4.246431000	-1.849545000
H	6.092417000	-1.366056000	-4.720206000
H	5.490398000	-3.708720000	-4.139416000
C	0.232971000	0.641154000	-2.076102000
H	-0.538105000	1.370091000	-2.342773000
H	1.131365000	0.856501000	-2.660112000
H	-0.123788000	-0.355522000	-2.341979000
C	-0.301658000	0.545411000	1.857939000
H	0.284424000	1.426294000	2.135751000
H	-1.221097000	0.541514000	2.448777000
H	0.275148000	-0.348208000	2.102719000
C	-4.550389000	-0.523778000	0.113880000
C	-5.633375000	0.099262000	-0.535001000
C	-4.830274000	-1.766832000	0.707482000
C	-6.901973000	-0.464830000	-0.582289000
C	-6.092010000	-2.349809000	0.664383000
C	-7.136274000	-1.697905000	0.018335000
F	-5.470559000	1.279391000	-1.155794000
F	-7.898462000	0.168443000	-1.215798000
F	-8.354123000	-2.247062000	-0.021963000
F	-6.307331000	-3.532374000	1.255759000
F	-3.872323000	-2.440793000	1.363737000

DTE^{o}-Ph

C	2.812527000	0.855769000	-0.761248000
C	2.309136000	-0.377667000	-1.129013000
S	3.409687000	-1.658617000	-0.678020000
C	4.570415000	-0.529144000	0.004769000
C	4.103049000	0.752507000	-0.137288000
H	4.644068000	1.616086000	0.233020000
C	1.024433000	-0.716272000	-1.818553000
H	0.254466000	-1.013755000	-1.097279000
H	0.649988000	0.156062000	-2.359213000
H	1.151308000	-1.538048000	-2.531275000
C	1.917961000	4.341767000	-1.953495000
C	0.653194000	3.975795000	-1.149703000
C	0.877329000	2.520256000	-0.768590000
C	2.166620000	2.158362000	-0.977611000
C	2.988323000	3.344673000	-1.462388000
H	2.215598000	5.387297000	-1.832379000
H	-0.272793000	4.128285000	-1.715851000
H	0.558222000	4.580663000	-0.235512000
H	3.707273000	3.066437000	-2.240871000
H	3.573495000	3.760029000	-0.628181000
H	1.730901000	4.171277000	-3.019746000
C	-1.535280000	1.710461000	-0.752434000
C	-2.435976000	0.913790000	-0.091904000
S	-1.662683000	0.182952000	1.305629000
C	-0.137013000	0.960634000	0.964774000
C	-0.216434000	1.731907000	-0.180771000
H	-1.795235000	2.261123000	-1.650639000
C	1.025920000	0.757770000	1.886624000
H	1.567891000	-0.165203000	1.649854000
H	1.732211000	1.585226000	1.785175000
H	0.705057000	0.700200000	2.931709000
P	-4.145696000	0.607735000	-0.648980000
C	-4.033787000	-1.107418000	-1.341153000
C	-5.200331000	-1.883387000	-1.458565000
C	-2.833768000	-1.612217000	-1.863897000
C	-5.159140000	-3.141077000	-2.061826000
C	-2.795423000	-2.869151000	-2.472177000
C	-3.955807000	-3.639737000	-2.569689000

H	-6.142363000	-1.511347000	-1.064154000
H	-1.925301000	-1.022670000	-1.796268000
H	-6.068097000	-3.732236000	-2.134028000
H	-1.854583000	-3.245821000	-2.864732000
H	-3.924925000	-4.619093000	-3.038850000
C	-5.027489000	0.335253000	0.955109000
C	-4.948653000	-0.855233000	1.697941000
C	-5.785791000	1.401985000	1.462580000
C	-5.606878000	-0.969101000	2.923338000
C	-6.441091000	1.288415000	2.690986000
C	-6.352590000	0.102534000	3.423067000
H	-4.378770000	-1.696705000	1.316207000
H	-5.864672000	2.325676000	0.894630000
H	-5.536948000	-1.894682000	3.488175000
H	-7.024008000	2.122659000	3.071341000
H	-6.865621000	0.010899000	4.376372000
C	5.832840000	-0.977663000	0.605914000
C	6.950937000	-0.120506000	0.619147000
C	5.965098000	-2.254036000	1.184550000
C	8.150935000	-0.523385000	1.201767000
C	7.171329000	-2.658241000	1.755568000
C	8.269417000	-1.794780000	1.771102000
H	6.880629000	0.857670000	0.153392000
H	5.113732000	-2.929019000	1.204816000
H	9.000727000	0.153762000	1.199773000
H	7.249379000	-3.647875000	2.197076000
H	9.207679000	-2.109436000	2.218804000

DTE^{c}-Ph

C	-2.709941000	1.312333000	-0.134644000
C	-1.646772000	0.269485000	0.263220000
S	-2.537282000	-1.372071000	0.100540000
C	-4.130630000	-0.558809000	0.120174000
C	-4.040200000	0.795714000	-0.016205000
H	-4.912383000	1.440122000	-0.045739000
C	-2.084986000	4.941673000	-0.303027000
C	-0.709196000	4.374351000	-0.730541000
C	-0.882822000	2.877174000	-0.589729000
C	-2.297067000	2.567351000	-0.457744000
C	-3.100661000	3.830304000	-0.666048000
H	-2.314834000	5.899321000	-0.778165000
H	0.121824000	4.768030000	-0.136614000
H	-0.498315000	4.622658000	-1.780036000
H	-4.013885000	3.866955000	-0.064534000
H	-3.399748000	3.918857000	-1.720387000
H	-2.093343000	5.095885000	0.782083000
C	1.483694000	1.999776000	-0.630933000
C	2.159571000	0.840391000	-0.399334000
S	1.087450000	-0.563696000	-0.127033000
C	-0.419768000	0.425004000	-0.661998000
C	0.052034000	1.890736000	-0.608070000
H	1.991952000	2.947231000	-0.781312000
P	3.986860000	0.770968000	-0.323123000
C	4.271775000	0.219209000	1.421622000
C	5.475418000	-0.425740000	1.756053000
C	3.372157000	0.542307000	2.449821000
C	5.760195000	-0.757270000	3.081335000
C	3.661103000	0.212411000	3.775996000
C	4.853051000	-0.440785000	4.096447000
H	6.188187000	-0.683278000	0.977141000
H	2.439798000	1.047820000	2.216956000
H	6.691146000	-1.264468000	3.320051000
H	2.949094000	0.462584000	4.557886000
H	5.074590000	-0.700115000	5.127892000
C	4.353691000	-0.758585000	-1.298523000
C	4.167366000	-2.064716000	-0.814835000
C	4.810912000	-0.581614000	-2.613664000
C	4.428764000	-3.165079000	-1.631714000
C	5.067227000	-1.683863000	-3.433183000
C	4.876839000	-2.977146000	-2.942866000
H	3.826064000	-2.223659000	0.203265000
H	4.968093000	0.422702000	-2.999357000
H	4.280324000	-4.169784000	-1.245512000
H	5.420220000	-1.531334000	-4.449339000
H	5.080116000	-3.835834000	-3.576737000
C	-0.702870000	0.070290000	-2.139807000
H	-1.544995000	0.659202000	-2.515426000
H	0.179733000	0.304045000	-2.740673000
H	-0.936738000	-0.988700000	-2.263500000
C	-1.321530000	0.475474000	1.761399000
H	-0.846333000	1.449209000	1.912033000
H	-2.249018000	0.449804000	2.338957000
H	-0.652296000	-0.299986000	2.138280000
C	-5.359119000	-1.352401000	0.241871000
C	-6.578795000	-0.857213000	-0.264703000
C	-5.358798000	-2.619016000	0.857816000
C	-7.752950000	-1.594901000	-0.141708000
C	-6.536787000	-3.355778000	0.976209000
C	-7.739331000	-2.847941000	0.480117000
H	-6.598659000	0.099591000	-0.776488000
H	-4.435715000	-3.020263000	1.265044000
H	-8.680518000	-1.196004000	-0.542674000
H	-6.513526000	-4.327800000	1.460682000
H	-8.655870000	-3.423798000	0.570125000

[$PdCl_2$(**DTE^{o}-COCF$_3$**)$_2$]

Pd	-0.061203000	-1.184500000	0.659183000
Cl	-0.642077000	-1.189271000	2.950424000
S	-4.926600000	-2.531676000	0.839954000
S	-8.061580000	0.660969000	-2.682137000

P	-1.795047000	-2.768581000	0.303599000
F	-12.498098000	2.776474000	-1.128824000
F	-10.695421000	3.966002000	-0.846071000
F	-11.079200000	2.246956000	0.436198000
O	-11.063608000	1.273202000	-2.738561000
C	-1.755246000	-4.298367000	1.308326000
C	-0.660572000	-4.551012000	2.146810000
H	0.140074000	-3.824384000	2.225011000
C	-0.605642000	-5.731713000	2.890848000
H	0.245895000	-5.918545000	3.538608000
C	-1.640869000	-6.663927000	2.804869000
H	-1.598823000	-7.579476000	3.387957000
C	-2.728832000	-6.423750000	1.960193000
H	-3.530713000	-7.151855000	1.880157000
C	-2.783229000	-5.251822000	1.207304000
H	-3.614229000	-5.097943000	0.525660000
C	-2.052433000	-3.370193000	-1.410400000
C	-1.507391000	-4.590411000	-1.835121000
H	-0.966455000	-5.222119000	-1.137461000
C	-1.670234000	-5.006212000	-3.158025000
H	-1.250527000	-5.955948000	-3.477031000
C	-2.372131000	-4.208947000	-4.064908000
H	-2.500821000	-4.537335000	-5.092311000
C	-2.906711000	-2.986863000	-3.647612000
H	-3.450762000	-2.359717000	-4.348228000
C	-2.742625000	-2.565522000	-2.328929000
H	-3.150992000	-1.611581000	-2.012671000
C	-3.317841000	-1.856396000	0.674979000
C	-3.378745000	-0.487683000	0.736957000
H	-2.500749000	0.139989000	0.659173000
C	-4.697643000	0.046418000	0.896585000
C	-5.653559000	-0.948953000	0.988411000
C	-7.129379000	-0.825027000	1.209623000
H	-7.357243000	0.146634000	1.654004000
H	-7.503206000	-1.607893000	1.876874000
H	-7.682873000	-0.896948000	0.266116000
C	-4.926611000	1.497515000	0.958795000
H	-4.342404000	2.162544000	2.919685000
C	-4.454117000	3.809155000	1.451291000
H	-3.726081000	4.165812000	0.715387000
C	-5.838064000	3.679377000	0.777545000
C	-5.869081000	2.229360000	0.320363000
C	-6.864726000	1.776959000	-0.661983000
C	-8.230198000	2.170997000	-0.589405000
H	-8.616407000	2.809461000	0.195143000
C	-9.017635000	1.645227000	-1.595007000
C	-6.616417000	0.966185000	-1.766784000
C	-5.318742000	0.373424000	-2.215111000
H	-4.484754000	0.945058000	-1.801891000
H	-5.234566000	0.363080000	-3.306063000
H	-5.221653000	-0.658617000	-1.860165000
C	-10.437234000	1.797696000	-1.829794000
C	-11.197685000	2.711099000	-0.828517000
Cl	0.520699000	-1.221932000	-1.626024000
S	3.596732000	2.172843000	-0.612047000
S	8.973797000	1.651865000	1.161031000
P	1.284970000	0.743014000	0.967715000
F	12.934895000	2.252319000	-2.081269000
F	12.133012000	0.237950000	-1.873660000
F	11.019601000	1.745090000	-2.985115000
O	11.587459000	2.842639000	0.097298000
C	0.355235000	2.224499000	0.402524000
C	-0.720126000	2.071553000	-0.487528000
H	-0.991424000	1.083905000	-0.842950000
C	-1.433561000	3.187681000	-0.927763000
H	-2.268880000	3.056756000	-1.609318000
C	-1.076049000	4.465319000	-0.490674000
H	-1.632797000	5.333038000	-0.832406000
C	-0.001485000	4.625660000	0.388051000
H	0.281562000	5.617042000	0.729420000
C	0.710761000	3.512969000	0.837113000
H	1.532118000	3.649888000	1.533106000
C	1.801071000	1.142470000	2.682684000
C	0.896560000	1.748477000	3.569788000
H	-0.098795000	2.019735000	3.234759000
C	1.276935000	2.011863000	4.885182000
H	0.572826000	2.487633000	5.561678000
C	2.553155000	1.659554000	5.333280000
H	2.845546000	1.865115000	6.359063000
C	3.449518000	1.040599000	4.459710000
H	4.443088000	0.763123000	4.800244000
C	3.076504000	0.781739000	3.139519000
H	3.780423000	0.305151000	2.466486000
C	2.823410000	0.736821000	0.023808000
C	3.589267000	-0.370882000	-0.227975000
H	3.286198000	-1.369199000	0.065423000
C	4.821093000	-0.089825000	-0.907078000
C	4.957778000	1.255020000	-1.205090000
C	6.053615000	1.950105000	-1.953315000
H	6.593253000	1.230904000	-2.573794000
H	5.659613000	2.739236000	-2.601440000
H	6.778456000	2.408588000	-1.270663000
C	5.782026000	-1.150153000	-1.244609000
C	5.319455000	-2.417227000	-1.944642000
H	5.050913000	-2.177902000	-2.983963000
H	4.421594000	-2.848423000	-1.487647000
C	6.548158000	-3.347398000	-1.863022000
H	6.641211000	-4.010111000	-2.727767000
H	6.467143000	-3.976365000	-0.969453000
C	7.749871000	-2.391467000	-1.700782000
H	8.197387000	-2.135813000	-2.672835000
H	8.553735000	-2.810504000	-1.085681000

C	7.125395000	-1.152218000	-1.077366000
C	7.971802000	-0.129006000	-0.446510000
C	9.189205000	0.310136000	-1.038848000
H	9.551961000	-0.069528000	-1.985732000
C	9.848706000	1.279581000	-0.308684000
C	7.731650000	0.501051000	0.772118000
C	6.591779000	0.297586000	1.718284000
H	6.144414000	-0.685434000	1.555439000
H	6.915426000	0.371082000	2.761016000
H	5.811862000	1.049431000	1.554595000
C	11.084971000	1.973039000	-0.598983000
C	11.811323000	1.550403000	-1.906151000
C	-4.081960000	2.371221000	1.871986000
H	-3.009711000	2.166028000	1.772539000
H	-4.450198000	4.512520000	2.288484000
H	-6.656078000	3.864228000	1.489535000
H	-5.979939000	4.382031000	-0.051070000

[$PdCl_2$(**DTE^o-COCF$_3$**)(**DTE^c-COCF$_3$**)]

C	7.496451000	-1.255225000	0.414066000
C	7.059525000	0.218059000	0.273332000
S	8.523588000	1.060693000	-0.550586000
C	9.576201000	-0.315011000	-0.124908000
C	8.903949000	-1.419369000	0.334506000
H	9.392217000	-2.355370000	0.578198000
C	5.377302000	-3.965380000	1.765995000
C	4.323032000	-3.055095000	1.089408000
C	5.138810000	-1.881174000	0.595335000
C	6.546567000	-2.210393000	0.643884000
C	6.700915000	-3.662854000	1.019390000
H	5.107487000	-5.023835000	1.732034000
H	3.511112000	-2.762510000	1.761911000
H	3.858138000	-3.564308000	0.234187000
H	7.596117000	-3.865391000	1.613658000
H	6.769208000	-4.269097000	0.105104000
H	5.484383000	-3.679654000	2.818398000
C	3.404076000	-0.132480000	0.105094000
C	3.332012000	1.188915000	-0.219768000
S	4.898097000	1.943686000	-0.565668000
C	5.750389000	0.263023000	-0.544703000
C	4.727198000	-0.673070000	0.120012000
H	2.530458000	-0.718258000	0.366855000
P	1.761066000	2.116120000	-0.140129000
C	1.941968000	3.094963000	1.400656000
C	1.200551000	4.276160000	1.558497000
C	2.757675000	2.645092000	2.448434000
C	1.287231000	5.002873000	2.745519000
C	2.841575000	3.377463000	3.633519000
C	2.108580000	4.556488000	3.784368000
H	0.562374000	4.633124000	0.755847000
H	3.331138000	1.729914000	2.342032000
H	0.713011000	5.917973000	2.857744000
H	3.483196000	3.026246000	4.436544000
H	2.176252000	5.125478000	4.707135000
C	1.781482000	3.375610000	-1.469809000
C	2.706979000	4.433626000	-1.438112000
C	0.846580000	3.305932000	-2.512570000
C	2.711383000	5.389548000	-2.452604000
C	0.850429000	4.271967000	-3.521050000
C	1.784296000	5.309044000	-3.495986000
H	3.411134000	4.525862000	-0.617041000
H	0.126727000	2.496163000	-2.541963000
H	3.433608000	6.200111000	-2.423716000
H	0.122825000	4.210383000	-4.325082000
H	1.787387000	6.057587000	-4.283226000
C	5.908109000	-0.179528000	-2.017885000
H	6.358996000	-1.175148000	-2.063041000
H	4.923485000	-0.222435000	-2.490431000
H	6.536826000	0.513230000	-2.579467000
C	6.919271000	0.808750000	1.696071000
H	6.115567000	0.303644000	2.240008000
H	7.852525000	0.657643000	2.243924000
H	6.702425000	1.878112000	1.667241000
Pd	0.024485000	0.503901000	-0.224333000
Cl	-0.780864000	1.194479000	1.880745000
Cl	0.870669000	-0.178957000	-2.326479000
C	11.001710000	-0.175701000	-0.337310000
O	11.542501000	0.828915000	-0.782003000
C	11.886583000	-1.398760000	0.021689000
F	13.178812000	-1.139350000	-0.201537000
F	11.745135000	-1.738293000	1.323828000
F	11.542311000	-2.481417000	-0.713658000
S	-4.180812000	-2.131408000	1.175161000
S	-9.076214000	-1.269271000	-1.683015000
P	-1.459940000	-1.342682000	-0.192112000
F	-13.542946000	-0.759027000	0.836014000
F	-12.377793000	1.058391000	0.548567000
F	-11.728030000	-0.434965000	1.995978000
O	-11.993223000	-1.871619000	-0.971863000
C	-0.783784000	-2.668548000	0.882767000
C	0.219229000	-2.360461000	1.815602000
H	0.594033000	-1.345635000	1.893349000
C	0.727004000	-3.354036000	2.654867000
H	1.501843000	-3.104523000	3.373788000
C	0.240481000	-4.660257000	2.570423000
H	0.638407000	-5.432497000	3.222454000
C	-0.758767000	-4.973197000	1.645101000
H	-1.140314000	-5.987579000	1.574876000
C	-1.268512000	-3.985439000	0.801867000
H	-2.031465000	-4.245955000	0.075265000
C	-1.796481000	-2.157237000	-1.801371000

C	-0.905163000	-3.107874000	-2.322913000
H	-0.028736000	-3.404674000	-1.756734000
C	-1.146998000	-3.682510000	-3.570635000
H	-0.455829000	-4.423067000	-3.962645000
C	-2.267513000	-3.304210000	-4.315101000
H	-2.452298000	-3.753806000	-5.286533000
C	-3.147043000	-2.345160000	-3.807939000
H	-4.019731000	-2.045021000	-4.380989000
C	-2.913028000	-1.772035000	-2.557138000
H	-3.601845000	-1.029767000	-2.168864000
C	-3.102010000	-0.955249000	0.453138000
C	-3.721854000	0.262671000	0.353344000
H	-3.226847000	1.137264000	-0.051373000
C	-5.075214000	0.273597000	0.828339000
C	-5.464184000	-0.957743000	1.325775000
C	-6.762249000	-1.351774000	1.960532000
H	-7.276445000	-0.463935000	2.335946000
H	-6.608403000	-2.042463000	2.795417000
H	-7.428402000	-1.840764000	1.240315000
C	-5.899564000	1.490354000	0.799237000
H	-5.300168000	2.727292000	2.450503000
C	-6.399639000	3.843389000	0.897962000
H	-6.081650000	4.276663000	-0.056934000
C	-7.695512000	3.032966000	0.678708000
C	-7.182810000	1.629621000	0.391552000
C	-8.069037000	0.623207000	-0.211268000
C	-9.420871000	0.463759000	0.205081000
H	-9.865766000	1.055214000	0.995482000
C	-10.103223000	-0.524788000	-0.476858000
C	-7.741224000	-0.245201000	-1.249661000
C	-6.445127000	-0.374437000	-1.983741000
H	-5.874301000	0.552865000	-1.898532000
H	-6.602285000	-0.597010000	-3.043511000
H	-5.837517000	-1.180166000	-1.557235000
C	-11.466690000	-0.982480000	-0.319456000
C	-12.300089000	-0.270998000	0.781918000
C	-5.360210000	2.798206000	1.354594000
H	-4.344875000	3.018479000	1.005944000
H	-6.522529000	4.663982000	1.610123000
H	-8.324472000	3.023233000	1.581410000
H	-8.317500000	3.426280000	-0.132806000

$[PdCl_2(\mathbf{DTE^c\text{-}COCF_3})_2]$

C	6.854347000	-2.166313000	0.508531000
C	6.709744000	-0.671777000	0.864529000
S	8.429968000	0.038160000	0.599200000
C	9.128936000	-1.602950000	0.609388000
C	8.201414000	-2.611861000	0.545441000
H	8.465102000	-3.660955000	0.485659000
C	4.077866000	-4.611946000	0.473209000
C	3.351611000	-3.306755000	0.064828000
C	4.436756000	-2.258543000	0.148683000
C	5.729681000	-2.898707000	0.250345000
C	5.557920000	-4.386801000	0.073037000
H	3.646207000	-5.500242000	0.004881000
H	2.486145000	-3.079393000	0.694317000
H	2.979809000	-3.369089000	-0.966130000
H	6.265912000	-4.978376000	0.659962000
H	5.710795000	-4.645552000	-0.984226000
H	4.014458000	-4.741417000	1.559324000
C	3.155616000	-0.098809000	0.091755000
C	3.375502000	1.235721000	0.254328000
S	5.082554000	1.680382000	0.442324000
C	5.618408000	-0.059774000	-0.040724000
C	4.338822000	-0.901331000	0.097184000
H	2.162824000	-0.520955000	-0.012873000
P	2.011559000	2.439173000	0.384310000
C	1.979122000	2.847197000	2.170736000
C	1.422710000	4.065758000	2.590188000
C	2.445470000	1.933230000	3.125908000
C	1.349056000	4.368861000	3.949089000
C	2.368683000	2.242401000	4.484935000
C	1.822423000	3.458996000	4.898727000
H	1.053749000	4.779268000	1.859641000
H	2.873199000	0.985764000	2.814151000
H	0.921143000	5.315660000	4.265604000
H	2.740691000	1.532439000	5.217984000
H	1.765703000	3.698302000	5.956753000
C	2.567302000	3.989029000	-0.420322000
C	3.596932000	4.760732000	0.146633000
C	1.951107000	4.421743000	-1.603392000
C	4.015536000	5.934846000	-0.477464000
C	2.369777000	5.603034000	-2.219268000
C	3.403580000	6.356913000	-1.661413000
H	4.062314000	4.459434000	1.079873000
H	1.155851000	3.833774000	-2.046609000
H	4.815164000	6.521822000	-0.035415000
H	1.886280000	5.930832000	-3.134918000
H	3.729497000	7.274174000	-2.143454000
C	5.992312000	-0.014096000	-1.540937000
H	6.265614000	-1.014425000	-1.889175000
H	5.130660000	0.330474000	-2.118280000
H	6.830586000	0.659762000	-1.724658000
C	6.388520000	-0.570493000	2.374063000
H	5.417029000	-1.025973000	2.587562000
H	7.151849000	-1.106690000	2.943114000
H	6.368645000	0.467385000	2.711697000
Pd	0.082184000	1.443394000	-0.565096000
Cl	-1.106472000	1.749215000	1.440343000
Cl	1.306136000	1.098080000	-2.575325000
C	-7.759714000	-0.148636000	1.072573000

C	-6.680846000	-1.162533000	0.643836000
S	-7.656738000	-2.642880000	0.017535000
C	-9.126813000	-2.038533000	0.826700000
C	-9.024298000	-0.752840000	1.295040000
H	-9.846212000	-0.221247000	1.759133000
C	-7.068931000	3.253015000	2.344480000
C	-5.904205000	3.053737000	1.343374000
C	-6.094985000	1.632516000	0.862656000
C	-7.407532000	1.161069000	1.243568000
C	-8.186677000	2.302863000	1.847121000
H	-7.398813000	4.292851000	2.409885000
H	-4.919250000	3.222611000	1.789648000
H	-5.996630000	3.745480000	0.494915000
H	-8.876981000	1.987590000	2.634417000
H	-8.782741000	2.791702000	1.063549000
H	-6.747997000	2.938775000	3.343761000
C	-3.907033000	1.101809000	-0.257683000
C	-3.254001000	0.026842000	-0.778795000
S	-4.219065000	-1.465324000	-0.829287000
C	-5.777891000	-0.496553000	-0.418013000
C	-5.255588000	0.838790000	0.140282000
H	-3.429264000	2.063153000	-0.116996000
P	-1.612120000	0.135671000	-1.562752000
C	-0.973188000	-1.576812000	-1.547927000
C	-0.374207000	-2.155377000	-2.676286000
C	-0.979152000	-2.276142000	-0.327564000
C	0.184452000	-3.431910000	-2.590265000
C	-0.422184000	-3.552536000	-0.250932000
C	0.157516000	-4.133393000	-1.382499000
H	-0.343283000	-1.616251000	-3.616332000
H	-1.419265000	-1.827849000	0.558558000
H	0.640435000	-3.876883000	-3.469788000
H	-0.440093000	-4.090888000	0.691996000
H	0.591875000	-5.126944000	-1.320544000
C	-2.089633000	0.567617000	-3.275595000
C	-2.787634000	-0.342233000	-4.086611000
C	-1.860698000	1.873735000	-3.731615000
C	-3.238788000	0.053560000	-5.346201000
C	-2.320043000	2.264499000	-4.989788000
C	-3.006560000	1.355399000	-5.798477000
H	-2.979602000	-1.352092000	-3.739662000
H	-1.318767000	2.576372000	-3.107343000
H	-3.773488000	-0.655294000	-5.971666000
H	-2.136488000	3.276497000	-5.338867000
H	-3.360322000	1.660200000	-6.779240000
C	-6.490918000	-0.196709000	-1.757875000
H	-7.378889000	0.416904000	-1.579828000
H	-5.813470000	0.355823000	-2.414132000
H	-6.797019000	-1.113887000	-2.263276000
C	-5.917163000	-1.607813000	1.912827000
H	-5.369038000	-0.764407000	2.342835000
H	-6.632121000	-1.969809000	2.655712000
H	-5.208252000	-2.408836000	1.695391000
C	-10.285024000	-2.905259000	0.877861000
O	-10.329277000	-4.034476000	0.405723000
C	10.570949000	-1.731401000	0.633043000
O	11.351506000	-0.788249000	0.661372000
C	11.147664000	-3.171989000	0.606377000
F	12.483549000	-3.155600000	0.656121000
F	10.697299000	-3.898893000	1.655058000
F	10.777505000	-3.823621000	-0.520540000
C	-11.551359000	-2.342672000	1.577127000
F	-12.539276000	-3.243461000	1.578330000
F	-11.291178000	-2.002693000	2.860561000
F	-11.999375000	-1.228898000	0.951937000

$[PdCl_2(\mathbf{DTE^o\text{-}C_6F_5})_2]$

C	5.205534000	-2.190946000	-1.849110000
C	4.043159000	-2.206101000	-1.097864000
S	4.116420000	-3.428369000	0.141493000
C	5.729884000	-3.935056000	-0.344291000
C	6.144963000	-3.182242000	-1.418326000
H	7.104732000	-3.319320000	-1.896998000
C	2.808994000	-1.372690000	-1.244260000
H	2.828424000	-0.493847000	-0.593101000
H	2.725133000	-1.010615000	-2.271624000
H	1.905098000	-1.937189000	-0.998317000
C	5.878928000	-0.791226000	-5.308541000
C	5.708511000	0.508748000	-4.495424000
C	5.283017000	0.018364000	-3.120252000
C	5.490146000	-1.314255000	-2.994047000
C	6.144442000	-1.879324000	-4.246711000
H	6.668148000	-0.724711000	-6.062834000
H	4.983647000	1.200183000	-4.940357000
H	6.653356000	1.065778000	-4.407706000
H	5.740259000	-2.858972000	-4.524229000
H	7.221890000	-2.020990000	-4.073911000
H	4.941086000	-1.018088000	-5.827731000
C	3.796377000	1.954171000	-2.421841000
C	3.456859000	2.761234000	-1.368679000
S	4.377934000	2.320435000	0.056259000
C	5.231036000	1.061436000	-0.801648000
C	4.798461000	0.972798000	-2.112300000
H	3.321005000	2.021734000	-3.392595000
C	6.278694000	0.260295000	-0.093268000
H	5.832407000	-0.565697000	0.472770000
H	6.968214000	-0.177002000	-0.819184000
H	6.853344000	0.876282000	0.605662000
P	2.093542000	3.943947000	-1.239744000
C	2.868155000	5.586739000	-0.998130000
C	2.026184000	6.678093000	-0.730993000

C	4.246397000	5.793933000	-1.143905000
C	2.559150000	7.960357000	-0.614526000
C	4.776339000	7.080757000	-1.018094000
C	3.935804000	8.163343000	-0.753909000
H	0.959263000	6.521739000	-0.607615000
H	4.906054000	4.961321000	-1.364701000
H	1.901784000	8.799580000	-0.406292000
H	5.845776000	7.233965000	-1.131592000
H	4.350232000	9.162767000	-0.656252000
C	1.389618000	4.081663000	-2.925012000
C	2.209591000	4.469833000	-3.998089000
C	0.020804000	3.871160000	-3.136921000
C	1.666450000	4.616958000	-5.273614000
C	-0.519804000	4.032233000	-4.414661000
C	0.301168000	4.397790000	-5.483017000
H	3.266776000	4.658163000	-3.835158000
H	-0.614799000	3.574016000	-2.310652000
H	2.306262000	4.909213000	-6.101273000
H	-1.581807000	3.867940000	-4.572654000
H	-0.120959000	4.517781000	-6.476764000
Pd	0.702581000	3.030168000	0.439570000
Cl	0.336920000	1.185208000	-1.012933000
Cl	1.121163000	4.813209000	1.912836000
C	-6.608150000	-1.155274000	1.355790000
C	-5.529675000	-1.897637000	0.909300000
S	-5.955138000	-2.844962000	-0.488377000
C	-7.619177000	-2.273144000	-0.462485000
C	-7.789991000	-1.396737000	0.583809000
H	-8.731327000	-0.907444000	0.793531000
C	-4.134938000	-1.967035000	1.450850000
H	-3.458148000	-1.304559000	0.899278000
H	-4.129830000	-1.650037000	2.496261000
H	-3.728549000	-2.981944000	1.392837000
C	-7.168915000	0.559205000	4.696831000
C	-6.071118000	1.453403000	4.081141000
C	-5.697461000	0.727108000	2.800108000
C	-6.607127000	-0.228076000	2.496669000
C	-7.750302000	-0.225349000	3.500052000
H	-7.925311000	1.126965000	5.245966000
H	-5.213747000	1.602523000	4.747919000
H	-6.447698000	2.457256000	3.834556000
H	-8.076828000	-1.236564000	3.766508000
H	-8.625054000	0.283577000	3.068335000
H	-6.709503000	-0.146047000	5.398399000
C	-3.220868000	1.261614000	2.603599000
C	-2.229750000	1.593031000	1.709697000
S	-2.902911000	1.799586000	0.109123000
C	-4.509051000	1.423332000	0.663093000
C	-4.520088000	1.133075000	2.017595000
H	-3.029625000	1.094334000	3.657348000
C	-5.652229000	1.427525000	-0.304675000
H	-5.707195000	0.483747000	-0.859219000
H	-6.594996000	1.547045000	0.234415000
H	-5.561672000	2.240275000	-1.032379000
P	-0.474559000	1.816784000	2.085293000
C	-0.525521000	2.484660000	3.792583000
C	0.234420000	1.925465000	4.828428000
C	-1.324993000	3.610799000	4.051761000
C	0.186065000	2.480032000	6.110305000
C	-1.373691000	4.155733000	5.332852000
C	-0.617445000	3.591829000	6.365516000
H	0.857235000	1.056275000	4.646380000
H	-1.913585000	4.054236000	3.254949000
H	0.773964000	2.035356000	6.908164000
H	-1.998321000	5.023467000	5.524407000
H	-0.655659000	4.018855000	7.363624000
C	0.276049000	0.151311000	2.242959000
C	1.676751000	0.055825000	2.212164000
C	-0.495266000	-1.006206000	2.403187000
C	2.296230000	-1.184878000	2.355293000
C	0.130220000	-2.248715000	2.530538000
C	1.523633000	-2.340106000	2.510252000
H	2.279407000	0.947177000	2.063235000
H	-1.577763000	-0.942457000	2.420350000
H	3.379385000	-1.252594000	2.328768000
H	-0.473958000	-3.144251000	2.644715000
H	2.007461000	-3.307303000	2.608240000
C	6.480399000	-4.976130000	0.361263000
C	7.887000000	-5.028161000	0.327126000
C	5.863742000	-5.989666000	1.115557000
C	8.618618000	-6.016983000	0.974025000
C	6.577040000	-6.981414000	1.778162000
C	7.965026000	-7.003526000	1.704682000
C	-8.630768000	-2.737875000	-1.414333000
C	-8.314842000	-3.216271000	-2.697586000
C	-10.002052000	-2.733912000	-1.096549000
C	-9.276995000	-3.656172000	-3.598923000
C	-10.980431000	-3.160698000	-1.986604000
C	-10.621587000	-3.626112000	-3.247164000
F	8.592200000	-4.096194000	-0.338514000
F	9.957100000	-6.014817000	0.905159000
F	8.662538000	-7.956918000	2.331892000
F	5.928573000	-7.921938000	2.478455000
F	4.522463000	-6.030198000	1.225924000
F	-10.424273000	-2.318132000	0.110575000
F	-12.271388000	-3.135447000	-1.627615000
F	-11.557275000	-4.041460000	-4.107666000
F	-8.911336000	-4.099445000	-4.809174000
F	-7.032544000	-3.269045000	-3.103239000

[$PdCl_2$(**DTE^o-C_6F_5**)(**DTE^c-C_6F_5**)]

C	-7.241439000	0.599706000	-0.373321000
C	-6.297781000	-0.333423000	0.408945000
S	-6.979302000	-2.050359000	0.089624000
C	-8.537170000	-1.367610000	-0.467371000
C	-8.498435000	-0.018590000	-0.663106000
H	-9.343699000	0.540391000	-1.044477000
C	-6.831455000	4.257746000	-0.614135000
C	-5.358063000	3.786992000	-0.539218000
C	-5.473650000	2.291150000	-0.345665000
C	-6.832480000	1.869059000	-0.640108000
C	-7.605506000	3.045338000	-1.188551000
H	-6.956822000	5.163245000	-1.213731000
H	-4.788486000	4.279589000	0.255336000
H	-4.835914000	3.993801000	-1.483543000
H	-8.663709000	3.035751000	-0.911526000
H	-7.554163000	3.047177000	-2.286604000
H	-7.196862000	4.471902000	0.396702000
C	-3.165790000	1.614062000	0.403961000
C	-2.530329000	0.522028000	0.907023000
S	-3.531377000	-0.950628000	0.954673000
C	-4.854463000	-0.116015000	-0.094812000
C	-4.521905000	1.384930000	-0.000142000
H	-2.687142000	2.584197000	0.332085000
P	-0.852846000	0.590393000	1.595952000
C	-1.136228000	0.618123000	3.408793000
C	-0.102203000	0.225024000	4.273992000
C	-2.347619000	1.076750000	3.944500000
C	-0.288218000	0.273333000	5.654452000
C	-2.526553000	1.127683000	5.328656000
C	-1.500502000	0.724428000	6.185005000
H	0.843186000	-0.123698000	3.870861000
H	-3.154296000	1.385184000	3.287436000
H	0.515692000	-0.037396000	6.315518000
H	-3.471948000	1.476674000	5.734120000
H	-1.643342000	0.761201000	7.261243000
C	-0.089757000	-1.053938000	1.290543000
C	-0.492999000	-2.178707000	2.031243000
C	0.899478000	-1.198156000	0.305864000
C	0.078446000	-3.426094000	1.780416000
C	1.468507000	-2.448959000	0.061231000
C	1.060717000	-3.563565000	0.795665000
H	-1.242382000	-2.082534000	2.810596000
H	1.217877000	-0.340828000	-0.275359000
H	-0.241958000	-4.288759000	2.357293000
H	2.231158000	-2.548922000	-0.704582000
H	1.508322000	-4.534786000	0.604565000
C	-4.624238000	-0.561332000	-1.557062000
H	-5.339803000	-0.063802000	-2.218303000
H	-3.613917000	-0.279166000	-1.863957000
H	-4.735758000	-1.640898000	-1.672752000
C	-6.481556000	-0.035471000	1.915915000
H	-6.146139000	0.981054000	2.141118000
H	-7.540903000	-0.114641000	2.172728000
H	-5.918442000	-0.734138000	2.537186000
Pd	0.478035000	2.316248000	0.656137000
Cl	1.107015000	3.087131000	2.794515000
Cl	-0.261012000	1.650879000	-1.490451000
C	-9.683307000	-2.237841000	-0.753492000
C	-9.991376000	-3.379831000	0.005881000
C	-10.541788000	-1.976838000	-1.838276000
C	-11.072480000	-4.203947000	-0.286896000
C	-11.629507000	-2.785807000	-2.142262000
C	-11.899063000	-3.907974000	-1.364982000
F	-9.245385000	-3.712501000	1.071393000
F	-11.327270000	-5.275432000	0.475616000
F	-12.944305000	-4.690387000	-1.650051000
F	-12.413689000	-2.495705000	-3.189154000
F	-10.326505000	-0.922321000	-2.641896000
C	6.791732000	-0.952200000	-1.611158000
C	5.453680000	-1.278697000	-1.742104000
S	5.174073000	-2.947995000	-1.333036000
C	6.874306000	-3.226002000	-0.975814000
C	7.584561000	-2.067506000	-1.189749000
H	8.653100000	-1.995954000	-1.040561000
C	4.304689000	-0.426703000	-2.189895000
H	3.755243000	-0.013742000	-1.336009000
H	4.675764000	0.414574000	-2.779831000
H	3.596070000	-0.993443000	-2.802403000
C	8.726646000	2.000546000	-3.018276000
C	7.863380000	2.689413000	-1.938511000
C	6.959224000	1.574954000	-1.443753000
C	7.392238000	0.365730000	-1.868939000
C	8.688352000	0.499555000	-2.652967000
H	9.742233000	2.402260000	-3.074672000
H	7.300442000	3.548850000	-2.321760000
H	8.471337000	3.066212000	-1.102688000
H	8.717854000	-0.156545000	-3.529819000
H	9.540798000	0.214891000	-2.018318000
H	8.259066000	2.142352000	-3.999001000
C	4.778766000	2.774356000	-0.936756000
C	3.719783000	2.814611000	-0.061475000
S	4.007045000	1.726021000	1.282841000
C	5.537395000	1.215705000	0.629477000
C	5.806739000	1.847619000	-0.571718000
H	4.809379000	3.349865000	-1.853860000
C	6.357532000	0.197379000	1.360069000
H	5.988037000	-0.817581000	1.173441000
H	7.394262000	0.237803000	1.018164000
H	6.340497000	0.367639000	2.441348000
P	2.157608000	3.712723000	-0.255177000
C	2.355403000	5.340373000	0.553972000
C	1.204920000	6.040480000	0.946643000

C	3.619674000	5.915425000	0.736452000
C	1.320535000	7.313271000	1.505179000
C	3.730288000	7.184967000	1.306928000
C	2.583107000	7.884869000	1.688557000
H	0.226006000	5.586704000	0.821827000
H	4.512178000	5.373441000	0.438335000
H	0.427557000	7.852578000	1.807605000
H	4.712377000	7.625695000	1.452536000
H	2.672359000	8.872320000	2.132465000
C	2.114395000	4.089318000	-2.050688000
C	1.856202000	5.387930000	-2.512959000
C	2.307364000	3.052654000	-2.981169000
C	1.802752000	5.646910000	-3.884918000
C	2.264452000	3.319827000	-4.347952000
C	2.009869000	4.617002000	-4.803535000
H	1.705526000	6.201481000	-1.811498000
H	2.497054000	2.042560000	-2.637137000
H	1.606995000	6.657731000	-4.231018000
H	2.423012000	2.512415000	-5.057015000
H	1.973426000	4.822097000	-5.869689000
C	7.380455000	-4.507958000	-0.480020000
C	8.557974000	-4.592060000	0.286789000
C	6.736329000	-5.733198000	-0.723577000
C	9.062061000	-5.798145000	0.758712000
C	7.218436000	-6.948664000	-0.253015000
C	8.392198000	-6.987155000	0.490910000
F	9.248932000	-3.483717000	0.607020000
F	10.189089000	-5.816580000	1.483461000
F	8.870161000	-8.150738000	0.944445000
F	6.558551000	-8.083057000	-0.522510000
F	5.595796000	-5.767218000	-1.437831000

$[PdCl_2(\mathbf{DTE^c\text{-}C_6F_5})_2]$

C	-6.781029000	-2.169103000	-0.437751000
C	-6.684611000	-0.661313000	-0.743637000
S	-8.421511000	-0.020869000	-0.449801000
C	-9.085706000	-1.680916000	-0.530729000
C	-8.126635000	-2.649983000	-0.503151000
H	-8.363547000	-3.706574000	-0.496927000
C	-3.925038000	-4.506255000	-0.535357000
C	-3.240046000	-3.196761000	-0.073925000
C	-4.359232000	-2.181696000	-0.103100000
C	-5.634934000	-2.866829000	-0.214504000
C	-5.404654000	-4.355789000	-0.100115000
H	-3.450647000	-5.400224000	-0.121384000
H	-2.384807000	-2.913368000	-0.694851000
H	-2.861190000	-3.294246000	0.951910000
H	-6.096579000	-4.949483000	-0.704640000
H	-5.527672000	-4.673055000	0.945124000
H	-3.876632000	-4.577445000	-1.627919000
C	-3.145152000	0.015984000	0.016837000
C	-3.406231000	1.345816000	-0.106554000
S	-5.137884000	1.734804000	-0.274848000
C	-5.609209000	-0.035458000	0.171330000
C	-4.301503000	-0.827959000	-0.003521000
H	-2.137705000	-0.376224000	0.100818000
P	-2.086747000	2.588212000	-0.225651000
C	-2.108752000	3.081247000	-1.992335000
C	-1.549606000	4.312585000	-2.369017000
C	-2.624606000	2.226093000	-2.975435000
C	-1.520938000	4.686261000	-3.711767000
C	-2.594167000	2.605902000	-4.318698000
C	-2.044711000	3.834794000	-4.689108000
H	-1.142962000	4.981548000	-1.616254000
H	-3.053354000	1.268923000	-2.696834000
H	-1.089393000	5.642157000	-3.994504000
H	-3.004019000	1.940510000	-5.073178000
H	-2.023636000	4.128941000	-5.734576000
C	-2.660918000	4.099071000	0.642807000
C	-3.730961000	4.850930000	0.126053000
C	-2.021327000	4.526318000	1.815007000
C	-4.166333000	5.997298000	0.789120000
C	-2.456496000	5.680463000	2.470242000
C	-3.530610000	6.413127000	1.962761000
H	-4.214539000	4.556182000	-0.800138000
H	-1.194668000	3.954673000	2.219910000
H	-4.997313000	6.568197000	0.385272000
H	-1.953824000	6.003610000	3.377275000
H	-3.869112000	7.309111000	2.475318000
C	-5.976223000	-0.044966000	1.672462000
H	-6.210849000	-1.063637000	1.995098000
H	-5.123476000	0.315287000	2.253561000
H	-6.836437000	0.593431000	1.881861000
C	-6.383074000	-0.504710000	-2.252989000
H	-5.396957000	-0.918048000	-2.483745000
H	-7.131486000	-1.054339000	-2.829328000
H	-6.403852000	0.541959000	-2.561632000
Pd	-0.101968000	1.601272000	0.621402000
Cl	0.944542000	1.831018000	-1.475004000
Cl	-1.216872000	1.241318000	2.690703000
C	7.838833000	0.674134000	-1.081883000
C	6.867387000	-0.445755000	-0.666254000
S	7.983690000	-1.805672000	-0.017219000
C	9.405044000	-1.066691000	-0.813212000
C	9.169598000	0.190382000	-1.285780000
H	9.939957000	0.792074000	-1.752035000
C	6.793136000	3.953936000	-2.409485000
C	5.642591000	3.639824000	-1.421945000
C	5.977363000	2.252908000	-0.919388000
C	7.348413000	1.928834000	-1.270751000
C	8.003748000	3.148158000	-1.876153000

H	6.999946000	5.024242000	-2.492556000
H	4.650765000	3.699304000	-1.881006000
H	5.650486000	4.346495000	-0.580436000
H	8.737792000	2.905730000	-2.650150000
H	8.526849000	3.718862000	-1.095677000
H	6.526540000	3.585564000	-3.406542000
C	3.838917000	1.497925000	0.174417000
C	3.296790000	0.364424000	0.694080000
S	4.423291000	-1.020705000	0.752718000
C	5.874469000	0.116584000	0.375077000
C	5.215671000	1.382414000	-0.205275000
H	3.263678000	2.404080000	0.028831000
P	1.669694000	0.308258000	1.496925000
C	1.108336000	-1.425286000	1.353153000
C	0.428049000	-2.061607000	2.403125000
C	1.245586000	-2.080346000	0.117070000
C	-0.077384000	-3.350360000	2.226184000
C	0.737479000	-3.368855000	-0.051814000
C	0.080037000	-4.007424000	1.002972000
H	0.293649000	-1.555359000	3.352526000
H	1.747787000	-1.587512000	-0.709879000
H	-0.595225000	-3.839712000	3.045912000
H	0.856303000	-3.871521000	-1.007123000
H	-0.315308000	-5.010267000	0.869761000
C	2.142645000	0.614209000	3.239411000
C	2.779337000	-0.368834000	4.012822000
C	1.984812000	1.909540000	3.754186000
C	3.241311000	-0.056548000	5.292641000
C	2.454392000	2.216945000	5.030895000
C	3.080842000	1.234179000	5.802299000
H	2.915583000	-1.371910000	3.623149000
H	1.489015000	2.669804000	3.159067000
H	3.729163000	-0.822726000	5.888251000
H	2.325293000	3.220988000	5.424668000
H	3.442476000	1.473624000	6.798258000
C	6.523932000	0.496149000	1.725409000
H	7.338677000	1.208220000	1.563908000
H	5.774006000	0.966707000	2.366665000
H	6.923111000	-0.378738000	2.241567000
C	6.186677000	-0.979870000	-1.948549000
H	5.556391000	-0.203326000	-2.391268000
H	6.954956000	-1.259194000	-2.673912000
H	5.567595000	-1.854615000	-1.741942000
C	10.696844000	-1.761539000	-0.850383000
C	11.904805000	-1.059326000	-0.681311000
C	10.818588000	-3.148282000	-1.042863000
C	13.143907000	-1.687027000	-0.709801000
C	12.049762000	-3.794179000	-1.069187000
C	13.220691000	-3.062804000	-0.903618000
C	-10.534082000	-1.915652000	-0.537524000
C	-11.445389000	-1.084332000	-1.211369000
C	-11.098536000	-3.001408000	0.158379000
C	-12.817260000	-1.311053000	-1.197212000
C	-12.465800000	-3.246971000	0.178471000
C	-13.333840000	-2.398380000	-0.501633000
F	9.728395000	-3.909292000	-1.228495000
F	12.111428000	-5.117555000	-1.267097000
F	14.408697000	-3.674051000	-0.933627000
F	14.265412000	-0.974069000	-0.539593000
F	11.899211000	0.267007000	-0.469396000
F	-11.012099000	-0.028583000	-1.918501000
F	-13.641195000	-0.492247000	-1.864176000
F	-14.650202000	-2.628446000	-0.488779000
F	-12.952990000	-4.292643000	0.859823000
F	-10.320021000	-3.846555000	0.853718000

$[PdCl_2(\mathbf{DTE^o\text{-}Ph})_2]$

C	5.914833000	-1.584349000	-1.505057000
C	5.223992000	-1.812995000	-0.329509000
S	6.174829000	-2.784059000	0.768493000
C	7.514501000	-2.898015000	-0.364009000
C	7.202497000	-2.220789000	-1.515852000
H	7.891124000	-2.134661000	-2.349192000
C	3.847299000	-1.379518000	0.064438000
H	3.853830000	-0.453265000	0.649007000
H	3.250316000	-1.196503000	-0.831689000
H	3.339081000	-2.139062000	0.665234000
C	4.619160000	-0.452781000	-4.891249000
C	4.442268000	0.835288000	-4.057986000
C	4.821423000	0.407732000	-2.649679000
C	5.423446000	-0.805271000	-2.650558000
C	5.598072000	-1.321269000	-4.070790000
H	4.968182000	-0.257609000	-5.909189000
H	3.426196000	1.243777000	-4.113720000
H	5.115851000	1.638167000	-4.392381000
H	5.392945000	-2.394309000	-4.153936000
H	6.638995000	-1.175156000	-4.395788000
H	3.657020000	-0.971613000	-4.967804000
C	3.308552000	1.908944000	-1.271096000
C	3.252766000	2.685180000	-0.138203000
S	4.803626000	2.699273000	0.663257000
C	5.512148000	1.653797000	-0.540489000
C	4.584763000	1.303127000	-1.507002000
H	2.447824000	1.738936000	-1.907962000
C	6.950521000	1.253931000	-0.425483000
H	7.072842000	0.403069000	0.254555000
H	7.330178000	0.948405000	-1.403331000
H	7.570238000	2.075589000	-0.052454000
P	1.714987000	3.365967000	0.533424000
C	2.140368000	4.257226000	2.074687000
C	1.465788000	3.969725000	3.268566000

C	3.091228000	5.291949000	2.043317000
C	1.754643000	4.697341000	4.425033000
C	3.384127000	6.006299000	3.204323000
C	2.716375000	5.709026000	4.396222000
H	0.730224000	3.174093000	3.295183000
H	3.593133000	5.545820000	1.114059000
H	1.228807000	4.469492000	5.347721000
H	4.125789000	6.799293000	3.175904000
H	2.942318000	6.270060000	5.298636000
C	1.226368000	4.730941000	-0.589150000
C	1.980542000	5.103773000	-1.708033000
C	0.048357000	5.429819000	-0.279437000
C	1.561307000	6.171299000	-2.507063000
C	-0.361989000	6.496064000	-1.076479000
C	0.393459000	6.867967000	-2.193576000
H	2.891539000	4.569291000	-1.955859000
H	-0.546895000	5.139278000	0.581968000
H	2.152249000	6.457092000	-3.372697000
H	-1.274087000	7.032326000	-0.830761000
H	0.070100000	7.696908000	-2.816790000
Pd	0.341764000	1.444771000	0.632541000
Cl	-0.988796000	2.216583000	-1.164186000
Cl	1.694075000	0.671736000	2.412786000
C	-7.436424000	-2.062665000	0.209549000
C	-6.839482000	-1.786238000	-1.006319000
S	-7.957437000	-0.974451000	-2.076026000
C	-9.250162000	-1.013947000	-0.885705000
C	-8.807169000	-1.635598000	0.254223000
H	-9.428052000	-1.754064000	1.135147000
C	-5.451605000	-2.093840000	-1.478455000
H	-4.785748000	-1.230645000	-1.363732000
H	-5.034039000	-2.913389000	-0.888657000
H	-5.438964000	-2.385134000	-2.533968000
C	-6.393939000	-4.500379000	2.927092000
C	-5.295723000	-3.422981000	3.055341000
C	-5.575077000	-2.489944000	1.888996000
C	-6.795106000	-2.728090000	1.352800000
C	-7.525350000	-3.810800000	2.133413000
H	-6.724136000	-4.892453000	3.893240000
H	-4.281120000	-3.838023000	3.030876000
H	-5.376546000	-2.862971000	3.998914000
H	-8.074741000	-4.499178000	1.481822000
H	-8.267910000	-3.352339000	2.803485000
H	-6.007525000	-5.342461000	2.341976000
C	-3.230979000	-1.736333000	1.267359000
C	-2.486793000	-0.649369000	0.872500000
S	-3.484301000	0.787233000	0.838440000
C	-4.895251000	-0.100691000	1.341467000
C	-4.610598000	-1.445137000	1.512821000
H	-2.813479000	-2.731711000	1.364007000
C	-6.202204000	0.609901000	1.514243000
H	-6.723730000	0.719138000	0.556497000
H	-6.853237000	0.034745000	2.176952000
H	-6.066134000	1.609184000	1.939803000
P	-0.735153000	-0.647149000	0.423802000
C	-0.071158000	-2.041363000	1.414019000
C	0.683077000	-3.065224000	0.825245000
C	-0.287722000	-2.054728000	2.802177000
C	1.209483000	-4.091566000	1.614532000
C	0.232257000	-3.084711000	3.583166000
C	0.984947000	-4.104314000	2.991644000
H	0.863459000	-3.070354000	-0.243950000
H	-0.866306000	-1.264431000	3.269315000
H	1.791436000	-4.880796000	1.147262000
H	0.054814000	-3.088024000	4.654751000
H	1.393555000	-4.903884000	3.602970000
C	-0.615596000	-1.227282000	-1.312495000
C	0.549321000	-0.924790000	-2.034667000
C	-1.617295000	-2.004833000	-1.906801000
C	0.715737000	-1.407398000	-3.332157000
C	-1.453395000	-2.473481000	-3.212319000
C	-0.287925000	-2.179574000	-3.924348000
H	1.320171000	-0.308795000	-1.583011000
H	-2.522501000	-2.241055000	-1.357549000
H	1.624192000	-1.173588000	-3.879774000
H	-2.237880000	-3.068715000	-3.670995000
H	-0.163240000	-2.547868000	-4.938684000
C	8.742418000	-3.638123000	-0.047436000
C	9.513840000	-4.199169000	-1.084390000
C	9.186043000	-3.805444000	1.277978000
C	10.691773000	-4.888721000	-0.803688000
C	10.358777000	-4.506887000	1.555791000
C	11.120315000	-5.048796000	0.517493000
H	9.174640000	-4.108429000	-2.111814000
H	8.620228000	-3.368484000	2.096272000
H	11.270365000	-5.314013000	-1.619187000
H	10.682041000	-4.621621000	2.586702000
H	12.035287000	-5.592324000	0.734878000
C	-10.578927000	-0.451611000	-1.158898000
C	-10.764347000	0.599476000	-2.076666000
C	-11.710089000	-0.959996000	-0.490157000
C	-12.034363000	1.122926000	-2.316596000
C	-12.975843000	-0.426042000	-0.723552000
C	-13.146291000	0.616452000	-1.639395000
H	-9.907838000	1.024081000	-2.593213000
H	-11.595238000	-1.789289000	0.201147000
H	-12.152414000	1.935126000	-3.028496000
H	-13.834298000	-0.834518000	-0.197385000
H	-14.134715000	1.026961000	-1.824577000

[$PdCl_2$(**DTE^o-Ph**)(**DTE^c-Ph**)]

C	7.512552000	0.025685000	-0.202578000
C	6.408326000	-1.039199000	-0.357158000
S	7.107409000	-2.547711000	0.507521000
C	8.763493000	-1.875736000	0.433417000
C	8.789792000	-0.561486000	0.066502000
H	9.710397000	0.007470000	-0.004448000
C	7.231216000	3.497880000	-1.417438000
C	5.765313000	3.188306000	-1.026767000
C	5.808996000	1.735269000	-0.607270000
C	7.190301000	1.331047000	-0.410934000
C	8.083288000	2.542980000	-0.544931000
H	7.493840000	4.549858000	-1.276572000
H	5.053535000	3.380458000	-1.836018000
H	5.452937000	3.804995000	-0.172690000
H	9.059919000	2.315243000	-0.982539000
H	8.263548000	2.990190000	0.443092000
H	7.385299000	3.252898000	-2.474580000
C	3.383156000	1.053010000	-0.607126000
C	2.636419000	-0.077603000	-0.496695000
S	3.577199000	-1.542268000	-0.105024000
C	5.100982000	-0.496676000	0.260276000
C	4.786505000	0.868366000	-0.381136000
H	2.949447000	2.012619000	-0.862080000
P	0.865907000	-0.169930000	-0.866631000
C	0.833428000	-0.920871000	-2.542481000
C	-0.322211000	-1.568754000	-3.010941000
C	1.943944000	-0.800389000	-3.392424000
C	-0.354309000	-2.103815000	-4.298213000
C	1.902416000	-1.329978000	-4.683437000
C	0.756298000	-1.985308000	-5.137802000
H	-1.193439000	-1.654000000	-2.374133000
H	2.843352000	-0.300904000	-3.048384000
H	-1.251362000	-2.608432000	-4.645435000
H	2.770797000	-1.235048000	-5.329048000
H	0.727562000	-2.401158000	-6.140959000
C	0.203067000	-1.444211000	0.285064000
C	0.132447000	-2.806078000	-0.045473000
C	-0.228969000	-1.022488000	1.554111000
C	-0.390590000	-3.723099000	0.869005000
C	-0.738799000	-1.944786000	2.467375000
C	-0.832941000	-3.295404000	2.122513000
H	0.474341000	-3.156530000	-1.013035000
H	-0.161974000	0.024439000	1.828865000
H	-0.451714000	-4.772986000	0.597671000
H	-1.070875000	-1.603360000	3.442869000
H	-1.247172000	-4.010417000	2.827509000
C	5.163873000	-0.299284000	1.791760000
H	6.007766000	0.345862000	2.053404000
H	4.242263000	0.181236000	2.130266000
H	5.275823000	-1.249245000	2.317627000
C	6.289112000	-1.378532000	-1.861832000
H	5.940674000	-0.503234000	-2.417666000
H	7.271828000	-1.663184000	-2.246020000
H	5.593325000	-2.201251000	-2.035663000
Pd	-0.412989000	1.810579000	-0.504296000
Cl	0.987319000	2.472302000	1.281914000
Cl	-1.869216000	1.212300000	-2.275148000
C	9.914463000	-2.718285000	0.778456000
C	9.854616000	-4.121759000	0.675903000
C	11.117319000	-2.133023000	1.226296000
C	10.960298000	-4.909226000	0.994905000
C	12.219387000	-2.922957000	1.541203000
C	12.148096000	-4.315342000	1.426607000
H	8.944675000	-4.598584000	0.324311000
H	11.179180000	-1.056437000	1.348293000
H	10.892425000	-5.989429000	0.902082000
H	13.134464000	-2.451216000	1.888135000
H	13.008060000	-4.929498000	1.677696000
C	-5.372105000	-2.480963000	1.209860000
C	-4.732207000	-2.376583000	-0.009942000
S	-5.654017000	-3.175614000	-1.261717000
C	-6.910896000	-3.668062000	-0.133939000
C	-6.594261000	-3.230271000	1.127423000
H	-7.238139000	-3.394941000	1.984329000
C	-3.419946000	-1.738721000	-0.341457000
H	-3.540725000	-0.761382000	-0.821914000
H	-2.839011000	-1.588558000	0.569525000
H	-2.834336000	-2.370436000	-1.016307000
C	-3.929072000	-1.955544000	4.686651000
C	-3.959629000	-0.507838000	4.146716000
C	-4.423326000	-0.666221000	2.708753000
C	-4.879460000	-1.918165000	2.474781000
C	-4.857339000	-2.754280000	3.743794000
H	-4.225725000	-2.022952000	5.737092000
H	-2.986430000	-0.006866000	4.216903000
H	-4.671185000	0.124553000	4.697703000
H	-4.503567000	-3.775256000	3.561415000
H	-5.875099000	-2.843947000	4.151659000
H	-2.912029000	-2.352729000	4.606617000
C	-3.238762000	1.292525000	1.603804000
C	-3.400311000	2.317531000	0.702627000
S	-5.020818000	2.303322000	0.052326000
C	-5.465067000	0.913907000	1.009108000
C	-4.403882000	0.479568000	1.785358000
H	-2.297909000	1.090277000	2.102563000
C	-6.850935000	0.355028000	0.913071000
H	-6.941710000	-0.338848000	0.069531000
H	-7.089103000	-0.203126000	1.821774000
H	-7.598347000	1.144107000	0.783117000
P	-2.049584000	3.381949000	0.137038000
C	-2.731463000	4.517400000	-1.126551000
C	-2.146464000	4.603201000	-2.396764000

C	-3.801999000	5.365456000	-0.793686000
C	-2.641601000	5.514276000	-3.332095000
C	-4.300444000	6.263400000	-1.736654000
C	-3.721202000	6.337735000	-3.006927000
H	-1.317806000	3.954271000	-2.655209000
H	-4.237405000	5.333247000	0.200806000
H	-2.184097000	5.576060000	-4.315210000
H	-5.133730000	6.909584000	-1.476576000
H	-4.107501000	7.041762000	-3.738514000
C	-1.681230000	4.519884000	1.527873000
C	-2.311251000	4.426788000	2.774466000
C	-0.726598000	5.525547000	1.304721000
C	-1.991156000	5.335631000	3.787110000
C	-0.414348000	6.430844000	2.316157000
C	-1.045349000	6.336382000	3.561122000
H	-3.052148000	3.655776000	2.956798000
H	-0.229930000	5.600312000	0.341307000
H	-2.486800000	5.259877000	4.750816000
H	0.324242000	7.206547000	2.135656000
H	-0.798921000	7.040906000	4.350368000
C	-8.086524000	-4.435973000	-0.563098000
C	-8.758603000	-5.268321000	0.354041000
C	-8.578479000	-4.364160000	-1.880143000
C	-9.887230000	-5.989024000	-0.031125000
C	-9.700890000	-5.096555000	-2.265201000
C	-10.364107000	-5.909703000	-1.342992000
H	-8.381031000	-5.362252000	1.367636000
H	-8.091417000	-3.717115000	-2.604534000
H	-10.388675000	-6.625100000	0.693218000
H	-10.062489000	-5.023419000	-3.287119000
H	-11.240253000	-6.477346000	-1.642914000

[$PdCl_2$(**DTE^c-Ph**)$_2$]

C	-6.781414000	-2.448113000	-0.515268000
C	-6.680707000	-0.936717000	-0.808150000
S	-8.425308000	-0.305582000	-0.543190000
C	-9.089784000	-1.961952000	-0.659716000
C	-8.125352000	-2.926952000	-0.625406000
H	-8.356509000	-3.985876000	-0.662385000
C	-3.912517000	-4.773463000	-0.578060000
C	-3.244555000	-3.466754000	-0.085309000
C	-4.366616000	-2.455378000	-0.131379000
C	-5.636201000	-3.143692000	-0.277177000
C	-5.402918000	-4.634032000	-0.177123000
H	-3.443682000	-5.670429000	-0.163910000
H	-2.374787000	-3.173613000	-0.680905000
H	-2.891359000	-3.574404000	0.948758000
H	-6.075989000	-5.221581000	-0.808753000
H	-5.550885000	-4.969811000	0.859232000
H	-3.837518000	-4.831057000	-1.669983000
C	-3.158772000	-0.257410000	0.038968000
C	-3.416338000	1.074418000	-0.075751000
S	-5.146586000	1.458347000	-0.294827000
C	-5.625588000	-0.314313000	0.132918000
C	-4.312685000	-1.102092000	-0.018490000
H	-2.153774000	-0.650978000	0.142858000
P	-2.095660000	2.317145000	-0.146505000
C	-2.144952000	2.906900000	-1.882995000
C	-1.653903000	4.183001000	-2.199127000
C	-2.608369000	2.070842000	-2.908362000
C	-1.640541000	4.619311000	-3.523689000
C	-2.595348000	2.513523000	-4.231943000
C	-2.112960000	3.786900000	-4.542216000
H	-1.288987000	4.838668000	-1.414092000
H	-2.983198000	1.079160000	-2.675894000
H	-1.262138000	5.609922000	-3.759243000
H	-2.964682000	1.862237000	-5.018961000
H	-2.104625000	4.129846000	-5.572899000
C	-2.632327000	3.785788000	0.814948000
C	-3.742197000	4.542844000	0.400271000
C	-1.913972000	4.184784000	1.951083000
C	-4.139591000	5.662694000	1.129184000
C	-2.310869000	5.313017000	2.672464000
C	-3.425693000	6.048570000	2.267576000
H	-4.286523000	4.275535000	-0.499723000
H	-1.054194000	3.611537000	2.276689000
H	-5.002147000	6.236834000	0.803672000
H	-1.746968000	5.613082000	3.550996000
H	-3.734854000	6.923988000	2.831654000
C	-6.025084000	-0.333333000	1.625461000
H	-6.264356000	-1.354422000	1.937020000
H	-5.185800000	0.025145000	2.227015000
H	-6.890948000	0.302014000	1.820501000
C	-6.347117000	-0.769480000	-2.309370000
H	-5.352972000	-1.174031000	-2.520528000
H	-7.078976000	-1.320862000	-2.904993000
H	-6.367885000	0.278962000	-2.612054000
Pd	-0.099527000	1.276982000	0.607791000
Cl	0.870058000	1.533615000	-1.522561000
Cl	-1.153164000	0.882457000	2.703716000
C	7.810953000	0.321394000	-1.298868000
C	6.848025000	-0.799498000	-0.863167000
S	7.980809000	-2.147128000	-0.219260000
C	9.389840000	-1.418618000	-1.045174000
C	9.136538000	-0.166955000	-1.526757000
H	9.888409000	0.427573000	-2.034125000
C	6.725828000	3.585769000	-2.637571000
C	5.594853000	3.274607000	-1.627015000
C	5.942946000	1.891747000	-1.121795000
C	7.309355000	1.571921000	-1.491663000
C	7.949115000	2.788624000	-2.120408000

H	6.926052000	4.656416000	-2.733246000
H	4.594255000	3.329071000	-2.067362000
H	5.616758000	3.986508000	-0.790044000
H	8.667069000	2.541401000	-2.908176000
H	8.487441000	3.369633000	-1.357845000
H	6.442339000	3.208262000	-3.626593000
C	3.823547000	1.139317000	0.012650000
C	3.291611000	0.008187000	0.548554000
S	4.423548000	-1.376436000	0.588264000
C	5.865526000	-0.235415000	0.187299000
C	5.193242000	1.024050000	-0.390882000
H	3.245065000	2.044903000	-0.123662000
P	1.689911000	-0.048508000	1.397142000
C	1.115439000	-1.777525000	1.244500000
C	0.450798000	-2.421343000	2.299998000
C	1.230612000	-2.422507000	0.001003000
C	-0.060145000	-3.707592000	2.120937000
C	0.716610000	-3.708475000	-0.170258000
C	0.075823000	-4.354835000	0.889955000
H	0.333157000	-1.922297000	3.255391000
H	1.721425000	-1.924368000	-0.829565000
H	-0.565553000	-4.202668000	2.945009000
H	0.818331000	-4.203245000	-1.131660000
H	-0.323562000	-5.355856000	0.755026000
C	2.212929000	0.226697000	3.131248000
C	2.851006000	-0.775369000	3.878497000
C	2.091900000	1.518819000	3.664011000
C	3.350553000	-0.485335000	5.149522000
C	2.598684000	1.804213000	4.931520000
C	3.226483000	0.802245000	5.676739000
H	2.959425000	-1.776465000	3.475463000
H	1.595146000	2.294597000	3.089995000
H	3.839485000	-1.266567000	5.724354000
H	2.497372000	2.806151000	5.338622000
H	3.617361000	1.024330000	6.665662000
C	6.530793000	0.154372000	1.526855000
H	7.340182000	0.869184000	1.350840000
H	5.787163000	0.625278000	2.175240000
H	6.940675000	-0.715571000	2.043052000
C	6.152534000	-1.342815000	-2.133364000
H	5.510948000	-0.571997000	-2.569871000
H	6.912211000	-1.620381000	-2.868386000
H	5.541326000	-2.220035000	-1.914077000
C	10.658540000	-2.151960000	-1.120738000
C	11.873177000	-1.457235000	-1.300157000
C	10.704016000	-3.555739000	-1.014861000
C	13.080611000	-2.144425000	-1.385740000
C	11.916267000	-4.239764000	-1.097953000
C	13.109622000	-3.539512000	-1.285681000
H	11.870640000	-0.373209000	-1.351130000
H	9.783660000	-4.117598000	-0.887632000
H	14.004497000	-1.588970000	-1.520506000
H	11.925771000	-5.323145000	-1.018919000
H	14.053744000	-4.072876000	-1.347881000
C	-10.540060000	-2.168950000	-0.746273000
C	-11.398661000	-1.165148000	-1.235166000
C	-11.110436000	-3.391399000	-0.333274000
C	-12.773600000	-1.380826000	-1.321462000
C	-12.483169000	-3.603230000	-0.423966000
C	-13.322902000	-2.599975000	-0.919246000
H	-10.986493000	-0.217764000	-1.569210000
H	-10.476276000	-4.168794000	0.080633000
H	-13.415392000	-0.593858000	-1.707280000
H	-12.901325000	-4.550935000	-0.096448000
H	-14.394277000	-2.766343000	-0.984260000

PhI

C	0.000000000	0.000000000	-0.579023000
C	0.000000000	1.218778000	-1.260023000
C	0.000000000	-1.218778000	-1.260023000
C	0.000000000	1.208622000	-2.658171000
C	0.000000000	-1.208622000	-2.658171000
C	0.000000000	0.000000000	-3.357848000
H	0.000000000	2.157824000	-0.717789000
H	0.000000000	-2.157824000	-0.717789000
H	0.000000000	2.152414000	-3.196150000
H	0.000000000	-2.152414000	-3.196150000
H	0.000000000	0.000000000	-4.443889000
I	0.000000000	0.000000000	1.564365000

0 [Pd(**DTE^o-COCF$_3$**)$_2$]

Pd	-0.083484000	2.249482000	0.539332000
S	4.961586000	2.411204000	0.881997000
S	7.556792000	-1.511742000	-2.342721000
P	1.956756000	3.231076000	0.209455000
F	11.531232000	-4.212687000	-0.478576000
F	9.545334000	-5.020709000	-0.095870000
F	10.230241000	-3.256594000	0.983435000
O	10.403212000	-2.644497000	-2.259922000
C	2.522114000	4.784745000	1.024381000
C	1.843178000	5.191278000	2.183031000
H	0.993117000	4.611431000	2.535041000
C	2.252149000	6.330093000	2.880602000
H	1.719186000	6.634790000	3.776916000
C	3.338468000	7.077876000	2.420914000
H	3.654364000	7.966783000	2.959756000
C	4.015462000	6.685068000	1.262403000
H	4.858341000	7.266839000	0.899861000
C	3.611241000	5.545017000	0.566367000
H	4.137781000	5.254906000	-0.337912000

C	2.293213000	3.513348000	-1.586838000
C	1.977028000	4.739342000	-2.193720000
H	1.626400000	5.571720000	-1.590095000
C	2.122978000	4.902584000	-3.572892000
H	1.883543000	5.859718000	-4.028138000
C	2.576048000	3.843664000	-4.364468000
H	2.689694000	3.973841000	-5.436937000
C	2.880995000	2.617122000	-3.768435000
H	3.233205000	1.787088000	-4.375210000
C	2.737855000	2.451283000	-2.390061000
H	2.965951000	1.492174000	-1.937618000
C	3.259472000	2.032417000	0.673907000
C	3.066131000	0.681080000	0.814069000
H	2.092145000	0.221354000	0.707266000
C	4.261032000	-0.073578000	1.063329000
C	5.379959000	0.735071000	1.147390000
C	6.797688000	0.357058000	1.450163000
H	6.824476000	-0.606983000	1.963803000
H	7.285749000	1.102073000	2.086611000
H	7.392228000	0.259818000	0.534186000
C	4.229843000	-1.534794000	1.223926000
H	3.472639000	-1.937959000	3.198106000
C	3.365646000	-3.694295000	1.861812000
H	2.608656000	-3.987718000	1.127828000
C	4.766914000	-3.846048000	1.229688000
C	5.053923000	-2.458814000	0.677322000
C	6.138555000	-2.253993000	-0.293669000
C	7.414038000	-2.866732000	-0.144500000
H	7.665138000	-3.502786000	0.695113000
C	8.303944000	-2.559731000	-1.155834000
C	6.060092000	-1.496585000	-1.460036000
C	4.893262000	-0.727605000	-1.990690000
H	3.965000000	-1.127441000	-1.578614000
H	4.842554000	-0.772231000	-3.082985000
H	4.959554000	0.326524000	-1.699523000
C	9.680804000	-2.967703000	-1.328506000
C	10.263671000	-3.881450000	-0.215271000
S	-3.412381000	-1.429581000	-0.986791000
S	-8.400051000	-2.126614000	1.553874000
P	-1.150071000	0.223661000	0.516792000
F	-12.568360000	-3.255005000	-1.259446000
F	-12.150988000	-1.141209000	-0.940919000
F	-10.916416000	-2.300793000	-2.310851000
O	-10.856863000	-3.733580000	0.677050000
C	-0.144405000	-0.963247000	-0.493485000
C	0.485039000	-0.479979000	-1.653742000
H	0.377782000	0.566302000	-1.926751000
C	1.267085000	-1.325298000	-2.440329000
H	1.752014000	-0.935119000	-3.330648000
C	1.439195000	-2.664174000	-2.074362000
H	2.059404000	-3.319584000	-2.679154000
C	0.814146000	-3.153646000	-0.925917000
H	0.936871000	-4.194423000	-0.640397000
C	0.026672000	-2.309229000	-0.136945000
H	-0.446411000	-2.702324000	0.757396000
C	-1.237926000	-0.631579000	2.153118000
C	-0.125963000	-0.497897000	3.004013000
H	0.720930000	0.107242000	2.691223000
C	-0.103053000	-1.133893000	4.245189000
H	0.767317000	-1.029418000	4.887038000
C	-1.199098000	-1.895022000	4.663436000
H	-1.185126000	-2.384286000	5.633244000
C	-2.314101000	-2.017945000	3.832155000
H	-3.171868000	-2.603170000	4.152249000
C	-2.332963000	-1.393992000	2.581356000
H	-3.202344000	-1.507204000	1.943081000
C	-2.809119000	0.021550000	-0.204413000
C	-3.778453000	0.991891000	-0.207683000
H	-3.614910000	1.977555000	0.215683000
C	-5.024669000	0.585068000	-0.792569000
C	-4.974645000	-0.707987000	-1.282348000
C	-6.032420000	-1.484061000	-2.005857000
H	-6.767870000	-0.800533000	-2.436770000
H	-5.606169000	-2.087850000	-2.813398000
H	-6.567107000	-2.161267000	-1.329465000
C	-6.190005000	1.479727000	-0.857326000
C	-6.066015000	2.882446000	-1.427518000
H	-5.911548000	2.819709000	-2.514744000
H	-5.203190000	3.425312000	-1.024694000
C	-7.416176000	3.541121000	-1.071087000
H	-7.752033000	4.261620000	-1.821948000
H	-7.317795000	4.074859000	-0.119317000
C	-8.392608000	2.358228000	-0.888162000
H	-8.930600000	2.128305000	-1.820037000
H	-9.155001000	2.544305000	-0.123768000
C	-7.472183000	1.203830000	-0.524039000
C	-8.009511000	-0.029698000	0.068166000
C	-9.187657000	-0.657514000	-0.423446000
H	-9.750124000	-0.273924000	-1.265463000
C	-9.531754000	-1.810203000	0.256278000
C	-7.477497000	-0.707661000	1.162455000
C	-6.276831000	-0.354340000	1.980363000
H	-6.083592000	0.718887000	1.913896000
H	-6.408427000	-0.626243000	3.031882000
H	-5.385802000	-0.870284000	1.606723000
C	-10.632833000	-2.720631000	0.030832000
C	-11.588426000	-2.354446000	-1.138426000
C	3.222021000	-2.185759000	2.156140000
H	2.203120000	-1.820347000	1.989425000
H	3.226803000	-4.317237000	2.749720000
H	5.525775000	-4.114992000	1.979551000
H	4.805549000	-4.620006000	0.454935000

0 [Pd(**DTE^{o}-COCF$_3$**)(**DTE^{c}-COCF$_3$**)]

C	-6.462111000	-1.967294000	0.035290000
C	-6.159461000	-0.690218000	-0.775028000
S	-7.835801000	-0.147332000	-1.429277000
C	-8.515437000	-1.761352000	-1.081443000
C	-7.701715000	-2.558032000	-0.312742000
H	-7.991534000	-3.541607000	0.037397000
C	-3.938942000	-3.898206000	1.928987000
C	-3.389687000	-2.456070000	2.061493000
C	-4.358350000	-1.636342000	1.238028000
C	-5.526434000	-2.422397000	0.925042000
C	-5.457940000	-3.729503000	1.675160000
H	-3.723754000	-4.516769000	2.804048000
H	-2.357173000	-2.365236000	1.710866000
H	-3.409743000	-2.121504000	3.107778000
H	-5.906850000	-4.565344000	1.131143000
H	-5.997281000	-3.630992000	2.627858000
H	-3.479364000	-4.376854000	1.058097000
C	-3.145081000	0.540513000	0.937932000
C	-3.241829000	1.691910000	0.210821000
S	-4.741161000	1.828337000	-0.725267000
C	-5.472602000	0.333073000	0.157010000
C	-4.260180000	-0.341454000	0.820011000
H	-2.253709000	0.288706000	1.501362000
P	-1.902586000	2.958038000	0.185950000
C	-2.290906000	3.893822000	-1.355037000
C	-2.744145000	5.220246000	-1.369169000
C	-2.068975000	3.231961000	-2.576411000
C	-2.981492000	5.868704000	-2.584394000
C	-2.320066000	3.877813000	-3.785879000
C	-2.775394000	5.200098000	-3.792256000
H	-2.917086000	5.750388000	-0.438481000
H	-1.701667000	2.208573000	-2.575668000
H	-3.332313000	6.896927000	-2.583291000
H	-2.154193000	3.352372000	-4.722179000
H	-2.964524000	5.706326000	-4.734632000
C	-2.393110000	4.073071000	1.566555000
C	-3.727104000	4.438328000	1.817010000
C	-1.379670000	4.552572000	2.410178000
C	-4.035807000	5.271931000	2.891977000
C	-1.691952000	5.391997000	3.482326000
C	-3.019382000	5.750580000	3.725045000
H	-4.522654000	4.075943000	1.173321000
H	-0.348555000	4.259636000	2.228656000
H	-5.069731000	5.547890000	3.079284000
H	-0.899732000	5.758076000	4.129238000
H	-3.263764000	6.398379000	4.562218000
C	-6.384792000	0.872613000	1.283814000
H	-6.797850000	0.040066000	1.860891000
H	-5.796547000	1.501941000	1.956738000
H	-7.211471000	1.461931000	0.884058000
C	-5.287887000	-1.094678000	-1.986884000
H	-4.317404000	-1.465996000	-1.645893000
H	-5.787918000	-1.892322000	-2.541714000
H	-5.121880000	-0.253350000	-2.662368000
Pd	0.051666000	1.775661000	0.335493000
C	-9.838295000	-2.066507000	-1.575326000
O	-10.535305000	-1.295521000	-2.225847000
C	-10.401591000	-3.474289000	-1.245884000
F	-11.625902000	-3.635109000	-1.759575000
F	-9.606265000	-4.448387000	-1.746273000
F	-10.480424000	-3.671660000	0.091437000
S	3.541745000	-2.045357000	-0.347797000
S	8.852385000	-1.116908000	1.552429000
P	1.151206000	-0.205015000	0.671685000
F	12.965190000	-2.535736000	-1.210677000
F	12.126828000	-0.574393000	-1.650063000
F	11.079493000	-2.374700000	-2.289224000
O	11.515098000	-2.520263000	0.981126000
C	0.159253000	-1.668689000	0.128316000
C	-0.785326000	-1.499151000	-0.895802000
H	-0.944601000	-0.510206000	-1.316847000
C	-1.526139000	-2.586819000	-1.363305000
H	-2.251803000	-2.441939000	-2.158223000
C	-1.338708000	-3.853502000	-0.804942000
H	-1.918286000	-4.698664000	-1.165044000
C	-0.408160000	-4.029686000	0.223265000
H	-0.263786000	-5.011230000	0.665743000
C	0.337689000	-2.944858000	0.688113000
H	1.050220000	-3.092718000	1.493998000
C	1.457112000	-0.567224000	2.456950000
C	0.355929000	-0.828343000	3.291046000
H	-0.643625000	-0.888057000	2.868466000
C	0.537638000	-1.024797000	4.659434000
H	-0.320844000	-1.235368000	5.291374000
C	1.818905000	-0.951474000	5.216334000
H	1.959376000	-1.103452000	6.282722000
C	2.915249000	-0.681408000	4.395357000
H	3.914026000	-0.622436000	4.819253000
C	2.736655000	-0.490168000	3.022471000
H	3.595227000	-0.278620000	2.393405000
C	2.765526000	-0.488564000	-0.118743000
C	3.574334000	0.511666000	-0.595252000
H	3.285130000	1.556812000	-0.556063000
C	4.832803000	0.061134000	-1.120588000
C	4.953745000	-1.316230000	-1.072527000
C	6.070217000	-2.183864000	-1.567499000
H	6.664438000	-1.641515000	-2.306699000
H	5.690538000	-3.099457000	-2.032191000

H	6.742826000	-2.477232000	-0.753080000
C	5.833987000	0.994569000	-1.657321000
H	5.212220000	1.562878000	-3.634709000
C	6.683306000	2.957149000	-2.765606000
H	6.576203000	3.790829000	-2.062738000
C	7.851483000	2.057388000	-2.308062000
C	7.167645000	1.023607000	-1.425909000
C	7.959921000	0.188717000	-0.511491000
C	9.201371000	-0.386378000	-0.903128000
H	9.621058000	-0.258474000	-1.893017000
C	9.808827000	-1.134466000	0.086575000
C	7.646137000	-0.108829000	0.812598000
C	6.456492000	0.323505000	1.608095000
H	6.039938000	1.242037000	1.188775000
H	6.712392000	0.496692000	2.657721000
H	5.672904000	-0.441312000	1.572493000
C	11.049834000	-1.877183000	0.051861000
C	11.825324000	-1.843388000	-1.294209000
C	5.437149000	2.051379000	-2.675146000
H	4.530608000	2.595330000	-2.386341000
H	6.833086000	3.380775000	-3.762507000
H	8.336172000	1.559211000	-3.161000000
H	8.636853000	2.607598000	-1.778361000

0 [Pd(**DTE^{c}-COCF$_3$**)$_2$]

C	-5.867033000	-1.507421000	0.942644000
C	-4.939774000	-1.531478000	-0.289751000
S	-5.862227000	-2.583512000	-1.544676000
C	-6.911773000	-3.232815000	-0.255332000
C	-6.808849000	-2.567305000	0.941472000
H	-7.419643000	-2.799700000	1.805747000
C	-5.185859000	0.383232000	4.045764000
C	-4.538549000	1.297534000	2.977450000
C	-4.721173000	0.519038000	1.693972000
C	-5.667237000	-0.552527000	1.901652000
C	-6.264323000	-0.424453000	3.280997000
H	-5.597644000	0.941395000	4.890419000
H	-3.489550000	1.522648000	3.191105000
H	-5.070840000	2.256028000	2.907741000
H	-6.499901000	-1.387674000	3.742160000
H	-7.200381000	0.148637000	3.221352000
H	-4.428791000	-0.306160000	4.434907000
C	-3.114706000	1.630146000	0.114493000
C	-2.587604000	1.444588000	-1.130411000
S	-3.328393000	0.109066000	-2.033725000
C	-4.680579000	-0.076202000	-0.739057000
C	-4.157983000	0.720374000	0.468848000
H	-2.716923000	2.366254000	0.804834000
P	-1.216671000	2.488340000	-1.777379000
C	-0.216946000	1.267811000	-2.736781000
C	0.320091000	1.564717000	-3.997989000
C	0.120456000	0.048822000	-2.121687000
C	1.161690000	0.650606000	-4.639033000
C	0.951304000	-0.864777000	-2.768506000
C	1.474359000	-0.567045000	-4.030771000
H	0.078470000	2.502742000	-4.488122000
H	-0.272538000	-0.186931000	-1.137237000
H	1.568173000	0.891245000	-5.617359000
H	1.189525000	-1.808596000	-2.286827000
H	2.120954000	-1.279386000	-4.534620000
C	-2.070410000	3.509960000	-3.050989000
C	-2.686338000	2.970762000	-4.193433000
C	-2.131468000	4.893520000	-2.827306000
C	-3.352820000	3.804904000	-5.090550000
C	-2.800980000	5.726960000	-3.726890000
C	-3.412706000	5.183051000	-4.857774000
H	-2.638528000	1.904242000	-4.387807000
H	-1.653383000	5.313678000	-1.945613000
H	-3.825794000	3.379903000	-5.971392000
H	-2.841674000	6.797083000	-3.544336000
H	-3.932830000	5.829500000	-5.559107000
C	-5.933457000	0.651023000	-1.280015000
H	-6.737633000	0.614444000	-0.539244000
H	-5.688853000	1.698348000	-1.475187000
H	-6.292230000	0.197256000	-2.205248000
C	-3.650247000	-2.290032000	0.103887000
H	-3.106989000	-1.737221000	0.875382000
H	-3.915908000	-3.271656000	0.503858000
H	-2.989628000	-2.431174000	-0.753574000
Pd	0.000007000	3.246442000	0.000006000
C	5.867002000	-1.507397000	-0.942716000
C	4.940043000	-1.531226000	0.289915000
S	5.862902000	-2.582830000	1.544891000
C	6.912259000	-3.232316000	0.255492000
C	6.808971000	-2.567150000	-0.941470000
H	7.419605000	-2.799685000	-1.805819000
C	5.184796000	0.382230000	-4.046200000
C	4.537466000	1.296680000	-2.978026000
C	4.720612000	0.518659000	-1.694328000
C	5.666841000	-0.552786000	-1.901924000
C	6.263618000	-0.424960000	-3.281423000
H	5.596256000	0.940258000	-4.891102000
H	3.488356000	1.521439000	-3.191527000
H	5.069508000	2.255343000	-2.908743000
H	6.499372000	-1.388242000	-3.742368000
H	7.199529000	0.148404000	-3.222111000
H	4.427828000	-0.307470000	-4.434989000
C	3.114358000	1.629922000	-0.114725000
C	2.587638000	1.444626000	1.130385000
S	3.329086000	0.109660000	2.033958000
C	4.680843000	-0.075852000	0.738883000

C	4.157731000	0.720273000	-0.469109000
H	2.716213000	2.365740000	-0.805166000
P	1.216645000	2.488274000	1.777385000
C	0.216669000	1.267684000	2.736470000
C	-0.321369000	1.565039000	3.997165000
C	-0.120098000	0.048404000	2.121650000
C	-1.163314000	0.651089000	4.637962000
C	-0.951349000	-0.865024000	2.768220000
C	-1.475392000	-0.566853000	4.029961000
H	-0.080288000	2.503322000	4.487073000
H	0.273665000	-0.187733000	1.137602000
H	-1.570543000	0.892076000	5.615893000
H	-1.189120000	-1.809043000	2.286712000
H	-2.122307000	-1.279053000	4.533600000
C	2.070280000	3.509561000	3.051343000
C	2.685168000	2.970143000	4.194243000
C	2.132448000	4.893030000	2.827427000
C	3.351731000	3.803987000	5.091580000
C	2.802050000	5.726169000	3.727222000
C	3.412745000	5.182043000	4.858560000
H	2.636436000	1.903701000	4.388829000
H	1.655150000	5.313356000	1.945386000
H	3.823895000	3.378825000	5.972777000
H	2.843606000	6.796227000	3.544484000
H	3.932927000	5.828259000	5.560066000
C	5.933834000	0.651656000	1.279186000
H	6.737764000	0.614922000	0.538156000
H	5.689201000	1.699019000	1.474111000
H	6.292963000	0.198206000	2.204438000
C	3.650467000	-2.289985000	-0.103181000
H	3.106963000	-1.737405000	-0.874667000
H	3.916093000	-3.271690000	-0.502973000
H	2.990100000	-2.430948000	0.754504000
C	7.790116000	-4.334732000	0.579380000
O	7.861409000	-4.868126000	1.680466000
C	-7.789403000	-4.335441000	-0.579106000
O	-7.860438000	-4.869104000	-1.680082000
C	-8.707413000	-4.857230000	0.558066000
F	-9.445525000	-5.892475000	0.143937000
F	-7.983259000	-5.260504000	1.627902000
F	-9.548972000	-3.888153000	0.988539000
C	8.707963000	-4.856703000	-0.557843000
F	9.446462000	-5.891594000	-0.143520000
F	7.983628000	-5.260570000	-1.627325000
F	9.549149000	-3.887568000	-0.988909000

1 [Pd(**DTE^o-COCF$_3$**)$_2$]·**PhI**

Pd	-0.241699000	1.560811000	1.068463000
S	4.505321000	2.399895000	-0.650597000
S	7.781285000	-1.873024000	-2.632086000
P	1.331927000	2.117657000	-0.555171000
F	12.620980000	-2.660286000	-1.046123000
F	11.042150000	-3.597749000	0.125034000
F	11.365289000	-1.447092000	0.255757000
O	10.806294000	-2.269431000	-2.905853000
C	1.549194000	3.880339000	-1.041877000
C	1.983903000	4.781444000	-0.053038000
H	2.245000000	4.412655000	0.935145000
C	2.075891000	6.144994000	-0.328778000
H	2.419552000	6.828706000	0.442595000
C	1.719428000	6.631078000	-1.591193000
H	1.784271000	7.694314000	-1.804314000
C	1.281975000	5.743328000	-2.576381000
H	1.008976000	6.113168000	-3.560978000
C	1.198794000	4.374678000	-2.306242000
H	0.861456000	3.695507000	-3.082741000
C	0.971147000	1.246508000	-2.143187000
C	-0.376308000	1.119806000	-2.523140000
H	-1.150546000	1.587725000	-1.922082000
C	-0.728935000	0.374468000	-3.648469000
H	-1.775688000	0.278627000	-3.922990000
C	0.260039000	-0.263917000	-4.403113000
H	-0.014395000	-0.859408000	-5.269291000
C	1.602404000	-0.135917000	-4.037071000
H	2.376494000	-0.627461000	-4.620158000
C	1.957193000	0.618911000	-2.916297000
H	3.001540000	0.699352000	-2.635658000
C	3.027658000	1.603570000	-0.139286000
C	3.329800000	0.477650000	0.583337000
H	2.566148000	-0.174159000	0.988775000
C	4.734038000	0.214541000	0.717745000
C	5.508269000	1.193696000	0.119856000
C	6.999456000	1.334352000	0.091685000
H	7.444561000	0.758025000	0.906231000
H	7.305772000	2.379776000	0.199880000
H	7.422189000	0.959217000	-0.847866000
C	5.227097000	-0.966715000	1.440166000
H	4.987188000	-0.576606000	3.542798000
C	5.234639000	-2.723822000	3.092162000
H	4.510189000	-3.480170000	2.773890000
C	6.491496000	-2.824159000	2.201367000
C	6.211922000	-1.826497000	1.087410000
C	7.004173000	-1.866719000	-0.150349000
C	8.410610000	-2.085361000	-0.133508000
H	8.973770000	-2.210469000	0.782823000
C	8.990077000	-2.104122000	-1.387366000
C	6.514004000	-1.751177000	-1.449465000
C	5.102950000	-1.550106000	-1.898317000
H	4.411971000	-1.885054000	-1.123875000
H	4.891310000	-2.096678000	-2.822418000
H	4.903390000	-0.488720000	-2.081160000

C	10.376136000	-2.280263000	-1.761874000
C	11.374368000	-2.500668000	-0.591864000
S	-2.713519000	-2.774495000	0.044174000
S	-8.126555000	-2.183016000	1.361117000
P	-0.636897000	-0.733421000	1.348009000
F	-11.794099000	-4.074753000	-1.725944000
F	-11.150361000	-2.031470000	-2.119927000
F	-9.852900000	-3.702321000	-2.640506000
O	-10.569862000	-3.862013000	0.588754000
C	0.562297000	-2.013365000	0.771107000
C	0.892178000	-1.997380000	-0.596591000
H	0.413011000	-1.284477000	-1.260155000
C	1.830244000	-2.890358000	-1.109260000
H	2.071576000	-2.861936000	-2.167761000
C	2.464275000	-3.806963000	-0.263175000
H	3.202921000	-4.497078000	-0.660670000
C	2.141764000	-3.829435000	1.094511000
H	2.617800000	-4.547827000	1.755700000
C	1.195571000	-2.938661000	1.612517000
H	0.951494000	-2.977597000	2.668837000
C	-1.012489000	-1.177686000	3.091993000
C	-0.020074000	-0.900873000	4.050803000
H	0.950556000	-0.529935000	3.730867000
C	-0.275239000	-1.081531000	5.409422000
H	0.504120000	-0.870910000	6.136432000
C	-1.536263000	-1.512055000	5.834640000
H	-1.740664000	-1.639944000	6.893810000
C	-2.533645000	-1.768325000	4.891242000
H	-3.517357000	-2.098367000	5.214009000
C	-2.274169000	-1.607096000	3.527276000
H	-3.061376000	-1.808263000	2.808506000
C	-2.119879000	-1.157063000	0.384743000
C	-2.922677000	-0.229684000	-0.230079000
H	-2.732675000	0.835957000	-0.168724000
C	-4.035084000	-0.782360000	-0.943789000
C	-4.052621000	-2.164076000	-0.898904000
C	-5.026491000	-3.111756000	-1.528733000
H	-5.564187000	-2.609198000	-2.336307000
H	-4.523527000	-3.992022000	-1.941719000
H	-5.770289000	-3.461894000	-0.803313000
C	-5.018915000	0.079942000	-1.613992000
C	-4.580557000	1.148100000	-2.601008000
H	-4.240666000	0.667073000	-3.530357000
H	-3.737467000	1.742575000	-2.230473000
C	-5.859290000	1.985655000	-2.817640000
H	-5.937961000	2.393888000	-3.828997000
H	-5.859222000	2.828470000	-2.116967000
C	-7.019743000	1.030178000	-2.457972000
H	-7.402194000	0.504851000	-3.345850000
H	-7.874215000	1.544150000	-2.004568000
C	-6.366324000	0.038631000	-1.508269000
C	-7.173757000	-0.841320000	-0.650550000
C	-8.309703000	-1.544653000	-1.138225000
H	-8.641860000	-1.481325000	-2.166891000
C	-8.933485000	-2.327596000	-0.185704000
C	-6.959300000	-1.075887000	0.705923000
C	-5.904282000	-0.498712000	1.595621000
H	-5.559697000	0.456341000	1.191961000
H	-6.276388000	-0.339302000	2.611983000
H	-5.034436000	-1.162670000	1.654528000
C	-10.086559000	-3.191858000	-0.311827000
C	-10.738253000	-3.255613000	-1.720998000
C	4.657801000	-1.321958000	2.804160000
H	3.561889000	-1.307160000	2.813818000
H	5.445993000	-2.890029000	4.152103000
H	7.400632000	-2.531616000	2.747478000
H	6.667473000	-3.836445000	1.820743000
C	-1.374766000	3.444693000	1.674808000
C	-0.542432000	4.417377000	2.299096000
C	-1.930759000	2.375523000	2.442945000
C	-0.207995000	4.273360000	3.632736000
C	-1.585105000	2.285793000	3.823694000
C	-0.729414000	3.202731000	4.400887000
H	-0.162214000	5.248658000	1.716662000
H	-2.781015000	1.810326000	2.077315000
H	0.453136000	5.000745000	4.096160000
H	-2.024499000	1.487610000	4.414829000
H	-0.477457000	3.123176000	5.454578000
I	-2.448960000	4.082754000	-0.126859000

1 [Pd(**DTE^{o}-COCF$_3$**)(**DTE^{c}-COCF$_3$**)]·**PhI**

C	5.878329000	2.926747000	0.325862000
C	5.808240000	1.667376000	-0.563121000
S	7.523893000	1.536981000	-1.319377000
C	7.862597000	3.236206000	-0.887821000
C	6.942488000	3.790961000	-0.031171000
H	7.035148000	4.792223000	0.372164000
C	3.099607000	4.147928000	2.433898000
C	2.897555000	2.616073000	2.515569000
C	3.960212000	2.078235000	1.583612000
C	4.918585000	3.114195000	1.284150000
C	4.605939000	4.331900000	2.118847000
H	2.791439000	4.667938000	3.344595000
H	1.888640000	2.298111000	2.240708000
H	3.078667000	2.252160000	3.536116000
H	4.837294000	5.274167000	1.614400000
H	5.195482000	4.302003000	3.046144000
H	2.508162000	4.546453000	1.601582000
C	3.180355000	-0.259425000	1.113819000
C	3.472462000	-1.312759000	0.298391000
S	4.962710000	-1.094618000	-0.641536000

C	5.399358000	0.464977000	0.316481000
C	4.102007000	0.827876000	1.057566000
H	2.274466000	-0.222588000	1.704075000
P	2.403533000	-2.814315000	0.252197000
C	2.602075000	-3.413934000	-1.478002000
C	2.609967000	-4.791100000	-1.755711000
C	2.555081000	-2.506386000	-2.549905000
C	2.589931000	-5.247743000	-3.074766000
C	2.541729000	-2.966222000	-3.867068000
C	2.558547000	-4.337769000	-4.134851000
H	2.640919000	-5.509930000	-0.941994000
H	2.523286000	-1.439089000	-2.358223000
H	2.603157000	-6.315895000	-3.273314000
H	2.516624000	-2.250737000	-4.684555000
H	2.548669000	-4.694609000	-5.160783000
C	3.431008000	-3.979054000	1.254110000
C	4.688022000	-4.453568000	0.843944000
C	2.927410000	-4.369012000	2.504544000
C	5.423773000	-5.301071000	1.672540000
C	3.667533000	-5.214651000	3.334989000
C	4.916344000	-5.681057000	2.919486000
H	5.088184000	-4.169137000	-0.124061000
H	1.952730000	-4.005560000	2.822345000
H	6.394142000	-5.664528000	1.345800000
H	3.267258000	-5.510004000	4.300950000
H	5.492744000	-6.340810000	3.562012000
C	6.454139000	0.068052000	1.375262000
H	6.704985000	0.931931000	1.997843000
H	6.045406000	-0.716186000	2.017811000
H	7.369218000	-0.302215000	0.910154000
C	4.806887000	1.953331000	-1.706332000
H	3.800671000	2.092169000	-1.303601000
H	5.101435000	2.868850000	-2.225516000
H	4.779540000	1.136597000	-2.430109000
Pd	0.214531000	-2.399108000	0.783118000
C	9.058115000	3.852326000	-1.415391000
O	9.858147000	3.299164000	-2.161979000
C	9.341514000	5.314840000	-0.980282000
F	10.458020000	5.779659000	-1.551395000
F	8.323017000	6.138290000	-1.322604000
F	9.490372000	5.403358000	0.362589000
S	-3.129424000	0.170448000	-1.062895000
S	-6.913554000	4.126215000	-0.243550000
P	-0.795890000	-0.327308000	0.973284000
F	-11.458211000	3.890398000	-2.662399000
F	-11.342374000	2.906433000	-0.723019000
F	-10.362442000	2.019391000	-2.454940000
O	-9.205592000	5.090078000	-2.032517000
C	-0.018242000	0.841878000	-0.246563000
C	0.396147000	0.295433000	-1.473224000
H	0.262297000	-0.766631000	-1.658542000
C	0.991731000	1.097741000	-2.447164000
H	1.304829000	0.656402000	-3.389362000
C	1.200796000	2.457672000	-2.202224000
H	1.679848000	3.080630000	-2.952088000
C	0.799415000	3.009162000	-0.983288000
H	0.961828000	4.064738000	-0.782986000
C	0.186062000	2.209895000	-0.014553000
H	-0.121310000	2.661512000	0.922002000
C	-0.676664000	0.551253000	2.594513000
C	0.218070000	0.043972000	3.550085000
H	0.773563000	-0.864254000	3.329390000
C	0.395480000	0.692966000	4.774765000
H	1.094936000	0.290176000	5.501970000
C	-0.328504000	1.851743000	5.062661000
H	-0.191993000	2.357791000	6.014220000
C	-1.239086000	2.353250000	4.127080000
H	-1.813186000	3.248106000	4.351142000
C	-1.416164000	1.706259000	2.903495000
H	-2.134080000	2.096698000	2.188967000
C	-2.570528000	-0.105535000	0.573619000
C	-3.638881000	-0.326429000	1.403996000
H	-3.528383000	-0.524040000	2.464435000
C	-4.918454000	-0.234786000	0.756367000
C	-4.806656000	0.003957000	-0.599985000
C	-5.885394000	0.146184000	-1.630232000
H	-6.814216000	-0.294150000	-1.259779000
H	-5.616205000	-0.355190000	-2.565856000
H	-6.088453000	1.198367000	-1.863014000
C	-6.182334000	-0.354686000	1.498552000
H	-6.643710000	-2.439094000	1.750382000
C	-7.741698000	-1.142073000	3.155724000
H	-7.452452000	-0.689362000	4.110612000
C	-8.407267000	-0.066659000	2.267978000
C	-7.240514000	0.487415000	1.465832000
C	-7.354875000	1.761713000	0.741213000
C	-8.497456000	2.092363000	-0.038684000
H	-9.343647000	1.426337000	-0.152670000
C	-8.417677000	3.328739000	-0.650875000
C	-6.410240000	2.785748000	0.739523000
C	-5.099097000	2.845805000	1.457772000
H	-5.119712000	2.182266000	2.325162000
H	-4.870824000	3.861946000	1.793490000
H	-4.282634000	2.511782000	0.807527000
C	-9.358988000	3.986300000	-1.530303000
C	-10.656013000	3.193602000	-1.852017000
C	-6.470295000	-1.555562000	2.382565000
H	-5.628730000	-1.805074000	3.039196000
H	-8.402185000	-1.985427000	3.375385000
H	-9.153912000	-0.505997000	1.589745000
H	-8.925080000	0.706774000	2.845758000
C	-1.831854000	-3.845677000	-0.722884000

C	-0.913372000	-4.518828000	0.105399000
C	-3.085765000	-3.445564000	-0.255981000
C	-1.266406000	-4.729374000	1.452650000
C	-3.426475000	-3.698700000	1.075736000
C	-2.512989000	-4.314618000	1.934852000
H	-0.013917000	-4.960362000	-0.308218000
H	-3.779888000	-2.927910000	-0.908007000
H	-0.571959000	-5.253503000	2.102664000
H	-4.400277000	-3.390155000	1.440639000
H	-2.774907000	-4.491649000	2.973908000
I	-1.279520000	-3.463695000	-2.749377000

1 [Pd(**DTE^{c}-COCF$_3$**)$_2$]·**PhI**

C	6.232804000	-1.777405000	-0.928220000
C	5.133993000	-2.287108000	0.027766000
S	5.936607000	-3.726483000	0.932148000
C	7.216796000	-3.814474000	-0.307392000
C	7.243704000	-2.743354000	-1.165903000
H	7.994584000	-2.618628000	-1.936923000
C	5.872007000	1.142338000	-3.164079000
C	5.014707000	1.575291000	-1.949813000
C	5.062688000	0.366926000	-1.040959000
C	6.108155000	-0.530383000	-1.476032000
C	6.888772000	0.124241000	-2.588928000
H	6.356189000	1.984843000	-3.664235000
H	3.994580000	1.863636000	-2.221513000
H	5.466252000	2.438680000	-1.442397000
H	7.265869000	-0.585650000	-3.330319000
H	7.756402000	0.650434000	-2.166460000
H	5.235073000	0.637424000	-3.899397000
C	3.141509000	0.753735000	0.525448000
C	2.436312000	0.085709000	1.483255000
S	3.142477000	-1.470888000	1.951650000
C	4.692819000	-1.121879000	0.941792000
C	4.305458000	0.073077000	0.053114000
H	2.793111000	1.687228000	0.096200000
P	0.831655000	0.691783000	2.130107000
C	-0.066391000	-0.905268000	2.368208000
C	-0.249625000	-1.533339000	3.609199000
C	-0.566893000	-1.523578000	1.210433000
C	-0.930256000	-2.752124000	3.686651000
C	-1.237036000	-2.743260000	1.288993000
C	-1.425665000	-3.358991000	2.530147000
H	0.139461000	-1.081236000	4.515299000
H	-0.423338000	-1.051467000	0.245479000
H	-1.069001000	-3.227746000	4.653441000
H	-1.612936000	-3.208887000	0.382439000
H	-1.953077000	-4.306335000	2.594735000
C	1.204264000	1.264382000	3.835463000
C	2.510669000	1.487549000	4.292557000
C	0.120783000	1.653509000	4.643402000
C	2.728872000	2.083917000	5.537347000
C	0.342207000	2.235010000	5.891025000
C	1.648189000	2.457071000	6.339815000
H	3.360011000	1.203632000	3.678816000
H	-0.897677000	1.504961000	4.292791000
H	3.746090000	2.251123000	5.880609000
H	-0.503912000	2.525502000	6.507490000
H	1.820999000	2.919426000	7.307409000
C	5.785388000	-0.644940000	1.926288000
H	6.698094000	-0.390102000	1.379638000
H	5.437257000	0.248782000	2.450962000
H	6.024615000	-1.412734000	2.663750000
C	3.983084000	-2.855706000	-0.835091000
H	3.507148000	-2.056405000	-1.408740000
H	4.384924000	-3.593437000	-1.534223000
H	3.220619000	-3.338271000	-0.220988000
Pd	0.100845000	2.394489000	0.686424000
C	-6.416750000	-1.974096000	0.485657000
C	-5.699597000	-1.529045000	-0.807048000
S	-7.025267000	-1.636879000	-2.134394000
C	-8.028411000	-2.663228000	-1.073067000
C	-7.596447000	-2.717938000	0.228874000
H	-8.128441000	-3.247591000	1.009960000
C	-4.825565000	-2.081212000	3.813547000
C	-4.112521000	-0.866849000	3.171396000
C	-4.678766000	-0.832073000	1.770130000
C	-5.845527000	-1.681852000	1.692954000
C	-6.184557000	-2.181207000	3.075194000
H	-4.939912000	-1.984787000	4.896221000
H	-3.023041000	-0.955399000	3.187949000
H	-4.373329000	0.062027000	3.697322000
H	-6.613684000	-3.187015000	3.079530000
H	-6.919920000	-1.507387000	3.537209000
H	-4.239833000	-2.985675000	3.615814000
C	-3.022452000	0.576246000	0.522672000
C	-2.709476000	0.911304000	-0.760961000
S	-3.953274000	0.467298000	-1.948987000
C	-5.120650000	-0.113521000	-0.589439000
C	-4.245660000	-0.146043000	0.675688000
H	-2.350616000	0.773290000	1.349491000
P	-1.107956000	1.690019000	-1.185831000
C	-0.178779000	0.380860000	-2.100267000
C	1.152625000	0.675036000	-2.447978000
C	-0.679794000	-0.902685000	-2.364956000
C	1.953993000	-0.284730000	-3.065480000
C	0.133152000	-1.868638000	-2.964518000
C	1.447538000	-1.562927000	-3.320569000
H	1.563018000	1.656375000	-2.227682000
H	-1.697133000	-1.163148000	-2.096068000
H	2.978246000	-0.040967000	-3.330601000

H	-0.266834000	-2.860909000	-3.153380000
H	2.076940000	-2.315676000	-3.786229000
C	-1.610479000	2.895014000	-2.486880000
C	-1.119155000	2.882998000	-3.799235000
C	-2.474555000	3.930704000	-2.089404000
C	-1.480858000	3.892861000	-4.695177000
C	-2.841265000	4.931185000	-2.988031000
C	-2.339246000	4.918421000	-4.293612000
H	-0.457093000	2.089140000	-4.128890000
H	-2.857546000	3.952910000	-1.072343000
H	-1.094779000	3.871794000	-5.710607000
H	-3.514035000	5.722482000	-2.669105000
H	-2.619007000	5.701256000	-4.992792000
C	-6.191031000	0.985565000	-0.405514000
H	-6.872899000	0.714319000	0.405795000
H	-5.702128000	1.928345000	-0.146531000
H	-6.775159000	1.133194000	-1.315483000
C	-4.619173000	-2.588354000	-1.133380000
H	-3.850234000	-2.598810000	-0.355098000
H	-5.082173000	-3.577319000	-1.173460000
H	-4.141731000	-2.389438000	-2.094676000
C	-9.201486000	-3.292701000	-1.638694000
O	-9.557727000	-3.180004000	-2.805567000
C	8.122345000	-4.942040000	-0.276882000
O	8.066979000	-5.857832000	0.535241000
C	9.246047000	-4.966743000	-1.346819000
F	9.995035000	-6.068436000	-1.232502000
F	8.733194000	-4.936511000	-2.598874000
F	10.059370000	-3.891827000	-1.222649000
C	-10.061344000	-4.159675000	-0.680505000
F	-11.101807000	-4.699646000	-1.323554000
F	-9.332364000	-5.165360000	-0.143184000
F	-10.541394000	-3.421819000	0.348033000
C	0.597854000	4.592885000	0.404623000
C	-0.566426000	5.413205000	0.452951000
C	1.244768000	4.199393000	1.615853000
C	-1.102488000	5.765624000	1.677768000
C	0.682784000	4.623040000	2.855384000
C	-0.474704000	5.374808000	2.886392000
H	-1.029548000	5.738634000	-0.471502000
H	2.261196000	3.820422000	1.603521000
H	-2.006760000	6.367659000	1.707521000
H	1.195257000	4.352930000	3.773719000
H	-0.891462000	5.693813000	3.837472000
I	1.812045000	4.722949000	-1.415867000

TS1 [Pd(**DTE^o-COCF$_3$**)$_2$]·**PhI**

Pd	-0.134768000	2.012621000	0.584561000
S	4.512281000	2.047059000	-1.499964000
S	7.414080000	-2.869905000	-2.158850000
P	1.316171000	2.068250000	-1.275992000
F	12.171608000	-3.713540000	-0.363721000
F	10.525453000	-4.093137000	1.010891000
F	11.085799000	-2.045618000	0.521137000
O	10.371918000	-3.665989000	-2.278315000
C	1.644988000	3.528824000	-2.355502000
C	2.394364000	4.603326000	-1.843471000
H	2.831618000	4.533920000	-0.853473000
C	2.582738000	5.762421000	-2.596622000
H	3.174228000	6.577211000	-2.187796000
C	2.011206000	5.876613000	-3.866627000
H	2.155049000	6.780607000	-4.451610000
C	1.254225000	4.820015000	-4.379101000
H	0.810423000	4.897023000	-5.368067000
C	1.072635000	3.654183000	-3.632156000
H	0.491575000	2.838933000	-4.051861000
C	0.847538000	0.752243000	-2.489811000
C	-0.520913000	0.540968000	-2.726009000
H	-1.253803000	1.169634000	-2.229530000
C	-0.948029000	-0.497264000	-3.555869000
H	-2.010546000	-0.657352000	-3.715208000
C	-0.010318000	-1.344974000	-4.152326000
H	-0.340593000	-2.166199000	-4.782175000
C	1.353972000	-1.136229000	-3.930349000
H	2.088107000	-1.791325000	-4.391563000
C	1.781399000	-0.091258000	-3.108521000
H	2.842827000	0.048669000	-2.934120000
C	2.994881000	1.575433000	-0.749467000
C	3.239858000	0.692392000	0.271908000
H	2.445695000	0.257051000	0.865684000
C	4.623621000	0.358611000	0.457039000
C	5.447625000	1.045333000	-0.416410000
C	6.943067000	1.044035000	-0.505045000
H	7.371981000	0.683980000	0.433118000
H	7.333630000	2.047854000	-0.701235000
H	7.300242000	0.385677000	-1.305841000
C	5.050835000	-0.598874000	1.486634000
H	4.914743000	0.414078000	3.379809000
C	4.990757000	-1.782472000	3.589442000
H	4.198969000	-2.535852000	3.534287000
C	6.194739000	-2.252509000	2.745427000
C	5.950775000	-1.606565000	1.389310000
C	6.697829000	-2.078556000	0.213768000
C	8.072117000	-2.440588000	0.303229000
H	8.640212000	-2.367982000	1.222014000
C	8.617719000	-2.875867000	-0.888634000
C	6.194656000	-2.278524000	-1.070792000
C	4.805678000	-2.059149000	-1.576056000
H	4.098674000	-2.075600000	-0.747041000
H	4.515660000	-2.824835000	-2.302051000
H	4.718464000	-1.082428000	-2.064454000

C	9.967396000	-3.304541000	-1.183024000
C	10.960386000	-3.292171000	0.012213000
S	-2.696600000	-2.409926000	-0.027084000
S	-8.054060000	-2.284985000	1.612846000
P	-0.752243000	-0.194923000	1.210892000
F	-11.722135000	-4.488505000	-1.261270000
F	-11.269041000	-2.401097000	-1.688041000
F	-9.872047000	-3.963632000	-2.284324000
O	-10.384839000	-4.171680000	0.980198000
C	0.406022000	-1.617591000	0.972499000
C	0.685418000	-2.040470000	-0.339487000
H	0.195525000	-1.563105000	-1.179675000
C	1.576673000	-3.086198000	-0.572860000
H	1.772840000	-3.399776000	-1.593895000
C	2.216571000	-3.719398000	0.496748000
H	2.915572000	-4.530439000	0.313798000
C	1.953793000	-3.298747000	1.801413000
H	2.436650000	-3.791737000	2.640006000
C	1.056247000	-2.254100000	2.040946000
H	0.857016000	-1.951824000	3.063563000
C	-1.242331000	-0.368479000	2.984218000
C	-0.427923000	0.269019000	3.936273000
H	0.447171000	0.824195000	3.607545000
C	-0.733191000	0.197373000	5.295958000
H	-0.090204000	0.690616000	6.019852000
C	-1.870633000	-0.495691000	5.721578000
H	-2.117438000	-0.542007000	6.778457000
C	-2.690209000	-1.124796000	4.781683000
H	-3.575633000	-1.665824000	5.104958000
C	-2.375360000	-1.068773000	3.421535000
H	-3.015802000	-1.574072000	2.707144000
C	-2.211426000	-0.745890000	0.267195000
C	-3.124136000	0.106848000	-0.298144000
H	-3.019369000	1.183356000	-0.251725000
C	-4.235937000	-0.539001000	-0.931031000
C	-4.136898000	-1.917643000	-0.883657000
C	-5.061216000	-2.946925000	-1.458419000
H	-5.682814000	-2.495811000	-2.235738000
H	-4.509123000	-3.783929000	-1.898098000
H	-5.732645000	-3.354975000	-0.693621000
C	-5.331668000	0.234009000	-1.533496000
C	-5.050685000	1.344117000	-2.531550000
H	-4.718505000	0.904479000	-3.483854000
H	-4.245845000	2.010994000	-2.200870000
C	-6.411485000	2.061669000	-2.668136000
H	-6.585023000	2.463490000	-3.670243000
H	-6.448986000	2.899837000	-1.963222000
C	-7.457136000	1.003535000	-2.249655000
H	-7.844301000	0.449367000	-3.117783000
H	-8.325491000	1.436585000	-1.741080000
C	-6.661729000	0.071444000	-1.349262000
C	-7.337902000	-0.874715000	-0.449657000
C	-8.434613000	-1.675761000	-0.872016000
H	-8.830001000	-1.645811000	-1.879773000
C	-8.932689000	-2.505535000	0.114614000
C	-7.027943000	-1.082262000	0.892742000
C	-5.980377000	-0.408585000	1.720677000
H	-5.741919000	0.569535000	1.296293000
H	-6.307111000	-0.274739000	2.756174000
H	-5.054166000	-0.992708000	1.733215000
C	-10.013128000	-3.465256000	0.054421000
C	-10.737116000	-3.586898000	-1.315049000
C	4.506832000	-0.488565000	2.901686000
H	3.415872000	-0.383950000	2.919395000
H	5.238696000	-1.638079000	4.644647000
H	7.147705000	-1.895776000	3.163757000
H	6.271881000	-3.343635000	2.679704000
C	-0.217852000	4.130772000	1.463874000
C	0.182432000	5.215076000	0.659305000
C	0.483770000	3.808758000	2.642253000
C	1.340957000	5.908594000	0.990341000
C	1.664737000	4.505837000	2.936414000
C	2.094262000	5.551045000	2.119464000
H	-0.389962000	5.480981000	-0.222576000
H	0.101514000	3.062057000	3.327675000
H	1.666498000	6.725247000	0.352095000
H	2.221233000	4.247700000	3.833732000
H	2.992876000	6.107030000	2.370462000
I	-2.435798000	3.604234000	1.442635000

TS1 [Pd(**DTE^{o}-COCF$_3$**)(**DTE^{c}-COCF$_3$**)]·**PhI**

C	5.545231000	3.180579000	0.579883000
C	5.556429000	2.056515000	-0.476367000
S	7.293694000	2.110344000	-1.191989000
C	7.534731000	3.748728000	-0.526314000
C	6.569891000	4.137255000	0.371351000
H	6.603153000	5.076215000	0.911141000
C	2.684931000	3.951166000	2.796222000
C	2.569052000	2.414164000	2.663134000
C	3.656796000	2.071578000	1.670505000
C	4.562092000	3.186552000	1.532360000
C	4.179598000	4.258140000	2.524161000
H	2.347063000	4.321249000	3.767624000
H	1.577674000	2.079351000	2.348440000
H	2.777910000	1.924243000	3.623720000
H	4.359990000	5.272519000	2.157546000
H	4.767331000	4.131786000	3.444412000
H	2.073281000	4.430136000	2.022780000
C	3.021893000	-0.231170000	0.898459000
C	3.382673000	-1.148018000	-0.044039000
S	4.829906000	-0.697538000	-0.967298000

C	5.186961000	0.724221000	0.212602000
C	3.868521000	0.914769000	0.980667000
H	2.134482000	-0.340082000	1.506964000
P	2.480731000	-2.737555000	-0.226317000
C	2.871019000	-3.261675000	-1.943288000
C	3.158921000	-4.601602000	-2.244663000
C	2.700228000	-2.346793000	-2.996524000
C	3.297415000	-5.011703000	-3.572254000
C	2.844705000	-2.759669000	-4.321371000
C	3.144461000	-4.092942000	-4.613856000
H	3.278501000	-5.327202000	-1.446002000
H	2.454375000	-1.311481000	-2.784071000
H	3.526729000	-6.050887000	-3.790903000
H	2.720665000	-2.038333000	-5.124415000
H	3.255056000	-4.414135000	-5.645584000
C	3.525333000	-3.814278000	0.849494000
C	4.879657000	-4.070925000	0.575317000
C	2.947495000	-4.349935000	2.010015000
C	5.636432000	-4.852687000	1.448095000
C	3.709217000	-5.130082000	2.884188000
C	5.053398000	-5.382333000	2.604099000
H	5.340449000	-3.665814000	-0.319803000
H	1.900075000	-4.157329000	2.224756000
H	6.681895000	-5.047981000	1.226505000
H	3.250481000	-5.541409000	3.779094000
H	5.646294000	-5.990787000	3.281341000
C	6.245226000	0.219038000	1.221699000
H	6.447572000	0.991503000	1.969593000
H	5.863943000	-0.668762000	1.733181000
H	7.182047000	-0.038593000	0.725177000
C	4.570280000	2.456578000	-1.597212000
H	3.549874000	2.485653000	-1.208888000
H	4.829025000	3.450970000	-1.969802000
H	4.600765000	1.753843000	-2.431950000
Pd	0.150427000	-2.710414000	0.123484000
C	8.710627000	4.484684000	-0.931849000
O	9.562490000	4.065607000	-1.707448000
C	8.891975000	5.903060000	-0.329164000
F	10.006556000	6.482145000	-0.788431000
F	7.845682000	6.703578000	-0.639518000
F	8.971267000	5.856088000	1.021751000
S	-3.245714000	-0.098327000	-1.423685000
S	-6.619473000	4.241070000	-0.477369000
P	-0.804283000	-0.571968000	0.483098000
F	-11.404348000	4.405295000	-2.384358000
F	-11.160877000	3.493894000	-0.421317000
F	-10.505800000	2.429109000	-2.205700000
O	-8.979006000	5.369170000	-2.072773000
C	-0.050542000	0.676548000	-0.662965000
C	0.255876000	0.223556000	-1.957509000
H	0.076450000	-0.816107000	-2.218377000
C	0.805775000	1.089102000	-2.904650000
H	1.034045000	0.720461000	-3.900814000
C	1.076192000	2.416689000	-2.565300000
H	1.518725000	3.088429000	-3.295127000
C	0.787567000	2.872729000	-1.276584000
H	1.004796000	3.901237000	-1.001450000
C	0.223818000	2.011685000	-0.332200000
H	0.008523000	2.389589000	0.659921000
C	-0.638897000	0.128025000	2.184356000
C	0.119094000	-0.591506000	3.121116000
H	0.567003000	-1.538072000	2.829060000
C	0.297813000	-0.103843000	4.418525000
H	0.890266000	-0.671261000	5.130537000
C	-0.288017000	1.105426000	4.797018000
H	-0.149634000	1.486671000	5.804727000
C	-1.064704000	1.819804000	3.879030000
H	-1.534023000	2.754582000	4.172559000
C	-1.245557000	1.332254000	2.584634000
H	-1.869912000	1.882070000	1.887797000
C	-2.585771000	-0.294363000	0.188454000
C	-3.602585000	-0.390179000	1.103480000
H	-3.429689000	-0.522019000	2.164797000
C	-4.917096000	-0.249973000	0.542024000
C	-4.892223000	-0.102727000	-0.830636000
C	-6.033939000	0.077775000	-1.783125000
H	-6.962324000	-0.262553000	-1.318075000
H	-5.882611000	-0.489364000	-2.707398000
H	-6.167560000	1.131521000	-2.056211000
C	-6.124672000	-0.229123000	1.381419000
H	-6.707049000	-2.261863000	1.775786000
C	-7.612864000	-0.818611000	3.181134000
H	-7.225455000	-0.357858000	4.096500000
C	-8.253112000	0.275336000	2.296710000
C	-7.109939000	0.697609000	1.387321000
C	-7.174171000	1.952118000	0.623384000
C	-8.352647000	2.368437000	-0.056120000
H	-9.262721000	1.781509000	-0.067298000
C	-8.222145000	3.577410000	-0.712676000
C	-6.146583000	2.885752000	0.500726000
C	-4.777652000	2.851579000	1.104331000
H	-4.781185000	2.219354000	1.995065000
H	-4.436869000	3.853543000	1.382479000
H	-4.049117000	2.428769000	0.403472000
C	-9.185913000	4.304211000	-1.509640000
C	-10.590974000	3.653034000	-1.637048000
C	-6.432686000	-1.361333000	2.344843000
H	-5.564323000	-1.634506000	2.955703000
H	-8.320526000	-1.597958000	3.477006000
H	-9.083003000	-0.123956000	1.694926000
H	-8.660128000	1.111479000	2.875956000
C	-1.500843000	-4.085183000	0.381120000

C	-0.807389000	-4.921345000	1.282335000
C	-2.803635000	-3.635354000	0.670905000
C	-1.366695000	-5.154733000	2.551010000
C	-3.343027000	-3.902138000	1.923584000
C	-2.621292000	-4.644367000	2.875533000
H	0.121173000	-5.401900000	0.996270000
H	-3.350733000	-3.047013000	-0.056032000
H	-0.824367000	-5.771758000	3.263364000
H	-4.331348000	-3.520584000	2.163911000
H	-3.058533000	-4.849355000	3.848928000
I	-0.968569000	-4.386961000	-1.895184000

TS1 [Pd(**DTE^{c}-COCF$_3$**)$_2$]·**PhI**

C	6.724757000	-1.397836000	-0.720981000
C	5.466068000	-2.060352000	-0.125785000
S	6.109488000	-3.626054000	0.693707000
C	7.633654000	-3.503090000	-0.226149000
C	7.802816000	-2.305519000	-0.876293000
H	8.699194000	-2.049783000	-1.428483000
C	6.771496000	1.868333000	-2.459956000
C	5.654718000	2.090279000	-1.410225000
C	5.534193000	0.739905000	-0.738277000
C	6.674675000	-0.078000000	-1.077583000
C	7.662402000	0.751684000	-1.860482000
H	7.331576000	2.779984000	-2.683032000
H	4.713423000	2.435039000	-1.849850000
H	5.958535000	2.845132000	-0.671910000
H	8.210926000	0.178090000	-2.612913000
H	8.402816000	1.182968000	-1.171942000
H	6.327359000	1.510477000	-3.395809000
C	3.346925000	0.903984000	0.487460000
C	2.480625000	0.105052000	1.173366000
S	3.070077000	-1.555985000	1.409538000
C	4.793197000	-1.060015000	0.841562000
C	4.573464000	0.275135000	0.109821000
H	3.099826000	1.921476000	0.208163000
P	0.843313000	0.692011000	1.759683000
C	-0.084520000	-0.900458000	1.862664000
C	-0.635073000	-1.394101000	3.053902000
C	-0.280709000	-1.618054000	0.669879000
C	-1.370021000	-2.583867000	3.049405000
C	-1.004670000	-2.808279000	0.670645000
C	-1.556875000	-3.292846000	1.861188000
H	-0.489502000	-0.860046000	3.987344000
H	0.139653000	-1.248426000	-0.258847000
H	-1.790777000	-2.956911000	3.978970000
H	-1.144924000	-3.350982000	-0.259775000
H	-2.128711000	-4.216331000	1.860514000
C	1.136265000	1.111496000	3.533454000
C	2.183018000	0.578407000	4.301376000
C	0.229898000	1.997468000	4.137177000
C	2.321503000	0.935037000	5.644299000
C	0.362707000	2.342121000	5.483367000
C	1.412702000	1.814347000	6.238586000
H	2.885951000	-0.120689000	3.861606000
H	-0.580607000	2.416775000	3.548014000
H	3.137862000	0.518648000	6.227710000
H	-0.347367000	3.027529000	5.937358000
H	1.523488000	2.087592000	7.284115000
C	5.624883000	-0.760457000	2.112248000
H	6.627795000	-0.424477000	1.832280000
H	5.141255000	0.036284000	2.683489000
H	5.718371000	-1.642088000	2.748152000
C	4.555409000	-2.485410000	-1.299843000
H	4.196249000	-1.603690000	-1.834138000
H	5.125860000	-3.106299000	-1.995265000
H	3.689317000	-3.053782000	-0.955719000
Pd	-0.001894000	2.424908000	0.384539000
C	-6.362498000	-1.999428000	0.634801000
C	-5.570550000	-1.888621000	-0.684523000
S	-6.833871000	-2.292153000	-2.017640000
C	-7.914533000	-3.018892000	-0.797735000
C	-7.547180000	-2.768030000	0.500688000
H	-8.129075000	-3.087698000	1.356883000
C	-4.978014000	-1.276696000	3.981789000
C	-4.224830000	-0.245736000	3.107960000
C	-4.683620000	-0.579470000	1.706598000
C	-5.852753000	-1.427063000	1.766642000
C	-6.285725000	-1.570700000	3.204704000
H	-5.161495000	-0.921436000	4.998956000
H	-3.139143000	-0.297708000	3.222945000
H	-4.533282000	0.778279000	3.361018000
H	-6.720693000	-2.548306000	3.430060000
H	-7.045556000	-0.810988000	3.436591000
H	-4.383631000	-2.195217000	4.046114000
C	-2.969770000	0.543485000	0.255794000
C	-2.581199000	0.594496000	-1.050630000
S	-3.702617000	-0.238638000	-2.154510000
C	-4.966842000	-0.469867000	-0.779869000
C	-4.174509000	-0.183802000	0.506854000
H	-2.376022000	0.987019000	1.047396000
P	-1.085900000	1.541655000	-1.546116000
C	0.047642000	0.359454000	-2.402275000
C	1.389332000	0.767072000	-2.512151000
C	-0.321586000	-0.894435000	-2.912087000
C	2.332599000	-0.046956000	-3.139365000
C	0.631187000	-1.720202000	-3.513952000
C	1.956836000	-1.297864000	-3.635447000
H	1.695449000	1.721237000	-2.092447000
H	-1.343826000	-1.245299000	-2.828806000
H	3.362662000	0.287867000	-3.220619000

H	0.332751000	-2.694450000	-3.890702000
H	2.694453000	-1.942710000	-4.104206000
C	-1.749409000	2.551903000	-2.943860000
C	-0.972660000	2.842389000	-4.076953000
C	-3.012486000	3.154076000	-2.817286000
C	-1.454189000	3.706274000	-5.063034000
C	-3.496491000	4.005971000	-3.810134000
C	-2.718286000	4.287637000	-4.936028000
H	0.005984000	2.388880000	-4.200114000
H	-3.620182000	2.959193000	-1.938945000
H	-0.842731000	3.916312000	-5.936432000
H	-4.481042000	4.452448000	-3.700253000
H	-3.093969000	4.953677000	-5.707613000
C	-6.019658000	0.652064000	-0.941088000
H	-6.756980000	0.593615000	-0.134948000
H	-5.524589000	1.625110000	-0.885530000
H	-6.541687000	0.579341000	-1.896421000
C	-4.506529000	-3.009846000	-0.688091000
H	-3.781511000	-2.843275000	0.112379000
H	-4.994402000	-3.973180000	-0.519759000
H	-3.971400000	-3.052695000	-1.638561000
C	-9.079193000	-3.743506000	-1.258455000
O	-9.375931000	-3.907583000	-2.435566000
C	8.557329000	-4.614611000	-0.172940000
O	8.363633000	-5.651981000	0.450066000
C	9.887597000	-4.458782000	-0.957500000
F	10.645001000	-5.554624000	-0.841680000
F	9.658875000	-4.244737000	-2.274202000
F	10.603427000	-3.404391000	-0.500671000
C	-10.012600000	-4.335417000	-0.168837000
F	-11.035960000	-4.996099000	-0.720209000
F	-9.344322000	-5.193165000	0.636402000
F	-10.519979000	-3.359860000	0.620638000
C	-0.515330000	4.639283000	0.363090000
C	-1.091870000	5.188157000	-0.797512000
C	-1.196699000	4.675197000	1.595475000
C	-2.395438000	5.668036000	-0.739495000
C	-2.519181000	5.144586000	1.621467000
C	-3.119110000	5.637071000	0.463466000
H	-0.540878000	5.191990000	-1.731402000
H	-0.703038000	4.374918000	2.512079000
H	-2.854557000	6.052408000	-1.645385000
H	-3.058774000	5.154285000	2.565312000
H	-4.134169000	6.022241000	0.495313000
I	1.802373000	4.680782000	0.494138000

2 [Pd(**DTE^o-COCF$_3$**)$_2$(**Ph**)**I**]

Pd	-0.343606000	2.026645000	0.770067000
S	4.481153000	2.415087000	-0.800882000
S	7.454096000	-2.204009000	-2.324179000
P	1.313603000	2.332523000	-0.823513000
F	12.035487000	-3.673141000	-0.478780000
F	10.281194000	-4.293288000	0.653246000
F	10.937125000	-2.216386000	0.710848000
O	10.382656000	-3.089608000	-2.437422000
C	1.637257000	4.022383000	-1.468571000
C	2.302050000	4.952510000	-0.651266000
H	2.653008000	4.661244000	0.331864000
C	2.489652000	6.262729000	-1.085310000
H	2.996770000	6.973318000	-0.439533000
C	2.016156000	6.661777000	-2.338534000
H	2.158176000	7.685232000	-2.673612000
C	1.358948000	5.741808000	-3.156644000
H	0.993082000	6.043385000	-4.133974000
C	1.168296000	4.426684000	-2.726258000
H	0.654419000	3.724830000	-3.374073000
C	0.935478000	1.353804000	-2.331790000
C	-0.406174000	1.265824000	-2.737083000
H	-1.181510000	1.747561000	-2.149573000
C	-0.749580000	0.547780000	-3.883205000
H	-1.791363000	0.478094000	-4.182037000
C	0.244256000	-0.092669000	-4.629229000
H	-0.022586000	-0.660934000	-5.515570000
C	1.580597000	-0.006178000	-4.229736000
H	2.355251000	-0.506733000	-4.803358000
C	1.927959000	0.715577000	-3.086610000
H	2.966818000	0.767428000	-2.781060000
C	2.938665000	1.788919000	-0.239800000
C	3.144615000	0.748882000	0.628494000
H	2.334508000	0.215709000	1.103447000
C	4.519623000	0.395516000	0.819387000
C	5.373705000	1.239545000	0.131726000
C	6.870789000	1.254383000	0.112381000
H	7.258828000	0.698415000	0.968812000
H	7.261617000	2.276030000	0.155222000
H	7.265234000	0.784116000	-0.795861000
C	4.889935000	-0.776586000	1.623796000
H	4.691494000	-0.286625000	3.709908000
C	4.634907000	-2.457870000	3.329305000
H	3.825075000	-3.119996000	3.003054000
C	5.894120000	-2.742746000	2.484545000
C	5.768281000	-1.763413000	1.325157000
C	6.582334000	-1.965902000	0.115657000
C	7.935567000	-2.402691000	0.206441000
H	8.434477000	-2.576713000	1.151476000
C	8.556535000	-2.567848000	-1.015507000
C	6.173537000	-1.828568000	-1.209939000
C	4.843185000	-1.416747000	-1.753042000
H	4.069616000	-1.533625000	-0.996236000
H	4.565170000	-2.011729000	-2.627758000
H	4.863334000	-0.364800000	-2.057176000

C	9.911098000	-2.978750000	-1.315550000
C	10.813016000	-3.297907000	-0.091149000
S	-2.633925000	-2.514130000	-0.499143000
S	-7.756950000	-2.175352000	1.583559000
P	-0.536350000	-0.453396000	0.710025000
F	-11.598919000	-4.402711000	-1.034673000
F	-11.166711000	-2.325359000	-1.524683000
F	-9.808454000	-3.902022000	-2.169287000
O	-10.126885000	-4.063173000	1.116371000
C	0.640488000	-1.689585000	-0.018427000
C	0.629704000	-1.921491000	-1.403596000
H	-0.041897000	-1.362325000	-2.044022000
C	1.458647000	-2.892035000	-1.966529000
H	1.428722000	-3.060376000	-3.039010000
C	2.315728000	-3.642015000	-1.158402000
H	2.958358000	-4.399622000	-1.597451000
C	2.353018000	-3.401057000	0.216233000
H	3.023085000	-3.970177000	0.853679000
C	1.522680000	-2.432763000	0.784139000
H	1.555658000	-2.277023000	1.856251000
C	-0.620952000	-1.029116000	2.456659000
C	0.284483000	-0.444519000	3.357996000
H	0.949712000	0.346283000	3.022627000
C	0.325840000	-0.859862000	4.688880000
H	1.034236000	-0.402955000	5.373903000
C	-0.554251000	-1.847658000	5.139296000
H	-0.532122000	-2.164685000	6.177937000
C	-1.467253000	-2.421084000	4.251340000
H	-2.158991000	-3.183742000	4.597614000
C	-1.497093000	-2.020172000	2.913361000
H	-2.212220000	-2.476921000	2.238519000
C	-2.084628000	-0.886731000	-0.125553000
C	-2.986584000	0.029109000	-0.606919000
H	-2.854860000	1.096779000	-0.485295000
C	-4.138856000	-0.544498000	-1.232622000
C	-4.089134000	-1.926271000	-1.259268000
C	-5.082947000	-2.890928000	-1.829087000
H	-5.715623000	-2.382717000	-2.560820000
H	-4.590105000	-3.734991000	-2.321939000
H	-5.738793000	-3.295040000	-1.049227000
C	-5.237989000	0.282617000	-1.751820000
C	-4.990114000	1.386667000	-2.763332000
H	-4.732939000	0.941464000	-3.736185000
H	-4.146784000	2.028886000	-2.482342000
C	-6.336829000	2.143115000	-2.809063000
H	-6.568019000	2.544242000	-3.799710000
H	-6.300232000	2.985290000	-2.109564000
C	-7.383424000	1.119352000	-2.311385000
H	-7.854117000	0.579076000	-3.146295000
H	-8.195101000	1.581287000	-1.739086000
C	-6.554643000	0.159933000	-1.473769000
C	-7.180359000	-0.776521000	-0.528213000
C	-8.303712000	-1.576288000	-0.872815000
H	-8.765165000	-1.550305000	-1.852098000
C	-8.735444000	-2.401382000	0.148962000
C	-6.777506000	-0.980019000	0.790407000
C	-5.675743000	-0.302158000	1.541820000
H	-5.451347000	0.664745000	1.087090000
H	-5.941806000	-0.142356000	2.590907000
H	-4.753402000	-0.892831000	1.518833000
C	-9.814499000	-3.363590000	0.163777000
C	-10.616544000	-3.505114000	-1.159676000
C	4.263376000	-1.000256000	2.990718000
H	3.181475000	-0.829648000	2.992092000
H	4.788330000	-2.624010000	4.398996000
H	6.815207000	-2.538774000	3.050455000
H	5.958601000	-3.782277000	2.144776000
C	-0.307906000	4.044125000	1.026202000
C	-1.020436000	4.909847000	0.185260000
C	0.430962000	4.586672000	2.086472000
C	-0.985011000	6.292666000	0.392338000
C	0.467031000	5.970947000	2.293387000
C	-0.237115000	6.828618000	1.444550000
H	-1.597640000	4.514291000	-0.646769000
H	0.983730000	3.935525000	2.759693000
H	-1.538856000	6.950266000	-0.273492000
H	1.047555000	6.375819000	3.119220000
H	-0.205366000	7.903294000	1.602147000
I	-2.473850000	2.112015000	2.549407000

2 [Pd(**DTE^{o}-COCF$_3$**)(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]

C	5.343246000	3.316404000	0.681905000
C	5.293300000	2.325674000	-0.499000000
S	7.004080000	2.435726000	-1.270519000
C	7.306909000	3.974431000	-0.420168000
C	6.382786000	4.272036000	0.550896000
H	6.456714000	5.138850000	1.196758000
C	2.592060000	3.855647000	3.099851000
C	2.446929000	2.345712000	2.794045000
C	3.480539000	2.112438000	1.715524000
C	4.397341000	3.226232000	1.666588000
C	4.076776000	4.177506000	2.793896000
H	2.306894000	4.112303000	4.123252000
H	1.436314000	2.057965000	2.492410000
H	2.695082000	1.744406000	3.679243000
H	4.255248000	5.226056000	2.539831000
H	4.704681000	3.938784000	3.663895000
H	1.952013000	4.428224000	2.418630000
C	2.807715000	-0.106563000	0.752399000
C	3.111839000	-0.916330000	-0.299086000
S	4.479969000	-0.341426000	-1.275211000

C	4.922770000	0.927315000	0.043043000
C	3.647390000	1.039571000	0.892715000
H	1.988944000	-0.302559000	1.430488000
P	2.323927000	-2.561233000	-0.521211000
C	2.867252000	-3.073060000	-2.197848000
C	3.415098000	-4.343471000	-2.432166000
C	2.642725000	-2.212190000	-3.285670000
C	3.743309000	-4.737739000	-3.730420000
C	2.975679000	-2.610586000	-4.580942000
C	3.525099000	-3.874724000	-4.806687000
H	3.585741000	-5.025030000	-1.606965000
H	2.221522000	-1.226357000	-3.125803000
H	4.170280000	-5.722358000	-3.897750000
H	2.806771000	-1.930361000	-5.410853000
H	3.783022000	-4.184755000	-5.815265000
C	3.376942000	-3.500551000	0.664118000
C	4.768623000	-3.591905000	0.491930000
C	2.790181000	-4.038462000	1.818597000
C	5.554860000	-4.217300000	1.459692000
C	3.581568000	-4.659226000	2.787617000
C	4.963592000	-4.749781000	2.609566000
H	5.237503000	-3.176638000	-0.394137000
H	1.714207000	-3.986574000	1.951302000
H	6.629143000	-4.287505000	1.315225000
H	3.114986000	-5.078069000	3.674681000
H	5.578647000	-5.235565000	3.361732000
C	6.015119000	0.286764000	0.933129000
H	6.268285000	0.961262000	1.756494000
H	5.639832000	-0.649667000	1.354088000
H	6.922108000	0.075544000	0.364811000
C	4.277246000	2.871665000	-1.526432000
H	3.274211000	2.874877000	-1.095246000
H	4.545429000	3.896861000	-1.793642000
H	4.258727000	2.268404000	-2.435969000
Pd	-0.062254000	-2.939623000	-0.072948000
C	8.488458000	4.729968000	-0.774092000
O	9.301614000	4.391868000	-1.625916000
C	8.728641000	6.055866000	-0.004490000
F	9.842056000	6.662971000	-0.427865000
F	7.694142000	6.912111000	-0.171637000
F	8.852034000	5.833840000	1.325325000
S	-3.232156000	-0.089065000	-1.528549000
S	-6.214030000	4.331728000	-0.352520000
P	-0.853424000	-0.802066000	0.357659000
F	-10.875598000	4.959512000	-2.456451000
F	-10.801679000	3.935924000	-0.535140000
F	-10.133225000	2.915330000	-2.340304000
O	-8.404575000	5.718784000	-1.980823000
C	-0.100436000	0.492197000	-0.713872000
C	0.171431000	0.135040000	-2.042650000
H	0.018578000	-0.890044000	-2.368923000
C	0.640364000	1.089400000	-2.947526000
H	0.847689000	0.801104000	-3.973910000
C	0.848174000	2.405091000	-2.529866000
H	1.221989000	3.146489000	-3.229656000
C	0.583801000	2.763525000	-1.205060000
H	0.751684000	3.783879000	-0.872686000
C	0.109536000	1.814347000	-0.299043000
H	-0.089162000	2.110840000	0.723808000
C	-0.642440000	-0.301937000	2.111507000
C	0.162392000	-1.095053000	2.944701000
H	0.624716000	-1.993965000	2.547276000
C	0.372290000	-0.734598000	4.277072000
H	0.999944000	-1.355612000	4.909288000
C	-0.228945000	0.415569000	4.792513000
H	-0.067476000	0.695714000	5.829330000
C	-1.047709000	1.200735000	3.975395000
H	-1.525843000	2.090125000	4.375199000
C	-1.259458000	0.844459000	2.643326000
H	-1.914142000	1.449396000	2.025213000
C	-2.618715000	-0.482836000	0.063399000
C	-3.651106000	-0.597472000	0.956810000
H	-3.505653000	-0.851678000	1.999105000
C	-4.940769000	-0.316468000	0.397234000
C	-4.880029000	-0.048814000	-0.957157000
C	-5.992201000	0.278076000	-1.905503000
H	-6.946744000	-0.040688000	-1.480500000
H	-5.859230000	-0.222743000	-2.869884000
H	-6.056000000	1.356205000	-2.094249000
C	-6.158110000	-0.266275000	1.221687000
H	-6.945727000	-2.252617000	1.429706000
C	-7.720721000	-0.854211000	2.953051000
H	-7.300412000	-0.505535000	3.902995000
C	-8.244247000	0.361818000	2.155543000
C	-7.053892000	0.744593000	1.291343000
C	-6.993173000	2.046625000	0.610156000
C	-8.106974000	2.589318000	-0.089176000
H	-9.059073000	2.078863000	-0.164229000
C	-7.853361000	3.812453000	-0.679654000
C	-5.890401000	2.897006000	0.571854000
C	-4.550093000	2.717758000	1.213878000
H	-4.629087000	2.016621000	2.047308000
H	-4.154283000	3.667439000	1.586905000
H	-3.825445000	2.306876000	0.501861000
C	-8.719305000	4.648277000	-1.482308000
C	-10.159406000	4.112060000	-1.711761000
C	-6.589892000	-1.440732000	2.079960000
H	-5.763110000	-1.861432000	2.662738000
H	-8.502891000	-1.582342000	3.184810000
H	-9.098503000	0.091219000	1.517251000
H	-8.580040000	1.184395000	2.796513000
C	-1.957646000	-3.490918000	0.437491000

C	-2.270985000	-3.715466000	1.784393000
C	-2.955163000	-3.670113000	-0.531084000
C	-3.560998000	-4.115095000	2.157589000
C	-4.242769000	-4.065663000	-0.157862000
C	-4.550420000	-4.290546000	1.187776000
H	-1.517643000	-3.573799000	2.555557000
H	-2.735808000	-3.497649000	-1.580950000
H	-3.788170000	-4.287200000	3.207250000
H	-5.006403000	-4.198083000	-0.920601000
H	-5.551883000	-4.596800000	1.476453000
I	0.328313000	-5.607050000	-0.663396000

2 [Pd(**DTE^{c}-COCF$_3$**)$_2$(**Ph**)**I**]]

C	7.036532000	-0.992411000	-0.653370000
C	5.789906000	-1.829156000	-0.302607000
S	6.485524000	-3.455123000	0.335330000
C	8.071515000	-3.080239000	-0.389086000
C	8.198834000	-1.787541000	-0.830889000
H	9.117198000	-1.386494000	-1.242467000
C	6.958154000	2.494121000	-1.876549000
C	5.727976000	2.467933000	-0.936223000
C	5.666031000	1.026901000	-0.481003000
C	6.906761000	0.359202000	-0.807905000
C	7.885799000	1.372811000	-1.345607000
H	7.449875000	3.469605000	-1.903781000
H	4.806721000	2.803295000	-1.423167000
H	5.886064000	3.120974000	-0.067506000
H	8.560323000	0.964719000	-2.103421000
H	8.507173000	1.751236000	-0.521777000
H	6.643477000	2.247924000	-2.896985000
C	3.356052000	0.826345000	0.483824000
C	2.503213000	-0.136626000	0.932875000
S	3.231335000	-1.759638000	1.019281000
C	4.944854000	-1.046131000	0.727398000
C	4.673993000	0.363855000	0.176255000
H	3.049197000	1.853993000	0.333619000
P	0.748119000	0.193283000	1.318925000
C	-0.058507000	-1.390905000	0.817979000
C	-0.984873000	-2.031162000	1.656379000
C	0.231430000	-1.958947000	-0.433334000
C	-1.609817000	-3.209893000	1.248604000
C	-0.399627000	-3.135268000	-0.839162000
C	-1.322297000	-3.763855000	-0.001375000
H	-1.209282000	-1.625274000	2.635773000
H	0.960048000	-1.497801000	-1.088167000
H	-2.321615000	-3.694521000	1.910764000
H	-0.163242000	-3.558002000	-1.811085000
H	-1.813824000	-4.678960000	-0.318419000
C	0.585051000	0.145049000	3.151403000
C	1.450747000	-0.580437000	3.981236000
C	-0.503105000	0.826031000	3.721123000
C	1.229450000	-0.620157000	5.359531000
C	-0.732806000	0.767167000	5.095973000
C	0.136270000	0.046060000	5.918578000
H	2.296313000	-1.114484000	3.562272000
H	-1.161437000	1.419669000	3.094449000
H	1.911982000	-1.177014000	5.995147000
H	-1.580266000	1.295589000	5.523015000
H	-0.034822000	0.007952000	6.990552000
C	5.620665000	-0.888187000	2.109741000
H	6.609652000	-0.435214000	1.993812000
H	5.011984000	-0.233094000	2.738354000
H	5.735319000	-1.849946000	2.612127000
C	5.036074000	-2.129295000	-1.619613000
H	4.650171000	-1.203837000	-2.054901000
H	5.724861000	-2.587207000	-2.333728000
H	4.198077000	-2.809941000	-1.459223000
Pd	0.006509000	2.397664000	0.479112000
C	-6.481993000	-1.891913000	0.618747000
C	-5.702824000	-1.714070000	-0.700093000
S	-7.002562000	-1.926429000	-2.041701000
C	-8.105884000	-2.693588000	-0.870890000
C	-7.712313000	-2.578376000	0.437728000
H	-8.302839000	-2.938743000	1.271307000
C	-5.025063000	-1.533764000	3.996341000
C	-4.216686000	-0.483302000	3.197475000
C	-4.706447000	-0.671613000	1.779100000
C	-5.925813000	-1.451527000	1.786225000
C	-6.353341000	-1.686495000	3.213920000
H	-5.180283000	-1.246687000	5.039198000
H	-3.134796000	-0.600694000	3.300797000
H	-4.461987000	0.533193000	3.535453000
H	-6.843623000	-2.652030000	3.365634000
H	-7.064755000	-0.905113000	3.516165000
H	-4.488557000	-2.489278000	3.986742000
C	-2.963721000	0.500325000	0.401038000
C	-2.598844000	0.643872000	-0.904072000
S	-3.757283000	-0.060759000	-2.054429000
C	-5.018251000	-0.329962000	-0.682800000
C	-4.194617000	-0.198431000	0.610027000
H	-2.351468000	0.864446000	1.216943000
P	-1.143130000	1.632412000	-1.390268000
C	-0.025559000	0.619516000	-2.435900000
C	1.343556000	0.928407000	-2.384933000
C	-0.465594000	-0.412452000	-3.277656000
C	2.260727000	0.203796000	-3.147060000
C	0.455986000	-1.143557000	-4.028011000
C	1.819364000	-0.842398000	-3.960155000
H	1.692482000	1.723208000	-1.733338000
H	-1.515602000	-0.673514000	-3.337465000
H	3.316455000	0.451201000	-3.095595000

H	0.107023000	-1.953011000	-4.662350000
H	2.533856000	-1.419399000	-4.539965000
C	-1.868928000	2.836756000	-2.571301000
C	-1.226964000	3.147743000	-3.777309000
C	-3.052343000	3.507306000	-2.223735000
C	-1.762835000	4.121217000	-4.623742000
C	-3.582092000	4.477257000	-3.071513000
C	-2.937505000	4.787870000	-4.272923000
H	-0.313397000	2.636393000	-4.061668000
H	-3.552053000	3.280601000	-1.287704000
H	-1.259617000	4.354727000	-5.557666000
H	-4.495951000	4.993292000	-2.792236000
H	-3.351075000	5.546145000	-4.931584000
C	-6.003521000	0.861021000	-0.736335000
H	-6.728446000	0.783632000	0.079319000
H	-5.450022000	1.796325000	-0.620344000
H	-6.545169000	0.891902000	-1.682859000
C	-4.707987000	-2.889990000	-0.819042000
H	-3.963402000	-2.831382000	-0.022946000
H	-5.248709000	-3.834738000	-0.722264000
H	-4.186687000	-2.882837000	-1.777973000
C	-9.312540000	-3.318104000	-1.375947000
O	-9.629393000	-3.357694000	-2.557306000
C	9.078120000	-4.120967000	-0.407006000
O	8.915143000	-5.252003000	0.033123000
C	10.453678000	-3.754979000	-1.025695000
F	11.288882000	-4.798234000	-0.991184000
F	10.319637000	-3.366153000	-2.314826000
F	11.033426000	-2.730779000	-0.357665000
C	-10.254282000	-3.973354000	-0.330610000
F	-11.319165000	-4.523215000	-0.922156000
F	-9.611983000	-4.940499000	0.363497000
F	-10.695421000	-3.061860000	0.567123000
C	-0.698117000	4.249168000	0.015771000
C	-0.110008000	5.075180000	-0.950620000
C	-1.826154000	4.713524000	0.706746000
C	-0.644678000	6.337951000	-1.227734000
C	-2.362049000	5.976664000	0.428488000
C	-1.774972000	6.791567000	-0.542333000
H	0.761697000	4.736404000	-1.504737000
H	-2.297154000	4.096491000	1.468785000
H	-0.178965000	6.963728000	-1.985365000
H	-3.238815000	6.320411000	0.972628000
H	-2.193137000	7.769974000	-0.762677000
I	1.563462000	3.690307000	2.356527000

3 [Pd(**DTE^{o}-COCF$_3$**)(**Ph**)**I**]

Pd	3.189422000	0.987559000	0.149111000
S	-0.754063000	-1.417469000	1.671046000
S	-5.504563000	-1.548380000	-1.481938000
P	2.051393000	-0.988878000	0.311279000
F	-10.073351000	-0.397986000	0.607978000
F	-8.919588000	1.271761000	-0.181912000
F	-8.308451000	0.306235000	1.673094000
O	-8.441524000	-1.971969000	-0.722562000
C	2.532280000	-2.067042000	1.708186000
C	3.134919000	-1.476036000	2.830482000
H	3.351784000	-0.410792000	2.830313000
C	3.459111000	-2.254430000	3.941324000
H	3.928593000	-1.792057000	4.804565000
C	3.186929000	-3.625321000	3.938094000
H	3.444213000	-4.231505000	4.801904000
C	2.587433000	-4.217294000	2.823887000
H	2.374798000	-5.282304000	2.819625000
C	2.259252000	-3.443715000	1.709096000
H	1.797127000	-3.912347000	0.846155000
C	1.992524000	-2.066555000	-1.166774000
C	3.116626000	-2.843943000	-1.493884000
H	3.991221000	-2.840016000	-0.851228000
C	3.111966000	-3.622175000	-2.650706000
H	3.984490000	-4.220353000	-2.896419000
C	1.995615000	-3.626234000	-3.492284000
H	1.996526000	-4.232369000	-4.393627000
C	0.880480000	-2.848395000	-3.173543000
H	0.009457000	-2.848342000	-3.822631000
C	0.876556000	-2.068673000	-2.015206000
H	0.007515000	-1.465279000	-1.775256000
C	0.347775000	-0.501162000	0.666780000
C	-0.269579000	0.628003000	0.184211000
H	0.229157000	1.339394000	-0.466308000
C	-1.638187000	0.765154000	0.587723000
C	-2.041800000	-0.266478000	1.418839000
C	-3.363790000	-0.472240000	2.091782000
H	-3.897285000	0.478643000	2.159637000
H	-3.242067000	-0.875383000	3.101990000
H	-3.995694000	-1.167724000	1.527509000
C	-2.464938000	1.902383000	0.157228000
H	-1.934052000	3.597472000	1.368509000
C	-2.984193000	4.163558000	-0.487504000
H	-2.629036000	4.296132000	-1.515383000
C	-4.263357000	3.298586000	-0.501819000
C	-3.729464000	1.885511000	-0.324468000
C	-4.579751000	0.724682000	-0.624802000
C	-5.945361000	0.669527000	-0.227685000
H	-6.427985000	1.464482000	0.326861000
C	-6.587904000	-0.495581000	-0.597778000
C	-4.199634000	-0.410637000	-1.336167000
C	-2.872837000	-0.725771000	-1.950498000
H	-2.321030000	0.197773000	-2.139588000
H	-2.983771000	-1.270171000	-2.893132000
H	-2.269578000	-1.342479000	-1.274809000

C	-7.951672000	-0.914710000	-0.354891000
C	-8.835416000	0.079068000	0.448728000
C	-1.955455000	3.326753000	0.302685000
H	-0.930827000	3.447654000	-0.067421000
H	-3.143703000	5.157539000	-0.061025000
H	-4.933141000	3.551219000	0.333629000
H	-4.849820000	3.412631000	-1.419910000
I	4.154324000	3.486636000	0.078645000
C	4.717995000	-0.019807000	-0.590855000
C	5.585461000	-0.724108000	0.249702000
C	4.919033000	-0.009366000	-1.975341000
C	6.662567000	-1.426337000	-0.306735000
C	5.998926000	-0.714701000	-2.517720000
C	6.868854000	-1.427153000	-1.688021000
H	5.423727000	-0.750910000	1.322339000
H	4.244659000	0.531648000	-2.631765000
H	7.333169000	-1.977184000	0.347891000
H	6.153401000	-0.706162000	-3.593577000
H	7.701598000	-1.978394000	-2.115433000

3 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]

Pd	3.068166000	0.977277000	0.309906000
C	-4.458699000	0.960711000	-0.233822000
C	-3.646062000	-0.186717000	0.398642000
S	-4.854960000	-1.624444000	0.479128000
C	-6.223735000	-0.507318000	0.242732000
C	-5.861533000	0.762157000	-0.127675000
H	-6.576160000	1.541736000	-0.362549000
C	-3.110159000	4.299180000	-1.057398000
C	-1.872918000	3.398736000	-1.295581000
C	-2.353422000	2.025096000	-0.883846000
C	-3.796446000	2.031412000	-0.762757000
C	-4.326526000	3.358638000	-1.244310000
H	-3.139330000	5.163271000	-1.725626000
H	-0.988699000	3.726506000	-0.740058000
H	-1.599014000	3.387123000	-2.359353000
H	-5.221560000	3.687241000	-0.709010000
H	-4.589163000	3.281807000	-2.308860000
H	-3.097336000	4.671099000	-0.027038000
C	-0.224986000	0.705436000	-0.645287000
C	0.183756000	-0.510910000	-0.180899000
S	-1.129401000	-1.599230000	0.298727000
C	-2.401263000	-0.446701000	-0.478559000
C	-1.645882000	0.881639000	-0.670010000
H	0.470536000	1.485135000	-0.941996000
P	1.936192000	-0.984865000	-0.044976000
C	1.984486000	-2.180542000	1.337580000
C	1.711240000	-3.544350000	1.148590000
C	2.244193000	-1.694263000	2.628910000
C	1.699688000	-4.409073000	2.243991000
C	2.228987000	-2.563724000	3.719492000
C	1.958394000	-3.921145000	3.527322000
H	1.510692000	-3.931635000	0.154949000
H	2.461901000	-0.639532000	2.776811000
H	1.488119000	-5.463525000	2.093094000
H	2.433651000	-2.182414000	4.715520000
H	1.951247000	-4.598455000	4.376452000
C	2.306060000	-1.938420000	-1.562100000
C	1.494800000	-1.833304000	-2.700873000
C	3.467956000	-2.727583000	-1.604173000
C	1.838287000	-2.519520000	-3.867328000
C	3.803238000	-3.410151000	-2.772672000
C	2.990199000	-3.308133000	-3.905131000
H	0.598737000	-1.220833000	-2.680950000
H	4.108331000	-2.806336000	-0.731547000
H	1.201560000	-2.439479000	-4.743565000
H	4.703411000	-4.017136000	-2.797623000
H	3.254786000	-3.840922000	-4.813942000
C	-2.725561000	-1.012342000	-1.881017000
H	-3.427595000	-0.351740000	-2.397993000
H	-1.807659000	-1.071512000	-2.471775000
H	-3.165350000	-2.008950000	-1.819998000
C	-3.305010000	0.218872000	1.851720000
H	-2.640132000	1.087697000	1.857740000
H	-4.224873000	0.485574000	2.377854000
H	-2.819715000	-0.595443000	2.392816000
C	-7.566316000	-1.027965000	0.409083000
O	-7.827580000	-2.185522000	0.708143000
C	-8.736788000	-0.034967000	0.179736000
F	-9.917050000	-0.630744000	0.375949000
F	-8.651624000	1.019683000	1.022170000
F	-8.717870000	0.456341000	-1.080974000
I	4.035252000	3.433068000	0.748502000
C	4.742497000	-0.003806000	-0.053698000
C	5.334650000	-0.796937000	0.933367000
C	5.326310000	0.117256000	-1.319007000
C	6.525082000	-1.477004000	0.644221000
C	6.515733000	-0.566707000	-1.593430000
C	7.114599000	-1.367080000	-0.617020000
H	4.875922000	-0.908604000	1.910313000
H	4.865570000	0.727844000	-2.089201000
H	6.982504000	-2.097121000	1.410906000
H	6.968586000	-0.471976000	-2.576940000
H	8.034369000	-1.901133000	-0.838003000

DTE^{o}-COCF$_3$

C	2.759474000	1.146499000	-0.626776000
C	2.330436000	-0.124591000	-1.002367000
S	3.456555000	-1.353428000	-0.519939000
C	4.540454000	-0.165924000	0.183190000

C	4.021628000	1.103704000	0.026042000
H	4.541023000	1.980872000	0.393614000
C	1.085029000	-0.516156000	-1.731234000
H	0.302608000	-0.814495000	-1.024929000
H	0.707569000	0.332691000	-2.305344000
H	1.261471000	-1.353653000	-2.413029000
C	1.735614000	4.568237000	-1.895034000
C	0.467114000	4.150027000	-1.123079000
C	0.749118000	2.712145000	-0.716607000
C	2.059692000	2.413509000	-0.884483000
C	2.839086000	3.629906000	-1.362331000
H	1.979148000	5.627741000	-1.776803000
H	-0.448903000	4.249424000	-1.716173000
H	0.316682000	4.757876000	-0.218698000
H	3.590682000	3.376159000	-2.117871000
H	3.381119000	4.082000000	-0.518352000
H	1.587967000	4.378331000	-2.964058000
C	-1.615689000	1.775484000	-0.764429000
C	-2.492160000	0.939035000	-0.121255000
S	-1.726874000	0.270930000	1.311848000
C	-0.235588000	1.126519000	1.009245000
C	-0.319648000	1.875814000	-0.150591000
H	-1.875433000	2.300345000	-1.677975000
C	0.902001000	1.008022000	1.977158000
H	1.491569000	0.101556000	1.796258000
H	1.573392000	1.863586000	1.872605000
H	0.545611000	0.971762000	3.011587000
P	-4.166195000	0.535141000	-0.726120000
C	-3.932337000	-1.165456000	-1.423994000
C	-5.045102000	-2.012456000	-1.568581000
C	-2.692776000	-1.590437000	-1.924753000
C	-4.912400000	-3.261460000	-2.176732000
C	-2.562801000	-2.838831000	-2.537727000
C	-3.670077000	-3.680461000	-2.662089000
H	-6.016487000	-1.702822000	-1.191748000
H	-1.825520000	-0.944350000	-1.836283000
H	-5.780515000	-3.908377000	-2.270096000
H	-1.592544000	-3.153535000	-2.912944000
H	-3.567892000	-4.653239000	-3.134769000
C	-5.069994000	0.197747000	0.852621000
C	-4.929200000	-0.987593000	1.594598000
C	-5.912756000	1.208078000	1.341864000
C	-5.609917000	-1.151012000	2.801916000
C	-6.590816000	1.044949000	2.552220000
C	-6.440235000	-0.134873000	3.283917000
H	-4.293419000	-1.786739000	1.226294000
H	-6.039755000	2.126399000	0.773991000
H	-5.491402000	-2.071828000	3.366396000
H	-7.239362000	1.835762000	2.918805000
H	-6.970361000	-0.265065000	4.223272000
C	5.804271000	-0.445722000	0.845731000
O	6.541197000	0.414126000	1.303171000
C	6.229047000	-1.931511000	0.984987000
F	6.318474000	-2.522273000	-0.228992000
F	7.412034000	-2.044746000	1.593510000
F	5.314202000	-2.622947000	1.702546000

DTE^{c}-COCF$_3$

C	-2.636506000	0.868282000	-0.317549000
C	-1.485089000	0.012566000	0.248517000
S	-2.265034000	-1.668849000	0.562527000
C	-3.896377000	-0.953212000	0.455368000
C	-3.916580000	0.333747000	-0.022354000
H	-4.831023000	0.886230000	-0.202583000
C	-2.289638000	4.368544000	-1.447604000
C	-0.899204000	3.789581000	-1.807754000
C	-0.962742000	2.370924000	-1.284535000
C	-2.333316000	2.028555000	-0.974453000
C	-3.237904000	3.144035000	-1.435361000
H	-2.617309000	5.148035000	-2.140092000
H	-0.071968000	4.365690000	-1.381373000
H	-0.753081000	3.775769000	-2.896435000
H	-4.118806000	3.277977000	-0.801450000
H	-3.594309000	2.927326000	-2.452373000
H	-2.253933000	4.805158000	-0.443270000
C	1.448426000	1.635979000	-1.268778000
C	2.210845000	0.606650000	-0.799063000
S	1.269132000	-0.750240000	-0.150381000
C	-0.333722000	0.001032000	-0.780546000
C	0.034818000	1.456037000	-1.122619000
H	1.882220000	2.544575000	-1.673765000
P	4.046675000	0.679307000	-0.777288000
C	4.378638000	0.984835000	1.018936000
C	5.688928000	0.787286000	1.489874000
C	3.412689000	1.492540000	1.900272000
C	6.017280000	1.071405000	2.815349000
C	3.746368000	1.782238000	3.225906000
C	5.046116000	1.569979000	3.688739000
H	6.453145000	0.397170000	0.822155000
H	2.396287000	1.661043000	1.558849000
H	7.032242000	0.904467000	3.165412000
H	2.984688000	2.169200000	3.897396000
H	5.302224000	1.792394000	4.720721000
C	4.487650000	-1.106304000	-0.970002000
C	4.485622000	-2.033865000	0.085037000
C	4.807585000	-1.547227000	-2.263833000
C	4.791082000	-3.374334000	-0.154319000
C	5.106598000	-2.890384000	-2.502607000
C	5.099508000	-3.805555000	-1.447767000
H	4.248678000	-1.710139000	1.093684000
H	4.822878000	-0.838422000	-3.088199000

H	4.784978000	-4.082844000	0.669397000
H	5.350494000	-3.218749000	-3.509093000
H	5.336623000	-4.849827000	-1.630975000
C	-0.682341000	-0.719738000	-2.104552000
H	-1.587232000	-0.287866000	-2.541981000
H	0.139958000	-0.592572000	-2.813042000
H	-0.847174000	-1.786926000	-1.947999000
C	-1.081048000	0.604006000	1.619485000
H	-0.678009000	1.613370000	1.494551000
H	-1.963091000	0.663831000	2.261753000
H	-0.330122000	-0.012413000	2.117173000
C	-5.028743000	-1.775774000	0.819537000
O	-4.950382000	-2.932555000	1.215979000
C	-6.434369000	-1.134151000	0.678429000
F	-6.679431000	-0.774979000	-0.603498000
F	-7.392360000	-1.985118000	1.060389000
F	-6.541368000	-0.015711000	1.432909000

TS3 [Pd(**DTE^{o}-COCF$_3$**)(**Ph**)**I**]

Pd	3.281795000	1.060855000	-0.021684000
S	-0.505011000	-1.449923000	1.693553000
S	-5.272374000	-1.743220000	-1.480775000
P	2.261728000	-0.921478000	0.314258000
F	-9.902638000	-0.759123000	0.558122000
F	-8.791852000	0.951064000	-0.206309000
F	-8.177780000	-0.003821000	1.653322000
O	-8.200231000	-2.273121000	-0.753785000
C	2.819592000	-1.865057000	1.776615000
C	3.378780000	-1.155143000	2.851703000
H	3.526650000	-0.081261000	2.772490000
C	3.747573000	-1.827583000	4.016120000
H	4.183602000	-1.274010000	4.842405000
C	3.561601000	-3.209493000	4.114650000
H	3.852830000	-3.732957000	5.020707000
C	3.003262000	-3.918344000	3.048642000
H	2.855598000	-4.991620000	3.124000000
C	2.631093000	-3.251711000	1.879697000
H	2.198345000	-3.810438000	1.056277000
C	2.204273000	-2.094939000	-1.087509000
C	3.316519000	-2.907925000	-1.363689000
H	4.191334000	-2.875114000	-0.722249000
C	3.298033000	-3.759786000	-2.467161000
H	4.159554000	-4.388144000	-2.672920000
C	2.181563000	-3.798910000	-3.307939000
H	2.172408000	-4.461979000	-4.168221000
C	1.079684000	-2.983270000	-3.041963000
H	0.209599000	-3.008931000	-3.691699000
C	1.088197000	-2.131908000	-1.935565000
H	0.229882000	-1.499666000	-1.734694000
C	0.547366000	-0.481602000	0.681830000
C	-0.125385000	0.616361000	0.203475000
H	0.337188000	1.355659000	-0.441243000
C	-1.494196000	0.690916000	0.618933000
C	-1.846874000	-0.361005000	1.446988000
C	-3.157558000	-0.631319000	2.118887000
H	-3.732376000	0.294618000	2.194818000
H	-3.018048000	-1.037885000	3.125373000
H	-3.758099000	-1.348696000	1.547574000
C	-2.366909000	1.799580000	0.205360000
H	-1.908708000	3.492073000	1.447488000
C	-2.969814000	4.048456000	-0.404812000
H	-2.616401000	4.209443000	-1.429261000
C	-4.215493000	3.135936000	-0.436360000
C	-3.628862000	1.741304000	-0.279051000
C	-4.434161000	0.553551000	-0.597028000
C	-5.800814000	0.447948000	-0.213508000
H	-6.316203000	1.221988000	0.341151000
C	-6.399539000	-0.735356000	-0.598989000
C	-4.009172000	-0.561709000	-1.314936000
C	-2.669250000	-0.824659000	-1.925346000
H	-2.143617000	0.118195000	-2.091613000
H	-2.758318000	-1.352278000	-2.879867000
H	-2.052905000	-1.438103000	-1.258553000
C	-7.751081000	-1.201651000	-0.375220000
C	-8.678535000	-0.241485000	0.419908000
C	-1.912849000	3.239677000	0.376884000
H	-0.890704000	3.406169000	0.018064000
H	-3.168390000	5.029342000	0.035463000
H	-4.896395000	3.350450000	0.400829000
H	-4.803804000	3.241722000	-1.354359000
I	2.912868000	3.760567000	-0.019549000
C	4.818182000	-0.007190000	-0.650642000
C	5.749980000	-0.557055000	0.236007000
C	5.013259000	-0.095120000	-2.034964000
C	6.901574000	-1.172586000	-0.271981000
C	6.168246000	-0.710685000	-2.528541000
C	7.111170000	-1.252714000	-1.650419000
H	5.585999000	-0.526461000	1.308329000
H	4.275697000	0.300466000	-2.727417000
H	7.626474000	-1.596942000	0.417971000
H	6.321364000	-0.773519000	-3.602786000
H	8.000663000	-1.740270000	-2.039194000

TS3 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]

Pd	3.267759000	1.042501000	0.144946000
C	-4.340711000	0.820715000	-0.202577000
C	-3.487951000	-0.312818000	0.402327000
S	-4.632253000	-1.804751000	0.408509000
C	-6.045536000	-0.743299000	0.179583000
C	-5.734662000	0.554398000	-0.135522000

H	-6.479354000	1.308989000	-0.358339000
C	-3.126666000	4.245584000	-0.870588000
C	-1.847358000	3.409310000	-1.120060000
C	-2.274573000	2.001375000	-0.771150000
C	-3.718448000	1.940391000	-0.675918000
C	-4.298103000	3.261751000	-1.115084000
H	-3.182536000	5.132699000	-1.506161000
H	-0.986708000	3.750994000	-0.536881000
H	-1.555636000	3.450738000	-2.178387000
H	-5.214936000	3.530259000	-0.583175000
H	-4.540307000	3.215669000	-2.186270000
H	-3.147065000	4.577863000	0.173063000
C	-0.094346000	0.770520000	-0.556029000
C	0.364122000	-0.440489000	-0.130868000
S	-0.907815000	-1.603346000	0.298094000
C	-2.219084000	-0.484683000	-0.462444000
C	-1.521547000	0.881673000	-0.591655000
H	0.564448000	1.597394000	-0.801089000
P	2.124687000	-0.891741000	-0.003028000
C	2.209562000	-1.936975000	1.495159000
C	1.949955000	-3.315575000	1.454212000
C	2.464832000	-1.311343000	2.726381000
C	1.951929000	-4.057566000	2.636656000
C	2.463672000	-2.059129000	3.903381000
C	2.209123000	-3.432577000	3.859040000
H	1.747865000	-3.810594000	0.510236000
H	2.667282000	-0.243922000	2.759498000
H	1.751306000	-5.124195000	2.600186000
H	2.665406000	-1.570049000	4.851763000
H	2.212052000	-4.014925000	4.775841000
C	2.437440000	-1.981563000	-1.437418000
C	1.638194000	-1.887830000	-2.585780000
C	3.535829000	-2.857210000	-1.421167000
C	1.928433000	-2.673041000	-3.702889000
C	3.816743000	-3.640466000	-2.539592000
C	3.014691000	-3.550379000	-3.681013000
H	0.793430000	-1.206718000	-2.610502000
H	4.169410000	-2.923642000	-0.542834000
H	1.301768000	-2.600417000	-4.586881000
H	4.666254000	-4.316682000	-2.519743000
H	3.237996000	-4.160885000	-4.551147000
C	-2.497141000	-1.013336000	-1.888909000
H	-3.221344000	-0.367232000	-2.393485000
H	-1.570067000	-1.009484000	-2.467647000
H	-2.891528000	-2.030389000	-1.869989000
C	-3.189434000	0.053581000	1.874979000
H	-2.562678000	0.948789000	1.924318000
H	-4.128920000	0.261485000	2.392868000
H	-2.678675000	-0.758382000	2.395700000
C	-7.365801000	-1.330998000	0.293026000
O	-7.579611000	-2.509798000	0.542859000
C	-8.575663000	-0.385304000	0.067680000
F	-9.731285000	-1.040987000	0.212854000
F	-8.561215000	0.642578000	0.946586000
F	-8.548456000	0.149376000	-1.175185000
I	2.938171000	3.704958000	0.577402000
C	4.863547000	-0.082943000	-0.147220000
C	5.499146000	-0.738319000	0.912035000
C	5.425362000	-0.081844000	-1.429657000
C	6.729979000	-1.368612000	0.687241000
C	6.656198000	-0.712653000	-1.638822000
C	7.307777000	-1.358523000	-0.584226000
H	5.047297000	-0.775019000	1.897932000
H	4.913913000	0.393091000	-2.262032000
H	7.226997000	-1.874664000	1.510812000
H	7.096184000	-0.706570000	-2.632597000
H	8.257393000	-1.857603000	-0.754927000

4 [Pd(**DTE^{o}-COCF$_3$**)(**Ph**)**I**]

Pd	3.529122000	1.099009000	-0.258587000
S	-0.418783000	-0.976142000	1.809205000
S	-5.138957000	-2.044666000	-1.149201000
P	2.305769000	-0.694416000	0.309279000
F	-9.761471000	-0.910938000	0.827538000
F	-8.784392000	0.658112000	-0.324704000
F	-8.057756000	0.155435000	1.666760000
O	-8.011550000	-2.566686000	-0.223071000
C	2.837246000	-1.472403000	1.877916000
C	3.476174000	-0.673531000	2.840054000
H	3.700034000	0.366306000	2.617999000
C	3.824911000	-1.213808000	4.077369000
H	4.321758000	-0.590968000	4.815282000
C	3.539514000	-2.551854000	4.362749000
H	3.815623000	-2.972565000	5.325296000
C	2.900070000	-3.348521000	3.410566000
H	2.674639000	-4.387944000	3.629963000
C	2.546853000	-2.814269000	2.170024000
H	2.050849000	-3.442535000	1.437738000
C	2.173137000	-2.040661000	-0.930507000
C	3.190998000	-3.002427000	-1.044374000
H	4.043521000	-2.980007000	-0.374071000
C	3.111158000	-3.989351000	-2.025632000
H	3.900413000	-4.731336000	-2.103135000
C	2.027991000	-4.018867000	-2.909096000
H	1.971260000	-4.787518000	-3.674465000
C	1.021269000	-3.056961000	-2.807003000
H	0.176969000	-3.072767000	-3.490149000
C	1.091258000	-2.070095000	-1.821695000
H	0.304325000	-1.328174000	-1.747956000
C	0.603866000	-0.176371000	0.630582000
C	-0.100653000	0.794724000	-0.033874000

H	0.341784000	1.420045000	-0.799602000
C	-1.471852000	0.901761000	0.369055000
C	-1.790567000	0.011631000	1.380701000
C	-3.086290000	-0.161087000	2.111837000
H	-3.685375000	0.748284000	2.024742000
H	-2.923592000	-0.368978000	3.173958000
H	-3.674061000	-0.986839000	1.694576000
C	-2.387132000	1.877977000	-0.240230000
H	-1.996142000	3.796909000	0.642277000
C	-3.084158000	3.937577000	-1.271442000
H	-2.742379000	3.905738000	-2.311983000
C	-4.292526000	2.989835000	-1.106719000
C	-3.648582000	1.677196000	-0.687431000
C	-4.404272000	0.417593000	-0.752278000
C	-5.754211000	0.323348000	-0.311059000
H	-6.296376000	1.163055000	0.105354000
C	-6.297796000	-0.939704000	-0.441798000
C	-3.937479000	-0.793991000	-1.255644000
C	-2.597499000	-1.104591000	-1.842504000
H	-2.123832000	-0.185174000	-2.193528000
H	-2.676229000	-1.804360000	-2.680139000
H	-1.938430000	-1.553302000	-1.091035000
C	-7.614802000	-1.419440000	-0.082598000
C	-8.577395000	-0.366298000	0.532644000
C	-1.992322000	3.340482000	-0.358431000
H	-0.978110000	3.474351000	-0.751065000
H	-3.319816000	4.977948000	-1.031576000
H	-4.976444000	3.338376000	-0.318501000
H	-4.890105000	2.890778000	-2.019512000
I	2.543423000	3.616820000	0.125335000
C	4.905648000	-0.226994000	-0.786194000
C	5.830730000	-0.736669000	0.133097000
C	5.057317000	-0.483603000	-2.156224000
C	6.931063000	-1.471031000	-0.327360000
C	6.162145000	-1.213511000	-2.606084000
C	7.097324000	-1.710645000	-1.693408000
H	5.697643000	-0.580657000	1.199294000
H	4.318754000	-0.131585000	-2.871816000
H	7.649932000	-1.862382000	0.387999000
H	6.281297000	-1.404348000	-3.669527000
H	7.946507000	-2.289735000	-2.045227000

4 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]

Pd	-3.416029000	-1.207734000	0.182672000
C	4.280280000	-0.684892000	-0.373426000
C	3.373858000	0.319718000	0.365855000
S	4.451954000	1.844581000	0.586385000
C	5.912653000	0.882700000	0.241323000
C	5.660368000	-0.373186000	-0.248616000
H	6.439490000	-1.059769000	-0.557255000
C	3.220198000	-4.038968000	-1.498854000
C	1.908756000	-3.231216000	-1.658988000
C	2.272440000	-1.864028000	-1.125025000
C	3.710810000	-1.756242000	-1.000917000
C	4.350642000	-2.984428000	-1.598657000
H	3.320790000	-4.835226000	-2.240529000
H	1.058635000	-3.678688000	-1.134575000
H	1.628890000	-3.149278000	-2.718269000
H	5.273497000	-3.281105000	-1.092732000
H	4.599792000	-2.790678000	-2.651604000
H	3.244481000	-4.499687000	-0.505245000
C	0.039042000	-0.770638000	-0.768449000
C	-0.475338000	0.340901000	-0.175571000
S	0.740721000	1.496584000	0.409983000
C	2.103681000	0.552292000	-0.482856000
C	1.469492000	-0.811540000	-0.807178000
H	-0.579340000	-1.584151000	-1.127078000
P	-2.253676000	0.704443000	-0.013737000
C	-2.366600000	1.740300000	1.490715000
C	-2.105480000	3.119465000	1.458949000
C	-2.649695000	1.113004000	2.714826000
C	-2.133718000	3.859215000	2.642175000
C	-2.674486000	1.858866000	3.893004000
C	-2.418597000	3.232090000	3.857324000
H	-1.881533000	3.616808000	0.521366000
H	-2.851400000	0.045438000	2.741115000
H	-1.931968000	4.925809000	2.611787000
H	-2.896428000	1.367551000	4.835664000
H	-2.441535000	3.812719000	4.774935000
C	-2.608765000	1.795451000	-1.444785000
C	-1.859775000	1.675118000	-2.624262000
C	-3.684289000	2.697786000	-1.394542000
C	-2.176885000	2.456913000	-3.736795000
C	-3.991490000	3.478633000	-2.507448000
C	-3.239982000	3.360005000	-3.680223000
H	-1.032078000	0.975469000	-2.678315000
H	-4.284657000	2.784716000	-0.495479000
H	-1.588812000	2.360163000	-4.644699000
H	-4.823581000	4.174772000	-2.458880000
H	-3.484617000	3.967737000	-4.546555000
C	2.363222000	1.283312000	-1.820483000
H	3.114626000	0.741959000	-2.402920000
H	1.437357000	1.321675000	-2.400184000
H	2.715825000	2.303168000	-1.659455000
C	3.081029000	-0.253405000	1.772291000
H	2.489808000	-1.170473000	1.694107000
H	4.024842000	-0.492067000	2.268602000
H	2.534777000	0.460619000	2.391137000
C	7.204979000	1.503407000	0.450882000
O	7.367425000	2.646645000	0.857167000
C	8.455890000	0.646158000	0.121647000

F	9.581369000	1.322393000	0.372395000
F	8.474899000	-0.490132000	0.855103000
F	8.466361000	0.281675000	-1.181786000
I	-2.052822000	-3.465373000	0.919712000
C	-4.988640000	-0.070819000	-0.225095000
C	-5.682719000	0.594276000	0.793347000
C	-5.511355000	-0.115435000	-1.524946000
C	-6.924996000	1.178476000	0.515250000
C	-6.755017000	0.466537000	-1.790547000
C	-7.460613000	1.116336000	-0.773401000
H	-5.262760000	0.673610000	1.791712000
H	-4.955059000	-0.586387000	-2.331227000
H	-7.464490000	1.690762000	1.307757000
H	-7.162650000	0.423367000	-2.797217000
H	-8.419092000	1.580847000	-0.987344000

$Sn(CH_2CH)Bu_3$

C	-3.241339000	-1.112243000	-0.072672000
Sn	-1.180453000	-0.460230000	-0.027951000
H	-3.452345000	-2.182047000	-0.147502000
C	-1.152939000	1.724910000	0.047426000
H	-1.971031000	2.097681000	-0.582153000
H	-1.387284000	2.034632000	1.073811000
C	-0.136280000	-1.150830000	-1.822821000
H	-0.448870000	-0.513501000	-2.659868000
H	-0.491997000	-2.162570000	-2.056340000
C	-0.170560000	-1.267522000	1.738469000
H	-0.890146000	-1.275590000	2.566858000
H	0.082457000	-2.316597000	1.538200000
C	1.090094000	-0.486861000	2.144639000
H	1.806213000	-0.464080000	1.311192000
H	0.832173000	0.562531000	2.346542000
C	1.793240000	-1.067837000	3.380174000
H	1.084959000	-1.087836000	4.220145000
H	2.061216000	-2.114788000	3.180831000
C	3.045695000	-0.282424000	3.779711000
H	3.530251000	-0.715596000	4.662080000
H	3.781894000	-0.273015000	2.966658000
H	2.799973000	0.760710000	4.013402000
C	1.395902000	-1.147977000	-1.697595000
H	1.704900000	-1.787350000	-0.858419000
H	1.753224000	-0.138084000	-1.451753000
C	2.111007000	-1.625519000	-2.970011000
H	1.764390000	-2.638431000	-3.218069000
H	1.811560000	-0.985080000	-3.811313000
C	3.636531000	-1.620441000	-2.836099000
H	3.963656000	-2.276471000	-2.020156000
H	4.124271000	-1.964389000	-3.755237000
H	4.010347000	-0.612522000	-2.618123000
C	0.178548000	2.348508000	-0.402814000
H	0.409274000	2.037552000	-1.431671000
H	1.002849000	1.968317000	0.216849000
C	0.183121000	3.882787000	-0.338886000
H	-0.634820000	4.270422000	-0.962114000
H	-0.039479000	4.199306000	0.689675000
C	1.511437000	4.496361000	-0.790703000
H	1.742316000	4.219401000	-1.826610000
H	1.490797000	5.590705000	-0.735788000
H	2.341121000	4.147308000	-0.163858000
C	-4.288666000	-0.280200000	-0.011953000
H	-4.172844000	0.801141000	0.064004000
H	-5.321119000	-0.634534000	-0.034905000

5 [Pd(**DTE^o-COCF$_3$**)(**Ph**)**I**]·**Sn(CH$_2$CH)Bu$_3$**

Pd	-1.650388000	0.314665000	-0.744168000
S	2.525395000	0.371927000	2.100538000
S	7.547359000	1.706051000	-0.158139000
P	-0.108924000	1.349319000	0.680812000
F	11.756736000	-1.107500000	0.803115000
F	10.563517000	-1.685575000	-0.924935000
F	9.844577000	-2.110638000	1.087195000
O	10.408686000	1.147620000	0.782449000
C	-0.651867000	1.474454000	2.426113000
C	-1.689219000	0.646023000	2.878781000
H	-2.173217000	-0.038326000	2.192464000
C	-2.093486000	0.693424000	4.213866000
H	-2.901228000	0.051116000	4.550932000
C	-1.464365000	1.564871000	5.105532000
H	-1.780582000	1.602163000	6.144076000
C	-0.429174000	2.391949000	4.660745000
H	0.061548000	3.072107000	5.350783000
C	-0.023445000	2.352061000	3.326461000
H	0.771793000	3.008802000	2.988703000
C	0.408081000	3.052250000	0.212360000
C	-0.350779000	4.162945000	0.612392000
H	-1.201571000	4.034432000	1.271997000
C	-0.025182000	5.437973000	0.150973000
H	-0.623762000	6.288843000	0.462849000
C	1.059384000	5.619584000	-0.711506000
H	1.309415000	6.613918000	-1.070212000
C	1.818641000	4.518103000	-1.110963000
H	2.665056000	4.650033000	-1.779063000
C	1.493974000	3.239347000	-0.654480000
H	2.086058000	2.390073000	-0.976805000
C	1.448509000	0.427937000	0.721957000
C	1.992751000	-0.251101000	-0.336583000
H	1.482395000	-0.357396000	-1.286738000
C	3.289387000	-0.804574000	-0.075512000
C	3.706902000	-0.565602000	1.222046000
C	4.960371000	-1.014477000	1.908476000

H	5.386013000	-1.871287000	1.381118000
H	4.767608000	-1.307497000	2.945262000
H	5.717707000	-0.221782000	1.919683000
C	4.037397000	-1.547986000	-1.099634000
H	3.235509000	-3.537805000	-1.198507000
C	4.390789000	-2.988387000	-2.995722000
H	4.126095000	-2.411688000	-3.889118000
C	5.745286000	-2.484114000	-2.451139000
C	5.338983000	-1.416725000	-1.446648000
C	6.325751000	-0.450899000	-0.941924000
C	7.641534000	-0.845105000	-0.569312000
H	7.984121000	-1.870725000	-0.623502000
C	8.428035000	0.193901000	-0.111317000
C	6.133232000	0.920327000	-0.791870000
C	4.917263000	1.731738000	-1.107788000
H	4.300909000	1.205702000	-1.840193000
H	5.182588000	2.714644000	-1.508987000
H	4.307523000	1.888574000	-0.211205000
C	9.792725000	0.176560000	0.368748000
C	10.508147000	-1.202602000	0.336461000
C	3.379631000	-2.679717000	-1.871080000
H	2.384282000	-2.414392000	-2.244989000
H	4.408528000	-4.045009000	-3.276389000
H	6.299601000	-3.285921000	-1.940921000
H	6.406131000	-2.094466000	-3.233253000
I	-1.092614000	-2.332528000	0.182272000
C	-2.224169000	2.177527000	-1.248089000
C	-3.241747000	2.791190000	-0.504477000
C	-1.678736000	2.848086000	-2.348732000
C	-3.709206000	4.061519000	-0.861110000
C	-2.143447000	4.121652000	-2.698046000
C	-3.158987000	4.731663000	-1.956618000
H	-3.678808000	2.287066000	0.353261000
H	-0.879550000	2.394782000	-2.929137000
H	-4.503070000	4.523260000	-0.279193000
H	-1.704447000	4.637385000	-3.548561000
H	-3.516312000	5.720824000	-2.229081000
C	-3.527459000	-0.225338000	-2.149431000
Sn	-5.016486000	-1.250437000	-0.914267000
H	-3.856849000	0.758995000	-2.480930000
C	-4.936102000	-3.396250000	-1.289195000
H	-5.779861000	-3.673600000	-1.932833000
H	-4.022141000	-3.578793000	-1.867079000
C	-6.830247000	-0.195686000	-1.532849000
H	-7.696210000	-0.639923000	-1.026674000
H	-6.982068000	-0.348024000	-2.608738000
C	-4.720389000	-0.783595000	1.195933000
H	-3.938050000	-1.450504000	1.572243000
H	-4.320413000	0.235324000	1.254798000
C	-5.987407000	-0.902244000	2.054822000
H	-6.773726000	-0.239112000	1.666734000
H	-6.393808000	-1.921927000	1.991428000
C	-5.738585000	-0.562496000	3.531969000
H	-4.965446000	-1.236697000	3.926081000
H	-5.323266000	0.452672000	3.600231000
C	-6.999487000	-0.663993000	4.394526000
H	-6.792474000	-0.418594000	5.442359000
H	-7.777580000	0.022518000	4.039035000
H	-7.416204000	-1.678110000	4.366377000
C	-6.733279000	1.305503000	-1.213323000
H	-5.841993000	1.737491000	-1.688734000
H	-6.590350000	1.449427000	-0.132439000
C	-7.957399000	2.118525000	-1.656989000
H	-8.112060000	1.975424000	-2.735414000
H	-8.855040000	1.722193000	-1.162399000
C	-7.811997000	3.612550000	-1.351387000
H	-6.936939000	4.034249000	-1.860727000
H	-8.692307000	4.180214000	-1.673587000
H	-7.680655000	3.784158000	-0.275794000
C	-4.928170000	-4.247289000	-0.010600000
H	-5.851596000	-4.079141000	0.562397000
H	-4.102293000	-3.930603000	0.640419000
C	-4.783797000	-5.750012000	-0.289884000
H	-5.604989000	-6.078334000	-0.942489000
H	-3.856082000	-5.918655000	-0.854049000
C	-4.769066000	-6.594419000	0.987505000
H	-5.697361000	-6.465828000	1.557676000
H	-4.660596000	-7.662028000	0.764907000
H	-3.937441000	-6.304176000	1.640976000
C	-2.401679000	-0.696719000	-2.766370000
H	-2.048251000	-1.715802000	-2.635111000
H	-1.894199000	-0.117991000	-3.540327000

5 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]·**Sn(CH$_2$CH)Bu$_3$**

Pd	-1.603912000	0.352943000	-0.527596000
C	6.013011000	-0.933803000	-1.035919000
C	5.305398000	-0.422134000	0.235071000
S	6.698897000	0.253343000	1.302298000
C	7.901080000	-0.625760000	0.320958000
C	7.400386000	-1.159763000	-0.839711000
H	8.012530000	-1.676433000	-1.569219000
C	4.287850000	-2.371810000	-3.969463000
C	3.250429000	-1.330702000	-3.480966000
C	3.879973000	-0.773201000	-2.223694000
C	5.271120000	-1.162512000	-2.160852000
C	5.650100000	-1.849358000	-3.449066000
H	4.275214000	-2.507082000	-5.053886000
H	2.260462000	-1.762595000	-3.304138000
H	3.126621000	-0.527286000	-4.220270000
H	6.399071000	-2.635042000	-3.317095000
H	6.067944000	-1.110634000	-4.147704000

H	4.074481000	-3.341633000	-3.506922000
C	1.970326000	0.403272000	-1.088717000
C	1.689750000	0.990746000	0.107467000
S	3.076139000	1.136916000	1.198791000
C	4.251475000	0.628166000	-0.181088000
C	3.335393000	0.010199000	-1.251676000
H	1.205422000	0.188411000	-1.826273000
P	0.034452000	1.637157000	0.525807000
C	-0.064656000	1.658044000	2.354027000
C	0.717813000	2.549314000	3.109391000
C	-0.925565000	0.766205000	3.010851000
C	0.648044000	2.533621000	4.501953000
C	-0.995388000	0.760433000	4.405068000
C	-0.207915000	1.639741000	5.150891000
H	1.370540000	3.261069000	2.614884000
H	-1.531815000	0.073600000	2.436868000
H	1.258996000	3.222350000	5.077888000
H	-1.664084000	0.067501000	4.906274000
H	-0.263050000	1.631675000	6.235686000
C	0.173838000	3.407334000	0.039968000
C	0.901961000	3.764801000	-1.104518000
C	-0.533262000	4.394457000	0.742796000
C	0.926314000	5.092165000	-1.535047000
C	-0.507728000	5.718733000	0.306031000
C	0.221448000	6.071563000	-0.832133000
H	1.449821000	3.011669000	-1.661675000
H	-1.114829000	4.132655000	1.619181000
H	1.498591000	5.358492000	-2.419102000
H	-1.063790000	6.473158000	0.854767000
H	0.238953000	7.103751000	-1.169754000
C	4.850819000	1.928341000	-0.766430000
H	5.501485000	1.691551000	-1.613407000
H	4.043222000	2.575172000	-1.119345000
H	5.433334000	2.472600000	-0.021594000
C	4.701741000	-1.642436000	0.969157000
H	3.909861000	-2.096848000	0.366789000
H	5.483742000	-2.387758000	1.133576000
H	4.281620000	-1.361478000	1.936523000
C	9.271179000	-0.659412000	0.786608000
O	9.667234000	-0.135560000	1.820457000
C	10.297796000	-1.399885000	-0.111062000
F	11.515372000	-1.389075000	0.441157000
F	9.938256000	-2.688896000	-0.309568000
F	10.384483000	-0.817106000	-1.329708000
I	-0.385826000	-2.114560000	0.321049000
C	-2.614812000	2.104310000	-0.599894000
C	-3.369013000	2.452849000	0.528693000
C	-2.562434000	2.990438000	-1.685028000
C	-4.068607000	3.665781000	0.565717000
C	-3.261943000	4.200019000	-1.644642000
C	-4.015025000	4.543199000	-0.517738000
H	-3.406136000	1.799954000	1.395233000
H	-1.962612000	2.753362000	-2.558810000
H	-4.649599000	3.920563000	1.448532000
H	-3.208179000	4.878313000	-2.492368000
H	-4.552494000	5.486314000	-0.485724000
C	-3.131083000	-1.130597000	-1.686429000
Sn	-5.004537000	-1.308178000	-0.575583000
H	-2.536048000	-2.042667000	-1.697343000
C	-6.516834000	-0.003294000	-1.453629000
H	-6.527054000	-0.234441000	-2.527027000
H	-7.483169000	-0.345596000	-1.060538000
C	-4.567053000	-1.018713000	1.545114000
H	-5.417117000	-0.527120000	2.033904000
H	-3.722219000	-0.324863000	1.603879000
C	-5.590593000	-3.387555000	-0.885044000
H	-5.582599000	-3.588305000	-1.963940000
H	-4.803944000	-4.014825000	-0.446943000
C	-6.957017000	-3.757483000	-0.287741000
H	-6.974388000	-3.530129000	0.788079000
H	-7.745936000	-3.138158000	-0.738753000
C	-7.321240000	-5.237017000	-0.480944000
H	-7.312170000	-5.471112000	-1.554573000
H	-6.538853000	-5.859437000	-0.025139000
C	-8.683398000	-5.602765000	0.115481000
H	-8.918230000	-6.662591000	-0.034804000
H	-8.707638000	-5.406494000	1.194373000
H	-9.487386000	-5.015339000	-0.344652000
C	-4.206871000	-2.329347000	2.260748000
H	-3.389146000	-2.832304000	1.726746000
H	-5.060063000	-3.021504000	2.237177000
C	-3.772625000	-2.116389000	3.717076000
H	-2.907711000	-1.440873000	3.727857000
H	-4.575184000	-1.602490000	4.264879000
C	-3.407850000	-3.421134000	4.429818000
H	-2.584098000	-3.930680000	3.915597000
H	-3.094235000	-3.241750000	5.464533000
H	-4.260172000	-4.111158000	4.454463000
C	-6.373351000	1.509978000	-1.241443000
H	-5.409510000	1.862751000	-1.630556000
H	-6.359800000	1.741724000	-0.168246000
C	-7.504161000	2.307017000	-1.909285000
H	-7.516527000	2.077130000	-2.984106000
H	-8.469015000	1.960555000	-1.512877000
C	-7.379821000	3.820232000	-1.711179000
H	-6.441589000	4.196693000	-2.133308000
H	-8.205520000	4.357083000	-2.192360000
H	-7.386981000	4.081774000	-0.646287000
C	-2.739167000	-0.155058000	-2.561390000
H	-3.343789000	0.726761000	-2.748624000
H	-1.896897000	-0.299096000	-3.241383000

TS5 [Pd(**DTE^{o}-COCF$_3$**)(**Ph**)**I**]·**Sn(CH$_2$CH)Bu$_3$**

Pd	-1.841621000	0.410348000	-1.298534000
S	2.167115000	0.463298000	2.031772000
S	7.469579000	1.435274000	-0.007771000
P	-0.387073000	1.391306000	0.433576000
F	11.404967000	-1.584479000	1.393574000
F	10.228446000	-2.254529000	-0.312449000
F	9.402718000	-2.385871000	1.699229000
O	10.243642000	0.754953000	1.104086000
C	-1.020874000	1.411268000	2.166393000
C	-1.535455000	0.208621000	2.677046000
H	-1.525964000	-0.683166000	2.061038000
C	-2.052002000	0.150148000	3.970544000
H	-2.448210000	-0.787691000	4.348902000
C	-2.064597000	1.294988000	4.772461000
H	-2.474288000	1.253130000	5.777601000
C	-1.541246000	2.490311000	4.277330000
H	-1.535386000	3.382152000	4.897257000
C	-1.017039000	2.550546000	2.983047000
H	-0.610371000	3.487215000	2.620516000
C	0.126816000	3.125162000	0.103316000
C	-0.841581000	4.142888000	0.136031000
H	-1.865238000	3.909256000	0.409249000
C	-0.500911000	5.450873000	-0.202243000
H	-1.261168000	6.226146000	-0.177153000
C	0.807596000	5.758652000	-0.590268000
H	1.069622000	6.777238000	-0.862564000
C	1.772247000	4.751236000	-0.633265000
H	2.790629000	4.980694000	-0.935936000
C	1.434972000	3.439873000	-0.287618000
H	2.189944000	2.662827000	-0.334805000
C	1.175774000	0.489145000	0.588223000
C	1.773415000	-0.235243000	-0.409924000
H	1.324409000	-0.360228000	-1.388433000
C	3.035383000	-0.813250000	-0.046488000
C	3.377952000	-0.533814000	1.265530000
C	4.571204000	-0.990881000	2.047299000
H	4.986305000	-1.896315000	1.598220000
H	4.310535000	-1.208536000	3.087811000
H	5.362341000	-0.231965000	2.052641000
C	3.805828000	-1.643539000	-0.983339000
H	2.882613000	-3.582989000	-1.038119000
C	4.187381000	-3.206489000	-2.775943000
H	4.021075000	-2.664054000	-3.713303000
C	5.532868000	-2.759227000	-2.164384000
C	5.133295000	-1.613919000	-1.246181000
C	6.149513000	-0.684347000	-0.732739000
C	7.414580000	-1.137239000	-0.263532000
H	7.692592000	-2.183441000	-0.242052000
C	8.242887000	-0.124071000	0.178192000
C	6.039782000	0.702671000	-0.670156000
C	4.892563000	1.566171000	-1.087053000
H	4.282692000	1.045119000	-1.828484000
H	5.233288000	2.515309000	-1.511685000
H	4.250085000	1.792078000	-0.228743000
C	9.574667000	-0.200098000	0.738402000
C	10.170246000	-1.627838000	0.884160000
C	3.127302000	-2.773323000	-1.741554000
H	2.179242000	-2.467009000	-2.197976000
H	4.153239000	-4.275997000	-3.000924000
H	5.997700000	-3.564718000	-1.576411000
H	6.268488000	-2.455837000	-2.917350000
I	-1.339954000	-2.268450000	-0.507146000
C	-2.088941000	2.232279000	-2.158995000
C	-3.229255000	3.035267000	-2.026446000
C	-1.021536000	2.718584000	-2.934306000
C	-3.288604000	4.305155000	-2.613982000
C	-1.082696000	3.982340000	-3.529504000
C	-2.214914000	4.785930000	-3.365971000
H	-4.080382000	2.687533000	-1.454051000
H	-0.121774000	2.121726000	-3.065308000
H	-4.178745000	4.916074000	-2.478669000
H	-0.239175000	4.340143000	-4.115671000
H	-2.258821000	5.771896000	-3.820742000
C	-2.991700000	-0.131512000	-2.904834000
Sn	-4.164666000	-1.084653000	-0.105518000
H	-3.910867000	0.427885000	-3.096540000
C	-5.170898000	-2.293429000	-1.614131000
H	-5.561487000	-1.620673000	-2.384559000
H	-4.402579000	-2.912628000	-2.086701000
C	-5.136137000	0.850283000	0.222268000
H	-6.108309000	0.546680000	0.635661000
H	-5.334683000	1.294181000	-0.757210000
C	-4.205421000	-2.135839000	1.813546000
H	-4.172062000	-3.205685000	1.573497000
H	-3.295406000	-1.909498000	2.373036000
C	-5.450757000	-1.796200000	2.645311000
H	-5.484669000	-0.716849000	2.850245000
H	-6.363838000	-2.027490000	2.077516000
C	-5.498778000	-2.551466000	3.982483000
H	-5.438580000	-3.630731000	3.788181000
H	-4.605758000	-2.294311000	4.568594000
C	-6.758366000	-2.242231000	4.796474000
H	-6.766020000	-2.783271000	5.749399000
H	-6.831538000	-1.171323000	5.020406000
H	-7.662450000	-2.526943000	4.245272000
C	-4.437246000	1.834868000	1.162510000
H	-3.453602000	2.098403000	0.758996000
H	-4.243545000	1.358717000	2.132594000

C	-5.239137000	3.124498000	1.387108000
H	-5.423397000	3.606519000	0.416718000
H	-6.226158000	2.871188000	1.797869000
C	-4.526512000	4.107406000	2.321116000
H	-3.561309000	4.418334000	1.904959000
H	-5.123907000	5.011304000	2.485856000
H	-4.329256000	3.650912000	3.298008000
C	-6.289872000	-3.160149000	-1.018184000
H	-7.053041000	-2.527143000	-0.542241000
H	-5.888866000	-3.803836000	-0.222900000
C	-6.972133000	-4.047147000	-2.072055000
H	-7.384103000	-3.409207000	-2.866054000
H	-6.211877000	-4.680456000	-2.549485000
C	-8.081174000	-4.924742000	-1.485086000
H	-8.868050000	-4.313857000	-1.025883000
H	-8.550284000	-5.548089000	-2.254857000
H	-7.686899000	-5.593226000	-0.709948000
C	-2.622067000	-1.037943000	-3.821129000
H	-1.719818000	-1.639378000	-3.723532000
H	-3.221357000	-1.225409000	-4.714936000

TS5 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]·**Sn(CH$_2$CH)Bu$_3$**

Pd	-1.589888000	-0.070767000	-1.124699000
I	-1.631622000	-2.263898000	0.676243000
C	-1.369990000	1.286239000	-2.618207000
C	-2.139990000	2.453781000	-2.719573000
C	-0.349059000	1.085484000	-3.563975000
C	-1.884394000	3.403604000	-3.715017000
C	-0.085227000	2.039255000	-4.553760000
C	-0.851449000	3.204403000	-4.633686000
H	-2.925432000	2.654472000	-2.002152000
H	0.253259000	0.181431000	-3.535595000
H	-2.486742000	4.308080000	-3.757580000
H	0.718396000	1.864618000	-5.265895000
H	-0.646839000	3.946029000	-5.401146000
C	-2.510435000	-1.125303000	-2.621606000
Sn	-4.334900000	-1.038054000	0.029010000
H	-3.267267000	-0.608398000	-3.218211000
C	-5.151730000	-2.794194000	-0.965351000
H	-5.360966000	-2.513514000	-2.003071000
H	-4.356340000	-3.544804000	-0.987919000
C	-4.974114000	0.862710000	-0.845852000
H	-6.064557000	0.737285000	-0.925141000
H	-4.581800000	0.942556000	-1.862824000
C	-4.869771000	-0.891388000	2.141619000
H	-4.657767000	-1.850835000	2.625505000
H	-4.216704000	-0.144710000	2.605018000
C	-6.343417000	-0.488558000	2.320208000
H	-6.558660000	0.427229000	1.751691000
H	-7.001491000	-1.264840000	1.906495000
C	-6.723977000	-0.248250000	3.789307000
H	-6.524643000	-1.161186000	4.366682000
H	-6.067903000	0.529014000	4.204903000
C	-8.188372000	0.165622000	3.961592000
H	-8.438137000	0.333921000	5.015166000
H	-8.403219000	1.092827000	3.416269000
H	-8.865645000	-0.607038000	3.578013000
C	-4.639135000	2.106729000	-0.017301000
H	-3.550404000	2.246354000	0.019006000
H	-4.961571000	1.975000000	1.024746000
C	-5.297042000	3.376992000	-0.579308000
H	-5.019449000	3.489902000	-1.636431000
H	-6.388289000	3.248825000	-0.562692000
C	-4.910014000	4.642496000	0.189788000
H	-3.831205000	4.822971000	0.124756000
H	-5.419988000	5.526526000	-0.209974000
H	-5.171965000	4.557778000	1.251974000
C	-6.410711000	-3.341444000	-0.276162000
H	-7.199823000	-2.576445000	-0.258581000
H	-6.194741000	-3.580881000	0.774303000
C	-6.960152000	-4.599539000	-0.966994000
H	-7.182569000	-4.364563000	-2.016770000
H	-6.175972000	-5.368579000	-0.983165000
C	-8.213778000	-5.153530000	-0.284068000
H	-9.023374000	-4.413597000	-0.282028000
H	-8.584429000	-6.050776000	-0.792299000
H	-8.009173000	-5.422354000	0.759306000
C	-2.177421000	-2.365679000	-3.012809000
H	-1.434717000	-2.966989000	-2.490430000
H	-2.648072000	-2.842736000	-3.875734000
C	5.925443000	-1.171466000	-0.320314000
C	5.150001000	-0.405588000	0.771638000
S	6.468609000	0.600280000	1.658239000
C	7.750203000	-0.414391000	0.944166000
C	7.317520000	-1.248219000	-0.055889000
H	7.980930000	-1.884892000	-0.628894000
C	4.384727000	-3.389069000	-2.847346000
C	3.269373000	-2.335230000	-2.635981000
C	3.824769000	-1.451327000	-1.541456000
C	5.234332000	-1.719540000	-1.364687000
C	5.695315000	-2.669059000	-2.442136000
H	4.415301000	-3.774212000	-3.869595000
H	2.302677000	-2.778816000	-2.377335000
H	3.116174000	-1.740467000	-3.547001000
H	6.485124000	-3.349361000	-2.111794000
H	6.091702000	-2.092231000	-3.289735000
H	4.217050000	-4.236663000	-2.173839000
C	1.818363000	-0.146394000	-0.777474000
C	1.458572000	0.729600000	0.204224000
S	2.801899000	1.216487000	1.259372000
C	4.052573000	0.438832000	0.086087000

C	3.206494000	-0.488031000	-0.803359000
H	1.097345000	-0.575047000	-1.464124000
C	4.603598000	1.577346000	-0.805128000
H	5.294594000	1.171090000	-1.549364000
H	3.777064000	2.062688000	-1.329692000
H	5.130303000	2.328630000	-0.214741000
C	4.594885000	-1.439574000	1.778224000
H	3.858855000	-2.086953000	1.292585000
H	5.414079000	-2.063005000	2.144714000
H	4.120110000	-0.952921000	2.632203000
C	9.104099000	-0.248994000	1.429155000
O	9.435376000	0.533242000	2.311356000
C	10.199600000	-1.124056000	0.763509000
F	11.397240000	-0.893668000	1.311333000
F	9.923449000	-2.441783000	0.897384000
F	10.287912000	-0.866659000	-0.562332000
P	-0.251886000	1.377732000	0.330646000
C	-0.529215000	1.617428000	2.136937000
C	-1.485475000	0.842144000	2.804595000
H	-2.067850000	0.117727000	2.252404000
C	-1.686335000	0.988279000	4.180213000
H	-2.428077000	0.373131000	4.683206000
C	-0.934785000	1.917780000	4.900375000
H	-1.084387000	2.028893000	5.971151000
C	0.005398000	2.714880000	4.238041000
H	0.582634000	3.451498000	4.789457000
C	0.203961000	2.572768000	2.864819000
H	0.916004000	3.218845000	2.360435000
C	-0.078794000	3.115016000	-0.254569000
C	-0.990147000	4.082438000	0.196393000
H	-1.727156000	3.830021000	0.952455000
C	-0.953671000	5.378636000	-0.318885000
H	-1.662892000	6.118872000	0.040729000
C	-0.009861000	5.720863000	-1.290228000
H	0.017685000	6.729809000	-1.691719000
C	0.897639000	4.760410000	-1.743331000
H	1.632185000	5.017664000	-2.500978000
C	0.863831000	3.462820000	-1.231090000
H	1.560883000	2.720067000	-1.603834000

6 [Pd(**DTE^o-COCF$_3$**)(**Ph**)(**CH$_2$CH**)(**SnBu$_3$**)**I**]

Pd	-1.847631000	1.014158000	-1.375774000
S	1.999572000	0.574236000	2.054326000
S	7.373463000	1.316859000	0.227450000
P	-0.446028000	1.781475000	0.444009000
F	11.099011000	-2.033813000	1.440513000
F	9.949441000	-2.460028000	-0.359717000
F	9.051304000	-2.757930000	1.602397000
O	10.070433000	0.384051000	1.349314000
C	-1.142481000	1.747432000	2.153353000
C	-2.104395000	0.779717000	2.480847000
H	-2.449643000	0.086499000	1.725065000
C	-2.621878000	0.701714000	3.774655000
H	-3.368754000	-0.050972000	4.009479000
C	-2.186102000	1.592570000	4.758160000
H	-2.591870000	1.535446000	5.764260000
C	-1.226918000	2.558093000	4.442893000
H	-0.881265000	3.252929000	5.203045000
C	-0.706251000	2.636605000	3.149705000
H	0.035166000	3.394463000	2.918698000
C	0.175595000	3.502856000	0.274930000
C	-0.736231000	4.562560000	0.412812000
H	-1.764346000	4.362099000	0.698945000
C	-0.332051000	5.873274000	0.168733000
H	-1.048404000	6.683526000	0.268864000
C	0.985338000	6.142782000	-0.217070000
H	1.296746000	7.165035000	-0.412292000
C	1.895523000	5.094007000	-0.354436000
H	2.920964000	5.294848000	-0.652378000
C	1.492399000	3.778096000	-0.112196000
H	2.202089000	2.967152000	-0.236687000
C	1.053677000	0.770400000	0.593100000
C	1.617558000	0.057981000	-0.433893000
H	1.186042000	0.031624000	-1.428554000
C	2.821874000	-0.638069000	-0.080379000
C	3.149779000	-0.467780000	1.253400000
C	4.286549000	-1.060016000	2.028636000
H	4.655937000	-1.955102000	1.522603000
H	3.980346000	-1.336456000	3.042493000
H	5.124401000	-0.357922000	2.112564000
C	3.561543000	-1.450980000	-1.056437000
H	2.524373000	-3.320784000	-1.273434000
C	3.891445000	-2.899465000	-2.952309000
H	3.779645000	-2.281232000	-3.849908000
C	5.246466000	-2.580576000	-2.283998000
C	4.894235000	-1.483130000	-1.291062000
C	5.951248000	-0.657252000	-0.689892000
C	7.177100000	-1.219472000	-0.235352000
H	7.394297000	-2.278756000	-0.291920000
C	8.051569000	-0.295064000	0.301974000
C	5.920711000	0.724937000	-0.519899000
C	4.838064000	1.686860000	-0.891666000
H	4.216364000	1.262151000	-1.682879000
H	5.246694000	2.641532000	-1.236253000
H	4.189773000	1.888326000	-0.031505000
C	9.362445000	-0.494793000	0.880319000
C	9.881711000	-1.959391000	0.894222000
C	2.834745000	-2.478261000	-1.909321000
H	1.919160000	-2.080135000	-2.361359000
H	3.799076000	-3.945714000	-3.256382000
H	5.649322000	-3.453609000	-1.749042000

H	6.015846000	-2.268044000	-2.998475000
I	-1.649237000	-1.728678000	-0.512983000
C	-1.926476000	2.856200000	-2.186783000
C	-3.070344000	3.662261000	-2.070621000
C	-0.800083000	3.402313000	-2.827398000
C	-3.074791000	4.984723000	-2.530669000
C	-0.806552000	4.718461000	-3.300597000
C	-1.941062000	5.520550000	-3.145269000
H	-3.968478000	3.265702000	-1.607436000
H	0.106264000	2.811769000	-2.934271000
H	-3.968250000	5.593181000	-2.406844000
H	0.083044000	5.120337000	-3.780194000
H	-1.940926000	6.547293000	-3.501544000
C	-3.081980000	0.522378000	-2.927440000
Sn	-4.438181000	-1.973835000	0.026277000
H	-3.935847000	1.189503000	-3.090693000
C	-4.977712000	-3.505049000	-1.414557000
H	-6.052175000	-3.693567000	-1.293158000
H	-4.839833000	-3.051490000	-2.403089000
C	-5.455339000	-0.074728000	-0.270507000
H	-6.495728000	-0.288490000	0.011764000
H	-5.448061000	0.132623000	-1.344862000
C	-4.317609000	-2.557907000	2.123906000
H	-4.326234000	-3.653533000	2.164076000
H	-3.330648000	-2.236501000	2.474476000
C	-5.422163000	-1.968957000	3.013268000
H	-5.412095000	-0.872643000	2.950038000
H	-6.412495000	-2.283284000	2.654941000
C	-5.272945000	-2.378149000	4.486156000
H	-5.320985000	-3.472913000	4.562254000
H	-4.271800000	-2.091480000	4.836688000
C	-6.335461000	-1.746479000	5.389391000
H	-6.210803000	-2.055282000	6.433221000
H	-6.280055000	-0.651513000	5.356824000
H	-7.345537000	-2.035371000	5.074720000
C	-4.914196000	1.118947000	0.521355000
H	-3.897529000	1.350363000	0.172605000
H	-4.822483000	0.870154000	1.585512000
C	-5.777556000	2.380268000	0.391658000
H	-5.907118000	2.625214000	-0.671395000
H	-6.783689000	2.175578000	0.783361000
C	-5.164980000	3.574407000	1.130253000
H	-4.180270000	3.824306000	0.718661000
H	-5.795933000	4.466754000	1.051716000
H	-5.030131000	3.350282000	2.195456000
C	-4.176851000	-4.807046000	-1.294367000
H	-4.319414000	-5.249528000	-0.298335000
H	-3.103111000	-4.592103000	-1.383648000
C	-4.563702000	-5.843960000	-2.359177000
H	-5.636315000	-6.066427000	-2.273969000
H	-4.418782000	-5.403676000	-3.355184000
C	-3.756635000	-7.140153000	-2.245774000
H	-3.905892000	-7.614983000	-1.268411000
H	-4.047782000	-7.863818000	-3.015353000
H	-2.682927000	-6.947337000	-2.358982000
C	-2.977759000	-0.515269000	-3.774103000
H	-2.164784000	-1.238750000	-3.720328000
H	-3.709363000	-0.693653000	-4.566834000

6 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)(**CH$_2$CH**)(**SnBu$_3$**)**I**]

C	5.400020000	-0.280362000	-0.817042000
C	4.512188000	-0.002133000	0.412695000
S	5.733321000	0.365690000	1.793867000
C	7.056833000	-0.358858000	0.841402000
C	6.733995000	-0.613817000	-0.468188000
H	7.442888000	-0.997603000	-1.192190000
C	4.123716000	-1.002884000	-4.207662000
C	3.041487000	-0.033554000	-3.670867000
C	3.480411000	0.227690000	-2.247021000
C	4.837514000	-0.235408000	-2.062331000
C	5.398408000	-0.664769000	-3.394761000
H	4.276195000	-0.913134000	-5.286122000
H	2.028352000	-0.443098000	-3.736006000
H	3.044802000	0.907398000	-4.237820000
H	6.104536000	-1.496346000	-3.320399000
H	5.931461000	0.179199000	-3.855044000
H	3.825499000	-2.035576000	-3.995331000
C	1.432635000	1.223305000	-1.178687000
C	0.980082000	1.559662000	0.062525000
S	2.196811000	1.446113000	1.343044000
C	3.557887000	1.164928000	0.074745000
C	2.805249000	0.822791000	-1.223824000
H	0.780712000	1.191789000	-2.045288000
C	4.271387000	2.520843000	-0.136135000
H	5.046189000	2.421626000	-0.901961000
H	3.545773000	3.265454000	-0.473640000
H	4.735722000	2.877808000	0.784441000
C	3.775487000	-1.313289000	0.775649000
H	3.082424000	-1.594572000	-0.022884000
H	4.506285000	-2.116374000	0.898314000
H	3.211558000	-1.212265000	1.704717000
C	8.332817000	-0.563874000	1.491456000
O	8.570535000	-0.285081000	2.660570000
C	9.471194000	-1.168432000	0.627331000
F	10.588412000	-1.324077000	1.345319000
F	9.120936000	-2.376958000	0.129461000
F	9.758211000	-0.369823000	-0.427359000
Pd	-2.263198000	1.072778000	-1.237957000
P	-0.753257000	2.041931000	0.385282000
C	-0.981875000	1.576706000	2.155752000
C	-1.499175000	0.308682000	2.460221000

H	-1.776000000	-0.364704000	1.659668000
C	-1.660964000	-0.092192000	3.786796000
H	-2.067295000	-1.075115000	4.004474000
C	-1.309042000	0.771500000	4.826297000
H	-1.439276000	0.462263000	5.859504000
C	-0.789134000	2.034789000	4.533314000
H	-0.509847000	2.709799000	5.337205000
C	-0.623940000	2.437391000	3.206874000
H	-0.219734000	3.421359000	2.993705000
C	-0.691727000	3.877453000	0.428545000
C	-1.818016000	4.563101000	0.913138000
H	-2.658368000	4.009286000	1.320252000
C	-1.871073000	5.953905000	0.856595000
H	-2.752160000	6.472645000	1.222806000
C	-0.801503000	6.676425000	0.317855000
H	-0.846740000	7.760688000	0.269587000
C	0.321610000	6.000179000	-0.160135000
H	1.157835000	6.555152000	-0.576091000
C	0.377568000	4.604725000	-0.108220000
H	1.250927000	4.088344000	-0.494018000
I	-1.034699000	-1.533781000	-0.981263000
C	-3.074072000	2.868775000	-1.651293000
C	-4.333235000	3.238191000	-1.152017000
C	-2.355938000	3.820608000	-2.396330000
C	-4.838453000	4.529289000	-1.346386000
C	-2.865047000	5.106840000	-2.603961000
C	-4.105029000	5.471162000	-2.071217000
H	-4.927727000	2.520224000	-0.595754000
H	-1.376184000	3.573725000	-2.797354000
H	-5.807640000	4.794918000	-0.929387000
H	-2.283951000	5.828110000	-3.174046000
H	-4.494370000	6.474516000	-2.222196000
C	-3.651909000	0.388299000	-2.569806000
Sn	-3.390008000	-2.741229000	0.087236000
H	-4.671005000	0.767561000	-2.435433000
C	-3.768213000	-4.243270000	-1.434694000
H	-4.670572000	-4.788217000	-1.129287000
H	-4.019238000	-3.692091000	-2.348611000
C	-4.980134000	-1.276908000	0.326285000
H	-5.811370000	-1.860226000	0.746528000
H	-5.282772000	-0.955630000	-0.674629000
C	-2.582235000	-3.422120000	1.993740000
H	-2.146961000	-4.415183000	1.832120000
H	-1.753436000	-2.748929000	2.237817000
C	-3.606163000	-3.452675000	3.138245000
H	-4.032171000	-2.451191000	3.287556000
H	-4.451890000	-4.105524000	2.880305000
C	-2.995478000	-3.934490000	4.462806000
H	-2.599928000	-4.950174000	4.326855000
H	-2.132215000	-3.301913000	4.711267000
C	-3.997147000	-3.917174000	5.620454000
H	-3.540203000	-4.268220000	6.552334000
H	-4.378098000	-2.903913000	5.796931000
H	-4.858773000	-4.561653000	5.408288000
C	-4.658186000	-0.073124000	1.216350000
H	-3.870091000	0.525701000	0.738053000
H	-4.250747000	-0.400645000	2.180706000
C	-5.867977000	0.831464000	1.483437000
H	-6.306184000	1.145390000	0.526241000
H	-6.646689000	0.255800000	2.002831000
C	-5.491732000	2.063526000	2.312496000
H	-4.749405000	2.675892000	1.787349000
H	-6.362654000	2.696363000	2.516261000
H	-5.055857000	1.770753000	3.275471000
C	-2.602875000	-5.209062000	-1.681385000
H	-2.360545000	-5.754494000	-0.758435000
H	-1.700392000	-4.642153000	-1.948440000
C	-2.896784000	-6.223555000	-2.796390000
H	-3.795986000	-6.798038000	-2.534524000
H	-3.137318000	-5.679149000	-3.719807000
C	-1.728577000	-7.180040000	-3.050877000
H	-1.486076000	-7.757094000	-2.150249000
H	-1.959149000	-7.892593000	-3.850754000
H	-0.825809000	-6.630669000	-3.344305000
C	-3.474795000	-0.471613000	-3.586431000
H	-2.505041000	-0.905574000	-3.827843000
H	-4.300646000	-0.786843000	-4.229832000

7 [Pd(**DTE^{o}-COCF$_3$**)(**Ph**)(**vinyl**)]

Pd	-3.688645000	1.633919000	-0.331746000
S	0.298460000	-1.330543000	-1.731930000
S	4.817218000	-1.421213000	1.718462000
P	-2.531742000	-0.454339000	-0.597483000
F	9.598979000	-0.960173000	-0.147483000
F	8.567002000	0.890089000	0.358169000
F	7.987134000	-0.230789000	-1.417835000
O	7.738691000	-2.202612000	1.232101000
C	-3.126095000	-1.527413000	-1.961874000
C	-3.905279000	-0.947015000	-2.974134000
H	-4.172894000	0.104961000	-2.912033000
C	-4.343174000	-1.716341000	-4.054188000
H	-4.947417000	-1.259090000	-4.832454000
C	-4.010330000	-3.070693000	-4.127397000
H	-4.353624000	-3.670215000	-4.965724000
C	-3.241107000	-3.657391000	-3.118037000
H	-2.985966000	-4.711943000	-3.170092000
C	-2.801704000	-2.892141000	-2.037437000
H	-2.217909000	-3.359160000	-1.249963000
C	-2.554145000	-1.537837000	0.884707000
C	-3.702033000	-2.296921000	1.162602000
H	-4.523432000	-2.324763000	0.453499000

C	-3.800339000	-3.006572000	2.358970000
H	-4.695966000	-3.584553000	2.567486000
C	-2.757020000	-2.966819000	3.288563000
H	-2.836720000	-3.519131000	4.220530000
C	-1.614564000	-2.210926000	3.017421000
H	-0.799109000	-2.175592000	3.734629000
C	-1.514077000	-1.494802000	1.822687000
H	-0.629832000	-0.897772000	1.624777000
C	-0.775405000	-0.182712000	-0.958656000
C	-0.081261000	0.947435000	-0.602773000
H	-0.552202000	1.786400000	-0.100152000
C	1.319241000	0.905370000	-0.914860000
C	1.673909000	-0.269181000	-1.555154000
C	3.007618000	-0.683772000	-2.096587000
H	3.635005000	0.196179000	-2.256019000
H	2.906760000	-1.214714000	-3.048439000
H	3.535162000	-1.345076000	-1.399421000
C	2.224673000	2.015618000	-0.583848000
H	1.935666000	3.563764000	-2.047783000
C	2.916284000	4.292676000	-0.211199000
H	2.513030000	4.596288000	0.761205000
C	4.104493000	3.332235000	0.011796000
C	3.450449000	1.959070000	-0.012015000
C	4.167829000	0.783918000	0.503879000
C	5.544271000	0.557421000	0.220842000
H	6.134476000	1.222782000	-0.396755000
C	6.048912000	-0.596698000	0.787572000
C	3.638686000	-0.205650000	1.328812000
C	2.252879000	-0.319767000	1.878760000
H	1.775007000	0.662233000	1.893443000
H	2.253998000	-0.727902000	2.893996000
H	1.641742000	-0.978636000	1.251997000
C	7.378380000	-1.161624000	0.703142000
C	8.406750000	-0.356912000	-0.138656000
C	1.864229000	3.444307000	-0.956657000
H	0.834428000	3.703107000	-0.684360000
H	3.194993000	5.200711000	-0.752820000
H	4.844170000	3.407597000	-0.799182000
H	4.642967000	3.523723000	0.946324000
C	-4.865460000	0.958640000	1.113629000
C	-6.133644000	0.440907000	0.810934000
C	-4.397394000	0.891664000	2.435019000
C	-6.903201000	-0.169981000	1.809337000
C	-5.173241000	0.284106000	3.428034000
C	-6.425740000	-0.253301000	3.119188000
H	-6.523676000	0.497044000	-0.201744000
H	-3.419473000	1.286785000	2.693741000
H	-7.878880000	-0.578811000	1.556804000
H	-4.790491000	0.226827000	4.444150000
H	-7.023506000	-0.729373000	3.891634000
C	-4.614080000	3.418252000	-0.188490000
H	-5.681086000	3.513721000	0.035374000
C	-3.931573000	4.545898000	-0.454086000
H	-2.858412000	4.548371000	-0.657926000
H	-4.407858000	5.529640000	-0.488237000

7 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)(**vinyl**)]

Pd	3.618446000	-1.439421000	-0.872987000
P	2.358548000	0.529117000	-0.308712000
C	2.439517000	1.910029000	-1.513487000
C	2.846108000	1.617879000	-2.824315000
H	3.138499000	0.603610000	-3.084955000
C	2.883862000	2.625725000	-3.790052000
H	3.201205000	2.391839000	-4.802174000
C	2.520956000	3.931081000	-3.451153000
H	2.553365000	4.716116000	-4.201324000
C	2.122297000	4.230109000	-2.144852000
H	1.844325000	5.245731000	-1.878427000
C	2.082482000	3.226219000	-1.177026000
H	1.784398000	3.468678000	-0.161666000
C	2.788995000	1.285071000	1.307285000
C	3.939719000	2.084010000	1.400567000
H	4.503845000	2.337248000	0.508341000
C	4.374414000	2.543230000	2.643345000
H	5.270612000	3.153599000	2.705125000
C	3.667136000	2.212145000	3.802518000
H	4.008887000	2.569732000	4.769582000
C	2.522618000	1.417089000	3.714073000
H	1.966627000	1.157910000	4.610702000
C	2.086034000	0.950006000	2.472580000
H	1.201969000	0.322121000	2.415820000
C	5.142255000	-0.975712000	0.309430000
C	6.254283000	-0.292695000	-0.204549000
C	5.070747000	-1.227403000	1.688066000
C	7.259430000	0.166532000	0.656284000
C	6.080972000	-0.770579000	2.541096000
C	7.175281000	-0.067307000	2.030583000
H	6.339056000	-0.102312000	-1.271018000
H	4.220175000	-1.755609000	2.108606000
H	8.109145000	0.706778000	0.245283000
H	6.004360000	-0.960580000	3.608925000
H	7.955249000	0.291451000	2.696588000
C	4.609224000	-3.110546000	-1.401874000
H	5.694684000	-3.132658000	-1.538713000
C	3.922508000	-4.231272000	-1.684930000
H	2.841863000	-4.308703000	-1.546512000
H	4.401611000	-5.132920000	-2.076209000
C	-4.161606000	-0.991166000	-0.018236000
C	-3.313366000	0.234374000	-0.412430000
S	-4.398002000	1.708858000	0.018025000
C	-5.830953000	0.651079000	0.107689000

C	-5.545076000	-0.690281000	0.090899000
H	-6.298243000	-1.462100000	0.193887000
C	-3.032345000	-4.502155000	-0.246667000
C	-1.707262000	-3.771635000	0.083177000
C	-2.104667000	-2.312213000	0.097271000
C	-3.547274000	-2.201754000	0.134637000
C	-4.143533000	-3.576248000	0.307330000
H	-3.076234000	-5.510259000	0.172864000
H	-0.907048000	-3.989988000	-0.631053000
H	-1.339472000	-4.062020000	1.076782000
H	-5.106479000	-3.697139000	-0.196383000
H	-4.305065000	-3.771897000	1.376831000
H	-3.142159000	-4.585485000	-1.333568000
C	0.100496000	-1.102133000	-0.003256000
C	0.574432000	0.166402000	-0.167688000
S	-0.683774000	1.414973000	-0.210613000
C	-1.978766000	0.174799000	0.363437000
C	-1.323740000	-1.196859000	0.117982000
H	0.750855000	-1.971633000	0.006148000
C	-2.133809000	0.355097000	1.892064000
H	-2.845103000	-0.376639000	2.285910000
H	-1.168411000	0.193611000	2.378308000
H	-2.488254000	1.355653000	2.144182000
C	-3.136777000	0.216834000	-1.948559000
H	-2.552316000	-0.656067000	-2.254101000
H	-4.118568000	0.157869000	-2.424748000
H	-2.631598000	1.116476000	-2.304715000
C	-7.132429000	1.274108000	0.236667000
O	-7.320899000	2.482955000	0.280206000
C	-8.357935000	0.327206000	0.336955000
F	-9.495703000	1.022767000	0.429539000
F	-8.444338000	-0.477775000	-0.746990000
F	-8.265326000	-0.473342000	1.424153000

SnIBu$_3$

I	1.169164000	-1.383911000	-1.741181000
Sn	-0.035112000	0.415328000	0.084233000
C	1.571952000	1.802191000	0.547585000
H	1.827317000	2.317440000	-0.385380000
H	1.146882000	2.556133000	1.222777000
C	-0.637727000	-0.897566000	1.708850000
H	-1.015381000	-0.251778000	2.512139000
H	0.268384000	-1.382892000	2.088465000
C	-1.706879000	1.226004000	-1.043259000
H	-1.294069000	1.822424000	-1.864446000
H	-2.226469000	0.373517000	-1.494627000
C	-2.671563000	2.062511000	-0.188095000
H	-3.060836000	1.458767000	0.643906000
H	-2.138127000	2.906410000	0.271918000
C	-3.856790000	2.608808000	-0.998510000
H	-3.472755000	3.218022000	-1.828033000
H	-4.393383000	1.767401000	-1.457700000
C	-4.825227000	3.439371000	-0.152001000
H	-5.660458000	3.817027000	-0.752287000
H	-5.246396000	2.843094000	0.666485000
H	-4.319002000	4.303497000	0.295097000
C	-1.689953000	-1.939926000	1.307718000
H	-1.308542000	-2.555875000	0.482109000
H	-2.590068000	-1.439156000	0.923853000
C	-2.090726000	-2.859025000	2.470891000
H	-1.193420000	-3.365366000	2.852284000
H	-2.473550000	-2.246638000	3.299065000
C	-3.139736000	-3.900274000	2.071047000
H	-2.768895000	-4.544487000	1.264778000
H	-3.408864000	-4.544814000	2.915377000
H	-4.058086000	-3.419063000	1.713270000
C	2.813926000	1.151640000	1.171160000
H	3.206273000	0.376810000	0.498925000
H	2.543010000	0.637752000	2.104079000
C	3.928641000	2.165663000	1.467379000
H	4.203155000	2.678255000	0.535226000
H	3.540845000	2.941449000	2.142062000
C	5.171441000	1.518682000	2.084995000
H	5.595229000	0.760245000	1.415831000
H	5.953017000	2.260081000	2.285529000
H	4.929939000	1.024149000	3.033679000

TS7 [Pd(**DTE^o-COCF$_3$**)(**Ph**)(**vinyl**)]

Pd	3.669729000	-1.121465000	-1.109665000
S	-0.328542000	2.214633000	-0.467744000
S	-4.709156000	-0.251870000	2.247583000
P	2.513018000	0.795665000	-0.397987000
F	-9.592962000	0.660684000	0.878492000
F	-8.573662000	-0.962439000	-0.156239000
F	-8.070349000	1.107581000	-0.613643000
O	-7.631579000	0.583262000	2.627086000
C	3.129131000	2.434530000	-0.959637000
C	3.801769000	2.501695000	-2.188935000
H	3.976671000	1.590693000	-2.756444000
C	4.250645000	3.729160000	-2.681394000
H	4.771737000	3.771434000	-3.633662000
C	4.036601000	4.897109000	-1.945793000
H	4.389676000	5.851585000	-2.325943000
C	3.374284000	4.836516000	-0.716000000
H	3.210939000	5.742624000	-0.139397000
C	2.922927000	3.611813000	-0.222573000
H	2.421437000	3.571735000	0.739965000
C	2.624230000	0.879875000	1.436759000
C	3.857205000	1.219772000	2.017954000
H	4.686951000	1.531220000	1.390266000

C	4.029876000	1.141273000	3.398837000
H	4.990869000	1.398890000	3.834599000
C	2.976848000	0.719329000	4.216148000
H	3.114767000	0.654042000	5.291698000
C	1.750783000	0.375290000	3.643762000
H	0.927913000	0.045702000	4.272265000
C	1.574497000	0.451406000	2.259727000
H	0.622363000	0.168082000	1.822960000
C	0.734330000	0.850944000	-0.759835000
C	0.018798000	-0.199151000	-1.277867000
H	0.481372000	-1.148520000	-1.528233000
C	-1.386863000	0.054009000	-1.424352000
C	-1.727862000	1.337422000	-1.036513000
C	-3.067236000	2.007265000	-1.067110000
H	-3.721974000	1.499381000	-1.779187000
H	-2.984677000	3.058464000	-1.360761000
H	-3.554849000	1.971593000	-0.085840000
C	-2.314244000	-0.960437000	-1.947512000
H	-2.131057000	-0.971504000	-4.089145000
C	-3.070140000	-2.804695000	-3.300073000
H	-2.644025000	-3.716605000	-2.867287000
C	-4.216536000	-2.303154000	-2.395307000
C	-3.517124000	-1.335578000	-1.452643000
C	-4.176601000	-0.897733000	-0.214118000
C	-5.559217000	-0.562087000	-0.174876000
H	-6.196430000	-0.591354000	-1.049999000
C	-6.006089000	-0.178218000	1.074654000
C	-3.582630000	-0.794988000	1.041856000
C	-2.169491000	-1.089320000	1.431347000
H	-1.727685000	-1.798852000	0.728038000
H	-2.105756000	-1.504775000	2.441475000
H	-1.565711000	-0.175842000	1.402448000
C	-7.324307000	0.246174000	1.493313000
C	-8.414945000	0.265515000	0.386814000
C	-2.016395000	-1.677937000	-3.253749000
H	-0.986730000	-2.050479000	-3.304115000
H	-3.398206000	-3.041746000	-4.315885000
H	-4.985444000	-1.770153000	-2.974354000
H	-4.729196000	-3.111386000	-1.862410000
C	4.892973000	-1.821381000	0.371528000
C	6.181468000	-1.273763000	0.511652000
C	4.277993000	-2.392230000	1.504044000
C	6.814045000	-1.251079000	1.759881000
C	4.911764000	-2.361499000	2.746276000
C	6.181952000	-1.788777000	2.882766000
H	6.690622000	-0.858869000	-0.354097000
H	3.296224000	-2.848982000	1.415792000
H	7.803833000	-0.809694000	1.849764000
H	4.409451000	-2.784736000	3.612847000
H	6.671796000	-1.767381000	3.852364000
C	4.746351000	-2.817994000	-1.439573000
H	5.705592000	-2.684623000	-1.947691000
C	4.139199000	-4.018047000	-1.502229000
H	3.231215000	-4.239542000	-0.943359000
H	4.546107000	-4.836904000	-2.097224000

TS7 [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)(**vinyl**)]

Pd	-3.723900000	1.225815000	-0.965410000
P	-2.284899000	-0.539315000	-0.394674000
C	-2.281583000	-2.017219000	-1.487840000
C	-2.571972000	-1.825155000	-2.847141000
H	-2.827949000	-0.831541000	-3.207503000
C	-2.538441000	-2.903035000	-3.734052000
H	-2.765301000	-2.745487000	-4.784637000
C	-2.221640000	-4.181022000	-3.267551000
H	-2.199704000	-5.021032000	-3.956068000
C	-1.939446000	-4.380780000	-1.913068000
H	-1.697000000	-5.374490000	-1.547383000
C	-1.969136000	-3.305281000	-1.024404000
H	-1.758377000	-3.470445000	0.027724000
C	-2.754613000	-1.191713000	1.259694000
C	-3.960591000	-1.902974000	1.373677000
H	-4.539663000	-2.139419000	0.486008000
C	-4.430329000	-2.292187000	2.627027000
H	-5.367879000	-2.834885000	2.703636000
C	-3.704851000	-1.973951000	3.779148000
H	-4.073804000	-2.275071000	4.755477000
C	-2.508011000	-1.263107000	3.671255000
H	-1.938853000	-1.013205000	4.562361000
C	-2.034260000	-0.869192000	2.417318000
H	-1.107920000	-0.307848000	2.345399000
C	-5.408589000	1.182547000	0.190508000
C	-6.476333000	0.348961000	-0.188670000
C	-5.271382000	1.525642000	1.550156000
C	-7.349506000	-0.170576000	0.773527000
C	-6.142808000	1.001039000	2.504423000
C	-7.184371000	0.146895000	2.123036000
H	-6.623697000	0.099327000	-1.235802000
H	-4.475007000	2.194647000	1.863658000
H	-8.159994000	-0.825147000	0.461900000
H	-6.006842000	1.259070000	3.551783000
H	-7.861364000	-0.258750000	2.869566000
C	-5.130251000	2.672494000	-1.229981000
H	-5.854891000	2.489183000	-2.028163000
C	-4.907168000	3.938698000	-0.831811000
H	-4.268891000	4.176316000	0.017608000
H	-5.379452000	4.787967000	-1.327419000
C	4.227904000	1.025457000	-0.138102000
C	3.385308000	-0.244546000	-0.370518000
S	4.460034000	-1.641423000	0.284988000
C	5.892979000	-0.580043000	0.248662000

C	5.608741000	0.745153000	0.036086000
H	6.361226000	1.524676000	0.042516000
C	3.106669000	4.468541000	-0.874191000
C	1.774414000	3.788655000	-0.472493000
C	2.169867000	2.346218000	-0.245615000
C	3.611227000	2.244455000	-0.166269000
C	4.205797000	3.630576000	-0.175193000
H	3.143332000	5.525301000	-0.598117000
H	0.989730000	3.902907000	-1.226962000
H	1.386012000	4.215073000	0.462496000
H	5.178506000	3.681655000	-0.672059000
H	4.346648000	3.973328000	0.859650000
H	3.238236000	4.400189000	-1.959724000
C	-0.034162000	1.128301000	-0.226261000
C	-0.505736000	-0.151021000	-0.224253000
S	0.752617000	-1.389757000	-0.054704000
C	2.036249000	-0.078622000	0.364184000
C	1.386852000	1.243373000	-0.084380000
H	-0.684647000	1.986237000	-0.364564000
C	2.163469000	-0.040573000	1.905506000
H	2.874164000	0.735274000	2.204701000
H	1.191585000	0.195779000	2.345724000
H	2.504235000	-0.997244000	2.304146000
C	3.237300000	-0.445084000	-1.896682000
H	2.659039000	0.374266000	-2.333860000
H	4.227761000	-0.452625000	-2.358302000
H	2.737779000	-1.386843000	-2.130909000
C	7.190223000	-1.176150000	0.489979000
O	7.376691000	-2.365864000	0.712139000
C	8.414899000	-0.223402000	0.470371000
F	9.549764000	-0.895259000	0.689295000
F	8.523041000	0.407368000	-0.721565000
F	8.303821000	0.733739000	1.420929000

8 [Pd(**DTE^{o}-COCF$_3$**)]·**Styrene**

Pd	3.591888000	-1.703151000	-0.260285000
S	-0.481475000	1.024434000	-1.788445000
S	-4.938260000	1.481651000	1.692108000
P	2.338946000	0.204629000	-0.563526000
F	-9.742616000	1.073955000	-0.126800000
F	-8.771261000	-0.774180000	0.493149000
F	-8.167962000	0.206294000	-1.356445000
O	-7.827972000	2.340695000	1.152041000
C	2.845907000	1.291586000	-1.965630000
C	3.442493000	0.696884000	-3.088286000
H	3.624033000	-0.375122000	-3.092745000
C	3.805180000	1.474431000	-4.189206000
H	4.266384000	1.004437000	-5.053379000
C	3.583858000	2.854208000	-4.174853000
H	3.871721000	3.460452000	-5.029195000
C	2.998095000	3.454145000	-3.057205000
H	2.827867000	4.527033000	-3.040470000
C	2.630293000	2.678457000	-1.955744000
H	2.180019000	3.154481000	-1.089780000
C	2.385812000	1.350701000	0.885221000
C	3.638747000	1.585240000	1.477959000
H	4.526535000	1.101097000	1.081993000
C	3.750727000	2.432562000	2.579875000
H	4.726658000	2.600572000	3.025977000
C	2.612976000	3.045683000	3.113519000
H	2.699264000	3.698493000	3.977661000
C	1.364106000	2.811398000	2.534601000
H	0.474857000	3.282830000	2.944171000
C	1.249987000	1.970646000	1.423871000
H	0.274207000	1.802807000	0.981946000
C	0.566565000	-0.059091000	-0.891012000
C	-0.148342000	-1.144507000	-0.451720000
H	0.305860000	-1.946873000	0.121030000
C	-1.543630000	-1.112804000	-0.787403000
C	-1.874819000	0.002764000	-1.535676000
C	-3.197784000	0.383441000	-2.126737000
H	-3.836353000	-0.499058000	-2.211447000
H	-3.081566000	0.823883000	-3.122187000
H	-3.723101000	1.112556000	-1.498807000
C	-2.472358000	-2.177011000	-0.378468000
H	-2.226370000	-3.828002000	-1.732745000
C	-3.223762000	-4.403322000	0.149123000
H	-2.827502000	-4.650305000	1.140282000
C	-4.386217000	-3.398518000	0.305830000
C	-3.695407000	-2.048740000	0.186660000
C	-4.373451000	-0.818590000	0.620391000
C	-5.740082000	-0.559313000	0.320901000
H	-6.354642000	-1.239833000	-0.255055000
C	-6.201211000	0.646416000	0.813533000
C	-3.806913000	0.200337000	1.382822000
C	-2.418121000	0.290136000	1.928617000
H	-2.001010000	-0.711761000	2.054880000
H	-2.393043000	0.808747000	2.891387000
H	-1.764454000	0.830534000	1.235970000
C	-7.508939000	1.253224000	0.694516000
C	-8.571769000	0.431123000	-0.085553000
C	-2.150119000	-3.636368000	-0.652288000
H	-1.126514000	-3.901795000	-0.363680000
H	-3.527443000	-5.338647000	-0.329052000
H	-5.129886000	-3.510270000	-0.497366000
H	-4.927090000	-3.510920000	1.251837000
C	6.297815000	-1.089405000	0.806551000
C	6.985323000	0.034498000	0.311705000
C	6.135076000	-1.207100000	2.200781000
C	7.476895000	1.015628000	1.173337000
C	6.627728000	-0.228703000	3.060550000

C	7.298788000	0.890526000	2.553394000
H	7.119633000	0.142193000	-0.761950000
H	5.606414000	-2.061257000	2.612257000
H	7.997870000	1.877747000	0.765995000
H	6.485265000	-0.336284000	4.132413000
H	7.679742000	1.652390000	3.227483000
C	5.755409000	-2.071362000	-0.159206000
H	6.113153000	-1.930828000	-1.179442000
C	5.086228000	-3.258150000	0.133710000
H	4.950136000	-3.602568000	1.157096000
H	5.003923000	-4.025027000	-0.634012000

8 [Pd(**DTE^{c}-COCF$_3$**)]·**Styrene**

Pd	-3.448200000	1.126844000	-1.230422000
P	-2.228000000	-0.522079000	-0.192580000
C	-2.206479000	-2.176720000	-1.006656000
C	-2.336102000	-2.218569000	-2.404359000
H	-2.476991000	-1.292804000	-2.957095000
C	-2.289442000	-3.438160000	-3.080778000
H	-2.388454000	-3.459560000	-4.162410000
C	-2.126021000	-4.627998000	-2.366365000
H	-2.096510000	-5.578299000	-2.891918000
C	-2.007322000	-4.594735000	-0.974744000
H	-1.883716000	-5.518011000	-0.415792000
C	-2.045944000	-3.375559000	-0.295029000
H	-1.952006000	-3.361357000	0.786174000
C	-2.718689000	-0.879591000	1.550566000
C	-4.083889000	-0.782897000	1.867490000
H	-4.799929000	-0.495629000	1.103518000
C	-4.527500000	-1.046586000	3.164020000
H	-5.586276000	-0.965264000	3.391915000
C	-3.613044000	-1.396031000	4.160860000
H	-3.957256000	-1.592340000	5.172445000
C	-2.252832000	-1.487018000	3.854688000
H	-1.536725000	-1.757375000	4.625712000
C	-1.805077000	-1.233456000	2.556257000
H	-0.746837000	-1.318573000	2.332816000
C	-6.341893000	1.215332000	-0.534972000
C	-7.055634000	0.007722000	-0.424864000
C	-6.381163000	2.112416000	0.550466000
C	-7.767912000	-0.304605000	0.733672000
C	-7.092470000	1.800591000	1.706062000
C	-7.787211000	0.589067000	1.807315000
H	-7.035262000	-0.696077000	-1.253422000
H	-5.839861000	3.051716000	0.493836000
H	-8.305806000	-1.246445000	0.797599000
H	-7.104676000	2.503652000	2.534501000
H	-8.339415000	0.348766000	2.711351000
C	-5.562662000	1.468987000	-1.767033000
H	-5.764796000	0.762890000	-2.572563000
C	-4.829440000	2.610503000	-2.074687000
H	-4.816188000	3.478613000	-1.418547000
H	-4.541144000	2.796448000	-3.107257000
C	4.285721000	1.089265000	-0.051442000
C	3.443182000	-0.152467000	-0.403658000
S	4.556212000	-1.605716000	0.026583000
C	5.979556000	-0.529549000	0.061656000
C	5.673318000	0.808416000	0.029915000
H	6.418335000	1.591660000	0.102369000
C	3.105824000	4.584546000	-0.302620000
C	1.799120000	3.842775000	0.072541000
C	2.215891000	2.388506000	0.094847000
C	3.657636000	2.295311000	0.095649000
C	4.242932000	3.678896000	0.231706000
H	3.149505000	5.598673000	0.102485000
H	0.978478000	4.041294000	-0.624110000
H	1.453130000	4.143481000	1.070991000
H	5.189818000	3.803131000	-0.300993000
H	4.433145000	3.891074000	1.293350000
H	3.184735000	4.654959000	-1.393166000
C	0.024429000	1.147082000	0.065467000
C	-0.439126000	-0.130612000	-0.057878000
S	0.835654000	-1.361994000	-0.112905000
C	2.126934000	-0.094787000	0.402944000
C	1.447436000	1.263474000	0.151784000
H	-0.636758000	2.008042000	0.053289000
C	2.320275000	-0.242989000	1.931526000
H	3.035412000	0.501846000	2.292466000
H	1.365579000	-0.075802000	2.436953000
H	2.689213000	-1.235247000	2.195558000
C	3.226421000	-0.165059000	-1.934614000
H	2.623290000	0.694875000	-2.240734000
H	4.194695000	-0.103586000	-2.437407000
H	2.723452000	-1.077086000	-2.261432000
C	7.289125000	-1.133353000	0.170364000
O	7.496291000	-2.339717000	0.228816000
C	8.503912000	-0.169693000	0.229540000
F	9.652943000	-0.849257000	0.307306000
F	8.557901000	0.621027000	-0.867376000
F	8.426453000	0.646572000	1.306787000

9 [Pd(**DTE^{o}-COCF$_3$**)]

Pd	4.507364000	1.929860000	-0.922858000
S	0.922959000	-0.636106000	1.544000000
S	-4.009181000	-1.810477000	-1.190099000
P	3.536350000	0.155235000	-0.076135000
F	-8.594726000	-1.150803000	1.068862000
F	-7.752871000	0.578465000	0.046535000
F	-6.917840000	-0.075780000	1.949419000
O	-6.804039000	-2.590722000	-0.206272000

C	4.267290000	-0.573496000	1.459522000
C	4.968174000	0.270849000	2.333931000
H	5.111025000	1.315252000	2.067657000
C	5.482040000	-0.222179000	3.534652000
H	6.023341000	0.441881000	4.202776000
C	5.307561000	-1.566925000	3.870885000
H	5.712356000	-1.952673000	4.802328000
C	4.616300000	-2.416420000	3.003273000
H	4.480204000	-3.463726000	3.258244000
C	4.097783000	-1.924674000	1.803800000
H	3.566713000	-2.596372000	1.136579000
C	3.457365000	-1.296704000	-1.220679000
C	4.638164000	-2.003597000	-1.506348000
H	5.566524000	-1.732177000	-1.010308000
C	4.625167000	-3.061707000	-2.414469000
H	5.543061000	-3.605708000	-2.619790000
C	3.437160000	-3.420344000	-3.060484000
H	3.429244000	-4.243274000	-3.769597000
C	2.263401000	-2.714572000	-2.790246000
H	1.335850000	-2.985299000	-3.287546000
C	2.272291000	-1.658773000	-1.875028000
H	1.355928000	-1.114849000	-1.673243000
C	1.791473000	0.388420000	0.414248000
C	0.947578000	1.343643000	-0.091388000
H	1.281079000	2.085180000	-0.809526000
C	-0.404554000	1.261030000	0.387532000
C	-0.568819000	0.239679000	1.306327000
C	-1.788520000	-0.142868000	2.087671000
H	-2.483687000	0.698811000	2.131577000
H	-1.533449000	-0.434906000	3.111396000
H	-2.316227000	-0.984025000	1.623226000
C	-1.445629000	2.200168000	-0.055165000
H	-1.138370000	4.052630000	0.990794000
C	-2.382718000	4.286537000	-0.814024000
H	-2.126011000	4.381840000	-1.874977000
C	-3.496111000	3.229523000	-0.656309000
C	-2.721285000	1.939705000	-0.428701000
C	-3.394610000	0.641603000	-0.579029000
C	-4.715074000	0.422421000	-0.094498000
H	-5.284127000	1.184651000	0.422695000
C	-5.193132000	-0.852222000	-0.327746000
C	-2.885457000	-0.485300000	-1.220175000
C	-1.558899000	-0.658809000	-1.886973000
H	-1.161533000	0.312971000	-2.188142000
H	-1.629861000	-1.302024000	-2.769256000
H	-0.839456000	-1.111666000	-1.195826000
C	-6.464118000	-1.441549000	0.033349000
C	-7.454979000	-0.512189000	0.787701000
C	-1.179369000	3.697185000	-0.049398000
H	-0.215236000	3.955733000	-0.501406000
H	-2.676431000	5.276214000	-0.453378000
H	-4.133658000	3.441461000	0.215075000
H	-4.161311000	3.171541000	-1.524809000

9 [Pd(**DTE^{c}-COCF$_3$**)]

Pd	-4.398312000	1.454495000	-1.569073000
C	3.255307000	0.957781000	-0.159860000
C	2.278157000	-0.202564000	-0.431883000
S	3.219469000	-1.738365000	0.106753000
C	4.755998000	-0.830373000	0.072632000
C	4.601709000	0.529072000	-0.051673000
H	5.431996000	1.225162000	-0.030197000
C	2.474927000	4.539468000	-0.657691000
C	1.093361000	3.975766000	-0.243308000
C	1.344394000	2.488558000	-0.120666000
C	2.765066000	2.234507000	-0.101776000
C	3.503437000	3.549463000	-0.057123000
H	2.632718000	5.567038000	-0.320389000
H	0.300197000	4.217708000	-0.957887000
H	0.783016000	4.380350000	0.729871000
H	4.456548000	3.529463000	-0.593029000
H	3.720045000	3.810435000	0.988443000
H	2.560545000	4.527841000	-1.749954000
C	-0.972861000	1.498477000	-0.089507000
C	-1.576423000	0.274220000	-0.124691000
S	-0.446276000	-1.090861000	-0.074532000
C	0.976611000	0.059025000	0.357449000
C	0.452620000	1.462580000	0.004536000
H	-1.534894000	2.422741000	-0.175215000
P	-3.402806000	0.046800000	-0.217983000
C	-3.521375000	-1.741086000	-0.676581000
C	-3.847829000	-2.753356000	0.237244000
C	-3.268393000	-2.083427000	-2.016685000
C	-3.913787000	-4.084504000	-0.182959000
C	-3.320618000	-3.414193000	-2.428676000
C	-3.646978000	-4.418328000	-1.511867000
H	-4.046886000	-2.511598000	1.275901000
H	-3.030380000	-1.302402000	-2.734808000
H	-4.170083000	-4.860285000	0.533139000
H	-3.114707000	-3.666340000	-3.465119000
H	-3.696566000	-5.454589000	-1.833997000
C	-3.883763000	0.087214000	1.566035000
C	-3.020800000	-0.328524000	2.593935000
C	-5.169739000	0.541960000	1.895868000
C	-3.439597000	-0.285508000	3.924578000
C	-5.588926000	0.575549000	3.227404000
C	-4.723438000	0.165435000	4.243972000
H	-2.026413000	-0.694806000	2.361052000
H	-5.838265000	0.874811000	1.105806000
H	-2.762600000	-0.606909000	4.711124000
H	-6.587236000	0.929221000	3.469279000

H	-5.046126000	0.198857000	5.280726000
C	1.151020000	0.000782000	1.894486000
H	1.943010000	0.686908000	2.208113000
H	0.219125000	0.306584000	2.376865000
H	1.408517000	-1.004415000	2.231736000
C	2.061192000	-0.296758000	-1.960039000
H	1.560945000	0.603260000	-2.329770000
H	3.030084000	-0.382080000	-2.458079000
H	1.456740000	-1.165633000	-2.227277000
C	5.988954000	-1.567815000	0.226030000
O	6.061653000	-2.782922000	0.372463000
C	7.303067000	-0.742932000	0.214280000
F	8.372197000	-1.538370000	0.326812000
F	7.428014000	-0.033116000	-0.931386000
F	7.331235000	0.143478000	1.237324000

Styrene

C	-0.515538000	-0.222795000	-0.000002000
C	0.407702000	-1.284288000	-0.000009000
C	-0.012020000	1.092865000	-0.000004000
C	1.782698000	-1.045776000	0.000017000
C	1.360006000	1.331669000	-0.000009000
C	2.265352000	0.264236000	-0.000003000
H	0.038917000	-2.307248000	-0.000007000
H	-0.697631000	1.934932000	0.000000000
H	2.475377000	-1.883001000	0.000045000
H	1.726997000	2.354482000	-0.000002000
H	3.334892000	0.454696000	0.000003000
C	-1.956087000	-0.533097000	-0.000010000
H	-2.189957000	-1.597810000	-0.000056000
C	-2.974585000	0.337329000	0.000021000
H	-2.830639000	1.414724000	0.000033000
H	-4.003115000	-0.011640000	-0.000016000

i [Pd(**DTE^o-COCF$_3$**)]·**PhI**

Pd	3.521250000	-0.333356000	0.101178000
S	-0.637712000	2.172059000	-1.323219000
S	-5.335990000	1.060100000	1.769642000
P	2.253530000	1.537495000	-0.141530000
F	-9.891425000	0.050129000	-0.419831000
F	-8.560400000	-1.644436000	-0.104378000
F	-8.134097000	-0.203078000	-1.681214000
O	-8.330922000	1.393304000	1.214334000
C	2.735235000	2.796546000	-1.400197000
C	3.581186000	2.398208000	-2.445566000
H	3.967690000	1.381973000	-2.461889000
C	3.928891000	3.298054000	-3.455243000
H	4.585580000	2.979104000	-4.259831000
C	3.440274000	4.606254000	-3.424658000
H	3.714464000	5.308260000	-4.207118000
C	2.602769000	5.013238000	-2.382101000
H	2.224000000	6.031045000	-2.352407000
C	2.251001000	4.114743000	-1.373669000
H	1.607749000	4.444179000	-0.563178000
C	1.992917000	2.543672000	1.385488000
C	3.013804000	3.404497000	1.822505000
H	3.912427000	3.529389000	1.224102000
C	2.876711000	4.111887000	3.016830000
H	3.669995000	4.780394000	3.339834000
C	1.724947000	3.961312000	3.795888000
H	1.620265000	4.512236000	4.726253000
C	0.711806000	3.098779000	3.372852000
H	-0.186562000	2.975350000	3.971590000
C	0.844148000	2.392856000	2.174465000
H	0.052679000	1.722520000	1.855762000
C	0.559868000	1.083641000	-0.646531000
C	0.020759000	-0.169025000	-0.499877000
H	0.590837000	-1.000444000	-0.099474000
C	-1.354351000	-0.278434000	-0.896584000
C	-1.851080000	0.915741000	-1.387099000
C	-3.206594000	1.214606000	-1.950261000
H	-3.688529000	0.288560000	-2.272664000
H	-3.144908000	1.890450000	-2.809179000
H	-3.857675000	1.683434000	-1.203073000
C	-2.088109000	-1.547552000	-0.786529000
H	-1.479993000	-2.808144000	-2.419351000
C	-2.411040000	-3.934858000	-0.768181000
H	-2.012920000	-4.301237000	0.184864000
C	-3.752212000	-3.214732000	-0.511335000
C	-3.333964000	-1.766461000	-0.303511000
C	-4.262607000	-0.808912000	0.314538000
C	-5.645568000	-0.779030000	-0.021139000
H	-6.085734000	-1.439903000	-0.757375000
C	-6.367028000	0.180471000	0.662144000
C	-3.947837000	0.128331000	1.295901000
C	-2.626374000	0.396000000	1.942018000
H	-1.983734000	-0.483082000	1.858634000
H	-2.738722000	0.653547000	2.999522000
H	-2.116501000	1.228291000	1.444161000
C	-7.772041000	0.514197000	0.575183000
C	-8.610745000	-0.331375000	-0.422529000
C	-1.479696000	-2.835260000	-1.319663000
H	-0.434856000	-2.965316000	-1.014750000
H	-2.506316000	-4.792373000	-1.440027000
H	-4.423769000	-3.289400000	-1.379808000
H	-4.301429000	-3.619540000	0.345709000
I	2.805962000	-3.536428000	0.056928000
C	4.525275000	-2.215641000	0.355394000
C	5.393621000	-1.961774000	-0.737067000
C	4.939278000	-1.919281000	1.680219000
C	6.677113000	-1.456183000	-0.485413000

C	6.228492000	-1.416379000	1.895407000
C	7.099706000	-1.203147000	0.822347000
H	5.096892000	-2.230470000	-1.744905000
H	4.290519000	-2.147708000	2.518486000
H	7.346691000	-1.280548000	-1.322481000
H	6.549471000	-1.207729000	2.911931000
H	8.104541000	-0.834684000	1.005429000

i [Pd(**DTE^{c}-COCF$_3$**)]·**PhI**

Pd	-3.317228000	-0.330795000	0.357298000
C	4.440808000	-1.195475000	-0.273072000
C	3.739568000	0.010409000	0.382766000
S	5.069853000	1.337578000	0.456535000
C	6.335713000	0.109403000	0.184760000
C	5.854443000	-1.119321000	-0.194489000
H	6.494776000	-1.953998000	-0.453219000
C	2.790412000	-4.395978000	-1.115502000
C	1.634209000	-3.386685000	-1.323589000
C	2.240546000	-2.067007000	-0.899470000
C	3.675409000	-2.200302000	-0.798276000
C	4.082569000	-3.562688000	-1.302319000
H	2.737205000	-5.248737000	-1.797024000
H	0.733553000	-3.644037000	-0.757048000
H	1.345059000	-3.337770000	-2.382360000
H	4.950351000	-3.976311000	-0.781036000
H	4.341803000	-3.494007000	-2.368314000
H	2.756920000	-4.782305000	-0.090747000
C	0.239342000	-0.562459000	-0.626903000
C	-0.061625000	0.683939000	-0.160923000
S	1.353756000	1.636719000	0.324627000
C	2.509542000	0.385501000	-0.472785000
C	1.636238000	-0.866846000	-0.666640000
H	-0.529517000	-1.279805000	-0.895138000
P	-1.786088000	1.299538000	-0.009690000
C	-1.611362000	2.581228000	1.307643000
C	-1.248913000	3.910120000	1.040620000
C	-1.827998000	2.181441000	2.636533000
C	-1.099451000	4.820847000	2.088974000
C	-1.669859000	3.091959000	3.681735000
C	-1.306403000	4.413683000	3.409030000
H	-1.083139000	4.237180000	0.019045000
H	-2.122789000	1.155925000	2.846081000
H	-0.820407000	5.848218000	1.872509000
H	-1.837028000	2.771791000	4.706367000
H	-1.189619000	5.124849000	4.221946000
C	-2.030580000	2.274578000	-1.557700000
C	-0.979742000	2.781440000	-2.338157000
C	-3.356209000	2.507295000	-1.960783000
C	-1.253521000	3.508996000	-3.498753000
C	-3.625834000	3.244107000	-3.114710000
C	-2.574412000	3.743877000	-3.887780000
H	0.051712000	2.617935000	-2.044722000
H	-4.175938000	2.102523000	-1.371985000
H	-0.431982000	3.893651000	-4.096638000
H	-4.655479000	3.418120000	-3.414322000
H	-2.783674000	4.309788000	-4.791166000
C	2.863623000	0.927925000	-1.878609000
H	3.504203000	0.214226000	-2.404755000
H	1.946407000	1.059800000	-2.458368000
H	3.384110000	1.885044000	-1.820715000
C	3.382567000	-0.377192000	1.836575000
H	2.645038000	-1.185219000	1.844683000
H	4.282375000	-0.726143000	2.349237000
H	2.975219000	0.470943000	2.390076000
C	7.717996000	0.507290000	0.331693000
O	8.089686000	1.633054000	0.641954000
C	8.791744000	-0.580733000	0.064422000
F	10.024274000	-0.095527000	0.247401000
F	8.630979000	-1.640387000	0.890673000
F	8.709610000	-1.047965000	-1.203629000
I	-6.150524000	-1.446996000	-0.861569000
C	-4.747484000	-1.880465000	0.755562000
C	-3.784885000	-2.906736000	0.571862000
C	-5.027002000	-1.390279000	2.057562000
C	-3.151530000	-3.457804000	1.694384000
C	-4.375251000	-1.964240000	3.157467000
C	-3.457528000	-3.003890000	2.980446000
H	-3.602442000	-3.312774000	-0.416912000
H	-5.791354000	-0.635218000	2.203911000
H	-2.429802000	-4.257151000	1.552030000
H	-4.606294000	-1.600338000	4.154553000
H	-2.977523000	-3.455810000	3.843164000

TSi [Pd(**DTE^{o}-COCF$_3$**)]·**PhI**

Pd	3.508072000	-0.389879000	0.095727000
S	-0.712601000	2.165077000	-1.274926000
S	-5.371941000	0.931874000	1.829606000
P	2.184636000	1.469173000	-0.144686000
F	-9.947306000	0.092057000	-0.390211000
F	-8.634109000	-1.633198000	-0.185335000
F	-8.195009000	-0.100231000	-1.669694000
O	-8.368145000	1.317560000	1.316511000
C	2.693867000	2.735465000	-1.383167000
C	3.564961000	2.342972000	-2.410333000
H	3.949800000	1.326032000	-2.426391000
C	3.940151000	3.249730000	-3.404001000
H	4.615804000	2.935089000	-4.194404000
C	3.453826000	4.558726000	-3.375535000
H	3.749222000	5.266009000	-4.145384000
C	2.591295000	4.959837000	-2.351181000

H	2.214585000	5.978409000	-2.322865000
C	2.212378000	4.054597000	-1.358961000
H	1.551401000	4.380291000	-0.561355000
C	1.932767000	2.449476000	1.399675000
C	2.938628000	3.329014000	1.833652000
H	3.820374000	3.492620000	1.219864000
C	2.806835000	4.007524000	3.045585000
H	3.587773000	4.691444000	3.366284000
C	1.676097000	3.809191000	3.844079000
H	1.575274000	4.338282000	4.787436000
C	0.678186000	2.927491000	3.423611000
H	-0.203892000	2.766983000	4.037545000
C	0.805232000	2.249885000	2.208797000
H	0.026200000	1.564125000	1.891756000
C	0.487860000	1.044339000	-0.657835000
C	-0.053399000	-0.211597000	-0.559423000
H	0.516458000	-1.060683000	-0.198309000
C	-1.432768000	-0.299370000	-0.946531000
C	-1.930604000	0.916140000	-1.380074000
C	-3.290868000	1.242230000	-1.915983000
H	-3.779741000	0.331537000	-2.270033000
H	-3.235685000	1.951843000	-2.747681000
H	-3.932089000	1.682937000	-1.143548000
C	-2.169946000	-1.569620000	-0.884810000
H	-1.581763000	-2.757559000	-2.577853000
C	-2.504989000	-3.953637000	-0.971304000
H	-2.099228000	-4.367045000	-0.041082000
C	-3.839542000	-3.239455000	-0.666507000
C	-3.411321000	-1.804262000	-0.398208000
C	-4.326872000	-0.870451000	0.273302000
C	-5.711990000	-0.812083000	-0.048983000
H	-6.164044000	-1.431487000	-0.813438000
C	-6.419364000	0.118092000	0.687452000
C	-3.995787000	0.014061000	1.297223000
C	-2.665858000	0.238986000	1.942377000
H	-2.031933000	-0.640454000	1.810098000
H	-2.765525000	0.445968000	3.012147000
H	-2.153803000	1.090281000	1.480111000
C	-7.820841000	0.471275000	0.625253000
C	-8.670871000	-0.302328000	-0.420269000
C	-1.572563000	-2.834447000	-1.480579000
H	-0.525780000	-2.982810000	-1.190967000
H	-2.612157000	-4.777925000	-1.681793000
H	-4.521994000	-3.271452000	-1.529001000
H	-4.380414000	-3.680375000	0.177982000
I	2.862984000	-3.245324000	0.201999000
C	4.788524000	-2.011485000	0.324348000
C	5.584811000	-1.917742000	-0.840804000
C	5.343163000	-1.774327000	1.603340000
C	6.928570000	-1.551963000	-0.711915000
C	6.690093000	-1.410104000	1.697123000
C	7.481280000	-1.305761000	0.548688000
H	5.166543000	-2.157910000	-1.812080000
H	4.740432000	-1.902338000	2.495691000
H	7.544381000	-1.474480000	-1.603754000
H	7.120459000	-1.220695000	2.676645000
H	8.530329000	-1.039368000	0.636868000

TSi [Pd(**DTE^{c}-COCF$_3$**)]·**PhI**

Pd	-3.317747000	-0.453930000	0.274663000
C	4.386386000	-1.097096000	-0.286726000
C	3.673391000	0.092498000	0.386822000
S	4.992340000	1.429251000	0.485060000
C	6.268741000	0.215800000	0.198421000
C	5.799368000	-1.010671000	-0.201697000
H	6.447339000	-1.835863000	-0.471707000
C	2.762914000	-4.298473000	-1.175010000
C	1.600091000	-3.295186000	-1.375518000
C	2.195986000	-1.976789000	-0.933030000
C	3.631582000	-2.100752000	-0.828513000
C	4.049843000	-3.453830000	-1.348218000
H	2.718144000	-5.143835000	-1.866279000
H	0.698611000	-3.564939000	-0.815755000
H	1.315167000	-3.235392000	-2.434913000
H	4.919159000	-3.867499000	-0.829553000
H	4.311241000	-3.370597000	-2.412637000
H	2.728789000	-4.696470000	-0.154755000
C	0.182208000	-0.496256000	-0.648039000
C	-0.135334000	0.735863000	-0.155937000
S	1.267845000	1.692701000	0.357649000
C	2.441266000	0.471807000	-0.464118000
C	1.582140000	-0.785207000	-0.685242000
H	-0.575500000	-1.217603000	-0.936604000
P	-1.871605000	1.309985000	0.015191000
C	-1.742144000	2.506961000	1.410992000
C	-1.389856000	3.853486000	1.234184000
C	-1.980398000	2.022072000	2.707320000
C	-1.270626000	4.697861000	2.340118000
C	-1.854111000	2.867217000	3.810306000
C	-1.499506000	4.206629000	3.627708000
H	-1.209483000	4.245181000	0.238032000
H	-2.264639000	0.981764000	2.847974000
H	-0.998560000	5.739407000	2.194186000
H	-2.038215000	2.482188000	4.809324000
H	-1.406754000	4.866635000	4.485568000
C	-2.138872000	2.366538000	-1.471816000
C	-1.102078000	2.954916000	-2.212907000
C	-3.470120000	2.576607000	-1.868005000
C	-1.396003000	3.742899000	-3.328088000
C	-3.759755000	3.373875000	-2.976033000
C	-2.722804000	3.956470000	-3.709602000

H	-0.067071000	2.807248000	-1.923487000
H	-4.277582000	2.107268000	-1.311421000
H	-0.585934000	4.191536000	-3.896237000
H	-4.793420000	3.530889000	-3.271119000
H	-2.947627000	4.570020000	-4.577436000
C	2.791761000	1.047290000	-1.857268000
H	3.440195000	0.351040000	-2.397126000
H	1.873914000	1.182549000	-2.435275000
H	3.302548000	2.008098000	-1.778418000
C	3.318059000	-0.322795000	1.833439000
H	2.586471000	-1.136245000	1.826731000
H	4.220012000	-0.674079000	2.340707000
H	2.904182000	0.512554000	2.401296000
C	7.647492000	0.623016000	0.356587000
O	8.008123000	1.747865000	0.681984000
C	8.731173000	-0.453641000	0.083883000
F	9.958932000	0.040092000	0.275382000
F	8.575649000	-1.521000000	0.900952000
F	8.657225000	-0.910948000	-1.188197000
I	-6.047021000	-1.015253000	-0.440940000
C	-4.346102000	-2.232537000	0.541617000
C	-3.623267000	-3.128504000	-0.278750000
C	-4.376271000	-2.396142000	1.944684000
C	-2.895745000	-4.159149000	0.325189000
C	-3.638846000	-3.436978000	2.517442000
C	-2.905232000	-4.316502000	1.714510000
H	-3.655076000	-3.031859000	-1.358416000
H	-4.978228000	-1.738077000	2.561661000
H	-2.331672000	-4.846590000	-0.299418000
H	-3.650375000	-3.563268000	3.596554000
H	-2.349273000	-5.129819000	2.171307000

ii [Pd(**DTE^o-COCF$_3$**)(**Ph**)**I**]

Pd	3.694897000	-0.418786000	-0.249680000
S	-0.758742000	2.053497000	-1.334461000
S	-5.366584000	0.774176000	1.726033000
P	2.120542000	1.419588000	-0.206150000
F	-9.923321000	0.025061000	-0.564526000
F	-8.637450000	-1.721202000	-0.363067000
F	-8.156296000	-0.176479000	-1.821987000
O	-8.351322000	1.206106000	1.179951000
C	2.553666000	2.796449000	-1.339783000
C	3.303502000	2.485340000	-2.485131000
H	3.630219000	1.462080000	-2.657979000
C	3.624427000	3.479790000	-3.410399000
H	4.205934000	3.229093000	-4.292887000
C	3.201045000	4.793767000	-3.196410000
H	3.453108000	5.569530000	-3.913688000
C	2.455162000	5.110969000	-2.057783000
H	2.124653000	6.131973000	-1.889940000
C	2.130930000	4.118760000	-1.131178000
H	1.556908000	4.375440000	-0.246222000
C	1.911206000	2.195753000	1.443707000
C	2.913481000	3.046120000	1.939145000
H	3.757593000	3.319439000	1.311702000
C	2.822269000	3.557220000	3.234013000
H	3.597310000	4.221632000	3.605492000
C	1.738461000	3.217279000	4.049387000
H	1.669598000	3.616198000	5.057339000
C	0.746743000	2.361828000	3.564958000
H	-0.097001000	2.091182000	4.193520000
C	0.832724000	1.849382000	2.268695000
H	0.064389000	1.177270000	1.902496000
C	0.452088000	0.941265000	-0.724837000
C	-0.064965000	-0.327378000	-0.649050000
H	0.510687000	-1.169614000	-0.282281000
C	-1.439684000	-0.428692000	-1.048834000
C	-1.951646000	0.785821000	-1.471234000
C	-3.309986000	1.098177000	-2.019973000
H	-3.781702000	0.184118000	-2.387918000
H	-3.254183000	1.816071000	-2.844472000
H	-3.965784000	1.523097000	-1.251230000
C	-2.168320000	-1.705033000	-1.004298000
H	-1.574461000	-2.872250000	-2.709695000
C	-2.499306000	-4.087931000	-1.118153000
H	-2.092401000	-4.512774000	-0.193946000
C	-3.834908000	-3.379781000	-0.803511000
C	-3.409415000	-1.947025000	-0.521312000
C	-4.325371000	-1.018322000	0.156910000
C	-5.705798000	-0.940415000	-0.179868000
H	-6.155770000	-1.543782000	-0.958212000
C	-6.410504000	-0.011668000	0.561070000
C	-3.995133000	-0.151988000	1.196174000
C	-2.668526000	0.048870000	1.856007000
H	-2.042195000	-0.834665000	1.714945000
H	-2.774694000	0.239630000	2.928142000
H	-2.143852000	0.902389000	1.412398000
C	-7.806221000	0.361225000	0.485266000
C	-8.652318000	-0.387214000	-0.581705000
C	-1.567596000	-2.961274000	-1.613262000
H	-0.522031000	-3.111820000	-1.321334000
H	-2.605640000	-4.902906000	-1.839402000
H	-4.519723000	-3.403818000	-1.664388000
H	-4.372658000	-3.830269000	0.037828000
I	2.842182000	-1.822729000	1.817526000
C	5.086997000	-1.798293000	-0.493115000
C	4.912780000	-2.728134000	-1.528662000
C	6.330124000	-1.671194000	0.142923000
C	6.011581000	-3.465801000	-1.986339000
C	7.422025000	-2.413382000	-0.322364000
C	7.263810000	-3.307144000	-1.385755000

H	3.935981000	-2.876467000	-1.983756000
H	6.452476000	-0.998504000	0.987834000
H	5.882046000	-4.174577000	-2.800406000
H	8.390984000	-2.302414000	0.157881000
H	8.110570000	-3.892413000	-1.733490000

ii [Pd(**DTE^{c}-COCF$_3$**)(**Ph**)**I**]

Pd	-3.686342000	-0.332679000	-0.074460000
C	4.242120000	-1.093444000	-0.336467000
C	3.528358000	0.113181000	0.305246000
S	4.858490000	1.438402000	0.410265000
C	6.127022000	0.209229000	0.164080000
C	5.655184000	-1.018919000	-0.225079000
H	6.300305000	-1.854387000	-0.468822000
C	2.605031000	-4.292599000	-1.194124000
C	1.453995000	-3.283523000	-1.430147000
C	2.054570000	-1.961479000	-1.007059000
C	3.489105000	-2.097320000	-0.877518000
C	3.901738000	-3.463021000	-1.367006000
H	2.561477000	-5.150902000	-1.869223000
H	0.543146000	-3.532866000	-0.876858000
H	1.184365000	-3.242080000	-2.494398000
H	4.760893000	-3.874264000	-0.829950000
H	4.176659000	-3.401733000	-2.429556000
H	2.553462000	-4.669785000	-0.166891000
C	0.049283000	-0.462745000	-0.767476000
C	-0.258045000	0.777323000	-0.294353000
S	1.146898000	1.740110000	0.208057000
C	2.317580000	0.492188000	-0.576251000
C	1.449179000	-0.760922000	-0.789094000
H	-0.709768000	-1.186458000	-1.042564000
P	-1.970160000	1.370097000	-0.125334000
C	-1.901477000	2.474935000	1.338125000
C	-1.526164000	3.824130000	1.243354000
C	-2.208945000	1.924597000	2.592976000
C	-1.455178000	4.610355000	2.394412000
C	-2.133455000	2.715646000	3.740353000
C	-1.757306000	4.057772000	3.642092000
H	-1.291517000	4.259382000	0.276580000
H	-2.500083000	0.880567000	2.669770000
H	-1.163759000	5.653816000	2.316113000
H	-2.371235000	2.284049000	4.708364000
H	-1.702638000	4.673270000	4.535513000
C	-2.245996000	2.495997000	-1.548872000
C	-1.254061000	2.836779000	-2.478414000
C	-3.550360000	2.994544000	-1.715090000
C	-1.563470000	3.670077000	-3.556419000
C	-3.852575000	3.830162000	-2.789917000
C	-2.858639000	4.168264000	-3.713369000
H	-0.242826000	2.461128000	-2.364568000
H	-4.327797000	2.733849000	-0.999733000
H	-0.788167000	3.931633000	-4.270847000
H	-4.862213000	4.212776000	-2.908294000
H	-3.094504000	4.815864000	-4.552834000
C	2.702636000	1.039883000	-1.970836000
H	3.355039000	0.328407000	-2.485426000
H	1.799079000	1.173849000	-2.571217000
H	3.220871000	1.997212000	-1.898206000
C	3.141303000	-0.277575000	1.750748000
H	2.401370000	-1.083291000	1.741915000
H	4.029832000	-0.630646000	2.279932000
H	2.725310000	0.570035000	2.298303000
C	7.507829000	0.606645000	0.341661000
O	7.871094000	1.731584000	0.661265000
C	8.587395000	-0.480503000	0.094877000
F	9.815203000	0.005135000	0.304686000
F	8.408956000	-1.541328000	0.915197000
F	8.530791000	-0.943675000	-1.175757000
I	-2.667130000	-2.195685000	1.492249000
C	-5.275047000	-1.491118000	-0.236211000
C	-6.395636000	-1.199906000	0.554690000
C	-5.382229000	-2.369868000	-1.323370000
C	-7.645891000	-1.717759000	0.195010000
C	-6.637030000	-2.882748000	-1.673387000
C	-7.766670000	-2.555434000	-0.917565000
H	-6.304509000	-0.571075000	1.437126000
H	-4.503508000	-2.648114000	-1.899839000
H	-8.519794000	-1.477690000	0.795359000
H	-6.725804000	-3.549389000	-2.527486000
H	-8.736093000	-2.967073000	-1.184323000

6. 4. Cartesian coordinates for the structures reported in Chapter 3

1oo

C	-5.206076000	0.129609000	1.391559000
C	-5.245031000	-0.473967000	0.136549000
S	-6.086581000	0.505179000	-1.022342000
C	-6.421350000	1.741112000	0.177617000
C	-5.894332000	1.373220000	1.399503000
H	-5.992557000	2.002972000	2.275795000
C	-4.677864000	-1.791093000	-0.287553000
H	-3.685776000	-1.659162000	-0.733313000
H	-4.566620000	-2.444786000	0.580277000
H	-5.316116000	-2.287354000	-1.024806000
C	-4.525758000	-1.367497000	4.807837000
C	-3.122854000	-1.438762000	4.168986000
C	-3.357431000	-0.993169000	2.734646000
C	-4.578464000	-0.423123000	2.600506000
C	-5.296201000	-0.349666000	3.939742000
H	-4.500782000	-1.096137000	5.866844000
H	-2.672256000	-2.435750000	4.232711000
H	-2.415132000	-0.748472000	4.651330000
H	-6.364697000	-0.576420000	3.856341000
H	-5.221317000	0.669052000	4.348461000
H	-5.010269000	-2.346929000	4.727035000
C	-1.586007000	-2.367770000	1.531347000
C	-0.650135000	-2.338636000	0.528582000
S	-0.607001000	-0.736987000	-0.192448000
C	-1.856597000	-0.140899000	0.869981000
C	-2.299134000	-1.135101000	1.723842000
H	-1.785671000	-3.259527000	2.116370000
C	-2.287123000	1.291407000	0.782615000
H	-3.012792000	1.444058000	-0.024840000
H	-2.764473000	1.596320000	1.716826000
H	-1.436608000	1.954608000	0.594981000
P	0.357183000	-3.779093000	0.038485000
C	-0.294240000	-4.179812000	-1.646559000
C	0.499572000	-4.929107000	-2.532196000
C	-1.606688000	-3.856664000	-2.022741000
C	-0.000422000	-5.319073000	-3.775265000
C	-2.106536000	-4.253150000	-3.264979000
C	-1.304533000	-4.980607000	-4.146973000
H	1.515150000	-5.200033000	-2.255794000
H	-2.240640000	-3.292473000	-1.346141000
H	0.630018000	-5.887782000	-4.453272000
H	-3.122712000	-3.987276000	-3.543588000
H	-1.692536000	-5.284416000	-5.115091000
C	1.974134000	-3.023712000	-0.337942000
C	3.010163000	-2.958049000	0.559465000
S	2.391661000	-2.130009000	-1.792857000
C	4.123831000	-2.163226000	0.126245000
C	3.942542000	-1.658811000	-1.148392000
C	4.878148000	-0.830313000	-1.974799000
H	4.871512000	-1.142829000	-3.023997000
H	4.608044000	0.231622000	-1.941913000
H	5.897299000	-0.923507000	-1.592239000
H	2.971982000	-3.432978000	1.534498000
C	5.296836000	-1.914808000	0.977662000
C	6.083422000	-3.055909000	1.597481000
H	6.638148000	-3.586015000	0.809340000
H	5.436071000	-3.801629000	2.073490000
C	7.027086000	-2.346676000	2.593383000
H	6.557552000	-2.324534000	3.583085000
H	7.993941000	-2.846939000	2.696703000
C	7.147409000	-0.901510000	2.059404000
H	7.257088000	-0.157189000	2.855684000
H	8.018168000	-0.785031000	1.397184000
C	5.864258000	-0.720693000	1.264418000
C	5.398471000	0.615360000	0.863621000
C	4.093073000	1.088666000	0.982962000
S	3.942571000	2.712043000	0.390740000
C	5.650151000	2.787679000	-0.008600000
C	6.268723000	1.596867000	0.318865000
H	7.326986000	1.437579000	0.147993000
C	2.894242000	0.393864000	1.546176000
H	2.304453000	-0.083330000	0.756030000
H	2.238035000	1.088482000	2.079327000
H	3.212352000	-0.390328000	2.236912000
C	6.340671000	3.919122000	-0.605310000
O	7.537424000	3.938511000	-0.849232000
C	5.495489000	5.170964000	-0.960338000
F	4.880744000	5.664374000	0.139548000
F	6.253163000	6.137130000	-1.484910000
F	4.529806000	4.856201000	-1.853656000
C	-7.144240000	2.982276000	-0.050109000
O	-7.369417000	3.811104000	0.818211000
C	-7.655254000	3.262373000	-1.488343000
F	-8.507280000	2.291080000	-1.890058000
F	-8.291709000	4.433768000	-1.559347000
F	-6.626919000	3.283858000	-2.366932000

1oc

C	5.901356000	-0.568951000	1.477025000
C	5.958782000	0.519547000	0.608955000
S	7.137319000	0.282083000	-0.641540000
C	7.591825000	-1.285740000	0.002643000

C	6.847760000	-1.570758000	1.130333000
H	6.974388000	-2.496565000	1.679108000
C	5.176847000	1.794289000	0.651189000
H	4.299619000	1.740185000	-0.003766000
H	4.818881000	1.974901000	1.667085000
H	5.782656000	2.648499000	0.333821000
C	4.428281000	-0.838278000	4.963983000
C	3.150831000	-0.709735000	4.106696000
C	3.683045000	-0.444379000	2.709051000
C	5.009759000	-0.702357000	2.638202000
C	5.532443000	-1.239653000	3.961232000
H	4.320263000	-1.547985000	5.788828000
H	2.475086000	0.079618000	4.455817000
H	2.562918000	-1.639357000	4.100623000
H	6.516556000	-0.833840000	4.219886000
H	5.647868000	-2.332091000	3.901925000
H	4.674016000	0.138217000	5.395933000
C	1.897987000	1.087440000	1.738803000
C	1.174416000	1.367774000	0.605895000
S	1.567267000	0.202567000	-0.649550000
C	2.698847000	-0.636687000	0.376893000
C	2.782707000	-0.035672000	1.620217000
H	1.830893000	1.689039000	2.639340000
C	3.431666000	-1.836001000	-0.141807000
H	4.285338000	-1.545745000	-0.765383000
H	3.817405000	-2.426209000	0.692589000
H	2.779207000	-2.474344000	-0.745914000
P	0.013585000	2.764829000	0.478493000
C	0.271702000	3.328260000	-1.266990000
C	-0.805374000	3.669011000	-2.098629000
C	1.581516000	3.533550000	-1.732919000
C	-0.577276000	4.182012000	-3.377308000
C	1.805974000	4.044996000	-3.011561000
C	0.727332000	4.368086000	-3.839392000
H	-1.825122000	3.532443000	-1.751697000
H	2.429581000	3.284484000	-1.100523000
H	-1.422288000	4.430895000	-4.013426000
H	2.824657000	4.188663000	-3.361180000
H	0.902893000	4.763405000	-4.835829000
C	8.592220000	-2.182502000	-0.553878000
O	8.920181000	-3.242205000	-0.042953000
C	9.260654000	-1.770702000	-1.892269000
F	9.859682000	-0.561864000	-1.783061000
F	10.181210000	-2.660457000	-2.270824000
F	8.334288000	-1.673539000	-2.872645000
C	-1.638505000	1.968413000	0.374063000
C	-2.730042000	2.526984000	0.973123000
H	-2.667094000	3.427148000	1.575987000
C	-3.954824000	1.805722000	0.794566000
C	-5.152841000	1.994414000	1.416387000
C	-6.253759000	1.085346000	1.184447000
C	-5.593628000	3.096231000	2.355322000
C	-6.928255000	2.564196000	2.933289000
C	-7.499191000	1.642065000	1.827713000
S	-1.990332000	0.456719000	-0.488027000
C	-3.840305000	0.725820000	-0.296449000
C	-4.351900000	1.338282000	-1.622078000
H	-3.819723000	2.271068000	-1.823127000
H	-5.420423000	1.559827000	-1.545848000
H	-4.196004000	0.660479000	-2.462639000
C	-4.628943000	-0.523097000	0.156980000
C	-4.021030000	-1.221905000	1.394990000
H	-3.918308000	-0.511584000	2.220589000
H	-4.851767000	3.321684000	3.127714000
H	-5.757376000	4.021998000	1.787017000
H	-7.618339000	3.364395000	3.212431000
H	-8.174673000	0.869878000	2.206119000
H	-8.057601000	2.233570000	1.088372000
H	-6.725414000	1.967717000	3.829685000
H	-4.683278000	-2.029935000	1.715443000
H	-3.038836000	-1.644129000	1.175005000
C	-6.064780000	-0.090053000	0.512839000
C	-7.040398000	-1.042046000	0.118884000
C	-6.573261000	-2.009916000	-0.734572000
S	-4.854853000	-1.828283000	-1.178219000
H	-8.073856000	-0.978561000	0.437672000
C	-7.322363000	-3.095997000	-1.329081000
O	-6.858325000	-3.911864000	-2.116140000
C	-8.819671000	-3.211197000	-0.937845000
F	-9.504461000	-2.100694000	-1.298916000
F	-9.392494000	-4.262846000	-1.532373000
F	-8.966982000	-3.353698000	0.399753000

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C	-4.578370000	-0.853654000	1.076233000
C	-3.797061000	-0.152523000	-0.053561000
S	-4.926547000	-0.287789000	-1.550827000
C	-5.869998000	-1.571602000	-0.745502000
C	-5.587159000	-1.722712000	0.589779000
H	-6.114232000	-2.415365000	1.234898000
C	-3.430970000	-1.112106000	4.578029000
C	-2.844703000	0.259843000	4.162401000
C	-3.219609000	0.373292000	2.700741000
C	-4.208952000	-0.627555000	2.373405000
C	-4.642643000	-1.326947000	3.637474000
H	-3.705640000	-1.153698000	5.635117000
H	-1.765986000	0.333729000	4.333488000
H	-3.316606000	1.073247000	4.730402000
H	-4.897938000	-2.379195000	3.484699000
H	-5.534008000	-0.827642000	4.043010000

H	-2.689116000	-1.896827000	4.392785000
C	-1.736288000	2.223443000	1.853176000
C	-1.350931000	2.769574000	0.663157000
S	-2.286179000	2.207805000	-0.731276000
C	-3.489784000	1.295383000	0.388612000
C	-2.783540000	1.254500000	1.755599000
H	-1.236671000	2.449228000	2.790120000
P	0.114753000	3.874895000	0.553561000
C	0.057339000	4.458071000	-1.197408000
C	1.096592000	4.228983000	-2.111780000
C	-1.034314000	5.253220000	-1.589081000
C	1.032116000	4.765479000	-3.399600000
C	-1.099467000	5.777829000	-2.879891000
C	-0.066457000	5.534385000	-3.789086000
H	1.956055000	3.631182000	-1.826383000
H	-1.840236000	5.456329000	-0.888678000
H	1.840653000	4.575317000	-4.099899000
H	-1.955330000	6.379182000	-3.173070000
H	-0.116278000	5.945212000	-4.793404000
C	-4.744549000	2.188385000	0.532025000
H	-5.463915000	1.719524000	1.209786000
H	-4.455016000	3.156046000	0.949620000
H	-5.231547000	2.353381000	-0.430396000
C	-2.529514000	-0.989414000	-0.346977000
H	-1.855696000	-0.977560000	0.514628000
H	-2.818003000	-2.024438000	-0.546060000
H	-1.987845000	-0.607563000	-1.214109000
C	1.438003000	2.603798000	0.525433000
C	2.612247000	2.772477000	1.198996000
H	2.841235000	3.674208000	1.757767000
C	3.538612000	1.686448000	1.072614000
C	4.848934000	1.636598000	1.442853000
C	5.654638000	0.471859000	1.145663000
C	5.677538000	2.643775000	2.210109000
C	7.127533000	2.131396000	2.027920000
C	6.986336000	0.600406000	1.841871000
S	1.321394000	1.059736000	-0.346865000
C	2.874334000	0.423142000	0.495038000
C	2.416989000	-0.452632000	1.685980000
H	1.793835000	0.145184000	2.356185000
H	3.285521000	-0.810767000	2.246504000
H	1.839840000	-1.315405000	1.349733000
C	3.874170000	-0.276147000	-0.451542000
C	4.198918000	0.544633000	-1.721733000
H	4.560213000	1.540593000	-1.448608000
H	5.537884000	3.670116000	1.856765000
H	5.389174000	2.626534000	3.269995000
H	7.778771000	2.395754000	2.864818000
H	7.811763000	0.148238000	1.285165000
H	6.936336000	0.100157000	2.819343000
H	7.556474000	2.566098000	1.118266000
H	4.983105000	0.037434000	-2.289076000
H	3.322793000	0.655318000	-2.363266000
C	5.192420000	-0.507751000	0.312670000
C	5.804230000	-1.747455000	-0.009197000
C	4.994865000	-2.613087000	-0.700976000
S	3.349583000	-1.994613000	-1.005475000
H	6.810383000	-1.995574000	0.306886000
C	5.314056000	-3.951832000	-1.150747000
O	4.530724000	-4.694447000	-1.729143000
C	-6.856242000	-2.285906000	-1.524640000
O	-7.091668000	-2.078646000	-2.709443000
C	6.751545000	-4.463802000	-0.868646000
F	7.013376000	-4.478840000	0.459385000
F	6.920877000	-5.703957000	-1.338197000
F	7.675816000	-3.664684000	-1.449460000
C	-7.673168000	-3.380553000	-0.787887000
F	-8.384569000	-2.852221000	0.236015000
F	-8.530214000	-3.982272000	-1.619541000
F	-6.863276000	-4.328728000	-0.262626000

4oo

C	5.332587000	0.747120000	-1.314119000
C	5.391930000	0.316789000	0.009474000
S	6.339350000	1.387927000	0.991604000
C	6.689718000	2.427914000	-0.377662000
C	6.089574000	1.932826000	-1.517915000
H	6.185007000	2.431341000	-2.475349000
C	4.771642000	-0.894778000	0.629729000
H	3.809339000	-0.644125000	1.089674000
H	4.586528000	-1.651413000	-0.135997000
H	5.413527000	-1.325851000	1.403839000
C	4.403550000	-1.161688000	-4.458149000
C	3.030561000	-1.049115000	-3.761849000
C	3.361864000	-0.422688000	-2.417792000
C	4.619994000	0.076125000	-2.410920000
C	5.278295000	-0.090102000	-3.771750000
H	4.344209000	-1.035782000	-5.542605000
H	2.519191000	-2.013532000	-3.662232000
H	2.342777000	-0.388766000	-4.310310000
H	6.331932000	-0.379316000	-3.694563000
H	5.252655000	0.864777000	-4.317344000
H	4.828595000	-2.152038000	-4.261237000
C	1.588322000	-1.495432000	-0.948269000
C	0.705699000	-1.248848000	0.073393000
S	0.769624000	0.437759000	0.543012000
C	1.998347000	0.786702000	-0.646064000
C	2.348359000	-0.349437000	-1.354946000
H	1.708471000	-2.477510000	-1.392883000
C	2.510440000	2.186222000	-0.791141000

H	3.286532000	2.406450000	-0.049257000
H	2.952626000	2.318839000	-1.781157000
H	1.709643000	2.921698000	-0.665813000
P	-0.369021000	-2.478515000	0.839968000
C	0.261019000	-2.740504000	2.537231000
C	-0.580287000	-3.328008000	3.496032000
C	1.588492000	-2.434582000	2.866177000
C	-0.097509000	-3.585803000	4.778692000
C	2.065081000	-2.698152000	4.151488000
C	1.223826000	-3.269850000	5.108410000
H	-1.607545000	-3.576993000	3.245211000
H	2.247884000	-1.994280000	2.125325000
H	-0.753532000	-4.033244000	5.519475000
H	3.092876000	-2.453545000	4.403148000
H	1.596392000	-3.471265000	6.108523000
C	-1.978846000	-1.690805000	1.034397000
C	-2.996457000	-1.760993000	0.115719000
S	-2.378335000	-0.556380000	2.308024000
C	-4.092650000	-0.882614000	0.394231000
C	-3.909479000	-0.170113000	1.566565000
C	-4.828404000	0.812278000	2.224410000
H	-4.836642000	0.689574000	3.312022000
H	-4.529971000	1.844021000	2.005548000
H	-5.846108000	0.675580000	1.851814000
H	-2.951291000	-2.396320000	-0.762419000
C	-5.248552000	-0.758875000	-0.506774000
C	-6.056110000	-1.971037000	-0.933432000
H	-6.638535000	-2.340857000	-0.076878000
H	-5.422159000	-2.804311000	-1.258673000
C	-6.961939000	-1.422699000	-2.058356000
H	-6.477709000	-1.591785000	-3.026398000
H	-7.942552000	-1.905205000	-2.089753000
C	-7.044360000	0.097881000	-1.793367000
H	-7.111692000	0.690815000	-2.711909000
H	-7.923226000	0.358164000	-1.185107000
C	-5.772911000	0.381075000	-1.010668000
C	-5.274474000	1.753004000	-0.831888000
C	-3.954837000	2.165487000	-1.003535000
S	-3.765202000	3.858269000	-0.676102000
C	-5.474968000	4.042331000	-0.323962000
C	-6.123858000	2.831770000	-0.467542000
H	-7.188291000	2.728843000	-0.291843000
C	-2.769268000	1.359239000	-1.431783000
H	-2.186495000	1.019643000	-0.568292000
H	-2.101433000	1.937632000	-2.077465000
H	-3.101582000	0.472162000	-1.975702000
C	-6.139379000	5.273120000	0.074469000
O	-7.340054000	5.366477000	0.277112000
C	-5.257682000	6.535294000	0.268602000
F	-4.581745000	6.831183000	-0.865623000
F	-5.994180000	7.596420000	0.605820000
F	-4.340517000	6.327678000	1.240866000
C	7.488435000	3.643423000	-0.347960000
O	7.719343000	4.332360000	-1.329210000
C	8.070509000	4.087775000	1.020032000
F	8.862400000	3.122770000	1.541648000
F	8.792516000	5.204269000	0.901972000
F	7.075992000	4.316371000	1.908267000
Au	-0.512885000	-4.380370000	-0.407084000
Cl	-0.699135000	-6.346947000	-1.685350000

4oc

C	-5.765281000	-1.070335000	-1.557425000
C	-5.866798000	-0.300949000	-0.400376000
S	-7.075876000	-0.921305000	0.677854000
C	-7.479082000	-2.222784000	-0.428318000
C	-6.698283000	-2.141687000	-1.564206000
H	-6.791004000	-2.856018000	-2.373796000
C	-5.106664000	0.932960000	-0.027214000
H	-4.241982000	0.690063000	0.601163000
H	-4.731365000	1.422613000	-0.928805000
H	-5.733477000	1.641466000	0.522500000
C	-4.172426000	-0.190833000	-4.890754000
C	-2.926611000	-0.360540000	-3.993714000
C	-3.512545000	-0.570002000	-2.608907000
C	-4.838950000	-0.825330000	-2.672711000
C	-5.313489000	-0.887111000	-4.115530000
H	-4.031568000	-0.593391000	-5.897510000
H	-2.245831000	0.497777000	-4.035808000
H	-2.331885000	-1.242087000	-4.274643000
H	-6.286440000	-0.404506000	-4.257563000
H	-5.433744000	-1.936192000	-4.423903000
H	-4.404325000	0.875377000	-4.988685000
C	-1.806170000	0.555110000	-1.099224000
C	-1.142623000	0.430120000	0.096934000
S	-1.542958000	-1.093814000	0.862740000
C	-2.609756000	-1.539575000	-0.442458000
C	-2.661848000	-0.549763000	-1.408949000
H	-1.715217000	1.431557000	-1.731889000
C	-3.334677000	-2.848778000	-0.396208000
H	-4.216209000	-2.793797000	0.252787000
H	-3.676622000	-3.117467000	-1.398155000
H	-2.691562000	-3.650889000	-0.020949000
P	-0.002381000	1.651292000	0.772654000
C	-0.267427000	1.616084000	2.582788000
C	0.813728000	1.635687000	3.473917000
C	-1.582306000	1.650892000	3.074171000
C	0.578526000	1.671396000	4.849480000
C	-1.808663000	1.686755000	4.449547000
C	-0.729487000	1.694470000	5.338181000

H	1.832779000	1.620378000	3.101069000
H	-2.424248000	1.644592000	2.387688000
H	1.419120000	1.677562000	5.537066000
H	-2.827042000	1.707539000	4.826089000
H	-0.908943000	1.719938000	6.409017000
C	-8.478144000	-3.256543000	-0.207497000
O	-8.743849000	-4.132584000	-1.015689000
C	-9.238220000	-3.244524000	1.145043000
F	-9.886853000	-2.070638000	1.322164000
F	-10.134184000	-4.232111000	1.208597000
F	-8.374577000	-3.386896000	2.176534000
C	1.677620000	1.015937000	0.503905000
C	2.696021000	1.781773000	0.020843000
H	2.559914000	2.816409000	-0.276153000
C	3.945126000	1.092059000	-0.105802000
C	5.080175000	1.508131000	-0.731758000
C	6.223767000	0.626124000	-0.846240000
C	5.411555000	2.848961000	-1.347456000
C	6.705505000	2.567493000	-2.150142000
C	7.393881000	1.402891000	-1.396019000
S	2.120093000	-0.668096000	0.849703000
C	3.946564000	-0.256850000	0.636688000
C	4.529349000	-0.019185000	2.049035000
H	3.989013000	0.797907000	2.533535000
H	5.584044000	0.261609000	1.976310000
H	4.448276000	-0.910381000	2.673043000
C	4.734460000	-1.286773000	-0.203034000
C	4.054052000	-1.645407000	-1.544780000
H	3.857047000	-0.739520000	-2.125586000
H	4.600391000	3.248388000	-1.963887000
H	5.599786000	3.580091000	-0.549525000
H	7.346835000	3.447543000	-2.240759000
H	8.053698000	0.801164000	-2.026959000
H	7.997860000	1.791207000	-0.563889000
H	6.443042000	2.236980000	-3.161123000
H	4.718809000	-2.289718000	-2.125337000
H	3.110500000	-2.171375000	-1.388681000
C	6.122349000	-0.695897000	-0.520757000
C	7.155989000	-1.670553000	-0.478735000
C	6.787643000	-2.856349000	0.101786000
S	5.106738000	-2.897777000	0.691902000
H	8.157075000	-1.467863000	-0.839612000
C	7.616434000	-4.026218000	0.321805000
O	7.236721000	-5.046508000	0.879900000
C	9.084286000	-3.952822000	-0.177394000
F	9.757971000	-2.960313000	0.448183000
F	9.727000000	-5.101723000	0.053236000
F	9.138057000	-3.699460000	-1.504989000
Au	-0.329620000	3.703669000	-0.167017000
Cl	-0.704360000	5.817912000	-1.126826000

4cc

C	4.861665000	-1.419499000	-1.065715000
C	3.913038000	-1.232086000	0.135863000
S	4.857534000	-1.953580000	1.592461000
C	5.962642000	-2.798280000	0.478062000
C	5.851496000	-2.411696000	-0.832630000
H	6.489210000	-2.790898000	-1.622074000
C	4.169312000	-0.253176000	-4.498267000
C	3.462152000	0.835823000	-3.654467000
C	3.647671000	0.355577000	-2.232553000
C	4.647493000	-0.692064000	-2.201119000
C	5.270145000	-0.821530000	-3.568538000
H	4.570374000	0.133841000	-5.438202000
H	2.410862000	0.975402000	-3.924884000
H	3.958227000	1.807915000	-3.779264000
H	5.566501000	-1.844848000	-3.814377000
H	6.172383000	-0.195800000	-3.619051000
H	3.455803000	-1.048898000	-4.739166000
C	1.957815000	1.690418000	-0.935235000
C	1.411891000	1.709733000	0.313366000
S	2.202525000	0.652157000	1.492806000
C	3.584096000	0.270894000	0.268777000
C	3.051054000	0.778600000	-1.083738000
H	1.555438000	2.269622000	-1.760068000
P	-0.122238000	2.608689000	0.691703000
C	-0.112550000	2.865181000	2.499144000
C	-1.179870000	2.451941000	3.307825000
C	0.975928000	3.549986000	3.064454000
C	-1.148448000	2.711472000	4.679530000
C	0.999999000	3.801307000	4.435078000
C	-0.061055000	3.381471000	5.243385000
H	-2.028791000	1.930740000	2.877591000
H	1.801066000	3.878902000	2.438575000
H	-1.974108000	2.385953000	5.305280000
H	1.845676000	4.324444000	4.871256000
H	-0.039856000	3.579143000	6.311091000
C	4.792197000	1.149725000	0.665699000
H	5.614180000	0.996271000	-0.039446000
H	4.502082000	2.203081000	0.633853000
H	5.147511000	0.914576000	1.670238000
C	2.667425000	-2.119088000	-0.098607000
H	2.104491000	-1.764595000	-0.966979000
H	2.986384000	-3.146488000	-0.289815000
H	2.004112000	-2.117236000	0.768054000
C	-1.438913000	1.407056000	0.345838000
C	-2.576407000	1.734091000	-0.330850000
H	-2.780497000	2.739526000	-0.683910000
C	-3.496439000	0.649058000	-0.495514000
C	-4.785854000	0.692781000	-0.930293000
C	-5.600699000	-0.505116000	-0.940498000

C	-5.580385000	1.849713000	-1.493052000
C	-7.035696000	1.320854000	-1.495148000
C	-6.898418000	-0.213896000	-1.651558000
S	-1.347828000	-0.288381000	0.865168000
C	-2.853149000	-0.714280000	-0.183819000
C	-2.325109000	-1.302955000	-1.512653000
H	-1.677492000	-0.570664000	-2.001911000
H	-3.160887000	-1.527798000	-2.181692000
H	-1.755071000	-2.218427000	-1.347294000
C	-3.892907000	-1.604464000	0.531434000
C	-4.284528000	-1.092947000	1.937647000
H	-4.635329000	-0.058163000	1.881186000
H	-5.457627000	2.772994000	-0.918619000
H	-5.241689000	2.060135000	-2.516623000
H	-7.647994000	1.771030000	-2.280277000
H	-7.747214000	-0.773341000	-1.249089000
H	-6.800875000	-0.481805000	-2.713052000
H	-7.506732000	1.544276000	-0.531577000
H	-5.094567000	-1.709648000	2.334514000
H	-3.442751000	-1.139389000	2.630951000
C	-5.172003000	-1.647393000	-0.328090000
C	-5.791106000	-2.926799000	-0.326170000
C	-5.007170000	-3.929480000	0.182624000
S	-3.385566000	-3.406503000	0.703948000
H	-6.780679000	-3.092070000	-0.734855000
C	-5.337240000	-5.338024000	0.289750000
O	-4.577204000	-6.195105000	0.718845000
C	6.894514000	-3.756865000	1.038734000
O	6.972032000	-4.031112000	2.228777000
C	-6.751086000	-5.765689000	-0.186306000
F	-6.928499000	-5.480217000	-1.496951000
F	-6.937635000	-7.078105000	-0.017415000
F	-7.714279000	-5.110610000	0.500819000
C	7.858692000	-4.461003000	0.047231000
F	8.644752000	-3.559736000	-0.586147000
F	8.650654000	-5.329720000	0.683154000
F	7.174044000	-5.134320000	-0.905255000
Au	-0.325207000	4.515072000	-0.536563000
Cl	-0.539704000	6.480005000	-1.807655000

[AuCl(**5o**)]

C	3.891249000	1.380627000	-0.093867000
C	3.621485000	0.316959000	-0.951421000
S	4.990606000	-0.735339000	-1.121488000
C	5.961080000	0.258253000	-0.048816000
C	5.227138000	1.341270000	0.391204000
H	5.644869000	2.078744000	1.066331000
C	2.361519000	0.009545000	-1.696048000
H	1.760501000	-0.725721000	-1.149429000
H	1.762254000	0.915934000	-1.805086000
H	2.568573000	-0.397906000	-2.690316000
C	2.129100000	4.713378000	0.313305000
C	1.085700000	3.752409000	0.920654000
C	1.665213000	2.373878000	0.646992000
C	2.962533000	2.460653000	0.269573000
C	3.443188000	3.903529000	0.302410000
H	2.211180000	5.656392000	0.860530000
H	0.084274000	3.881900000	0.494646000
H	0.980238000	3.891248000	2.006683000
H	4.092910000	4.147718000	-0.544968000
H	4.034287000	4.078341000	1.213641000
H	1.844979000	4.950866000	-0.717817000
C	-0.481258000	1.044602000	0.368253000
C	-1.087061000	-0.149379000	0.668799000
S	-0.020282000	-1.152666000	1.628585000
C	1.240502000	0.053889000	1.602007000
C	0.854695000	1.168026000	0.875736000
H	-0.969395000	1.815344000	-0.218553000
C	2.519756000	-0.196554000	2.339204000
H	3.214221000	-0.797431000	1.740708000
H	3.011822000	0.752706000	2.562751000
H	2.344214000	-0.727217000	3.280138000
P	-2.714422000	-0.676506000	0.095370000
C	-2.424410000	-1.782238000	-1.336605000
C	-3.480168000	-2.585844000	-1.797009000
C	-1.200086000	-1.783194000	-2.016145000
C	-3.300860000	-3.393427000	-2.919203000
C	-1.028084000	-2.592057000	-3.141701000
C	-2.074907000	-3.398213000	-3.592604000
H	-4.433691000	-2.586826000	-1.275997000
H	-0.386471000	-1.153856000	-1.672282000
H	-4.118119000	-4.017594000	-3.268546000
H	-0.074974000	-2.590884000	-3.662570000
H	-1.938929000	-4.027344000	-4.467448000
C	-3.375543000	-1.745164000	1.422320000
C	-2.984289000	-3.089348000	1.530866000
C	-4.236859000	-1.188825000	2.379953000
C	-3.448357000	-3.863876000	2.594735000
C	-4.696813000	-1.969641000	3.440926000
C	-4.302706000	-3.305682000	3.549260000
H	-2.330281000	-3.533741000	0.786856000
H	-4.546173000	-0.150806000	2.292856000
H	-3.144584000	-4.903439000	2.674861000
H	-5.366212000	-1.535763000	4.177819000
H	-4.664814000	-3.912995000	4.373769000
C	7.337306000	-0.000791000	0.345416000
O	7.990688000	0.734545000	1.068753000
C	8.000289000	-1.303520000	-0.175045000
F	7.989486000	-1.344235000	-1.527481000
F	9.266053000	-1.403901000	0.236772000

F	7.322178000	-2.387838000	0.265567000
Au	-4.035595000	1.103630000	-0.438668000
Cl	-5.398743000	2.931356000	-1.025325000

[AuCl(**5c**)]

C	3.831529000	-1.001954000	0.104303000
C	2.973199000	0.249202000	0.378189000
S	4.092070000	1.691141000	-0.072061000
C	5.517738000	0.622123000	-0.025491000
C	5.222018000	-0.714139000	0.053424000
H	5.973714000	-1.493986000	0.036429000
C	2.664341000	-4.483123000	0.491663000
C	1.363467000	-3.769052000	0.048733000
C	1.772153000	-2.315837000	-0.040645000
C	3.217218000	-2.215861000	-0.009779000
C	3.809150000	-3.601627000	-0.066236000
H	2.719820000	-5.516655000	0.141331000
H	0.526286000	-3.936374000	0.733337000
H	1.044379000	-4.120242000	-0.941932000
H	4.746327000	-3.695201000	0.489111000
H	4.018493000	-3.865997000	-1.112359000
H	2.719583000	-4.495422000	1.585798000
C	-0.423268000	-1.091471000	-0.125973000
C	-0.888569000	0.187069000	-0.053516000
S	0.376079000	1.433163000	-0.038863000
C	1.685462000	0.149555000	-0.468718000
C	1.004462000	-1.199450000	-0.173401000
H	-1.079909000	-1.955049000	-0.108265000
P	-2.654394000	0.613068000	0.038928000
C	-2.840522000	1.519974000	1.618341000
C	-3.916729000	2.406059000	1.784566000
C	-1.972010000	1.268979000	2.690629000
C	-4.108677000	3.045644000	3.009107000
C	-2.171293000	1.912810000	3.913093000
C	-3.236206000	2.801898000	4.073518000
H	-4.596131000	2.605397000	0.961126000
H	-1.141616000	0.579395000	2.575362000
H	-4.938864000	3.735295000	3.129941000
H	-1.490819000	1.720376000	4.737304000
H	-3.387226000	3.303125000	5.025143000
C	-2.924534000	1.833464000	-1.295395000
C	-2.513381000	3.169319000	-1.157326000
C	-3.499805000	1.401834000	-2.500145000
C	-2.676769000	4.059249000	-2.218479000
C	-3.658720000	2.297907000	-3.558442000
C	-3.247281000	3.625093000	-3.418558000
H	-2.079490000	3.519424000	-0.226088000
H	-3.824019000	0.370354000	-2.607603000
H	-2.359071000	5.091673000	-2.106950000
H	-4.107694000	1.958893000	-4.487301000
H	-3.374141000	4.322522000	-4.241524000
C	1.923946000	0.236546000	-1.993843000
H	2.644173000	-0.525931000	-2.304426000
H	0.982344000	0.057540000	-2.519270000
H	2.306114000	1.216083000	-2.285145000
C	2.709172000	0.320771000	1.900491000
H	2.101989000	-0.530787000	2.221384000
H	3.661604000	0.285333000	2.434864000
H	2.191322000	1.241545000	2.175073000
C	6.830140000	1.231593000	-0.119572000
O	7.027858000	2.435563000	-0.212429000
C	8.052112000	0.274735000	-0.116062000
F	8.004637000	-0.575106000	-1.167699000
F	9.197536000	0.959827000	-0.186401000
F	8.080122000	-0.478438000	1.007339000
Au	-3.981820000	-1.236610000	-0.111501000
Cl	-5.360082000	-3.137230000	-0.284264000

6. 5. Cartesian coordinates for the structures reported in Chapter 4

i

N	-0.304780000	-4.512239000	0.164414000
N	0.925679000	-4.493918000	-0.034645000
C	1.625617000	-3.312907000	-0.462674000
C	1.806974000	-2.259258000	0.451169000
C	2.272561000	-3.342834000	-1.700012000
C	2.687242000	-1.210193000	0.099068000
C	3.079867000	-2.268866000	-2.064625000
C	3.297769000	-1.222652000	-1.166117000
H	3.562100000	-2.257644000	-3.037729000
H	3.967786000	-0.416944000	-1.446519000
C	-1.180610000	-3.416785000	-0.201195000
C	-2.099980000	-3.835946000	-1.172720000
C	-1.233924000	-2.119768000	0.362025000
C	-3.049832000	-2.956893000	-1.674475000
C	-2.217760000	-1.239876000	-0.161698000
C	-3.101117000	-1.663632000	-1.165376000
H	-3.747119000	-3.279643000	-2.441615000
H	-3.843296000	-0.972119000	-1.549701000
P	3.087935000	0.087744000	1.371556000
P	-2.370576000	0.516311000	0.462118000
C	1.883139000	1.438061000	1.006772000
C	1.451995000	2.220488000	2.089738000
C	1.428646000	1.755264000	-0.284694000
C	0.597850000	3.307425000	1.886883000
C	0.584902000	2.847285000	-0.487416000
C	0.168539000	3.624569000	0.597271000
H	1.786490000	1.978551000	3.095426000
H	1.738997000	1.151114000	-1.132194000
H	0.269473000	3.902415000	2.734575000
H	0.235355000	3.081610000	-1.487506000
H	-0.498925000	4.465677000	0.434357000
C	4.678110000	0.771441000	0.716865000
C	4.824408000	2.061412000	0.185547000
C	5.819881000	-0.043947000	0.830234000
C	6.078049000	2.519655000	-0.231621000
C	7.066389000	0.409220000	0.401156000
C	7.200032000	1.696045000	-0.130434000
H	3.962592000	2.713657000	0.091031000
H	5.730578000	-1.043769000	1.248953000
H	6.172950000	3.522153000	-0.640340000
H	7.934518000	-0.238570000	0.487514000
H	8.172223000	2.053244000	-0.458417000
C	-2.348964000	1.473708000	-1.117259000
C	-2.864882000	2.782713000	-1.115682000
C	-1.679035000	1.021995000	-2.265626000
C	-2.732099000	3.605676000	-2.233927000
C	-1.541546000	1.849000000	-3.383468000
C	-2.067844000	3.142280000	-3.374030000
H	-3.374340000	3.162467000	-0.234085000
H	-1.252338000	0.024884000	-2.291098000
H	-3.144710000	4.610730000	-2.213610000
H	-1.020007000	1.478788000	-4.262029000
H	-1.961421000	3.784084000	-4.244007000
C	-4.158255000	0.540633000	0.953145000
C	-4.438971000	0.243818000	2.297523000
C	-5.229357000	0.812192000	0.086007000
C	-5.755659000	0.199087000	2.759946000
C	-6.545327000	0.780182000	0.551705000
C	-6.812708000	0.469368000	1.887627000
H	-3.621658000	0.046620000	2.987444000
H	-5.038308000	1.058022000	-0.953821000
H	-5.954180000	-0.036982000	3.801814000
H	-7.362629000	0.995347000	-0.131487000
H	-7.837578000	0.443555000	2.247225000
C	1.012894000	-2.290912000	1.733168000
H	0.933206000	-3.314800000	2.107351000
H	1.522421000	-1.714866000	2.510541000
C	-0.388919000	-1.673408000	1.548039000
H	-0.968283000	-1.853050000	2.463974000
H	-0.267320000	-0.590318000	1.483545000
H	2.130176000	-4.193564000	-2.359496000
H	-2.041881000	-4.860195000	-1.528633000

ii

N	-0.333984000	-3.103134000	1.058975000
N	0.200811000	-3.658634000	0.064911000
C	1.544618000	-3.213519000	-0.081524000
C	1.668797000	-1.820526000	-0.312161000
C	2.627125000	-4.089039000	-0.126695000
C	2.976696000	-1.308070000	-0.483987000
C	3.903141000	-3.563610000	-0.311388000
C	4.073929000	-2.187911000	-0.470978000
H	4.767642000	-4.220936000	-0.320966000
H	5.077049000	-1.797835000	-0.600658000
C	-1.723235000	-2.855333000	0.904854000
C	-2.683481000	-3.296276000	1.812662000
C	-1.993725000	-1.888215000	-0.095144000
C	-3.979215000	-2.797557000	1.706036000
C	-3.292421000	-1.331332000	-0.125169000
C	-4.272372000	-1.813766000	0.760617000
H	-4.754951000	-3.147054000	2.381121000
H	-5.274402000	-1.401098000	0.730299000
P	3.207610000	0.504425000	-0.828552000
P	-3.691768000	0.008820000	-1.358578000

C	5.046387000	0.687552000	-0.783407000
C	5.725577000	0.720659000	-2.012044000
C	5.788256000	0.792363000	0.404885000
C	7.116353000	0.844226000	-2.053639000
C	7.176881000	0.924814000	0.362510000
C	7.843887000	0.948761000	-0.866045000
H	5.164267000	0.649644000	-2.940509000
H	5.279929000	0.769712000	1.364055000
H	7.628611000	0.866319000	-3.011514000
H	7.738994000	1.006731000	1.288862000
H	8.924977000	1.052442000	-0.896669000
C	2.719779000	1.305824000	0.767947000
C	2.431784000	0.611678000	1.952933000
C	2.629665000	2.708321000	0.768515000
C	2.058232000	1.303964000	3.108181000
C	2.276851000	3.400422000	1.927528000
C	1.983787000	2.698798000	3.100690000
H	2.493203000	-0.471747000	1.977894000
H	2.837295000	3.262941000	-0.143496000
H	1.832069000	0.750610000	4.015592000
H	2.220173000	4.485387000	1.911967000
H	1.698647000	3.235624000	4.001135000
C	-2.585181000	1.378674000	-0.777688000
C	-2.251871000	2.373817000	-1.710917000
C	-2.022093000	1.443145000	0.508109000
C	-1.380781000	3.409981000	-1.367598000
C	-1.137788000	2.469446000	0.845644000
C	-0.815770000	3.454733000	-0.091029000
H	-2.665090000	2.331011000	-2.715818000
H	-2.258310000	0.679542000	1.242259000
H	-1.131096000	4.170666000	-2.102131000
H	-0.687457000	2.491881000	1.833600000
H	-0.119016000	4.244867000	0.171586000
C	-5.362172000	0.570287000	-0.799049000
C	-6.475416000	0.048606000	-1.478651000
C	-5.574854000	1.476833000	0.252313000
C	-7.771990000	0.411202000	-1.106871000
C	-6.870411000	1.848313000	0.615517000
C	-7.971436000	1.314018000	-0.060037000
H	-6.327647000	-0.646168000	-2.301945000
H	-4.728590000	1.894591000	0.788719000
H	-8.622981000	-0.004724000	-1.639133000
H	-7.020323000	2.553358000	1.428734000
H	-8.978947000	1.603675000	0.225438000
C	0.444044000	-0.897342000	-0.395490000
H	0.223109000	-0.486044000	0.593814000
H	0.740311000	-0.031492000	-0.996533000
C	-0.874548000	-1.440561000	-1.044195000
H	-1.259368000	-0.640799000	-1.676389000
H	-0.636647000	-2.255740000	-1.733050000
H	-2.411685000	-4.019481000	2.575186000
H	2.462626000	-5.152446000	0.016892000

iii

N	0.770127000	3.722880000	-1.840428000
N	-0.440547000	3.938773000	-1.623910000
C	-1.116763000	3.268926000	-0.534088000
C	-0.907296000	3.527107000	0.835646000
C	-2.064215000	2.338054000	-0.965629000
C	-1.642901000	2.738674000	1.732256000
C	-2.764440000	1.538423000	-0.053393000
C	-2.535645000	1.752120000	1.312621000
H	-1.497858000	2.896409000	2.798085000
H	-3.055443000	1.158189000	2.057106000
C	1.543599000	2.905772000	-0.936334000
C	1.944042000	1.634328000	-1.347318000
C	1.962518000	3.452214000	0.288101000
C	2.742987000	0.848626000	-0.504886000
C	2.818935000	2.684586000	1.083849000
C	3.201114000	1.399156000	0.702491000
H	3.164416000	3.091918000	2.030805000
H	3.840076000	0.815878000	1.357518000
C	-0.002111000	4.614501000	1.387154000
H	-0.522683000	5.579048000	1.326909000
H	0.135646000	4.406059000	2.452372000
C	1.401821000	4.775997000	0.734799000
H	1.336269000	5.459901000	-0.116475000
H	2.067759000	5.242559000	1.466256000
P	-4.015111000	0.351202000	-0.727079000
P	3.035162000	-0.904028000	-1.013661000
H	-2.208619000	2.216236000	-2.035891000
H	1.596175000	1.251261000	-2.303129000
C	4.549136000	-1.340807000	-0.043649000
C	5.792316000	-1.080058000	-0.644815000
C	4.524465000	-1.907805000	1.240581000
C	6.982094000	-1.363845000	0.027350000
C	5.716017000	-2.200943000	1.908355000
C	6.946314000	-1.927626000	1.305627000
H	5.829876000	-0.652552000	-1.644138000
H	3.574653000	-2.119853000	1.721639000
H	7.935249000	-1.152899000	-0.449743000
H	5.681771000	-2.640056000	2.901802000
H	7.871738000	-2.156325000	1.826903000
C	1.702565000	-1.776913000	-0.067093000
C	0.828166000	-1.147640000	0.833270000
C	1.544101000	-3.153117000	-0.310641000
C	-0.176243000	-1.877909000	1.474101000
C	0.550494000	-3.883635000	0.340937000
C	-0.314862000	-3.246051000	1.234525000
H	0.916012000	-0.084798000	1.032262000

H	2.201676000	-3.655862000	-1.016241000
H	-0.857846000	-1.372481000	2.151942000
H	0.444819000	-4.946689000	0.142888000
H	-1.098098000	-3.809539000	1.733100000
C	-2.987817000	-0.731258000	-1.819747000
C	-1.588807000	-0.832505000	-1.749014000
C	-3.673895000	-1.502483000	-2.773271000
C	-0.894640000	-1.682706000	-2.611890000
C	-2.980319000	-2.362798000	-3.626532000
C	-1.588095000	-2.451409000	-3.550007000
H	-1.035525000	-0.252626000	-1.019632000
H	-4.756222000	-1.429051000	-2.850173000
H	0.186415000	-1.750414000	-2.540141000
H	-3.525967000	-2.954425000	-4.356519000
H	-1.046081000	-3.113681000	-4.219424000
C	-4.349903000	-0.736006000	0.731202000
C	-5.367758000	-0.335682000	1.614121000
C	-3.659081000	-1.929627000	0.991318000
C	-5.670052000	-1.096727000	2.745196000
C	-3.973036000	-2.697578000	2.114712000
C	-4.973874000	-2.281750000	2.996644000
H	-5.924706000	0.577568000	1.417923000
H	-2.872679000	-2.260334000	0.322035000
H	-6.454598000	-0.769771000	3.422016000
H	-3.433032000	-3.621930000	2.301446000
H	-5.214592000	-2.880551000	3.870659000

iv

N	0.809932000	-0.317178000	-0.121184000
N	-0.159267000	0.276177000	-0.661063000
C	-1.397783000	-0.344694000	-0.342706000
C	-1.506690000	-1.661025000	-0.853895000
C	-2.469029000	0.320598000	0.244487000
C	-2.747907000	-2.286781000	-0.703036000
C	-3.700611000	-0.334281000	0.398199000
C	-3.823656000	-1.647122000	-0.080623000
H	-2.881057000	-3.295348000	-1.087337000
H	-4.768854000	-2.171874000	0.011087000
C	1.974516000	-0.268955000	-0.934802000
C	3.201568000	0.218783000	-0.490997000
C	1.823647000	-0.953188000	-2.164569000
C	4.330631000	0.108657000	-1.312694000
C	2.971506000	-1.073611000	-2.956027000
C	4.195289000	-0.535853000	-2.553662000
H	2.905784000	-1.595305000	-3.907624000
H	5.058993000	-0.636640000	-3.206194000
C	-0.354362000	-2.374917000	-1.570396000
H	0.318854000	-2.820610000	-0.829523000
H	-0.801492000	-3.217867000	-2.106343000
C	0.496116000	-1.572947000	-2.616711000
H	0.741144000	-2.269049000	-3.424833000
H	-0.133451000	-0.801110000	-3.073435000
P	-5.061113000	0.609251000	1.225635000
H	-2.327937000	1.339916000	0.594407000
P	6.007213000	0.743637000	-0.854323000
H	3.256998000	0.694307000	0.482612000
C	-5.718683000	1.627644000	-0.172117000
C	-6.540410000	2.717757000	0.160993000
C	-5.446625000	1.374753000	-1.526224000
C	-7.089462000	3.526847000	-0.835079000
C	-5.987841000	2.191398000	-2.521857000
C	-6.811797000	3.266533000	-2.179640000
H	-6.751435000	2.934965000	1.205518000
H	-4.812441000	0.539162000	-1.805608000
H	-7.725459000	4.364172000	-0.561269000
H	-5.767214000	1.985083000	-3.565733000
H	-7.231355000	3.900610000	-2.955743000
C	-6.366356000	-0.686698000	1.422469000
C	-6.334670000	-1.452236000	2.600750000
C	-7.371309000	-0.943075000	0.476549000
C	-7.274245000	-2.460512000	2.821118000
C	-8.318586000	-1.944430000	0.703412000
C	-8.270933000	-2.706960000	1.873022000
H	-5.569473000	-1.259553000	3.349144000
H	-7.415288000	-0.362977000	-0.439848000
H	-7.233375000	-3.046639000	3.735092000
H	-9.092389000	-2.130095000	-0.036641000
H	-9.008352000	-3.485715000	2.046703000
C	6.760464000	-0.726696000	-0.020349000
C	8.146964000	-0.690510000	0.207419000
C	6.037877000	-1.858103000	0.390185000
C	8.792800000	-1.751040000	0.844420000
C	6.687203000	-2.924348000	1.017373000
C	8.063783000	-2.872717000	1.248848000
H	8.724474000	0.173223000	-0.113965000
H	4.966489000	-1.908998000	0.223643000
H	9.864493000	-1.705112000	1.017577000
H	6.114830000	-3.794240000	1.328234000
H	8.566319000	-3.702711000	1.737668000
C	5.616558000	1.848936000	0.577355000
C	5.617949000	1.431967000	1.917780000
C	5.296201000	3.185729000	0.284620000
C	5.300414000	2.330555000	2.939295000
C	4.968662000	4.079795000	1.304900000
C	4.972406000	3.654089000	2.636034000
H	5.863489000	0.404355000	2.166699000
H	5.300756000	3.528459000	-0.747523000
H	5.306025000	1.993801000	3.972447000
H	4.718325000	5.108729000	1.061597000
H	4.724860000	4.350689000	3.432153000

v

N	0.655787000	-2.095124000	1.030592000
N	-0.567796000	-2.188993000	1.259480000
C	-1.528969000	-2.331363000	0.187234000
C	-1.636235000	-3.588639000	-0.436639000
C	-2.405089000	-1.276922000	-0.111399000
C	-2.644068000	-3.769430000	-1.386225000
C	-3.371970000	-1.483449000	-1.109491000
C	-3.504490000	-2.723866000	-1.729876000
H	-2.737599000	-4.735063000	-1.876585000
H	-4.015038000	-0.659979000	-1.404145000
H	-4.268232000	-2.873991000	-2.487242000
C	1.157603000	-1.981680000	-0.322719000
C	1.767772000	-0.740288000	-0.615463000
C	1.145556000	-3.043570000	-1.246941000
C	2.257696000	-0.526035000	-1.907365000
C	1.667428000	-2.783013000	-2.524722000
C	2.195213000	-1.541025000	-2.863378000
H	2.695103000	0.431466000	-2.166861000
H	1.653195000	-3.579783000	-3.263691000
H	2.578086000	-1.368108000	-3.865041000
P	-2.121496000	0.352017000	0.713910000
P	1.851911000	0.538540000	0.738965000
C	-1.907670000	1.420034000	-0.794002000
C	-1.123122000	0.933229000	-1.856594000
C	-2.364744000	2.745846000	-0.856412000
C	-0.810285000	1.745886000	-2.945971000
C	-2.050681000	3.557681000	-1.950290000
C	-1.271324000	3.063645000	-2.998463000
H	-0.748961000	-0.084576000	-1.836343000
H	-2.977543000	3.153104000	-0.058961000
H	-0.197930000	1.346676000	-3.749857000
H	-2.421290000	4.578858000	-1.980722000
H	-1.024932000	3.698096000	-3.845049000
C	-3.768122000	0.847748000	1.396259000
C	-3.789365000	2.037416000	2.150131000
C	-4.948462000	0.092311000	1.311411000
C	-4.966376000	2.486922000	2.749627000
C	-6.121511000	0.533650000	1.929174000
C	-6.139113000	1.735749000	2.639090000
H	-2.875874000	2.613320000	2.277509000
H	-4.961154000	-0.848412000	0.773151000
H	-4.961699000	3.413918000	3.316324000
H	-7.024090000	-0.066767000	1.852880000
H	-7.054283000	2.077266000	3.114521000
C	3.333345000	-0.058043000	1.676258000
C	3.494621000	0.428205000	2.984163000
C	4.289962000	-0.949798000	1.165113000
C	4.591809000	0.045165000	3.757639000
C	5.382682000	-1.340313000	1.942555000
C	5.538000000	-0.842223000	3.238644000
H	2.754709000	1.107164000	3.401325000
H	4.184264000	-1.340626000	0.157833000
H	4.702261000	0.431993000	4.767006000
H	6.113957000	-2.032650000	1.533816000
H	6.388536000	-1.147340000	3.842002000
C	2.525111000	2.003020000	-0.172700000
C	1.592105000	2.949348000	-0.629777000
C	3.890138000	2.226311000	-0.417791000
C	2.011162000	4.079902000	-1.333566000
C	4.309072000	3.364024000	-1.110911000
C	3.370894000	4.290907000	-1.574110000
H	0.533241000	2.800680000	-0.440246000
H	4.628404000	1.510934000	-0.068771000
H	1.273668000	4.794282000	-1.688342000
H	5.368620000	3.524828000	-1.291574000
H	3.698993000	5.174399000	-2.114964000
C	-0.616767000	-4.652480000	-0.124738000
H	-0.390875000	-4.649198000	0.945373000
H	-1.022375000	-5.641115000	-0.358293000
C	0.691881000	-4.462164000	-0.939714000
H	1.503221000	-4.984268000	-0.416060000
H	0.571327000	-4.970829000	-1.900845000

vi

N	-0.187475000	1.563981000	0.007251000
N	0.807545000	1.695729000	-0.751183000
C	1.993074000	1.935614000	-0.009006000
C	1.968367000	3.148933000	0.716445000
C	3.129805000	1.121110000	-0.117225000
C	3.156056000	3.522017000	1.354276000
C	4.287994000	1.523651000	0.562497000
C	4.296915000	2.716631000	1.287119000
H	3.189632000	4.457048000	1.907692000
H	5.180863000	0.908843000	0.523680000
H	5.203722000	3.026368000	1.798958000
C	-1.385960000	2.058661000	-0.575763000
C	-2.549105000	1.284831000	-0.715948000
C	-1.353421000	3.458313000	-0.776984000
C	-3.706328000	1.934495000	-1.166492000
C	-2.542565000	4.063473000	-1.198862000
C	-3.699592000	3.310109000	-1.407040000
H	-4.618080000	1.369265000	-1.325535000
H	-2.560958000	5.137532000	-1.365774000
H	-4.609074000	3.800607000	-1.742255000

P	2.984107000	-0.375028000	-1.186413000
P	-2.409936000	-0.545697000	-0.422391000
C	4.632429000	-1.175232000	-0.946094000
C	5.612210000	-0.956273000	-1.927497000
C	4.950473000	-1.971191000	0.166667000
C	6.887271000	-1.511420000	-1.795595000
C	6.222110000	-2.532189000	0.293611000
C	7.193170000	-2.302155000	-0.685754000
H	5.376757000	-0.349950000	-2.798755000
H	4.203515000	-2.151455000	0.933942000
H	7.636418000	-1.332698000	-2.561944000
H	6.456168000	-3.147114000	1.158438000
H	8.182244000	-2.740408000	-0.585056000
C	1.866870000	-1.483995000	-0.215552000
C	1.449936000	-2.666749000	-0.849835000
C	1.400047000	-1.211134000	1.079438000
C	0.603939000	-3.564327000	-0.197543000
C	0.539751000	-2.102015000	1.724476000
C	0.144467000	-3.281933000	1.091371000
H	1.787662000	-2.887450000	-1.859812000
H	1.697241000	-0.299595000	1.587153000
H	0.294259000	-4.476279000	-0.700660000
H	0.167618000	-1.866527000	2.717152000
H	-0.529052000	-3.968854000	1.594984000
C	-2.595608000	-0.677574000	1.415393000
C	-2.916330000	-1.939445000	1.949232000
C	-2.305781000	0.369878000	2.301467000
C	-2.949532000	-2.145524000	3.327605000
C	-2.326950000	0.158846000	3.683408000
C	-2.647146000	-1.096741000	4.202307000
H	-3.141797000	-2.766868000	1.282016000
H	-2.057794000	1.355022000	1.922935000
H	-3.205960000	-3.126395000	3.718893000
H	-2.096531000	0.982906000	4.353393000
H	-2.664650000	-1.257789000	5.276563000
C	-4.050537000	-1.156208000	-1.016249000
C	-4.089864000	-1.756110000	-2.284967000
C	-5.243925000	-1.047333000	-0.281335000
C	-5.293781000	-2.228893000	-2.812980000
C	-6.445096000	-1.526736000	-0.805668000
C	-6.472745000	-2.116814000	-2.073118000
H	-3.173169000	-1.856873000	-2.860756000
H	-5.231863000	-0.589759000	0.703168000
H	-5.308059000	-2.690482000	-3.796423000
H	-7.360147000	-1.437607000	-0.226375000
H	-7.408710000	-2.490412000	-2.479145000
C	0.730430000	4.053008000	0.784443000
H	0.057879000	3.692686000	1.570976000
H	1.084476000	5.030756000	1.125858000
C	-0.098272000	4.304426000	-0.523128000
H	-0.433037000	5.345722000	-0.488319000
H	0.570699000	4.238634000	-1.388151000

vii

N	-0.750993000	1.952385000	0.890446000
N	0.492536000	1.863062000	0.970256000
C	1.394980000	2.270312000	-0.070120000
C	1.483990000	3.637374000	-0.378893000
C	2.336409000	1.339224000	-0.572260000
C	2.463752000	4.050674000	-1.290506000
C	3.276224000	1.785046000	-1.504965000
C	3.334582000	3.133142000	-1.869289000
H	2.536476000	5.106073000	-1.539544000
H	3.974710000	1.084565000	-1.947709000
H	4.078203000	3.463949000	-2.587818000
C	-1.491610000	2.298787000	-0.302033000
C	-2.368094000	1.265212000	-0.742768000
C	-1.526010000	3.570804000	-0.902927000
C	-3.203962000	1.491624000	-1.834477000
C	-2.404803000	3.754626000	-1.987015000
C	-3.226010000	2.741116000	-2.455892000
H	-3.838833000	0.697429000	-2.208589000
H	-2.433474000	4.730075000	-2.464983000
H	-3.885079000	2.916320000	-3.300632000
P	2.298816000	-0.424884000	-0.013074000
P	-2.289289000	-0.422342000	0.015928000
C	3.451916000	-1.366357000	-1.079822000
C	2.947214000	-2.312265000	-1.983716000
C	4.842398000	-1.190220000	-0.965373000
C	3.821901000	-3.060035000	-2.774849000
C	5.710382000	-1.935713000	-1.762218000
C	5.201024000	-2.870740000	-2.668418000
H	1.876401000	-2.457656000	-2.070511000
H	5.244490000	-0.476874000	-0.252450000
H	3.422934000	-3.792143000	-3.470982000
H	6.782980000	-1.791056000	-1.670728000
H	5.879254000	-3.454539000	-3.284298000
C	3.149637000	-0.416260000	1.608827000
C	3.489547000	-1.656989000	2.173996000
C	3.453007000	0.763361000	2.300910000
C	4.135527000	-1.712571000	3.407051000
C	4.095625000	0.701324000	3.539957000
C	4.438250000	-0.532831000	4.094105000
H	3.253624000	-2.577005000	1.647915000
H	3.200767000	1.730169000	1.880477000
H	4.397259000	-2.676428000	3.833986000
H	4.330346000	1.621344000	4.067687000
H	4.939009000	-0.577373000	5.057082000

C	-3.130838000	-0.283703000	1.635617000
C	-3.331845000	-1.463876000	2.370823000
C	-3.599939000	0.934919000	2.143866000
C	-3.998468000	-1.422496000	3.594030000
C	-4.263199000	0.970967000	3.372523000
C	-4.463264000	-0.204445000	4.098714000
H	-2.967657000	-2.410996000	1.986900000
H	-3.459630000	1.853568000	1.585949000
H	-4.150184000	-2.340382000	4.154611000
H	-4.626011000	1.919684000	3.757643000
H	-4.980067000	-0.172996000	5.053741000
C	-3.427462000	-1.486207000	-0.949026000
C	-2.899617000	-2.452400000	-1.817861000
C	-4.821261000	-1.368113000	-0.808206000
C	-3.755511000	-3.282684000	-2.544572000
C	-5.670956000	-2.197422000	-1.539369000
C	-5.139170000	-3.155167000	-2.408358000
H	-1.824949000	-2.549191000	-1.928183000
H	-5.239835000	-0.632119000	-0.128464000
H	-3.338710000	-4.029979000	-3.213613000
H	-6.746850000	-2.099086000	-1.427044000
H	-5.803233000	-3.803269000	-2.973280000
C	0.563854000	4.626459000	0.292972000
H	0.384055000	4.325693000	1.329270000
H	1.055320000	5.603160000	0.334679000
C	-0.774931000	4.807771000	-0.442103000
H	-1.443093000	5.398132000	0.199224000
H	-0.594212000	5.418799000	-1.332726000
Pd	0.010928000	-0.962889000	-0.044920000
Cl	0.003552000	-0.425125000	-2.370381000
Cl	0.030564000	-1.831829000	2.137490000

viii

N	-0.537255000	2.049244000	0.722706000
N	0.451883000	1.905685000	-0.028943000
C	1.630785000	2.208083000	0.687155000
C	1.661461000	3.524596000	1.190040000
C	2.675196000	1.282631000	0.781197000
C	2.859132000	3.897176000	1.814991000
C	3.834053000	1.688297000	1.451223000
C	3.918571000	2.993056000	1.949890000
H	2.960654000	4.900816000	2.219927000
H	4.660838000	1.001950000	1.595454000
H	4.825684000	3.308027000	2.457148000
C	-1.712376000	2.340990000	0.008127000
C	-2.707673000	1.415143000	-0.301546000
C	-1.749952000	3.715059000	-0.295882000
C	-3.875238000	1.925429000	-0.899077000
C	-2.933253000	4.177196000	-0.876665000
C	-3.986757000	3.293193000	-1.155183000
H	-4.684297000	1.257214000	-1.174089000
H	-3.031503000	5.228581000	-1.135375000
H	-4.898661000	3.675678000	-1.603782000
P	2.392402000	-0.386719000	0.014220000
P	-2.384192000	-0.388584000	-0.006173000
C	3.160384000	-0.227555000	-1.643249000
C	3.311754000	1.020180000	-2.263598000
C	3.543753000	-1.391232000	-2.329898000
C	3.850669000	1.102386000	-3.549222000
C	4.084418000	-1.302945000	-3.611422000
C	4.239035000	-0.056096000	-4.224406000
H	3.016580000	1.929344000	-1.750635000
H	3.425465000	-2.364139000	-1.862699000
H	3.969019000	2.074542000	-4.019255000
H	4.381779000	-2.208504000	-4.132387000
H	4.659247000	0.010769000	-5.223893000
C	3.476245000	-1.582746000	0.878100000
C	2.912115000	-2.613171000	1.643661000
C	4.874351000	-1.508714000	0.740229000
C	3.736389000	-3.543390000	2.280507000
C	5.691757000	-2.436437000	1.384602000
C	5.123955000	-3.453791000	2.157228000
H	1.835525000	-2.682036000	1.746141000
H	5.322996000	-0.740217000	0.118632000
H	3.290276000	-4.338942000	2.870222000
H	6.770315000	-2.369705000	1.275277000
H	5.762560000	-4.178992000	2.653588000
C	-3.250448000	-0.804113000	1.551834000
C	-2.943358000	-2.024806000	2.174442000
C	-4.226211000	0.032188000	2.111433000
C	-3.622958000	-2.413404000	3.328384000
C	-4.892695000	-0.354750000	3.276073000
C	-4.596444000	-1.577322000	3.882374000
H	-2.168783000	-2.662380000	1.760262000
H	-4.468238000	0.981762000	1.645584000
H	-3.381861000	-3.360704000	3.801868000
H	-5.644560000	0.300424000	3.706634000
H	-5.117817000	-1.875645000	4.787532000
C	-3.368437000	-1.213370000	-1.319395000
C	-3.269932000	-0.758610000	-2.646252000
C	-4.178304000	-2.322946000	-1.034066000
C	-3.982921000	-1.394667000	-3.661382000
C	-4.881296000	-2.962368000	-2.057573000
C	-4.787833000	-2.499667000	-3.371137000
H	-2.642940000	0.092580000	-2.884505000
H	-4.273648000	-2.688830000	-0.017591000
H	-3.903529000	-1.028803000	-4.681026000
H	-5.507686000	-3.817996000	-1.821928000
H	-5.339150000	-2.995784000	-4.164861000
C	0.461368000	4.500892000	1.129734000

H	-0.145801000	4.345544000	2.027814000
H	0.894178000	5.501213000	1.237324000
C	-0.495915000	4.599277000	-0.123395000
H	-0.843971000	5.636577000	-0.153001000
H	0.114995000	4.468023000	-1.025666000
Pd	0.023352000	-0.769061000	0.016376000
Cl	0.117791000	-0.676838000	2.400326000
Cl	0.003517000	-1.189074000	-2.302109000

ix

N	0.624112000	4.626899000	-0.358345000
N	-0.624043000	4.626914000	-0.358261000
C	-1.359941000	3.505006000	-0.898965000
C	-1.475675000	2.310453000	-0.167855000
C	-2.027739000	3.714951000	-2.106712000
C	-2.269335000	1.279496000	-0.729258000
C	-2.796634000	2.687121000	-2.642213000
C	-2.911377000	1.476252000	-1.960213000
H	-3.305254000	2.824922000	-3.591352000
H	-3.499706000	0.679714000	-2.399291000
C	1.359911000	3.504967000	-0.899131000
C	2.027555000	3.714861000	-2.106972000
C	1.475714000	2.310431000	-0.168004000
C	2.796342000	2.686991000	-2.642553000
C	2.269291000	1.279449000	-0.729476000
C	2.911149000	1.476138000	-1.960534000
H	3.304829000	2.824749000	-3.591770000
H	3.499382000	0.679564000	-2.399675000
P	-2.305930000	-0.397501000	0.048316000
P	2.305961000	-0.397474000	0.048224000
C	-3.405389000	-1.467390000	-0.953434000
C	-2.889495000	-2.610472000	-1.579193000
C	-4.781636000	-1.191708000	-1.036851000
C	-3.738005000	-3.460362000	-2.292532000
C	-5.621980000	-2.038367000	-1.757888000
C	-5.100820000	-3.173728000	-2.386756000
H	-1.829747000	-2.829517000	-1.514513000
H	-5.194405000	-0.319670000	-0.538237000
H	-3.331029000	-4.345202000	-2.773341000
H	-6.683194000	-1.816213000	-1.823015000
H	-5.758509000	-3.835220000	-2.943536000
C	-3.258678000	-0.232285000	1.604631000
C	-3.380423000	-1.367188000	2.422891000
C	-3.898318000	0.958969000	1.973706000
C	-4.133852000	-1.307824000	3.593579000
C	-4.648602000	1.014112000	3.151036000
C	-4.766827000	-0.116252000	3.961425000
H	-2.881981000	-2.290822000	2.146318000
H	-3.818420000	1.841673000	1.347618000
H	-4.221604000	-2.189367000	4.222016000
H	-5.142328000	1.940785000	3.429416000
H	-5.350064000	-0.071007000	4.876753000
C	3.405208000	-1.467603000	-0.953484000
C	4.781379000	-1.191770000	-1.037613000
C	2.889229000	-2.611134000	-1.578352000
C	5.621559000	-2.038734000	-1.758487000
C	3.737579000	-3.461341000	-2.291503000
C	5.100316000	-3.174559000	-2.386447000
H	5.194215000	-0.319375000	-0.539686000
H	1.829539000	-2.830295000	-1.513102000
H	6.682714000	-1.816456000	-1.824187000
H	3.330544000	-4.346538000	-2.771603000
H	5.757882000	-3.836292000	-2.943085000
C	3.258878000	-0.232064000	1.604418000
C	3.380692000	-1.366827000	2.422859000
C	3.898551000	0.959250000	1.973239000
C	4.134214000	-1.307260000	3.593481000
C	4.648930000	1.014594000	3.150497000
C	4.767216000	-0.115628000	3.961074000
H	2.882228000	-2.290505000	2.146487000
H	3.818596000	1.841848000	1.347012000
H	4.222015000	-2.188690000	4.222067000
H	5.142677000	1.941313000	3.428675000
H	5.350521000	-0.070225000	4.876351000
C	-0.785522000	2.234697000	1.178921000
H	-1.123660000	3.095600000	1.766391000
H	-1.114392000	1.354065000	1.727822000
C	0.785697000	2.234710000	1.178846000
H	1.123882000	3.095632000	1.766258000
H	1.114627000	1.354100000	1.727744000
H	-1.925958000	4.668724000	-2.615247000
H	1.925736000	4.668623000	-2.615518000
Pd	0.000028000	-0.914815000	0.116045000
Cl	0.000125000	-0.816485000	-2.264028000
Cl	0.000088000	-1.228587000	2.447515000

x

N	0.784056000	-2.310407000	2.453609000
N	1.093948000	-3.133934000	1.553601000
C	2.401733000	-2.868684000	1.064528000
C	2.533289000	-1.589454000	0.473428000
C	3.411326000	-3.828605000	1.036091000
C	3.794691000	-1.258085000	-0.075807000
C	4.641264000	-3.482534000	0.483598000
C	4.831659000	-2.207078000	-0.051432000
H	5.456908000	-4.199618000	0.475701000
H	5.800871000	-1.953653000	-0.466421000
C	-0.602858000	-2.016292000	2.468823000

C	-1.399482000	-2.172610000	3.602114000
C	-1.041721000	-1.355038000	1.299420000
C	-2.717141000	-1.728652000	3.566995000
C	-2.380563000	-0.899108000	1.303010000
C	-3.204917000	-1.096316000	2.423744000
H	-3.365893000	-1.866627000	4.426068000
H	-4.232274000	-0.754323000	2.412943000
P	4.021085000	0.394117000	-0.902046000
P	-3.088808000	-0.070843000	-0.173331000
C	5.848717000	0.454327000	-1.174242000
C	6.317227000	0.102711000	-2.451273000
C	6.779732000	0.827799000	-0.191540000
C	7.684481000	0.108145000	-2.735963000
C	8.145470000	0.843717000	-0.479759000
C	8.601256000	0.481009000	-1.750380000
H	5.608683000	-0.177605000	-3.226919000
H	6.439951000	1.109331000	0.800021000
H	8.031030000	-0.170115000	-3.727412000
H	8.854316000	1.137837000	0.289541000
H	9.664858000	0.493747000	-1.971812000
C	3.768626000	1.565522000	0.507515000
C	3.957343000	1.218276000	1.855348000
C	3.318136000	2.858674000	0.198289000
C	3.702570000	2.144808000	2.868166000
C	3.069161000	3.787276000	1.211199000
C	3.257980000	3.430443000	2.548534000
H	4.289145000	0.217601000	2.115401000
H	3.150351000	3.137931000	-0.839096000
H	3.846501000	1.860293000	3.906937000
H	2.718241000	4.783401000	0.956362000
H	3.053455000	4.148076000	3.338079000
C	-4.882303000	0.119108000	0.104374000
C	-5.809091000	-0.716399000	-0.534474000
C	-5.330615000	1.135521000	0.966322000
C	-7.174423000	-0.541015000	-0.300222000
C	-6.694370000	1.298103000	1.198662000
C	-7.617804000	0.460753000	0.564619000
H	-5.476870000	-1.495235000	-1.211578000
H	-4.615828000	1.795720000	1.449111000
H	-7.889478000	-1.188652000	-0.798656000
H	-7.035658000	2.082854000	1.866986000
H	-8.681082000	0.594492000	0.741116000
C	-2.845553000	-1.273810000	-1.529645000
C	-2.507615000	-0.878607000	-2.830926000
C	-2.989640000	-2.640859000	-1.228664000
C	-2.323146000	-1.842393000	-3.823219000
C	-2.811519000	-3.595095000	-2.229285000
C	-2.475156000	-3.197965000	-3.526180000
H	-2.386347000	0.170662000	-3.069661000
H	-3.236150000	-2.960808000	-0.221436000
H	-2.055996000	-1.529458000	-4.828141000
H	-2.927829000	-4.648151000	-1.991316000
H	-2.327095000	-3.944467000	-4.301030000
C	1.357656000	-0.604231000	0.408490000
H	1.344510000	0.027665000	1.299870000
H	1.570084000	0.085049000	-0.413872000
C	-0.086239000	-1.133869000	0.119935000
H	-0.531835000	-0.381933000	-0.530493000
H	-0.038477000	-2.045268000	-0.484107000
H	-0.985843000	-2.653677000	4.482803000
H	3.235175000	-4.807097000	1.471869000
Pd	-2.256743000	1.971650000	-0.570243000
Cl	-3.671396000	2.371694000	-2.377919000
Cl	-0.785450000	2.113038000	1.213176000

xi

N	0.623942000	-2.896644000	4.292493000
N	-0.623881000	-2.896779000	4.292423000
C	-1.351660000	-1.749501000	3.796037000
C	-1.470268000	-1.529140000	2.414584000
C	-1.995062000	-0.954124000	4.745142000
C	-2.258426000	-0.426951000	2.004571000
C	-2.739209000	0.139166000	4.317587000
C	-2.864472000	0.405202000	2.955237000
H	-3.222613000	0.787982000	5.040832000
H	-3.425853000	1.278411000	2.650685000
C	1.351548000	-1.749231000	3.796176000
C	1.994697000	-0.953673000	4.745296000
C	1.470289000	-1.528941000	2.414719000
C	2.738733000	0.139697000	4.317749000
C	2.258324000	-0.426665000	2.004721000
C	2.864140000	0.405645000	2.955396000
H	3.221937000	0.788646000	5.041008000
H	3.425443000	1.278898000	2.650837000
P	-2.272630000	0.073942000	0.232124000
P	2.272586000	0.074006000	0.232226000
C	-3.377464000	1.522494000	0.045970000
C	-2.965116000	2.675073000	-0.631922000
C	-4.716999000	1.466736000	0.449996000
C	-3.828816000	3.746481000	-0.841737000
C	-5.596249000	2.523084000	0.253822000
C	-5.144093000	3.670762000	-0.394057000
C	-3.206499000	-1.148884000	-0.768151000
C	-3.305617000	-0.885088000	-2.139377000
C	-3.812174000	-2.317369000	-0.302081000
C	-3.953531000	-1.741753000	-3.017371000
C	-4.465207000	-3.195367000	-1.163629000
C	-4.535826000	-2.906646000	-2.522586000
C	3.377046000	1.522843000	0.045890000
C	4.716533000	1.467596000	0.450127000

C	2.964513000	2.675074000	-0.632485000
C	5.595542000	2.524108000	0.253737000
C	3.827960000	3.746633000	-0.842537000
C	5.143188000	3.671437000	-0.394615000
C	3.206853000	-1.148730000	-0.767743000
C	3.306180000	-0.885106000	-2.138987000
C	3.812663000	-2.317042000	-0.301404000
C	3.954474000	-1.741744000	-3.016728000
C	4.466092000	-3.194997000	-1.162693000
C	4.536934000	-2.906441000	-2.521673000
C	-0.786716000	-2.507325000	1.481858000
H	-1.127794000	-3.511076000	1.755864000
H	-1.111070000	-2.355336000	0.453455000
C	0.786976000	-2.507286000	1.481995000
H	1.128067000	-3.510978000	1.756199000
H	1.111501000	-2.355428000	0.453620000
H	-1.889721000	-1.188750000	5.799668000
H	1.889261000	-1.188228000	5.799830000
Pd	-0.000037000	0.353557000	-0.240888000
Cl	-0.000080000	2.070294000	1.410062000
Cl	0.000219000	-1.313917000	-1.905790000
F	-5.976774000	4.690969000	-0.596645000
F	-6.864623000	2.443086000	0.668459000
F	-5.186065000	0.362205000	1.053098000
F	-3.407832000	4.836533000	-1.490363000
F	-1.733685000	2.780891000	-1.145164000
F	-5.033713000	-4.308863000	-0.687685000
F	-3.789383000	-2.642987000	0.997851000
F	-5.164844000	-3.741321000	-3.350822000
F	-4.023629000	-1.458748000	-4.322129000
F	-2.770577000	0.242389000	-2.637366000
F	3.406785000	4.836347000	-1.491611000
F	1.733141000	2.780390000	-1.146001000
F	5.975607000	4.691812000	-0.597422000
F	6.863862000	2.444579000	0.668626000
F	5.185815000	0.363398000	1.053689000
F	5.034737000	-4.308302000	-0.686471000
F	3.789620000	-2.642540000	0.998553000
F	2.771004000	0.242178000	-2.637253000
F	4.024769000	-1.458890000	-4.321507000
F	5.166309000	-3.741082000	-3.349667000

xii

N	-0.393108000	0.506063000	3.919937000
N	-0.901634000	1.641403000	3.759310000
C	-2.253780000	1.527927000	3.316072000
C	-2.369997000	0.984515000	2.017430000
C	-3.340819000	2.028687000	4.026619000
C	-3.664460000	0.929456000	1.448704000
C	-4.612025000	1.907512000	3.470300000
C	-4.771205000	1.359724000	2.196722000
H	-5.483026000	2.243536000	4.024543000
H	-5.772898000	1.275790000	1.791853000
C	1.005001000	0.463014000	3.663156000
C	1.956189000	0.072633000	4.602163000
C	1.298063000	0.610197000	2.290297000
C	3.271655000	-0.125269000	4.188600000
C	2.611292000	0.277939000	1.888347000
C	3.596018000	-0.044967000	2.835651000
H	4.040542000	-0.376642000	4.911761000
H	4.617049000	-0.237881000	2.530702000
P	-3.792037000	0.485788000	-0.355651000
P	2.990529000	0.148186000	0.098422000
C	-5.614604000	0.475104000	-0.683209000
C	-6.223970000	1.737309000	-0.713069000
C	-6.429941000	-0.601662000	-1.047019000
C	-7.558673000	1.933004000	-1.040880000
C	-7.770725000	-0.434673000	-1.388918000
C	-8.339500000	0.833448000	-1.384211000
C	-3.283426000	-1.291745000	-0.367107000
C	-3.768920000	-2.265743000	0.508885000
C	-2.238475000	-1.676112000	-1.212509000
C	-3.263800000	-3.560205000	0.533160000
C	-1.718887000	-2.963727000	-1.215109000
C	-2.227306000	-3.907411000	-0.331877000
C	4.710472000	-0.451715000	-0.103341000
C	5.699046000	0.165720000	-0.881139000
C	5.026488000	-1.714145000	0.422370000
C	6.947888000	-0.416095000	-1.075323000
C	6.265002000	-2.312762000	0.239434000
C	7.234857000	-1.655076000	-0.512027000
C	2.914594000	1.876890000	-0.504681000
C	1.954460000	2.360516000	-1.399897000
C	3.792799000	2.815371000	0.052351000
C	1.899068000	3.705341000	-1.754965000
C	3.759102000	4.158792000	-0.289607000
C	2.805978000	4.604201000	-1.203500000
C	-1.169663000	0.449714000	1.237854000
H	-1.067090000	-0.621287000	1.425465000
H	-1.423649000	0.533167000	0.177461000
C	0.236576000	1.115726000	1.314200000
H	0.624170000	0.989854000	0.307463000
H	0.129990000	2.197433000	1.446441000
H	1.665407000	-0.053026000	5.640163000
H	-3.188272000	2.465396000	5.008406000
Pd	1.770459000	-1.344268000	-1.026244000
Cl	2.786306000	-0.717012000	-3.029933000
Cl	0.812559000	-2.398918000	0.803507000
F	8.428234000	-2.213484000	-0.698664000
F	6.523484000	-3.510668000	0.769536000

F	7.867895000	0.208238000	-1.815619000
F	5.484338000	1.333223000	-1.498178000
F	4.105325000	-2.394749000	1.118451000
F	1.003062000	1.564833000	-1.903591000
F	0.964393000	4.136887000	-2.605623000
F	4.722198000	2.411390000	0.932645000
F	4.628712000	5.019602000	0.245994000
F	2.756953000	5.891428000	-1.538613000
F	-3.755592000	-4.471983000	1.381747000
F	-1.711568000	-5.137087000	-0.297304000
F	-0.684087000	-3.275757000	-2.013578000
F	-1.639670000	-0.775989000	-2.017104000
F	-4.767470000	-1.966303000	1.352568000
F	-5.962783000	-1.859052000	-1.101219000
F	-5.495095000	2.825104000	-0.397260000
F	-8.091201000	3.160997000	-1.033991000
F	-9.624823000	0.996297000	-1.707580000
F	-8.515019000	-1.496227000	-1.724576000

xiii

N	-0.510280000	4.333909000	-1.223275000
N	0.714908000	4.418128000	-0.999085000
C	1.481997000	3.477470000	-0.223587000
C	1.637805000	2.147515000	-0.650817000
C	2.239054000	4.019804000	0.821067000
C	2.494185000	1.283103000	0.090680000
C	3.141243000	3.199443000	1.478799000
C	3.258619000	1.854443000	1.116539000
H	3.755584000	3.593045000	2.282968000
H	3.958869000	1.254531000	1.673103000
C	-1.422280000	3.373957000	-0.627416000
C	-2.453106000	4.029885000	0.066312000
C	-1.443495000	1.978550000	-0.819384000
C	-3.492511000	3.303648000	0.622709000
C	-2.469995000	1.231453000	-0.158615000
C	-3.494123000	1.912567000	0.508784000
H	-4.297863000	3.809448000	1.146299000
H	-4.308847000	1.362743000	0.958226000
P	2.376342000	-0.605103000	-0.011690000
P	-2.376251000	-0.633948000	0.041837000
C	0.933148000	1.807639000	-1.938143000
H	0.957834000	2.688227000	-2.583968000
H	1.496480000	1.056309000	-2.479322000
C	-0.514509000	1.311982000	-1.809875000
H	-0.975585000	1.392754000	-2.801481000
H	-0.476598000	0.243101000	-1.586146000
H	2.122178000	5.066966000	1.082398000
H	-2.423191000	5.112765000	0.139006000
Pd	0.015385000	-0.987884000	0.254416000
Cl	0.003336000	0.741256000	1.898224000
Cl	0.031579000	-3.129452000	-0.776725000
C	3.199516000	-1.136042000	-1.700357000
C	2.137516000	-1.344007000	-2.807328000
H	2.652355000	-1.360634000	-3.775581000
H	1.624548000	-2.295200000	-2.671124000
H	1.366325000	-0.580622000	-2.859962000
C	3.947820000	-2.483745000	-1.629876000
H	3.282791000	-3.303143000	-1.352538000
H	4.324498000	-2.698375000	-2.637454000
H	4.809339000	-2.477771000	-0.962778000
C	4.205051000	-0.037335000	-2.102214000
H	4.726135000	-0.351701000	-3.014607000
H	3.722073000	0.920488000	-2.308464000
H	4.959042000	0.127565000	-1.326289000
C	3.352347000	-1.391243000	1.463120000
C	2.755053000	-0.910758000	2.805786000
H	1.725890000	-1.254103000	2.922710000
H	3.356772000	-1.350996000	3.610556000
H	2.753746000	0.169348000	2.938028000
C	3.089818000	-2.918833000	1.424739000
H	3.375701000	-3.329176000	2.400323000
H	2.034716000	-3.150433000	1.258622000
H	3.679486000	-3.440290000	0.674199000
C	4.876592000	-1.144211000	1.453534000
H	5.333529000	-1.799465000	2.205150000
H	5.341833000	-1.372383000	0.494499000
H	5.150396000	-0.121431000	1.716915000
C	-3.325609000	-1.202329000	1.638594000
C	-2.997101000	-0.319272000	2.860561000
H	-3.317510000	0.717205000	2.748346000
H	-3.530450000	-0.738973000	3.722499000
H	-1.932455000	-0.316277000	3.083597000
C	-4.860982000	-1.282996000	1.509486000
H	-5.194119000	-1.987057000	0.747575000
H	-5.260611000	-1.635452000	2.468022000
H	-5.324643000	-0.314819000	1.306470000
C	-2.769498000	-2.613203000	1.951843000
H	-3.262269000	-2.983223000	2.859176000
H	-2.950888000	-3.339418000	1.159105000
H	-1.692812000	-2.582478000	2.141553000
C	-3.285417000	-1.351242000	-1.506412000
C	-2.391794000	-1.179275000	-2.751983000
H	-1.395959000	-1.604604000	-2.611578000
H	-2.868150000	-1.708536000	-3.586034000
H	-2.304093000	-0.133720000	-3.047664000
C	-3.563406000	-2.859402000	-1.347579000
H	-4.009655000	-3.222802000	-2.281360000
H	-2.641779000	-3.419029000	-1.176395000
H	-4.269143000	-3.087219000	-0.548575000
C	-4.599678000	-0.588401000	-1.772162000

H	-5.045144000	-0.981637000	-2.694495000
H	-5.337646000	-0.705732000	-0.978601000
H	-4.423288000	0.480719000	-1.920099000

xiv

N	0.822664000	3.571351000	-0.612876000
N	1.403340000	3.576973000	0.500410000
C	2.725021000	3.054077000	0.420514000
C	2.776325000	1.688175000	0.031179000
C	3.826596000	3.753168000	0.906978000
C	4.021631000	1.023955000	0.139410000
C	5.058926000	3.108831000	0.943416000
C	5.144288000	1.769349000	0.563952000
H	5.945606000	3.637929000	1.279676000
H	6.106626000	1.269791000	0.620730000
C	-0.580356000	3.358974000	-0.500185000
C	-1.522586000	4.277933000	-0.946600000
C	-0.906246000	2.043806000	-0.077669000
C	-2.866989000	3.920818000	-0.913274000
C	-2.272388000	1.674429000	-0.142083000
C	-3.230559000	2.635134000	-0.521332000
H	-3.633019000	4.630517000	-1.209110000
H	-4.282049000	2.389345000	-0.520881000
P	4.488216000	-0.783418000	-0.076787000
P	-2.891938000	-0.032910000	0.250069000
C	1.509217000	0.982210000	-0.445242000
H	1.287839000	1.255574000	-1.478430000
H	1.735452000	-0.075871000	-0.473610000
C	0.217318000	1.133465000	0.423949000
H	-0.185469000	0.128107000	0.548376000
H	0.495182000	1.452123000	1.431951000
H	-1.200824000	5.257653000	-1.285238000
H	3.710505000	4.785112000	1.223962000
Pd	-1.404954000	-1.565558000	-0.537900000
Cl	-1.447811000	-3.191043000	1.117215000
Cl	-0.953002000	-0.411764000	-2.515662000
C	-3.145295000	-0.020959000	2.156970000
C	-3.881727000	1.278905000	2.556754000
H	-4.880493000	1.361261000	2.127584000
H	-3.993499000	1.266810000	3.647048000
H	-3.313018000	2.173053000	2.292079000
C	-1.767949000	-0.012537000	2.848543000
H	-1.217321000	0.906847000	2.642782000
H	-1.938121000	-0.053403000	3.930489000
H	-1.154836000	-0.872258000	2.573012000
C	-3.947408000	-1.241690000	2.640645000
H	-3.990852000	-1.199931000	3.735135000
H	-4.975878000	-1.242334000	2.276892000
H	-3.470039000	-2.181289000	2.361734000
C	-4.536392000	-0.418186000	-0.693390000
C	-4.417471000	0.018658000	-2.166550000
H	-5.334980000	-0.294642000	-2.678040000
H	-4.322176000	1.098286000	-2.290766000
H	-3.572770000	-0.455982000	-2.666170000
C	-4.721640000	-1.954035000	-0.668798000
H	-3.920398000	-2.466467000	-1.208086000
H	-4.771726000	-2.364724000	0.340346000
H	-5.667829000	-2.184704000	-1.171587000
C	-5.790883000	0.228652000	-0.066614000
H	-6.647140000	-0.054471000	-0.689106000
H	-5.992022000	-0.130813000	0.942728000
H	-5.757026000	1.318757000	-0.045274000
C	3.772308000	-1.533301000	-1.705090000
C	4.822250000	-2.600474000	-2.102678000
H	4.549485000	-3.040761000	-3.070564000
H	5.823405000	-2.168602000	-2.198904000
H	4.876119000	-3.415486000	-1.373741000
C	2.394285000	-2.221584000	-1.701072000
H	2.337542000	-3.032693000	-0.971249000
H	1.567311000	-1.535002000	-1.520546000
H	2.219095000	-2.663035000	-2.691545000
C	3.794969000	-0.418731000	-2.768749000
H	3.025965000	0.336806000	-2.593413000
H	4.765948000	0.088583000	-2.806491000
H	3.611747000	-0.855557000	-3.758833000
C	3.734126000	-1.628169000	1.474153000
C	4.489379000	-1.017749000	2.675514000
H	5.573270000	-1.148322000	2.586557000
H	4.283989000	0.051757000	2.786395000
H	4.166499000	-1.515290000	3.599073000
C	2.226579000	-1.453340000	1.718055000
H	1.938747000	-1.999971000	2.626354000
H	1.969697000	-0.403539000	1.878643000
H	1.615420000	-1.842375000	0.901926000
C	4.080543000	-3.128701000	1.397578000
H	3.816872000	-3.611581000	2.347341000
H	3.528740000	-3.644539000	0.607565000
H	5.150727000	-3.291130000	1.228527000

xv

N	0.951885000	4.275485000	2.330994000
N	-0.276811000	4.173177000	2.542922000
C	-1.149253000	3.432678000	1.646494000
C	-1.195263000	2.030622000	1.505249000
C	-2.026465000	4.269524000	0.946939000
C	-2.075733000	1.507421000	0.522948000
C	-2.906169000	3.732895000	0.015754000
C	-2.910800000	2.360024000	-0.215671000

H	-3.569855000	4.381831000	-0.546776000
H	-3.551573000	1.958522000	-0.989177000
C	1.575963000	3.537931000	1.258079000
C	2.128899000	4.262598000	0.203715000
C	1.664694000	2.135721000	1.342289000
C	2.709240000	3.566995000	-0.854635000
C	2.196555000	1.441013000	0.233075000
C	2.713677000	2.174274000	-0.854258000
H	3.128917000	4.106516000	-1.697778000
H	3.095066000	1.650628000	-1.722701000
P	-1.883199000	-0.221983000	-0.097273000
P	1.911508000	-0.357190000	-0.108995000
C	-3.412000000	-0.682649000	-1.024458000
C	-3.323047000	-1.523113000	-2.142012000
C	-4.673322000	-0.368485000	-0.495804000
C	-4.482280000	-2.024463000	-2.735600000
C	-5.830223000	-0.855820000	-1.105043000
C	-5.737249000	-1.685228000	-2.225243000
H	-2.353610000	-1.774594000	-2.557300000
H	-4.757432000	0.250750000	0.391796000
H	-4.401901000	-2.672416000	-3.603651000
H	-6.802081000	-0.593642000	-0.696825000
H	-6.638399000	-2.068829000	-2.695042000
C	-2.190366000	-1.425155000	1.271175000
C	-2.062917000	-2.790863000	0.970102000
C	-2.719673000	-1.042708000	2.510320000
C	-2.410098000	-3.756188000	1.913126000
C	-3.066917000	-2.013151000	3.453572000
C	-2.904434000	-3.368298000	3.162542000
H	-1.698430000	-3.101360000	-0.005679000
H	-2.876406000	0.005234000	2.741110000
H	-2.299510000	-4.808984000	1.670410000
H	-3.470439000	-1.704715000	4.413625000
H	-3.173851000	-4.120004000	3.898603000
C	3.447676000	-1.007964000	-0.881593000
C	4.698372000	-0.412173000	-0.676812000
C	3.365116000	-2.233964000	-1.558486000
C	5.854036000	-1.032767000	-1.159199000
C	4.521162000	-2.852671000	-2.029315000
C	5.768531000	-2.251034000	-1.834134000
H	4.780550000	0.530517000	-0.146544000
H	2.396710000	-2.694863000	-1.727556000
H	6.819696000	-0.560520000	-1.002668000
H	4.447622000	-3.798935000	-2.557427000
H	6.668416000	-2.730738000	-2.208289000
C	1.995655000	-1.351069000	1.430442000
C	1.081608000	-2.386911000	1.624143000
C	3.056961000	-1.181518000	2.338211000
C	1.183387000	-3.220210000	2.741588000
C	3.156802000	-2.012313000	3.451043000
C	2.214759000	-3.027987000	3.659476000
H	0.294536000	-2.545170000	0.901771000
H	3.793421000	-0.399365000	2.177770000
H	0.451852000	-4.009104000	2.888139000
H	3.970286000	-1.870352000	4.156496000
H	2.295373000	-3.670646000	4.531392000
C	-0.376219000	1.112202000	2.389690000
H	-0.860846000	1.031176000	3.369865000
H	-0.390223000	0.105968000	1.975501000
C	1.096080000	1.507156000	2.589220000
H	1.191249000	2.206863000	3.420290000
H	1.651850000	0.621379000	2.882159000
H	-1.985430000	5.339144000	1.128447000
H	2.071810000	5.346589000	0.206655000
Pd	0.022998000	-0.124672000	-1.518193000
Cl	-1.487587000	0.994480000	-3.024817000
Cl	1.587829000	-0.083604000	-3.334283000

xvi

N	-0.952783000	-2.294106000	4.888776000
N	0.273422000	-2.072211000	4.990189000
C	1.166062000	-2.066673000	3.844778000
C	1.206005000	-1.099141000	2.821680000
C	2.094206000	-3.115056000	3.892143000
C	2.134569000	-1.307844000	1.771428000
C	3.023728000	-3.272477000	2.873425000
C	3.028580000	-2.385420000	1.800169000
H	3.730712000	-4.095262000	2.899990000
H	3.711817000	-2.561068000	0.980611000
C	-1.590975000	-2.422570000	3.601549000
C	-2.183124000	-3.647116000	3.294428000
C	-1.686935000	-1.302996000	2.754423000
C	-2.822334000	-3.793643000	2.066775000
C	-2.275267000	-1.491709000	1.483682000
C	-2.844368000	-2.736942000	1.160216000
H	-3.282457000	-4.739340000	1.799251000
H	-3.280670000	-2.900064000	0.183405000
P	1.894942000	-0.445176000	0.159949000
P	-1.951307000	-0.386323000	0.036126000
C	3.411312000	-0.692202000	-0.860229000
C	3.359798000	-0.906759000	-2.242235000
C	4.678800000	-0.484427000	-0.302976000
C	4.514592000	-0.995836000	-3.012996000
C	5.846084000	-0.573696000	-1.051396000
C	5.760942000	-0.835277000	-2.415678000
C	2.129400000	1.384626000	0.314821000
C	1.956575000	2.143467000	-0.848574000
C	2.575863000	2.073391000	1.446961000
C	2.067116000	3.526766000	-0.863374000
C	2.705901000	3.459351000	1.458597000

C	2.435720000	4.189170000	0.304578000
C	-3.408583000	-0.446798000	-1.088380000
C	-4.723509000	-0.681322000	-0.675252000
C	-3.213421000	-0.150639000	-2.442874000
C	-5.786246000	-0.684083000	-1.574764000
C	-4.258274000	-0.146192000	-3.356988000
C	-5.552097000	-0.418428000	-2.919591000
C	-2.122347000	1.391908000	0.497482000
C	-1.414242000	2.348611000	-0.230688000
C	-3.027051000	1.876437000	1.449086000
C	-1.486754000	3.708632000	0.047172000
C	-3.133617000	3.232159000	1.740032000
C	-2.349597000	4.151481000	1.044975000
C	0.364771000	0.157563000	2.866645000
H	0.844913000	0.877268000	3.536797000
H	0.364803000	0.626283000	1.881750000
C	-1.098644000	-0.020330000	3.285830000
H	-1.180604000	-0.015803000	4.373052000
H	-1.654787000	0.850599000	2.960496000
H	2.058963000	-3.806076000	4.728672000
H	-2.120382000	-4.467282000	4.002568000
Pd	-0.008298000	-1.499656000	-0.786855000
Cl	1.523529000	-3.325478000	-0.993976000
Cl	-1.536679000	-2.882842000	-1.982855000
F	4.430478000	-1.212268000	-4.329552000
F	6.870203000	-0.915333000	-3.150721000
F	7.039051000	-0.391546000	-0.474881000
F	4.798017000	-0.174871000	0.999322000
F	2.194416000	-1.007114000	-2.892581000
F	-1.988466000	0.146180000	-2.902320000
F	-4.031705000	0.125832000	-4.646378000
F	-6.565672000	-0.410708000	-3.785959000
F	-7.030763000	-0.924915000	-1.146959000
F	-5.015136000	-0.913225000	0.612457000
F	-3.804123000	1.031960000	2.142039000
F	-3.979805000	3.657017000	2.682348000
F	-0.754387000	4.583349000	-0.652393000
F	-0.661001000	1.965660000	-1.269043000
F	2.902447000	1.420594000	2.570497000
F	3.106669000	4.089222000	2.568043000
F	1.674783000	1.523641000	-2.005858000
F	1.833962000	4.216932000	-1.982167000
F	2.546128000	5.516909000	0.312764000
F	-2.440859000	5.450142000	1.323755000

xvii

N	-0.939149000	4.241020000	-0.238303000
N	-2.173989000	4.210429000	-0.091790000
C	-2.901261000	3.002417000	-0.356416000
C	-2.673269000	1.795158000	0.341712000
C	-3.903105000	3.146075000	-1.318843000
C	-3.430203000	0.663044000	-0.070233000
C	-4.666878000	2.042484000	-1.676497000
C	-4.416841000	0.818483000	-1.061390000
H	-5.446582000	2.132903000	-2.426731000
H	-5.015806000	-0.034015000	-1.350851000
C	-0.150060000	3.111714000	-0.660594000
C	0.231904000	3.057048000	-2.005817000
C	0.365948000	2.255958000	0.335394000
C	1.215533000	2.158307000	-2.380745000
C	1.480245000	1.462493000	-0.015432000
C	1.878665000	1.428588000	-1.387161000
H	1.530690000	2.069364000	-3.414457000
H	2.850517000	1.009997000	-1.689244000
P	-3.066424000	-1.019431000	0.653947000
P	2.551031000	0.223880000	0.860540000
C	-1.824820000	1.761564000	1.610692000
H	-2.390329000	2.299523000	2.382068000
H	-1.791036000	0.722816000	1.935512000
C	-0.363998000	2.326895000	1.647981000
H	-0.394502000	3.376142000	1.961803000
H	0.164361000	1.789994000	2.425523000
H	-4.055768000	4.117807000	-1.778549000
H	-0.229935000	3.726819000	-2.724036000
Pd	2.328606000	-0.923249000	-1.107932000
Cl	2.004652000	-1.534614000	-3.417779000
Cl	2.962970000	-3.062676000	-0.417173000
C	4.315859000	0.956431000	1.079979000
C	5.325594000	-0.202755000	0.950905000
H	6.334895000	0.207007000	1.074919000
H	5.187887000	-0.976653000	1.707180000
H	5.267914000	-0.675721000	-0.033001000
C	4.451049000	1.638199000	2.454588000
H	4.333488000	0.940317000	3.283979000
H	5.459899000	2.061033000	2.524141000
H	3.738481000	2.459250000	2.578244000
C	4.635286000	1.998796000	-0.007634000
H	5.631242000	2.402323000	0.206283000
H	4.678989000	1.559725000	-1.007136000
H	3.931204000	2.834656000	-0.014318000
C	1.883666000	-0.540027000	2.464699000
C	2.842048000	-1.667642000	2.909736000
H	2.361487000	-2.189634000	3.745676000
H	3.026945000	-2.393244000	2.116178000
H	3.795843000	-1.281283000	3.274659000
C	0.537777000	-1.184185000	2.080112000
H	0.679157000	-1.994538000	1.360954000
H	0.078370000	-1.607719000	2.979809000
H	-0.164507000	-0.469523000	1.655363000
C	1.718469000	0.463333000	3.645138000

H	0.748015000	0.305935000	4.125804000
H	2.488813000	0.293637000	4.400928000
H	1.782329000	1.514115000	3.365272000
C	-4.746788000	-1.634464000	1.357442000
C	-5.769722000	-2.229079000	0.377207000
H	-5.386794000	-3.125735000	-0.117188000
H	-6.671729000	-2.523056000	0.931037000
H	-6.082550000	-1.516970000	-0.390678000
C	-4.383754000	-2.713684000	2.402388000
H	-5.294944000	-3.061280000	2.906631000
H	-3.907312000	-3.586700000	1.946340000
H	-3.704849000	-2.321997000	3.167217000
C	-5.383488000	-0.440396000	2.097005000
H	-6.239265000	-0.791155000	2.687813000
H	-4.679029000	0.036203000	2.789099000
H	-5.745768000	0.324583000	1.404291000
C	-2.526863000	-2.023226000	-0.892175000
C	-2.250853000	-3.460082000	-0.404753000
H	-1.730491000	-4.019701000	-1.192323000
H	-1.614858000	-3.474488000	0.487369000
H	-3.176086000	-3.998454000	-0.175659000
C	-1.193779000	-1.378206000	-1.326702000
H	-0.456817000	-1.377391000	-0.520615000
H	-0.759777000	-1.941880000	-2.159884000
H	-1.330726000	-0.345275000	-1.664401000
C	-3.442126000	-2.076275000	-2.128371000
H	-2.985345000	-2.742329000	-2.872401000
H	-4.438807000	-2.464029000	-1.912389000
H	-3.544943000	-1.096667000	-2.601118000