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Supplementary information

Table S1

^{1}H (600 MHz) and ^{13}C NMR (150 MHz) data (δ in ppm, *J* in Hz) of rosmarinine in $CDCl_3$

Id	^{1}H		^{13}C
	δ_H	multiplicity[1]	δ_C
1	2.59	m, br	48.60
2	4.29	dd, $J_{2,1}$ = 8.21, $J_{2,3b}$ = 8.20	68.93
3a	3.26	m, br	60.36
3b	3.01	dd, $J_{3b,3a}$ = 11.24, $J_{3b,2}$ = 8,21	60.36
4	-	-	
5a	2.69	m, br	53.28
5b	3.49	m, br	53.28
6a	2.16	m, br	34.12
6b	2.32	dd, $J_{6b,6a}$=13.68, $J_{6b,x}$ = 5.80	34.12
7	5.10	br	74.73
8	3.81	m, br	69.39
9a	4.92	dd, $J_{9a,9b}$ = 12.67, $J_{9a,1}$ = 5.00	61.40
9b	4.13	dbr, $J_{9b,9a}$ = 12.67	61.40
10	-		
11	-		179.96
12	-		76.86
13	1.79	m	37.72
14a	2.26	dbr, $J_{14a,14b}$ = 13. 94	39.27
14b	1.95	dd, $J_{14b,14a}$ = 13.94, $J_{14b,13}$ = 9.62	39.27
15	-		131.27
16	-		166.33
17	-		
18	1.34	d, $J_{18,13}$ = 6.5	25.69
19	0.97	d, $J_{19,13}$ = 6.78	11.43
20	5.81	q, $J_{20,21}$ = 7.04	134.84
21	1.85	d, $J_{21,20}$ = 7.04	14.81

[1] Multiplicity $^{3/4}J_{H,H}$: s (singlet), d (doublet), dd (double doublet), q (quartet), m (multiplet), br (broad signal)

Fig. S1 Rosmarinine chemical structure and stereochemistry determined by NMR spectroscopy: A) ^{1}H NMR spectrum with the assignment of signals corresponding to rosmarinine, B) 1D selective ^{1}H NOE spectrum when proton 7 signal is saturated, and C) 1D selective ^{1}H NOE spectrum when proton 1 signal is saturated. Spectra acquired at 298.0 K and at a magnetic field of 600 MHz.

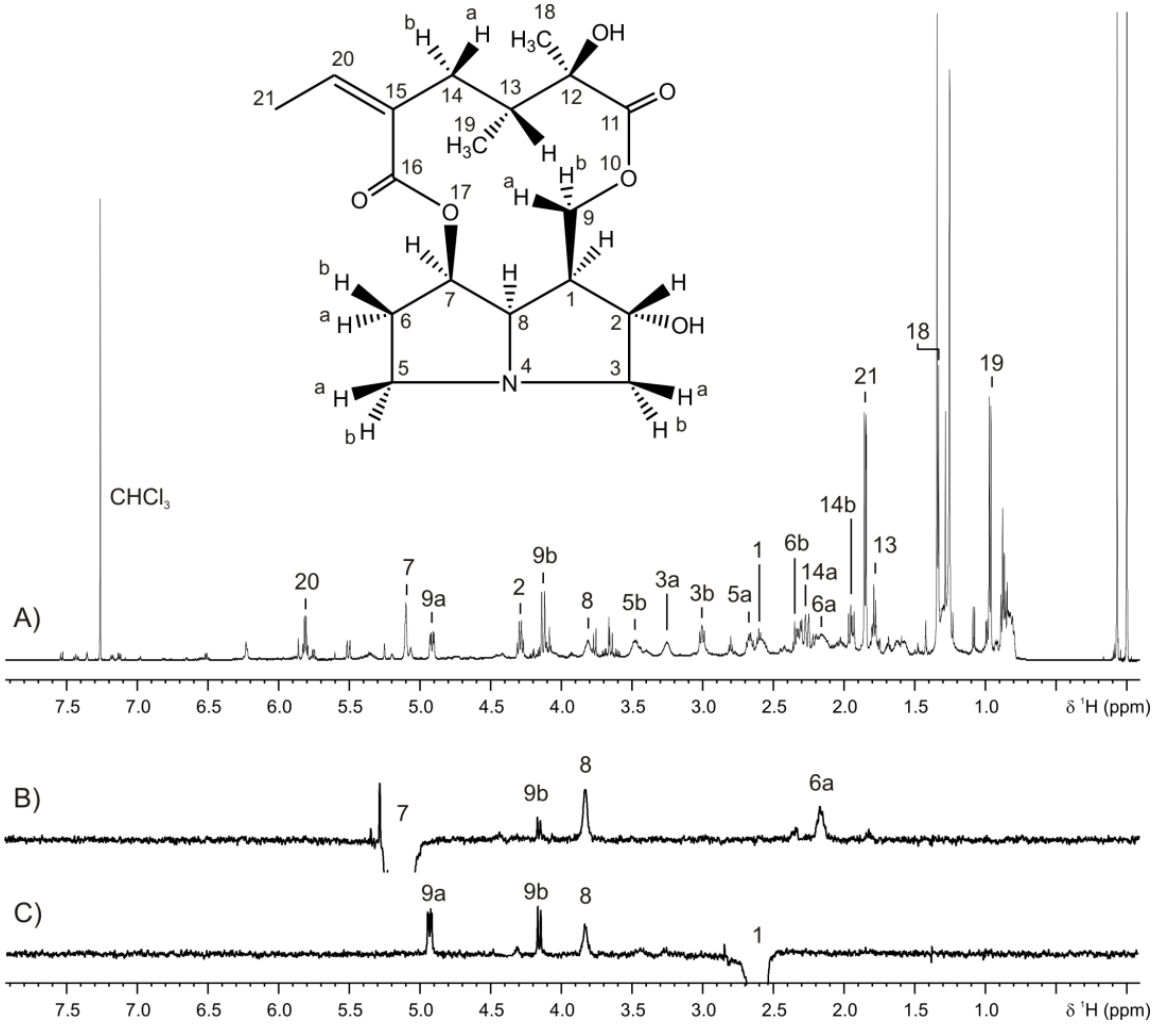

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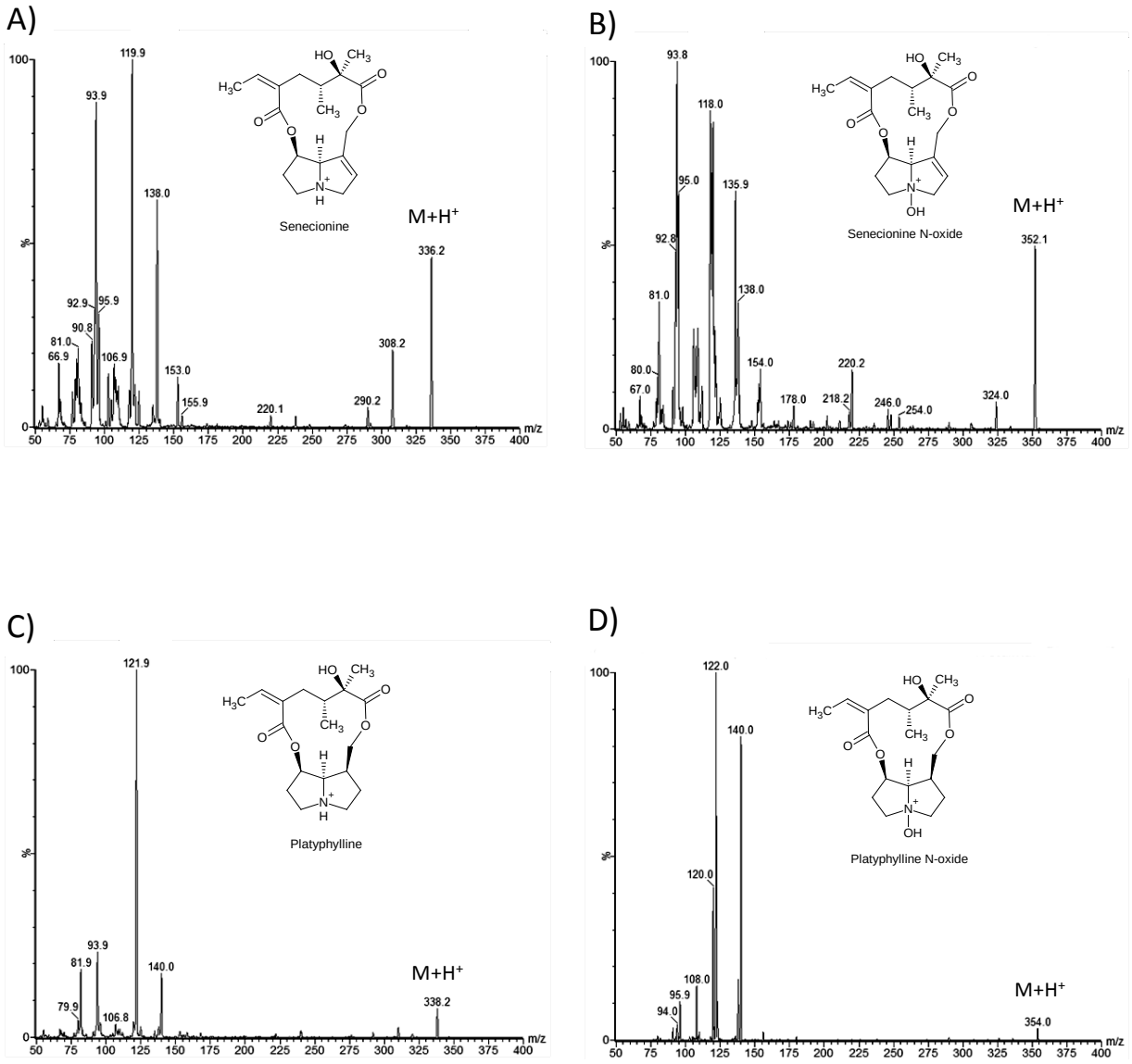
Fig. S2 Typical mass fragmentation of A) senecionine and B) senecionine N-oxide as representatives of retronecine PAs; C) platyphilline and D) platyphilline N-oxide as representatives of platynecine PAs; E) rosmarinine and F) rosmarinine N-oxide as representatives of rosmarinecine PAs; G) senkirkine as representative of otonecine PAs; H) 1,2-dihydrosenkirkine as representative of dihydrootonecine PAs; I) 2-hydroxy-1,2-senkirkine and J) 1,2-dihydro senkirkine, 2-C_5H_7O-ester as representatives of hydroxydihydrootonecine PAs.



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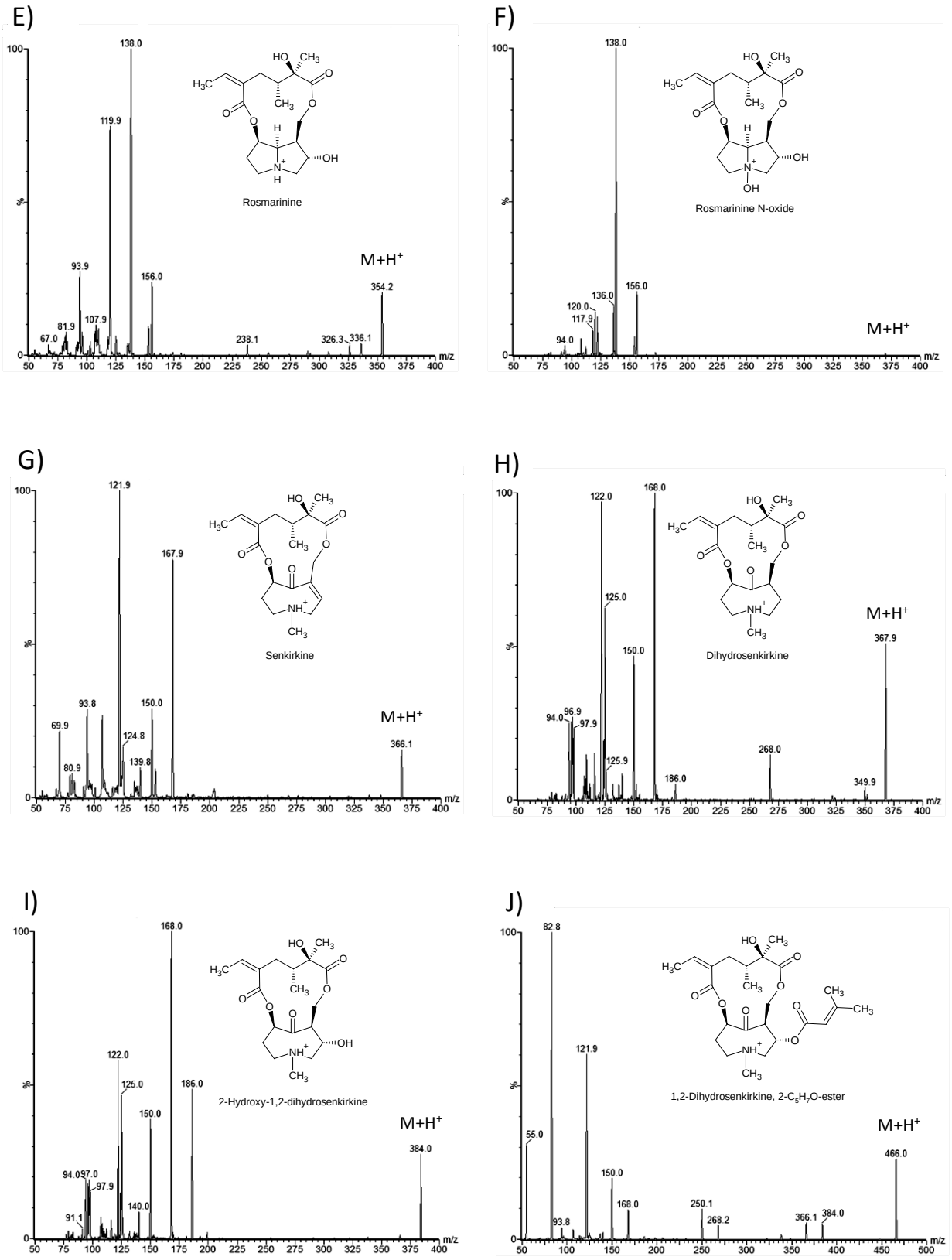

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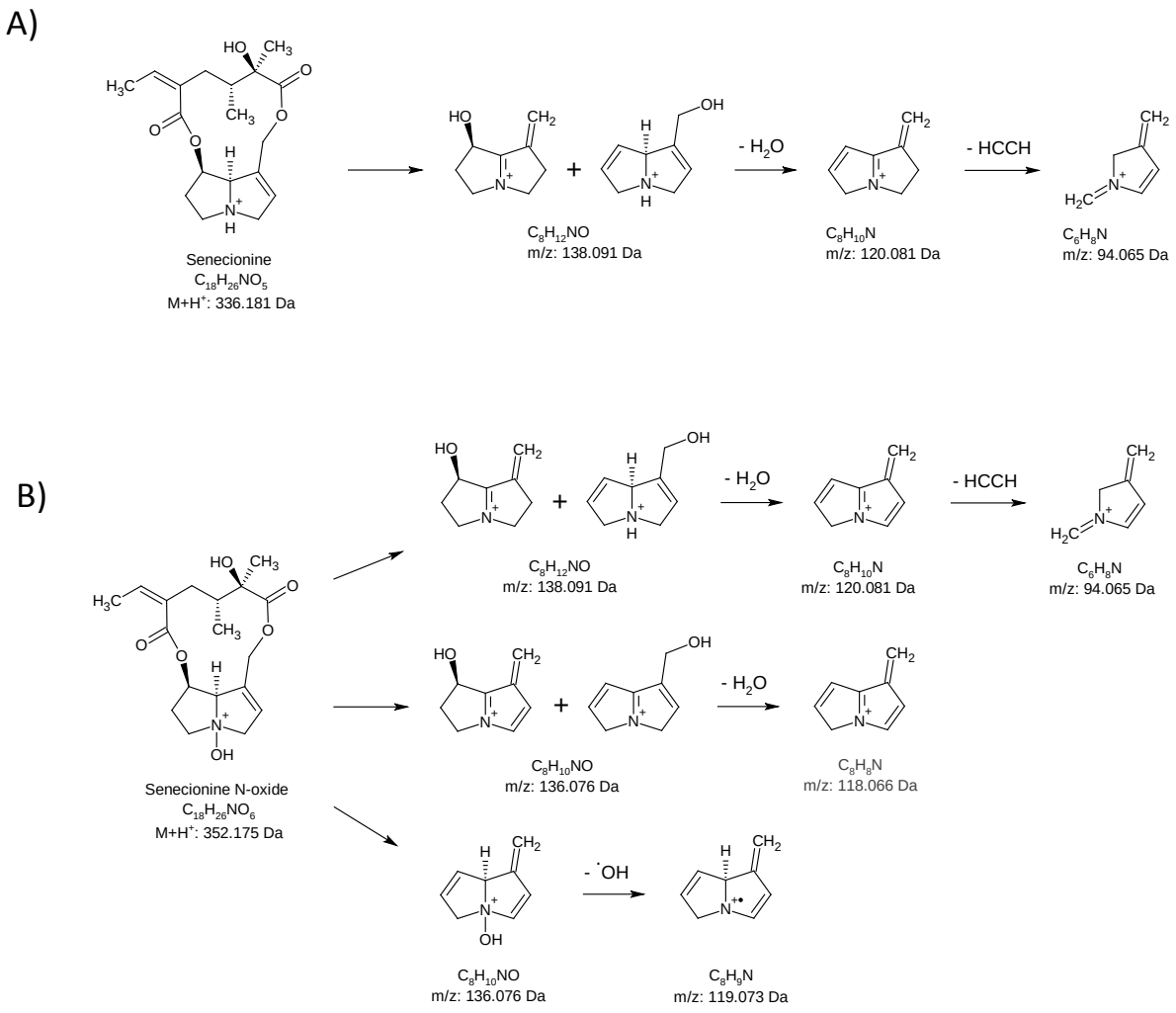
Fig. S3 Putative fragmentation pathways for A) senecionine and B) senecionine N-oxide as representatives of retronecine PAs; C) platyphilline and D) platyphilline N-oxide as representatives of platynecine PAs; E) rosmarinine and F) rosmarinine N-oxide as representatives of rosmarinecine PAs; G) senkirkine as representative of otonecine PAs; H) 1,2-dihydrosenkirkine as representative of dihydrootonecine PAs; I) 2-hydroxy-1,2-senkirkine and J) 1,2-dihydro senkirkine, 2-C_5H_7O-ester as representatives of hydroxydihydrootonecine PAs.



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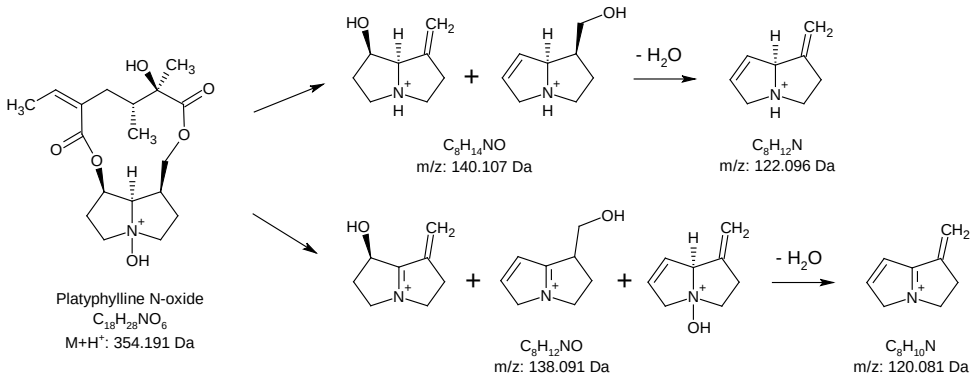
D)



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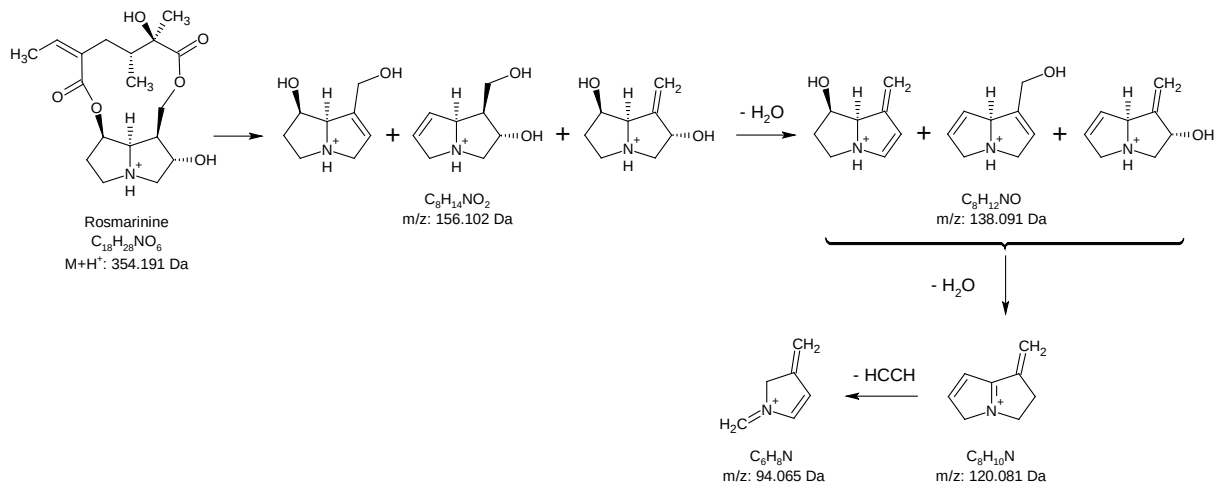

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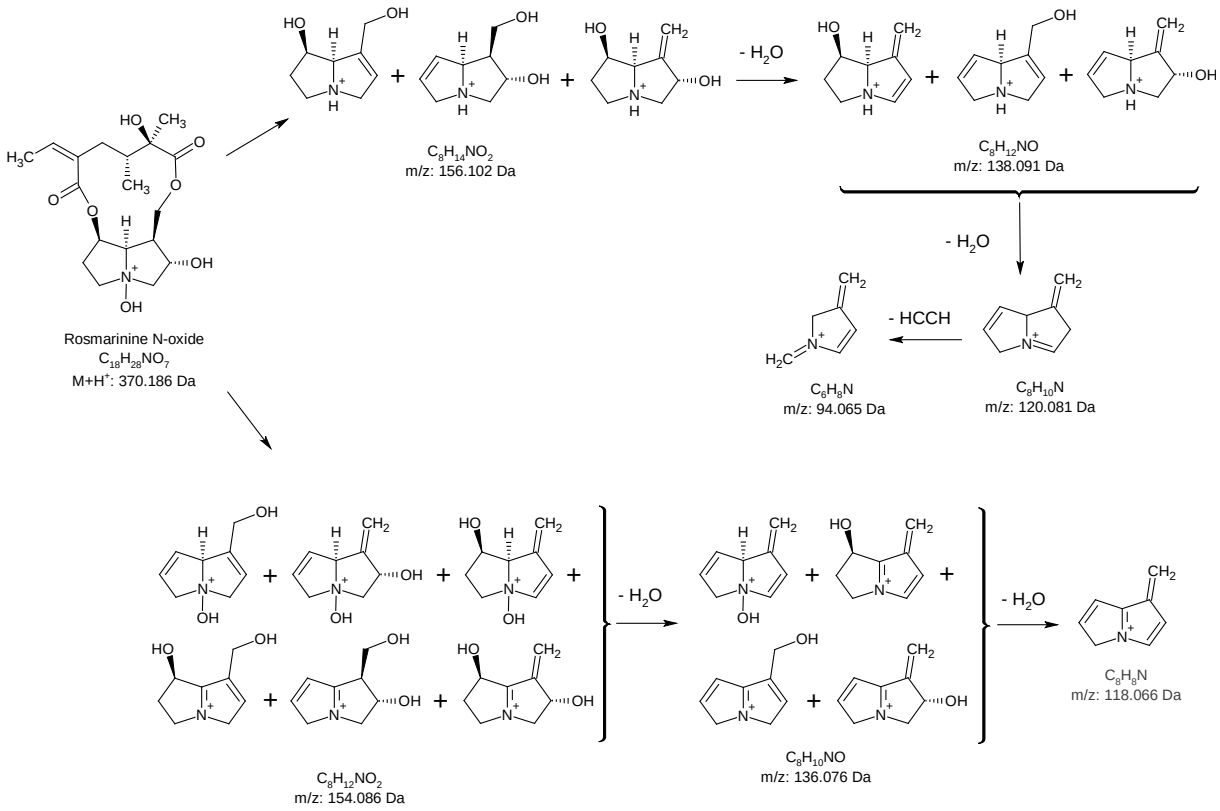

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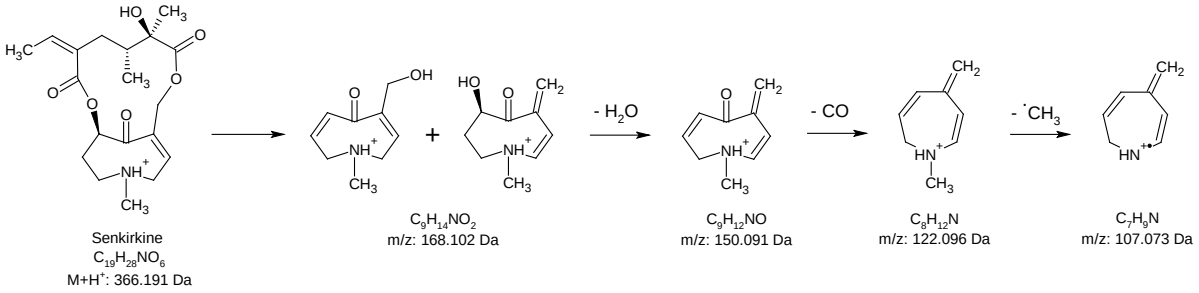
G)



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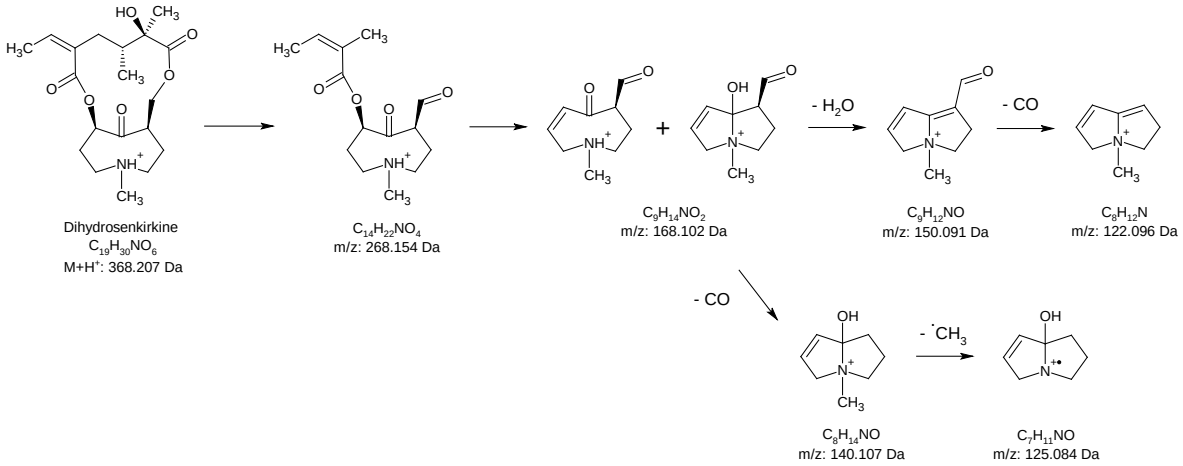

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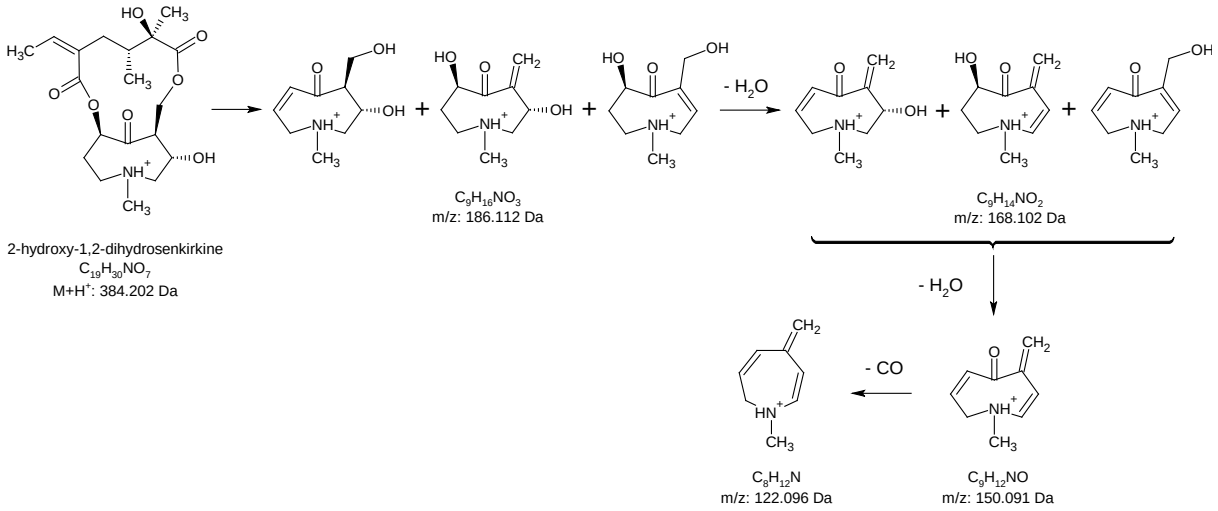

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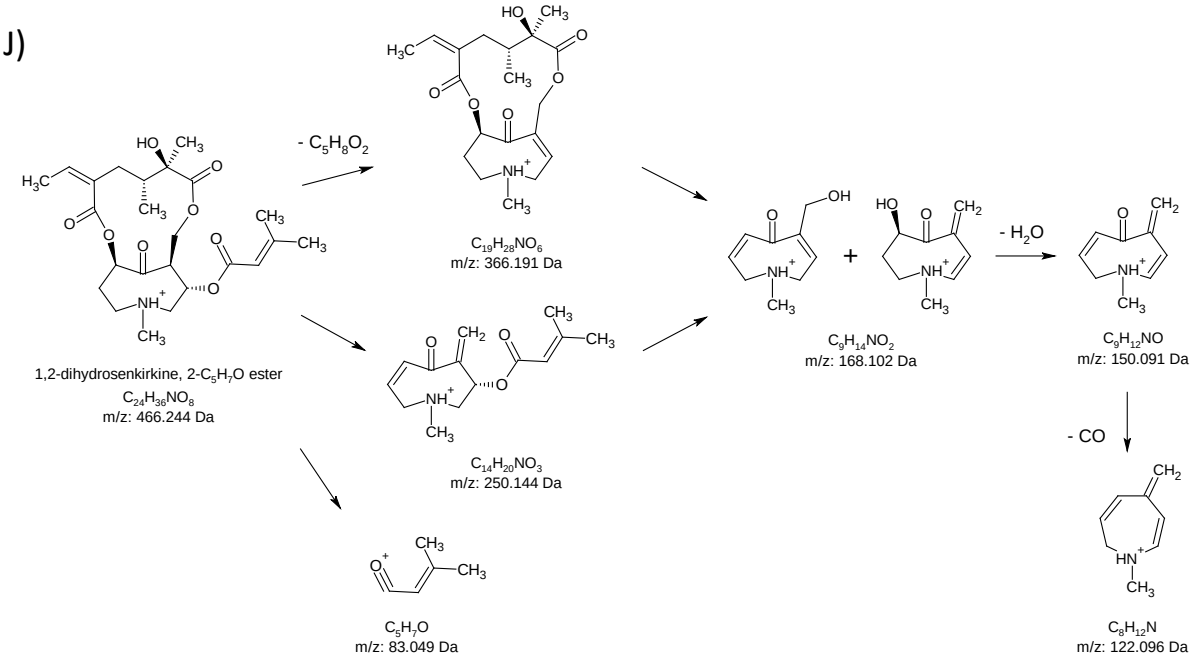
J)



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