

**Biomimetic Synthesis of the Non-Canonical PPAP Natural Products Yezo'otogirin C and
Hypermogin D, and Studies Towards the Synthesis of Norascyronone A**

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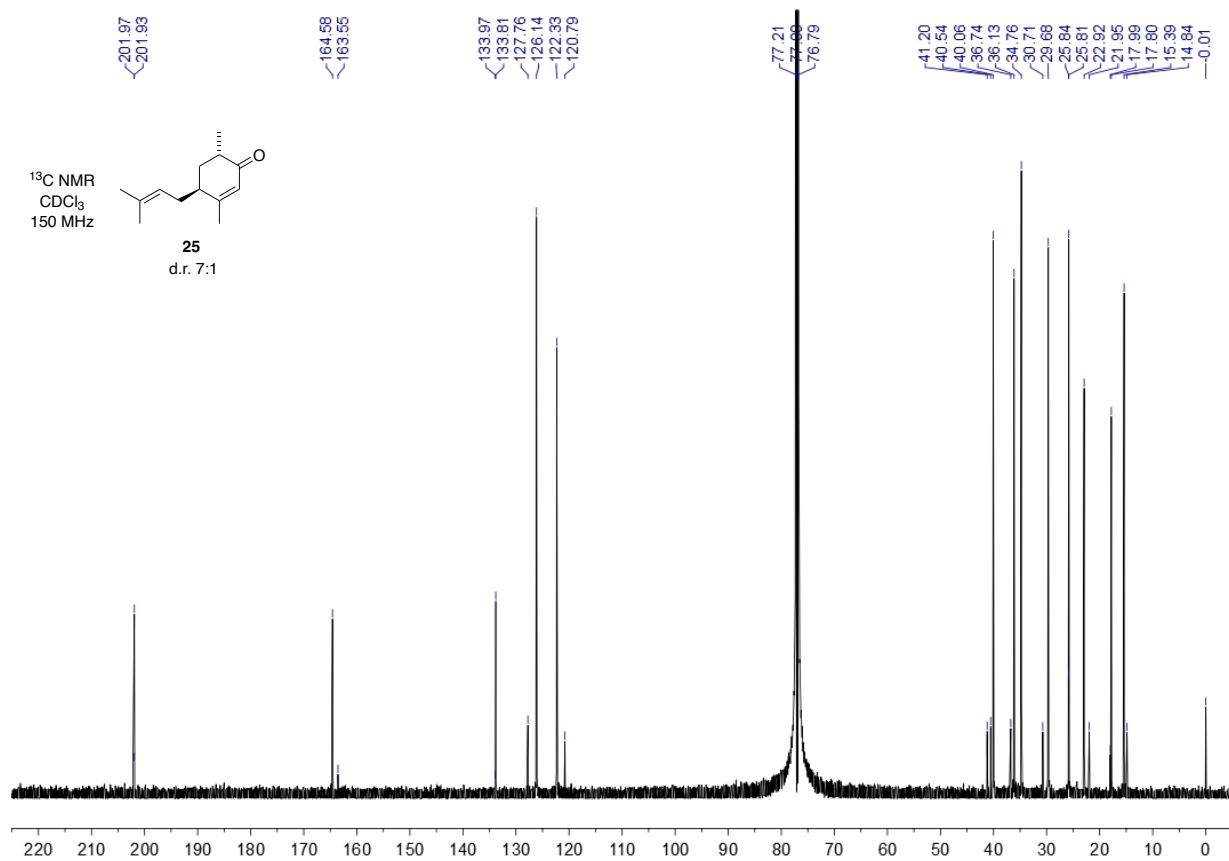
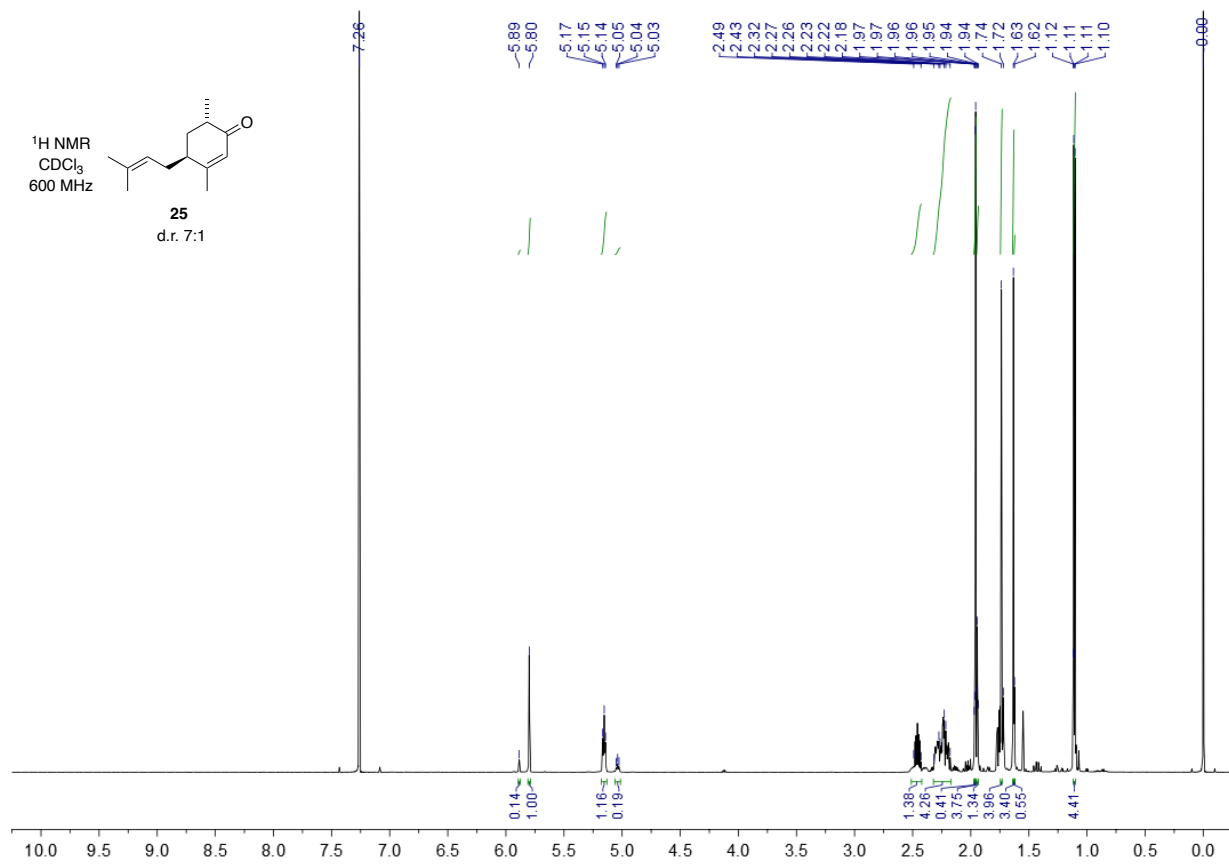
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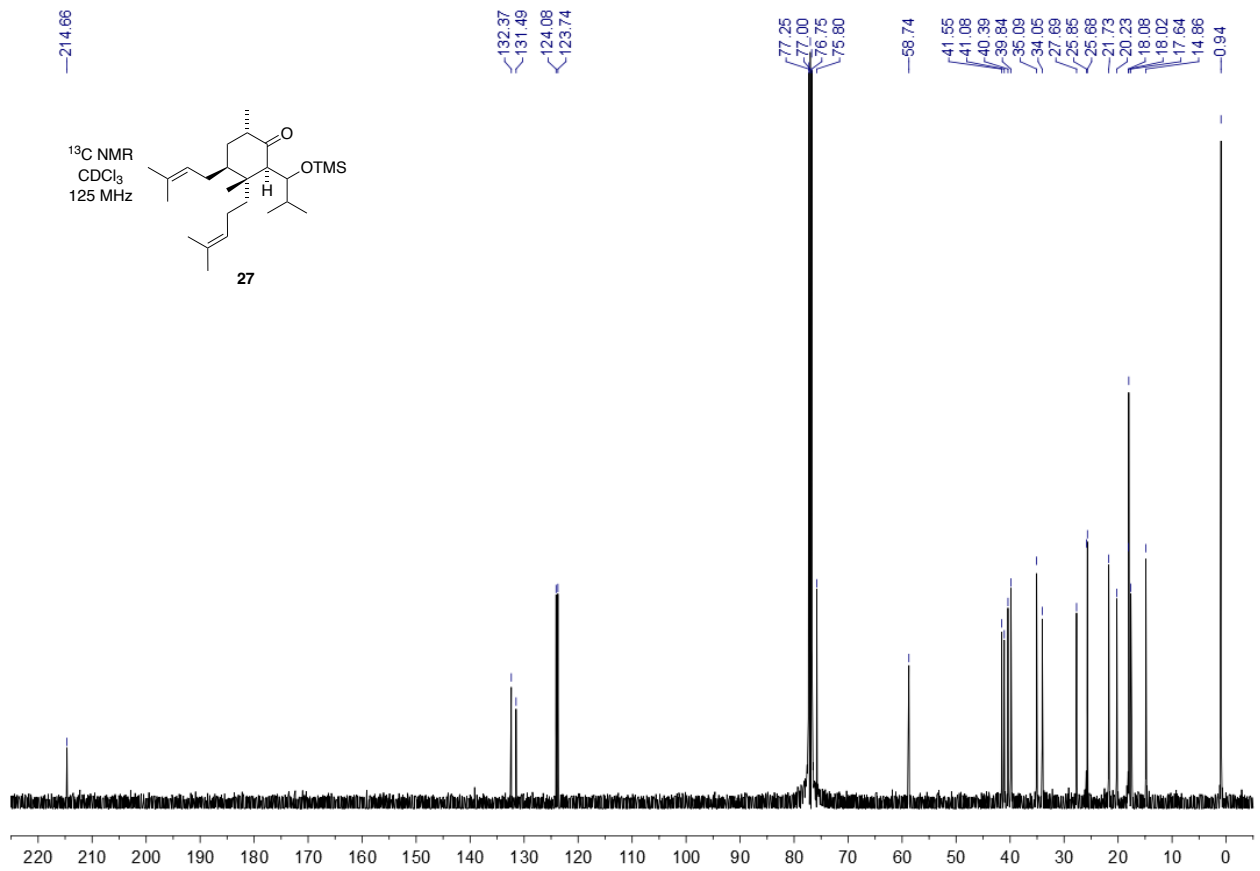
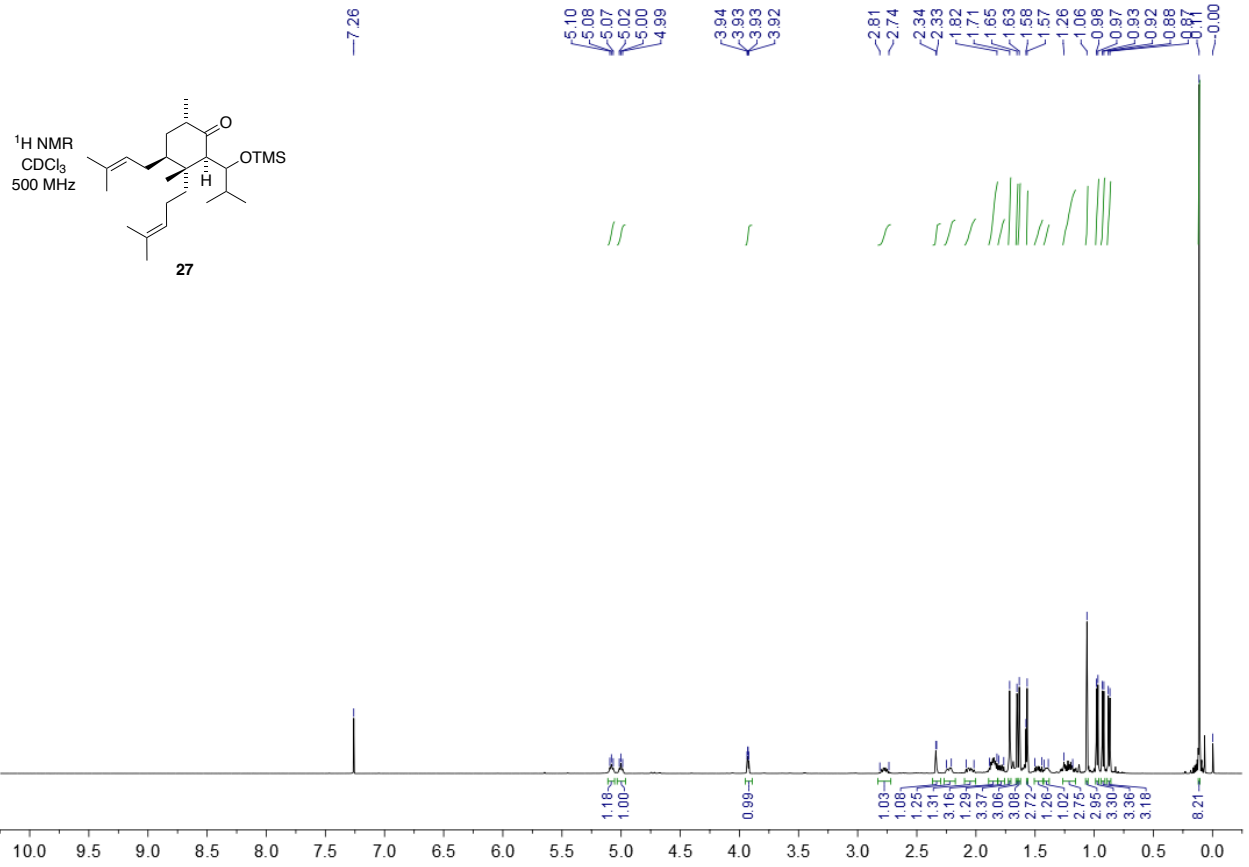
Supporting Information

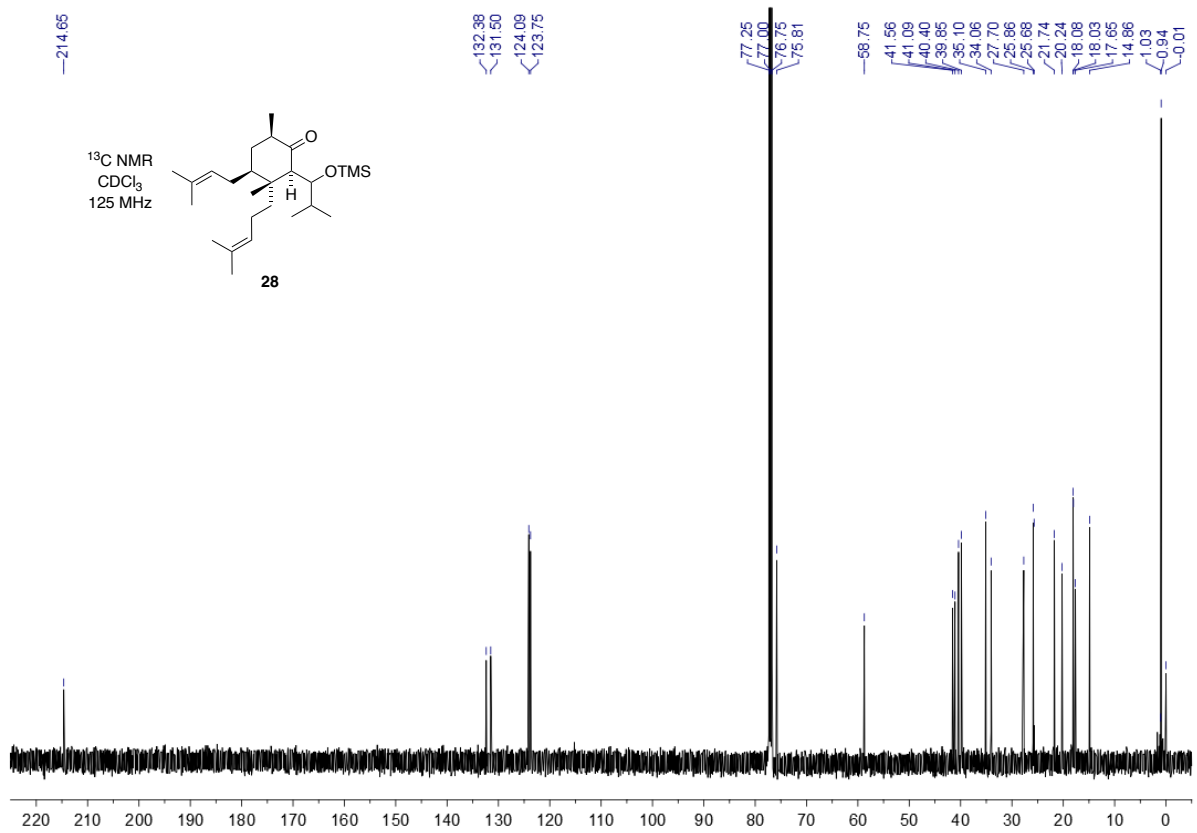
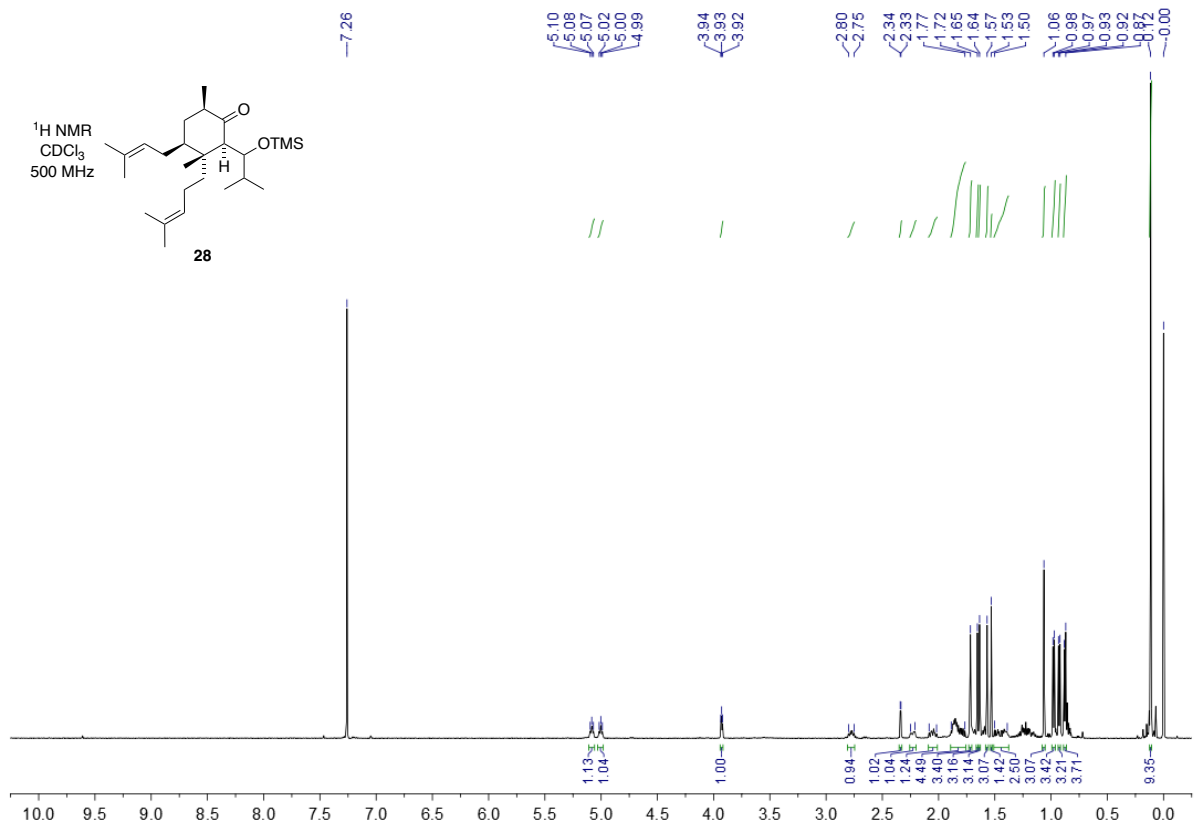
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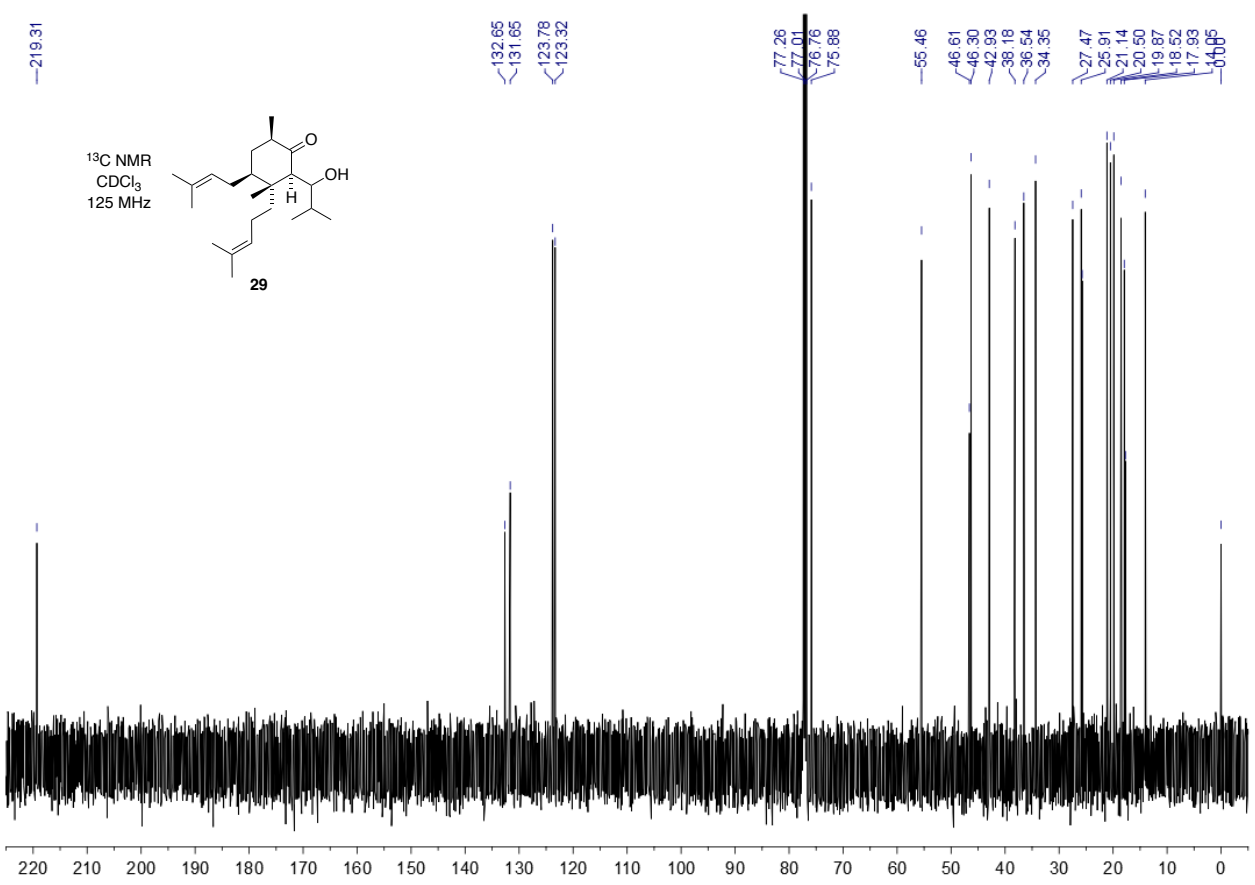
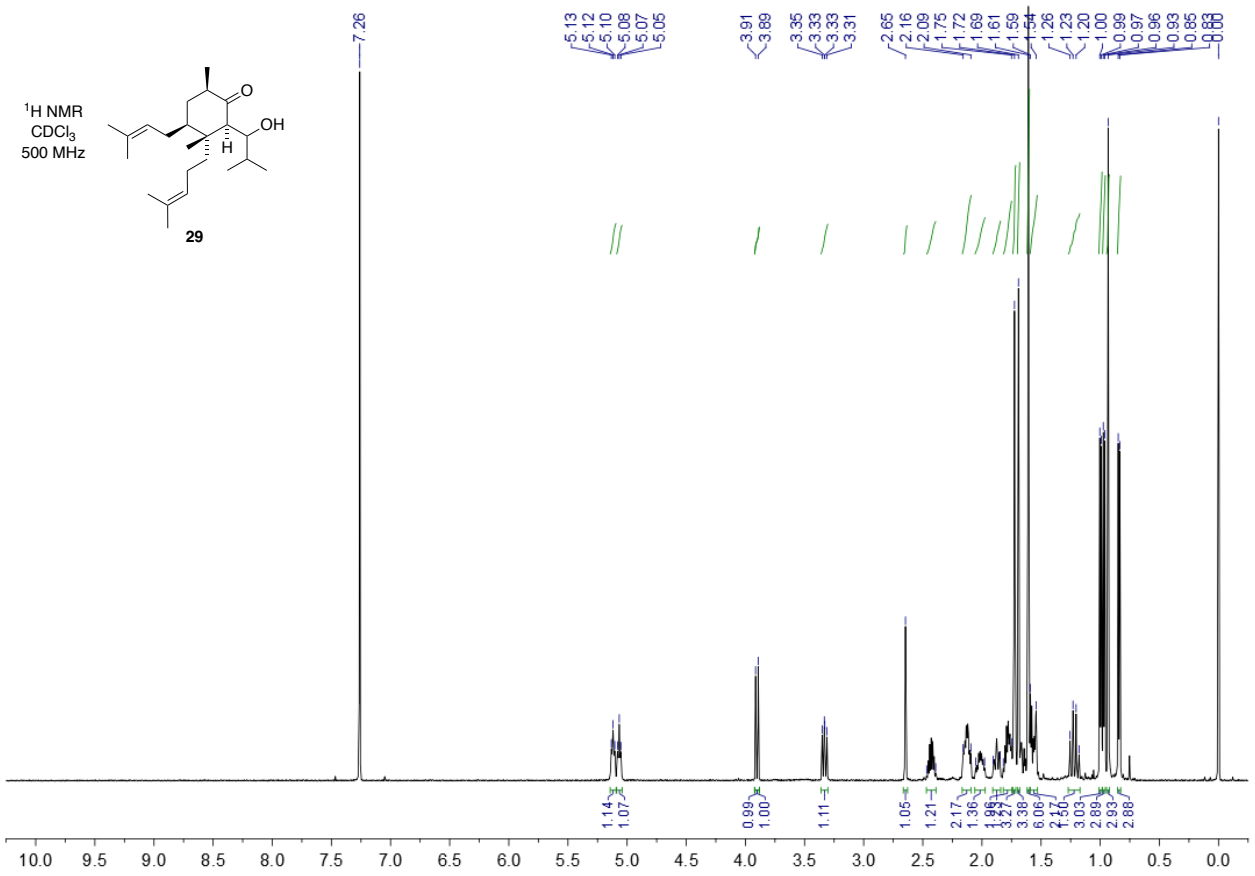
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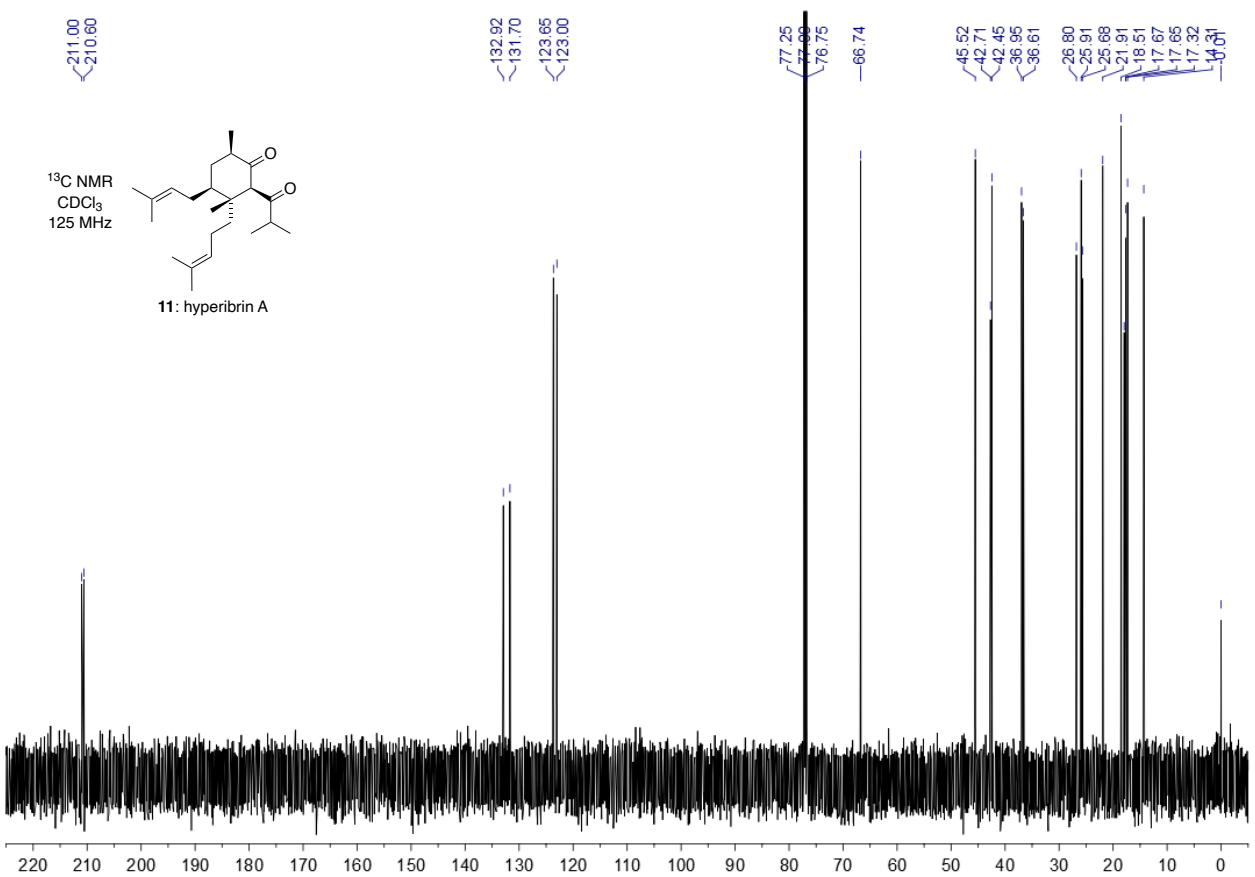
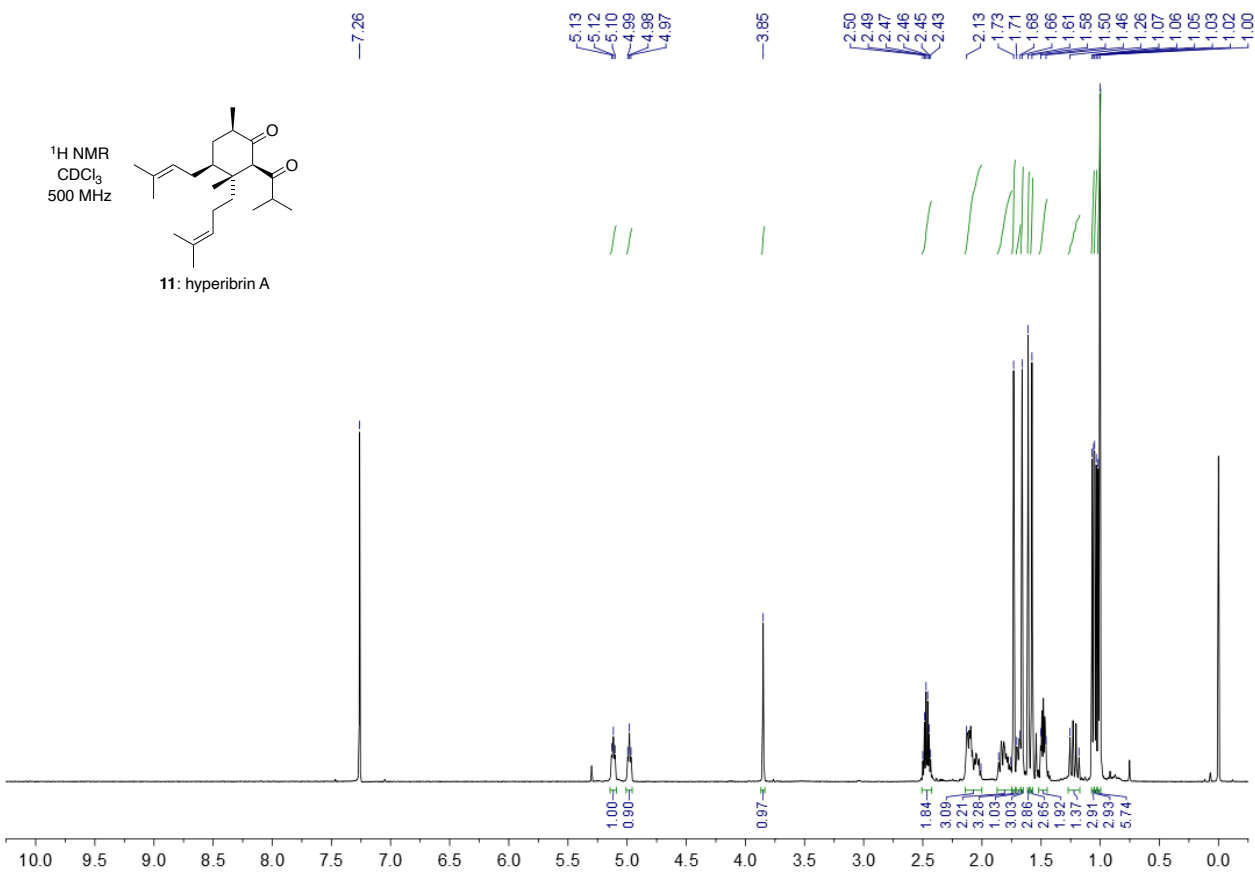
1. NMR spectra

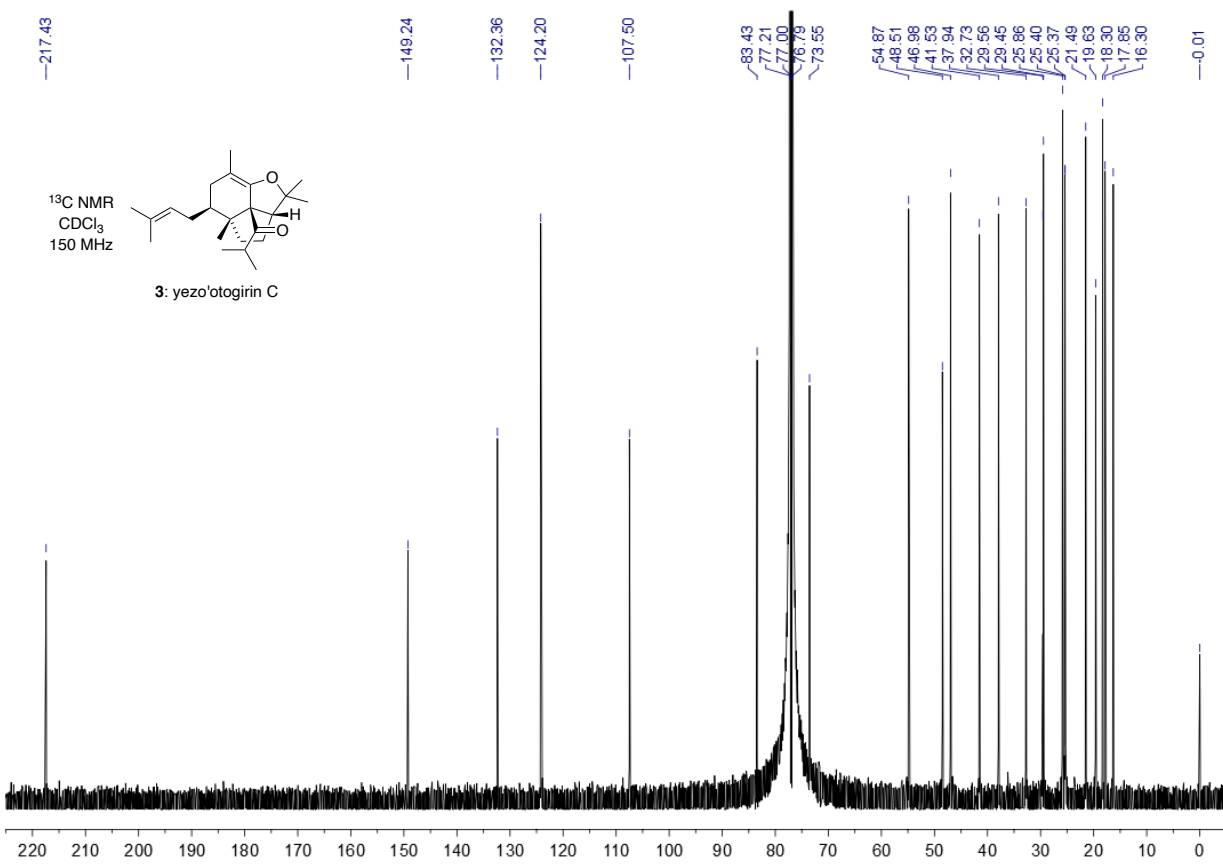
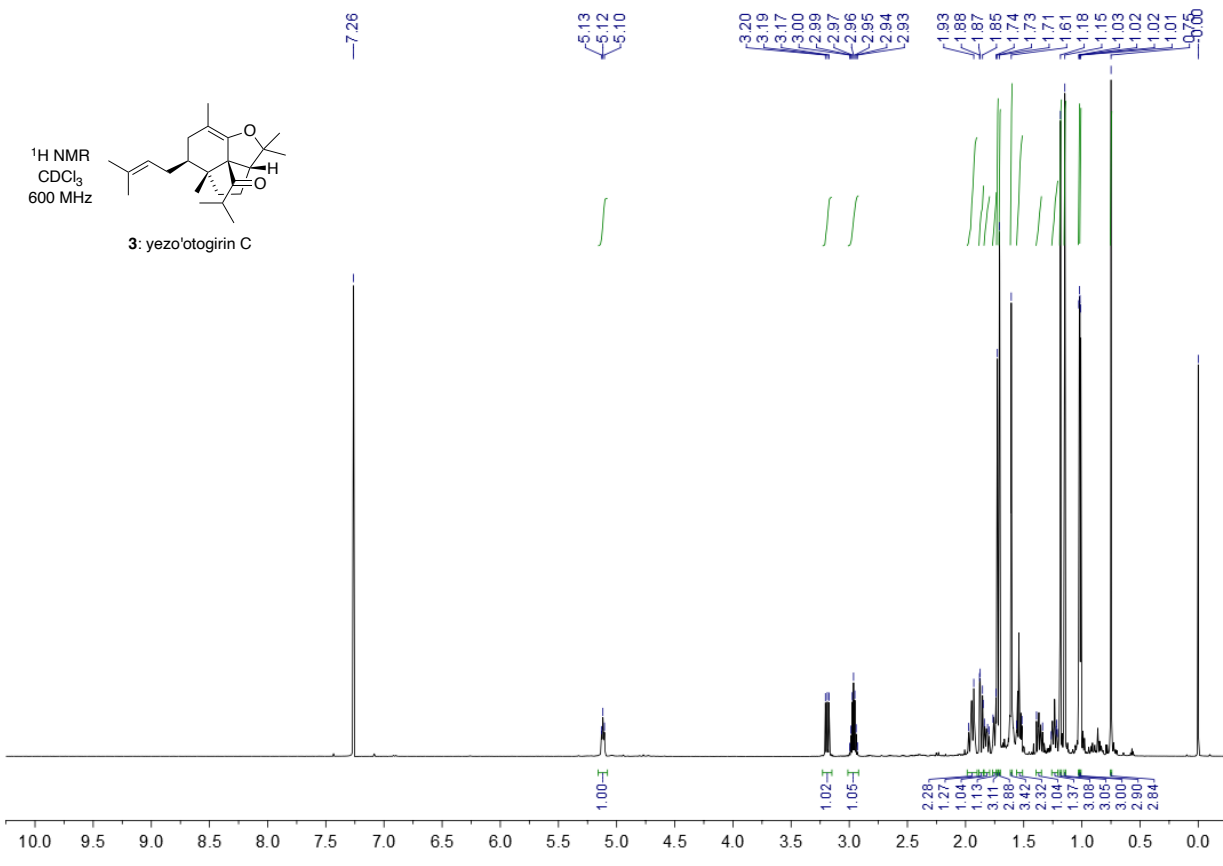


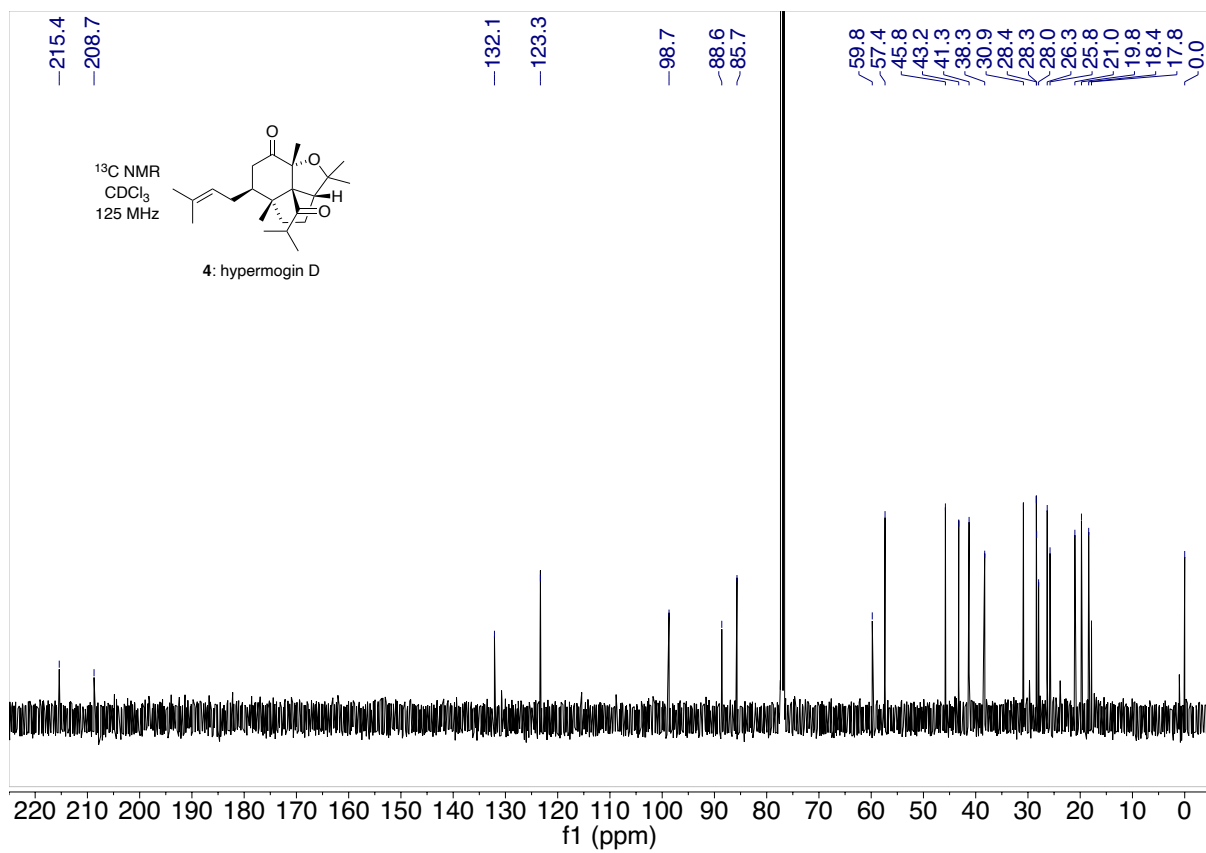
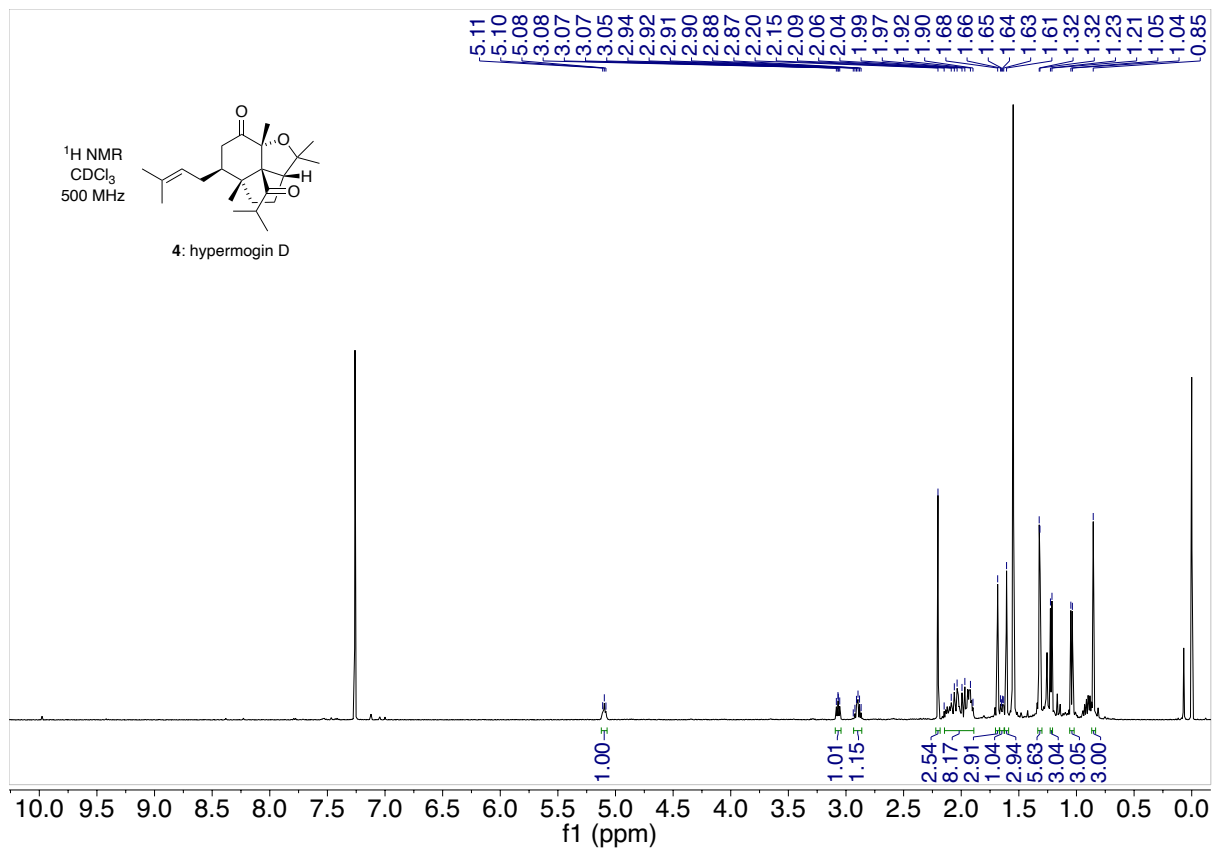


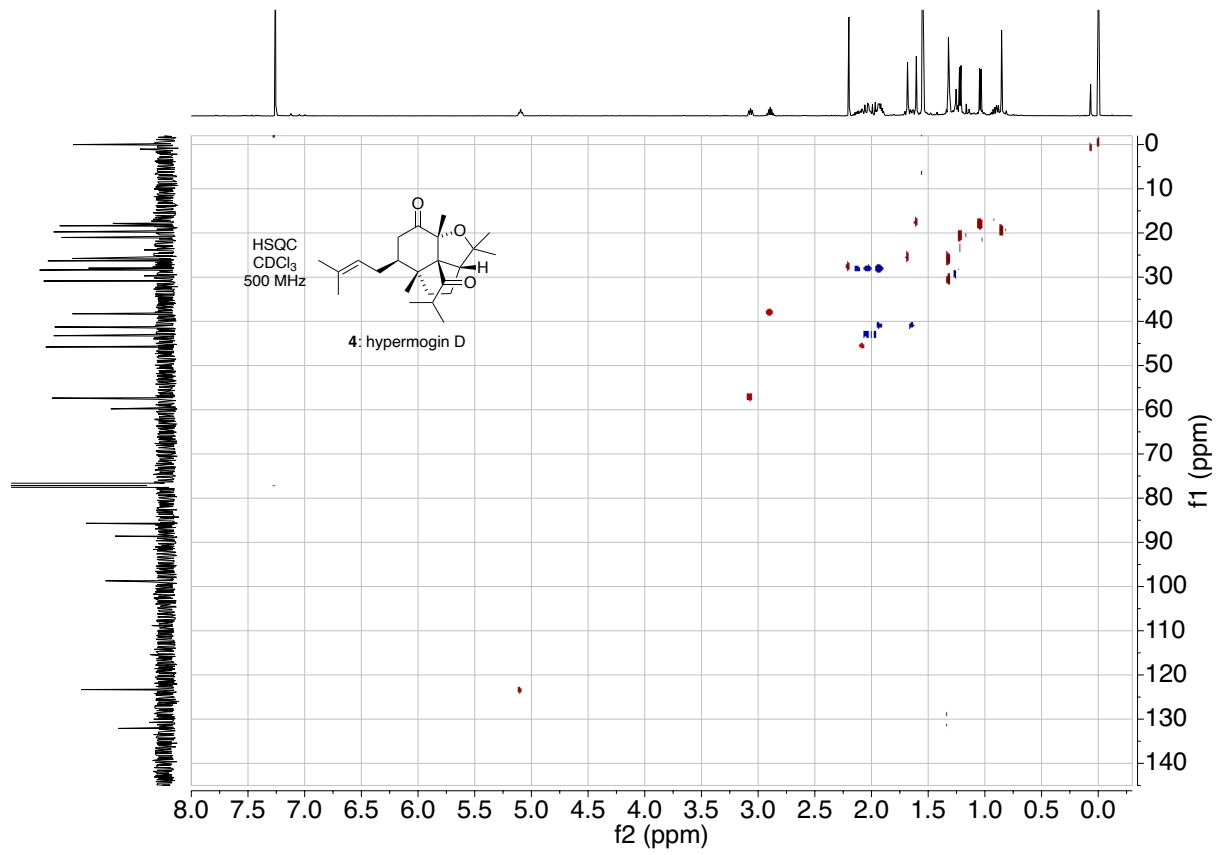
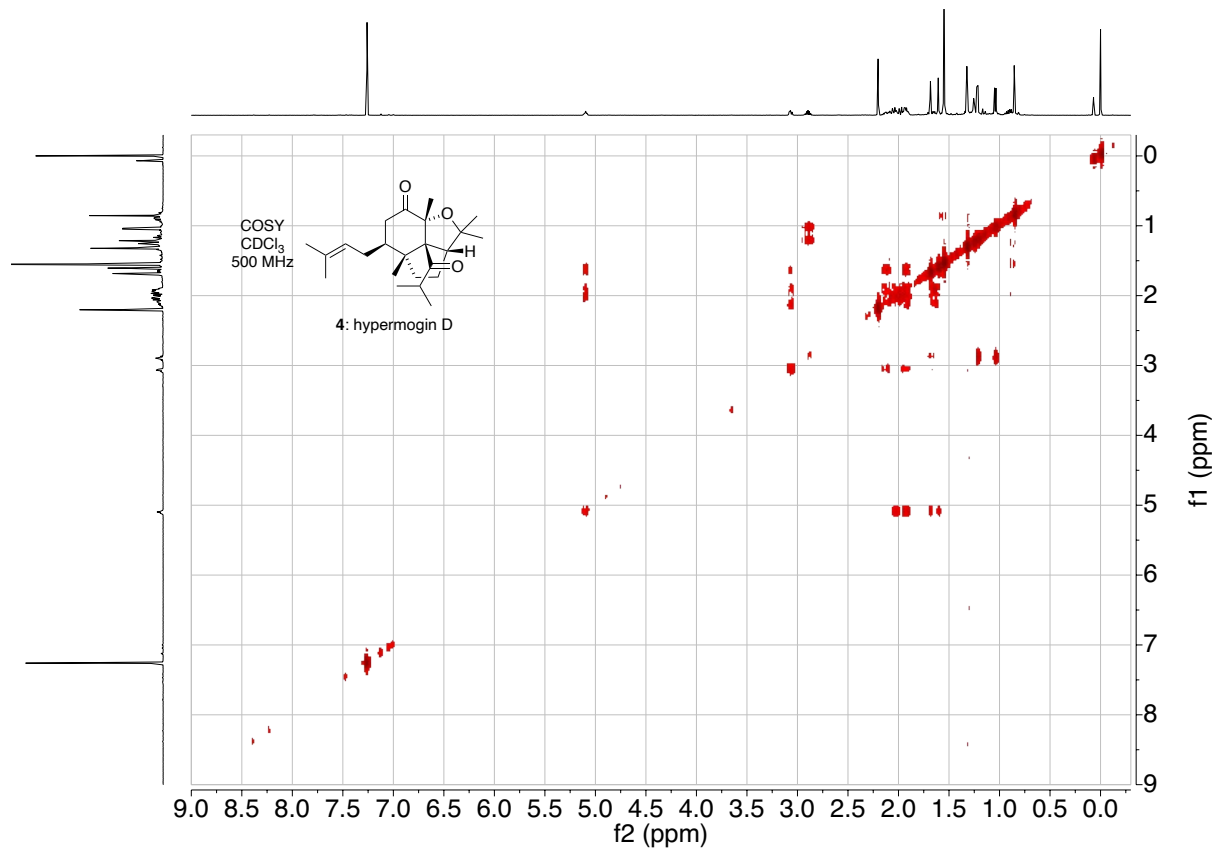


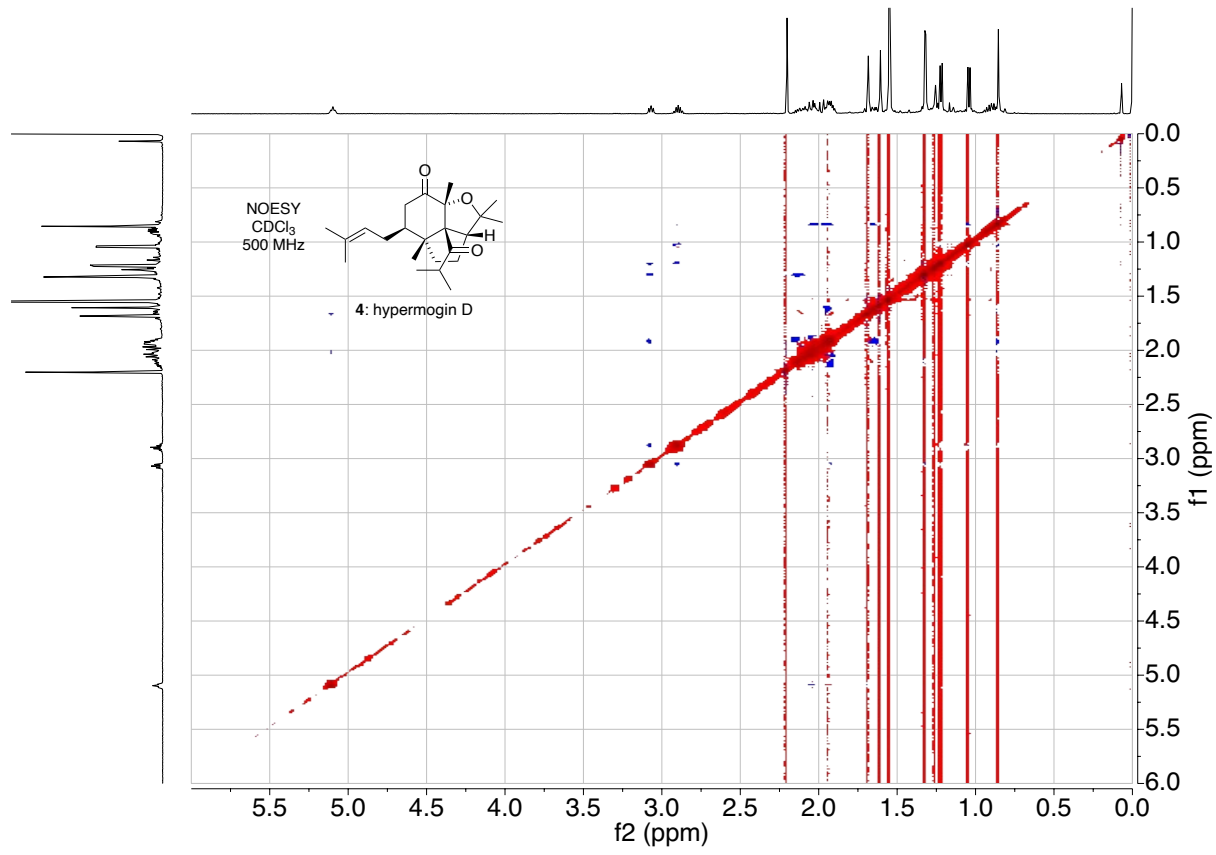
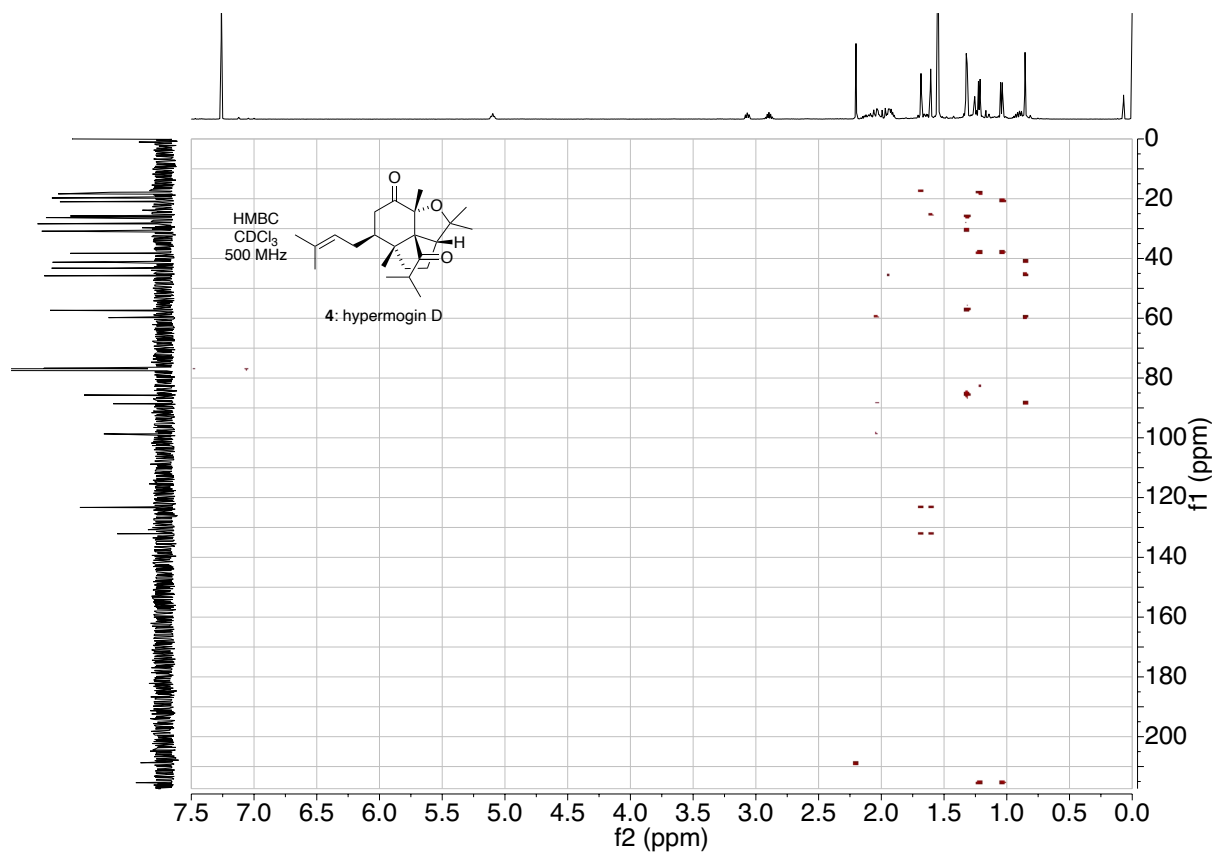


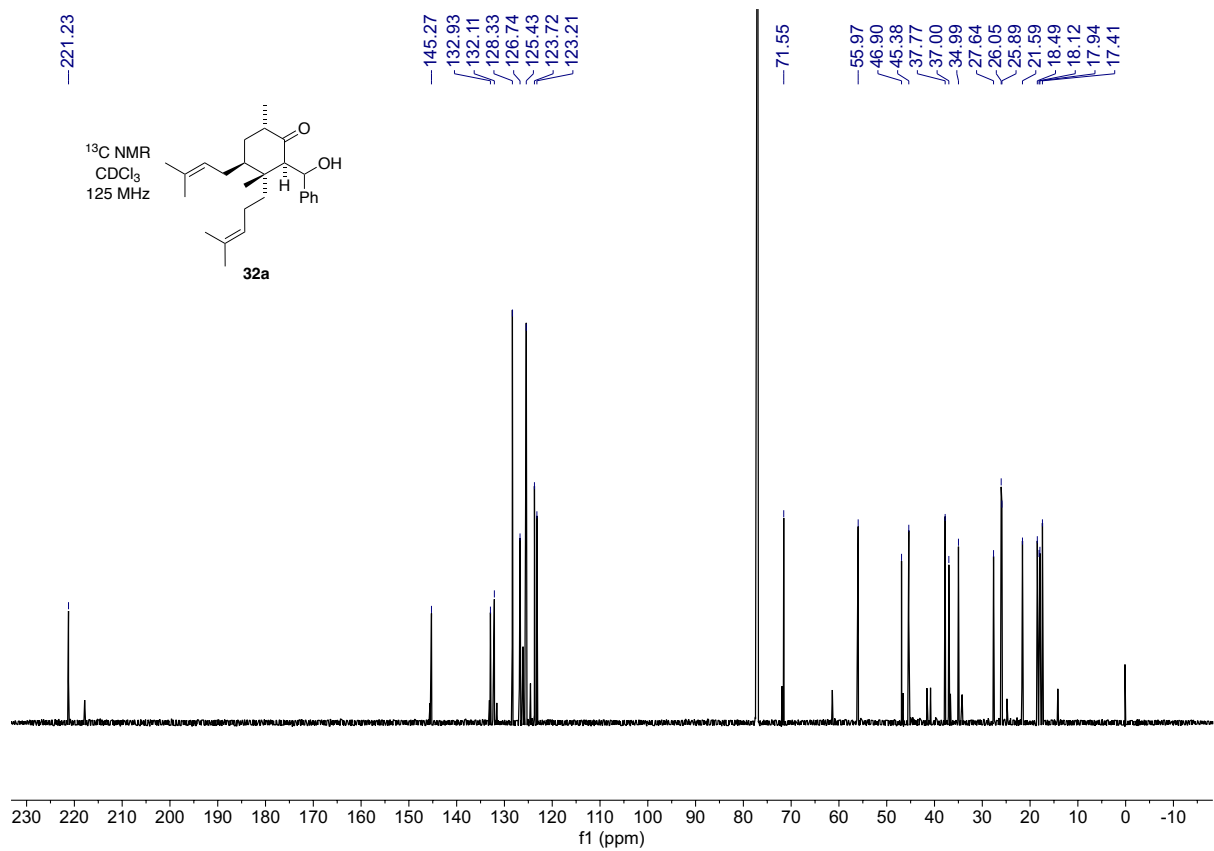
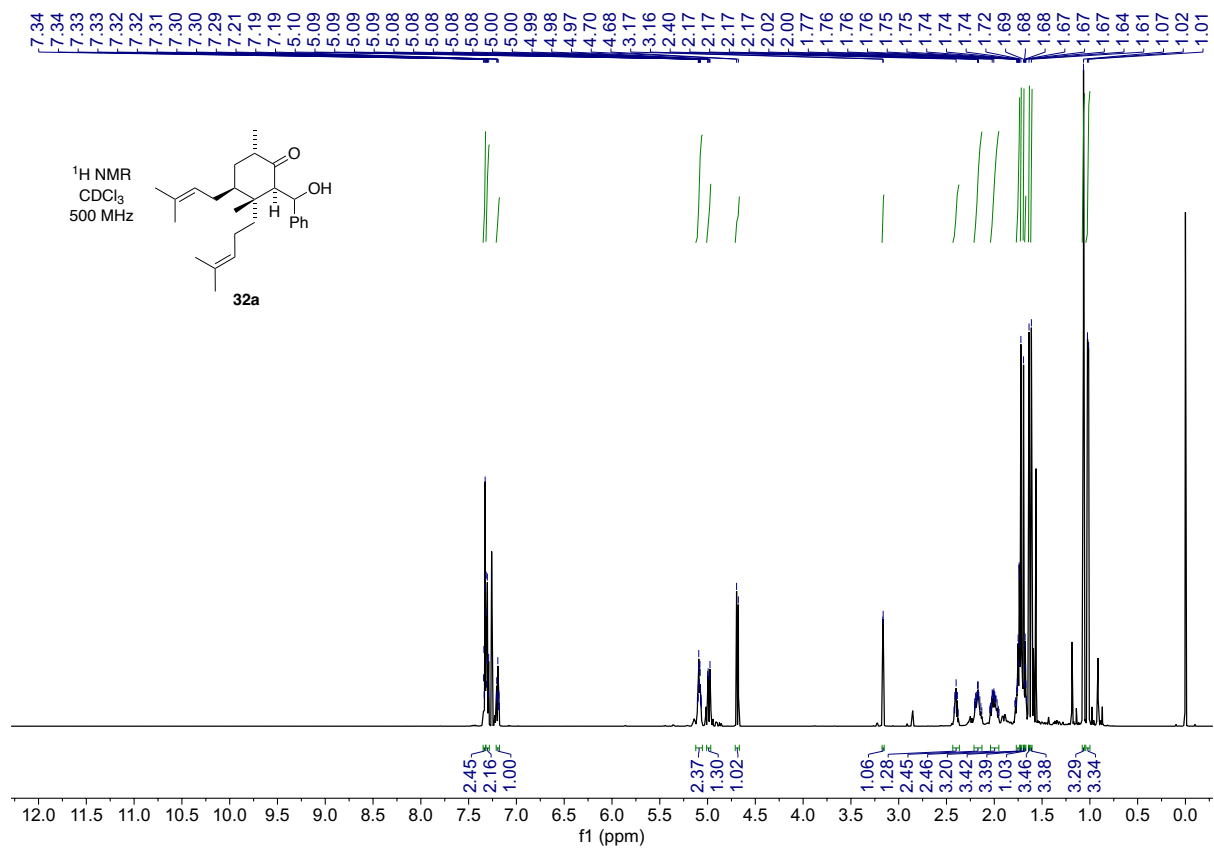


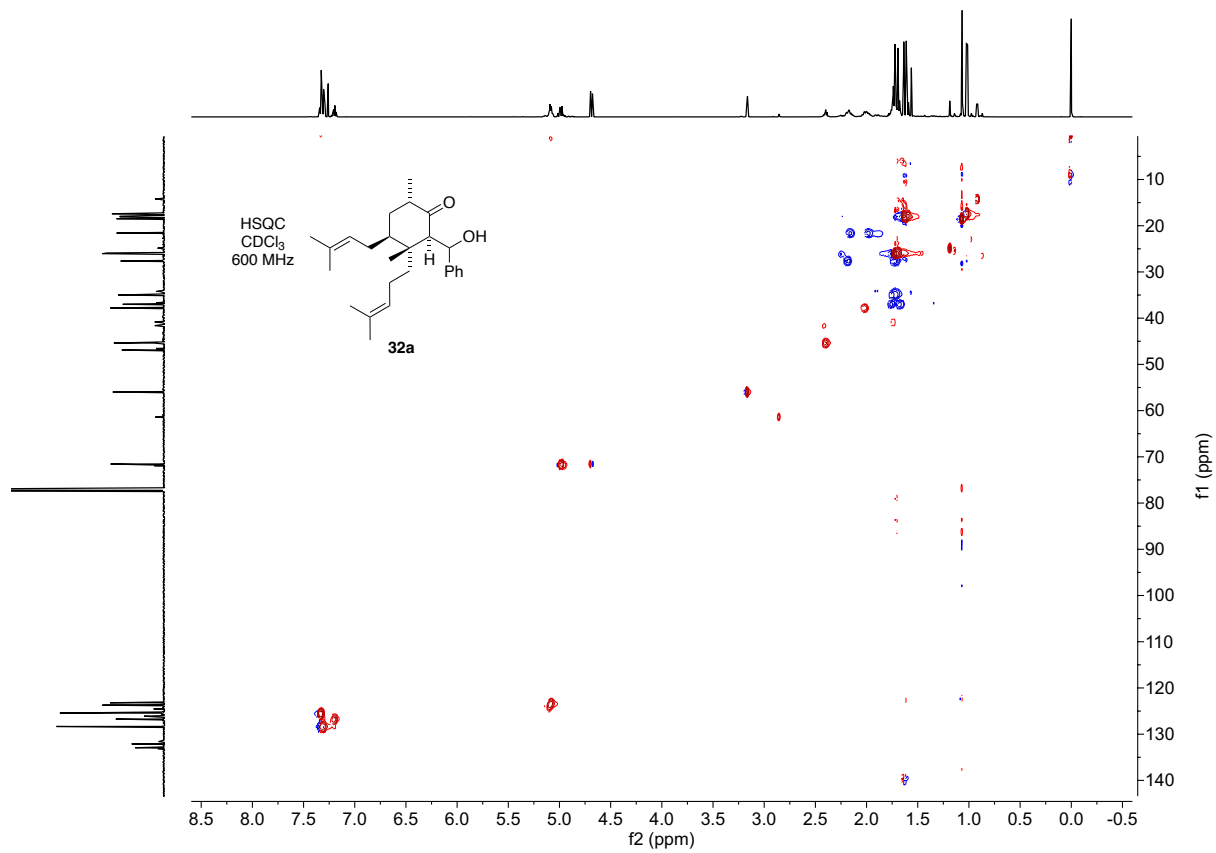
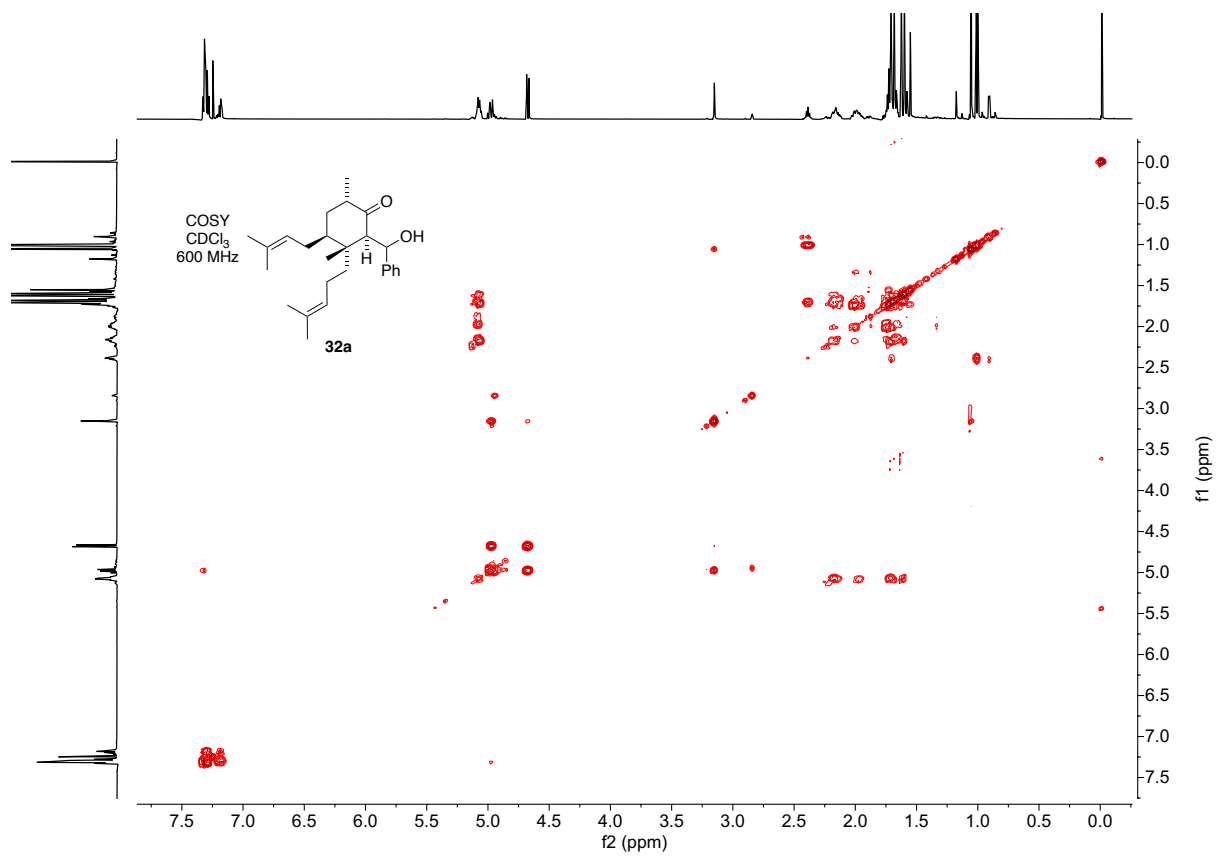


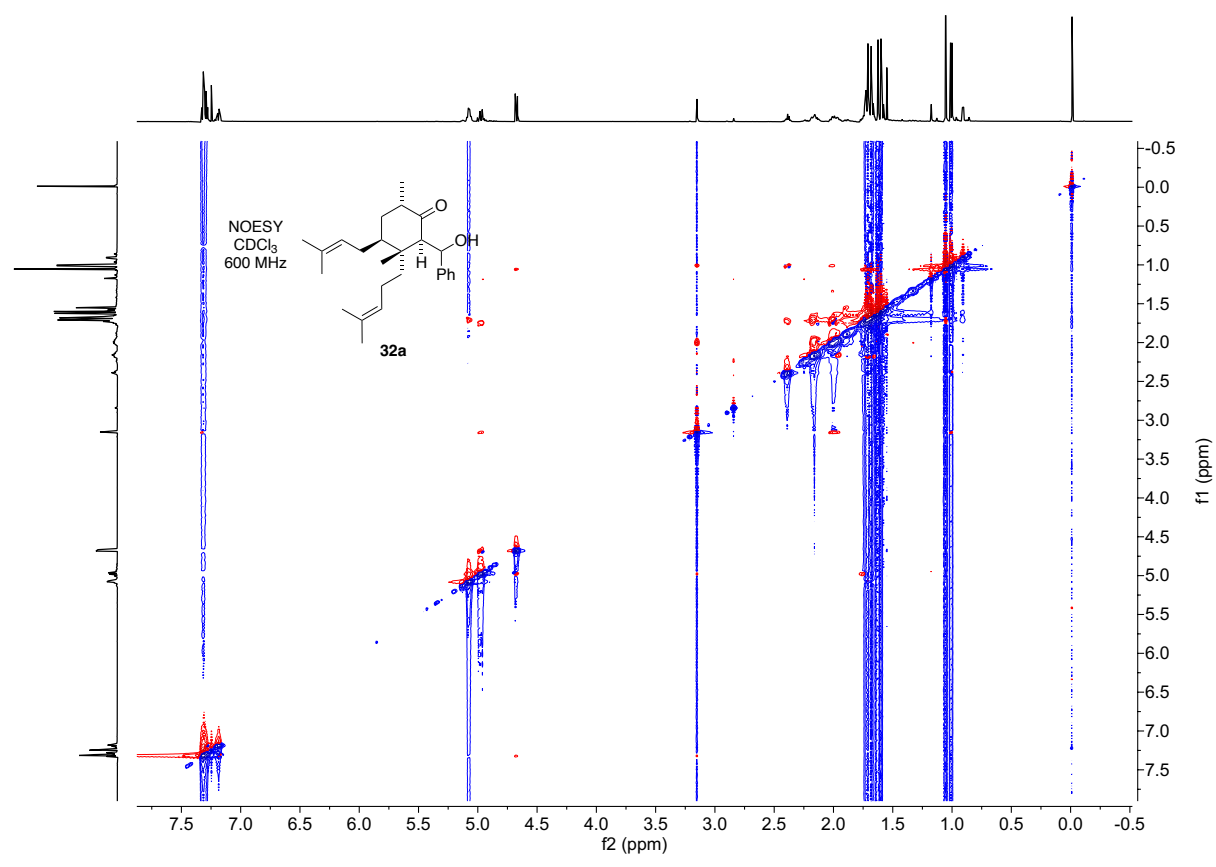
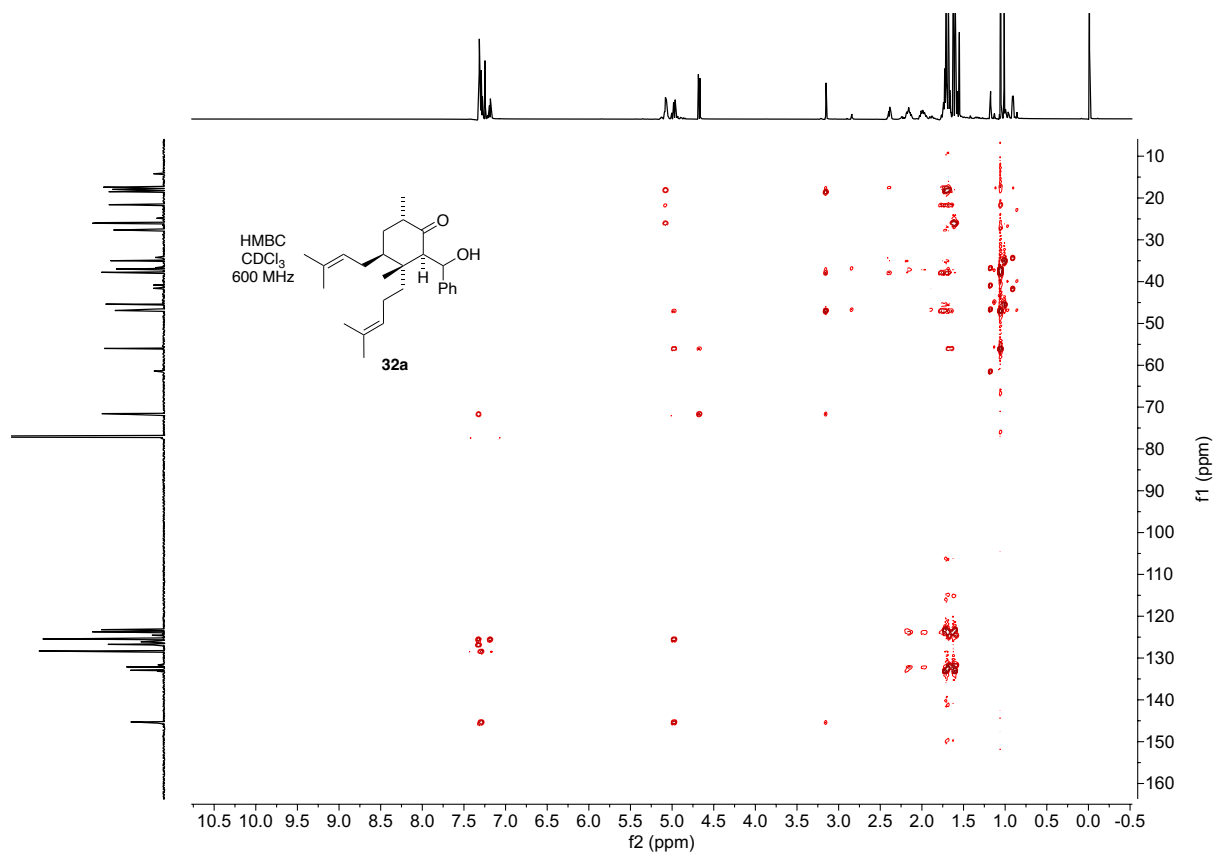


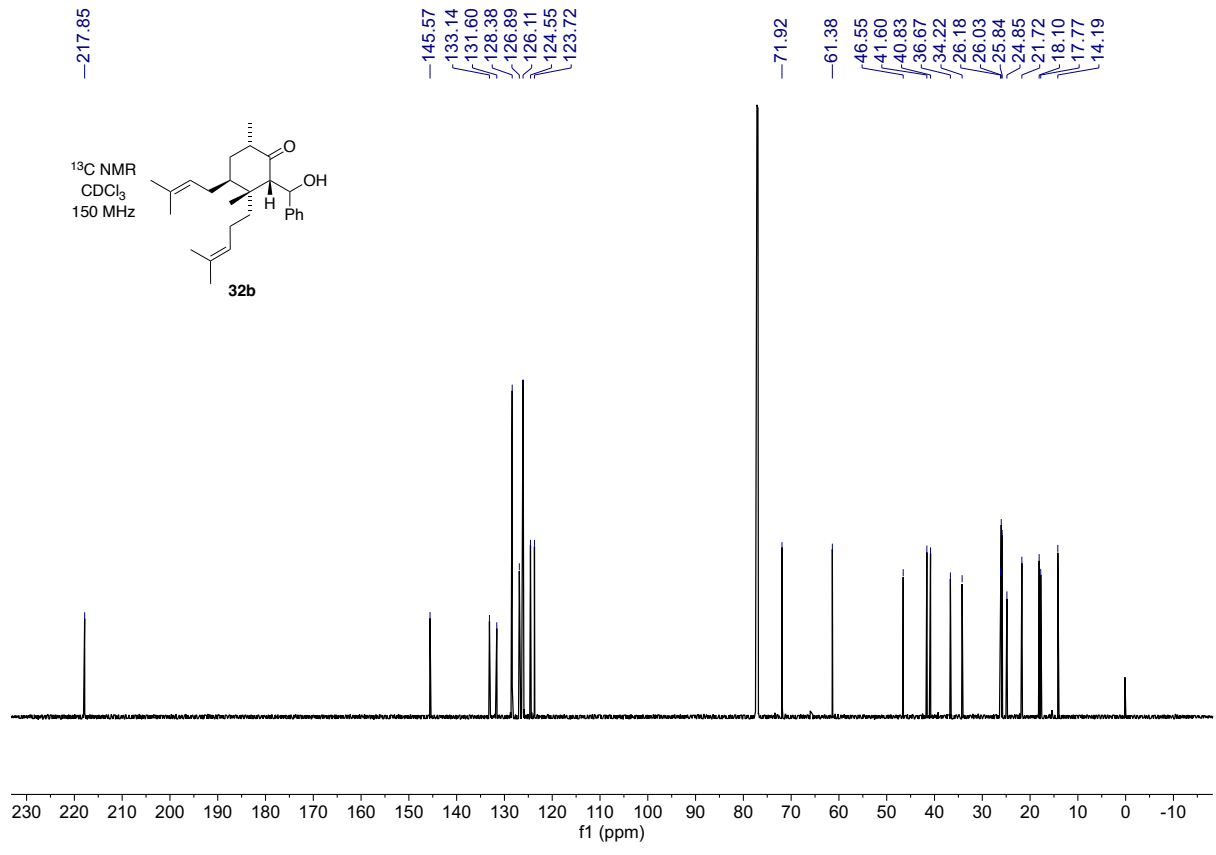
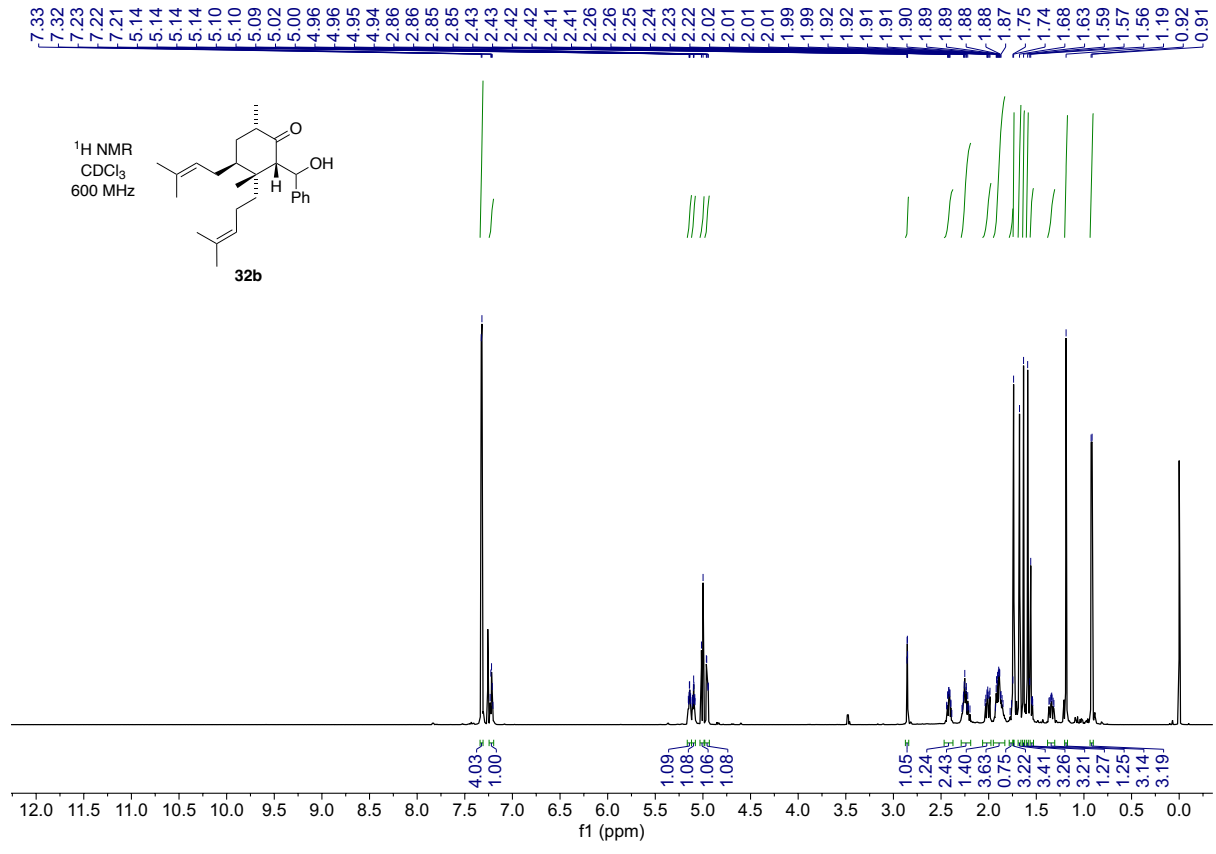


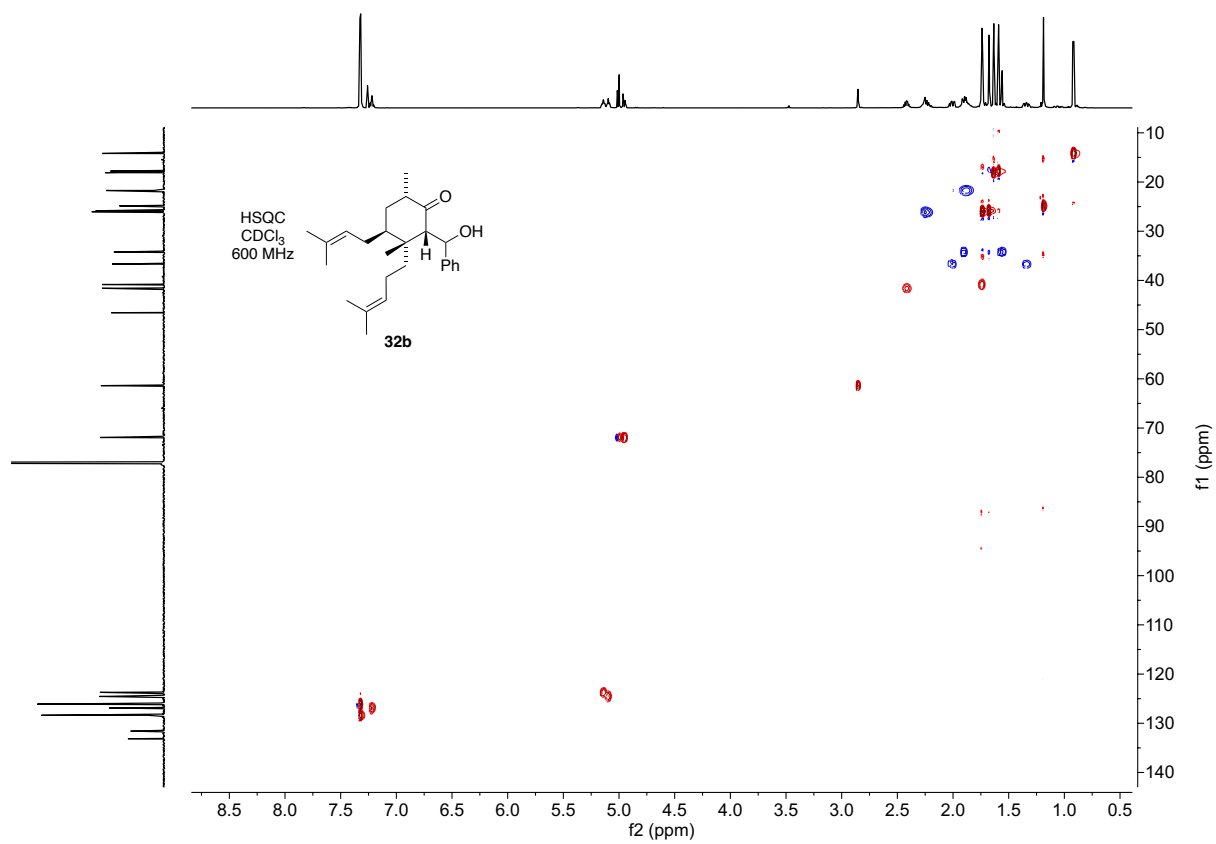
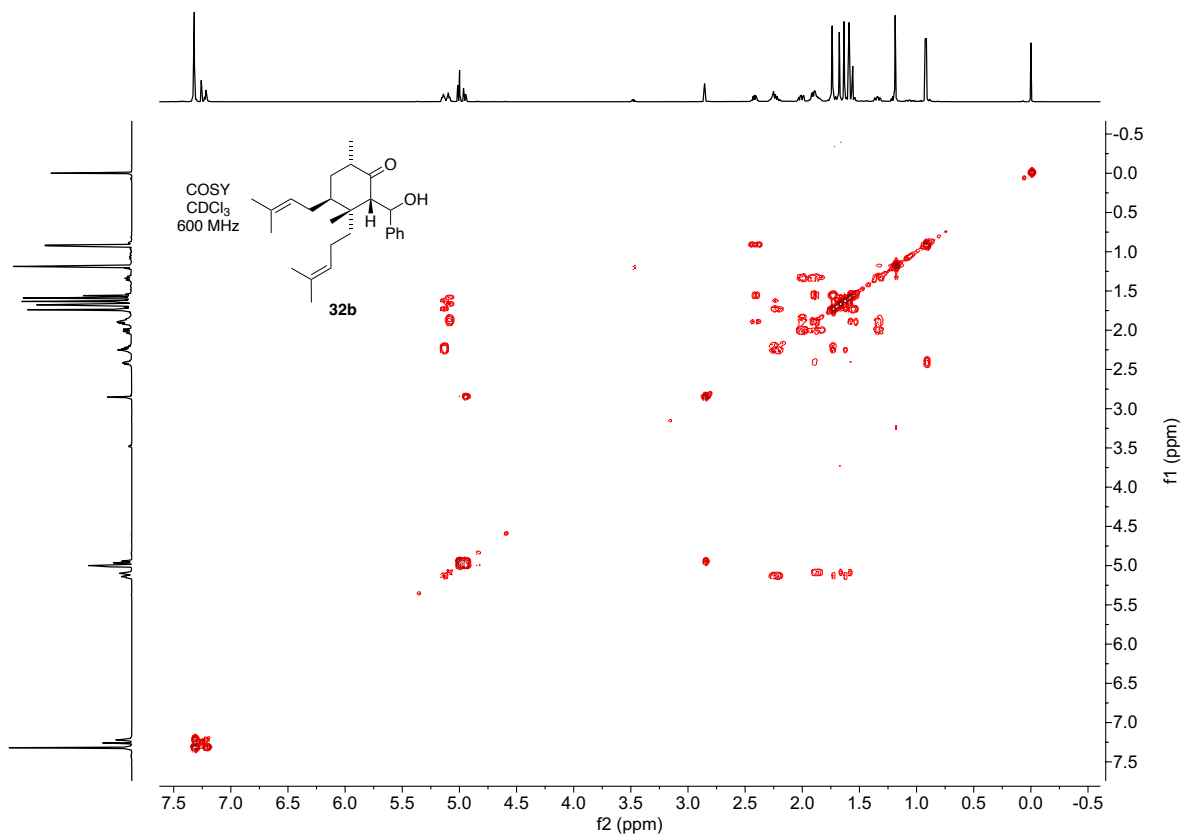


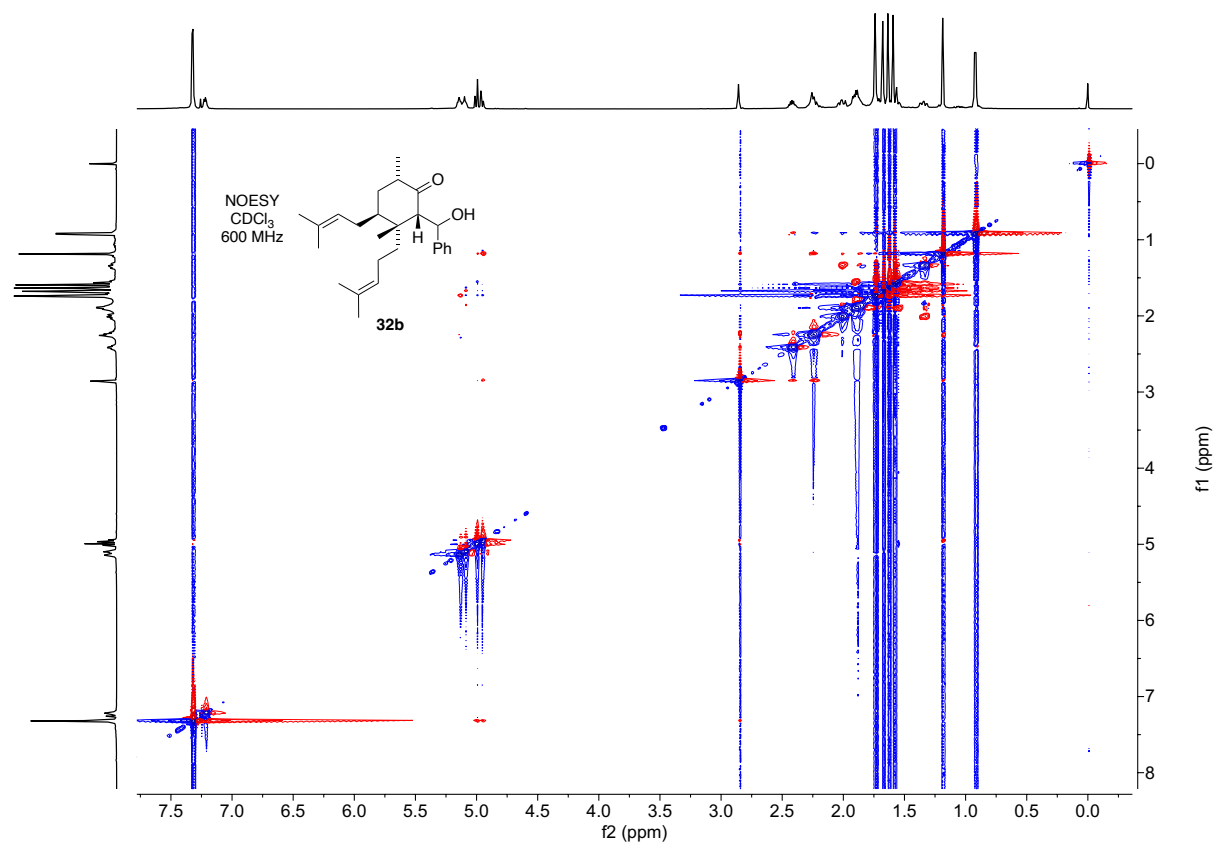
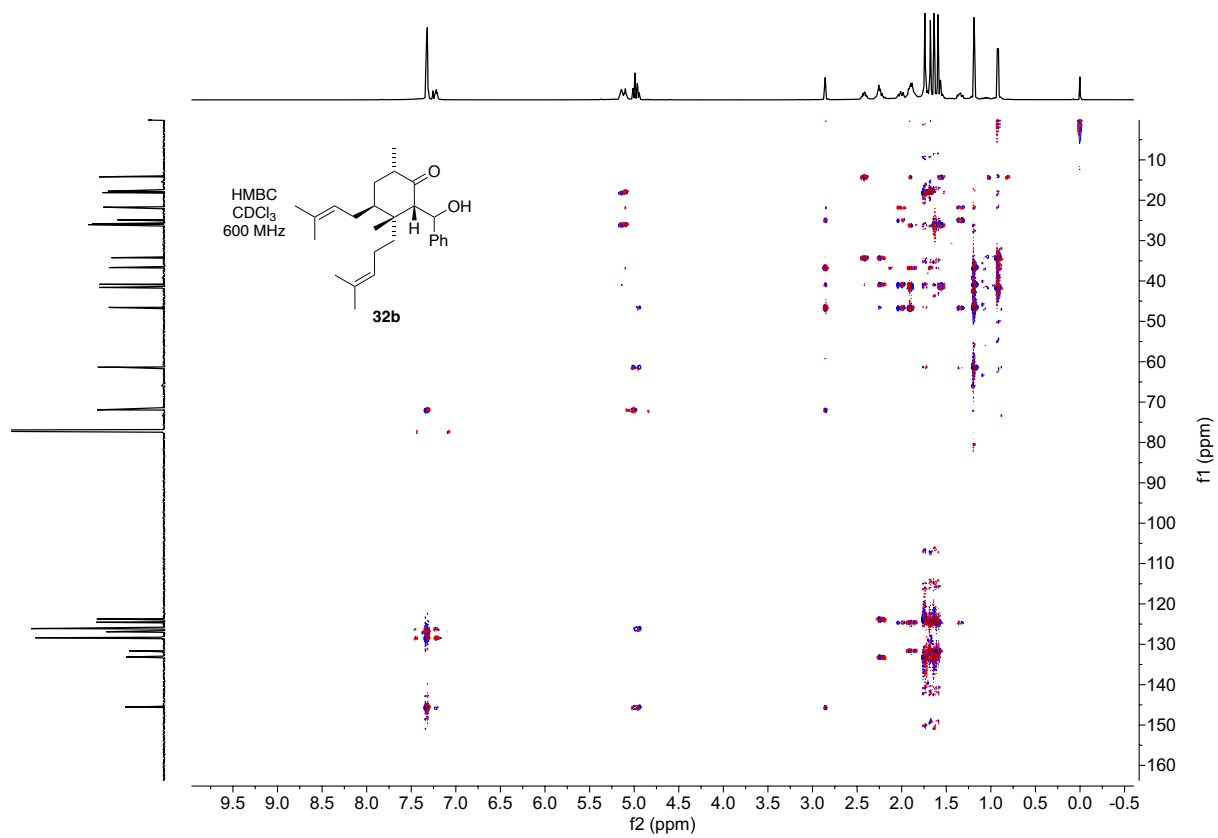


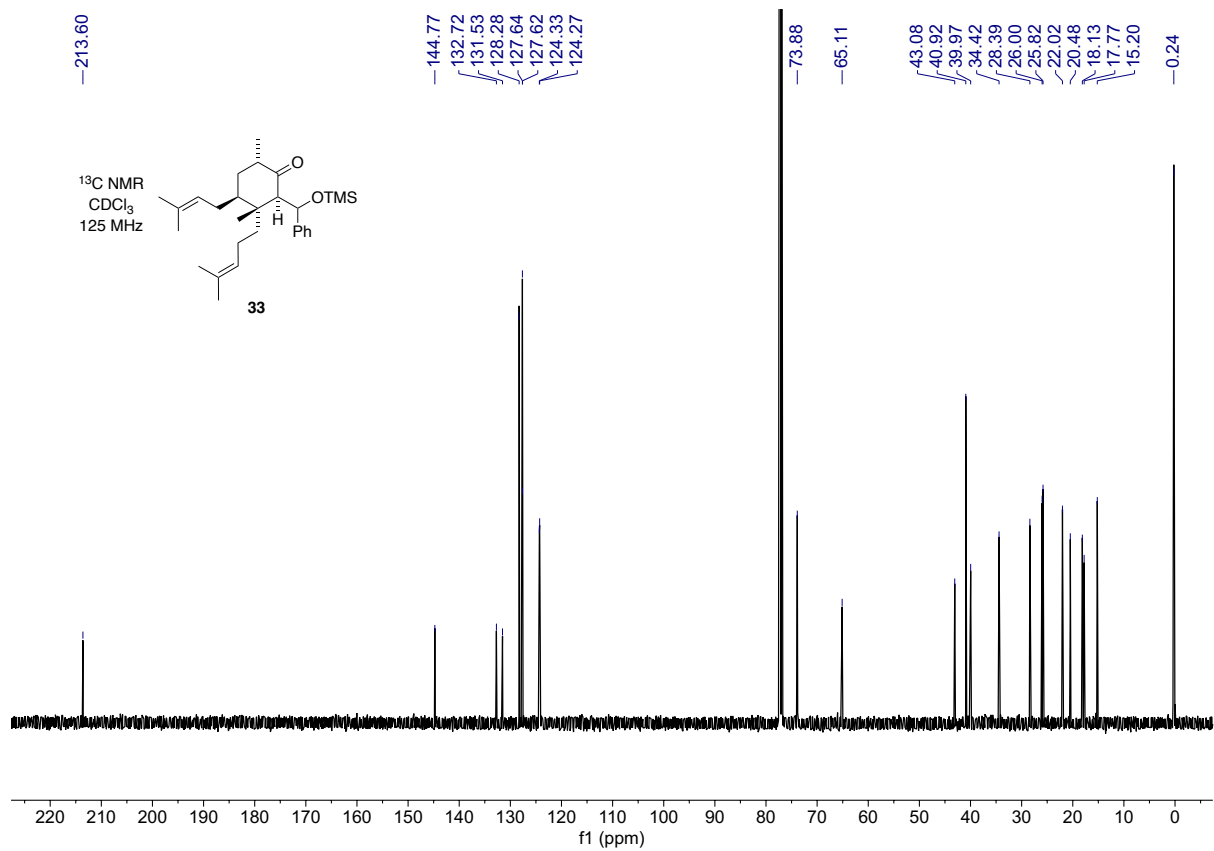
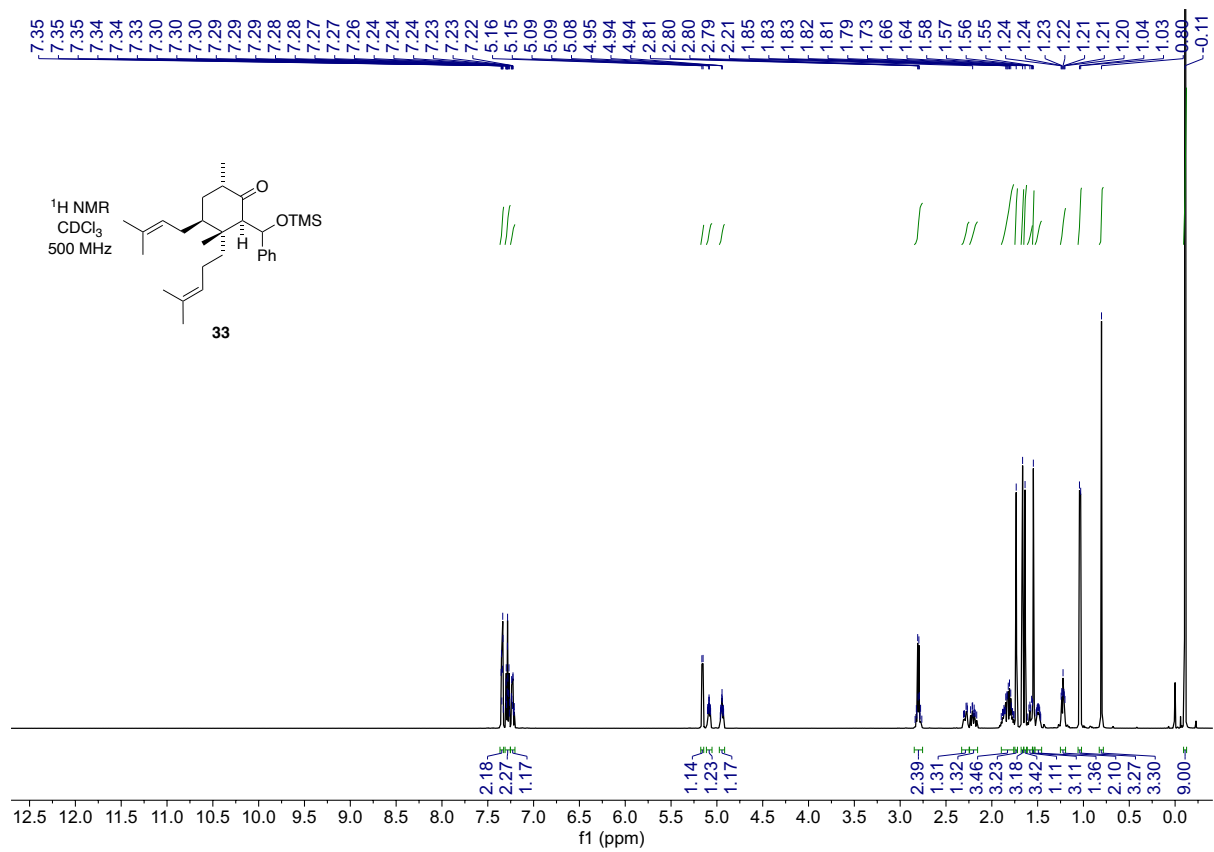


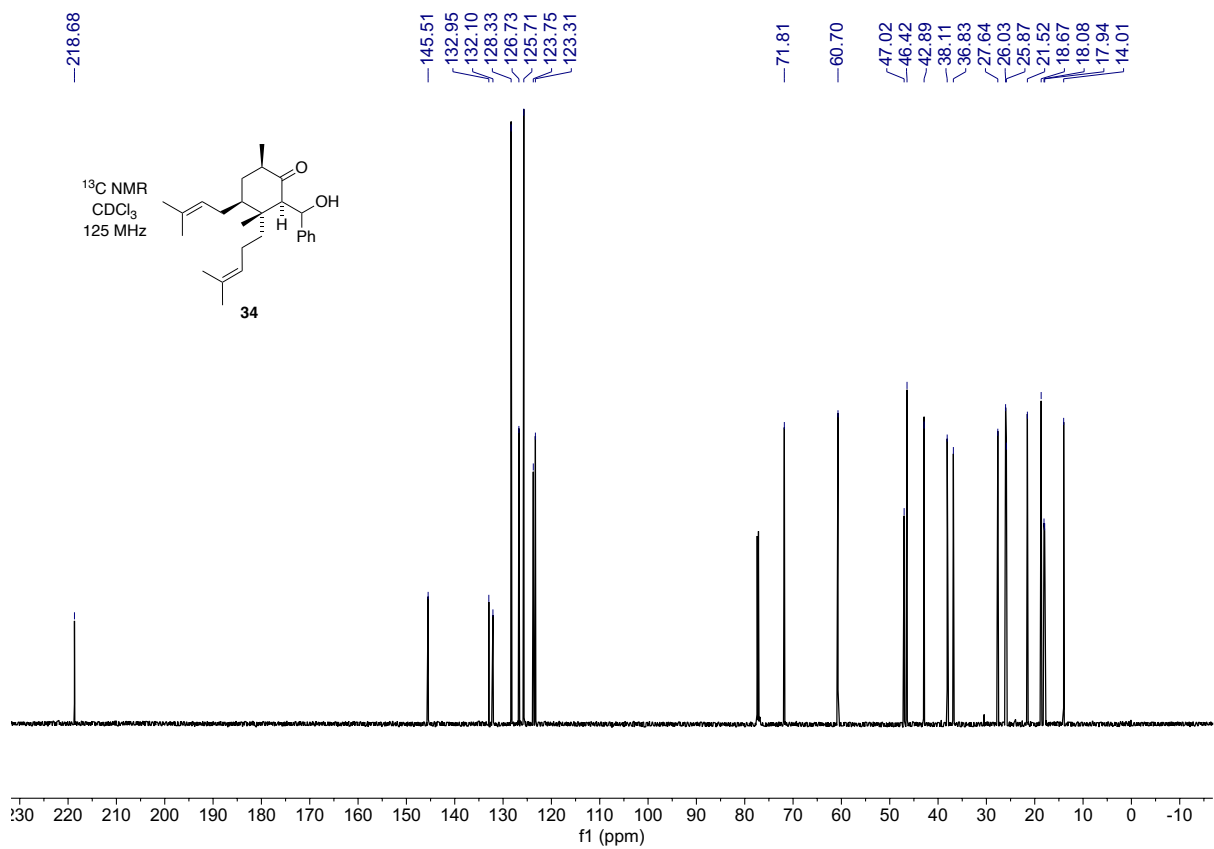
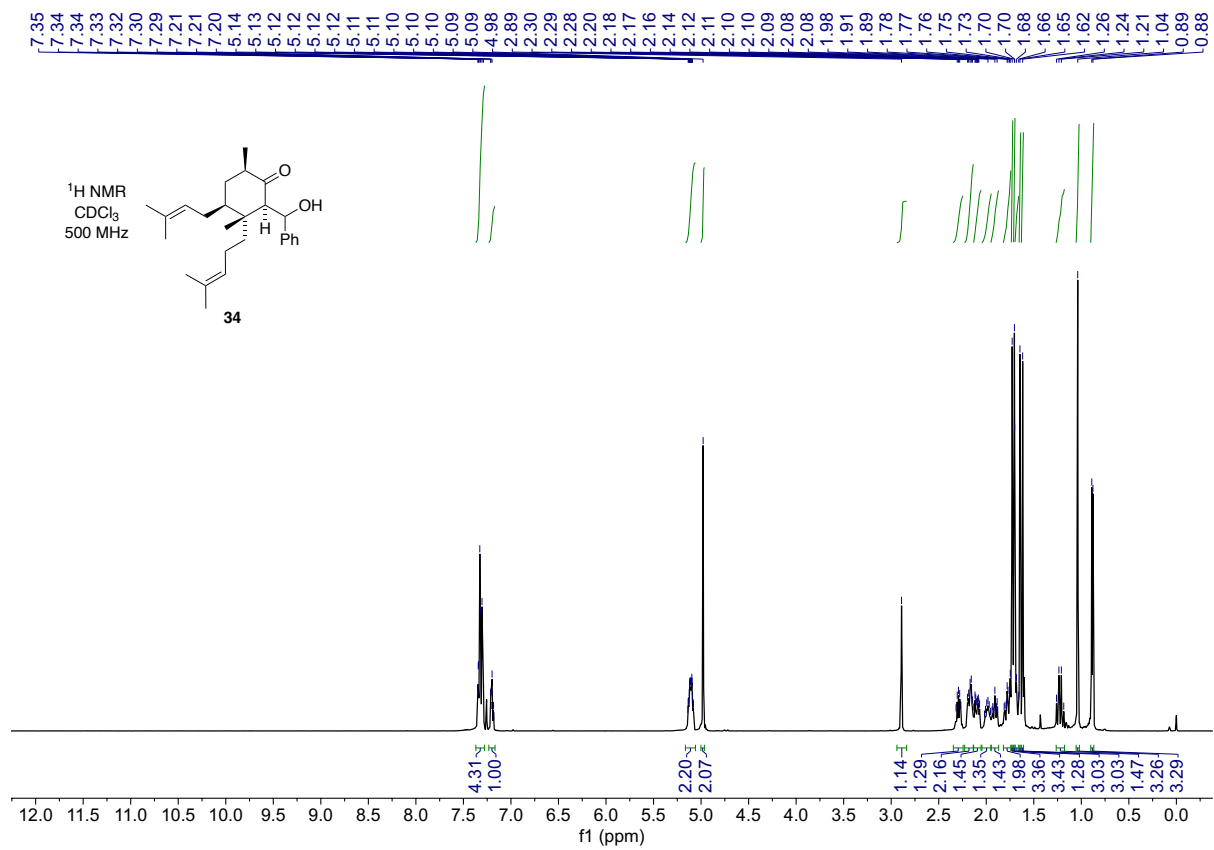


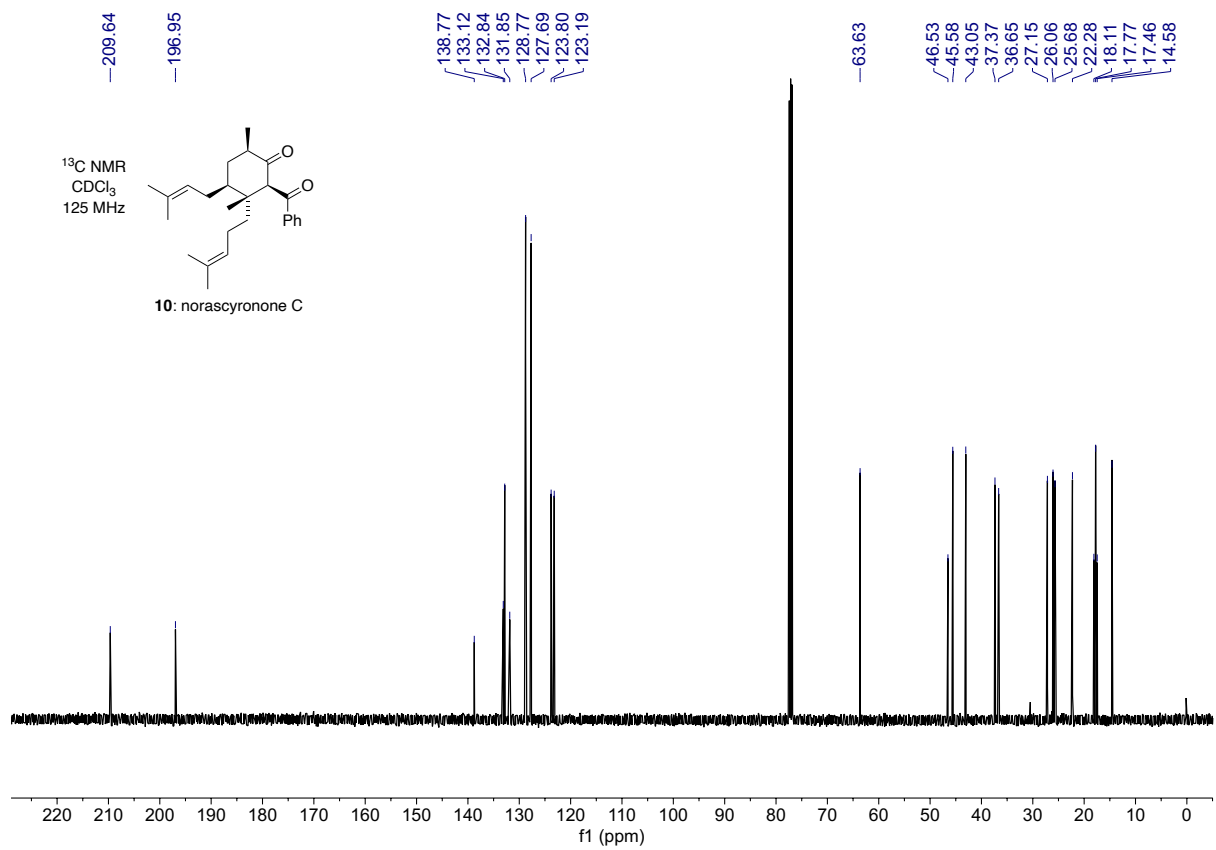
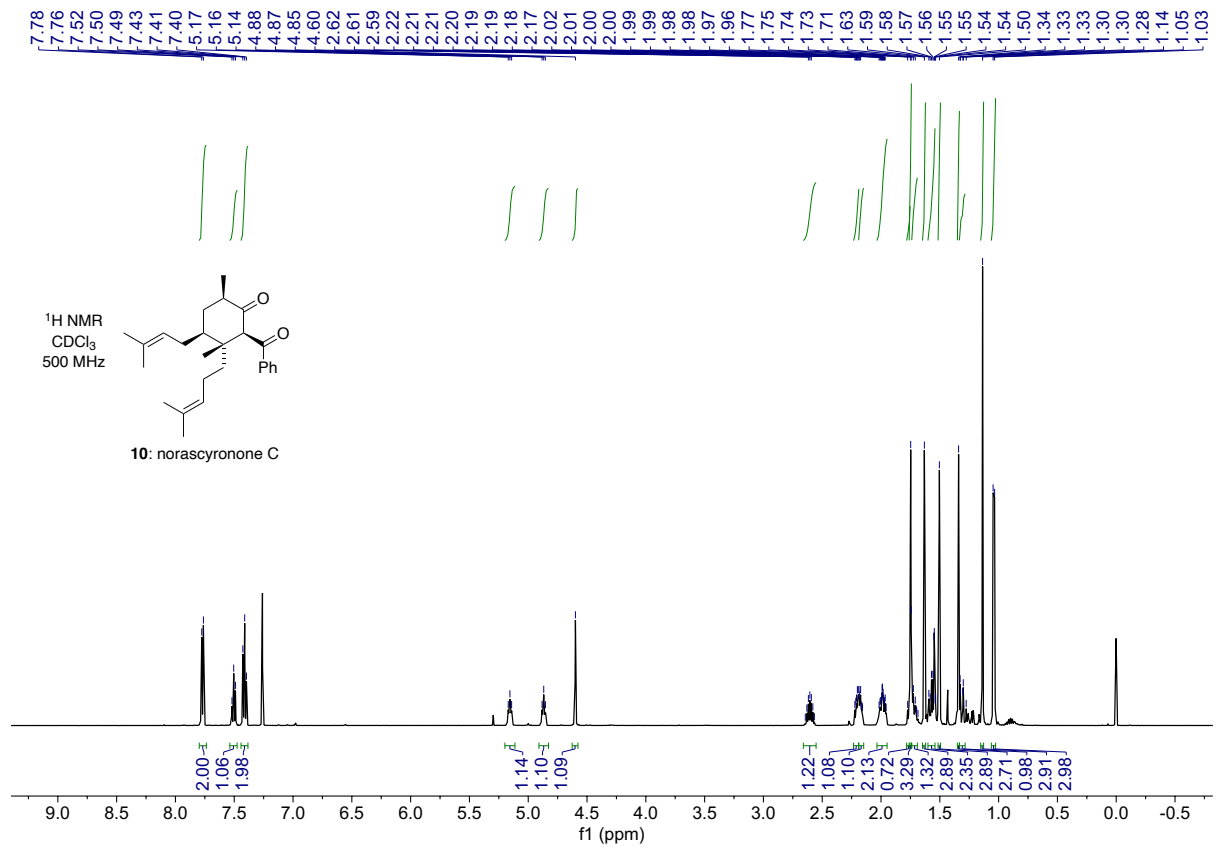


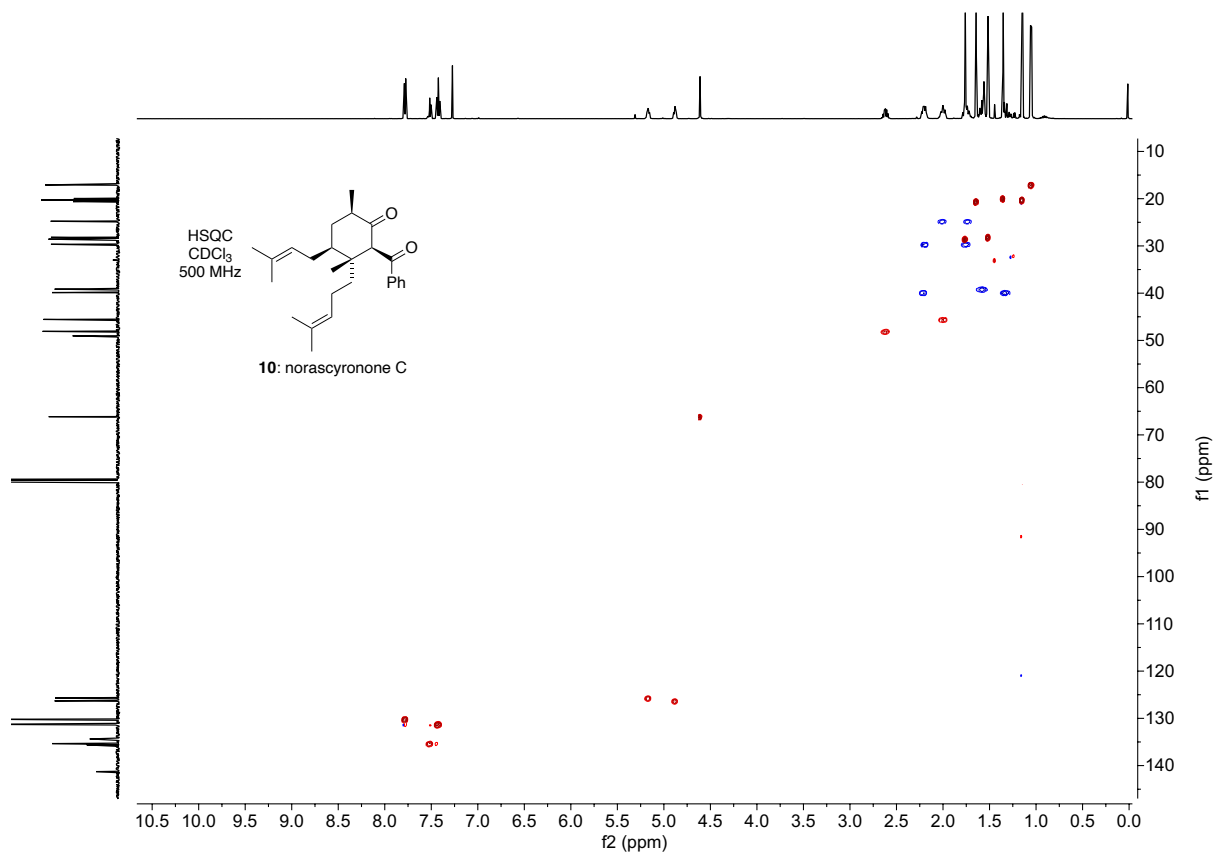
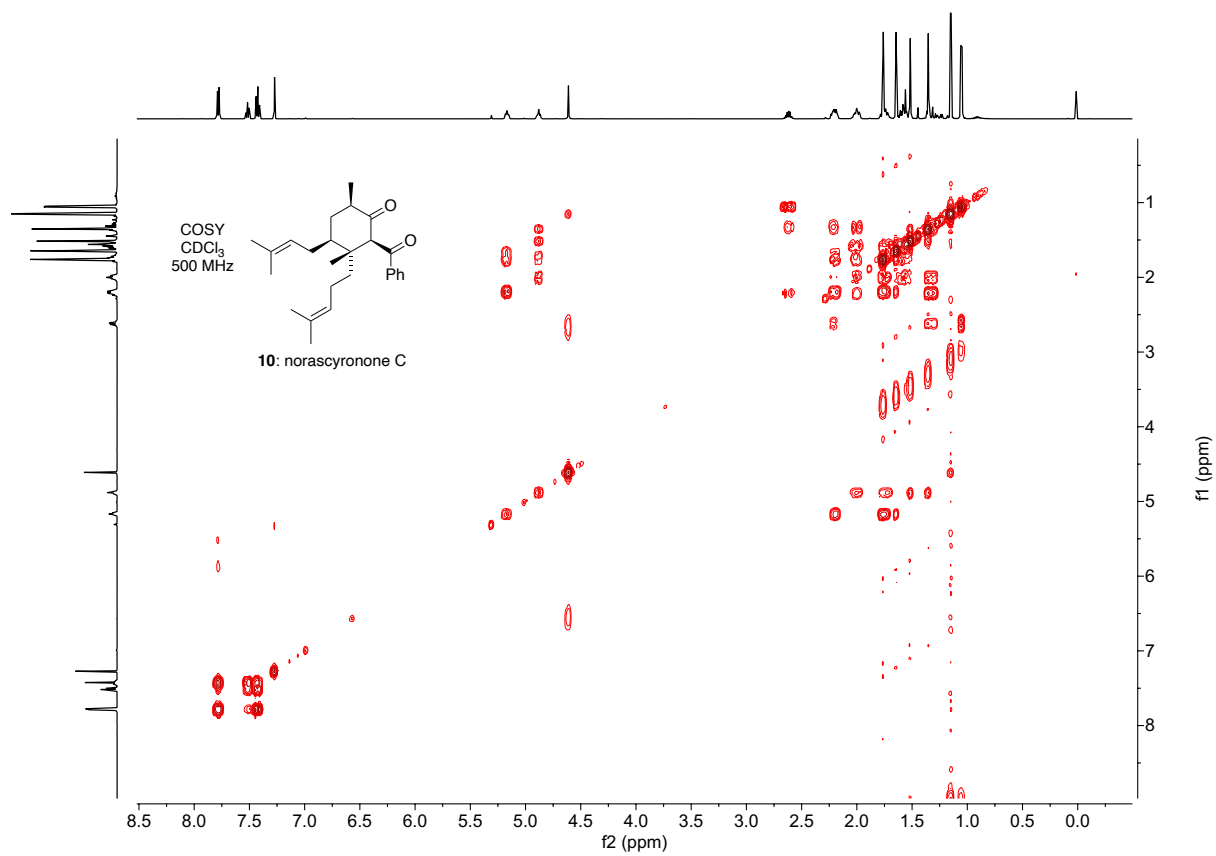


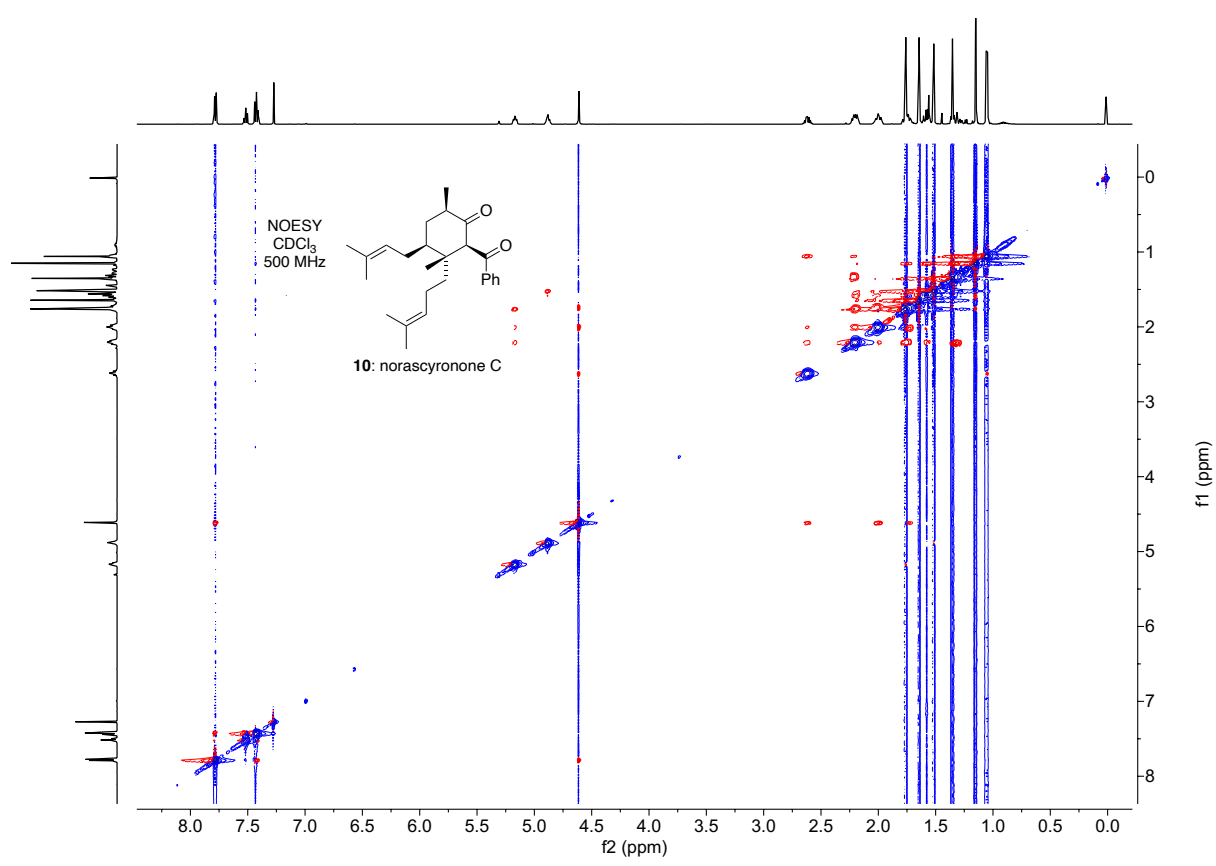
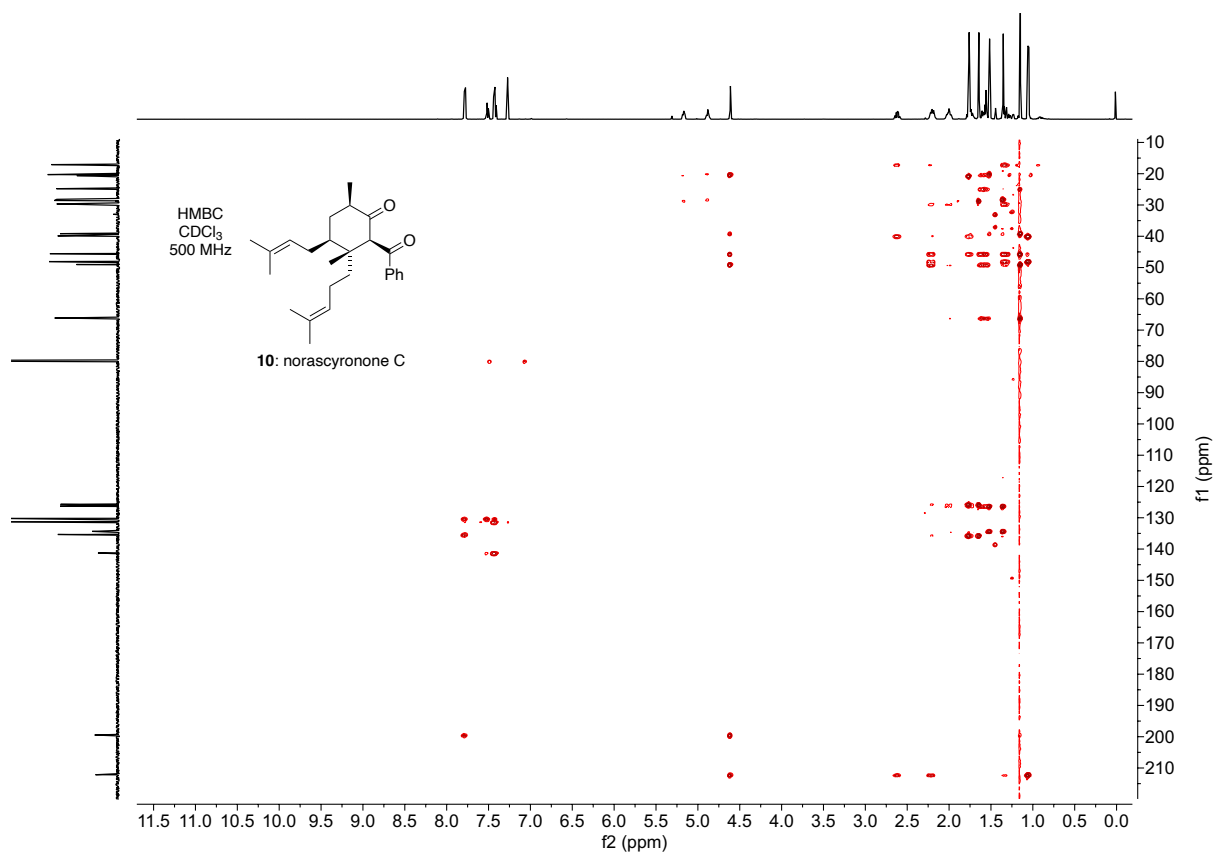


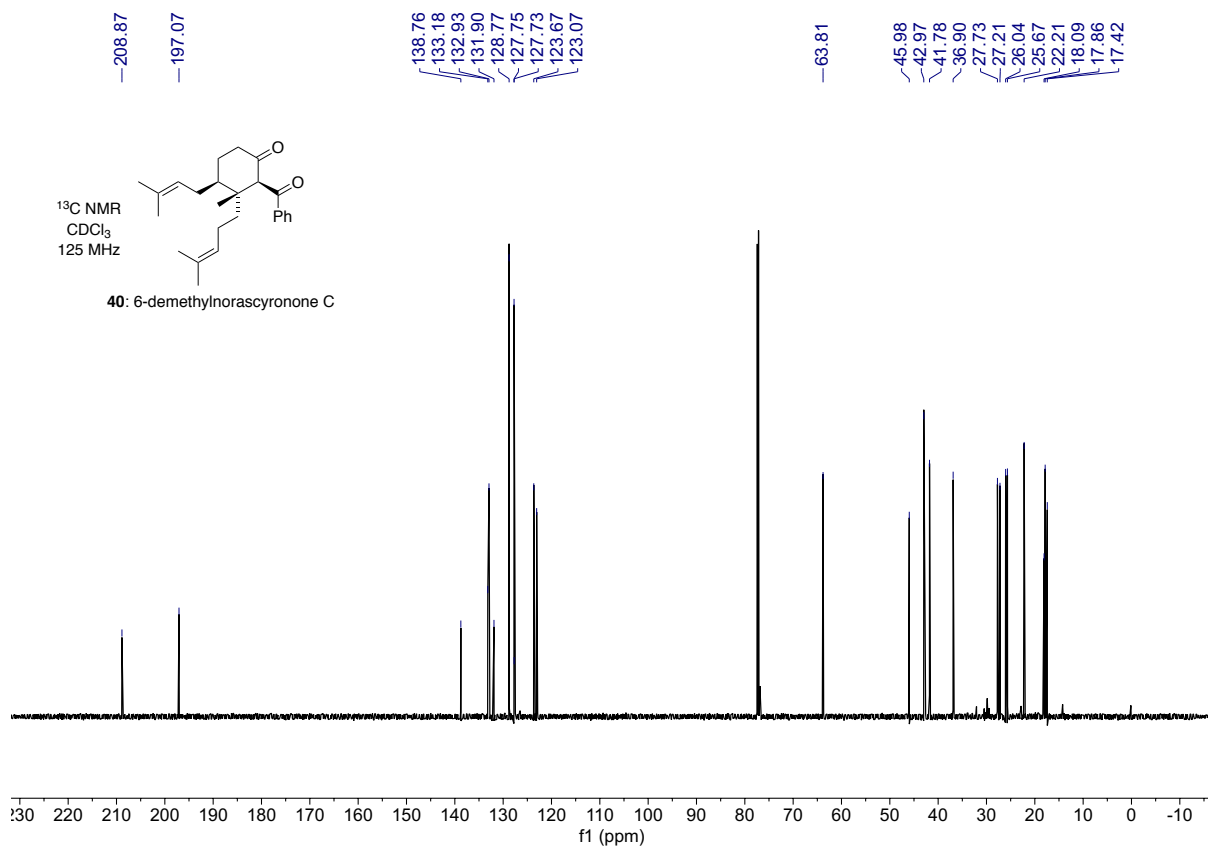
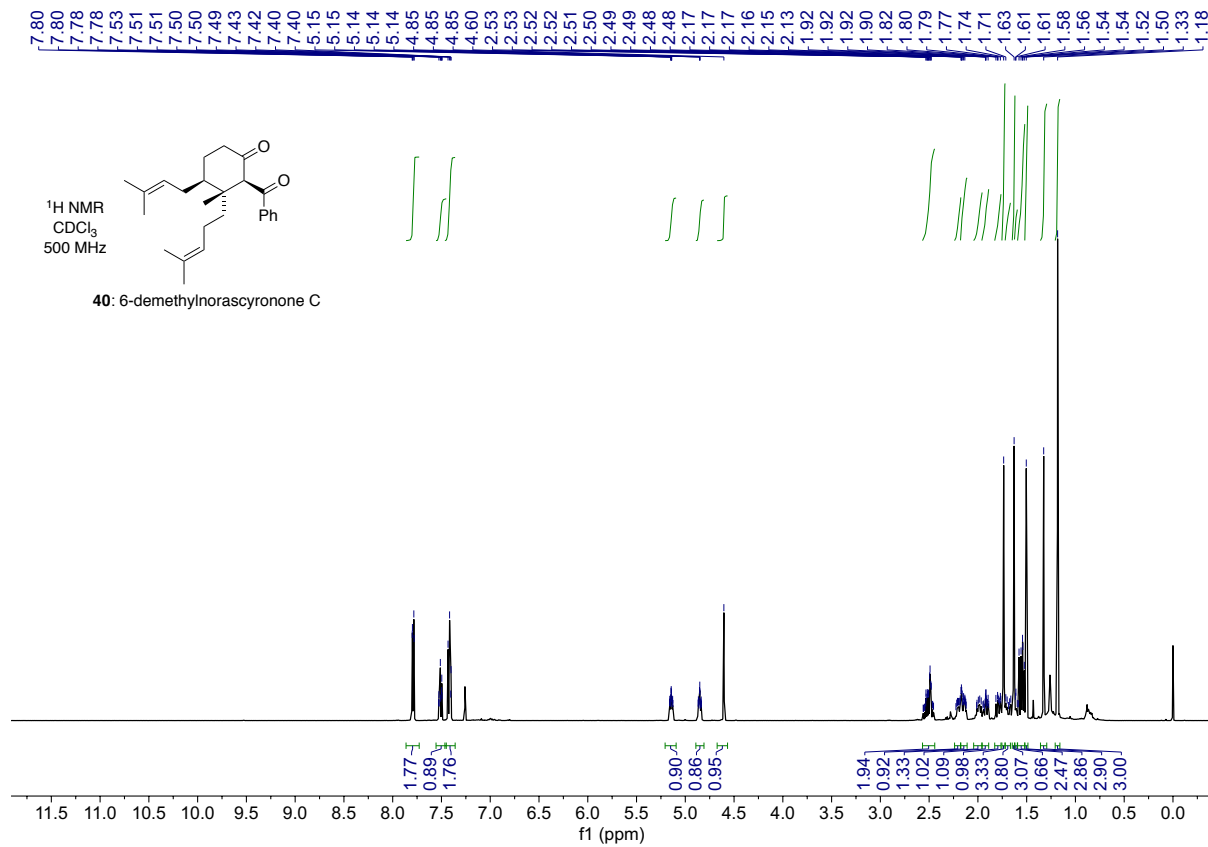


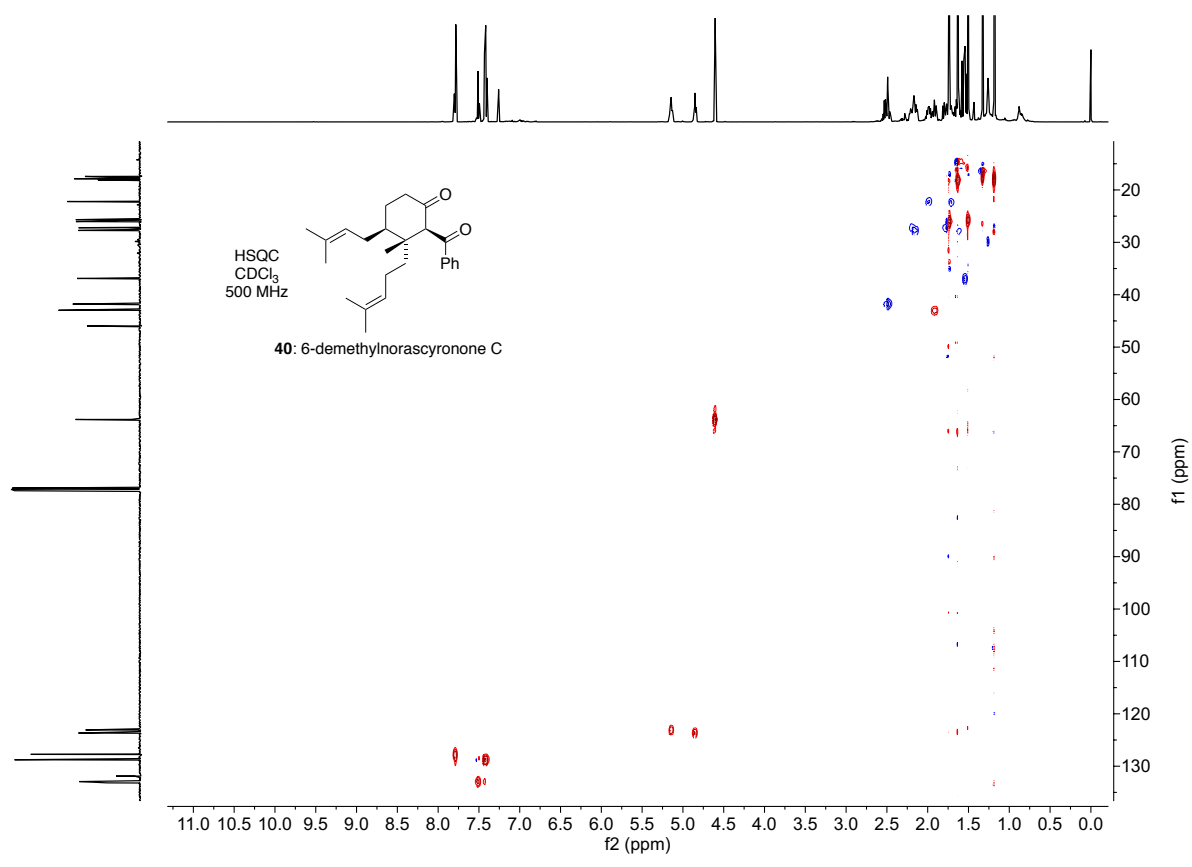
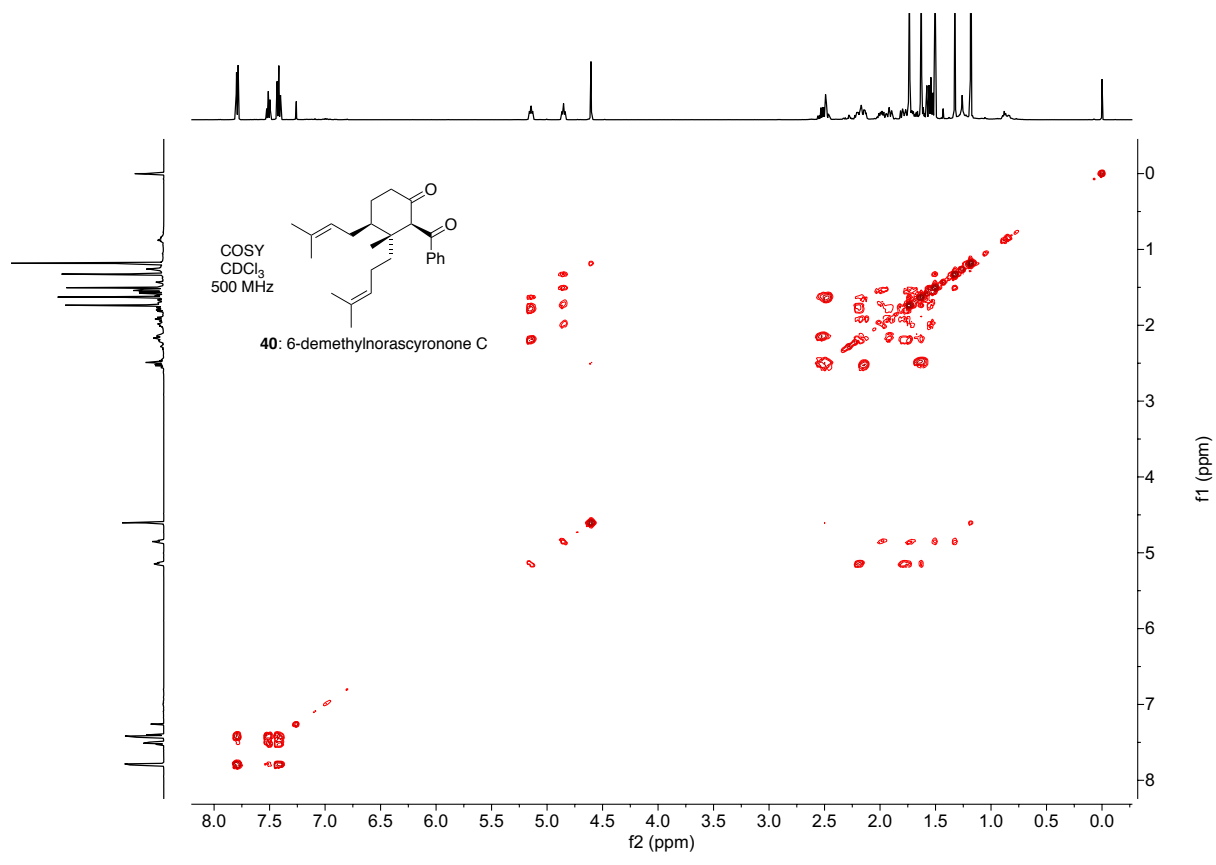


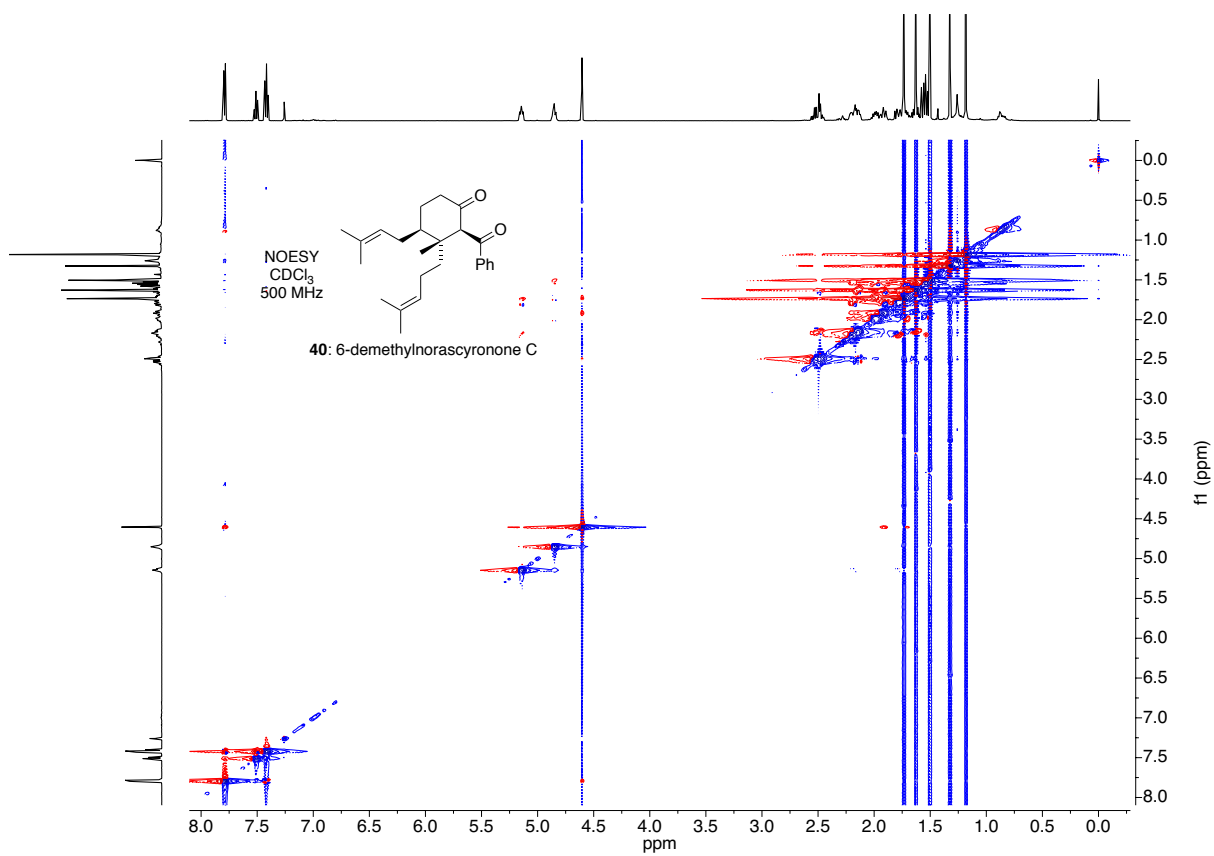
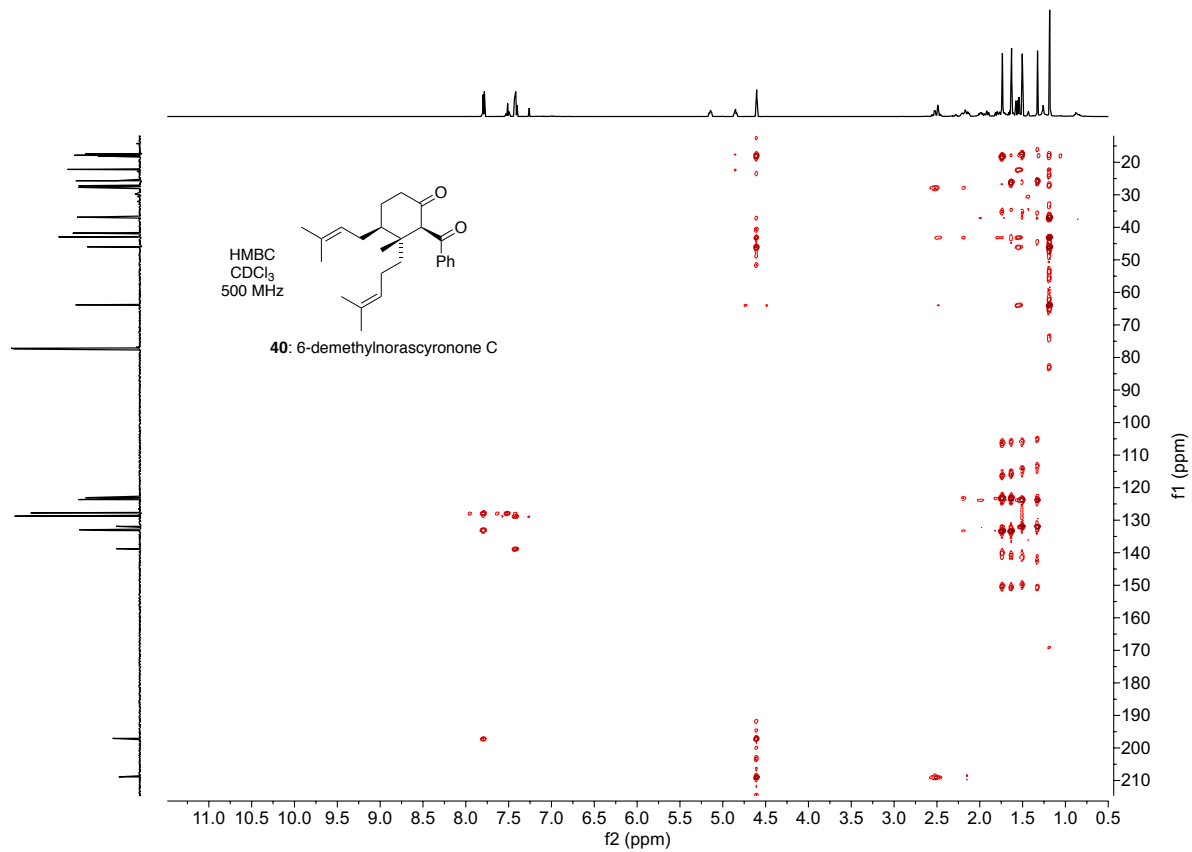


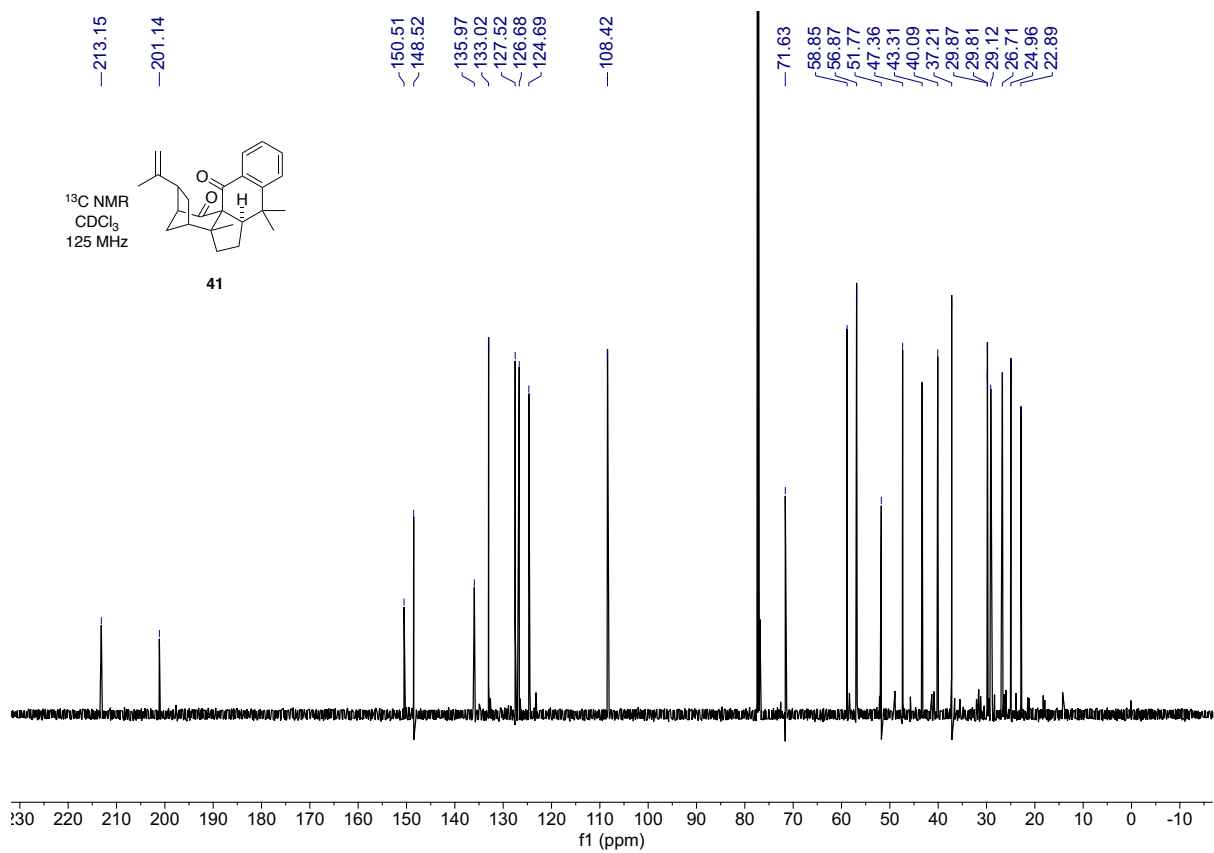
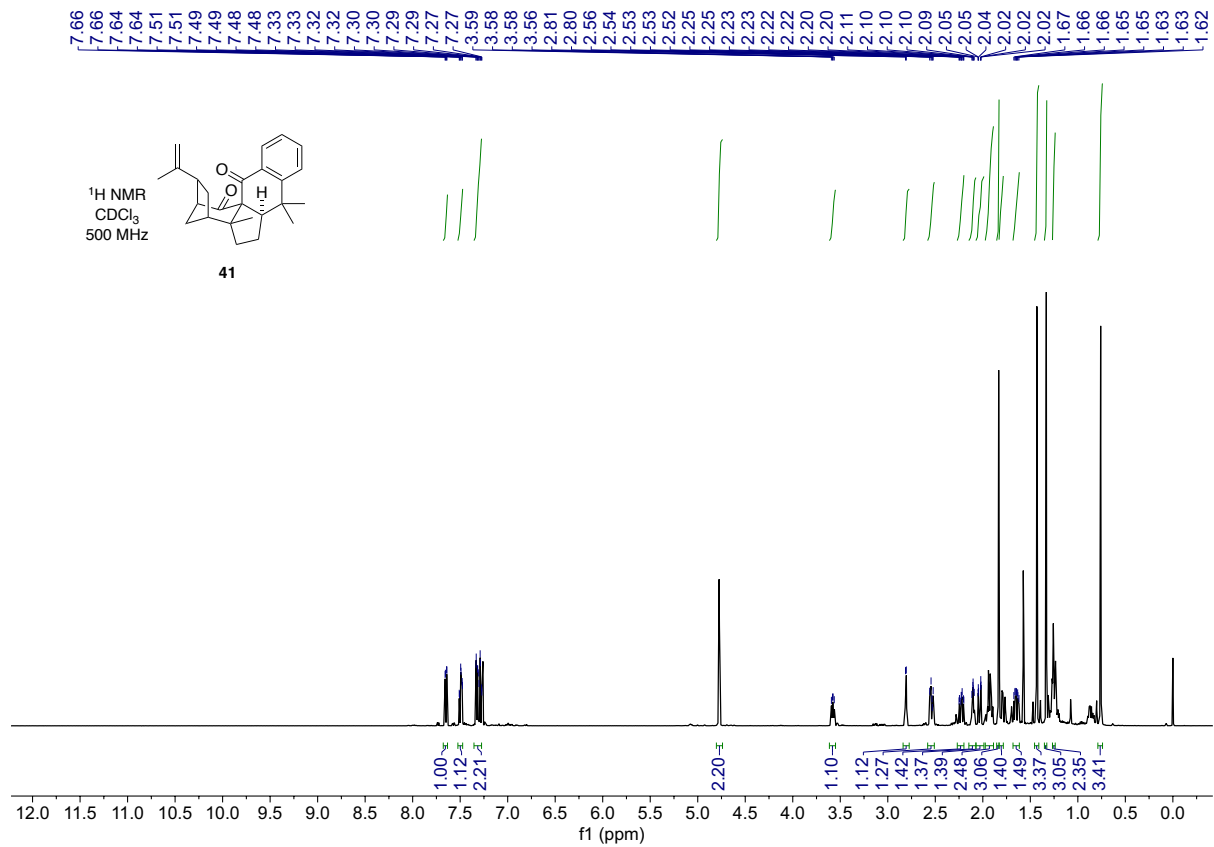


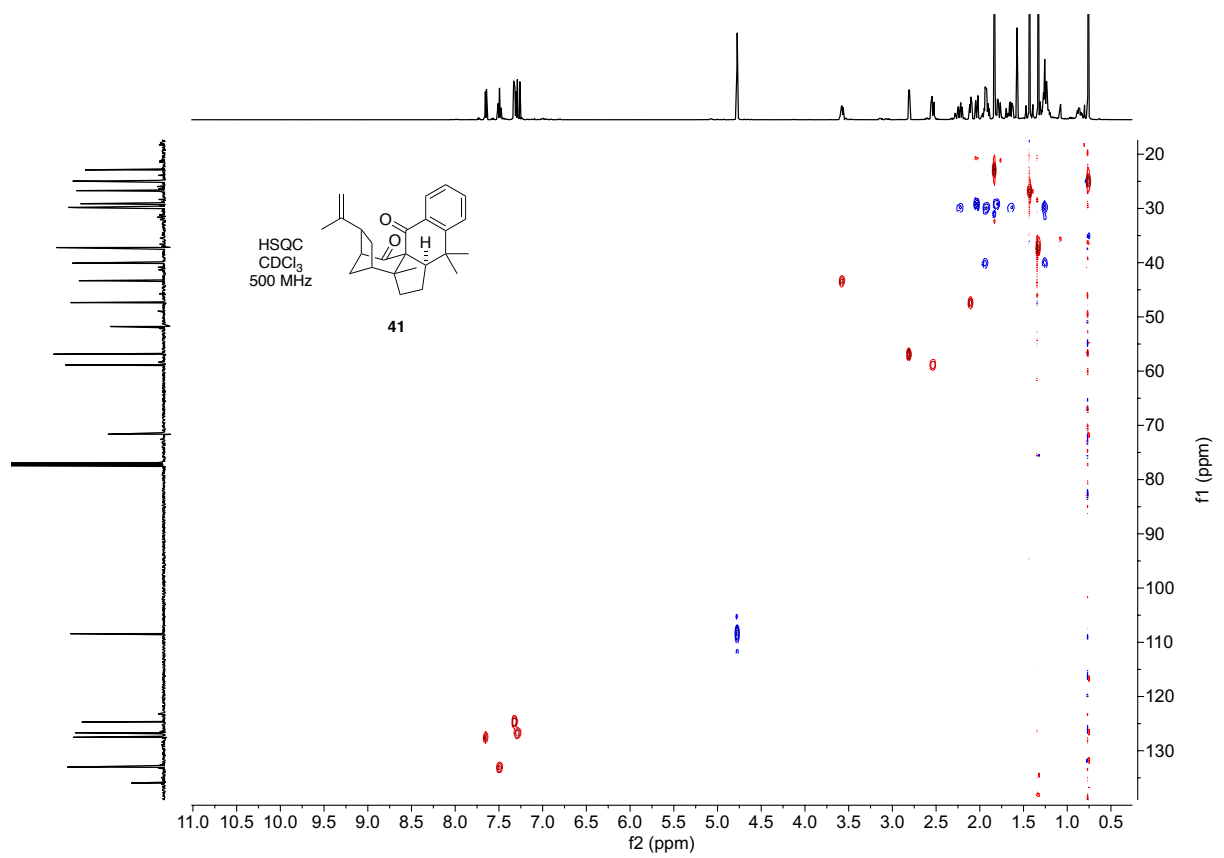
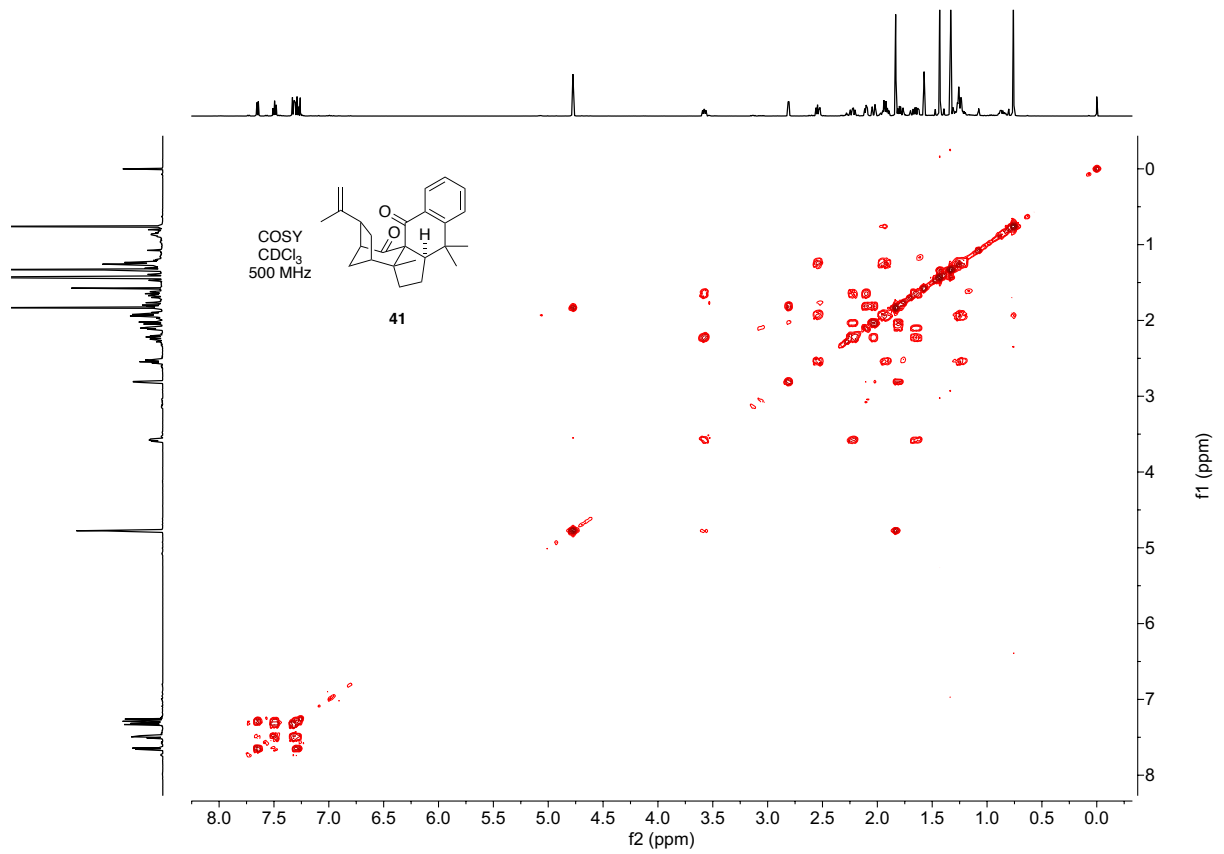


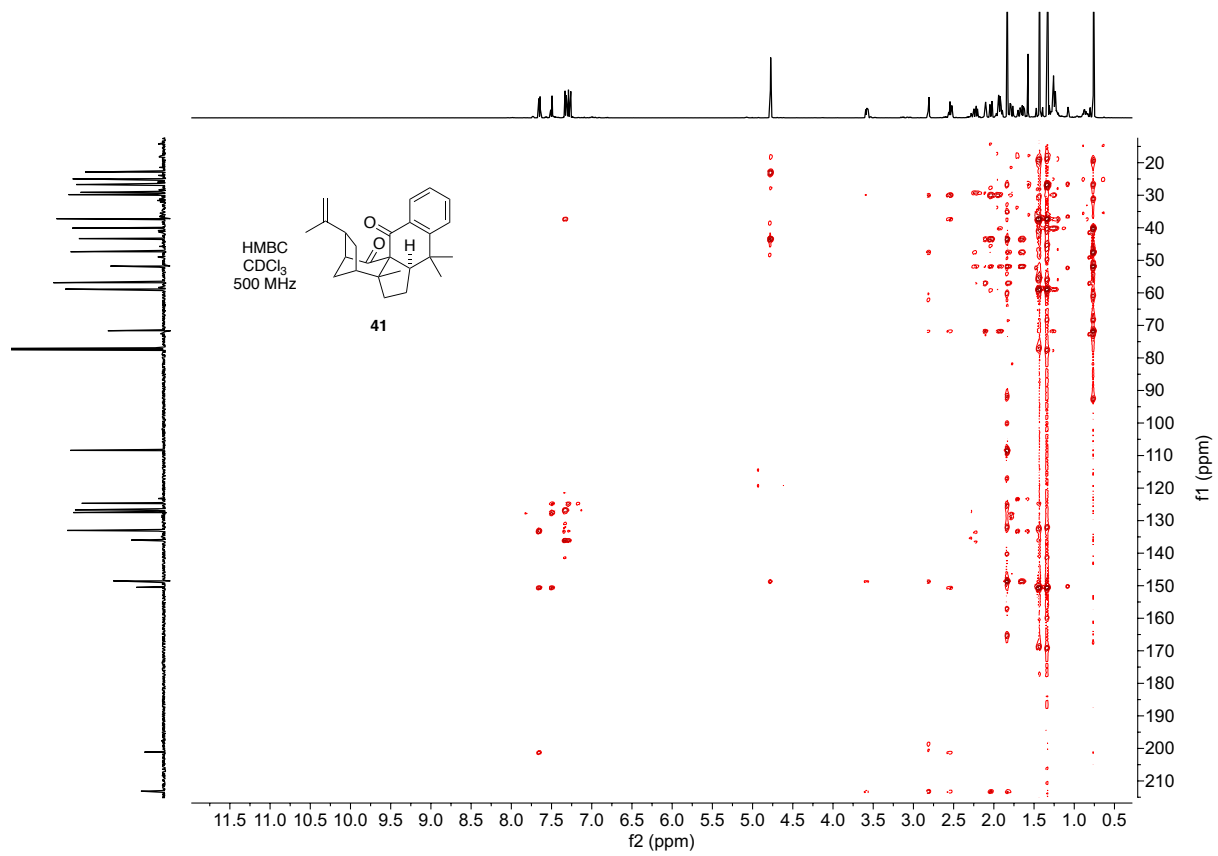






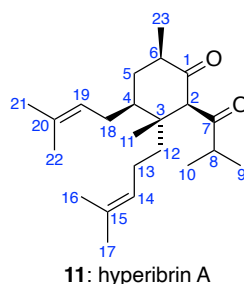






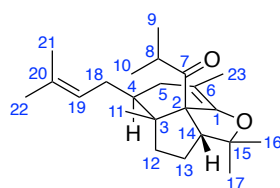
2. Tables of NMR data for natural products

Comparison of the ^1H and ^{13}C NMR spectra of natural¹ and synthetic hyperibrin A (**11**).



Assignment	Natural ^1H NMR CDCl_3 , 400 MHz	Synthetic ^1H NMR CDCl_3 , 500 MHz	Natural ^{13}C NMR CDCl_3 , 125 MHz	Synthetic ^{13}C NMR CDCl_3 , 125 MHz
1			210.6	210.6
2	3.85 (s)	3.85 (s)	66.7	66.7
3			45.5	45.5
4	1.84 (m)	1.86 – 1.75 (m)	42.4	42.5
5	2.13 (m) 1.68 (m)	2.13 – 2.01 (m) 1.71 – 1.68 (m)	36.9	37.0
6	2.45 (m)	2.50 – 2.43 (m)	42.7	42.7
7			211.0	211.0
8	2.47 (m)	2.50 – 2.43 (m)	45.5	
9	1.06 (d, $J = 8.4$)	1.04 (d, $J = 8.0$ Hz)	18.5	18.5
10	1.08 (d, $J = 8.4$)	1.06 (d, $J = 8.0$ Hz)	17.9	18.0
11	1.00 (s)	1.00 (s)	17.3	17.3
12	1.50 (m) 1.25 (m)	1.50 – 1.46 (m) 1.26 – 1.18 (m)	36.6	36.6
13	2.07 (m) 1.49 (m)	2.13 – 2.01 (m) 1.50 – 1.46 (m)	21.9	21.9
14	4.98 (t, $J = 5.6$)	4.98 (t, $J = 6.7$ Hz)	123.6	123.7
15			131.6	131.7
16	1.66 (s)	1.66 (s)	17.6	17.7
17	1.58 (s)	1.58 (s)	25.6	25.7
18	2.12 (m) 1.71 (m)	2.13 – 2.01 (m) 1.71 – 1.68 (m)	26.8	26.8
19	5.12 (t, $J = 5.6$)	5.12 (t, $J = 7.0$ Hz)	122.9	123.0
20			132.9	132.9
21	1.61 (s)	1.61 (s)	25.9	25.9
22	1.74 (s)	1.73 (s)	14.3	14.3
23	1.01 (d, $J = 5.2$)	1.01 (d, $J = 8.0$ Hz)	17.6	17.7

Comparison of the ^1H and ^{13}C NMR spectra of natural² and synthetic yezo'otogirin C (**3**).

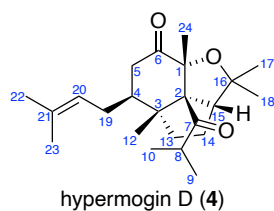


3: yezo'otogirin C

Assignment	Natural ^1H NMR CDCl_3^*	Synthetic ^1H NMR CDCl_3 , 600 MHz	Natural ^{13}C NMR CDCl_3^*	Synthetic ^{13}C NMR CDCl_3 , 150 MHz
1			149.3	149.2
2			73.6	73.6
3			48.5	48.5
4	1.22 (m)	1.23 (tt, $J = 11.4, 3.0$ Hz)	47.0	47.0
5	1.98 (dd, $J = 15.3, 11.4$ Hz) 1.86 (dd, $J = 15.3, 3.0$ Hz)	1.96 (dd, $J = 14.8, 11.6$ Hz) 1.86 (dd, $J = 15.5, 3.3$ Hz)	32.8	32.7
6			107.5	107.5
7			217.4	217.4
8	2.96 (hept, $J = 6.6$ Hz)	2.96 (hept, $J = 6.6$ Hz)	37.9	37.9
9	1.01 (d, $J = 6.6$ Hz)	1.02 (d, $J = 6.6$ Hz)	18.3	18.3
10	1.01 (d, $J = 6.6$ Hz)	1.01 (d, $J = 6.6$ Hz)	21.5	21.5
11	0.75 (s)	0.75 (s)	19.6	19.6
12	1.75 (m) 1.46 (m)	1.76 – 1.74 (m) 1.56 – 1.52 (m)	41.5	41.5
13	1.54 (m)	1.56 – 1.52 (m)	25.4	25.4
14	3.18 (t, $J = 9.6$ Hz)	3.19 (dd, $J = 10.2, 9.0$ Hz)	54.9	54.9
15			83.4	83.4
16	1.14 (s)	1.15 (s)	29.4	29.5
17	1.18 (s)	1.18 (s)	25.4	25.4
18	1.93 (m) 1.81 (m)	1.94 (dd, $J = 11.1, 1.0$ Hz) 1.84 – 1.80 (m)	29.6	29.6
19	5.11 (t, $J = 6.9$ Hz)	5.13 – 5.10 (m)	124.2	124.2
20			132.3	132.4
21	1.72 (s)	1.73 (s)	25.8	25.9
22	1.60 (s)	1.61 (s)	17.8	17.9
23	1.70 (s)	1.71 (s)	16.3	16.3

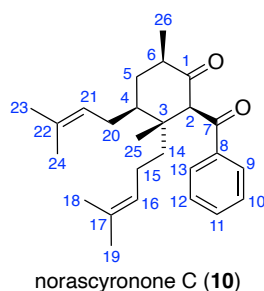
*The operation frequency is not specified in the isolation paper.

Comparison of the ^1H and ^{13}C NMR spectra of natural³ and synthetic hypermogenin D (**4**)



Assignment	Natural ^1H NMR CDCl_3 , 600 MHz	Synthetic ^1H NMR CDCl_3 , 500 MHz	Natural ^{13}C NMR CDCl_3 , 150 MHz	Synthetic ^{13}C NMR CDCl_3 , 125 MHz
1			98.7	98.7
2			85.7	85.7
3			59.8	59.8
4	2.10 (m)	2.13 – 2.06 (m)	45.8	45.8
5	1.93 (m) 1.66 (m)	2.17 – 1.89 (m)	43.2	43.2
6			208.7	208.7
7			215.4	215.4
8	2.91 (m)	2.94 – 2.85 (m)	38.3	38.3
9	1.06 (d, $J = 6.5$)	1.04 (d, $J = 6.6$ Hz)	18.4	18.4
10	1.24 (d, $J = 6.5$)	1.22 (d, $J = 6.6$ Hz)	21.1	21.0
11				
12	0.87 (s)	0.85 (s)	19.7	19.8
13	2.13 (m)	2.17 – 1.89 (m) 1.66 – 1.63 (m)	41.2	41.3
14	2.05 (m) 1.94 (m)	2.17 – 1.89 (m)	28.4	28.4
15	3.09 (dd, $J = 8.2, 6.2$)	3.07 (dd, $J = 8.3, 6.4$ Hz)	57.3	57.4
16			88.6	88.6
17	1.34 (s)	1.32 (s)	25.8	25.8
18	1.33 (s)	1.32 (s)	30.9	30.9
19	2.05 (m) 1.99 (m)	2.17 – 1.89 (m)	28.3	28.3
20	5.11 (t, $J = 6.5$)	5.10 (t, $J = 7.1$ Hz)	123.3	123.3
21			132.1	132.1
22	1.70 (s)	1.68 (s)	17.8	17.8
23	1.62 (s)	1.61 (s)	26.3	26.3
24	2.22 (s)	2.20 (s)	28.0	28.0

Comparison of the ^1H and ^{13}C NMR spectra of natural⁴ and synthetic norascyronone C (**10**)



Assignment	Natural ^1H NMR CDCl_3 , 600 MHz	Synthetic ^1H NMR CDCl_3 , 500 MHz	Natural ^{13}C NMR CDCl_3 , 150 MHz	Synthetic ^{13}C NMR CDCl_3 , 125 MHz
1	-	-	209.6	209.6
2	4.55 (s)	4.60 (s)	63.7	63.6
3	-	-	46.3	46.5
4	1.94 (m)	2.03 – 1.95 (m)	42.8	43.1
5	2.13, m 1.25 (q, $J = 12.3$ Hz)	2.23 – 2.19 (m) 1.33 – 1.28 (m)	37.1	37.4
6	2.55 (m)	2.60 (dp, $J = 12.8$, 6.6 Hz)	45.4	45.6
7	-	-	196.8	197.0
8	-	-	138.5	138.8
9	7.71 (d, $J = 7.8$ Hz)	7.77 (d, $J = 7.3$ Hz)	127.5	127.7
10	7.35 (t, $J = 7.8$ Hz)	7.41 (t, $J = 7.7$ Hz)	128.6	128.8
11	7.44 (t, $J = 7.8$ Hz)	7.50 (t, $J = 7.4$ Hz)	132.7	132.8
12	7.35 (t, $J = 7.8$ Hz)	7.41 (t, $J = 7.7$ Hz)	128.6	128.8
13	7.71 (d, $J = 7.8$ Hz)	7.77 (d, $J = 7.3$ Hz)	127.5	127.7
14	1.50 (m)	1.60 – 1.54 (m)	36.4	36.7
15	1.91 (overlap) 1.65 (m)	2.03 – 1.95 (m) 1.74 – 1.69 (m)	22.0	22.3
16	4.80 (t, $J = 7.0$ Hz)	4.87 (t, $J = 7.1$ Hz)	123.6	123.8
17	-	-	131.7	131.9
18	1.44 (s)	1.50 (s)	25.5	25.7
19	1.27 (s)	1.34 (s)	17.3	17.5
20	2.11 (m) 1.70 (overlap)	2.19 – 2.15 (m) 1.78 – 1.75 (m)	26.9	27.2
21	5.09 (t, $J = 7.2$ Hz)	5.16 (t, $J = 7.2$ Hz)	123.0	123.2
22	-	-	132.9	133.1
23	1.56 (s)	1.63 (s)	17.9	18.1
24	1.68 (s)	1.75 (s)	25.9	26.1
25	1.07 (s)	1.14 (s)	17.6	17.8
26	0.98 (d, $J = 6.6$ Hz)	1.04 (d, $J = 6.4$ Hz)	14.4	14.6

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