Biomimetic Synthetic Studies on the Bruceol Family of Meroterpenoid Natural Products

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Supporting Information

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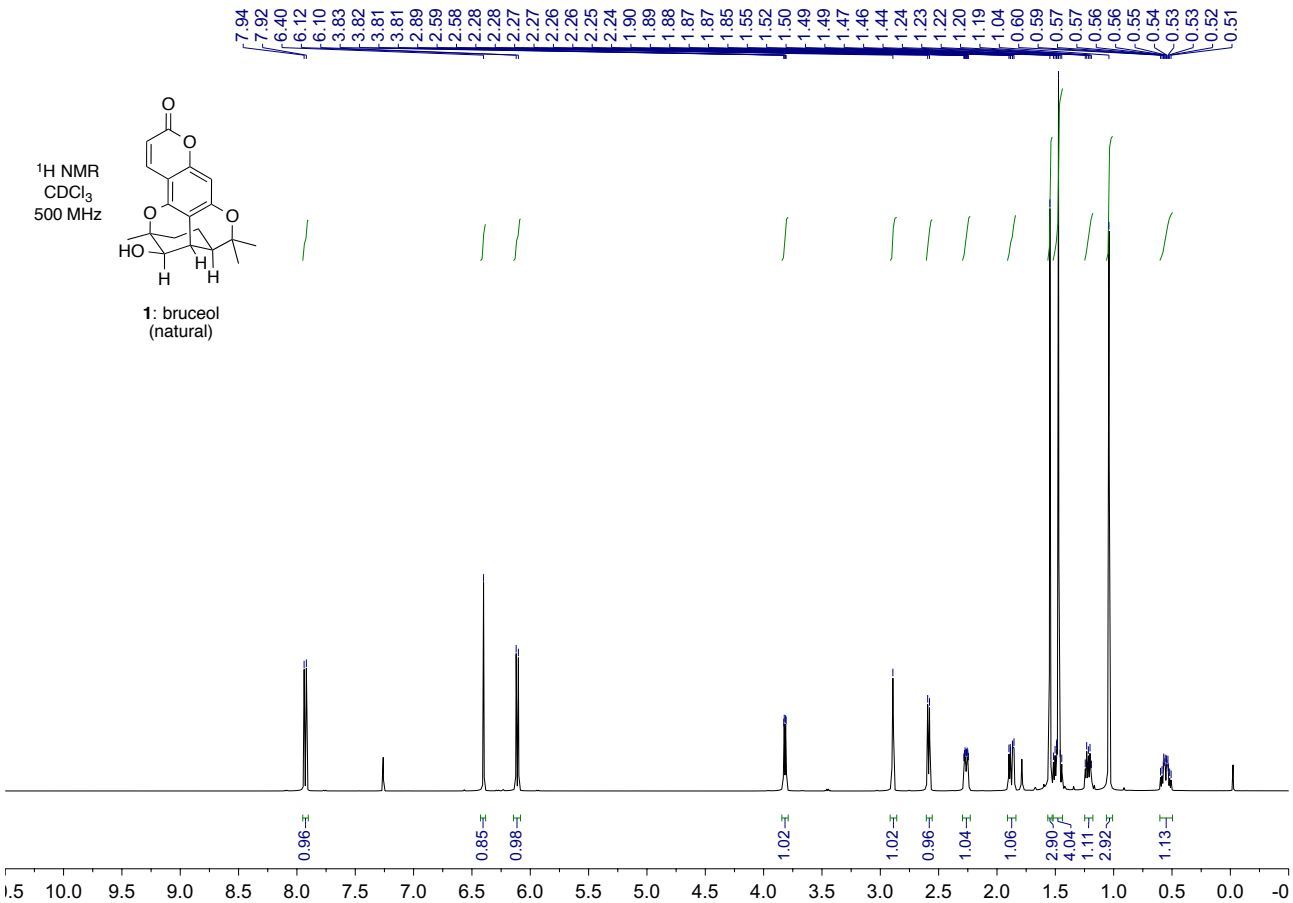
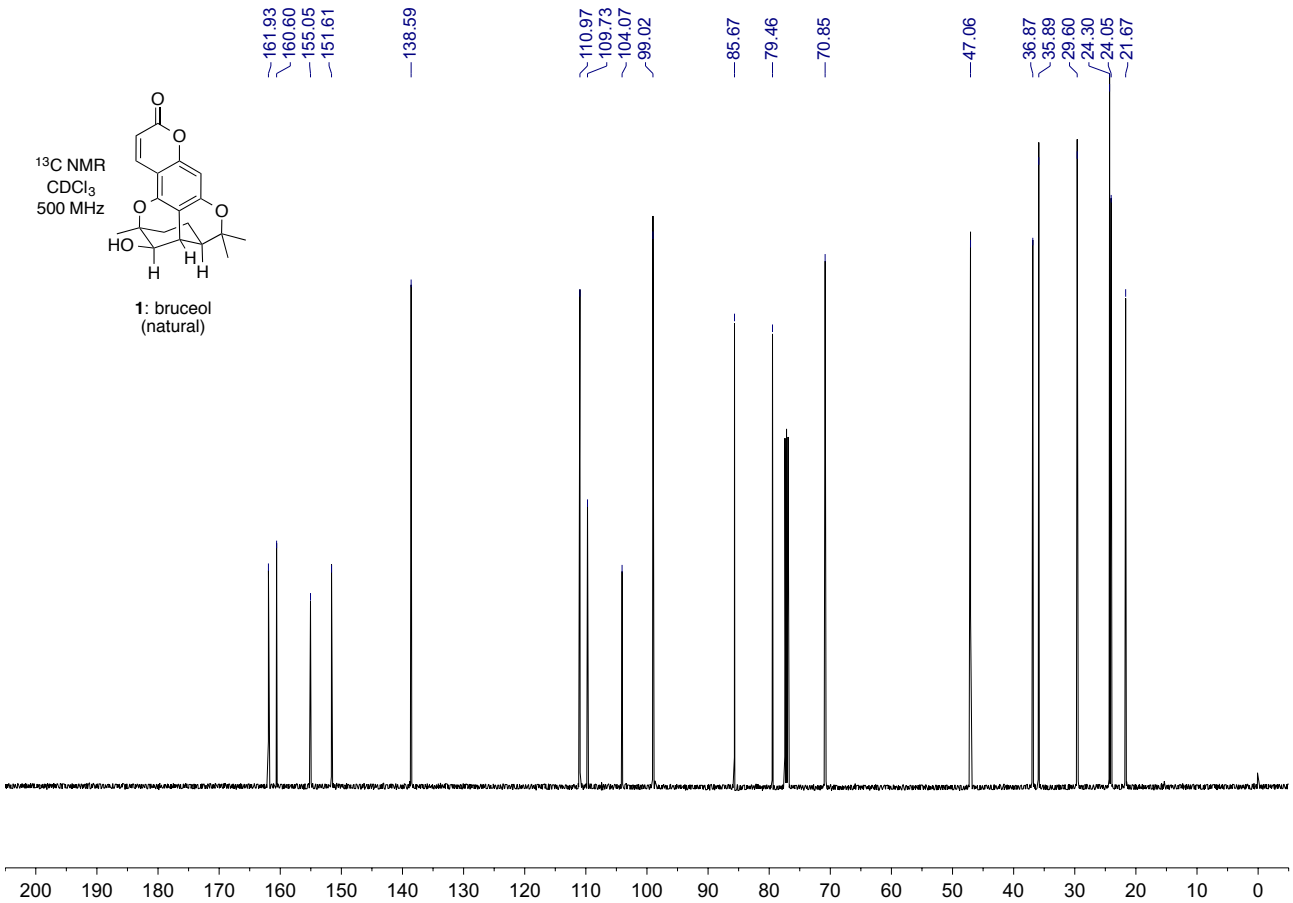
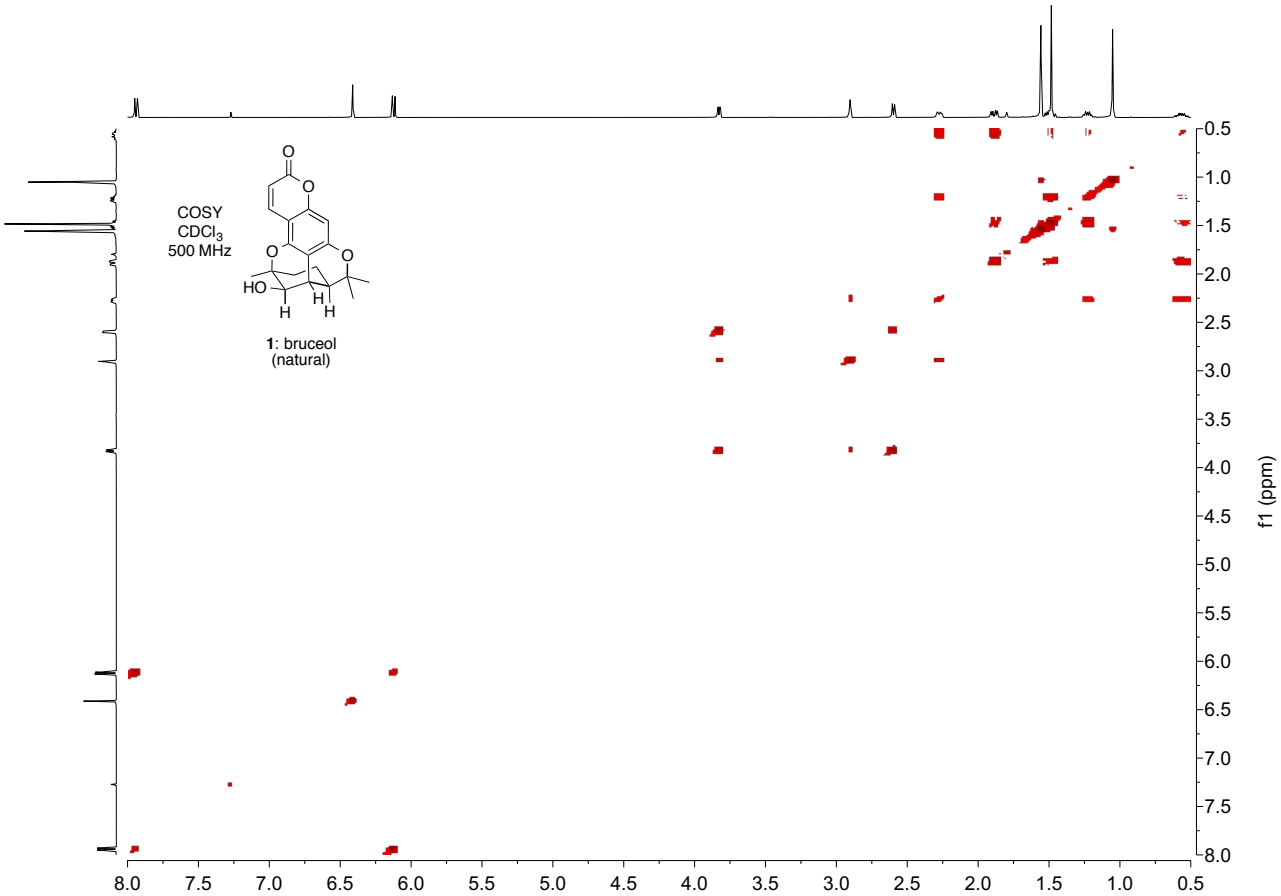
1. NMR spectra



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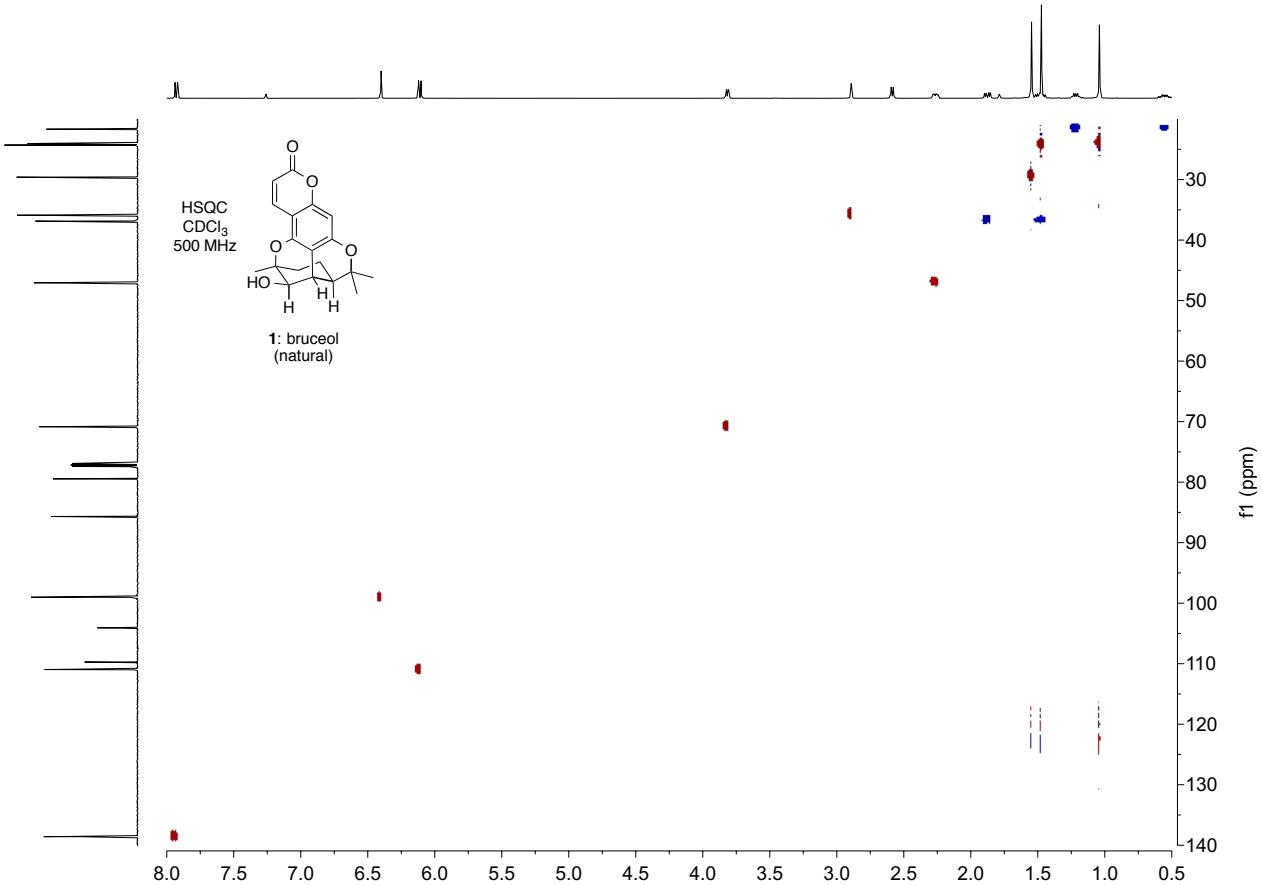
CDCl3
500 MHz
1: bruceol
(natural)
f1 (ppm)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CDCl3
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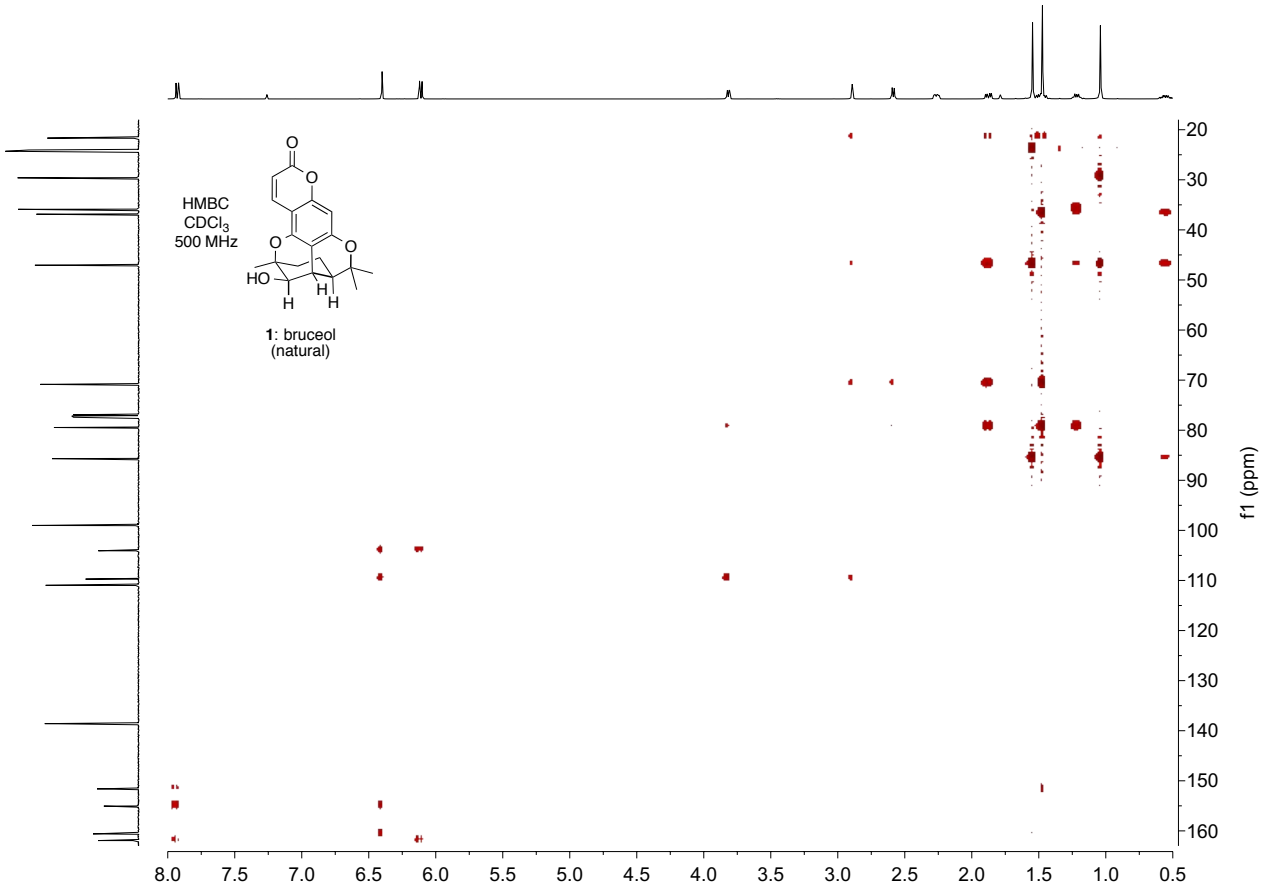
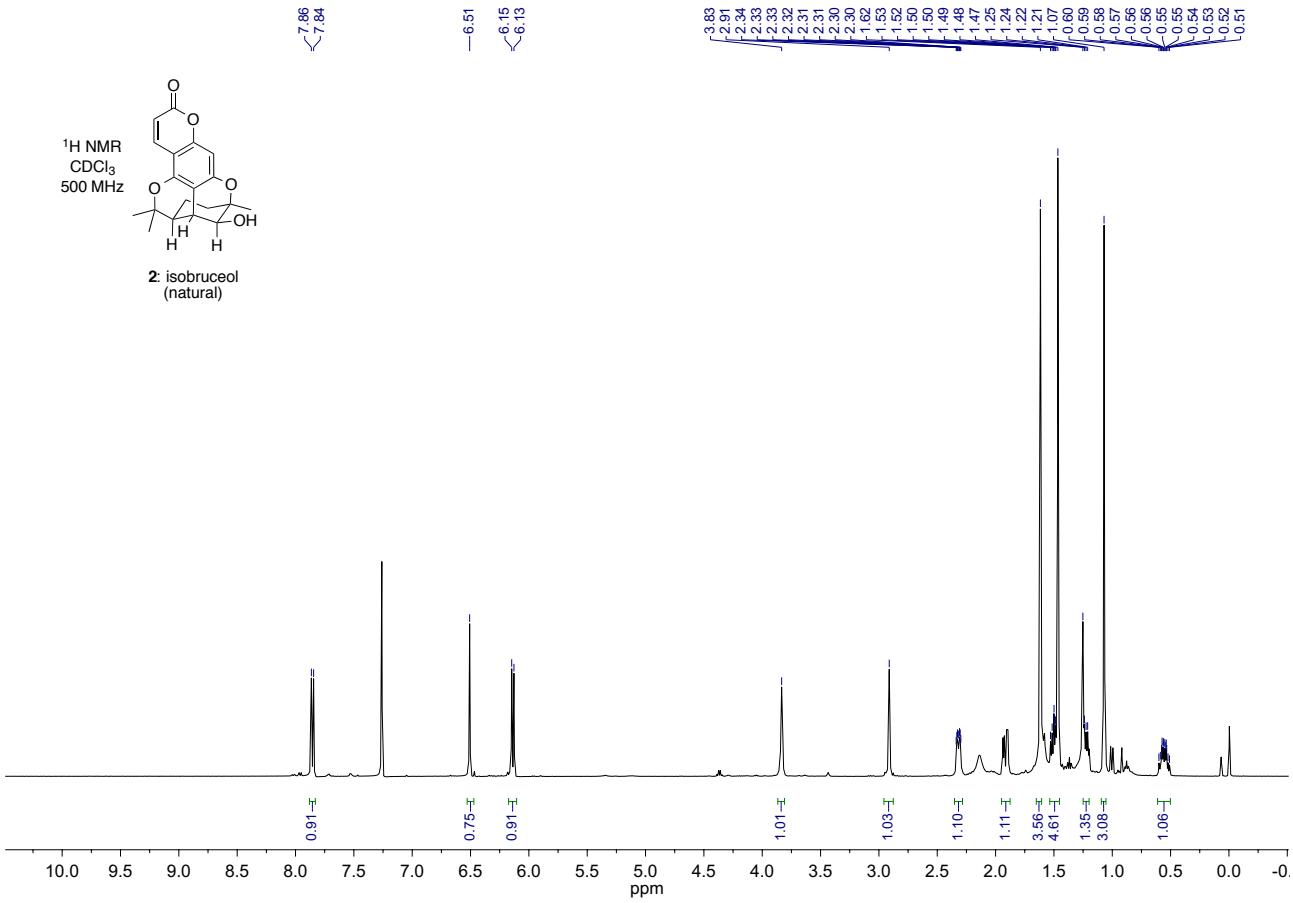
1: bruceol
(natural)
f1 (ppm)


HMBC
CDCl3
500 MHz
1: bruceol
(natural)
f1 (ppm)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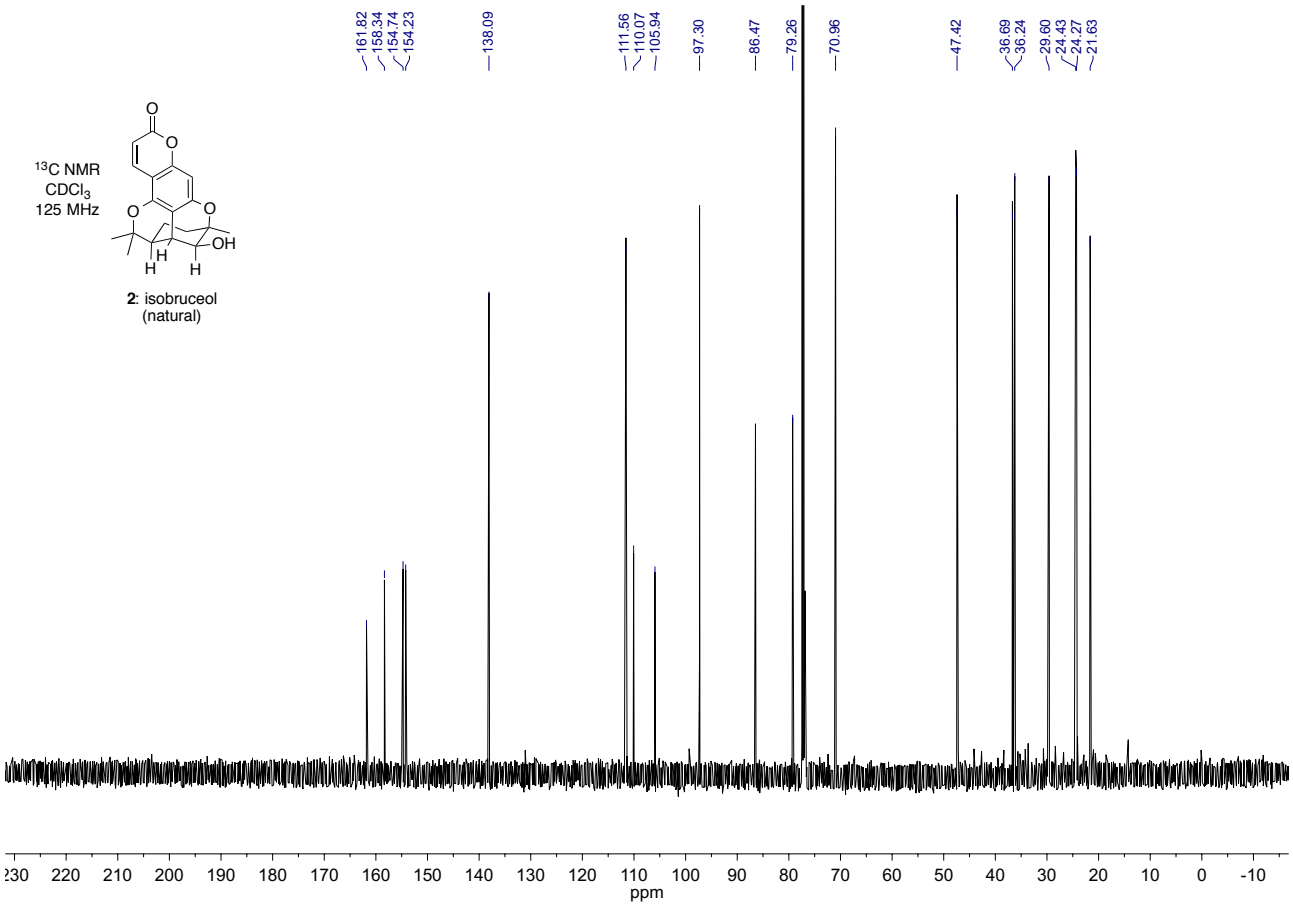
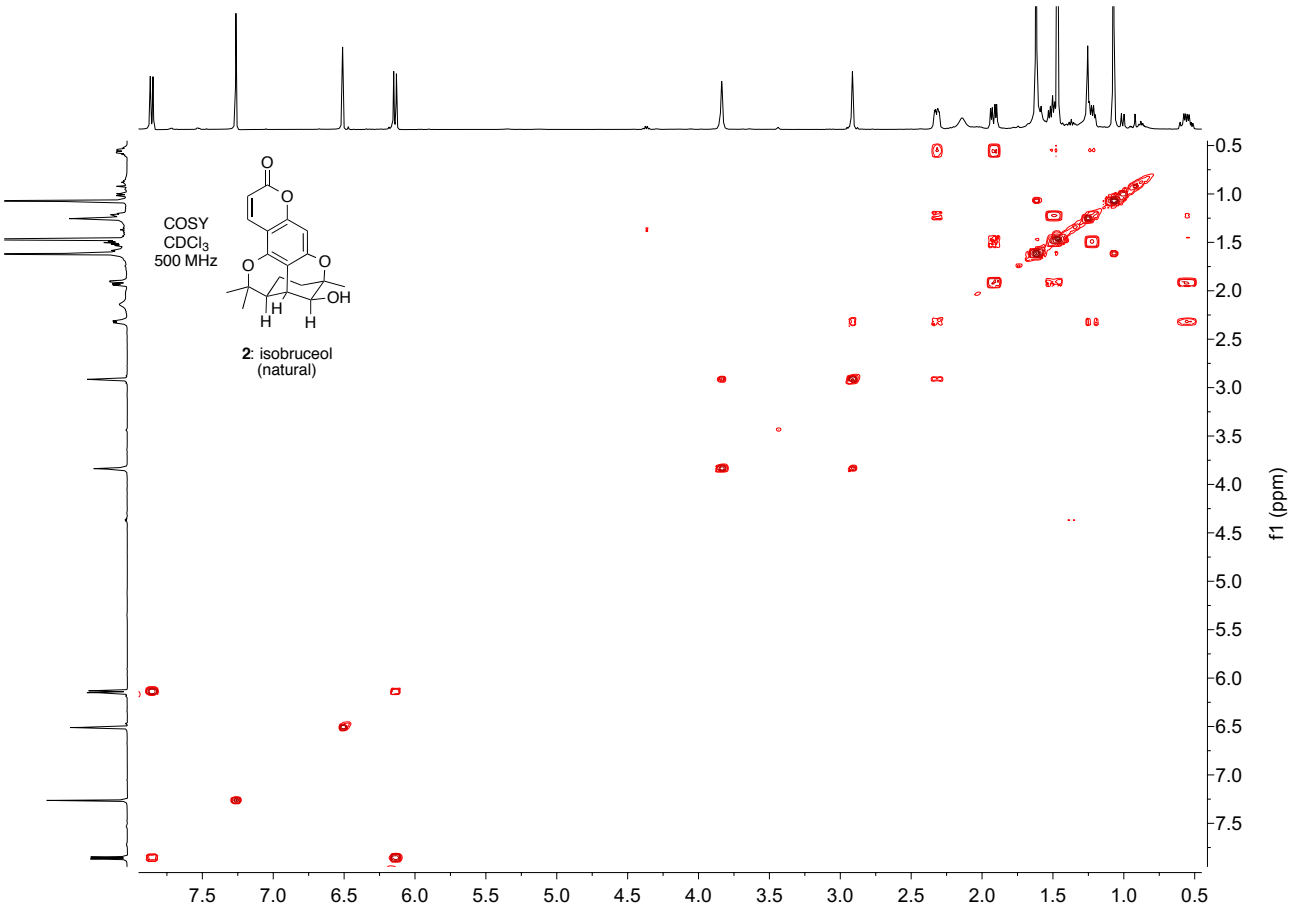
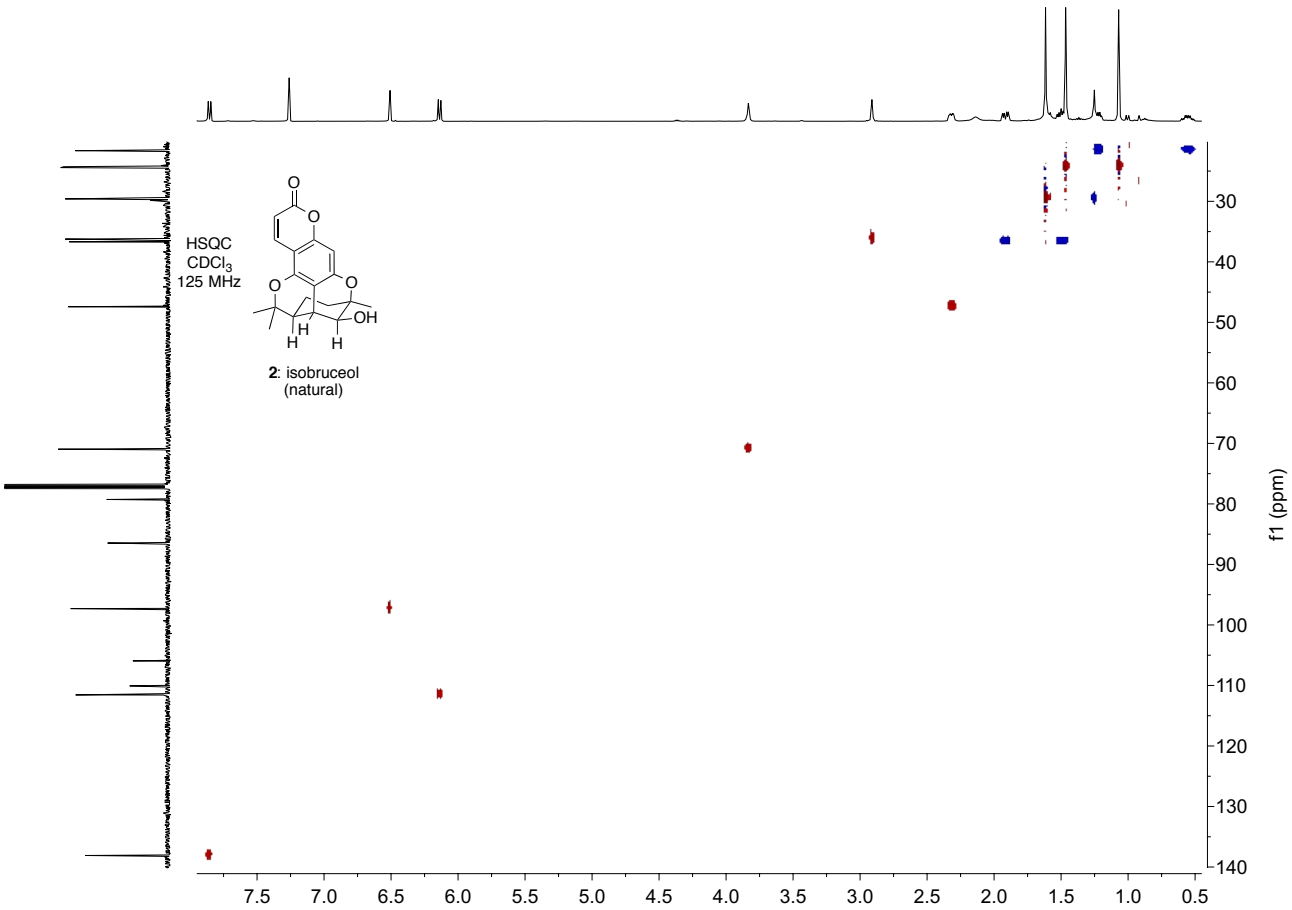
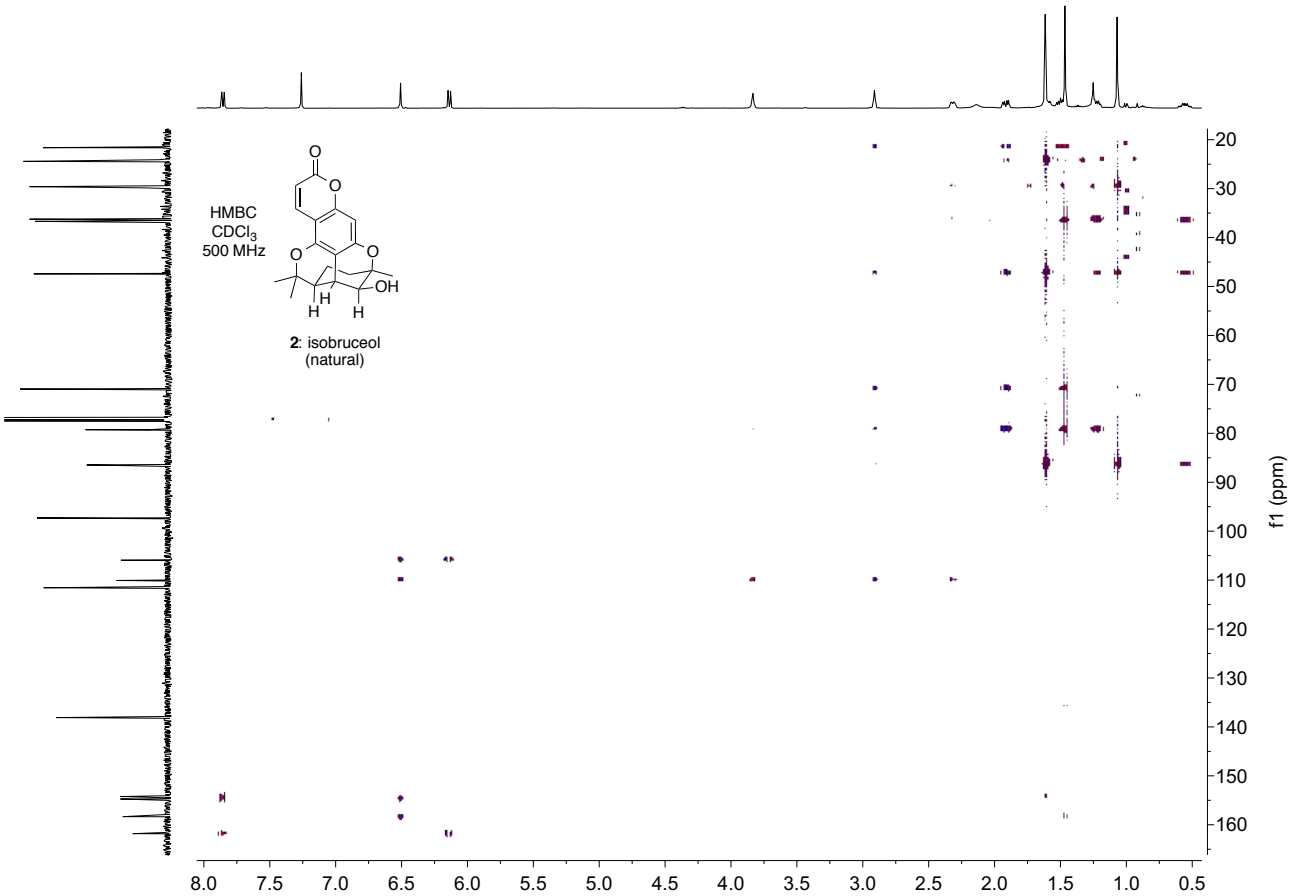
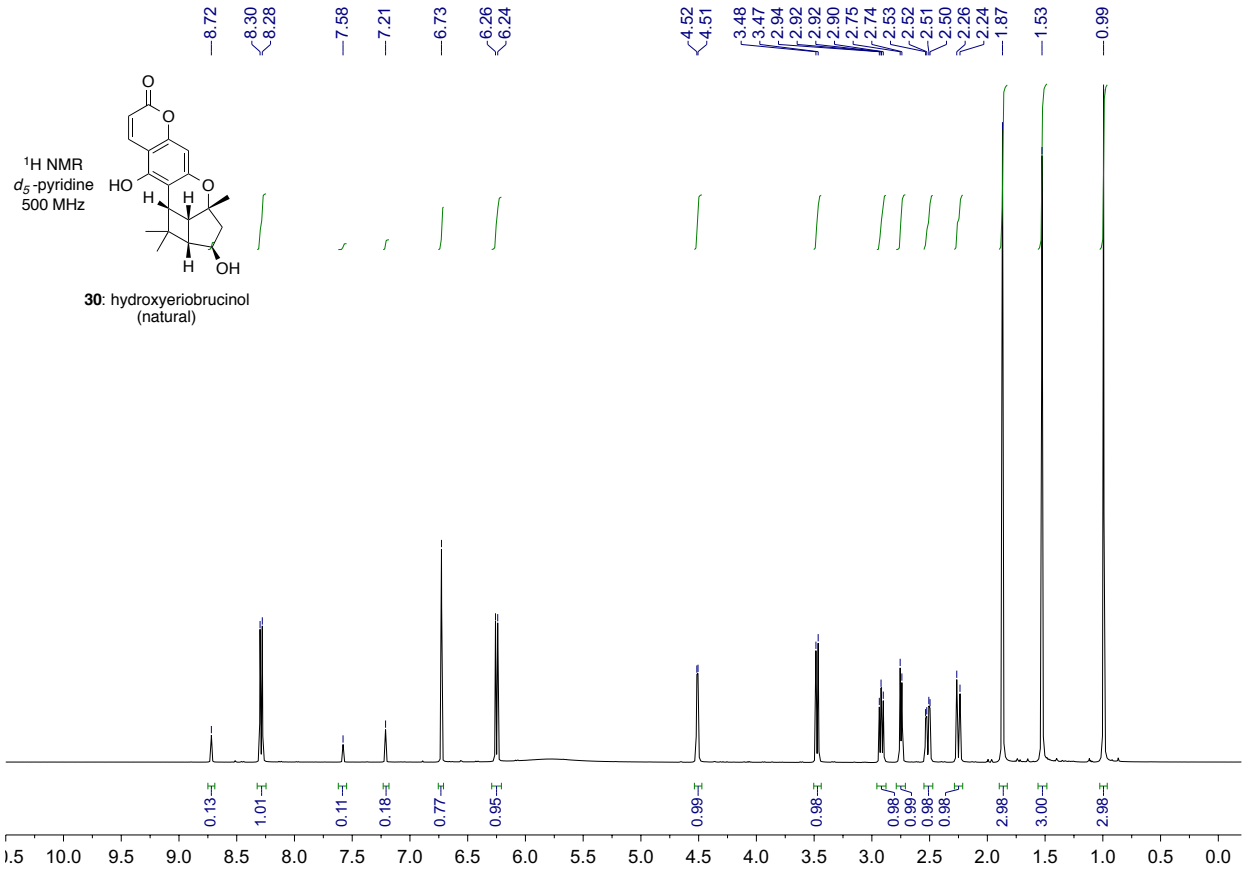
7.84
6.51
6.15
6.13
3.83
2.91
2.34
2.33
2.33
2.32
2.31
2.31
2.30
2.30
1.62
1.53
1.52
1.50
1.50
1.49
1.48
1.47
1.25
1.24
1.22
1.21
1.07
0.60
0.59
0.58
0.57
0.56
0.56
0.55
0.55
0.54
0.53
0.52
0.51
^{1}H NMR
$CDCl_3$
500 MHz
O
O
O
O
OH
H
H
H
2: isobruceol
(natural)
0.91
0.75
0.91
1.01
1.03
1.10
1.11
3.56
4.61
1.35
3.08
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

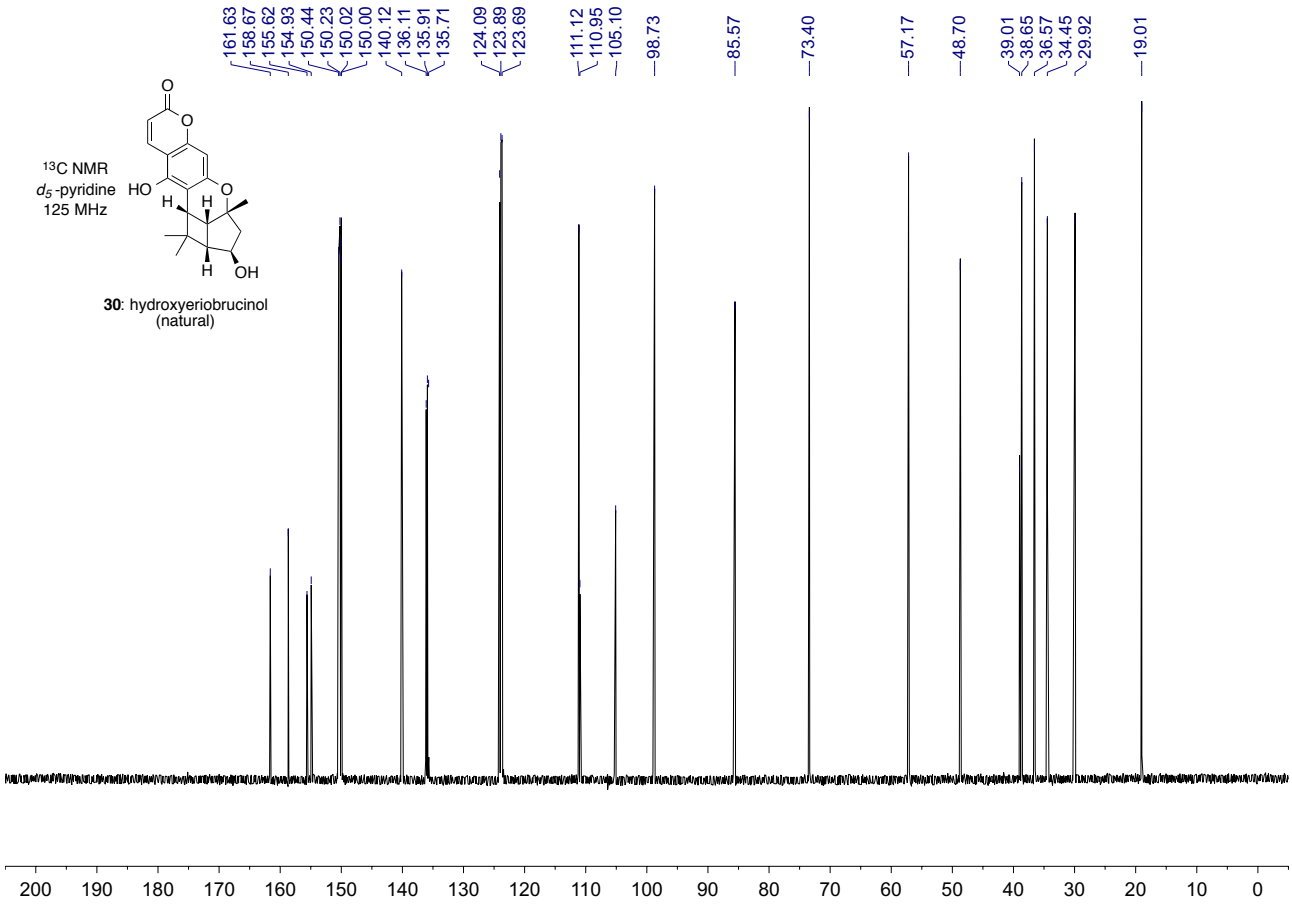

161.82
158.34
154.74
154.23
138.09
111.56
110.07
105.94
97.30
86.47
79.26
70.96
47.42
36.69
36.24
29.60
24.43
24.27
21.63
^{13}C NMR
$CDCl_3$
125 MHz
O
O
O
O
OH
H
H
H
2: isobruceol
(natural)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

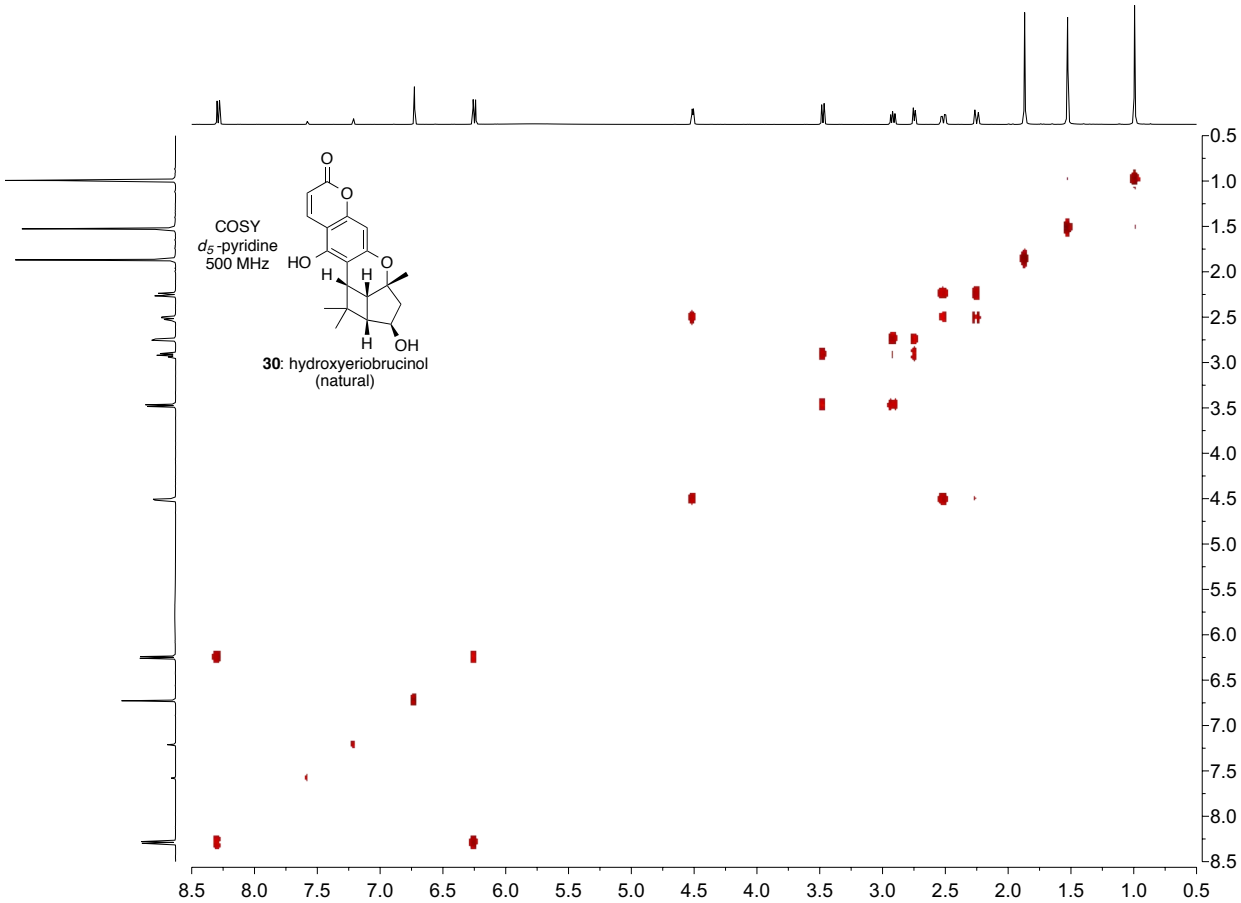

COSY
CDCl3
500 MHz
2: isobruceol
(natural)
f1 (ppm)

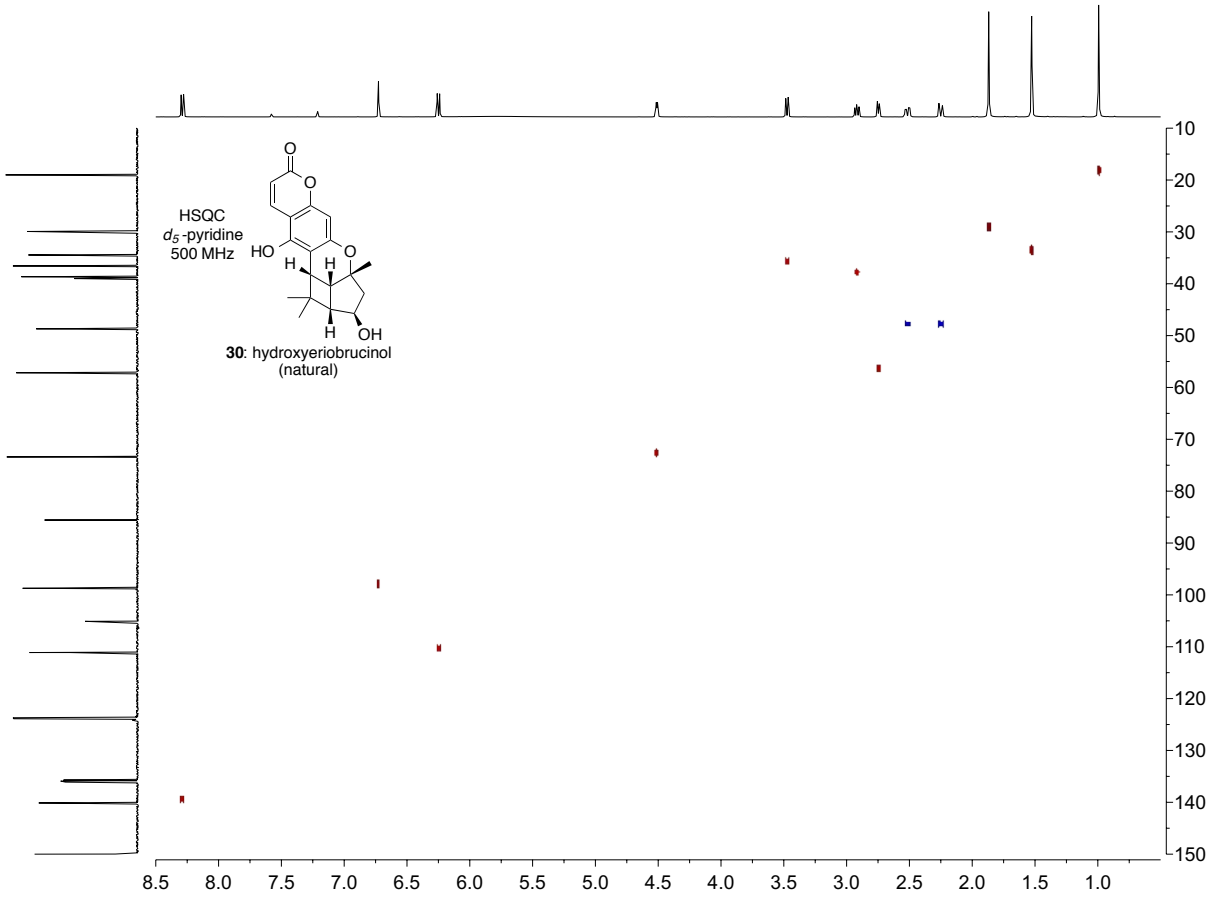

HSQC
CDCl3
125 MHz
2: isobruceol
(natural)
f1 (ppm)

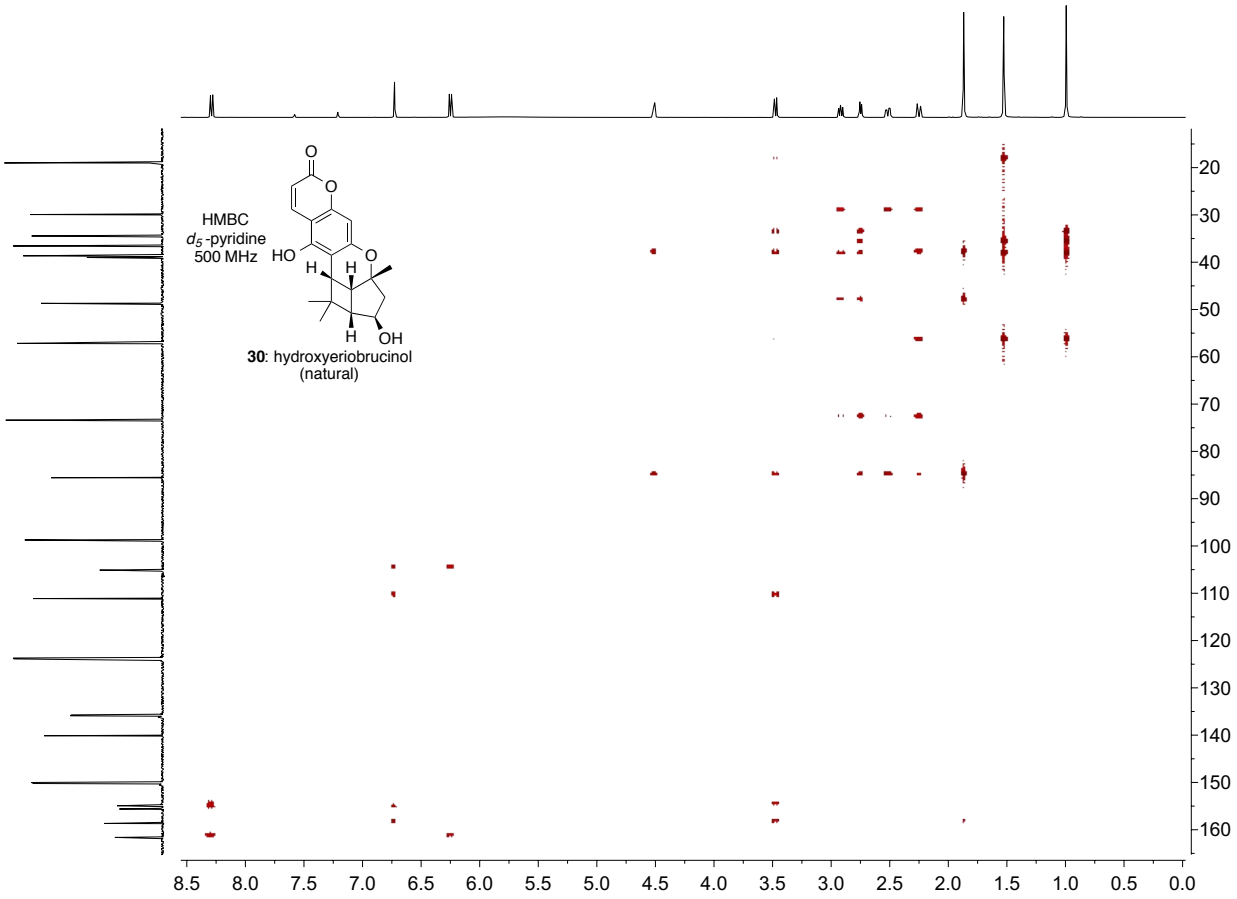

HMBC
CDCl3
500 MHz
2: isobruceol
(natural)
f1 (ppm)

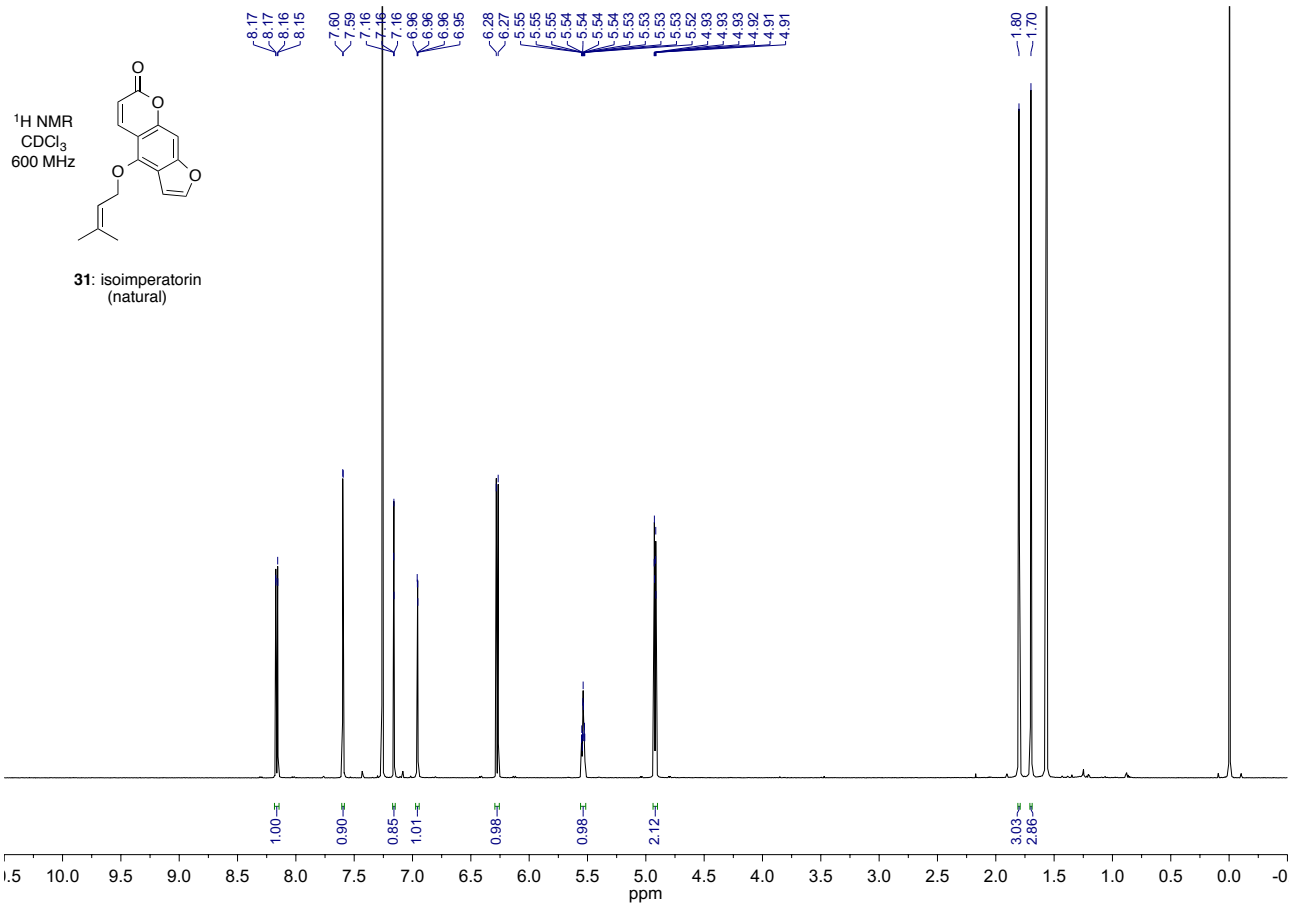

8.72
8.30
8.28
7.58
7.21
6.73
6.26
6.24
4.52
4.51
3.48
3.47
2.94
2.92
2.92
2.90
2.75
2.74
2.53
2.52
2.51
2.50
2.26
2.24
1.87
1.53
0.99
^{1}H NMR
d_5-pyridine
500 MHz
HO
O
H
H
OH
30: hydroxyeriobrucinol
(natural)
0.13
1.01
0.11
0.18
0.77
0.95
0.99
0.98
0.98
0.99
0.98
0.98
2.98
3.00
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

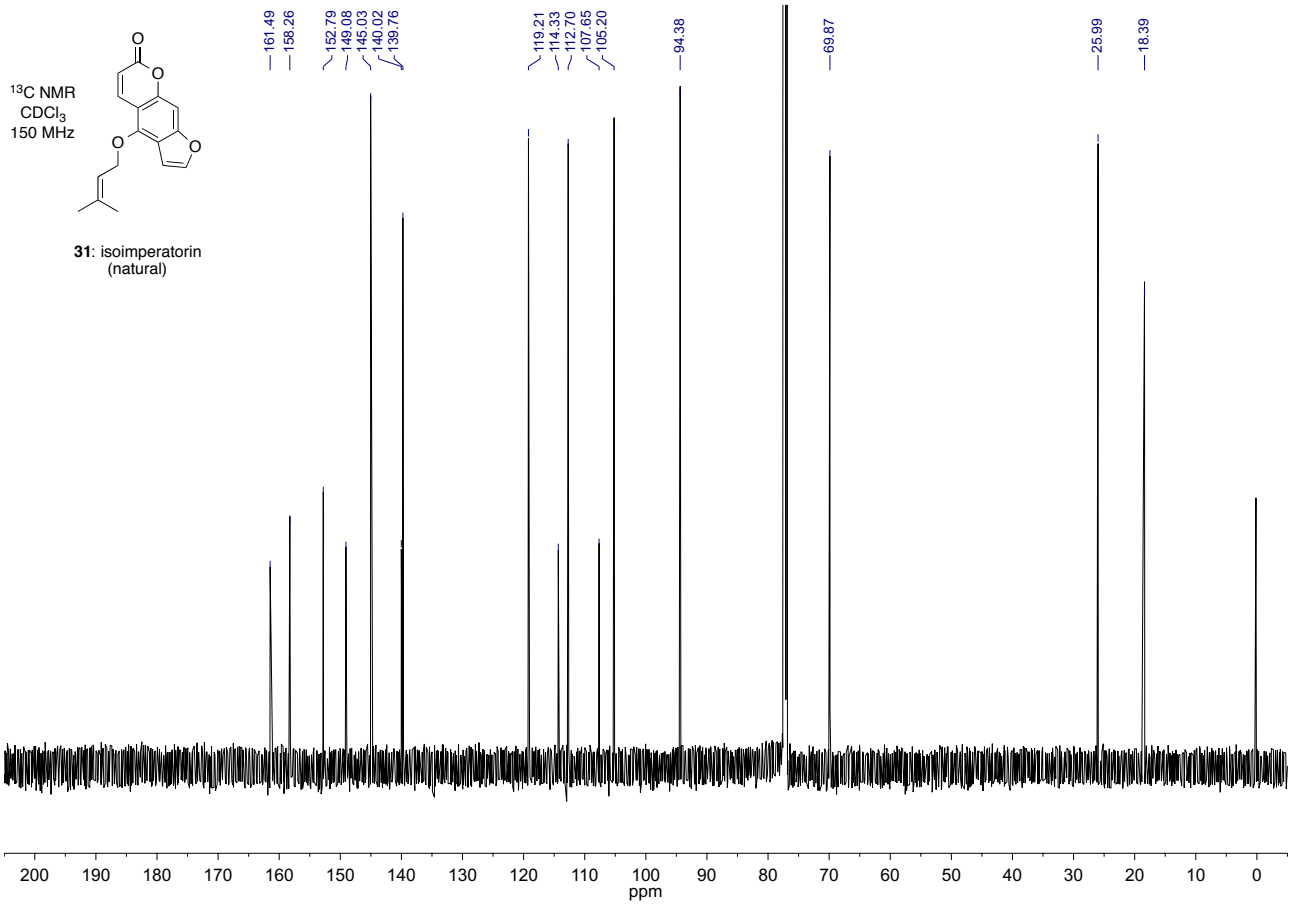

161.63
158.67
155.62
154.93
150.44
150.23
150.02
150.00
140.12
136.11
135.91
135.71
124.09
123.89
123.69
111.12
110.95
105.10
98.73
85.57
73.40
57.17
48.70
39.01
38.65
36.57
34.45
29.92
19.01
^{13}C NMR
d_5-pyridine
125 MHz
HO
O
H
H
OH
30: hydroxyeriobrucinol
(natural)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

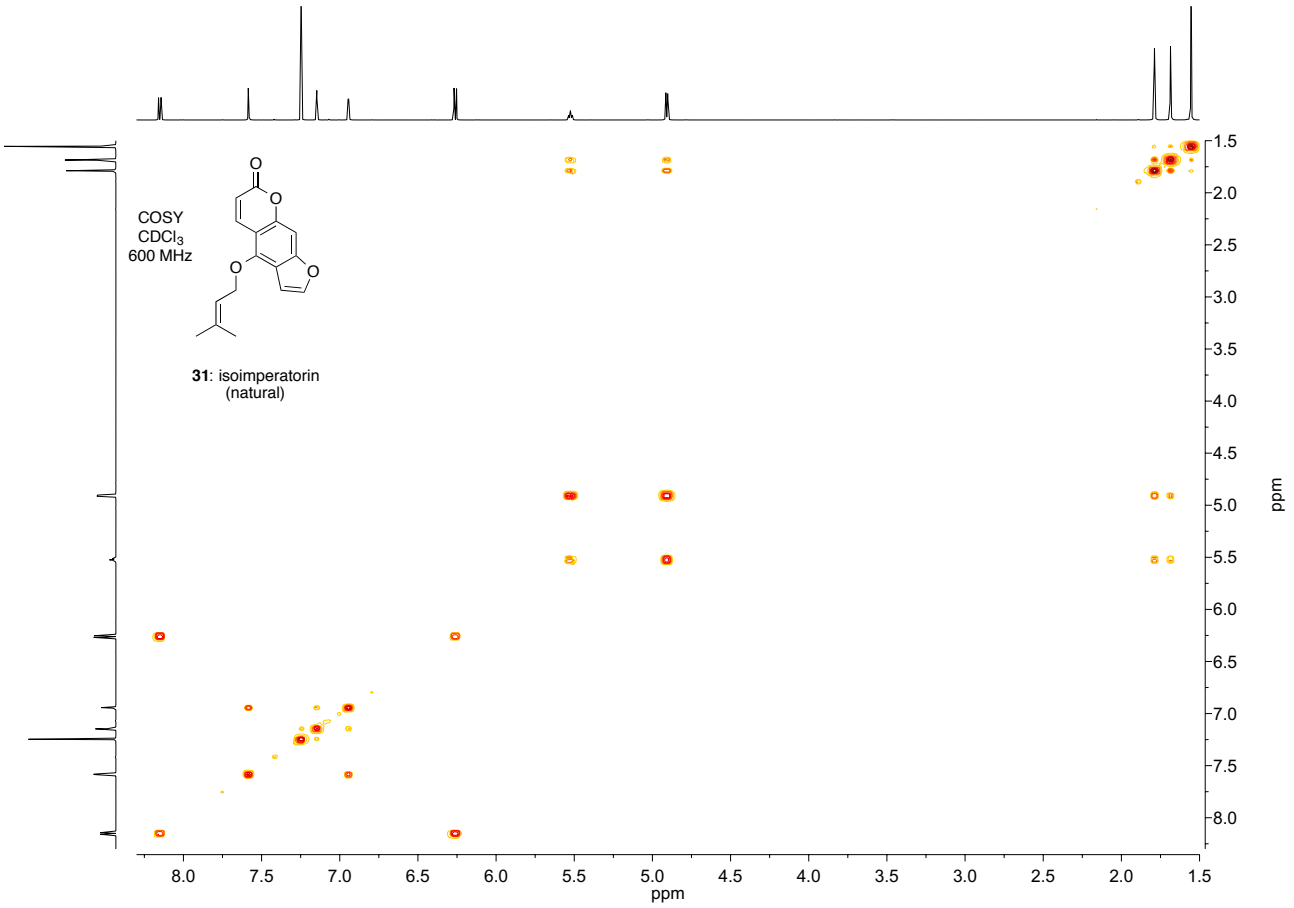

COSY
d_5-pyridine
500 MHz
30: hydroxyeriobrucinol
(natural)

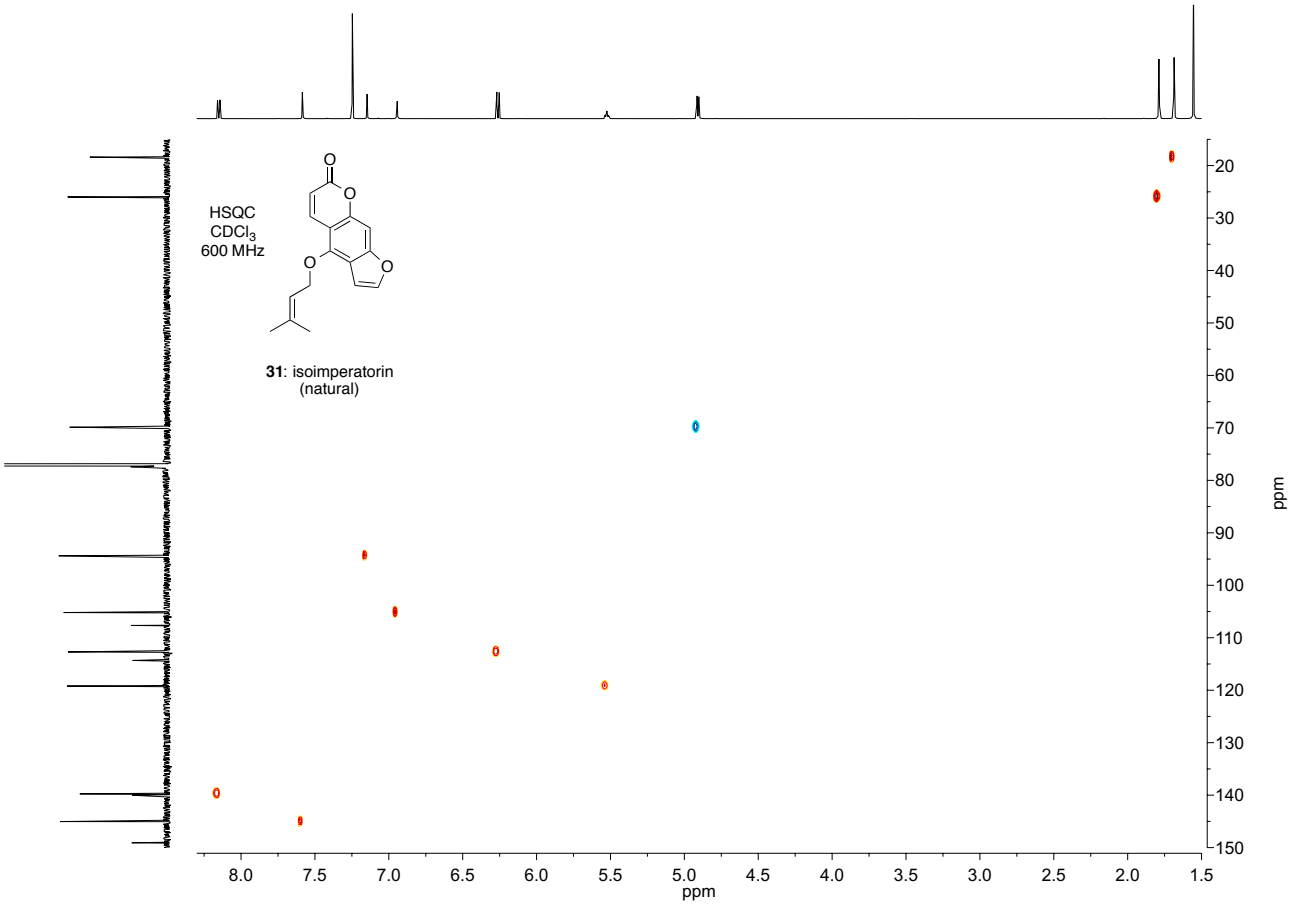

HSQC
d_5-pyridine
500 MHz
30: hydroxyeriobrucinol
(natural)

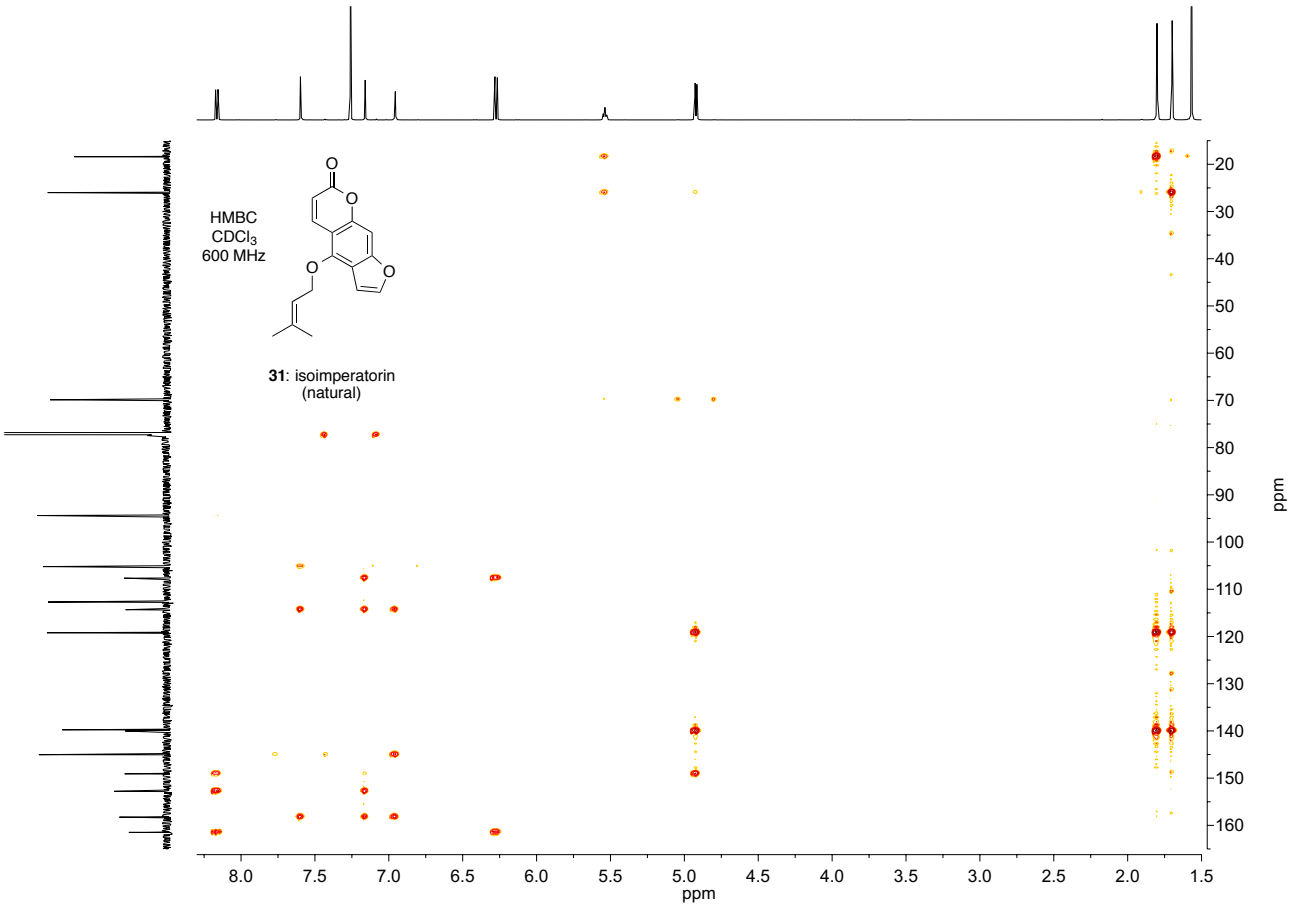

HMBC
d_5-pyridine
500 MHz
HO
O
H
H
H
OH
30: hydroxyeriobrucinol
(natural)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

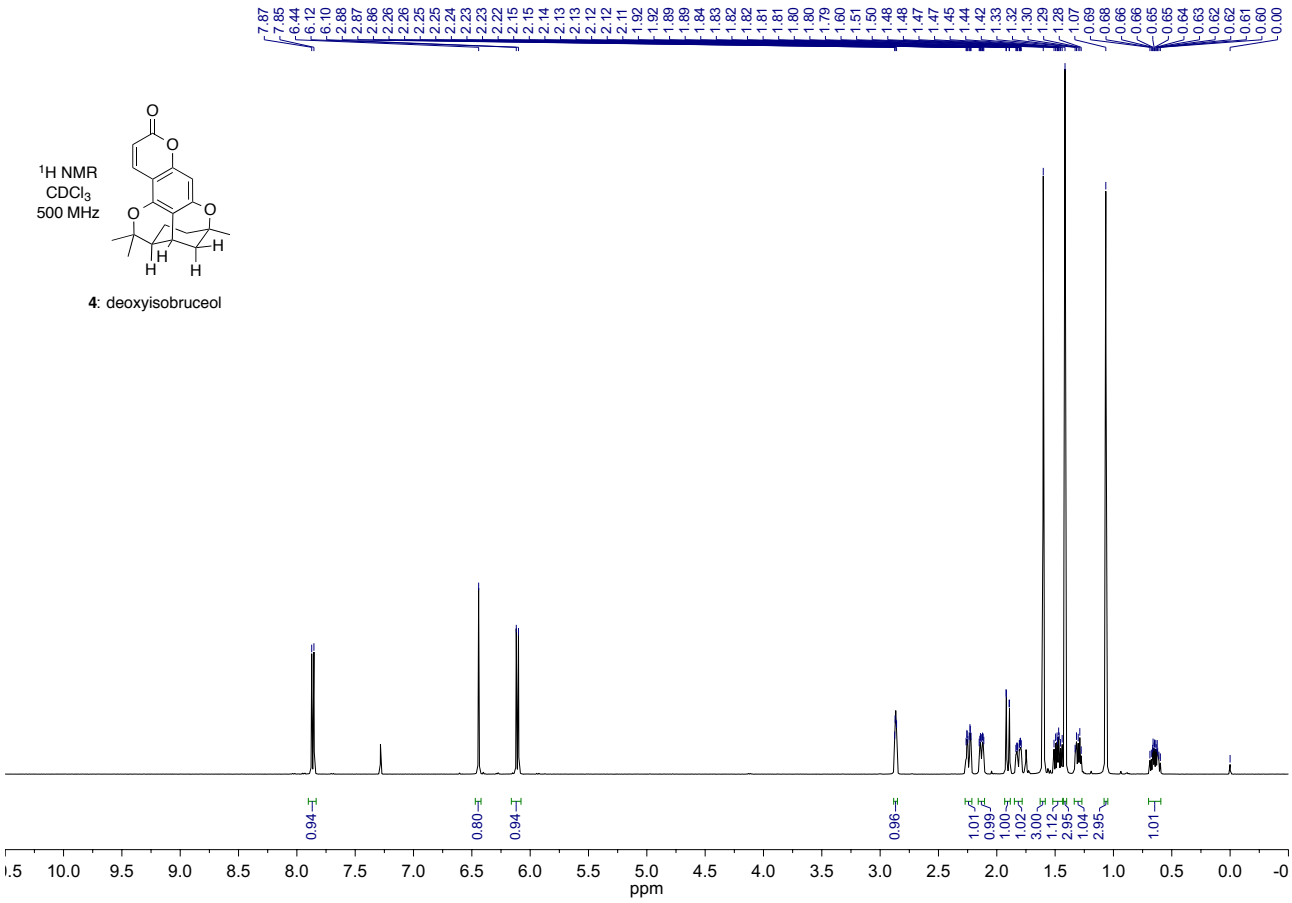

^{1}H NMR
$CDCl_3$
600 MHz
31: isoimperatorin
(natural)
8.17
8.17
8.16
8.15
7.60
7.59
7.16
7.16
7.16
6.96
6.96
6.96
6.95
6.28
6.27
5.55
5.55
5.55
5.54
5.54
5.54
5.54
5.53
5.53
5.53
5.53
5.52
4.93
4.93
4.93
4.92
4.91
4.91
1.80
1.70
1.00
0.90
0.85
1.01
0.98
0.98
2.12
3.03
2.86
ppm

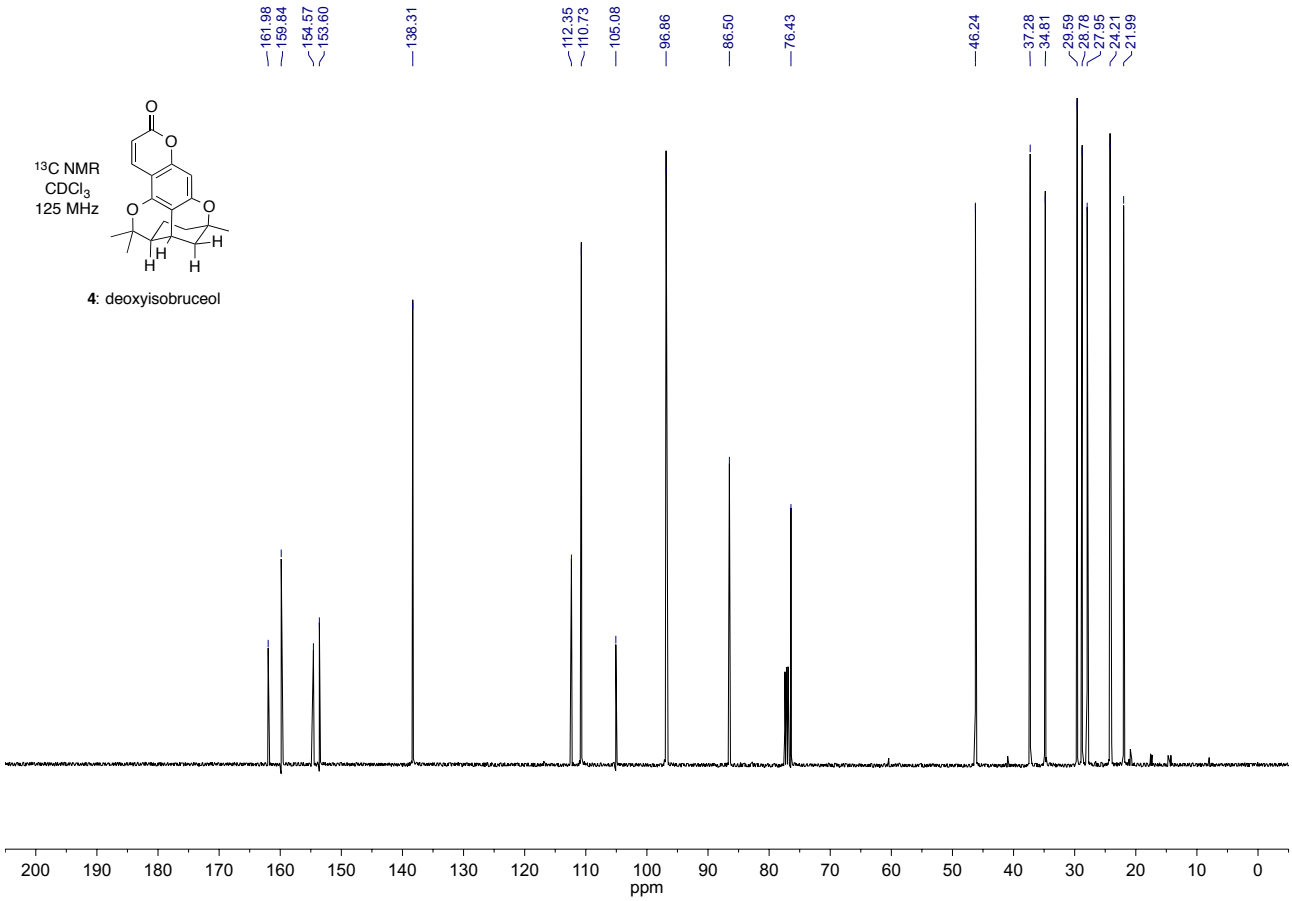

^{13}C NMR
$CDCl_3$
150 MHz
31: isoimperatorin
(natural)
161.49
158.26
152.79
149.08
145.03
140.02
139.76
119.21
114.33
112.70
107.65
105.20
94.38
69.87
25.99
18.39
ppm

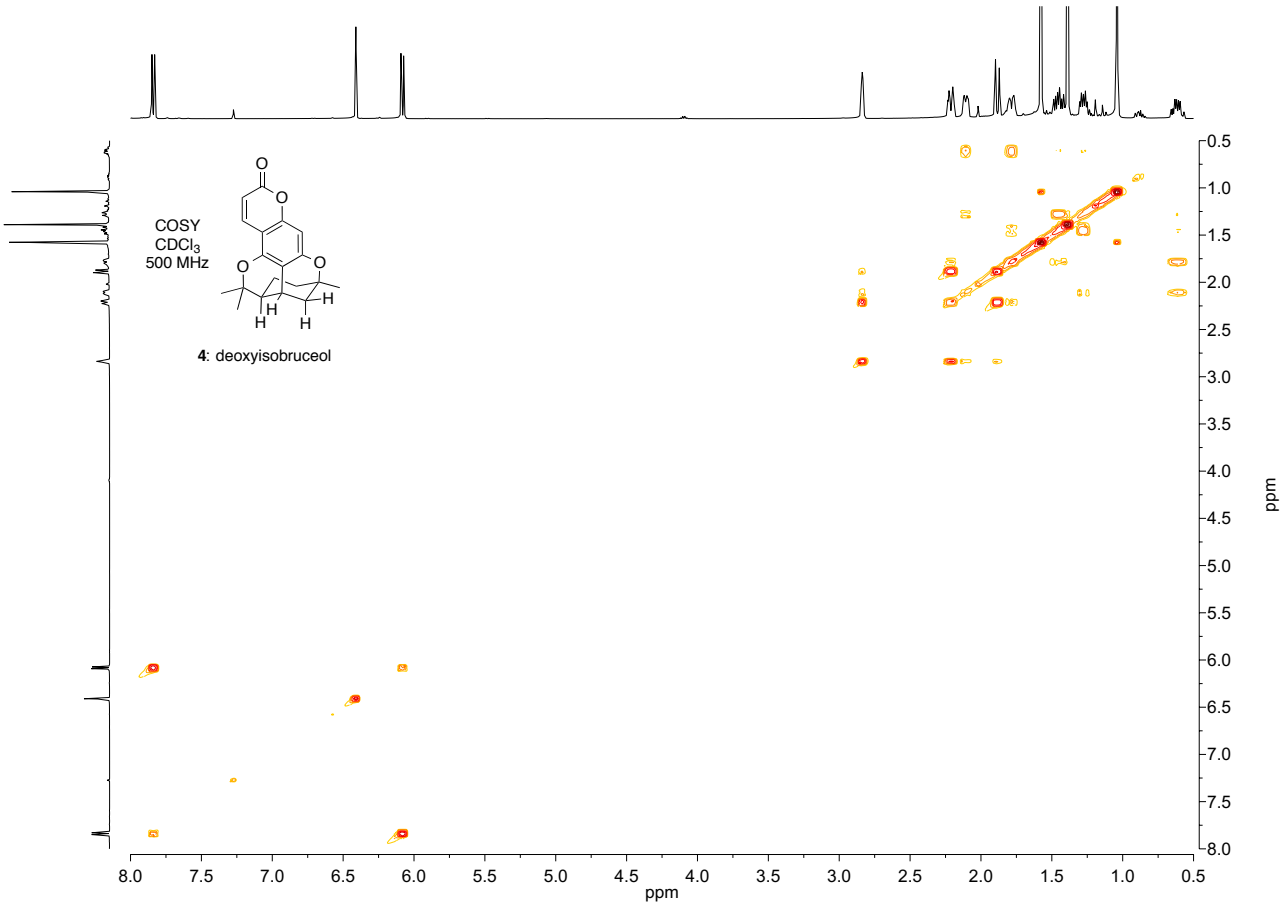

COSY
CDCl3
600 MHz
31: isoimperatorin
(natural)
ppm
ppm

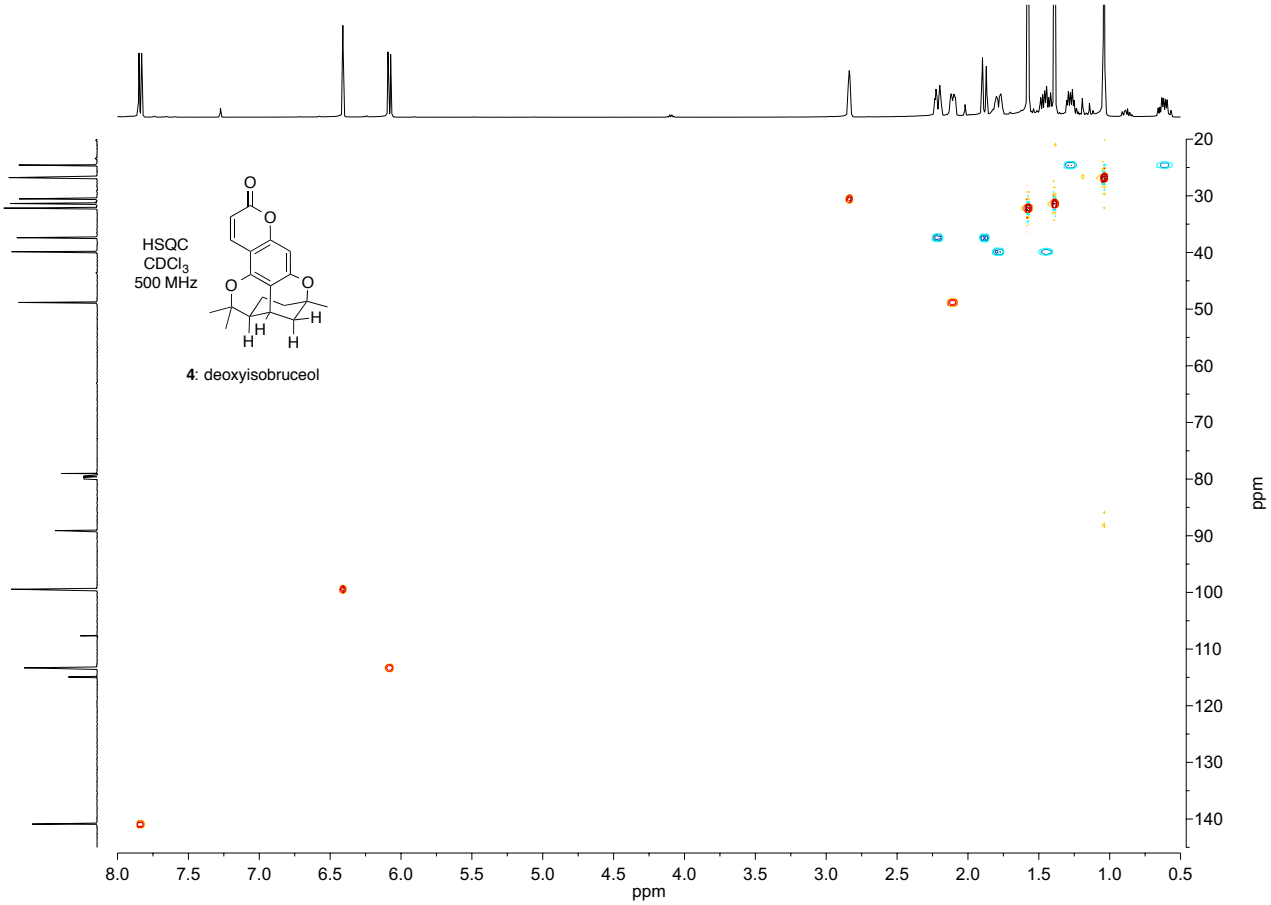

HSQC
CDCl3
600 MHz
31: isoimperatorin
(natural)
ppm
ppm

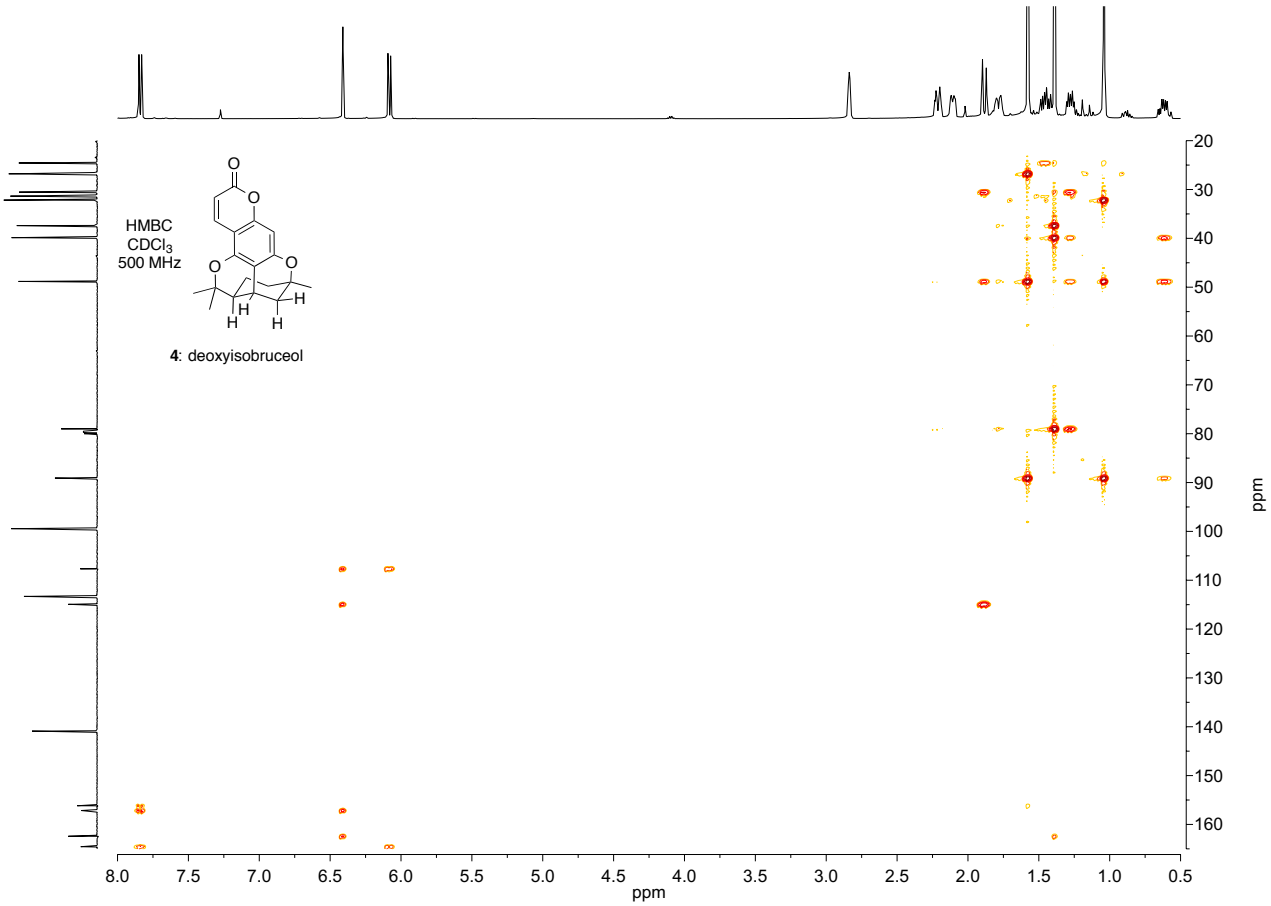

HMBC
CDCl3
600 MHz
31: isoimperatorin
(natural)
ppm
ppm


^{1}H NMR
$CDCl_3$
500 MHz
4: deoxyisobruceol
ppm


^{13}C NMR
$CDCl_3$
125 MHz
4: deoxyisobruceol
ppm


COSY
CDCl3
500 MHz
4: deoxyisobruceol
ppm
ppm


HSQC
CDCl3
500 MHz
4: deoxyisobruceol
ppm
ppm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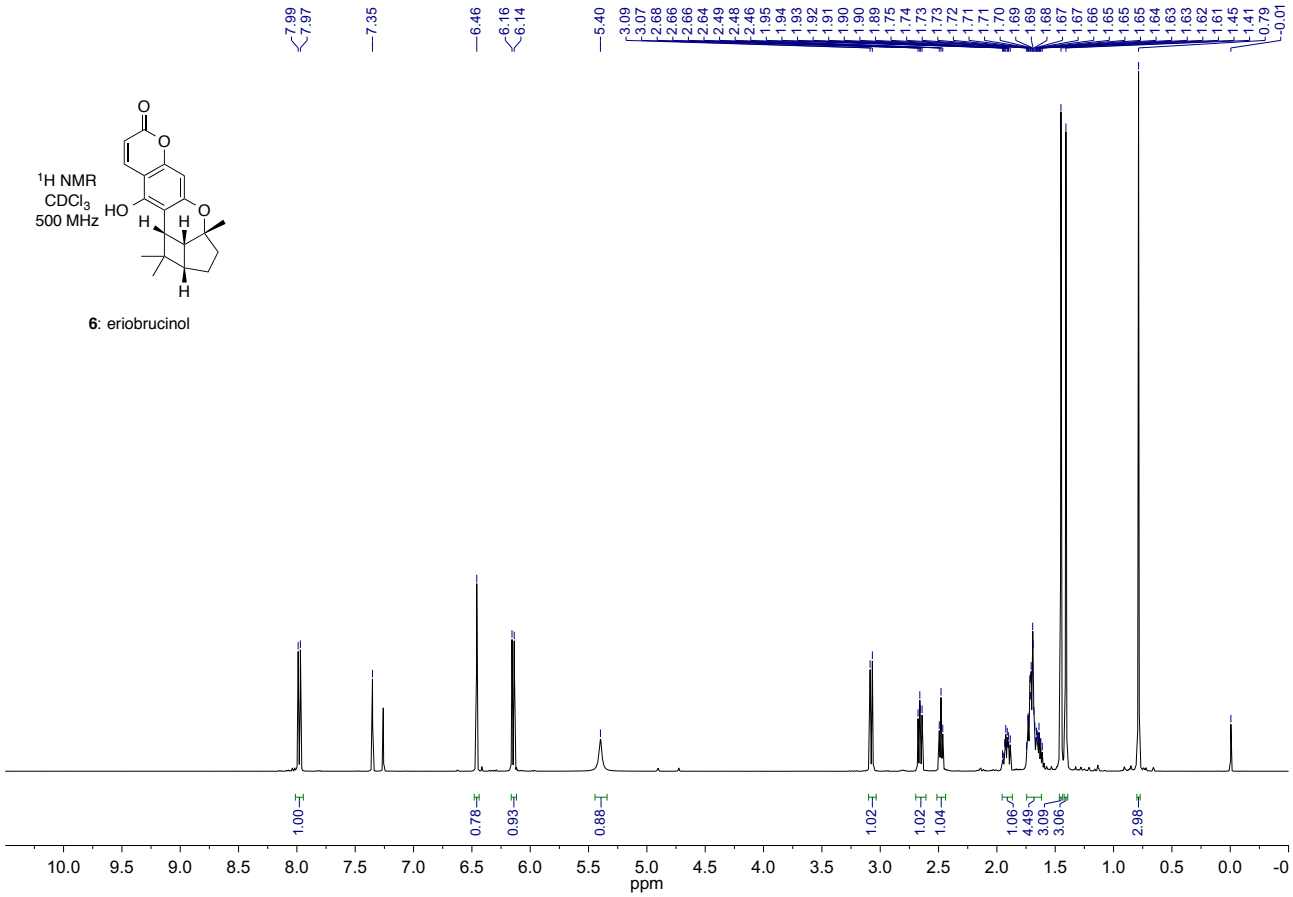
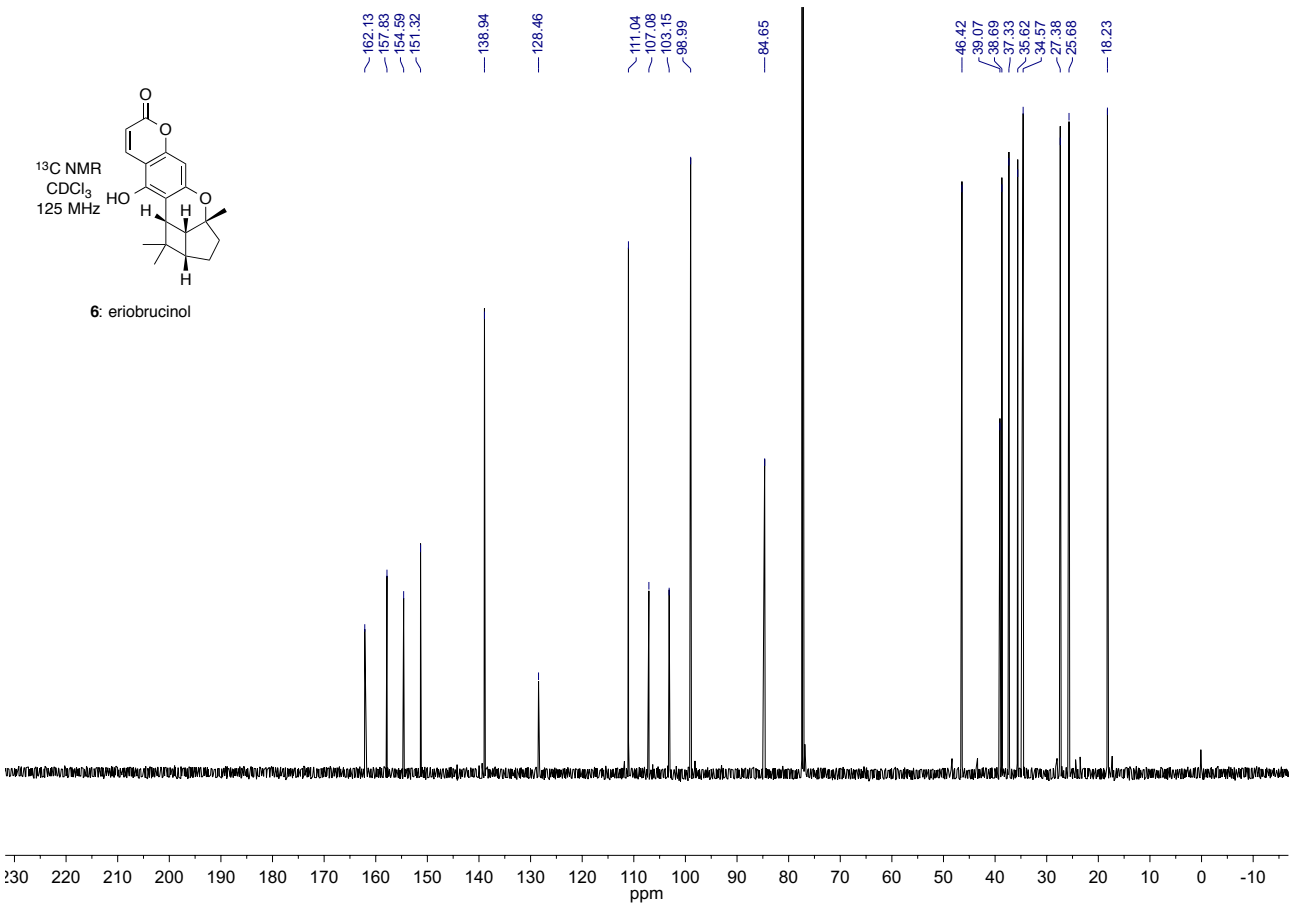
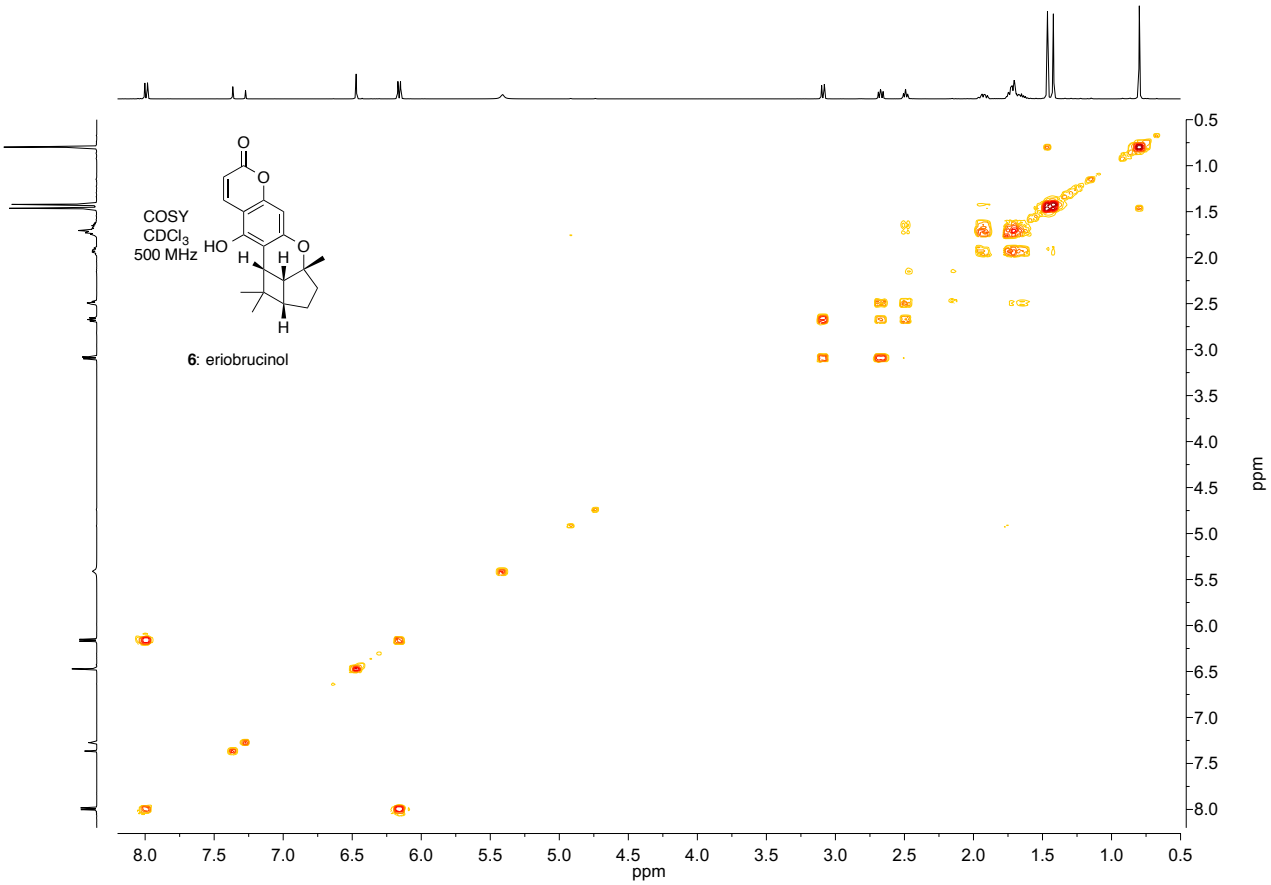
CDCl3
500 MHz
4: deoxyisobruceol
ppm
ppm

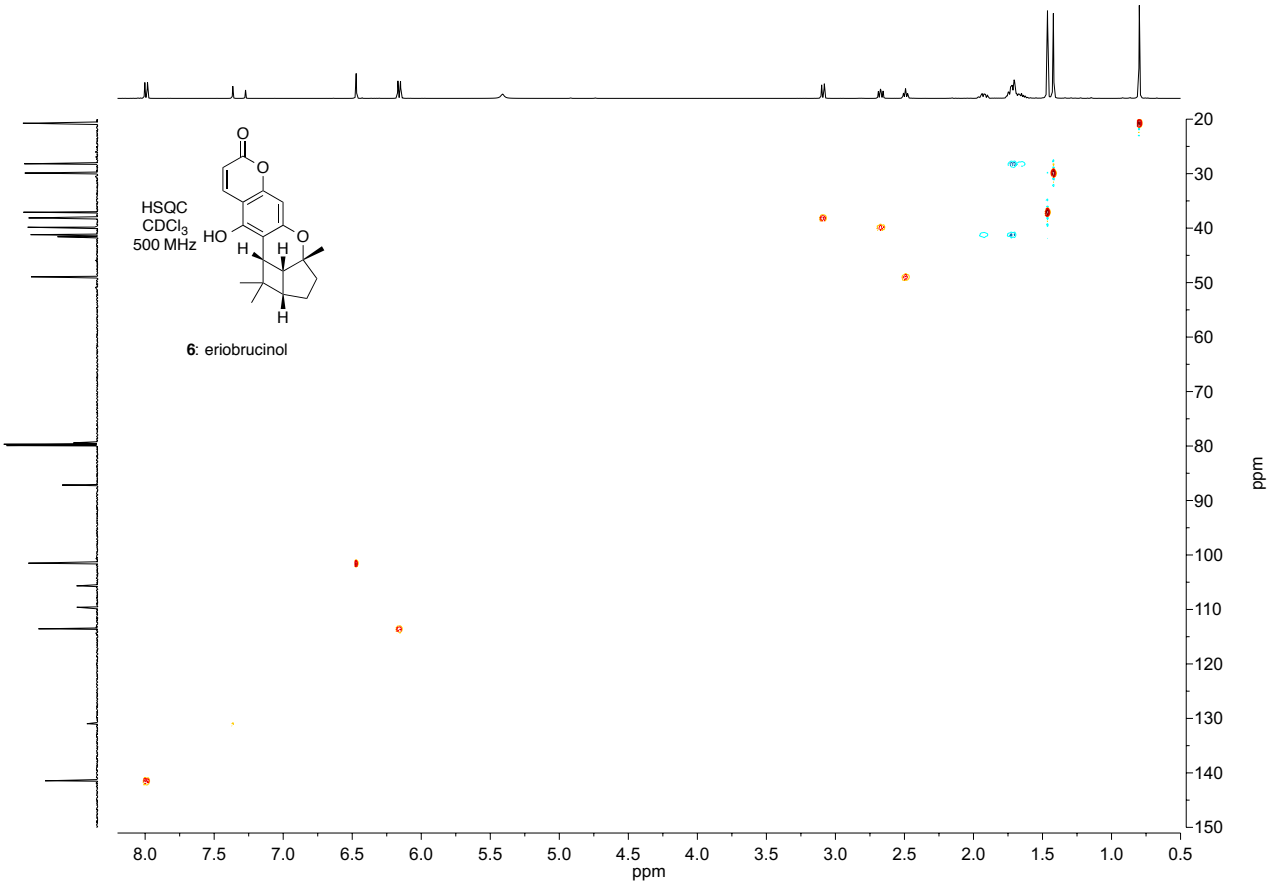


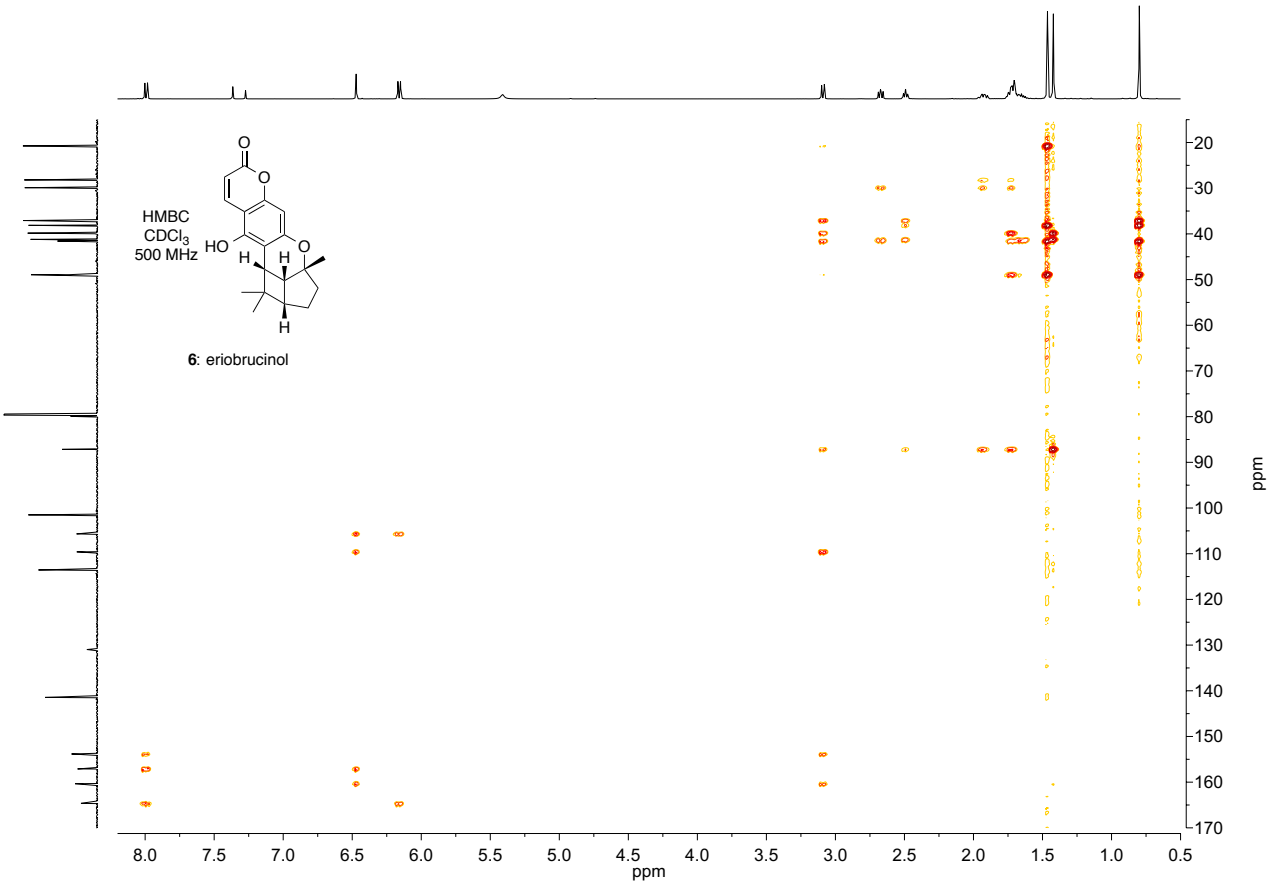
6: eriobrucinol

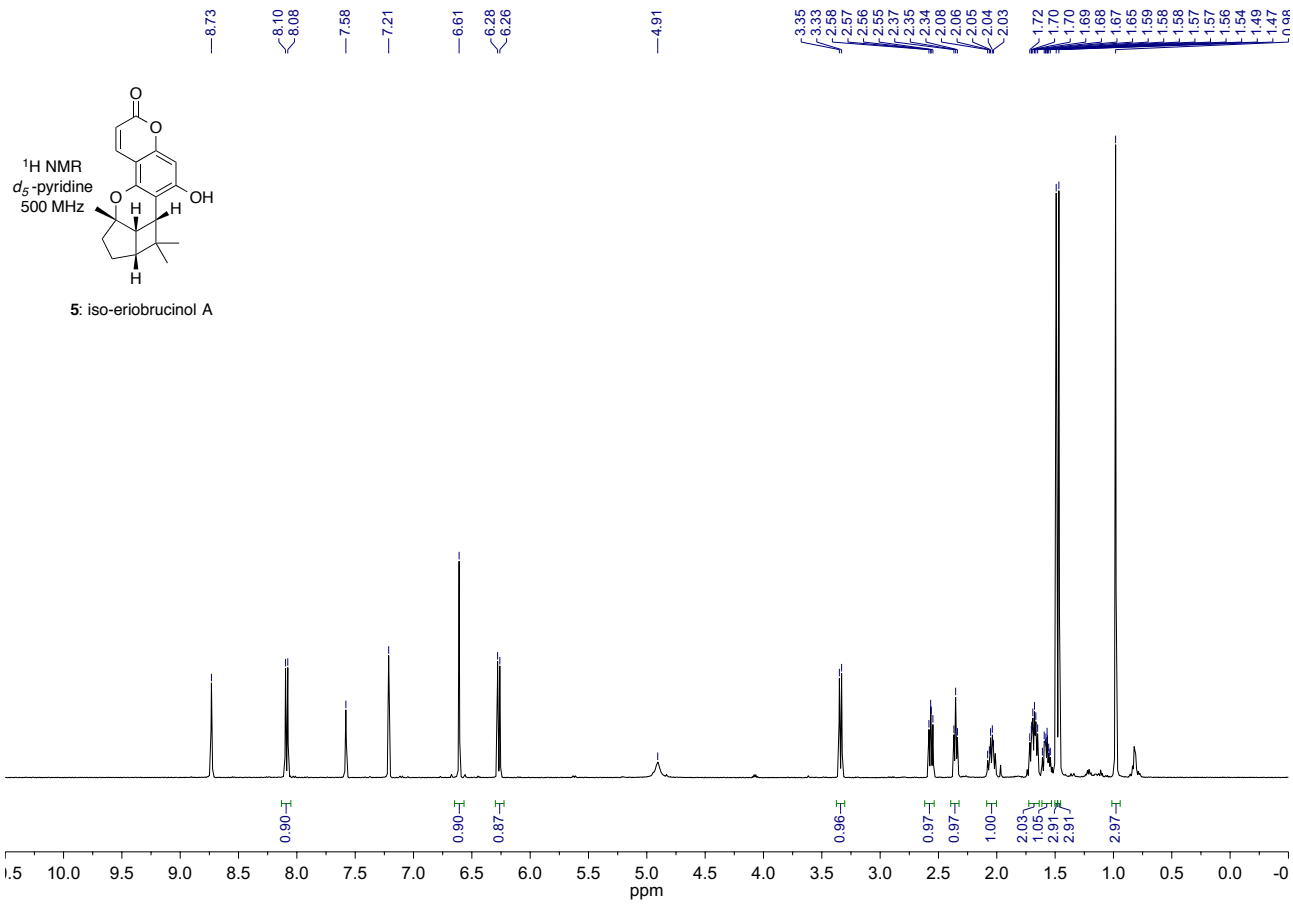


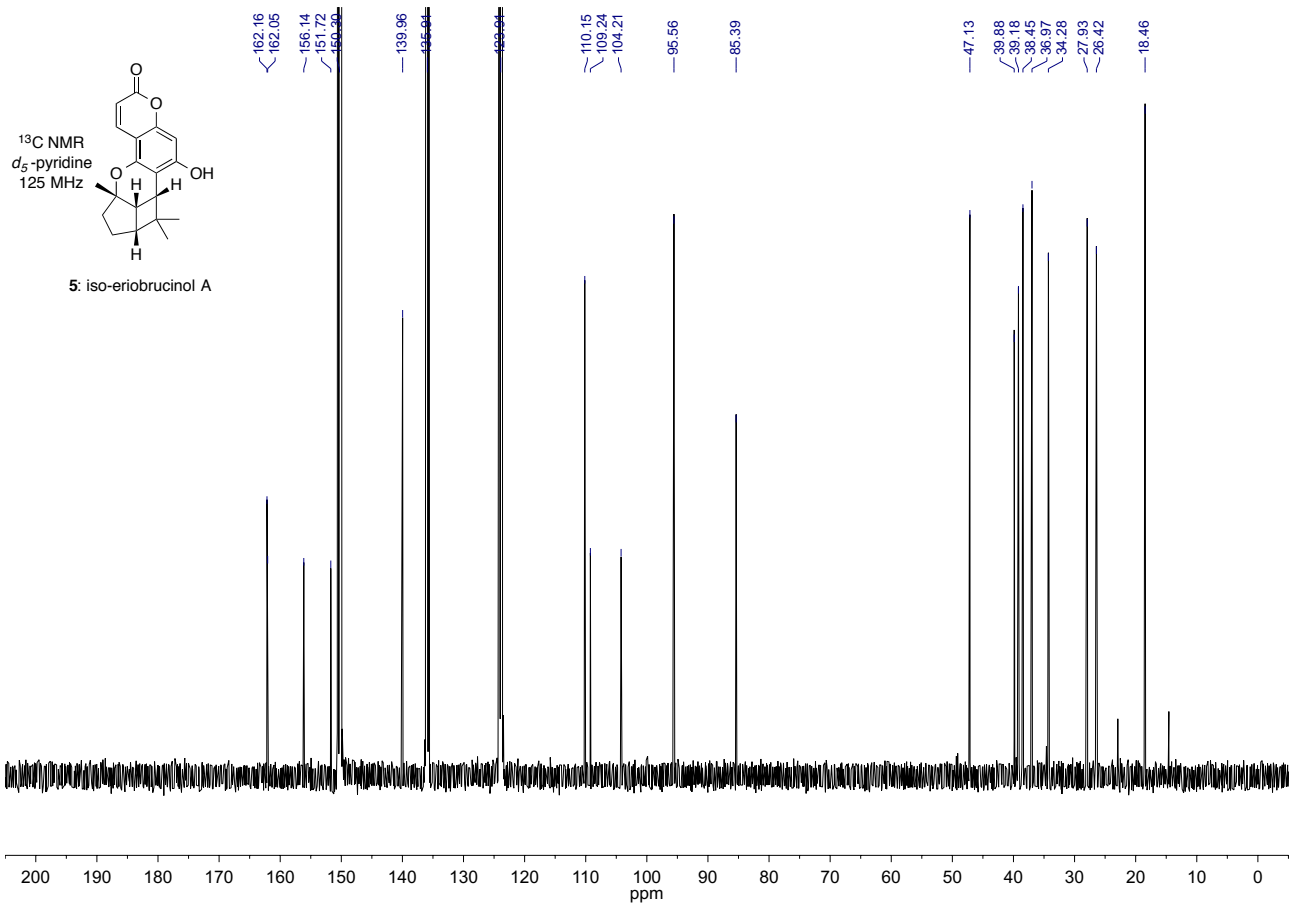
6: eriobrucinol

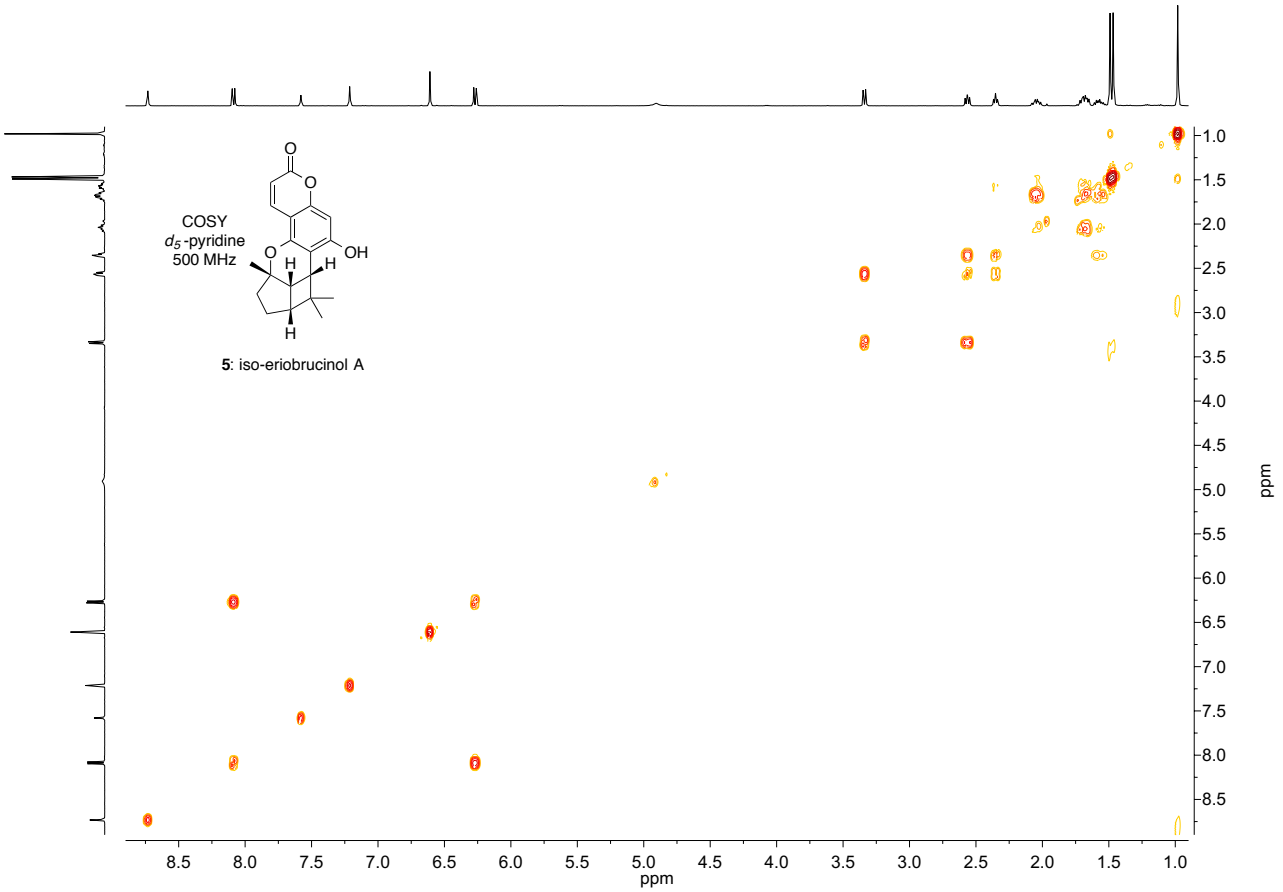

COSY
CDCl3
500 MHz
HO
O
H
6: eriobrucinol
ppm

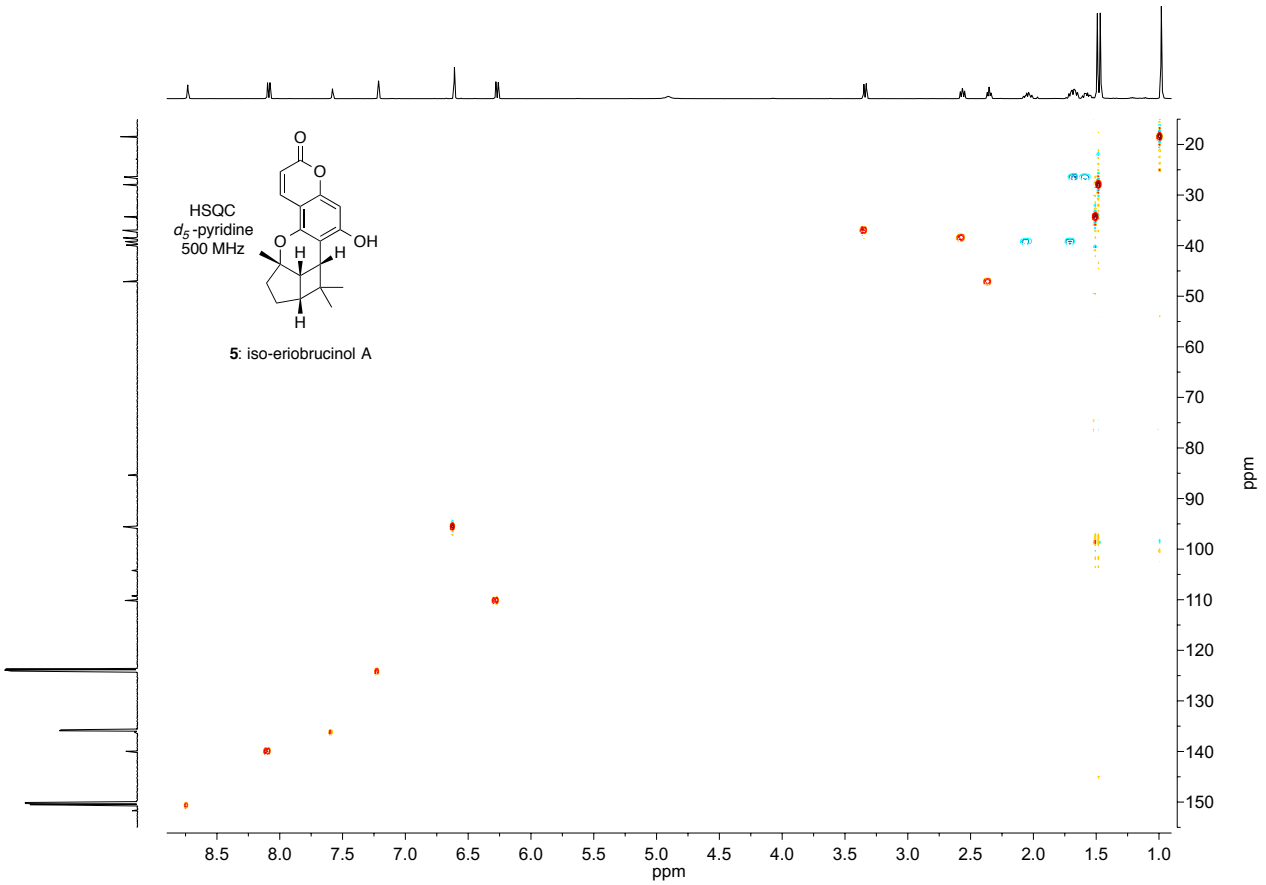

HSQC
CDCl3
500 MHz
HO
O
H
6: eriobrucinol
ppm

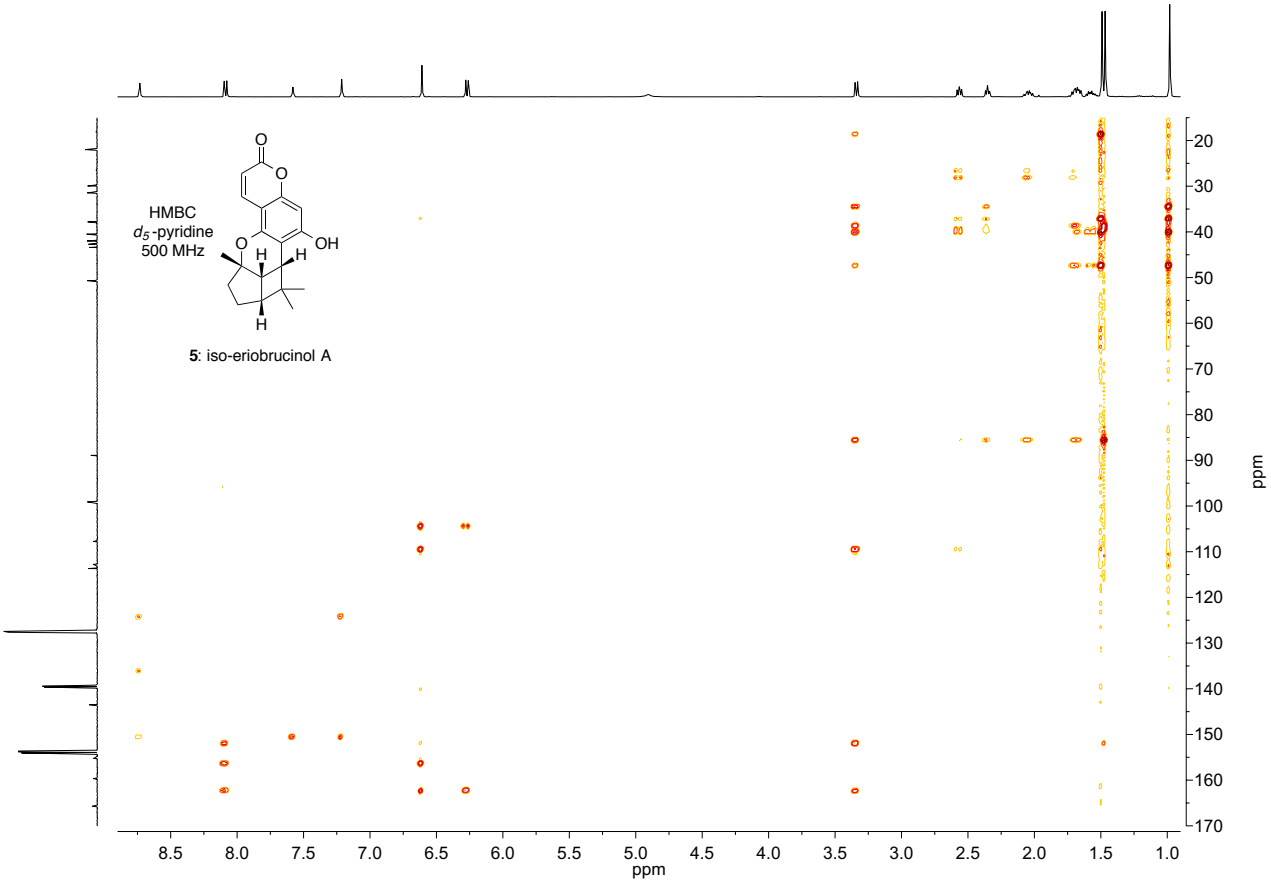

HMBC
CDCl3
500 MHz
HO
O
H
H
O
H
6: eriobrucinol
ppm
ppm

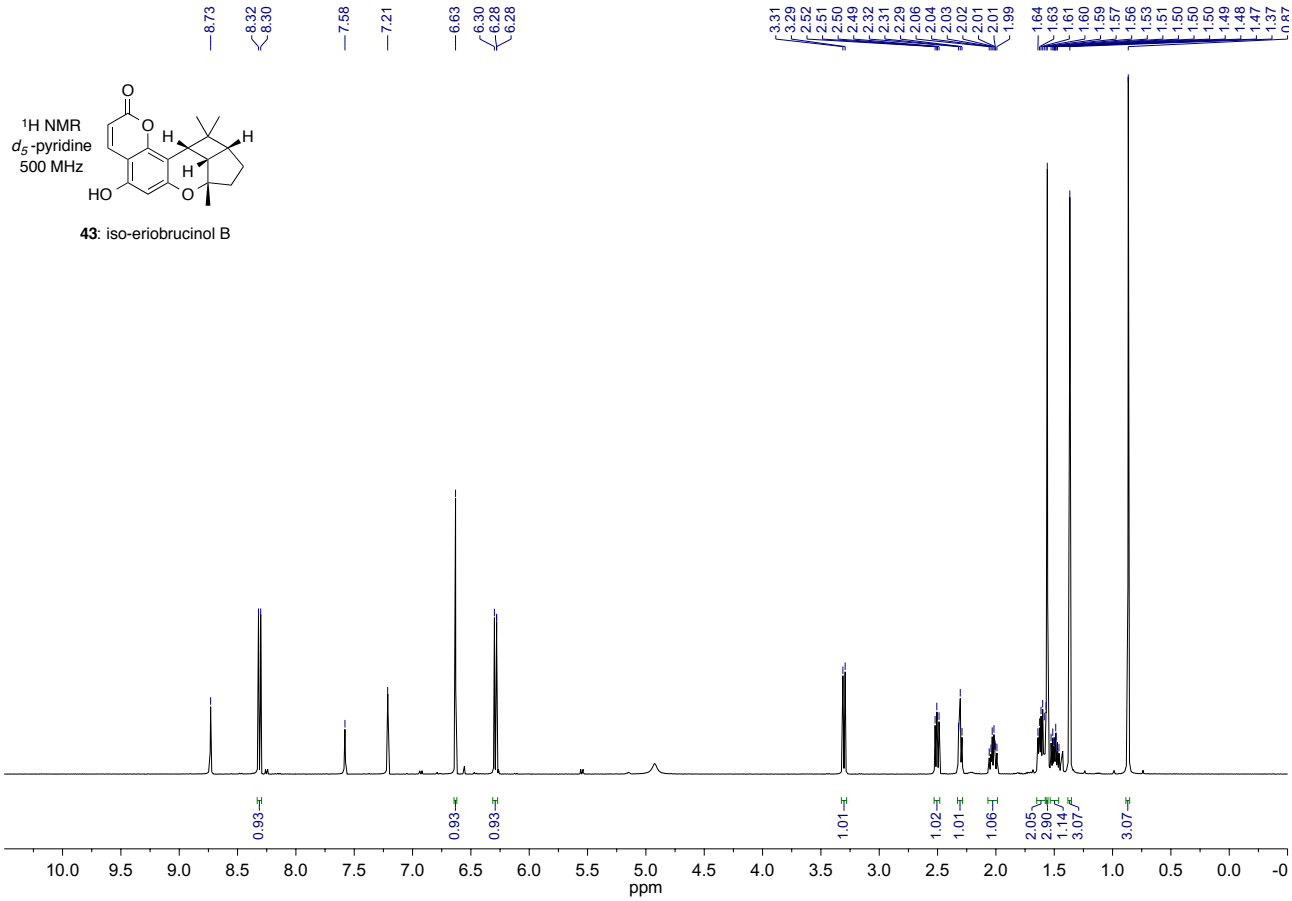

8.73
8.10
8.08
7.58
7.21
6.61
6.28
6.26
4.91
3.35
3.33
2.58
2.57
2.56
2.55
2.37
2.35
2.34
2.08
2.06
2.05
2.04
2.03
1.72
1.70
1.70
1.69
1.68
1.67
1.65
1.59
1.58
1.58
1.57
1.57
1.56
1.54
1.49
1.47
0.98
^{1}H NMR
d_5-pyridine
500 MHz
O
O
O
H
H
OH
H
5: iso-eriobrucinol A
0.90
0.90
0.87
0.96
0.97
0.97
1.00
2.03
1.05
2.91
2.91
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

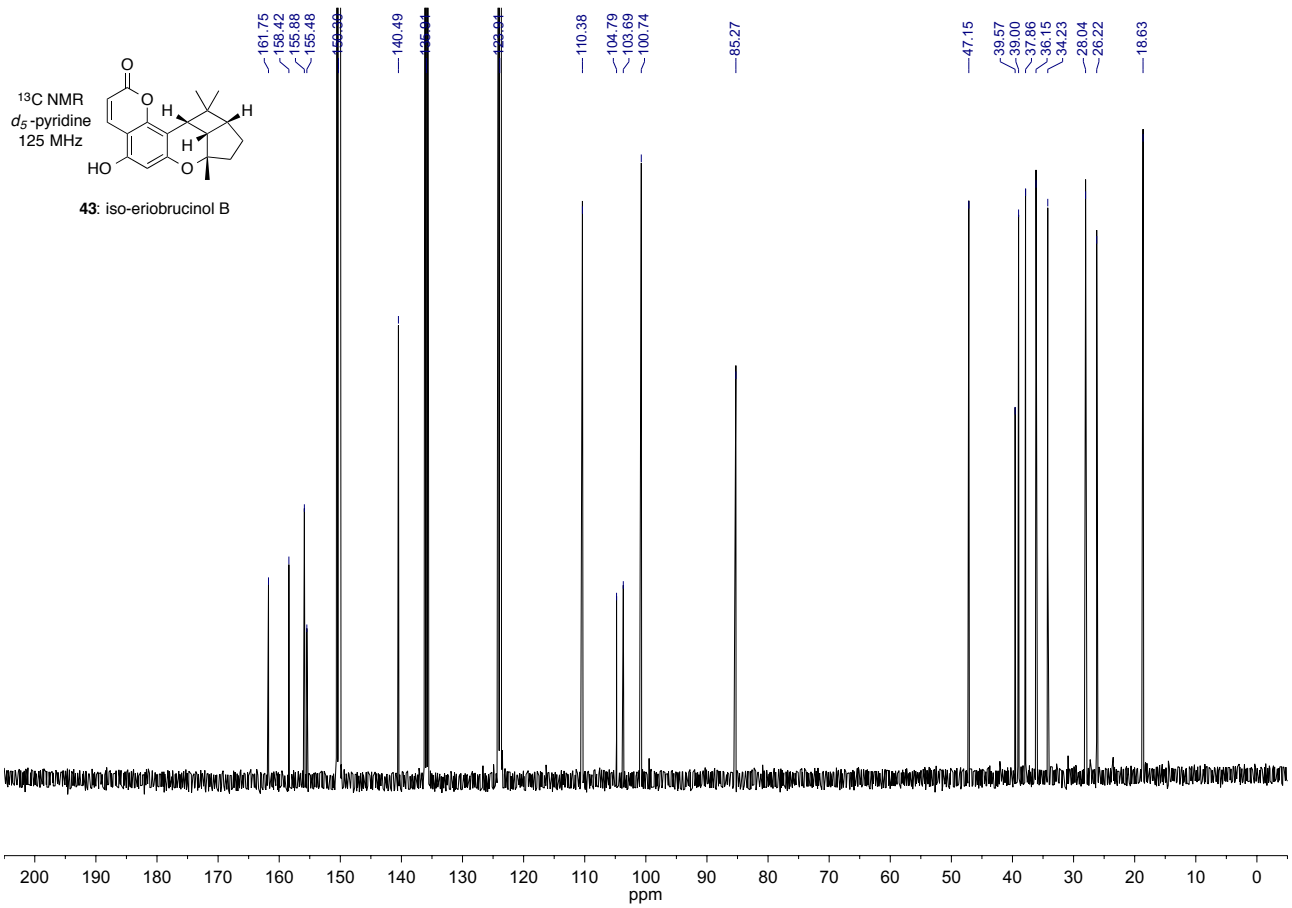

162.16
162.05
156.14
151.72
150.90
139.96
135.91
123.91
110.15
109.24
104.21
95.56
85.39
47.13
39.88
39.18
38.45
36.97
34.28
27.93
26.42
18.46
^{13}C NMR
d_5-pyridine
125 MHz
O
O
O
H
H
OH
H
5: iso-eriobrucinol A
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

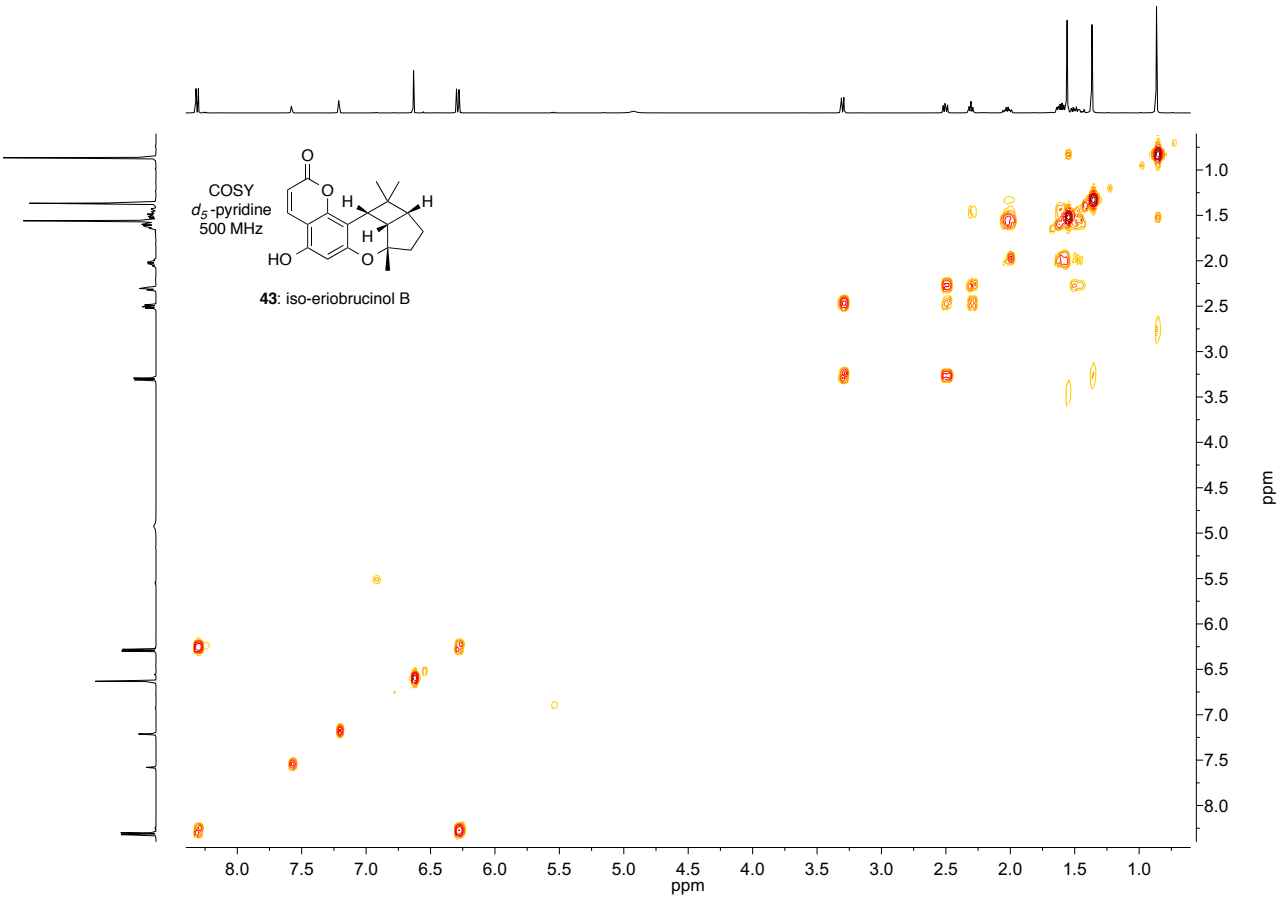

COSY
d_5-pyridine
500 MHz
5: iso-eriobrucinol A
ppm
ppm

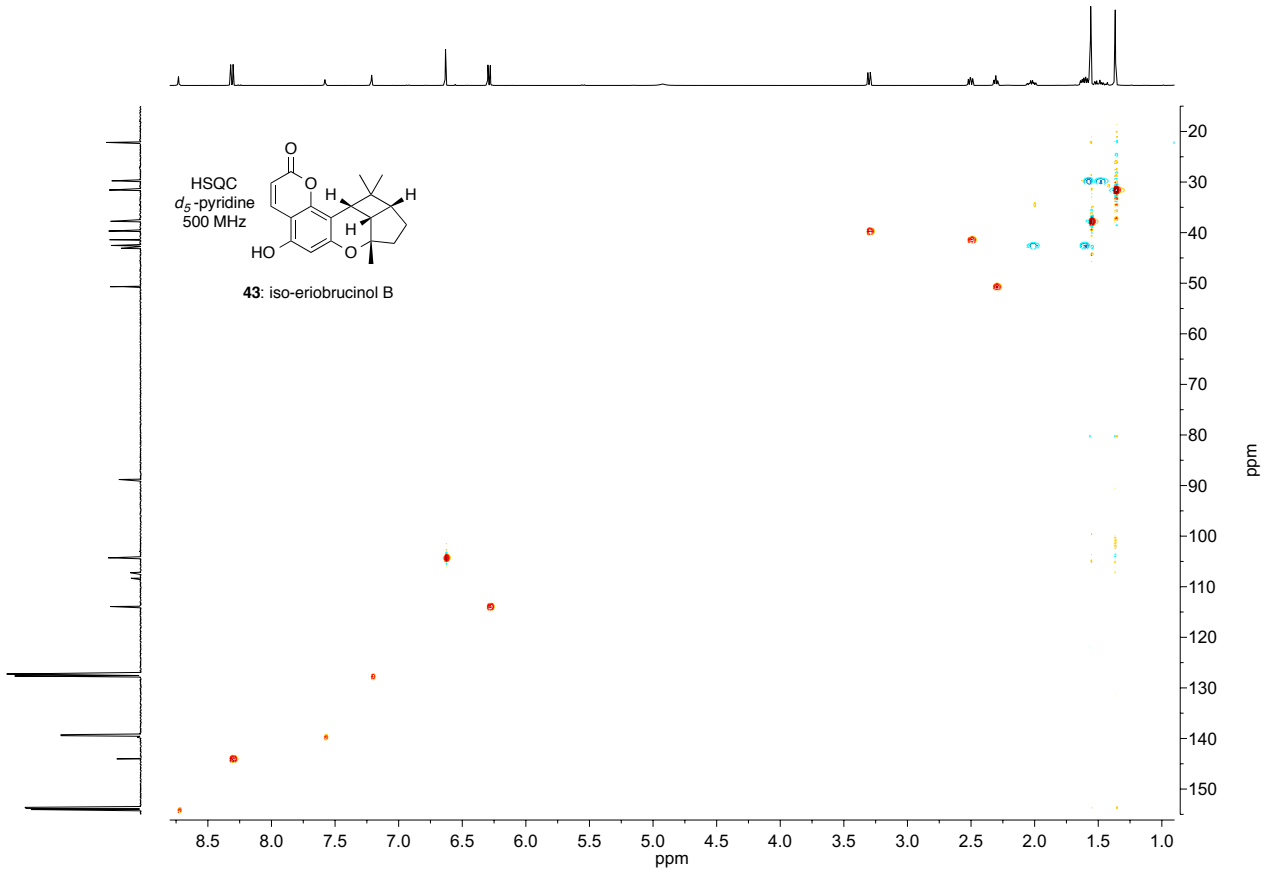

HSQC
d_5-pyridine
500 MHz
5: iso-eriobrucinol A
ppm
ppm

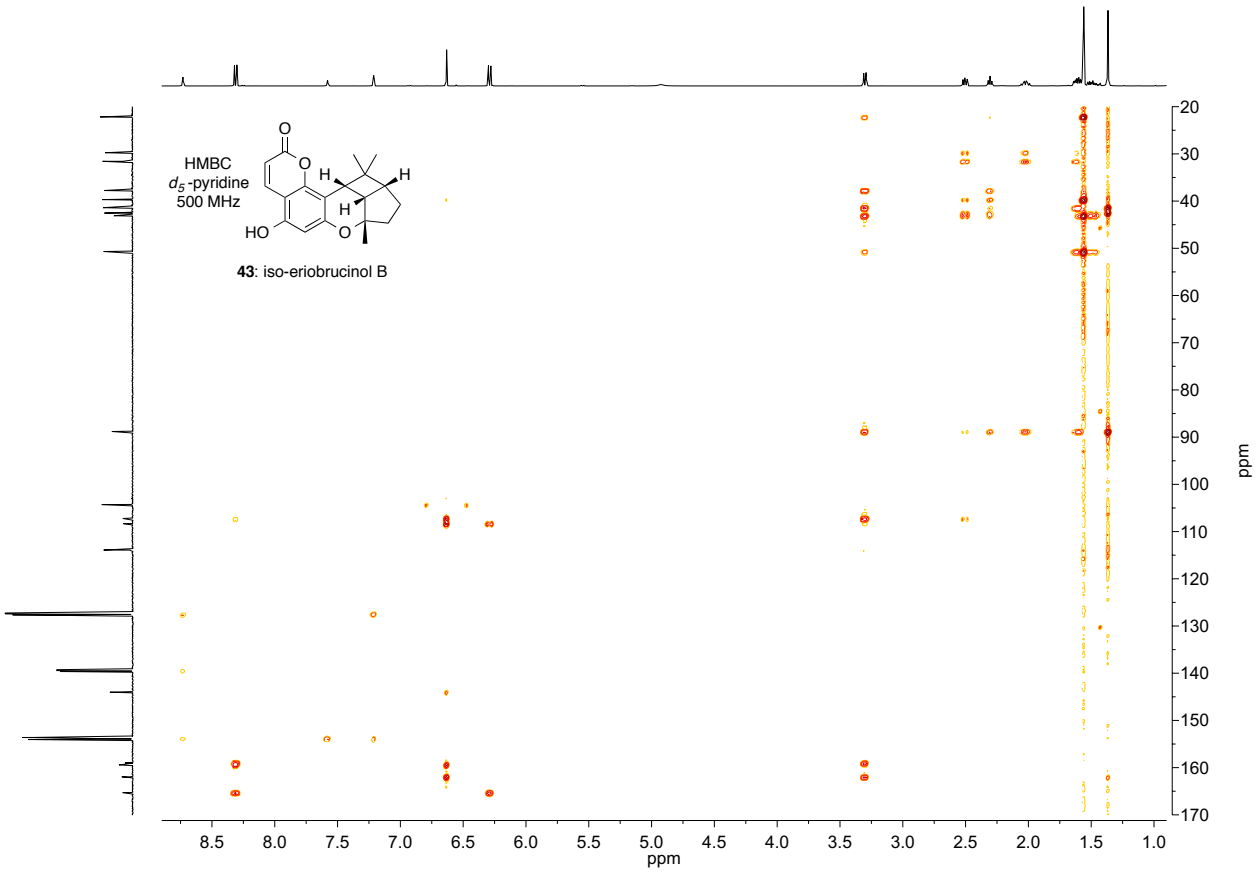

HMBC
d_5-pyridine
500 MHz
O
O
O
H
H
OH
H
5: iso-eriobrucinol A
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

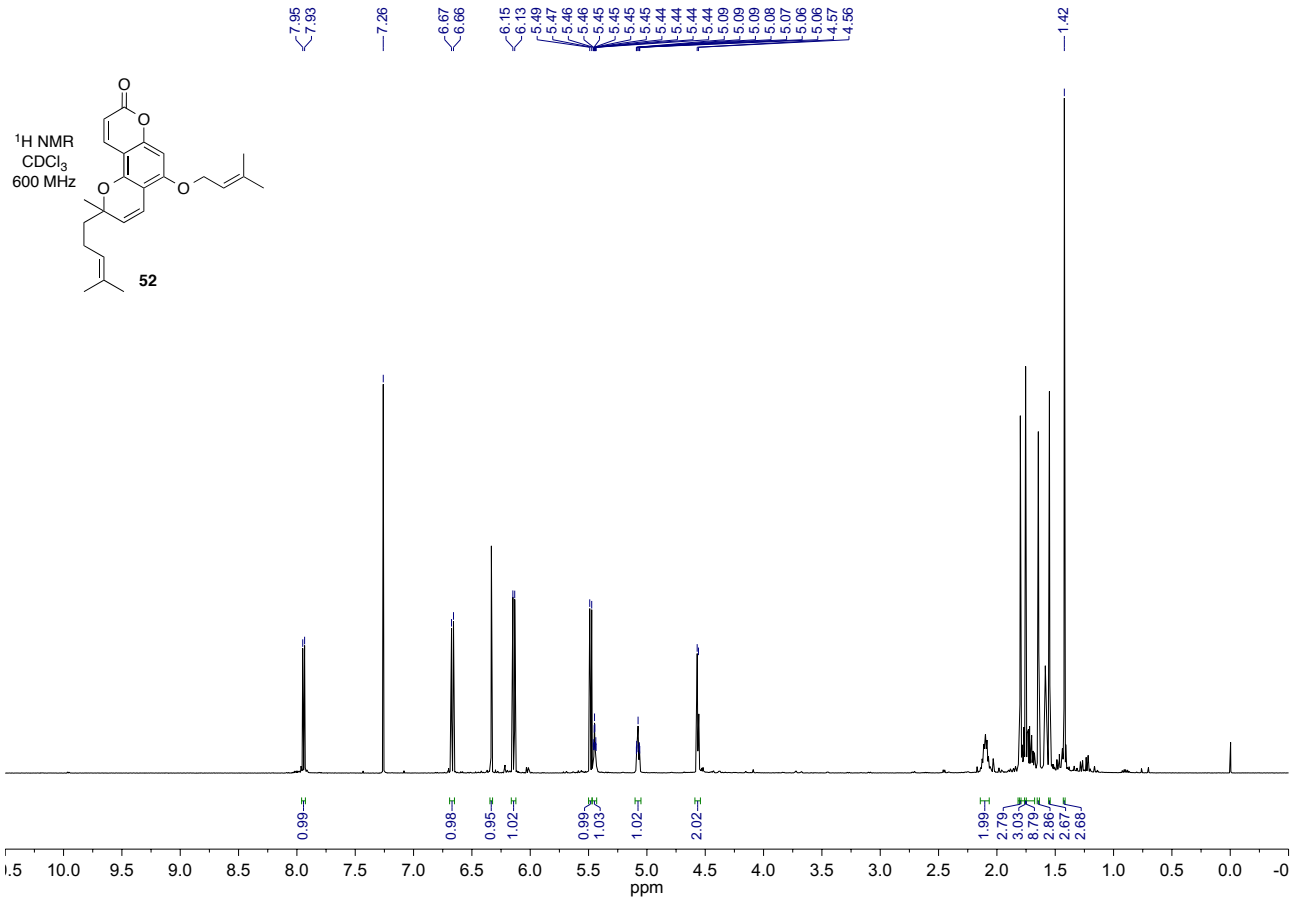

1H NMR
d5-pyridine
500 MHz
43: iso-eriobrucinol B
8.73
8.32
8.30
7.58
7.21
6.63
6.30
6.28
6.28
3.31
3.29
3.29
2.52
2.51
2.50
2.49
2.32
2.31
2.29
2.06
2.04
2.03
2.02
2.01
2.01
1.99
1.64
1.63
1.61
1.60
1.59
1.57
1.56
1.53
1.51
1.50
1.50
1.50
1.49
1.48
1.47
1.37
0.93
0.93
0.93
1.01
1.02
1.01
1.06
2.05
2.90
1.14
3.07
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm

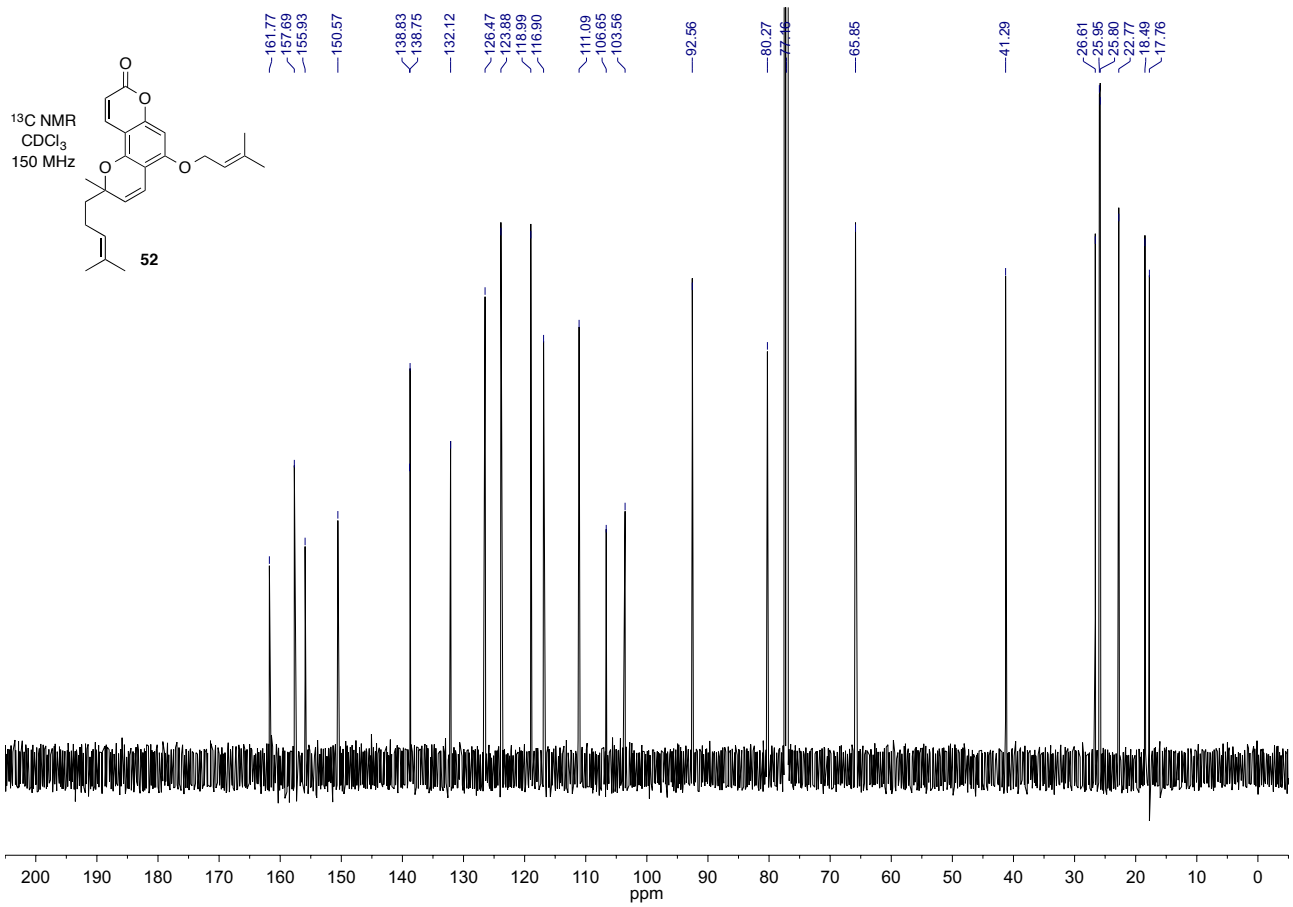

13C NMR
d5-pyridine
125 MHz
43: iso-eriobrucinol B
161.75
158.42
155.88
155.48
150.36
140.49
135.01
123.94
110.38
104.79
103.69
100.74
85.27
47.15
39.57
39.00
37.86
36.15
34.23
28.04
26.22
18.63
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

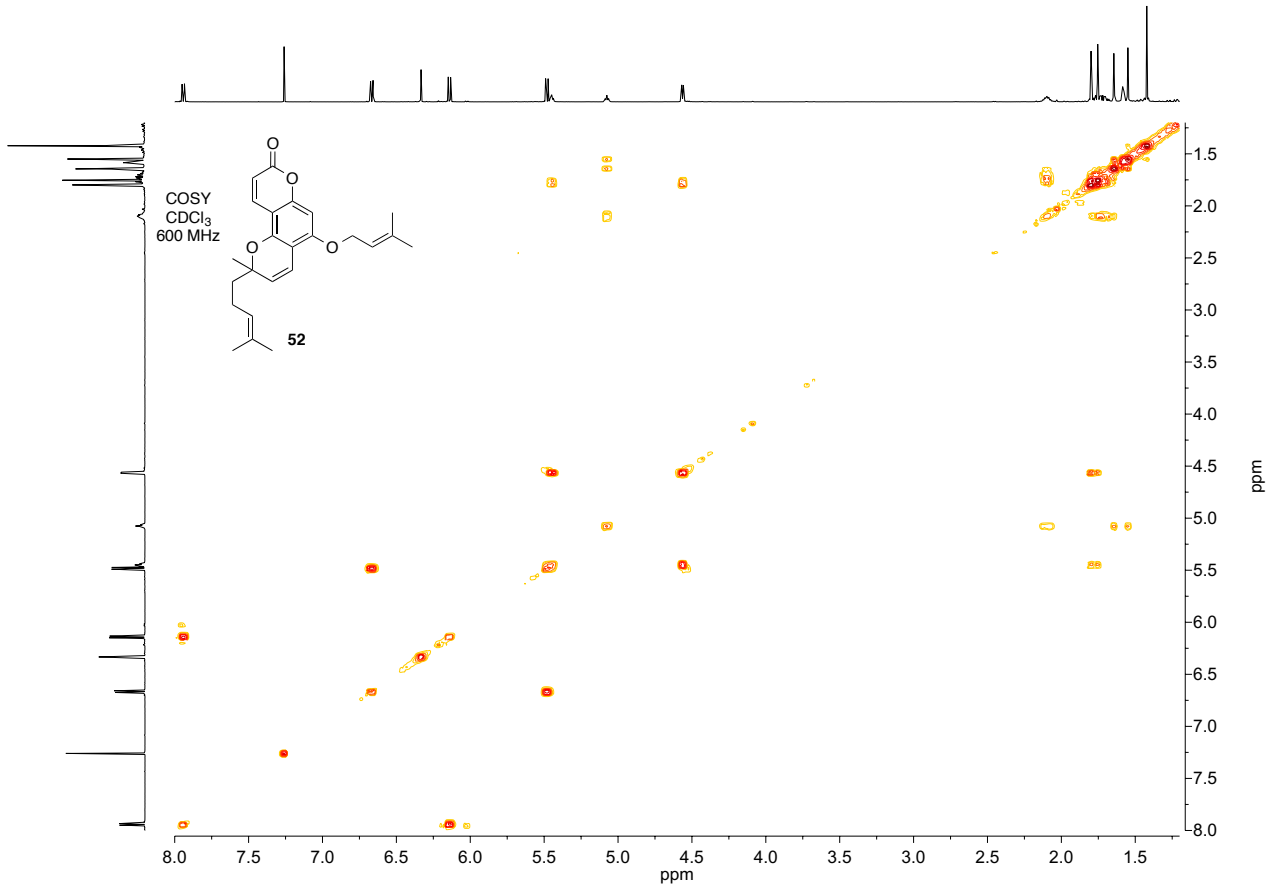

COSY
d_5-pyridine
500 MHz
43: iso-eriobrucinol B
ppm
ppm

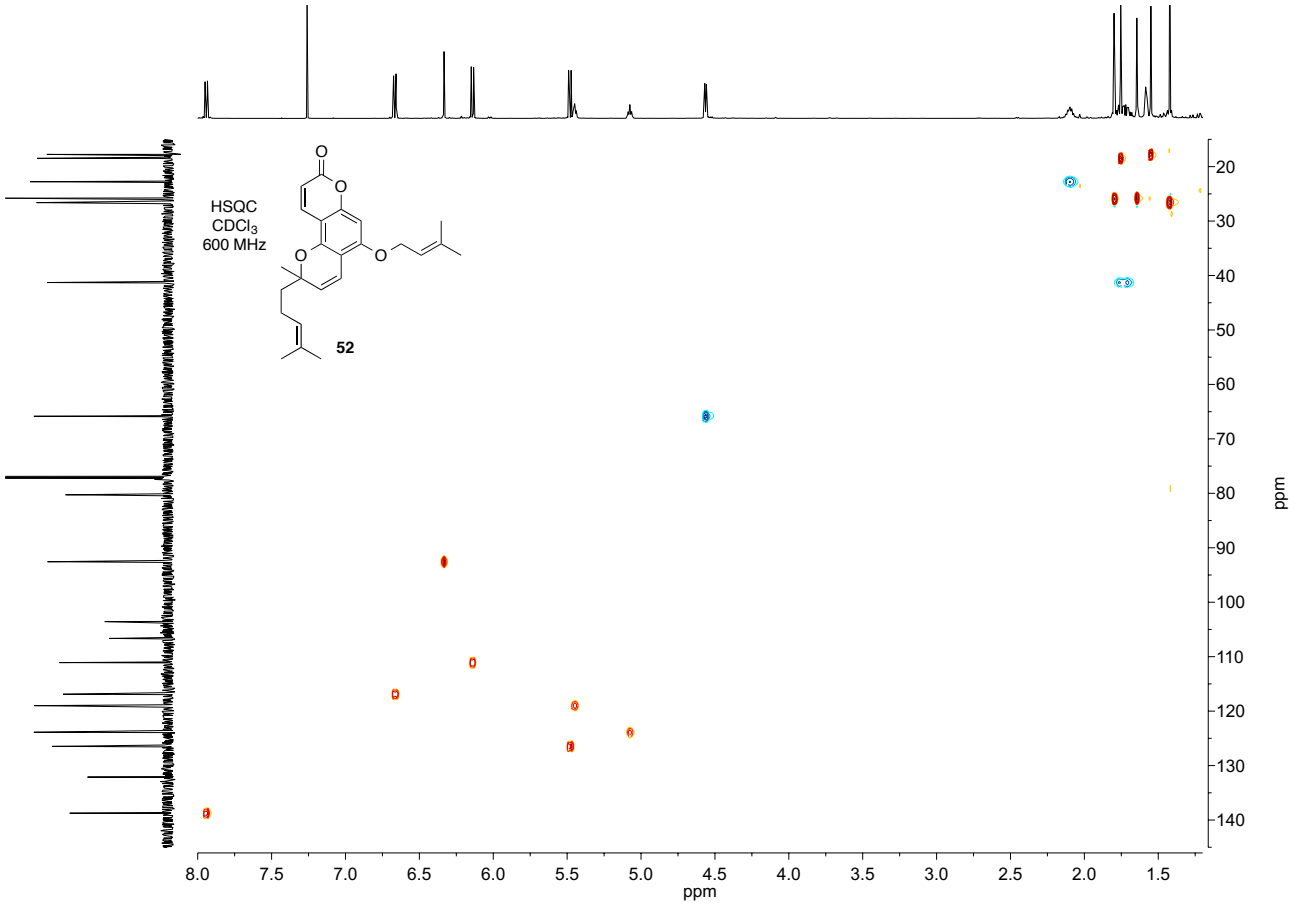

HSQC
d_5-pyridine
500 MHz
43: iso-eriobrucinol B
ppm
ppm

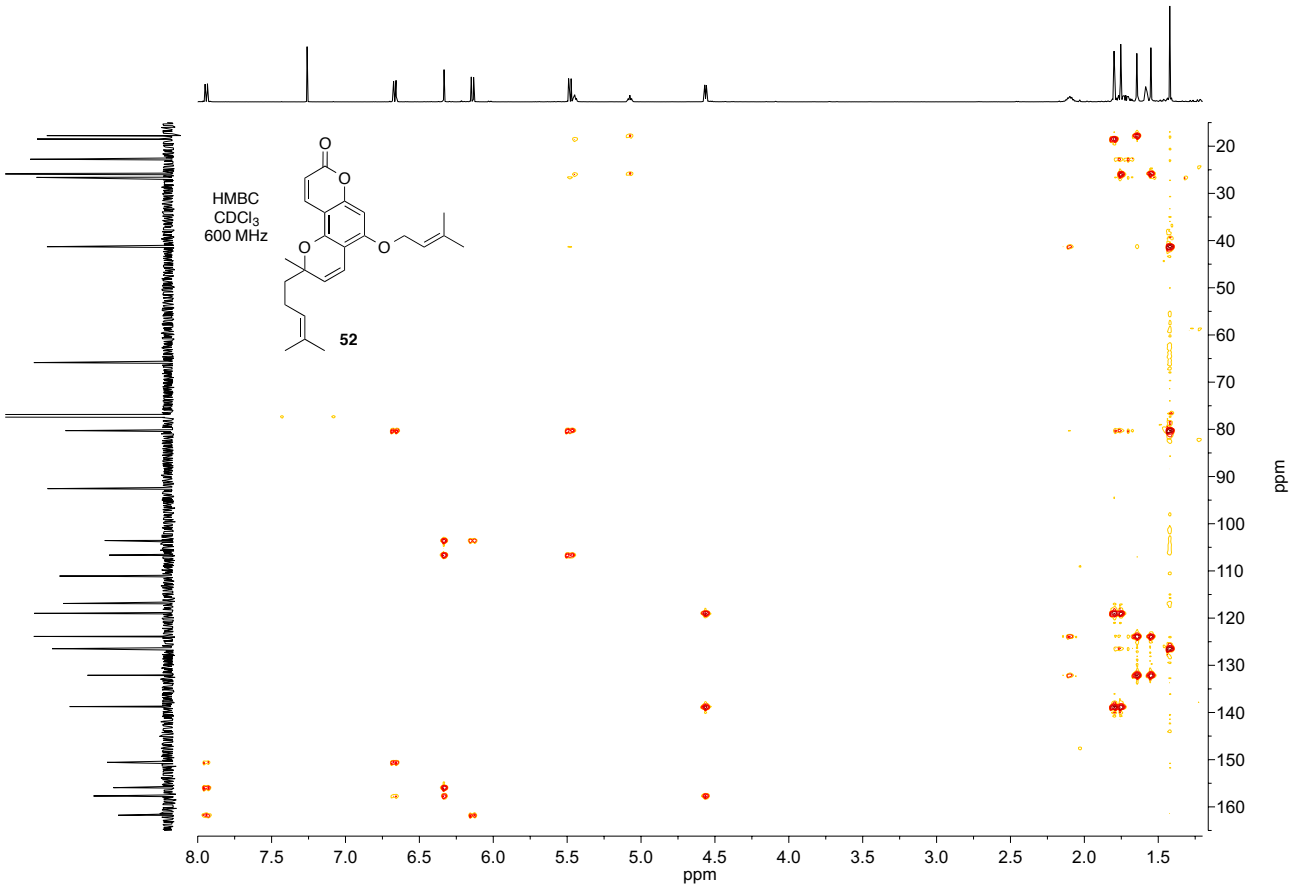

HMBC
d_5-pyridine
500 MHz
O
O
H
H
H
HO
O
43: iso-eriobrucinol B
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

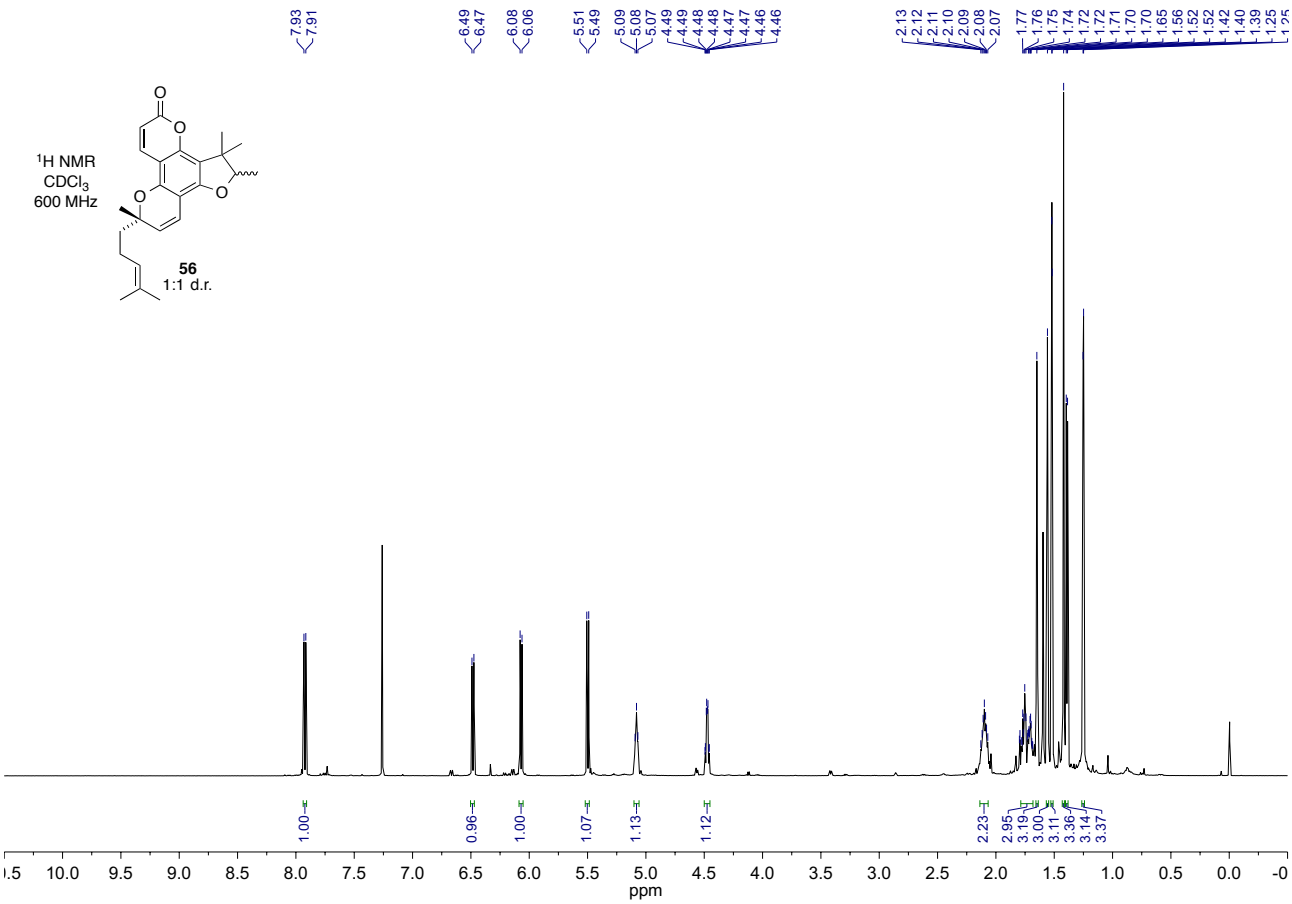

7.95
7.93
7.26
6.67
6.66
6.15
6.13
5.49
5.47
5.46
5.46
5.45
5.45
5.45
5.45
5.44
5.44
5.44
5.44
5.09
5.09
5.09
5.08
5.07
5.06
5.06
4.57
4.56
1.42
^{1}H NMR
$CDCl_3$
600 MHz
52
0.99
0.98
0.95
1.02
0.99
1.03
1.02
2.02
1.99
2.79
3.03
8.79
2.86
2.67
2.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

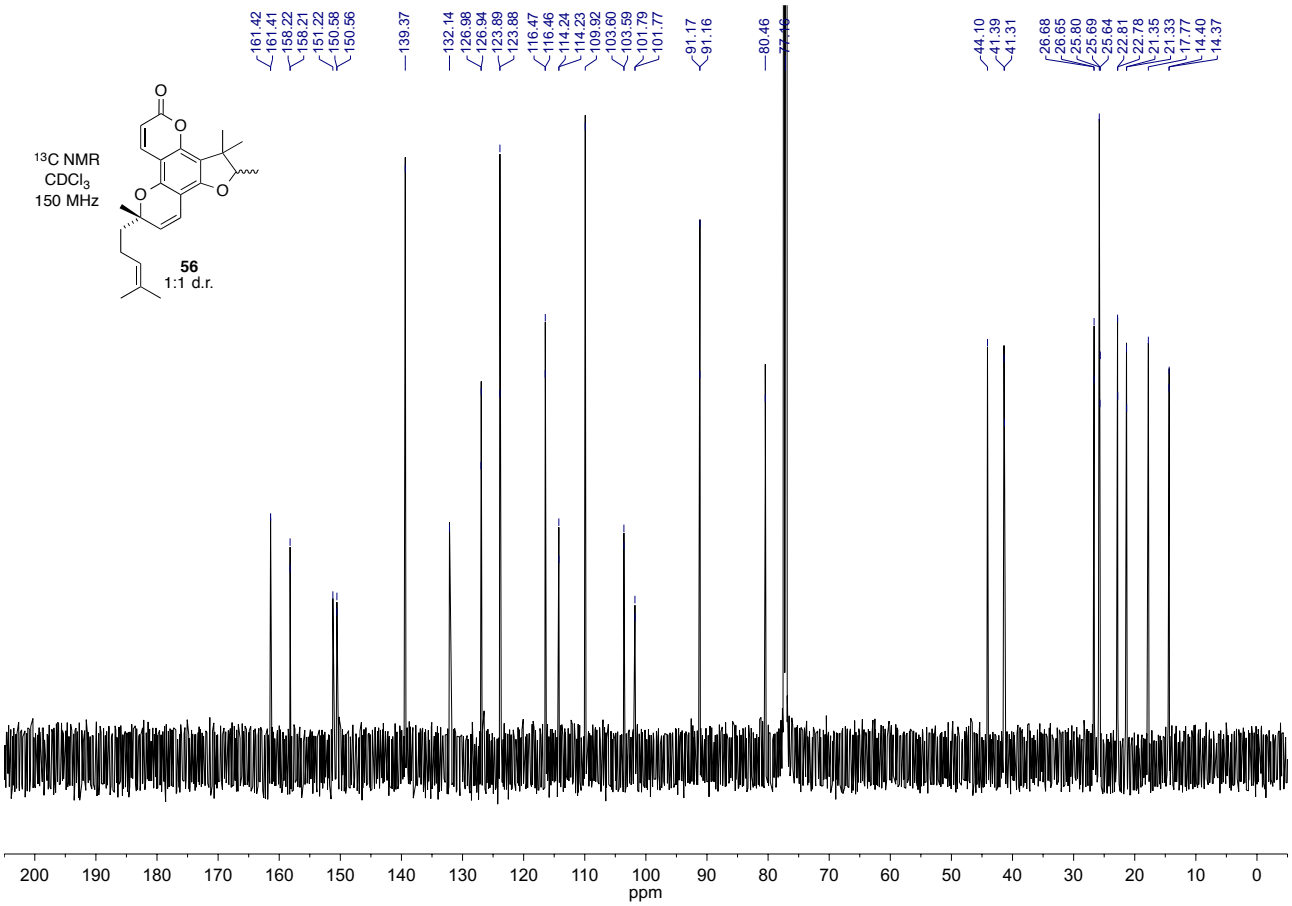

161.77
157.69
155.93
150.57
138.83
138.75
132.12
126.47
123.88
118.99
116.90
111.09
106.65
103.56
92.56
80.27
77.16
65.85
41.29
26.61
25.95
25.80
22.77
18.49
17.76
^{13}C NMR
$CDCl_3$
150 MHz
52
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

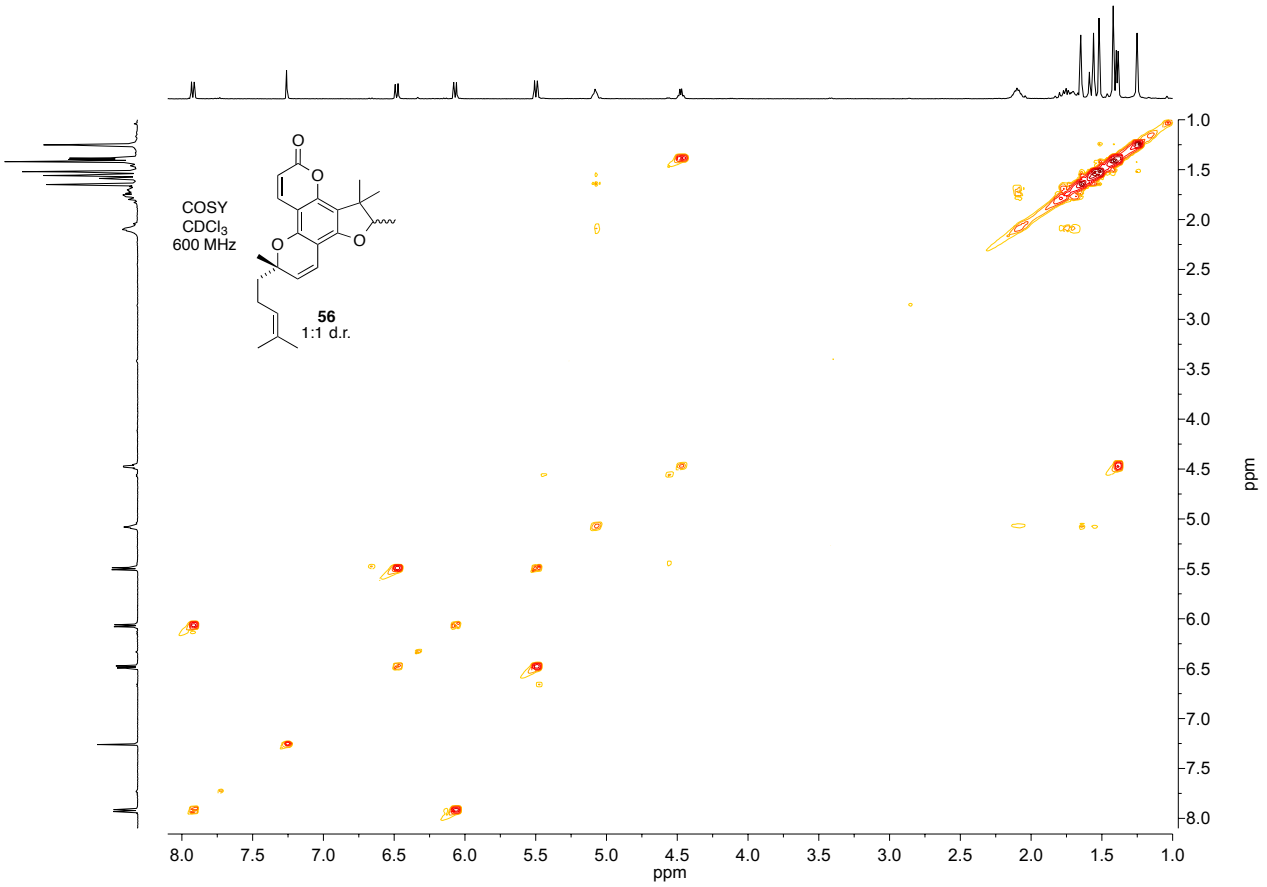

COSY
CDCl3
600 MHz
52
ppm
ppm

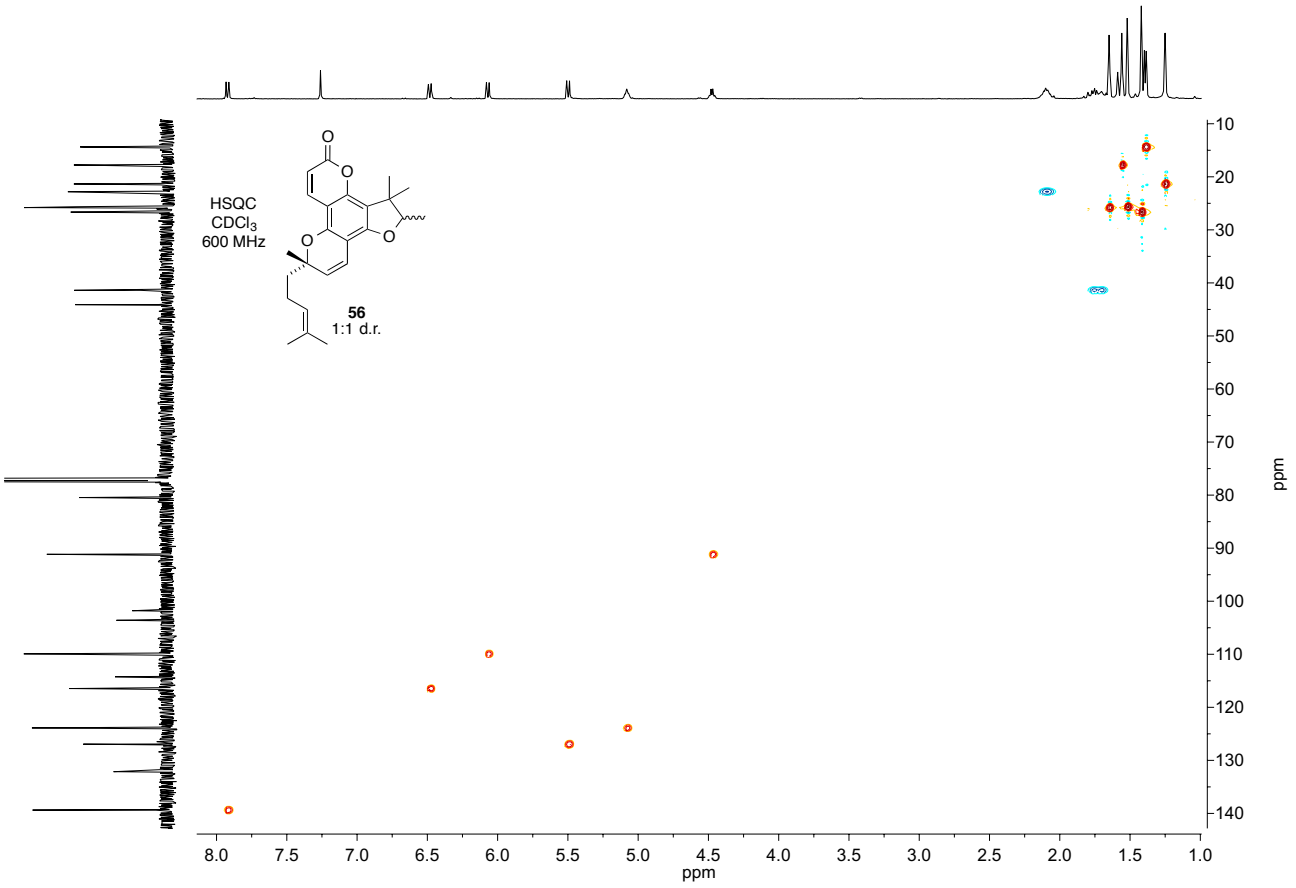

HSQC
CDCl3
600 MHz
52
ppm
ppm

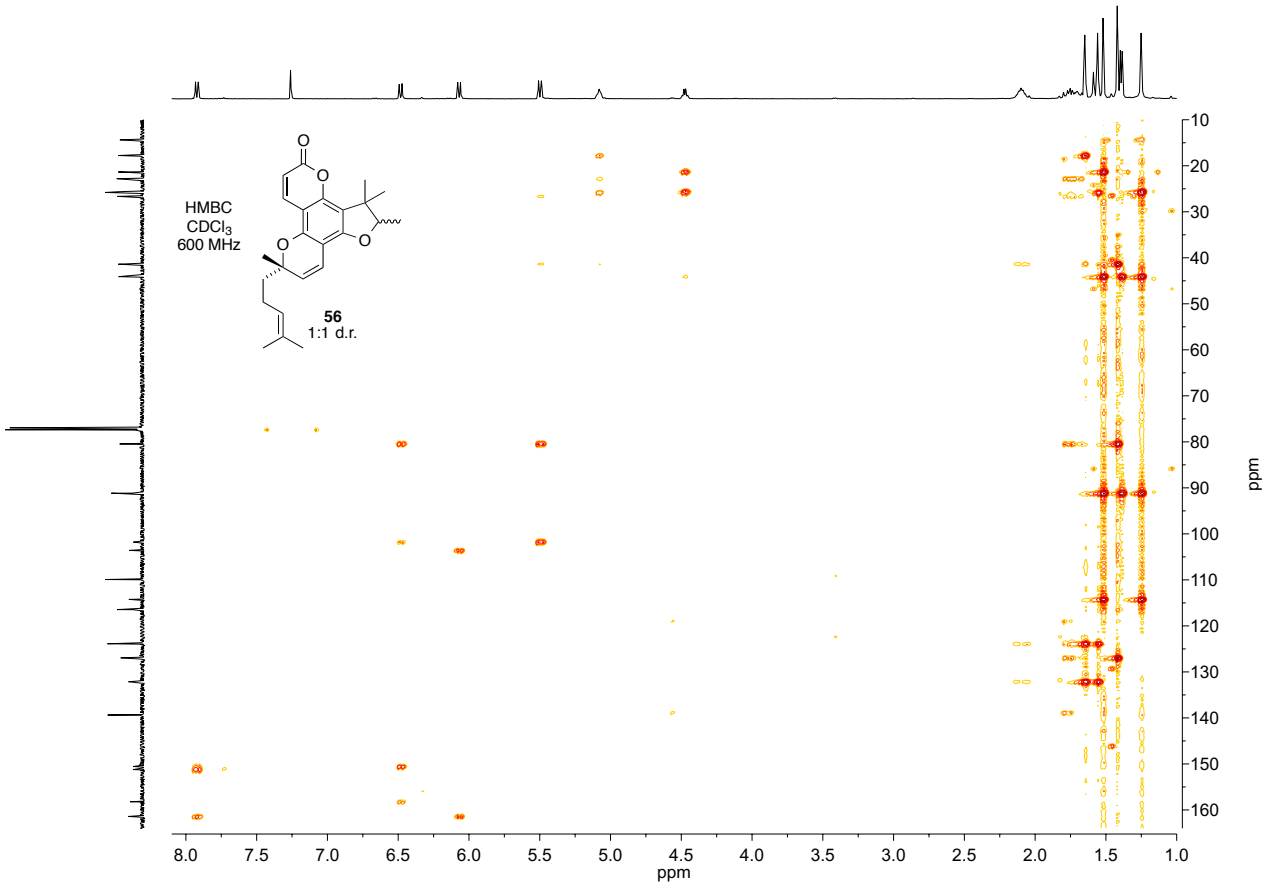

HMBC
CDCl3
600 MHz
52
ppm
ppm

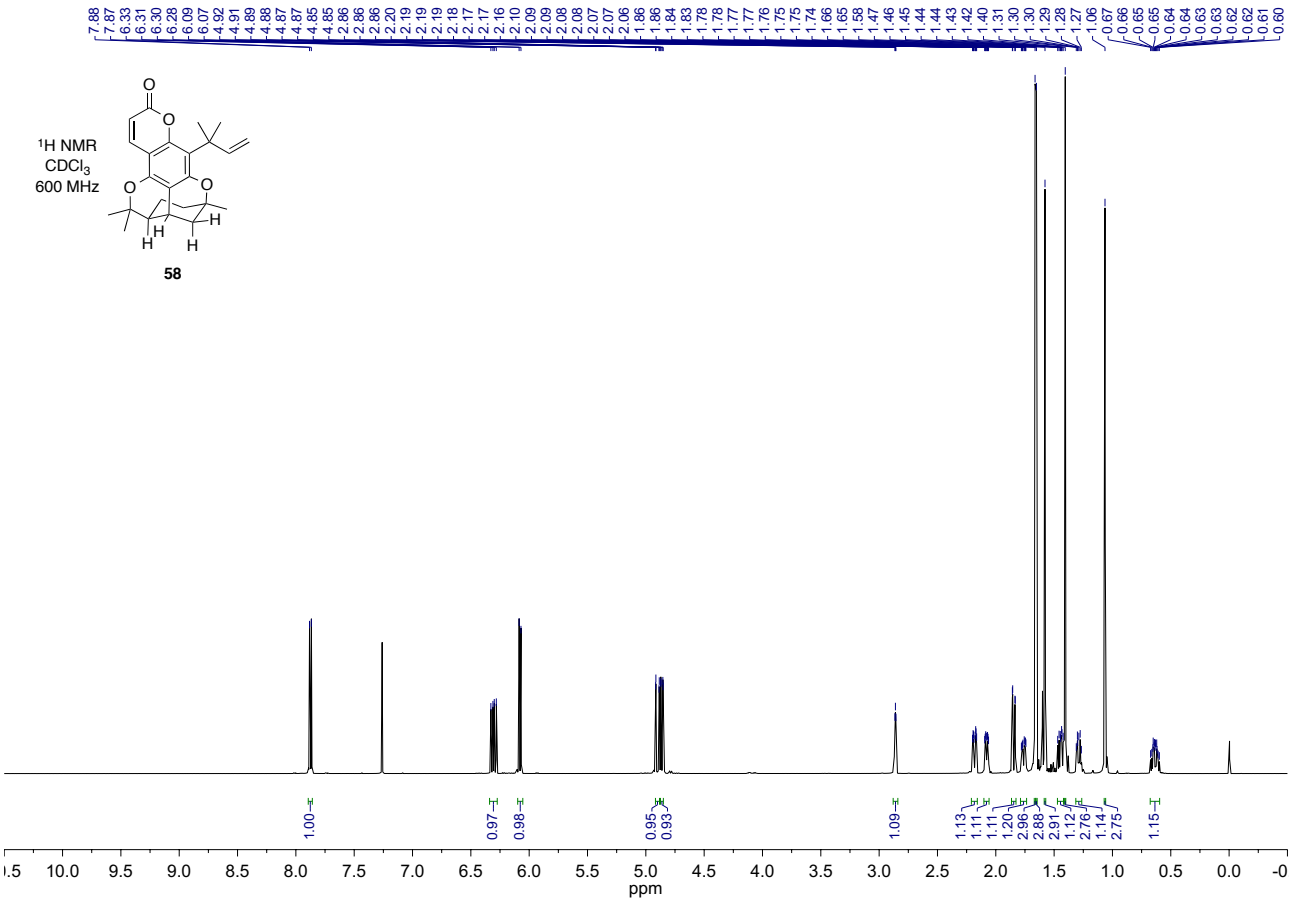

7.93
7.91
6.49
6.47
6.08
6.06
5.51
5.49
5.09
5.08
5.07
4.49
4.49
4.48
4.48
4.47
4.47
4.46
4.46
2.13
2.12
2.11
2.10
2.09
2.08
2.07
1.77
1.76
1.75
1.74
1.72
1.72
1.71
1.70
1.70
1.65
1.56
1.52
1.52
1.42
1.40
1.39
1.25
1.00
0.96
1.00
1.07
1.13
1.12
2.23
2.95
3.19
3.00
3.11
3.36
3.14
3.37
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
^{1}H NMR
$CDCl_3$
600 MHz
56
1:1 d.r.

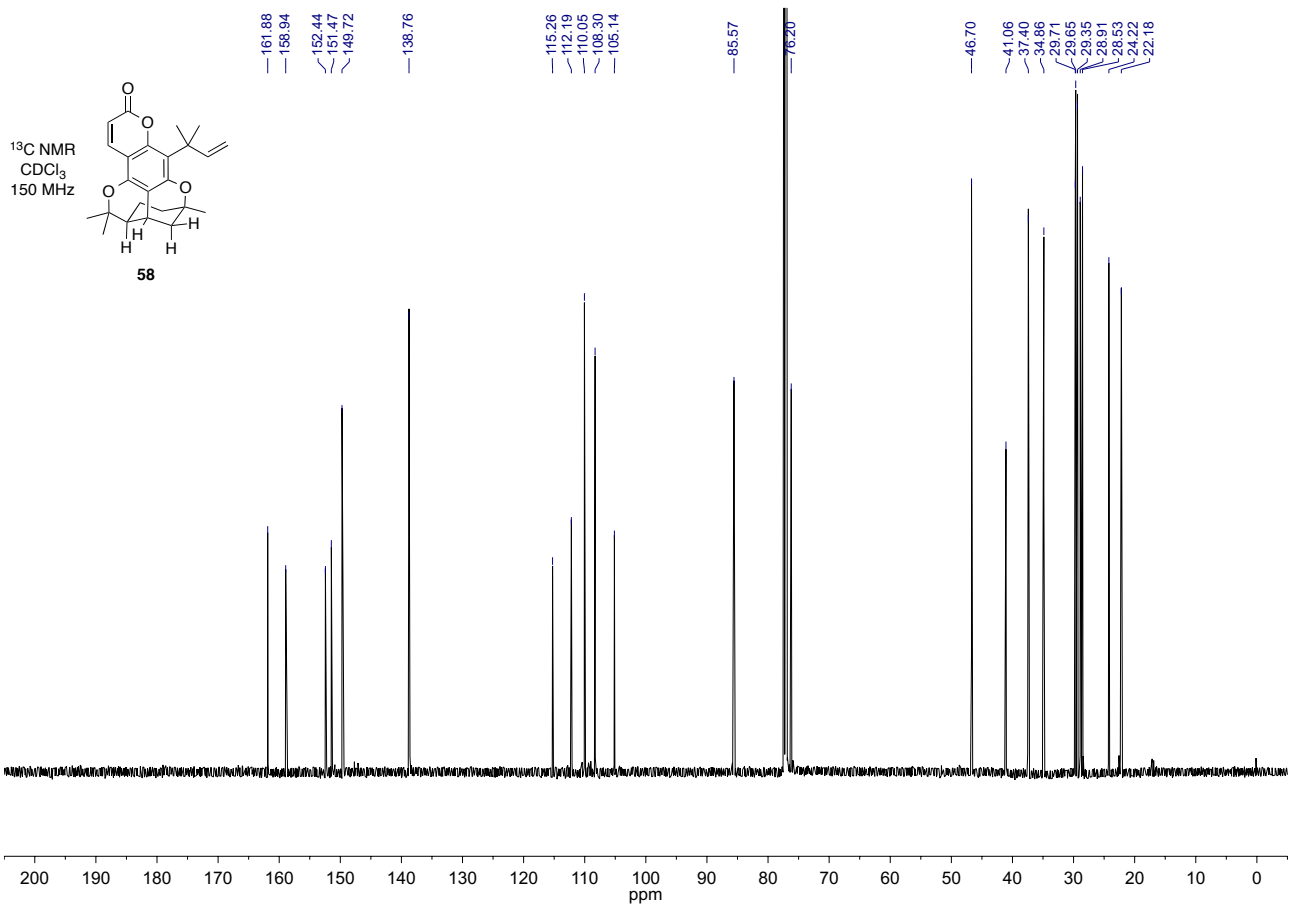

161.42
161.41
158.22
158.21
151.22
150.58
150.56
139.37
132.14
126.98
126.94
123.89
123.88
116.47
116.46
114.24
114.23
109.92
103.60
103.59
101.79
101.77
91.17
91.16
80.46
77.46
44.10
41.39
41.31
26.68
26.65
25.80
25.69
25.64
22.81
22.78
21.35
21.33
17.77
14.40
14.37
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
^{13}C NMR
$CDCl_3$
150 MHz
56
1:1 d.r.

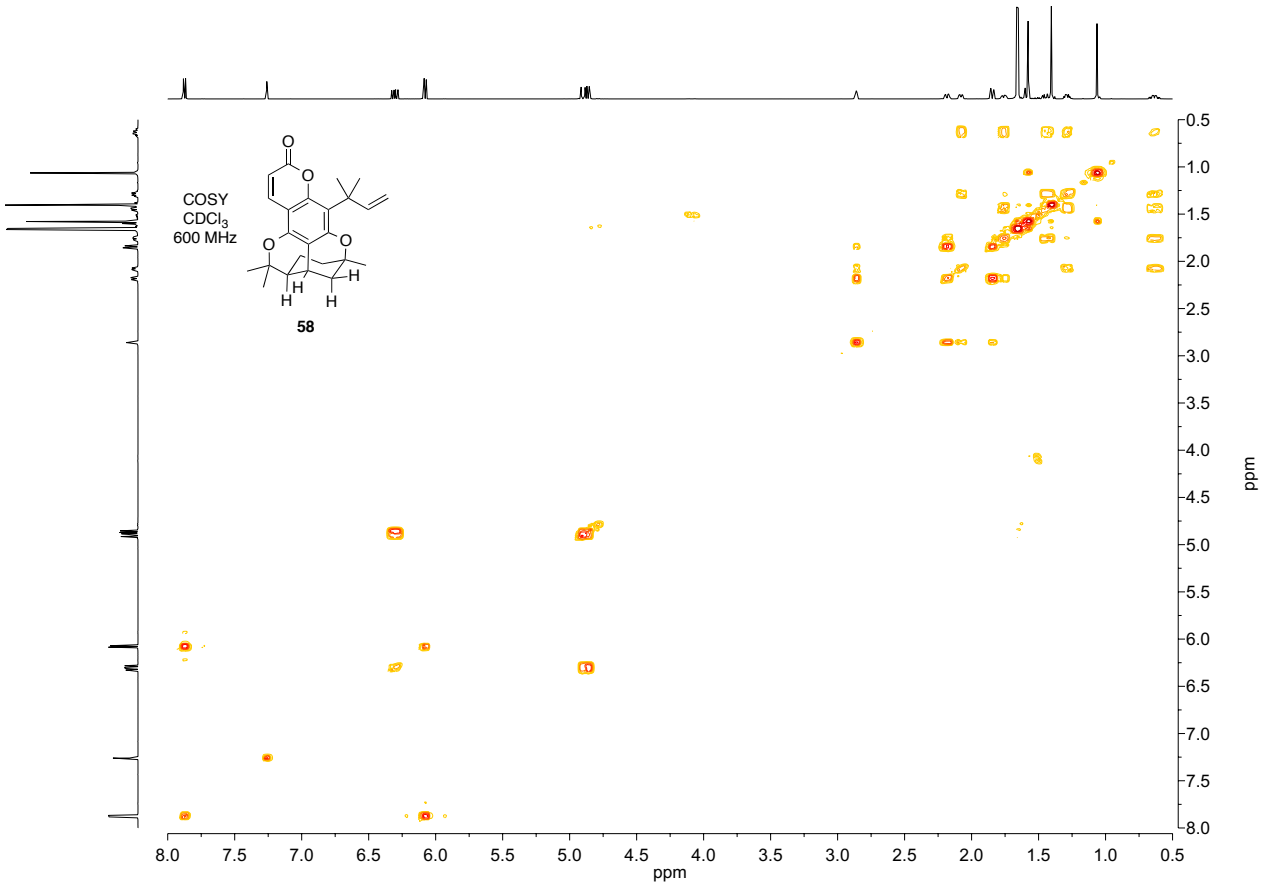

COSY
CDCl3
600 MHz
56
1:1 d.r.
ppm

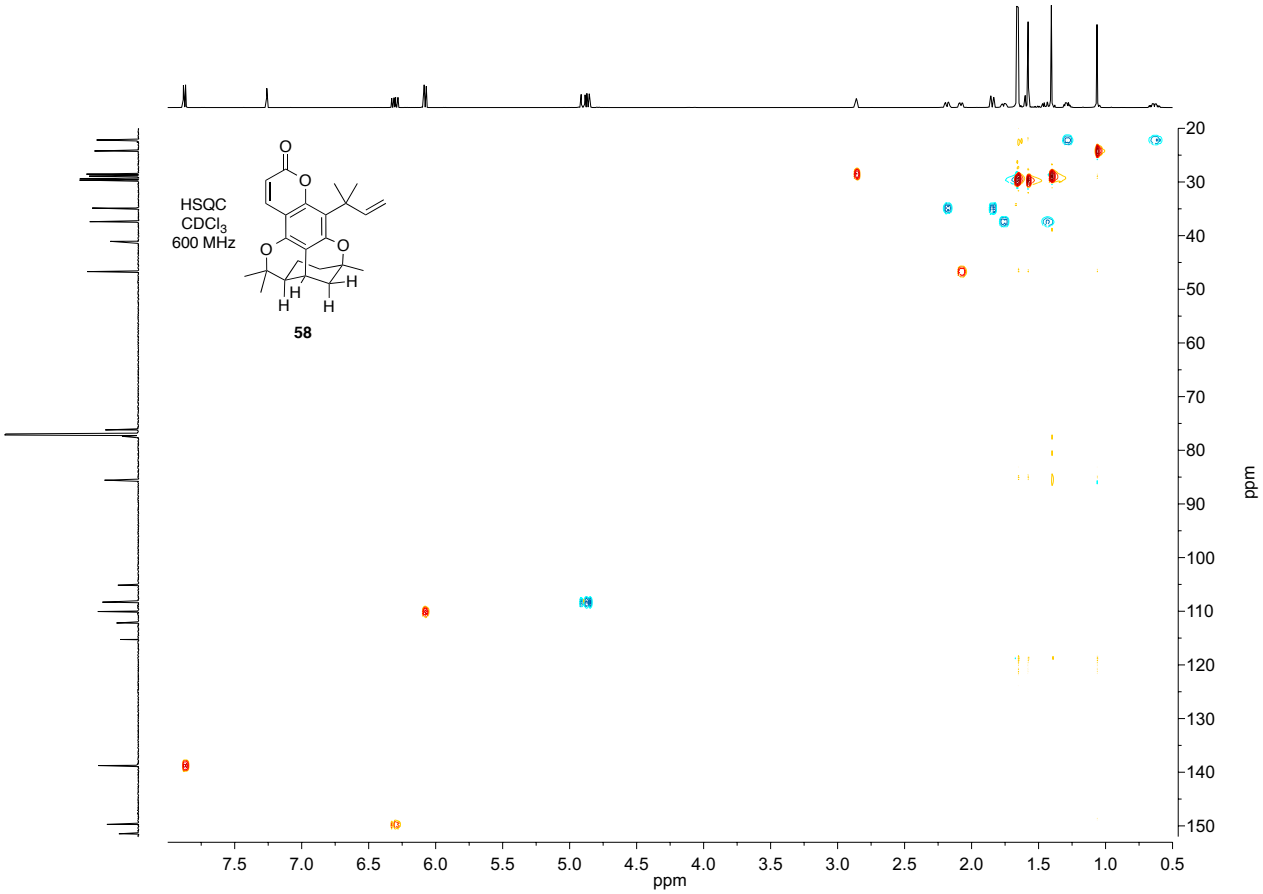

HSQC
CDCl3
600 MHz
56
1:1 d.r.
ppm

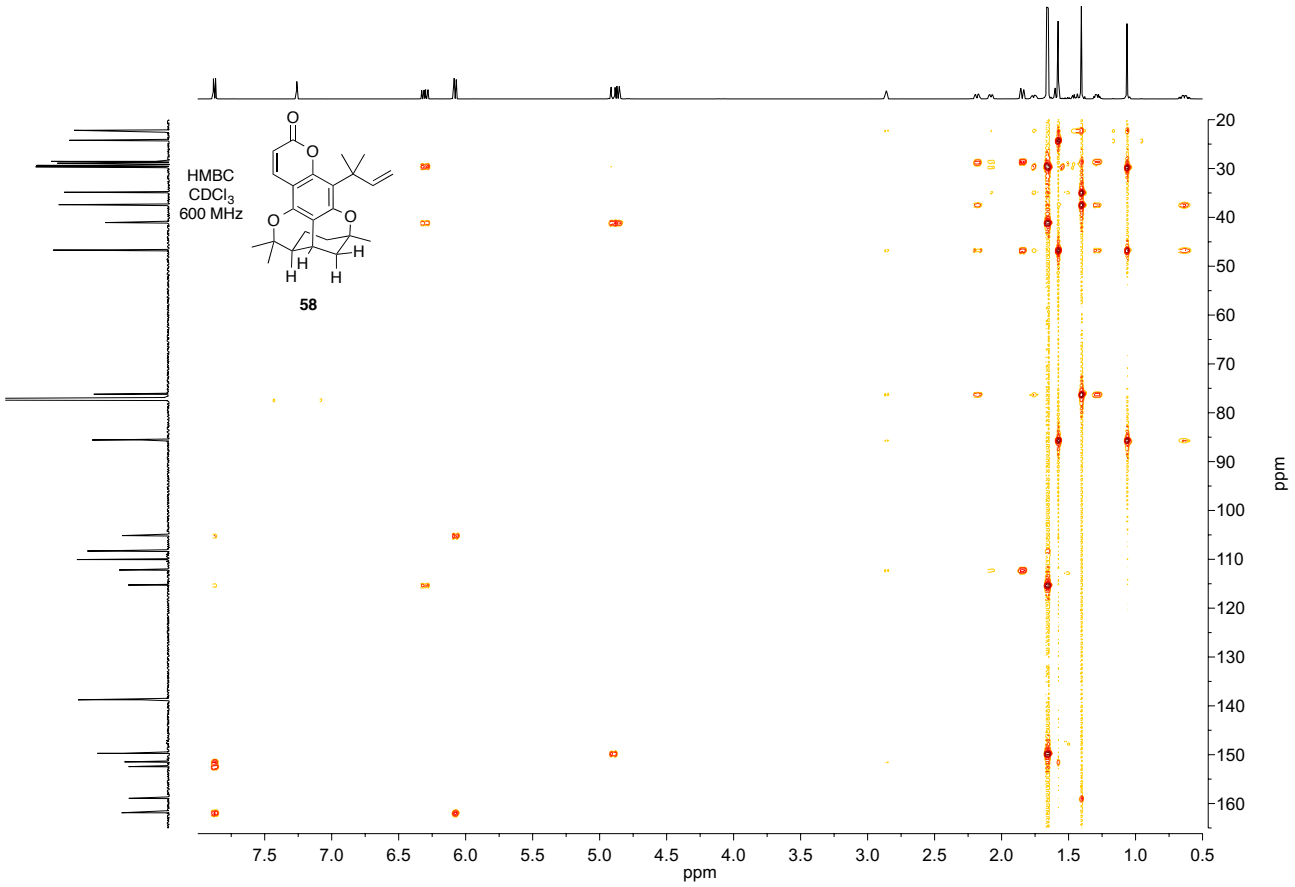

HMBC
CDCl3
600 MHz
56
1:1 d.r.
ppm
ppm

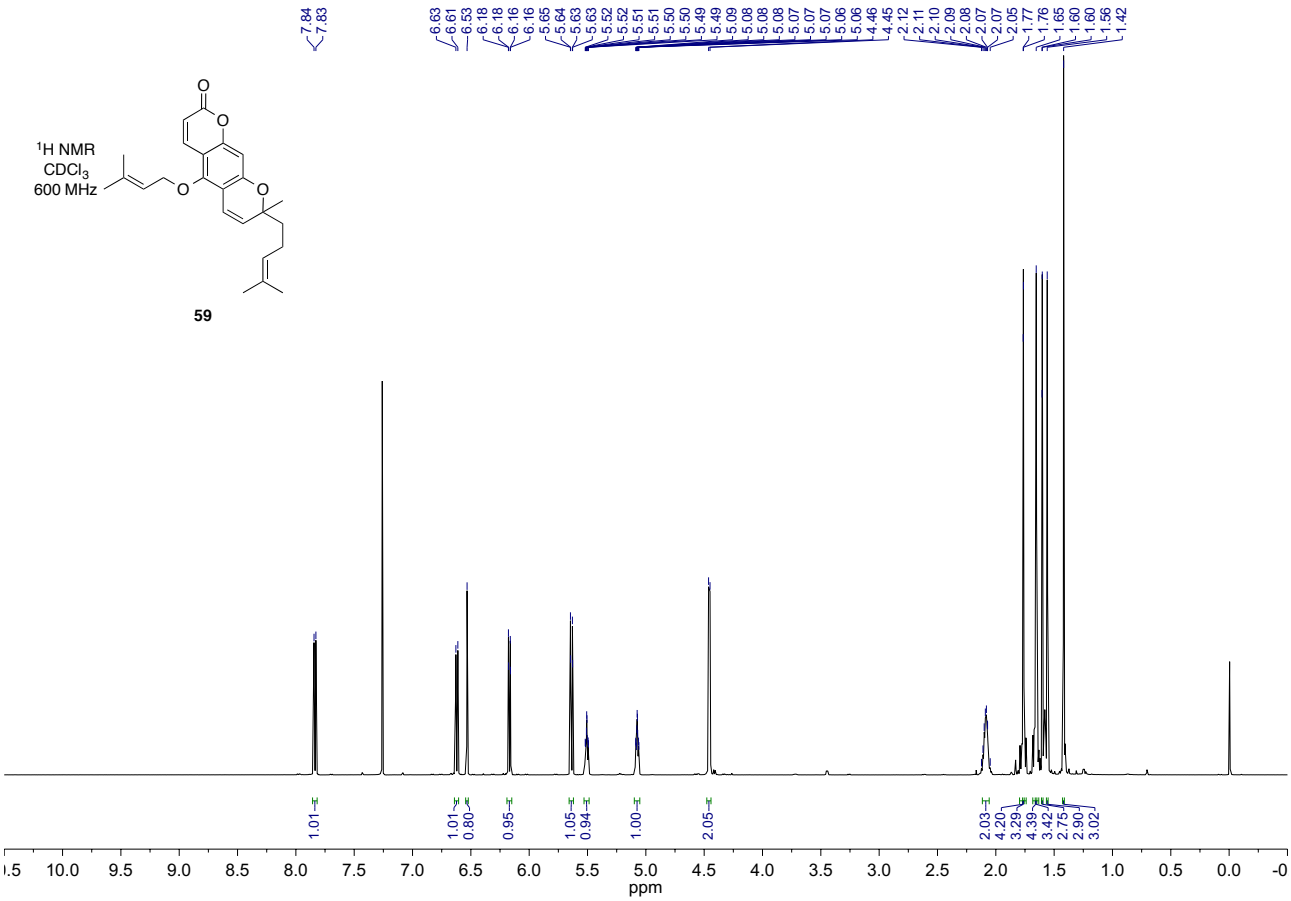

7.88 7.87 6.33 6.31 6.30 6.28 6.09 6.07 4.92 4.91 4.89 4.88 4.87 4.87 4.85 4.85 2.86 2.86 2.86 2.20 2.19 2.19 2.19 2.18 2.17 2.17 2.16 2.10 2.09 2.09 2.08 2.08 2.08 2.07 2.07 2.06 1.86 1.86 1.84 1.83 1.78 1.78 1.77 1.77 1.76 1.75 1.75 1.74 1.66 1.65 1.58 1.47 1.46 1.45 1.44 1.44 1.43 1.42 1.40 1.31 1.30 1.30 1.29 1.28 1.27 1.06 0.67 0.66 0.65 0.65 0.64 0.64 0.63 0.63 0.62 0.62 0.61 0.60
^{1}H NMR
$CDCl_3$
600 MHz
58
1.00
0.97
0.98
0.95
0.93
1.09
1.13
1.11
1.11
1.20
2.96
2.88
2.91
1.12
2.76
1.14
2.75
1.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

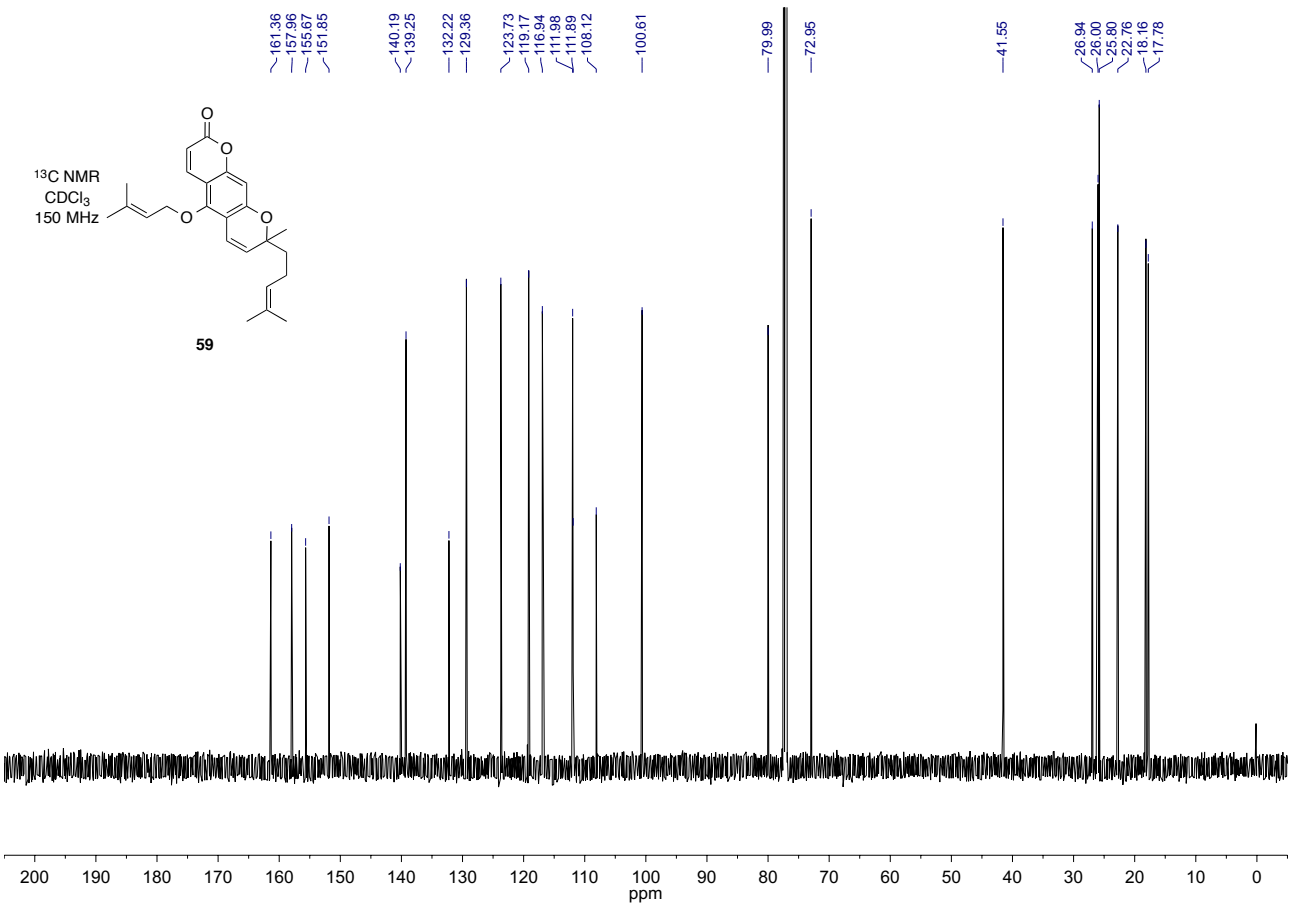

161.88
158.94
152.44
151.47
149.72
138.76
115.26
112.19
110.05
108.30
105.14
85.57
76.20
46.70
41.06
37.40
34.86
29.71
29.65
29.35
28.91
28.53
24.22
22.18
^{13}C NMR
$CDCl_3$
150 MHz
58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


COSY
CDCl3
600 MHz
58
ppm
ppm


HSQC
CDCl3
600 MHz
58
ppm
ppm


HMBC
CDCl3
600 MHz
58
ppm
ppm


^{1}H NMR
$CDCl_3$
600 MHz
59
ppm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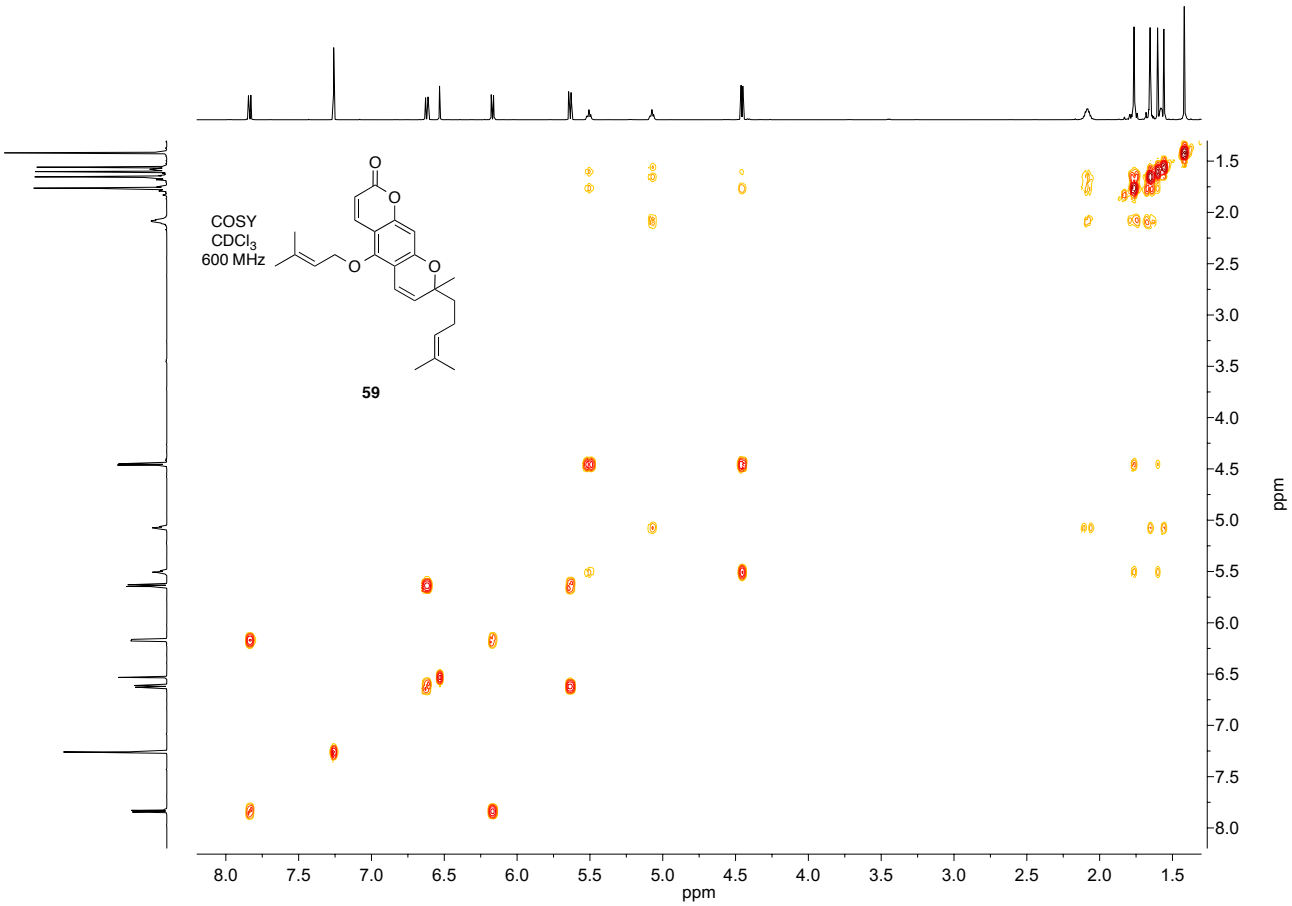
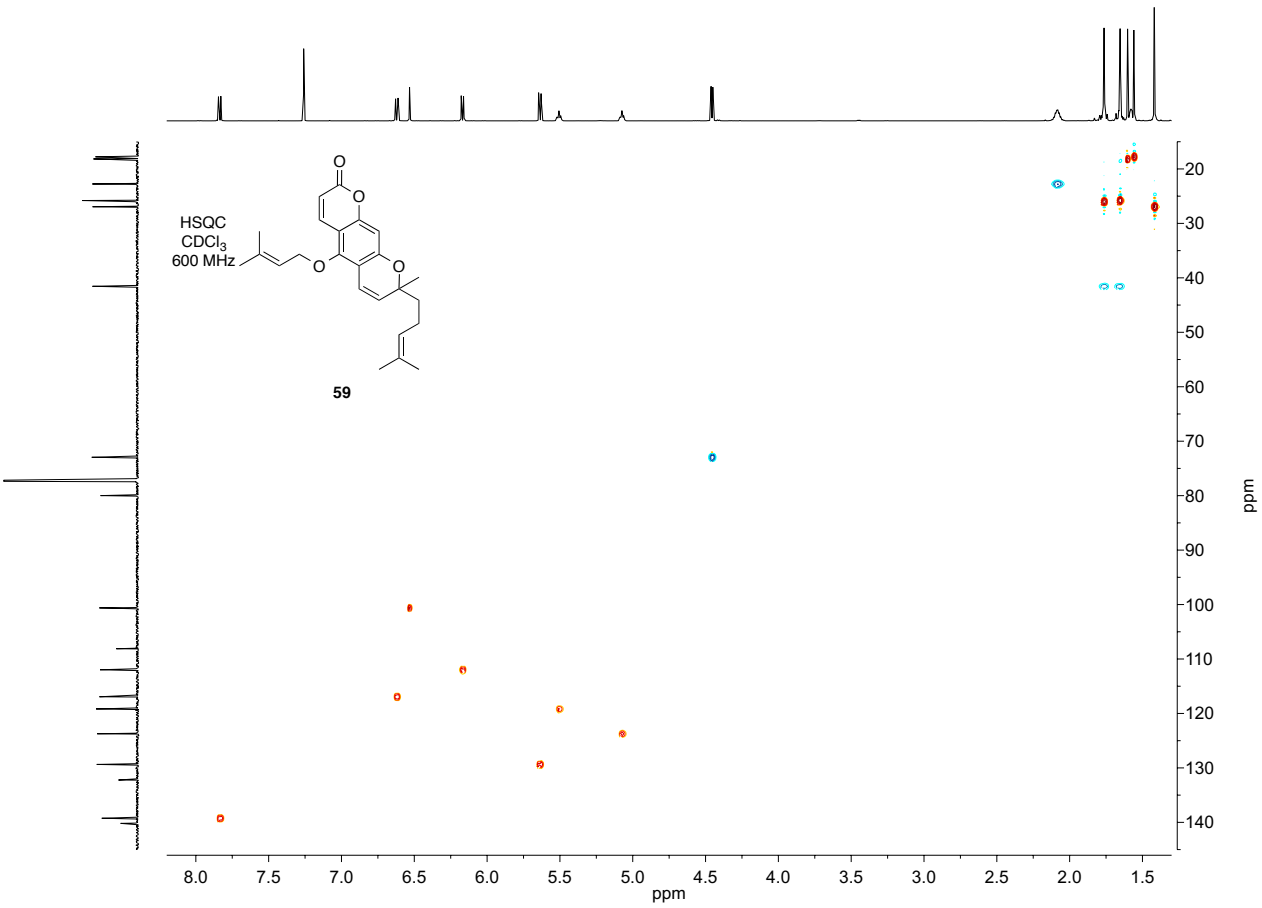
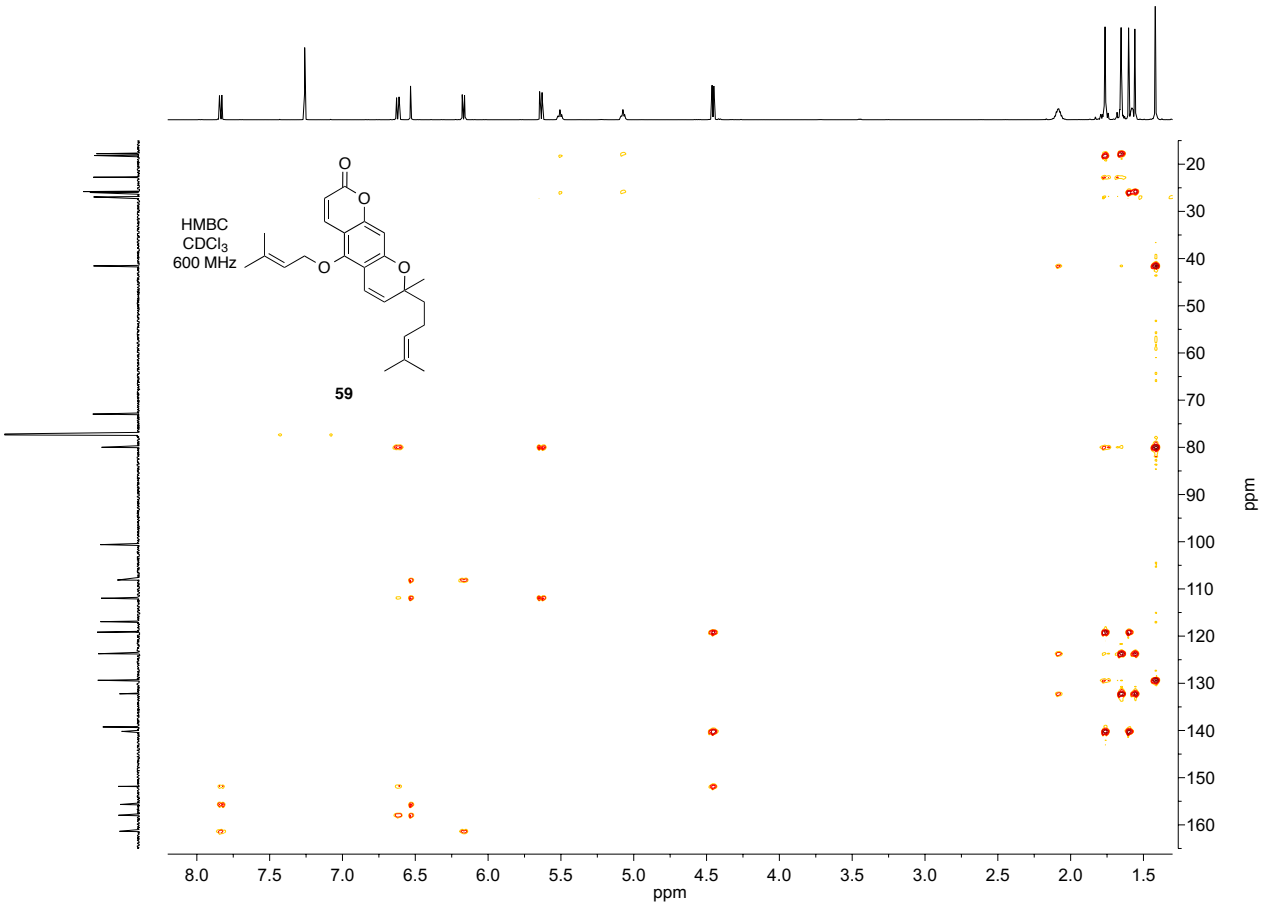
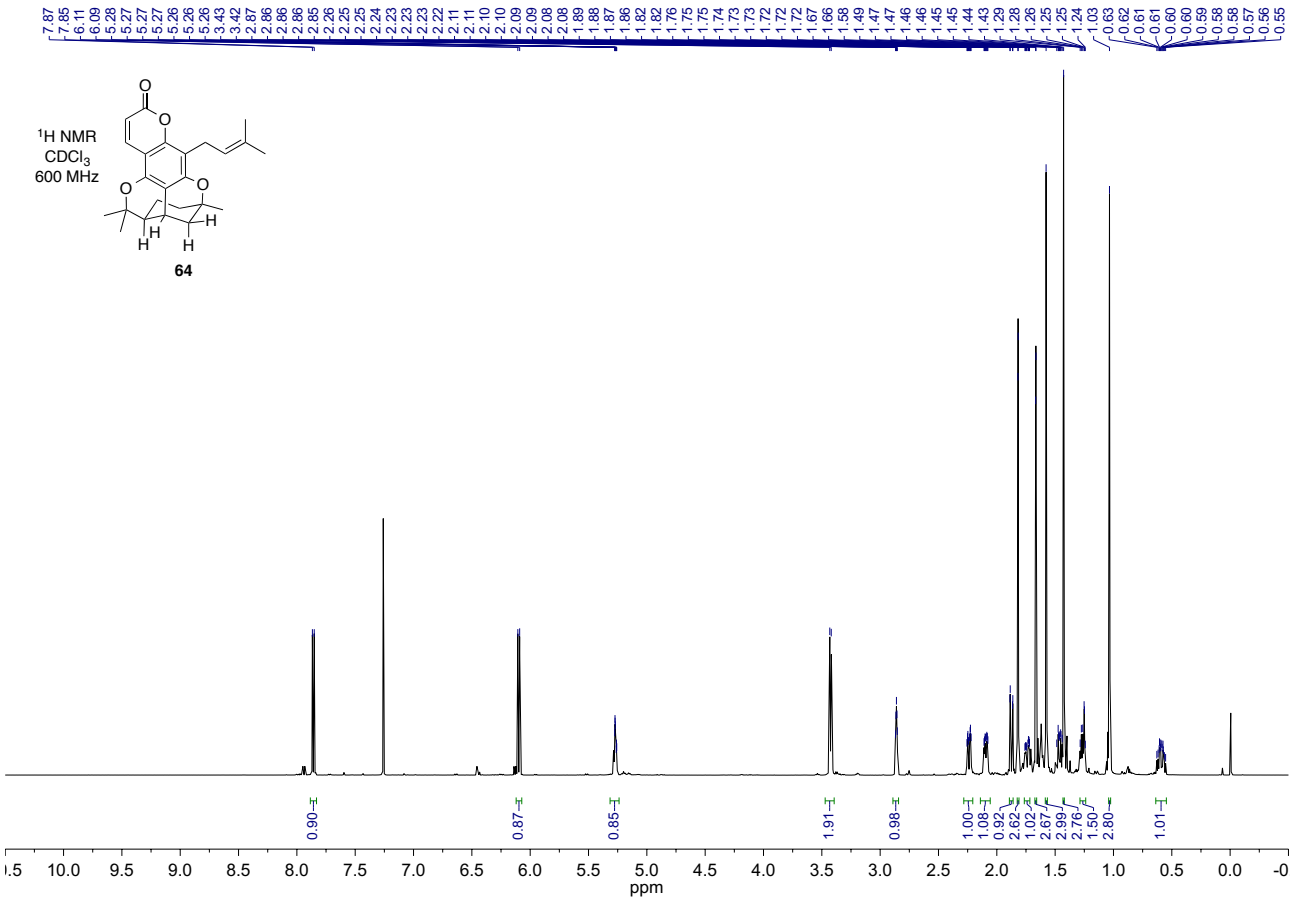
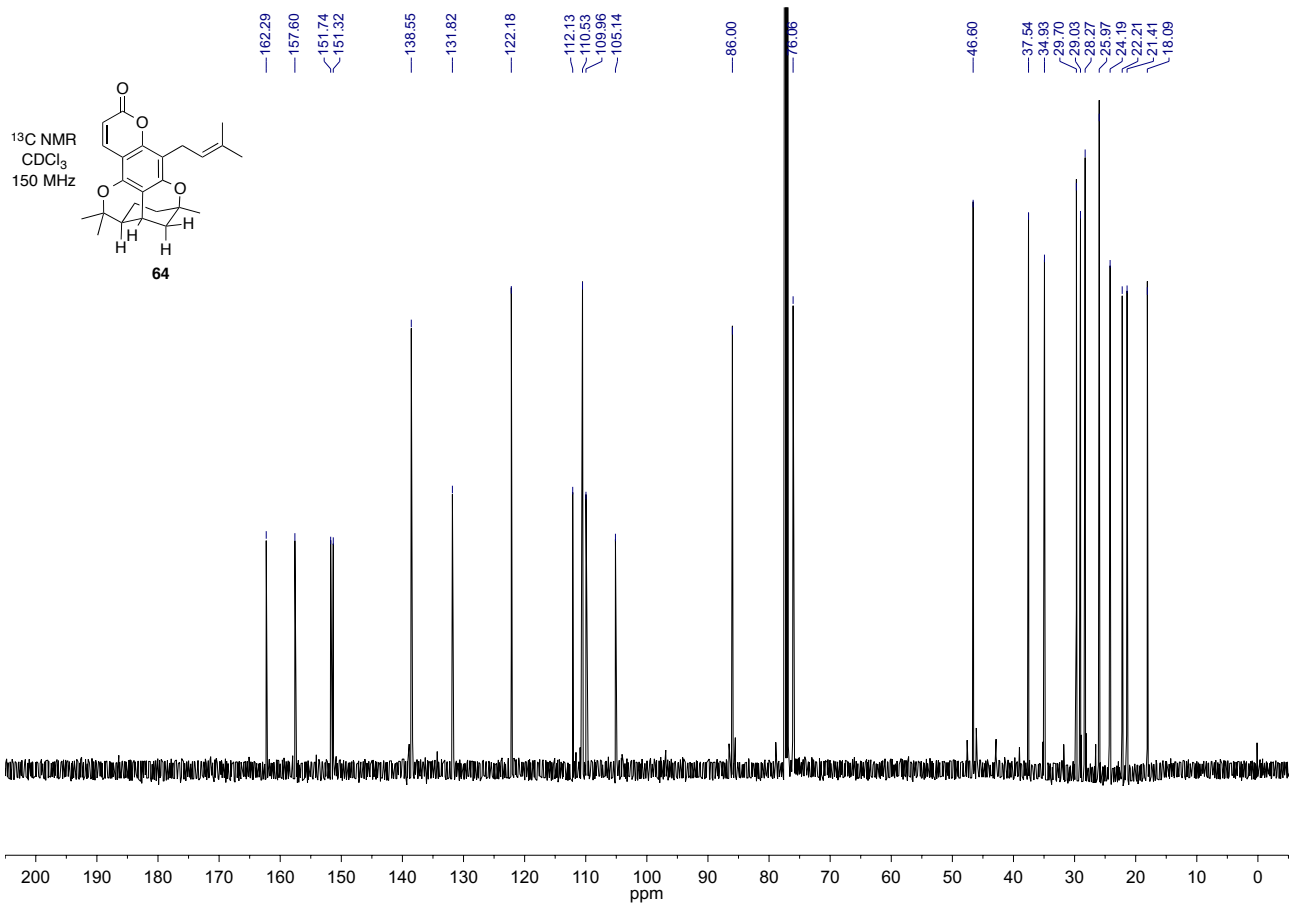
$CDCl_3$
150 MHz
59
ppm

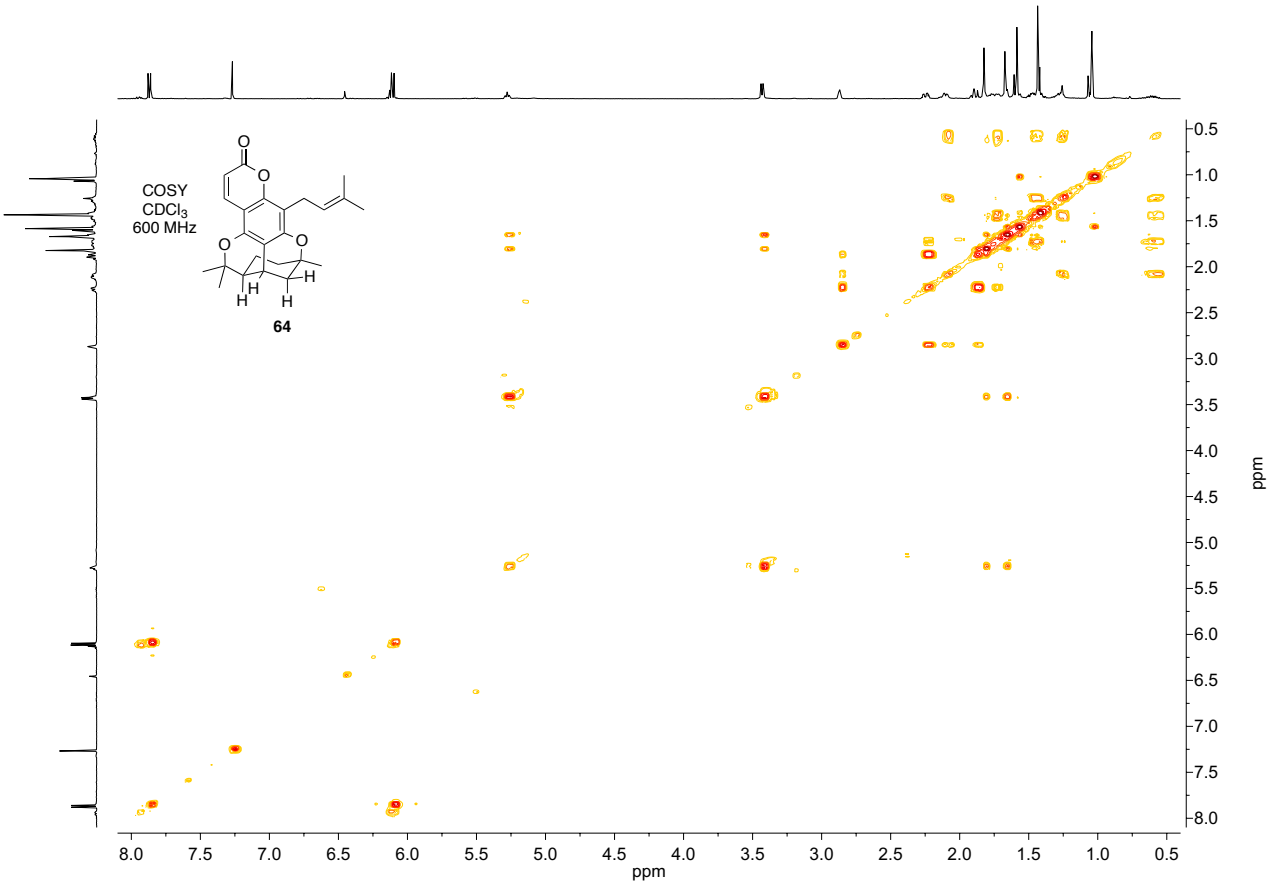

COSY
CDCl3
600 MHz
59
ppm
ppm


HSQC
CDCl3
600 MHz
59
ppm
ppm


HMBC
CDCl3
600 MHz
59
ppm
ppm


^{1}H NMR
$CDCl_3$
600 MHz
64
ppm


^{13}C NMR
$CDCl_3$
150 MHz
64
ppm


COSY
CDCl3
600 MHz
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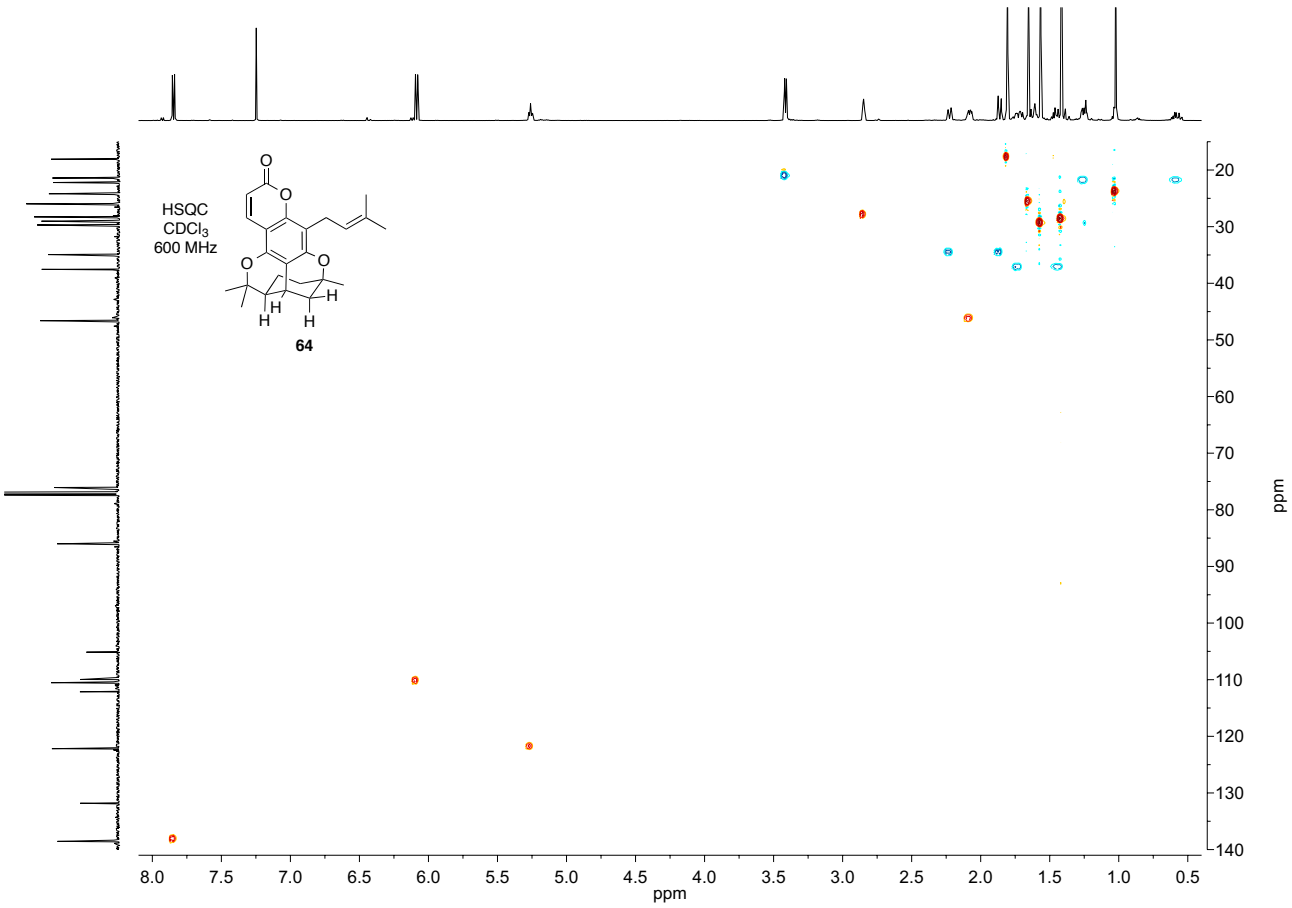
ppm
ppm


HSQC
CDCl3
600 MHz
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ppm
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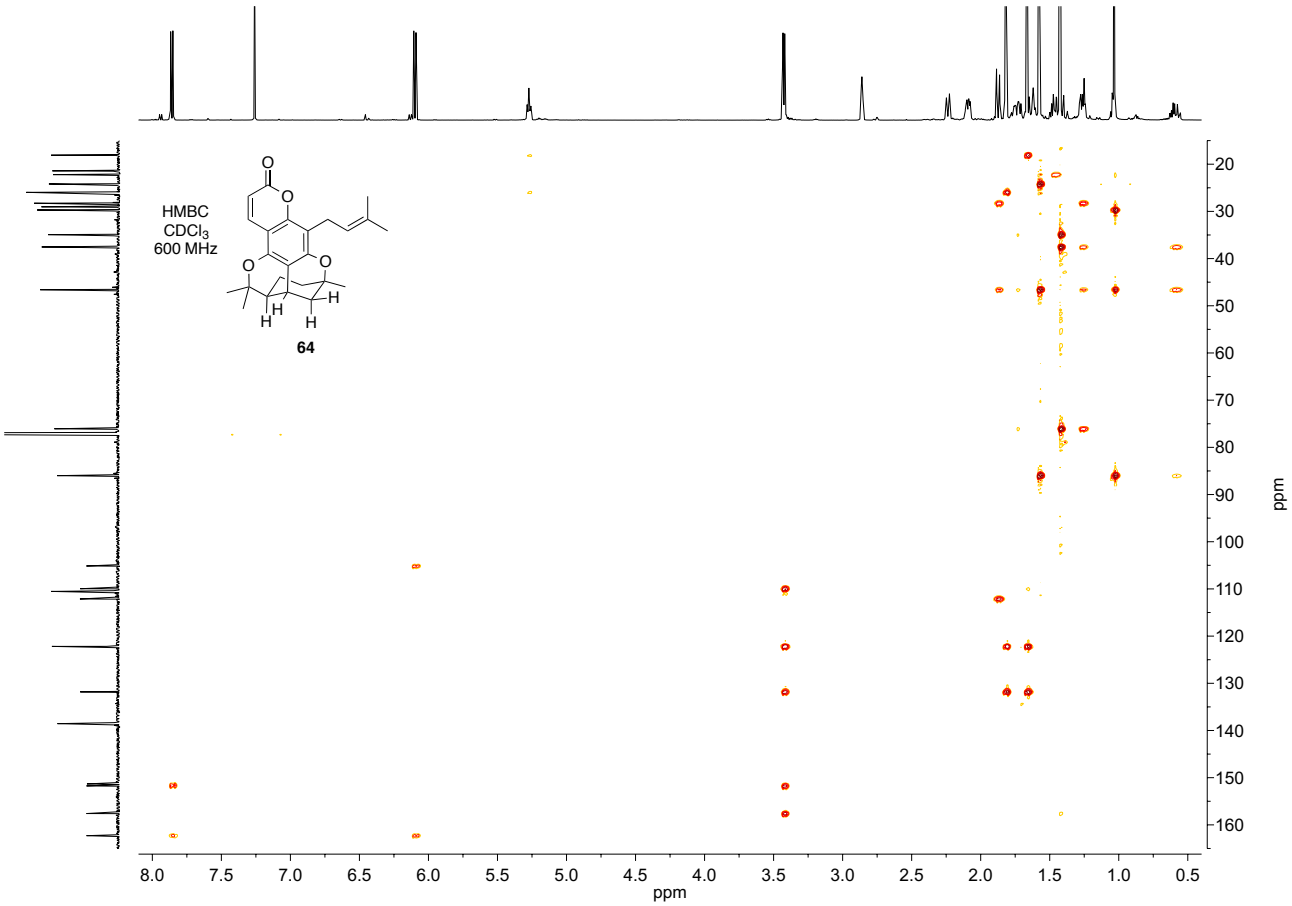
HMBC
CDCl3
600 MHz
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ppm
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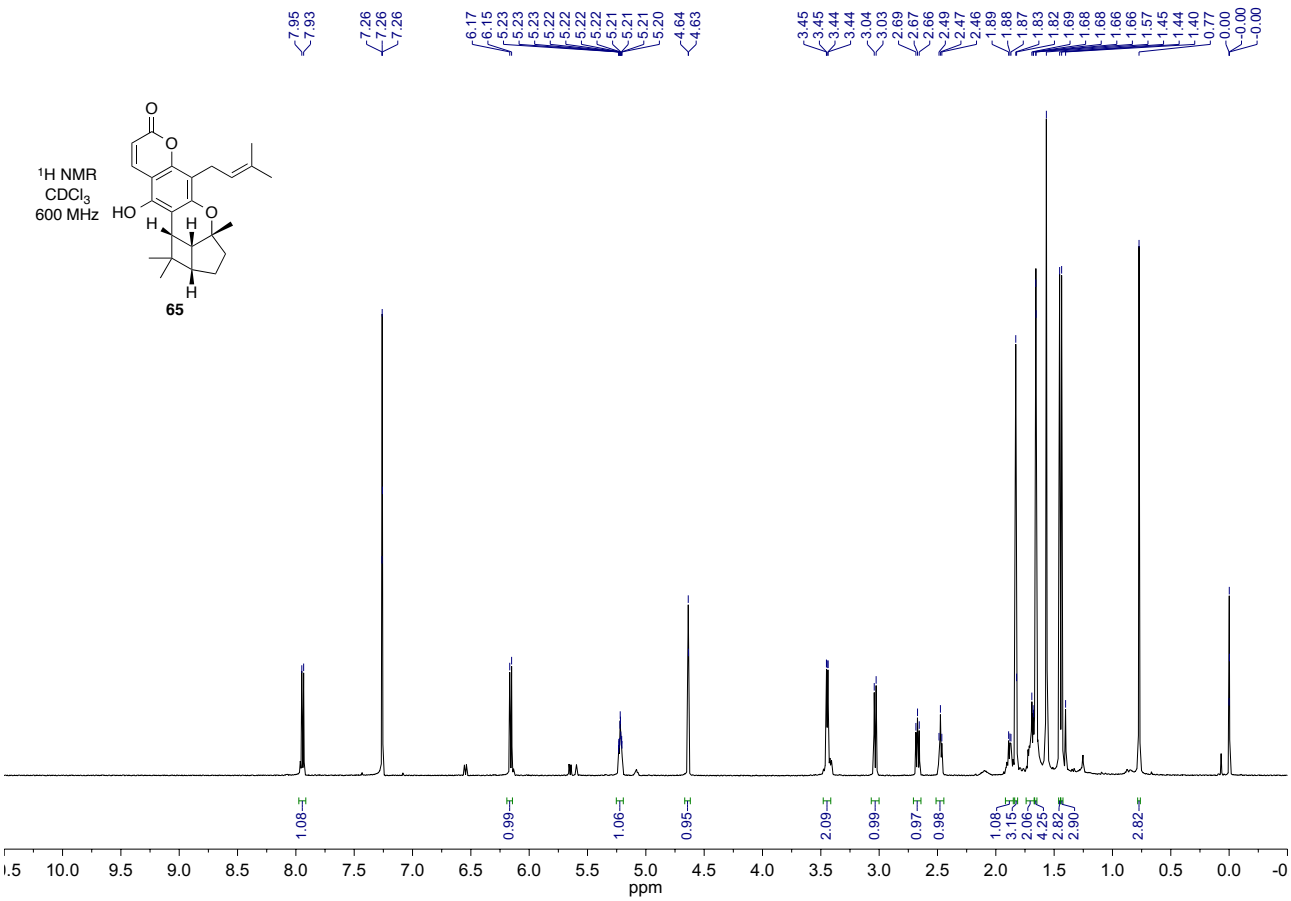
^{1}H NMR
$CDCl_3$
600 MHz
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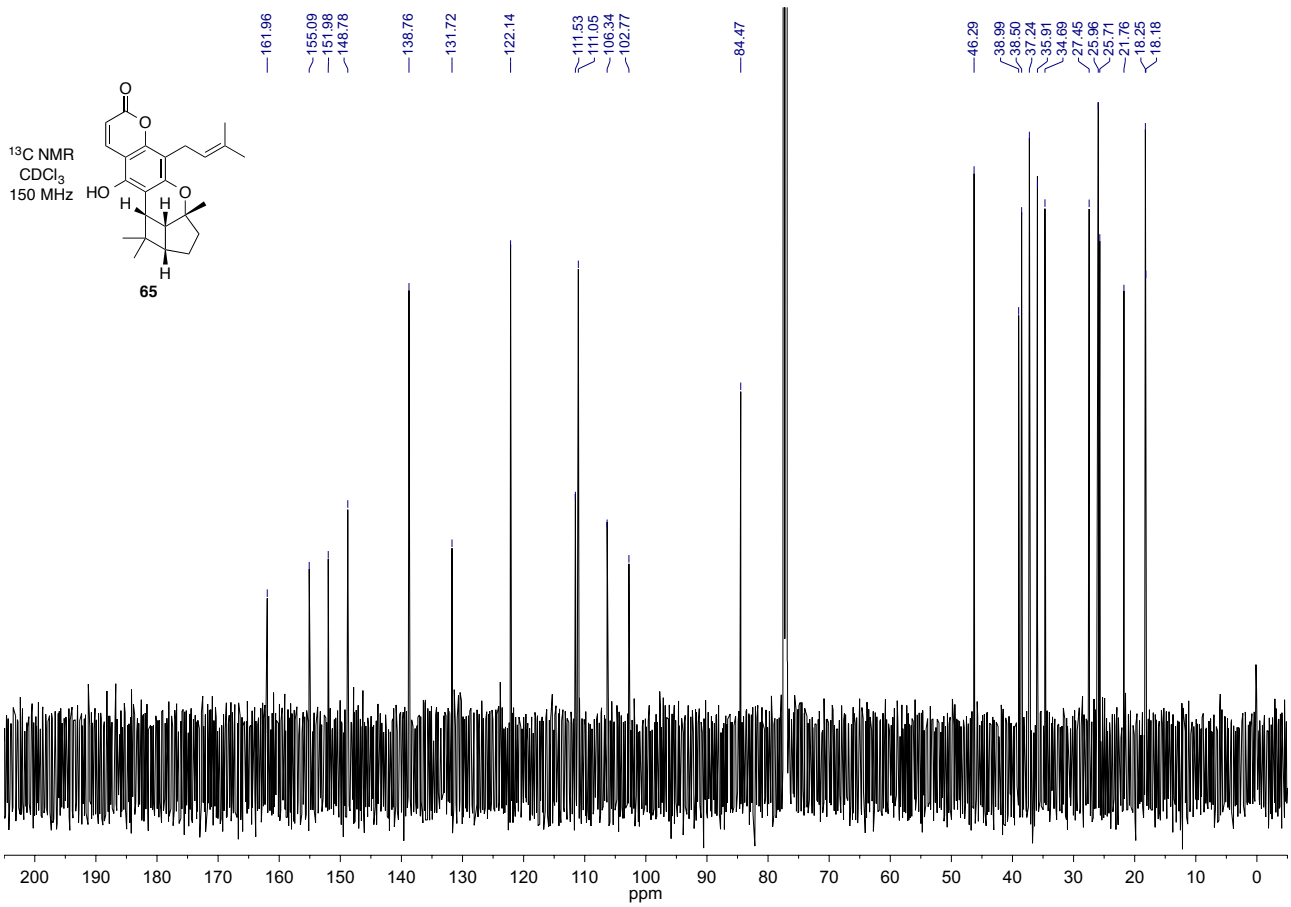
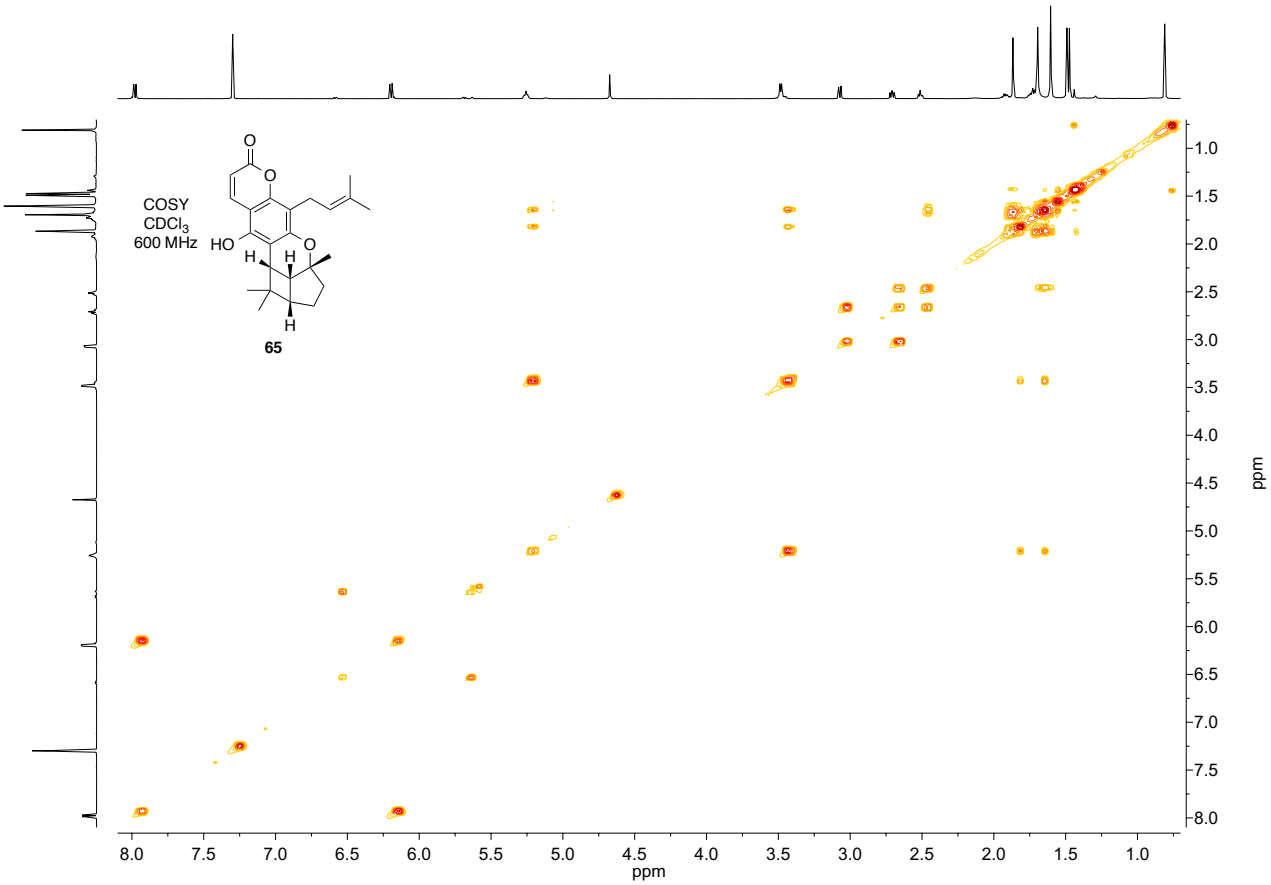
ppm


^{13}C NMR
$CDCl_3$
150 MHz
65
ppm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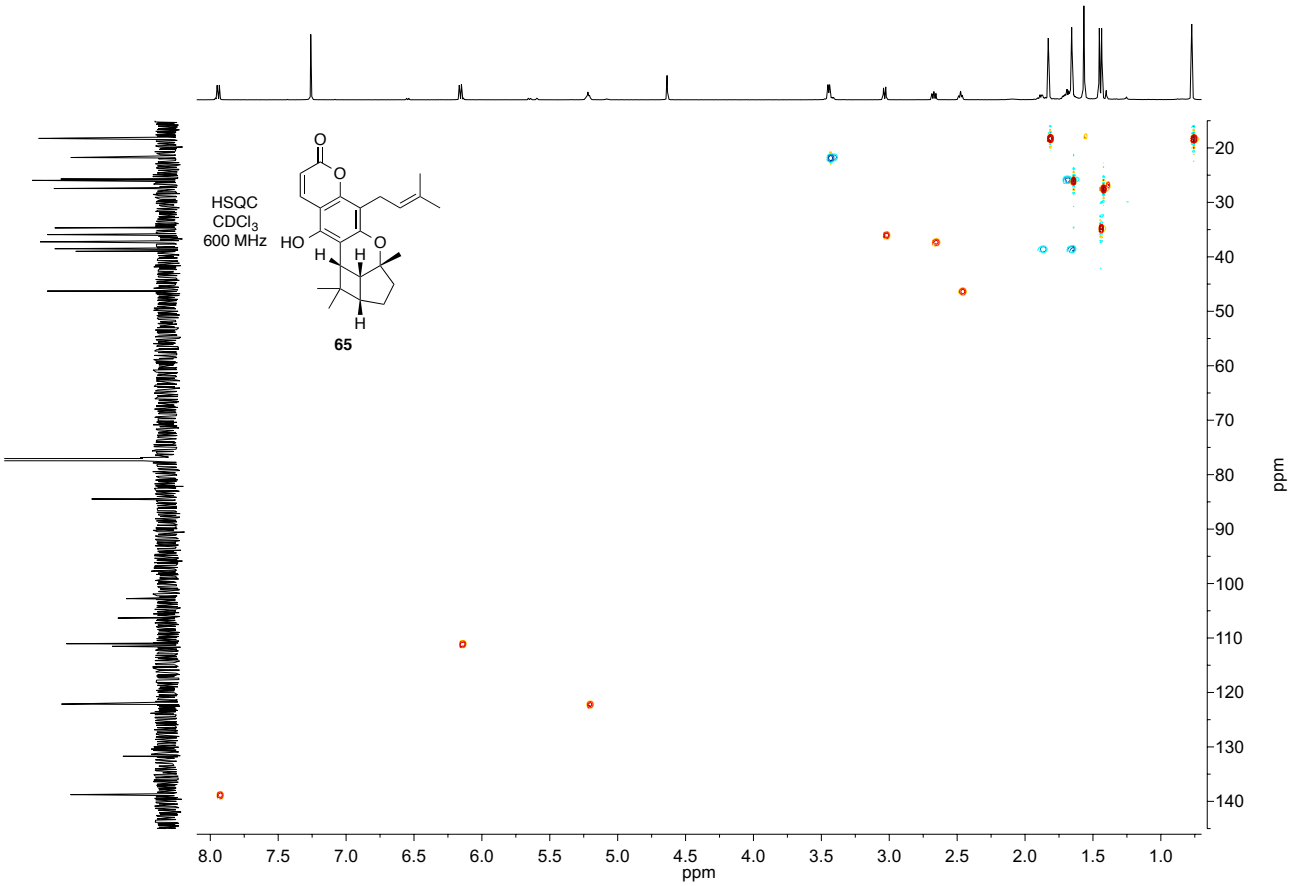
CDCl3
600 MHz
HO
O
H
65
ppm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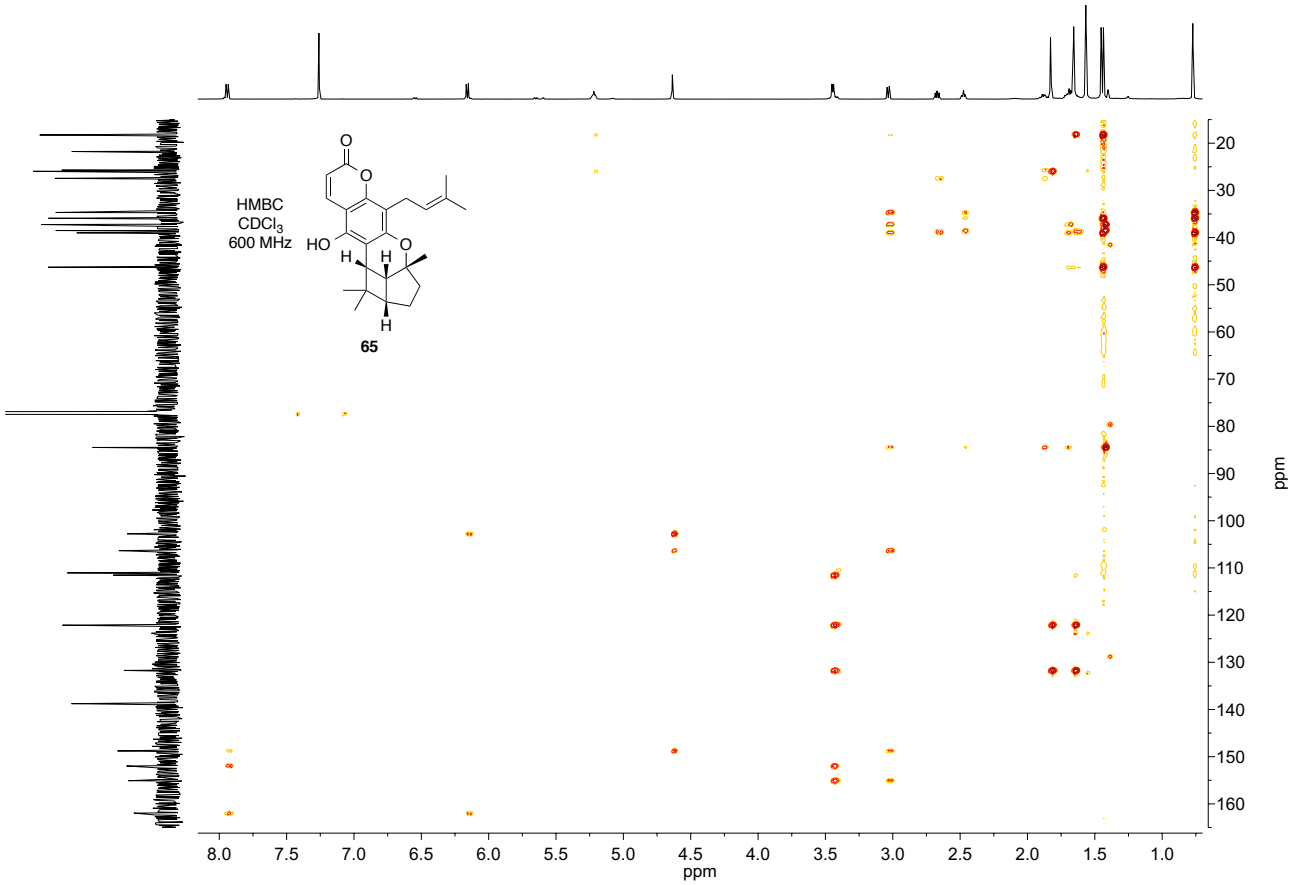
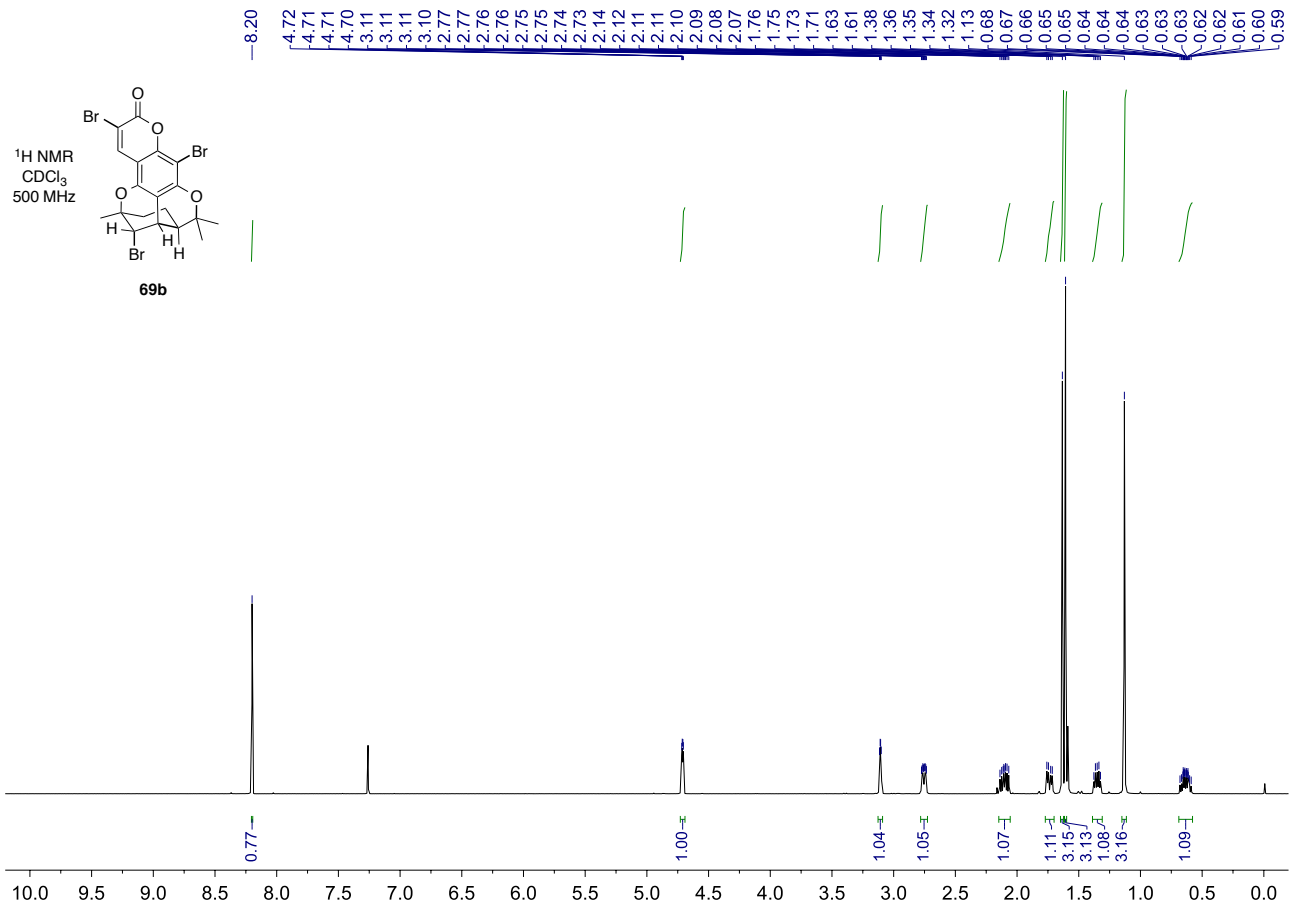
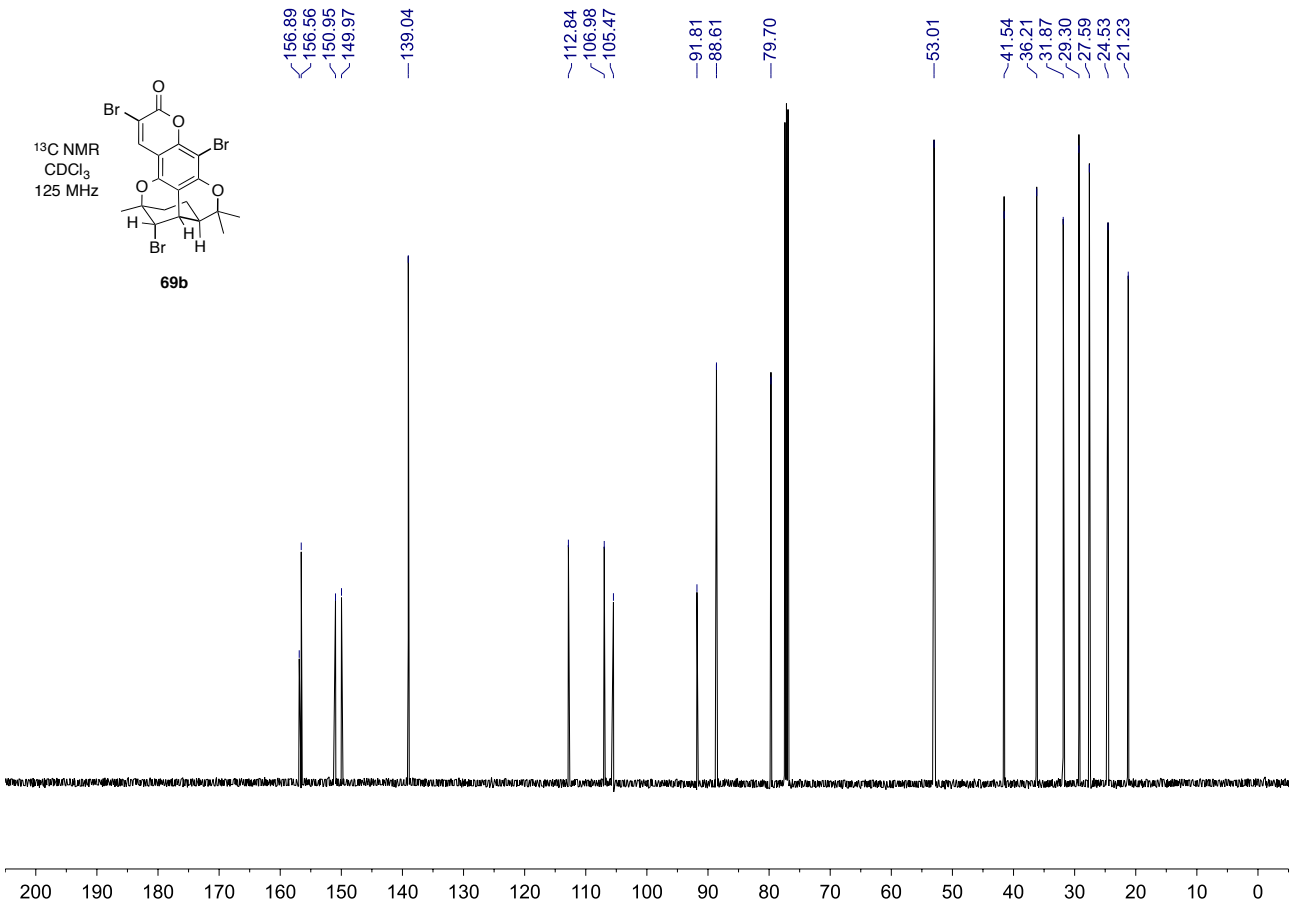
CDCl3
600 MHz
HO
O
H
65
ppm


HMBC
CDCl3
600 MHz
65
ppm
ppm


8.20
4.72
4.71
4.71
4.70
3.11
3.11
3.11
3.10
2.77
2.77
2.76
2.76
2.75
2.75
2.74
2.73
2.14
2.12
2.11
2.11
2.10
2.09
2.08
2.07
1.76
1.75
1.73
1.71
1.63
1.61
1.38
1.36
1.35
1.34
1.32
1.13
0.68
0.67
0.66
0.65
0.65
0.64
0.64
0.64
0.63
0.63
0.63
0.62
0.62
0.61
0.60
0.59
^{1}H NMR
$CDCl_3$
500 MHz
69b
0.77
1.00
1.04
1.05
1.07
1.11
3.15
3.13
1.08
3.16
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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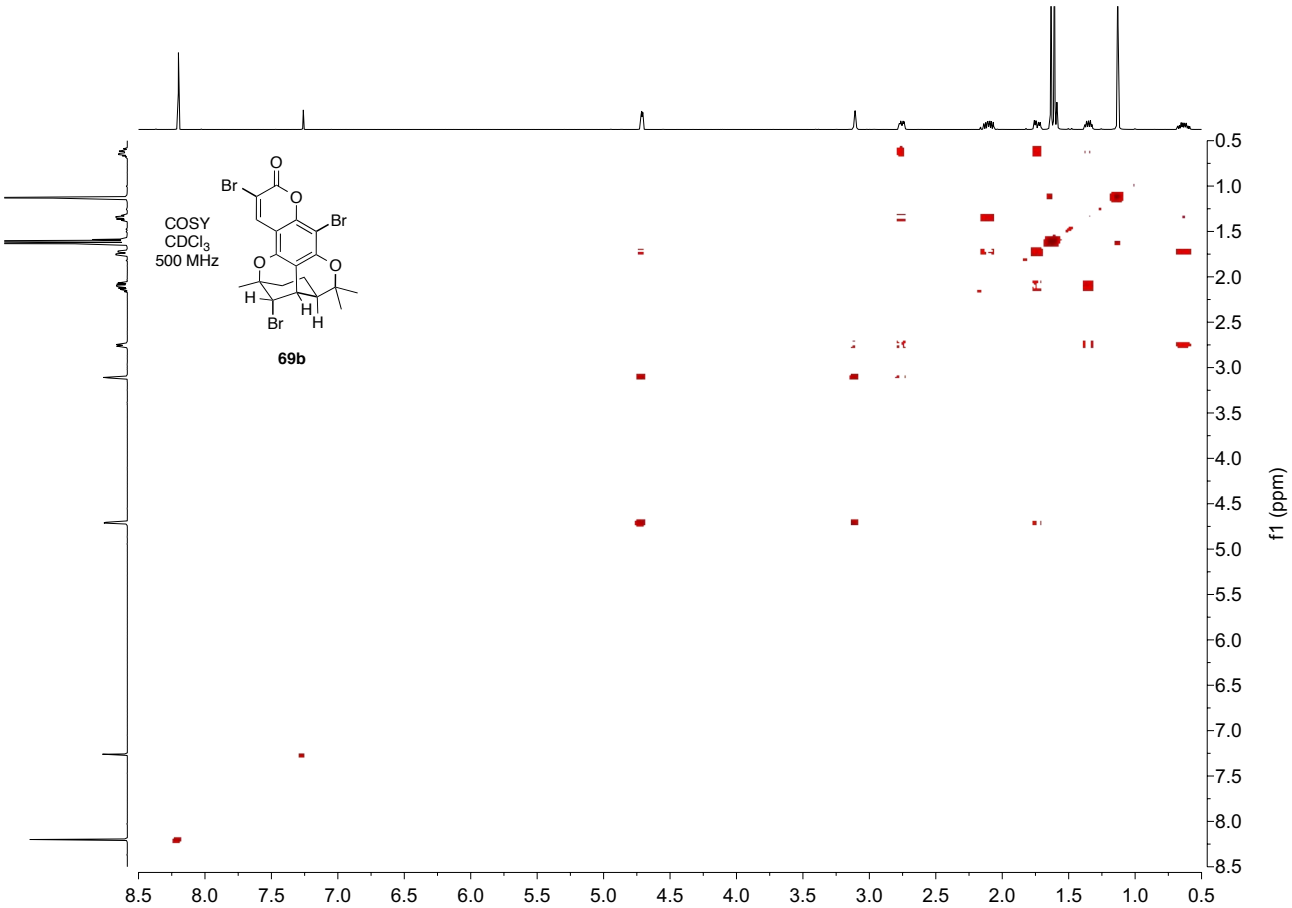
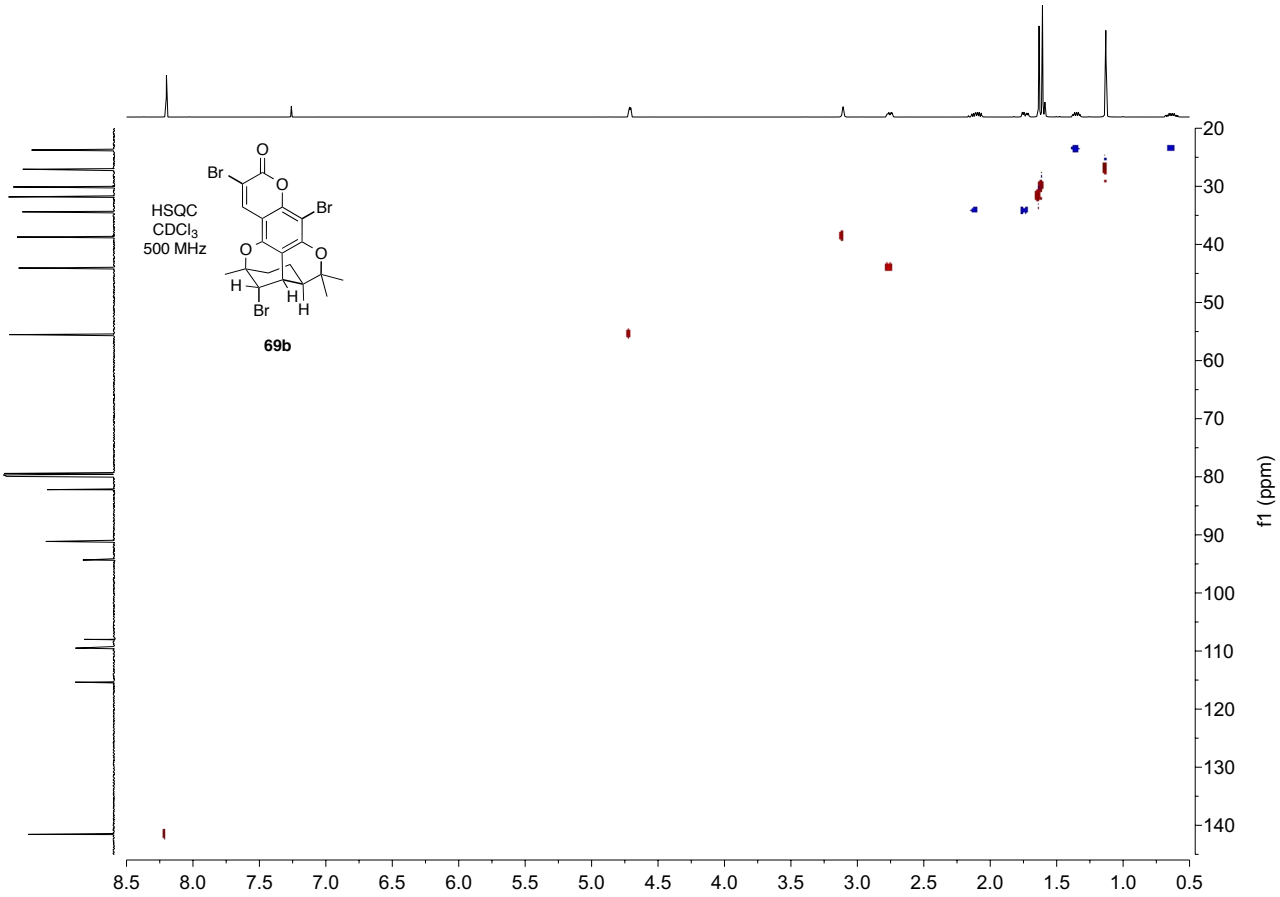
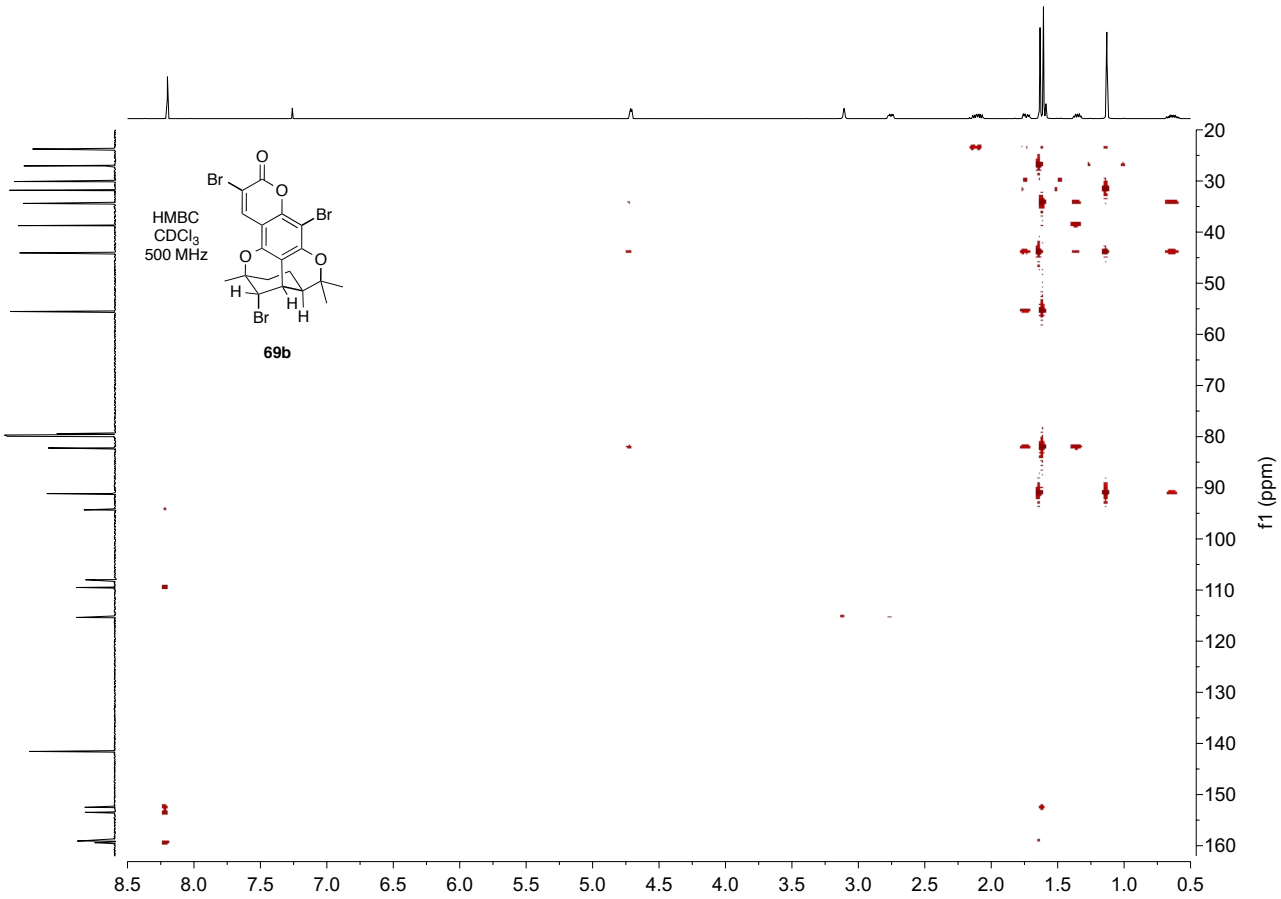
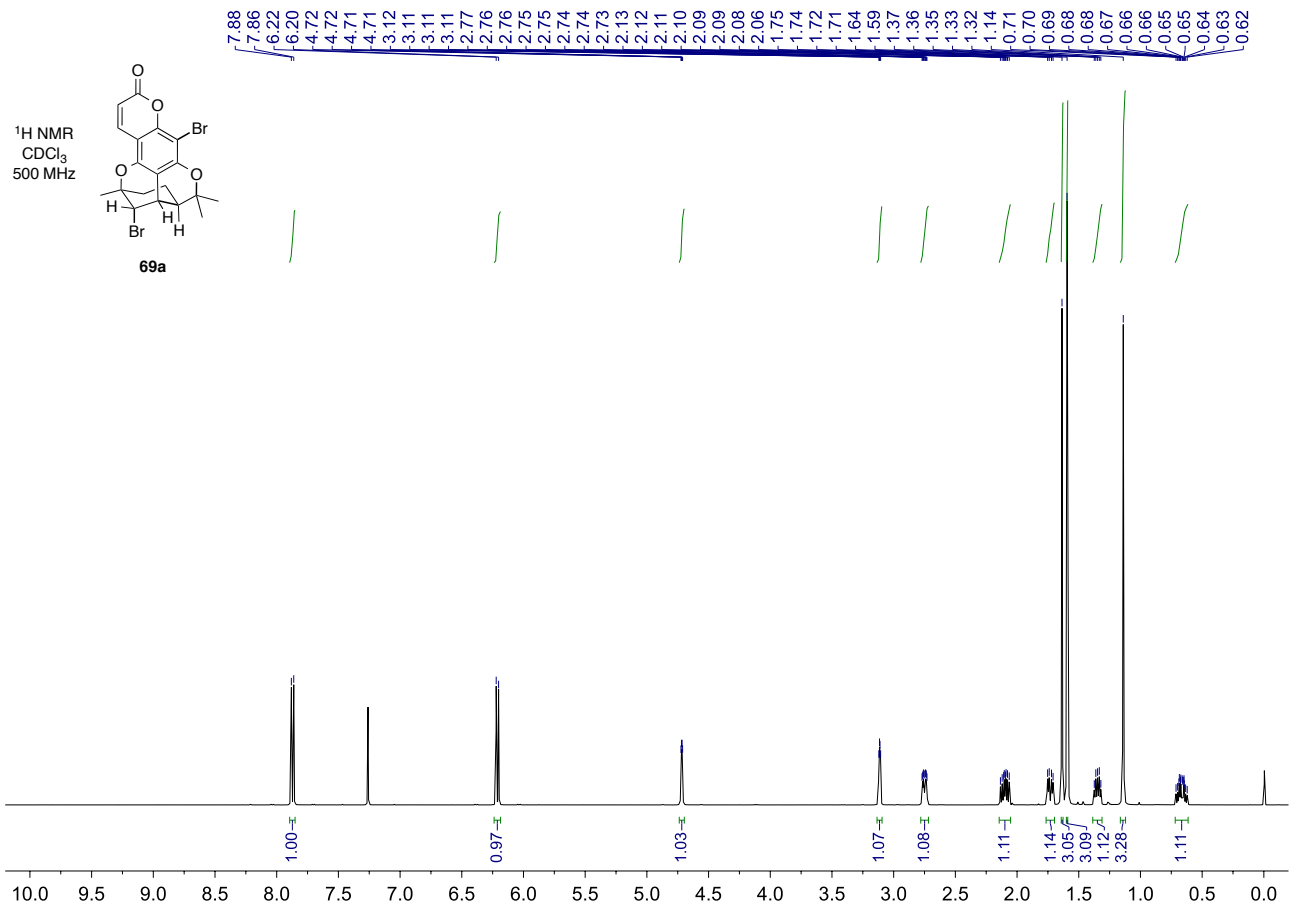
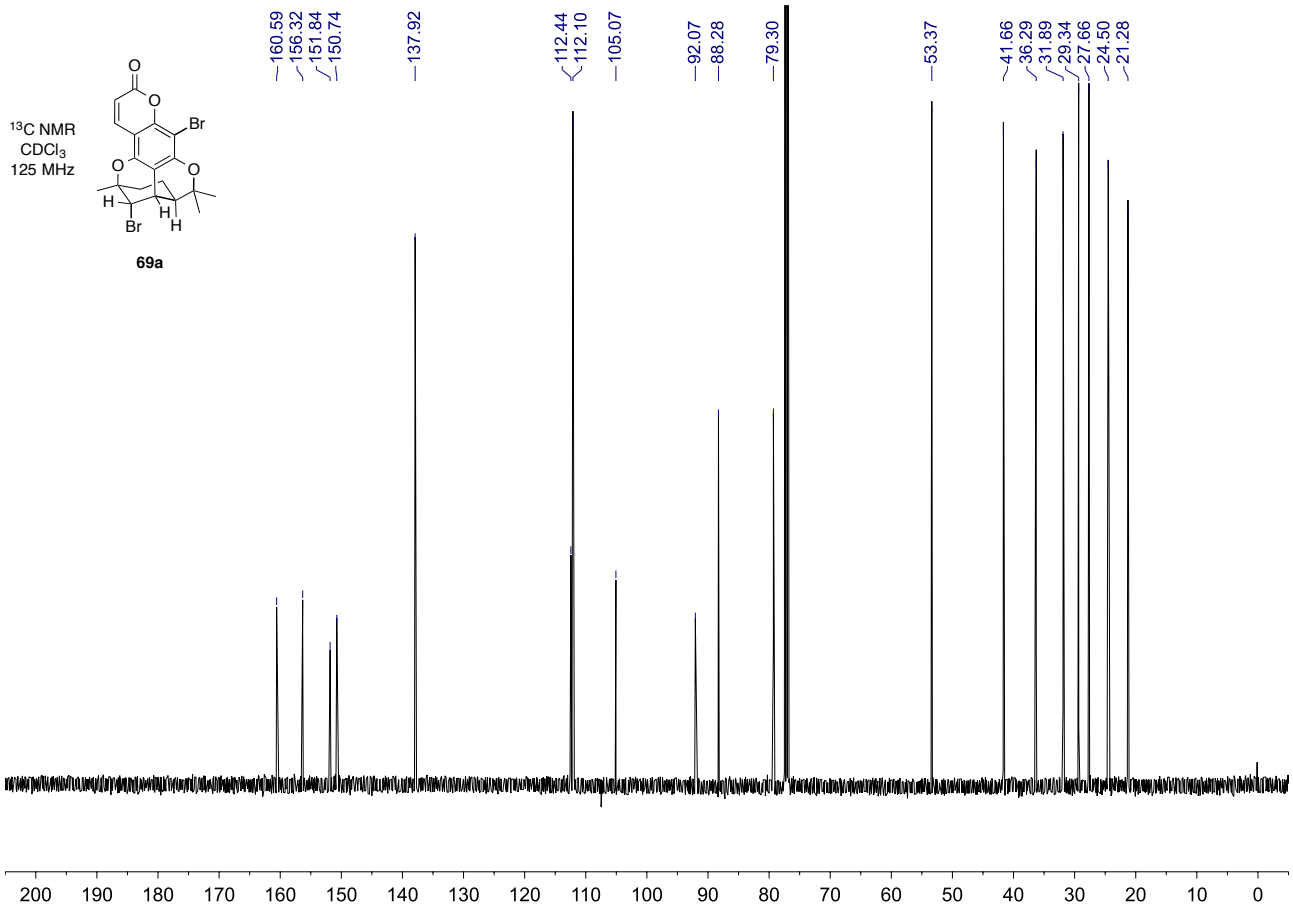
156.56
150.95
149.97
139.04
112.84
106.98
105.47
91.81
88.61
79.70
53.01
41.54
36.21
31.87
29.30
27.59
24.53
21.23
^{13}C NMR
$CDCl_3$
125 MHz
69b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

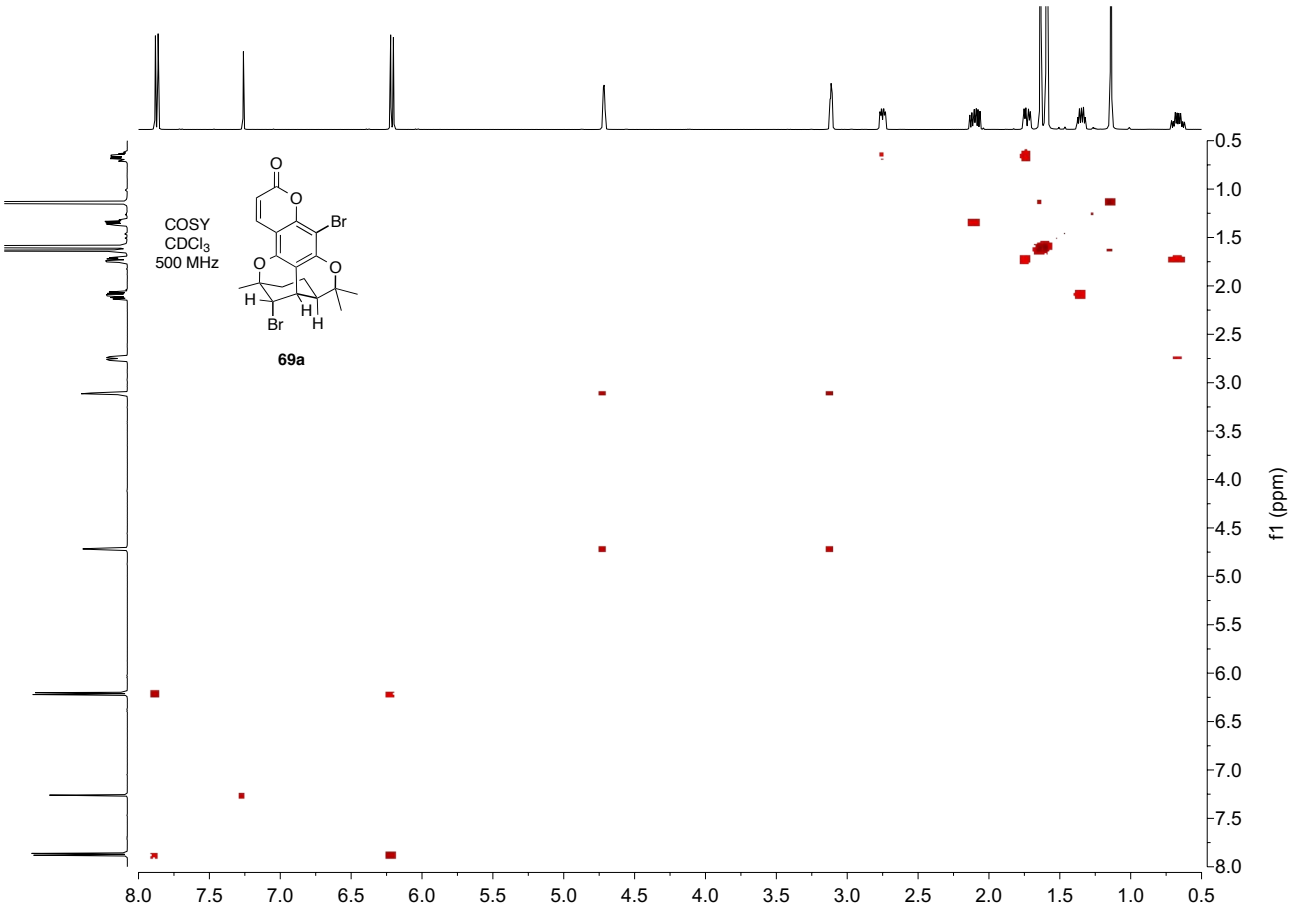

COSY
CDCl3
500 MHz
69b
f1 (ppm)

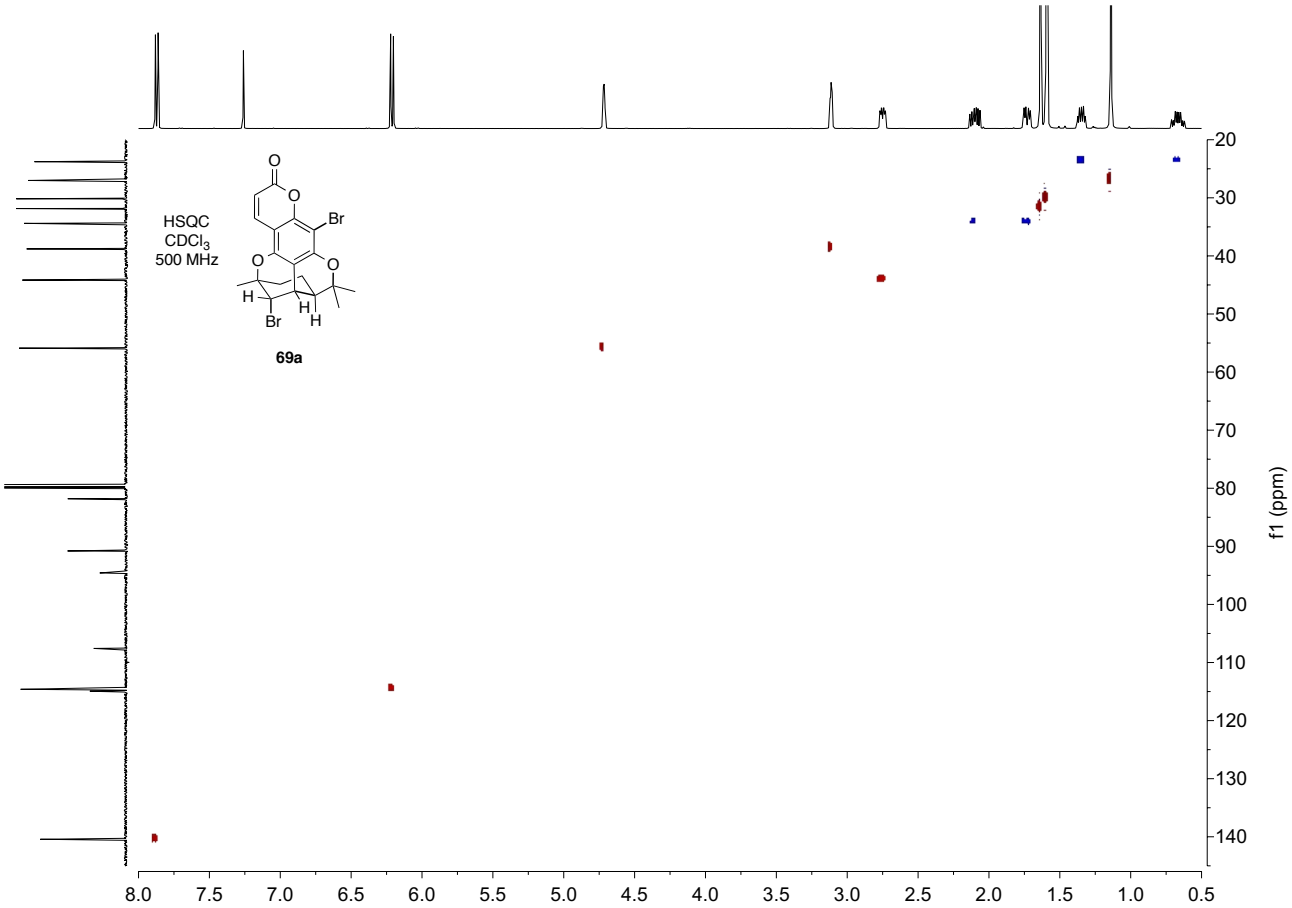

HSQC
CDCl3
500 MHz
69b
f1 (ppm)

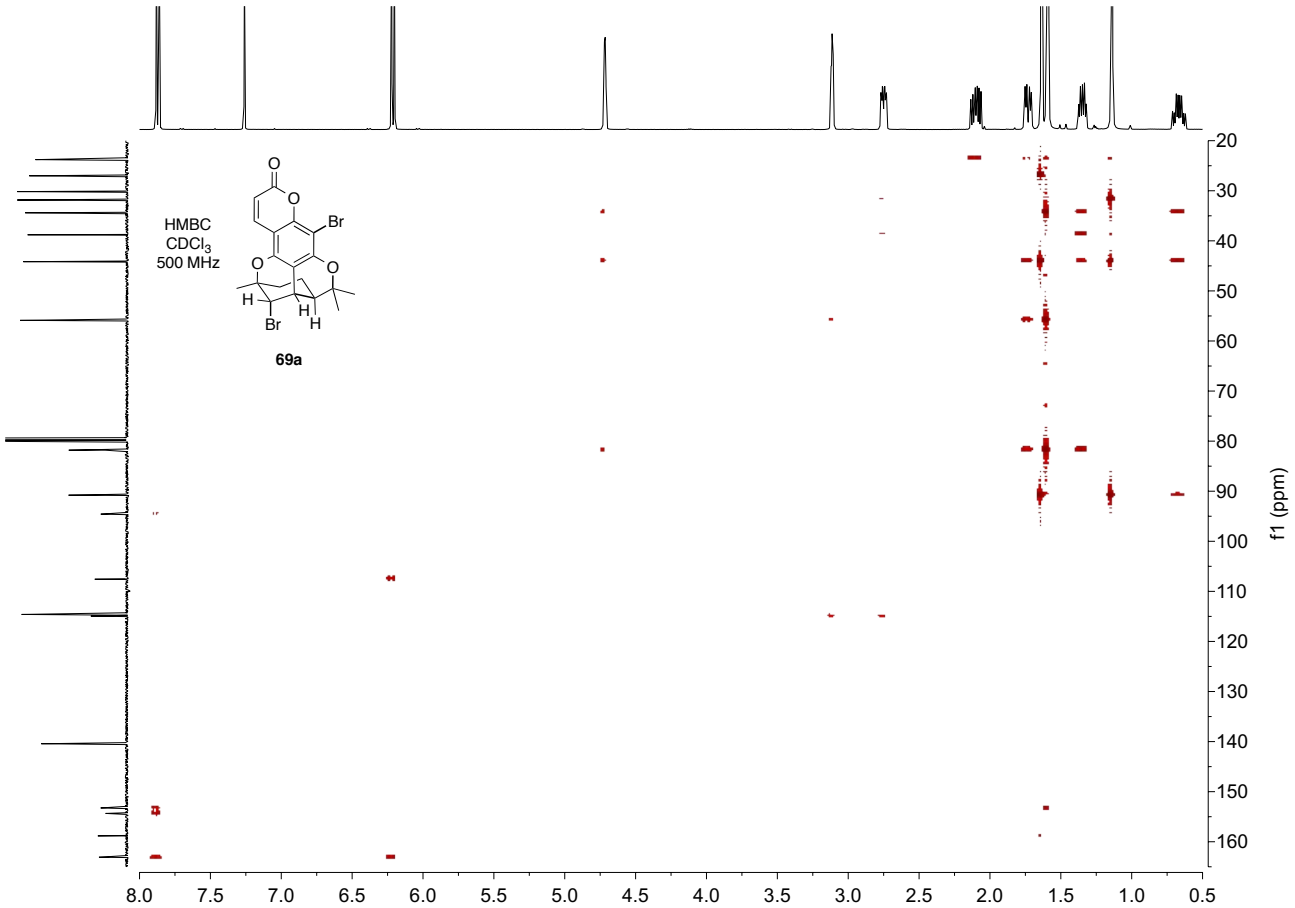

HMBC
CDCl3
500 MHz
69b
f1 (ppm)

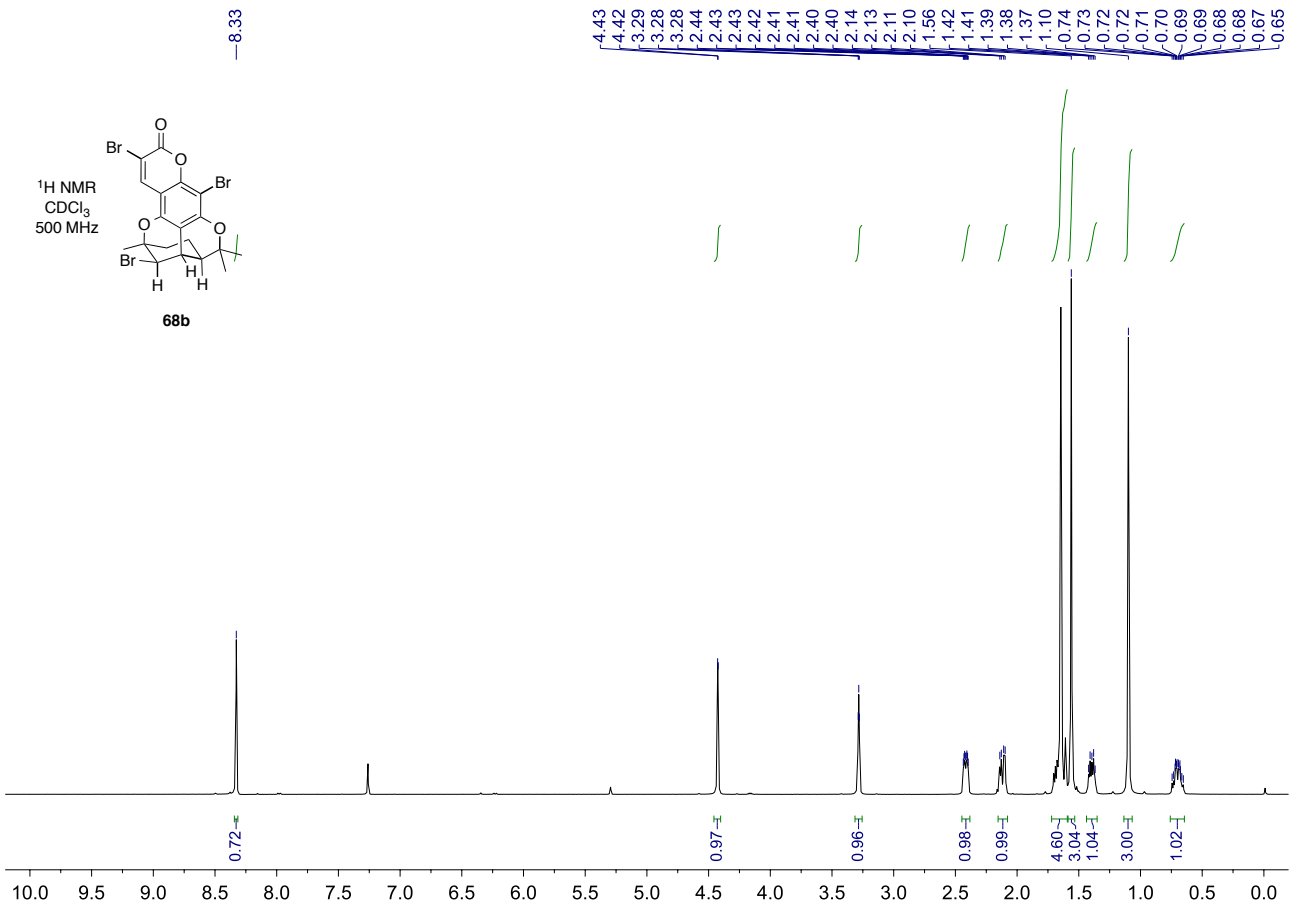

^{1}H NMR
$CDCl_3$
500 MHz
69a
7.88 7.86 6.22 6.20 4.72 4.72 4.71 4.71 3.12 3.11 3.11 3.11 2.77 2.76 2.76 2.75 2.75 2.74 2.74 2.73 2.13 2.12 2.11 2.10 2.09 2.09 2.08 2.06 1.75 1.74 1.72 1.71 1.64 1.59 1.37 1.36 1.35 1.33 1.32 1.14 0.71 0.70 0.69 0.68 0.68 0.67 0.66 0.66 0.65 0.65 0.64 0.63 0.62
1.00 0.97 1.03 1.07 1.08 1.11 1.14 3.05 3.09 1.12 3.28 1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


^{13}C NMR
$CDCl_3$
125 MHz
69a
160.59 156.32 151.84 150.74 137.92 112.44 112.10 105.07 92.07 88.28 79.30 53.37 41.66 36.29 31.89 29.34 27.66 24.50 21.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


COSY
CDCl3
500 MHz
69a
f1 (ppm)


HSQC
CDCl3
500 MHz
69a
f1 (ppm)


HMBC
CDCl3
500 MHz
69a
f1 (ppm)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4.43
4.42
3.29
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3.28
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2.43
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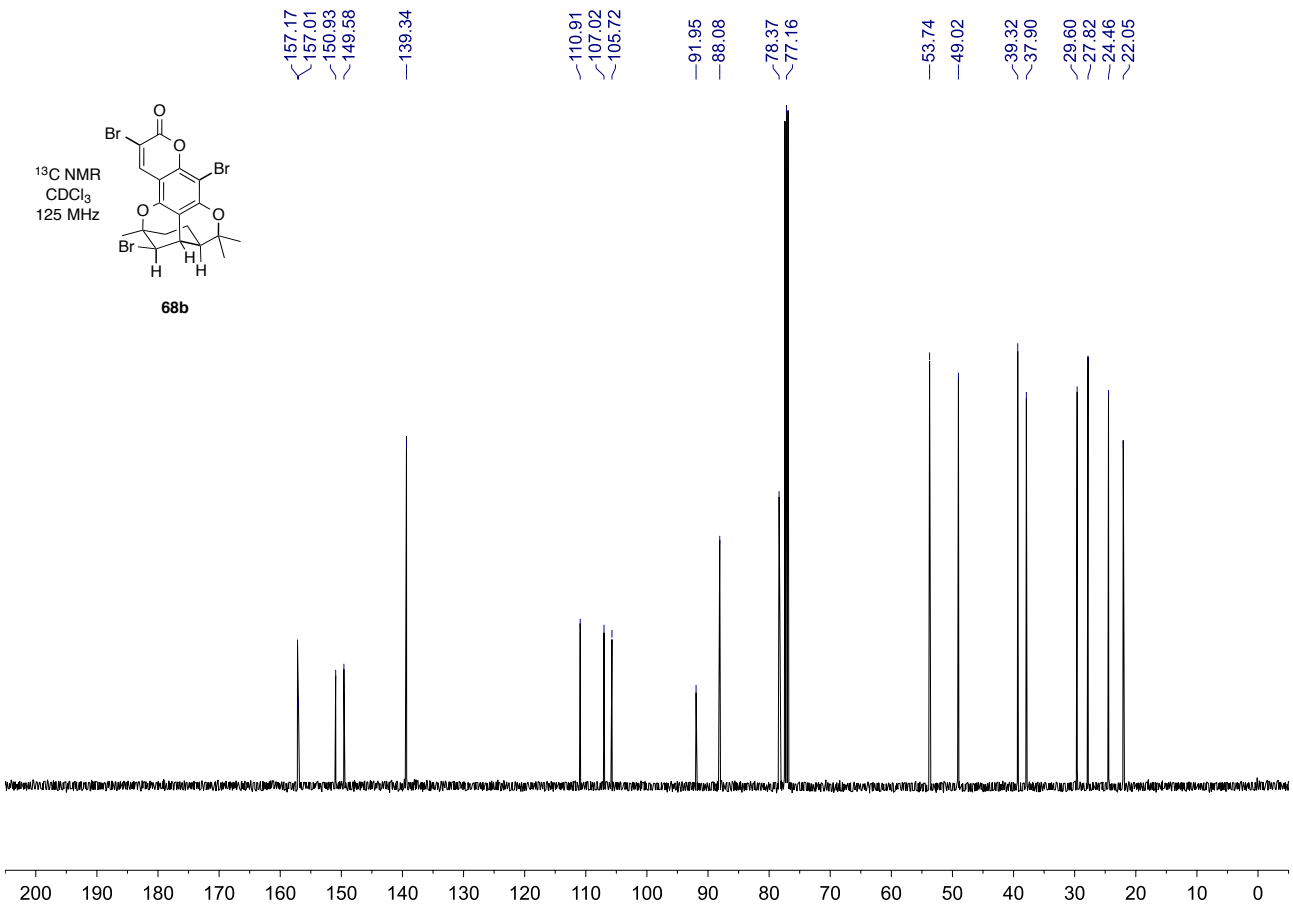
2.13
2.11
2.10
1.56
1.42
1.41
1.39
1.38
1.37
1.10
0.74
0.73
0.72
0.72
0.71
0.70
0.69
0.69
0.68
0.68
0.67
0.65
0.72
0.97
0.96
0.98
0.99
4.60
3.04
1.04
3.00
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
^{1}H NMR
$CDCl_3$
500 MHz
68b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157.01
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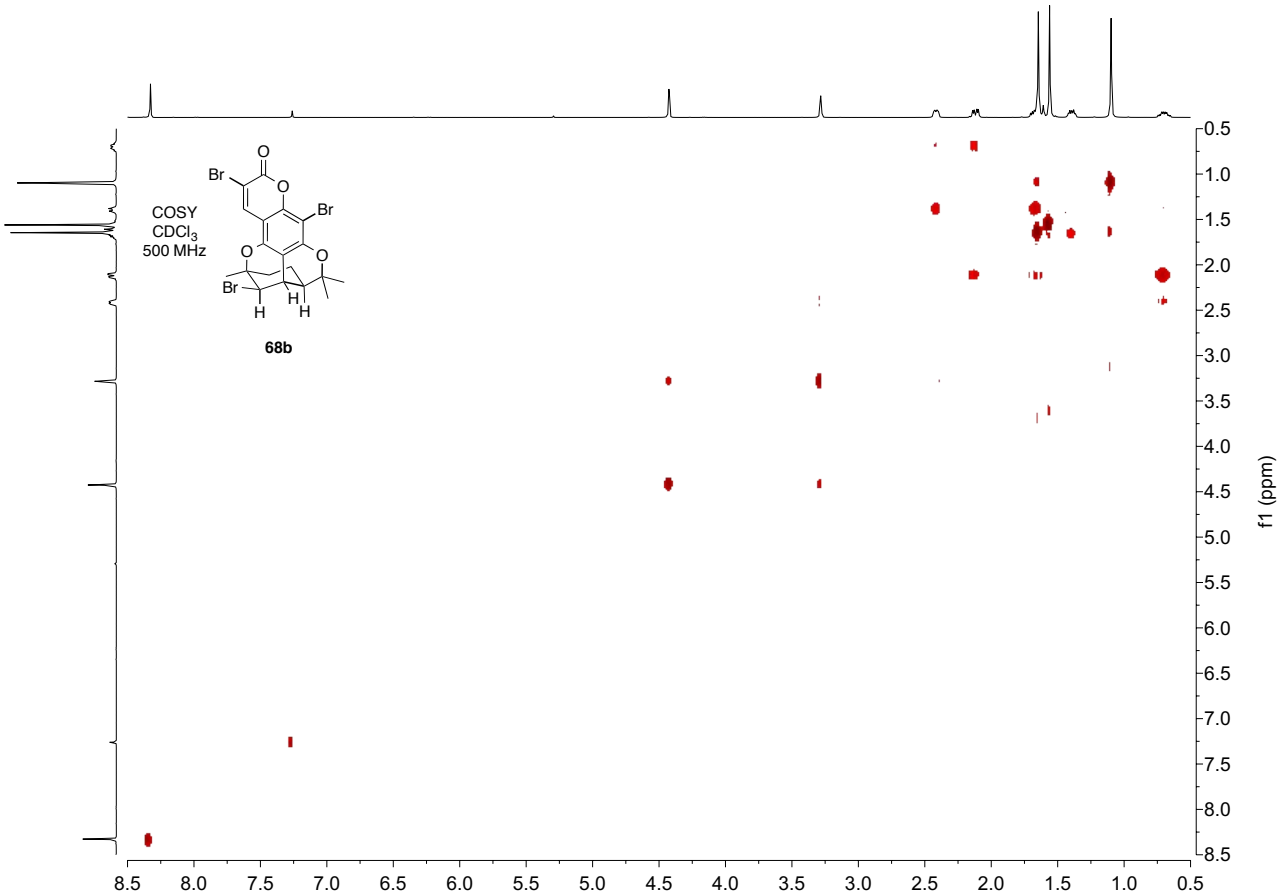
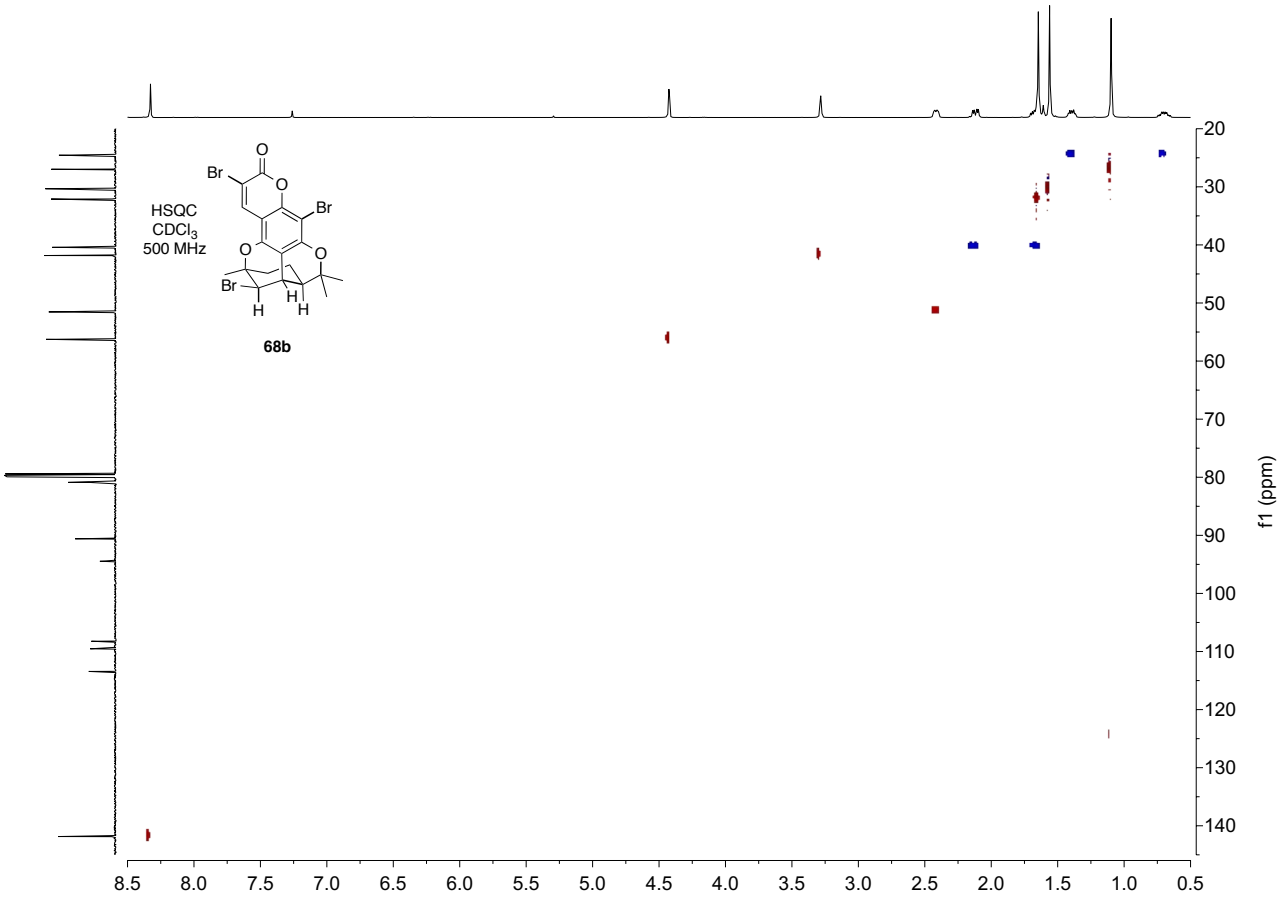
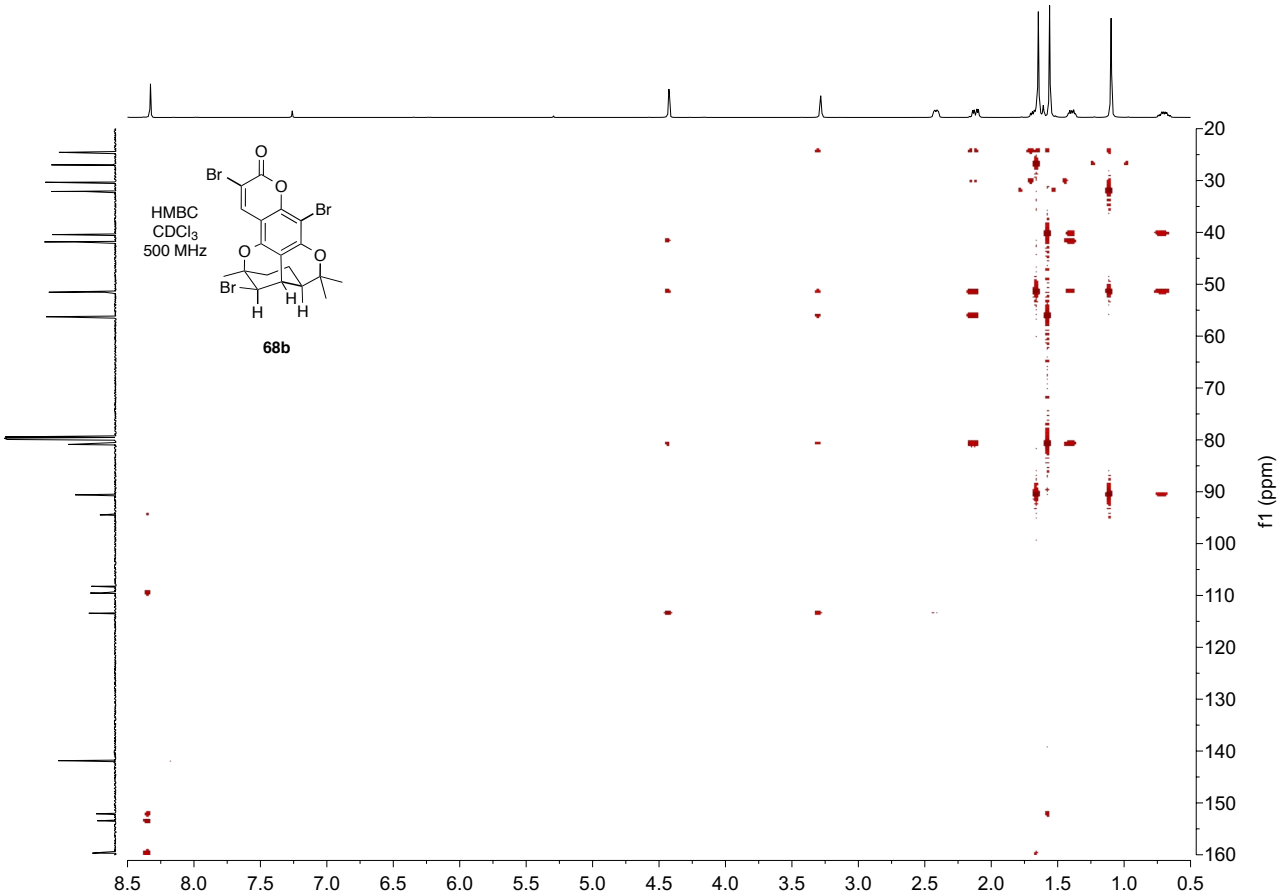
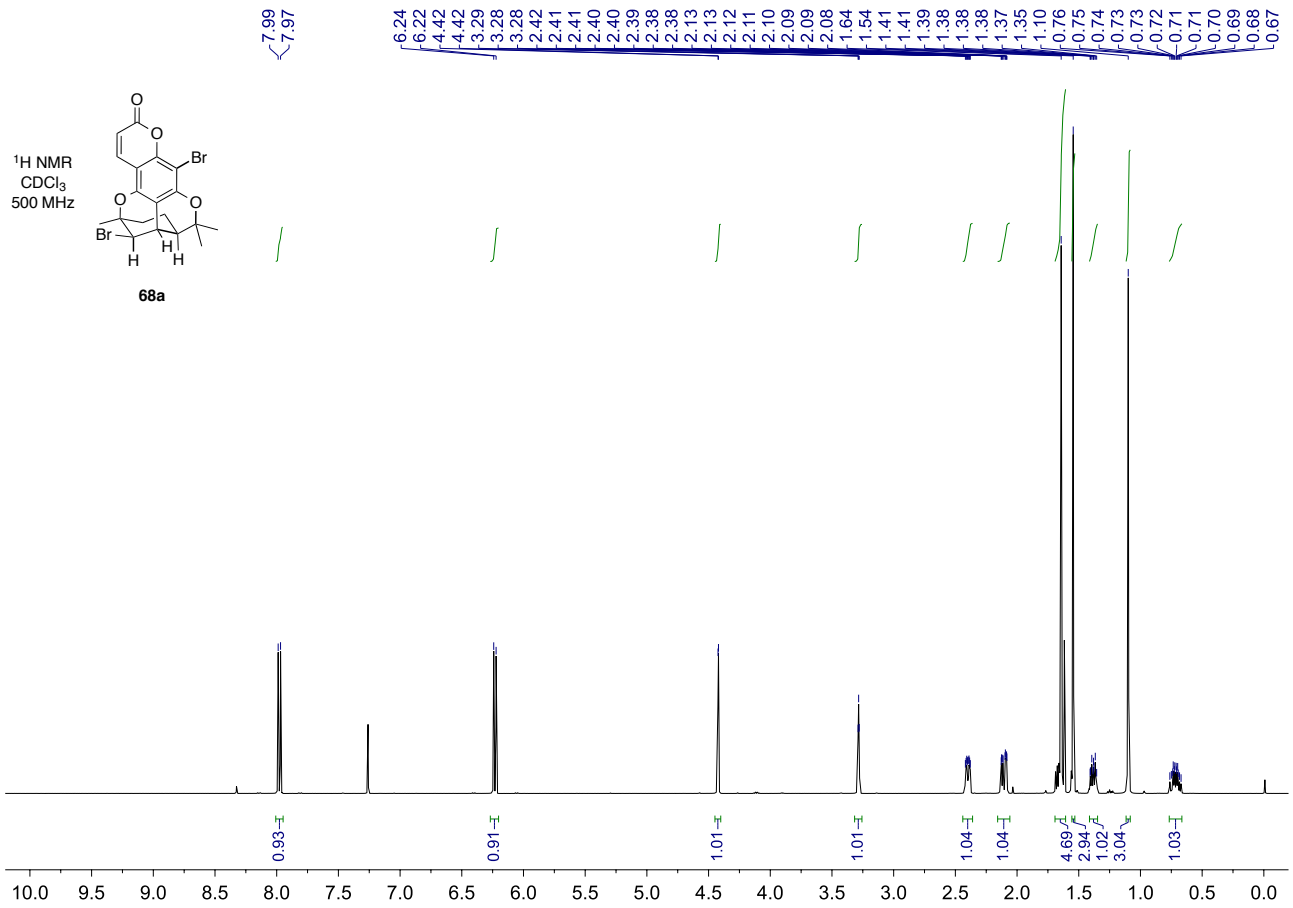
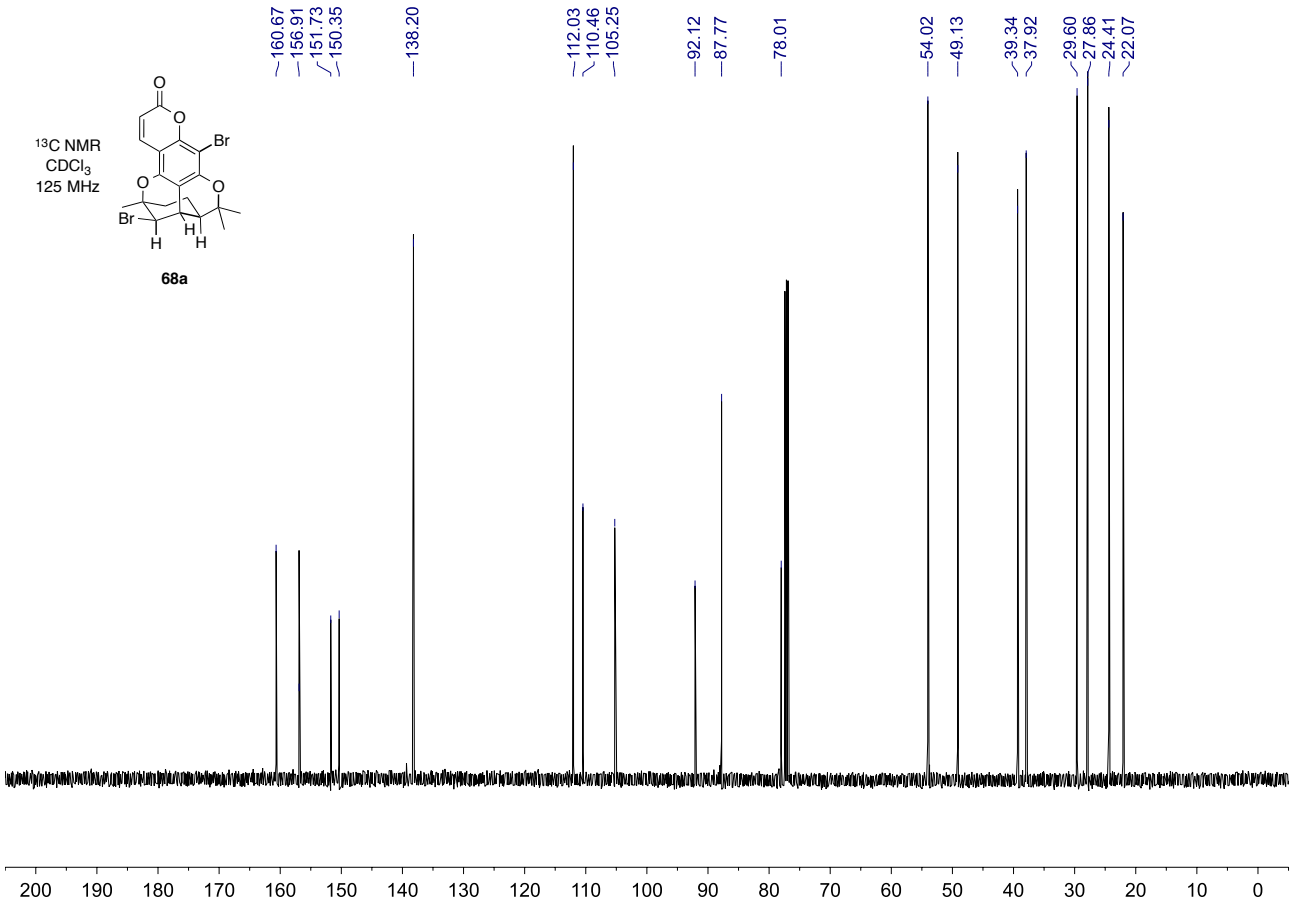
149.58
139.34
110.91
107.02
105.72
91.95
88.08
78.37
77.16
53.74
49.02
39.32
37.90
29.60
27.82
24.46
22.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
^{13}C NMR
$CDCl_3$
125 MHz
68b


COSY
CDCl3
500 MHz
68b
f1 (ppm)


HSQC
CDCl3
500 MHz
68b
f1 (ppm)


HMBC
CDCl3
500 MHz
68b
f1 (ppm)


^{1}H NMR
$CDCl_3$
500 MHz
68a
7.99
7.97
6.24
6.22
4.42
4.42
3.29
3.28
3.28
2.42
2.41
2.41
2.40
2.40
2.39
2.38
2.38
2.13
2.13
2.12
2.11
2.10
2.09
2.09
2.08
1.64
1.54
1.41
1.41
1.39
1.38
1.38
1.37
1.35
1.10
0.76
0.75
0.74
0.73
0.73
0.72
0.71
0.71
0.70
0.69
0.68
0.67
0.93
0.91
1.01
1.01
1.04
1.04
4.69
2.94
1.02
3.04
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


^{13}C NMR
$CDCl_3$
125 MHz
68a
160.67
156.91
151.73
150.35
138.20
112.03
110.46
105.25
92.12
87.77
78.01
54.02
49.13
39.34
37.92
29.60
27.86
24.41
22.07
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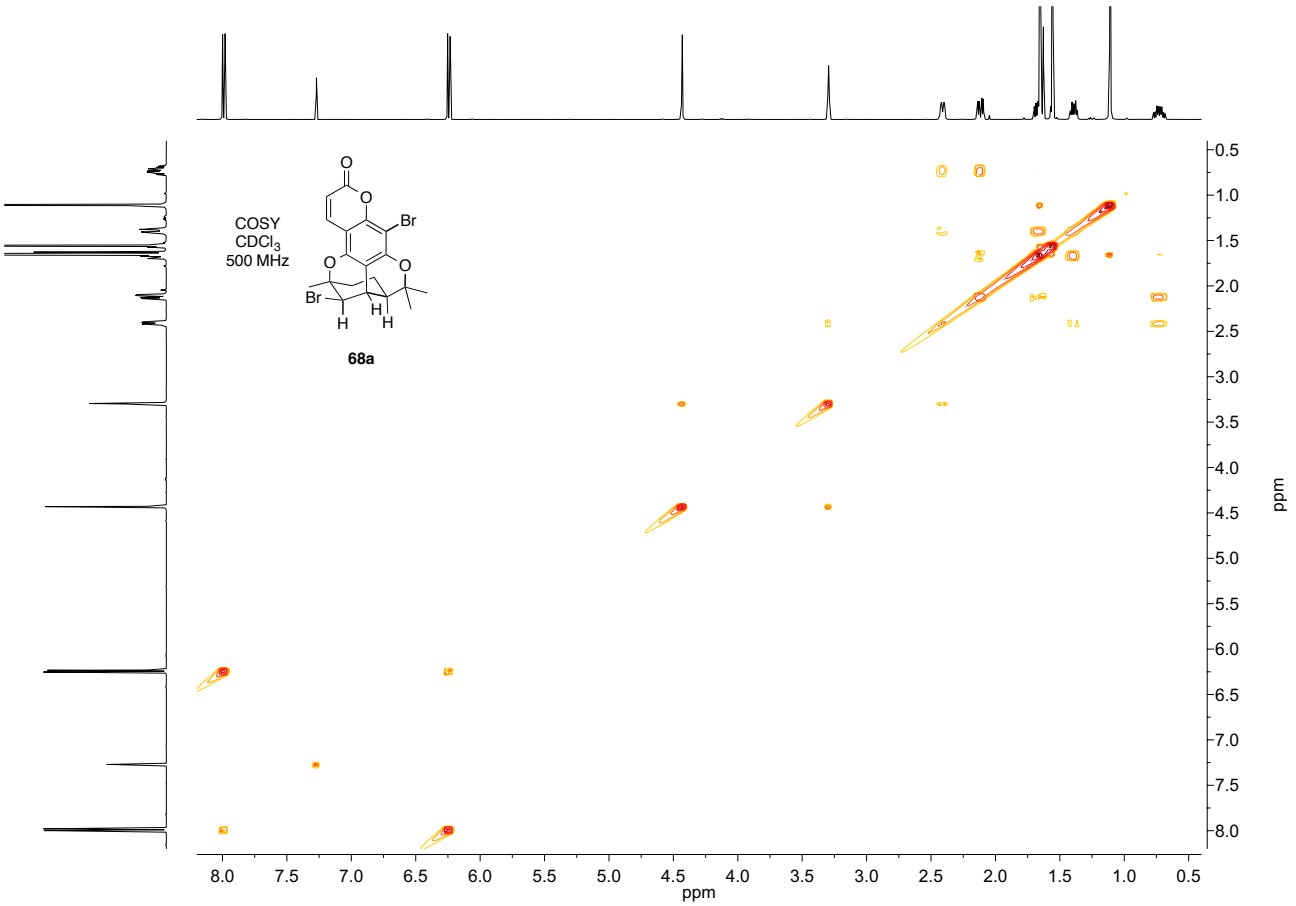
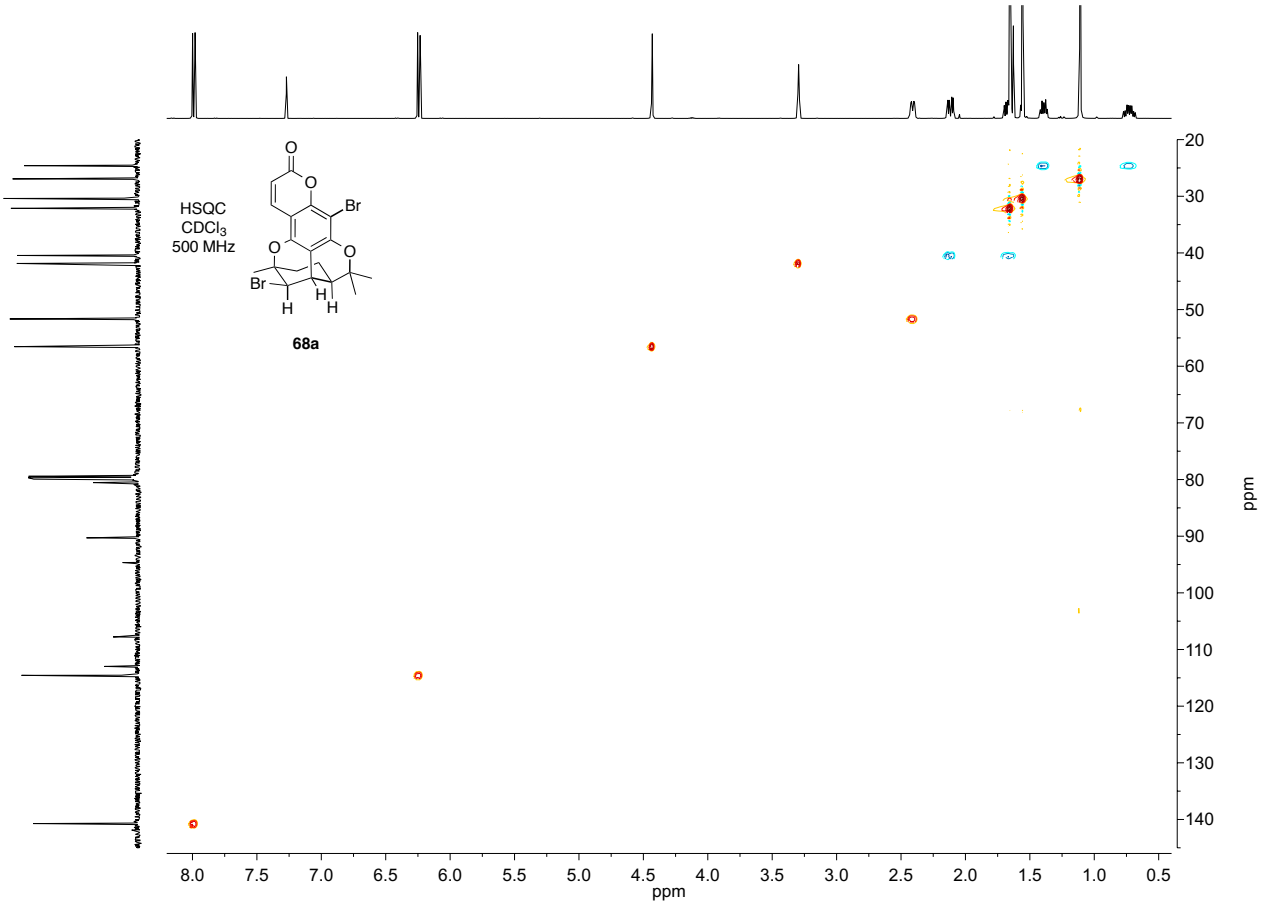
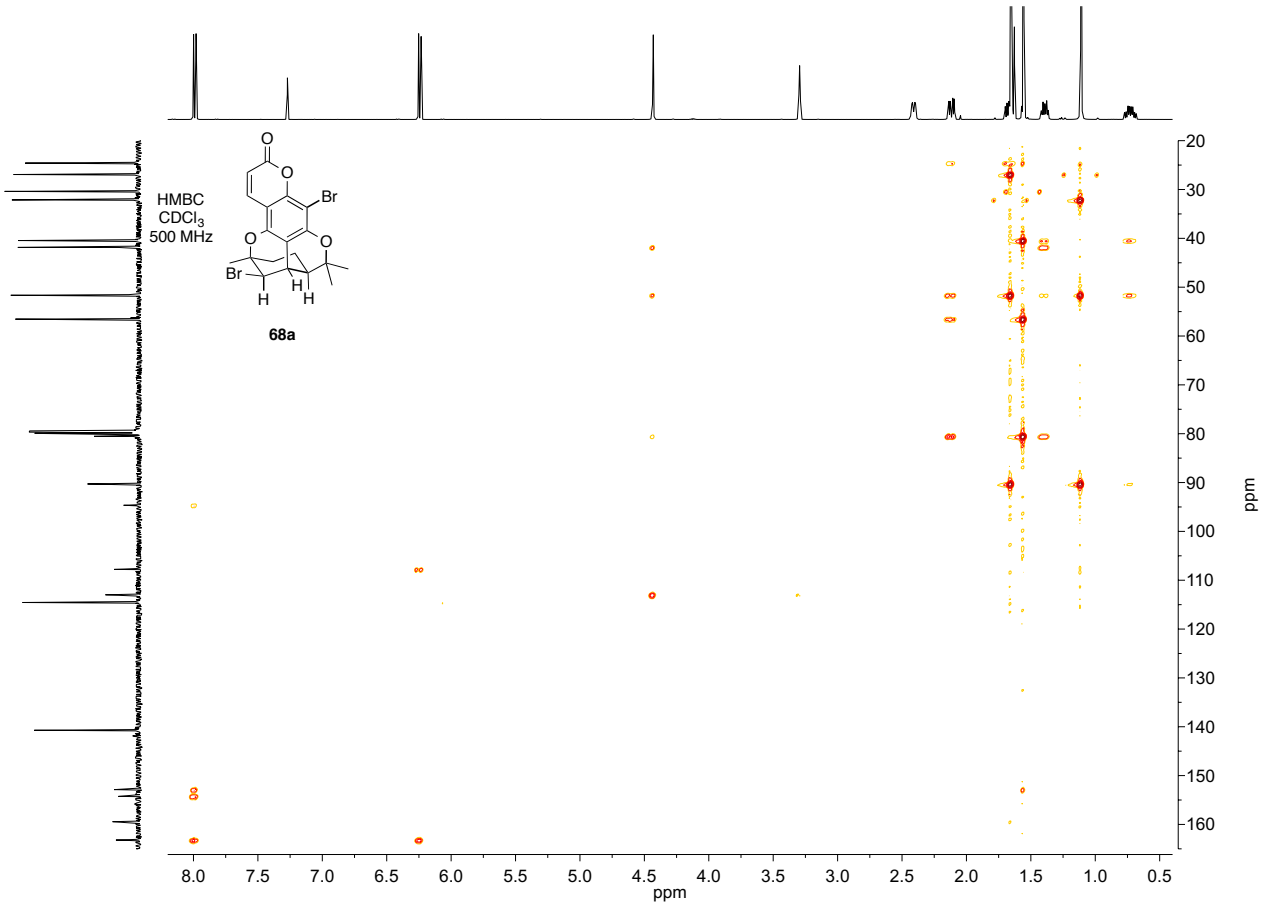
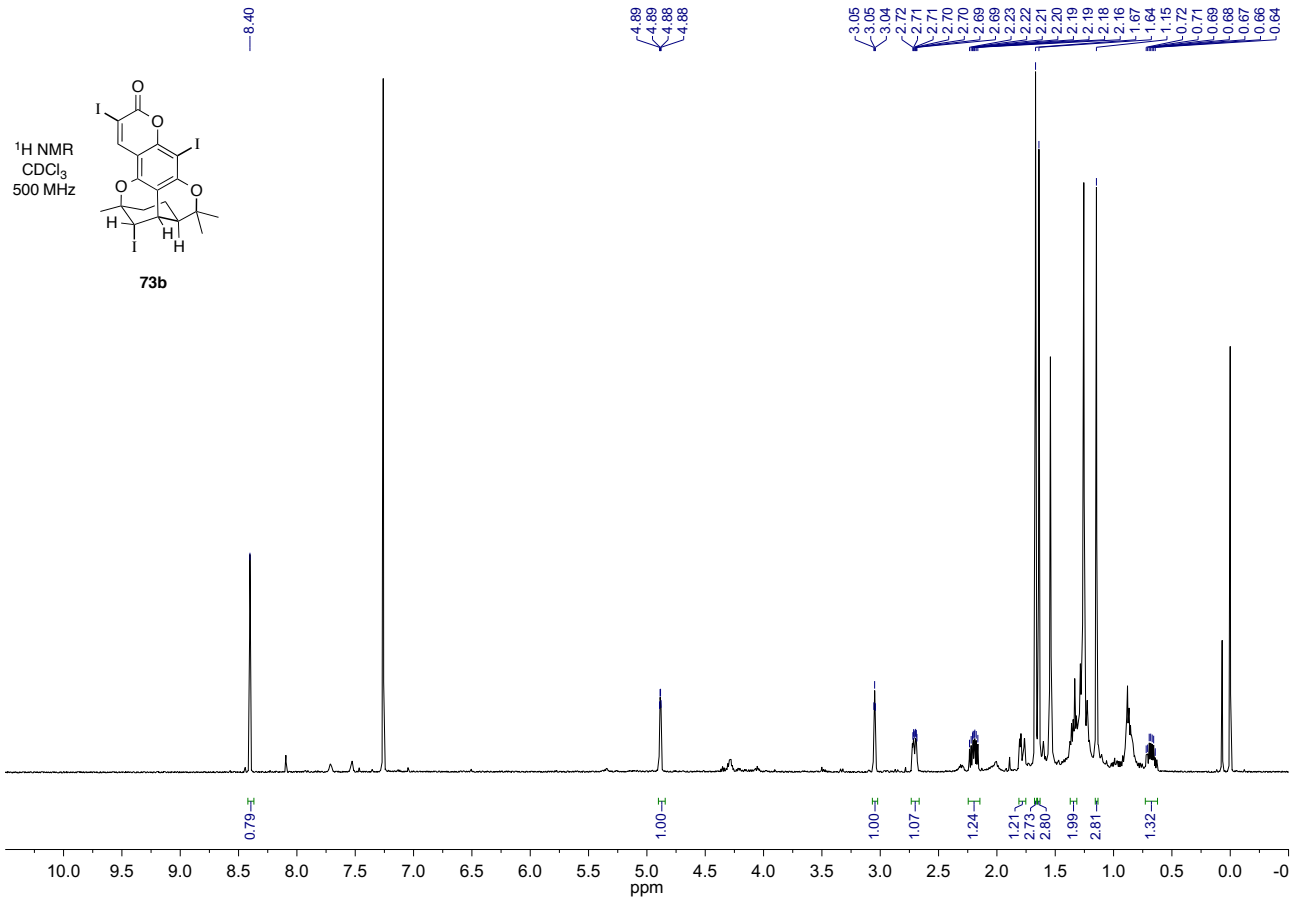

COSY
CDCl3
500 MHz
68a
ppm
ppm


HSQC
CDCl3
500 MHz
68a
ppm
ppm


HMBC
CDCl3
500 MHz
68a
ppm
ppm


^{1}H NMR
$CDCl_3$
500 MHz
73b
8.40
4.89
4.88
3.05
3.04
2.72
2.71
2.70
2.69
2.23
2.22
2.21
2.20
2.19
2.18
2.16
1.67
1.64
1.15
0.72
0.71
0.69
0.68
0.67
0.66
0.64
0.79
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1.00
1.07
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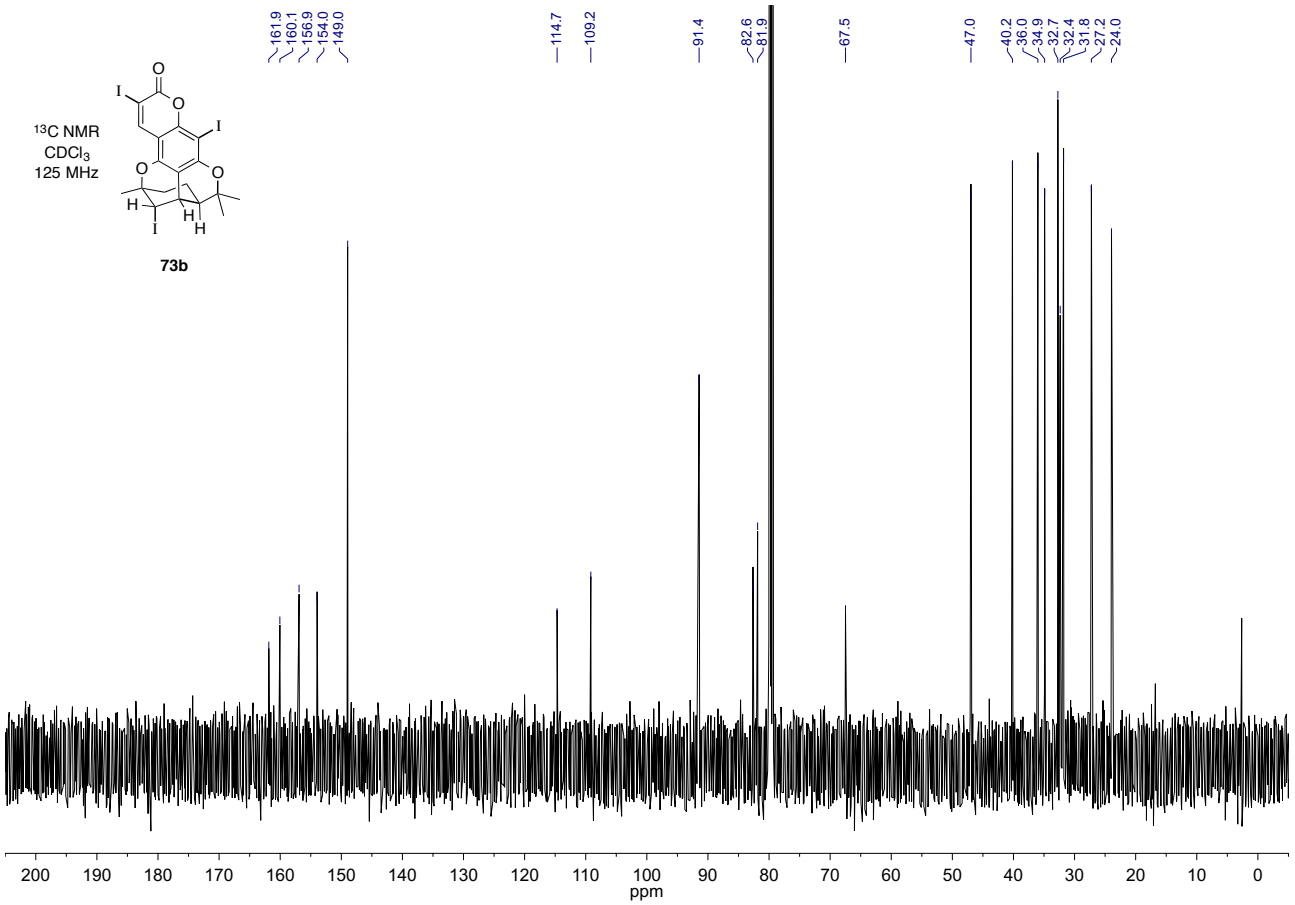
2.81
1.32
ppm


^{13}C NMR
$CDCl_3$
125 MHz
73b
161.9
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149.0
114.7
109.2
91.4
82.6
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40.2
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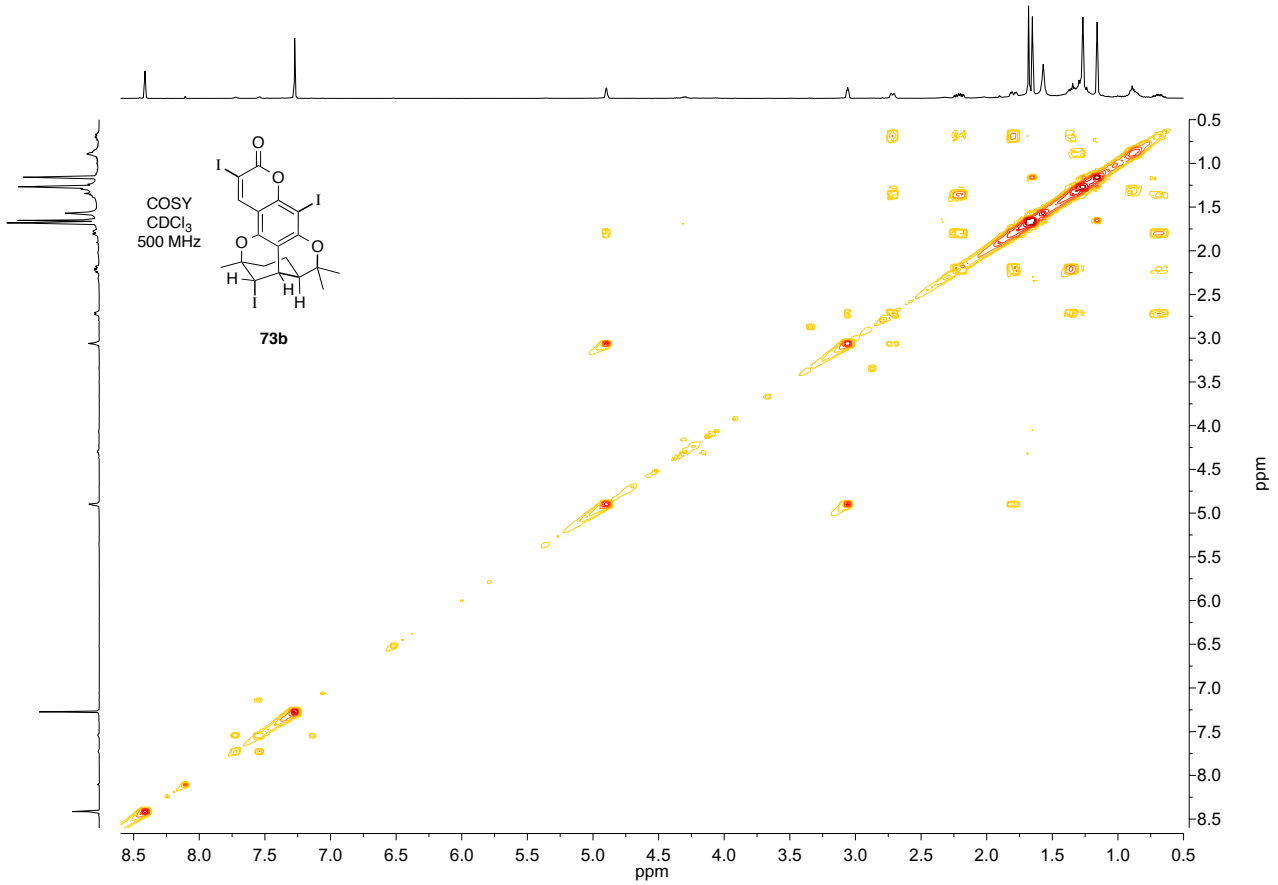
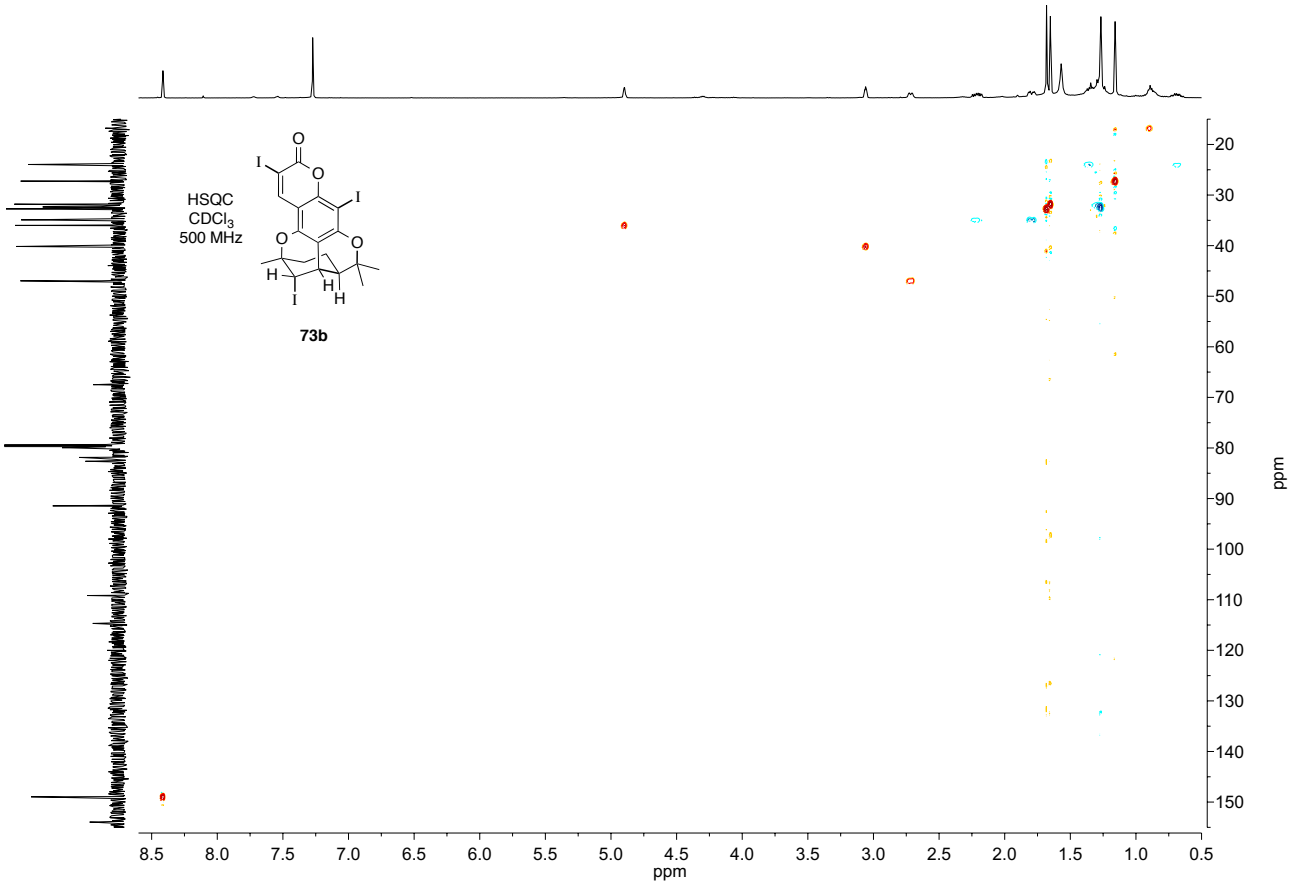
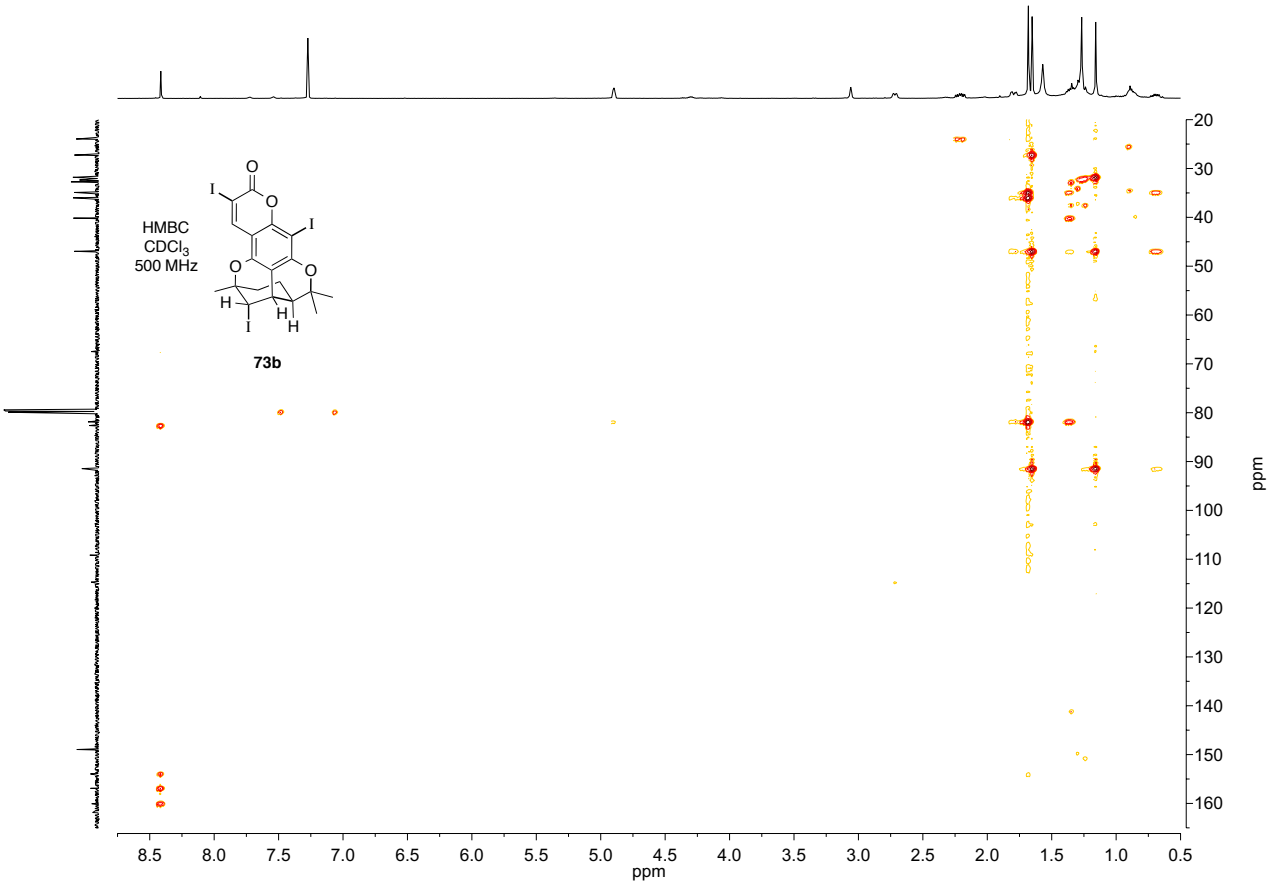
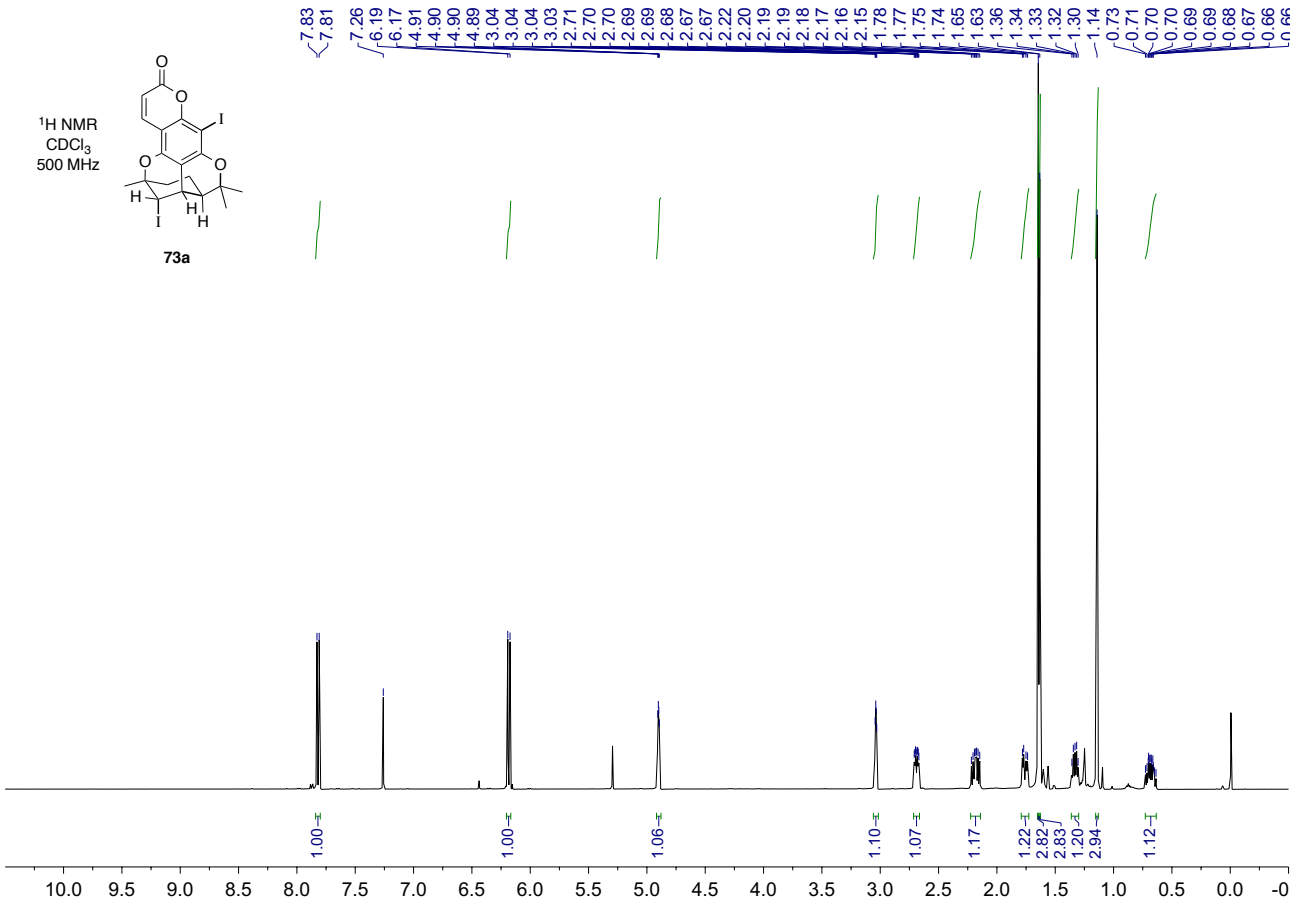
32.4
31.8
27.2
24.0
ppm


COSY
CDCl3
500 MHz
73b
ppm
ppm


HSQC
CDCl3
500 MHz
73b
ppm
ppm


HMBC
CDCl3
500 MHz
73b
ppm
ppm


^{1}H NMR
$CDCl_3$
500 MHz
73a
7.83
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7.26
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6.17
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4.89
3.04
3.04
3.04
3.03
2.71
2.70
2.70
2.69
2.69
2.68
2.67
2.67
2.22
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2.19
2.19
2.18
2.17
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1.77
1.75
1.74
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1.00
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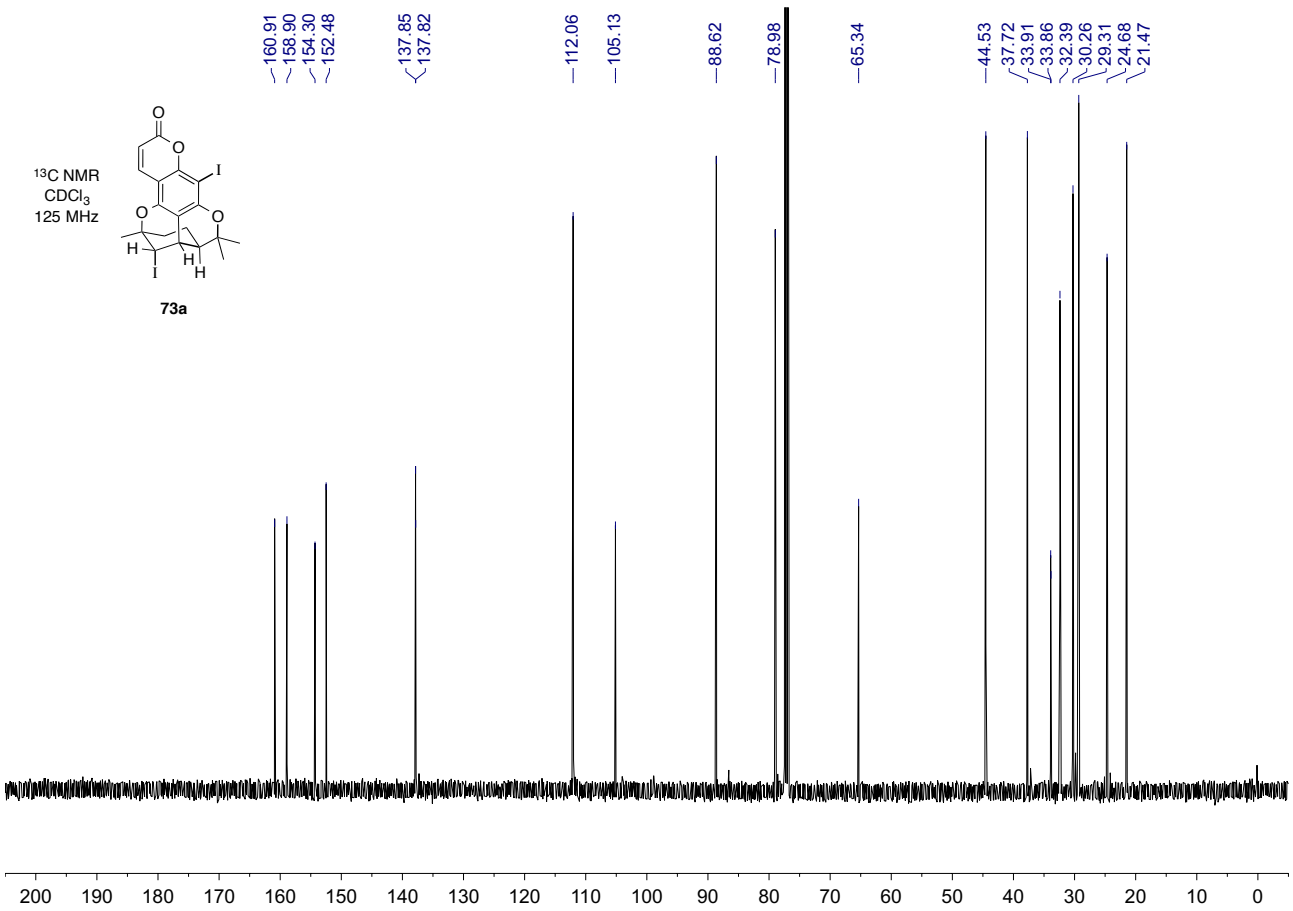
1.10
1.07
1.17
1.22
2.82
2.83
1.20
2.94
1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0


^{13}C NMR
$CDCl_3$
125 MHz
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160.91
158.90
154.30
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137.85
137.82
112.06
105.13
88.62
78.98
65.34
44.53
37.72
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32.39
30.26
29.31
24.68
21.47
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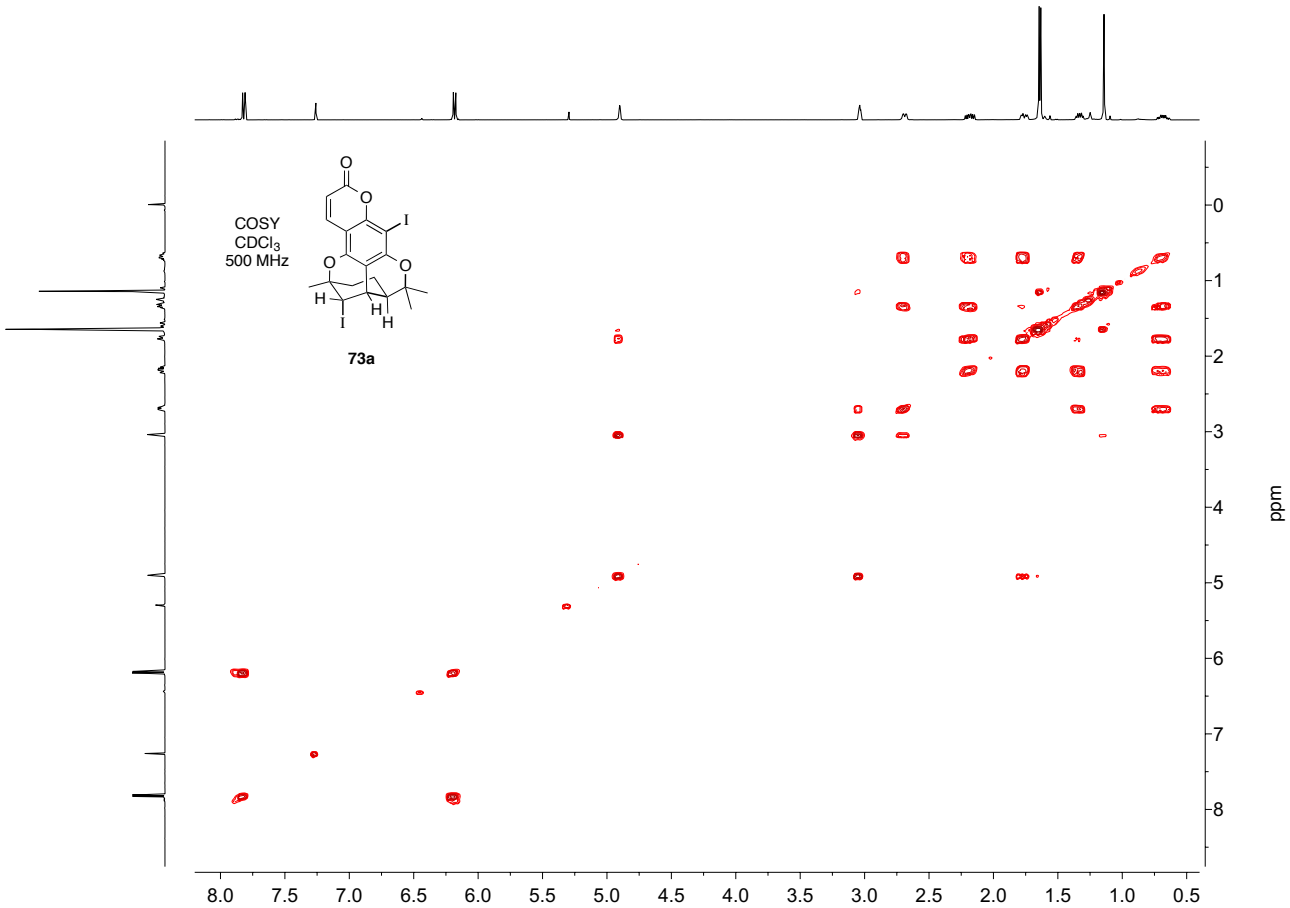
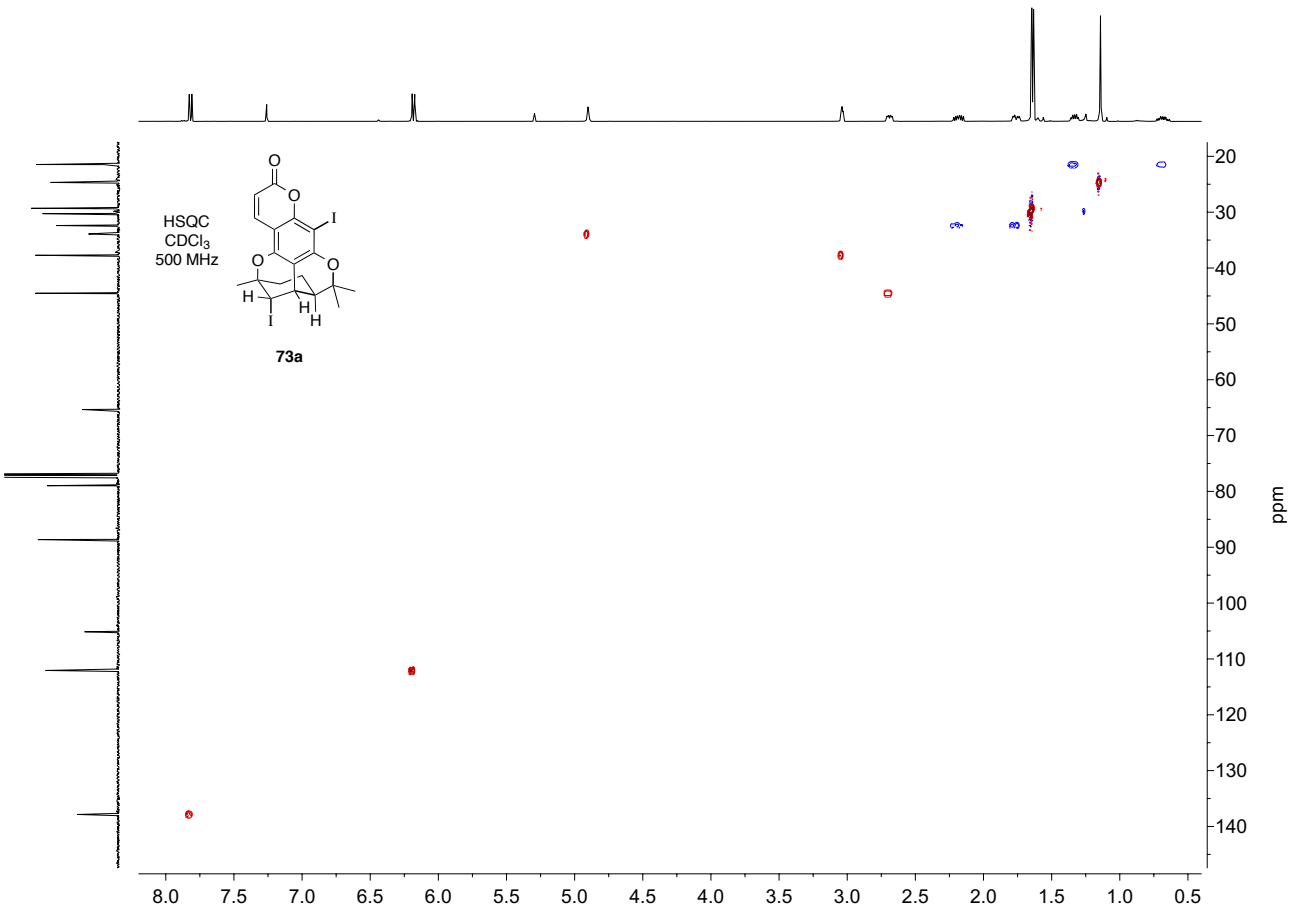
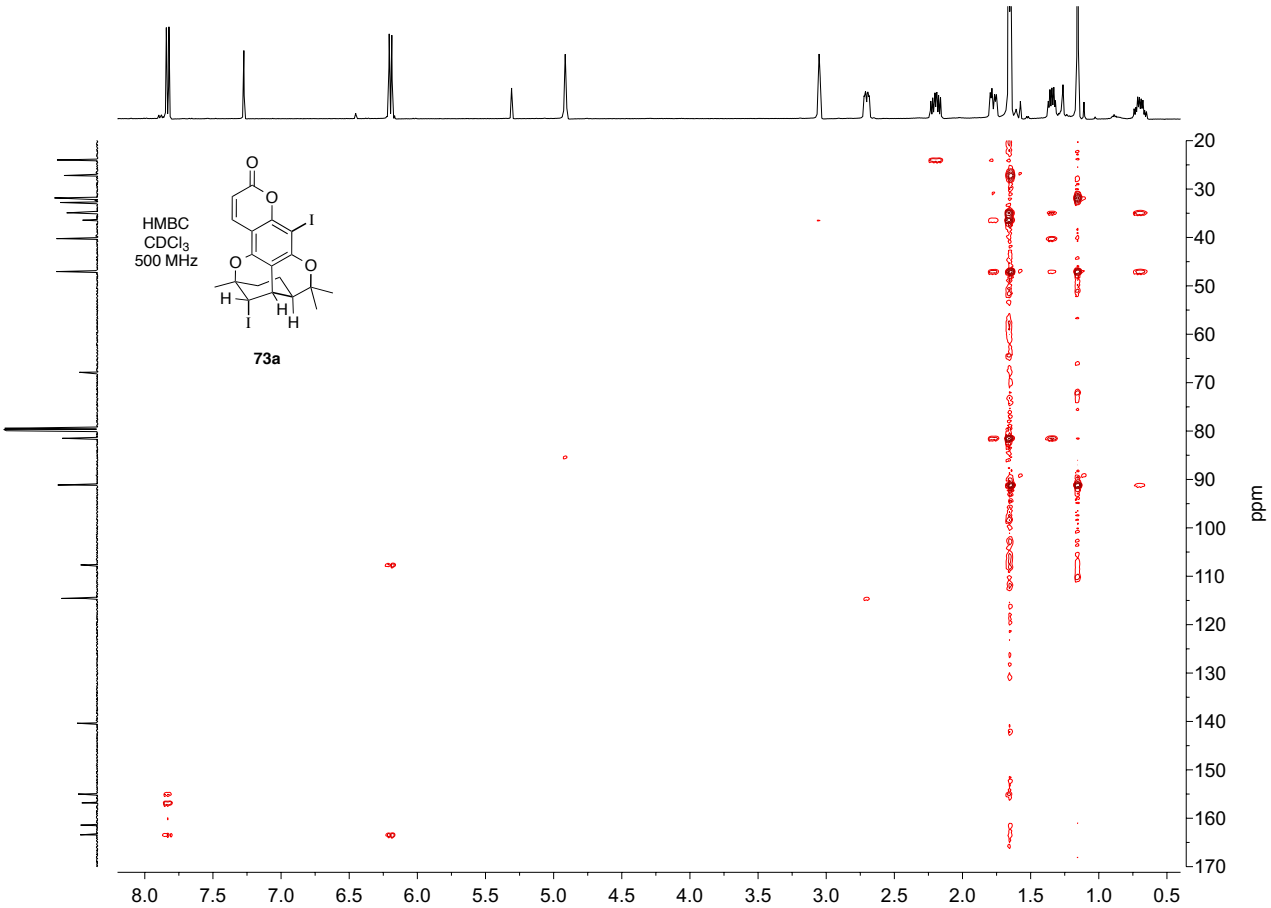

COSY
CDCl3
500 MHz
73a
ppm


HSQC
CDCl3
500 MHz
73a
ppm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500 MHz
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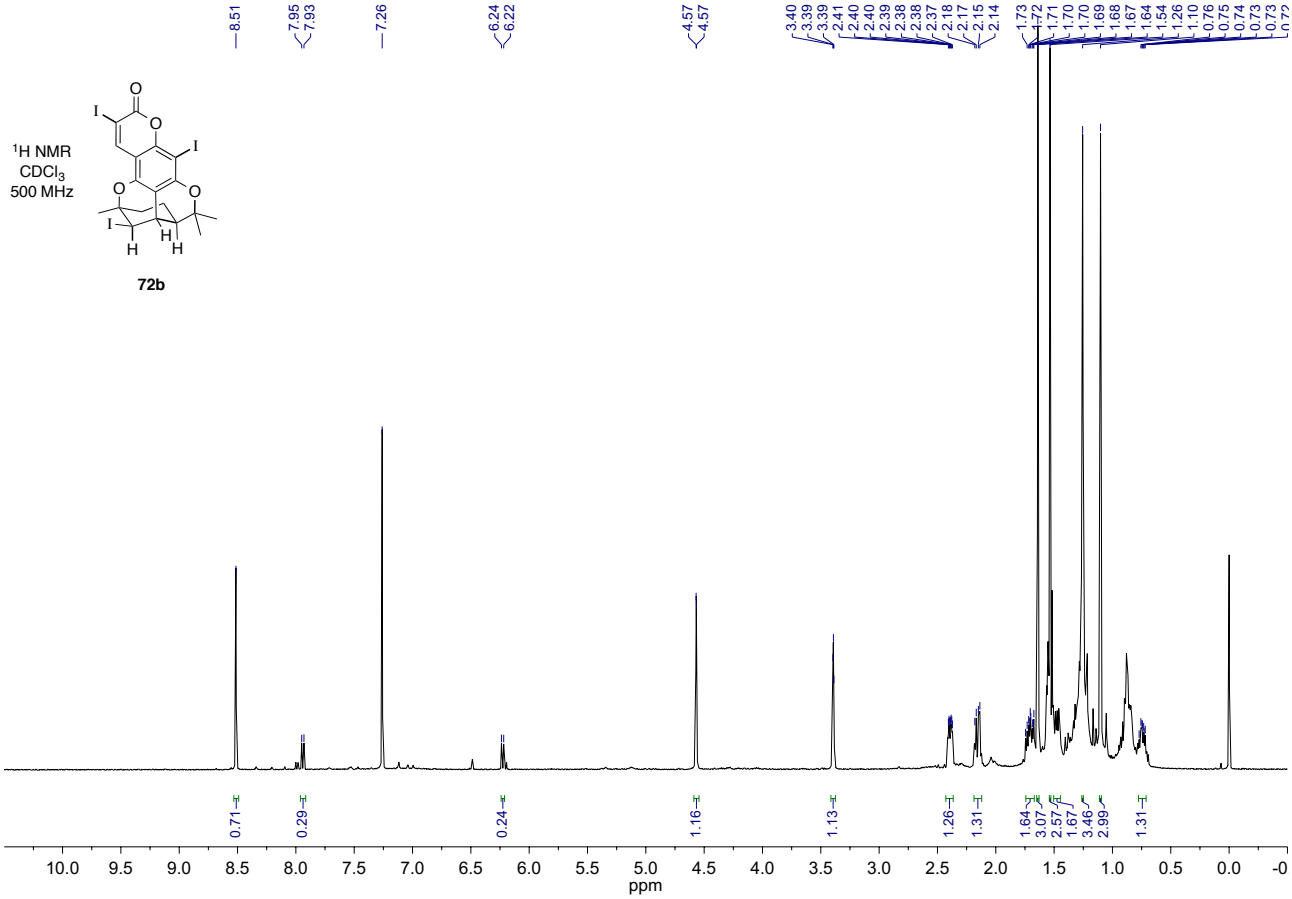
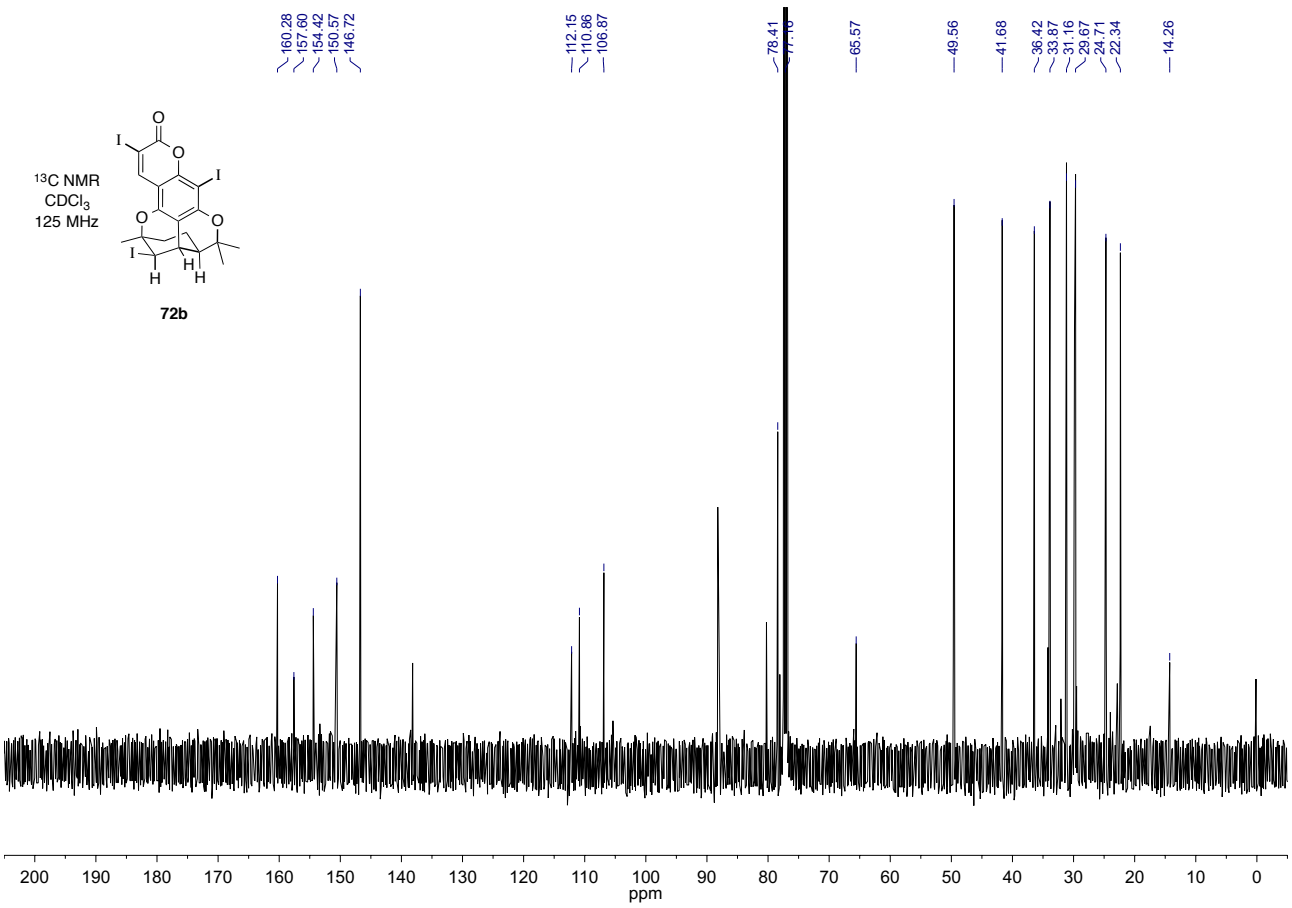
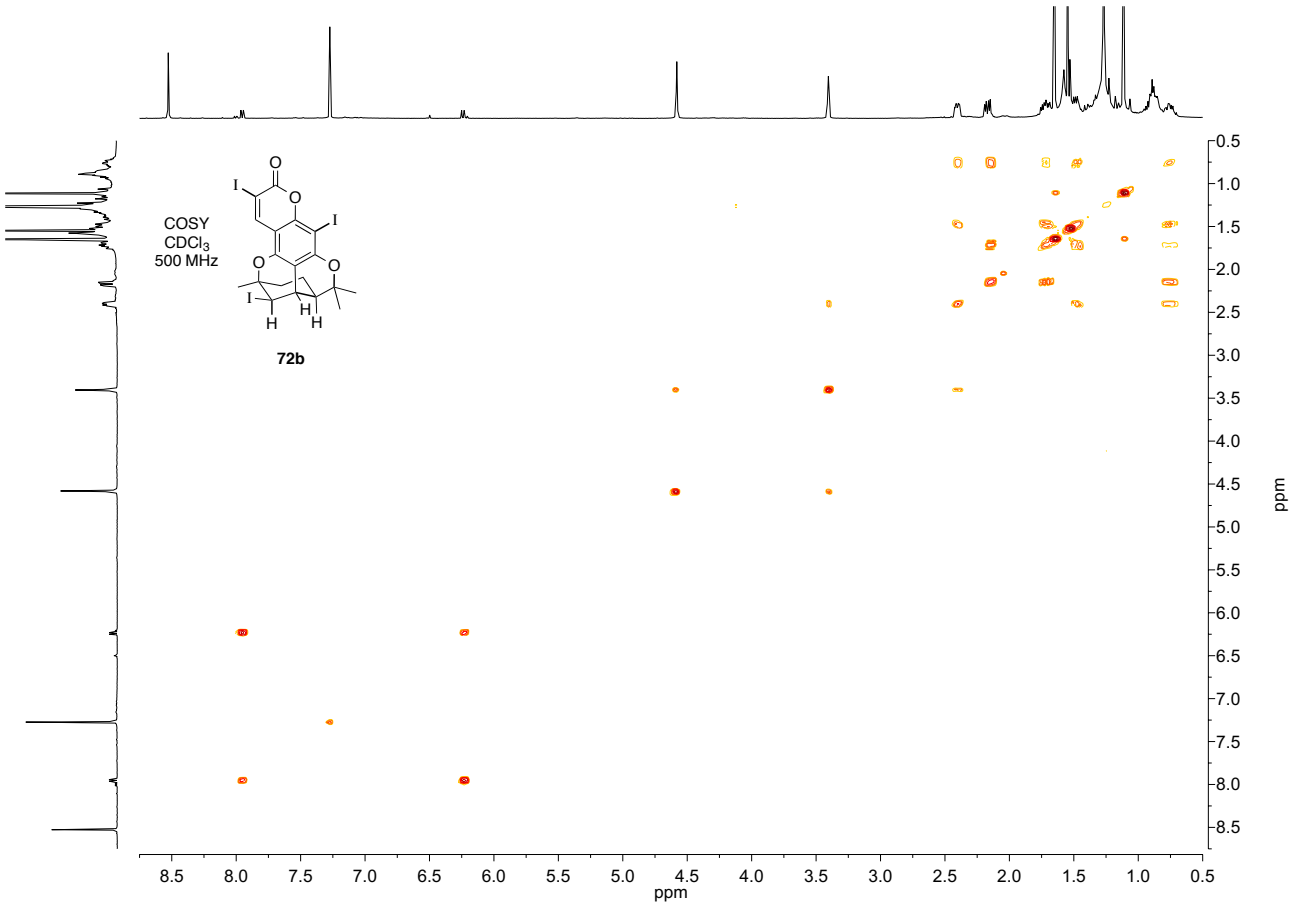
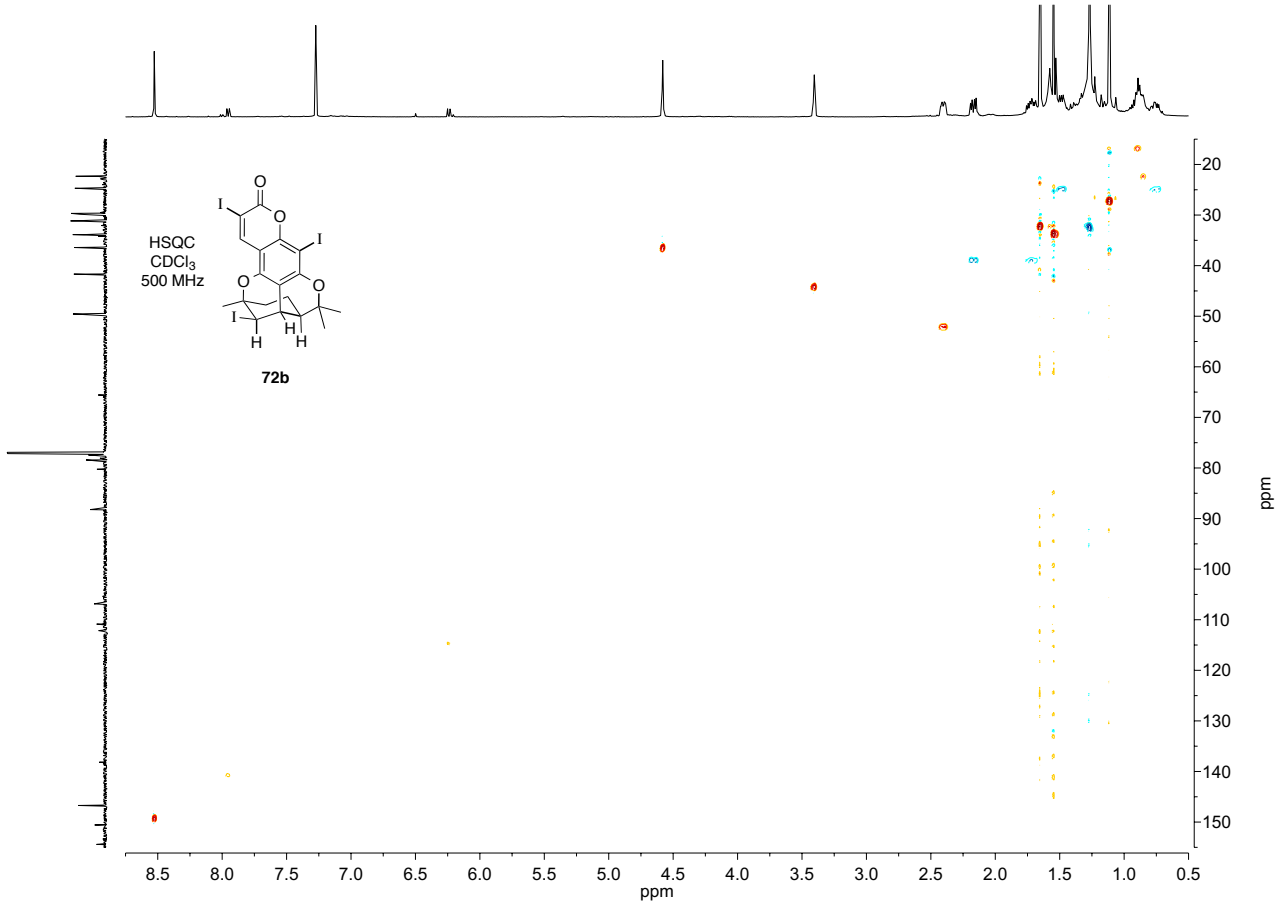
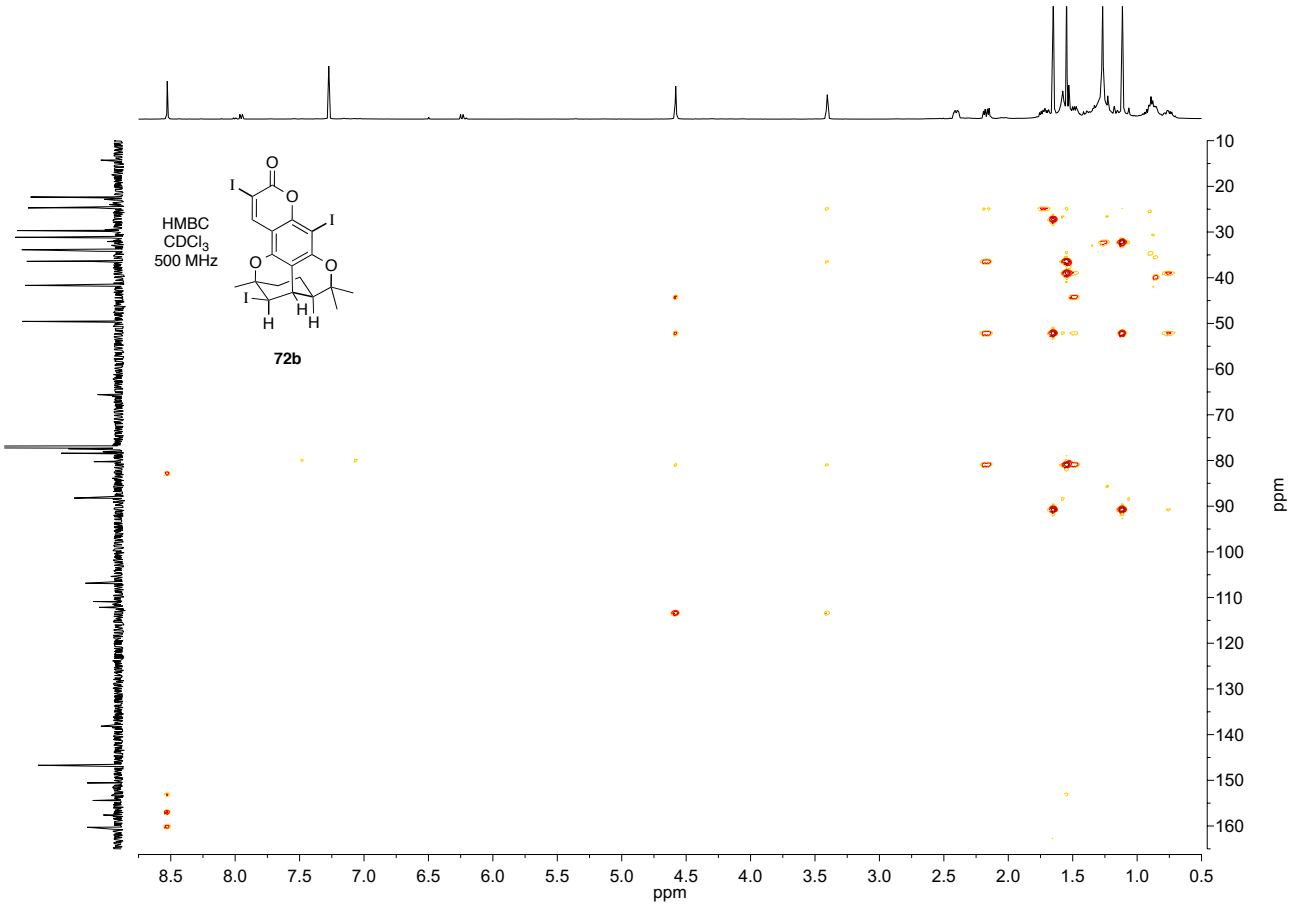
ppm

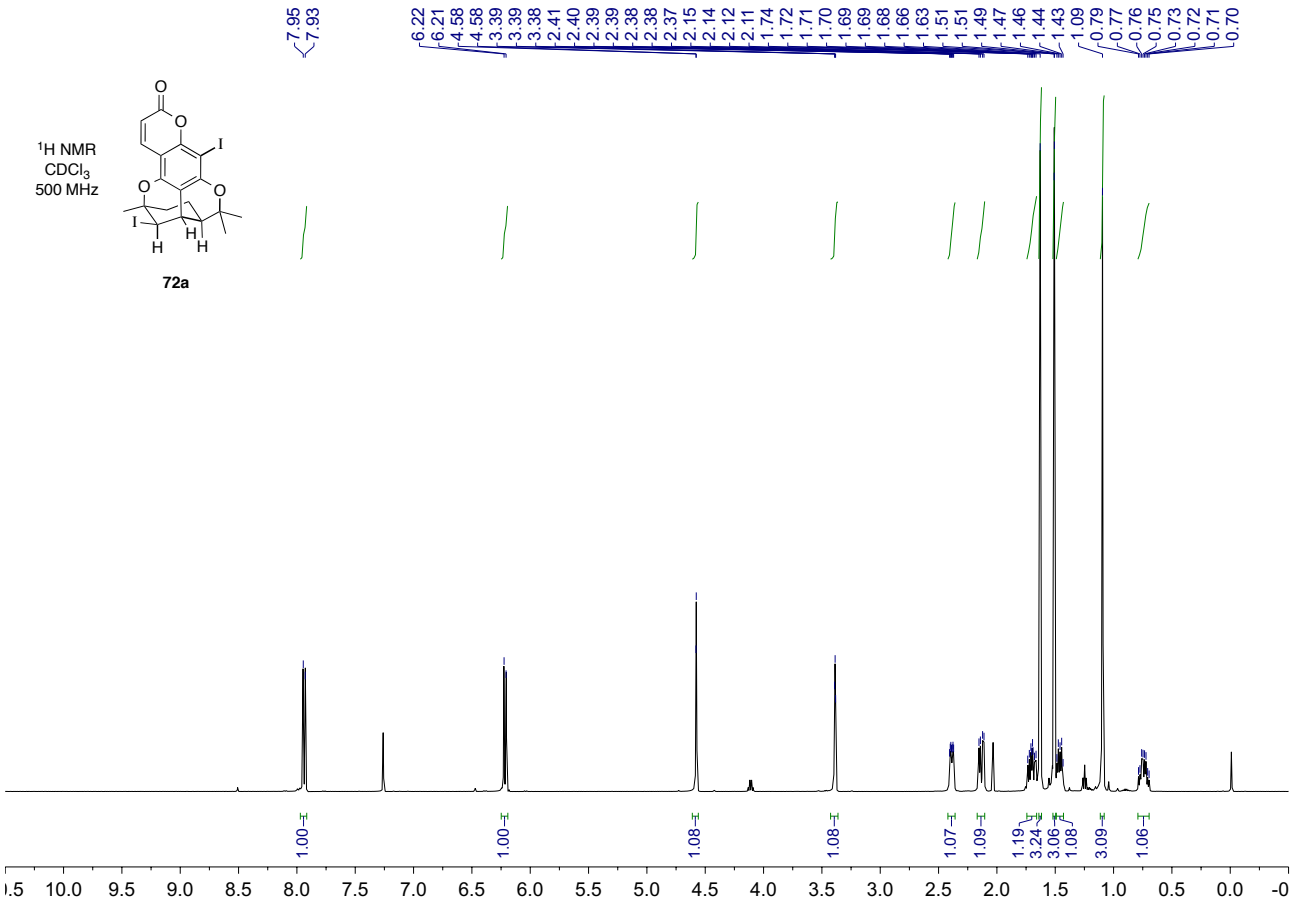

^{1}H NMR
$CDCl_3$
500 MHz
72b
8.51
7.95
7.93
7.26
6.24
6.22
4.57
4.57
3.40
3.39
3.39
2.41
2.40
2.40
2.39
2.38
2.38
2.37
2.18
2.17
2.15
2.14
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.67
1.64
1.54
1.26
1.10
0.76
0.75
0.74
0.73
0.73
0.72
0.71
0.29
0.24
1.16
1.13
1.26
1.31
1.64
3.07
2.57
1.67
3.46
2.99
1.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm

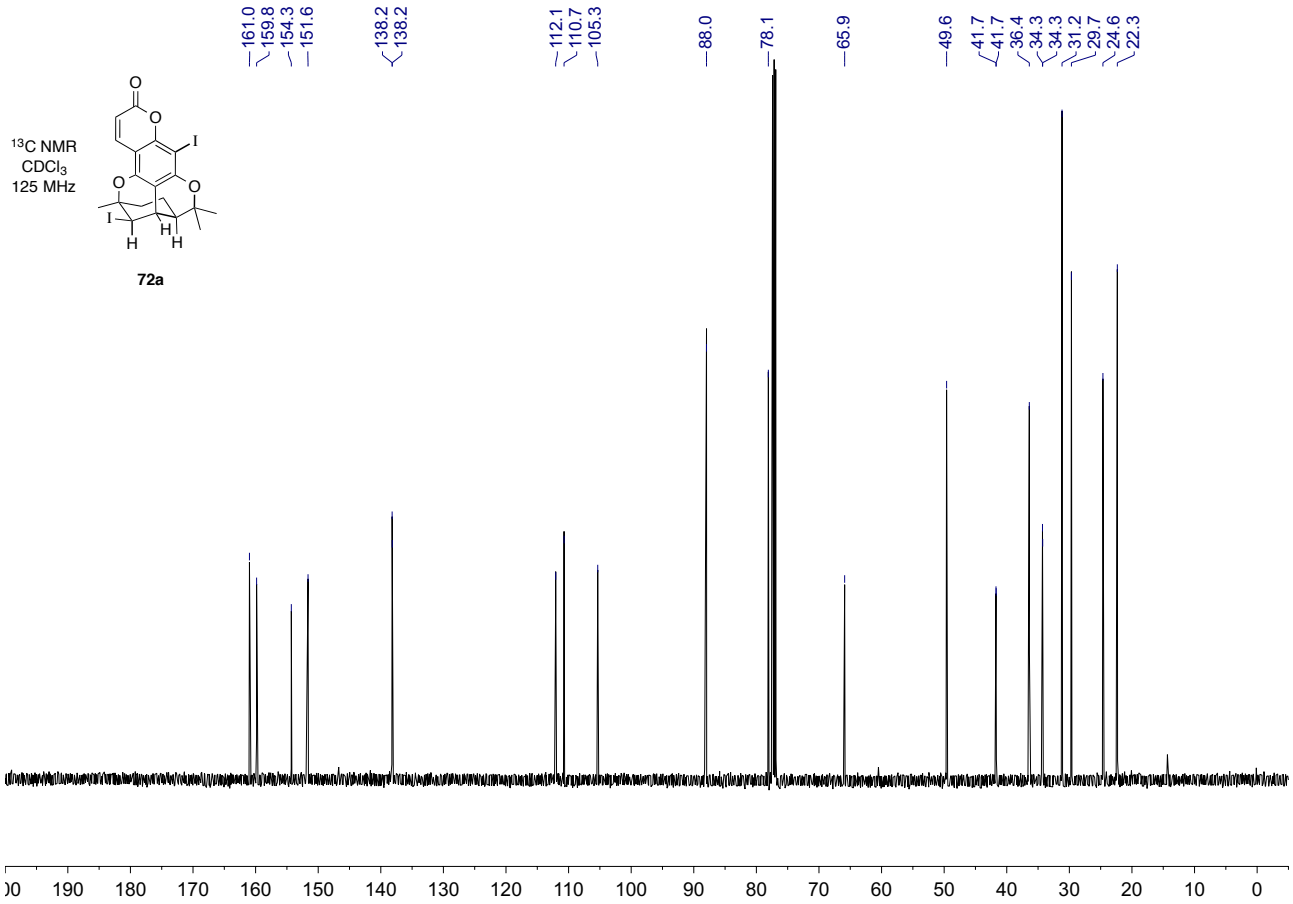

^{13}C NMR
$CDCl_3$
125 MHz
72b
160.28
157.60
154.42
150.57
146.72
112.15
110.86
106.87
78.41
65.57
49.56
41.68
36.42
33.87
31.16
29.67
24.71
22.34
14.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

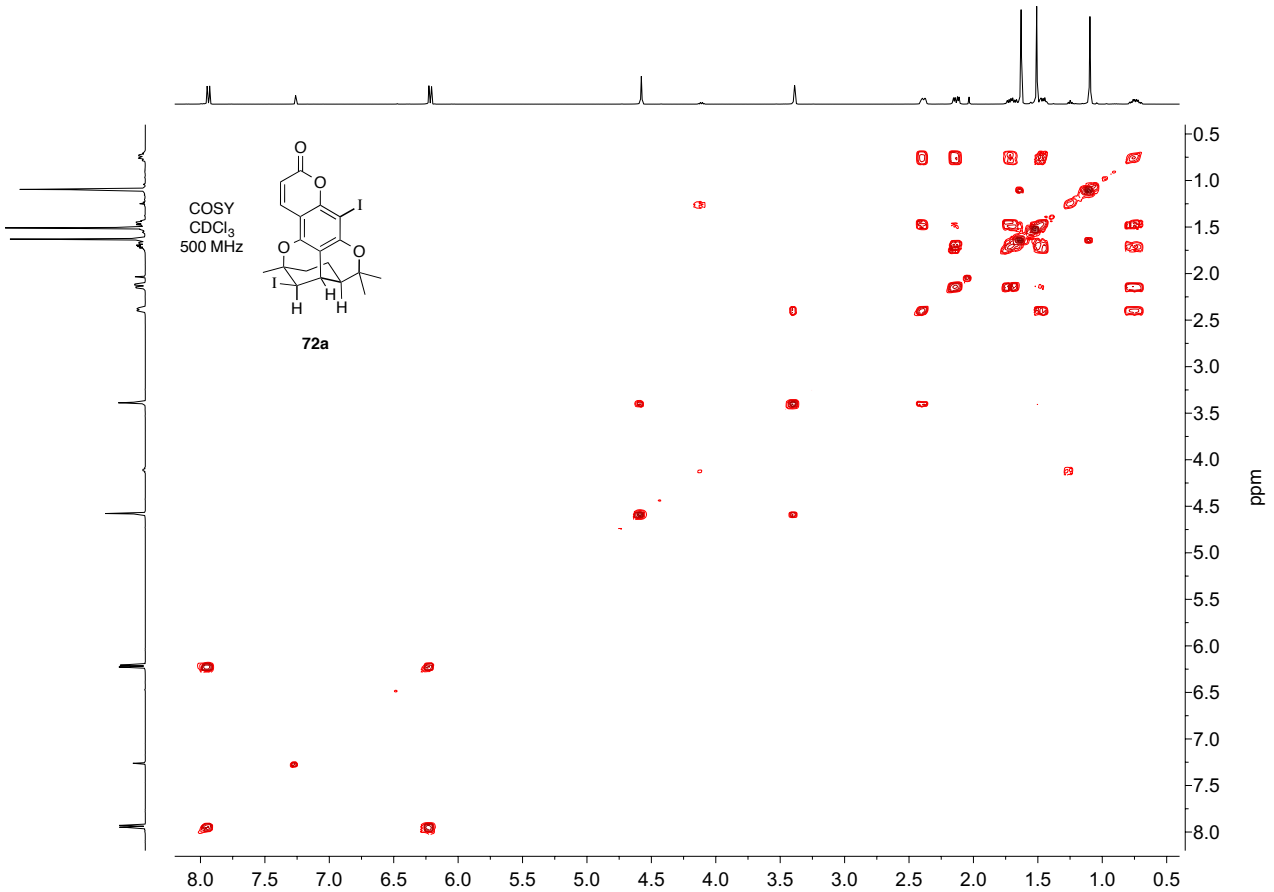

COSY
CDCl3
500 MHz
72b
ppm
ppm

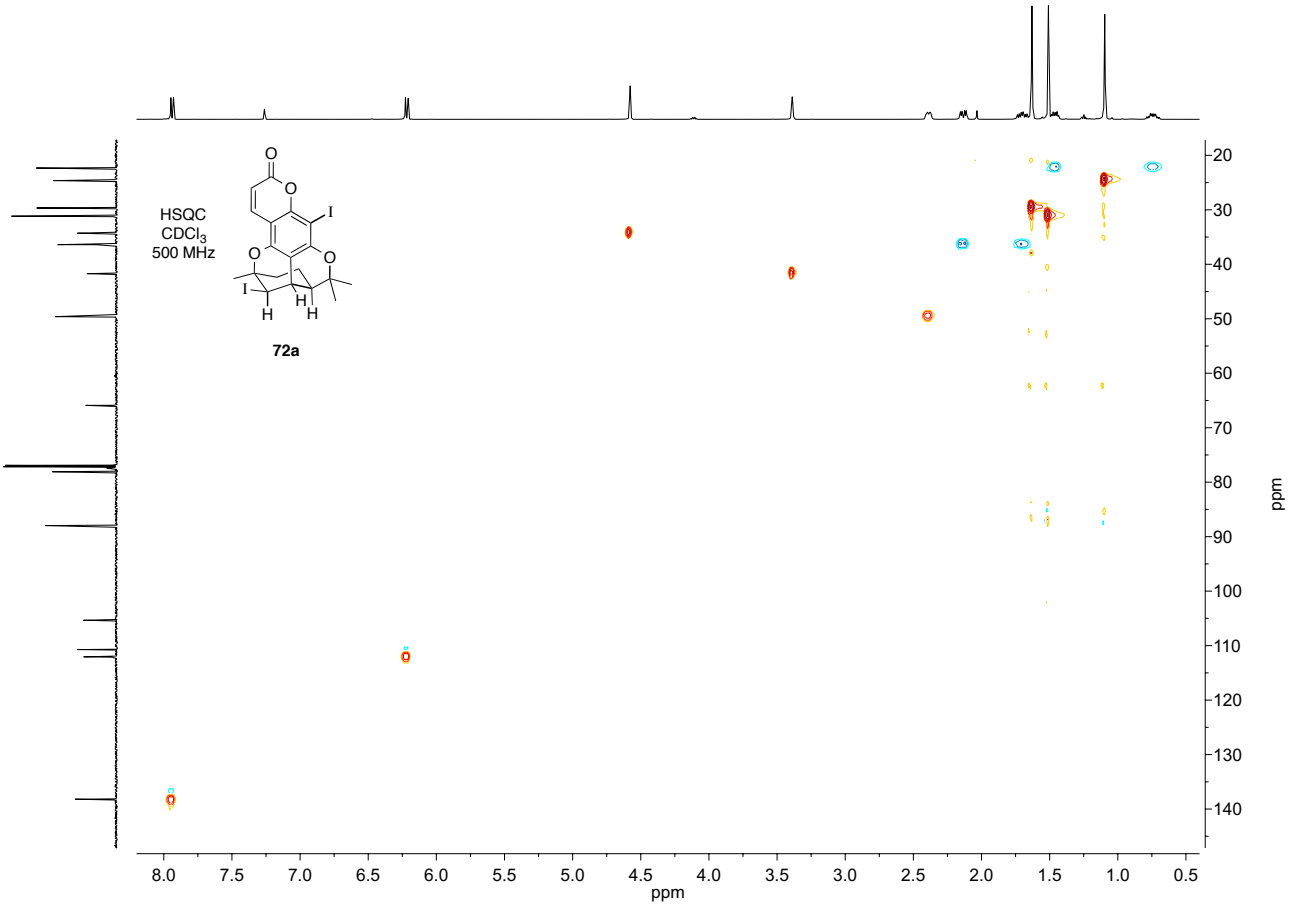

HSQC
CDCl3
500 MHz
72b
ppm
ppm

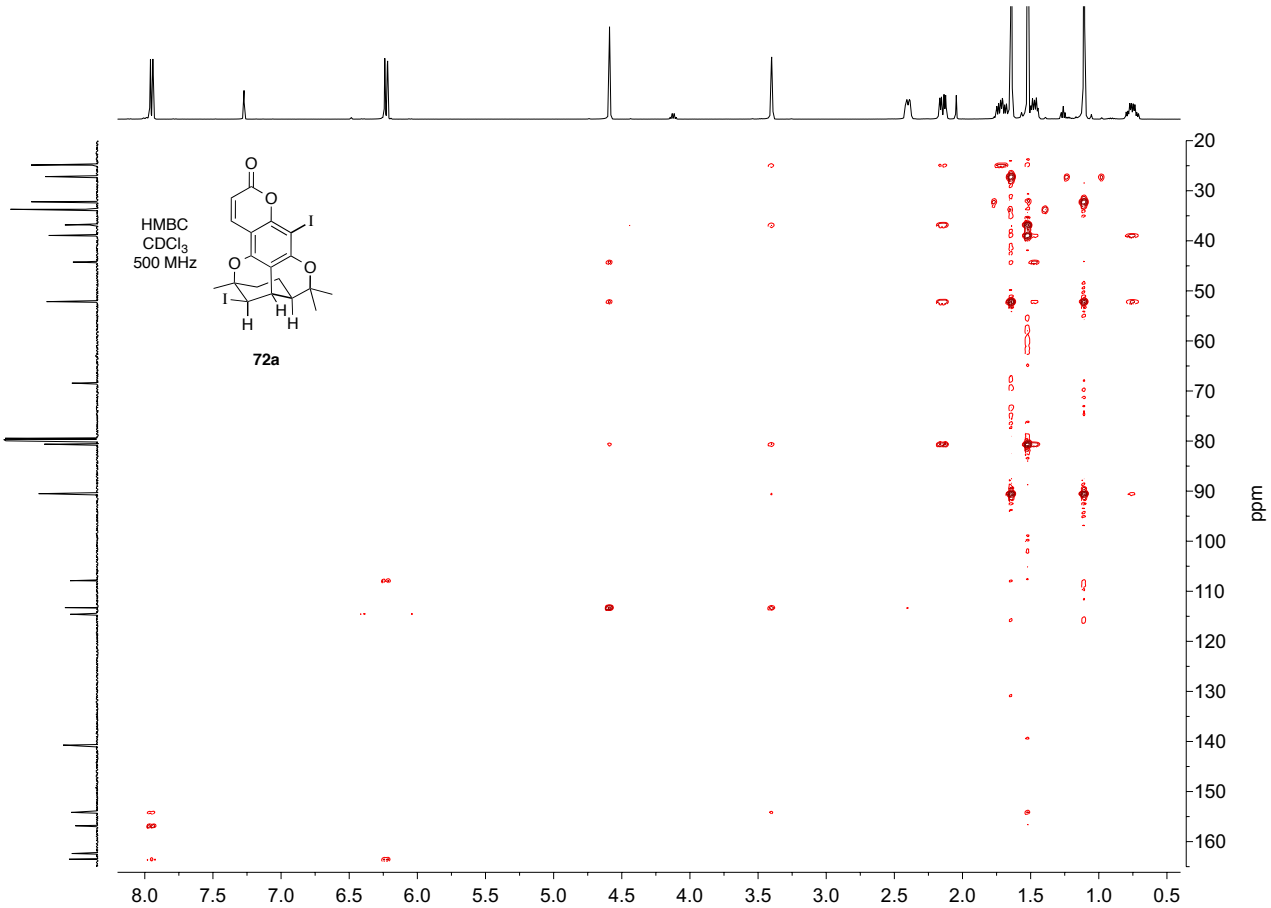

HMBC
CDCl3
500 MHz
72b
ppm
ppm

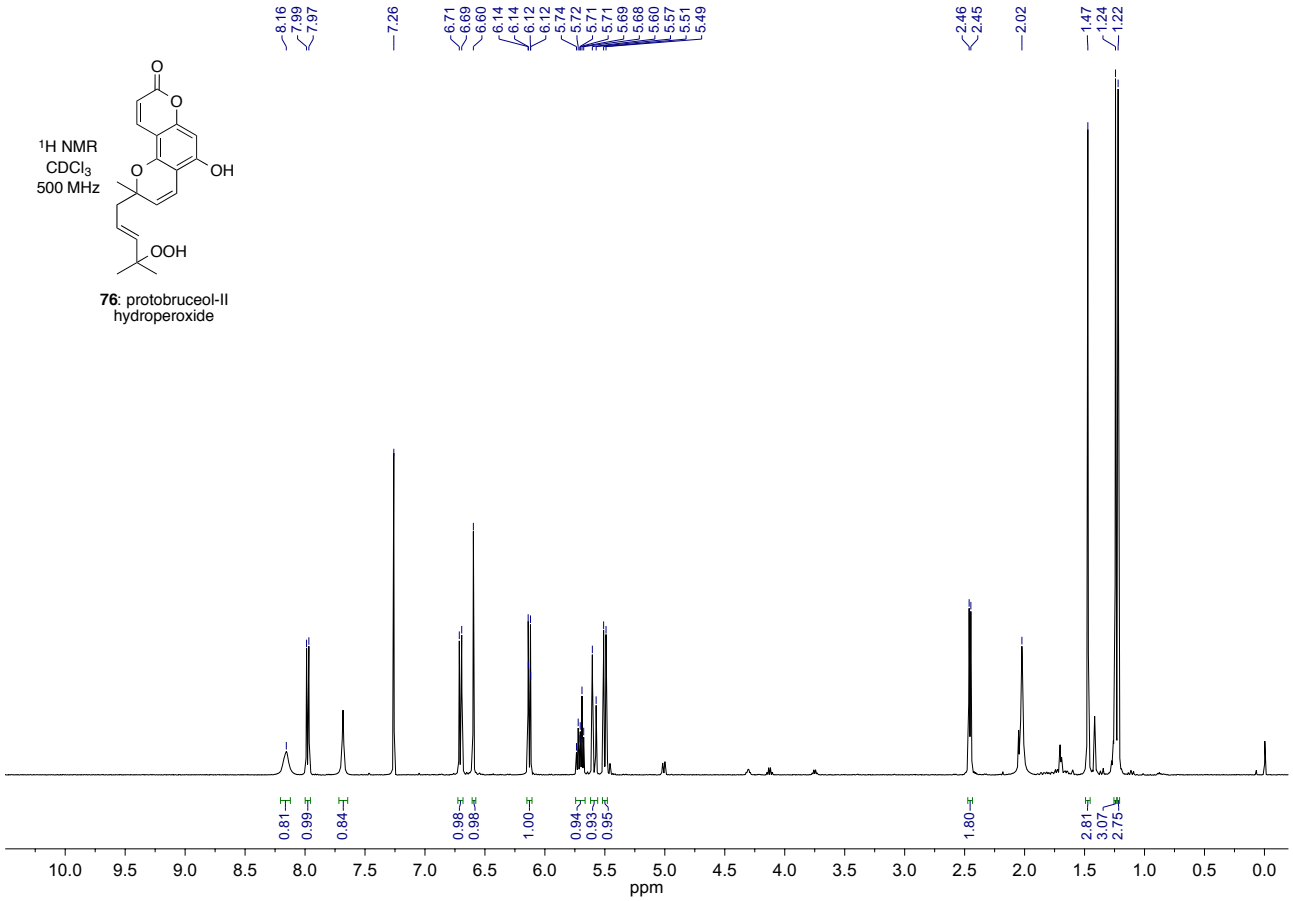

^{1}H NMR
$CDCl_3$
500 MHz
72a
7.95
7.93
6.22
6.21
4.58
4.58
3.39
3.39
3.38
2.41
2.40
2.39
2.39
2.38
2.38
2.37
2.15
2.14
2.12
2.11
1.74
1.72
1.71
1.70
1.69
1.69
1.68
1.66
1.63
1.51
1.51
1.49
1.47
1.46
1.44
1.43
1.09
0.79
0.77
0.76
0.75
0.73
0.72
0.71
0.70
1.00
1.00
1.08
1.08
1.07
1.09
1.19
3.24
3.06
1.08
3.09
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

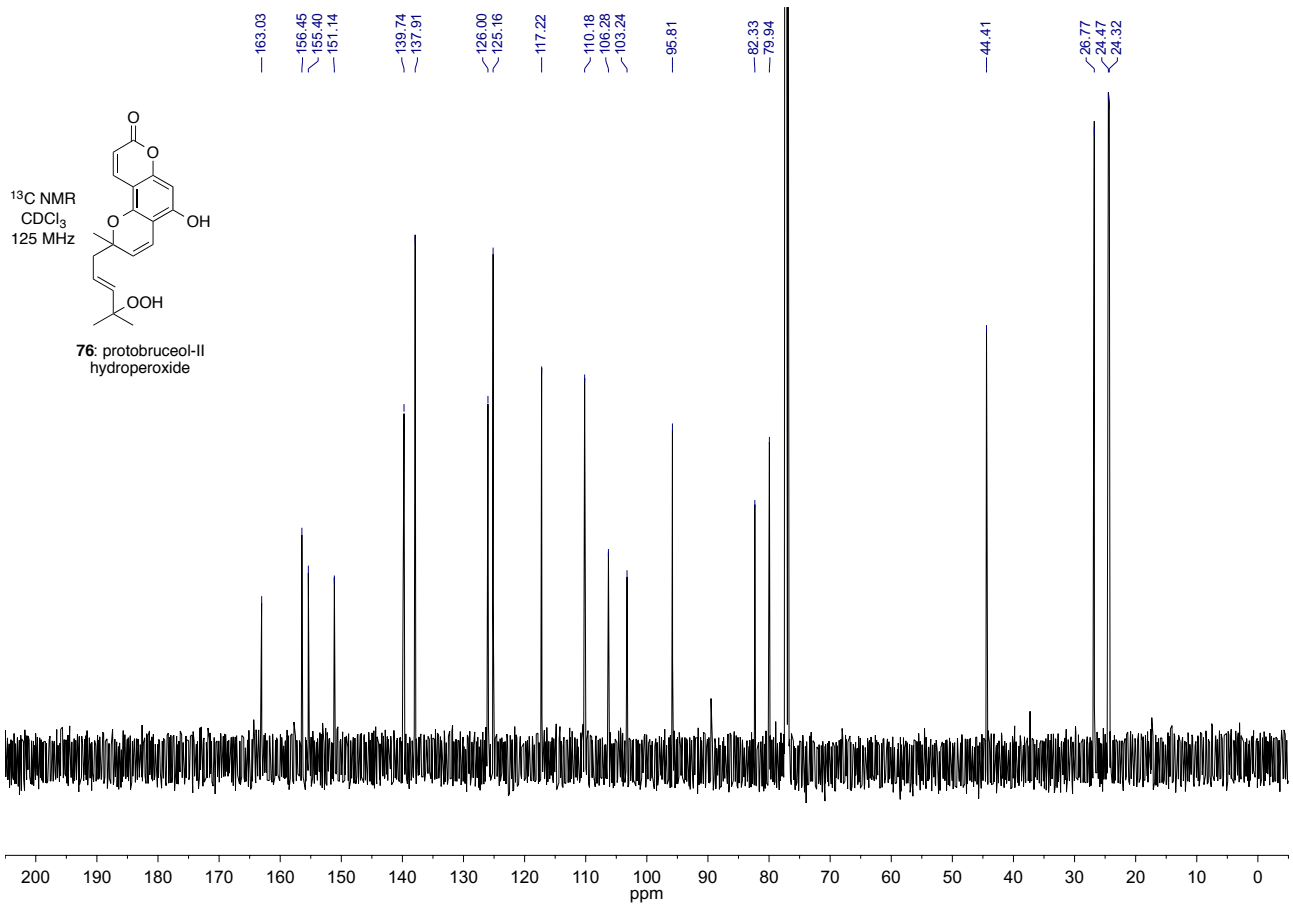

^{13}C NMR
$CDCl_3$
125 MHz
72a
161.0
159.8
154.3
151.6
138.2
138.2
112.1
110.7
105.3
88.0
78.1
65.9
49.6
41.7
41.7
36.4
34.3
34.3
31.2
29.7
24.6
22.3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

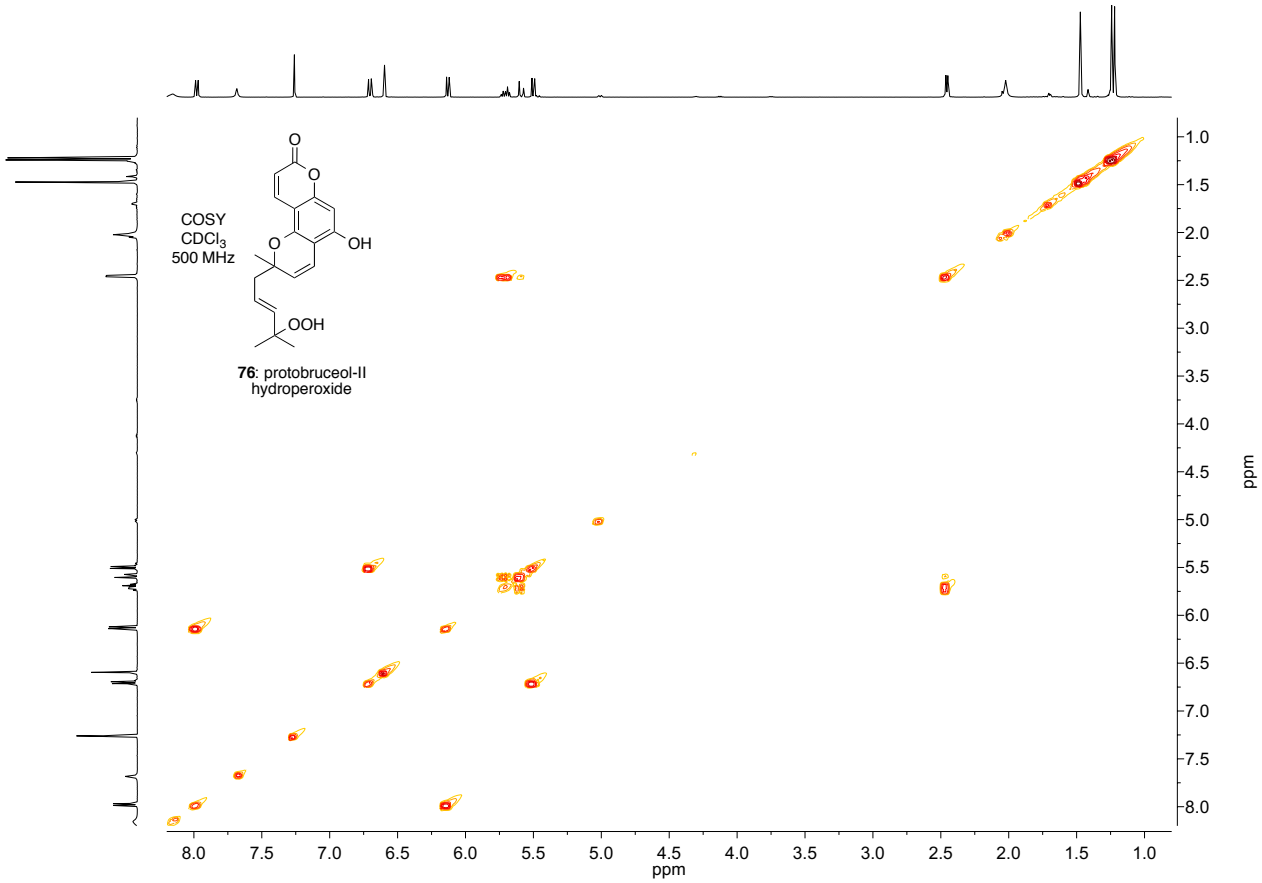

COSY
CDCl3
500 MHz
72a
ppm

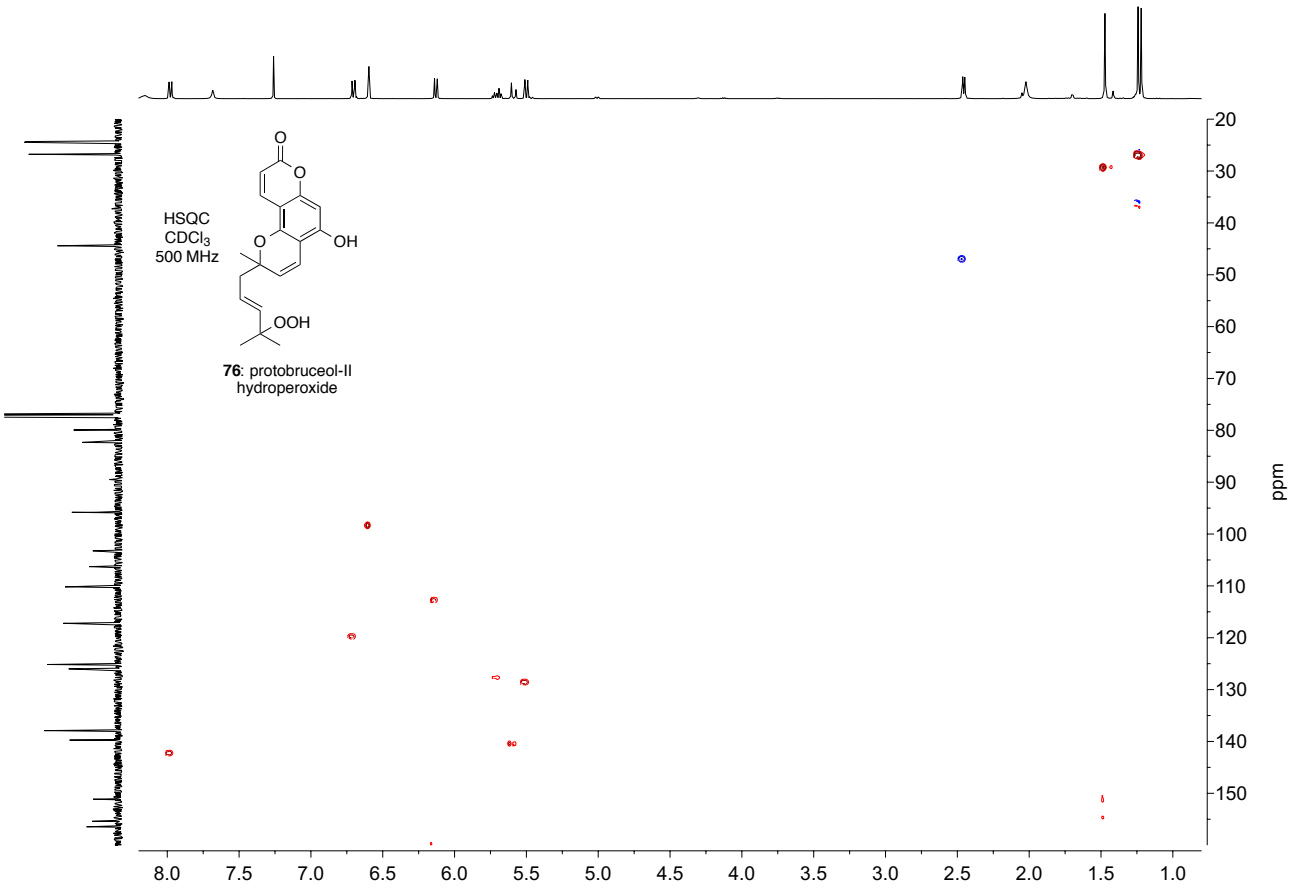

HSQC
CDCl3
500 MHz
72a
ppm

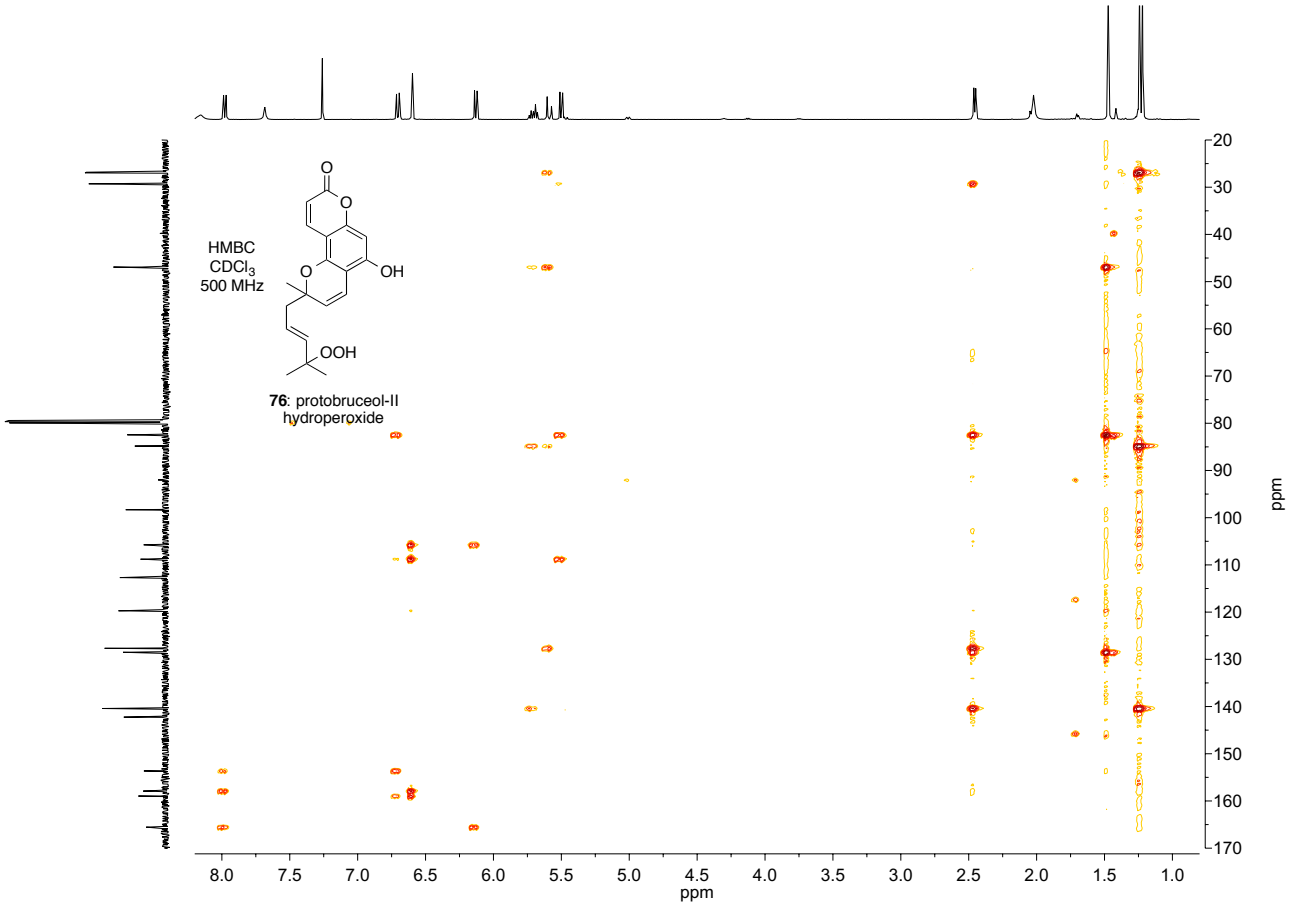

HMBC
CDCl3
500 MHz
72a
ppm

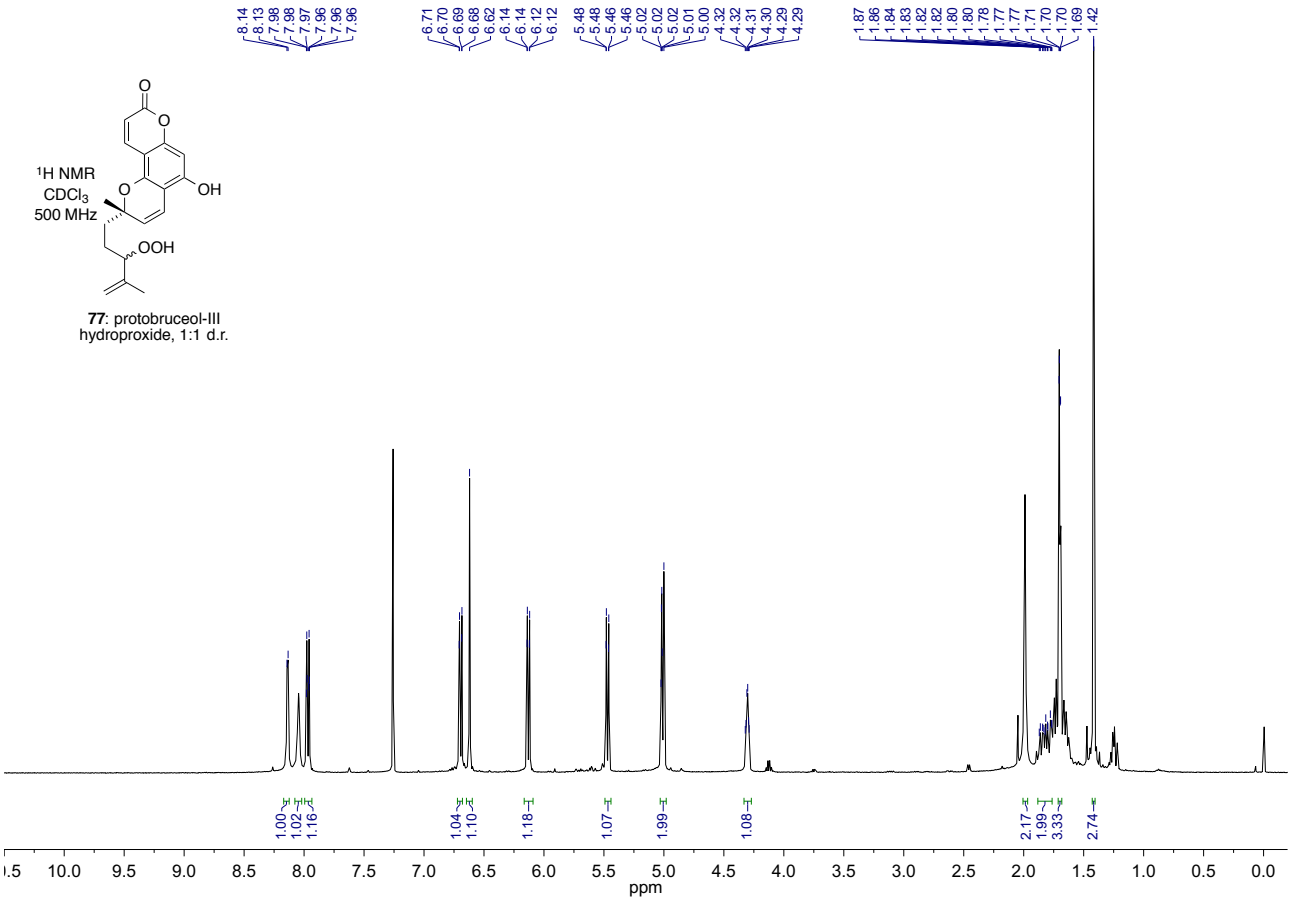

8.16
7.99
7.97
7.26
6.71
6.69
6.60
6.14
6.14
6.12
6.12
5.74
5.72
5.71
5.71
5.69
5.68
5.60
5.57
5.51
5.49
2.46
2.45
2.02
1.47
1.24
1.22
0.81
0.99
0.84
0.98
0.98
1.00
0.94
0.93
0.95
1.80
2.81
3.07
2.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
^{1}H NMR
$CDCl_3$
500 MHz
OH
OOH
76: protobruceol-II
hydroperoxide

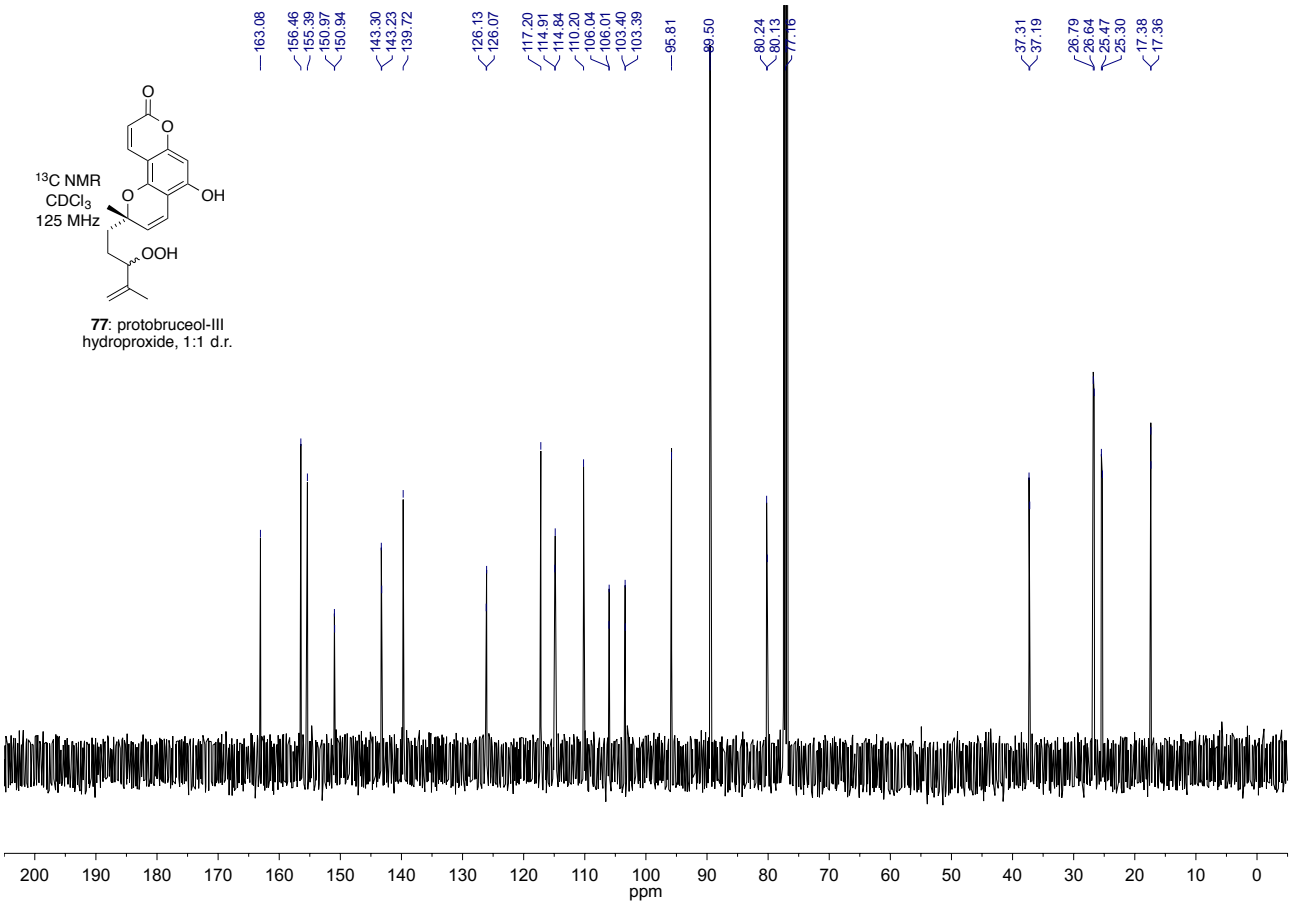

163.03
156.45
155.40
151.14
139.74
137.91
126.00
125.16
117.22
110.18
106.28
103.24
95.81
82.33
79.94
44.41
26.77
24.47
24.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
^{13}C NMR
$CDCl_3$
125 MHz
OH
OOH
76: protobruceol-II
hydroperoxide

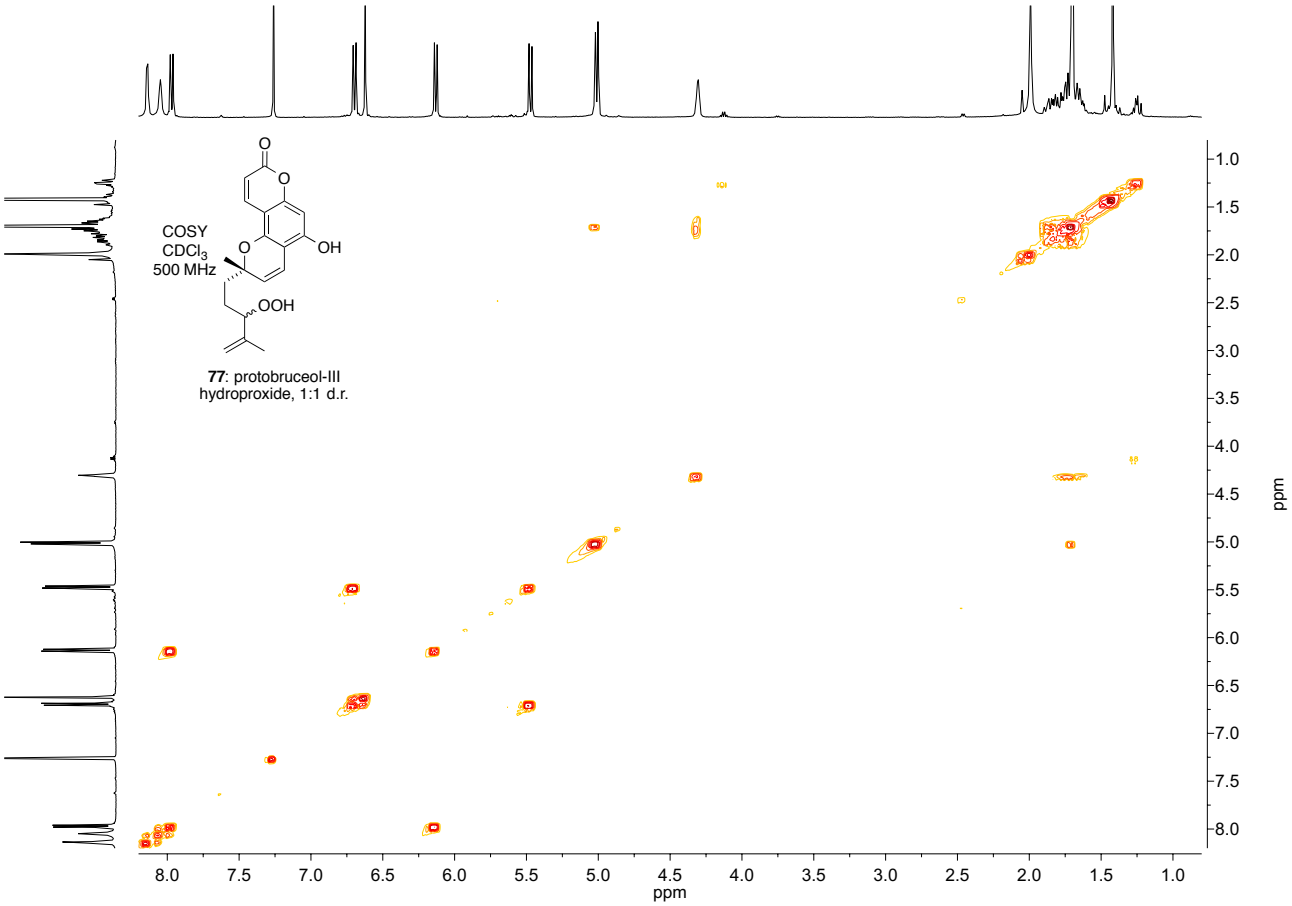

COSY
CDCl3
500 MHz
O
O
O
OH
OOH
76: protobruceol-II
hydroperoxide
ppm
ppm

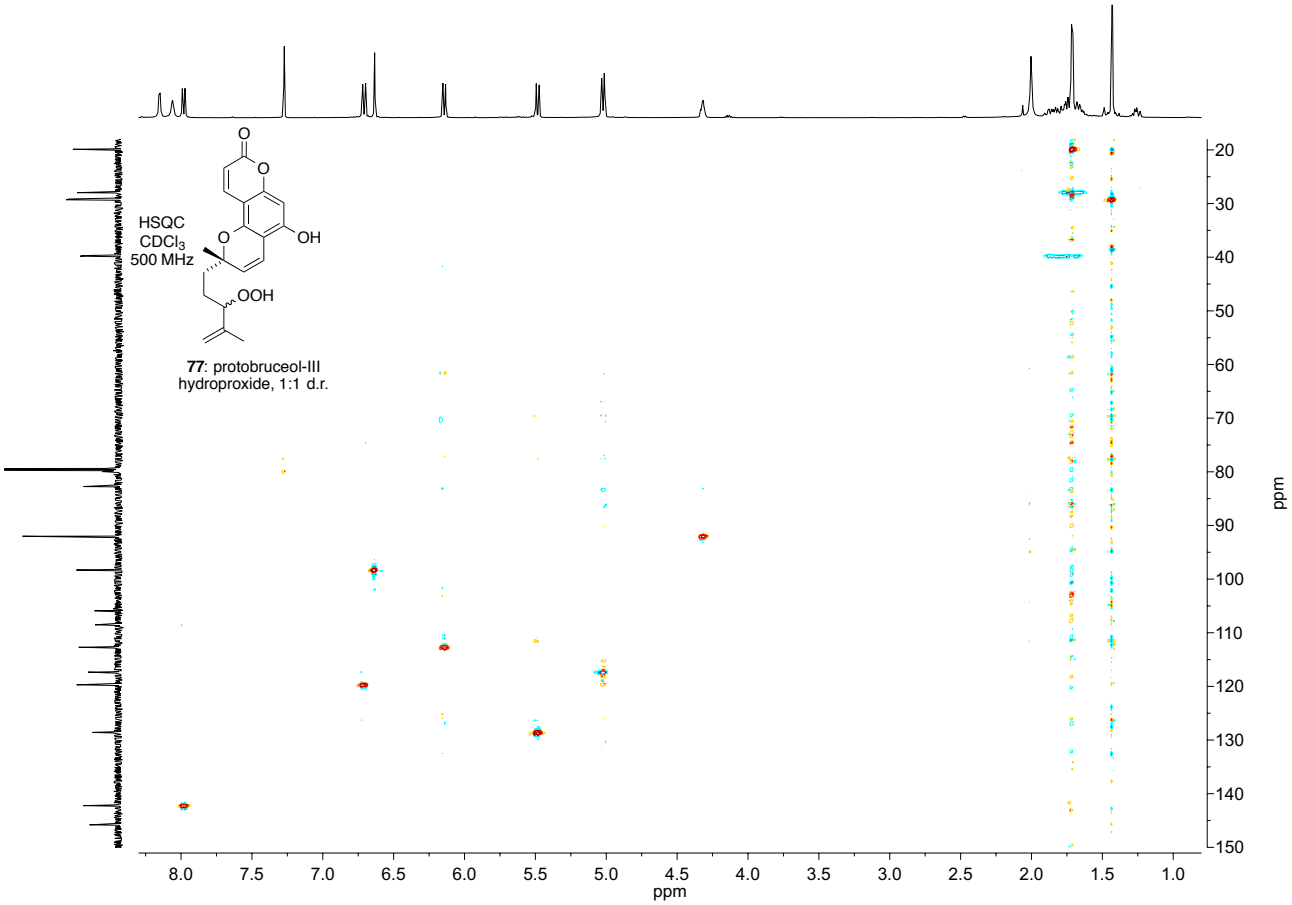

HSQC
CDCl3
500 MHz
O
O
O
OH
OOH
76: protobruceol-II
hydroperoxide
ppm
ppm

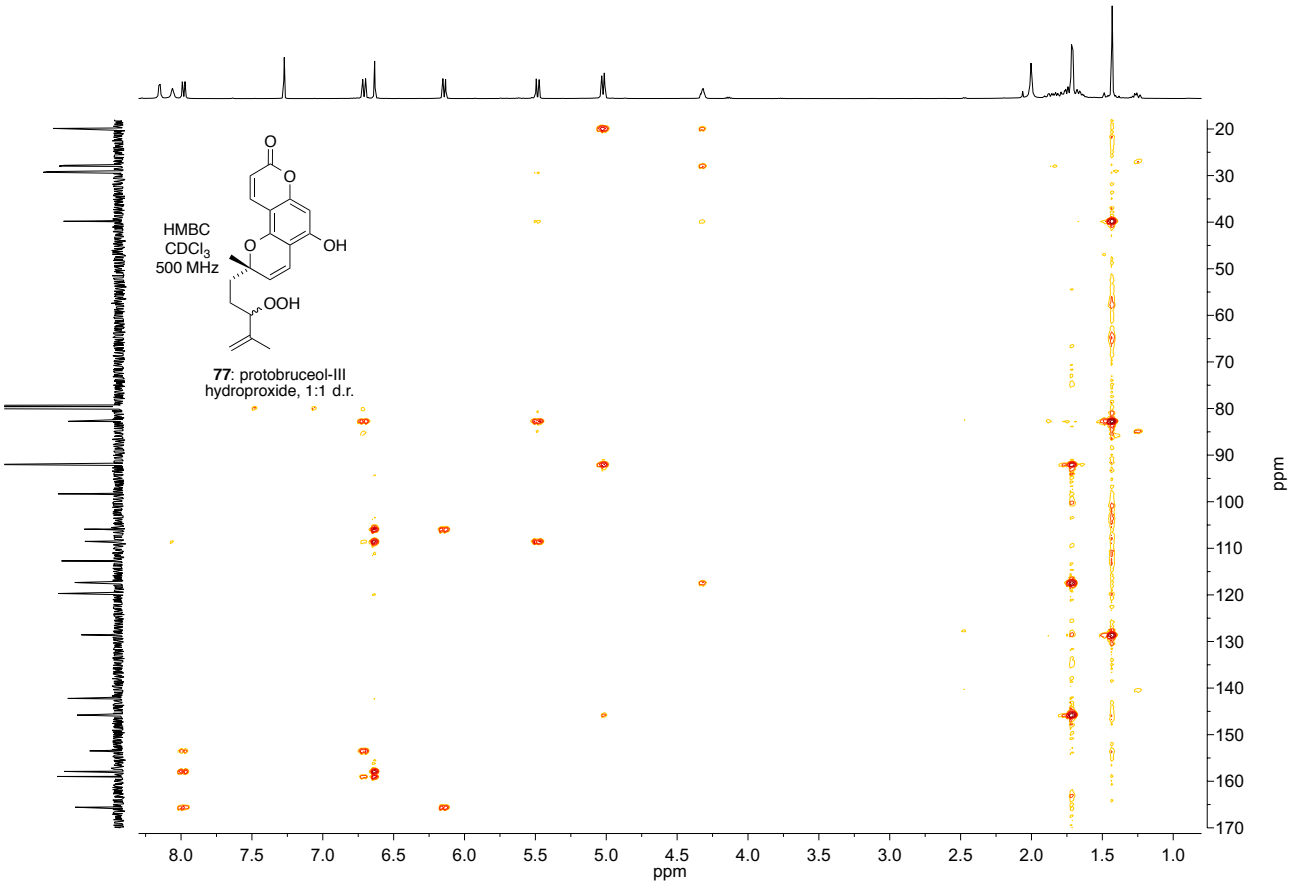

HMBC
CDCl3
500 MHz
OH
OOH
76: protobruceol-II
hydroperoxide
ppm
ppm

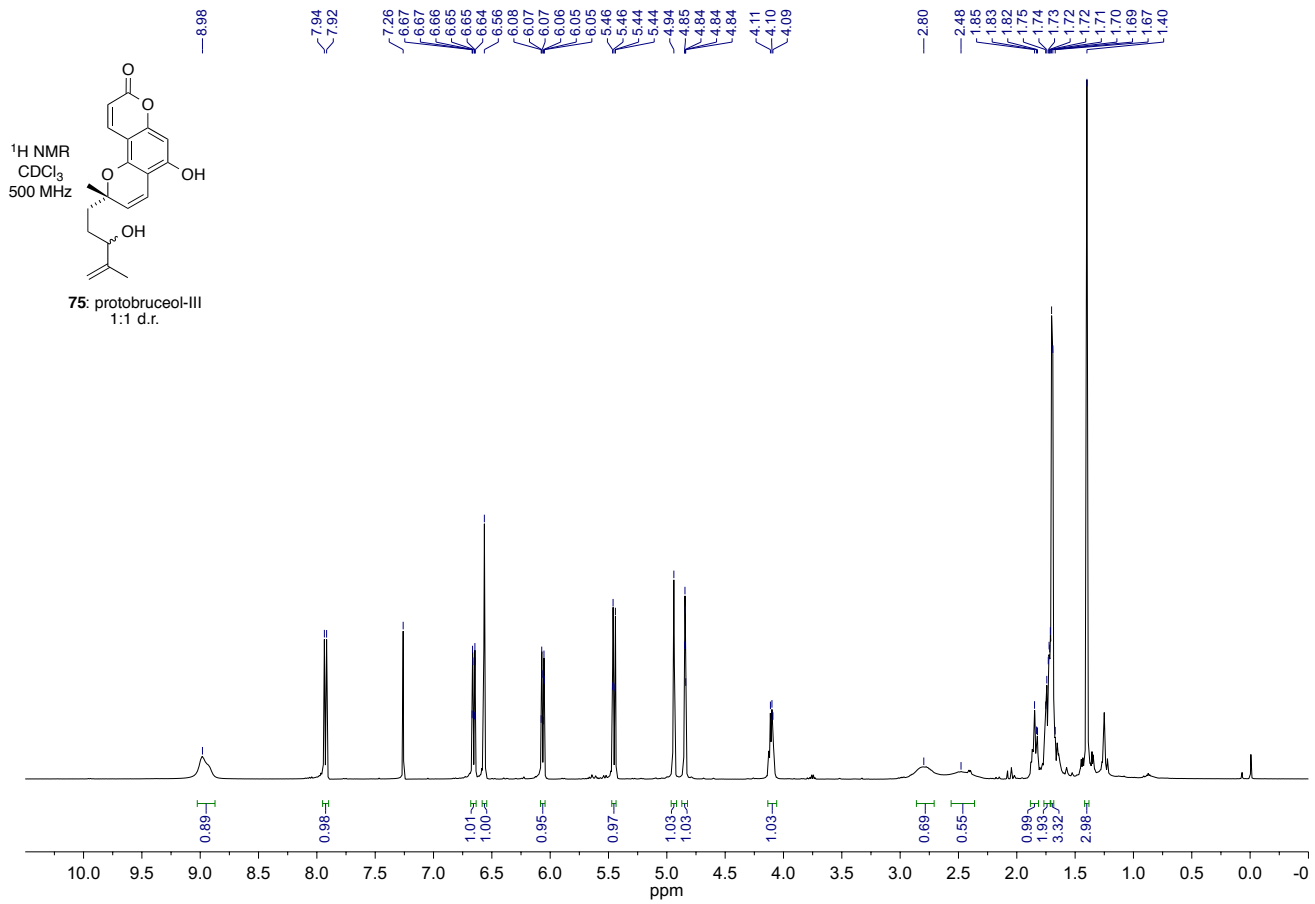

8.14
8.13
7.98
7.98
7.97
7.96
7.96
7.96
6.71
6.70
6.69
6.68
6.62
6.14
6.14
6.12
6.12
5.48
5.48
5.46
5.46
5.02
5.02
5.02
5.01
5.00
4.32
4.32
4.31
4.30
4.29
4.29
1.87
1.86
1.84
1.83
1.82
1.82
1.80
1.80
1.78
1.77
1.77
1.71
1.70
1.70
1.69
1.42
^{1}H NMR
$CDCl_3$
500 MHz
OH
OOH
77: protobruceol-III
hydroproxide, 1:1 d.r.
1.00
1.02
1.16
1.04
1.10
1.18
1.07
1.99
1.08
2.17
1.99
3.33
2.74
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

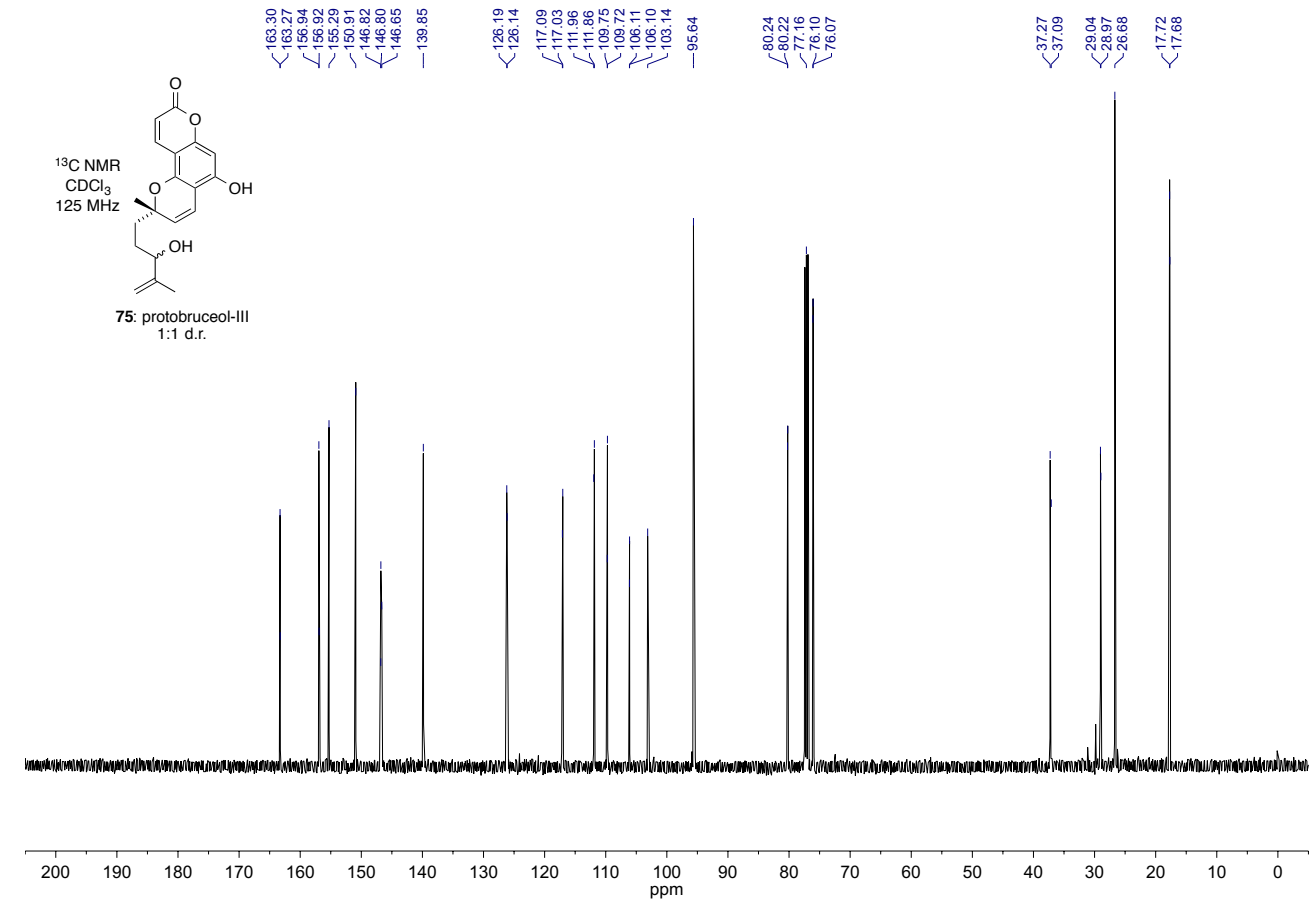

163.08
156.46
155.39
150.97
150.94
143.30
143.23
139.72
126.13
126.07
117.20
114.91
114.84
110.20
106.04
106.01
103.40
103.39
95.81
89.50
80.24
80.13
77.16
37.31
37.19
26.79
26.64
25.47
25.30
17.38
17.36
^{13}C NMR
$CDCl_3$
125 MHz
OH
OOH
77: protobruceol-III
hydroproxide, 1:1 d.r.
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

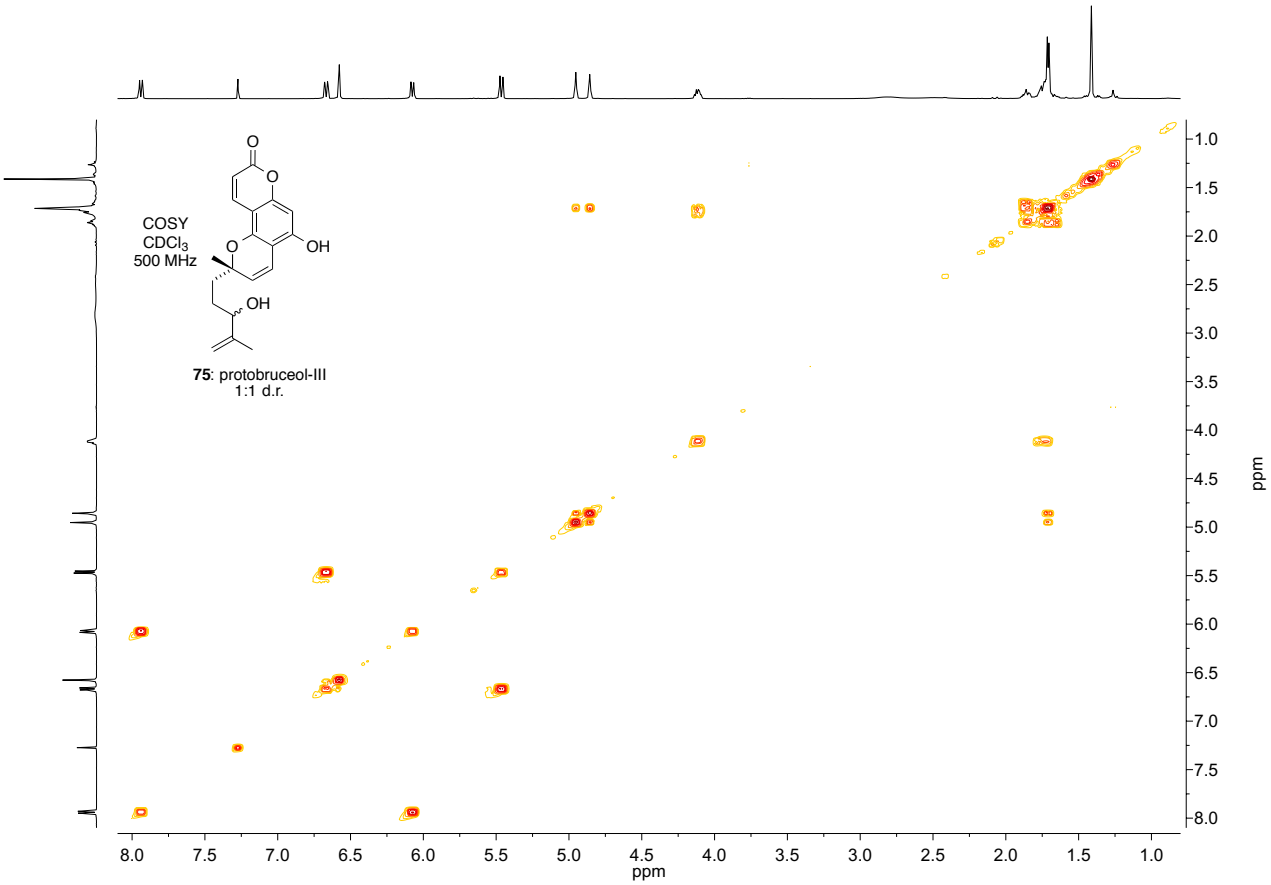

COSY
$CDCl_3$
500 MHz
77: protobruceol-III
hydroproxide, 1:1 d.r.
ppm

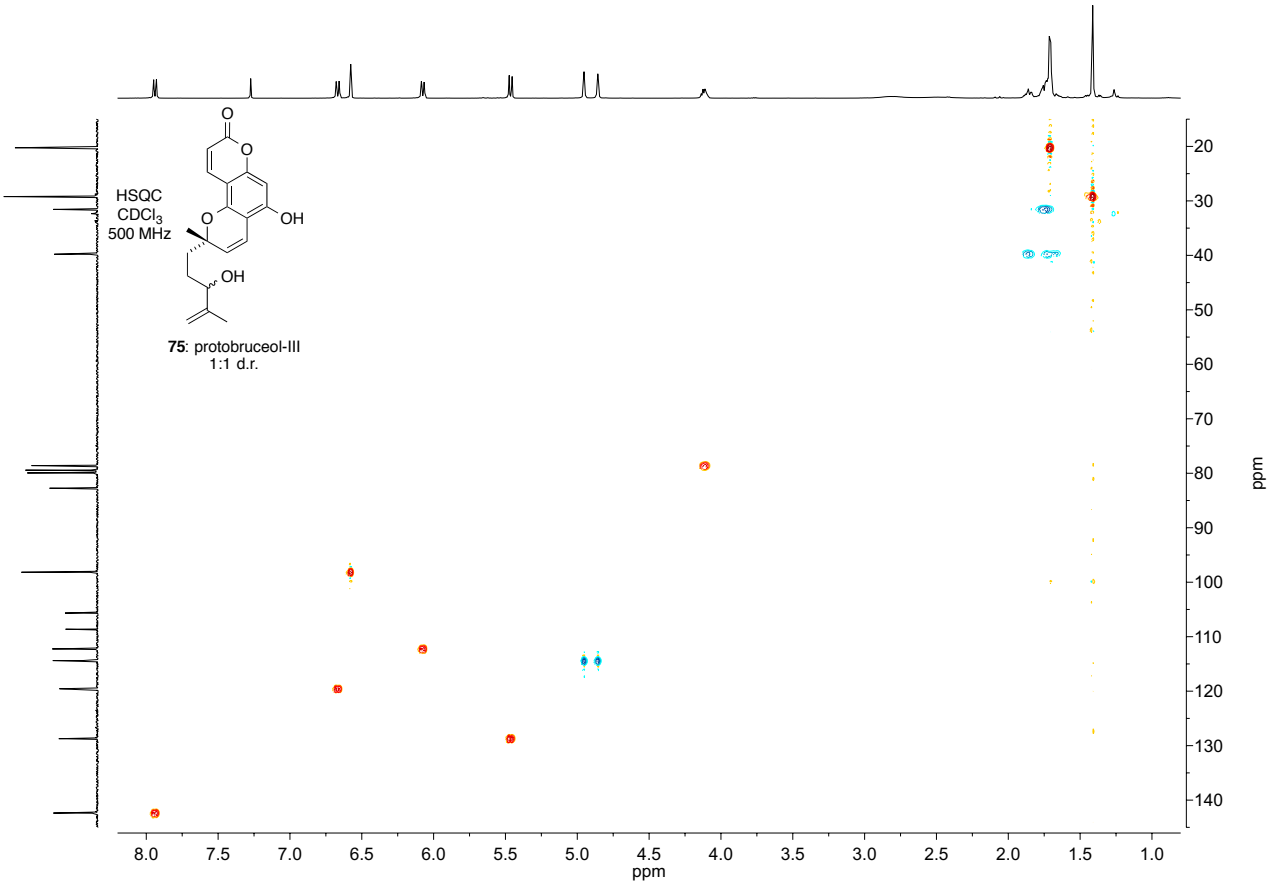

HSQC
$CDCl_3$
500 MHz
77: protobruceol-III
hydroproxide, 1:1 d.r.
ppm

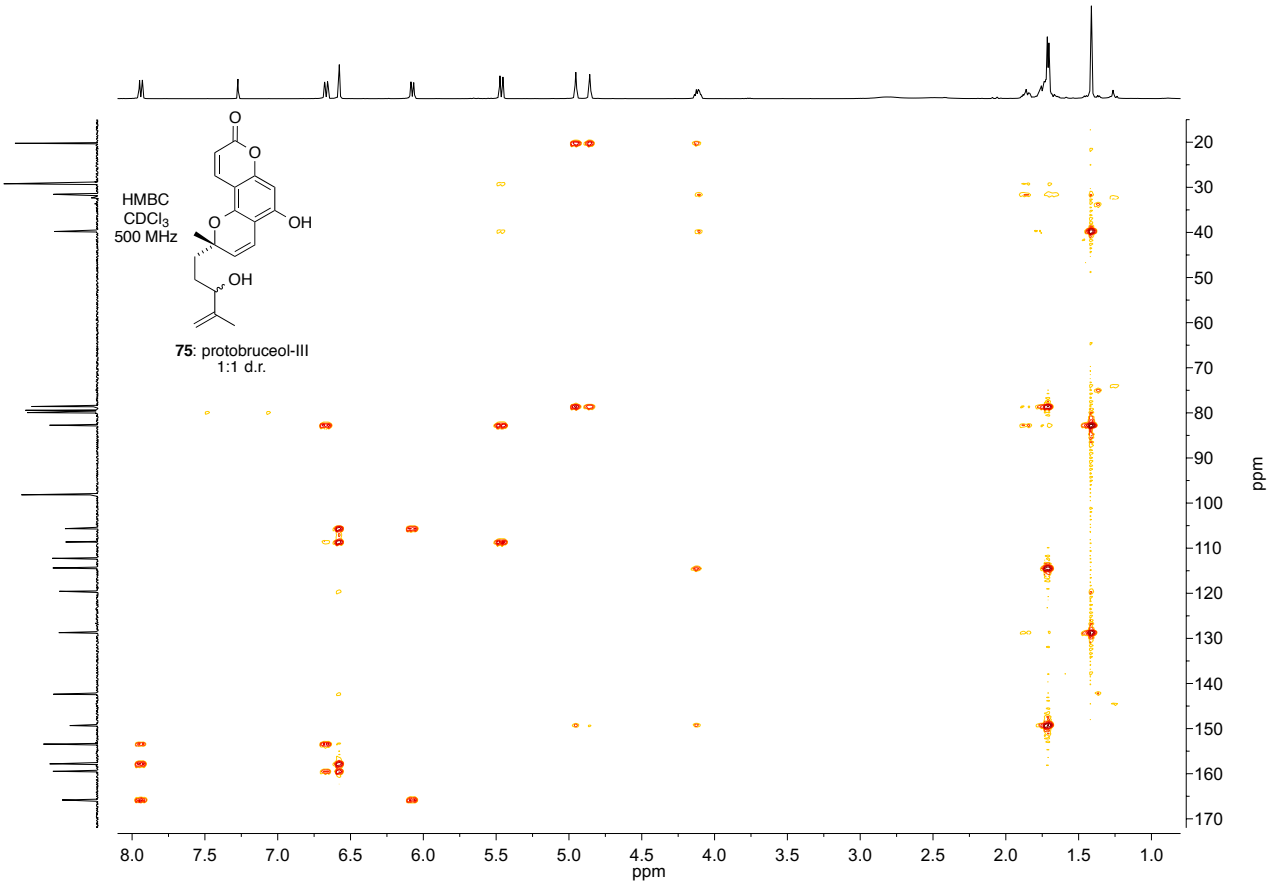

HMBC
CDCl3
500 MHz
OH
OOH
77: protobruceol-III
hydroproxide, 1:1 d.r.
ppm
ppm

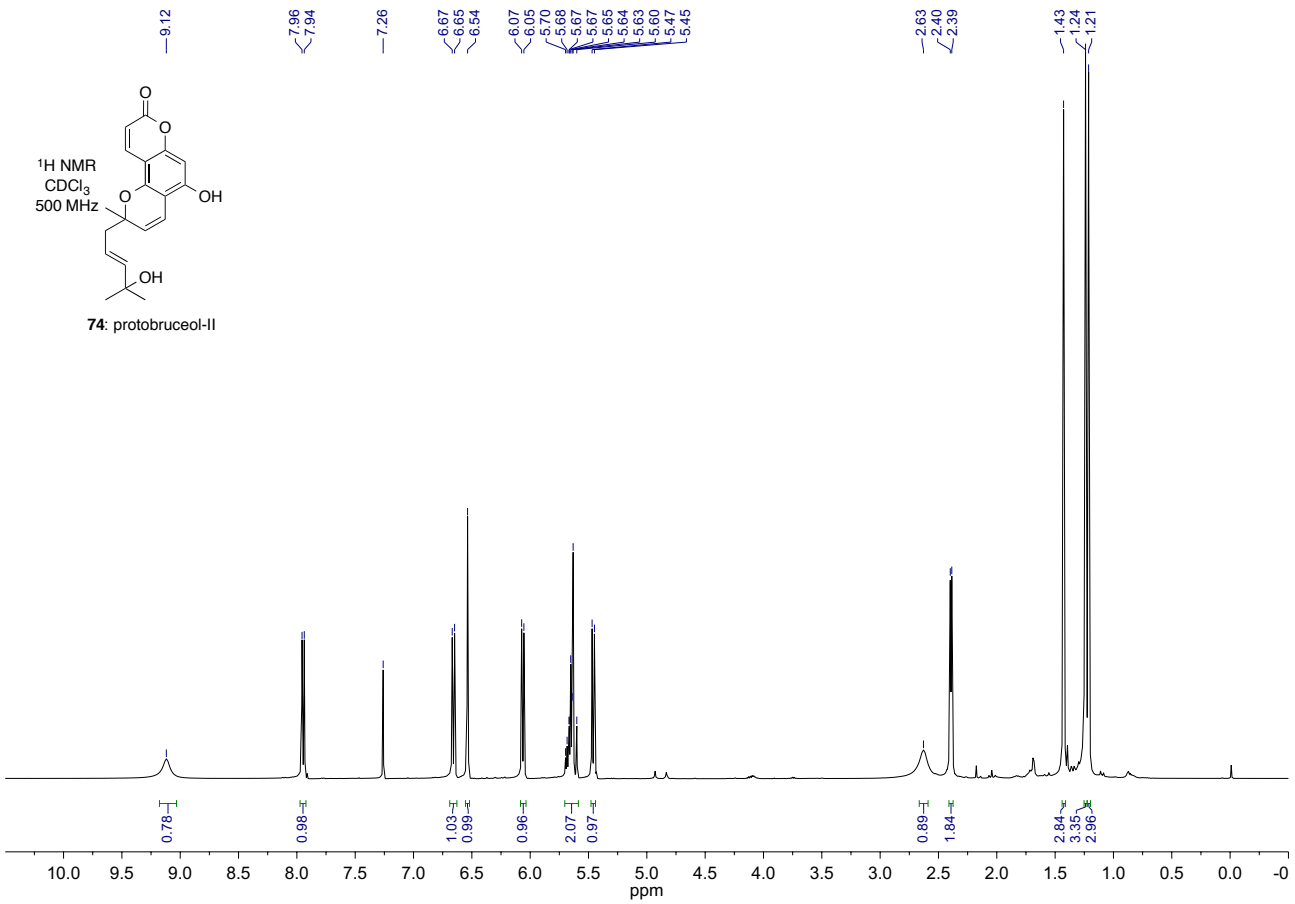

^{1}H NMR
$CDCl_3$
500 MHz
75: protobruceol-III
1:1 d.r.
ppm

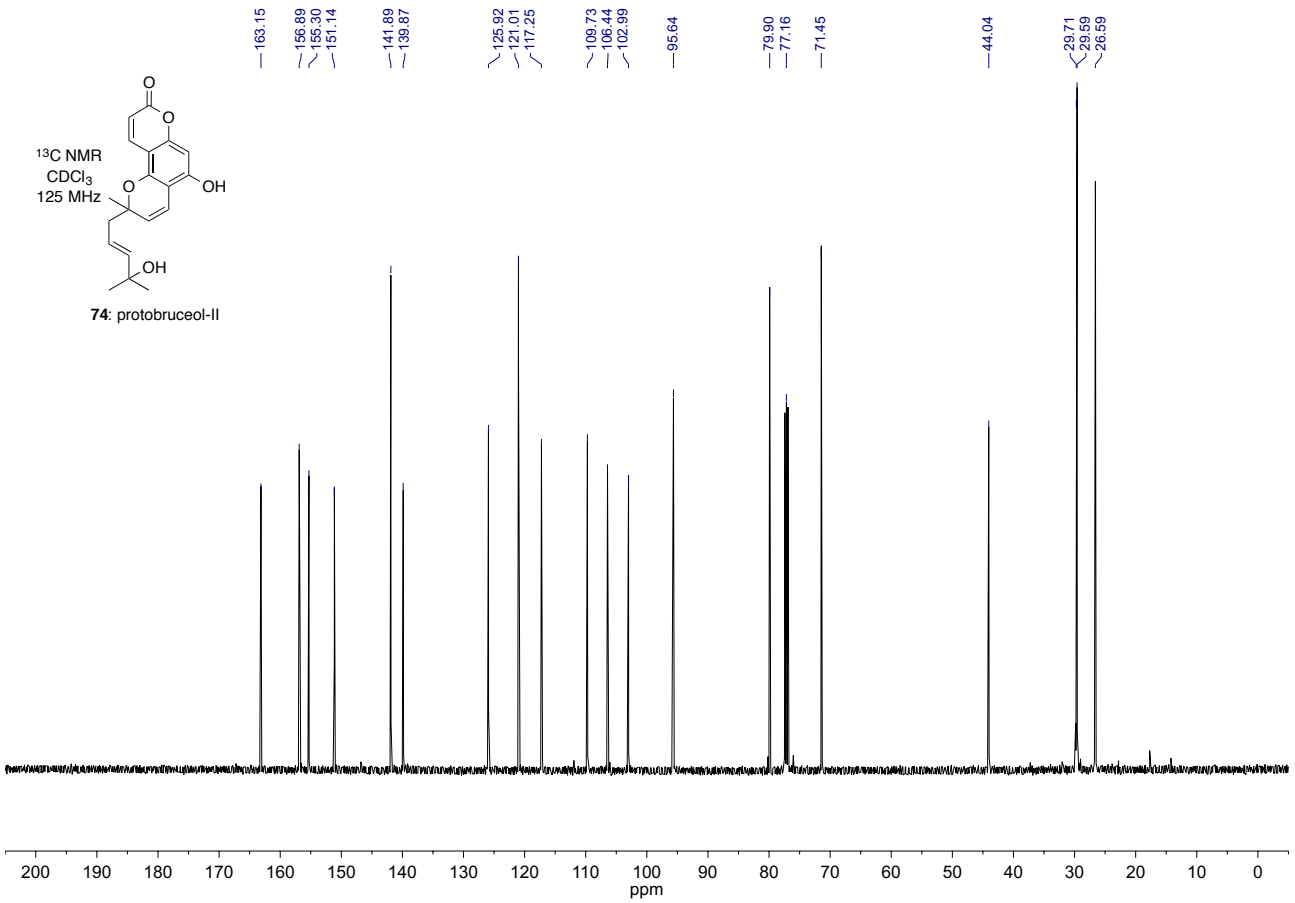

^{13}C NMR
$CDCl_3$
125 MHz
75: protobruceol-III
1:1 d.r.
ppm

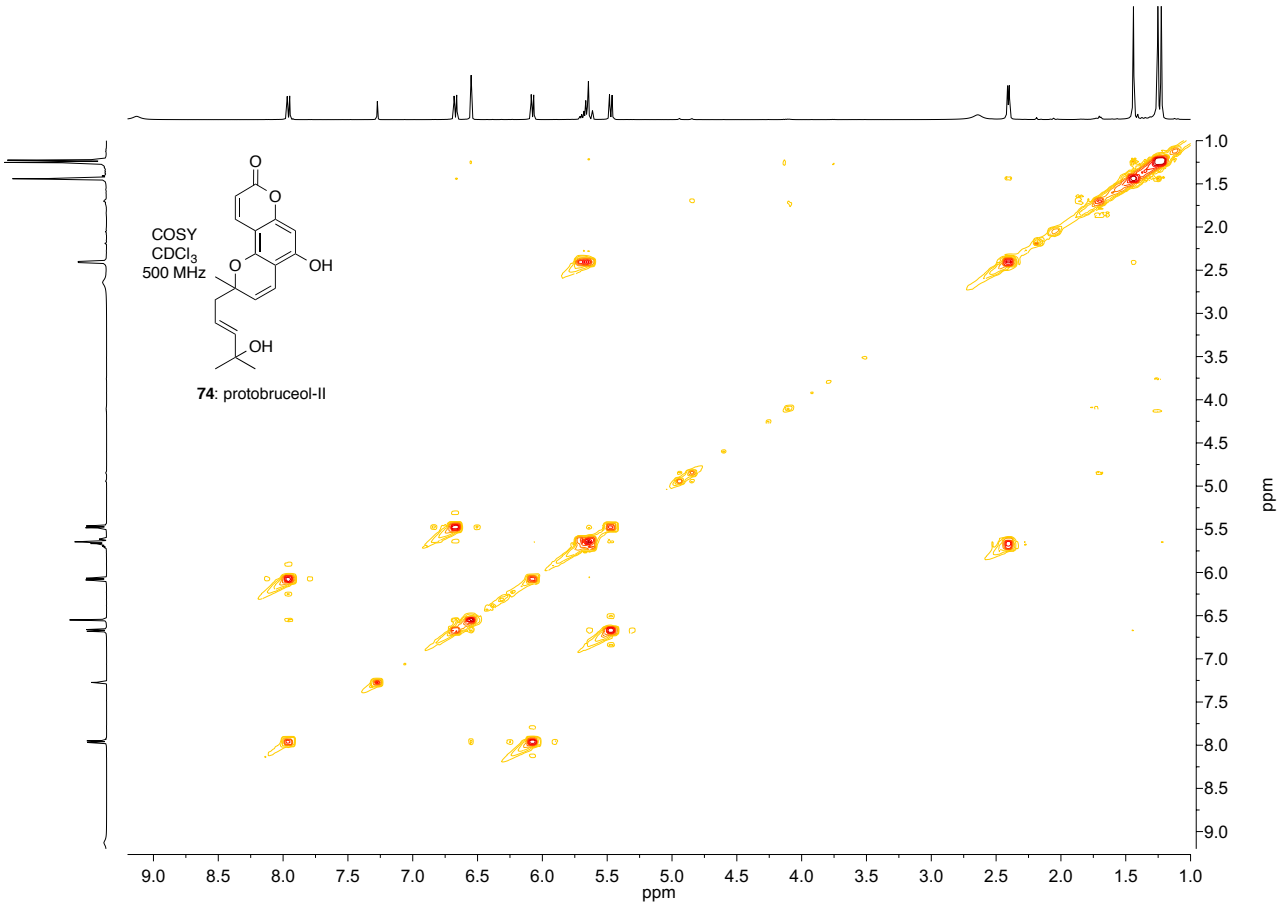

COSY
CDCl3
500 MHz
75: protobruceol-III
1:1 d.r.
ppm

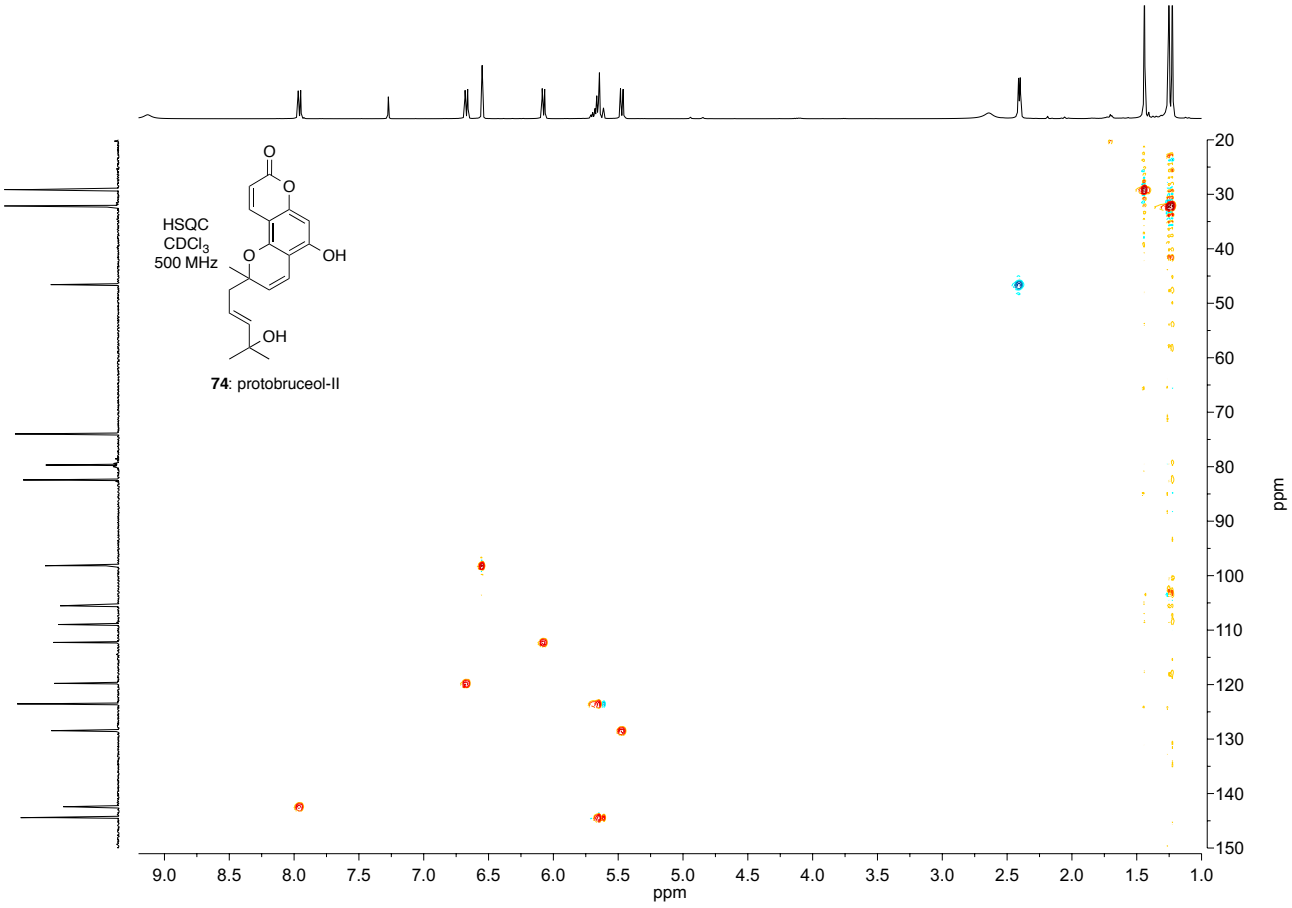

HSQC
CDCl3
500 MHz
75: protobruceol-III
1:1 d.r.
ppm

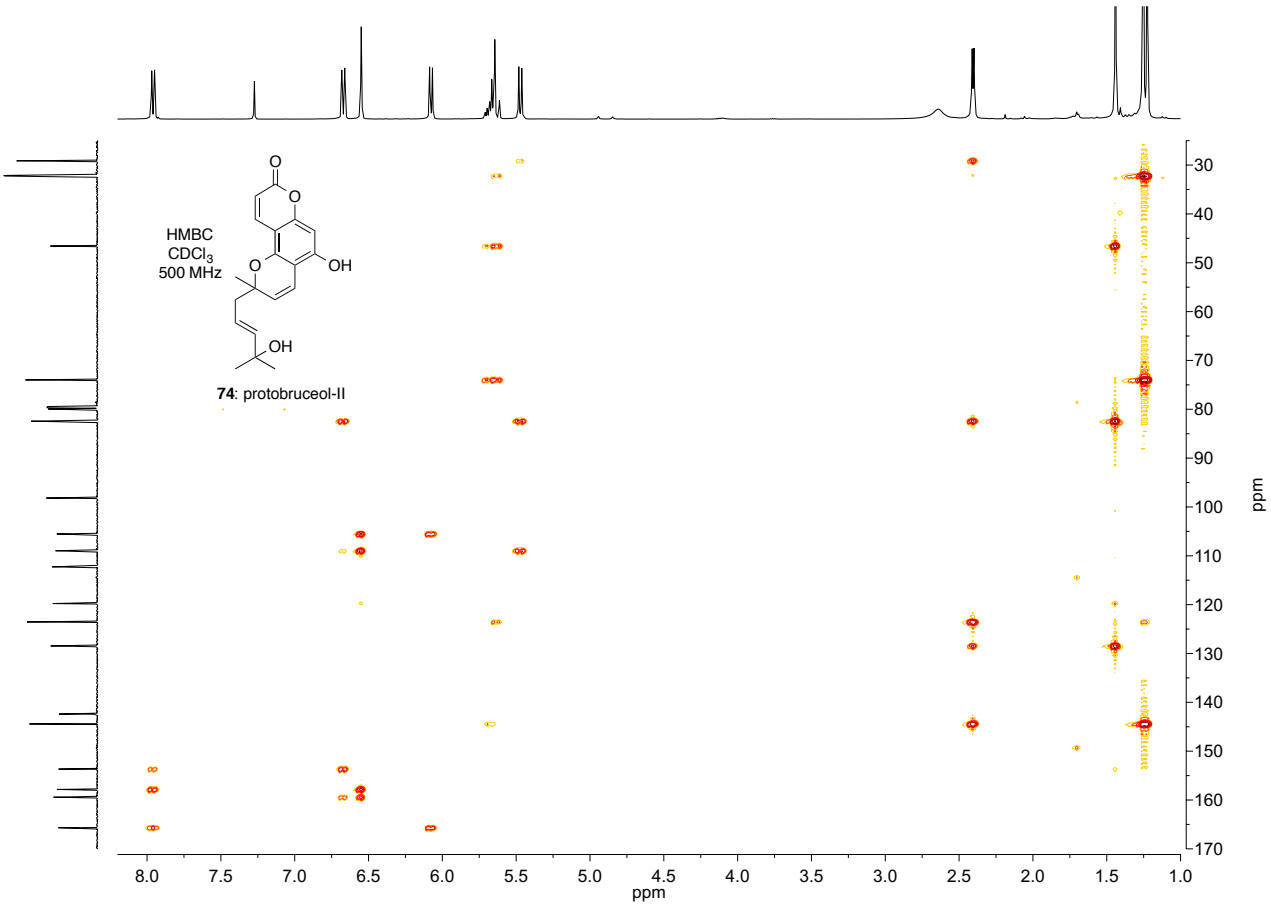

HMBC
CDCl3
500 MHz
O
O
O
OH
OH
75: protobruceol-III
1:1 d.r.
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

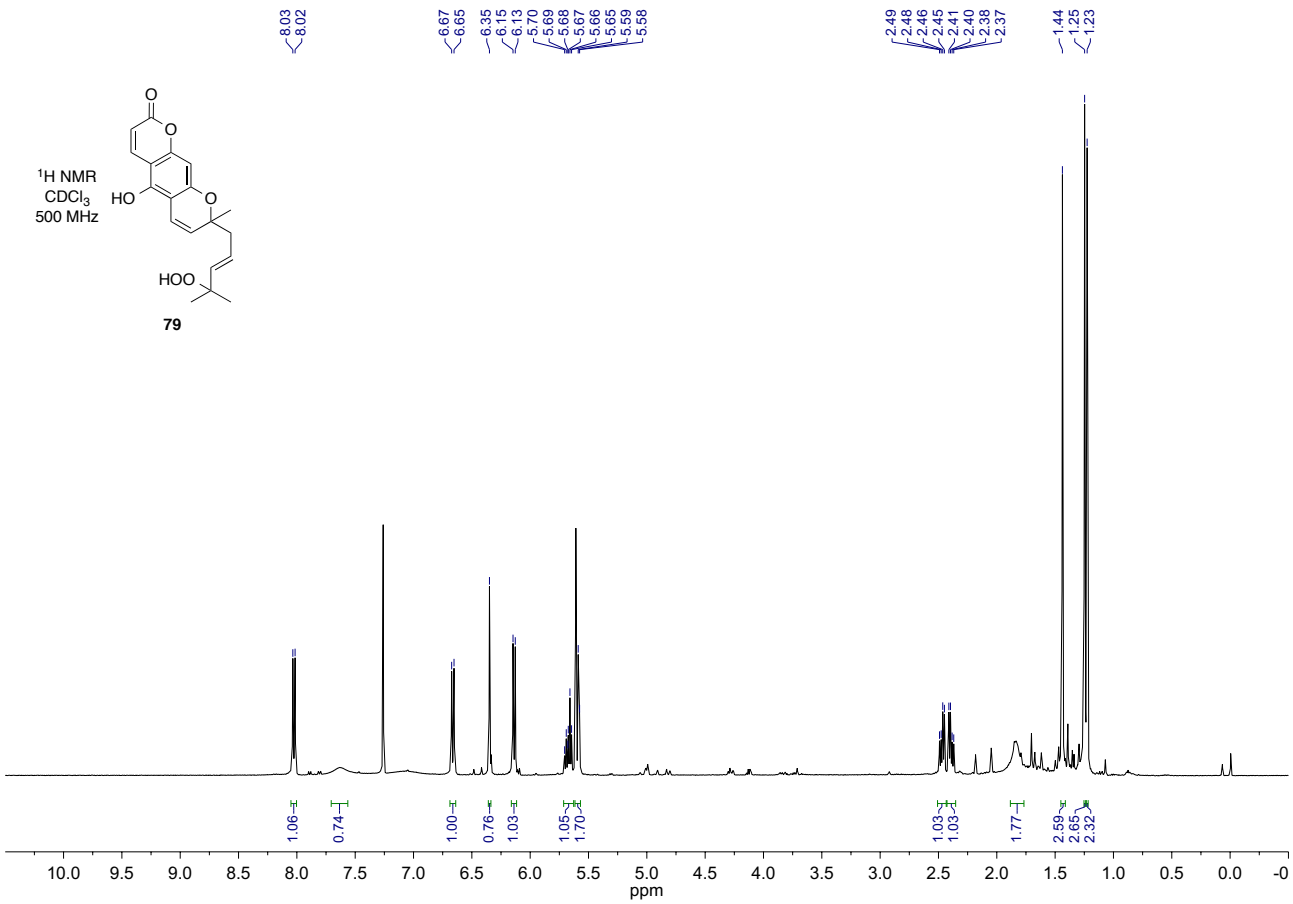

9.12
7.96
7.94
7.26
6.67
6.65
6.54
6.07
6.05
5.70
5.68
5.67
5.67
5.65
5.64
5.63
5.60
5.47
5.45
2.63
2.40
2.39
1.43
1.24
1.21
^{1}H NMR
$CDCl_3$
500 MHz
O
O
O
OH
OH
74: protobruceol-II
0.78
0.98
1.03
0.99
0.96
2.07
0.97
0.89
1.84
2.84
3.35
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm

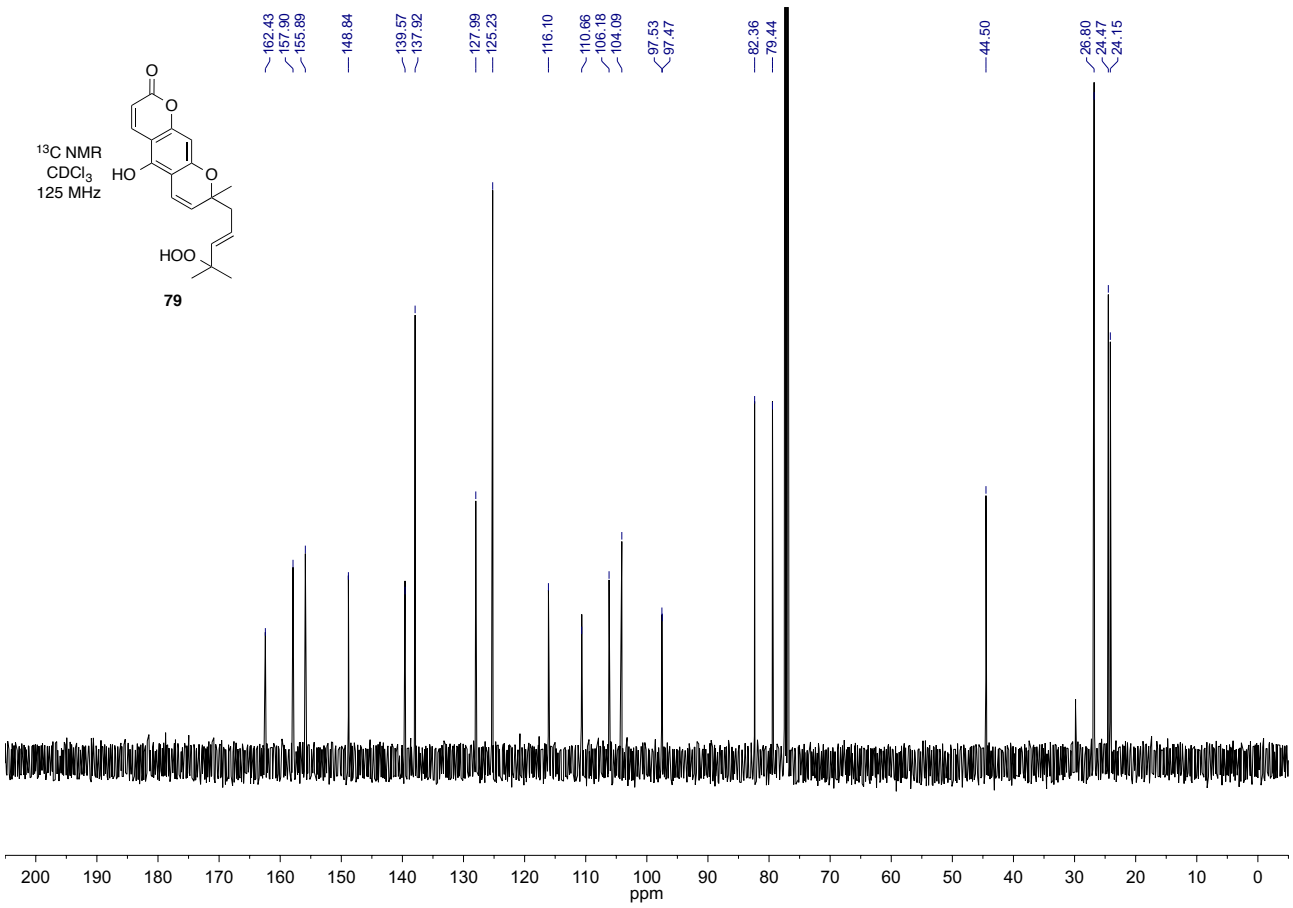

163.15
156.89
155.30
151.14
141.89
139.87
125.92
121.01
117.25
109.73
106.44
102.99
95.64
79.90
77.16
71.45
44.04
29.71
29.59
26.59
^{13}C NMR
$CDCl_3$
125 MHz
O
O
O
OH
OH
74: protobruceol-II
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


COSY
CDCl3
500 MHz
74: protobruceol-II
ppm


HSQC
CDCl3
500 MHz
74: protobruceol-II
ppm


HMBC
CDCl3
500 MHz
O
O
O
OH
OH
74: protobruceol-II
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm


8.03
8.02
6.67
6.65
6.35
6.15
6.13
5.70
5.69
5.68
5.67
5.66
5.65
5.59
5.58
2.49
2.48
2.46
2.45
2.41
2.40
2.38
2.37
1.44
1.25
1.23
^{1}H NMR
$CDCl_3$
500 MHz
HO
HOO
79
1.06
0.74
1.00
0.76
1.03
1.05
1.70
1.03
1.03
1.77
2.59
2.65
2.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm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157.90
155.89
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139.57
137.92
127.99
125.23
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110.66
106.18
104.09
97.53
97.47
82.36
79.44
44.50
26.80
24.47
24.15
^{13}C NMR
$CDCl_3$
125 MHz
HO
HOO
79
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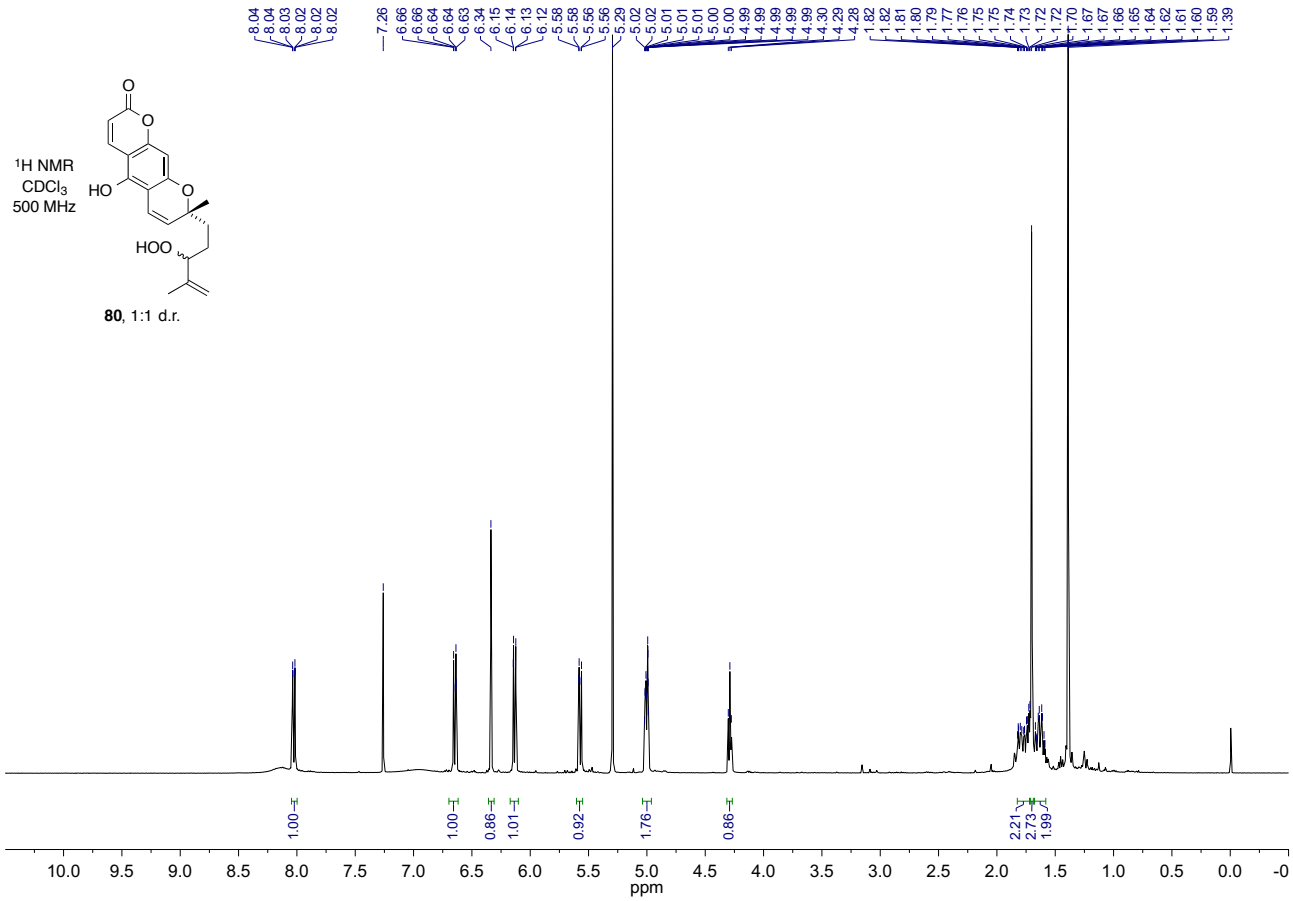
ppm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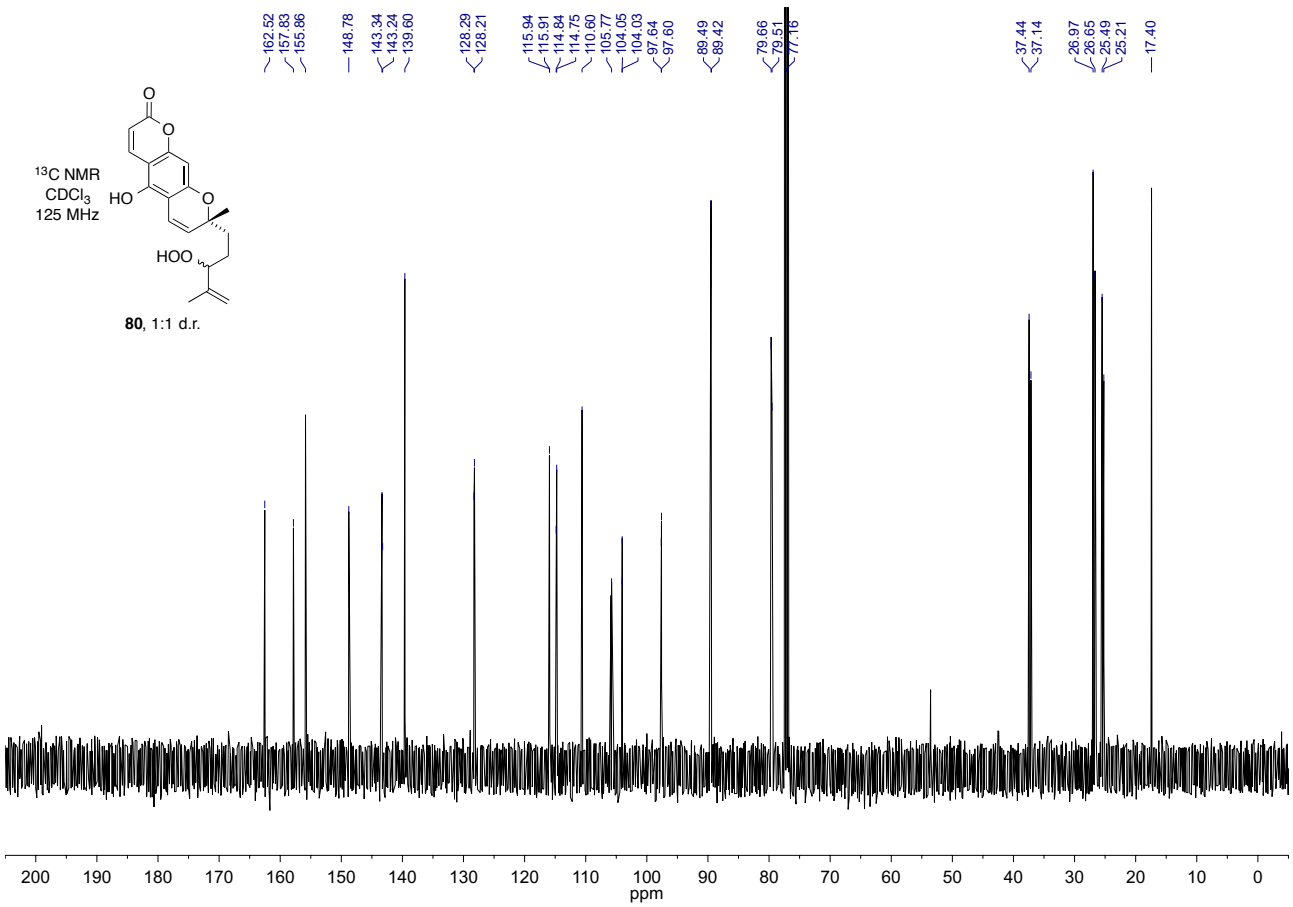
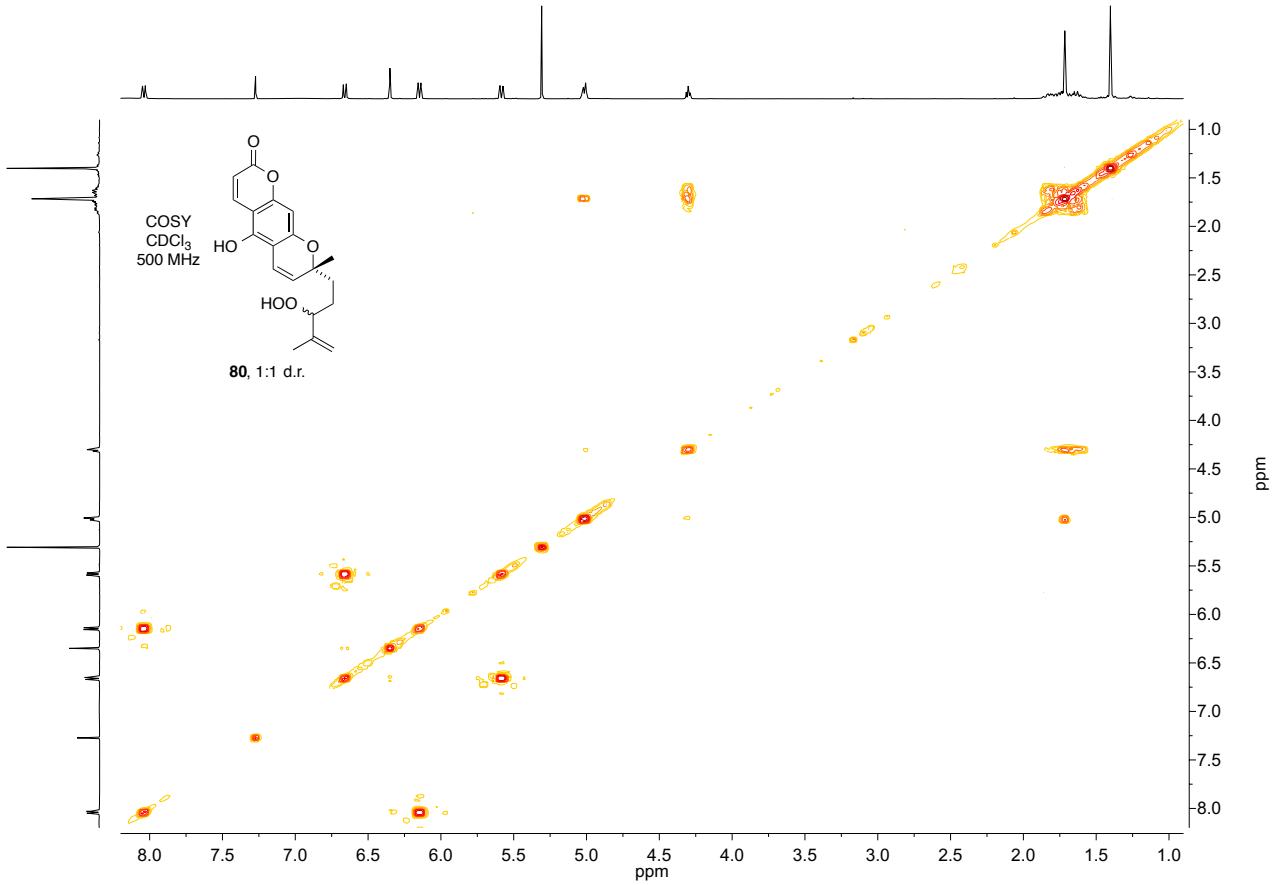
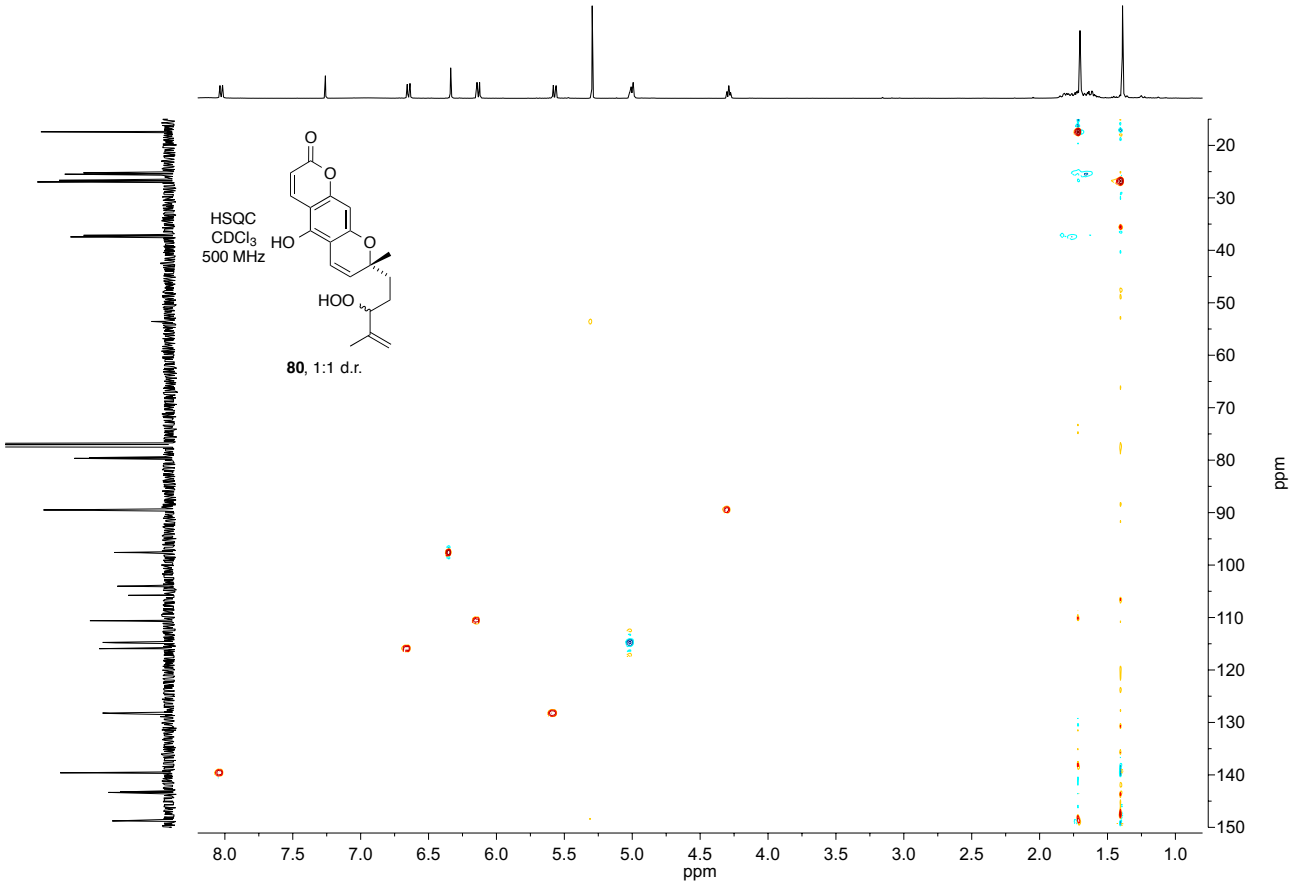
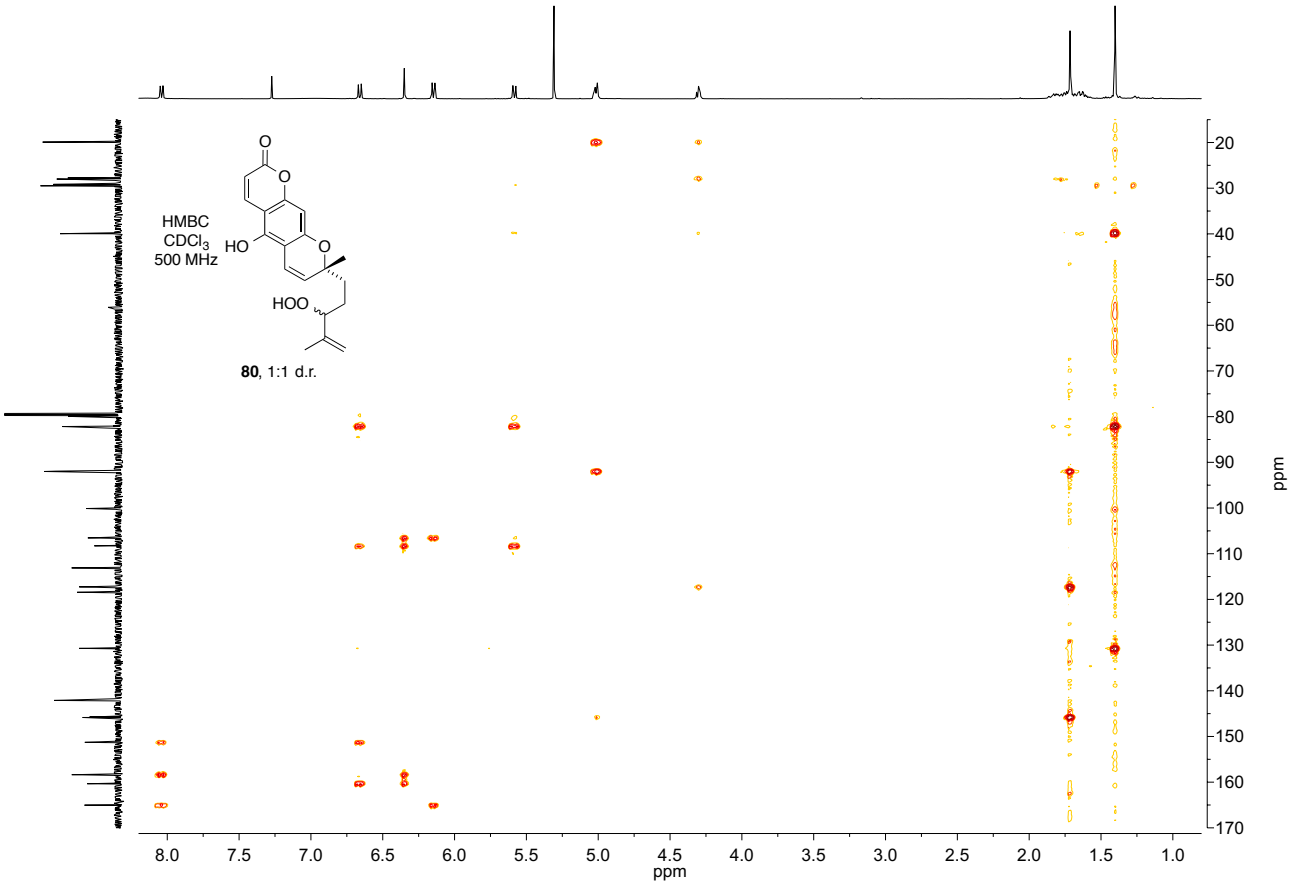
$CDCl_3$
500 MHz
HO
HOO
80, 1:1 d.r.
ppm


^{13}C NMR
$CDCl_3$
125 MHz
HO
HOO
80, 1:1 d.r.
ppm


COSY
CDCl3
500 MHz
HO
HOO
80, 1:1 d.r.
ppm


HSQC
CDCl3
500 MHz
HO
HOO
80, 1:1 d.r.
ppm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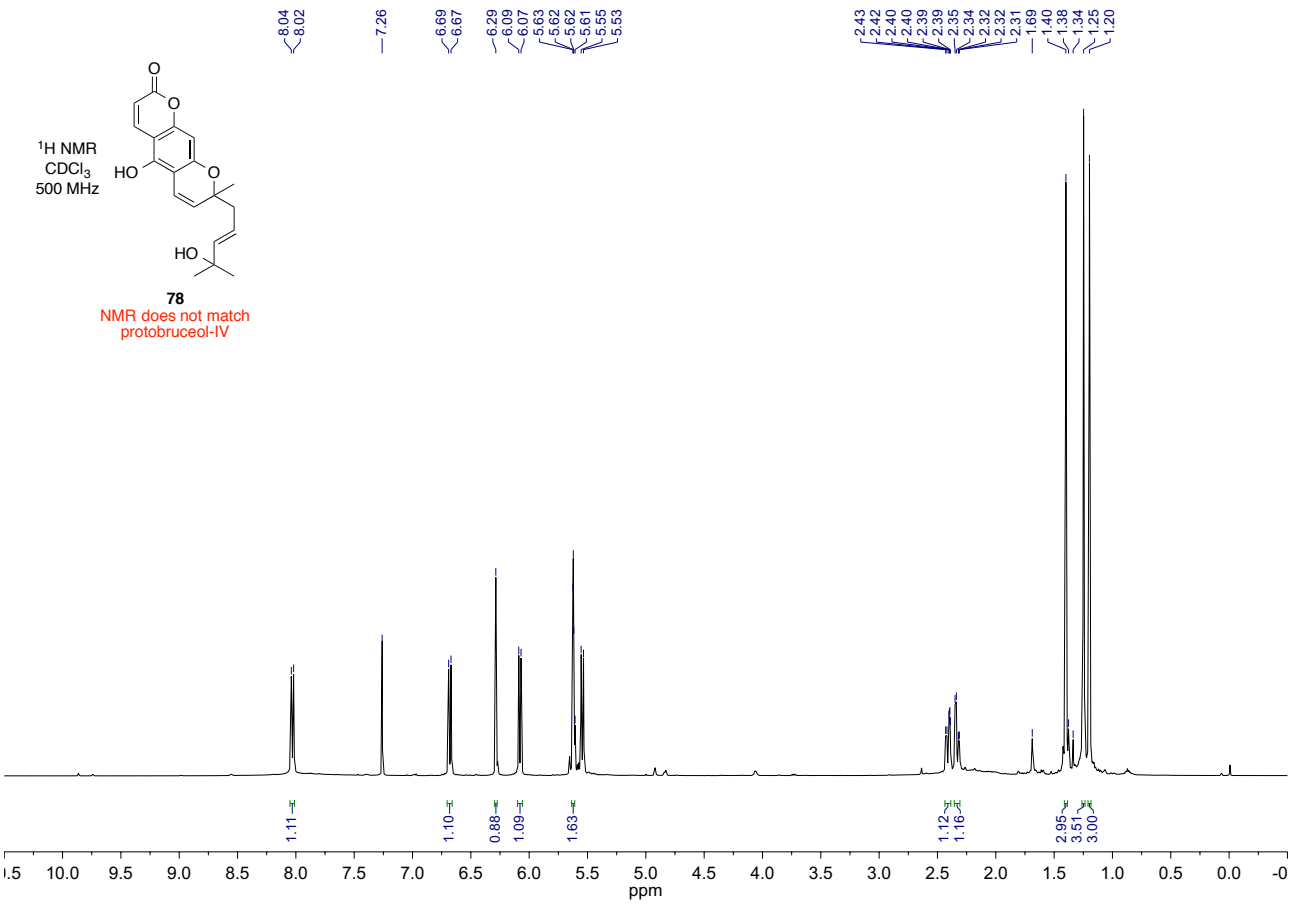
CDCl3
500 MHz
HO
HOO
O
O
O
80, 1:1 d.r.
ppm
ppm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8.02
7.26
6.69
6.67
6.29
6.09
6.07
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5.62
5.62
5.61
5.55
5.53
2.43
2.42
2.40
2.40
2.39
2.39
2.35
2.34
2.32
2.32
2.31
1.69
1.40
1.38
1.34
1.25
1.20
^{1}H NMR
$CDCl_3$
500 MHz
HO
O
HO
78
NMR does not match
protobruceol-IV
1.11
1.10
0.88
1.09
1.63
1.12
1.16
2.95
3.51
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
3.5
3.0
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1.5
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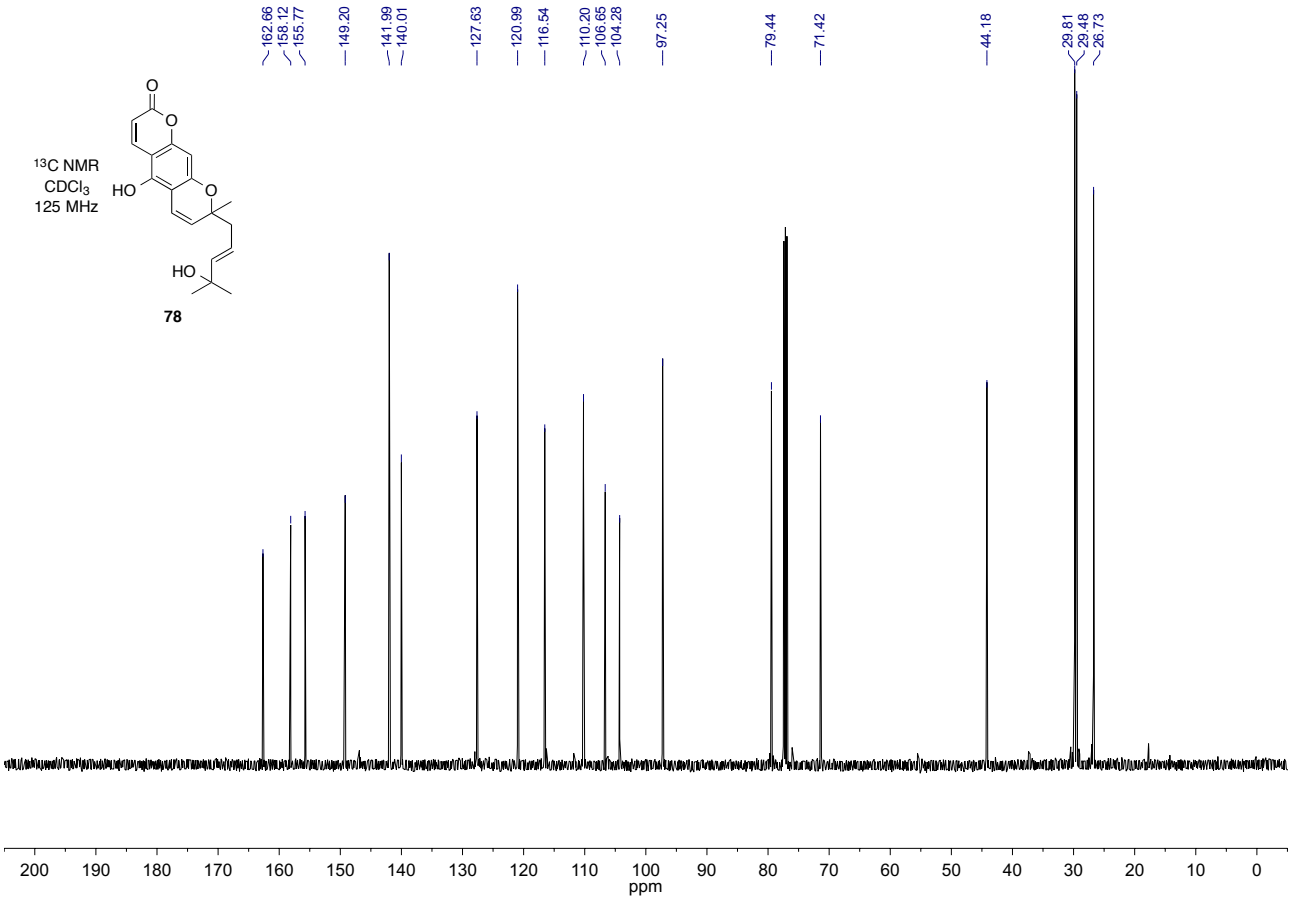
0.0
ppm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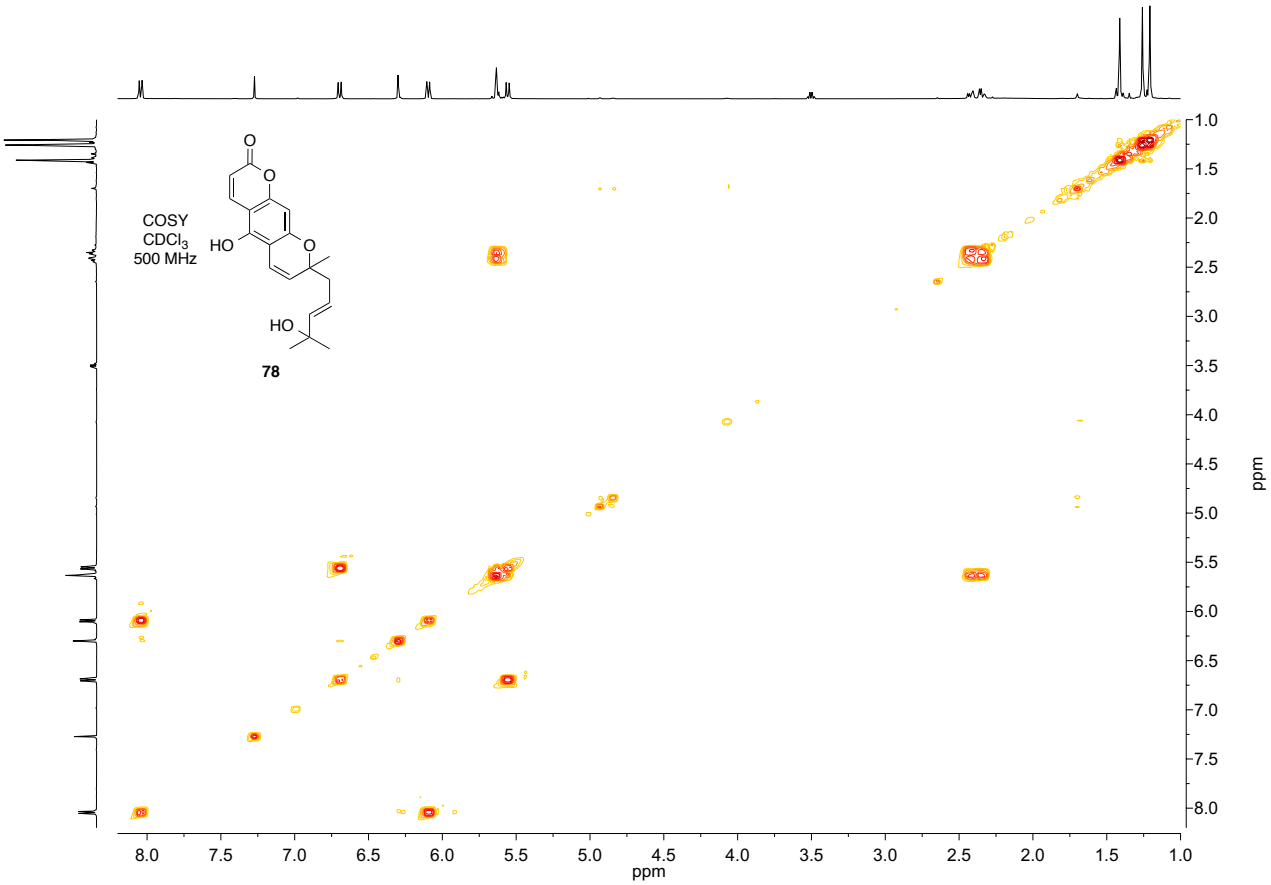
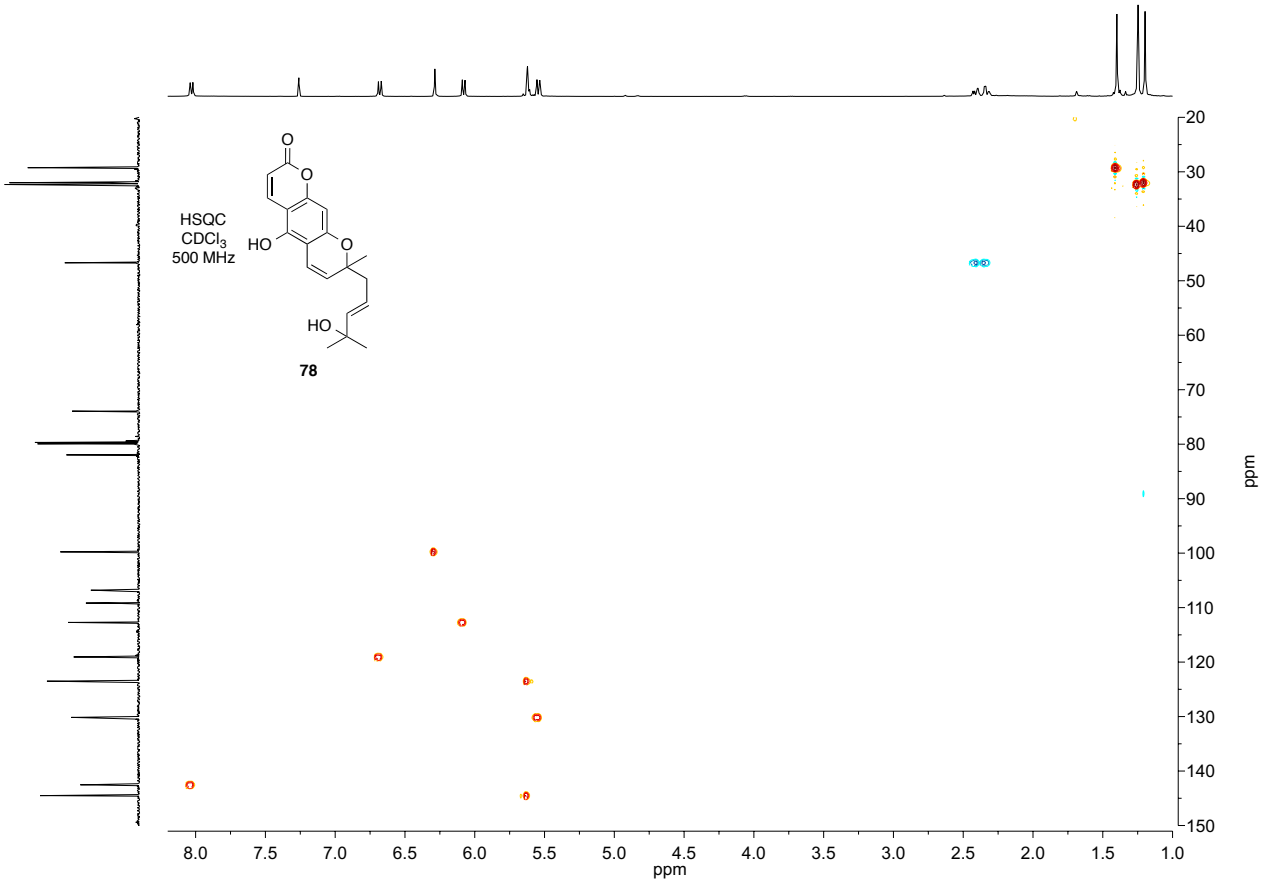
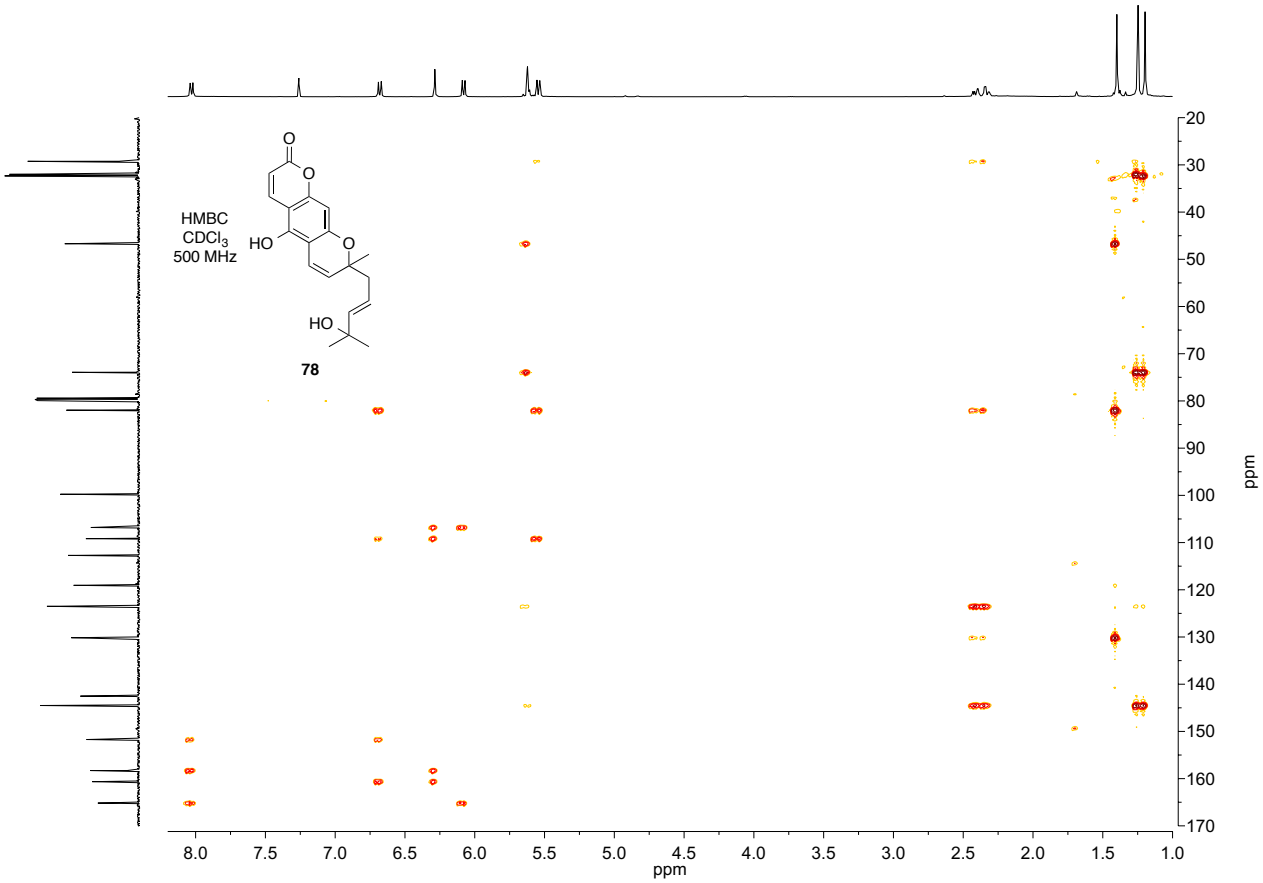
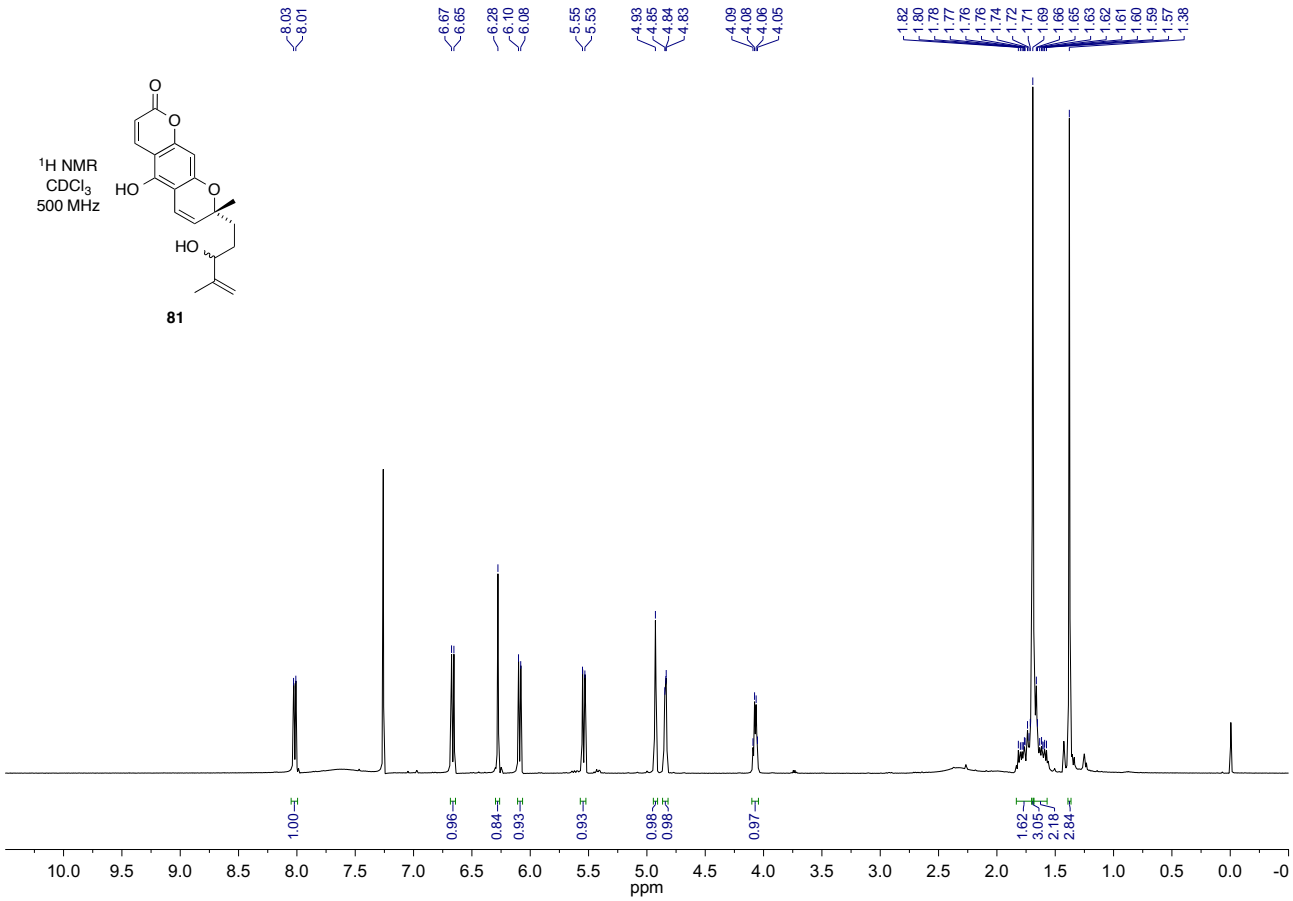
140.01
127.63
120.99
116.54
110.20
106.65
104.28
97.25
79.44
71.42
44.18
29.81
29.48
26.73
^{13}C NMR
$CDCl_3$
125 MHz
HO
O
HO
78
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


COSY
CDCl3
500 MHz
HO
O
O
O
HO
78
ppm
ppm


HSQC
CDCl3
500 MHz
HO
O
O
O
HO
78
ppm
ppm


HMBC
CDCl3
500 MHz
HO
O
O
O
HO
78
ppm
ppm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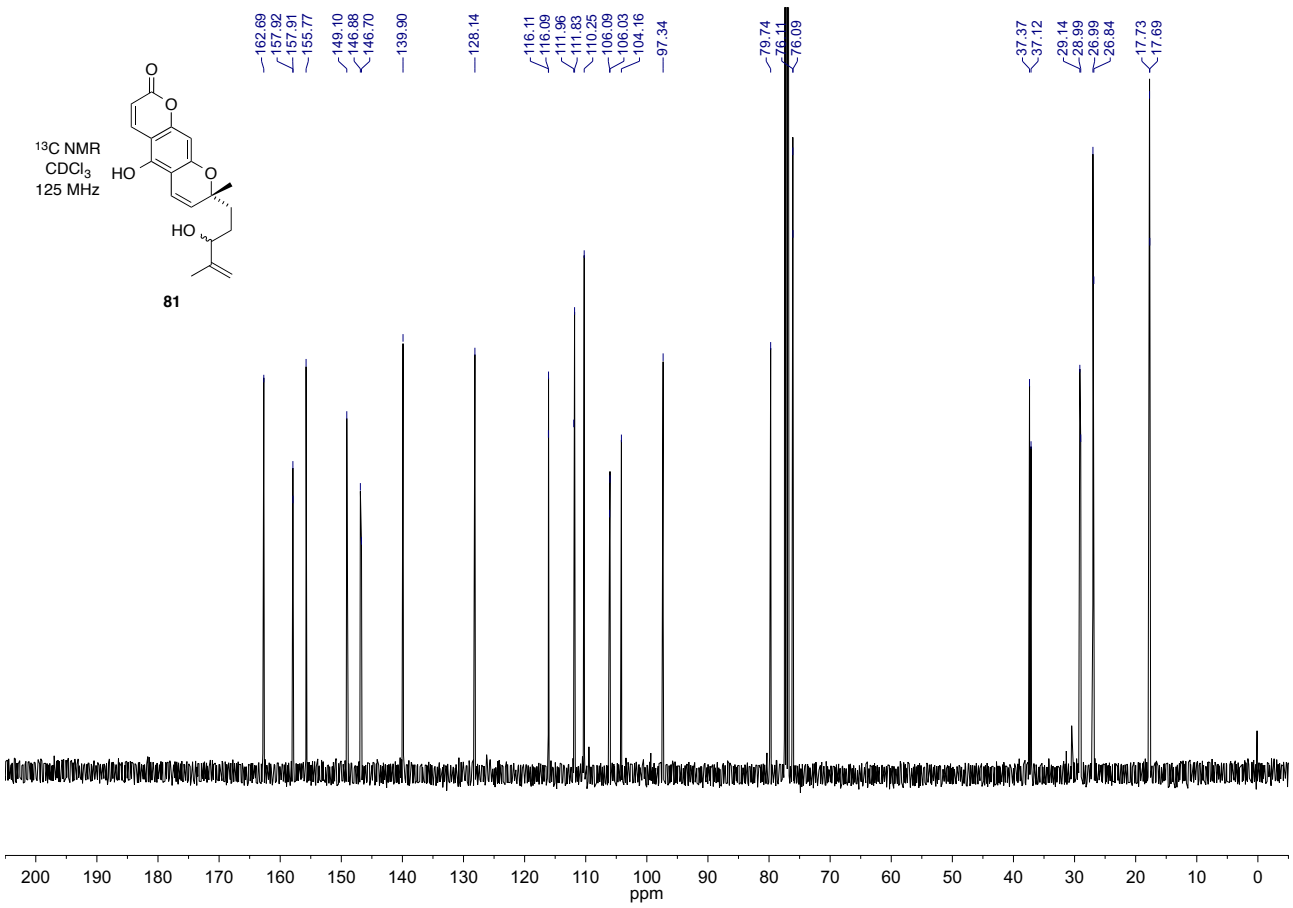
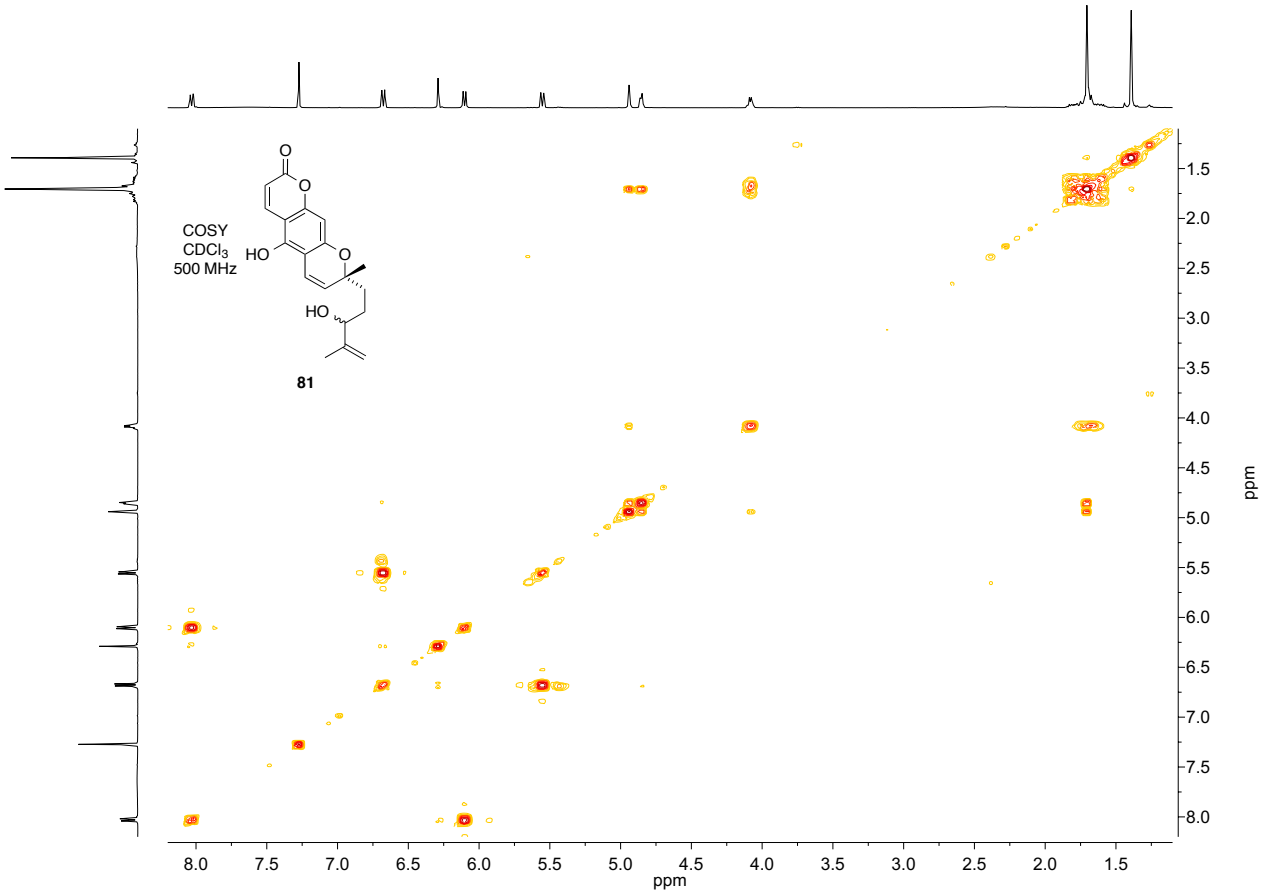
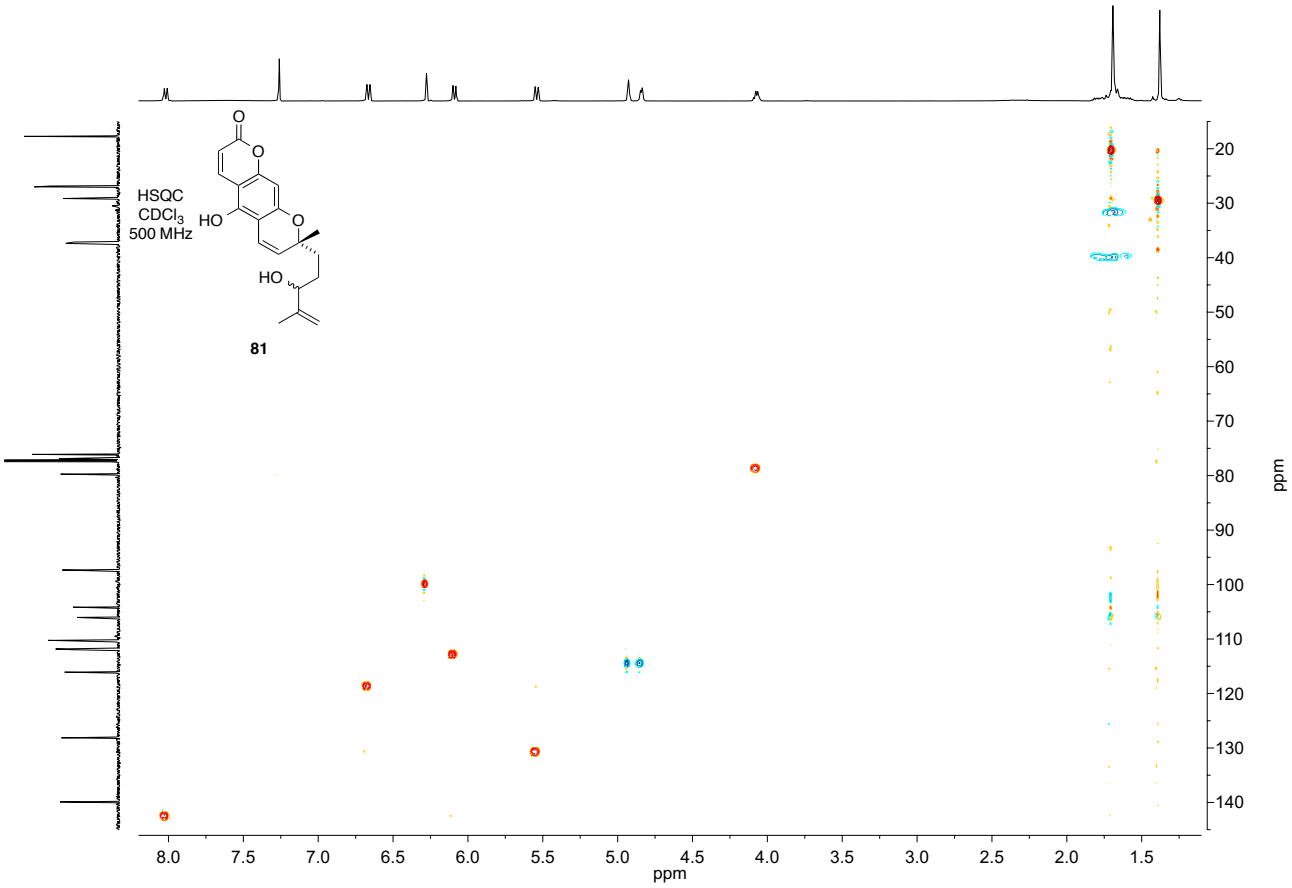
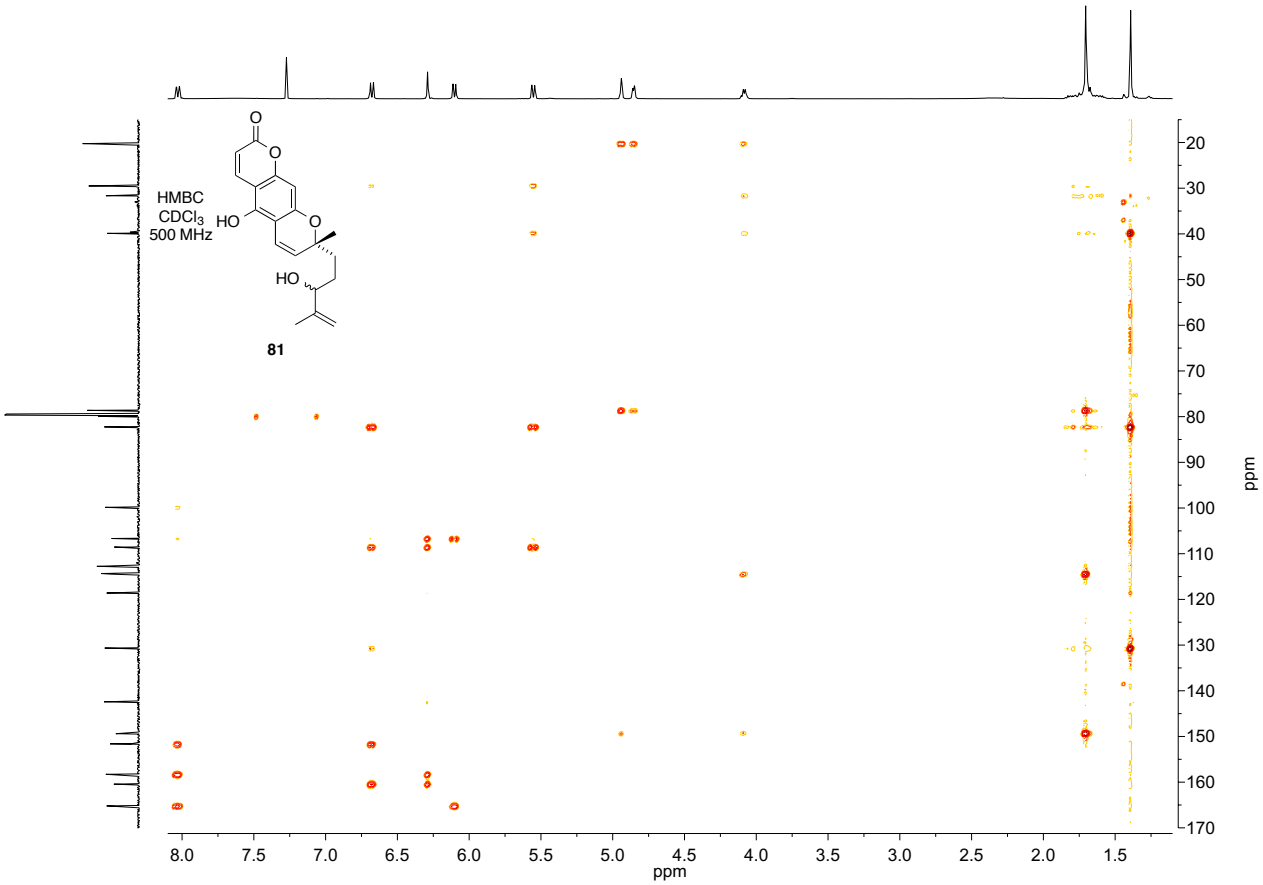
8.01
6.67
6.65
6.28
6.10
6.08
5.55
5.53
4.93
4.85
4.84
4.83
4.09
4.08
4.06
4.05
1.82
1.80
1.78
1.77
1.76
1.76
1.74
1.72
1.71
1.69
1.66
1.65
1.63
1.62
1.61
1.60
1.59
1.57
1.38
^{1}H NMR
$CDCl_3$
500 MHz
HO
HO
81
1.00
0.96
0.84
0.93
0.93
0.98
0.98
0.97
1.62
3.05
2.18
2.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm

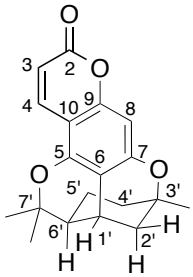

162.69
157.92
157.91
155.77
149.10
146.88
146.70
139.90
128.14
116.11
116.09
111.96
111.83
110.25
106.09
106.03
104.16
97.34
79.74
76.11
76.09
37.37
37.12
29.14
28.99
26.99
26.84
17.73
17.69
^{13}C NMR
$CDCl_3$
125 MHz
HO
HO
81
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


COSY
CDCl3
500 MHz
HO
O
O
O
HO
81
ppm
ppm


HSQC
CDCl3
500 MHz
HO
O
O
O
HO
81
ppm
ppm


HMBC
CDCl3
500 MHz
HO
O
O
O
HO
81
ppm
ppm

2. Tables of ^{1}H and ^{13}C NMR data



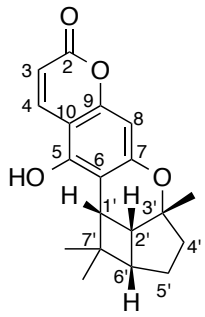
4: deoxyisobruceol
previously known as deoxybruceol

Table SI-1: Deoxyisobruceol (4) ^{1}H NMR comparison

	Crombie 1971 100 MHz ($CDCl_3$)[1]	Waterman 1992 400 MHz ($CDCl_3$)[2]	George 2019 500 MHz ($CDCl_3$)
3	6.11 d (10)	6.11 d (9.7)	6.11 d (9.5)
4	7.87 d (10)	7.86 dd (9.7, 0.6)	7.86 d (9.5)
8	6.44 s	6.44 d (0.6)	6.44 s
1’	2.82 s	2.86 ddd (4.6, 2.8, 1.7)	2.90-2.84 m
2’-ax.	n.r.	1.90 dd (13.4, 1.7)	1.91 dd (13.4, 1.7)
2’-eq.	n.r.	2.24 ddd (13.1, 4.6, 3.2)	2.24 ddd (13.4, 4.7, 3.2)
3’-Me	1.42 s	1.41 s	1.42 s
4’-ax.	n.r.	1.48 ddd (14.9, 11.6, 5.4)	1.47 ddd (15.1, 13.1, 6.8)
4’-eq.	n.r.	1.81 ddd (14.9, 6.4, 2.8)	1.81 ddd (14.9, 5.6, 3.4)
5’-ax.	n.r.	0.64 dtd (14.0, 11.6, 6.4)	0.64 tdd (13.4, 11.6, 6.1)
5’-eq.	n.r.	1.31 dt (1.40, 5.4)	1.30 dt (12.8, 6.0)
6’	n.r.	2.13 ddd (11.6, 5.4, 2.8)	2.13 ddd (11.6, 5.4, 2.8)
7’-Me	1.60 s	1.60 s	1.60 s
7’-Me	1.09 s	1.06 s	1.07 s

Table SI-2: Deoxyisobruceol (4) ^{13}C NMR comparison

	Waterman 1992 100 MHz ($CDCl_3$)[2]	George 2019 500 MHz ($CDCl_3$)
2	162.1	162.0
3	110.9	110.7
4	138.4	138.3
5	153.7	153.6
6	112.5	112.4
7	160.0	159.8
8	97.1	96.9
9	154.7	154.6
10	105.2	105.1
1’	28.1	28.0
2’	35.0	34.8
3’	76.5	76.4
3’-Me	28.9	28.8
4’	37.4	37.3
5’	22.1	22.0
6’	46.4	46.2
7’	86.6	86.5
7’-Me	24.3	24.4
7’-Me	29.7	29.6



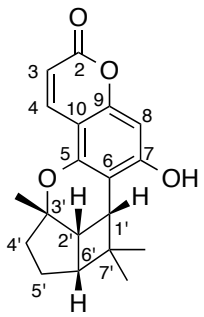
6: eriobrucinol

Table SI-3: Eriobrucinol (6) ^{1}H NMR comparison

	Jefferies 1973 90 MHz (d_5-pyridine)[3]	Waterman 1992 400 MHz ($CDCl_3$)[4]	Hsung 2013 400 MHz ($CDCl_3$)[5]	George 2019 500 MHz ($CDCl_3$)
3	6.18 d (10)	6.16 d (9.6)	6.15 (9.5)	6.14 d (9.6)
4	8.33 d (10)	8.01 dd (9.6, 0.6)	7.97 d (9.5)	8.02 d (9.6)
8	6.46 s	6.47 d (0.6)	6.47 s	6.44 s
1’	3.4 m (10)	3.09 d (9.7)	3.06 d (9.7)	3.10 d (9.7)
2’	2.54, t (~8.5)	2.67 dd (12.0, 6.8)	2.66 dd (9.5, 7.5)	2.64 dd (9.7, 7.6)
3’-Me	1.39 s	1.42 s	1.41 s	1.40 s
4’-α	n.r.	1.74 m	1.56-1.80 m	1.7 m (2H)
4’-β	n.r.	1.71 m	1.56-1.80 m	1.7 m (2H)
5’-α	n.r.	1.92 dt (12.0, 6.8)	1.84 – 1.98 m	1.9 m
5’-β	n.r.	1.65 m	1.56-1.80 m	1.63 td (8.0, 6.9, 4.4)
6’	n.r.	2.49 t (7.4)	2.48 t (7.5)	2.46 t (7.6)
7’-Me	0.86 s	0.80 s	0.79 s	0.77 s
7’-Me	1.48 s	1.46 s	1.45 s	1.44 s

Table SI-4: Eriobrucinol (6) ^{13}C NMR comparison

	Waterman 1992 100 MHz ($CDCl_3$)[4]	Hsung 2013 100 MHz ($CDCl_3$)[5]	George 2019 125 MHz ($CDCl_3$)
2	162.3	162.0	162.1
3	111.1	111.1	111.0
4	139.1	139.0	138.9
5	151.5	151.2	151.3
6	107.2	106.8	107.1
7	157.9	157.7	157.8
8	99.1	99.0	99.0
9	154.7	154.6	154.6
10	103.2	103.1	103.2
1’	35.7	35.6	35.6
2’	37.4	37.2	37.3
3’	84.7	84.6	84.7
3’-Me	27.4	27.4	27.4
4’	38.8	38.6	38.7
5’	25.7	25.7	25.7
6’	46.5	46.4	46.4
7’	39.1	39.0	39.1
7’-Me	18.3	18.2	18.2
7’-Me	34.6	34.6	34.6



5: isoeriobrucinol A

Table SI-5: Iso-eriobrucinol A (5) ^{1}H NMR comparison

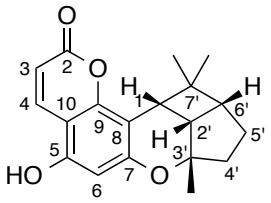
	Crombie 1983 (d_5-pyridine)[6]	Waterman 1992 250 MHz (d_5-pyridine)[4]	Hsung 2013 600 MHz (d_5-pyridine)[5]	George 2019 500 MHz (d_5-pyridine)
3	6.24 d (10)	6.25 d (9.6)	6.26 d (9.6)	6.27 d (9.6)
4	8.08 d (10)	8.06 dd (9.6, 0.6)	8.04 d (9.6)	8.09 d (9.6)
8	6.59 s	6.60 d (0.6)	6.60 s	6.61 s
1’	3.34 d (10)	3.31 d (9.5)	3.32 d (9.6)	3.34 d (9.6)
2’	n.r.	2.56 dd (9.5, 7.6)	2.55 dd (9.0, 7.8)	2.56 dd (9.6, 7.5)
3’-Me	1.45 s	1.44 s	1.45 s	1.47 s
4’-α	n.r.	1.55 dt (11.8, 7.6)	1.56 dt (12.6, 7.8)	1.57 ddd (13.7, 12.3, 7.6)
4’-β	n.r.	1.62 m	1.70 – 1.64 m	1.72-1.65 (overlapped)
5’-α	n.r.	2.12 m	2.11 – 2.00 m	2.04 td (12.6, 7.5)
5’-β	n.r.	1.68 dt (13.9, 7.6)	1.70 – 1.64 m	1.74-1.68 (overlapped)
6’	n.r.	2.31 t (7.6)	2.34 t (7.8)	2.35 t (7.5)
7’-Me	0.96 s	0.96 s	0.97 s	0.98 s
7’-Me	1.48 s	1.46 s	1.48 s	1.47 s

Table SI-6: Iso-eriobrucinol A (5) ^{13}C NMR comparison

	Hsung 2013 150 MHz (d_5-pyridine)[5]	George 2019 125 MHz (d_5-pyridine)
2	161.7	162.2
3	109.7	110.2
4	139.5	140.0
5	151.3	151.7
6	108.8	109.2
7	161.6	162.1
8	95.1	95.6
9	155.7	156.1
10	103.7	104.2
1’	36.5	37.0
2’	38.0	38.5
3’	84.9	85.4
3’-Me	27.4	27.9
4’	38.7	39.2
5’	25.9	26.4
6’	46.6	47.1
7’	39.4	39.9
7’-Me	18.0	18.5
7’-Me	33.8	34.3

Note. The residual pyridine ^{13}C NMR peak at 135.91 was used as a reference (our chemical shift values for **5** are ~0.4 – 0.5 ppm higher than for Hsungs’ synthetic **5**).

^{13}C NMR data for **5** was not reported by Waterman and co-workers.



43: isoeriobrucinol B

Table SI-7: Iso-eriobrucinol B (43) ^{1}H NMR comparison table

	Crombie 1983 (d_5-pyridine)[6]	Waterman 1992 250 MHz ($CDCl_3$)[4]	Hsung 2013 600 MHz (d_5-pyridine)[5]	George 2019 500 MHz (d_5-pyridine)
3	6.25 d (10)	6.16 d (9.7)	6.28 d (9.6)	6.29 d (9.5
4	8.30 d (10)	7.98 d (9.7)	8.30 d (9.6)	8.31 d (9.5)
6	6.60 s	6.21 s	6.63 s	6.63 s
1’	3.29 d (10)	3.26 d (9.4)	3.29 d (9.6)	3.30 d (9.6)
2’	2.30 – 1.7 m	2.60 dd (9.4, 7.4)	2.49 dd (7.2, 8.1)	2.50 dd (9.7, 7.3)
3’-Me	1.34 s	1.42 s	1.35 s	1.37 s
4’-α	2.30 – 1.7 m	1.75 – 1.50	1.62 – 1.57 m	1.61 – 1.55 overlapped
4’-β	2.30 – 1.7 m	1.75 – 1.50	1.62 – 1.57 m	1.53 – 1.44 m
5’-α	2.30 – 1.7 m	1.90 m	2.04 – 1.98 m	2.02 td (12.8, 7.8)
5’-β	2.30 – 1.7 m	1.75 – 1.50	1.62 – 1.57 m	1.64 – 1.47 overlapped
6’	2.30 – 1.7 m	2.46 t (7.4)	2.29 t (7.2)	2.31 t (7.4)
7’-Me	0.84	0.77 s	0.85 s	0.87 s
7’-Me	1.34	1.52 s	1.55 s	1.56 s

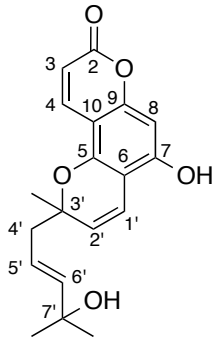
Table SI-8: Iso-eriobrucinol B (43) ^{13}C NMR comparison table

	Hsung 2013 125 MHz (d_5-pyridine)[5]	George 2019 500 MHz (d_5-pyridine)
2	161.3	161.8
3	109.9	110.4
4	140.1	140.5
5	155.4	155.9
6	100.3	100.7
7	-*	158.4
8	-	103.7
9	155.1	155.5
10	-	104.8
1’	35.7	36.2
2’	37.4	37.9
3’	84.8	85.3
3’-Me	27.6	28.0
4’	25.8	26.2
5’	38.5	39.0
6’	46.7	47.2
7’	39.1	39.6
7’-Me	18.2	18.6
7’-Me	33.8	34.2

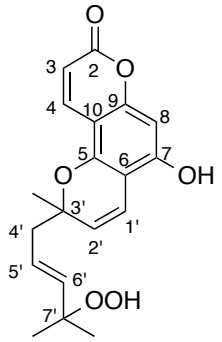
Note: The residual pyridine ^{13}C NMR peak at 135.91 was used as a reference (our chemical shift values for **43** are ~0.4 – 0.6 ppm higher than for Hsung’s synthetic **43**).

* Only 18 ^{13}C peaks were reported. Signals were reported at 79.7 and 79.5 are possibly misassigned residual chloroform.

^{13}C NMR data for **43** was not reported by Waterman and co-workers.



74: protobruceol-II



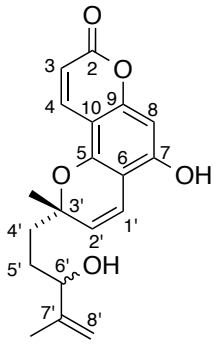
76: protobruceol-II hydroperoxide

Table SI-9: Protobruceol-II and (74) -II hydroperoxide (76) ^{1}H NMR comparison

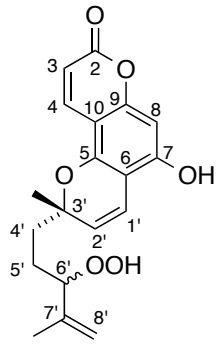
	Waterman 1992 400 MHz ($CDCl_3$) **74**[7]	George 2019 500 MHz ($CDCl_3$) **74**	Waterman 1992 400 MHz ($CDCl_3$) **76**[7]	George 2019 500 MHz ($CDCl_3$) **76**
3	6.10 d (7.6)	6.09 d (9.5)	6.14 (7.6)	6.13 d (9.6)
4	7.97 br d (7.6)	7.96 d (9.6)	7.98 bd (7.6)	7.98 d (9.6)
8	6.50 br s	6.55 s	6.54 br s	6.60 s
1’	6.69 d (10.0)	6.68 d (10.1)	6.61 d (10.0)	6.70 d (10.0)
2’	5.49 d (10.0)	5.48 d (10.1)	5.53 d (10.0)	5.50 d (10.1)
3’-Me	1.47 s	1.45 s	1.49 s	1.47
4’-α/ β	2.43 br d (6.7)	2.42 d (7.1)	2.47 br d (6.9)	2.46 d (7.2)
5’	5.69 dt (15.4, 6.7)	5.72-5.64 m (overlapped)	5.70 dt (15.8, 6.9)	5.71 dt (15.9, 7.2)
6’	5.63 d (15.4)	5.63 d (15.6)	5.59 d (15.8)	5.59 d (15.8)
7’-Me	1.21 s	1.22 s	1.23 s	1.22 s
7’-Me	1.23 s	1.25 s	1.25 s	1.24 s

Table SI-10: Protobruceol II and (74) II hydroperoxide (76) ^{13}C NMR comparison

	Waterman 1992 400 MHz ($CDCl_3$) **74**[8]	George 2019 500 MHz ($CDCl_3$) **74**	Waterman 1992 400 MHz ($CDCl_3$) (as C7 methyl ether of **76**)[8]	George 2019 500 MHz ($CDCl_3$) **76**
2	162.8	163.2	161.6	163.0
3	110.2	109.7	111.5	110.2
4	139.6	139.9	138.6	139.7
5	151.3	151.1	150.6	151.1
6	106.3	106.4	106.6	106.3
7	156.4	156.9	158.5	155.4
8	95.7	95.6	91.8	95.8
9	155.4	155.3	156.2	156.5
10	103.2	103.0	103.6	103.2
1’	117.2	117.3	117.2	117.2
2’	126.0	125.9	126.2	126.0
3’	80.0	79.9	79.9	79.9
3’-Me	26.8	26.6	26.8	26.8
4’	44.2	44.0	44.4	44.4
5’	121.0	121.0	125.2	125.2
6’	142.1	141.9	138.4	137.9
7’	71.4	71.5	82.3	82.3
7’-Me	29.7	29.6	24.4	24.5
7’-Me	29.9	29.7	24.4	24.3



75: protobruceol-III



77: protobruceol-III hydroperoxide

Table SI-11: Protobruceol-III (75) and -III hydroperoxide (77) ^{1}H NMR comparison

	Waterman 1992 400 MHz ($CDCl_3$) **75**[8]	George 2019 500 MHz ($CDCl_3$) **75**	Waterman 1992 400 MHz ($CDCl_3$) **77**[8]	George 2019 500 MHz ($CDCl_3$) **77**
3	6.11 d (9.6)	6.08 d (9.5)	6.15 d (9.6)	6.13 d (9.6)
4	7.96 br d (9.6)	7.94 d (9.5)	7.95 br d (9.6)	7.97 d (9.6)
8	6.54 br s	6.58 s	6.44 br s	6.62 s
1’	6.67 d (10.0)	6.67 d (10.1)	6.68 d(10.0)	6.70 d (10.1)
2’	5.49 d (10.0)	5.47 d (10.1)	5.50 d (10.0)	5.47 d (10.1)
3’-Me	1.43 s	1.42 s	1.44 s	1.42 s
4’-α/β	2.00 – 1.60 m	1.90 – 1.60 m	2.00 – 1.50 m	1.92 – 1.63 m
5’-α/β	2.00 – 1.60 m	1.79 – 1.70 m	2.00 – 1.50 m	1.80 – 1.63 m
6’	4.10 br s	4.12 m	4.30 br t	4.30 t (6.4)
7’-Me	1.71 t*	1.71 d (5.2)	1.71 br s	1.70 d (5.0)
8’	4.87 br s	4.86 br s	5.02 br s	5.00 br s
8’	4.97 br s	4.95 br s	5.04 br s	5.02 br s

^{13}C NMR was not reported for protobruceol-III (**75**) or hydroperoxide (**77**)

*coupling constant was not specified

5. Single crystal X-ray data

General experimental

Single crystals of each sample were mounted under paratone-N oil on a nylon loop, and X-ray diffraction data were collected at 150(2) K with Mo Kα radiation (λ = 0.7107 Å) on an Oxford Diffraction X-calibur small molecule diffractometer.[8] The data sets were corrected for absorption, the structures solved by direct methods using SHELXS-2014 and refined by full matrix least-squares on F^2 by SHELXL-2014, interfaced through the programs X-Seed and/or Olex.[9] In general, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as invariants at geometrically estimated positions. Details of data collection and structure refinement are given below (Table SI-12 and Figures). CCDC numbers 1958707-1958710 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

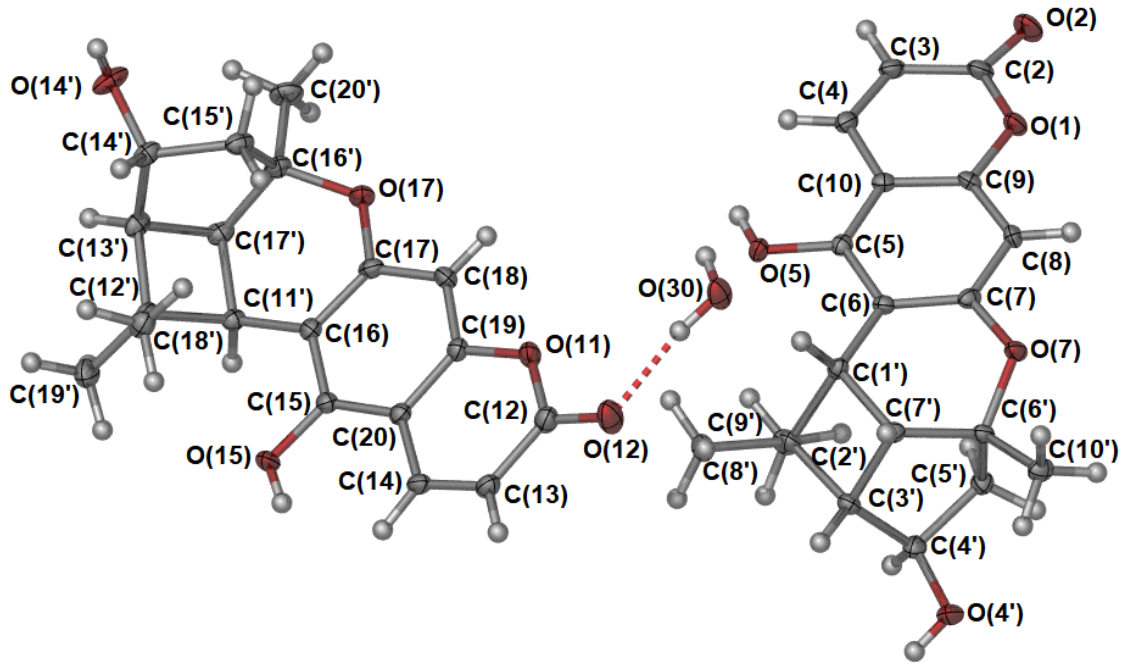
Specific refinement details

30. The absolute structure of this compound was determined by anomalous dispersion effects using Mo Kα radiation. When the reported enantiomer is chosen the Flack parameter is -0.2(2) for the refined structure and the Hooft parameter is -0.1(2). Further support for the absolute structure comes from analysing the Bijvoet pair data; the slope in a Bijvoet plot is positive (1.830) with P2(true) = 1.000 and P3(true) 0.993, suggesting the correct enantiomer has been assigned.[10] Two molecules, with the same absolute structure are present in the asymmetric unit but are involved in unique sets of hydrogen bonding interactions with the single water molecule and symmetry-related molecules of **30**.

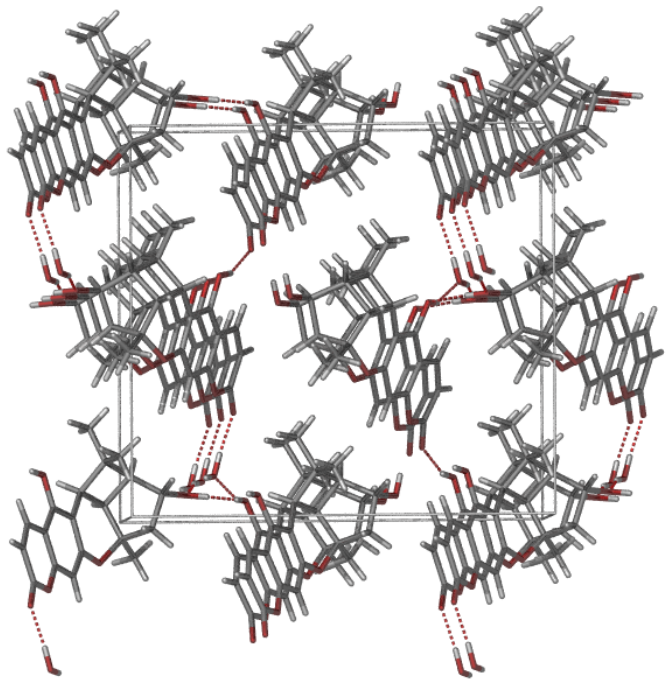
68a. Compounds **68a** and **68b** are isomorphous but not isostructural. A small residual amount of **68b** has co-crystallised with **68a** resulting in a peak in the electron density map adjacent to atom C3. This was refined satisfactorily as a low occupancy bromine atom (2.5% occupancy) at this position consistent with co-crystallisation.

Table SI-12. X-ray experimental data for **30**, **69a**, **68a** and **68b**.

Compound	**30**	**69a**	**68a**	**68b**
Data code	AD3-190-76	Br2epicitran	Br2citran	Br3citran
CCDC #	1958707	1958708	1958709	1958710
Empirical formula	$C_{38}H_{42}O_{11}$	$C_{19}H_{18}Br_2O_4$	$C_{19}H_{17.98}O_4Br_{2.02}$	$C_{19}H_{17}O_4Br_3$
Formula weight	674.71	470.15	472.13	549.05
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1$	P-1	$P2_1/c$	$P2_1/c$
a/Å	6.33660(10)	7.0199(2)	11.3644(6)	11.2865(2)
b/Å	15.3568(2)	8.2476(2)	8.7153(5)	8.9228(2)
c/Å	16.6789(2)	15.7704(4)	17.5002(11)	18.4922(4)
α/°	90	88.837(2)	90	90
β/°	99.6180(10)	78.506(2)	90.885(5)	95.950(2)
γ/°	90	76.606(3)	90	90
Volume/Å^3	1600.21(4)	870.10(4)	1733.09(17)	1852.26(7)
Z	2	2	4	4
ρ_{calc}g/cm^3	1.400	1.795	1.809	1.969
μ/mm^{-1}	0.103	4.680	4.757	6.556
F(000)	716.0	468.0	939.0	1072.0
Crystal size/mm^3	0.40 × 0.18 × 0.14	0.40 × 0.30 × 0.11	0.47 × 0.32 × 0.23	0.44 × 0.30 × 0.18
2θ range for data collection/°	7.042 to 58.714	6.966 to 58.762	7.172 to 58.756	7.094 to 58.538
Reflections collected	56739	30830	20229	21055
Independent reflections	8066 [R_{int} = 0.0391]	4360 [R_{int} = 0.0573]	4303 [R_{int} = 0.0361]	4533 [R_{int} = 0.0388]
Data/restraints/parameters	8066/3/458	4360/0/229	4303/1/239	4533/0/238
Goodness-of-fit on F^2	1.032	1.057	1.044	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0354, wR_2 = 0.0822	R_1 = 0.0367, wR_2 = 0.0719	R_1 = 0.0323, wR_2 = 0.0684	R_1 = 0.0315, wR_2 = 0.0620
Final R indexes [all data]	R_1 = 0.0404, wR_2 = 0.0846	R_1 = 0.0567, wR_2 = 0.0777	R_1 = 0.0464, wR_2 = 0.0738	R_1 = 0.0475, wR_2 = 0.0672
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25	0.72/-0.50	0.97/-0.57	0.80/-0.58
Flack parameter	-0.2(2)			



(a)



(b)

Figure SI-1. (a) A representation of the structure of **30**, showing the two molecules of WW and the water solvate in the asymmetric unit with ellipsoids presented with 50% probability level. Carbon - grey; hydrogen - white; and oxygen - red. (b) A view slightly off the *a*-axis showing the ABA layers in the crystal packing and the crystallographically distinct environments for the two molecules in the asymmetric unit. Single crystals were grown from neat ethanol.

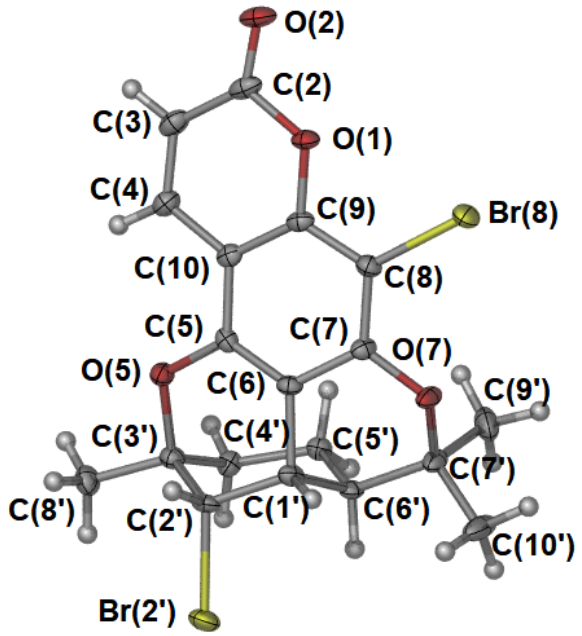


Figure SI-2. A representation of the structure of **69a** with ellipsoids presented with 50% probability level. Carbon - grey; hydrogen - white; oxygen - red; and bromine - yellow. Single crystals were grown from a petrol/ethyl acetate mixture.

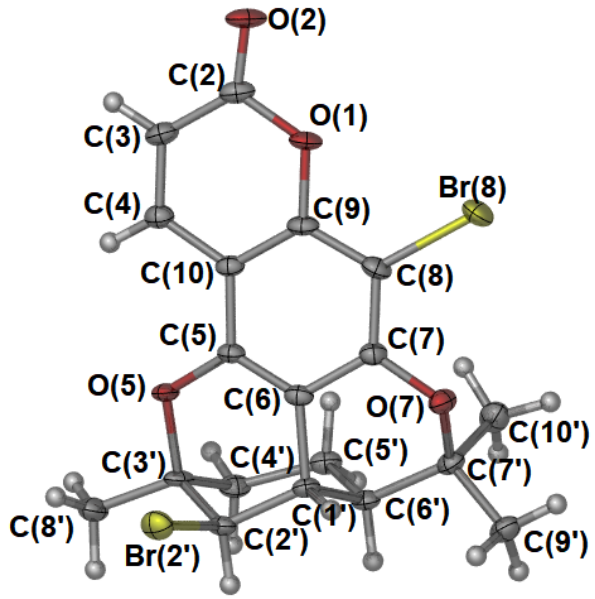


Figure SI-3. A representation of the structure of **68a** with ellipsoids presented with 50% probability level. Carbon - grey; hydrogen - white; oxygen - red; and bromine - yellow. The disorder arising from co-crystallisation is not shown. Single crystals were grown from a petrol/ethyl acetate mixture.

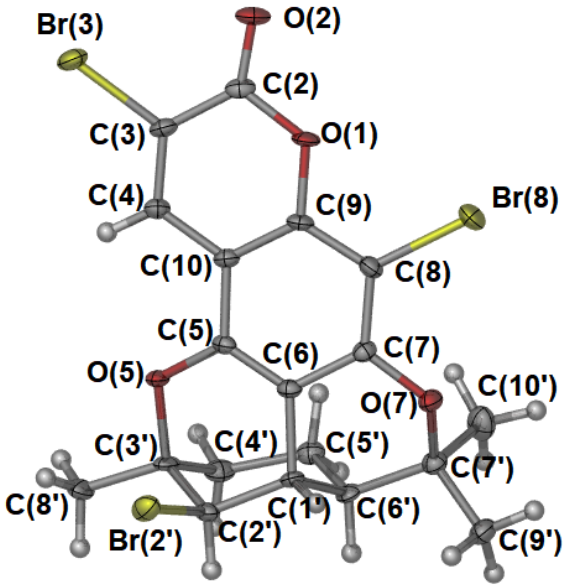


Figure SI-4. A representation of the structure of **68b** with ellipsoids presented with 50% probability level. Carbon - grey; hydrogen - white; oxygen - red; and bromine - yellow. Single crystals were grown from a petrol/ethyl acetate mixture.

6. References

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