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– SUPPORTING INFORMATION –

Terpene Cyclase Mimicking Chlorine-Induced Polyene Cyclizations

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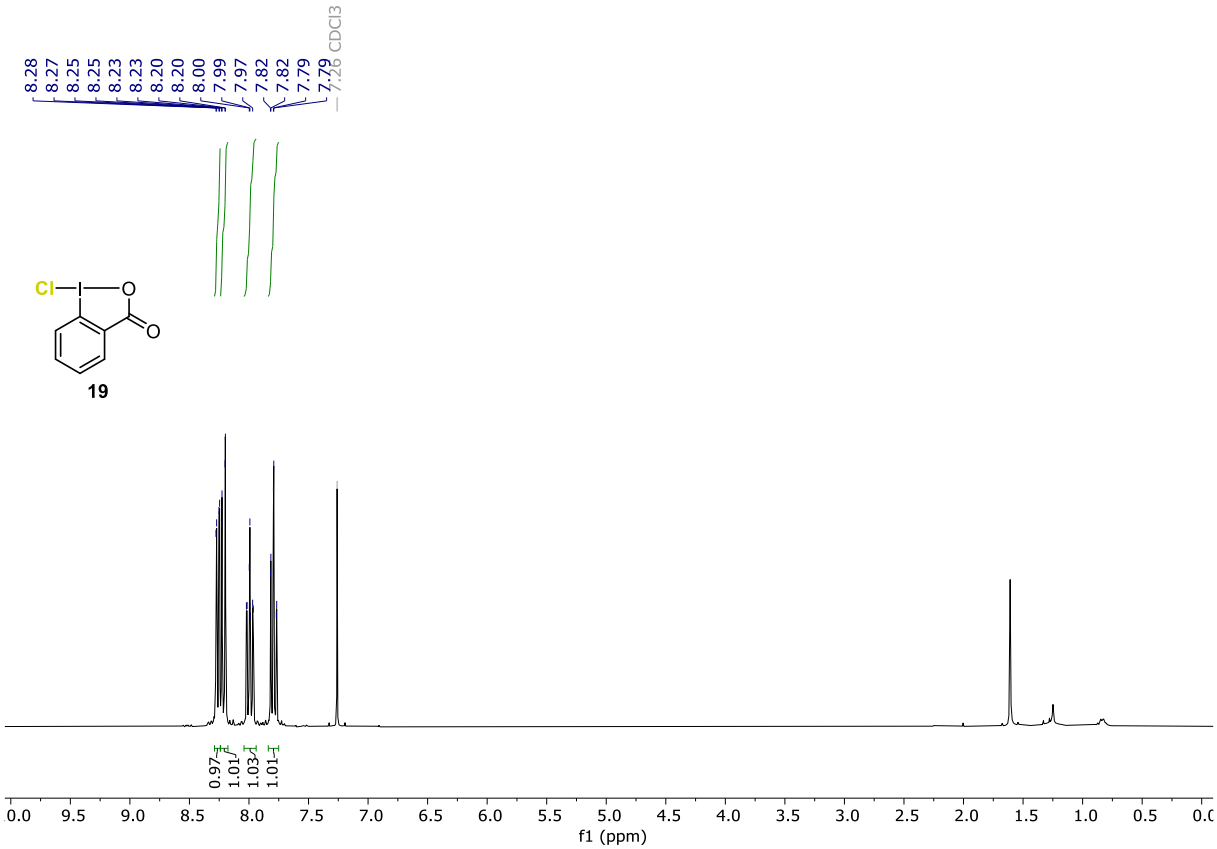
[b]Biomimetic Catalysis, Department of Chemistry and Catalysis Research Center, Technical University Munich, Lichtenbergstrasse 4, 85748 Garching, Germany

NMR spectra of reagents 19, 21, S6 – S12 and compounds 16, 24 – 43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7.82
7.79
7.79
7.26 CDCl3
Cl
I
O
O
19
0.97
1.01
1.03
1.01
0.0 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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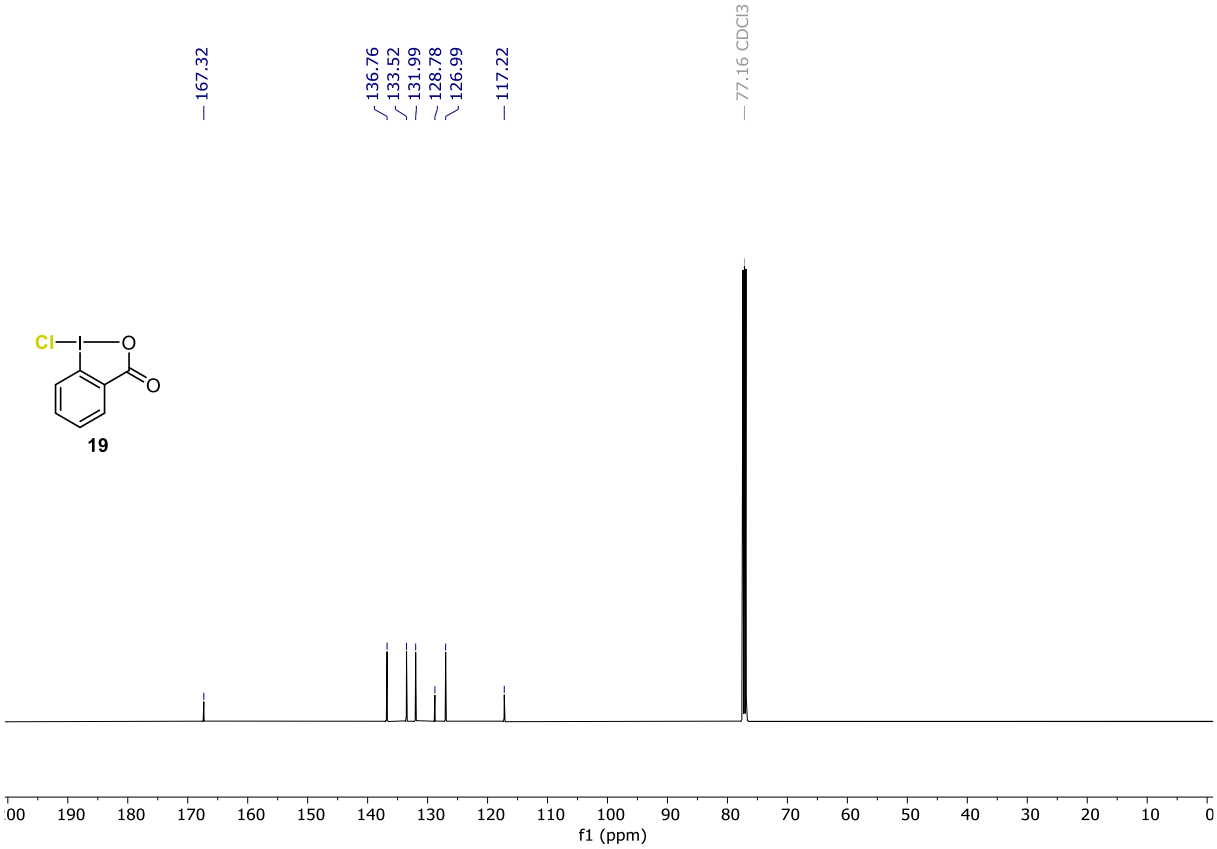
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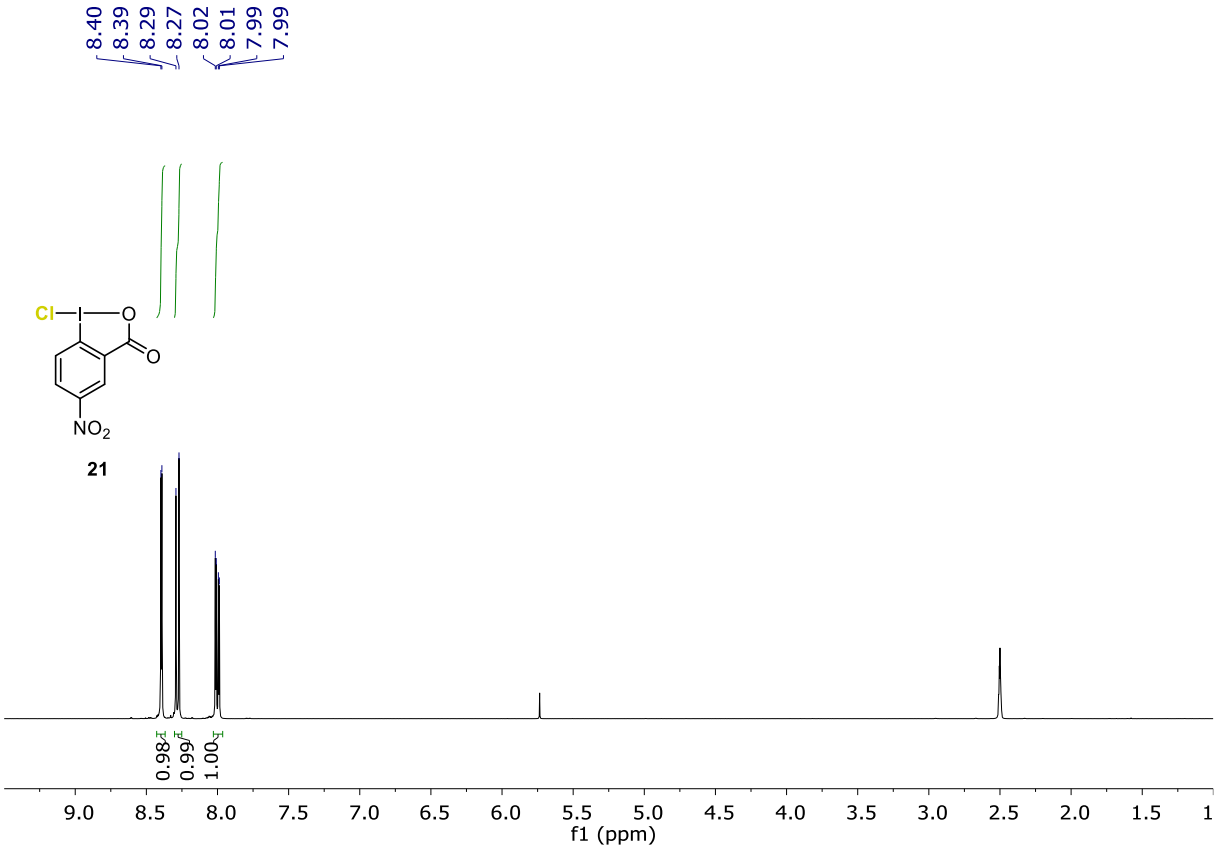
f1 (ppm)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0.99
1.00
9.0
8.5
8.0
7.5
7.0
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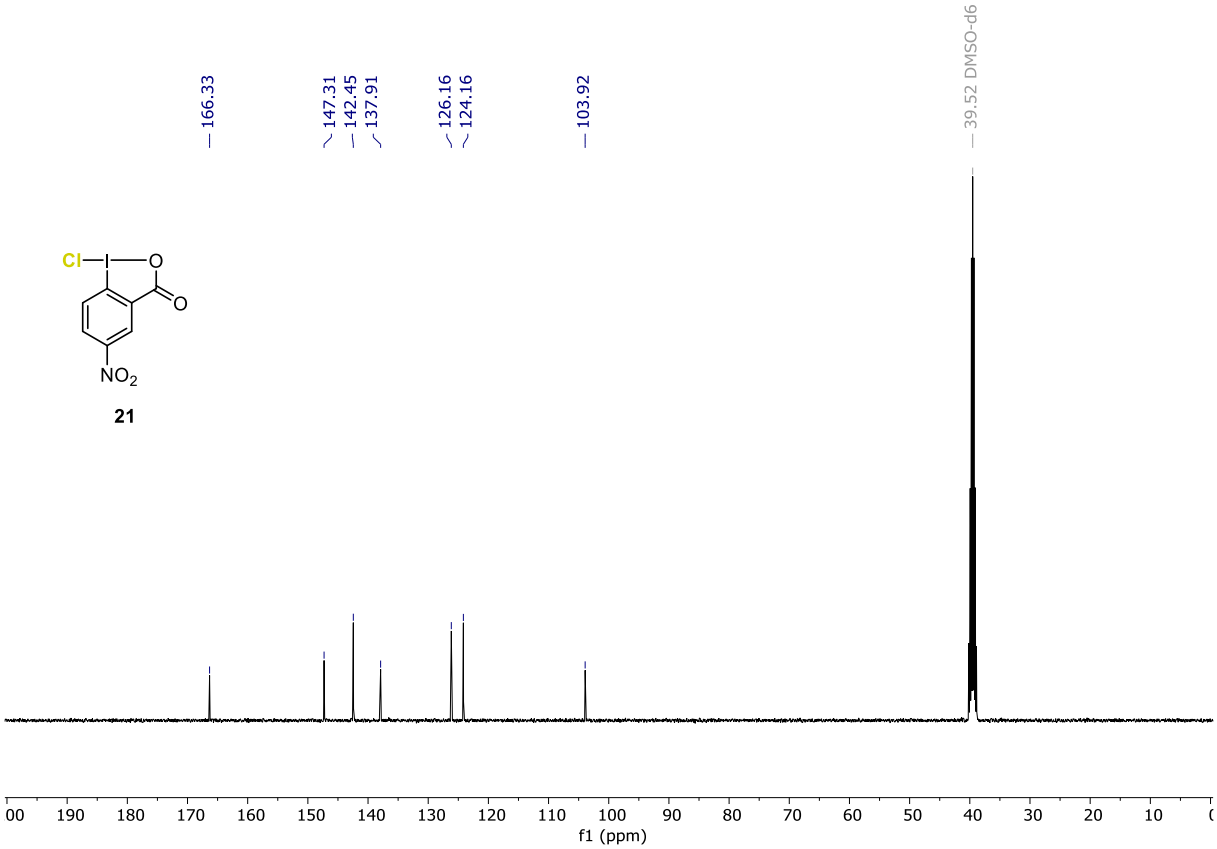
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I
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21
190
180
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130
120
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100
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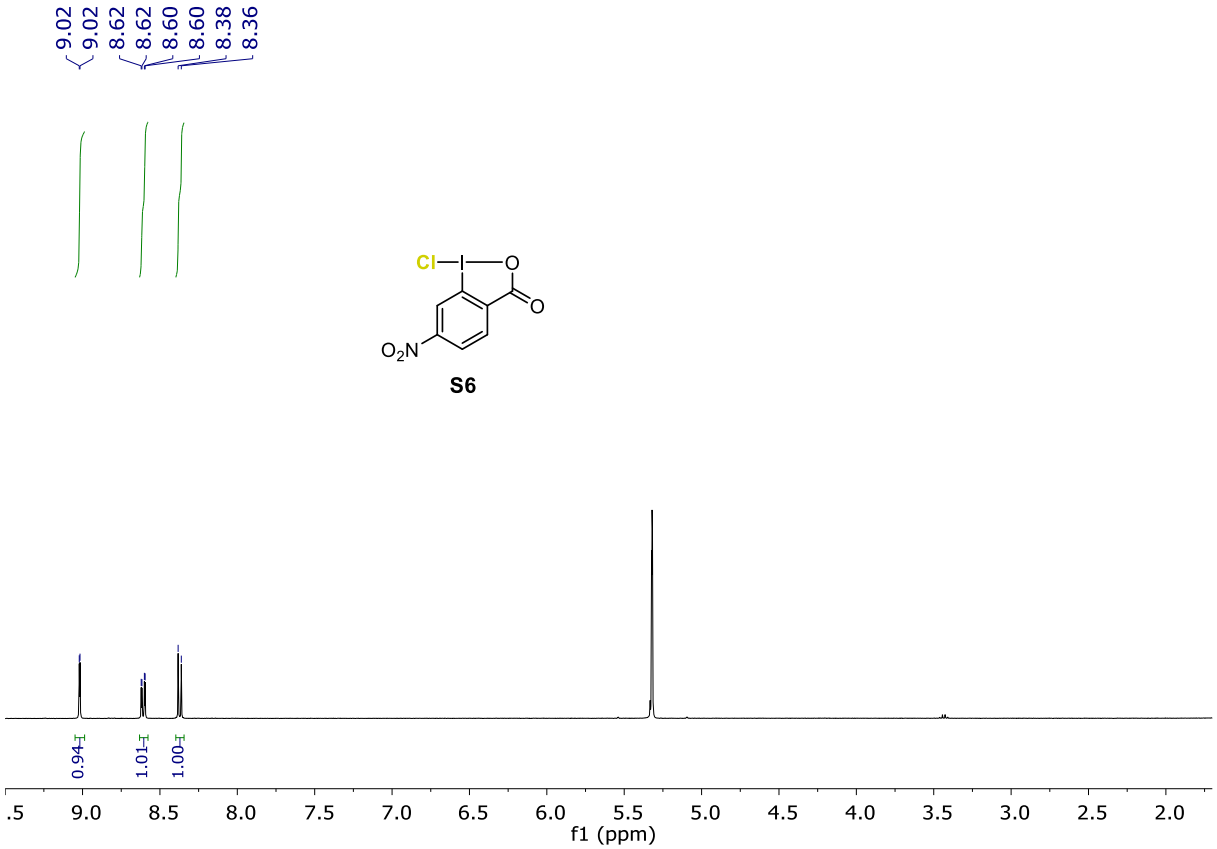
20
10
f1 (ppm)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S6
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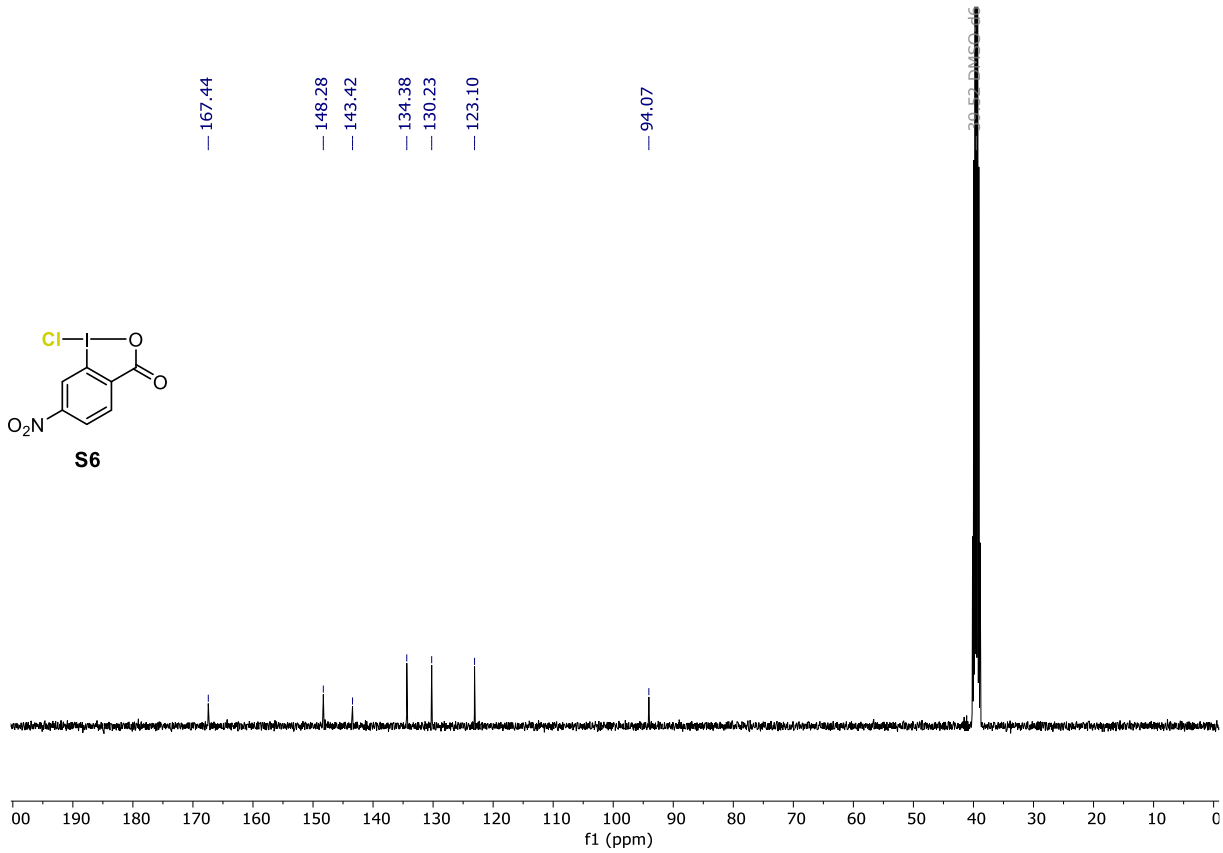
f1 (ppm)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O
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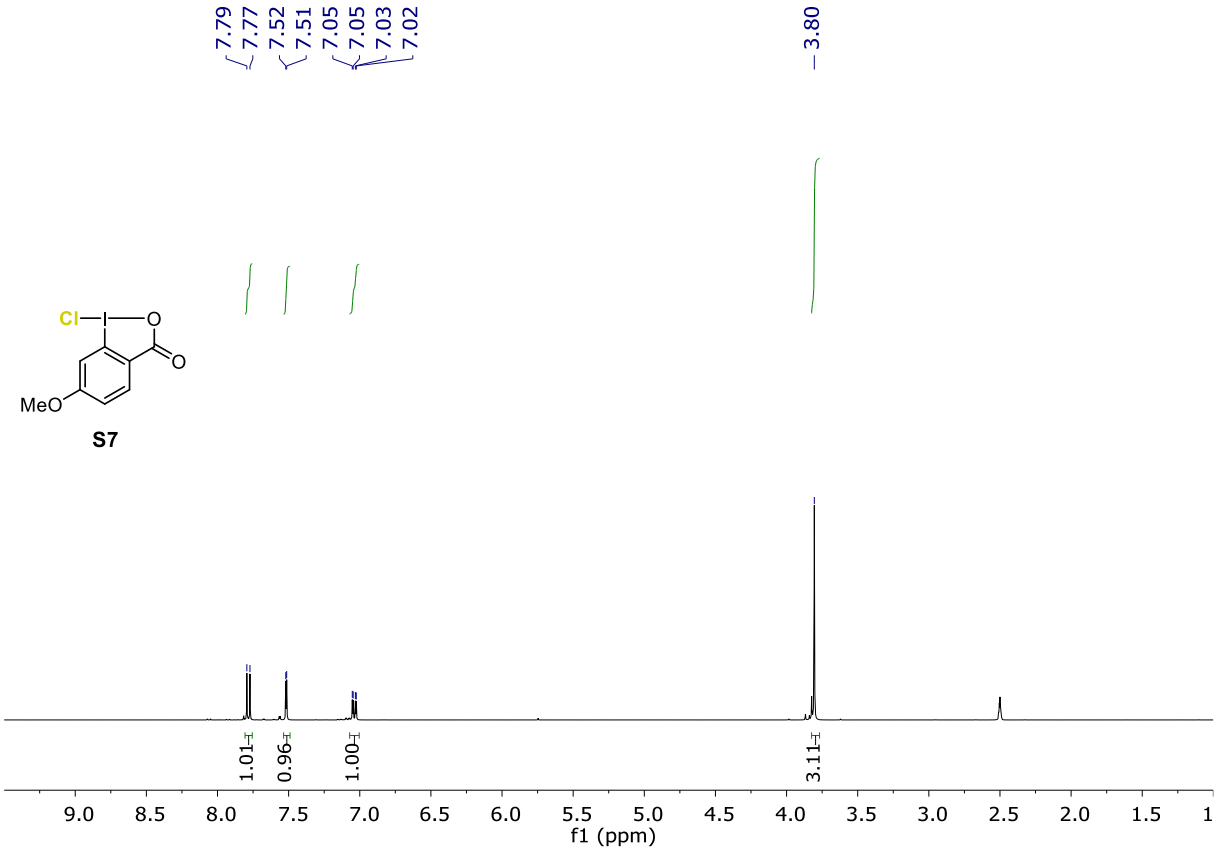
S6
f1 (ppm)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S7
1.01
0.96
1.00
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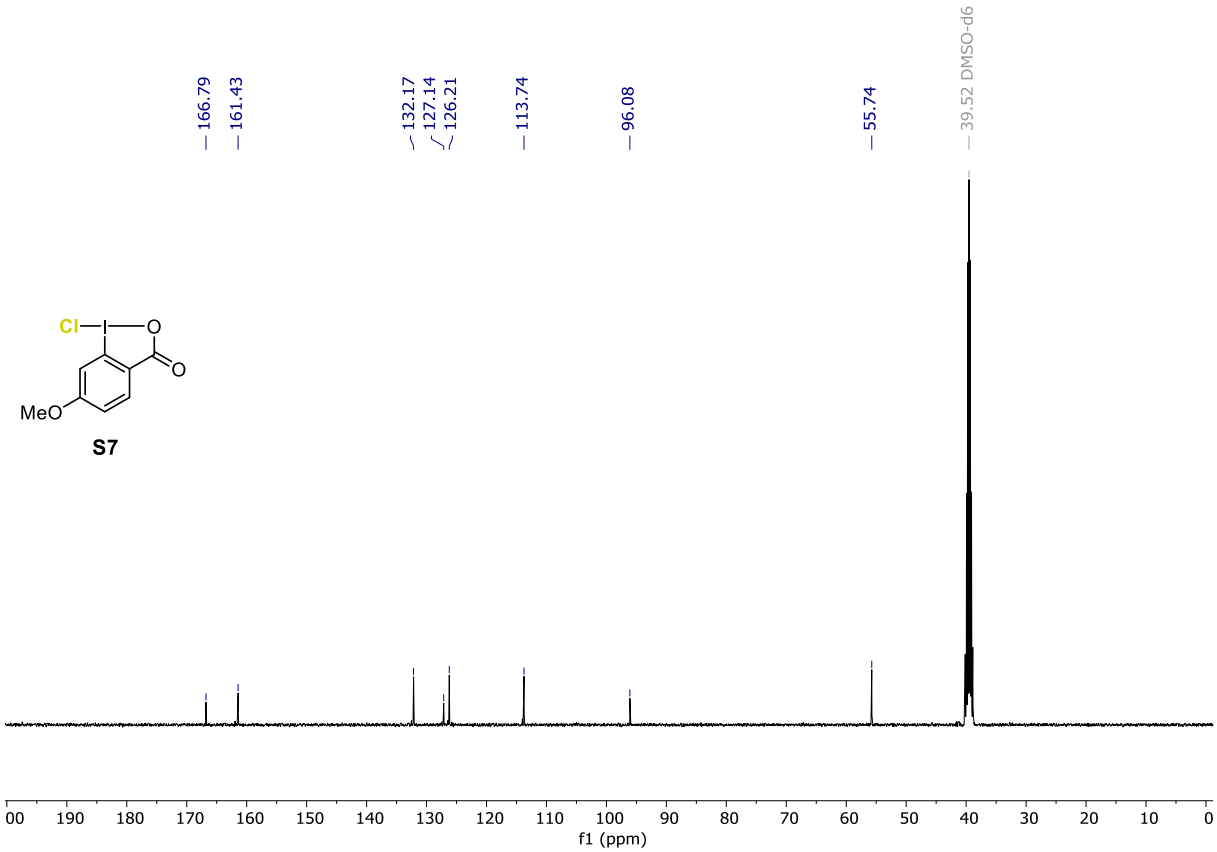
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MeO
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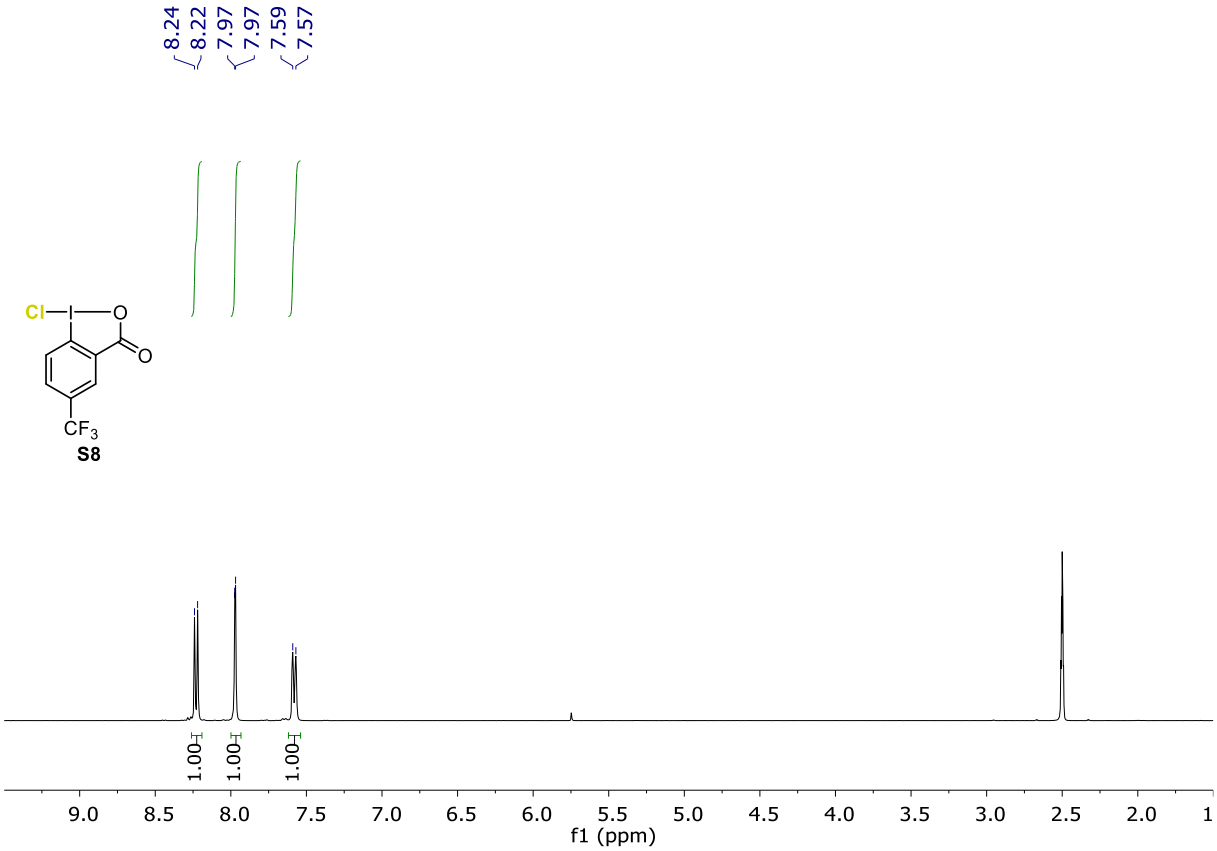
f1 (ppm)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S8
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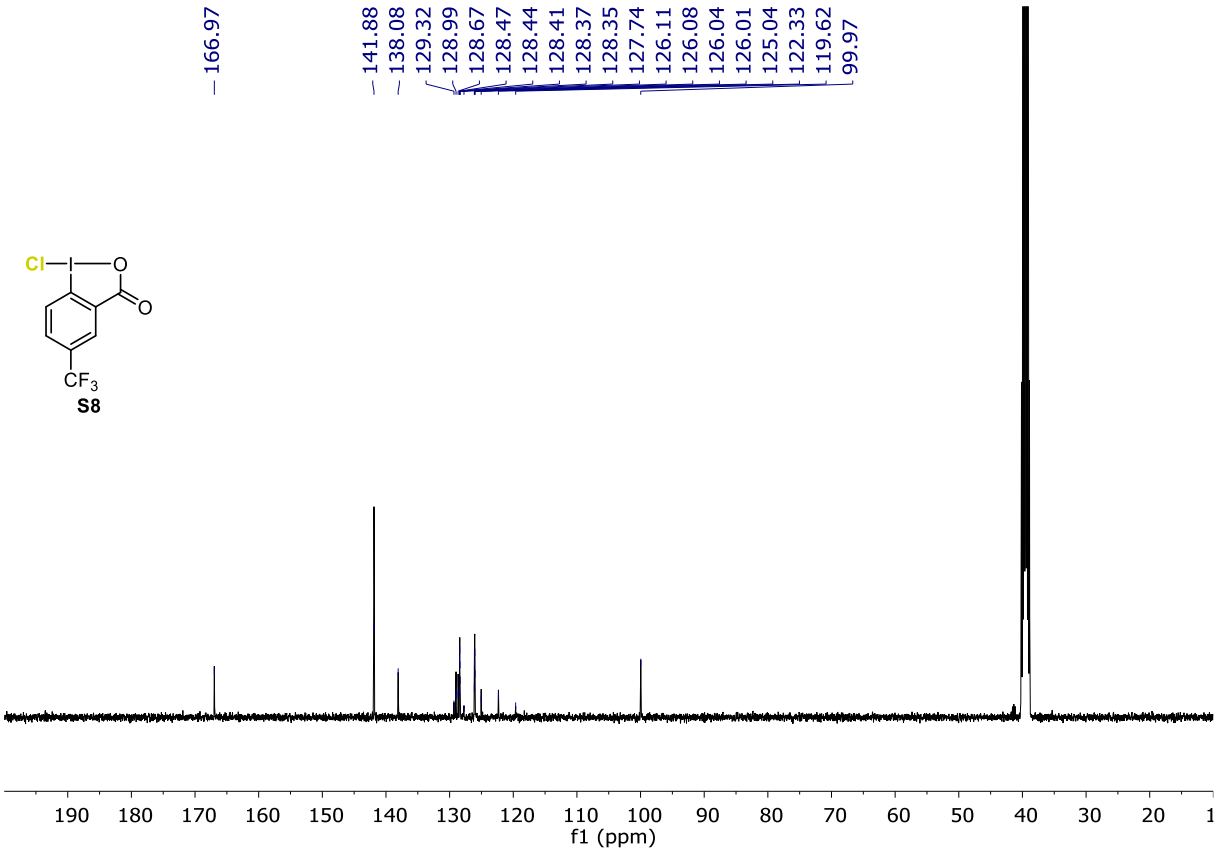
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126.08
126.04
126.01
125.04
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Cl
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O
CF3
S8
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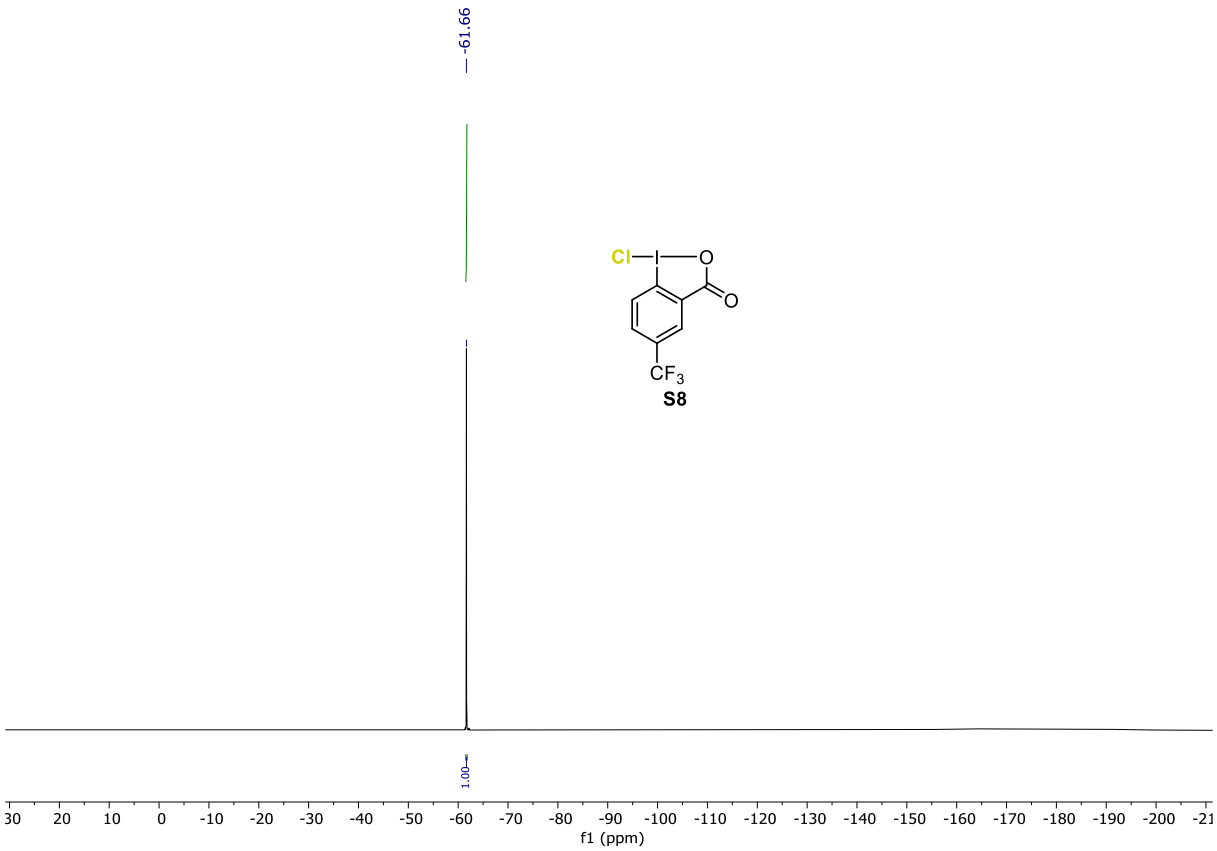
f1 (ppm)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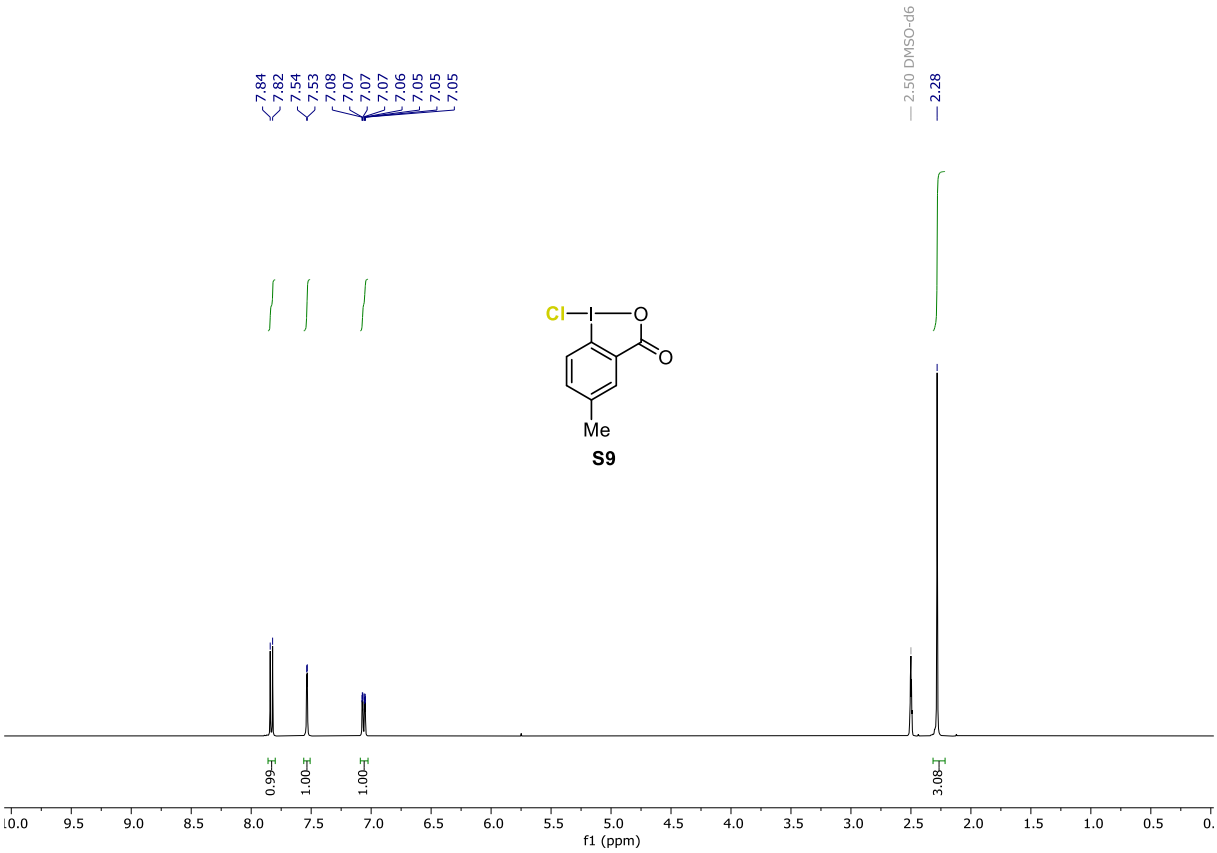
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7.05
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7.05
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Cl
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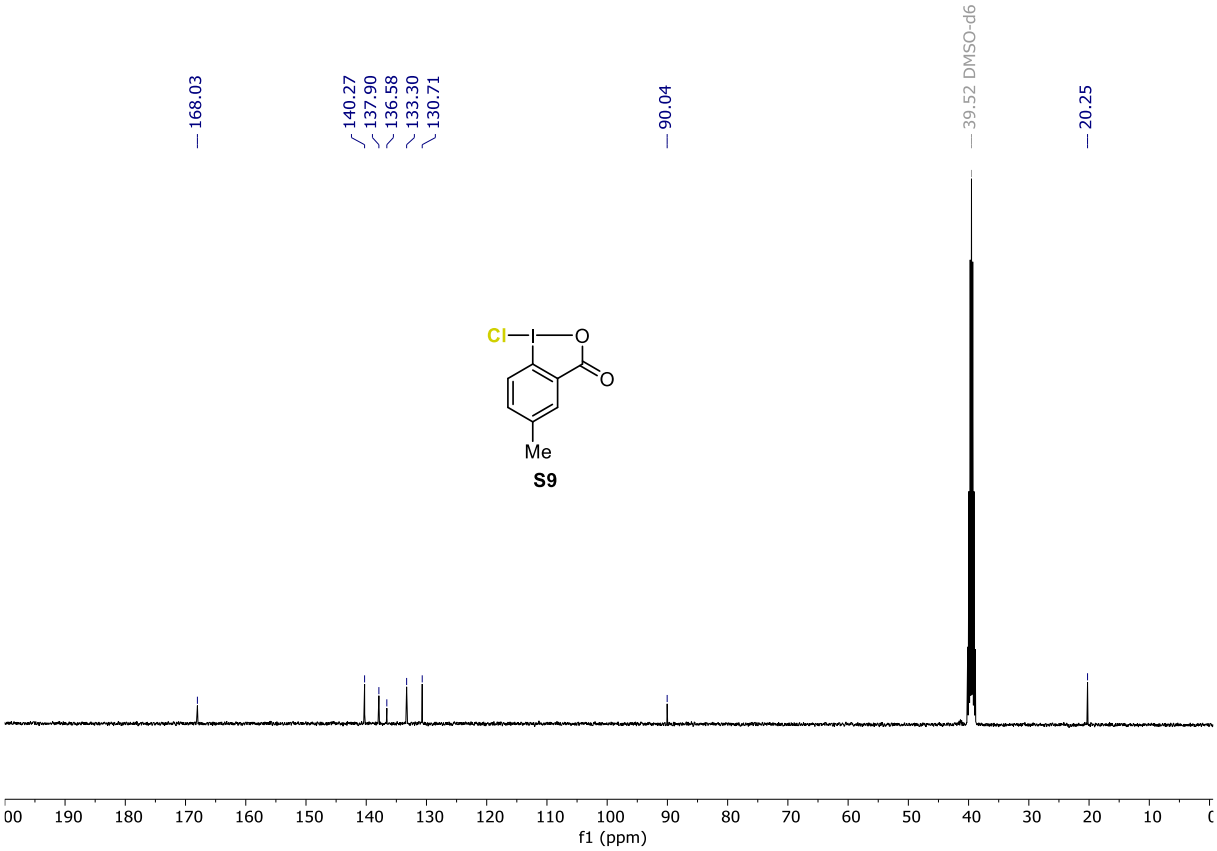
f1 (ppm)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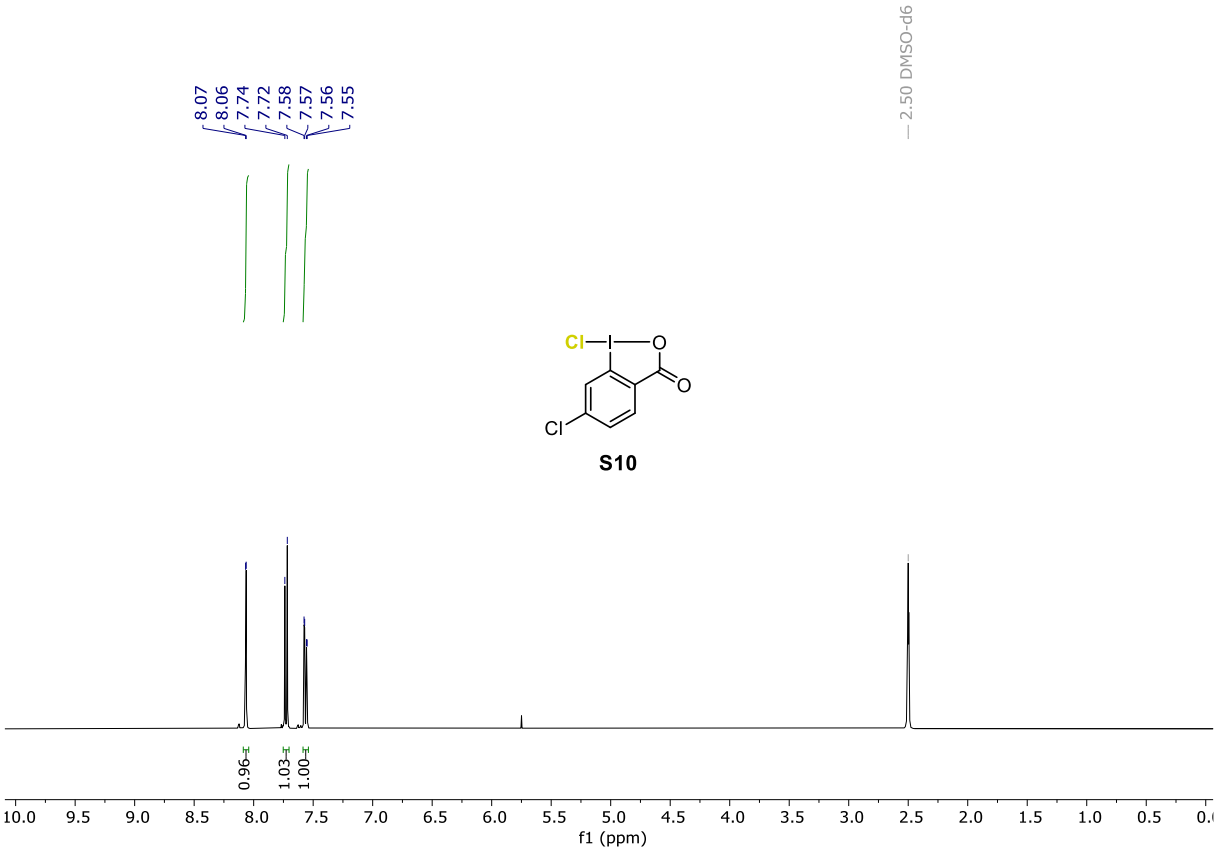
Me
S9
f1 (ppm)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O
Cl
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1.03
1.00
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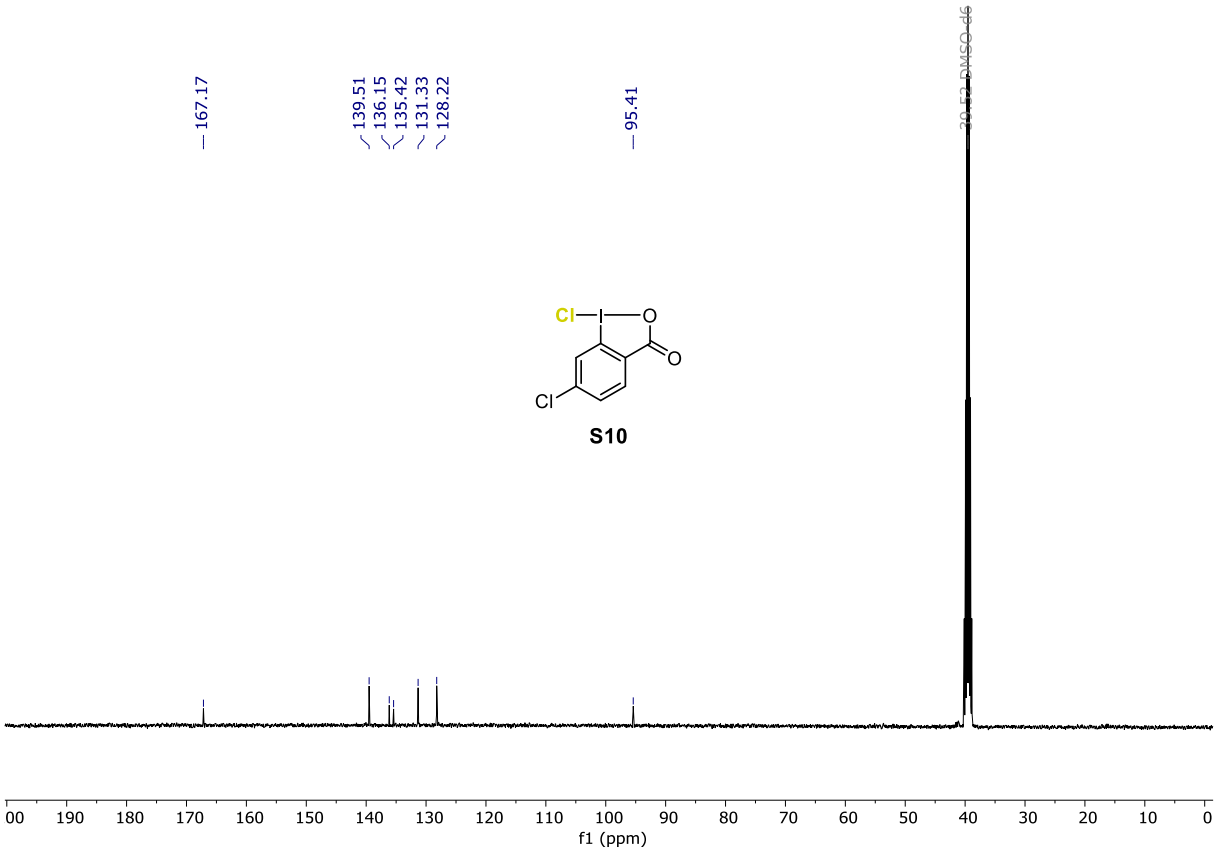
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I
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O
Cl
S10
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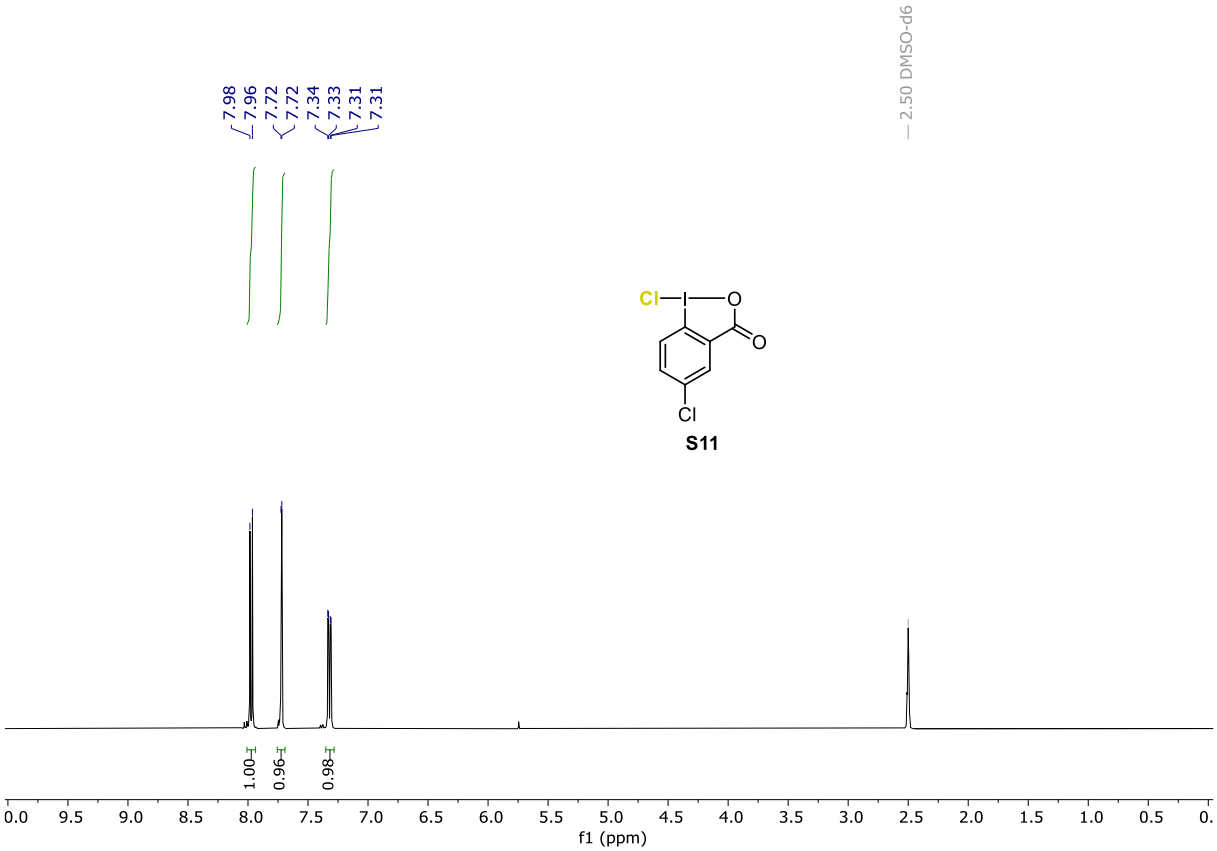
f1 (ppm)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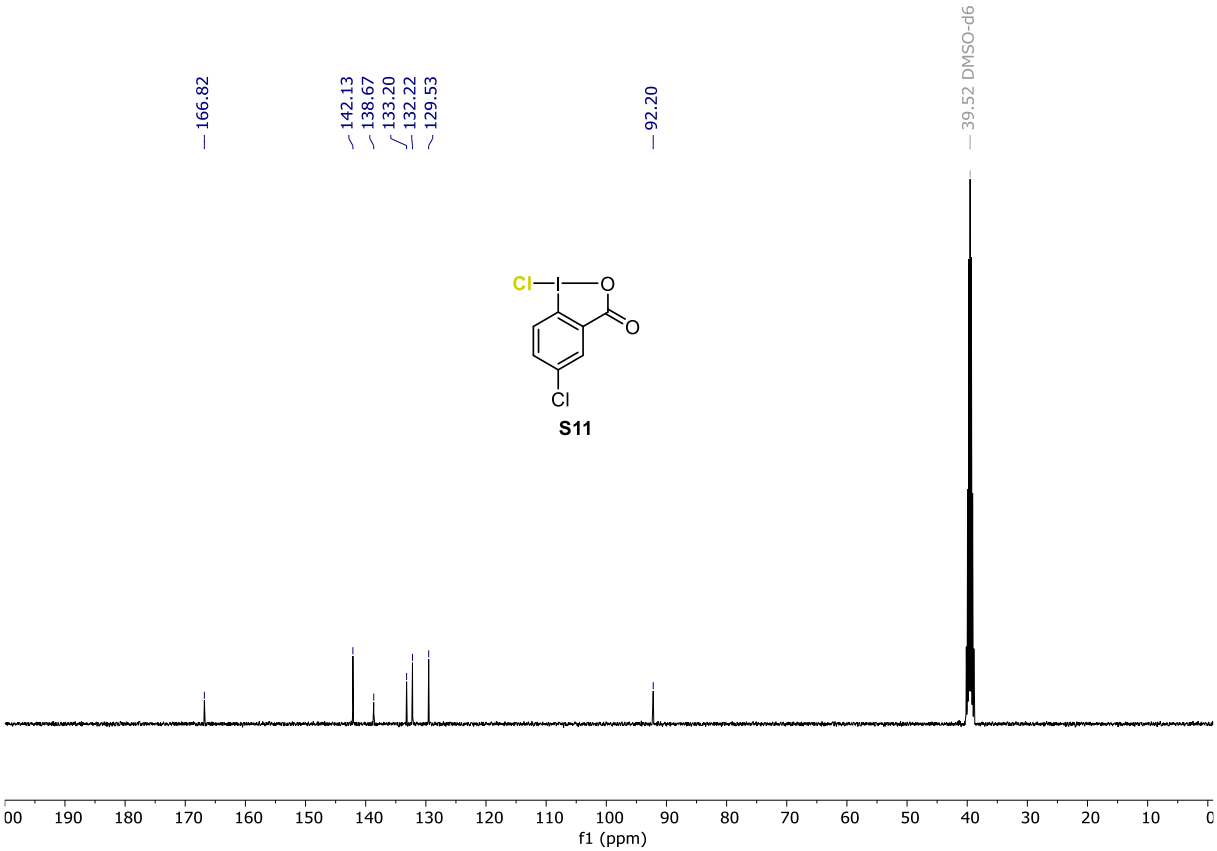
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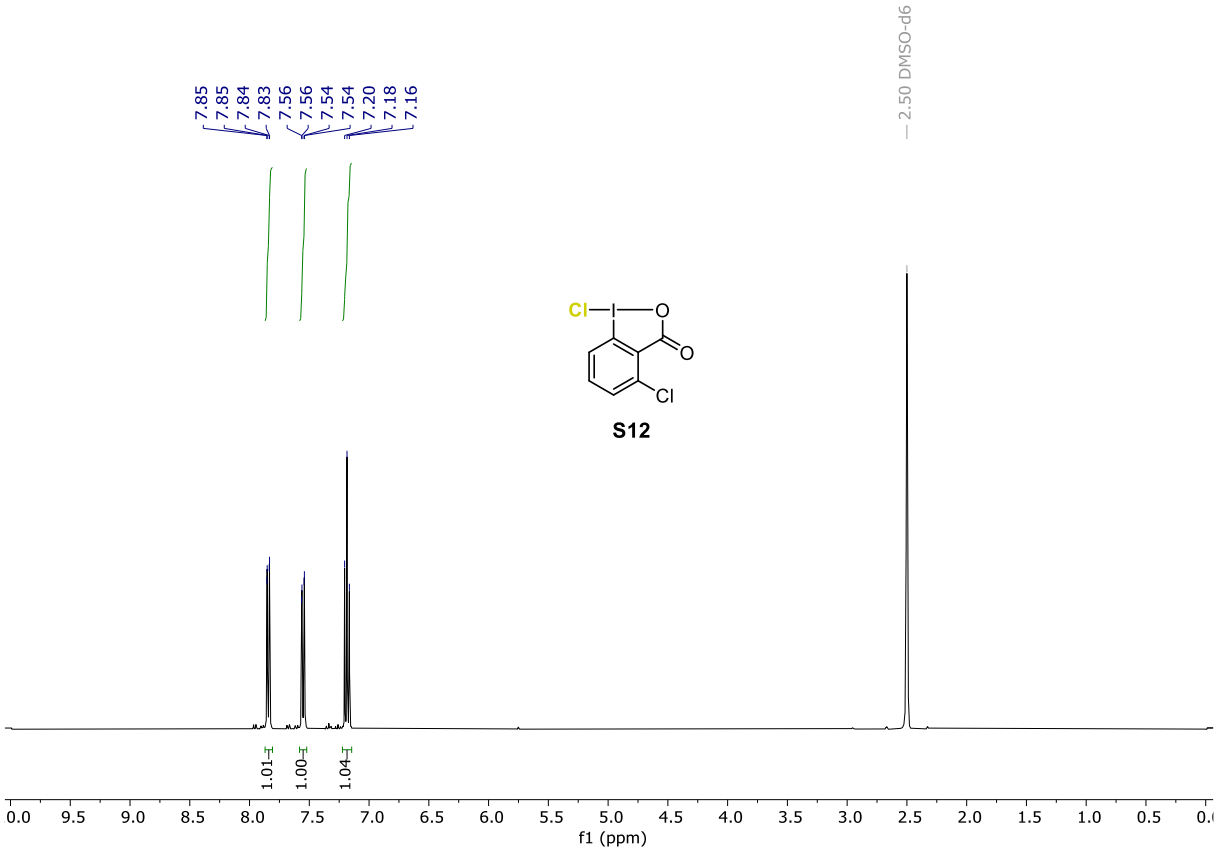
Cl
S11
f1 (ppm)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7.18
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Cl
I
O
O
Cl
S12
1.01
1.00
1.04
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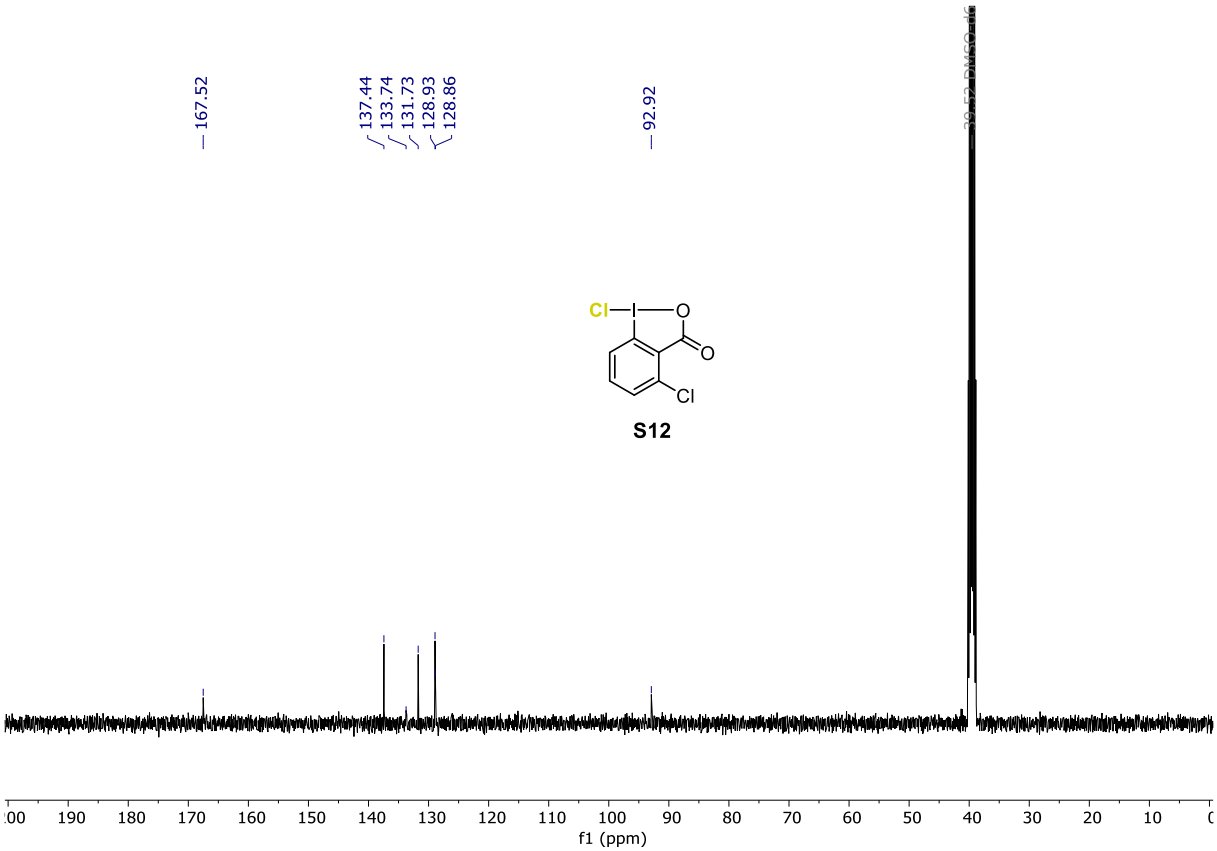
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O
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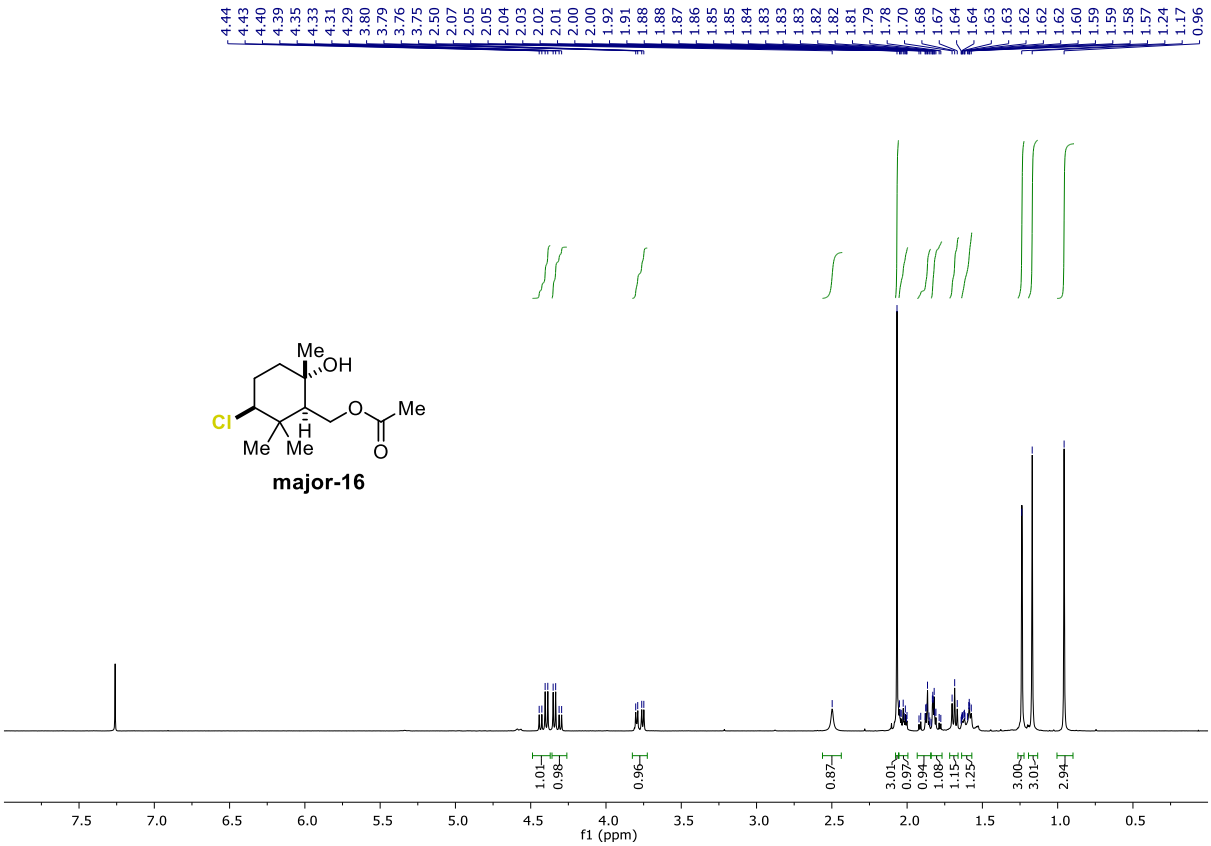
f1 (ppm)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Me
OH
Cl
O
Me
H
Me Me
O
major-16
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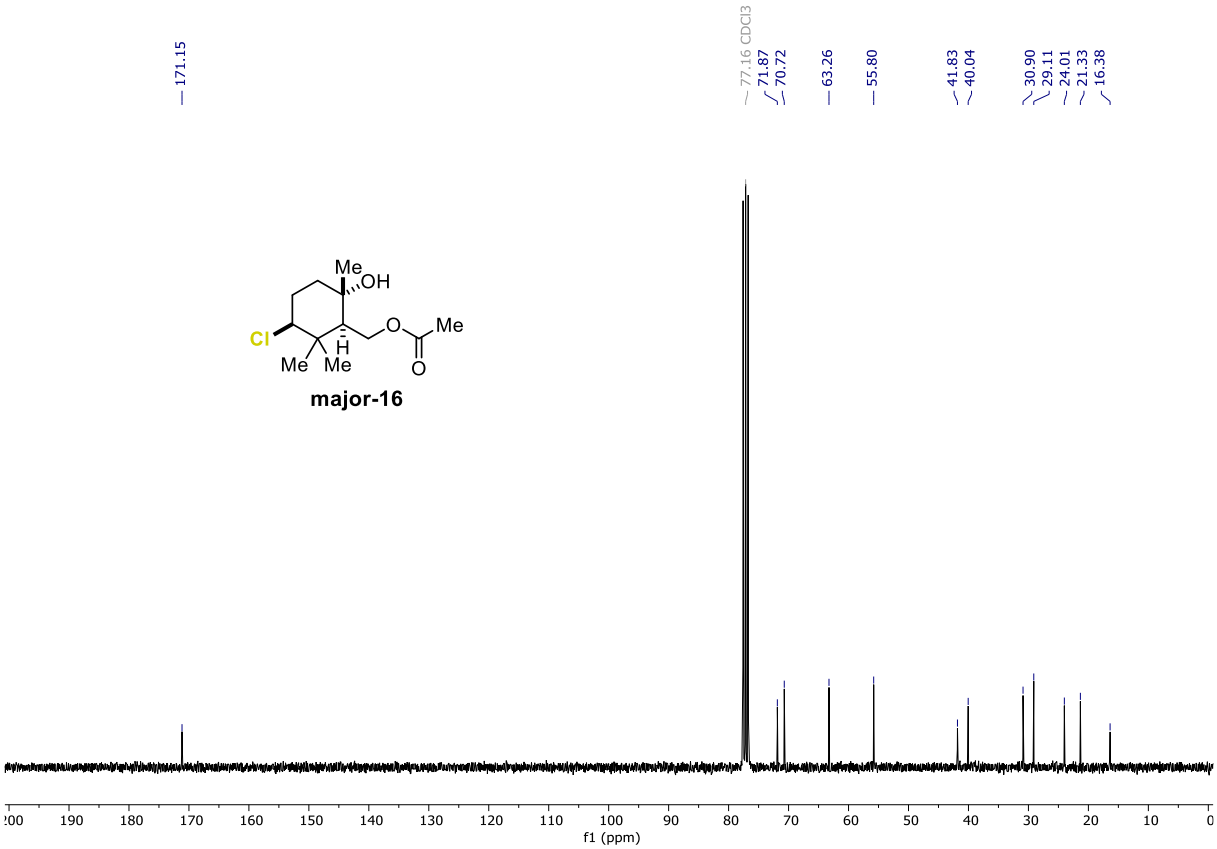
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40.04
30.90
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24.01
21.33
16.38
Me
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O
Me
H
Me Me
O
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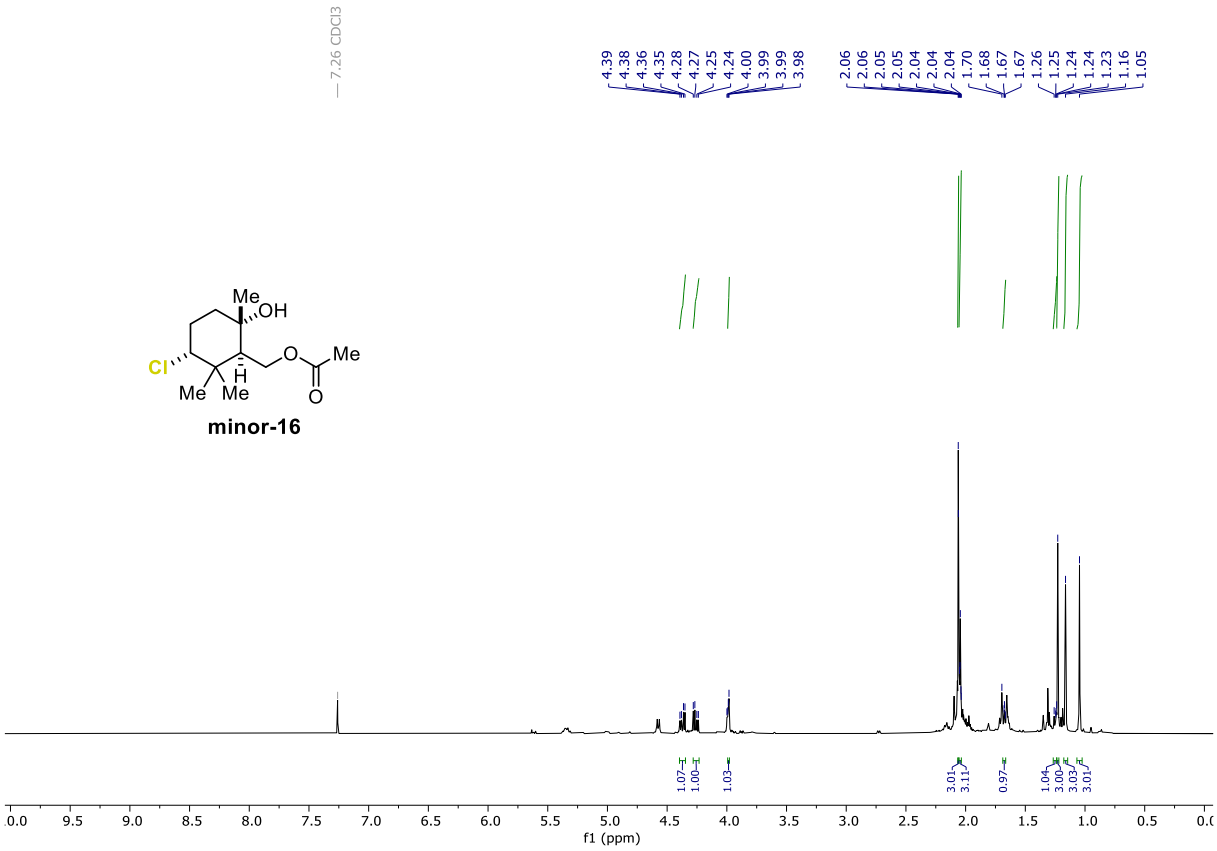
f1 (ppm)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1.05
Me
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Me
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Me
Me
O
minor-16
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1.00
1.03
3.01
3.11
0.97
1.04
3.00
3.03
3.01
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8.5
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7.5
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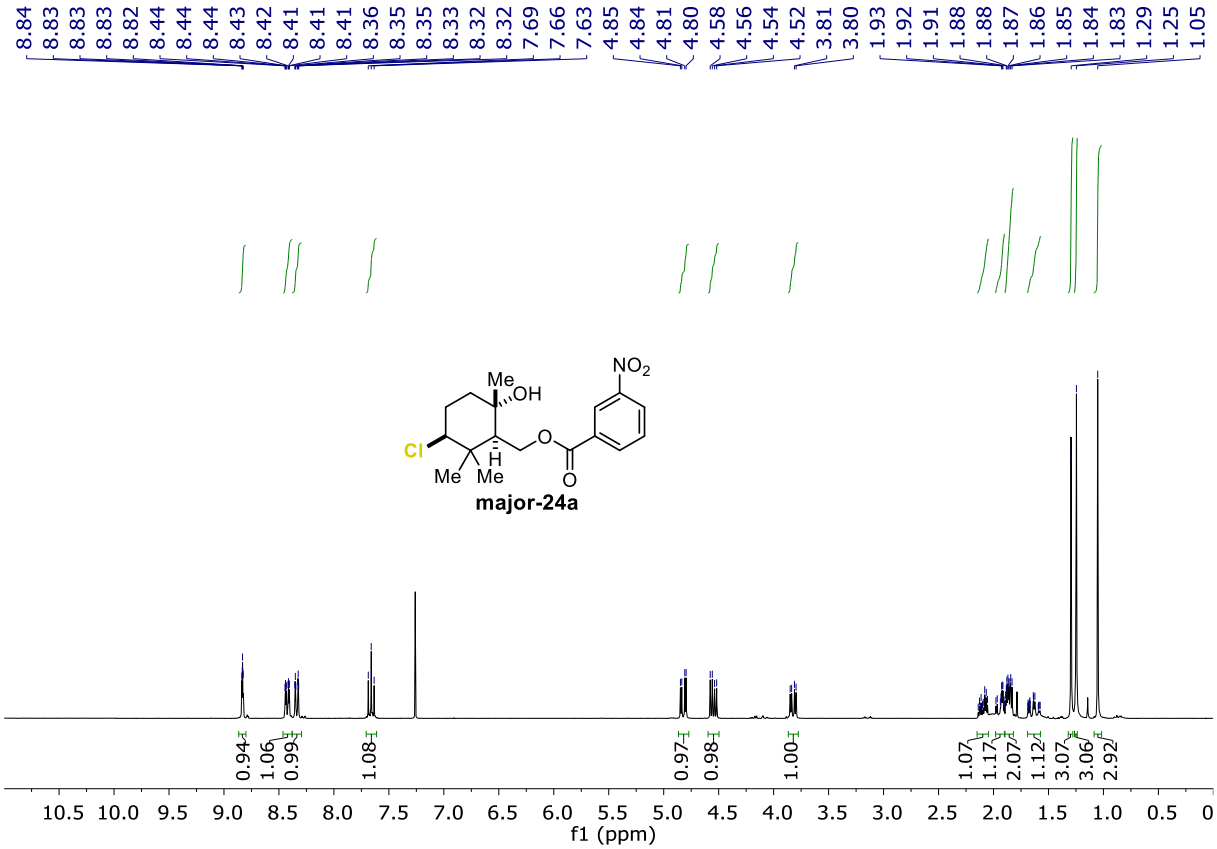
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4.85 4.84 4.81 4.80 4.58 4.56 4.54 4.52 3.81 3.80
1.93 1.92 1.91 1.88 1.88 1.87 1.86 1.85 1.84 1.83 1.29 1.25 1.05
NO2
Me
OH
Cl
O
H
Me Me
O
major-24a
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10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
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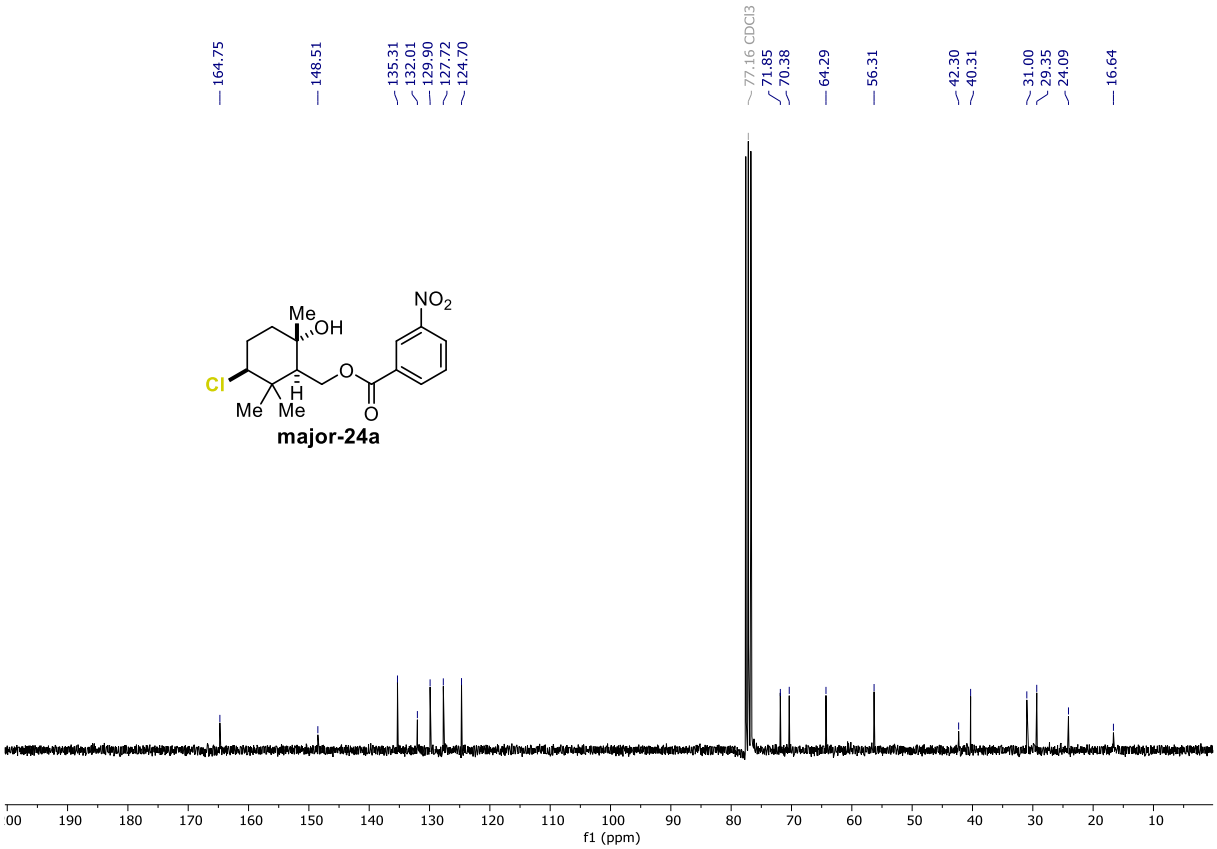
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135.31 132.01 129.90 127.72 124.70
77.16 CDCl3
71.85 70.38
64.29
56.31
42.30 40.31
31.00 29.35 24.09
16.64
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Me Me
O
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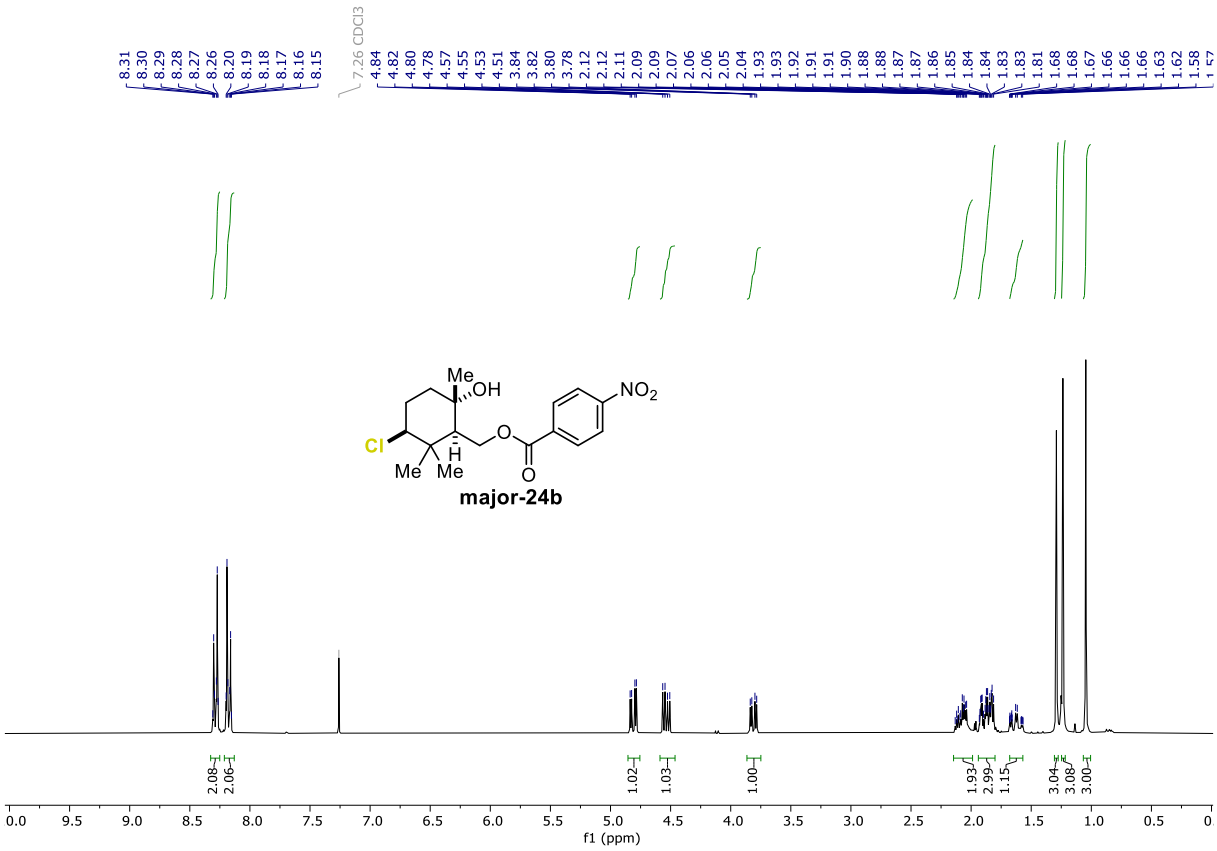
f1 (ppm)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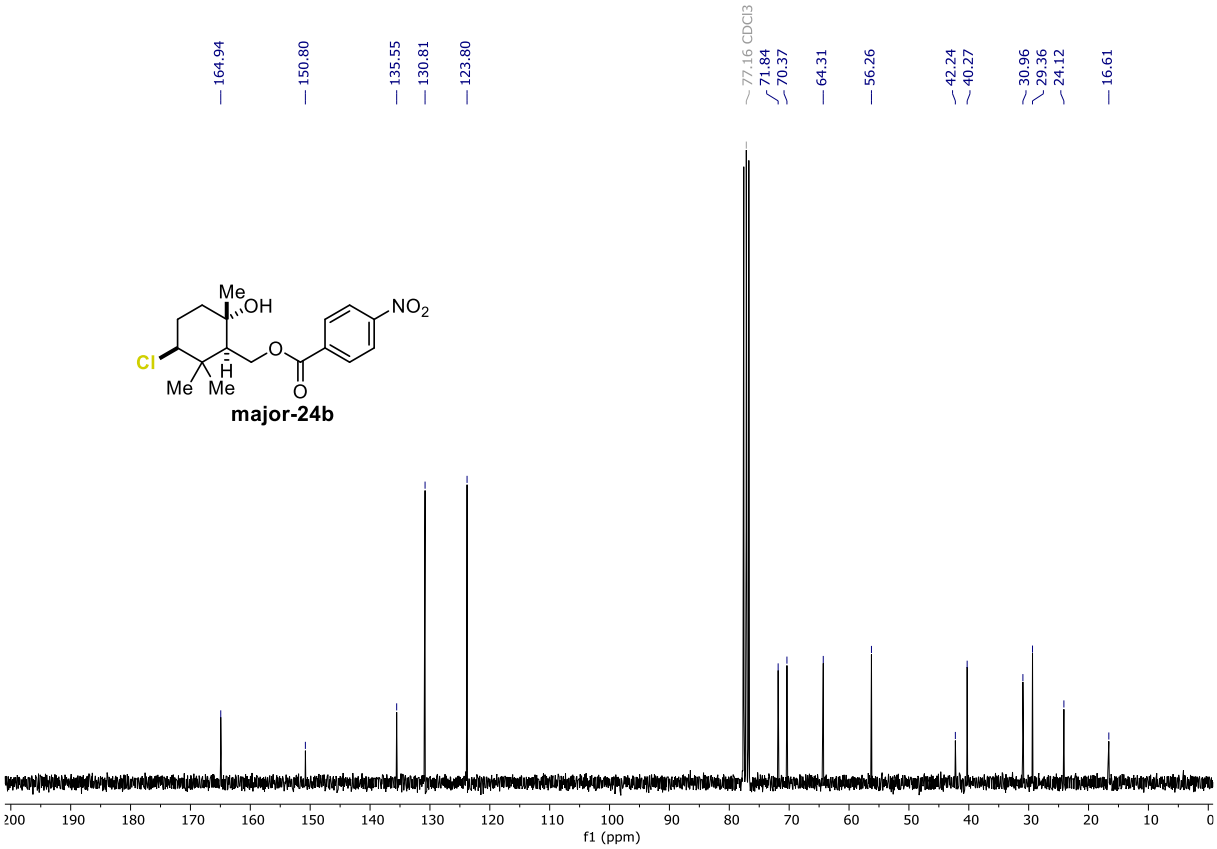
4.84 4.82 4.80 4.78 4.57 4.55 4.53 4.51 3.84 3.82 3.80 3.78 2.12 2.12 2.11 2.09 2.09 2.07 2.06 2.06 2.05 2.04 1.93 1.93 1.92 1.91 1.91 1.90 1.88 1.88 1.87 1.87 1.86 1.85 1.84 1.84 1.83 1.83 1.81 1.68 1.68 1.67 1.66 1.66 1.66 1.63 1.62 1.58
Me
OH
NO2
Cl
O
H
Me Me
O
major-24b
2.08 2.06 1.02 1.03 1.00 1.93 2.99 1.15 3.04 3.08 3.00
0.0 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
f1 (ppm)


164.94
150.80
135.55
130.81
123.80
77.16 CDCl3
71.84
70.37
64.31
56.26
42.24
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30.96
29.36
24.12
16.61
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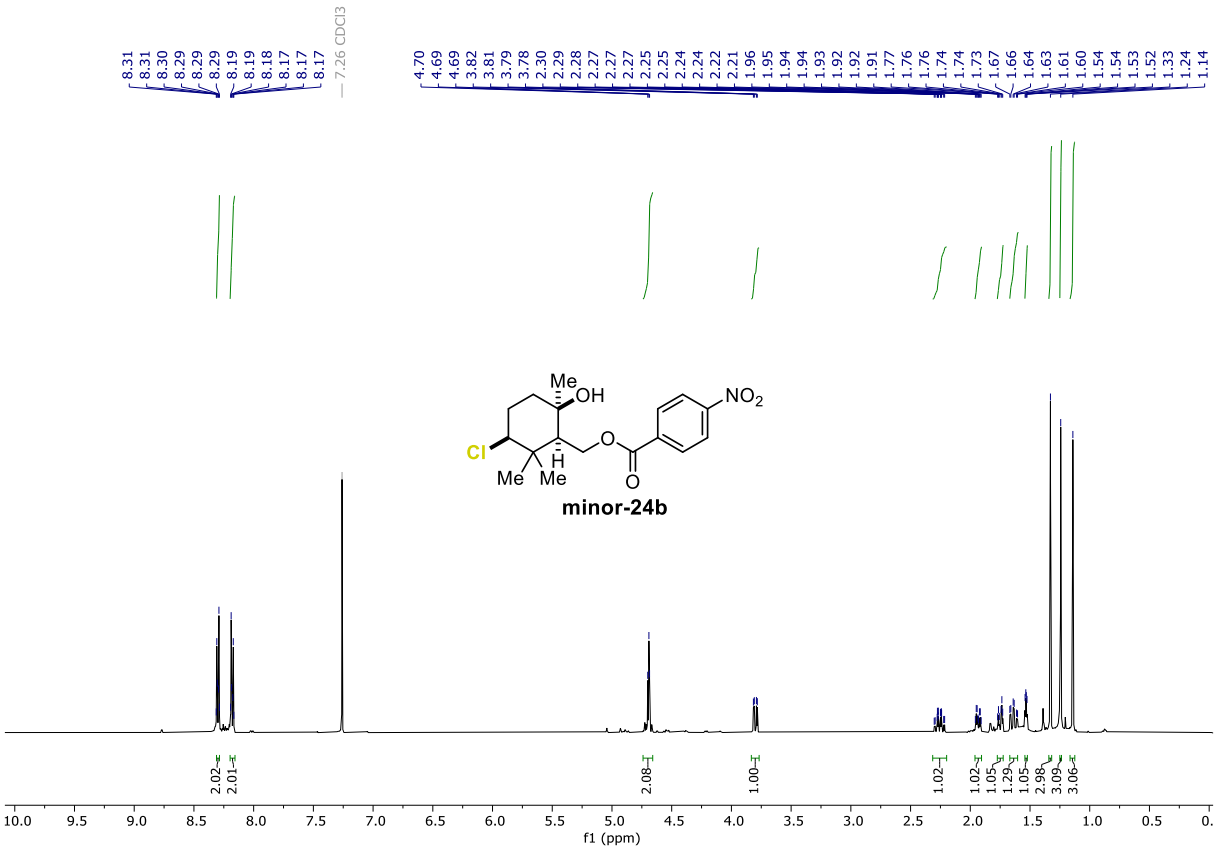
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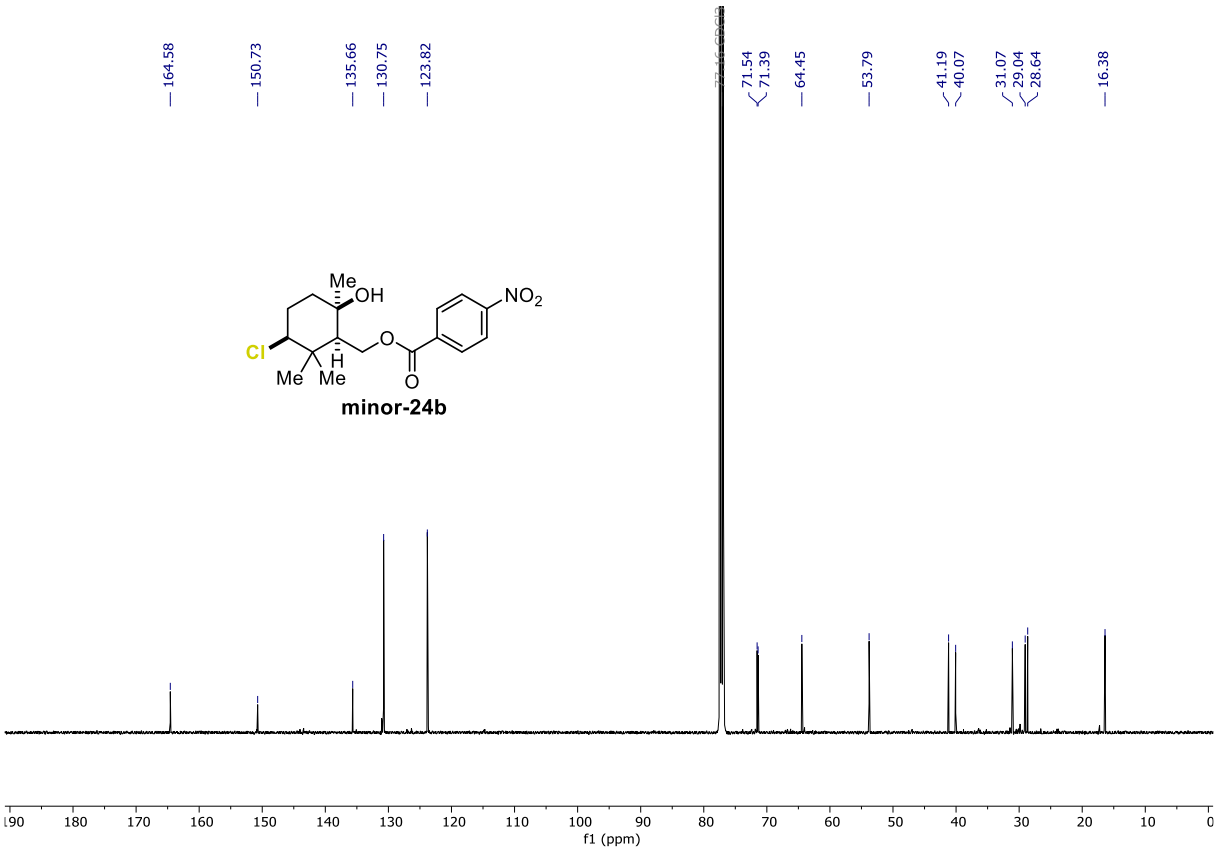
1.33
1.24
1.14
Me
OH
NO2
Cl
O
H
Me Me
O
minor-24b
2.02
2.01
2.08
1.00
1.02
1.02
1.05
1.29
1.05
2.98
3.09
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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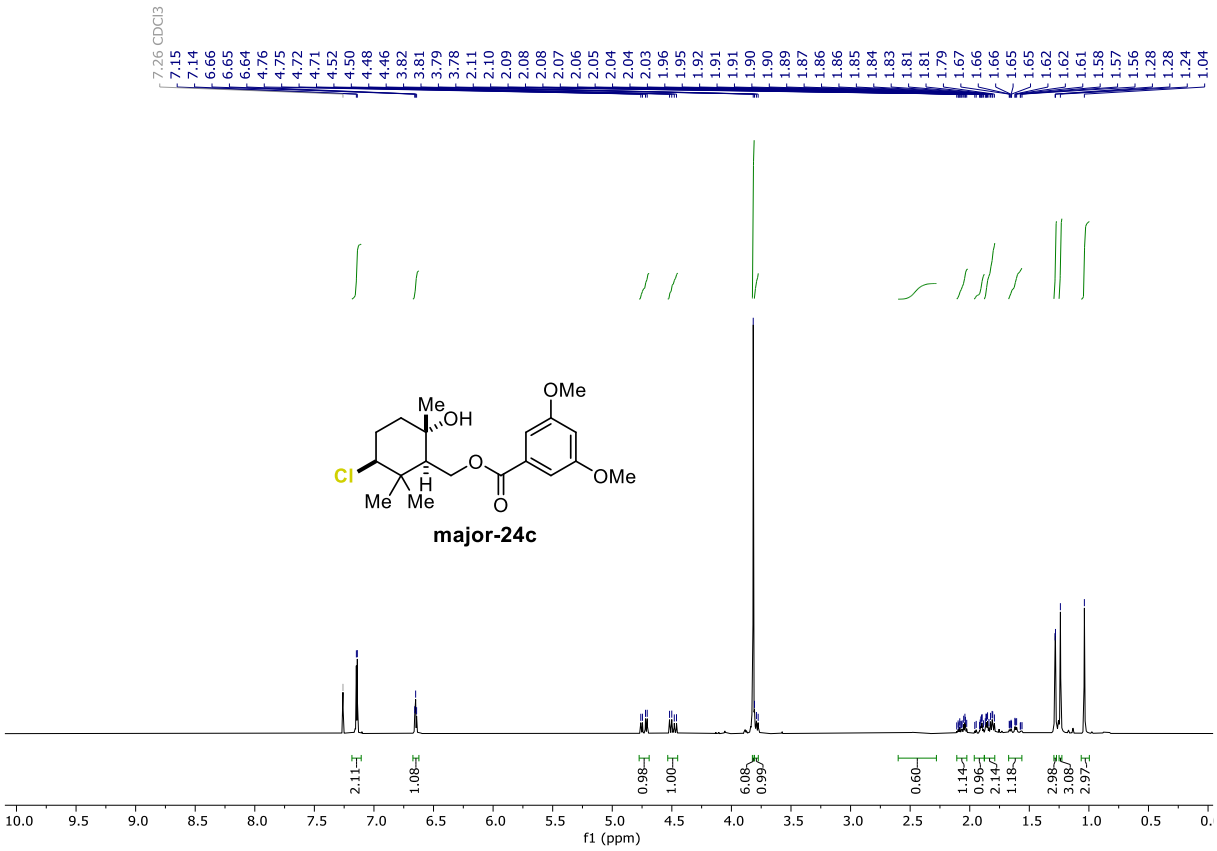
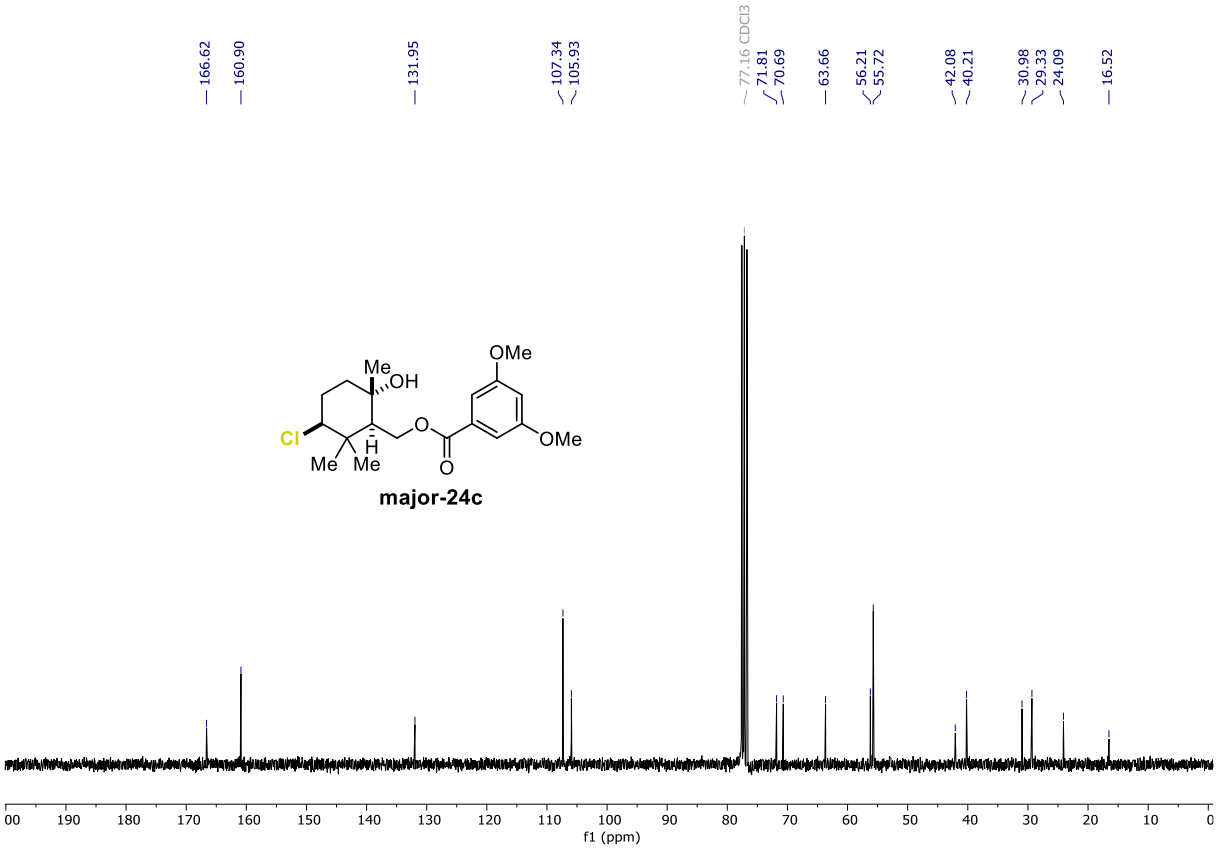
150.73
135.66
130.75
123.82
77.16 CDCl3
71.54
71.39
64.45
53.79
41.19
40.07
31.07
29.04
28.64
16.38
Me
OH
NO2
Cl
O
H
Me Me
O
minor-24b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 CDCl3
7.15 7.14 6.66 6.65 6.64 4.76 4.75 4.72 4.71 4.52 4.50 4.48 4.46 3.82 3.81 3.79 3.78 2.11 2.10 2.09 2.08 2.08 2.07 2.06 2.05 2.04 2.04 2.03 1.96 1.95 1.92 1.91 1.91 1.90 1.90 1.89 1.87 1.86 1.86 1.85 1.84 1.83 1.81 1.81 1.79 1.67 1.66 1.66 1.65 1.65 1.62 1.62 1.61 1.58 1.57 1.56 1.28 1.28 1.24 1.04
Me
OH
OMe
Cl
O
OMe
H
Me Me
O
major-24c
2.11 1.08 0.98 1.00 6.08 0.99 0.60 1.14 0.96 2.14 1.18 2.98 3.08 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.
f1 (ppm)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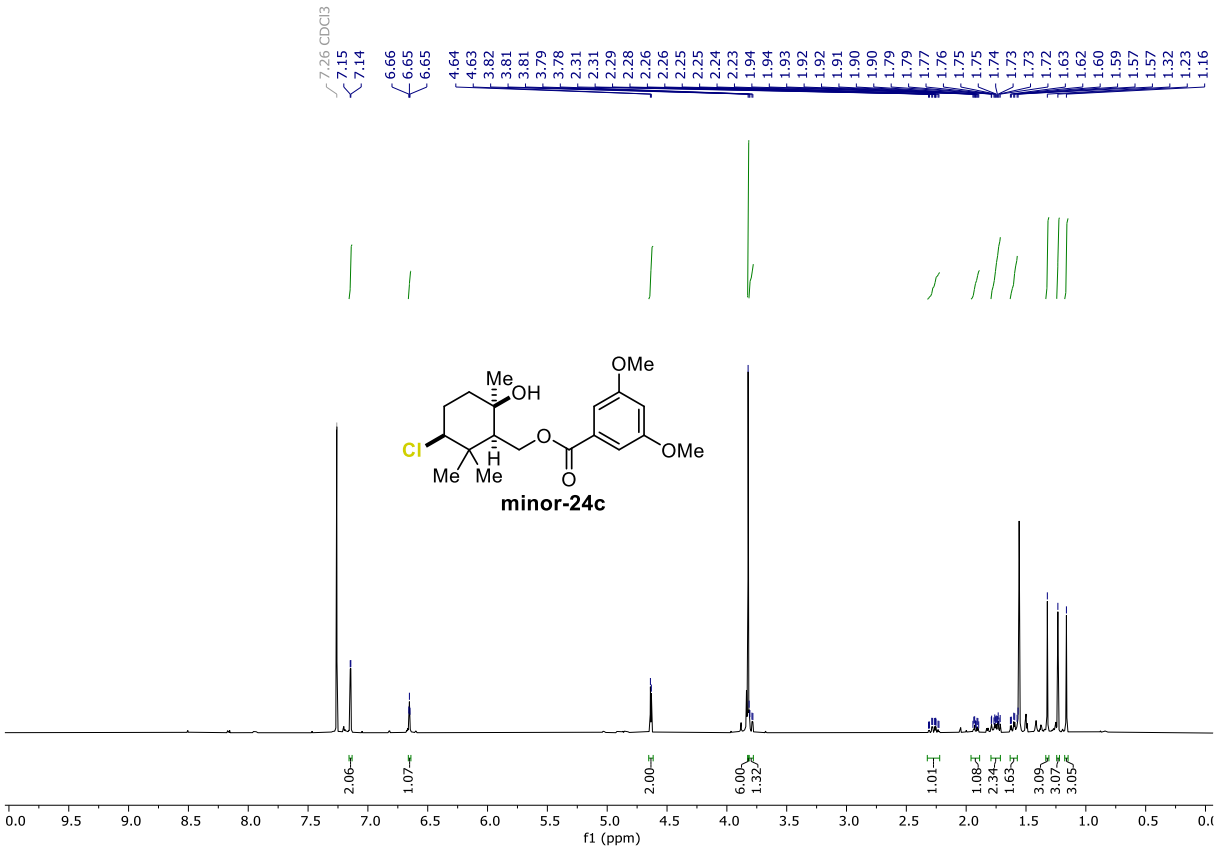
Me
OH
OMe
Cl
O
OMe
H
Me Me
O
major-24c
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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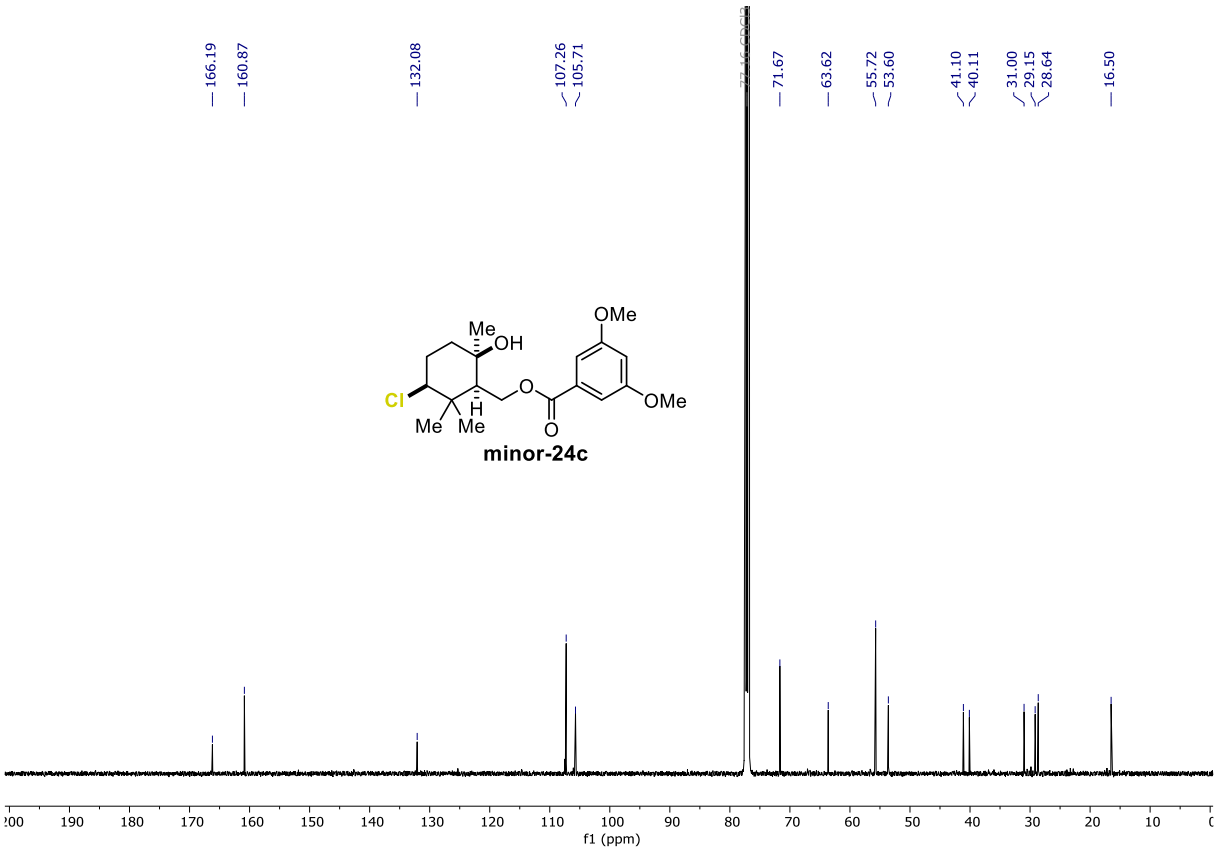
7.14
6.66
6.65
6.65
4.64
4.63
3.82
3.81
3.81
3.79
3.78
2.31
2.31
2.29
2.28
2.26
2.26
2.25
2.25
2.24
2.23
1.94
1.94
1.93
1.92
1.92
1.91
1.90
1.90
1.79
1.79
1.77
1.76
1.75
1.75
1.74
1.73
1.73
1.72
1.63
1.62
1.60
1.59
1.57
1.57
1.32
1.23
1.16
Me
OH
OMe
Cl
O
OMe
H
Me
Me
O
minor-24c
2.06
1.07
2.00
6.00
1.32
1.01
1.08
2.34
1.63
3.09
3.07
3.05
f1 (ppm)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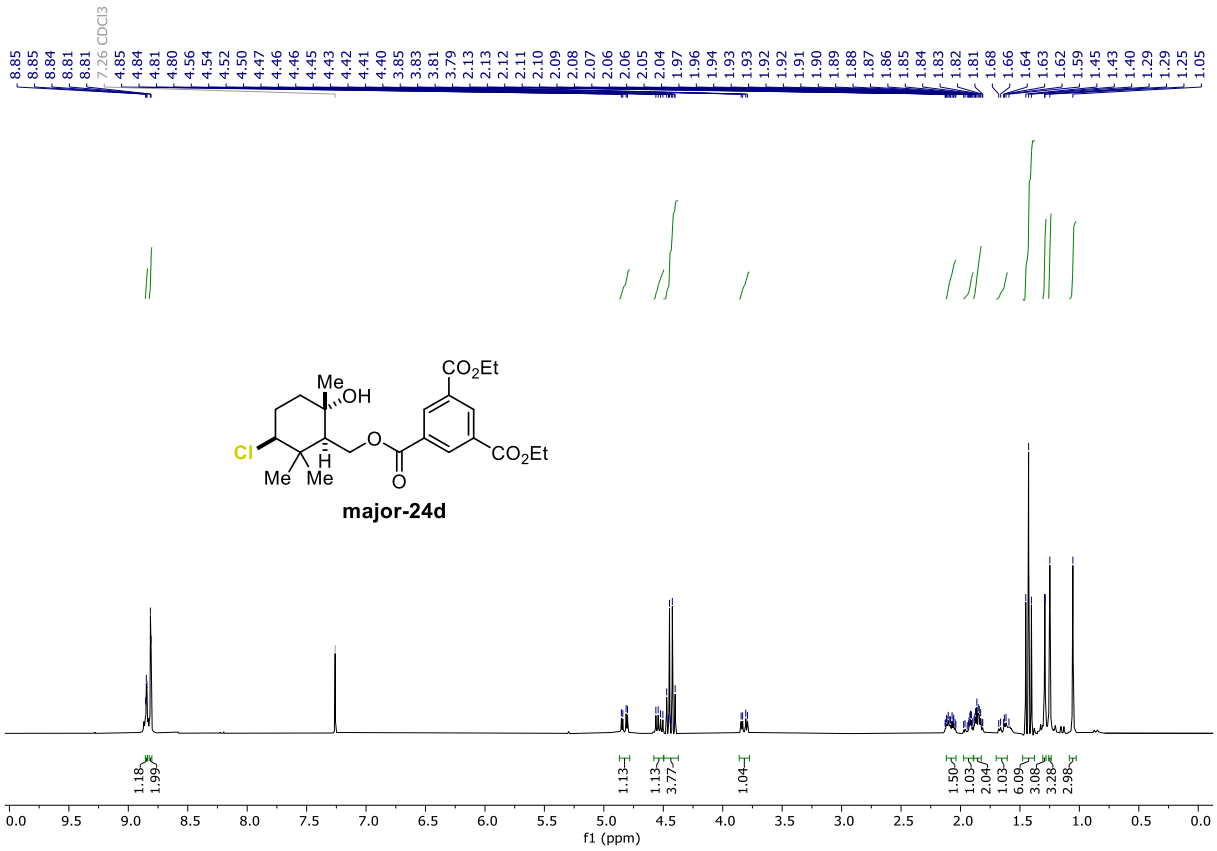
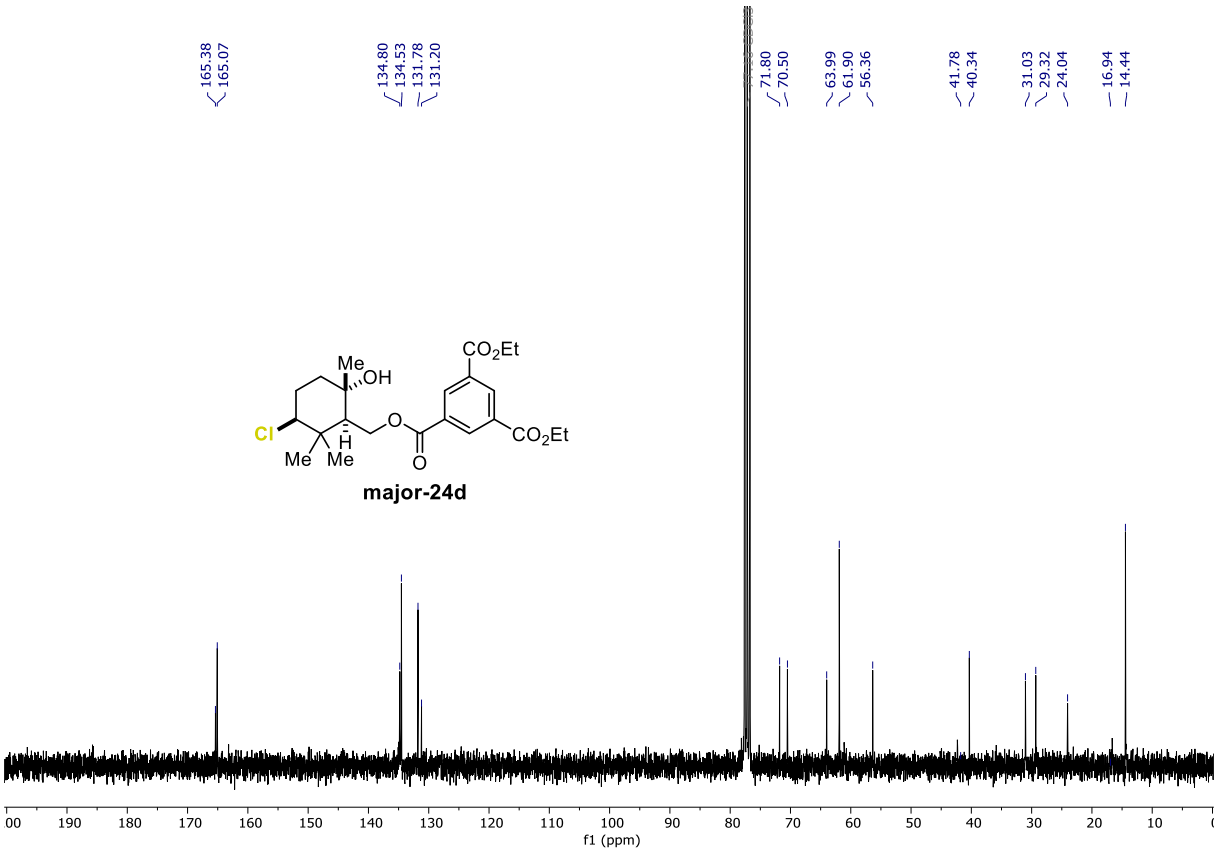
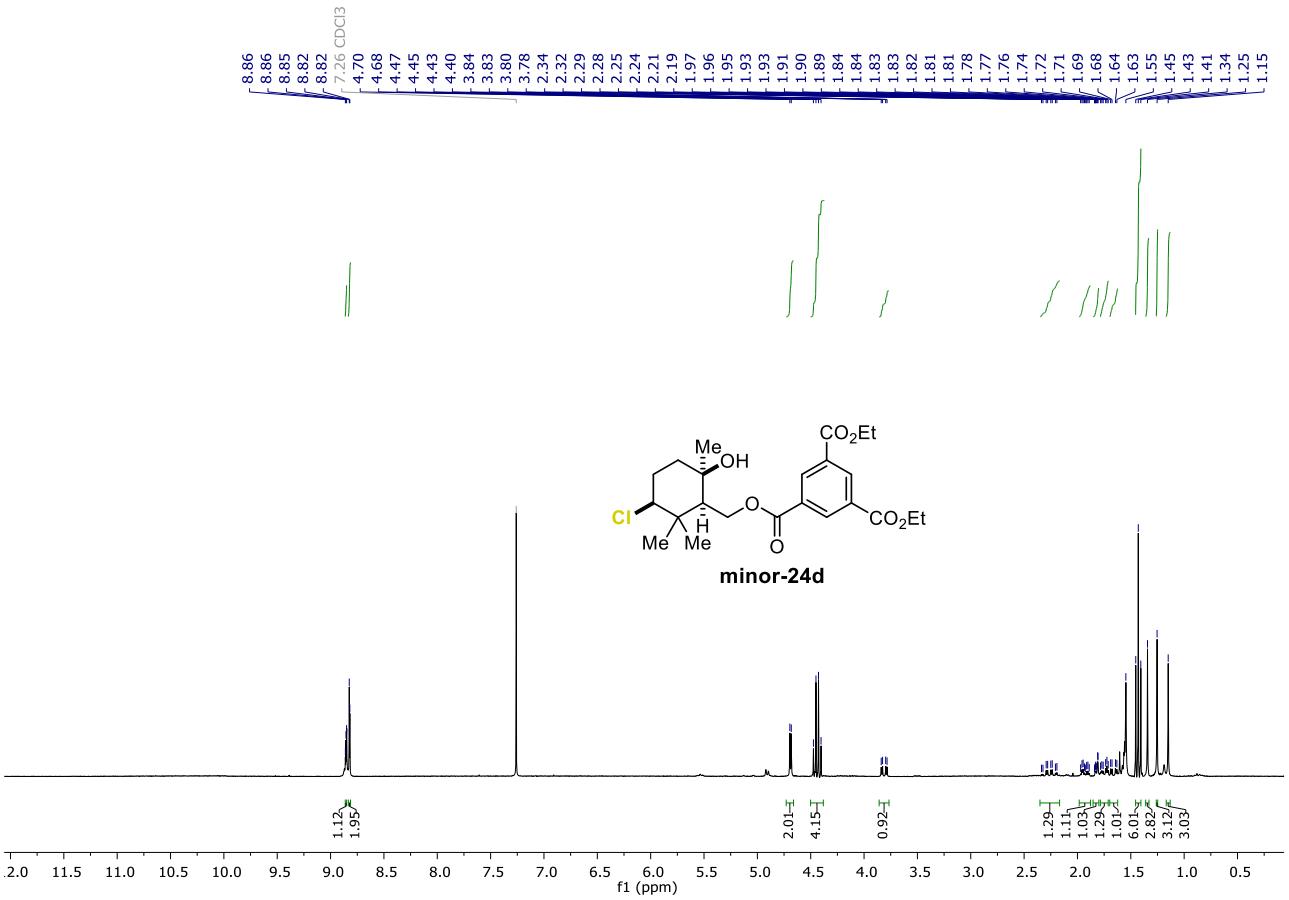
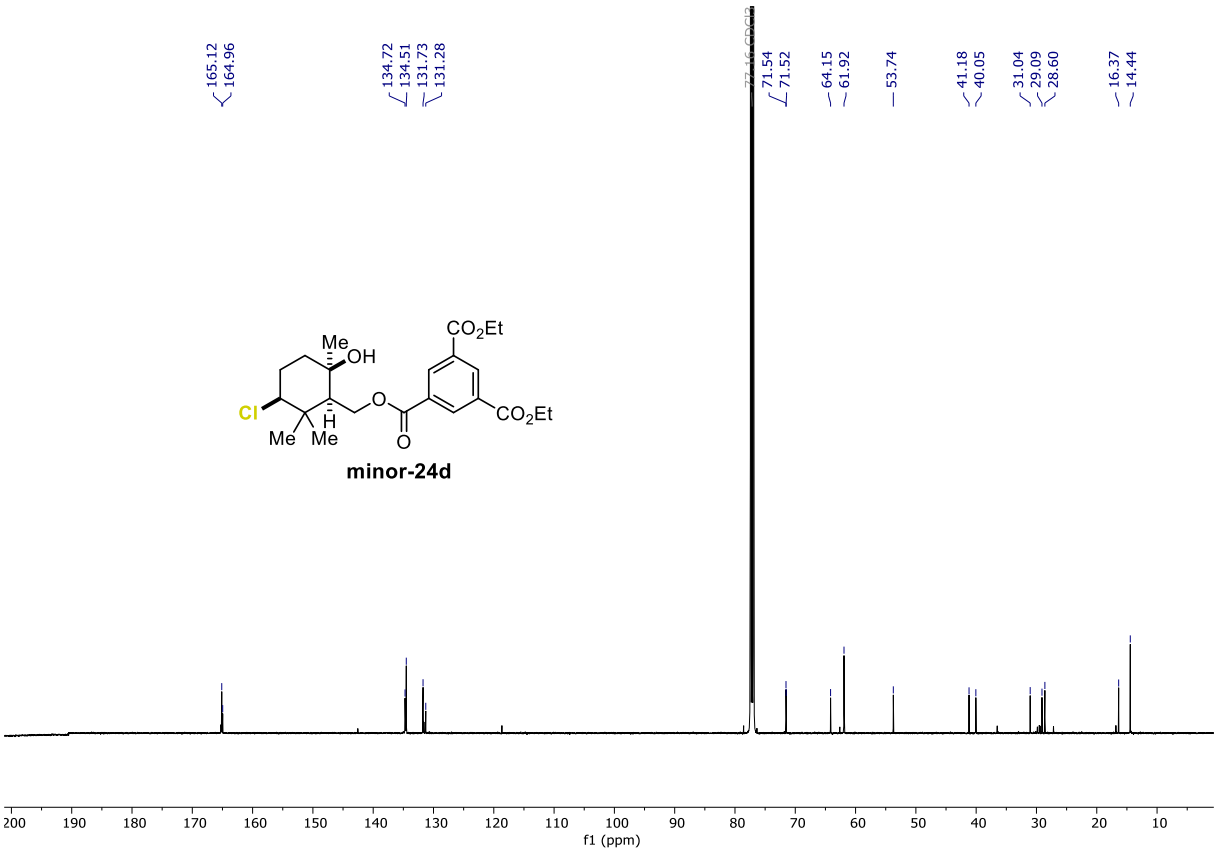
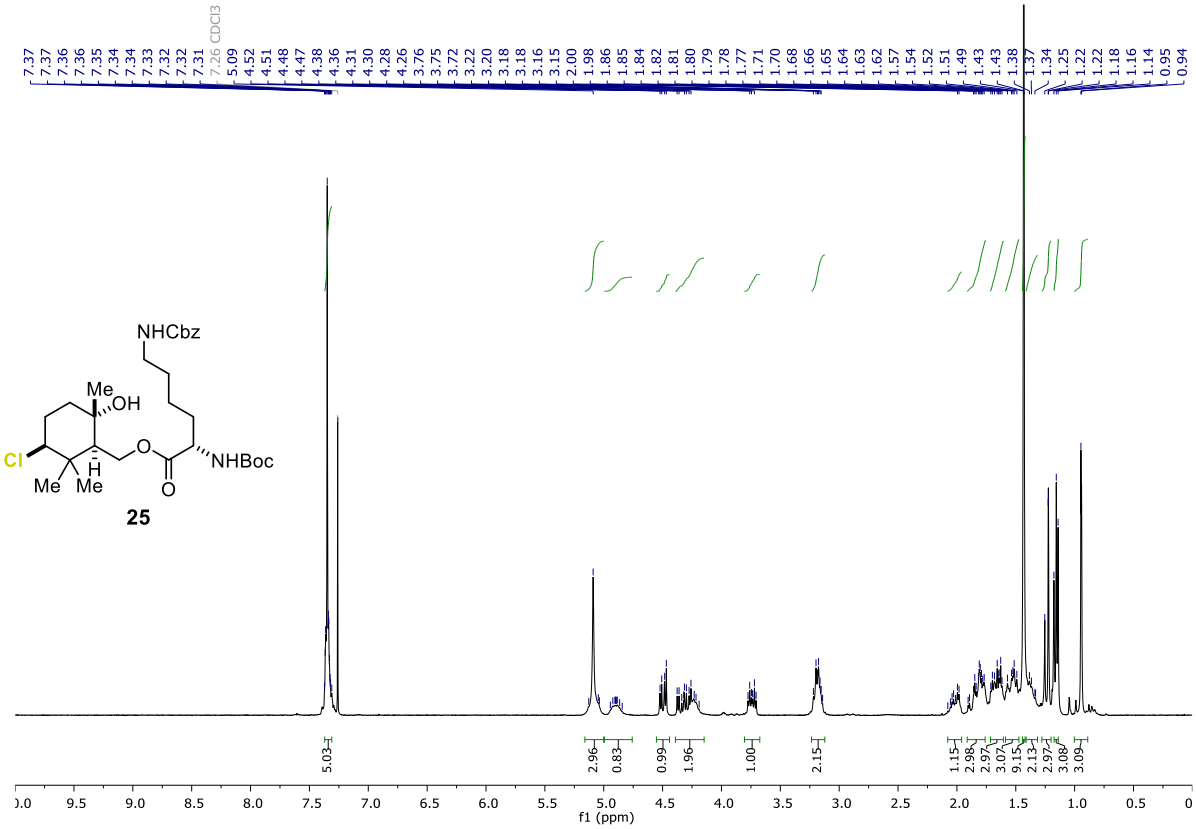
107.26
105.71
71.67
63.62
55.72
53.60
41.10
40.11
31.00
29.15
28.64
16.50
Me
OH
OMe
Cl
O
OMe
H
Me
Me
O
minor-24c
f1 (ppm)

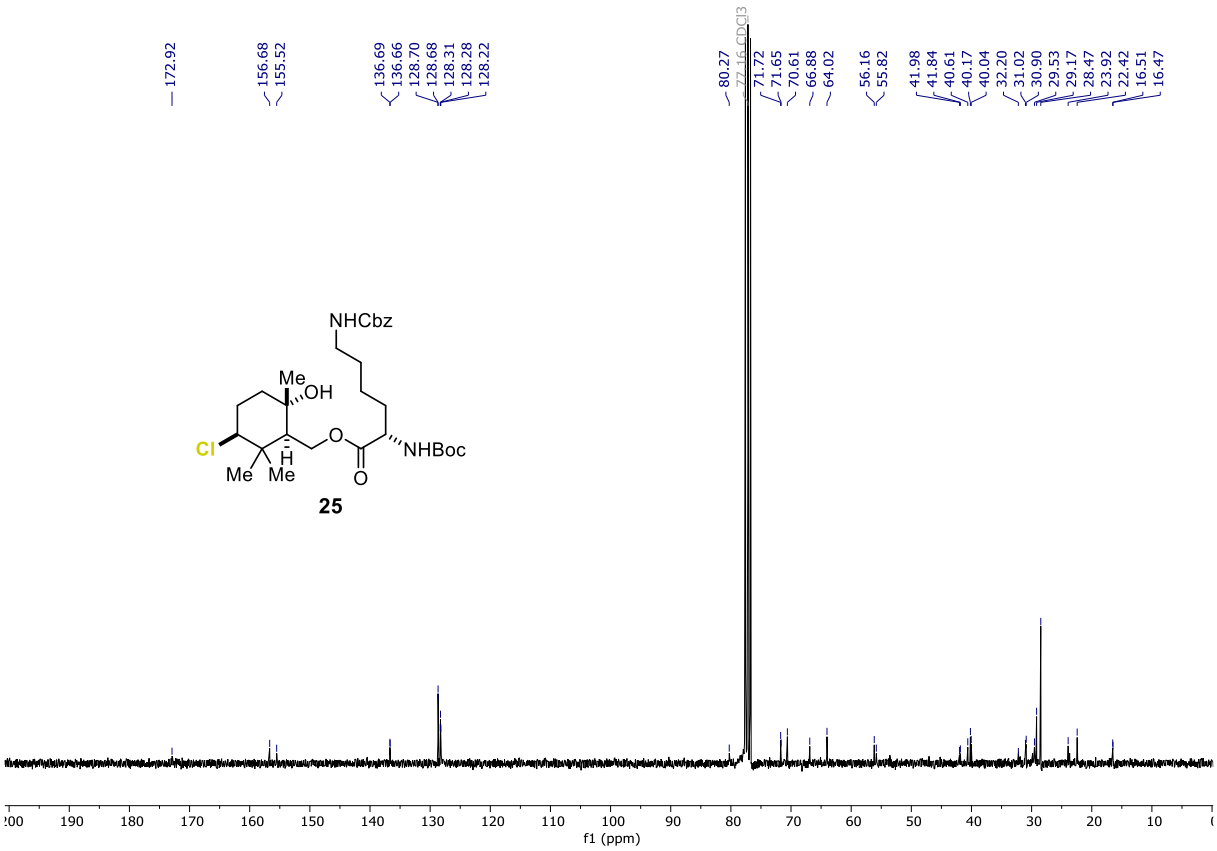

8.85 8.85 8.84 8.81 8.81 7.26 CDCl3 4.85 4.84 4.81 4.80 4.56 4.54 4.52 4.50 4.47 4.46 4.46 4.45 4.43 4.42 4.41 4.40 3.85 3.83 3.81 3.79 2.13 2.13 2.12 2.11 2.10 2.09 2.08 2.07 2.06 2.06 2.05 2.04 1.97 1.96 1.94 1.93 1.93 1.92 1.92 1.91 1.90 1.89 1.88 1.87 1.86 1.85 1.84 1.83 1.82 1.81 1.68 1.66 1.64 1.63 1.62 1.59 1.45 1.43 1.40 1.29 1.29 1.25 1.05
Me
OH
CO2Et
Cl
O
H
CO2Et
Me Me
O
major-24d
1.18
1.99
1.13
1.13
3.77
1.04
1.50
1.03
2.04
1.03
6.09
3.08
3.28
2.98
0.0 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
f1 (ppm)


165.38
165.07
134.80
134.53
131.78
131.20
71.80
70.50
63.99
61.90
56.36
41.78
40.34
31.03
29.32
24.04
16.94
14.44
Me
OH
CO2Et
Cl
O
H
CO2Et
Me Me
O
major-24d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.86 8.86 8.85 8.82 8.82 7.26 CDCl3 4.70 4.68 4.47 4.45 4.43 4.40 3.84 3.83 3.80 3.78 2.34 2.32 2.29 2.28 2.25 2.24 2.21 2.19 1.97 1.96 1.95 1.93 1.93 1.91 1.90 1.89 1.84 1.84 1.83 1.83 1.82 1.81 1.81 1.78 1.77 1.76 1.74 1.72 1.71 1.69 1.68 1.64 1.63 1.55 1.45 1.43 1.41 1.34 1.25 1.15
Me
OH
Cl
H
Me Me
O
O
CO2Et
CO2Et
minor-24d
1.12 1.95 2.01 4.15 0.92 1.29 1.11 1.03 1.29 1.01 6.01 2.82 3.12 3.03
12.0 11.5 11.0 10.5 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
f1 (ppm)


165.12 164.96 134.72 134.51 131.73 131.28 77.16 CDCl3 71.54 71.52 64.15 61.92 53.74 41.18 40.05 31.04 29.09 28.60 16.37 14.44
Me
OH
Cl
H
Me Me
O
O
CO2Et
CO2Et
minor-24d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.26 CDCl3 5.09 4.52 4.51 4.48 4.47 4.38 4.36 4.31 4.30 4.28 4.26 3.76 3.75 3.72 3.22 3.20 3.18 3.18 3.16 3.15 2.00 1.98 1.86 1.85 1.84 1.82 1.81 1.80 1.79 1.78 1.77 1.71 1.70 1.68 1.66 1.65 1.64 1.63 1.62 1.57 1.54 1.52 1.51 1.49 1.43 1.43 1.38 1.37 1.34 1.25 1.22 1.22 1.18 1.16 1.14 0.95 0.94
NHCbz
Me
OH
Cl
O
NHBoc
H
Me Me
O
25
5.03
2.96
0.83
0.99
1.96
1.00
2.15
1.15
2.98
2.97
3.07
9.15
2.13
2.97
3.08
3.09
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
f1 (ppm)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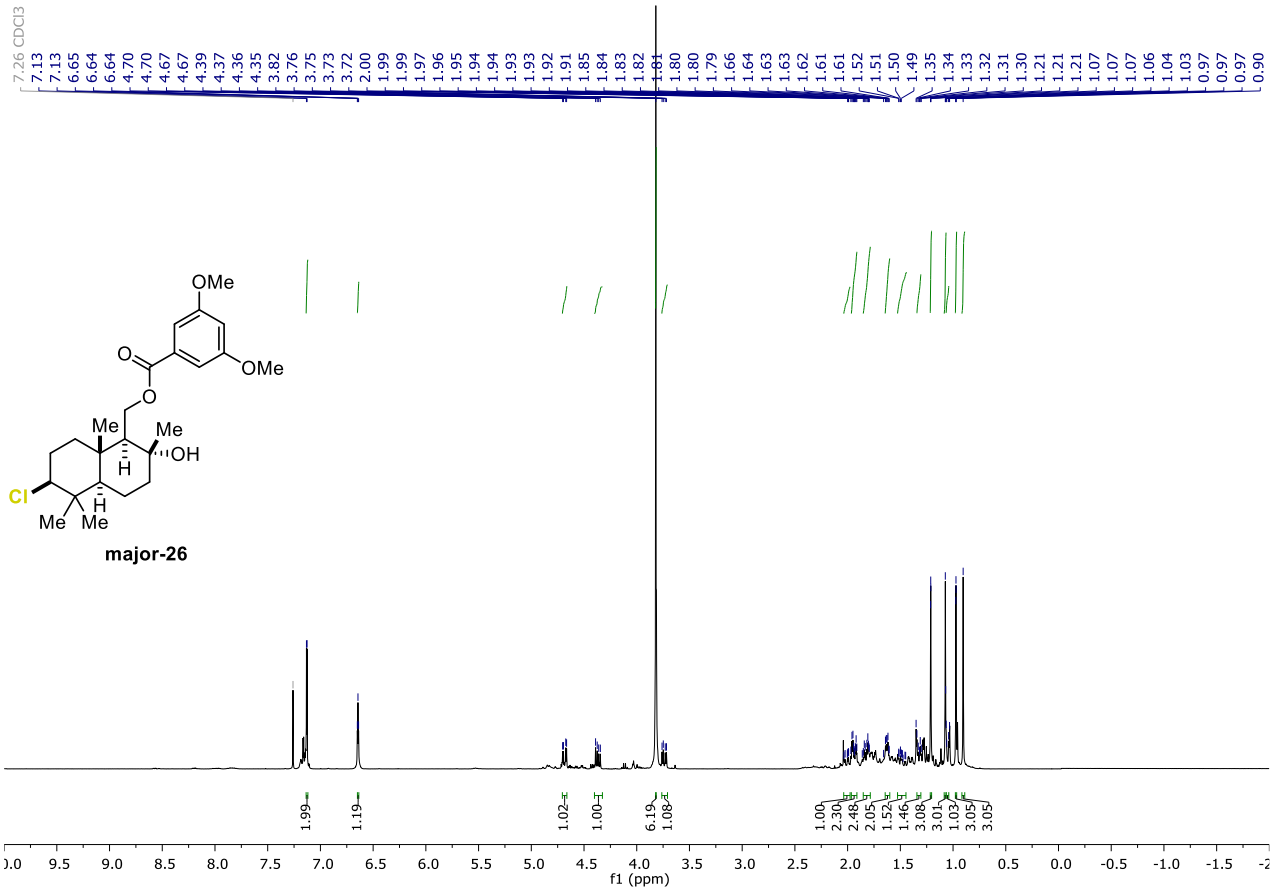
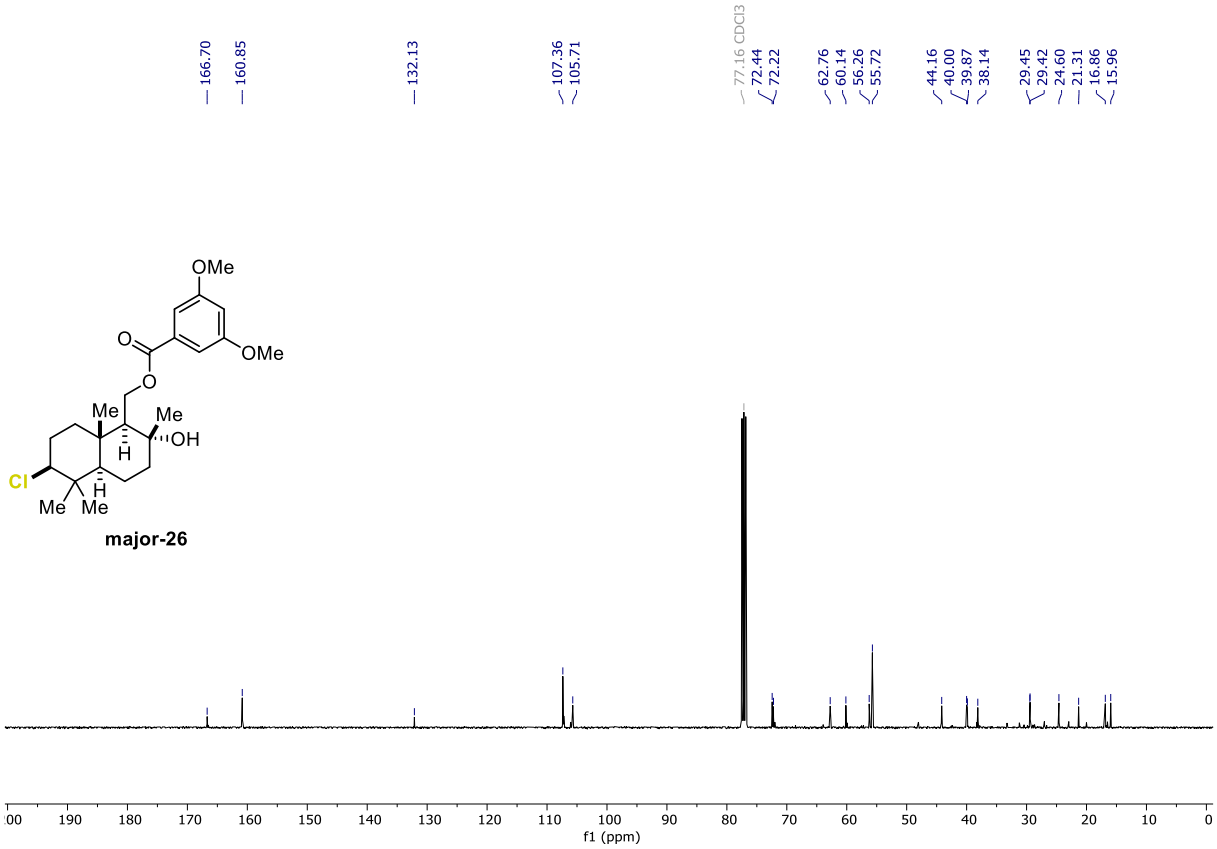
155.52
136.69
136.66
128.70
128.68
128.31
128.28
128.22
80.27
77.16 CDCl3
71.72
71.65
70.61
66.88
64.02
56.16
55.82
41.98
41.84
40.61
40.17
40.04
32.20
31.02
30.90
29.53
29.17
28.47
23.92
22.42
16.51
16.47
NHCbz
Me
OH
Cl
O
NHBoc
H
Me Me
O
25
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.26 CDCl3
7.13 7.13 6.65 6.64 6.64 4.70 4.70 4.67 4.67 4.39 4.37 4.36 4.35 3.82 3.76 3.75 3.73 3.72 2.00 1.99 1.99 1.97 1.96 1.95 1.94 1.94 1.93 1.93 1.92 1.91 1.85 1.84 1.83 1.82 1.81 1.80 1.80 1.79 1.66 1.64 1.63 1.63 1.62 1.61 1.61 1.52 1.51 1.50 1.49 1.35 1.34 1.33 1.32 1.31 1.30 1.21 1.21 1.21 1.07 1.07 1.07 1.06 1.04 1.03 0.97 0.97 0.97 0.90
OMe
OMe
O
O
Me
Me
OH
H
Cl
H
Me
Me
major-26
1.99
1.19
1.02
1.00
6.19
1.08
1.00
2.30
2.48
2.05
1.52
1.46
3.08
3.01
1.03
3.05
3.05
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 -0.5 -1.0 -1.5
f1 (ppm)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160.85
132.13
107.36
105.71
77.16 CDCl3
72.44
72.22
62.76
60.14
56.26
55.72
44.16
40.00
39.87
38.14
29.45
29.42
24.60
21.31
16.86
15.96
OMe
OMe
O
O
Me
Me
OH
H
Cl
H
Me
Me
major-26
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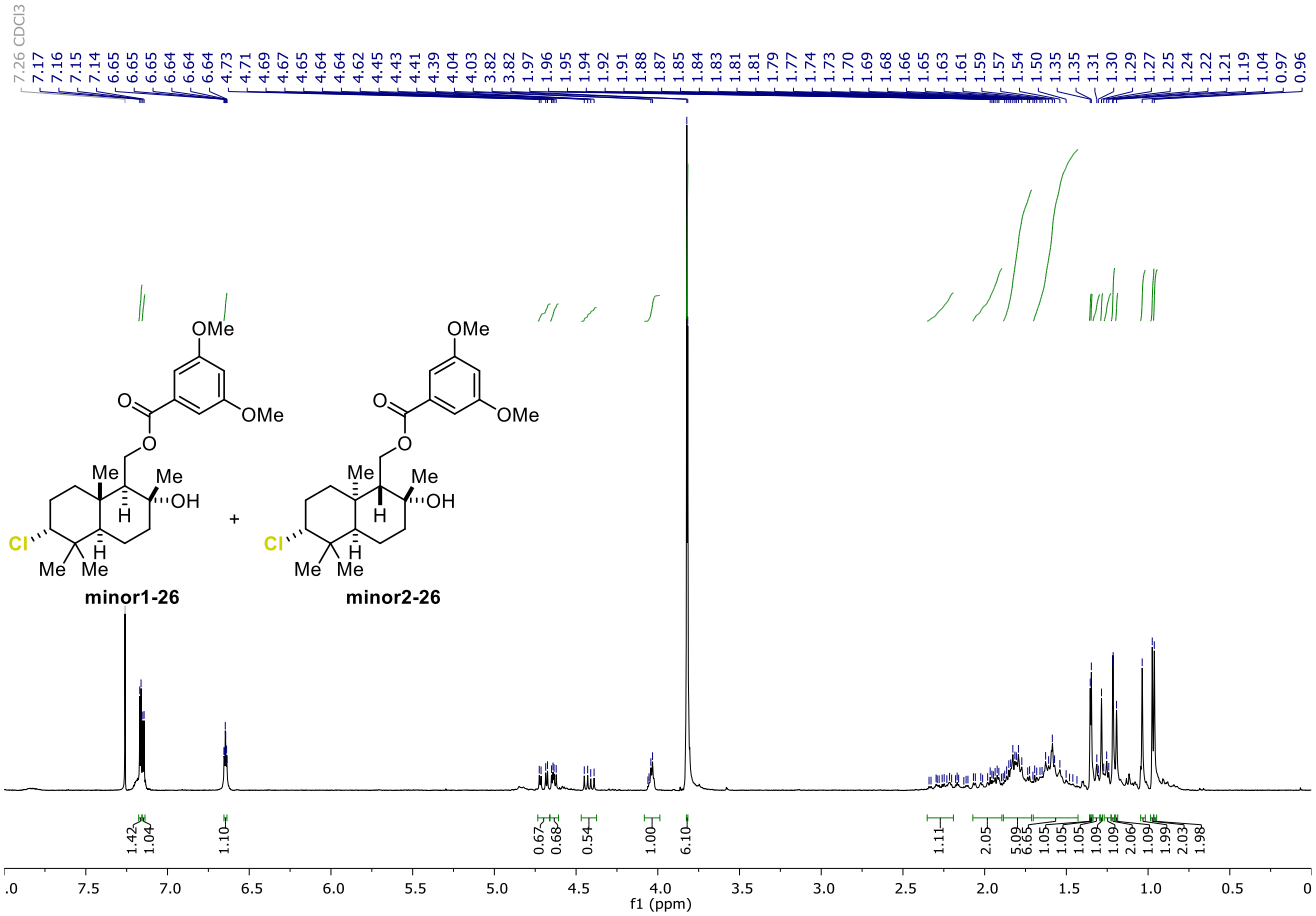
f1 (ppm)


7.26 CDCl3
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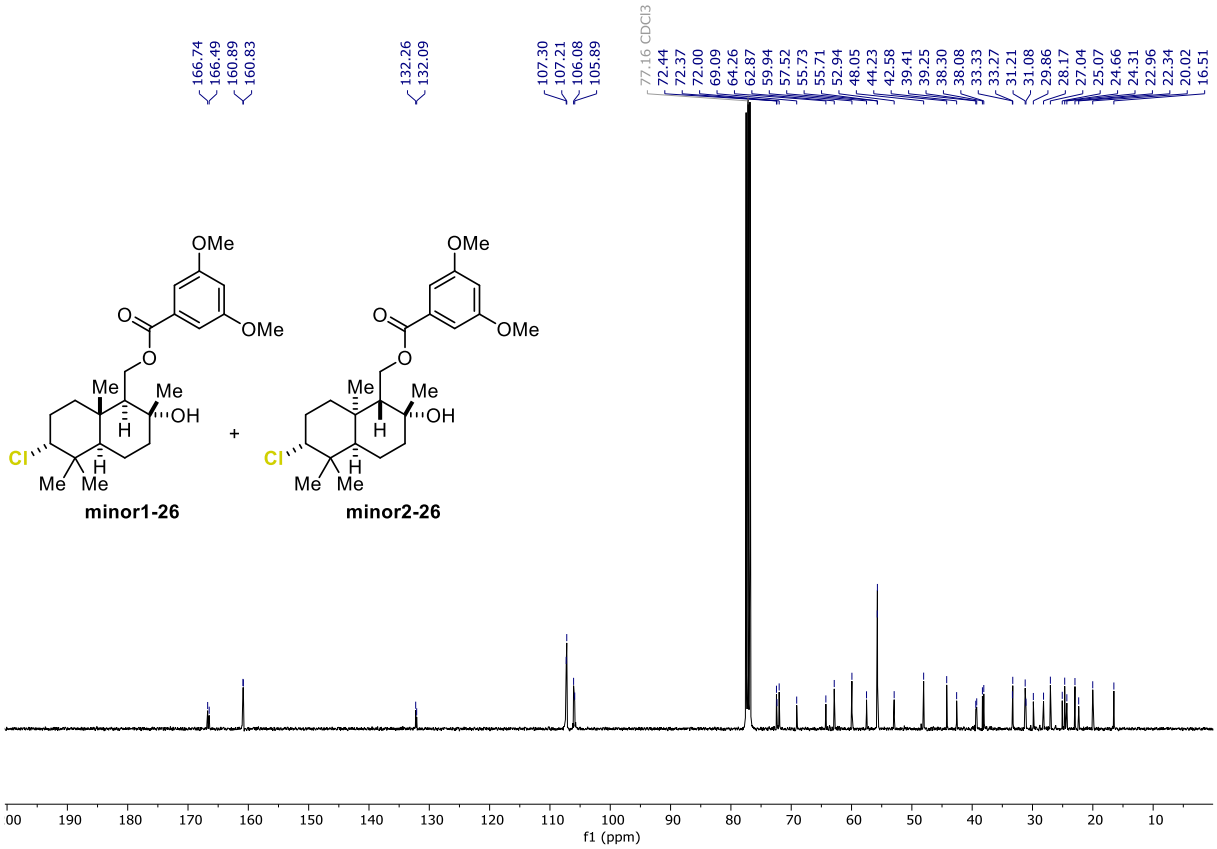
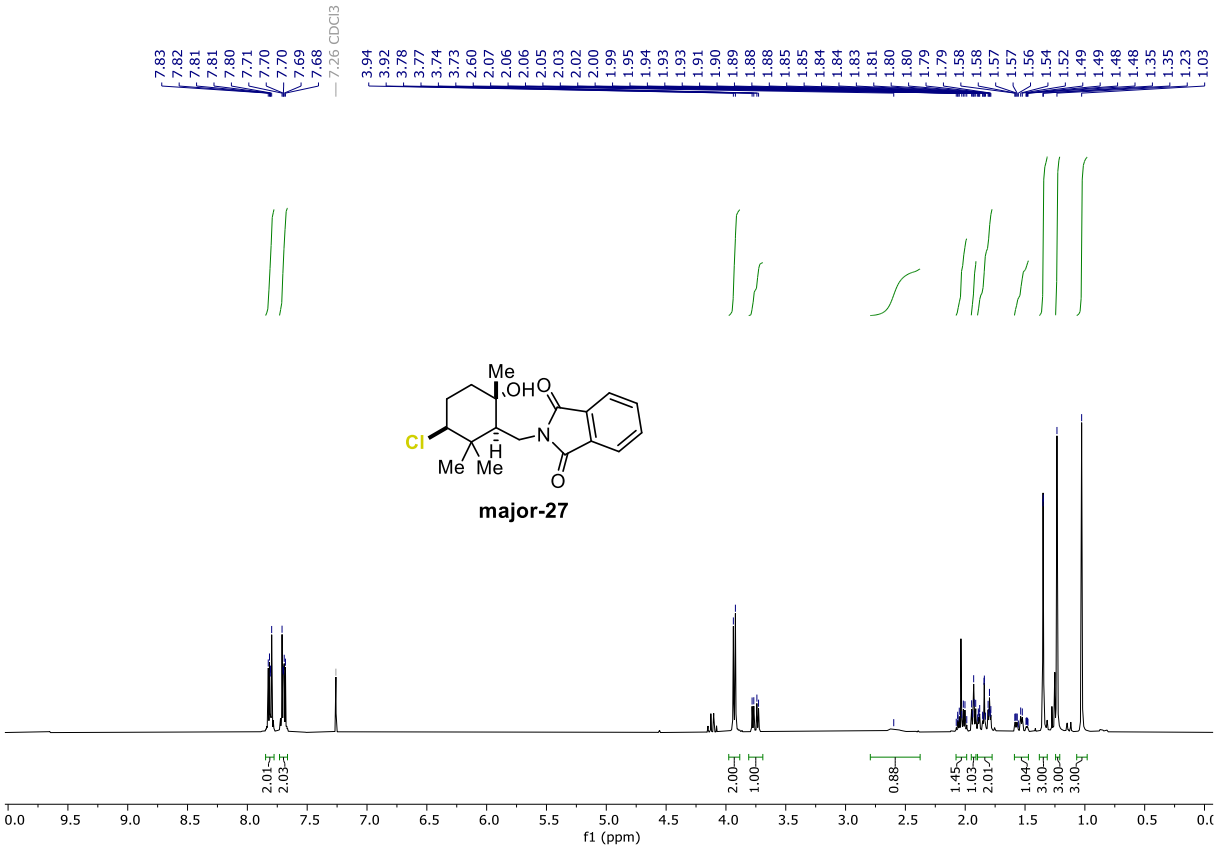
OMe
OMe
O
O
Me
Me
OH
H
Cl
H
Me Me
minor1-26
+
minor2-26
1.42 1.04 1.10 0.67 0.68 0.54 1.00 6.10 1.11 2.05 5.09 6.65 1.05 1.05 1.09 1.09 2.06 1.09 1.99 2.03 1.98
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


166.74 166.49 160.89 160.83 132.26 132.09 107.30 107.21 106.08 105.89
77.16 CDCl3
72.44 72.37 72.00 69.09 64.26 62.87 59.94 57.52 55.73 55.71 52.94 48.05 44.23 42.58 39.41 39.25 38.30 38.08 33.33 33.27 31.21 31.08 29.86 28.17 27.04 25.07 24.66 24.31 22.96 22.34 20.02 16.51
OMe
OMe
O
O
Me
Me
OH
H
Cl
H
Me Me
minor1-26
+
minor2-26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.83
7.82
7.81
7.81
7.80
7.71
7.70
7.70
7.69
7.68
7.26 CDCl3
3.94
3.92
3.78
3.77
3.74
3.73
2.60
2.07
2.06
2.06
2.05
2.03
2.02
2.00
1.99
1.95
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1.52
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1.49
1.48
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1.23
1.03
Me
OH
O
Cl
N
H
Me Me
O
major-27
2.01
2.03
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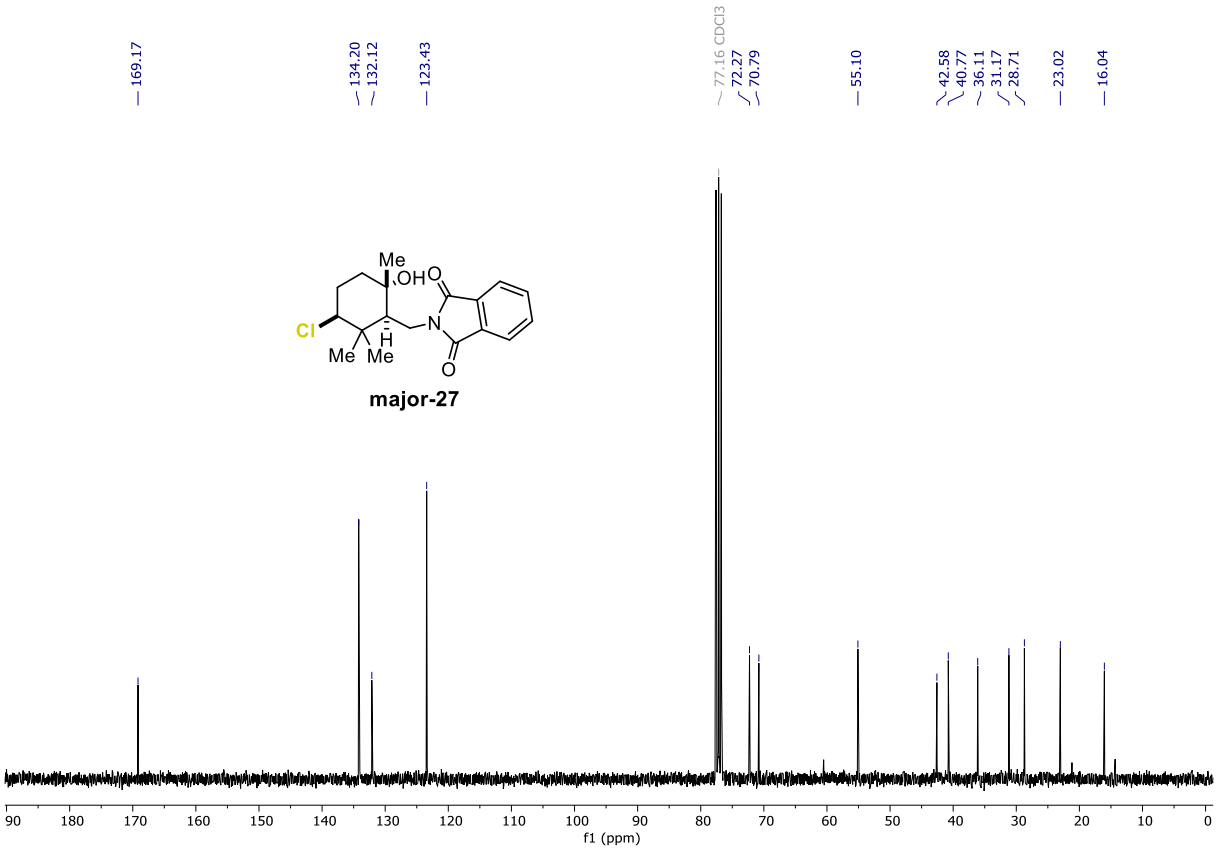
1.45
1.03
2.01
1.04
3.00
3.00
3.00
f1 (ppm)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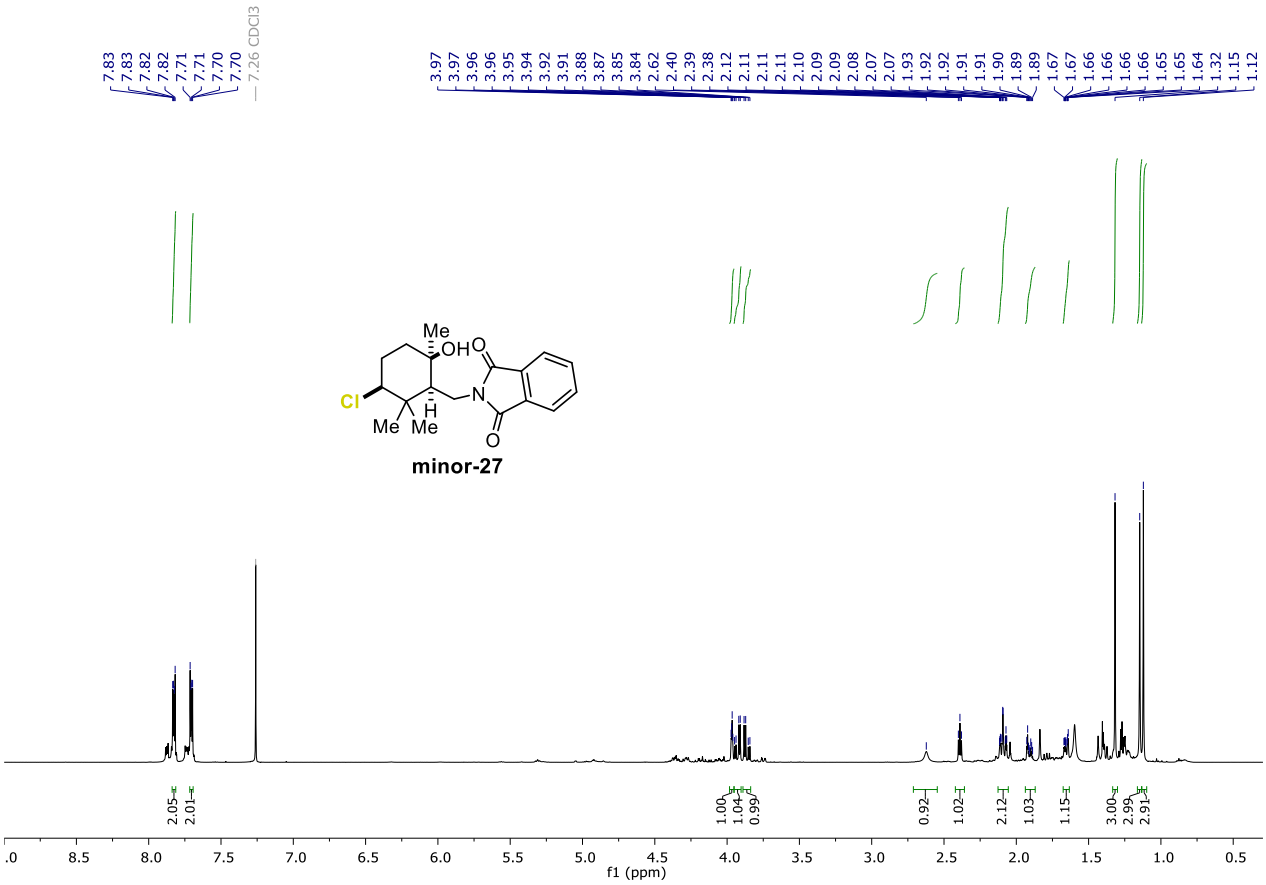
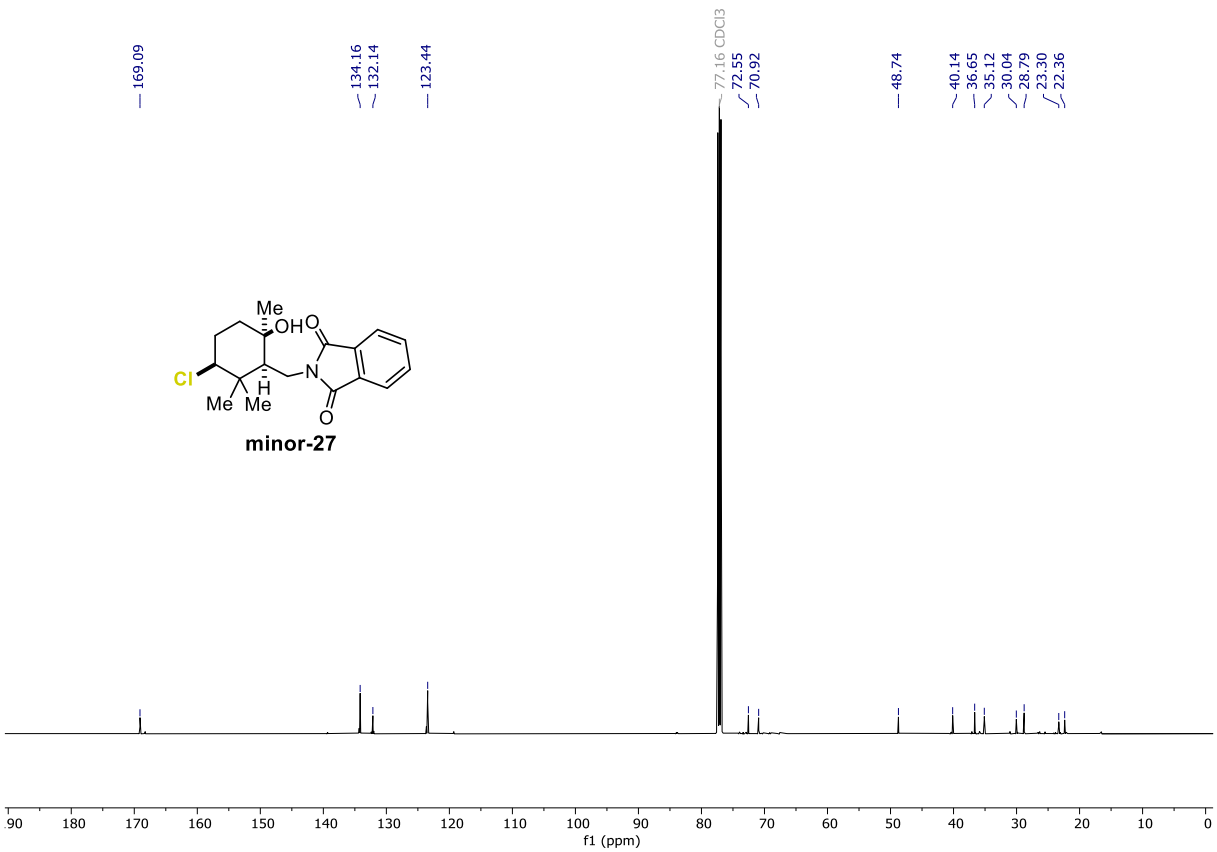
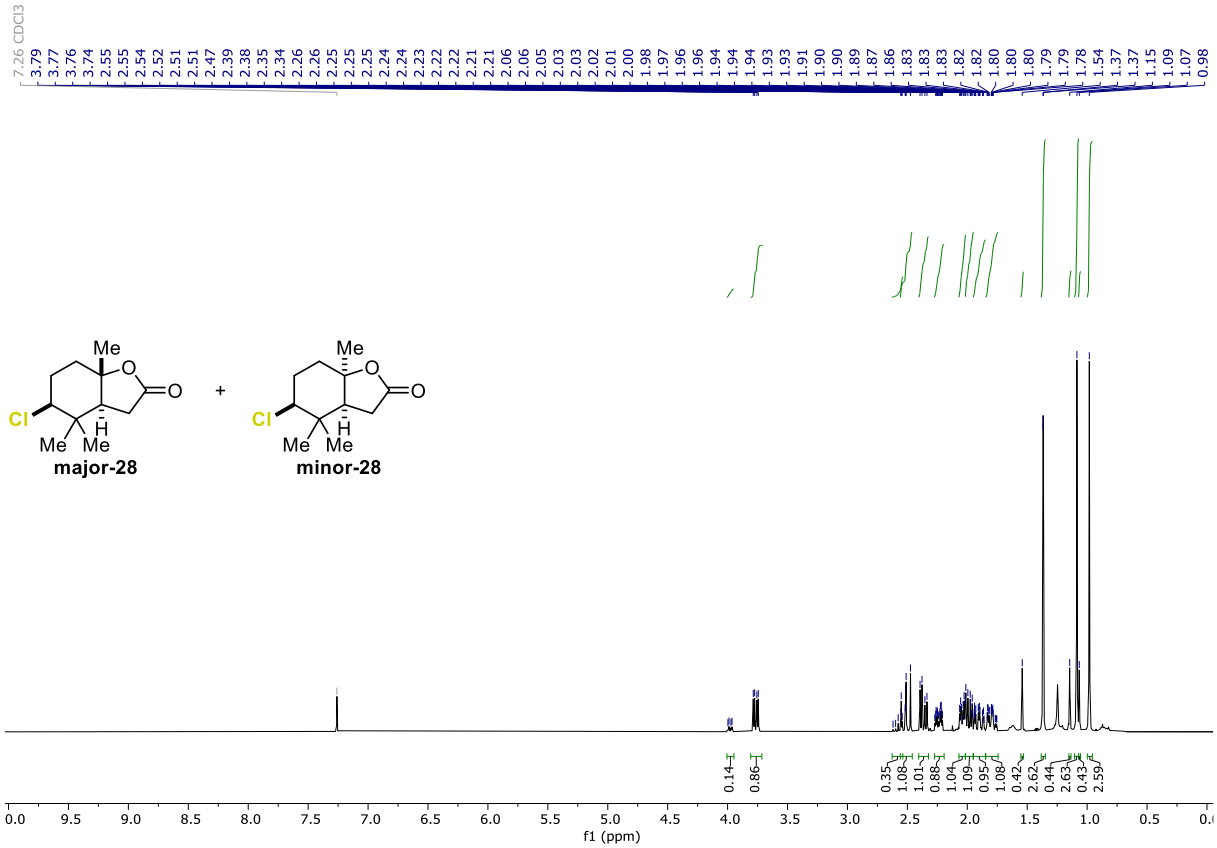
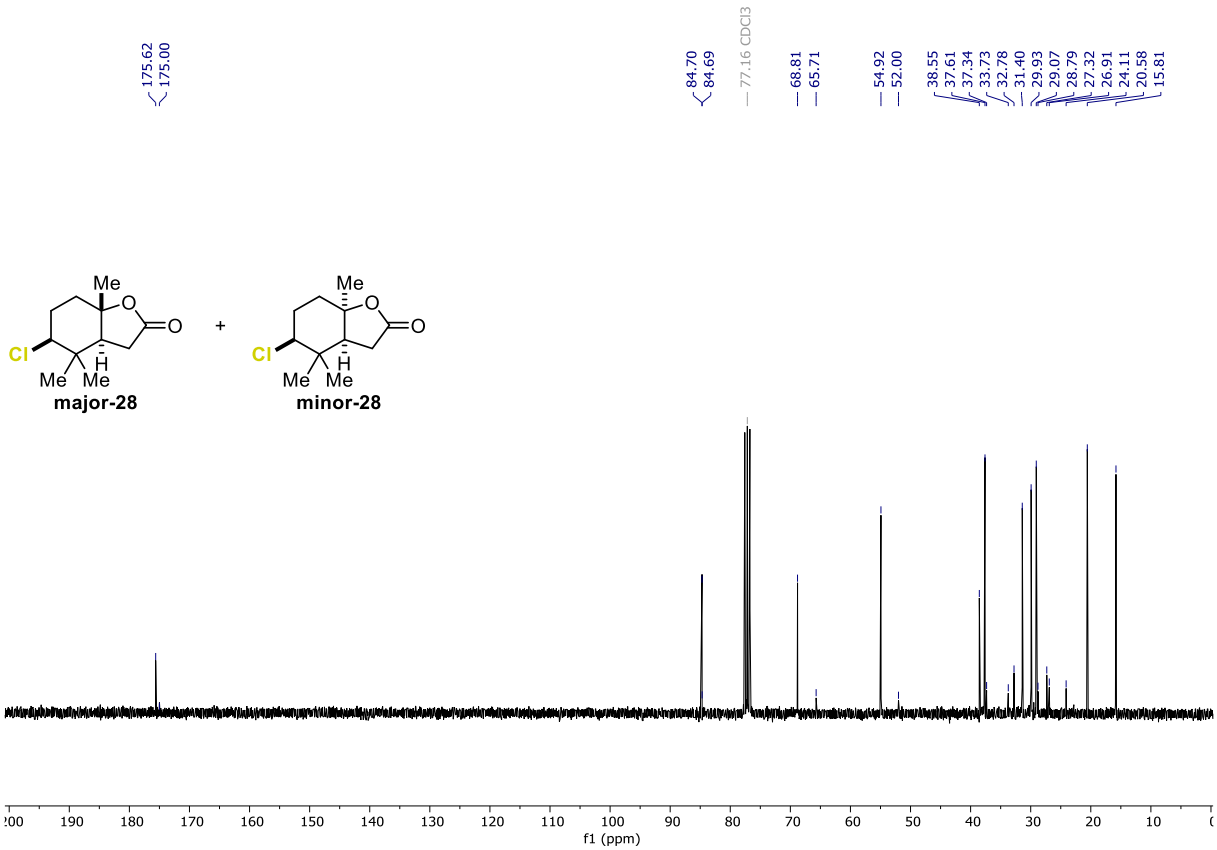
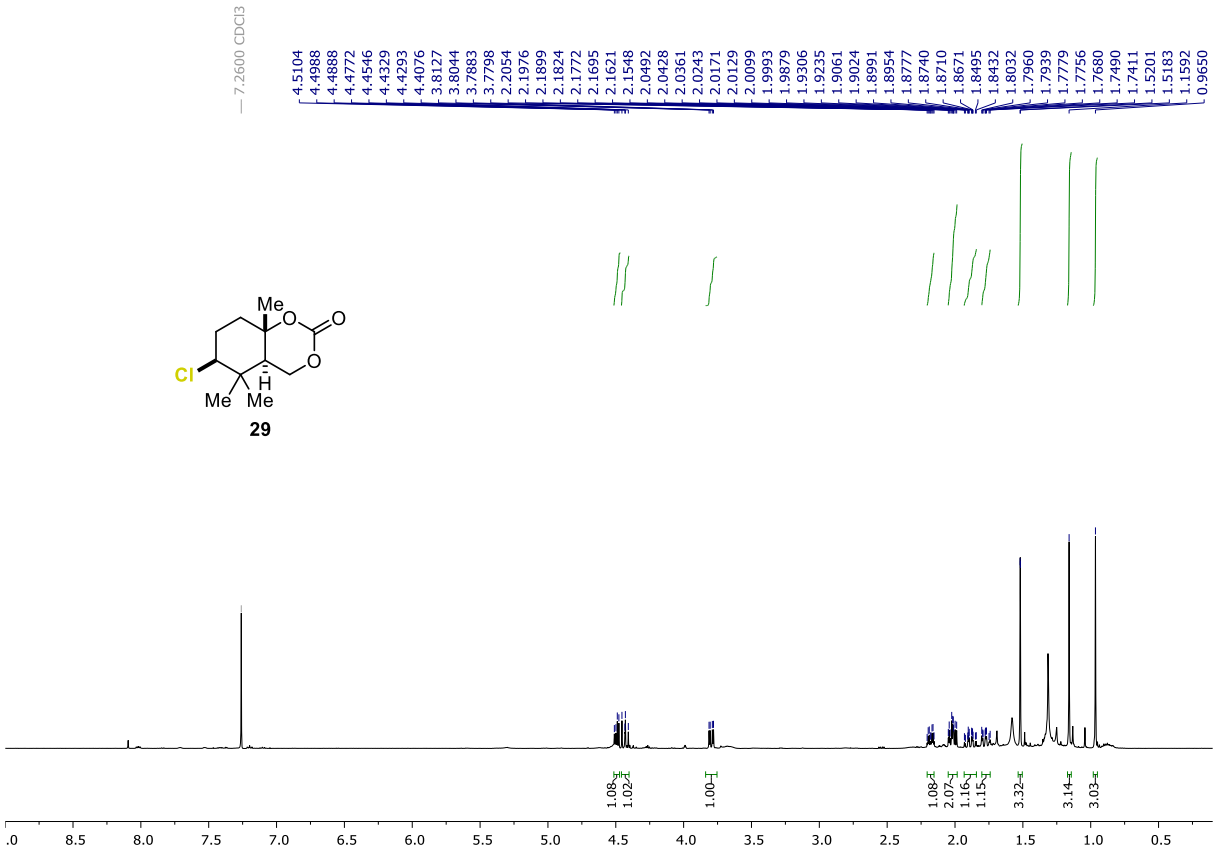
132.12
123.43
77.16 CDCl3
72.27
70.79
55.10
42.58
40.77
36.11
31.17
28.71
23.02
16.04
Me
OH
O
Cl
N
H
Me Me
O
major-27
f1 (ppm)


7.83 7.83 7.82 7.82 7.71 7.71 7.70 7.70
7.26 CDCl3
3.97 3.97 3.96 3.96 3.95 3.94 3.92 3.91 3.88 3.87 3.85 3.84 2.62 2.40 2.39 2.38 2.12 2.11 2.11 2.10 2.09 2.09 2.08 2.07 2.07 1.93 1.92 1.92 1.91 1.91 1.90 1.89 1.89 1.67 1.67 1.66 1.66 1.66 1.66 1.65 1.65 1.64 1.32 1.15 1.12
Me
OH
O
Cl
N
H
Me Me
O
minor-27
2.05 2.01 1.00 1.04 0.99 0.92 1.02 2.12 1.03 1.15 3.00 2.99 2.91
f1 (ppm)

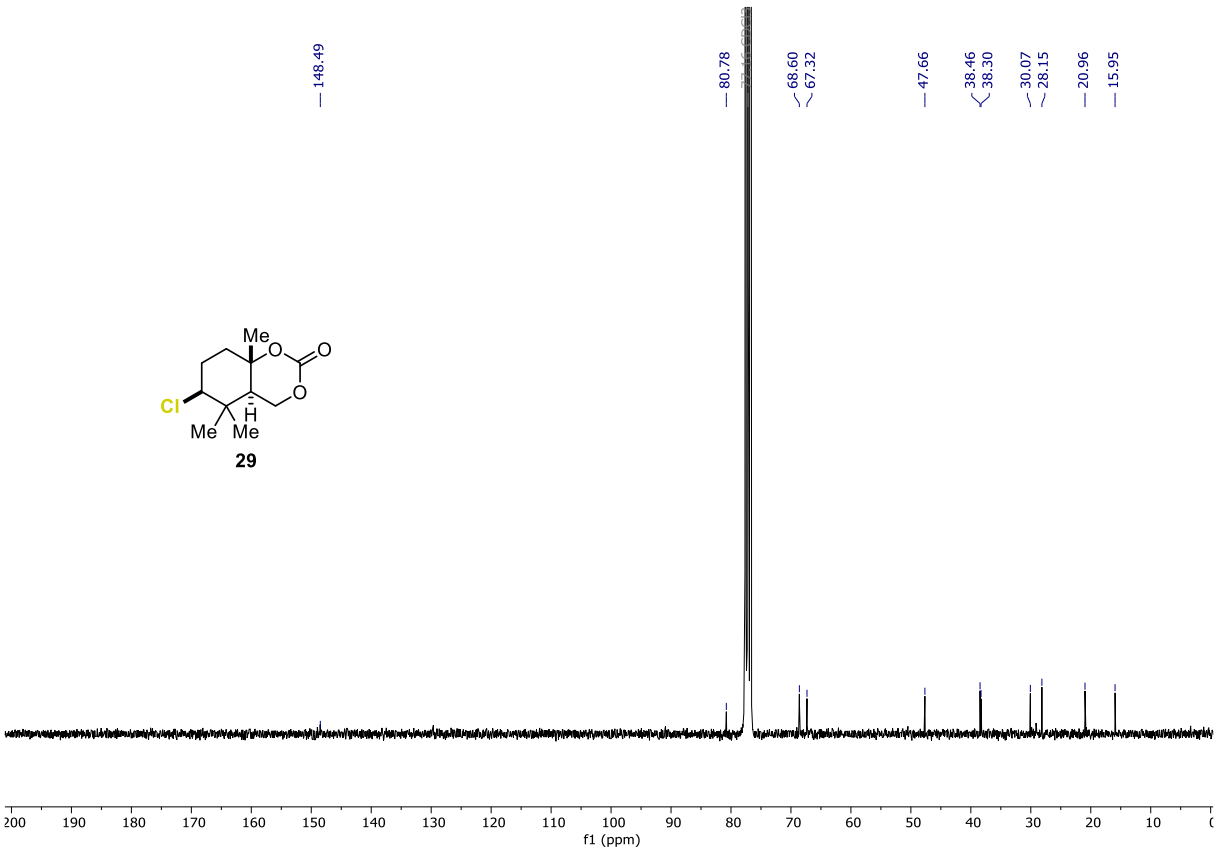

169.09
134.16
132.14
123.44
77.16 CDCl3
72.55
70.92
48.74
40.14
36.65
35.12
30.04
28.79
23.30
22.36
Me
OH
O
Cl
N
H
Me Me
O
minor-27
f1 (ppm)

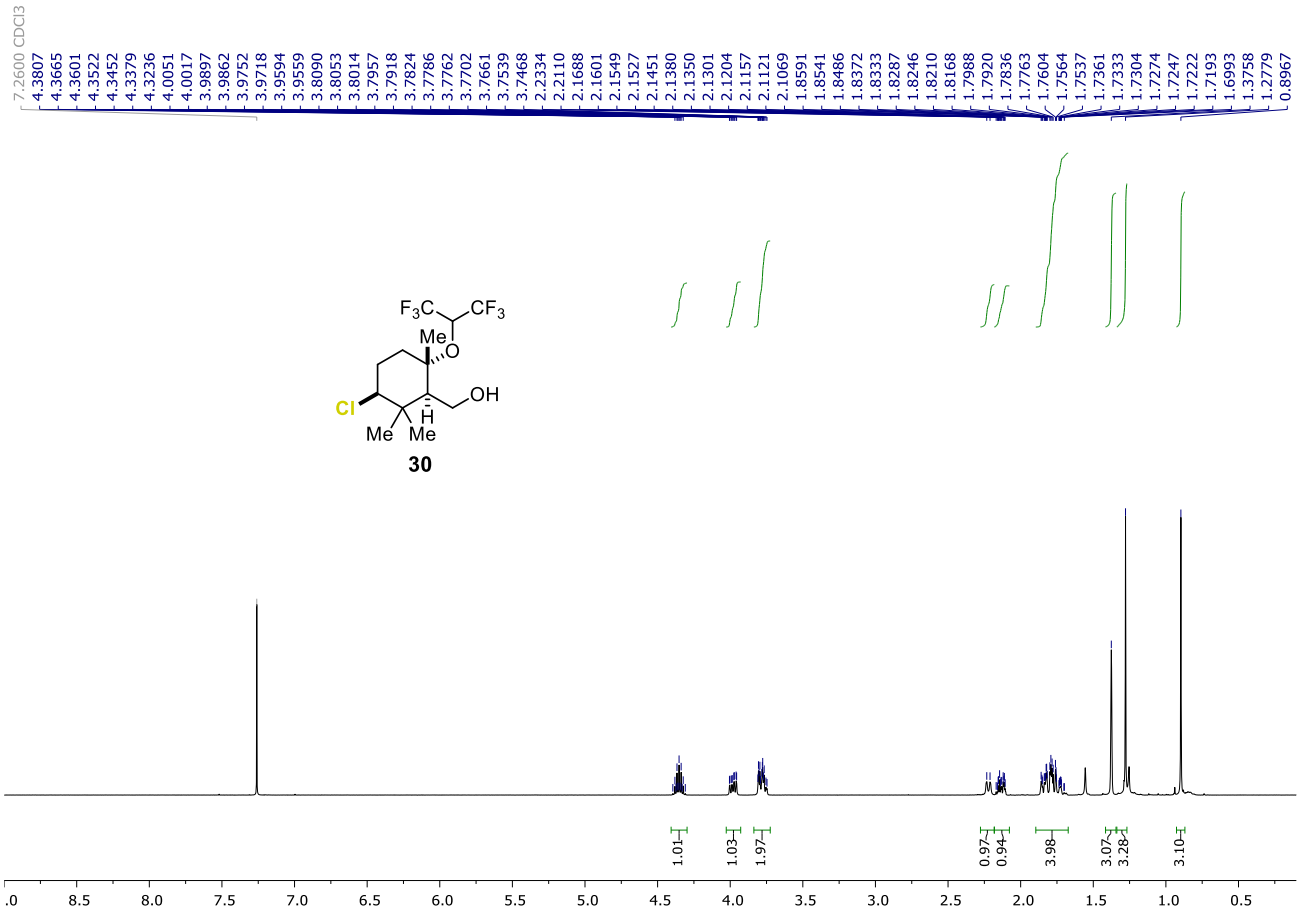

7.26 CDCl3
3.79 3.77 3.76 3.74 2.55 2.55 2.54 2.52 2.51 2.51 2.47 2.39 2.38 2.35 2.34 2.26 2.26 2.25 2.25 2.25 2.24 2.24 2.23 2.22 2.22 2.21 2.21 2.06 2.06 2.05 2.03 2.03 2.02 2.01 2.00 1.98 1.97 1.96 1.96 1.94 1.94 1.94 1.93 1.93 1.91 1.90 1.90 1.89 1.87 1.86 1.83 1.83 1.83 1.82 1.82 1.80 1.80 1.80 1.79 1.79 1.78 1.54 1.37 1.37 1.15 1.09 1.07 0.98
Me
O
O
Cl
H
Me Me
major-28
+
Me
O
O
Cl
H
Me Me
minor-28
0.14 0.86 0.35 1.08 1.01 0.88 1.04 1.09 0.95 1.08 0.42 2.62 0.44 2.63 0.43 2.59
0.0 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
f1 (ppm)

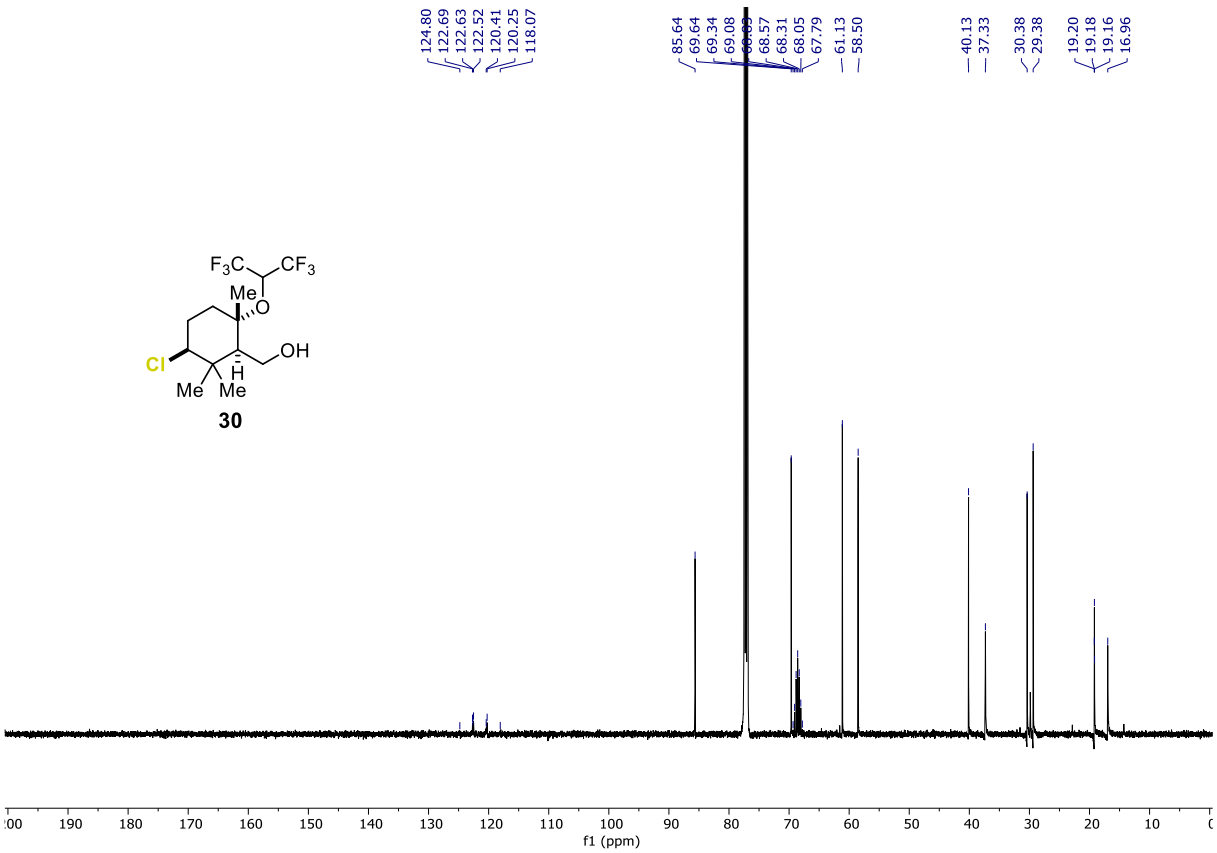

175.62
175.00
84.70
84.69
77.16 CDCl3
68.81
65.71
54.92
52.00
38.55
37.61
37.34
33.73
32.78
31.40
29.93
29.07
28.79
27.32
26.91
24.11
20.58
15.81
Me
O
O
Cl
H
Me Me
major-28
+
Me
O
O
Cl
H
Me Me
minor-28
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

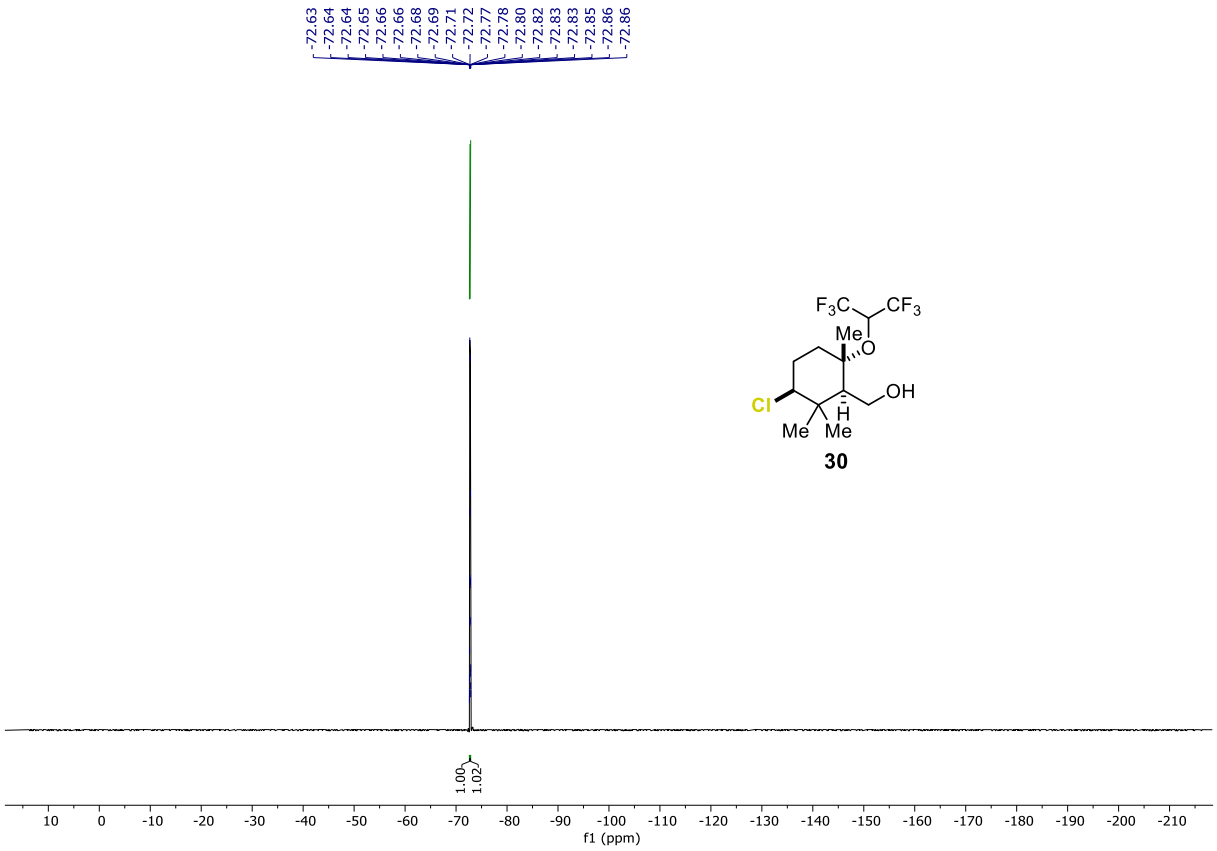

7.2600 CDCl3
4.5104
4.4988
4.4888
4.4772
4.4546
4.4329
4.4293
4.4076
3.8127
3.8044
3.7883
3.7798
2.2054
2.1976
2.1899
2.1824
2.1772
2.1695
2.1621
2.1548
2.0492
2.0428
2.0361
2.0243
2.0171
2.0129
2.0099
1.9993
1.9879
1.9306
1.9235
1.9061
1.9024
1.8991
1.8954
1.8777
1.8740
1.8710
1.8671
1.8495
1.8432
1.8032
1.7960
1.7939
1.7779
1.7756
1.7680
1.7490
1.7411
1.5201
1.5183
1.1592
0.9650
Me
O
O
O
Cl
H
Me
Me
29
1.08
1.02
1.00
1.08
2.07
1.16
1.15
3.32
3.14
3.03
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

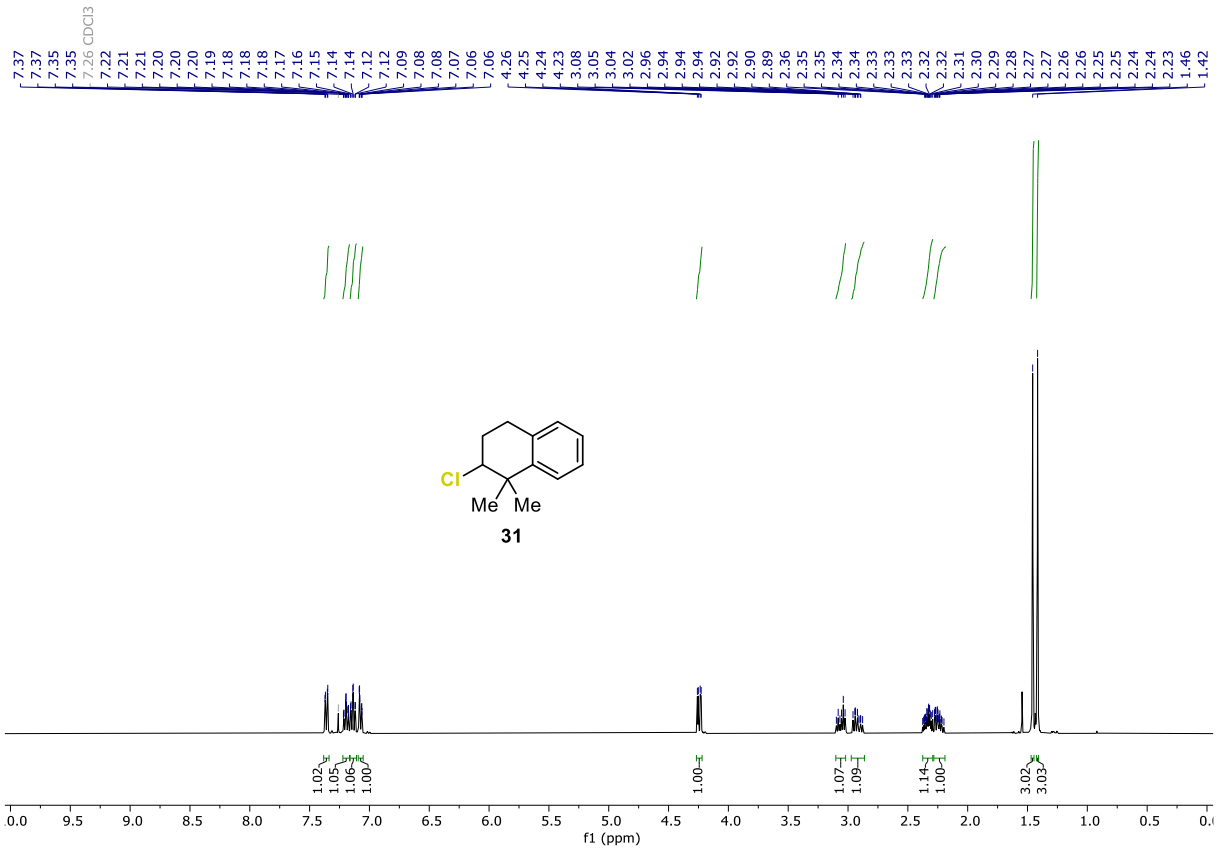
389

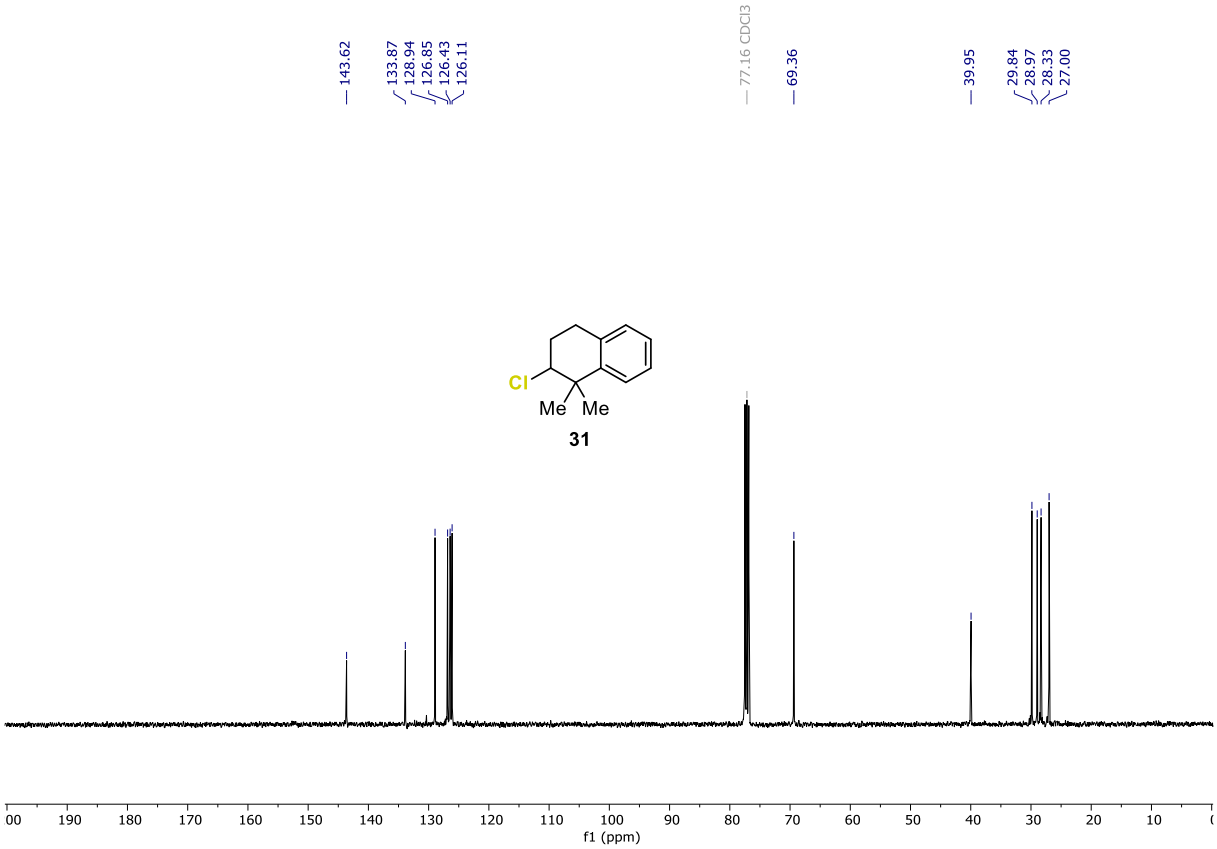

148.49
80.78
68.60
67.32
47.66
38.46
38.30
30.07
28.15
20.96
15.95
Me
O
O
O
Cl
H
Me
Me
29
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

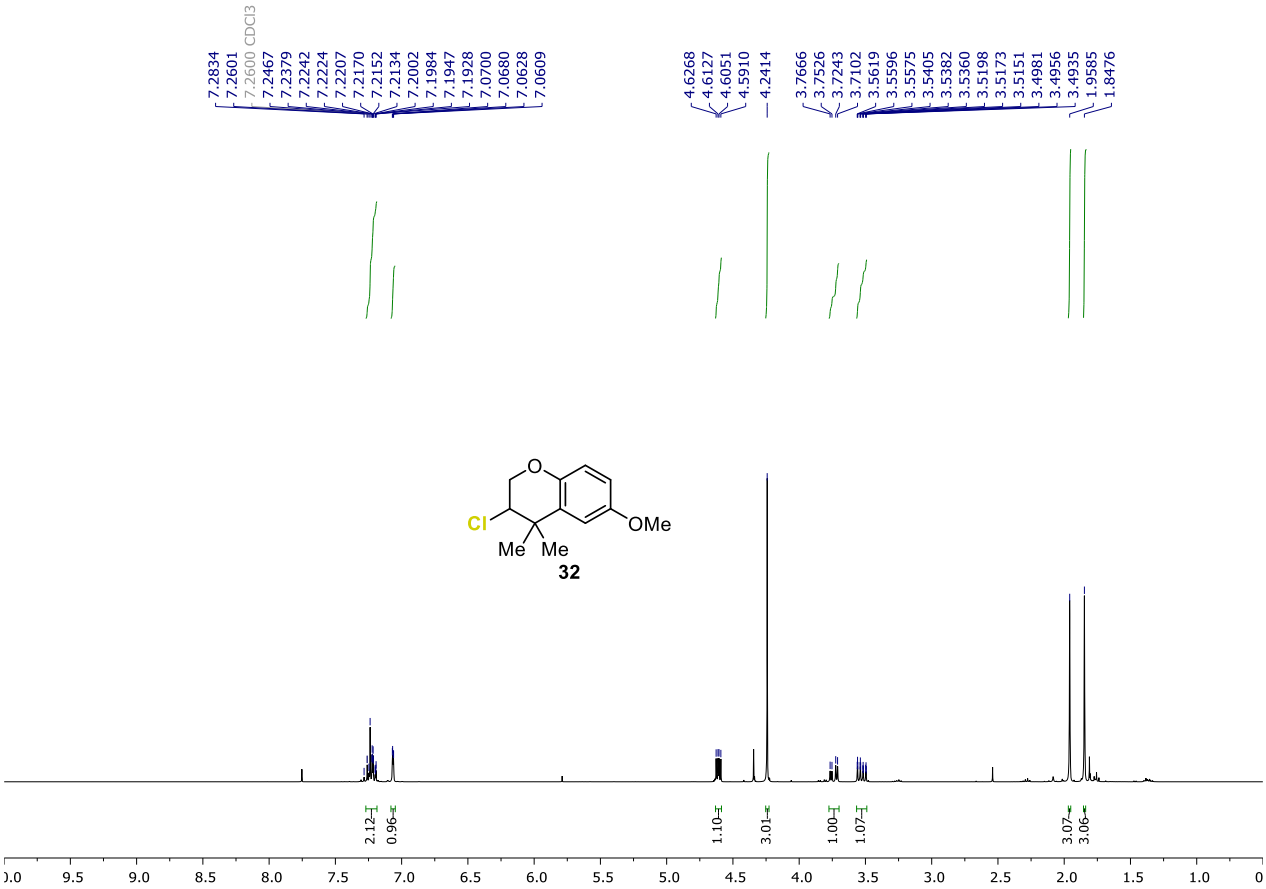

7.2600 CDCl3
4.3807
4.3665
4.3601
4.3522
4.3452
4.3379
4.3236
4.0051
4.0017
3.9897
3.9862
3.9752
3.9718
3.9594
3.9559
3.8090
3.8053
3.8014
3.7957
3.7918
3.7824
3.7786
3.7762
3.7702
3.7661
3.7539
3.7468
2.2334
2.2110
2.1688
2.1601
2.1549
2.1527
2.1451
2.1380
2.1350
2.1301
2.1204
2.1157
2.1121
2.1069
1.8591
1.8541
1.8486
1.8372
1.8333
1.8287
1.8246
1.8210
1.8168
1.7988
1.7920
1.7836
1.7763
1.7604
1.7564
1.7537
1.7361
1.7333
1.7304
1.7274
1.7247
1.7222
1.7193
1.6993
1.3758
1.2779
0.8967
F3C
CF3
Me
O
Cl
OH
H
Me
Me
30
1.01
1.03
1.97
0.97
0.94
3.98
3.07
3.28
3.10
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

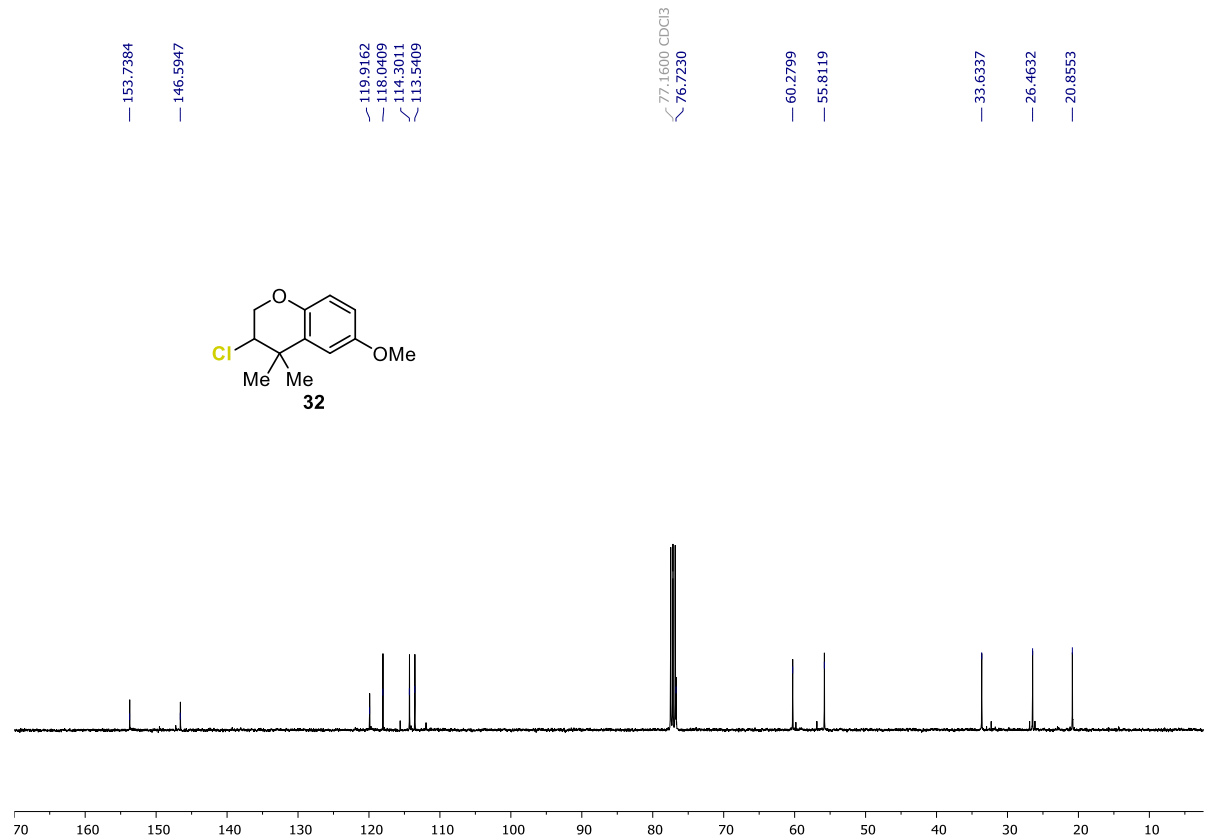

124.80
122.69
122.63
122.52
120.41
120.25
118.07
85.64
69.64
69.34
69.08
68.57
68.31
68.05
67.79
61.13
58.50
40.13
37.33
30.38
29.38
19.20
19.18
19.16
16.96
F3C
CF3
Me
O
Cl
OH
H
Me
Me
30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-72.63
-72.64
-72.64
-72.65
-72.66
-72.66
-72.68
-72.69
-72.71
-72.72
-72.77
-72.78
-72.80
-72.82
-72.83
-72.83
-72.85
-72.86
-72.86
F3C
CF3
Me
O
OH
Cl
H
Me
Me
30
1.00
1.02
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.37 7.37 7.35 7.35 7.26 CDCl3 7.22 7.21 7.21 7.20 7.20 7.20 7.19 7.18 7.18 7.18 7.17 7.16 7.15 7.14 7.14 7.12 7.12 7.09 7.08 7.08 7.07 7.06 7.06
4.26 4.25 4.24 4.23 3.08 3.05 3.04 3.02 2.96 2.94 2.94 2.94 2.92 2.92 2.90 2.89 2.36 2.35 2.35 2.34 2.34 2.33 2.33 2.32 2.32 2.31 2.30 2.29 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.24 2.24 2.23 1.46 1.42
Cl
Me Me
31
1.02 1.05 1.06 1.00
1.00
1.07 1.09
1.14 1.00
3.02 3.03
f1 (ppm)


143.62
133.87 128.94 126.85 126.43 126.11
77.16 CDCl3
69.36
39.95
29.84 28.97 28.33 27.00
Cl
Me Me
31
f1 (ppm)


7.2834
7.2601
7.2600 CDCl3
7.2467
7.2379
7.2242
7.2224
7.2207
7.2170
7.2152
7.2134
7.2002
7.1984
7.1947
7.1928
7.0700
7.0680
7.0628
7.0609
4.6268
4.6127
4.6051
4.5910
4.2414
3.7666
3.7526
3.7243
3.7102
3.5619
3.5596
3.5575
3.5405
3.5382
3.5360
3.5198
3.5173
3.5151
3.4981
3.4956
3.4935
1.9585
1.8476
O
Cl
OMe
Me Me
32
2.12
0.96
1.10
3.01
1.00
1.07
3.07
3.06
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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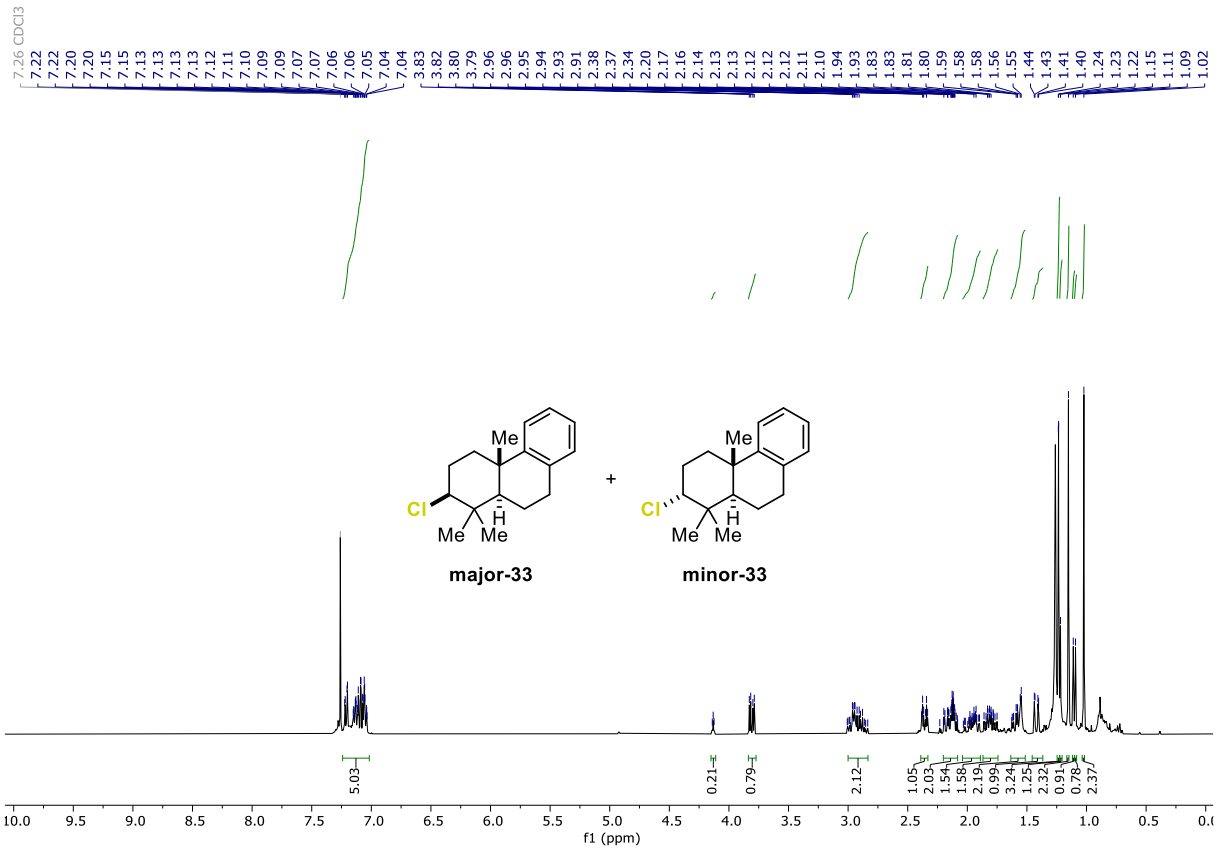
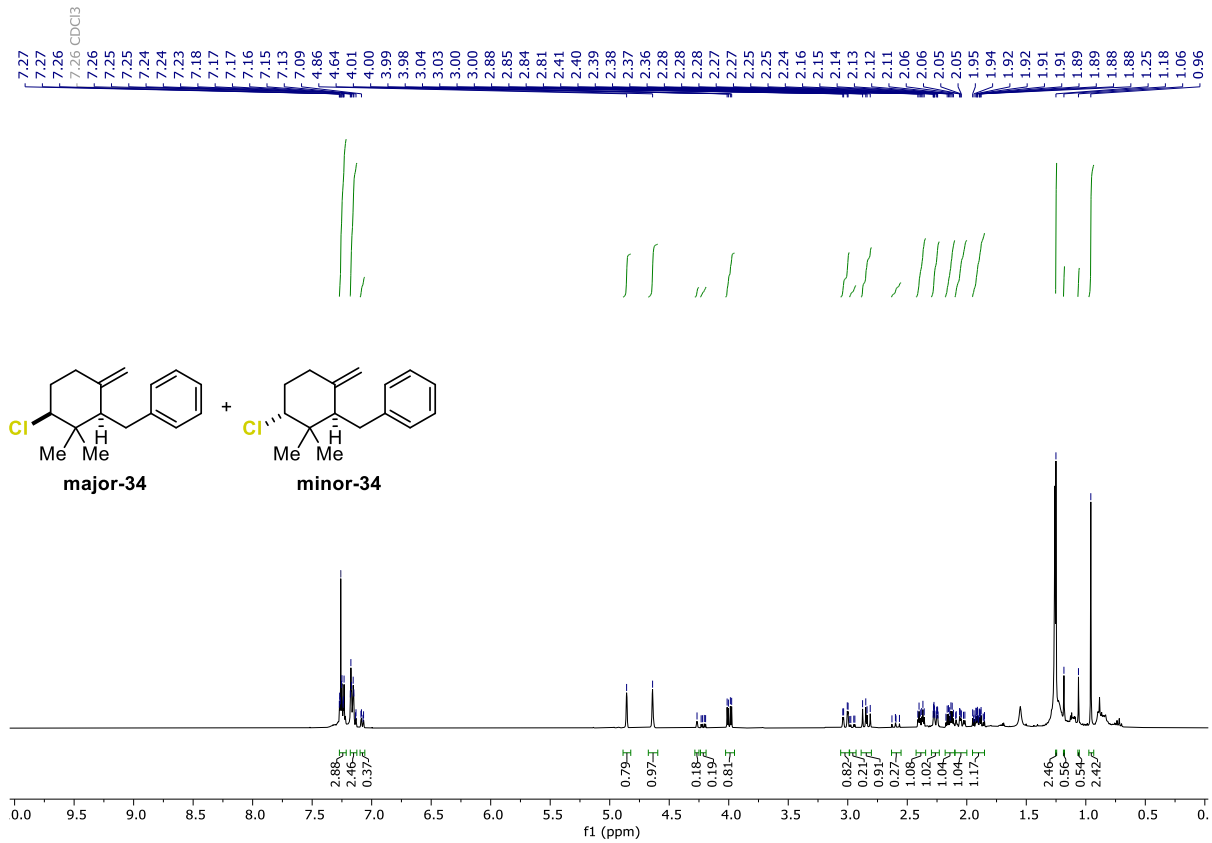
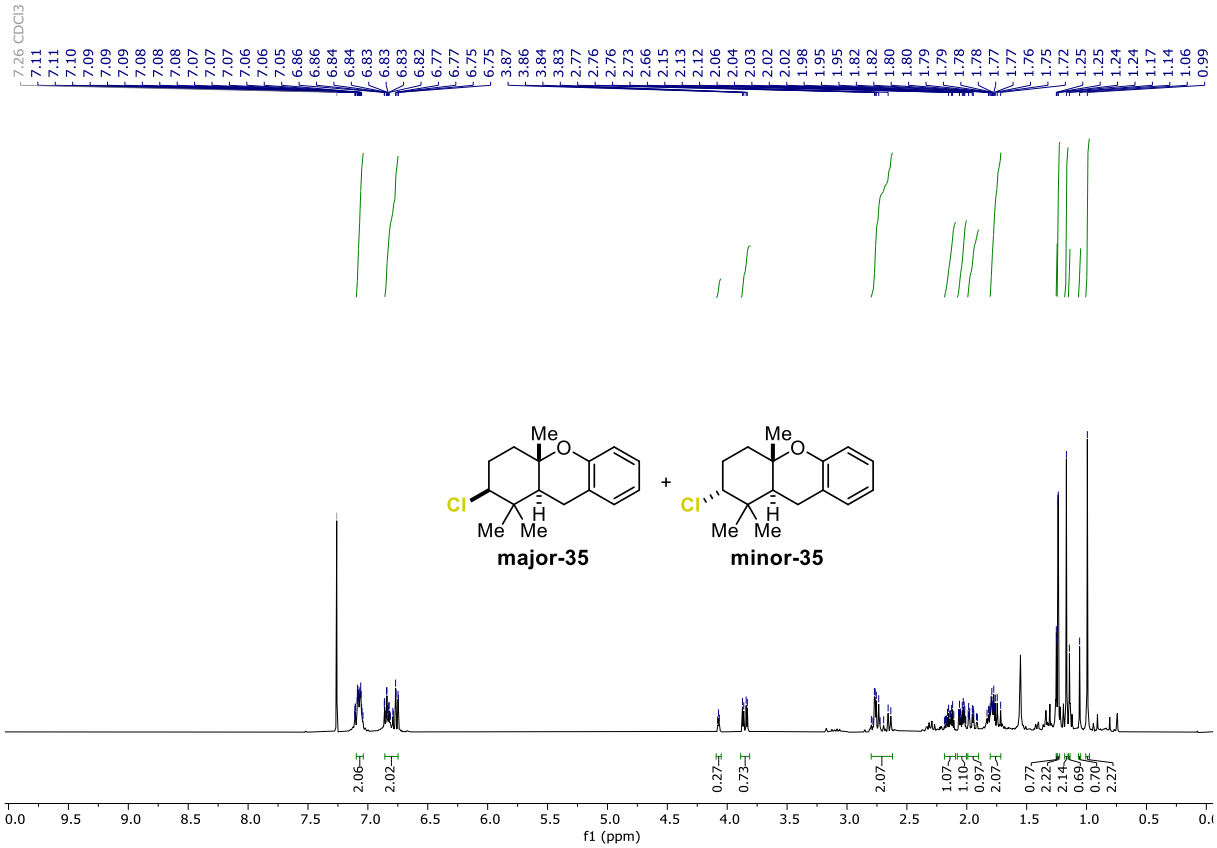
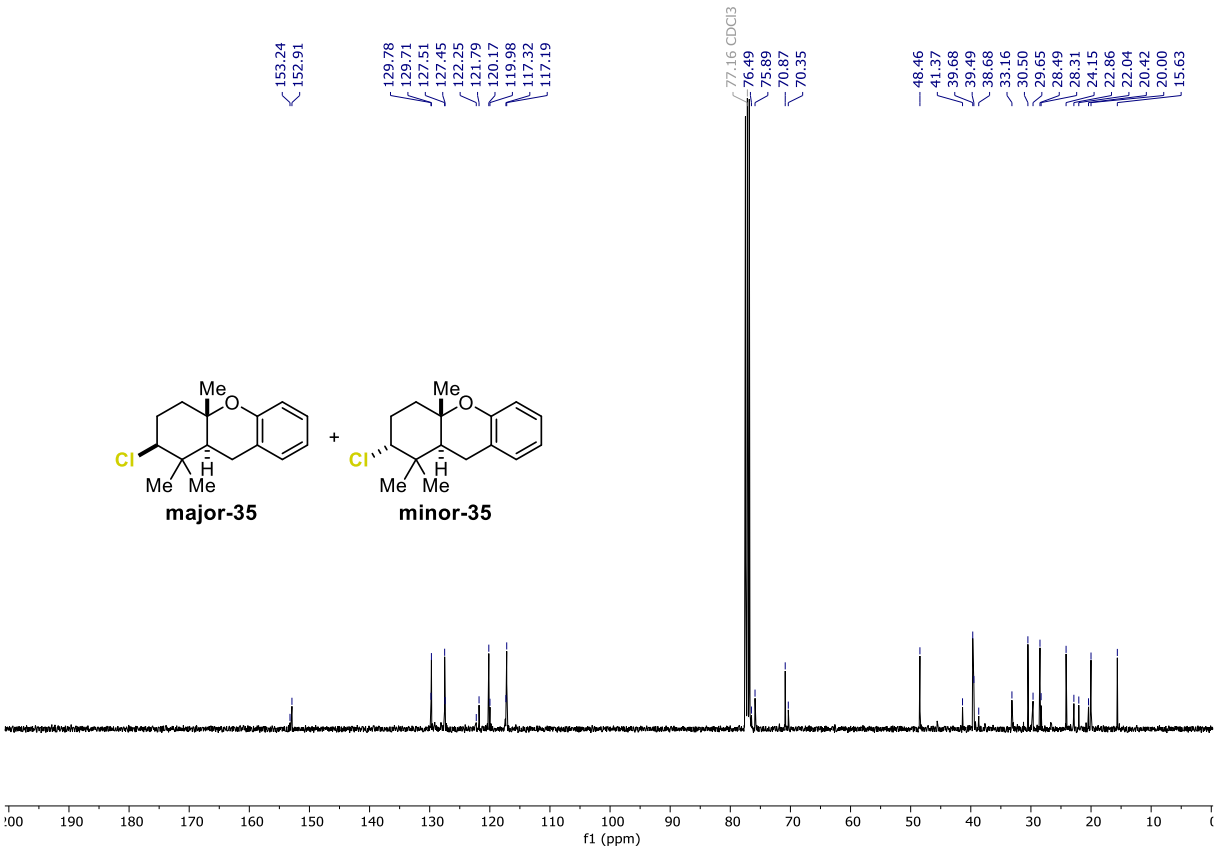
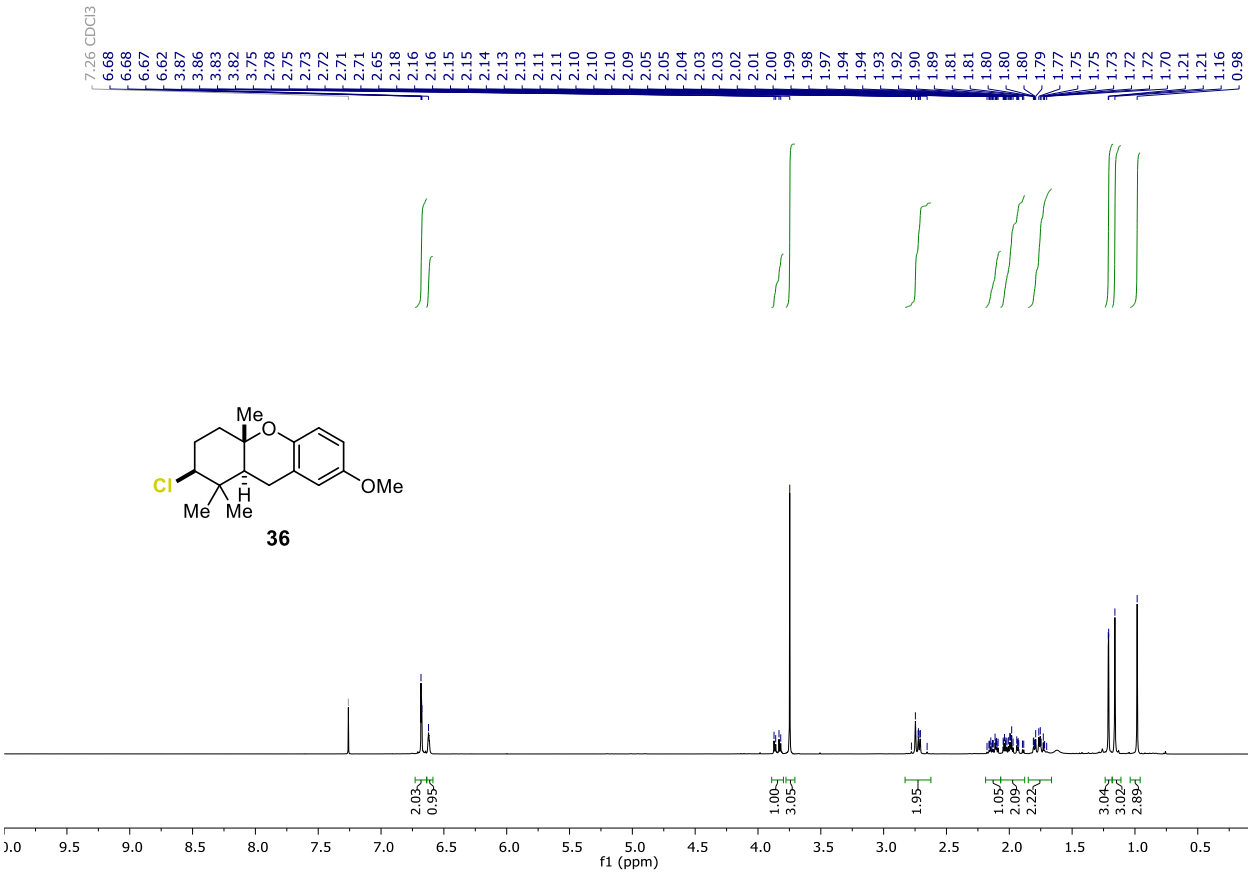
146.5947
119.9162
118.0409
114.3011
113.5409
77.1600 CDCl3
76.7230
60.2799
55.8119
33.6337
26.4632
20.8553
O
Cl
OMe
Me Me
32
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

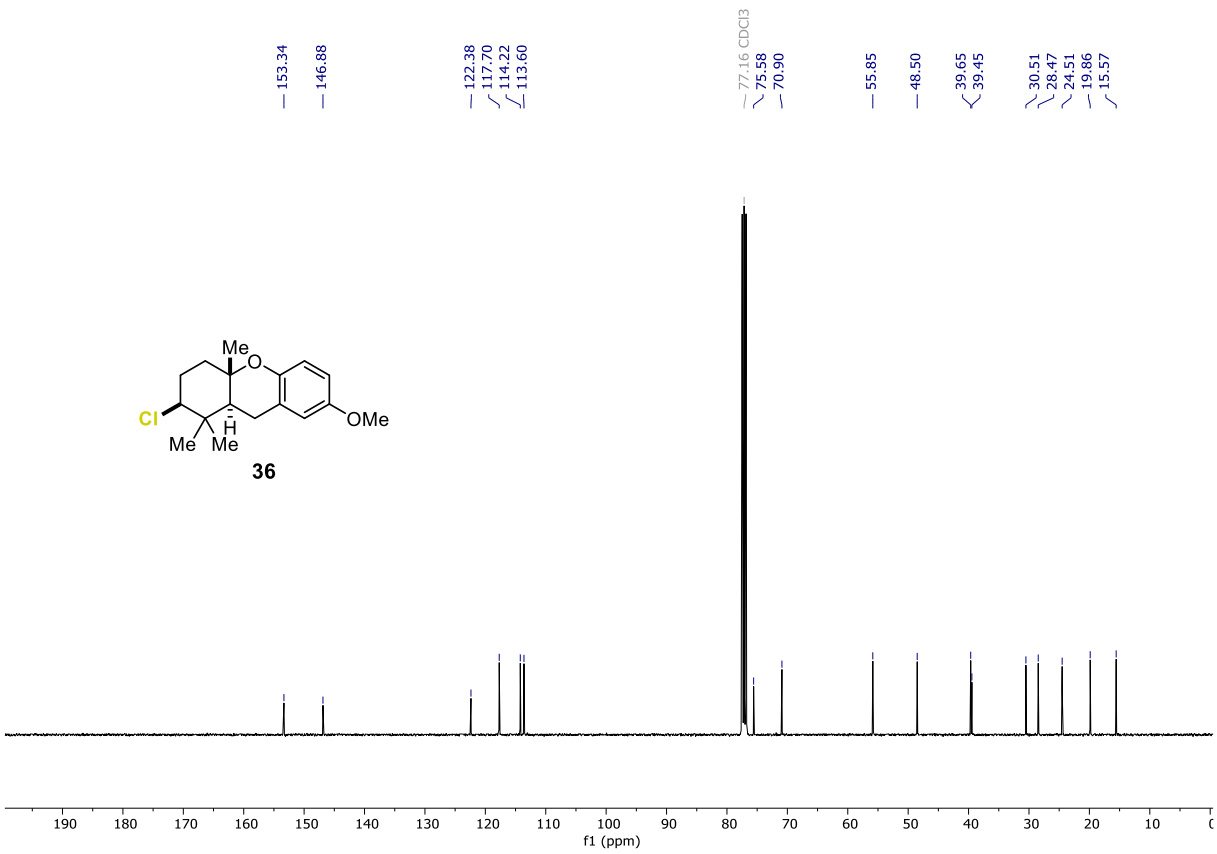

7.26 CDCl3
Me
Cl
H
Me Me
major-33
+
minor-33
5.03
0.21
0.79
2.12
f1 (ppm)

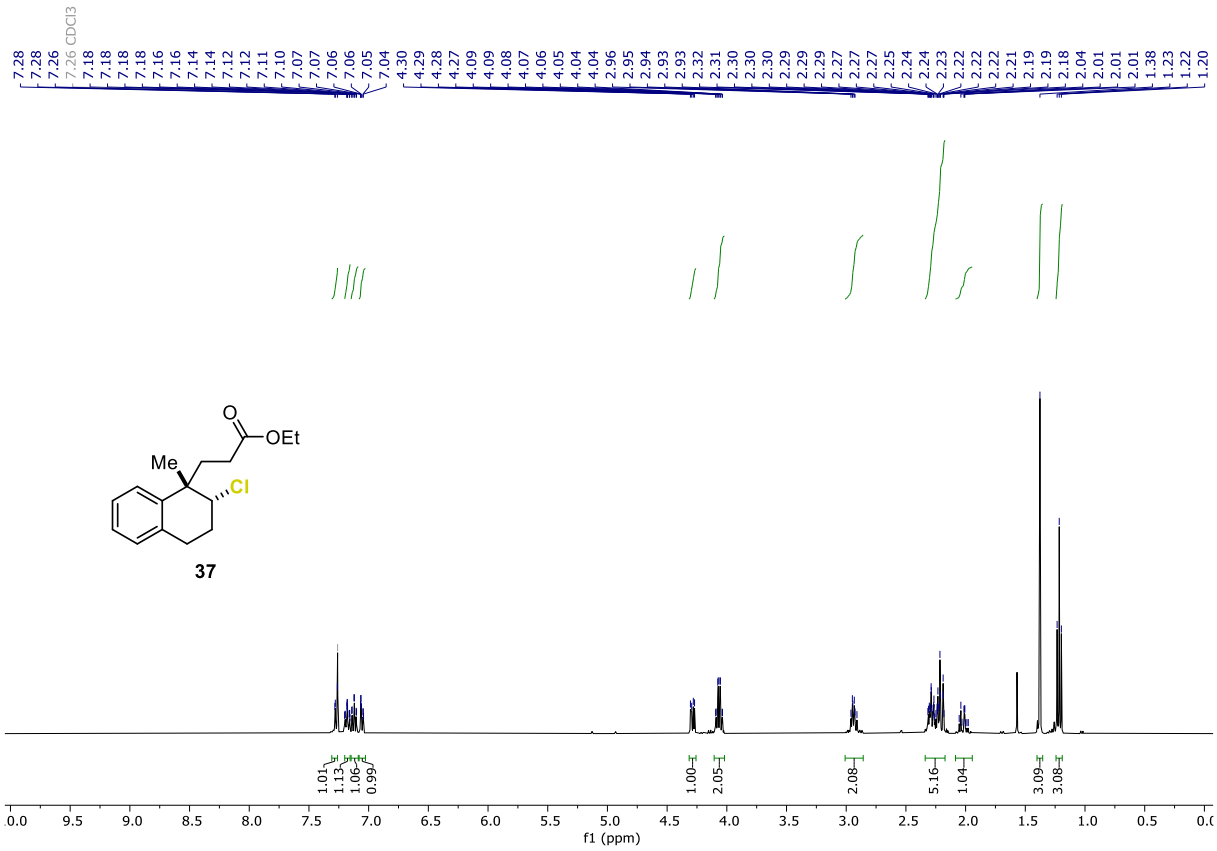

7.26 CDCl3
Cl
H
Me Me
major-34
+
minor-34
2.88
2.46
0.37
0.79
0.97
0.18
0.19
0.81
0.82
0.21
0.91
0.27
1.08
1.02
1.04
1.04
1.17
2.46
0.56
0.54
2.42
f1 (ppm)

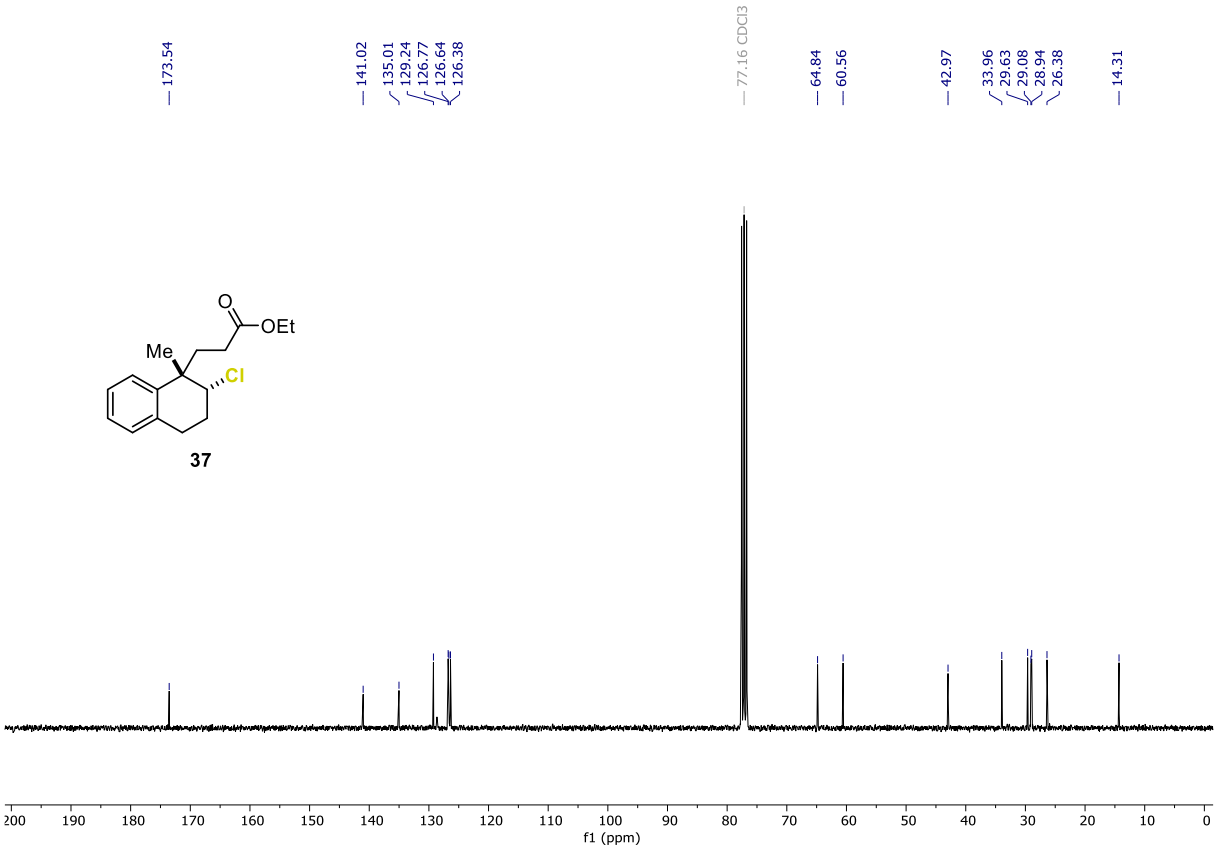

7.26 CDCl3
7.11 7.11 7.10 7.09 7.09 7.09 7.08 7.08 7.08 7.07 7.07 7.07 7.06 7.06 7.05 6.86 6.86 6.84 6.84 6.83 6.83 6.83 6.82 6.77 6.77 6.75 6.75 3.87 3.86 3.84 3.83 2.77 2.76 2.76 2.73 2.66 2.15 2.13 2.12 2.06 2.04 2.03 2.02 2.02 1.98 1.95 1.95 1.82 1.82 1.80 1.80 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.75 1.72 1.25 1.25 1.24 1.24 1.17 1.14 1.06 0.99
Me
O
Cl
H
Me Me
major-35
+
minor-35
2.06 2.02 0.27 0.73 2.07 1.07 1.10 0.97 2.07 0.77 2.22 2.14 0.69 0.70 2.27
0.0 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
f1 (ppm)

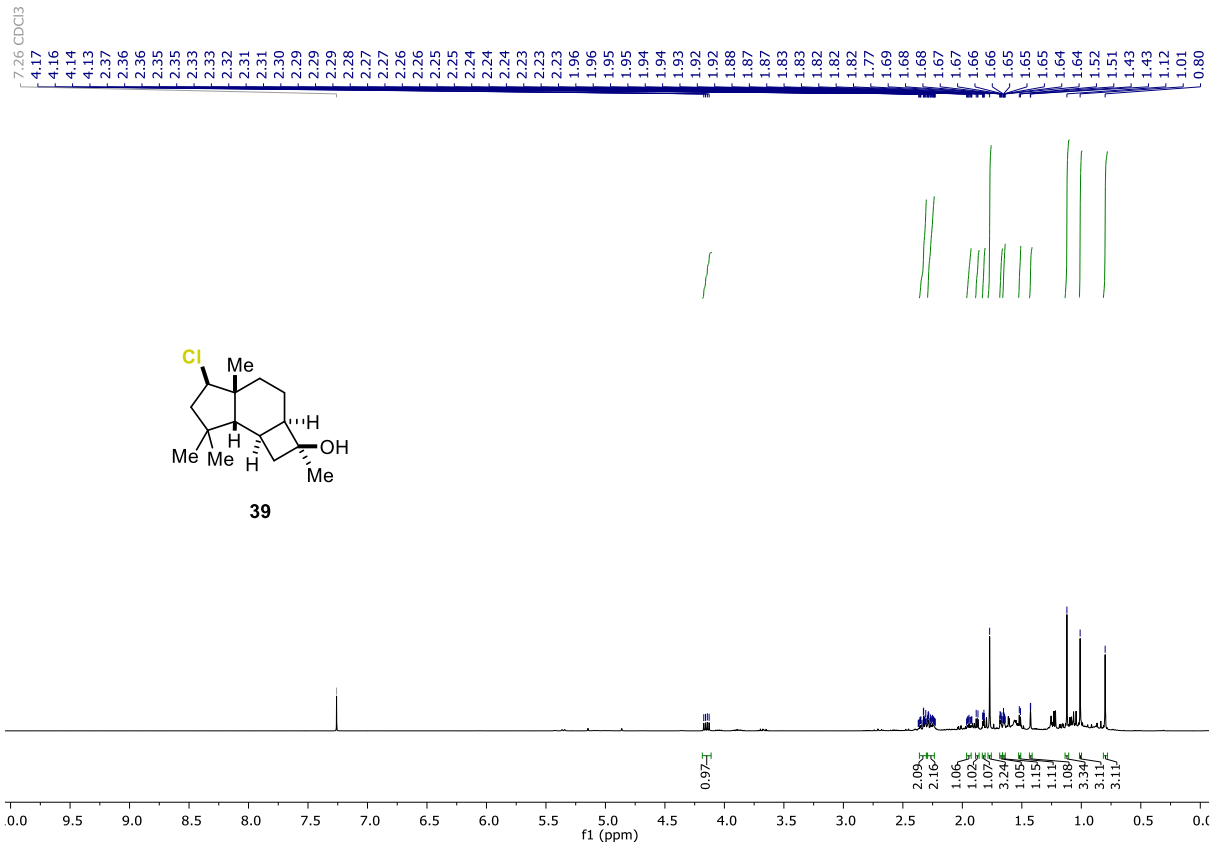

153.24 152.91
129.78 129.71 127.51 127.45 122.25 121.79 120.17 119.98 117.32 117.19
77.16 CDCl3
76.49 75.89 70.87 70.35
48.46 41.37 39.68 39.49 38.68 33.16 30.50 29.65 28.49 28.31 24.15 22.86 22.04 20.42 20.00 15.63
Me
O
Cl
H
Me Me
major-35
+
minor-35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

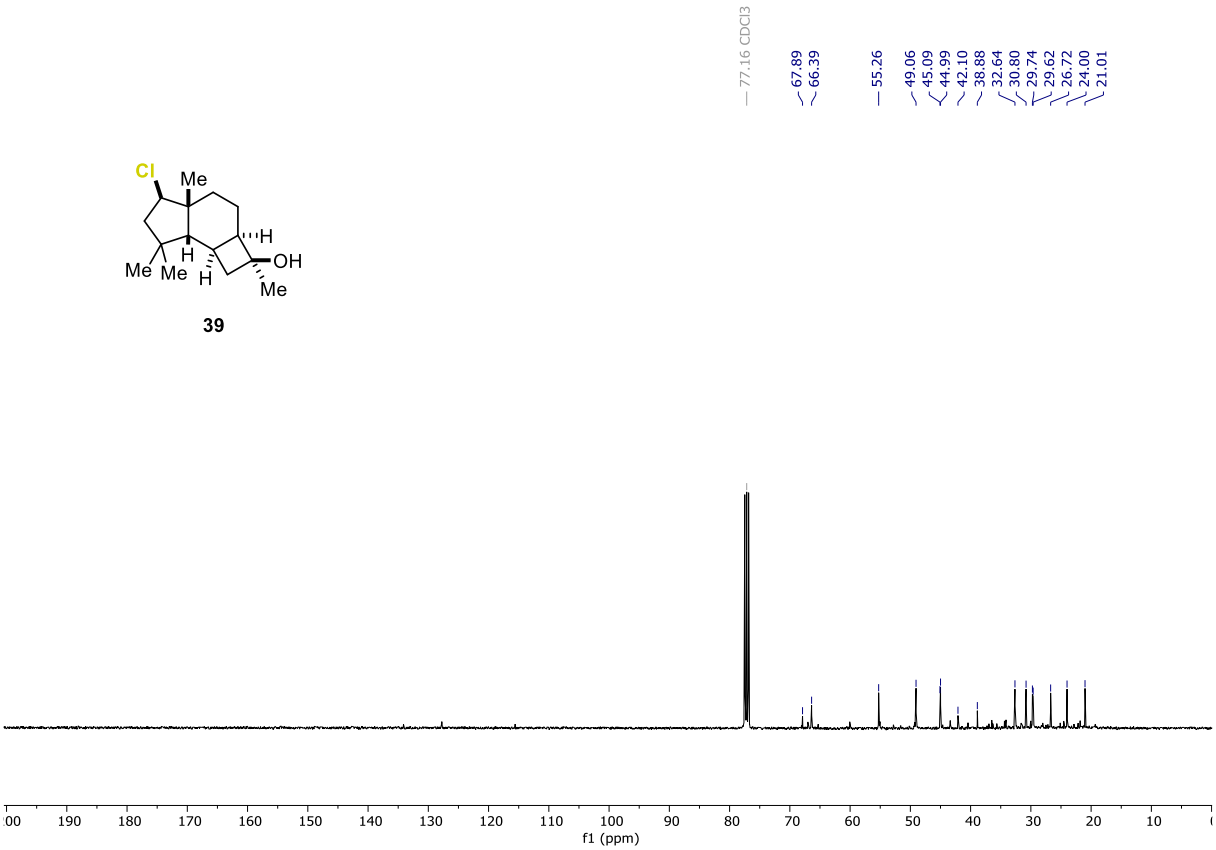

7.26 CDCl3
6.68 6.68 6.67 6.62 3.87 3.86 3.83 3.82 3.75 2.78 2.75 2.73 2.72 2.71 2.71 2.65 2.18 2.16 2.16 2.15 2.15 2.14 2.13 2.13 2.11 2.11 2.10 2.10 2.10 2.09 2.05 2.05 2.04 2.03 2.03 2.02 2.01 2.00 1.99 1.98 1.97 1.94 1.94 1.93 1.92 1.90 1.89 1.81 1.81 1.80 1.80 1.80 1.79 1.77 1.75 1.75 1.73 1.72 1.72 1.70 1.21 1.21 1.16 0.98
Me
O
Cl
H
Me Me
OMe
36
2.03
0.95
1.00
3.05
1.95
1.05
2.09
2.22
3.04
3.02
2.89
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
f1 (ppm)

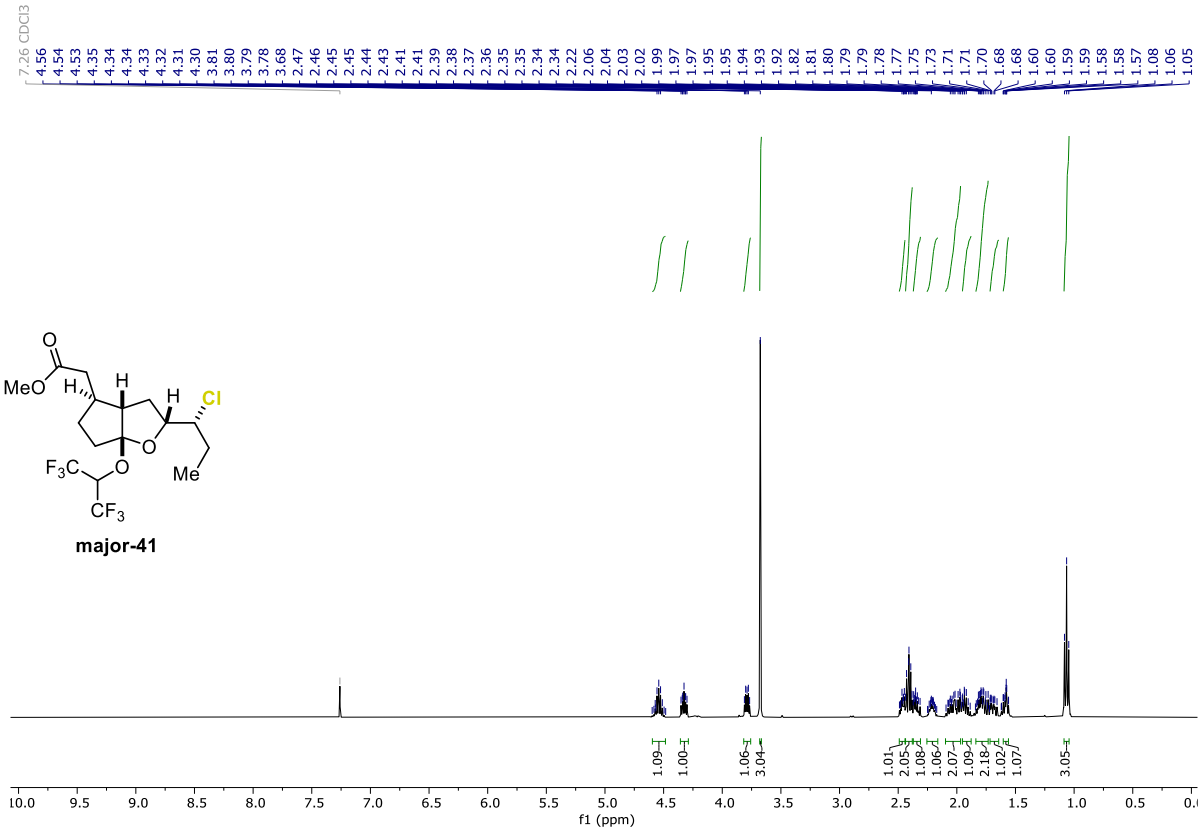

153.34
146.88
122.38
117.70
114.22
113.60
77.16 CDCl3
75.58
70.90
55.85
48.50
39.65
39.45
30.51
28.47
24.51
19.86
15.57
Me
O
Cl
H
Me Me
OMe
36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

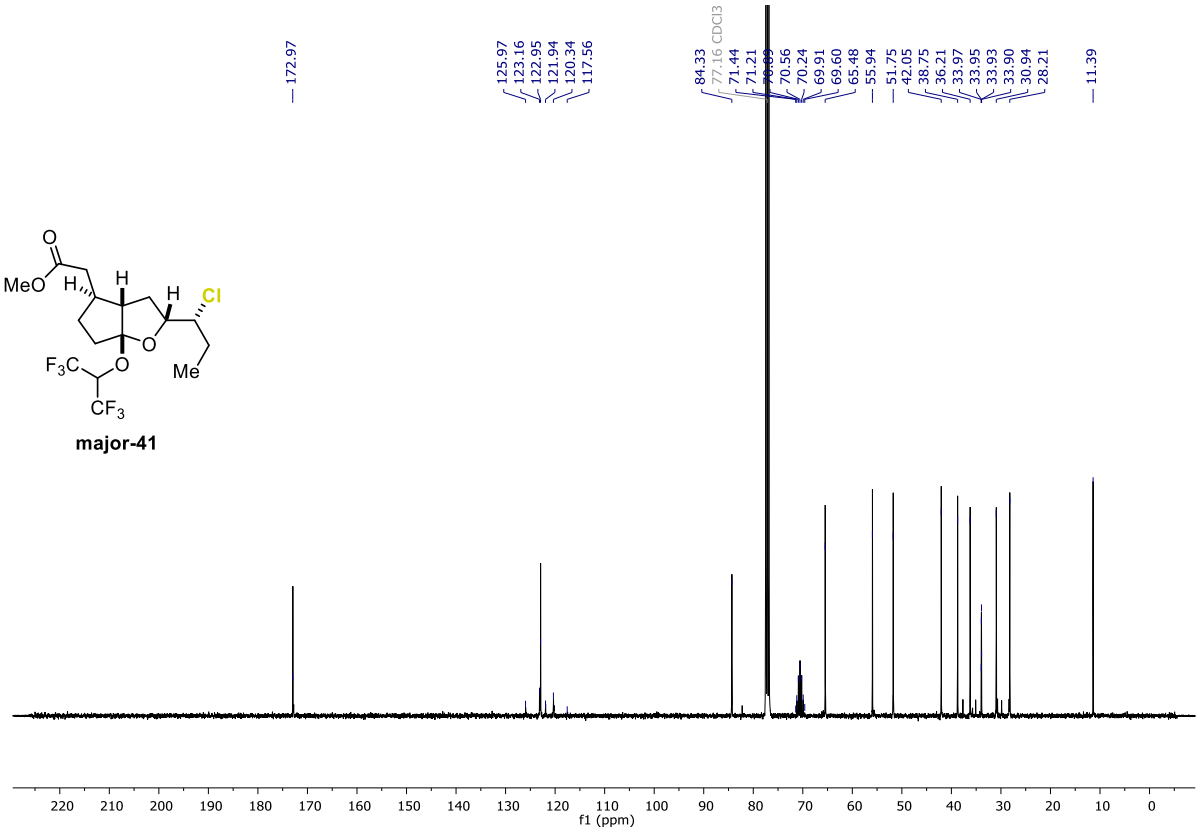

7.28 7.28 7.26 7.26 CDCl3 7.18 7.18 7.18 7.18 7.16 7.14 7.14 7.12 7.12 7.11 7.10 7.07 7.07 7.06 7.06 7.05 7.04 4.30 4.29 4.28 4.27 4.09 4.09 4.08 4.07 4.06 4.05 4.04 4.04 2.96 2.95 2.94 2.93 2.93 2.32 2.31 2.30 2.30 2.30 2.29 2.29 2.29 2.27 2.27 2.27 2.25 2.24 2.24 2.23 2.22 2.22 2.22 2.21 2.19 2.19 2.18 2.04 2.01 2.01 2.01 1.38 1.23 1.22 1.20
O
OEt
Me
Cl
37
1.01 1.13 1.06 0.99 1.00 2.05 2.08 5.16 1.04 3.09 3.08
f1 (ppm)

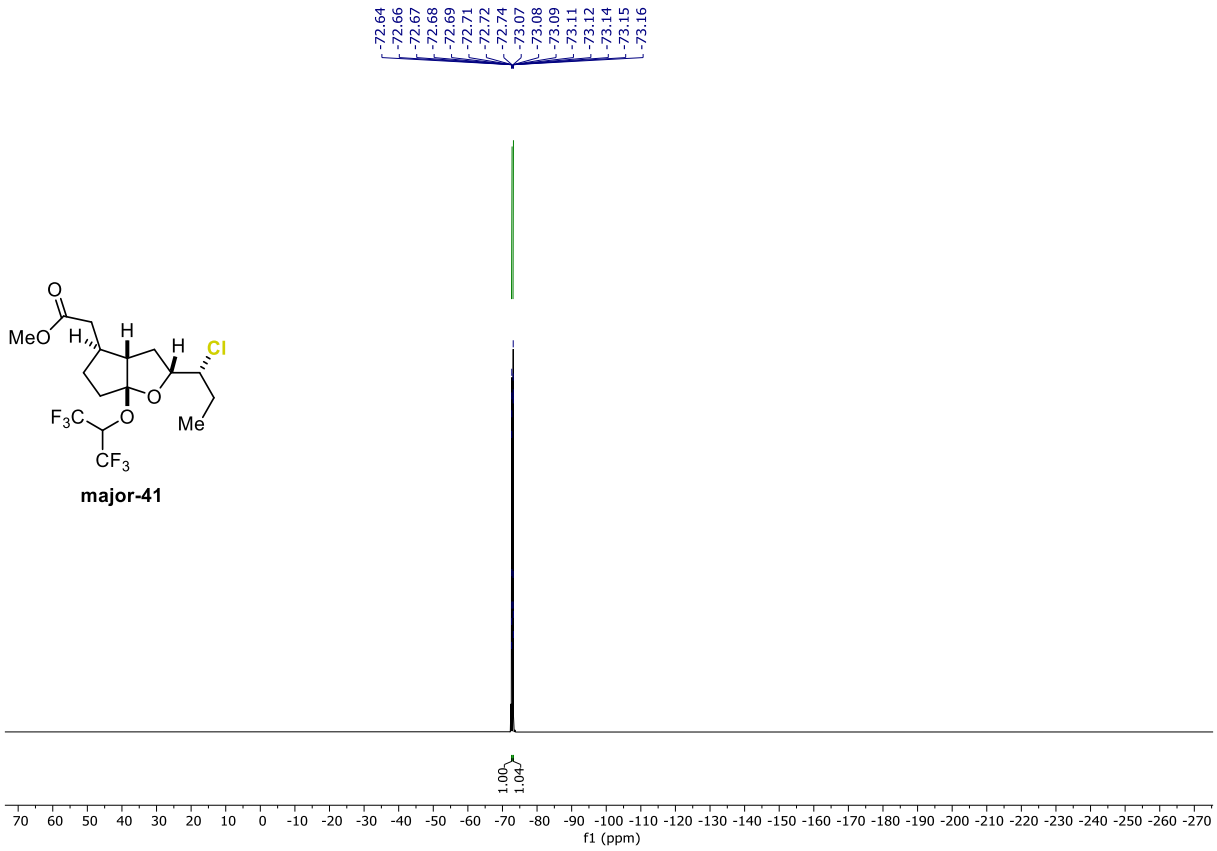

173.54 141.02 135.01 129.24 126.77 126.64 126.38 77.16 CDCl3 64.84 60.56 42.97 33.96 29.63 29.08 28.94 26.38 14.31
O
OEt
Me
Cl
37
f1 (ppm)

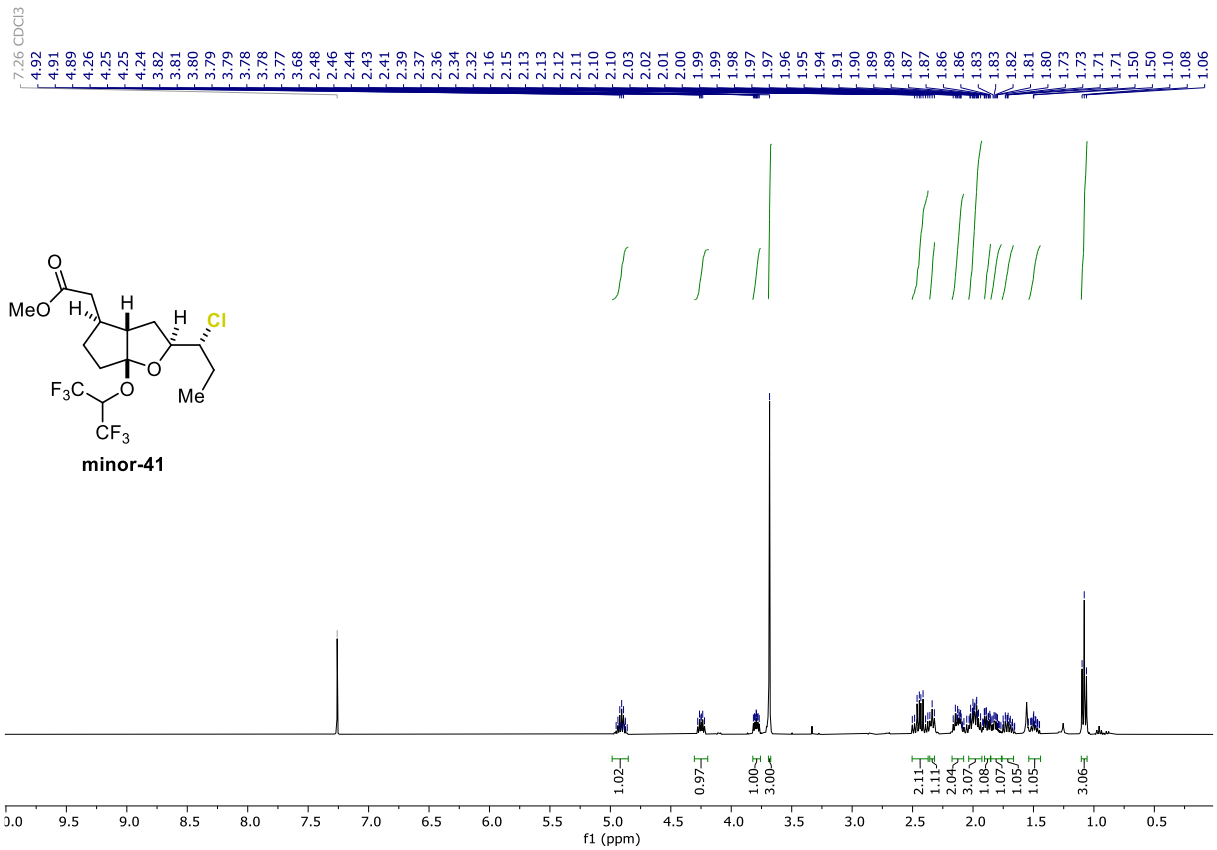

7.26 CDCl3
4.17 4.16 4.14 4.13 2.37 2.36 2.36 2.35 2.35 2.33 2.33 2.32 2.31 2.31 2.30 2.29 2.29 2.29 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.24 2.24 2.24 2.23 2.23 2.23 1.96 1.96 1.95 1.95 1.94 1.94 1.93 1.92 1.92 1.88 1.87 1.87 1.83 1.83 1.82 1.82 1.82 1.77 1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.52 1.51 1.43 1.43 1.12 1.01 0.80
Cl
Me
H
OH
Me
Me
Me
H
H
39
0.97
2.09
2.16
1.06
1.02
1.07
3.24
1.05
1.15
1.11
1.08
3.34
3.11
3.11
f1 (ppm)

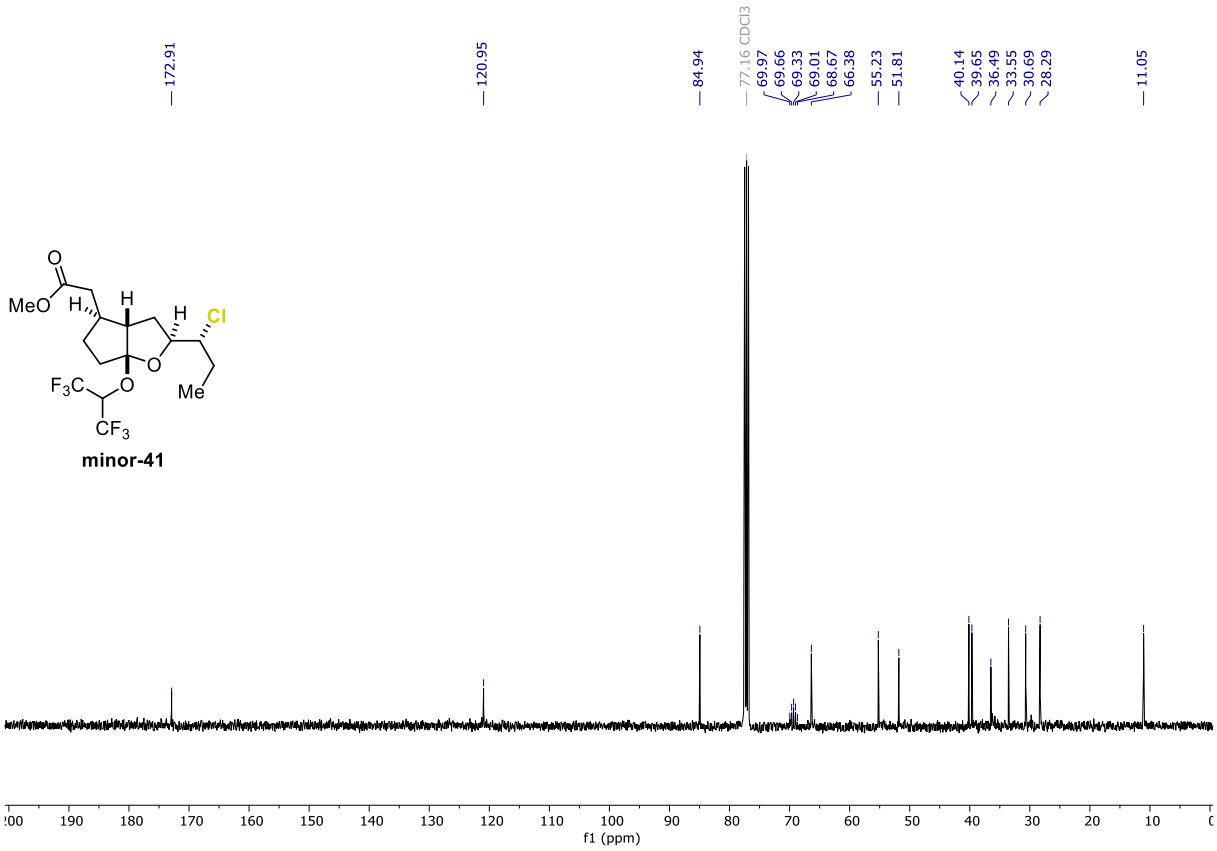

77.16 CDCl3
67.89
66.39
55.26
49.06
45.09
44.99
42.10
38.88
32.64
30.80
29.74
29.62
26.72
24.00
21.01
Cl
Me
H
OH
Me
Me
Me
H
H
39
f1 (ppm)

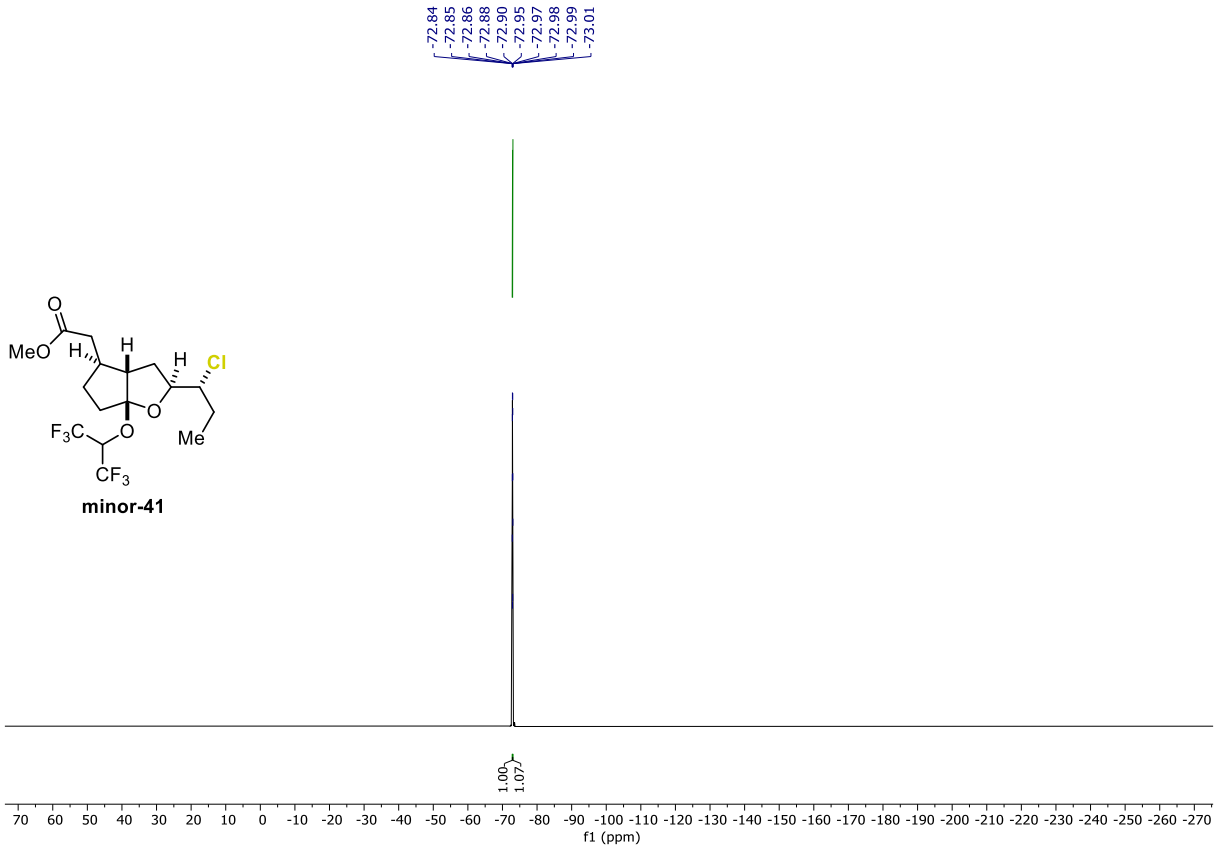

7.26 CDCl3
4.56 4.54 4.53 4.35 4.34 4.34 4.33 4.32 4.31 4.30 3.81 3.80 3.79 3.78 3.68 2.47 2.46 2.45 2.45 2.44 2.43 2.41 2.41 2.39 2.38 2.37 2.36 2.35 2.35 2.34 2.34 2.22 2.06 2.04 2.03 2.02 1.99 1.97 1.97 1.95 1.95 1.94 1.93 1.92 1.82 1.81 1.80 1.79 1.79 1.78 1.77 1.75 1.73 1.71 1.71 1.70 1.68 1.68 1.60 1.60 1.59 1.59 1.58 1.58 1.57 1.08 1.06 1.05
MeO
O
H
H
H
Cl
O
O
F3C
CF3
Me
major-41
1.09 1.00 1.06 3.04 1.01 2.05 1.08 1.06 2.07 1.09 2.18 1.02 1.07 3.05
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
f1 (ppm)

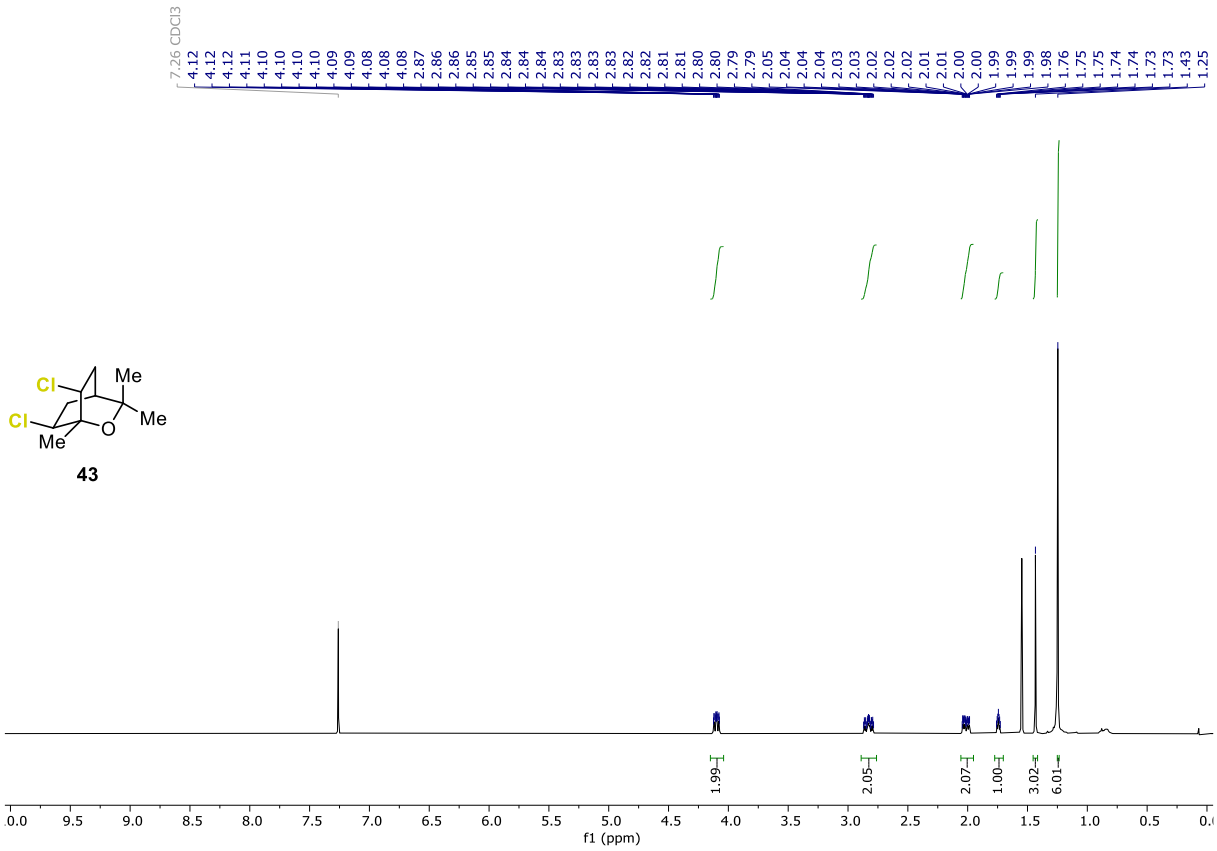

172.97
125.97 123.16 122.95 121.94 120.34 117.56
84.33 77.16 CDCl3 71.44 71.21 70.56 70.24 69.91 69.60 65.48 55.94 51.75 42.05 38.75 36.21 33.97 33.95 33.93 33.90 30.94 28.21
11.39
MeO
O
H
H
H
Cl
O
O
F3C
CF3
Me
major-41
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

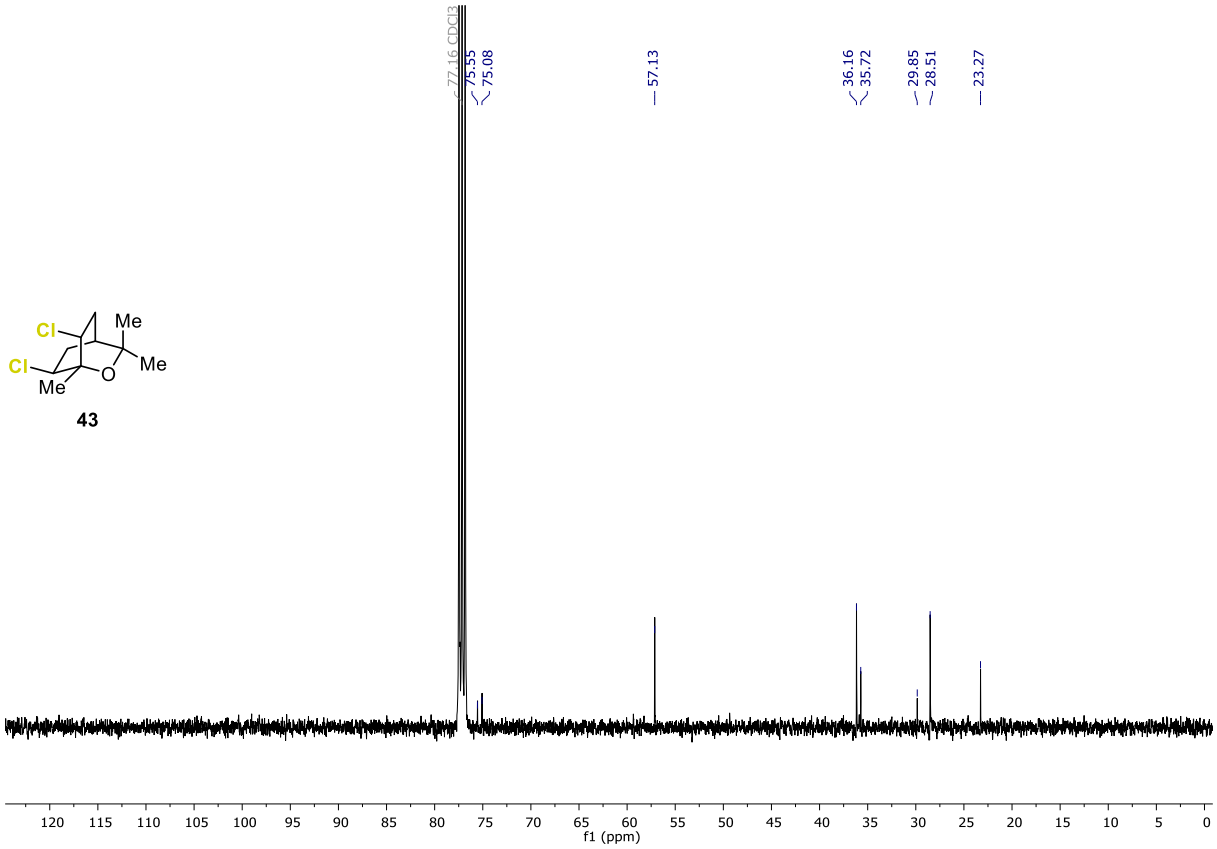

-72.64
-72.66
-72.67
-72.68
-72.69
-72.71
-72.72
-72.74
-73.07
-73.08
-73.09
-73.11
-73.12
-73.14
-73.15
-73.16
MeO
O
H
H
H
Cl
O
F3C
O
Me
CF3
major-41
1.00
1.04
f1 (ppm)


7.26 CDCl3
4.92
4.91
4.89
4.26
4.25
4.25
4.24
3.82
3.81
3.80
3.79
3.79
3.78
3.78
3.77
3.68
2.48
2.46
2.44
2.43
2.41
2.39
2.37
2.36
2.34
2.32
2.16
2.15
2.13
2.13
2.12
2.11
2.10
2.10
2.03
2.02
2.01
2.00
1.99
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.91
1.90
1.89
1.89
1.87
1.87
1.86
1.86
1.83
1.83
1.82
1.81
1.80
1.73
1.73
1.71
1.71
1.50
1.50
1.10
1.08
1.06
MeO
O
H
H
H
Cl
O
F3C
O
Me
CF3
minor-41
1.02
0.97
1.00
3.00
2.11
1.11
2.04
3.07
1.08
1.07
1.05
1.05
3.06
f1 (ppm)


172.91
120.95
84.94
77.16 CDCl3
69.97
69.66
69.33
69.01
68.67
66.38
55.23
51.81
40.14
39.65
36.49
33.55
30.69
28.29
11.05
MeO
H
H
H
Cl
O
O
O
F3C
CF3
Me
minor-41
f1 (ppm)


-72.84
-72.85
-72.86
-72.88
-72.90
-72.95
-72.97
-72.98
-72.99
-73.01
MeO
H
H
H
Cl
O
O
O
F3C
CF3
Me
minor-41
1.00
1.07
f1 (ppm)


7.26 CDCl3
4.12 4.12 4.12 4.11 4.10 4.10 4.10 4.10 4.09 4.09 4.08 4.08 4.08 2.87 2.86 2.86 2.85 2.85 2.84 2.84 2.84 2.83 2.83 2.83 2.83 2.82 2.82 2.81 2.81 2.80 2.80 2.79 2.79 2.05 2.04 2.04 2.04 2.03 2.03 2.02 2.02 2.02 2.01 2.01 2.00 2.00 1.99 1.99 1.99 1.98 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.43 1.25
Cl
Cl
Me
Me
Me
O
43
1.99
2.05
2.07
1.00
3.02
6.01
f1 (ppm)


77.16 CDCl3
75.55
75.08
57.13
36.16
35.72
29.85
28.51
23.27
Cl
Cl
Me
Me
Me
O
43
f1 (ppm)