Angewandte Chemie
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Supporting Information

Reductive Cyclization of Unactivated Alkyl Chlorides with Tethered Alkenes under Visible-Light Photoredox Catalysis

Miguel Claros, Felix Ungeheuer, Federico Franco, Vlad Martin-Diaconescu, Alicia Casitas, and Julio Lloret-Fillol**

ange_201812702_sm_miscellaneous_information.pdf

Supporting Information

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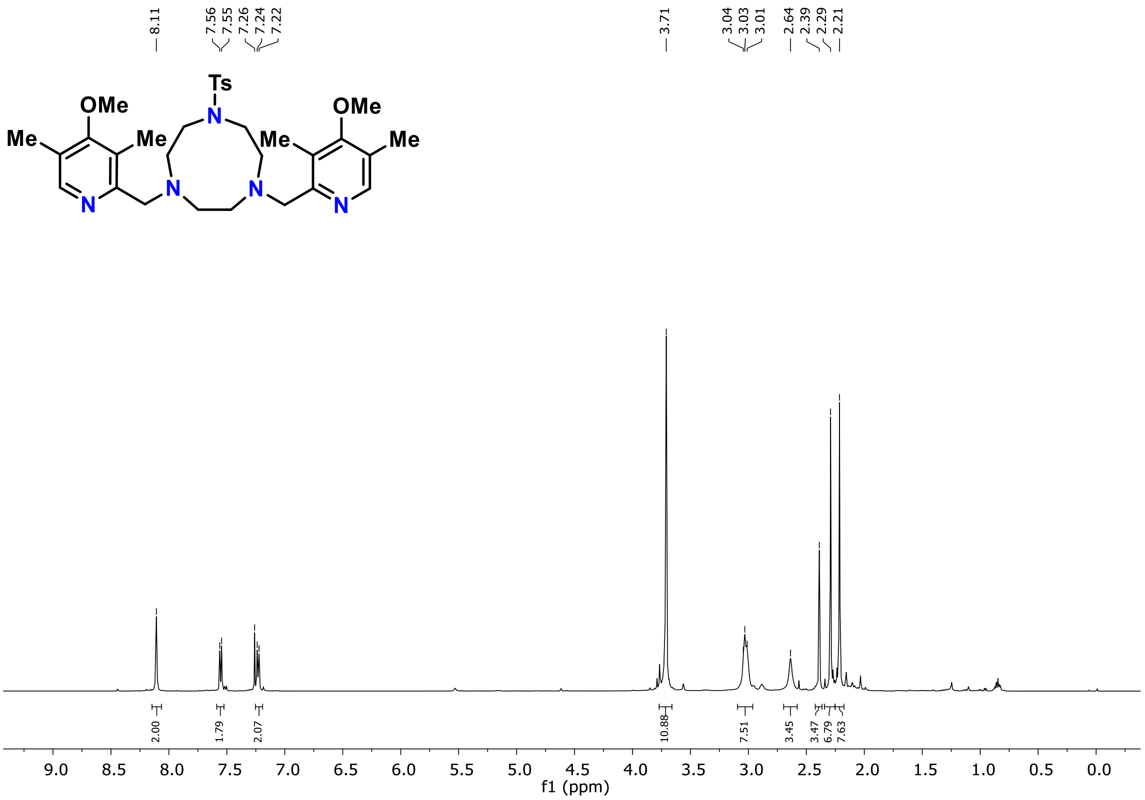
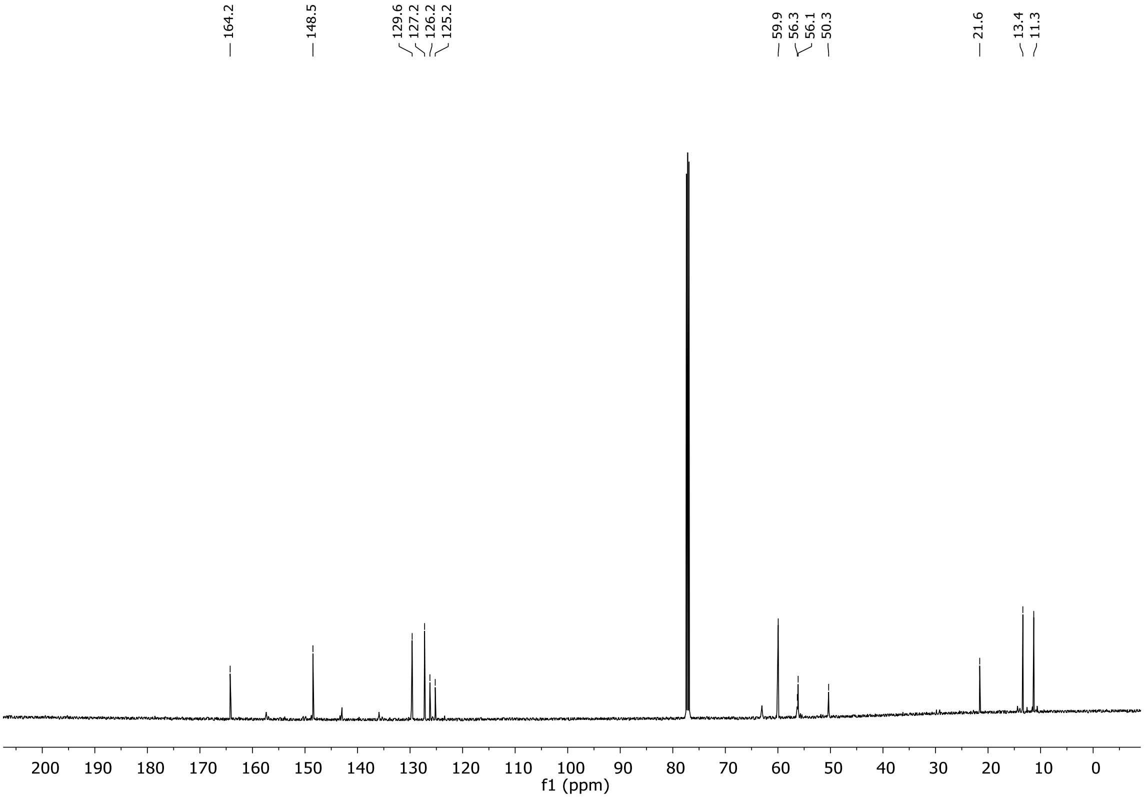
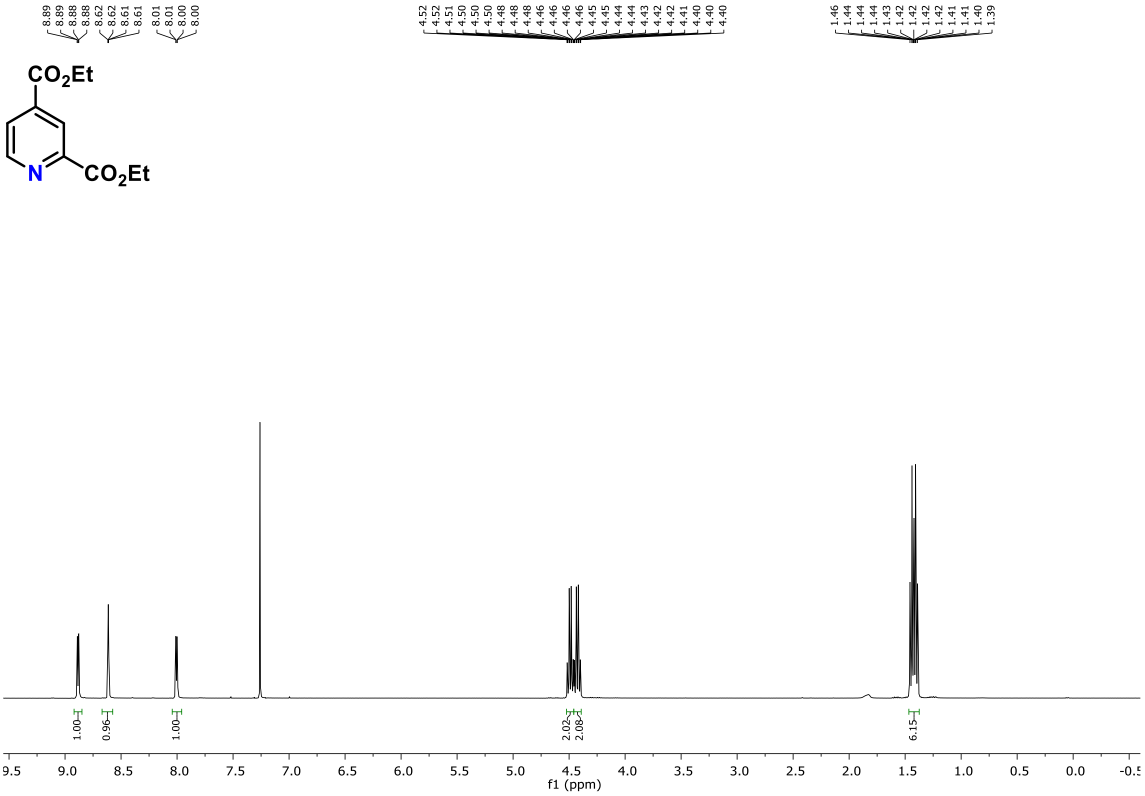
1. Spectra of Ligands



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4.51
4.50
4.50
4.48
4.48
4.48
4.46
4.46
4.46
4.45
4.44
4.44
4.43
4.42
4.42
4.41
4.40
4.40
1.46
1.44
1.44
1.44
1.43
1.42
1.42
1.42
1.42
1.41
1.41
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CO2Et
N
CO2Et
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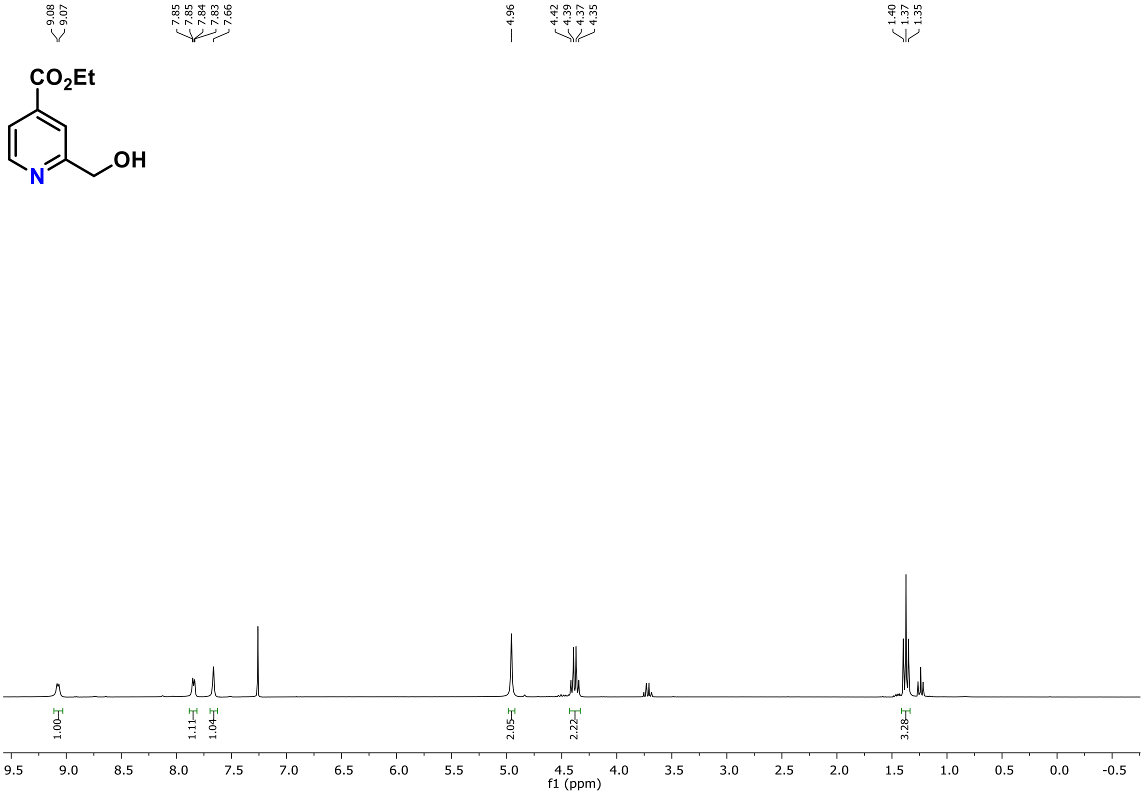
2.02
2.08
6.15
f1 (ppm)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2.05
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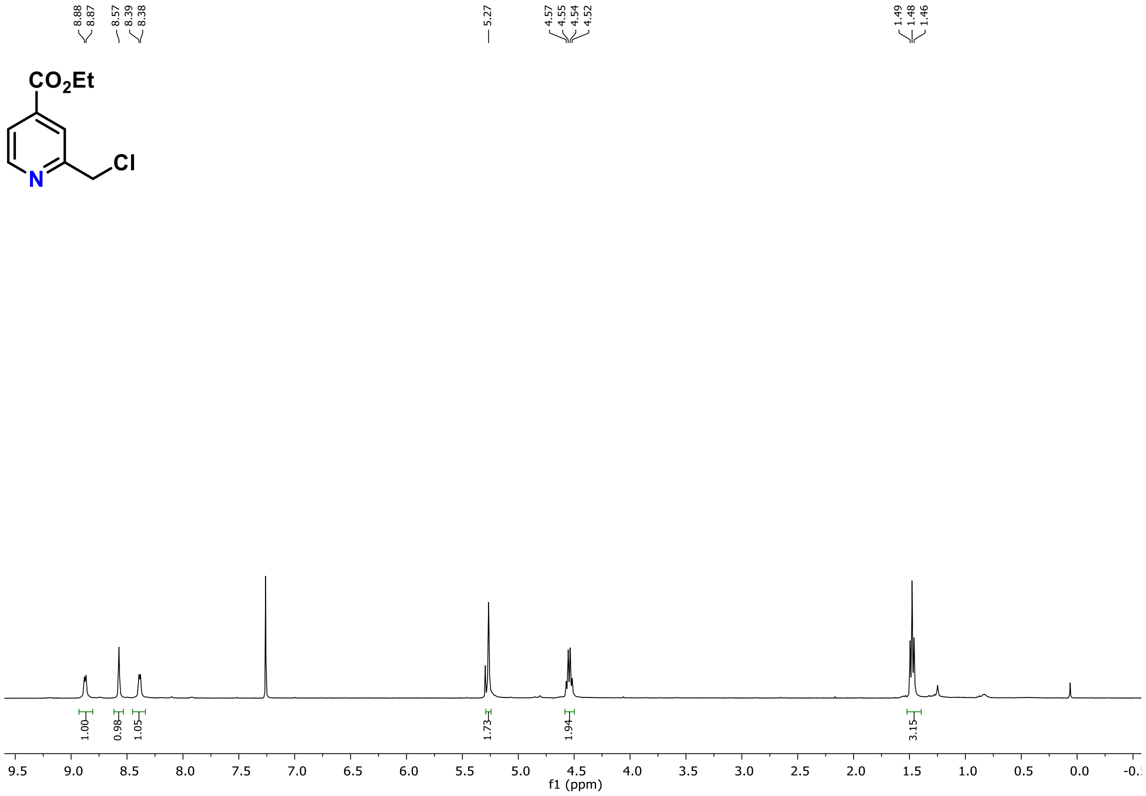
3.28
f1 (ppm)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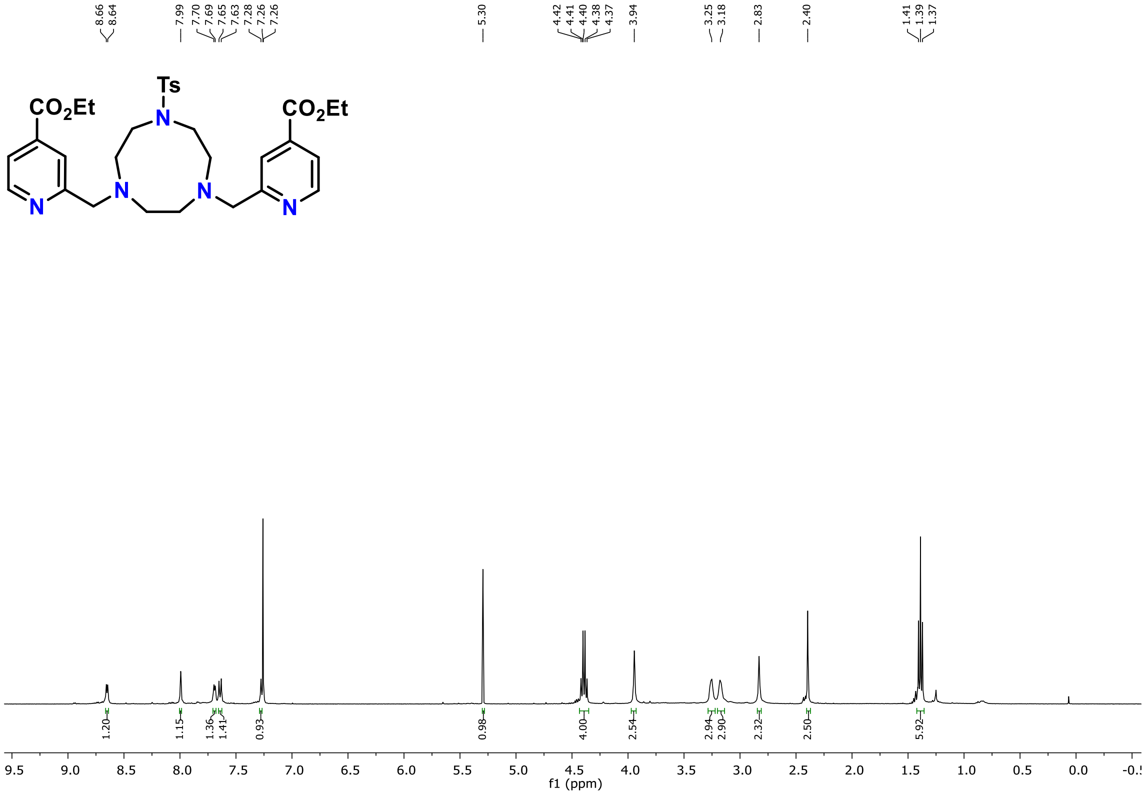
CO2Et
N
Cl
1.00
0.98
1.05
1.73
1.94
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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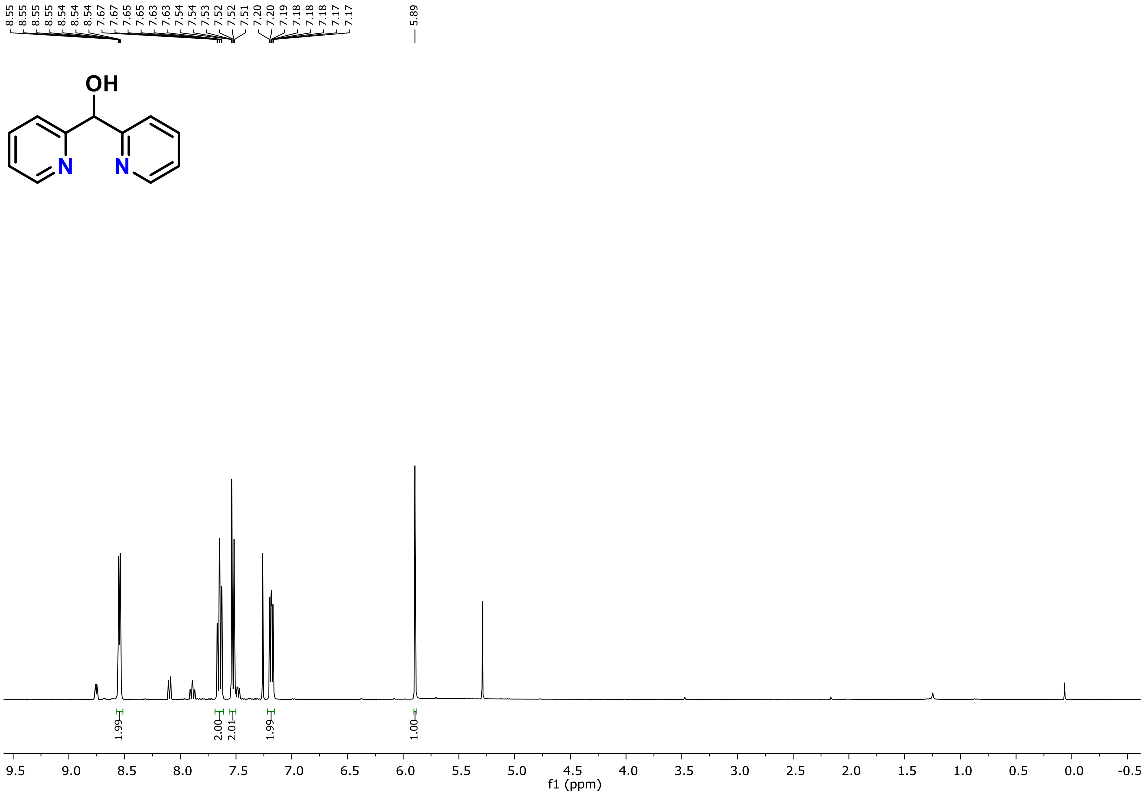
4.40
4.38
4.37
3.94
3.25
3.18
2.83
2.40
1.41
1.39
1.37
Ts
N
CO2Et
CO2Et
N
N
N
N
1.20
1.15
1.36
1.41
0.93
0.98
4.00
2.54
2.94
2.90
2.32
2.50
5.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.54
7.53
7.52
7.52
7.51
7.20
7.20
7.19
7.18
7.18
7.18
7.17
7.17
5.89
OH
N
N
1.99
2.00
2.01
1.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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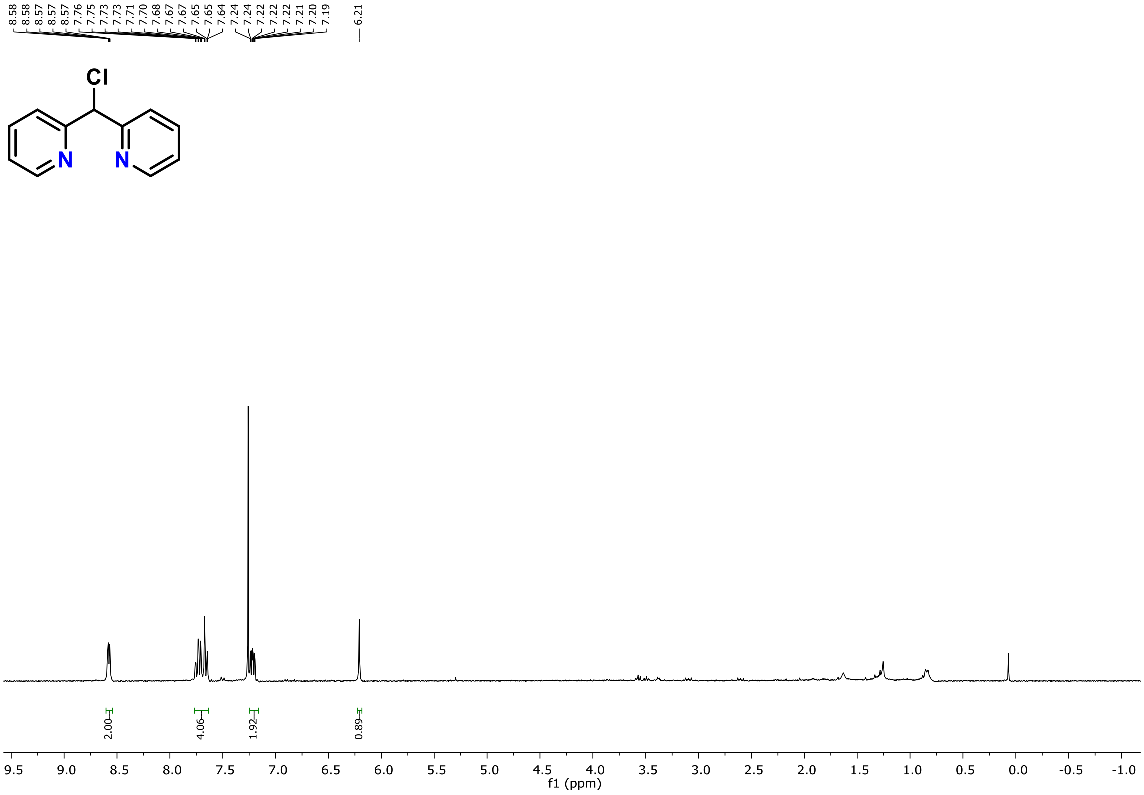
-0.5
f1 (ppm)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7.22
7.22
7.22
7.21
7.20
7.19
6.21
Cl
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N
2.00
4.06
1.92
0.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
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0.0
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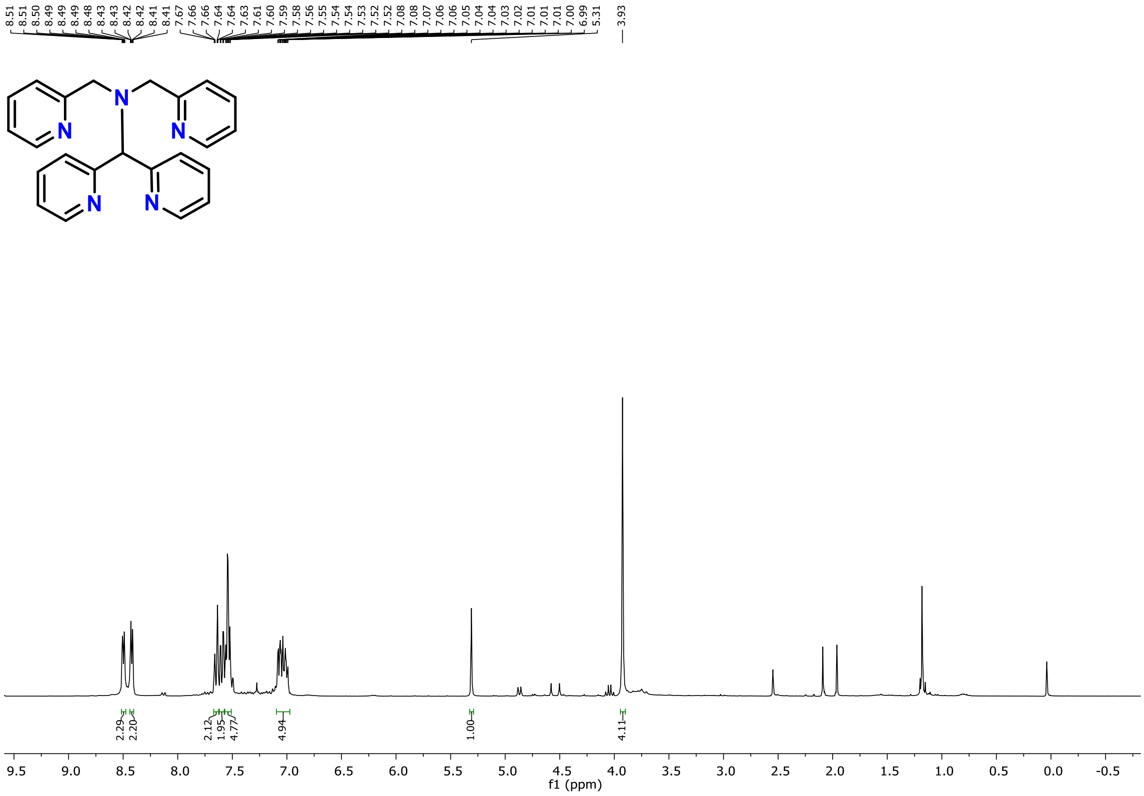
f1 (ppm)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7.66
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7.64
7.63
7.61
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7.54
7.54
7.53
7.52
7.52
7.08
7.08
7.07
7.06
7.06
7.05
7.04
7.04
7.03
7.02
7.01
7.01
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N
N
N
N
2.29
2.20
2.12
1.95
4.77
4.94
1.00
4.11
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
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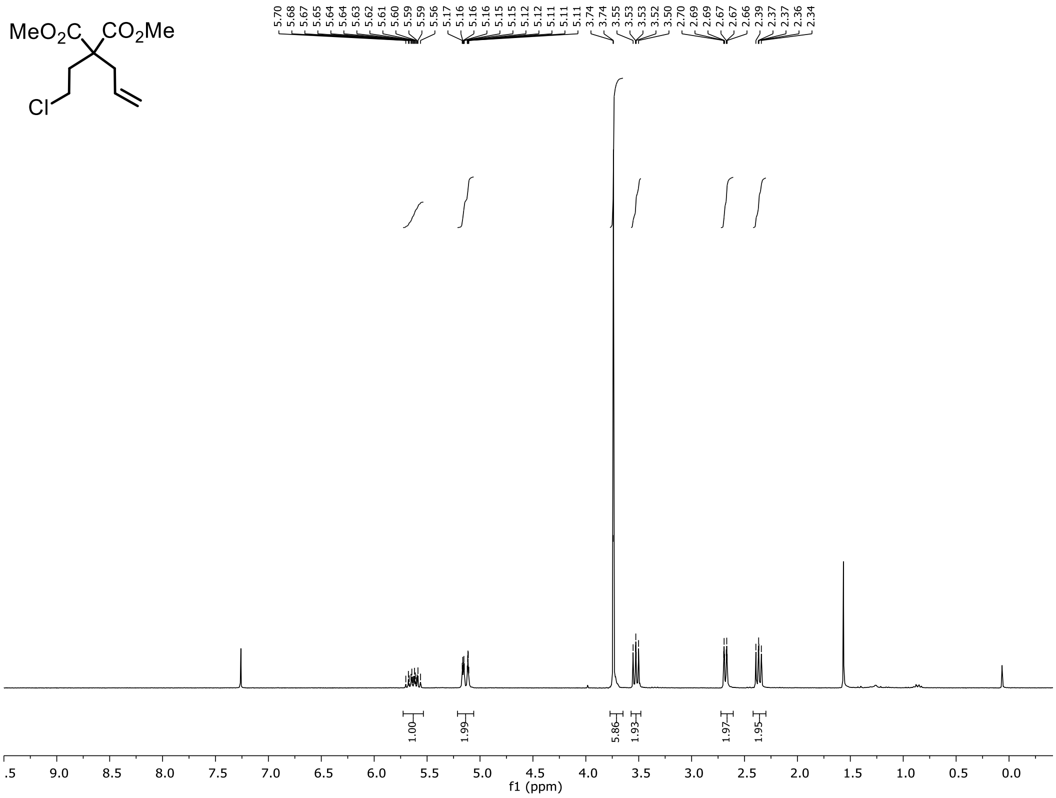
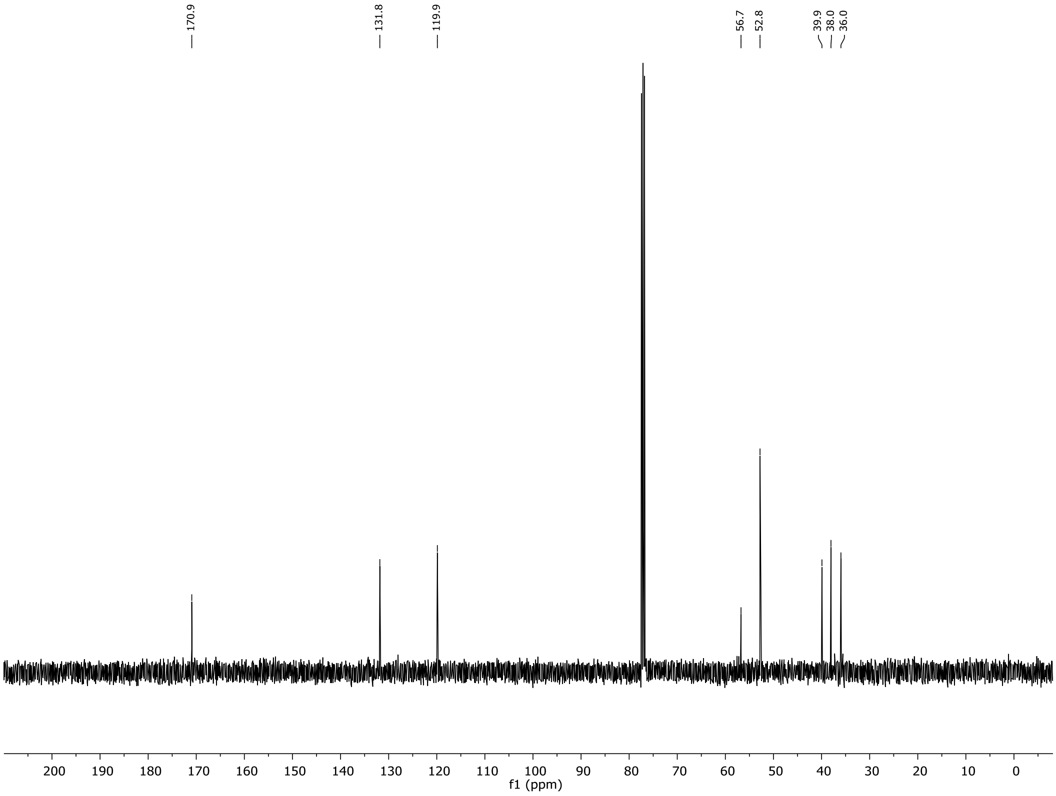
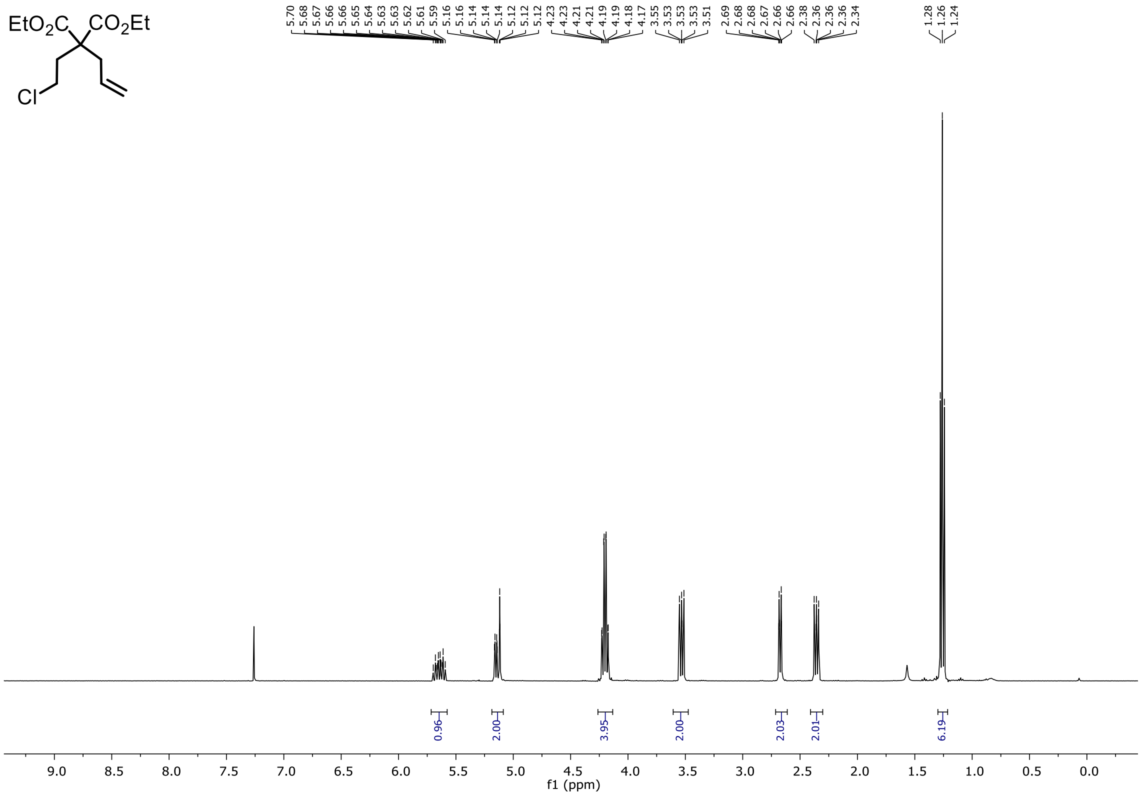
0.0
-0.5
f1 (ppm)

2. Spectra of substrates



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5.66
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5.64
5.63
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5.62
5.61
5.59
5.16
5.16
5.14
5.14
5.14
5.12
5.12
5.12
4.23
4.23
4.21
4.21
4.19
4.19
4.18
4.17
3.55
3.53
3.53
3.53
3.51
2.69
2.68
2.68
2.67
2.66
2.66
2.38
2.36
2.36
2.36
2.34
1.28
1.26
1.24
0.96
2.00
3.95
2.00
2.03
2.01
6.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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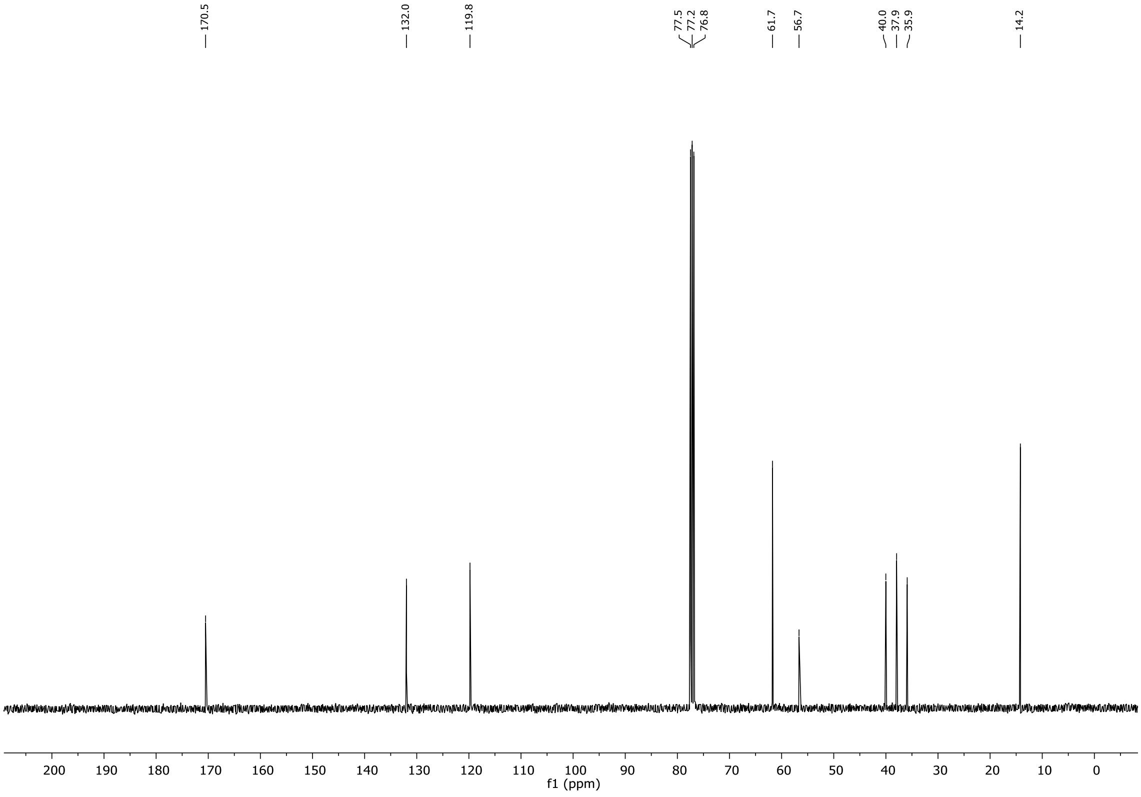
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.5
77.2
76.8
61.7
56.7
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37.9
35.9
14.2
200
190
180
170
160
150
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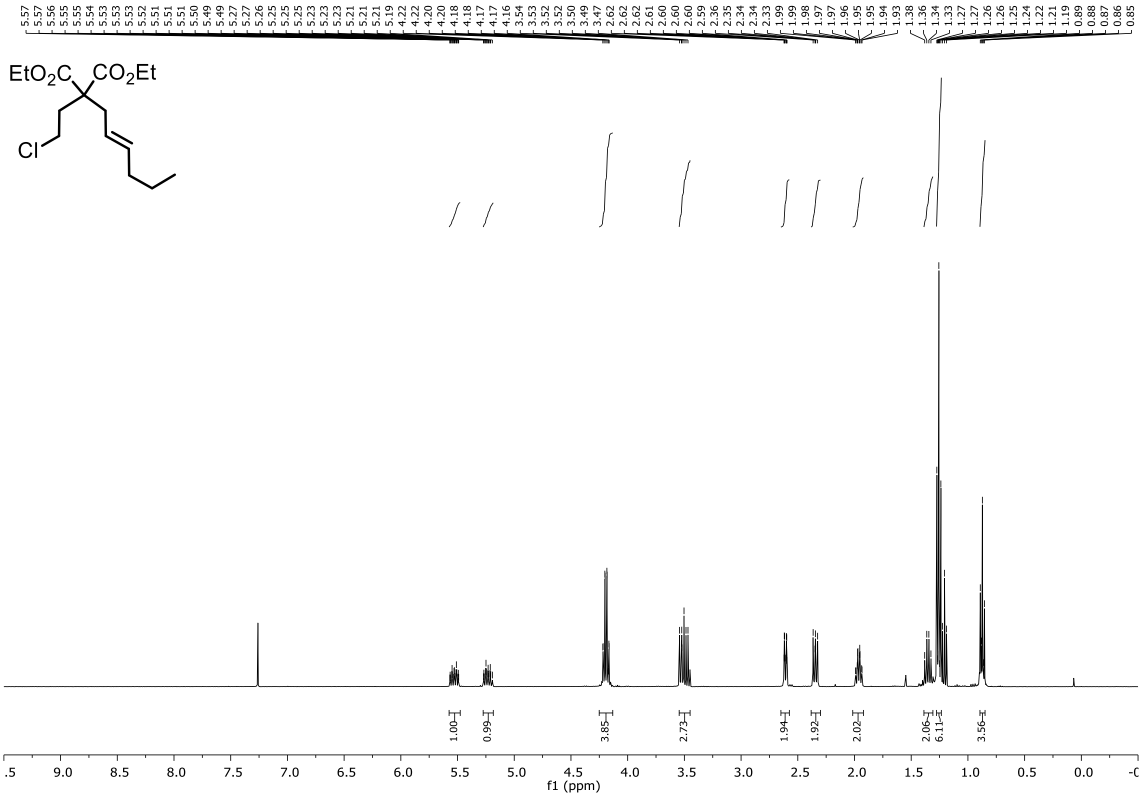
0
f1 (ppm)


EtO2C
CO2Et
Cl
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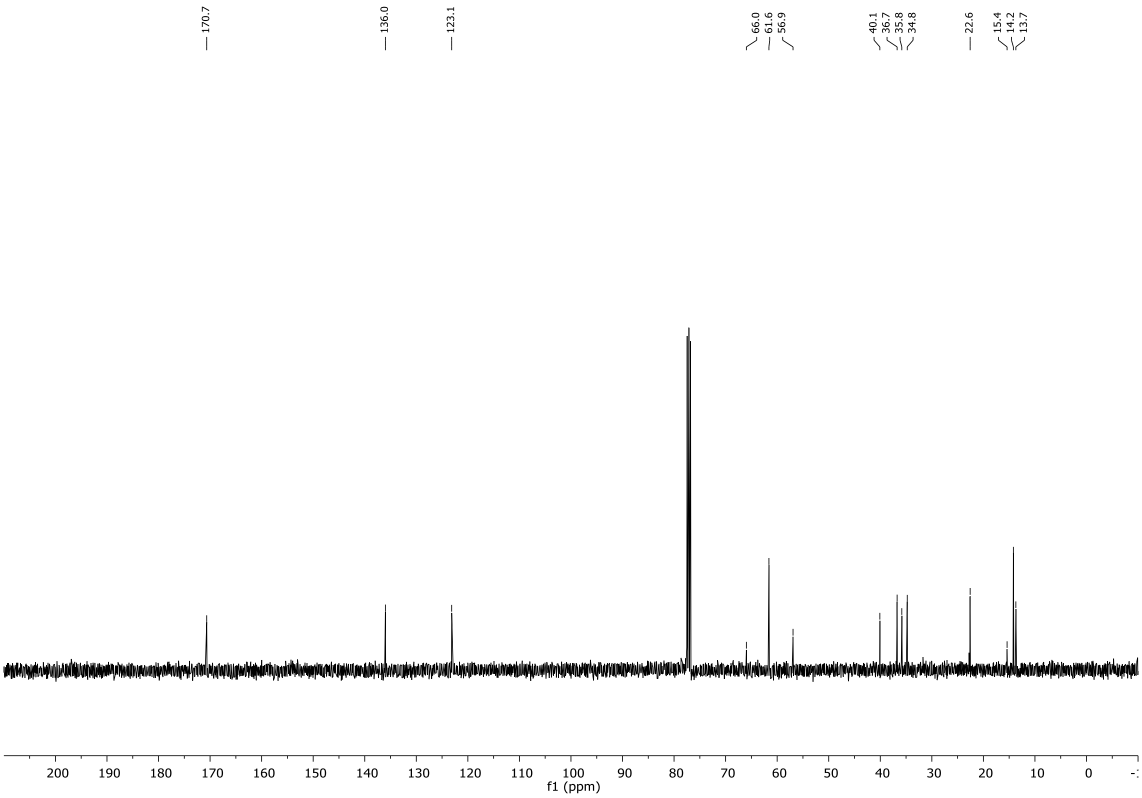
1.00
0.99
3.85
2.73
1.94
1.92
2.02
2.06
6.11
3.56
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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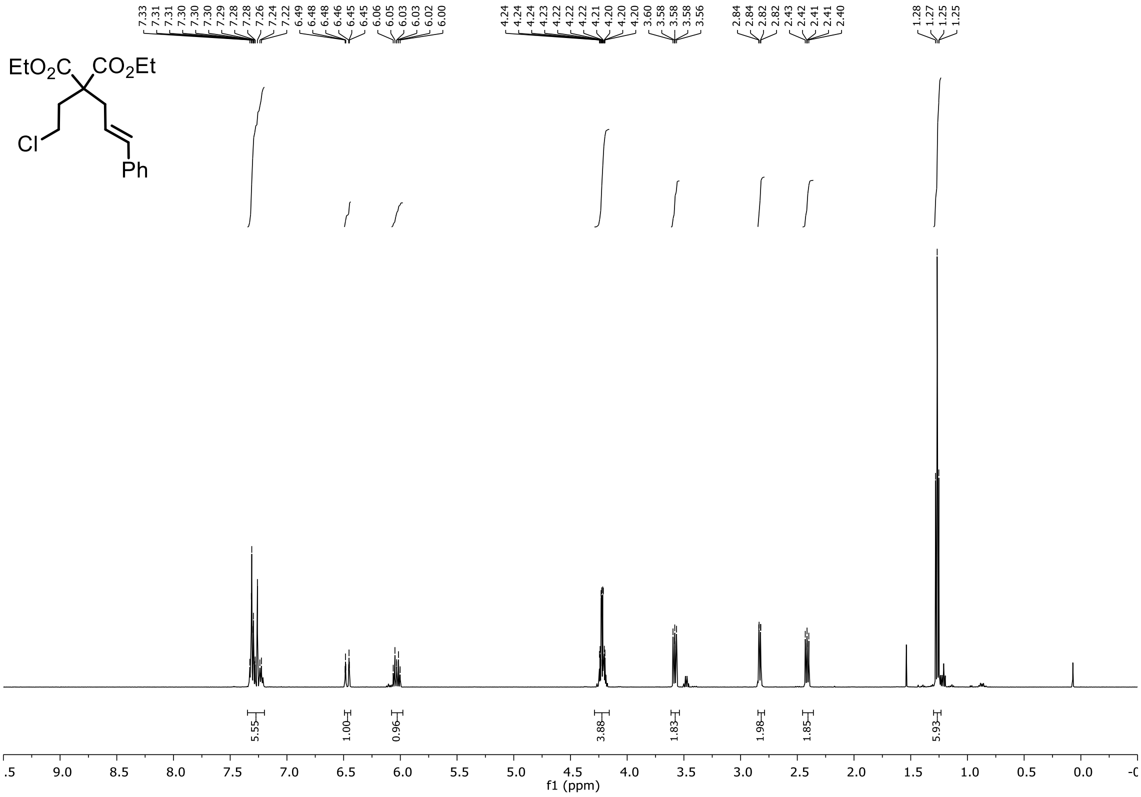
123.1
66.0
61.6
56.9
40.1
36.7
35.8
34.8
22.6
15.4
14.2
13.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.26
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7.22
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6.46
6.45
6.45
6.06
6.05
6.03
6.03
6.02
6.00
4.24
4.24
4.24
4.23
4.22
4.22
4.22
4.21
4.20
4.20
4.20
3.60
3.58
3.58
3.58
3.56
2.84
2.84
2.82
2.82
2.43
2.42
2.42
2.41
2.40
1.28
1.27
1.25
1.25
EtO2C
CO2Et
Cl
Ph
5.55
1.00
0.96
3.88
1.83
1.98
1.85
5.93
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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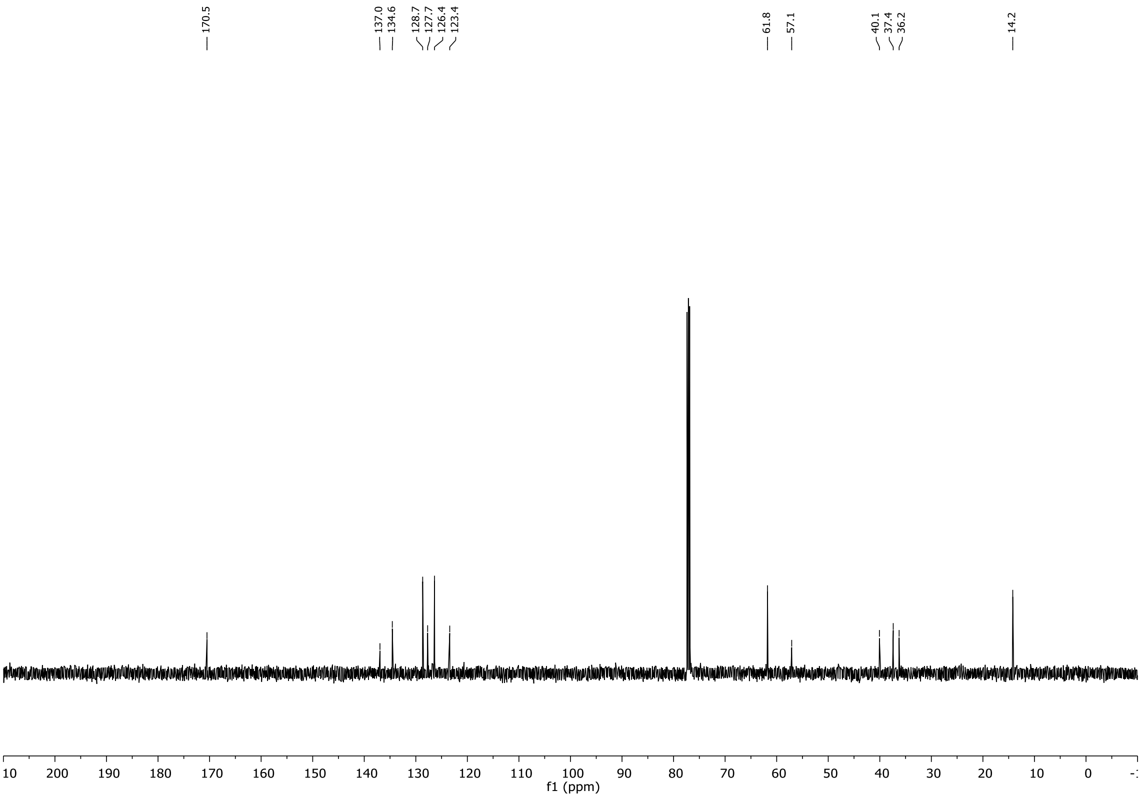
1.5
1.0
0.5
0.0
-0
f1 (ppm)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127.7
126.4
123.4
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40.1
37.4
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10
200
190
180
170
160
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120
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30
20
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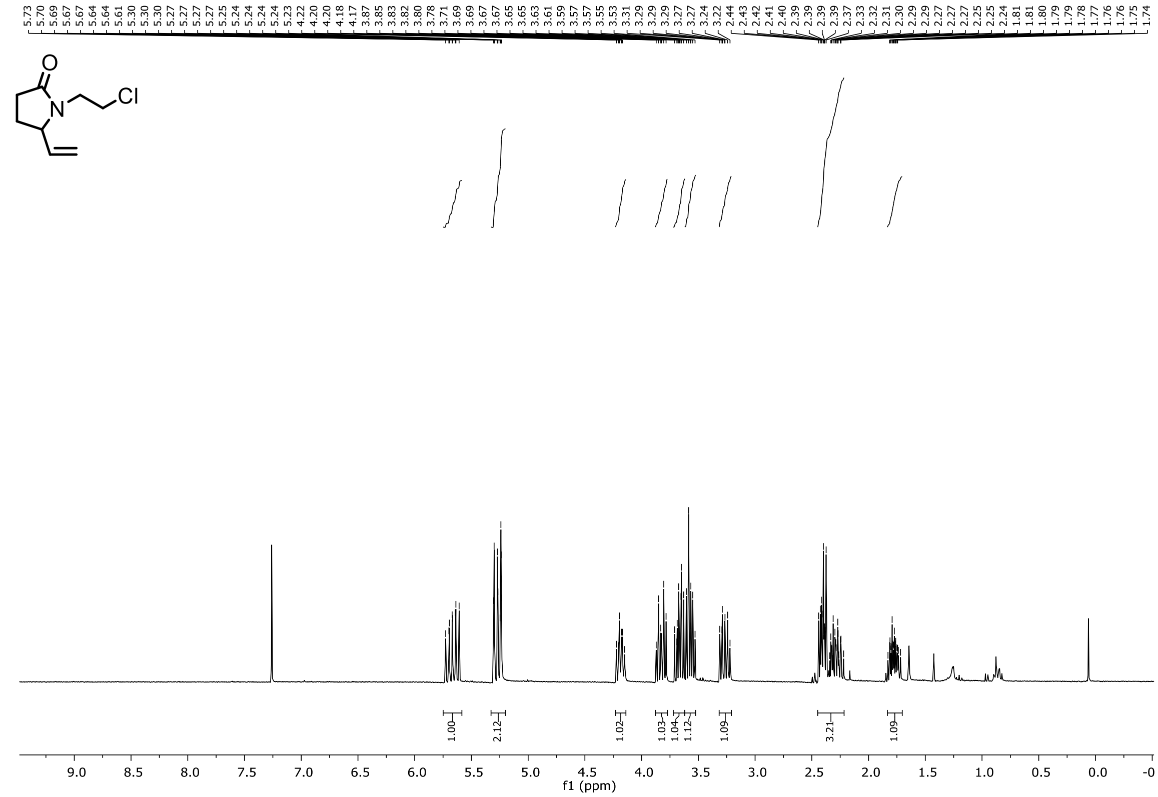
0
-:
f1 (ppm)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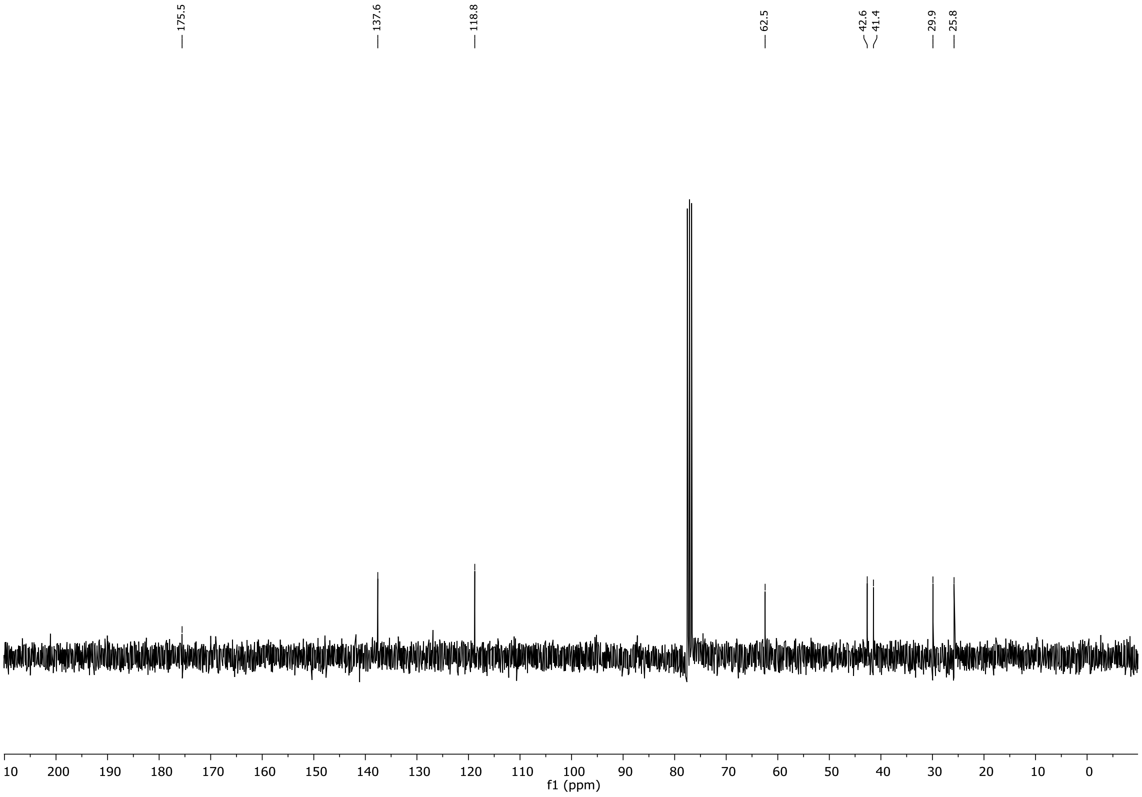
O
N
Cl
1.00
2.12
1.02
1.03
1.04
1.12
1.09
3.21
1.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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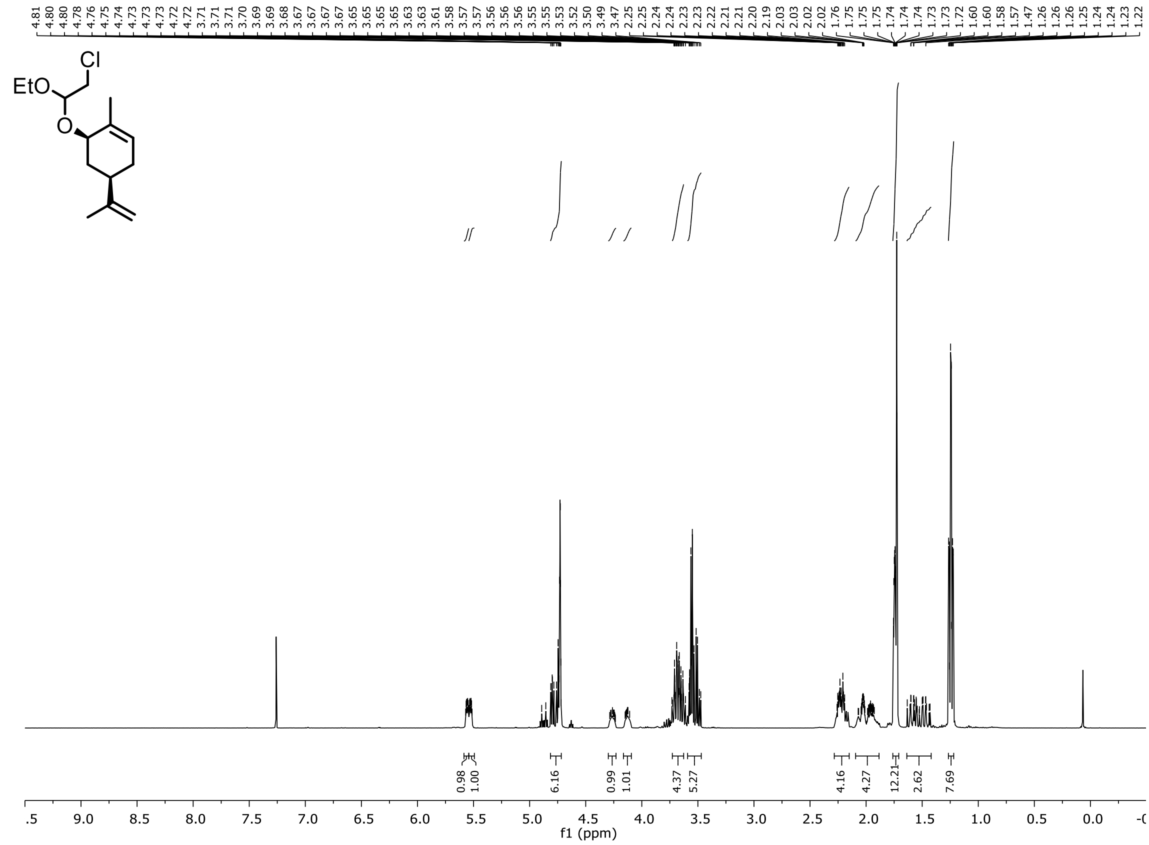
f1 (ppm)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EtO
O
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0.98
1.00
6.16
0.99
1.01
4.37
5.27
4.16
4.27
12.21
2.62
7.69
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
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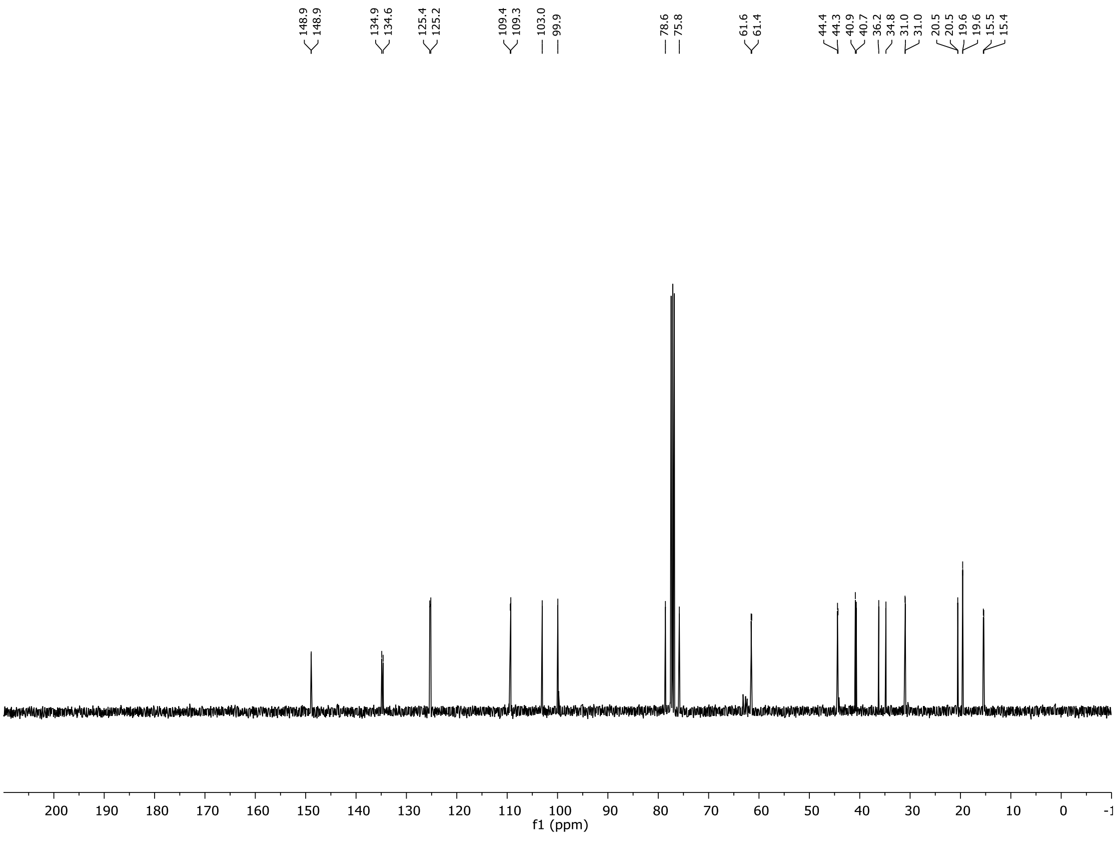
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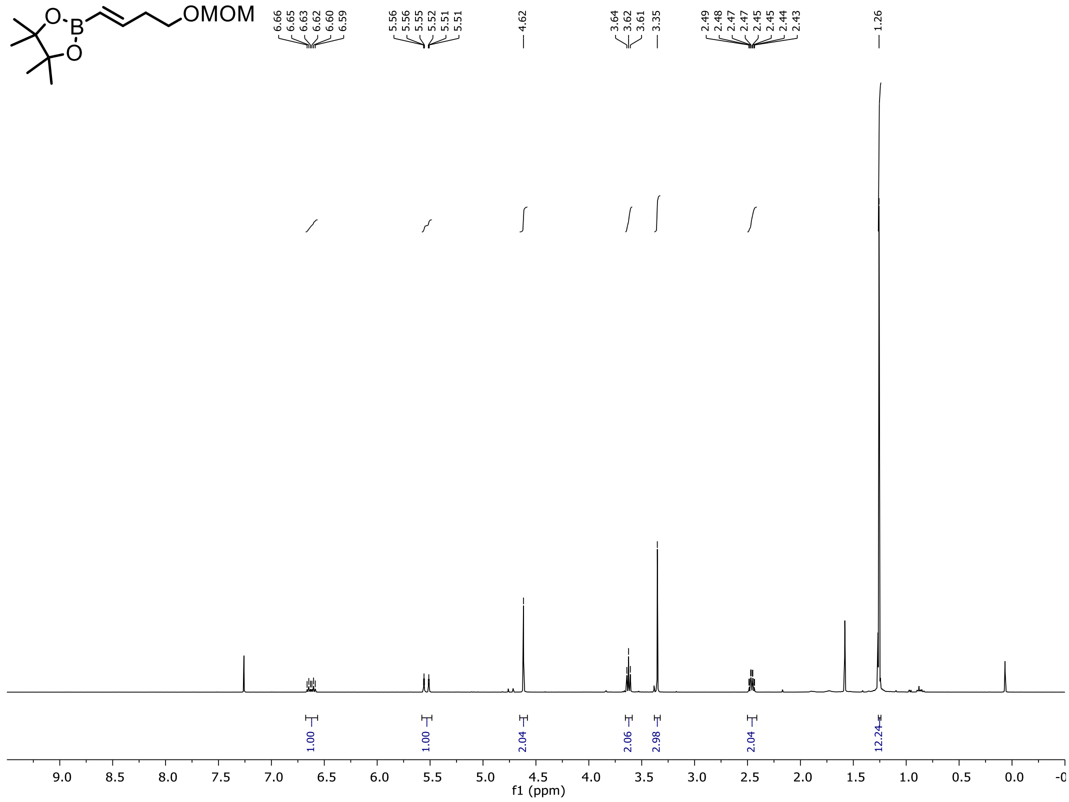
f1 (ppm)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B
O
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5.56
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5.51
5.51
4.62
3.64
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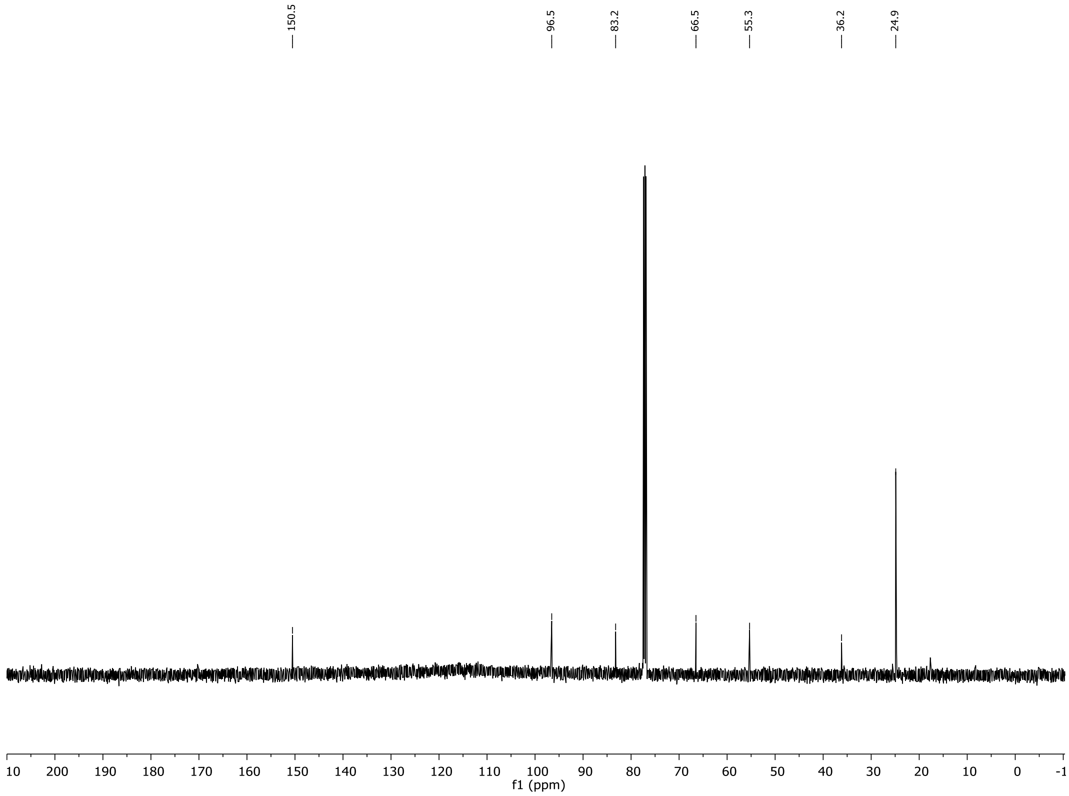
2.45
2.45
2.44
2.43
1.26
1.00
1.00
2.04
2.06
2.98
2.04
12.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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83.2
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55.3
36.2
24.9
10
200
190
180
170
160
150
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120
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100
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80
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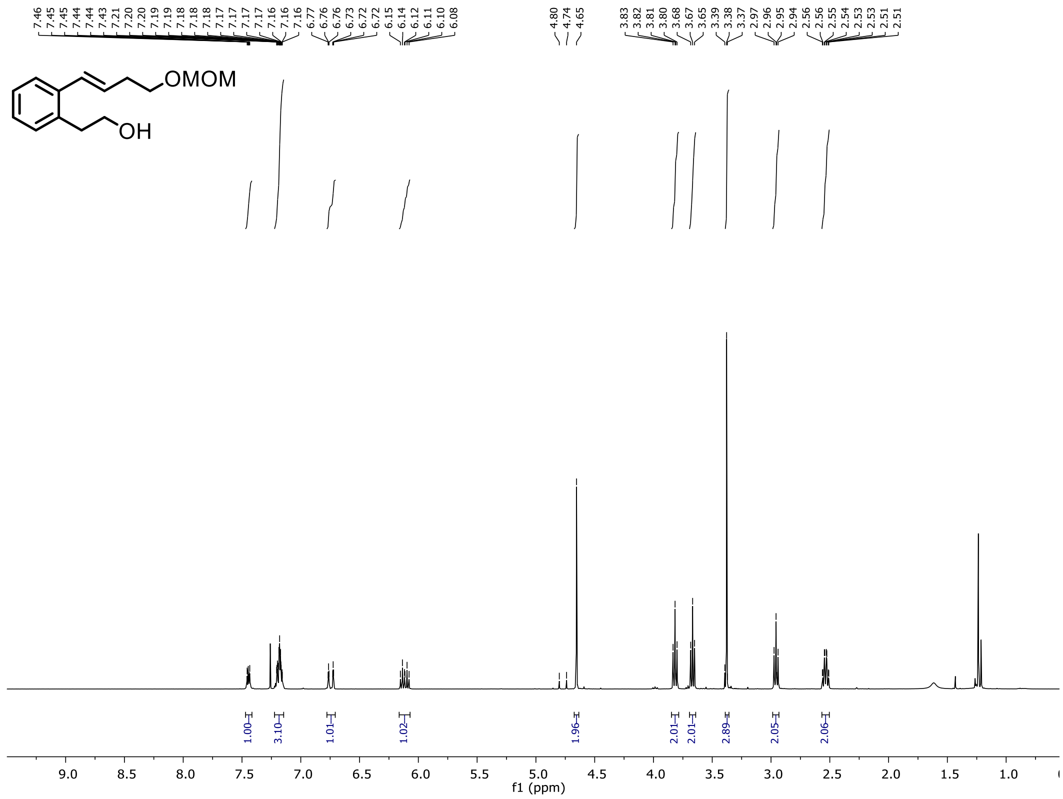
60
50
40
30
20
10
0
-1
f1 (ppm)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7.19
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6.11
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3.37
2.97
2.96
2.95
2.94
2.56
2.56
2.55
2.54
2.53
2.53
2.51
2.51
OMOM
OH
1.00
3.10
1.01
1.02
1.96
2.01
2.01
2.89
2.05
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
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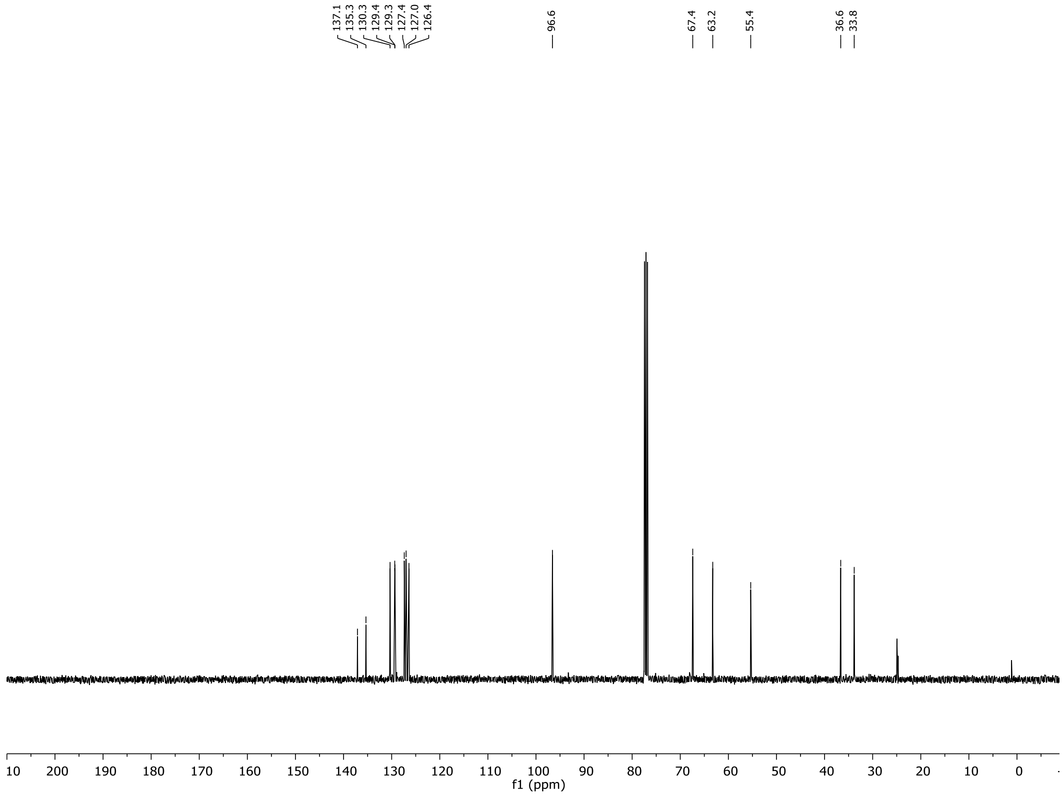
2.5
2.0
1.5
1.0
f1 (ppm)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129.4
129.3
127.4
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126.4
96.6
67.4
63.2
55.4
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180
170
160
150
140
130
120
110
100
90
80
70
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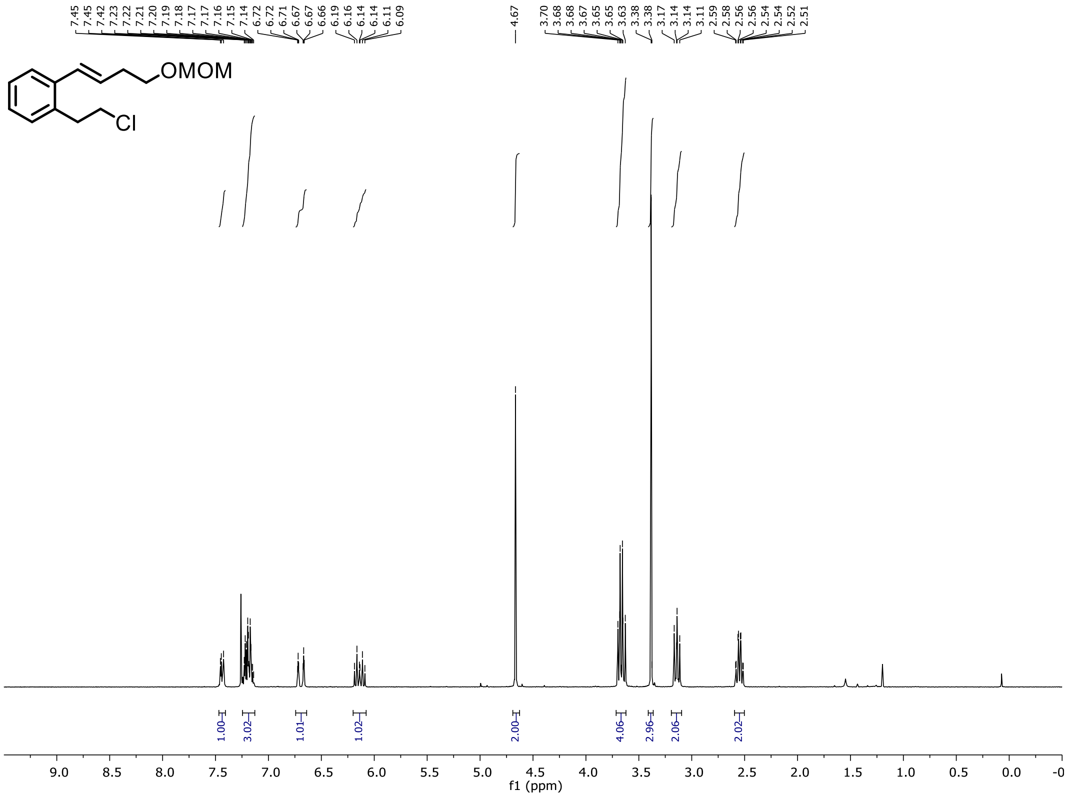
50
40
30
20
10
0
f1 (ppm)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7.19
7.18
7.17
7.17
7.16
7.15
7.14
6.72
6.72
6.71
6.67
6.67
6.66
6.19
6.16
6.14
6.14
6.11
6.09
4.67
3.70
3.68
3.68
3.67
3.65
3.65
3.63
3.38
3.38
3.17
3.14
3.14
3.11
2.59
2.58
2.56
2.56
2.54
2.54
2.52
2.51
OMOM
Cl
1.00
3.02
1.01
1.02
2.00
4.06
2.96
2.06
2.02
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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1.0
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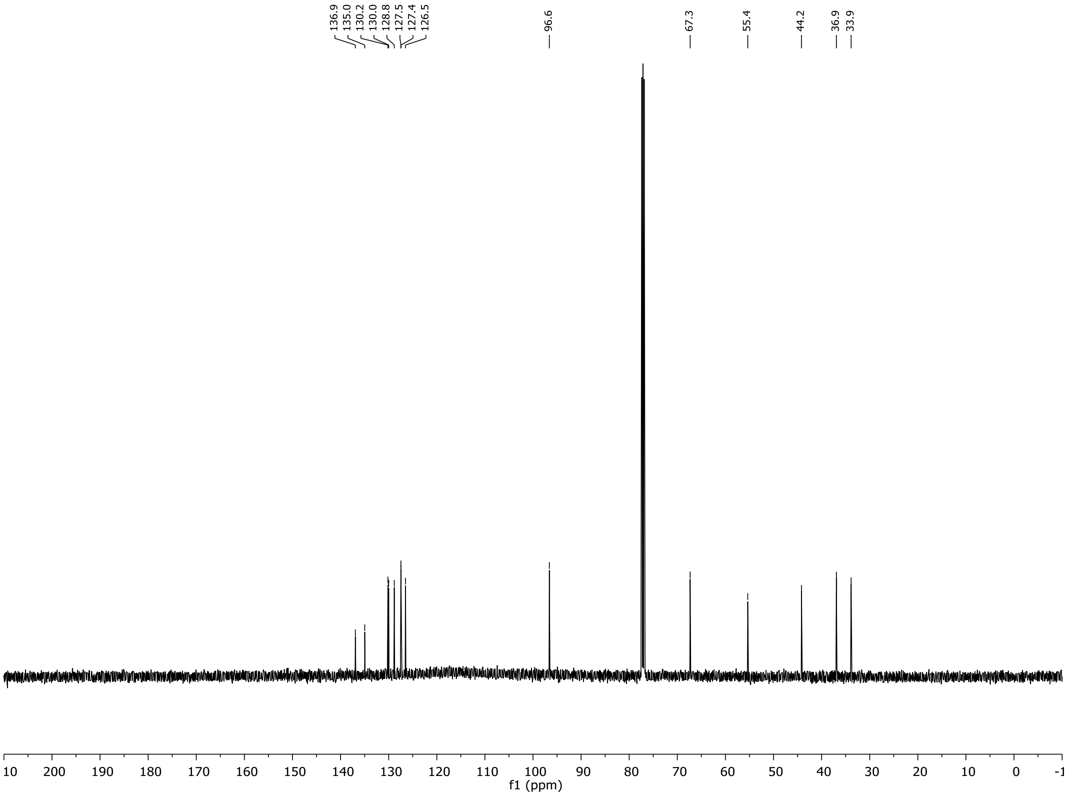
f1 (ppm)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127.4
126.5
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67.3
55.4
44.2
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33.9
10
200
190
180
170
160
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120
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100
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80
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30
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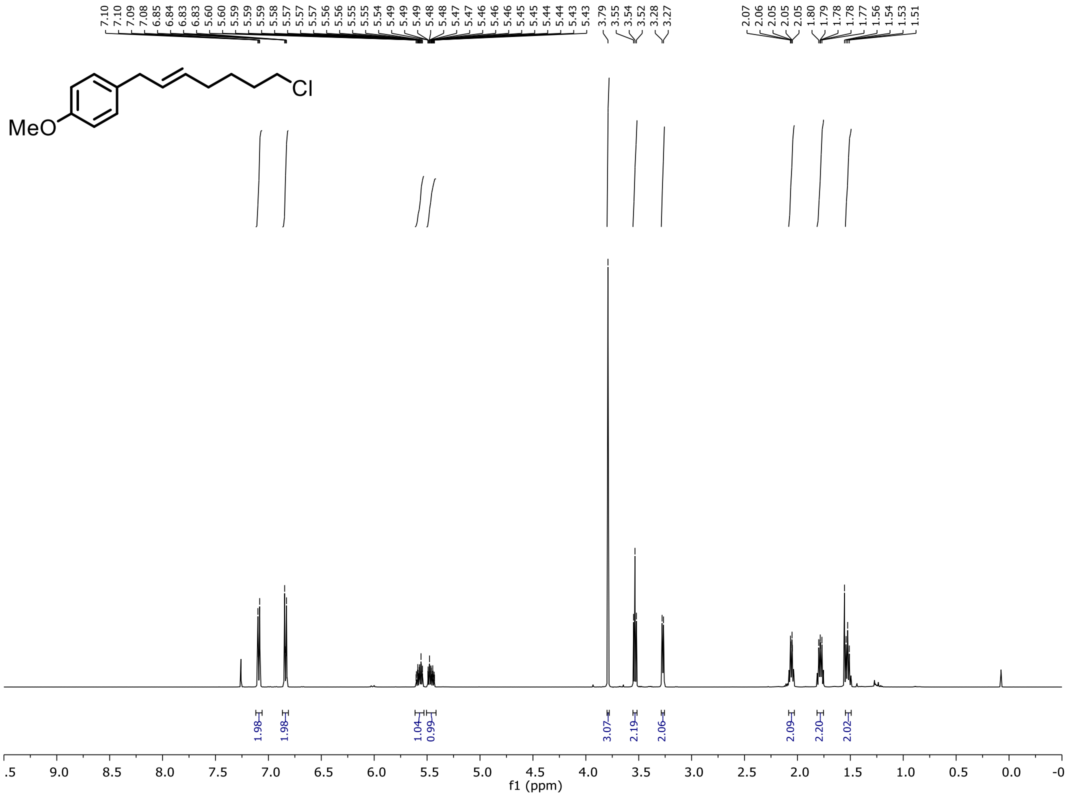
-1
f1 (ppm)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5.55
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5.49
5.48
5.48
5.47
5.46
5.46
5.46
5.45
5.45
5.45
5.44
5.44
5.43
5.43
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3.55
3.54
3.52
3.28
3.27
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2.06
2.05
2.05
2.05
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1.79
1.78
1.78
1.77
1.56
1.54
1.53
1.51
MeO
Cl
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1.98
1.04
0.99
3.07
2.19
2.06
2.09
2.20
2.02
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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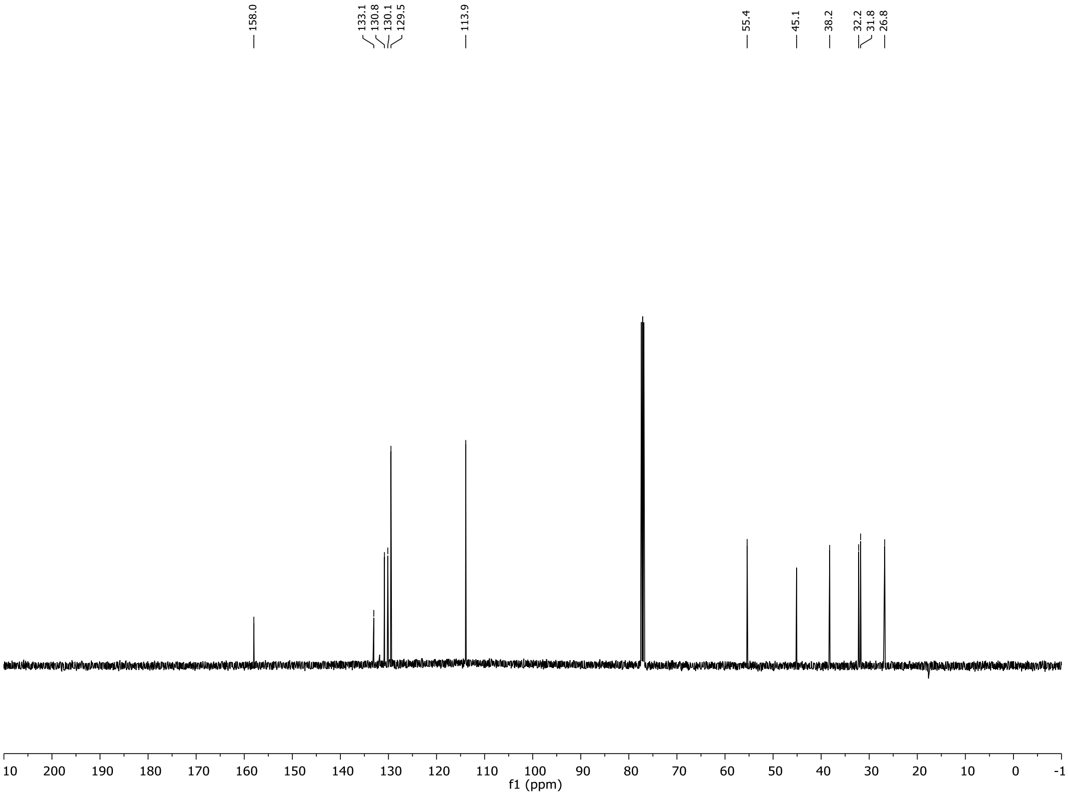
f1 (ppm)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32.2
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26.8
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200
190
180
170
160
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140
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120
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100
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80
70
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30
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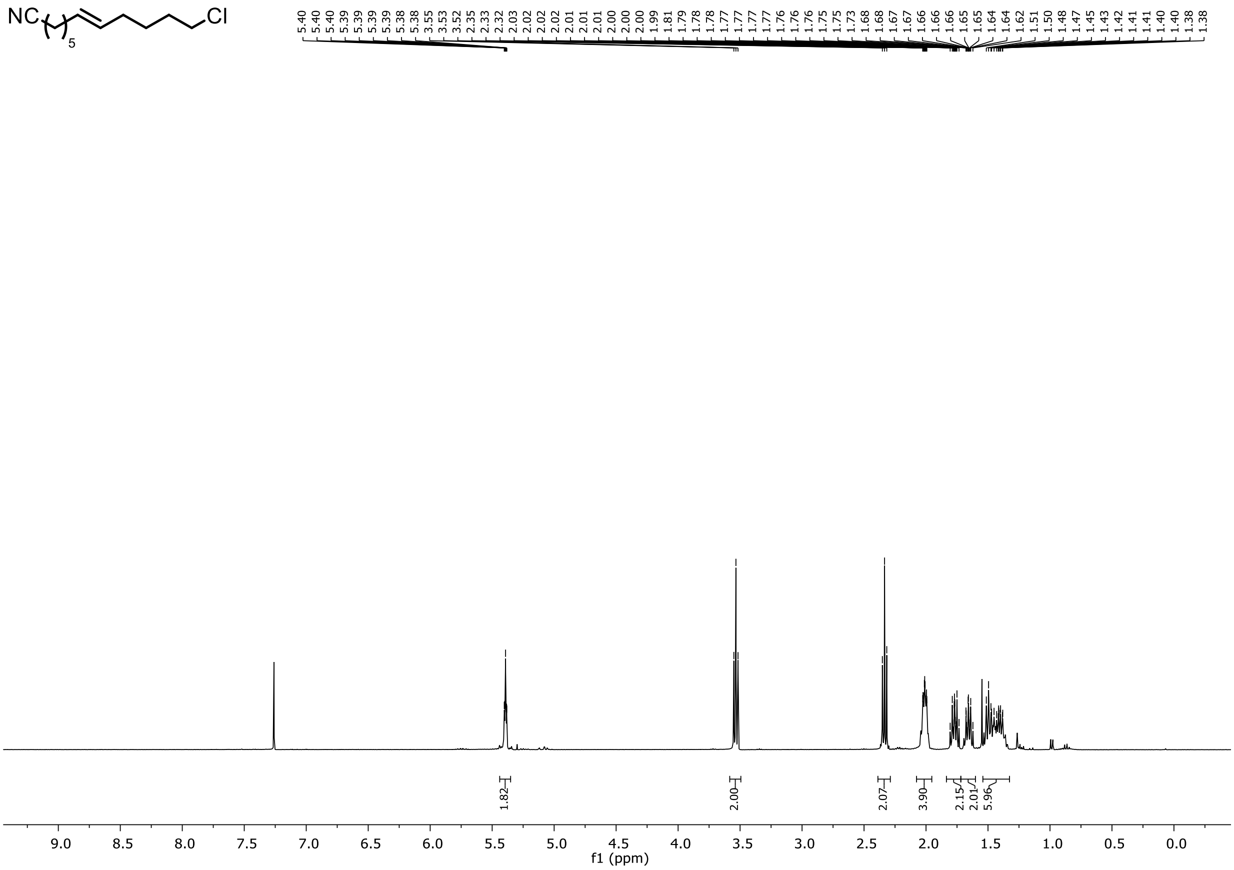
f1 (ppm)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3.52
2.35
2.33
2.32
2.03
2.02
2.02
2.02
2.01
2.01
2.01
2.00
2.00
2.00
1.99
1.81
1.79
1.78
1.78
1.77
1.77
1.77
1.77
1.76
1.76
1.76
1.75
1.75
1.73
1.68
1.68
1.67
1.67
1.66
1.66
1.66
1.65
1.65
1.64
1.64
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1.47
1.45
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1.41
1.40
1.40
1.38
1.38
1.82
2.00
2.07
3.90
2.15
2.01
5.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
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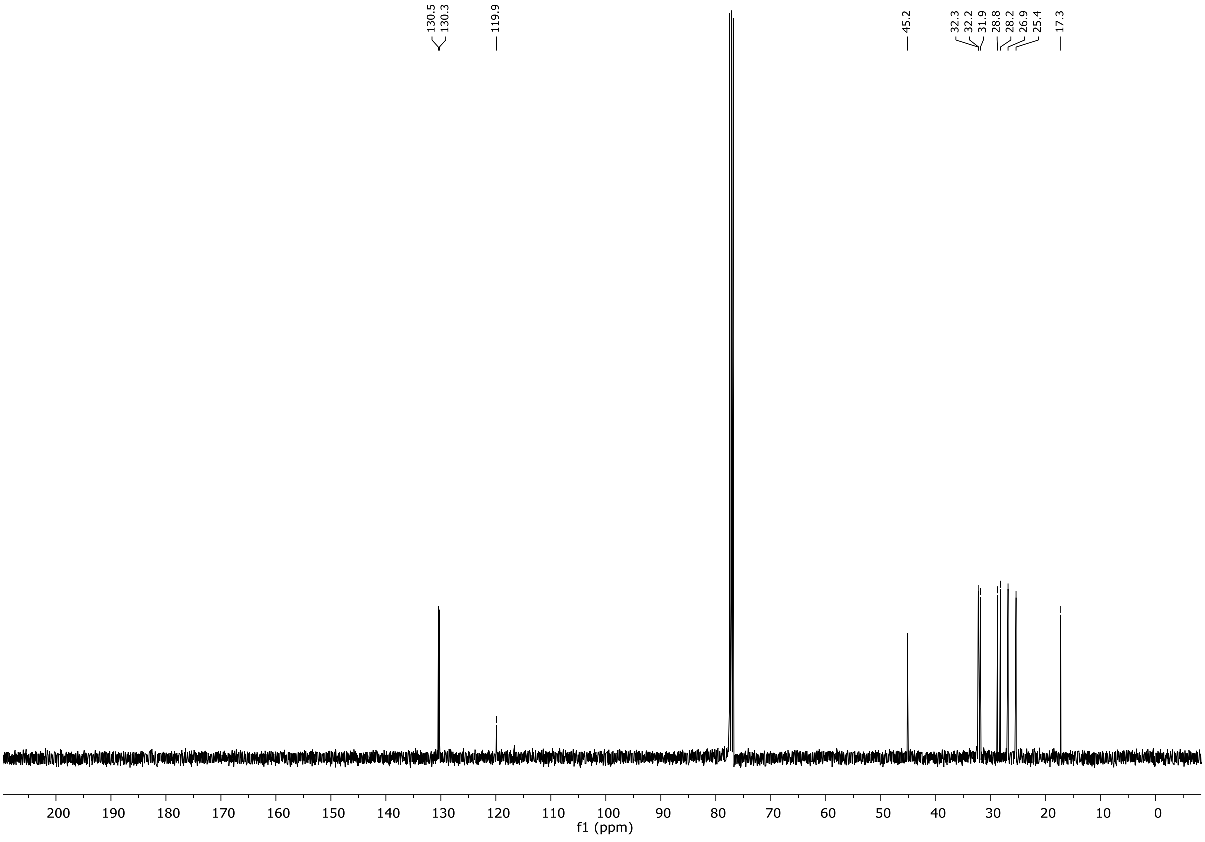
0.0
f1 (ppm)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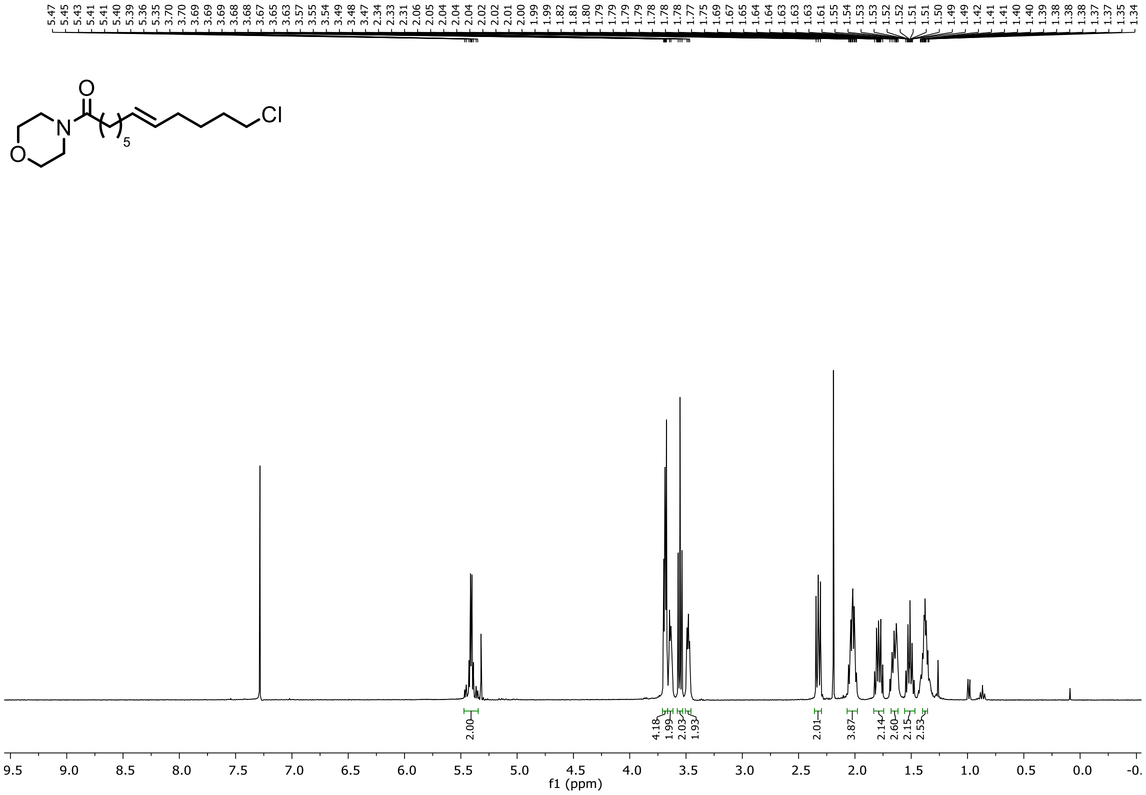
32.2
31.9
28.8
28.2
26.9
25.4
17.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.69
3.69
3.69
3.68
3.67
3.65
3.63
3.57
3.55
3.54
3.49
3.48
3.47
2.34
2.33
2.31
2.06
2.05
2.04
2.04
2.04
2.02
2.02
2.01
2.00
1.99
1.99
1.82
1.81
1.80
1.79
1.79
1.79
1.79
1.78
1.78
1.77
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1.64
1.64
1.63
1.63
1.63
1.61
1.55
1.54
1.53
1.53
1.53
1.52
1.52
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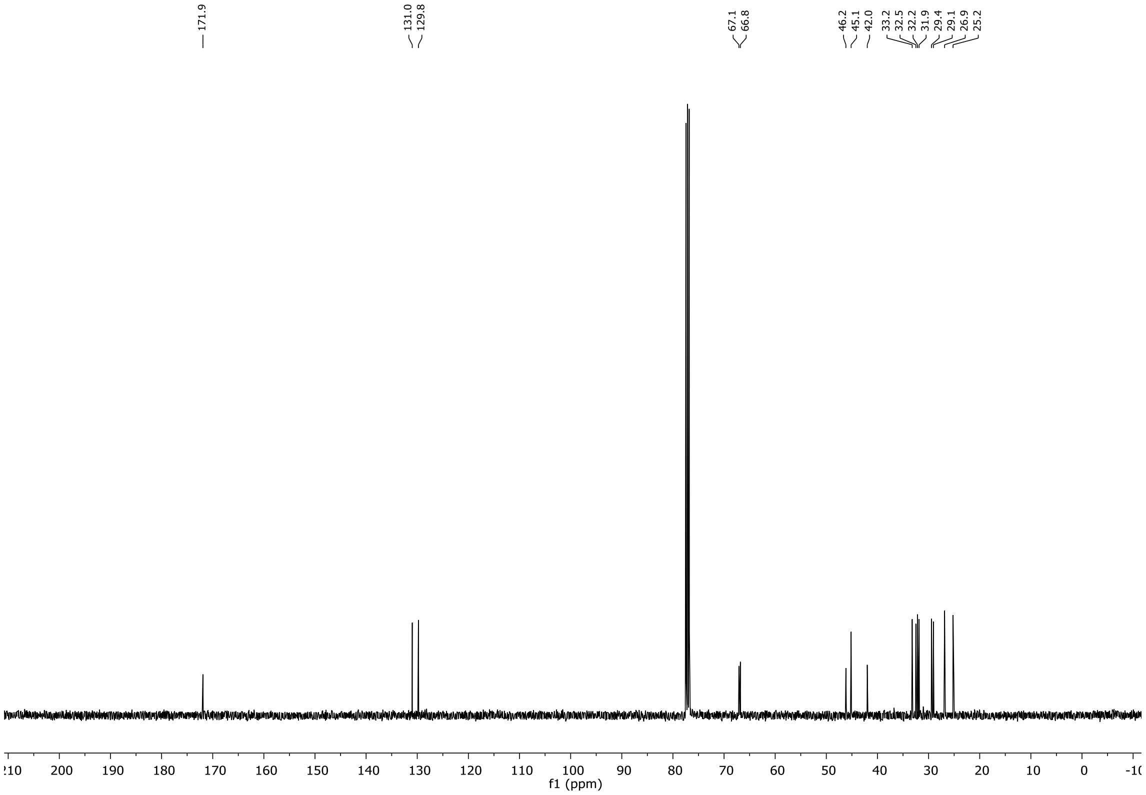
1.41
1.41
1.40
1.40
1.39
1.38
1.38
1.38
1.37
1.37
1.35
1.34
O
N
O
5
Cl
2.00
4.18
1.99
2.03
1.93
2.01
3.87
2.14
2.60
2.15
2.53
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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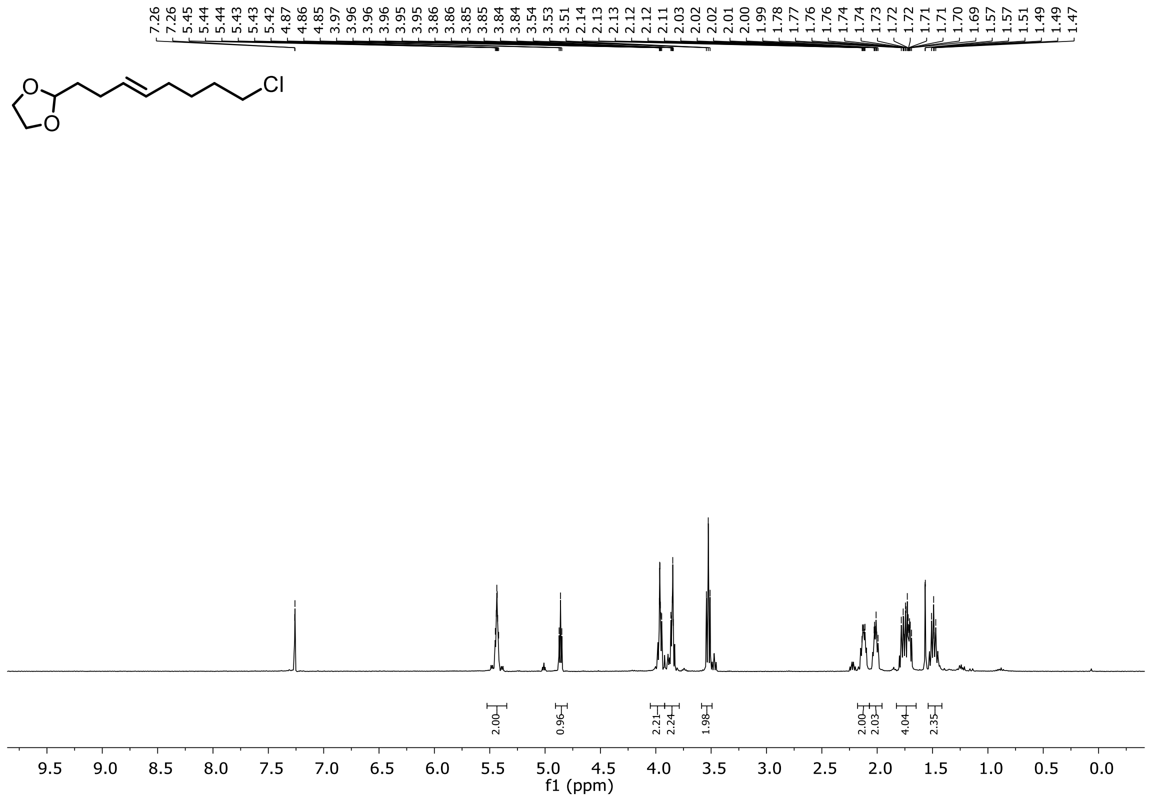
67.1
66.8
46.2
45.1
42.0
33.2
32.5
32.2
31.9
29.4
29.1
26.9
25.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
O
O
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5.44
5.44
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5.42
4.87
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4.85
3.97
3.96
3.96
3.95
3.95
3.86
3.86
3.85
3.85
3.84
3.84
3.54
3.53
3.51
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2.13
2.13
2.12
2.12
2.11
2.03
2.02
2.02
2.01
2.00
1.99
1.78
1.77
1.76
1.76
1.74
1.74
1.73
1.72
1.72
1.71
1.71
1.70
1.69
1.57
1.57
1.51
1.49
1.49
1.47
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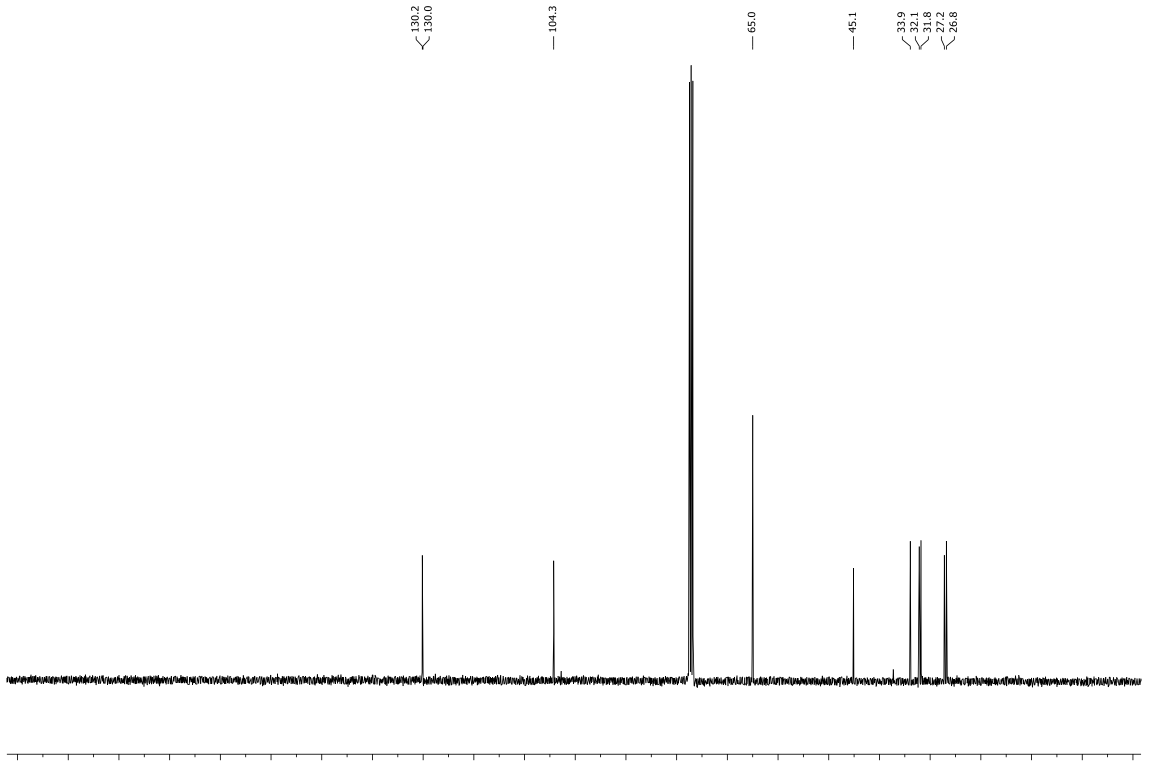
0.96
2.21
2.24
1.98
2.00
2.03
4.04
2.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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65.0
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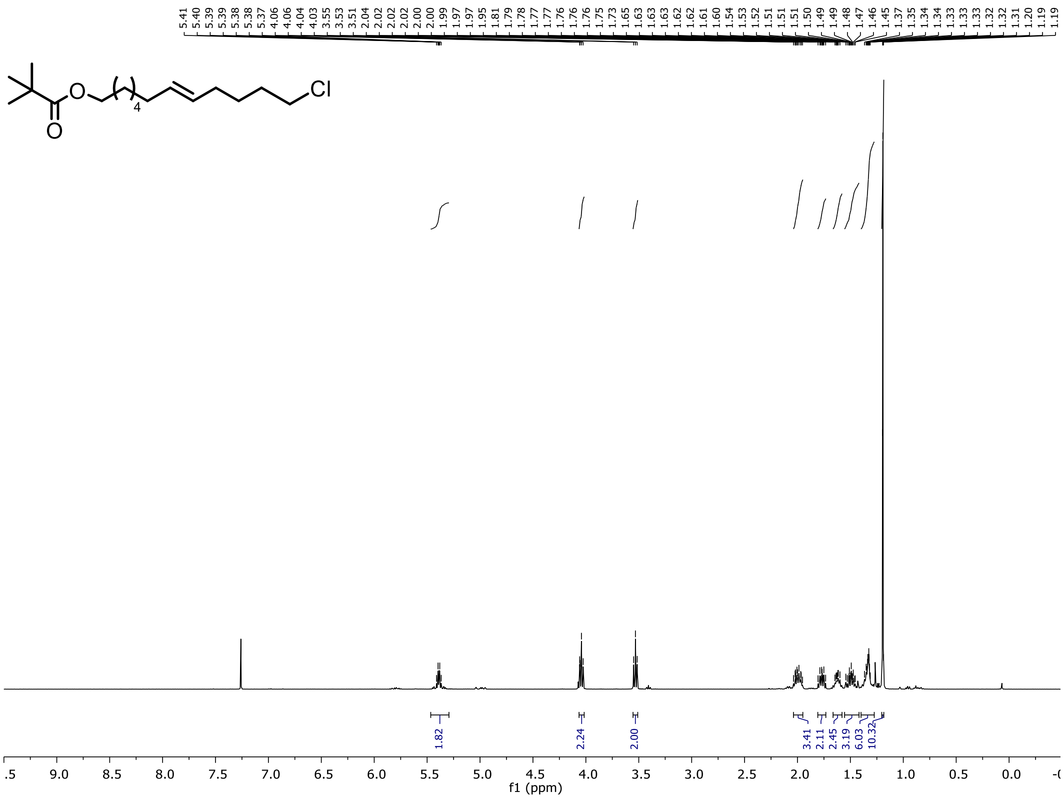
33.9
32.1
31.8
27.2
26.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
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O
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5.39
5.39
5.38
5.38
5.37
4.06
4.06
4.04
4.03
3.55
3.53
3.51
2.04
2.02
2.02
2.02
2.00
2.00
1.99
1.97
1.97
1.95
1.81
1.79
1.78
1.77
1.77
1.76
1.76
1.76
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1.63
1.63
1.62
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1.54
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1.52
1.51
1.51
1.51
1.50
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1.47
1.46
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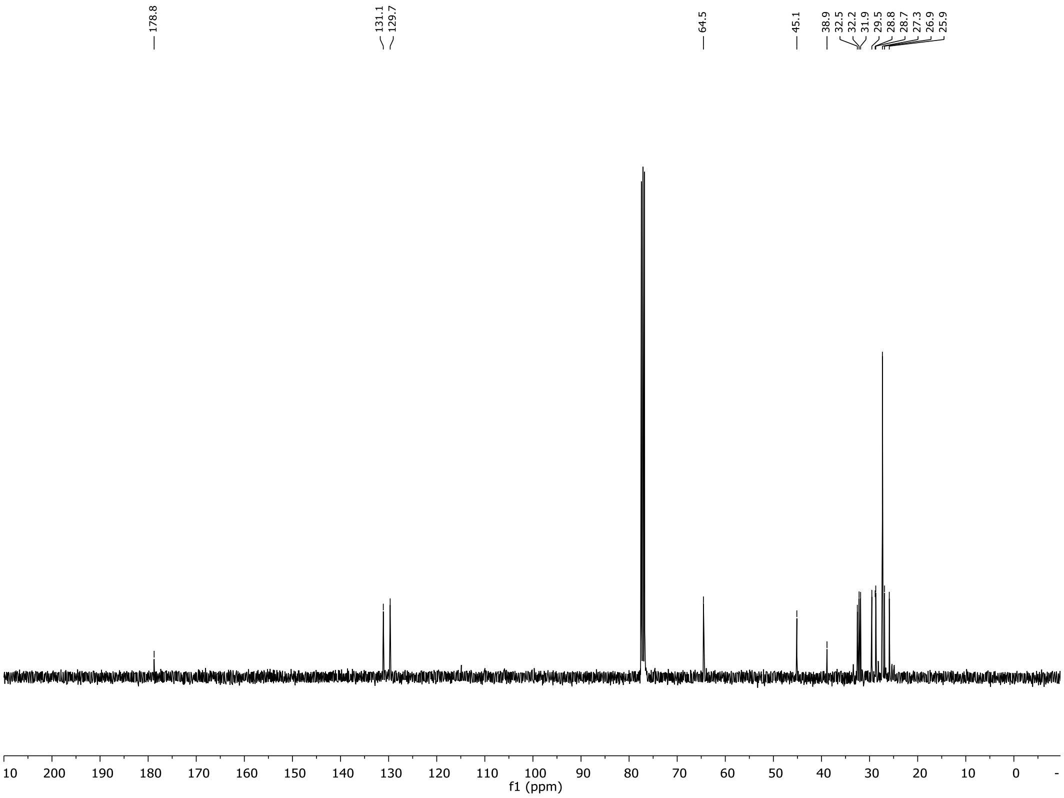
1.37
1.35
1.34
1.34
1.33
1.33
1.32
1.32
1.31
1.20
1.19
1.19
1.82
2.24
2.00
3.41
2.11
2.45
3.19
6.03
10.32
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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64.5
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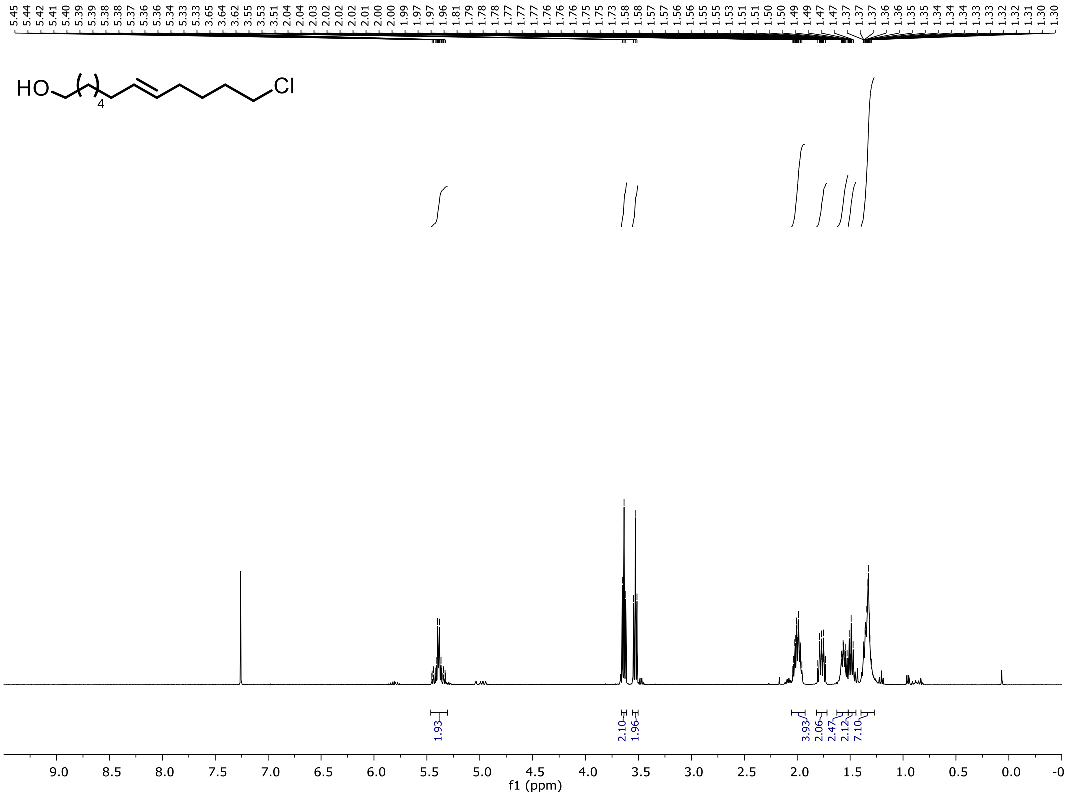
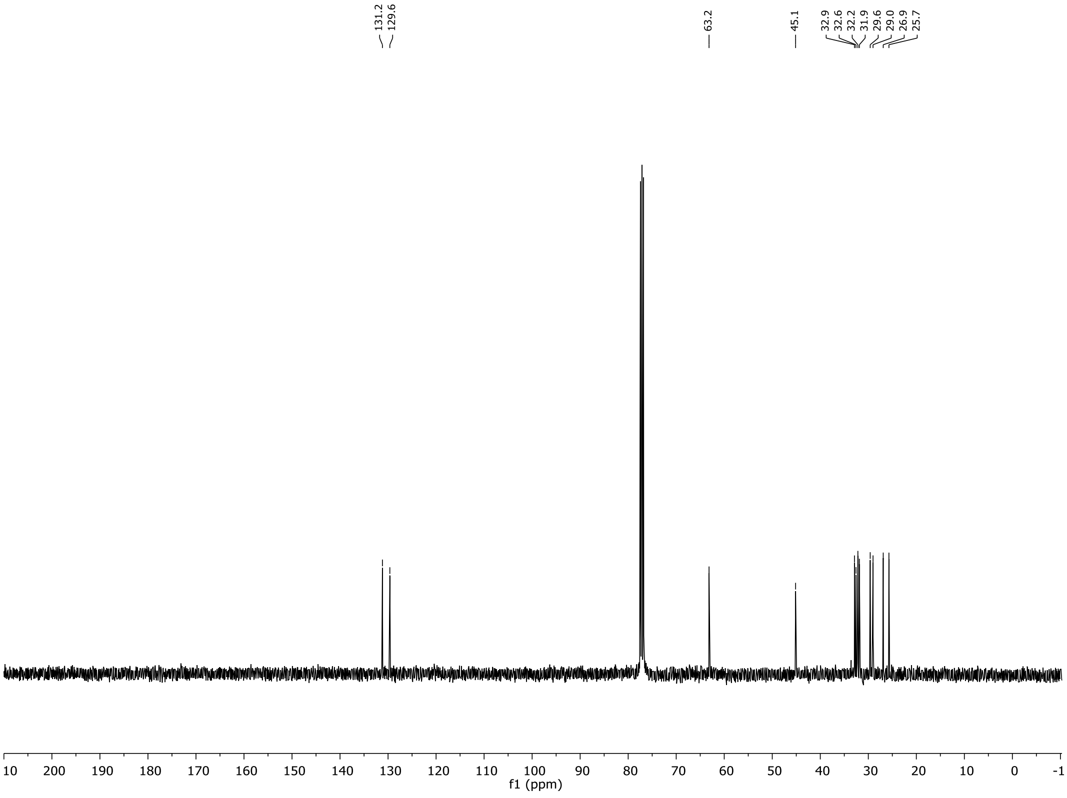
38.9
32.5
32.2
31.9
29.5
28.8
28.7
27.3
26.9
25.9
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5.45 5.44 5.42 5.41 5.40 5.39 5.39 5.38 5.38 5.37 5.36 5.36 5.34 5.33 5.33 3.65 3.64 3.62 3.55 3.53 3.51 2.04 2.04 2.03 2.02 2.02 2.02 2.01 2.00 2.00 1.99 1.97 1.97 1.96 1.81 1.79 1.78 1.78 1.77 1.77 1.77 1.76 1.76 1.75 1.75 1.73 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.53 1.51 1.51 1.50 1.50 1.49 1.49 1.47 1.47 1.37 1.37 1.37 1.36 1.35 1.35 1.34 1.34 1.34 1.33 1.33 1.32 1.32 1.31 1.30 1.30
HO
4
Cl
1.93
2.10
1.96
3.93
2.06
2.47
2.12
7.10
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
f1 (ppm)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63.2
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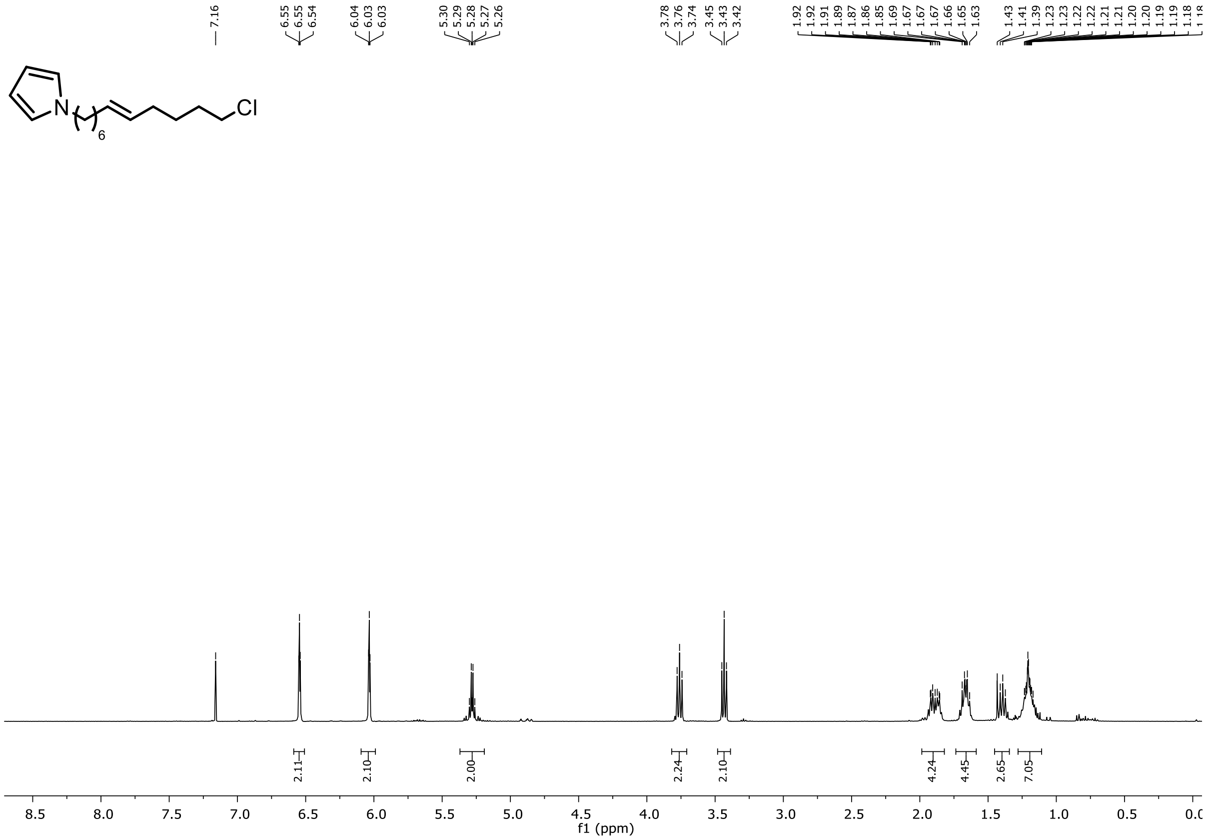
32.9
32.6
32.2
31.9
29.6
29.0
26.9
25.7
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


N
Cl
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6.54
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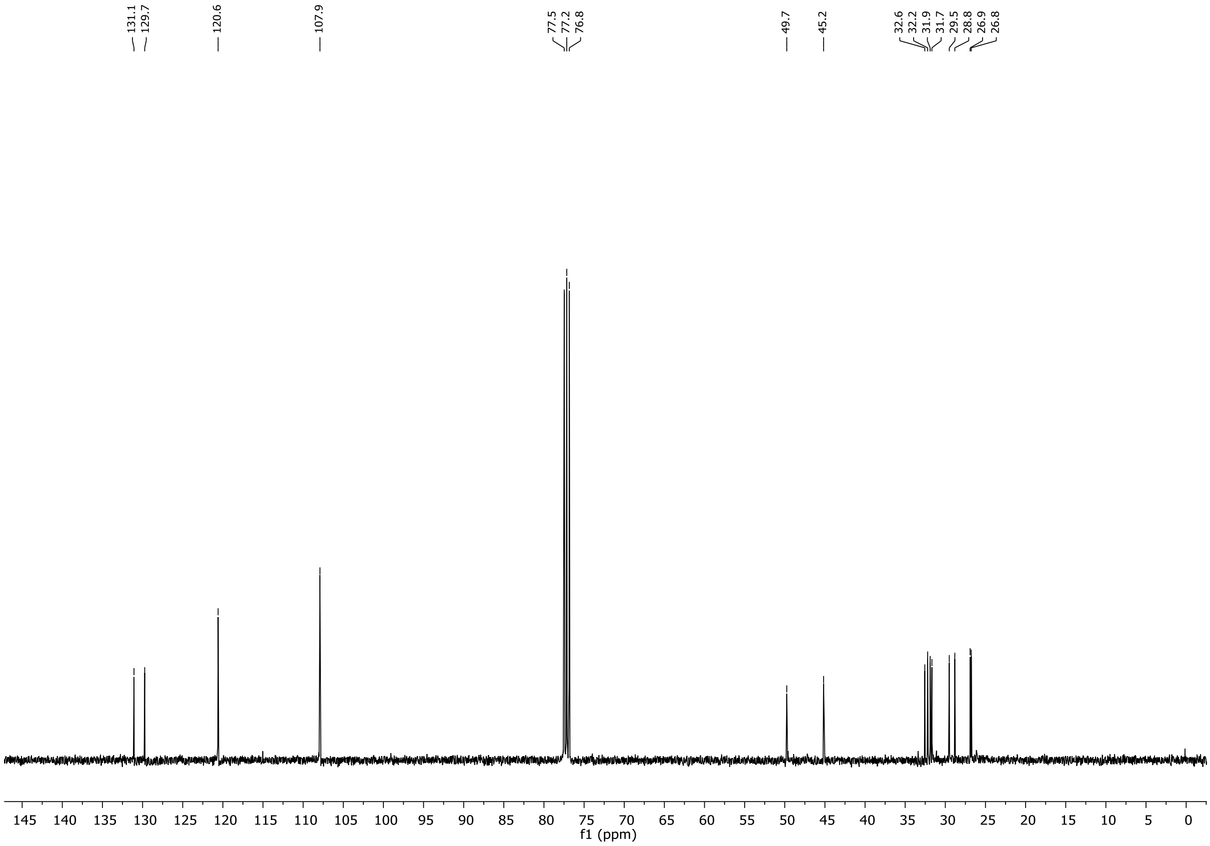
6.03
6.03
5.30
5.29
5.28
5.27
5.26
3.78
3.76
3.74
3.45
3.43
3.42
1.92
1.92
1.91
1.89
1.87
1.86
1.85
1.69
1.67
1.67
1.67
1.66
1.65
1.63
1.43
1.41
1.39
1.23
1.23
1.22
1.22
1.21
1.21
1.20
1.20
1.19
1.19
1.18
2.11
2.10
2.00
2.24
2.10
4.24
4.45
2.65
7.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


131.1
129.7
120.6
107.9
77.5
77.2
76.8
49.7
45.2
32.6
32.2
31.9
31.7
29.5
28.8
26.9
26.8
145
140
135
130
125
120
115
110
105
100
95
90
85
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45
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25
20
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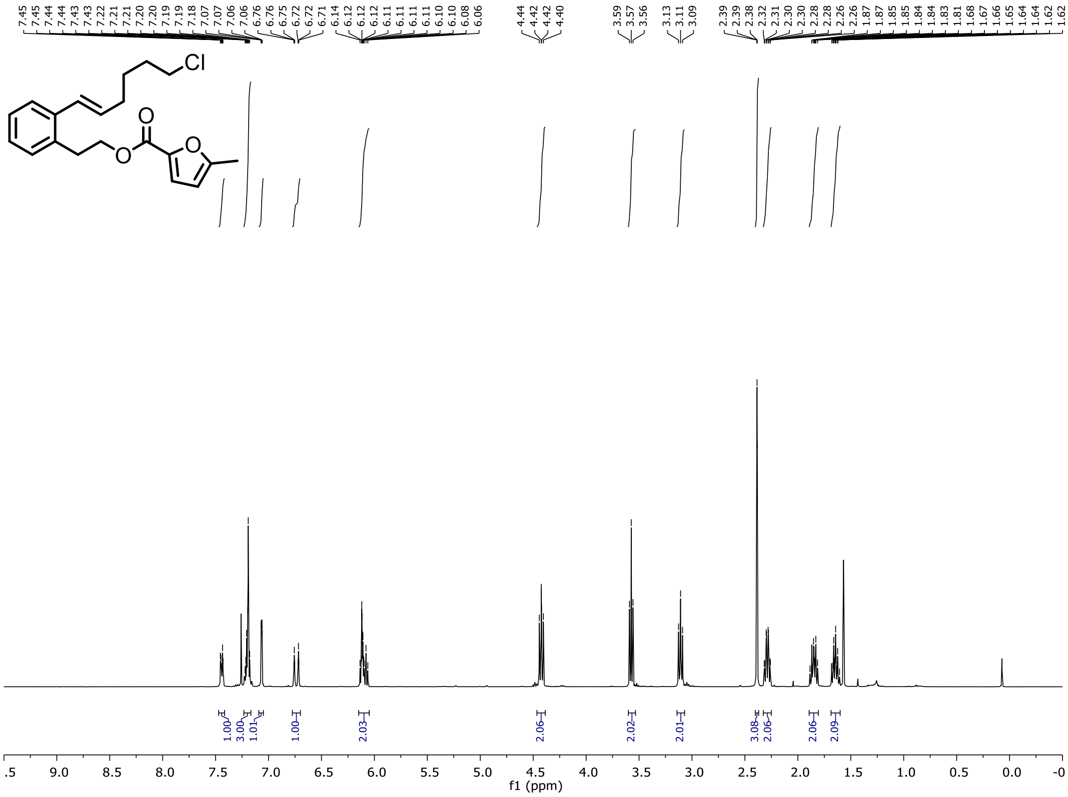
10
5
0
f1 (ppm)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7.44
7.44
7.43
7.43
7.22
7.21
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7.20
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7.19
7.19
7.18
7.07
7.06
7.06
6.76
6.76
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6.72
6.71
6.14
6.12
6.12
6.11
6.11
6.11
6.11
6.10
6.10
6.08
6.06
4.44
4.42
4.42
4.40
3.59
3.57
3.56
3.13
3.11
3.09
2.39
2.39
2.38
2.32
2.31
2.30
2.30
2.28
2.28
2.26
2.26
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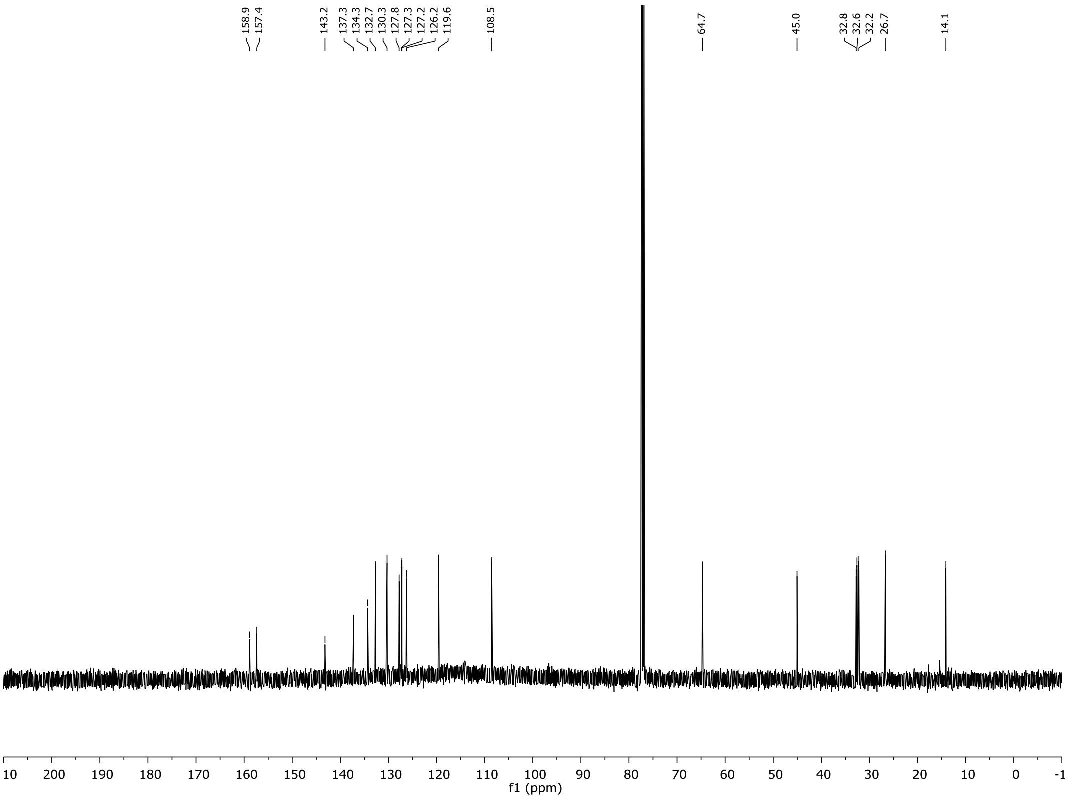
1.87
1.85
1.85
1.84
1.84
1.83
1.81
1.68
1.67
1.66
1.65
1.64
1.64
1.62
1.62
Cl
O
O
O
1.00
3.00
1.01
1.00
2.03
2.06
2.02
2.01
3.08
2.06
2.06
2.09
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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132.7
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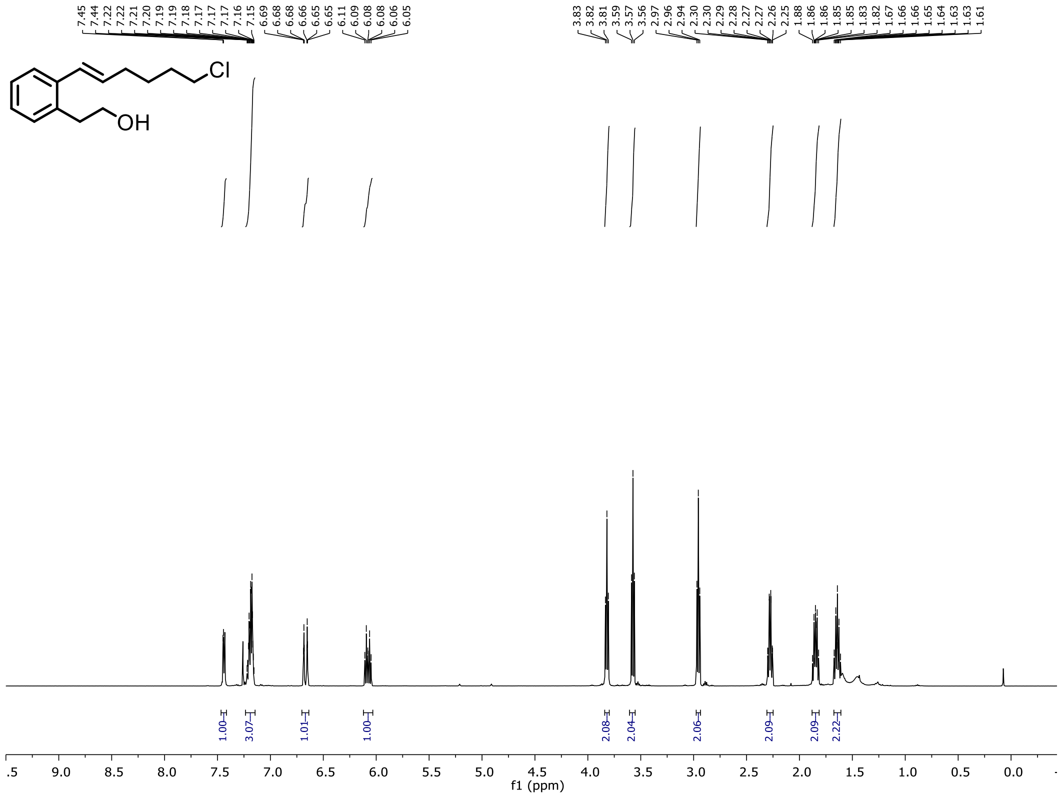
127.8
127.3
127.2
126.2
119.6
108.5
64.7
45.0
32.8
32.6
32.2
26.7
14.1
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Cl
OH
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7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.15
6.69
6.68
6.68
6.66
6.65
6.65
6.11
6.09
6.08
6.08
6.06
6.05
3.83
3.82
3.81
3.59
3.57
3.56
2.97
2.96
2.94
2.30
2.29
2.28
2.27
2.27
2.26
2.25
1.88
1.86
1.86
1.85
1.83
1.82
1.67
1.66
1.66
1.65
1.64
1.63
1.63
1.61
1.00
3.07
1.01
1.00
2.08
2.04
2.06
2.09
2.09
2.22
.5
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8.5
8.0
7.5
7.0
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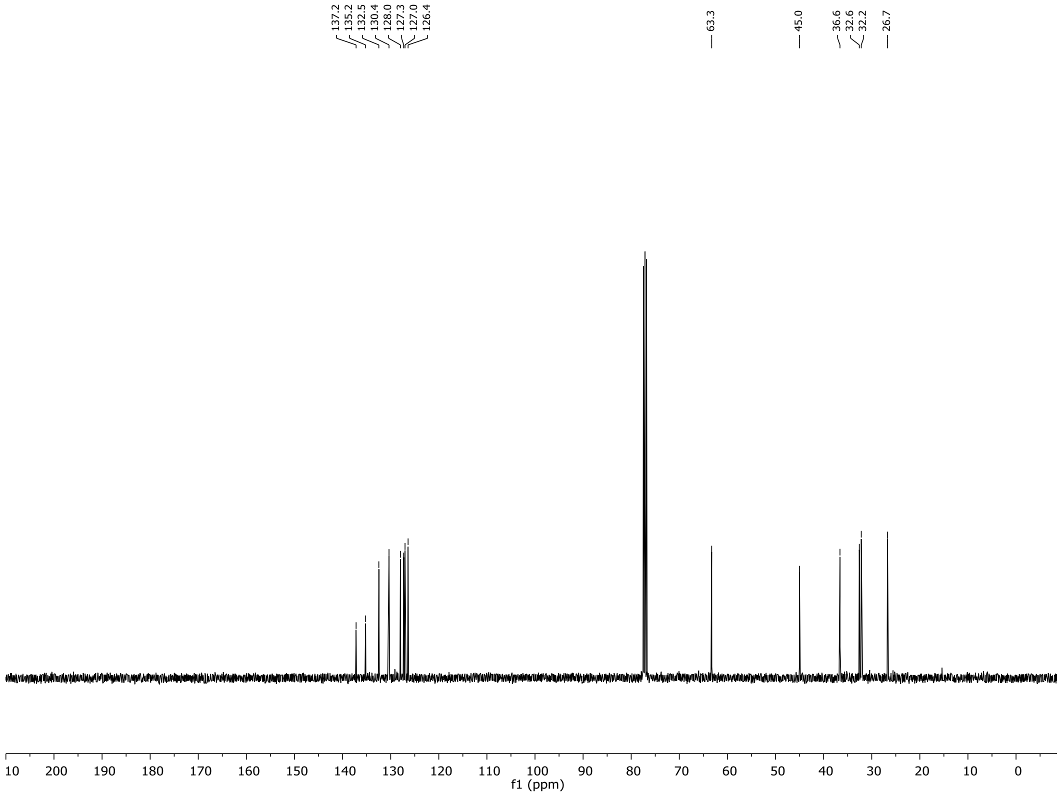
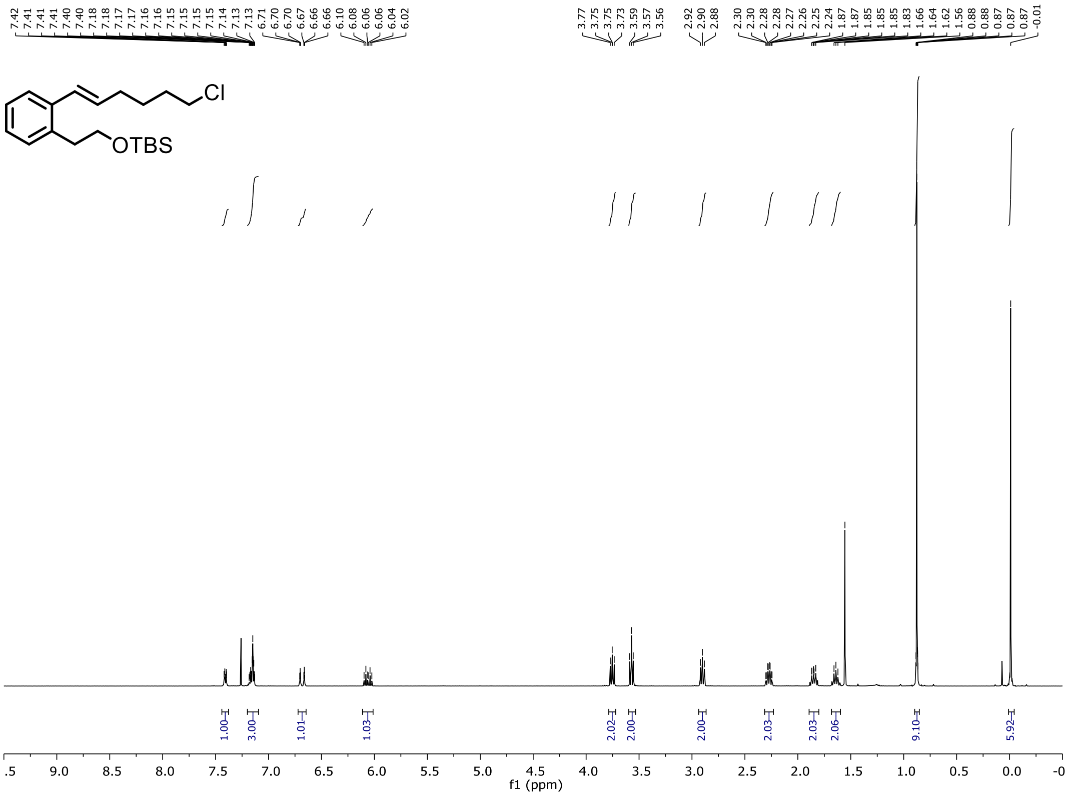
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.2
135.2
132.5
130.4
128.0
127.3
127.0
126.4
63.3
45.0
36.6
32.6
32.2
26.7
10
200
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
7.13
7.13
6.71
6.70
6.70
6.67
6.66
6.66
6.10
6.08
6.06
6.06
6.04
6.02
3.77
3.75
3.75
3.73
3.59
3.57
3.56
2.92
2.90
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2.30
2.30
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2.28
2.27
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2.25
2.24
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1.87
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1.85
1.85
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1.64
1.62
1.56
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0.88
0.87
0.87
0.87
-0.01
Cl
OTBS
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3.00
1.01
1.03
2.02
2.00
2.00
2.03
2.03
2.06
9.10
5.92
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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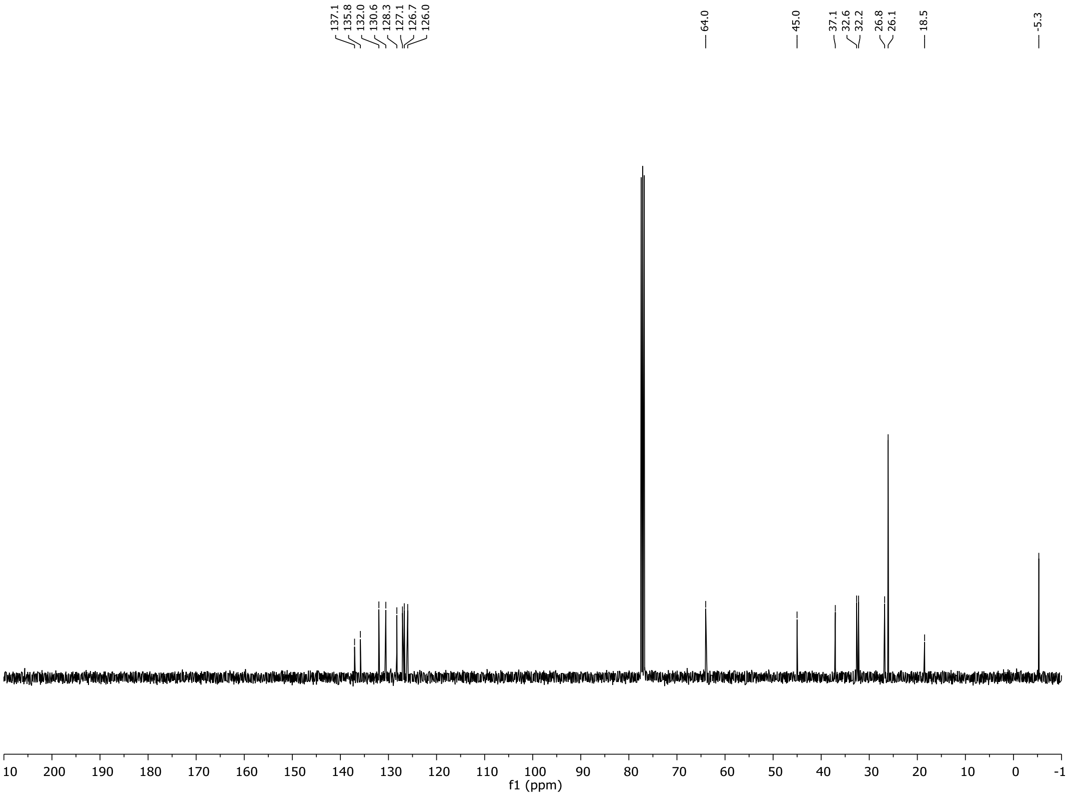
f1 (ppm)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126.0
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45.0
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32.2
26.8
26.1
18.5
-5.3
10
200
190
180
170
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100
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80
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30
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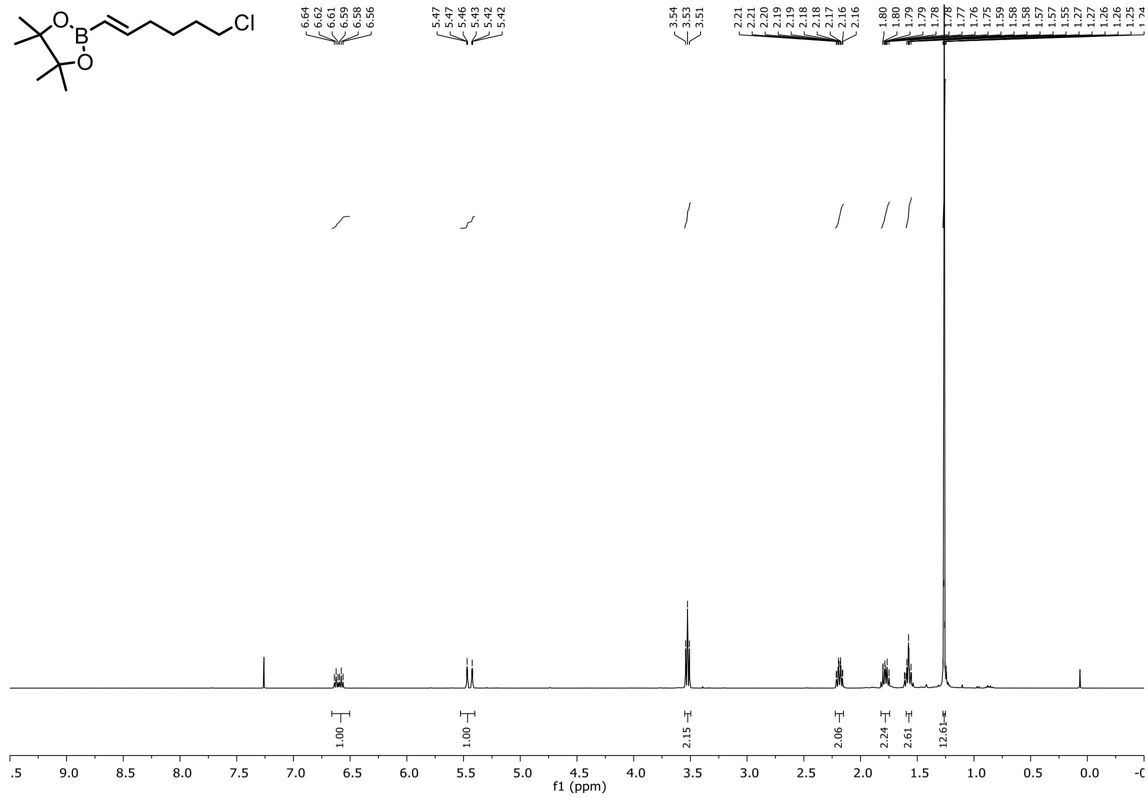
f1 (ppm)


O
B
O
Cl
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5.47
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5.42
5.42
3.54
3.53
3.51
2.21
2.21
2.20
2.19
2.19
2.18
2.18
2.17
2.16
2.16
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1.80
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1.79
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1.78
1.77
1.76
1.75
1.59
1.58
1.58
1.57
1.55
1.27
1.27
1.26
1.26
1.25
1.00
1.00
2.15
2.06
2.24
2.61
12.61
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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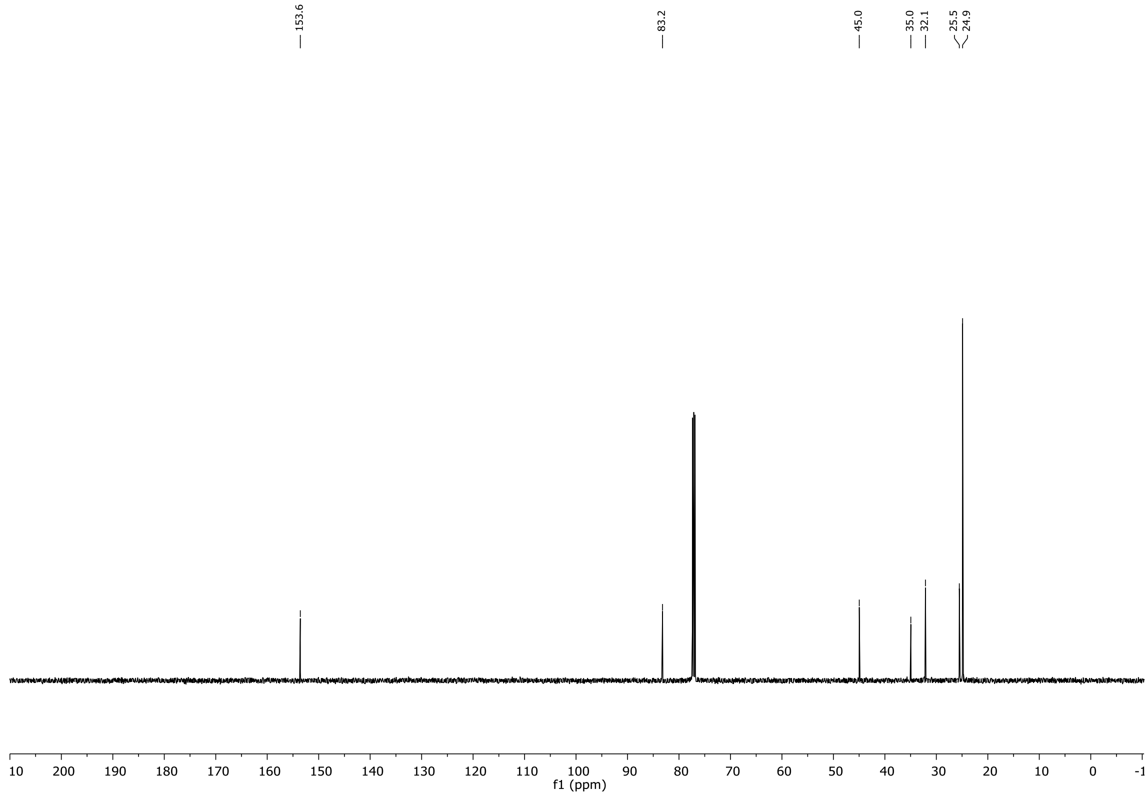
0.0
f1 (ppm)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10
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180
170
160
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120
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100
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80
70
60
50
40
30
20
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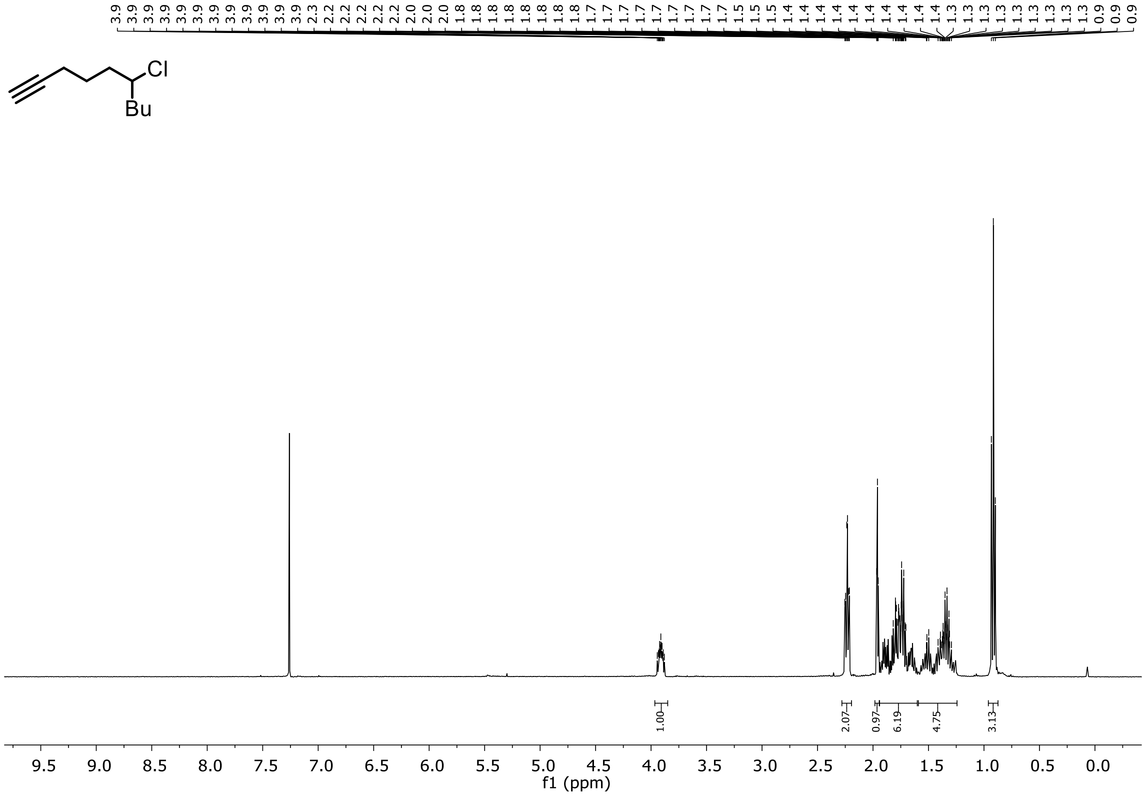
0
-1
f1 (ppm)


Cl
Bu
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3.9
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3.9
3.9
2.3
2.2
2.2
2.2
2.2
2.2
2.0
2.0
2.0
1.8
1.8
1.8
1.8
1.8
1.8
1.8
1.8
1.7
1.7
1.7
1.7
1.7
1.7
1.7
1.7
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1.5
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1.4
1.4
1.4
1.4
1.4
1.4
1.4
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1.3
1.3
1.3
1.3
1.3
1.3
1.3
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0.9
0.9
1.00
2.07
0.97
6.19
4.75
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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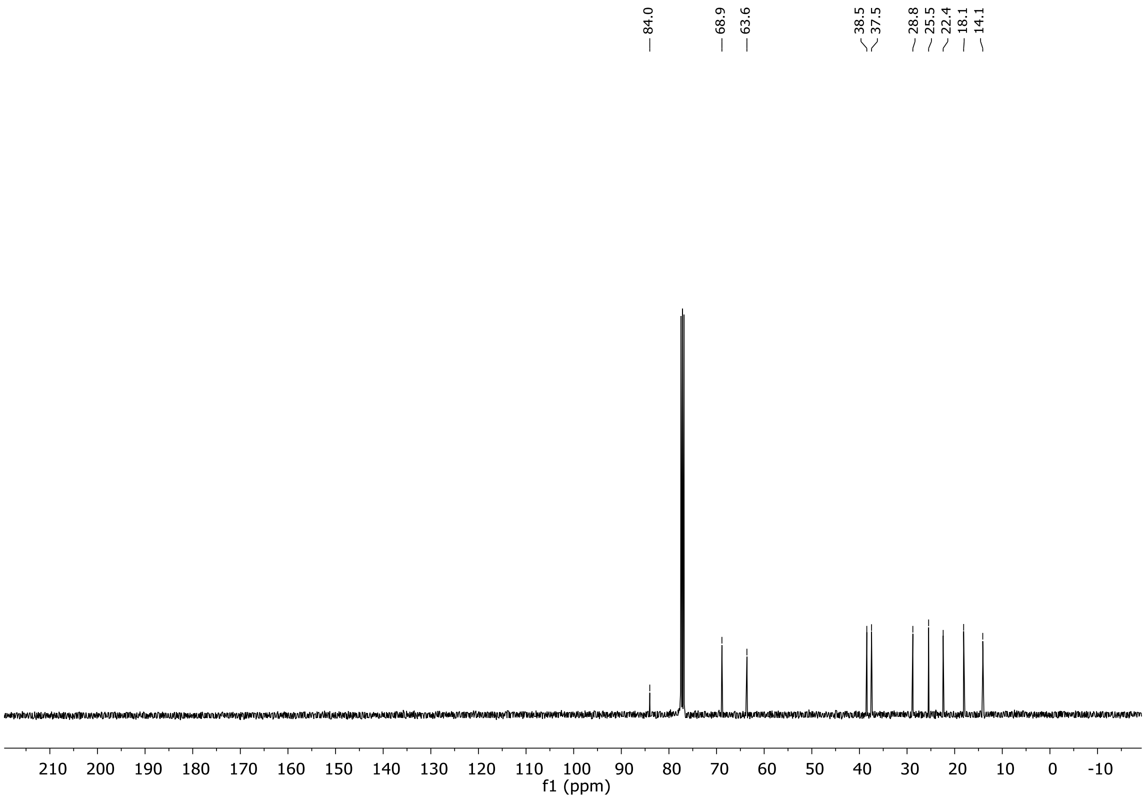
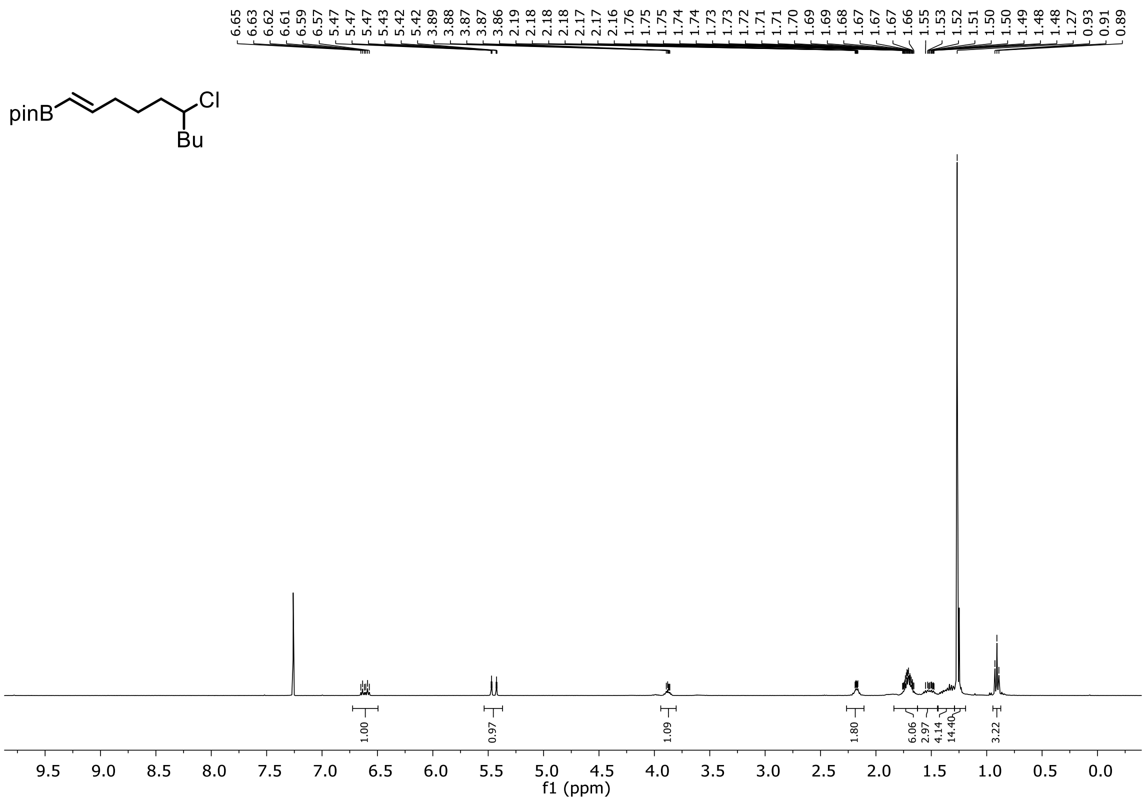
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


84.0
68.9
63.6
38.5
37.5
28.8
25.5
22.4
18.1
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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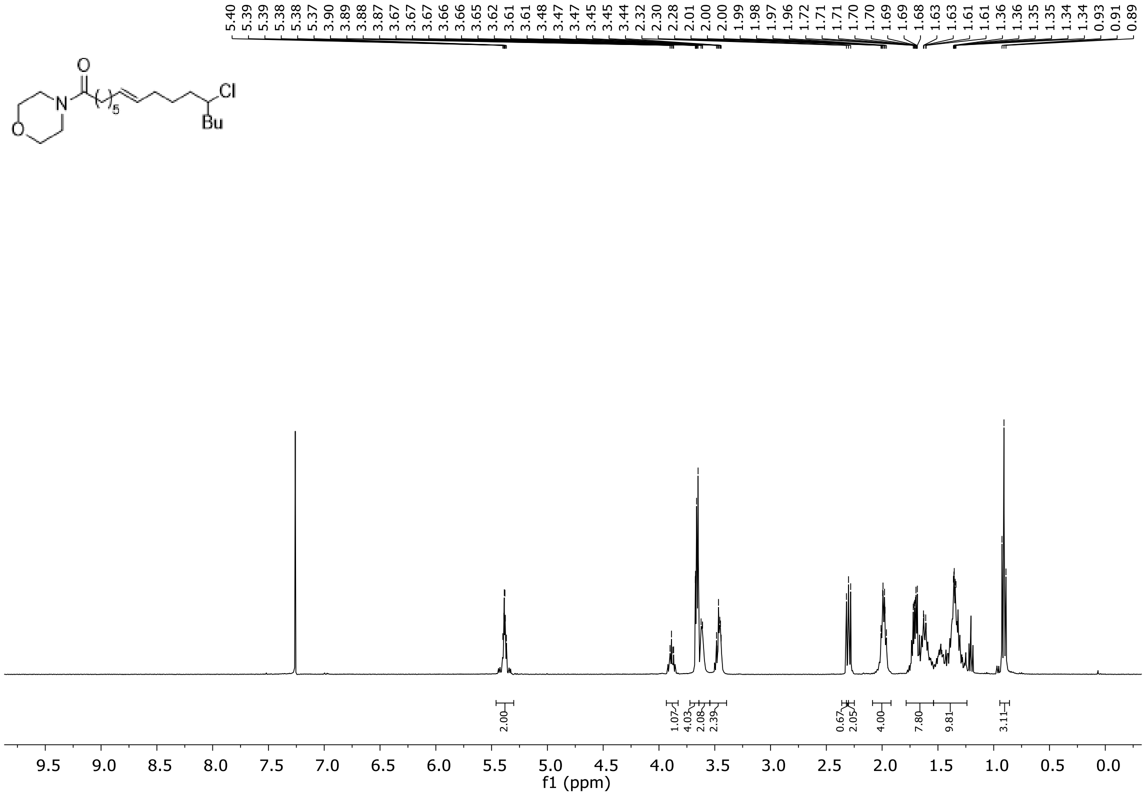
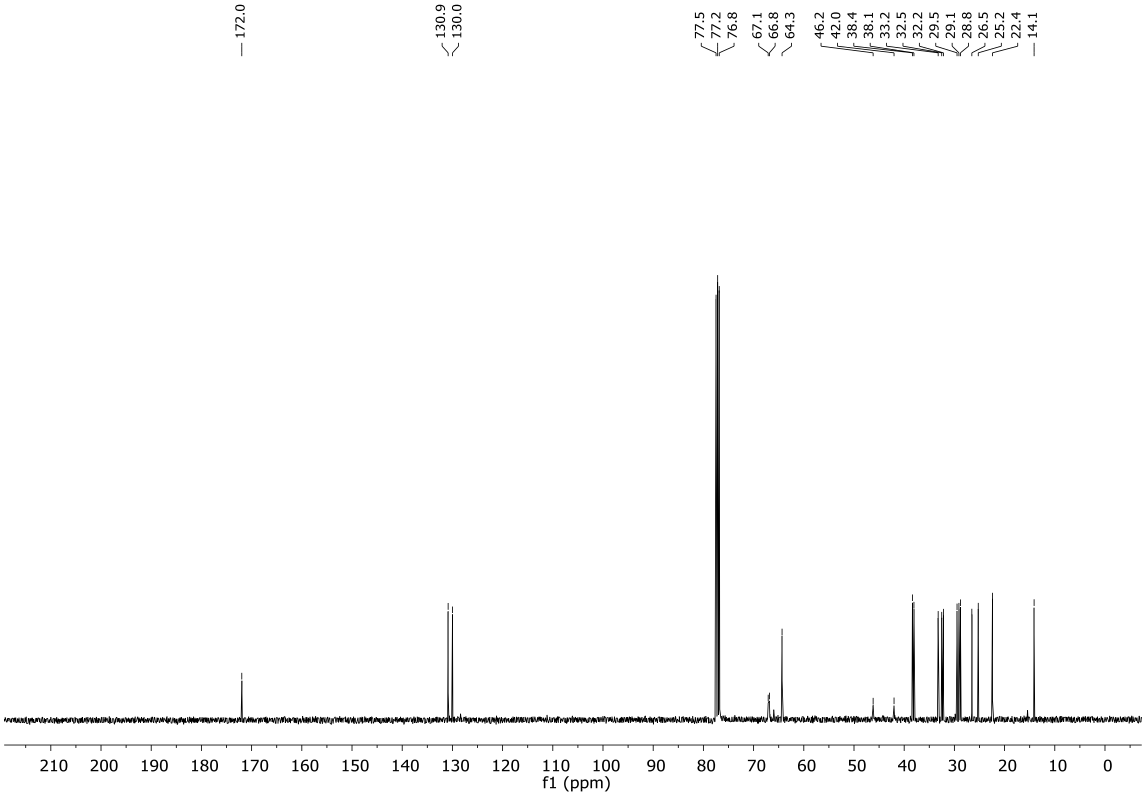
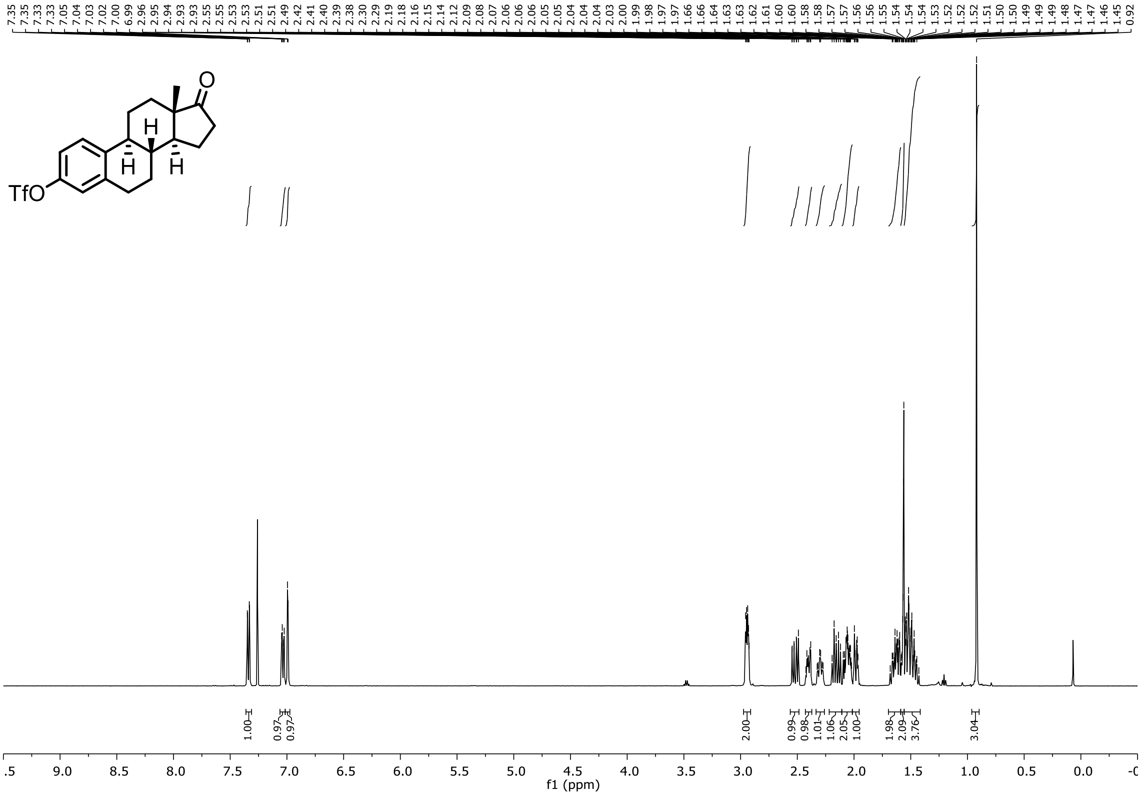
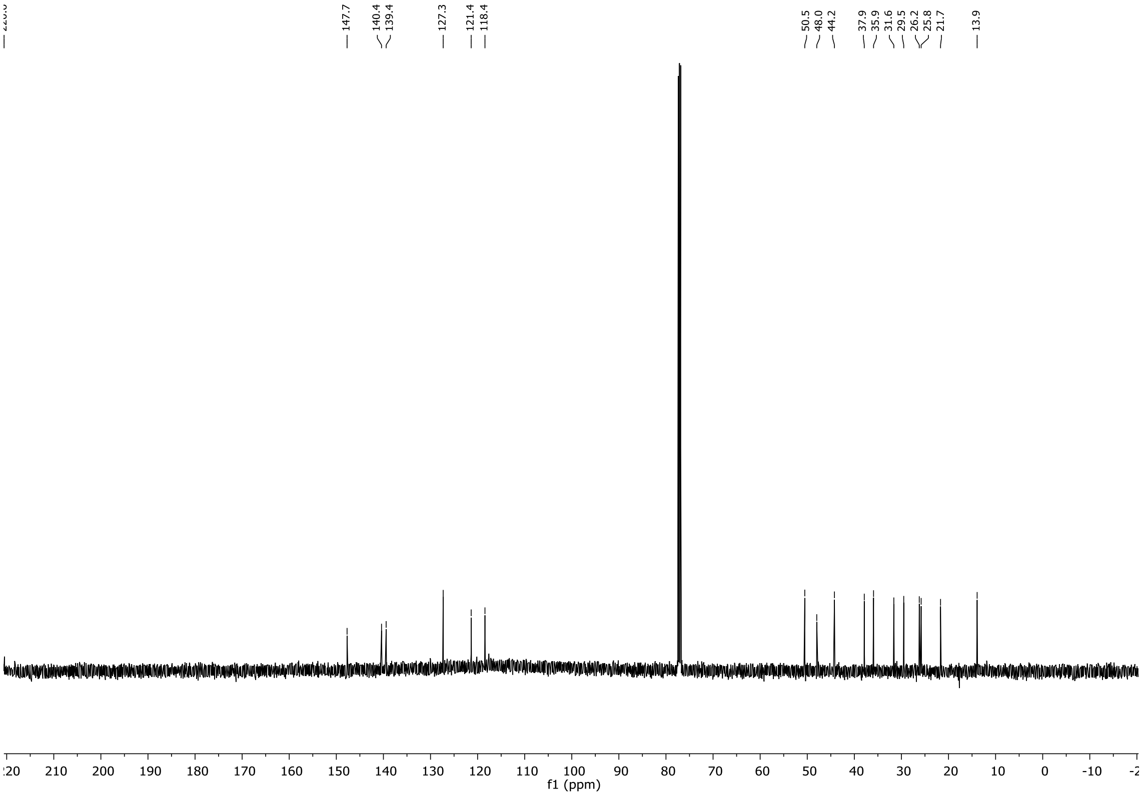
6.62
6.61
6.59
6.57
5.47
5.47
5.43
5.42
3.89
3.88
3.87
3.86
2.19
2.18
2.18
2.17
2.17
2.16
1.76
1.75
1.74
1.73
1.73
1.72
1.71
1.71
1.70
1.69
1.69
1.68
1.67
1.67
1.67
1.66
1.55
1.53
1.52
1.51
1.50
1.50
1.49
1.48
1.48
1.27
0.93
0.91
0.89
pinB
Cl
Bu
1.00
0.97
1.09
1.80
6.06
2.97
4.14
14.40
3.22
9.5
9.0
8.5
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)

O
N
O
5
Cl
Bu


5.40 5.39 5.39 5.38 5.38 5.37 3.90 3.89 3.88 3.87 3.67 3.67 3.67 3.66 3.66 3.65 3.62 3.61 3.61 3.48 3.47 3.47 3.45 3.45 3.44 2.32 2.30 2.28 2.01 2.00 2.00 1.99 1.98 1.97 1.96 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.68 1.63 1.63 1.61 1.61 1.36 1.36 1.35 1.35 1.34 1.34 0.93 0.91 0.89
2.00
1.07
4.03
2.08
2.39
0.67
2.05
4.00
7.80
9.81
3.11
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)


172.0
130.9 130.0
77.5 77.2 76.8
67.1 66.8 64.3
46.2 42.0 38.4 38.1 33.2 32.5 32.2 29.5 29.1 28.8 26.5 25.2 22.4
14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35 7.35 7.33 7.33 7.05 7.04 7.03 7.02 7.00 6.99 2.96 2.95 2.94 2.93 2.93 2.55 2.55 2.53 2.53 2.51 2.51 2.49 2.42 2.41 2.40 2.39 2.38 2.30 2.29 2.19 2.18 2.16 2.15 2.14 2.12 2.09 2.08 2.07 2.06 2.06 2.06 2.05 2.05 2.04 2.04 2.04 2.03 2.00 1.99 1.98 1.97 1.97 1.66 1.66 1.64 1.63 1.63 1.62 1.61 1.60 1.60 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.54 1.54 1.54 1.53 1.52 1.52 1.52 1.51 1.50 1.50 1.49 1.49 1.48 1.47 1.47 1.46 1.45 0.92
O
H
H
H
TfO
1.00
0.97
0.97
2.00
0.99
0.98
1.01
1.06
2.05
1.00
1.98
2.09
3.76
3.04
.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)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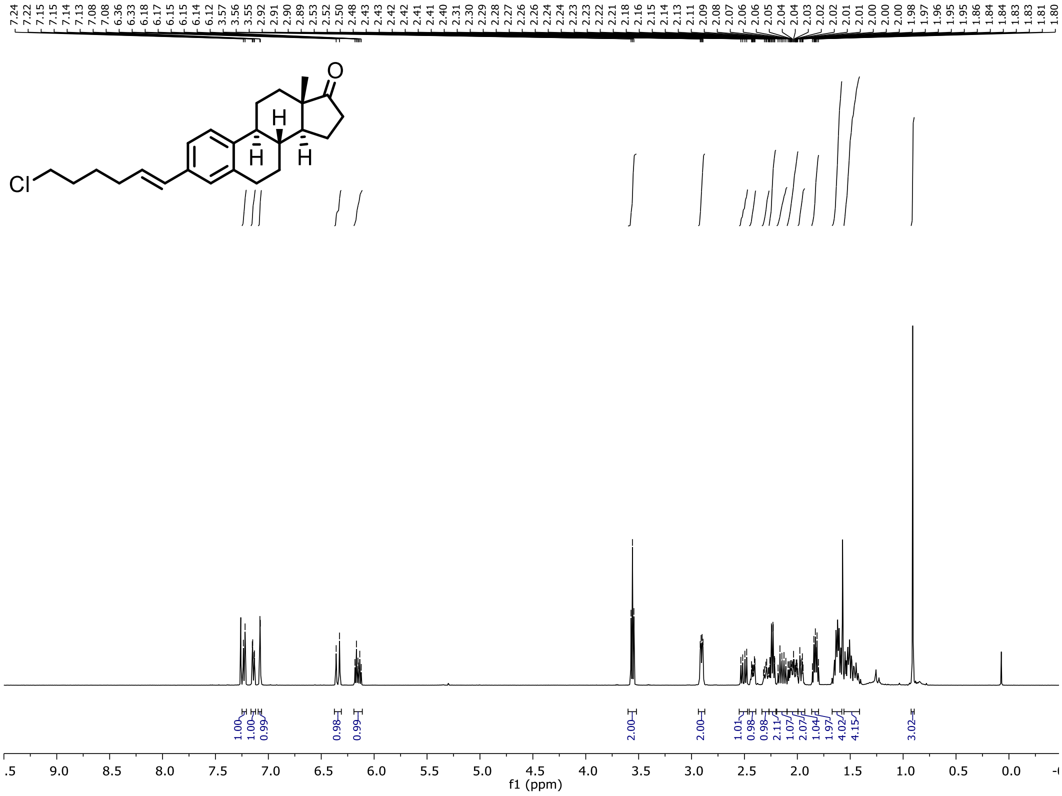
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.13
7.08
7.08
6.36
6.33
6.18
6.17
6.15
6.15
6.14
6.12
3.57
3.56
3.55
2.92
2.91
2.90
2.89
2.53
2.52
2.50
2.48
2.43
2.43
2.42
2.42
2.41
2.40
2.31
2.30
2.29
2.28
2.27
2.26
2.24
2.24
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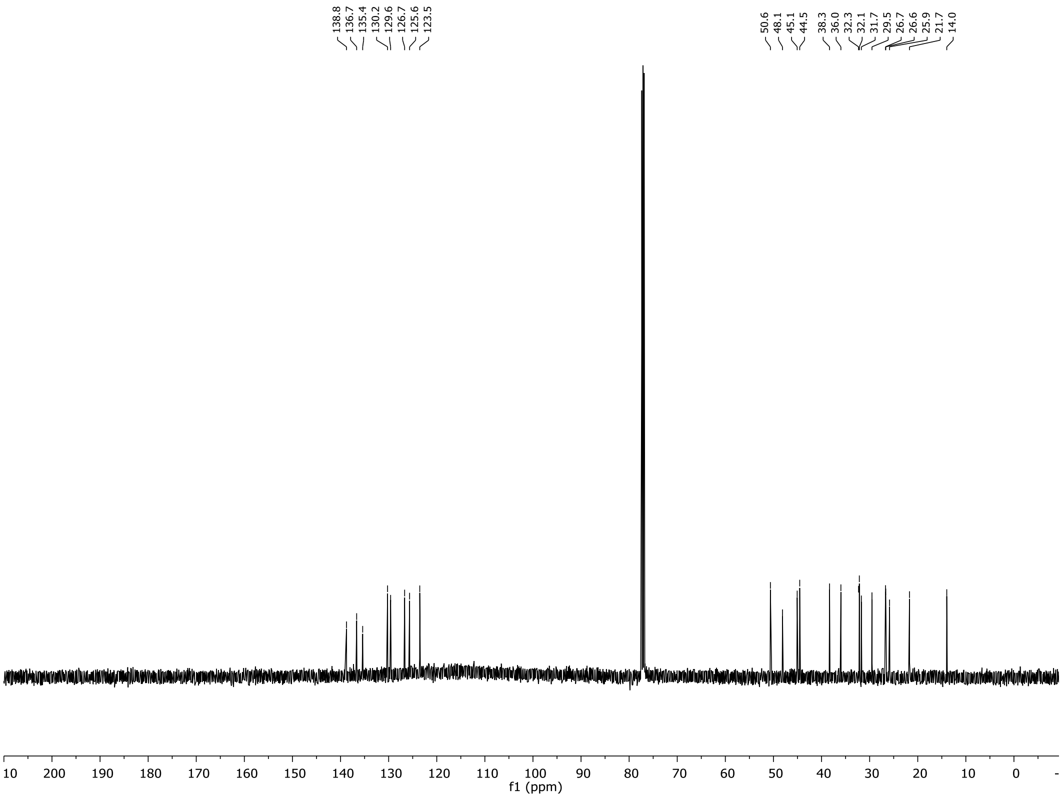
2.21
2.18
2.16
2.15
2.14
2.13
2.11
2.09
2.08
2.07
2.06
2.06
2.05
2.04
2.04
2.03
2.02
2.02
2.01
2.01
2.00
2.00
2.00
1.98
1.97
1.96
1.95
1.95
1.86
1.84
1.84
1.83
1.83
1.81
1.80
O
H
H
H
Cl
1.00
1.00
0.99
0.98
0.99
2.00
2.00
1.01
0.98
0.98
2.11
1.07
2.07
1.04
1.97
4.02
4.15
3.02
.5
9.0
8.5
8.0
7.5
7.0
6.5
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)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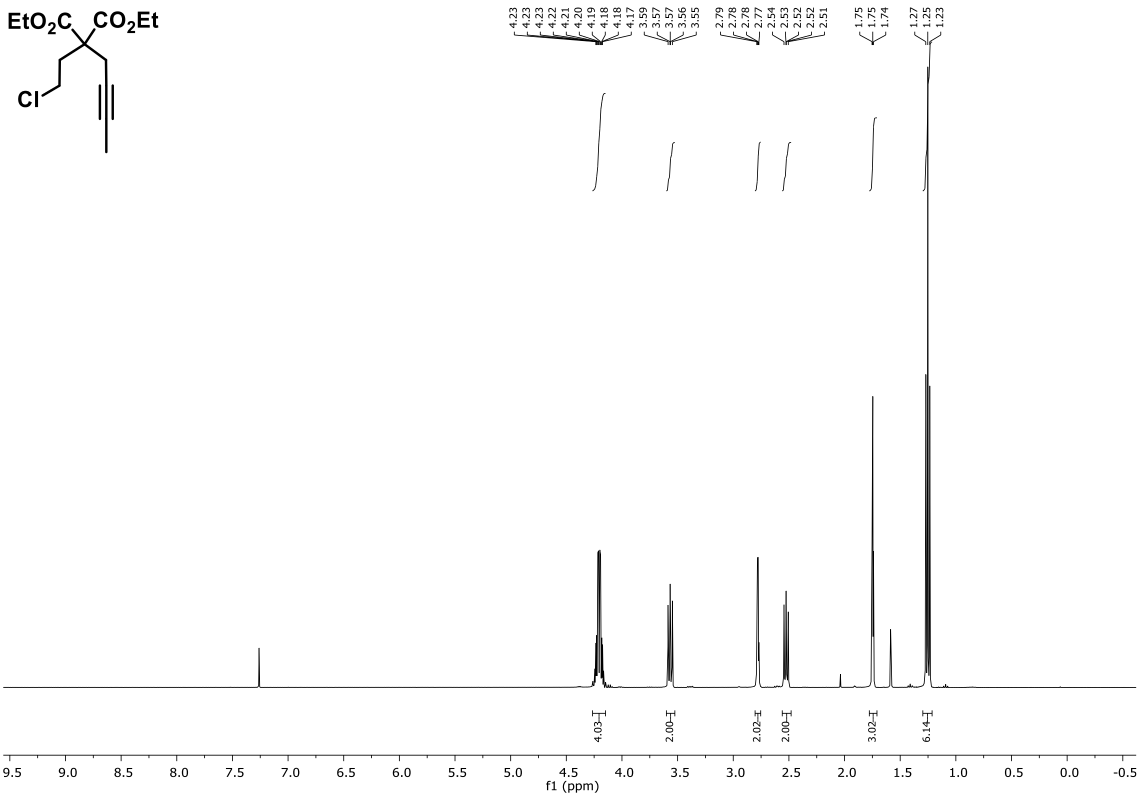
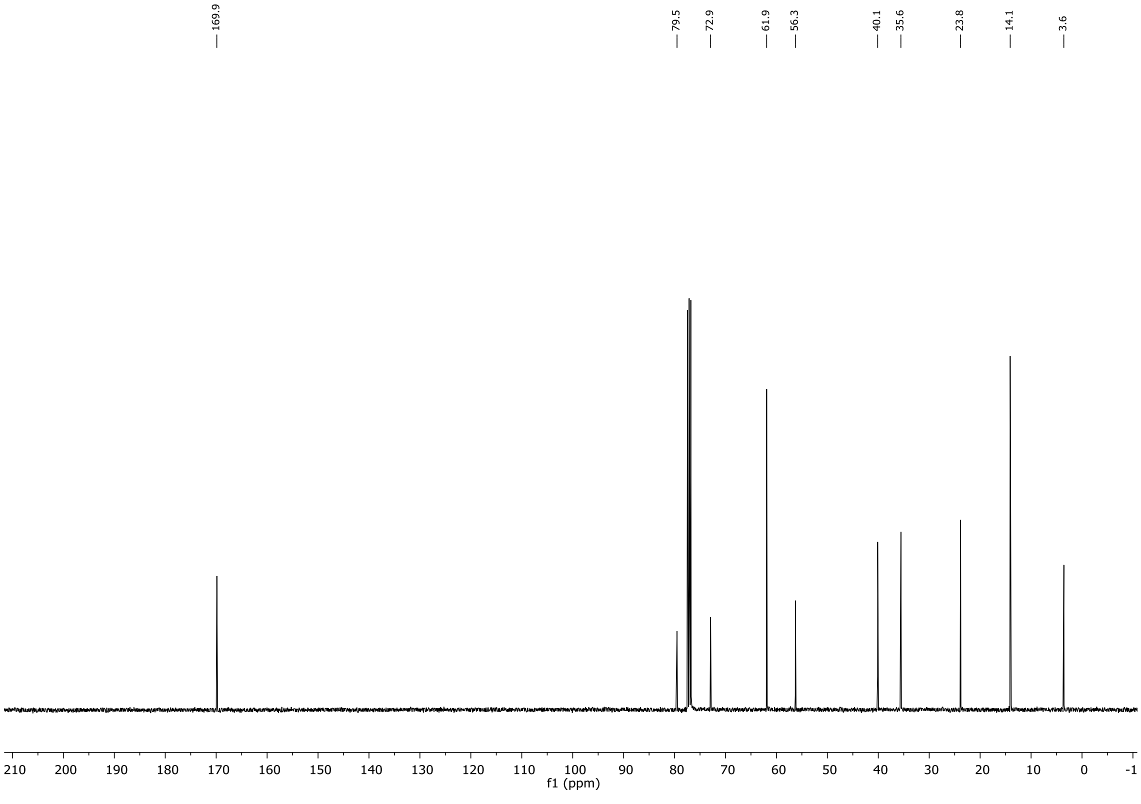
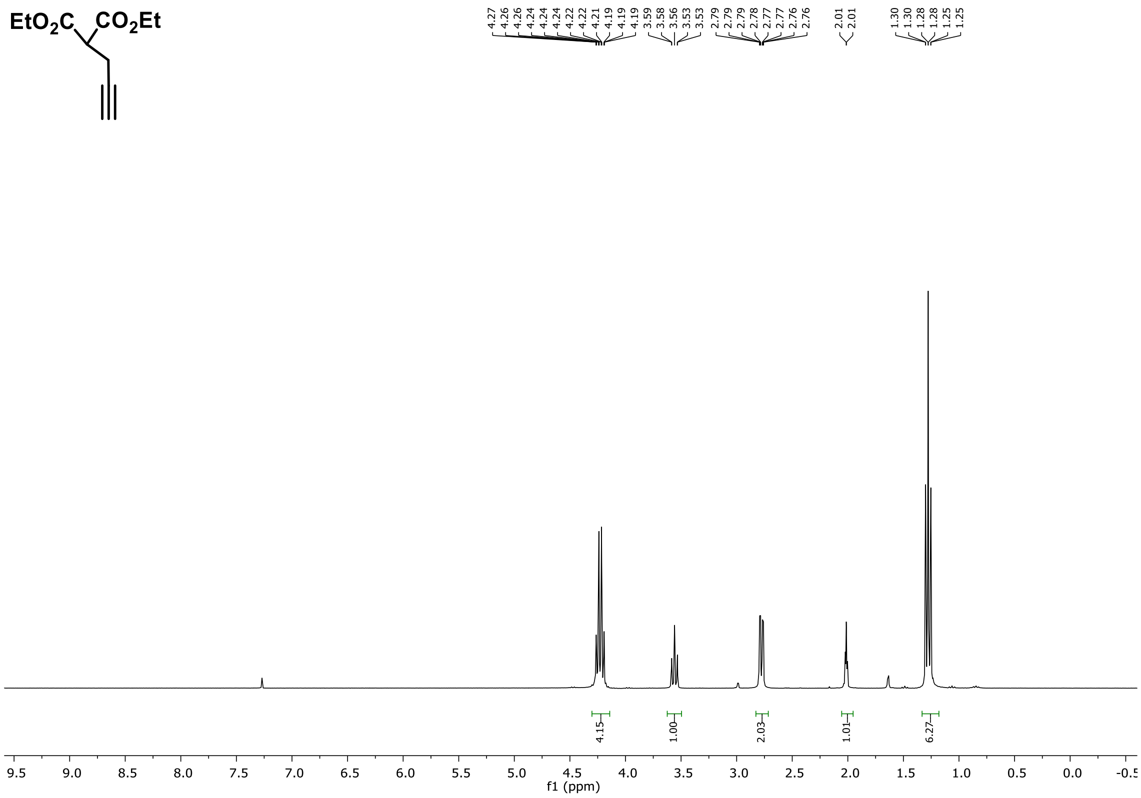
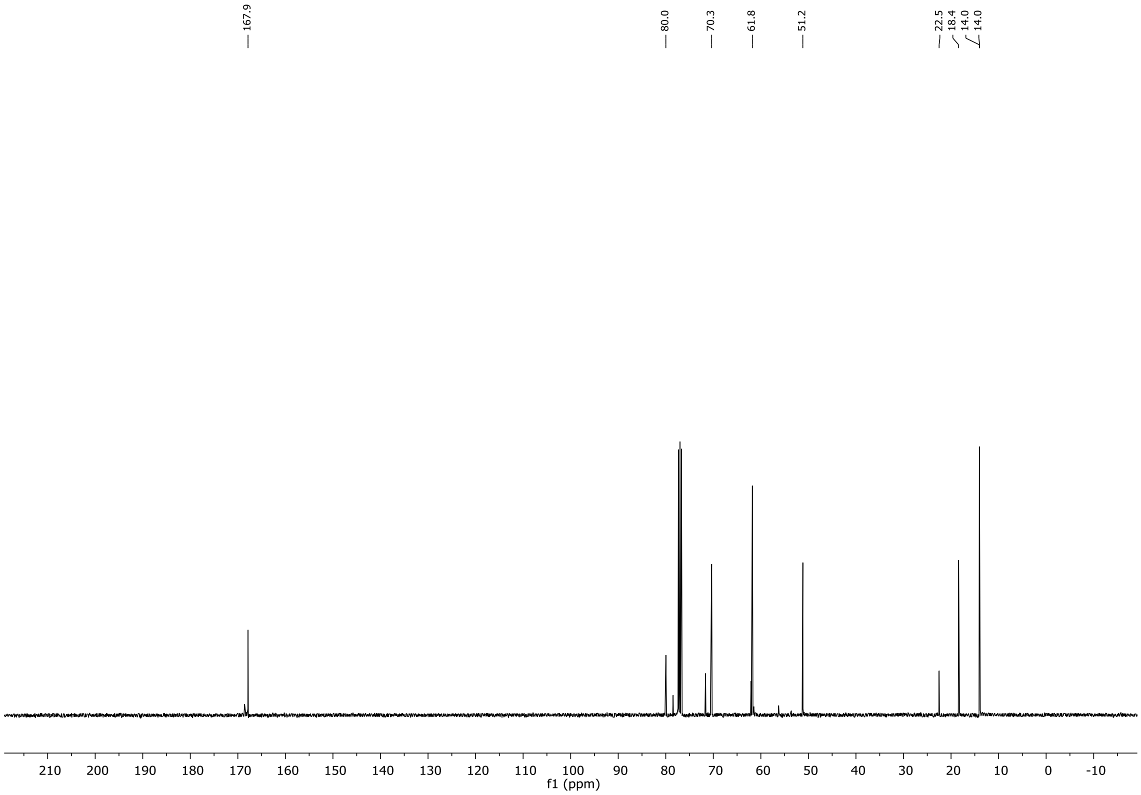
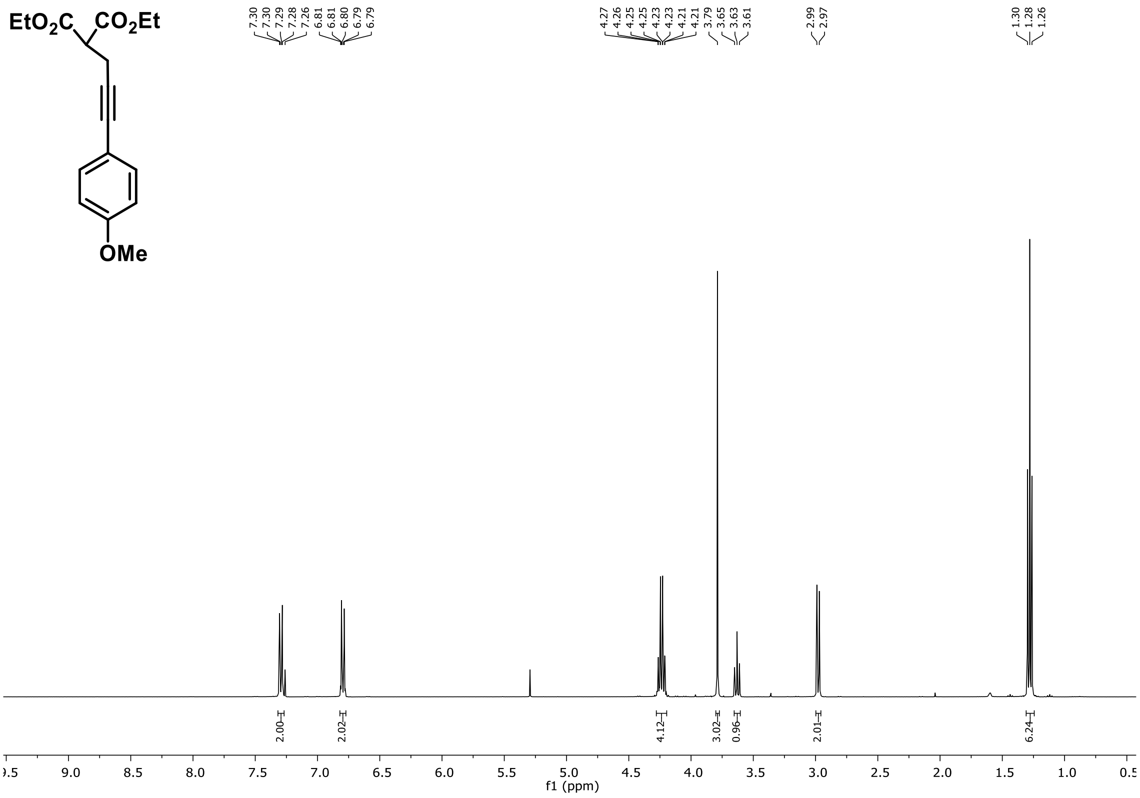
130.2
129.6
126.7
125.6
123.5
50.6
48.1
45.1
44.5
38.3
36.0
32.3
32.1
31.7
29.5
26.7
26.6
25.9
21.7
14.0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

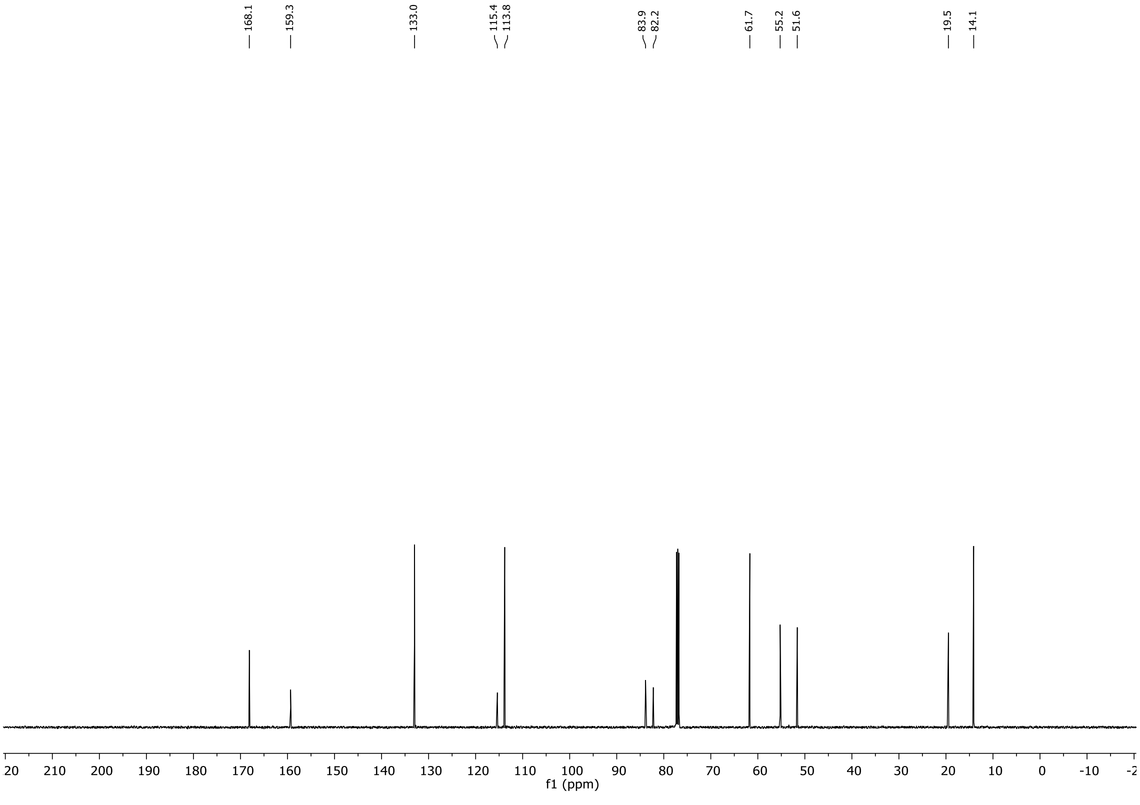

EtO2C
CO2Et
Cl
4.23
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.18
4.17
3.59
3.57
3.57
3.56
3.55
2.79
2.78
2.78
2.77
2.54
2.53
2.52
2.52
2.51
1.75
1.75
1.74
1.27
1.25
1.23
4.03
2.00
2.02
2.00
3.02
6.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

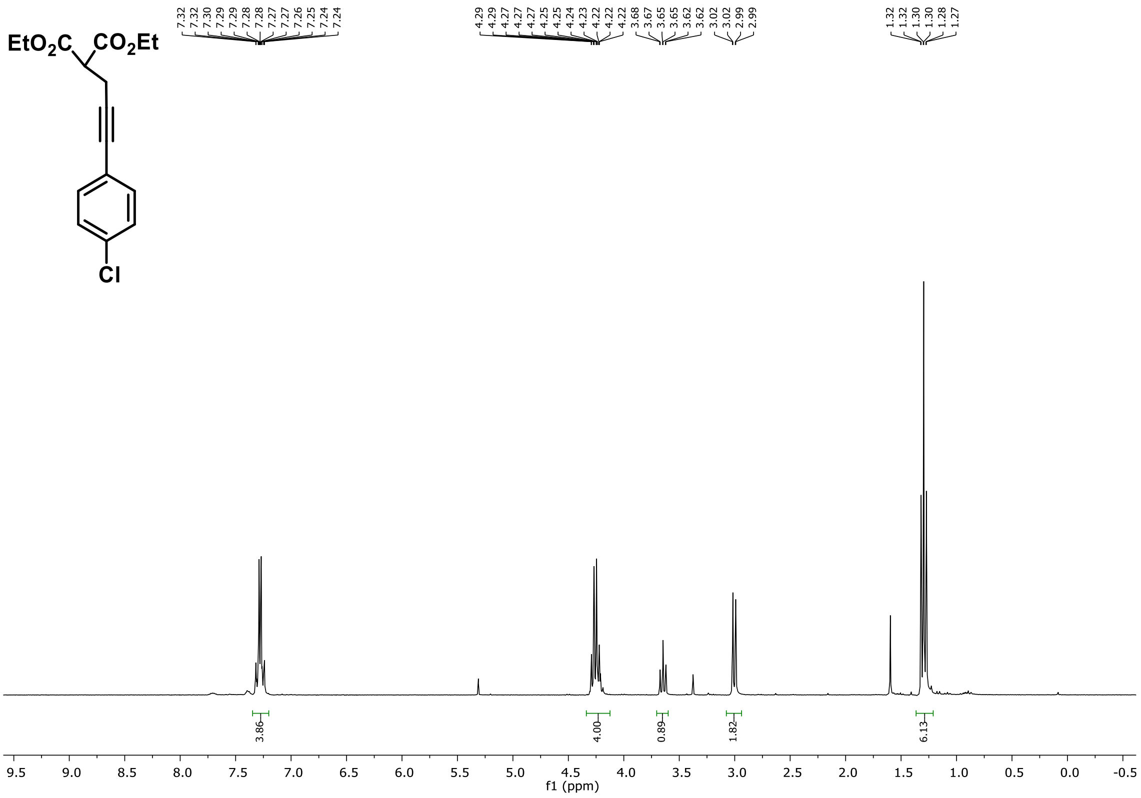

169.9
79.5
72.9
61.9
56.3
40.1
35.6
23.8
14.1
3.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

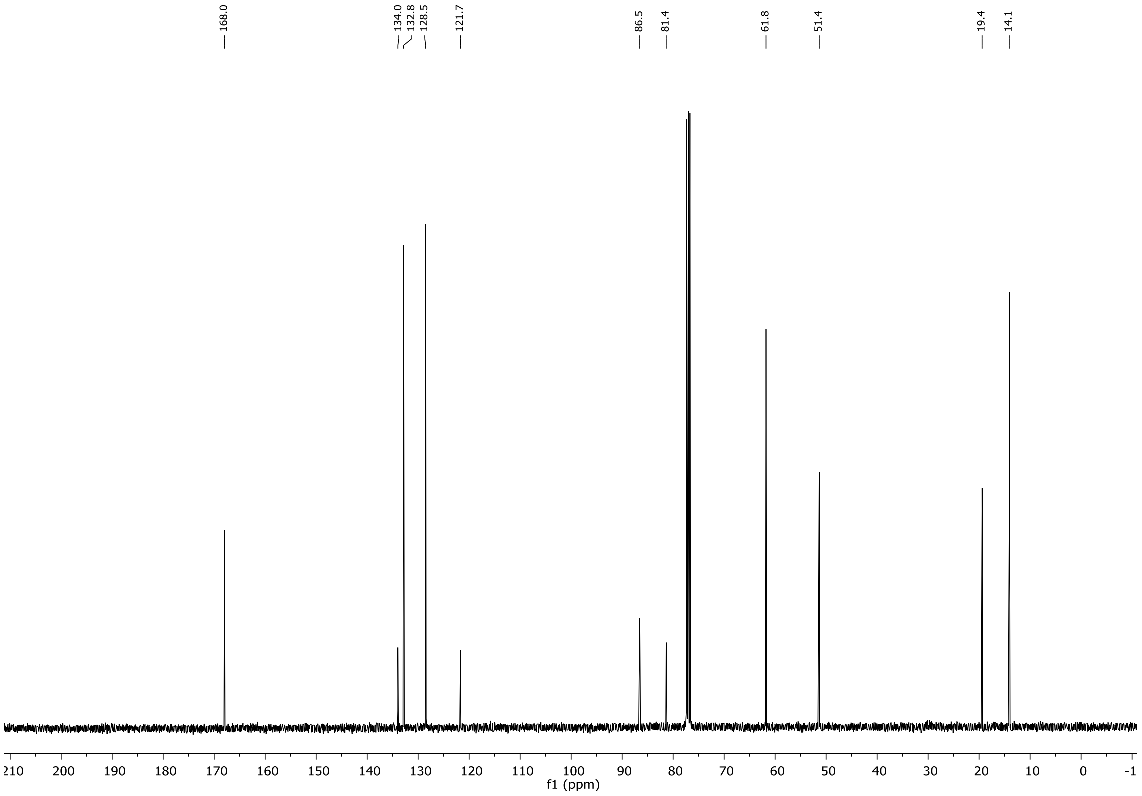

EtO2C
CO2Et
4.27
4.26
4.26
4.24
4.24
4.24
4.22
4.22
4.21
4.19
4.19
4.19
3.59
3.58
3.56
3.53
3.53
2.79
2.79
2.79
2.78
2.77
2.77
2.76
2.76
2.01
2.01
1.30
1.30
1.28
1.28
1.25
1.25
4.15
1.00
2.03
1.01
6.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

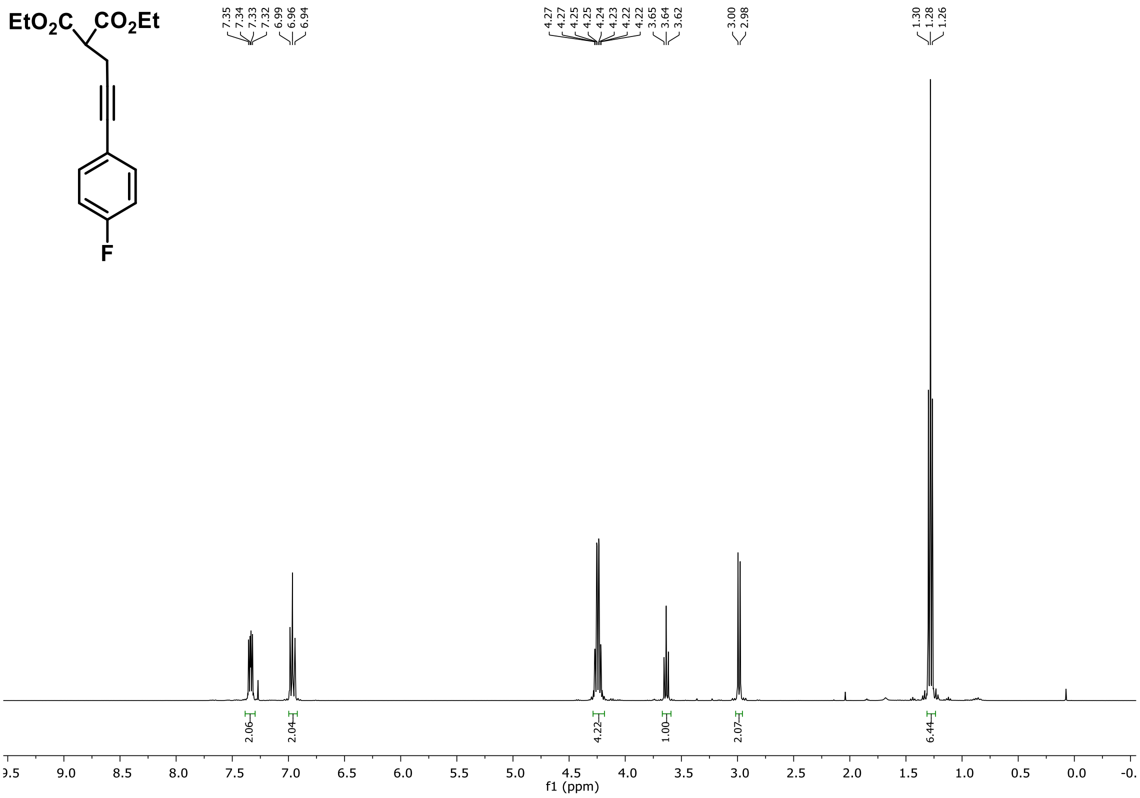

167.9
80.0
70.3
61.8
51.2
22.5
18.4
14.0
14.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

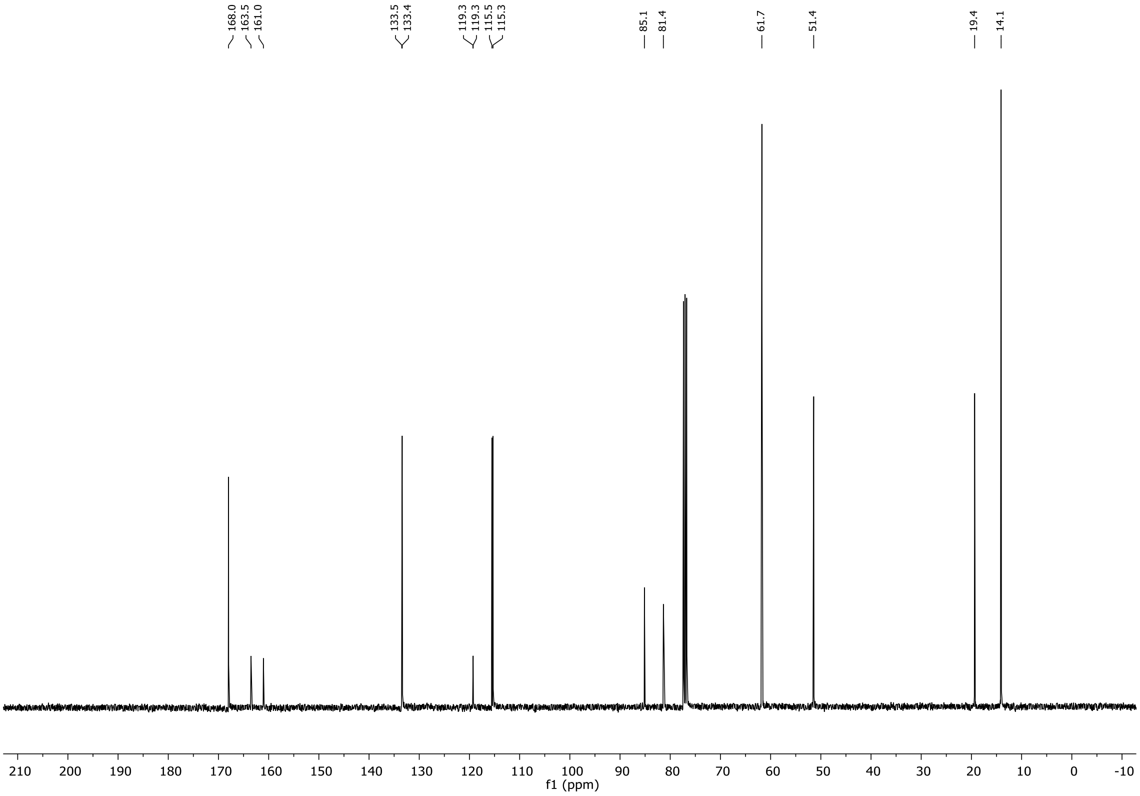

EtO2C CO2Et
OMe
7.30
7.30
7.29
7.28
7.26
6.81
6.81
6.80
6.79
6.79
4.27
4.26
4.25
4.25
4.23
4.23
4.21
4.21
3.79
3.65
3.63
3.61
2.99
2.97
1.30
1.28
1.26
2.00
2.02
4.12
3.02
0.96
2.01
6.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

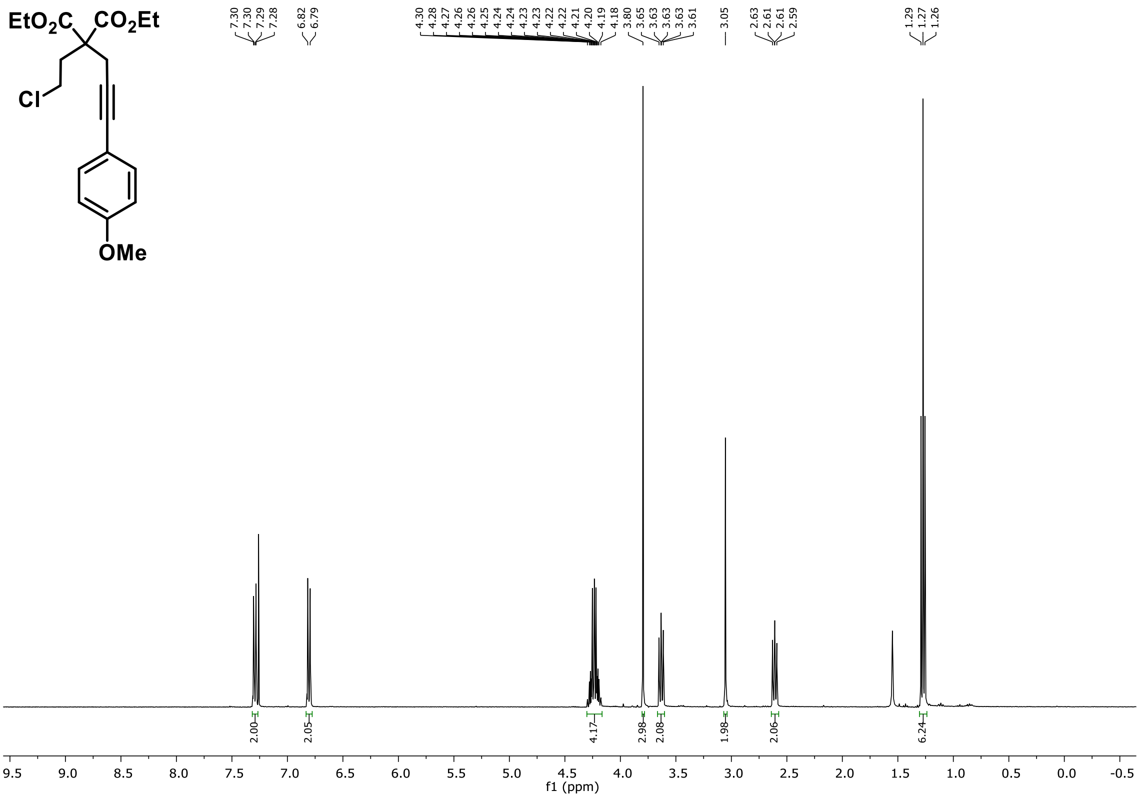

168.1
159.3
133.0
115.4
113.8
83.9
82.2
61.7
55.2
51.6
19.5
14.1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

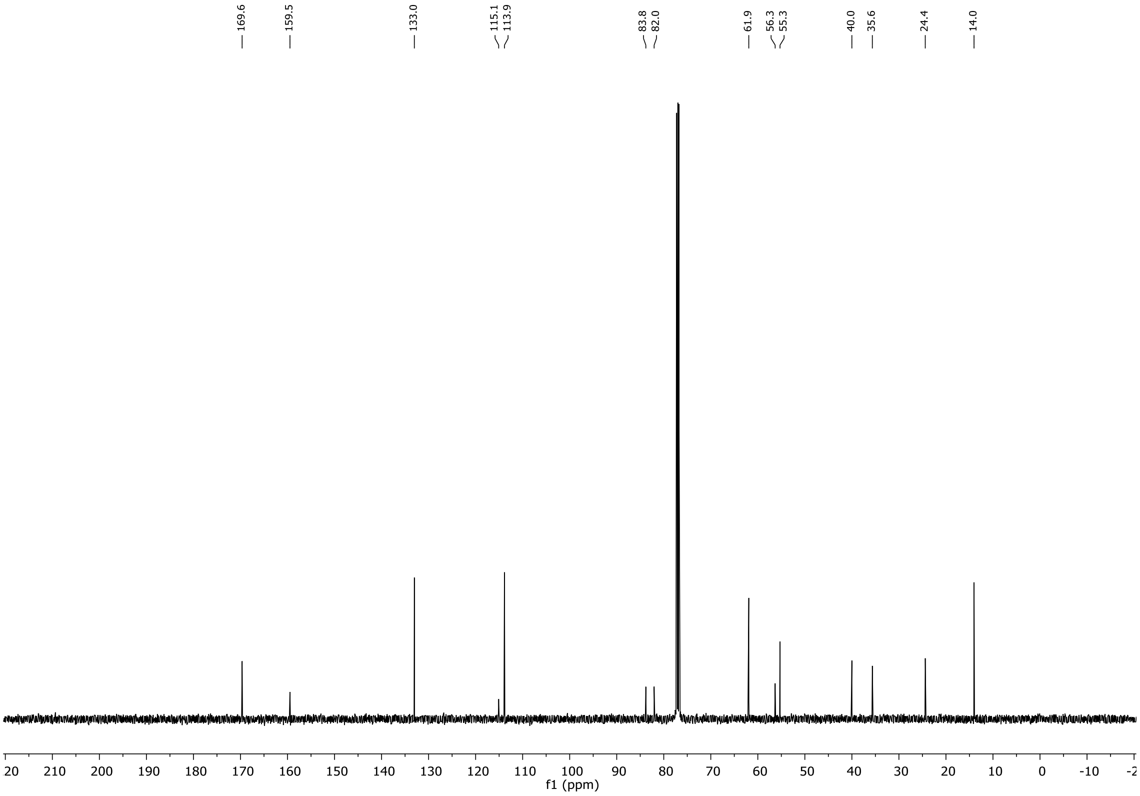

EtO$_2$C
CO$_2$Et
Cl
7.32
7.32
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.24
7.24
4.29
4.29
4.27
4.27
4.27
4.25
4.25
4.24
4.23
4.22
4.22
4.22
4.22
3.68
3.67
3.65
3.65
3.62
3.62
3.02
3.02
2.99
2.99
1.32
1.32
1.30
1.30
1.28
1.27
3.86
4.00
0.89
1.82
6.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

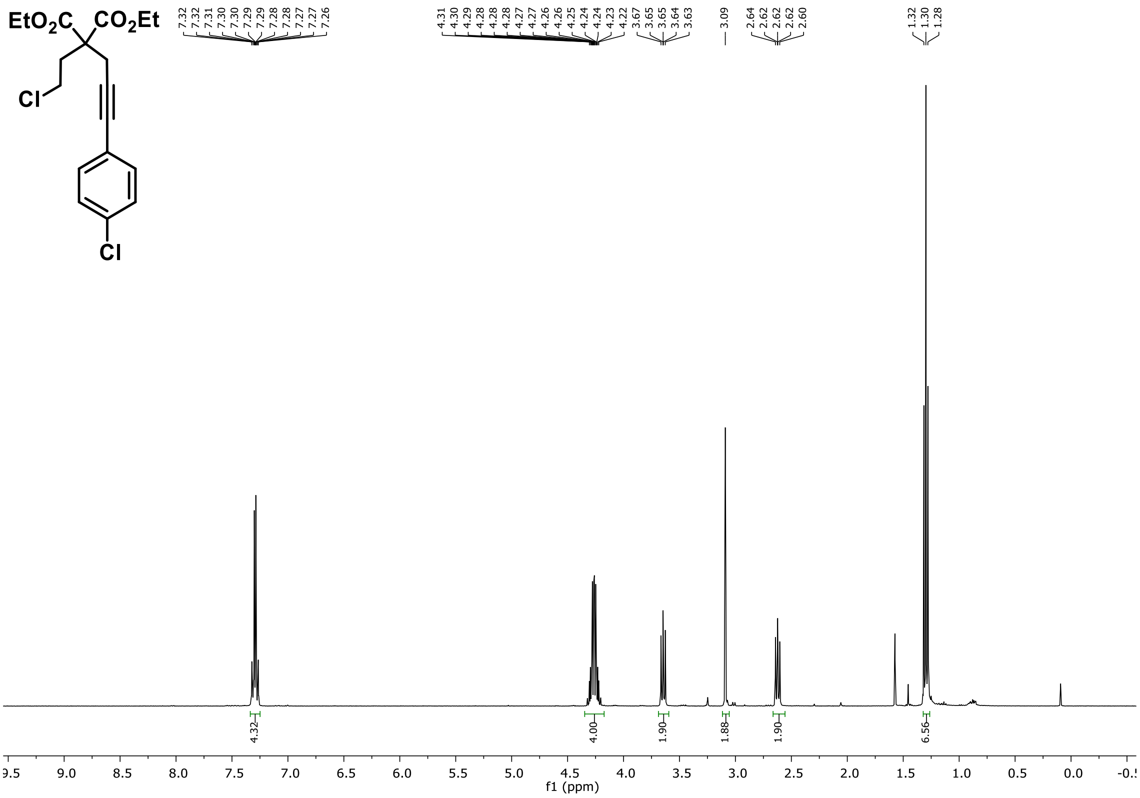

168.0
134.0
132.8
128.5
121.7
86.5
81.4
61.8
51.4
19.4
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

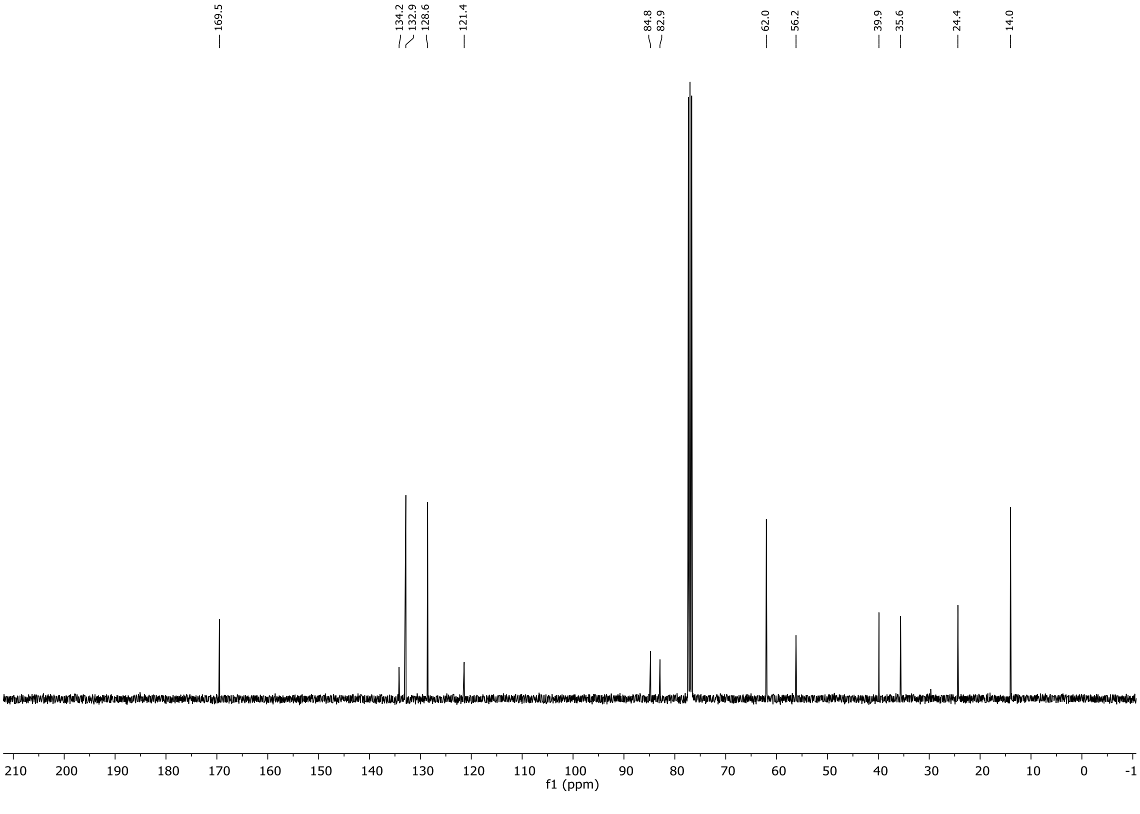

EtO2C CO2Et
F
7.35
7.34
7.33
7.32
6.99
6.96
6.94
4.27
4.27
4.25
4.25
4.24
4.23
4.22
4.22
3.65
3.64
3.62
3.00
2.98
1.30
1.28
1.26
2.06
2.04
4.22
1.00
2.07
6.44
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

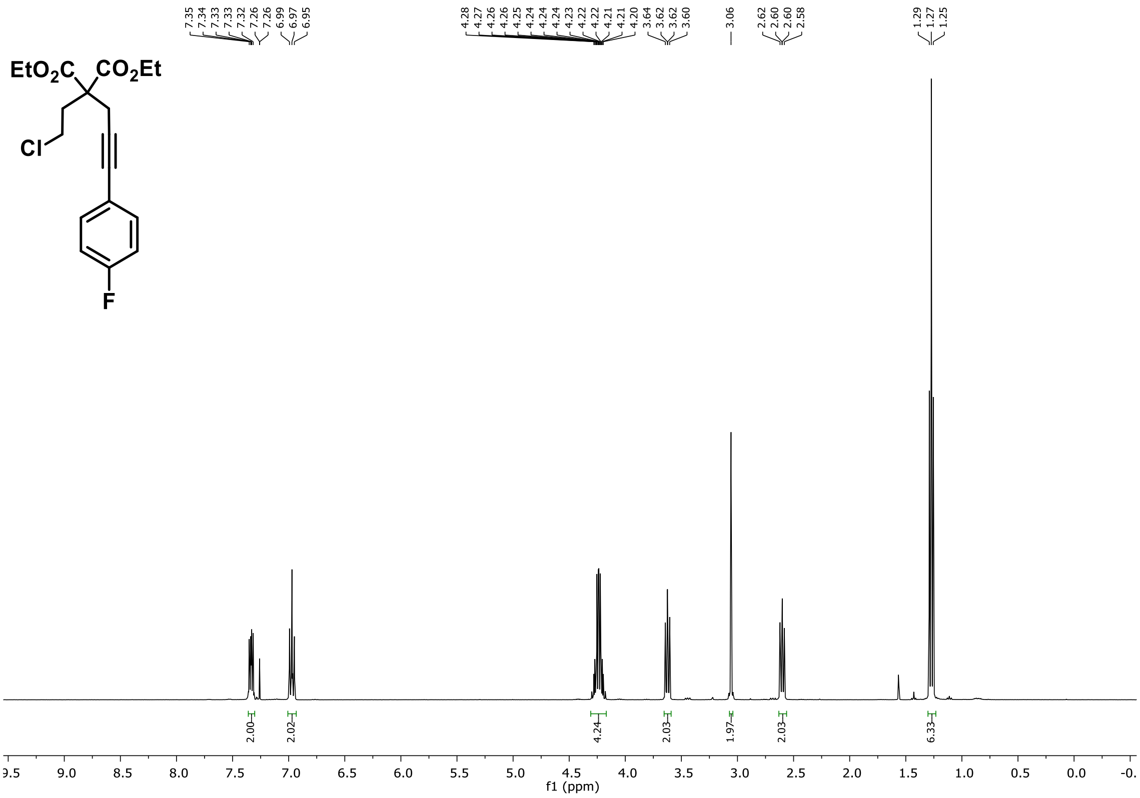

168.0
163.5
161.0
133.5
133.4
119.3
119.3
115.5
115.3
85.1
81.4
61.7
51.4
19.4
14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

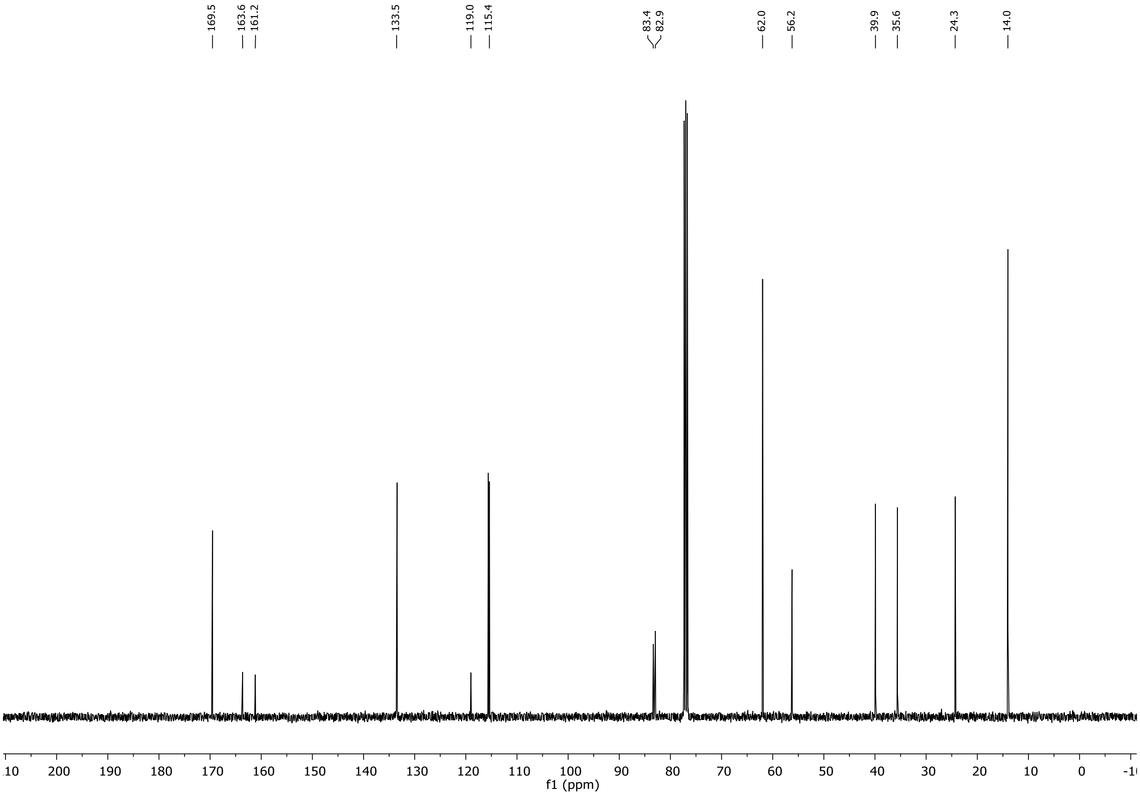

EtO₂C CO₂Et
Cl
OMe
7.30 7.30 7.29 7.28
6.82 6.79
4.30 4.28 4.27 4.26 4.26 4.25 4.24 4.24 4.23 4.23 4.22 4.22 4.21 4.20 4.19 4.18
3.80
3.65 3.63 3.63 3.63 3.61
3.05
2.63 2.61 2.61 2.59
1.29 1.27 1.26
2.00 2.05 4.17 2.98 2.08 1.98 2.06 6.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

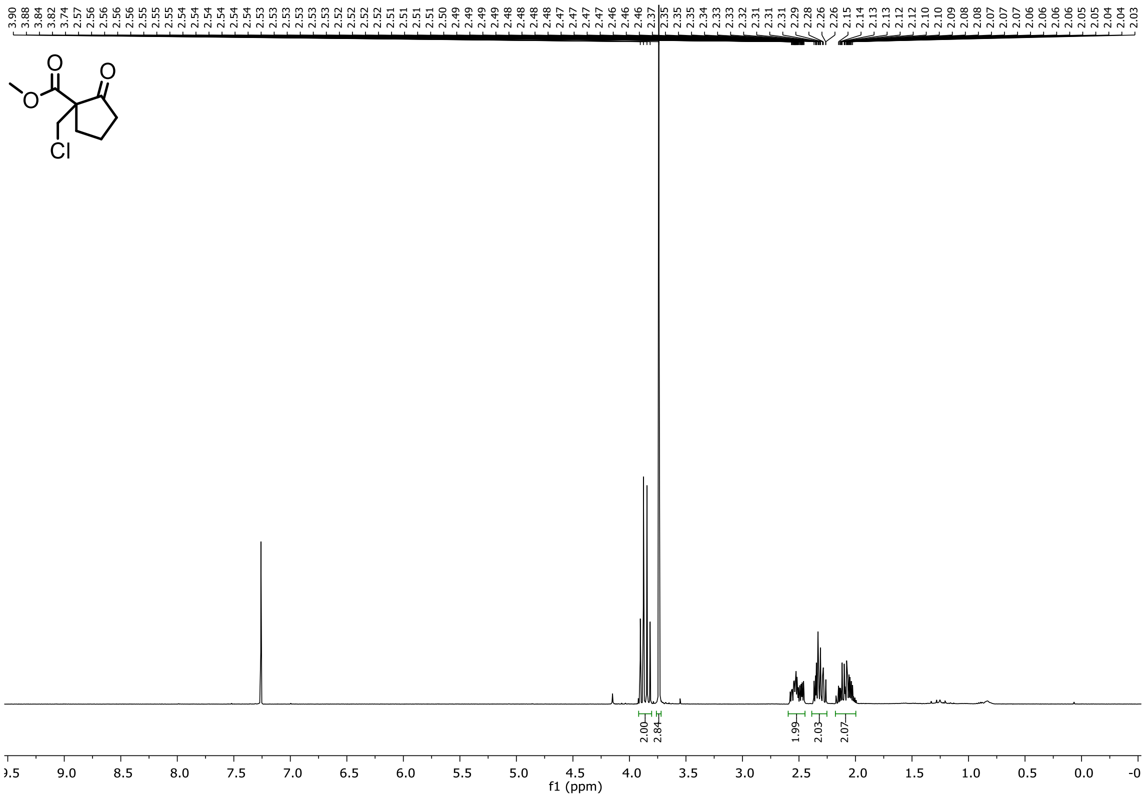

169.6
159.5
133.0
115.1 113.9
83.8 82.0
61.9
56.3 55.3
40.0
35.6
24.4
14.0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

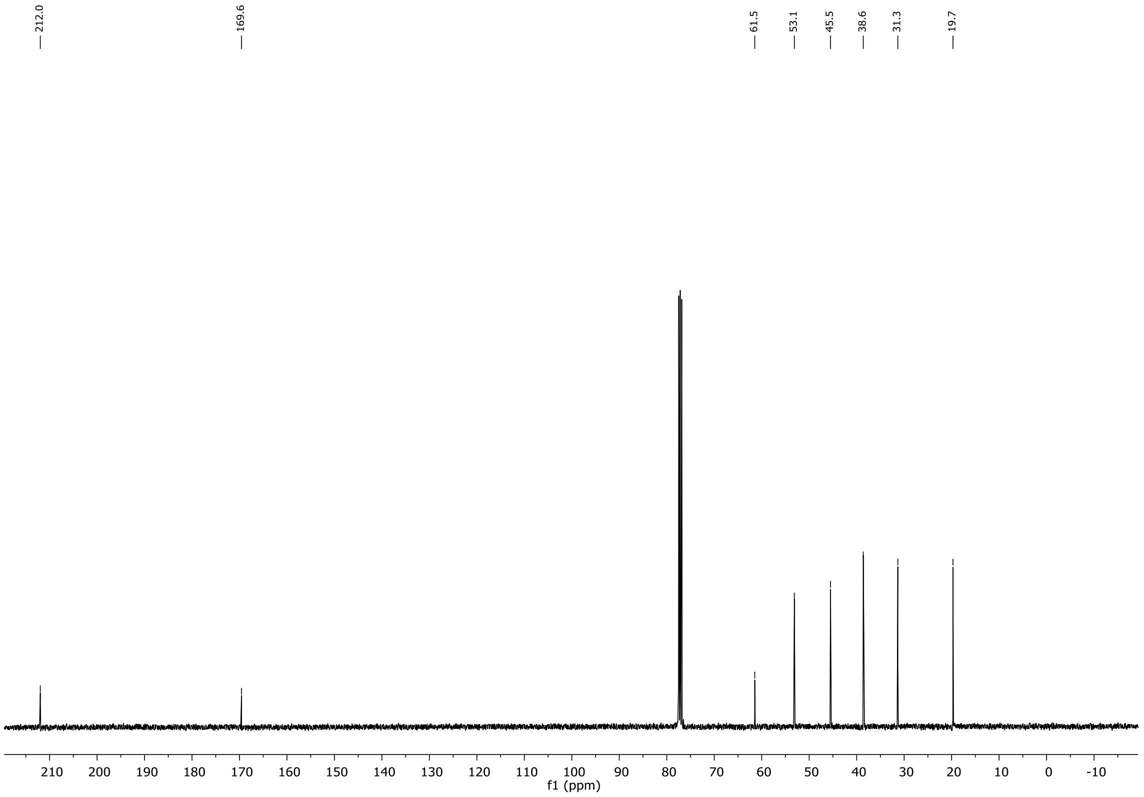

EtO2C
CO2Et
Cl
Cl
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
4.31
4.30
4.29
4.28
4.28
4.28
4.27
4.27
4.26
4.26
4.25
4.24
4.24
4.23
4.22
3.67
3.65
3.65
3.64
3.63
3.09
2.64
2.62
2.62
2.62
2.60
1.32
1.30
1.28
4.32
4.00
1.90
1.88
1.90
6.56
f1 (ppm)

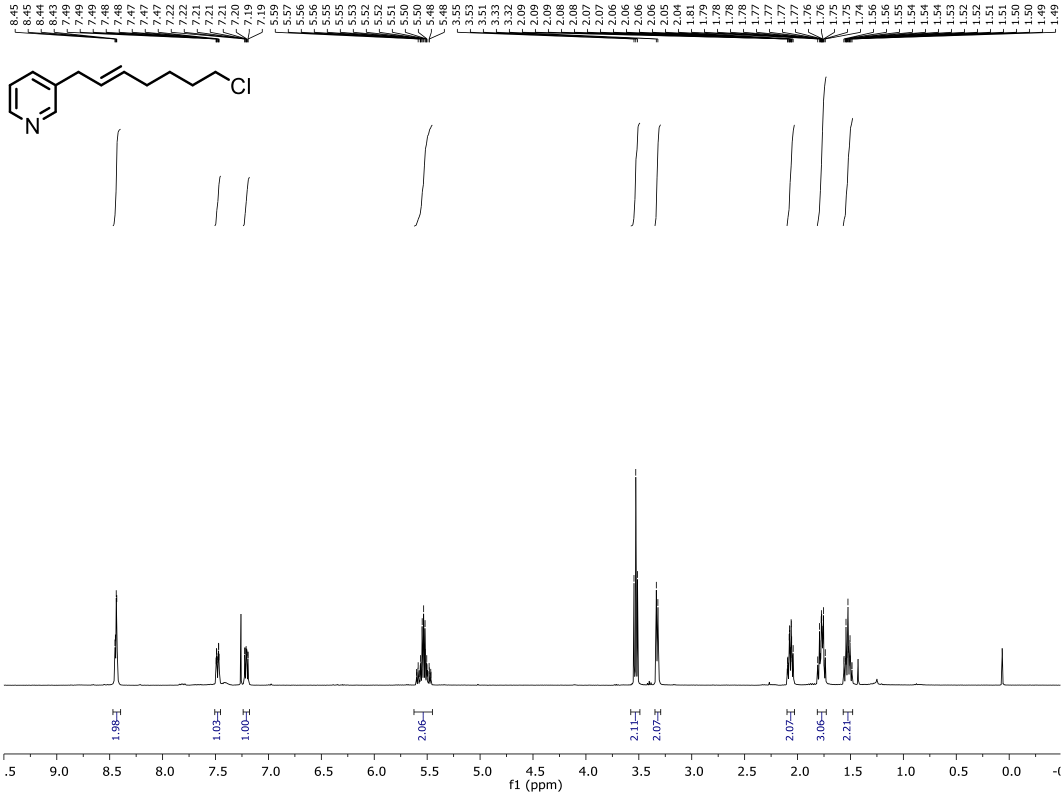

169.5
134.2
132.9
128.6
121.4
84.8
82.9
62.0
56.2
39.9
35.6
24.4
14.0
f1 (ppm)

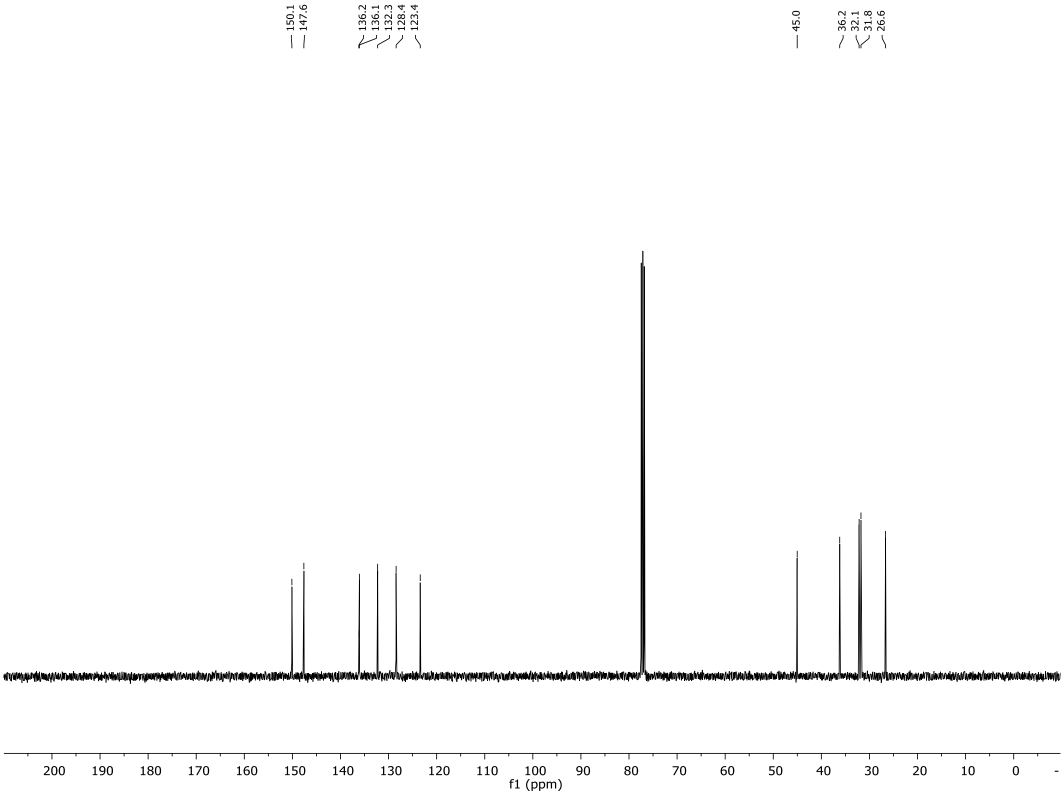

EtO$_2$C
CO$_2$Et
Cl
F
7.35
7.34
7.33
7.33
7.32
7.26
7.26
6.99
6.97
6.95
4.28
4.27
4.26
4.26
4.25
4.24
4.24
4.24
4.23
4.22
4.22
4.21
4.21
4.20
3.64
3.62
3.62
3.60
3.06
2.62
2.60
2.60
2.58
1.29
1.27
1.25
2.00
2.02
4.24
2.03
1.97
2.03
6.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

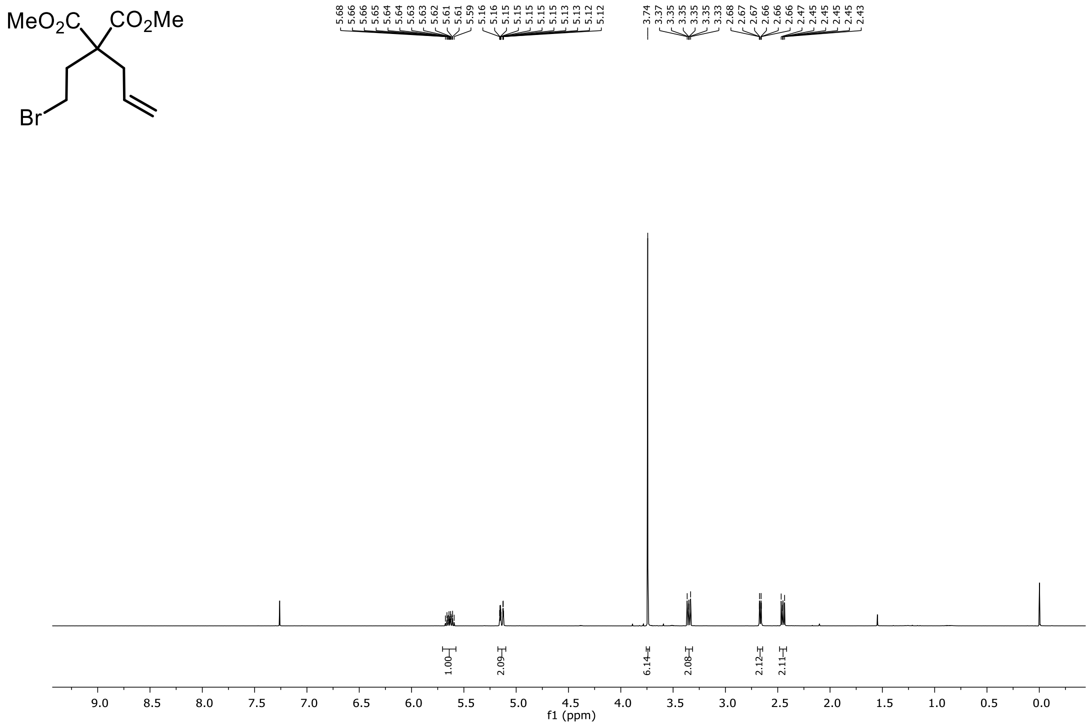

169.5
163.6
161.2
133.5
119.0
115.4
83.4
82.9
62.0
56.2
39.9
35.6
24.3
14.0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

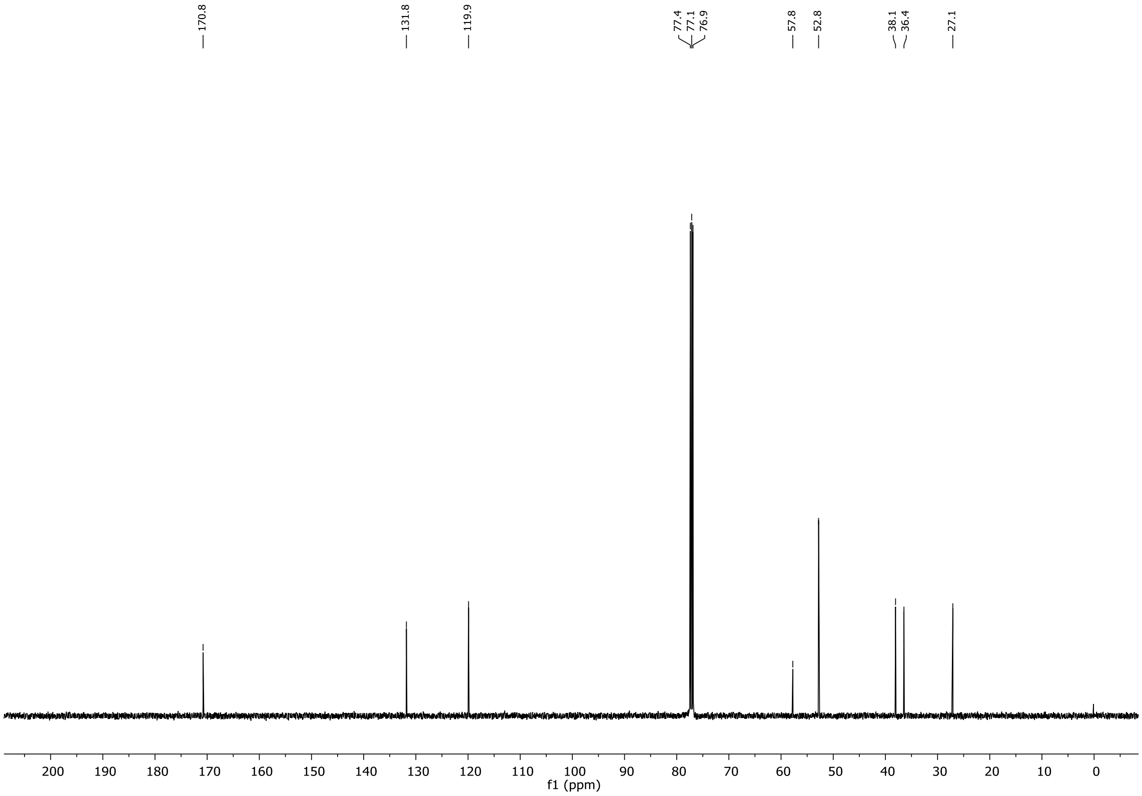

3.90 3.88 3.84 3.82 3.74 2.57 2.56 2.56 2.56 2.55 2.55 2.55 2.54 2.54 2.54 2.54 2.54 2.53 2.53 2.53 2.53 2.53 2.53 2.52 2.52 2.52 2.51 2.51 2.51 2.50 2.49 2.49 2.49 2.49 2.48 2.48 2.48 2.48 2.47 2.47 2.47 2.47 2.46 2.46 2.46 2.37 2.35 2.35 2.35 2.34 2.33 2.33 2.32 2.31 2.31 2.31 2.29 2.28 2.26 2.26 2.15 2.14 2.13 2.13 2.13 2.12 2.12 2.10 2.10 2.09 2.08 2.07 2.07 2.07 2.06 2.06 2.06 2.06 2.05 2.05 2.04 2.04 2.03
O
O
O
Cl
2.00
2.84
1.99
2.03
2.07
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
f1 (ppm)


212.0
169.6
61.5
53.1
45.5
38.6
31.3
19.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

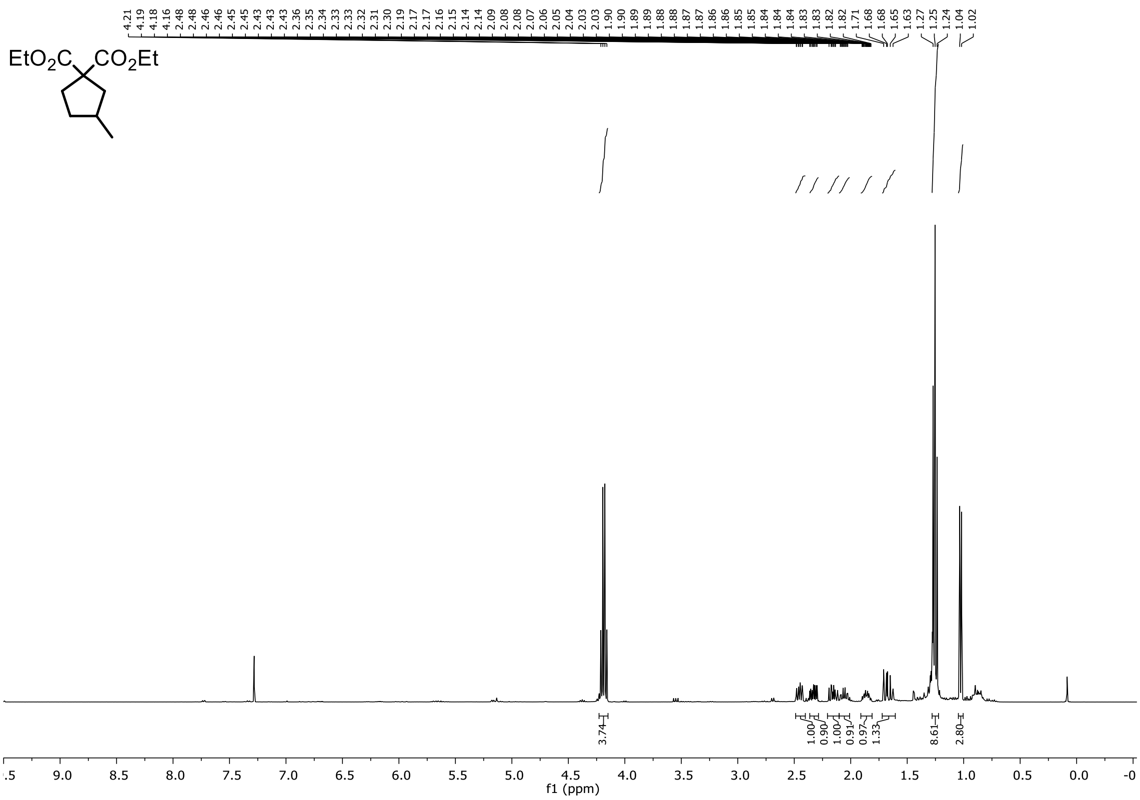

8.45
8.45
8.44
8.43
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.22
7.21
7.21
7.21
7.20
7.19
7.19
5.59
5.57
5.56
5.56
5.55
5.55
5.55
5.53
5.52
5.52
5.51
5.50
5.50
5.48
5.48
3.55
3.53
3.51
3.33
3.32
2.09
2.09
2.09
2.08
2.08
2.07
2.07
2.06
2.06
2.06
2.06
2.05
2.04
1.81
1.79
1.78
1.78
1.78
1.77
1.77
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.56
1.56
1.55
1.54
1.54
1.54
1.53
1.52
1.52
1.51
1.51
1.50
1.50
1.49
1.49
N
Cl
1.98
1.03
1.00
2.06
2.11
2.07
2.07
3.06
2.21
.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)

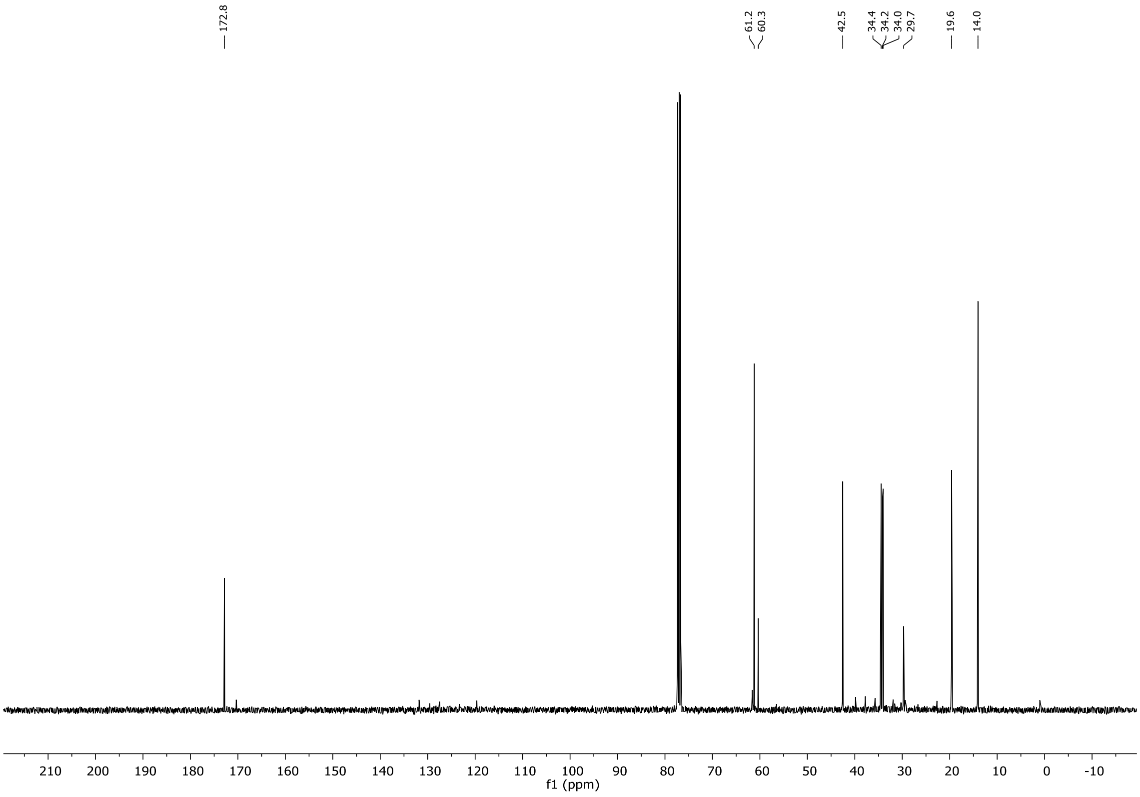

150.1
147.6
136.2
136.1
132.3
128.4
123.4
45.0
36.2
32.1
31.8
26.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

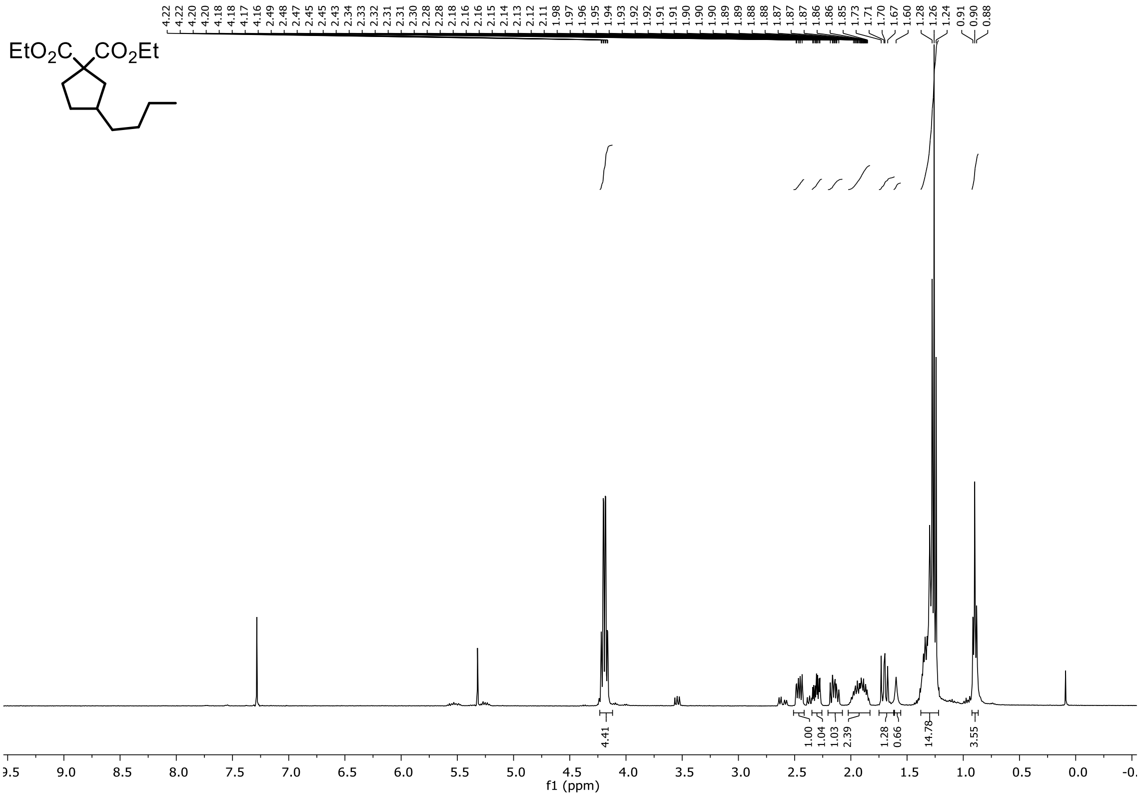

MeO$_2$C
CO$_2$Me
Br
5.68
5.66
5.65
5.64
5.64
5.63
5.63
5.62
5.61
5.61
5.59
5.16
5.16
5.15
5.15
5.15
5.15
5.15
5.13
5.13
5.12
5.12
3.74
3.37
3.35
3.35
3.35
3.35
3.33
2.68
2.67
2.67
2.66
2.66
2.47
2.45
2.45
2.45
2.45
2.43
1.00
2.09
6.14
2.08
2.12
2.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

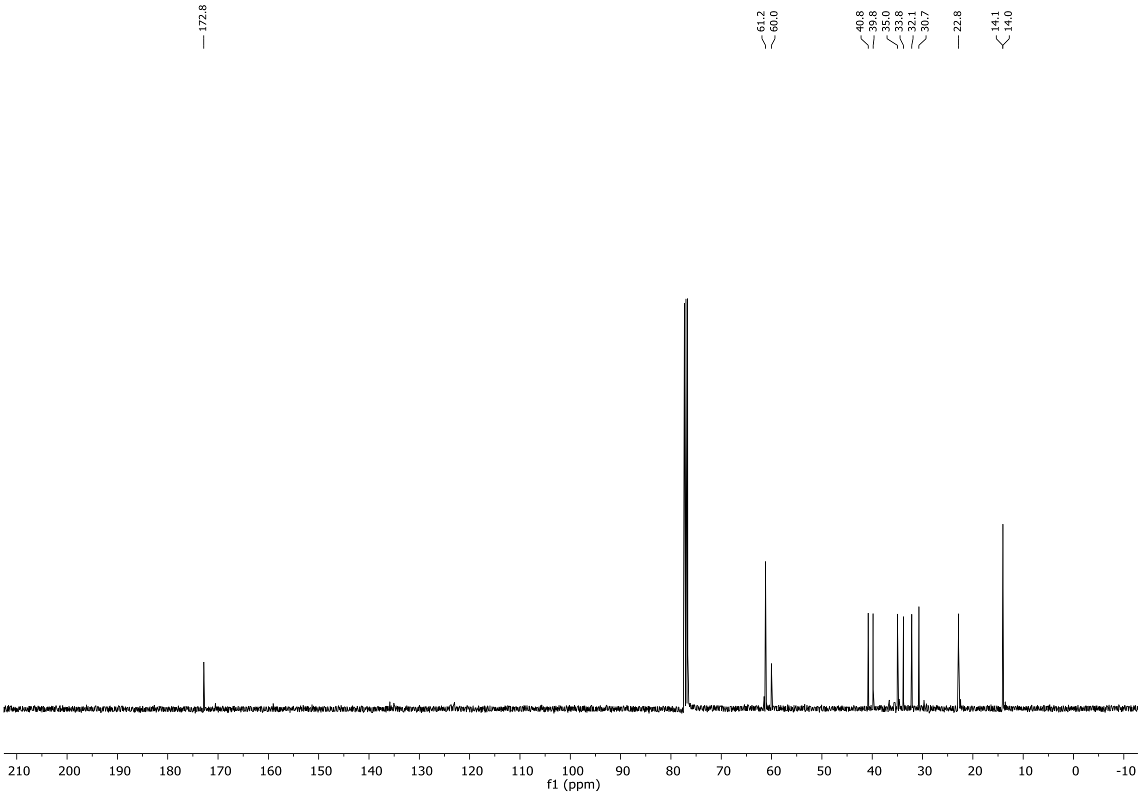

170.8
131.8
119.9
77.4
77.1
76.9
57.8
52.8
38.1
36.4
27.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

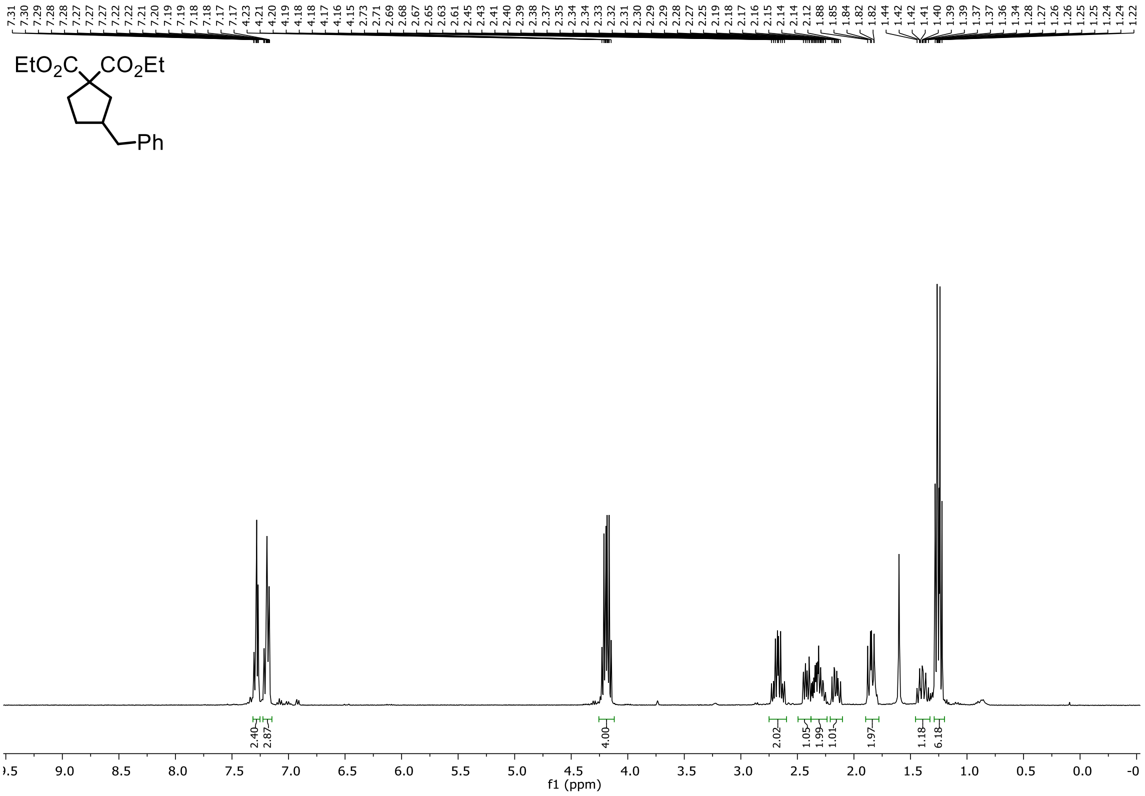
3. Spectra of products

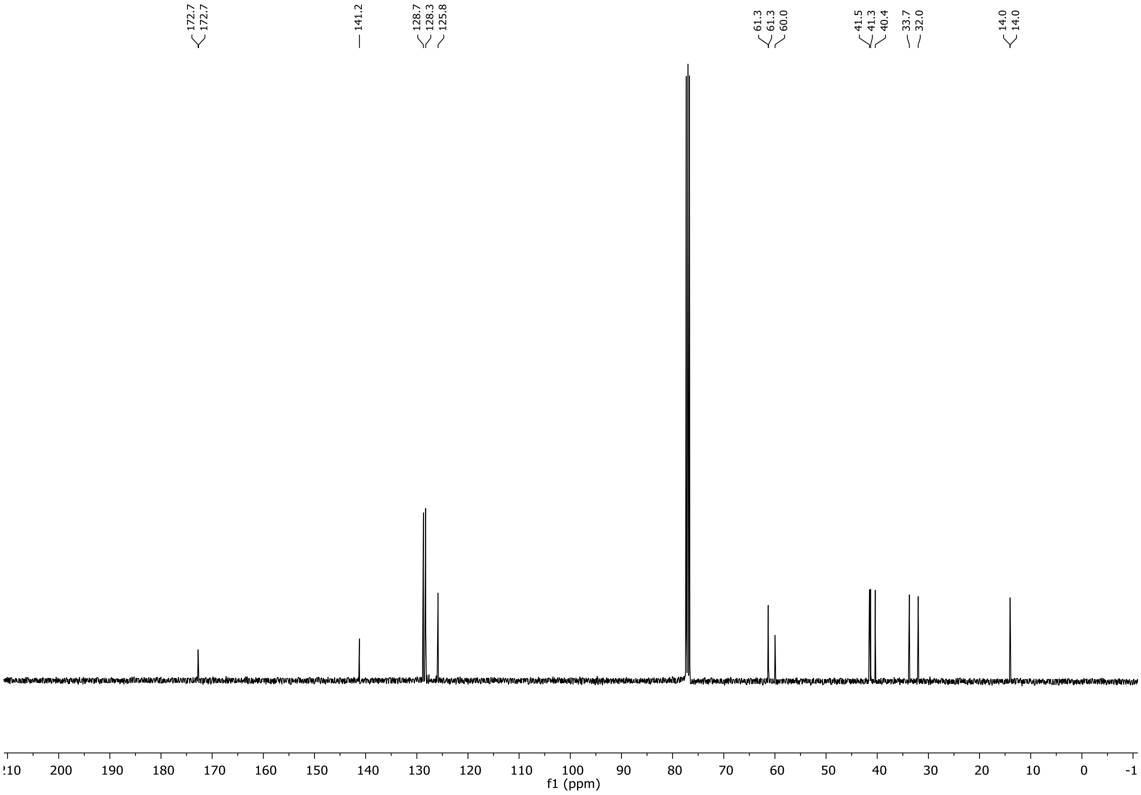


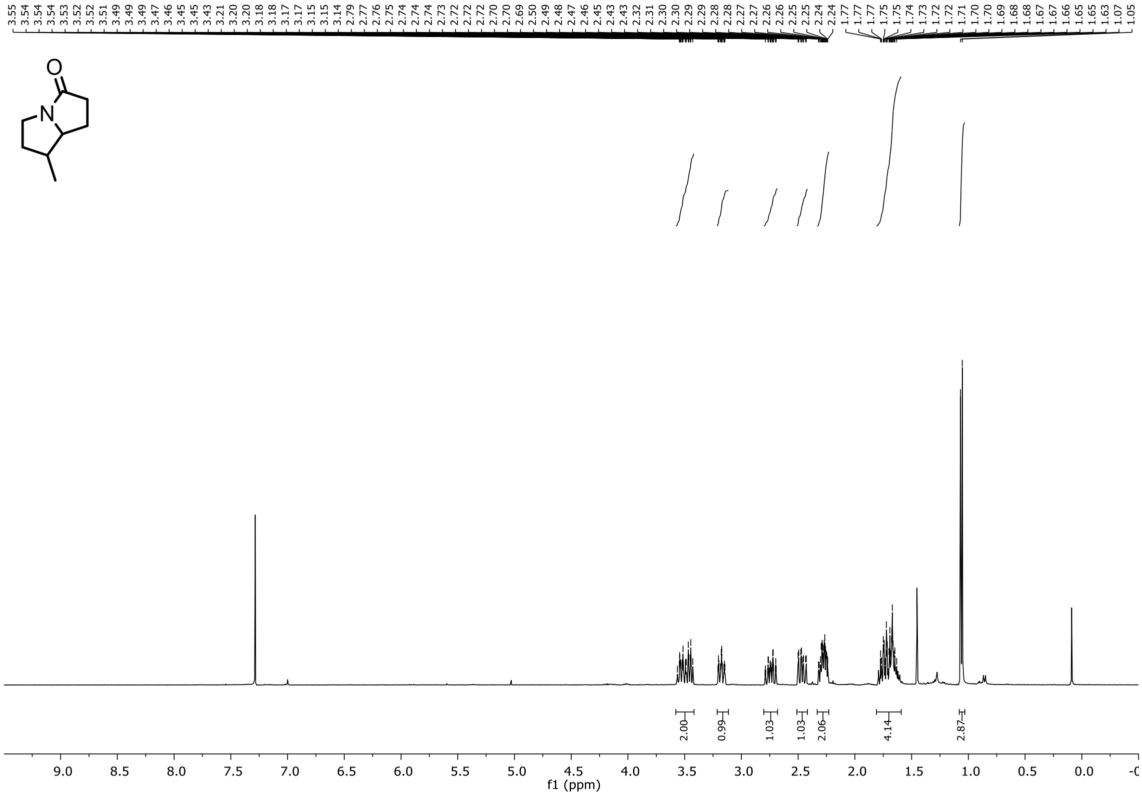


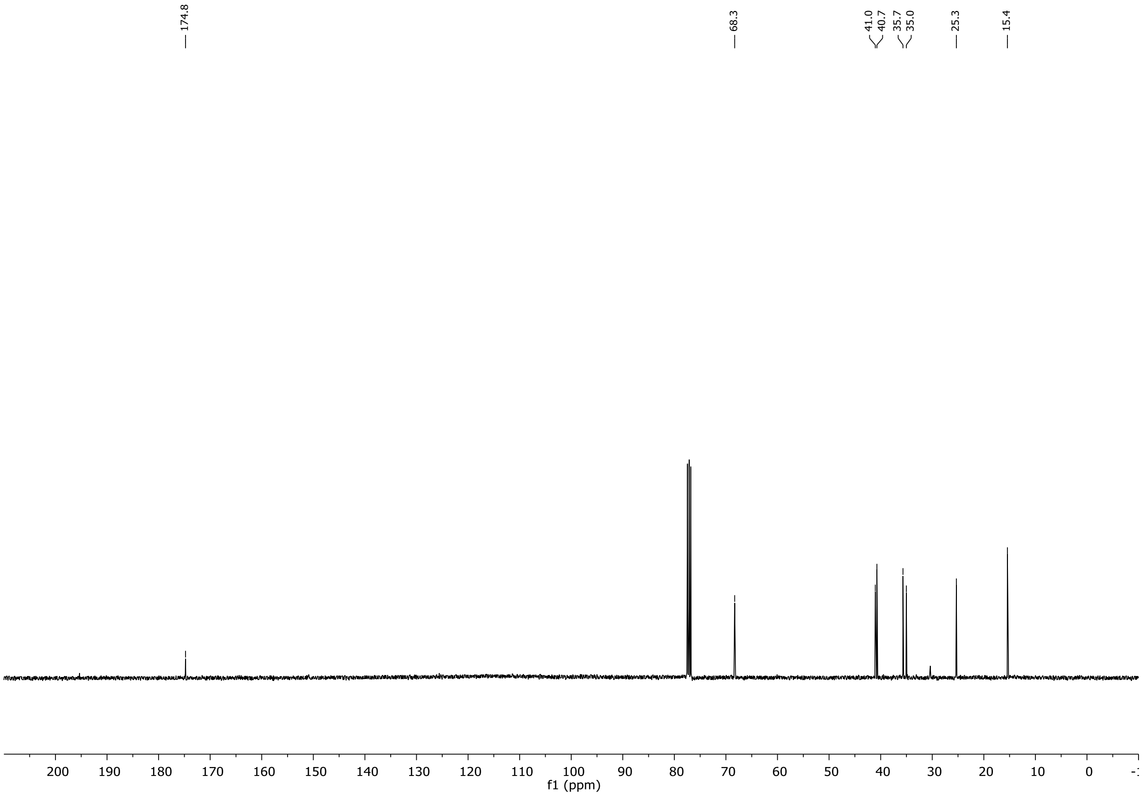

EtO2C CO2Et
4.22
4.22
4.20
4.20
4.18
4.18
4.17
4.16
2.49
2.48
2.47
2.45
2.45
2.43
2.34
2.33
2.32
2.31
2.31
2.30
2.28
2.28
2.18
2.16
2.16
2.15
2.14
2.13
2.12
2.11
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.92
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.87
1.86
1.86
1.85
1.73
1.71
1.70
1.67
1.60
1.28
1.26
1.24
0.91
0.90
0.88
4.41
1.00
1.04
1.03
2.39
1.28
0.66
14.78
3.55
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.
f1 (ppm)

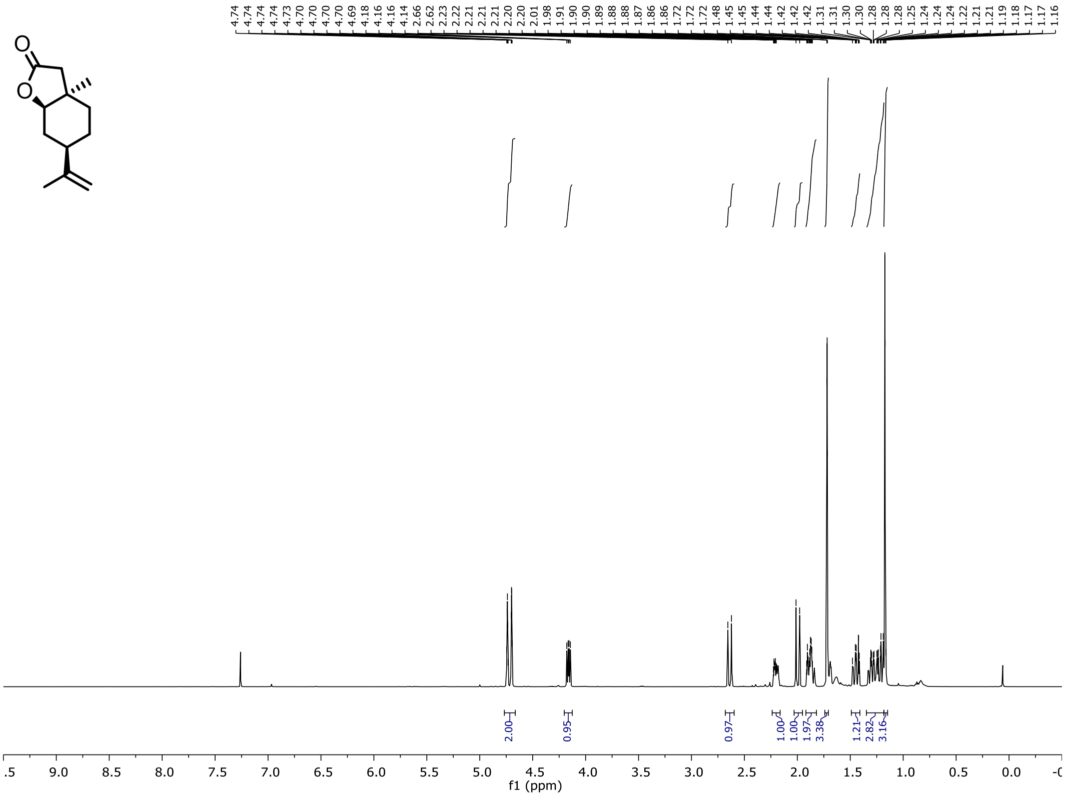

172.8
61.2
60.0
40.8
39.8
35.0
33.8
32.1
30.7
22.8
14.1
14.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

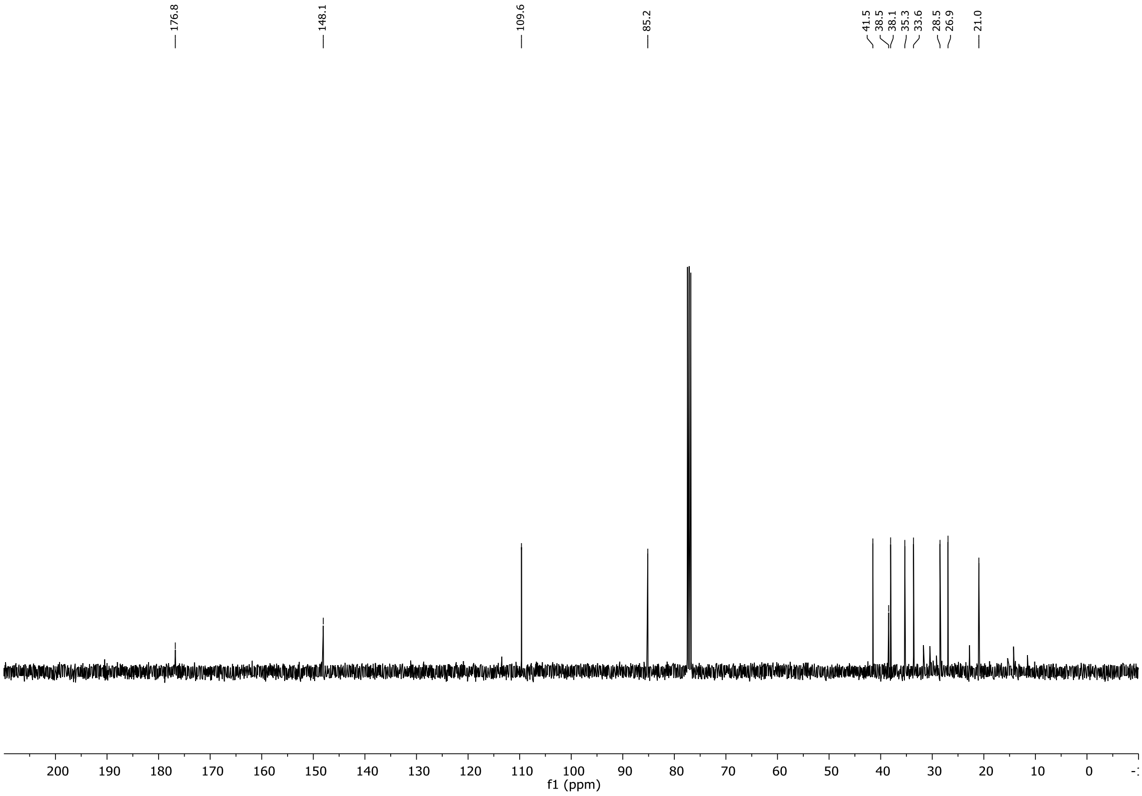

7.31 7.30 7.29 7.28 7.28 7.27 7.27 7.27 7.22 7.22 7.21 7.20 7.19 7.19 7.18 7.18 7.17 7.17 4.23 4.21 4.20 4.19 4.18 4.18 4.17 4.16 4.15 2.73 2.71 2.69 2.68 2.67 2.65 2.63 2.61 2.45 2.43 2.41 2.40 2.39 2.38 2.37 2.35 2.34 2.34 2.33 2.32 2.31 2.30 2.29 2.29 2.28 2.27 2.25 2.19 2.18 2.17 2.16 2.15 2.14 2.14 2.12 1.88 1.85 1.84 1.82 1.82 1.44 1.42 1.42 1.41 1.40 1.39 1.39 1.37 1.37 1.36 1.34 1.28 1.27 1.26 1.26 1.25 1.25 1.24 1.24 1.22
EtO2C
CO2Et
Ph
2.40
2.87
4.00
2.02
1.05
1.99
1.01
1.97
1.18
6.18
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
f1 (ppm)

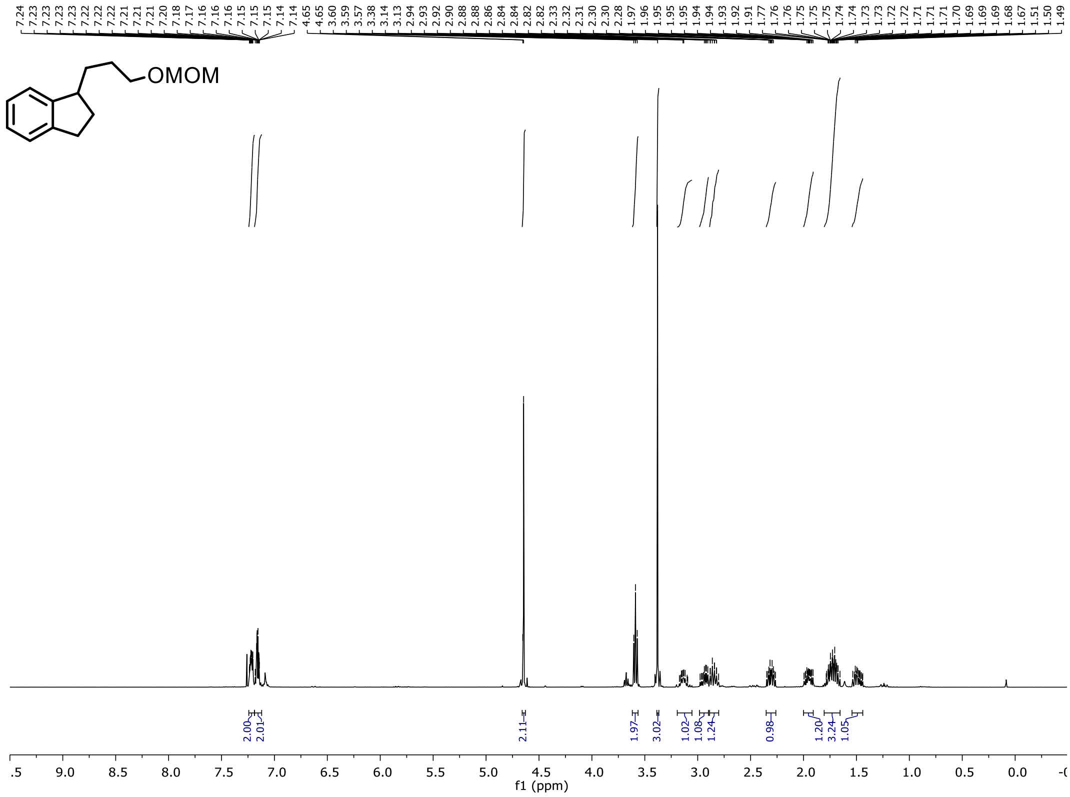

172.7 172.7
141.2
128.7 128.3 125.8
61.3 61.3 60.0
41.5 41.3 40.4
33.7 32.0
14.0 14.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


O
N
3.55 3.54 3.54 3.54 3.53 3.52 3.52 3.51 3.49 3.49 3.49 3.47 3.46 3.45 3.45 3.43 3.21 3.20 3.20 3.18 3.18 3.17 3.17 3.15 3.15 3.14 2.79 2.77 2.76 2.75 2.74 2.74 2.74 2.73 2.72 2.72 2.72 2.70 2.70 2.69 2.50 2.49 2.48 2.47 2.46 2.45 2.43 2.43 2.32 2.31 2.30 2.30 2.29 2.29 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.24 2.24 1.77 1.77 1.77 1.75 1.75 1.74 1.73 1.72 1.72 1.71 1.70 1.70 1.69 1.68 1.68 1.67 1.67 1.66 1.65 1.65 1.63 1.07 1.05
2.00
0.99
1.03
1.03
2.06
4.14
2.87
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
f1 (ppm)


174.8
68.3
41.0
40.7
35.7
35.0
25.3
15.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
4.74
4.74
4.74
4.74
4.73
4.70
4.70
4.70
4.69
4.18
4.16
4.16
4.14
2.66
2.62
2.23
2.22
2.21
2.21
2.21
2.20
2.20
2.01
1.98
1.91
1.90
1.89
1.88
1.88
1.87
1.86
1.86
1.72
1.72
1.72
1.48
1.45
1.45
1.44
1.44
1.42
1.42
1.42
1.31
1.31
1.30
1.30
1.28
1.28
1.28
1.25
1.24
1.24
1.24
1.22
1.21
1.21
1.19
1.18
1.17
1.17
1.16
2.00
0.95
0.97
1.00
1.00
1.97
3.38
1.21
2.82
3.16
.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)


176.8
148.1
109.6
85.2
41.5
38.5
38.1
35.3
33.6
28.5
26.9
21.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:
f1 (ppm)


7.24
7.23
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.18
7.17
7.16
7.16
7.15
7.15
7.15
7.14
7.14
4.65
4.65
3.60
3.59
3.57
3.38
3.14
3.13
2.94
2.93
2.92
2.90
2.88
2.88
2.86
2.84
2.84
2.82
2.82
2.33
2.32
2.31
2.30
2.30
2.28
1.97
1.96
1.95
1.95
1.95
1.94
1.94
1.93
1.92
1.91
1.77
1.76
1.75
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.71
1.71
1.71
1.70
1.69
1.69
1.68
1.67
1.51
1.50
1.49
OMOM
2.00
2.01
2.11
1.97
3.02
1.02
1.08
1.24
0.98
1.20
3.24
1.05
.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
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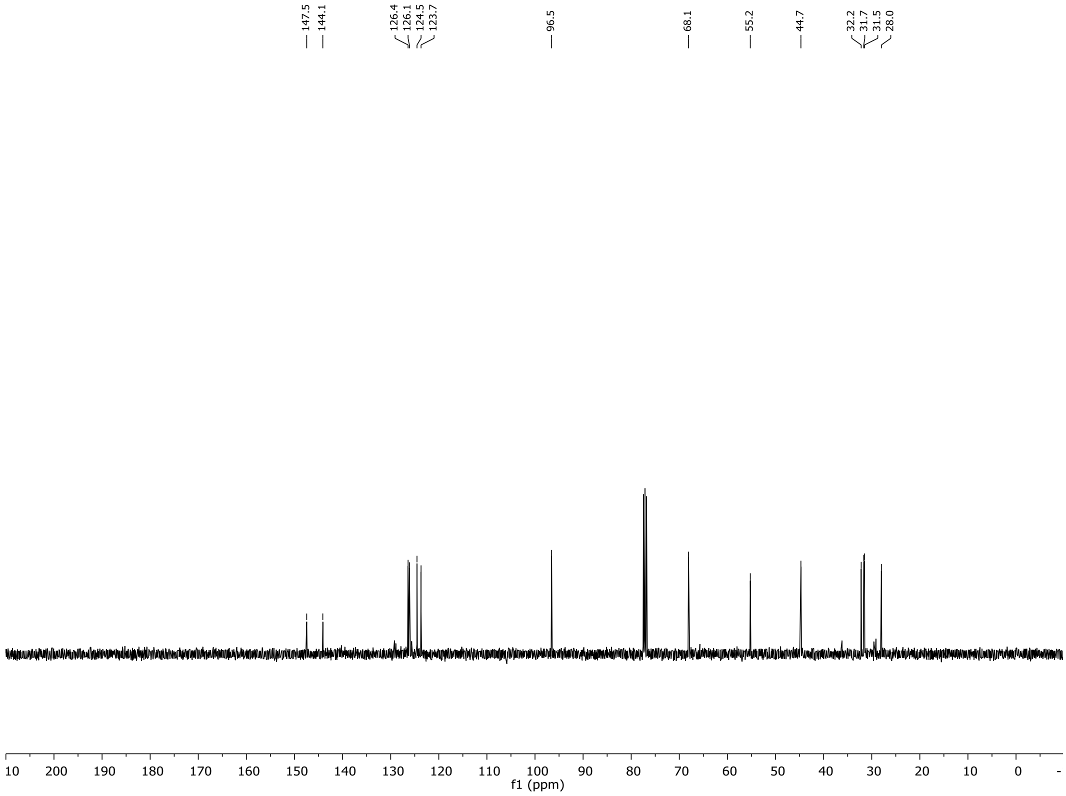
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31.5
28.0
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200
190
180
170
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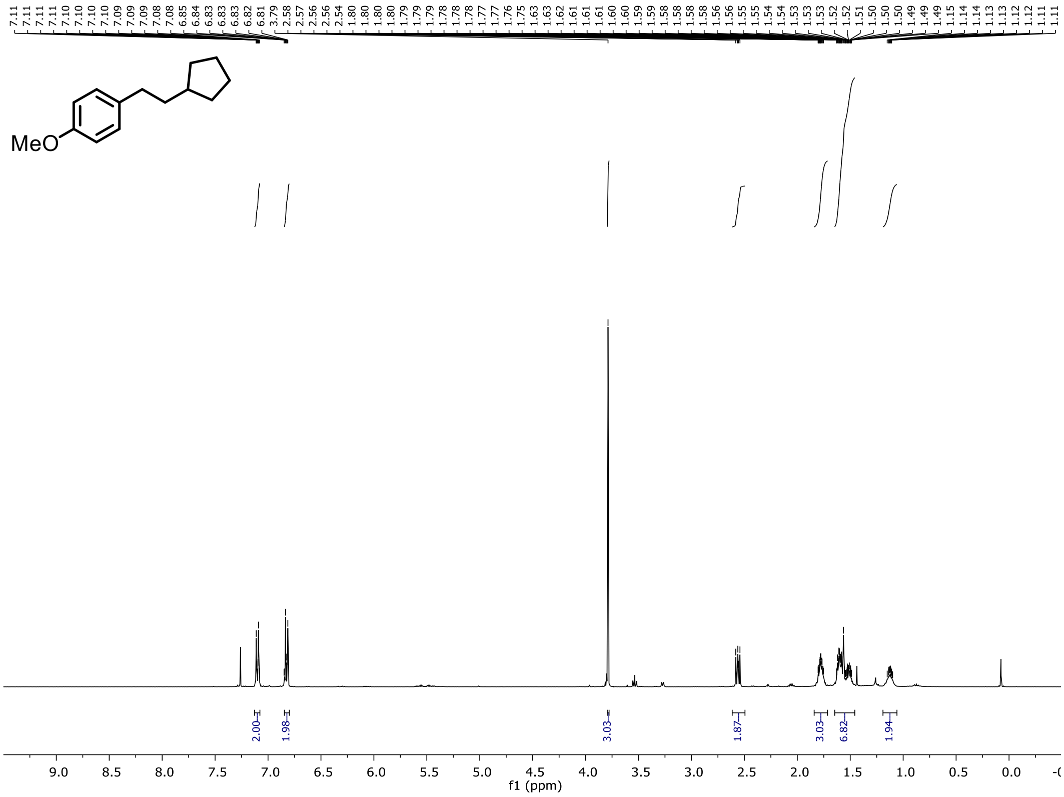
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1.12
1.12
1.11
1.11
MeO
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1.87
3.03
6.82
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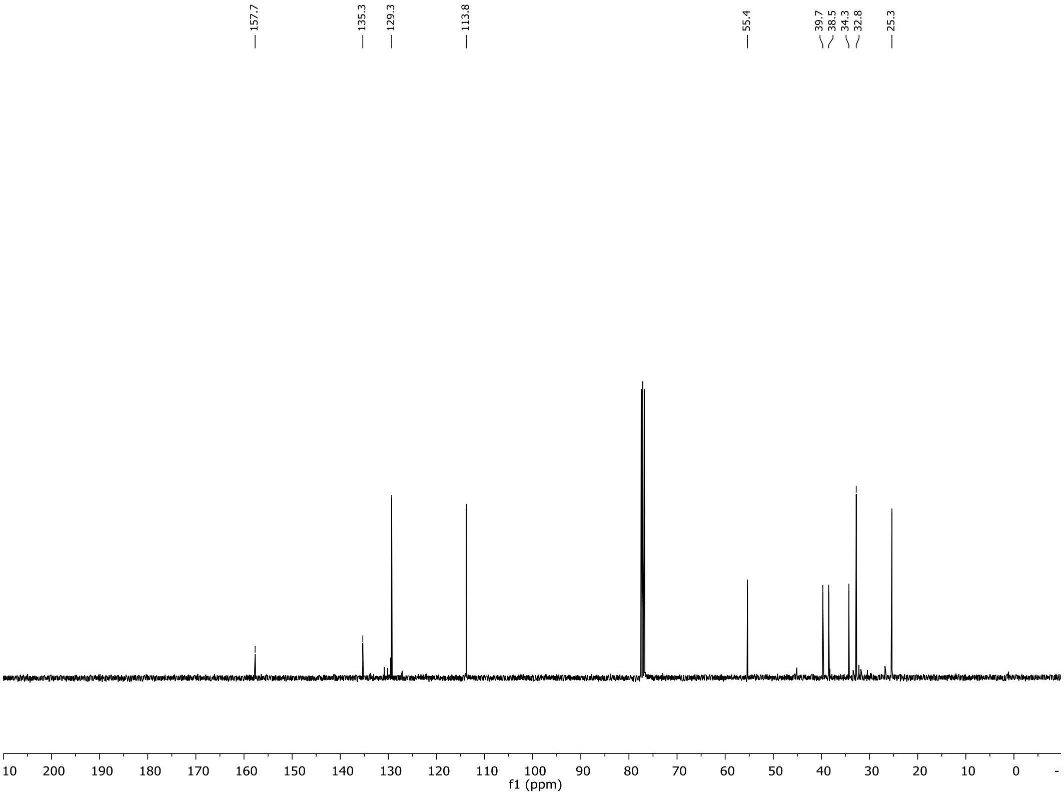
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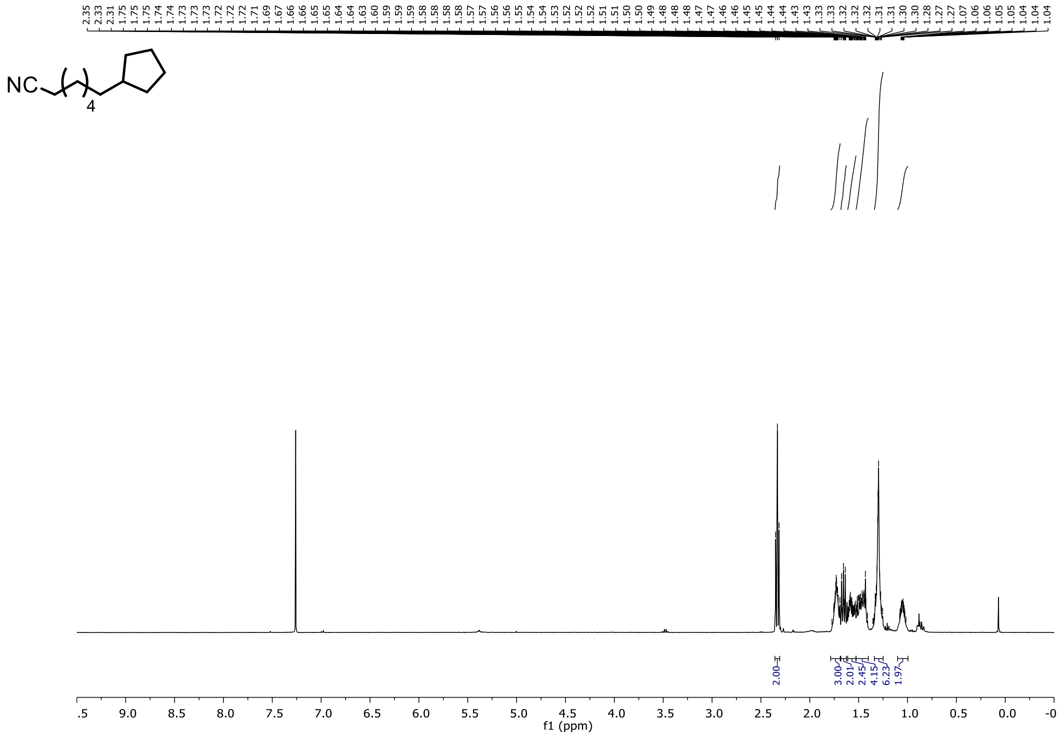
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1.05
1.05
1.04
1.04
1.04
2.00
3.00
2.01
2.45
4.15
6.23
1.97
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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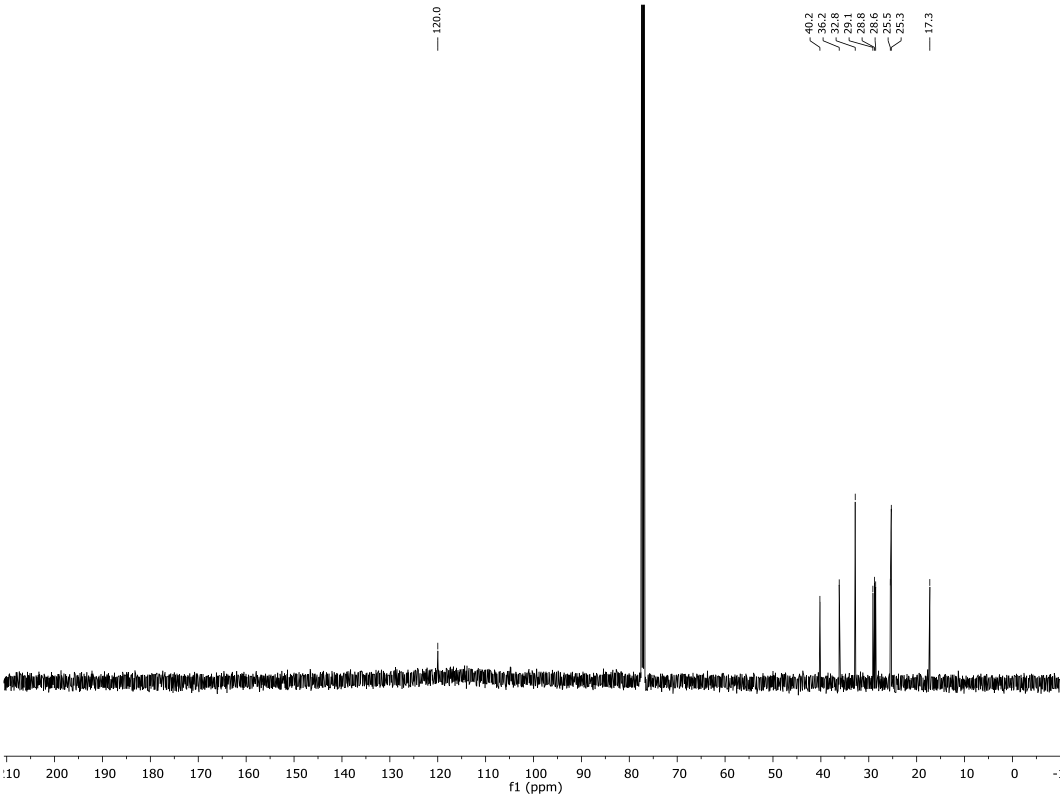
f1 (ppm)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190
180
170
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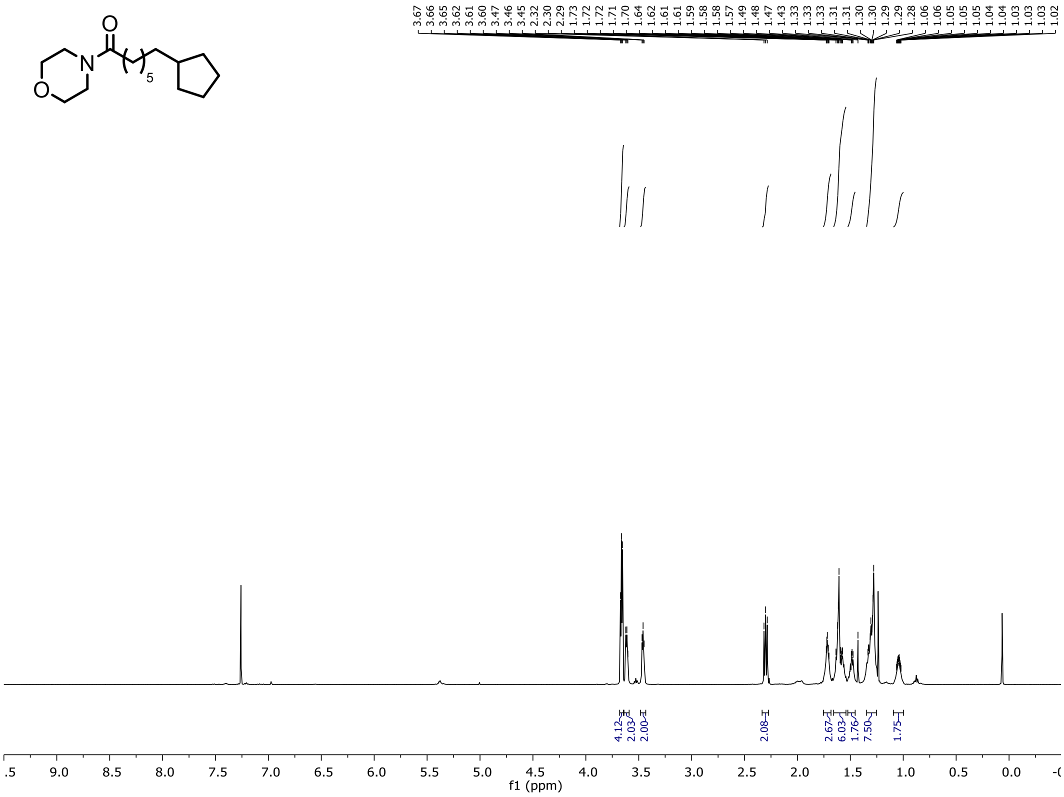
-:
f1 (ppm)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2.30
2.29
1.73
1.72
1.72
1.71
1.70
1.64
1.62
1.61
1.61
1.59
1.58
1.58
1.57
1.49
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1.47
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1.30
1.30
1.29
1.29
1.28
1.06
1.06
1.05
1.05
1.05
1.04
1.04
1.03
1.03
1.03
1.02
4.12
2.03
2.00
2.08
2.67
6.03
1.76
7.50
1.75
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
1.0
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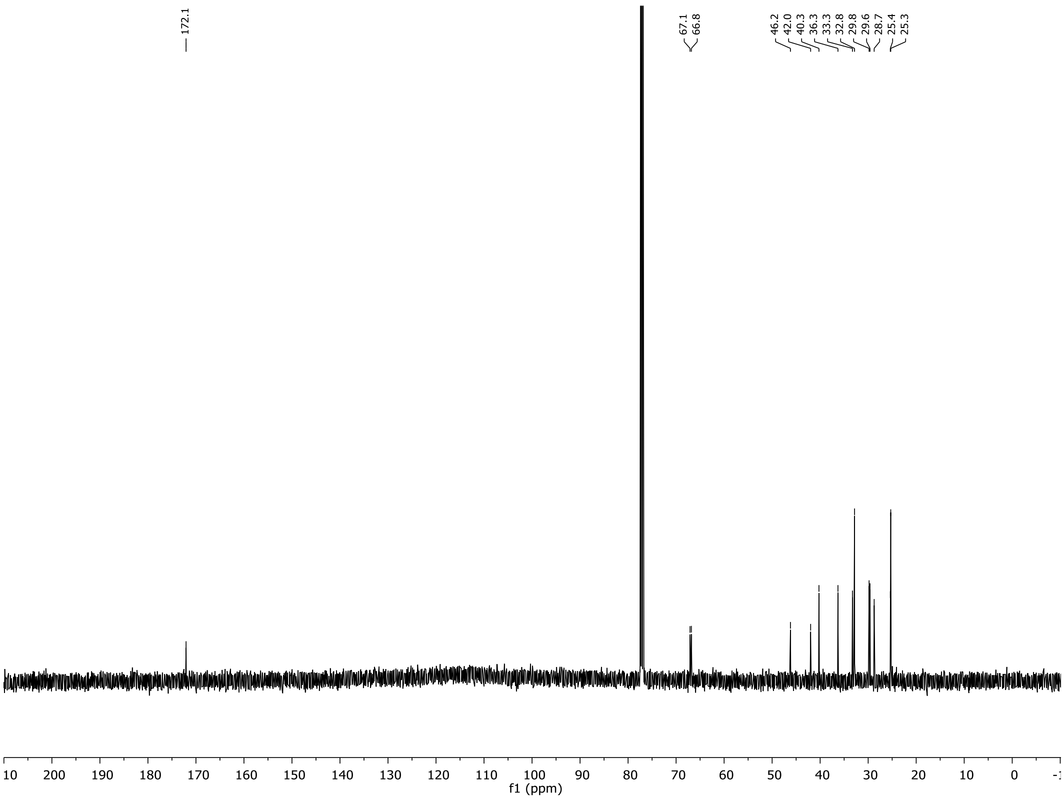
f1 (ppm)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67.1
66.8
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36.3
33.3
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29.8
29.6
28.7
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25.3
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200
190
180
170
160
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140
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120
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100
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80
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20
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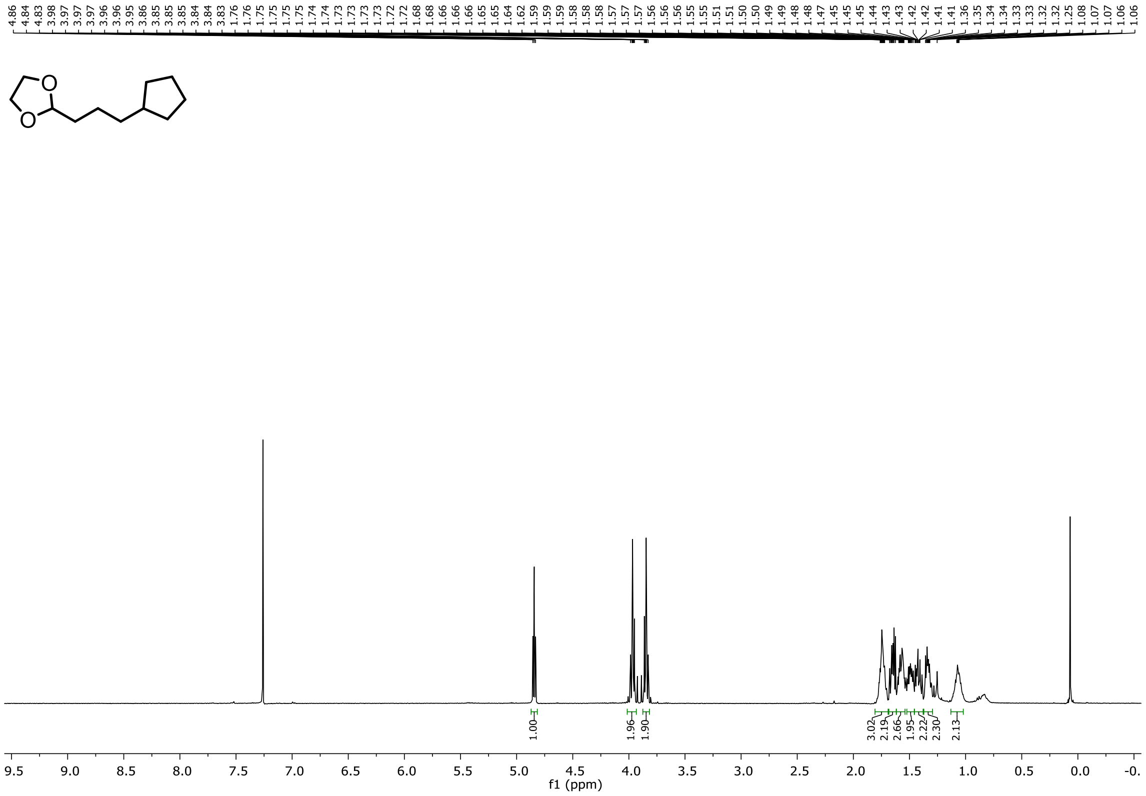
-1
f1 (ppm)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3.86
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3.85
3.85
3.84
3.84
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1.06
1.06
O
O
1.00
1.96
1.90
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1.95
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2.30
2.13
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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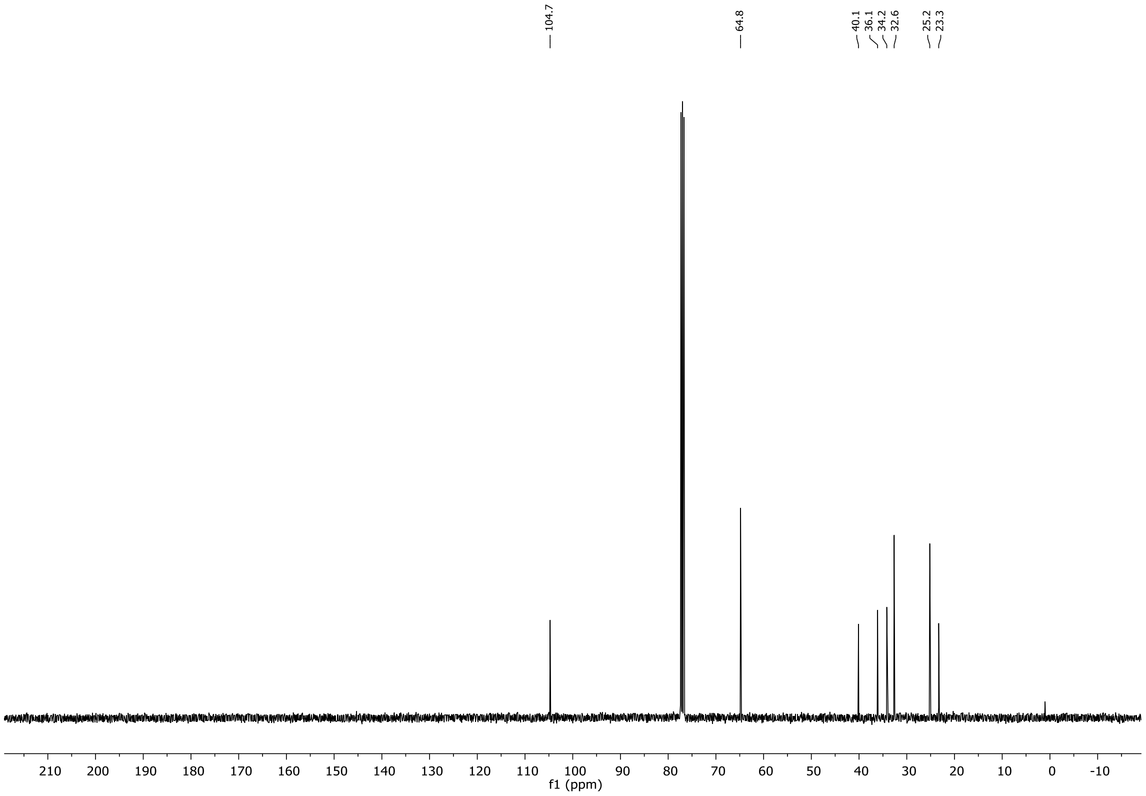
f1 (ppm)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36.1
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23.3
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180
170
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140
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120
110
100
90
80
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40
30
20
10
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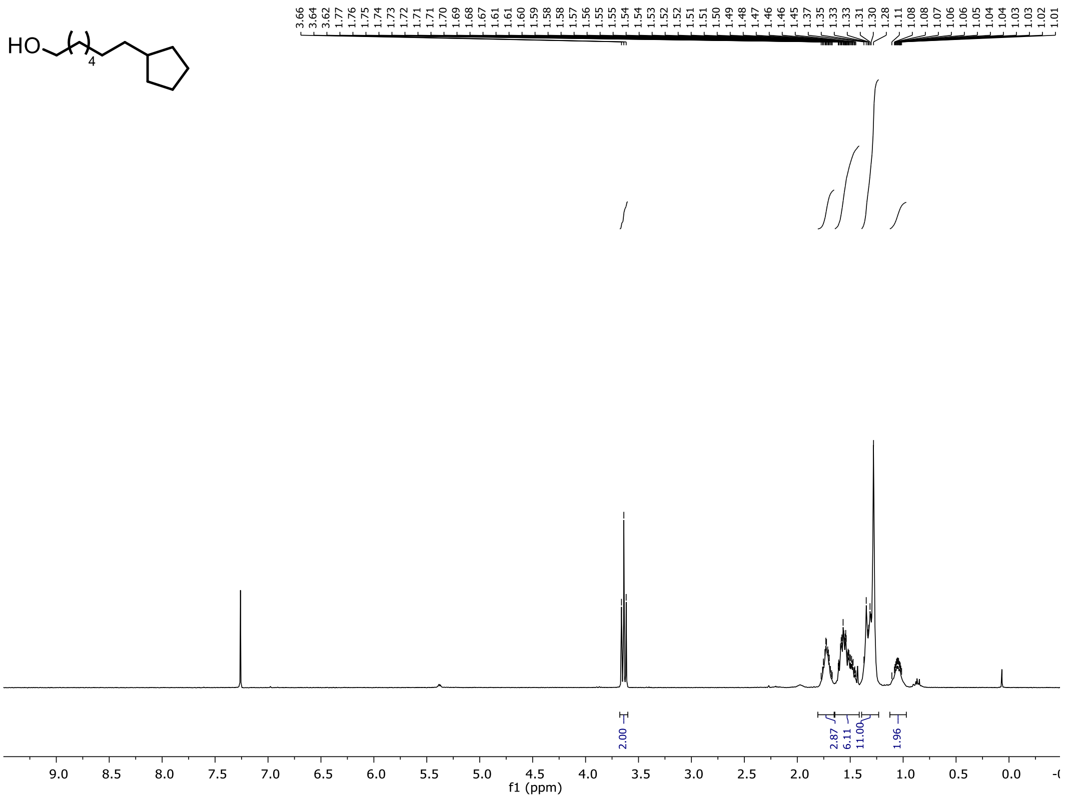
-10
f1 (ppm)


HO
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1.08
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1.06
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1.02
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11.00
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8.0
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1.0
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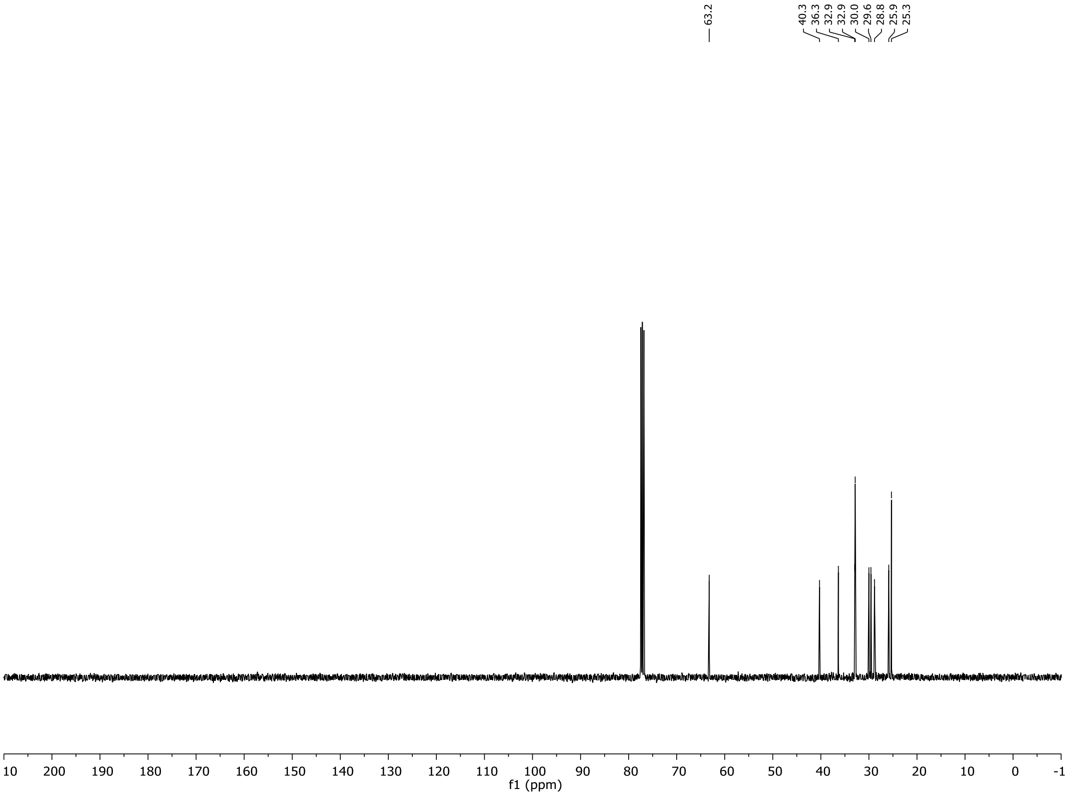
0.0
f1 (ppm)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25.3
10
200
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180
170
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140
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120
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100
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80
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60
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40
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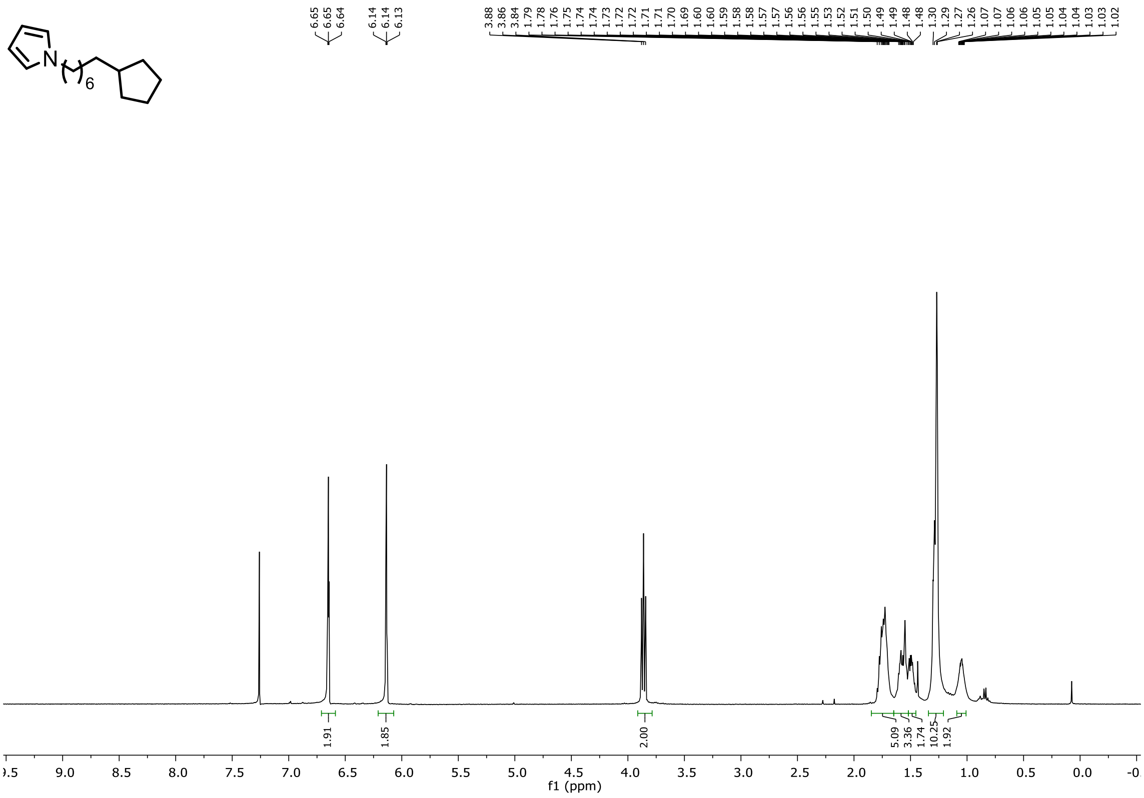
20
10
0
-1
f1 (ppm)


N
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1.29
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1.07
1.07
1.06
1.06
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1.04
1.04
1.03
1.03
1.02
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2.00
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3.36
1.74
10.25
1.92
9.5
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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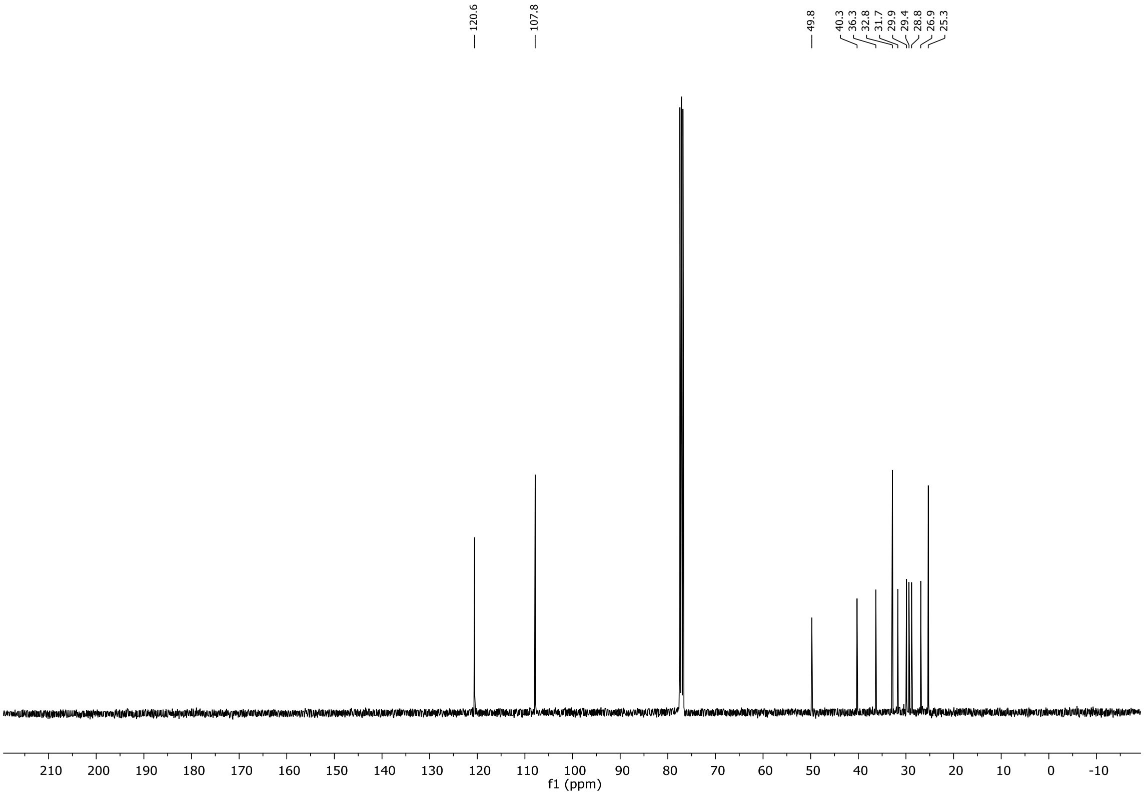
f1 (ppm)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29.9
29.4
28.8
26.9
25.3
210
200
190
180
170
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140
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120
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100
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80
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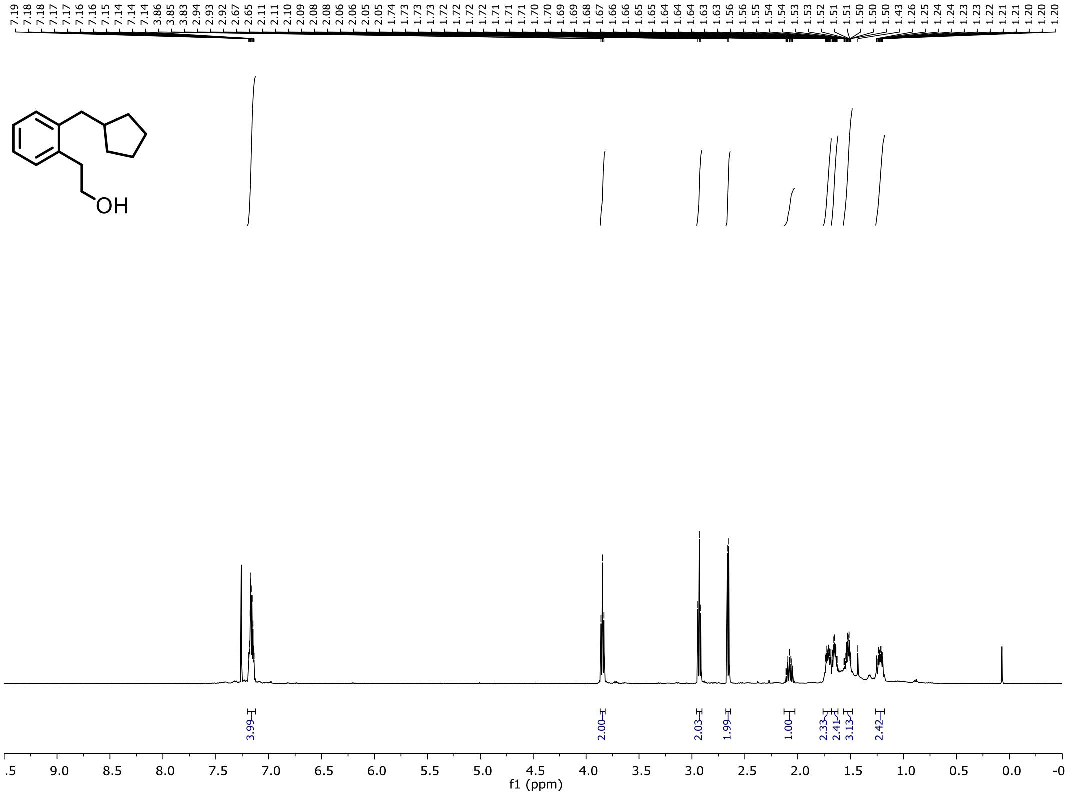
30
20
10
0
-10
f1 (ppm)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7.14
7.14
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2.11
2.11
2.10
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2.08
2.06
2.06
2.05
2.05
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1.20
OH
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5.0
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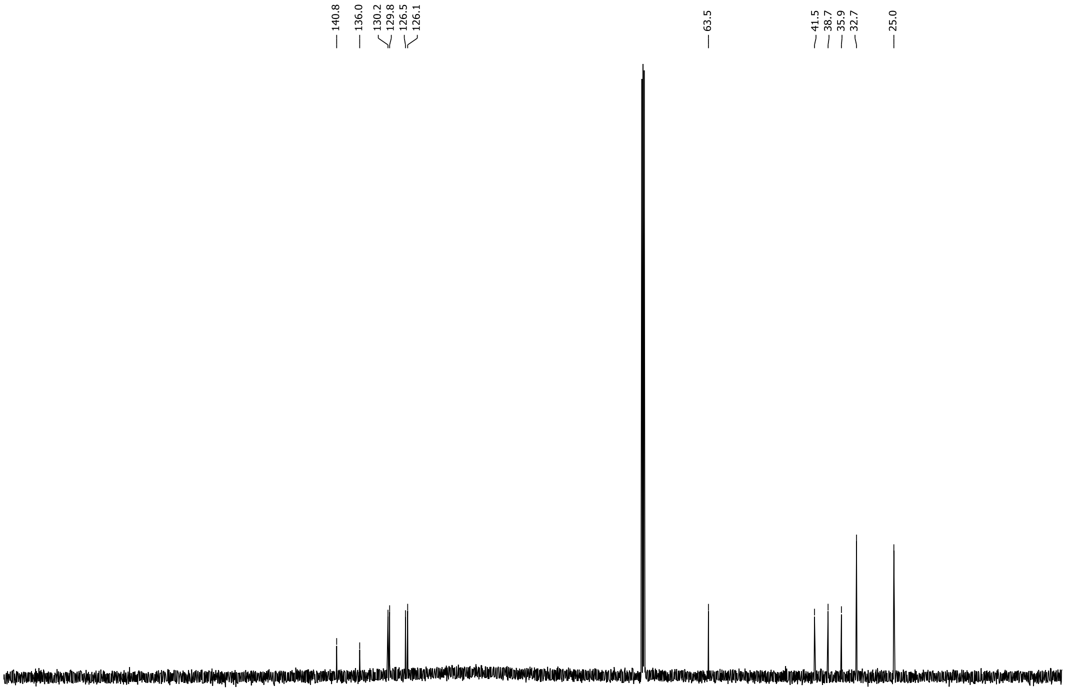
-0
f1 (ppm)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25.0
10
200
190
180
170
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120
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100
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80
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60
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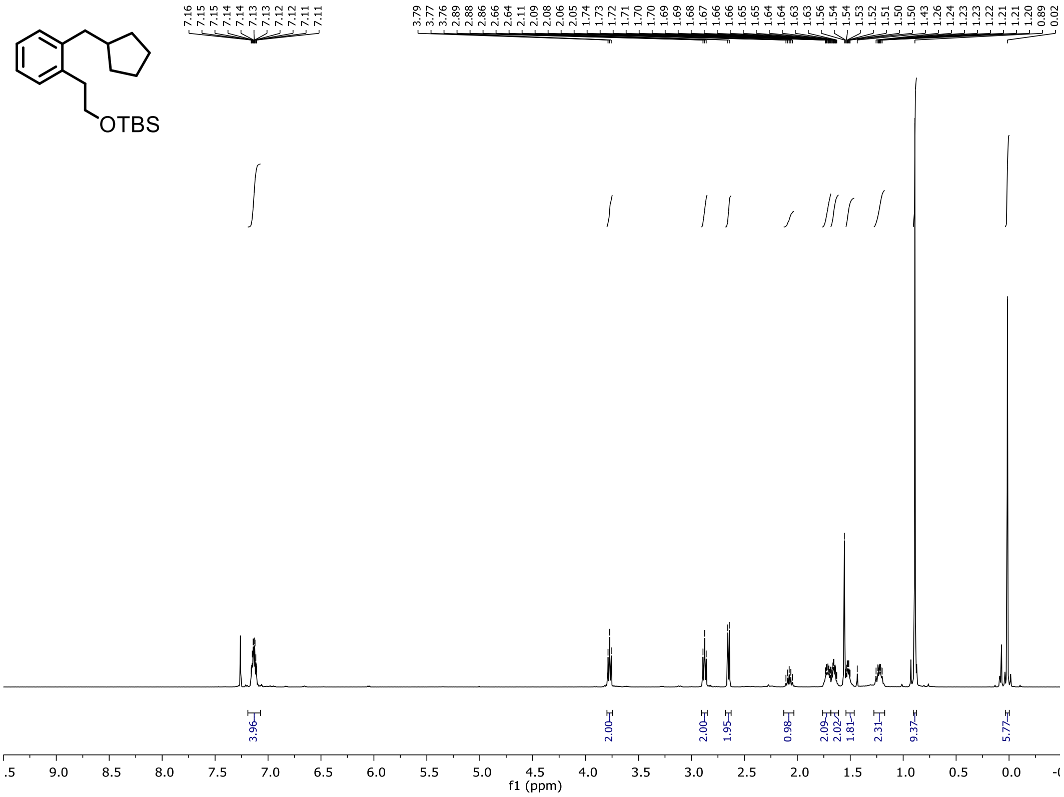
30
20
10
0
-1
f1 (ppm)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2.06
2.05
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1.21
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1.20
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2.00
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2.02
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.5
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8.5
8.0
7.5
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6.5
6.0
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5.0
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3.0
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2.0
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1.0
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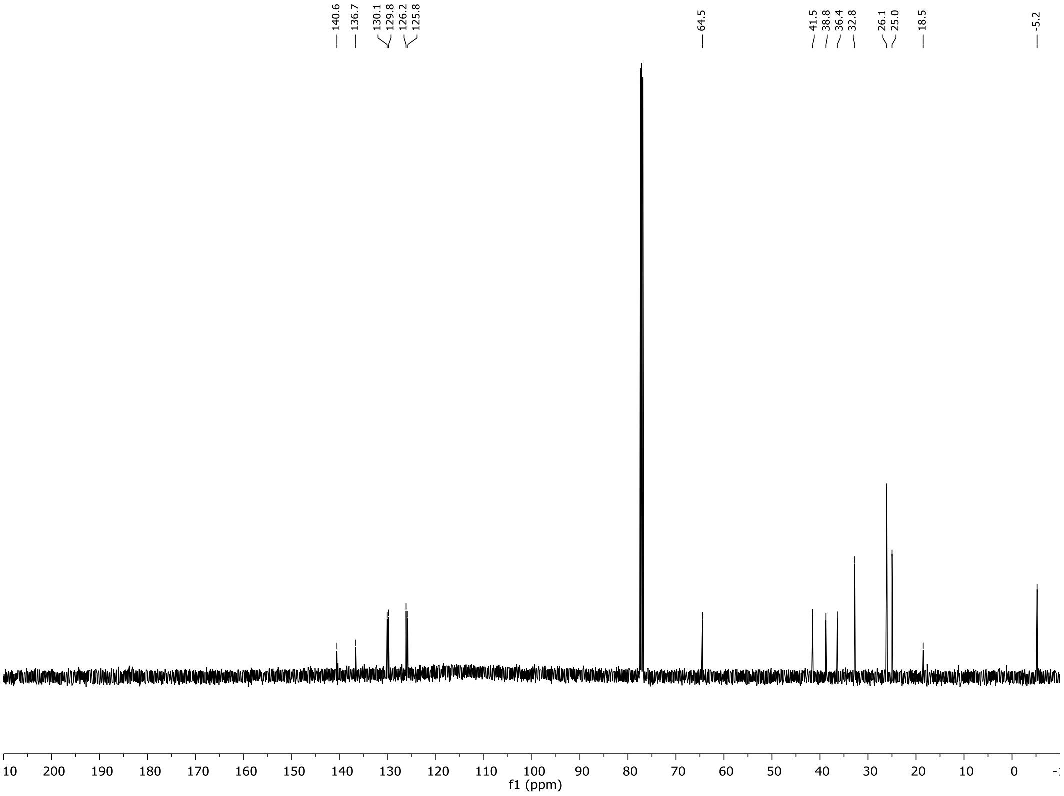
f1 (ppm)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125.8
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41.5
38.8
36.4
32.8
26.1
25.0
18.5
-5.2
10
200
190
180
170
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100
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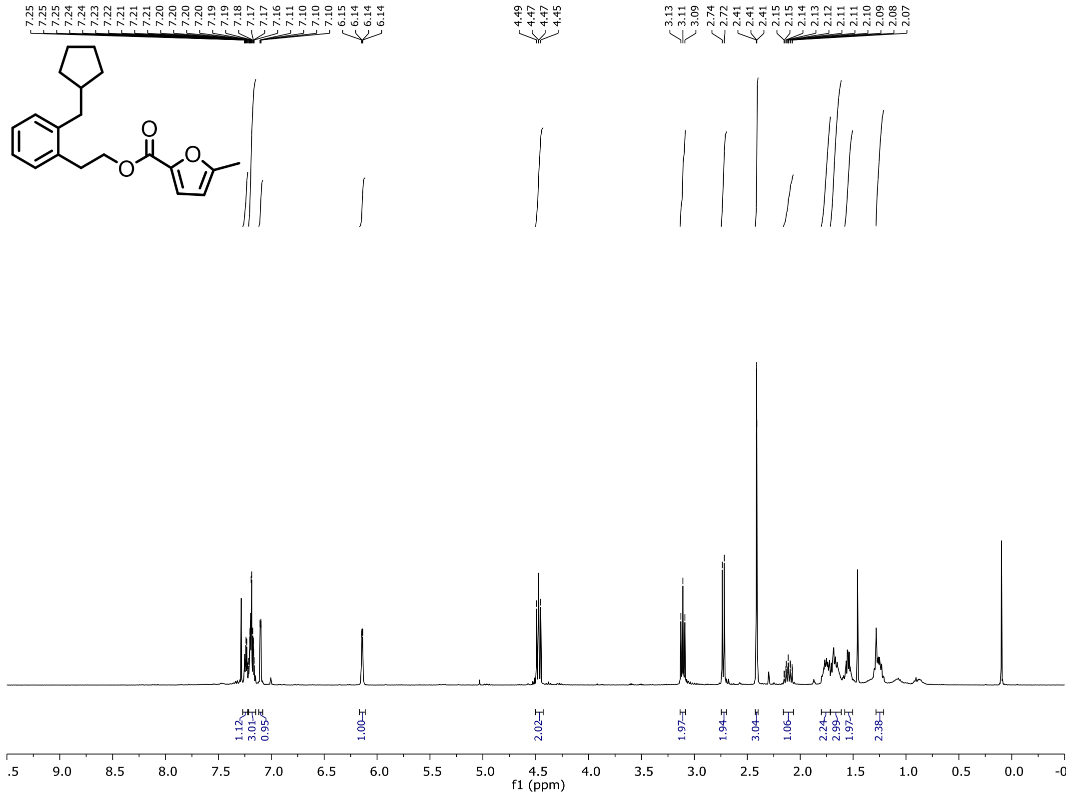
-:
f1 (ppm)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7.21
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6.14
6.14
6.14
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4.47
4.47
4.45
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2.72
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2.14
2.13
2.12
2.11
2.11
2.10
2.09
2.08
2.07
O
O
O
1.12
3.01
0.95
1.00
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1.94
3.04
1.06
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2.38
.5
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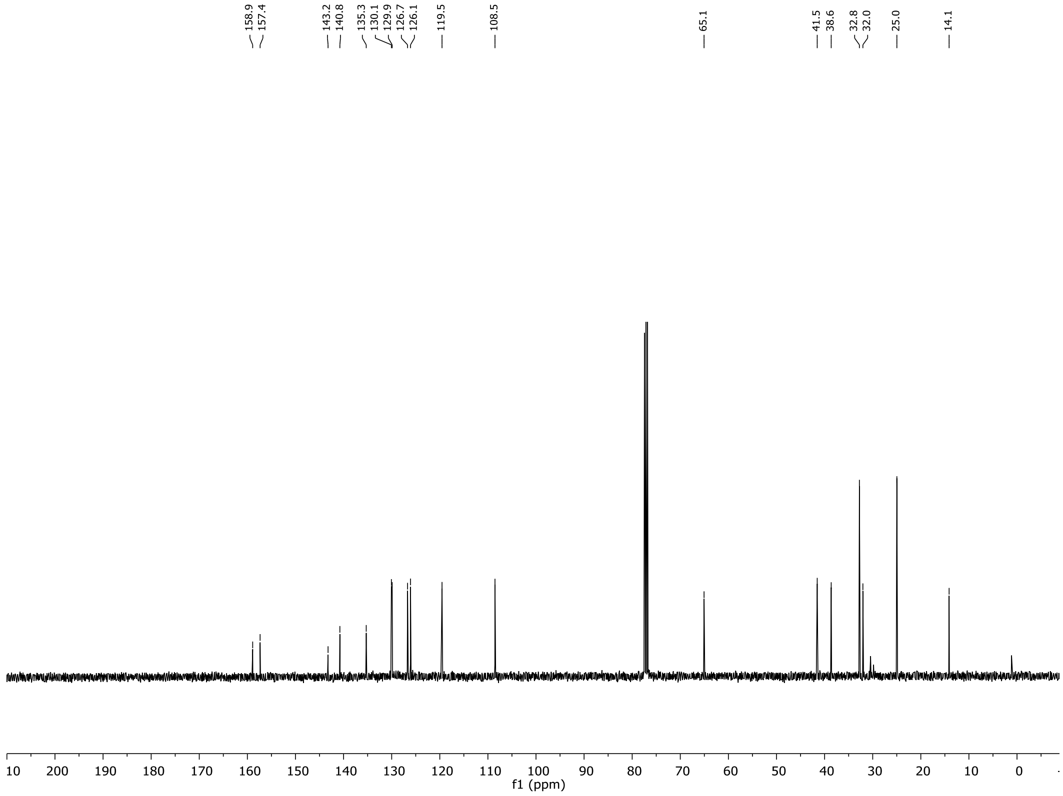
f1 (ppm)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32.8
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25.0
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200
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180
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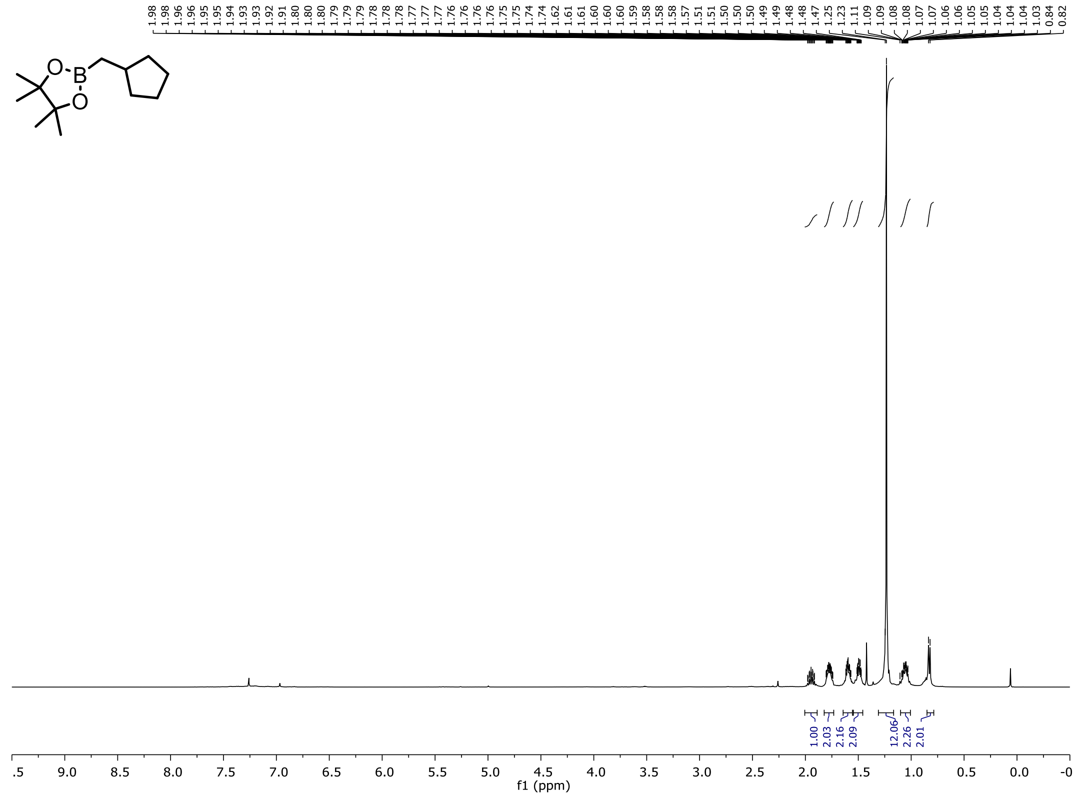
f1 (ppm)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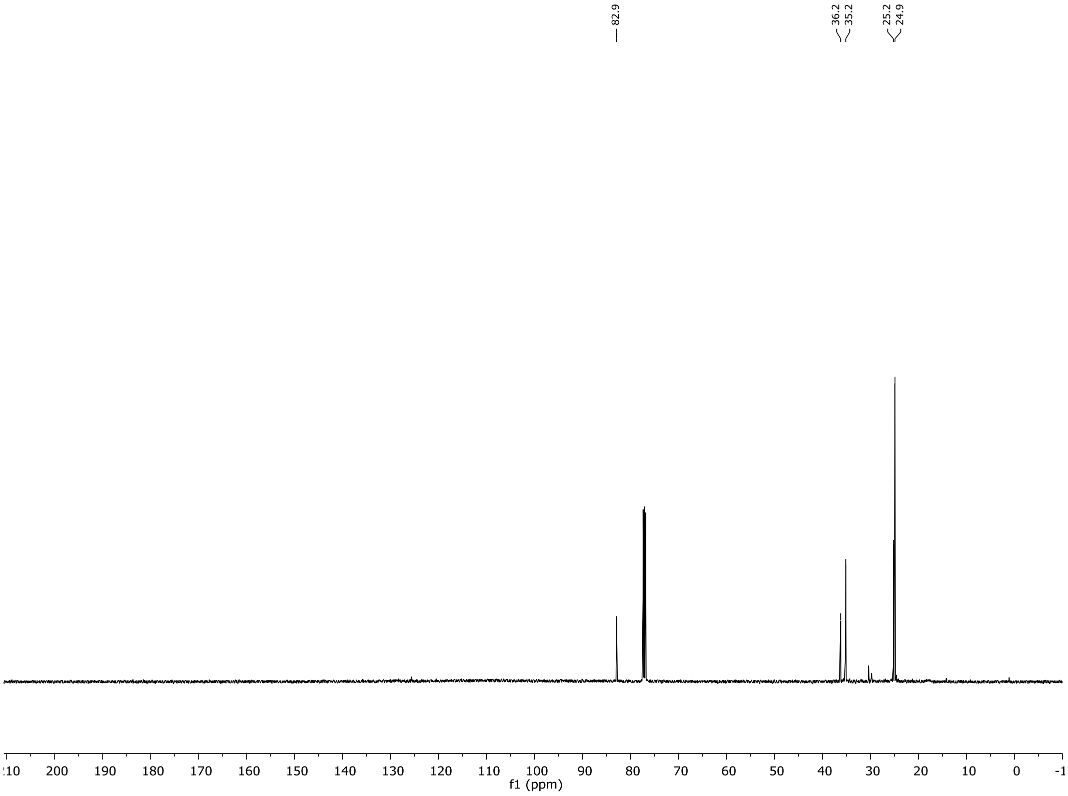
1.48
1.48
1.47
1.25
1.23
1.11
1.09
1.09
1.08
1.08
1.07
1.07
1.06
1.05
1.05
1.04
1.04
1.04
1.03
0.84
0.82
O
B
O
1.00
2.03
2.16
2.09
12.06
2.26
2.01
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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35.2
25.2
24.9
:10
200
190
180
170
160
150
140
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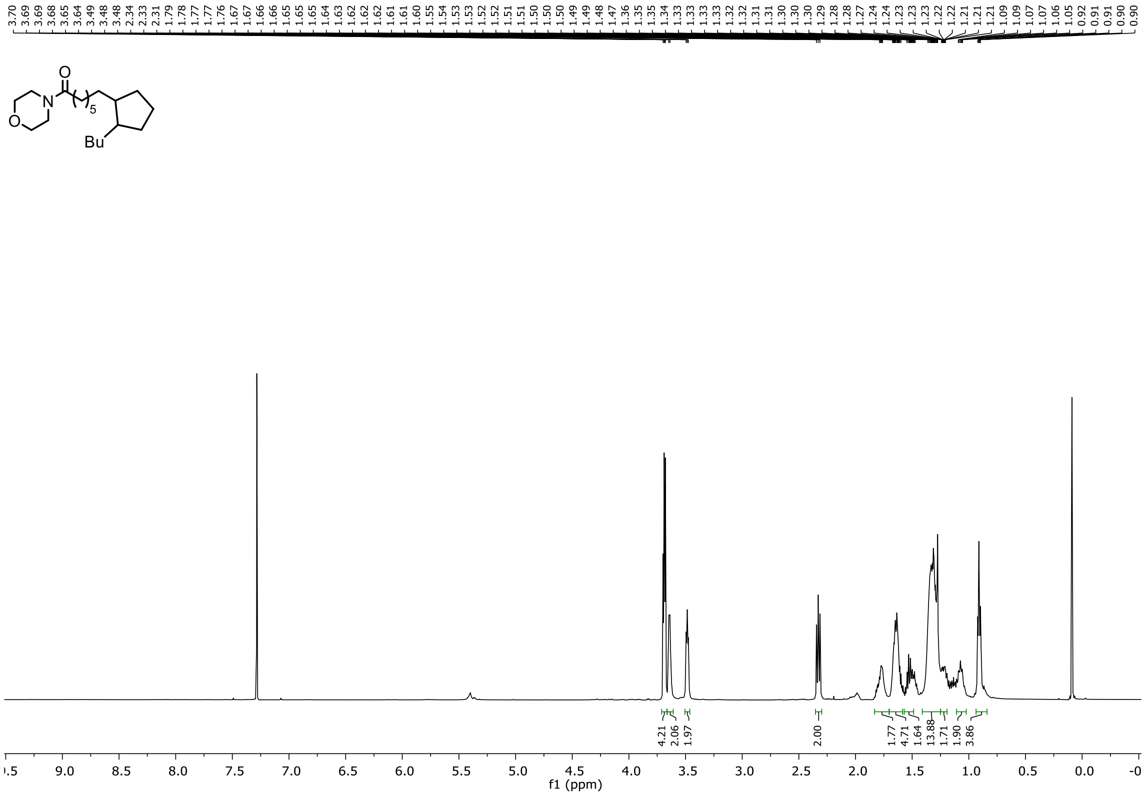
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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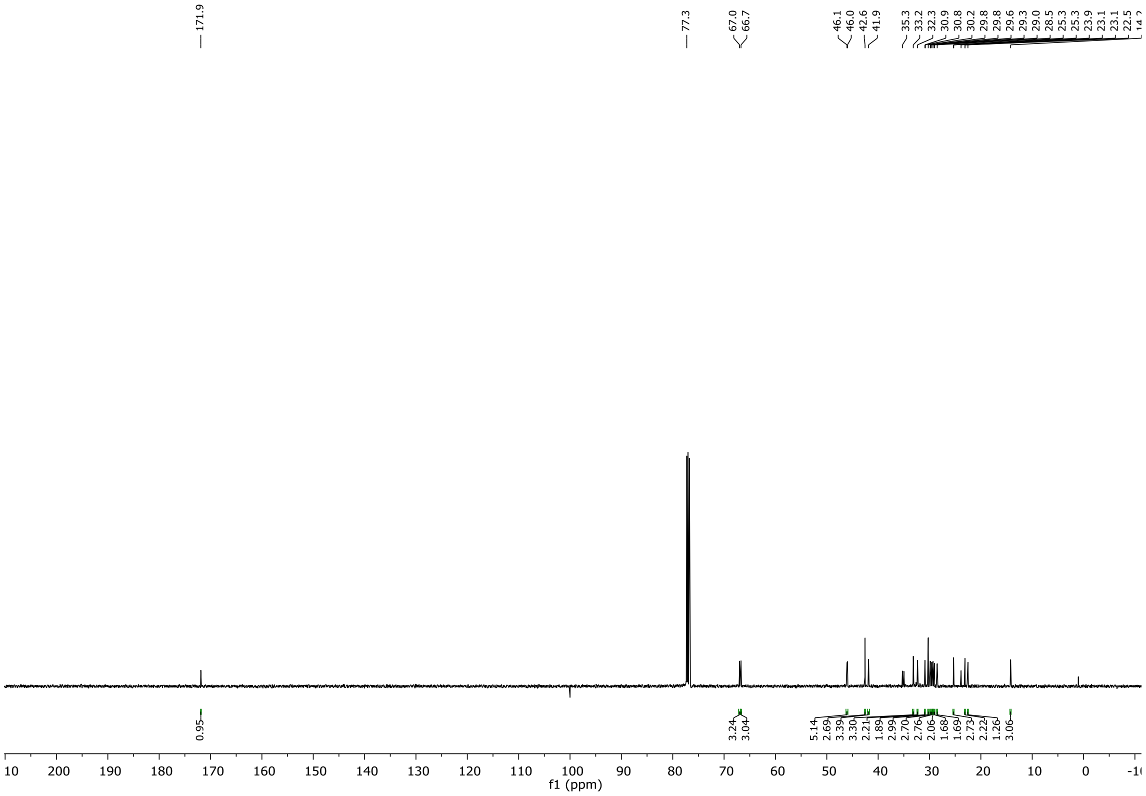
3.69
3.69
3.68
3.65
3.64
3.49
3.48
2.34
2.33
2.31
1.79
1.78
1.77
1.77
1.76
1.67
1.67
1.66
1.65
1.65
1.65
1.64
1.63
1.62
1.62
1.61
1.61
1.60
1.55
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.50
1.50
1.49
1.49
1.48
1.47
1.36
1.35
1.35
1.34
1.33
1.33
1.33
1.33
1.32
1.32
1.31
1.31
1.30
1.30
1.30
1.29
1.28
1.28
1.27
1.24
1.24
1.23
1.23
1.23
1.22
1.22
1.21
1.21
1.21
1.09
1.07
1.07
1.06
1.05
0.92
0.91
0.91
0.90
0.90
O
N
O
5
Bu
4.21
2.06
1.97
2.00
1.77
4.71
1.64
13.88
1.71
1.90
3.86
.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
f1 (ppm)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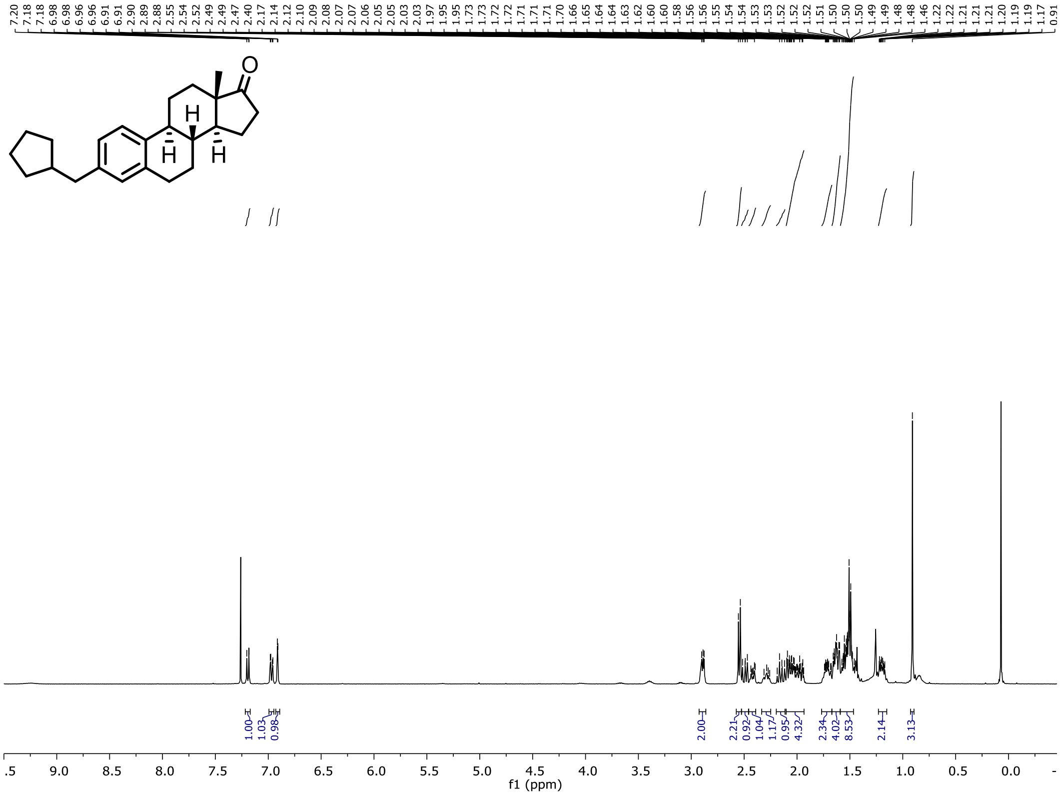
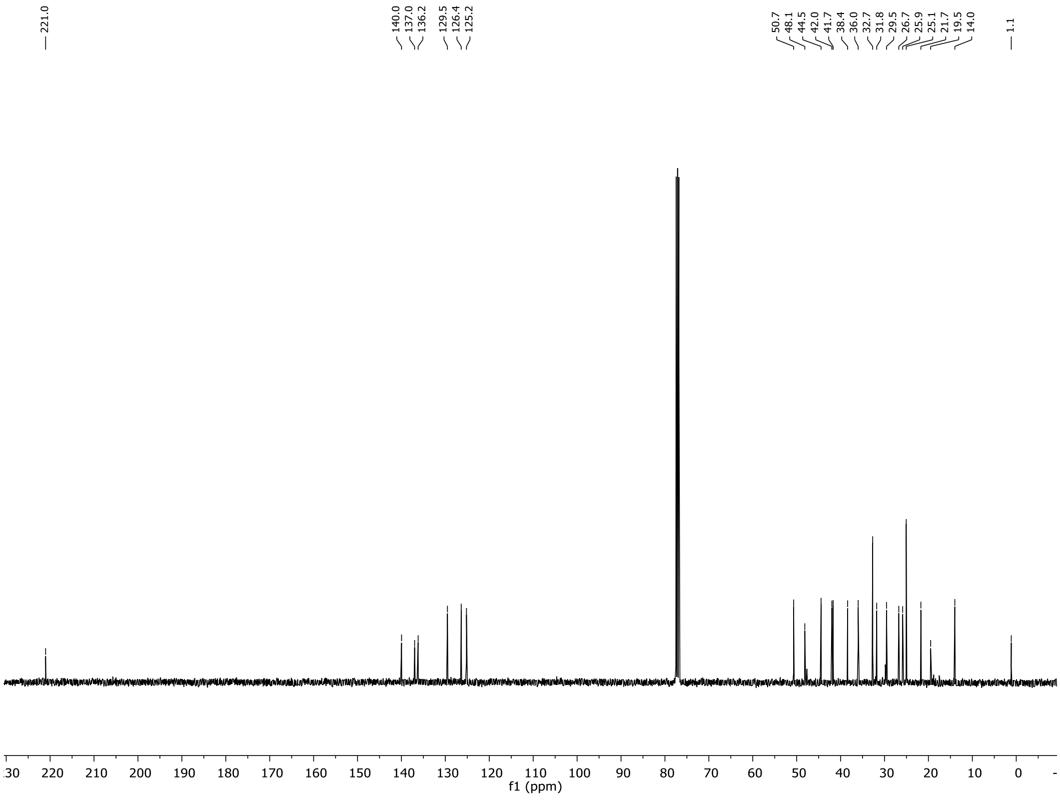
77.3
67.0
66.7
46.1
46.0
42.6
41.9
35.3
33.2
32.3
30.9
30.8
30.2
29.8
29.8
29.6
29.3
29.0
28.5
25.3
25.3
23.9
23.1
23.1
22.5
14.
0.95
3.24
3.04
5.14
2.69
3.39
3.30
2.21
1.89
2.99
2.70
2.76
2.06
1.68
1.69
2.73
2.22
1.26
3.06
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.20
7.18
7.18
6.98
6.98
6.96
6.96
6.91
6.91
2.90
2.89
2.88
2.55
2.54
2.52
2.49
2.49
2.47
2.40
2.17
2.14
2.12
2.10
2.09
2.08
2.07
2.07
2.06
2.05
2.05
2.03
2.03
1.97
1.95
1.95
1.73
1.73
1.72
1.71
1.71
1.71
1.70
1.66
1.65
1.64
1.64
1.63
1.62
1.60
1.60
1.58
1.56
1.56
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.52
1.51
1.50
1.50
1.50
1.49
1.49
1.48
1.46
1.22
1.22
1.21
1.21
1.21
1.20
1.19
1.19
1.17
0.91
O
H
H
H
1.00
1.03
0.98
2.00
2.21
0.92
1.04
1.17
0.95
4.32
2.34
4.02
8.53
2.14
3.13
.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)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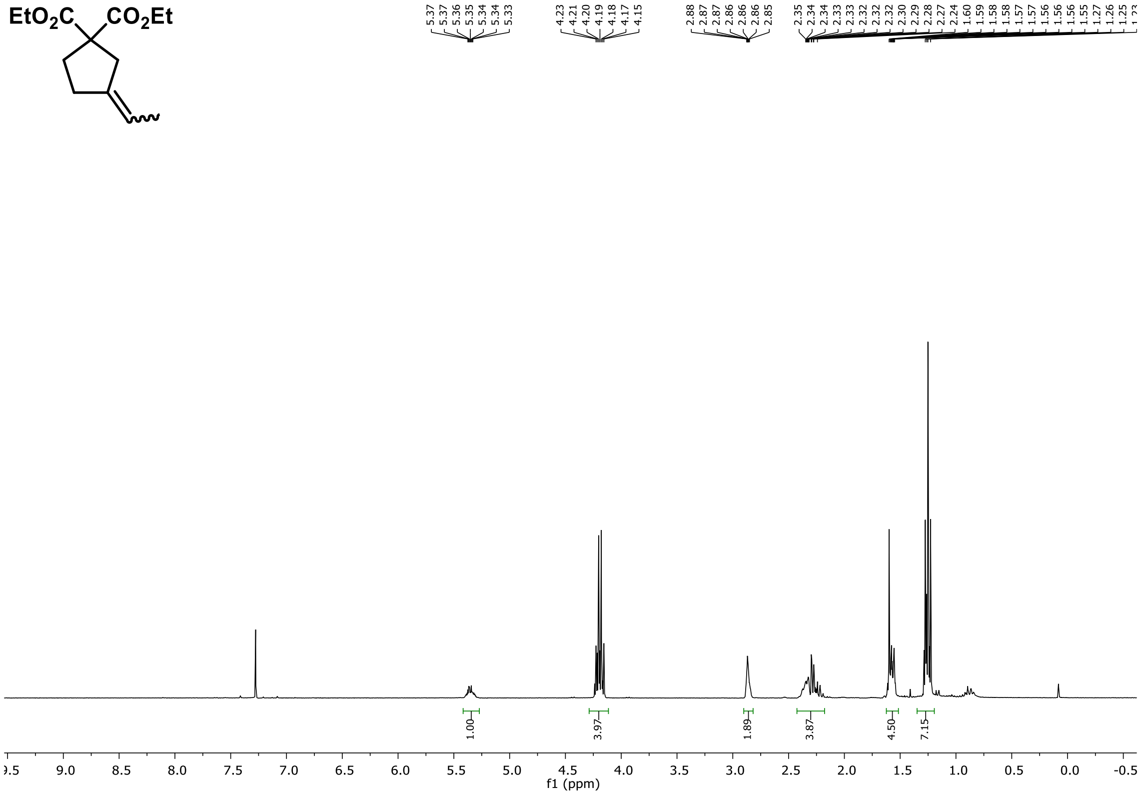
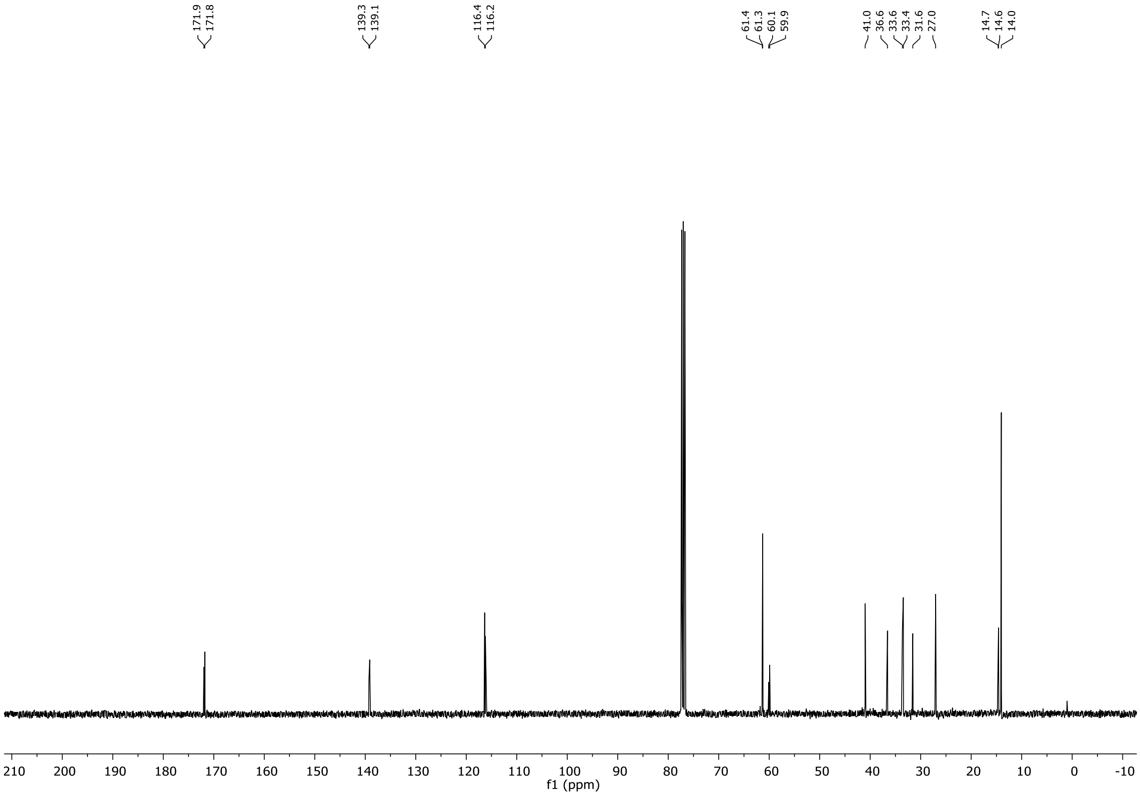
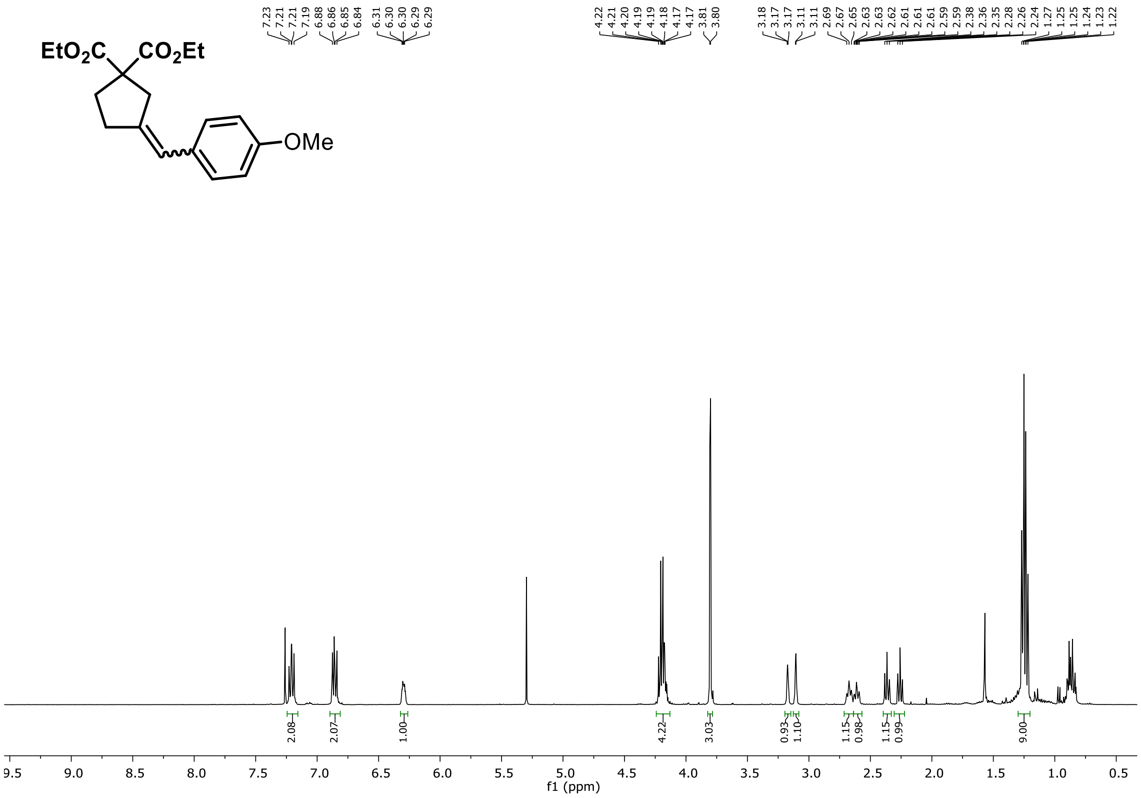
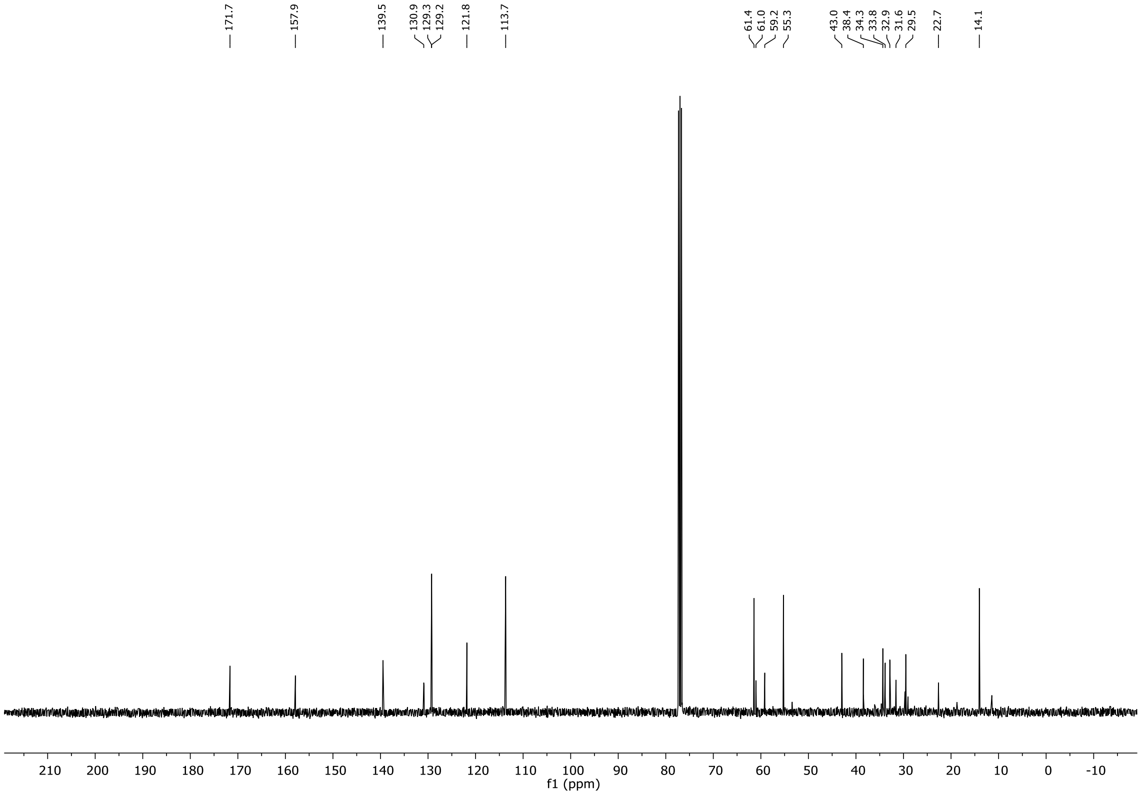
137.0
136.2
129.5
126.4
125.2
50.7
48.1
44.5
42.0
41.7
38.4
36.0
32.7
31.8
29.5
26.7
25.9
25.1
21.7
19.5
14.0
1.1
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


EtO2C
CO2Et




EtO2C
CO2Et
OMe
7.23
7.21
7.21
7.19
6.88
6.86
6.85
6.84
6.31
6.30
6.30
6.29
6.29
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.17
3.81
3.80
3.18
3.17
3.17
3.11
3.11
2.69
2.67
2.65
2.63
2.62
2.61
2.61
2.61
2.59
2.59
2.38
2.36
2.35
2.28
2.26
2.24
1.27
1.25
1.24
1.23
1.22
2.08
2.07
1.00
4.22
3.03
0.93
1.10
1.15
0.98
1.15
0.99
9.00
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)


171.7
157.9
139.5
130.9
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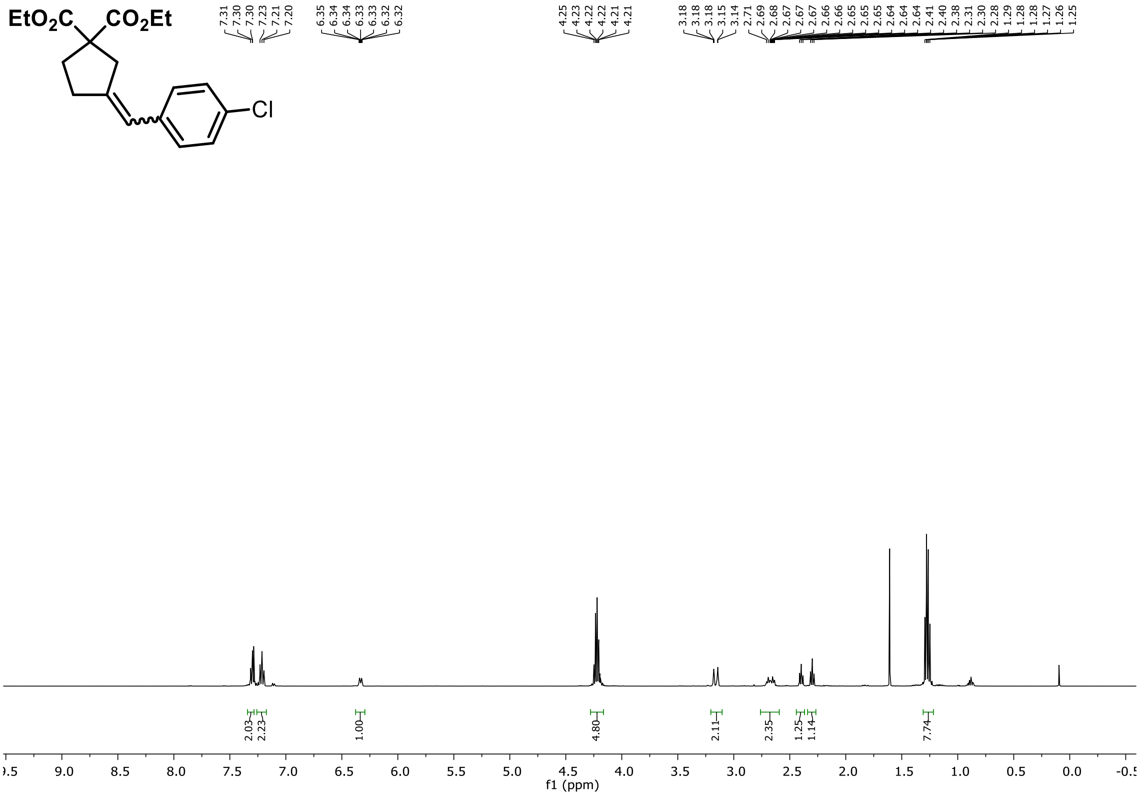
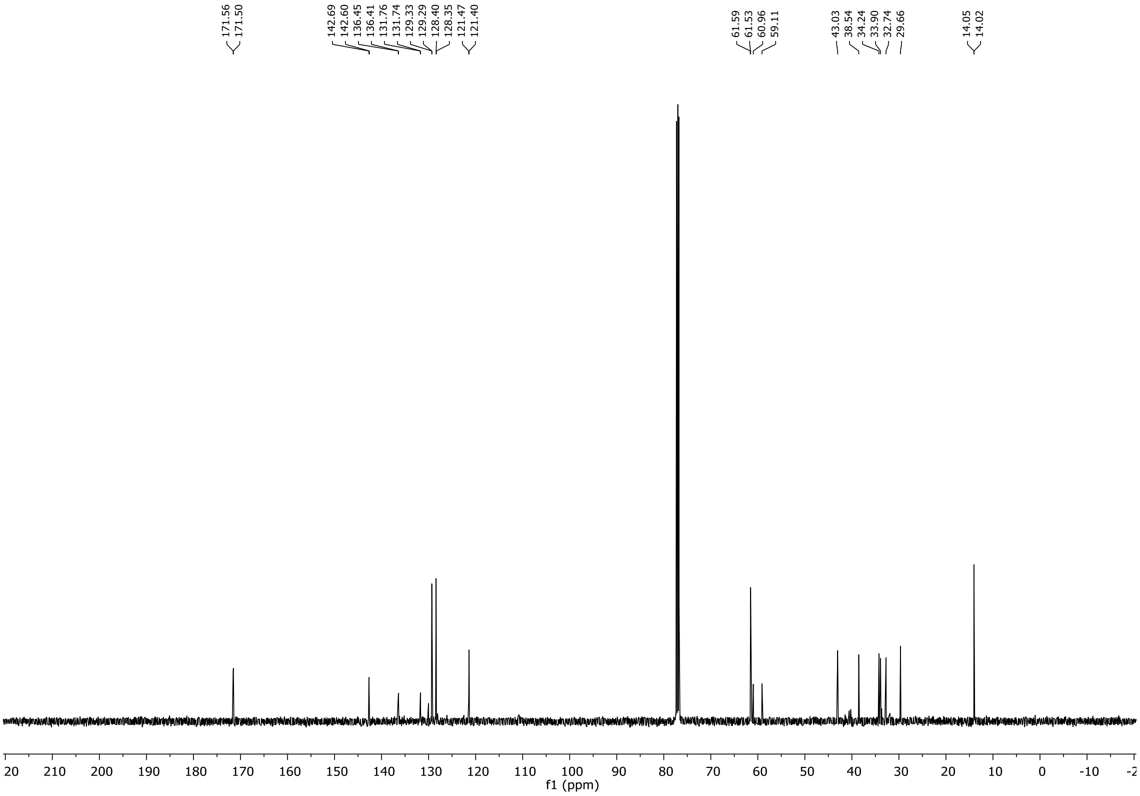
129.2
121.8
113.7
61.4
61.0
59.2
55.3
43.0
38.4
34.3
33.8
32.9
31.6
29.5
22.7
14.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


EtO2C
CO2Et
Cl
7.31
7.30
7.30
7.23
7.21
7.20
6.35
6.34
6.34
6.33
6.33
6.32
6.32
4.25
4.23
4.22
4.22
4.21
4.21
3.18
3.18
3.18
3.15
3.14
2.71
2.69
2.68
2.67
2.67
2.67
2.66
2.65
2.65
2.65
2.64
2.64
2.64
2.41
2.40
2.38
2.31
2.30
2.28
1.29
1.28
1.28
1.27
1.26
1.25
2.03
2.23
1.00
4.80
2.11
2.35
1.25
1.14
7.74
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
f1 (ppm)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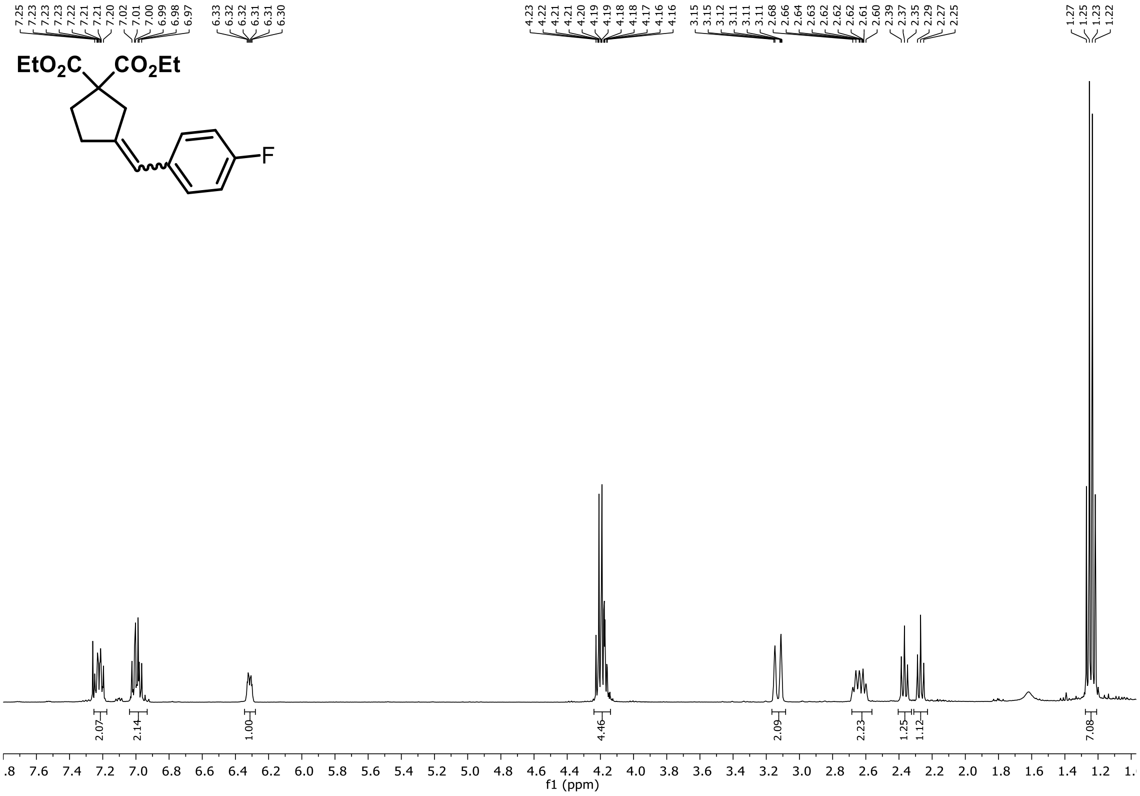
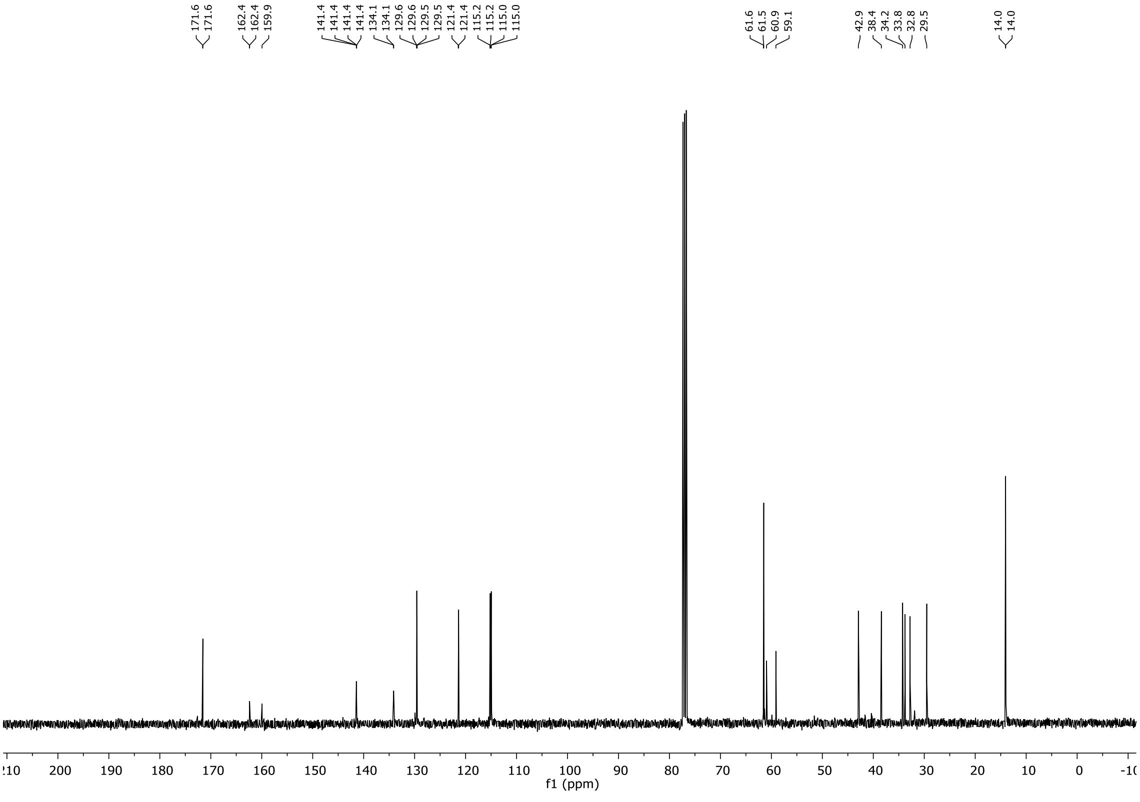
171.50
142.69
142.60
136.45
136.41
131.76
131.74
129.33
129.29
128.40
128.35
121.47
121.40
61.59
61.53
60.96
59.11
43.03
38.54
34.24
33.90
32.74
29.66
14.05
14.02
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.25
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.02
7.01
7.00
6.99
6.98
6.97
6.33
6.32
6.32
6.31
6.31
6.30
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.18
4.18
4.17
4.16
4.16
3.15
3.15
3.12
3.11
3.11
3.11
2.68
2.66
2.64
2.63
2.62
2.62
2.62
2.61
2.60
2.39
2.37
2.35
2.29
2.27
2.25
1.27
1.25
1.23
1.22
EtO2C
CO2Et
F
2.07
2.14
1.00
4.46
2.09
2.23
1.25
1.12
7.08
.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.
f1 (ppm)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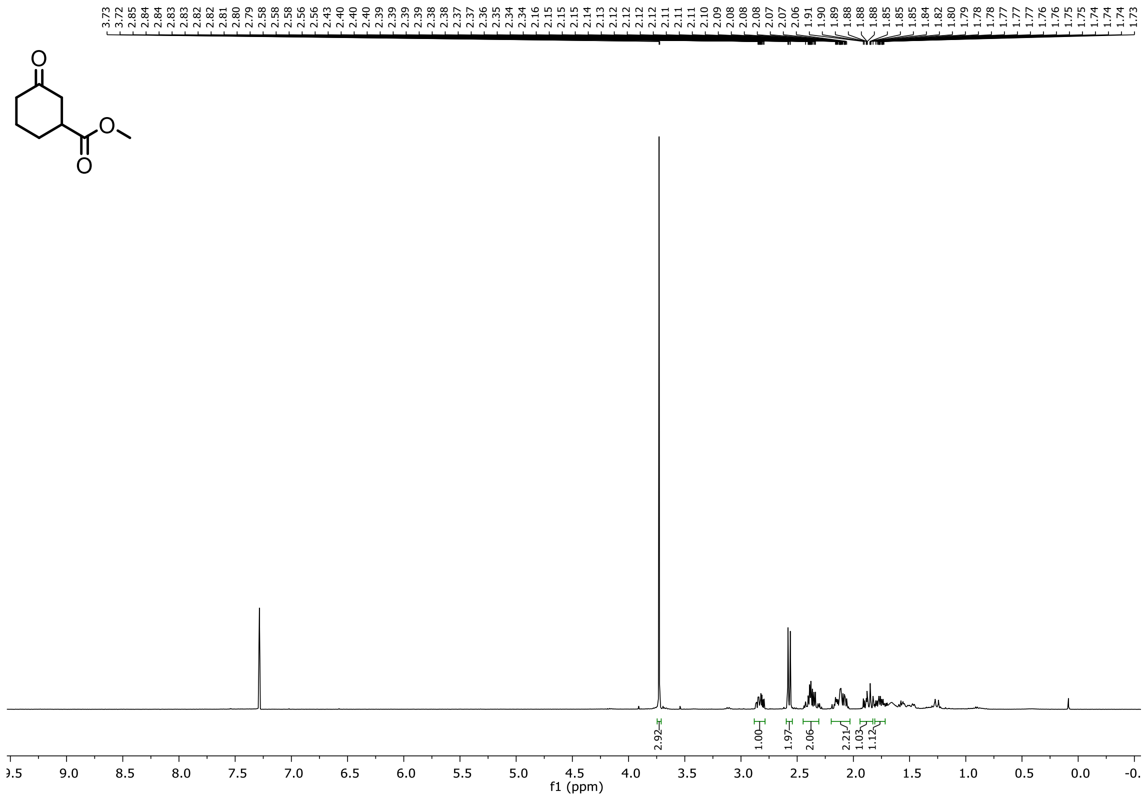
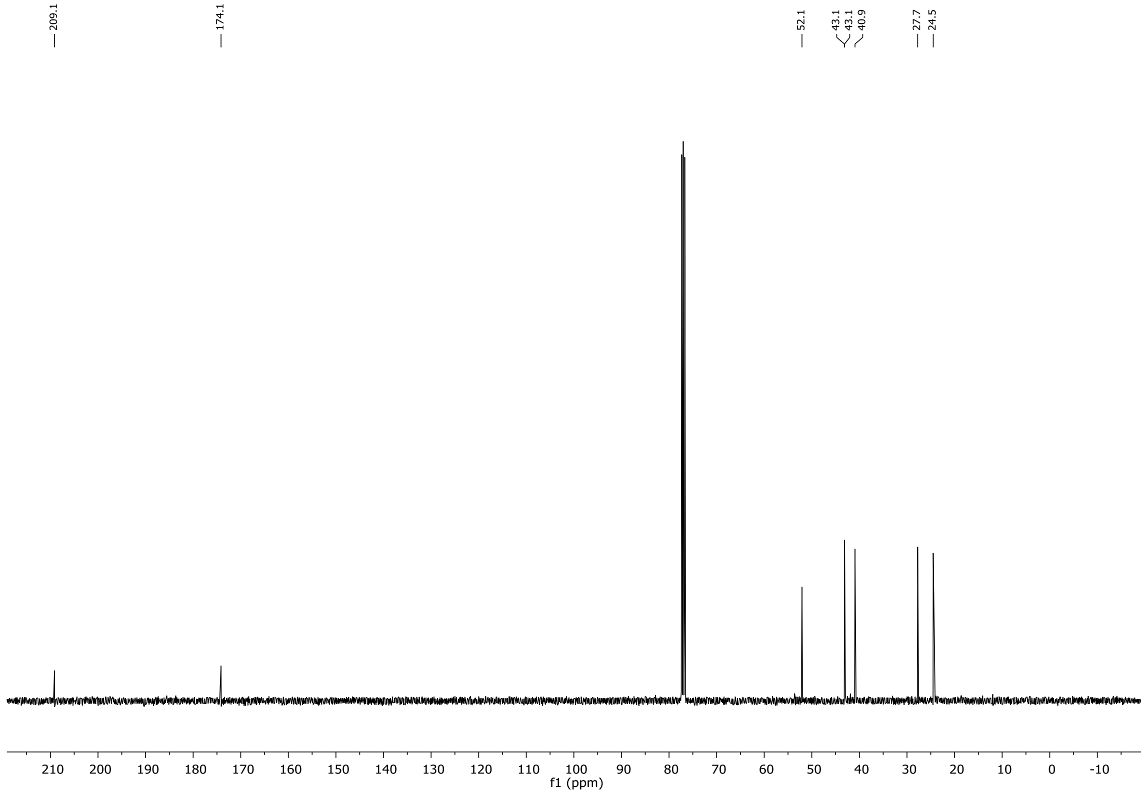
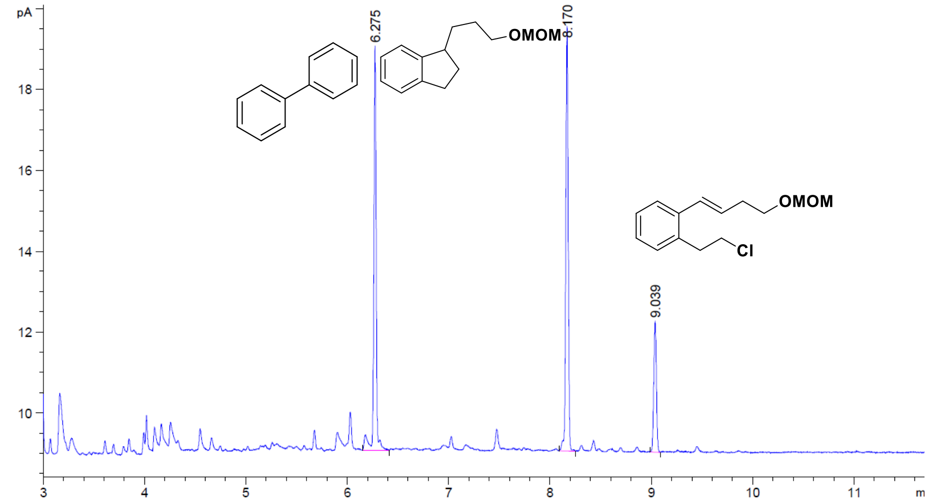
171.6
162.4
162.4
159.9
141.4
141.4
141.4
141.4
134.1
134.1
129.6
129.6
129.5
129.5
121.4
121.4
115.2
115.2
115.0
115.0
61.6
61.5
60.9
59.1
42.9
38.4
34.2
33.8
32.8
29.5
14.0
14.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.73
3.72
2.85
2.84
2.84
2.83
2.83
2.82
2.81
2.80
2.79
2.58
2.58
2.58
2.58
2.56
2.56
2.43
2.40
2.40
2.40
2.39
2.39
2.39
2.39
2.38
2.38
2.37
2.37
2.36
2.35
2.34
2.34
2.16
2.15
2.15
2.15
2.14
2.13
2.12
2.12
2.12
2.12
2.11
2.11
2.11
2.10
2.09
2.08
2.08
2.08
2.07
2.07
2.06
1.91
1.90
1.89
1.88
1.88
1.88
1.85
1.85
1.84
1.82
1.80
1.79
1.78
1.78
1.77
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.74
1.74
1.73
O
O
O
2.92
1.00
1.97
2.06
2.21
1.03
1.12
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.
f1 (ppm)

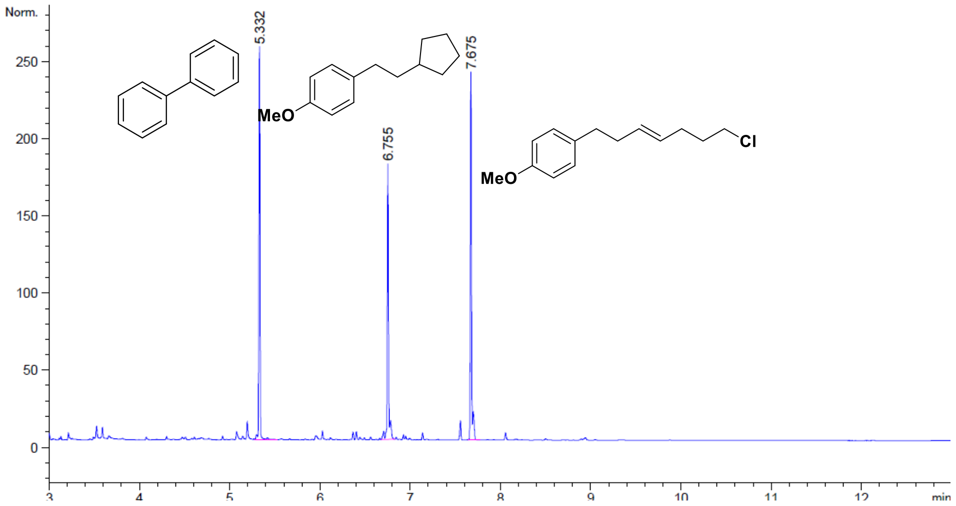

209.1
174.1
52.1
43.1
43.1
40.9
27.7
24.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4. GC-FID chromatograms



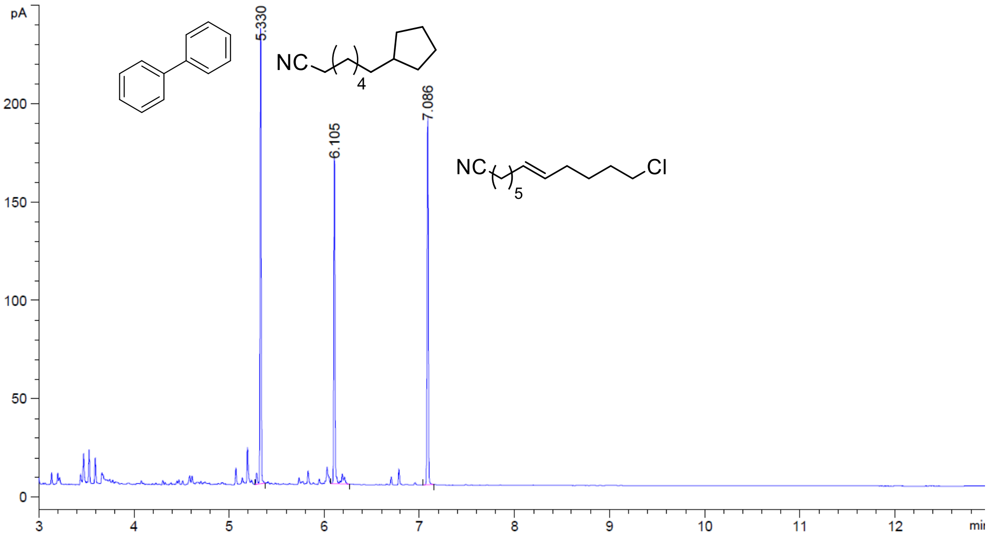
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   6.275 VV R  0.0229   16.51272    9.99282 41.18545
   2   8.170 BB    0.0267   17.71652   10.50463 44.18792
   3   9.039 BB    0.0281    5.86434    3.23761 14.62663

Totals :                    40.09358   23.73505
```

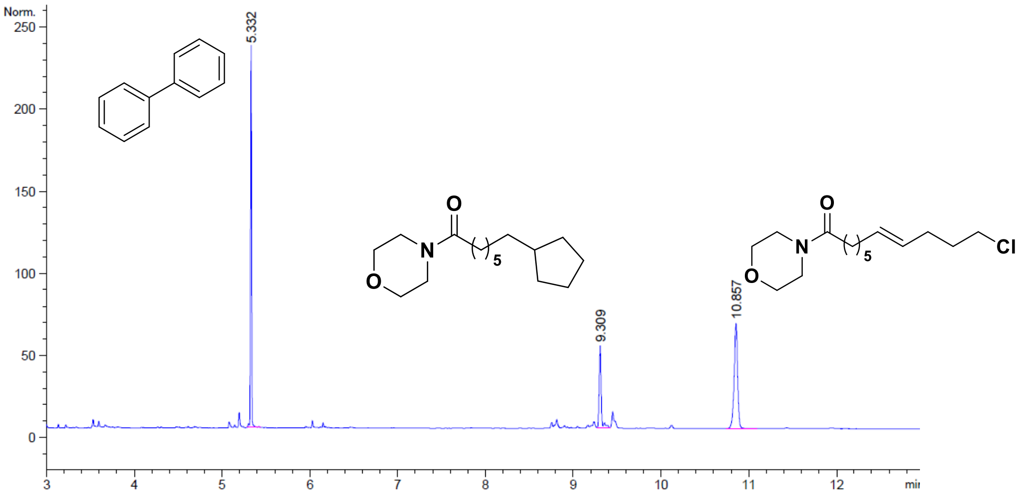


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   5.332 VV R  0.0123  208.60773  253.67999 34.47136
   2   6.755 VV R  0.0129  172.13979  178.11925 28.44522
   3   7.675 BV R  0.0135  224.41501  237.99486 37.08343
```

```
Totals :                       605.16252   669.79410
```

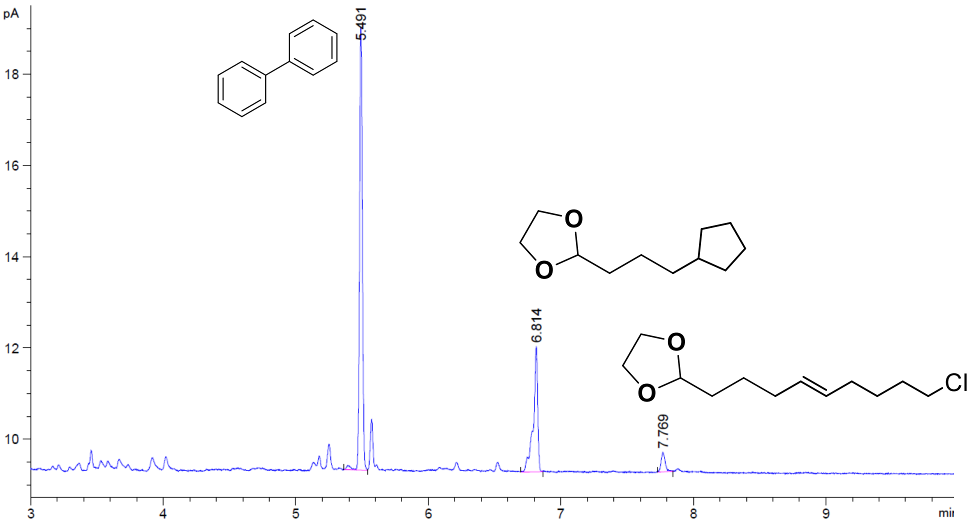


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1    5.330 VB  R  0.0133  185.34430  227.05916 37.12191
   2    6.105 BV  R  0.0141  151.30867  163.49706 30.30504
   3    7.086 BB     0.0144  162.63248  183.27374 32.57305
Totals :                     499.28545  573.82996
```



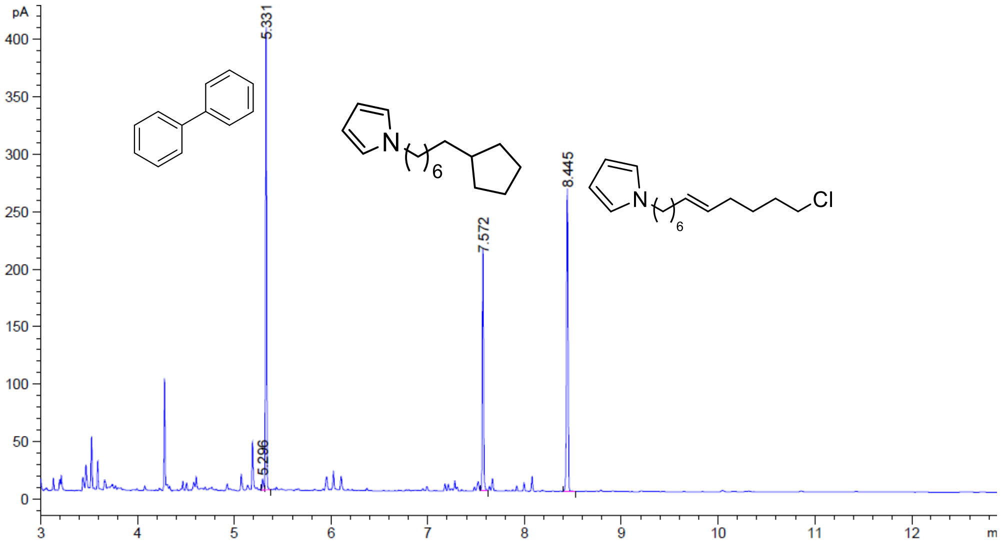
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1    5.332 VV  R  0.0124  188.51582  231.59004 42.38409
   2    9.309 BV  R  0.0233   80.29534   49.75000 18.05283
   3   10.857 BB     0.0374  175.96852   64.40415 39.56308

Totals :                     444.77969  345.74419
```



```
 Peak RetTime Type  Width     Area       Height      Area
   #   [min]        [min]   [pA*s]      [pA]         %
 ----|-------|----|-------|----------|----------|--------|
    1   5.491 VV  R 0.0235   14.54990    9.68141 66.80300
    2   6.814 BB    0.0324    6.33101    2.75026 29.06760
    3   7.769 BB    0.0307 8.99395e-1 4.25427e-1  4.12939

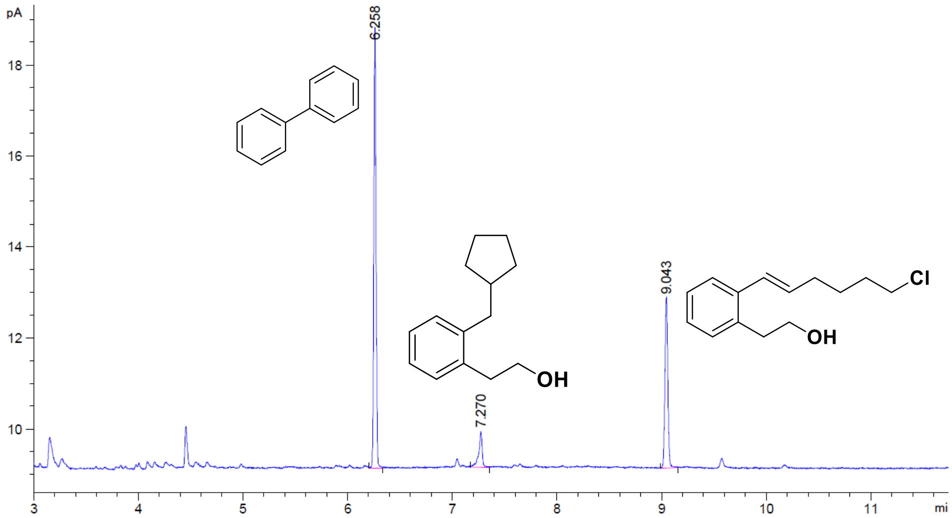
Totals :                     21.78030   12.85709
```



```
 Peak RetTime Type  Width     Area       Height      Area
   #   [min]        [min]   [pA*s]      [pA]         %
 ----|-------|----|-------|----------|----------|--------|
    1   5.296 BV  E 0.0156    9.16505    9.21018  1.16119
    2   5.331 VB  R 0.0122  311.91507  393.84573 39.51893
    3   7.572 BB    0.0146  184.24258  203.69937 23.34311
```

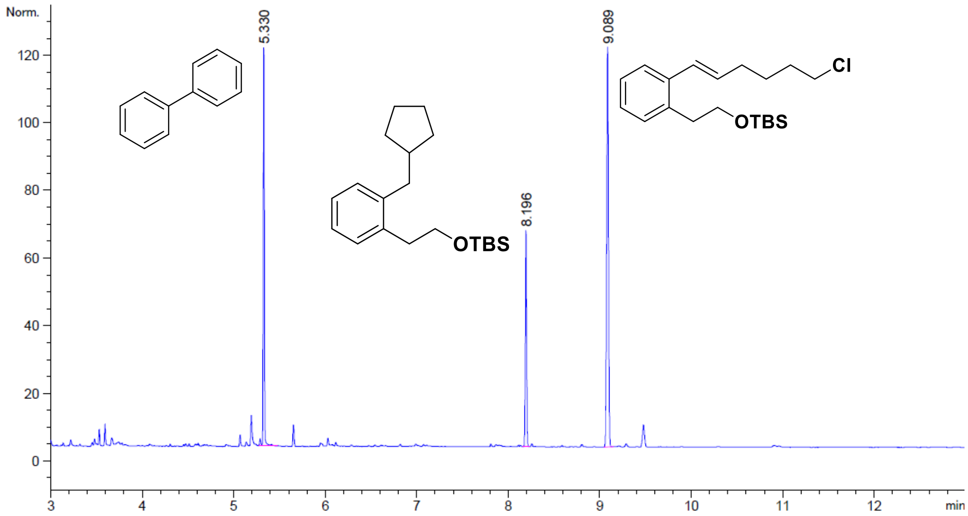
```
   4    8.445 BB    0.0177  283.95752  260.84375 35.97677

 Totals :                   789.28022  867.59903
```

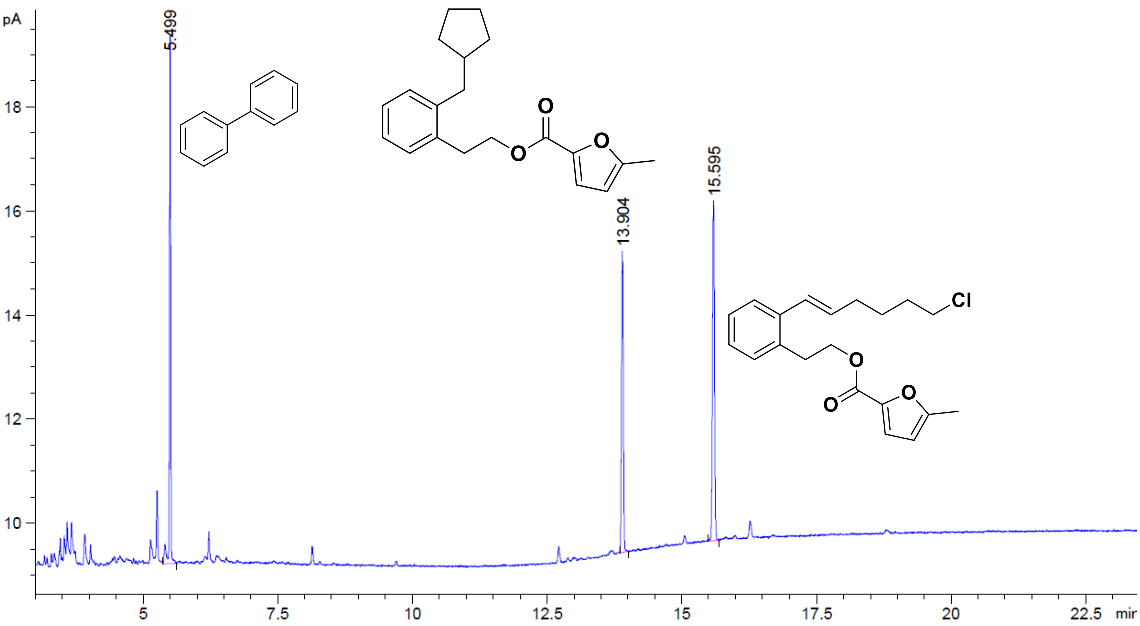


```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]    [pA*s]     [pA]        %
 ----|-------|----|-------|----------|----------|--------|
    1   6.258 BB    0.0227   14.28197    9.67704 61.42316
    2   7.270 BB    0.0319    1.77505 7.84199e-1  7.63405
    3   9.043 BB    0.0295    7.19475    3.72815 30.94279

 Totals :                    23.25177   14.18939
```



```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]    [pA*s]     [pA]        %
 ----|-------|----|-------|----------|----------|--------|
    1   5.330 VV R  0.0129   97.02084  117.84389 29.46816
    2   8.196 BB    0.0156   63.73653   63.92062 19.35871
    3   9.089 BB    0.0216  168.48224  118.17670 51.17314
 Totals :                   329.23962  299.94120
```



```
Peak RetTime Type  Width     Area      Height     Area
  #    [min]       [min]    [pA*s]     [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   5.499 VB R  0.0237   16.41653   10.13132 35.04998
   2  13.904 BB    0.0343   13.53111    5.78759 28.88948
   3  15.595 BB    0.0386   16.88985    6.54095 36.06054

Totals :                    46.83749   22.45986
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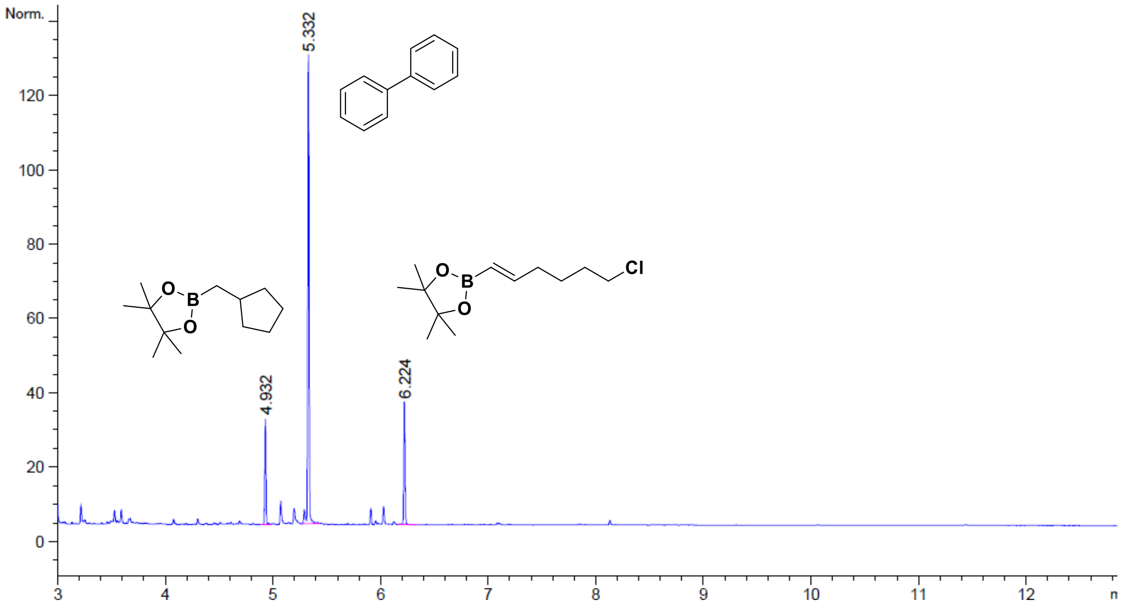

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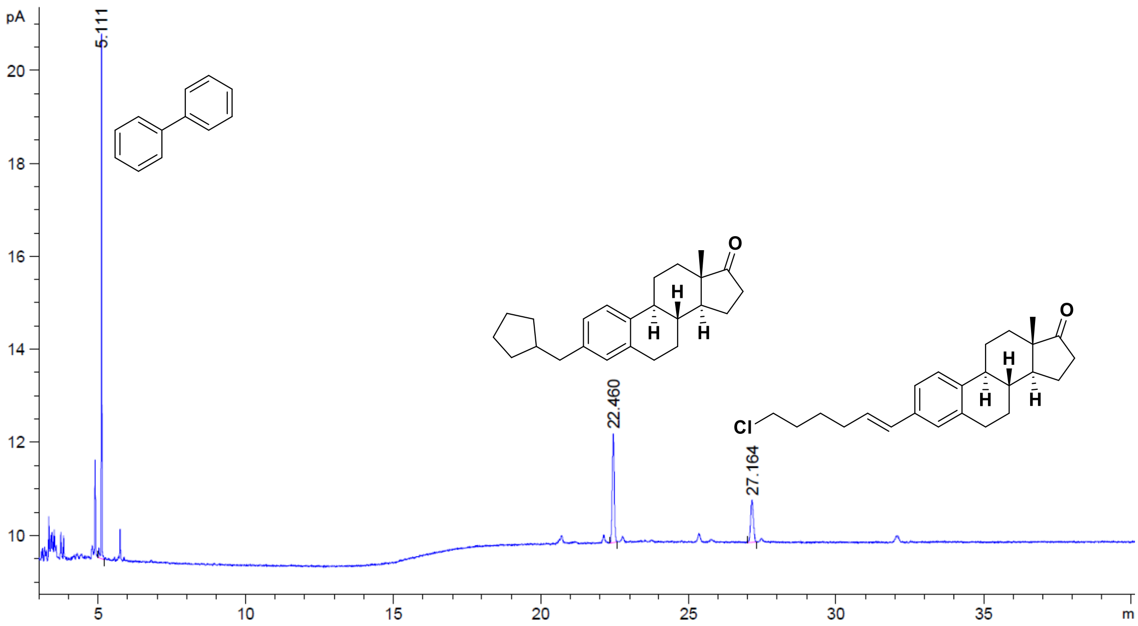
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   4.932 BV R  0.0129   23.15867   28.35225 15.05854
   2   5.332 VV R  0.0127  103.26064  125.97087 67.14350
   3   6.224 VV R  0.0132   27.37164   32.81668 17.79796

Totals :                   153.79095  187.13980
```

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   6.259 BB    0.0234   83.41785   56.07837 92.51344
   2   7.595 BB    0.0304 3.56103e-1 1.63600e-1  0.39493
   3   9.571 BB    0.0327    6.39441    3.07662  7.09163

Totals :                    90.16837   59.31859
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   5.111 VB R  0.0237   17.54341   11.27078 50.60866
   2  22.460 BB    0.0605   11.22521    2.33752 32.38212
   3  27.164 BB    0.0794    5.89622 9.12106e-1 17.00922

Totals :                    34.66483   14.52041
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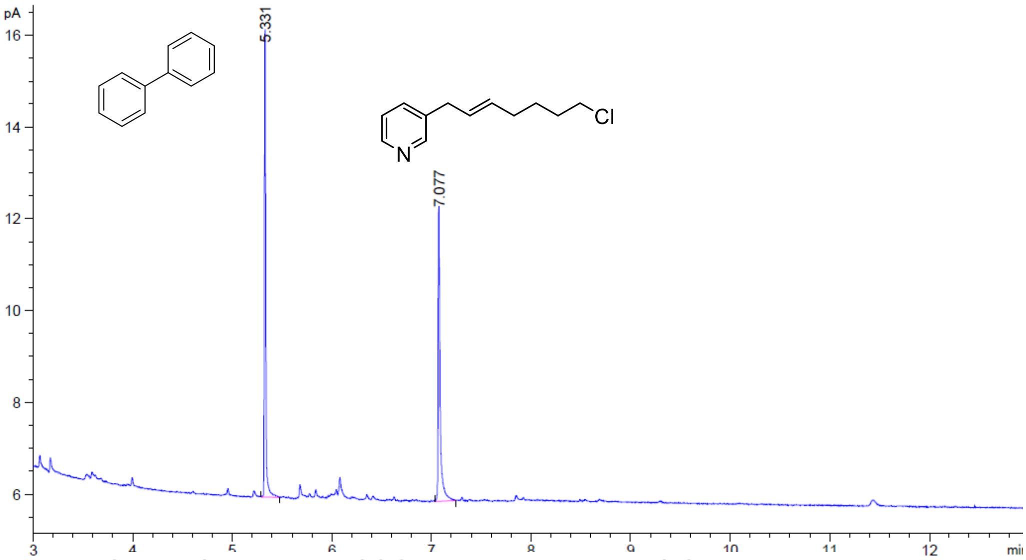

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   5.331 BB    0.0140    9.42540   10.01193 52.25809
   2   7.077 BB    0.0199    8.61085    6.32609 47.74191

Totals :                    18.03624   16.33803
```

Supporting Information

Experimental Procedures

Contents

6. Synthesis and characterization of complexes

13. Mechanistic Studies

   - 13.2. Spectroelectrochemistry Studies

1. General procedures

Reagents and solvents were used as received from the commercial supplier unless otherwise stated. Triethylamine and *di*-isopropylethylamine were distilled over potassium hydroxide and were stored under argon. Photosensitizers [Ir(bpy)(ppy)$_2$](PF$_6$) (**PC$_{Ir2}$**),[1] [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (**PC$_{Ir3}$**),[2] Ir[dF(CF)$_3$ppy]$_2$(dtbbpy)(PF$_6$) (**PC$_{Ir4}$**),[3] [Cu(bathocuproine)(Xantphos)](PF$_6$)[4] (**PC$_{Cu}$**) and complexes [Co(OTf)(Py$_2$Tstacn)](OTf)[5] (**1^{H}Co**), [Ni(OTf)(Py$_2$Tstacn)](OTf) (**1^{H}Ni**),[5] [Co(OTf)(^{DMM}Py$_2$Tstacn)](OTf) (**1^{DMM}Co**),[6] [Co(OTf)(^{CO2Et}Py$_2$Tstacn)](OTf) (**1^{CO2Et}Co**),[6] CoN4Py (**5Co**),[7] [Co(OTf)$_2$(Me$_2$^{H}Pytacn)] (**7^{H}Co**),[8] [Co(OTf)$_2$(Me$_2$^{DMM}Pytacn)] (**7^{DMM}Co**),[8] [Co(OTf)$_2$(Me$_2$^{CO2Et}Pytacn)] (**7^{CO2Et}Co**),[8] [Co(TPA)(OTf)$_2$] (**8Co-OTf**),[9] [Co(TPA)Cl$_2$] (**8Co-Cl**),[9] [Co(MCP)Cl$_2$] (**9Co-Cl**),[10] Co-(PDP)OTf$_2$ (**10Co-OTf**),[11] Co-TPP (**11Co**),[12] Ni-TTP (**11Ni**),[13] Co-Salen (**13Co**),[14] Ni-Salen (**13Ni**)[15] were synthesized according to the literature procedures.

For the synthesis of reagents the solvents (hexane, Et$_2$O, CH$_2$Cl$_2$, MeCN, DMF and toluene) were used from a SPS-400, Innovative Technology solvent purification system and stored under argon with activated 4 Å molecular sieves.

Anhydrous acetonitrile was purchased from Sigma-Aldrich® and water was purified with a Milli-Q Millipore Gradient AIS system. Water, methanol, ethanol, isopropanol, butironitrile, isobutironitrile and trimethylacetonitrile used for photoreactions were degassed by freeze-pump-thaw method (repeated 3 cycles) and were stored under argon.

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[1] Lowry, M. S.; Hudson, W. R.; Pascal, R. A., Jr.; Bernhard, S. *J. Am. Chem. Soc.* **2004**, *126*, 14129.

[2]Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763.

[3]Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, Jr. R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005,** *17,* 5712.

[4] Luo, S.-P.; Mejía, E.; Friedrich, A.; Pazidis, A.; Junge, H.; Surkus, A.-E.; Jackstell, R.; Denurra, S.; Gladiali, S.; Lochbrunner, S.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 419.

[5] Call, A.; Codolà, Z.; Acuña-Parés, F.; Lloret-Fillol, J. *Chem. Eur. J.* **2014**, *20*, 6171.

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[9] Davies, C. J.; Solan, G. A.; Fawcett, J. *Polyhedron* **2004**, *23*, 3105.

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[11] Call, A.; Casadevall, C.; Acuña-Parrés, F.; Casitas, A; Lloret-Fillol, J. *Chem. Sci.* **2017**, *8*, 4739.

[12] Fu, L.; Chen, Y.; Liu, Z. *Journal of Molecular Catalysis A: Chemical* **2015**, *408*, 91.

[13] Schlabach, M.; Wehrle, B.; Rumpel, H.; Braun, J.; Scherer, G.; Limbach, H-H. - *Berichte der Bunsen-Gesellschaft* **1992**, *6*, 821.

[14] Jayaseeli, M. I.; Ramdass, A.; Rajagopal, S. *Polyhedron* **2015**, *100*, 59.

[15] Shehata; M.; Khalil; A-G. *Journal of Molecular Liquids* **2014**, *194*, 149.

The synthesis of air sensitive reagents as well as the preparation of visible light photocatalytic reactions were conducted inside a nitrogen-filled glove box (mBraun Unilab) with concentrations of O_2 and H_2O lower than 0.5 ppm and using Schlenk techniques under argon atmosphere.

NMR spectra were recorded on a Bruker 300MHz, 400MHz or 500MHz spectrometers at room temperature. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm), relative to the residual solvent peak as internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublet (dd), triplet of doublets (td), triplet (t), broad signal (br) and multiplet (m). Deuterated solvents ($CDCl_3$, CD_3CN, EtOD) were stored with activated 4 Å molecular sieves and they were degassed by freeze-pump-thaw method when it was required for photocatalytic reactions.

High resolution Mass Spectrometry (HRMS) data was collected on a HPLC-QqTOF (Maxis Impact, Bruker Daltonics) or HPLC-TOF (MicroTOF Focus, Bruker Daltonics) mass spectrometer using 1 mM solution of the analyzed compound.

The analysis and quantification of the starting materials and products were carried out on an Agilent 7820A gas chromatograph (HP5 capillary column, 30 m x 320 µm x 0.25 µm or Sapiens 5MS capillary column, 30 m x 250 µm x 0.25 µm) and a flame ionization detector (FID). GC-MS spectral analyses were performed on an Agilent 7890A gas chromatograph interfaced (HP5 capillary column, 30 m x 320 µm x 0.25 µm) with an Agilent 5975c MS mass spectrometer.

Electron Paramagnetic Resonance (EPR) was collected on solutions of 1mM **1^{H}Ni** complex with or without substrate **2h** (10 mM) in a reaction mixture containing **PC_{Cu}** (0.4mM), DIPEA (114.5 mM) as sacrificial electron donor and a 3:2 ratio ethanol:butyronitrile solvent mixture. Samples were prepared anaerobically under dark conditions and investigated before and after irradiation with a 476 nm lamp (40 W) at room temperature. An EMX Micro X-band EPR spectrometer from Bruker was used to collect the data using a finger dewar for measurements at 77 K. Data was acquired in perpendicular mode with a modulation frequency of 100 KHz, a modulation amplitude of 10 G, a 5.1 ms time constant and 21.4 ms conversion time and a microwave power of 0.18 mW. Spectra was simulated using the EasySpin software package.[16]

Cyclic Voltammetry (CV) measurements were carried out with a VSP potentiostat from Bio-Logic, equipped with the EC-Lab software. The experiments were performed under inert (Ar) atmosphere in a custom double-wall jacketed single-compartment cell.

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[16] Stoll, S.; Schweiger, A. *Journal of Magnetic Resonance* **2006**, *178*, 42.

0.1 M TBAH electrolyte solutions were employed using CH_3CN or CH_3CN:EtOH (2:3) as a solvent mixture. A 3 mm diameter glassy carbon (GC) disk and a Pt wire were used as working and counter electrodes, respectively. An Ag wire was employed as a pseudo-reference, immerged in a bridge tube containing the same electrolyte solution as the main compartment (0.1 M TBAH/CH_3CN) and separated from it by a porous tip. Ferrocene (Fc) was used as an internal standard and all the potentials are referenced *vs.* the $Fc^{+/0}$ redox couple.[17]

UV-Vis spectra were recorded on an Agilent 8453 diode array spectrophotometer (190-1100 nm range) in a 1 cm quartz cells.

UV-Vis measurements with on-line irradiation were performed in a house-built apparatus using 1 cm quartz fluorescence cuvette in a fluorescence cuvette holder. LED (Royal blue, 447 nm.) was placed perpendicular to the optical pathway of the Agilent 8453 diode array spectrophotometer (190-1100 nm range).

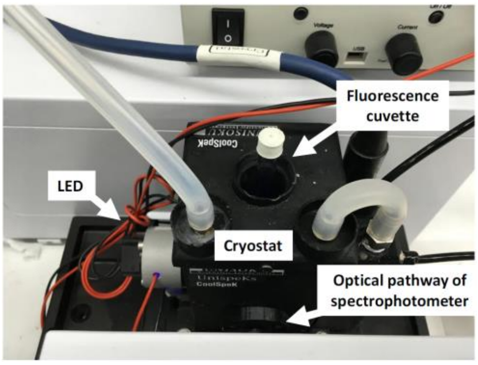

Figure SI.EP.EP-1. Setup for UV-Vis measurement with on-line irradiation.

The solutions of **PC_{Cu}** were prepared in ethanol acetonitrile mixture (3:2). The concentraton of **PC_{Cu}** was fixed to 20 µM. As a blank the same ethanol-acetonitrile mixture was used. The absorption kinetics were studied on an Agilent 8453 diode array spectrophotometer (190-1100 nm range) in 1cm quartz cell.

UV-Vis Spectroelectrochemistry (UV-Vis SEC) experiments were performed by using a SP-50 potentiostat from Bio-Logic under an Ar atmosphere. A 4 mM solution of complex in 0.2 M TBAH/CH_3CN or solvent mixture is introduced in an optically transparent thin-layer electrode (OTTLE) cell, equipped with Pt minigrid working and auxiliary electrodes, an Ag microwire pseudo-reference electrode and a CaF_2 window.[18] Blank 0.2 M TBAH/CH_3CN solutions were used for solvent subtractions. UV/Vis spectra

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[17] V. V. Pavlishchuk, A.W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97–102.
[18] M. Krejcik, M. Danek, F. Hartl, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *317*, 179.

were measured with an Agilent 8453 diode array spectrophotometer (λ=190–1100 nm range), with a cycle time equal to 2 s.

1.1. In-house developed parallel photoreactor

Light source: The reactions were performed using Royal-Blue (λ = 447±20 nm) LUXEON Rebel ES LED, mounted on a 20 mm Square Saber - 1030 mW @ 700mA (Datasheet: https://www.luxeonstar.com/assets/downloads/ds68.pdf) as a light source.

Temperature Control: Reaction temperature was controlled by a high precision thermoregulation Hubber K6 cryostat. Likewise, aiming at ensuring a stable irradiation the temperature of the LEDs was controlled and set at 22 ºC.

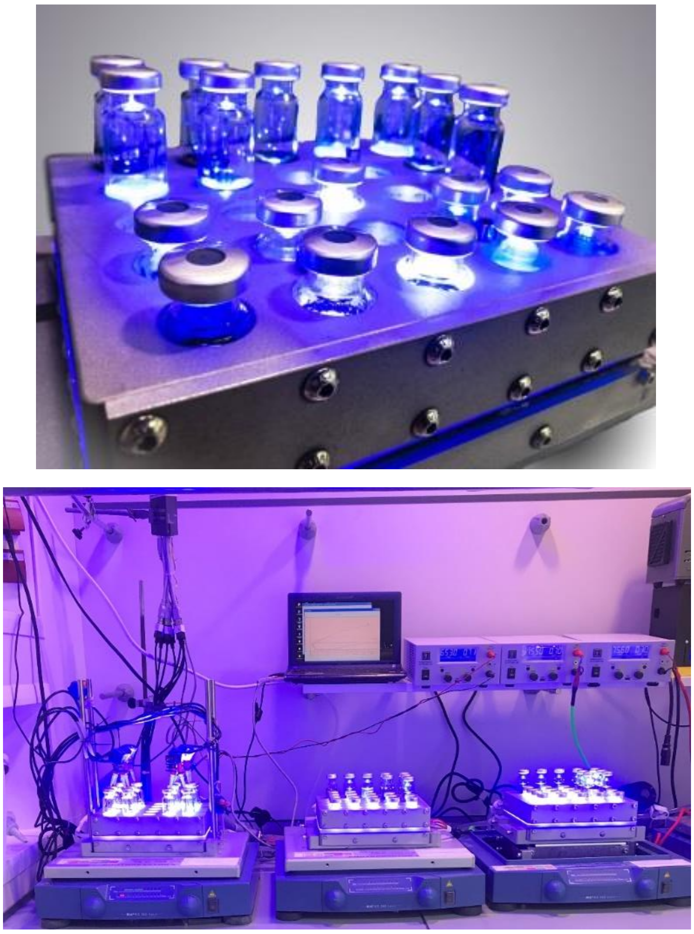


Figure SI.EP.EP-2. In-house developed parallel photoreactors.

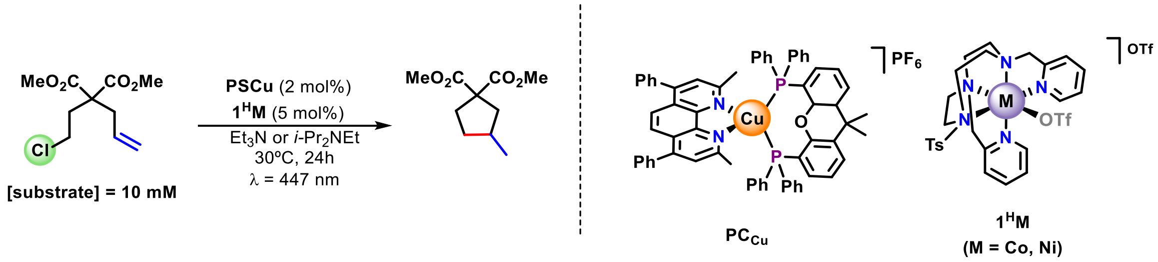
1.2. Parallel pressure transducer hardware

The parallel pressure transducer device is composed of 8 differential pressure transducers (Honeywell-ASCX15DN, ± 15 psi) connected to a hardware data-acquisition system (based on an Atmega microcontroller) controlled by a home-developed software program. The differential pressure transducer Honeywell-ASCX15DN gives a 100 microseconds response with a signal-conditioned output (high level span, 4.5 V), and contains a calibrated sensor that is temperature compensated (from 0 ºC to 70 ºC). The differential sensor has two sensing ports that can be used for differential pressure measurements.

The pressure calibration device was offset within ± 0.5 matm and the span adjusted *via* software with a high precision pressure transducer (PX409-030GUSB, 0.08 % of accuracy). Each of the 8 differential 4 pressure transducers (Honeywell-ASCX15DN, ±15 psi) produce a voltage output that can be directly transformed to a pressure difference between two measuring ports. The voltage output is digitalized with a resolution of 0.25 matm from 0 to 175 matm, and 1 matm from 176 to 1000 matm using an Atmega microcontroller with an independent voltage auto-calibration. The firmware for the Atmega microcontroller and the control software were developed in-house.

Gases at the headspace were analyzed with an Agilent 7820A GC System equipped with columns Washed Molecular Sieve 5Å, 2m x 1/8'' OD, Mesh 60/80 SS and Porapak Q, 4m x 1/8'' OD, SS. Mesh: 80/100 SS and a Thermal Conductivity Detector. The quantification of the H_2 obtained was measured through the interpolation of a previous calibration using different H_2/N_2 mixtures.

2. Optimization of conditions for reductive cyclization reactions



General procedure for optimization screening: Inside an anaerobic box, aliquots from stock solutions of dimethyl allyl chloroethylmalonate (0.2 mL, 0.02 mmol, 1.0 eq.), **1^HM** catalyst (M = Co or Ni, 0.1 mL, 0.001 mmol, 5 mol %), **PC$_{Cu}$** (0.1 mL, $4x10^{-4}$ mmol, 2 mol %) and acetonitrile (0.4 mL) were equally distributed into a vial (10 mL of headspace) that contained glass beads. The vial was sealed with a septum and removed from the anaerobic box. Degassed protic solvent was added to the vial to reach a total volume of

2 mL (total concentration of substrate 10 mM). Et_3N (40 µL, 0.286 mmol, 14.4 eq.) or *i*-Pr_2NEt (40 µL, 0.229 mmol, 11.4 eq.) was added to each vial, which was placed in the photoreactor at the indicated temperature (30 ºC). After irradiating for 24h with blue LEDs (λ = 447 nm), the sample was diluted with ethyl acetate (2 mL). A solution of biphenyl in ethyl acetate was added as internal standard (8.7×10^{-3} mmol in 0.25 mL). Then, addition of 1 mL of H_2O formed a biphasic solution and an aliquot of the organic phase was passed through a plug of $MgSO_4$ and eluted with EtOAc. The resulting solution was analyzed by gas chromatography. The yields reported for each reaction are given as an average of at least two runs.

2.1. Solvent screening

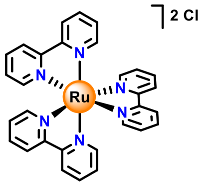
Table SI.EP-1.

Catalyst (mol%)	**PC (%)**	**Solvent (mL)**	**ED**	**Conv. (%)^a**	**Yield (%)^a**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	MeCN	Et_3N (14.4)	24	**17**
[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HNi **(5)**	**PC$_{Cu}$** (2)	MeCN	Et_3N (14.4)	19	**6**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	H_2O : MeCN (3:2)	Et_3N (14.4)	67	**22**
[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HNi **(5)**	**PC$_{Cu}$** (2)	H_2O : MeCN (3:2)	Et_3N (14.4)	56	**4**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	MeOH : MeCN (3:2)	Et_3N (14.4)	39	**27**
[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HNi **(5)**	**PC$_{Cu}$** (2)	MeOH : MeCN (3:2)	Et_3N (14.4)	17	**9**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	*i*-PrOH : MeCN (3:2)	Et_3N (14.4)	75	**61**
[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HNi **(5)**	**PC$_{Cu}$** (2)	*i*-PrOH : MeCN (3:2)	Et_3N (14.4)	76	**62**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et_3N (14.4)	96	**83**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	93	**78**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	EtOH : *i*-BuCN (3:2)	Et_3N (14.4)	84	**74**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	EtOH : *n*-BuCN (3:2)	Et_3N (14.4)	98	**85**
[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HCo **(5)**	**PC$_{Cu}$** (2)	EtOH : *t*-BuCN (3:2)	Et_3N (14.4)	68	**58**
[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HNi **(5)**	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et_3N (14.4)	100	**74**
[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], 1^HNi **(5)**	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	99	**96**

a) Conversion and yield were determined by GC using biphenyl as internal standard. PC = photoredox catalyst. ED = electron donor.

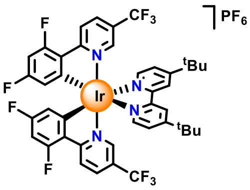
2.2. Photosensitizer screening

Table SI.EP-2.



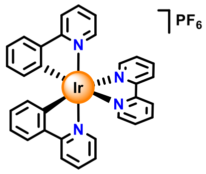
PC$_{Ru}$

E$_{1/2}$ (PS^n/PS^{n-1}) = -1.33 V



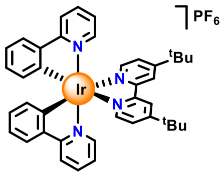
PC$_{Ir1}$

E$_{1/2}$ (PS^n/PS^{n-1}) = -1.37 V



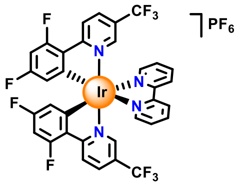
PC$_{Ir2}$

E$_{1/2}$ (PS^n/PS^{n-1}) = -1.42 V



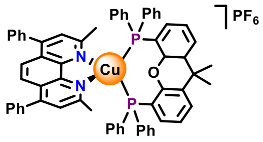
PCIr$_3$

E$_{1/2}$ (PS^n/PS^{n-1}) = -1.51 V



PC$_{Ir4}$

E$_{1/2}$ (PS^n/PS^{n-1}) = -1.37 V



PC$_{Cu}$

E$_{1/2}$ (PS^n/PS^{n-1}) = -1.60 V

PS (%)	E$_{1/2}$ (PS^n/PS^{n-1}) (V vs SCE)	Catalyst (mol%)	ED (equiv)	Conv. (%)^a	Yield (%)^a
PC$_{Cu}$ (2)	-1.6[11]	[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Co** (5)	Et$_3$N (14.4)	96	**83**
PC$_{Cu}$ (2)	-1.6[11]	[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Ni** (5)	*i*-Pr$_2$NEt (11.4)	99	**96**
PC$_{Ir1}$ (2)	-1.37[19]	[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Co** (5)	Et$_3$N (14.4)	63	**46**
PC$_{Ir1}$ (2)	-1.37[16]	[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Ni** (5)	*i*-Pr$_2$NEt (11.4)	100	**73**
PC$_{Ir2}$ (2)	-1.42[20]	[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Co** (5)	Et$_3$N (14.4)	17	**12**
PC$_{Ir2}$ (2)	-1.42[17]	[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Ni** (5)	*i*-Pr$_2$NEt (11.4)	86	**72**
PC$_{Ir2}$ (2)	-1.42[17]	----	Et$_3$N (14.4)	13	**6**
PC$_{Ir3}$ (2)	-1.51[21]	[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Co** (5)	Et$_3$N (14.4)	45	**37**
PC$_{Ir3}$ (2)	-1.51[18]	[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Ni** (5)	*i*-Pr$_2$NEt (11.4)	29	**21**
PC$_{Ir4}$ (2)	-1.37[22]	[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Co** (5)	Et$_3$N (14.4)	46	**37**
PC$_{Ir4}$ (2)	-1.37[19]	[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Ni** (5)	*i*-Pr$_2$NEt (11.4)	100	**76**
PC$_{Ru}$ (2)	-1.33[23]	[Co(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Co** (5)	Et$_3$N (14.4)	5	**5**
PC$_{Ru}$ (2)	-1.33[20]	[Ni(OTf)$_2$(Ts^{H}Py$_2$tacn)], **1^{H}Ni** (5)	*i*-Pr$_2$NEt (11.4)	13	**1**

a) Conversion and yield were determined by GC using biphenyl as internal standard. PC = photoredox catalyst. ED = electron donor.

2.3. Catalyst screening

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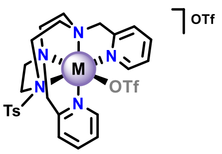
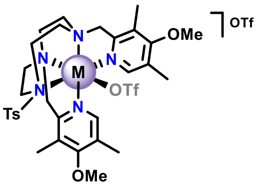
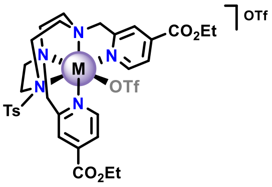
Table SI.EP-3.



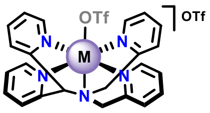
1^{H}M



1^{DMM}M



1^{CO2Et}M



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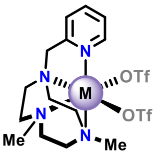

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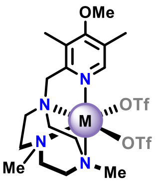

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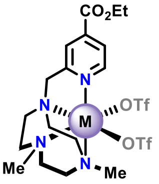

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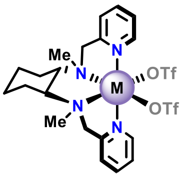

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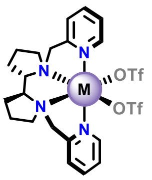

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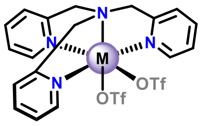
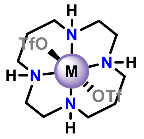
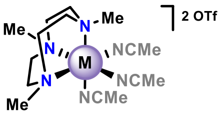


9M-OTf



10M



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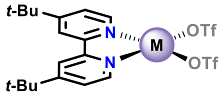
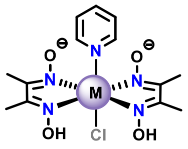


12M-OTf



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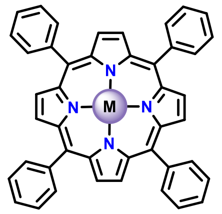

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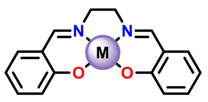

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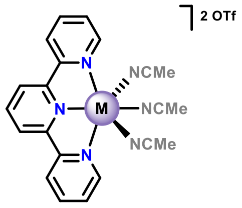
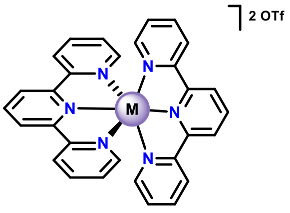


20M-OTf



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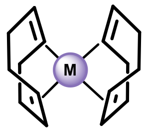


22M

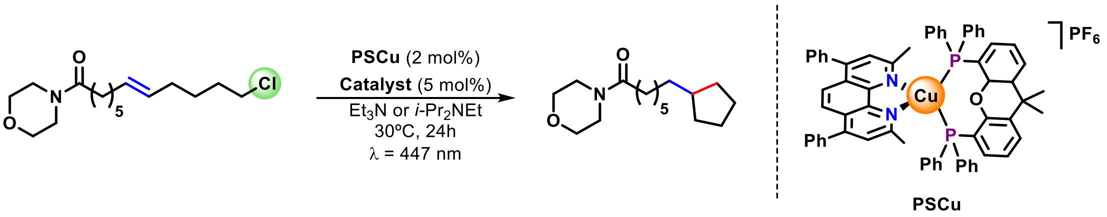
Catalyst (mol%)	PS (%)	Solvent	ED (equiv)	Conv. (%)[a]	Yield (%)[a]
[Co(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	96	**83**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.4)	99	**96**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.4)	100	**91**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)[c]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.4)	100	**90**
[Co(OTf)(Ts^{H}Py$_2$tacn)],(OTf) 1^{H}Co (10)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	84	**80**
[Co(OTf)(Ts^{DMM}Py$_2$tacn)](OTf), 1^{DMM}Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	87	**80**
[Ni(OTf)(Ts^{DMM}Py$_2$tacn)](OTf), 1^{DMM}Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.4)	70	**52**
[Co(OTf)(Ts^{CO2Et}Py$_2$tacn)](OTf), 1^{CO2Et}Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	83	**70**
[Ni(OTf)(Ts^{CO2Et}Py$_2$tacn)],(OTf) 1^{CO2Et}Ni (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.4)	73	**63**
[CoN4Py], 5Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	43	**36**
[NiN4Py], 5Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.4)	73	**33**

[Co(OTf)$_2$(Me$_2$^{H}Pytacn)], 6^{H}Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	42	**30**
[Co(OTf)$_2$(Me$_2$^{DMM}Pytacn)], 6^{DMM}Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	22	**18**
[Co(OTf)$_2$(Me$_2$^{CO2Et}Pytacn)], 6^{CO2Et}Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	50	**41**
[Co-(MCP)OTf$_2$], 7Co-OTf (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	71	**68**
[Co-(MCP)Cl$_2$], 7Co-Cl (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	71	**64**
[Ni-(MCP)OTf$_2$], 7Ni-OTf (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	90	**55**
[Co-(PDP)OTf$_2$], 8Co-OTf (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	67	**60**
[Ni-(PDP)OTf$_2$], 8Ni-OTf (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	94	**68**
[Co-TPA_OTf$_2$], 9Co-OTf (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	16	**16**
[Co-TPA_Cl$_2$], 9Co-Cl (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	13	**11**
[Ni-TPA_OTf$_2$], 9Ni-OTf (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	96	**54**
[Co-Cyclam], 10Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	18	**10**
[Ni-Cyclam], 10Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	100	**82**
[Co-tacnMe$_3$(MeCN)$_3$](OTf)$_2$, 11Co-OTf (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	48	**36**
[Ni- tacnMe$_3$(MeCN)$_3$](OTf)$_2$, 11Ni-OTf (5)[b]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	19	**2**
[Co(dtbbpy)(OTf)$_2$], 12Co-OTf (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	21	**10**
[Co(dtbbpy)(OTf)$_2$], 12Co-OTf (5)[d]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	87	**80**
[Co(dtbbpy)(OTf)$_2$], 12Co-OTf (5)	**PC$_{Cu}$** (2)	EtOH : DMF (3:2)	Et$_3$N (14.4)	25	**4**
[Co(dtbbpy)(OTf)$_2$], 12Co-OTf (5)	**PC$_{Ir1}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	38	**13**
[Co(dtbbpy)(OTf)$_2$], 12Co-OTf (5)[d]	**PC$_{Ir1}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	100	**88**
[Co(dtbbpy)(OTf)$_2$], 12Co-OTf (5)	**PC$_{Ir1}$** (2)	EtOH : DMF (3:2)	Et$_3$N (14.4)	52	**2**
[Ni(dtbbpy)(OTf)$_2$], 12Ni-OTf (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	13	**3**
[Ni(dtbbpy)(OTf)$_2$], 12Ni-OTf (5)[d]	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	55	**8**
[Ni(dtbbpy)(OTf)$_2$], 12Ni-OTf (5)	**PC$_{Cu}$** (2)	EtOH : DMF (3:2)	Et$_3$N (14.4)	21	**3**
[Ni(dtbbpy)(OTf)$_2$], 12Ni-OTf (5)	**PC$_{Ir1}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	11	**4**
[Ni(dtbbpy)(OTf)$_2$], 12Ni-OTf (5)[d]	**PC$_{Ir4}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	72	**58**
[Ni(dtbbpy)(OTf)$_2$], 12Ni-OTf (5)	**PC$_{Ir4}$** (2)	EtOH : DMF (3:2))	Et$_3$N (14.4)	17	**3**
[Co(DMG)PyCl], 17Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.4)	7	**6**
[Co(DMG)PyCl], 17Co (5)	**PC$_{Cu}$** (2)	MeCN	Et$_3$N (14.4)	21	**6**
[Co-TTP], 18Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	100	**74**
[Co-TTP], 18Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3	100	**80**
[Ni-TTP], 18Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	13	**7**
[Ni-TTP], 18Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	30	**19**
[Co-Salem], 19Co (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	Et$_3$N (14.3)	33	**12**
[Ni-Salem], 19Ni (5)	**PC$_{Cu}$** (2)	EtOH : MeCN (3:2)	*i*-Pr$_2$NEt (11.3)	20	**10**

[Co-Terpyridine(MeCN)$_3$](OTf)$_2$ 20Co-OTf (5)^b	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	Et_3N (14.3)	57	**42**
[Ni-Terpyridine(MeCN)$_3$](OTf)$_2$ 20Ni-OTf (5)^b	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.3)	29	**12**
[Co-Terpyridine$_2$] 21Co (5)^e	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	Et_3N (14.3)	57	**42**
[Ni-Terpyridine$_2$] 21Ni (5)^e	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.3)	29	**12**
[Ni-Cod$_2$] 22Ni (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.3)	19	**5**
[Ni-Cod$_2$] 22Ni (5)^f	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.3)	26	**13**
--	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	Et_3N (14.4)	10	**1**
[Co(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Co (5)	**--**	EtOH : MeCN (3:2)	Et_3N (14.4)	0	0
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)	**--**	EtOH : MeCN (3:2)	Et_3N (14.4)	0	0
[Co(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Co (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	**--**	0	0
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	**--**	2	**2**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)^g	**--**	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	20	**14**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)^h	**--**	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	7	**0**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)^i	**--**	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	15	**0**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)^j	**--**	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	13	**0**

a) Conversion and yield were determined by GC using biphenyl as internal standard. dtbbpy = 4,4′-Di-*tert*-butyl-2,2′-dipyridyl. DMG = Dimethylglyoximato. b) Complex formed *in situ* by reacting equimolar amounts of ligand and the triflate metal salt. c) Reactions was carried out in presence of 500 eq oh mercury. d) Using 3a as substrate. e) Complex formed *in situ* by reacting two equivalents of the ligand with one equivalent of the triflate metal salt. f) Reaction was carried out with one equivalent of the ^{H}Py$_2$tacn ligand. g) Reaction was carried out using two equivalents of zinc as reductant in presence of light. h) Reaction was carried out using two equivalents of zinc as reductant in absence of light. i) Reaction was carried out using two equivalents of manganese as reductant in presence of light. j) Reaction was carried out using two equivalents of manganese as reductant in absence of light.

Table SI.EP-4.



Catalyst (mol%)	PS (%)	Solvent	ED (equiv)	Conv. (%)^a	Yield (%)^a
[Co(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Co (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	Et_3N (14.4)	42	**23**
[Co-TTP], 18Co (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	83	**39**
[Ni(OTf)(Ts^{H}Py$_2$tacn)](OTf), 1^{H}Ni (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	Et_3N (14.4)	94	**87**
[Ni-Cyclam], 10Ni (5)	**PC_{Cu}** (2)	EtOH : MeCN (3:2)	*i*-Pr_2NEt (11.4)	100	**73**

a) Conversion and yield were determined by GC using biphenyl as internal standard. PS = photosensitizer

3. Single-point experiment monitoring

General Procedure A: Cobalt (5 mol%), PC_{Cu} (2 mol%), Et_3N (14.4 eq).

General Procedure B: Nickel (5 mol%), PC_{Cu} (2 mol%), i-Pr_2NEt (11.4 eq).

Inside an anaerobic box, aliquots from stock solutions of dimethyl allyl chloroethylmalonate (0.2 mL, 0.02 mmol, 1.0 eq.), complex **1^HCo** or **1^HNi** (0.1 mL, 0.002 mmol, 5 mol%), **PC_{Cu}** (0.1 mL, 4×10^{-4} mmol, 2 mol%) and acetonitrile (0.4 mL) were equally distributed into 8 vials (10 mL of headspace) that contained glass beads. The vials were sealed with a septum and removed from the anaerobic box. Degassed ethanol was added to each vial to reach a total volume of 2 mL (total concentration of substrate 10 mM). Et_3N (40 µL, 0.29 mmol, 14.4 eq.) or *i*-Pr_2NEt (40 µL, 0.23 mmol, 11.4 eq.) was added to each vial, which was placed in the photoreactor at the indicated temperature (30 ºC). At specific points of time (see plot), aliquots of 100 µL were taken from the sealed vials and mixed with 29 µL of solution of biphenyl in EtOAc (34.8 mM) and the resulting mixture was analyzed by GC-FID. Light irradiation was switched off and on at specific points of the single-point monitoring experiment, which indicates that the reaction stops when the vial is not irradiated with visible light.

3.1. Kinetic monitoring

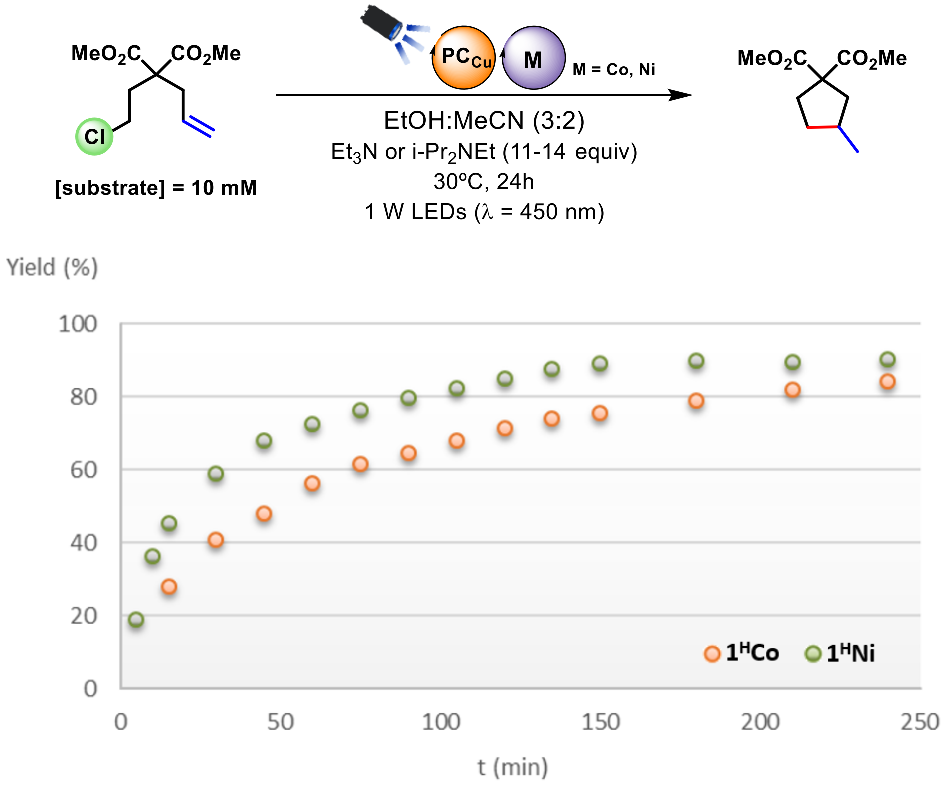


Figure SI.EP-3. *Single-point monitoring experiments.*

3.2. Single-point experiment through light-dark cycles

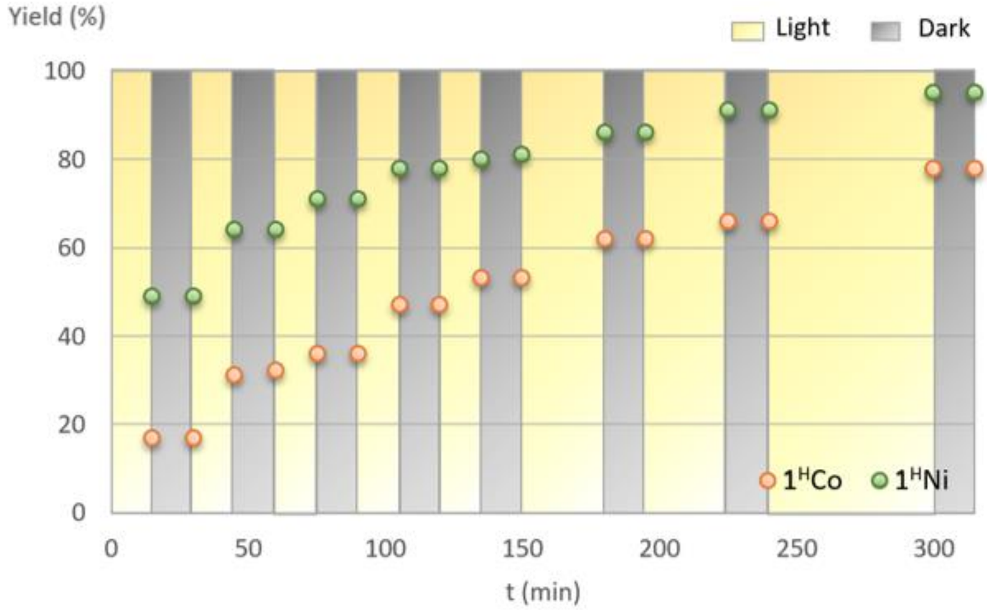


Figure SI.EP-4. *Single-point monitoring experiment throughout light-dark cycles.*

4. H_2 evolution monitoring

General Procedure A: Cobalt (5 mol%), PC_{Cu} (2 mol%), Et_3N (14.4 eq).

General Procedure B: Nickel (5 mol%), PC_{Cu} (2 mol%), i-Pr_2NEt (11.4 eq).

General procedure: Inside an anaerobic box, aliquots from stock solutions of dimethyl allyl chloroethylmalonate (**2a**, 1.5 mL, 0.15 mmol, 1.0 eq.), complex **1^HCo** or **1^HNi** (0.75 mL, $7.5x10^{-3}$ mmol, 5 mol%), photosensitizer **PC_{Cu}** (0.75 mL, $3x10^{-3}$ mmol, 2 mol%) and acetonitrile (3 mL) were equally distributed into 3 vials (22 mL of headspace) that contained glass beads. The vials were sealed with a septum and removed from the anaerobic box. Degassed ethanol was added to each vial to reach a total volume of 15 mL (total concentration of substrate 10 mM). Et_3N (300 µL, 2.16 mmol, 14.4 eq.) or *i*-Pr_2NEt (300 µL, 1.72 mmol, 11.4 eq.) was added to each vial, which was placed in the photoreactor at 30 ºC. Each reaction vial was connected to a differential pressure transducer sensor (Honeywell-ASCX15DN) with a reference vial that contains only **PC_{Cu}**, electron donor and solvents. The reaction and reference vials were kept under the same experimental conditions to compensate the noise due to temperature-pressure fluctuations. The dihydrogen generated in the reaction vessels were monitored by recording the increase of pressure in the headspace, which is measured as the difference in pressure between the reaction and the reference vial. Also blank experiments in order to monitor the dihydrogen evolution in the absence of substrate **2a** were performed at the same reaction conditions.

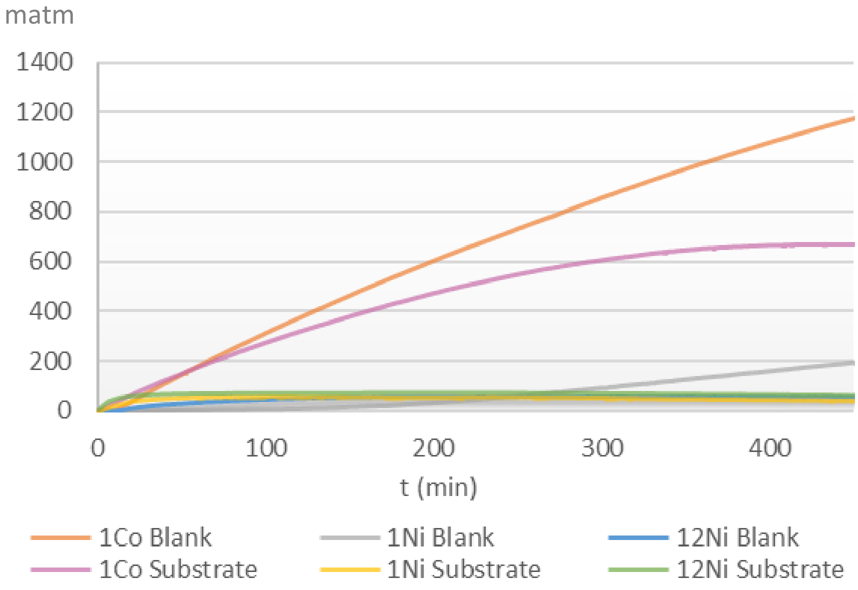
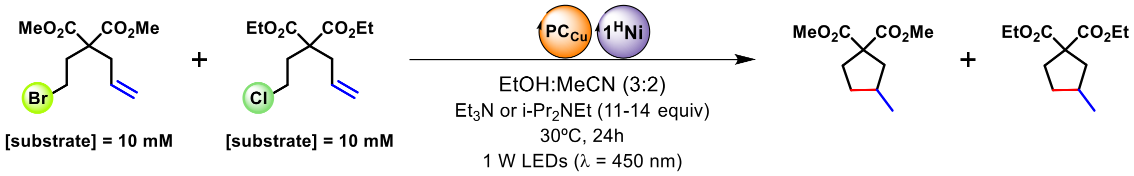


Figure SI.EP-5. *Hydrogen evolution monitoring.*

5. Competitive Studies



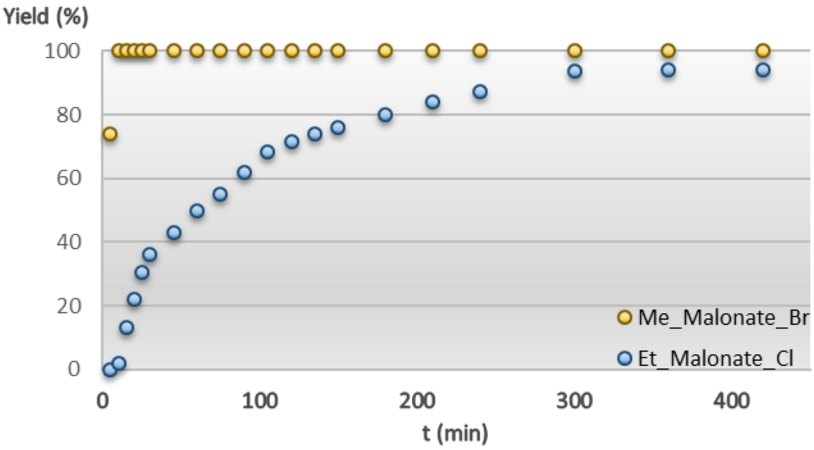
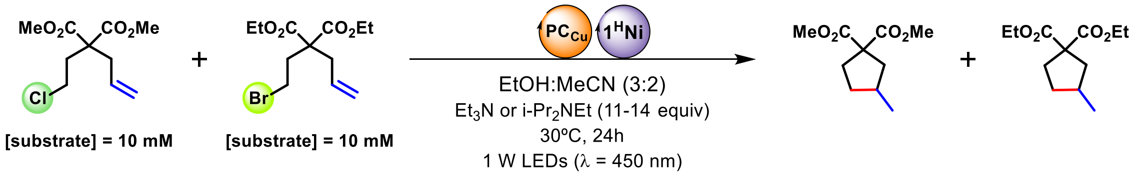


Figure SI.EP-6. *Single-point monitoring experiment of bromine/chlorine selectivity.*



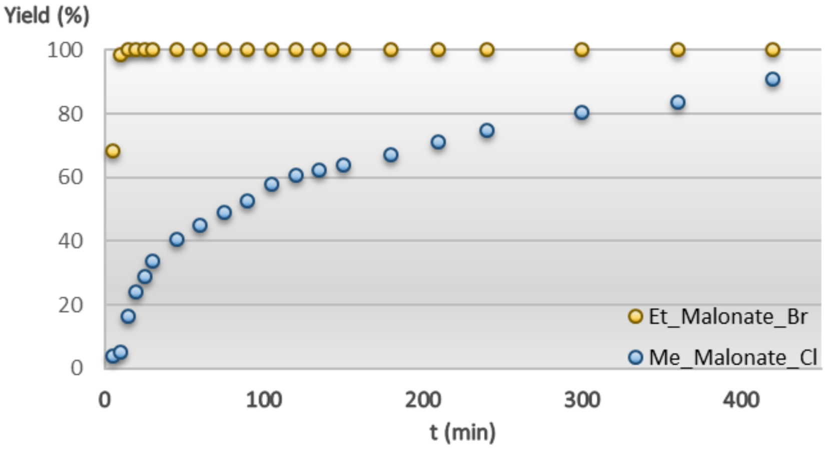
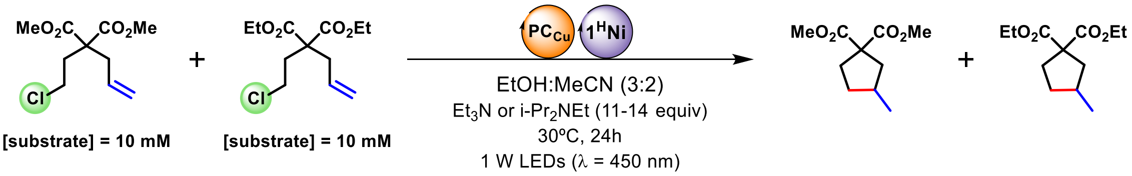


Figure SI.EP-7. *Single-point monitoring experiment of bromine/chlorine selectivity.*



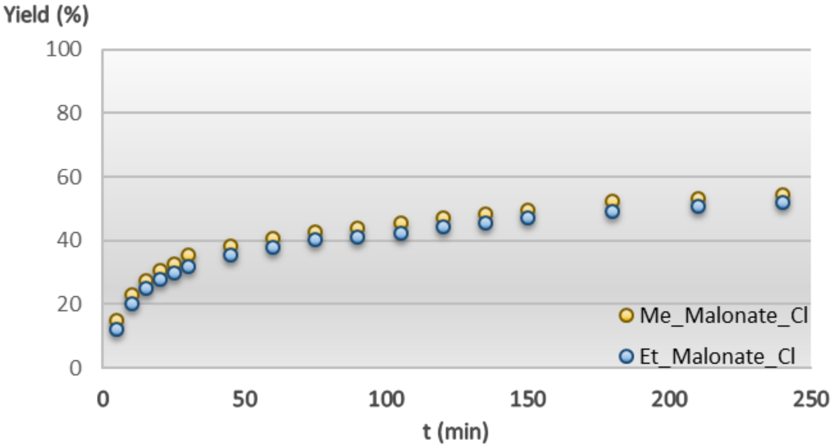
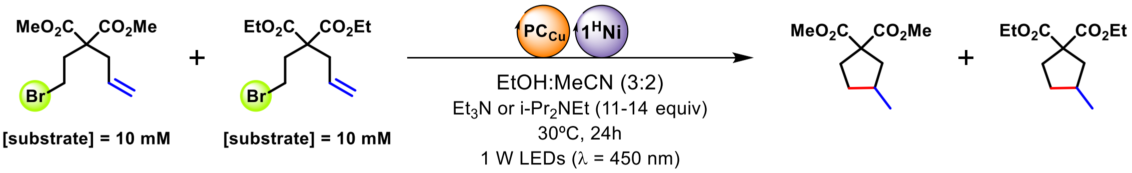


Figure SI.EP-8. *Single-point monitoring experiment of bromine/chlorine selectivity.*



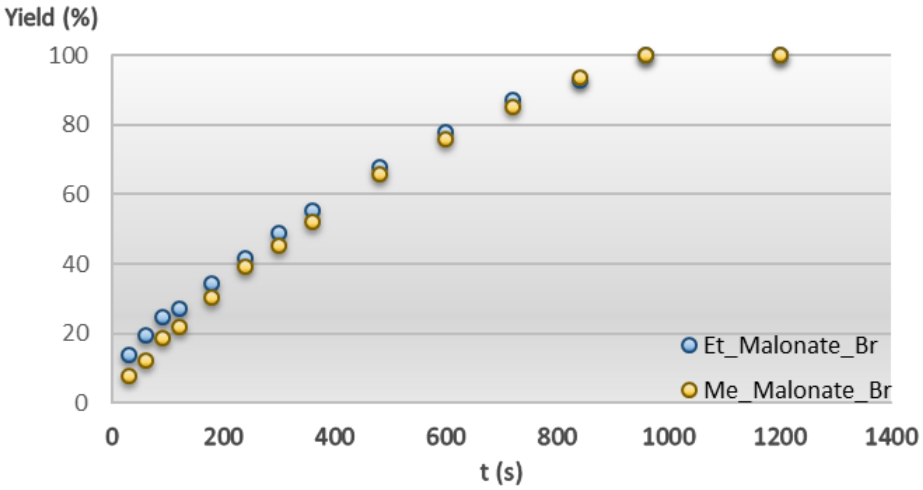
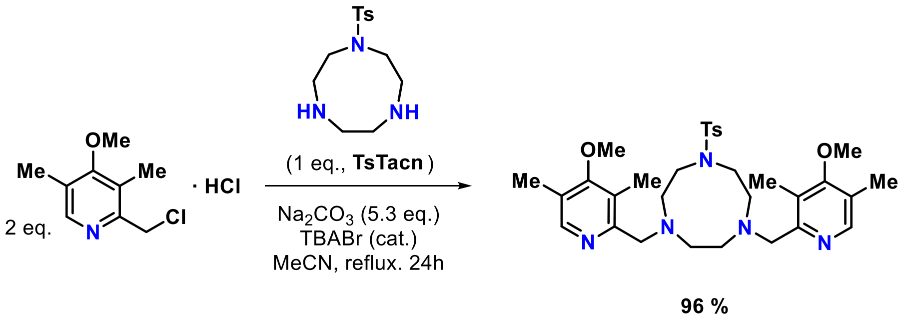


Figure SI.EP-9. *Single-point monitoring experiment of bromine/chlorine selectivity.*

6. Synthesis and characterization of complexes

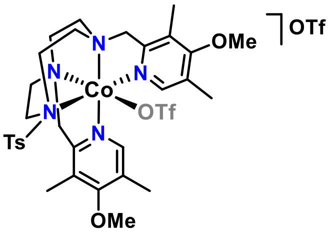
6.1. Synthesis of ligand Ts^{DMM}Py$_2$tacn



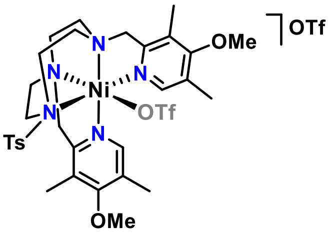
Ts^{DMM}Py$_2$tacn was synthesized following a reported procedure with the introduction of small modifications in the purification steps.[6] 2-Chloromethyl-4-methoxy-3,5-dimethylpyridine hydrochloride (2.59 g, 11.64 mmol), Tstacn (1.5 g, 5.29 mmol) and anhydrous acetonitrile (80 mL) were mixed in a 150 mL flask. Na_2CO_3 (3 g, 28.3 mmol) and tetrabutylammonium bromide (TBABr, 130 mg, 0.54 mmol) were added directly as solids and the resulting mixture was heated at reflux for 24 h under N_2 atmosphere. After cooling at room temperature, the resulting orange mixture was filtered and the filter cake was washed with CH_2Cl_2. The combined filtrates were evaporated under reduce pressure. Then, a solution of HCl 1 M (20 mL) was added to the residue and the aqueous phase was washed with dichloromethane (3 x 20 mL). The aqueous phase was basified to pH 10 with a solution of NaOH 2 M and dichloromethane (30 mL) was added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the oil residue was dissolved with 5 mL of dichloromethane and the addition of hexane (20 mL) caused the precipitation of a brownish oil. The solution was decanted and the solvent was removed under reduced pressure, which gave 1.78 g of the title compound. The remaining brownish oil was redissolved again in 3 mL of dichloromethane and addition of hexane (10 mL) caused the formation of an oil residue. The organic solution was decanted, the solvent removed and another fraction of 1.10 g of the title compound was obtained (overall yield of the reaction 96%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (s, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 10H), 3.09 - 2.97 (m, 8H), 2.64 (s, 4H), 2.39 (s, 3H), 2.29 (s, 6H), 2.21 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 164.2, 157.4, 148.5, 143.0, 135.9, 129.6, 127.2, 126.2, 125.2, 63.0, 59.9, 56.3, 56.1, 50.3, 21.6, 13.4, 11.3 ppm. **IR** (film): 2925, 2832, 1563, 1450, 1334, 1252, 1156, 1090, 998, 711, 694, 547 cm^{-1}. **MS:** *m/z* calcd for $C_{31}H_{44}N_5O_4S$ $[M+H]^+$:582,3114, found 582.3109. The spectroscopic data is in agreement with previously reported data for this compound.[6]

6.2. Synthesis of [Co(OTf)(Ts^{DMM}Py$_2$tacn)](OTf) and [Ni(OTf)(Ts^{DMM}Py$_2$tacn)](OTf)

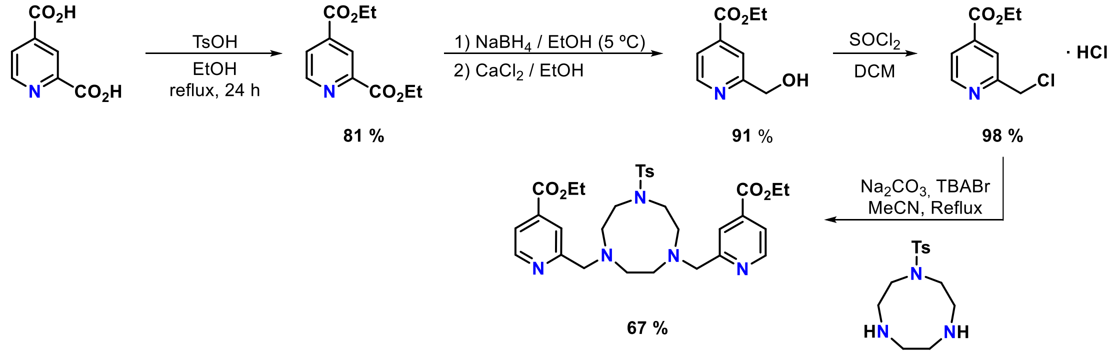


1^{DMM}Ni was synthesized following the reported procedure.[6] A solution of $Co(OTf)_2(MeCN)_2$ (374 mg, 0.851 mmol) in anhydrous tetrahydrofuran (THF) (1 mL) was added dropwise to a vigorously stirred solution of ^{DMM}Py$_2$Tstacn (550 mg, 0.945 mmol) in THF(1 mL). After stirring for 2 h the solution was filtered off and the resulting solid dried under vacuum. This solid was dissolved in CH_2Cl_2 and the slow diffusion of diethyl ether into this solution gave 0.672 g of the title complex as a pale pink solid (76 %). **Anal.** Calcd for $C_{33}H_{47}CoF_6N_5O_{12}S_3$: C, 40.69; N, 7.19; H, 4.86 %. Found: C, 41.04; N, 7.20; H, 4.46 %. **HR-ESI-MS** (m/z): 789.1882 $[M - OTf]^+$.



1^{DMM}Ni was synthesized following an analogous synthetic procedure as described for complex **1^{DMM}Co**, obtaining 0.213 g of the targeted complex as a pale blue solid (68 %). **Anal.** Calcd for $C_{33}H_{45}NiF_6N_5O_{11}S_3$: C, 41.50; N, 7.33; H, 4.75 %. Found: C, 41.77; N, 7.28; H, 4.56 %. **HR-ESI-MS** (m/z): 788.1904 $[M - OTf]^+$.

6.3. Synthesis of ligand Ts^{CO2Et}Py$_2$tacn



4-ethoxycarbonyl-2-chloromethylpyridine hydrochloride was synthesized following the reported procedure starting from *2,4-Pyridine dicarboxylic acid*.[24]

1,4-dimethyl-7-(4-ethoxycarbonyl-2-pyridylmethyl)-1,4,7-triazacyclononane, (Ts^{CO2Et}Py$_2$tacn) was synthesized following a reported procedure with slight modifications in the purification steps.[6] Ethyl 2-(chloromethyl)isonicotinatehydrochloride (2,17 g, 9.25 mmol), Tstacn (1.31g, 4.63 mmol) and anhydrous acetonitrile (80 mL) were mixed in a 250 mL flask. Na_2CO_3 (2.4 g) and tetrabutylammonium bromide (TBABr, 160 mg) were added directly as solids and the resulting mixture was heated at reflux for 22 hours under N_2. After cooling at room temperature, the resulting orange mixture was filtered and the filter cake was washed with CH_2Cl_2. The combined filtrates were evaporated under reduce pressure. To the resulting residue, 2 M NaOH (15 mL) was added and the mixture was extracted with CH_2Cl_2 (4 x 40 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The remaining oil residue was dissolved with 5 mL of dichloromethane and the addition of hexane (20 mL) caused the precipitation of a yellowish oil that was dried under reduced pressure to yield 3.8 g of a pale yellow oil (6.4 mmol, 67 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 - 8-64 (m, 2H), 7.99 (s, 2H), 7.72 - 7.68 (m, 2H), 7.67 - 7.61 (m, 2H), 7.29 - 7.24 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 4H), 3.94 (s, 4H), 3.31 - 3.12 (m, 8H), 2.85 (s, 4H), 2.40 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 165.2 (2C), 161.1 (2C), 149.8 (2C), 143.0, 138.14 (2C), 135.8, 129.6 (2C), 127.0 (2C), 122.4 (2C), 121.2 (2C), 63.1 (br, 2C), 61.7 (2C), 55.5 (br, 4C), 50.5 (br, 2C), 21.4, 14.6 (2C) ppm. **IR** (film): 2929, 1723, 1599, 1562, 1287, 1203, 1156, 1902, 1018, 914, 763, 728, 694, 548cm^{-1}. **MS:** *m/z* calcd for $C_{31}H_{40}N_5O_6S$ $[M+H]^+$: 610,2699, found

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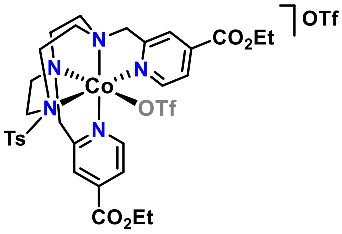
[24] Prat, I.; Company, A.; Corona, T.; Parella, T.; Ribas, X.; Costas, M., *Inorg. Chem.* **2013**, *52*, 9229.

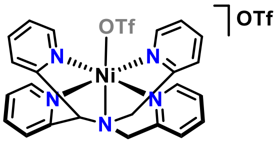
610.2694. The spectroscopic data is in agreement with previously reported data for this compound.[6]

6.4. Synthesis of [Co(OTf)(Ts^{CO2Et}Py$_2$tacn)](OTf)



1^{CO2Et}Co was synthesized following the analogous procedure to the described for complex **1^{DMM}Co** obtaining 0.210 g of the desired product as a brown crystalline solid (66 %). **HR-ESI-MS** (m/z): 817.1468 [M -OTf]$^+$. The spectroscopic data is in agreement with previously reported data for this compound.[6]

6.5. Synthesis of [Ni(OTf)(N4Py)](OTf)



Inside a glovebox, a suspension of Ni(OTf)$_2$(MeCN)$_2$ (269 mg, 0.612 mmol) in anhydrous THF (2 mL) was added dropwise to a vigorously stirred solution of N4Py ligand[25] (250 mg, 0.680 mmol) in THF (2 mL), causing a colour change from light yellow to brown after few minutes. After stirring overnight, Et$_2$O (3 mL) was added causing the precipitation of a brown solid. The solution was siphoned off and the solid was dried under vacuum. This solid was dissolved in CH$_2$Cl$_2$, filtered through Celite®, and the slow diffusion of diethyl ether into a saturated solution of complex caused the formation of a pale brown solid, which was dried under vacuum to give 282 mg of the title compound (0.489 mmol, 72 %).

Anal. Calcd for $C_{25}H_{23}NiF_6N_5O_7S_2$: C, 40.84; N, 9.52; H, 3.04; S, 8.72 %. Found: C, 40.84; N, 10.05; H, 3.23; S, 8.35 %. **HR-ESI-MS** (m/z): 574.0665 [M - OTf]$^+$.

6.6. Synthesis of [Co(MCP)(OTf)$_2$]

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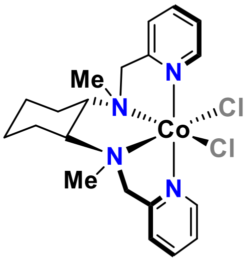
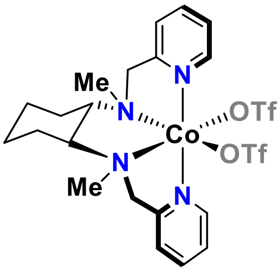
[22] Lubben, M.; Meetsma, A.; Wilkinson, E. C.;Feringa, B.;Lawrence Que Jr, L. *Angew. Chem. Int. Ed.* **1995**, *34*, 1512.



Complex **[Co(MCP)Cl$_2$]** was synthesized following a reported procedure with slight modifications.[10] In a glovebox, a solution of MCP ligand[26] (357 mg, 1.1 mmol) in THF (1 mL) was added dropwise to a vigorously stirred suspension of $CoCl_2$ (130 mg, 1 mmol) in THF (1 mL). After few minutes, a purple solid precipitated. After stirring for an additional 2 hours, the solid was allowed to settle down and the solution was filtered washed with dichloromethane (3x2 mL) and dried under vacuum. This solid was dissolved in dichloromethane, filtered through Celite®, and the slow diffusion of diethyl ether into a solution of the complex produced a crystalline pink solid, which was dried under vacuum to give 447 mg of the title compound (0.889 mmol, 89 %).

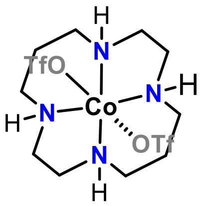
^{1}H NMR (400 MHz, $CDCl_3$): δ = 164.91, 101.2, 62.66, 50.65, 23.76, 21.23, 18.40, 8.23, 6.45, 2.14, 0.22, -16.95 ppm. **MS:** *m/z* calcd for $C_{20}H_{28}ClCoN_4$ [M-Cl]$^+$: 418.1329, found 418.1321. **Anal. Calcd** (%) for $C_{20}H_{28}Cl_2CoN_4$: C, 52.87; H, 6.21; N, 12.33. Found: C, 52.37; H, 6.04; N, 12.08. The spectroscopic data is in agreement with that reported.[10]



[Co(MCP)(OTf)$_2$] In a glovebox, to a stirred suspension of AgOTf (0.71 g, 0.660 mmol) in CH_2Cl_2 (1 mL) was added a solution of [Co(MCP)Cl$_2$] complex (0.1 g, 0.220 mmol) in CH_2Cl_2 (1 mL) at room temperature. After stirring overnight, the solution was filtered to remove the silver salts. The resulting pale pink solution was evaporated under vacuum to give 118 mg of the title compound asas a pink solid (0.173 mmol, 79 %).

HR-ESI-MS (m/z): 532.1161 [M - OTf]$^+$. **Anal. Calcd** (%) for $C_{22}H_{28}CoF_6N_4O_6S_2$: C, 38.77; H, 4.14; N, 8.22. Found: C, 38.28; H, 4.06; N, 8.05.

6.7. Synthesis of [Co-Cyclam]



[Co-Cyclam]. Compound has been synthesized according to the procedure described in the literature with slight modifications.[27] Co(OTf)$_2$ (0.7 g, 1.598 mmol) dissolved in warm ethanol (20 mL) was added to a solution of the ligand (0.326 g, 1.630 mmol) in ethanol (10 mL). The resulting light brown solution was warmed for a one hour in a sealed tube before ether was added. The resultant mauve precipitate

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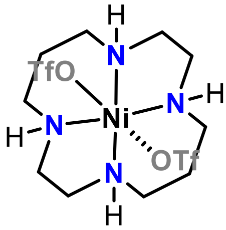
[26]Maity, N. C.; Kumar Bera, P.; Ghosh, D.; Abdi, S. H. R.; Kureshy, R. I.; Khan, N.-u. H.; Bajaj, H. C.; Suresh, E. *Catal. Sci. Technol.* **2014**, *4*, 208.

[27] Bosnich, B.; Poon, C. K.; Tobe, M.L. *Inorganic Chemistry* **1965**, *4*, 1102.

was filtered off and washed with ether yielded a brown solid (496 mg, 0.897 mmol, 56 %).

Anal. Calcd for $C_{12}H_{24}F_6N_4CoO_6S_2$: C, 25.86; N, 10.05; H, 4.33 %. Found: C, 25.69; N, 10.10; H, 4.23 %. **ESI-MS** (m/z): 408.0 [M - OTf]$^+$.

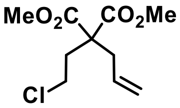
6.8. Synthesis of [Ni-Cyclam]



[Ni-Cyclam]. Compound has been synthesized according to the procedure described in the literature with slight modifications.[24] $Ni(OTf)_2(MeCN)_2$ (0.65 g, 1.415 mmol) was dissolved in warm ethanol (20 mL) and added to a solution of the ligand (0.289 g, 1.443 mmol) in ethanol (10 mL). The resulting light brown solution was warmed for a one hour in a sealed tube before ether was added. The resultant dark yellow precipitate was filtered off and washed with ether yielded a yellow solid (597 mg, 1.115 mmol, 76 %).

Anal. Calcd for $C_{12}H_{24}F_6N_4NiO_6S_2$: C, 26.05; N, 10.13; H, 4.37 %. Found: C, 25.94; N, 10.18; H, 4.24 %. **ESI-MS** (m/z): 407.1 [M - OTf]$^+$, 129.1 [M-2·OTf]$^{2+}$.

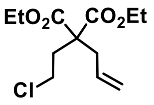
7. Synthesis and characterization of substrates



Substrate (**2a**): To a suspension of NaH (176 mg, 7.32 mmol, 1.1 eq.) in DMF (10 mL) was added at 0 ºC a solution of dimethyl allylmalonate (1.2 g, 6.97 mmol, 1.0 eq.) in THF (5 mL). The mixture was stirred at room temperature for 30 min in which it became a clear solution. To this solution was added dropwise a solution of freshly distilled 1-bromo-2-chloroethane (1.5 g, 10.45 mmol, 1.5 eq.) in THF (2 mL). The solution was stirred overnight at room temperature. The reaction was quenched by addition of H_2O (15 mL) and extracted with Et_2O (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 10 % diethyl ether in hexane) to yield 1.05 g (64 %) of the title compound as colorless oil.

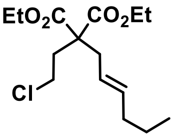
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73 - 5.52 (m, 1H), 5.23 - 5.02 (m, 2H), 3.74 (s, 6H), 3.53 (t, *J* = 7.6 Hz, 2H), 2.68 (dt, *J* = 7.4, 1.2 Hz, 2H), 2.37 (d, *J* = 7.6 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 170.9 (2C), 131.8, 119.9, 56.7, 52.8 (2C), 39.9, 38.0, 36.0

ppm. **IR** (film): 2955, 1730, 1435, 1208, 1172, 925, 648 cm^{-1}. **MS:** *m*/*z* calcd for $C_{10}H_{15}ClNaO_4$ [M + Na]$^+$: 257.0551, found 257.0549.



Substrate (**2b**): A solution of dimethyl allylmalonate (1.59 g, 7.98 mmol, 1 eq.) in THF (30 mL) was added dropwise to a suspension of NaH (286 mg, 11.91 mmol, 1.5 eq.) in THF at 0 ºC. The cooling bath was removed and the mixture was stirred for 60 min at room temperature. Freshly distilled 1-bromo-2-chloroethane (3.4 g, 23.82 mmol, 3.0 eq.) was added over 15 min and the resulting mixture was stirred for 48 h at rt. The reaction was quenched with saturated aqueous NH_4Cl. The aqueous solution was extracted with CH_2Cl_2 (2 ×15 mL) and the combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 3 % ethyl acetate in hexane) to yield 1.6 g (75 %) of title compound as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 - 5.58 (m, 1H), 5.19 - 5.09 (m, 2H), 4.20 (qd, *J* = 7.1, 1.3 Hz, 4H), 3.53 (t, *J* = 7.80 Hz, 2H), 2.67 (dt, J = 7.4, 1.2 Hz, 2H), 2.35 (t, *J* = 8.14 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 170.5 (2C), 132.0, 119.8, 61.7 (2C), 56.7, 40.0, 37.9, 35.9, 14.2 (2C) ppm. **IR** (film): 2981, 1727, 1641, 1203, 1177, 923, 858 cm^{-1}. **MS:** m/z calcd for $C_{12}H_{19}ClNaO_4$ [M + Na]$^+$: 285.0864, found 285.0877.



Substrate (**2c**): A solution of diethyl (*E*)-2-(hex-2-en-1-yl)malonate[28] (0.69 g, 2,9 mmol. 1.0 eq.) in THF (5 mL) was added dropwise at 0 ºC to a suspension of NaH (72.5 mg, 2,9 mmol. 1.1 eq.) in DMF (10 mL). The cooling bath was removed and the mixture was stirred at room temperature for 1h. The suspension was again cooled to 0 ºC and 1-bromo-2-chloroethane (0.49 g, 3.4 mmol, 1.2 eq.) was added and stirring was continued overnight at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 2 % → 5 % →10 % Et_2O in hexane) to yield 0.48 g (55 %) of title compound as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (dtt, *J* = 15.0, 6.9, 1.3 Hz, 1H), 5.23 (dtt, *J* = 15.0, 7.4, 1.4 Hz, 1H), 4.19 (qd, *J* = 7.1, 0.9 Hz, 4H), 3.56 - 3.43 (m, 2H), 2.61 (dt, *J* = 7.4, 1.1

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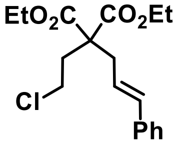
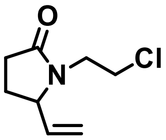
[28] Takeuchi, R.; Kashio M. *J. Am. Chem. Soc.* **1998**, *120*, 8647.

Hz, 2H), 2.37 - 2.31 (m, 2H), 2.01 - 1.91 (m, 2H), 1.35 (q, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 0.87 ppm (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.1 (2C), 136.0, 123.2, 61.6 (2C), 56.9, 40.1, 36.8, 35.9, 34.8, 22.6, 14.2 (2C), 13.7 ppm. **IR** (film): 2960, 1728, 1446, 1367, 1229, 1176, 971, 859, 731 cm^{-1}. **MS:** *m*/*z* calcd for $C_{15}H_{25}ClNaO_4$ [M + Na]$^+$: 327.1334, found 327.1349



Substrate (**2d**): A solution of diethyl cinnamylmalonate[29] (0.82 g, 3,0 mmol. 1.0 eq.) in THF (3 mL) was added dropwise at 0 ºC to a suspension of NaH (78.1 mg, 3.3 mmol. 1.1 eq.) in DMF (12 mL). The cooling bath was removed and the mixture was stirred at room temperature for 1h. The suspension was again cooled to 0 ºC and 1-bromo-2-chloroethane (0.55 g, 3.9 mmol, 1.3 eq.) was added and the mixture was stirred overnight at room temperature. After 24 h another portion of NaH (78.1 mg, 3.3 mmol. 1.1 eq.) and 1-bromo-2-chloroethane (0.55 g, 3.9 mmol, 1.3 eq.) was added since TLC revealed incomplete conversion. Stirring was continued for additional 18 h and the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 2 % → 5 % Et_2O in hexane) to yield 0.48 g (78 %) of title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 - 7.19 (m, 5H), 6.47 (dt, *J* = 15.7, 1.4 Hz, 1H), 6.03 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.22 (m, 4H), 3.61 - 3.56 (m, 2H), 2.83 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.44 - 2.38 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.5 (2C), 137.0, 134.6, 128.7 (2C), 127.7, 126.4 (2C), 123.4, 61.8 (2C), 57.1, 40.1, 37.4, 36.3, 14.2 (2C) ppm. **IR** (film): 2980, 1726, 1447, 1367, 1177, 1094, 967, 739, 693 cm^{-1}. **MS:** *m*/*z* calcd. for $C_{18}H_{23}ClNaO_4$ [M + Na]$^+$: 361.1177, found 361.1191.



Substrate (**2e**): Thionyl chloride (0.35 mL, 4.8 mmol, 1.5 eq.) was added dropwise to a solution of 1-(2-hydroxyethyl)-5-vinylpyrrolidin-2-one[30] (0.5 g, 3.2 mmol, 1.0 eq.) in CH_2Cl_2 (15 mL) at 0 ºC. The cooling bath was removed and the mixture was warmed to 40 ºC and maintained at this temperature for 2 h. The reaction was carefully quenched by addition of saturated aqueous $NaHCO_3$ (10 mL) and diluted with CH_2Cl_2 (15 mL). The organic layer was separated and the aqueous

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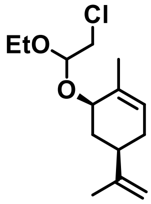
[29] Yip, K.-T.; Zhu, N.-Y.; Yang, D. *Org. Lett.*, **2009**, *11*, 1911.

[30] a) Toja, E.; Gorini, C.; Zirotti, C.; Barzaghi, F.; Galliani, G. *Eur. J. Med. Chem.* **1991**, *26*, 403;
b) Z. Y. Wei, E. E. Knaus, *Org. Prep.Proc. Int.* **1993**, *25*, 255;
c) P. F. Keusenkothen, M. B. Smith, *J. Chem. Soc. Perkin. Trans.1*, **1994**, 2485.

layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 80 % → 90 → 100 % Et_2O in hexane) to yield 0.49 g (88 %) of the desired product as light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.67 (ddd, *J* = 17.1, 9.9, 8.5 Hz, 1H), 5.38 - 5.11 (m, 2H), 4.19 (td, *J* = 8.0, 5.8 Hz, 1H), 3.83 (dt, *J* = 14.0, 6.1 Hz, 1H), 3.72 - 3.52 (m, 2H), 3.36 - 3.17 ppm (m, 1H), 2.45 - 2.36 (m, 2H), 2.36 - 2.21 (m, 1H), 1.87 - 1.71 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 175.6, 137.6, 118.8, 62.5, 42.7, 41.4, 29.9, 25.8 ppm. **IR** (film) cm^{-1}: 2971, 1682, 1408, 1258, 929, 666, 564, 506 cm^{-1}. **MS:** *m*/*z* calcd. for $C_8H_{13}ClNO$ [M + H]$^+$: 174.0680, found 174.0680.



Substrate (**2f**): *N*-Chlorosuccinimide (0.43 g, 3.2 mmol, 1.4 eq.) was added to a solution of (*R*,*R*)-carveol[31] (0.35 g, 2.3 mmol, 1.0 eq.) and ethyl vinyl ether (0.55 mL, 5.8 mmol, 2.5 eq.) in CH_2Cl_2 (8 mL) at -45 ºC. The solution was allowed to reach room temperature over the course of 2 h. Stirring was continued until no further conversion was observed as judged by TLC. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 10 % → 20 % Et_2O in hexane) to yield 0.25 g (42 %) as a 1:1 diastereomeric mixture of title compound and 0.16 g (47 %) of recovered starting material.

(1:1 mixture of diastereoisomers) **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.56 - 5.55 (m, 1H {isomer A}), 5.53 - 5.52, (m, 1H {isomer B}) 4.81 - 4.73 (m, 3 H, each), 4.26 (s, 1H {isomer A}), 4.13 (s, 1H {isomer B}), 3.73 - 3.61 (m, 2H, each), 3.58 - 3.47 (m, 2H, each) 2.26 - 2.16 (m, 2H, each), 2.07 - 1.88 (m, 2H, each), 1.76 - 1.73 (m, 6H, each), 1.63 - 1.43 (m, 1H, each), 1.27 - 1.22 (td, *J* = 7.0, 2.4 Hz, 3H each) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.0, 148.9, 134.9, 134.7, 125.4, 125.2, 109.4, 109.3, 103.0, 99.9, 78.6, 75.8, 61.6, 61.4, 44.4, 44.3, 40.9, 40.7, 36.2, 34.8, 31.0, 31.0, 20.5, 20.5, 19.6, 19.6, 15.5, 15.4 ppm. **IR** (film): 2971, 2918, 2885, 1112, 1035, 889, 759 cm^{-1}. **MS:** *m*/*z* calcd. for $C_{14}H_{23}ClNaO_2$ [M + Na]$^+$: 281.1279, found 281.1283.

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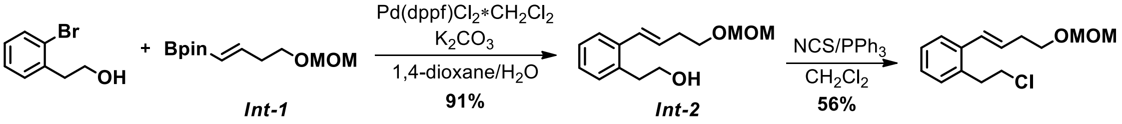
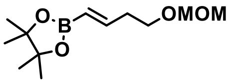
[31] Elamparuthi, E.; Fellay, C.; Neuburger, M.; Gardemann K. *Angew. Chem. Int. Ed*. **2012**, 51, 4071.

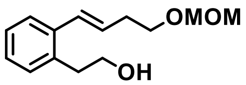
Substrate (**2g**)





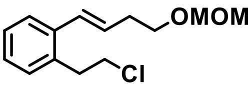
Int-1: A Schlenk flask was charged with dicyclohexylborane (55 mg, 0.31 mmol, 7 mol%) and to this flask was added pinacolborane (0.67 mL, 4.82 mmol, 1.1 eq.) and 4-(methoxy)but-1-yne (0.5 g, 4.38 mmol, 1.0 eq.) at 0 ºC. The mixture was stirred for 24 h at room temperature, diluted with hexane (25 mL) followed by bubbling air through the solution for 2 h. The organic layer was washed with H_2O (3 × 20 mL) and the solvent was removed under reduced pressure to yield 0.61 g (58 %) of title compound as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.53 (dt, *J* = 18.1, 1.6 Hz, 1H), 4.62 (s, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.35 (s, 3H), 2.46 (qd, *J* = 6.6, 1.6 Hz, 2H), 1.26 (s, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 150.5, 96.5, 83.2 (2C), 66.5, 55.3, 36.2, 24.9 (4C) ppm. **IR** (film): 2979, 1641, 1361, 1146 cm^{-1}. **MS:** *m/z* calcd for $C_{12}H_{23}NaO_4B$ [M + Na]$^+$: 264.1618, found 264.1611.



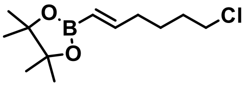
Int-2: Inside an anaerobic box, a Schlenk flask was charged with $PdCl_2$(dppf)·CH_2Cl_2 (91 mg, 0.11 mmol, 0.05 eq.). The flask was removed from the glovebox and degassed 1,4-dioxane/H_2O (5:1, 18 mL), intermediate 1 (0.59 g, 2.4 mmol, 1.1 eq.), aryl bromide (0.45 g, 2.24 mmol, 1.0 eq.) and K_2CO_3 (0.93 g, 6.71 mmol, 3.0 eq.) were successively added. The mixture was stirred at 70 °C for 18 h. After reaching room temperature the reaction was quenched with saturated aqueous NH_4Cl (20 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 5 % → 10 % Et_2O in hexane) to yield 0.48 g (91 %) of the title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 - 7.40 (m, 1H), 7.22 - 7.14 (m, 3H), 6.74 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.11 (dt, *J* = 15.7, 7.0 Hz, 1H), 4.65 (s, 2H), 3.85 - 3.79 (m, 2H), 3.67 (t, *J* = 6.6 Hz, 2H), 3.38 (s, 3H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.54 (qd, *J* = 6.7, 1.5 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 137.1, 135.4, 130.3, 129.4, 129.3, 127.4, 127.0, 126.4, 96.6, 67.4, 63.3, 55.4, 36.6, 33.8 ppm. **IR** (film): 2934, 2881, 1148, 1108, 1037, 966 cm^{-1}. **MS:** *m/z* calcd. for $C_{14}H_{20}NaO_3$ 259.1305, found 259.1303.



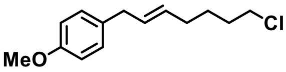
Substrate (**2g**): *N*-Chlorosuccinimide (0.37 g, 2.81 mmol, 1.4 eq.) was added at 0 ºC to a solution of PPh_3 (0.74 g, 2.81 mmol, 1.4 eq.) and alcohol (0.47 g, 2.0 mmol, 1.0 eq.) in CH_2Cl_2 (10 mL). The mixture was stirred at 0 ºC for 5 h until complete consumption of starting material was observed on TLC. Hexane (10 mL) was added and the suspension was stirred for additional 10 min and then filtered. The solvent was removed under reduced pressure and the crude material was purified by flash chromatography (10 % → 20 % Et_2O in hexane) to yield 287 mg (56 %) of title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.41 (m, 1H), 7.24 – 7.13 (m, 3H), 6.69 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.14 (dt, *J* = 15.6, 7.0 Hz, 1H), 4.67 (s, 2H), 3.83 – 3.60 (m, 4H), 3.38 (s, 3H), 3.14 (dd, *J* = 8.5, 7.2 Hz, 2H), 2.55 (qd, *J* = 6.6, 1.5 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 136.9, 135.0, 130.2, 130.0, 128.8, 127.5, 127.5, 126.5, 96.6, 67.3, 55.4, 44.2, 36.9, 33.9 ppm. **IR** (film): 2932, 2883, 1149, 1110, 1035, 965 cm^{-1}. **MS:** *m*/*z* calcd for $C_{14}H_{19}ClNaO_2$ [M + Na]$^+$: 277.0966, found 277.0975.



Substrate (**2q**): A Schlenk flask was charged with dicyclohexylborane (0.274 g, 1.54 mmol, 7 mol%) and to this flask was added pinacolborane (3.35 mL, 23.10 mmol, 1.05 eq.) and 6-chlorohex-1-yne (2.67 mL, 22 mmol, 1.0 eq.) at 0 ºC. The mixture was stirred for 24 h at room temperature, diluted hexane (25 mL) followed by bubbling air through the solution for 2 h. The organic layer was washed with H_2O (3 × 20 mL) and the solvent was removed under reduced pressure to yield 5.01 g (93 %) of title compound as a colorless oil.

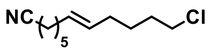
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.45 (dt, *J* = 18.0, 1.7 Hz, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.28 - 2.08 (m, 2H), 1.89 - 1.70 (m, 2H), 1.64 - 1.51 (m, 2H), 1.26 (s, 12H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 153.6, 83.2 (2C), 45.0, 35.0, 32.1, 25.5, 24.9 (4C) ppm. **IR** (film): 2978, 2905, 1639, 1357, 1319, 1144, 968, 849 cm^{-1}. **MS:** *m*/*z* calcd for $C_{12}H_{22}NaO_2BCl$ [M + Na]$^+$: 266.1330, found 266.1325.



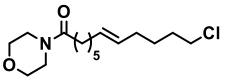
Substrate (**2h**): A Schlenk flask was charged with Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (0.11 g, 0.13 mmol, 0.05 eq.), K_2CO_3 (1.1 g, 7.98 mmol, 3.0 eq.) benzyl bromide (0.54 g, 2,66 mmol, 1.0 eq.) and substrate **2q** (0.72 g, 2,93 mmol, 1.1 eq.) and 1,4-dioxane/H_2O (4:1, 15 mL). The mixture was stirred at 70 ºC for 18 h. After cooling down to room temperature the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL) and diluted with Et_2O (20 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (5 % Et_2O in hexane) to yield 0.315 g (49 %) of title compound.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 - 7.06 (m, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.65 – 5.52 (m, 1H), 5.52 - 5.42 (m, 1H), 3.79 (s, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.27 (d, *J* = 6.6 Hz, 2H), 2.23 - 1.94 (m, 2H), 1.82 - 1.73 (m, 2H), 1.53 (dt, *J* = 10.1, 7.1 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 158.0, 133.1, 130.8, 130.1, 129.5, 113.9, 55.4, 45.1, 38.2, 32.2, 31.8, 26.8 ppm. **IR** (film): 2932, 2835, 1509, 1243, 1036 cm^{-1}. **MS:** *m*/*z* calcd for $C_{14}H_{20}ClO$ [M + H]$^+$: 239.1197, found 239,1195.

Substrates **2i-2m**: A slightly modified procedure from Nishibara and co-workers was followed for Suzuki-Miyaura Cross-Coupling reaction of (*E*)-6-chloro-1-hexen-1-ylboronic acid pinacol ester (**2q**) with alkyl bromides.[32] To a solution of bis(dibenzylidene)palladium ($Pd(dba)_2$) (5 mol%), [HP*t*-Bu_2Me]BF_4 (10 mol%), and substrate **2q** (1.5 eq.) in THF (3.5 mL) in a 25 mL Schlenk flask were added the corresponding alkyl bromide (1 eq.) and KOH (3 eq.) at room temperature under argon atmosphere. After stirring for 24h, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (10 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography in silica gel gave the corresponding cross-coupling products.



Substrate (**2i**): Isolated as colorless liquid in 65 % yield (236 mg, 1.1 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.43 - 5.35 (m, 2H), 3.53 (t, *J* = 6.7 Hz, 1H), 2.33 (t, *J* = 7.1 Hz, 1H), 2.07 - 1.96 (m, 2H), 1.82 - 1.72 (m, 2H), 1.71 - 1.60 (m, 2H), 1.54 - 1.33 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 130.5, 130.3, 119.9, 45.2, 32.3, 32.2, 31.9, 28.8, 28.2, 26.9, 25.4, 17.3 ppm. **IR** (film): 2930, 2856, 2244, 1457, 1457, 968, 724, 649 cm^{-1}. **MS:** *m*/*z* calcd for $C_{12}H_{20}ClNNa$ [M + Na]$^+$: 236.1176, found 236.1172.



Substrate (**2j**): Isolated as colorless liquid in 45 % yield (560 mg, 1.85 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.47 - 5.32 (m, 2H), 3.68 - 3.65 (m, 4H), 3.64 - 3.59 (m, 2H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.48 - 3.43 (m, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.06 - 1.95 (m, 4H), 1.82 - 1.72 (m, 2H), 1.68 - 1.59 (m, 2H), 1.54 - 1.44 (m, 2H), 1.41 - 1.29 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.9, 131.0, 129.8,

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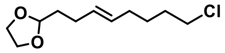
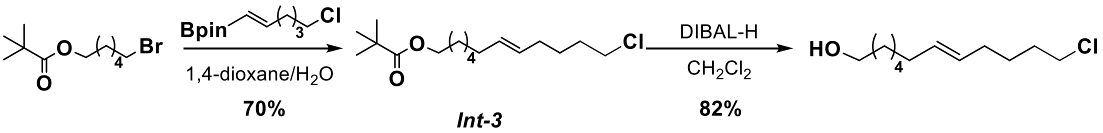
[32] Nishihara, Y.; Okada, Y.; Jiao, J.; Suetsugu, M.; Lan, M.-T.; Kinoshita, M.; Iwasaki, M.; Takagi, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 8660.

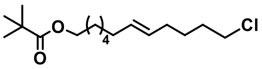
67.1, 66.8, 46.2, 45.2, 42.0, 33.2, 32.5, 32.2, 31.9, 29.5, 29.1, 26.9, 25.2 ppm. **IR** (film): 2923, 2853, 1641, 1441, 1429, 1228, 1115, 967, 848 cm^{-1}. **MS:** *m*/*z* calcd for $C_{16}H_{28}ClNNaO_2$ [M + Na]$^+$: 324.1701, found 324.1699.



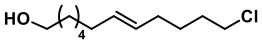
Substrate (**2k**): Isolated as light yellow liquid in 74 % yield (662 mg, 3 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.53 - 5.39 (m, 2H), 4.89 (t, *J* = 4.8 Hz, 1H), 4.02 - 3.95 (m, 2H), 3.92 - 3.82 (m, 2H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.20 - 2.10 (m, 2H), 2.08 - 1.98 (m, 2H), 1.84 - 1.70 (m, 4H), 1.59 - 1.46 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 130.2, 130.0, 104.3, 65.0 (2C), 45.1, 33.9, 32.1, 31.8, 27.2, 26.8 ppm. **IR** (film): 2933, 2882, 1446, 1407, 1133, 1034, 967 cm^{-1}. **MS:** *m*/*z* calcd for $C_{11}H_{20}ClO2$ [M + H]$^+$: 219.1146, found 219.1152.

Substrate (**2l**)



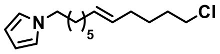


***Int-3*.** Isolated as light yellow liquid in 70 % yield (320 mg, 1.06 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.47 - 5.32 (m, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.06 - 1.93 (m, 4H), 1.82 - 1.73 (m, 2H), 1.68 - 1.57 (m, 2H), 1.56 - 1.45 (m, 3H), 1.38 - 1.30 (m, 6H), 1.19 (s + m, 9 + 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 178.8, 131.1, 129.7, 64.5, 45.1, 38.9, 32.5, 32.2, 31.9, 29.5, 28.8, 28.7, 27.3 (3C), 26.9, 25.9 ppm. **IR** (film): 2931, 1728, 1284, 1154 cm^{-1}. **MS:** *m*/*z* calcd for $C_{17}H_{31}ClNaO_2$ [M + Na]$^+$: 325.1905, found 325.1901.

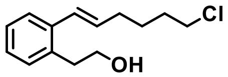


Substrate (**2l**): To a solution of pivalate derivate ***Int-3*** (0.3 g, 0.99 mmol, 1.0 eq.) in CH_2Cl_2 (10 mL) was added at -78 ºC dropwise DIBAL-H (1 M in THF, 1.98 mL, 1.98 mmol, 2.0 eq.) and the mixture was stirred at -78 ºC for 30 min. The reaction was quenched by addition of aqueous saturated Na/K tartrate (10 mL). The suspension was allowed to reach room temperature, stirred at room temperature for 30 min and then filtered through Celite®, which was rinsed several times with CH_2Cl_2 (30 mL). The solvent was removed under reduced pressure and the crude material was purified via flash chromatography (SiO_2, 20 % Et_2O in hexane) to yield 177 mg (82 %) of title compound as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46 - 5.32 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.05 - 1.95 (m, 4H), 1.81 - 1.73 (m, 2H), 1.60 - 1.54 (m, 2H), 1.54 - 1.46 (m, 2H), 1.39 - 1.29 (m, 7H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 131.2, 129.6, 63.2, 45.1, 32.9, 32.6, 32.2, 31.9, 29.6, 29.0, 26.9, 25.7 ppm. **IR** (film): 2927, 2855, 1456, 1055, 967 cm^{-1}. **MS:** *m*/*z* calcd. for $C_{12}H_{24}ClO$ [M + H]$^+$: 219.1510, found 219.1501.

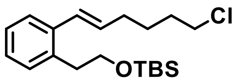


Substrate (**2m**): Isolated as pale yellow liquid in 66 % yield (383 mg, 1.4 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.55 (t, *J* = 2.1 Hz, 2H), 6.03 (t, *J* = 2.1 Hz, 2H), 5.35 - 5.22 (m, 2H), 3.76 (t, *J* = 7.2 Hz, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 1.98 - 1.82 (m, 4H), 1.74 - 1.59 (m, 4H), 1.45 - 1.35 (m, 2H), 1.28 - 1.12 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 131.1, 129.7, 120.6, 107.9, 49.7, 45.2, 32.6, 32.2, 31.9, 31.7, 29.5, 28.8, 26.9, 26.8 ppm. **IR** (film): 2978, 2931, 2857, 1638, 1358, 1318, 1144, 968, 849, 717, 640 cm^{-1}. **MS:** *m*/*z* calcd for $C_{16}H_{27}ClN$: [M + H]$^+$: 268.1827, found 268.1838.



Substrate (**2n**): A Schlenk flask was charged with $Pd(dppf)Cl_2·CH_2Cl_2$ (0.1 g, 0.122 mmol, 0.1 eq.), NaOH (0.245 g, 6.12 mmol, 2.0 eq.) aryl bromide (0.615 g, 3,06 mmol, 1.0 eq.) and substrate **4q** (0.86 g, 3,52 mmol, 1.15 eq.) and 1,4-dioxane/H_2O (4:1, 15 mL). The mixture was stirred at 70 ºC for 18 h. After reaching room temperature the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL) and diluted with Et_2O (20 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (5 % Et_2O in hexane) to yield 0.68 g (93 %) of title compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.42 (m, 1H), 7.27 – 7.16 (m, 3H), 6.69 (dt, *J* = 15.6 Hz, 1H), 6.10 (dt, *J* = 15.6, 7.0 Hz, 1H), 3.85 (t, *J* = 6.8 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.30 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.94 – 1.82 (m, 2H), 1.71 – 1.62 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.2, 135.2, 132.5, 130.3, 128.0, 127.3, 127.0, 126.4, 63.3, 45.0, 36.6, 32.6, 32.2, 26.7 ppm. **IR** (film): 3321, 2933, 1447, 1041 cm^{-1}. **MS:** *m*/*z* calcd for $C_{14}H_{19}ClNaO$ [M + Na]$^+$: 261.1017, found 261.1025.



Substrate (**2o**): A Schlenk flask was charged with $PdCl_2(dppf)·CH_2Cl_2$ (0.11 g, 0.13 mmol, 5 mol%). The flask was removed from the anaerobic box and degassed 1,4-dioxane/H_2O (5:1, 24 mL), substrate **4q** (0.716 g, 2.93 mmol, 1.1 eq.), aryl bromide[33] (0.84 g, 2.66 mmol, 1.0 eq.) and K_2CO_3

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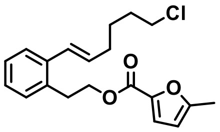
[33] Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C., *J. Org. Chem.* **1996**, *61*, 5440.

(1.1 g, 7.98 mmol, 3.0 eq.) were added. The reaction mixture was stirred for 6 h at 70 °C. After reaching room temperature the reaction was quenched with saturated aqueous NH_4Cl (20 mL) and diluted with Et_2O (20 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3×15 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 5 % Et_2O in hexane) to yield 0.47 g (50 %) of the title compound as a colorless oil.

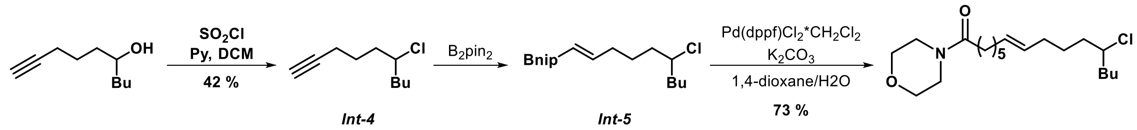
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 - 7.38 (m, 1H), 7.21 - 7.11 (m, 3H), 6.68 (dt, *J* = 15.6, 1.6 Hz, 1H), 6.06 (dt, *J* = 15.6, 7.0 Hz, 1H), 3.75 (t, *J* = 7.9 Hz, 2H), 3.57 (t, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.27 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.95 - 1.78 (m, 2H), 1.71 - 1.59 (m, 2H), 0.88 (s, 9H), -0.01 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 137.1, 135.8, 132.0, 130.6, 128.3, 127.1, 126.7, 126.0, 64.0, 45.0, 37.1, 32.6, 32.2, 26.8, 26.1 (3C), 18.5, -5.3 (2C) ppm. **IR** (film): 2928, 2856, 1461, 1252, 1089, 834 cm^{-1}. **MS:** *m*/*z* calcd for $C_{20}H_{33}ClNaOSi$ $[M + Na]^+$: 375.1881, found 375.1900.

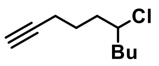


Substrate (**2p**): *N*,*N'*-Dicyclohexylcarbodiimide (145 mg, 0.7 mmol, 1.2 eq.) and DMAP (21 mg, 0,17 mmol, 0,3 eq.) were added to a solution of alcohol **4n** (140 mg, 0.58 mmol, 1.0 eq.) and 5-methylfuran-2-carboxylic acid (89 mg, 0.7 mmol, 1.2 eq.) in CH_2Cl_2 (5 mL). The mixture was stirred overnight and the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (5 % → 10 % Et_2O in hexane) to yield 160 mg (79 %) of title compound as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 - 7.42 (m, 1H), 7.24 – 7.17 (m, 3H), 7.06 (d, *J* = 3.4 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.15 - 6.04 (m, 2H), 4.42 (dd, *J* = 8.0, 7.2 Hz, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 2.29 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.85 (dq, *J* = 8.7, 6.5 Hz, 2H), 1.69 - 1.60 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 158.9, 157.4, 143.2, 137.3, 134.3, 132.7, 130.3, 127.8, 127.3, 127.2, 126.2, 119.6, 108.5, 64.7, 45.1, 32.8, 32.6, 32.2, 26.7, 14.1 ppm. **IR** (film): 1712, 1530, 1297, 1208, 1182 cm^{-1}. **MS:** *m*/*z* calcd for $C_{20}H_{23}ClNaO_3$ $[M + Na]^+$: 369.1228, found 369.1236.

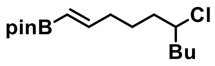
Substrate (**2r**)





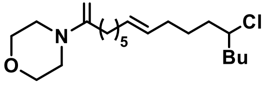
Int-4: Over a solution of dec-9-yn-5-ol[34] (1.4 g,9.08 mmol) and pyridine (0.1 mL, 1.24 mmol) in dichloromethane (10 mL) is added dropwise a solution of thionyl chloride (6.6 mL, 90 mmol) in dichloromethane (10 mL) at 0ºC. Then, the reaction mixture was allowed to warm up to room temperature and it is stirred overnight. The crude was diluted with dichloromethane (30 mL) and the residual thionyl chloride was quenched by adding slowly ice/water into the flask. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (5 % AcOEt in hexane) to yield 0.66 g (42 %) of title compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96-3.86 (m, 1H), 2.23 (td, *J* = 6.8, 2.7 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1 H), 1.95-1.60 (m, 6H), 1.59-1.30 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 84.0, 68.9, 63.6, 38.5, 37.5, 28.8, 25.5, 22.4, 18.1, 14.1 ppm. **MS:** *m*/*z* calcd for $C_{10}H_{17}$ $[M - Cl]^+$: 137.1325, found 137.1321.



Int-5: Following the procedure above described for substrate **2q** with intermediate ***Int-4*** gave intermediate ***Int-5***: as a white solid that was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.45 (dt, *J* = 17.9, 1.6 Hz, 1H), 3.93-3.83 (m, 1H), 2.24-2.11 (m, 2H), 1.80-1.63 (m, 6H), 1.60-1.44 (m, 2H), 1.44-1.19 (m, 14H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm.



Substrate (**2r**): Isolated as colorless liquid in 73 % yield (261 mg, 0.7 mmol) following the analogous procedure to **2j**.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46-4.30 (m, 2H), 3.95-3.82 (m, 1H), 3.71-3.64 (m, 4H), 3.63-3.57 (m, 2H), 3.49-3.41 (m, 2H), 2.30 (t, *J* = 8.0 Hz, 2H), 2.08-1.92 (m, 4H), 1.78-1.24 (m, 16H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 172.0, 130.9, 130.0, 67.1, 66.8, 64.3, 46.2, 42.0, 38.4, 38.1, 33.2, 32.5, 32.2, 29.5, 29.1, 28.8,

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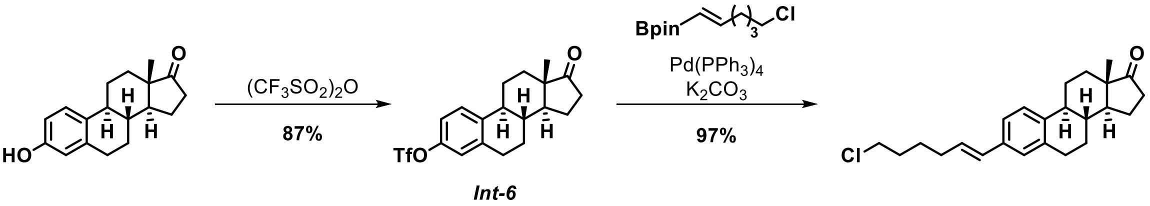
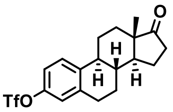
[34] Rizk,T; Bilodeau, E.J.-F.;Beauchemin, A. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 8325.

26.5, 25.2, 22.4, 14.1 ppm. **IR** (film): 3452, 2961, 2921, 2855, 1638, 1429, 1271, 1235, 1113, 1068, 1028, 913, 847, 701, 571 cm^{-1}. **MS:** *m/z* calcd for $C_{20}H_{36}ClNNaO_2$ $[M + Na]^+$: 380.2332, found 380.2327.

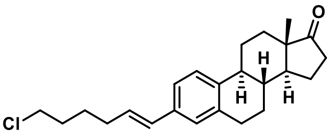
Substrate (**2s**)





Int-6: Triflic anhydride (0.36 mL, 2.17 mmol, 1.15 eq.) was added at 0°C to a Schlenk flask containing estrone (0.5 g, 1,85 mmol, 1.0 eq.) and NEt_3 (0.52 mL, 3.7 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at 0°C for 1 h before the reaction was quenched by addition of saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, 10 % → 20 % → 30 % Et_2O in hexane) to yield 0.65 g (87 %) of title compound as an off-white solid. Spectral data is in agreement with previously reported data for this compound.[35]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.07 – 6.96 (m, 2H), 2.98 - 2.88 (m, 2H), 2.57 - 2.48 (m, 1H), 2.46 - 2.37 (m, 1H), 2.30 (td, *J* = 10.6, 4.3 Hz, 1H), 2.22 - 1.95 (m, 4H), 1.70 - 1.39 (m, 6H), 0.92 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 220.6, 147.7, 140.4, 139.4, 127.3, 121.4, 118.4 (2C), 50.5, 48.0, 44.2, 37.9, 35.9, 31.6, 29.5, 26.2, 25.8, 21.7, 13.9 ppm.



Substrate (**2s**): K_2CO_3 (103 mg, 0.75 mmol, 3.0 eq.) was added to a solution of $Pd(PPh_3)_4$ (29 mg, 0.025 mmol, 10 mol%), estrone derivate ***Int-6*** (100 mg, 0.25 mmol, 1.0 eq.) and substrate **4q** (73 mg, 0.3 mmol, 1.2 eq.) in 1,4-dioxane/H_2O (4:1, 3.5 mL). The mixture was heated for 18 h at 100 ºC in a sealed flask. The reaction was allowed to reach room temperature and the solvent was removed under reduced pressure. The

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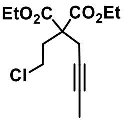
[35] Van der Born, D.; Sewing, C.; Herscheid, J. D. M.; Windhorst, A. D.; Orru, R. V. A.; Vugts, D. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 11046.

crude material was directly purified by flash chromatography (10 % → 20 % Et$_2$O in hexane) to yield 89 mg (97 %) of title compound as a white solid.

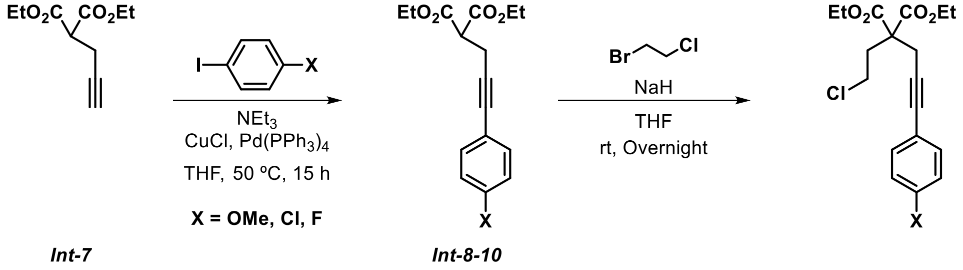
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.23 (d, J = 8.1 Hz, 1H), 7.14 (dd, J = 8.2, 1.9 Hz, 1H), 7.08 (s, 1H), 6.34 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.7, 6.9 Hz, 1H), 3.56 (t, J = 6.7 Hz, 2H), 2.90 (dd, J = 9.1, 4.2 Hz, 2H), 2.51 (dd, J = 19.0, 8.7 Hz, 1H), 2.46 - 2.38 (m, 1H), 2.33 – 2.20 (m, 3H), 2.15 (dt, J = 18.8, 8.9 Hz, 1H), 2.09 - 1.99 (m, 2H), 1.98 - 1.94 (m, 1H), 1.83 (dt, J = 14.5, 6.8 Hz, 2H), 1.68 – 1.58 (m, 4H), 1.56 – 1.48 (m, 3H), 1.48 – 1.39 (m, 1H), 0.91 (s, 3H) ppm. **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 221.0, 138.8, 136.6, 135.4, 130.2, 129.6, 126.7, 125.6, 123.5, 50.6, 48.1, 45.1, 44.5, 38.3, 36.0, 32.3, 32.2, 31.7, 29.5, 26.7, 26.7, 25.9, 21.7, 14.0 ppm. **IR** (film): 2931, 2860, 1739, 966 cm^{-1}. **MS:** m/z calcd for $C_{24}H_{31}ClNaO$ [M + Na]$^+$: 393.1956, found 393.1956.

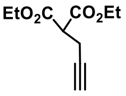


Substrate (**2t**): To a suspension of NaH (0.09 g, 3.61 mmol) in DMF (5 mL) was added at rt a solution of diethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (3.3 mmol, 1 g) in DMF (3 mL). The mixture was stirred at rt for 30 min in which it became a clear solution. To this solution was added dropwise a solution of 1-bromo-2-chloroethane (6.6 mmol, 0.9 g) in THF (3 mL). The mixture was stirring at room temperature overnight. Them, the reaction was quenched by addition of 15 mL of water and extracted with diethyl ether (3*15 mL). The combined organic extracts were dried over MgSO4, the solvent was removed under reduce pressure. The crude material was directly purified by flash chromatography (5 % Et$_2$O in hexane) to yield 569 mg (60 %) of title compound as a colourless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.20 (qd, J = 7.1, 2.9 Hz, 4H), 3.60 – 3.51 (m, 2H), 2.78 (q, J = 2.6 Hz, 2H), 2.58 – 2.47 (m, 2H), 1.75 (t, J = 2.6 Hz, 3H), 1.25 (t, J = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 169.9 (2C), 79.5, 72.9, 61.9 (2C), 56.3, 40.1, 35.6, 23.8, 14.1 (2C), 3.6 ppm. **IR** (film): 2981, 2937, 1730, 1446, 1327, 1300, 1264, 1230, 1195, 1179, 1066, 1030, 859, 751, 526 cm^{-1}. **MS:** m/z calcd for $C_{13}H_{19}ClNaO_4$ [M + Na]$^+$: 297.0870, found 297.0864.

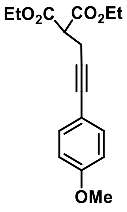
Substrates **2u-2w**:





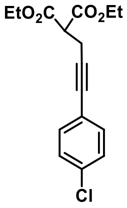
***Int-7*:** Diethyl malonate (25.9 g; 161 mmol) was added dropwise to an ice-cold suspension of sodium hydride (6.46 g, 60 wt % in mineral oil, 161 mmol) in dry THF. The reaciton mixture was allowed to stir for 2 h at room temperature. To this solution propargyl bromide (8 g; 53.8 mmol) were added dropwise at 0ºC and the solution was allowed to warm to room temperature with continuous stirring 24 h. The solvent was removed under reduce pressure. The reaction was quenched by addition of 50 mL of water, extracted with AcOEt (3x 15mL). The combines organic layer were the concentrated in redced pressure. The required product was purified by fractional distillation in vifreux column at 80ºC ($1.6x10^{-1}$ mbar), yielding 9.75 g (91 %) of the desired product as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.23 (q, *J* = 7.1, 0.8 Hz, 4H), 3.64 – 3.42 (m, 1H), 2.78 (ddd, *J* = 7.7, 2.7, 0.6 Hz, 2H), 2.01 (d, *J* = 0.7 Hz, 1H), 1.28 (td, *J* = 7.1, 0.7 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.9 (2C), 78.0, 70.4, 61.8 (2C), 51.2, 22.5, 18.1, 14.0 (2C). ppm.



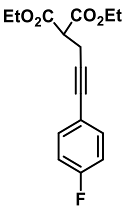
***Int-8*:** Diethyl 2-(prop-2-yn-1-yl)malonate (2.0 g; 10.09 mmol) and 1-iodo-4-methoxybenzene (2.66 g; 11.37 mmol) were added to a stirring solution of $Pd(PPh_3)_4$ (0.583 g; 0.504 mmol), CuI (0.288 g; 1.513 mmol) and Et_3N (1.021 g; 10.09 mmol) in THF (20 mL). The mixture was heated for 15 h at 50 ºC. The reaction was quenched by addition of 15 mL of water, extracted with Et_2O (3x 15mL). The crude materiasl was purifies by flash chroatography (10 % of AcOEt in hexane) yo wield 1.46 g (48 %) of title compound as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.27 (m, 2H), 6.86 – 6.69 (m, 2H), 4.24 (qd, *J* = 7.1, 0.9 Hz, 4H), 3.79 (s, 3H), 3.63 (t, *J* = 7.8 Hz, 1H), 2.98 (d, *J* = 7.8 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 168.1 (2C), 159.3, 133.0 (2C), 115.4, 113.8 (2C), 83.9, 82.2, 61.7 (2C), 55.3, 51.6, 19.5, 14.1 (2C) ppm. **IR** (film): 2981, 1731, 1606, 1509, 1464, 1369, 1290, 1244, 1172, 1030, 832, 539 cm^{-1}.



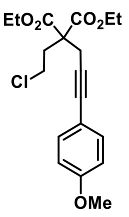
***Int-9*:** Diethyl 2-(prop-2-yn-1-yl)malonate (0.650 g; 3.28 mmol) and 1-chloro-4-iodobenzene (0.860 g; 3.61 mmol) were added to a stirring solution of $Pd(PPh_3)_4$ (0.094 g; 0.492 mmol), CuI (0.094 g; 0.492 mmol) and Et_3N (0.332 g; 3.28 mmol) in THF (10 mL). The mixture was heated for 15 h at 50 ºC. The eraction was quenched by addition of 15 mL of water, extracted with Et_2O (3x 15mL). The crude materiasl was purifies by flash chroatography (10 % of AcOEt in hexane) yo wield 605 mg (78 %) of title compound as a pale yellow oil.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.59 – 7.14 (m, 4H), 4.42 – 4.09 (m, 4H), 3.65 (t, *J* = 7.7 Hz, 1H), 3.01 (dd, *J* = 7.7, 1.3 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 168.0 (2C), 133.0, 132.8 (2C), 128.5 (2C), 121.7, 86.6, 81.4, 61.8 (2C), 51.4, 19.41, 14.1 (2C) ppm. **IR** (film): 2982, 1731, 1489, 1639, 1231, 1153, 1059, 1032, 1015, 828, 526 cm^{-1}. **MS:** *m*/*z* calcd for $C_{16}H_{17}ClNaO_4$ [M + Na]$^+$: 331.0713, found 331.0708.



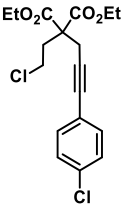
***Int-10*:** Diethyl 2-(prop-2-yn-1-yl)malonate (0.50 g; 2.52 mmol) and 1-fluoro-4-iodobenzene (0.618 g; 2.77 mmol) were added to a stirring solution of Pd(PPh$_3$)$_4$ (0.146 g; 0.126 mmol), CuI (0.037 g; 0.376 mmol) and Et$_3$N (0.255 g; 2.52 mmol) in THF (10 mL). The mixture was heated for 15 h at 50 ºC. The eraction was quenched by addition of 15 mL of water, extracted with Et$_2$O (3x 15mL). The crude materiasl was purifies by flash chroatography (10 % of AcOEt in hexane) yo wield 632 mg (86 %) of title compound as a pale yellow oil.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.34 (dd, *J* = 8.9, 5.4 Hz, 2H), 6.96 (t, *J* = 8.8 Hz, 2H), 4.24 (qd, *J* = 7.1, 0.6 Hz, 4H), 3.63 (t, *J* = 7.7 Hz, 1H), 2.98 (d, *J* = 7.7 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 168.0, 163.5, 161.1, 133.5, 133.40, 119.3, 119.3 (2C), 115.5, 115.3, 85.1, 81.4, 61.8, 51.4, 19.4, 14.1 ppm **IR** (film): 2982, 1731, 1601, 1507, 1335, 1221, 1154, 1032, 837, 532 cm^{-1}. **MS:** *m*/*z* calcd for $C_{16}H_{17}FNaO_4$ [M + Na]$^+$: 315.1009, found 315.1003.



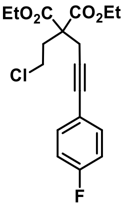
Substrate (**2u**): To a suspension of NaH (0.06 g, 2.30 mmol) in DMF (5 mL) was added at rt a solution of diethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (2.3 mmol, 0,7 g) in DMF (3 mL). The mixture was stirred at rt for 30 min in which it became a clear solution. To this solution was added dropwise a solution of 1-bromo-2-chloroethane (4.6 mmol, 0.67 g) in DMF (3 mL). The mixture was stirring at room temperature overnight. Them, the reaction was quenched by addition of 15 mL of water and extracted with Et$_2$O (3x15 mL). The combined organic extracts were dried over MgSO4, the solvent was removed under reduce pressure and the crude material was purified by Column Cromatography (5 % of Et$_2$O in hexane) to yield 533 mg (63 %) of title compound as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.24 (qd, *J* = 7.1, 5.6 Hz, 4H), 3.80 (s, 3H), 3.68 – 3.60 (m, 2H), 3.05 (s, 2H), 2.61 (m, 7.2 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 169.7, 159.5, 133.0, 115.1, 113.9, 83.8, 82.0, 61.9, 56.3, 55.38, 40.0, 35.7, 24.4, 14.0 ppm. **IR** (film): 2980, 2937, 2906, 2838, 1730, 1606, 1509, 0444, 1289, 1245, 1173, 1030, 832, 537 cm^{-1}. **MS:** *m*/*z* calcd for $C_{24}H_{31}ClNaO$ [M + Na]$^+$: 389.1132, found 389.1126.



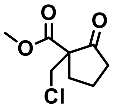
Substrate (**2v**): To a suspension of NaH (0.09 g, 3.61 mmol) in DMF (5 mL) was added at rt a solution of diethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)malonate (3.3 mmol, 1 g) in DMF (3 mL). The mixture was stirred at rt for 30 min in which it became a clear solution. To this solution was added dropwise a solution of 1-bromo-2-chloroethane (6.6 mmol, 0.9 g) in DMF (3 mL). The mixture was stirring at room temperature overnight. Them, the reaction was quenched by addition of 15 mL of water and extracted with Et_2O (3x15 mL). The combined organic extracts were dried over MgSO4, the solvent was removed under reduce pressure and the crude material was purified by Column Cromatography (5 % of Et_2O in hexane) to yield 543 mg (77 %) of title compound as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.25 (m, 4H), 4.33 – 4.20 (m, 4H), 3.68 – 3.62 (m, 2H), 3.09 (s, 2H), 2.66 – 2.59 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 169.5, 134.2, 132.8, 128.6, 121.4, 84.8, 82.9, 62.0, 56.2, 39.9, 35.6, 24.48, 14.0.ppm. **IR** (film): 2980, 2935, 2873, 1730, 1489, 1367, 1327, 1299, 1264, 1230, 1193, 1179, 1088, 1067, 1015, 828, 526 cm^{-1}. **MS:** *m*/*z* calcd for $C_{18}H_{20}Cl_2NaO_4$ $[M + Na]^+$: 393.0636, found 393.0631.



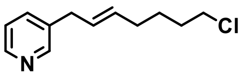
Substrate (**2w**): To a suspension of NaH (0.05 g, 2.05 mmol) in DMF (5 mL) was added at rt a solution of diethyl 2-(3-(4-fluoroyphenyl)prop-2-yn-1-yl)malonate (1.7 mmol, 0.5 g) in DMF (3 mL). The mixture was stirred at rt for 30 min in which it became a clear solution. To this solution was added dropwise a solution of 1-bromo-2-chloroethane (3.4 mmol, 0.5 g) in DMF (3 mL). The mixture was stirring at room temperature overnight. Them, the reaction was quenched by addition of 15 mL of water and extracted with Et_2O (3x15 mL). The combined organic extracts were dried over MgSO4, the solvent was removed under reduce pressure and the crude material was purified by Column Cromatography (5 % of Et_2O in hexane) to yield to yield 237 mg (40 %) of title compound as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 8.8, 5.3 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 4.24 (qd, *J* = 7.1, 5.0 Hz, 4H), 3.74 – 3.54 (m, 2H), 3.06 (s, 2H), 2.68 – 2.53 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 169.5 (2C), 163.6, 161.2, 133.5 (2C), 119.0 (2C), 115.4, 83.4, 82.9, 62.0 (2C), 56.2, 39.9, 35.6, 24.3, 14.0 (2C) ppm. **IR** (film): 2981, 1730, 1601, 1507, 1220, 1179, 1067, 1015, 836, 653, 531 cm^{-1}. **MS:** *m*/*z* calcd for $C_{18}H_{20}ClFNaO_4$ $[M + Na]^+$: 377.0932, found 377.0926.



Substrate (**2x**): A solution of the corresponding alcohol[36] (1 g, 5.81 mmol) in dry acetonitrile was added triphenylphosphine (1.83 g, 6.97 mmol) and tetraclorocarbon (1.54 mL, 11.62 mmol, 2 eq.). The resulting mixture was stirred for 48h at room temperature. Then, the solvent was removed under vacuum and the residue was extracted with pentane (3 x 40 mL) and filtered through Celite®. The organic solvent was removed under reduced pressure and the crude material was purified by flash chromatography (SiO_2, 15 % EtOAc in hexane) to yield 1.1 g (31 %) of title compound as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (q, *J* = 8 Hz, 2H), 3.74 (s, 3H), 2.60 – 2.43 (m, 2H), 2.40 – 2.24 (m, 2H), 2.18 – 1.99 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 212.0, 169.6, 61.5, 53.1, 45.5, 38.6, 31.3, 19.7 ppm. **IR** (film): 2957, 1754, 1724, 1434, 1225, 1152, 1098, 1010, 516 cm^{-1}. **MS:** *m*/*z* calcd for $C_8H_{11}ClNaO_3$ $[M + Na]^+$: 213.0284, found 213.0289.



Substrate (**2y**): 3-Bromomethyl pyridine hydrobromide (0.37 g, 1,46 mmol, 1.0 eq.) was added to a Schlenk flask containing, Na_2CO_3 (0.74 g, 7,02 mmol, 4.8 eq.), $Pd(PPh_3)_4$ (0.15 g, 0,13 mmol, 9 mol%) and (*E*)-6-chloro-1-hexen-1-ylboronic acid pinacol ester (0.36 g, 1,46 mmol, 1.0 eq.) in 1,4-dioxane/H_2O (4:1, 5 mL). The mixture was stirred for 18 h at 80 ºC. After reaching room temperature the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic extracts were washed with saturated aqueous NaCl (2×10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by flash chromatography (SiO_2, 10 % Et_2O → 20 % Et_2O) to yield 130 mg (42 %) of title compound as yellow oil which darkens on standing.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 5.1, 1.9 Hz, 2H), 7.52 - 7.43 (m, 1H), 7.21 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 5.62 - 5.44 (m, 2H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.33 (d, *J* = 5.8 Hz, 2H), 2.12 - 2.02 (m, 2H), 1.83 - 1.72 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.1, 147.6, 136.2, 136.1, 132.3, 128.4, 123.4, 45.0, 36.2, 32.1, 31.8, 26.6 ppm. **IR** (film): 2937, 1478, 1422, 970 cm^{-1}. **MS:** *m*/*z* calcd. for $C_{12}H_{17}ClN$ $[M + H]^+$: 210.1044, found 210.1047.

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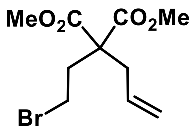
[36] V. Lecomte, C. Bolm *Adv. Synth. Catal.* **2005**, *347*, 1666.



Substrate (**3a**): A solution of dimethyl allylmalonate (500 mg, 2.90 mmol) in THF (5 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 139 mg, 3.48 mmol) in THF (10 mL) at 0 ºC under Ar. The ice bath was removed and the mixture was stirred for 60 min at ambient temperature. Then, freshly distilled 1,2-dibromoethane (0.36 mL, 3.78 mmol) was added via syringe slowly over 15 min and the resulting mixture was stirred overnight. The reaction mixture was quenched with saturated aq. NH_4Cl. The aqueous solution was extracted with dichloromethane and the combined filtrates were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 2% EtOAc in hexane) to give 600 mg (74%) of the title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.69 - 5.58 (m, 1H), 5.18 - 5.10 (m, 1H), 3.74 (s, 6H), 2.67 (dt, J = 7.4, 1.2 Hz, 2H), 2.48 - 2.42 ppm (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 170.8 (2C), 131.8, 119.9, 57.8, 52.8 (2C), 38.1, 36.4, 27.1 ppm. **IR** (film): 2953, 1729, 1640, 1434, 1208, 1162, 925, 643, 545 cm^{-1}. **MS:** *m/z* calcd for $C_{10}H_{15}BrNaO_4$: 301.0046, found 301.0049.

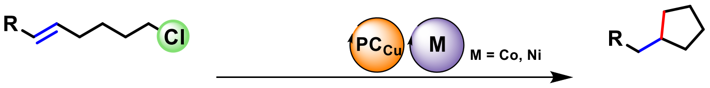
8. General Procedure for reductive cyclization reactions

General Procedure A: 1^{H}Co (5 mol%), PC_{Cu} (2 mol%), Et_3N (14.4 eq).

General Procedure B: 1^{H}Ni (5 mol%), PC_{Cu} (2 mol%), i-Pr_2NEt (11.4 eq).

A solution of chloroalkane **2b-y** (0.6 mL, 0.06 mmol, 1.0 eq.), **1^{H}Co** or **1^{H}Ni** (0.3 mL, 0.003 mmol, 5 mol%), **PC_{Cu}** (0.3 mL, 1.2×10^{-3} mmol, 2 mol%) and acetonitrile (1.2 mL) was equally distributed into vials (10 mL of headspace) containing glass beads. The vials were sealed with a septum and removed from the glovebox. Degased EtOH was added to each vial to reach a total volume of 6 mL (total concentration of substrate 10 mM). To these vials Et_3N (120 µL, 0.865 mmol, 14.4 eq.) or *i*-Pr_2NEt (120 µL, 0.687 mmol, 11.4 eq.) was added and the vials were placed in the photoreactor at the indicated temperature (30 ºC) and stirring was switched on. After irradiating the vials for 24 h with visible light (blue LED, 447 nm), they were opened and the content was combined in a separatory funnel. H_2O (15 mL) and Et_2O (15 mL) was added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 x 15 mL), and the combined organic extracts were washed with brine (15 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified via column chromatography.

Table SI.EP.EP-5.

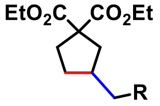


R = alkyl, aryl
2b-w

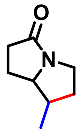
EtOH : MeCN (3:2)
Et_3N or i-Pr_2NEt (11-14 equiv)
30ºC, 24h
1 W LEDs (λ = 450 nm)

4b-w

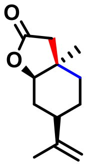
Alkenes



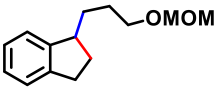
1^{H}Co: R = H, 88 % (4b)[a]
Bu, 50 % (4c)[a]
Ph, 73 % (4d)[a]
1^{H}Ni: R = H, 93 % (4b)[a]
Bu, 79 % (4c)[a]
Ph, 93 % (4d)[a]



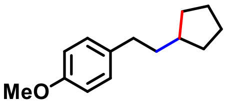
1^{H}Co: 83 % (4e)[a]
1^{H}Ni: 83 % (4e)[a]



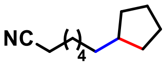
1^{H}Co: 62 % (4f)[b]
1^{H}Ni: 66 % (4f)[b]



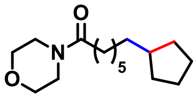
1^{H}Co: 65 % (4g)[c]
1^{H}Ni: 52 % (4g)[b]



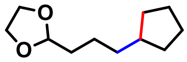
1^{H}Co: 37 % (4h)[c]
1^{H}Ni: 76 % (4h)[a]



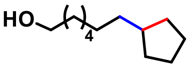
1^{H}Co: 26 % (4i)[c]
1^{H}Ni: 52% (4i)[a]



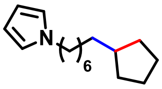
1^{H}Co: 23 % (4j)[c]
1^{H}Ni: 81 % (4j)[a]



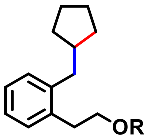
1^{H}Co: 5% (4k)[c]
1^{H}Ni: 40 % (4k)[a]



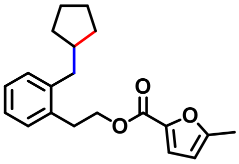
1^{H}Co: 43 % (4l)[c]
1^{H}Ni: 77 % (4l)[a]



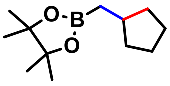
1^{H}Co: 21 % (4m)[c]
1^{H}Ni: 48 % (4m)[a]



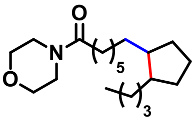
1^{H}Co: R = H, 15 % (4n)[c]
TBS, 23% (4o)[c]
1^{H}Ni: R = H, 90 % (4n)[a]
TBS, 91 % (4o)[a]



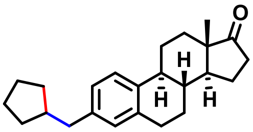
1^{H}Co: 38 % (4p)[c]
1^{H}Ni: 88 % (4p)[a]



1^{H}Co: 14 % (4q)[c]
1^{H}Ni: 61 % (4q)[a]

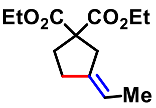


1^{H}Co: 18 % (4r)[c]
1^{H}Ni: 67 % (4r)[a]

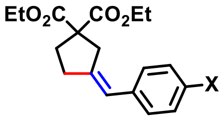


1^{H}Co: 43 % (4s)[c]
1^{H}Ni: 79 % (4s)[a]

Alkynes



1^{H}Co: 84 % (4t)[a]
1^{H}Ni: 83 % (4t)[a]

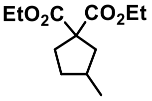


1^{H}Co: X = Cl; 76 % (4u)[a]
X = OMe; 82 % (4v)[a]
X = F; 80% (4w)[a]

1^{H}Ni: X = Cl; 72 % (4u)[a]
X = OMe; 78 % (4v)[a]
X = F; 82% (4w)[a]

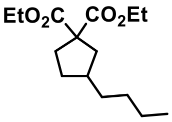
Standard conditions: substrate (10 mM), **PC$_{Cu}$** (2 mol%), **1^{H}Co** or **1^{H}Ni** catalyst (5 mol%), ED [Et_3N (14.4 eq.) or *i*-Pr_2NEt (11.4 eq.)], EtOH:MeCN (3:2), visible light irradiation with blue LEDs (λ = 447 nm) at 30 ºC for 24 h. a) Isolated yield. b) Isolated yield over two steps. c) Yield was determined by GC using biphenyl as internal standard.

9. Characterization of products



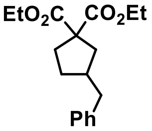
Product (**4b**): Cyclization according to general procedure **A**: scale 0.4 mmol, flash chromatography (SiO_2, 100 % hexane) yielded 85 mg (88 %) of the title compound as a colorless liquid. The same substrate was also tested according to general procedure **B**: scale 0.3 mmol, flash chromatography (SiO_2, 100 % hexane) yielded 64 mg (93 %) of the title compound as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (q, *J* = 7.1 Hz, 4H), 2.51 - 2.41 (m, 1H), 2.33 (ddd, *J* = 13.6, 8.5, 3.8 Hz, 1H), 2.21 - 2.12 (m, 1H), 2.10 - 2.01 (m, 1H), 1.91 – 1.80 (m, 1H), 1.72 - 1.60 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.03 (d, *J* = 6.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.8 (2C), 61.2 (2C), 60.5, 42.5, 34.5, 34.2, 34.0, 29.7, 19.6, 14.0 (2C) ppm. **IR** (film): 2955, 2928, 2871, 1728, 1446, 1252, 1158, 859 cm^{-1}. **MS** (ESI-pos): *m/z* 229.1 [M + H$^+$]. The spectroscopic characterization is in agreement with the literature reported.[37]



Product (**4c**): Cyclization according to general procedure **A**: scale 0.3 mmol, flash chromatography (SiO_2, 100 % hexane) yielded 69 mg (71 %) of the title compound as a light yellow liquid. The same substrate was also tested according to general procedure **B**: scale 0.3 mmol, flash chromatography (SiO_2, 0 % → 2 % Et_2O in hexane) yielded 79 mg (79 %) of the title compound as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (qd, *J* = 7.1, 1.6 Hz, 4H), 2.50 - 2.43 (m, 1H), 2.31 (ddd, *J* = 13.5, 8.5, 3.6 Hz, 1H), 2.14 (ddd, *J* = 13.5, 9.4, 7.3 Hz, 1H), 2.01 - 1.83 (m, 2H), 1.70 (dd, *J* = 13.3, 9.9 Hz, 1H), 1.60 (s, 1H), 1.29 - 1.21 (m, 9H), 0.96 - 0.85 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.8 (2C), 61.2 (2C), 60.0, 40.8, 39.8, 35.0, 33.8, 32.2, 30.7, 22.8, 14.1, 14.0 (2C) ppm. **IR** (film): 2957, 2927, 1728, 1465, 1446, 1253, 1175, 1157, 860 cm^{-1}. **MS:** *m/z* calcd for $C_{13}H_{29}NaO_4$ [M + Na]$^+$: 293.1729, found 293.1723.



Product (**4d**): Cyclization according to general procedure **A**: scale 0.3 mmol, flash chromatography (SiO_2, 2 % of Et_2O in hexane) yielded 80 mg (73 %) of the title compound as a light yellow liquid. The same substrate was also tested according to general procedure **B**: scale 0.2 mmol, flash chromatography

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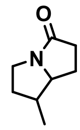
[37] Revol, G.; McCallum, T.; Morin, M.; Gagosz, F.; Barriault, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 13342.

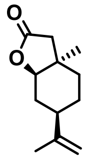
(SiO_2, 0 % → 5 % Et_2O in hexane) yielded 73 mg (93 %) of the title compound as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 - 7.25 (m, 2H), 7.24 - 7.14 (m, 3H), 4.19 (dq, *J* = 11.5, 7.0 Hz, 4H), 2.67 (qd, *J* = 13.5, 7.4 Hz, 2H), 2.48 - 2.38 (m, 1H), 2.38 - 2.25 (m, 2H), 2.23 - 2.10 (m, 1H), 1.85 (dd, *J* = 13.3, 9.6 Hz, 2H), 1.47 - 1.32 (m, 1H), 1.25 (dt, *J* = 10.0, 7.5 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.7, 172.7, 141.2, 128.7, 128.3, 125.8, 61.3, 61.3, 60.0, 41.5, 41.3, 40.4, 33.7, 32.0, 14.0 (2C) ppm. **IR** (film): 3027, 2981, 2937, 1726, 1603, 1496, 1453, 1366, 1248, 1207, 1176, 1097, 1029, 860, 745, 700 cm^{-1}. **MS:** *m*/*z* calcd for $C_{18}H_{24}NaO_4$ $[M + Na]^+$: 327.1572, found 327.1567.



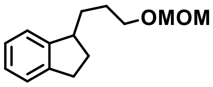
Product (**4e**): Cyclization according to general procedure **A**: scale 0.3 mmol, flash chromatography (SiO_2, 100 % hexane) yielded 49 mg (83 %) of the title compound as an orange/brown liquid. The same substrate was also tested according to general procedure **B**: scale 0.24 mmol, flash chromatography (SiO_2, 90 % Et_2O →100 % in hexane, then 10 % MeOH in Et_2O) yielded 27.7 mg (83 %) of title compound as an orange/brown liquid, which darkens rapidly on standing.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 - 3.28 (m, 2H), 3.15 (ddt, *J* = 11.5, 9.5, 1.8 Hz, 1H), 2.72 (dddt, *J* = 16.7, 10.7, 9.4, 1.3 Hz, 1H), 2.44 (ddd, *J* = 16.7, 9.7, 2.3 Hz, 1H), 2.36 – 2.19 (m, 2H), 1.78 - 1.56 (m, 3H), 1.04 ppm (d, *J* = 6.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 174.8, 68.3, 41.1, 40.7, 35.7, 35.0, 25.3, 15.4 ppm. **IR** (film): 3458, 2957, 2930, 2872, 1679, 1562, 1409, 1250 cm^{-1}. **MS:** *m*/*z* calcd. for $C_8H_{14}NO$ $[M + H]^+$: 140.1070, found 140.1071.



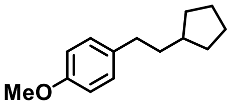
Product (**4f**): Cyclization according to general procedure **A**: scale 0.3 mmol, yielded 48 mg (62 % over 2 steps) of the title compound as a light yellow liquid. The same substrate was also tested according to general procedure **B**: scale 0.24 mmol yielded 41 mg (66 % over 2 steps) of the title compound a light yellow liquid. The reaction crude containing a mixture of diastereoisomeric hemiacetals was dissolved in acetone (4 mL), cooled to 0 ºC and Jones reagent (2 M CrO_3 in aqueous H_2SO_4, 0.26 mL, 0.53 mmol, 2.2 eq.) was added dropwise. The mixture was stirred for 90 min at 0 ºC. After complete conversion of starting material as judged by TLC the reaction was diluted with Et_2O (10 mL) and carefully quenched by addition of 2-propanol (1 mL). Saturated aqueous $NaHCO_3$ (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by column chromatography (SiO_2, 5 % → 10 % → 20 % Et_2O in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.78 - 4.65 (m, 2H), 4.17 (dd, *J* = 10.6, 6.4 Hz, 1H), 2.64 (dd, *J* = 17.0, 0.9 Hz, 1H), 2.21 (ddt, *J* = 13.3, 6.4, 2.6 Hz, 1H), 2.00 (d, *J* = 17.0 Hz, 1H), 1.93 - 1.82 (m, 2H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.52 - 1.40 (m, 1H), 1.37 - 1.21 (m, 1H), 1.18 (d, *J* = 0.8 Hz, 3H), 0.90 - 0.82 ppm (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 176.8, 148.1, 109.6, 85.2, 41.5, 38.5, 38.1, 35.3, 33.6, 28.5, 26.9, 21.0 ppm. **IR** (film): 2931, 2858, 1774, 1456, 1158, 979, 886 cm^{-1}. **MS:** *m*/*z* calcd. for $C_{12}H_{18}NaO_2$ $[M + Na]^+$: 217.1199, found 217.1199.



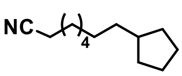
Product (**4g**): Cyclization according to general procedure **B** (Scale 0.24 mmol). Flash chromatography (SiO_2, 5 % → 10 % Et_2O in hexane) yielded 27.3 mg (52 %) of title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 - 7.19 (m, 2H), 7.19 - 7.14 (m, 2H), 4.65 (s, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.38 (s, 3H), 3.14 (m, 1H), 2.94 (ddd, *J* = 15.1, 8.5, 4.8 Hz, 1H), 2.86 (m, 1H), 2.31 (dtd, *J* = 12.6, 7.9, 4.8 Hz, 1H), 2.04 - 1.90 (m, 1H), 1.85 - 1.65 (m, 3H), 1.55 - 1.43 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 147.5, 144.1, 126.4, 126.1, 124.5, 123.7, 96.6, 68.1, 55.2, 44.7, 32.2, 31.7, 31.5, 28.0 ppm. **IR** (film): 2930, 1146, 1109, 1041, 918 cm^{-1}. **MS:** *m*/*z* calcd for $C_{14}H_{20}NaO_2$ $[M + Na]^+$: 243.1356, found 243.1350.



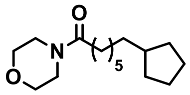
Product (**4h**): Cyclization according to general procedure **B**: scale 0.3 mmol, flash chromatography (SiO_2, 5 % →10 % Et_2O in hexane) yielded 46 mg (76 %) of the title compound as a light liquid yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 - 7.07 (m, 2H), 6.86 - 6.79 (m, 2H), 3.79 (s, 3H), 2.86 - 2.45 (m, 2H), 1.95 - 1.73 (m, 3H), 1.64 - 1.48 (m, 6H), 1.20 - 1.06 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 157.7, 135.1, 129.3 (2C), 113.8 (2C), 55.4, 39.7, 38.5, 34.3, 32.8 (2C), 25.4 (2C) ppm. **IR** (film): 2946, 1511, 1246, 1039 cm^{-1}. **MS:** *m*/*z* calcd for $C_{14}H_{21}O$ $[M + H]^+$: 205.1587, found 205.1585.



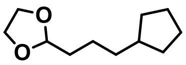
Product (**4i**): Cyclization according to general procedure **B**: scale 0.24 mmol, flash chromatography (SiO_2, 5 % → 10 % → 20 % Et_2O in hexane) yielded 22.3 mg (52 %) of title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (t, *J* = 7.1 Hz, 2H), 1.79 - 1.68 (m, 3H), 1.68 - 1.61 (m, 2H), 1.61 - 1.53 (m, 2H), 1.53 - 1.39 (m, 4H), 1.37 - 1.25 (m, 6H), 1.11 - 0.99 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 120.0, 40.2, 36.2, 32.8 (2C), 29.2, 28.8, 28.6, 25.5, 25.3 (2C), 17.3 ppm. **IR** (film): 2927, 2857, 1818, 1452, 1064 cm^{-1}. **MS:** *m*/*z* calcd. for $C_{12}H_{22}N$ 180.1747, found 180.1750.



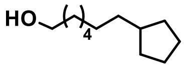
Product (**4j**): Cyclization according to general procedure **B**: scale 0.24 mmol, flash chromatography (SiO_2, 5 % → 10 % → 20 % Et_2O in hexane) yielded 52.2 mg (81 %) of title compound as a light liquid yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70 - 3.64 (m, 4H), 3.61 (d, *J* = 4.9 Hz, 2H), 3.46 (t, *J* = 4.8 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.76 - 1.69 (m, 2H), 1.67 - 1.55 (m, 6H), 1.54 - 1.46 (m, 2H), 1.37 - 1.25 (m, 7H), 1.10 - 1.00 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 172.1, 67.1, 66.8, 46.2, 42.0, 40.3, 36.3, 33.3, 32.8 (2C), 29.8, 29.6, 28.8, 25.4, 25.3 (2C) ppm. **IR** (film): 2922, 2853, 1649, 1430, 1116 cm^{-1}. **MS:** *m*/*z* calcd for $C_{16}H_{29}NNaO_2$ $[M + Na]^+$: 290.2091, found 290.2093.



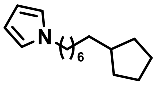
Product (**4k**): Cyclization according to general procedure **B**: 0.3 mmol, flash chromatography (SiO_2, 5 % of Et_2O in hexane) yielded 22 mg (40 % + 36 % of the starting material) of title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84 (t, *J* = 4.8 Hz, 1H), 4.19 - 3.92 (m, 2H), 3.90 - 3.81 (m, 2H), 1.83 - 1.69 (m, 3H), 1.69 - 1.61 (m, 2H), 1.61 - 1.54 (m, 2H), 1.53 - 1.46 (m, 2H), 1.46 - 1.38 (m, 2H), 1.37 - 1.29 (m, 2H), 1.13 - 1.01 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 104.7, 64.8, 40.1, 36.1, 34.2, 32.6, 25.2, 23.3 ppm. **IR** (film): 2945, 2864, 1737, 1454, 1409, 1260, 1130, 1033, 943, 805 cm^{-1}. **MS:** *m*/*z* calcd for $C_{11}H_{21}O_2$ $[M + H]^+$: 185.1, found 185.2*.*



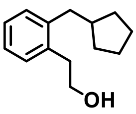
Product (**4l**): Cyclization according to general procedure **B**: scale 0.3 mmol, flash chromatography (SiO_2, 5 % → 10 % → 20 % Et_2O in hexane) yielded 42.5 mg (77 %) of title compound as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 (t, *J* = 6.6 Hz, 2H), 1.79 - 1.66 (m, 3H), 1.62 - 1.44 (m, 6H), 1.31 (d, *J* = 20.7 Hz, 11H), 1.12 - 1.00 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 63.2, 40.3, 36.4, 33.0, 32.9 (2C), 30.0, 29.6, 28.8, 25.9, 25.3 (2C) ppm. **IR** (film): 2922, 2854, 1453, 1057 cm^{-1}. **IR** (film): 2922, 2854, 1453, 1057 cm^{-1}. **MS:** *m*/*z* calcd. For $C_{12}H_{25}O$ $[M + H]^+$: 185.1905, found 185.1888*.*



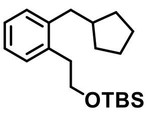
Product (**4m**): Cyclization according to general procedure **B**: 0.24 mmol, flash chromatography (SiO_2, 5 % of Et_2O in hexane) yielded 27 mg (48 %) of title compound as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.65 (t, *J* = 2.1 Hz, 2H), 6.14 (t, *J* = 2.1 Hz, 2H), 3.86 (t, *J* = 7.2 Hz, 2H), 1.82 – 1.68 (m, 5H), 1.64 - 1.53 (m, 2H), 1.50 (dq, *J* = 7.2, 2.9, 2.5 Hz, 2H), 1.32 – 1.22 (m, 10H), 1.11 - 1.00 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 120.6, 107.9, 49.8, 40.3, 36.3, 32.9, 31.7, 29.9, 29.4, 28.8, 26.9, 25.3 ppm. **IR** (film): 3114, 2922, 2853, 1705, 1499, 1451, 1356, 1281, 1088, 1062, 967, 717, 616 cm^{-1}. **MS:** *m*/*z* calcd for $C_{16}H_{28}N$ $[M + H]^+$: 234.2222, found 234,2216.



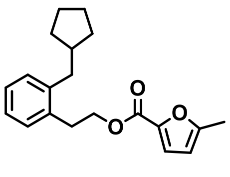
Product (**4n**): Cyclization according to general procedure **B**: 0.24 mmol. Aqueous work up including several washings with saturated aqueous NaCl (4 x 10 mL), drying over $MgSO_4$ and removal of the solvent under reduced pressure yielded 44 mg (90 %) of title compound as a light liquid yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 - 7.13 (m, 4H), 3.85 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.66 (d, *J* = 7.4 Hz, 2H), 2.12 - 2.04 (m, 1H), 1.75 - 1.68 (m, 2H), 1.68 - 1.62 (m, 2H), 1.56 - 1.49 (m, 3H), 1.28 - 1.17 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.8, 136.0, 130.2, 129.8, 126.5, 126.1, 63.5, 41.5, 38.7, 35.9, 32.8 (2C), 25.0 (2C) ppm. **IR** (film): 2948, 2867, 1450, 1043, 750 cm^{-1}. **MS:** *m*/*z* calcd for $C_{14}H_{19}$ $[M - H_2O]$: 187.1481, found 187.1481.



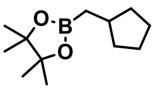
Product (**4o**): Cyclization according to general procedure **B**: 0.24 mmol. Aqueous work up including several washings with saturated aqueous NaCl (4 x 10 mL), drying over $MgSO_4$ and removal of the solvent under reduced pressure yielded 70 mg (91 %) of title compound as a light liquid yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 - 7.04 (m, 4H), 3.77 (t, *J* = 7.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.65 (d, *J* = 7.4 Hz, 2H), 2.08 (p, *J* = 7.7 Hz, 1H), 1.76 - 1.68 (m, 2H), 1.68 - 1.62 (m, 2H), 1.54 - 1.49 (m, 2H), 1.27 - 1.19 (m, 2H), 0.89 (s, 9H), 0.02 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.6, 136.7, 130.1, 129.8, 126.2, 125.8, 64.5, 41.5, 38.8, 36.4, 32.8 (2C), 26.1 (3C), 25.0 (2C), 18.5, -5.2 (2C) ppm. **IR** (film): 2952, 2858, 1471, 1254, 1093 cm^{-1}. **MS:** *m*/*z* calcd for $C_{20}H_{34}NaOSi$ $[M + Na]^+$: 341.2277 found 341.2273.



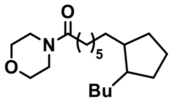
Product (**4p**): Cyclization according to general procedure B: 0.04 mmol. Aqueous work up including several washings with saturated aqueous NaCl (3 x 10 mL), drying over $MgSO_4$ and removal of the solvent under reduced pressure yielded 11 mg (88 %) of title compound as a light liquid yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 - 7.12 (m, 4H), 7.08 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.12 (dt, *J* = 3.4, 1.0 Hz, 1H), 4.45 (dd, *J* = 8.0, 7.2 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.70 (d, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.09 (dtd, *J* = 14.6, 7.2, 1.4 Hz, 1H), 1.78 - 1.69 (m, 2H), 1.69 - 1.59 (m, 2H), 1.56 - 1.47 (m, 2H), 1.28 - 1.18 (m, 2H) **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 158.9, 157.3, 143.2, 140.8, 135.3, 130.1, 129.9, 126.7, 126.1, 119.5, 108.5, 65.1, 41.5, 38.6, 32.8 (2C), 32.1, 25.0 (2C), 14.1. **IR** (film): cm^{-1} 2949, 2860, 1718, 1530, 1298, 1134, 755. **MS:** *m/z* calcd for $C_{20}H_{24}NaO_3$ [M + Na]$^+$: 335.1618, found 335.1616.



Product (**4q**): Cyclization according to general procedure **B**: 0.3 mmol. Aqueous work up including several washings with saturated aqueous NaCl (3 x 10 mL) and filtration through a short pad of Celite® yielded 37.8 mg (61 %) of title compound as a yellow/brownish oil. Spectral data is in agreement with previously reported data for this compound.[38]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 - 1.91 (m, 1H), 1.82 - 1.73 (m, 2H), 1.65 - 1.56 (m, 2H), 1.49 (ddq, *J* = 7.5, 4.6, 2.3, 1.8 Hz, 2H), 1.23 (s, 12H), 1.10 - 1.02 (m, 2H), 0.83 (d, *J* = 7.5 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 82.9 (2C), 36.2, 35.2 (2C), 25.2 (2C), 24.9 (4C) ppm.



Product (**4r**): Cyclization according to general procedure **B**: 0.11 mmol, flash chromatography (SiO_2, 10 % → 20 % Et_2O in hexane) yielded 23.1 mg (67 %) of title compound as a light brown oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.69 (dd, *J* = 5.7, 4.0 Hz, 4H), 3.64 (d, *J* = 5.2 Hz, 2H), 3.49 (t, *J* = 4.8 Hz, 2H), 2.35 - 2.31 (m, 2H), 1.84 - 1.73 (m, 2H), 1.71 - 1.60 (m, 4H), 1.56 - 1.47 (m, 1H), 1.37 - 1.26 (m, 14H), 1.24 - 1.20 (m, 1H), 1.07 (td, *J* = 7.3, 5.6, 2.7 Hz, 2H), 0.93 - 0.86 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9 {mayor and minor}, 67.0 {mayor}, 66.7 {mayor}, 46.1 {mayor}, 46.0 {mayor}, 42.6 {mayor and minor}, 41.8 {mayor}, 35.3 {minor}, 35.0 {minor}, 33.2 {mayor}, 32.3 {mayor}, 30.9 {mayor}, 30.8 {minor}, 30.2 {mayor and minor}, 29.9 {mayor}, 29.8 {minor}, 29.6 {mayor}, 29.5 {minor},

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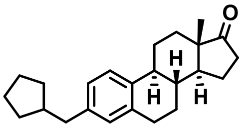
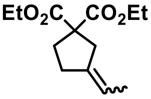
[38] Kubota, K.; Yamamoto, E.; Ito H. *J. Am. Chem. Soc.* **2013**, *135*, 2635.

29.3 {mayor}, 29.0 {mayor}, 28.5 {mayor}, 28.4 {minor}, 25.3 {mayor and minor}, 25.3 {minor}, 23.9 {minor}, 23.1 {mayor}, 23.1 {minor}, 22.5 {mayor}, 14.2 {mayor}. **IR** (film): 2958, 2924, 2854, 1720, 1643, 1458, 1361, 1258, 1175, 1084, 1010, 791, 682, 661, 570 cm^{-1}. **MS:** *m*/*z* calcd for $C_{20}H_{38}NO_2$ [M + H]$^+$: 324.2903 found 324.2897.



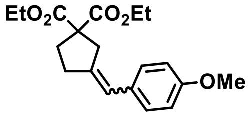
Product (**4s**): Cyclization according to general procedure **B**: scale 0.06 mmol, flash chromatography (SiO_2, 5 % → 10 % Et_2O in hexane) yielded 15.9 mg (79 %) of title compound as a white solid, which darkens at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 - 7.17 (m, 1H), 6.97 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.91 (s, 1H), 2.93 - 2.85 (m, 2H), 2.55 (d, *J* = 7.3 Hz, 2H), 2.53 - 2.46 (m, 1H), 2.45 - 2.39 (m, 1H), 2.34 - 2.25 (m, 1H), 2.21 - 2.11 (m, 1H), 2.10 - 1.93 (m, 4H), 1.77 - 1.67 (m, 2H), 1.67 - 1.59 (m, 4H), 1.58 - 1.46 (m, 6H), 1.24 - 1.15 (m, 2H), 0.91 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 221.0, 140.0, 137.0, 136.2, 129.5, 126.4, 125.2, 50.7, 48.1, 44.5, 42.0, 41.7, 38.4, 36.0, 32.7, 31.8, 29.6, 26.8, 25.9, 25.1, 21.7, 19.5, 14.0, 1.1 ppm. **IR** (film): 2928, 2864, 1741, 1453 cm^{-1}. **MS:** *m*/*z* calcd for $C_{24}H_{32}NaO$ [M + Na]$^+$: 359.2345, found 359.2337.



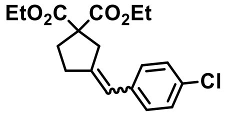
Product (**4t**): Cyclization according to general procedure **A**: scale 0.3 mmol, flash chromatography (SiO_2, 100 % hexane) yielded 61 mg (84 %) of the title compound as a colourless oil as a mixure of E/Z isomers (1:1). The same substrate was also tested according to general procedure **B**: scale 0.36 mmol, flash chromatography (SiO_2, 2 % Et_2O in hexane) yielded 70 mg (83 %) of title compound as a colourless oil as a mixure of E/Z isomers (1:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.35 (dq, *J* = 6.7, 2.2 Hz, 1H), 4.78 - 3.75 (m, 4H), 3.17 - 2.69 (m, 2H), 2.56 - 1.96 (m, 4H), 1.72 - 1.38 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 172.0, 139.3, 139.1, 116.4, 116.2, 61.4, 61.3, 60.1, 59.9, 41.0, 36.6, 33.6, 33.4, 31.6, 27.0, 14.7, 14.6, 14.0 ppm. **IR** (film): 2980, 2931, 29007, 2838, 1726, 1607, 1510, 1443, 1366, 1245, 1157, 1034, 833, 530 cm^{-1}. M**S:** *m*/*z* calcd for $C_{13}H_{20}NaO_4$ [M + Na]$^+$: 263.1259, found 263.1254.



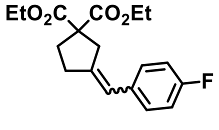
Product (**4u**): Cyclization according to general procedure **A**: scale 0.3 mmol, flash chromatography (SiO_2, 100 % hexane to 2% of AcOEt in hexane) yielded 88 mg (82 %) of the title compound as a yellow oil as a mixure of E/Z isomers (1:1). The same substrate was also tested according to general procedure **B**: scale 0.3 mmol, flash chromatography (SiO_2, 2 % Et_2O in hexane) yielded 78 mg (78 %) of title compound as a colourless oil as a mixure of E/Z isomers (1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 8.9, 7.3 Hz, 2H), 6.86 (dd, *J* = 8.7, 6.0 Hz, 2H), 6.33 – 6.27 (m, 1H), 4.24 – 4.14 (m, 4H), 3.80 (d, *J* = 2.6 Hz, 3H), 3.21 – 3.15 (m, 1H), 3.11 (d, *J* = 1.6 Hz, 1H), 2.67 (t, *J* = 7.6 Hz, 1H), 2.61 (td, *J* = 7.5, 1.7 Hz, 1H), 2.36 (t, *J* = 7.5 Hz, 1H), 2.26 (t, *J* = 7.5 Hz, 1H), 1.24 (td, *J* = 7.1, 5.9 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 171.6, 157.9, 139.5, 130.9, 129.3, 129.2, 121.8, 113. 7, 61.4, 61.0, 59.2, 55.3, 43.0, 38.4, 34.4, 33.9, 32.9, 31.6, 29.5, 22.7, 14.1 ppm. **IR** (film): 2980, 2937, 2907, 2838, 1726, 1607, 1510, 1443, 1245, 1157, 1034, 833, 530 cm^{-1}. **MS:** *m*/*z* calcd for $C_{19}H_{24}NaO_5$ [M + Na]$^+$: 355.1521, found 355.1516.



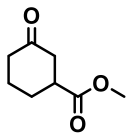
Product (**4v**): Cyclization according to general procedure **A**: scale 0.27 mmol, flash chromatography (SiO_2, 100 % hexane to 2% of AcOEt in hexane) yielded 77 mg (76 %) of the title compound as a yellow oil as a mixure of E/Z isomers (1:1). The same substrate was also tested according to general procedure **B**: scale 0.24 mmol, flash chromatography (SiO_2, 2 % Et_2O in hexane) yielded 65 mg (72 %) of title compound as a yellow oil as a mixure of E/Z isomers (1:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 - 7.29 (m, 2H), 7.21 (t, *J* = 8.7 Hz, 2H), 6.33 (dt, *J* = 9.2, 2.4 Hz,1H), 4.62 - 4.08 (m, 4H), 3.39 - 3.13 (m, 2H), 2.84 - 2.57 (m, 24H), 2.40 (t, *J* = 7.6 Hz, 1H), 2.30 (t, *J* = 7.5 Hz, 1H), 1.27 (dt, *J* = 8.2, 7.1 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 171. 6, 171.5, 142.7, 142.6, 136. 5, 136.4, 131.8, 131.7, 129.3, 129.3, 128.4, 128.4, 121.5, 121.4, 61.6, 61.5, 60.9, 59.1, 43.0, 38.5, 34.2, 33.9, 32.7, 29.7, 14.0, 14.0 ppm. **MS:** *m*/*z* calcd for $C_{18}H_{21}ClNaO_4$ [M + Na]$^+$: 359.1026, found 359.1021.



Product (**4w**): Cyclization according to general procedure **A**: scale 0.33 mmol, flash chromatography (SiO_2, 100 % hexane to 2% of AcOEt in hexane) yielded 93 mg (80 %) of the title compound as a pale-yellow oil as a mixure of E/Z isomers (1:1). The same substrate was also tested according to general procedure **B**: scale 0.3 mmol, flash chromatography (SiO_2, 2 % Et_2O in hexane) yielded 85 mg (82 %) of title compound as a pale-yellow oil as a mixure of E/Z isomers (1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 - 7.14 (m, 2H), 6.99 (td, *J* = 8.7, 6.1 Hz, 2H), 6.35 – 6.28 (m, 1H), 4.24 - 4.14 (m, 4H), 3.17 - 3.09 (m, 2H), 2.68 - 2.58 (m, 2H), 2.37 (t, *J* = 7.5 Hz, 1H), 2.27 (t, *J* = 7.5 Hz, 1H), 1.24 (dt, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 171.6, 171.5, 162.4, 162.4, 159.9, 141.4, 141.4, 141.4, 141.4, 134.2, 134.1, 129.6, 129.6, 129.5, 129.5, 121.4, 121.4, 115.2, 115.2, 115.0, 114.9, 61.6, 61.5, 60.9, 59.1, 42.9, 38.4, 34.2, 33.8, 32.8, 29.5, 14.1, 14.0 ppm. **IR** (film): 2980, 2937, 2873, 1727, 1602, 1508, 1446, 1272, 1245, 1221, 1157, 1065, 862, 522 cm^{-1}. **MS:** *m*/*z* calcd for $C_{18}H_{21}FNaO_4$ $[M + Na]^+$: 343.1322, found 343.1316.



Product (**4x**):The reductive cyclization reaction of substrate **2t** was carried out following the general procedure **B** obtaining the ring expansion product. Scale: 0.3 mmol, flash chromatography (SiO_2, (5 % → 10% of Et_2O in hexane) yielded 15 mg (33 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 2.89 - 2.76 (m, 1H), 2.57 (d, *J* = 8.0 Hz, 2H), 2.46 - 2.28 (m, 2H), 2.22 – 2.04 (m, 2H), 1.95 - 1.82 (m, 1H), 1.82 - 1.71 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 209.1, 174.2, 52.1, 43.1, 43.1, 40.9, 27.8, 24.5 ppm. **IR** (film): 2950, 2870, 1740, 1720 cm^{-1}. **MS:** *m*/*z* calcd for $C_8H_{13}O_3$ $[M + H]^+$: 157.2, found 157.2. The spectroscopic characterization is in agreement with the literature reported.[39]

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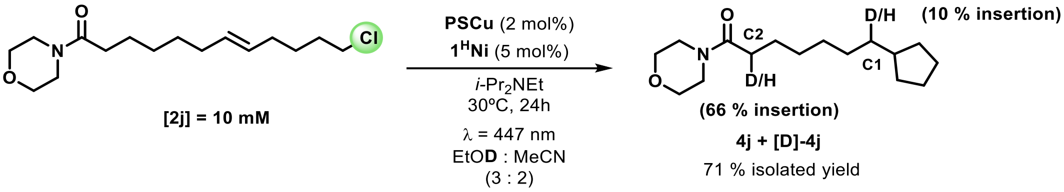
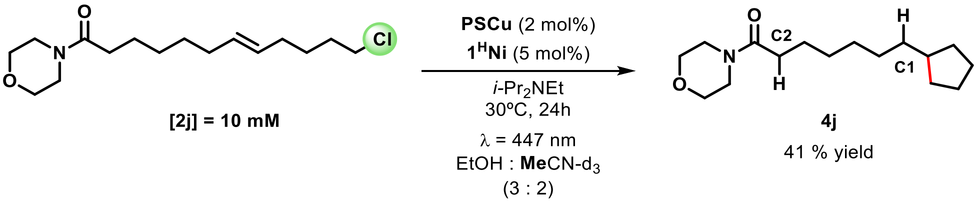
[39] Moteki, S.A.; Usui,A.; Zhang, T; Solorio-Alvarado, C.R.; Maruoka, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 1.

10. Experiments with deuterated solvents

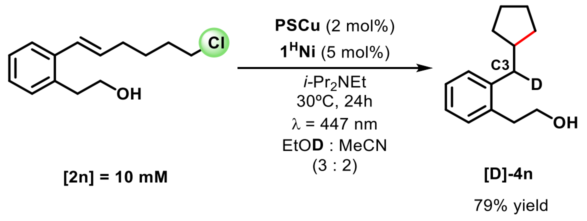


The reductive cyclization reaction of substrate **2j** was carried out following the general procedure **B** but using EtOD as protic solvent. Scale: 0.024 mmol, flash chromatography (SiO_2, (10 % of Et_2O in hexane) yielded 46 mg (71 %) of the pure product with a deuterium insertion of 10 % and 15 mg of the starting material (80 % of conversion). See Figure SI.EP-5 and SI-6 for the detailed ^{1}H-NMR and ^{2}H-NMR spectra and Figure SI.EP-7 for the ^{13}C-NMR spectrum of the mixture **4j/[D]-4j**.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (dd, *J* = 5.8, 3.9 Hz, 4H), 3.62 (d, *J* = 5.1 Hz, 2H), 3.52 – 3.37 (m, 2H), 2.67 – 2.16 (m, 2H), 2.00 – 1.65 (m, 2H), 1.65 – 1.52 (m, 4H), 1.51 – 1.43 (m, 2H), 1.40 – 1.21 (m, 8H), 1.04 (td, *J* = 4.2, 2.3 Hz, 2H).**^{2}H NMR** (500 MHz, $CHCl_3$): δ = 0.92 ppm. **^{13}C NMR** (10 MHz, $CDCl_3$) δ = 171.9, 67.0, 66.7, 46.1, 41.9, 40.1, 36.2, 33.2 (singlet of the non-deuterated product and t of the deuterated product), 32.7 (singlet of the non-deuterated product and t of the deuterated product), 29.7, 29.5, 29.5, 28.6, 25.3, 25.2, 25.2 ppm.

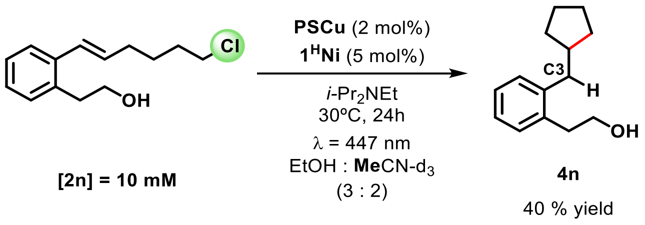


As control experiment, the reductive cyclization reaction of substrate **2j** was carried out following the general procedure **B** but using deuterated acetonitrile in this case. Scale: 0.21 mmol, flash chromatography (SiO_2, (10 % of Et_2O in hexane) yielded 23 mg (41 %) of the pure product **4j** without deuterium insertion and 28 mg of the starting material (55 % of conversion). See Figure SI.EP-8 and SI-9 for the detailed ^{1}H-NMR and ^{2}H-NMR spectra of the product **4j**.



The reductive cyclization reaction of substrate **2n** was carried out following the general procedure **B** but using CH_3CH_2OD as protic solvent. Scale: 0.24 mmol, flash chromatography (SiO_2, (20 % of Et_2O in hexane) yielded 38 mg (79 %) of the pure product with a deuterium insertion of 100 %. See Figure SI.EP-11 and SI-12 for the detailed ^{1}H-NMR and ^{2}H-NMR spectra and Figure SI.EP-13 for the ^{13}C-NMR spectrum of product **[D]-4n**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 - 7.09 (m, 4H), 4.28 - 3.75 (m, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.63 (dd, *J* = 5.3, 3.4 Hz, 1H), 2.07 (q, *J* = 7.6 Hz, 1H), 1.81 - 1.60 (m, 4H), 1.59 – 1.47 (m, 2H), 1.29 – 1.12 (m, 2H) ppm. **^{2}H NMR** (500 MHz, $CHCl_3$): δ = 2.62 ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.7, 135.9, 130.0, 129.7, 126.4, 125.9, 63.4, 41.3, 38.2 (t), 35.8, 32.6, 32.6, 24.9 ppm.



As a control experiment, the reductive cyclization reaction of substrate **2n** was carried out following the general procedure **B** but using deuterated acetonitrile instead. Scale: 0.24 mmol, flash chromatography (SiO_2, (10 % of Et_2O in hexane) yielded 12 mg (40 %) of the pure product **4n** without deuterium insertion and 12 mg of the starting material (75 % of conversion). See Figure SI.EP-14 and SI-15 for the detailed ^{1}H-NMR and ^{2}H-NMR spectra of the product **4n** and Figure SI.EP-16 for the ^{13}C-NMR spectrum of product **4n**.

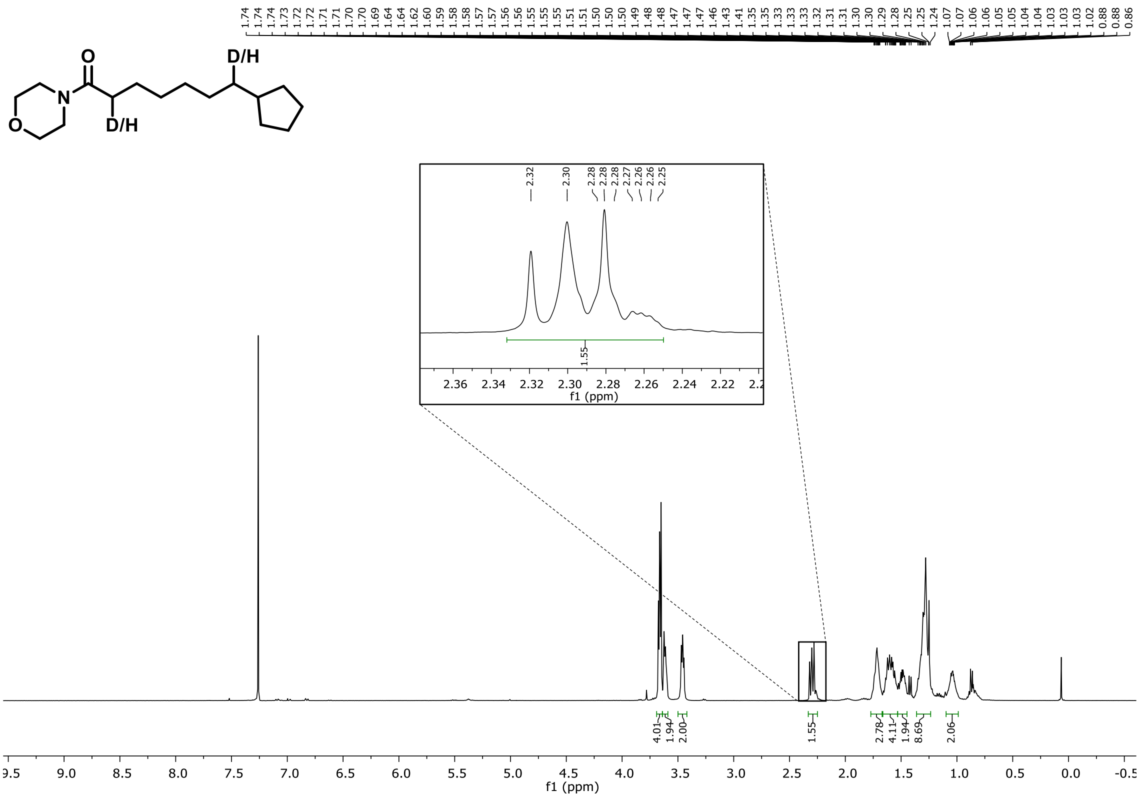


Figure SI.EP-10: ^{1}H-NMR ($CDCl_3$, 400 MHz, 298K) of isolated product **[D]-4j**.

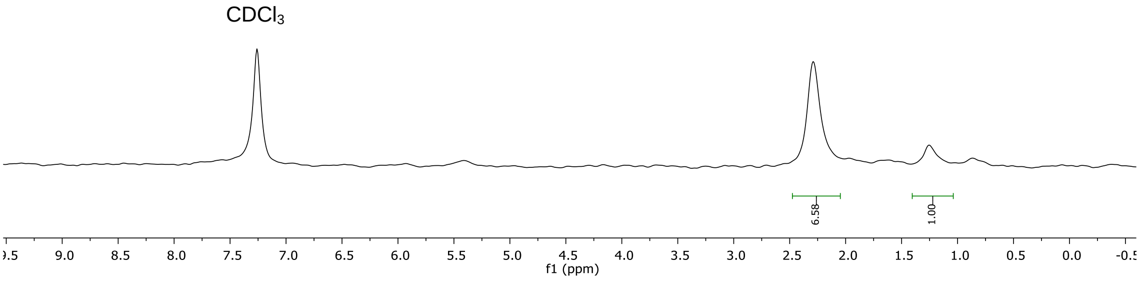


Figure SI.EP-11: ^{2}H-NMR ($CDCl_3$, 500 MHz, 298K) of isolated product **[D]-4j.**

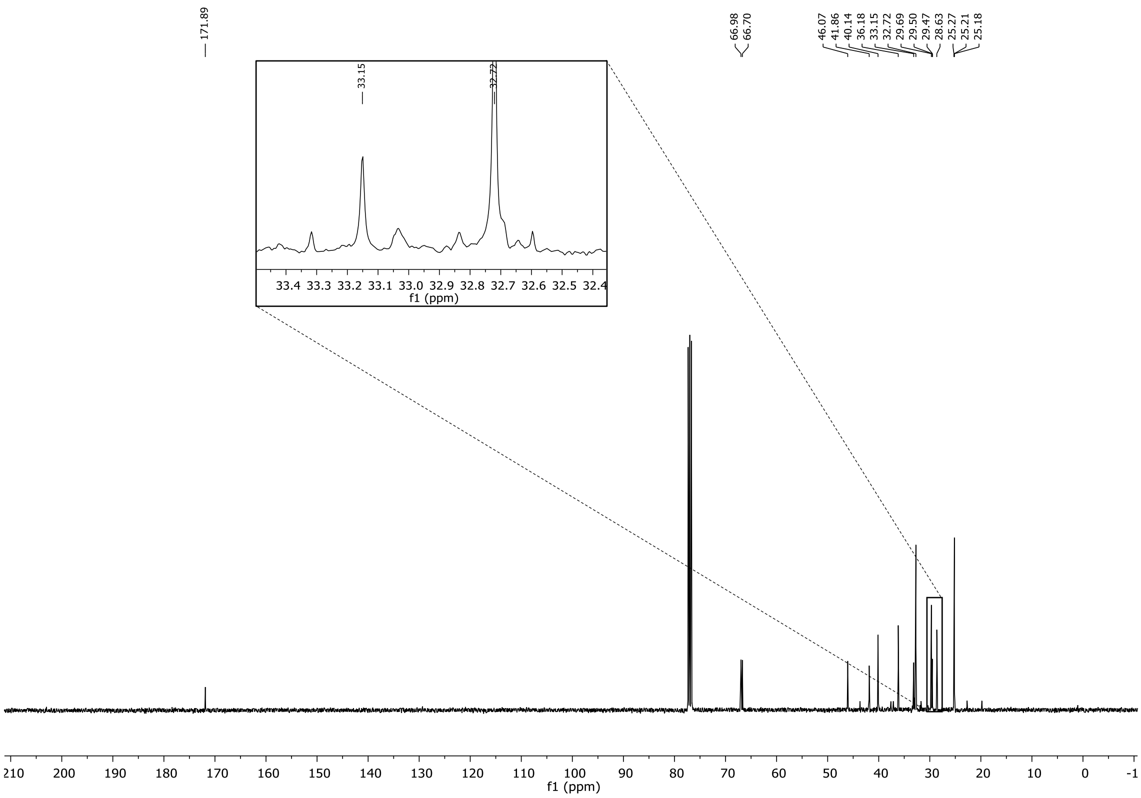
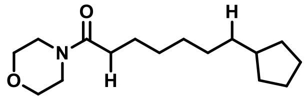


Figure SI.EP-12: ^{13}C-NMR (CDCl$_3$, 101 MHz, 298K) of isolated product **[D]-4j**.



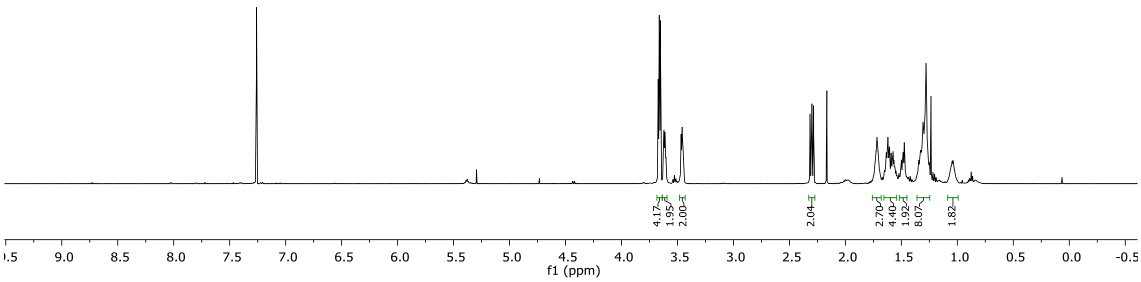


Figure SI.EP-13: ^{1}H-NMR (CDCl$_3$, 500 MHz, 298K) of isolated product **4j**.

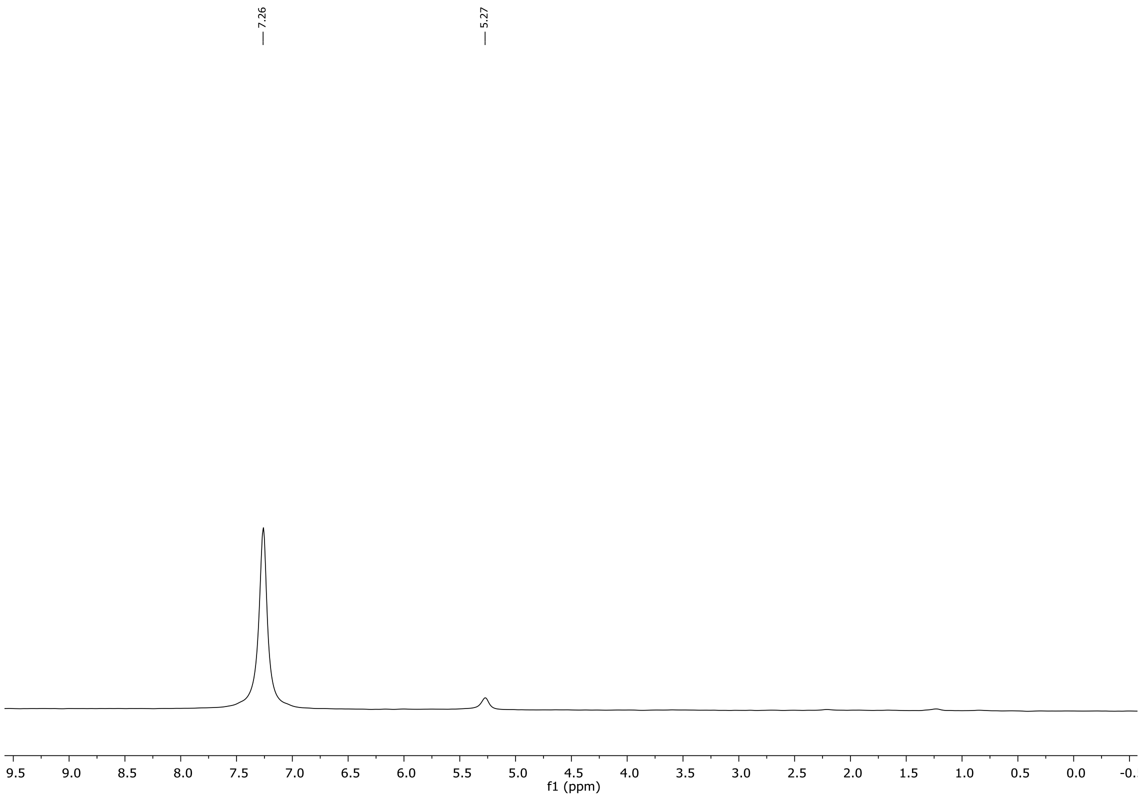


Figure SI.EP-14: ^{2}H-NMR ($CDCl_3$, 500 MHz, 298K) of isolated product **4j**.

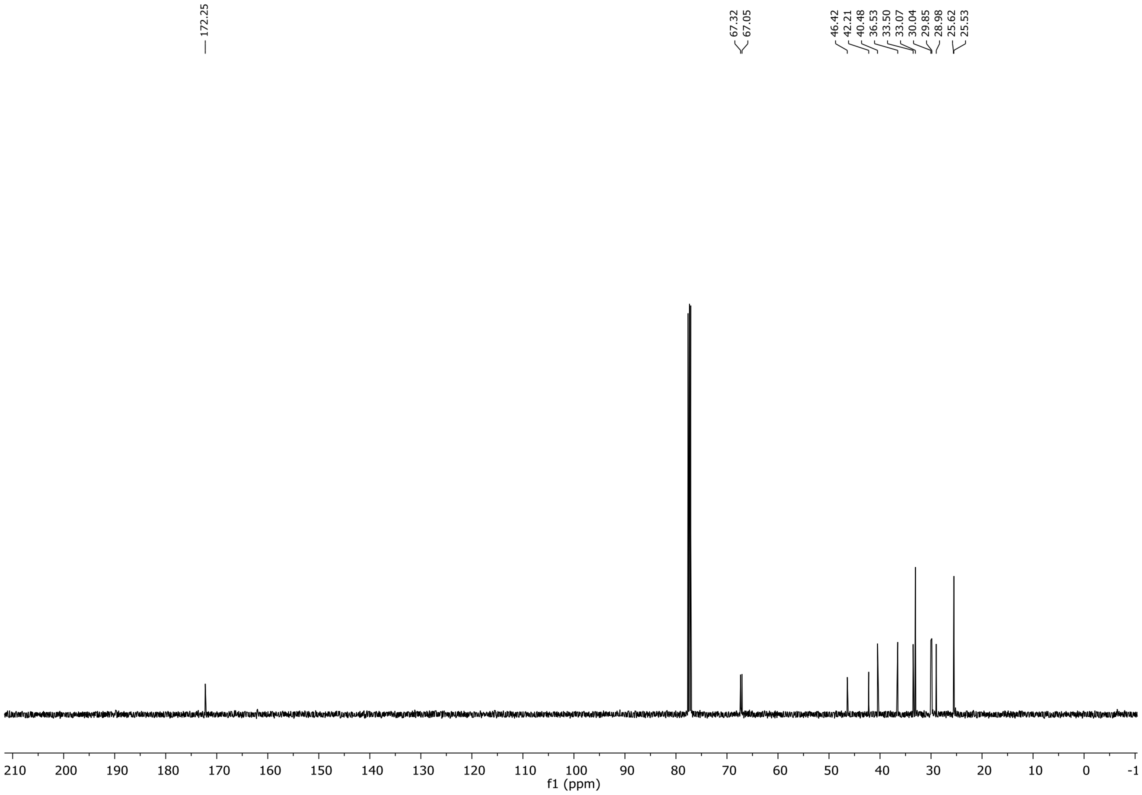


Figure SI.EP-15: ^{13}C-NMR ($CDCl_3$, 126 MHz, 298K) of isolated product **4j**.

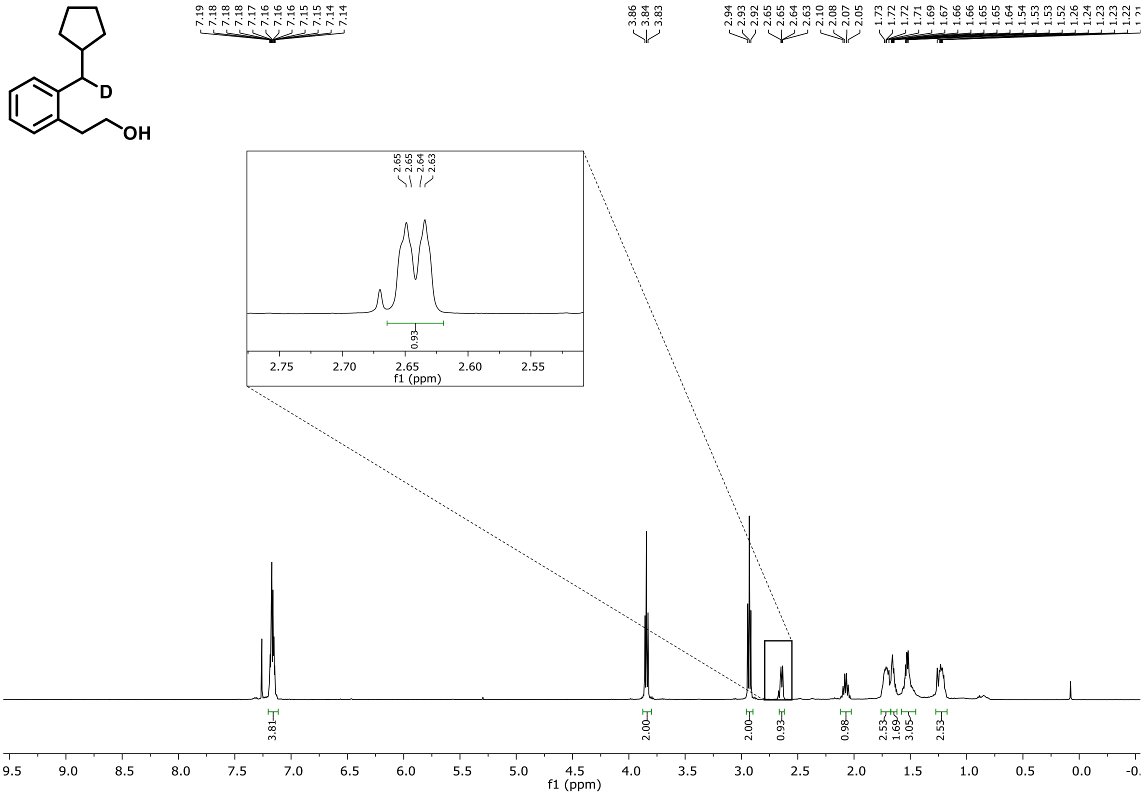


Figure SI.EP-16: ^{1}H-NMR (CDCl$_3$, 300 MHz, 298K) of product **[D]-4n**.

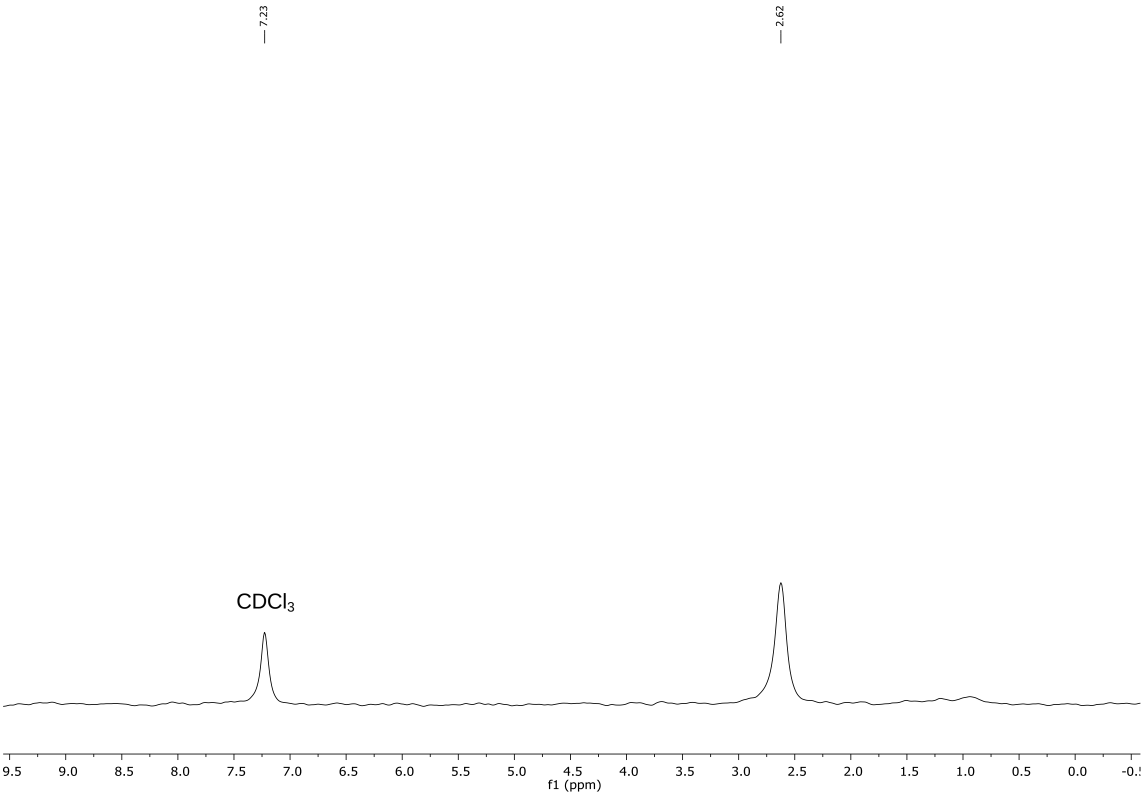


Figure SI.EP-17: ^{2}H-NMR (CDCl$_3$, 500 MHz, 298K) of isolated product **[D]-4n**.

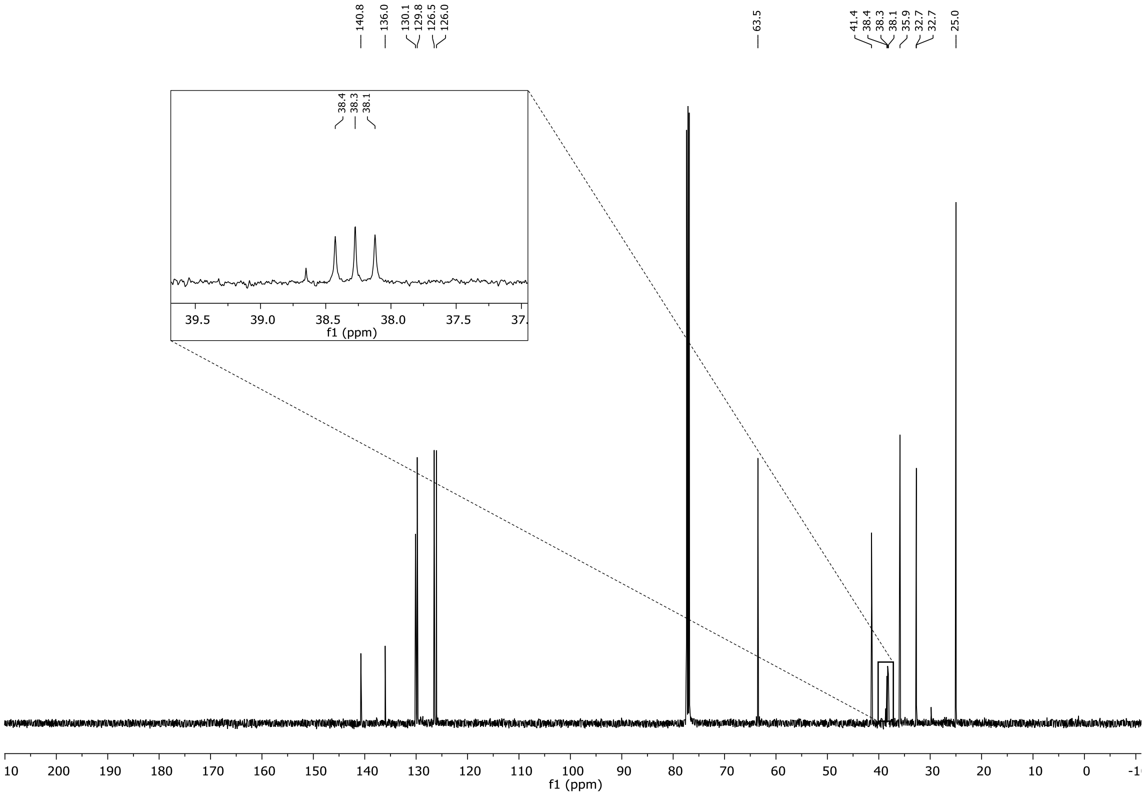


Figure SI.EP-18: ^{13}C-NMR (CDCl$_3$, 126 MHz, 298K) of isolated product **[D]-4n**.

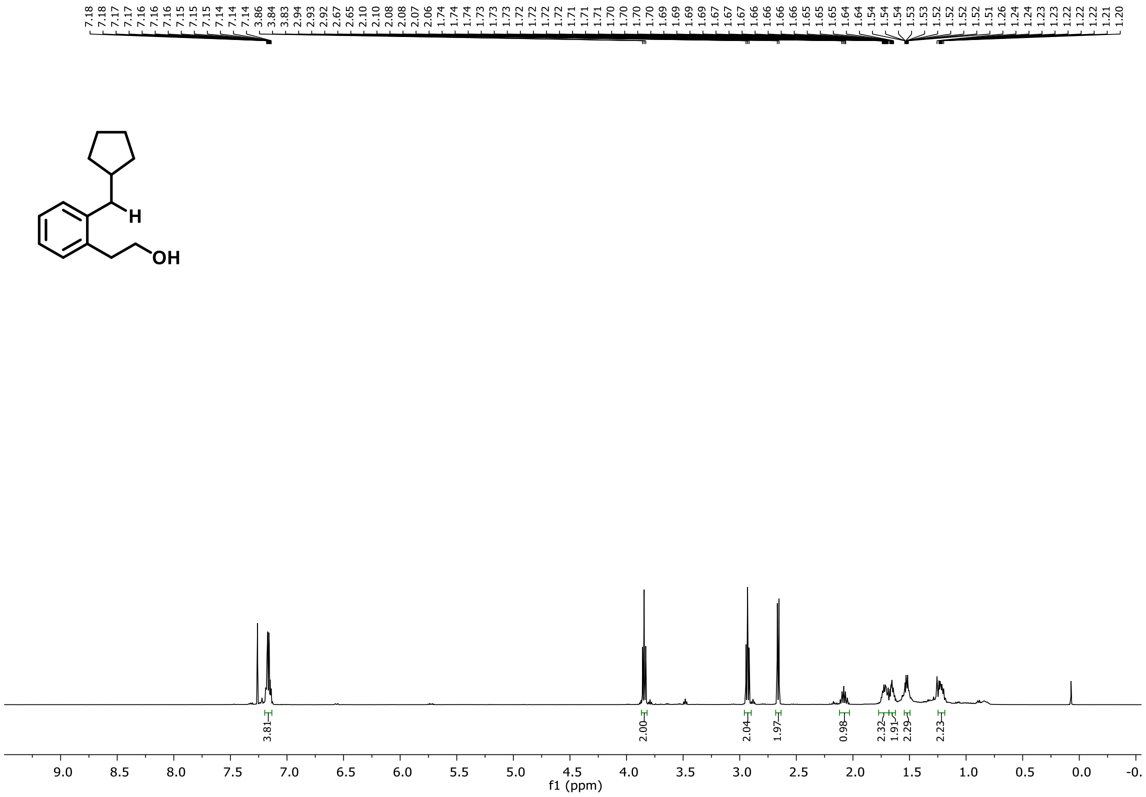


Figure SI.EP-19: ^{1}H-NMR (CDCl$_3$, 500 MHz, 298) of product **4n**.

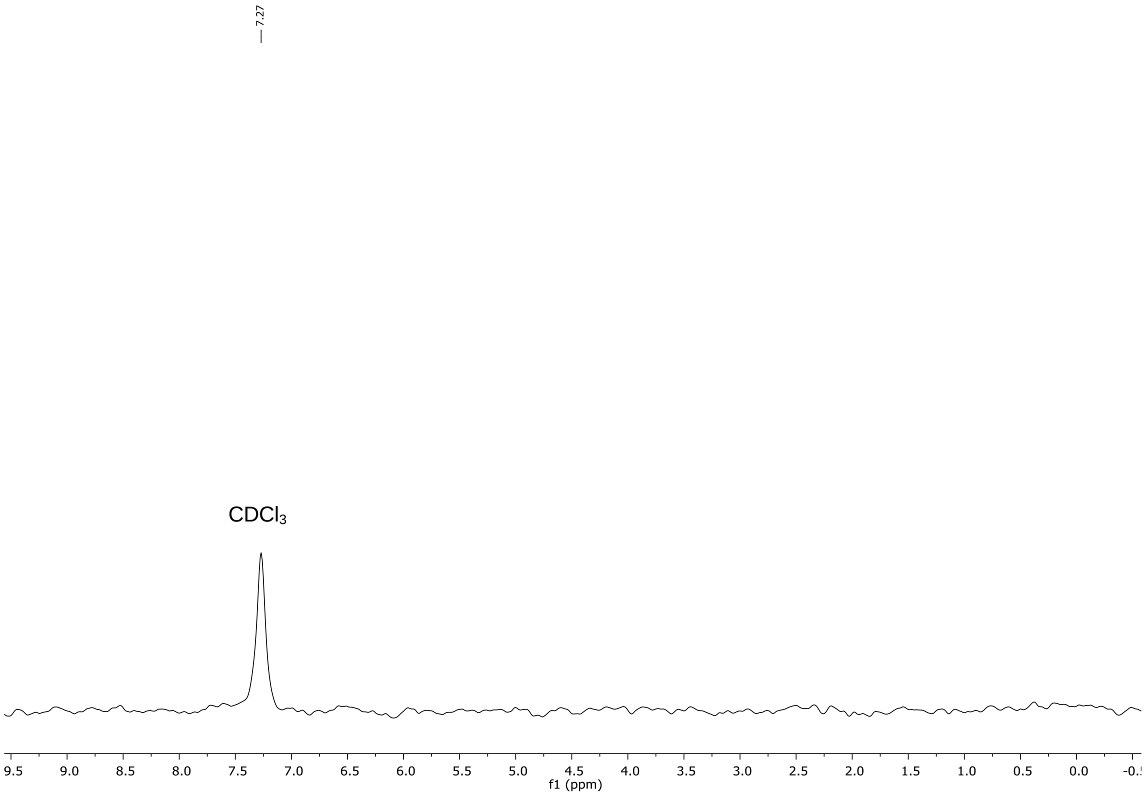


Figure SI.EP-20: ^{2}H-NMR ($CDCl_3$, 400 MHz, 298) of product **4n**.

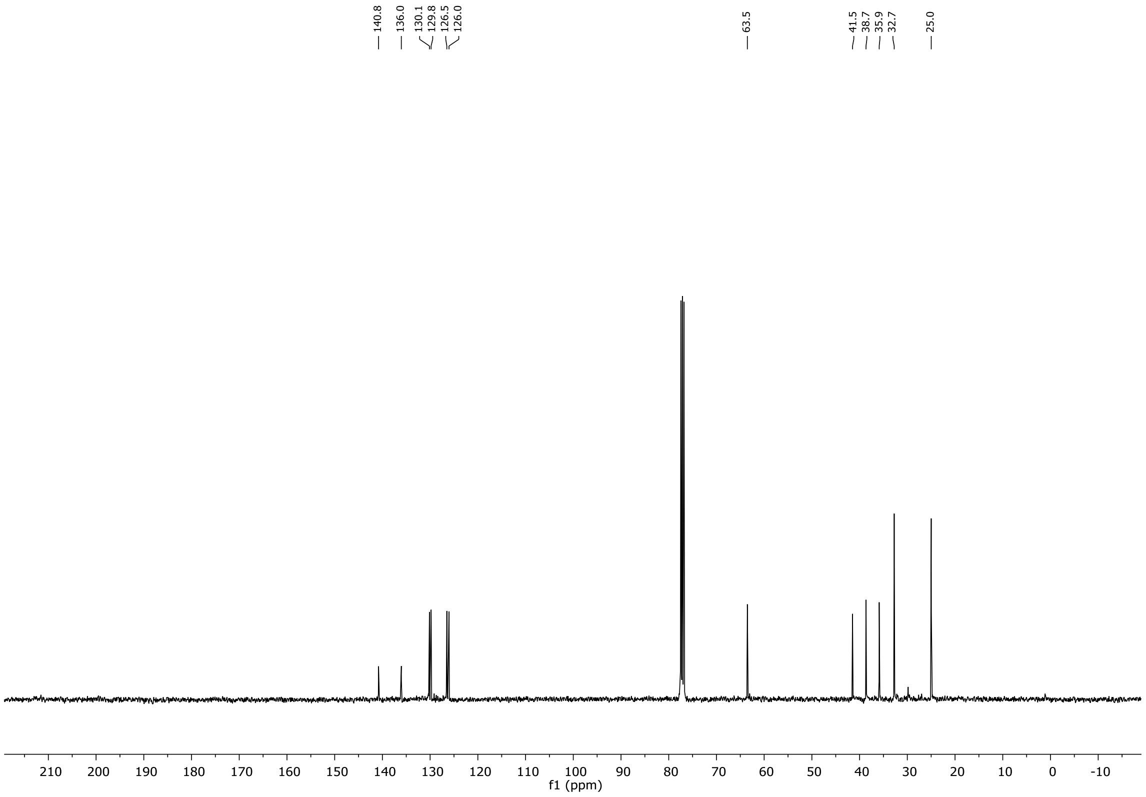


Figure SI.EP-21: ^{13}C-NMR ($CDCl_3$, 126 MHz, 298) of product **4n**.

11. Light-Sources Experiments

We have compared four different light irradiation sources, an in-house built parallel photoreactor, the commercial available KESSIL® lamp, a blue LEDs tape and a white-light desk lamp. The reactions were carried out with **2a** (20 μmol, 1.0 eq.), **1^HNi** (1 μmol, 5 mol %), **PC_{Cu}** (0.4 μmol, 2 mol %) and CH_3CN:EtOH:i-Pr_2NEt (0.8:1.2:0.04 mL) in crimped vials. The obtained conversion (and yield) were 91%(91%), 92%(85%), 84%(64%) and 69%(52%) for the in-house built parallel photoreactor (24 h irradiation), KESSIL® lamp (24 h irradiation), conventional LEDs tape (48 h irradiation) and common flexo-desk lamp (48 h irradiation), respectively.

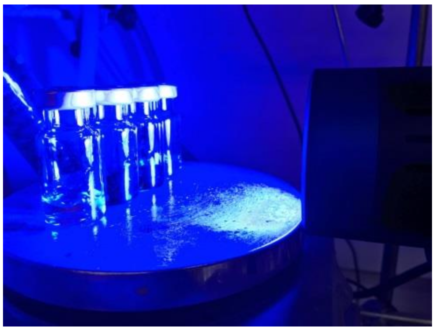


Figure SI.EP-22. *KESSIL® lamp irradiation experiments*

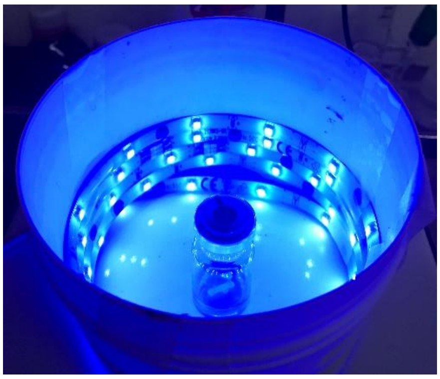
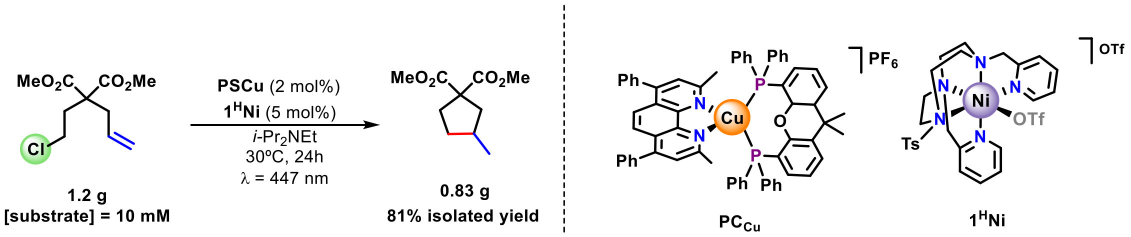


Figure SI.EP-23. *LEDs tape irradiation experiment*

Figure SI.EP-24. *Desk lamp irradiation experiment*

12. Gram Scale



Inside an anaerobic box, 1.2 g of dimethyl allyl chloroethylmalonate (5.12 mmol, 1.0 eq.), **1^{H}Ni** catalyst (210 mg, 0.255 mmol, 5 mol %), **PC_{Cu}** (117 mg, 0.102 mmol, 2 mol %) and acetonitrile (204.7 mL) were equally distributed into a 1 L 2-necked round bottom flask. Degassed ethanol (307.1 mL) was added (out of the anaerobic box) to the flask (total concentration of substrate 10 mM). *i*-Pr_2NEt (10 mL, 58.6 mmol, 11.4 eq.) was finally added to the solution flask, which was placed between 2 KESSIL lamps (λ = 467 nm), separated 7 cm from each other (to maintain a temperature close to 30ºC). After irradiating for 48 h, H_2O (150 mL) and Et_2O (150 mL) were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 x 100 mL), and the combined organic extracts were washed with brine (150 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified via column chromatography yielding 0.83 g (81% yield) of the pure cyclic product.

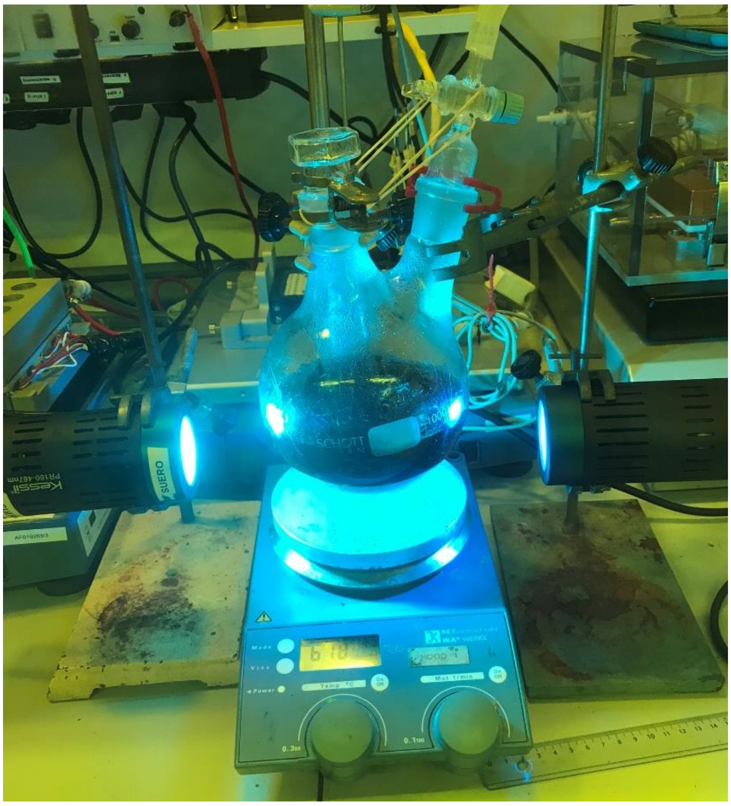


Figure SI.EP-25. *Gram Scale experiment*

13. Spectroscopic and electrochemical studies

13.1. EPR Studies

Control experiments performed in the absence of the **1^HNi** complex (PC_{Cu}, 4 mol% in $^nBuN:EtOH:^iPrNEt_2$ 2:3:0.2) before and after irradiation did not yield any EPR signal. However, 3 min of irradiation (at 467 nm with a KESIL® lamp) of an EPR tube containing the **1^HNi** complex (10 mol%), the photoredox catalyst **PC_{Cu}** (4 mol%) in the reaction mixture of $^nBuN:EtOH:^iPrNEt_2$ (2:3:0.2) gave an EPR signal with an almost axial symmetry consistent with a unpaired electron predominantly localized in the $d_x2_{-y}2$ orbital. Spectra simulations yield g-values centered at 2.06, 2.08 and 2.29. The obtained values combined with the performed UV-Vis experiments (an absorption band at 535 nm), is consistent with the presence of Ni(I) species as previously reported.[40]

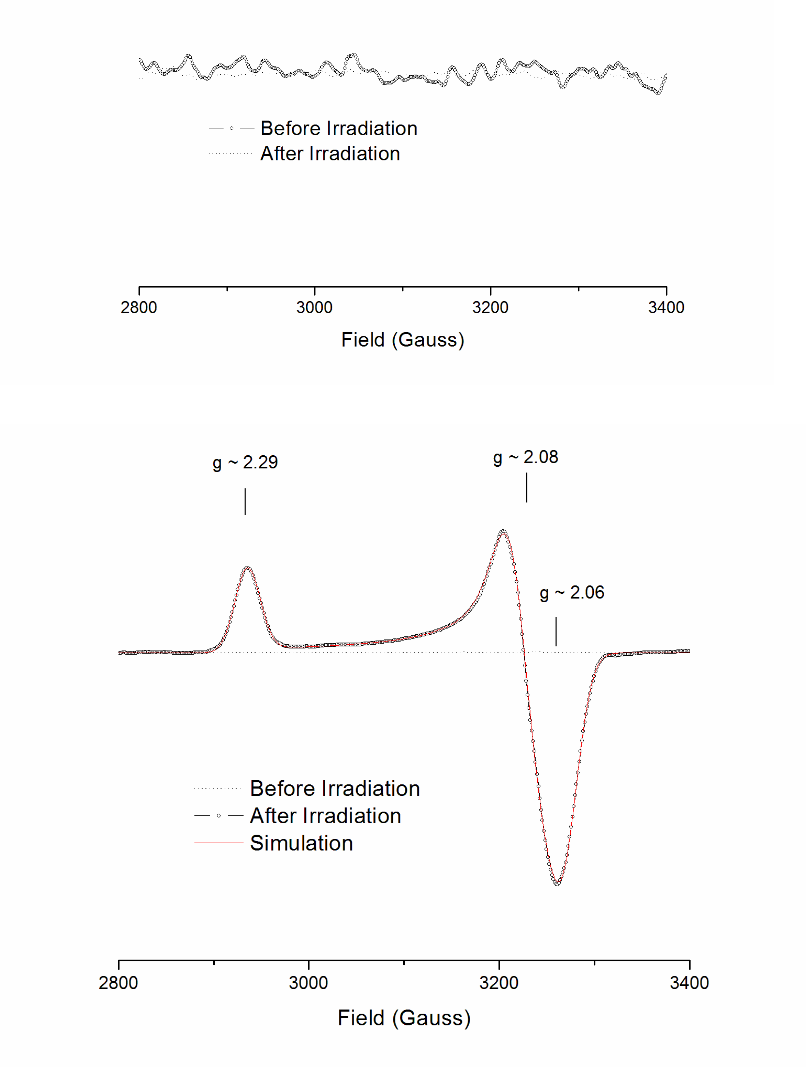


Figure SI.EP-26. *EPR spectra and simulations of (top) reaction mixture without **1^HNi** complex, (bottom) reaction mixture with **1^HNi** complex. Reaction conditions: **1^HNi** complex (10 mol%), the photoredox catalyst **PC_{Cu}** (4 mol%) in the reaction mixture of $^nBuN:EtOH:^iPrNEt_2$ (2:3:0.2).*

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[40] Mishra, V.; Mishra, H.; Mukherjee, R. *Eur. J. Inorg. Chem.* **2009**, 2973.

13.2. Spectroelectrochemical Studies

13.2.1. Cyclic Voltammetry

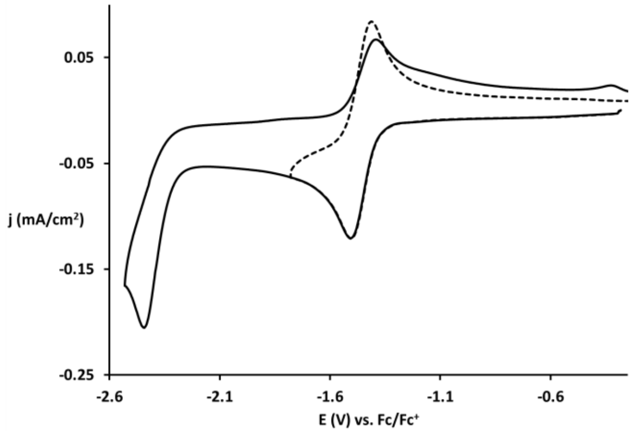


Figure SI.EP-27. *CVs of* ***1^HNi*** *(0.5 mM) in 0.1 M TBAH/CH_3CN electrolyte at 0.1 V s^{-1}. $E_{1/2}$($Ni^{II/I}$) = –1.46 V vs. Fc/Fc^+ (–1.08 V vs. SCE), ΔE_p= 91 mV; E_p($Ni^{I/0}$) = –2.44 V vs. Fc/Fc^+ (–2.06 V vs. SCE).*

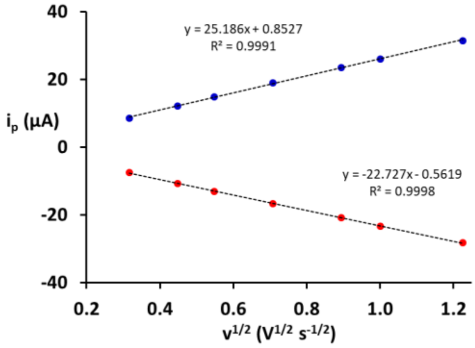


Figure SI.EP-28. *CVs of* ***1^HNi*** *(0.5 mM) in 0.1 M TBAH/CH_3CN electrolyte at varying scan rates (0.1–1.5 V s^{-1}). Plot of the peak current (ip) as a function of the square root of the scan rate ($v^{1/2}$).*

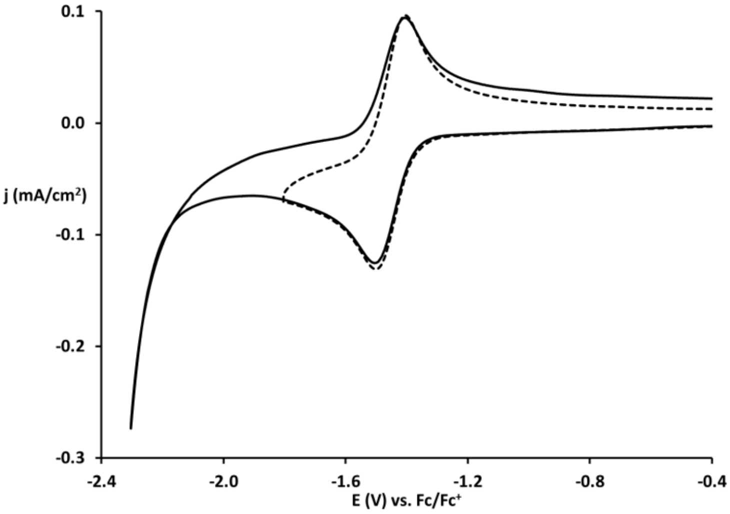


Figure SI.EP-29. *CVs of* ***1^HNi*** *(0.5 mM) in 0.1 M TBAH/CH_3CN:EtOH (2:3) electrolyte at 0.1 V s^{-1}. $E_{1/2}$($Ni^{II/I}$) = –1.45 V vs. Fc/Fc^+ (–1.07 V vs. SCE), ΔE_p= 89 mV. Catalytic current increase due to H_2 evolution starts to be observed at –2.15 V vs. Fc/Fc^+ (–1.77 V vs. SCE).*

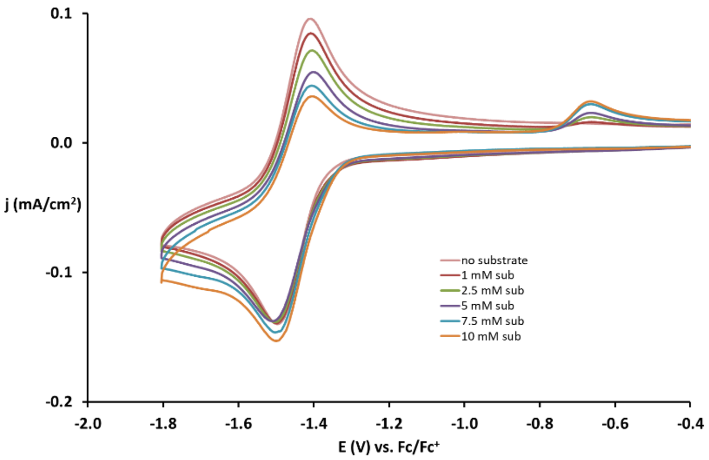


Figure SI.EP-30. *CVs of **1^HNi** (0.5 mM) in 0.1 M TBAH/CH_3CN:EtOH (2:3) electrolyte at 0.1 V s^{-1} in the absence of substrate (pink) and upon the addition of 2 (magenta), 5 (green), 10 (violet), 15 (cyan) and 20 (orange) eq. of substrate **2a**. The $Ni^{II/I}$ wave tends to lose reversibility by increasing the amount of added organic substrate, whereas a new anodic oxidation appears at –0.66 V vs. Fc/Fc^+ (–0.28 V vs. SCE) and progressively increases.*

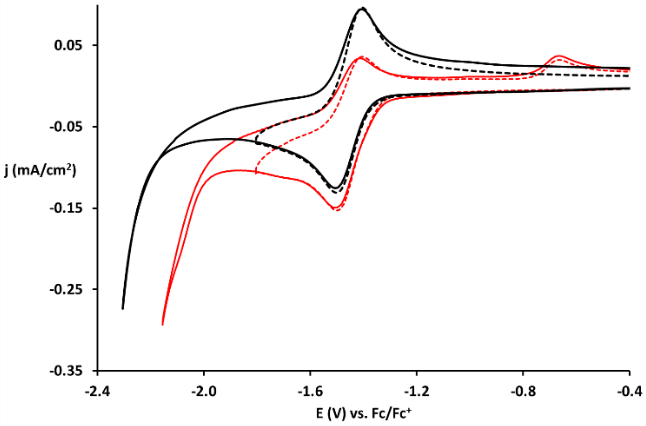


Figure SI.EP-31. *CVs of **1^HNi** (0.5 mM) in 0.1 M TBAH/CH_3CN:EtOH (2:3) electrolyte at 0.1 V s^{-1} in the absence (black) and presence (red) of 20 eq. of substrate **2a**. The increase in current starting at the Ni(I/II) redox potential in the presence of 20 eq. of **2a** when compared with the CV without **2a**, stand for a Ni(I)-**2a** reaction. In addition, the new reoxidation feature at -0.66 V vs Fc/Fc^+ is consistent with the DFT calculated redox potential for the **$[Ni^{II}(Ts^HPy_2tacn)(CH_2)_3Ph]^{2+}$** oxidation (-0.7 V vs Fc/Fc^+).*

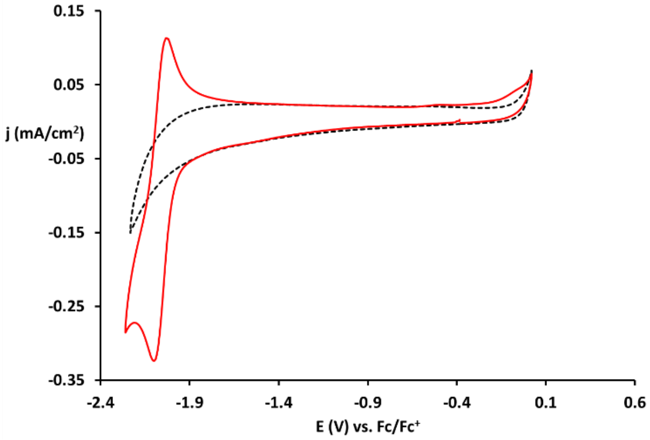


Figure SI.EP-32. *CVs of **PC_{Cu}** (1.0 mM) in 0.1 M TBAH/CH_3CN:EtOH (2:3) electrolyte with 114.5 mM DIPEA at 0.1 V s^{-1}. $E_{1/2}(Cu^{I/0})$ = –1.69 V vs. SCE, (-2.07 vs Fc/Fc^+) ΔE_p= 69 mV. Blank electrolyte is represented by dashed black curve.*

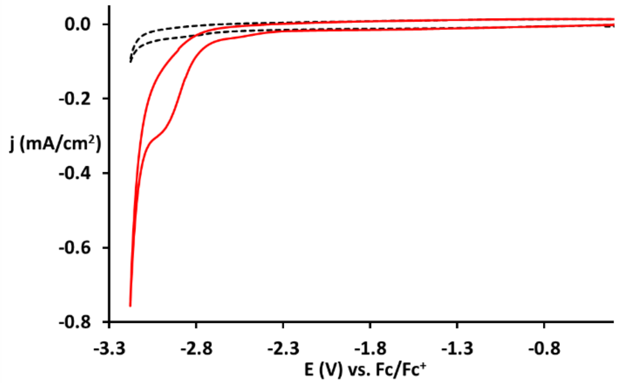


Figure SI.EP-33. *CVs of substrate **2a** (10 mM) in 0.1 M TBAH/CH_3CN at 0.1 V s^{-1}. Blank electrolyte is represented by dashed black curve.*

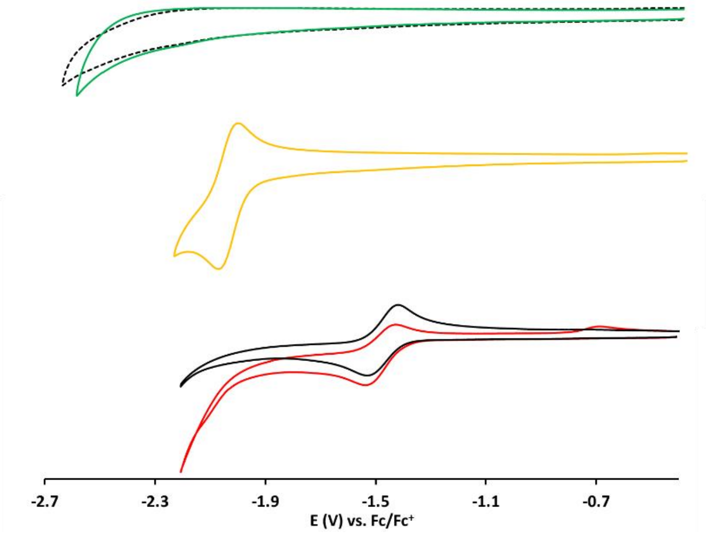


Figure SI.EP-34. *CVs of substrate **2a** (10 mM, green), **PC_{Cu}** (1.0 mM, yellow), **1^{H}Ni** (0.5 mM) and DIPEA (114.5 mM) in the absence (black) and presence (red) of 20 eq. of **2a** in in 0.1 M TBAH/CH_3CN:EtOH (2:3) electrolyte at 0.1 V. Blank electrolyte is represented by dashed black curve.*

13.2.2. UV-Vis Spectroelectrochemistry

The initial UV-Vis spectrum of **1^{H}Ni** shows intense absorptions at λ_{max} of 235 and 260 nm. In the absence of substrate, a broad band starts to grow in the visible region (λ_{max}= 535 nm) when the applied reduction potential matches the $Ni^{II/I}$ wave (*ca.* –1.5 V *vs.* Fc/Fc^{+}), indicating the bulk formation of a Ni^{I} species (*Figure SI.EP-35*, up). Other minor features also appear at λ_{max}= 299 and 361 nm. In agreement with CV data, the $Ni^{II/I}$ transition is reversible, since the initial spectrum of **1^{H}Ni** is recovered upon reoxidation by switching the potential after the $Ni^{II/I}$ wave (*Figure SI.EP-35*, bottom).

The evidence of Ni^{I} formation is also observed during reduction of **1^{H}Ni** in the presence of 20 equivalents of the substrate **2h**, as indicated by the growth of characteristic bands at λ_{max}= 535 and 361 nm (*Figure SI.EP-36*). However, the strong absorption at 278 nm of **2h** slowly decreases in the course of reduction, suggesting a slow reaction between the Ni^{I} species and **2h**. Interestingly, SEC of **1^{H}Ni** in the presence of the more reactive substrate **2a** shows that only a small amount of unreacted Ni^{I} is accumulated during reduction, whereas new intense bands at λ_{max}= 290 and 359 nm appear in the final spectrum (*Figure SI.EP-37*, up), likely corresponding to an adduct derived from reaction of the electrogenerated Ni^{I} species and **2a**. The spectral changes observed during the backward scan confirm the presence of a mixture of species in solution. Indeed, as suggested by CV data (*Figure SI.EP-30*), at the Ni^{I} reoxidation potential the band at λ_{max}= 535 nm rapidly decrease, while the features at λ_{max}= 290 and 359 nm only disappear at a more positive applied potential (*Figure SI.EP-37*, bottom).

The results of SEC experiments on **1^{H}Ni** in the 0.2 M TBAH/CH_3CN:EtOH (2:3) electrolyte are analogous to the ones obtained in pure CH_3CN, showing the reversible formation of a Ni^{I} species in the absence of substrates (*Figure SI.EP-38*). While maintaining the applied potential close to the $Ni^{II/I}$ wave (*ca.* –1.5 V *vs.* Fc/Fc^{+}) in the presence of 20 equivalents of substrate **2h**, after an initial accumulation of the Ni^{I} species the band at λ_{max}= 535 nm starts to decrease concomitantly to the absorption at 278 nm. This suggests that a slow reaction between Ni^{I} and **2h** occurs in solution (*Figure SI.EP-39*). Conversely, the enhanced reactivity of the electrogenerated Ni^{I} species with the substrate **2a** is indicated by the lack of free Ni^{I} in the final spectrum and the appearance of new bands at λ_{max}= 290 and 359 nm (*Figure SI.EP-40*). Analogous results are obtained repeating the experiment by using the solvent mixture employed under catalytic conditions (*Figure SI.EP-41*).

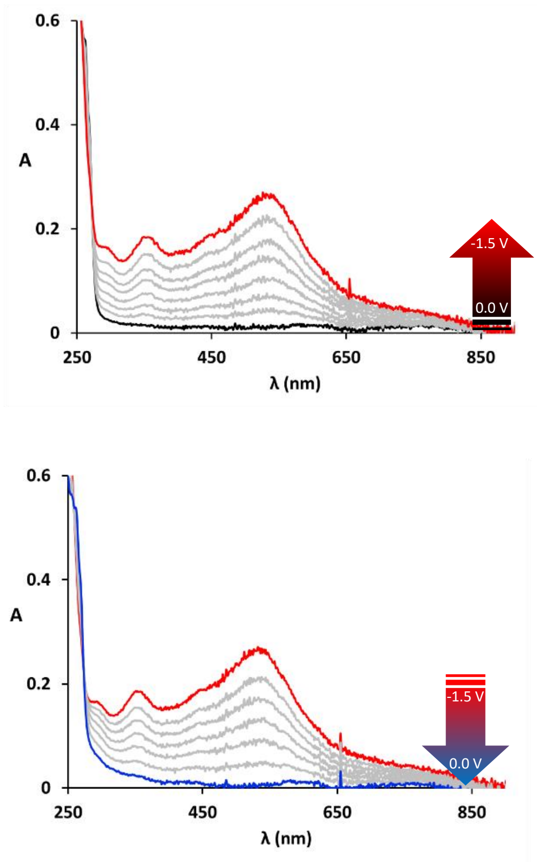


Figure SI.EP-35. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/CH_3CN electrolyte. The applied potential is slowly increased from the open circuit voltage (black) to the value corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+, red) and finally back to zero again (blue). The intermediate spectra are depicted in grey.*

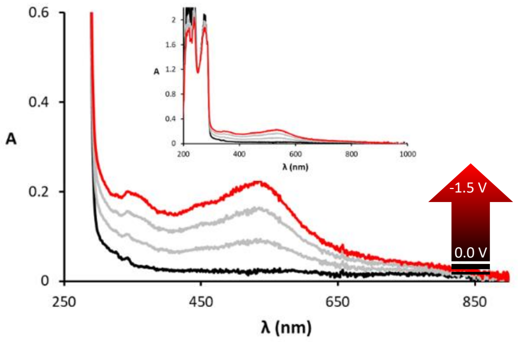
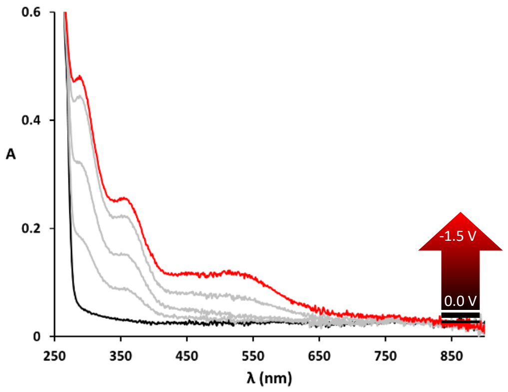


Figure SI.EP-36. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/CH_3CN electrolyte in the presence of 20 equivalents of substrate* ***2h*** *(80 mM). The applied potential is slowly increased from the open circuit voltage (black) to the value corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+, red). The intermediate spectra are depicted in grey.*



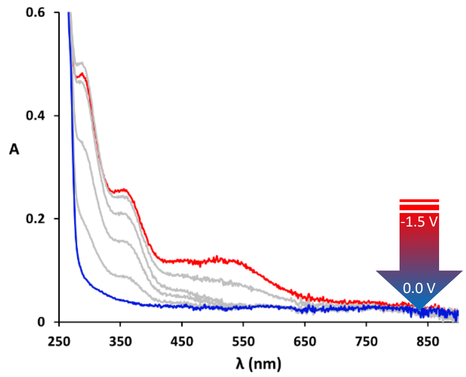


Figure SI.EP-37. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/CH_3CN electrolyte in the presence of 20 equivalents of substrate* ***2a*** *(80 mM). The applied potential is slowly increased from the open circuit voltage (black) to the value corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+, red) and finally back to zero again (blue). The intermediate spectra are depicted in grey.*

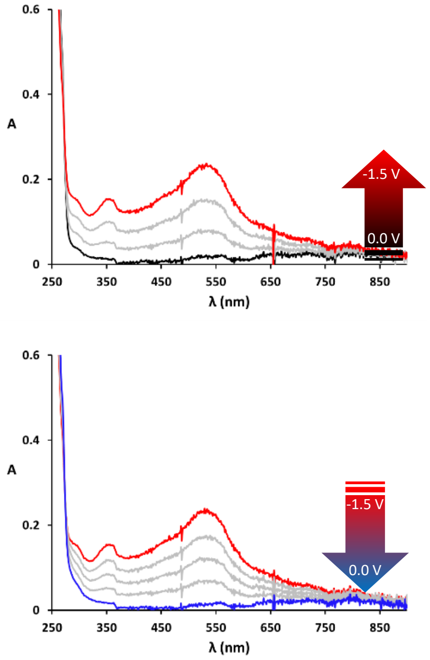


Figure SI.EP-38. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/CH_3CN:EtOH (2:3) electrolyte. The applied potential is slowly increased from the open circuit voltage (black) to the value corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+, red) and finally back to zero again (blue). The intermediate spectra are depicted in grey.*

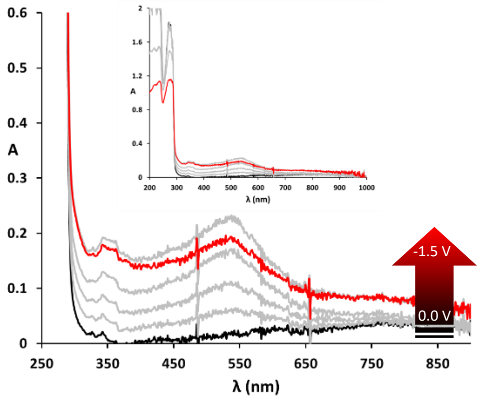


Figure SI.EP-39. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/CH_3CN:EtOH (2:3) electrolyte in the presence of 20 equivalents of substrate* ***2h*** *(80 mM). The applied potential is slowly increased from the open circuit voltage (black) to the value corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+, red). The intermediate spectra are depicted in grey.*

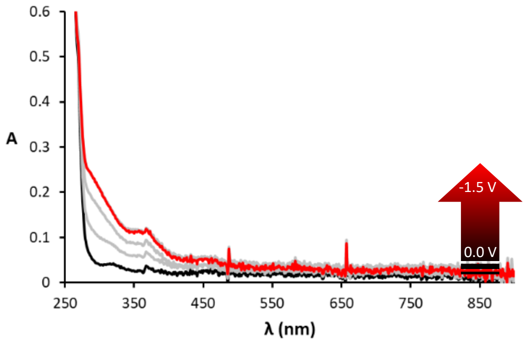


Figure SI.EP-40. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/ CH_3CN:EtOH (2:3) electrolyte in the presence of 20 equivalents of substrate* ***2a*** *(80 mM) monitoring the reduction at a potential corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+). The starting and final spectra are described by black and red curves, respectively, whereas the intermediate spectra are depicted in grey.*

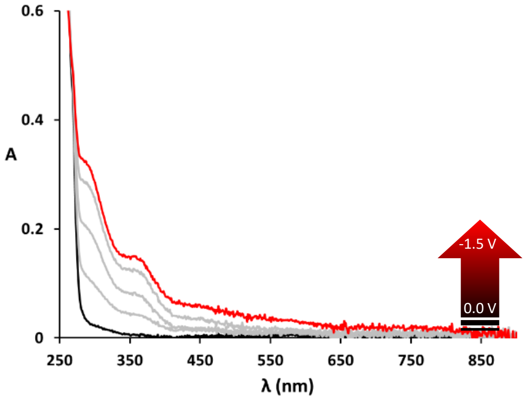


Figure SI.EP-41. *UV-Vis SEC of* ***1^HNi*** *(4 mM) in 0.2 M TBAH/ CH_3CN:EtOH (2:3) electrolyte with 114.5 mM DIPEA in the presence of 20 equivalents of substrate* ***2a*** *(80 mM) monitoring the reduction at a potential corresponding to the $Ni^{II/I}$ wave (ca. –1.5 V vs. Fc/Fc^+). The starting and final spectra are described by black and red curves, respectively, whereas the intermediate spectra are depicted in grey.*

13.2.3. UV-Vis Spectroscopy

UV-Vis monitoring with on-line continuous irradiation (LED λ_{max} 447 nm) shows the generation of an intense band with a λ_{max} at 536 nm that corresponds with the photogeneration of Ni^I species which drastically decreases with the addition of substrate **2a**. Analogous results are obtained in ethanol-acetonitrile mixture and in pure acetonitrile.

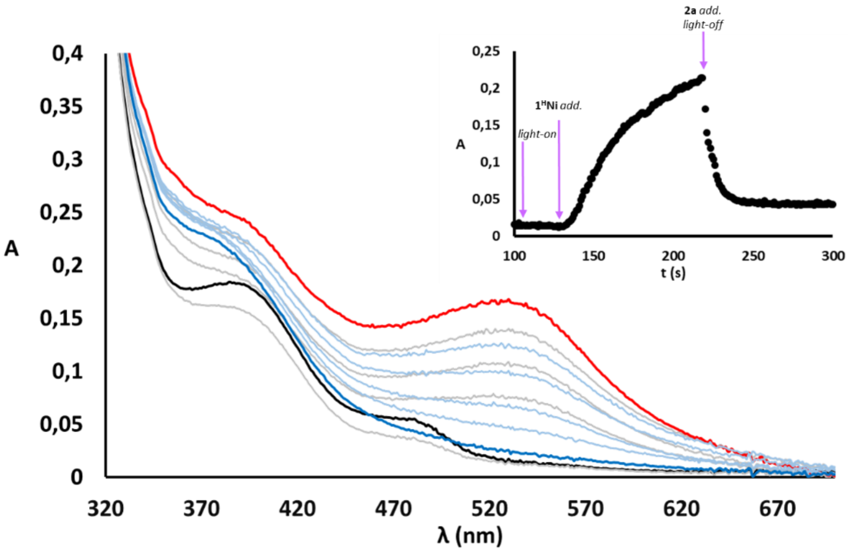


Figure SI.EP-42. *UV-Vis of* ***1^HNi*** *(50 µM) in a solution of* ***PC_{Cu}*** *(20 µM) in CH_3CN:EtOH (2:3) with 11.4 mM DIPEA. 20 equivalents of substrate* ***2a*** *(1 mM) were added after 218 s of monitoring. The starting and final spectra are described by black and red curves, respectively, whereas the intermediate spectra are depicted in grey. Blue lines corresponds to the spectra after the addition of the substrate, and the dark-blue line is the final spectra. Insert: Absorbance monitored at 536 nm.*

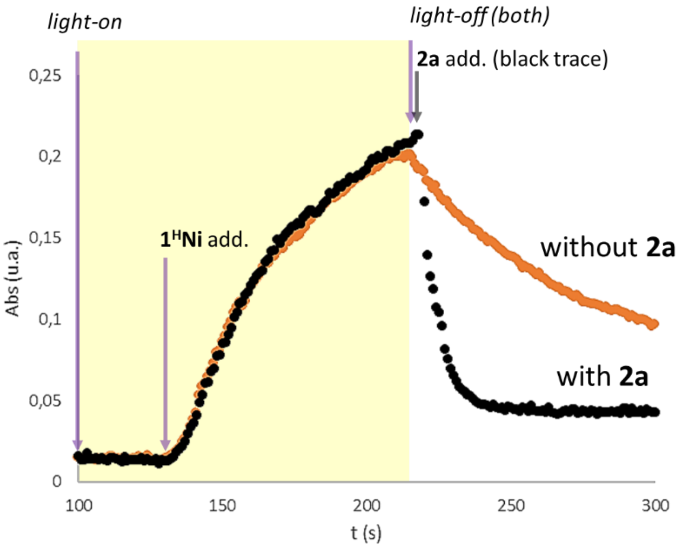


Figure SI-43. *Absorbance monitored at 536 nm of an irradiated (447 nm) solution containing* ***PC_{Cu}*** *(20 µM) in CH_3CN:EtOH (2:3) with DIPEA (11.4 mM) after the addition of* ***1^HNi*** *(50 µM) (40 s from irradiation started). After the addition of* ***1^HNi*** *the UV-Vis features corresponding to the* ***1^HNi^I*** *complex progressively increase. After 80 s from the* ***1^HNi*** *the light is switch off. At this point the addition of 20 eq. of* ***2a*** *(1 mM) triggers a rapid drop of the* ***1^HNi^I*** *band. In comparison, in the absence of substrate* ***2a*** *the decay in the dark of the* ***1^HNi^I*** *complex is significantly slower (orange trace).*

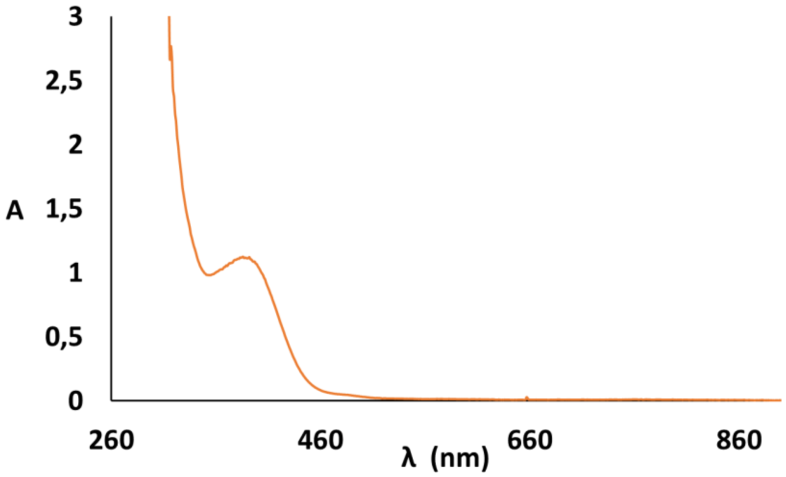


Figure SI.EP-44. *UV-Vis of* ***PC$_{Cu}$*** *(0.1 mM) with 28.6 mM DIPEA in CH$_3$CN.*

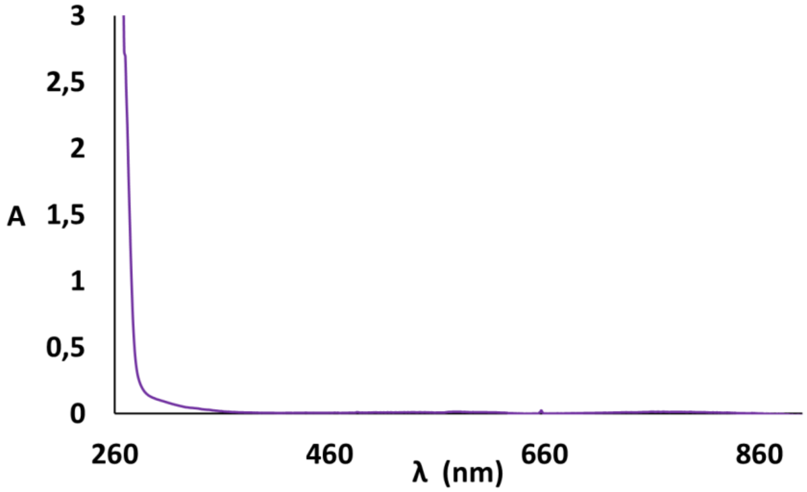


Figure SI.EP-45. *UV-Vis of* ***1^{H}Ni*** *(0.4 mM) in CH$_3$CN.*

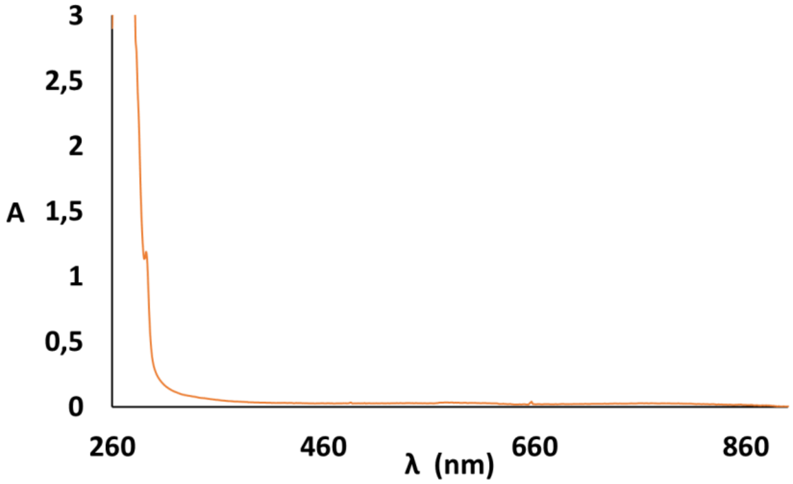


Figure SI.EP-46. 1^{H}Ni *(0.4 mM) with 28.6 mM DIPEA in CH$_3$CN.*

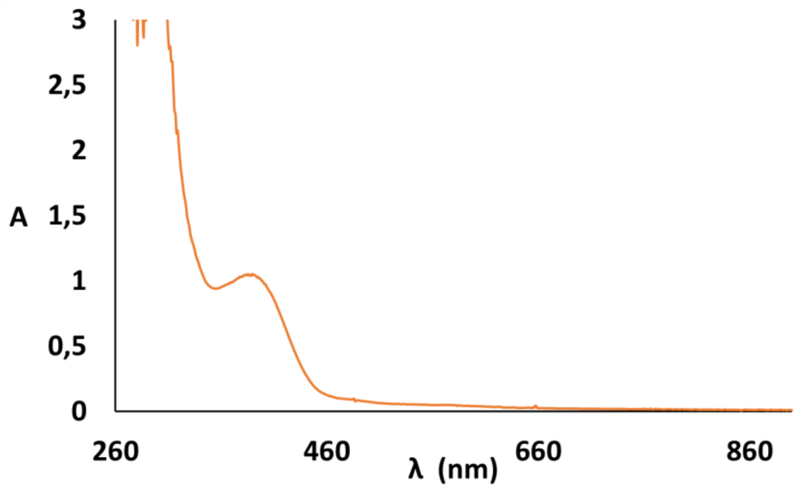


Figure SI.EP-47. *UV-Vis of* ***PC$_{Cu}$*** *(0.4 mM) with 28.6 mM DIPEA in CH$_3$CN:EtOH (2:3).*

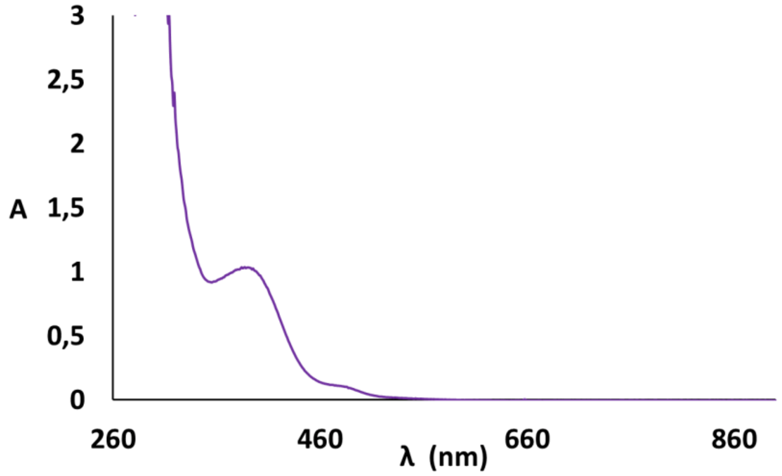


Figure SI.EP-48. *UV-Vis of* ***PC$_{Cu}$*** *(0.4 mM) and* ***1^{H}Ni*** *(1 mM) in CH$_3$CN:EtOH (2:3).*

Supporting Information

Theoretical Studies

Contents

1. Computational Details.

DFT calculations have been performed with the *Gaussian09* software package.[1] Geometry optimizations and frequency calculations of the ground state structure have been performed at the B3LYP/6-31+G* level of theory. Solvent effects (CH_3CN) and London interactions are considered through the SMD model[2] and Grimme-D_3 dispersion correction,[3] respectively.

Redox potentials (E°) have been evaluated through the Nernst equation in standard state conditions using the Standard Hydrogen Electrode (SHE) as reference following the equation.

$$\mathrm{E^o(V)} = -\left(\frac{\Delta \mathrm{G}^\circ}{\mathrm{nF}} - \frac{\Delta \mathrm{G}^\circ{}_{\mathrm{SHE}}}{\mathrm{F}}\right)$$

where *n* is the number of electrons involved in the reduction step, *F* is the Faraday constant, $\Delta G^\circ_{SHE} = -4.24$ eV.

Bond dissociation energy/enthalpy (BDE) is defined as the enthalpy change of the dissociation reaction of homolytic bonds at 298.15 K, 1 atm.

$$\mathrm{R{-}X} \rightarrow \mathrm{R^\bullet} + \mathrm{X^\bullet}$$

$$\mathrm{BDE(R{-}X)} = \mathrm{H(R^\bullet)} + \mathrm{H(X^\bullet)} - \mathrm{H(R{-}X)}$$

where $H(R^\bullet)$ and $H(X^\bullet)$ and H(R—X) are enthalpies of the radicals and the molecule. The experimental data was obtained from bibliography.[4]

For the molecules involving the modeling of the reaction mechanism, the energy of the geometry optimized molecules at B3LYP-D_3/6-31G* was refined by single point calculation at 6-311+G** level of theory.

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[1] Gaussian 09, Revision E.01, Frisch et. al. Gaussian, Inc., Wallingford CT, **2009**.

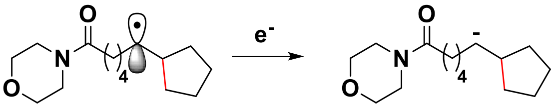
[2] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. J. Phys. Chem. B, **2009**, *113*, 6378.

[3] Grimme, S.; Ehrlich S.; Goerigk, L. *J. Comp. Chem*. **2011**, *32*, 1456.

[4] Y.-R. Luo, Y.-R. Luo, Comprehensive handbook of chemical bond energies, CRC Press, Boca Raton, **2007**.

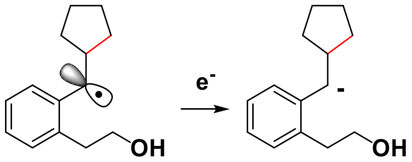
1.1. Redox potentials.

We have found that the level of theory B3LYP/6-31+G*, including solvent (SMD, CH_3CN) and dispersion effects reproduce correctly reported experimental values of reduction potentials for *para* substituted benzyl radicals to benzyl anions (Table SI.TS-1 and Figure SI.TS-2.). Based on this finding, we have estimated the redox potential of the reduction of the radicals **2j** and **2n.**



2j

Theoretical $E_{(1/2)}$ = -2.0 V vs SCE



2n

Theoretical $E_{(1/2)}$ = -1.6 V vs SCE

Figure SI.TS-1. Calculate redox potentials for benzyl radicals **2j** and **2n**.

Table SI.TS-1. Calculate and experimental redox potentials of substituted benzyl radicals.

$$R^{\bullet} + e^{-} \rightarrow R^{-}$$

Entry	$R^{\bullet}$	$E_{1/2}^{(0/-I)}$ exp.^{a}	$E_{1/2}^{(0/-I)}$ theo.^{b}
1	[*p*-MeO-$PhCH_2^{\bullet}$]	-1.75	-1.75
2	[*p*-Me-$PhCH_2^{\bullet}$]	-1.62	-1.59
3	[*p*-F-$PhCH_2^{\bullet}$]	-1.50	-1.50
4	[$PhCH_2^{\bullet}$]	-1.43	-1.50
5	[*p*-Cl-$PhCH_2^{\bullet}$]	-1.40	-1.42
6	[*o*-NC-$PhCH_2^{\bullet}$]	-1.11	-1.28
7	[*p*-NC-$PhCH_2^{\bullet}$]	-0.77	-0.97
8	[*p*-C(O)CH_3-$PhCH_2^{\bullet}$]	-0.71	-1.03
9	[2j-Cl]$^{\cdot}$		-1.6
10	[2n-Cl]$^{\cdot}$		-2.0

All redox potentials are given in V vs SCE. a) Redox potentials obtained from reference: *J. Am. Chem. Soc.* **1989**, *111*, 755-757. b) Theoretical redox potentials calculated at B3LYP/6-31+g* level including solvent effects (SMD) and Grimme-D_3 dispersion correction.

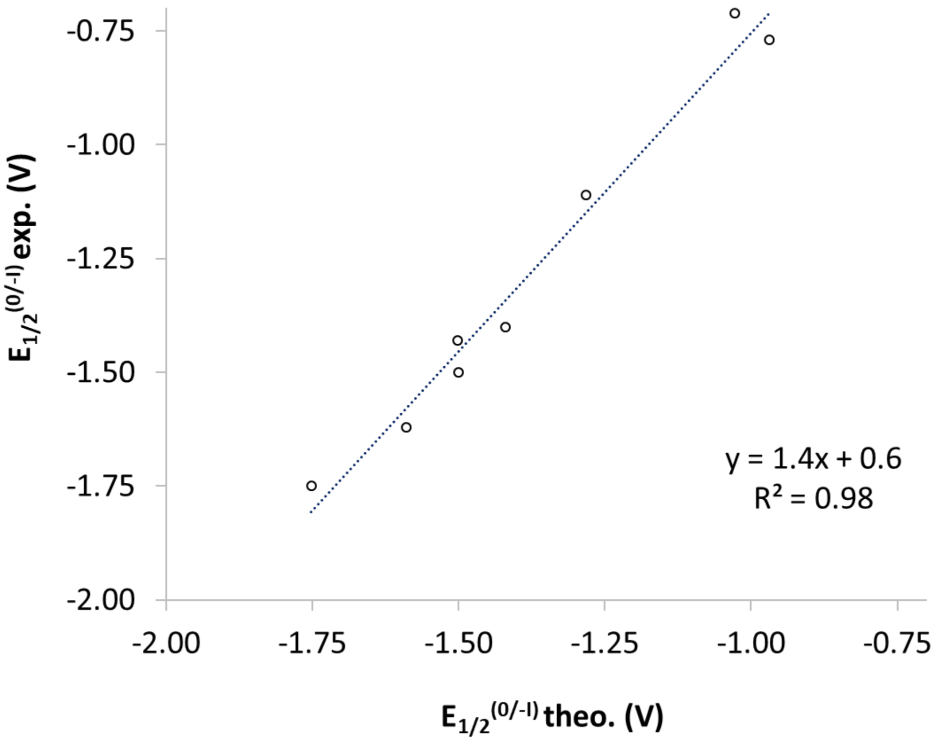


Figure SI.TS-2. Correlation between experimental and calculate redox potentials of benzyl radicals in Table SI.TS-1.

1.2. Bond Dissociation Energies BDE.

The level of theory B3LYP/6-31+G*, including solvent (SMD, CH_3CN) and dispersion effects reproduce correctly reported experimental values of DBE for *para* substituted toluenes, CH_4 and ethanol (Table SI.TS-1 and Figure SI.TS-.2.). Therefore, the methodology is reliable to estimate the BDE of **4j** and **4n.**

Table SI.TS-2. Calculate and experimental bond dissociation energies (BDE).

$$R{-}H \rightarrow R^{\bullet} + H^{\bullet}$$

Entry	R-H	BDE reported.[a]	BDE theo.[b]
1	[*p*-MeO-PhCH_3]	86.6	84.3
2	[*p*-Me-PhCH_3]	87.7	87.5
3	[*p*-F-PhCH_3]	87.6	88.1
4	[PhCH_3]	88.5	88.0
5	[*p*-Cl-PhCH_3]	87.5	88.0
6	[*o*-NC-PhCH_3]	88.7	88.9
7	[*p*-NC-PhCH_3]	88.0	87.5
8	CH_4	105.0	104.7
9	CH_3CH_2OH	95.9	93.4
10	CH_3CH_2OD	-	93.4
11	CH_3CH_2OH	100.8	101.4
12	CH_3CH_2OH	105.4	-
13	CH_3CN	97	-
14	**[4j]**	-	96.5
15	**[4n]**	-	83.6

All redox potentials are given in V vs SCE. a) BDE obtained from reference: .-R. Luo, Y.-R. Luo, *Comprehensive handbook of chemical bond energies*, CRC Press, Boca Raton, **2007**. b) Theoretical redox potentials calculated at B3LYP/6-31+g* level including solvent effects (SMD) and Grimme-D_3 dispersion correction.

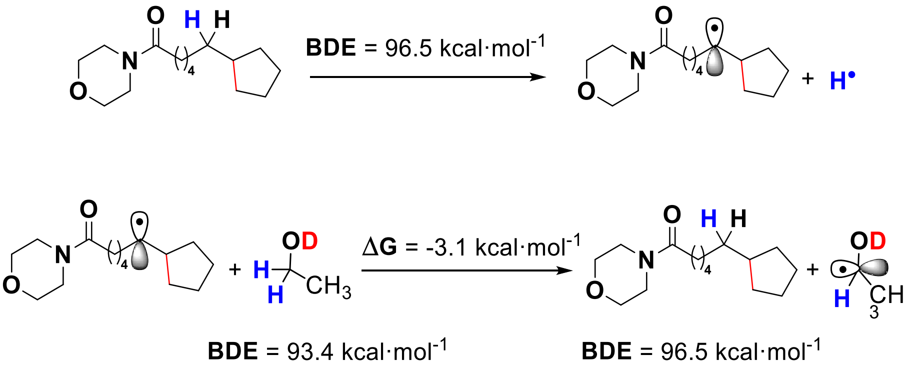


Figure SI.TS-3. Calculate BDE for **4j** and the energy balance of HAT reaction with CH_3CH_2OD. Energies do not include correction by concentration, which should favor the products. The energy value for the HAT reaction from CH_3CH_2OD to **2j** benzyl radical (-3.1 kcal·mol^{-1}) is clearly thermodynamically favor.

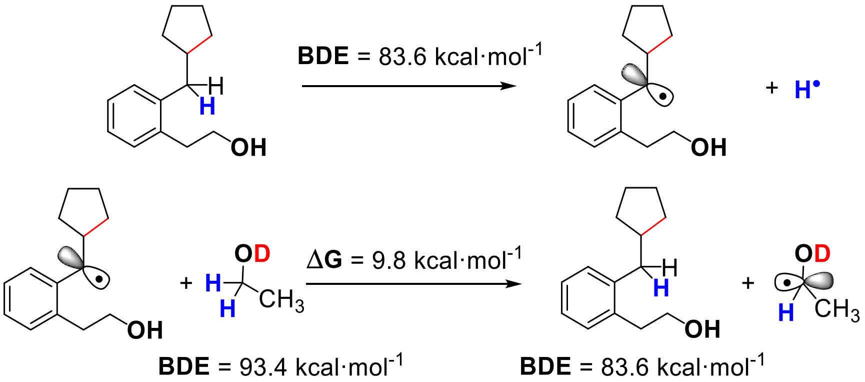


Figure SI.TS-4. Calculate BDE for **4n** and the energy balance of HAT reaction with CH_3CH_2OD. Energies do not include correction by concentration, which should favor the products. The energy value for the HAT reaction from CH_3CH_2OD to **2n** benzyl radical (9.8 kcal·mol^{-1}) is thermodynamically unfavorable.

1.3. Computational study of the reactivity of [Ni^{I}(Ts^{H}Py$_2$tacn)]$^+$ with (3-chloropropyl)benzene.

In order to determine the feasibility of the Ni(I) species based on the TsPy$_2$^{H}tacn ligand to activate C$_{sp3}$-Cl bonds, we have computed the reaction of the low valent intermediate Ni(I) (d^9, S = 1/2) species, formed by single electron reduction starting from the **1^{H}Ni** complex, with a model substrate ((3-chloropropyl)benzene). First we examined the thermodynamics of both the Cl$^-$ and CH$_3$CN coordination to the pentacoordinate **[Ni^{I}(Ts^{H}Py$_2$tacn)]$^+$** species (**I1**), which is endergonic in both cases (Figure SI.TS-4). Experimental studies based on cyclic voltammetry are in agreement with the endergonic coordination of Cl$^-$ to the Ni(I) metal center (See Figure SI.TS-5).

$$[\mathrm{Ni^{I}(Ts^{H}Py_2tacn)NCCH_3}] \longrightarrow [\mathrm{Ni^{I}(Ts^{H}Py_2tacn)}]^+ + \mathrm{NCCH_3} \qquad \Delta G = -9.7\ \mathrm{kcal{\cdot}mol^{-1}}$$

$$[\mathrm{Ni^{I}(Ts^{H}Py_2tacn)Cl}] \longrightarrow \underset{\text{ion pair}}{[\mathrm{Ni^{I}(Ts^{H}Py_2tacn)}]^+ \cdots \mathrm{Cl^-}} \qquad \Delta G = -9.0\ \mathrm{kcal{\cdot}mol^{-1}}$$

<**Figure SI.TS-5.** Thermodynamics of the coordination of CH$_3$CN and Cl$^-$ to **[Ni^{I}(Ts^{H}Py$_2$tacn)]$^+$**. Energies are given in kcal·mol^{-1}.

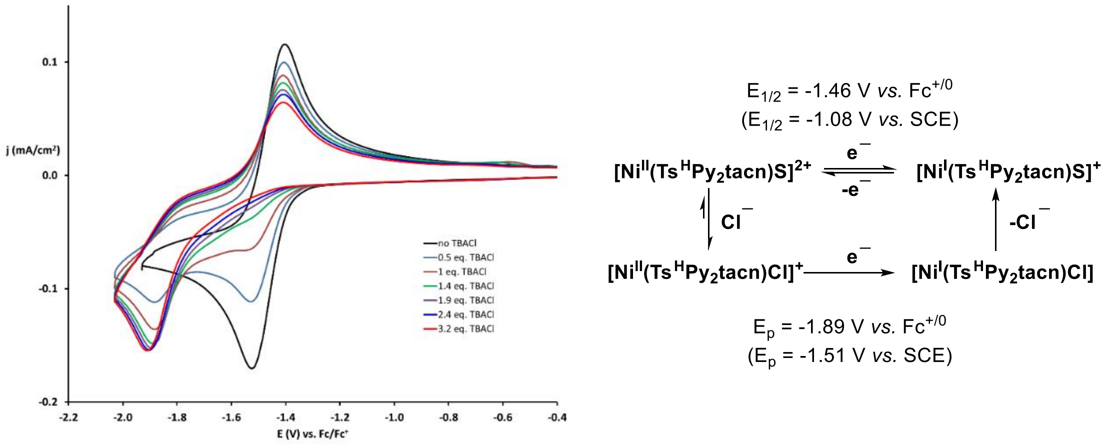


Figure SI.TS-6. CVs of **1^{H}Ni** (0.5 mM) in 0.1 M TBAH/CH$_3$CN electrolyte at 0.1 V s^{-1} in the absence (black) and presence of 0.25 mM (0.5 eq, cyan), 0.49 mM (1 eq, brown), 0.73 mM (1.4 eq, green), 1.0 mM (1.9 eq, violet), 1.2 mM (2.4 eq, blue) and 1.6 mM (3.2 eq, red) of TBACl.

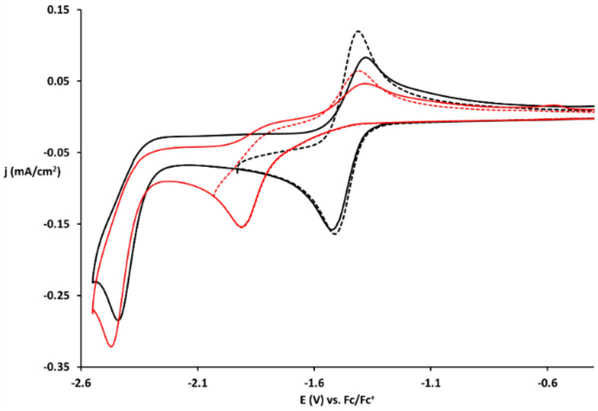


Figure SI.TS-7. CVs of **1^HNi** (0.5 mM) in 0.1 M TBAH/CH_3CN electrolyte at 0.1 V s^{-1} in the absence (black) and presence (red) of 1.6 mM (3.2 eq) of TBACl. Doted CV are done under the same conditions using a potential window from the open circuit potential to the first reduction wave.

Upon the addition of increasing aliquots of TBACl to a solution of **1^HNi**, the $Ni^{II/I}$ reduction peak progressively disappears, giving rise to a new peak at E_p = –1.89 V *vs.* $Fc^{+/0}$ (–1.51 V *vs.* SCE) which describes the **$[Ni^{II}(Ts^{H}Py_2tacn)Cl]^+$/$[Ni^{I}(Ts^{H}Py_2tacn)Cl]$** event. The irreversibility of the latter suggests a fast $Cl^–$ dissociation after reduction, which is also consistent with the anodic peak at –1.41 V *vs.* $Fc^{+/0}$ upon the backward scan representing the **$[Ni^{I}(Ts^{H}Py_2tacn)(S)]^+$** reoxidation. In line with this interpretation, the $Ni^{I/0}$ process occurring at a more cathodic potential, remains almost unchanged after the addition of TBACl.

Therefore, we started to model the reaction from the pentacoordinate **$[Ni^{I}(Ts^{H}Py_2tacn)]^+$** species (**I1**). Along the reaction pathway of **I1** with (3-chloropropyl)benzene we found two different mechanisms. The lowest in energy ($\Delta G^‡$ = 12.9 kcal·mol^{-1}) can be described as an oxidative S_N2-type attack of the Ni(I) center to the aliphatic carbon center bearing the chlorine atom to give an organometallic Ni(III) S = 3/2 species (**$I3_{Ni(III)\text{-}C \cdots Cl^-}$**) and chloride anion (Figure SI.TS-7, green energy profile). At the transition state the Ni – C(1) – Cl angle is 151° and the carbon center has a close sp^2-hybridation. The second mechanism ($\Delta G^‡$ = 19.3 kcal·mol^{-1}) can be described as a concerted halogen atom abstraction (Figure SI.TS-7, red energy profile) leading to the formation of **$[Ni^{II}(Ts^{H}Py_2tacn)Cl]$** (**$1^H$Ni-Cl**) complex and the free radical. Both mechanisms can be accessible at room temperature, nevertheless for this substrate the formed is favored by 6.4 kcal·mol^{-1}. The next step is the reaction of **$I3_{Ni(III)\text{-}C \cdots Cl^-}$**. A direct C-Ni homolytic cleavage of **$[Ni^{III}(Ts^{H}Py_2tacn)(CH_2)_3Ph]^{2+}$** is slightly endergonic (1.7 kcal·mol^{-1}), and just considering acetonitrile coordination is virtually isoenergetic (-0.5 kcal·mol^{-1}). Further reduction of the formed organic radical (**$Ph(CH_2)_3^•$**) and **$[Ni^{II}(Ts^{H}Py_2tacn)(CH_2)_3Ph]^+$** act as an expected large driving force, regenerating the Ni(I) catalytically active species.

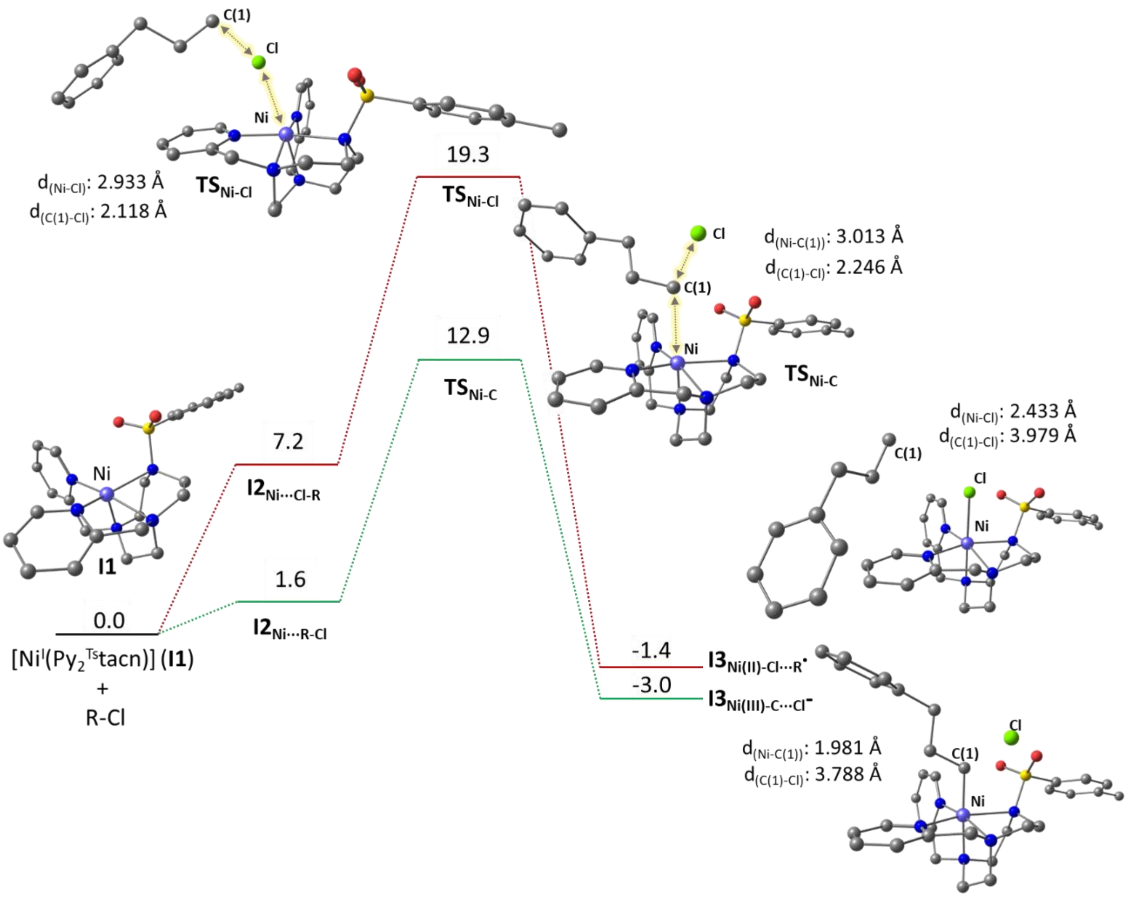
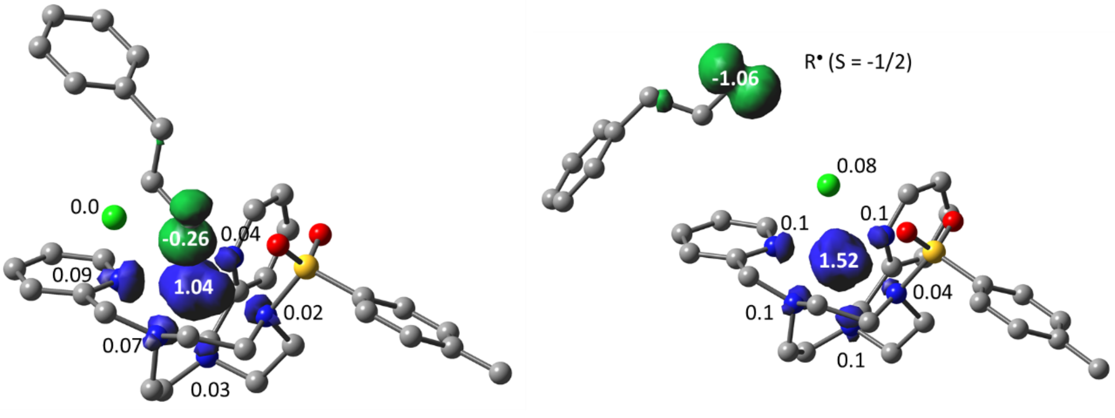


Figure SI.TS-8. Comparison between DFT(uB3LYP/6-31g*//uB3LYP/6-311+g**) calculated free energy barriers for the reaction of **$[Ni^{I}(Ts^{H}Py_{2}tacn)]$** (**I1**) with the model substrates (3-chloropropyl)benzene as an oxidative S_N2-type reaction (green profile) or concerted halogen atom abstraction (red). Energies are given in kcal·mol^{-1}.



Ni(II) (S = 1)

Ni(III) (S = 3/2)

Figure SI.TS-8. B3LYP-D$_3$/6-311+G** spin densities of intermediates **$I3_{Ni(III)-C\cdots Cl^{-}}$** (left) and **$I3_{Ni(II)-Cl\cdots R^{\bullet}}$** (right).Hydrogen atoms have been omitted for clarity. Isosurfaces calculated at values of 0.01. Alfa and beta spin density is represented by the green and blue colors. Relevant spin densities are represented in the figure.

On the other hand, one can expect that the reduction of the formed organometallic **[Ni^{III}(Ts^{H}Py$_2$tacn)(CH$_2$)$_3$Ph]$^+$** species is quickly reduced to **[Ni^{II}(Ts^{H}Py$_2$tacn)(CH$_2$)$_3$Ph]$^+$** (E$_{theo}$ = - 0.12 V vs NHE, -0.36 vs SCE) in the reaction medium, which also leads to a significant thermodynamic stabilization (considering the experimental redox potential of the **PC$_{Cu}$** of -1.45 V vs NHE (-1.69 V vs SCE) the driving force is -30.7 kcal·mol^{-1}. Now, the C-Ni homolytic cleavage in **[Ni^{II}(Ts^{H}Py$_2$tacn)(CH$_2$)$_3$Ph]$^+$** is endergonic, but still thermodynamically accessible at room temperature (22.1 kcal·mol^{-1}), which leads to the formation of Ni(I) species, regenerating the Ni(I) catalytically active species.

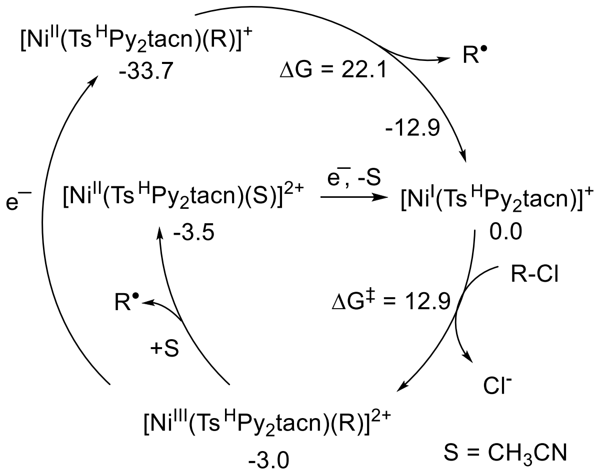


Figure SI.TS-9. Summary of the DFT data. Values represent thermodynamic energies respect [Ni^{I}(Ts^{H}Py$_2$tacn)]$^+$ and are given in kcal·mol^{-1}.

T.1.4. Cartesian Coordinates of optimized geometries for molecules related to redox potentials and BDE calculations

FORMAT

Name
E; Ezp; H; G in hartrees
Charge, multiplicity
Element x y z

[CH$_2$CH$_2$OH]$^-$
E = -154.4866539; Ezp = -154.423297; H = -154.417776; G = -154.448994
-1,1

C	+0.06603	+0.48780	-0.13406
H	+0.34156	+0.90874	-1.11665
H	+0.05710	+1.31724	+0.59433
C	-1.20904	-0.27358	-0.16436
H	-1.95240	+0.06701	+0.56856
H	-1.66490	-0.34572	-1.16071
O	+1.24637	-0.36244	+0.26526
H	+2.03236	+0.21878	+0.25709

[CH$_2$CH$_2$OH]$^•$
E = -154.3830054; Ezp = -154.318596; H = -154.312998; G = -154.34488
0,2

C	+0.08544	+0.58097	-0.02477
H	+0.26292	+1.29909	-0.84954
H	+0.09803	+1.16879	+0.90779
C	-1.22326	-0.09248	-0.19603
H	-2.13720	+0.42727	+0.07663
H	-1.28849	-1.01796	-0.76218
O	+1.13240	-0.40637	-0.01588
H	+1.98724	+0.05852	-0.02653

CH$_3$CH$_2$OH
E = -155.0567653; Ezp = -154.977155; H = -154.97193; G = -155.002532
0,1

C	+1.402e-	-0.00760	+0.00118
H	+0.88994	-0.53240	-0.37703
H	-0.88994	-0.53241	-0.37703
C	-2.14e-0	+0.00658	+1.51817
H	-0.89054	+0.51907	+1.90294
H	+2.68e-0	-1.02025	+1.90446
H	+0.89054	+0.51907	+1.90294
O	-4.5e-08	+1.35682	-0.45887
H	+4.221e-	+1.35389	-1.43183

[CH$_3$CH$_2$O]$^-$
E = -154.539947; Ezp = -154.474624; H = -154.469905; G = -154.499544
-1,1

C	+0.14821	+0.49616	+2.14821
H	+0.12438	+1.19579	-0.88521
H	+0.12549	+1.19369	+0.88695
C	-1.22396	-0.21935	-1.85942
H	-2.06471	+0.49522	+0.00183
H	-1.32087	-0.86057	-0.88887
O	+1.22547	-0.34106	-0.00167
H	-1.31932	-0.86338	+0.88697

[CH$_3$CH$_2$O]$^•$
E = -154.3901362; Ezp = -154.325843; H = -154.320459; G = -154.352127
0,2

C	+0.09247	+0.49866	-1.41809
H	+0.18211	+1.19197	-0.86539
H	+0.18298	+1.19028	+0.86665
C	-1.24111	-0.23737	-2.37362
H	-2.07003	+0.48179	+0.00229
H	-1.33385	-0.86877	-0.89196
O	+1.21398	-0.28777	-0.00118
H	-1.33186	-0.87227	+0.88962

[CH$_3$CHOH]$^•$
E = -154.3967257; Ezp = -154.33103; H = -154.32572; G = -154.356996
0,2

C	-0.09585	+0.07500	+0.04901
H	-0.76323	-0.58856	-0.50189
C	-0.01859	+0.02076	+1.53255
H	-0.85652	+0.55815	+2.01478
H	-0.05140	-1.01939	+1.87612
H	+0.90992	+0.47710	+1.90268
O	+0.07521	+1.33899	-0.48192
H	-0.09397	+1.31710	-1.44066

CH$_4$
E = -40.5201554; Ezp = -40.47549; H = -40.471678; G = -40.494129
0,1

C	+2.45578	-1.0001e	-0.00052
H	+2.82189	+0.89402	+0.51651
H	+2.82189	-0.89488	+0.51504
H	+2.82142	+0.00085	-1.03346
H	+1.36017	-9.881e-	-0.00018

[CH$_3$]$^•$
E = -39.8411813; Ezp = -39.811433; H = -39.807434; G = -39.830196
0,2

C	+2.70470	-1.0003e	-0.00059
H	+2.70494	+0.93975	+0.54300
H	+2.70494	-0.94065	+0.54145
H	+2.70444	+0.00089	-1.08625

[*p*-Cl-PhCH2]$^-$

E = -730.6526127; Ezp = -730.550003; H = -730.54158; G = -730.582028

-1,1

C	+1.04104	-1.21481	+2.76605
C	-0.34834	-1.21263	-0.00017
C	-1.05442	-7.5971e	-0.00026
C	-0.34834	+1.21262	-0.00017
C	+1.04103	+1.21481	+2.75148
C	+1.82993	+4.39e-0	+0.00010
H	+1.55940	+2.17327	+0.00014
C	+3.23005	+4.6531e	+0.00023
H	+3.79348	-0.93168	+0.00022
H	+1.55942	-2.17327	+0.00015
H	-0.88812	-2.15763	-0.00022
H	-0.88813	+2.15762	-0.00021
H	+3.79347	+0.93169	+0.00022
Cl	-2.84000	-1.36731	-0.00059

[*p*-Cl-PhCH$_2$]$^\bullet$

E = -730.542558; Ezp = -730.437447; H = -730.429638; G = -730.469437

0,2

C	+1.04644	-1.22063	-1.21883
C	-0.34114	-1.22316	-0.00015
C	-1.02758	-7.6711e	-0.00018
C	-0.34115	+1.22315	-0.00015
C	+1.04643	+1.22062	-1.49501
C	+1.79111	+4.417e-	+9.14724
H	+1.58233	+2.16654	+8.6959e
C	+3.19897	+4.6544e	+0.00025
H	+3.75753	-0.93188	+0.00032
H	+1.58235	-2.16654	+1.10876
H	-0.89039	-2.15996	-0.00025
H	-0.89040	+2.15995	-0.00025
H	+3.75753	+0.93190	+0.00032
Cl	-2.79155	-1.34341	-0.00048

[*p*-Cl-PhCH$_3$]

E = -731.1938875; Ezp = -731.075489; H = -731.067221; G = -731.107897

0,1

C	+1.09055	-1.20551	-0.02263
C	-0.30878	-1.21759	-0.02063
C	-0.99089	-0.00234	-0.00275
C	-0.30671	+1.21443	+0.01222
C	+1.09013	+1.20153	+0.00998
C	+1.81253	-0.00322	-0.00608
H	+1.62536	+2.14865	+0.02018
C	+3.32228	+0.00529	+0.01448
H	+3.73087	-0.98546	-0.21124
H	+1.62415	-2.15311	-0.03834
H	-0.85211	-2.15768	-0.03486
H	-0.85042	+2.15437	+0.02344
H	+3.72690	+0.71825	-0.71413
Cl	-2.76262	-0.00035	-0.00234
H	+3.69841	+0.30524	+1.00196

[*p*-F-PhCH2]$^-$

E = -370.2911651; Ezp = -370.188054; H = -370.179649; G = -370.220049

-1,1

C	+0.69995	-1.21518	-0.05593
C	-0.69244	-1.21366	-0.00681
C	-1.37622	+3.80316	+0.01776
C	-0.69237	+1.21369	-0.00686
C	+0.70002	+1.21513	-0.05598
C	+1.48555	-4.66005	-0.08231
H	+1.21988	+2.17238	-0.07449
C	+2.89094	-8.79103	-0.12623
H	+3.45260	-0.93202	-0.16707
H	+1.21975	-2.17245	-0.07440
H	-1.24794	-2.14934	+0.01202
H	-1.24781	+2.14941	+0.01193
H	+3.45265	+0.93181	-0.16711
F	-2.77335	+7.94577	+0.06663

[*p*-F-PhCH$_2$]$^\bullet$

E = -370.1855713; Ezp = -370.079359; H = -370.071888; G = -370.110419

0,2

C	+0.35557	+1.28765	+0.14360
C	-0.37418	+2.45802	+0.30754
C	-1.74282	+2.42911	+0.04161
C	-2.40969	+1.27924	-0.38043
C	-1.67510	+0.11173	-0.54250
C	-0.26805	+0.07446	-0.28715
H	-2.17567	-0.79561	-0.87090
C	+0.47496	-1.11191	-0.45255
H	+1.54333	-1.13329	-0.25614
H	+1.42369	+1.28905	+0.34546
H	+0.09505	+3.38145	+0.63399
H	-3.47790	+1.31240	-0.57350
H	-0.00420	-2.03045	-0.77961
F	-2.46463	+3.58174	+0.20264

[*p*-F-PhCH$_3$]

E = -370.8371651; Ezp = -370.717621; H = -370.709703; G = -370.749113

0,1

C	+0.64511	-1.20155	+0.03498
C	-0.75269	-1.21657	+0.03910
C	-1.41974	+0.00128	-0.00010
C	-0.75760	+1.21909	-0.04415
C	+0.64274	+1.20780	-0.04746
C	+1.36481	+0.00515	-0.00693
H	+1.17733	+2.15415	-0.08329
C	+2.87565	-0.00115	+0.01281
H	+3.28155	-0.72787	-0.70141
H	+1.18346	-2.14637	+0.06412
H	-1.31338	-2.14616	+0.06977
H	-1.32004	+2.14753	-0.07705
H	+3.28231	+0.98524	-0.23497
F	-2.79358	-0.00219	+0.00156
H	+3.25498	-0.27856	+1.00564

H$^{\bullet}$

E = -0.4997539; Ezp = -0.499754; H = -0.497393; G = -0.510408

0,2

H	-2.22182	-0.79089	-0.85454

[PhCH2]$^{-}$

E = -271.0499452; Ezp = -270.938002; H = -270.930803; G = -270.967622

-1,1

C	+0.24383	-1.21495	+0.11196
C	-1.13970	-1.20402	-0.01991
C	-1.87224	-6.54407	-0.08953
C	-1.13974	+1.20391	-0.01988
C	+0.24379	+1.21488	+0.11200
C	+1.02901	-2.60884	+0.18676
H	+0.76600	+2.17108	+0.16173
C	+2.42498	-8.0521e	+0.32009
H	+2.98689	-0.93163	+0.37144
H	+0.76606	-2.17114	+0.16167
H	-1.66818	-2.15687	-0.07026
H	-2.95454	-8.0872e	-0.19239
H	-1.66825	+2.15675	-0.07020
H	+2.98687	+0.93163	+0.37146

[PhCH$_2$]$^{\bullet}$

E = -270.9429635; Ezp = -270.828324; H = -270.821691; G = -270.858024

0,2

C	+0.35577	+1.28724	+0.14323
C	-0.38236	+2.45319	+0.30509
C	-1.76461	+2.46419	+0.04797
C	-2.40115	+1.28441	-0.37699
C	-1.67424	+0.11222	-0.54300
C	-0.26748	+0.07369	-0.28639
H	-2.17156	-0.79782	-0.87166
C	+0.47479	-1.11247	-0.45247
H	+1.54385	-1.13526	-0.25798
H	+1.42496	+1.28459	+0.34411
H	+0.11379	+3.36346	+0.63381
H	-2.33768	+3.37883	+0.17626
H	-3.47010	+1.28904	-0.57715
H	-0.00327	-2.03192	-0.77954

[*p*-MeO-PhCH2]$^{-}$

E = -385.5741893; Ezp = -385.429796; H = -385.420037; G = -385.46319

-1,1

C	+0.35884	+1.27314	+0.13537
C	-0.38508	+2.43535	+0.32348
C	-1.76835	+2.45786	+0.08638
C	-2.39108	+1.27332	-0.33693
C	-1.65924	+0.10411	-0.52908
C	-0.23167	+0.03110	-0.31119
H	-2.17953	-0.79273	-0.86633
C	+0.51750	-1.14176	-0.52314
H	+1.58454	-1.17424	-0.30725
H	+1.43256	+1.29965	+0.32297
H	+0.10888	+3.34869	+0.65411
H	-3.46488	+1.27847	-0.52249
H	+0.03419	-2.07229	-0.81773
O	-2.50111	+3.64244	+0.22800
C	-3.04481	+3.83592	+1.53801
H	-2.24788	+3.88617	+2.29419
H	-3.58915	+4.78612	+1.52321
H	-3.73853	+3.02467	+1.80278

[*p*-MeO-PhCH$_2$]$^{\bullet}$

E = -385.4764362; Ezp = -385.329275; H = -385.319997; G = -385.362793

0,2

C	+0.54627	+1.27128	-0.08427
C	-0.06683	+2.43465	+0.34066
C	-1.46181	+2.47170	+0.55794
C	-2.22948	+1.31200	+0.33850
C	-1.60935	+0.14279	-0.08915
C	-0.20162	+0.07147	-0.31808
H	-2.21415	-0.74604	-0.25486
C	+0.42017	-1.11520	-0.75093
H	+1.49259	-1.15627	-0.92159
H	+1.62179	+1.26038	-0.24674
H	+0.51185	+3.33823	+0.51445
H	-3.30201	+1.31574	+0.49840
H	-0.15898	-2.01821	-0.92442
O	-1.96437	+3.66715	+0.97587
C	-3.37339	+3.77505	+1.21514
H	-3.69190	+3.08741	+2.00801
H	-3.53917	+4.80509	+1.53591
H	-3.94438	+3.57878	+0.29950

[*p*-MeO-PhCH$_3$]

E = -386.1217118; Ezp = -385.961696; H = -385.951809; G = -385.996434

0,1

C	-1.14321	-1.20003	-0.03597
C	+0.24184	-1.20575	-0.22457
C	+0.93513	+0.00609	-0.30787
C	+0.24433	+1.21565	-0.19593
C	-1.14197	+1.20752	-0.00688
C	-1.85958	+0.00367	+0.07372
H	-1.67273	+2.15380	+0.07741
C	-3.36136	-0.00210	+0.24388
H	-3.68693	-0.81940	+0.89833
H	-1.67597	-2.14714	+0.02534
H	+0.78935	-2.14098	-0.31046
H	+0.79278	+2.15208	-0.25974
H	-3.71910	+0.94182	+0.67024
O	+2.30008	+0.00705	-0.54013
C	+3.09787	-0.00569	+0.65559
H	+2.89737	-0.90743	+1.24960
H	+4.14247	-0.00432	+0.33386
H	+2.90034	+0.88520	+1.26669
H	-3.86726	-0.13927	-0.72202

[*p*-Me-PhCH2]$^{-}$

E = -310.3675685; Ezp = -310.228434; H = -310.219294; G = -310.261635

-1,1

C	+0.75622	+1.20963	-0.03867
C	-0.63660	+1.19627	-0.02845
C	-1.38697	+0.00215	-0.02158
C	-0.63721	-1.19400	-0.02904
C	+0.75421	-1.20821	-0.03906
C	+1.54637	+0.00061	-0.03976
H	+1.27284	-2.16779	-0.05095
C	+2.95410	-0.00249	-0.03590
H	+3.51779	+0.92743	-0.10201
H	+1.27516	+2.16902	-0.05058
H	-1.16605	+2.15101	-0.02851
H	-1.16748	-2.14840	-0.02933
H	+3.51354	-0.93492	-0.10260
C	-2.89823	-0.00131	+0.04238
H	-3.33280	-0.79834	-0.57728
H	-3.28150	-0.15594	+1.06453
H	-3.31523	+0.95146	-0.31004

[*p*-CH$_3$-PhCH$_2$]$^{\bullet}$

E = -310.2649402; Ezp = -310.122917; H = -310.114485; G = -310.155286

0,2

C	+0.34983	+1.28490	+0.14972
C	-0.38772	+2.45288	+0.29748
C	-1.77047	+2.48943	+0.02687
C	-2.38957	+1.29541	-0.40462
C	-1.66925	+0.12064	-0.55769
C	-0.26539	+0.07039	-0.28476
H	-2.17095	-0.78476	-0.89301
C	+0.47356	-1.11836	-0.43919
H	+1.53965	-1.14587	-0.22971
H	+1.41649	+1.28590	+0.36438
H	+0.11147	+3.36152	+0.62886
H	-3.45642	+1.30111	-0.62162
H	-0.00508	-2.03597	-0.77088
C	-2.57597	+3.75049	+0.21101
H	-3.22745	+3.93931	-0.65178
H	-3.22876	+3.67625	+1.09255
H	-1.92882	+4.62348	+0.34976

[*p*-CH$_3$-PhCH$_3$]

E = -310.9155769; Ezp = -310.760279; H = -310.751365; G = -310.793254

0,1

C	+0.73757	+1.20571	+0.02902
C	-0.66353	+1.20651	+0.01759
C	-1.38929	+0.00790	-0.00651
C	-0.66213	-1.19549	-0.02117
C	+0.73406	-1.19629	-0.01009
C	+1.46228	+0.00630	+0.01425
H	+1.26957	-2.14433	-0.02182
C	+2.97327	-0.00421	+0.00155
H	+3.38207	+0.98788	+0.22339
H	+1.27211	+2.15378	+0.04837
H	-1.19723	+2.15519	+0.02900
H	-1.19848	-2.14294	-0.04018
H	+3.37550	-0.71143	+0.73771
C	-2.90029	-0.00168	+0.00583
H	-3.30313	-0.68427	-0.75290
H	-3.28562	-0.33930	+0.97783
H	-3.30821	+0.99745	-0.18366
H	+3.35831	-0.31042	-0.98090

[*o*-NC-PhCH2]$^{-}$

E = -363.3115393; Ezp = -363.200194; H = -363.191531; G = -363.2323

-1,1

C	+1.04495	-1.23127	-4.1576e
C	-0.35229	-1.21017	-0.00024
C	-1.10152	-0.00787	-0.00033
C	-0.36027	+1.18949	-0.00022
C	+1.02622	+1.19914	-2.6556e
C	+1.82395	-0.01392	+9.30182
H	+1.54917	+2.15500	+5.36674
C	+3.21947	-0.01018	+0.00034
H	+3.78610	-0.93957	+0.00035
H	+1.56138	-2.18907	+2.20631
H	-0.89295	+2.13976	-0.00029
H	+3.77854	+0.92373	+0.00036
H	-2.18630	-0.01943	-0.00048
C	-1.05430	-2.46035	-0.00034
N	-1.63268	-3.47356	-0.00042

[*o*-NC-PhCH$_2$]$^{\bullet}$

E = -363.1956484; Ezp = -363.082184; H = -363.073833; G = -363.114629

0,2

C	+1.05319	-1.23520	-2.63914
C	-0.34372	-1.22242	-0.00023
C	-1.06538	-0.00783	-0.00033
C	-0.35522	+1.19913	-0.00022
C	+1.03419	+1.20538	-1.67234
C	+1.78348	-0.01203	+8.39284
H	+1.57274	+2.14973	+6.78928
C	+3.19323	-0.00984	+0.00028
H	+3.75283	-0.94076	+0.00035
H	+1.58930	-2.17998	+4.66842
H	-0.90073	+2.13885	-0.00029
H	+3.74752	+0.92428	+0.00036
H	-2.15067	-0.01861	-0.00049
C	-1.05906	-2.46553	-0.00034
N	-1.64224	-3.47343	-0.00043

[*o*-NC-PhCH$_3$]

E = -363.8484213; Ezp = -363.721721; H = -363.712873; G = -363.754769

0,1

C	+1.02848	-1.22400	-0.04275
C	-0.37998	-1.21886	-0.03117

C	-1.09622	-0.01098	+0.02263
C	-0.38482	+1.18880	+0.06452
C	+1.01233	+1.18196	+0.05329
C	+1.73893	-0.02115	+2.94616
H	+1.55334	+2.12521	+0.08630
C	+3.24838	-0.00352	-0.00519
H	+3.66163	-1.01353	-0.09276
H	+1.56066	-2.17035	-0.08510
H	-0.92271	+2.13200	+0.10580
H	+3.62973	+0.59716	-0.84023
H	-2.18188	-0.01823	+0.03077
C	-1.08971	-2.46275	-0.07513
N	-1.66635	-3.47439	-0.11062
H	+3.63522	+0.44438	+0.91901

[*p*-NC-PhCH2]$^-$

E = -363.3267403; Ezp = -363.214642; H = -363.206095; G = -363.24677

-1,1

C	+0.34405	+1.31107	+0.14592
C	-0.38283	+2.46454	+0.30216
C	-1.79133	+2.50276	+0.04412
C	-2.41249	+1.28529	-0.38473
C	-1.69089	+0.12876	-0.54280
C	-0.25737	+0.05649	-0.28883
H	-2.20101	-0.77603	-0.87067
C	+0.47132	-1.10532	-0.44736
H	+1.54159	-1.13226	-0.25087
H	+1.41337	+1.32396	+0.35264
H	+0.11701	+3.37457	+0.62960
H	-3.48194	+1.28356	-0.58837
H	-0.00249	-2.02941	-0.77348
C	-2.53171	+3.68368	+0.20438
N	-3.15339	+4.67526	+0.33892

[*p*-NC-PhCH$_2$]$^\bullet$

E = -363.1986829; Ezp = -363.085131; H = -363.076786; G = -363.117577

0,2

C	+0.34754	+1.30465	+0.14474
C	-0.38009	+2.46803	+0.30336
C	-1.77190	+2.47186	+0.03971
C	-2.41694	+1.28462	-0.38603
C	-1.68657	+0.12287	-0.54372
C	-0.27797	+0.08934	-0.28441
H	-2.18280	-0.78721	-0.87043
C	+0.46204	-1.09081	-0.44496
H	+1.53011	-1.11155	-0.24703
H	+1.41532	+1.30334	+0.34740
H	+0.10745	+3.38206	+0.62935
H	-3.48428	+1.29529	-0.58623
H	-0.01639	-2.01020	-0.77076
C	-2.52404	+3.67116	+0.20293
N	-3.13962	+4.65347	+0.33671

[*p*-NC-PhCH$_3$]

E = -363.8491427; Ezp = -363.722463; H = -363.713637; G = -363.755289

0,1

C	+0.97618	-1.20935	-0.01591
C	-0.41751	-1.21922	-0.01325
C	-1.11936	-0.00047	-0.00112
C	-0.41426	+1.21894	+0.00789
C	+0.97706	+1.20649	+0.00515
C	+1.69545	-0.00303	-0.00545
H	+1.51807	+2.14979	+0.01052
C	+3.20260	+0.00565	+0.01402
H	+3.61295	-0.98487	-0.20756
H	+1.51441	-2.15381	-0.02727
H	-0.96137	-2.15918	-0.02233
H	-0.95738	+2.15936	+0.01515
H	+3.60418	+0.72029	-0.71435
C	-2.55027	+0.00103	-0.00025
N	-3.71563	+0.00245	+0.00066
H	+3.57314	+0.31072	+1.00210

[*p*-MeC(O)-PhCH$_2$]$^-$

E = -423.7374117; Ezp = -423.586407; H = -423.576247; G = -423.620595

-1,1

C	+1.04142	-1.22745	-3.44577
C	-0.32980	-1.21140	-0.00011
C	-1.08956	+0.00450	-7.70102
C	-0.32485	+1.21649	-6.9885e
C	+1.04912	+1.22119	+9.14566
C	+1.83492	-0.00474	+0.00010
H	+1.58220	+2.17160	+0.00016
C	+3.21530	-0.00976	+0.00026
H	+3.77770	-0.94180	+0.00028
H	+1.56985	-2.18088	-7.911e-
H	-0.87661	-2.15214	-0.00019
H	-0.84041	+2.17461	-2.35213
H	+3.78450	+0.91819	+0.00037
C	-2.52885	-0.02914	+9.75393
O	-3.19047	-1.10098	-0.00012
C	-3.30059	+1.28956	-0.00040
H	-3.06415	+1.89673	+0.88300
H	-3.06256	+1.89721	-0.88304
H	-4.37335	+1.07530	-0.00139

[*p*-MeC(O)-PhCH2]$^\bullet$

E = -423.6110053; Ezp = -423.458616; H = -423.44859; G = -423.49356

0,2

C	+1.04473	-1.22554	-0.00014
C	-0.33547	-1.20989	-0.00021
C	-1.05441	+0.01105	-4.44883
C	-0.32490	+1.22421	+0.00023
C	+1.05879	+1.22108	+0.00036
C	+1.79777	-0.00522	+0.00015
H	+1.60394	+2.16183	+0.00063
C	+3.19911	-0.01126	+0.00026
H	+3.75480	-0.94505	+0.00010

H	+1.58038	-2.17205	-0.00031
H	-0.89174	-2.14239	-0.00043
H	-0.84571	+2.17652	+0.00043
H	+3.76256	+0.91788	+0.00051
C	-2.54082	-0.02204	-5.93761
O	-3.14647	-1.09878	+0.00040
C	-3.30537	+1.28387	-0.00068
H	-3.05262	+1.88381	+0.88246
H	-3.05262	+1.88320	-0.88422
H	-4.37814	+1.07585	-0.00056

[*p*-MeC(O)-PhCH$_3$]

E = -424.2608946; Ezp = -424.095429; H = -424.084907; G = -424.130855

0,1

C	-1.46347	+1.18607	+0.06369
C	-0.07389	+1.24552	+0.06836
C	+0.69763	+0.06889	+0.00416
C	+0.03024	-1.16606	-0.06558
C	-1.36546	-1.21930	-0.07055
C	-2.13613	-0.04890	-0.00459
H	-1.86273	-2.18493	-0.12719
C	-3.64294	-0.10147	+0.01151
H	-4.07231	+0.60694	-0.70755
H	-2.04216	+2.10625	+0.11319
H	+0.43202	+2.20503	+0.12074
H	+0.58931	-2.09503	-0.11851
H	-4.01332	-1.10401	-0.22674
C	+2.18823	+0.17157	+0.01126
O	+2.74212	+1.27101	+0.06736
C	+3.01057	-1.09651	-0.05067
H	+2.78019	-1.75073	+0.79932
H	+2.78642	-1.66002	-0.96488
H	+4.07308	-0.84183	-0.03407
H	-4.02970	+0.17363	+1.00224

[PhCH$_3$]

E = -271.5943509; Ezp = -271.466398; H = -271.459311; G = -271.49654

0,1

C	+0.19785	-1.20160	+0.03513
C	-1.20028	-1.20712	+0.04201
C	-1.90970	+0.00021	+0.00527
C	-1.20644	+1.20835	-0.03911
C	+0.19409	+1.20796	-0.04590
C	+0.91713	+0.00552	-0.00748
H	+0.73237	+2.15315	-0.08248
C	+2.42803	-1.19192	+0.00942
H	+2.83338	-0.72972	-0.70234
H	+0.74085	-2.14477	+0.06235
H	-1.73642	-2.15302	+0.07395
H	-2.99713	-0.00244	+0.00880
H	-1.74551	+2.15258	-0.07066
H	+2.83534	+0.98552	-0.24157
H	+2.80866	-0.27477	+1.00272

[4j]

E = -832.4790949; Ezp = -832.040483; H = -832.019701; G = -832.092849

0,1

C	-3.94037	-3.59307	-2.42036
C	-4.01092	-2.07406	-2.30084
N	-2.65933	-1.51608	-2.19073
C	-1.76444	-1.96263	-3.26371
C	-1.77726	-3.48814	-3.34785
O	-3.10403	-3.99617	-3.51030
C	-2.39104	-0.51852	-1.29589
O	-3.25242	-0.12111	-0.49437
C	-0.98894	+0.08519	-1.31148
C	-0.78105	+1.16078	-0.24339
C	+0.64024	+1.73736	-0.27918
C	+0.87162	+2.88976	+0.71302
C	+0.64536	+2.53855	+2.19552
C	+1.47084	+1.35111	+2.72291
C	+2.98903	+1.50023	+2.57948
C	+3.79123	+0.32112	+3.16411
C	+5.24013	+0.84966	+3.30865
C	+5.11919	+2.40558	+3.34009
C	+3.60391	+2.70513	+3.31533
H	-4.93430	-4.00328	-2.62108
H	-3.55815	-4.02688	-1.48217
H	-4.58718	-1.79217	-1.41878
H	-4.50196	-1.65456	-3.19153
H	-0.74343	-1.62707	-3.08631
H	-2.10844	-1.53746	-4.21814
H	-1.32551	-3.91511	-2.43764
H	-1.20494	-3.82171	-4.21832
H	-0.25084	-0.71713	-1.17679
H	-0.79899	+0.50705	-2.30839
H	-1.50947	+1.96935	-0.38932
H	-0.99008	+0.73124	+0.74289
H	+1.36391	+0.93211	-0.08820
H	+0.85319	+2.10363	-1.29457
H	+1.89578	+3.26565	+0.58242
H	+0.20433	+3.72360	+0.44836
H	+0.87147	+3.42875	+2.79910
H	-0.41947	+2.32442	+2.36148
H	+1.23588	+1.20953	+3.78912
H	+1.15252	+0.42864	+2.21595
H	+3.24274	+1.58803	+1.51155
H	+3.72594	-0.58303	+2.54597
H	+3.37948	+0.06942	+4.15268
H	+5.85384	+0.53139	+2.45710
H	+5.72324	+0.45694	+4.21124
H	+5.59802	+2.83888	+2.45270
H	+5.61261	+2.84597	+4.21454
H	+3.37085	+3.66598	+2.84175
H	+3.20186	+2.73806	+4.33960

[2j]$^-$

E = -831.8956303; Ezp = -831.472969; H = -831.452254; G = -831.524875

-1,1

C	-3.98360	-3.55878	-2.50441
C	-4.00001	-2.04171	-2.35159
N	-2.63429	-1.53706	-2.17235
C	-1.70524	-2.00360	-3.20762
C	-1.77978	-3.52441	-3.32827
O	-3.11712	-3.97042	-3.56706
C	-2.38805	-0.51427	-1.29755
O	-3.28043	-0.07258	-0.55597
C	-0.97258	+0.05576	-1.25919
C	-0.78845	+1.16422	-0.22042
C	+0.64386	+1.71502	-0.21587
C	+0.85649	+2.88956	+0.75244
C	+0.62133	+2.56246	+2.25731
C	+1.42231	+1.40757	+2.88913
C	+2.92907	+1.53937	+2.66334
C	+3.78208	+0.36362	+3.18402
C	+5.24408	+0.87935	+3.20936
C	+5.13538	+2.43604	+3.24016
C	+3.62328	+2.73682	+3.34712
H	-4.98354	-3.92339	-2.75672
H	-3.65953	-4.02943	-1.56210
H	-4.60125	-1.75755	-1.48705
H	-4.43900	-1.58334	-3.25061
H	-0.68081	-1.72153	-2.96749
H	-1.97612	-1.54304	-4.16953
H	-1.39245	-3.99183	-2.40849
H	-1.17970	-3.86257	-4.17796
H	-0.26301	-0.75897	-1.06014
H	-0.72149	+0.43776	-2.25890
H	-1.49559	+1.97929	-0.42517
H	-1.04524	+0.77483	+0.77117
H	+1.34058	+0.90256	+0.03549
H	+0.90416	+2.03852	-1.23580
H	+1.88159	+3.26601	+0.62107
H	+0.18950	+3.71698	+0.45526
H	+0.81156	+3.50242	+2.80510
H	-0.45635	+2.37407	+2.39285
H	+1.10073	+0.46914	+2.39146
H	+3.18809	+1.63477	+1.58040
H	+3.66418	-0.54569	+2.57880
H	+3.44669	+0.11737	+4.20388
H	+5.79221	+0.54969	+2.31749
H	+5.79407	+0.49128	+4.07610
H	+5.54037	+2.86245	+2.31285
H	+5.70752	+2.87766	+4.06592
H	+3.35448	+3.70460	+2.90398
H	+3.30941	+2.76352	+4.40354

[2j-Cl]$^\bullet$

E = -831.8134828; Ezp = -831.389835; H = -831.368532; G = -831.44387

0,2

C	-3.94092	-3.59958	-2.40126
C	-4.02849	-2.07853	-2.32215
N	-2.68370	-1.50447	-2.21576
C	-1.77868	-1.96663	-3.27331
C	-1.77258	-3.49407	-3.31779
O	-3.09228	-4.02207	-3.47437
C	-2.42405	-0.49941	-1.32713
O	-3.29101	-0.09941	-0.53285
C	-1.02471	+0.11081	-1.34134
C	-0.82389	+1.19001	-0.27543
C	+0.59343	+1.77592	-0.31533
C	+0.82864	+2.91564	+0.68757
C	+0.66216	+2.51404	+2.17967
C	+1.55530	+1.39125	+2.61269
C	+3.04359	+1.51523	+2.56092
C	+3.82218	+0.33764	+3.18192
C	+5.26271	+0.86900	+3.39777
C	+5.15401	+2.42494	+3.35376
C	+3.64389	+2.73324	+3.30539
H	-4.92884	-4.02617	-2.59769
H	-3.56039	-4.00378	-1.44925
H	-4.61517	-1.77989	-1.45254
H	-4.51567	-1.68726	-3.22757
H	-0.76324	-1.61193	-3.10178
H	-2.12530	-1.57106	-4.23936
H	-1.32107	-3.89135	-2.39413
H	-1.19119	-3.84326	-4.17608
H	-0.28302	-0.68726	-1.20215
H	-0.83488	+0.52991	-2.33945
H	-1.55854	+1.99293	-0.42084
H	-1.02725	+0.75962	+0.71179
H	+1.32312	+0.97343	-0.13201
H	+0.79713	+2.15332	-1.32843
H	+1.84307	+3.31199	+0.54384
H	+0.13557	+3.74195	+0.47130
H	+0.87447	+3.41422	+2.77945
H	-0.38581	+2.25330	+2.37204
H	+1.12524	+0.40047	+2.75774
H	+3.36016	+1.61030	+1.50264
H	+3.78789	-0.56308	+2.55722
H	+3.36141	+0.08254	+4.14677
H	+5.93475	+0.50909	+2.60951
H	+5.67577	+0.51762	+4.35052
H	+5.63820	+2.81044	+2.44735
H	+5.64640	+2.90426	+4.20789
H	+3.41702	+3.68789	+2.81714
H	+3.22397	+2.77077	+4.32114

[4n]

E = -620.8235323; Ezp = -620.511108; H = -620.495727; G = -620.553302

0,1

C	+0.18515	+0.10980	-1.72315
C	-0.29501	+0.62849	-2.93088
C	-1.42099	+0.06348	-3.53154
C	-2.05160	-1.01516	-2.90588
C	-1.58230	-1.54167	-1.69256
C	-0.43479	-0.97407	-1.07933
C	-2.36076	-2.68123	-1.06194
C	-3.46243	-2.16763	-0.13358
O	-4.12149	-3.30837	+0.44155
C	+0.07136	-1.56700	+0.23256

C	+1.28926	-0.96628	+0.95882
C	+1.18597	+0.53453	+1.38653
C	+2.55723	+1.17231	+1.04431
C	+3.52376	-0.02152	+0.91246
C	+2.65914	-1.10627	+0.24902
H	+1.06160	+0.57112	-1.28693
H	+0.21572	+1.46884	-3.39569
H	-1.80371	+0.45181	-4.47248
H	-2.92966	-1.46495	-3.36621
H	-2.83212	-3.28387	-1.84793
H	-1.70831	-3.35001	-0.49161
H	-3.03687	-1.53444	+0.65762
H	-4.17865	-1.56098	-0.70651
H	-4.83149	-2.99059	+1.02561
H	+0.29190	-2.63026	+0.05584
H	-0.76569	-1.56829	+0.94405
H	+1.36947	-1.55381	+1.88370
H	+0.98610	+0.60016	+2.46293
H	+0.36210	+1.05326	+0.88426
H	+2.88315	+1.90438	+1.79284
H	+2.50036	+1.69874	+0.08182
H	+3.84183	-0.35871	+1.90979
H	+4.42851	+0.22155	+0.34179
H	+3.07159	-2.11649	+0.36378
H	+2.57667	-0.91232	-0.82717

[2n-Cl]$^{-}$

E = -620.2821762; Ezp = -619.985069; H = -619.970169; G = -620.026062

-1,1

C	+0.23986	+1.73073	-0.01183
C	-0.73490	+2.71957	+0.10599
C	-2.08322	+2.45383	-0.17730
C	-2.41136	+1.13879	-0.57057
C	-1.46960	+0.11914	-0.67985
C	-0.05793	+0.37440	-0.41313
C	-1.95694	-1.28267	-1.00335
C	-2.13661	-2.17972	+0.23311
O	-0.92520	-2.50225	+0.93066
C	+0.92038	-0.64841	-0.49595
C	+2.41190	-0.46113	-0.29354
C	+2.87648	+0.04718	+1.12264
C	+3.97816	+1.10826	+0.87933
C	+4.46494	+0.84453	-0.55994
C	+3.17204	+0.46423	-1.29584
H	+1.26838	+2.00293	+0.19990
H	-0.43154	+3.72116	+0.41294
H	-2.84630	+3.22459	-0.09932
H	-3.45351	+0.89853	-0.78799
H	-2.94405	-1.22050	-1.48218
H	-1.29534	-1.78910	-1.72160
H	-2.83142	-1.68151	+0.92936
H	-2.59993	-3.13027	-0.07049
H	-0.21747	-1.85904	+0.65980
H	+0.65700	-1.53784	-1.06706
H	+2.86238	-1.45638	-0.42201
H	+3.26882	-0.79574	+1.70659
H	+2.03925	+0.46115	+1.69489
H	+4.78757	+1.06553	+1.61897
H	+3.54643	+2.11764	+0.93143
H	+5.16290	-0.00616	-0.56996
H	+4.98724	+1.70460	-0.99928
H	+3.34921	-0.04193	-2.25387
H	+2.58350	+1.36655	-1.50688

[2n-Cl]$^{\bullet}$

E = -620.1798578; Ezp = -619.88038; H = -619.865172; G = -619.922513

0,2

C	+0.18236	+0.17299	-1.77710
C	-0.30368	+0.68611	-2.97277
C	-1.42574	+0.10764	-3.58365
C	-2.04318	-0.99259	-2.97187
C	-1.58022	-1.53288	-1.77072
C	-0.42797	-0.94623	-1.12550
C	-2.33080	-2.70312	-1.16870
C	-3.29294	-2.27153	-0.06030
O	-3.93104	-3.45414	+0.44990
C	+0.06725	-1.46615	+0.10116
C	+1.23483	-0.97262	+0.90815
C	+1.20262	+0.53651	+1.35821
C	+2.61850	+1.10020	+1.08164
C	+3.52219	-0.14178	+0.98215
C	+2.63732	-1.16001	+0.24820
H	+1.05415	+0.63807	-1.33351
H	+0.19222	+1.53772	-3.43324
H	-1.81244	+0.50122	-4.52025
H	-2.91205	-1.44546	-3.44610
H	-2.91634	-3.19995	-1.95116
H	-1.64211	-3.45317	-0.76191
H	-2.75066	-1.75461	+0.74330
H	-4.04218	-1.57736	-0.46794
H	-4.55942	-3.18880	+1.14349
H	-0.43971	-2.33507	+0.50800
H	+1.24878	-1.57591	+1.82322
H	+0.96497	+0.58497	+2.42727
H	+0.42713	+1.10626	+0.83692
H	+2.94695	+1.80850	+1.85153
H	+2.63133	+1.63383	+0.12163
H	+3.76444	-0.51454	+1.98777
H	+4.46841	+0.05607	+0.46369
H	+2.98901	-2.19419	+0.34074
H	+2.59659	-0.91984	-0.82092

T.1.5 Cartesian coordinates of optimized geometries for the Ni(I) reaction mechanism with (3-chloropropyl)benzene.

The geometries were optimized at the B3LYP-D$_3$/6-31G* level of theory for different spin states and only the lowest in energy structures are considered. The associated free energy values (G = E$_{elec}$ (**6-311+G****) + ΔG$_{corr}$ (**6-31G***), in Hartrees) are indicated.

----FORMAT---
Name
G, in Hartrees
Charge, multiplicity
Element x y z

CH_3CN
G = -132.787307
0, 1

C	-1.810932	-1.154317	0.8411222
N	-1.810932	-0.129039	0.2959727
C	-1.810933	-2.440822	1.5251684
H	-0.902585	-2.544904	2.1275145
H	-2.683376	-2.515709	2.1824224
H	-1.846836	-3.254330	0.7932777

$Ph(CH_2)_3Cl$
G = -809.8081101
0, 1

C	3.6956235	-2.427245	-0.929970
H	3.5257357	-2.305099	0.1460488
H	3.5141322	-1.455929	-1.404511
C	5.1566773	-2.860070	-1.176259
H	5.3247367	-3.835341	-0.702276
H	5.3169584	-2.991609	-2.253359
C	6.1384104	-1.846573	-0.629660
C	6.6578684	-0.833503	-1.448044
C	6.5139032	-1.872616	0.7219341
C	7.5307468	0.1281703	-0.932201
H	6.3763509	-0.800267	-2.498484
C	7.3858576	-0.913529	1.2422023
H	6.1208675	-2.654212	1.3688582
C	7.8978688	0.0913507	0.4157954
H	7.9258767	0.9035917	-1.583842
H	7.6689779	-0.953303	2.2911908
H	8.5786253	0.8369550	0.8183823
H	2.8530314	-4.435630	-1.014396
H	2.8285859	-3.569146	-2.571272
C	2.7320124	-3.459823	-1.489145
Cl	0.9833400	-2.971514	-1.189887

$[Ni^{I}(Ts^{H}Py_{2}tacn)]Cl$
G = -3762.361183
0, 2

S	1.9183079	-0.030442	0.8341984
N	1.1461054	-0.416194	-0.643279
O	1.6888223	1.3992932	1.0744131
N	-1.242297	1.8956157	-0.070080
N	-2.857413	-0.617205	0.6583876
N	-1.053441	0.3683171	-2.357488
N	-1.187453	-2.131553	-0.940035
O	1.4428656	-1.030876	1.8007451
C	1.3697122	0.5699764	-1.734514
H	2.3784509	0.4707535	-2.155854
H	1.2689239	1.5613958	-1.294005
C	-2.274116	-2.815395	-0.194198
H	-1.821857	-3.286790	0.6859603
H	-2.728340	-3.617640	-0.787127
C	-1.371319	2.5511852	-1.246433
C	-3.739651	0.2302601	1.2562621
H	-3.341861	1.2021635	1.5260204
C	-1.022086	2.6110724	1.0469454
H	-0.917158	2.0365258	1.9603801
C	-1.715133	1.6846095	-2.437498
H	-2.800489	1.5163907	-2.420362
H	-1.477466	2.2069587	-3.373753
C	-4.643832	-2.238298	0.5068768
H	-4.959991	-3.229350	0.1930721
C	0.3391681	0.3949674	-2.856292
H	0.4817630	1.2183230	-3.567571
H	0.5370017	-0.525285	-3.408314
C	-5.542089	-1.354041	1.1152720
H	-6.577156	-1.636599	1.2803709
C	1.3095043	-1.846998	-1.032818
H	2.2283592	-2.272488	-0.617006

H	1.4360500	-1.878017	-2.114380
C	3.6702889	-0.276797	0.5918961
C	-1.873721	-0.728384	-2.918004
H	-1.859420	-0.729809	-4.018705
H	-2.904405	-0.549083	-2.601430
C	-1.414414	-2.103908	-2.416426
H	-2.173104	-2.842106	-2.697716
H	-0.492994	-2.405609	-2.918868
C	4.2641225	-1.475686	0.9924850
H	3.6741201	-2.238916	1.4882835
C	-3.325022	-1.854843	0.3101088
C	0.1312123	-2.702378	-0.575806
H	0.2566771	-3.716882	-0.982746
H	0.1634402	-2.761797	0.5125469
C	4.4181008	0.7299758	-0.031688
H	3.9493167	1.6639570	-0.322688
C	-5.063285	-0.097760	1.5043558
H	-5.710930	0.6276761	1.9876492
C	-1.038240	4.6741891	-0.168582
H	-0.953122	5.7562202	-0.211454
C	-0.922928	3.9982684	1.0466088
H	-0.748943	4.5302392	1.9762131
C	-1.262668	3.9373570	-1.331828
H	-1.356108	4.4244699	-2.297579
C	5.6267662	-1.664787	0.7611499
H	6.0952795	-2.593162	1.0763931
C	6.3997986	-0.677745	0.1346705
C	5.7750800	0.5201112	-0.254171
H	6.3630596	1.2989694	-0.733032
C	7.8719753	-0.881707	-0.117197
H	8.2108202	-1.855334	0.2491611
H	8.4653344	-0.103654	0.3787676
H	8.0976255	-0.820973	-1.189086
Ni	-1.257997	-0.104092	-0.259787
Cl	-5.369780	0.8756571	-2.581967

[Ni^{I}(Ts^{H}Py$_2$tacn)Cl]

G = -3762.34688

0, 2

S	-2.355247	-0.195808	-1.196656
N	-1.310184	-0.468095	0.0992719
O	-2.185202	1.2050927	-1.606796
N	1.1505805	2.0544045	-0.324277
N	3.5963806	-0.468321	-0.054778
N	1.0995760	0.4566118	1.8521622
N	1.3474489	-1.934314	0.4332673
O	-2.132938	-1.288645	-2.154565
C	-1.367840	0.5759034	1.1483749
H	-2.348790	0.5713367	1.6471814
H	-1.240820	1.5335258	0.6472856
C	2.4788603	-2.597093	-0.246640
H	2.2473207	-2.618795	-1.316696
H	2.6166474	-3.631174	0.1001243
C	1.1756420	2.6955264	0.9030109
C	4.6858132	0.3126594	0.0293643
H	4.4991955	1.3821694	0.0487837
C	0.7947495	2.8227714	-1.403422
H	0.7962228	2.2981436	-2.352093
C	1.6827187	1.8088181	2.0098136
H	2.7701827	1.6971481	1.9089987
H	1.4786018	2.2379085	3.0005979
C	5.0104227	-2.402512	-0.006326
H	5.0953771	-3.484739	-0.016049
C	-0.328464	0.4286989	2.2598768
H	-0.521921	1.2493509	2.9625987
H	-0.514669	-0.488750	2.8196276
C	6.1402325	-1.589256	0.0783761
H	7.1310712	-2.030246	0.1363876
C	-1.196885	-1.886338	0.5035356
H	-2.037099	-2.470296	0.1171243
H	-1.278384	-1.947053	1.5891224
C	-4.020768	-0.370032	-0.559578
C	1.8736175	-0.608190	2.5117396
H	1.7075810	-0.628581	3.5990137
H	2.9292833	-0.395564	2.3432107
C	1.5163527	-1.982156	1.9167525
H	2.3026719	-2.695389	2.1870120
H	0.5978772	-2.358164	2.3703231
C	-4.662368	-1.608971	-0.629704
H	-4.181299	-2.446633	-1.122898
C	3.7524422	-1.806128	-0.079045
C	0.0794021	-2.548991	-0.019202
H	0.0433159	-3.614051	0.2630417
H	0.0662548	-2.482324	-1.109439
C	-4.642749	0.7276389	0.0480062
H	-4.143611	1.6902121	0.0789275
C	5.9766543	-0.202963	0.0948119
H	6.8272278	0.4671816	0.1637219
C	0.4100890	4.7828569	-0.040459
H	0.1142099	5.8212804	0.0694939
C	0.4283315	4.1513218	-1.299738
H	0.1447840	4.6926372	-2.198826
C	0.7986659	4.0131256	1.0724517
H	0.8172095	4.4419637	2.0715151
C	-5.937592	-1.745759	-0.080440
H	-6.442029	-2.706615	-0.139851
C	-6.580654	-0.665041	0.5388089
C	-5.914867	0.5710941	0.5907145
H	-6.403427	1.4223176	1.0584060
C	-7.957715	-0.810848	1.1353416
H	-8.351501	-1.822272	0.9964521
H	-8.660794	-0.103906	0.6777977
H	-7.942938	-0.595119	2.2110858
Ni	1.6550150	0.2126430	-0.232644
Cl	1.8019705	-0.271933	-2.749927

$[\mathrm{Ni^{I}(Ts^{H}Py_{2}tacn)NCCH_{3}}]^{+}$

G = -3434.713652

1, 2

S	2.3215605	-0.209511	0.9923899
N	1.2839901	-0.412958	-0.309743
O	2.1368461	1.1603538	1.4940339
N	-1.378147	2.0980015	0.4276206
N	-3.640490	-0.464859	0.1356837
N	-1.222612	0.6028682	-1.856308
N	-1.395018	-1.881958	-0.610472
O	2.1186786	-1.362865	1.8839407
C	1.2676159	0.7138160	-1.269071
H	2.2270481	0.7838606	-1.803660
H	1.1355705	1.6247739	-0.685762
C	-2.497427	-2.587773	0.0788052
H	-2.222086	-2.665593	1.1370650
H	-2.636445	-3.607944	-0.306775
C	-1.390813	2.7736748	-0.750379
C	-4.744805	0.3032998	0.0924831
H	-4.582604	1.3698719	0.2209765
C	-1.026734	2.7775403	1.5382306
H	-1.023441	2.2034124	2.4580196
C	-1.849068	1.9385779	-1.918913
H	-2.931929	1.7948106	-1.826515
H	-1.658268	2.4498789	-2.872503
C	-5.023203	-2.395977	-0.239101
H	-5.088209	-3.471258	-0.374479
C	0.1817021	0.6273496	-2.341349
H	0.3321963	1.4956175	-2.995975
H	0.3528688	-0.247225	-2.970542
C	-6.164032	-1.591896	-0.282110
H	-7.142056	-2.032554	-0.451777
C	1.1487531	-1.800601	-0.795111
H	2.0090915	-2.403392	-0.488252
H	1.1802911	-1.789329	-1.884819
C	3.9860031	-0.324792	0.3404885
C	-2.017994	-0.425052	-2.555950
H	-1.905540	-0.361534	-3.648751
H	-3.066735	-0.240638	-2.321822
C	-1.624910	-1.833020	-2.083806
H	-2.415656	-2.533975	-2.373332
H	-0.723137	-2.165697	-2.599852
C	4.6409739	-1.558610	0.3287243
H	4.1759100	-2.428502	0.7798163
C	-3.783392	-1.801187	-0.021193
C	-0.100904	-2.511820	-0.262655
H	-0.069378	-3.551833	-0.626335
H	-0.033344	-2.531089	0.8262905
C	4.5852092	0.8124471	-0.214772
H	4.0752230	1.7694149	-0.183852
C	-6.020929	-0.213924	-0.111637
H	-6.877561	0.4519182	-0.141711
C	-0.654412	4.8036823	0.3056605
H	-0.363492	5.8486477	0.2546207
C	-0.662477	4.1197027	1.5225760
H	-0.383724	4.6120863	2.4489851
C	-1.025486	4.1104919	-0.849856
H	-1.032022	4.5965431	-1.820768
C	5.9077730	-1.649711	-0.249087
H	6.4227985	-2.606782	-0.253347
C	6.5277421	-0.528860	-0.818671
C	5.8488574	0.7009414	-0.787573
H	6.3198245	1.5827265	-1.214810
C	7.8919771	-0.626653	-1.453557
H	8.3119044	-1.632206	-1.353570
H	8.5909506	0.0838465	-0.995588
H	7.8434019	-0.383012	-2.522439
C	-0.551302	-0.644482	3.0141492
N	-0.996121	-0.342132	1.9837928
C	0.0713416	-1.021517	4.2719873
H	1.0178264	-0.483947	4.3860872
H	-0.585953	-0.785001	5.1152089
H	0.2784321	-2.096447	4.2710188
Ni	-1.658448	0.1326708	0.2435164

$[\mathrm{Ni^{I}(Ts^{H}Py_{2}tacn)}]^{+}$

G = -3301.941763

1, 2

S	-1.976087	-0.071895	-0.879784
N	-1.139445	-0.420179	0.5772953
O	-1.764485	1.3532614	-1.159612
N	1.1619252	1.9448760	-0.083320
N	2.9175026	-0.511396	-0.650399
N	1.0919499	0.4267920	2.2219386
N	1.2030595	-2.090165	0.8360329
O	-1.529310	-1.090880	-1.839968
C	-1.352412	0.5789462	1.6603602
H	-2.346289	0.4640964	2.1110980
H	-1.288420	1.5640470	1.2002611
C	2.2905221	-2.733412	0.0580664
H	1.8481938	-3.069233	-0.887283
H	2.6917086	-3.617135	0.5692848
C	1.3296463	2.6081315	1.0831133
C	3.8480479	0.3914577	-1.072116
H	3.4559918	1.3571327	-1.372720
C	0.8896411	2.6507668	-1.194085
H	0.7596466	2.0716291	-2.101005
C	1.7409717	1.7500758	2.2616671
H	2.8223705	1.5930480	2.1818366
H	1.5542370	2.2752032	3.2073037
C	4.7273516	-2.076962	-0.281362
H	5.0306372	-3.069192	0.0408588
C	-0.288266	0.4478658	2.7578713
H	-0.422389	1.2904355	3.4472391

H	-0.456571	-0.457252	3.3433868
C	5.6731901	-1.134048	-0.704566
H	6.7320977	-1.372396	-0.716544
C	-1.280568	-1.846228	0.9995819
H	-2.211028	-2.286039	0.6277447
H	-1.366211	-1.855646	2.0853845
C	-3.714108	-0.322139	-0.559027
C	1.9410088	-0.654796	2.7690168
H	1.9723758	-0.638600	3.8682971
H	2.9551283	-0.477102	2.4025803
C	1.4830529	-2.044124	2.3019835
H	2.2633688	-2.767573	2.5624293
H	0.5862448	-2.350140	2.8440418
C	-4.312960	-1.539120	-0.893271
H	-3.736914	-2.315184	-1.385498
C	3.3807947	-1.748672	-0.278426
C	-0.108961	-2.697715	0.5203618
H	-0.204197	-3.705117	0.9518506
H	-0.170711	-2.780389	-0.565621
C	-4.443934	0.6996757	0.0608984
H	-3.971099	1.6459031	0.3012795
C	5.2069725	0.1216986	-1.114217
H	5.8912166	0.8897340	-1.462786
C	0.9183099	4.7192304	0.0130795
H	0.8166064	5.7997479	0.0552244
C	0.7688919	4.0367771	-1.194096
H	0.5520963	4.5618474	-2.118547
C	1.2011707	3.9916317	1.1698228
H	1.3260315	4.4848043	2.1287738
C	-5.662009	-1.731323	-0.596584
H	-6.133949	-2.674894	-0.856517
C	-6.417470	-0.728808	0.0275318
C	-5.788400	0.4865765	0.3481860
H	-6.362388	1.2761334	0.8262936
C	-7.879480	-0.931344	0.3334306
H	-8.174716	-1.977814	0.2107531
H	-8.503451	-0.325028	-0.336147
H	-8.114690	-0.621838	1.3583005
Ni	1.2222918	-0.065799	0.1233127

I2$_{\mathbf{Ni\cdots Cl\text{-}R}}$

G = -4111.738401

1, 2

S	2.842276	-0.877489	0.663401
N	2.372332	0.145898	-0.645864
O	2.748817	-0.068778	1.884203
N	0.478473	2.020931	1.285146
N	-1.739521	0.664987	-0.224597
N	0.928928	2.530589	-1.37233
N	-0.000049	-0.029144	-2.233593
O	2.035739	-2.095219	0.512146
C	3.07747	1.460622	-0.648596
H	4.125269	1.344647	-0.951622
H	3.048039	1.839309	0.372456
C	-1.367164	-0.606555	-2.235565
H	-1.296201	-1.594426	-1.76527
H	-1.75034	-0.746972	-3.253608
C	0.739603	3.306681	0.962589
C	-2.566599	1.321569	0.639825
H	-2.112023	1.63437	1.573323
C	0.521316	1.657196	2.577815
H	0.306013	0.614739	2.78122
C	0.546564	3.654364	-0.497842
H	-0.52296	3.841198	-0.644668
H	1.080333	4.579038	-0.752408
C	-3.618823	0.478582	-1.742789
H	-3.998586	0.114758	-2.693532
C	2.392097	2.454141	-1.594277
H	2.859725	3.434297	-1.441303
H	2.581996	2.181982	-2.633328
C	-4.446576	1.185025	-0.859037
H	-5.484346	1.38164	-1.102727
C	2.412176	-0.576119	-1.957777
H	3.108455	-1.418911	-1.932313
H	2.812301	0.114162	-2.698988
C	4.557939	-1.301135	0.408547
C	0.119331	2.454396	-2.609173
H	0.430484	3.201901	-3.352968
H	-0.912864	2.673719	-2.325838
C	0.174233	1.05744	-3.244079
H	-0.605523	0.993396	-4.010757
H	1.12615	0.91104	-3.758063
C	4.887271	-2.501449	-0.227018
H	4.10824	-3.193276	-0.528885
C	-2.300908	0.227093	-1.399305
C	1.030012	-1.084898	-2.35021
H	1.075653	-1.498932	-3.367883
H	0.753177	-1.885675	-1.6634
C	5.550594	-0.409691	0.833337
H	5.283714	0.508249	1.346051
C	-3.896703	1.595398	0.362414
H	-4.496887	2.121755	1.09885
C	1.131278	3.869926	3.263651
H	1.394968	4.590592	4.032237
C	0.832824	2.549085	3.599248
H	0.850698	2.209148	4.629421
C	1.084756	4.253802	1.922932
H	1.306796	5.272348	1.620381
C	6.230916	-2.804214	-0.443
H	6.492824	-3.739973	-0.929437
C	7.246876	-1.927175	-0.036564
C	6.885292	-0.731619	0.607222
H	7.661366	-0.047925	0.941215
C	8.697345	-2.245394	-0.294211
H	9.320988	-1.983126	0.567713

H	9.071998	-1.669532	-1.150889
H	8.842343	-3.306713	-0.518501
Ni	0.166923	0.856801	-0.333229
C	-3.668926	-2.407326	0.96075
H	-3.456838	-2.236704	-0.100771
H	-3.500697	-1.457889	1.481823
C	-5.137161	-2.851033	1.138025
H	-5.281537	-3.811419	0.627334
H	-5.330944	-3.021813	2.204346
C	-6.120634	-1.836639	0.597569
C	-6.619873	-0.812657	1.415545
C	-6.532424	-1.881492	-0.742497
C	-7.514383	0.135456	0.912581
H	-6.307943	-0.762755	2.456578
C	-7.427057	-0.936421	-1.250479
H	-6.152514	-2.668997	-1.38997
C	-7.923576	0.075028	-0.422756
H	-7.894378	0.918384	1.564165
H	-7.738502	-0.991893	-2.290556
H	-8.62346	0.808597	-0.814413
H	-2.861676	-4.427565	0.992933
H	-2.884688	-3.629116	2.582901
C	-2.736559	-3.474542	1.511772
Cl	-0.975273	-3.014811	1.301833

TS$_{\text{Ni-Cl}}$

G = -4111.719074

1, 2

S	2.9732191	-1.024001	0.7613066
N	2.3867291	-0.104431	-0.601761
O	2.7501401	-0.189086	1.9466786
N	0.4195994	1.8139333	1.1447974
N	-1.779164	0.6928473	-0.621535
N	0.8863942	2.1839700	-1.547201
N	0.0734036	-0.459757	-2.224072
O	2.3586182	-2.348840	0.6358288
C	3.0407266	1.2394011	-0.682657
H	4.0988395	1.1431994	-0.951749
H	2.9706768	1.6838853	0.3096110
C	-1.281922	-1.049731	-2.207372
H	-1.246301	-1.920903	-1.545068
H	-1.597025	-1.384599	-3.203625
C	0.5931928	3.0905557	0.7350710
C	-2.622414	1.5165137	0.0298462
H	-2.179058	2.1182208	0.8165027
C	0.4414403	1.5456118	2.4613539
H	0.2971962	0.5060809	2.7264610
C	0.4293630	3.3351128	-0.751523
H	-0.642240	3.4643806	-0.938826
H	0.9280480	4.2672953	-1.046937
C	-3.617032	-0.047536	-1.981823
H	-3.970135	-0.687139	-2.784978
C	2.3557178	2.1425412	-1.712126
H	2.7867795	3.1457717	-1.608118
H	2.5913308	1.8092850	-2.723781
C	-4.487924	0.8071331	-1.302308
H	-5.541447	0.8419192	-1.560660
C	2.4833367	-0.904942	-1.868825
H	3.2123247	-1.713319	-1.777764
H	2.8645406	-0.246149	-2.647702
C	4.7368341	-1.205339	0.5355208
C	0.1354456	1.9962661	-2.806310
H	0.4766906	2.6806461	-3.595912
H	-0.908855	2.2281280	-2.593270
C	0.2401470	0.5503584	-3.316452
H	-0.519138	0.3965696	-4.090596
H	1.2073806	0.3898015	-3.795755
C	5.2368144	-2.362129	-0.069717
H	4.5643650	-3.158169	-0.370219
C	-2.276032	-0.083969	-1.611589
C	1.1279724	-1.495637	-2.240801
H	1.2028947	-1.987153	-3.221187
H	0.8606737	-2.243070	-1.492209
C	5.5933036	-0.184653	0.9637950
H	5.1964760	0.6970630	1.4552493
C	-3.977421	1.6005954	-0.271987
H	-4.616185	2.2742413	0.2899465
C	0.8469365	3.8441790	3.0019230
H	1.0216183	4.6368571	3.7235916
C	0.6437434	2.5300010	3.4230719
H	0.6506802	2.2652891	4.4752925
C	0.8215413	4.1276469	1.6364530
H	0.9710843	5.1377470	1.2681925
C	6.6123990	-2.485935	-0.255603
H	7.0069846	-3.386486	-0.718245
C	7.4942175	-1.473313	0.1505310
C	6.9637260	-0.327939	0.7666866
H	7.6340159	0.4586545	1.1028511
C	8.9776379	-1.598929	-0.084747
H	9.5502510	-1.134930	0.7253753
H	9.2629733	-1.091941	-1.016354
H	9.2828460	-2.646428	-0.172947
Ni	0.2119941	0.5115870	-0.384664
C	-3.820414	-1.870765	1.4109967
H	-3.693353	-1.976120	0.3261756
H	-3.791267	-0.794743	1.6232980
C	-5.220478	-2.408327	1.7966280
H	-5.272269	-3.482225	1.5797983
H	-5.373943	-2.283967	2.8756402
C	-6.289948	-1.666123	1.0250884
C	-6.806662	-0.453055	1.5049847
C	-6.715529	-2.120745	-0.231944
C	-7.723807	0.2849321	0.7529409
H	-6.483136	-0.083970	2.4760363
C	-7.633547	-1.387321	-0.987969
H	-6.321194	-3.057283	-0.620963

C	-8.140429	-0.179507	-0.498505
H	-8.113724	1.2214087	1.1441702
H	-7.953426	-1.758652	-1.958491
H	-8.855869	0.3917627	-1.084292
H	-2.516955	-3.594719	1.8602844
H	-2.597990	-2.359258	3.1836036
C	-2.675298	-2.545947	2.1123030
Cl	-0.978416	-1.573139	1.2996362

I3$_{\text{Ni(II)-Cl}\cdots\text{R}^{\bullet}}$

G = -4111.752100

1, 2

S	-3.281364	-1.151047	-0.762166
N	-2.473901	-0.277890	0.5312294
O	-3.088067	-0.344570	-1.971303
N	-0.638319	1.7162404	-1.376329
N	1.7754872	0.6408550	0.3111743
N	-0.815100	1.9771281	1.3301697
N	0.0173692	-0.631433	1.9347594
O	-2.817227	-2.537005	-0.672013
C	-3.078846	1.0789864	0.6963158
H	-4.101137	1.0104568	1.0842192
H	-3.110171	1.5305850	-0.295008
C	1.3785249	-1.199758	1.8274308
H	1.3281529	-2.047615	1.1380581
H	1.7458051	-1.559608	2.7955997
C	-0.766563	2.9793812	-0.916911
C	2.5599383	1.5188235	-0.331755
H	2.0667465	2.1503591	-1.063901
C	-0.834543	1.4681909	-2.681113
H	-0.725455	0.4318968	-2.975116
C	-0.437324	3.1728195	0.5451753
H	0.6464648	3.2997362	0.6293426
H	-0.905527	4.0825828	0.9382983
C	3.6761487	-0.126788	1.5485610
H	4.0835489	-0.796385	2.2986380
C	-2.269579	1.9545019	1.6468141
H	-2.684172	2.9674669	1.6026101
H	-2.398368	1.6122175	2.6737443
C	4.4894052	0.7933092	0.8870327
H	5.5484033	0.8483160	1.1156896
C	-2.421881	-1.097597	1.7891165
H	-3.136007	-1.921942	1.7531143
H	-2.736262	-0.465234	2.6181893
C	-5.025402	-1.130988	-0.361087
C	0.0121891	1.8060096	2.5494171
H	-0.300401	2.4949620	3.3446017
H	1.0402348	2.0488128	2.2836245
C	-0.071622	0.3597754	3.0544584
H	0.7348865	0.1866350	3.7738091
H	-1.005969	0.1976784	3.5920596
C	-5.575366	-2.189244	0.3689822
H	-4.960299	-3.031652	0.6660252
C	2.3225700	-0.183813	1.2288457
C	-1.026936	-1.679753	2.0042234
H	-0.999665	-2.212198	2.9645894
H	-0.820546	-2.387188	1.1988583
C	-5.815687	-0.059065	-0.788592
H	-5.380707	0.7440631	-1.373631
C	3.9232898	1.6285609	-0.076009
H	4.5208454	2.3531145	-0.618925
C	-1.316233	3.7758348	-3.112332
H	-1.588334	4.5813990	-3.788073
C	-1.167397	2.4717973	-3.585020
H	-1.315778	2.2298480	-4.632115
C	-1.115159	4.0338202	-1.756220
H	-1.222930	5.0340052	-1.349074
C	-6.932405	-2.157944	0.6825391
H	-7.367128	-2.981389	1.2428587
C	-7.747538	-1.088927	0.2791934
C	-7.170017	-0.048108	-0.465400
H	-7.789648	0.7792145	-0.800773
C	-9.206387	-1.048119	0.6559724
H	-9.797566	-0.506693	-0.089799
H	-9.339547	-0.533097	1.6168640
H	-9.619650	-2.056060	0.7658065
Ni	-0.265692	0.3343313	0.0915547
C	4.5555438	-1.656182	-1.923469
H	3.9980230	-1.769853	-0.984810
H	4.6768224	-0.578091	-2.094073
C	5.9777384	-2.267765	-1.717608
H	5.8729152	-3.341898	-1.524463
H	6.5435343	-2.157683	-2.650518
C	6.7188577	-1.605169	-0.579103
C	7.4858042	-0.450799	-0.797116
C	6.6102424	-2.095302	0.7308226
C	8.1326225	0.1925407	0.2610168
H	7.5783065	-0.056399	-1.806911
C	7.2532031	-1.455411	1.7932774
H	6.0162533	-2.987528	0.9172544
C	8.0177210	-0.307667	1.5619872
H	8.7267994	1.0827995	0.0702321
H	7.1597262	-1.853941	2.8005155
H	8.5221245	0.1897471	2.3862854
H	3.2373267	-3.192249	-2.899773
H	4.0153850	-1.984049	-4.078434
C	3.8162016	-2.285271	-3.052730
Cl	0.2896180	-1.527027	-1.373195

I2$_{\text{Ni}\cdots\text{R-Cl}}$

G = -4111.747352

1, 2

S	-1.322744	0.3121659	-0.384923
N	-0.764552	-0.079181	1.1843057

O	-0.836117	1.6667940	-0.678895
N	1.8951949	2.0132647	0.9063829
N	3.4216192	-0.617613	0.6140730
N	1.2441266	0.5805081	3.1739220
N	1.3373708	-1.958616	1.8368293
O	-0.924760	-0.818509	-1.234817
C	-1.039155	0.9667054	2.2063275
H	-2.100515	0.9746710	2.4850923
H	-0.788351	1.9265661	1.7548529
C	2.4640493	-2.736072	1.2653610
H	2.1512664	-3.077433	0.2721770
H	2.6909733	-3.626859	1.8633474
C	1.9019862	2.6924749	2.0760242
C	4.4850523	0.1568804	0.2716239
H	4.2402979	1.1469514	-0.097389
C	1.9146002	2.7107830	-0.242003
H	1.9112262	2.1215182	-1.149579
C	2.0075071	1.8324580	3.3173860
H	3.0640885	1.5658443	3.4331365
H	1.7115490	2.3990097	4.2098490
C	4.9809082	-2.358910	1.2254231
H	5.1312895	-3.366342	1.6030593
C	-0.195377	0.7516714	3.4685077
H	-0.358359	1.6168431	4.1232133
H	-0.553126	-0.120517	4.0174421
C	6.0685884	-1.546080	0.8838635
H	7.0876377	-1.902731	0.9975332
C	-1.108209	-1.474605	1.5882563
H	-2.003105	-1.833305	1.0704918
H	-1.368161	-1.453498	2.6460136
C	-3.105152	0.3671933	-0.317046
C	1.8740573	-0.566861	3.8627201
H	1.7209111	-0.531114	4.9514355
H	2.9482115	-0.498857	3.6729463
C	1.3625715	-1.911030	3.3290112
H	2.0048699	-2.705266	3.7250026
H	0.3581983	-2.111964	3.7059074
C	-3.847403	-0.760817	-0.675943
H	-3.348564	-1.651995	-1.041330
C	3.6893251	-1.880317	1.0655052
C	0.0409611	-2.439636	1.3068792
H	-0.220128	-3.427291	1.7149551
H	0.1514811	-2.530560	0.2256560
C	-3.732353	1.5359142	0.1320100
H	-3.145609	2.4113326	0.3889053
C	5.8014441	-0.266177	0.3851472
H	6.6044996	0.4028227	0.0902849
C	1.9061207	4.8017237	0.9253039
H	1.9003748	5.8878118	0.9365238
C	1.9303512	4.1013439	-0.280432
H	1.9456660	4.6128299	-1.236772
C	1.8912238	4.0835239	2.1222800
H	1.8766227	4.5890957	3.0828019
C	-5.237678	-0.712036	-0.578602
H	-5.821056	-1.582866	-0.865154
C	-5.893709	0.4413983	-0.125405
C	-5.120235	1.5617503	0.2234619
H	-5.614380	2.4677548	0.5645957
C	-7.395004	0.4845248	0.0026263
H	-7.867410	-0.354368	-0.517322
H	-7.801060	1.4181543	-0.403256
H	-7.693499	0.4367220	1.0581647
Ni	1.6957543	0.0247827	1.1299044
C	2.4826154	-0.193952	-3.098365
H	3.0635369	-0.402821	-4.002892
H	3.1262915	0.3772798	-2.418818
C	1.2209995	0.6153479	-3.452945
H	0.6498390	0.0497235	-4.203638
H	0.5773714	0.6825260	-2.573083
C	1.4884314	2.0138989	-3.973600
C	0.7138754	3.0887003	-3.509913
C	2.4789123	2.2753881	-4.933237
C	0.9206246	4.3857624	-3.987879
H	-0.050066	2.9040610	-2.759034
C	2.6916761	3.5712177	-5.409896
H	3.0904122	1.4619625	-5.315132
C	1.9136135	4.6330749	-4.939163
H	0.3083310	5.2018927	-3.612030
H	3.4662417	3.7515940	-6.151275
H	2.0801739	5.6411332	-5.309838
H	1.3324266	-2.045367	-3.011363
H	1.7288261	-1.350767	-1.414303
C	2.0844705	-1.503310	-2.434868
Cl	3.5195461	-2.647288	-2.303588

$TS_{Ni\text{-}C}$

G = -4111.72926

1, 2

S	2.4190907	-0.946101	-0.541659
N	2.1384806	0.6542649	0.0676006
O	1.7335836	-1.863992	0.3751061
N	-0.590940	-0.171425	1.7701951
N	-1.967131	1.8821442	-0.130437
N	0.5854820	2.3304002	1.8780116
N	0.4666141	2.7739534	-0.945741
O	2.0415453	-0.891961	-1.958860
C	2.5399271	0.7905303	1.5007271
H	3.6310314	0.7633728	1.6034759
H	2.1178641	-0.065625	2.0261360
C	-0.699448	3.0905964	-1.800265
H	-0.692861	2.3976755	-2.649249
H	-0.640780	4.1053581	-2.212160
C	-0.490253	0.4056757	2.9903483
C	-3.089332	1.6338736	0.5790346
H	-3.019008	0.8294389	1.3030865

C	-0.850926	-1.487881	1.6996036
H	-0.898608	-1.907141	0.7045323
C	-0.276615	1.9043803	2.9938816
H	-1.257083	2.3718017	2.8500772
H	0.1081965	2.2373615	3.9661401
C	-3.125817	3.6568494	-1.263359
H	-3.094786	4.4586440	-1.994642
C	2.0252258	2.0908781	2.1266854
H	2.2260919	2.0341031	3.2032225
H	2.5962771	2.9422054	1.7528489
C	-4.292125	3.3765452	-0.545805
H	-5.194250	3.9574250	-0.711894
C	2.7074895	1.6966374	-0.848520
H	3.4898695	1.2806781	-1.487920
H	3.1990668	2.4484955	-0.232948
C	4.1749124	-1.246582	-0.436369
C	0.2836414	3.6927488	1.3934802
H	0.7026778	4.4662348	2.0524345
H	-0.802432	3.8019178	1.3994286
C	0.8066289	3.9096020	-0.031805
H	0.3864051	4.8436780	-0.419108
H	1.8888828	4.0409650	-0.022331
C	4.9794896	-1.019932	-1.558238
H	4.5362760	-0.702732	-2.495988
C	-1.986506	2.8955714	-1.033157
C	1.6279860	2.3098269	-1.735995
H	2.0719219	3.1261741	-2.323336
H	1.2655193	1.5426264	-2.422597
C	4.7240178	-1.679627	0.7749259
H	4.0884976	-1.867639	1.6337269
C	-4.267702	2.3468576	0.3965677
H	-5.143439	2.0996732	0.9878152
C	-0.915526	-1.690805	4.0852440
H	-1.035341	-2.281337	4.9887861
C	-1.028926	-2.282269	2.8276649
H	-1.241980	-3.339813	2.7137288
C	-0.636360	-0.326484	4.1656483
H	-0.532194	0.1715715	5.1242903
C	6.3522571	-1.227186	-1.454365
H	6.9824681	-1.056563	-2.323141
C	6.9339781	-1.655363	-0.250362
C	6.1005112	-1.877687	0.8568443
H	6.5335739	-2.214488	1.7947653
C	8.4185427	-1.901857	-0.165222
H	8.9805022	-1.141546	-0.718758
H	8.6722097	-2.875462	-0.605215
H	8.7663504	-1.906325	0.8724315
Ni	-0.184029	1.1185314	0.2429970
C	-2.577101	-1.019265	-1.438628
H	-3.364228	-0.492627	-1.991623
H	-2.643096	-0.663659	-0.403099
C	-2.858342	-2.533962	-1.431469
H	-2.854627	-2.905413	-2.460164
H	-2.040908	-3.041818	-0.902506
C	-4.178843	-2.845249	-0.762778
C	-4.297920	-2.801104	0.6355081
C	-5.323492	-3.131750	-1.519413
C	-5.523579	-3.040278	1.2596468
H	-3.420830	-2.575383	1.2373346
C	-6.553502	-3.371963	-0.899428
H	-5.249440	-3.168055	-2.604336
C	-6.657811	-3.327036	0.4930559
H	-5.593182	-3.004607	2.3442146
H	-7.428607	-3.595003	-1.504961
H	-7.612596	-3.515398	0.9772594
H	-1.048280	0.4042670	-2.204534
H	-0.362346	-1.194315	-1.661039
C	-1.232699	-0.631356	-1.973649
Cl	-1.240713	-1.291969	-4.119907

I3$_{Ni(III)\text{-}C\cdots Cl^-}$

G = -4111.754635

1, 2

S	2.3483631	-1.378779	-0.143164
N	2.0374717	0.3519166	-0.052368
O	1.7840507	-1.939866	1.0905974
N	-0.374670	0.2625605	2.1845107
N	-1.993128	1.9361457	0.1116710
N	0.7263596	2.5682808	1.3051237
N	0.2223081	2.1188884	-1.388540
O	1.8492909	-1.792344	-1.457816
C	2.6448439	0.9259661	1.1896224
H	3.7388863	0.9062460	1.1360783
H	2.3237122	0.2970298	2.0195595
C	-1.071666	2.2170822	-2.106985
H	-1.256098	1.2741988	-2.638624
H	-1.043415	3.0116885	-2.860339
C	-0.128774	1.1945983	3.1397502
C	-2.973736	2.0186485	1.0260910
H	-2.767297	1.5726955	1.9928167
C	-0.648102	-0.997110	2.5694384
H	-0.829128	-1.717890	1.7851509
C	0.0799006	2.5984375	2.6396975
H	-0.899356	3.0745790	2.5315362
H	0.6558710	3.1964511	3.3531125
C	-3.379644	3.0793722	-1.466553
H	-3.500457	3.4864298	-2.465147
C	2.2078156	2.3665951	1.4161419
H	2.5492893	2.6683203	2.4107339
H	2.6994932	3.0297225	0.7060616
C	-4.396102	3.1693482	-0.517764
H	-5.334808	3.6555146	-0.765581
C	2.4601062	1.0381242	-1.322694
H	3.1193167	0.4007030	-1.913861
H	3.0547047	1.9088133	-1.049573

C	4.1170893	-1.591647	-0.110469
C	0.4097192	3.7771652	0.4981353
H	0.9931416	4.6408789	0.8379911
H	-0.644862	4.0041124	0.6456673
C	0.6963258	3.4934148	-0.973374
H	0.2076917	4.2503799	-1.592302
H	1.7638142	3.5640723	-1.177409
C	4.8158384	-1.700581	-1.317792
H	4.2875175	-1.681124	-2.264714
C	-2.187378	2.4471302	-1.121002
C	1.2577224	1.4129586	-2.185896
H	1.5967656	2.0405980	-3.019292
H	0.8034202	0.5149608	-2.606005