Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

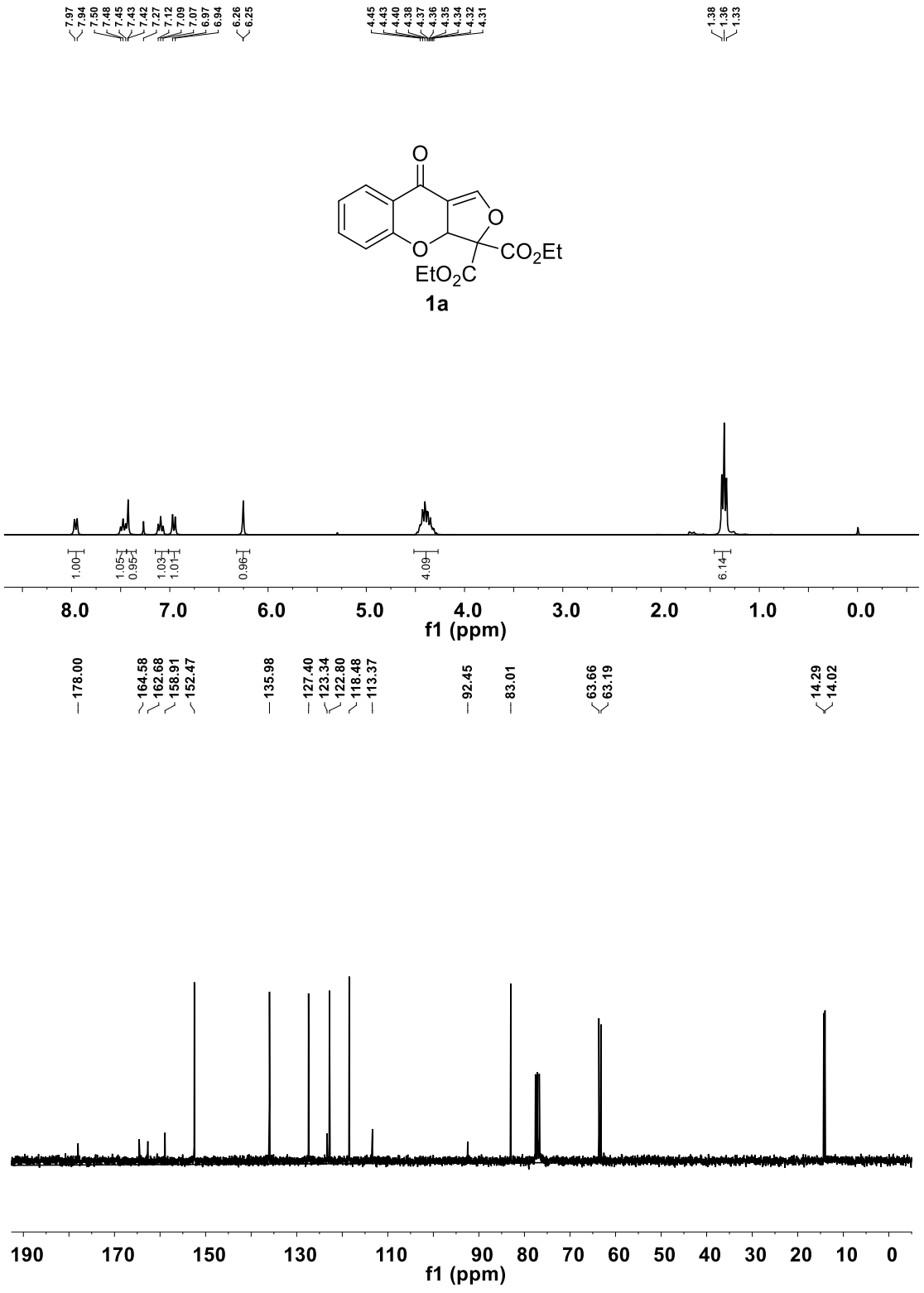
Supplementary Information

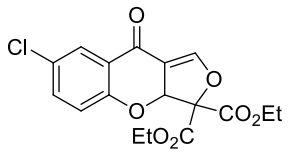
Unprecedented formation of 3-(tetrahydrofuran-2-yl)-4*H*-chromen-4-one in the reaction between 3,3*a*-dihydro-9*H*-furo[3,4-*b*]chromen-9-one with malononitrile

Table of Contents

1. NMR spectra

1.1 ^{1}H and ^{13}C NMR spectra of compounds 1-10

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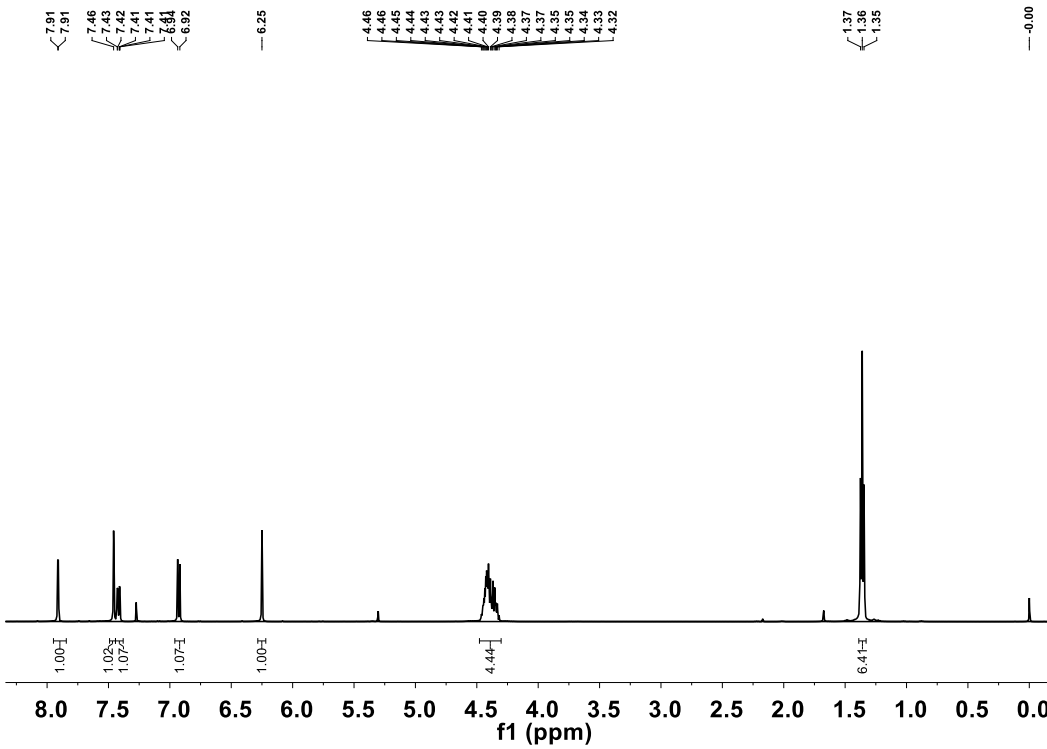
1b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4.33
4.32
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1.07
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1.00
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6.41
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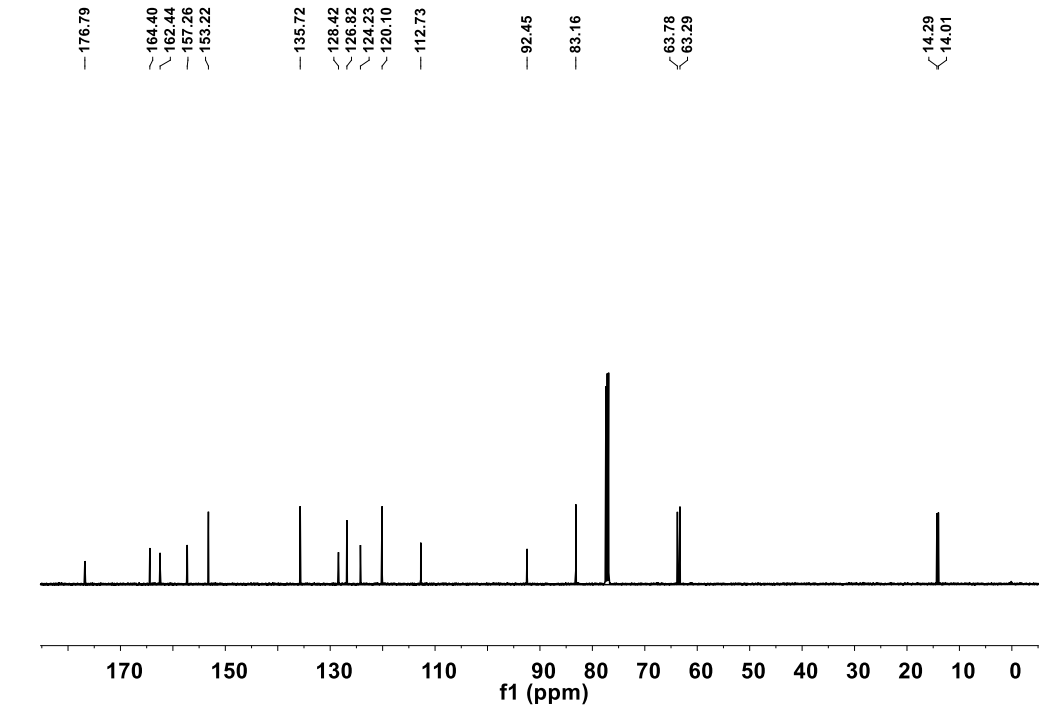
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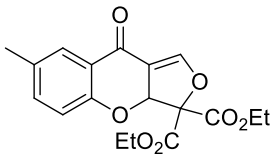
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CO2Et
EtO2C

1c


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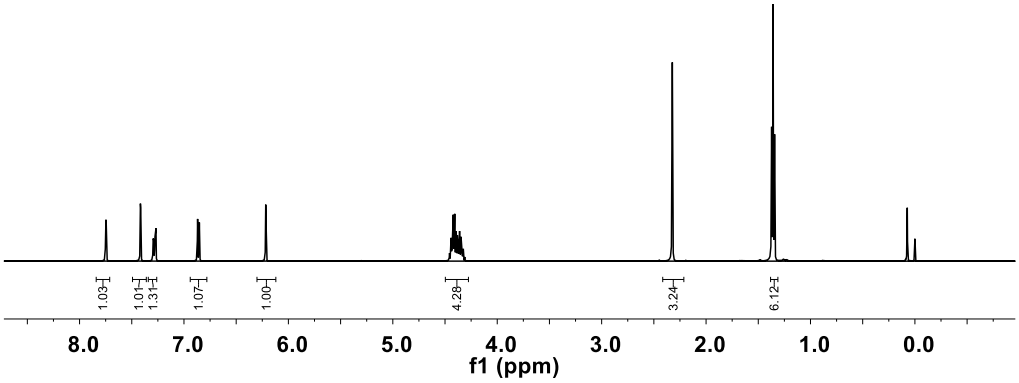
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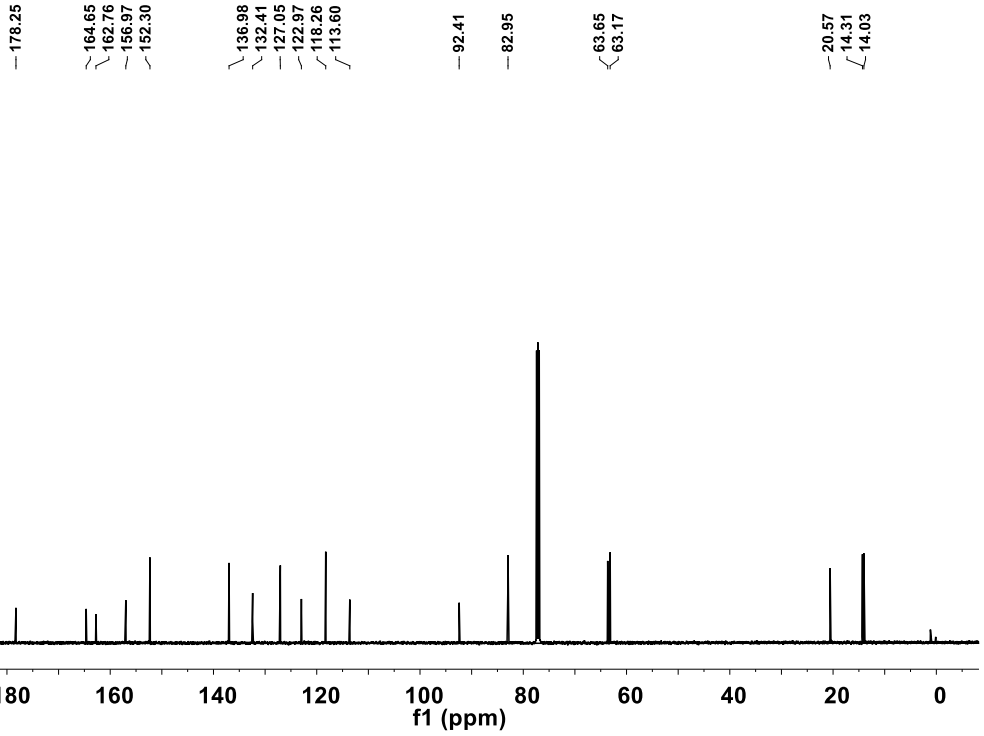
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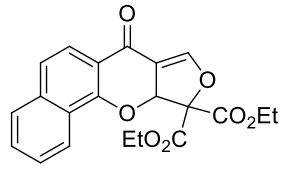
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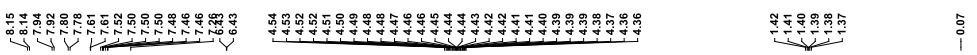
EtO2C

1d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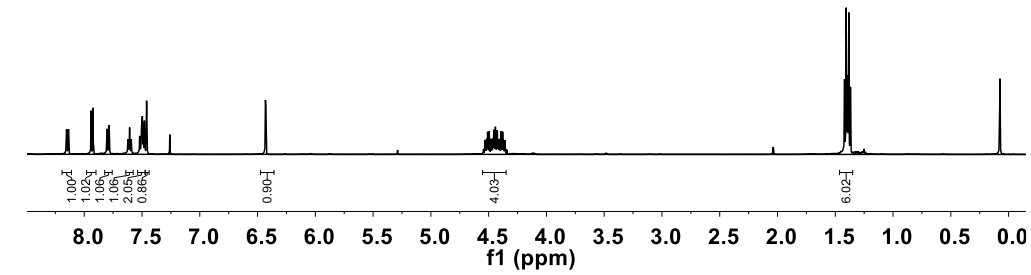
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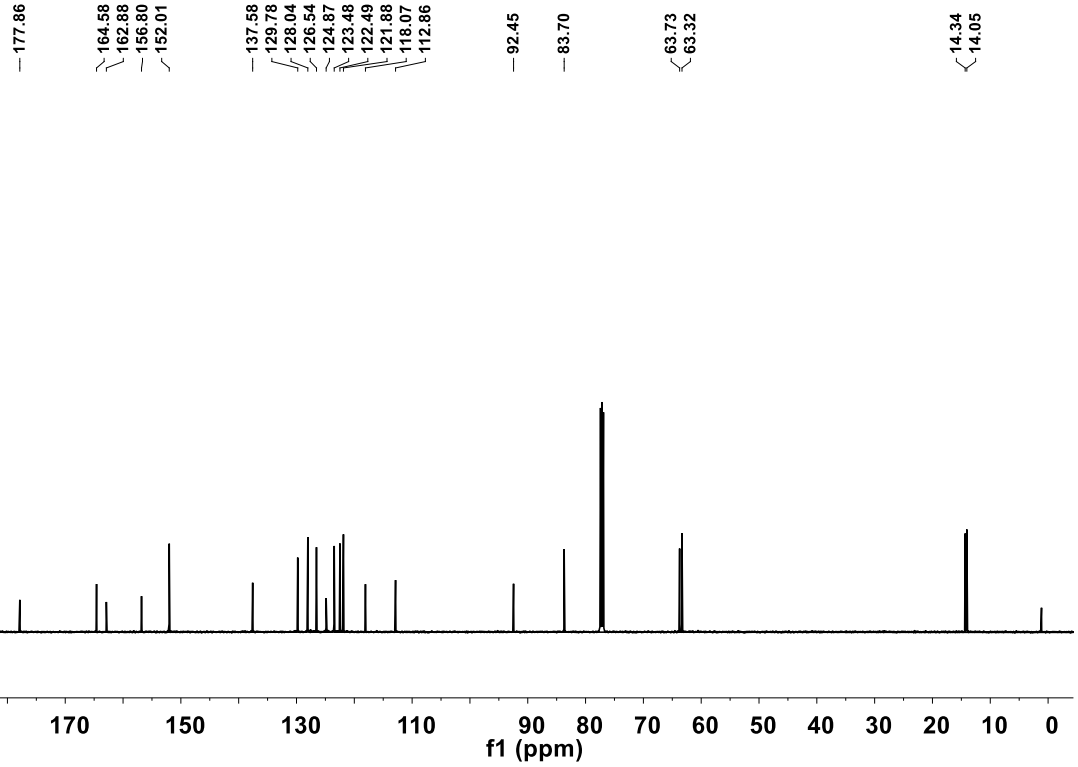
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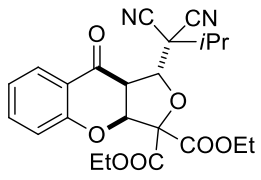
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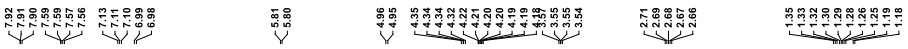
3a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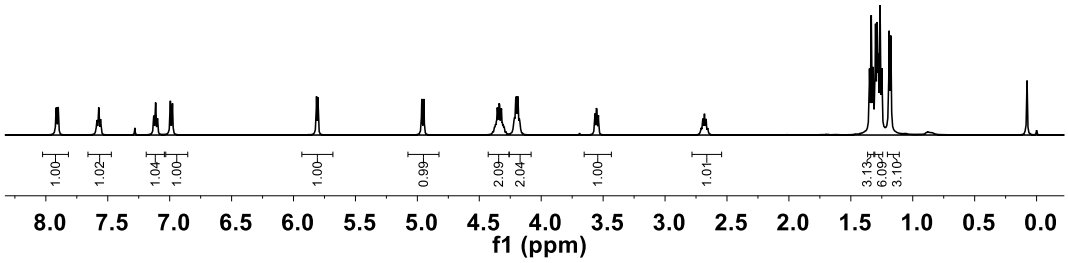
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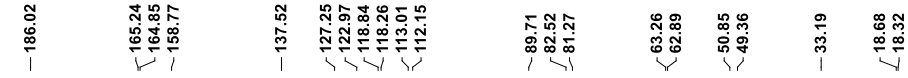
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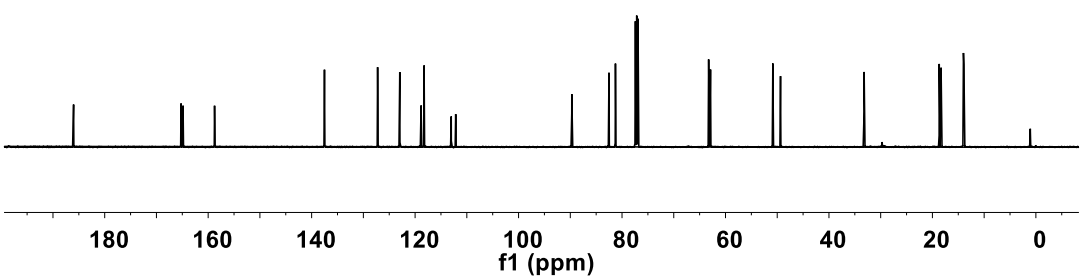
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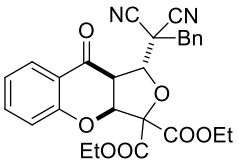
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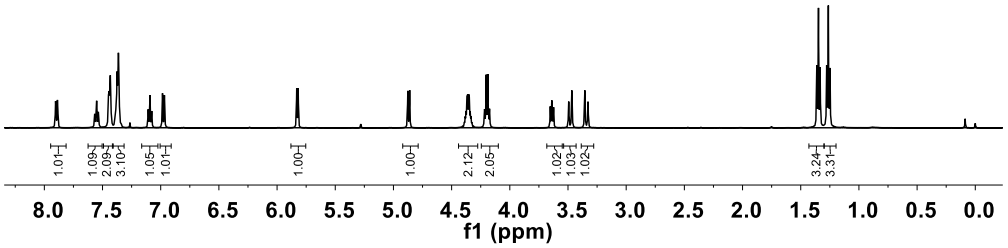
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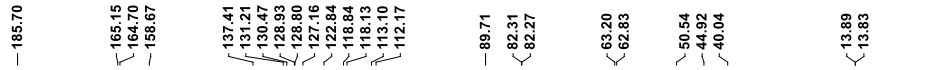
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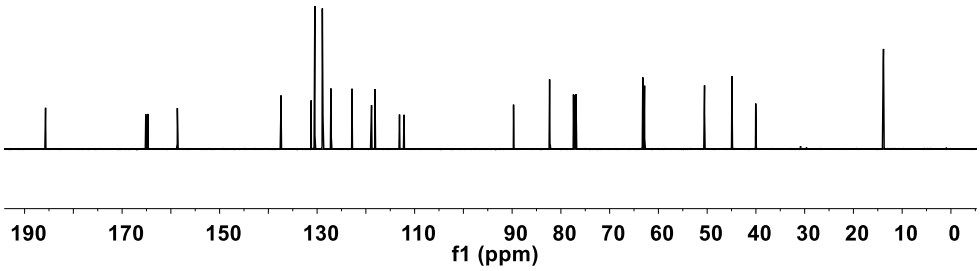
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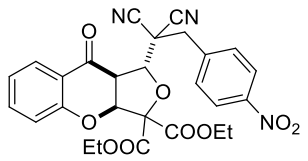
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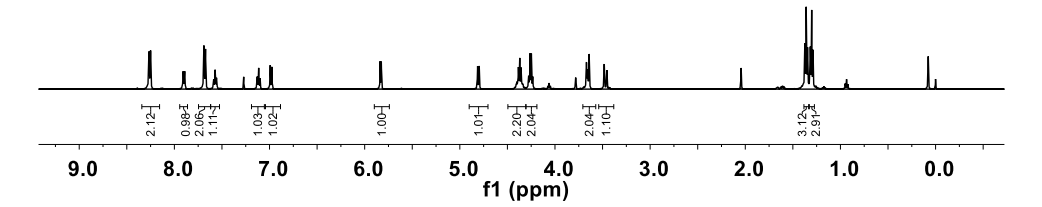
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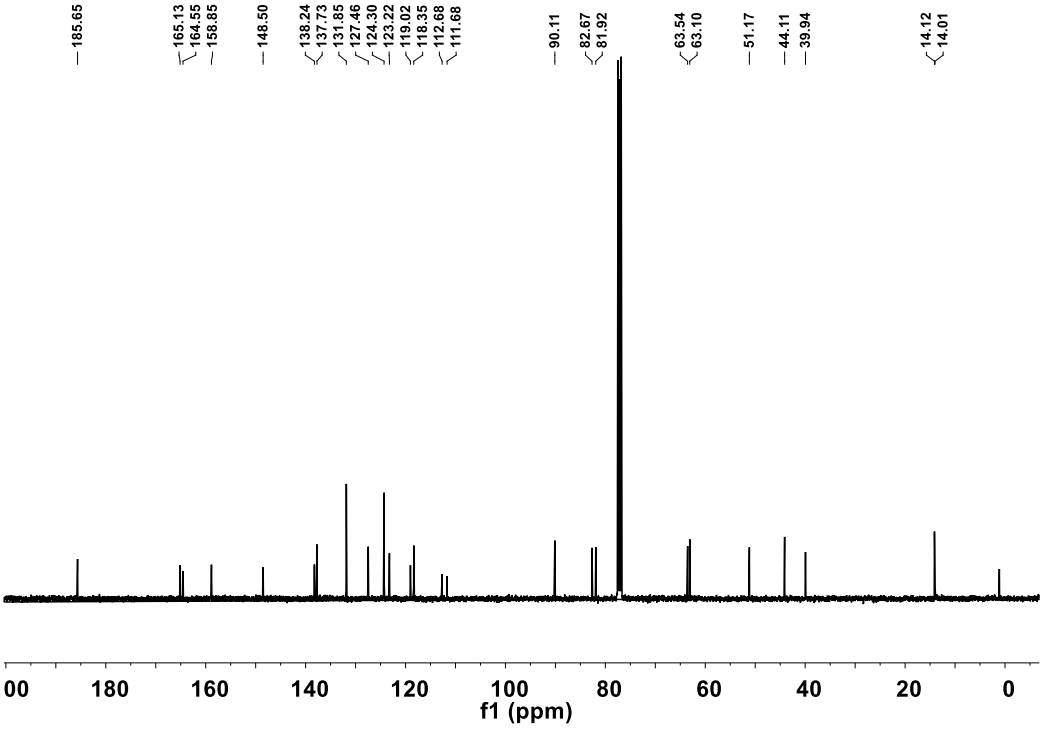
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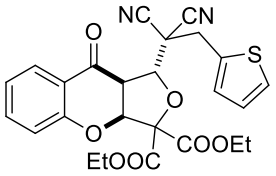
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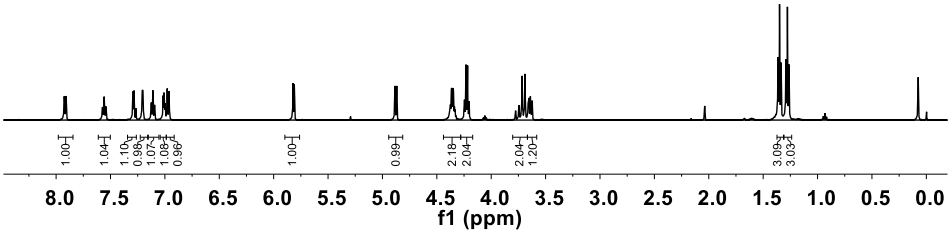
3d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f1 (ppm)


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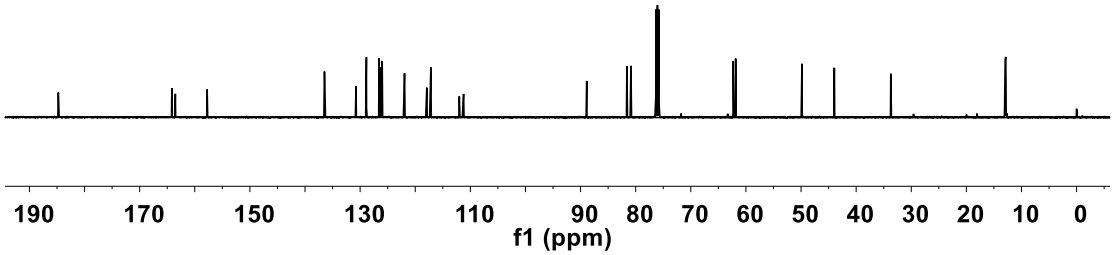
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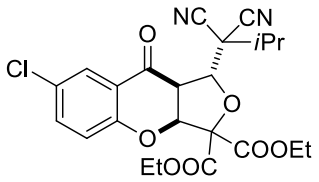
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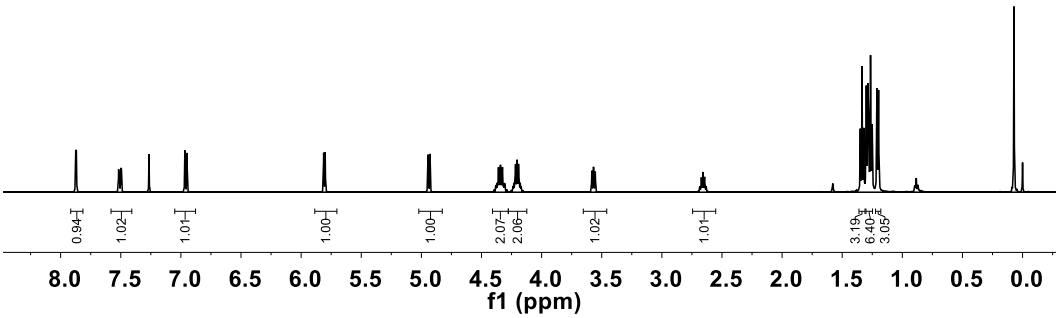
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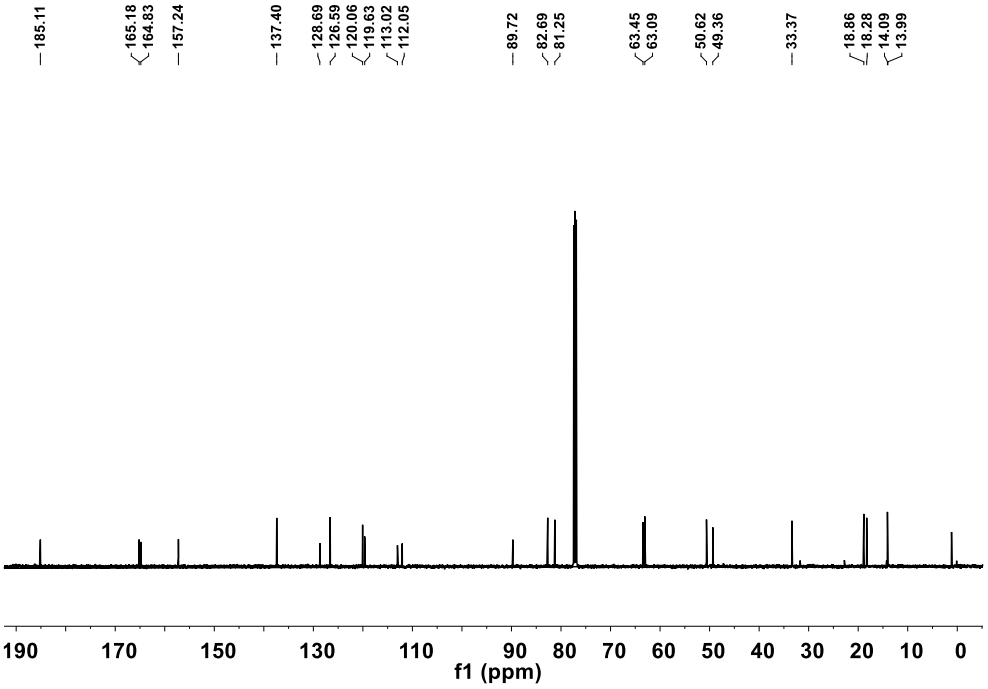
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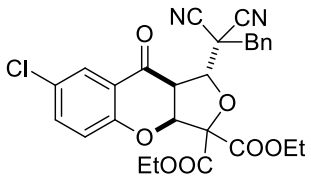
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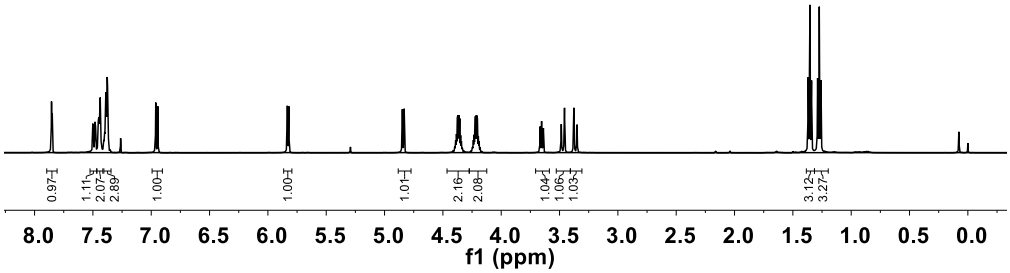
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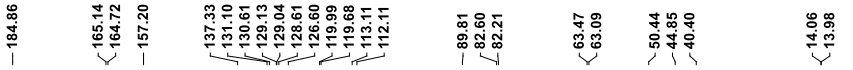
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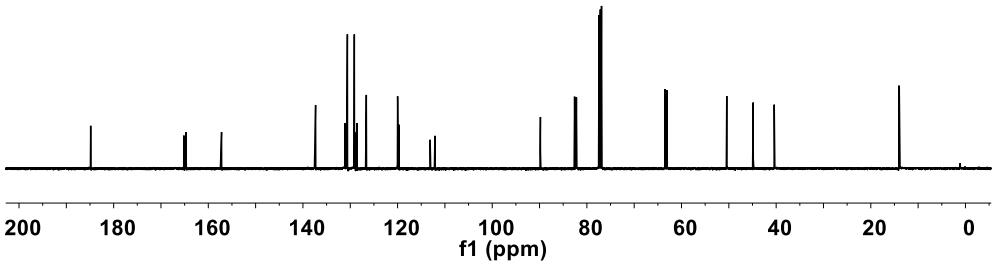
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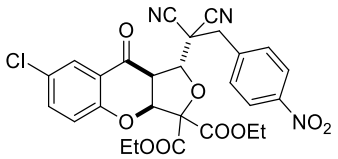
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O
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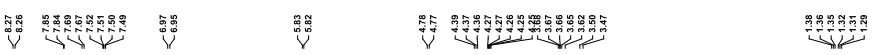
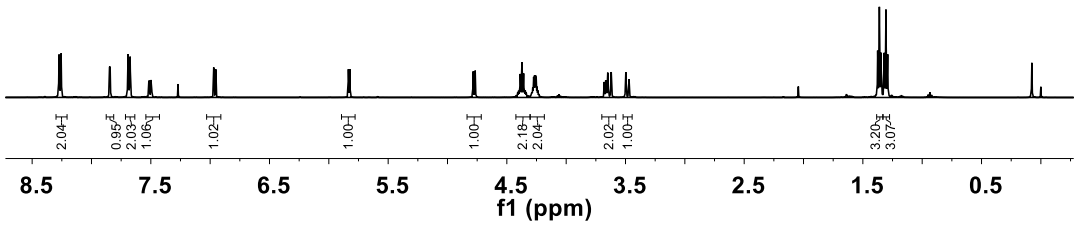
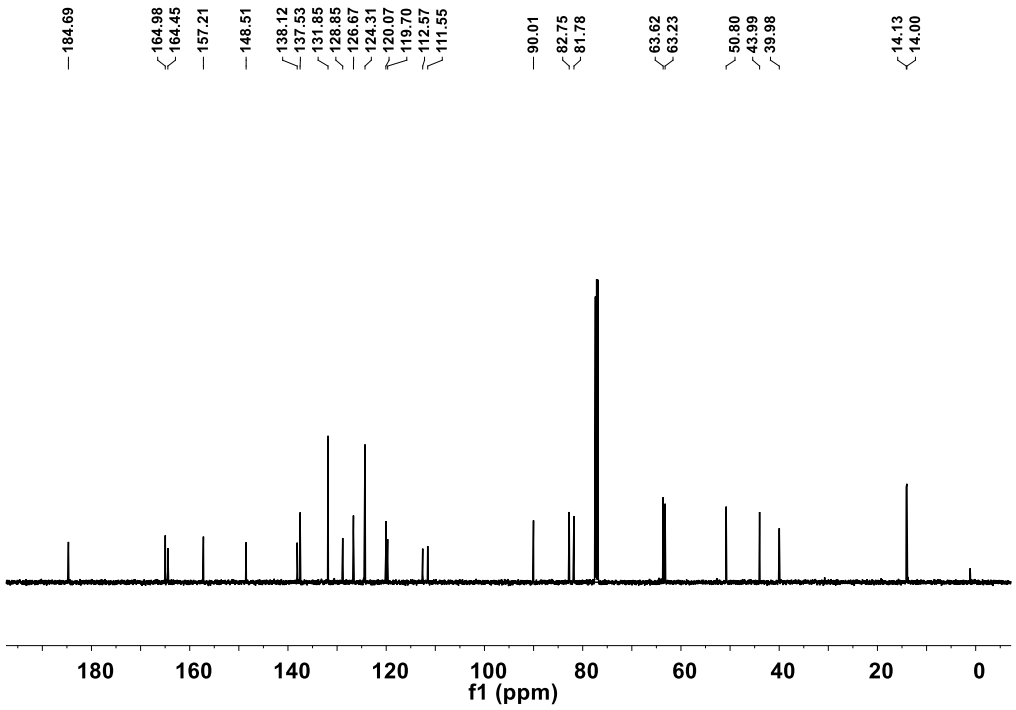
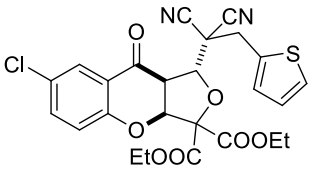
COOEt
NO2
EtOOC

3g

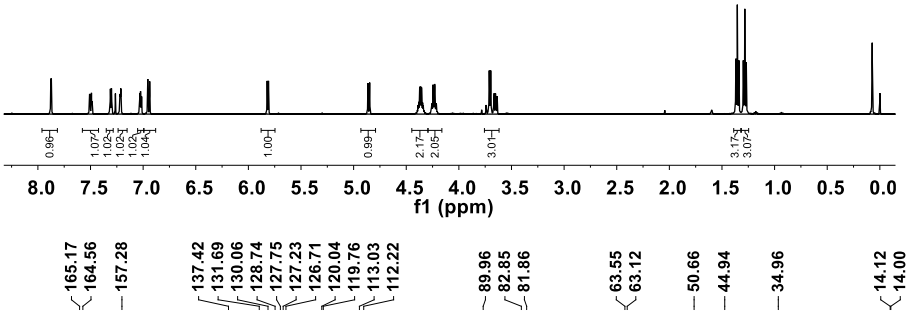

8.27
8.26
7.85
7.84
7.69
7.67
7.52
7.51
7.50
7.48
6.97
6.95
5.83
5.82
4.78
4.77
4.39
4.37
4.36
4.27
4.27
4.26
4.25
3.68
3.67
3.66
3.62
3.50
3.47
1.38
1.36
1.35
1.32
1.31
1.29


2.04
0.95
2.03
1.06
1.02
1.00
1.00
2.18
2.04
2.02
1.00
3.20
3.07
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

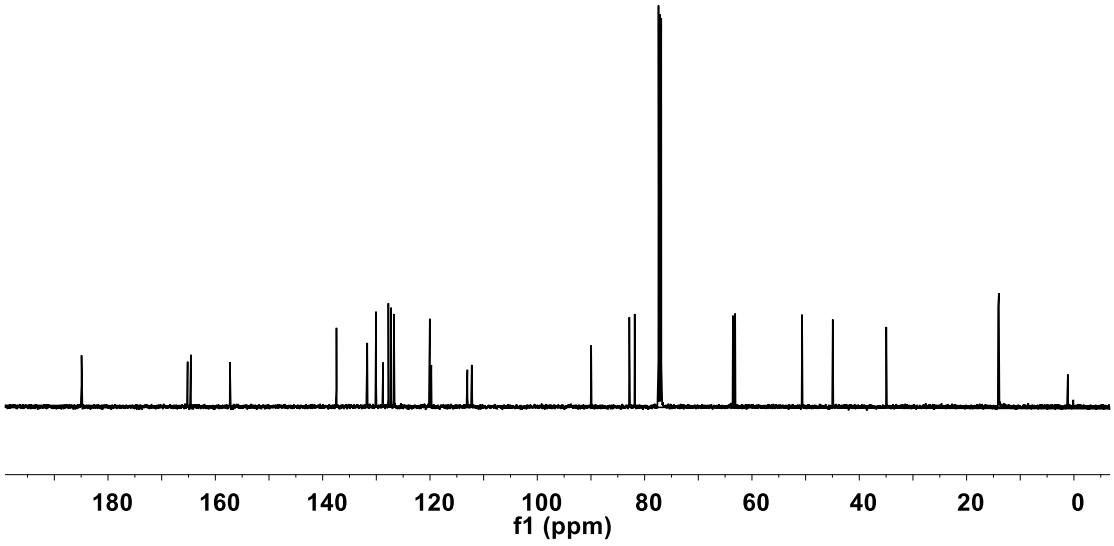

184.69
164.98
164.45
157.21
148.51
138.12
137.53
131.85
128.85
126.67
124.31
120.07
119.70
112.57
111.55
90.01
82.75
81.78
63.62
63.23
50.80
43.99
39.98
14.13
14.00
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

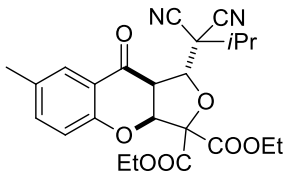

NC
CN
O
Cl
S
O
O
COOEt
EtOOC

3h

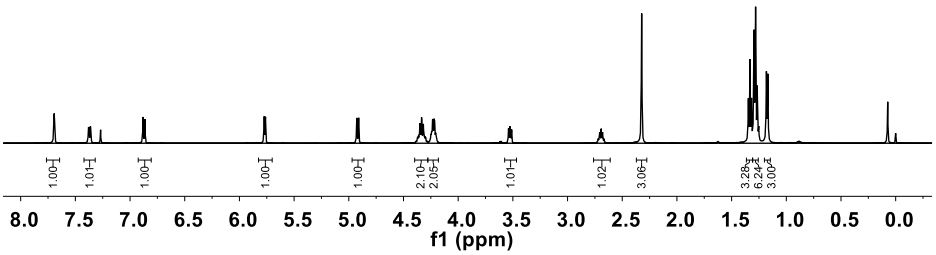

0.96
1.07
1.02
1.02
1.02
1.04
1.00
0.99
2.17
2.05
3.01
3.17
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

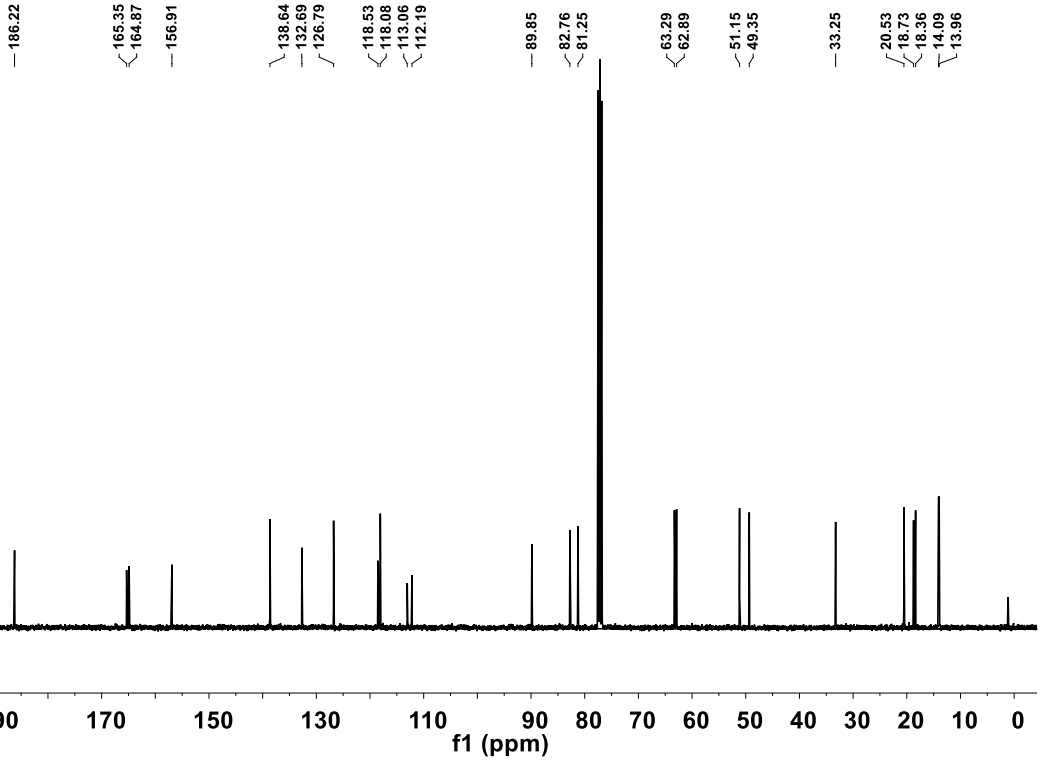
184.93
165.17
164.56
157.28
137.42
131.69
130.06
128.74
127.75
127.23
126.71
120.04
119.76
113.03
112.22
89.96
82.85
81.86
63.55
63.12
50.66
44.94
34.96
14.12
14.00

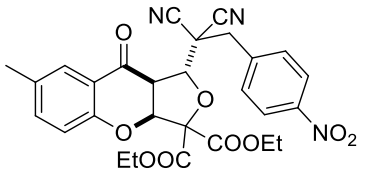

180
160
140
120
100
80
60
40
20
0
f1 (ppm)


NC
CN
iPr
O
O
O
COOEt
EtOOC

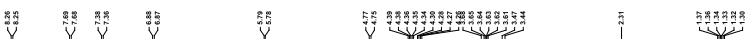
3i

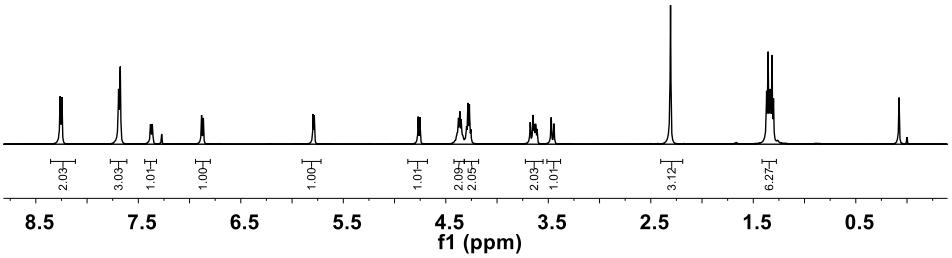

1.00
1.01
1.00
1.00
1.00
2.10
2.06
1.01
1.02
3.06
3.28
6.24
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


186.22
165.35
164.87
156.91
138.64
132.69
126.79
118.53
118.08
113.06
112.19
89.85
82.76
81.25
63.29
62.89
51.15
49.35
33.25
20.53
18.73
18.36
14.09
13.96
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

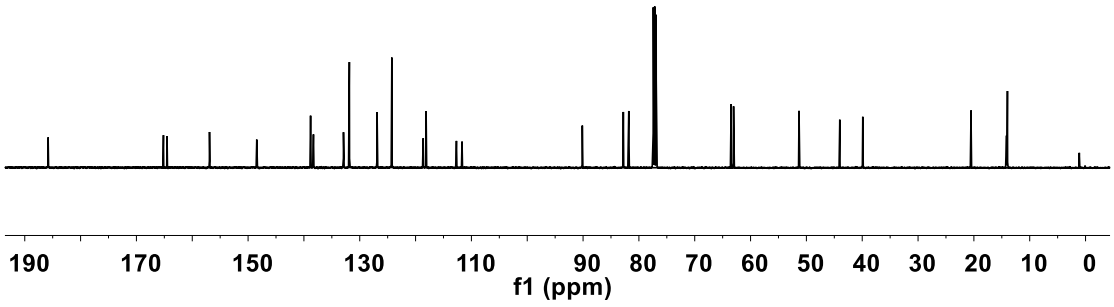

NC
CN
O
O
O
NO2
EtOOC
COOEt

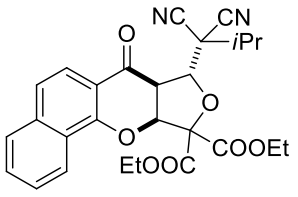
3j



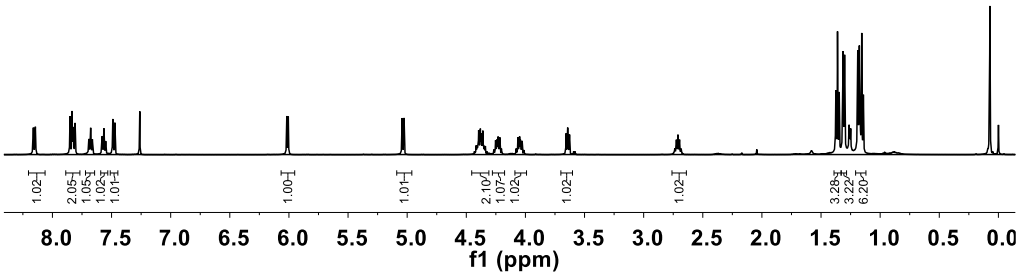

2.03
3.03
1.01
1.00
1.00
1.01
2.09
2.05
2.03
1.01
3.12
6.27
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

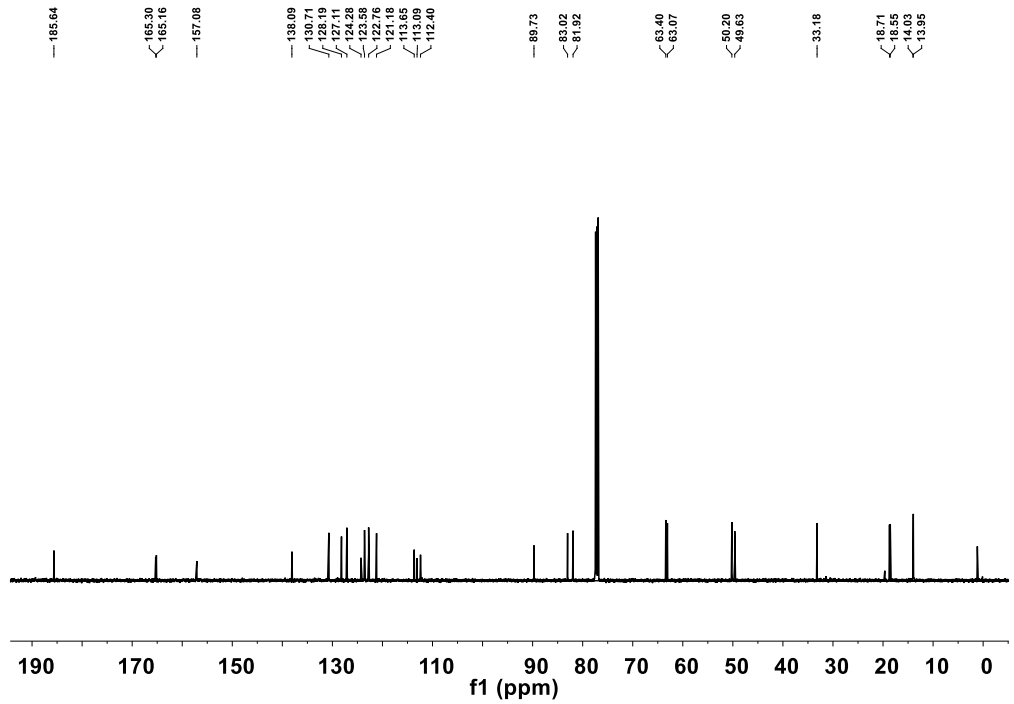

185.81
165.16
164.52
156.91
148.45
138.80
138.29
132.91
131.86
126.89
124.25
118.63
118.11
112.68
111.68
90.13
82.79
81.81
63.48
63.04
51.32
44.02
39.90
20.51
14.14
13.99

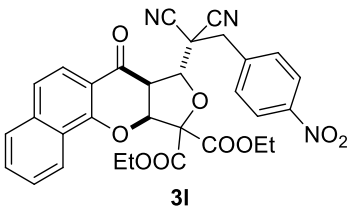

190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NC
CN
iPr
O
O
O
COOEt
EtOOC

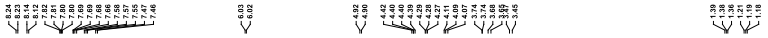
3k

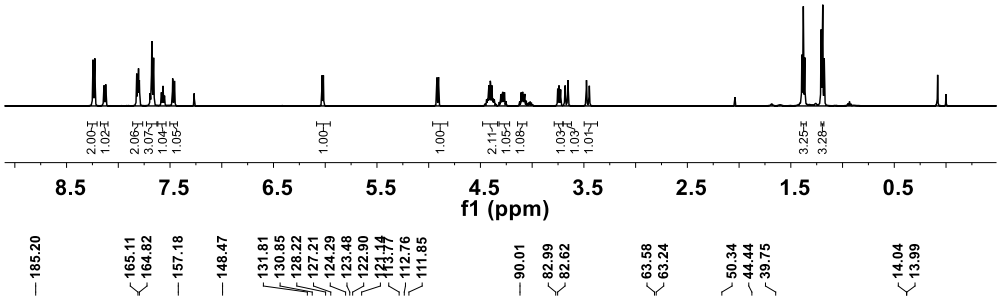

1.02
2.05
1.05
1.02
1.01
1.00
1.01
2.10
1.07
1.02
1.02
1.02
3.28
3.22
6.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


185.64
165.30
165.16
157.08
138.09
130.71
128.19
127.11
124.28
123.58
122.76
121.18
113.65
113.09
112.40
89.73
83.02
81.92
63.40
63.07
50.20
49.63
33.18
18.71
18.55
14.03
13.95
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NC
CN
O
O
O
NO2
COOEt
EtOOC

3l




2.00
1.02
2.06
3.07
1.04
1.05
1.00
1.00
2.11
1.05
1.08
1.03
1.03
1.01
3.25
3.28
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

185.20
165.11
164.82
157.18
148.47
131.81
130.85
128.22
127.21
124.29
123.48
122.90
112.76
111.85
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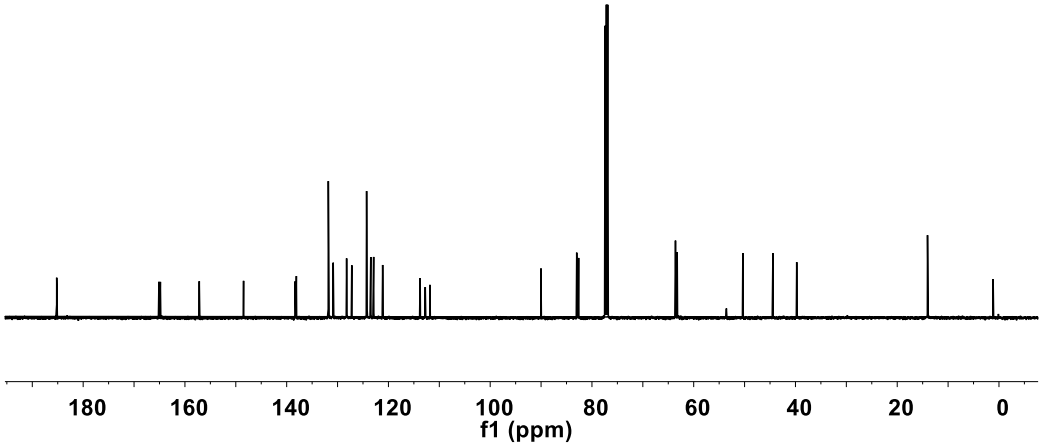
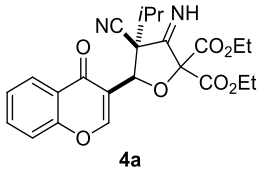
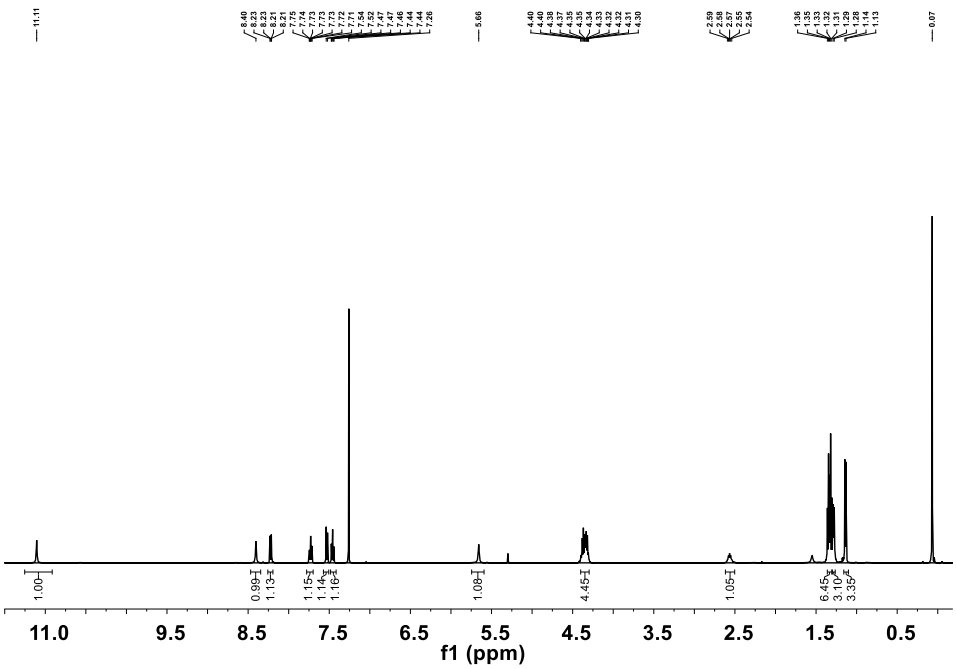
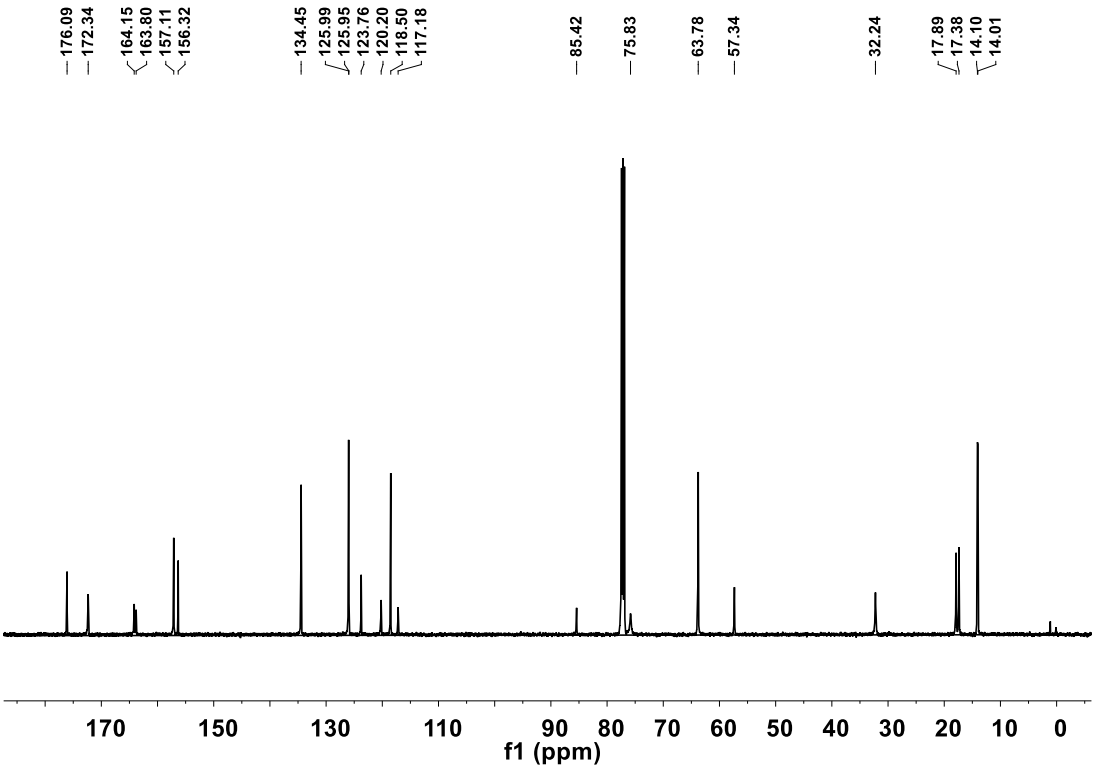
63.24
50.34
44.44
39.75
14.04
13.99

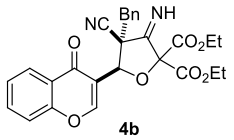

180
160
140
120
100
80
60
40
20
0
f1 (ppm)


NC
iPr NH
O
CO2Et
CO2Et
O
O

4a


11.11
8.40
8.23
8.23
8.21
8.21
7.75
7.74
7.73
7.73
7.72
7.72
7.71
7.71
7.54
7.52
7.47
7.47
7.46
7.45
7.44
7.44
7.28
5.66
4.40
4.40
4.38
4.37
4.37
4.35
4.34
4.33
4.32
4.32
4.31
4.30
2.59
2.58
2.57
2.56
2.55
2.54
1.38
1.35
1.33
1.32
1.31
1.29
1.28
1.14
1.13
0.07
1.00
0.99
1.13
1.15
1.14
1.16
1.18
1.08
4.45
1.05
6.45
3.15
3.33
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


176.09
172.34
164.15
163.80
157.11
156.32
134.45
125.99
125.95
123.76
120.20
118.50
117.18
85.42
75.83
63.78
57.34
32.24
17.89
17.38
14.10
14.01
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NC
Bn
NH
O
CO2Et
CO2Et
O
O

4b


11.29
8.29
8.28
8.27
7.74
7.72
7.60
7.59
7.53
7.51
7.49
7.48
7.32
7.30
7.29
7.27
7.68
5.69
4.36
4.35
4.35
4.34
4.32
3.98
3.97
3.96
3.96
3.94
3.90
3.89
3.88
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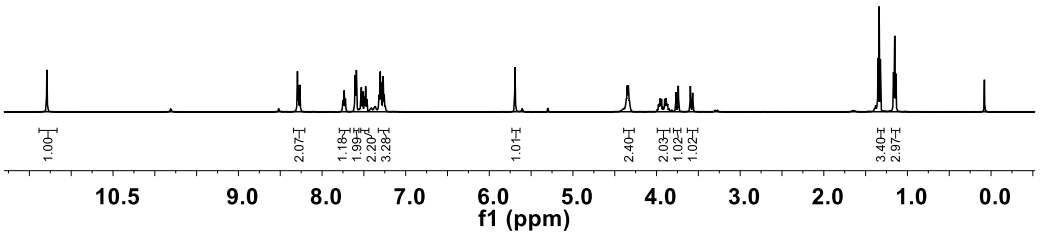
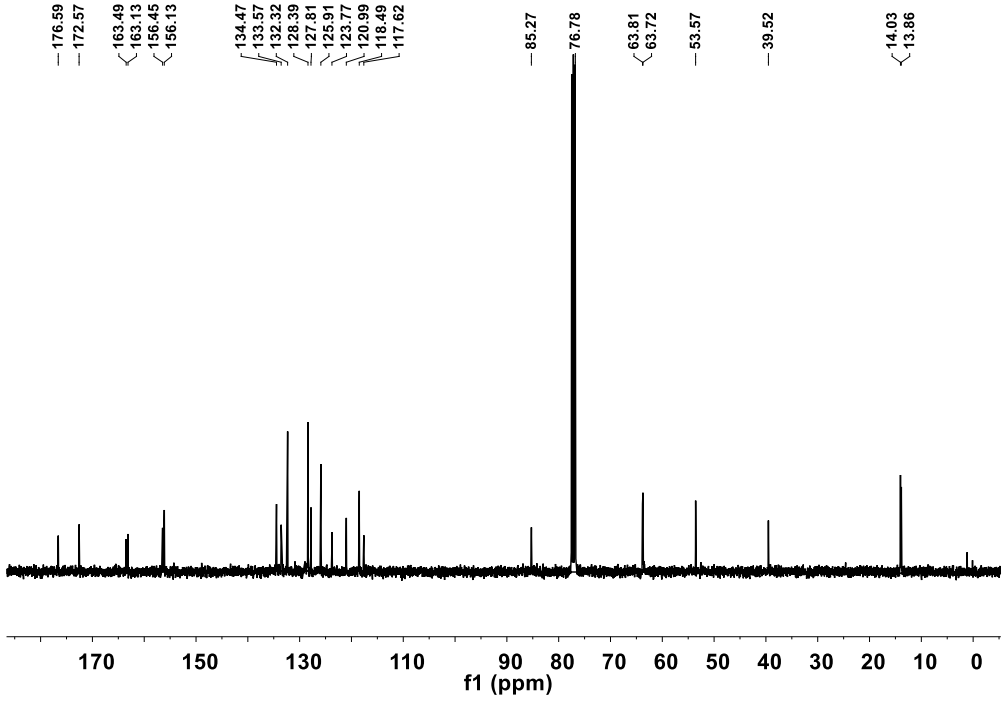
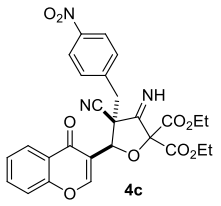
1.35
1.34
1.32
1.17
1.15
1.14

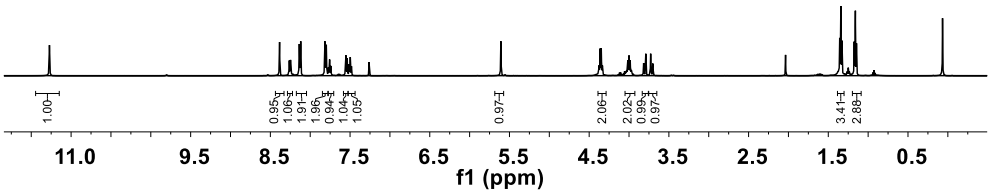

1.00
2.07
1.18
1.99
2.20
3.28
1.01
2.40
2.03
1.02
1.02
3.40
2.97
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


176.59
172.57
163.49
163.13
156.45
156.13
134.47
133.57
132.32
128.39
127.81
125.91
123.77
120.99
118.49
117.62
85.27
76.78
63.81
63.72
53.57
39.52
14.03
13.86
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

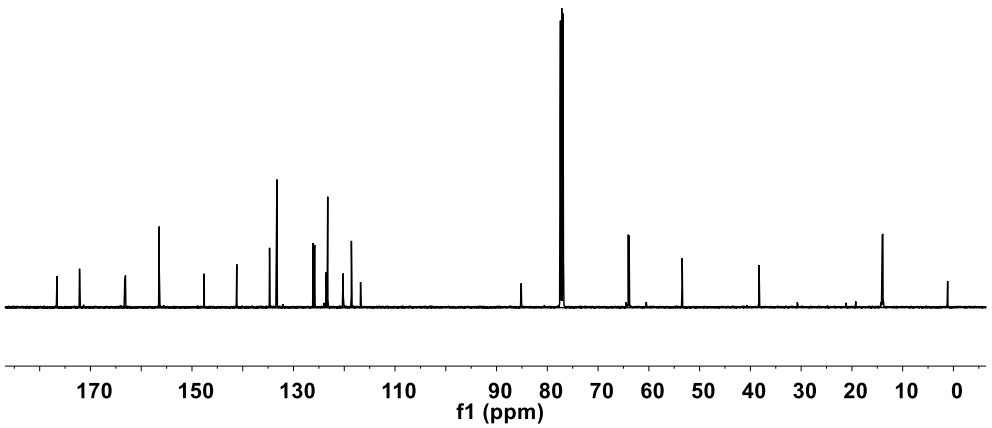

O2N
NC
NH
CO2Et
CO2Et
O
O
O

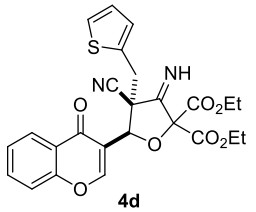
4c


11.27
8.38
8.26
8.25
8.14
8.12
7.82
7.80
7.77
7.77
7.76
7.74
7.74
7.55
7.54
7.51
7.50
7.48
7.26
5.61
4.38
4.36
4.35
4.33
4.04
4.03
4.02
4.02
4.00
3.98
3.98
3.97
3.82
3.79
3.73
3.70
2.04
1.36
1.34
1.33
1.17
1.16
1.15

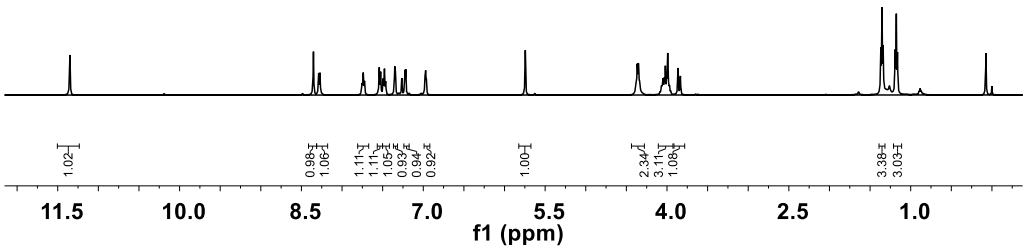

1.00
0.95
1.06
1.91
1.96
0.94
1.04
1.05
0.97
2.06
2.02
0.99
0.97
3.41
2.88
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

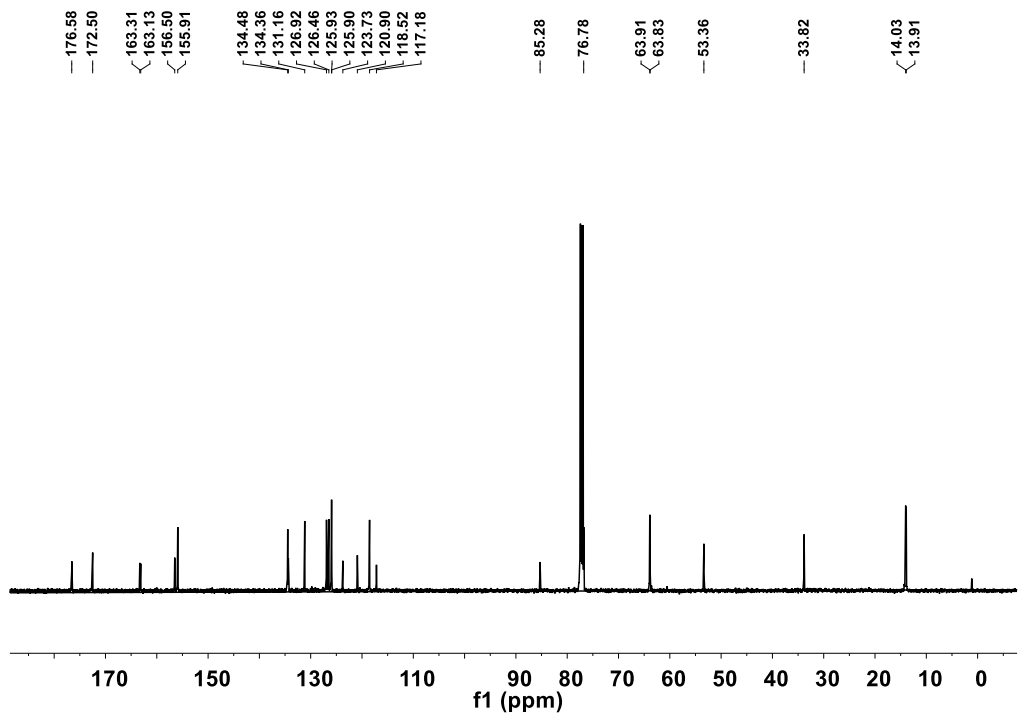

176.60
172.15
163.25
163.10
156.45
147.59
141.18
134.71
133.26
126.11
125.83
123.58
123.26
120.22
118.59
116.79
85.14
76.81
64.05
63.89
53.43
38.28
14.01
13.90

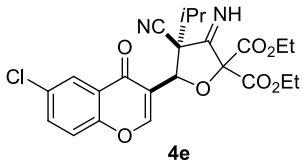

170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
NC
NH
O
CO2Et
CO2Et
O
O

4d


1.02
0.98
1.06
1.11
1.11
1.05
0.93
0.94
0.92
1.00
2.34
3.11
1.08
3.38
3.03
11.5
10.0
8.5
7.0
5.5
4.0
2.5
1.0
f1 (ppm)


176.58
172.50
163.31
163.13
156.50
155.91
134.48
134.36
131.16
126.92
126.46
125.93
125.90
123.73
120.90
118.52
117.18
85.28
76.78
63.91
63.83
53.36
33.82
14.03
13.91
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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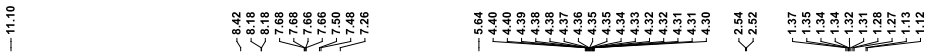
iPr NH
O
CO2Et
Cl
O
CO2Et
O

4e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8.42
8.18
8.18
7.68
7.68
7.66
7.66
7.50
7.48
7.26
5.64
4.40
4.39
4.38
4.38
4.37
4.36
4.35
4.35
4.34
4.33
4.32
4.32
4.31
4.31
4.30
2.54
2.52
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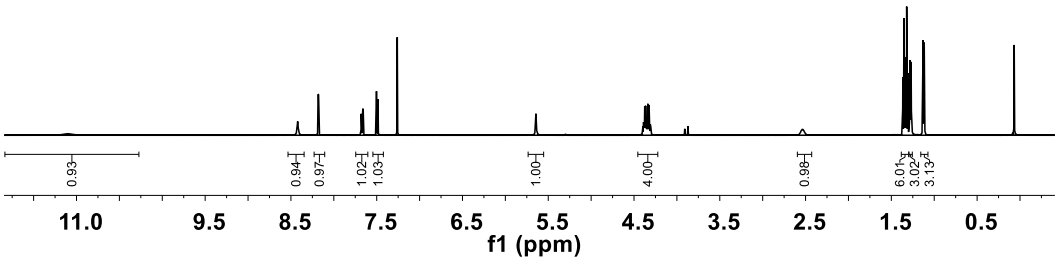
1.35
1.34
1.34
1.32
1.31
1.28
1.27
1.13
1.12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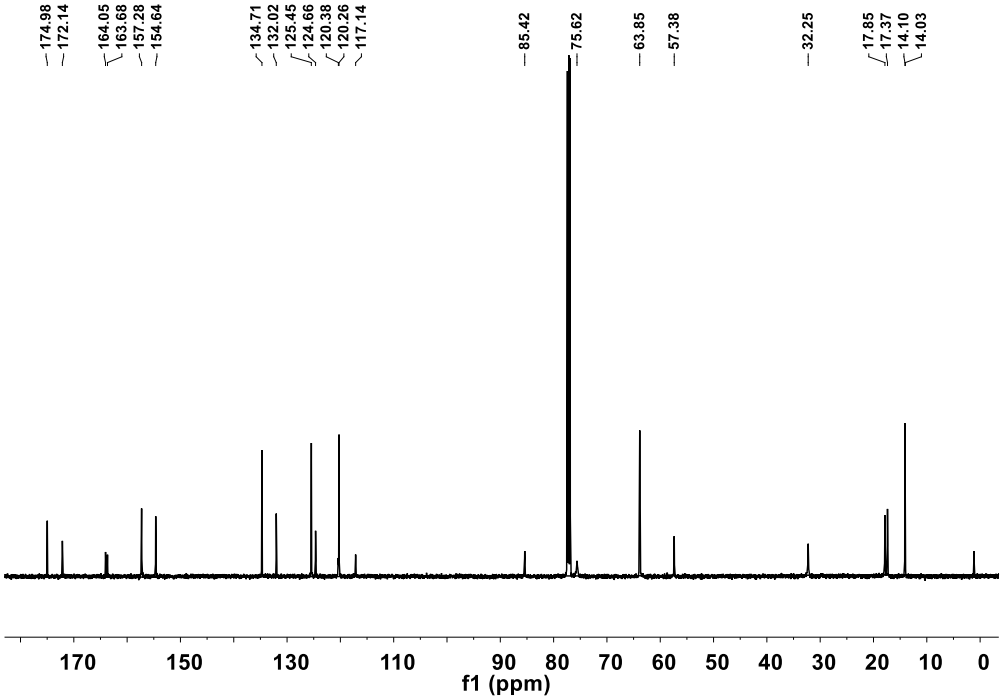
0.94
0.97
1.02
1.03
1.00
4.00
0.98
6.01
3.02
3.13
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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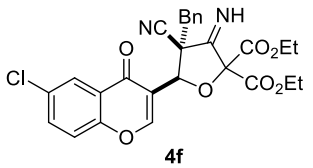
154.64
134.71
132.02
125.45
124.66
120.38
120.26
117.14
85.42
75.62
63.85
57.38
32.25
17.85
17.37
14.10
14.03
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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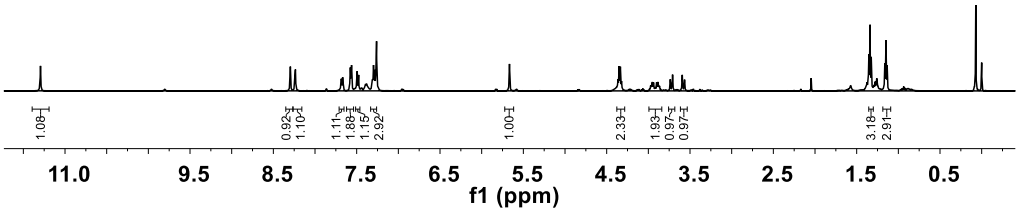
Bn
NH
O
CO2Et
CO2Et
Cl
O
O

4f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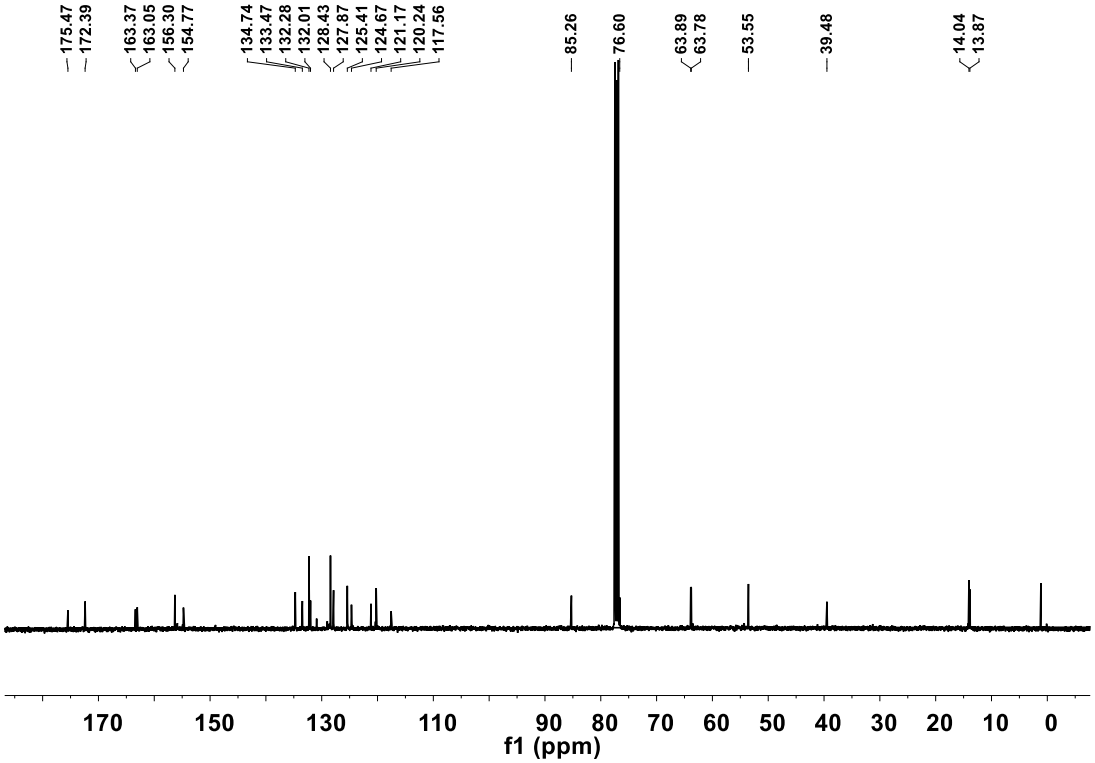
0.92
1.10
1.11
1.88
1.15
2.92
1.00
2.33
1.93
0.97
0.97
3.18
2.91
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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172.39
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163.05
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154.77
134.74
133.47
132.28
132.01
128.43
127.87
125.41
124.67
121.17
120.24
117.56
85.26
76.60
63.89
63.78
53.55
39.48
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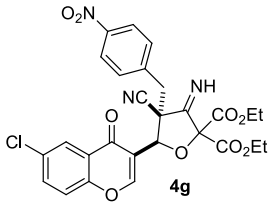
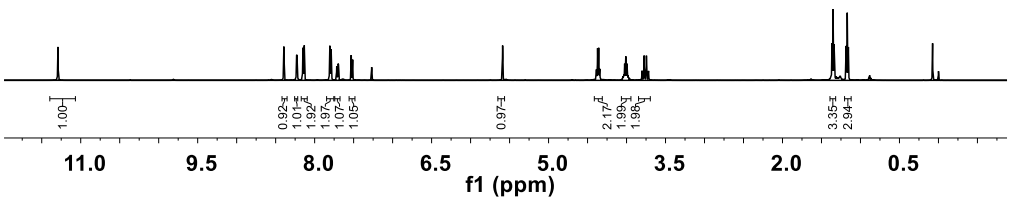
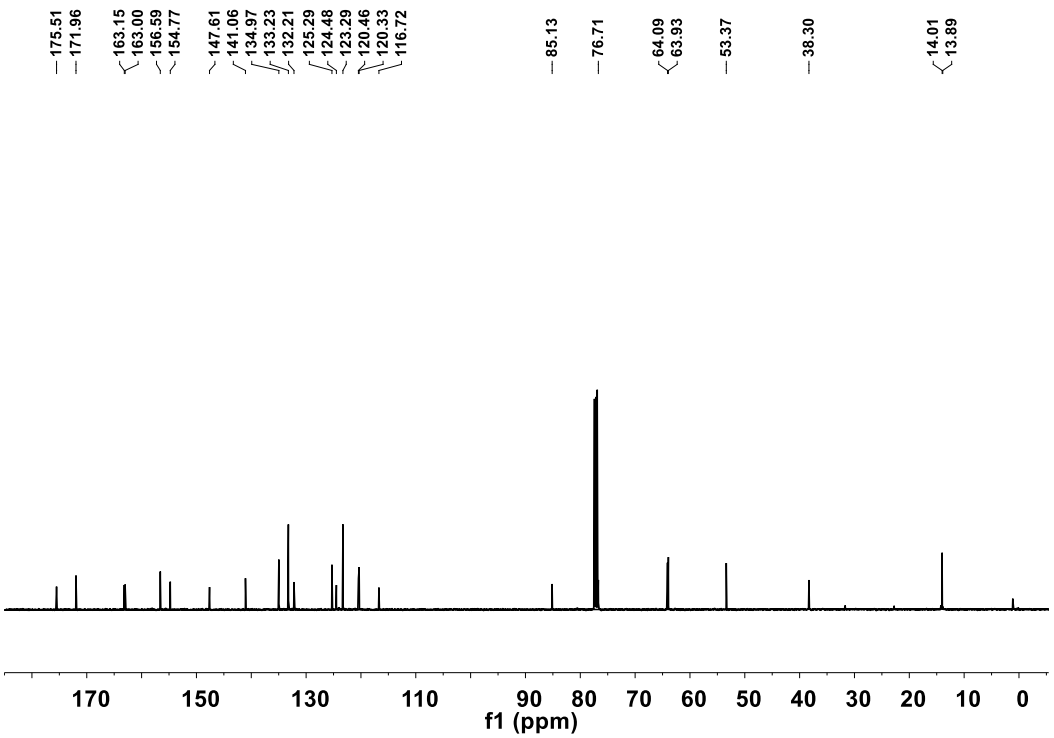
13.87
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O2N
NC
NH
CO2Et
CO2Et
O
Cl
O
O
4g


11.29
8.39
8.23
8.23
8.15
8.13
7.81
7.79
7.72
7.71
7.70
7.69
7.53
7.51
5.59
4.39
4.37
4.36
4.34
4.05
4.04
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.80
3.77
3.74
3.72
1.37
1.35
1.34
1.18
1.17
1.16


1.00
0.92
1.01
1.92
1.97
1.07
1.05
0.97
2.17
1.99
1.98
3.35
2.94
11.0
9.5
8.0
6.5
5.0
3.5
2.0
0.5
f1 (ppm)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171.96
163.15
163.00
156.59
154.77
147.61
141.06
134.97
133.23
132.21
125.29
124.48
123.29
120.46
120.33
116.72
85.13
76.71
64.09
63.93
53.37
38.30
14.01
13.89
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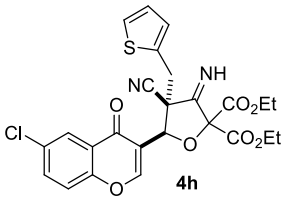
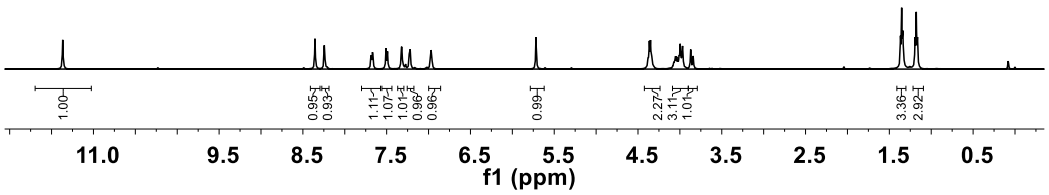
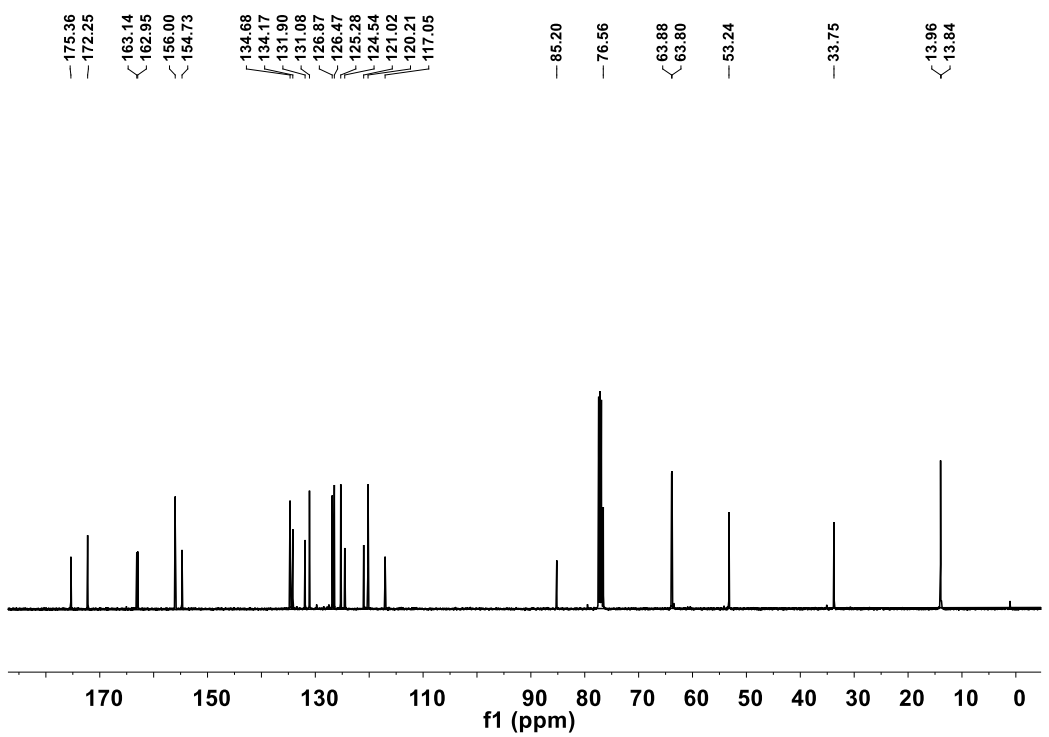
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
NC
NH
O
CO2Et
Cl
CO2Et
O
O
4h


11.37
8.36
8.24
8.24
7.69
7.68
7.67
7.51
7.49
7.23
7.22
7.23
6.98
6.97
5.72
4.38
4.36
4.35
4.34
4.07
4.05
4.04
4.02
4.00
3.98
3.97
3.87
3.84
1.37
1.35
1.34
1.19
1.18
1.16


1.00
0.95
0.93
1.11
1.07
1.01
0.96
0.96
0.99
2.27
3.11
1.01
3.36
2.92
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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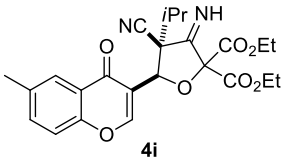
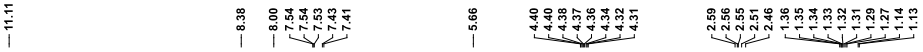
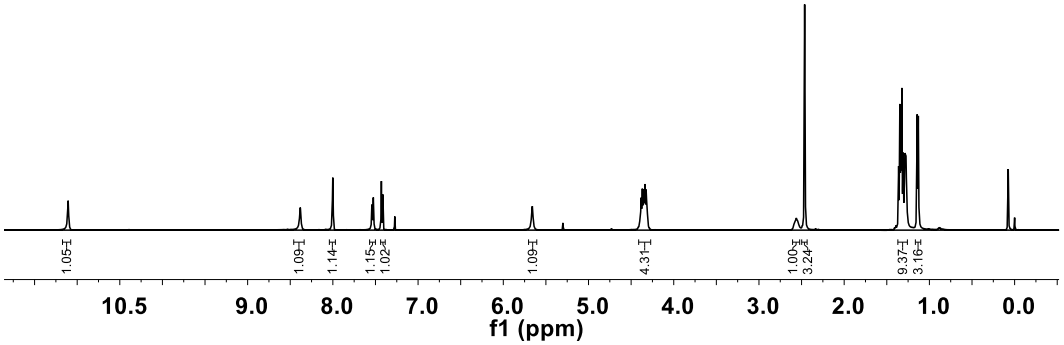
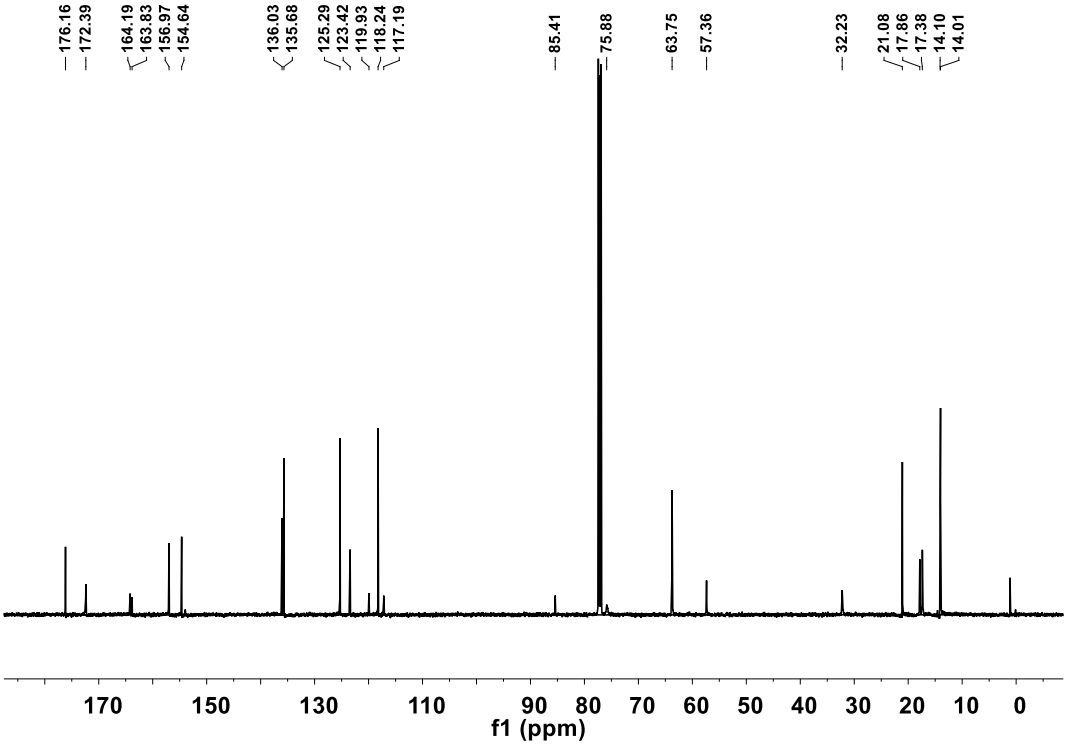
172.25
163.14
162.95
156.00
154.73
134.68
134.17
131.90
131.08
126.87
126.47
125.28
124.54
121.02
120.21
117.05
85.20
76.56
63.88
63.80
53.24
33.75
13.96
13.84
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NC
iPr NH
O
CO2Et
CO2Et
O
O

4i


11.11
8.38
8.00
7.54
7.54
7.53
7.43
7.41
5.66
4.40
4.40
4.38
4.37
4.36
4.34
4.32
4.31
2.59
2.56
2.55
2.51
2.46
1.36
1.35
1.34
1.33
1.32
1.31
1.29
1.27
1.14
1.13


1.05
1.09
1.14
1.15
1.02
1.09
4.31
1.00
3.24
9.37
3.16
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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156.97
154.64
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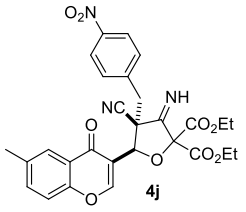
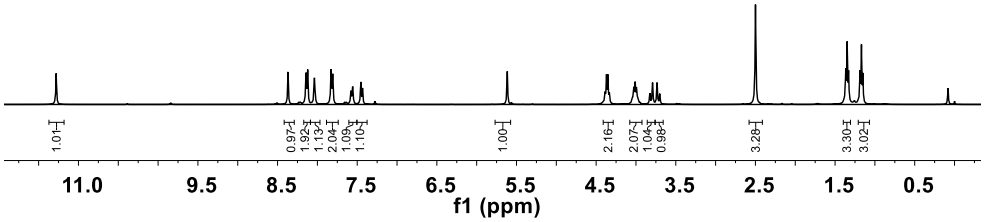
135.68
125.29
123.42
119.93
118.24
117.19
85.41
75.88
63.75
57.36
32.23
21.08
17.86
17.38
14.10
14.01
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O2N
NC
NH
O
CO2Et
CO2Et
O
O
4j


11.28
8.37
8.14
8.12
8.04
7.83
7.81
7.58
7.56
7.45
7.43
5.62
4.39
4.37
4.35
4.33
4.04
4.03
4.01
3.99
3.98
3.83
3.79
3.73
3.70
2.50
1.37
1.35
1.33
1.19
1.17
1.15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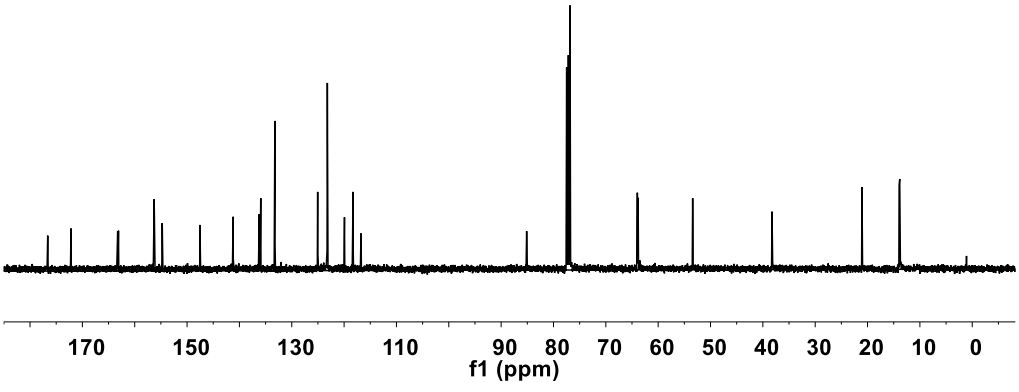
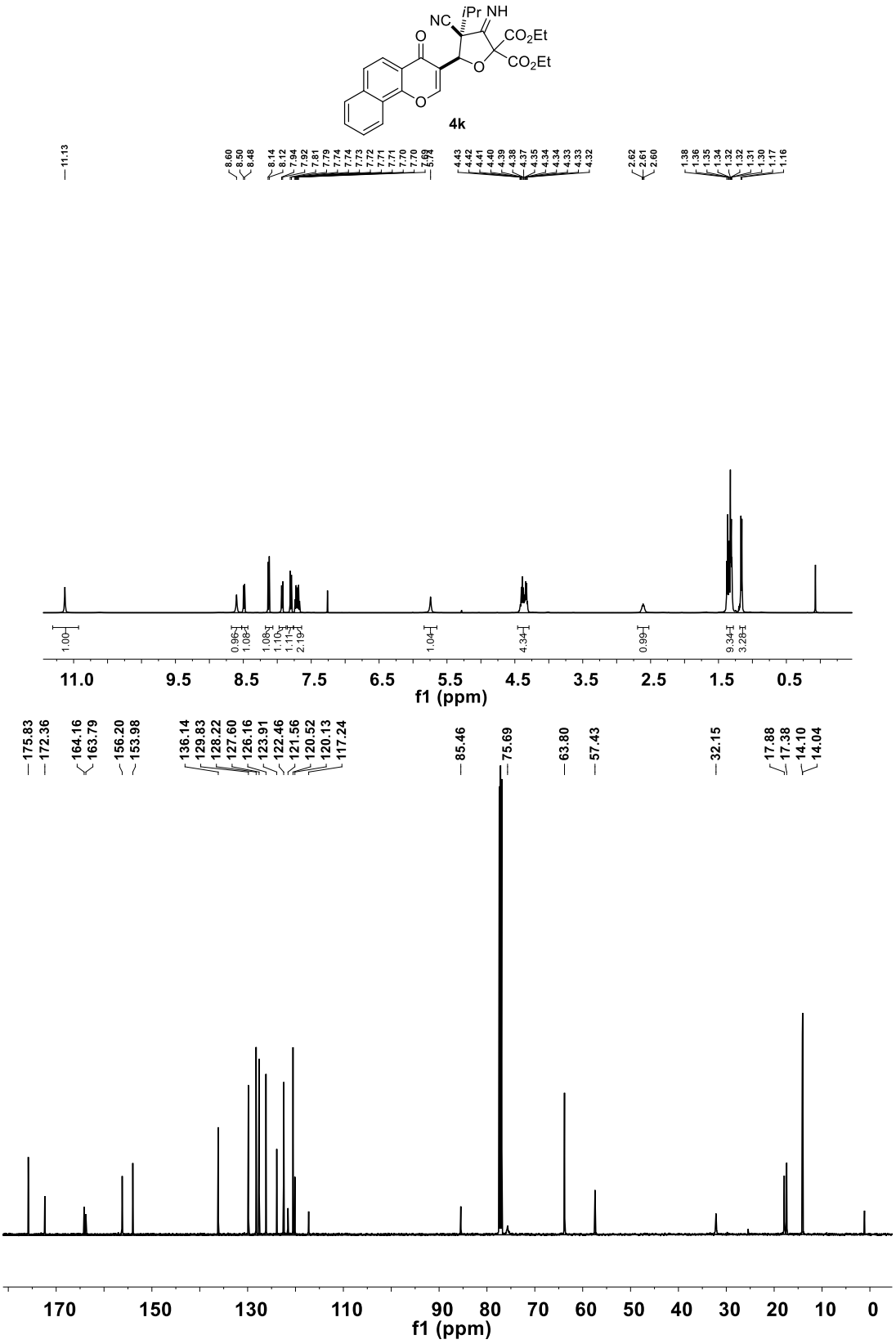
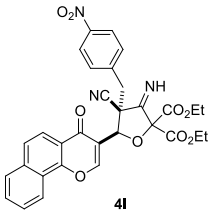
0.97
1.92
1.13
2.04
1.09
1.10
1.00
2.16
2.07
1.04
0.99
3.28
3.30
3.02
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


176.62
172.17
163.25
163.10
156.28
154.74
147.54
141.20
136.22
135.93
133.22
125.05
123.20
119.93
118.29
116.77
85.12
76.84
63.97
63.83
53.41
38.25
21.07
13.97
13.85


170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NC
iPr NH
O
CO2Et
CO2Et
O
O
4k
11.13
8.60
8.50
8.48
8.14
8.12
7.94
7.92
7.81
7.79
7.74
7.74
7.73
7.72
7.71
7.71
7.70
7.70
7.69
7.69
5.14
4.43
4.42
4.41
4.40
4.39
4.38
4.37
4.35
4.34
4.34
4.33
4.33
4.32
2.62
2.61
2.60
1.38
1.36
1.35
1.34
1.32
1.32
1.31
1.30
1.17
1.16
1.00
0.96
1.08
1.08
1.10
1.11
2.19
1.04
4.34
0.99
9.34
3.28
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
175.83
172.36
164.16
163.79
156.20
153.98
136.14
129.83
128.22
127.60
126.16
123.91
122.46
121.56
120.52
120.13
117.24
85.46
75.69
63.80
57.43
32.15
17.88
17.38
14.10
14.04
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O2N
NC
NH
CO2Et
CO2Et
O
O
O

4l


11.31
8.58
8.52
8.50
8.18
8.16
8.15
8.13
7.97
7.96
7.86
7.86
7.85
7.84
7.77
7.75
7.74
7.73
7.71
7.70
5.69
4.41
4.40
4.38
4.37
4.05
4.04
4.03
4.01
4.00
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3.75
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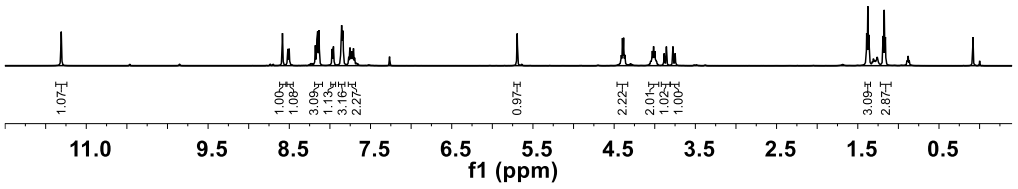
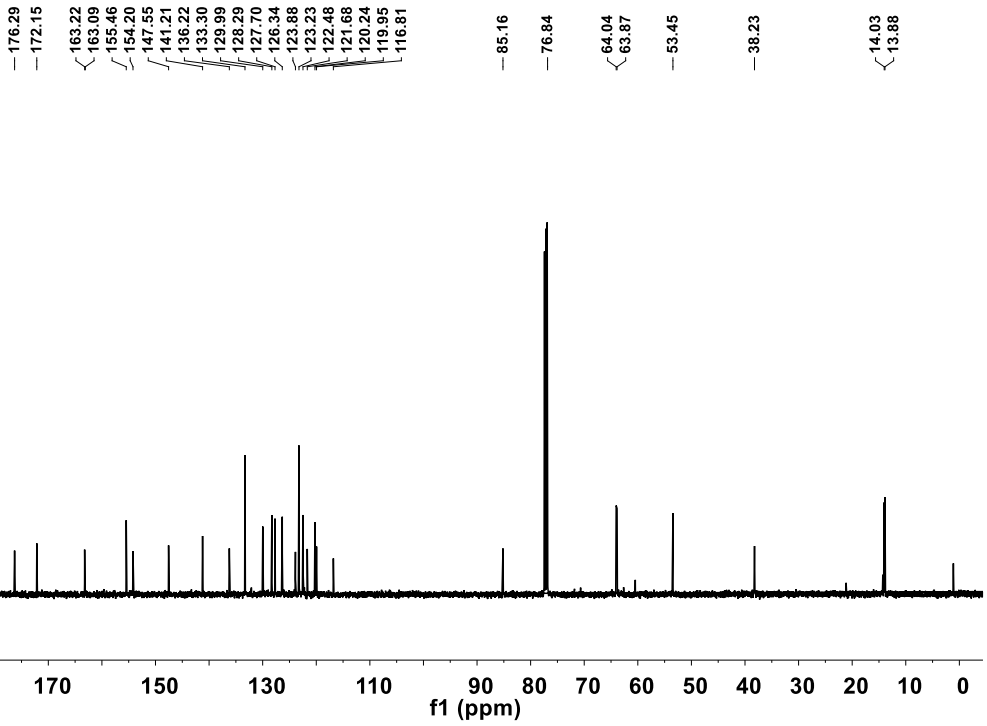
1.38
1.36
1.19
1.17
1.16


1.07
1.00
1.08
3.09
1.13
3.16
2.27
0.97
2.22
2.01
1.02
1.00
3.09
2.87
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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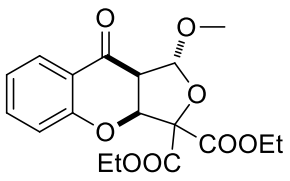
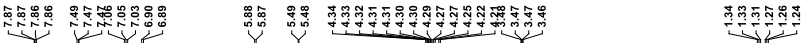
163.09
155.46
154.20
147.55
141.21
136.22
133.30
129.99
128.29
127.70
126.34
123.88
123.23
122.48
121.68
120.24
119.95
116.81
85.16
76.84
64.04
63.87
53.45
38.23
14.03
13.88
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O—
O
O
COOEt
EtOOC

6a


7.87
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7.86
7.86
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7.47
7.05
7.03
6.90
6.89
5.88
5.87
5.49
5.48
4.34
4.33
4.32
4.31
4.31
4.30
4.30
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4.27
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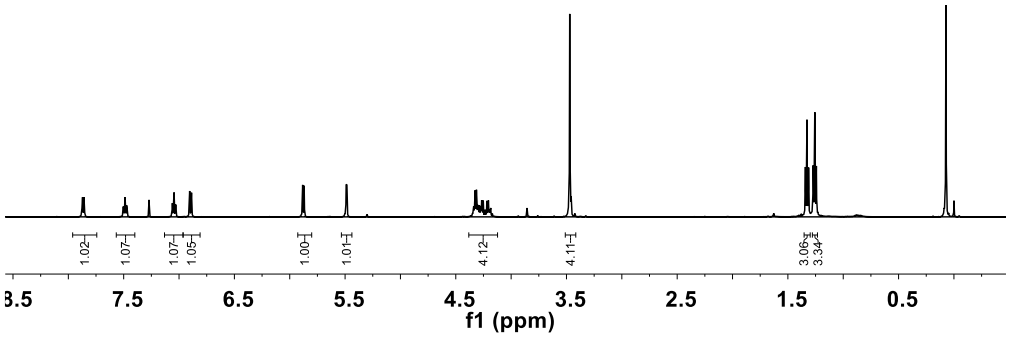
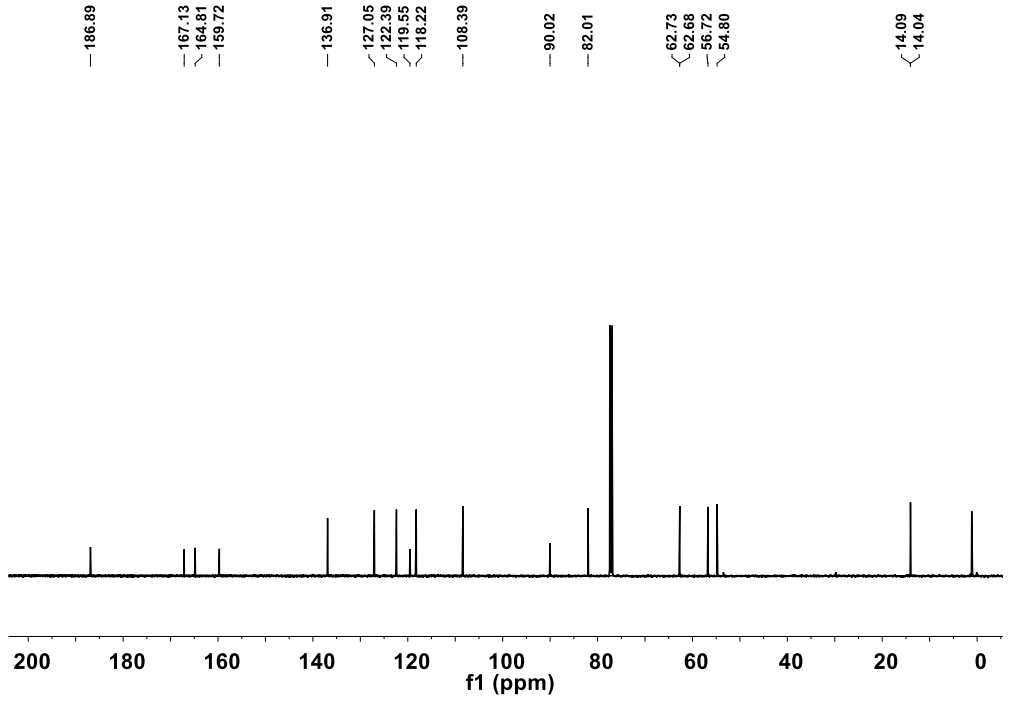
1.34
1.33
1.31
1.27
1.26
1.24


1.02
1.07
1.07
1.05
1.00
1.01
4.12
4.11
3.06
3.34
3.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


186.89
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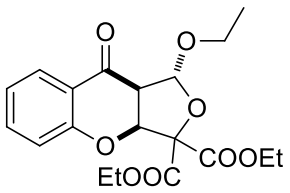
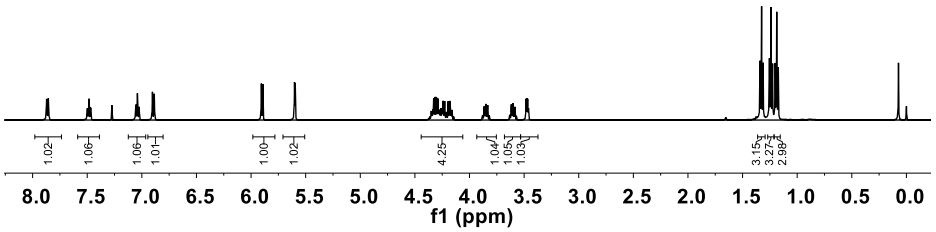
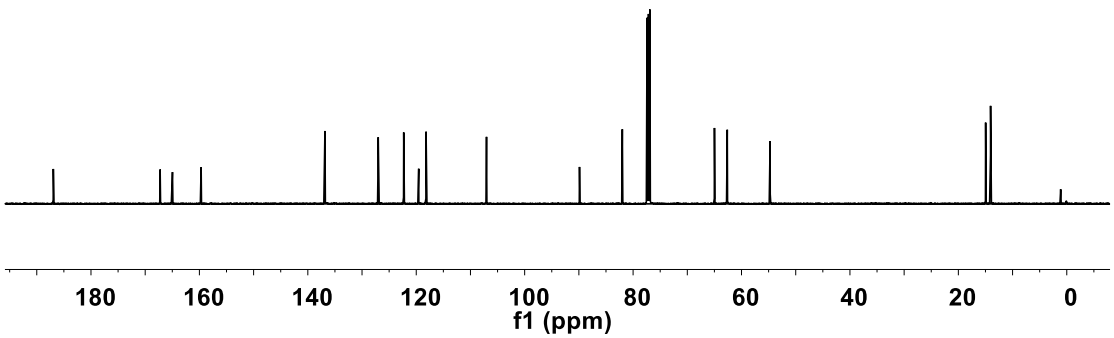
136.91
127.05
122.39
119.55
118.22
108.39
90.02
82.01
62.73
62.68
56.72
54.80
14.09
14.04
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

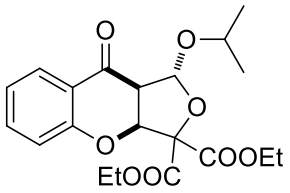

O
O
O
O
COOEt
EtOOC

6b

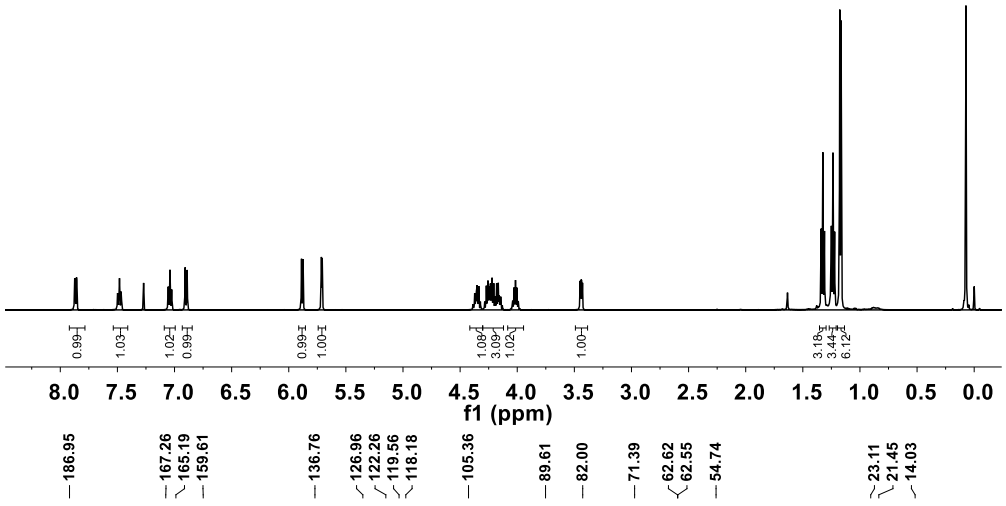

1.02
1.06
1.06
1.01
1.00
1.02
4.25
1.04
1.05
1.03
3.15
3.27
2.98
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


186.94
167.24
164.97
159.68
136.84
127.01
122.31
119.55
118.19
107.03
89.88
81.98
64.99
62.68
62.63
54.72
14.97
14.05
14.04


180 160 140 120 100 80 60 40 20 0
f1 (ppm)


O
O
O
O
COOEt
EtOOC

6c


0.99
1.03
1.02
0.99
0.99
1.00
1.08
3.09
1.02
1.00
3.18
3.44
6.12
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)
186.95
167.26
165.19
159.61
136.76
126.96
122.26
119.56
118.18
105.36
89.61
82.00
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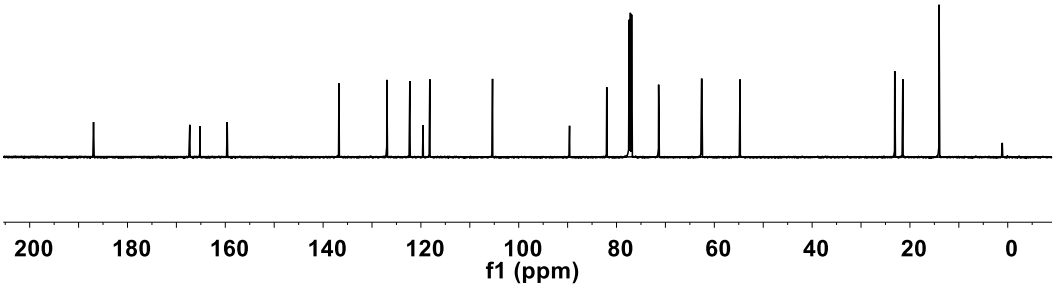
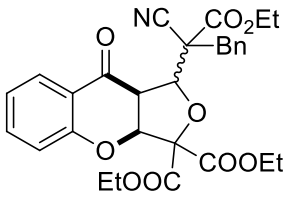
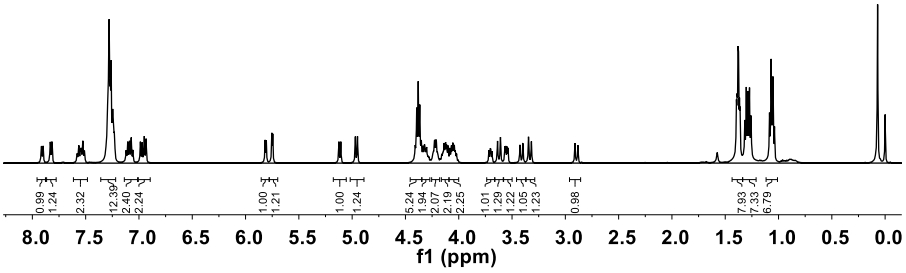
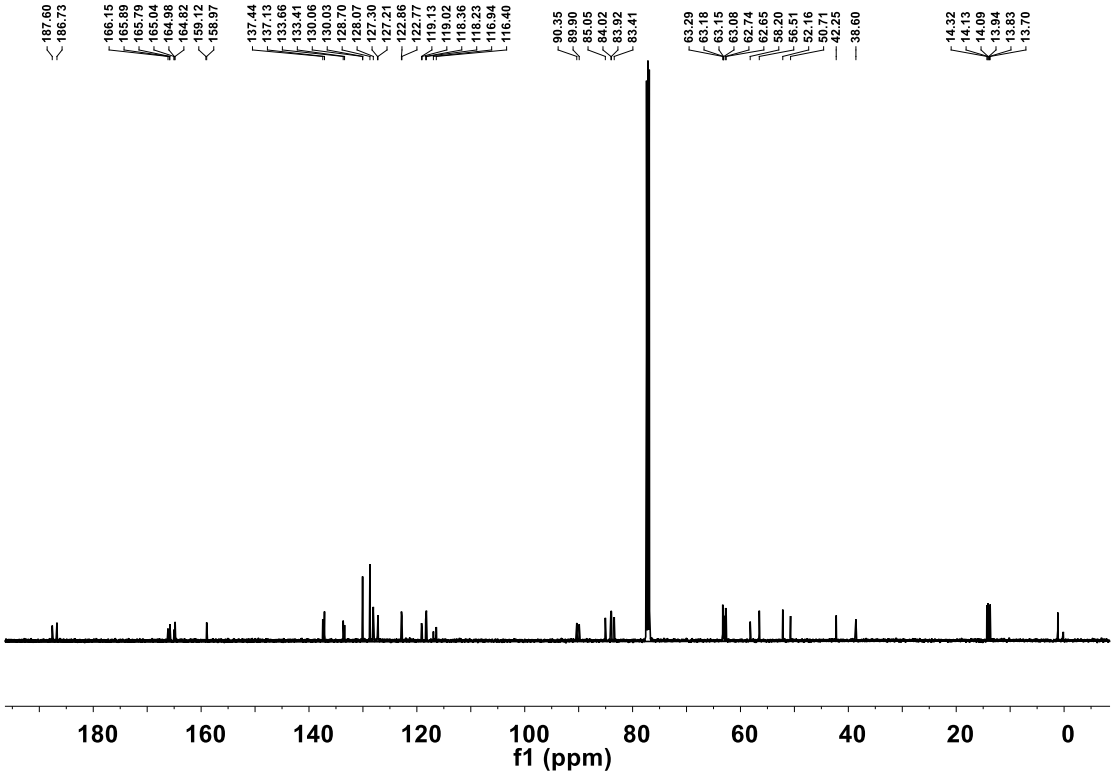
62.62
62.55
54.74
23.11
21.45
14.03

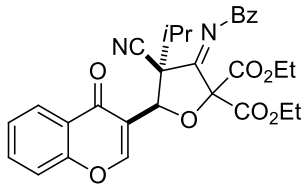

200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


NC
CO2Et
Bn
O
O
O
COOEt
EtOOC

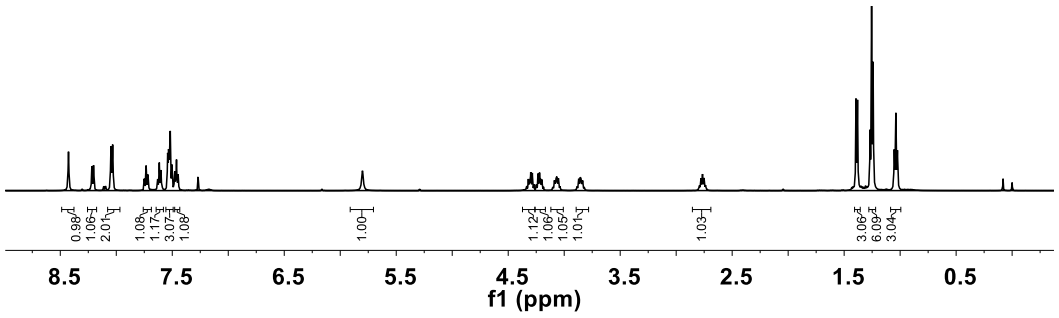
8

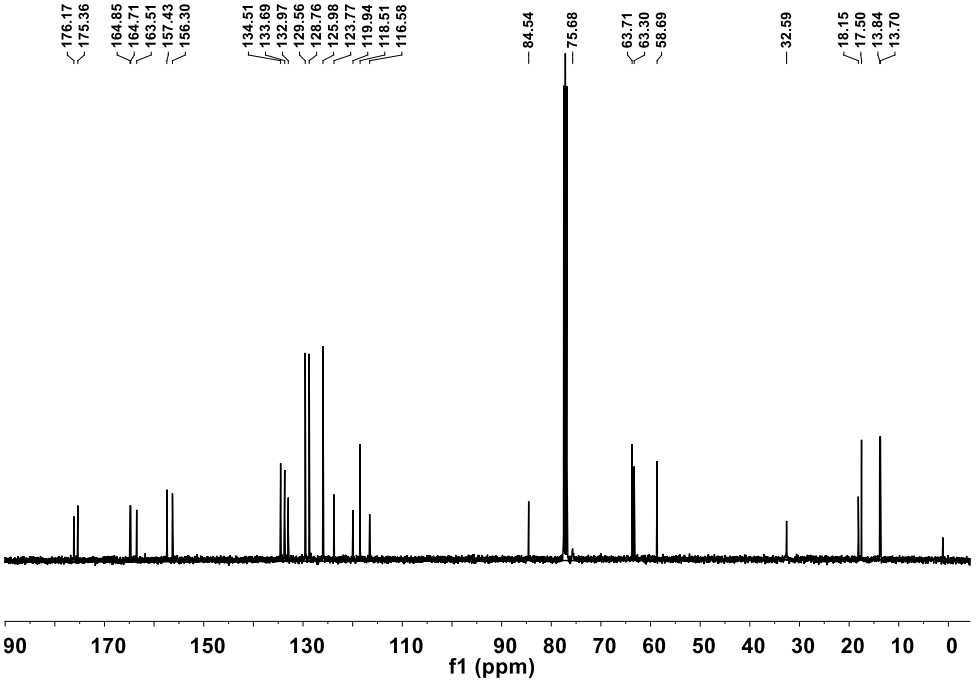

0.99
1.24
2.32
12.39
2.40
2.24
1.00
1.21
1.00
1.24
5.24
1.94
2.07
2.19
2.25
1.01
1.29
1.22
1.05
1.23
0.98
7.93
7.33
6.79
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

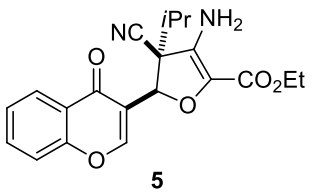

187.60
186.73
166.15
165.89
165.79
165.04
164.98
164.82
159.12
158.97
137.44
137.13
133.66
133.41
130.06
130.03
128.70
128.07
127.30
127.21
122.86
122.77
119.13
119.02
118.36
118.23
116.94
116.40
90.35
89.90
85.05
84.02
83.92
83.41
63.29
63.18
63.15
63.08
62.74
62.65
58.20
56.51
52.16
50.71
42.25
38.60
14.32
14.13
14.09
13.94
13.83
13.70
180 160 140 120 100 80 60 40 20 0
f1 (ppm)


Bz
N
iPr
NC
O
CO2Et
CO2Et
O
O

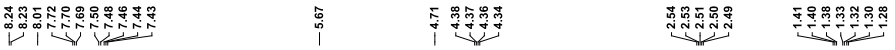
9

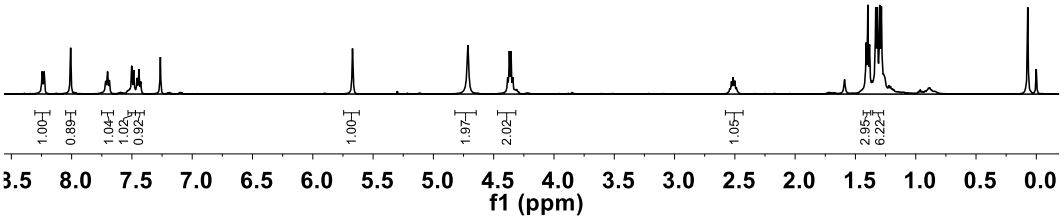

0.98
1.06
2.01
1.08
1.17
3.07
1.08
1.00
1.12
1.06
1.05
1.01
1.03
3.06
6.09
3.04
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

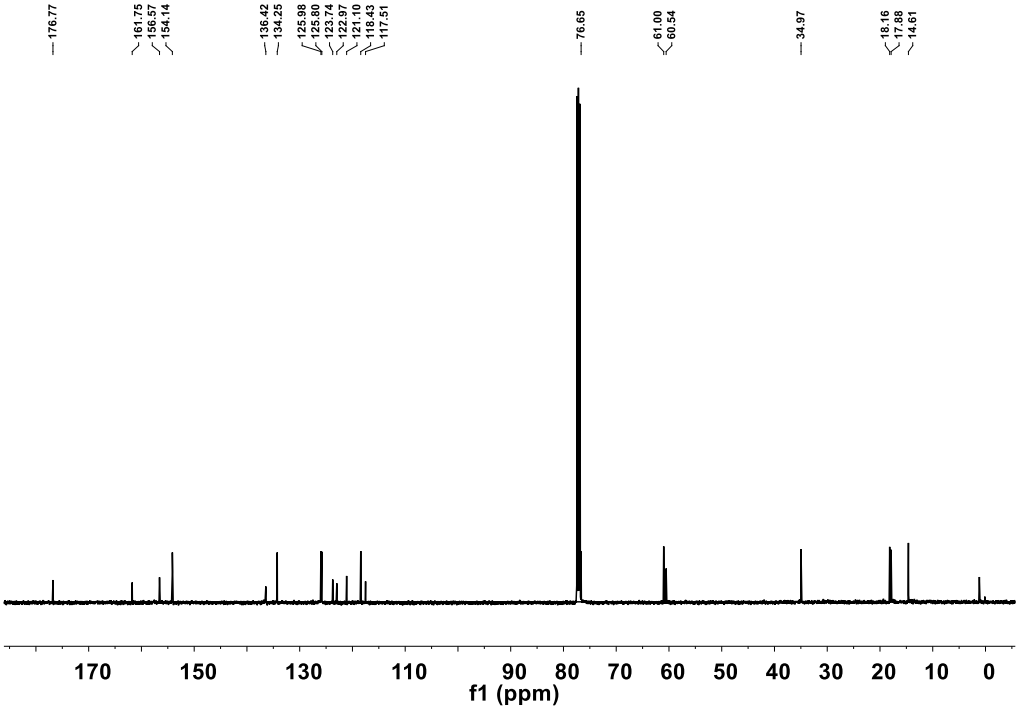

176.17
175.36
164.85
164.71
163.51
157.43
156.30
134.51
133.69
132.97
129.56
128.76
125.98
123.77
119.94
118.51
116.58
84.54
75.68
63.71
63.30
58.69
32.59
18.15
17.50
13.84
13.70
90
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

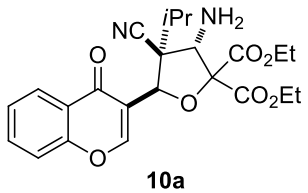

NC
iPr
NH2
O
CO2Et
O
O

5

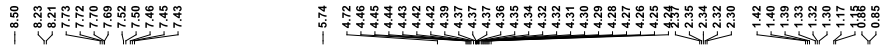

8.24
8.23
8.01
7.72
7.70
7.69
7.50
7.48
7.46
7.44
7.43
5.67
4.71
4.38
4.37
4.36
4.34
2.54
2.53
2.51
2.50
2.49
1.41
1.40
1.38
1.33
1.32
1.30
1.28

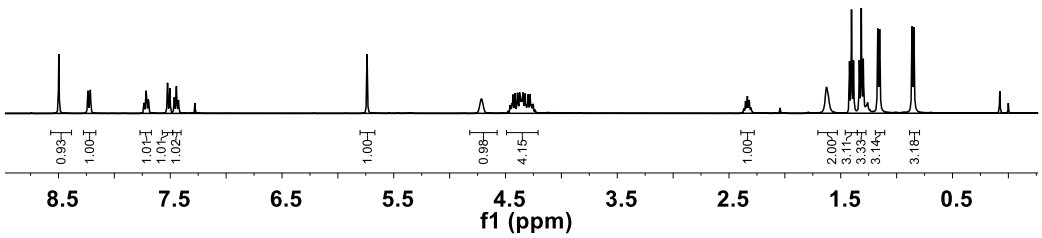

1.00
0.89
1.04
1.02
0.92
1.00
1.97
2.02
1.05
2.95
6.22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

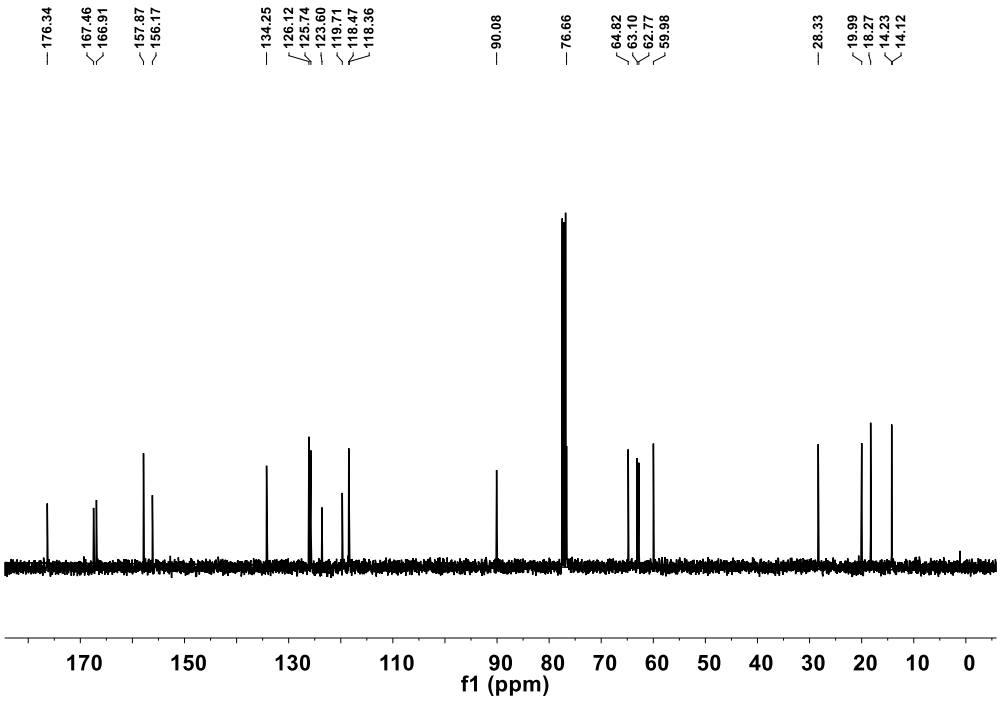

176.77
161.75
156.57
154.14
136.42
134.25
125.98
125.80
123.74
122.97
121.10
118.43
117.51
76.65
61.00
60.54
34.97
18.16
17.88
14.61
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

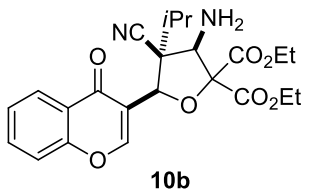

NC
iPr
NH2
O
CO2Et
CO2Et
O
O

10a

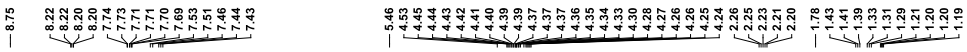

8.50
8.23
8.21
7.73
7.72
7.70
7.69
7.52
7.50
7.46
7.45
7.43
5.74
4.72
4.46
4.45
4.44
4.43
4.42
4.42
4.39
4.37
4.37
4.37
4.36
4.35
4.34
4.32
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.25
2.35
2.34
2.32
2.30
1.42
1.40
1.39
1.33
1.32
1.30
1.17
1.16
1.15
0.85

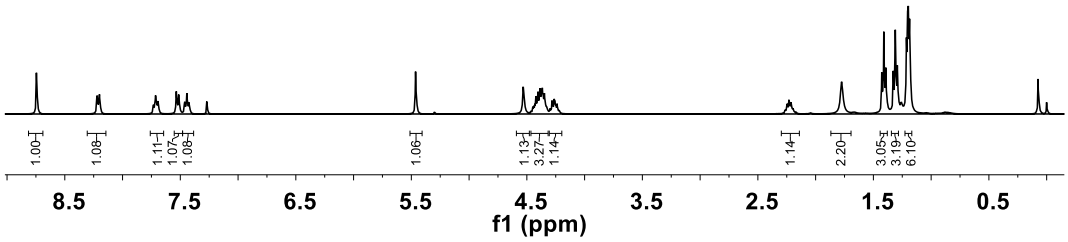

0.93
1.00
1.01
1.01
1.02
1.00
0.98
4.15
1.00
2.00
3.11
3.33
3.14
3.18
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

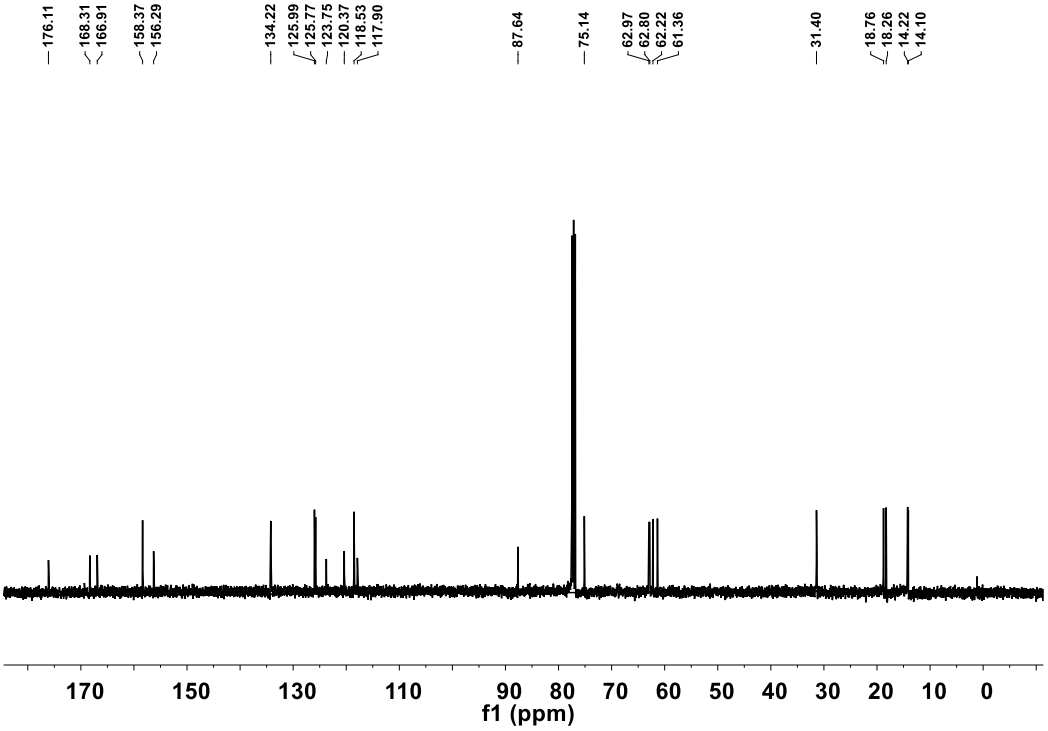

176.34
167.46
166.91
157.87
156.17
134.25
126.12
125.74
123.60
119.71
118.47
118.36
90.08
76.66
64.82
63.10
62.77
59.98
28.33
19.99
18.27
14.23
14.12
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NC
iPr
NH2
O
CO2Et
CO2Et
O
O

10b

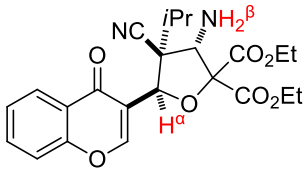

8.75
8.22
8.22
8.20
8.20
7.74
7.73
7.71
7.71
7.70
7.69
7.53
7.51
7.46
7.44
7.43
5.46
4.53
4.45
4.44
4.43
4.42
4.41
4.40
4.39
4.39
4.37
4.37
4.37
4.36
4.35
4.34
4.33
4.30
4.28
4.27
4.26
4.26
4.25
4.24
2.26
2.25
2.23
2.21
2.20
1.78
1.43
1.41
1.39
1.33
1.31
1.29
1.21
1.20
1.20
1.19


1.00
1.08
1.11
1.07
1.08
1.06
1.13
3.27
1.14
1.14
2.20
3.05
3.19
6.10
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

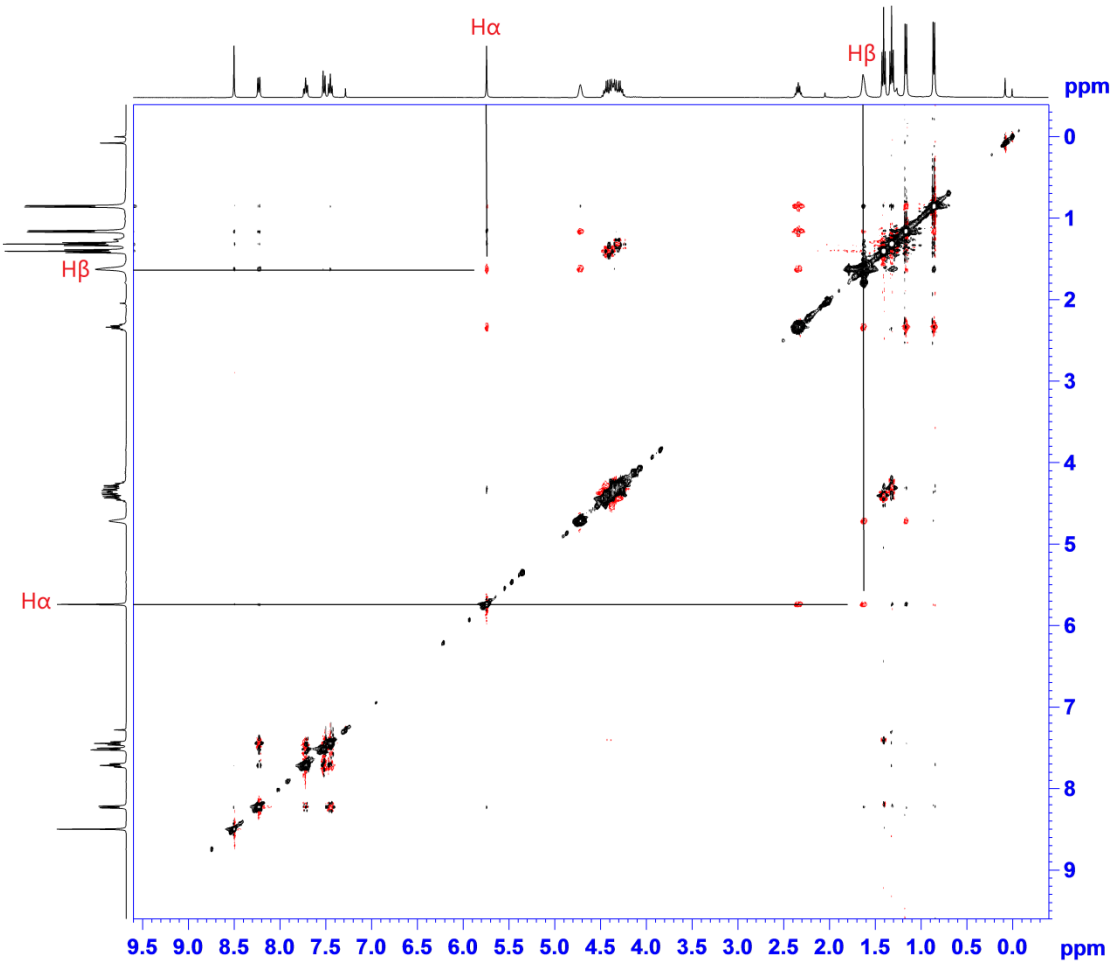

176.11
168.31
166.91
158.37
156.29
134.22
125.99
125.77
123.75
120.37
118.53
117.90
87.64
75.14
62.97
62.80
62.22
61.36
31.40
18.76
18.26
14.22
14.10
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1.2 NOESY spectra of compound (±)-10a, (±)-10b

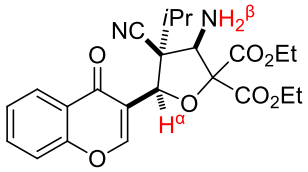
NOESY spectra of (±)-10a



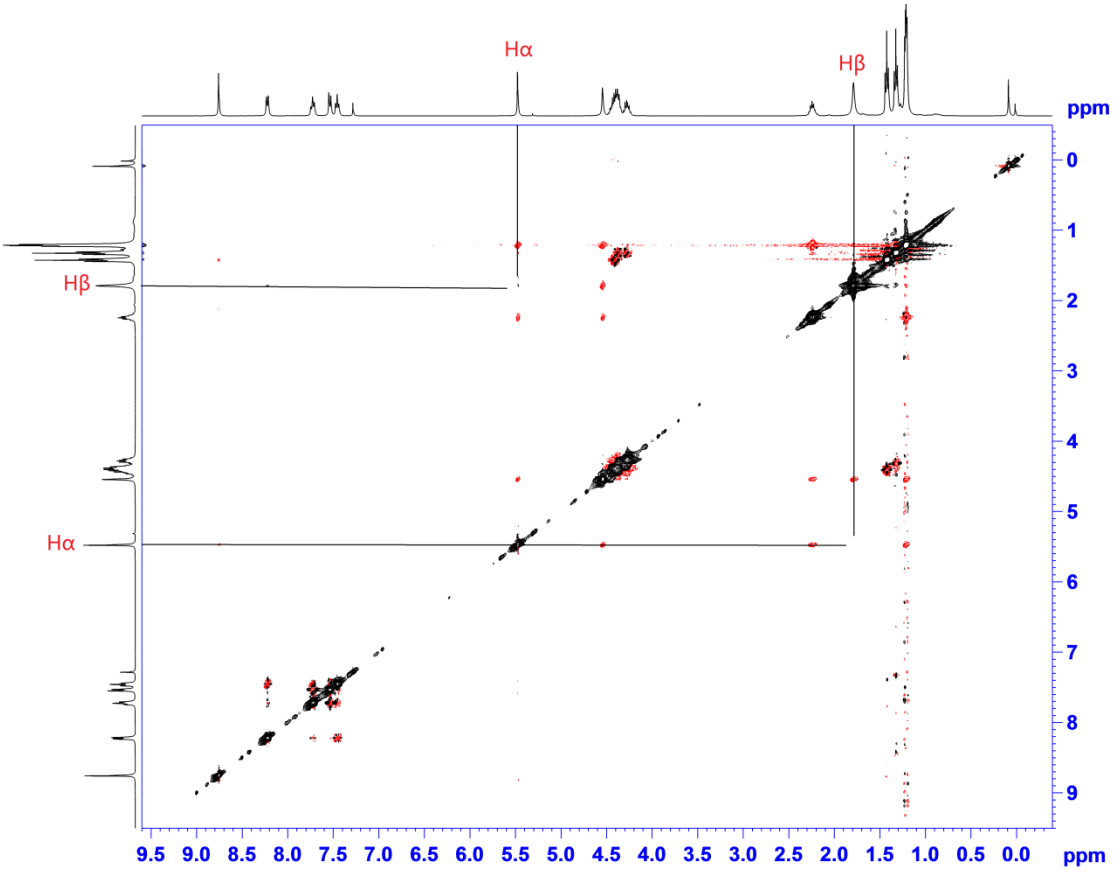
10a



NOESY spectra of (±)-10b

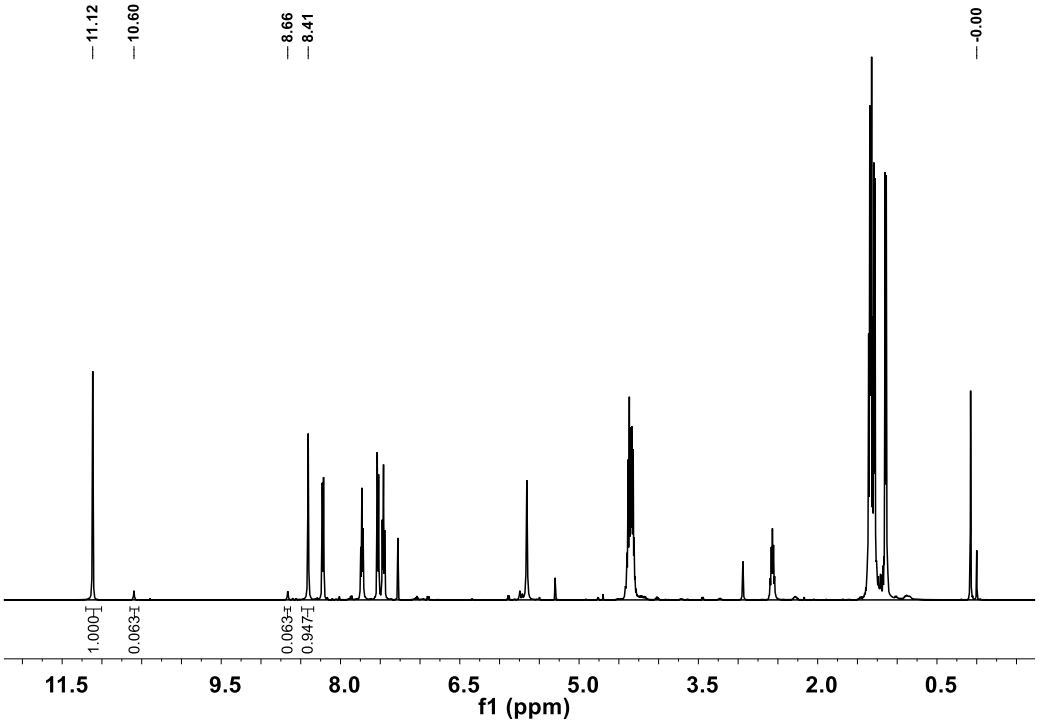


10b

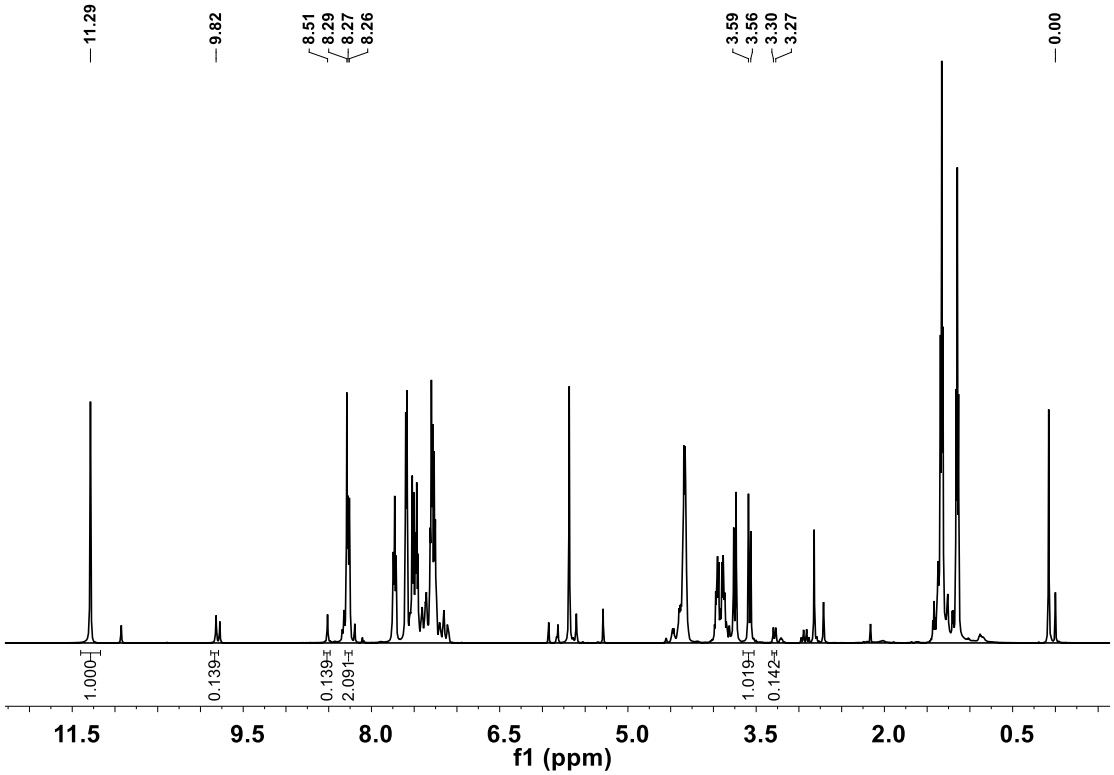


1.3 ^{1}H NMR spectra of the crude reaction mixture ((±)-4a-4l) for dr determination

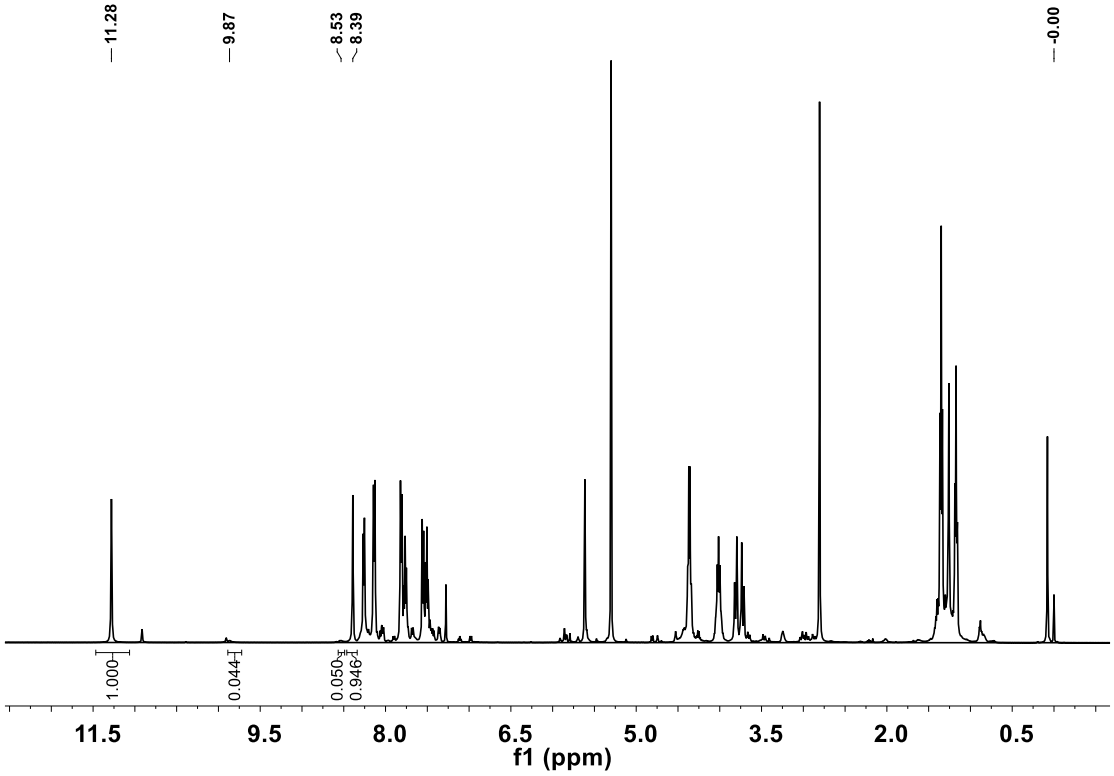
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4a**):



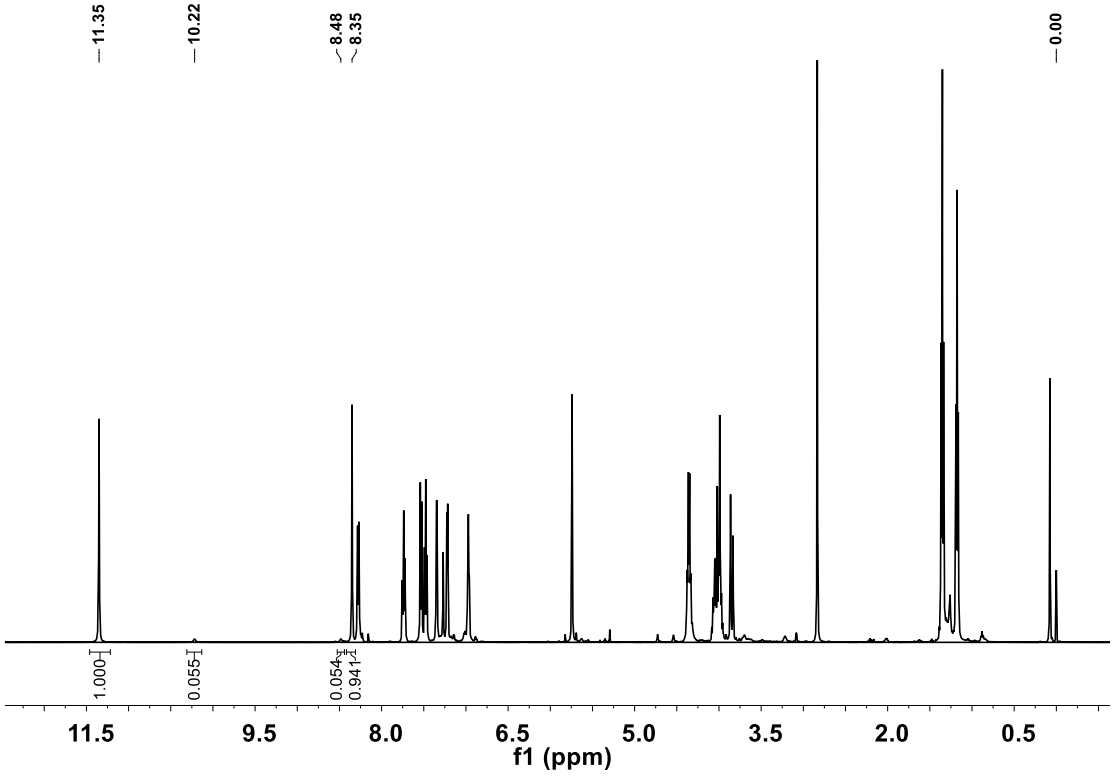
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4b**):



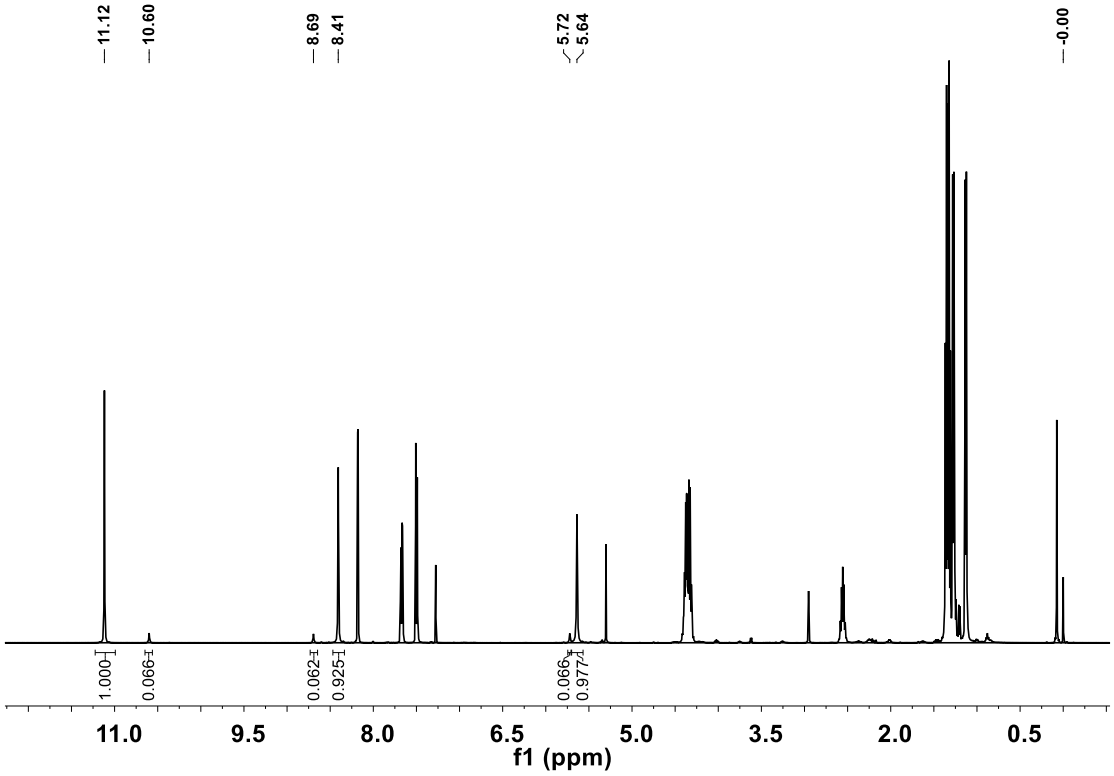
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4c**):



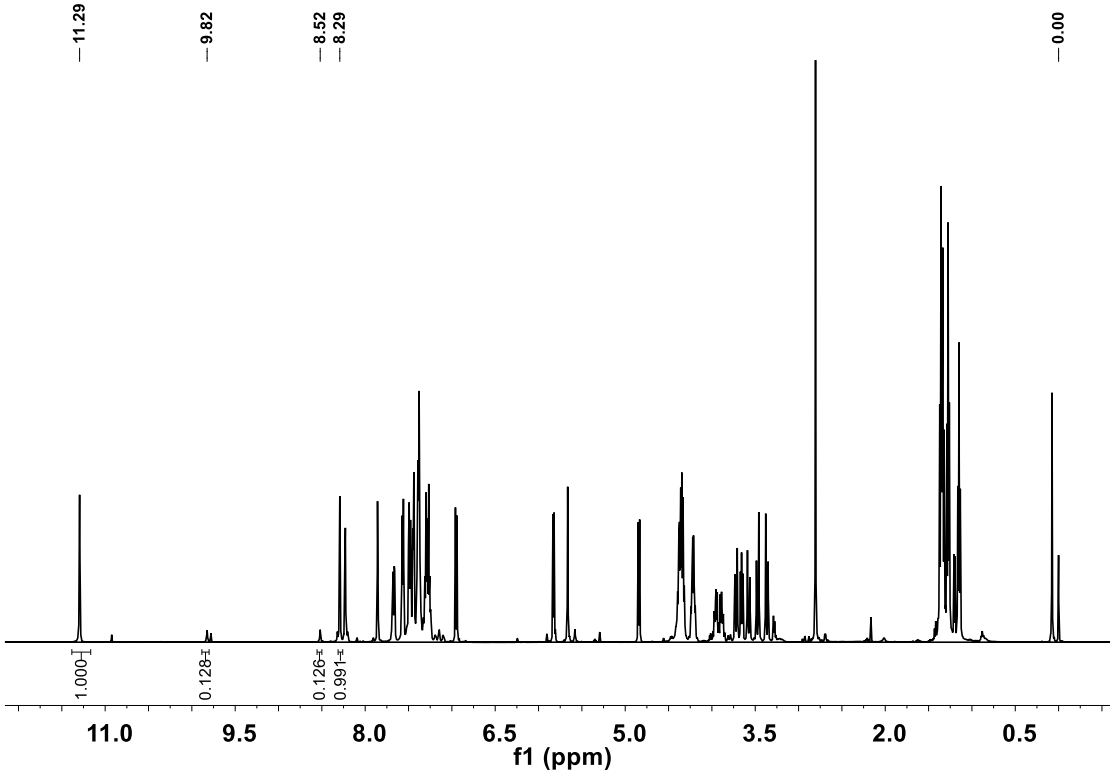
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4d**):



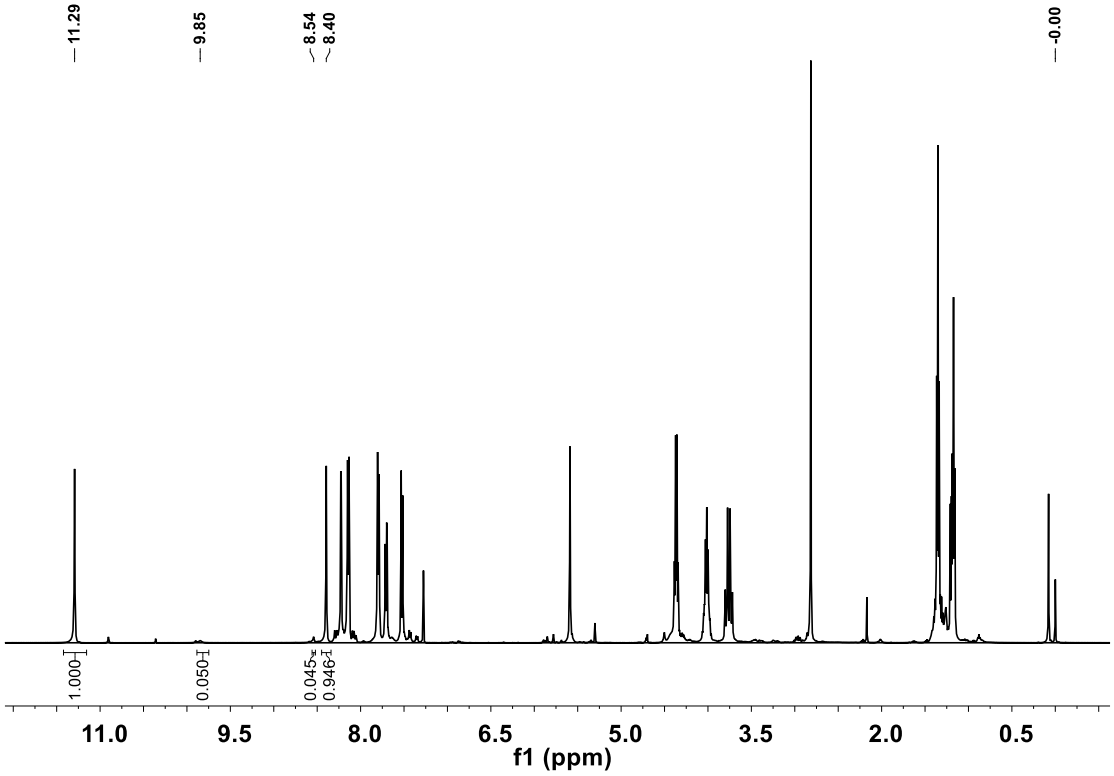
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4e**):



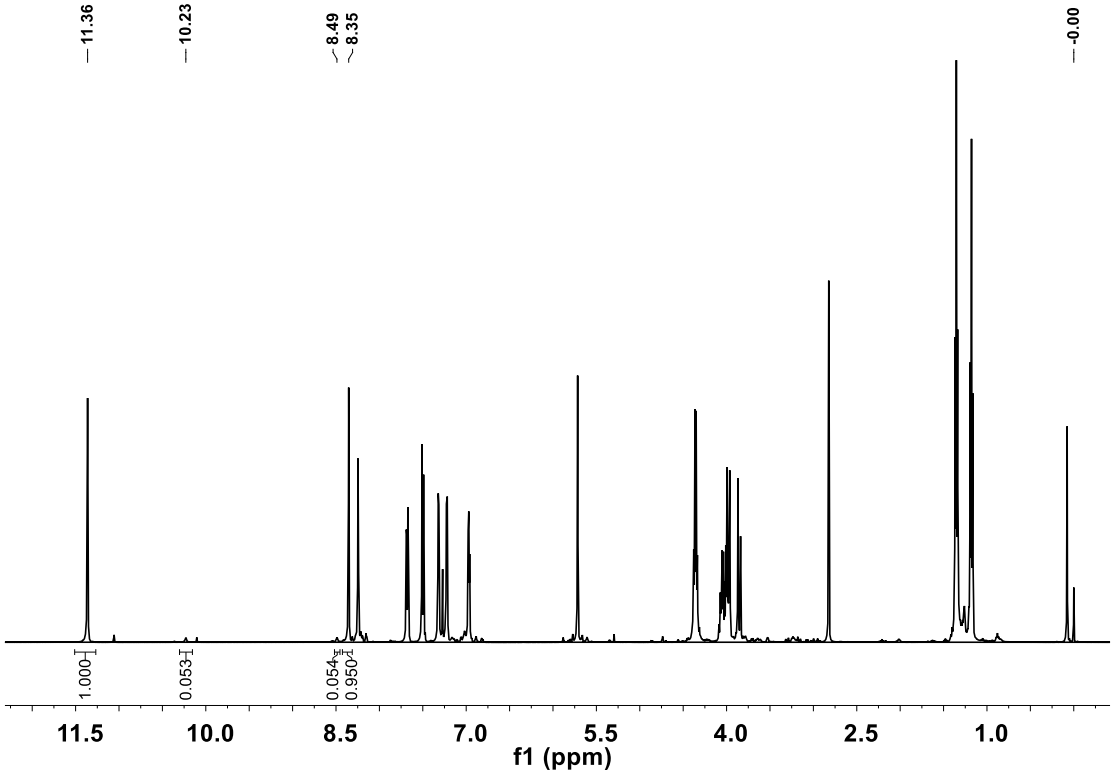
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4f**):



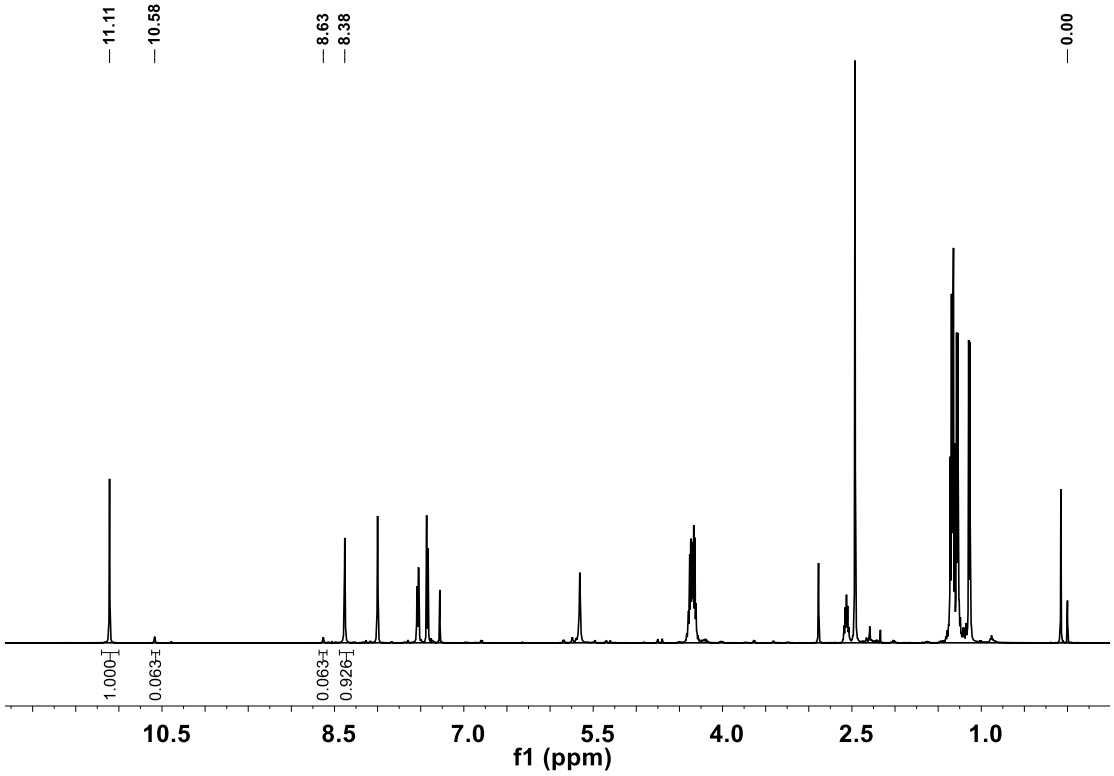
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4g**):



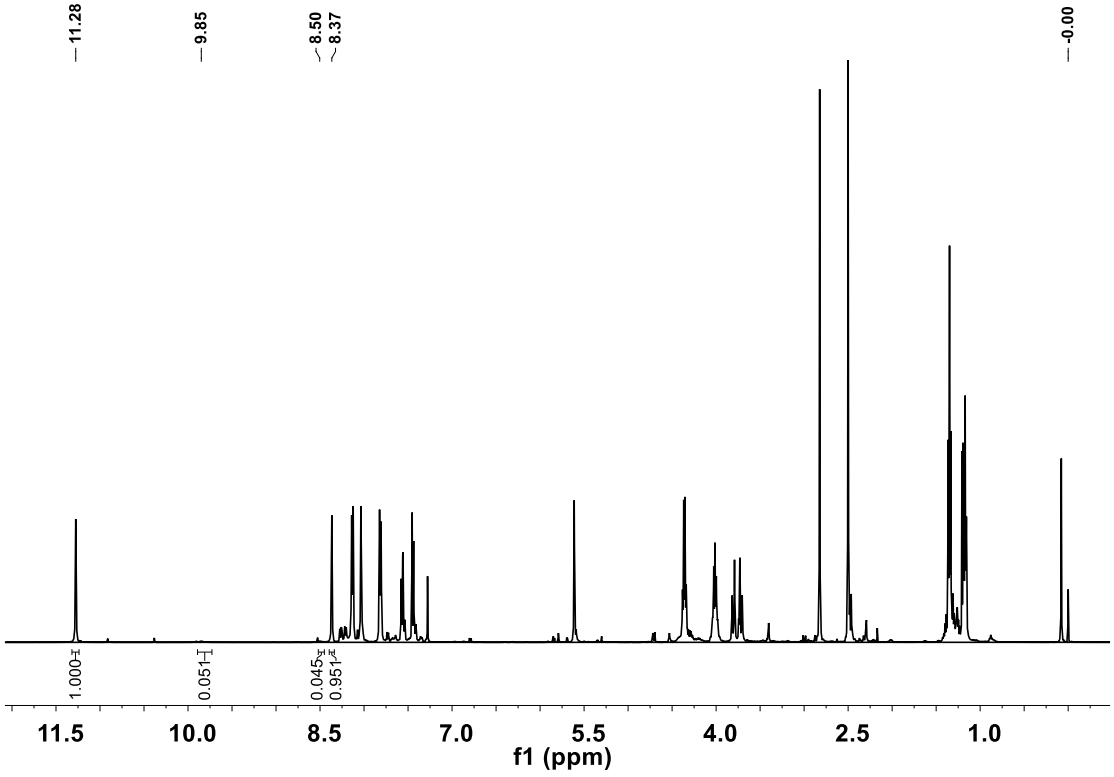
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4h**):



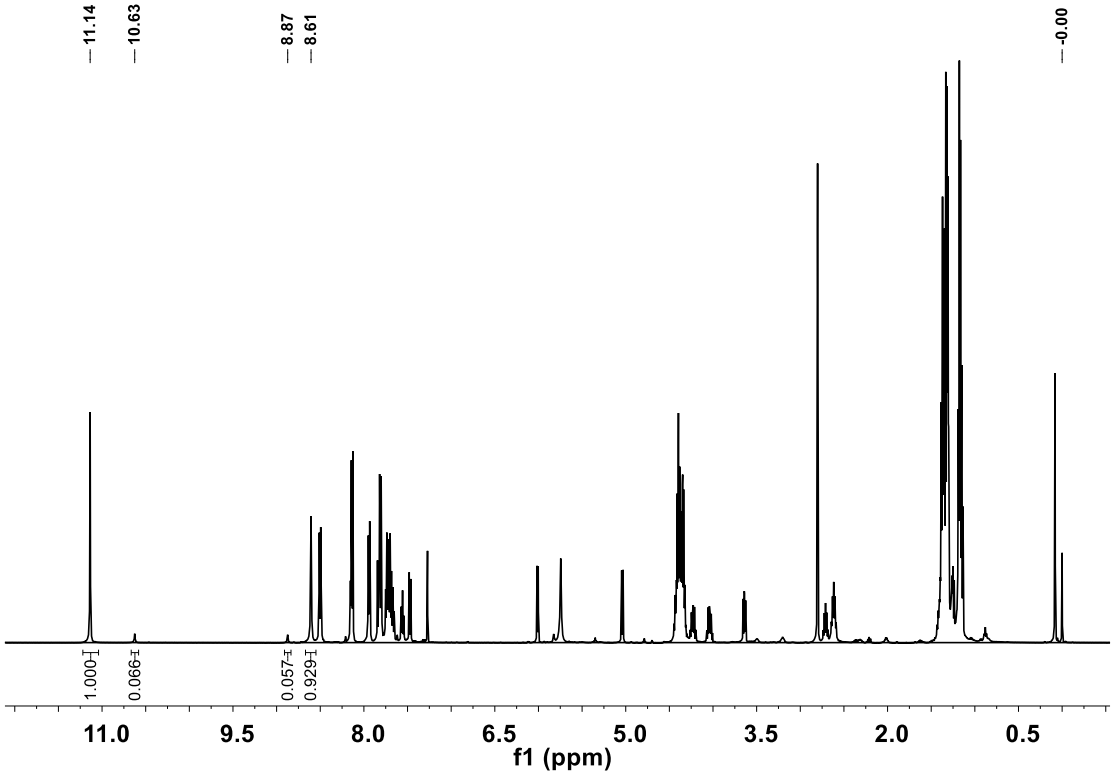
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4i**):



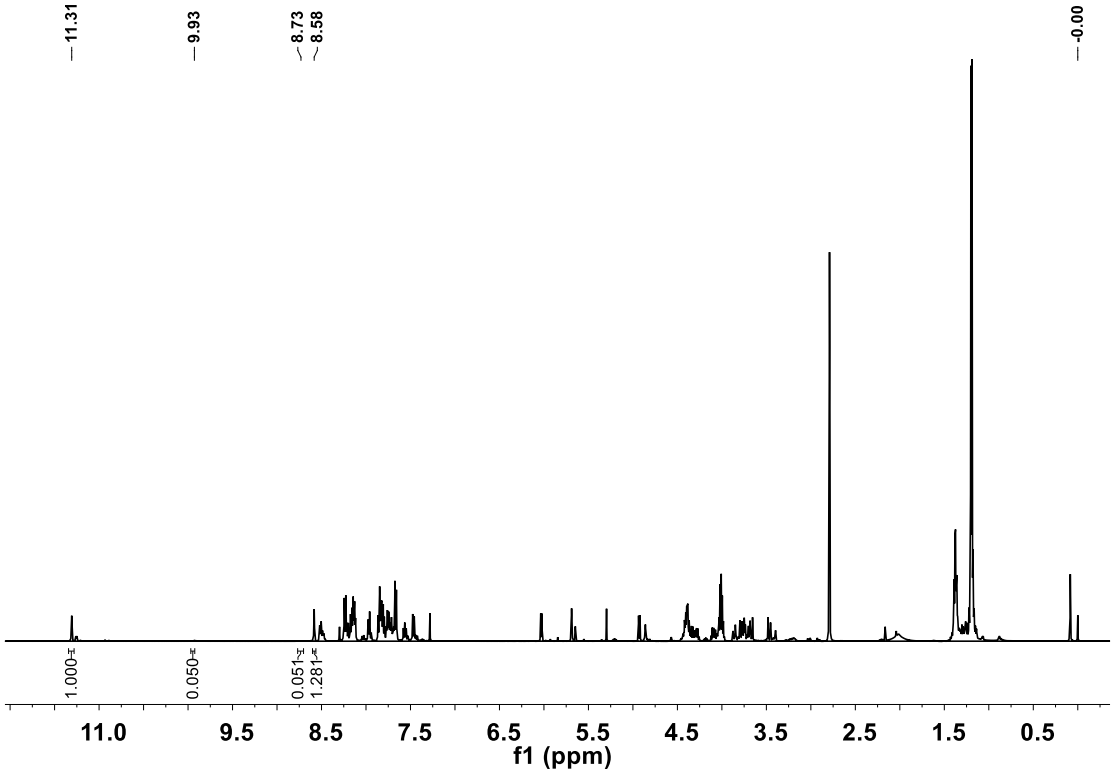
^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4j**):



^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4k**):

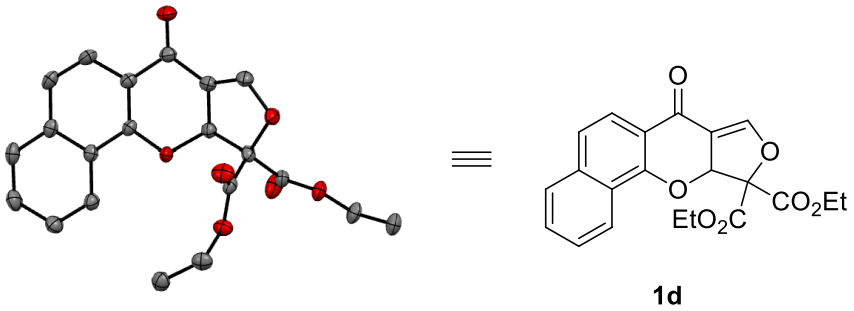


^{1}H NMR spectroscopy of the crude reaction mixture ((±)-**4l**):



2. X-ray crystallography of compound 1d, (±)-3f, (±)-5

2.1 X-ray crystallography of compound 1d



1d

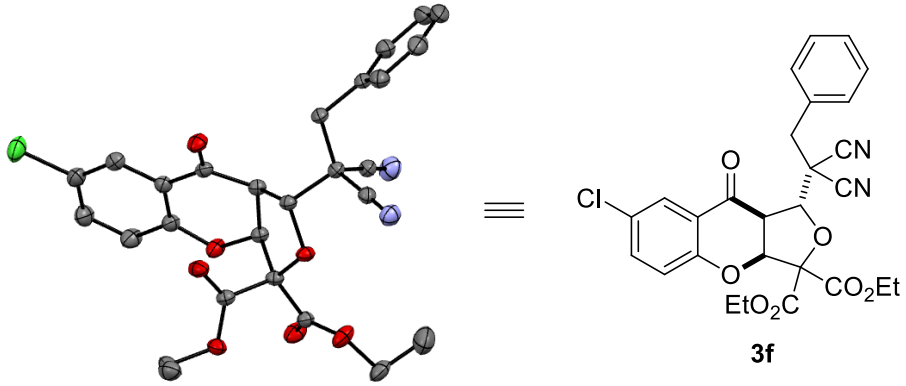
CCDC deposition number: 1541448

Table 1. Crystal data and structure refinement for A.

Identification code	a	
Empirical formula	C21 H18 O7	
Formula weight	382.35	
Temperature	173.1500 K	
Wavelength	0.710747 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6133(15) Å	α= 103.557(8)°.
	b = 10.8331(17) Å	β= 95.557(9)°.
	c = 11.794(2) Å	γ = 108.701(7)°.
Volume	880.0(3) $Å^3$	
Z	2	
Density (calculated)	1.443 Mg/m^3	

Absorption coefficient	0.109 mm^{-1}
F(000)	400
Crystal size	0.237 x 0.153 x 0.115 mm^3
Theta range for data collection	1.808 to 27.475°.
Index ranges	-9<=h<=9, -14<=k<=14, -15<=l<=15
Reflections collected	12308
Independent reflections	4002 [R(int) = 0.0325]
Completeness to theta = 25.242°	9940.00 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8967
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4002 / 0 / 255
Goodness-of-fit on F^2	1.143
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1110
R indices (all data)	R1 = 0.0569, wR2 = 0.1149
Extinction coefficient	n/a
Largest diff. peak and hole	0.296 and -0.197 $e.Å^{-3}$

2.2 X-ray crystallography of compound (±)-3f



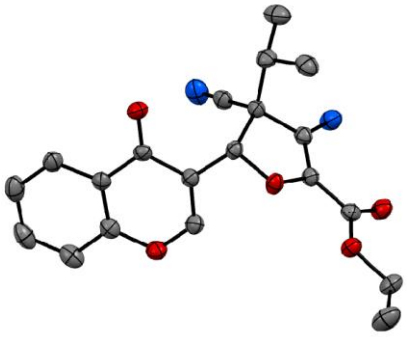
CCDC deposition number: 1541449

Table 1. Crystal data and structure refinement for mx5721b.

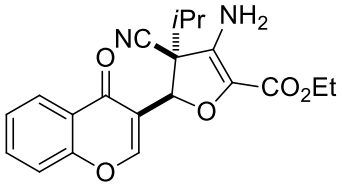
Identification code	mx5721b	
Empirical formula	C27 H23 Cl N2 O7	
Formula weight	522.92	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.668(3) Å	α= 90°.
	b = 14.731(3) Å	β= 111.59(3)°.
	c = 13.261(3) Å	γ = 90°.
Volume	2482.6(10) $Å^3$	
Z	4	

Density (calculated)	1.399 Mg/m^3
Absorption coefficient	0.205 mm^{-1}
F(000)	1088
Crystal size	? x ? x ? mm^3
Theta range for data collection	2.116 to 27.480°.
Index ranges	-17<=h<=17, -18<=k<=19, -16<=l<=17
Reflections collected	19385
Independent reflections	5674 [R(int) = 0.0554]
Completeness to theta = 25.242°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5674 / 0 / 336
Goodness-of-fit on F^2	1.154
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1215
R indices (all data)	R1 = 0.0648, wR2 = 0.1264
Extinction coefficient	n/a
Largest diff. peak and hole	0.238 and -0.295 $e.Å^{-3}$

2.3 X-ray crystallography of compound (±)-5



≡



5

CCDC deposition number: 1541450

Table 1. Crystal data and structure refinement for mx5525.

Identification code	mx5525	
Empirical formula	C20 H20 N2 O5	
Formula weight	368.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.7770(17) Å	α= 90°.
	b = 16.254(2) Å	β= 90°.
	c = 17.725(2) Å	γ = 90°.
Volume	3680.9(8) $Å^3$	
Z	8	
Density (calculated)	1.329 Mg/m^3	

Absorption coefficient	0.097 mm^{-1}
F(000)	1552
Crystal size	0.41 x 0.33 x 0.21 mm^3
Theta range for data collection	2.331 to 27.473°.
Index ranges	-10<=h<=16, -14<=k<=21, -19<=l<=23
Reflections collected	12304
Independent reflections	4166 [R(int) = 0.0434]
Completeness to theta = 25.242°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7740
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4166 / 0 / 247
Goodness-of-fit on F^2	1.138
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1268
R indices (all data)	R1 = 0.0675, wR2 = 0.1323
Extinction coefficient	n/a
Largest diff. peak and hole	0.268 and -0.247 e.$Å^{-3}$