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Electronic Supporting Information for

Selective synthesis of functionalized pyrroles from 3-aza-1,5-enynes

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*E-mail: bswan@dicp.ac.cn; xyxin@dicp.ac.cn

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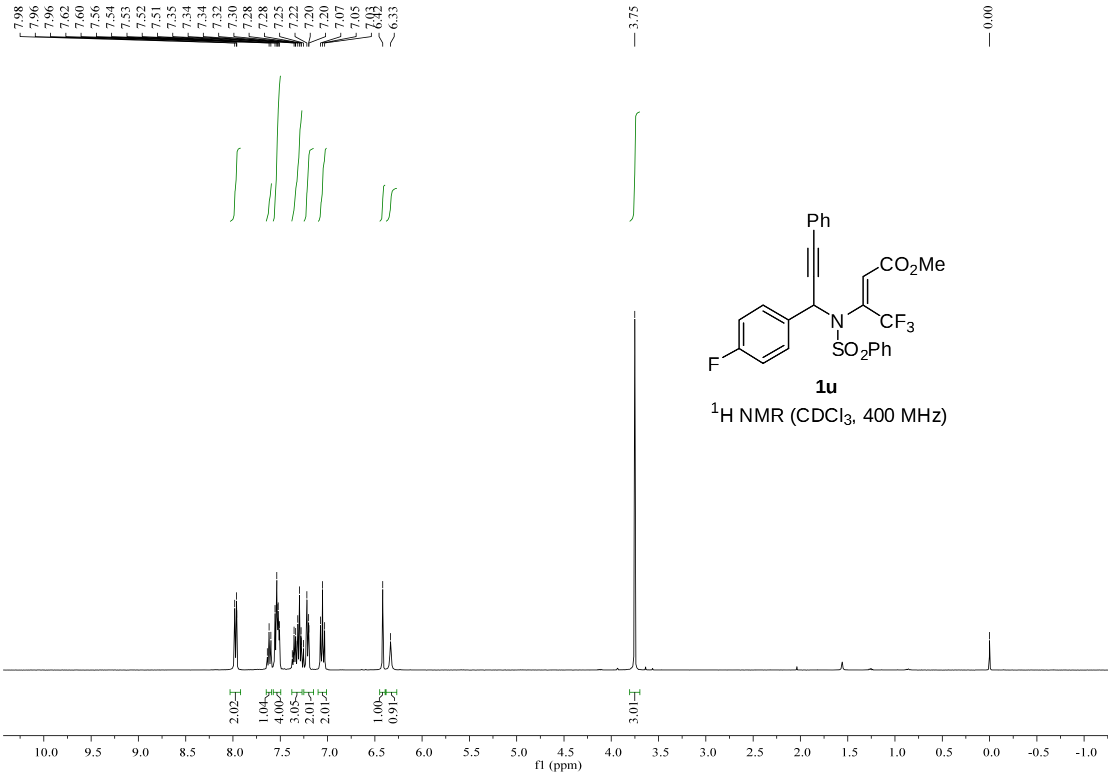

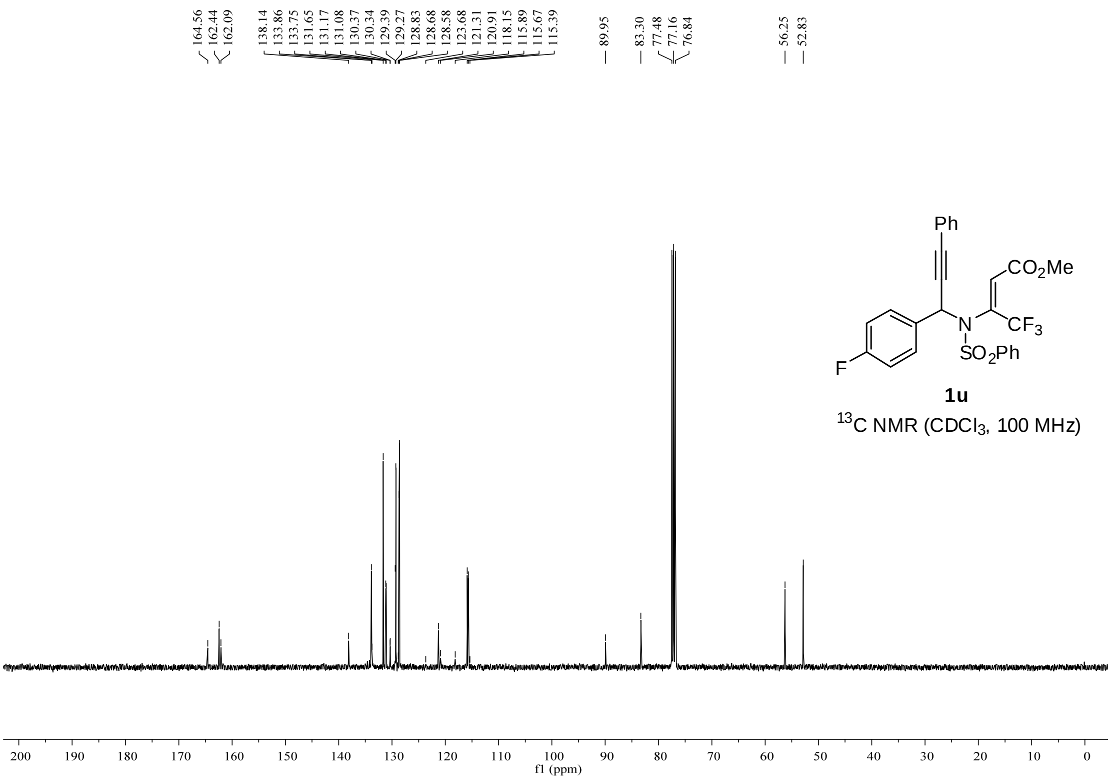

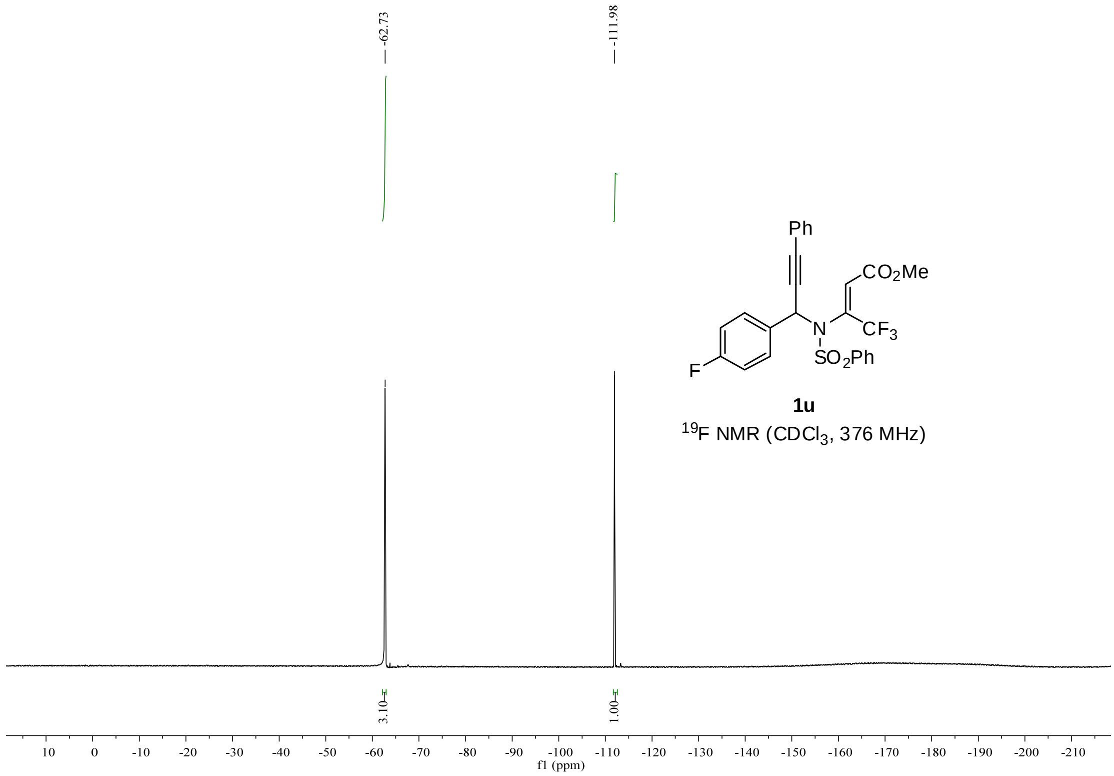
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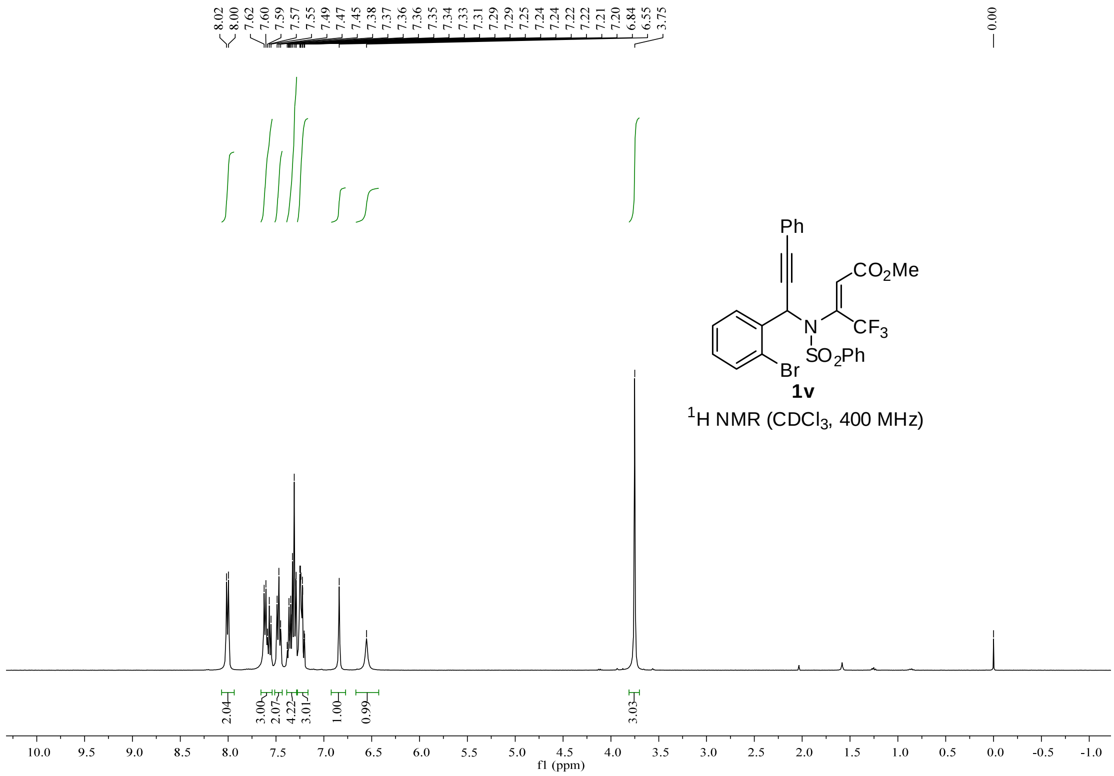
f1 (ppm)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7.31
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7.29
7.25
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7.22
7.21
7.20
6.84
6.55
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0.00
Ph
CO2Me
CF3
N
SO2Ph
Br
1v
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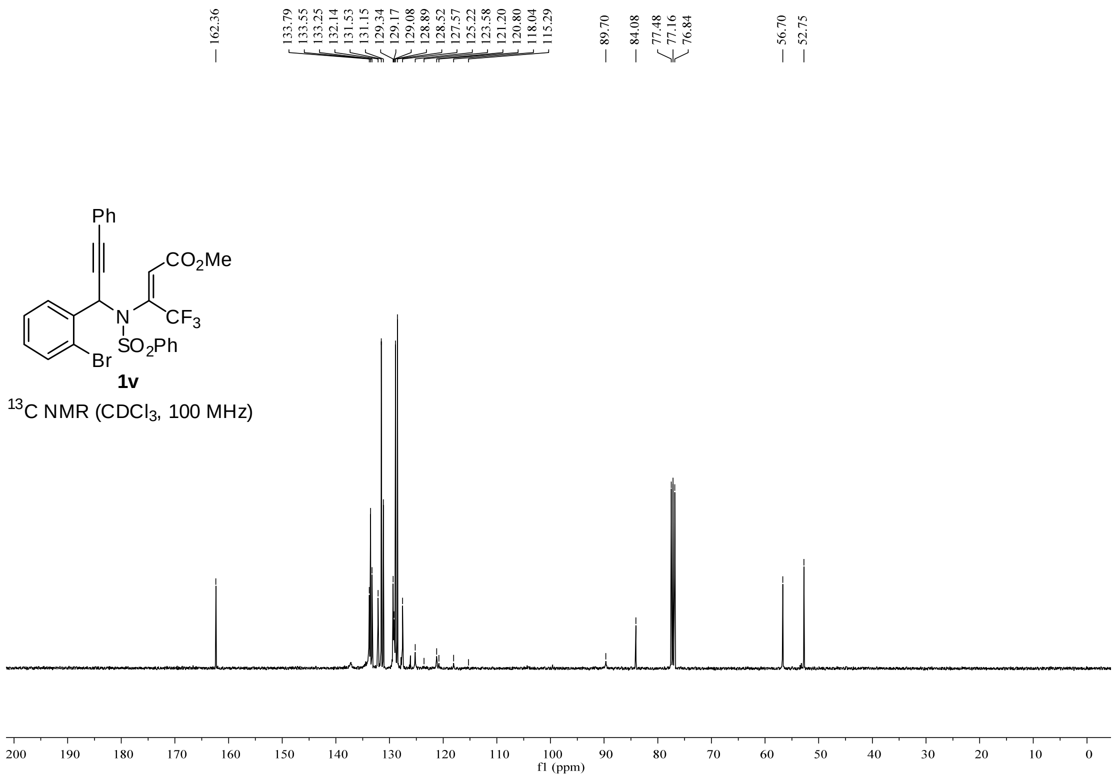
f1 (ppm)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120.80
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89.70
84.08
77.48
77.16
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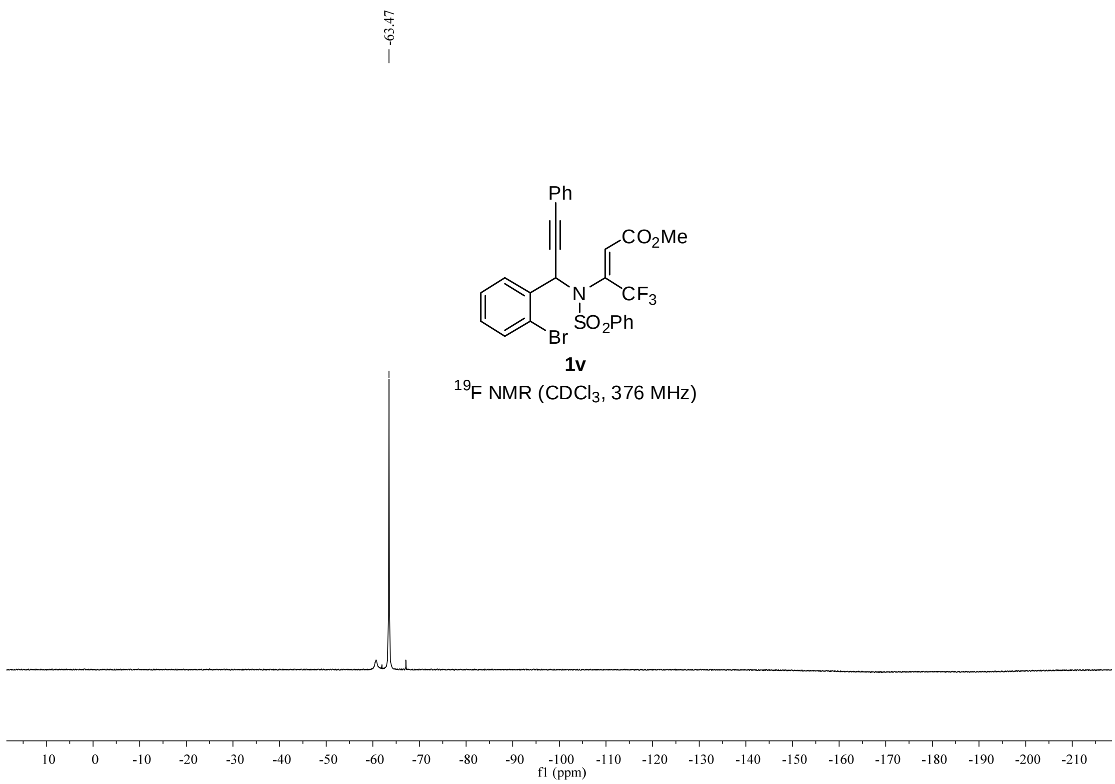
N
CF3
SO2Ph
Br
1v
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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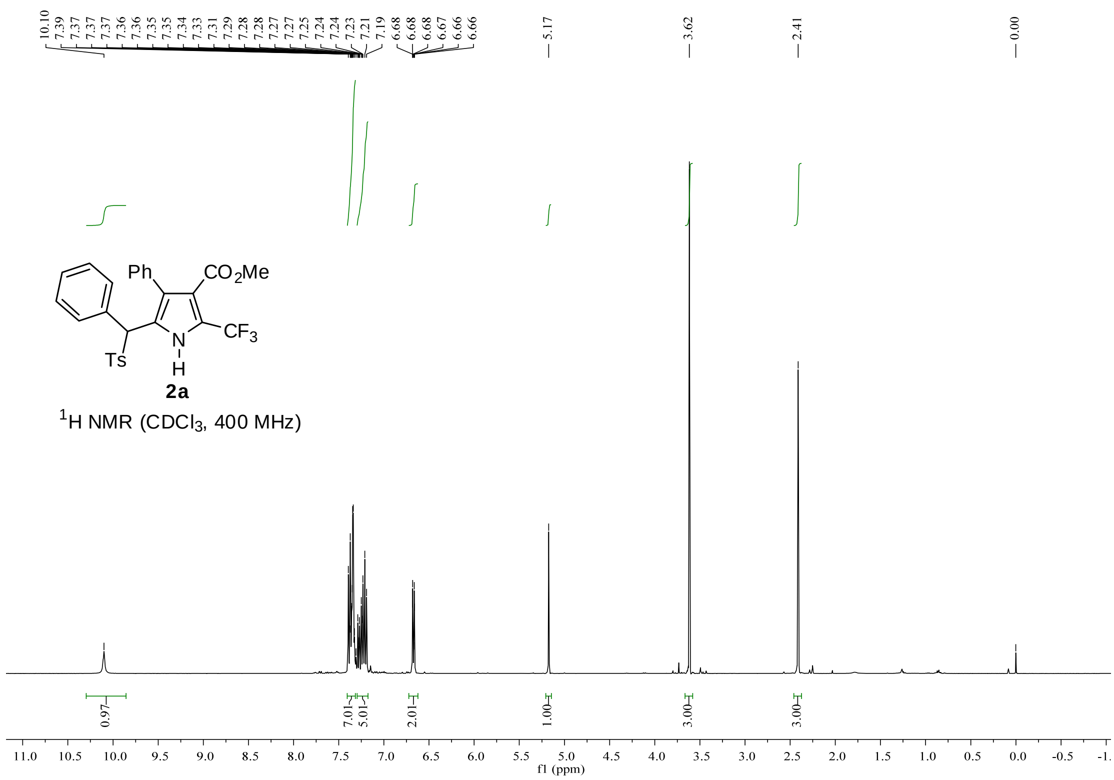
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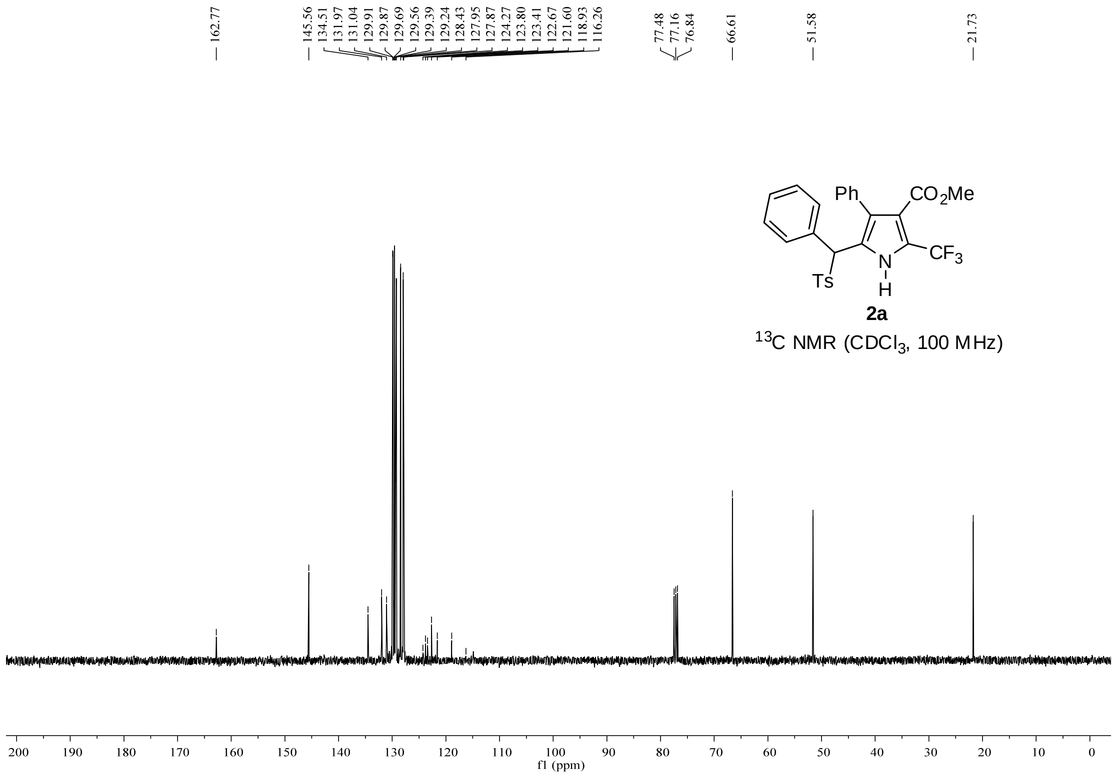
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Ts
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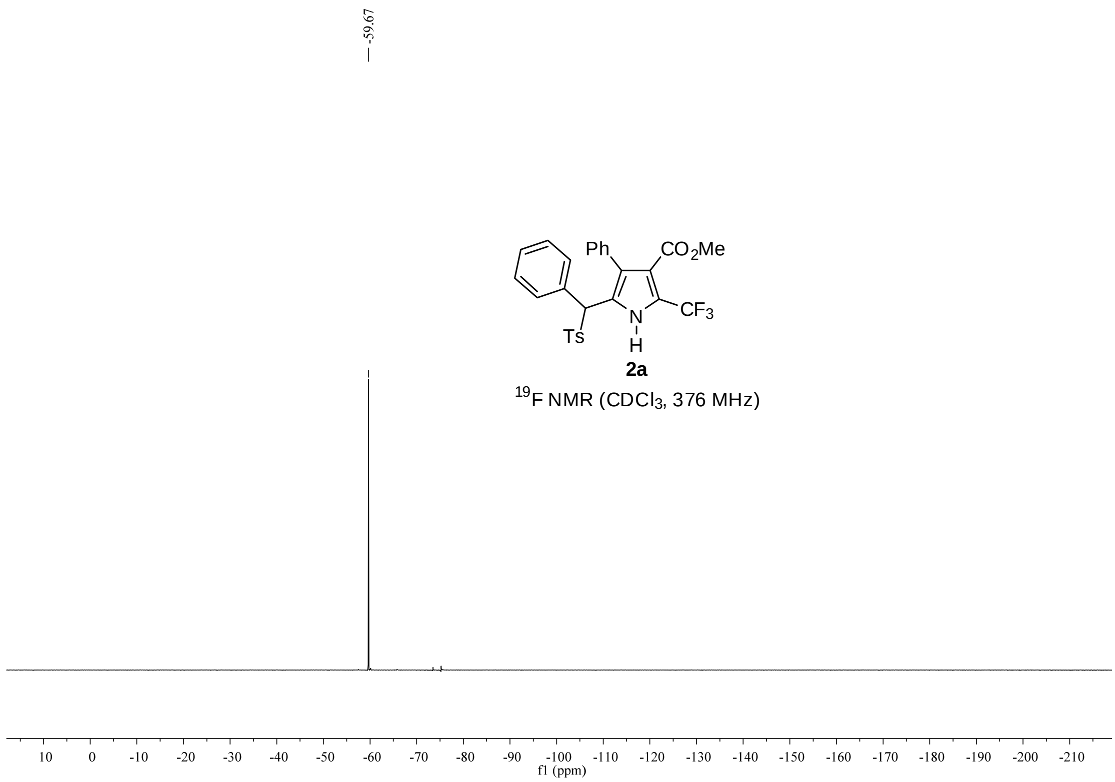
13C NMR (CDCl3, 100 MHz)
f1 (ppm)



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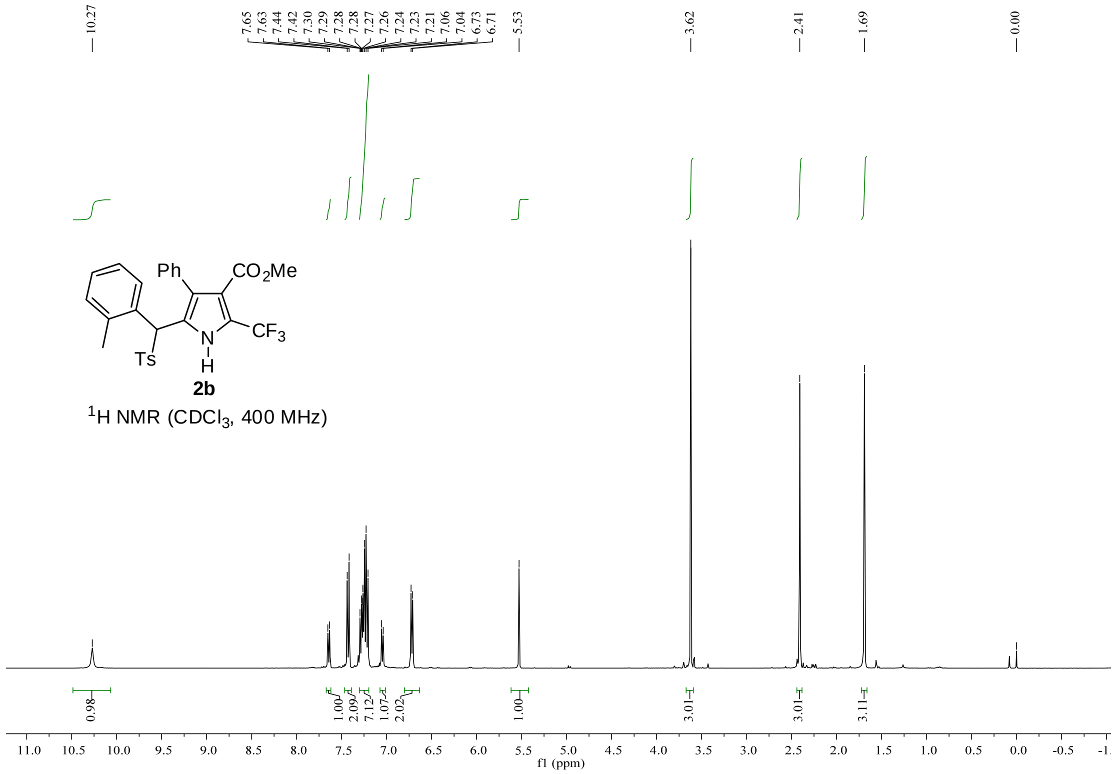
f1 (ppm)



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7.23
7.21
7.06
7.04
6.73
6.71
5.53
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CO2Me
CF3
N
H
Ts
2b
1H NMR (CDCl3, 400 MHz)
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3.01
3.11
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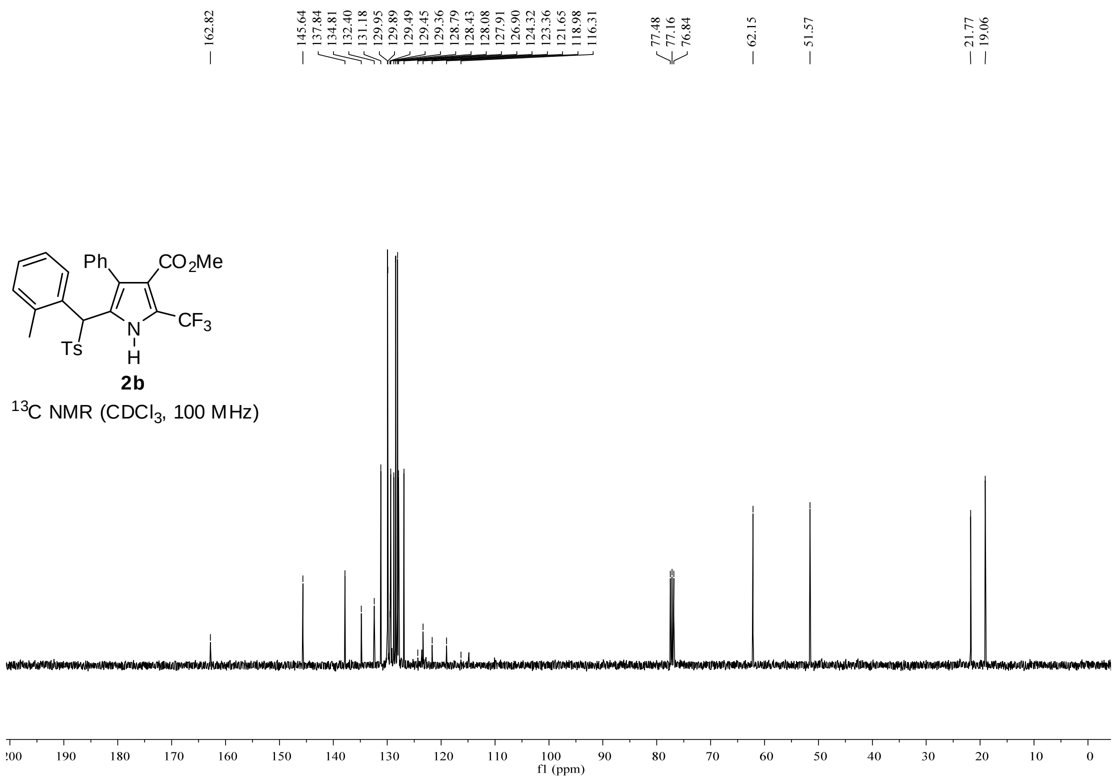
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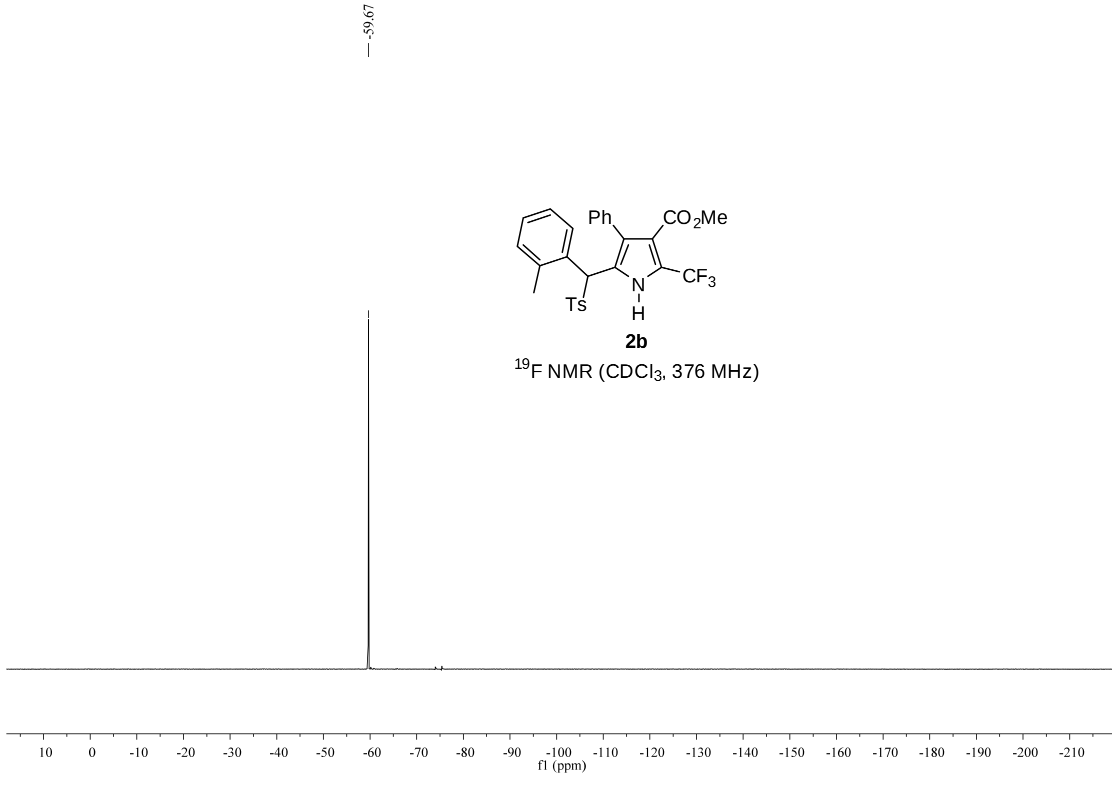
128.43
128.08
127.91
126.90
124.32
123.36
121.65
118.98
116.31
77.48
77.16
76.84
62.15
51.57
21.77
19.06
Ph
CO_2Me
CF_3
Ts
N
H
2b
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)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CF_3
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2b
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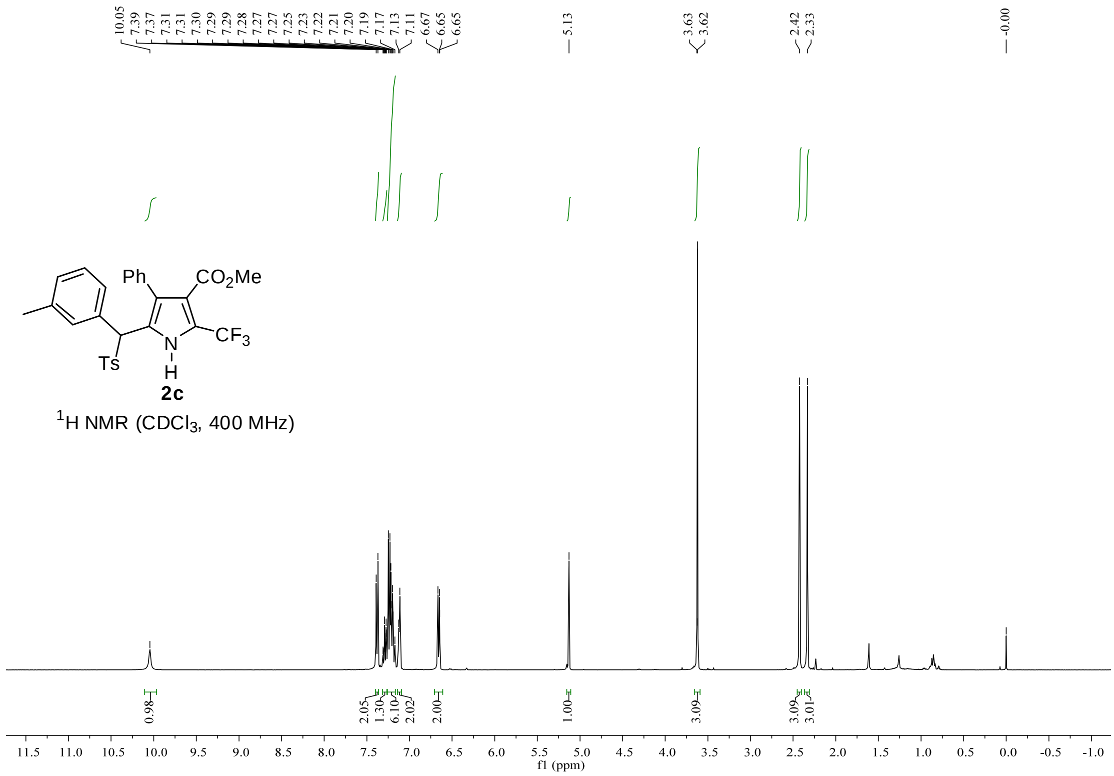
f1 (ppm)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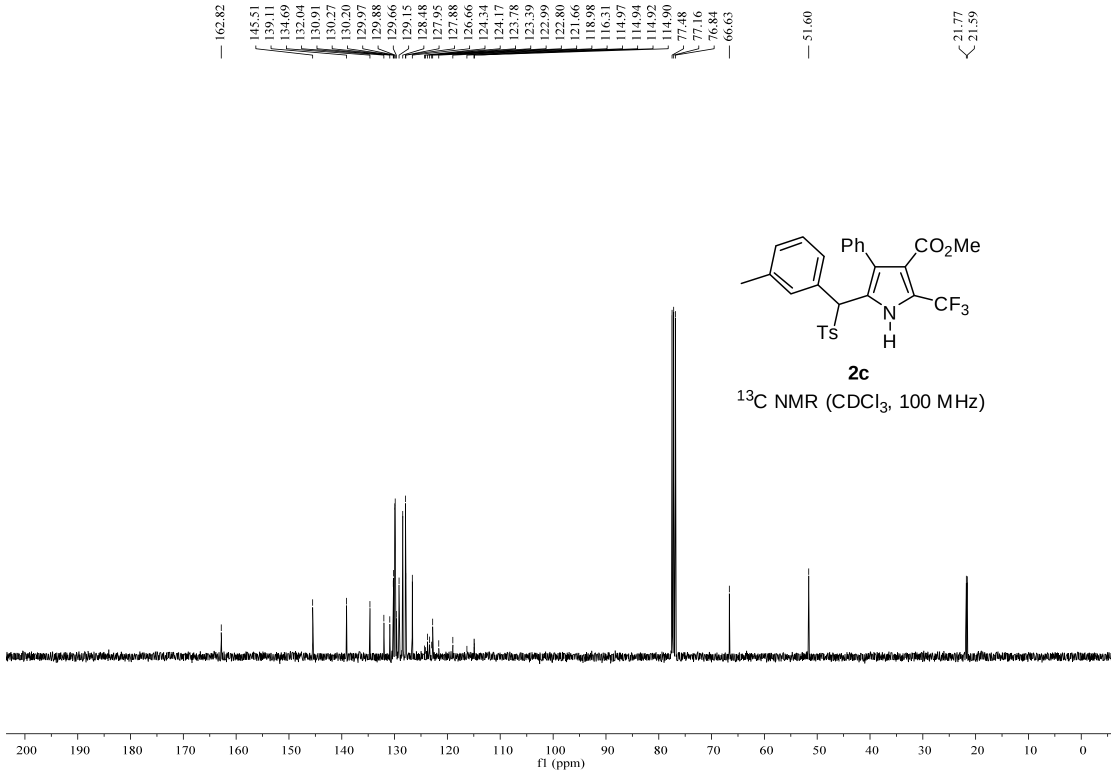
5.13
3.63 3.62
2.42 2.33
-0.00
Ph
CO2Me
CF3
Ts
N
H
2c
1H NMR (CDCl3, 400 MHz)
0.98
2.05 1.30 6.10 2.02
2.00
1.00
3.09
3.09 3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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51.60
21.77 21.59
Ph
CO2Me
CF3
Ts
N
H
2c
13C NMR (CDCl3, 100 MHz)
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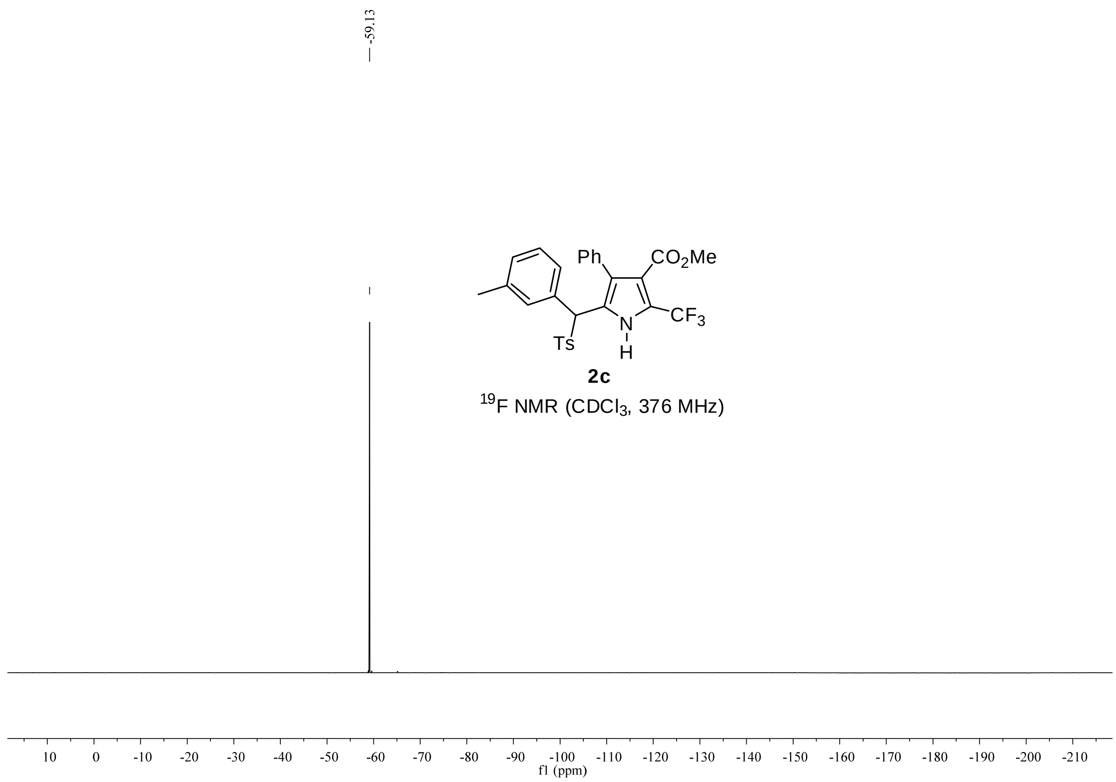
f1 (ppm)



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H
2c
19F NMR (CDCl3, 376 MHz)
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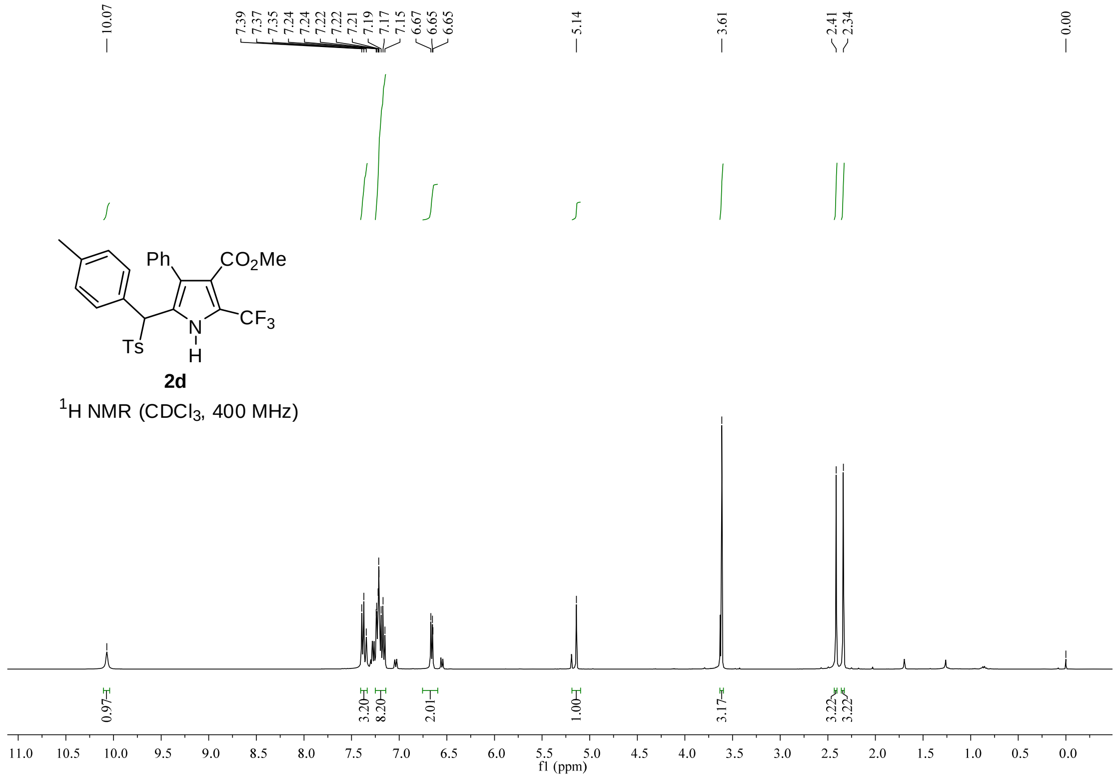
f1 (ppm)



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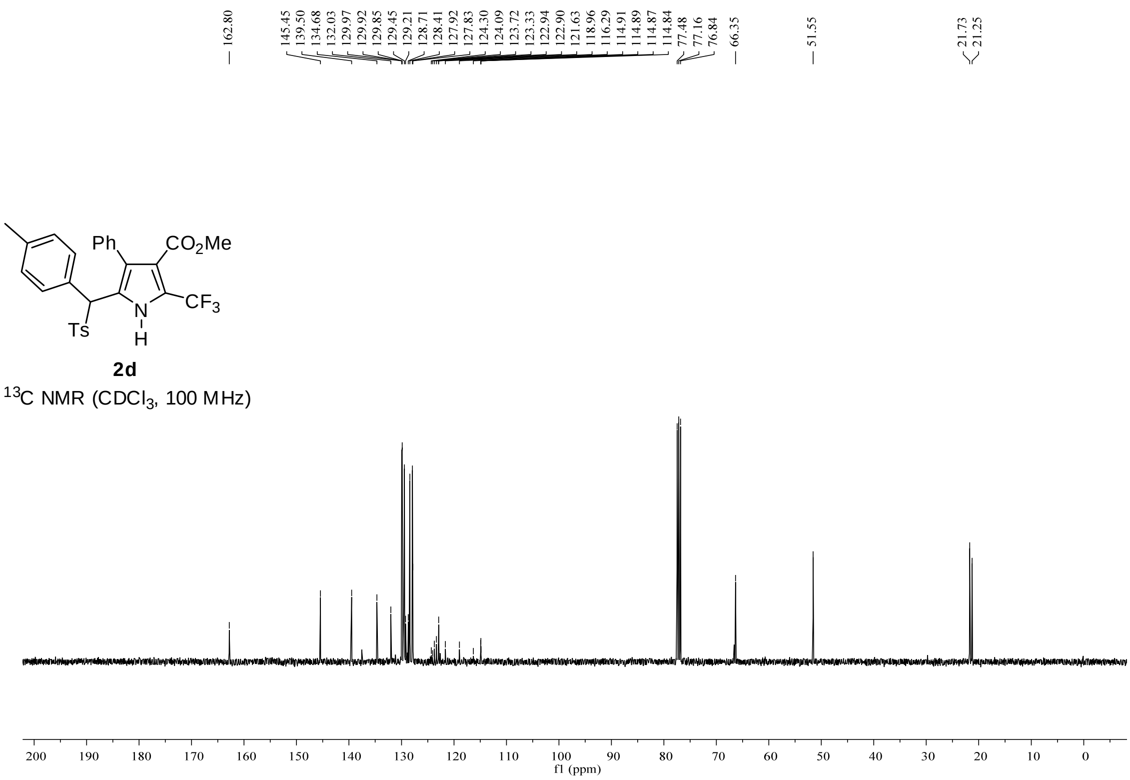
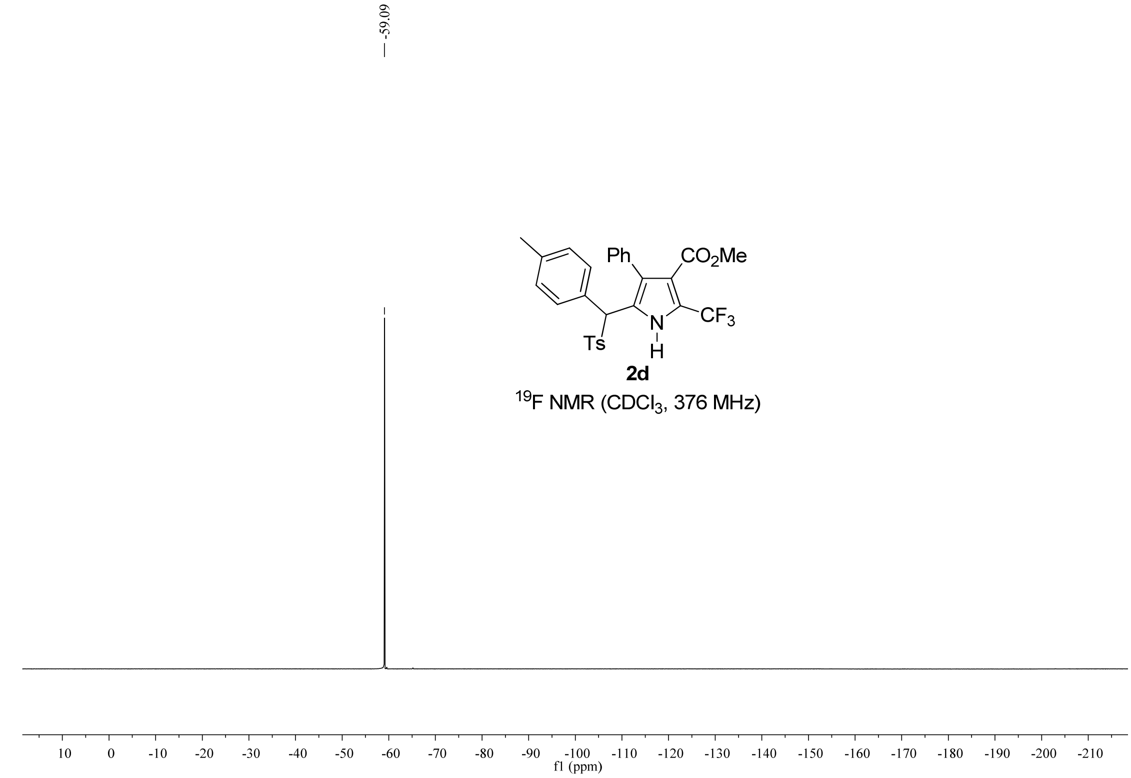
5.14
3.61
2.41 2.34
0.00
Ph
CO2Me
CF3
Ts
N
H
2d
1H NMR (CDCl3, 400 MHz)
0.97 3.20 8.20 2.01 1.00 3.17 3.22 3.22
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



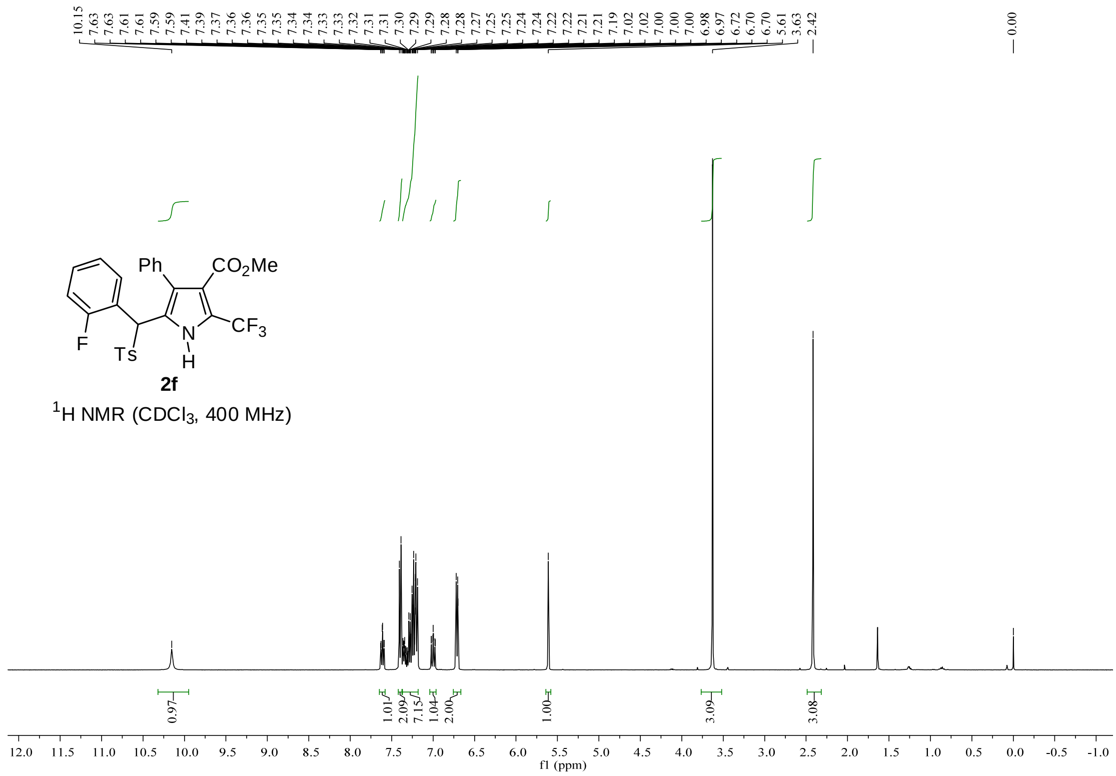
2d

^{13}C NMR ($CDCl_3$, 100 MHz)



2d

^{19}F NMR ($CDCl_3$, 376 MHz)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0.00
Ph
CO2Me
F
Ts
N
H
CF3
2f
1H NMR (CDCl3, 400 MHz)
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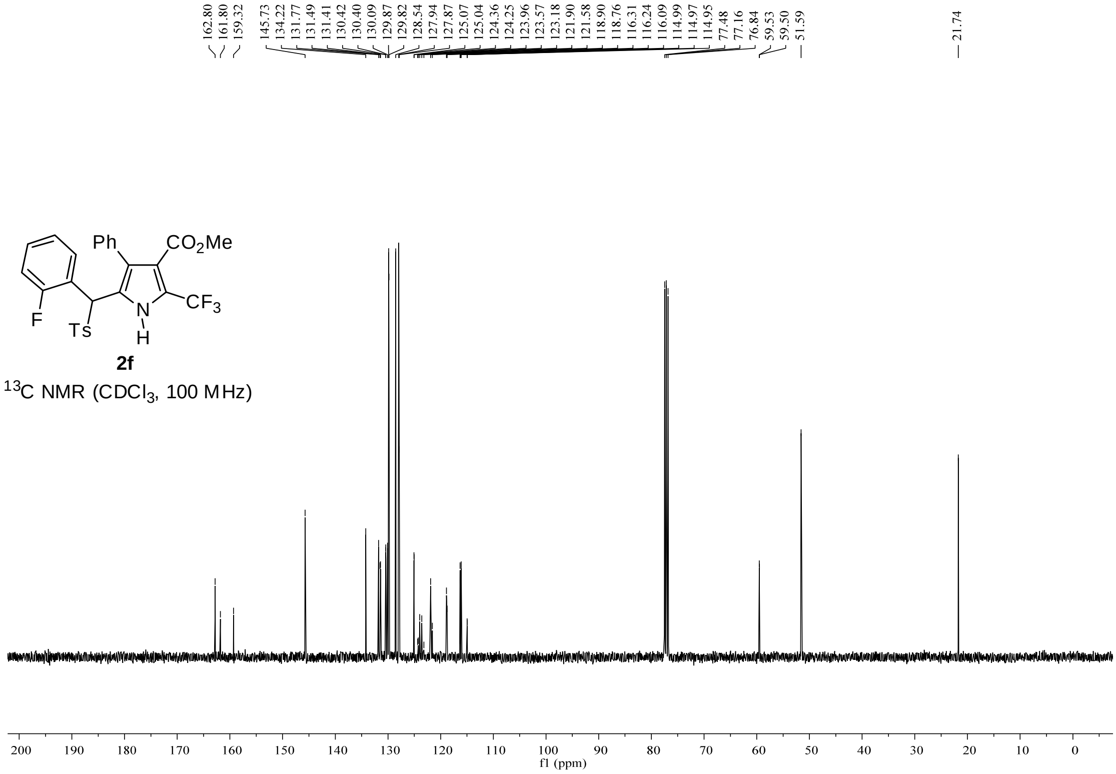
1.01
2.09
7.15
1.04
2.00
1.00
3.09
3.08
fl (ppm)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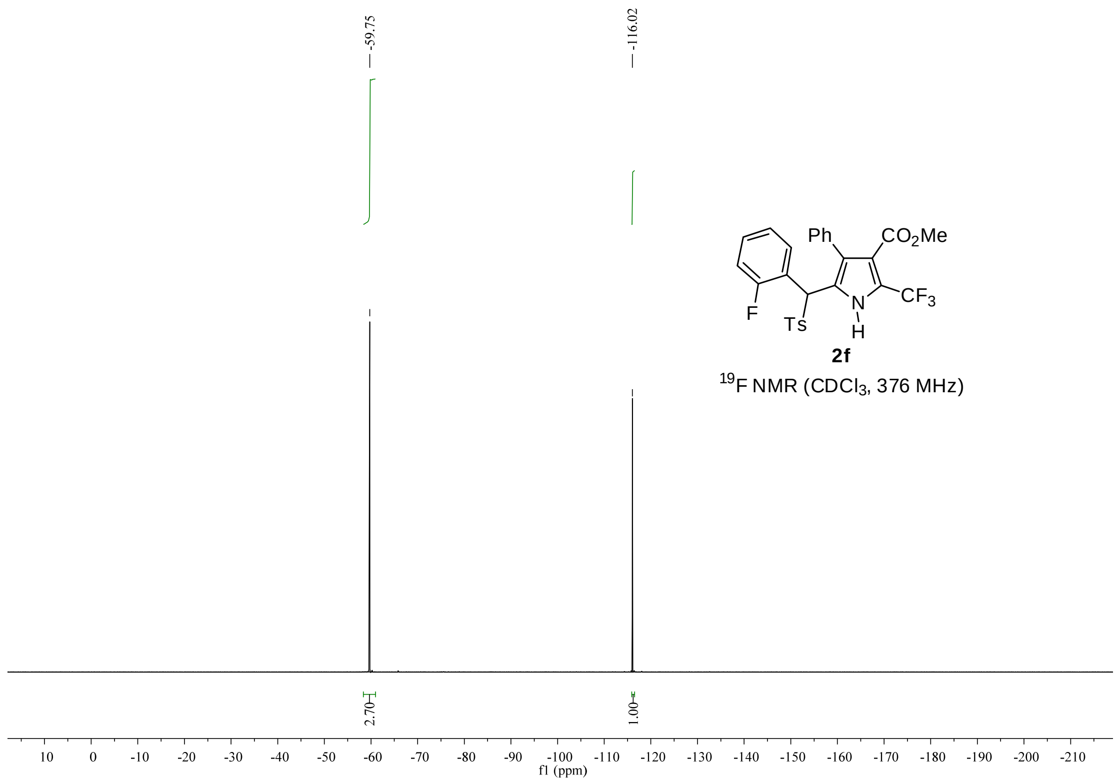
145.73 134.22 131.77 131.49 131.41 130.42 130.40 130.09 129.87 129.82 128.54 127.94 127.87 125.07 125.04 124.36 124.25 123.96 123.57 123.18 121.90 121.58 118.90 118.76 116.31 116.24 116.09 114.99 114.97 114.95 77.48 77.16 76.84 59.53 59.50 51.59
21.74
Ph
CO2Me
F
Ts
N
H
CF3
2f
13C NMR (CDCl3, 100 MHz)
fl (ppm)


Ph
CO2Me
CF3
F
Ts
N
H
2f
19F NMR (CDCl3, 376 MHz)
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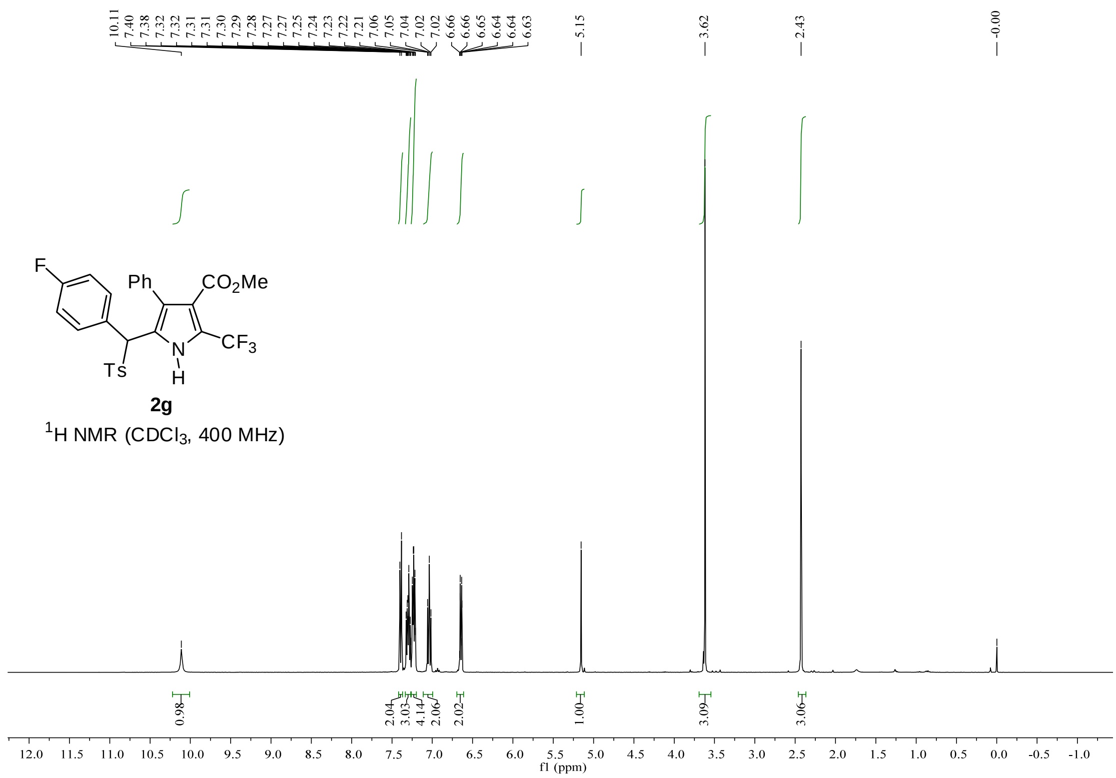
-116.02
2.70
1.00
f1 (ppm)


F
Ph
CO2Me
CF3
Ts
N
H
2g
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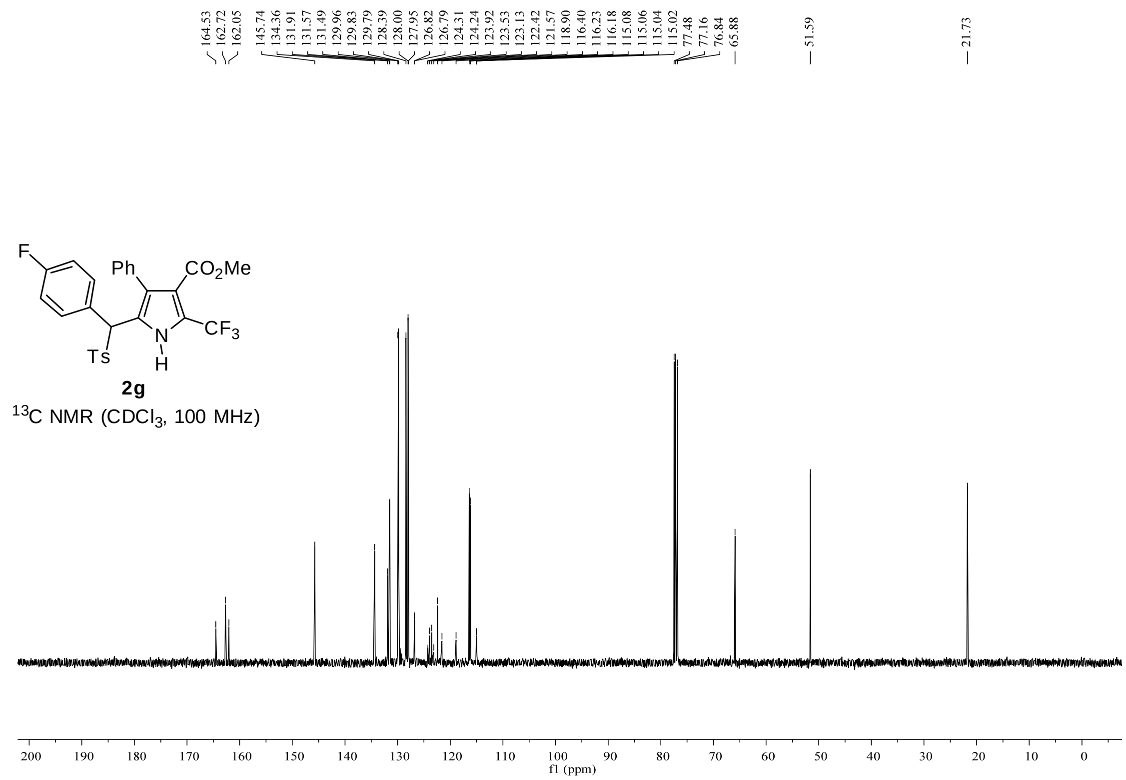
2.04
3.03
4.14
2.06
2.02
1.00
3.09
3.06
f1 (ppm)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127.95
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126.79
124.31
124.24
123.92
123.53
123.13
122.42
121.57
118.90
116.40
116.23
116.18
115.08
115.06
115.04
115.02
77.48
77.16
76.84
65.88
51.59
21.73
F
Ph
CO_2Me
CF_3
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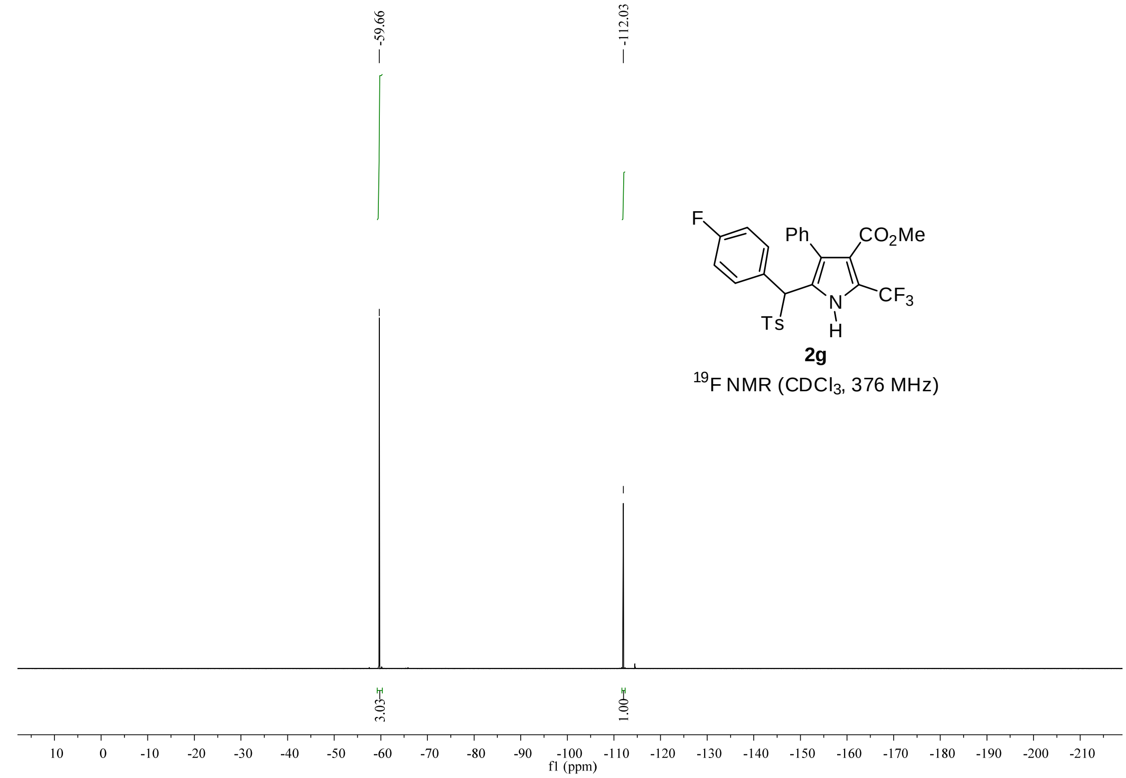
f1 (ppm)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1.00
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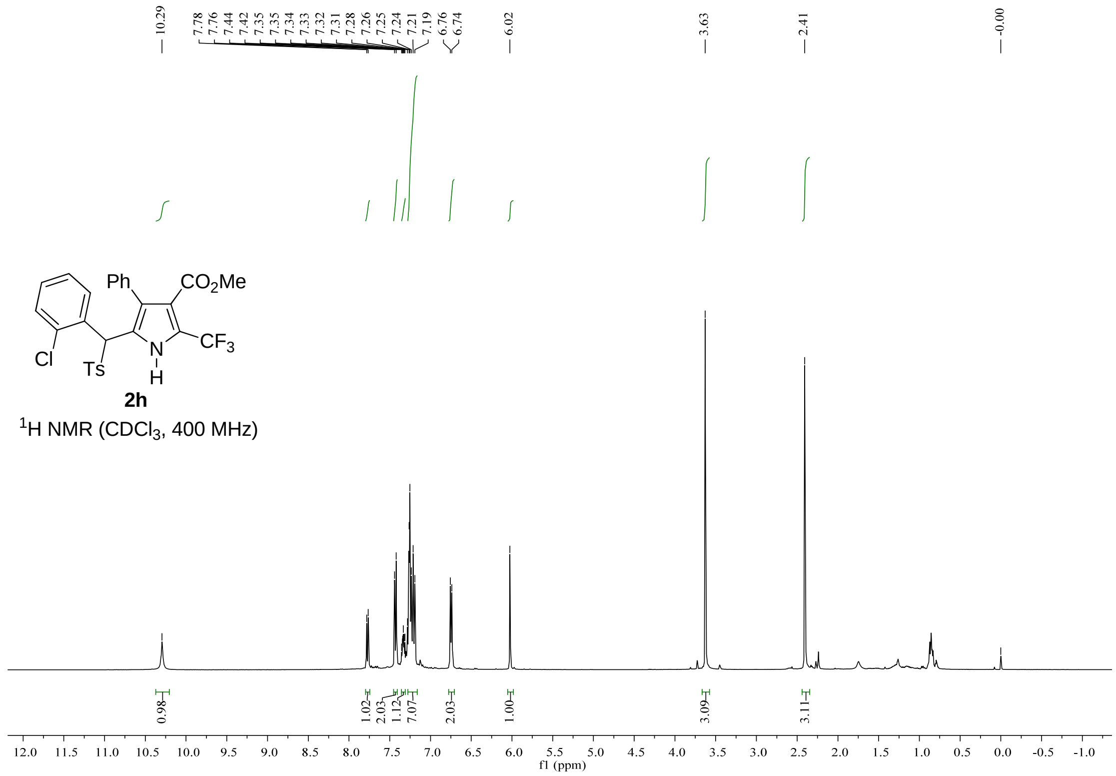
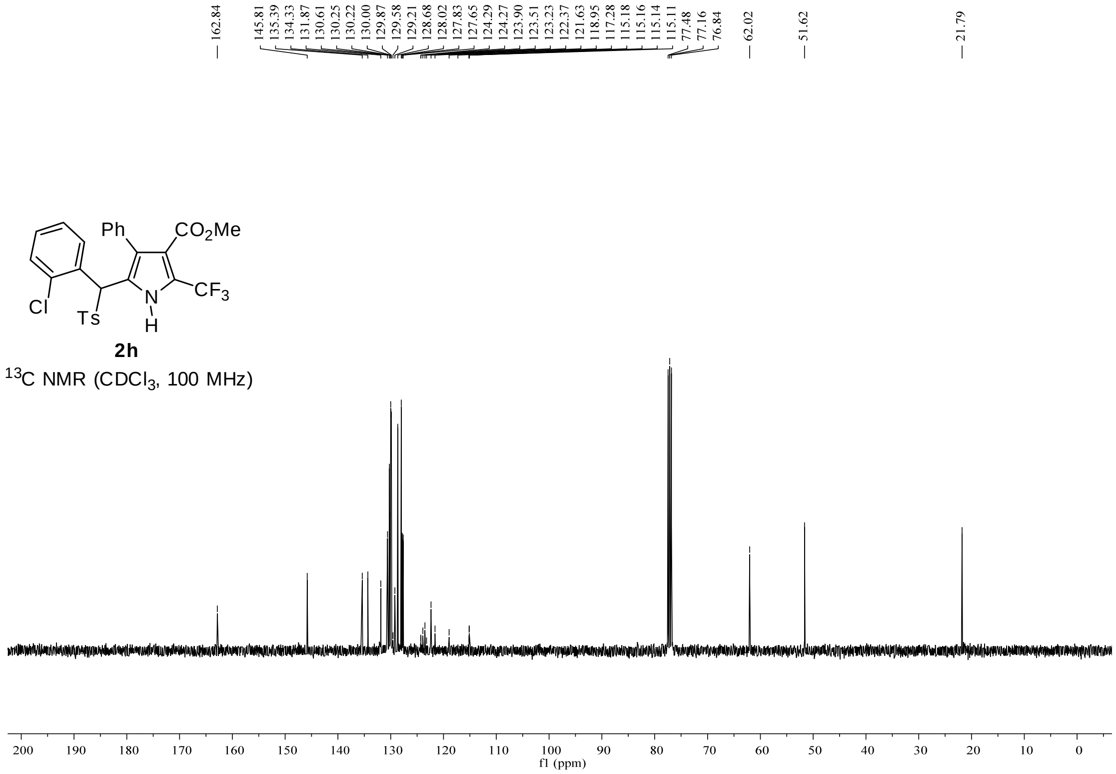
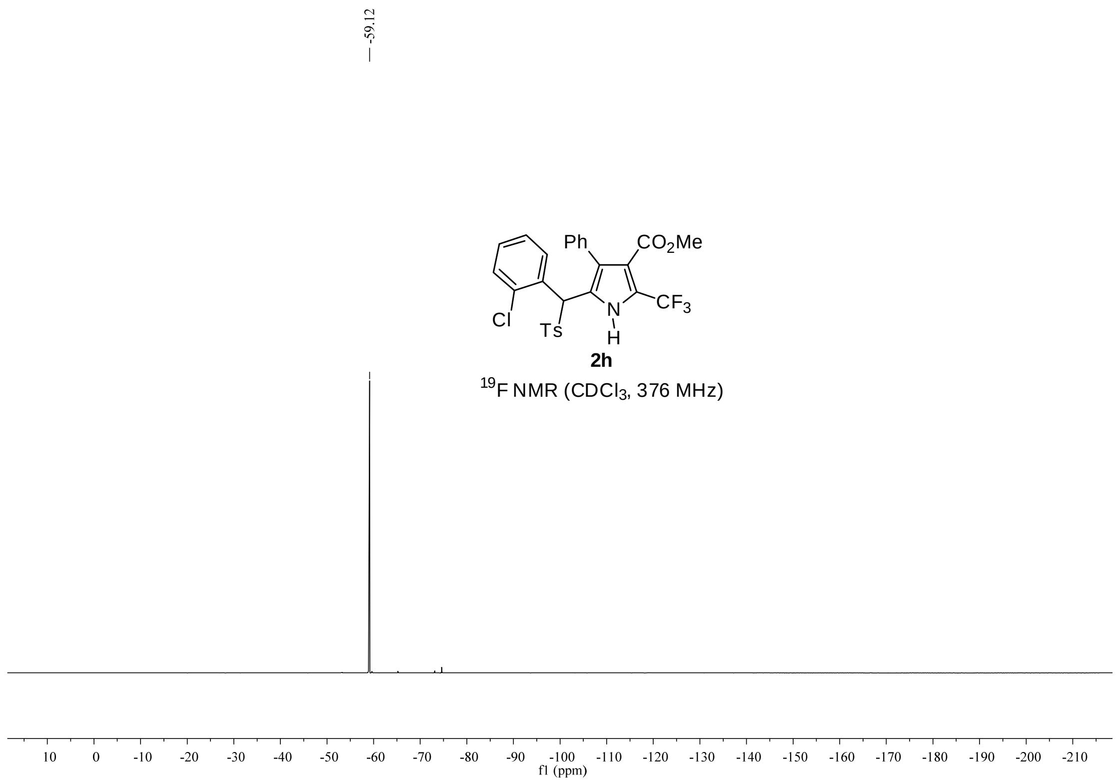
f1 (ppm)



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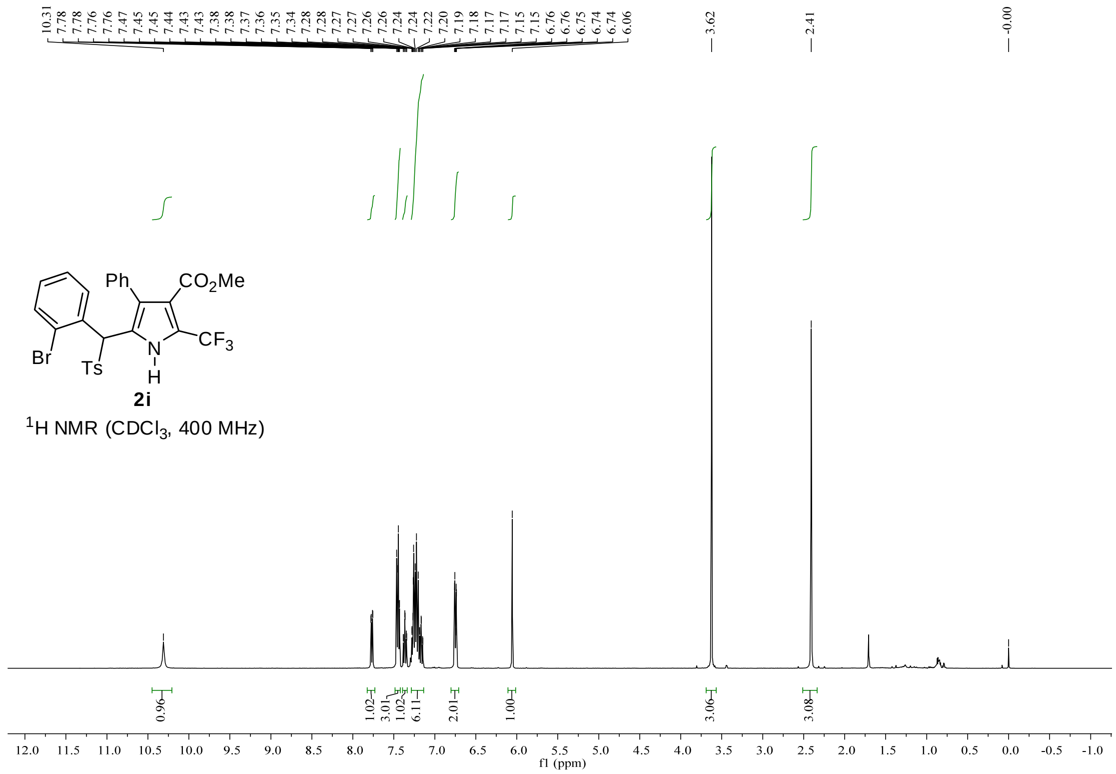
f1 (ppm)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3.62
2.41
-0.00
Ph
CO_2Me
Br
Ts
N
H
CF_3
2i
^{1}H NMR ($CDCl_3$, 400 MHz)
0.96
1.02
3.01
1.02
6.11
2.01
1.00
3.06
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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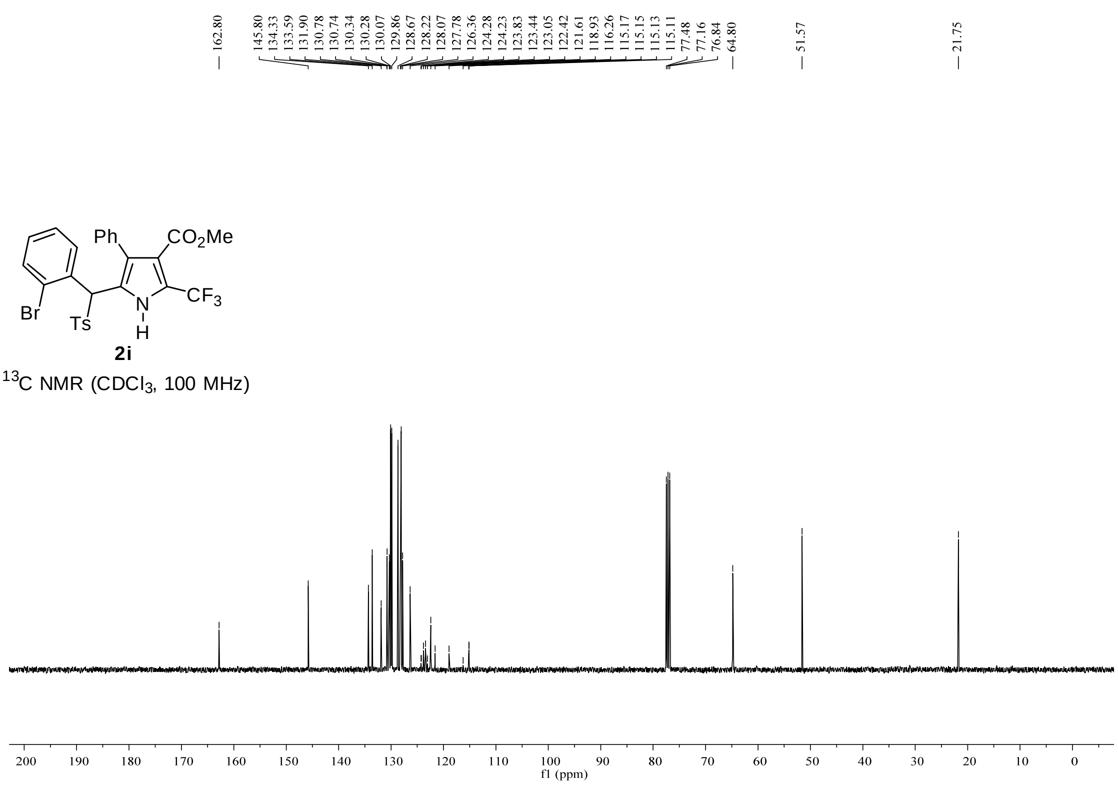
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133.59
131.90
130.78
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130.34
130.28
130.07
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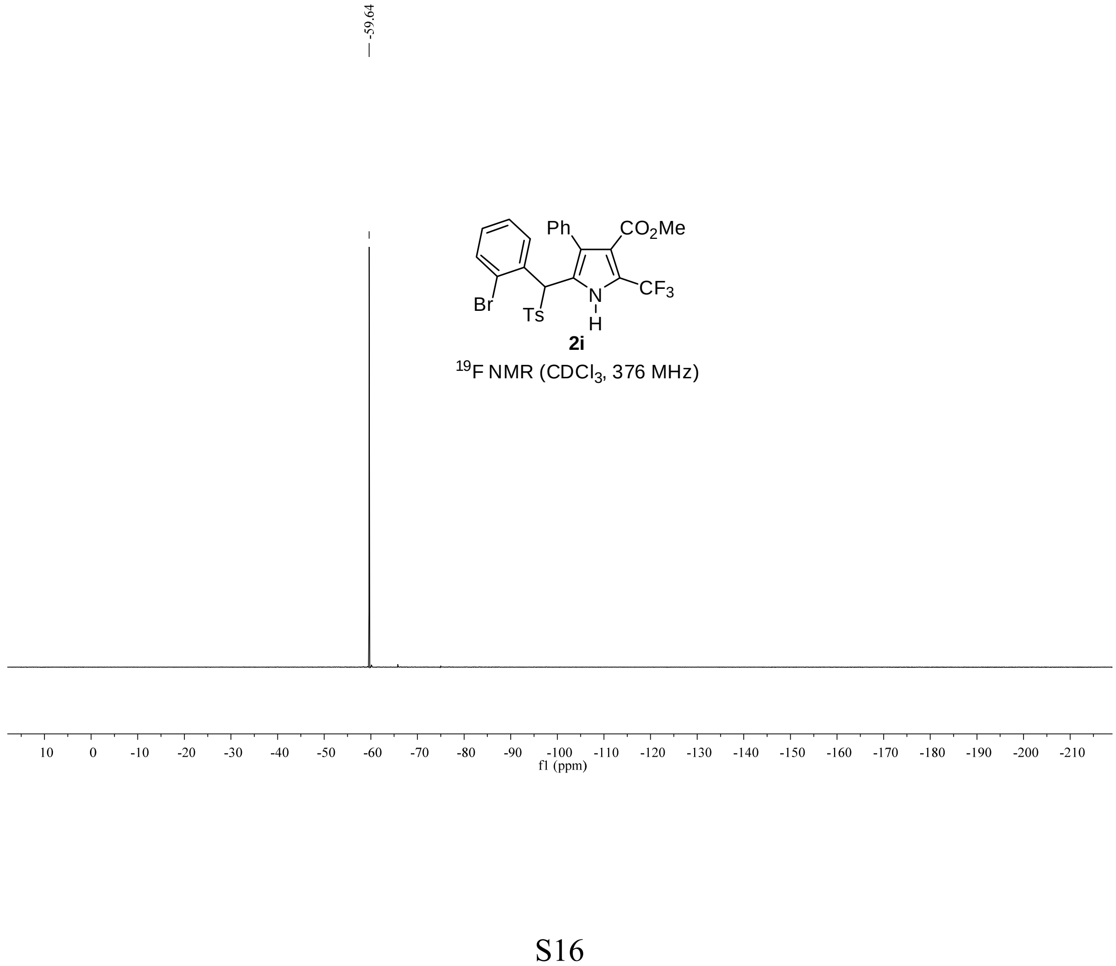
128.22
128.07
127.78
126.36
124.28
124.23
123.83
123.44
123.05
122.42
121.61
118.93
116.26
115.17
115.15
115.13
115.11
77.48
77.16
76.84
64.80
51.57
21.75
Ph
CO2Me
CF3
Br
Ts
N
H
2i
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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CF3
Br
Ts
N
H
2i
19F NMR (CDCl3, 376 MHz)
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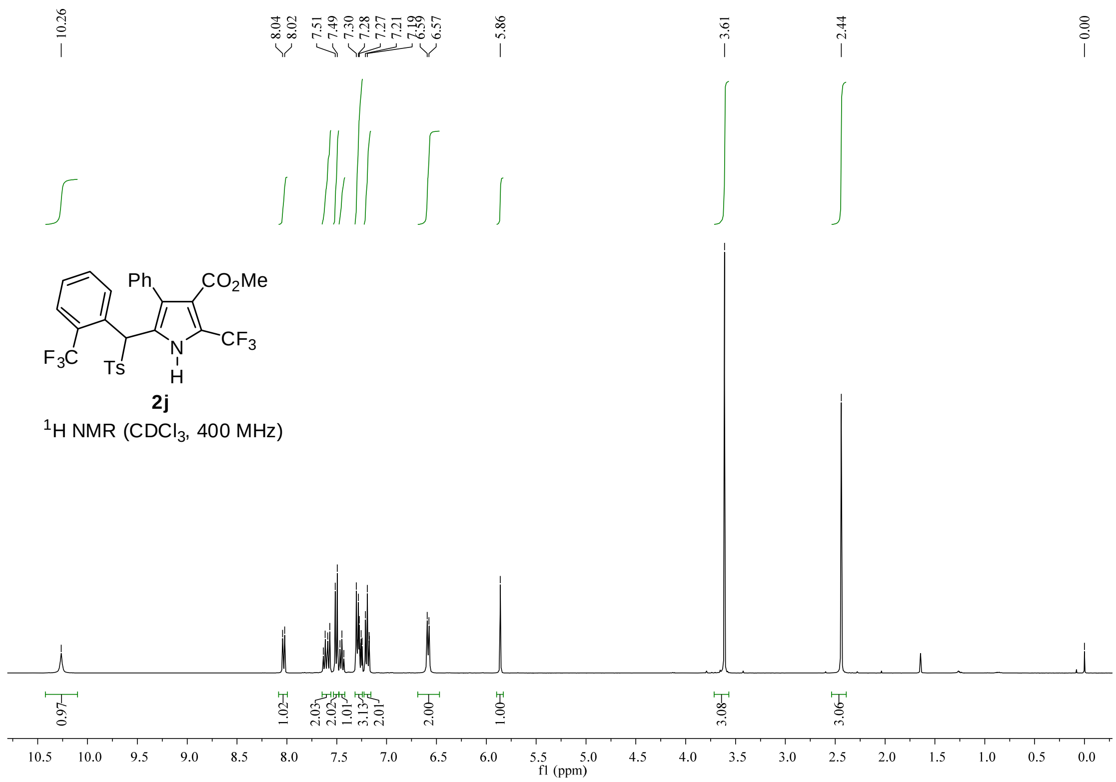
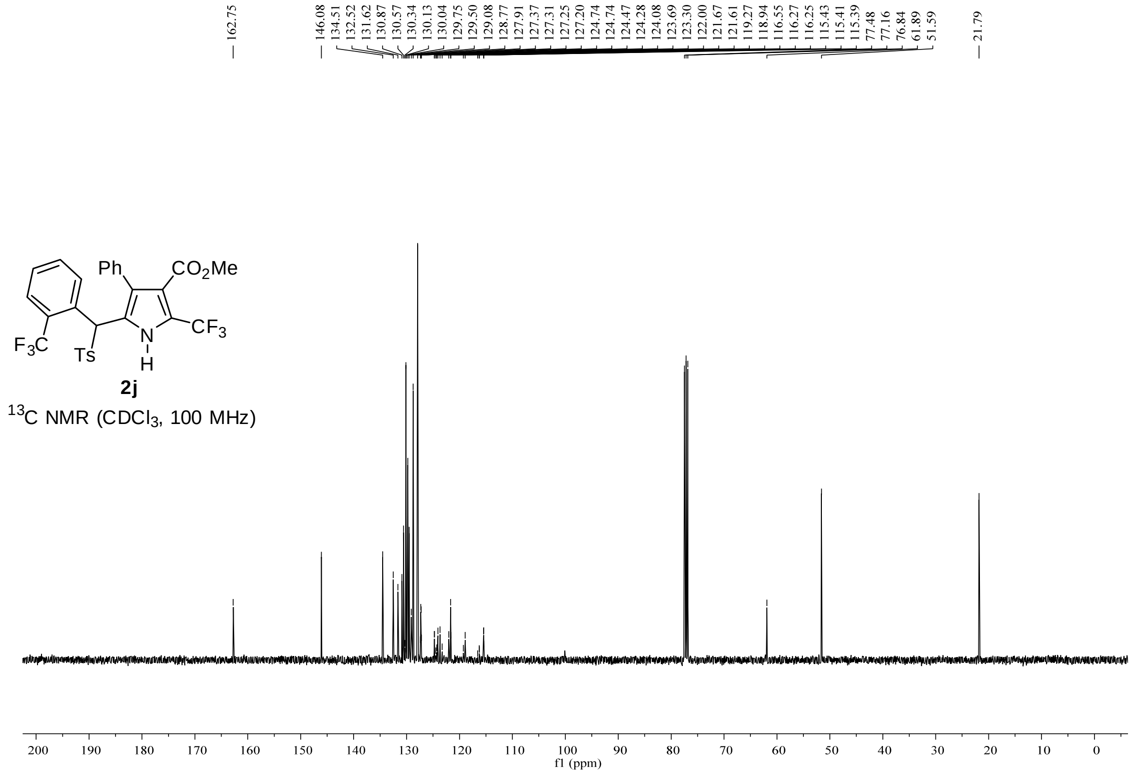
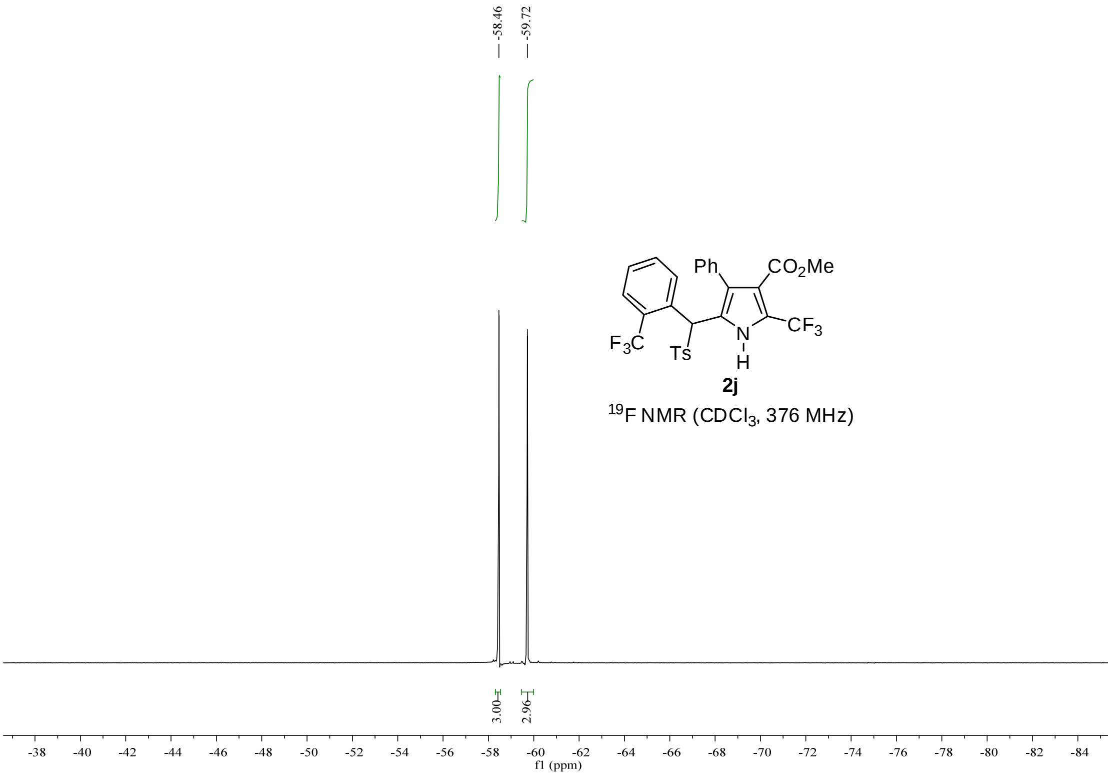
f1 (ppm)



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Ph
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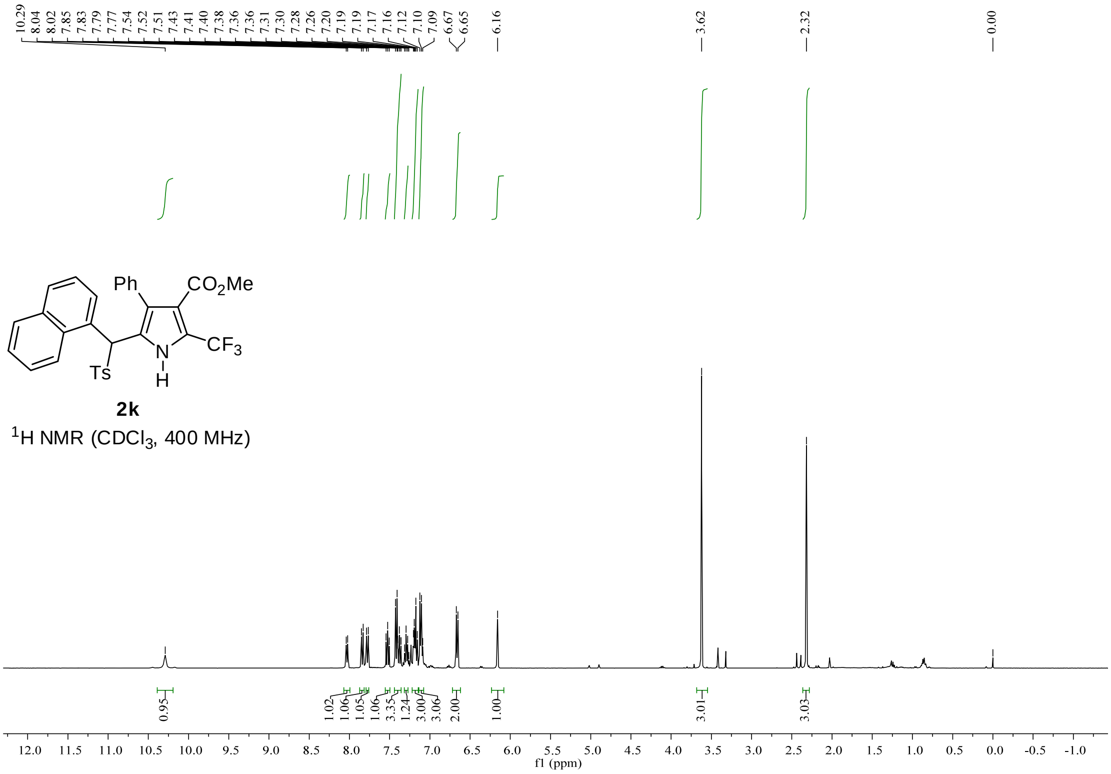
F3C
Ts
N
H
2j
19F NMR (CDCl3, 376 MHz)
3.00
2.96
f1 (ppm)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7.38
7.36
7.36
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7.28
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7.19
7.19
7.17
7.16
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7.10
7.09
6.67
6.65
6.16
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2.32
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Ph
CO2Me
CF3
Ts
N
H
2k
1H NMR (CDCl3, 400 MHz)
0.95
1.02
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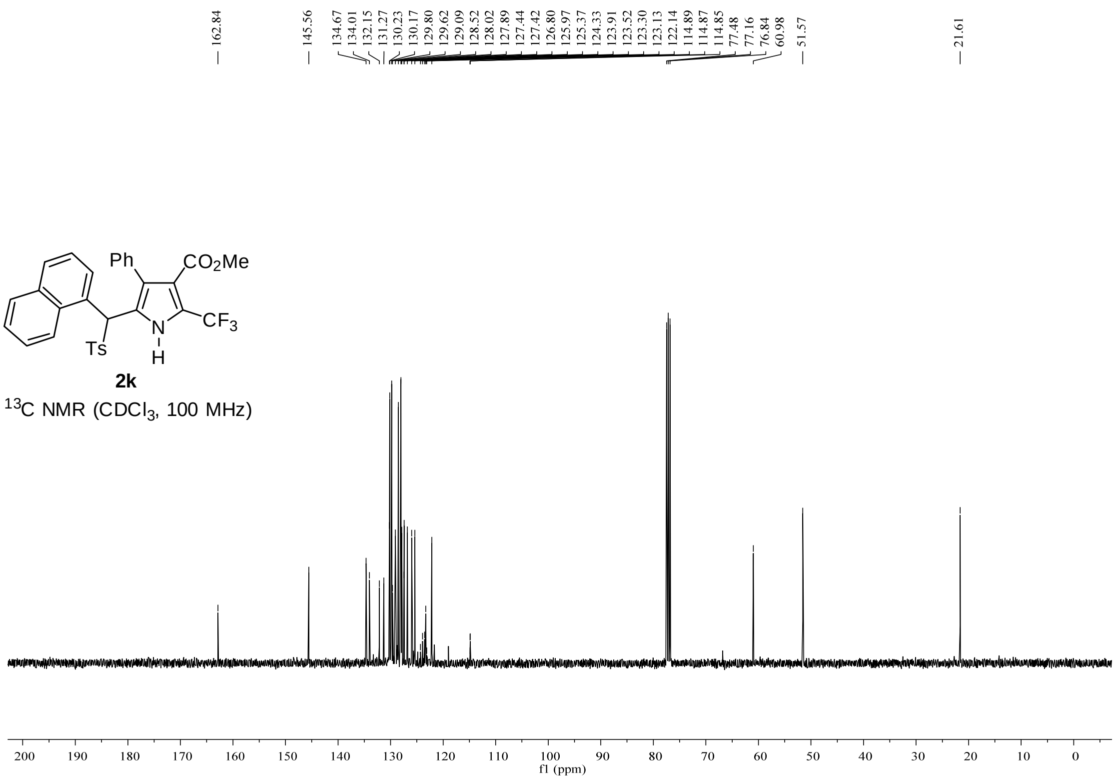
1.00
3.01
3.03
f1 (ppm)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127.42
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123.91
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123.30
123.13
122.14
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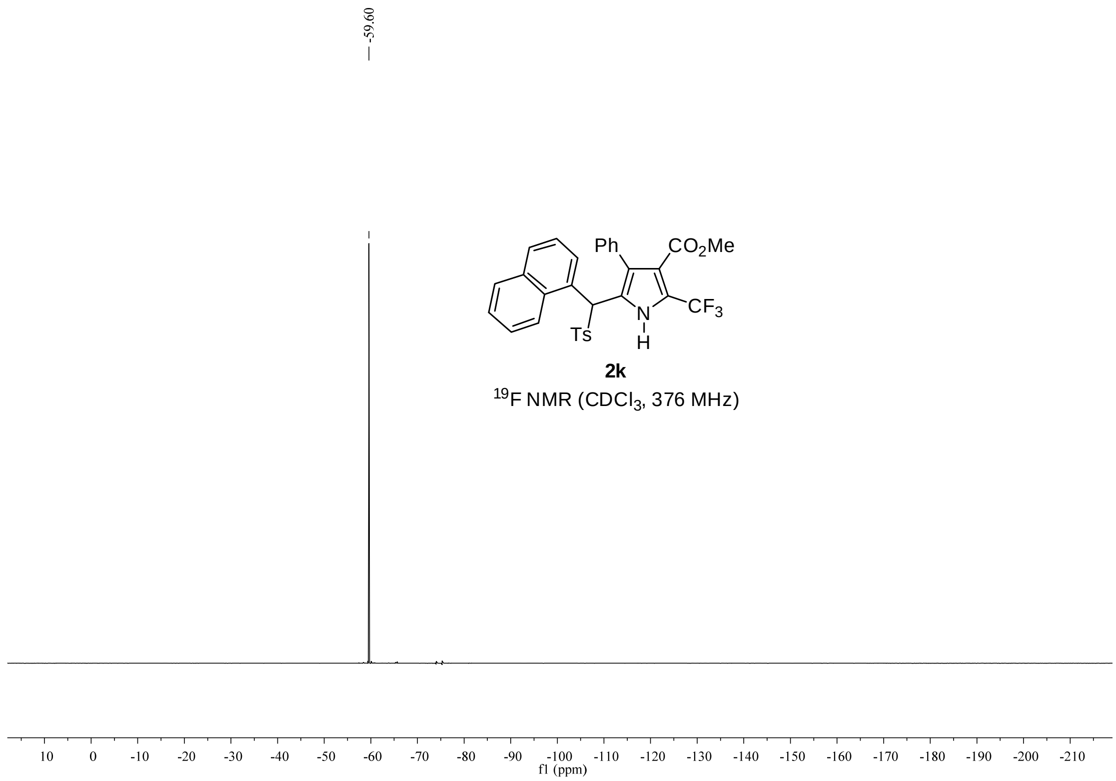
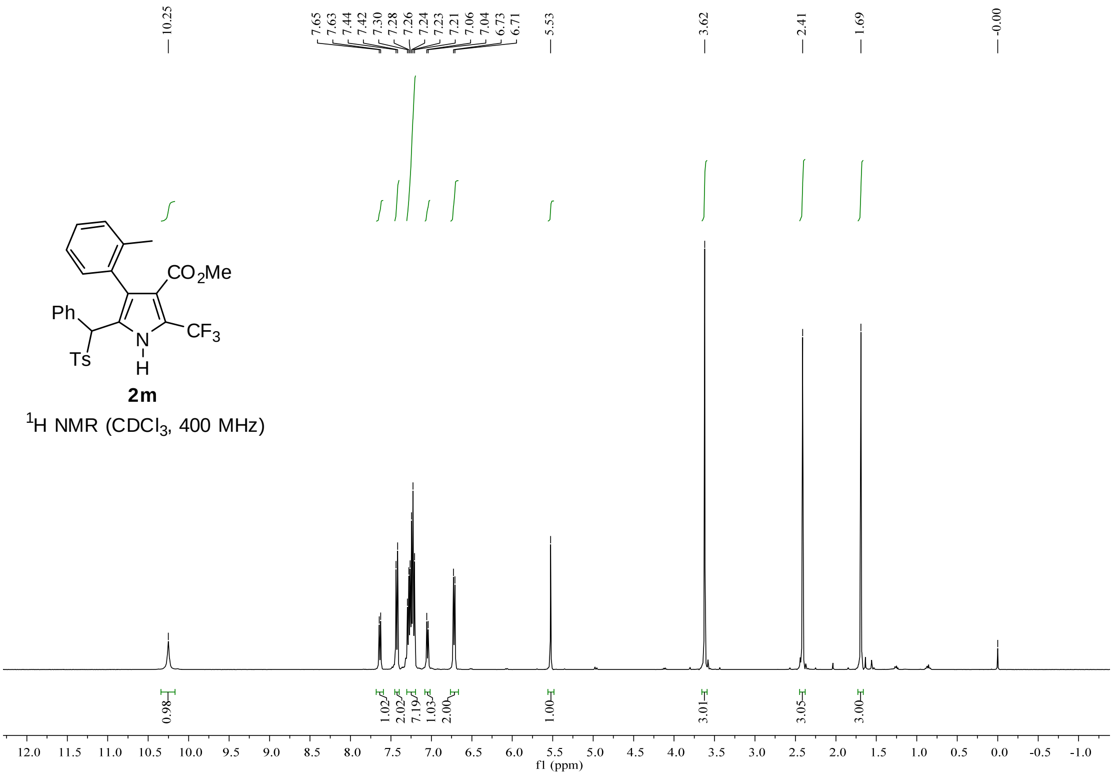
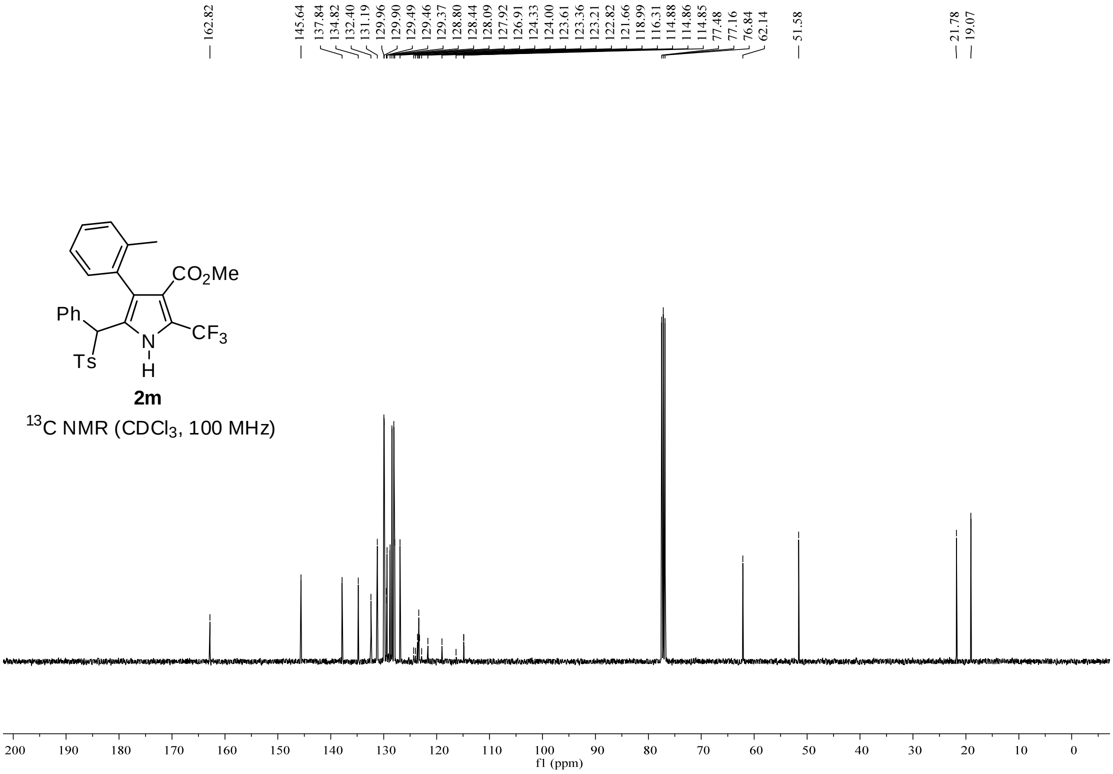
114.87
114.85
77.48
77.16
76.84
60.98
51.57
21.61
Ph
CO2Me
CF3
Ts
N
H
2k
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-59.60
Ph
CO2Me
CF3
Ts
N
H
2k
19F NMR (CDCl3, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



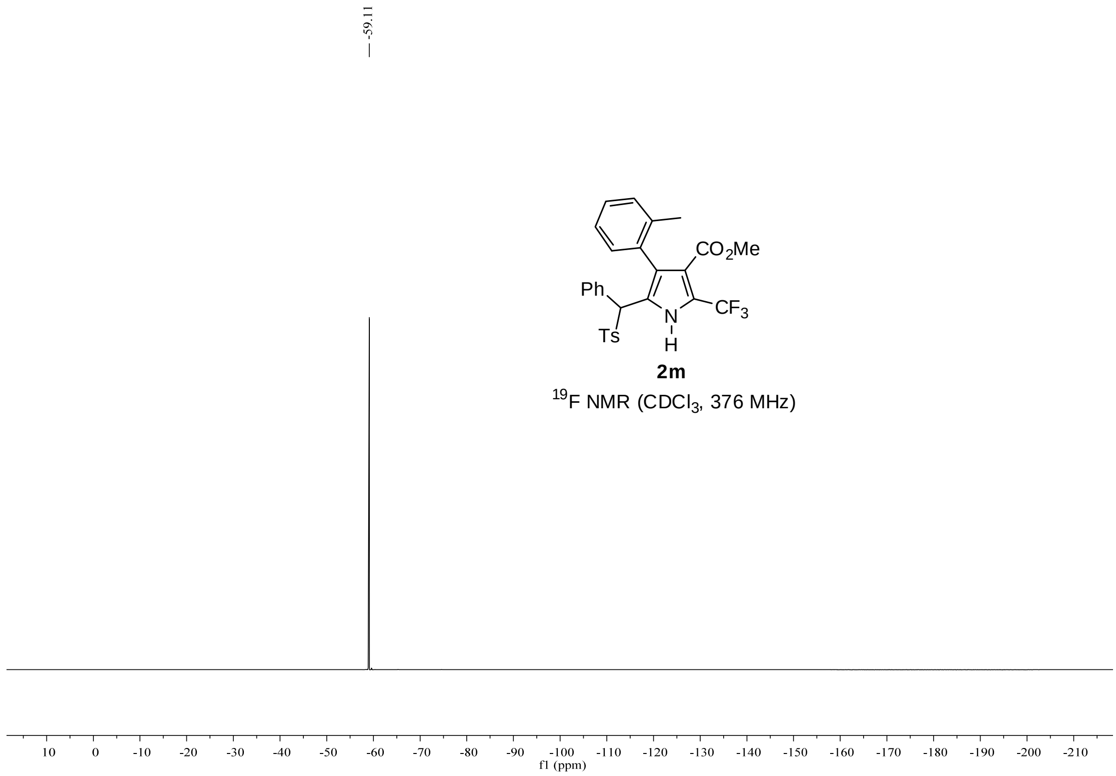
2m

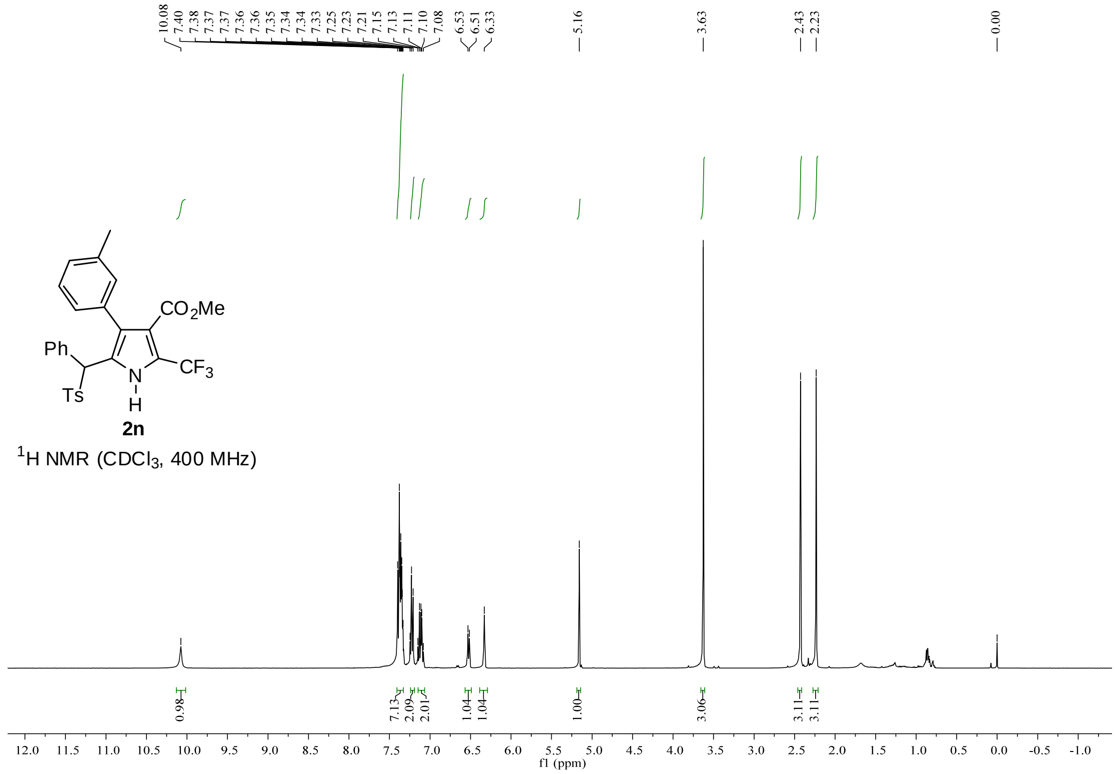
^{1}H NMR ($CDCl_3$, 400 MHz)

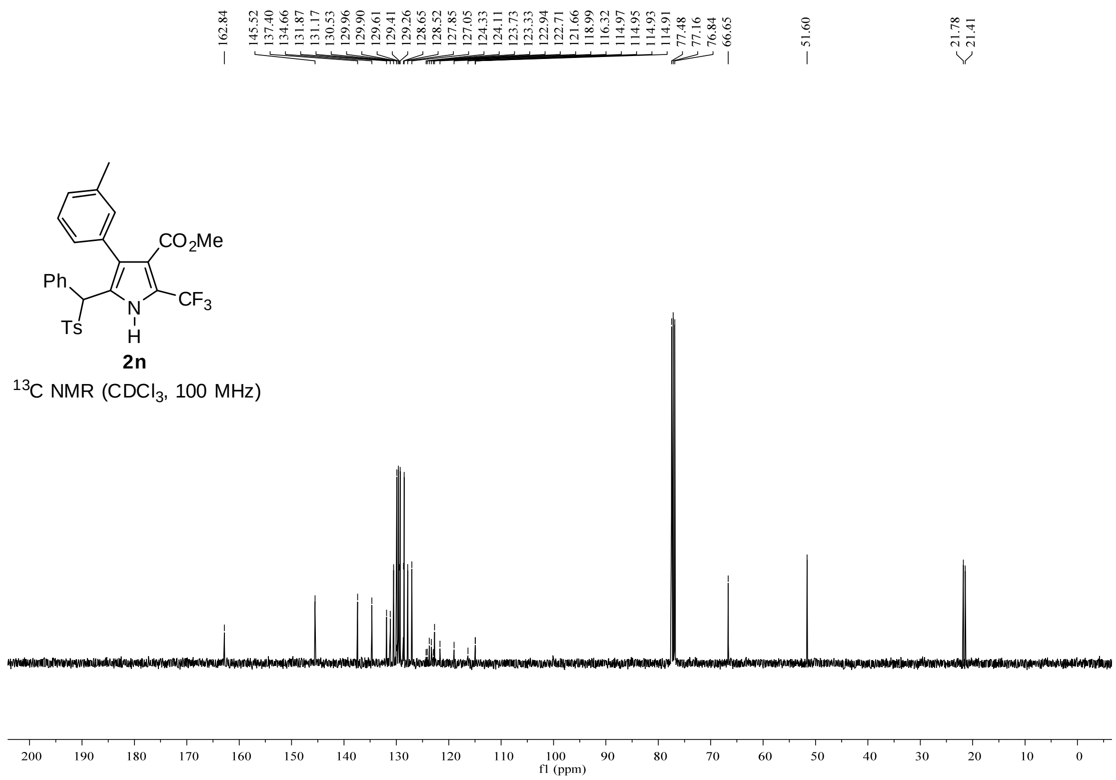


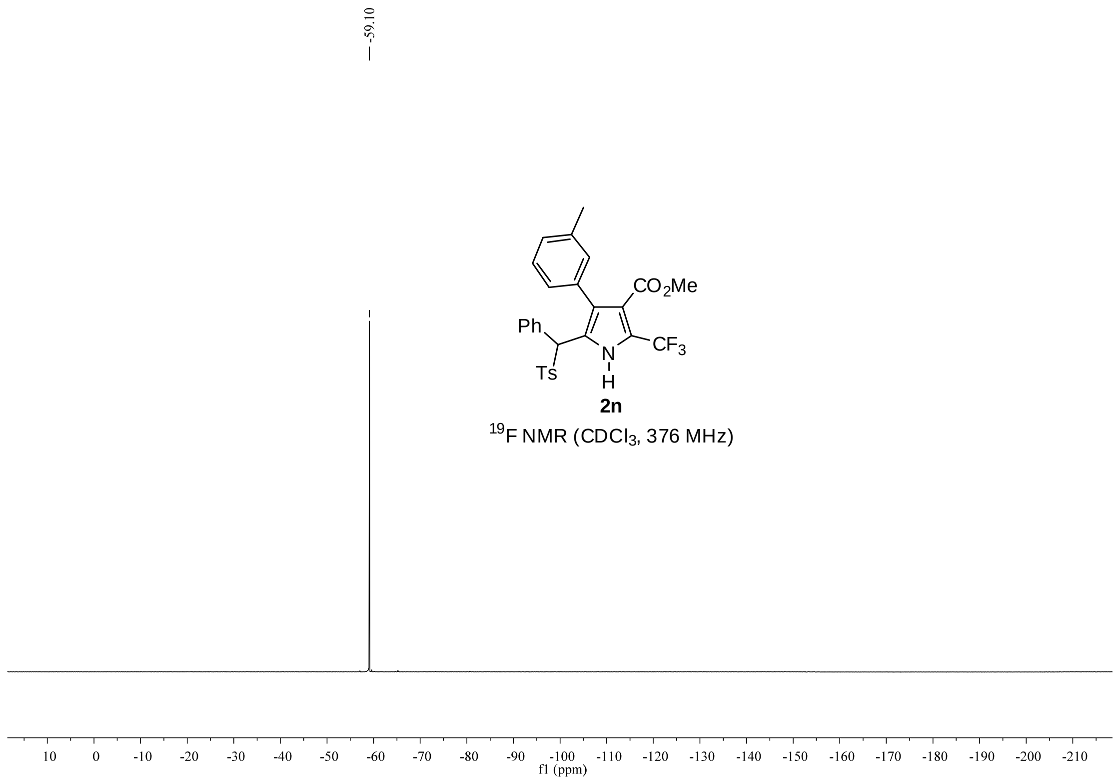
2m

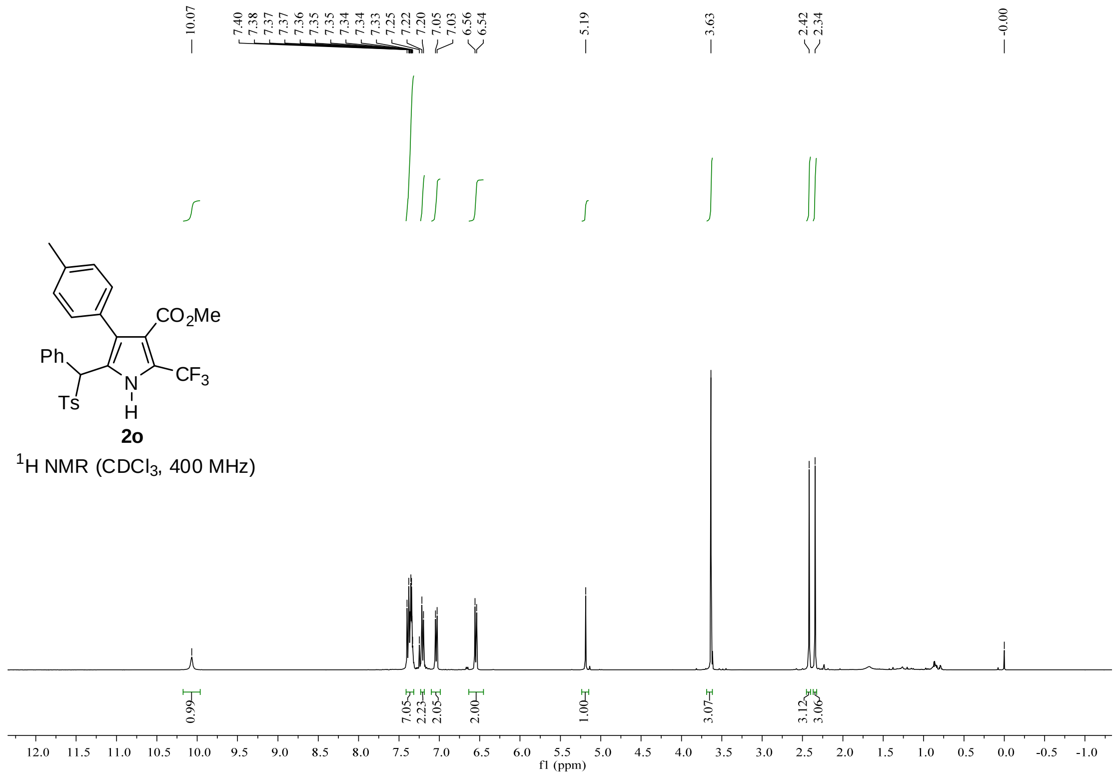
^{13}C NMR ($CDCl_3$, 100 MHz)

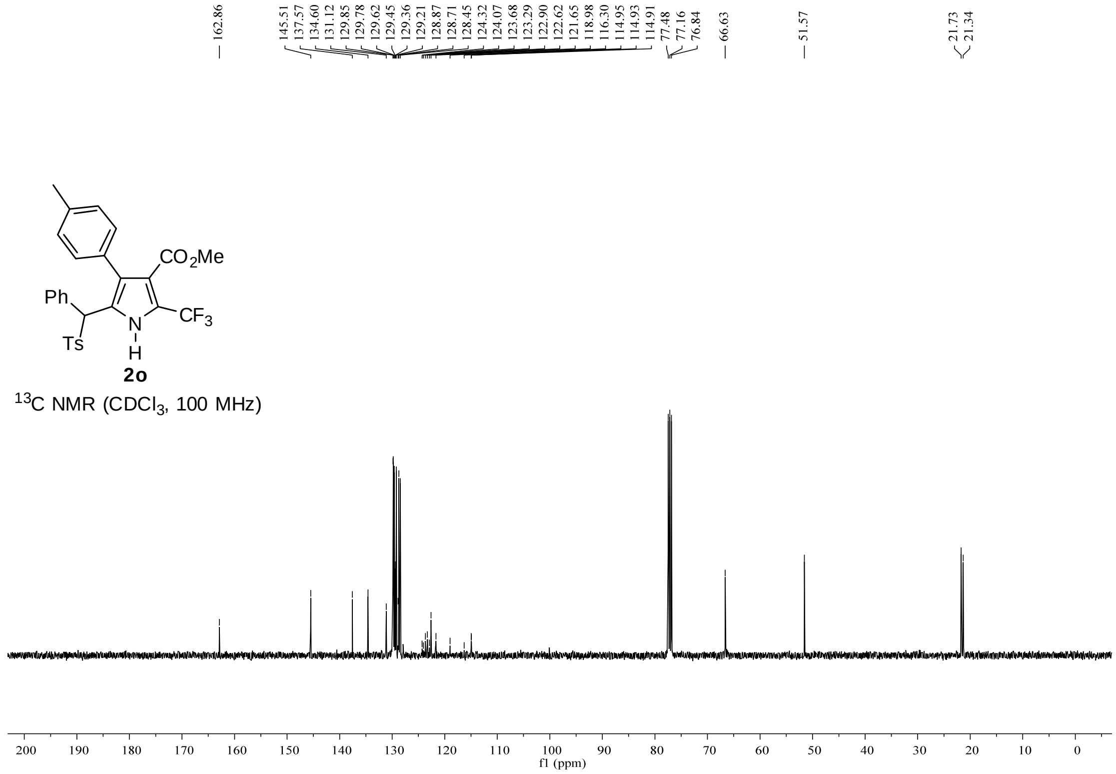

-59.11
CO2Me
Ph
CF3
Ts
N
H
2m
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

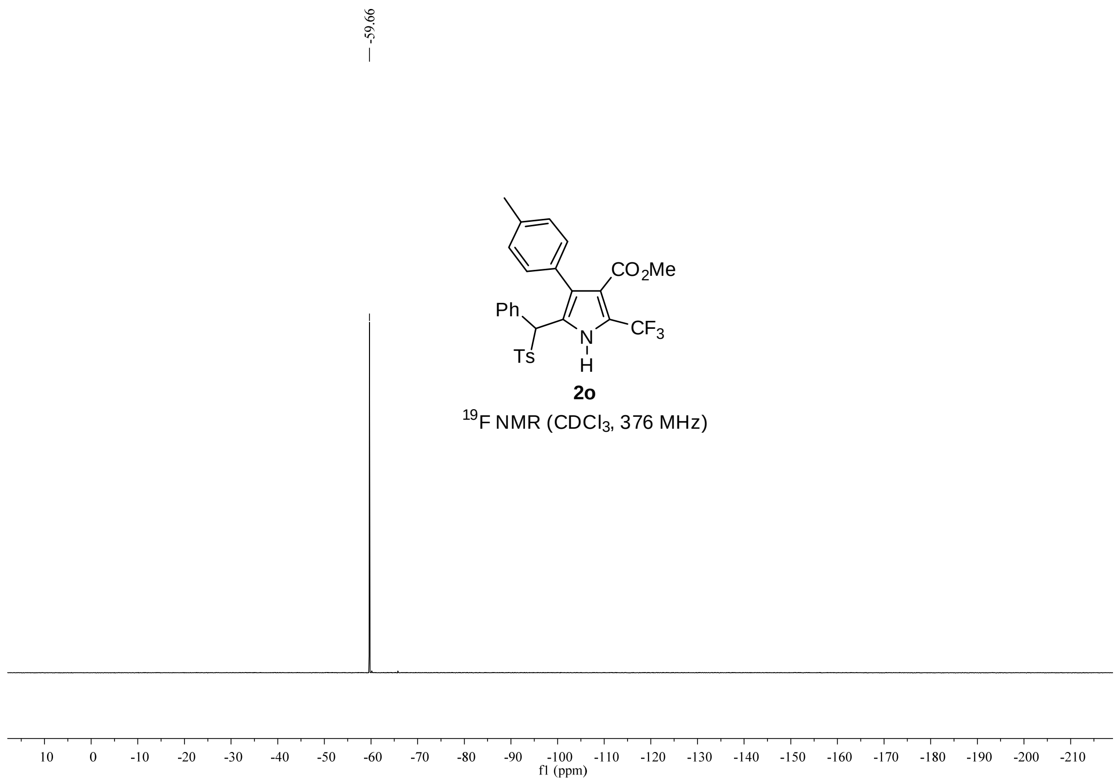

CO2Me
Ph
CF3
Ts
N
H
2n
1H NMR (CDCl3, 400 MHz)
f1 (ppm)


162.84
145.52
137.40
134.66
131.87
131.17
130.53
129.96
129.90
129.61
129.41
129.26
128.65
128.52
127.85
127.05
124.33
124.11
123.73
123.33
122.94
122.71
121.66
118.99
116.32
114.97
114.95
114.93
114.91
77.48
77.16
76.84
66.65
51.60
21.78
21.41
CO2Me
Ph
CF3
Ts
N
H
2n
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


-59.10
CO2Me
Ph
CF3
Ts
N
H
2n
19F NMR (CDCl3, 376 MHz)
f1 (ppm)


10.07
7.40
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.25
7.22
7.20
7.05
7.03
6.56
6.54
5.19
3.63
2.42
2.34
-0.00
CO2Me
Ph
CF3
Ts
N
H
2o
1H NMR (CDCl3, 400 MHz)
0.99
7.05
2.23
2.05
2.00
1.00
3.07
3.12
3.06
f1 (ppm)


162.86
145.51
137.57
134.60
131.12
129.85
129.78
129.62
129.45
129.36
129.21
128.87
128.71
128.45
124.32
124.07
123.68
123.29
122.90
122.62
121.65
118.98
116.30
114.95
114.93
114.91
77.48
77.16
76.84
66.63
51.57
21.73
21.34
CO2Me
Ph
CF3
Ts
N
H
2o
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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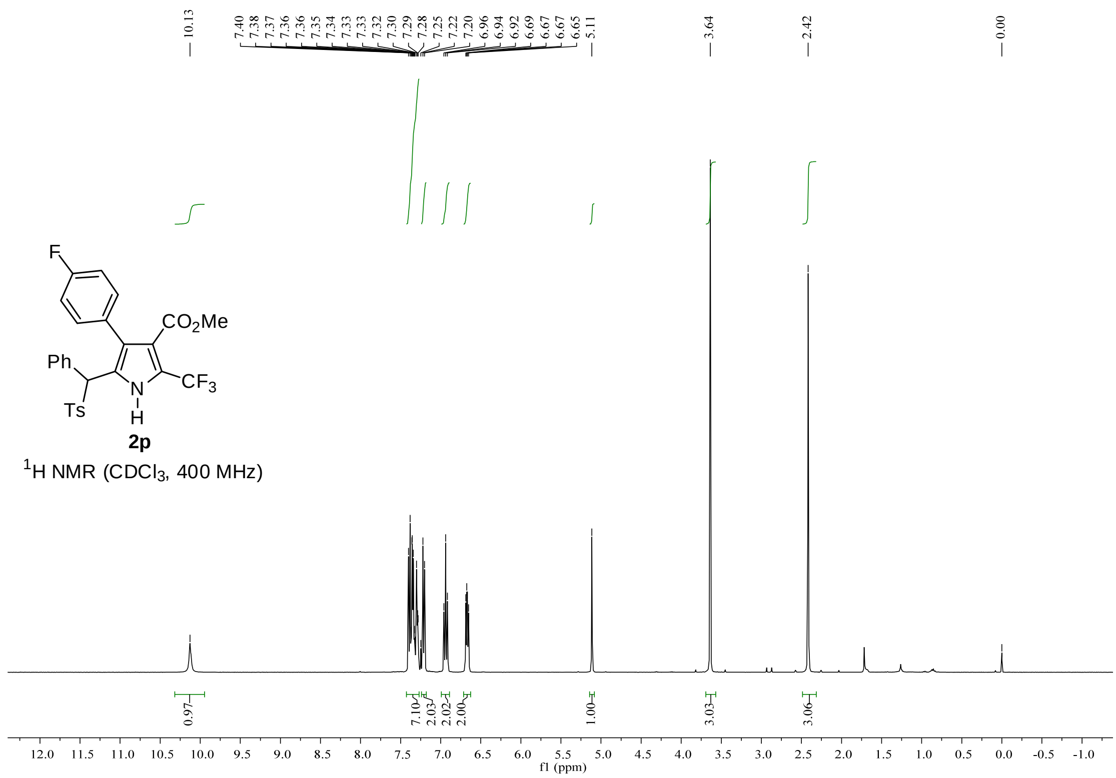
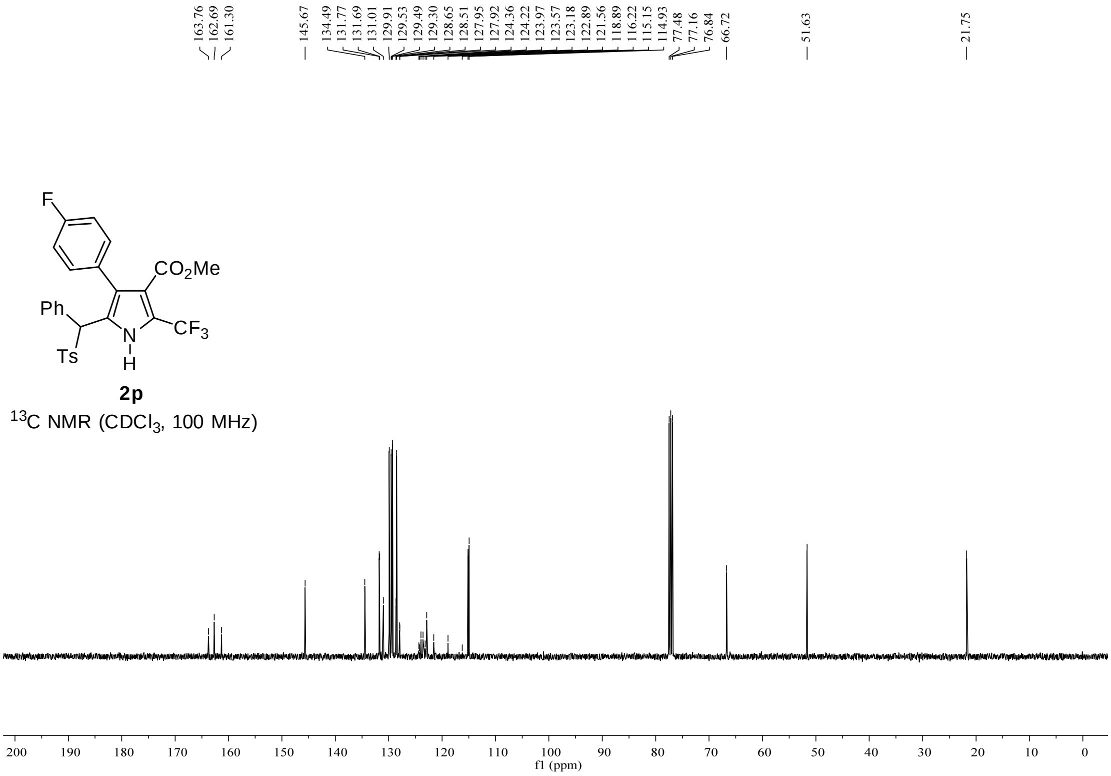
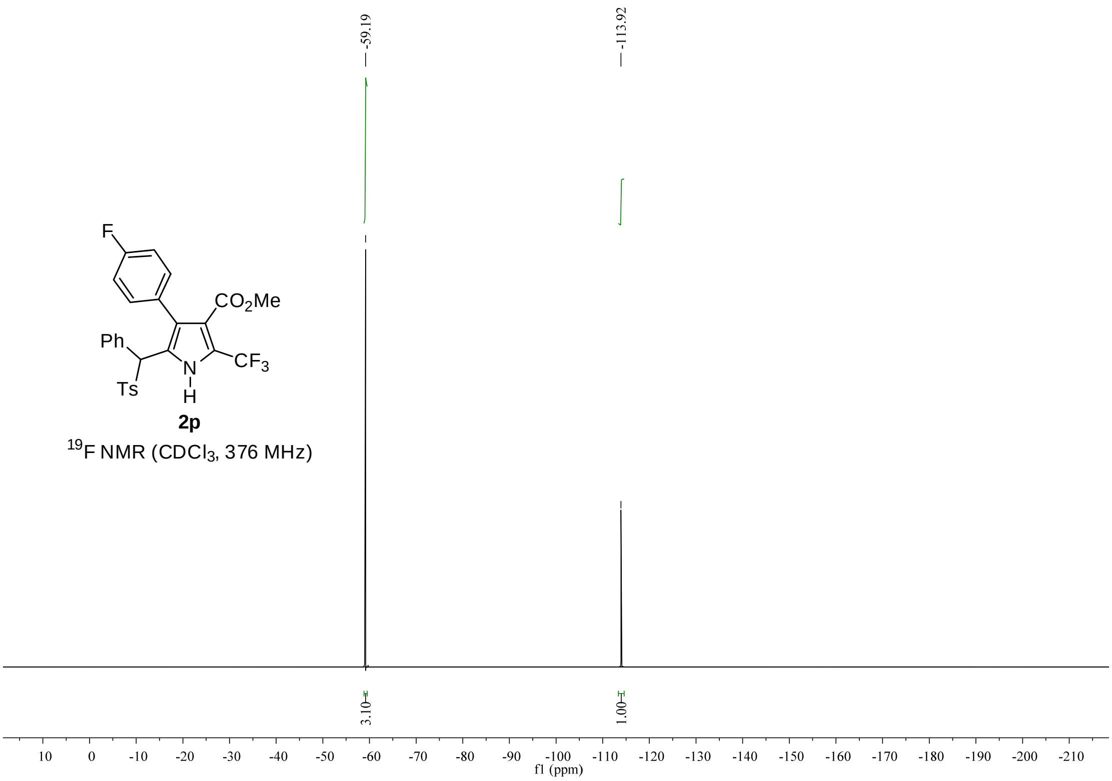
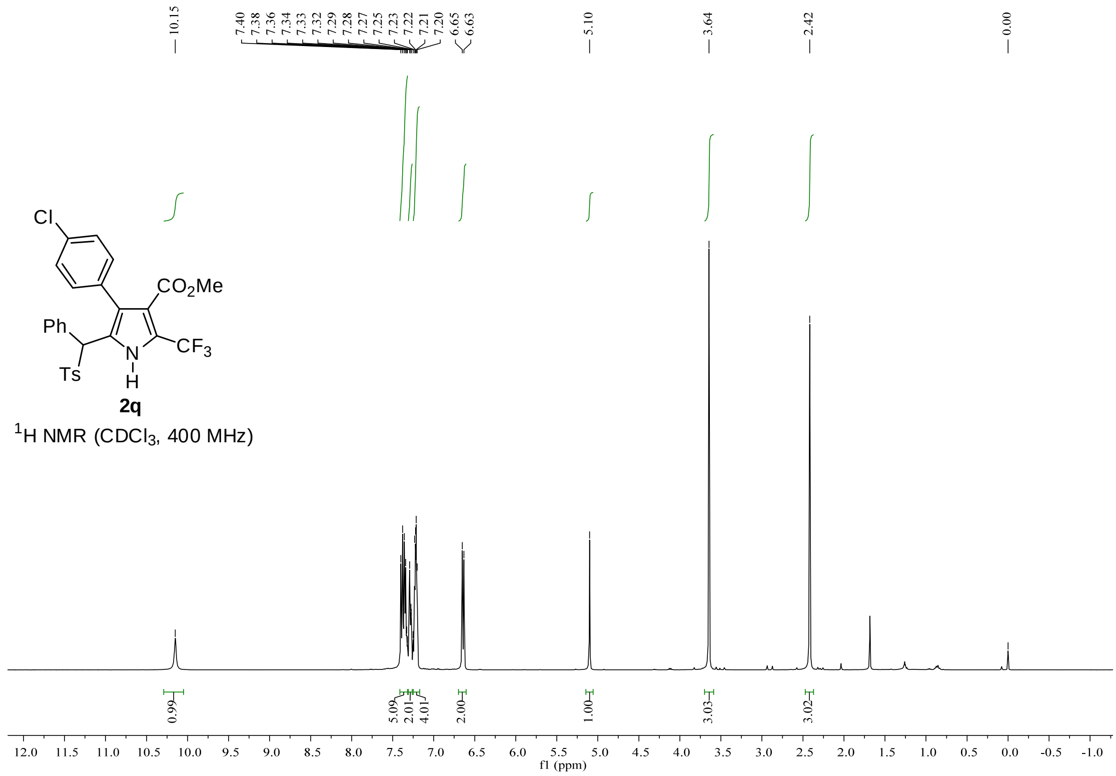
CO2Me
Ph
CF3
Ts
N
H
2o
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

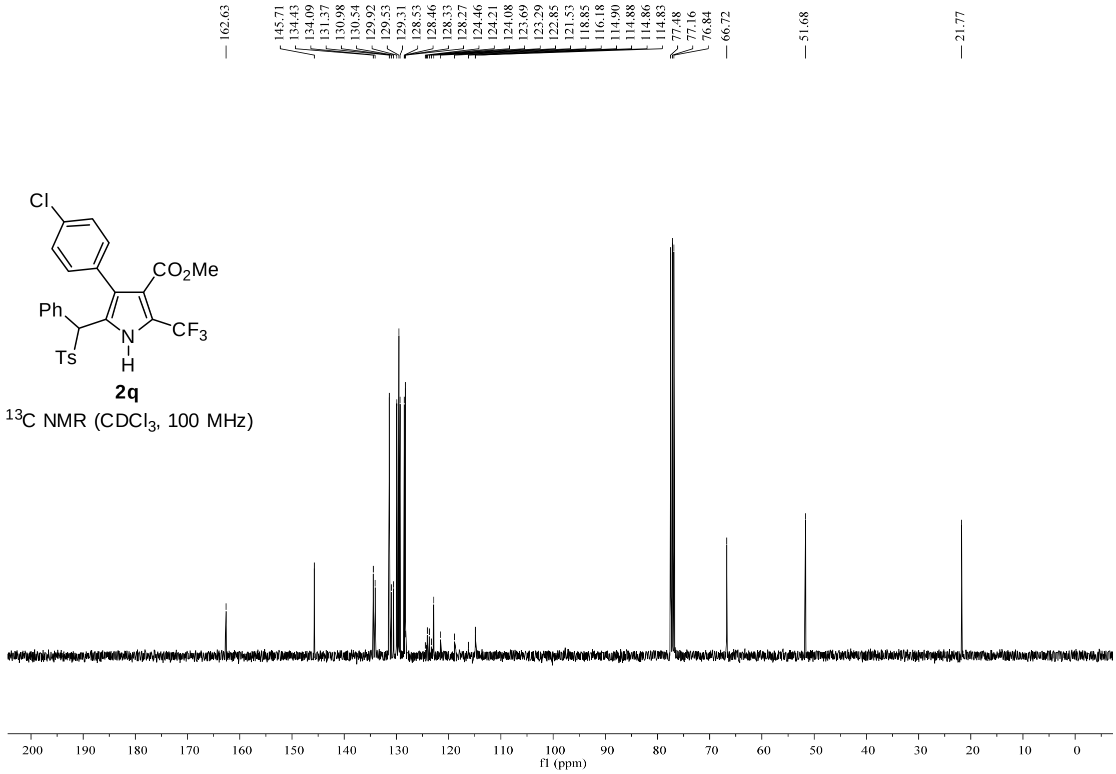

10.13
7.40
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.30
7.29
7.28
7.25
7.22
7.20
6.96
6.94
6.92
6.69
6.67
6.67
6.65
5.11
3.64
2.42
0.00
F
CO2Me
Ph
CF3
Ts
N
H
2p
1H NMR (CDCl3, 400 MHz)
0.97
7.10
2.03
2.02
2.00
1.00
3.03
3.06
f1 (ppm)


163.76
162.69
161.30
145.67
134.49
131.77
131.69
131.01
129.91
129.53
129.49
129.30
128.65
128.51
127.95
127.92
124.36
124.22
123.97
123.57
123.18
122.89
121.56
118.89
116.22
115.15
114.93
77.48
77.16
76.84
66.72
51.63
21.75
F
CO2Me
Ph
CF3
Ts
N
H
2p
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

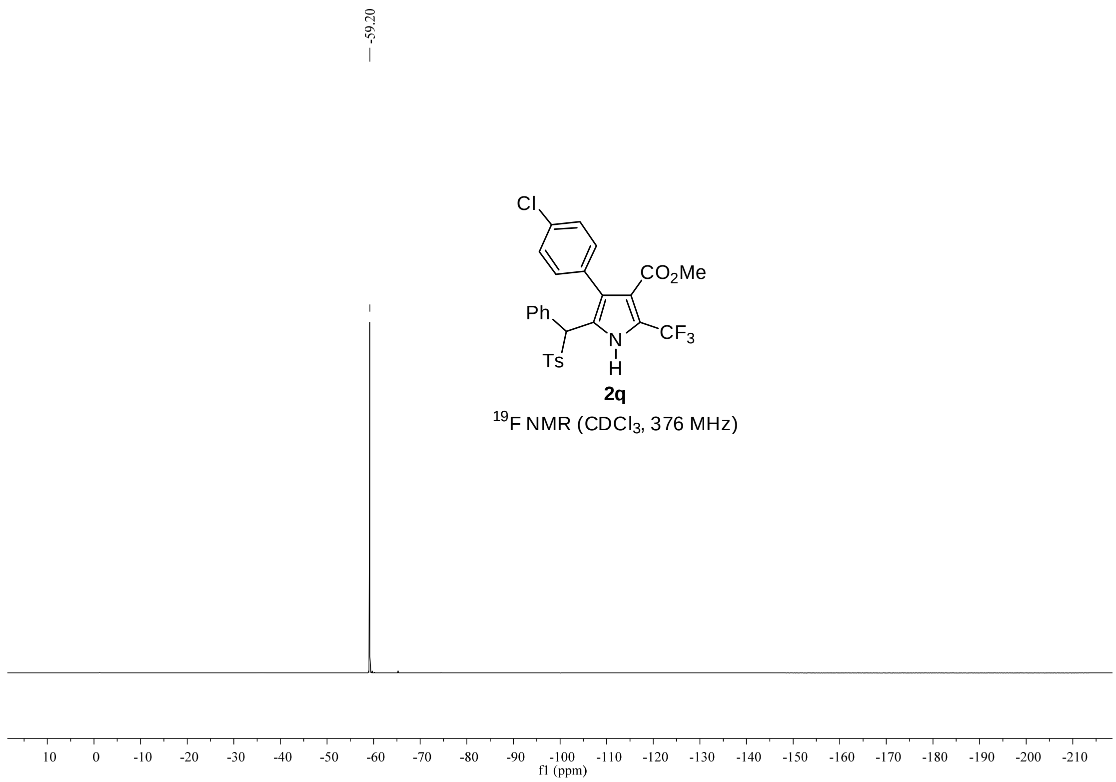

-59.19
-113.92
F
CO2Me
Ph
CF3
Ts
N
H
2p
19F NMR (CDCl3, 376 MHz)
3.10
1.00
f1 (ppm)

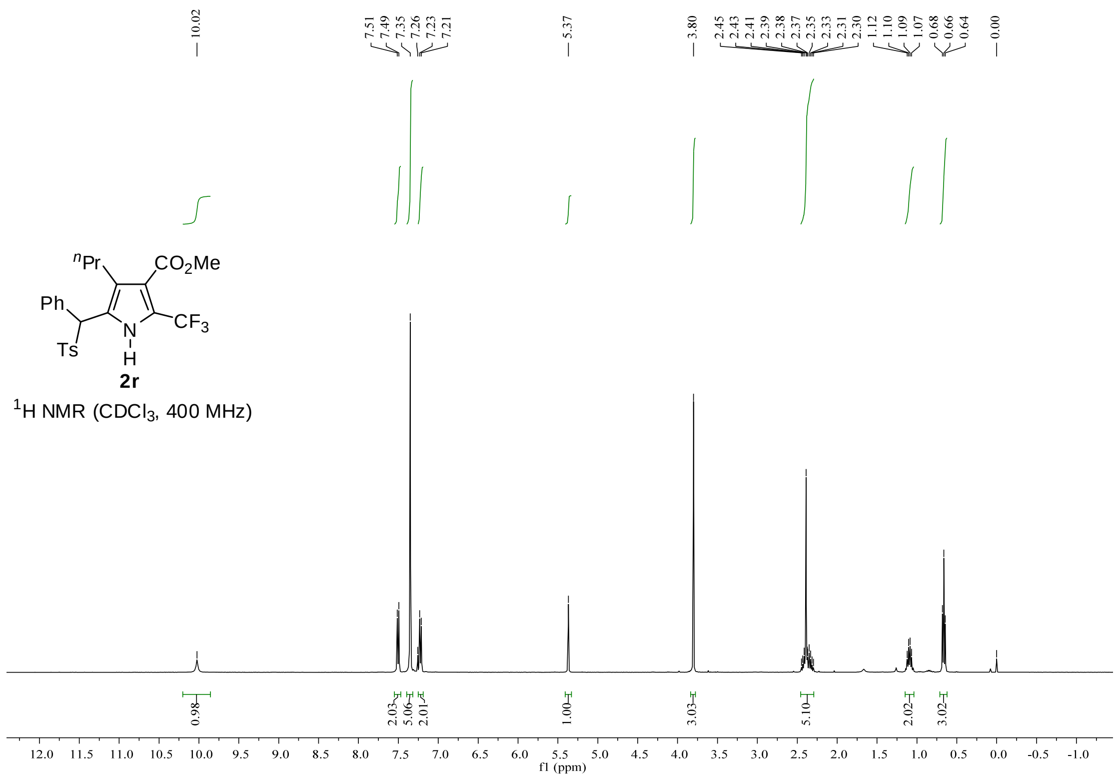


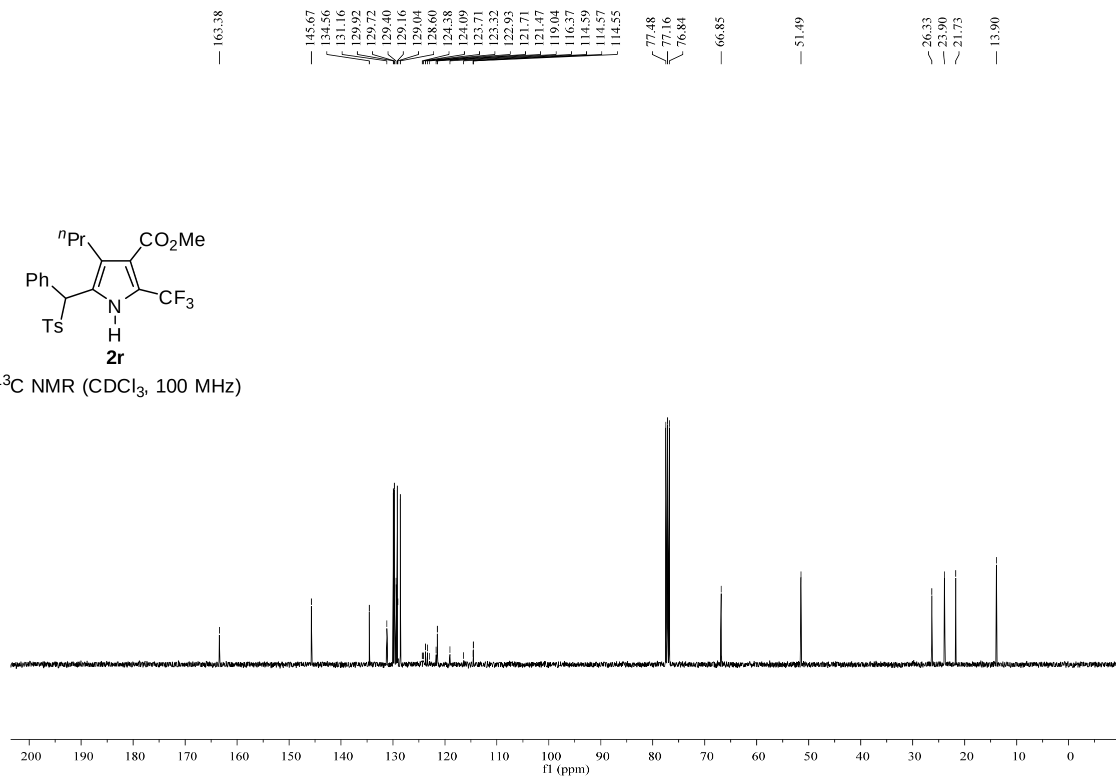
10.15
7.40 7.38 7.36 7.34 7.33 7.32 7.29 7.28 7.27 7.25 7.23 7.22 7.21 7.20
6.65 6.63
5.10
3.64
2.42
0.00
Cl
CO2Me
Ph
CF3
N
H
Ts
2q
1H NMR (CDCl3, 400 MHz)
0.99
5.09
2.01
4.01
2.00
1.00
3.03
3.02
f1 (ppm)



162.63
145.71 134.43 134.09 131.37 130.98 130.54 129.92 129.53 129.31 128.53 128.46 128.33 128.27 124.46 124.21 124.08 123.69 123.29 122.85 121.53 118.85 116.18 114.90 114.88 114.86 114.83
77.48 77.16 76.84
66.72
51.68
21.77
Cl
CO2Me
Ph
CF3
N
H
Ts
2q
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

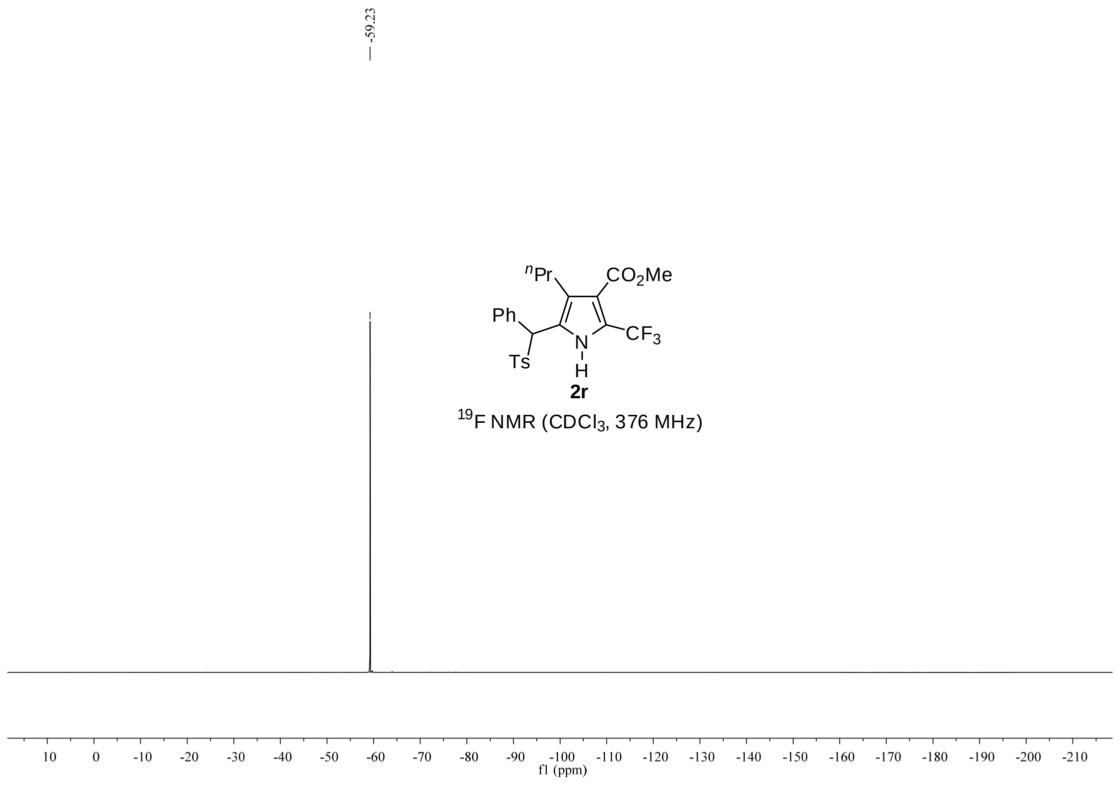

2q
^{19}F NMR (CDCl$_3$, 376 MHz)


2r
^{1}H NMR (CDCl$_3$, 400 MHz)



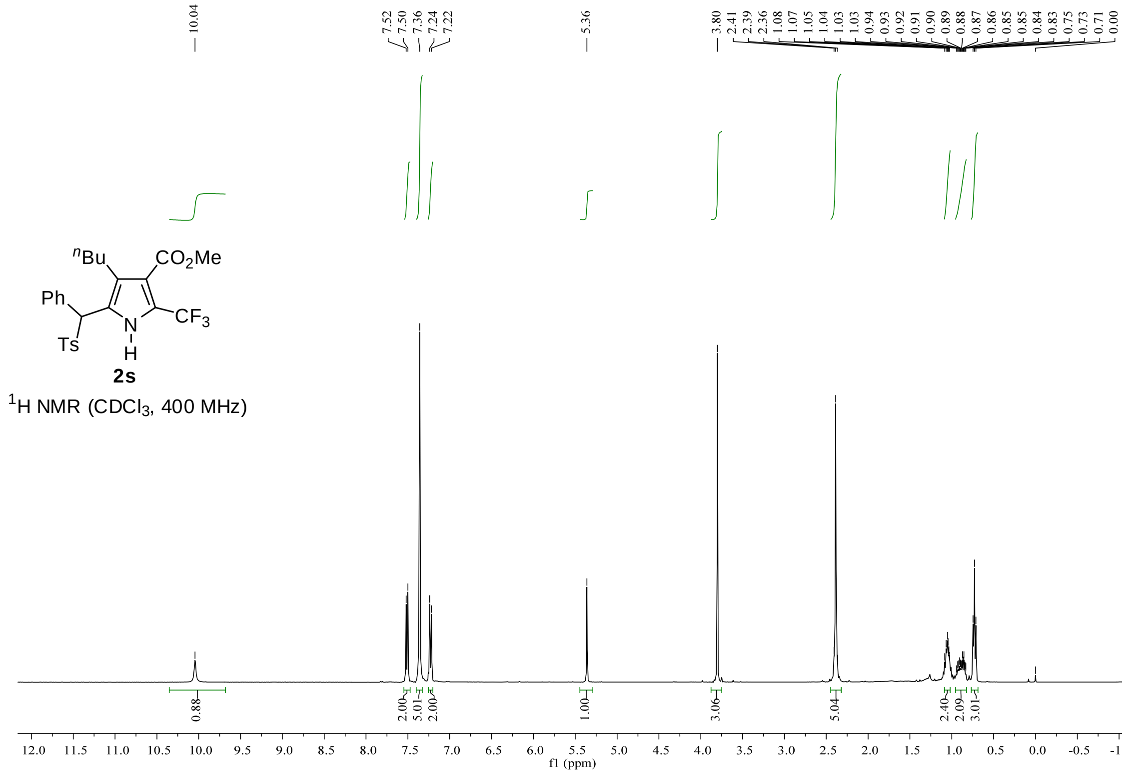
2r

^{13}C NMR ($CDCl_3$, 100 MHz)

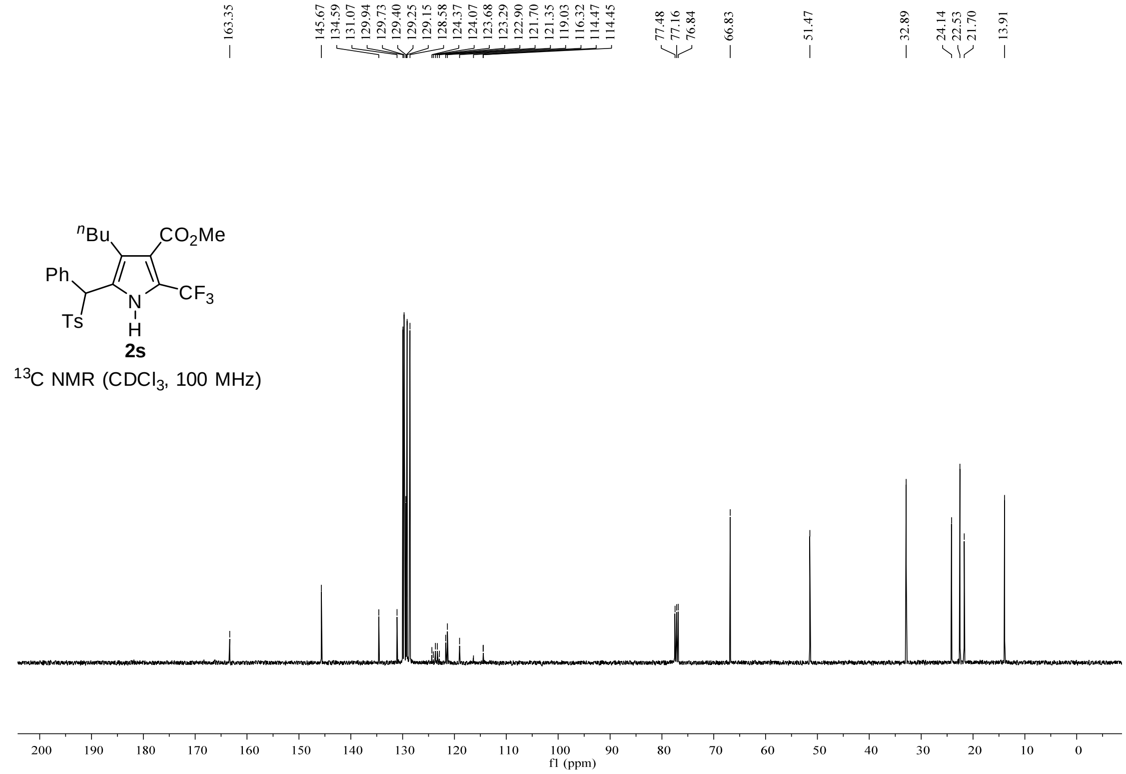


2r

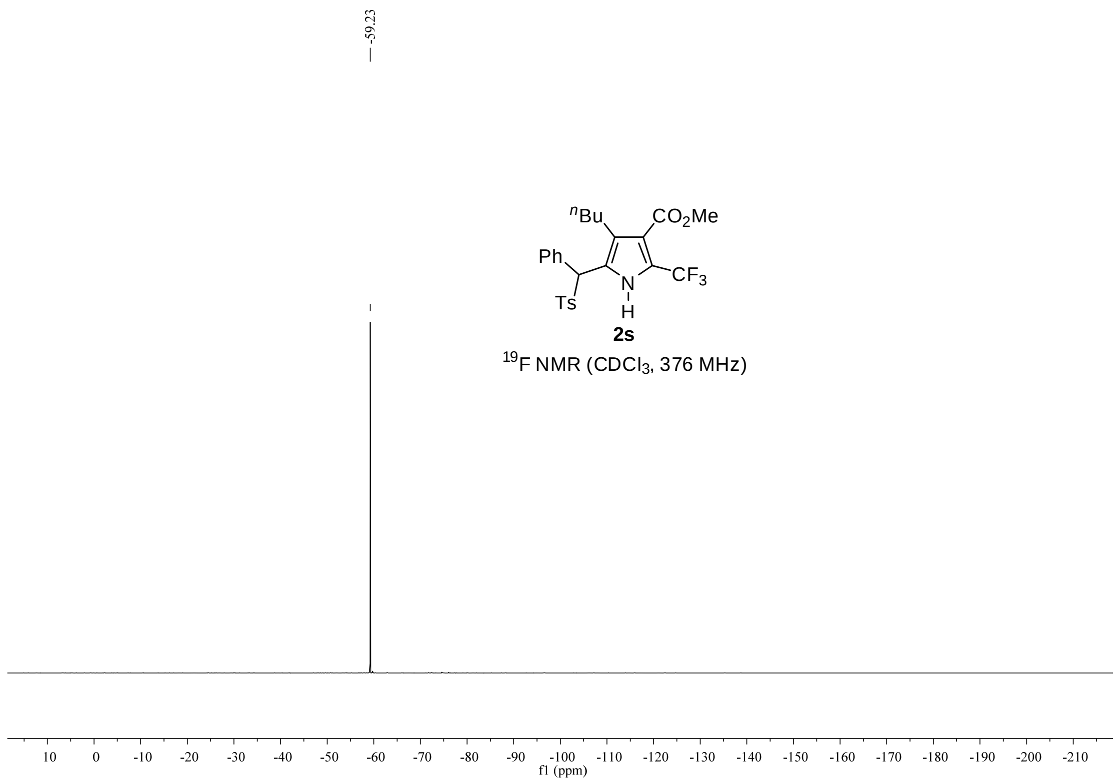
^{19}F NMR ($CDCl_3$, 376 MHz)



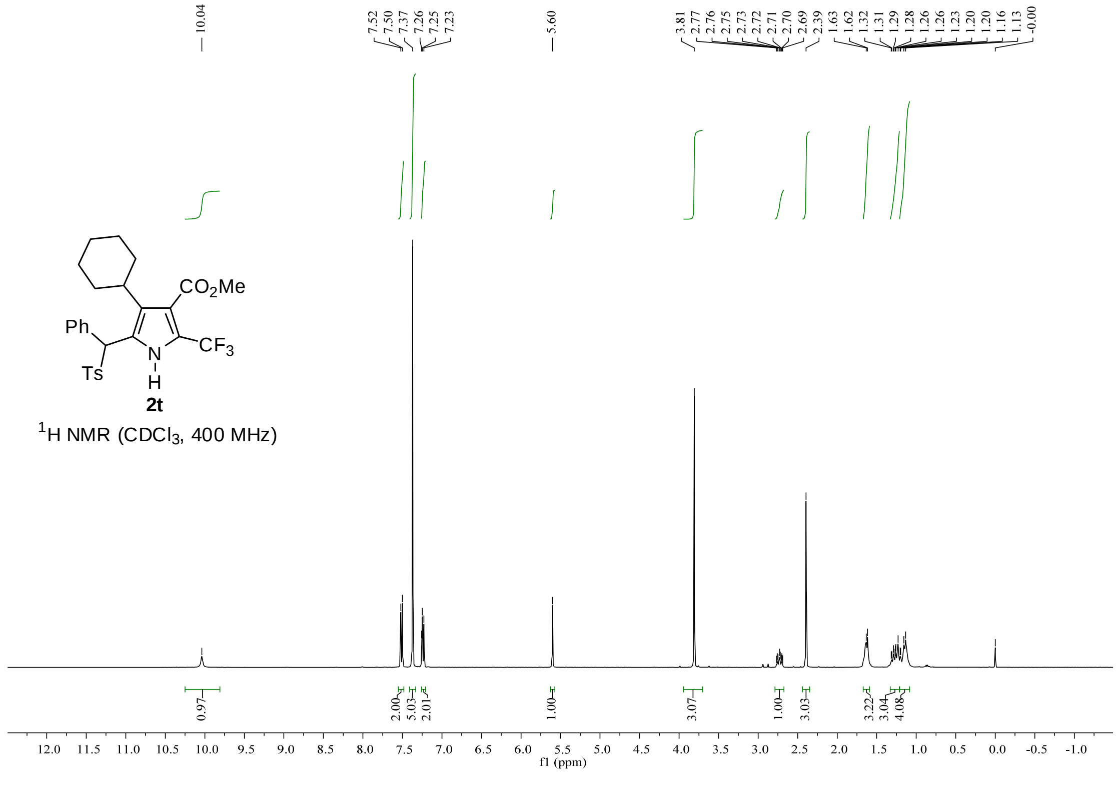
^{n}Bu
CO_2Me
Ph
CF_3
Ts
N
H
2s
^{1}H NMR ($CDCl_3$, 400 MHz)
f1 (ppm)



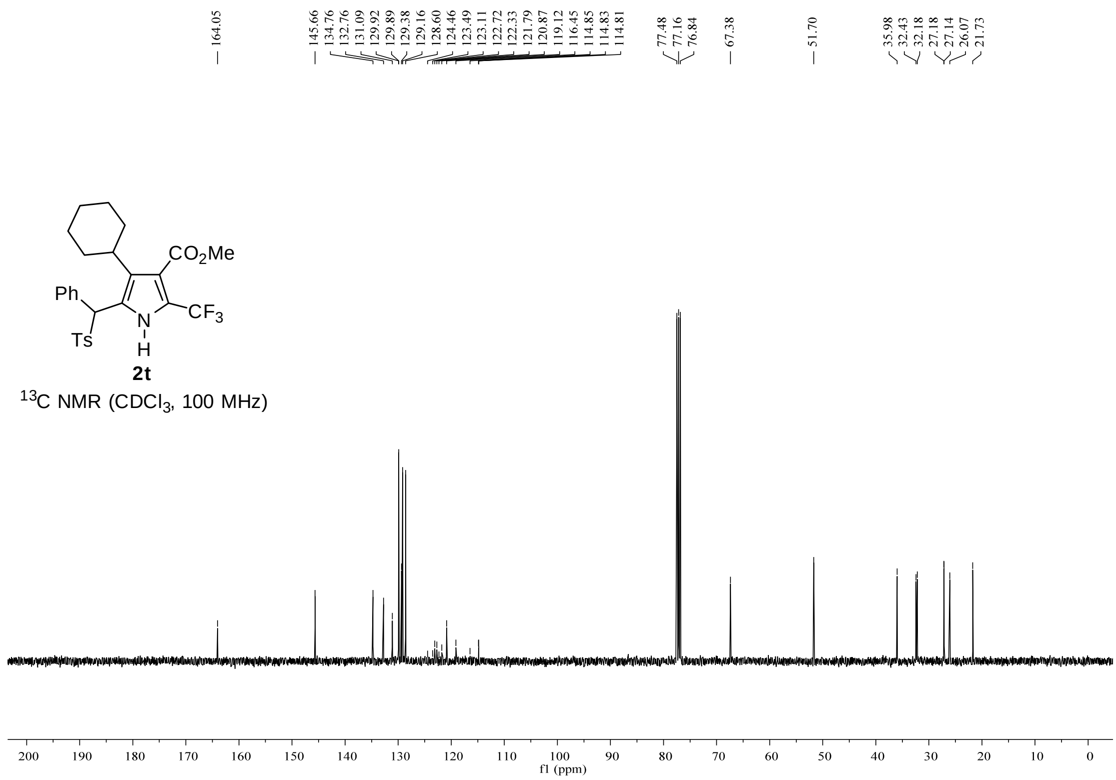
^{n}Bu
CO_2Me
Ph
CF_3
Ts
N
H
2s
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)

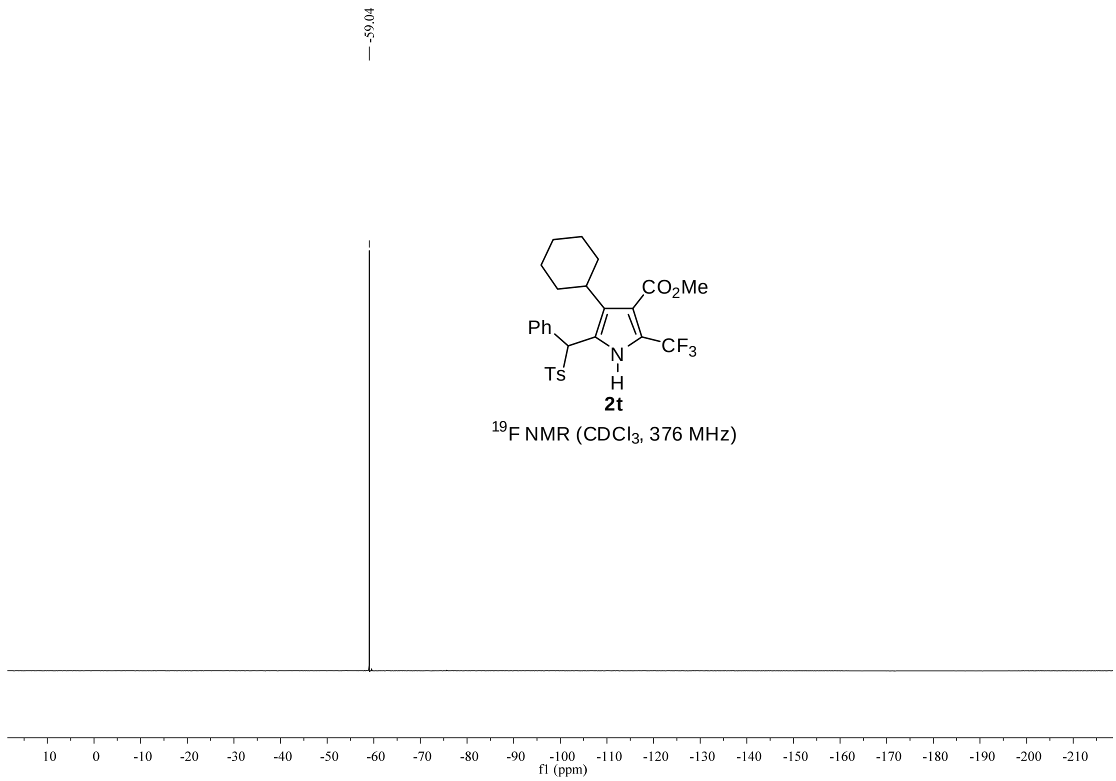


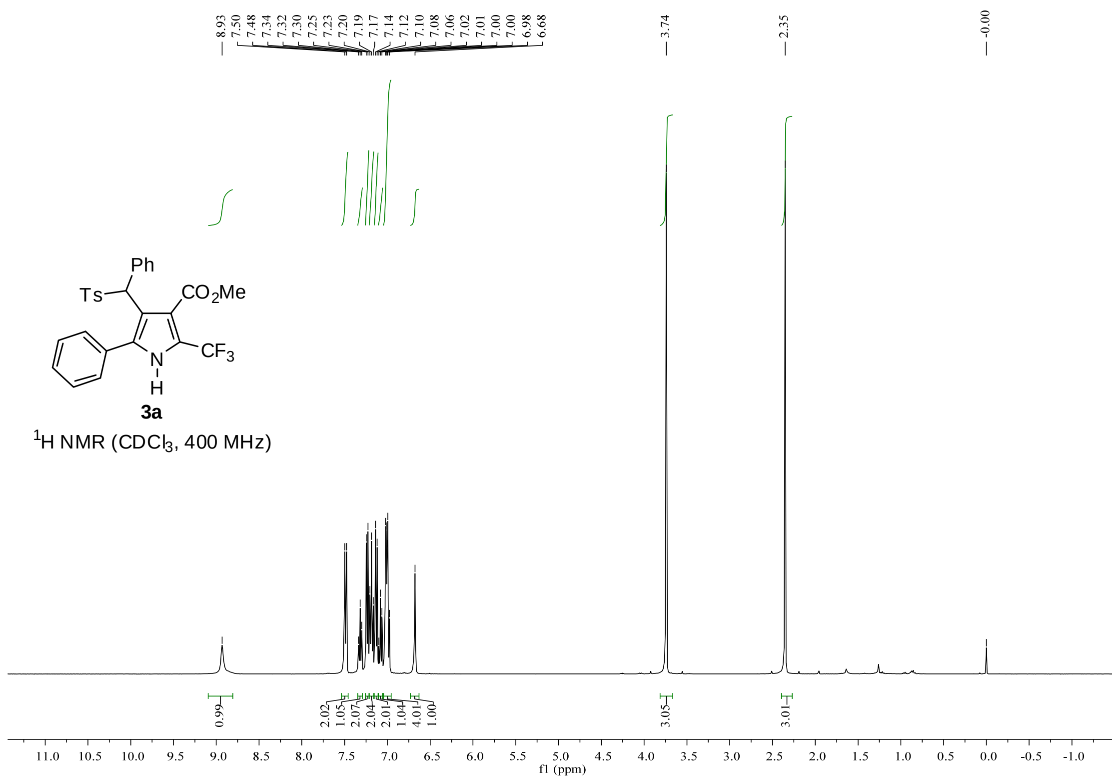
-59.23
^{n}Bu
CO_2Me
Ph
CF_3
N
H
Ts
2s
^{19}F NMR ($CDCl_3$, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



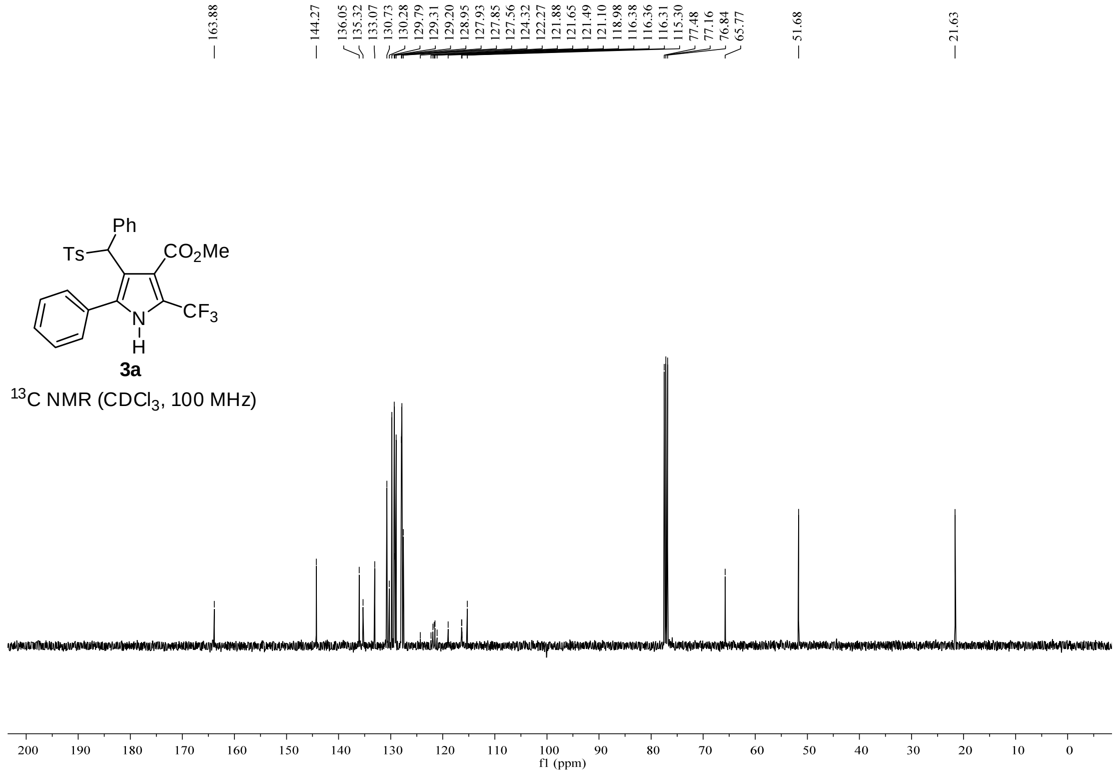
10.04
7.52 7.50 7.37 7.26 7.25 7.23
5.60
3.81 2.77 2.76 2.75 2.73 2.72 2.71 2.70 2.69 2.39 1.63 1.62 1.32 1.31 1.29 1.28 1.26 1.26 1.23 1.20 1.20 1.16 1.13 -0.00
CO_2Me
Ph
CF_3
N
H
Ts
2t
^{1}H NMR ($CDCl_3$, 400 MHz)
0.97
2.00 5.03 2.01
1.00
3.07
1.00 3.03
3.22 3.04 4.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


164.05
145.66
134.76
132.76
131.09
129.92
129.89
129.38
129.16
128.60
124.46
123.49
123.11
122.72
122.33
121.79
120.87
119.12
116.45
114.85
114.83
114.81
77.48
77.16
76.84
67.38
51.70
35.98
32.43
32.18
27.18
27.14
26.07
21.73
CO2Me
Ph
CF3
Ts
N
H
2t
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

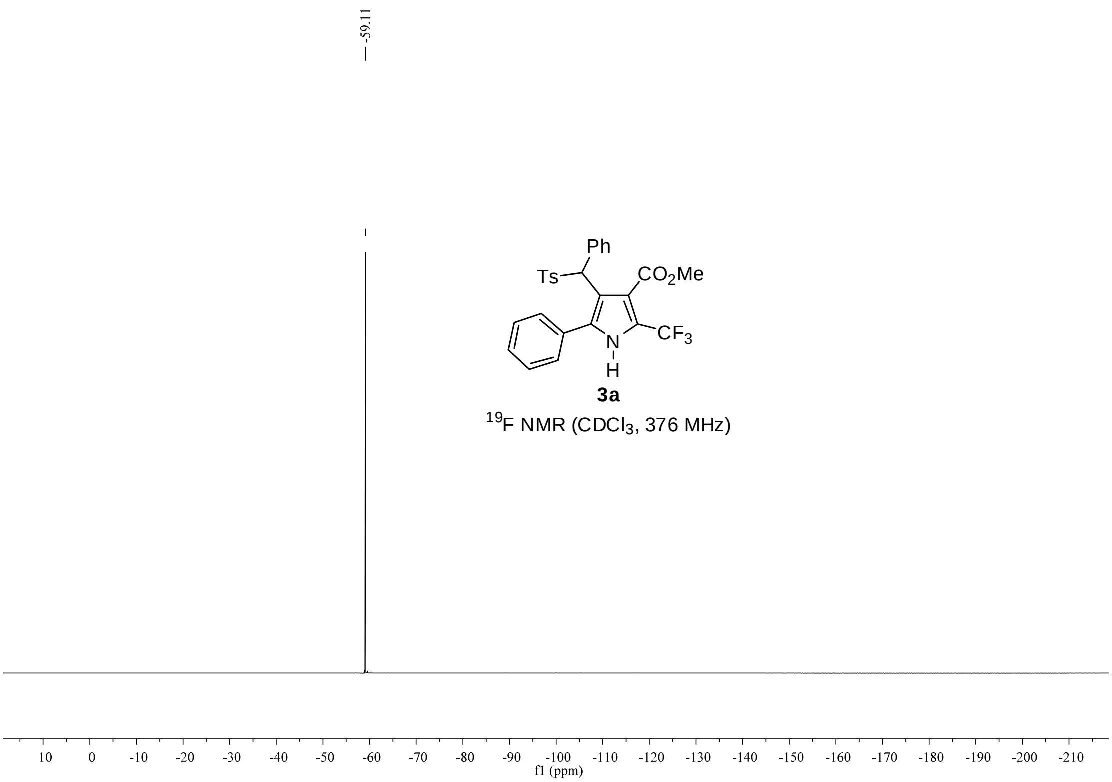

-59.04
CO2Me
Ph
CF3
Ts
N
H
2t
19F NMR (CDCl3, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



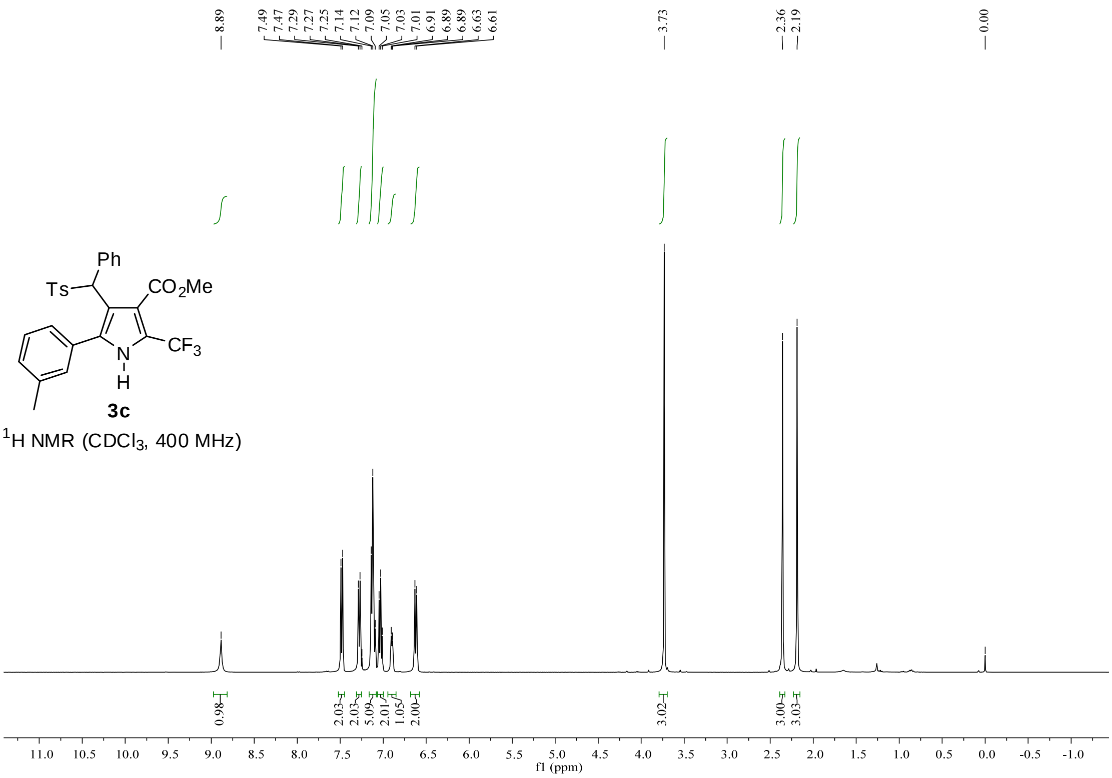
3a
^{1}H NMR (CDCl$_3$, 400 MHz)
f1 (ppm)



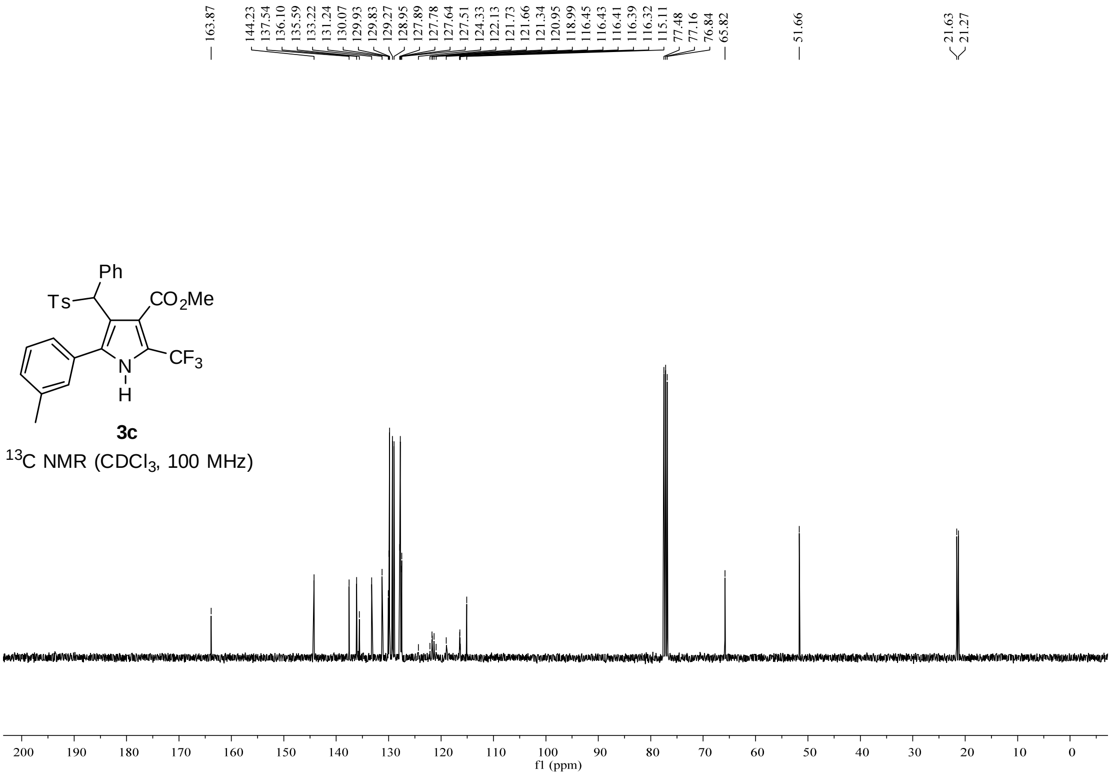
3a
^{13}C NMR (CDCl$_3$, 100 MHz)
f1 (ppm)

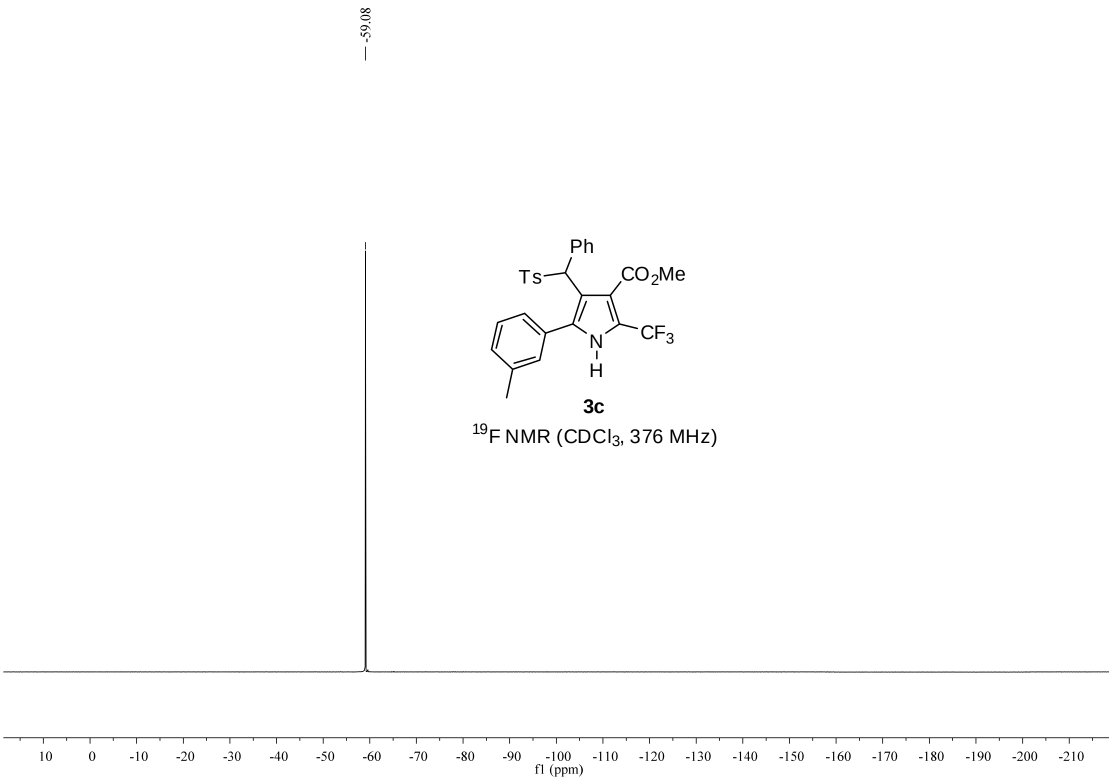


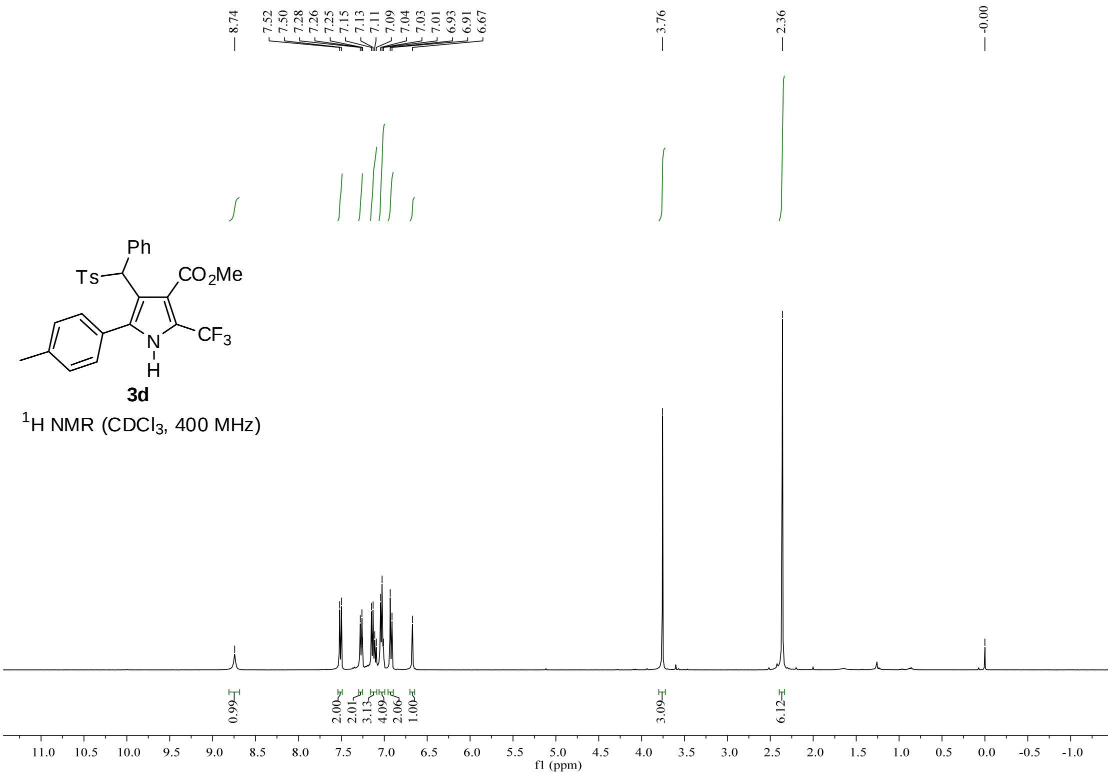
-59.11
Ph
Ts
CO2Me
CF3
N
H
3a
19F NMR (CDCl3, 376 MHz)
f1 (ppm)



8.89
7.49
7.47
7.29
7.27
7.25
7.14
7.12
7.09
7.05
7.03
7.01
6.91
6.89
6.89
6.63
6.61
3.73
2.36
2.19
0.00
Ph
Ts
CO2Me
CF3
N
H
3c
1H NMR (CDCl3, 400 MHz)
0.98
2.03
2.03
5.09
2.01
1.05
2.00
3.02
3.00
3.03
f1 (ppm)

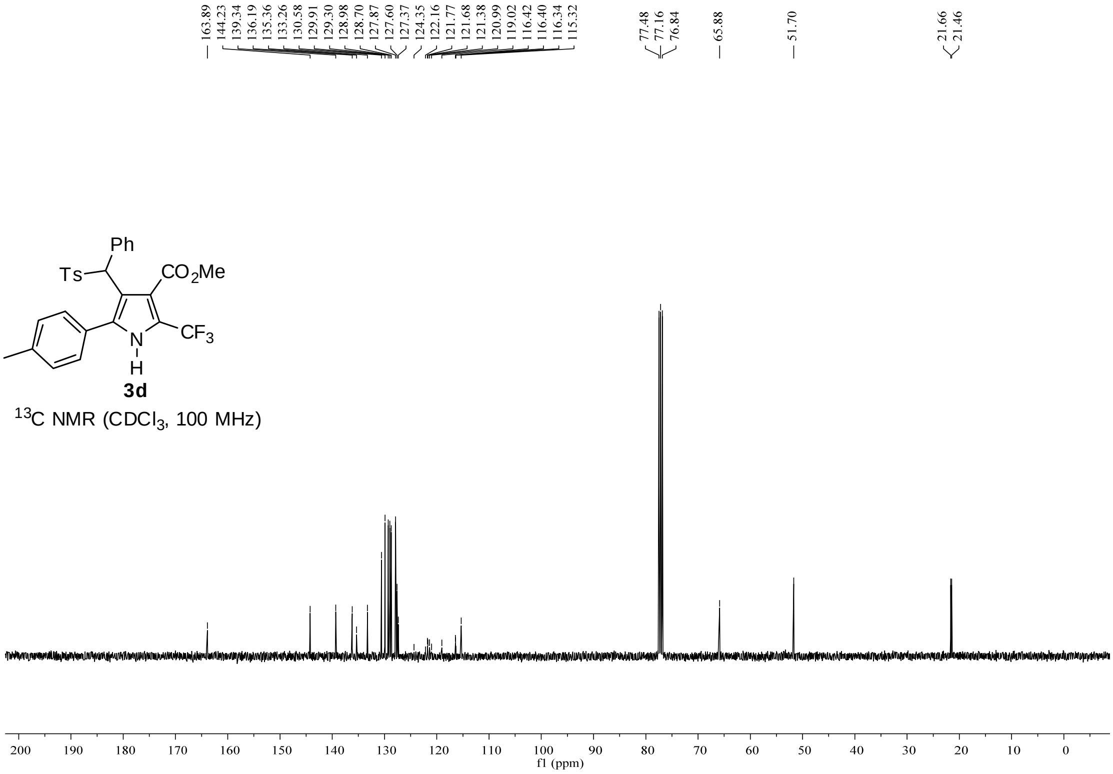

163.87
144.23
137.54
136.10
135.59
133.22
131.24
130.07
129.93
129.83
129.27
128.95
127.89
127.78
127.64
127.51
124.33
122.13
121.73
121.66
121.34
120.95
118.99
116.45
116.43
116.41
116.39
116.32
115.11
77.48
77.16
76.84
65.82
51.66
21.63
21.27
Ph
Ts
CO2Me
CF3
N
H
3c
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-59.08
Ph
Ts
CO2Me
CF3
N
H
3c
19F NMR (CDCl3, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



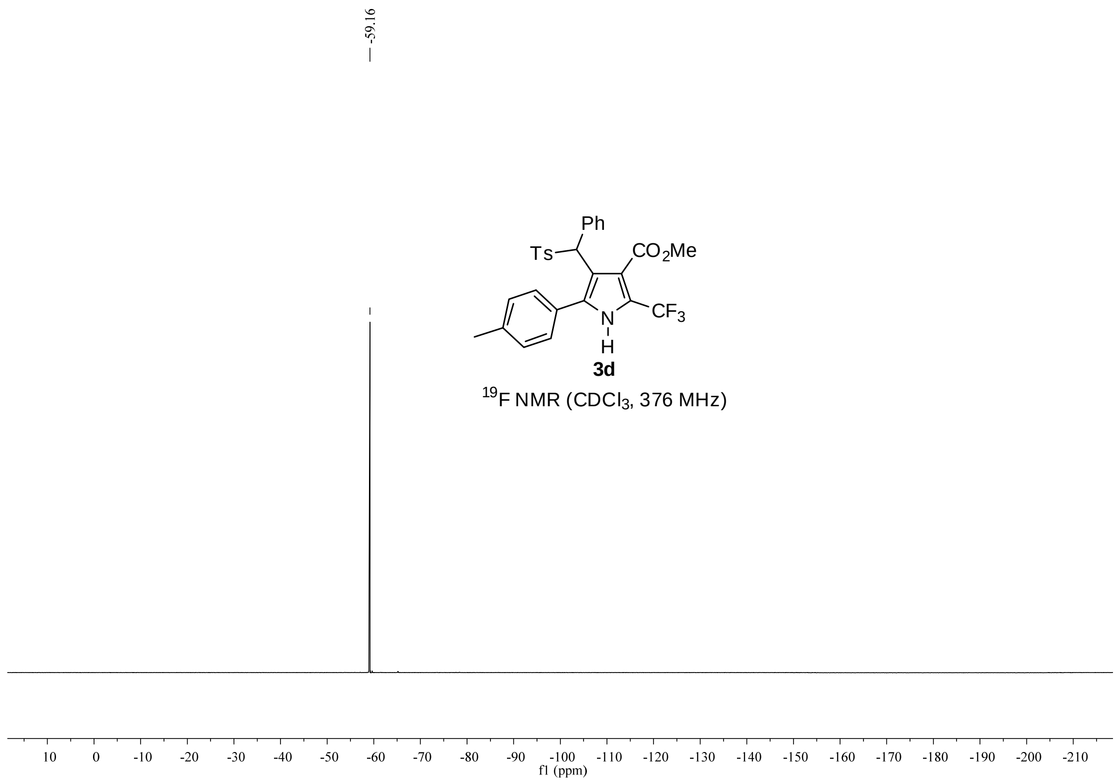
3d

^{1}H NMR ($CDCl_3$, 400 MHz)

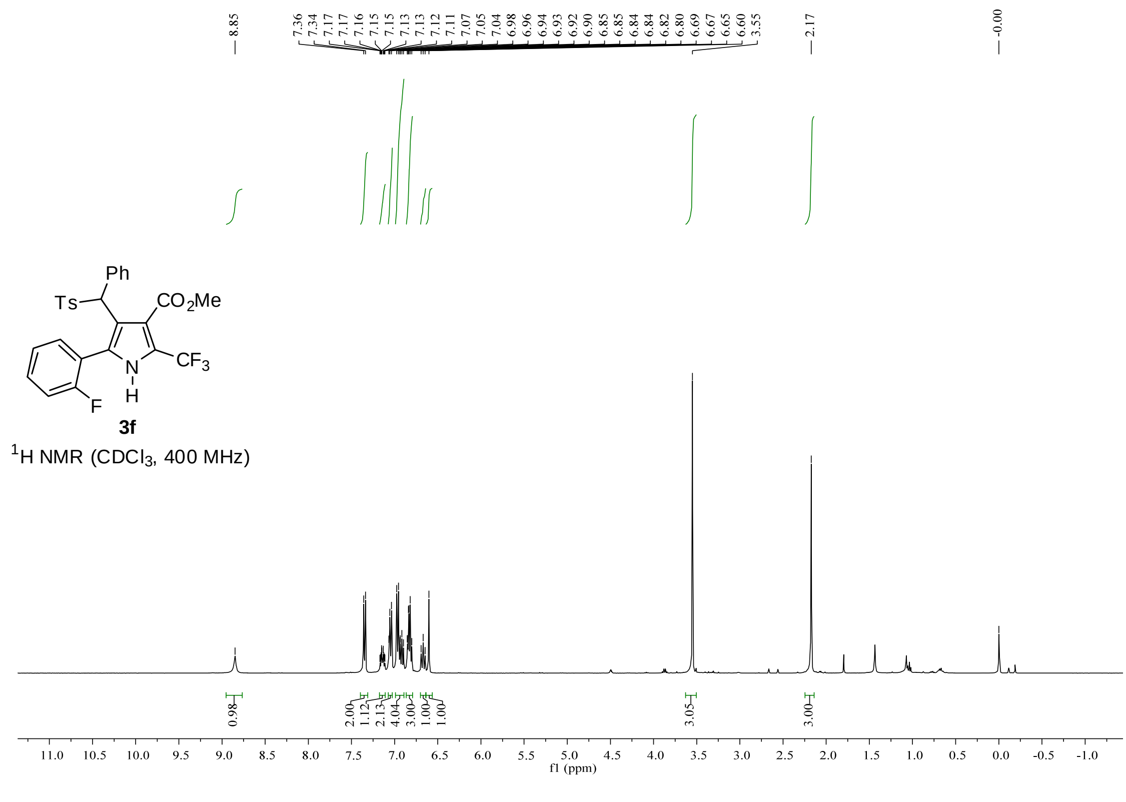


3d

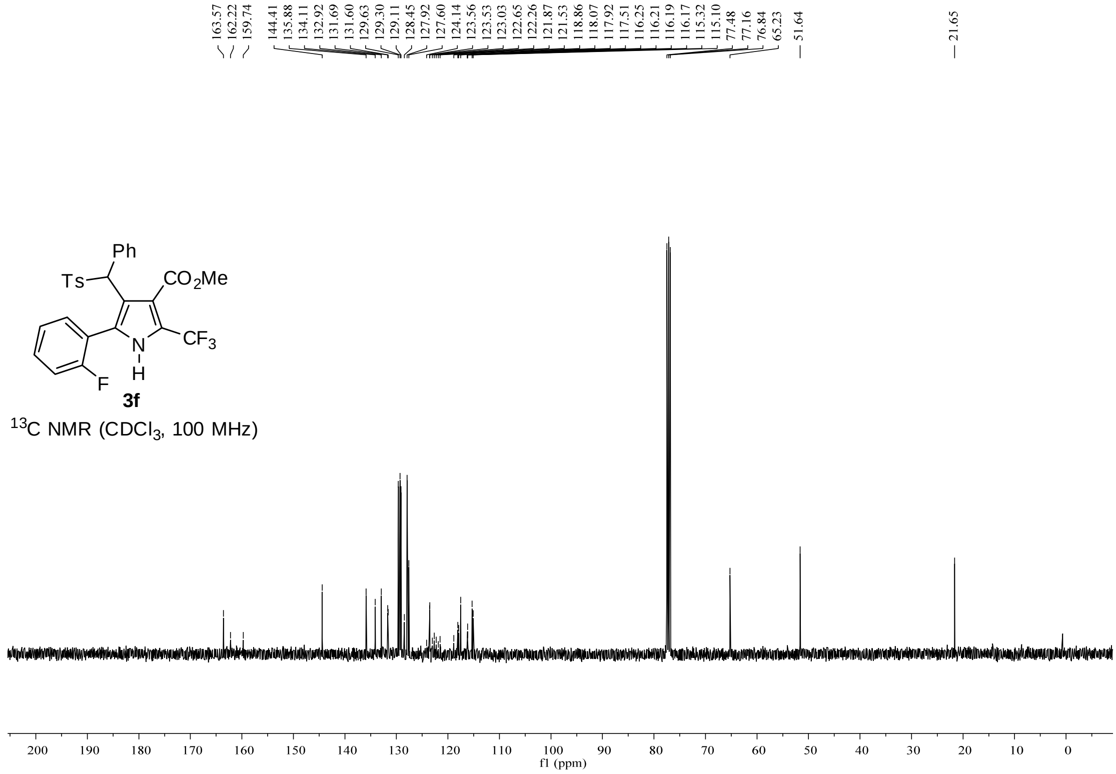
^{13}C NMR ($CDCl_3$, 100 MHz)

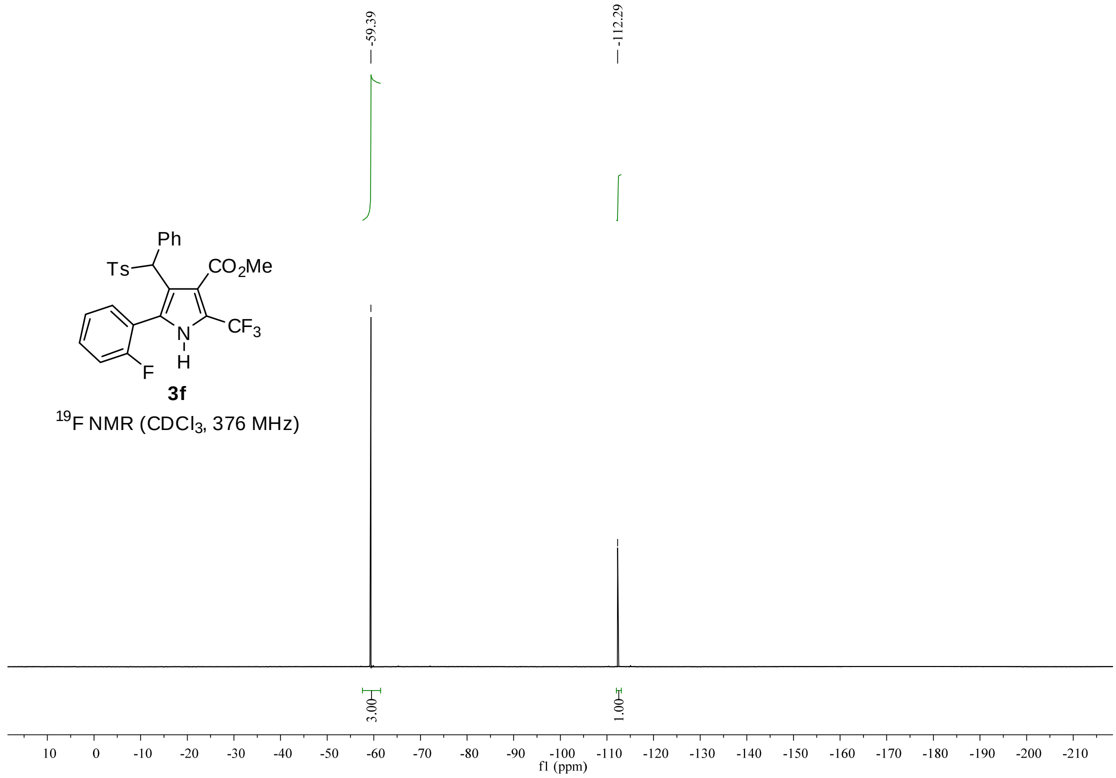


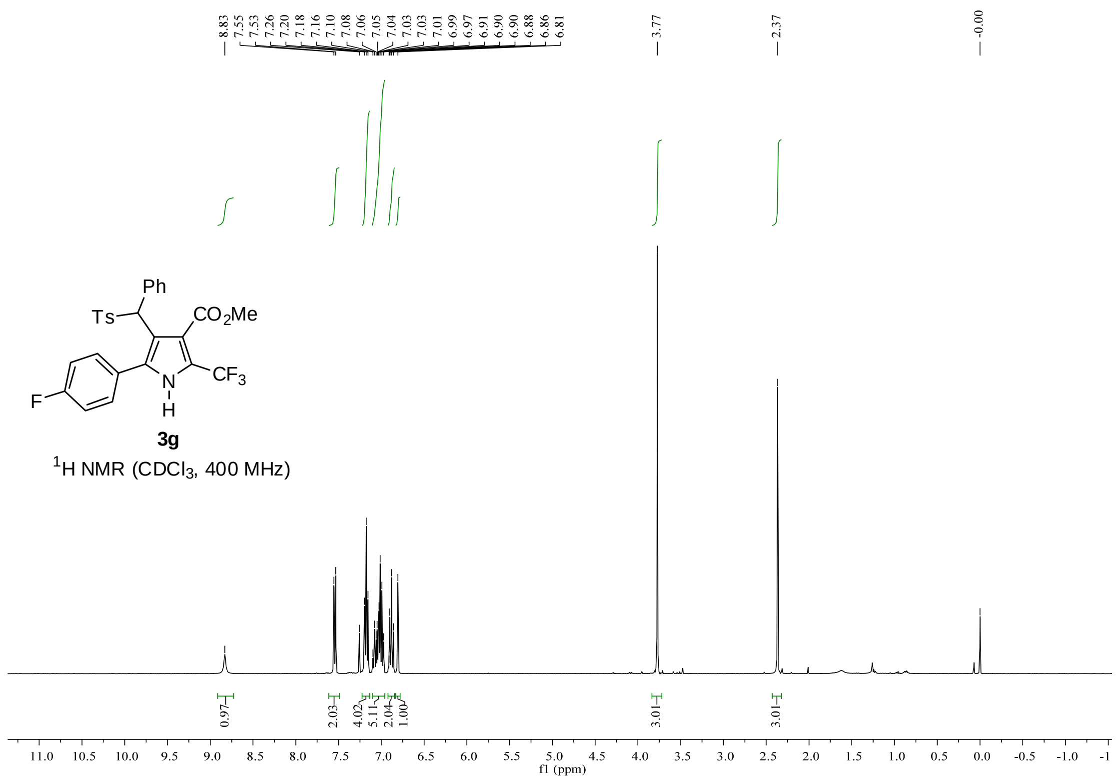
-59.16
Ph
Ts
CO2Me
CF3
N
H
3d
19F NMR (CDCl3, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

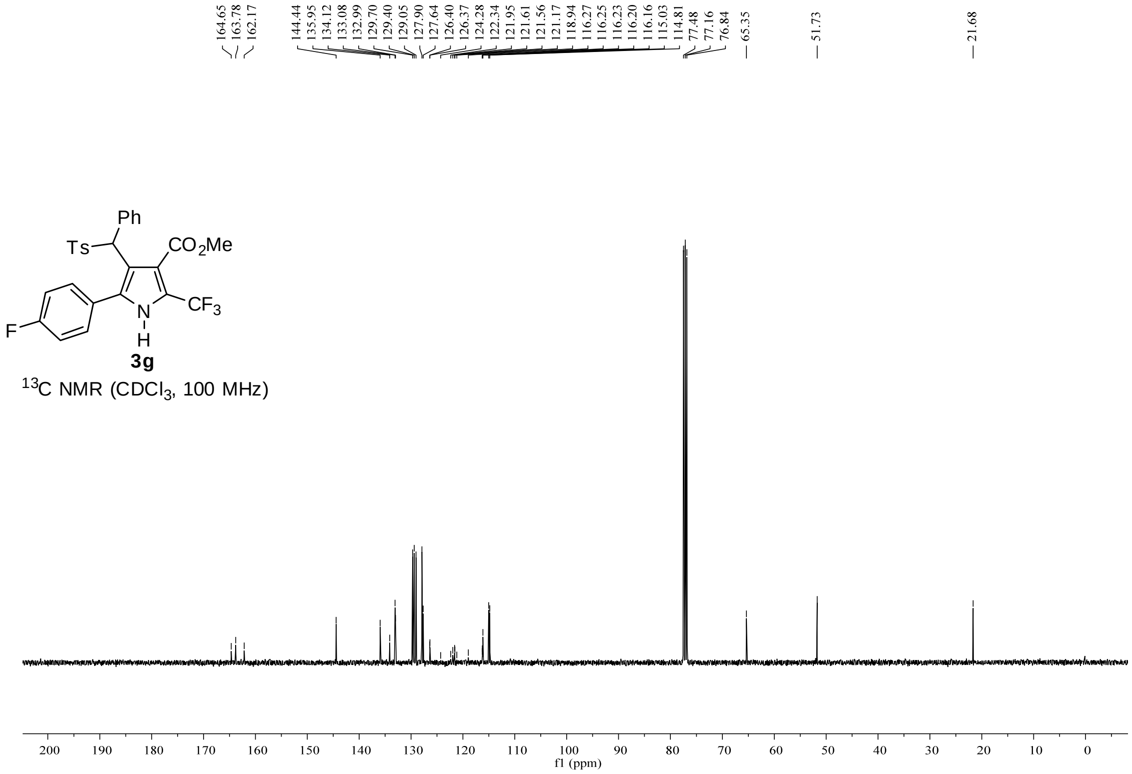


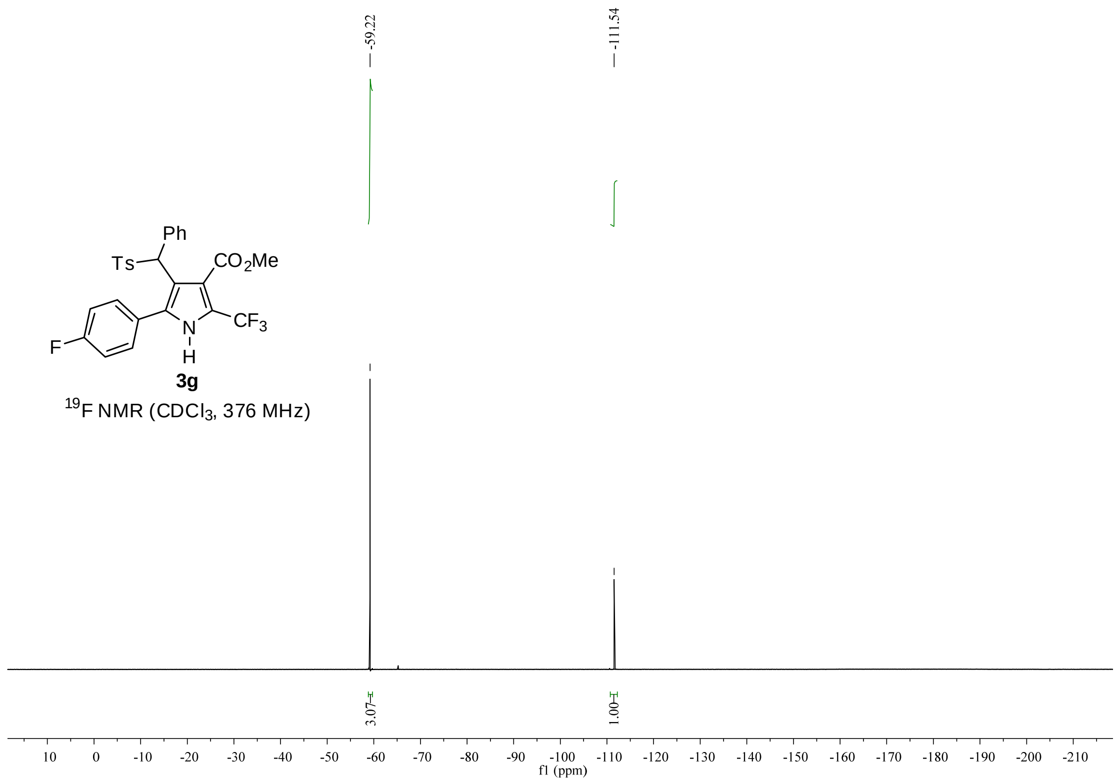
8.85
7.36 7.34 7.17 7.17 7.16 7.15 7.15 7.13 7.13 7.12 7.11 7.07 7.05 7.04 6.98 6.96 6.94 6.93 6.92 6.90 6.85 6.85 6.84 6.82 6.80 6.69 6.67 6.65 6.60 3.55
2.17
-0.00
Ph
Ts
CO2Me
CF3
N
H
F
3f
1H NMR (CDCl3, 400 MHz)
0.98
2.00 1.12 2.13 4.04 3.00 1.00 1.00
3.05
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


163.57
162.22
159.74
144.41
135.88
134.11
132.92
131.69
131.60
129.63
129.30
129.11
128.45
127.92
127.60
124.14
123.56
123.53
123.03
122.65
122.26
121.87
121.53
118.86
118.07
117.92
117.51
116.25
116.21
116.19
116.17
115.32
115.10
77.48
77.16
76.84
65.23
51.64
21.65
Ph
Ts
CO2Me
CF3
N
H
F
3f
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

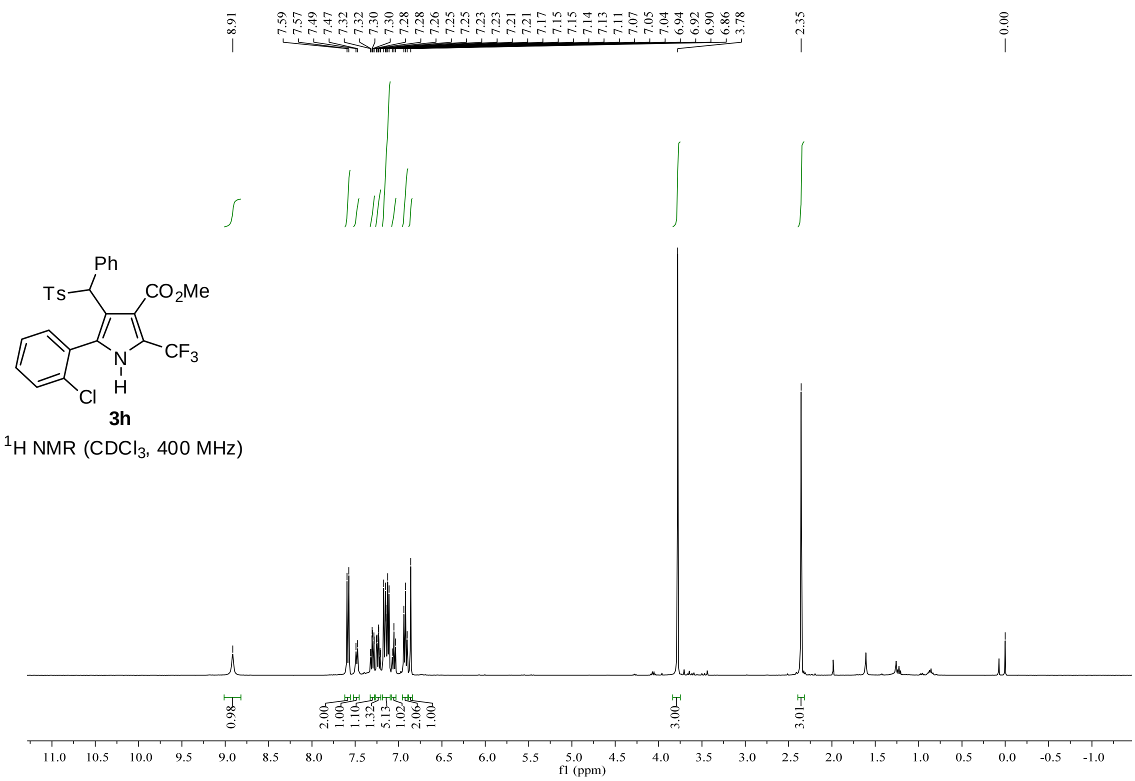

-59.39
-112.29
Ph
Ts
CO2Me
CF3
N
H
F
3f
19F NMR (CDCl3, 376 MHz)
3.00
1.00
f1 (ppm)


3g
^{1}H NMR (CDCl$_3$, 400 MHz)
f1 (ppm)

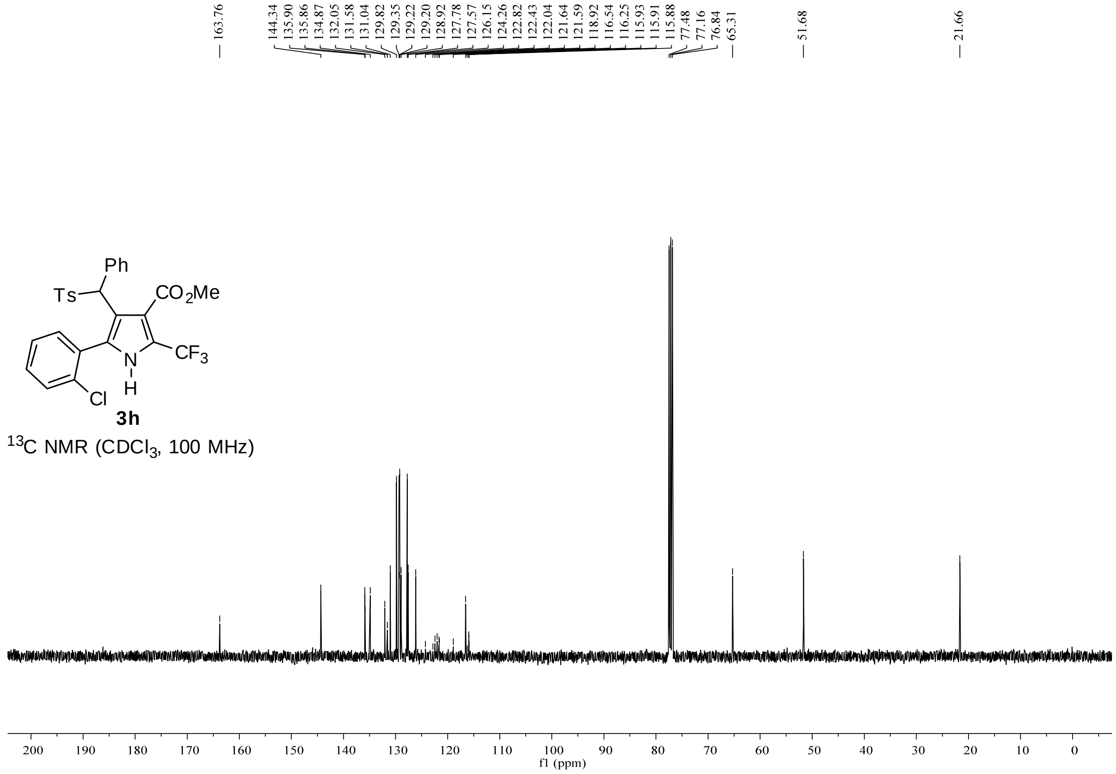

3g
^{13}C NMR (CDCl$_3$, 100 MHz)
f1 (ppm)

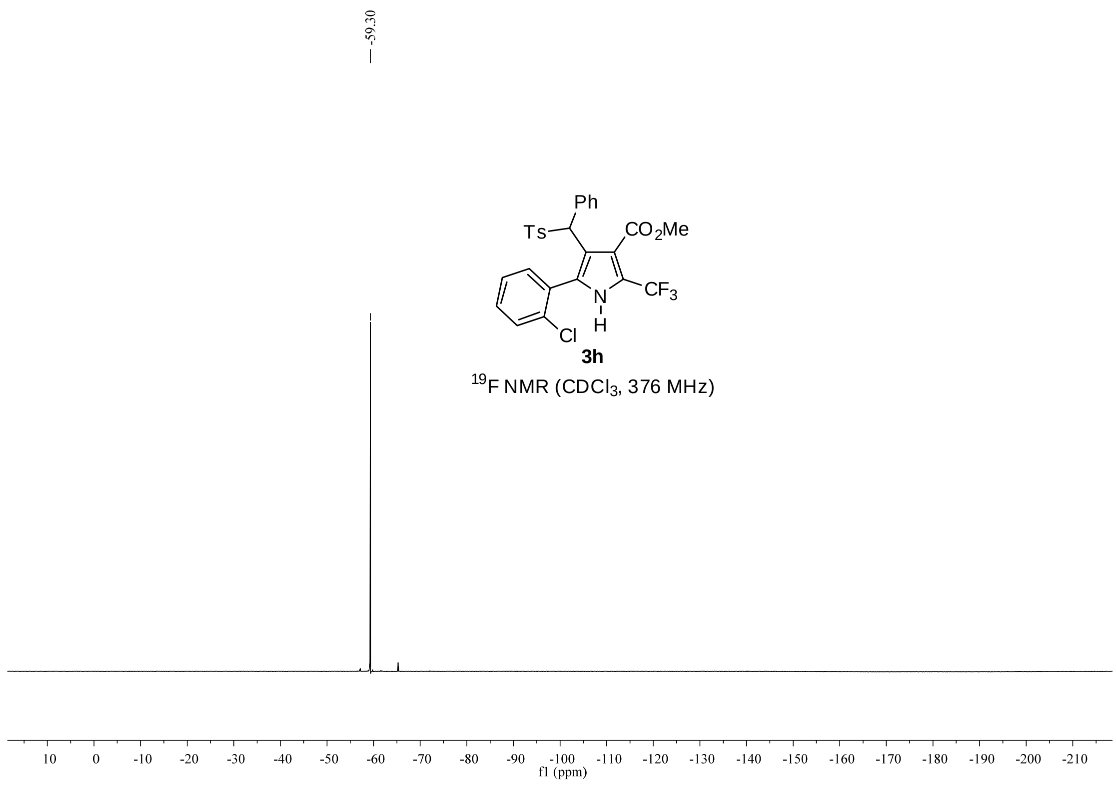


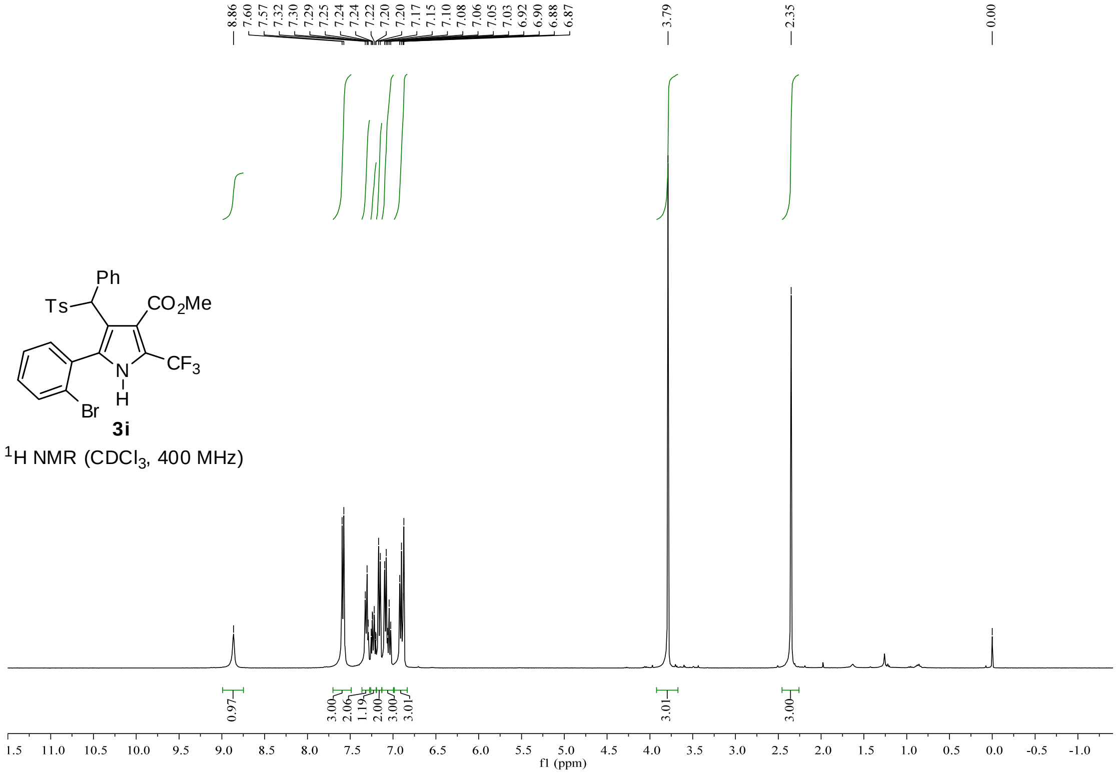
-59.22
-111.54
Ph
Ts
CO2Me
CF3
F
N
H
3g
19F NMR (CDCl3, 376 MHz)
3.07
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

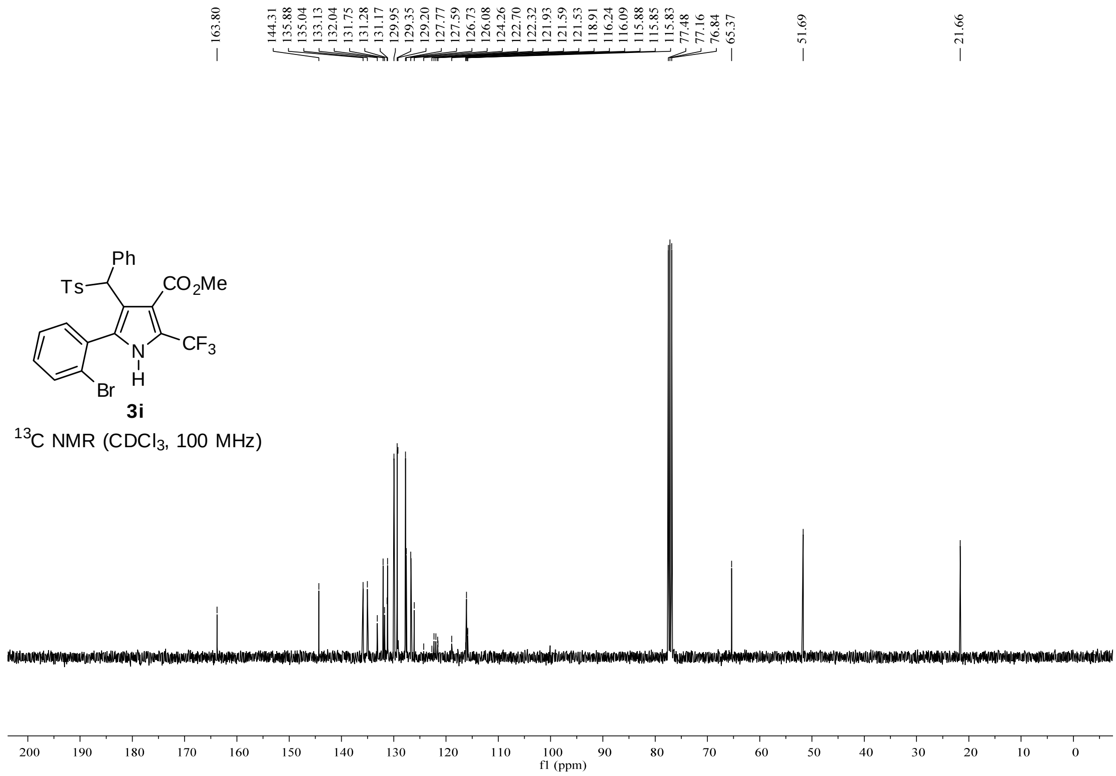


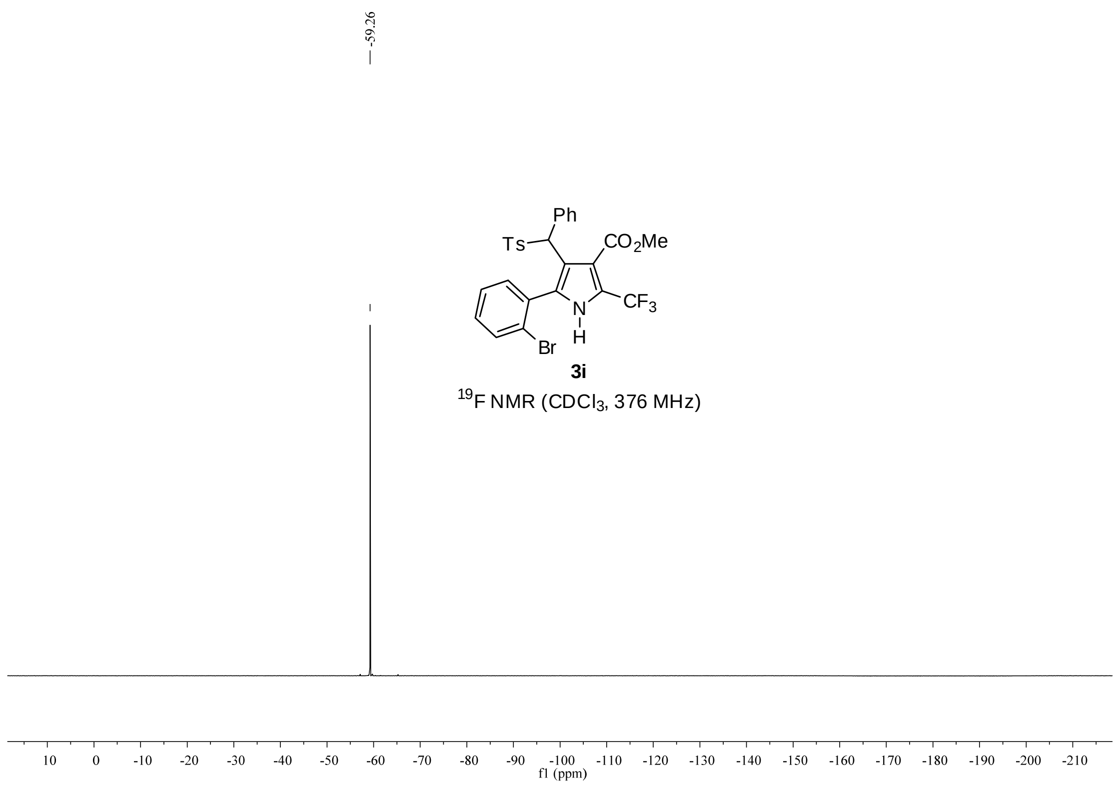
8.91
7.59 7.57 7.49 7.47 7.32 7.32 7.30 7.30 7.28 7.28 7.26 7.25 7.25 7.23 7.23 7.21 7.21 7.17 7.15 7.15 7.14 7.13 7.11 7.07 7.05 7.04 6.94 6.92 6.90 6.86 3.78
2.35
0.00
Ph
Ts
CO2Me
CF3
N
H
Cl
3h
1H NMR (CDCl3, 400 MHz)
0.98
2.00 1.00 1.10 1.32 5.13 1.02 2.06 1.00
3.00
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


163.76
144.34
135.90
135.86
134.87
132.05
131.58
131.04
129.82
129.35
129.22
129.20
128.92
128.92
127.78
127.57
126.15
124.26
122.82
122.43
122.04
121.64
121.59
118.92
116.54
116.25
115.93
115.91
115.88
77.48
77.16
76.84
65.31
51.68
21.66
Ph
Ts
CO2Me
N
H
CF3
Cl
3h
13C NMR (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-59.30
Ph
Ts
CO2Me
N
H
CF3
Cl
3h
19F NMR (CDCl3, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

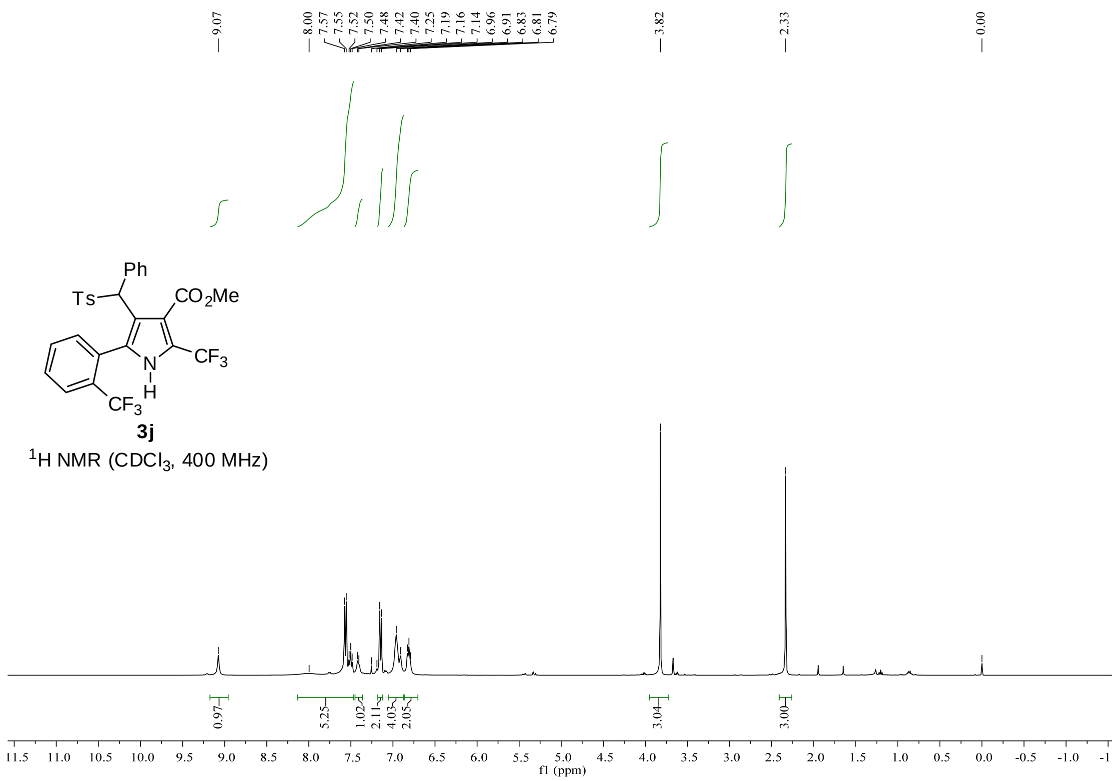

8.86 7.60 7.57 7.32 7.30 7.29 7.25 7.24 7.24 7.22 7.20 7.20 7.17 7.15 7.10 7.08 7.06 7.05 7.03 6.92 6.90 6.88 6.87
3.79
2.35
0.00
Ph
Ts
CO2Me
N
H
CF3
Br
3i
1H NMR (CDCl3, 400 MHz)
0.97
3.00 2.06 1.19 2.00 3.00 3.01
3.01
3.00
f1 (ppm)


163.80
144.31 135.88 135.04 133.13 132.04 131.75 131.28 131.17 129.95 129.35 129.20 127.77 127.59 126.73 126.08 124.26 122.70 122.32 121.93 121.59 121.53 118.91 116.24 116.09 115.88 115.85 115.83 77.48 77.16 76.84 65.37
51.69
21.66
Ph
Ts
CO2Me
N
H
CF3
Br
3i
13C NMR (CDCl3, 100 MHz)
f1 (ppm)



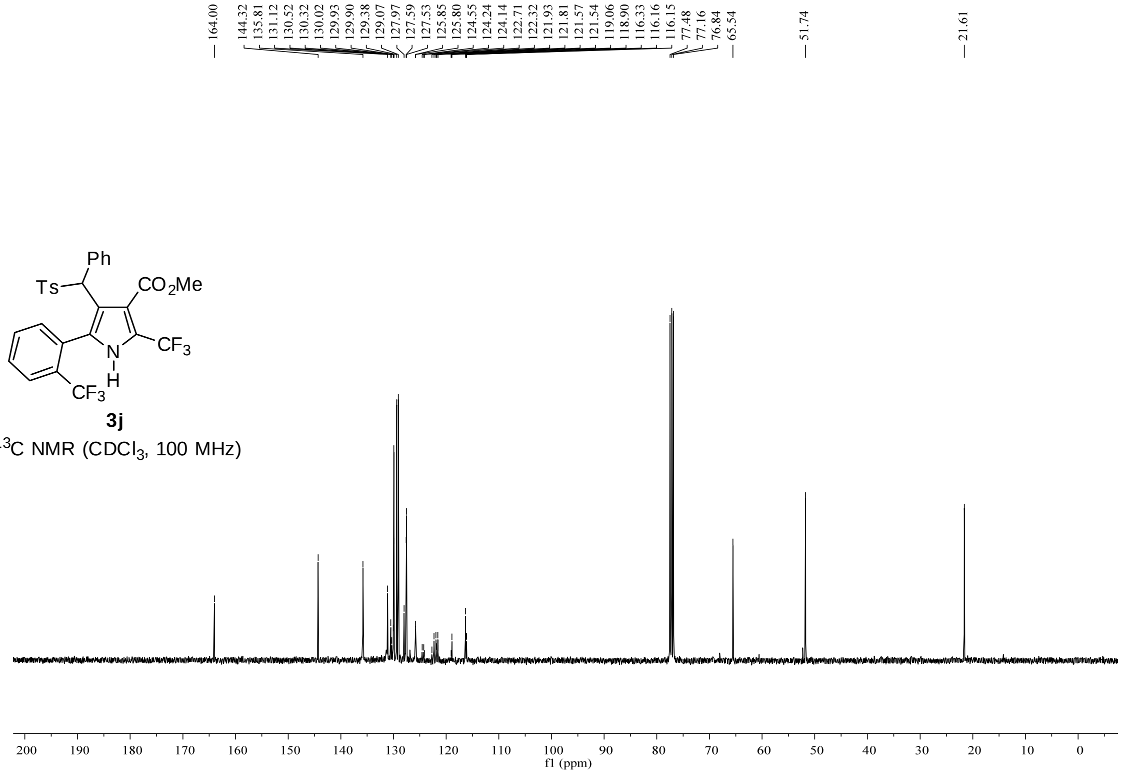
3i

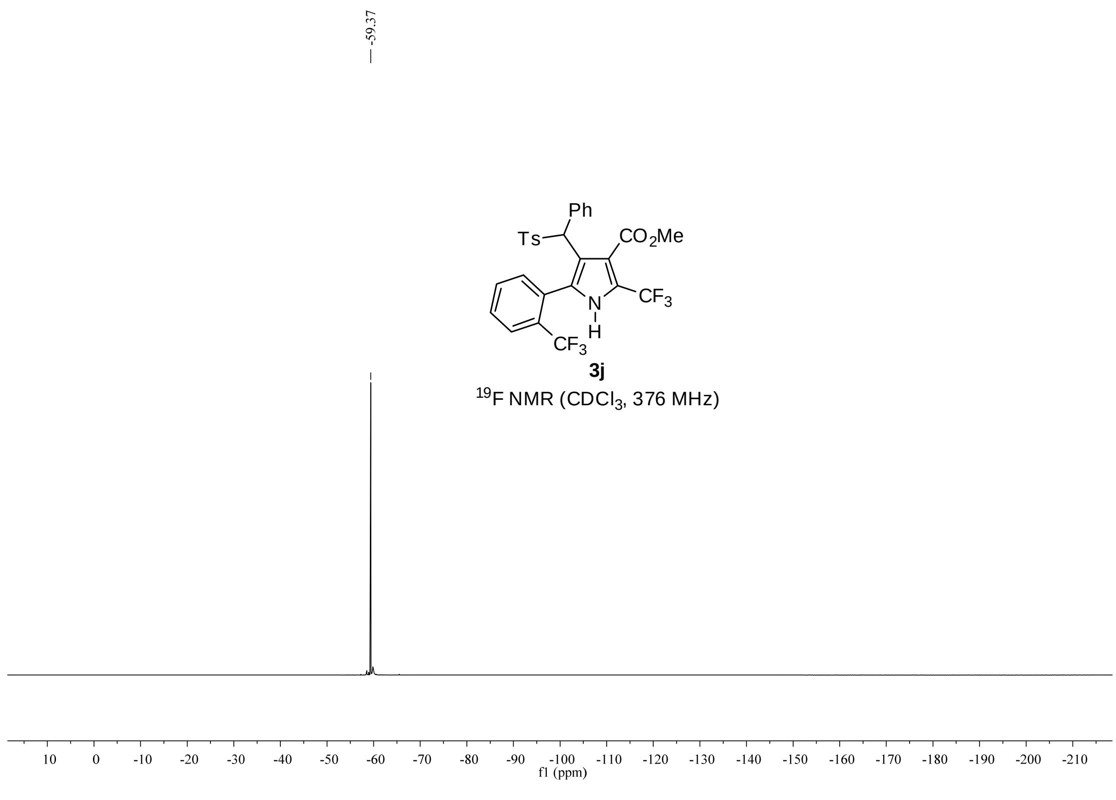
^{19}F NMR ($CDCl_3$, 376 MHz)

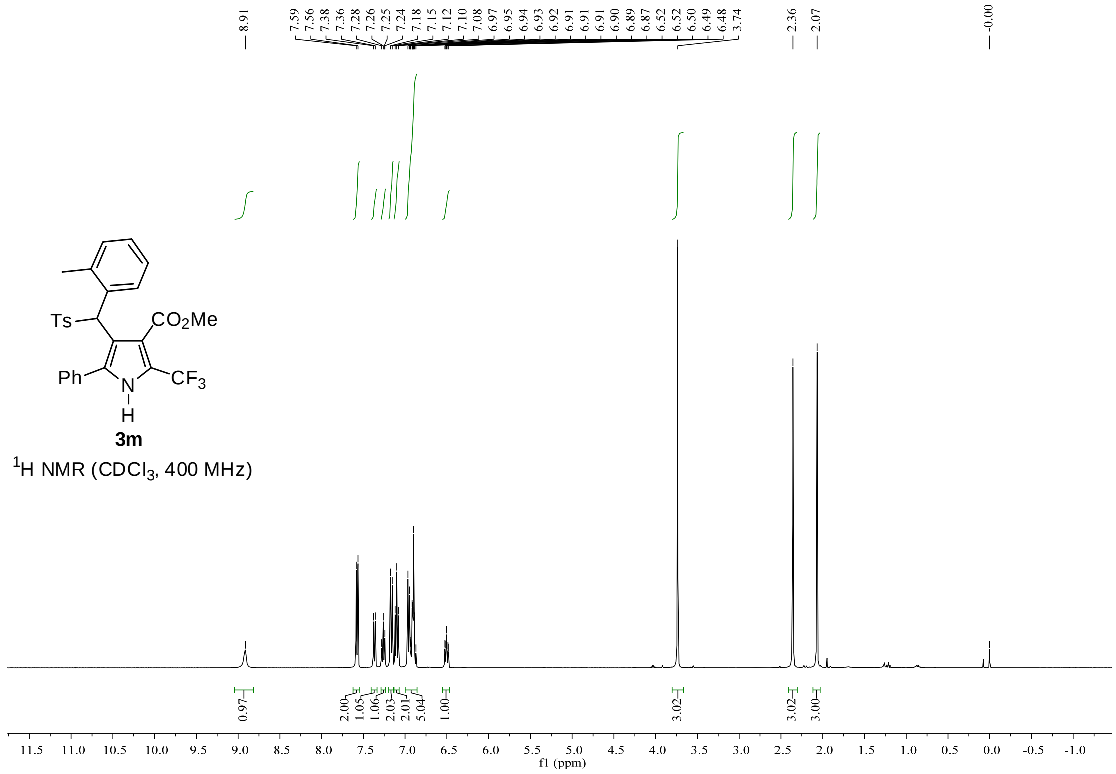


3j

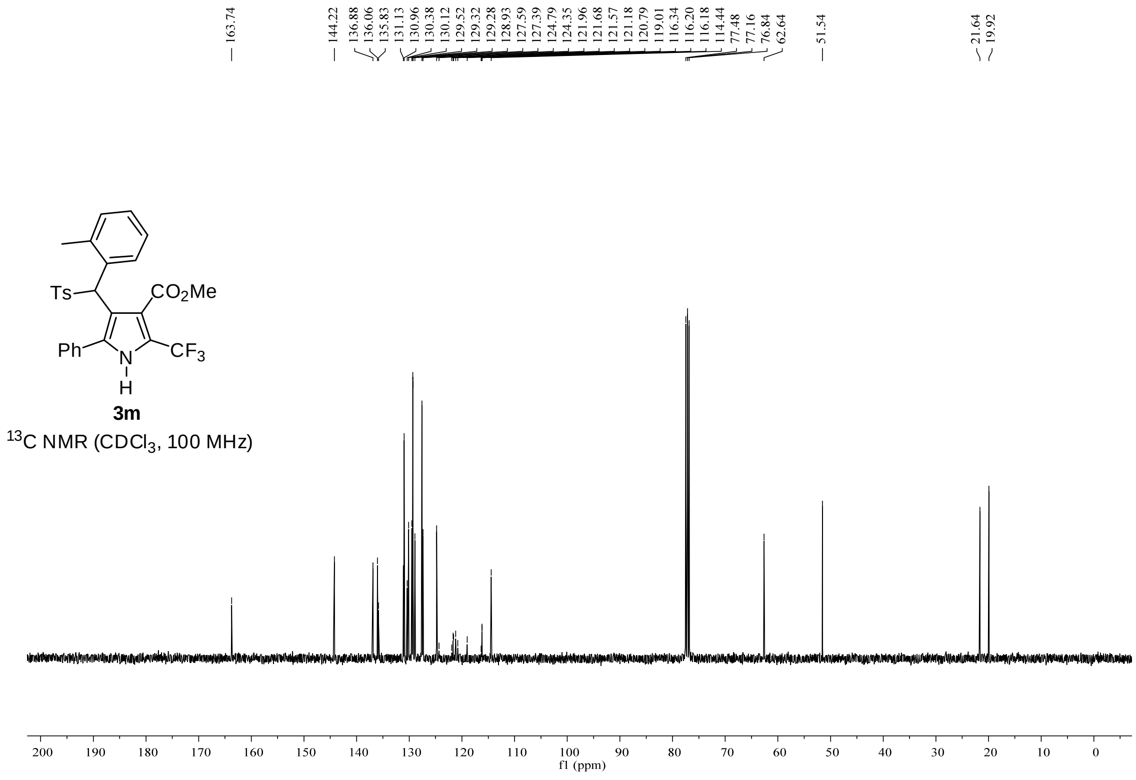
^{1}H NMR ($CDCl_3$, 400 MHz)


164.00
144.32
135.81
131.12
130.52
130.32
130.02
129.93
129.90
129.38
129.07
127.97
127.59
127.53
125.85
125.80
124.55
124.24
124.14
122.71
122.32
121.93
121.81
121.57
121.54
119.06
118.90
116.33
116.16
116.15
77.48
77.16
76.84
65.54
51.74
21.61
Ph
Ts
CO2Me
N
H
CF3
CF3
3j
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

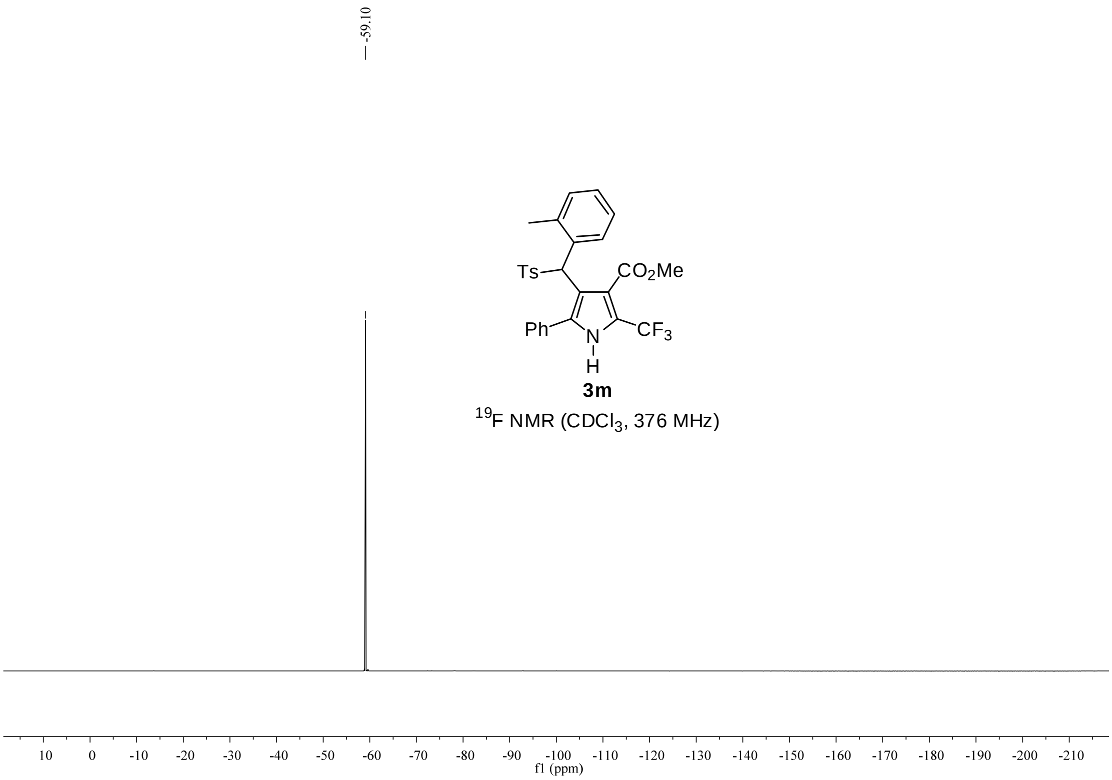

-59.37
Ph
Ts
CO2Me
N
H
CF3
CF3
3j
19F NMR (CDCl3, 376 MHz)
f1 (ppm)

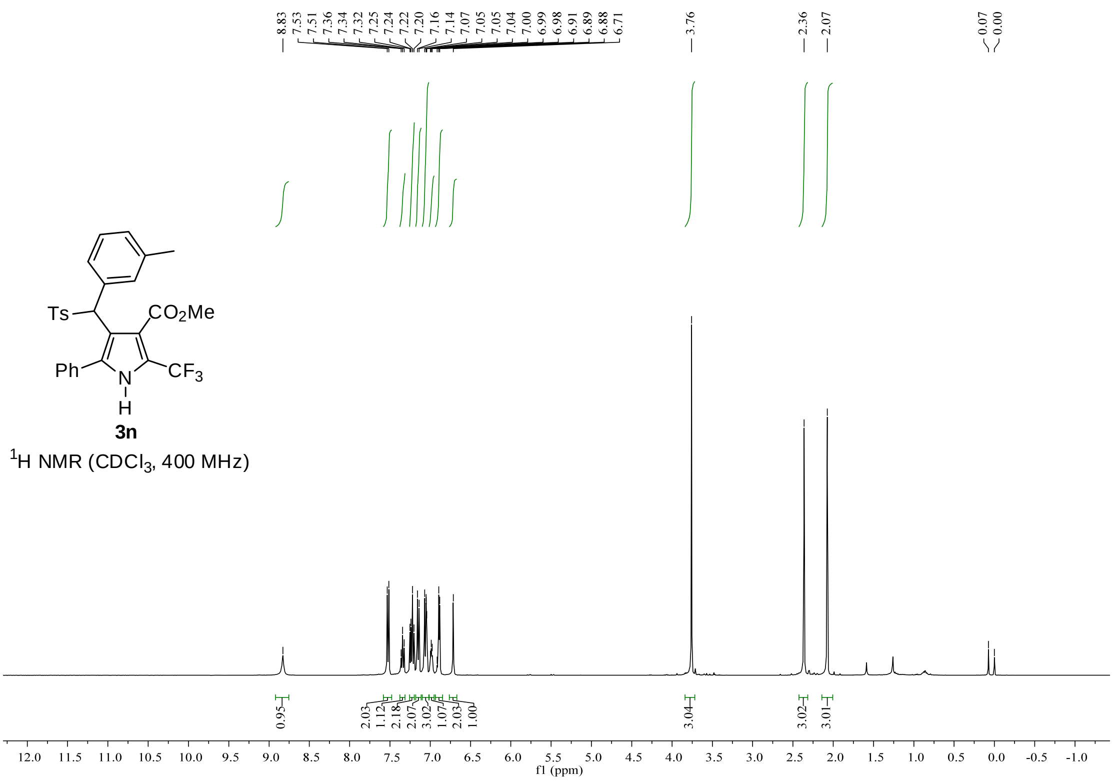


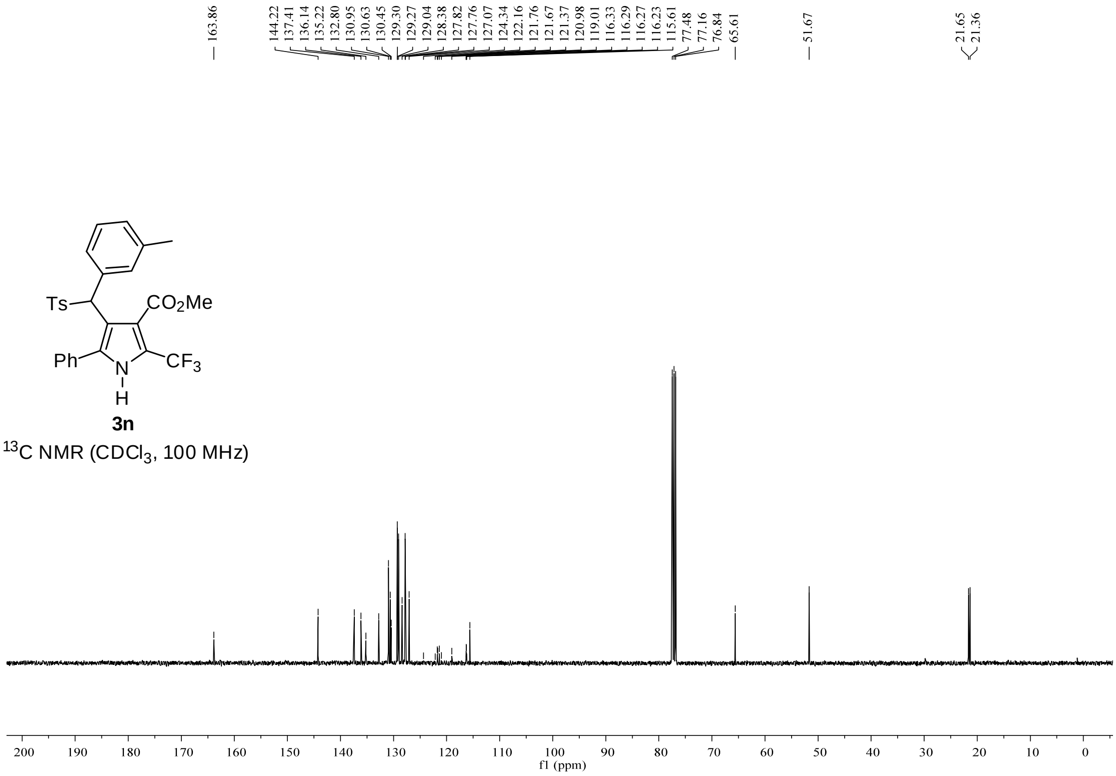
8.91
7.59 7.56 7.38 7.36 7.28 7.26 7.25 7.24 7.18 7.15 7.12 7.10 7.08 6.97 6.95 6.94 6.93 6.92 6.91 6.91 6.91 6.90 6.89 6.87 6.52 6.52 6.50 6.49 6.48 3.74
2.36 2.07
-0.00
Ts
CO2Me
Ph
CF3
N
H
3m
1H NMR (CDCl3, 400 MHz)
0.97 2.00 1.05 1.06 2.03 2.01 5.04 1.00 3.02 3.02 3.00
f1 (ppm)

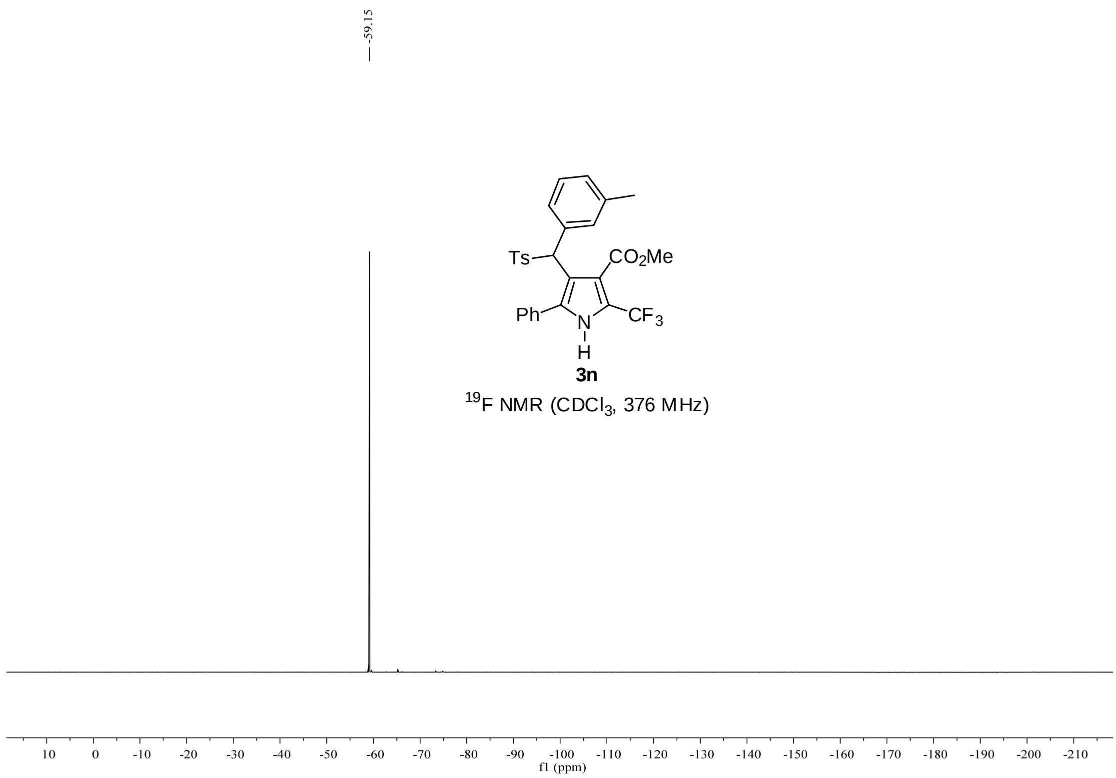


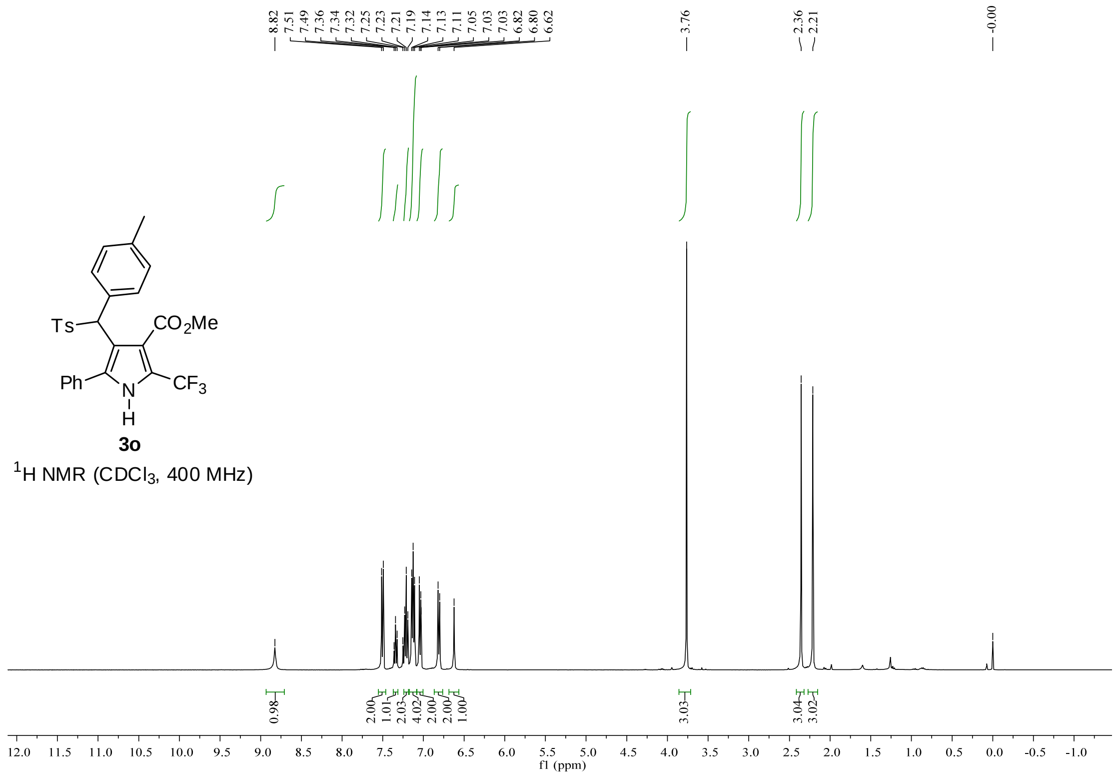
163.74
144.22 136.88 136.06 135.83 131.13 130.96 130.38 130.12 129.52 129.32 129.28 128.93 127.59 127.39 124.79 124.35 121.96 121.68 121.57 121.18 120.79 119.01 116.34 116.20 116.18 114.44 77.48 77.16 76.84 62.64
51.54
21.64 19.92
Ts
CO2Me
Ph
CF3
N
H
3m
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


-59.10
Ts
CO_2Me
Ph
N
H
CF_3
3m
^{19}F NMR ($CDCl_3$, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

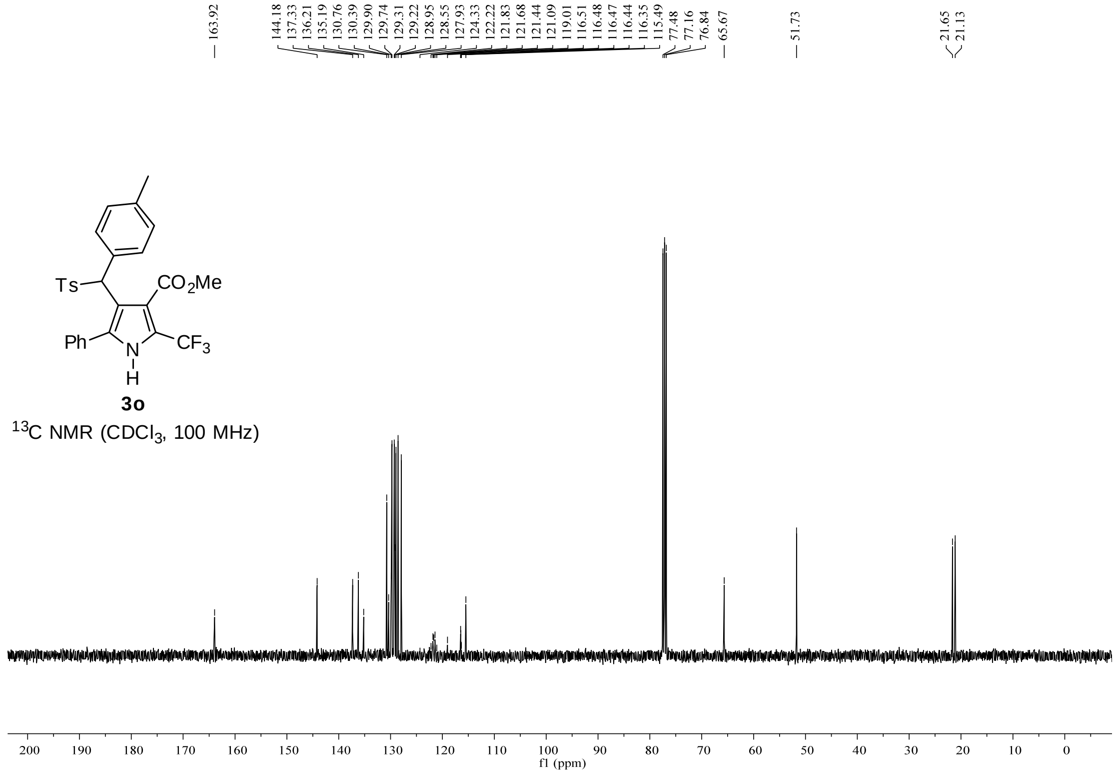

8.83 7.53 7.51 7.36 7.34 7.32 7.25 7.24 7.22 7.20 7.16 7.14 7.07 7.05 7.05 7.04 7.00 6.99 6.98 6.91 6.89 6.88 6.71
3.76
2.36 2.07
0.07 0.00
Ts
CO_2Me
Ph
N
H
CF_3
3n
^{1}H NMR ($CDCl_3$, 400 MHz)
0.95 2.03 1.12 2.18 2.07 3.02 1.07 2.03 1.00 3.04 3.02 3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


163.86
144.22
137.41
136.14
135.22
132.80
130.95
130.63
130.45
129.30
129.27
129.04
128.38
127.82
127.76
127.07
124.34
122.16
121.76
121.67
121.37
120.98
119.01
116.33
116.29
116.27
116.23
115.61
77.48
77.16
76.84
65.61
51.67
21.65
21.36
Ts
CO_2Me
Ph
N
H
CF_3
3n
^{13}C NMR ($CDCl_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

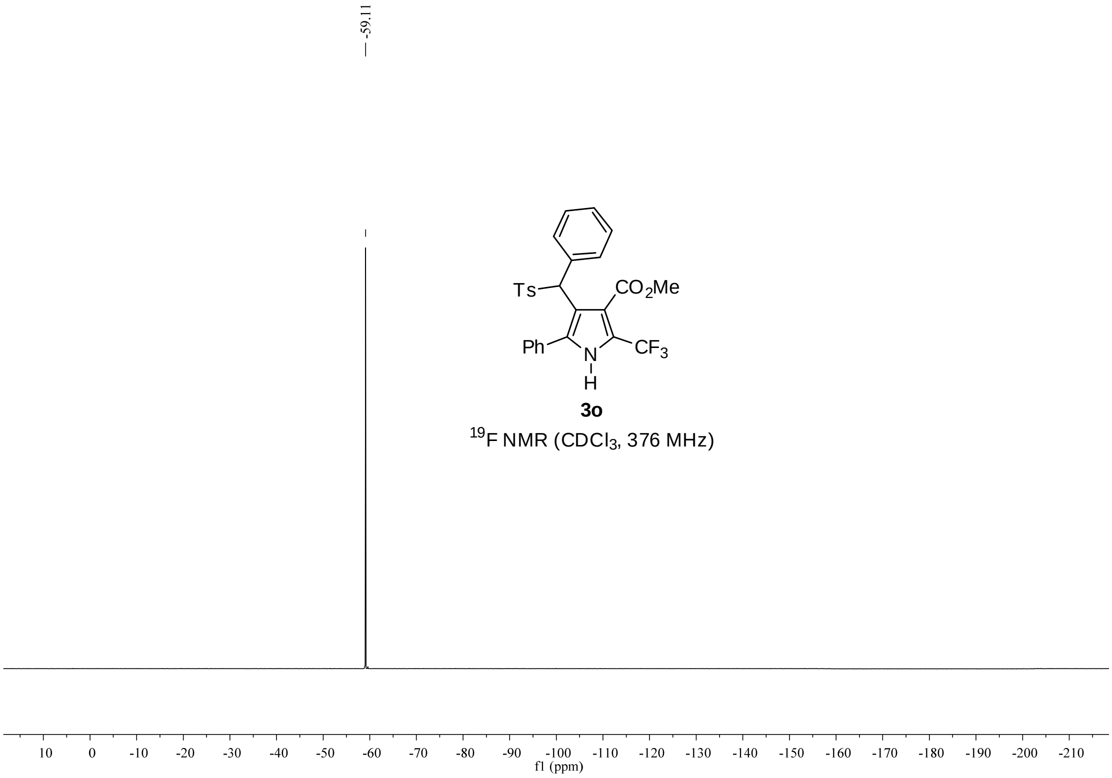

-59.15
Ts
CO_2Me
Ph
N
H
CF_3
3n
^{19}F NMR ($CDCl_3$, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



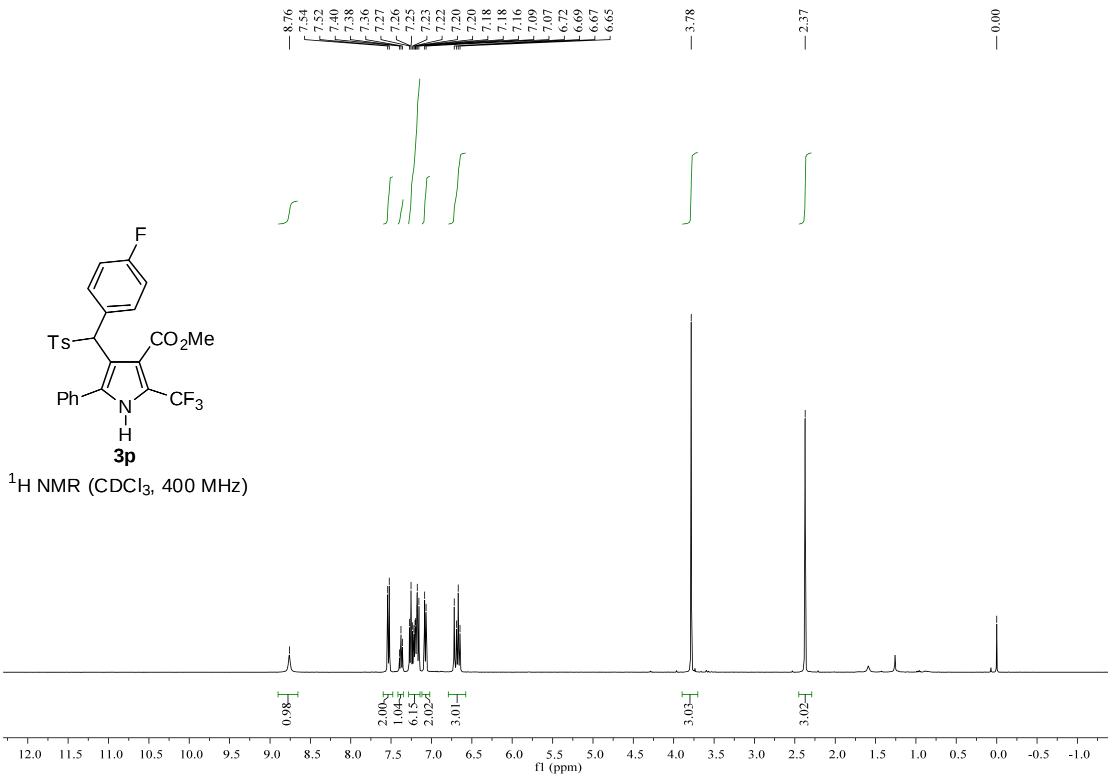
Ts
CO2Me
Ph
N
H
CF3
3o
1H NMR (CDCl3, 400 MHz)
f1 (ppm)



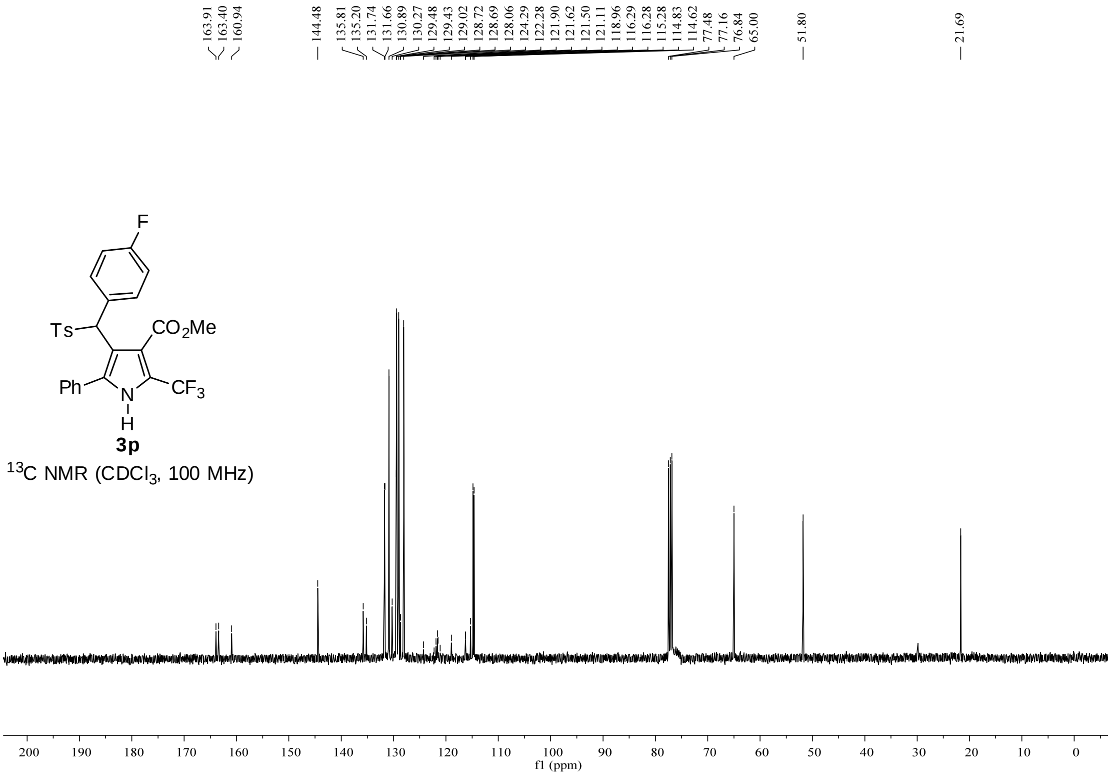
Ts
CO2Me
Ph
N
H
CF3
3o
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

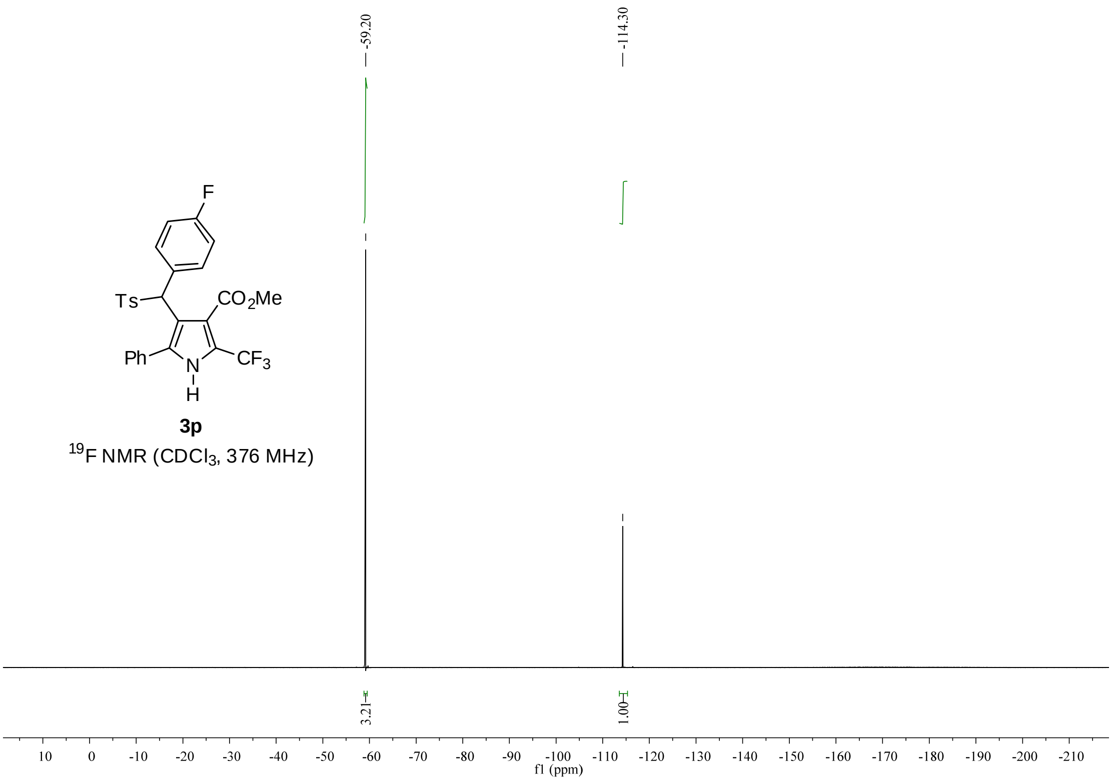


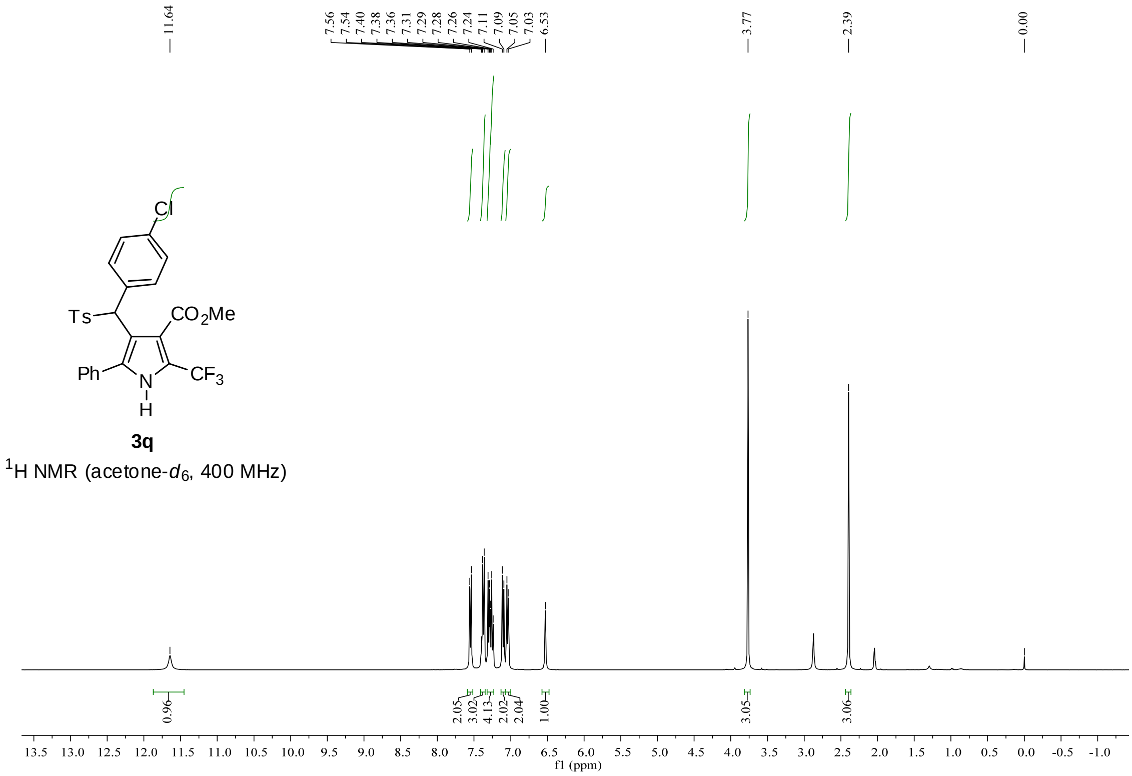
-59.11
Ts
CO2Me
Ph
CF3
N
H
3o
19F NMR (CDCl3, 376 MHz)
f1 (ppm)



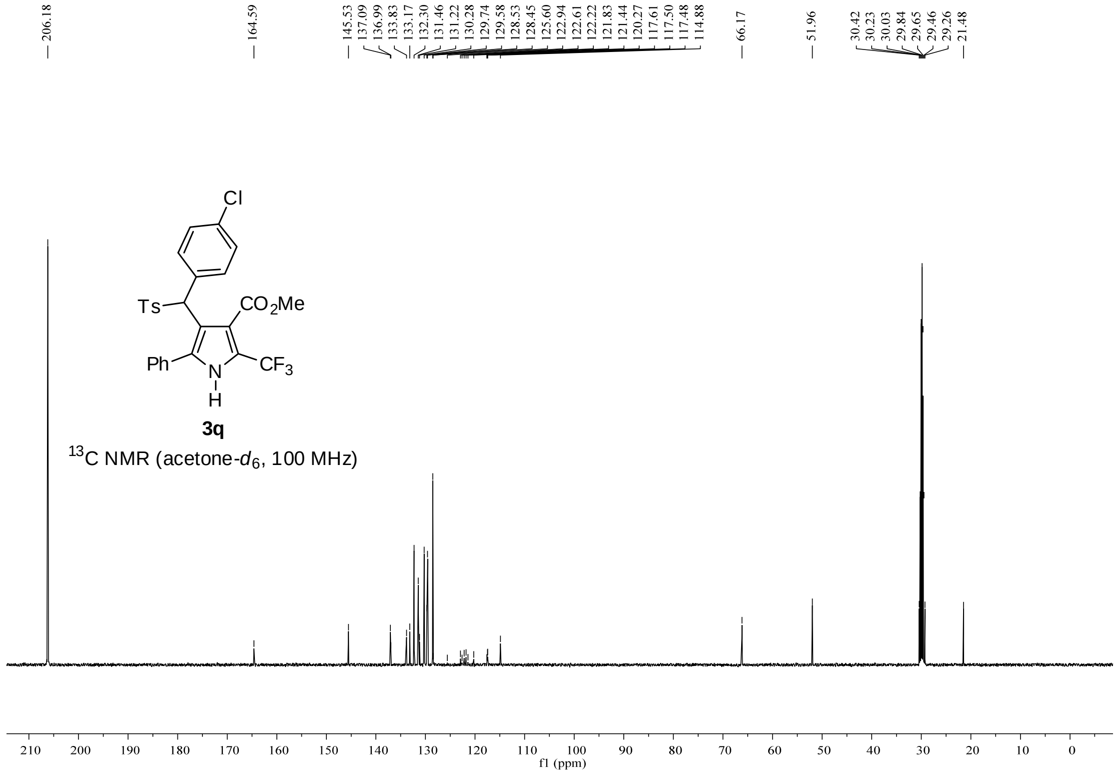
8.76 7.54 7.52 7.40 7.38 7.36 7.27 7.26 7.25 7.23 7.22 7.20 7.20 7.18 7.18 7.16 7.09 7.07 6.72 6.69 6.67 6.65
3.78
2.37
0.00
F
Ts
CO2Me
Ph
CF3
N
H
3p
1H NMR (CDCl3, 400 MHz)
0.98 2.00 1.04 6.15 2.02 3.01 3.03 3.02
f1 (ppm)


163.91
163.40
160.94
144.48
135.81
135.20
131.74
131.66
130.89
130.27
129.48
129.43
129.02
128.72
128.69
128.06
124.29
122.28
121.90
121.62
121.50
121.11
118.96
116.29
116.28
115.28
114.83
114.62
77.48
77.16
76.84
65.00
51.80
21.69
F
Ts
CO2Me
Ph
N
H
CF3
3p
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

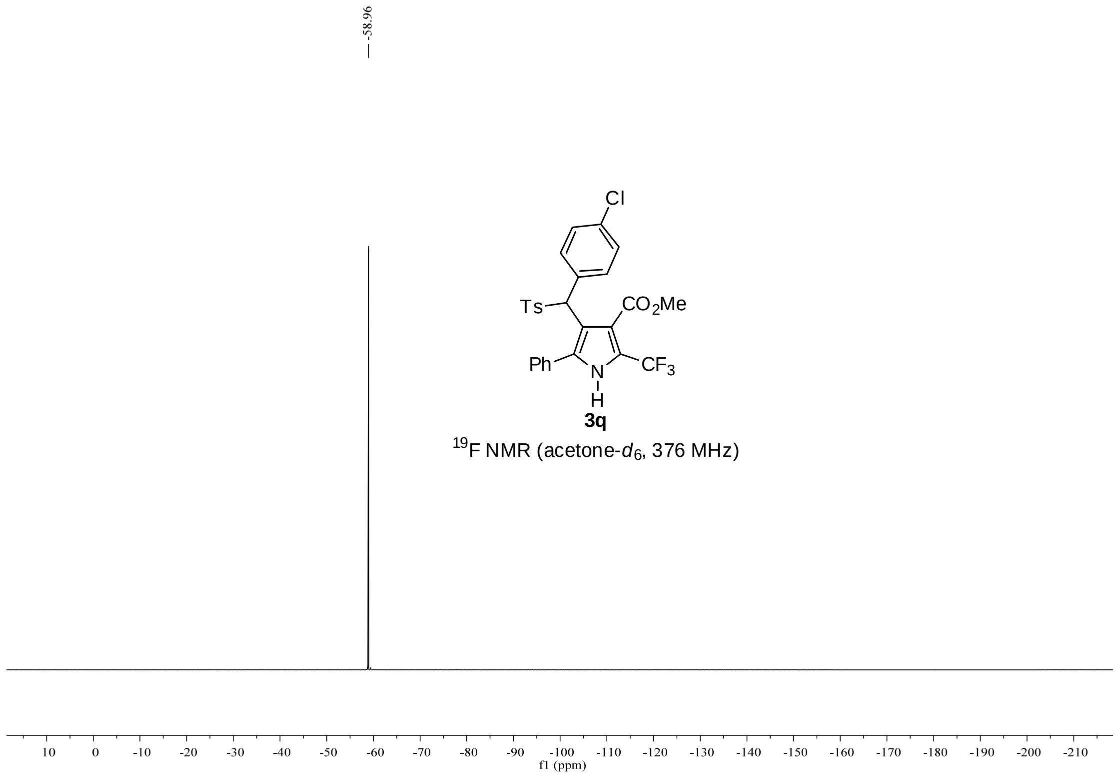

-59.20
-114.30
F
Ts
CO2Me
Ph
N
H
CF3
3p
19F NMR (CDCl3, 376 MHz)
3.21
1.00
f1 (ppm)

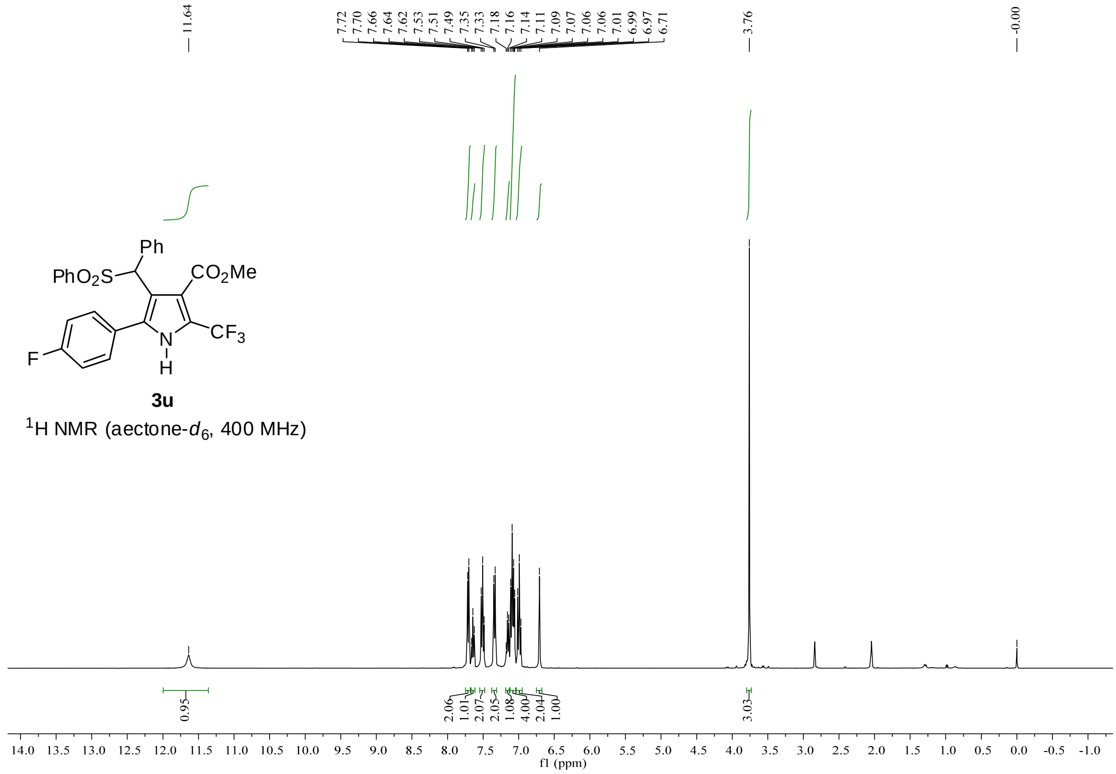


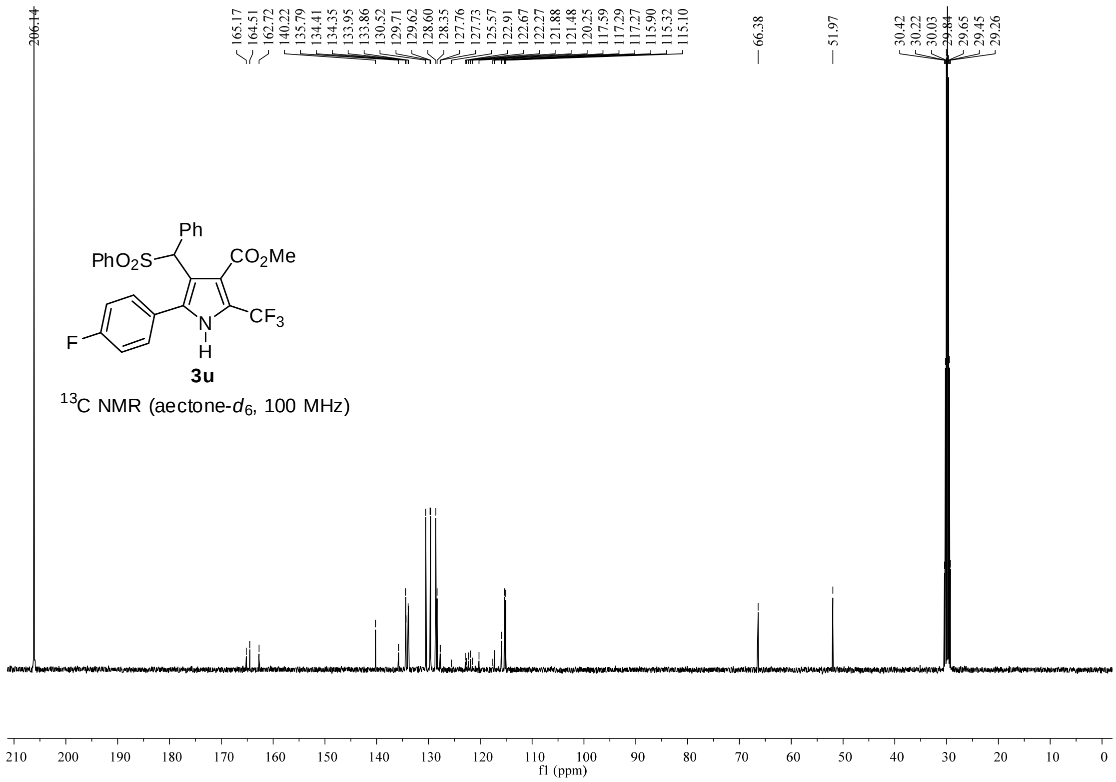
11.64
7.56 7.54 7.40 7.38 7.36 7.31 7.29 7.28 7.26 7.24 7.11 7.09 7.05 7.03 6.53
3.77
2.39
0.00
Cl
Ts
CO2Me
Ph
N
H
CF3
3q
1H NMR (acetone-d6, 400 MHz)
0.96
2.05 3.02 4.13 2.02 2.04 1.00
3.05
3.06
f1 (ppm)

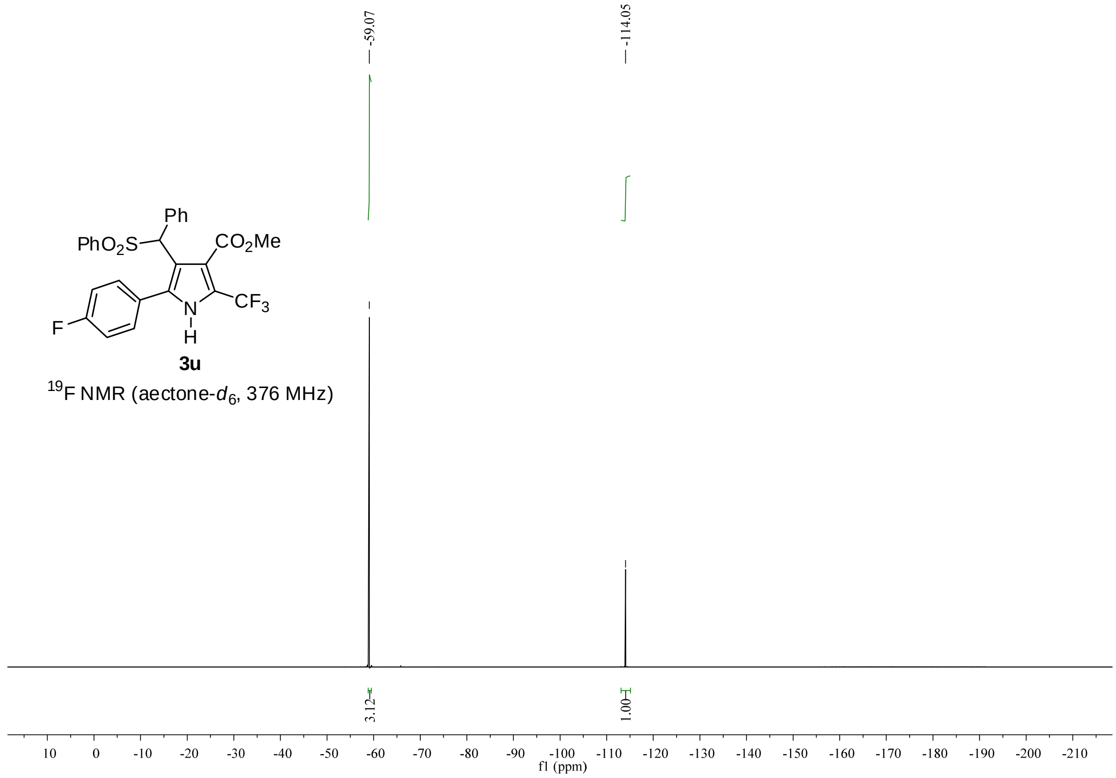


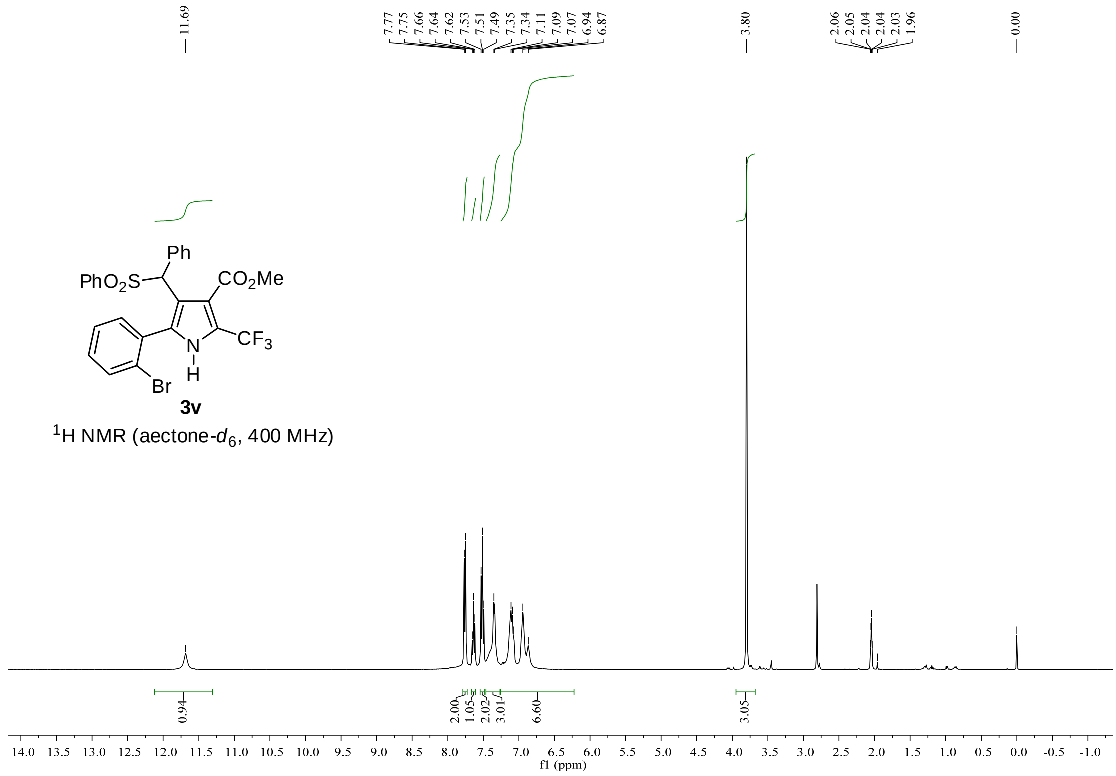
206.18
164.59
145.53 137.09 136.99 133.83 133.17 132.30 131.46 131.22 130.28 129.74 129.58 128.53 128.45 125.60 122.94 122.61 122.22 121.83 121.44 120.27 117.61 117.50 117.48 114.88
66.17
51.96
30.42 30.23 30.03 29.84 29.65 29.46 29.26 21.48
Cl
Ts
CO2Me
Ph
N
H
CF3
3q
13C NMR (acetone-d6, 100 MHz)
f1 (ppm)


-58.96
Cl
Ts
CO2Me
Ph
N
H
CF3
3q
19F NMR (acetone-d6, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


11.64
7.72 7.70 7.66 7.64 7.62 7.53 7.51 7.49 7.35 7.33 7.18 7.16 7.14 7.11 7.09 7.07 7.06 7.06 7.01 6.99 6.97 6.71
3.76
-0.00
Ph
PhO2S
CO2Me
F
N
H
CF3
3u
1H NMR (aectone-d6, 400 MHz)
0.95
2.06 1.01 2.07 2.05 1.08 4.00 2.04 1.00
3.03
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

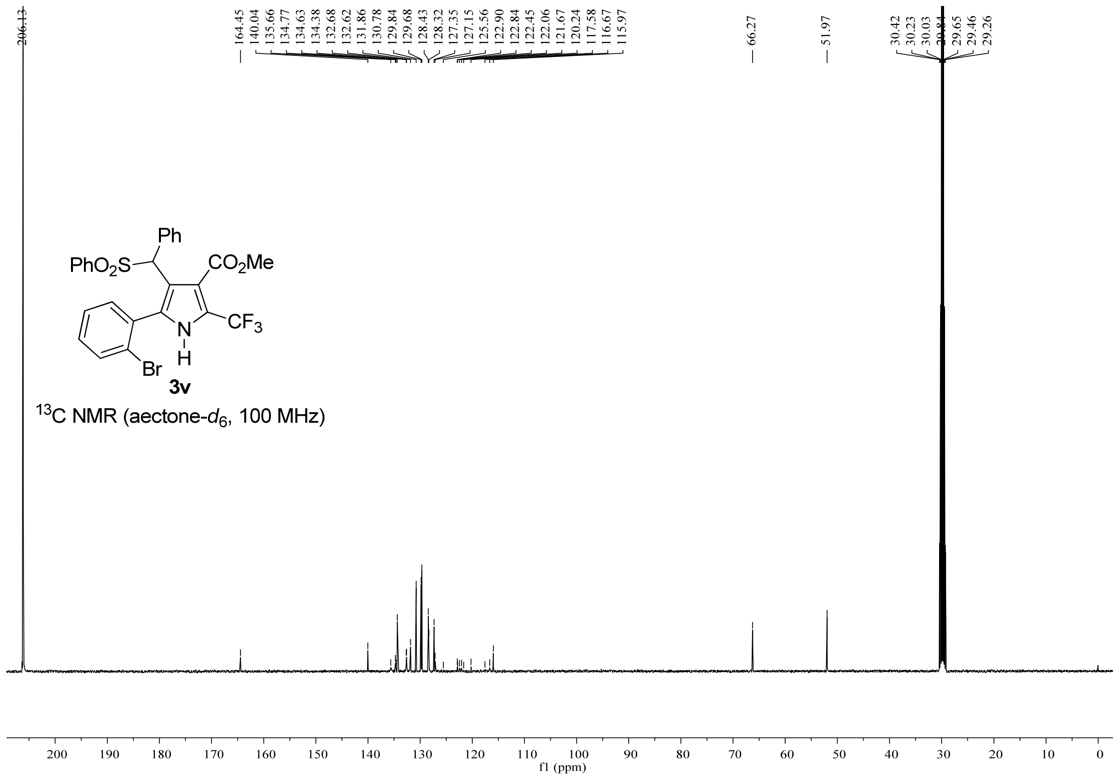

206.14
165.17
164.51
162.72
140.22
135.79
134.41
134.35
133.95
133.86
130.52
129.71
129.62
128.60
128.35
127.76
127.73
125.57
122.91
122.67
122.27
121.88
121.48
120.25
117.59
117.29
117.27
115.90
115.32
115.10
66.38
51.97
30.42
30.22
30.03
29.84
29.65
29.45
29.26
Ph
PhO_2S
CO_2Me
CF_3
F
N
H
3u
^{13}C NMR (aectone-d_6, 100 MHz)
f1 (ppm)


-59.07
-114.05
Ph
PhO_2S
CO_2Me
CF_3
F
N
H
3u
^{19}F NMR (aectone-d_6, 376 MHz)
3.12
1.00
f1 (ppm)



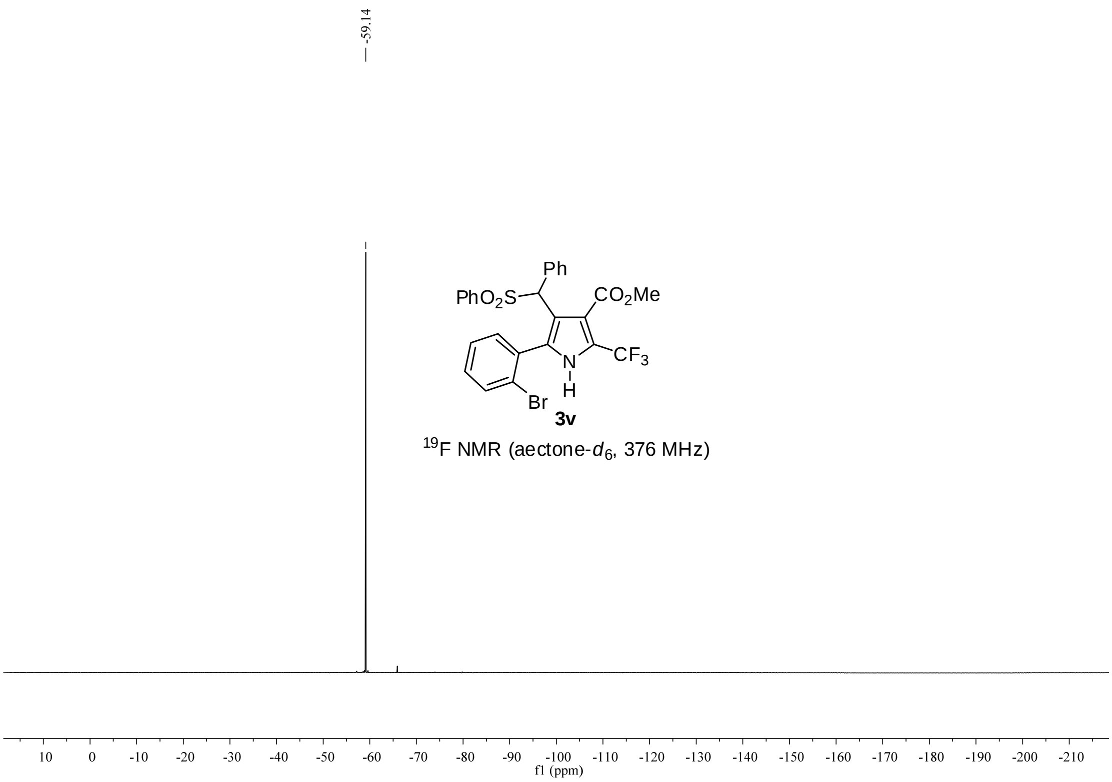
3v

^{1}H NMR (aectone-d_6, 400 MHz)

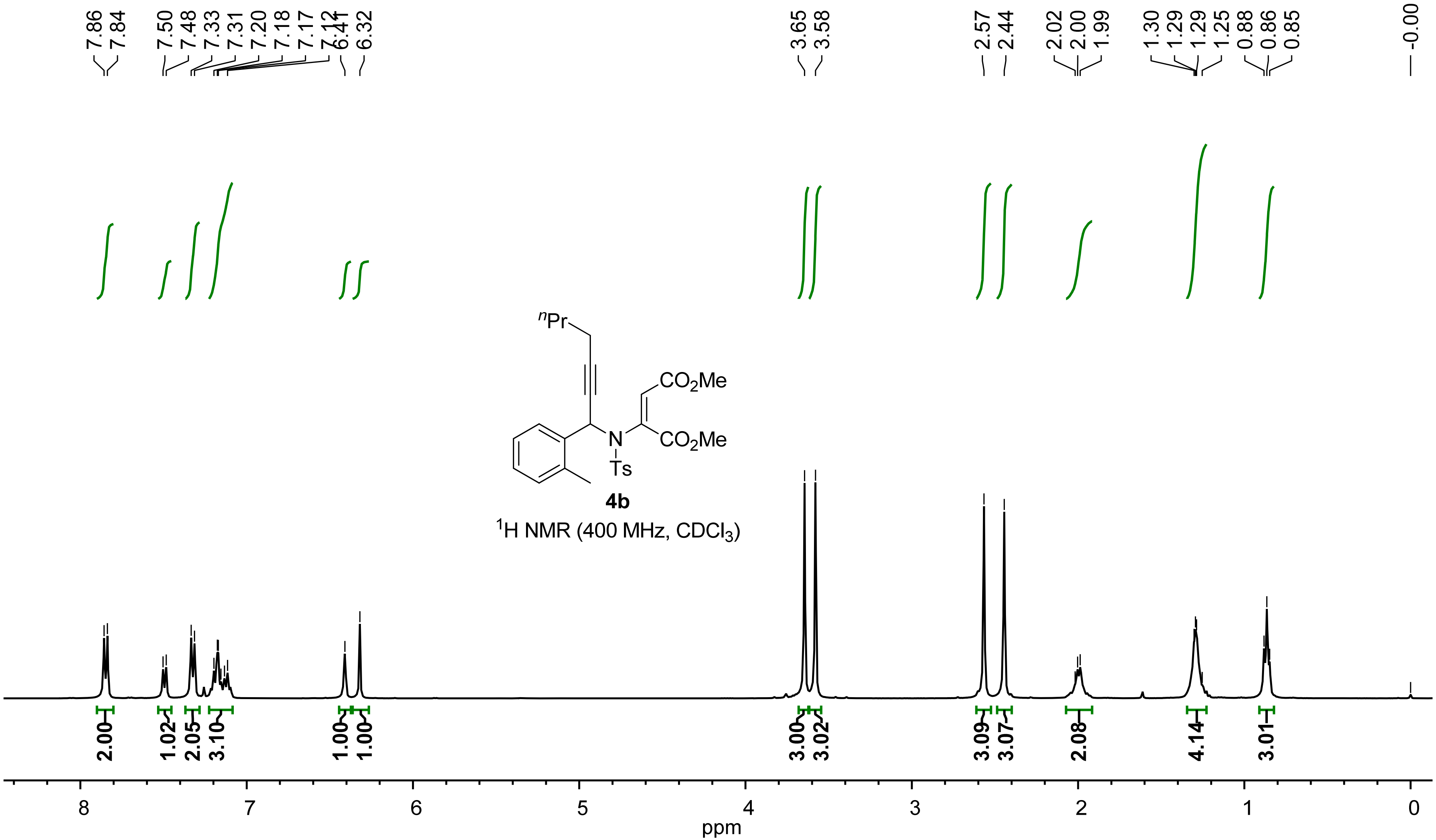


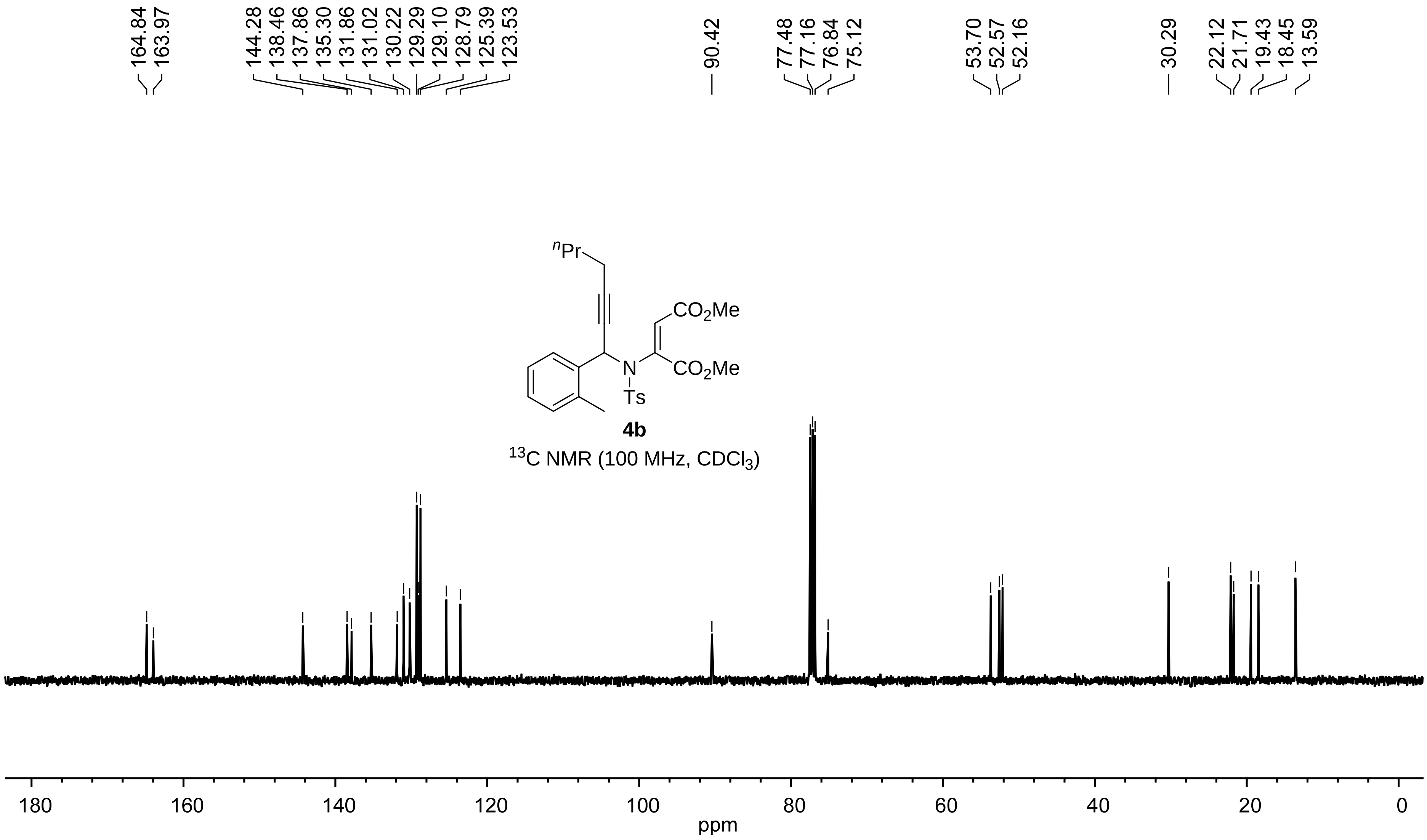
3v

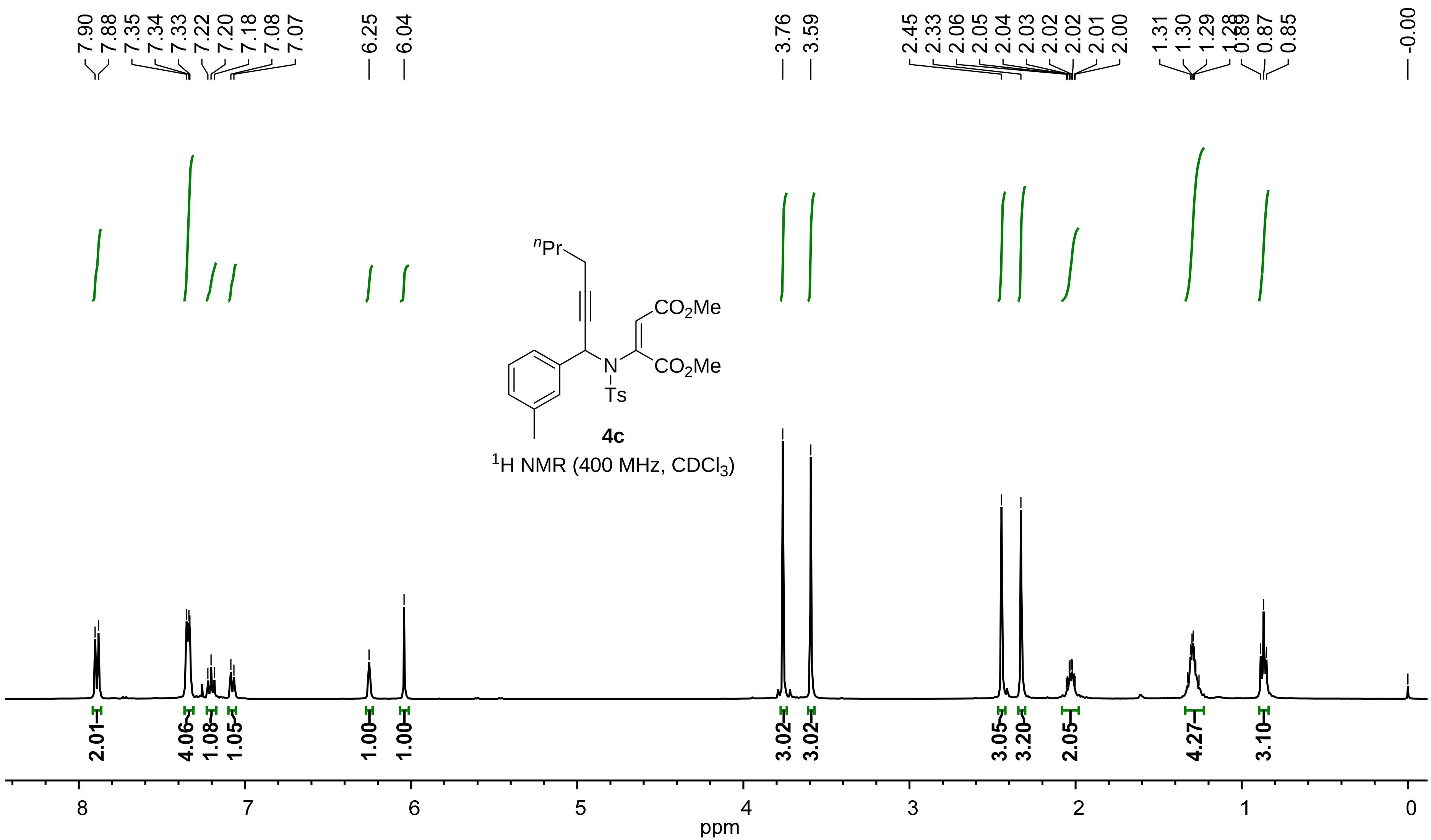
^{13}C NMR (aectone-d_6, 100 MHz)



^{19}F NMR (aectone-d_6, 376 MHz)

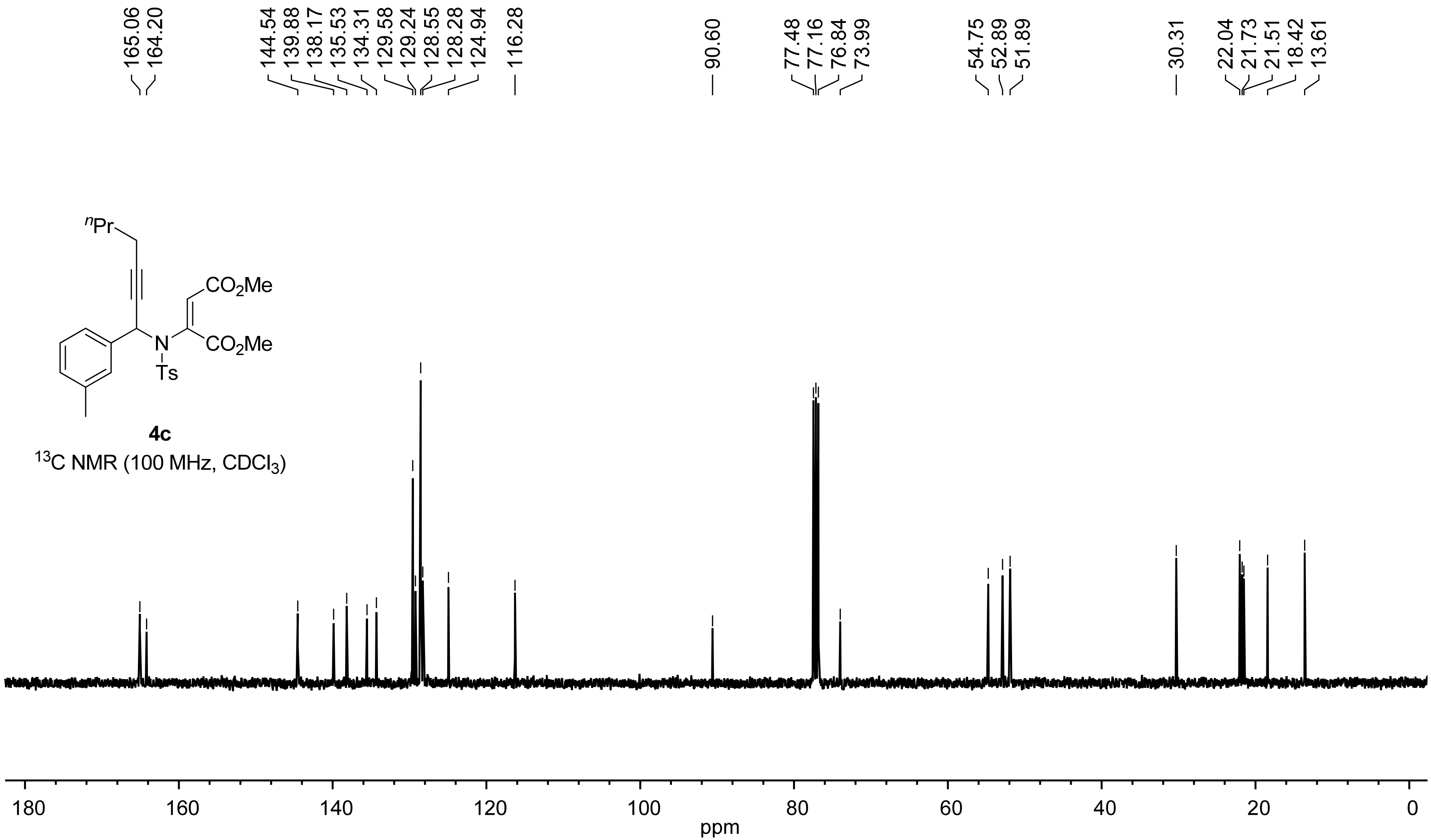

7.86
7.84
7.50
7.48
7.33
7.31
7.20
7.18
7.17
7.12
6.41
6.32
3.65
3.58
2.57
2.44
2.02
2.00
1.99
1.30
1.29
1.29
1.25
0.88
0.86
0.85
-0.00
nPr
CO2Me
CO2Me
N
Ts
4b
1H NMR (400 MHz, CDCl3)
2.00
1.02
2.05
3.10
1.00
1.00
3.00
3.02
3.09
3.07
2.08
4.14
3.01
8
7
6
5
4
3
2
1
0
ppm


164.84
163.97
144.28
138.46
137.86
135.30
131.86
131.02
130.22
129.29
129.10
128.79
125.39
123.53
90.42
77.48
77.16
76.84
75.12
53.70
52.57
52.16
30.29
22.12
21.71
19.43
18.45
13.59
^{n}Pr
CO_2Me
CO_2Me
N
Ts
4b
^{13}C NMR (100 MHz, $CDCl_3$)
180 160 140 120 100 80 60 40 20 0
ppm



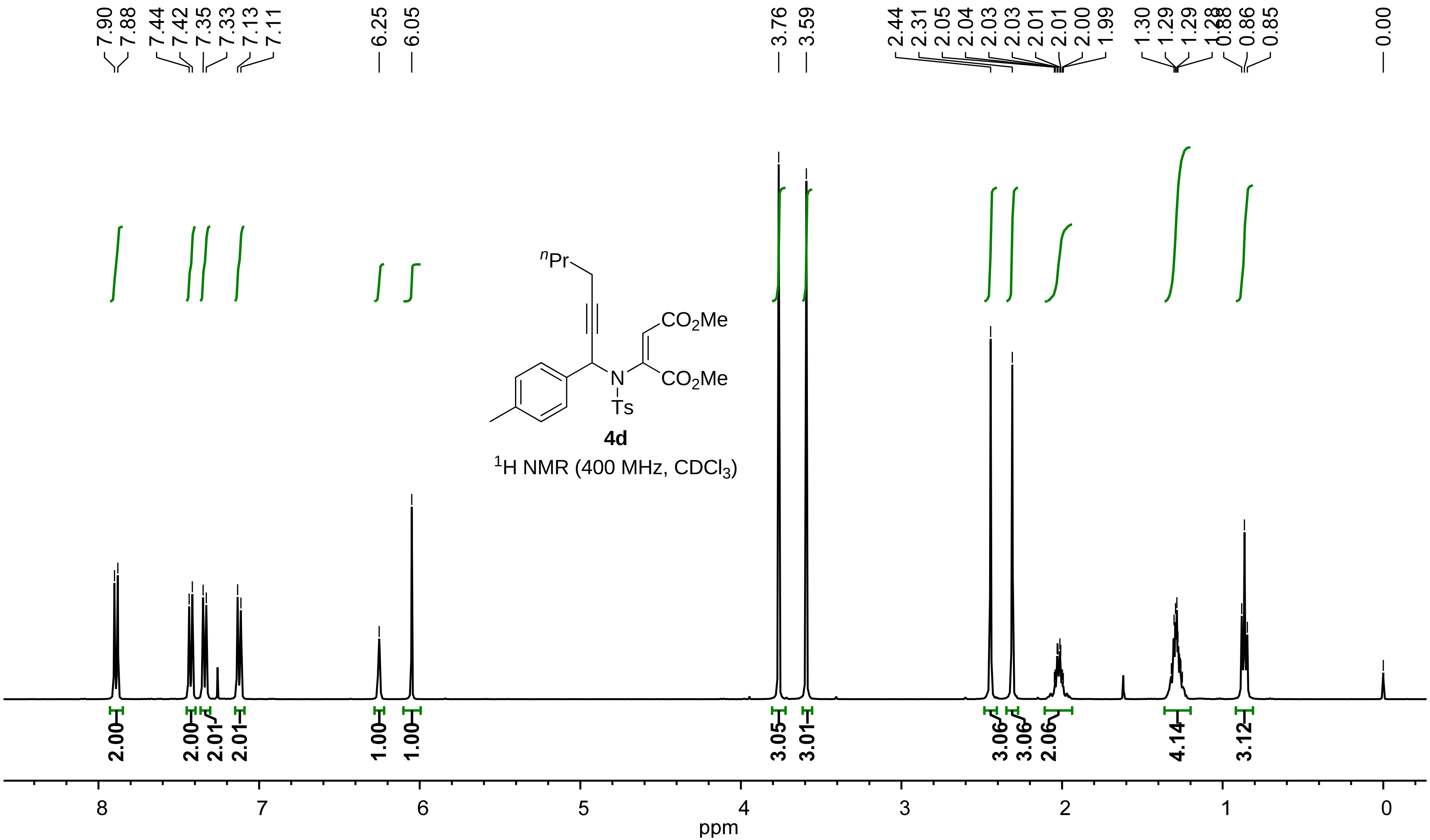
4c

^{1}H NMR (400 MHz, $CDCl_3$)

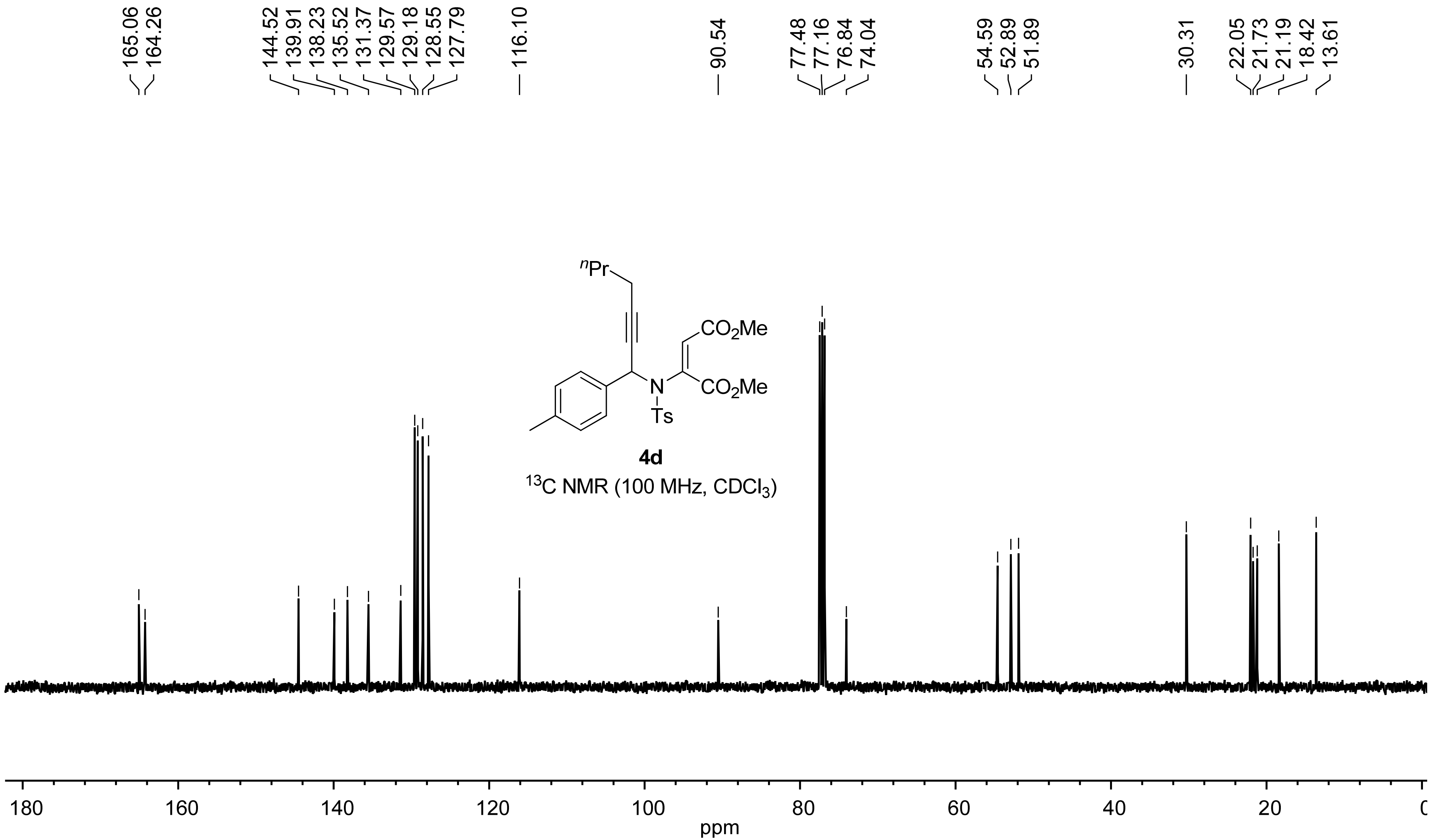


4c

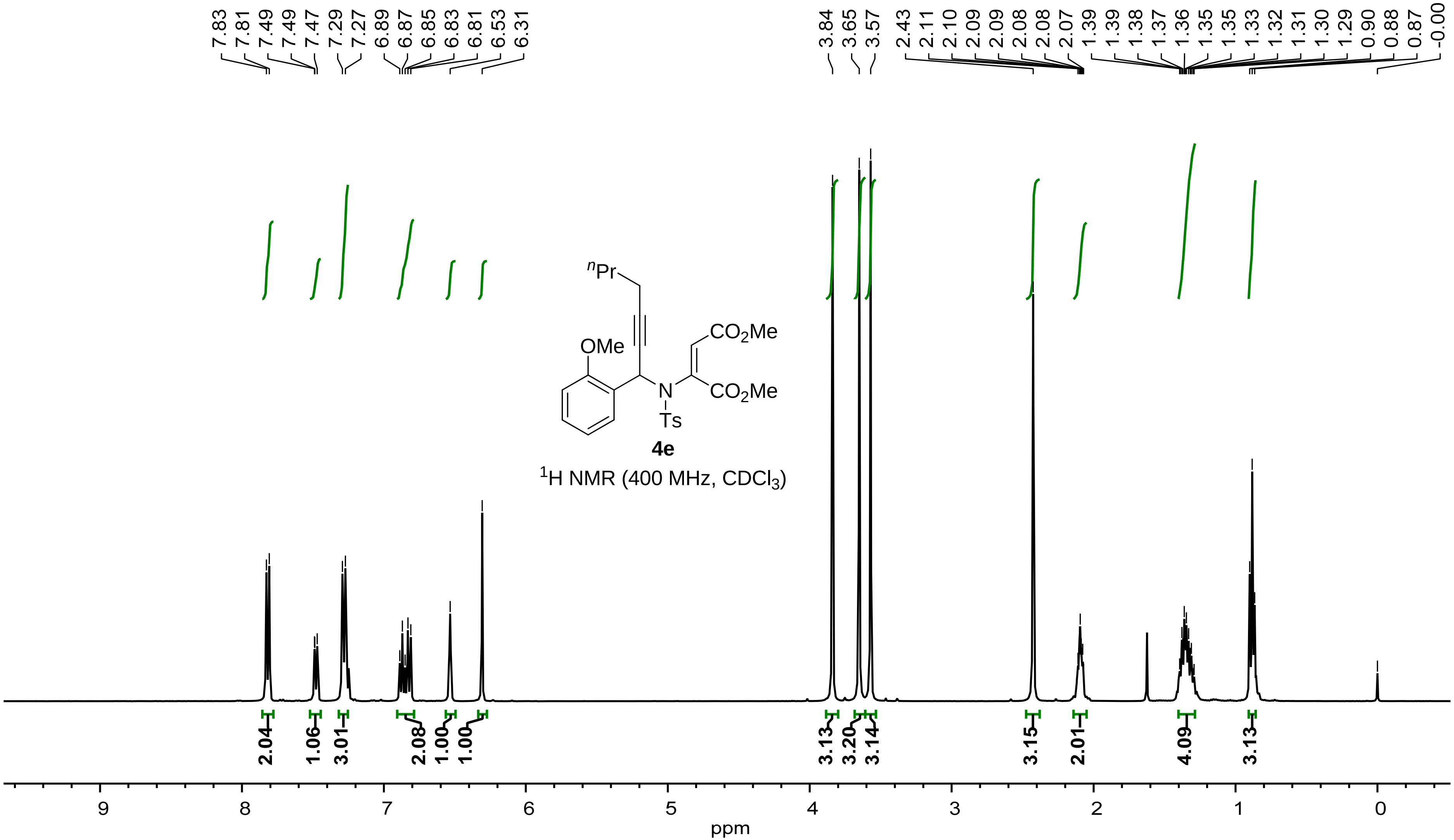
^{13}C NMR (100 MHz, $CDCl_3$)



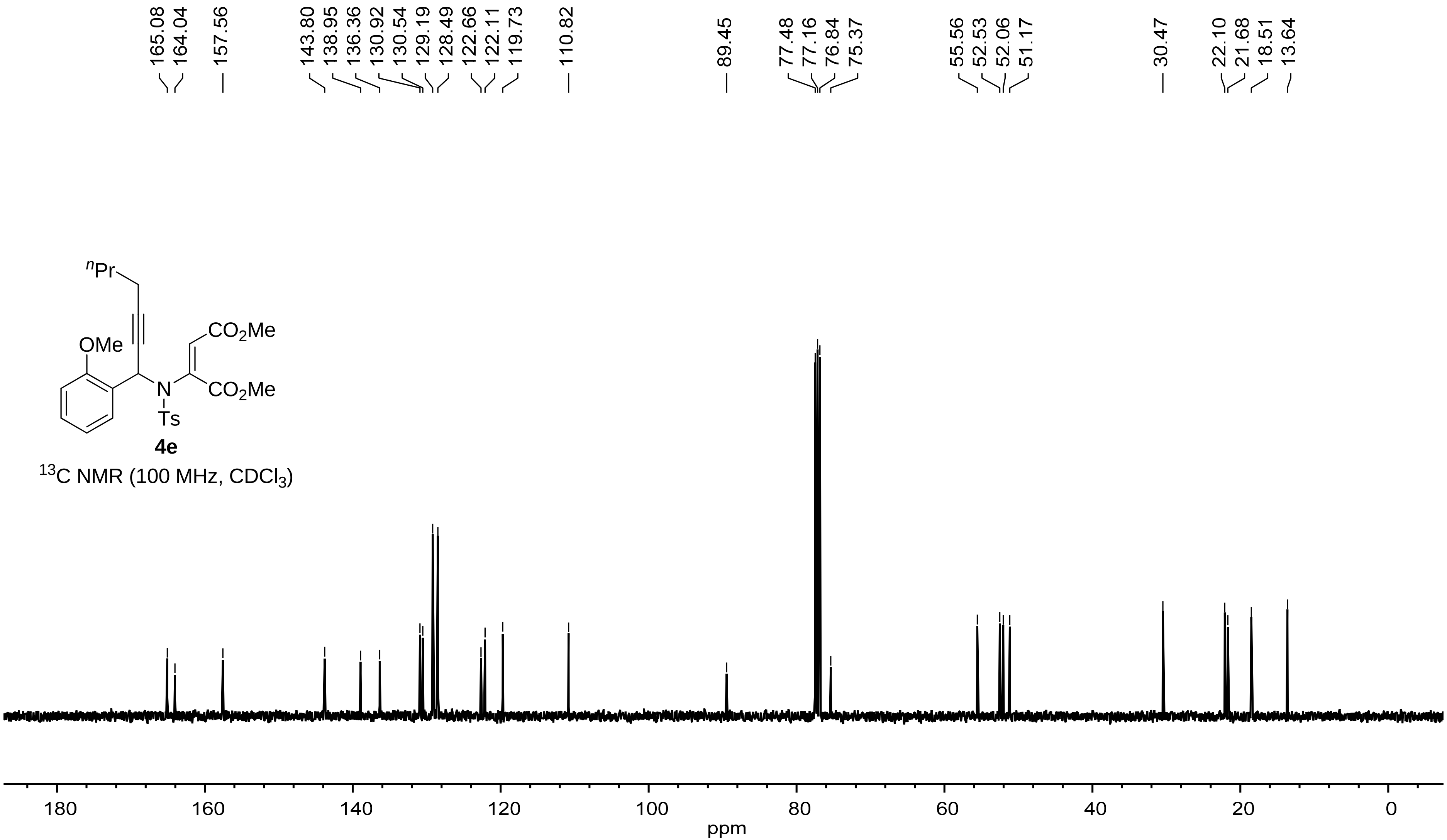
7.90
7.88
7.44
7.42
7.35
7.33
7.13
7.11
6.25
6.05
3.76
3.59
2.44
2.31
2.05
2.04
2.03
2.03
2.01
2.01
2.00
1.99
1.30
1.29
1.29
1.28
0.88
0.86
0.85
0.00
^{n}Pr
CO$_2$Me
CO$_2$Me
N
Ts
4d
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.00
2.01
2.01
1.00
1.00
3.05
3.01
3.06
3.06
2.06
4.14
3.12
8
7
6
5
4
3
2
1
0
ppm



165.06
164.26
144.52
139.91
138.23
135.52
131.37
129.57
129.18
128.55
127.79
116.10
90.54
77.48
77.16
76.84
74.04
54.59
52.89
51.89
30.31
22.05
21.73
21.19
18.42
13.61
^{n}Pr
CO_2Me
CO_2Me
N
Ts
4d
^{13}C NMR (100 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
ppm

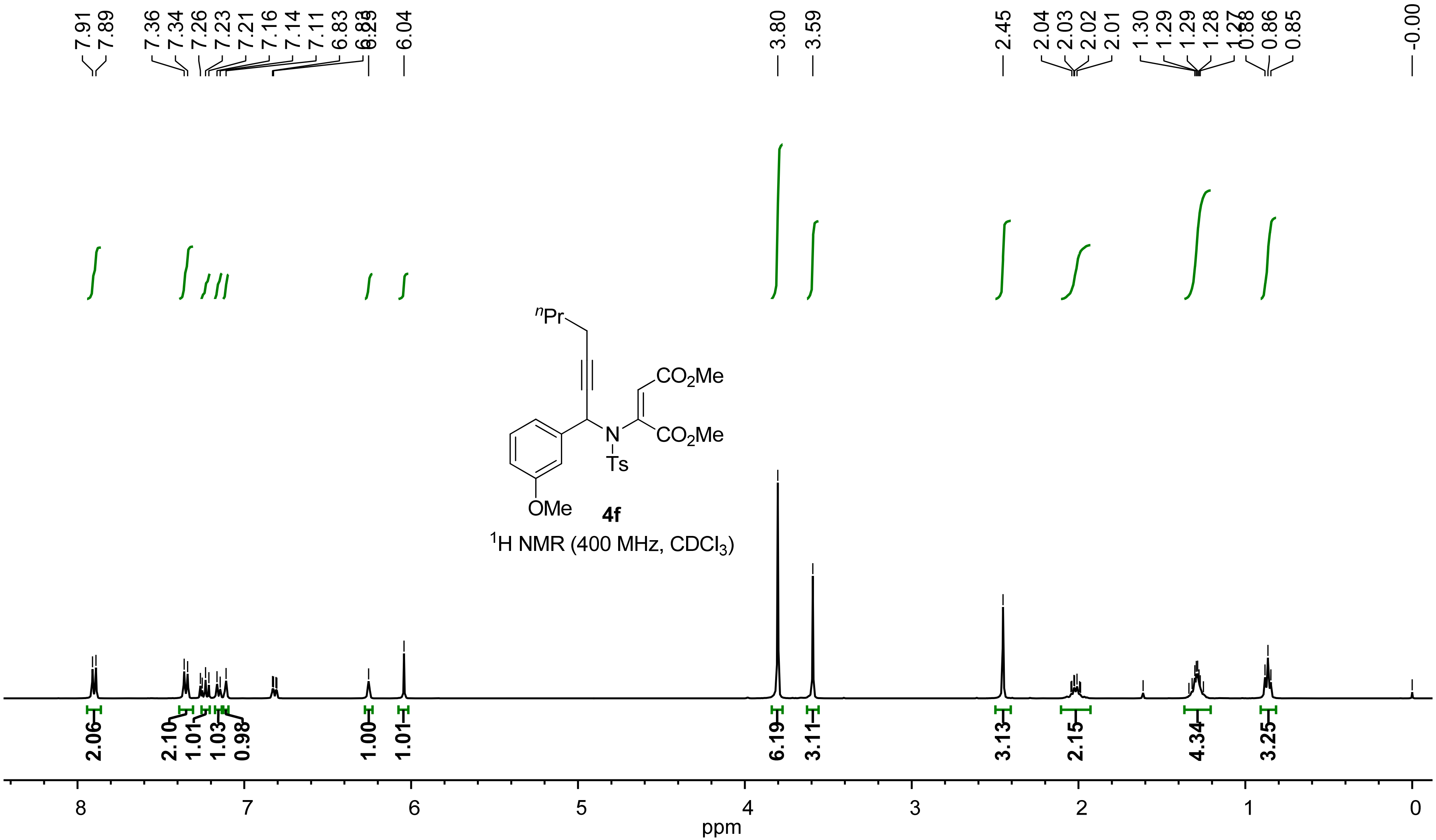


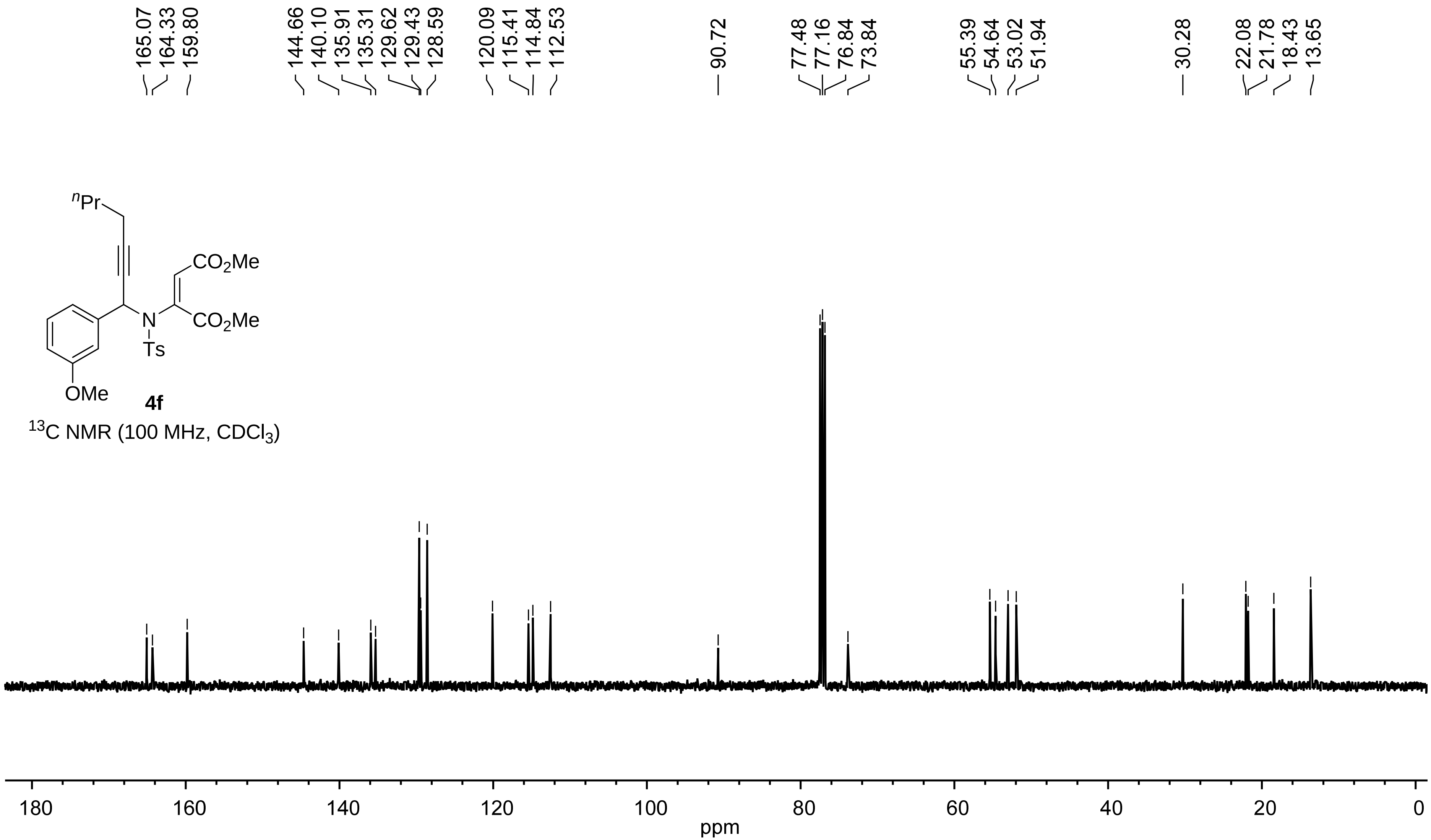
7.83 7.81 7.49 7.49 7.47 7.29 7.27 6.89 6.87 6.85 6.83 6.81 6.53 6.31
3.84 3.65 3.57 2.43 2.11 2.10 2.09 2.09 2.08 2.08 2.07 1.39 1.39 1.38 1.37 1.36 1.35 1.35 1.33 1.32 1.31 1.30 1.29 0.90 0.88 0.87 -0.00
nPr
OMe
CO2Me
N
Ts
CO2Me
4e
1H NMR (400 MHz, CDCl3)
2.04 1.06 3.01 2.08 1.00 1.00 3.13 3.20 3.14 3.15 2.01 4.09 3.13
9 8 7 6 5 4 3 2 1 0
ppm

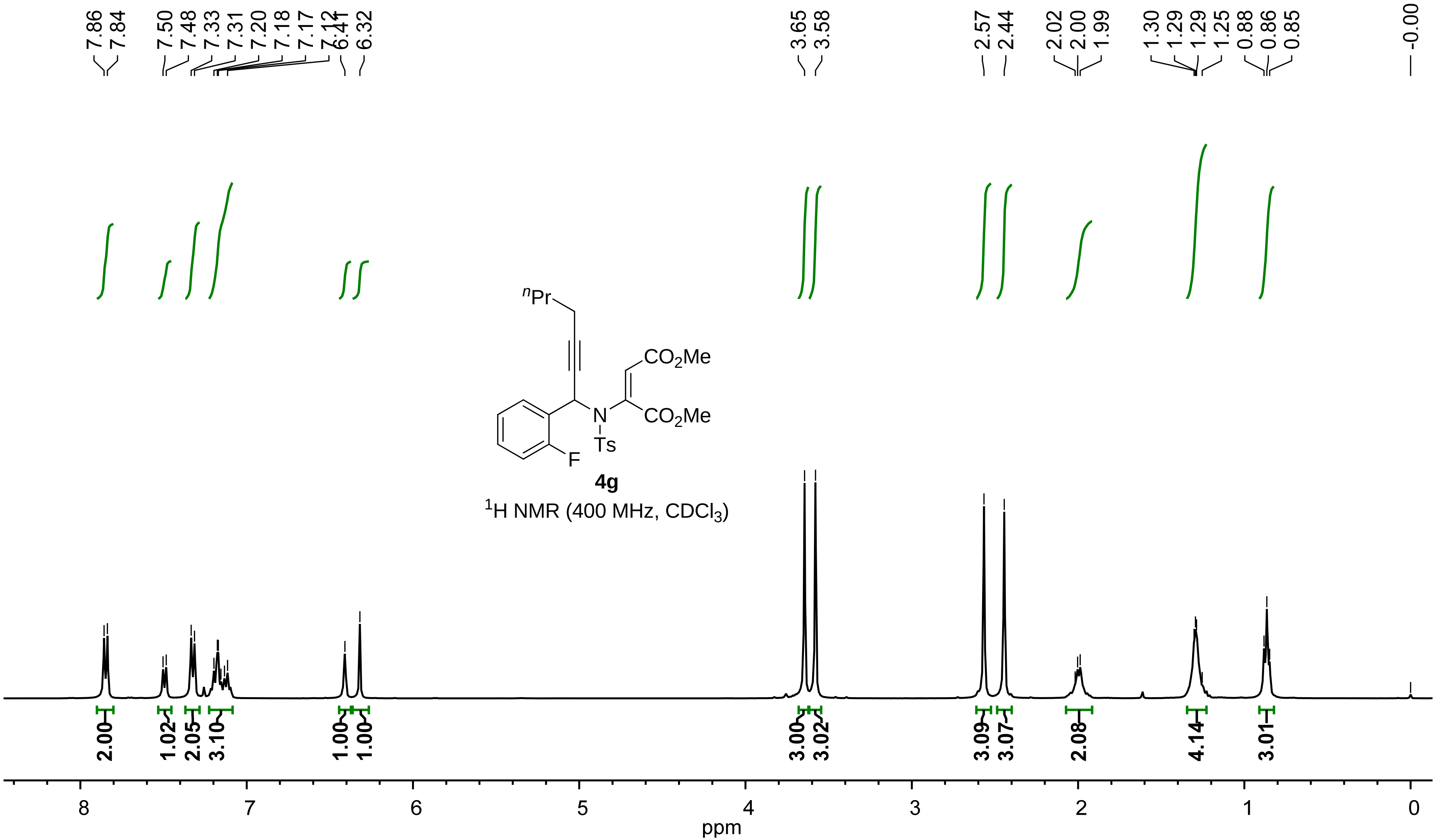


4e

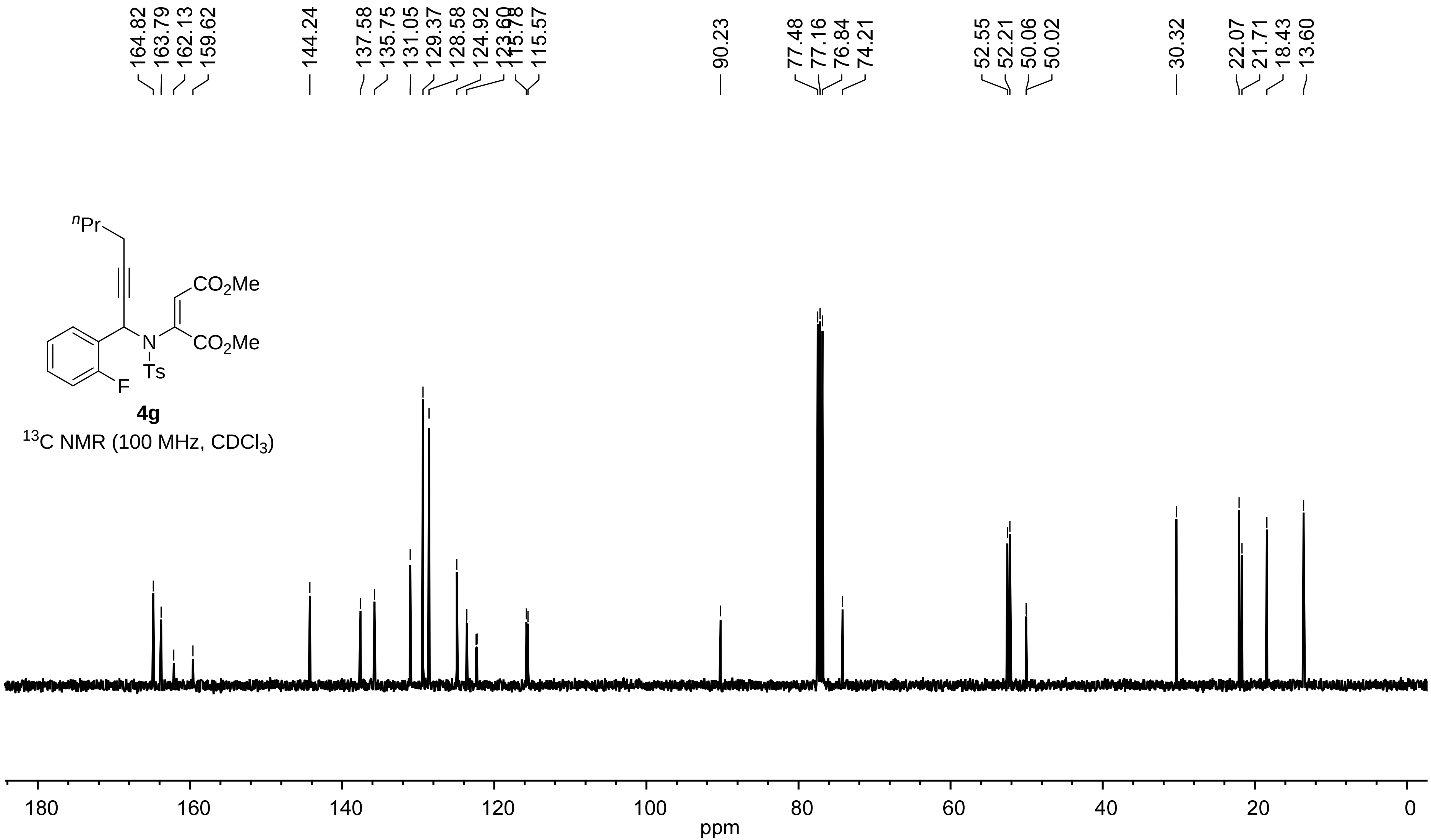
^{13}C NMR (100 MHz, $CDCl_3$)


7.91
7.89
7.36
7.34
7.26
7.23
7.21
7.16
7.14
7.11
6.83
6.29
6.04
3.80
3.59
2.45
2.04
2.03
2.02
2.01
1.30
1.29
1.29
1.28
1.27
0.88
0.86
0.85
-0.00
^nPr
CO_2Me
CO_2Me
N
Ts
OMe
4f
^1H NMR (400 MHz, $CDCl_3$)
2.06
2.10
1.01
1.03
0.98
1.00
1.01
6.19
3.11
3.13
2.15
4.34
3.25
8
7
6
5
4
3
2
1
0
ppm

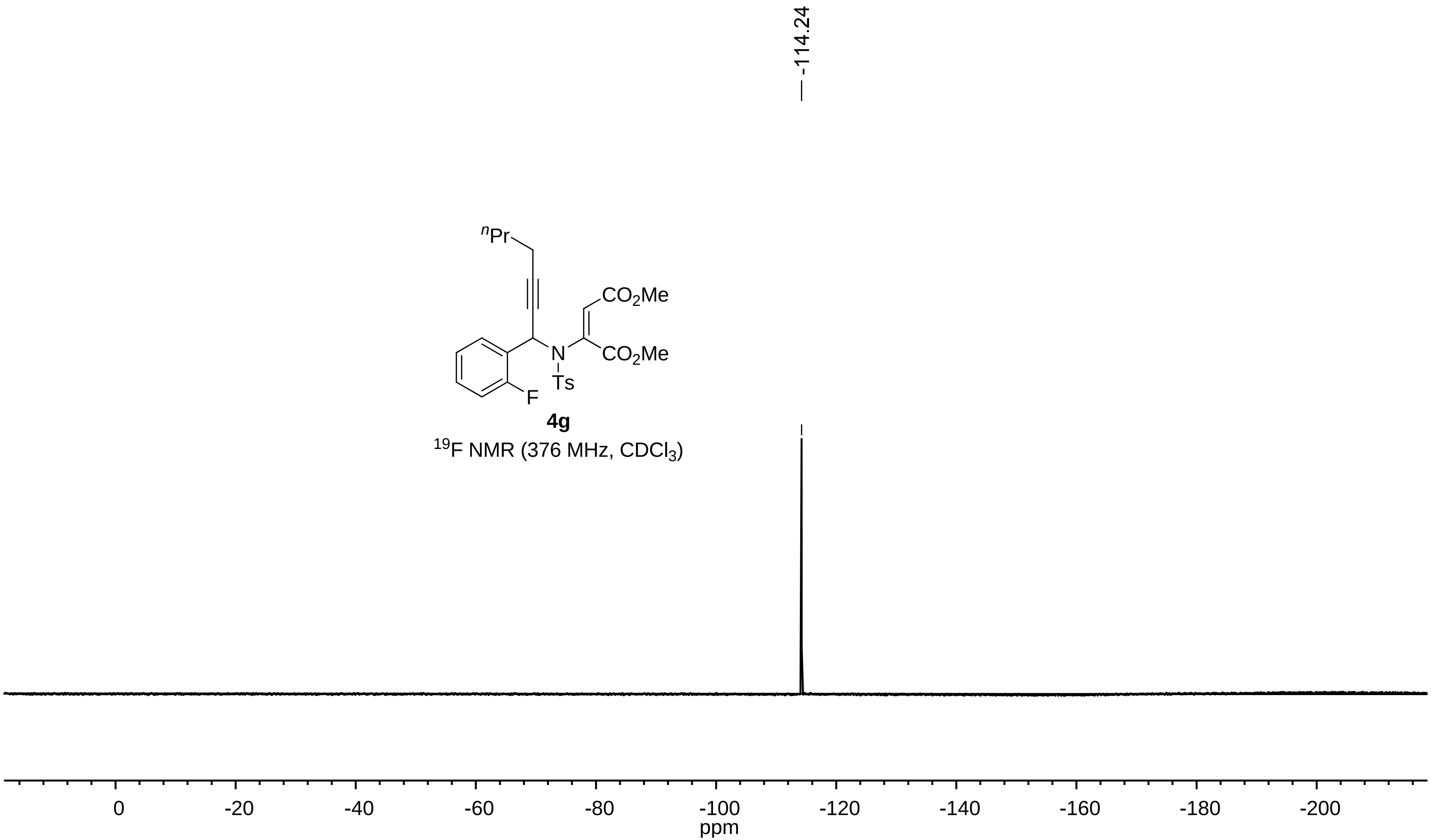

165.07
164.33
159.80
144.66
140.10
135.91
135.31
129.62
129.43
128.59
120.09
115.41
114.84
112.53
90.72
77.48
77.16
76.84
73.84
55.39
54.64
53.02
51.94
30.28
22.08
21.78
18.43
13.65
nPr
CO2Me
N
CO2Me
Ts
OMe
4f
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm



7.86
7.84
7.50
7.48
7.33
7.31
7.20
7.18
7.17
7.12
6.41
6.32
3.65
3.58
2.57
2.44
2.02
2.00
1.99
1.30
1.29
1.29
1.25
0.88
0.86
0.85
-0.00
nPr
CO2Me
CO2Me
N
Ts
F
4g
1H NMR (400 MHz, CDCl3)
2.00
1.02
2.05
3.10
1.00
1.00
3.00
3.02
3.09
3.07
2.08
4.14
3.01
8
7
6
5
4
3
2
1
0
ppm

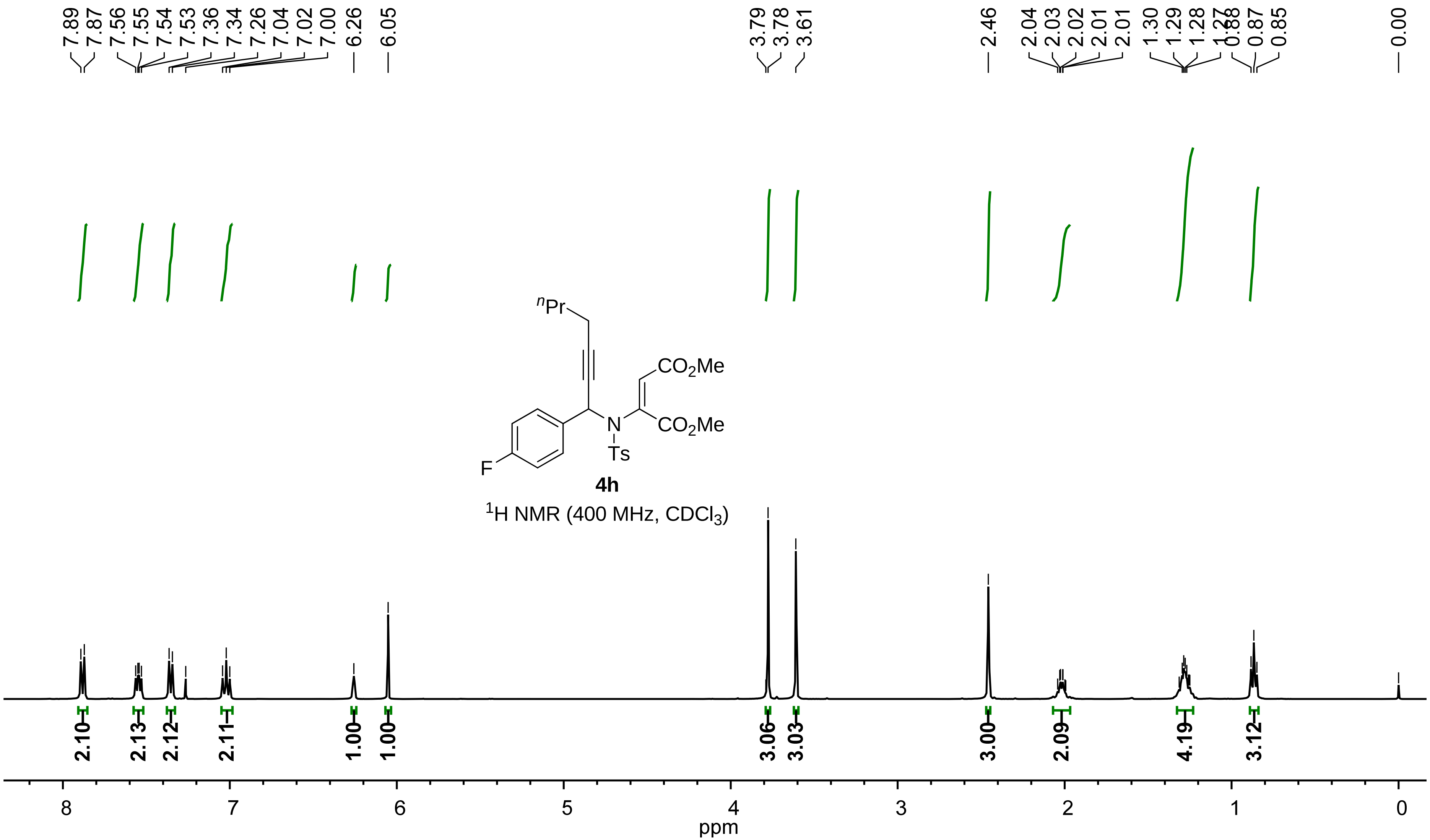


164.82
163.79
162.13
159.62
144.24
137.58
135.75
131.05
129.37
128.58
124.92
123.60
115.78
115.57
90.23
77.48
77.16
76.84
74.21
52.55
52.21
50.06
50.02
30.32
22.07
21.71
18.43
13.60
nPr
CO2Me
N
CO2Me
Ts
F
4g
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm



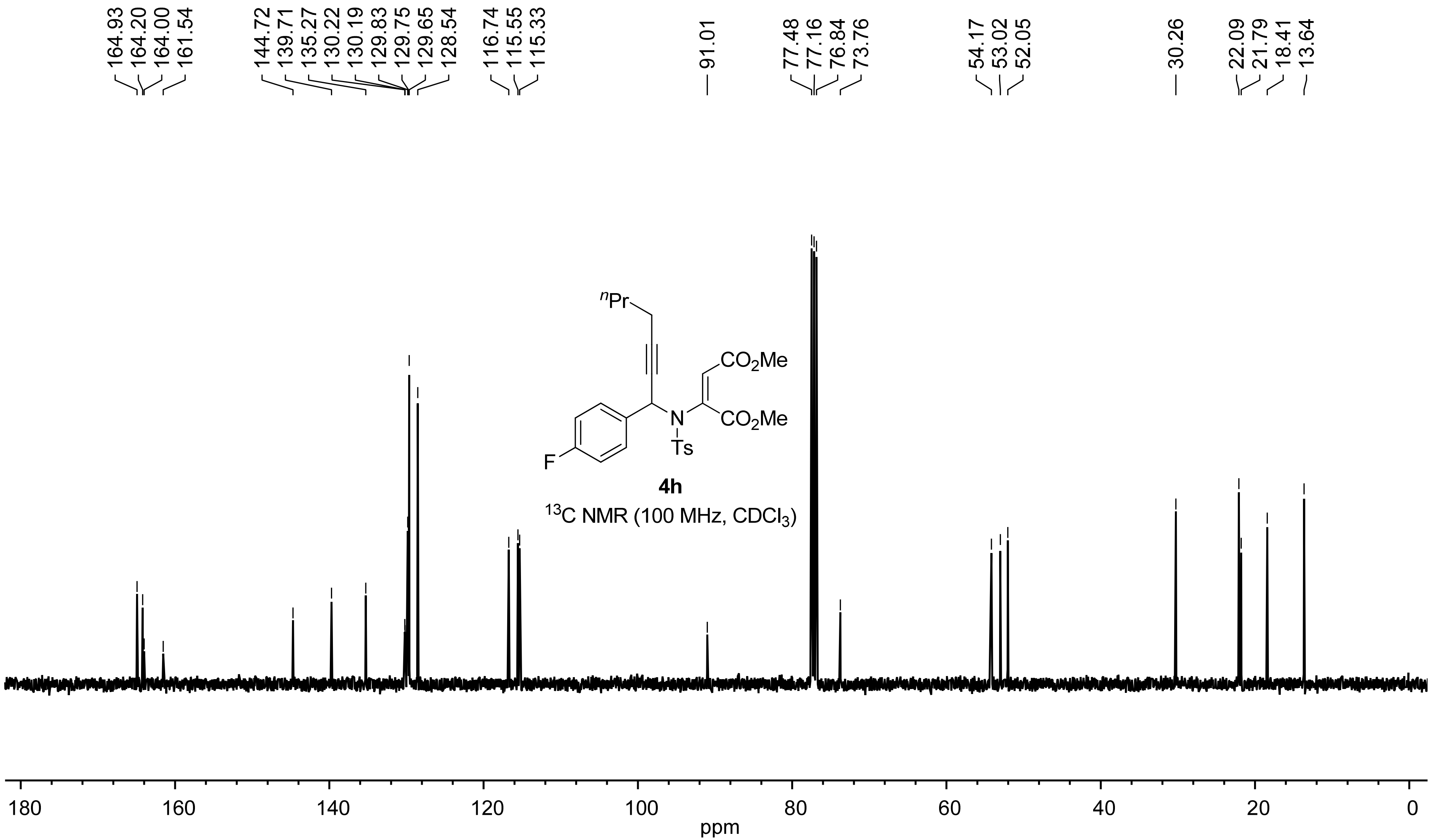
4g

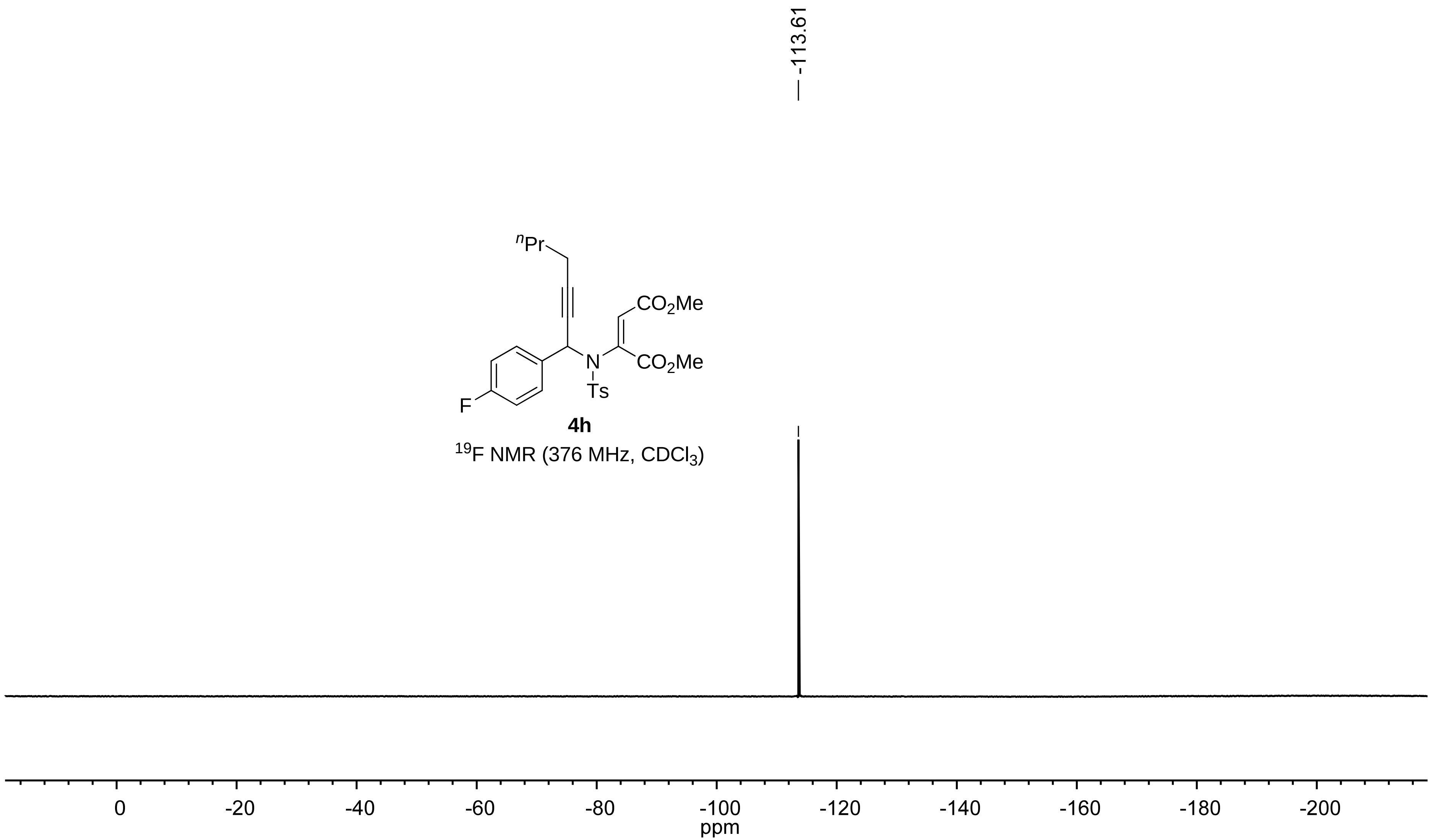
^{19}F NMR (376 MHz, $CDCl_3$)



4h

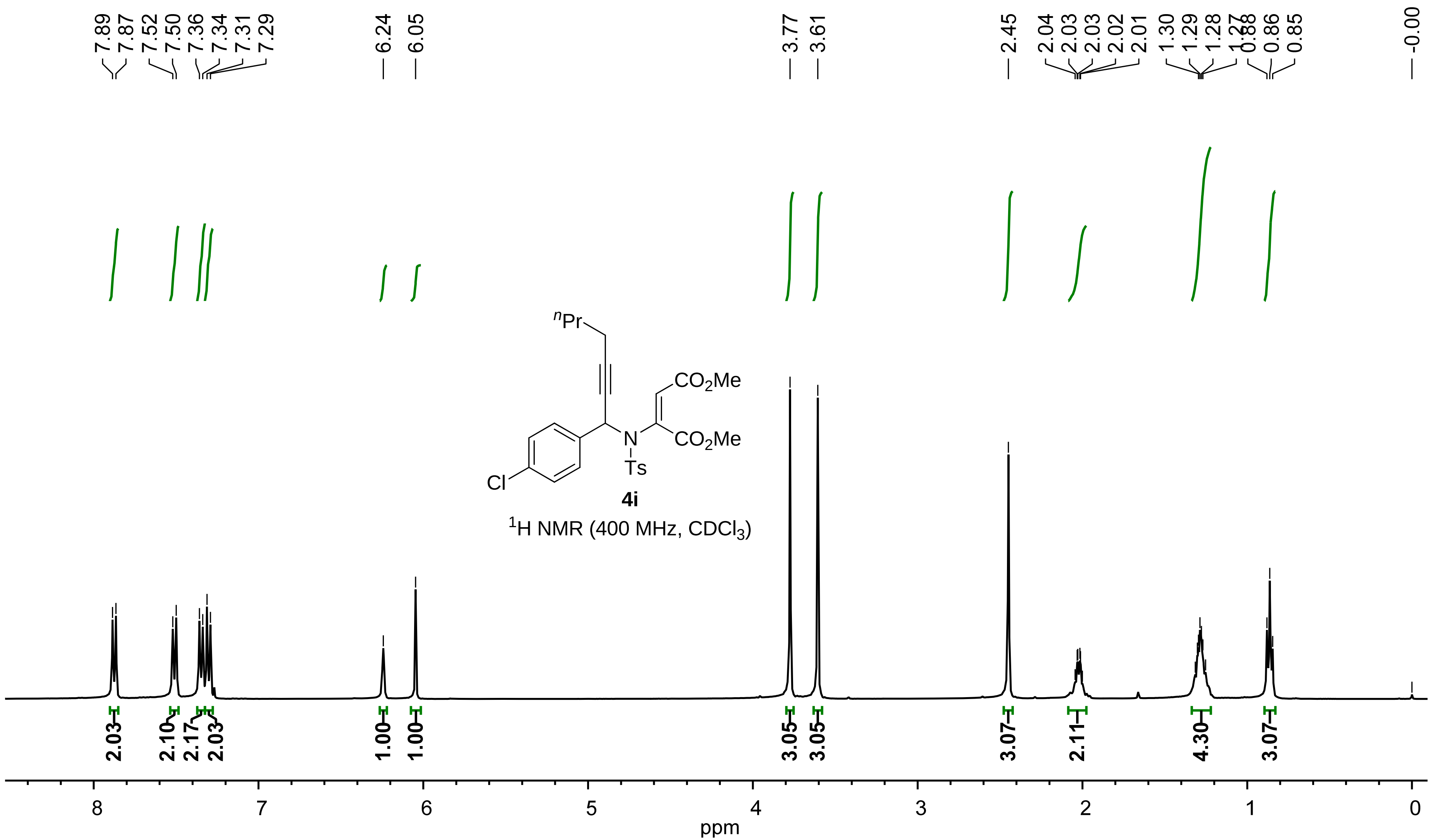
^{1}H NMR (400 MHz, $CDCl_3$)

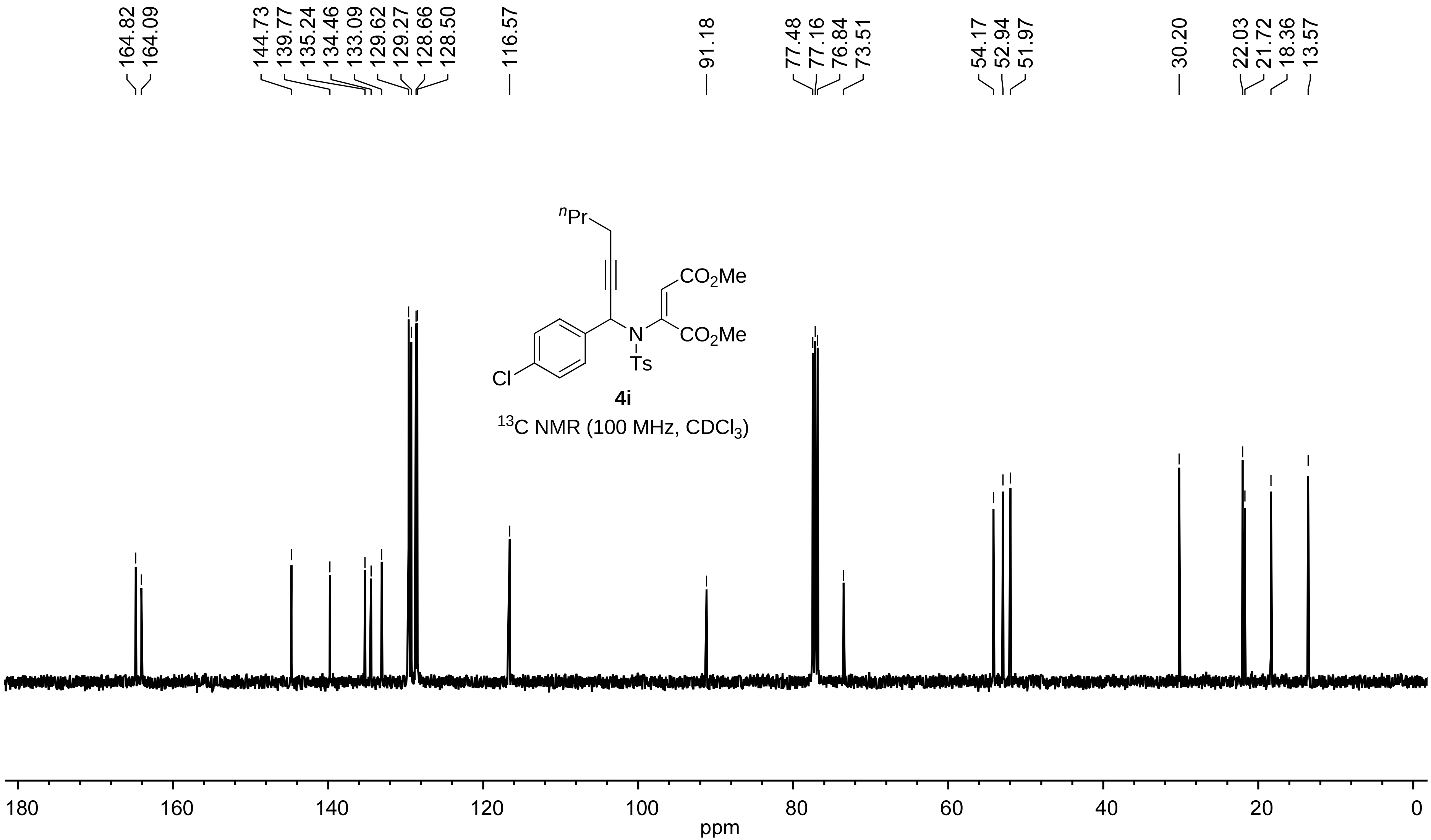

164.93
164.20
164.00
161.54
144.72
139.71
135.27
130.22
130.19
129.83
129.75
129.65
128.54
116.74
115.55
115.33
91.01
77.48
77.16
76.84
73.76
54.17
53.02
52.05
30.26
22.09
21.79
18.41
13.64
^{n}Pr
CO_2Me
N
CO_2Me
Ts
F
4h
^{13}C NMR (100 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
0
ppm

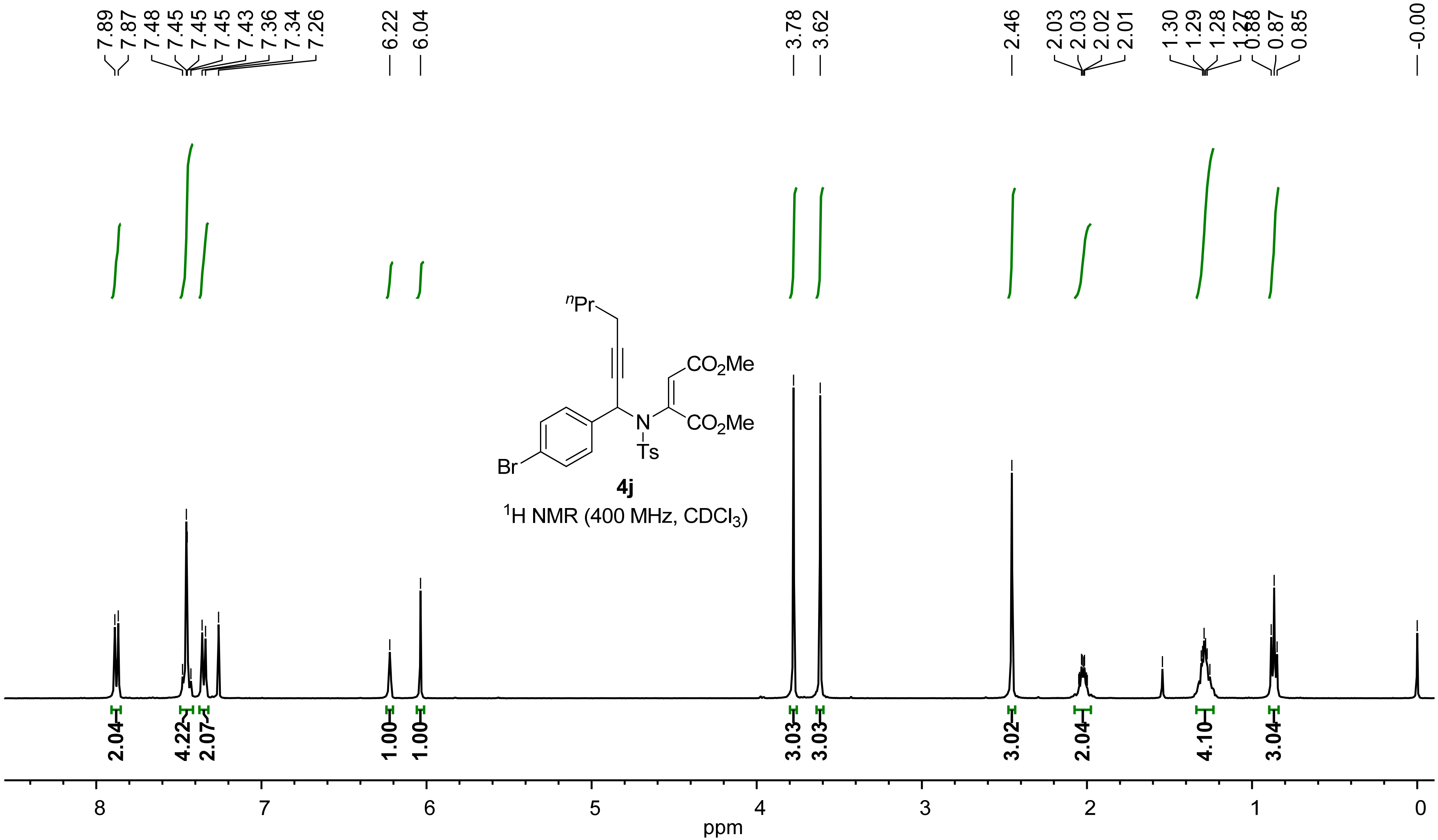


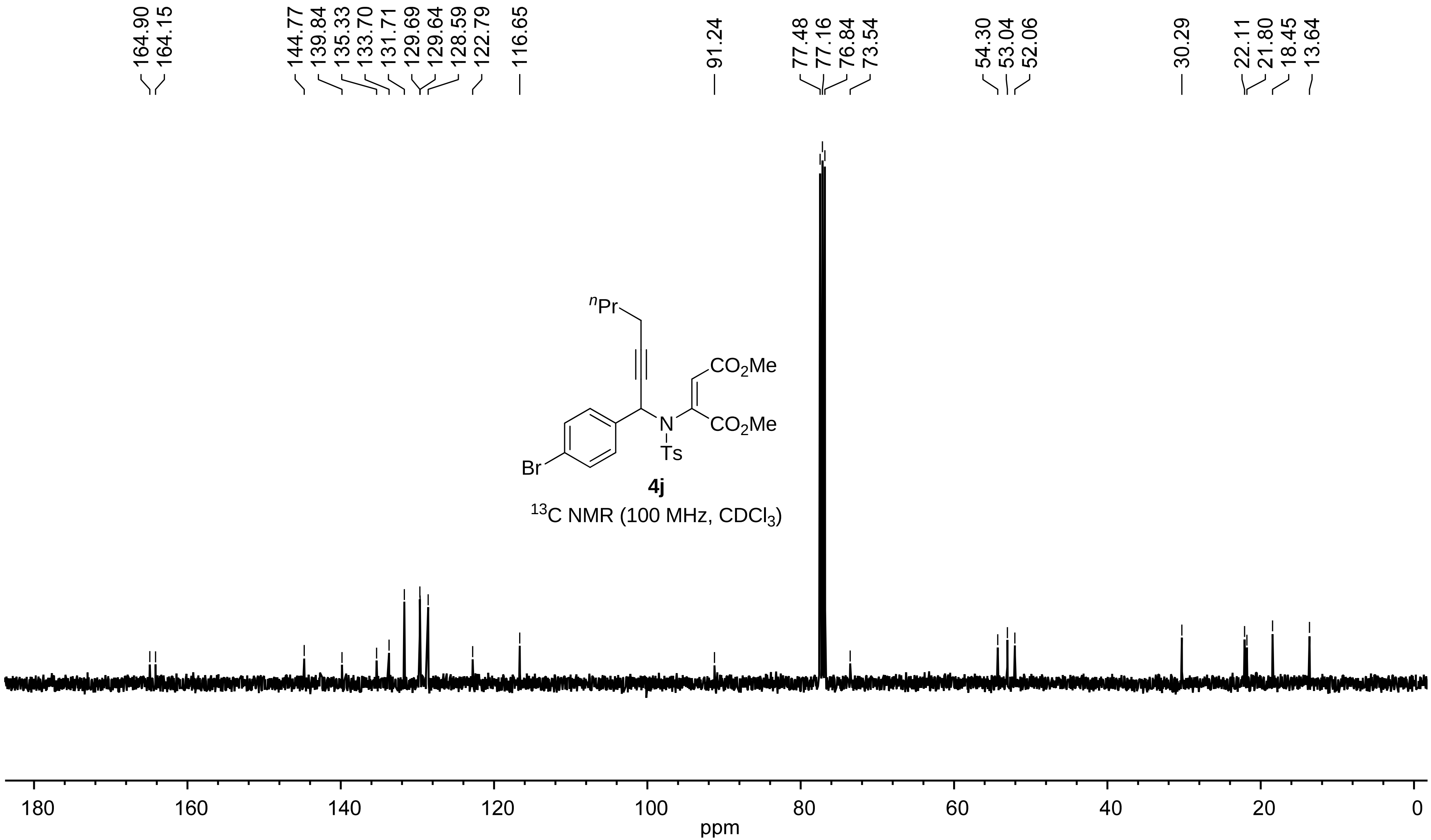
4h

^{19}F NMR (376 MHz, $CDCl_3$)

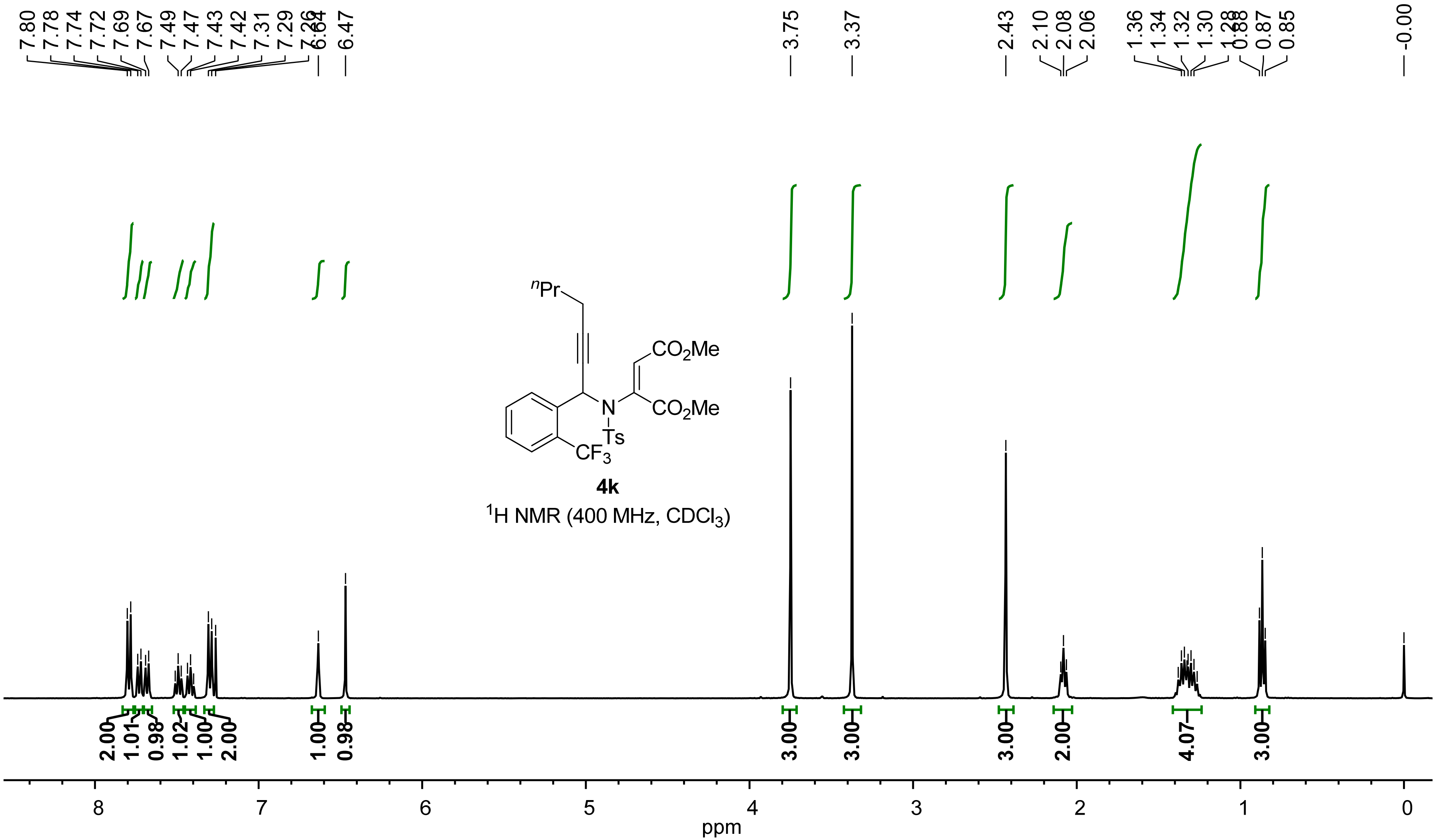

7.89
7.87
7.52
7.50
7.36
7.34
7.31
7.29
6.24
6.05
3.77
3.61
2.45
2.04
2.03
2.03
2.02
2.01
1.30
1.29
1.28
1.27
0.88
0.86
0.85
-0.00
ⁿPr
CO2Me
CO2Me
N
Ts
Cl
4i
1H NMR (400 MHz, CDCl3)
2.03
2.10
2.17
2.03
1.00
1.00
3.05
3.05
3.07
2.11
4.30
3.07
8
7
6
5
4
3
2
1
0
ppm


164.82
164.09
144.73
139.77
135.24
134.46
133.09
129.62
129.27
128.66
128.50
116.57
91.18
77.48
77.16
76.84
73.51
54.17
52.94
51.97
30.20
22.03
21.72
18.36
13.57
nPr
CO2Me
CO2Me
N
Ts
Cl
4i
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm


7.89
7.87
7.48
7.45
7.45
7.45
7.43
7.36
7.34
7.26
6.22
6.04
3.78
3.62
2.46
2.03
2.03
2.02
2.01
1.30
1.29
1.28
1.27
0.88
0.87
0.85
-0.00
ⁿPr
CO2Me
CO2Me
N
Ts
Br
4j
1H NMR (400 MHz, CDCl3)
2.04
4.22
2.07
1.00
1.00
3.03
3.03
3.02
2.04
4.10
3.04
8
7
6
5
4
3
2
1
0
ppm

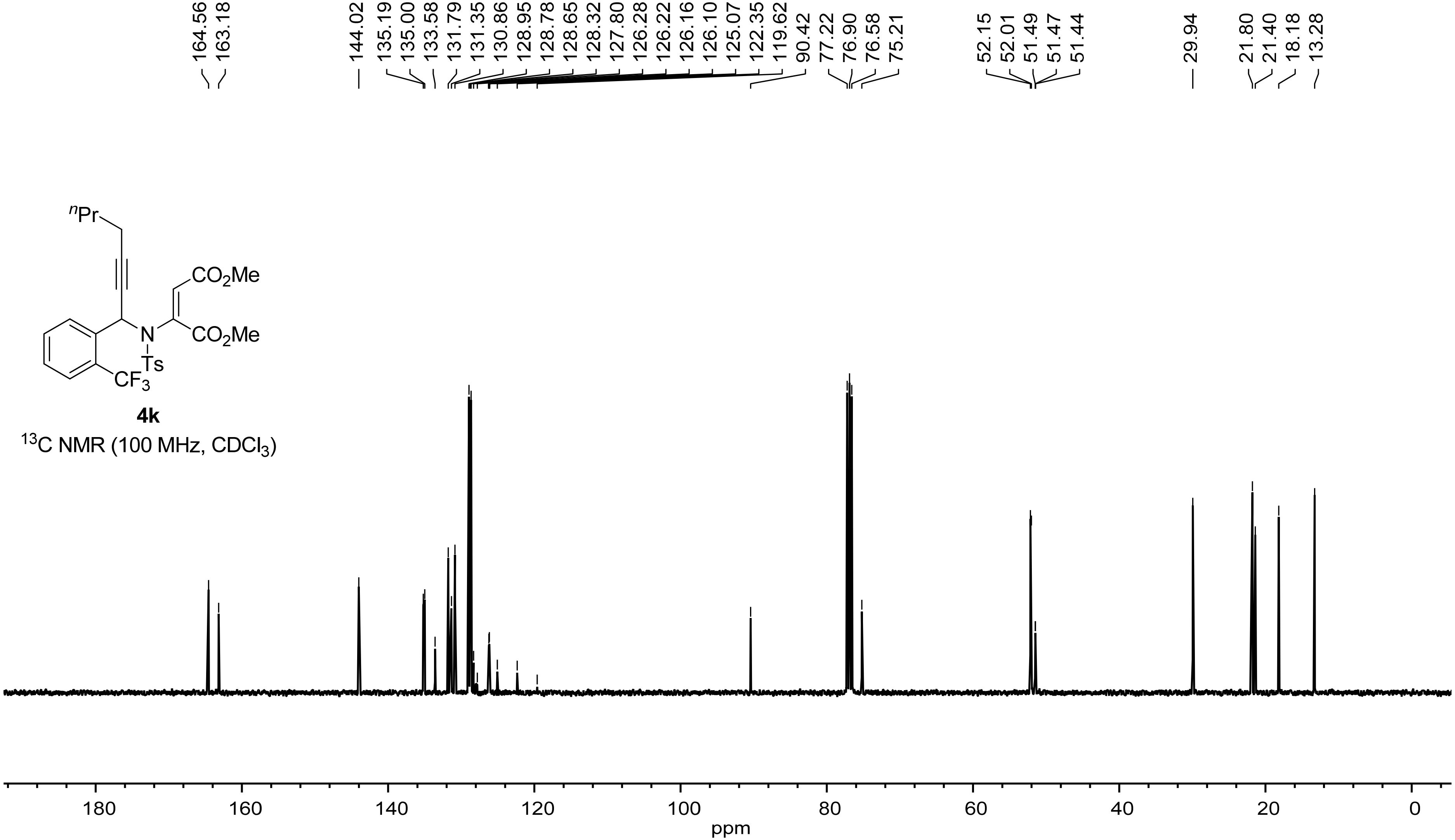


164.90
164.15
144.77
139.84
135.33
133.70
131.71
129.69
129.64
128.59
122.79
116.65
91.24
77.48
77.16
76.84
73.54
54.30
53.04
52.06
30.29
22.11
21.80
18.45
13.64
^{n}Pr
CO$_2$Me
CO$_2$Me
N
Ts
Br
4j
^{13}C NMR (100 MHz, CDCl$_3$)
180
160
140
120
100
80
60
40
20
0
ppm

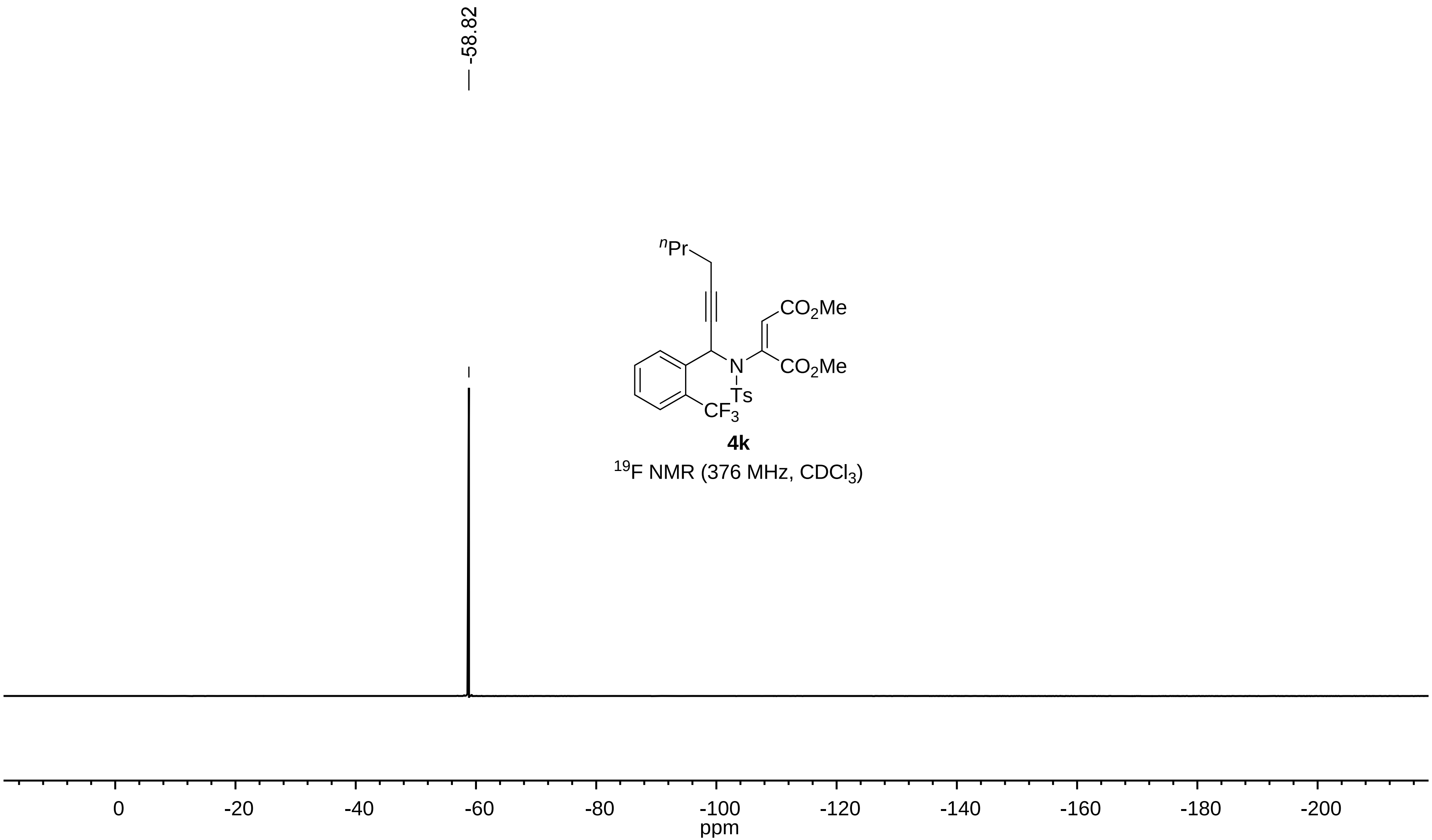


4k

^{1}H NMR (400 MHz, $CDCl_3$)

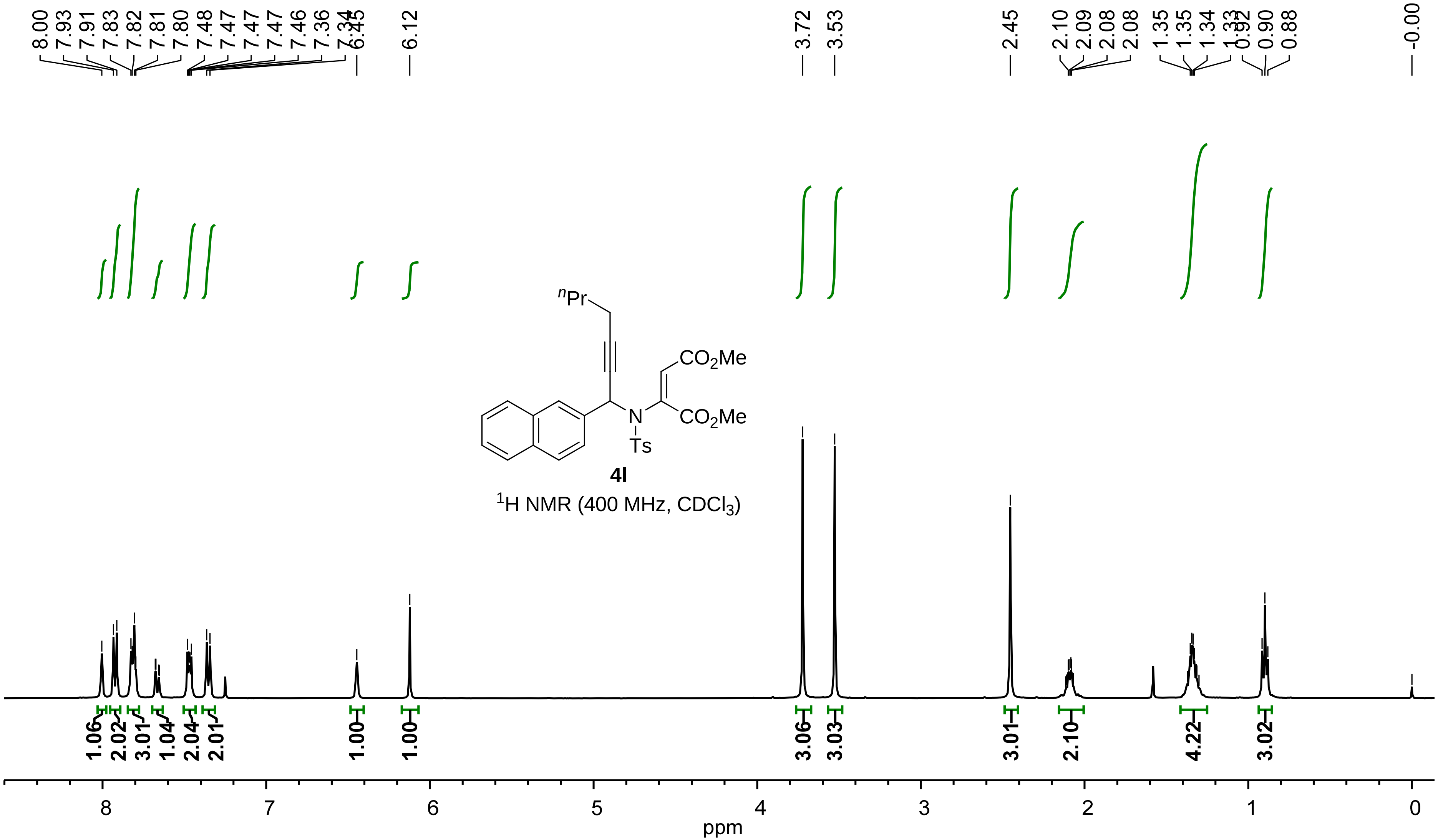


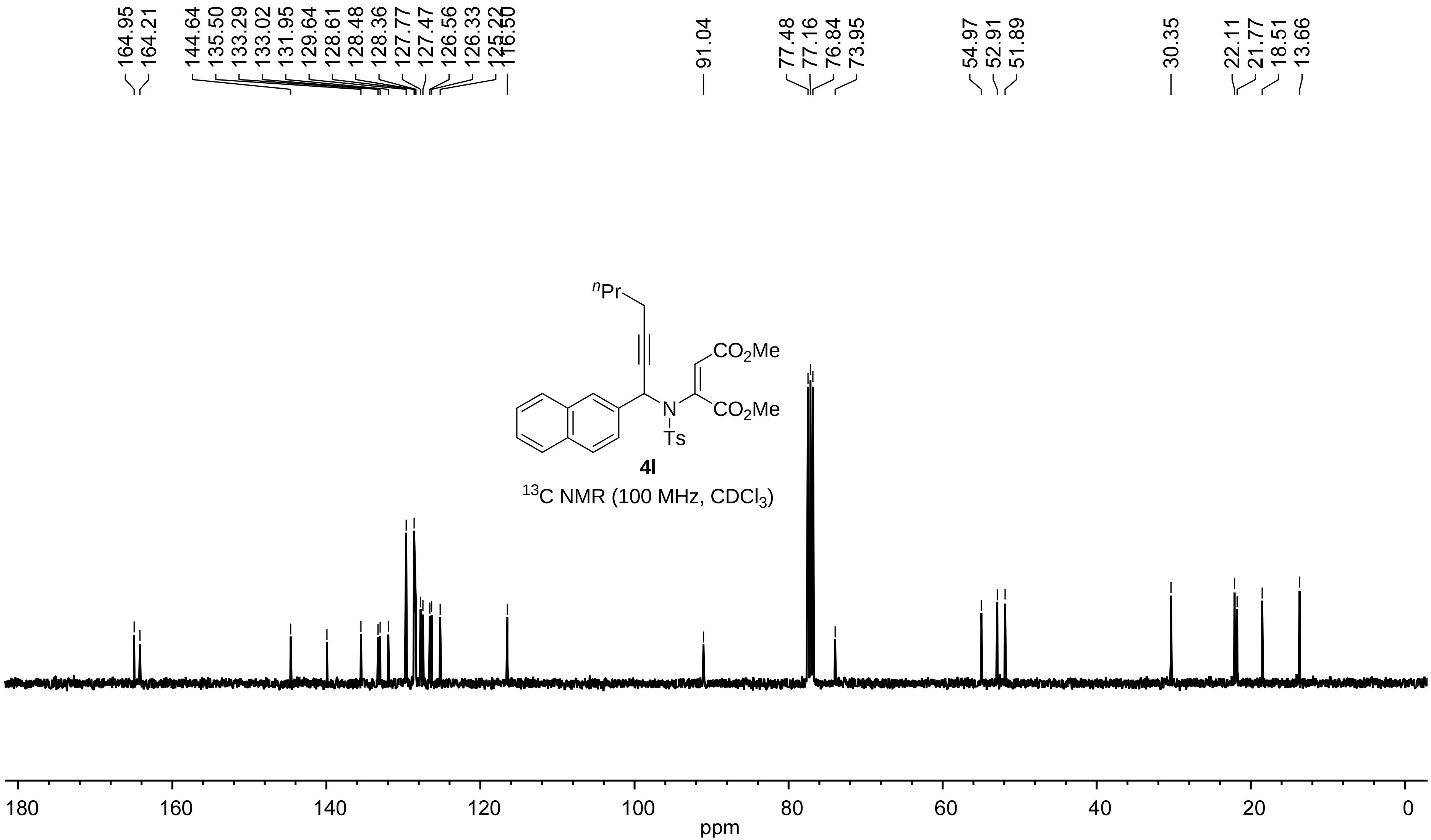
164.56
163.18
144.02
135.19
135.00
133.58
131.79
131.35
130.86
128.95
128.78
128.65
128.32
127.80
126.28
126.22
126.16
126.10
125.07
122.35
119.62
90.42
77.22
76.90
76.58
75.21
52.15
52.01
51.49
51.47
51.44
29.94
21.80
21.40
18.18
13.28
ⁿPr
CO2Me
CO2Me
N
Ts
CF3
4k
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm

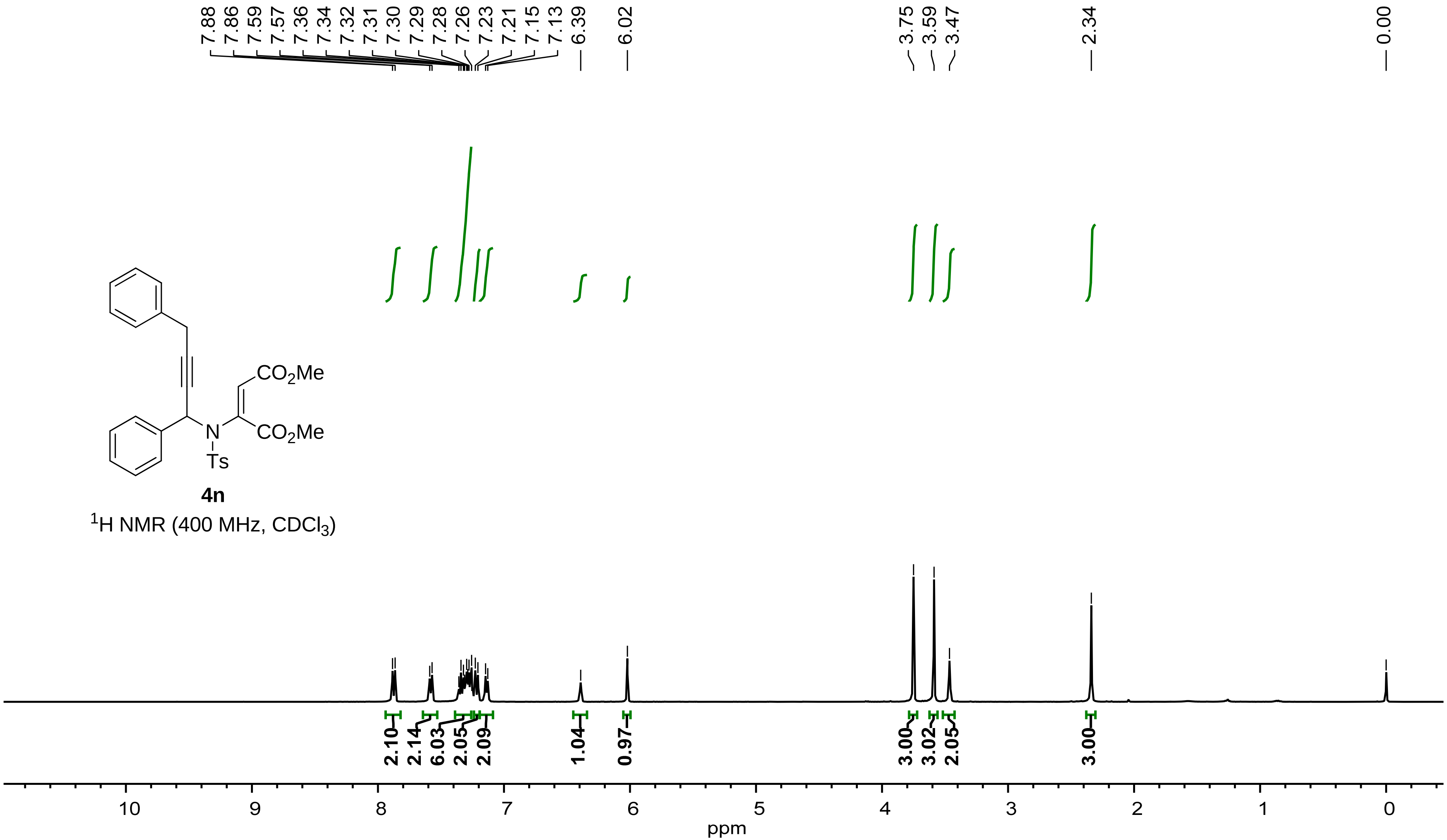


4k

^{19}F NMR (376 MHz, $CDCl_3$)

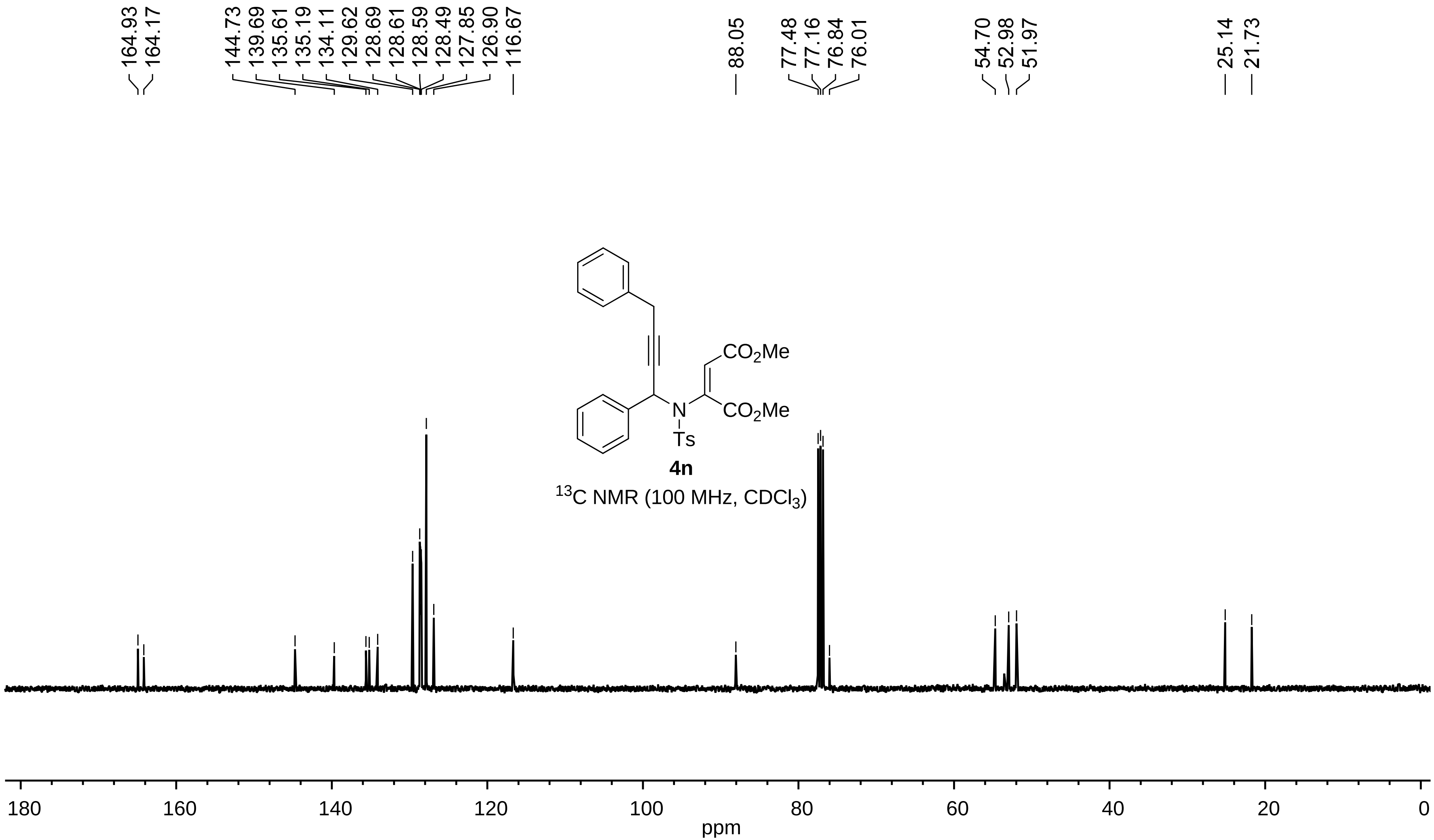

8.00
7.93
7.91
7.83
7.82
7.81
7.80
7.48
7.47
7.47
7.47
7.46
7.36
7.34
6.45
6.12
3.72
3.53
2.45
2.10
2.09
2.08
2.08
1.35
1.35
1.34
1.33
0.92
0.90
0.88
-0.00
nPr
CO2Me
CO2Me
N
Ts
4l
1H NMR (400 MHz, CDCl3)
1.06
2.02
3.01
1.04
2.04
2.01
1.00
1.00
3.06
3.03
3.01
2.10
4.22
3.02
8
7
6
5
4
3
2
1
0
ppm

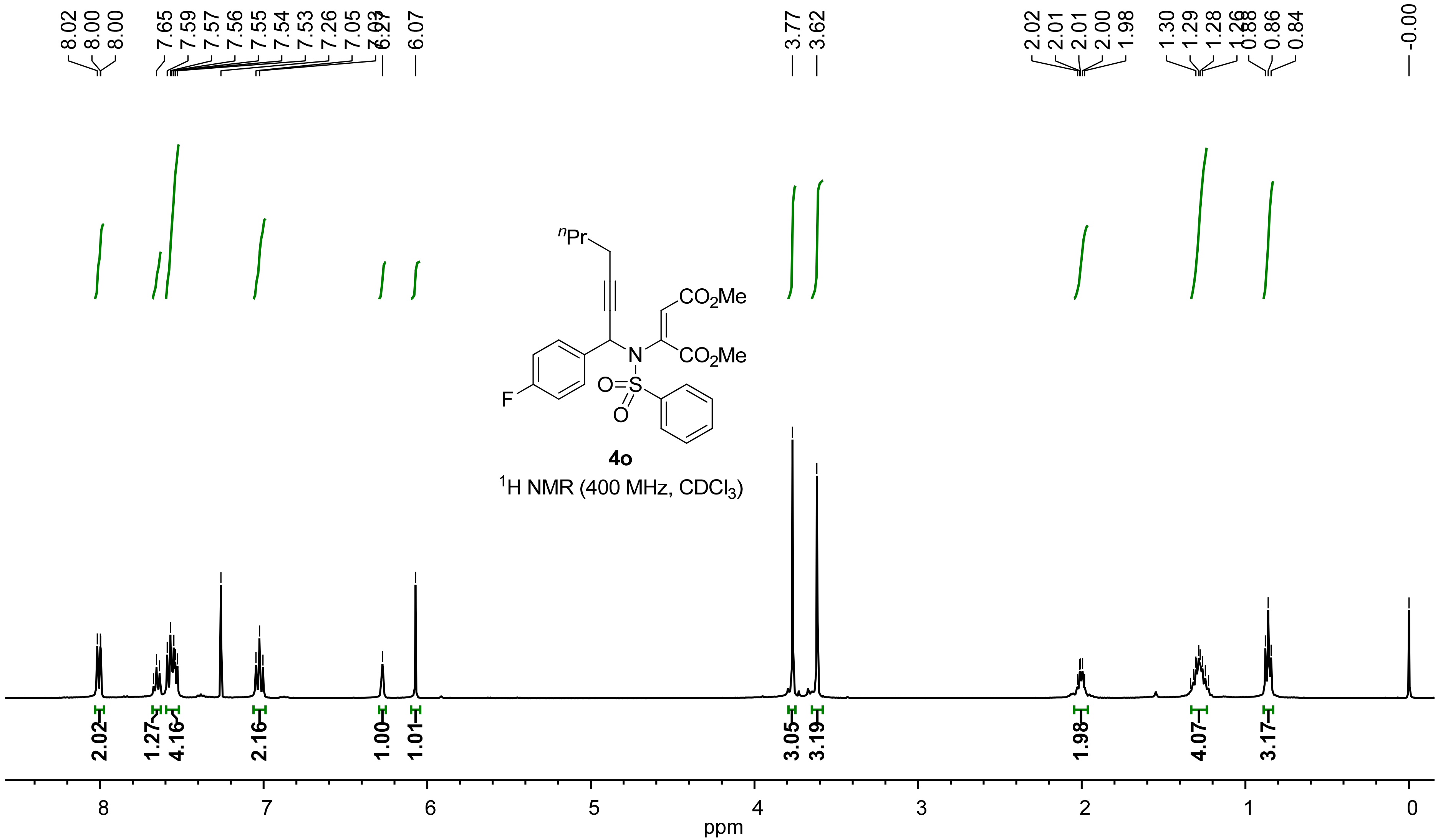

164.95
164.21
144.64
135.50
133.29
133.02
131.95
129.64
128.61
128.48
128.36
127.77
127.47
126.56
126.33
125.22
116.50
91.04
77.48
77.16
76.84
73.95
54.97
52.91
51.89
30.35
22.11
21.77
18.51
13.66
^{n}Pr
CO_2Me
N
CO_2Me
Ts
4l
^{13}C NMR (100 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
0
ppm

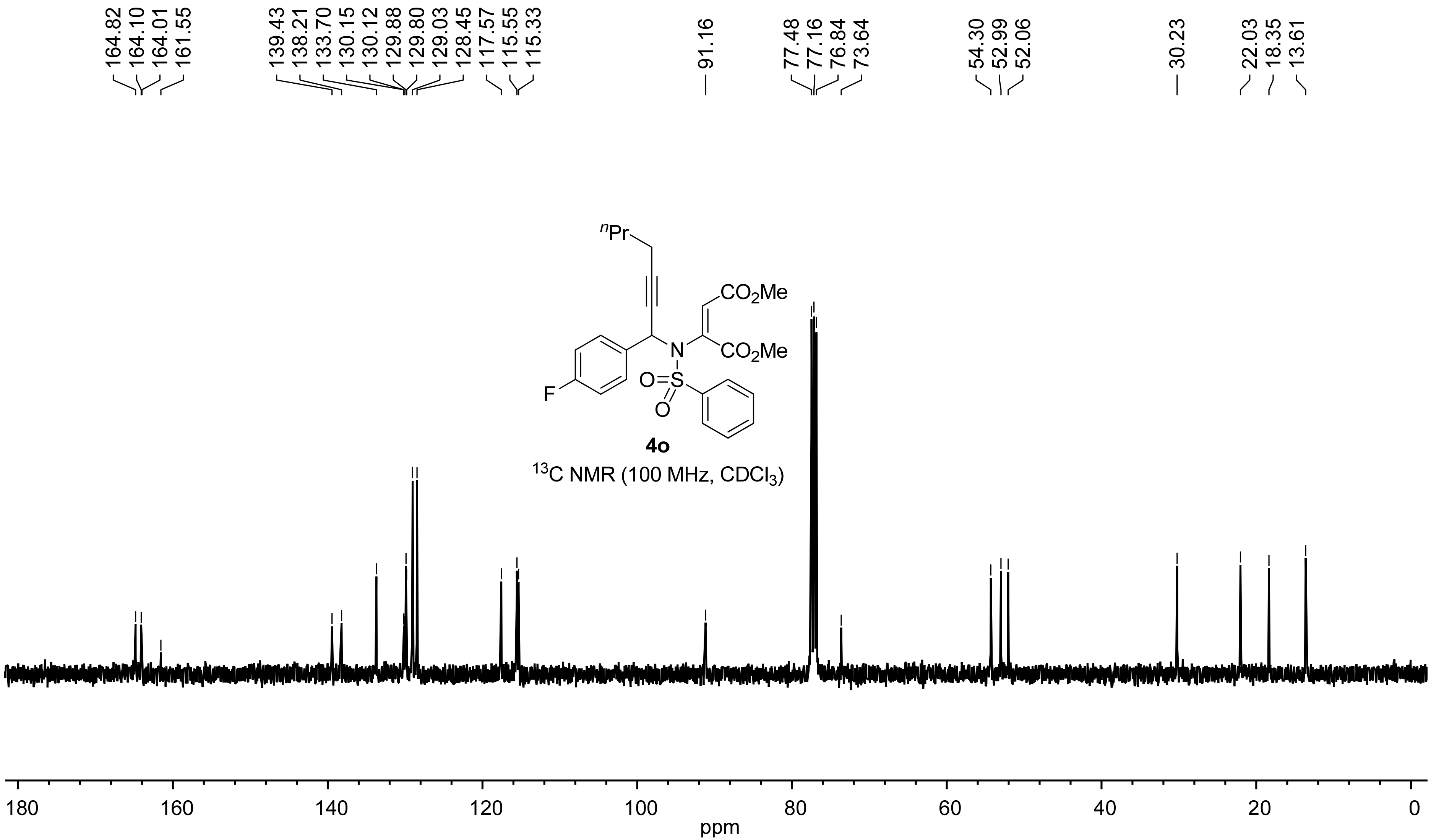


4n

^{1}H NMR (400 MHz, $CDCl_3$)

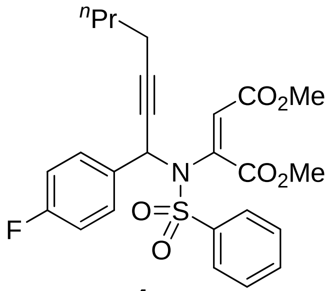

164.93
164.17
144.73
139.69
135.61
135.19
134.11
129.62
128.69
128.61
128.59
128.49
127.85
126.90
116.67
88.05
77.48
77.16
76.84
76.01
54.70
52.98
51.97
25.14
21.73
CO2Me
CO2Me
N
Ts
4n
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm


8.02 8.00 8.00 7.65 7.59 7.57 7.56 7.55 7.54 7.53 7.26 7.05 7.03 6.27 6.07
3.77 3.62
2.02 2.01 2.01 2.00 1.98 1.30 1.29 1.28 1.26 0.88 0.86 0.84
-0.00
^{n}Pr
CO_2Me
CO_2Me
N
O=S
O
F
4o
^{1}H NMR (400 MHz, $CDCl_3$)
2.02 1.27 4.16 2.16 1.00 1.01 3.05 3.19 1.98 4.07 3.17
8 7 6 5 4 3 2 1 0
ppm



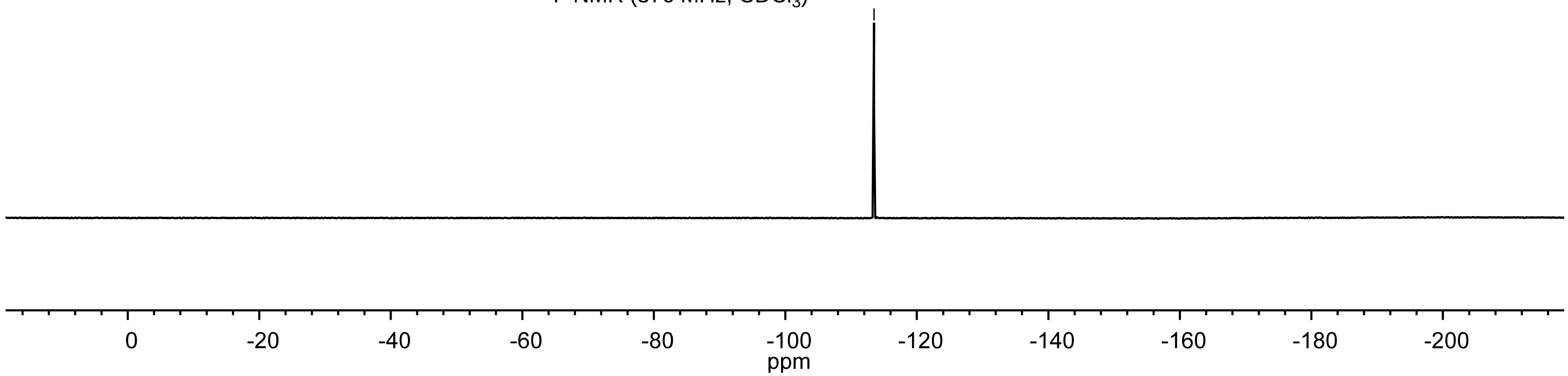
4o

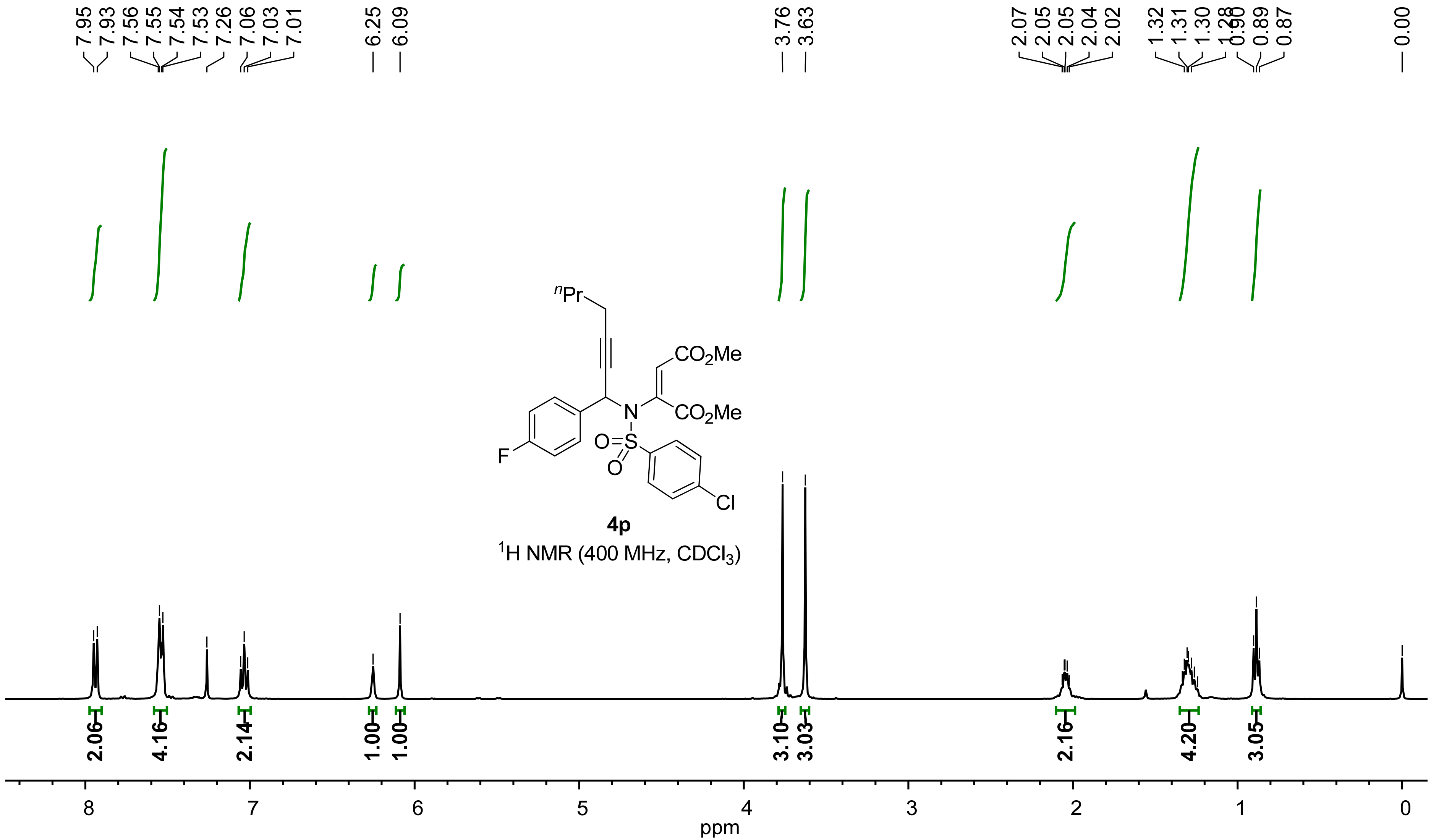
^{13}C NMR (100 MHz, $CDCl_3$)



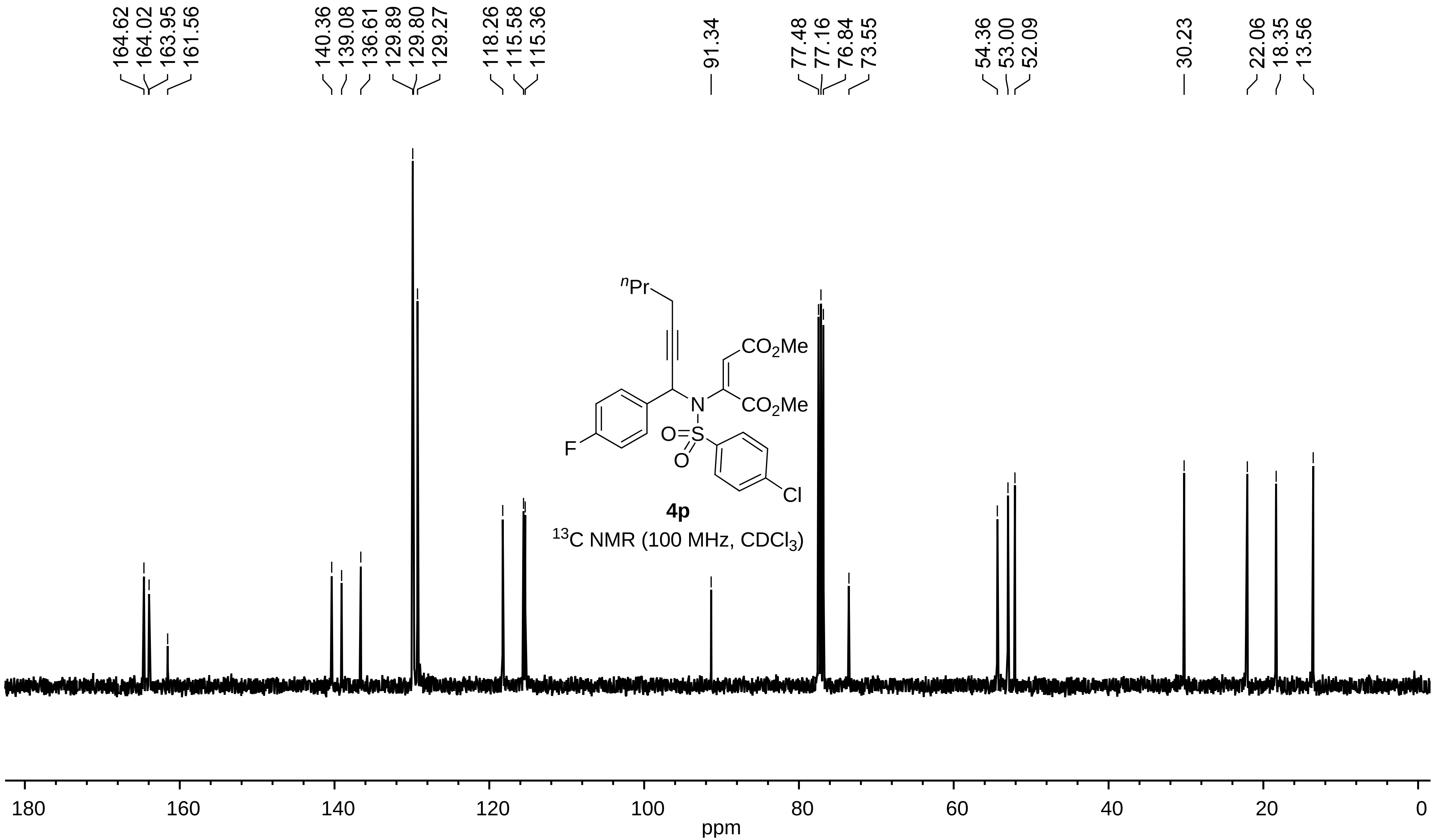
4o

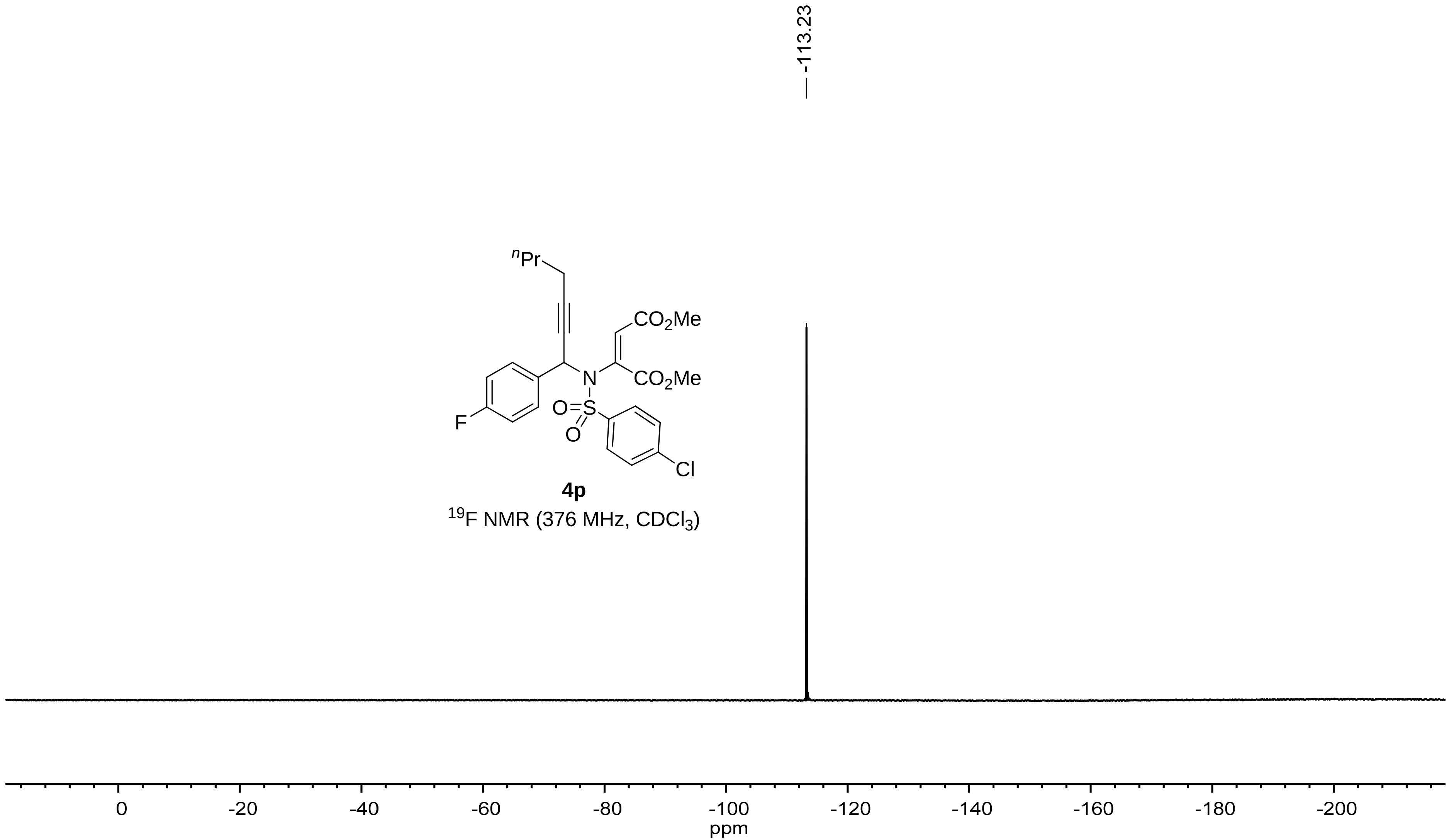
^{19}F NMR (376 MHz, $CDCl_3$)





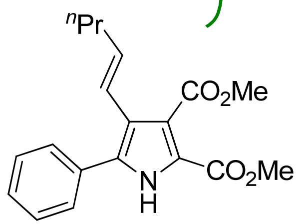
7.95
7.93
7.56
7.55
7.54
7.53
7.26
7.06
7.03
7.01
6.25
6.09
3.76
3.63
2.07
2.05
2.05
2.04
2.02
1.32
1.31
1.30
1.28
0.90
0.89
0.87
0.00
^{n}Pr
CO_2Me
CO_2Me
N
O=S
O
F
Cl
4p
^{1}H NMR (400 MHz, $CDCl_3$)
2.06
4.16
2.14
1.00
1.00
3.10
3.03
2.16
4.20
3.05
8
7
6
5
4
3
2
1
0
ppm


164.62
164.02
163.95
161.56
140.36
139.08
136.61
129.89
129.80
129.27
118.26
115.58
115.36
91.34
77.48
77.16
76.84
73.55
54.36
53.00
52.09
30.23
22.06
18.35
13.56
nPr
CO2Me
CO2Me
N
O=S
O
F
Cl
4p
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm



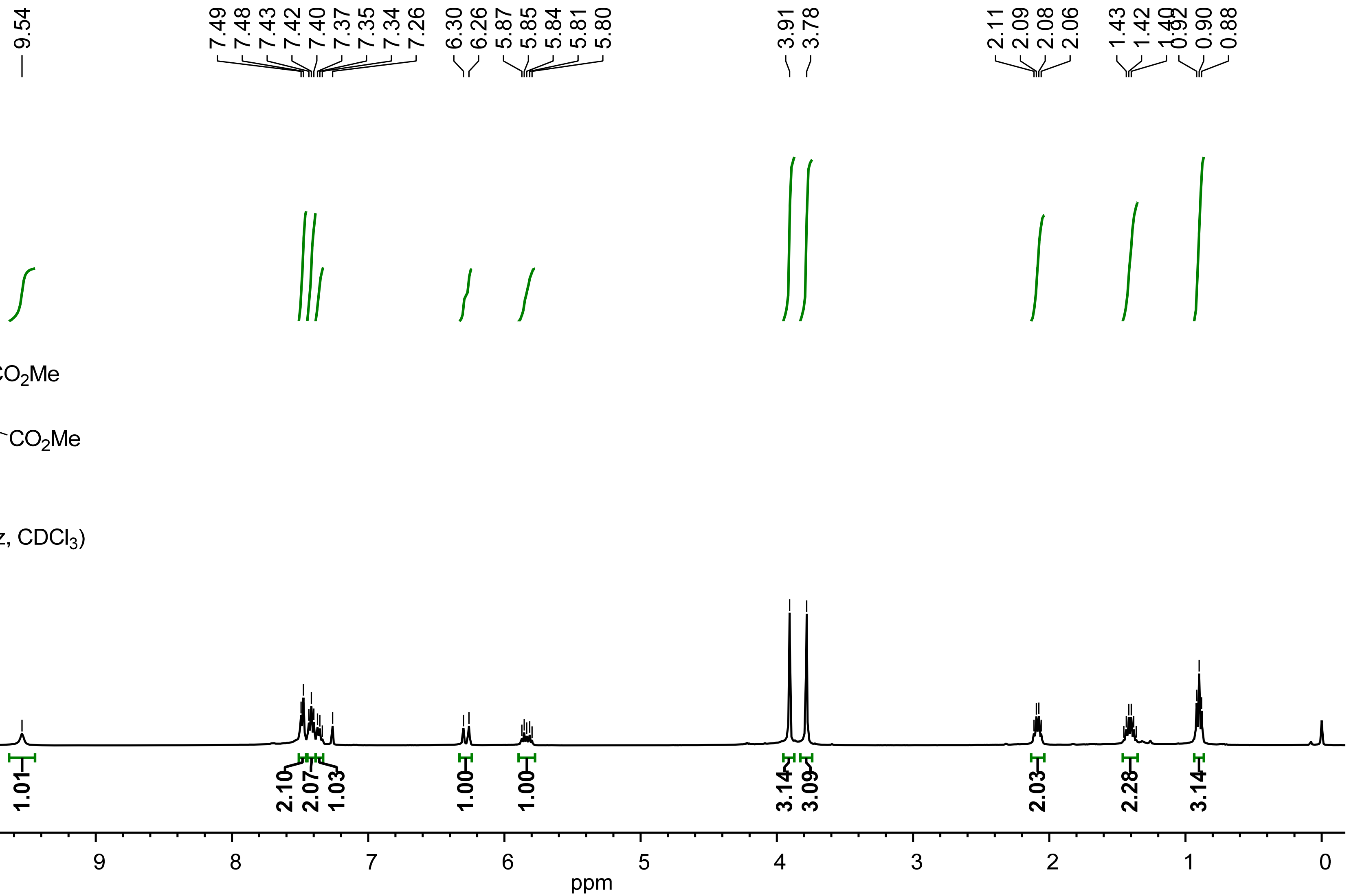
4p

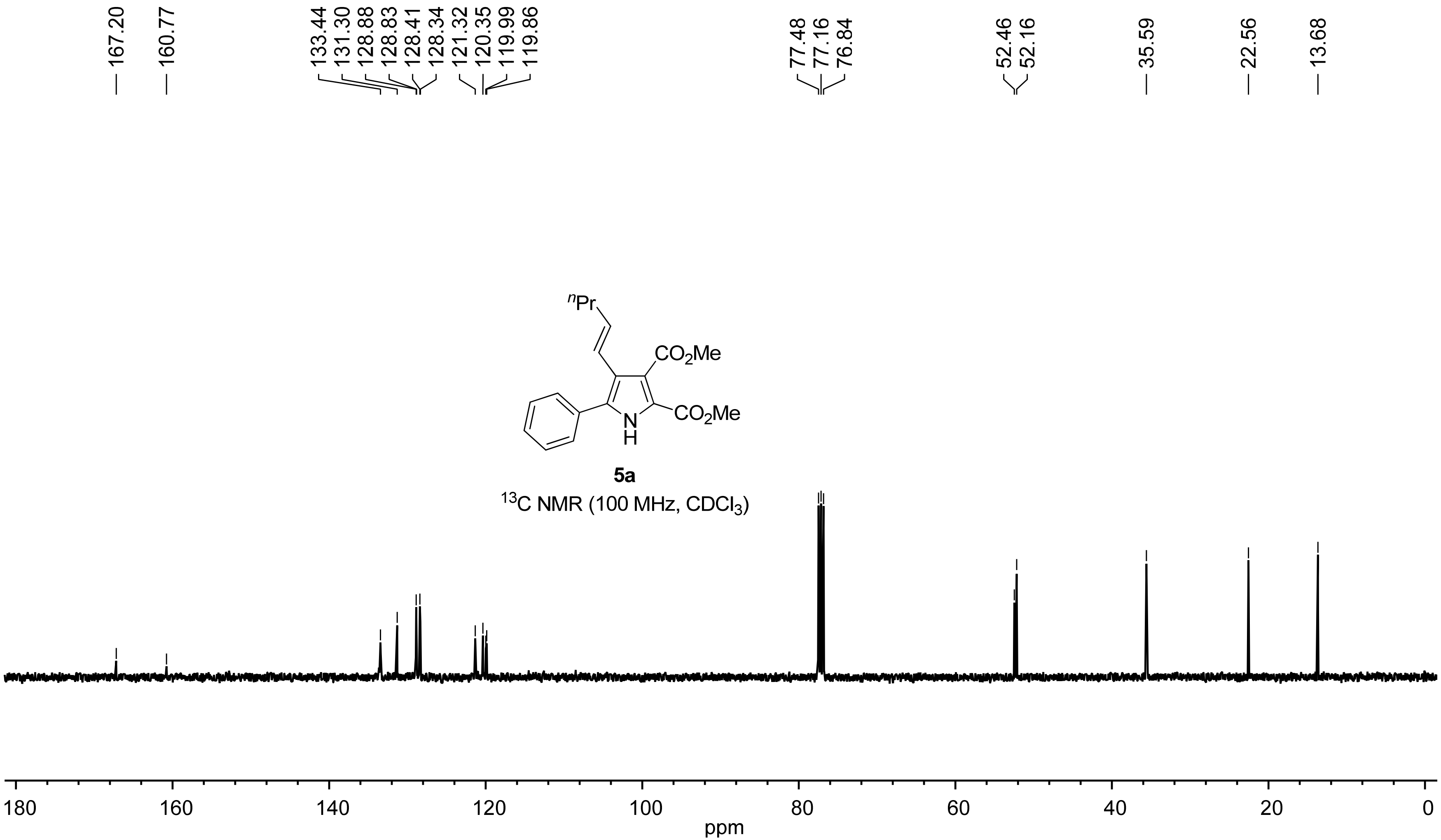
^{19}F NMR (376 MHz, $CDCl_3$)

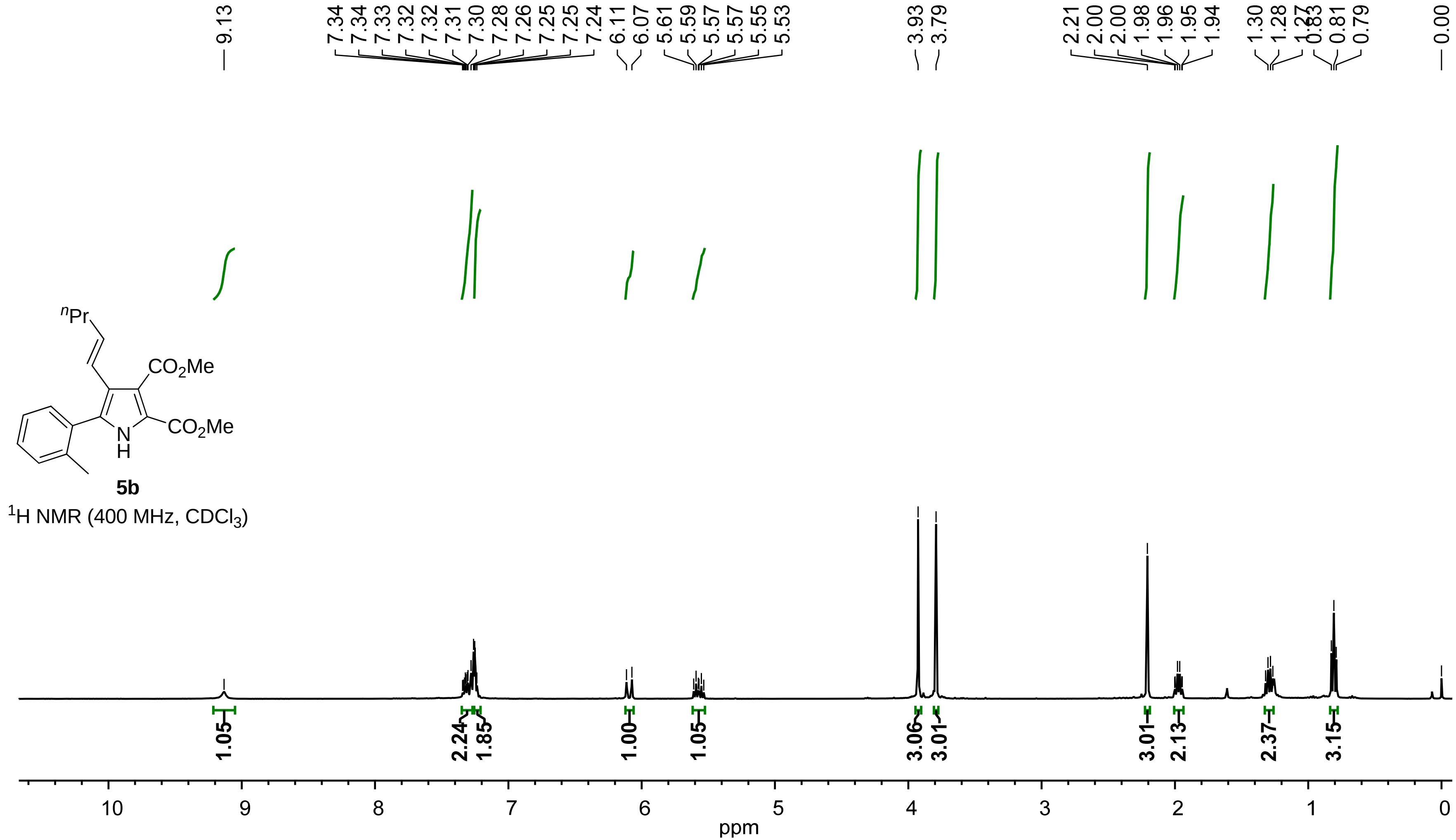


5a

^{1}H NMR (400 MHz, $CDCl_3$)

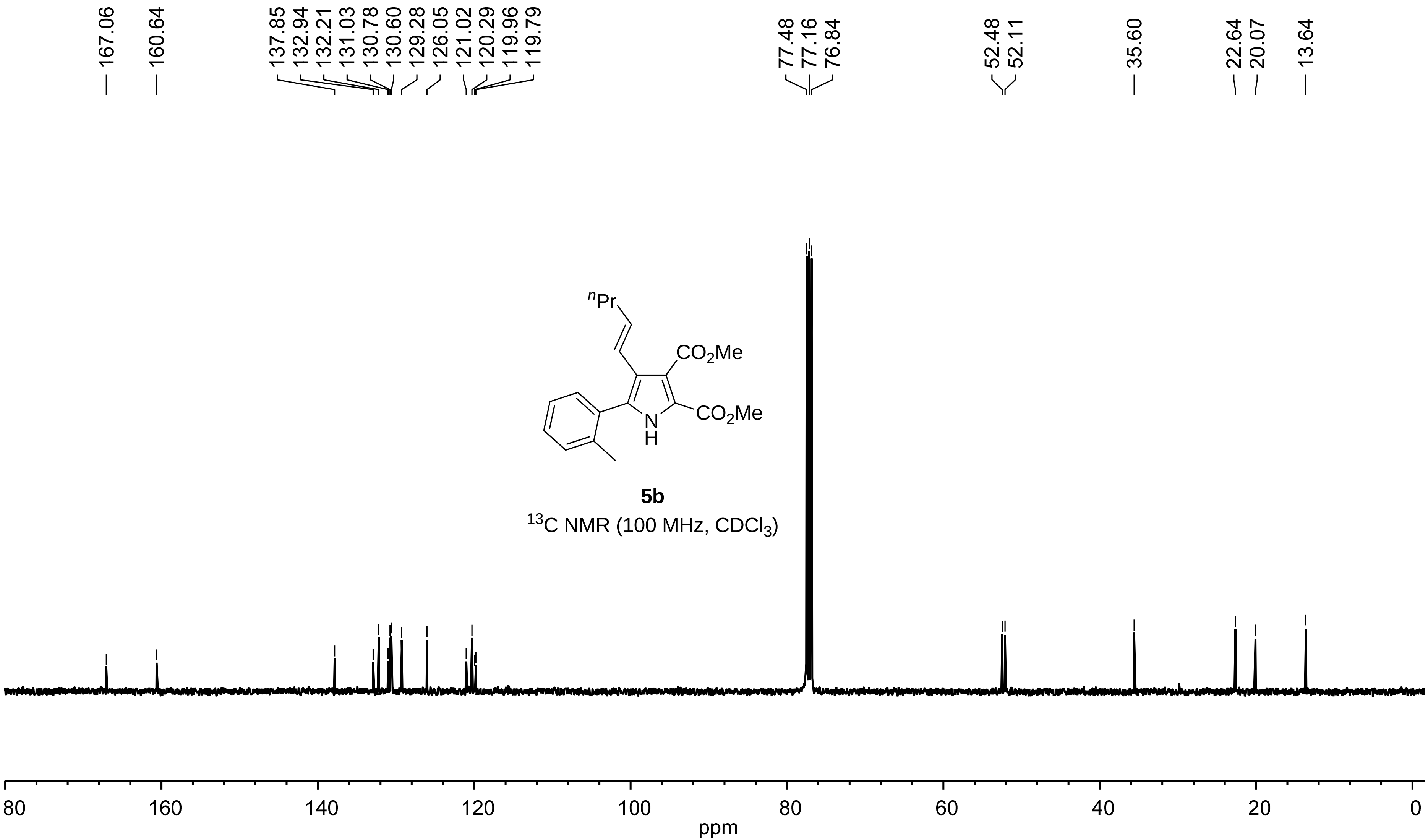


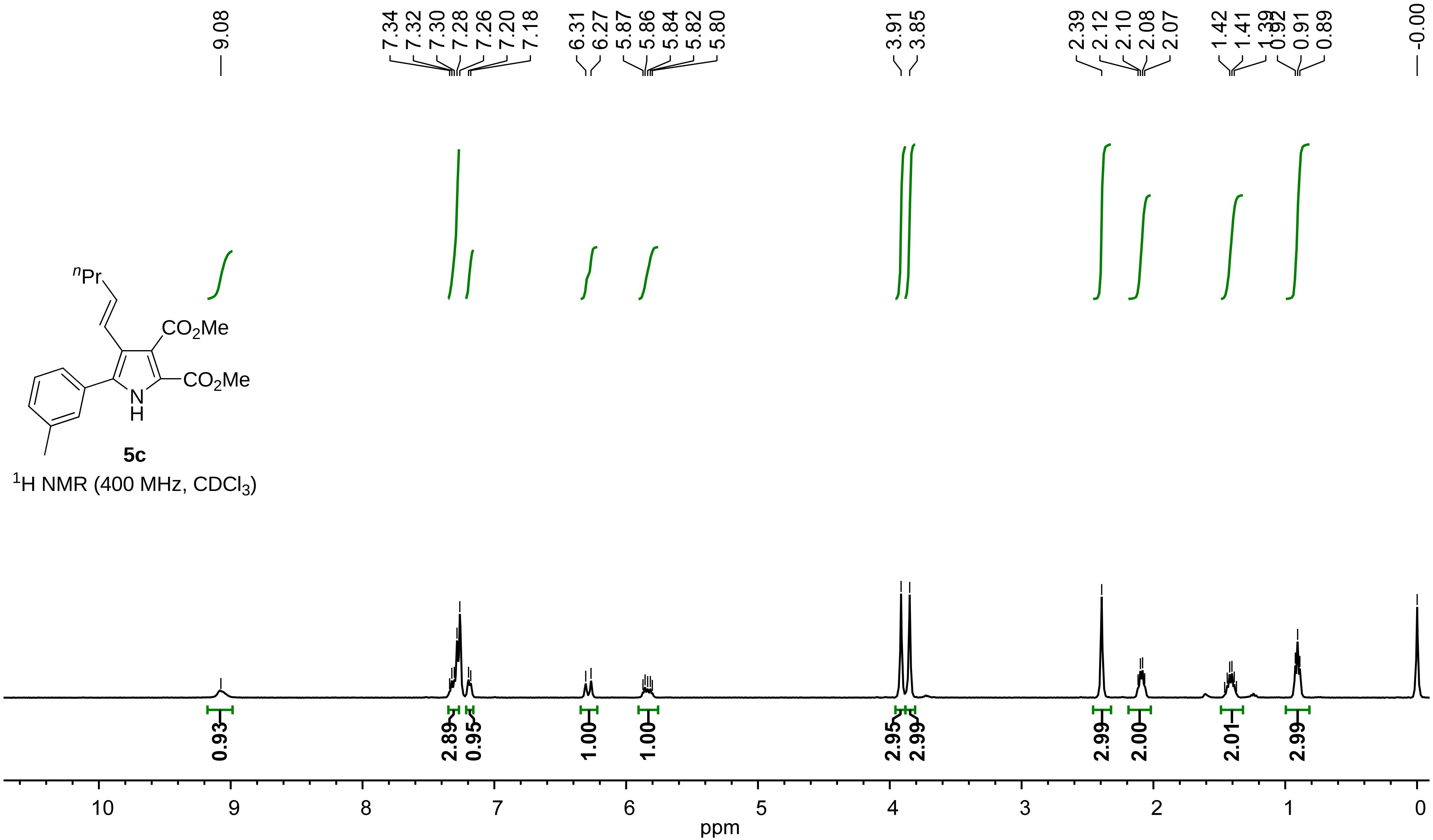

167.20
160.77
133.44
131.30
128.88
128.83
128.41
128.34
121.32
120.35
119.99
119.86
77.48
77.16
76.84
52.46
52.16
35.59
22.56
13.68
nPr
CO2Me
CO2Me
N
H
5a
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm



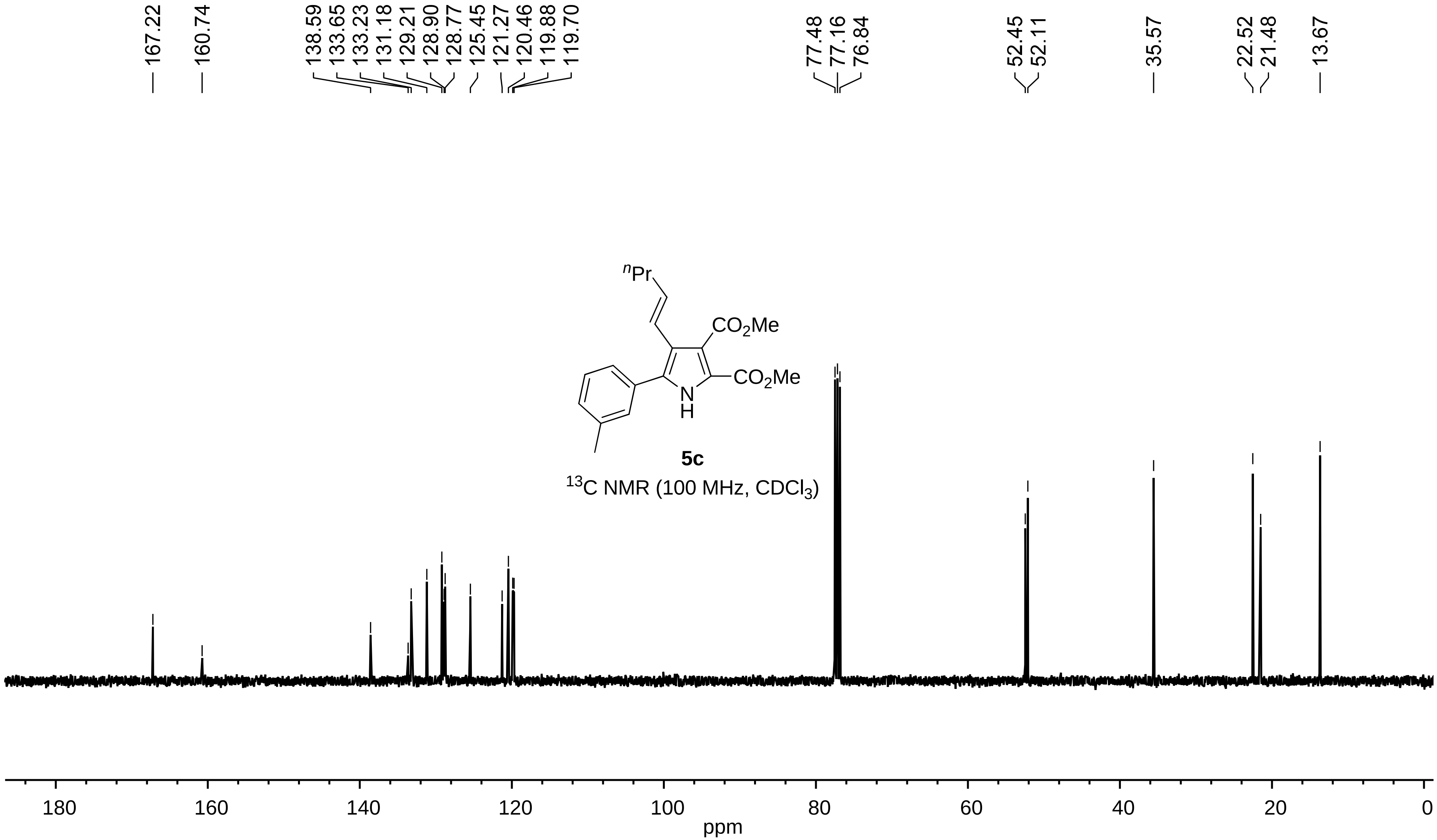
5b

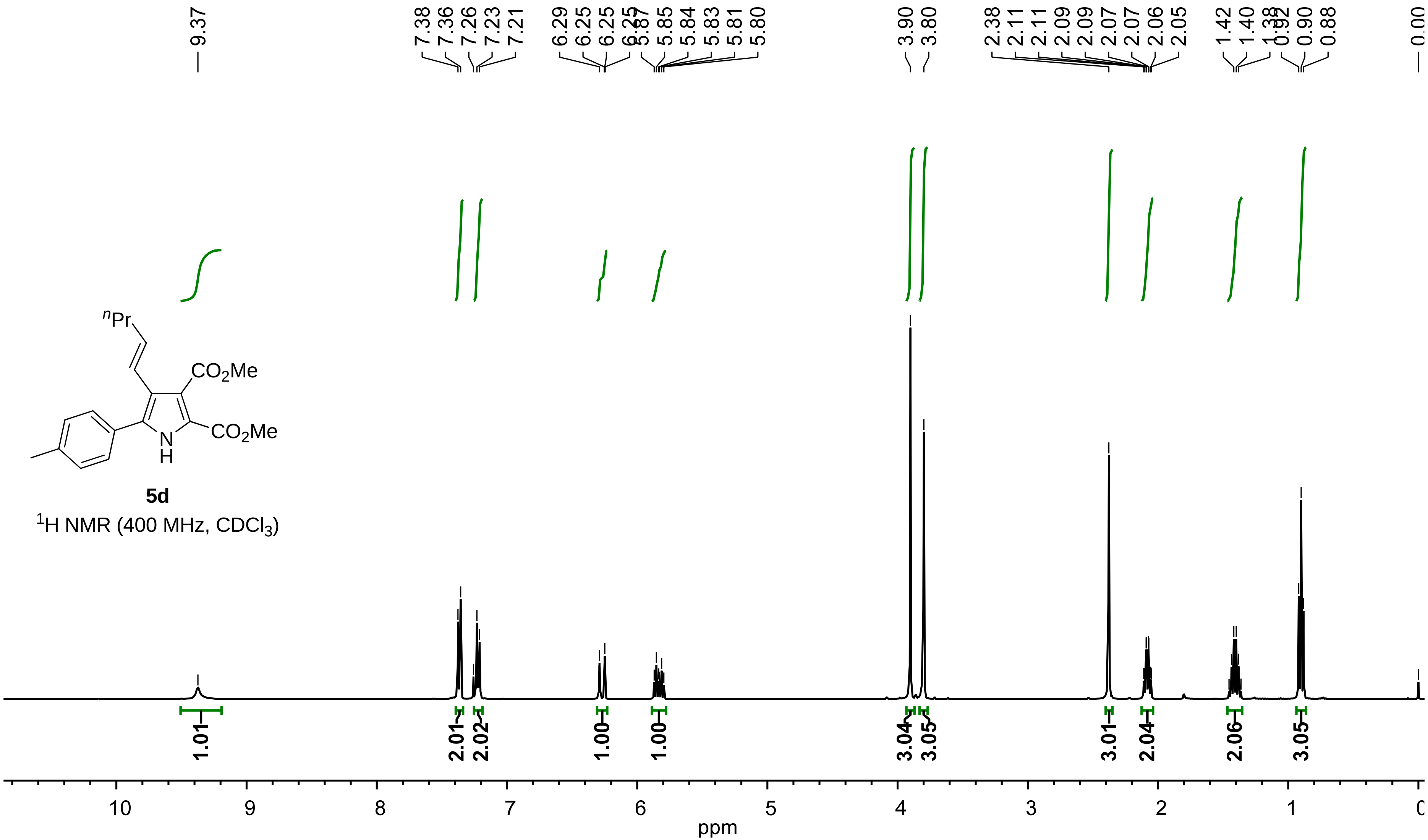
^{1}H NMR (400 MHz, $CDCl_3$)


167.06
160.64
137.85
132.94
132.21
131.03
130.78
130.60
129.28
126.05
121.02
120.29
119.96
119.79
77.48
77.16
76.84
52.48
52.11
35.60
22.64
20.07
13.64
nPr
CO2Me
CO2Me
N
H
5b
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm

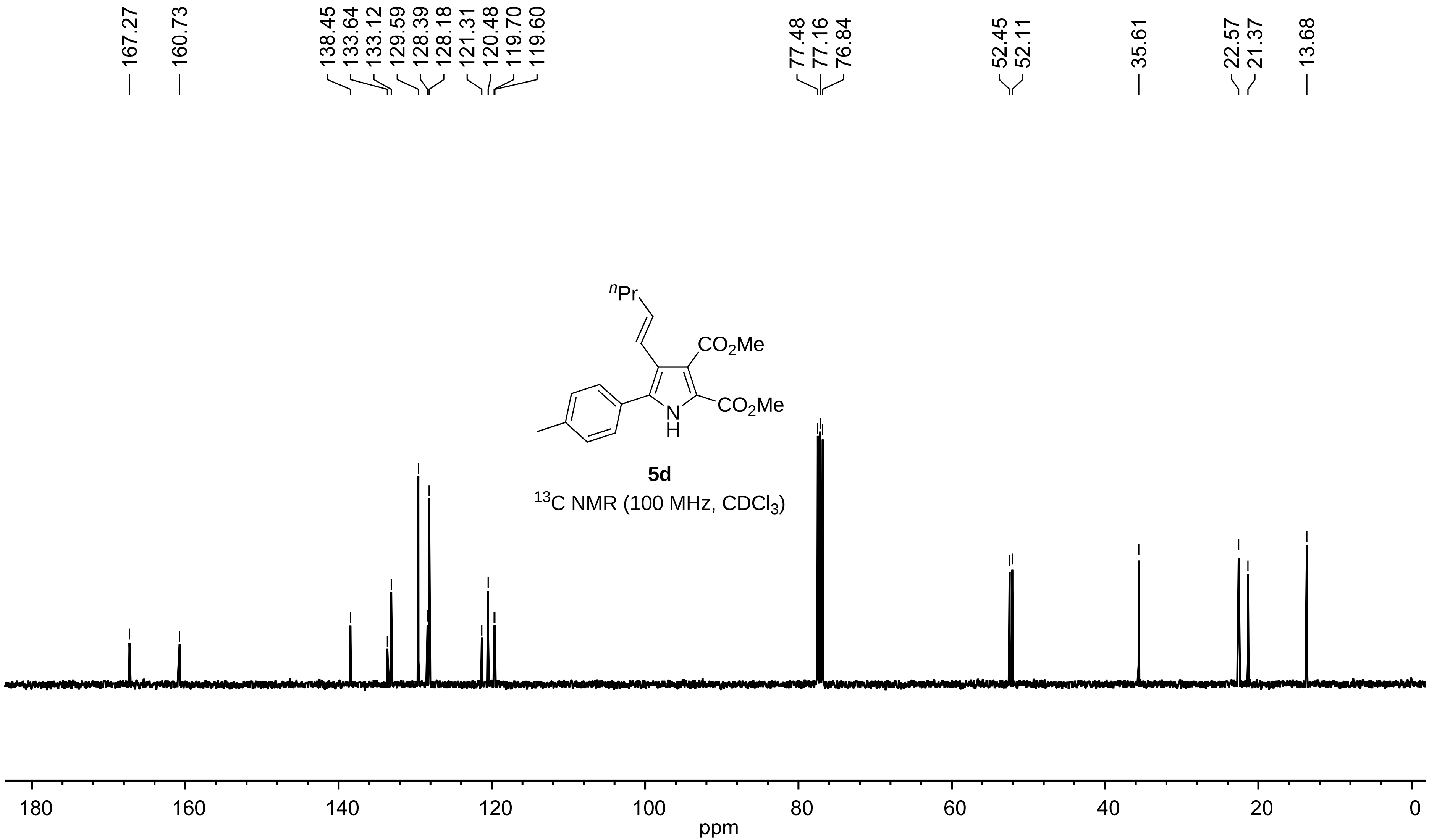


9.08
7.34
7.32
7.30
7.28
7.26
7.20
7.18
6.31
6.27
5.87
5.86
5.84
5.82
5.80
3.91
3.85
2.39
2.12
2.10
2.08
2.07
1.42
1.41
1.39
0.92
0.91
0.89
-0.00
nPr
CO2Me
CO2Me
N
H
5c
1H NMR (400 MHz, CDCl3)
0.93
2.89
0.95
1.00
1.00
2.95
2.99
2.99
2.00
2.01
2.99
10
9
8
7
6
5
4
3
2
1
0
ppm


167.22
160.74
138.59
133.65
133.23
131.18
129.21
128.90
128.77
125.45
121.27
120.46
119.88
119.70
77.48
77.16
76.84
52.45
52.11
35.57
22.52
21.48
13.67
nPr
CO2Me
CO2Me
N
H
5c
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm

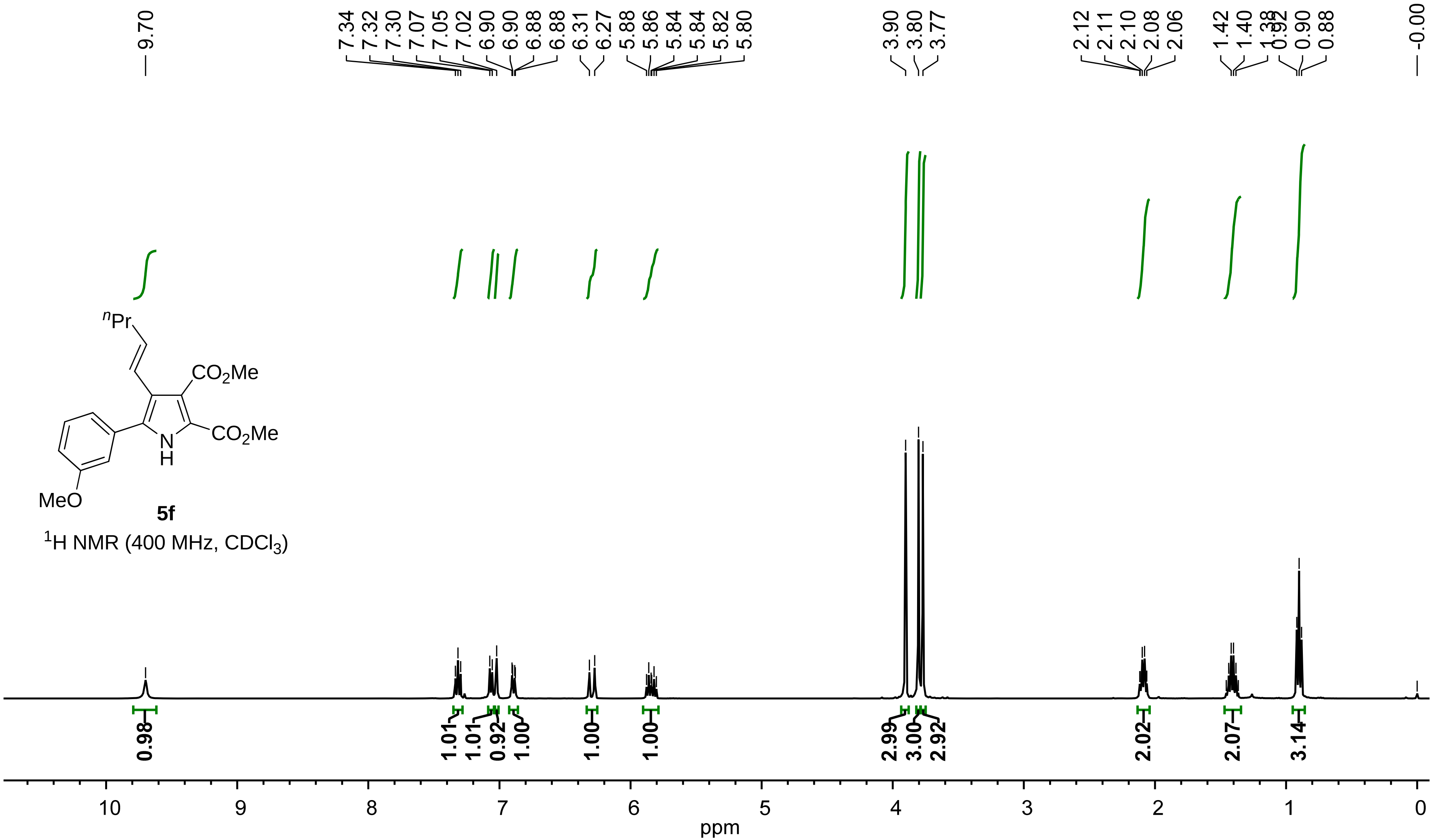


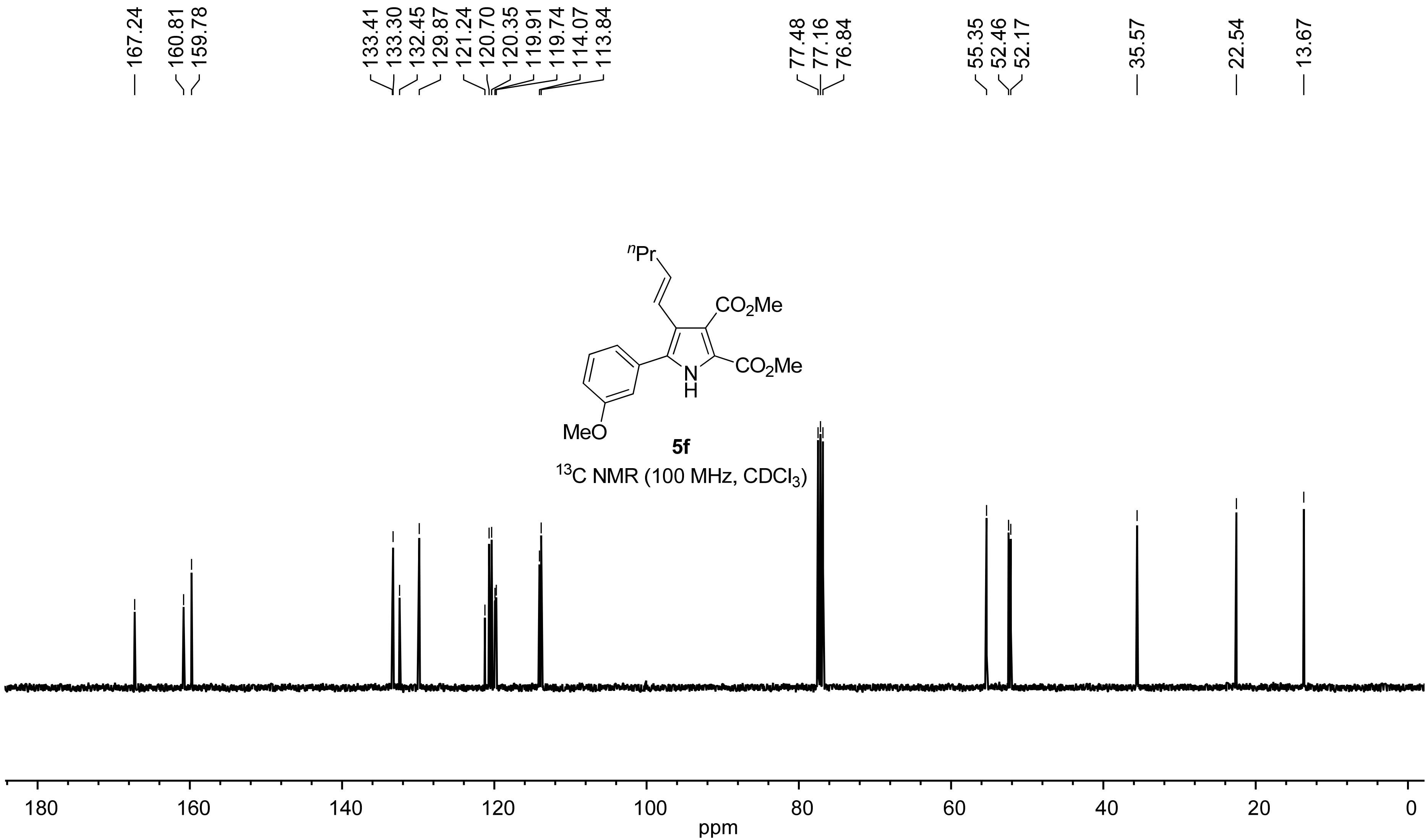
9.37
7.38
7.36
7.26
7.23
7.21
6.29
6.25
6.25
6.25
5.87
5.85
5.84
5.83
5.81
5.80
3.90
3.80
2.38
2.11
2.11
2.09
2.09
2.07
2.07
2.06
2.05
1.42
1.40
1.38
0.92
0.90
0.88
0.00
nPr
CO2Me
CO2Me
N
H
5d
1H NMR (400 MHz, CDCl3)
1.01
2.01
2.02
1.00
1.00
3.04
3.05
3.01
2.04
2.06
3.05
10
9
8
7
6
5
4
3
2
1
ppm

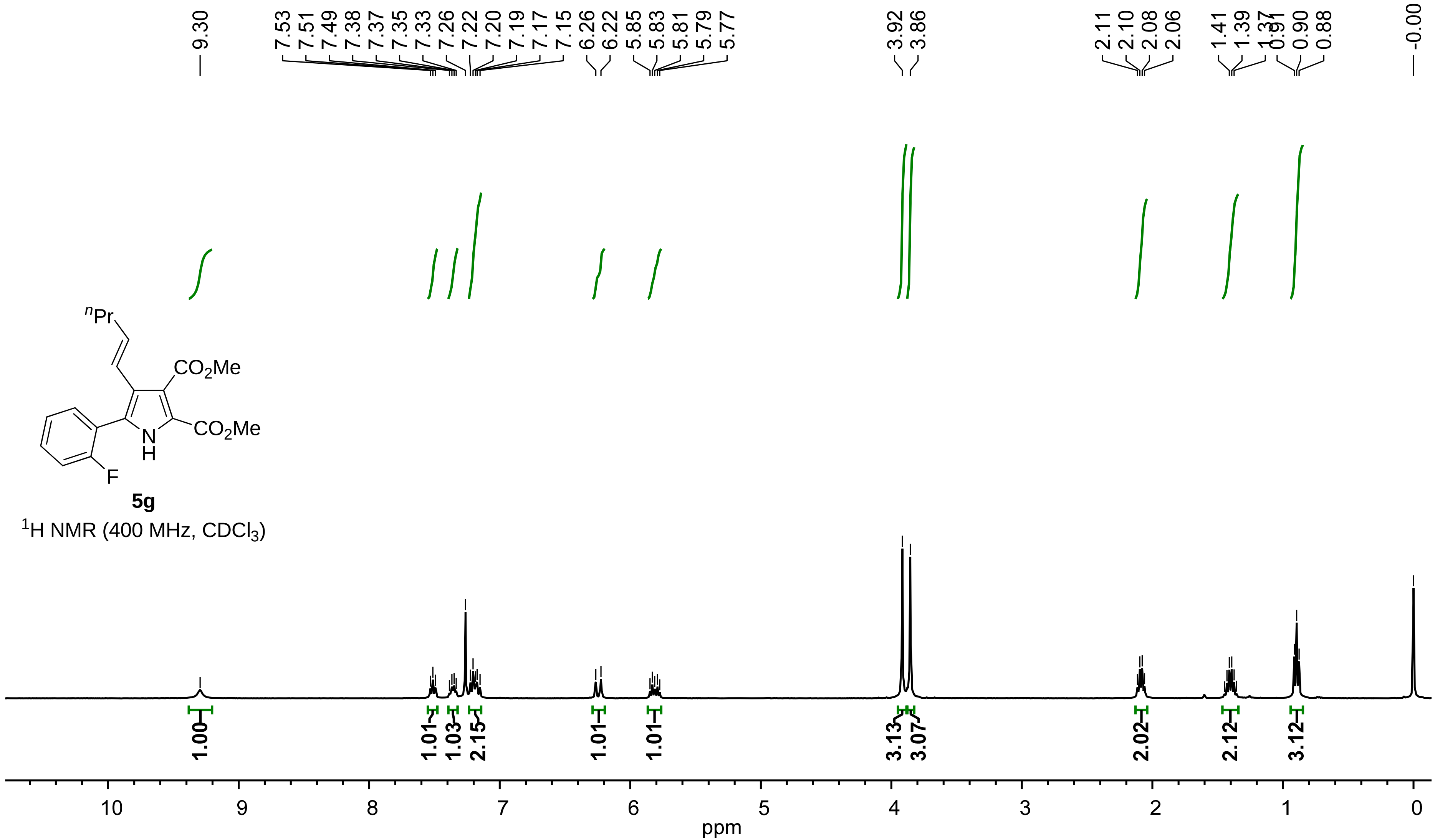


5d

^{13}C NMR (100 MHz, $CDCl_3$)

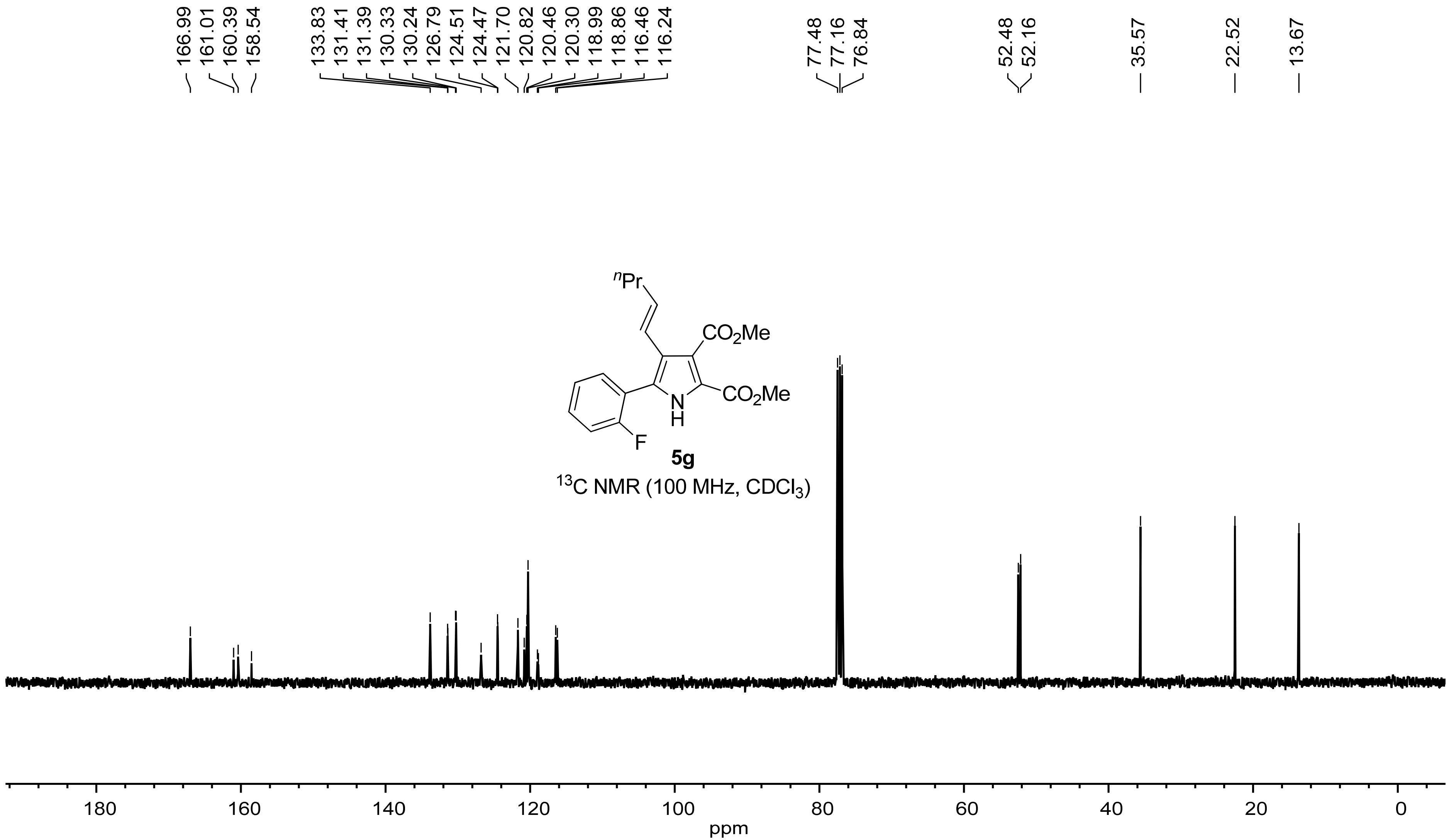

9.70
7.34 7.32 7.30 7.07 7.05 7.02 6.90 6.90 6.88 6.88 6.31 6.27 5.88 5.86 5.84 5.84 5.82 5.80
3.90 3.80 3.77
2.12 2.11 2.10 2.08 2.06 1.42 1.40 1.38 0.92 0.90 0.88
-0.00
^{n}Pr
CO$_2$Me
CO$_2$Me
N
H
MeO
5f
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
1.01
1.01
0.92
1.00
1.00
1.00
2.99
3.00
2.92
2.02
2.07
3.14
10
9
8
7
6
5
4
3
2
1
0
ppm

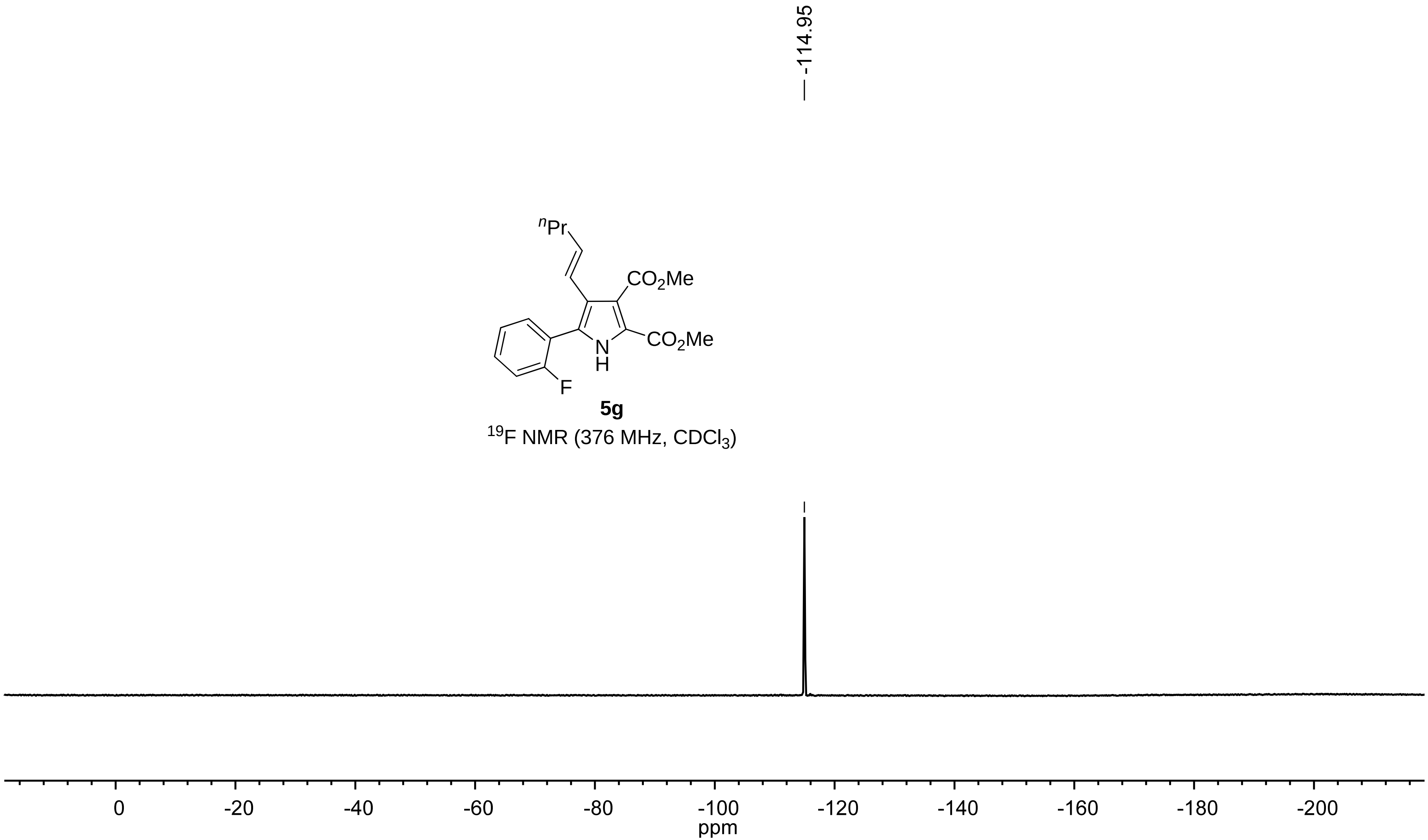

167.24
160.81
159.78
133.41
133.30
132.45
129.87
121.24
120.70
120.35
119.91
119.74
114.07
113.84
77.48
77.16
76.84
55.35
52.46
52.17
35.57
22.54
13.67
nPr
CO2Me
CO2Me
N
H
MeO
5f
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm



5g

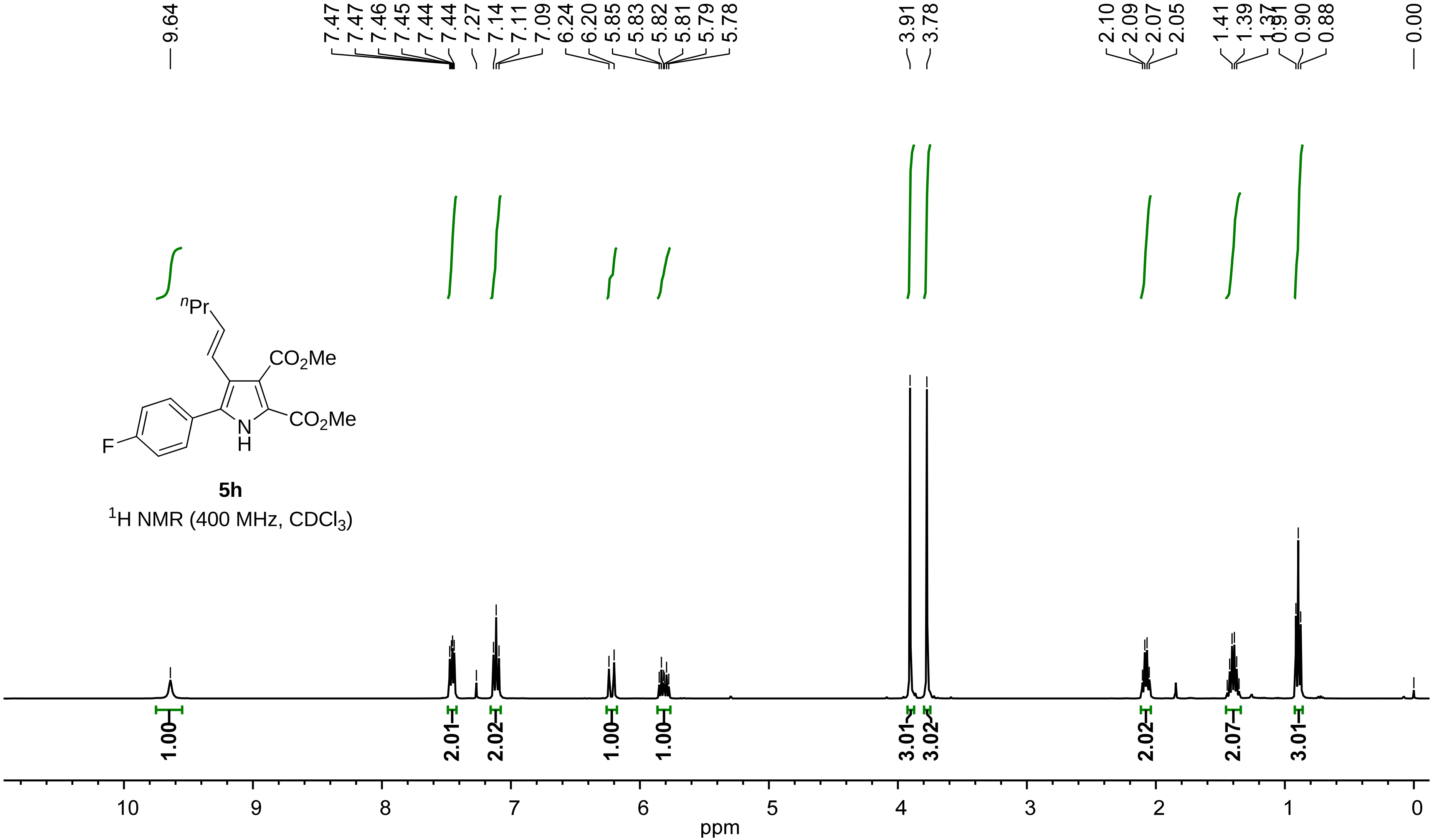
^{1}H NMR (400 MHz, CDCl$_3$)


166.99
161.01
160.39
158.54
133.83
131.41
131.39
130.33
130.24
126.79
124.51
124.47
121.70
120.82
120.46
120.30
118.99
118.86
116.46
116.24
77.48
77.16
76.84
52.48
52.16
35.57
22.52
13.67
^{n}Pr
CO_2Me
CO_2Me
N
H
F
5g
^{13}C NMR (100 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
0
ppm

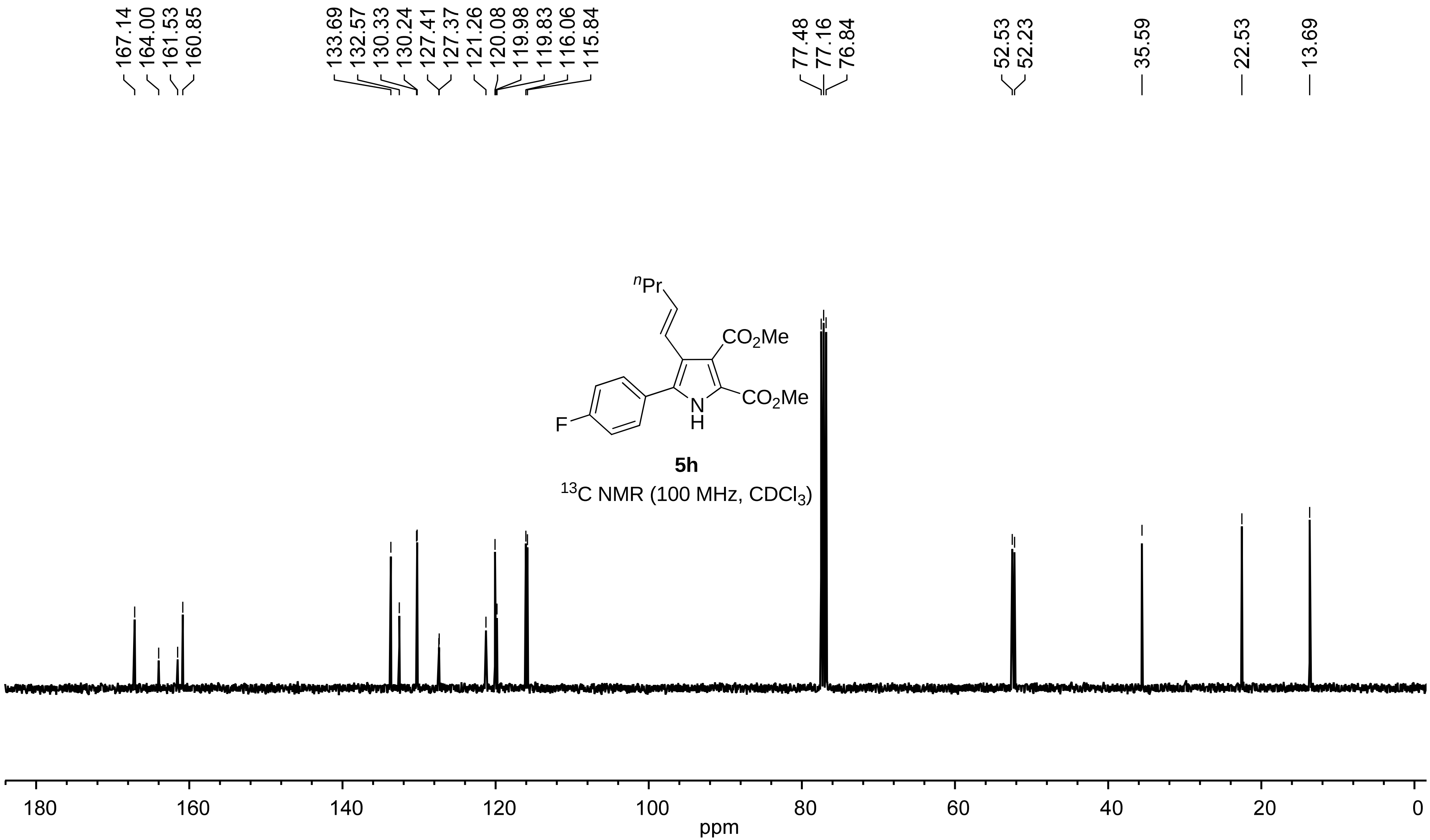


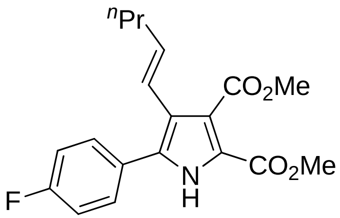
5g

^{19}F NMR (376 MHz, $CDCl_3$)



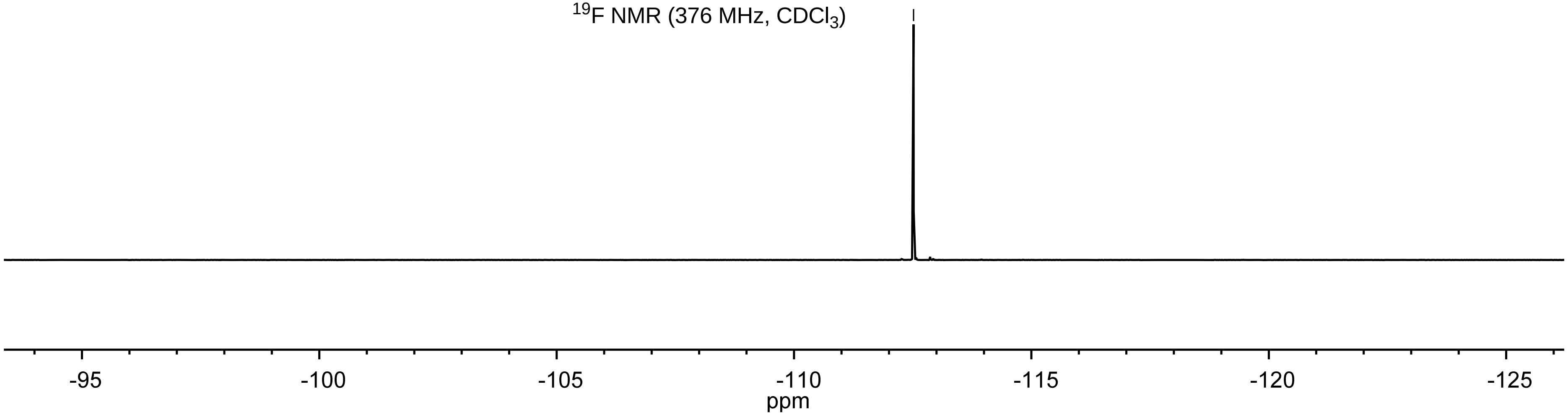
9.64
7.47
7.47
7.46
7.45
7.44
7.44
7.27
7.14
7.11
7.09
6.24
6.20
5.85
5.83
5.82
5.81
5.79
5.78
3.91
3.78
2.10
2.09
2.07
2.05
1.41
1.39
1.37
0.91
0.90
0.88
0.00
nPr
CO2Me
CO2Me
F
N
H
5h
1H NMR (400 MHz, CDCl3)
1.00
2.01
2.02
1.00
1.00
3.01
3.02
2.02
2.07
3.01
10
9
8
7
6
5
4
3
2
1
0
ppm

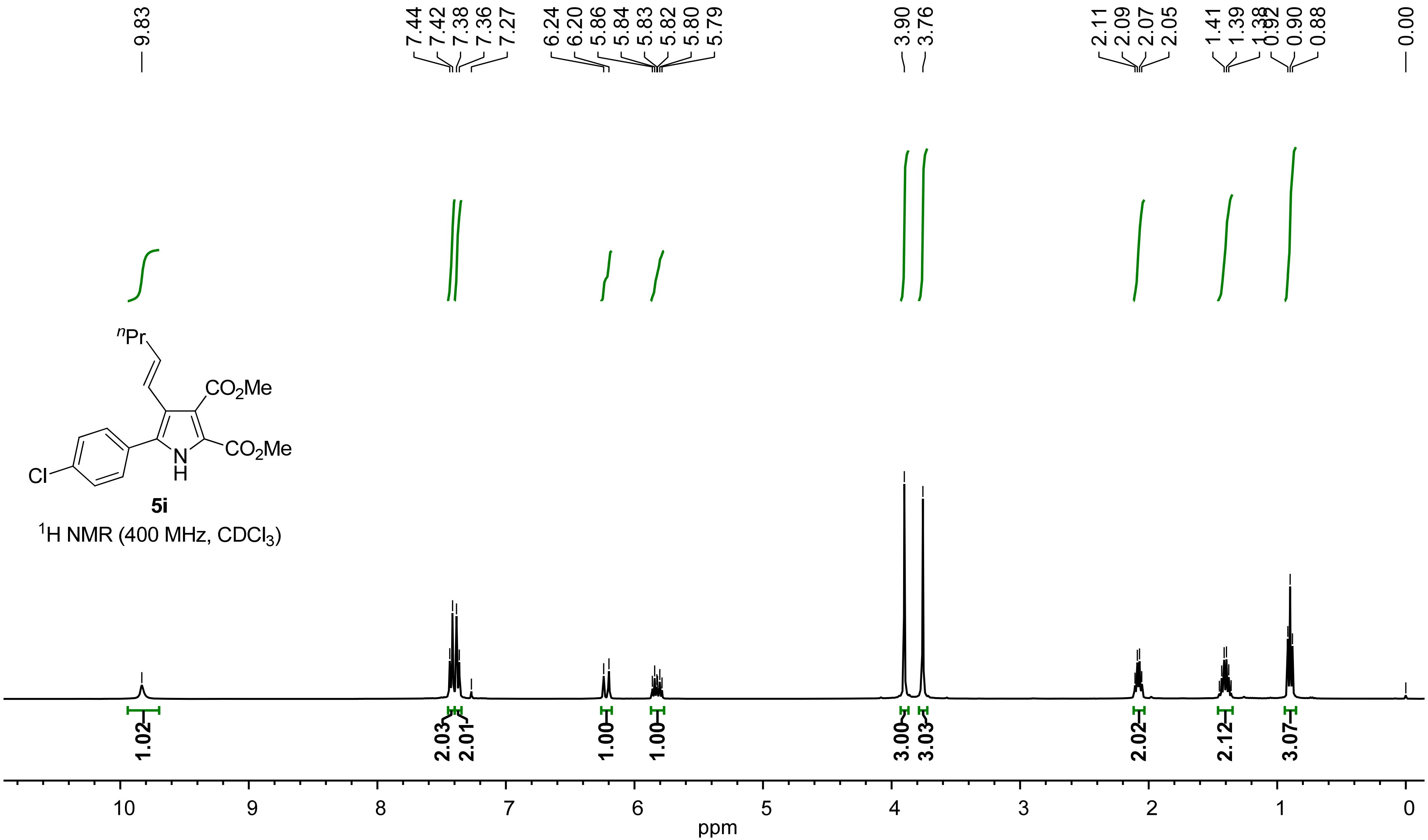

167.14
164.00
161.53
160.85
133.69
132.57
130.33
130.24
127.41
127.37
121.26
120.08
119.98
119.83
116.06
115.84
77.48
77.16
76.84
52.53
52.23
35.59
22.53
13.69
nPr
CO2Me
CO2Me
F
N
H
5h
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm

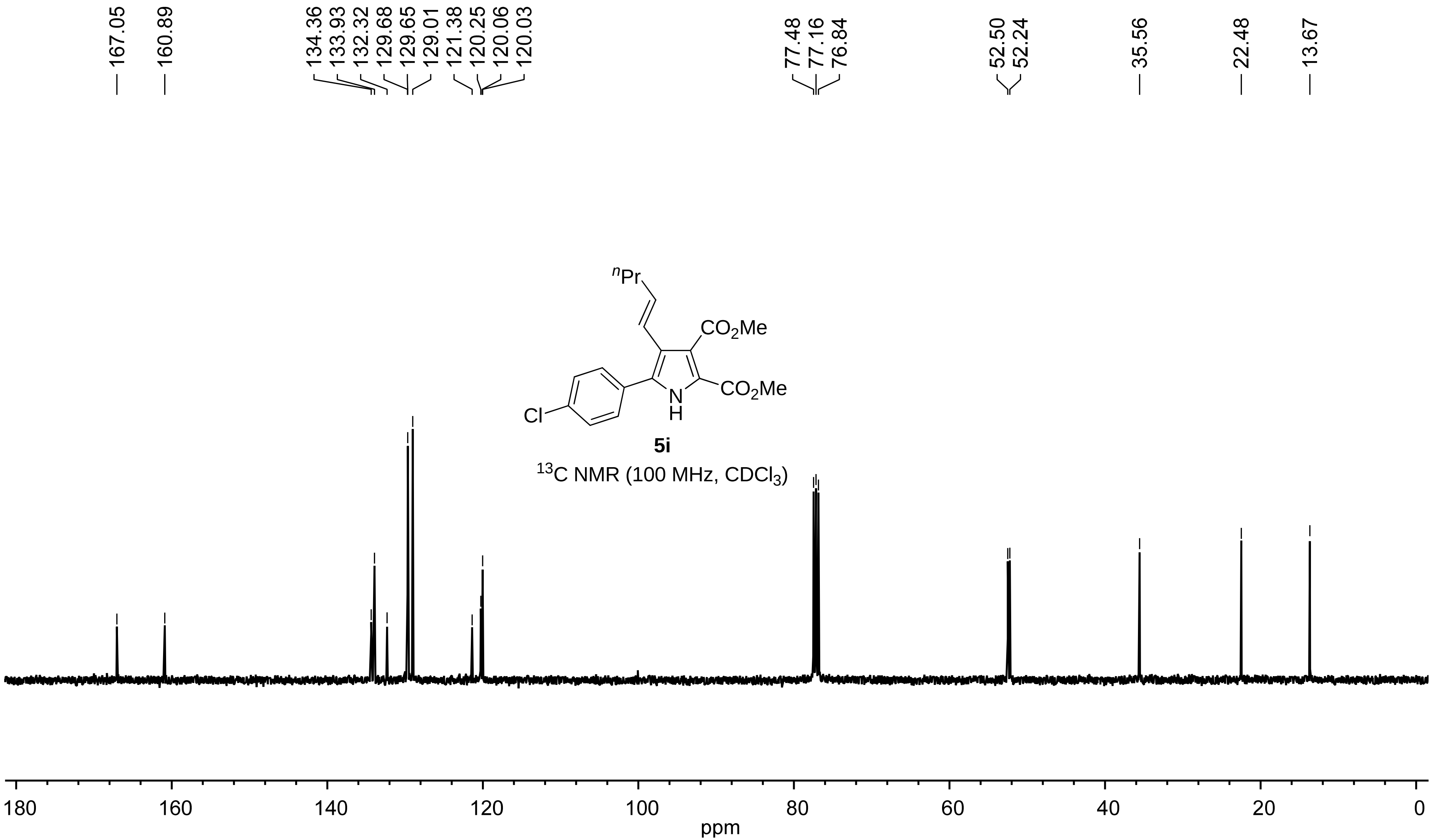


5h

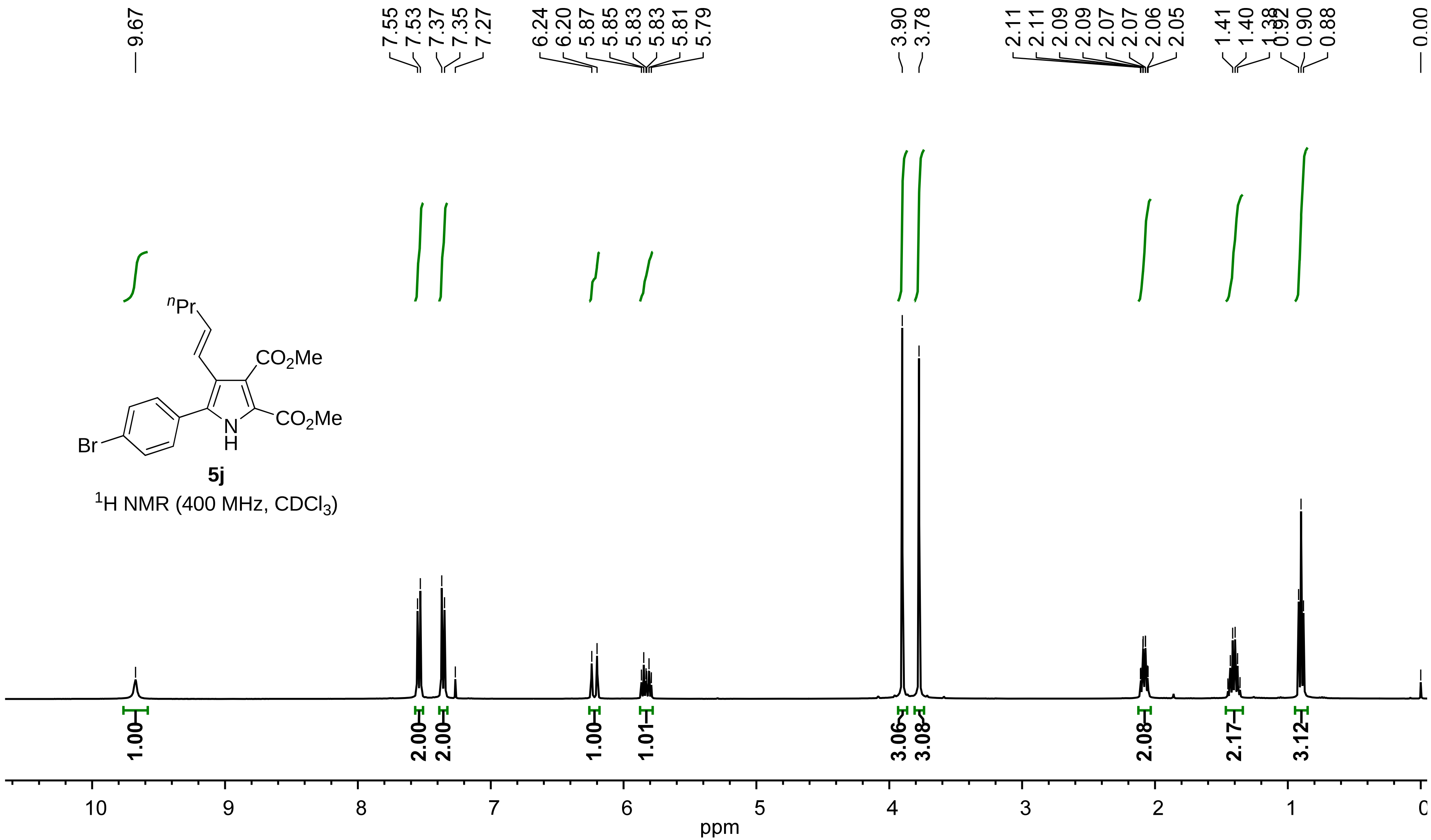
^{19}F NMR (376 MHz, $CDCl_3$)



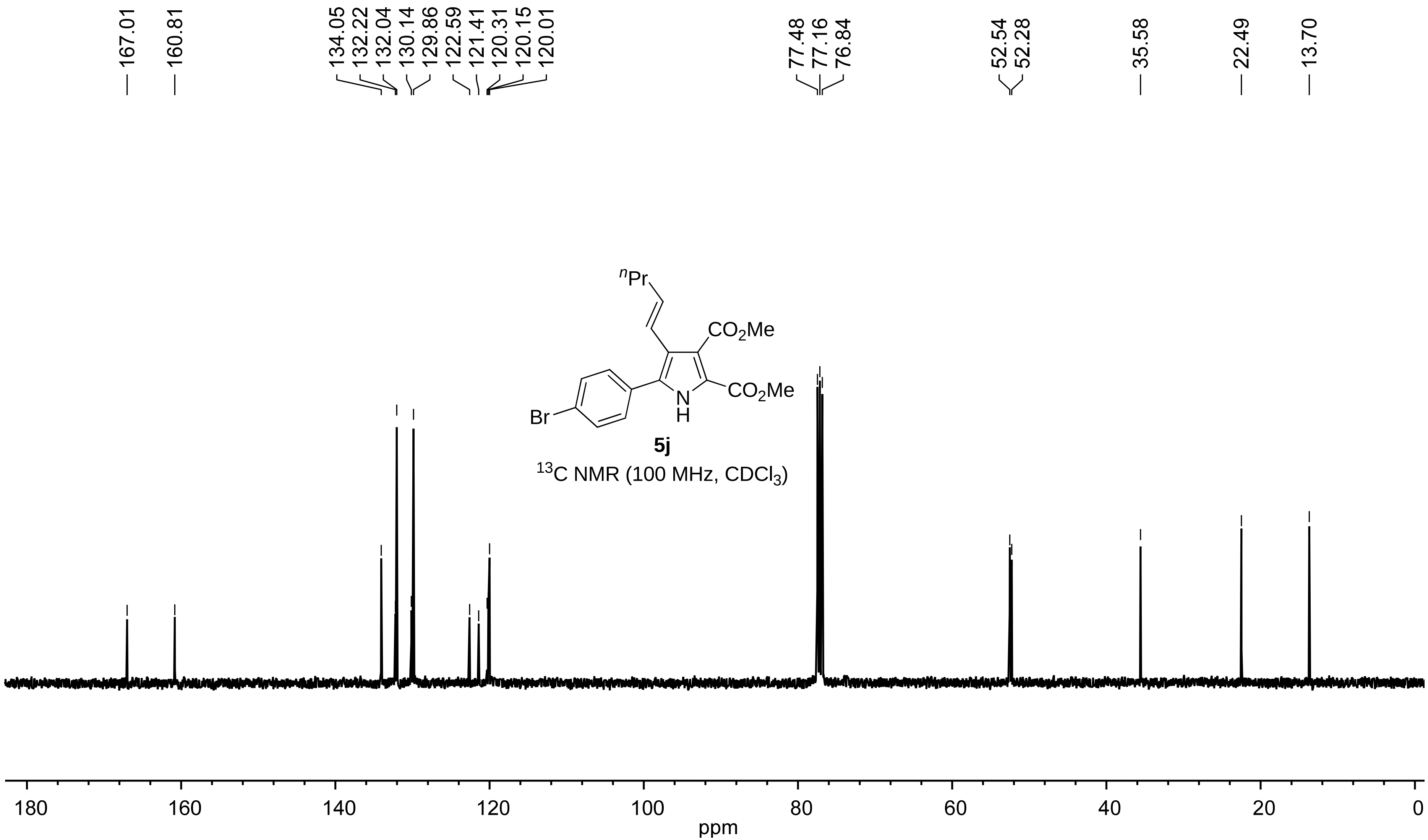

9.83
7.44
7.42
7.38
7.36
7.27
6.24
6.20
5.86
5.84
5.83
5.82
5.80
5.79
3.90
3.76
2.11
2.09
2.07
2.05
1.41
1.39
1.38
0.92
0.90
0.88
0.00
^{n}Pr
CO_2Me
CO_2Me
N
H
Cl
5i
^{1}H NMR (400 MHz, $CDCl_3$)
1.02
2.03
2.01
1.00
1.00
3.00
3.03
2.02
2.12
3.07
10
9
8
7
6
5
4
3
2
1
0
ppm

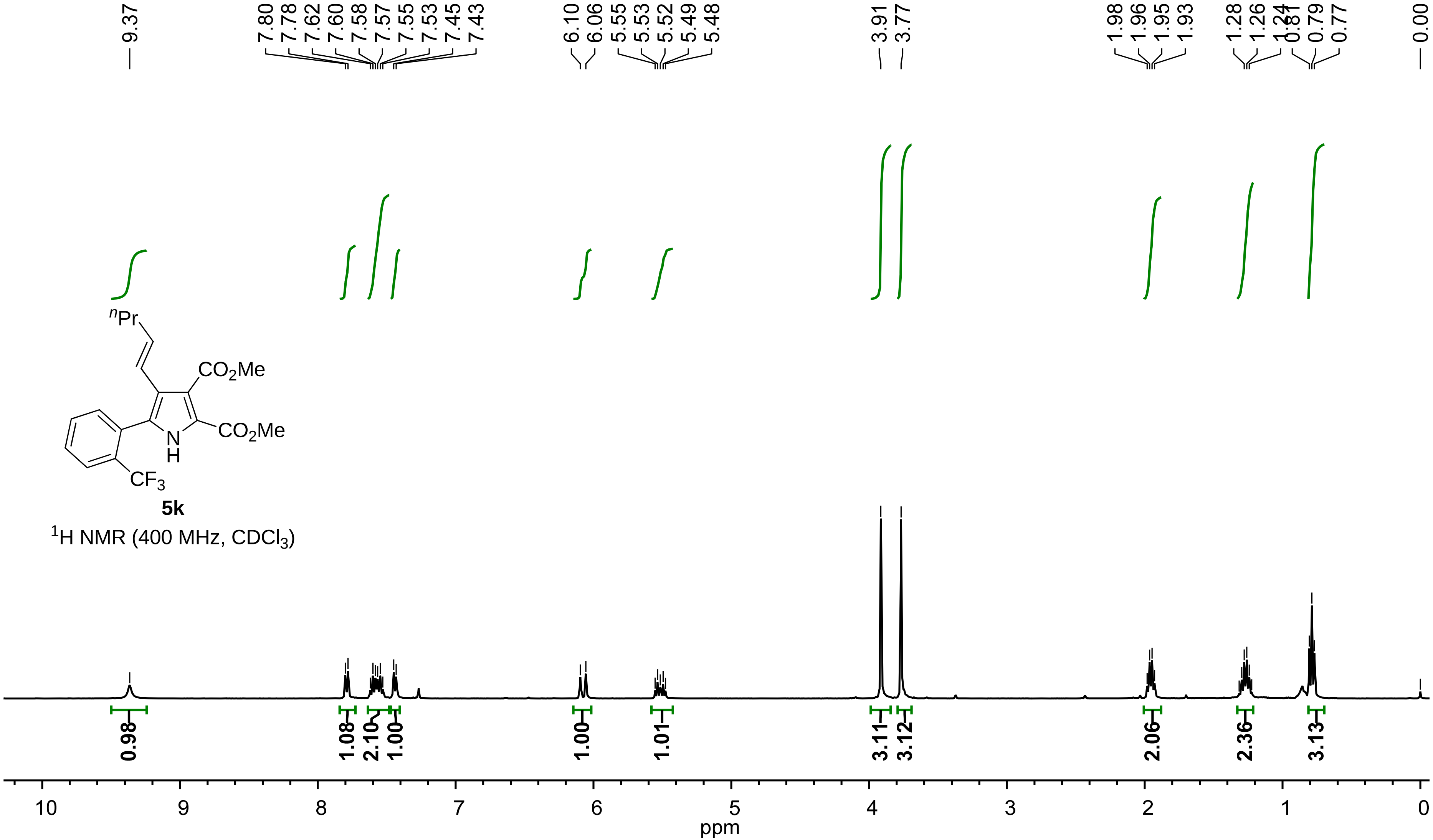


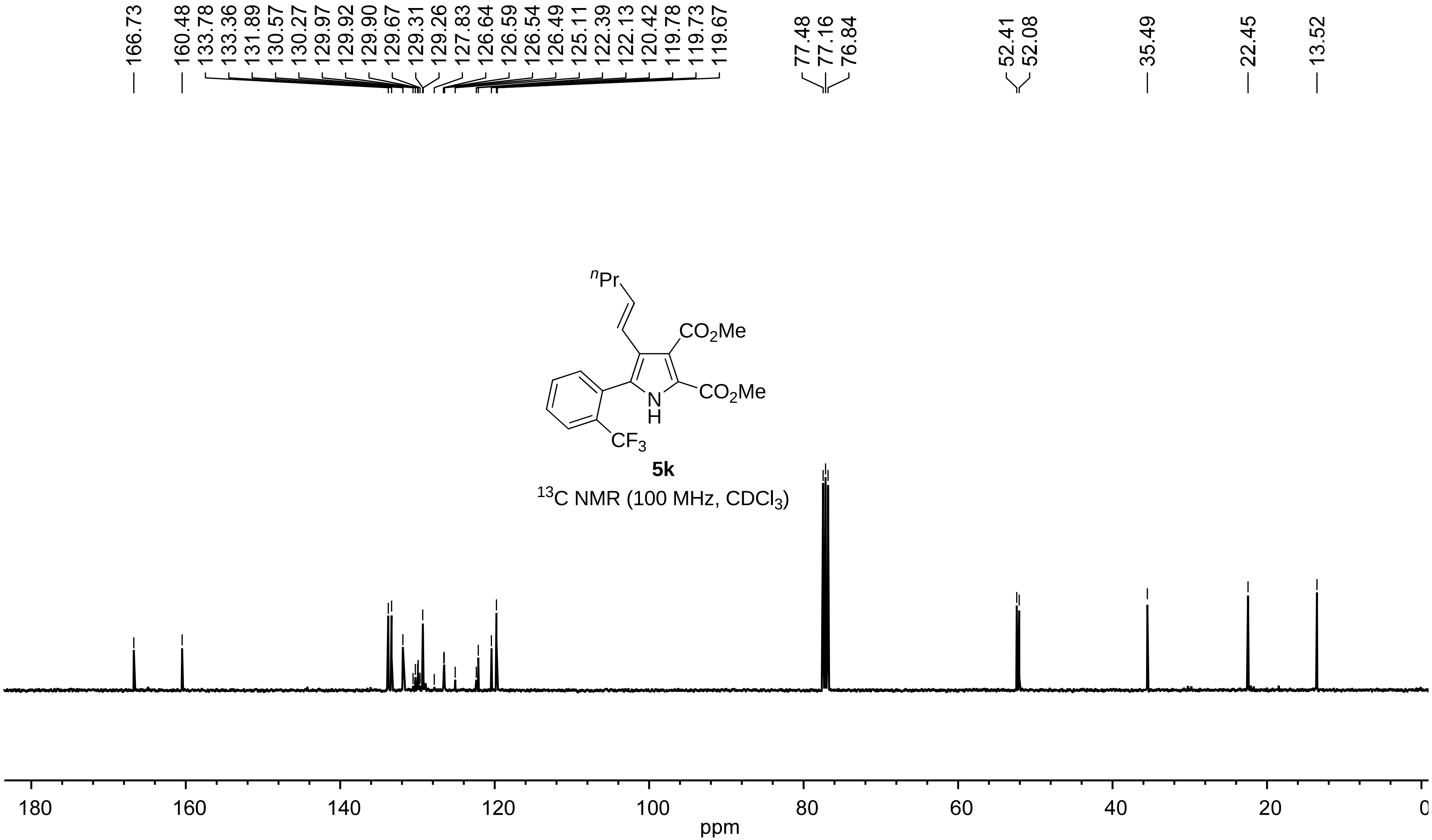
167.05
160.89
134.36
133.93
132.32
129.68
129.65
129.01
121.38
120.25
120.06
120.03
77.48
77.16
76.84
52.50
52.24
35.56
22.48
13.67
^{n}Pr
CO_2Me
CO_2Me
Cl
N
H
5i
^{13}C NMR (100 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
0
ppm



9.67
7.55
7.53
7.37
7.35
7.27
6.24
6.20
5.87
5.85
5.83
5.83
5.81
5.79
3.90
3.78
2.11
2.11
2.09
2.09
2.07
2.07
2.06
2.05
1.41
1.40
1.38
0.92
0.90
0.88
0.00
nPr
CO2Me
CO2Me
Br
N
H
5j
1H NMR (400 MHz, CDCl3)
1.00
2.00
2.00
1.00
1.01
3.06
3.08
2.08
2.17
3.12
10
9
8
7
6
5
4
3
2
1
0
ppm

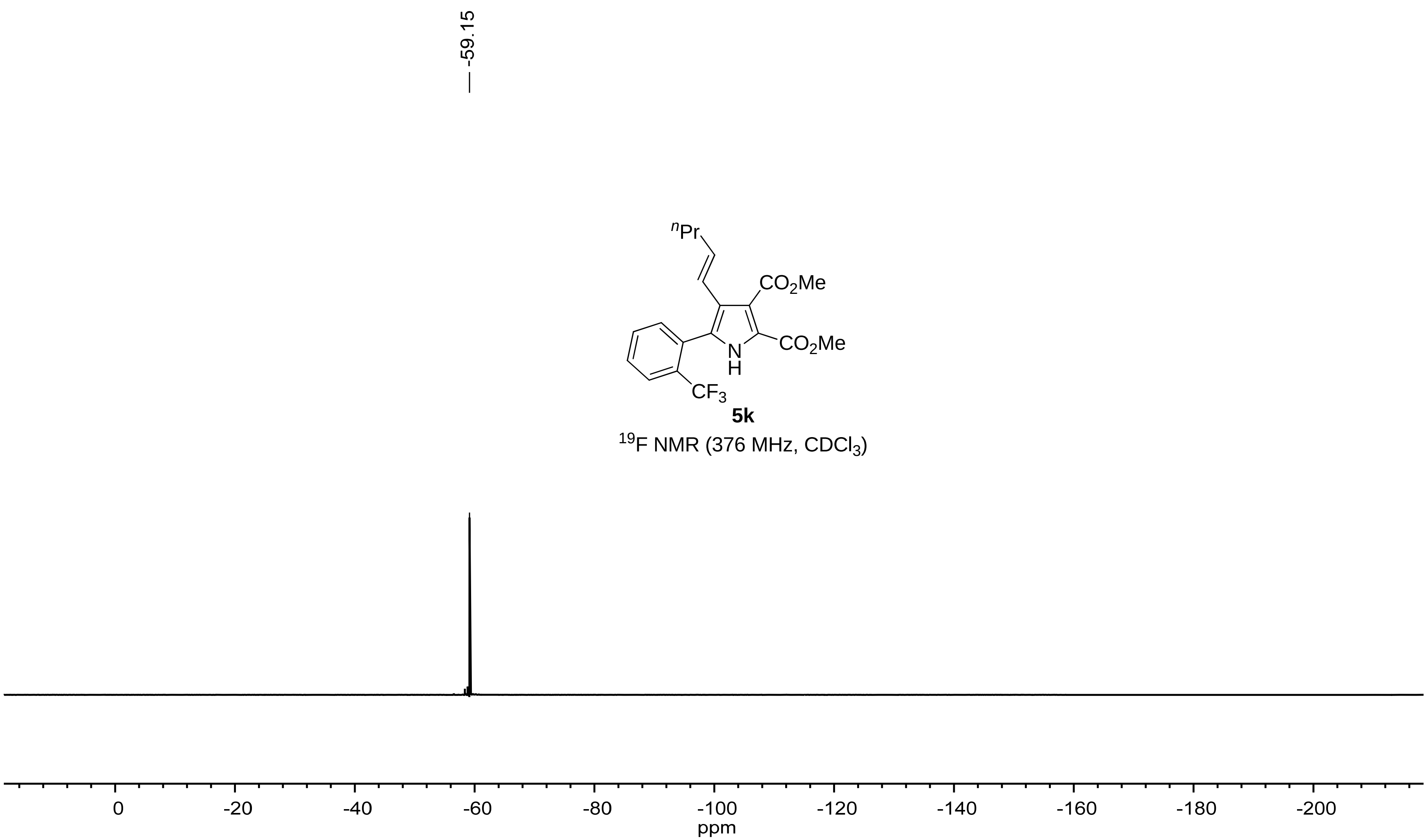

167.01
160.81
134.05
132.22
132.04
130.14
129.86
122.59
121.41
120.31
120.15
120.01
77.48
77.16
76.84
52.54
52.28
35.58
22.49
13.70
nPr
CO2Me
CO2Me
Br
N
H
5j
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm


9.37
7.80 7.78 7.62 7.60 7.58 7.57 7.55 7.53 7.45 7.43
6.10 6.06 5.55 5.53 5.52 5.49 5.48
3.91 3.77
1.98 1.96 1.95 1.93 1.28 1.26 1.24 0.81 0.79 0.77
0.00
^nPr
CO_2Me
CO_2Me
N
H
CF_3
5k
^1H NMR (400 MHz, $CDCl_3$)
0.98
1.08
2.10
1.00
1.00
1.01
3.11
3.12
2.06
2.36
3.13
10
9
8
7
6
5
4
3
2
1
0
ppm



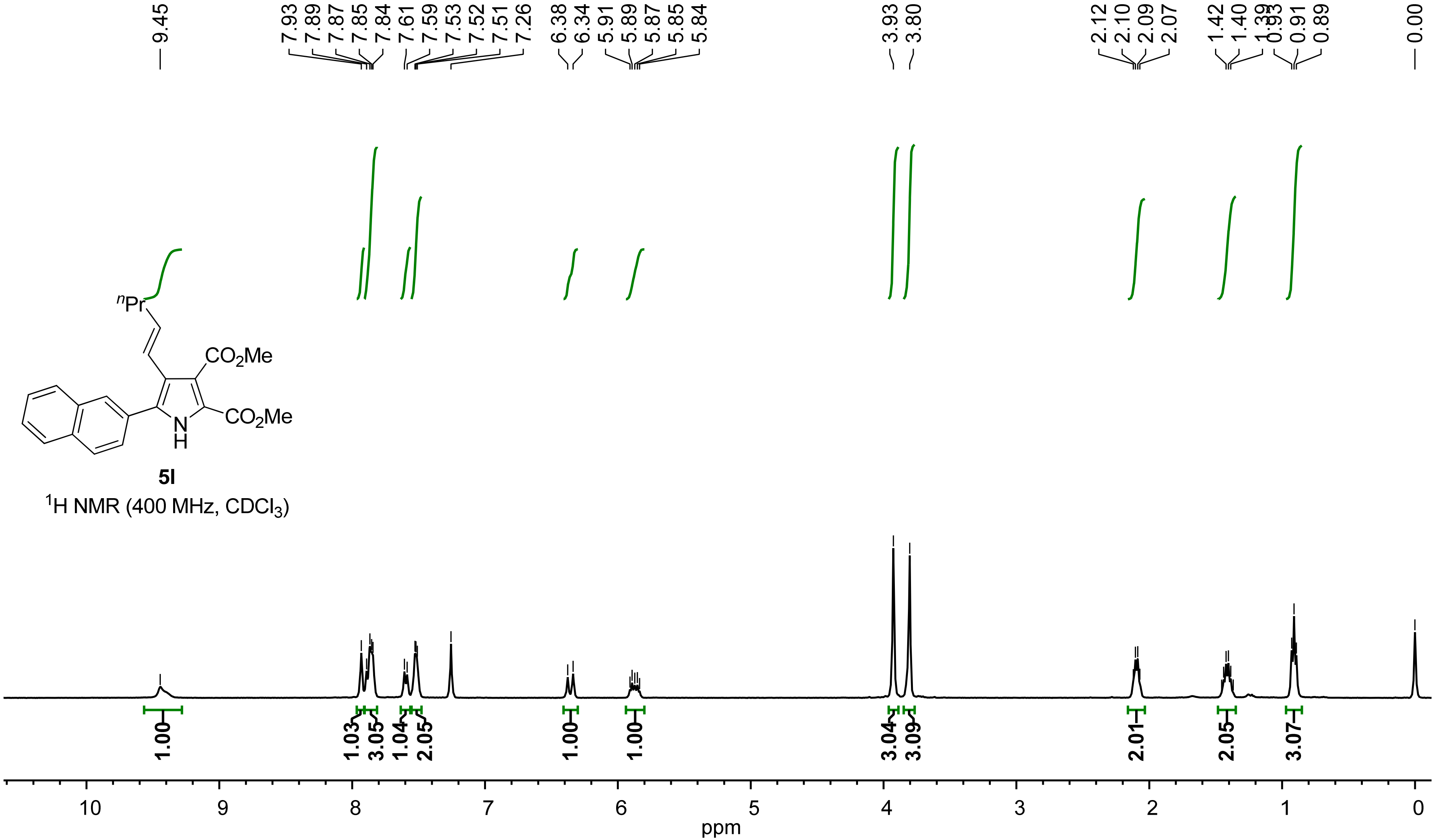
5k

^{13}C NMR (100 MHz, $CDCl_3$)

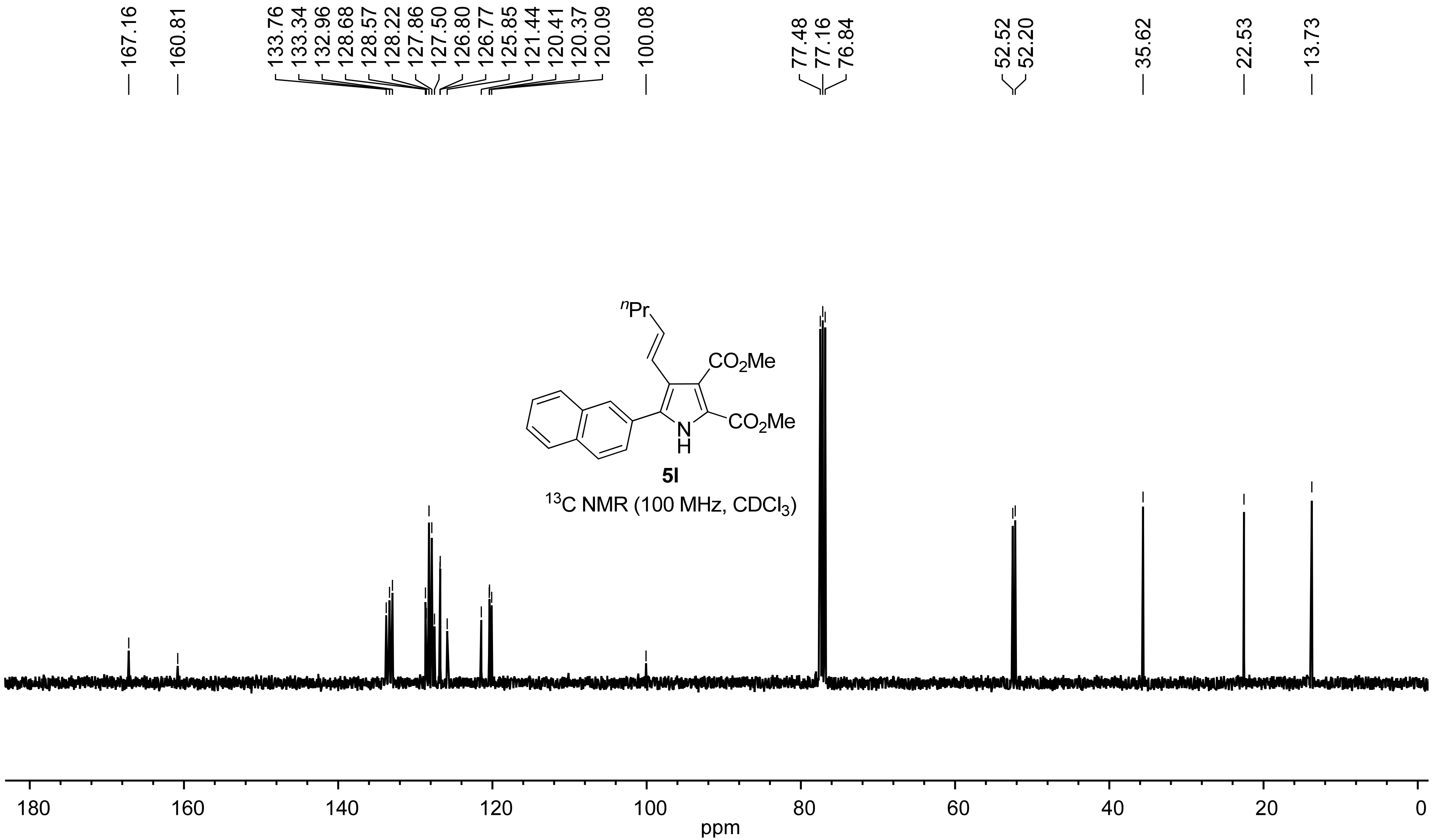


5k

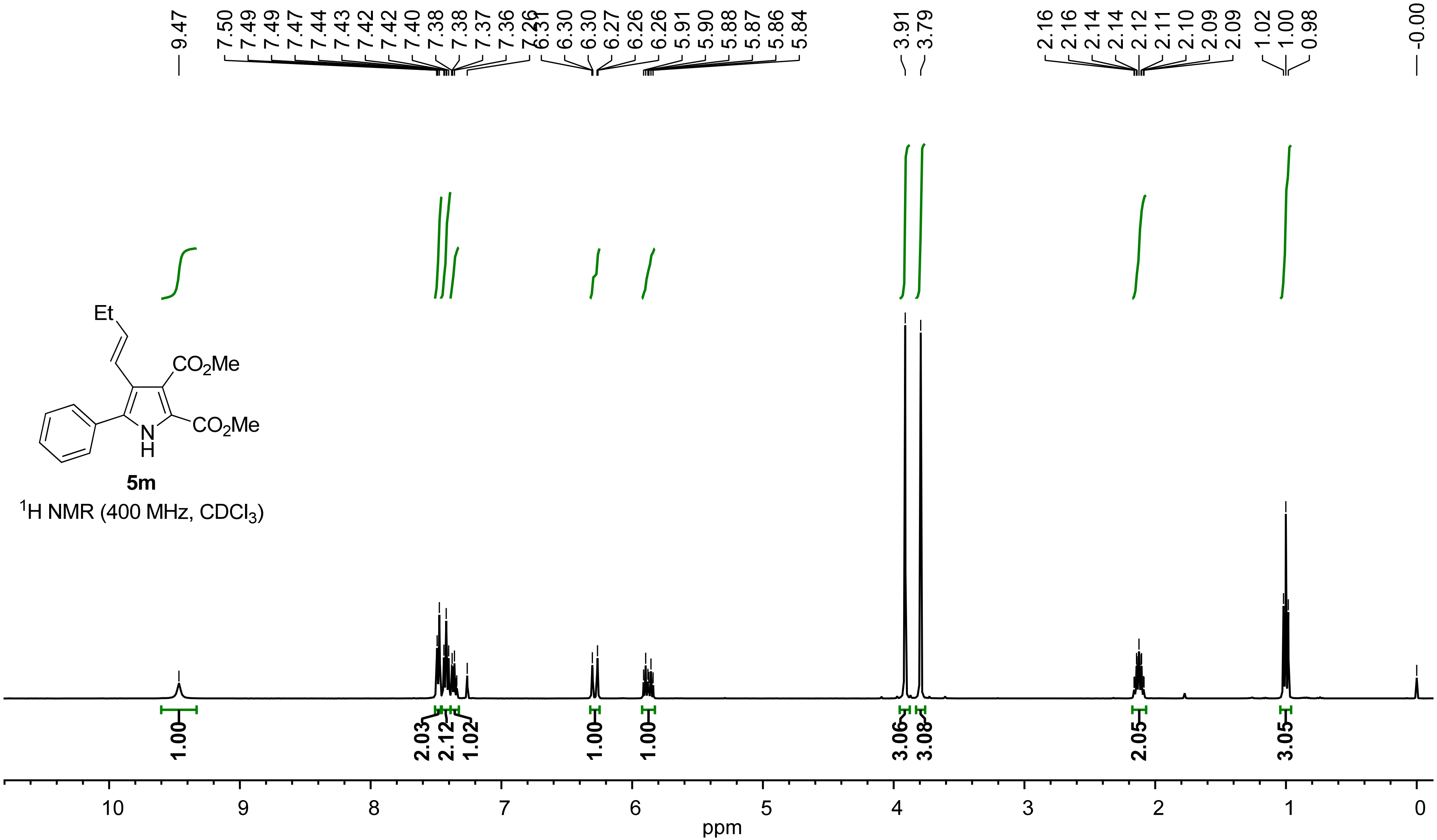
^{19}F NMR (376 MHz, $CDCl_3$)

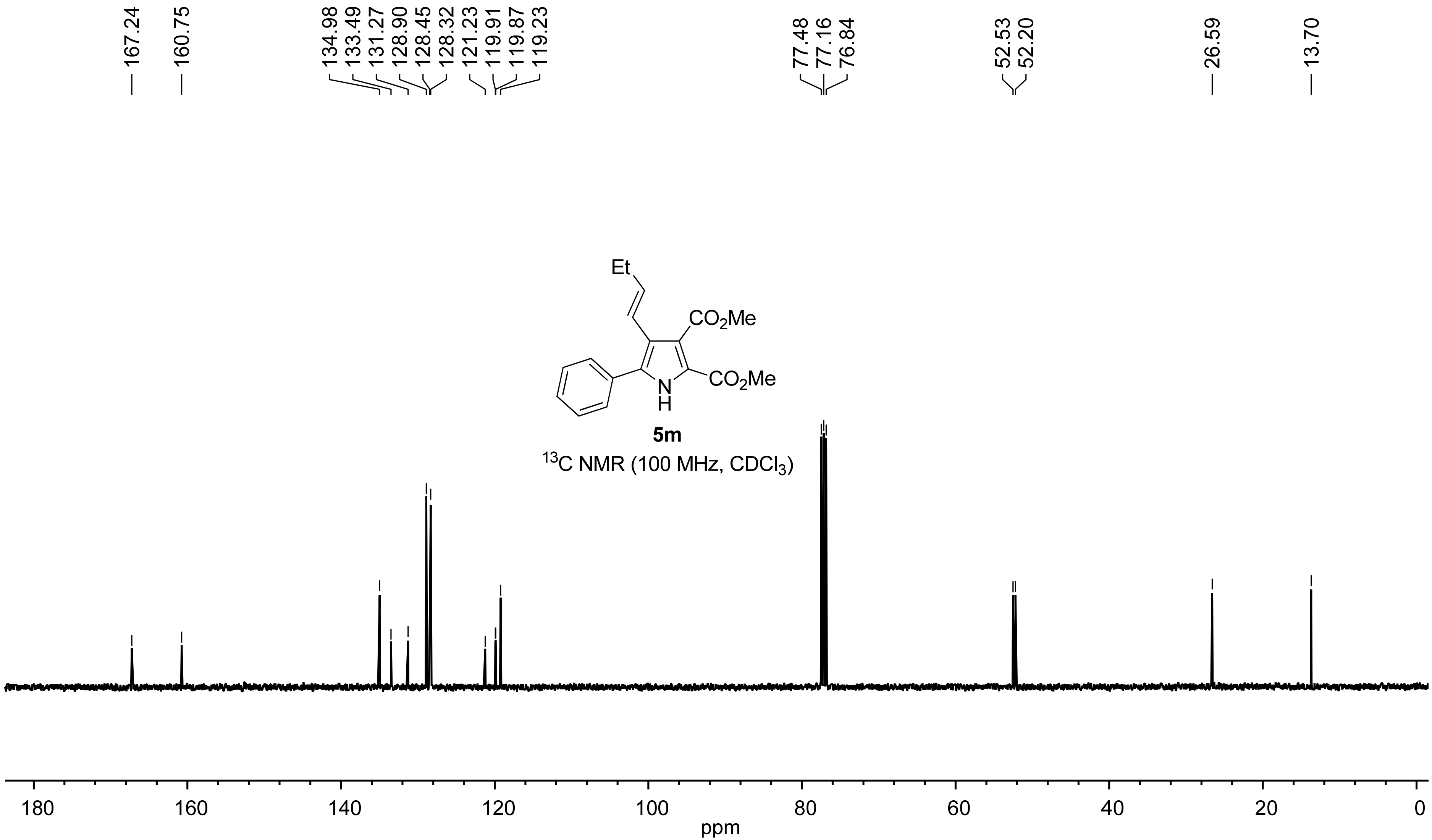


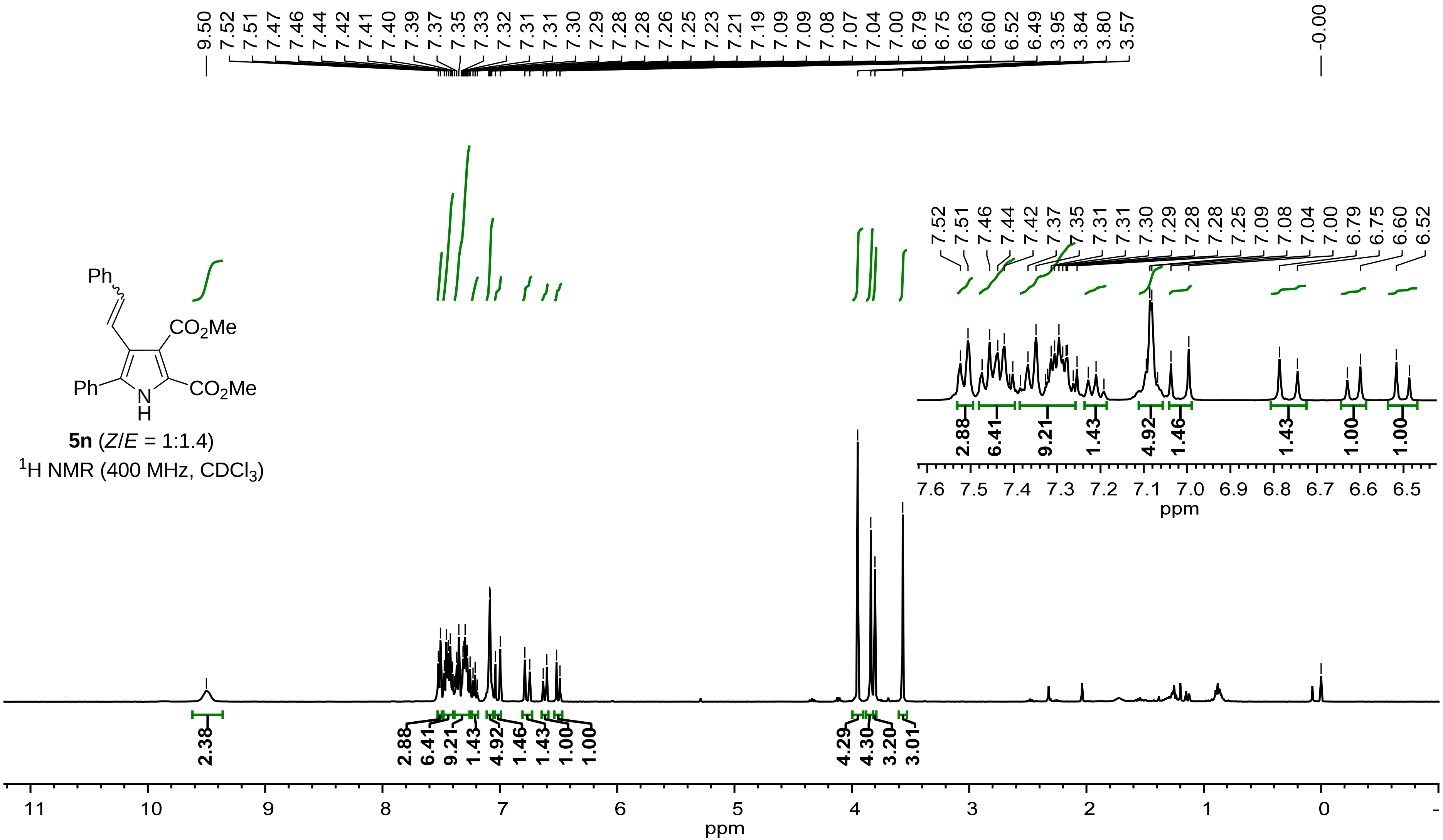
9.45
7.93 7.89 7.87 7.85 7.84 7.61 7.59 7.53 7.52 7.51 7.26
6.38 6.34 5.91 5.89 5.87 5.85 5.84
3.93 3.80
2.12 2.10 2.09 2.07
1.42 1.40 1.39 0.93 0.91 0.89
0.00
^{n}Pr
CO_2Me
CO_2Me
N
H
5l
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.03 3.05 1.04 2.05
1.00
1.00
3.04 3.09
2.01
2.05
3.07
10 9 8 7 6 5 4 3 2 1 0
ppm



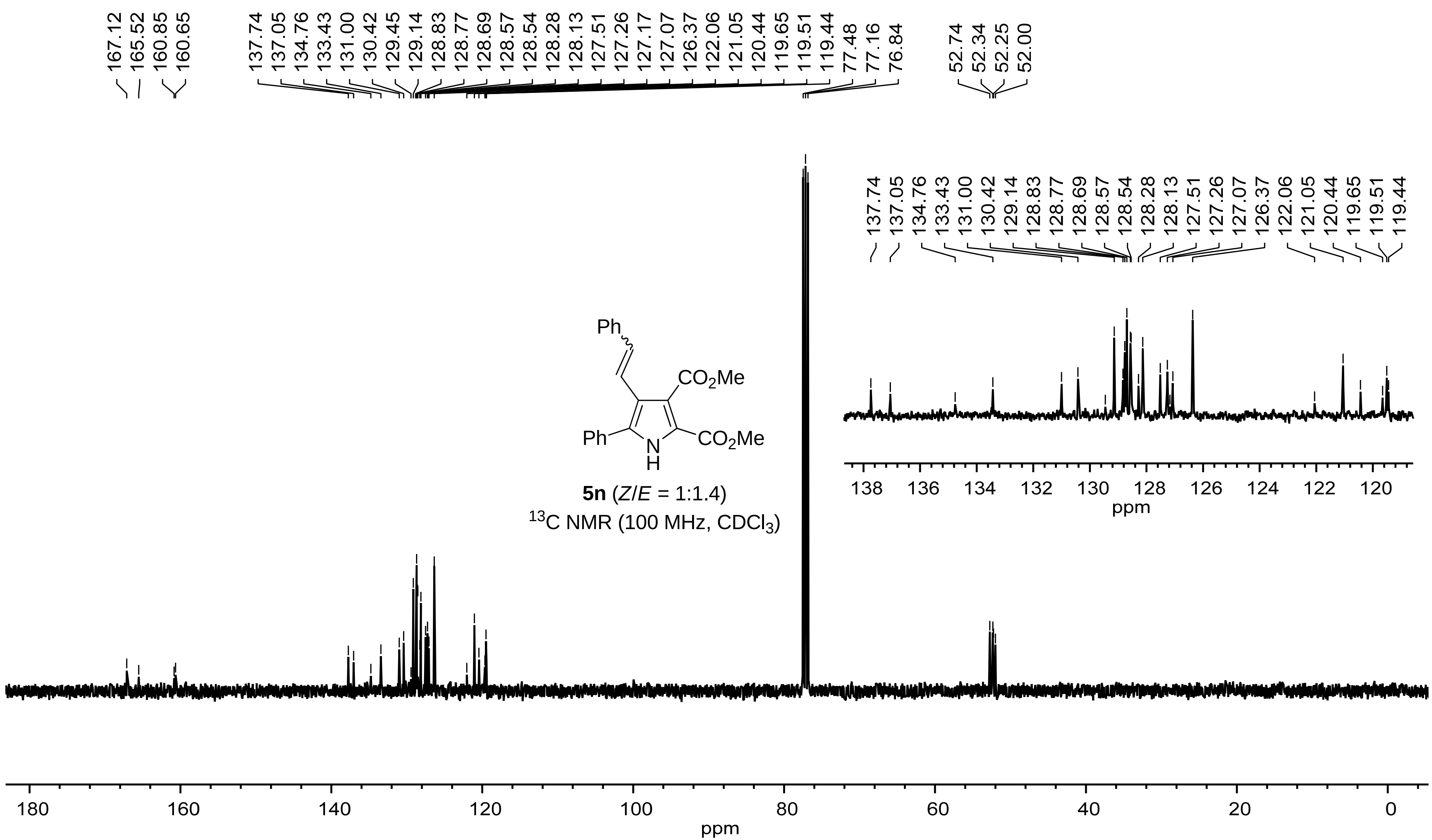
167.16
160.81
133.76
133.34
132.96
128.68
128.57
128.22
127.86
127.50
126.80
126.77
125.85
121.44
120.41
120.37
120.09
100.08
77.48
77.16
76.84
52.52
52.20
35.62
22.53
13.73
ⁿPr
CO2Me
CO2Me
N
H
5l
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm


9.47
7.50 7.49 7.49 7.47 7.44 7.43 7.42 7.42 7.40 7.38 7.38 7.37 7.36 7.26
6.31 6.30 6.30 6.27 6.26 6.26 5.91 5.90 5.88 5.87 5.86 5.84
3.91 3.79
2.16 2.16 2.14 2.14 2.12 2.11 2.10 2.09 2.09 1.02 1.00 0.98
-0.00
Et
CO2Me
CO2Me
N
H
5m
1H NMR (400 MHz, CDCl3)
1.00
2.03 2.12 1.02
1.00
1.00
3.06 3.08
2.05
3.05
10 9 8 7 6 5 4 3 2 1 0
ppm

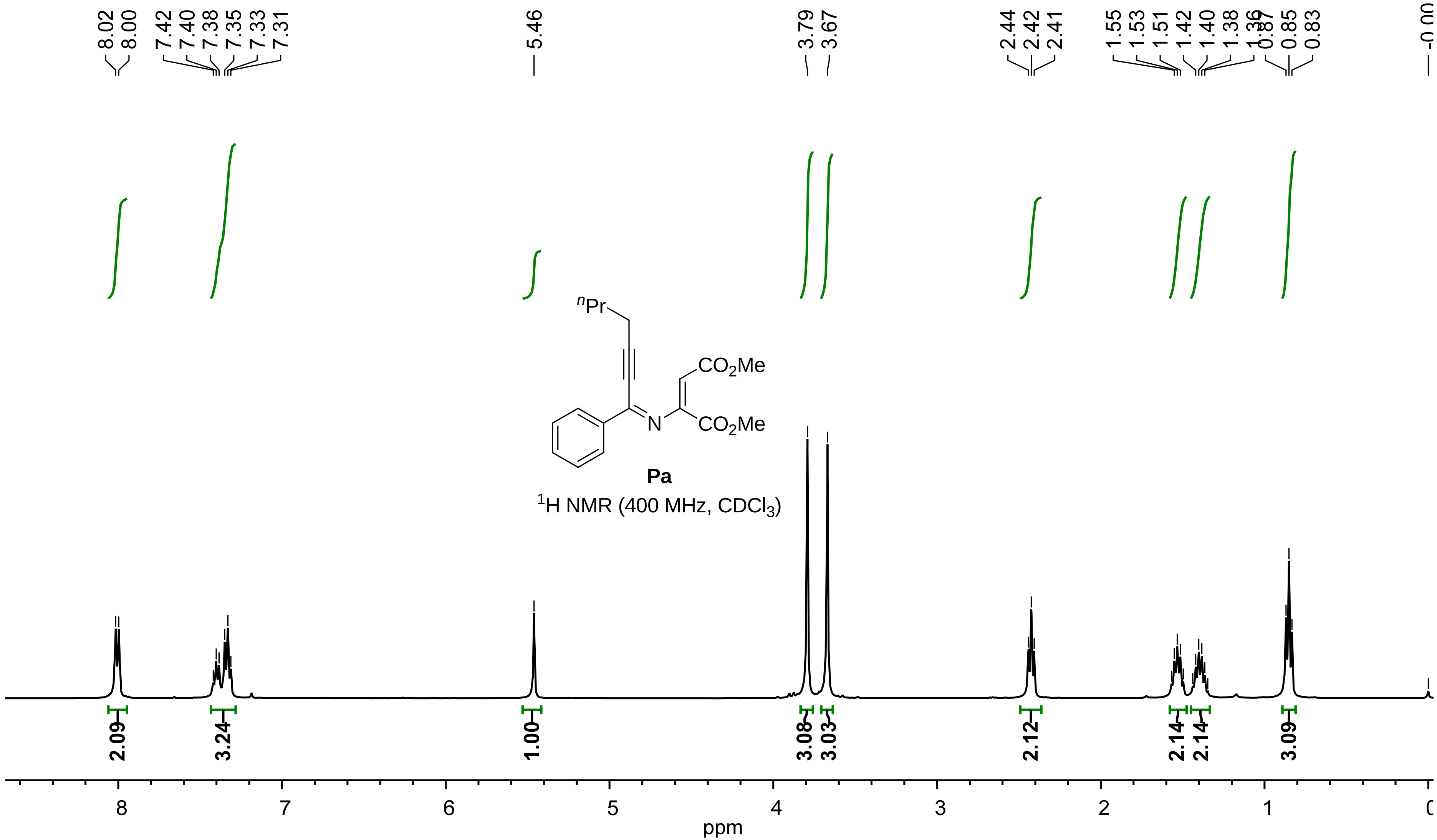

167.24
160.75
134.98
133.49
131.27
128.90
128.45
128.32
121.23
119.91
119.87
119.23
77.48
77.16
76.84
52.53
52.20
26.59
13.70
Et
CO2Me
CO2Me
N
H
5m
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
ppm

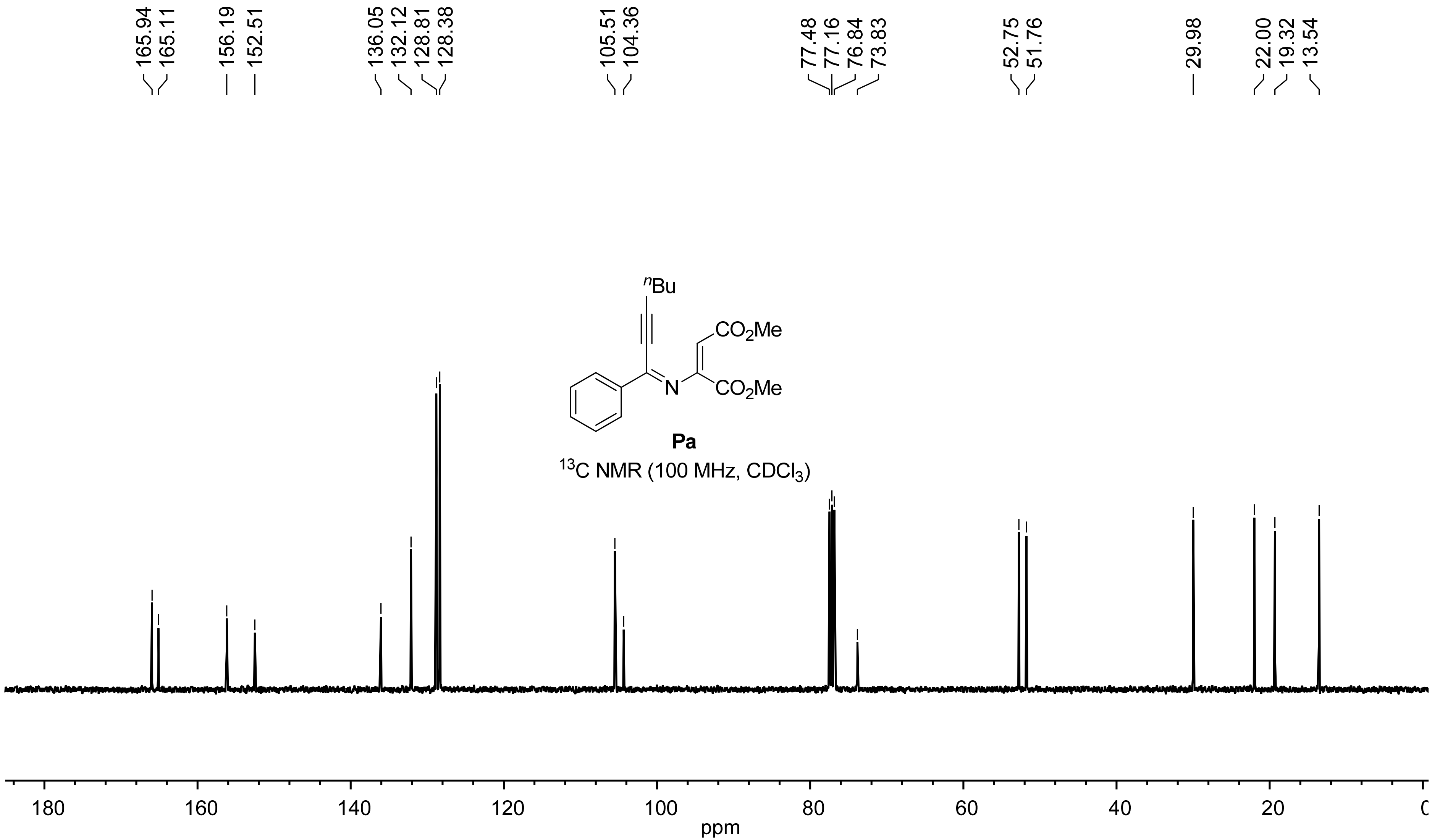


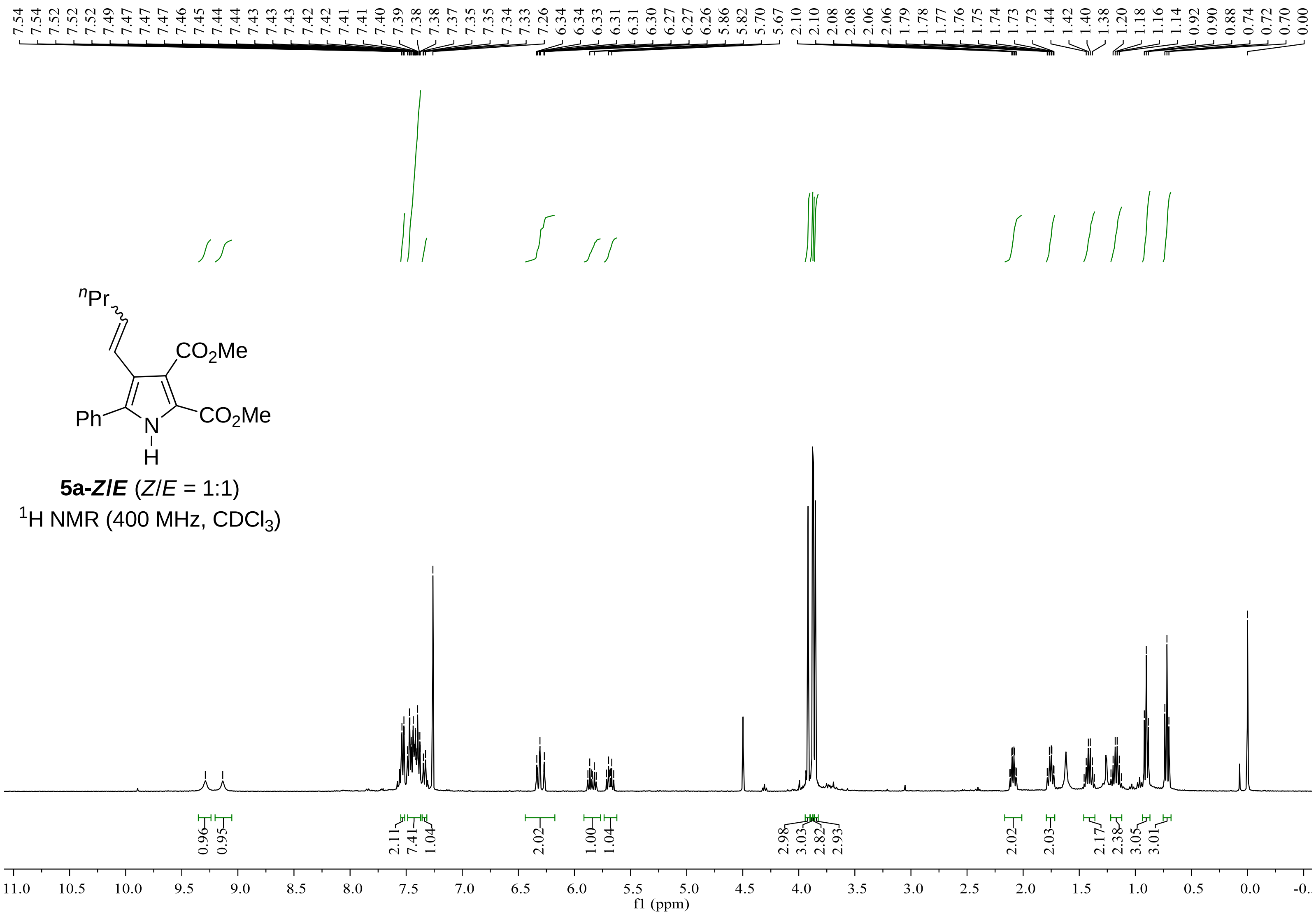
5n (*Z*/*E* = 1:1.4)
^{1}H NMR (400 MHz, $CDCl_3$)



5n (Z/E = 1:1.4)
^{13}C NMR (100 MHz, $CDCl_3$)

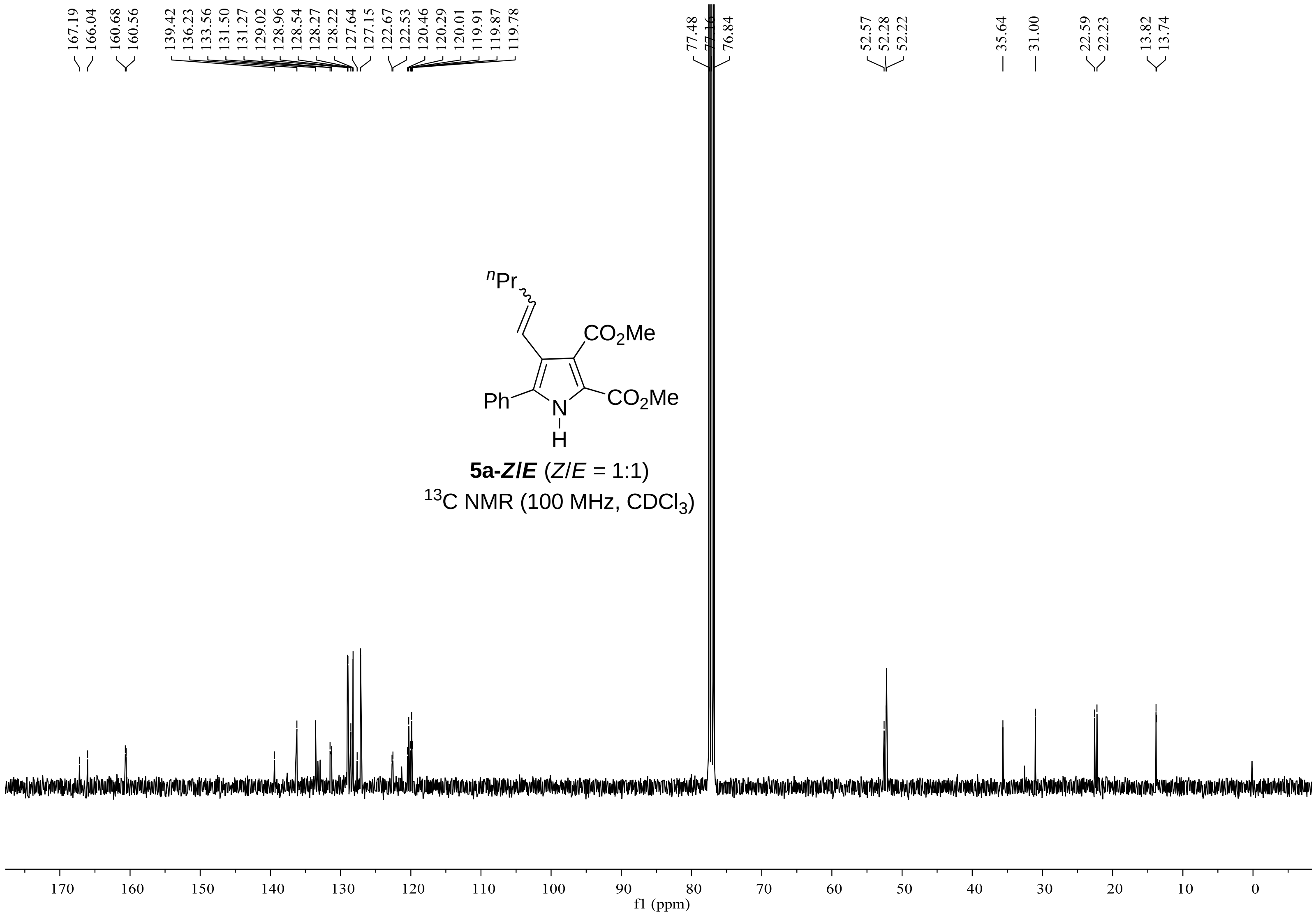

8.02
8.00
7.42
7.40
7.38
7.35
7.33
7.31
5.46
3.79
3.67
2.44
2.42
2.41
1.55
1.53
1.51
1.42
1.40
1.38
1.36
0.87
0.85
0.83
-0.00
nPr
CO2Me
N
CO2Me
Pa
1H NMR (400 MHz, CDCl3)
2.09
3.24
1.00
3.08
3.03
2.12
2.14
2.14
3.09
8
7
6
5
4
3
2
1
0
ppm


165.94
165.11
156.19
152.51
136.05
132.12
128.81
128.38
105.51
104.36
77.48
77.16
76.84
73.83
52.75
51.76
29.98
22.00
19.32
13.54
nBu
CO2Me
N
CO2Me
Pa
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
ppm

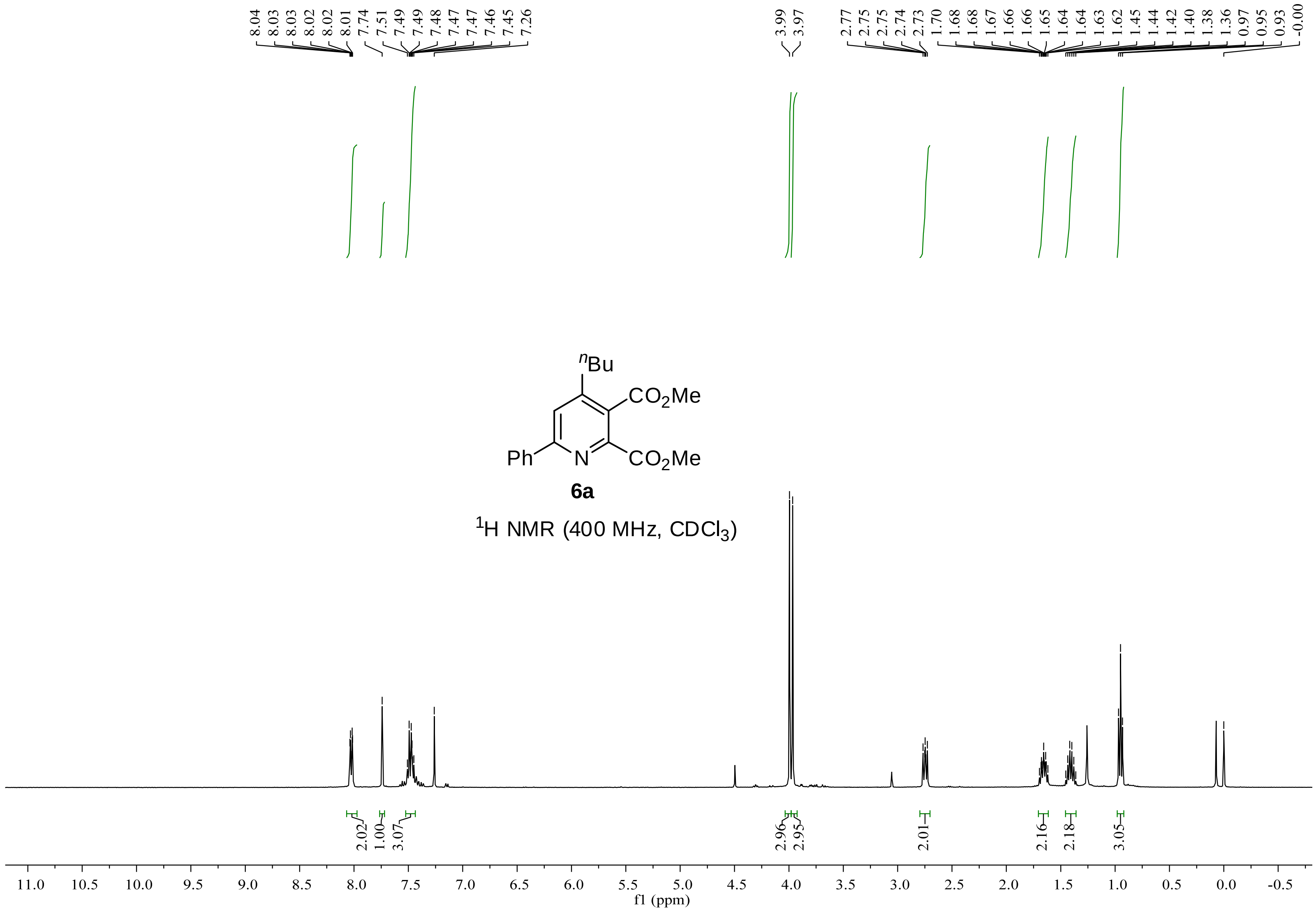


5a-*Z*/*E* (*Z*/*E* = 1:1)

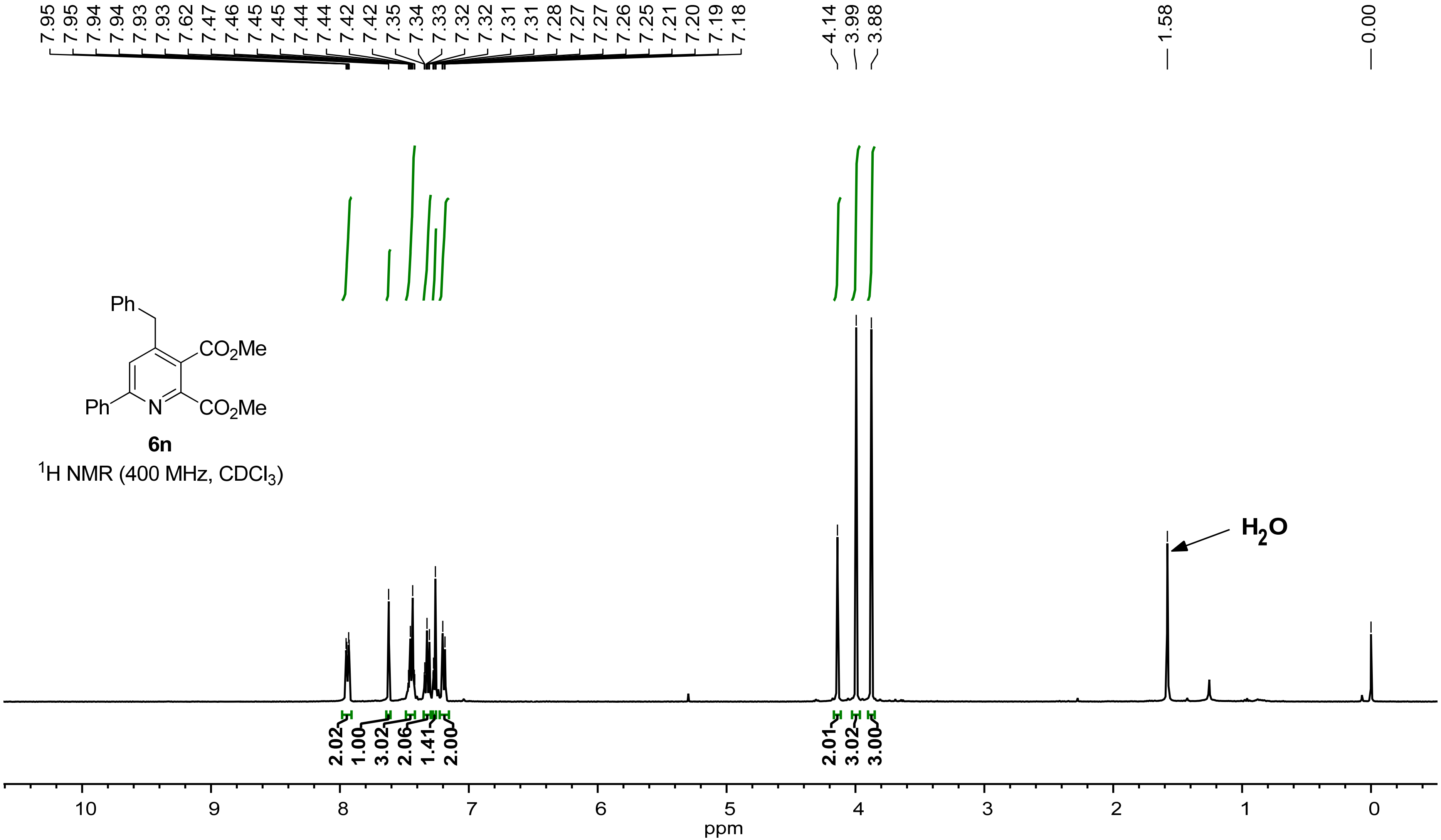
^{1}H NMR (400 MHz, $CDCl_3$)

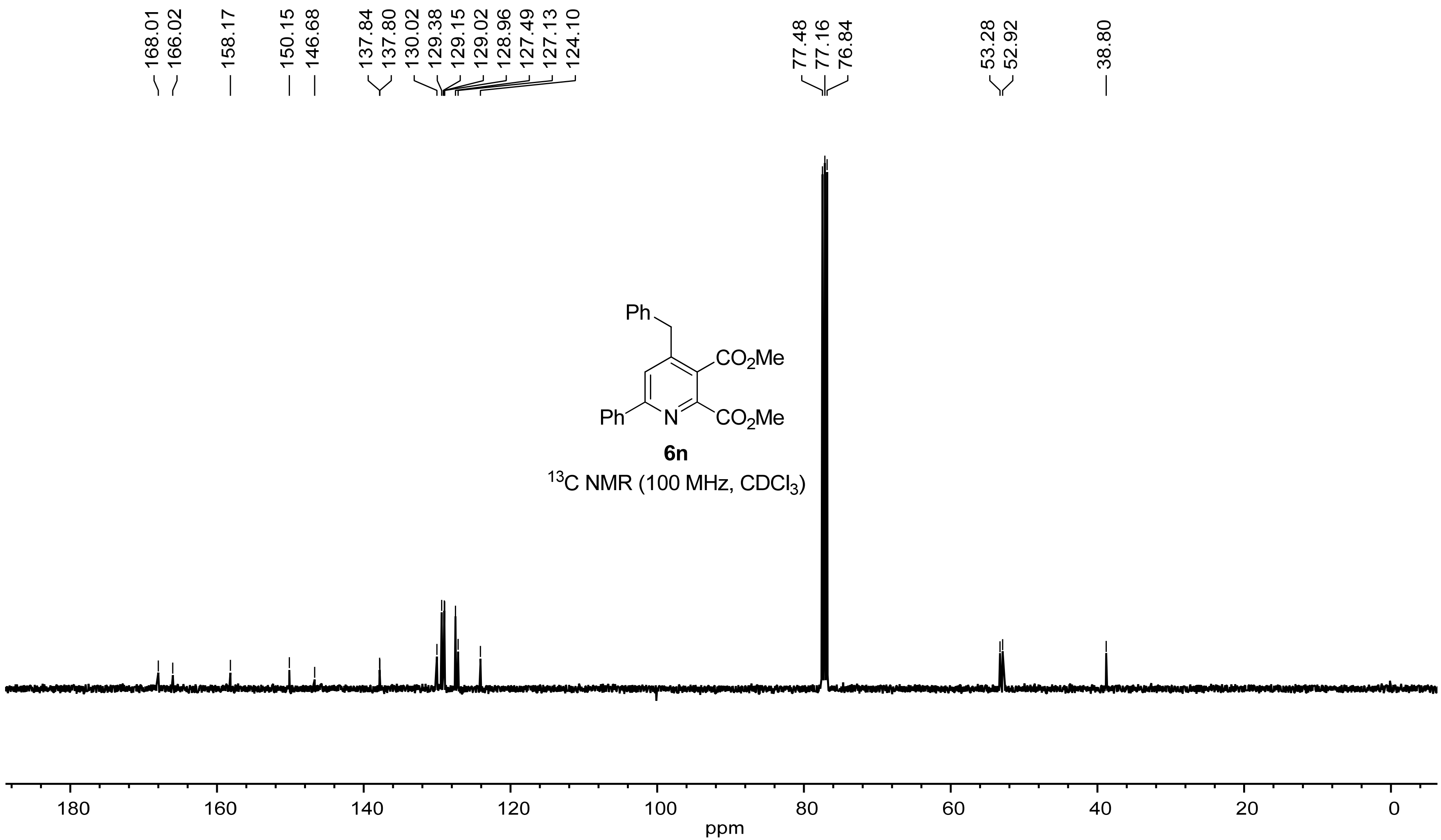


167.19
166.04
160.68
160.56
139.42
136.23
133.56
131.50
131.27
129.02
128.96
128.54
128.27
128.22
127.64
127.15
122.67
122.53
120.46
120.29
120.01
119.91
119.87
119.78
77.48
77.16
76.84
52.57
52.28
52.22
35.64
31.00
22.59
22.23
13.82
13.74
ⁿPr
CO2Me
CO2Me
Ph
N
H
5a-*Z*/*E* (*Z*/*E* = 1:1)
13C NMR (100 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



8.04 8.03 8.03 8.02 8.02 8.01 7.74 7.51 7.49 7.49 7.48 7.47 7.47 7.46 7.45 7.26
3.99 3.97
2.77 2.75 2.75 2.74 2.73 1.70 1.68 1.68 1.67 1.66 1.66 1.65 1.64 1.64 1.63 1.62 1.45 1.44 1.42 1.40 1.38 1.36 0.97 0.95 0.93 -0.00
^{n}Bu
CO2Me
CO2Me
Ph
N
6a
^{1}H NMR (400 MHz, $CDCl_3$)
2.02 1.00 3.07 2.96 2.95 2.01 2.16 2.18 3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.95
7.95
7.94
7.94
7.93
7.93
7.62
7.47
7.46
7.45
7.45
7.44
7.44
7.42
7.42
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.28
7.27
7.27
7.26
7.25
7.21
7.20
7.19
7.18
4.14
3.99
3.88
1.58
0.00
Ph
CO2Me
Ph
N
CO2Me
6n
1H NMR (400 MHz, CDCl3)
H2O
2.02
1.00
3.02
2.06
1.41
2.00
2.01
3.02
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

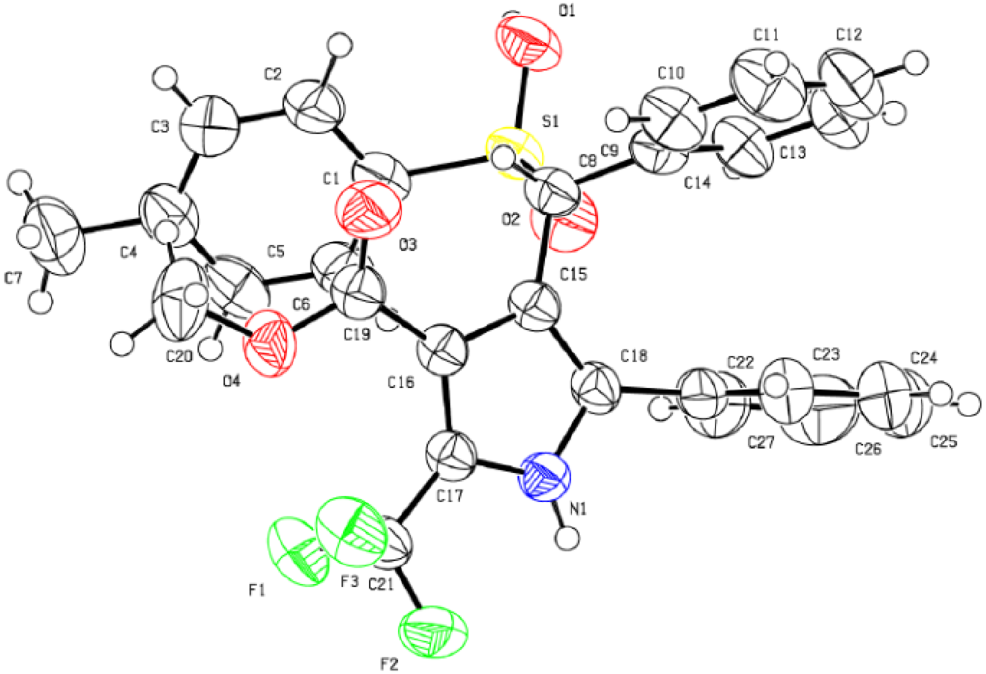


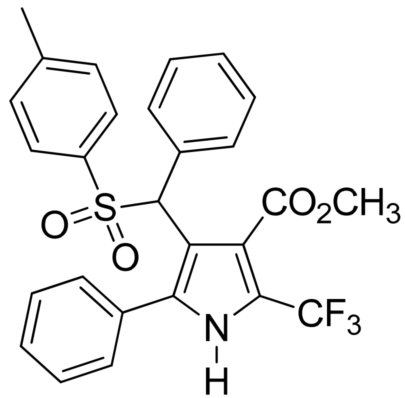
6n

^{13}C NMR (100 MHz, $CDCl_3$)

2. Crystal Structures of 3a and 5m

Molecular structure of **3a** with thermal ellipsoids at the 50% probability level.



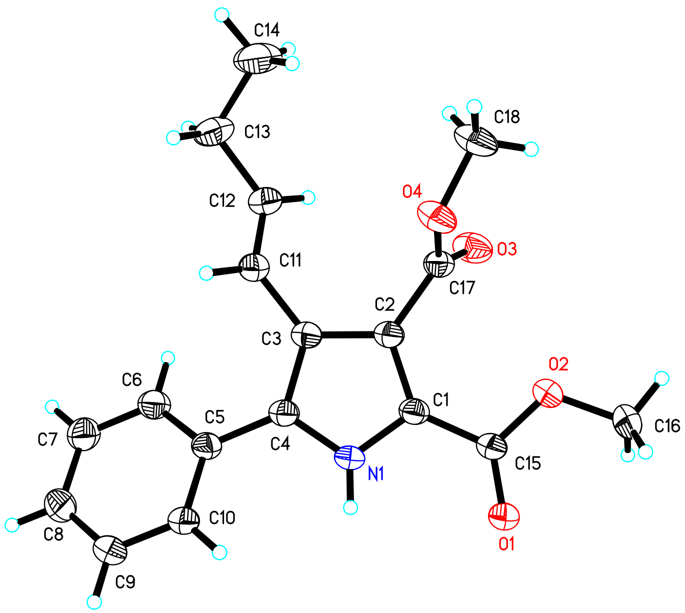


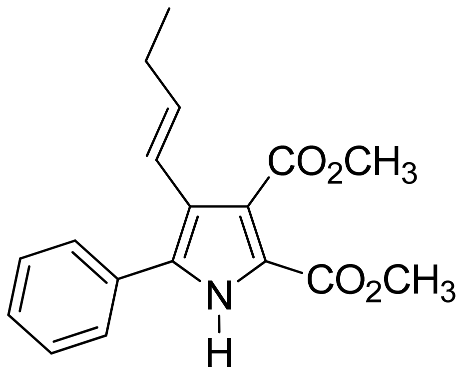
3a

CCDC 962702

CCDC 962702 (**3a**) contains the supplementary crystallographic data for this paper. These datacan be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Molecular structure of **5m** with thermal ellipsoids at the 50% probability level.





5m

CCDC 978572

CCDC 978572 (**5m**) contains the supplementary crystallographic data for this paper. These datacan be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Procedures for Calculating the HPLC Yields

Take the procedure for calculating the HPLC yields of product **3a** (Table 3 in the main text) for example:

HPLC conditions: instrument: Agilent 1200 series; column: Extend-C18, 5 μm, 4.6 × 150 mm; eluent: H_2O/MeCN = 45/55, 1 mL/min; UV detector wavelength: 254 nm; inject volume: 5 μL; constant temperature: 25 °C.

Step 1: calculating the standard curve equation (the relationship between the ratio of HPLC peak area with the weight of the desired product). We prepared the pure product **3a** beforehand. To four reaction tubes, marked as No. 1, No. 2, No. 3, and No. 4, we added 10.0, 25.0, 40.0, and 55.0 mg **3a**, respectively. Then to each of these four tubes, we added 30.0 mg naphthalene as internal standard, and each sample was diluted with 10.5 mL acetonitrile. After homogeneous mixing, the samples were then analyzed with HPLC. The ratio of $A_{\mathbf{3a}}/A_{nap}$ could be calculated based on the peak areas of **3a** and naphthalene ($A_{\mathbf{3a}}$: peak area of **3a**; A_{nap}: peak area of naphthalene). The results are described as the below table ($m_{\mathbf{3a}}$: the weight of **3a**; m_{nap}: the weight of naphthalene):

Experiment No.	$m_{\mathbf{3a}}$ (mg)	m_{nap} (mg)	$m_{\mathbf{3a}}/m_{nap}$	$A_{\mathbf{3a}}/A_{nap}$
No. 1	10.0	30.0	0.3333	0.3547
No. 2	25.0	30.0	0.8333	0.8632
No. 3	40.0	30.0	1.3333	1.3553

No. 4	55.0	30.0	1.8333	1.8699

According the equation: $m_{\mathbf{3a}}/m_{nap} = f \times (A_{\mathbf{3a}}/A_{nap})$, and base on the results in the above table, we could calculate that f = 0.9780. Therefore, the standard curve equation was: $m_{\mathbf{3a}}/m_{nap} = 0.9780 \times (A_{\mathbf{3a}}/A_{nap})$. Thus, $m_{\mathbf{3a}} = 0.9780 \times m_{nap} \times (A_{\mathbf{3a}}/A_{nap})$.

Step 2: carrying out the experiments in Table 3 of the main text. After termination of the reactions, the samples were cooled down to room temperature. To each reaction tube, 30.0 mg naphthalene (as internal standard) and 10.0 mL acetonitrile were added. After homogeneous mixing, the samples were then analyzed with HPLC. The ratio value of $A_{\mathbf{3a}}/A_{nap}$ of each sample could be calculated based on the peak areas of **3a** and naphthalene.

Step 3: calculating the HPLC yields. After putting the numerical value of $A_{\mathbf{3a}}/A_{nap}$ in to the equation $m_{\mathbf{3a}} = 0.9780 \times m_{nap} \times (A_{\mathbf{3a}}/A_{nap})$, we could get the calculated weight of **3a**. Thus, the yield was calculated as following: **3a**% = $(m_{\mathbf{3a}}/m_{theo}) \times 100\% = 0.9780 \times (m_{nap}/m_{theo}) \times (A_{\mathbf{3a}}/A_{nap}) \times 100\%$ (*note*: m_{theo} was the theoretical weight of **3a** in 100% yield).

One example: take the experiment of entry 2, Table 3 in the main text for example: the ration of $A_{\mathbf{3a}}/A_{nap}$ was 0.8463, $m_{nap} = 30.0$, $m_{theo} = 51.4$ (in 0.1 mmol scale). Thus, the HPLC yield of **3a** was following:

3a% = $0.9780 \times (m_{nap}/m_{theo}) \times (A_{\mathbf{3a}}/A_{nap}) \times 100\% = 0.9780 \times (30.0/51.4) \times 0.8463 \times 100\% = 48.3083\% \approx 48\%$.