Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Data

CHEMOSELECTIVE FLOW HYDROGENATION APPROACHES TO HIGHLY DECORATED 7-OXA-BICYCLIO[2.2.1]HEPTANES

Lacey Hizartzidis,[a] Mark Tarleton,[a] Christopher P. Gordon[a] and Adam McCluskey[a,*]

[a]*Chemistry, Centre for Chemical Biology, The University of Newcastle, University Drive, Callaghan, NSW 2308 Australia.*

* Corresponding author. Tel: +61 249 216486; Fax: +61 249 215472.

E-mail address: Adam.McCluskey@newcastle.edu.au

Supporting Information

1. GCMS Data

Gas chromatography-mass spectrometry (GC-MS) was performed using a Schimadzu GC-MS QF2010 EI/NCI System fitted with a ZB-5MS column [30 m x 0.25 mm], 5% phenylarylene stationary phase. The injector temperature was set at 250 °C and an oven program starting at 160 °C, with a hold time of 1 min. The temperature was then rapidly increased to 230 °C (35 °C/min) and it was held for 18.5 – 22 min. The flow rate was set at 23mL/min, with a column flow rate of 0.95 mL/min.

Table i: Details of compounds including molecular weight and retention times observed in GC-MS traces (Fig 1-32).

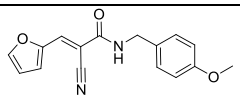
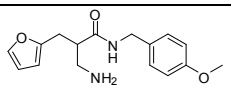
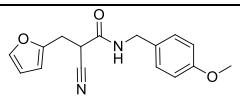
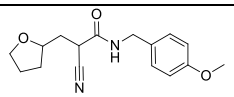
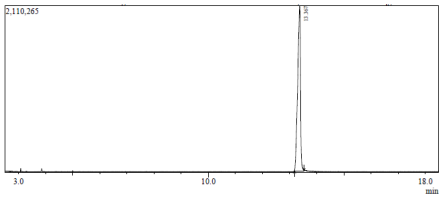
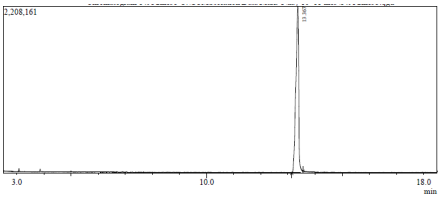
Compound	Structure	Retention Time (mins)
22a	 Chemical Formula: $C_{16}H_{14}N_2O_3$ Molecular Weight: 282.29	15.46
23a	 Chemical Formula: $C_{16}H_{20}N_2O_3$ Molecular Weight: 288.34	13.19
25a	 Chemical Formula: $C_{16}H_{16}N_2O_3$ Molecular Weight: 284.31	10.09
28a	 Chemical Formula: $C_{16}H_{20}N_2O_3$ Molecular Weight: 288.34	13.28

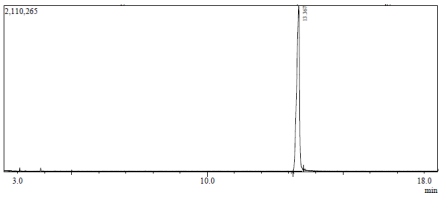
Table S2. Optimisation of temperature and H_2 pressure, for the reduction of **22a** to **25a** and **28a** and using a 10% Pd/C hydrogenation catalyst at 1.0 mL.min^{-1} flow rate. Reactions were conducted for 10 minutes and analysed using GC-MS.



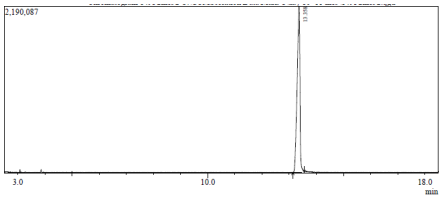
A. Entry 1, Table 2



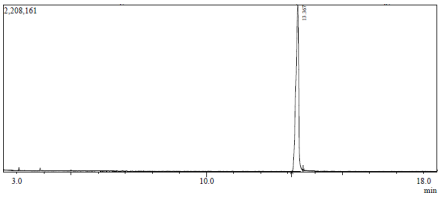
B. Entry 2, Table 2



C. Entry 3, Table 2



D. Entry 4, Table 2



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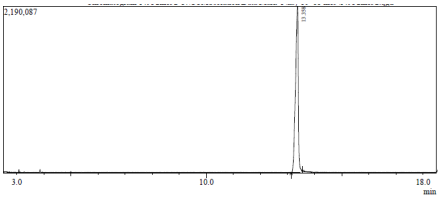

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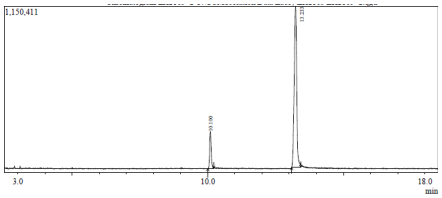
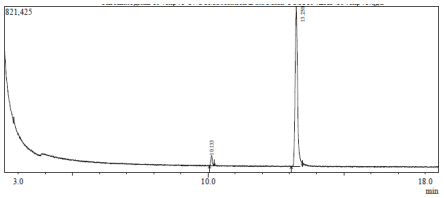
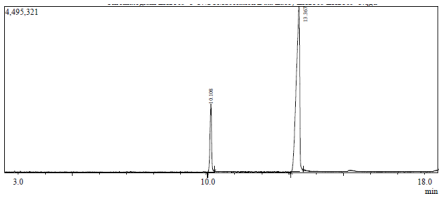


G. Entry 7, Table 2



H. Entry 8, Table 2



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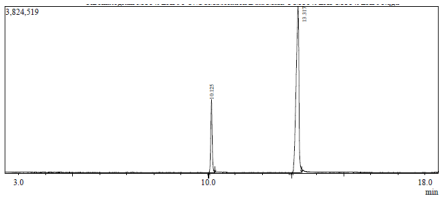
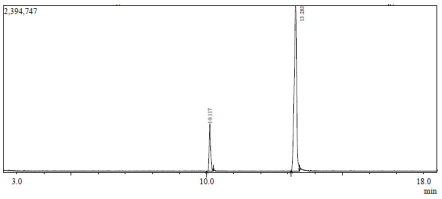
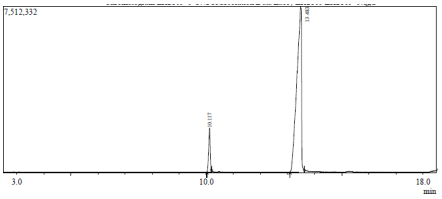


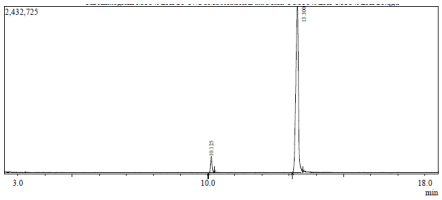
J. Entry 10, Table 2



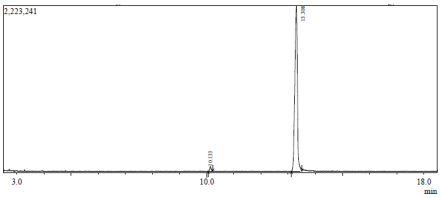
K. Entry 11, Table 2



L. Entry 12, Table 2



M. Entry 13, Table 2



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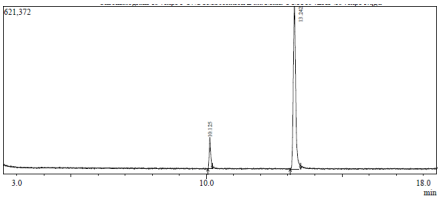
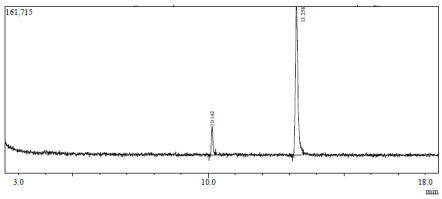
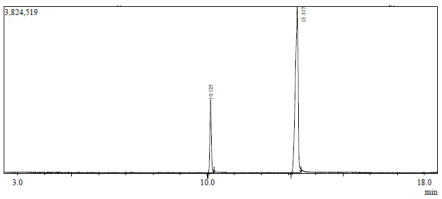


O. Entry 15, Table 2

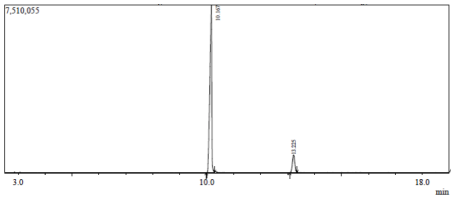


P. Entry 16, Table 2

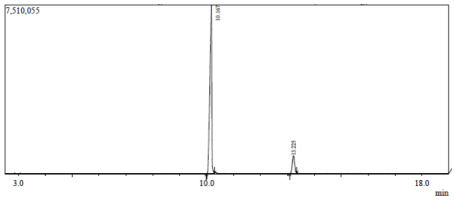


Q. Entry 17, Table 2

Table 3. Optimisation of the reduction of **22a** to **25a**. Reactions were conducted at flow rates of 1.33 – 8 mL.min^{-1}, 25 ºC, 10 bar $^{H}_{2}$ and analysed using GC-MS.



A. Entry 1, Table 3



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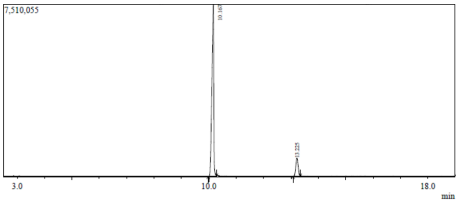
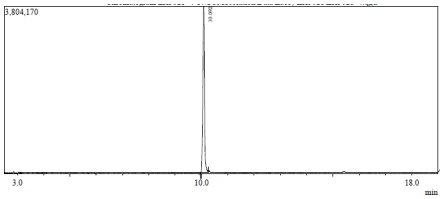


C. Entry 3, Table 3



D. Entry 4, Table 3

Table S5: Details of compounds including molecular weight and retention times observed in GC-MS traces.

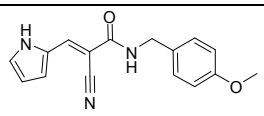
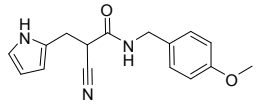
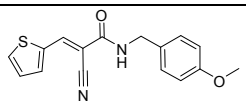
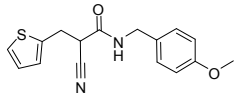
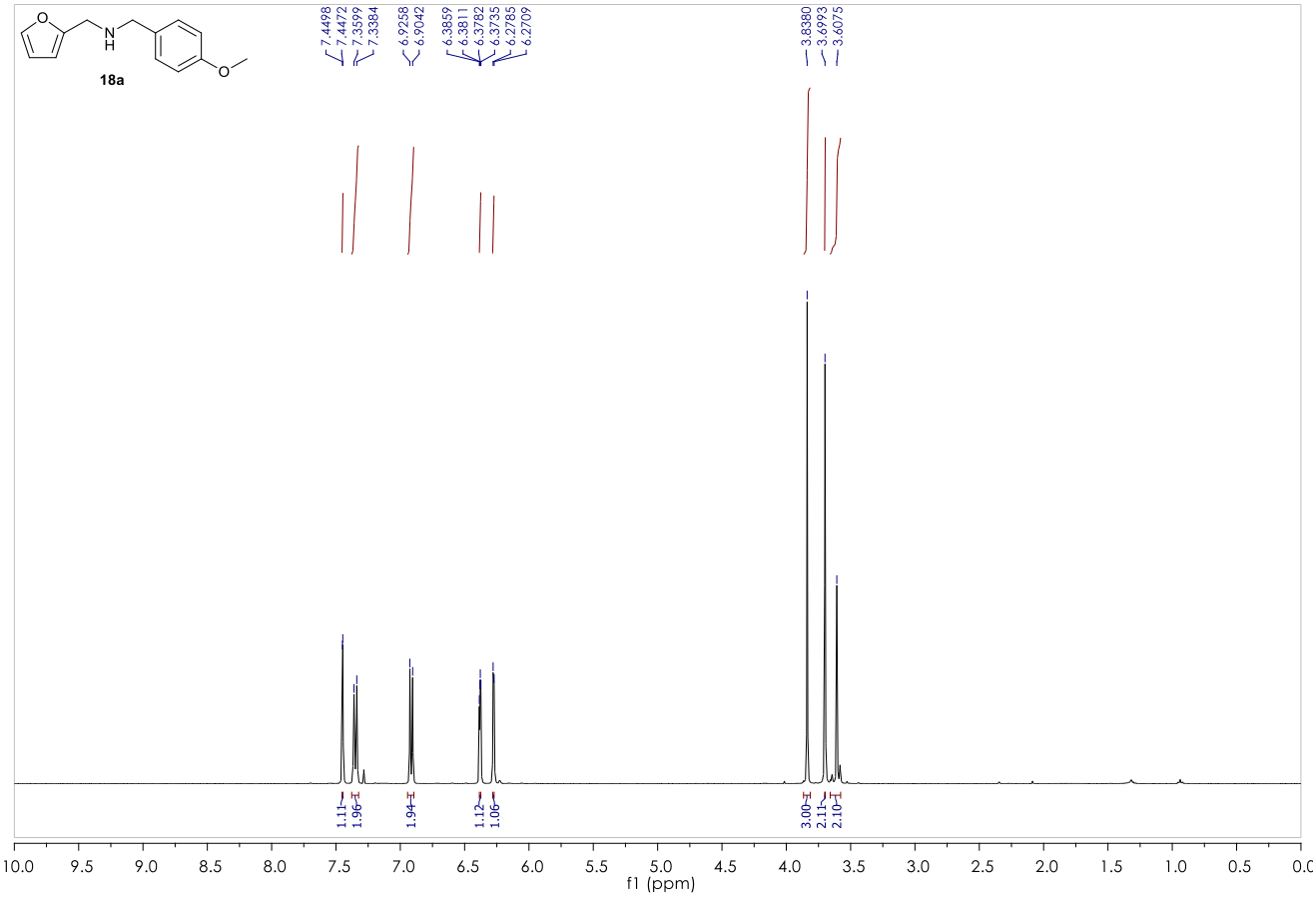
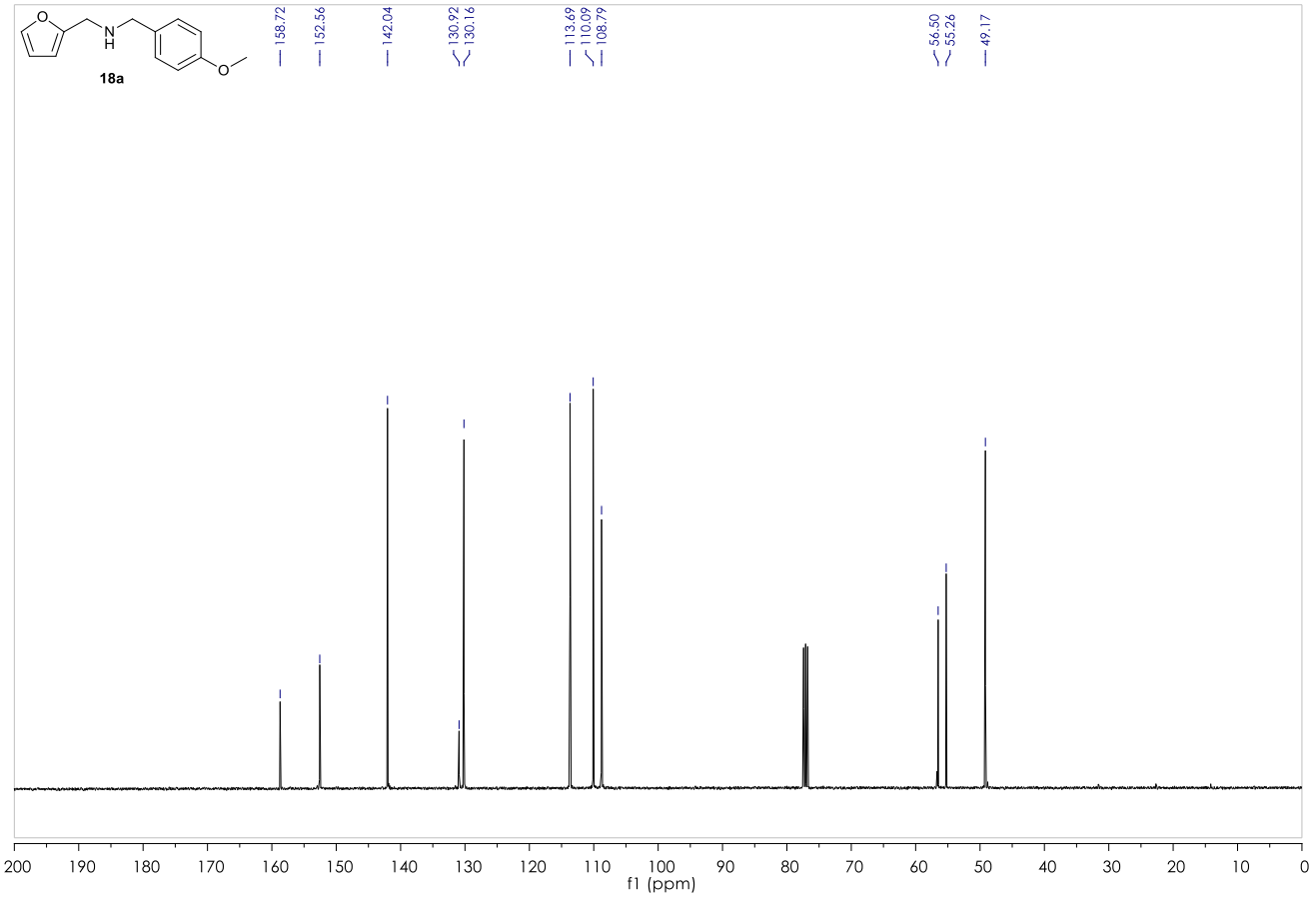
Compound	Structure	Retention Time (mins)
31	 Chemical Formula: $C_{16}H_{15}N_3O_2$ Molecular Weight: 281.31	19.08
33	 Chemical Formula: $C_{16}H_{17}N_3O_2$ Molecular Weight: 283.33	14.11

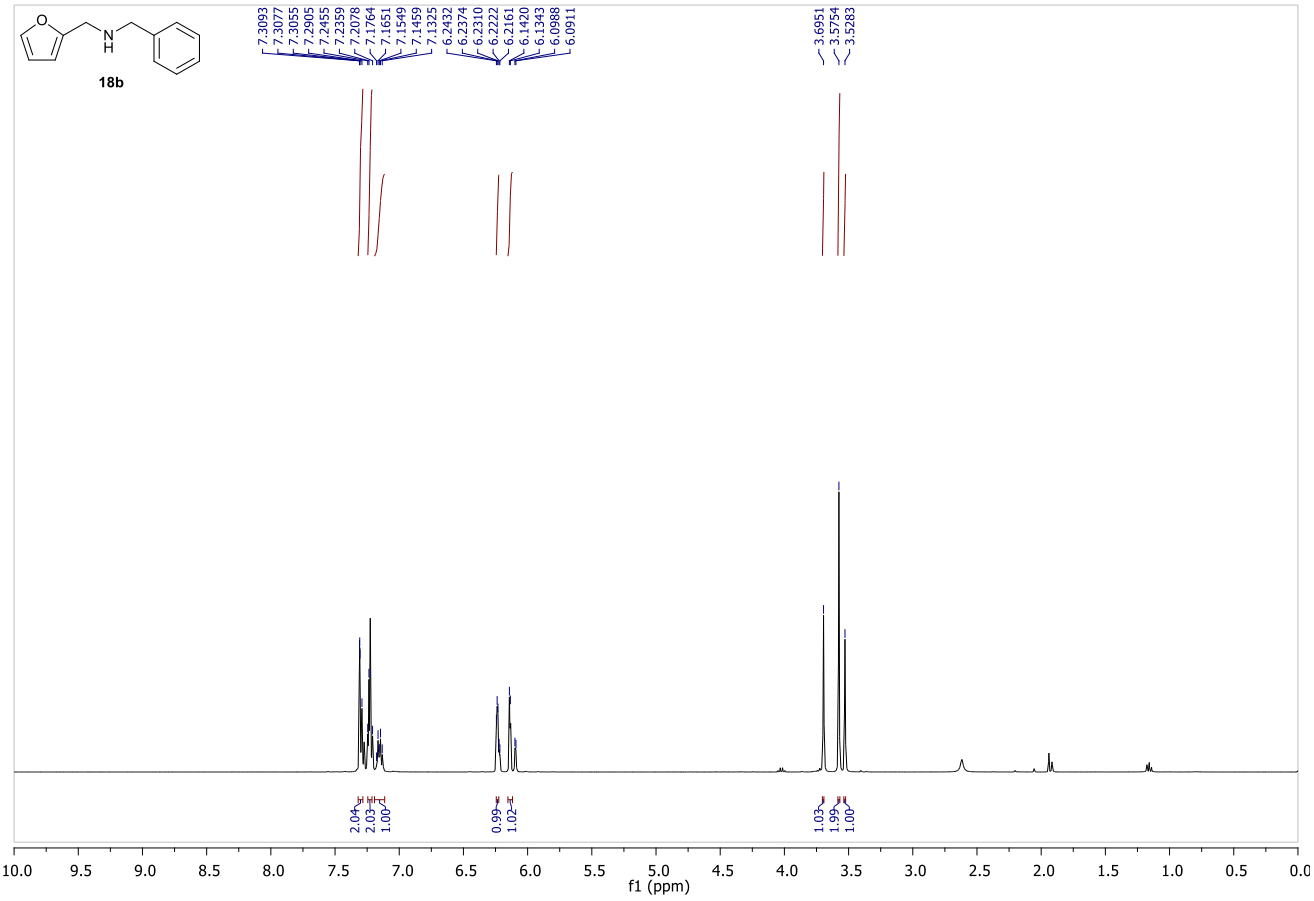
Table S6: Details of compounds including molecular weight and retention times observed in GC-MS traces (Fig 34).

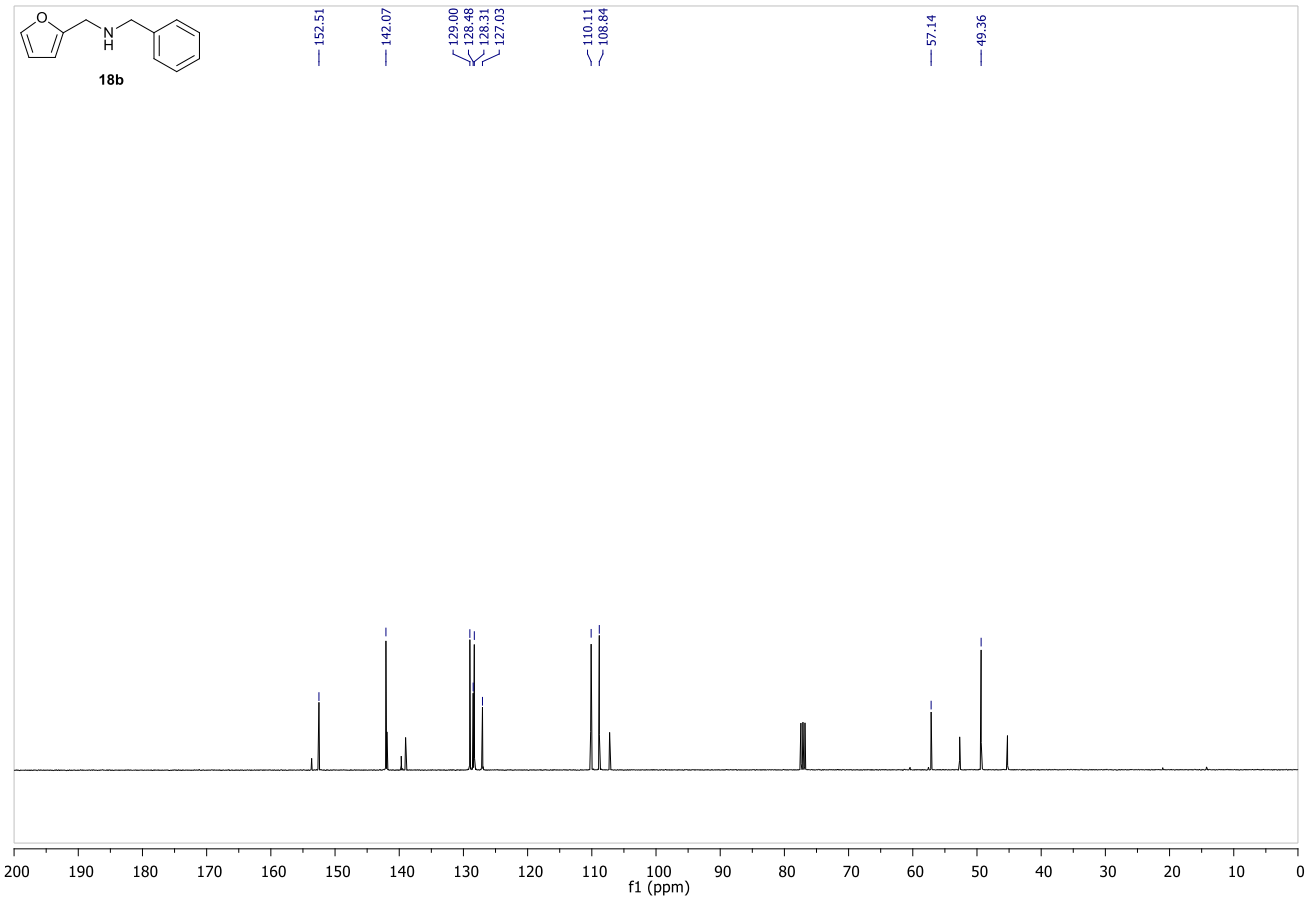
Compound	Structure	Retention Time (mins)
32	 Chemical Formula: $C_{16}H_{14}N_2O_2S$ Molecular Weight: 298.36	8.19
34	 Chemical Formula: $C_{16}H_{16}N_2O_2S$ Molecular Weight: 300.38	16.11

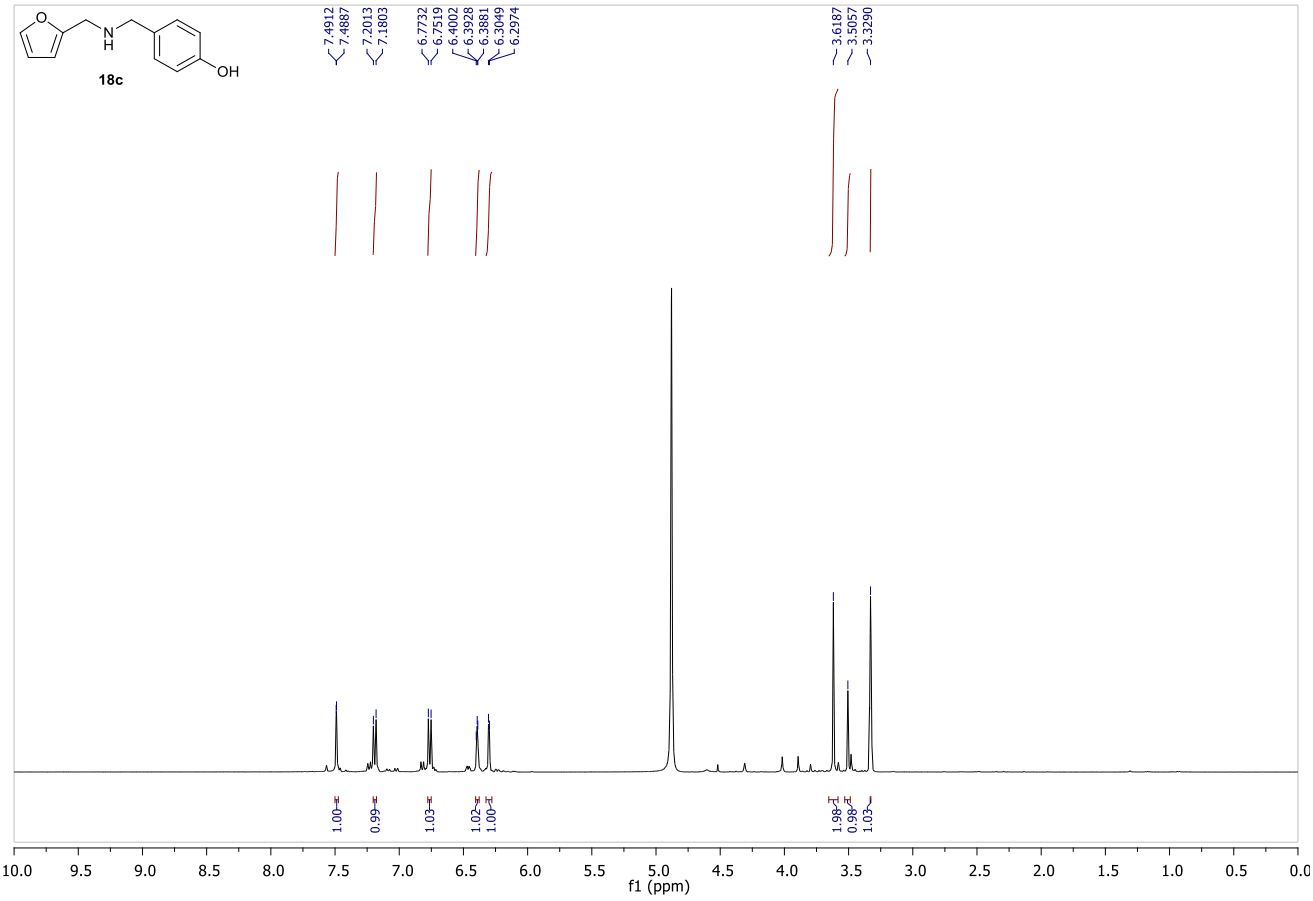
NMR Spectra

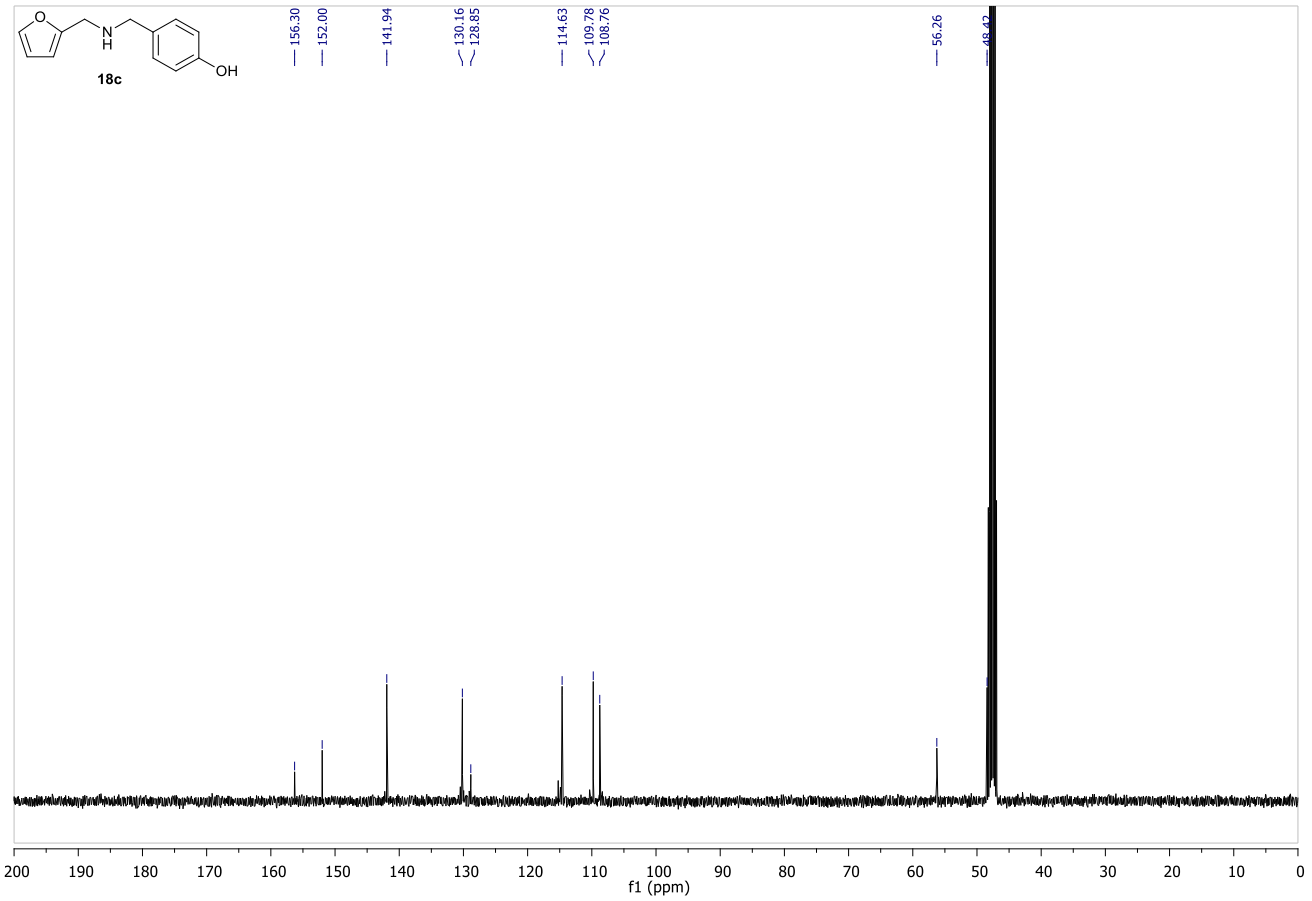


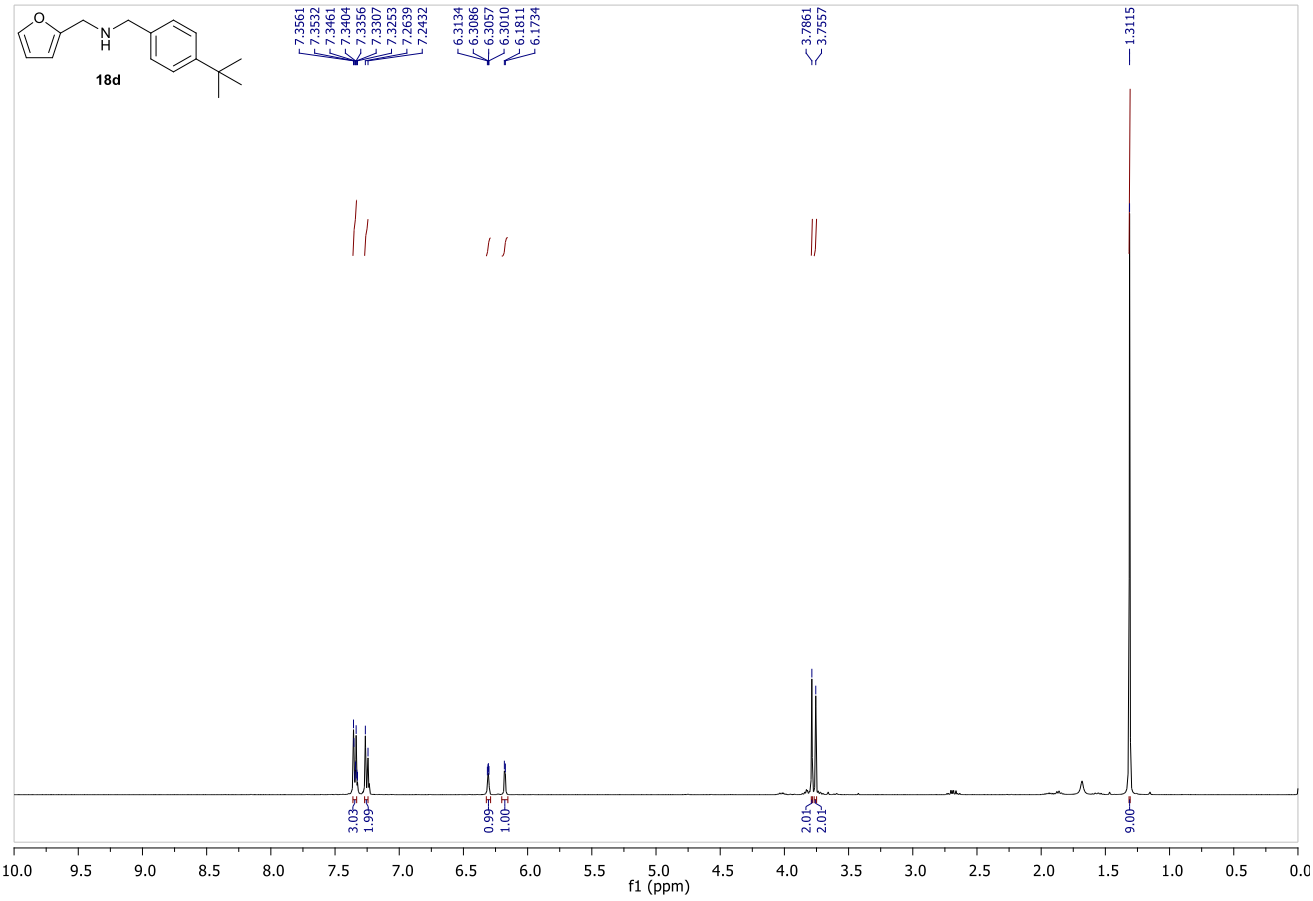


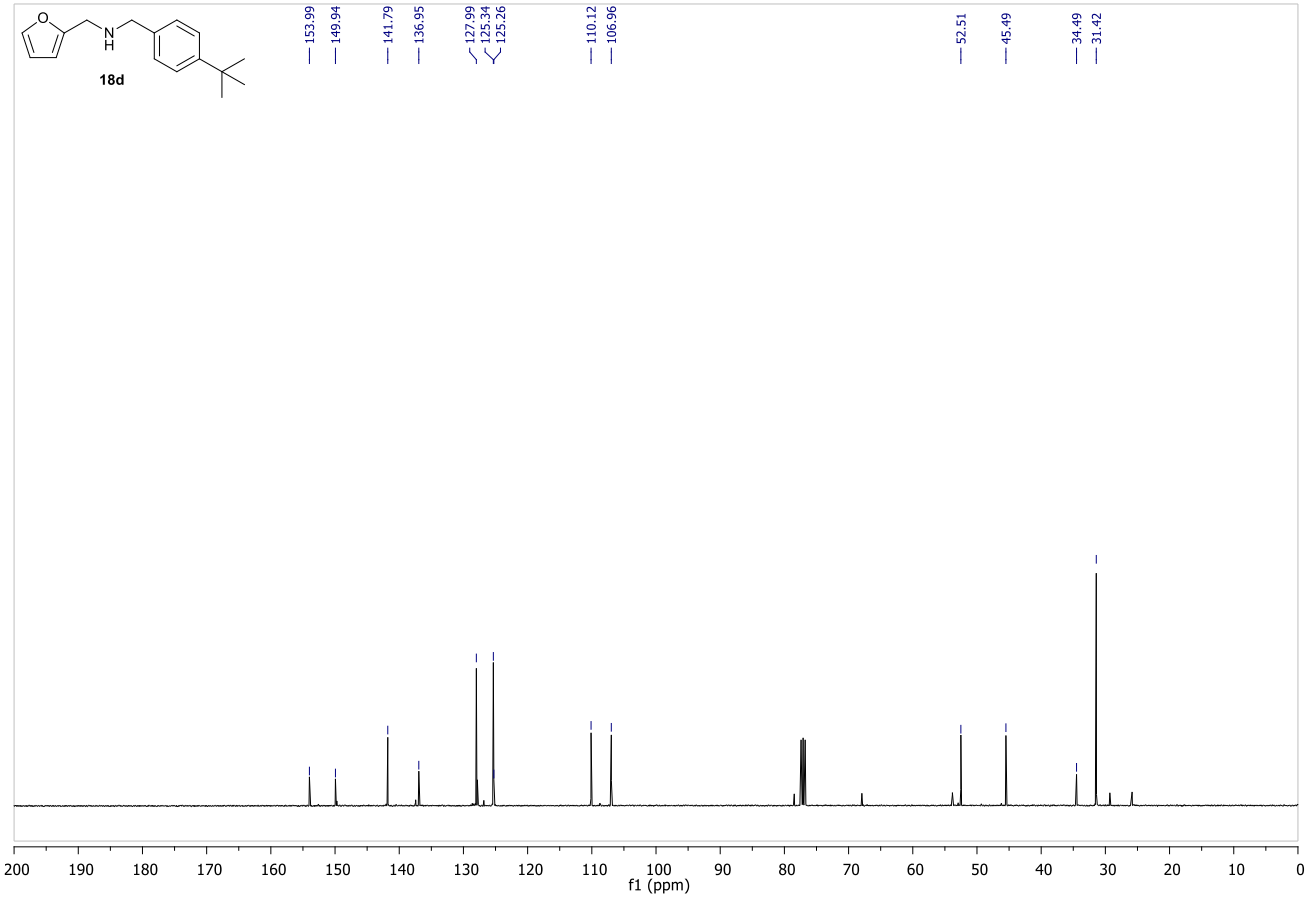


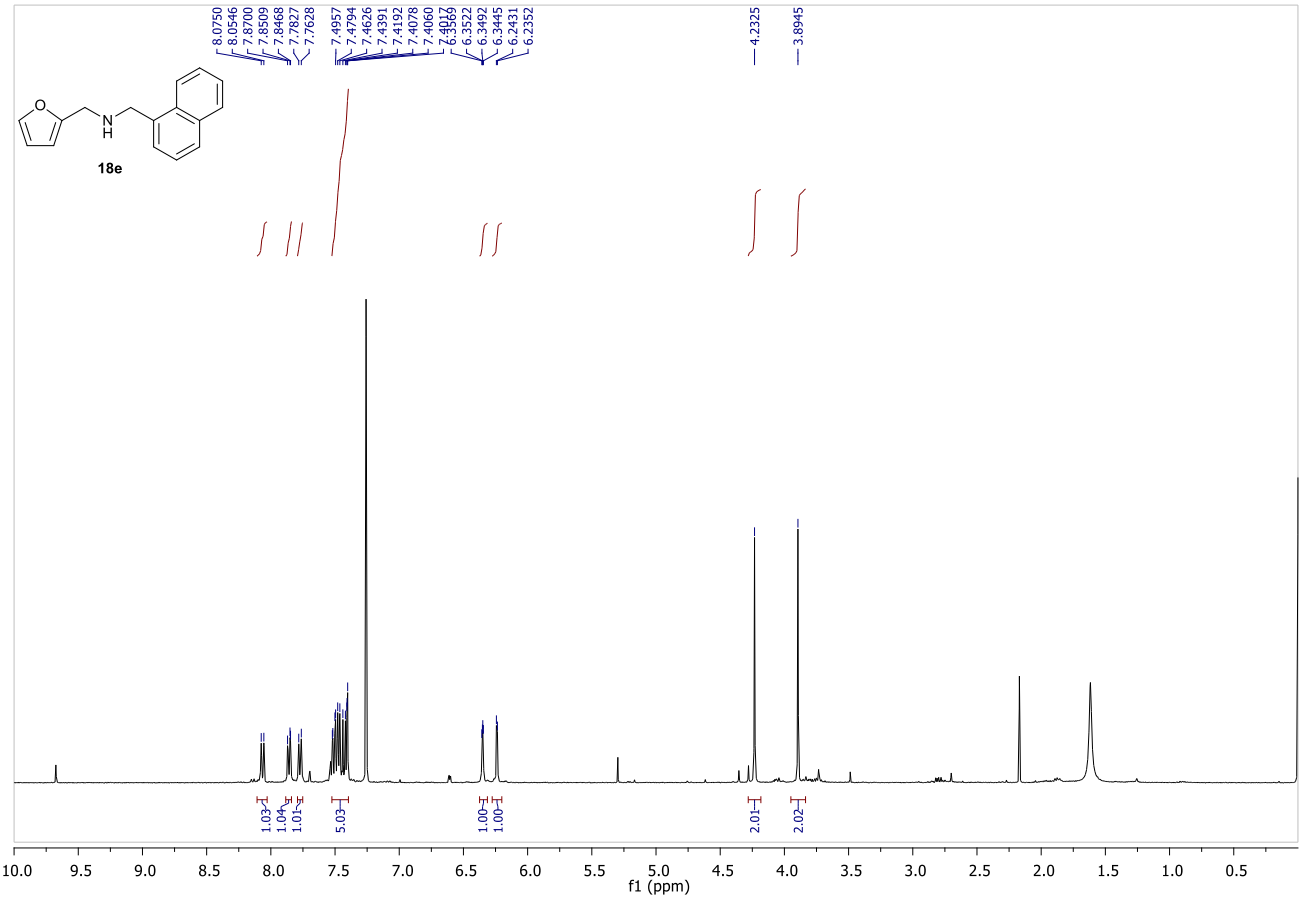


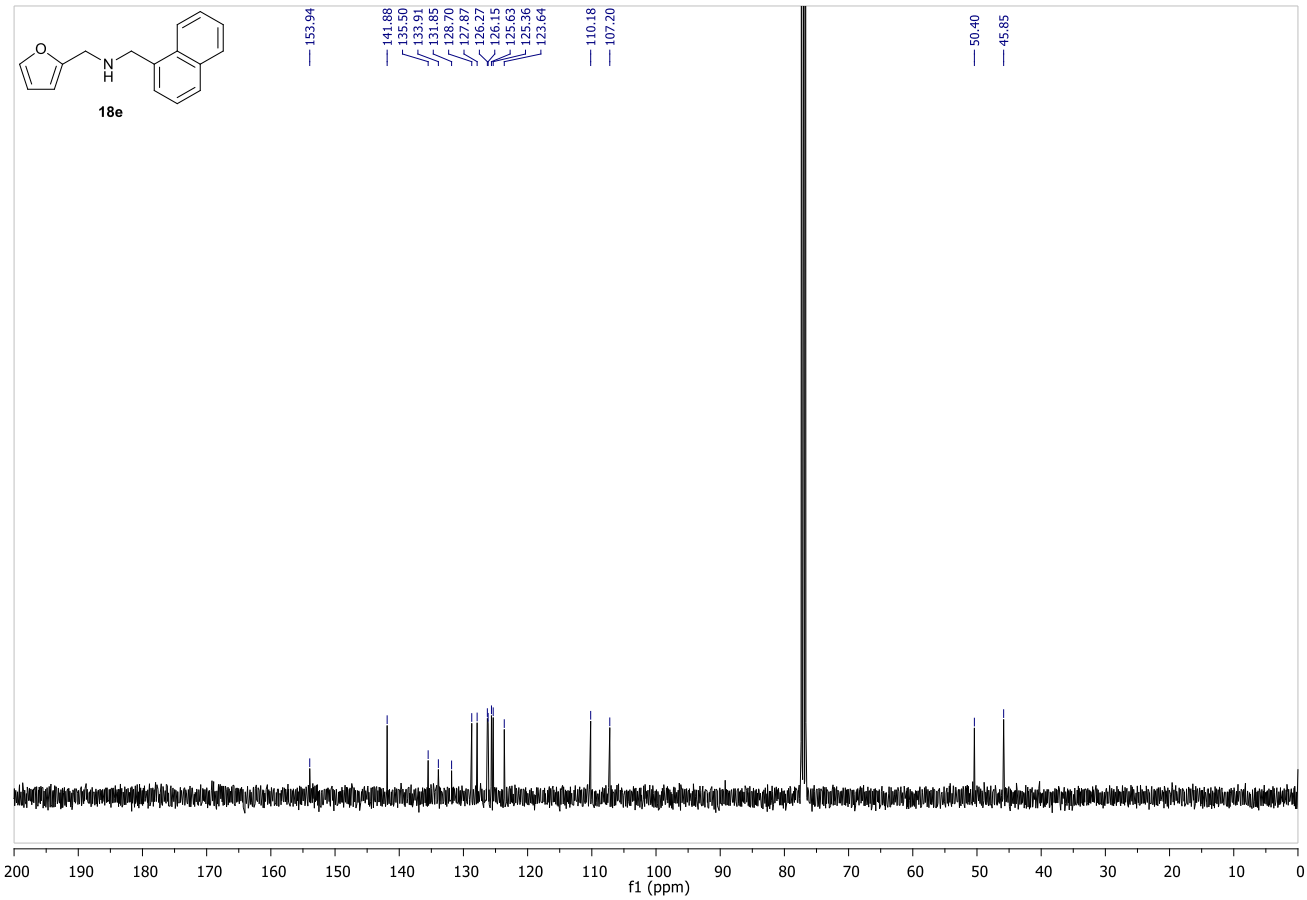


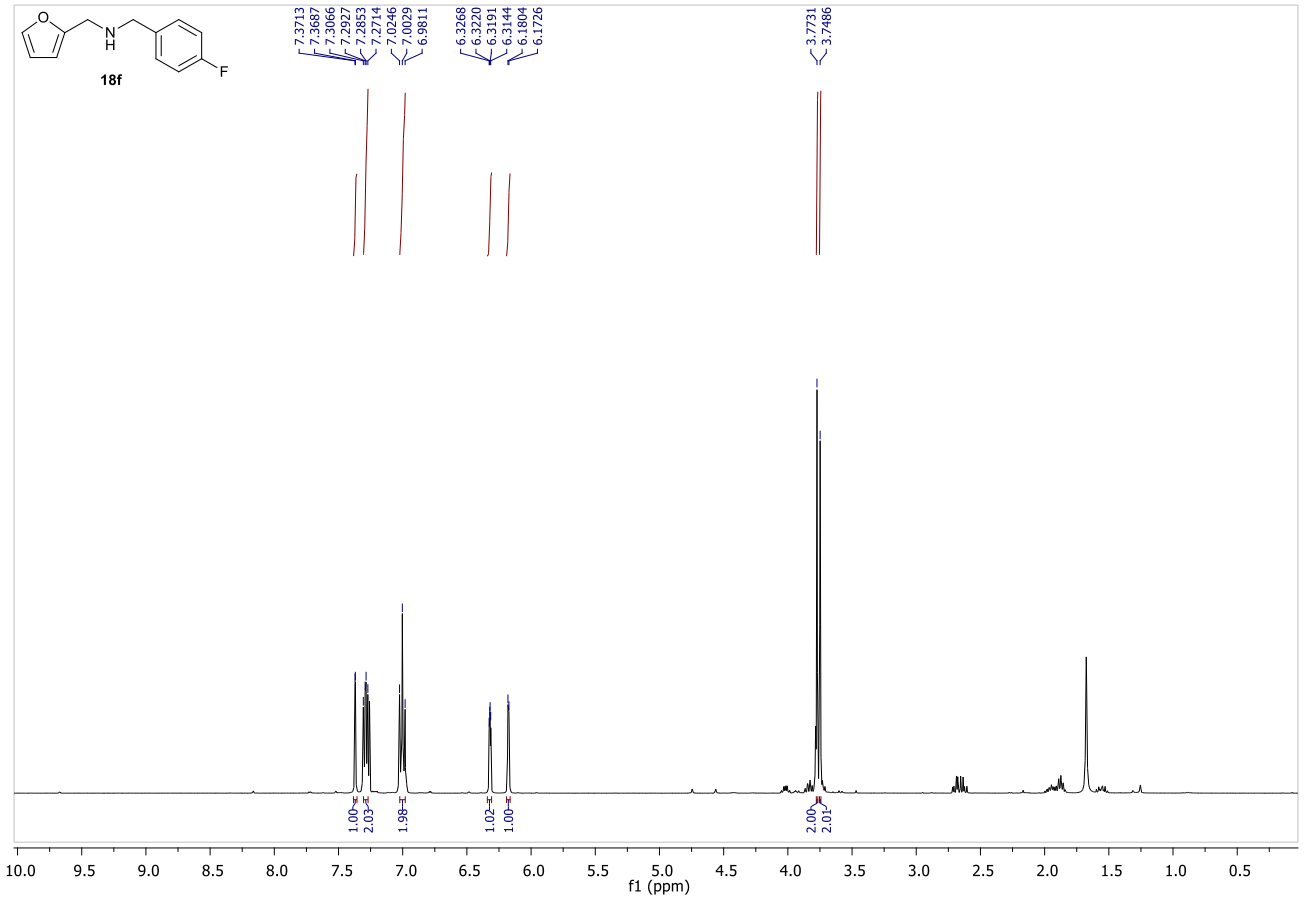


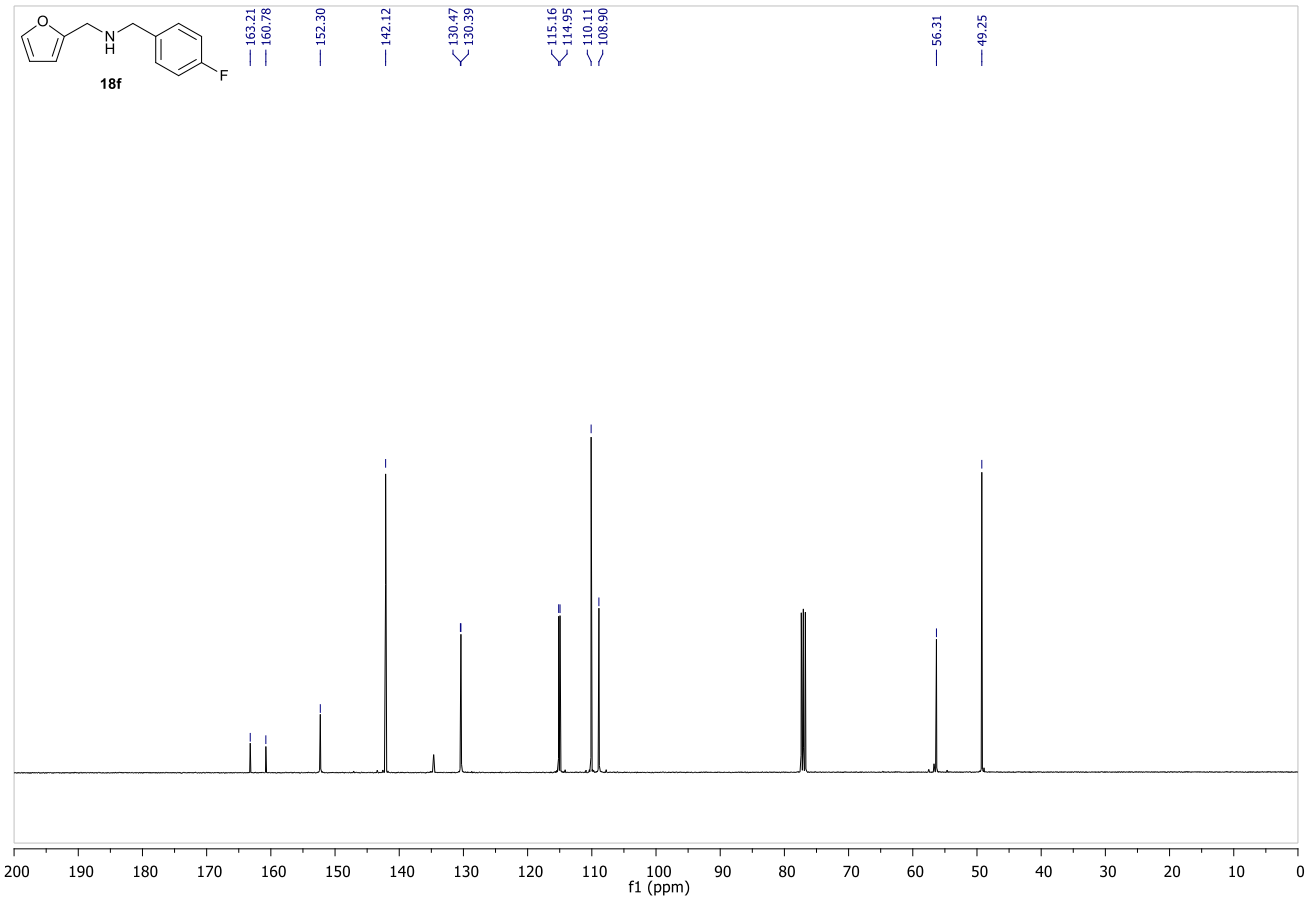


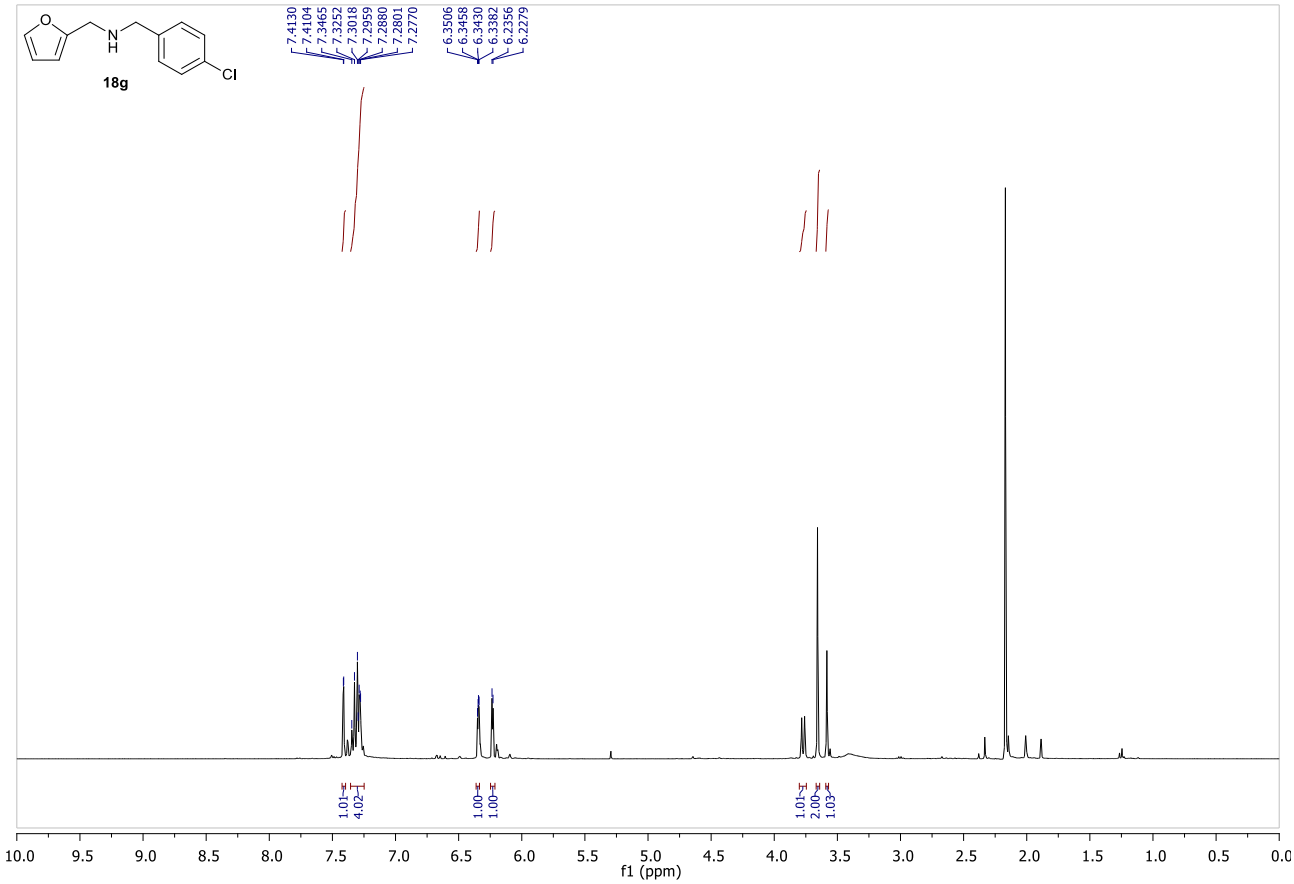


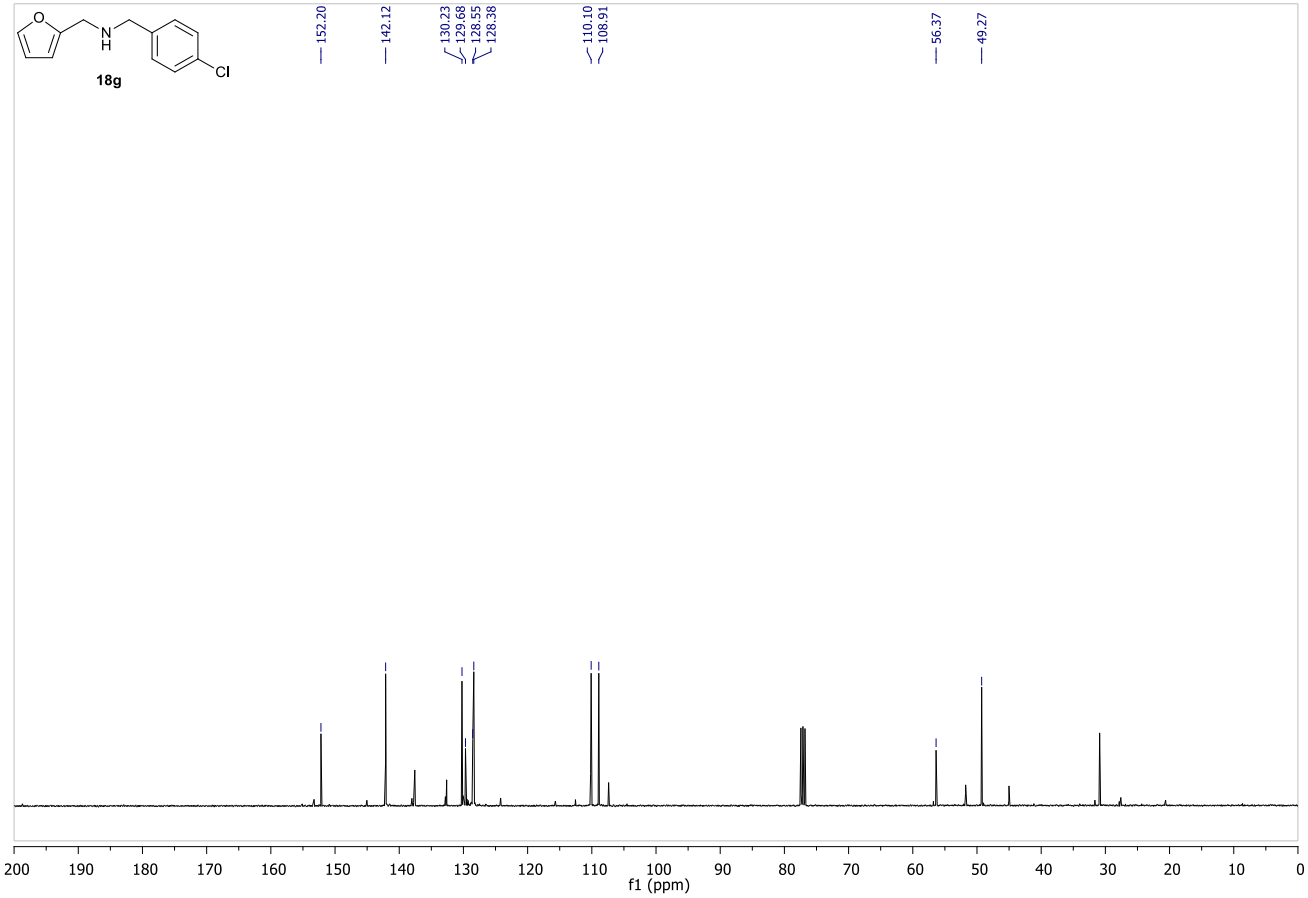


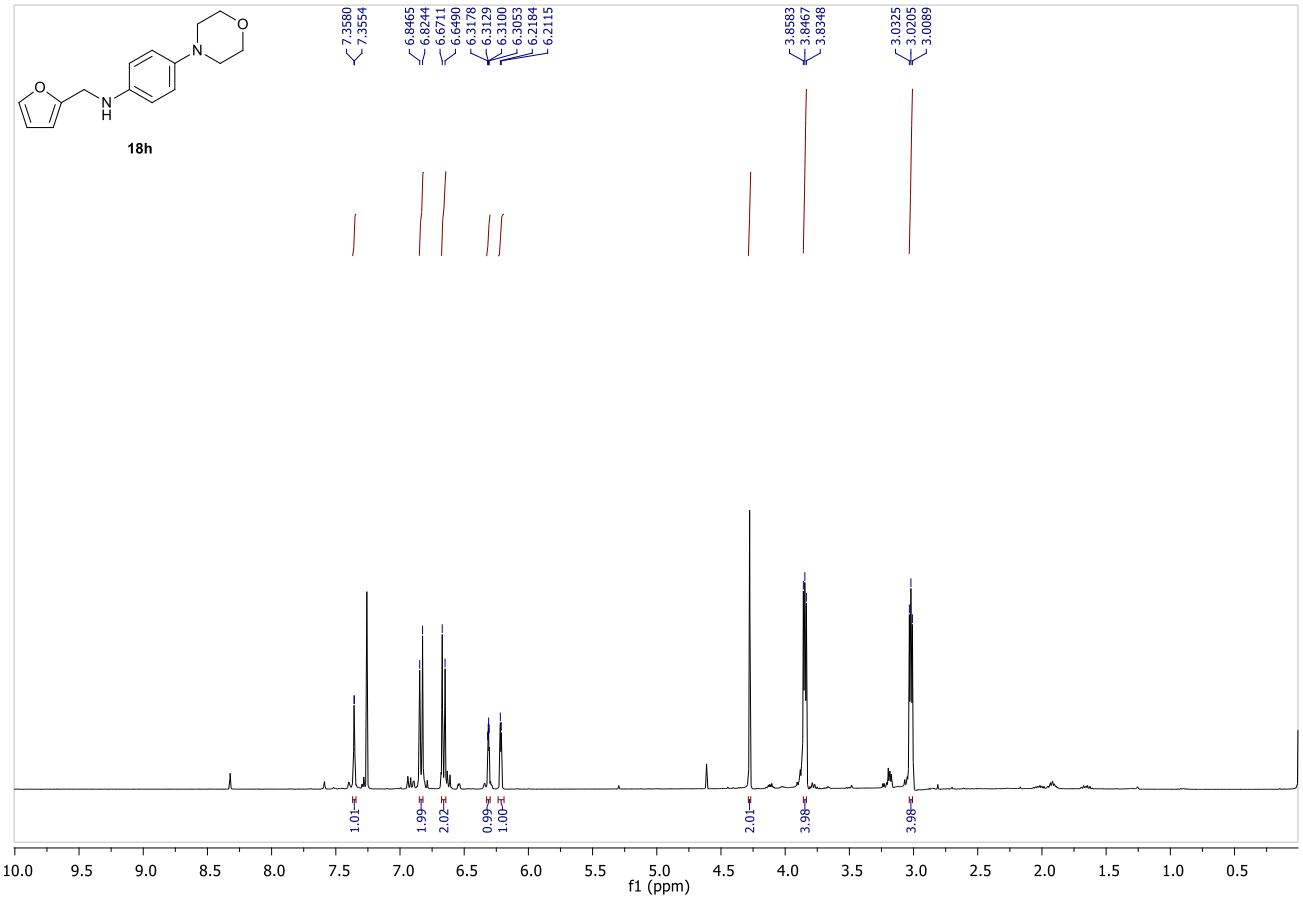


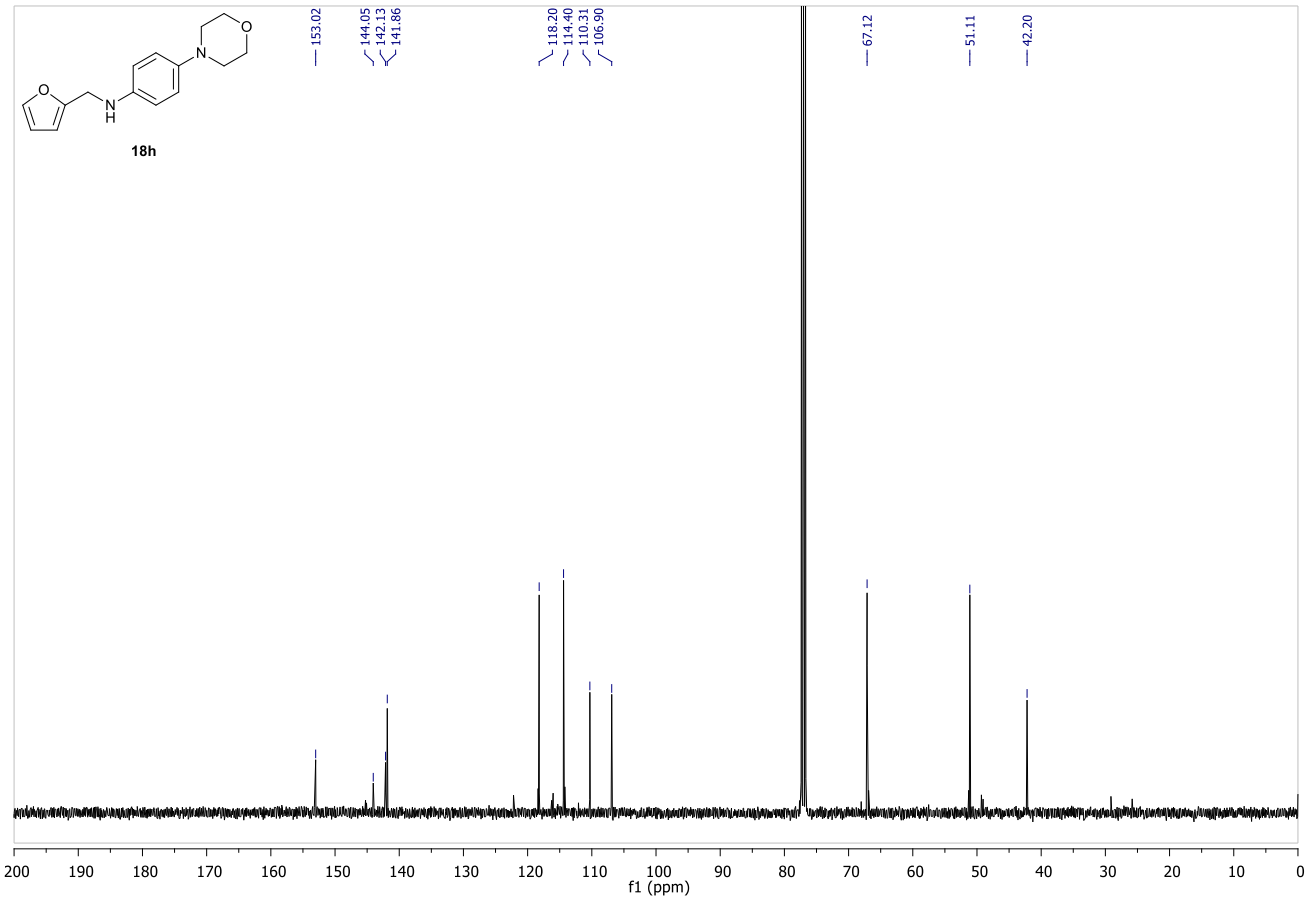


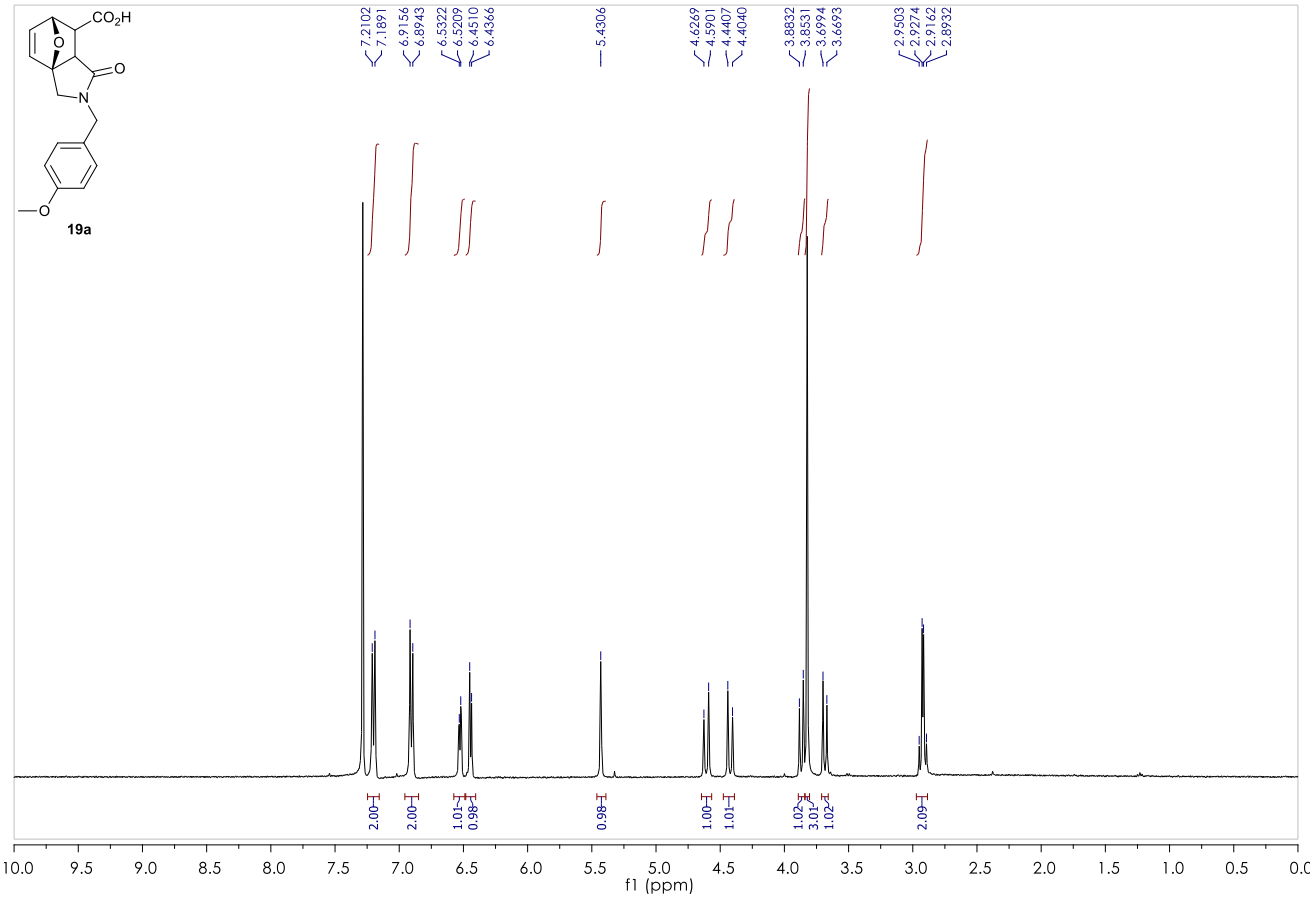


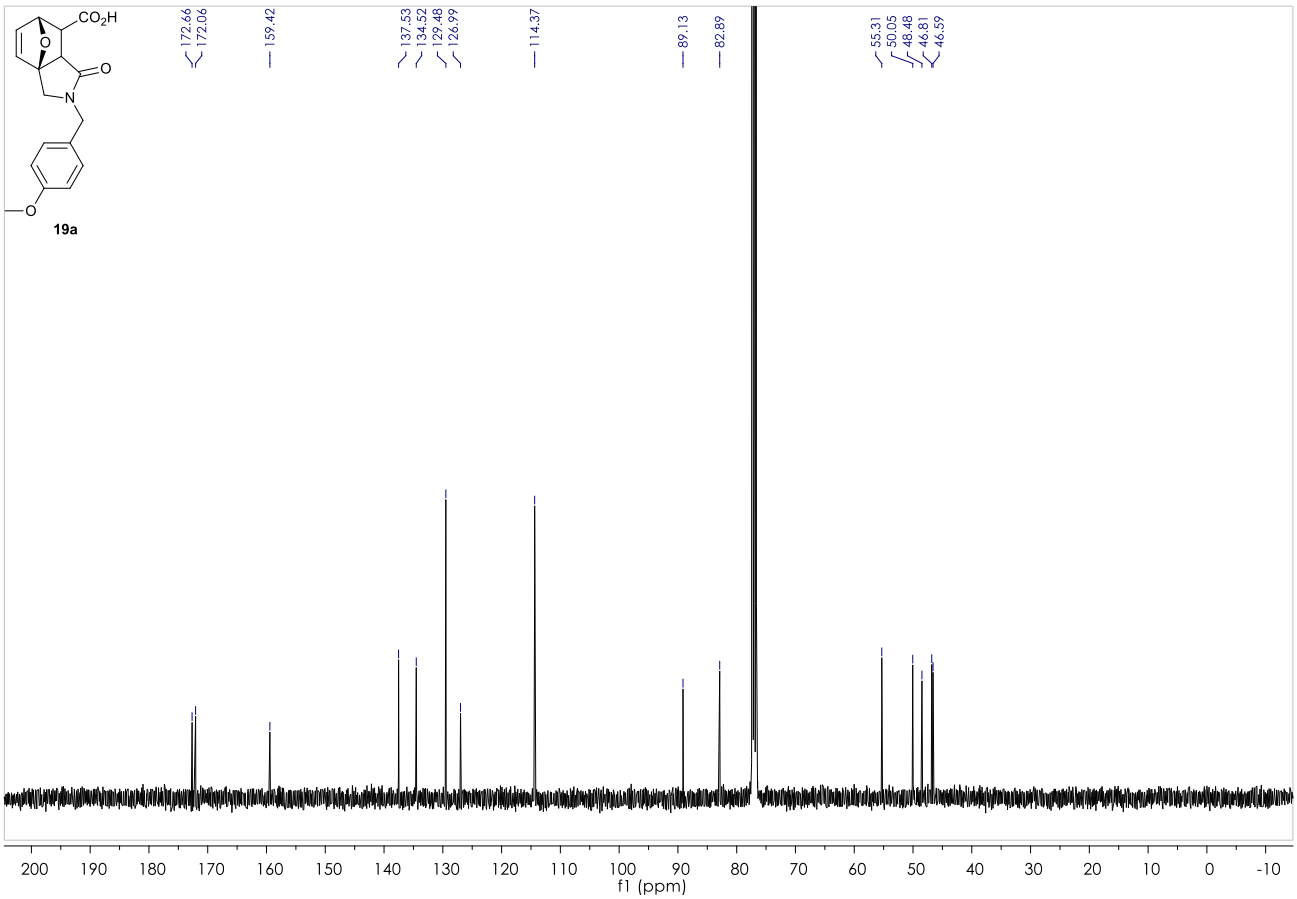


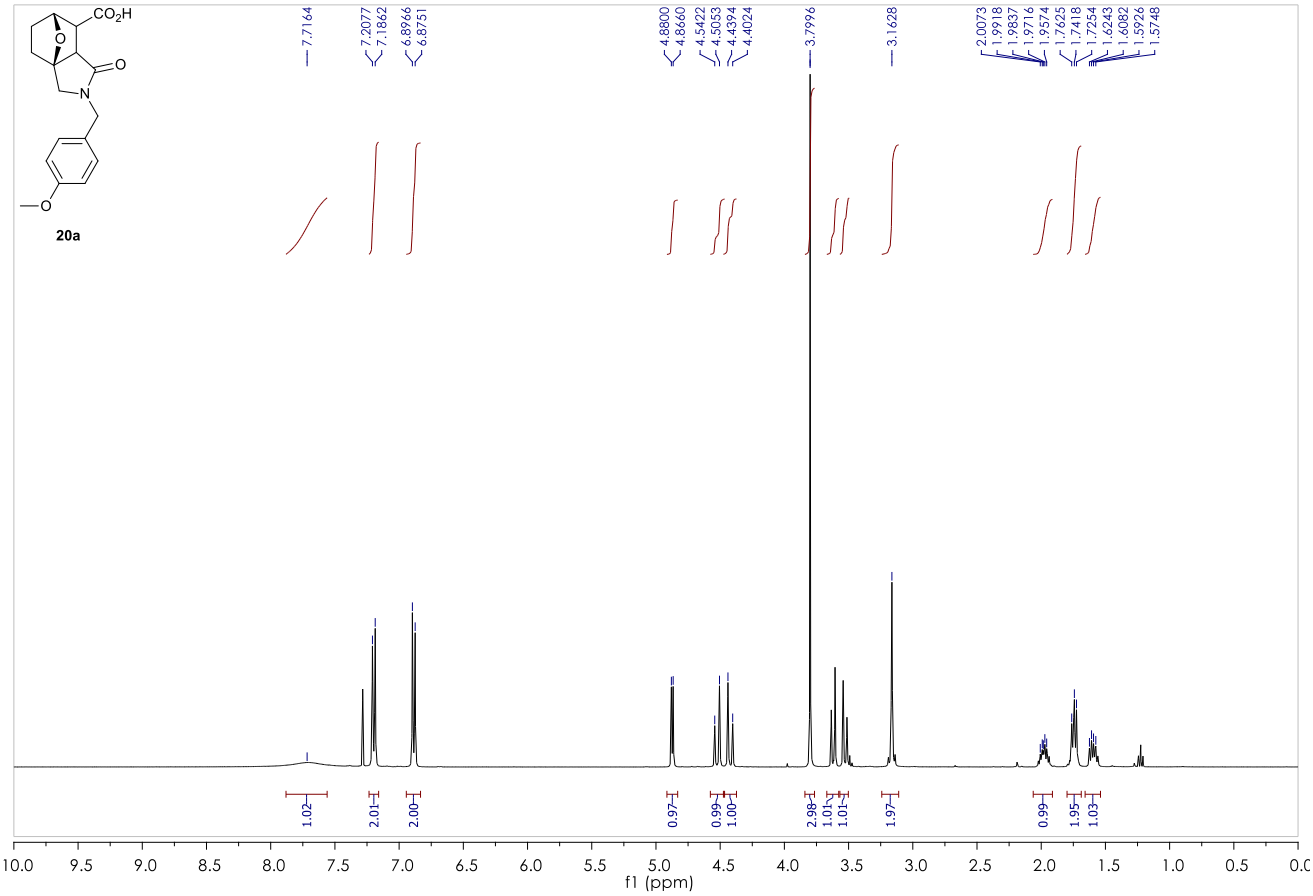


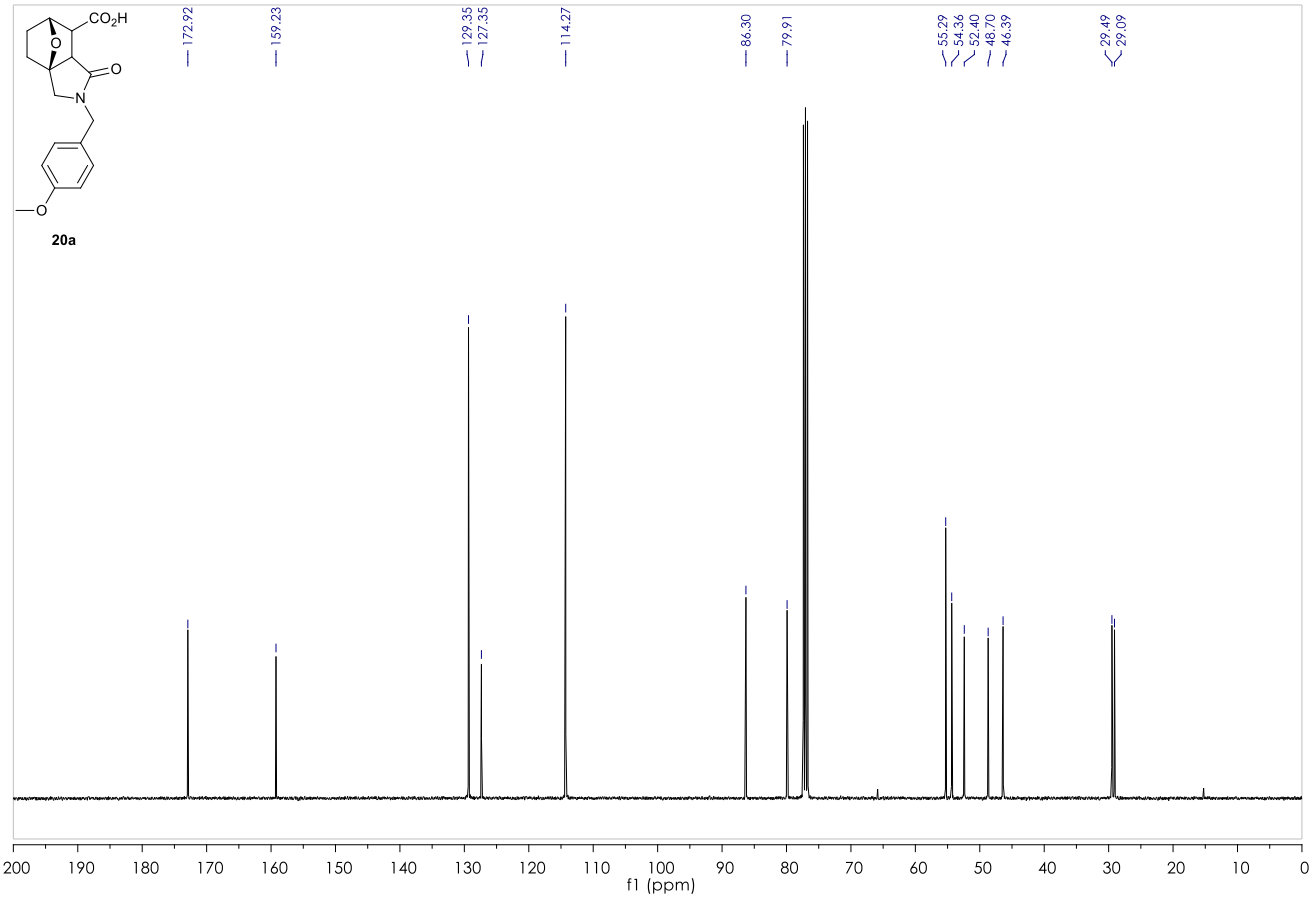


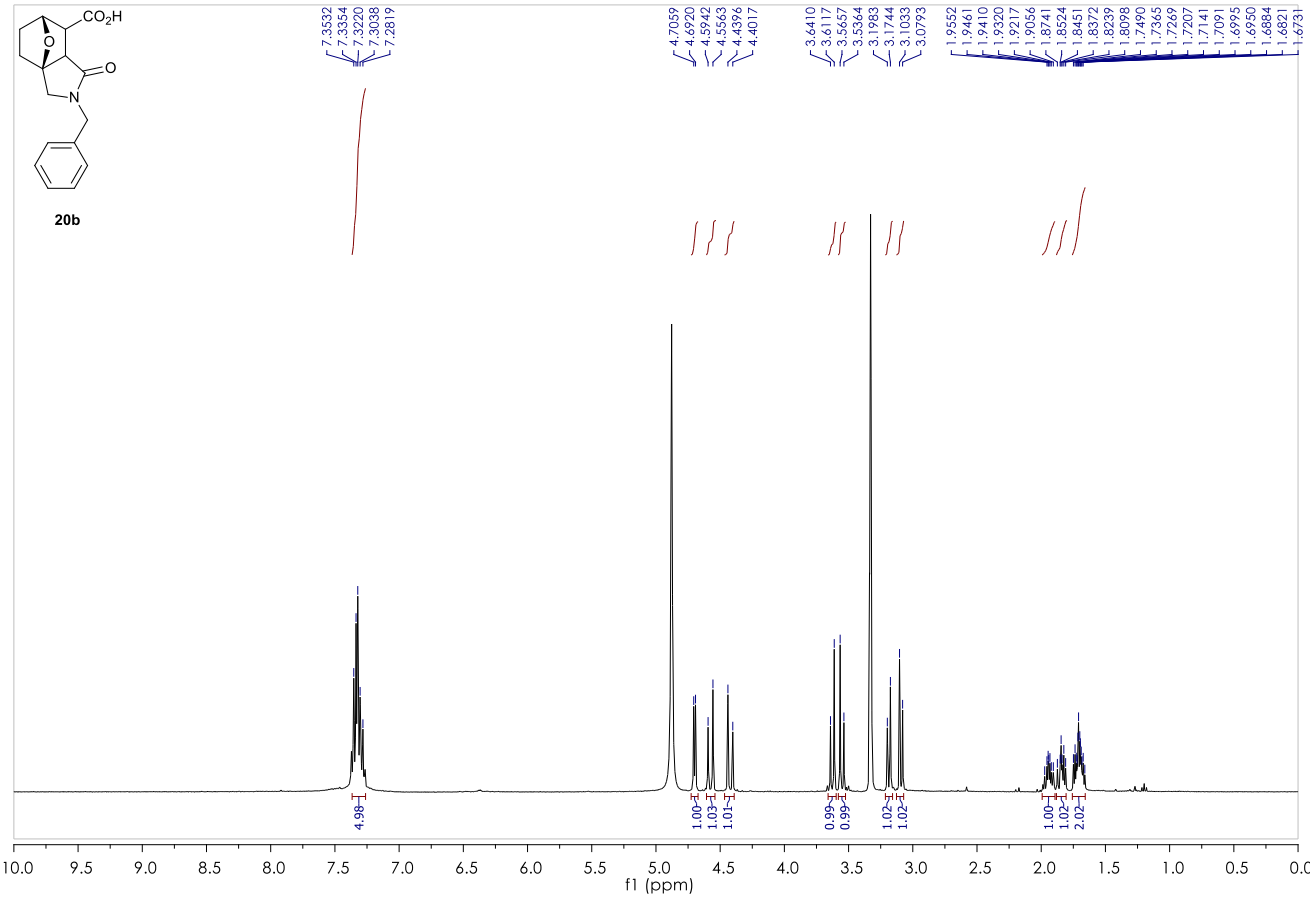


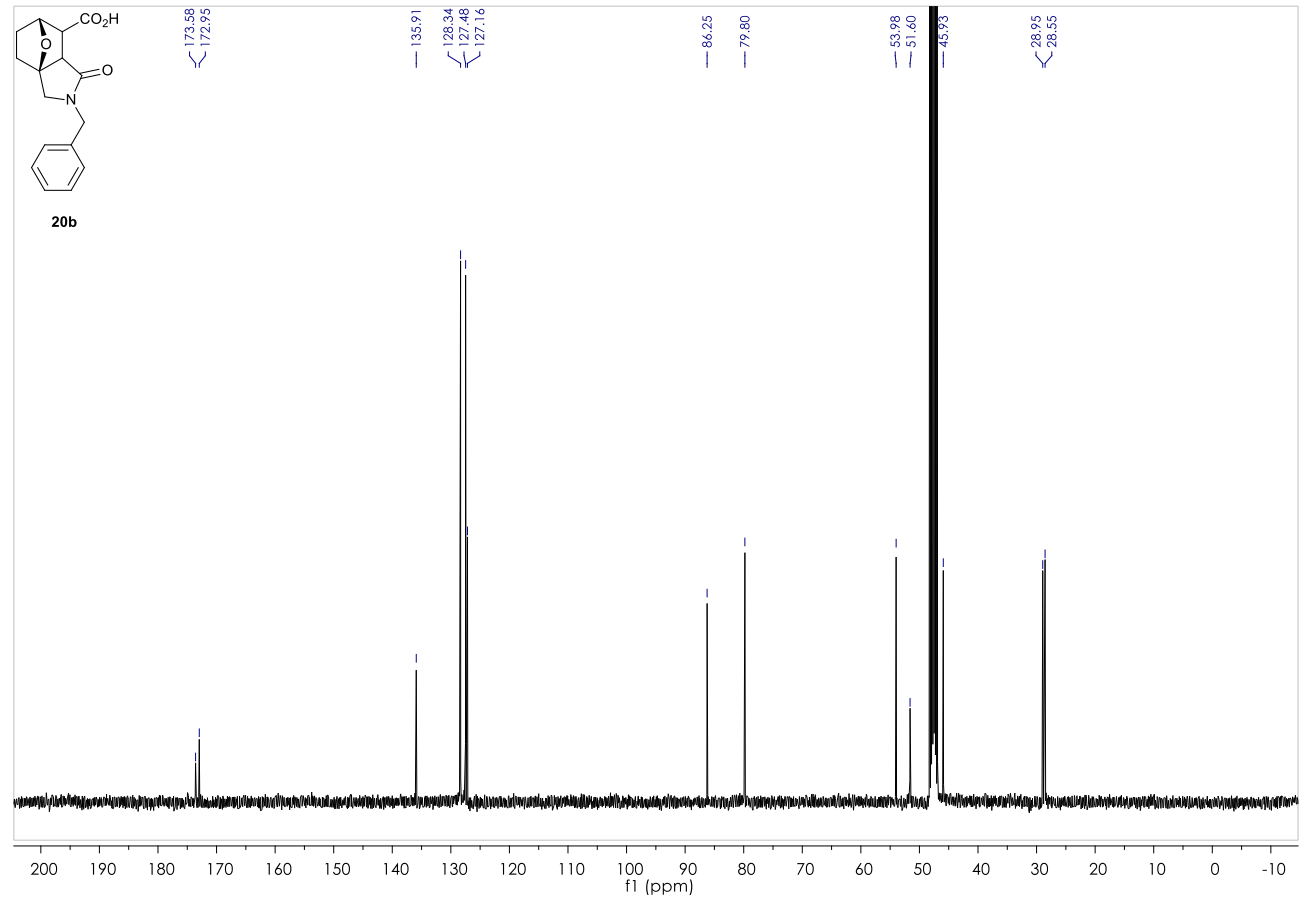


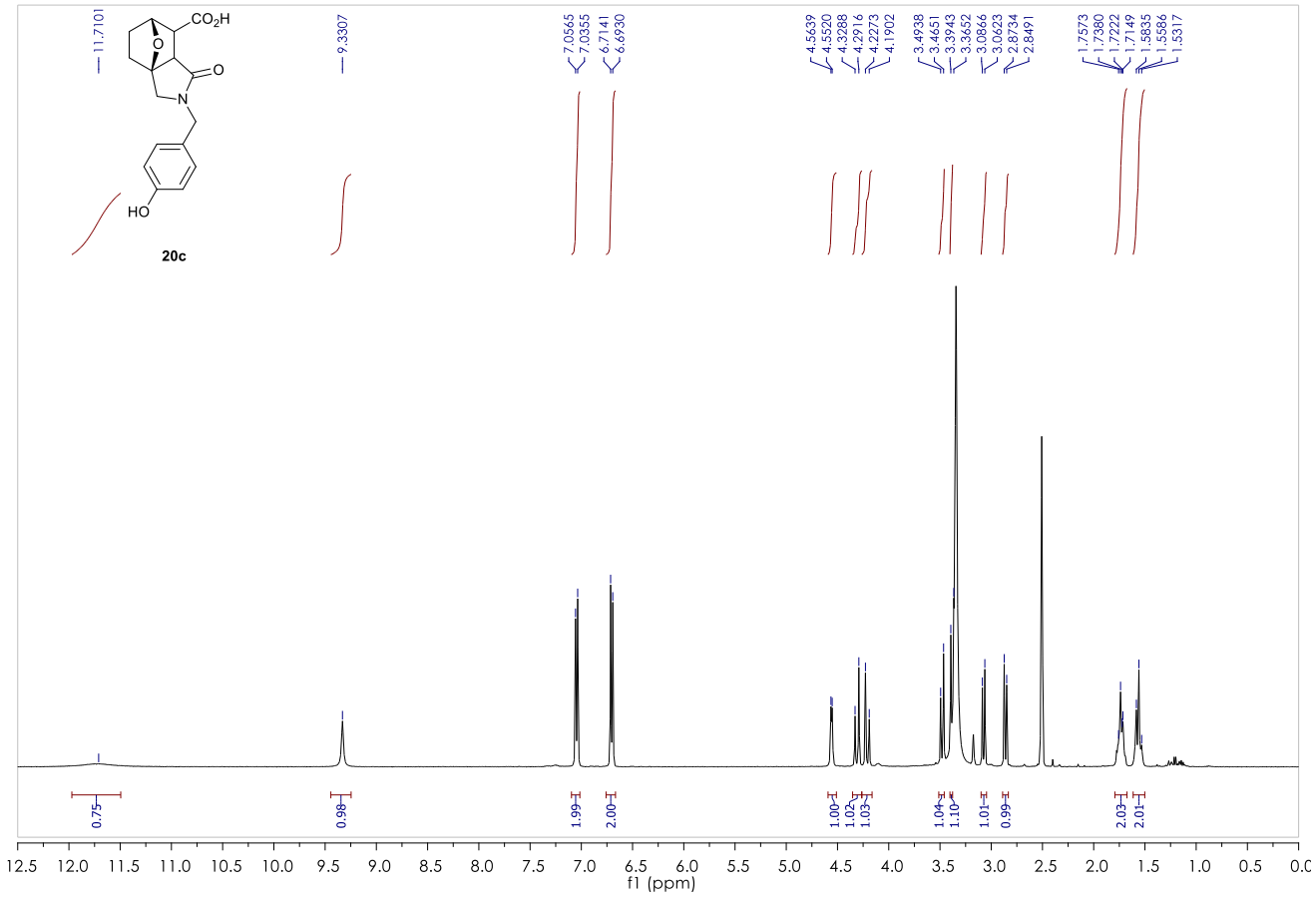







CO2H
O
O
N
20b
7.3532
7.3354
7.3220
7.3038
7.2819
4.7059
4.6920
4.5942
4.5563
4.4396
4.4017
3.6410
3.6117
3.5657
3.5364
3.1983
3.1744
3.1033
3.0793
1.9552
1.9461
1.9410
1.9320
1.9217
1.9056
1.8741
1.8524
1.8451
1.8372
1.8239
1.8098
1.7490
1.7365
1.7269
1.7207
1.7141
1.7091
1.6995
1.6950
1.6884
1.6821
1.6731
4.98
1.00
1.03
1.01
0.99
0.99
1.02
1.02
1.00
1.02
2.02
f1 (ppm)


CO2H
O
O
N
20b
173.58
172.95
135.91
128.34
127.48
127.16
86.25
79.80
53.98
51.60
45.93
28.95
28.55
f1 (ppm)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3.3652
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2.8491
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1.7380
1.7222
1.7149
1.5835
1.5586
1.5317
CO2H
O
O
N
HO
20c
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0.98
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1.01
0.99
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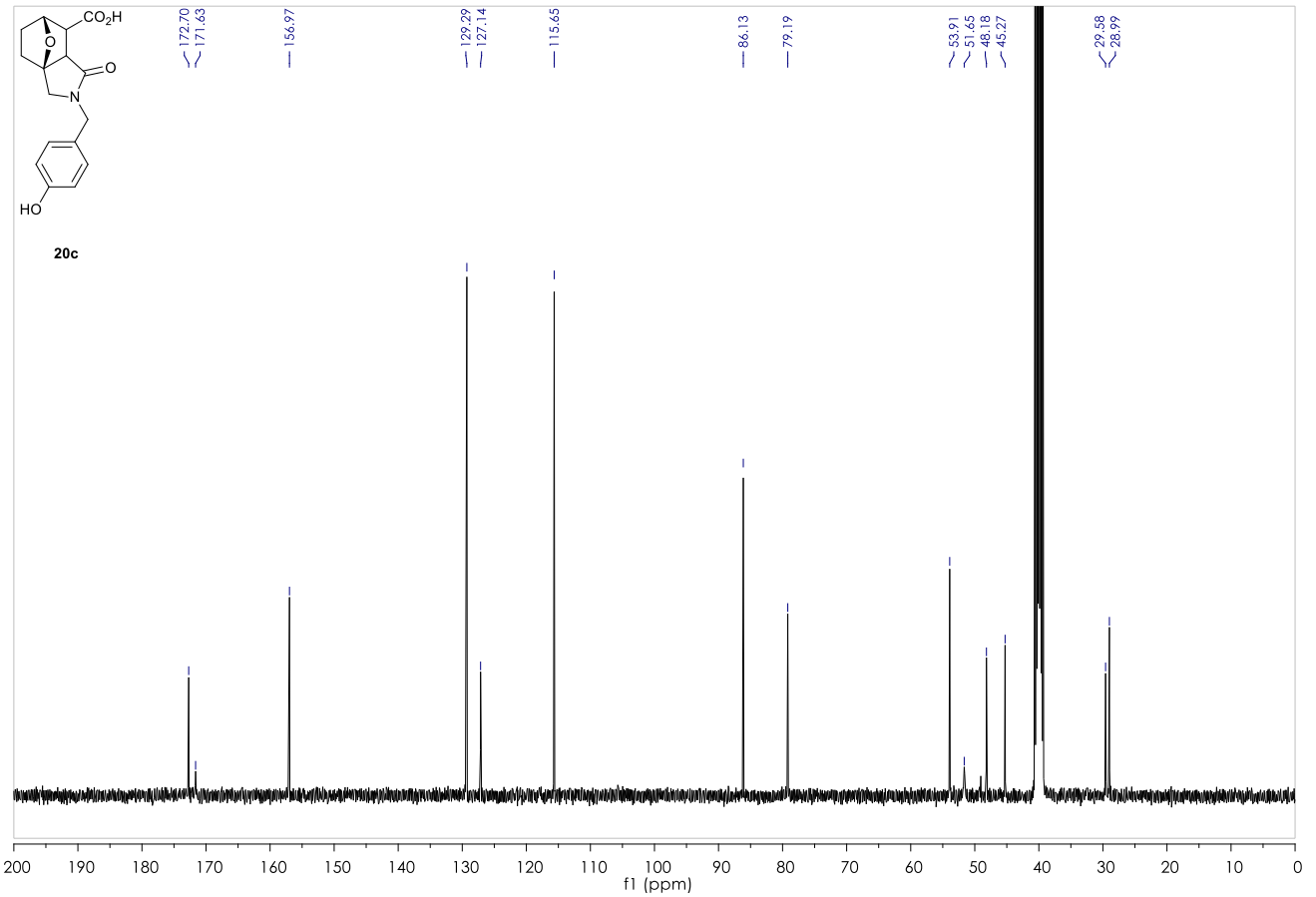
2.01
f1 (ppm)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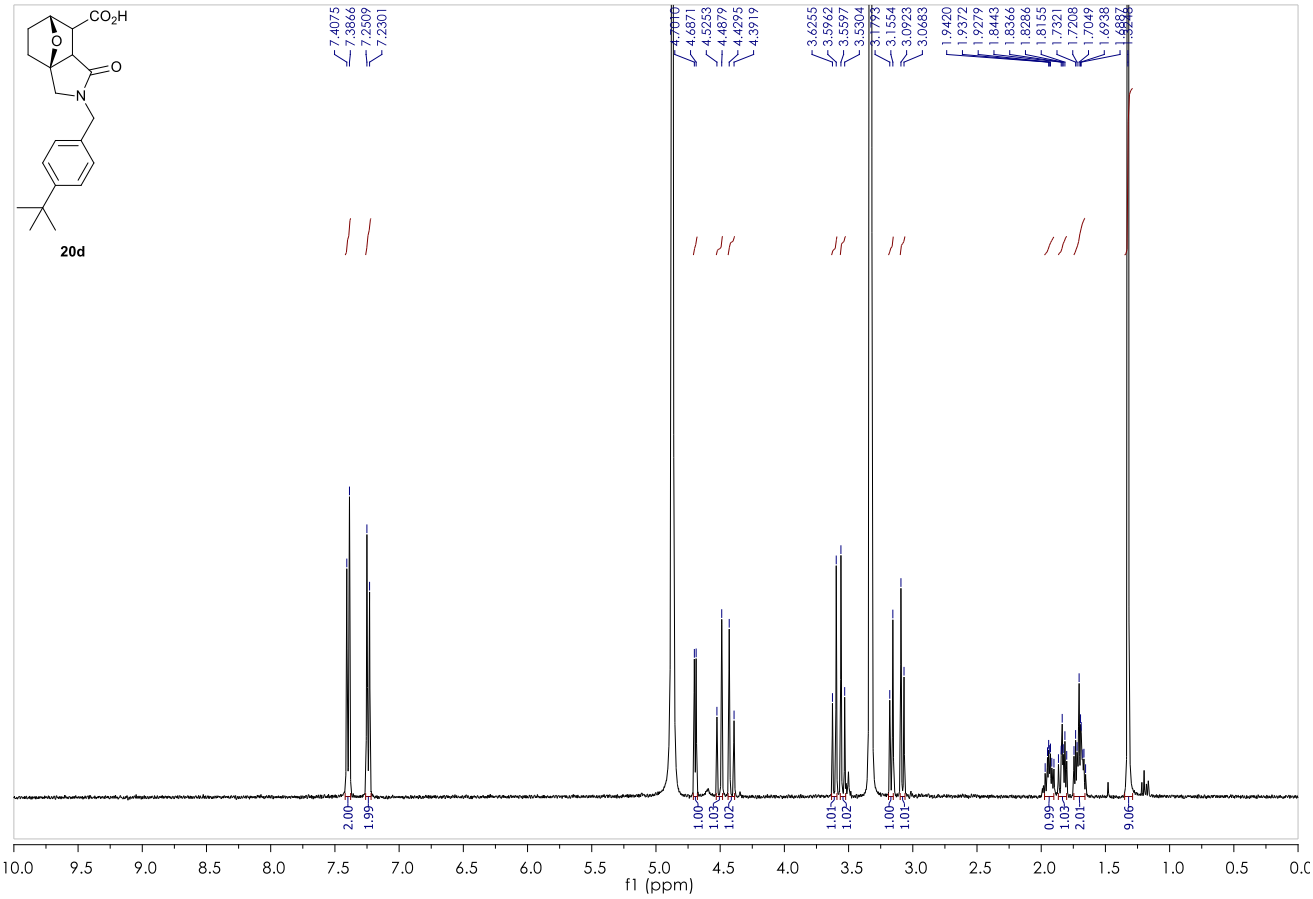
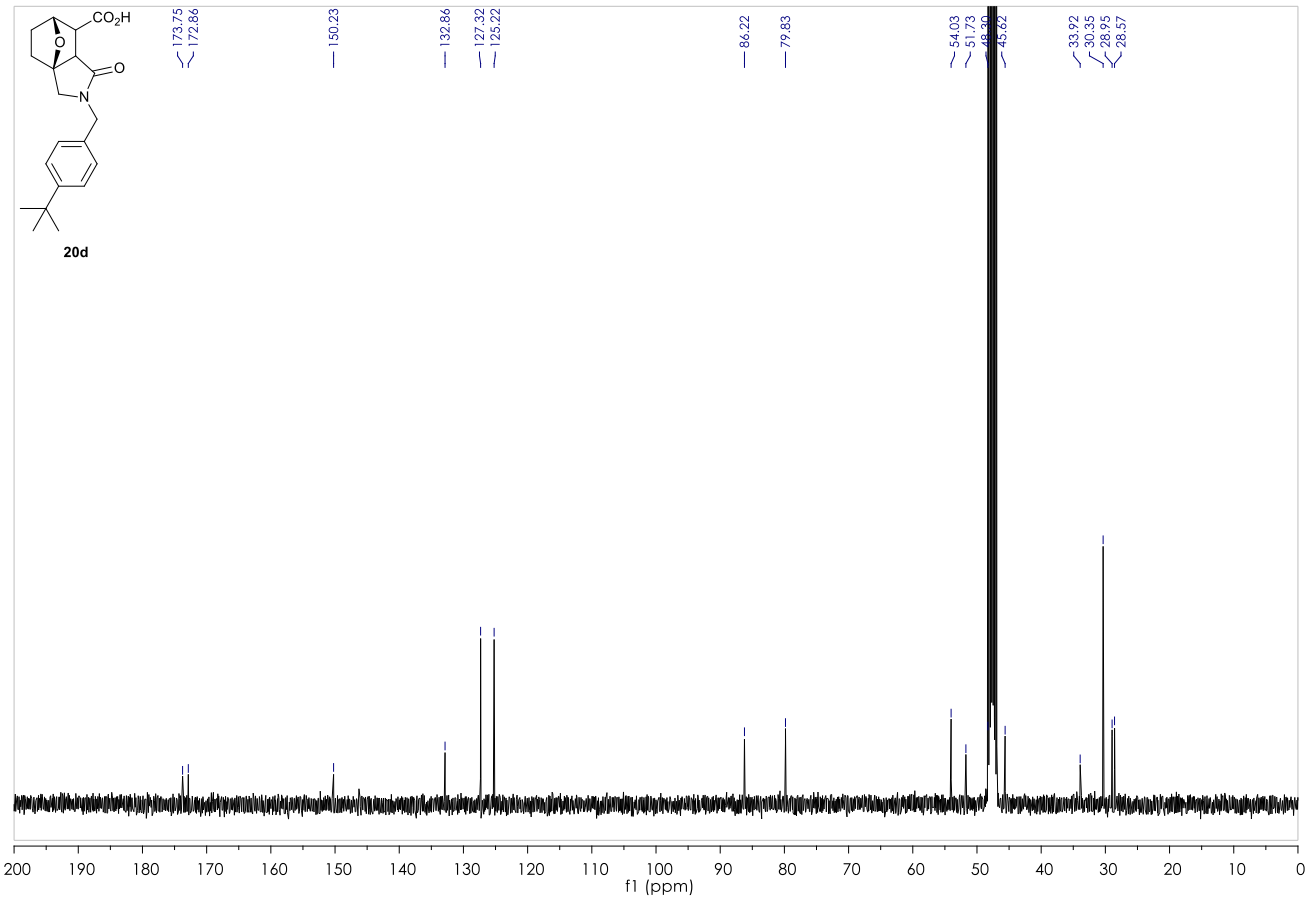
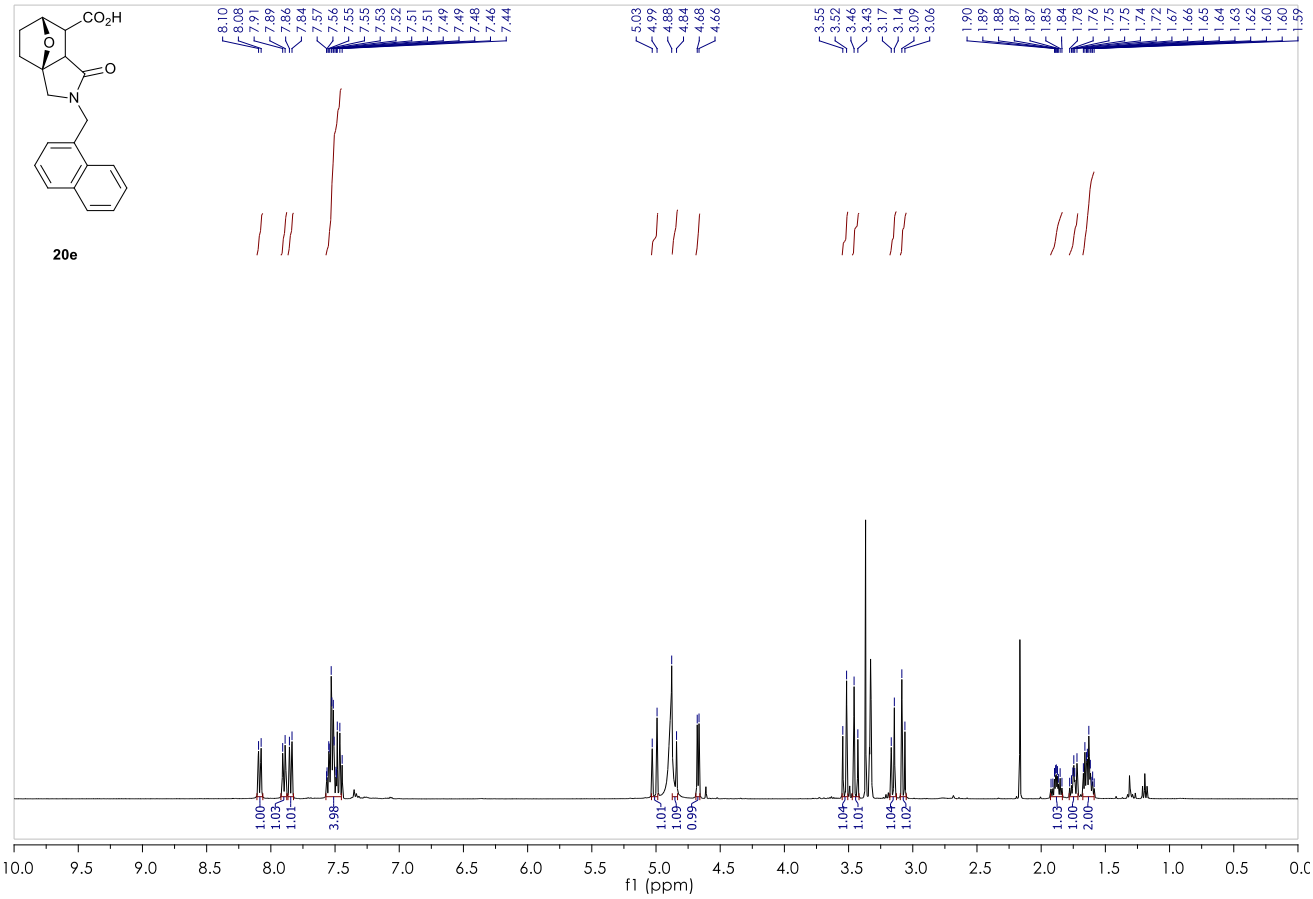
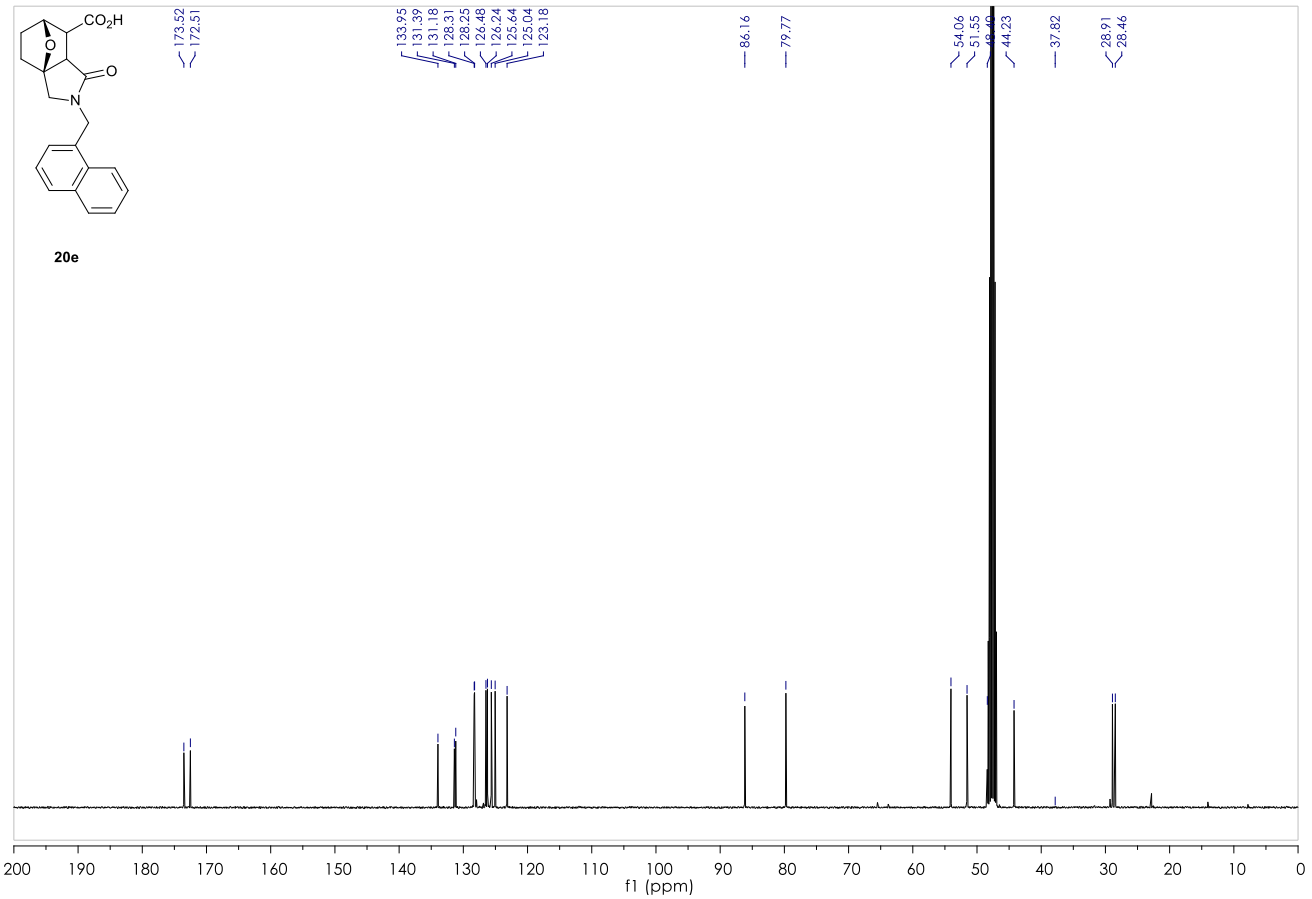
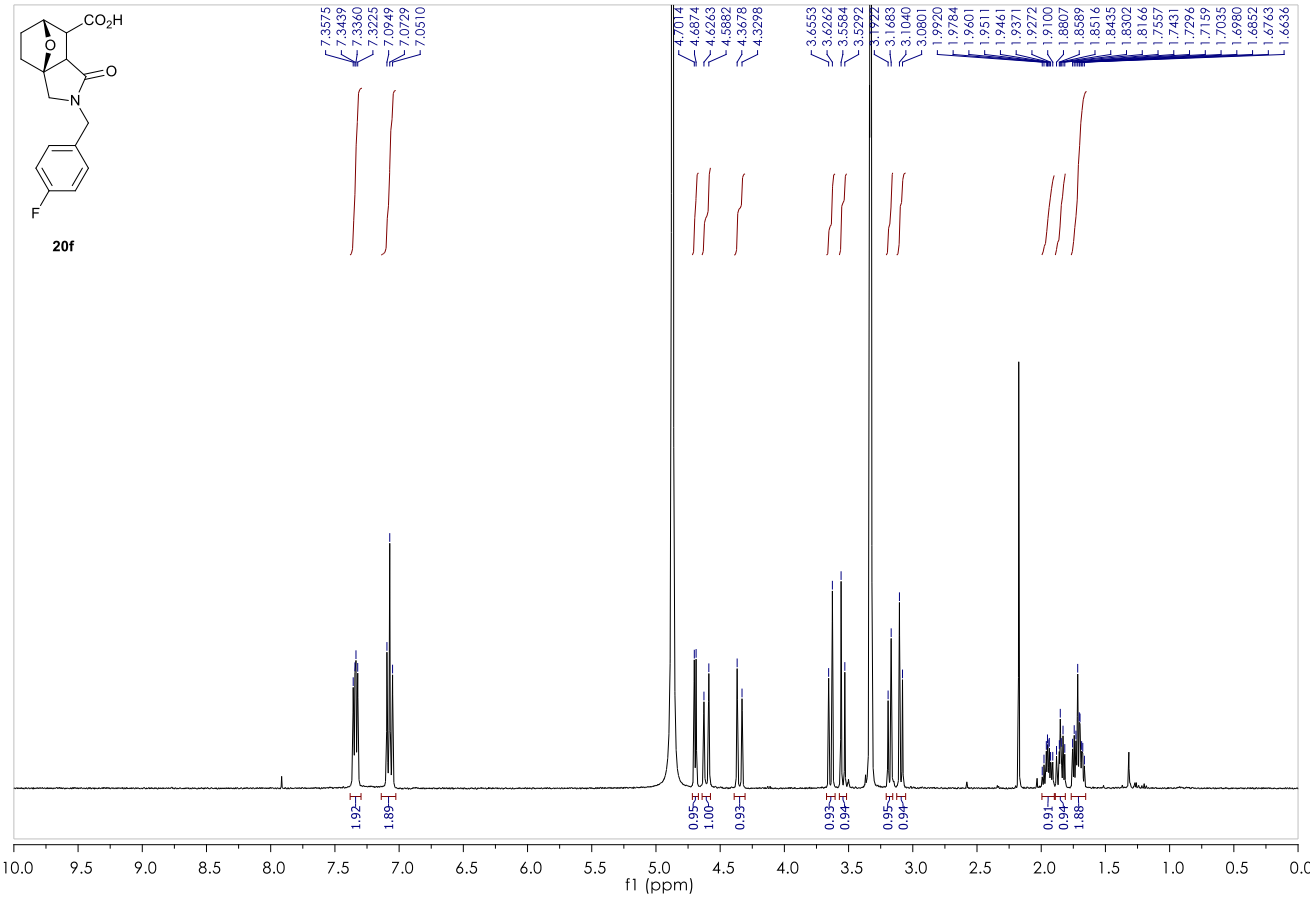
O
O
N
HO
20c
f1 (ppm)

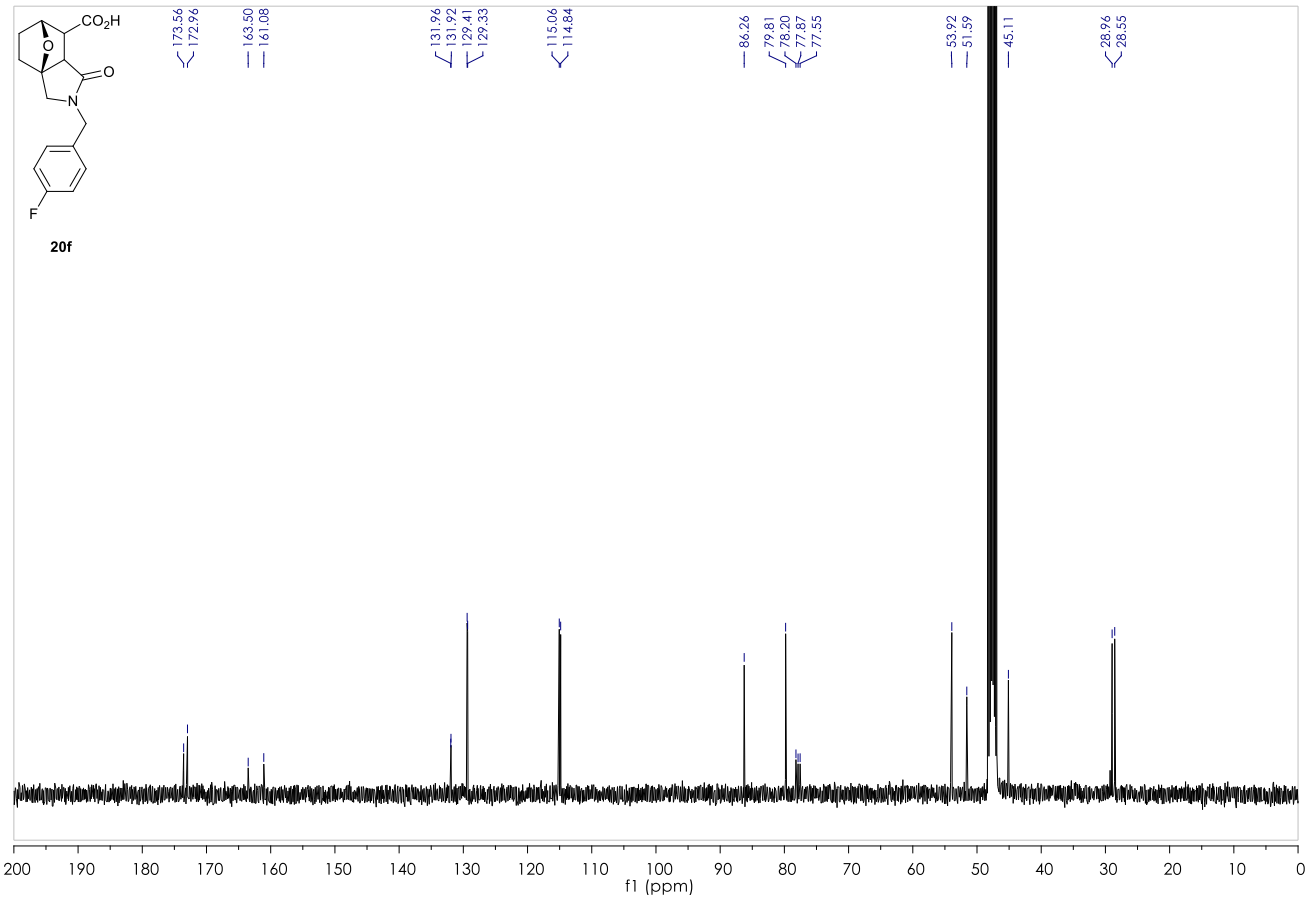


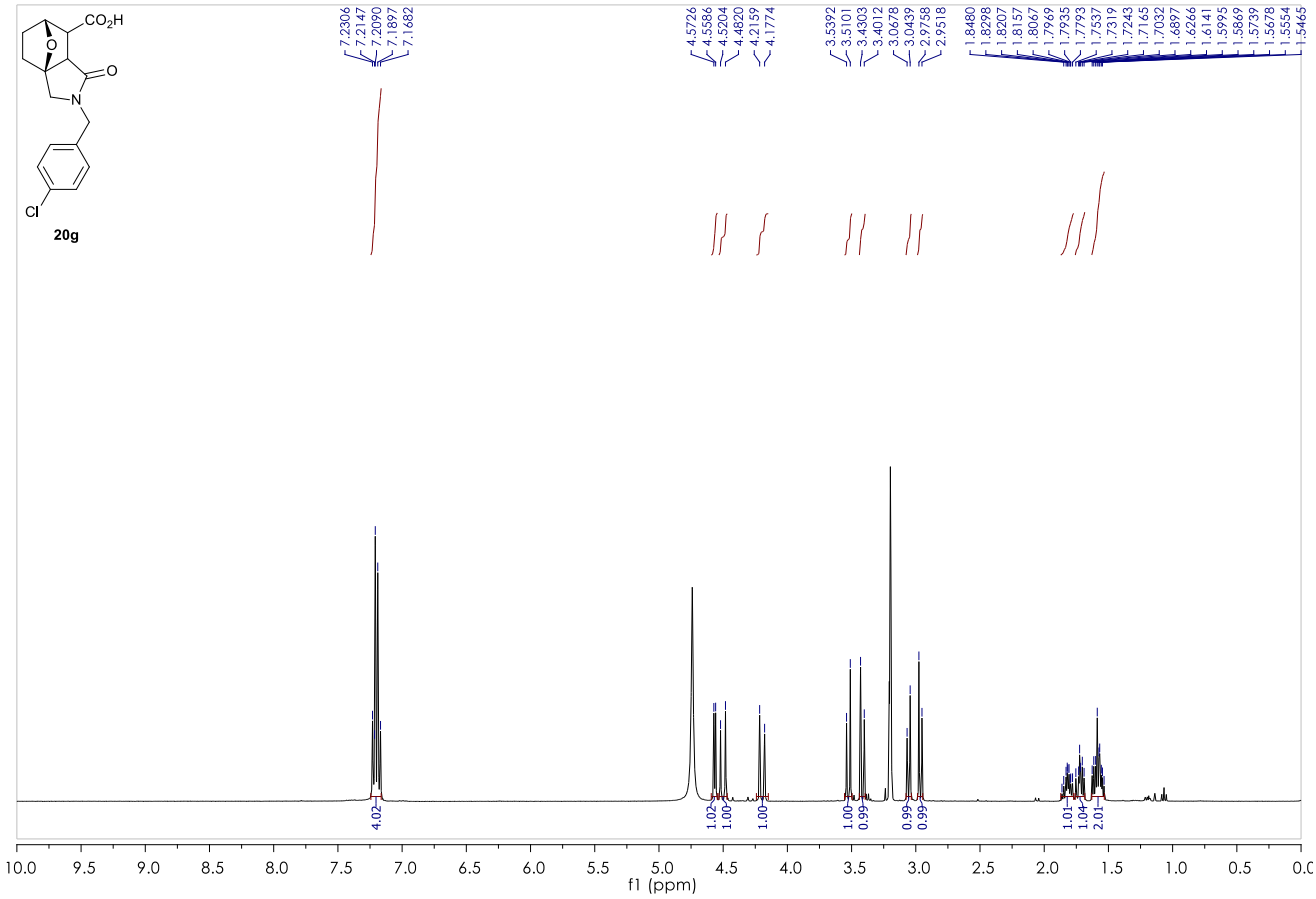


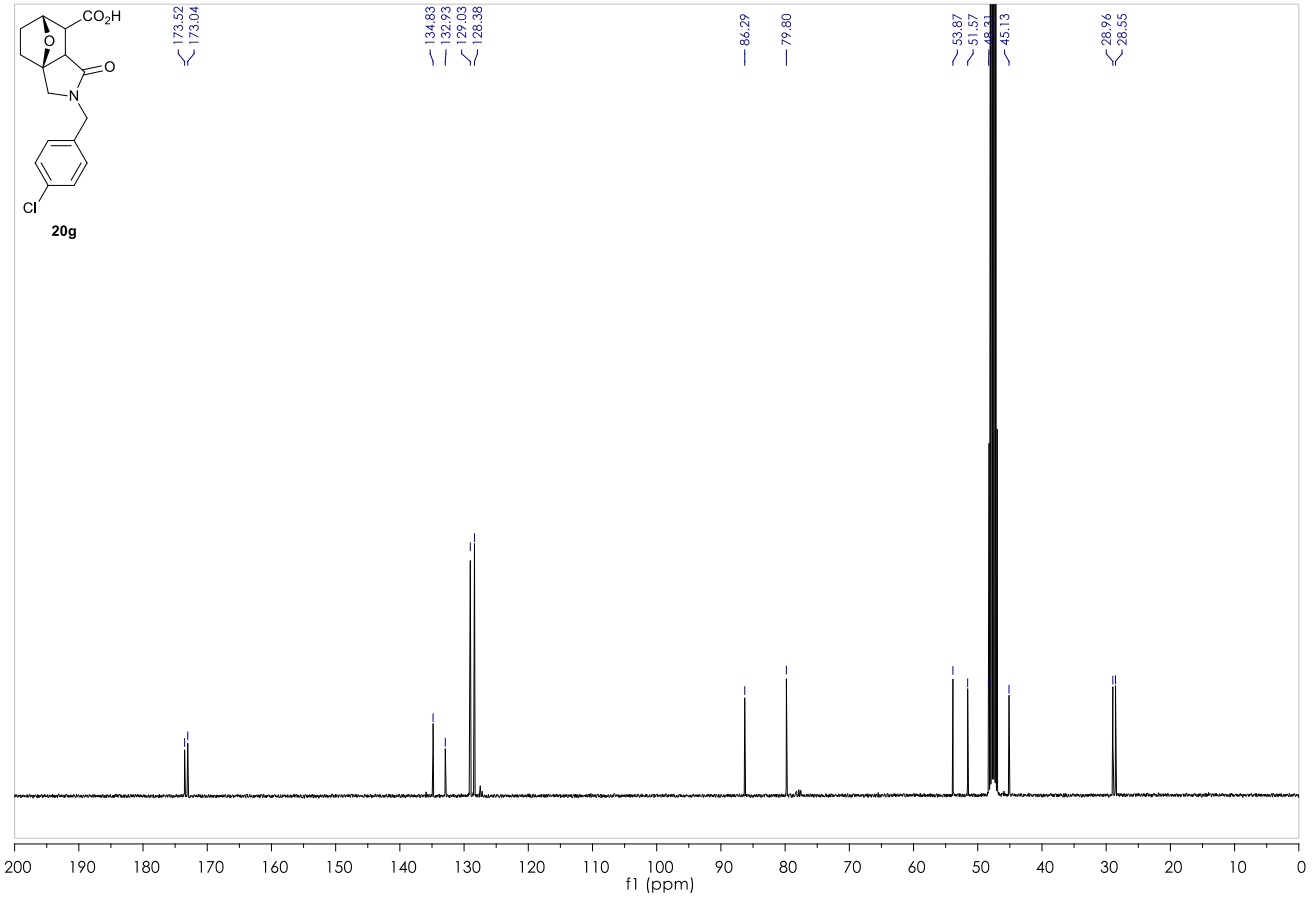


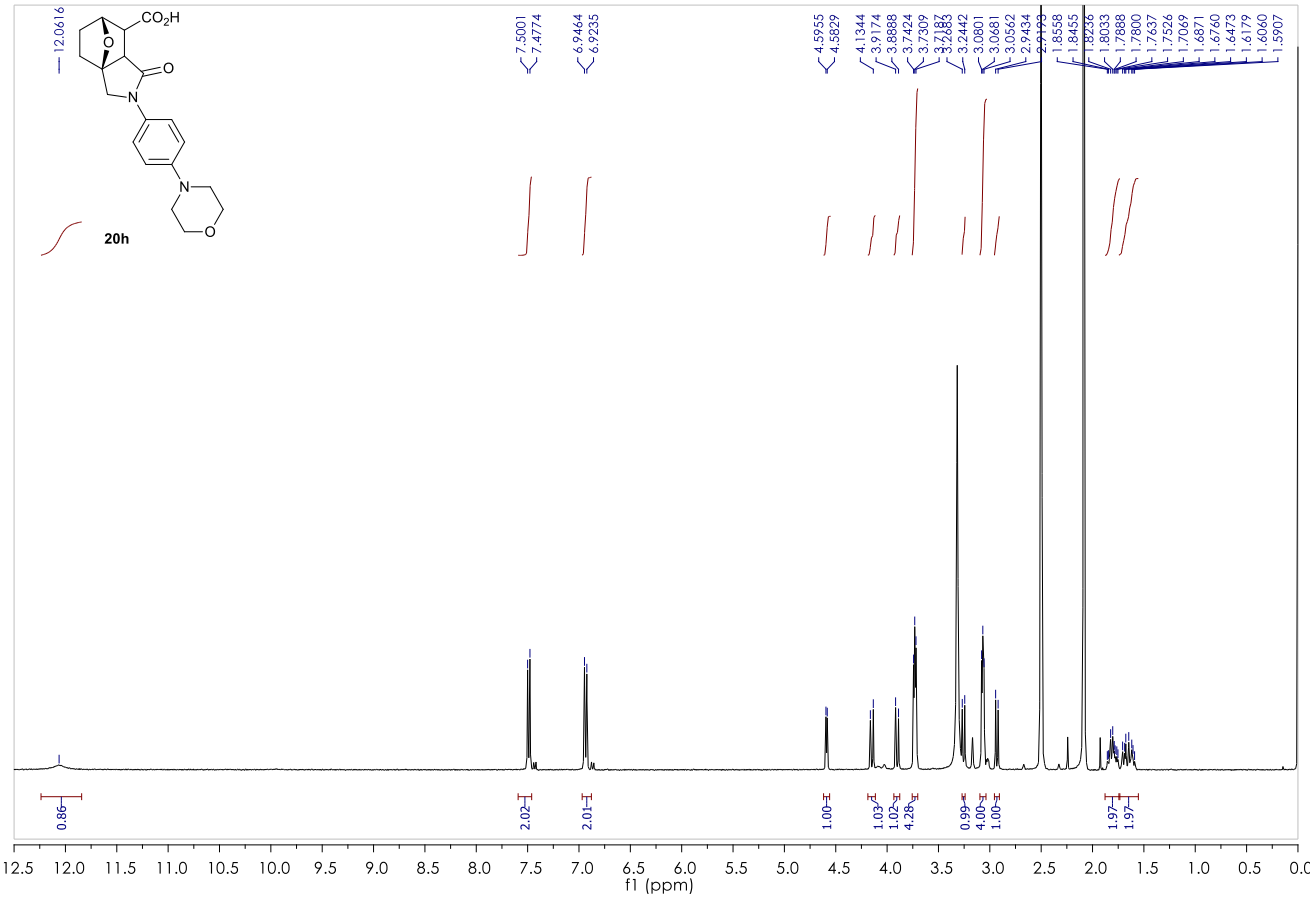


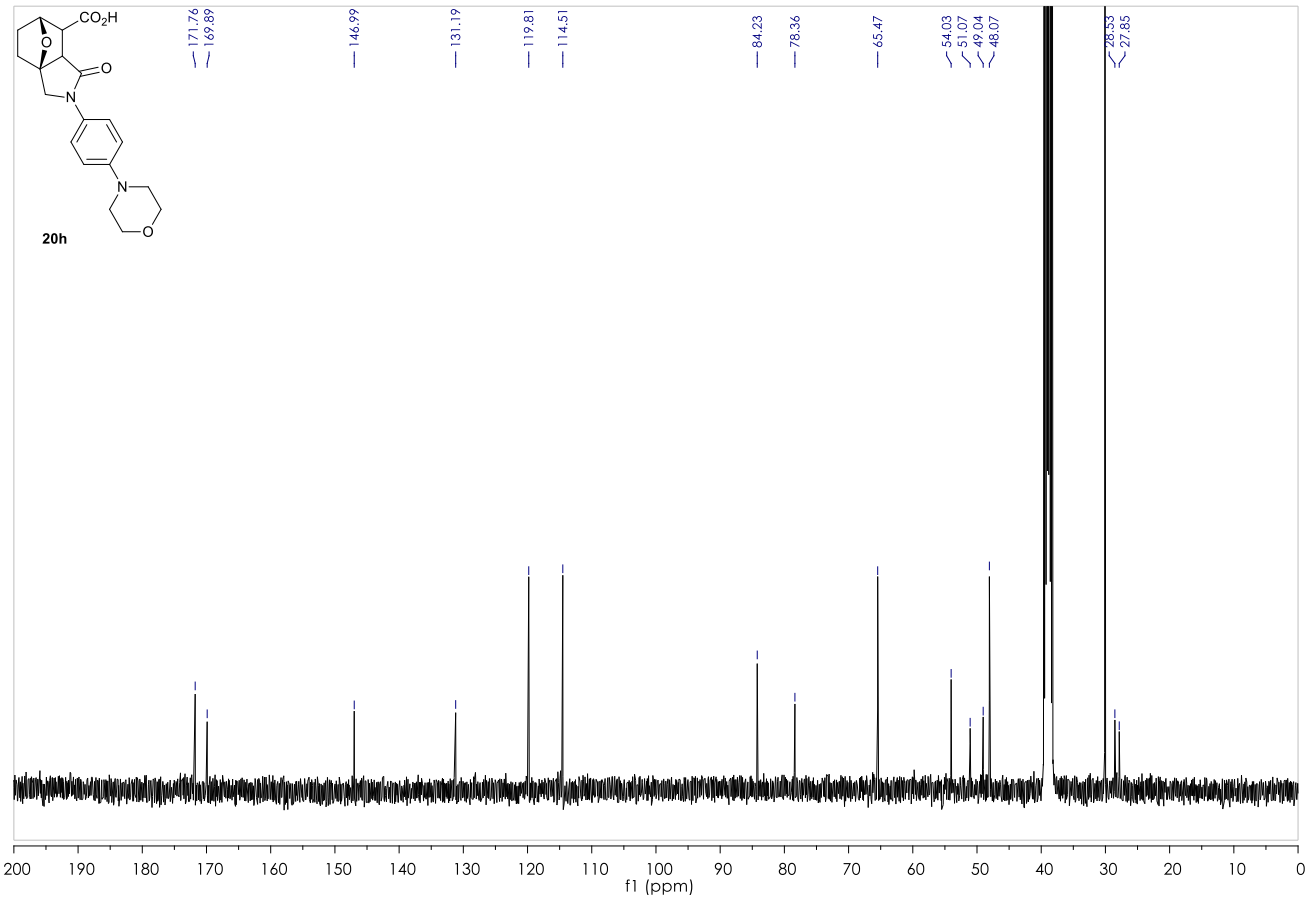


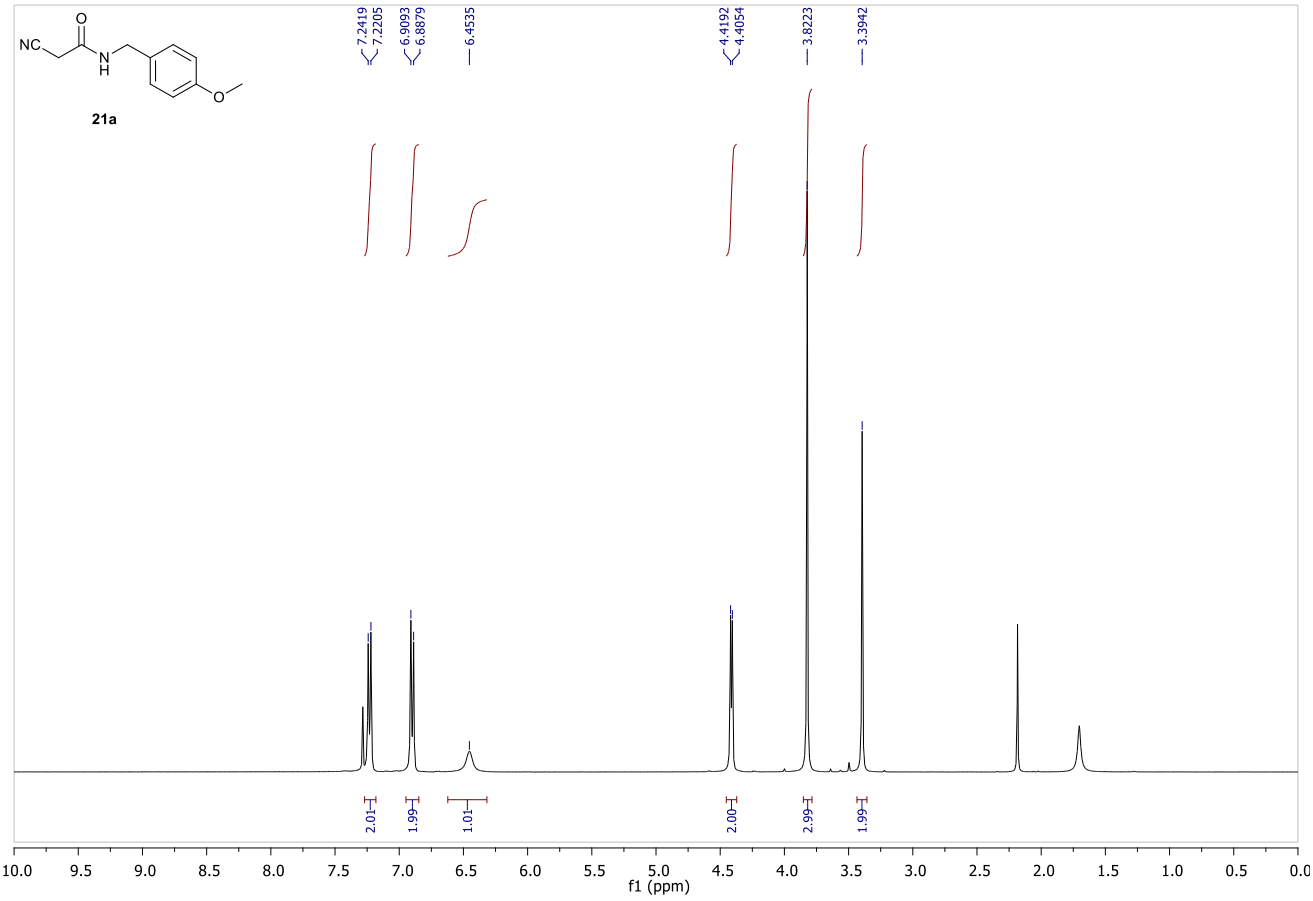


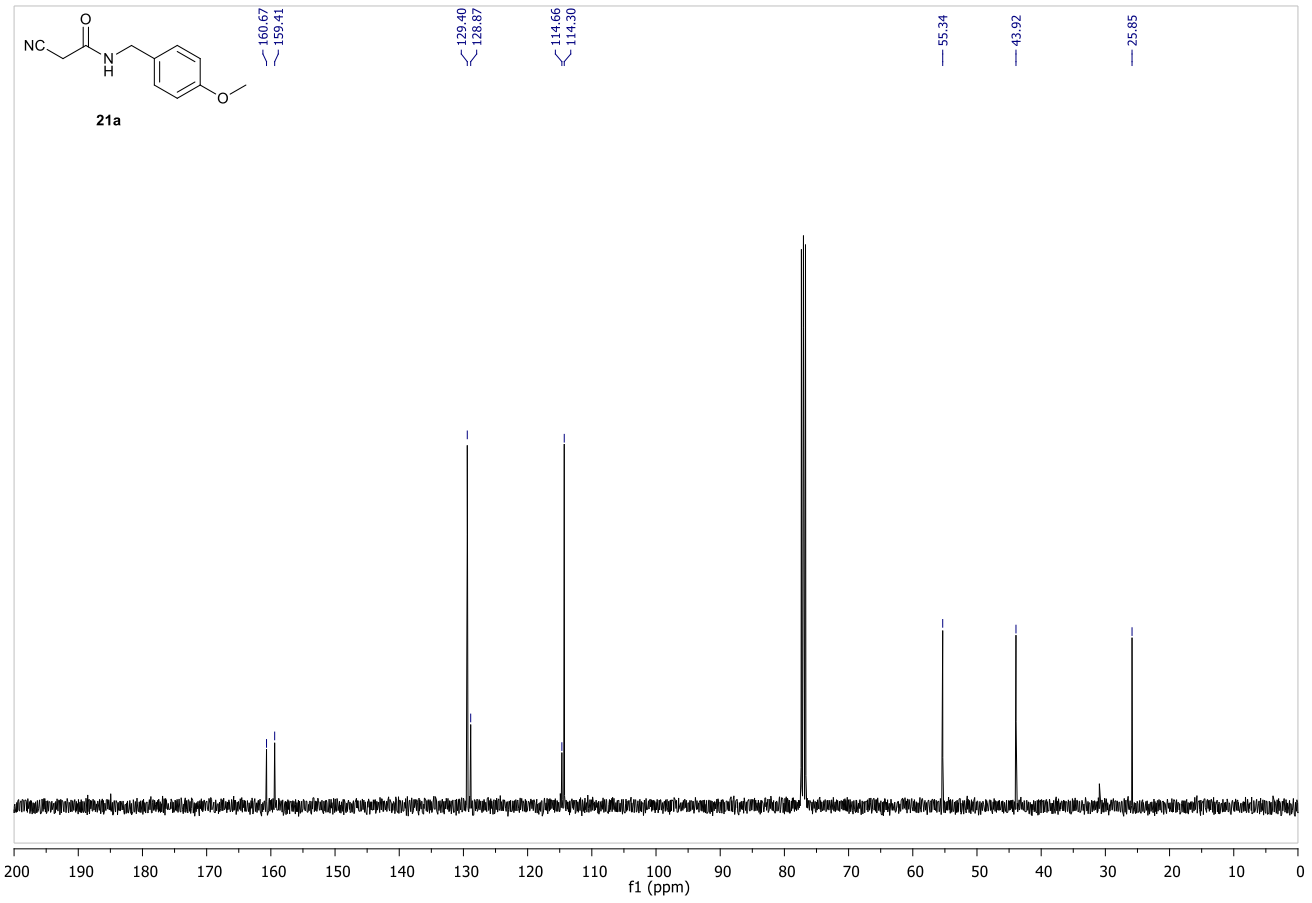


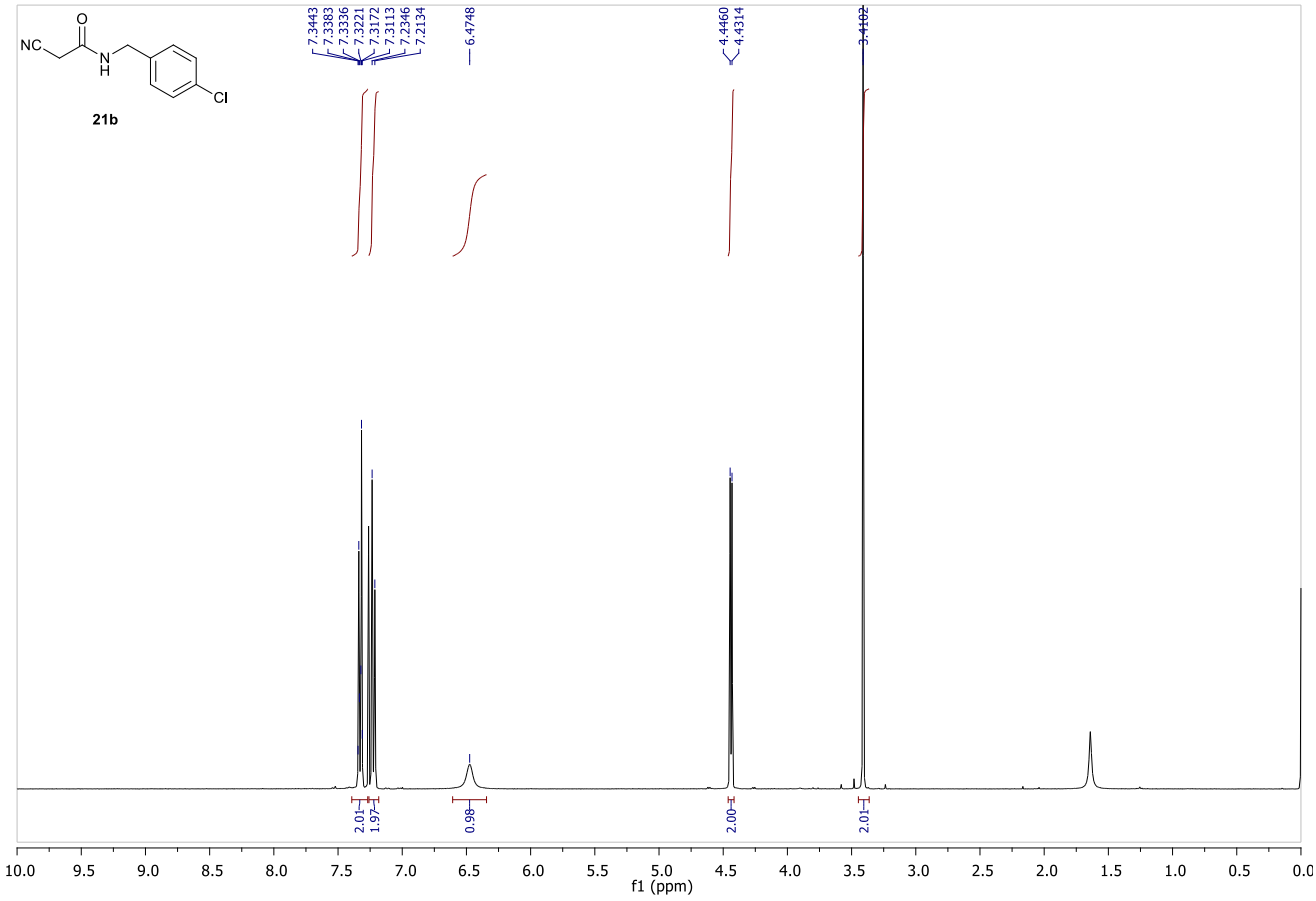


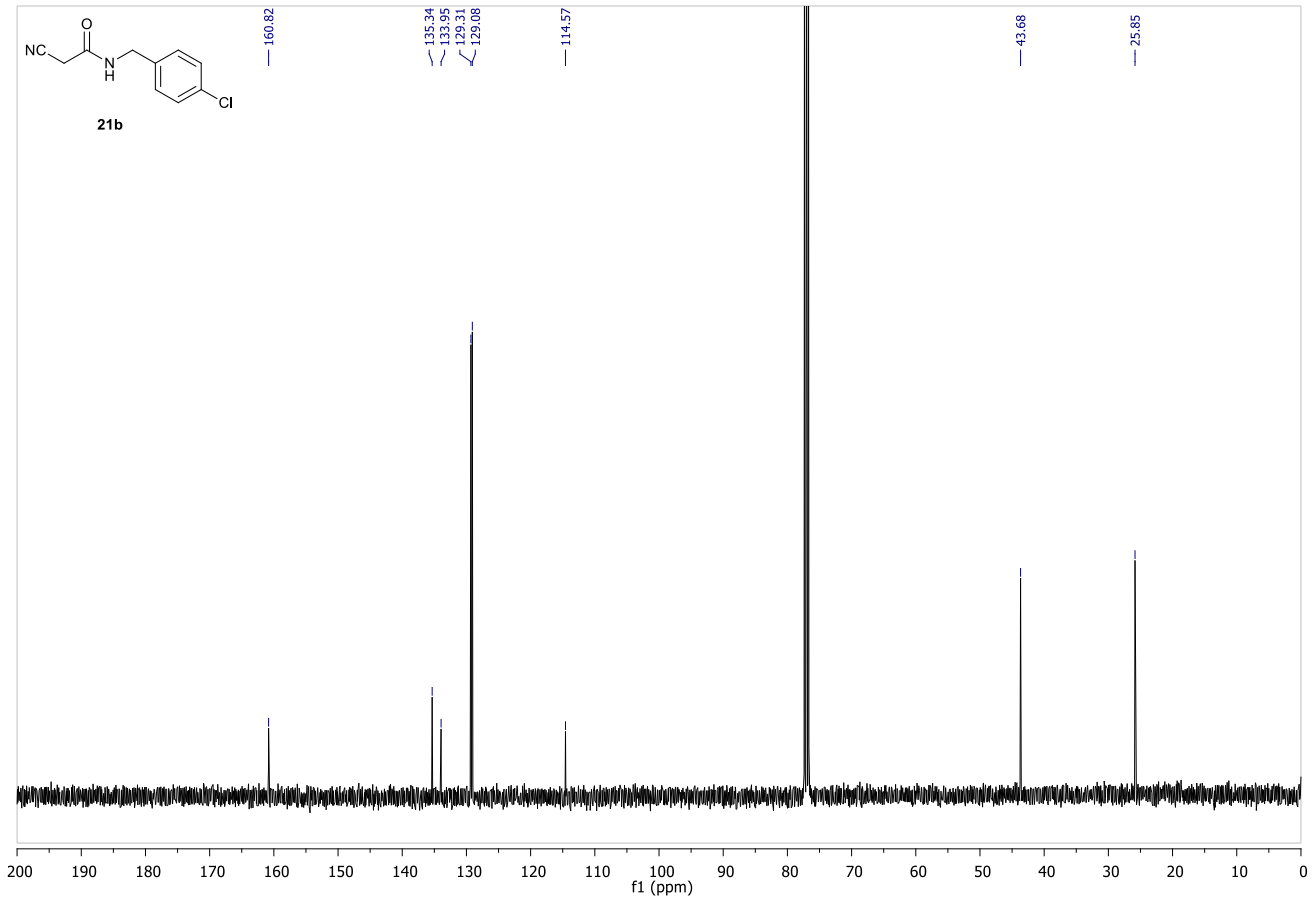


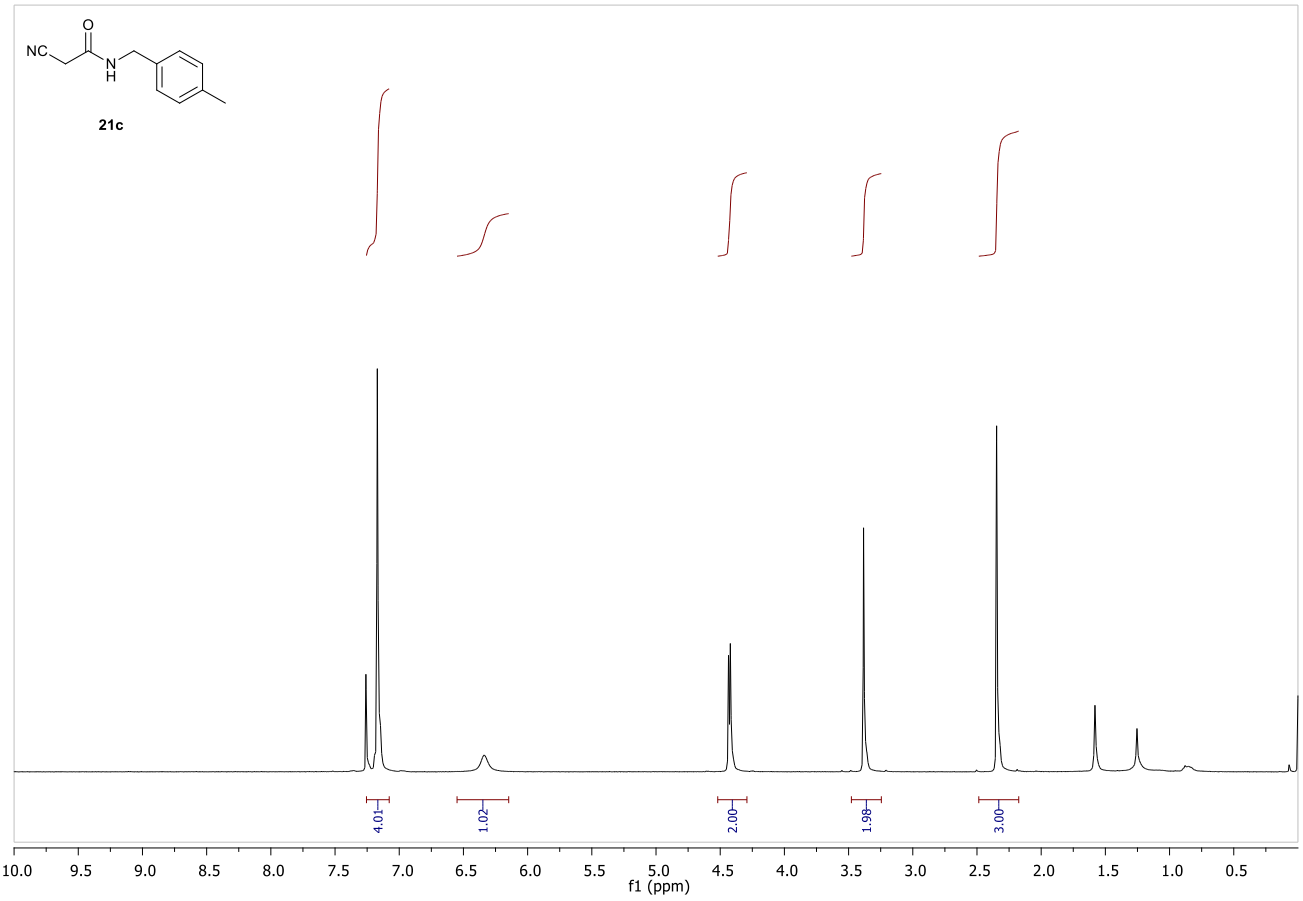


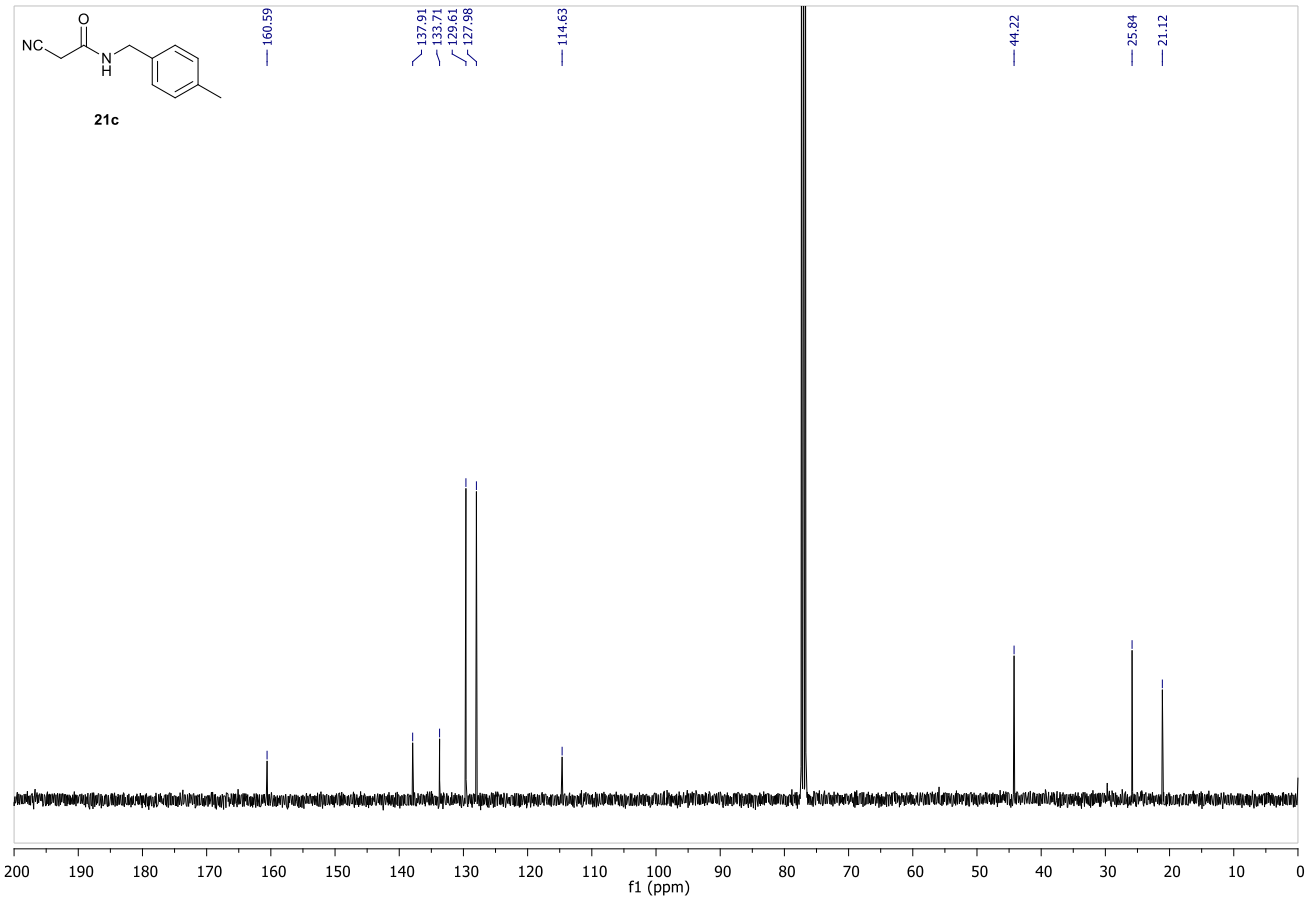


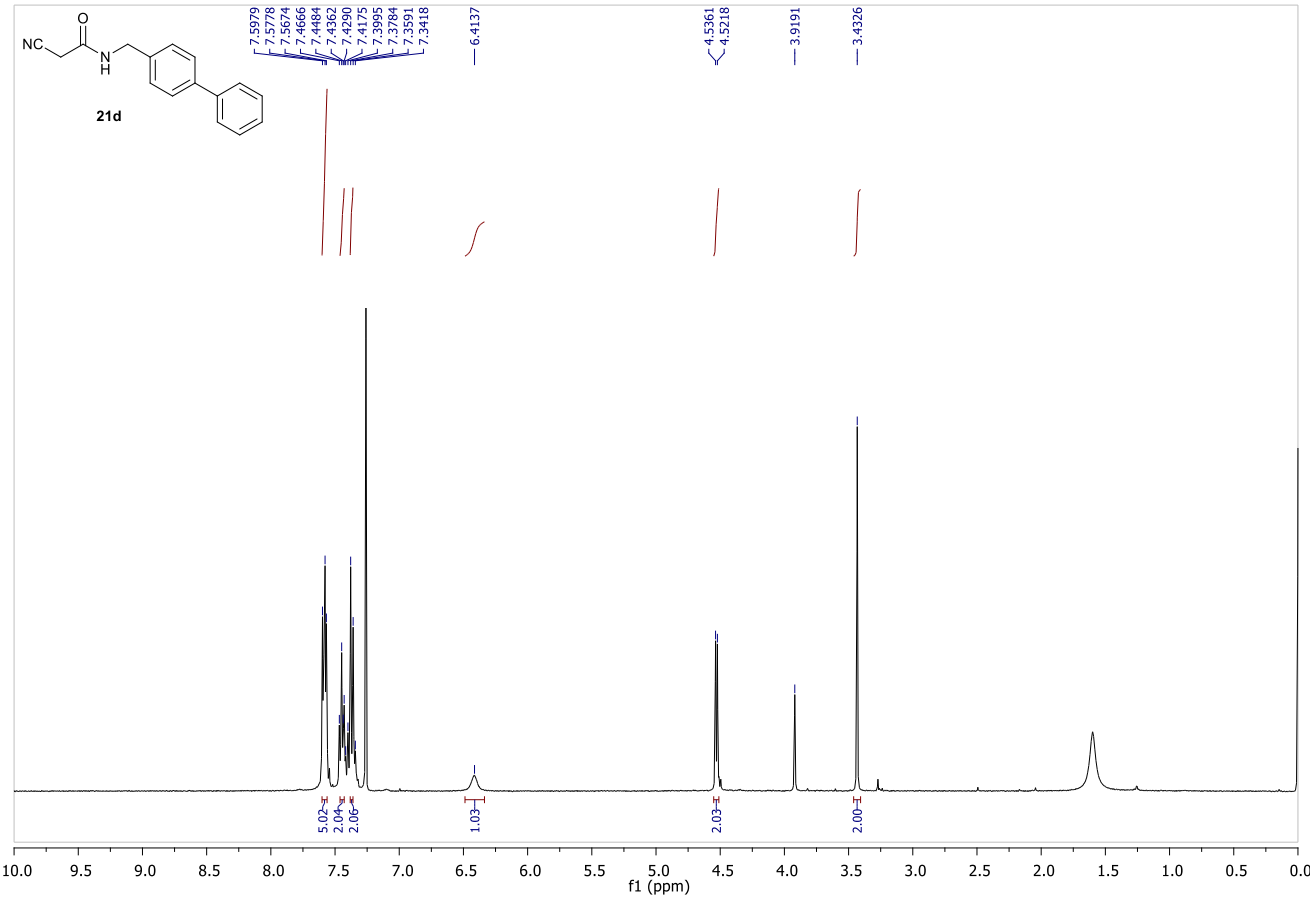


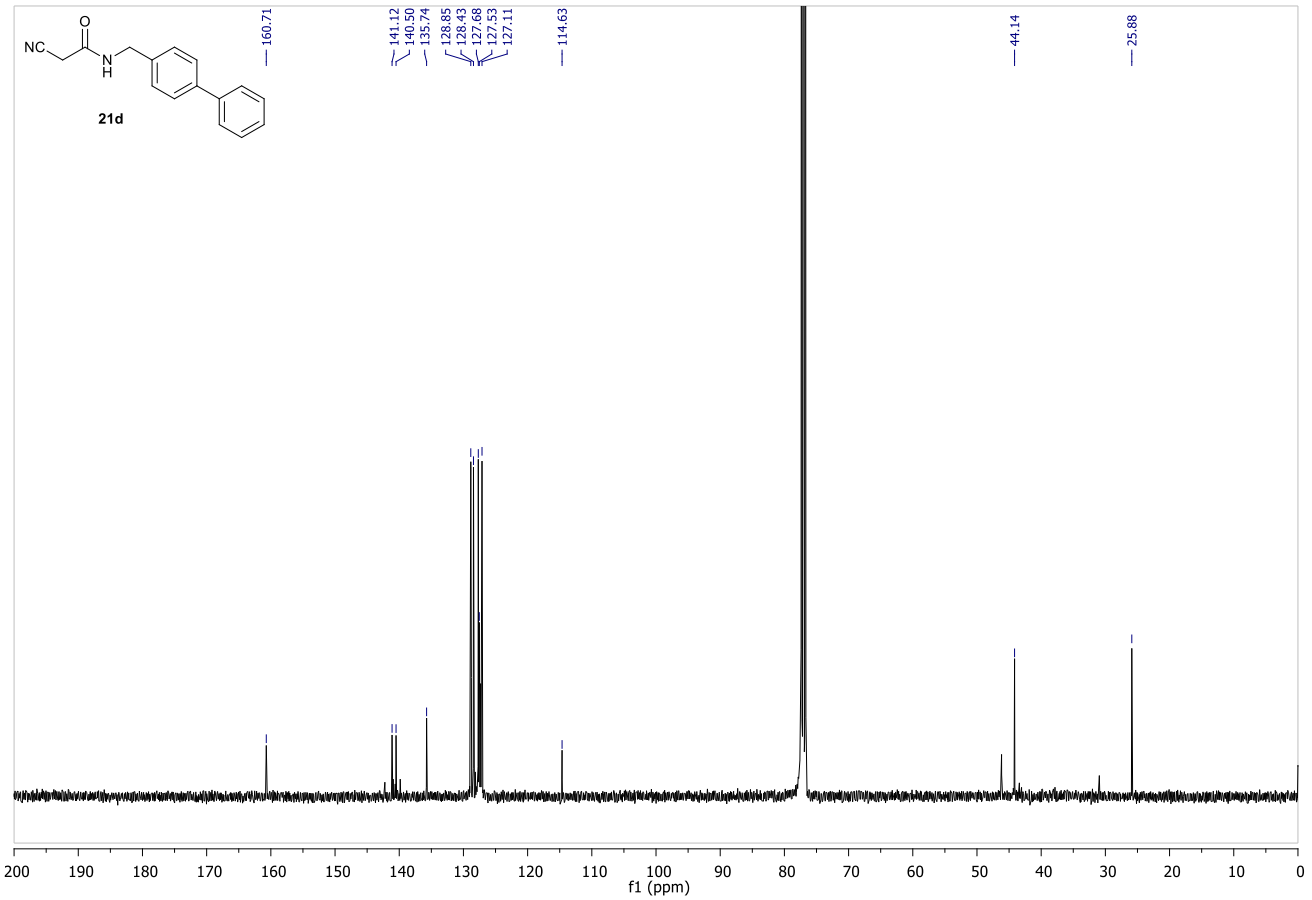


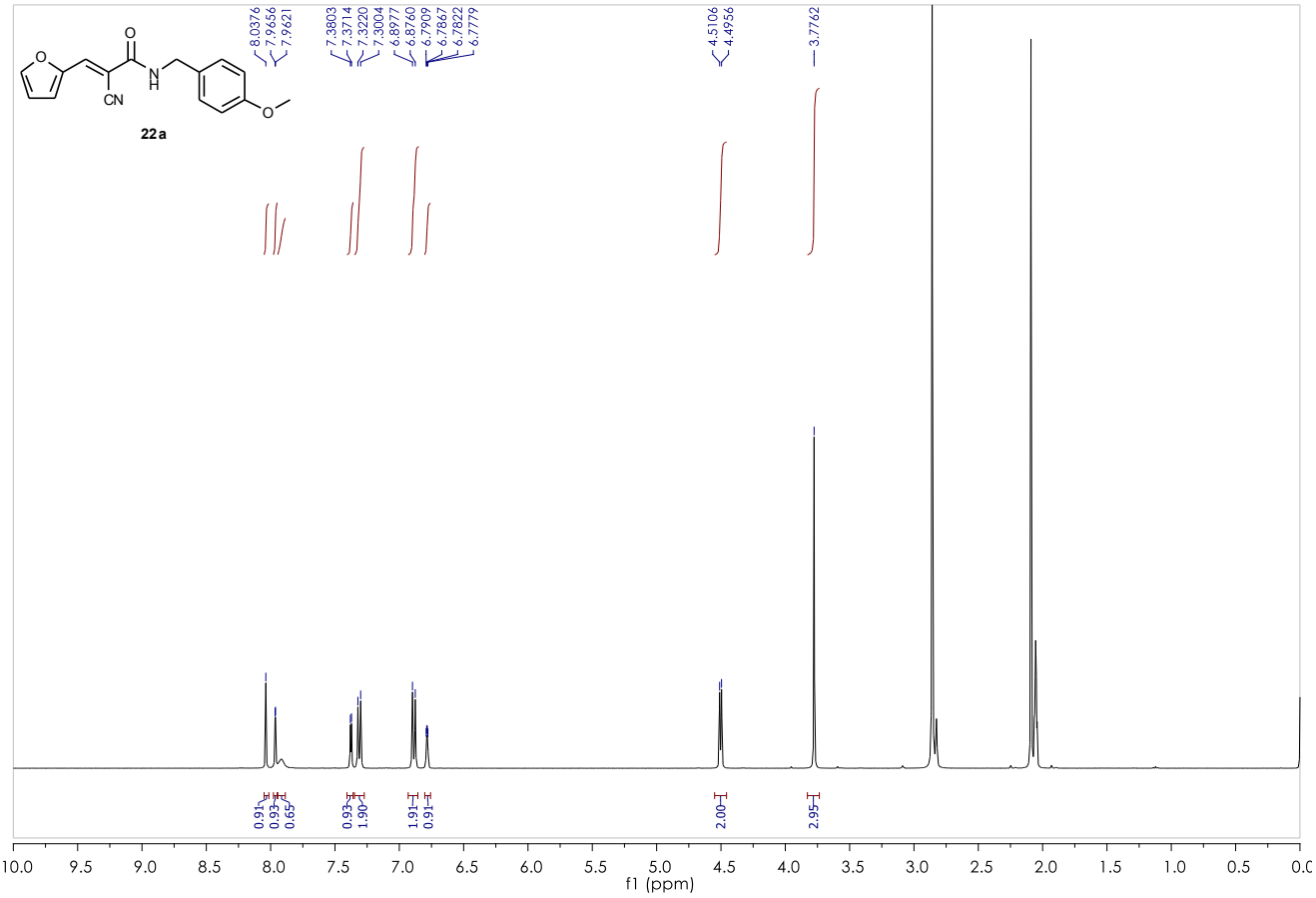


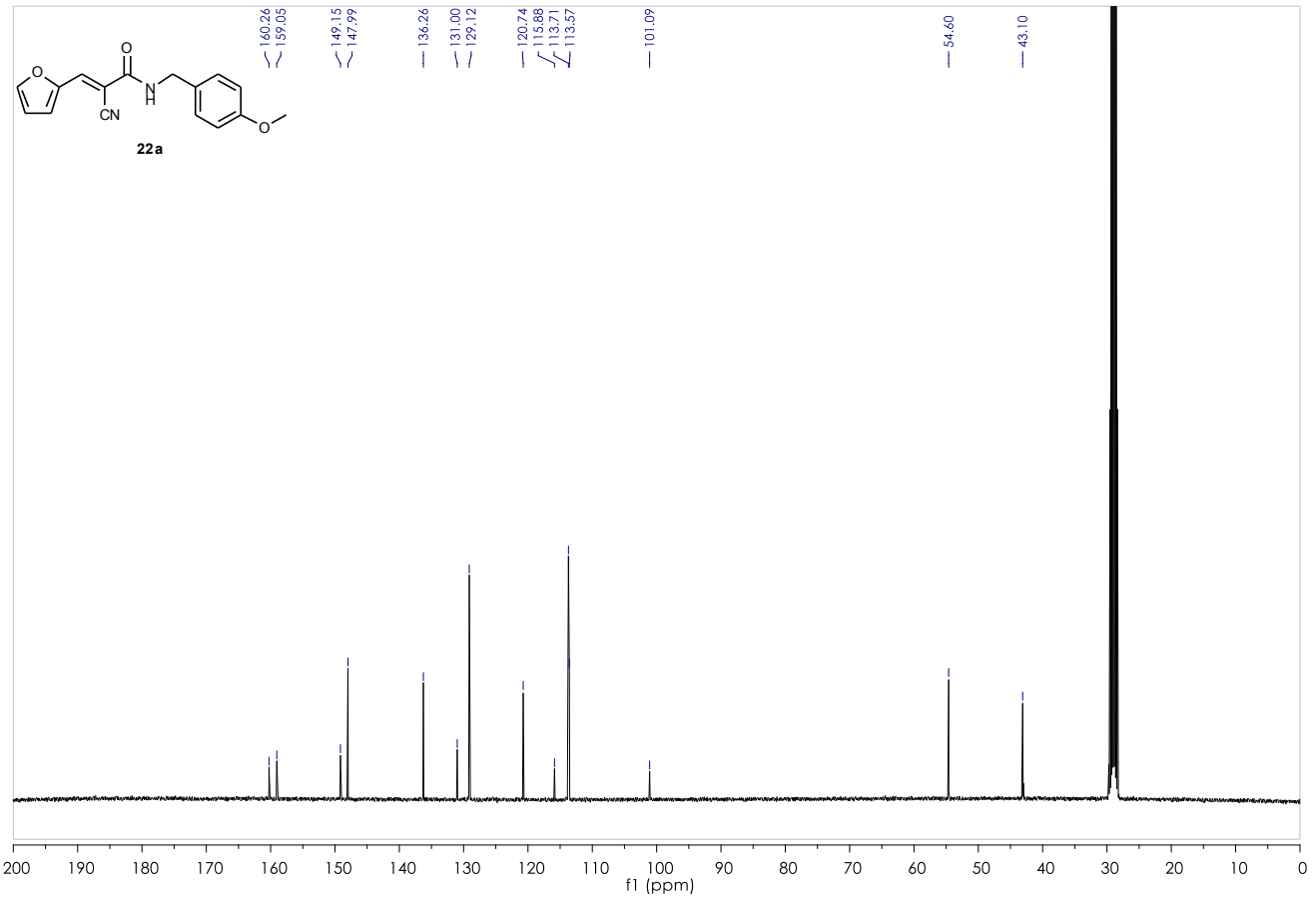


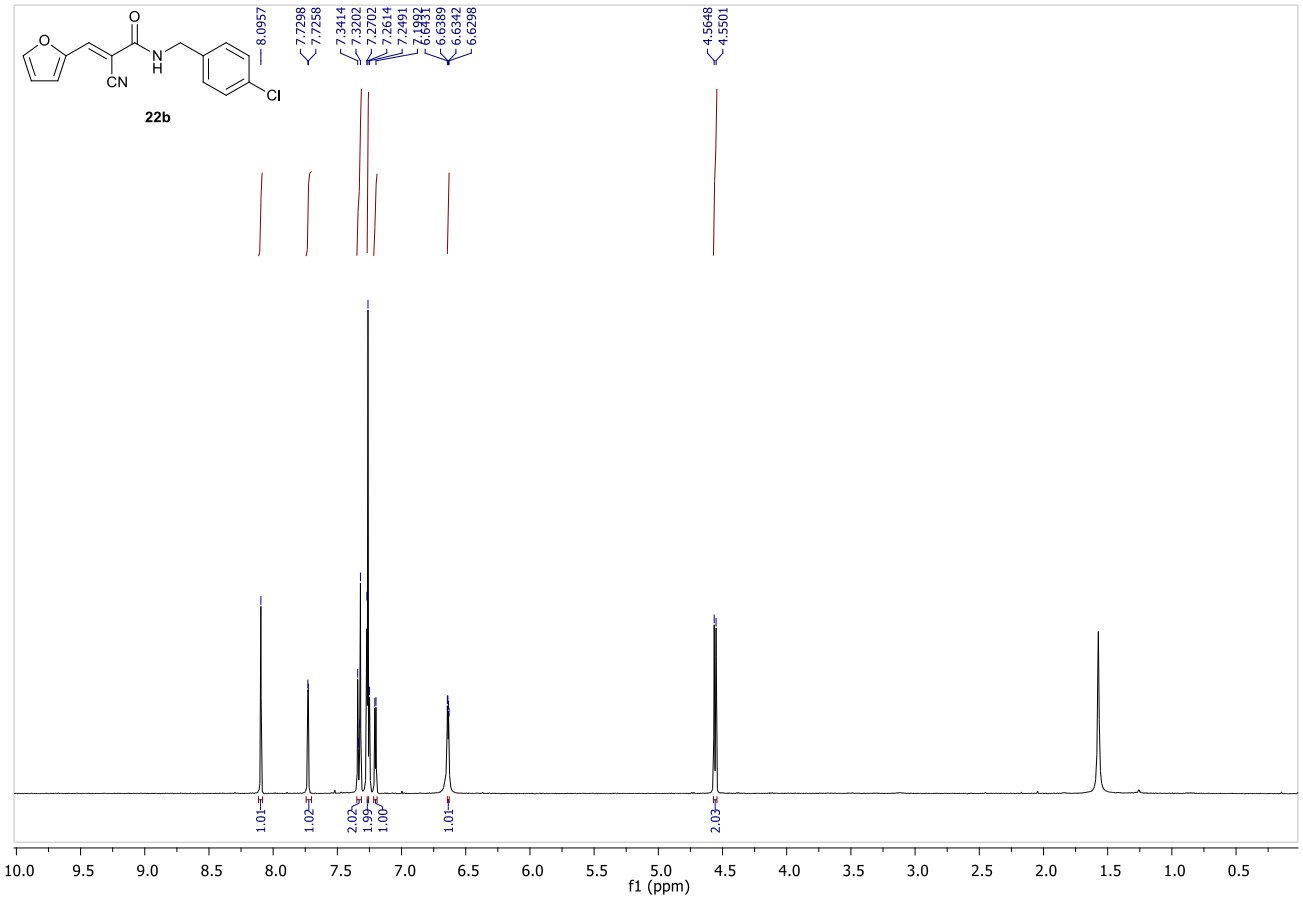








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6.6342
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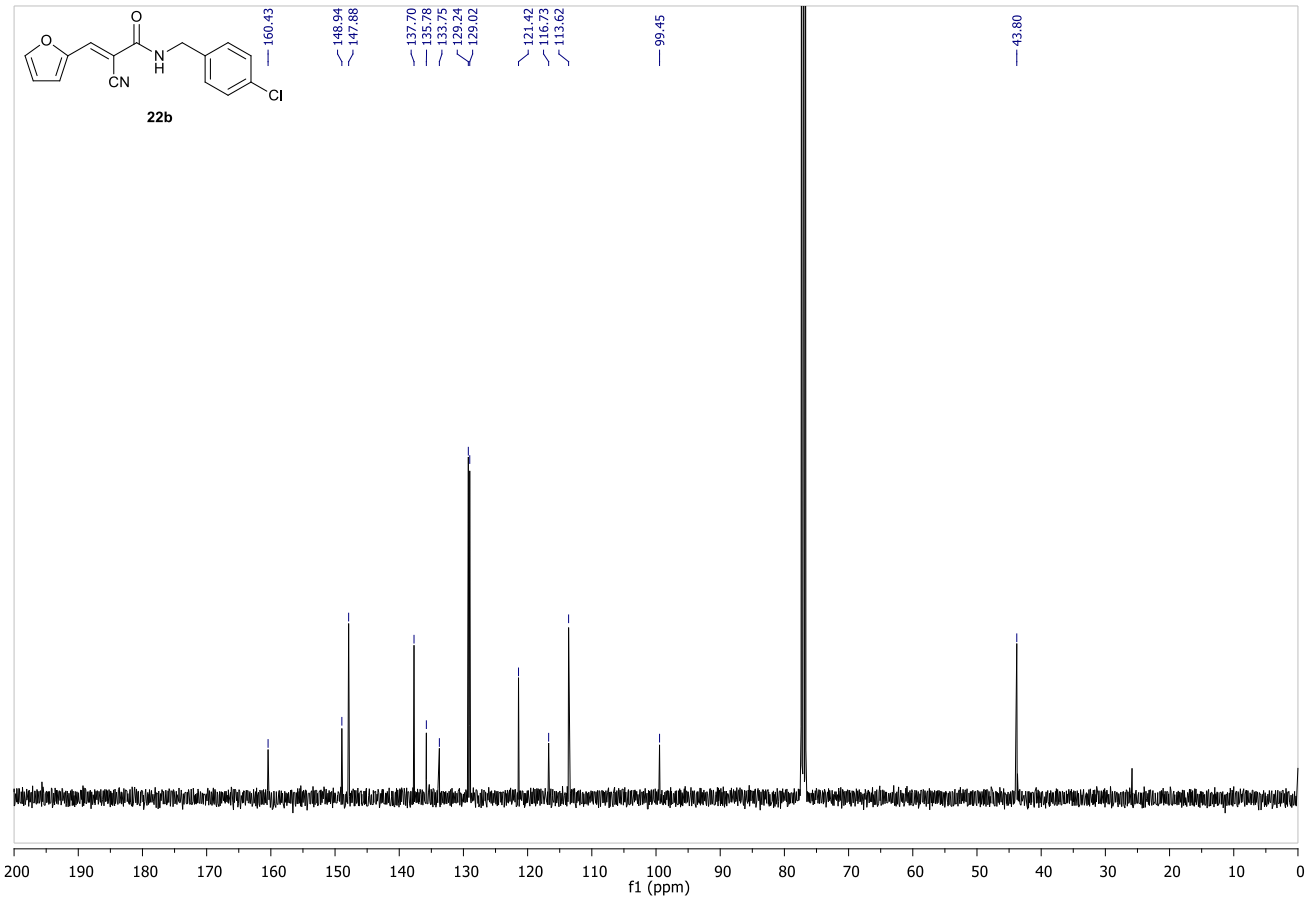
1.02
2.02
1.99
1.00
1.01
2.03
f1 (ppm)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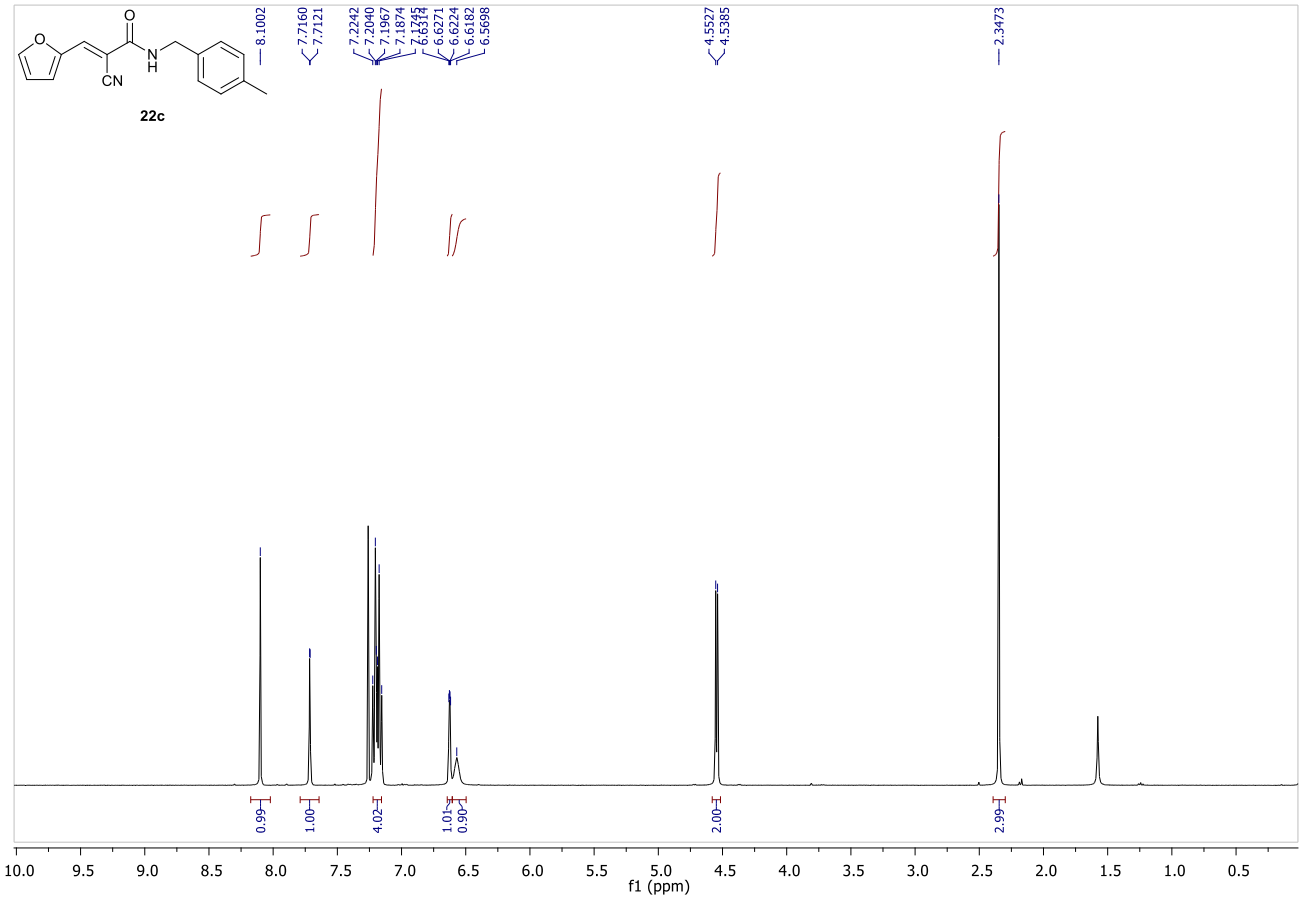
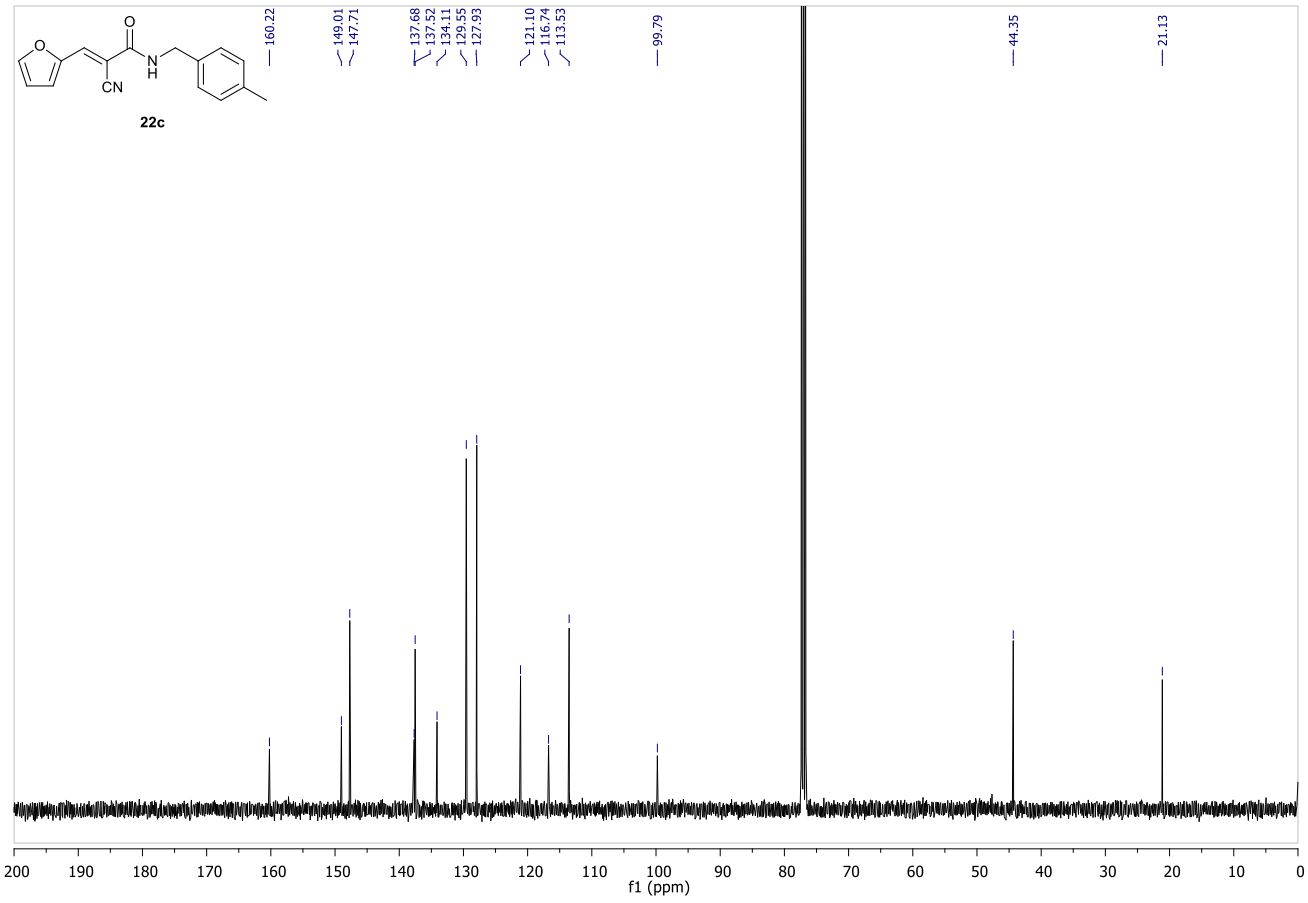
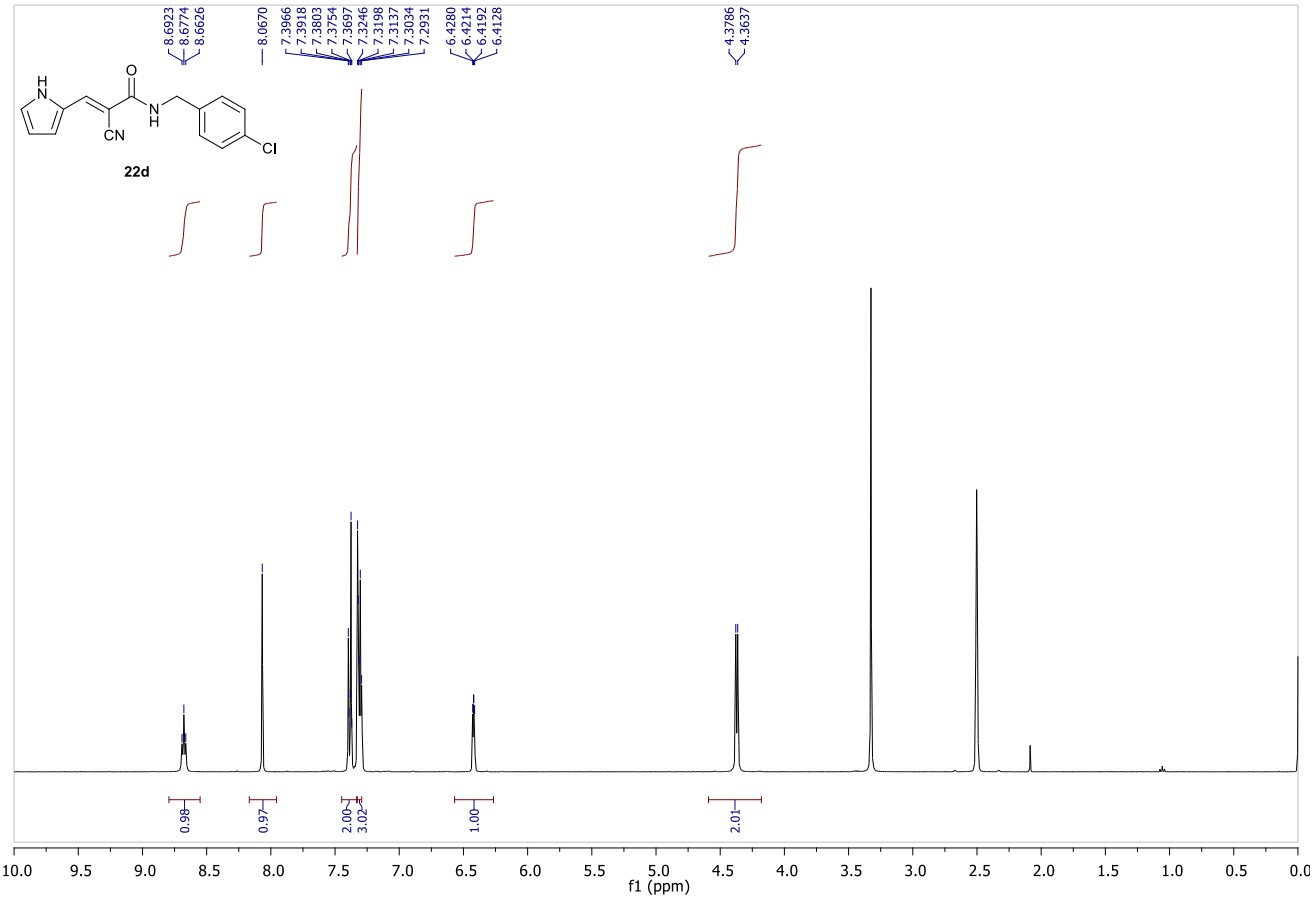
43.80
f1 (ppm)



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7.2931
6.4280
6.4214
6.4192
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0.97
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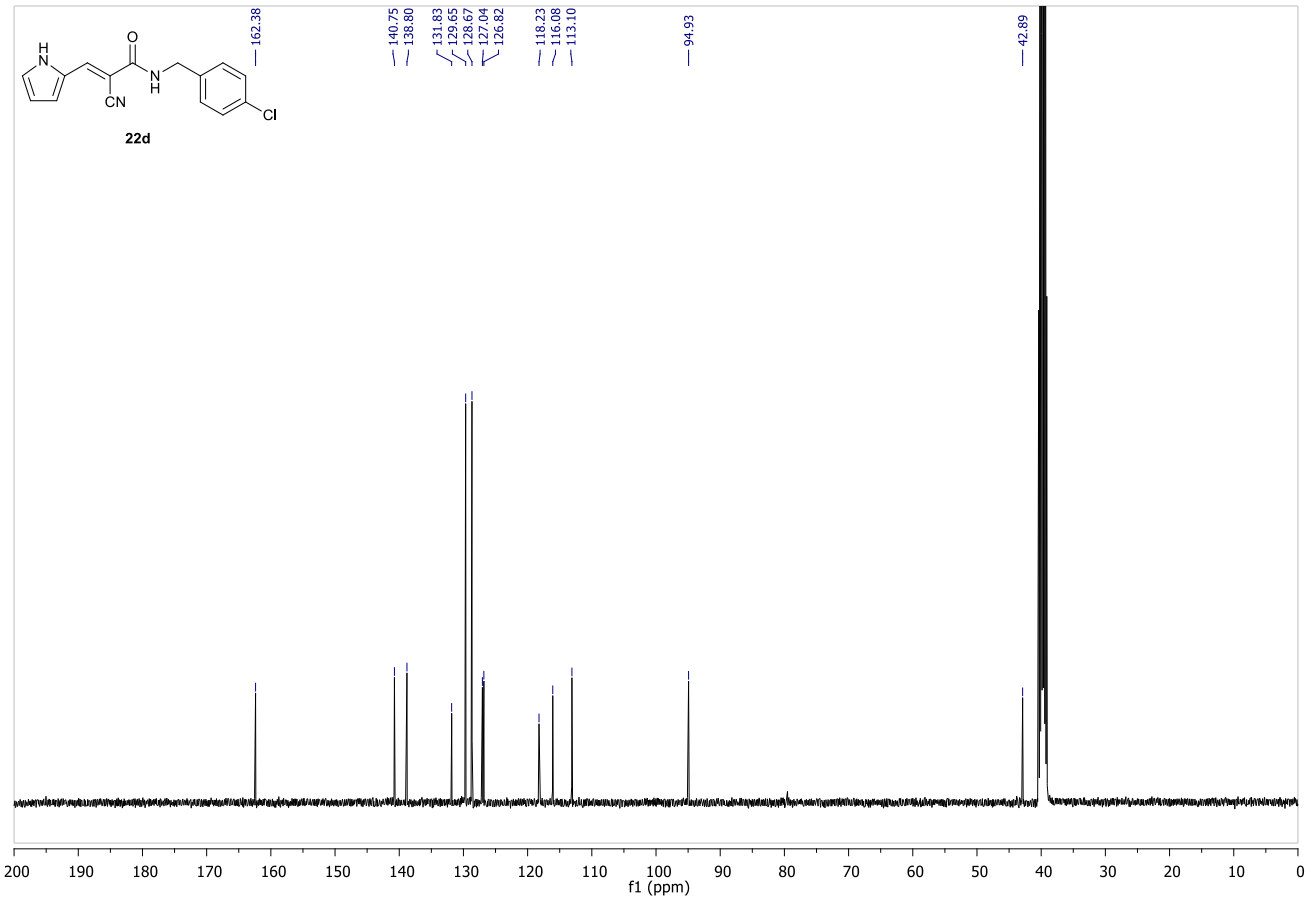
3.02
1.00
2.01
f1 (ppm)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113.10
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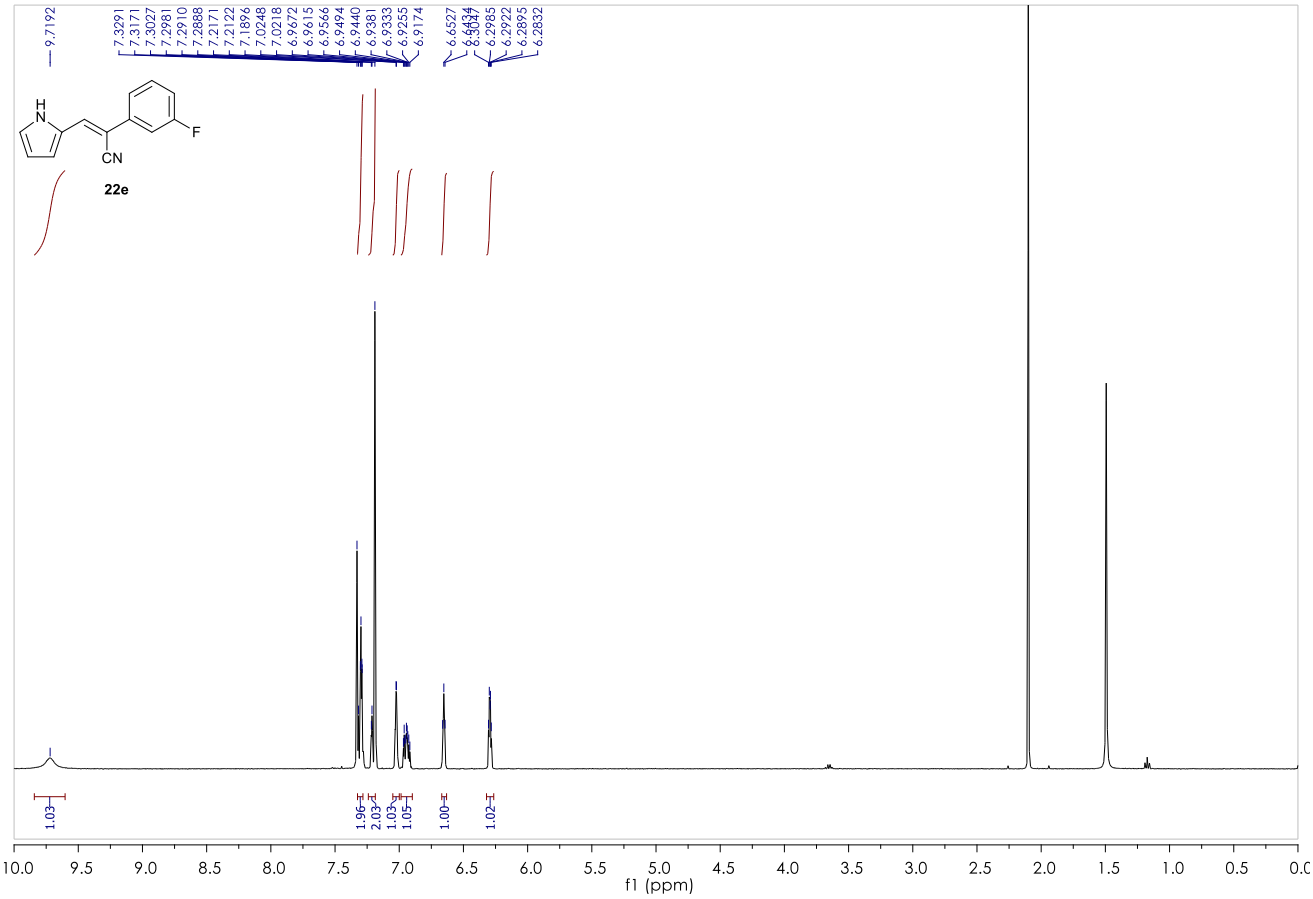
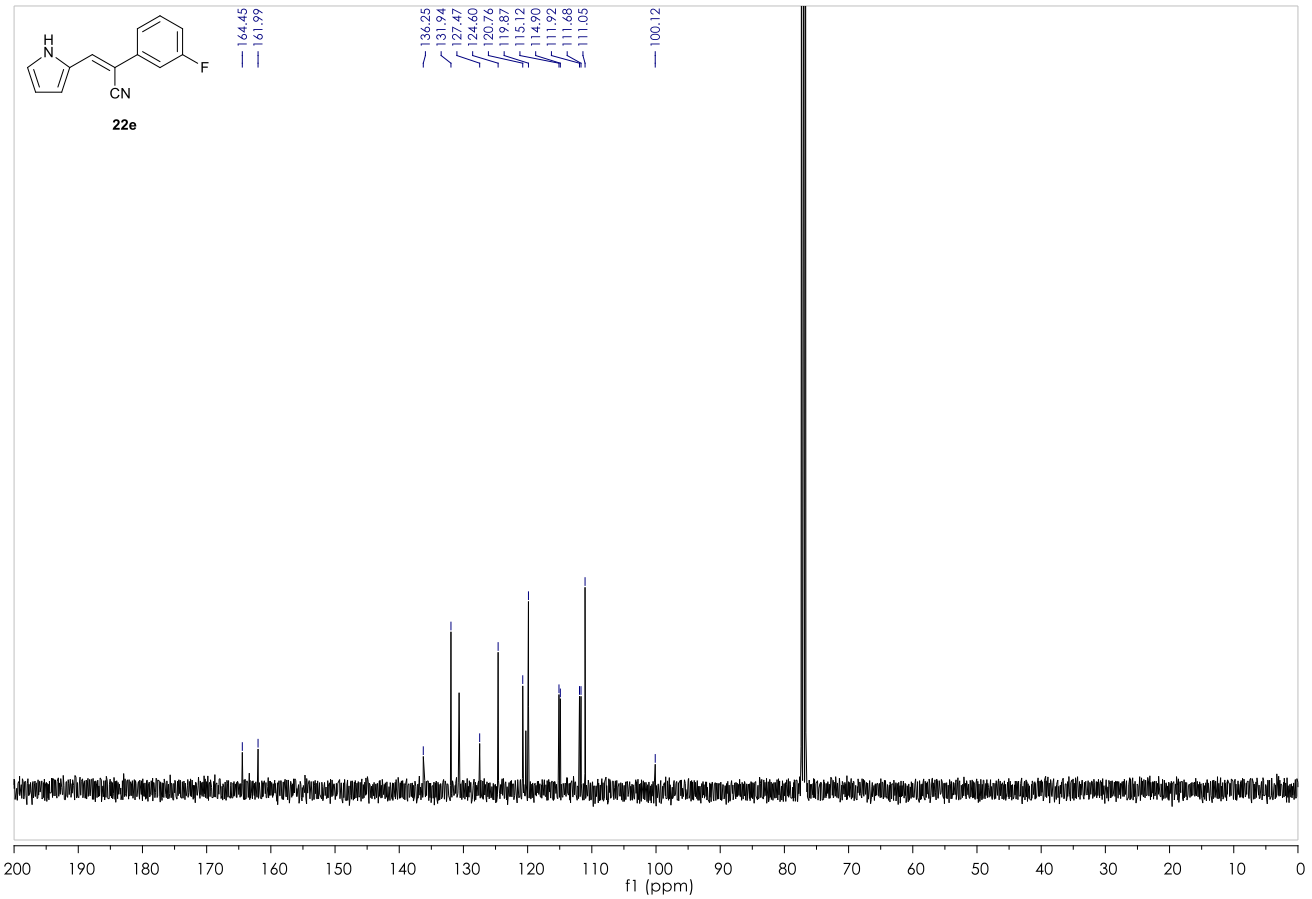
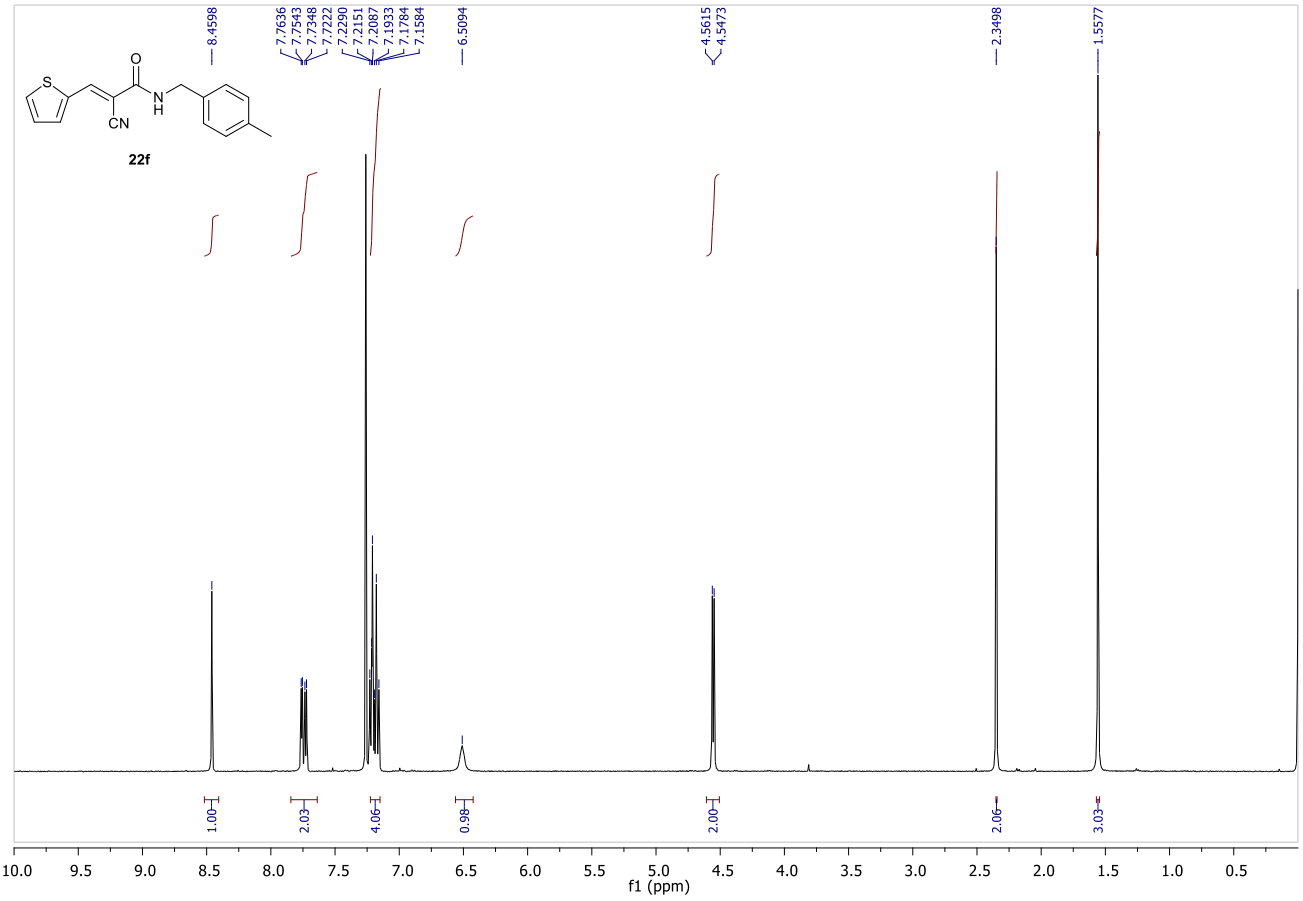
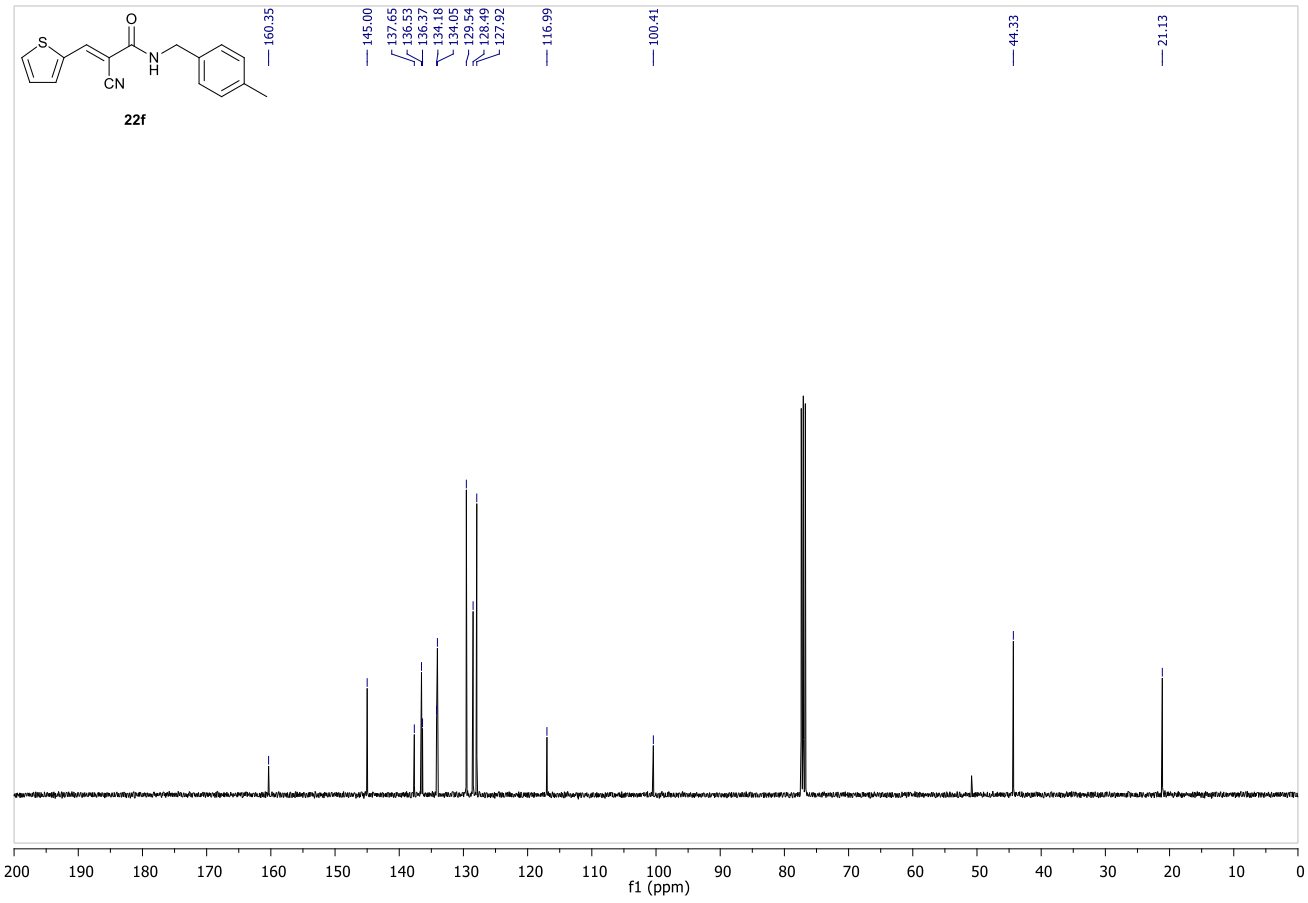
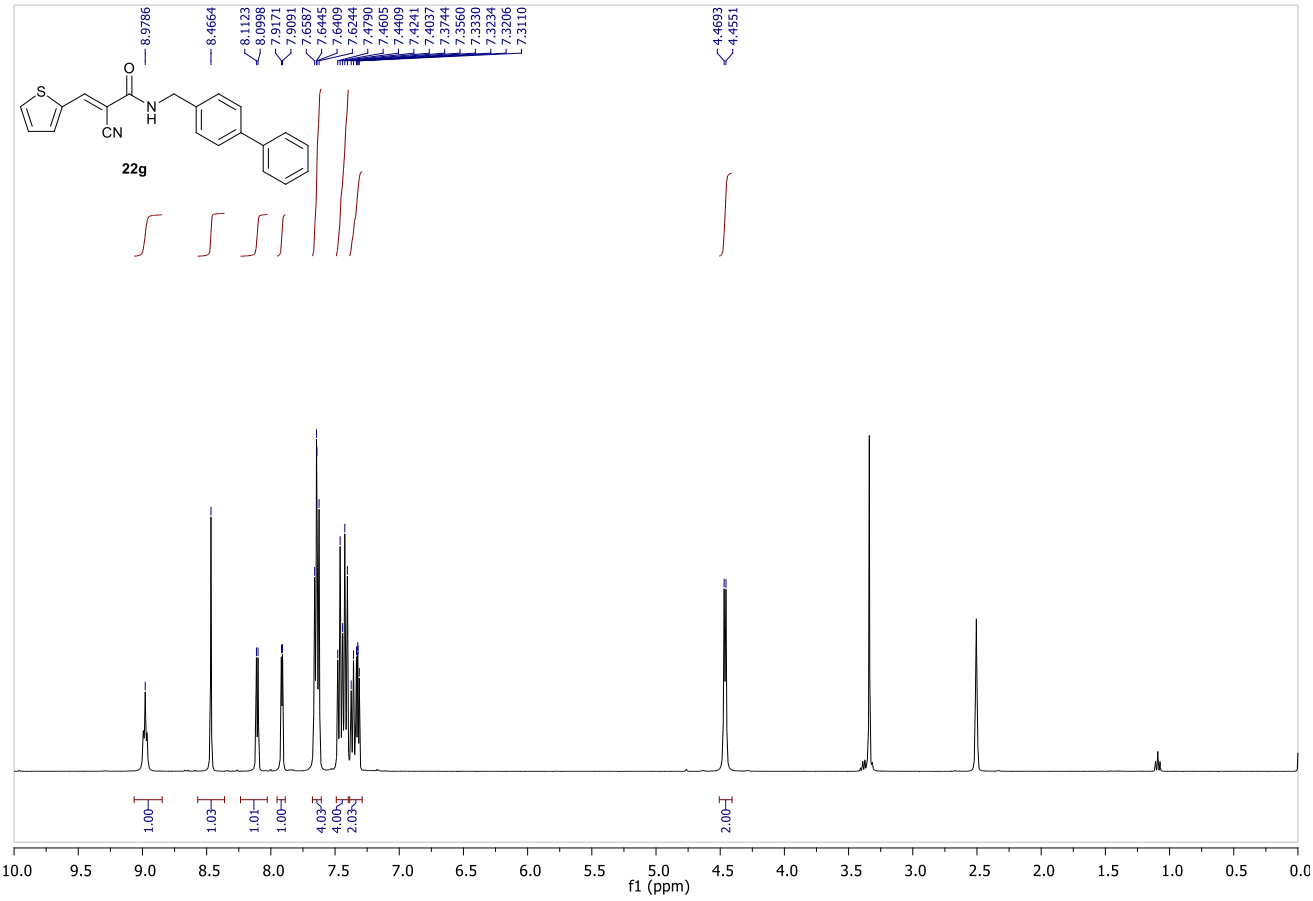
22d
f1 (ppm)







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7.3110
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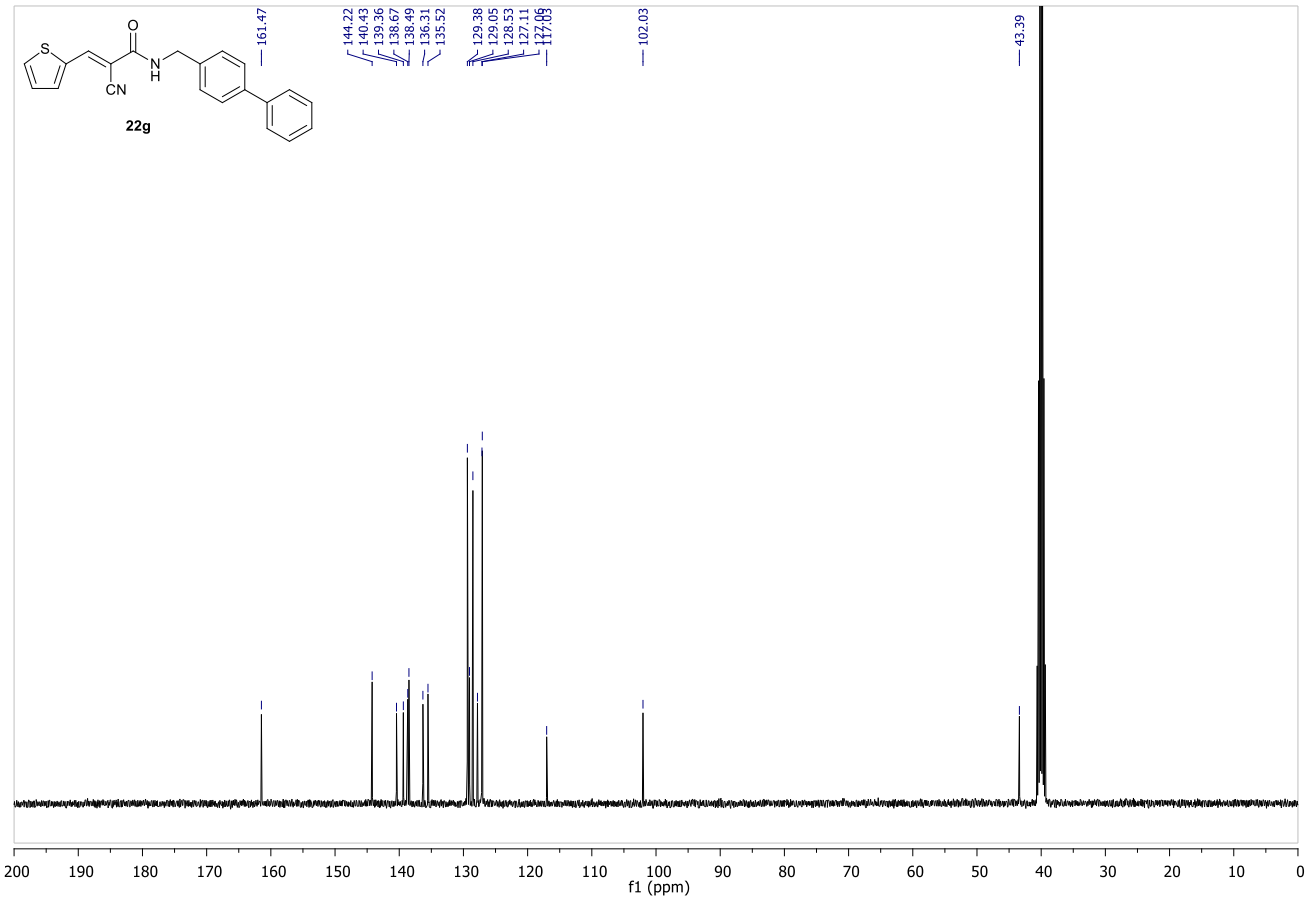
2.00
f1 (ppm)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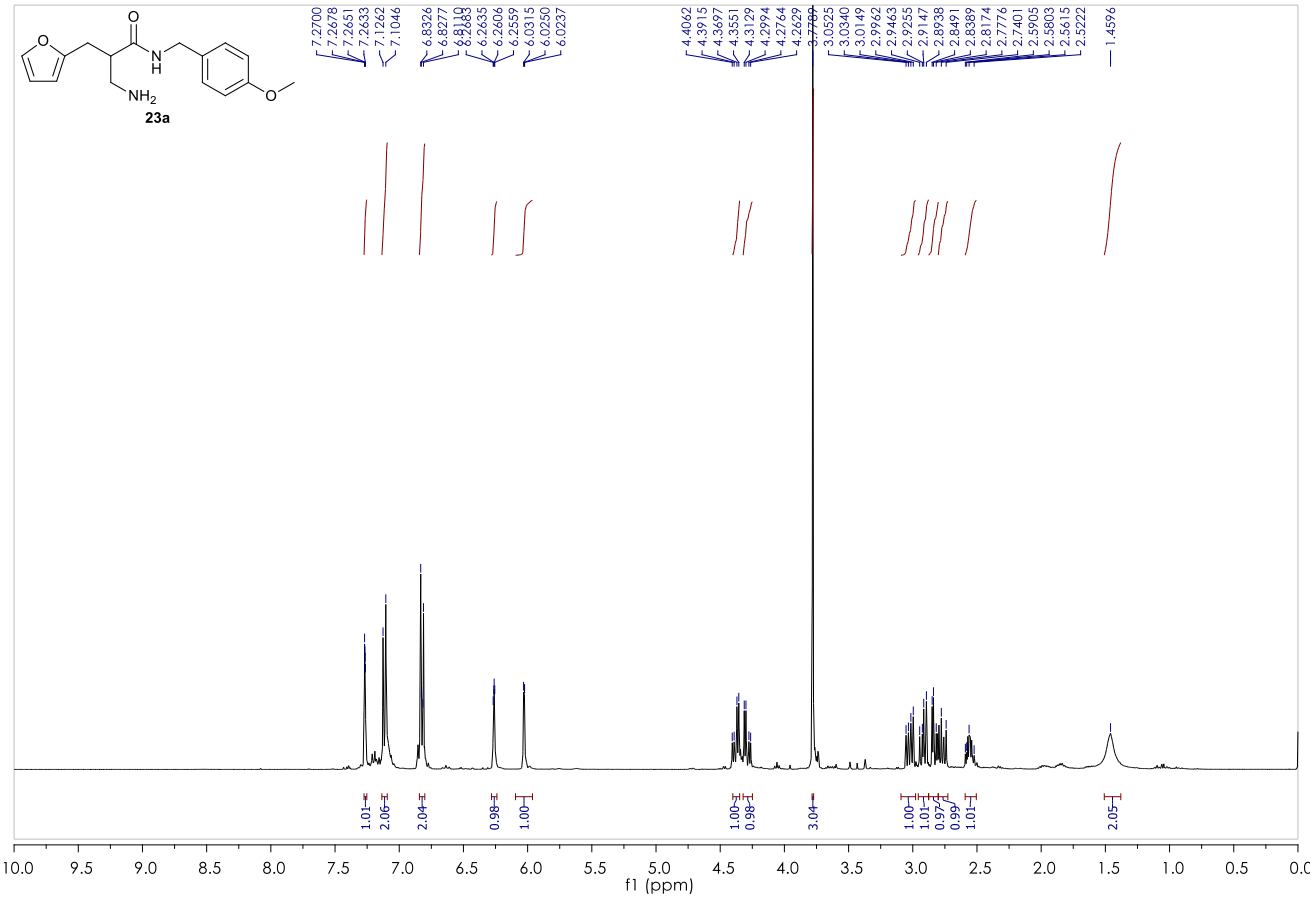
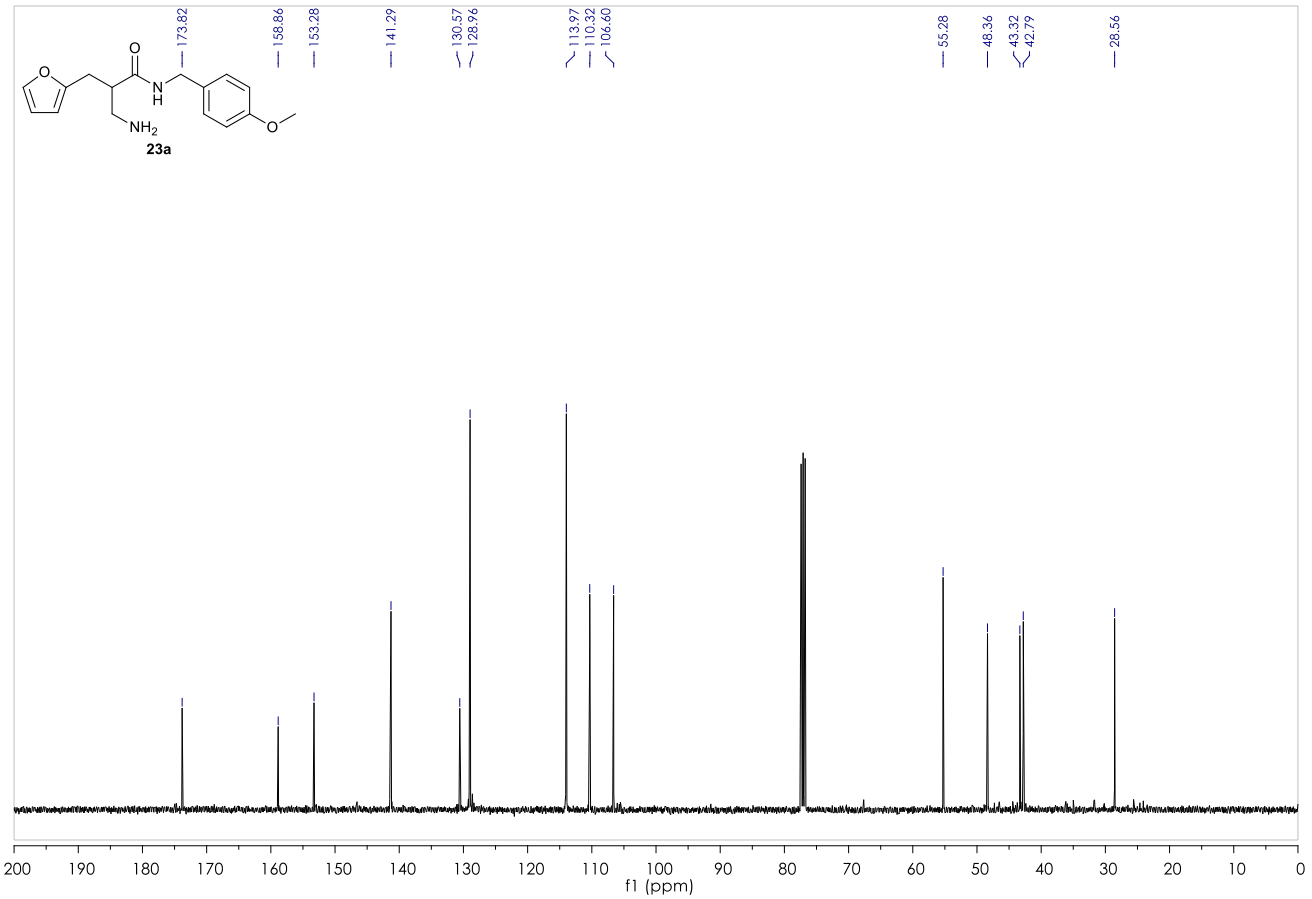
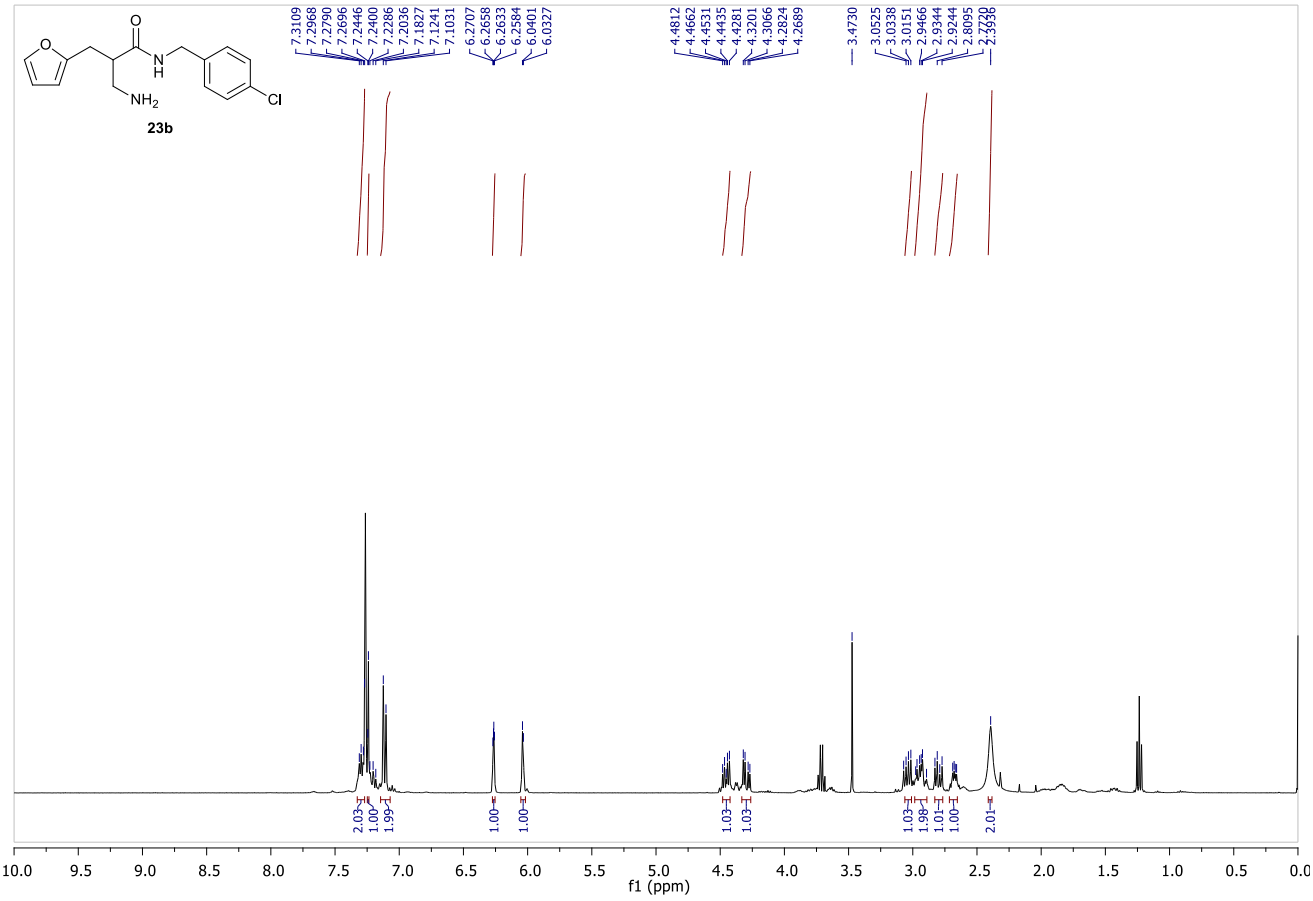
22g
f1 (ppm)



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6.0327
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1.03
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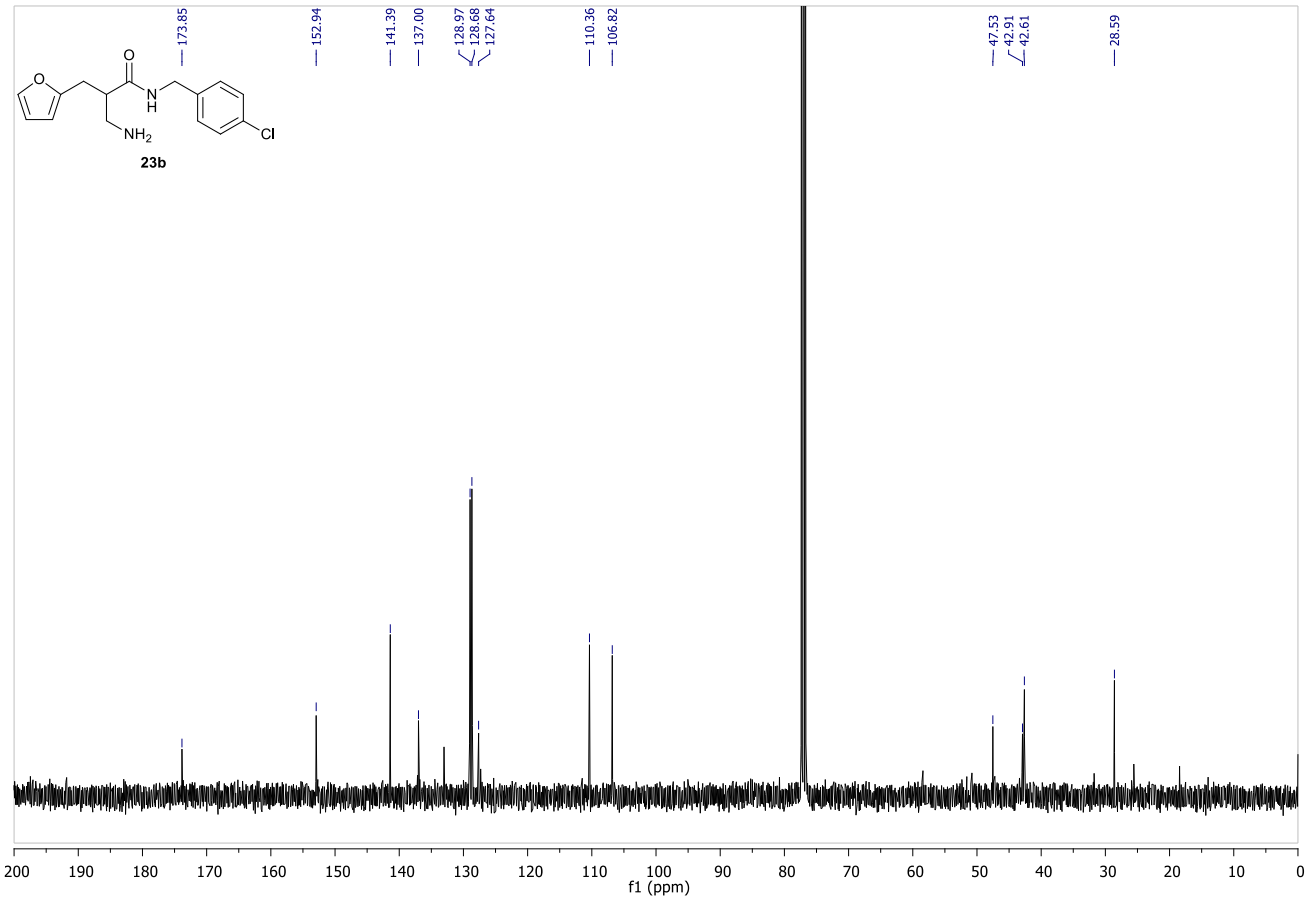
2.01
f1 (ppm)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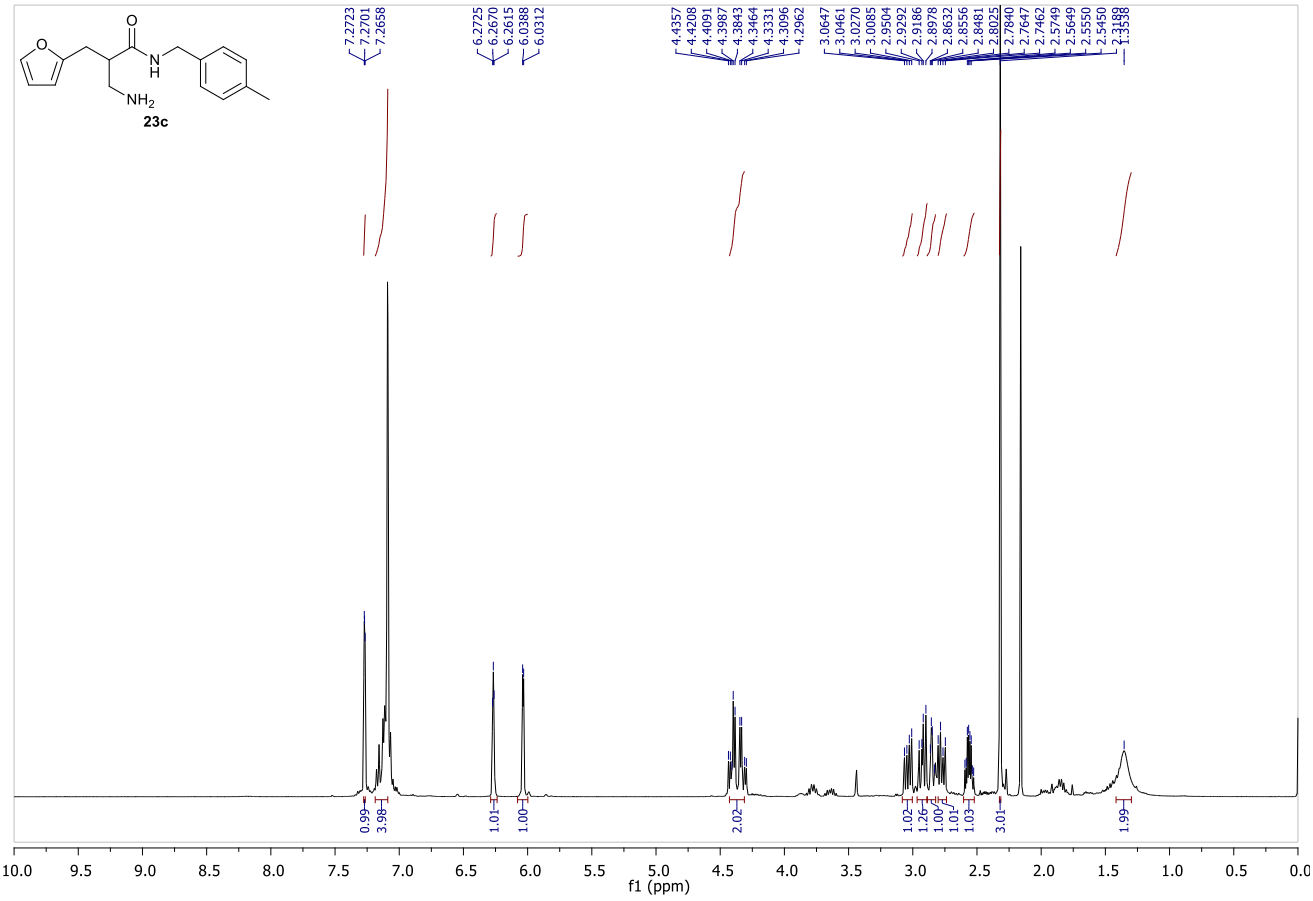
28.59
f1 (ppm)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1.03
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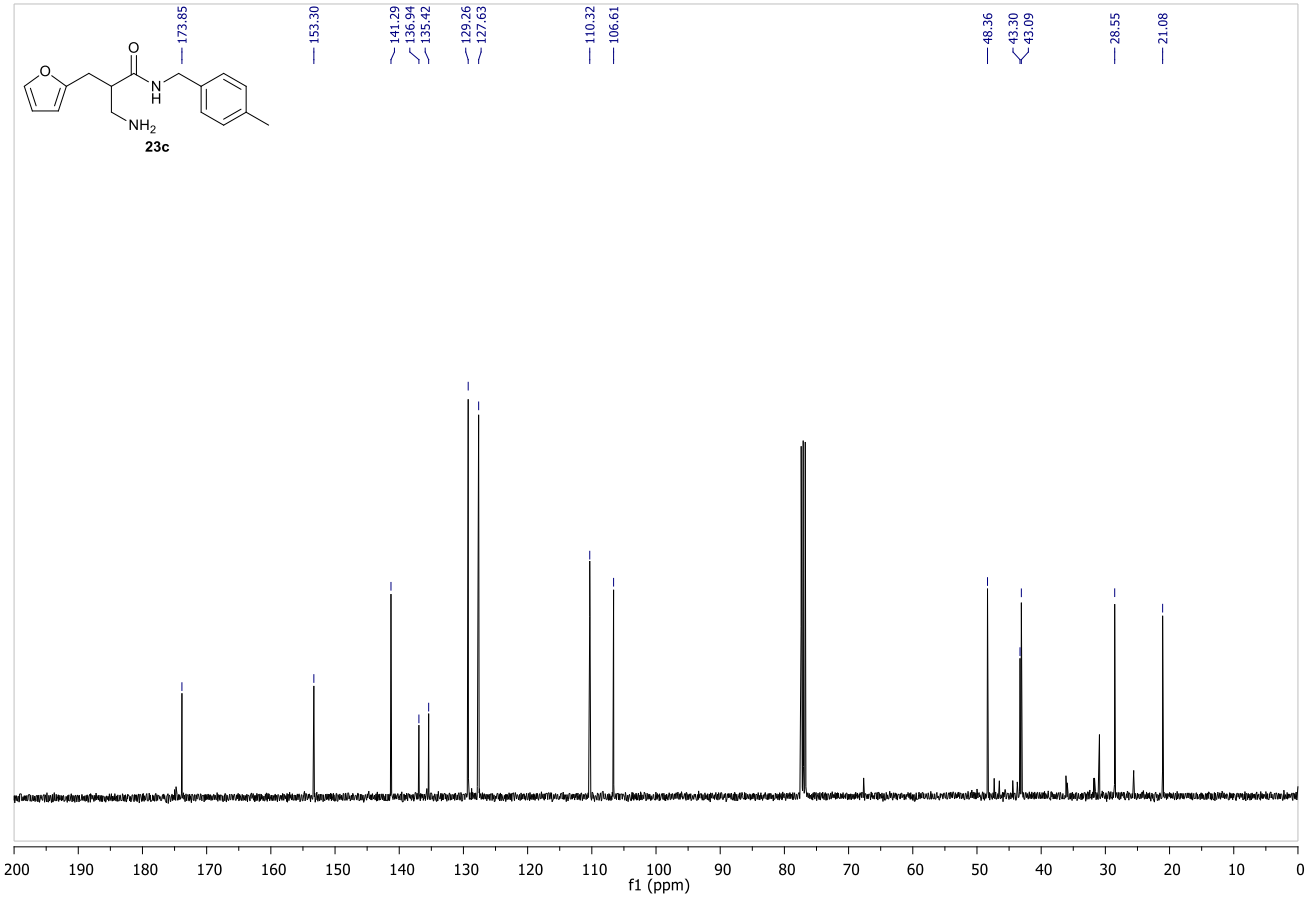
f1 (ppm)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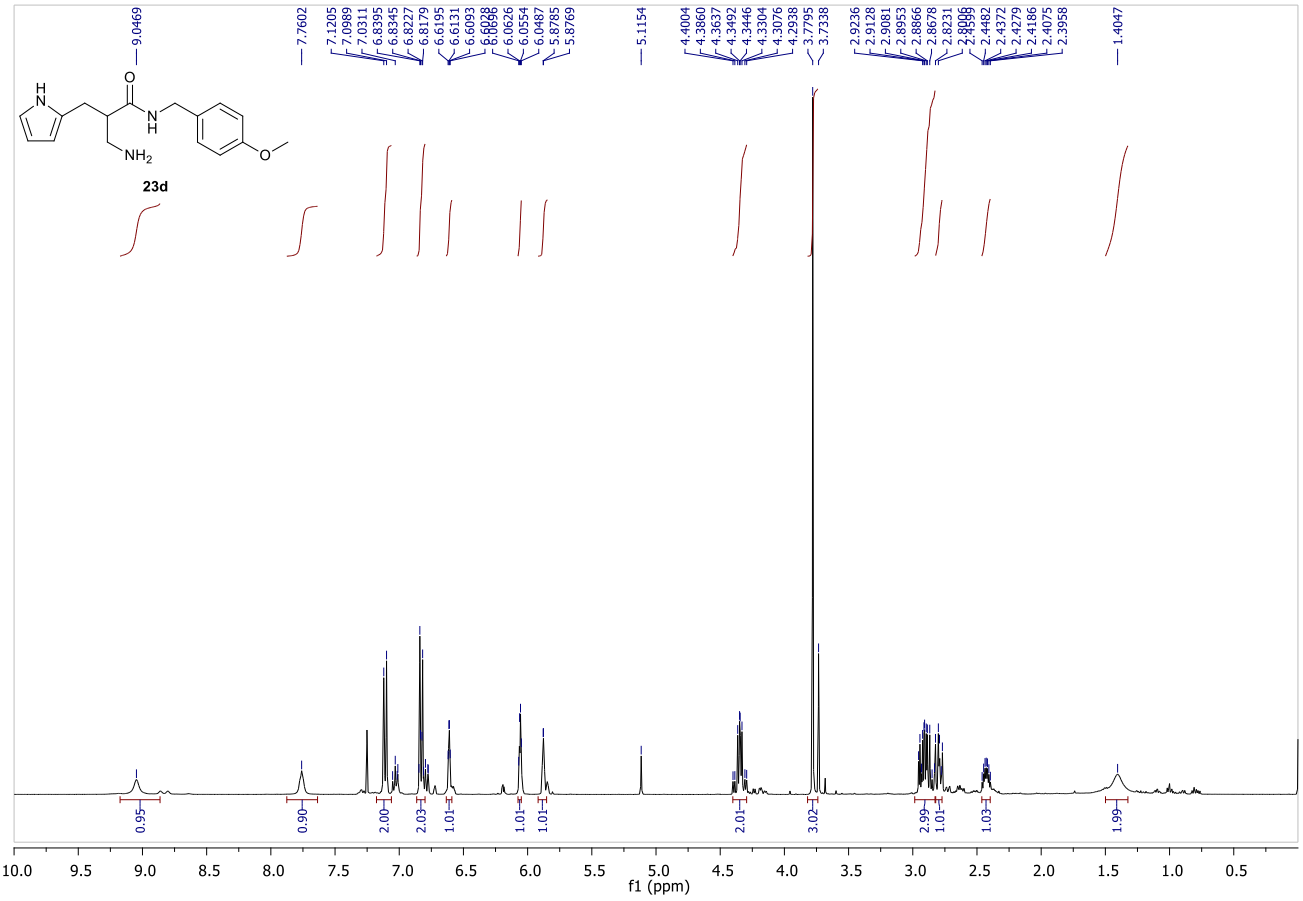
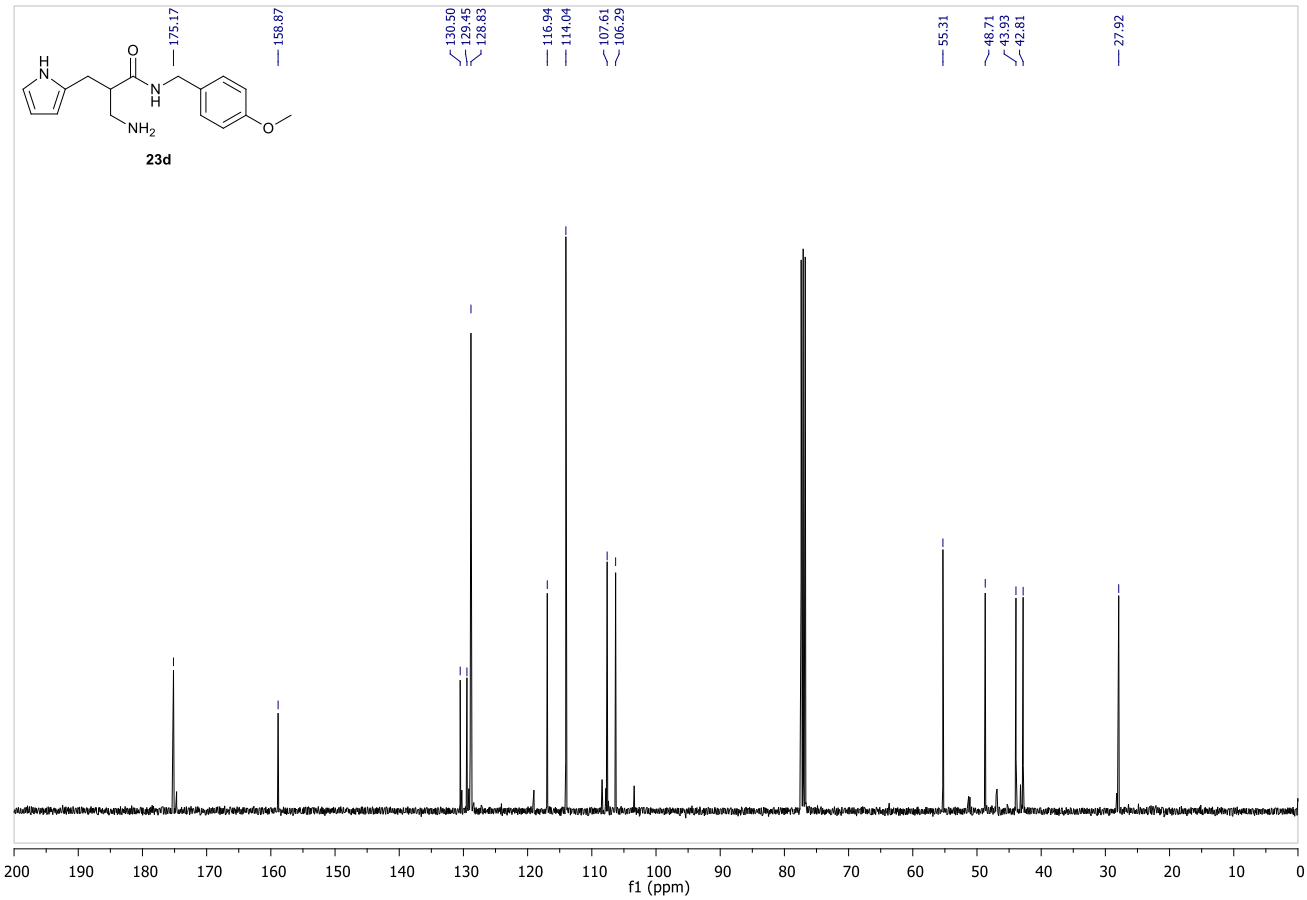
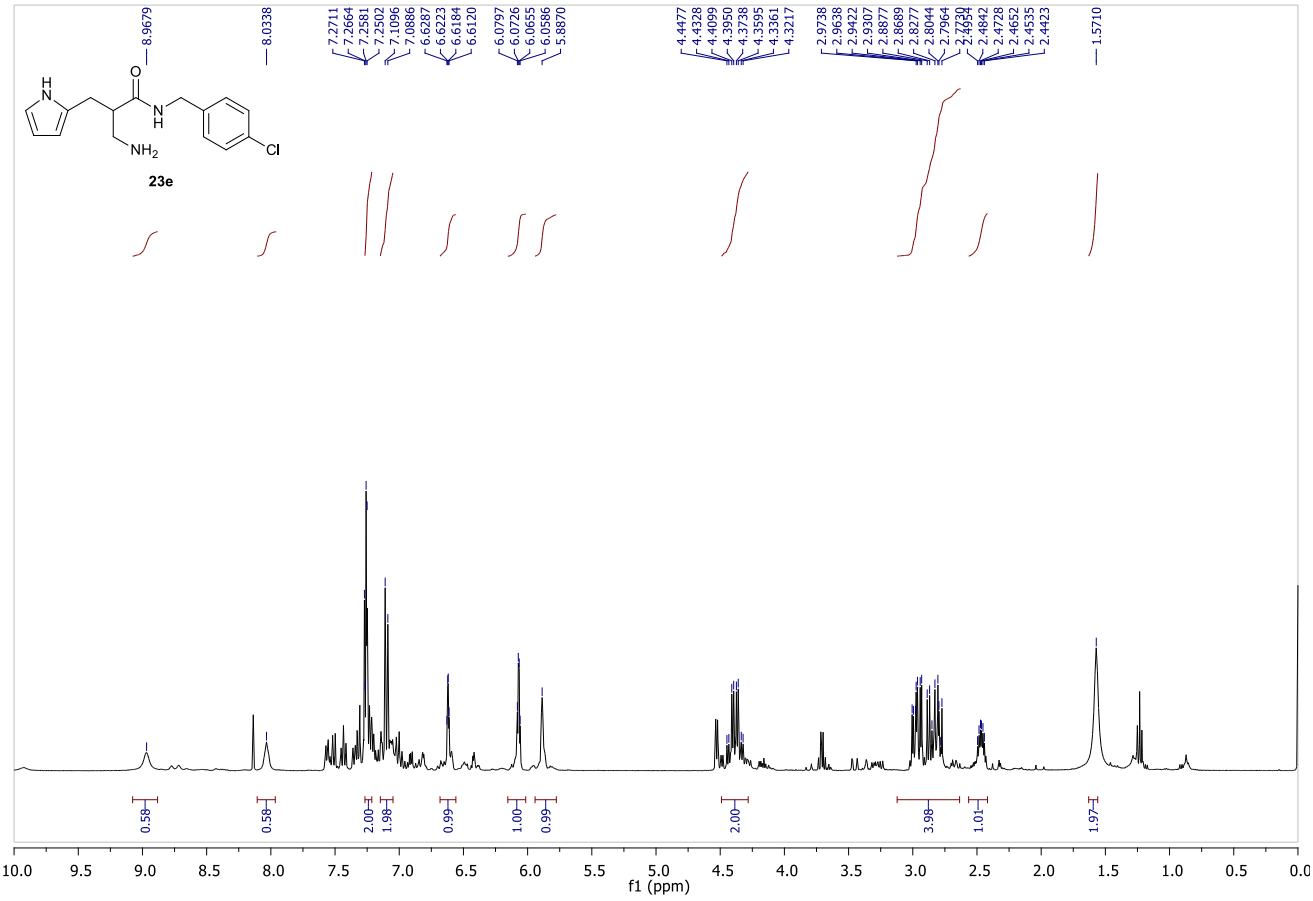
f1 (ppm)



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2.4535
2.4423
1.5710
23e
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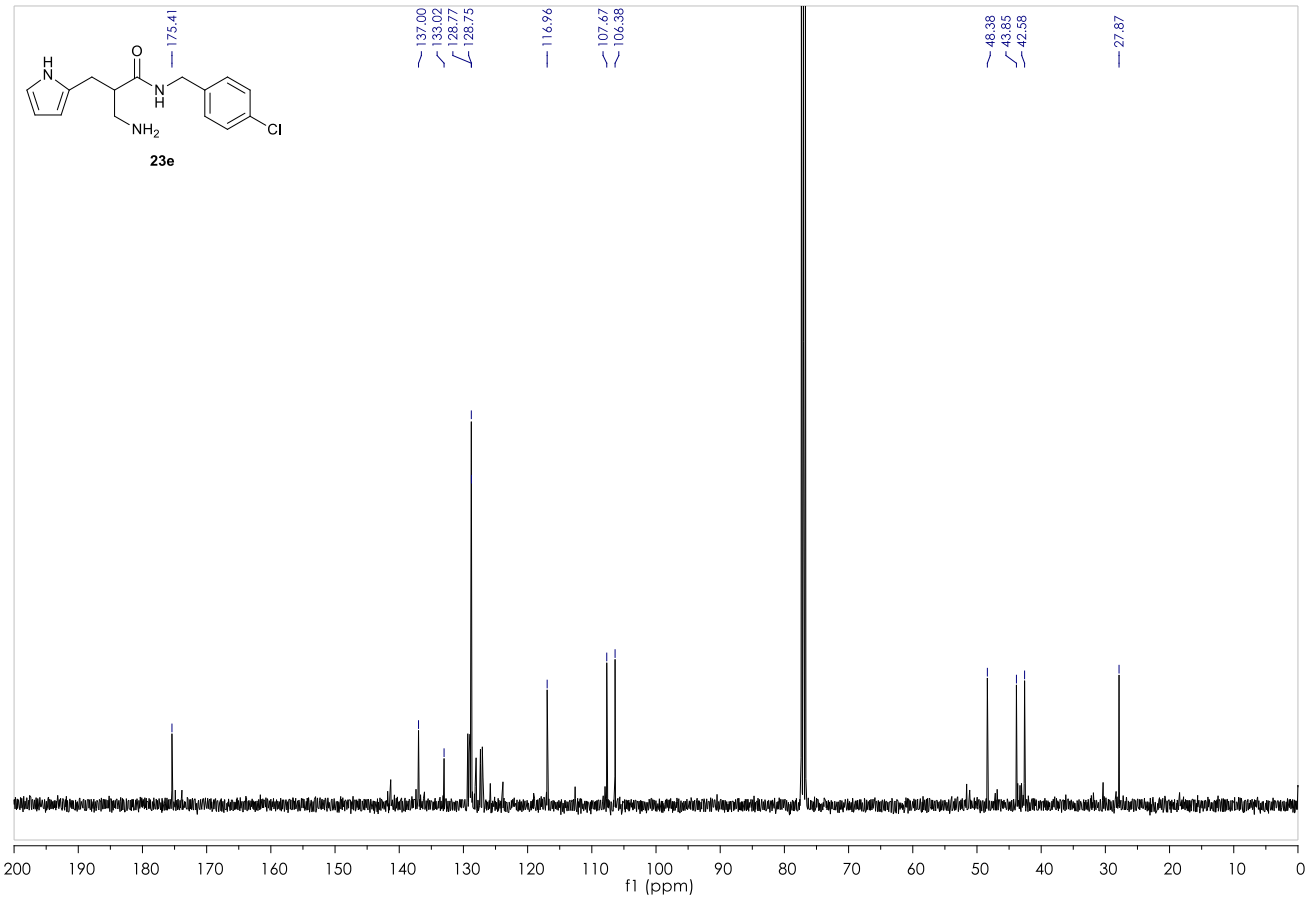
1.97
f1 (ppm)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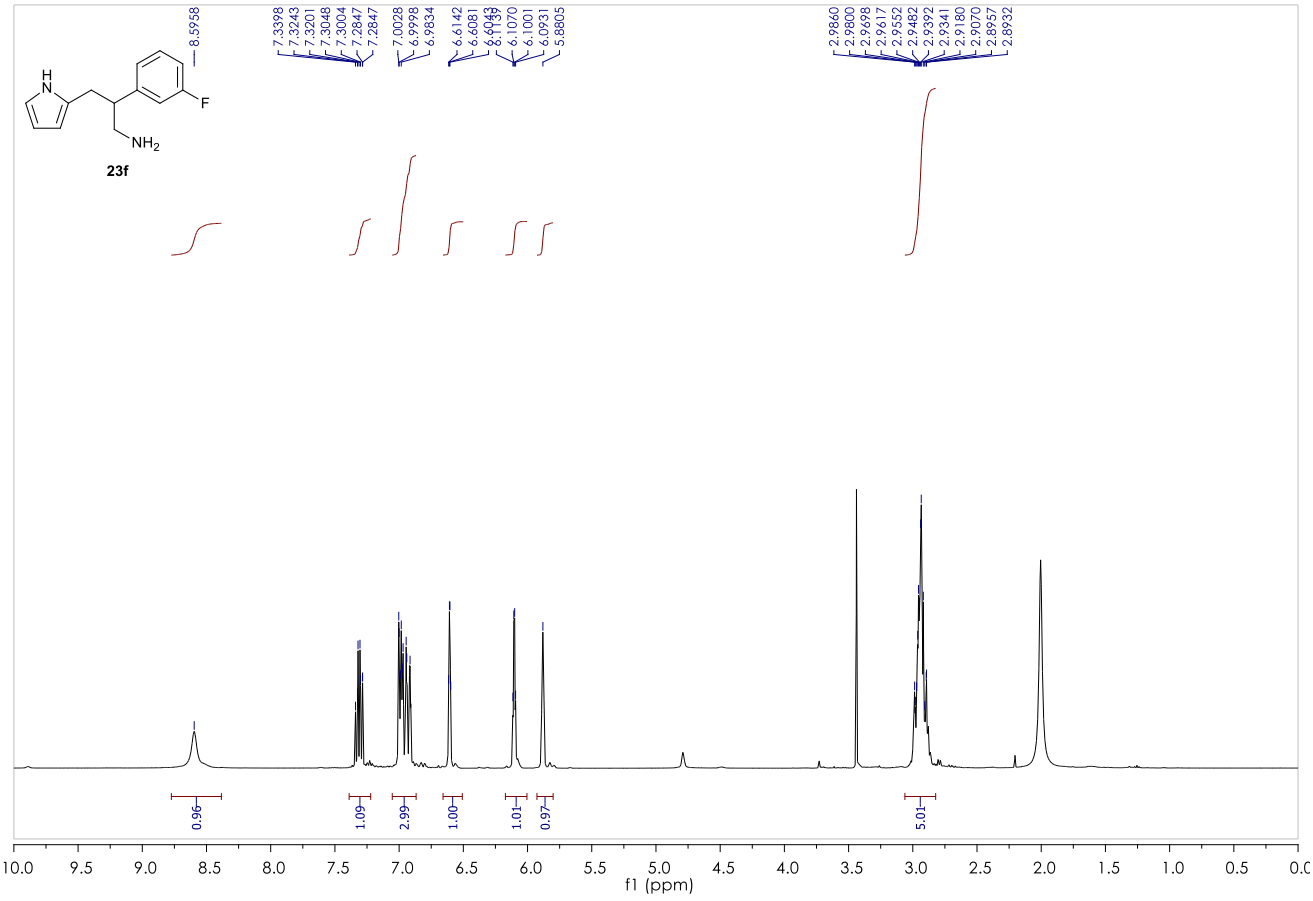
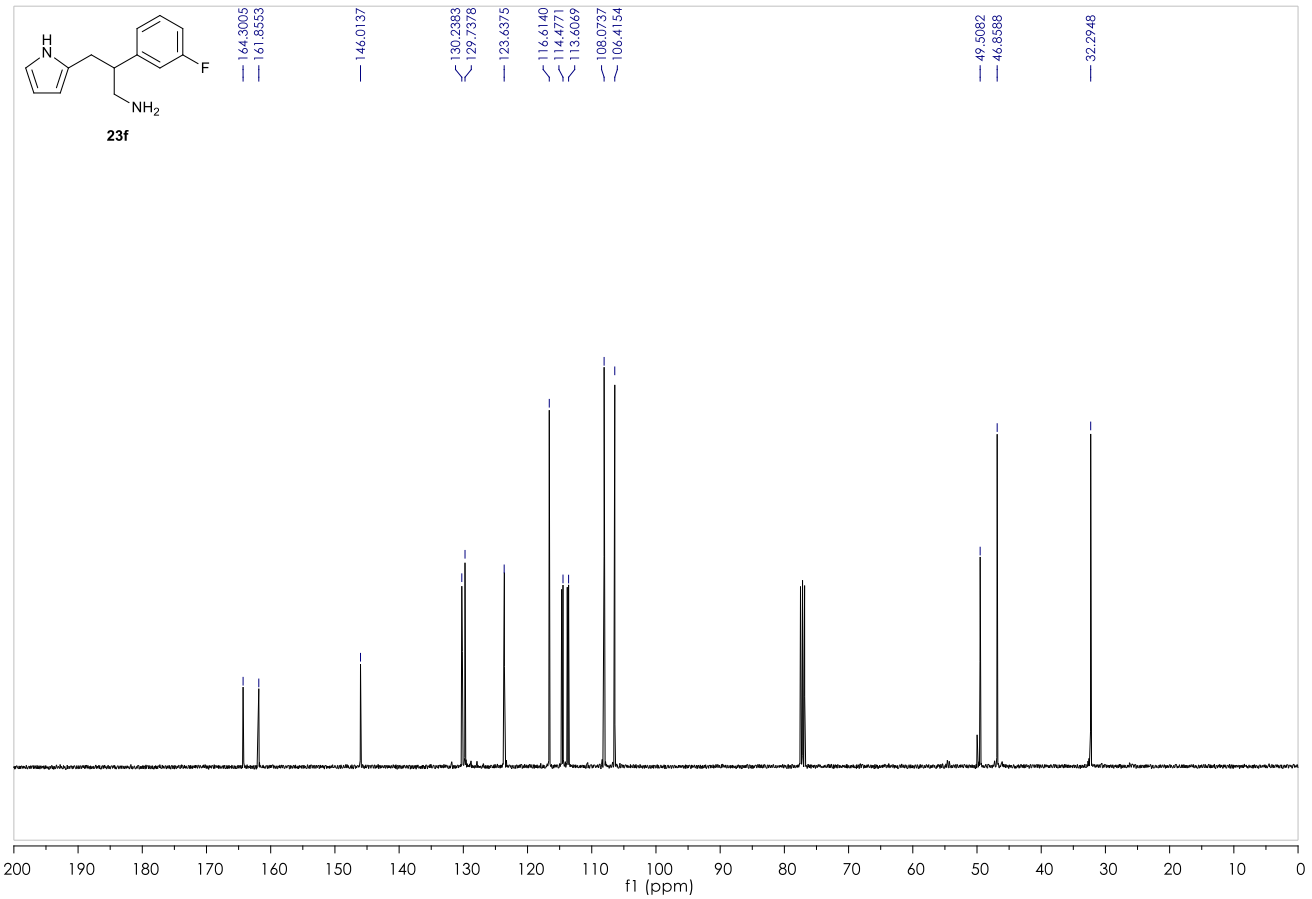
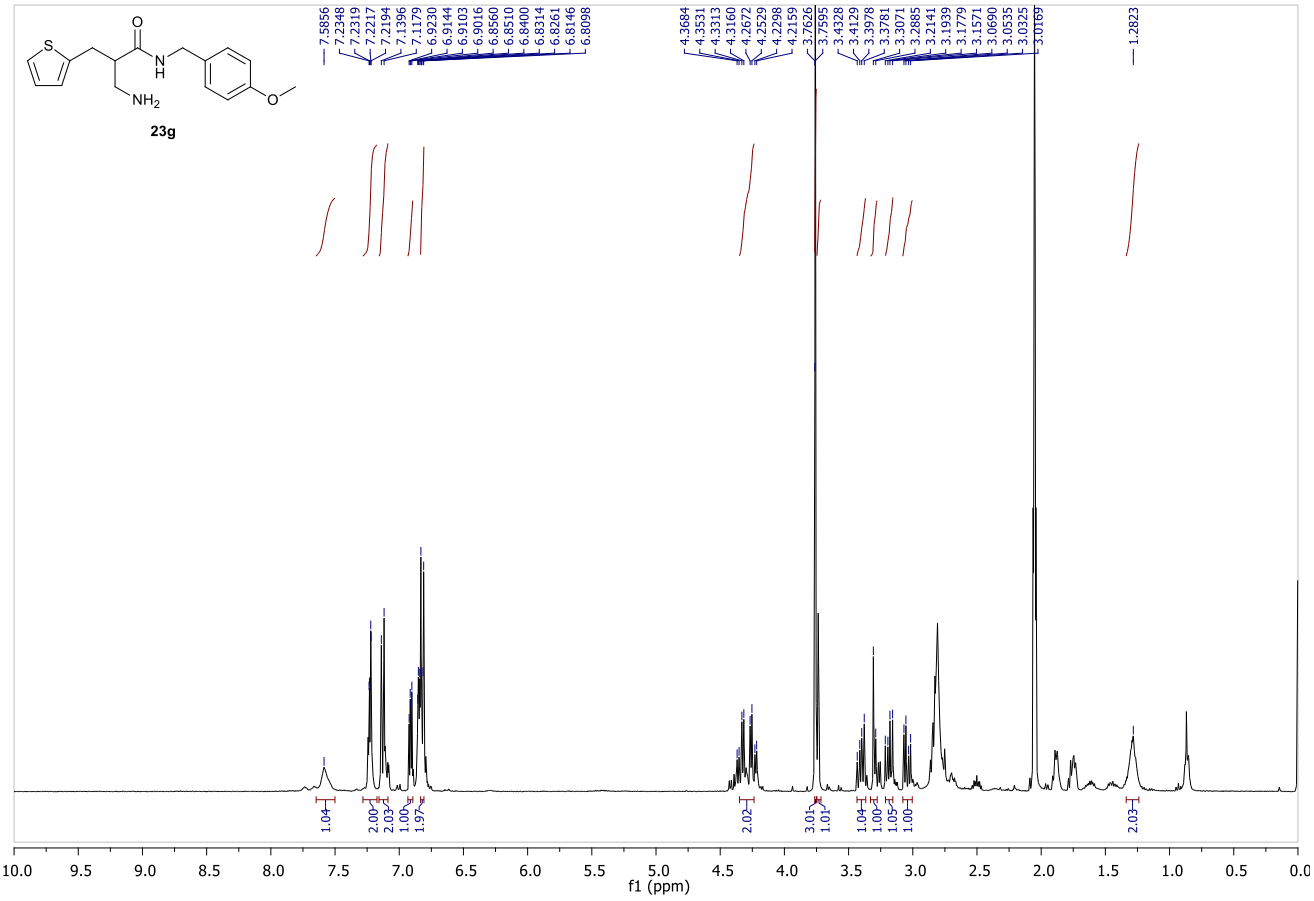
f1 (ppm)



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7.2348
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6.9016
6.8560
6.8510
6.8400
6.8314
6.8261
6.8146
6.8098
4.3684
4.3531
4.3313
4.3160
4.2672
4.2529
4.2298
4.2159
3.7626
3.7595
3.4328
3.4129
3.3978
3.3781
3.3071
3.2885
3.2141
3.1939
3.1779
3.1571
3.0690
3.0535
3.0325
3.0169
1.2823
1.04
2.00
2.03
1.00
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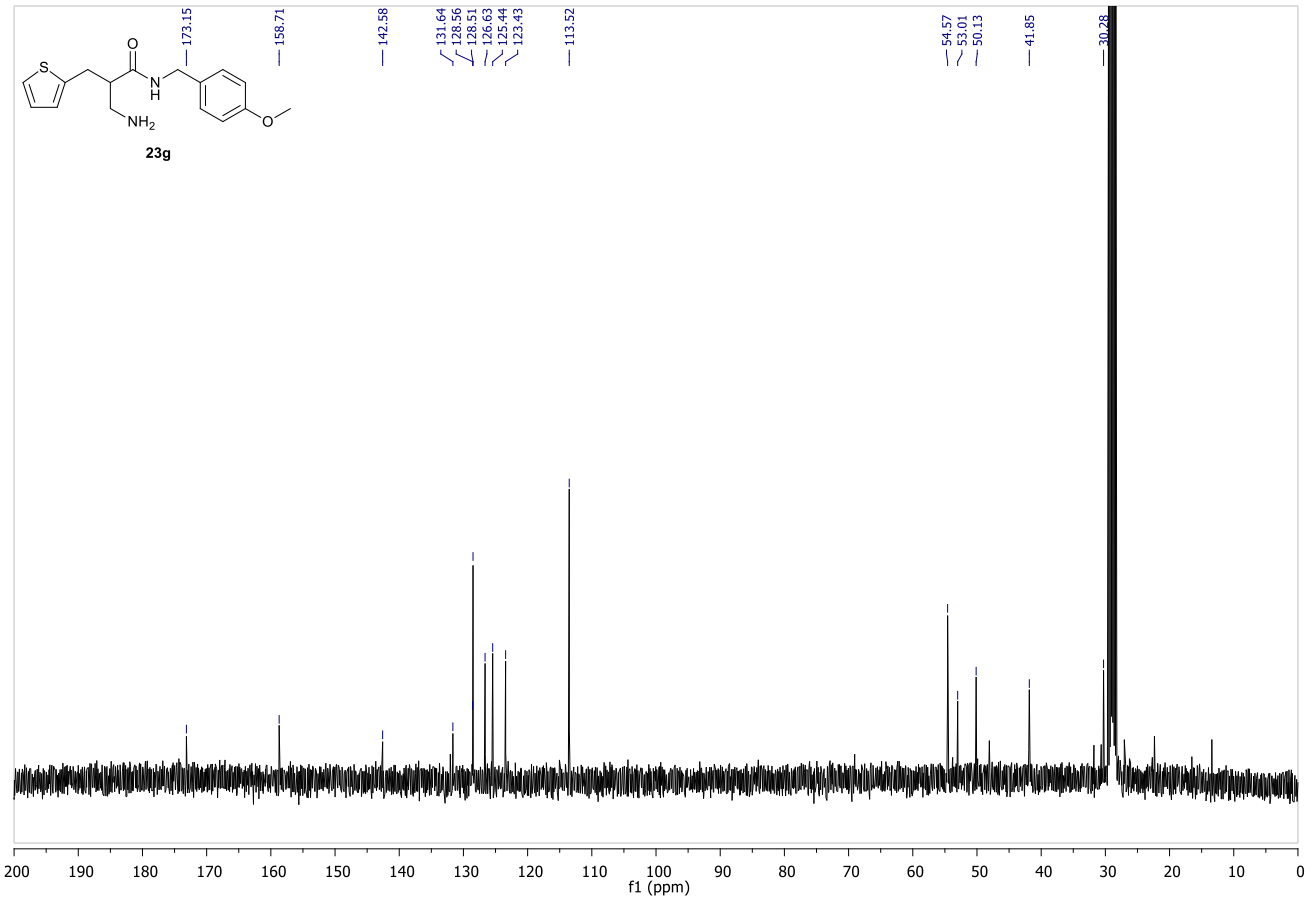
2.02
3.01
1.01
1.04
1.00
1.05
1.00
2.03
f1 (ppm)


23g
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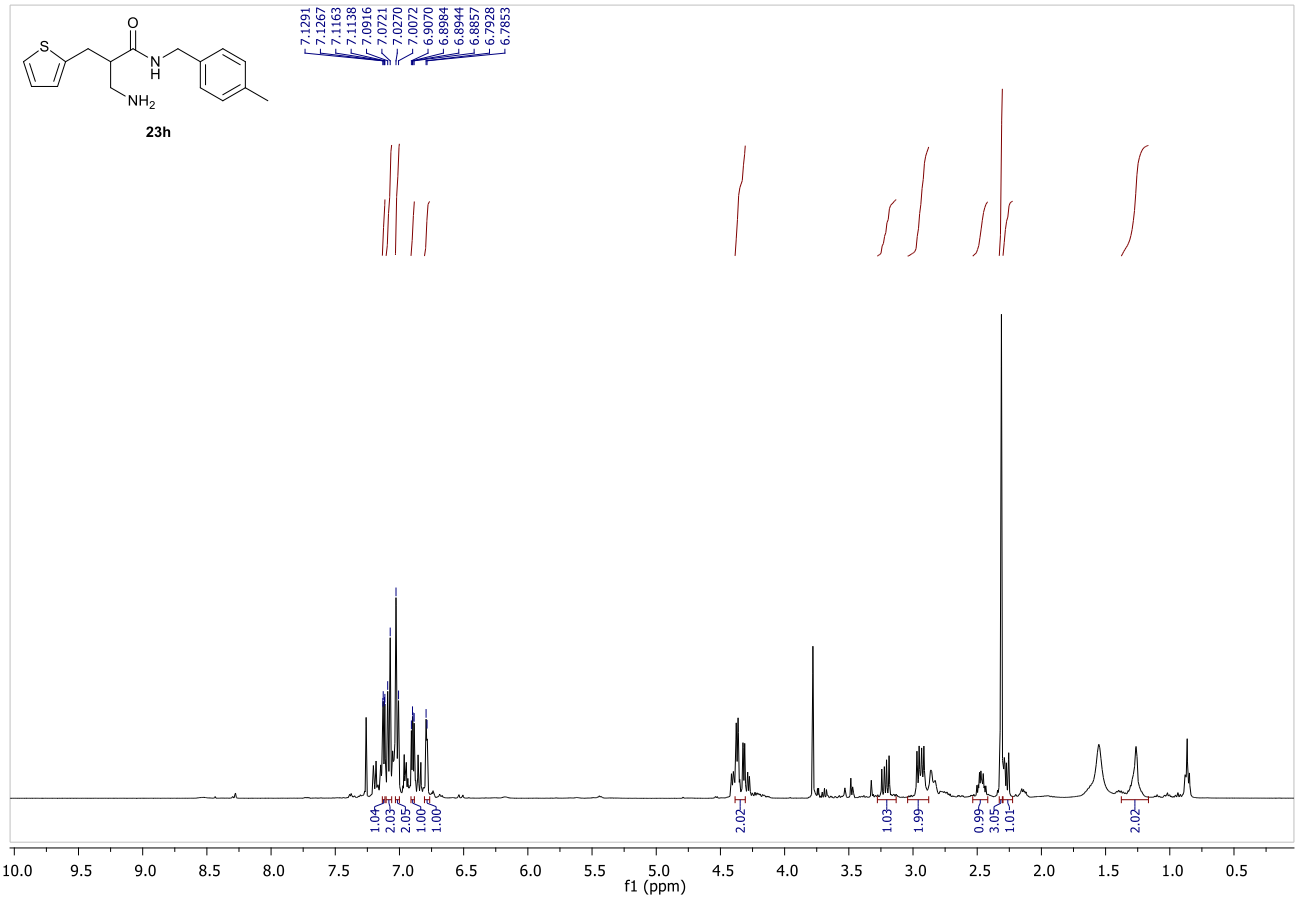
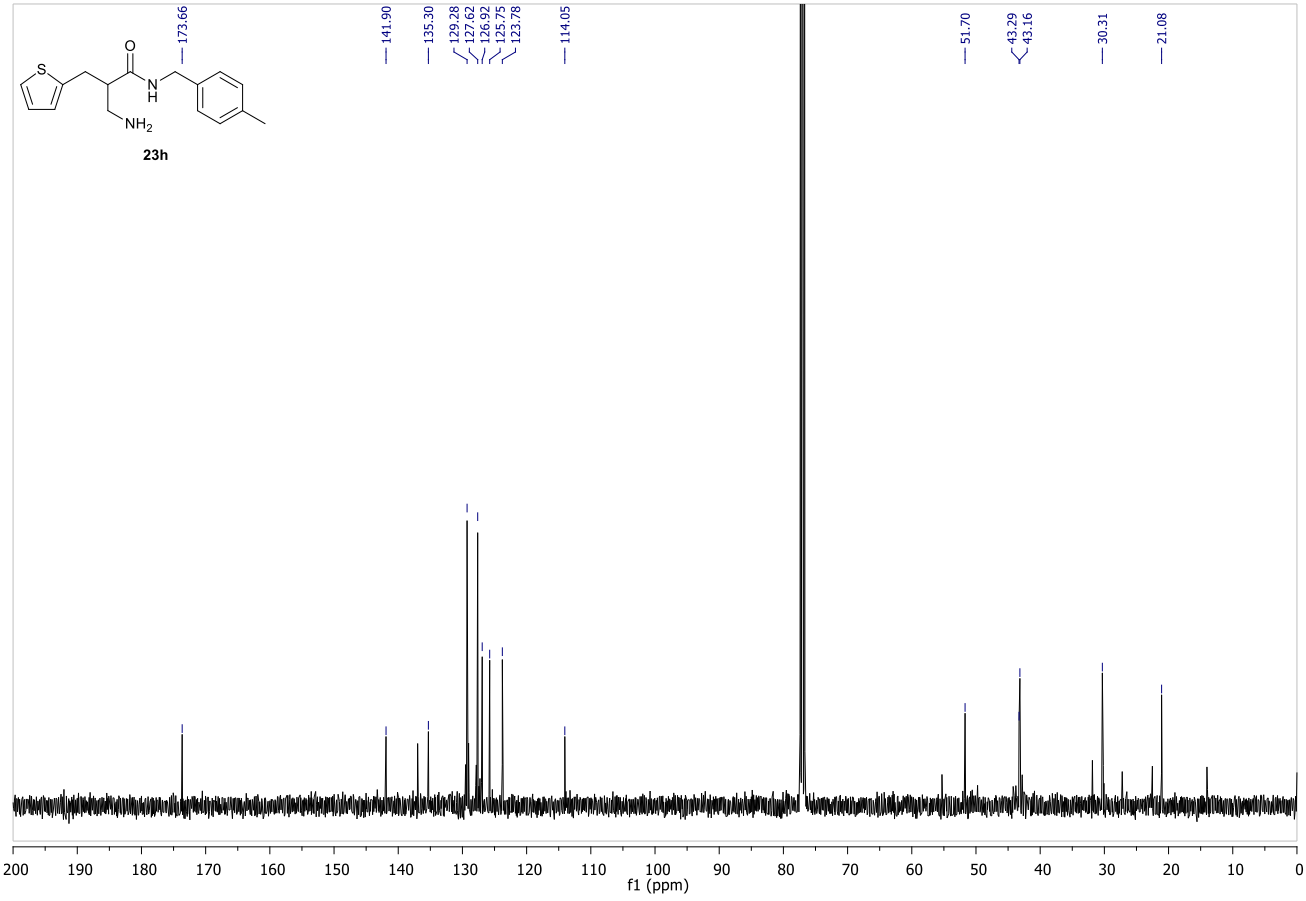
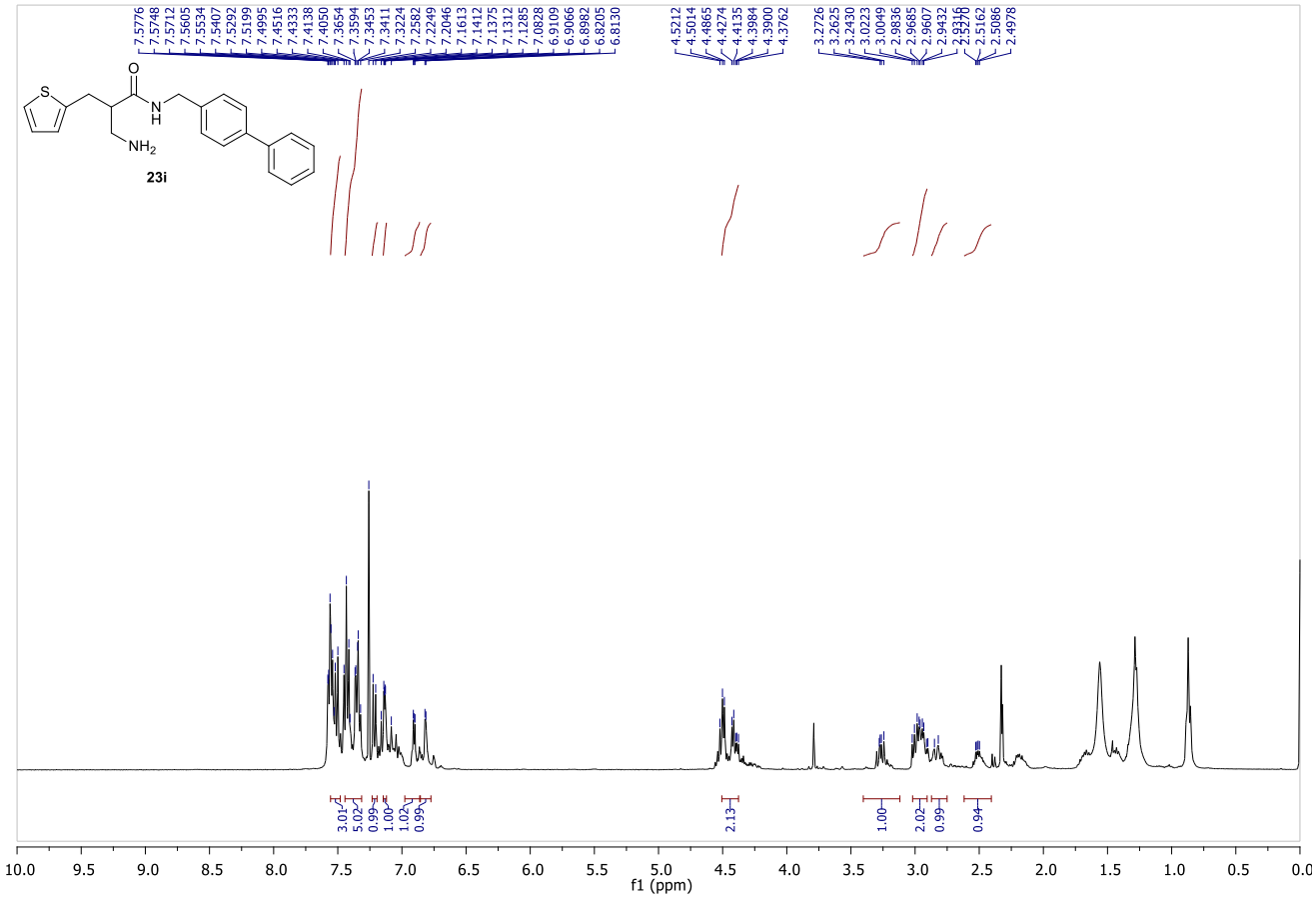
158.71
142.58
131.64
128.56
128.51
126.63
125.44
123.43
113.52
54.57
53.01
50.13
41.85
30.28
f1 (ppm)



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7.4516
7.4333
7.4138
7.4050
7.3654
7.3594
7.3453
7.3411
7.3224
7.2582
7.2249
7.2046
7.1613
7.1412
7.1375
7.1312
7.1285
7.0828
6.9109
6.9066
6.8982
6.8205
6.8130
4.5212
4.5014
4.4865
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4.4135
4.3984
4.3900
4.3762
3.2726
3.2625
3.2430
3.0223
3.0049
2.9836
2.9685
2.9607
2.9432
2.5162
2.5086
2.4978
23i
3.01
5.02
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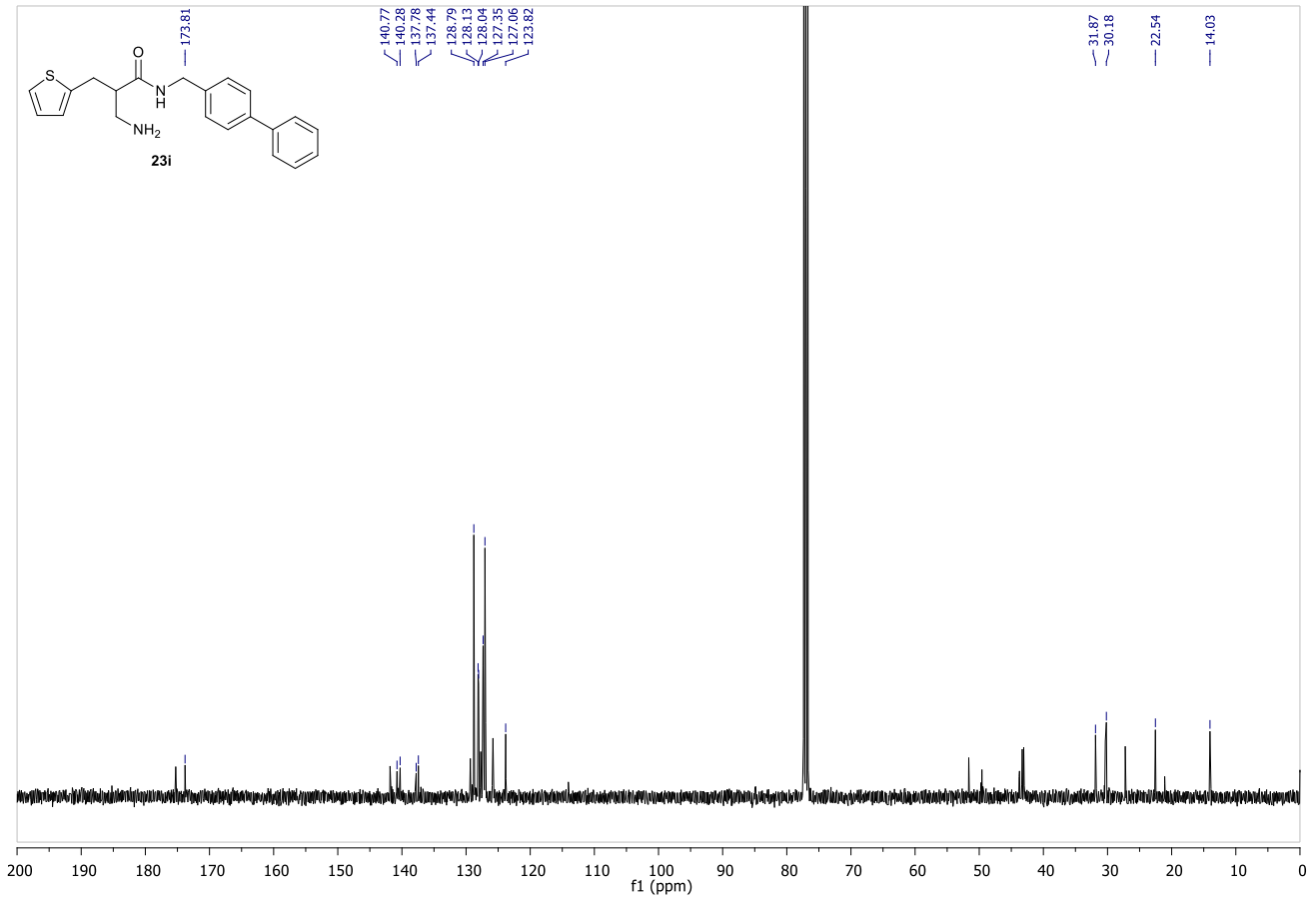
1.00
1.02
0.99
2.13
1.00
2.02
0.99
0.94
f1 (ppm)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123.82
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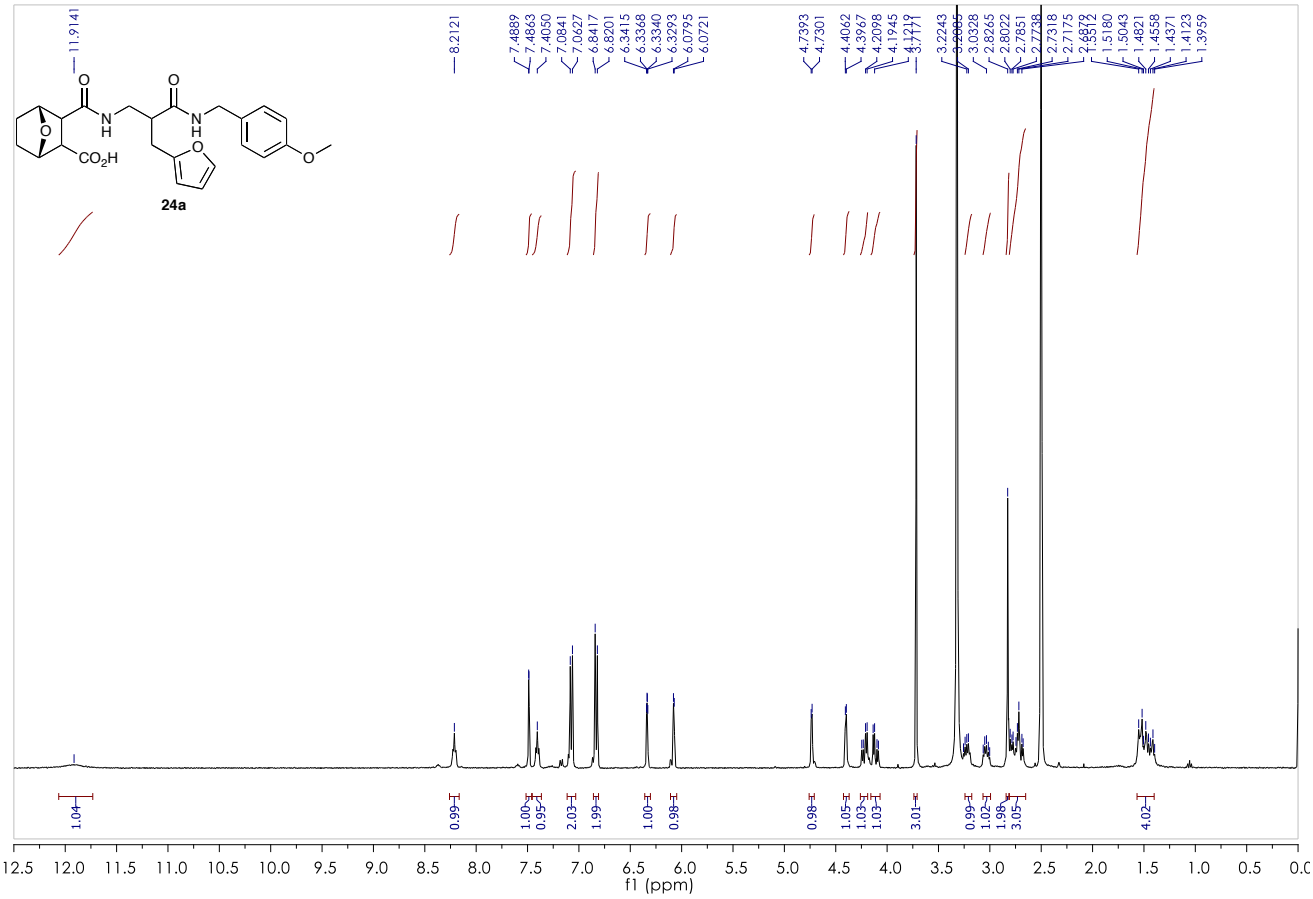
30.18
22.54
14.03
23i
f1 (ppm)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6.8201
6.3415
6.3368
6.3340
6.3293
6.0795
6.0721
4.7393
4.7301
4.4062
4.3967
4.2098
4.1945
4.1219
3.7171
3.2243
3.2085
3.0328
2.8265
2.8022
2.7851
2.7738
2.7318
2.7175
2.6872
2.6712
1.5180
1.5043
1.4821
1.4558
1.4371
1.4123
1.3959
1.04
0.99
1.00
0.95
2.03
1.99
1.00
0.98
0.98
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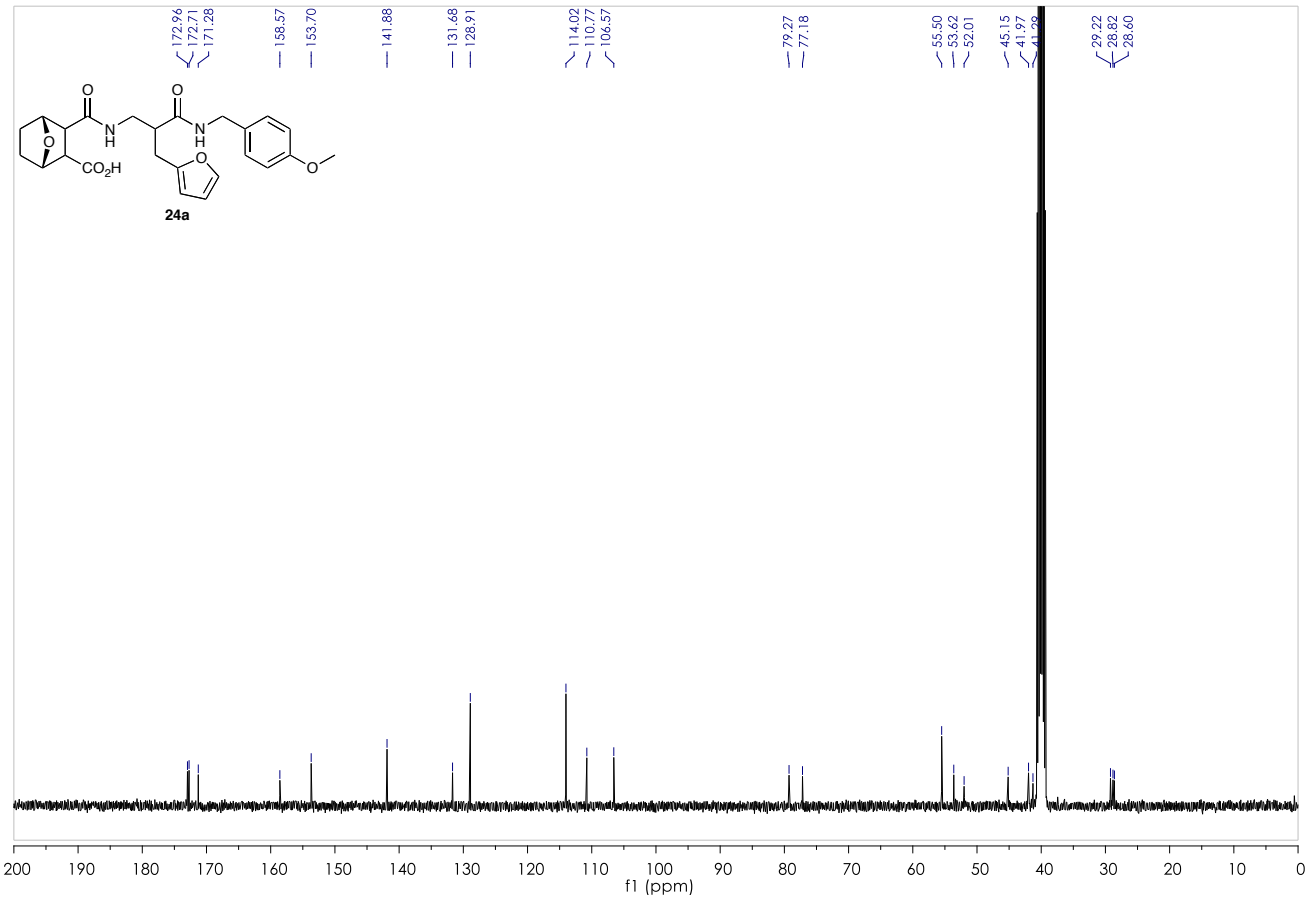
1.03
1.03
3.01
0.99
1.02
1.98
3.05
4.02
f1 (ppm)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158.57
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128.91
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110.77
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79.27
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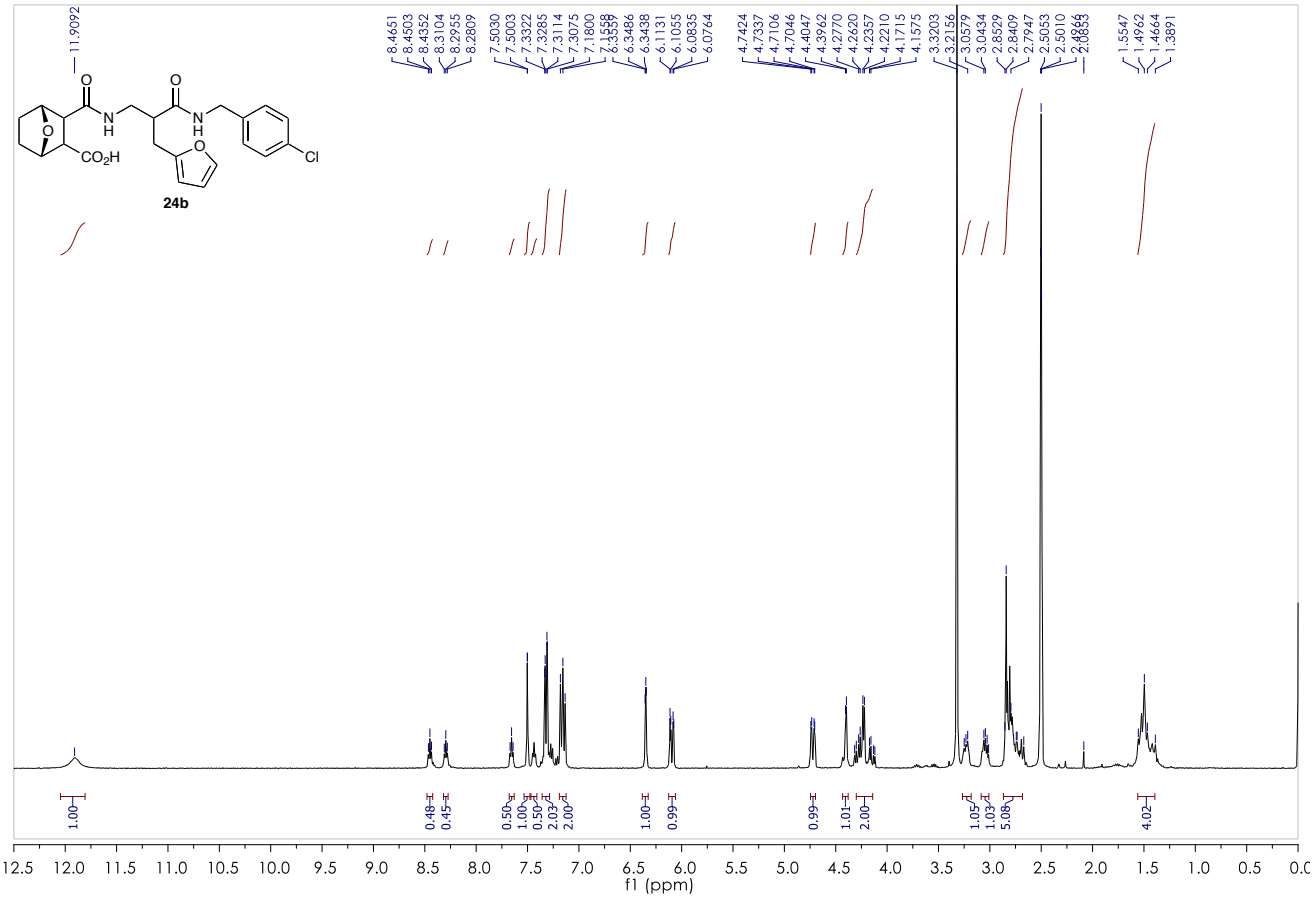
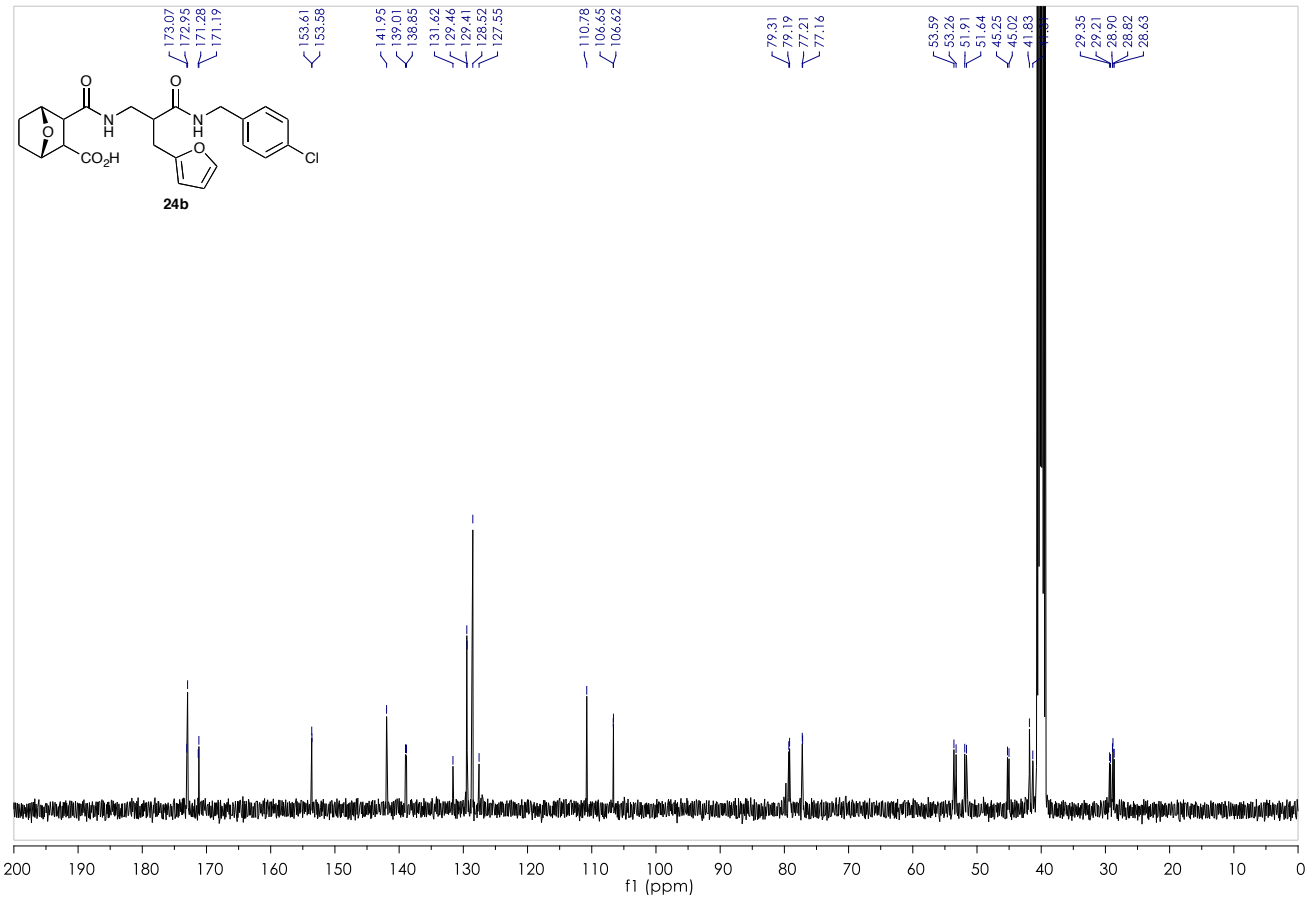
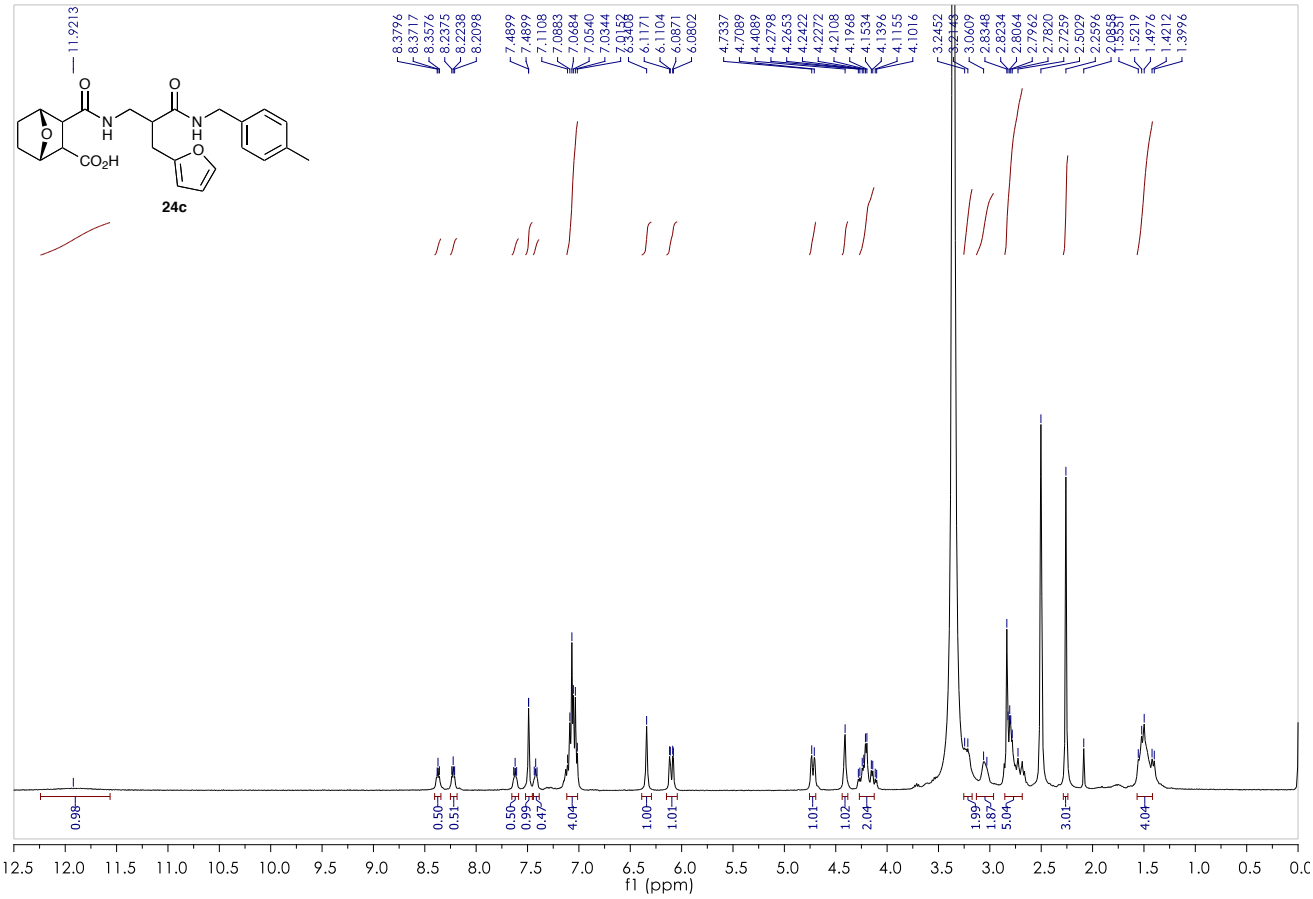
55.50
53.62
52.01
45.15
41.97
29.22
28.82
28.60
f1 (ppm)



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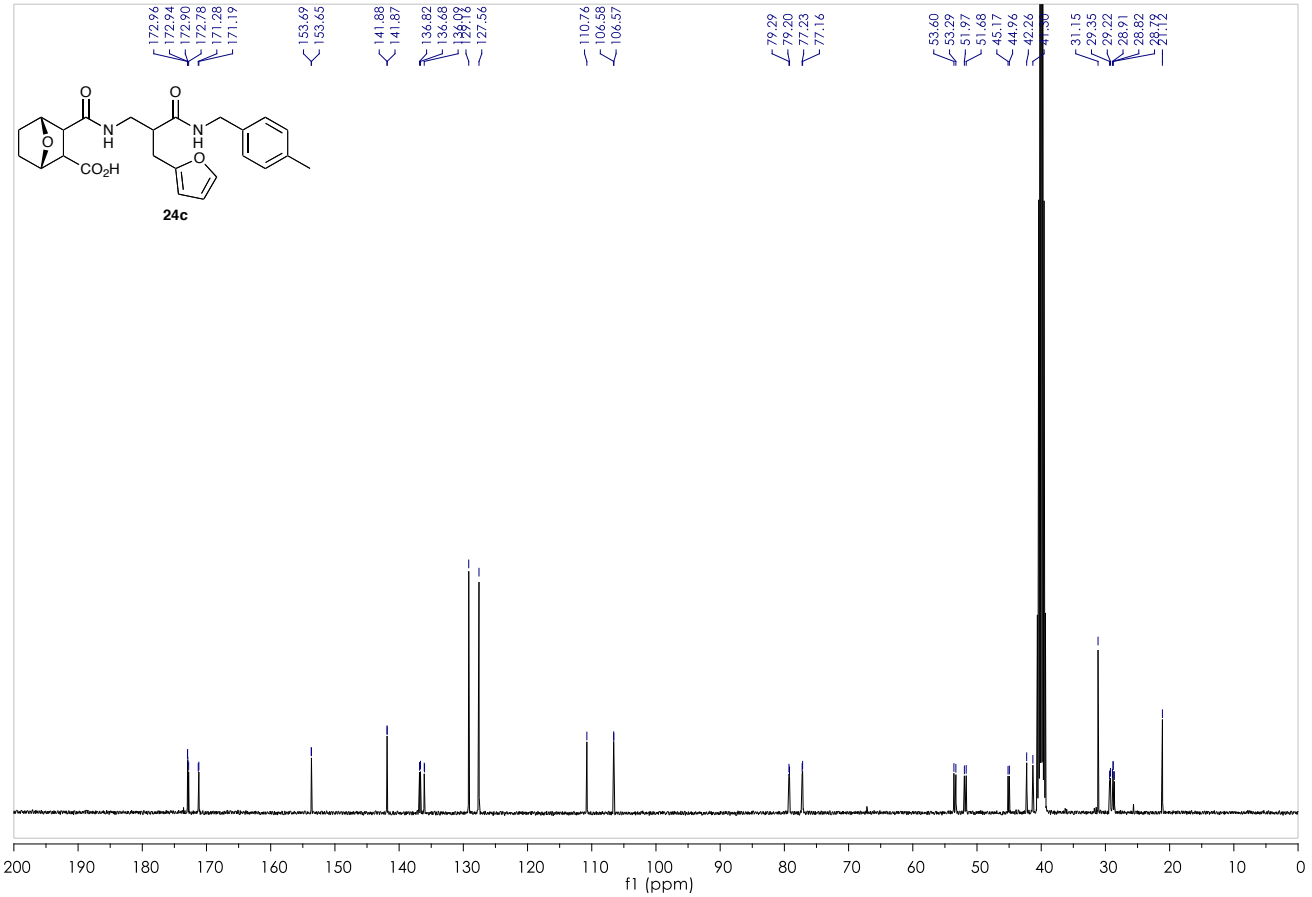
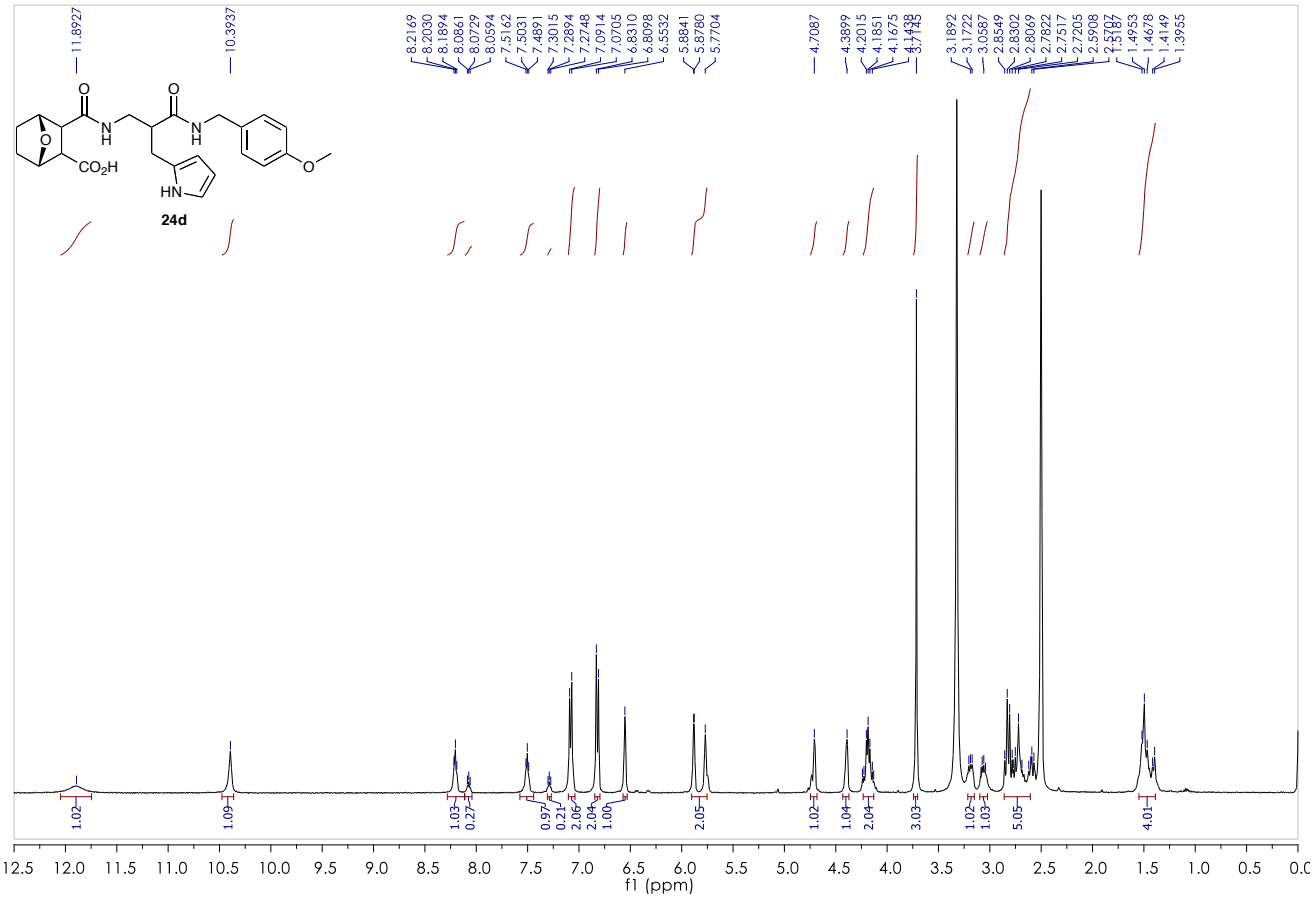
f1 (ppm)


24c
f1 (ppm)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6.8310
6.8098
6.5532
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4.3899
4.2015
4.1851
4.1675
4.1438
3.1892
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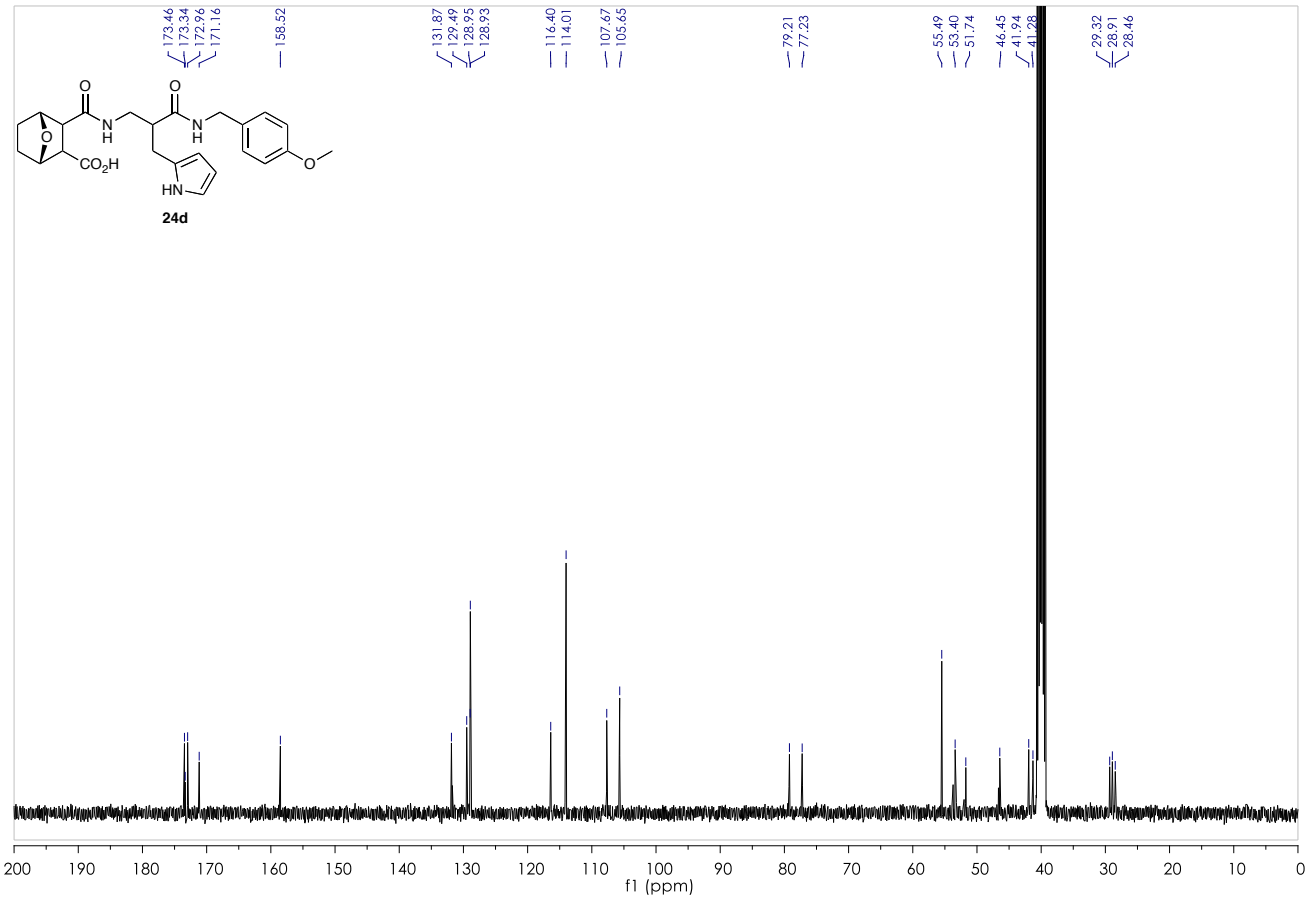
1.09
1.03
0.27
0.97
0.21
2.06
2.04
1.00
2.05
1.02
1.04
2.04
3.03
1.02
1.03
5.05
4.01
f1 (ppm)
24d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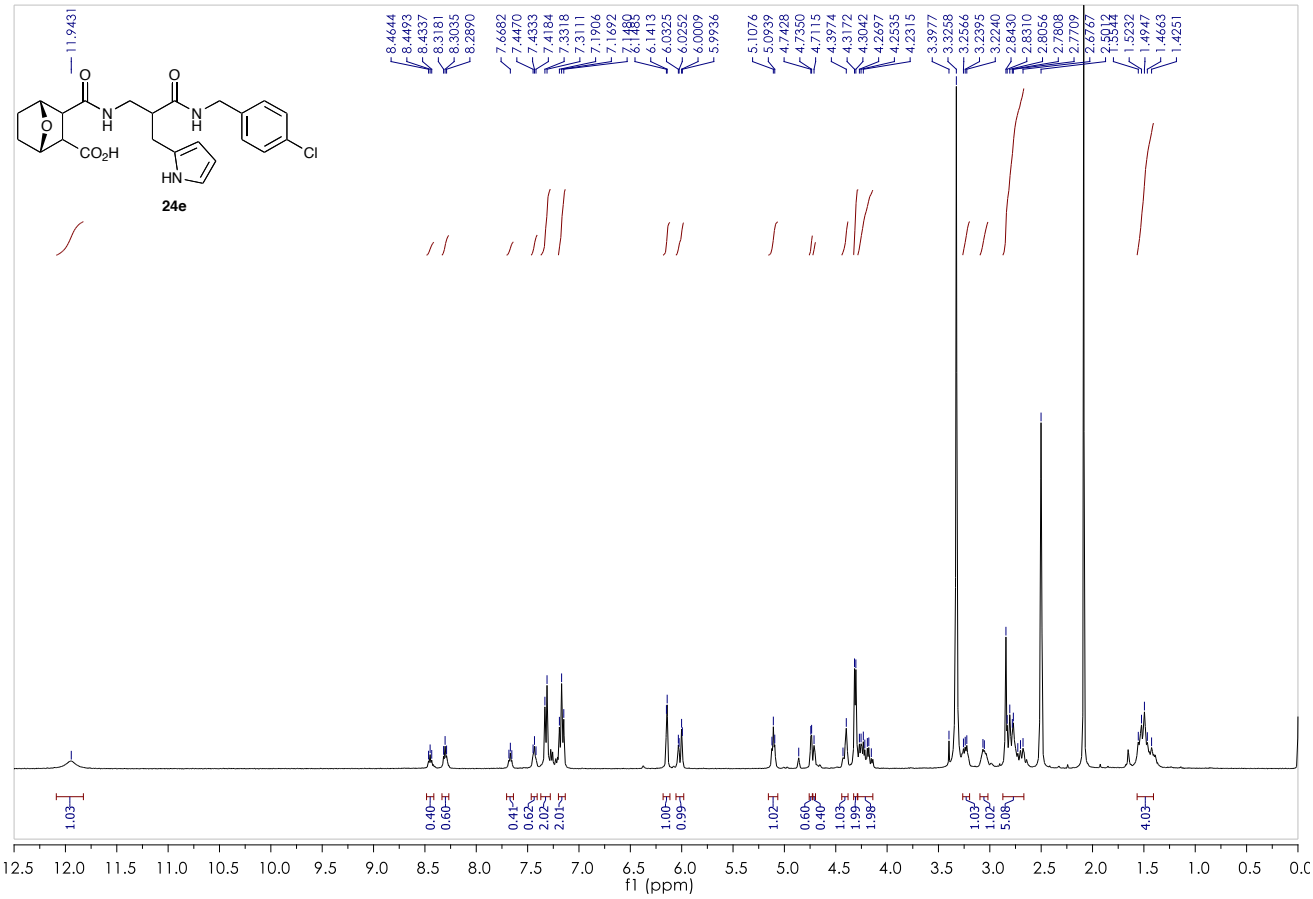
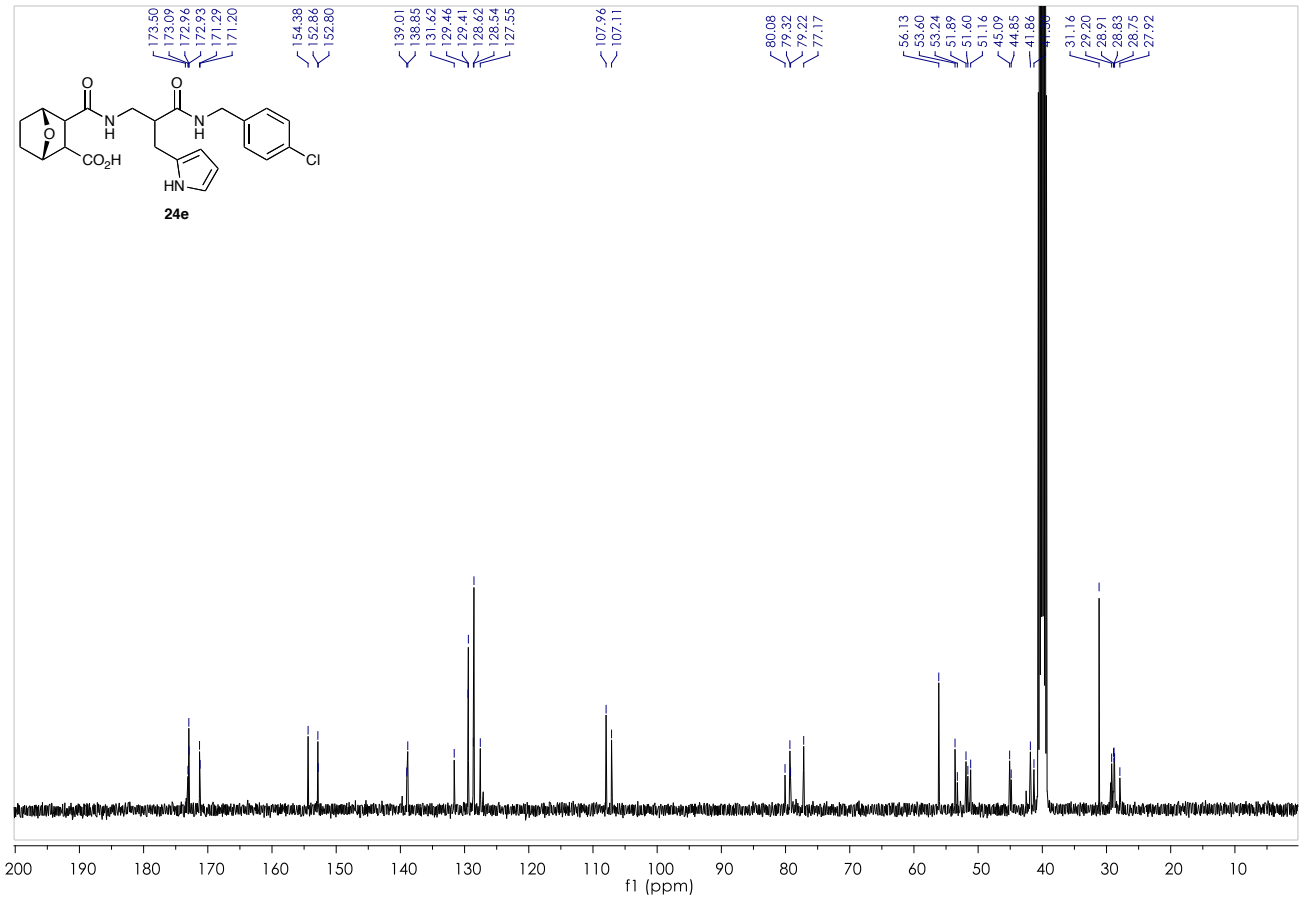
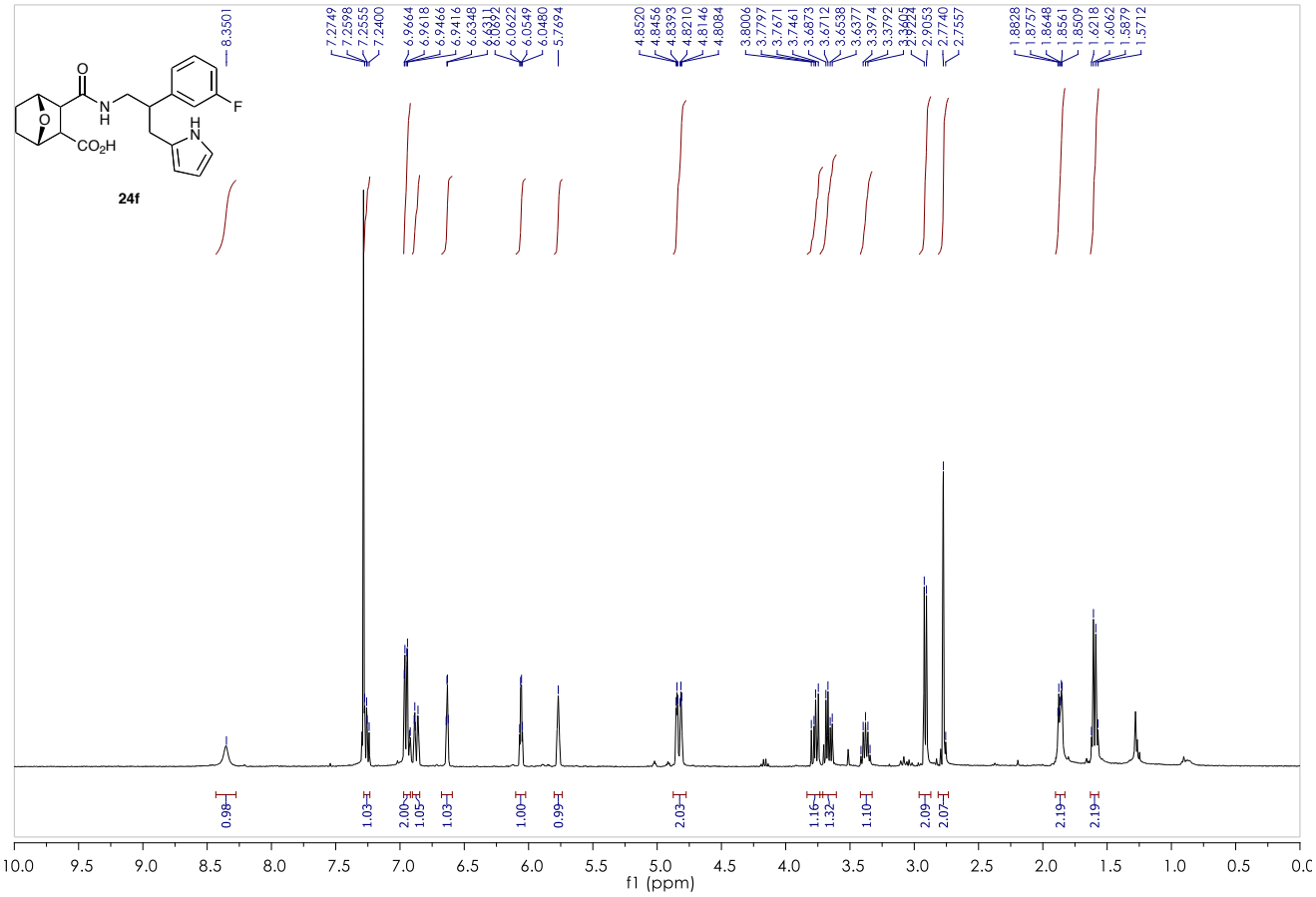
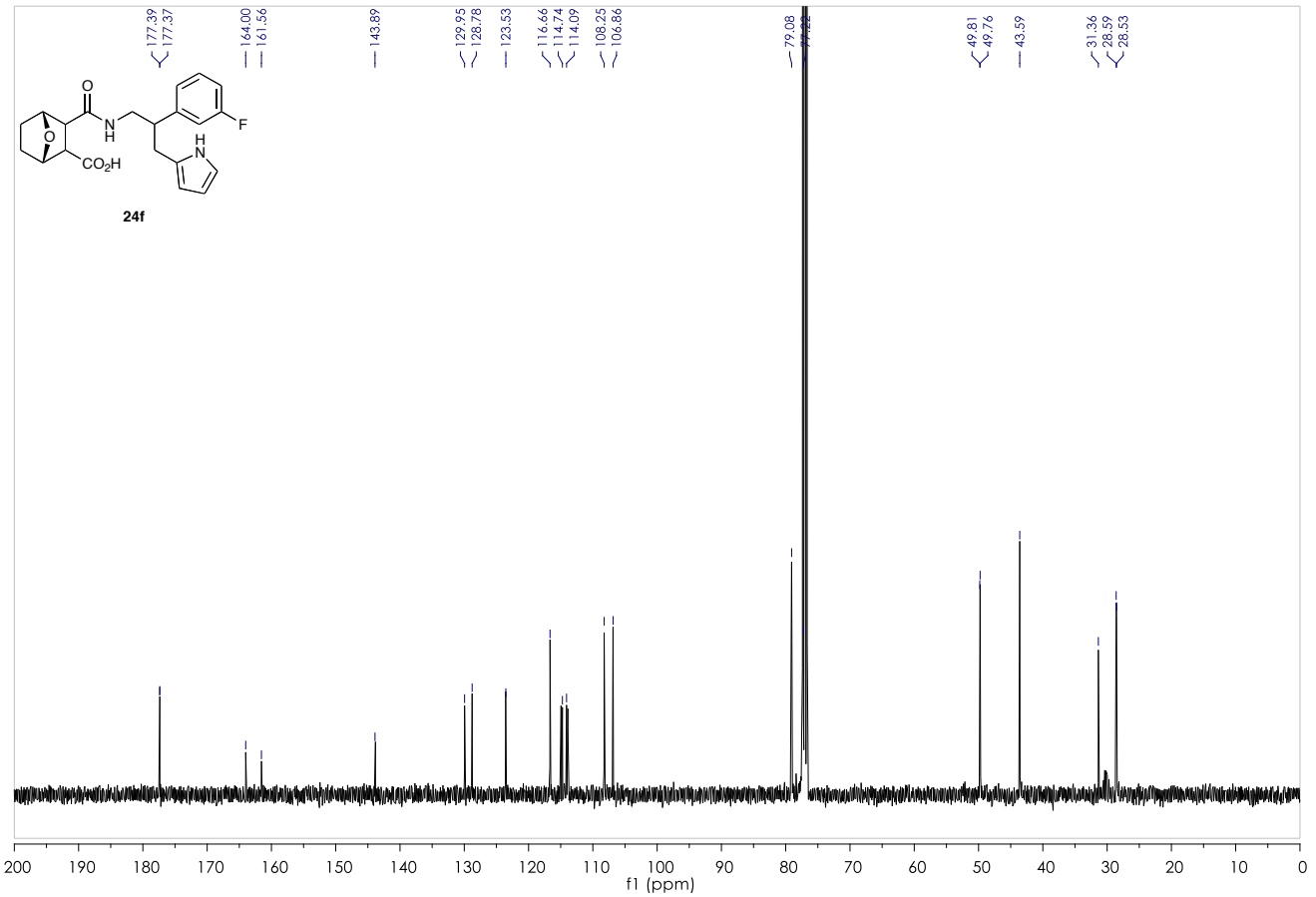
172.96
171.16
158.52
131.87
129.49
128.95
128.93
116.40
114.01
107.67
105.65
79.21
77.23
55.49
53.40
51.74
46.45
41.94
41.28
29.32
28.91
28.46
f1 (ppm)
24d






24f
f1 (ppm)


24f
f1 (ppm)