

Electronic Supplementary Information for

**The N-alkylation of Sulfonamides with Alcohols in Water Catalyzed by a  
Water-soluble Metal-ligand Bifunctional Iridium Catalyst  
[Cp\*Ir(biimH<sub>2</sub>)(H<sub>2</sub>O)][OTf]<sub>2</sub>**

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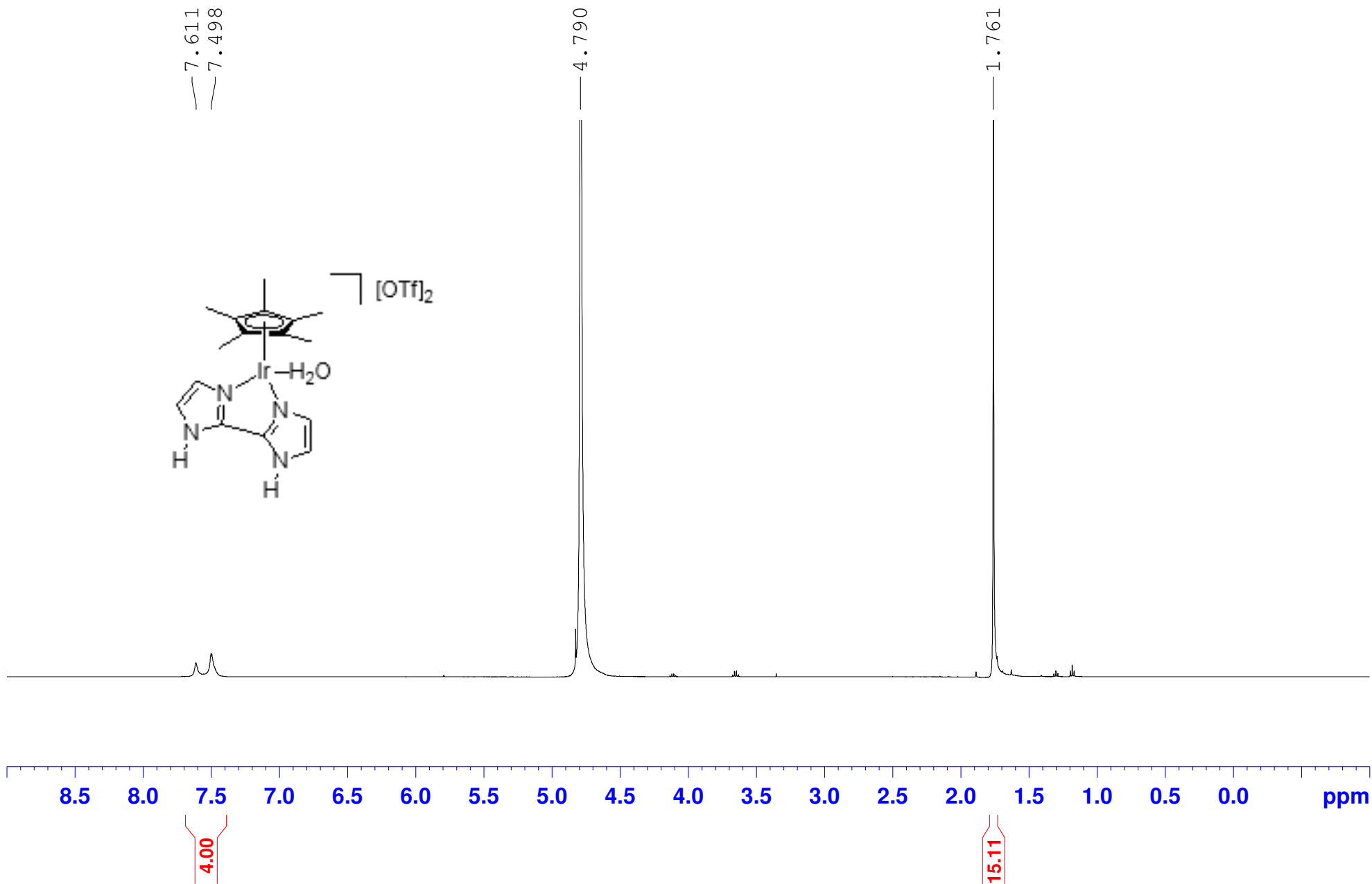
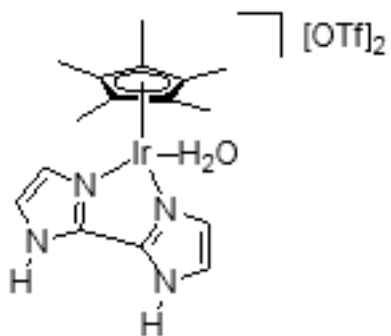
Copies of <sup>1</sup>NMR and <sup>13</sup>NMR spectra of all products S2-S61

[Cp\*Ir(bimH2)(H2O)] [OTf]2  
Proton D2O

7.611  
7.498

4.790

1.761



[Cp\*Ir(biimH2)(H2O)] [OTf]2  
C13CPD D2O

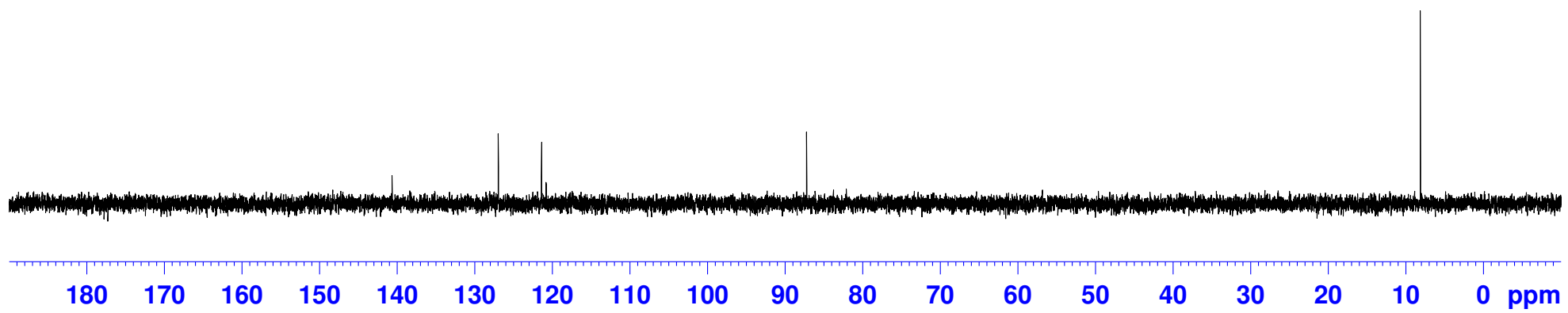
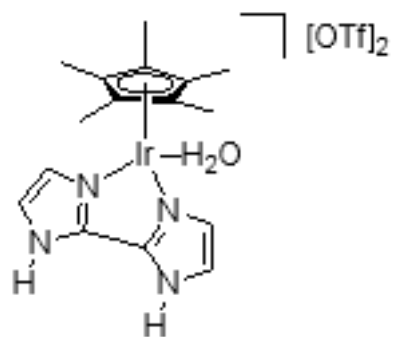
—140.643

—126.941

—121.355

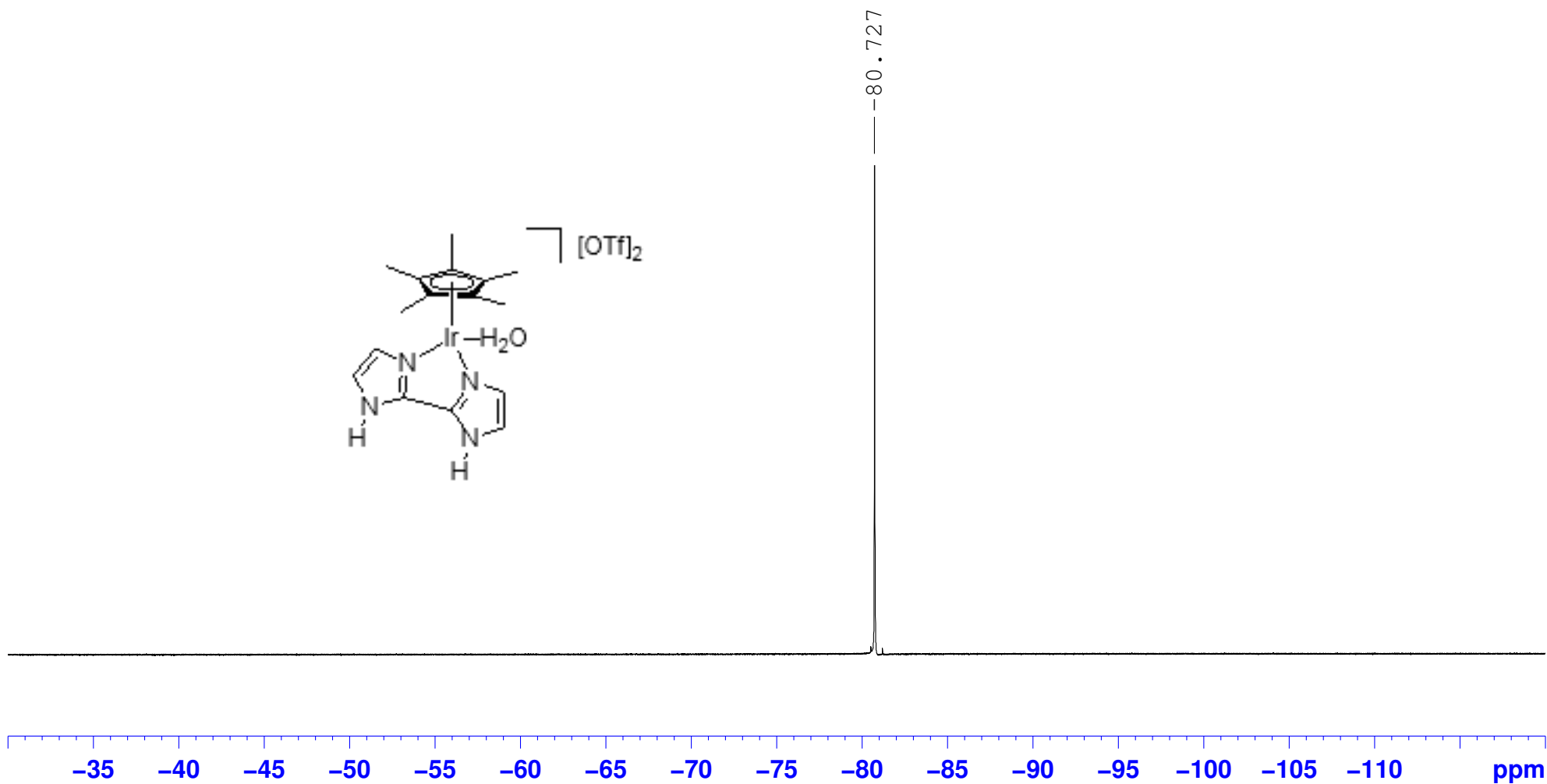
—87.264

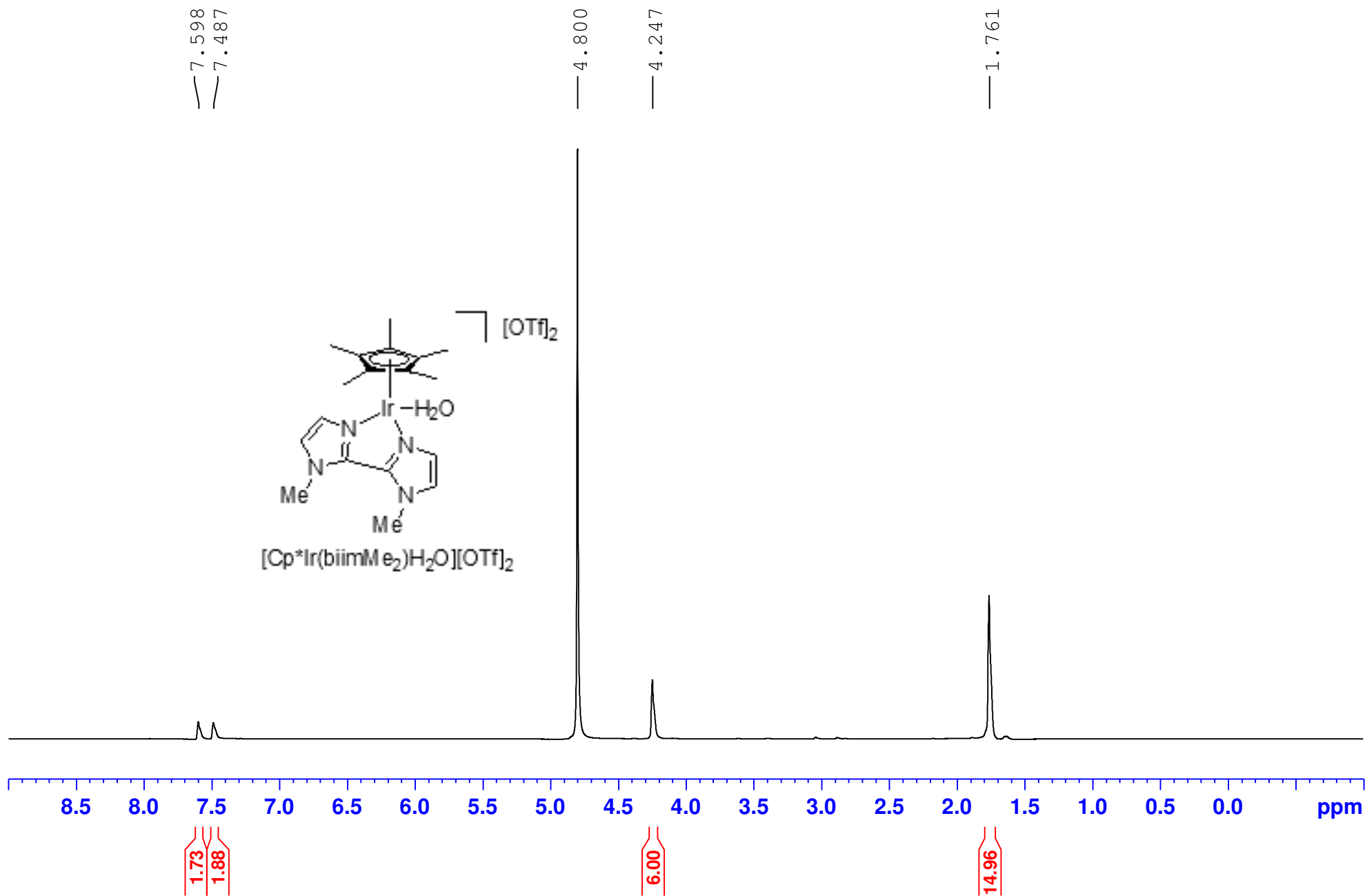
—8.169



[Cp\*Ir(bimH2)(H2O)][OTf]2

<sup>19</sup>F D2O





[Cp\*Ir(biimH2) (H2O) ] [OTf]2  
C13CPD D2O

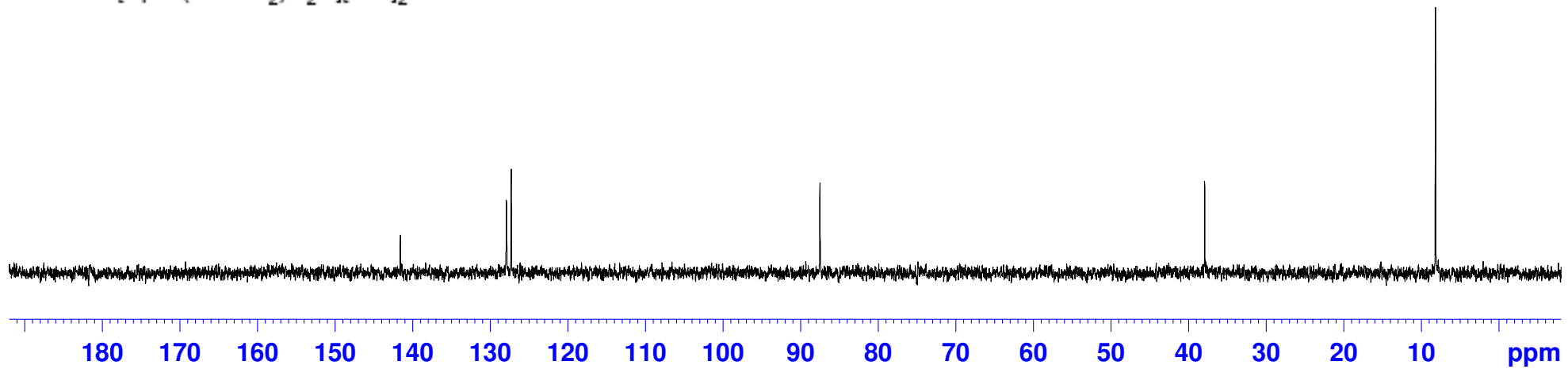
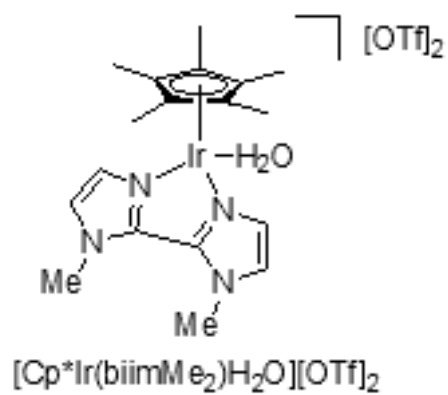
— 141.563

< 127.903  
127.275

— 87.546

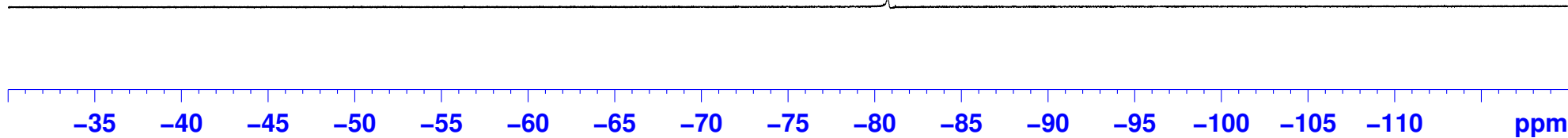
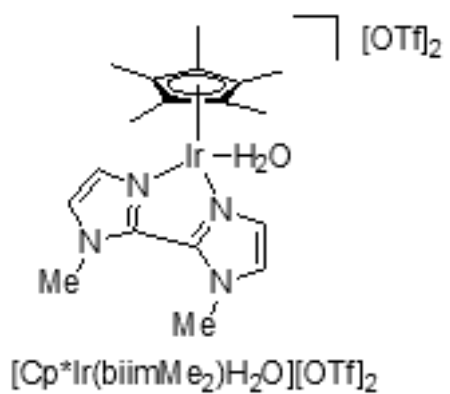
— 37.956

— 8.218



[Cp\*Ir(bimMe<sub>2</sub>)(H<sub>2</sub>O)] [OTf]<sub>2</sub>  
19F-D<sub>2</sub>O

---80.727

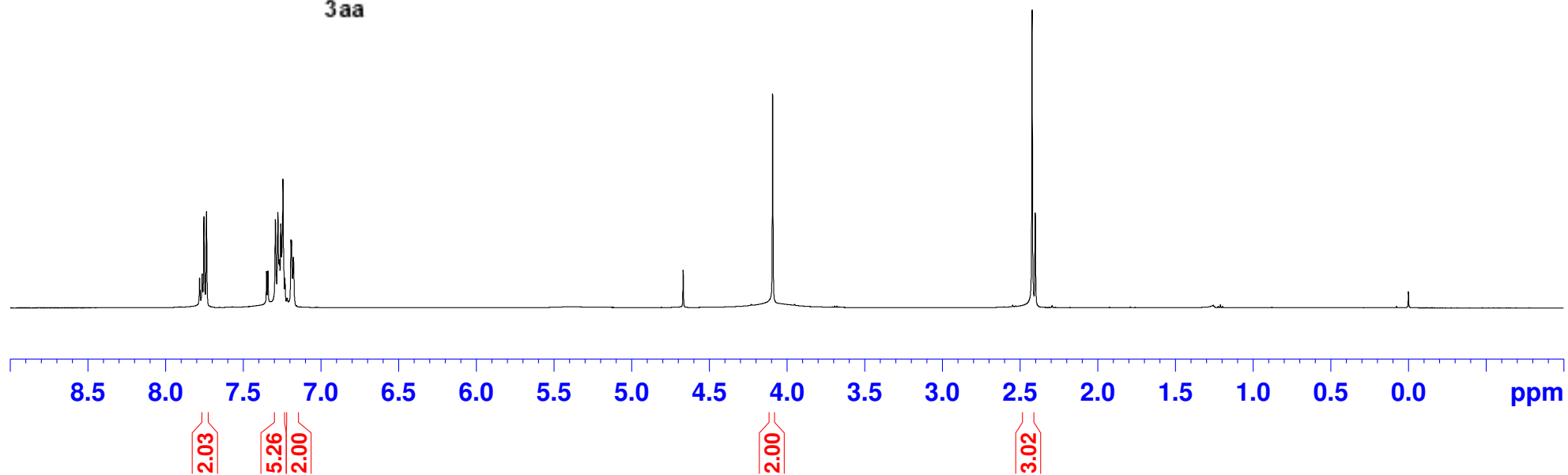
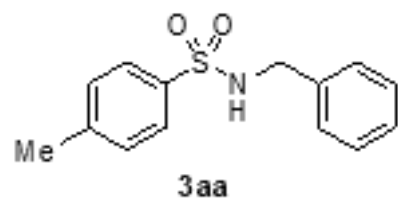


N-Benzyl-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.750  
7.734  
7.291  
7.275  
7.242  
7.191  
7.187  
7.175

4.093

2.422



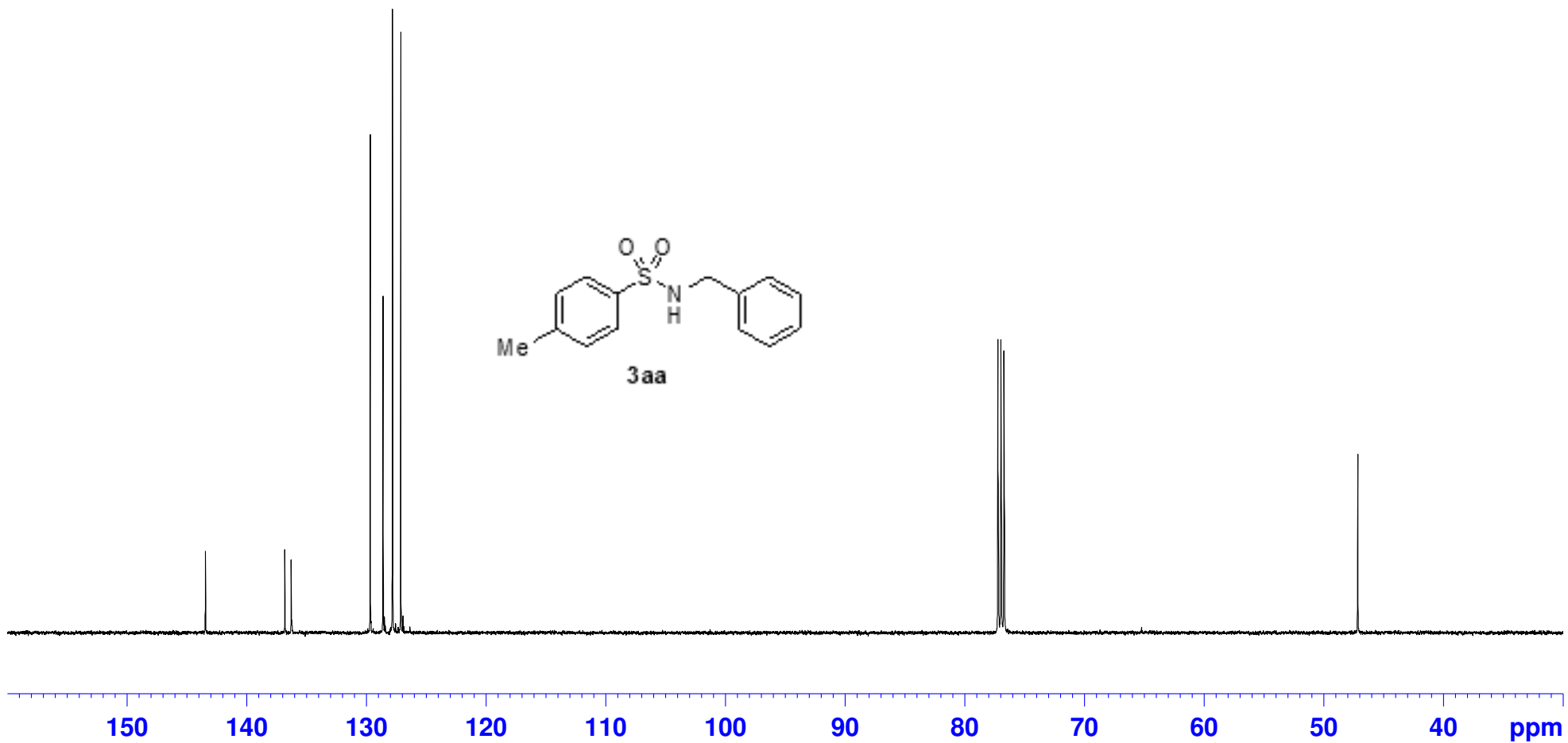
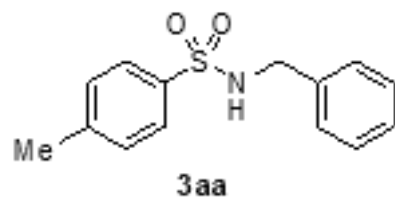


N-benzyl-4-methylbenzenesulfonamide  
C13CPD CDC13

— 143.424  
— 136.808  
— 136.280  
— 129.670  
— 128.587  
— 127.806  
— 127.777  
— 127.120

— 77.000

— 47.161

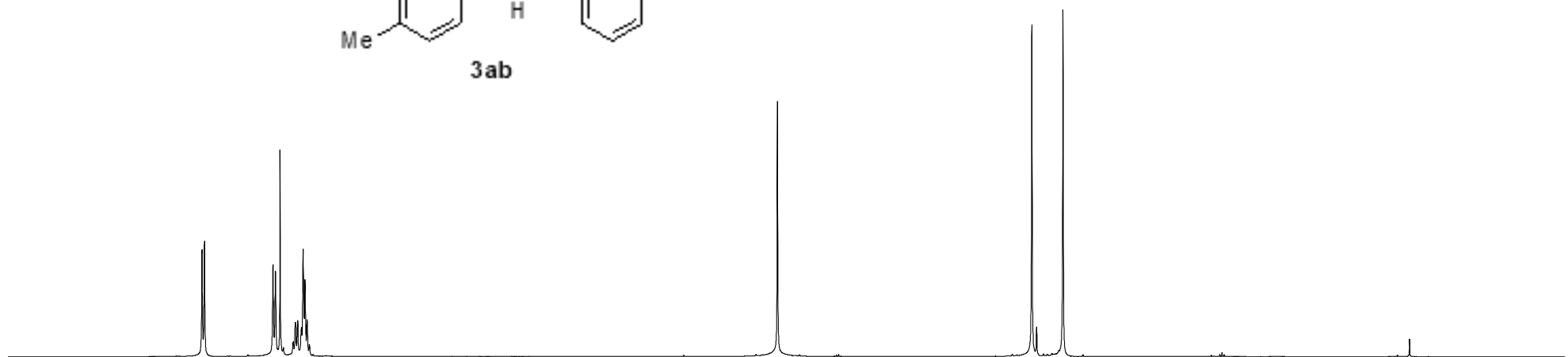
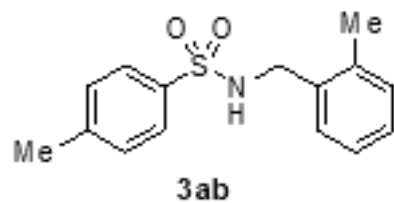


N-(2-Methylbenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.752  
7.735  
7.296  
7.280  
7.165  
7.151  
7.136  
7.113  
7.090  
7.062

4.059

2.425  
2.226



8.5

8.0

2.00

7.5

2.01

0.99

3.01

7.0

6.5

6.0

6.0

5.5

5.0

1.99

4.5

4.0

3.5

3.0

3.00

2.99

2.5

2.0

1.5

1.0

0.5

0.0

ppm

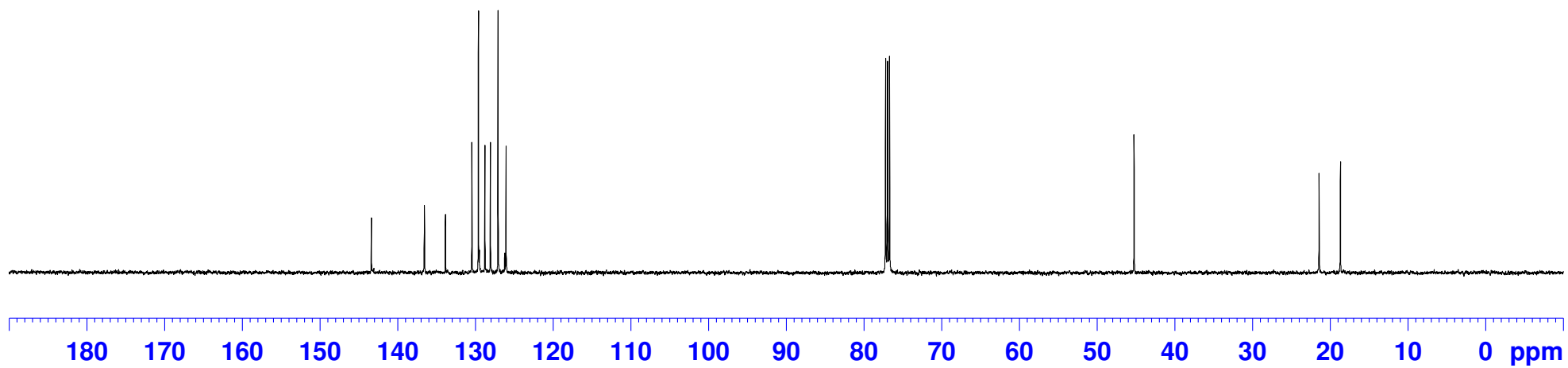
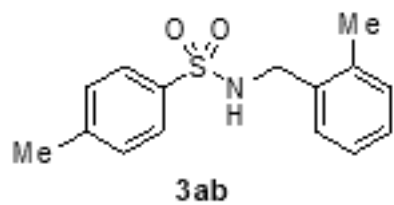
N-(2-Methylbenzyl)-4-methylbenzenesulfonamide  
C13CPD-1 CDCl3

143.429  
136.614  
133.905  
130.497  
129.651  
128.815  
128.111  
127.128  
126.099

— 77.000

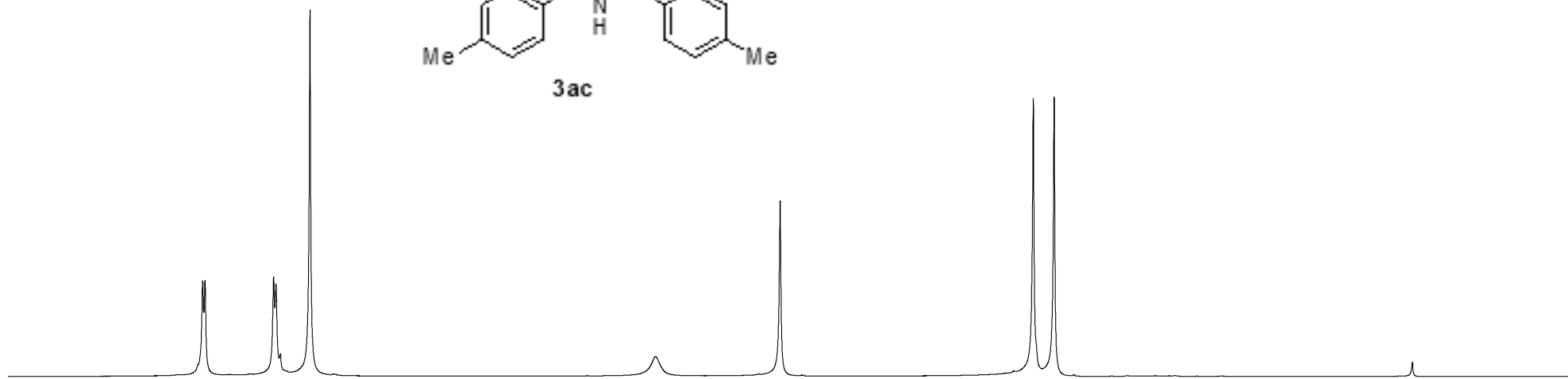
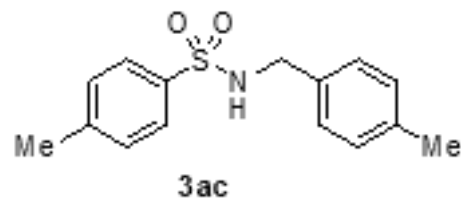
— 45.278

— 21.474  
— 18.722



N-(4-Methylbenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.752  
7.737  
7.297  
7.282  
7.064  
4.849  
4.051  
2.429  
2.295



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 ppm

1.98

2.00

3.99

0.99

2.00

3.00

3.02

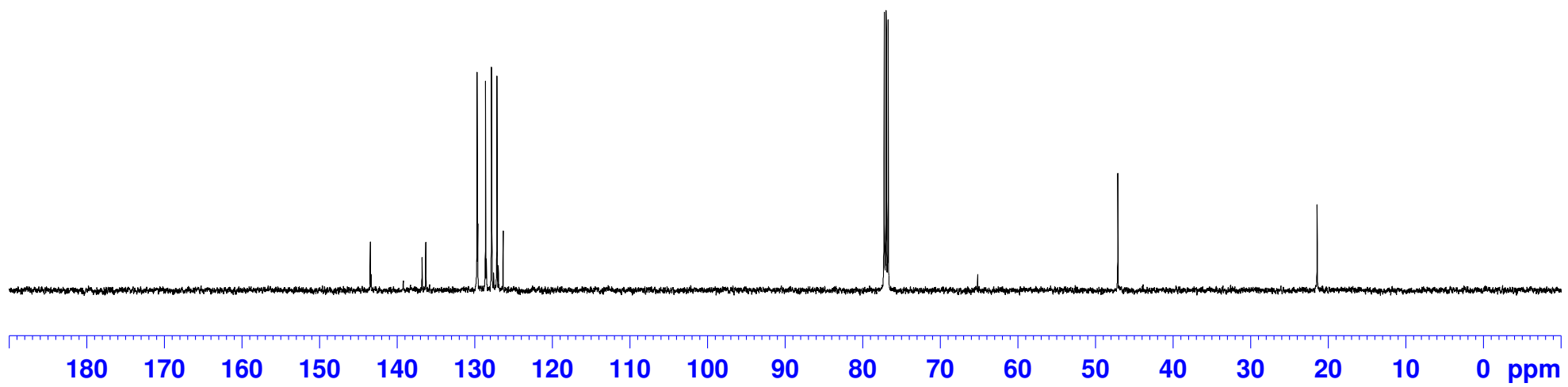
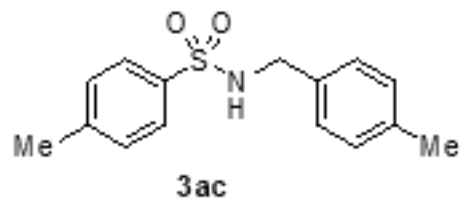
N-Benzyl-4-methylbenzenesulfonamide  
C13CPD-1 CDC13

143.437  
136.776  
136.280  
129.671  
128.586  
127.813  
127.772  
127.112

77.001

47.145

21.467



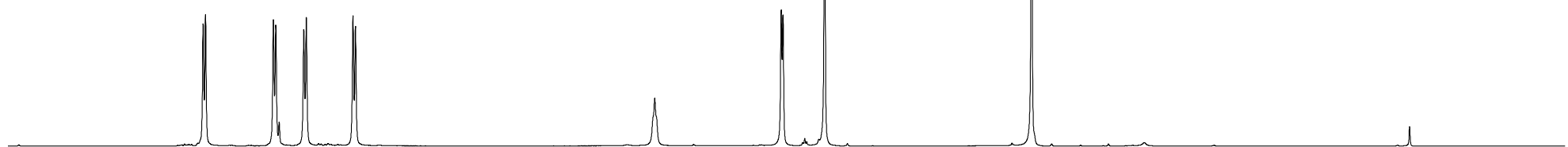
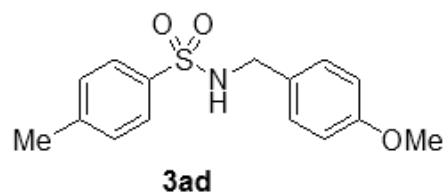
N-(4-Methoxybenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.744  
7.729  
7.296  
7.280  
7.100  
7.084  
6.784  
6.768

4.846

4.035  
4.023  
3.756

2.427



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

ppm

2.00

2.00

2.01

1.99

0.99

2.00

3.01

2.99

N-Benzyl-4-methoxybenzenesulfonamide  
C13CPD-1 CDC13

— 162.858

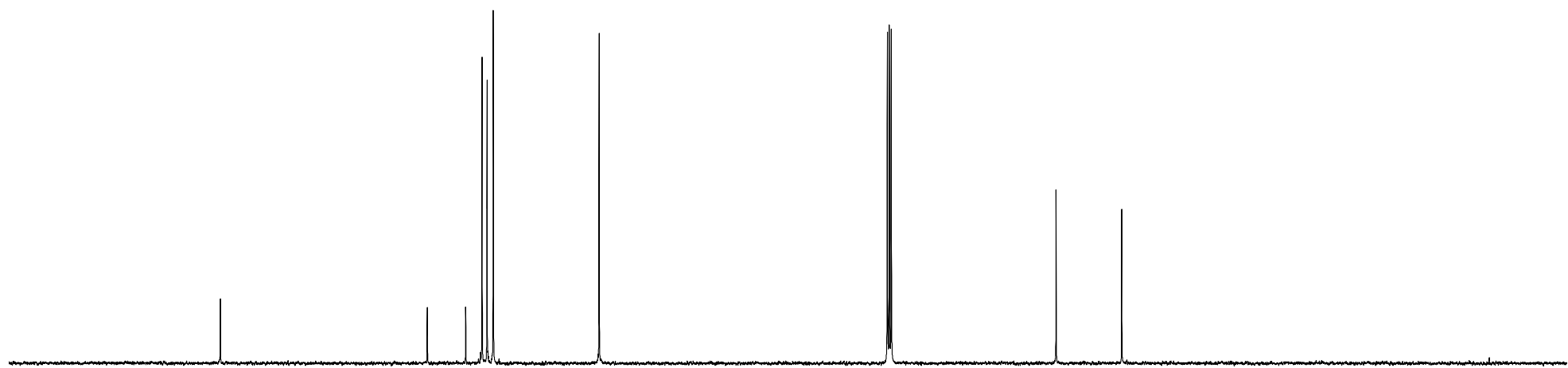
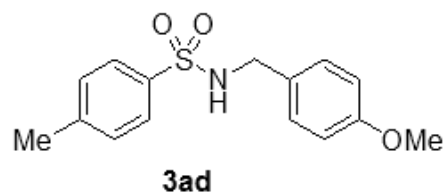
136.297  
131.359  
129.253  
128.614  
127.824

— 114.219

— 77.007

— 55.590

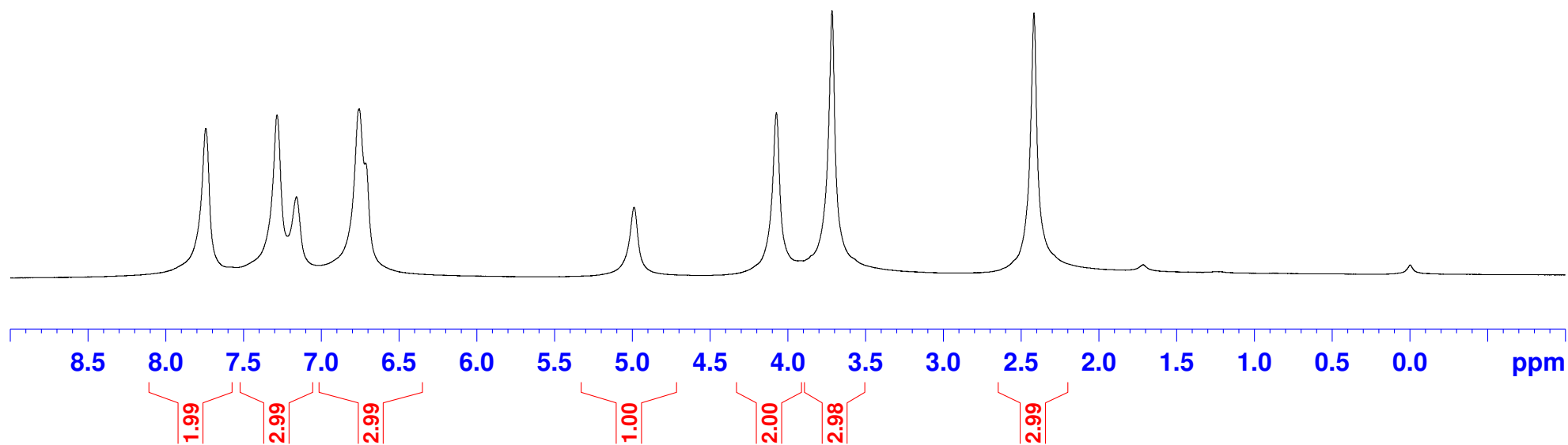
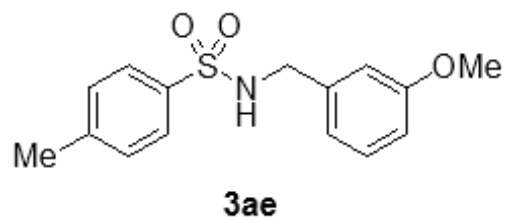
— 47.157



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

N-(3-methoxybenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

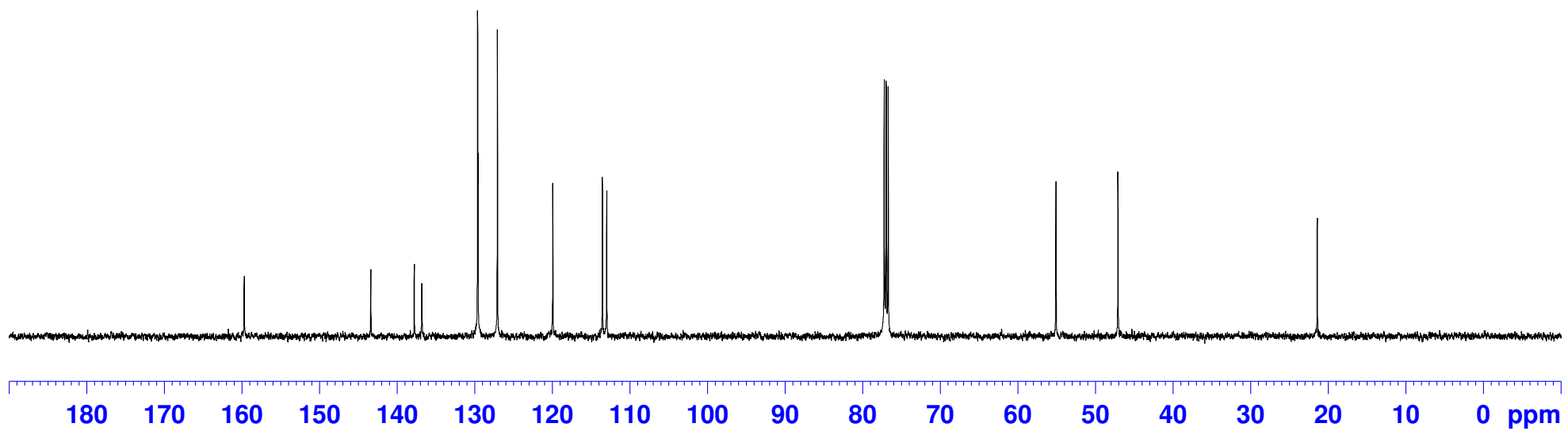
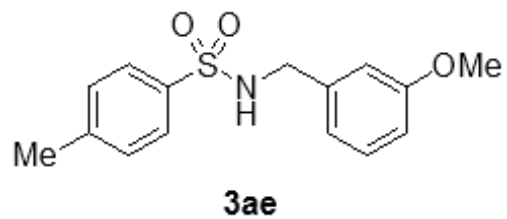
— 7.740  
— 7.282  
— 7.157  
— 6.756  
— 6.714  
  
— 4.988  
  
— 4.073  
— 3.715  
  
— 2.417





N-(3-Methoxybenzyl)-4-methylbenzenesulfonamide  
C13CPD-1 CDCl3

— 159.740  
— 143.421  
— 137.824  
— 136.847  
— 129.655  
— 129.604  
— 127.109  
— 119.973  
— 113.576  
— 113.020  
— 77.001  
— 55.113  
— 47.130  
— 21.446



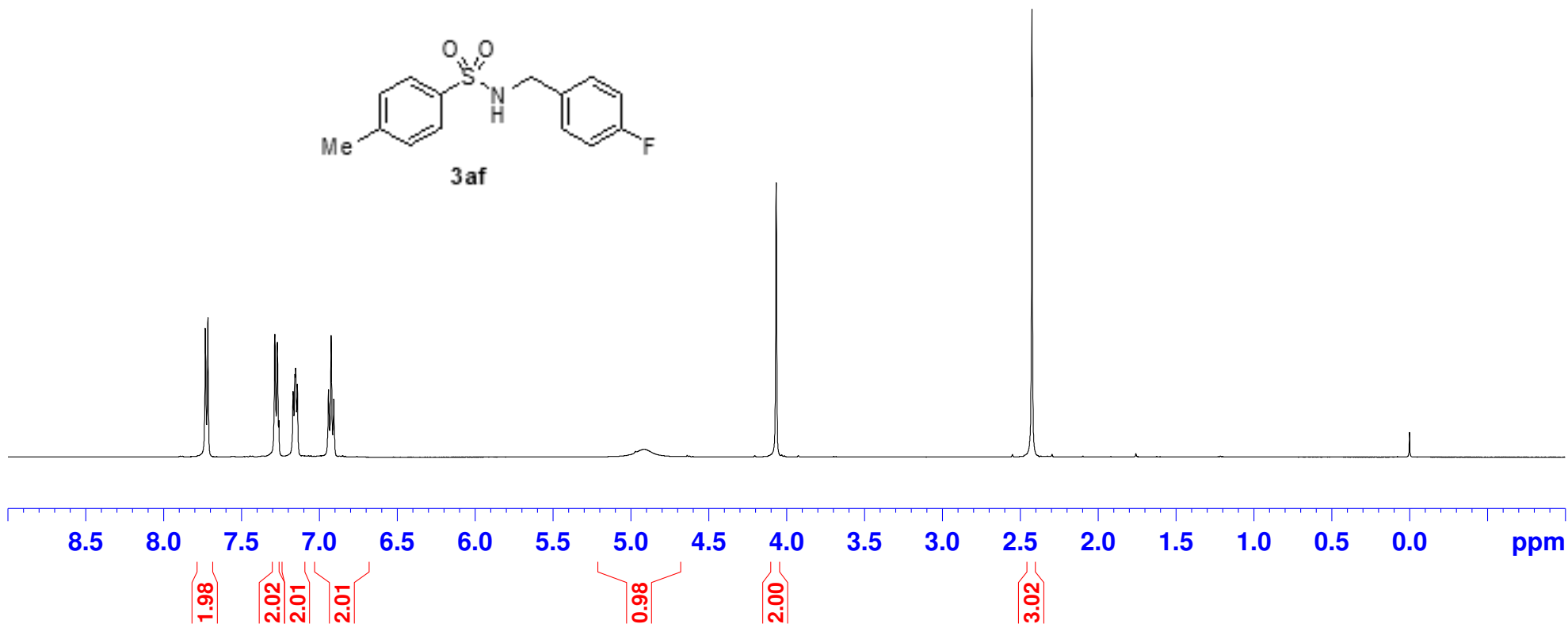
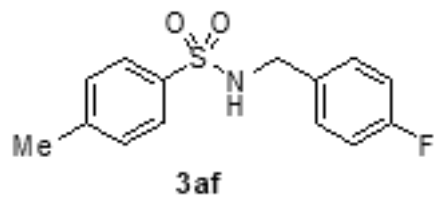
N-(4-fluorobenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.730  
7.713  
7.286  
7.270  
7.169  
7.158  
7.152  
7.142  
6.942  
6.925  
6.908

4.913

4.067

2.424



N-(4-Fluorobenzyl)-4-methylbenzenesulfonamide  
C13CPD-1 CDCl3

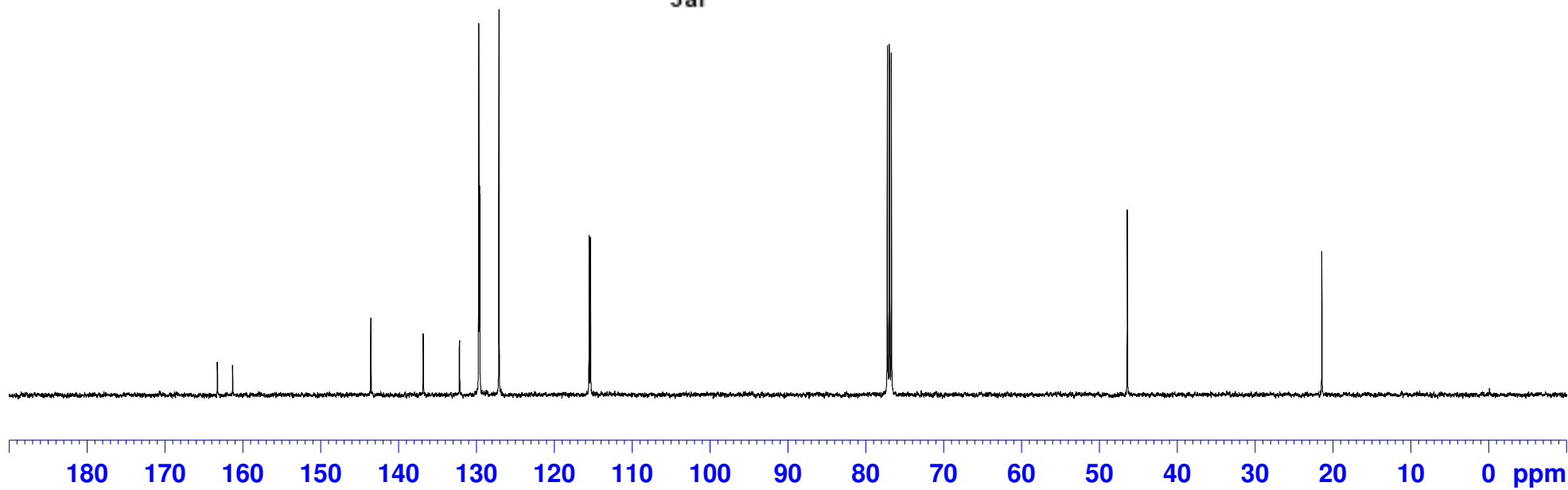
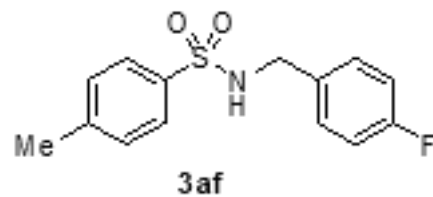
163.252  
161.294

143.535  
136.816  
132.156  
129.686  
129.604  
129.539  
127.083  
115.510  
115.339

77.000

46.444

21.457



N-(3-chlorobenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

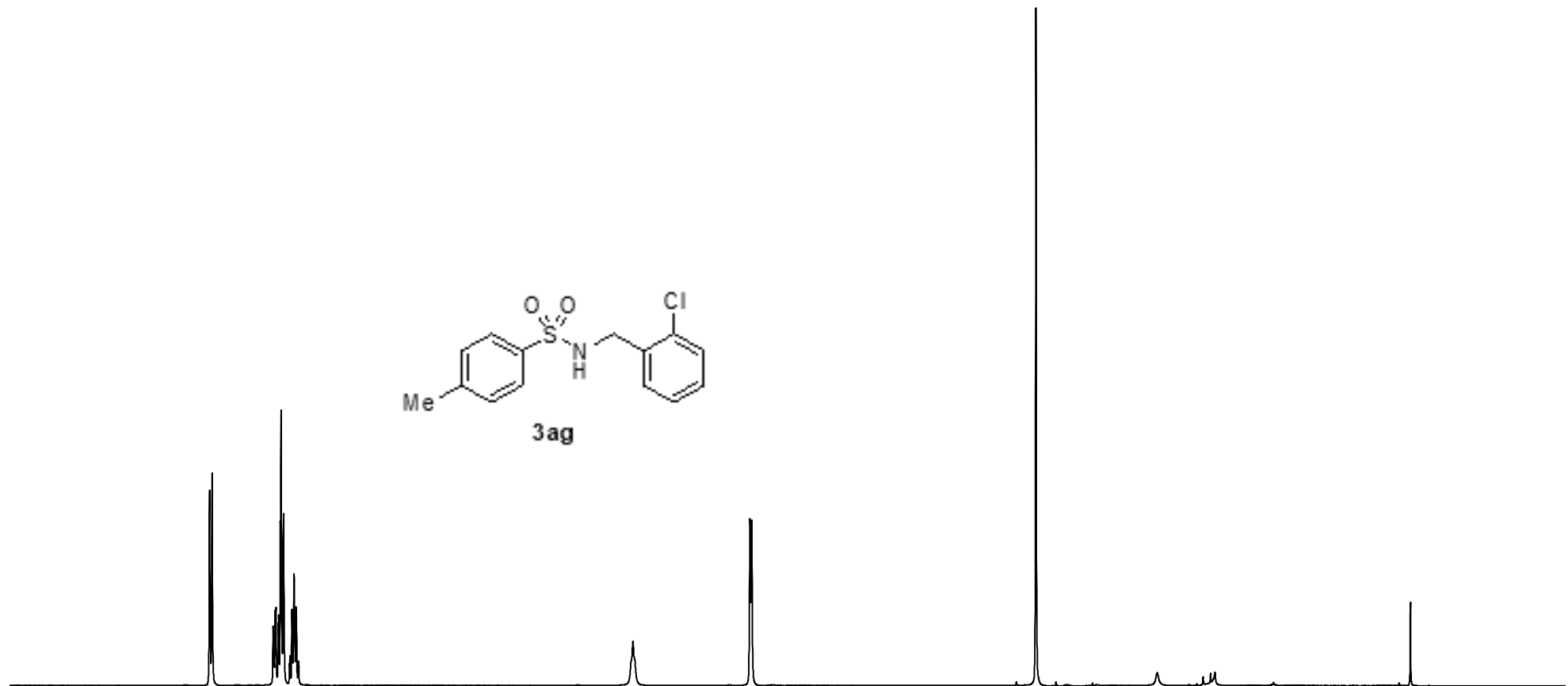
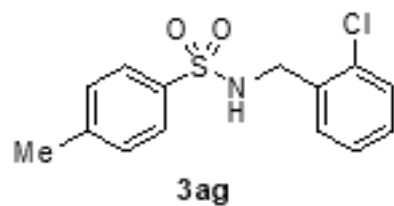
7.699  
7.307  
7.303  
7.294  
7.289  
7.274  
7.271  
7.261  
7.256  
7.240  
7.201  
7.198  
7.187  
7.183  
7.173  
7.171  
7.160  
7.157  
7.145  
7.142  
7.105

— 4.995

< 4.244  
4.232

— 2.406

— -0.000



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

ppm

1.92

4.09

2.01

0.91

2.00

2.98

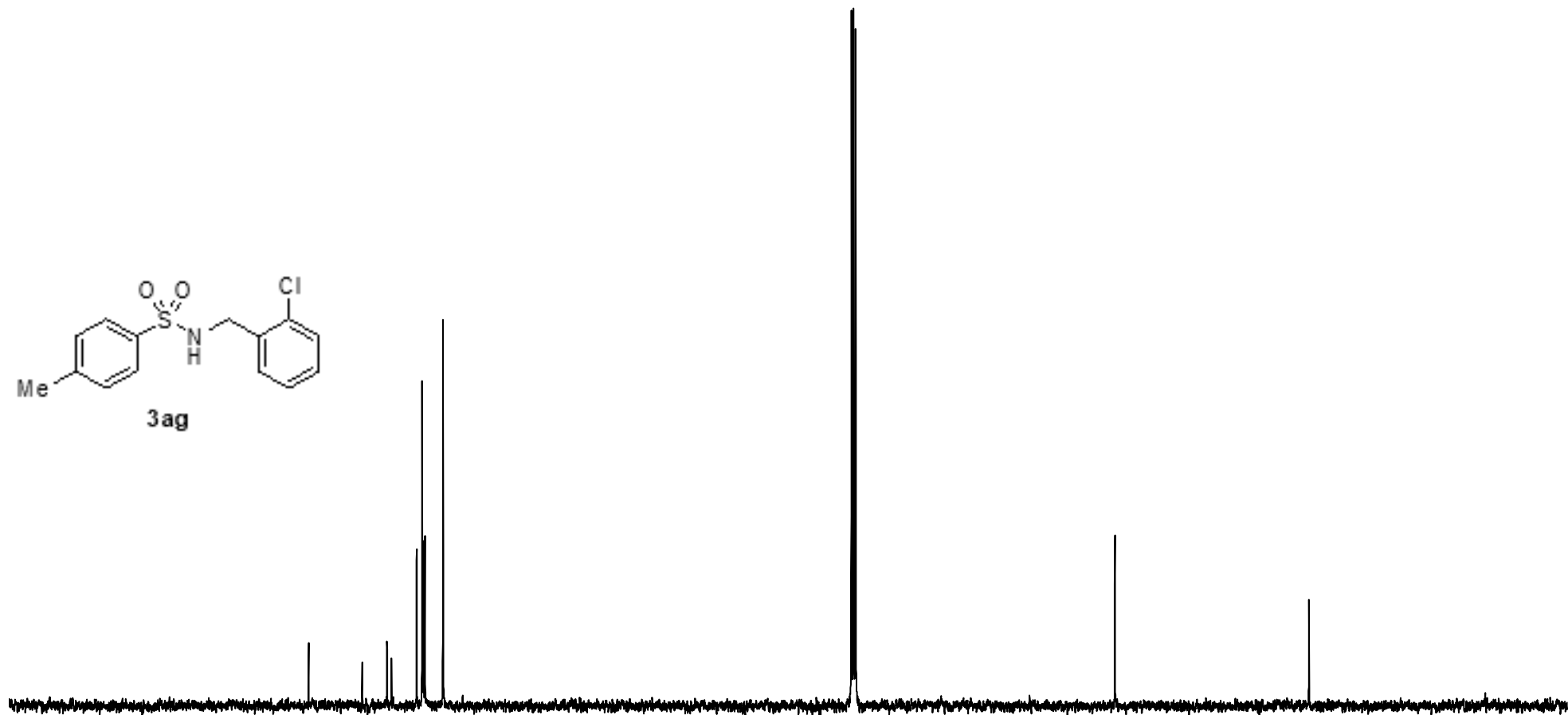
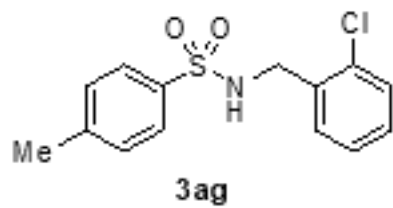
N-(3-chlorobenzyl)-4-methylbenzenesul  
C13CPD CDC13

143.427  
136.893  
133.873  
133.336  
130.257  
129.597  
129.450  
129.245  
127.052

77.000

45.136

21.483



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

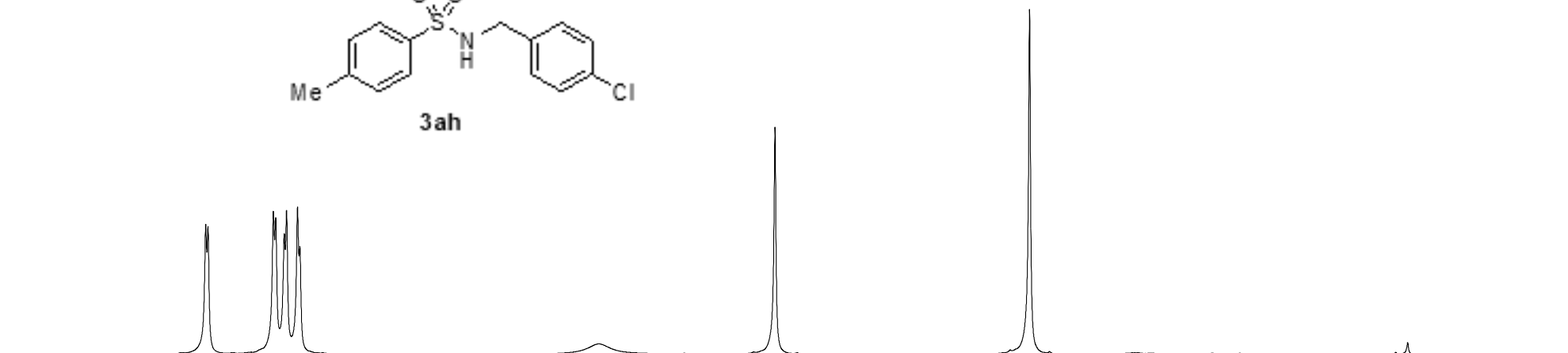
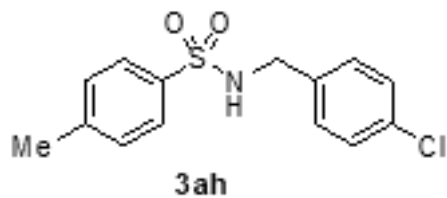
N-(4-Chlorobenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.727  
7.713  
7.293  
7.278  
7.223  
7.208  
7.138  
7.123

5.204

4.074

2.440



8.5

8.0

7.5

7.0

6.5

6.0

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

ppm

2.01

1.98

2.02

1.98

0.98

2.00

2.98

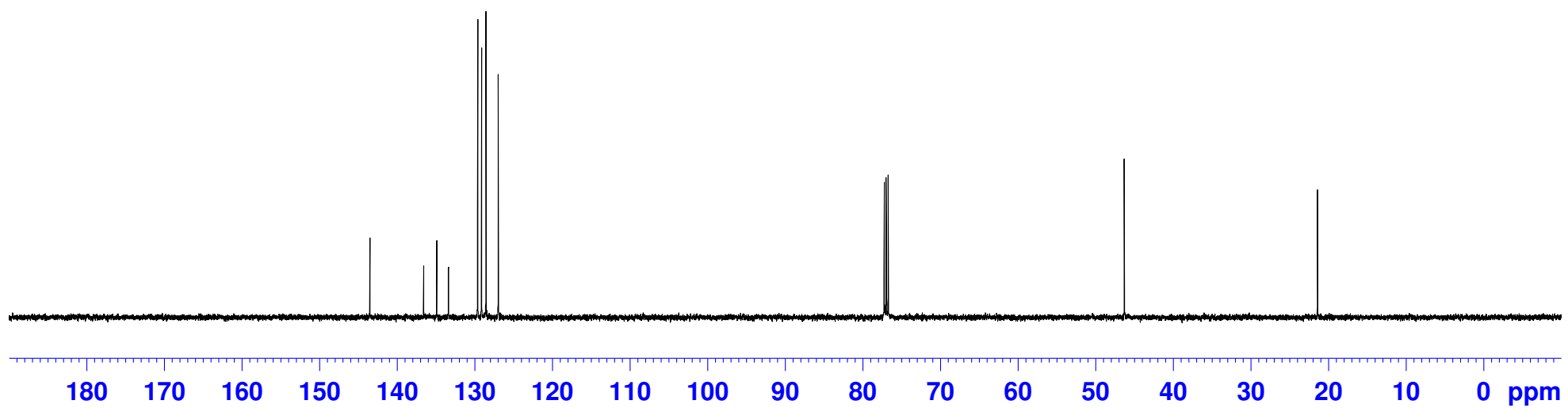
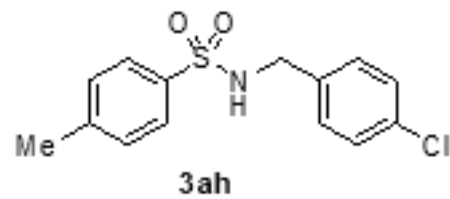
N-(4-Chlorobenzyl)-4-methylbenzenesulfonamide  
C13CPD-1 CDCl3

143.502  
136.571  
134.884  
133.378  
129.618  
129.115  
128.541  
126.964

77.236  
76.981  
76.727

46.307

21.413



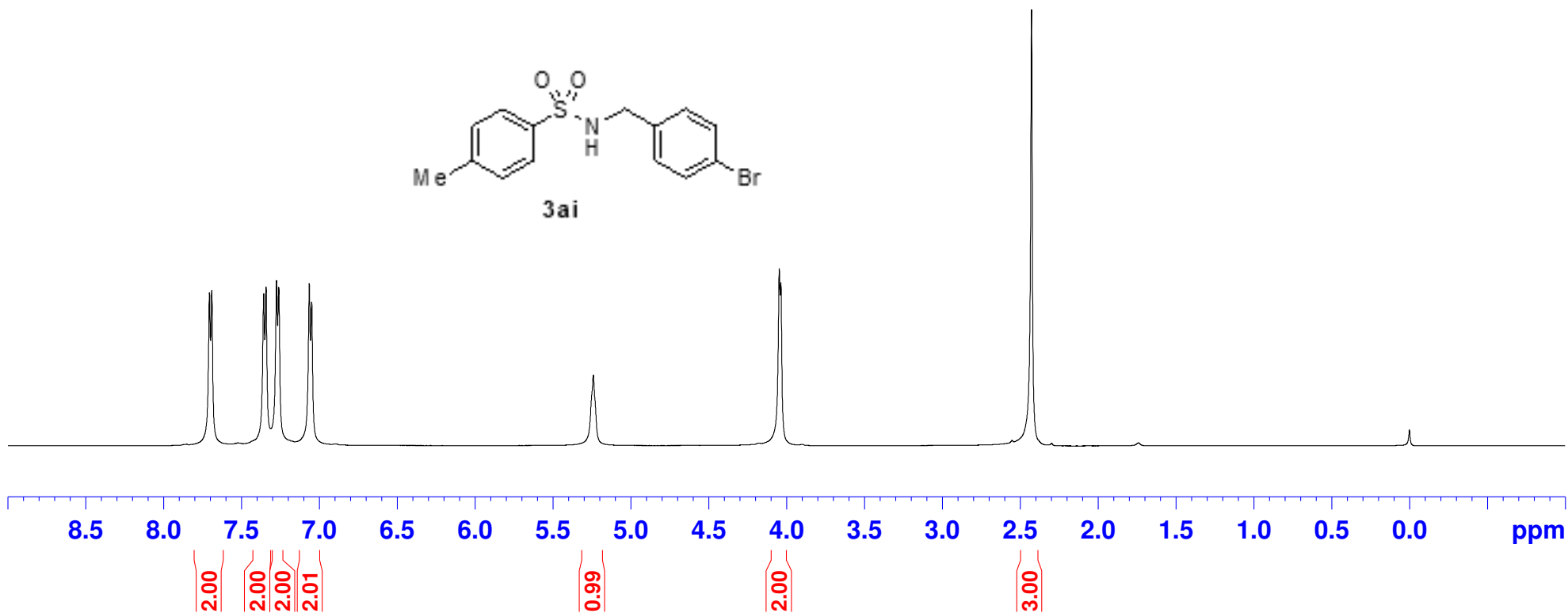
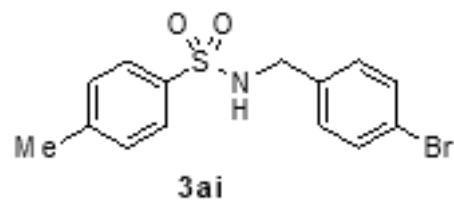
N-(4-Bromobenzyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.704  
7.688  
7.356  
7.340  
7.273  
7.258  
7.063  
7.047

5.241

4.047

2.427





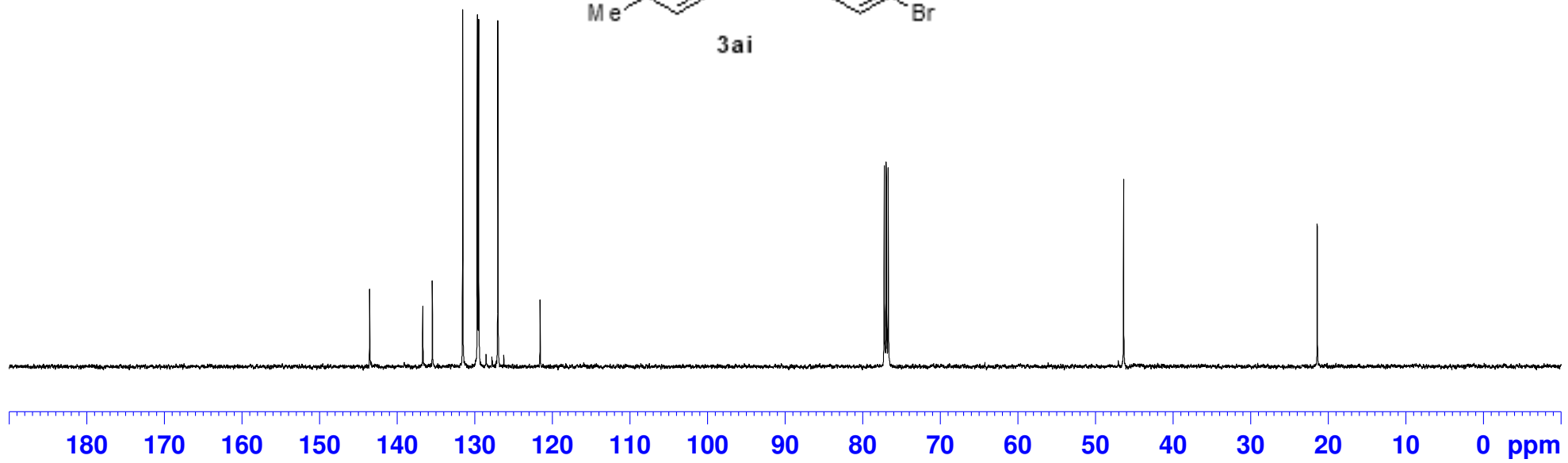
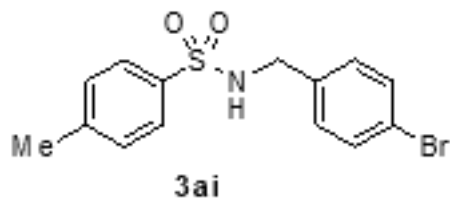
N-(4-Bromobenzyl)-4-methylbenzenesulfonamide  
C13CPD-1 CDCl3

143.527  
136.681  
135.447  
131.540  
129.649  
129.476  
127.002  
121.560

77.000

46.407

21.447

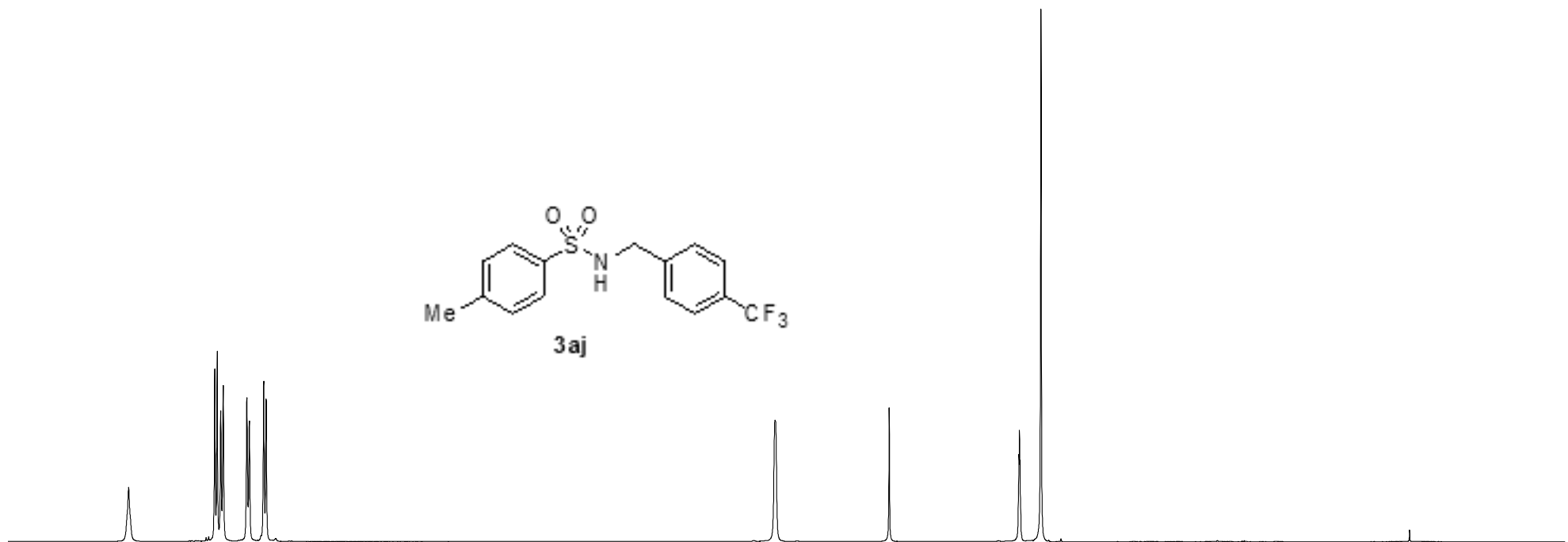
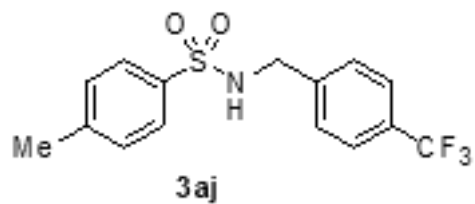


N-[4-(Trifluoromethyl)benzyl]-4-methylbenzenesulfonamide  
Proton DMSO-d6

8.223  
7.670  
7.653  
7.631  
7.615  
7.463  
7.447  
7.356  
7.339

4.075

2.367



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 ppm

0.99

2.00

2.00

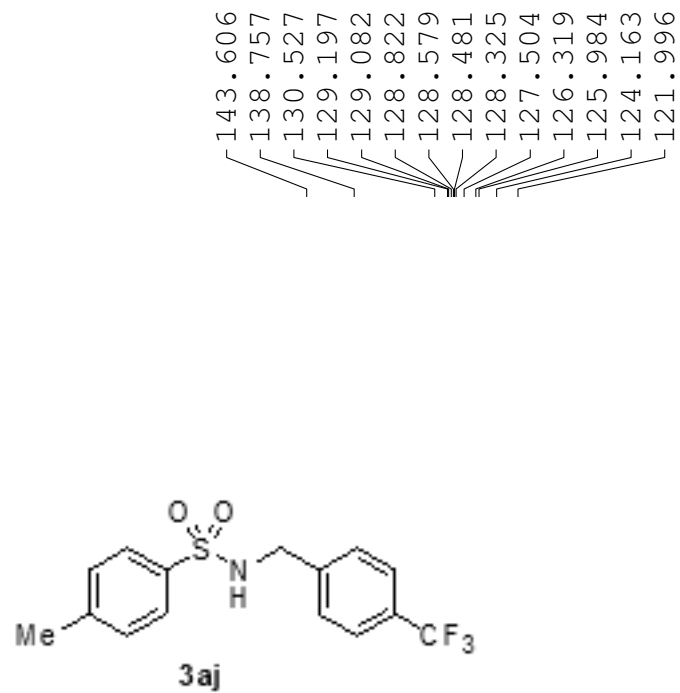
2.00

2.01

2.00

3.00

N-[4-(Trifluoromethyl)benzyl]-4-methylbenzenesulfonamide  
C13CPD-1 DMSO

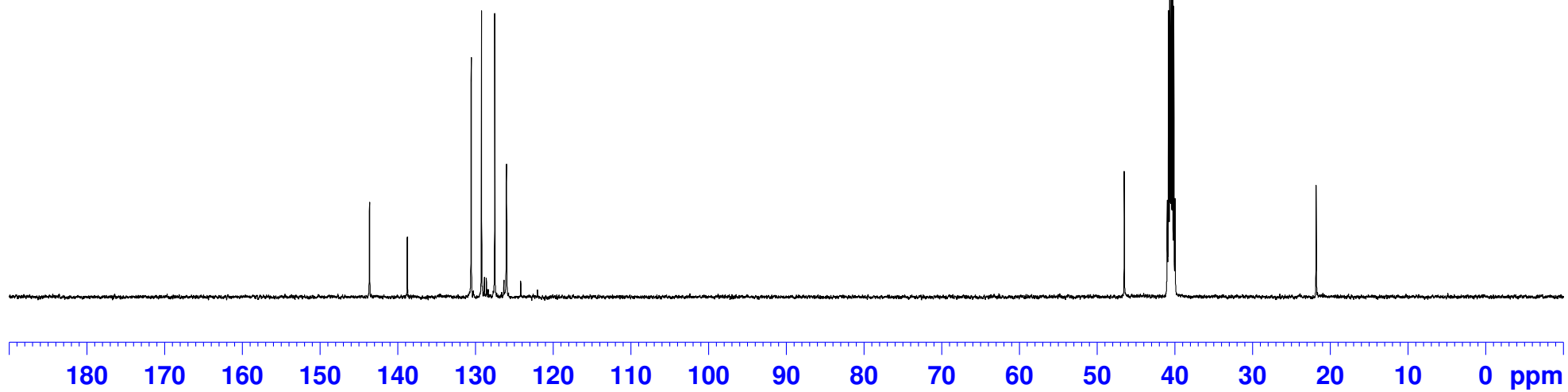
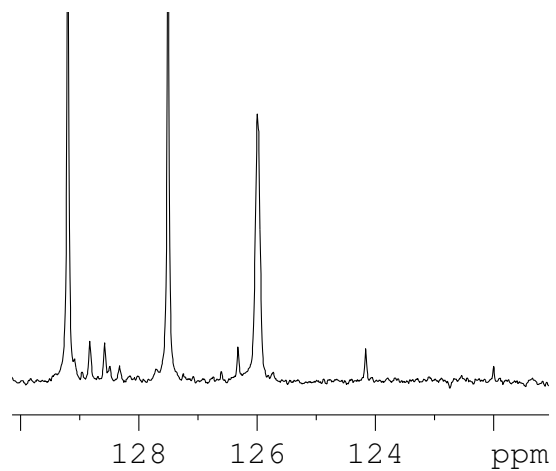


143.606  
138.757  
130.527  
129.197  
129.082  
128.822  
128.579  
128.481  
128.325  
127.504  
126.319  
125.984  
124.163  
121.996

—46.539

—40.499

—21.848

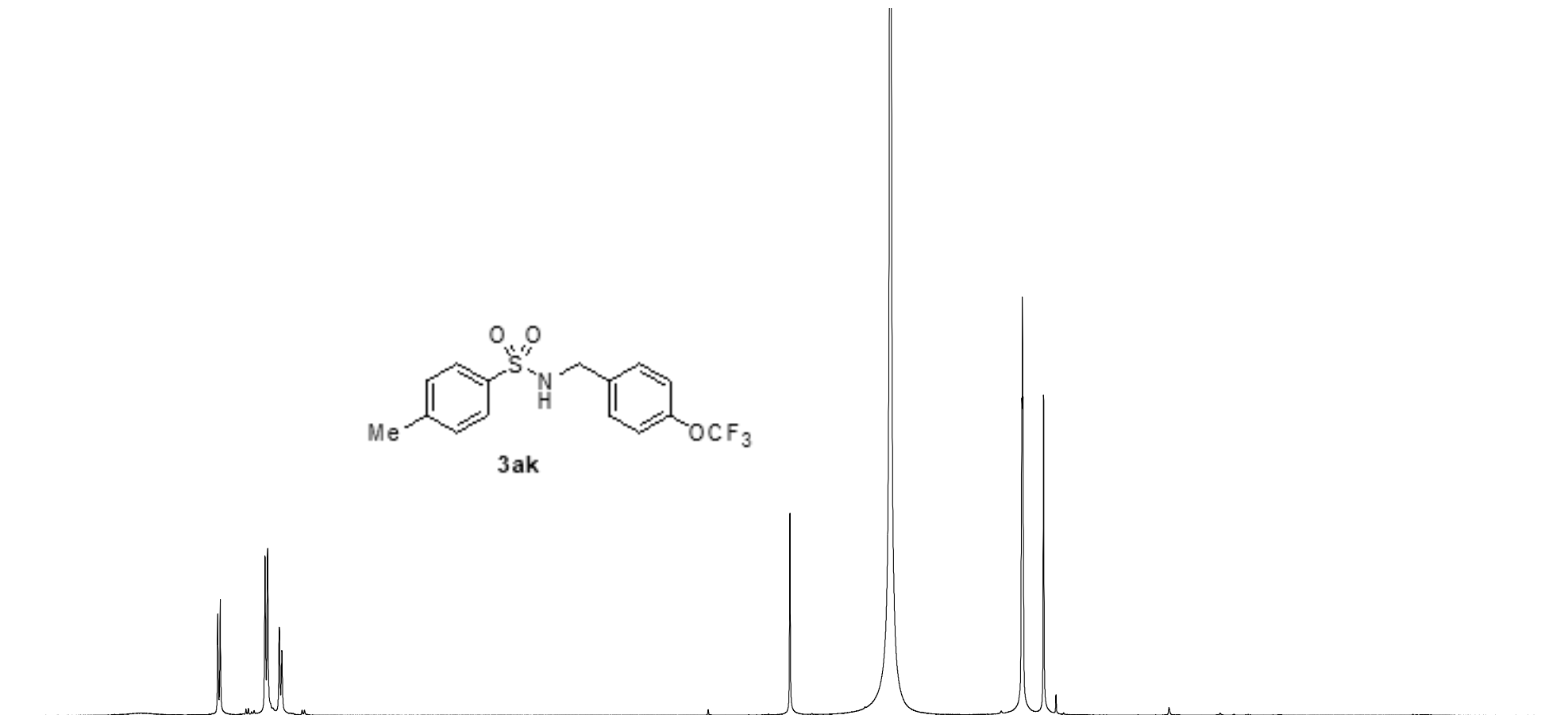
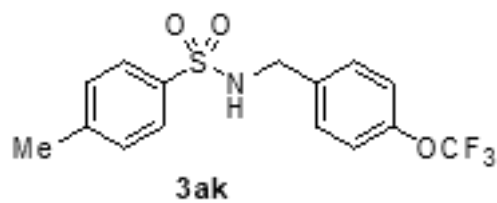


N-[4-(Trifluoromethoxy)benzyl]-4-methylbenzenesulfonamide  
Proton DMSO

8.155  
7.656  
7.639  
7.353  
7.335  
7.261  
7.245

3.989

2.364



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 ppm

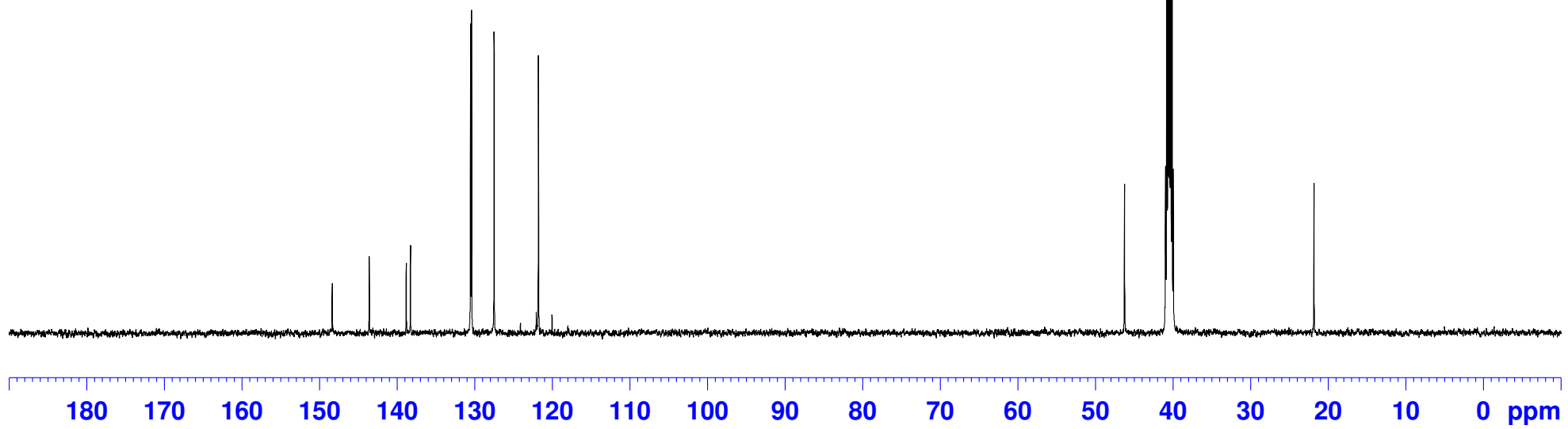
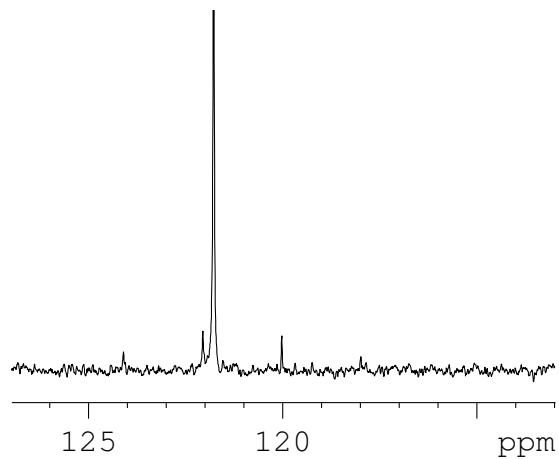
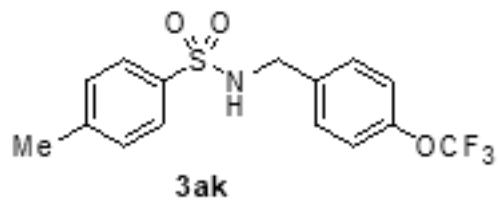
1.00  
1.98  
3.99  
2.02

2.09

3.00

N-[4-(Trifluoromethoxy)benzyl]-4-methylbenzenesulfonamide  
C13CPD-1 DMSO

148.340  
143.575  
138.810  
138.267  
130.517  
130.390  
127.483  
124.091  
122.051  
121.772  
120.015

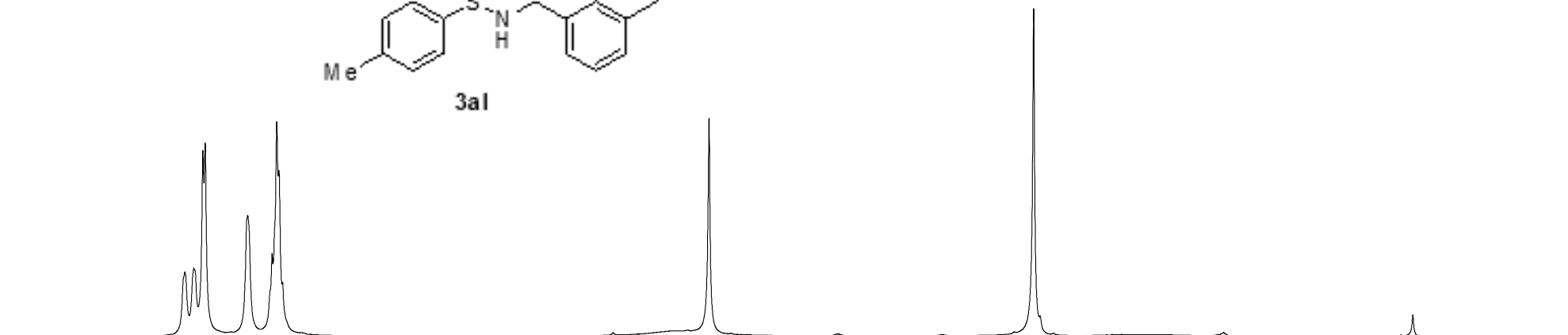
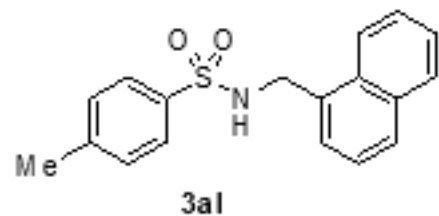


4-Methyl-N-(naphthalen-2-ylmethyl) benzenesulfonamide  
Proton CDCl<sub>3</sub>

7.877  
7.820  
7.762  
7.747  
7.474  
7.317  
7.287  
7.273

4.516

2.432



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 ppm

4.89  
2.00  
4.05  
2.05  
3.01

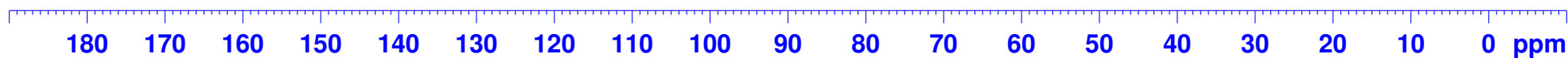
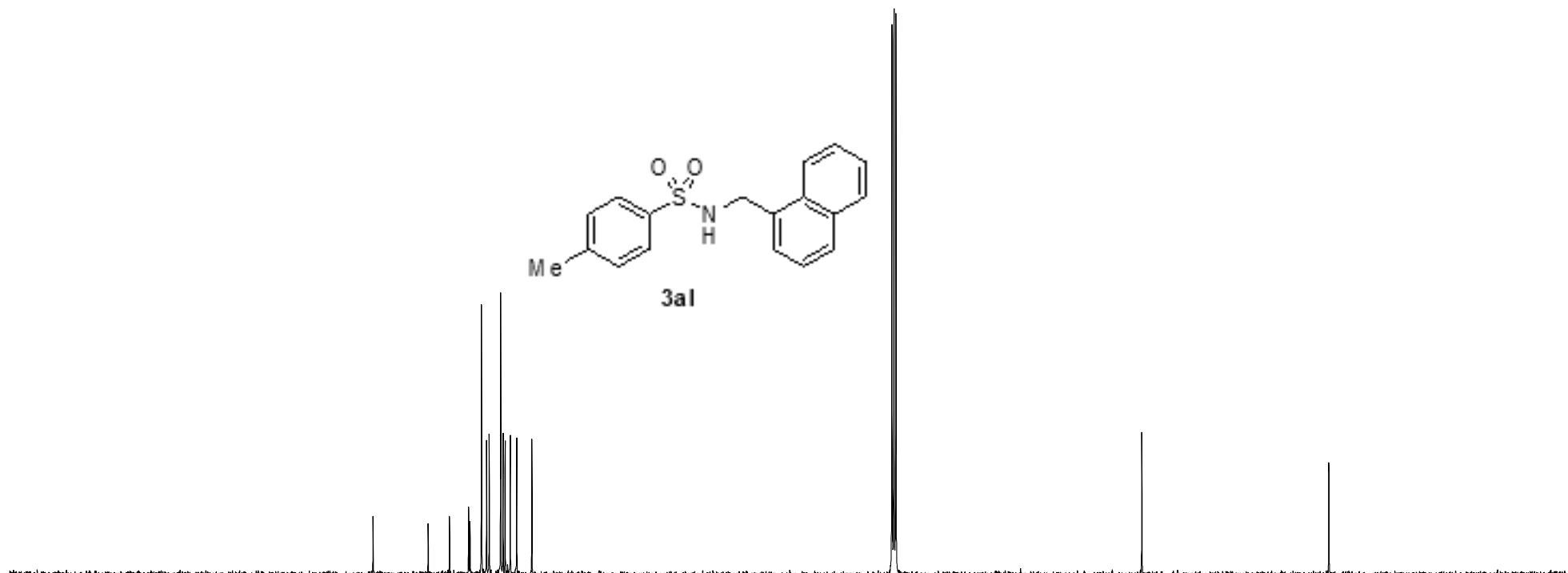
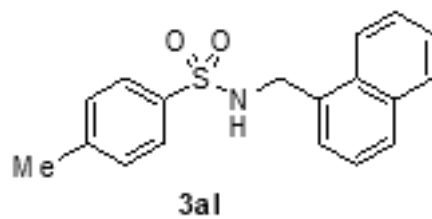
4-Methyl-N-(naphthalen-2-ylmethyl) benzenesulfonamide  
C13CPD-1 CDCl3

143.527  
136.491  
133.755  
131.321  
131.137  
129.680  
129.027  
128.691  
127.225  
126.913  
126.654  
125.999  
125.172  
123.237

— 77.001

— 45.395

— 21.512



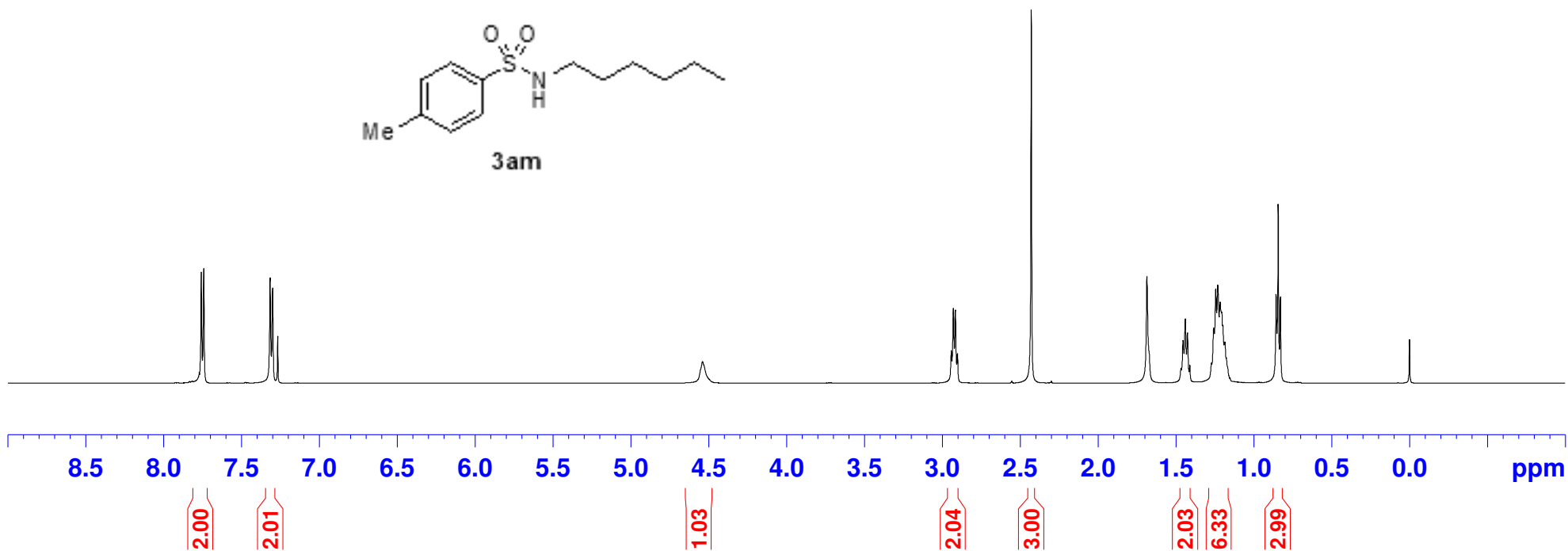
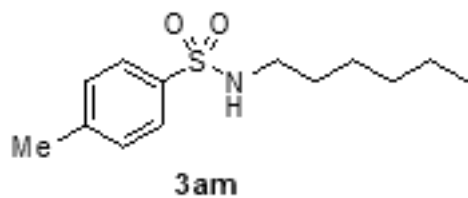
N-Hexyl-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.758  
7.742  
7.316  
7.300

4.540

2.942  
2.929  
2.916  
2.902  
2.429

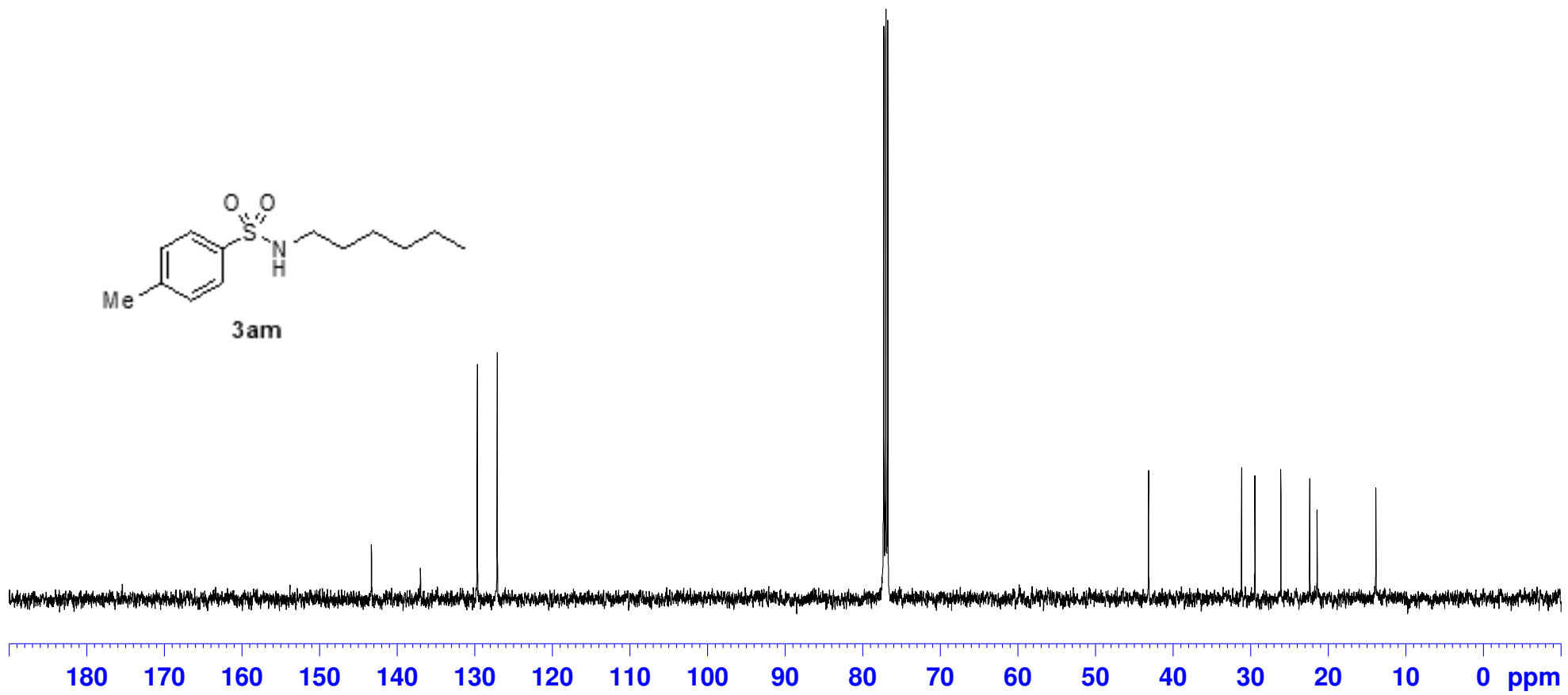
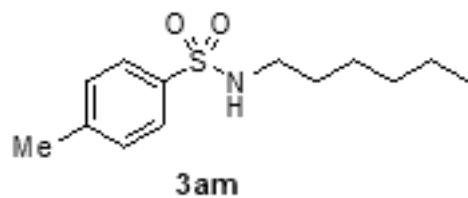
1.468  
1.440  
1.411  
1.257  
1.231  
1.188  
1.185  
0.857  
0.843  
0.829





N-Hexyl-4-methylbenzenesulfonamide  
C13CPD-1 CDC13

— 143.291  
— 136.988  
— 129.643  
— 127.075  
  
— 77.000  
  
— 43.194  
— 31.194  
— 29.483  
— 26.143  
— 22.410  
— 21.469  
— 13.893

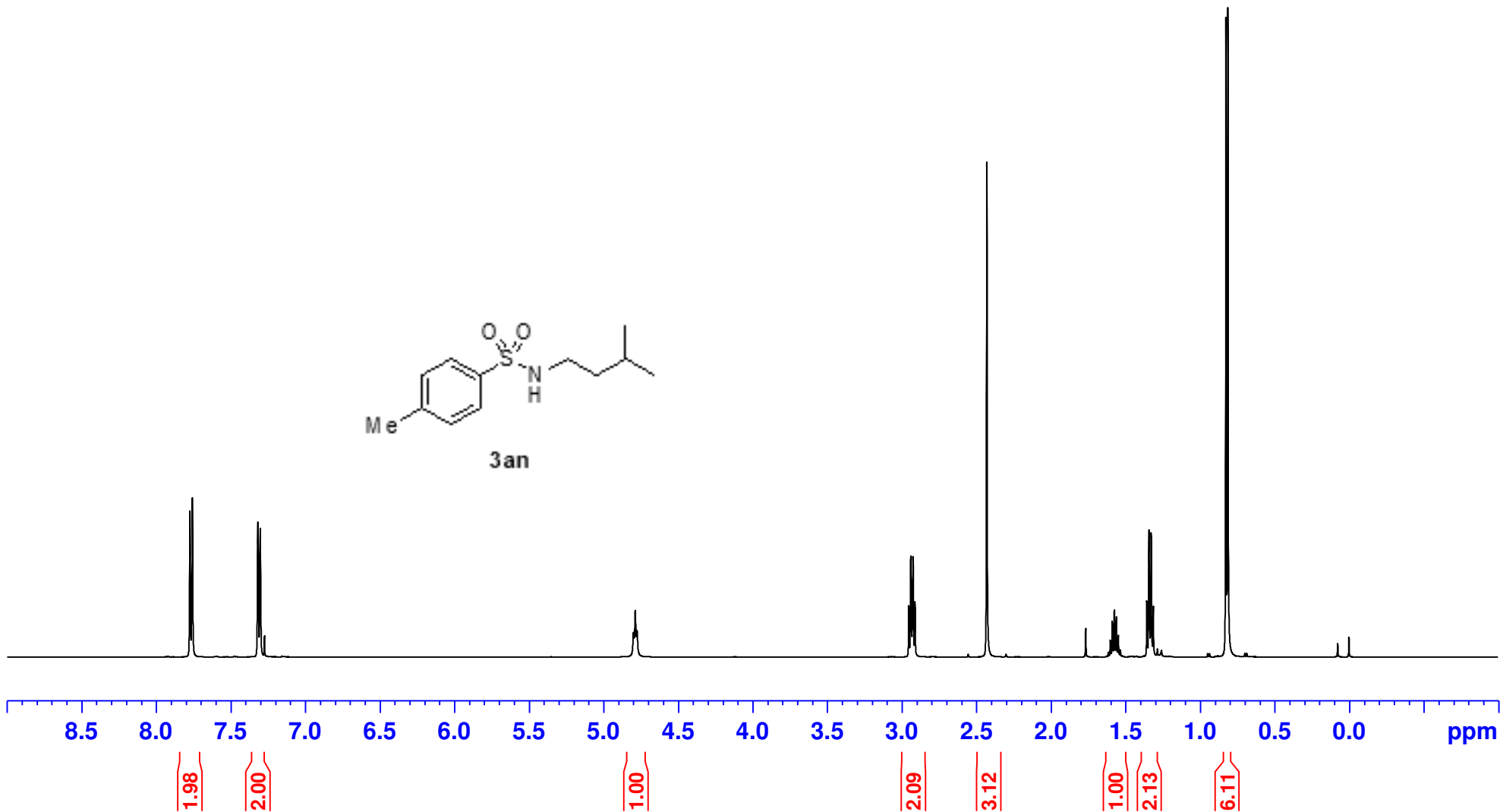
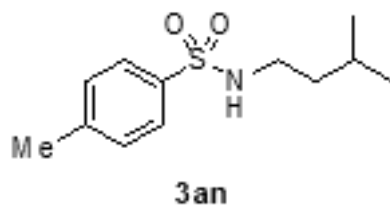


N-isopentyl-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

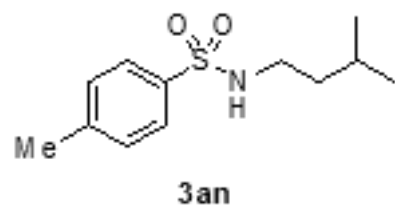
7.773  
7.757  
7.317  
7.301  
7.273

4.798  
4.787  
4.775

2.952  
2.939  
2.924  
2.910  
2.429  
1.628  
1.614  
1.601  
1.587  
1.574  
1.560  
1.547  
1.534  
1.520  
1.356  
1.341  
1.326  
1.312  
0.825  
0.812  
0.000



N-isopentyl-4-methylbenzenesulfonamide  
C13CPD CDC13

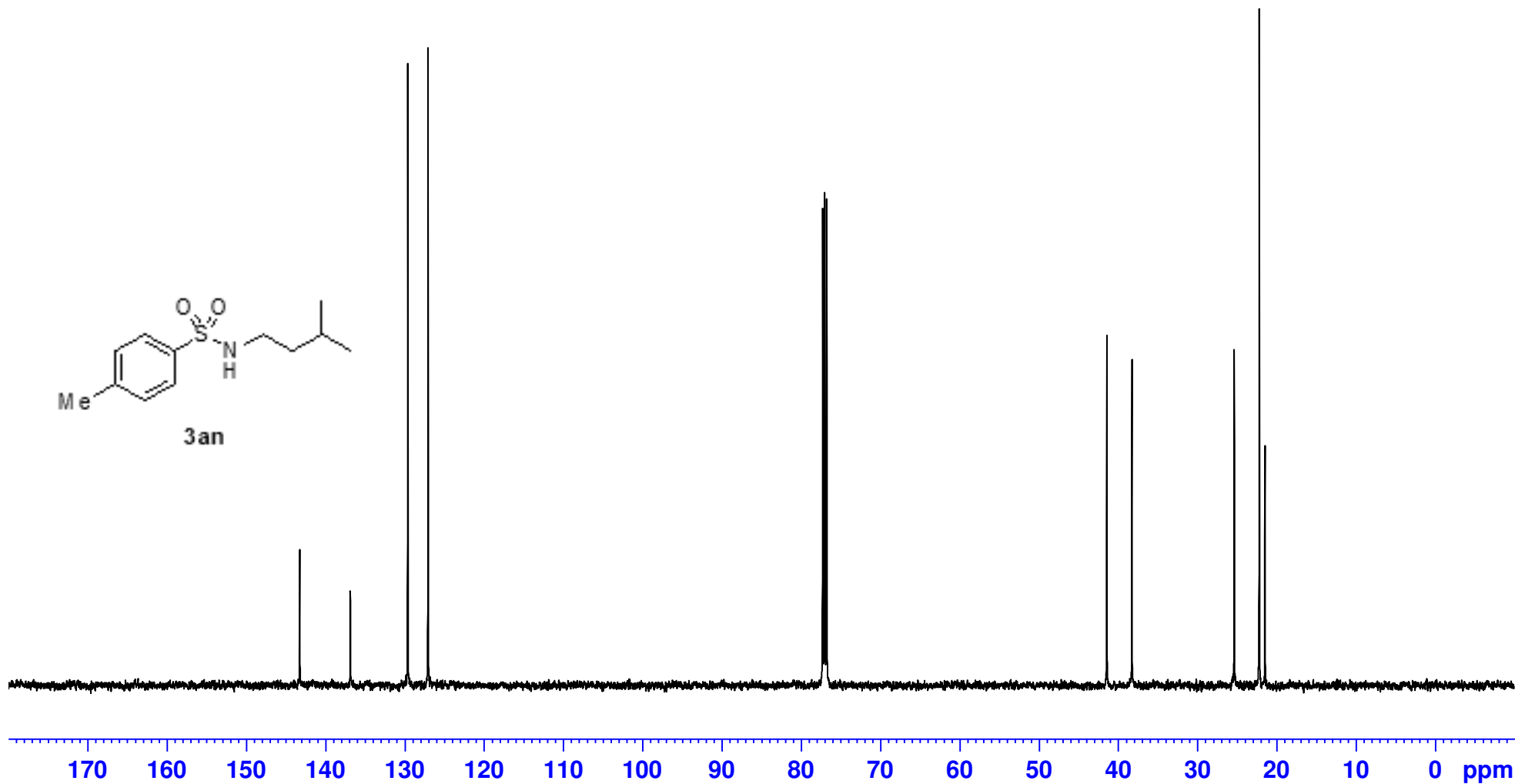


— 143.237  
— 136.864  
— 129.613  
— 127.050

— 77.000

— 41.407  
— 38.235

— 25.322  
— 22.168  
— 21.450



N-(Cyclohexylmethyl)-4-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

< 7.760  
< 7.744

< 7.305  
< 7.289

— 4.915

< 2.743  
< 2.731

— 2.421

1.675

1.653

1.605

1.404

1.398

1.377

1.170

1.120

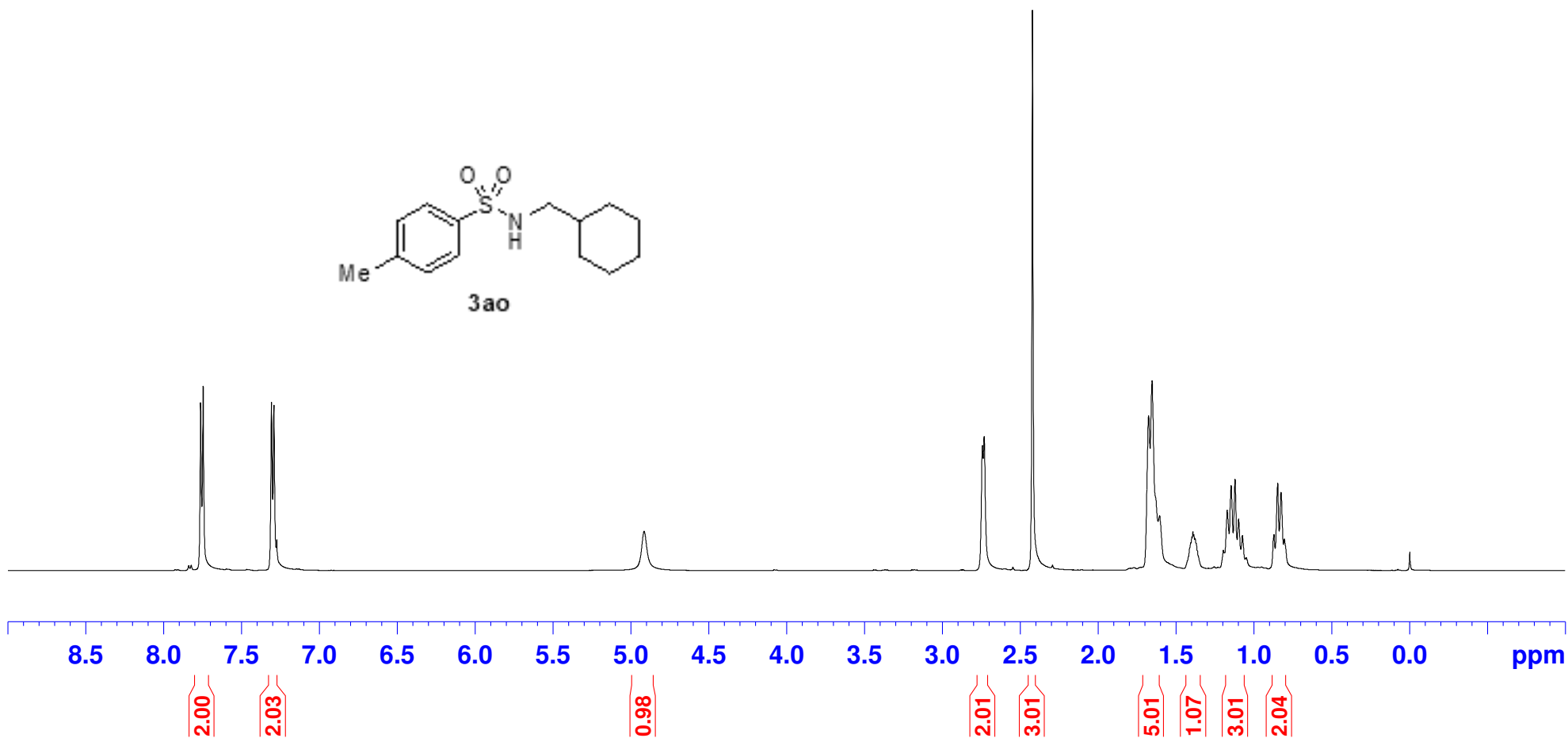
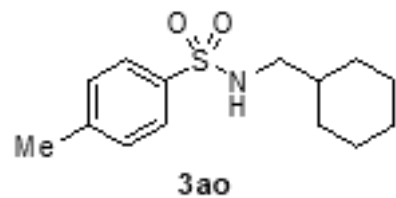
1.073

0.870

0.847

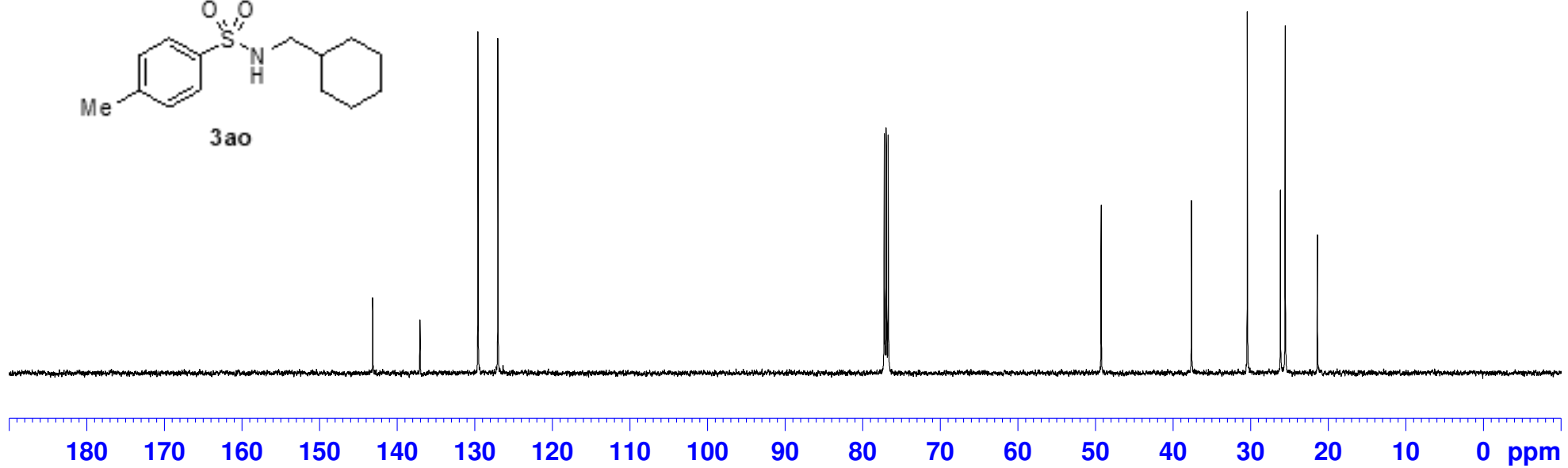
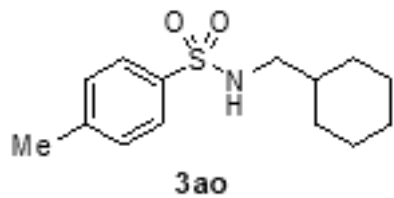
0.825

0.804



N-(Cyclohexylmethyl)-4-methylbenzenesulfonamide  
C13CPD-1 CDCl3

— 143.127  
— 137.045  
— 129.566  
— 127.001  
  
— 77.000  
  
— 49.300  
  
— 37.653  
— 30.462  
— 26.192  
— 25.578  
— 21.428



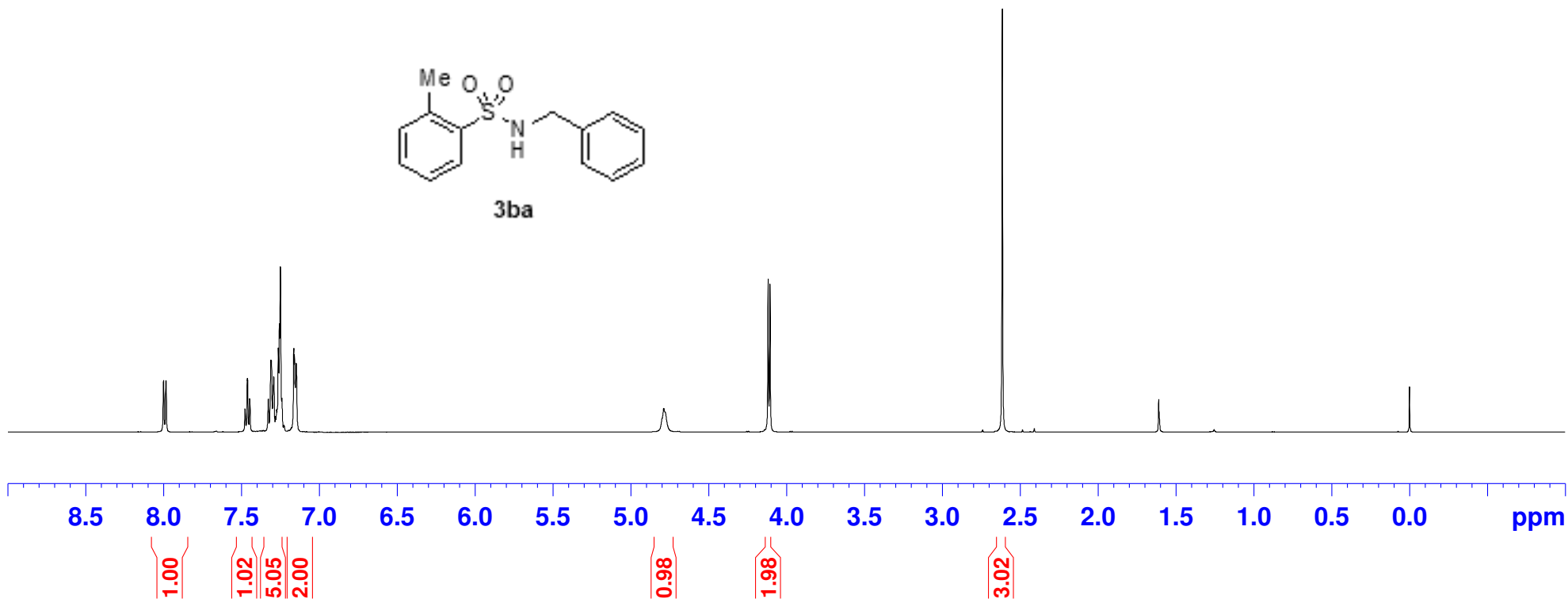
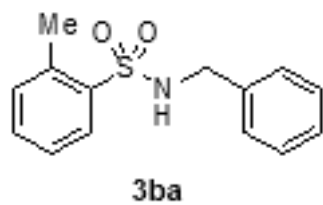
N-Benzyl-2-methylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.998  
7.982  
7.478  
7.463  
7.448  
7.328  
7.293  
7.251  
7.165  
7.160  
7.149

— 4.789

< 4.119  
4.106

— 2.615



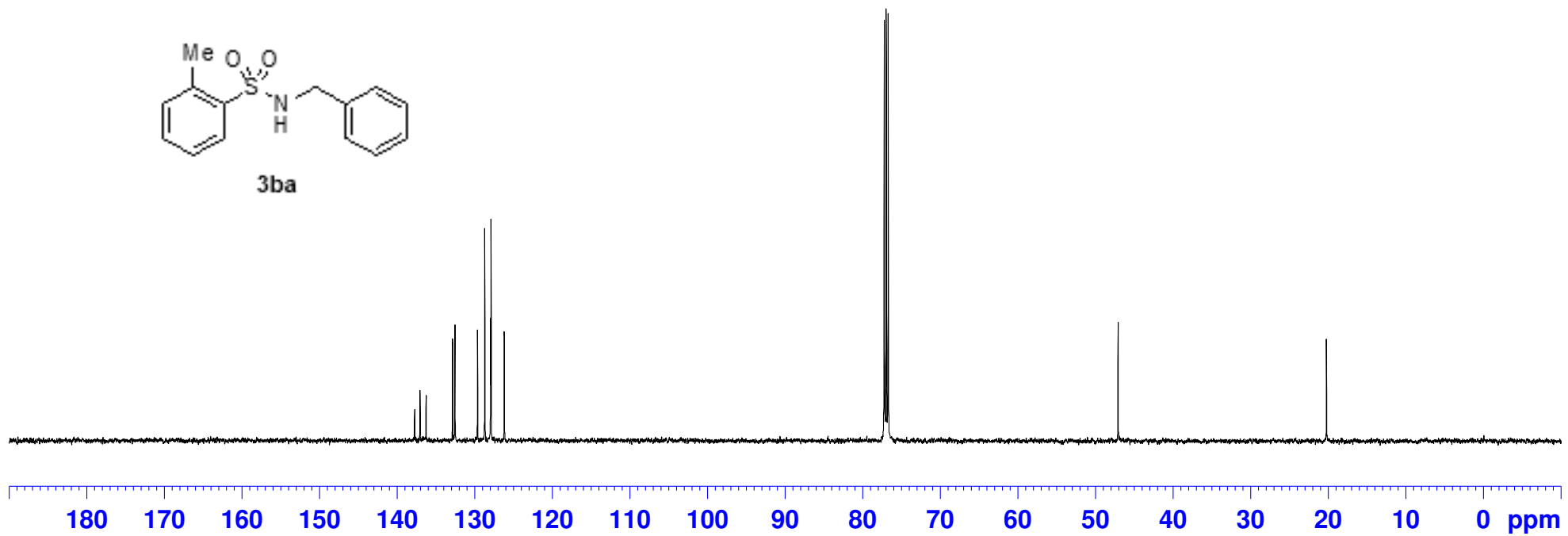
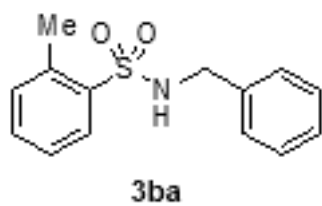
N-Benzyl-2-methylbenzenesulfonamide  
C13CPD-1 CDC13

137.717  
137.029  
136.247  
132.823  
132.521  
129.618  
128.684  
127.931  
127.869  
126.169

— 77.000

— 47.119

— 20.258

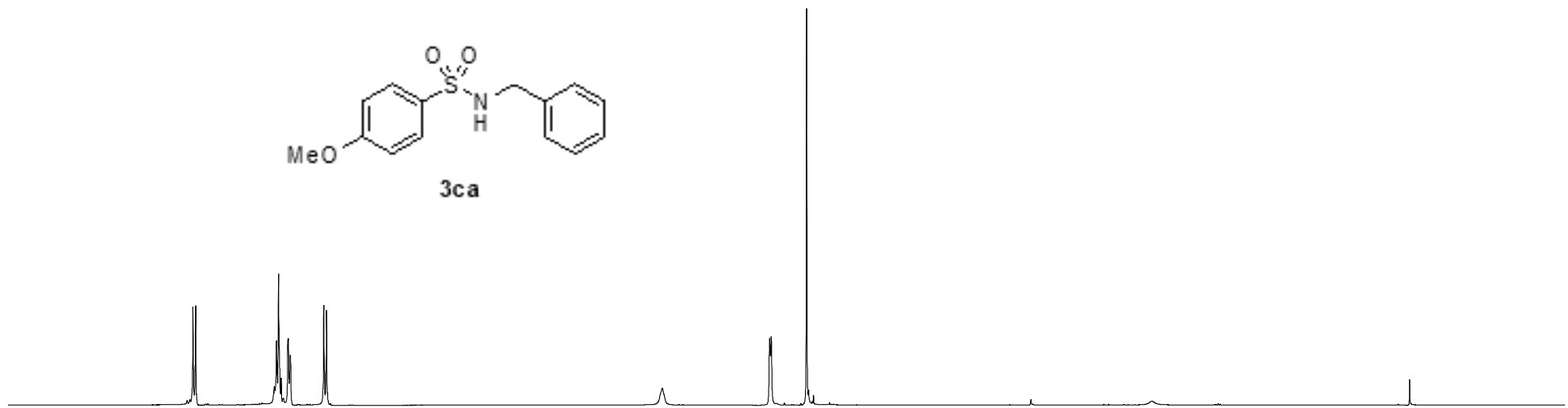
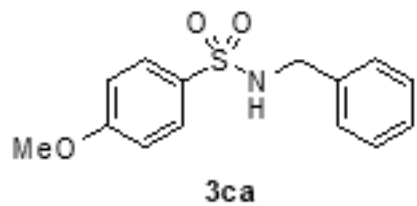


N-Benzyl-4-methoxybenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.809  
7.792  
7.286  
7.274  
7.259  
7.243  
7.200  
7.184  
6.972  
6.954

4.798

4.109  
4.099  
3.872



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

ppm

2.00

3.00

2.01

1.99

0.99

1.98

2.99



N-Benzyl-4-methoxybenzenesulfonamide  
C13CPD-1 CDC13

— 162.858

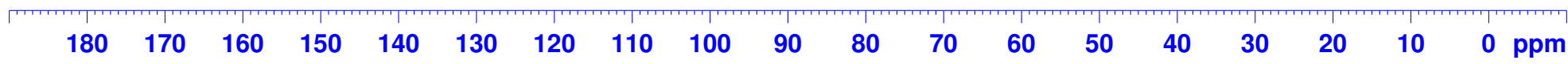
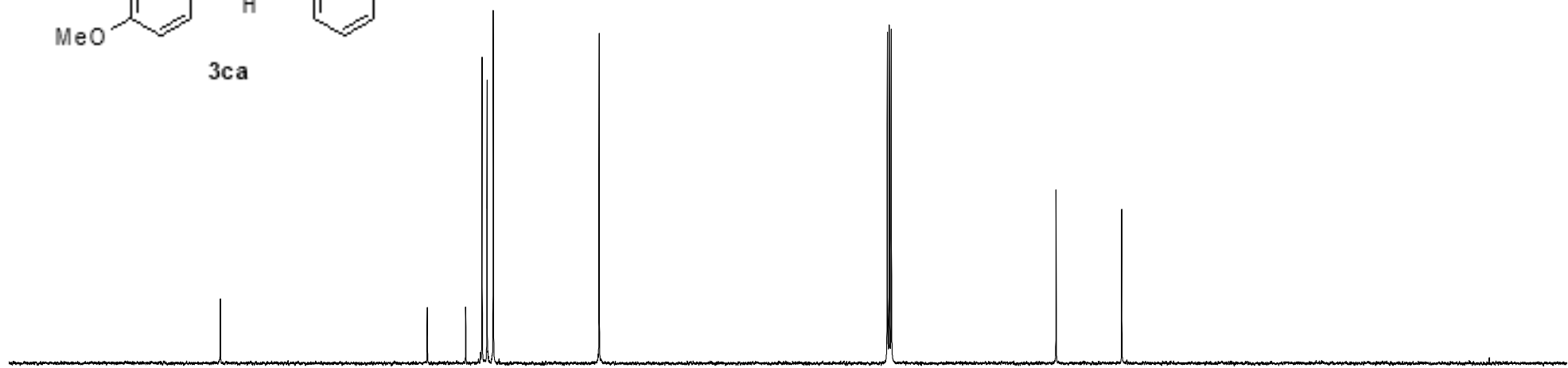
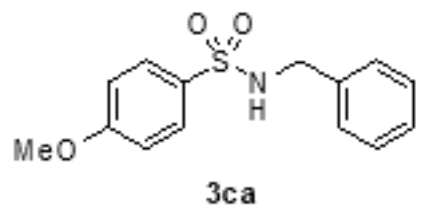
136.297  
131.359  
129.253  
128.614  
127.824

— 114.219

— 77.007

— 55.590

— 47.157

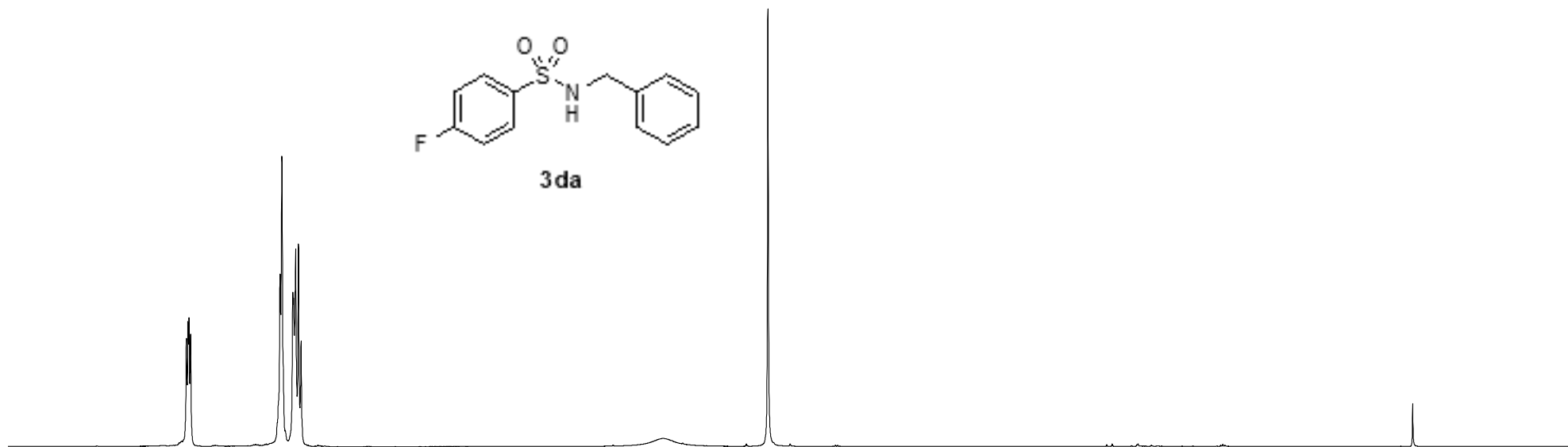
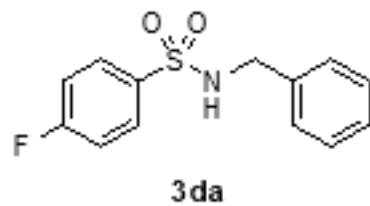


N-benzyl-4-fluorobenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.854  
7.844  
7.837  
7.827  
7.255  
7.244  
7.175  
7.170  
7.156  
7.138  
7.121

— 4.803

— 4.130



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

ppm

2.01

3.00

4.04

1.01

2.00

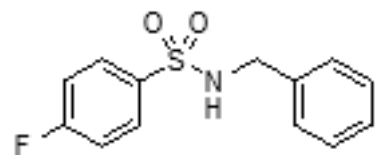
N-Benzyl-4-fluorobenzenesulfonamide  
C13CPD-1 CDCl3

165.992  
163.965

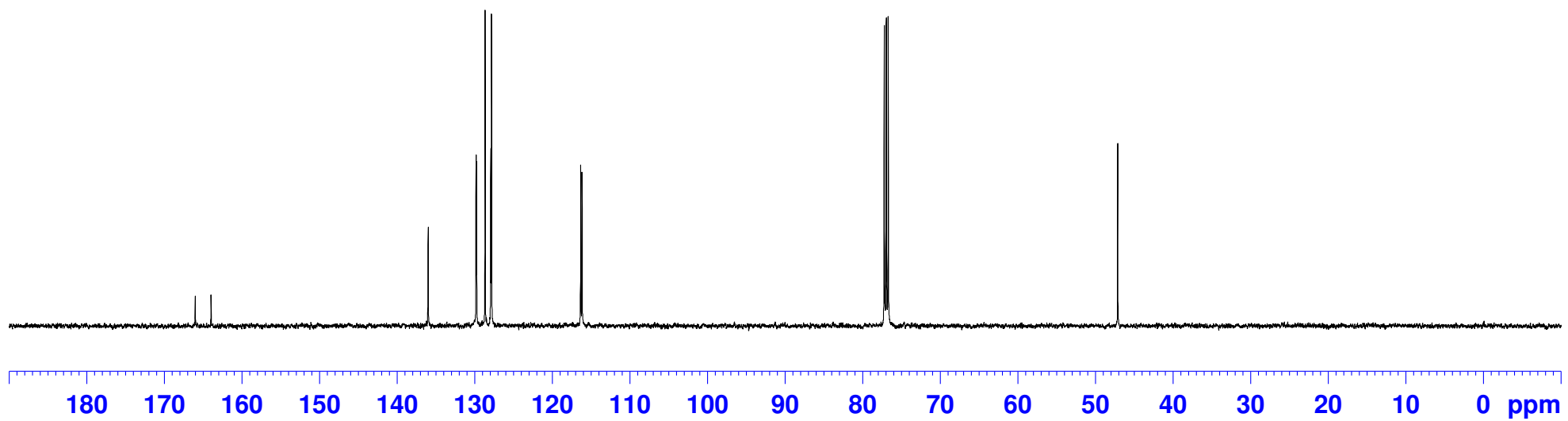
135.976  
129.816  
129.743  
128.649  
127.911  
127.814  
116.326  
116.146

77.001

47.170



3da

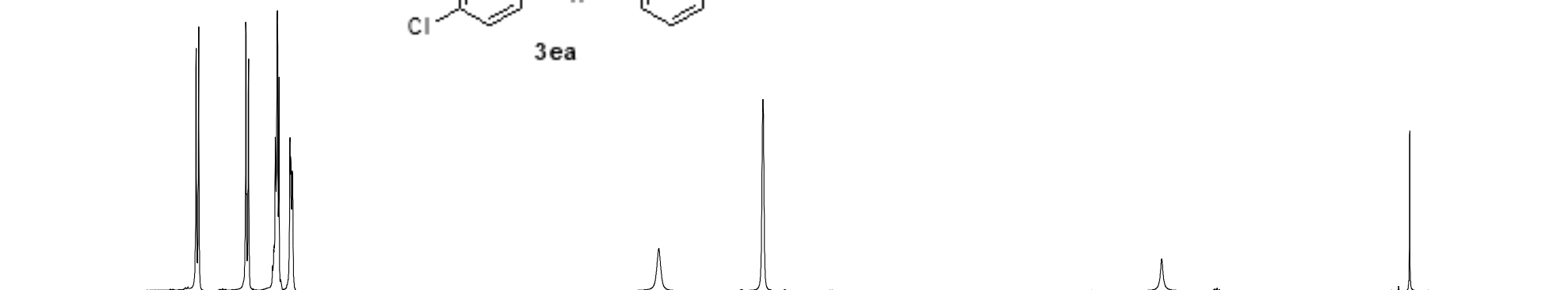
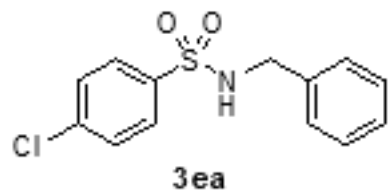


N-benzyl-4-chlorobenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.789  
7.772  
7.472  
7.455  
7.283  
7.271  
7.269  
7.259  
7.189  
7.184  
7.174

— 4.821

— 4.152



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

ppm

2.00

2.00

3.03

1.85

1.01

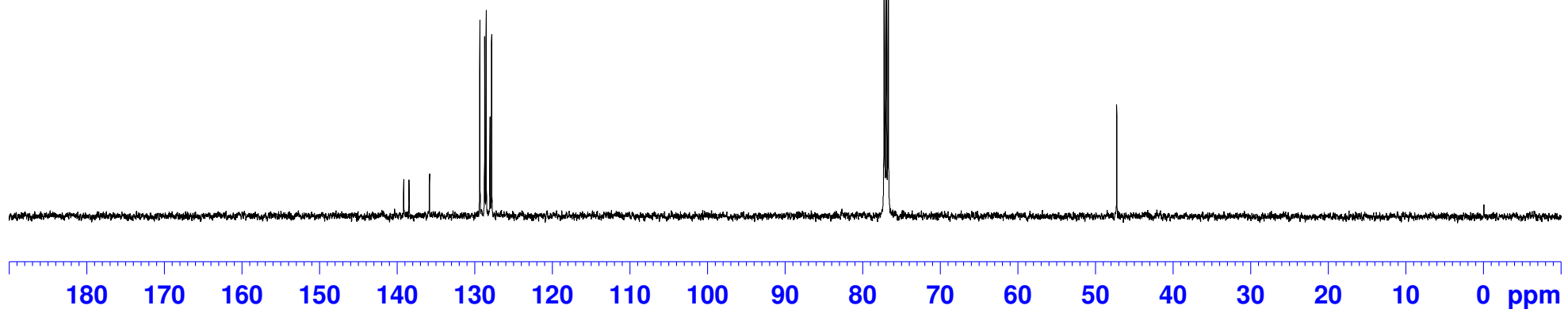
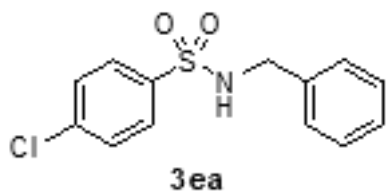
2.00

N-Benzyl-4-chlorobenzenesulfonamide  
C13CPD-1 CDC13

139.185  
138.514  
135.866  
129.377  
128.758  
128.558  
128.063  
127.853

77.000

47.290

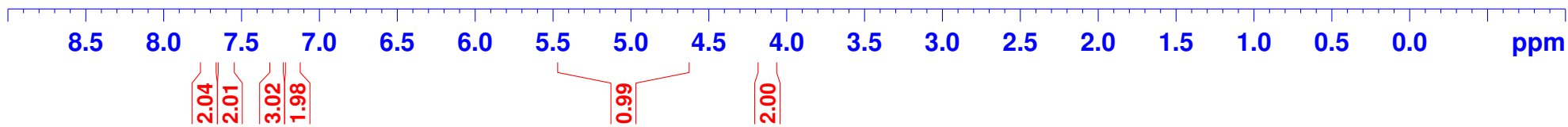
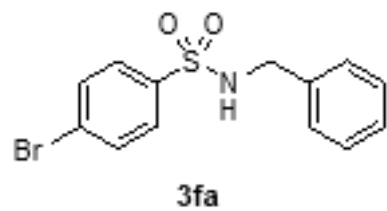


N-Benzyl-4-bromobenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.691  
7.675  
7.610  
7.594  
7.252  
7.170

5.033

4.127

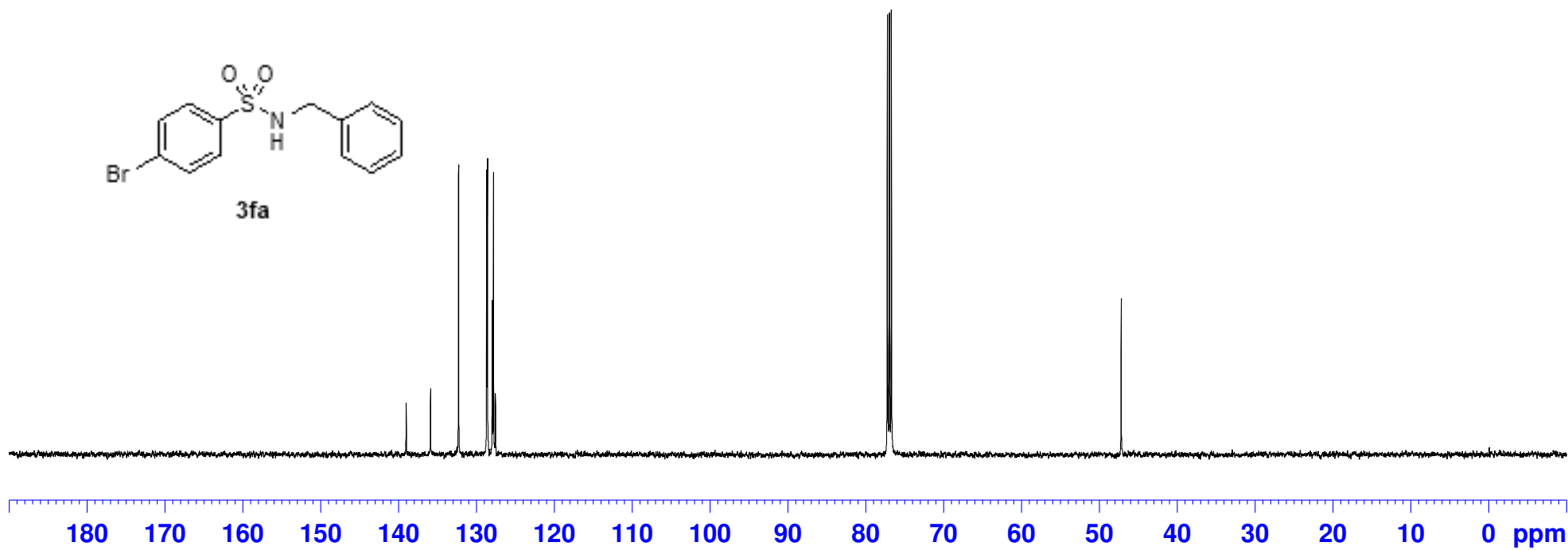
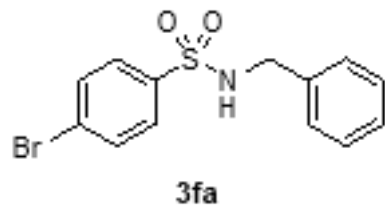


N-Benzyl-4-bromobenzenesulfonamide  
C13CPD-1 CDC13

139.003  
135.869  
132.326  
128.707  
128.614  
127.990  
127.836  
127.593

77.000

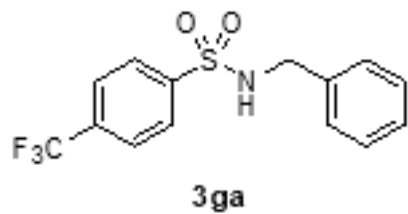
47.230



N-Benzyl-4-(trifluoromethyl)benzenesulfonamide  
Proton CDCl<sub>3</sub>

7.955  
7.938  
7.741  
7.725  
7.260  
7.251  
7.246  
7.171  
7.164  
7.156

4.187



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 ppm

2.00

1.99

3.00

2.00

1.99

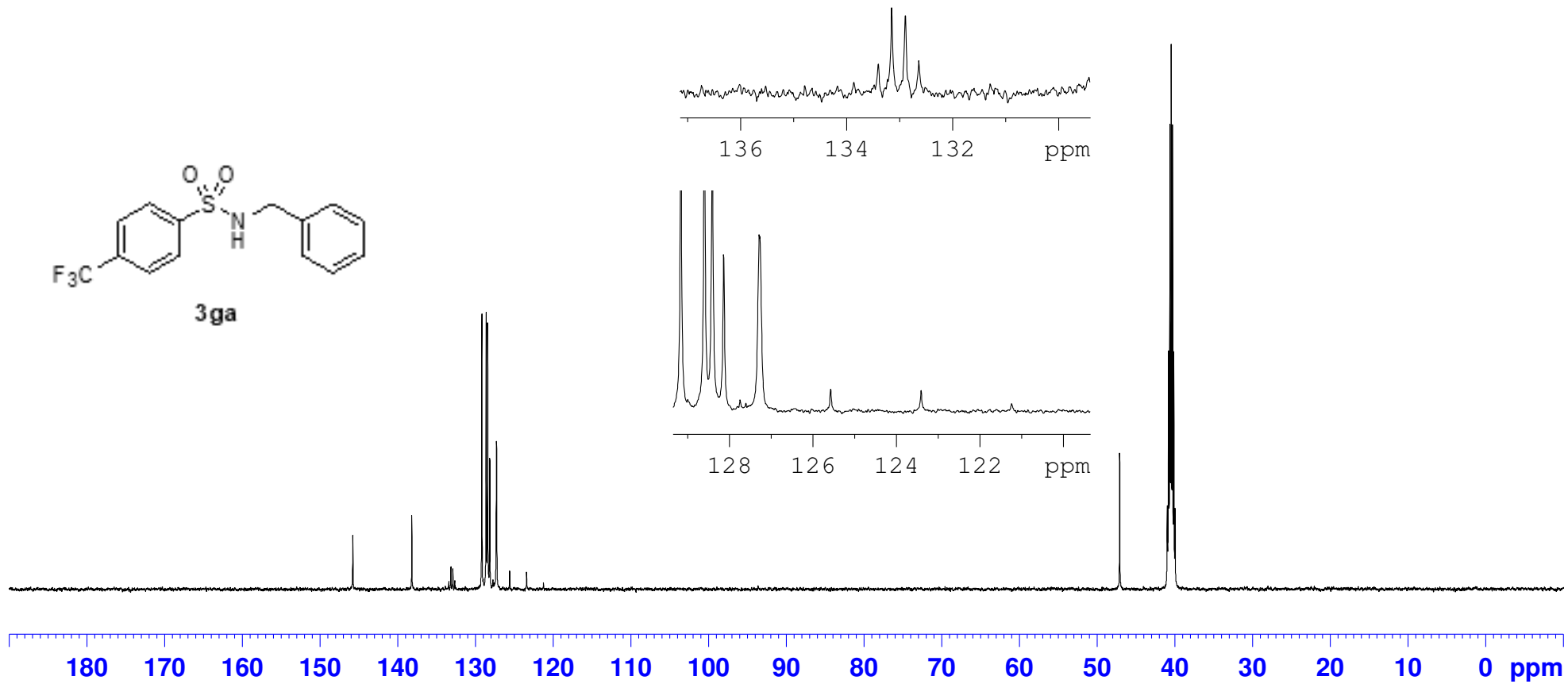
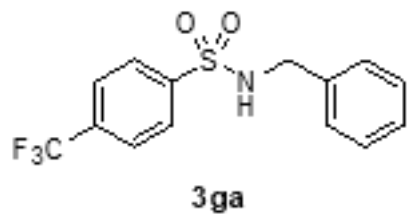


N-Benzyl-4-(trifluoromethyl)benzenesulfonamide  
C13CPD-1 DMSO

145.766  
138.171  
133.401  
133.145  
132.888  
132.633  
129.163  
128.598  
128.409  
128.136  
127.742  
127.284  
125.572  
123.403  
121.233

—47.131

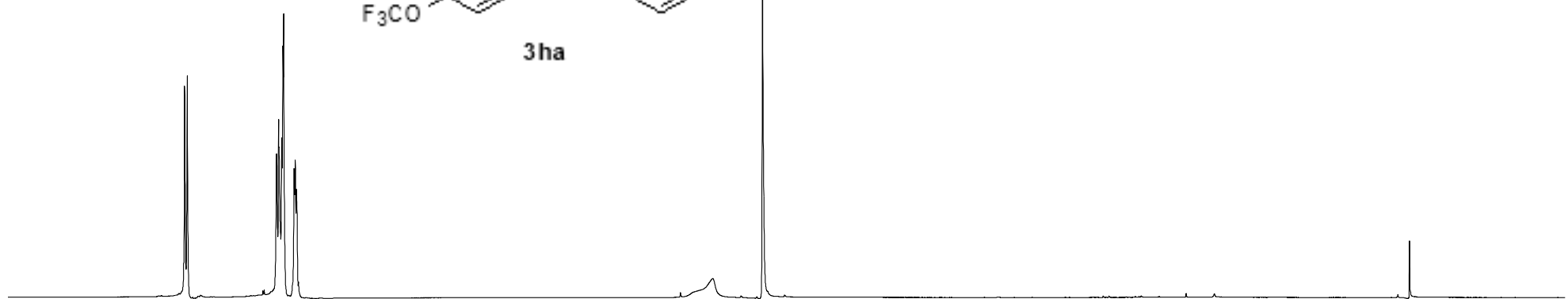
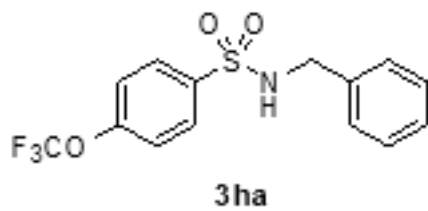
—40.500



N-Benzyl-4-(trifluoromethoxy) benzenesulfonamide  
Proton CDCl<sub>3</sub>

7.863  
7.845  
7.273  
7.231  
7.227  
7.160  
7.153  
7.145

4.475  
4.154



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

ppm

2.00

5.01

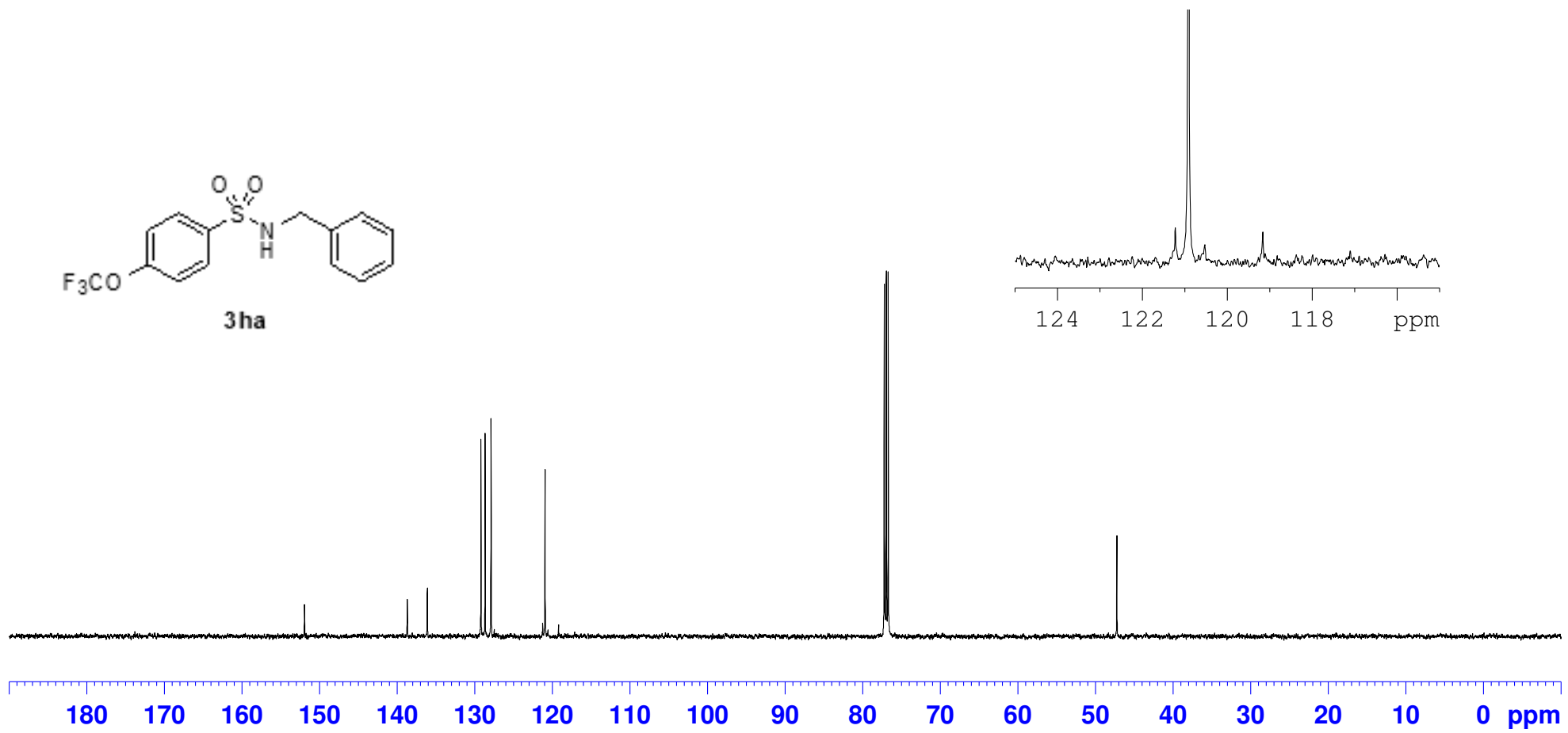
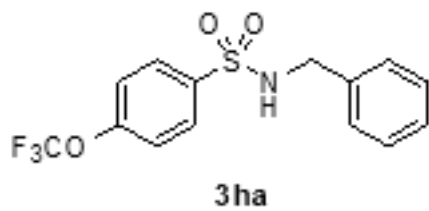
1.97

1.01

2.01

N-Benzyl-4-(trifluoromethoxy) benzenesulfonamide  
C13CPD-1 CDCl3

— 151.926  
— 138.682  
— 136.090  
— 129.177  
— 128.643  
— 127.899  
— 127.867  
— 121.224  
— 120.914  
— 119.162  
— 47.276

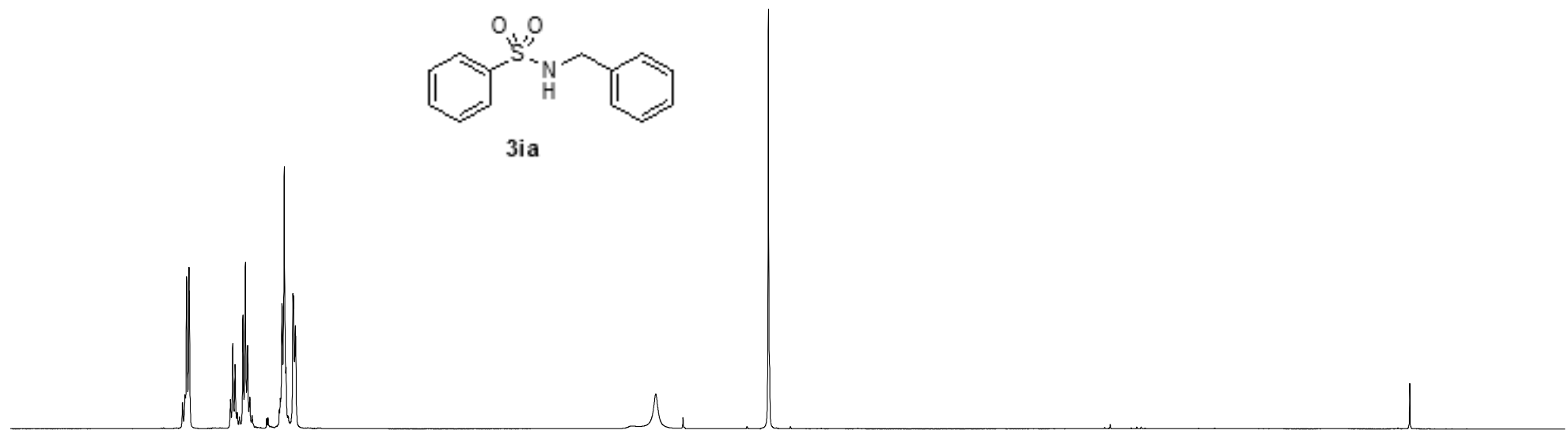
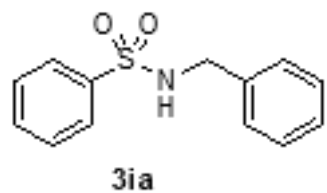


N-benzylbenzenesulfonamide  
Proton CDCl<sub>3</sub>

7.866  
7.851  
7.584  
7.569  
7.555  
7.504  
7.488  
7.473  
7.253  
7.238  
7.182  
7.178  
7.167

— 4.849

— 4.125



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 ppm

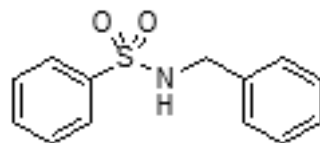
2.00  
1.00  
1.99  
2.98  
2.00  
1.00  
2.01

N-Benzylbenzenesulfonamide  
C13CPD-1 CDCl3

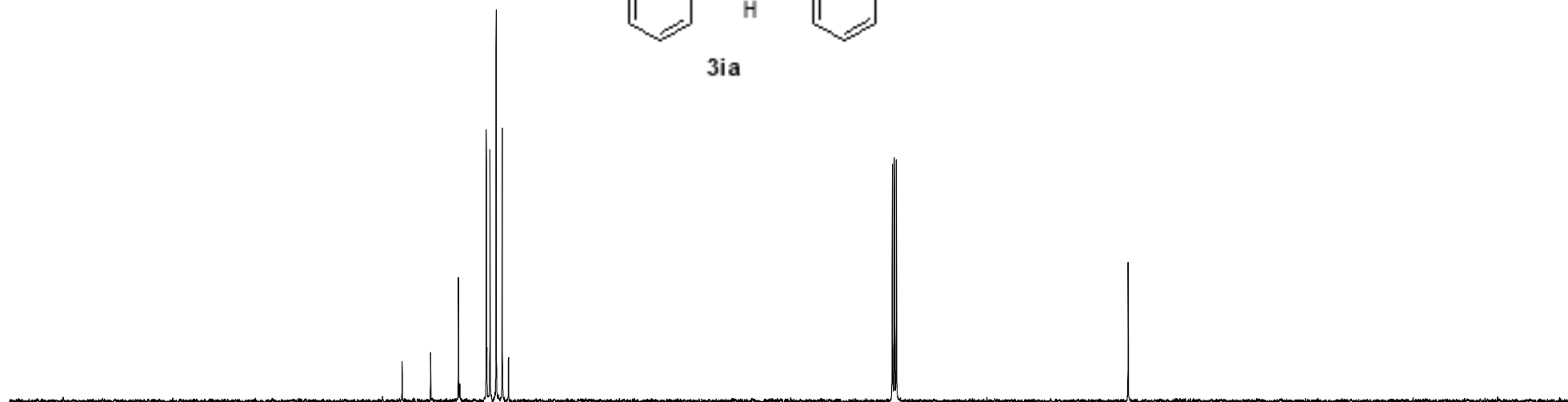
139.813  
136.173  
132.617  
129.061  
128.593  
127.799  
127.021

—77.001

—47.146



3ia

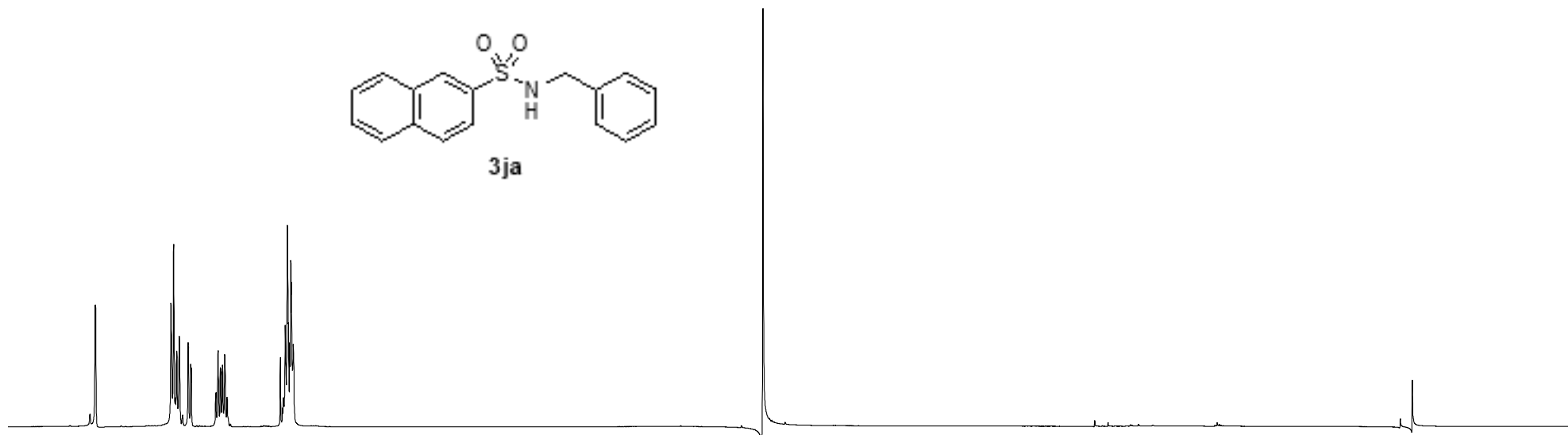
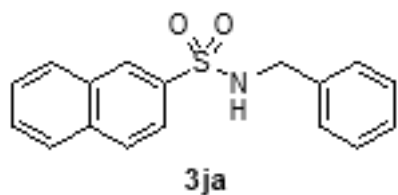


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

N-Benzyl-naphthalene-2-sulfonamide  
Proton CDCl<sub>3</sub>

7.952  
7.936  
7.915  
7.899  
7.843  
7.840  
7.826  
7.822  
7.666  
7.664  
7.594  
7.592  
7.254  
7.223  
7.208  
7.172

4.161



1.01

3.01

0.97

2.00

4.88

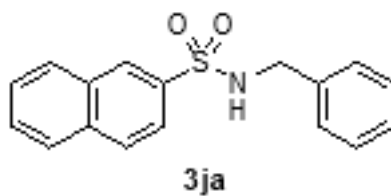
1.99

N-Benzyl-naphthalene-2-sulfonamide  
C13CPD-1 CDCl3

136.613  
136.097  
134.820  
132.131  
129.548  
129.247  
128.827  
128.675  
128.610  
127.945  
127.873  
127.562  
122.274

77.006

47.355

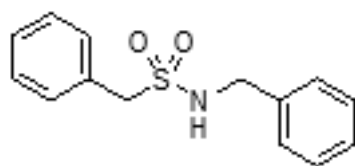


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

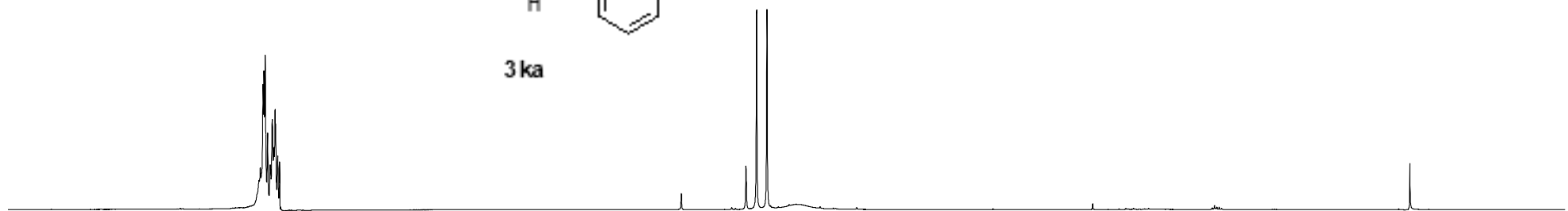
N-Benzyl (phenyl)methanesulfonamide  
Proton CDCl<sub>3</sub>

7.376  
7.346  
7.265

4.193  
4.126



3ka



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 ppm

10.48

2.00  
2.07



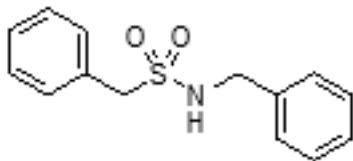
N-Benzyl (phenyl)methanesulfonamide  
C13CPD-1 CDCl3

136.825  
130.625  
129.150  
128.790  
128.028

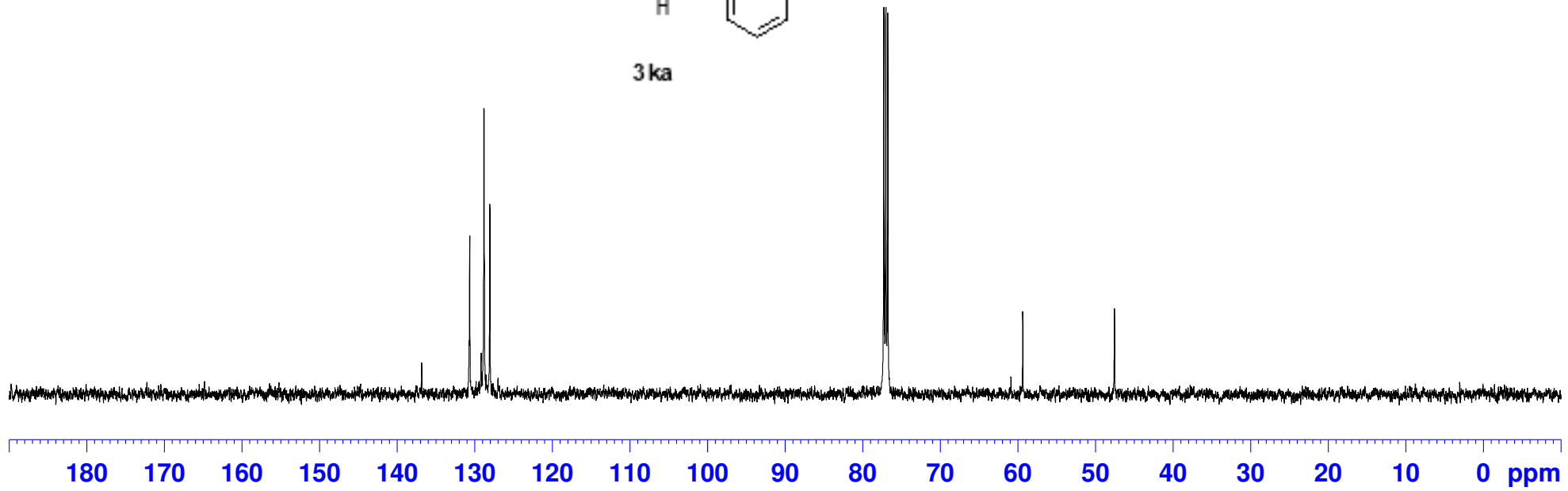
77.000

59.350

47.584



3ka

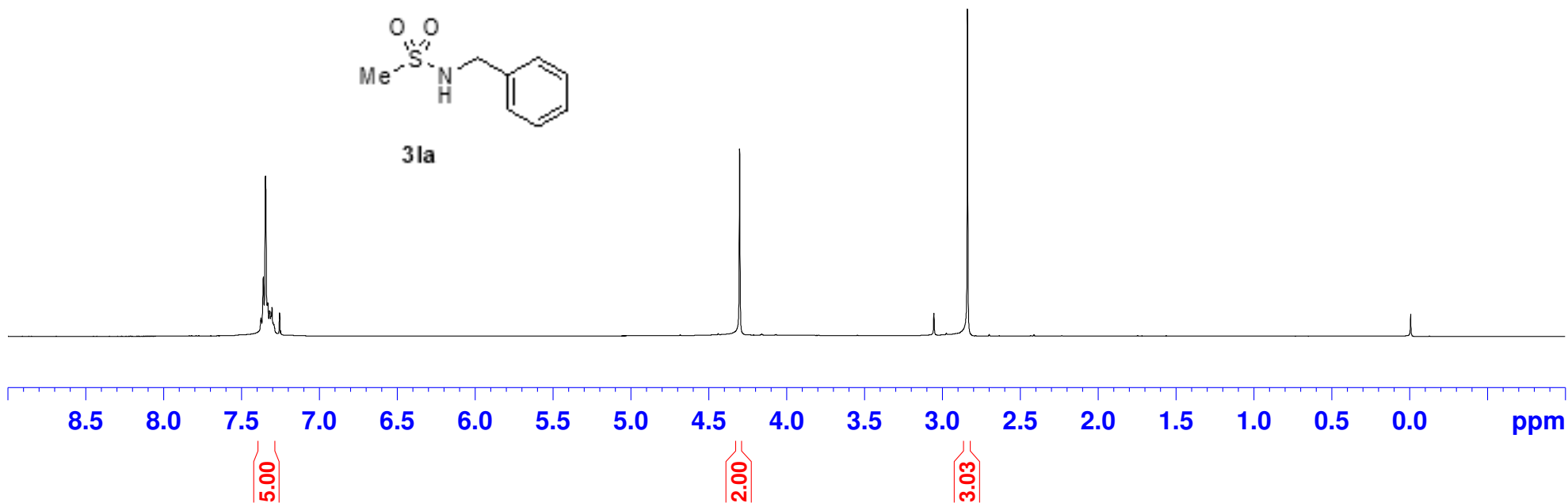
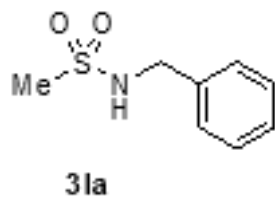


N-Benzylmethanesulfonamide  
Proton CDCl<sub>3</sub>

7.373  
7.344  
7.302

4.302

2.838



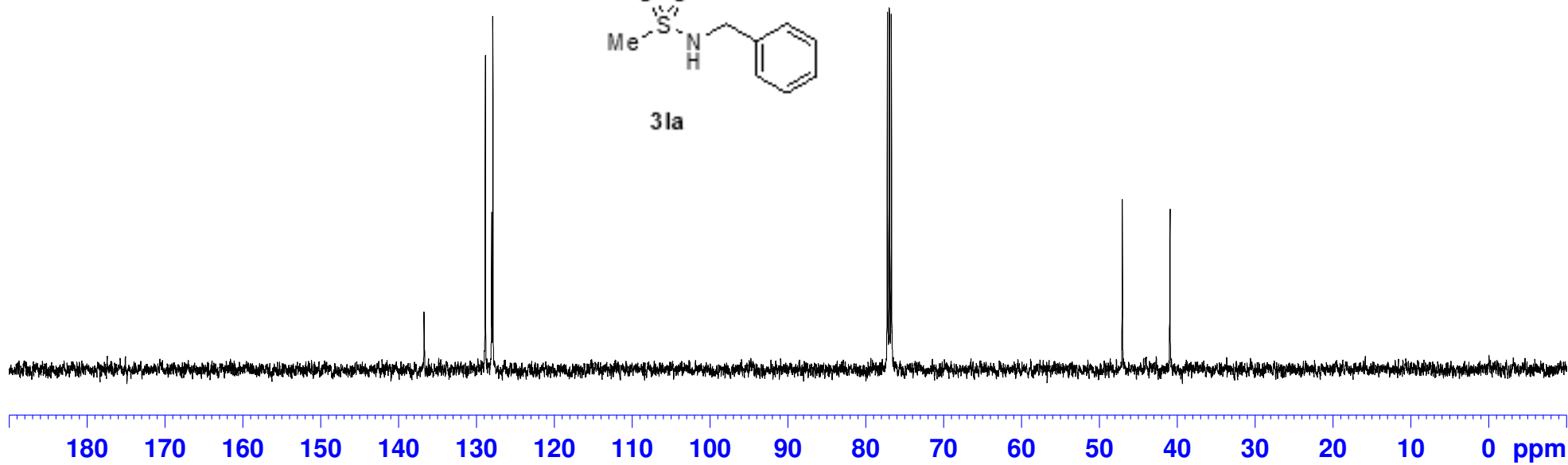
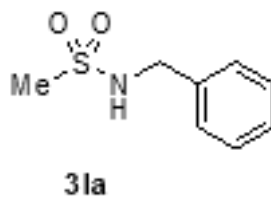
N-Benzylmethanesulfonamid  
C13CPD-1 CDCl3

— 136.710  
— 128.826  
— 128.004  
— 127.865

— 76.999

— 47.085

— 40.957



N-Benzylcyclopropanesulfonamide  
Proton CDC13

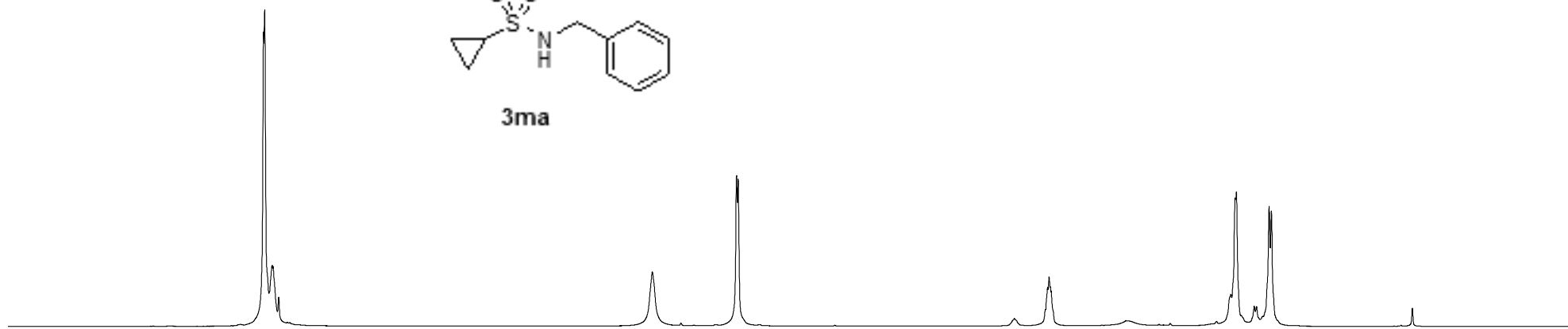
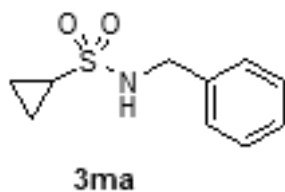
7.359  
7.352  
7.304  
7.299

4.870

4.331  
4.321

2.339  
2.336  
2.329  
2.327  
2.320  
2.314

1.137  
1.134  
1.131  
1.128  
0.918  
0.903



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 ppm

5.01

1.04

2.00

0.98

2.05

2.07

N-Benzylcyclopropanesulfonamide  
C13CPD-1 CDCl3

— 137.150  
128.722  
127.873  
127.751

— 76.999

— 47.225

— 30.455

— 5.422

