Supporting Information

Visible-light-mediated difunctionalization of C−C bond for the synthesis of 1-sulfonylmethyl-3,4-dihydronaphthalenes

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1. General Information

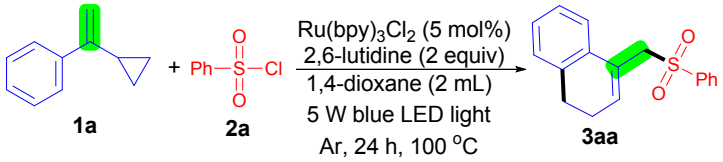
All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, for ^{13}C NMR: $CDCl_3$ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experiment Section

2.1 General procedure for the synthesis of vinylcyclopropanes (1):

All vinylcyclopropanes (**1**) were synthesized according to the known methods.[1]

2.2 Typical Experimental Procedure for the visible-light-mediated C−C *σ*–bond sulfonylation/arylation of vinylcyclopropanes with sulfonyl chlorides for the synthesis of 1-sulfonylmethyl-3,4-dihydronaphthalenes

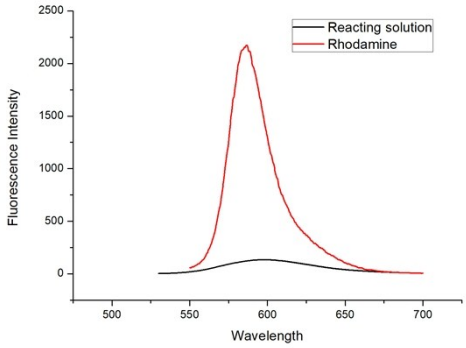


1a **2a** **3aa**

To a Schlenk tube were added **1a** (0.2 mmol), **2a** (2.0 equiv, 0.4 mmol), $Ru(bpy)_3Cl_2$ (5 mol %, 0.01 mmol), 2,6-lutidine (2 equiv, 0.4 mmol) in 1,4-dioxane (2 mL). Then the mixture was stirred at 100 °C (oil bath temperature) in argon atmosphere (1 atm) under 5 W blue LED light for 24 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The

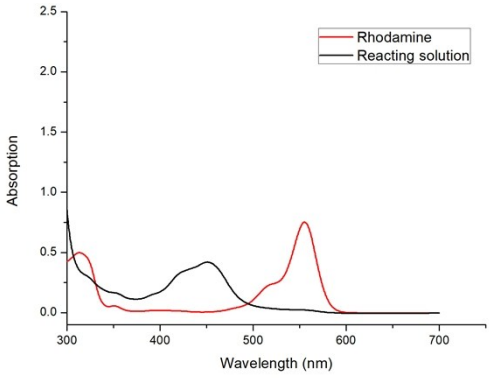
aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10 : 1 to 5 : 1) to afford the desired products **3**.

2.3 The Quantum Yield of the reaction of substrate 1a and benzenesulfonyl chloride 2a under the optimal conditions



Fs Integrated area of fluorescence of Rhodamine B: 79780 (red line)

Fu Integrated area of fluorescence of reaction system: 9673 (black line)



As UV-Vis absorbtion of Rhodamine B at 350nm: 0.054 (red line)

Au UV-Vis absorbtion of reaction system at 450nm: 0.42 (black line)

Yu = Ys*(Fu/Fs)*(As/Au)

Fu = 9673，Fs = 79780，As (350 nm) = 0.054, Au (450 nm) = 0.42

Yu = Ys*(Fu/Fs)*(As/Au) = 0.016Ys

3. References

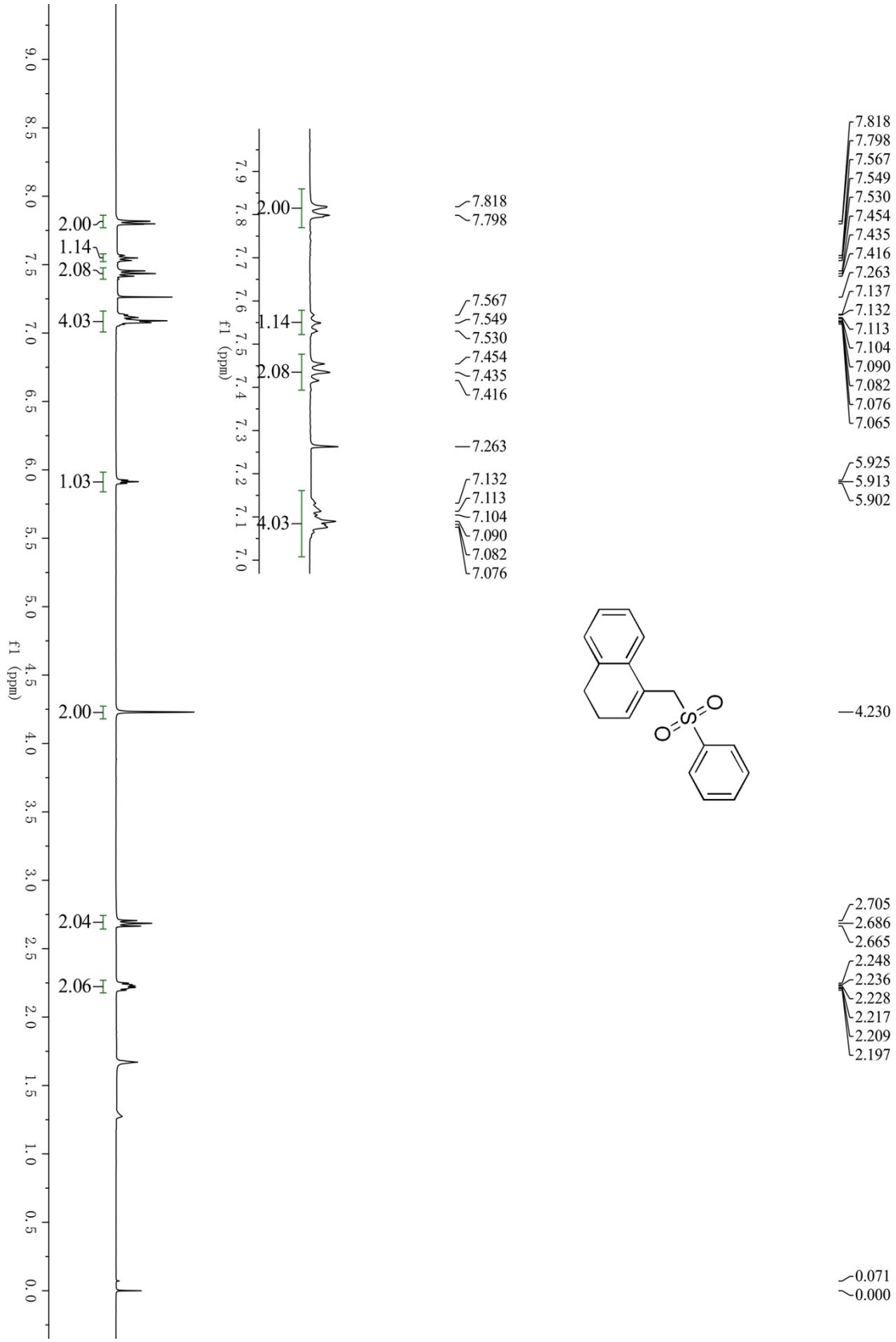
[1] J. Li, J.-Z. Chen, W. Jiao, G.-Q. Wang, Y. Li, X. Cheng and G.-G. Li, *J. Org. Chem.,* 2016, **81**, 9992.

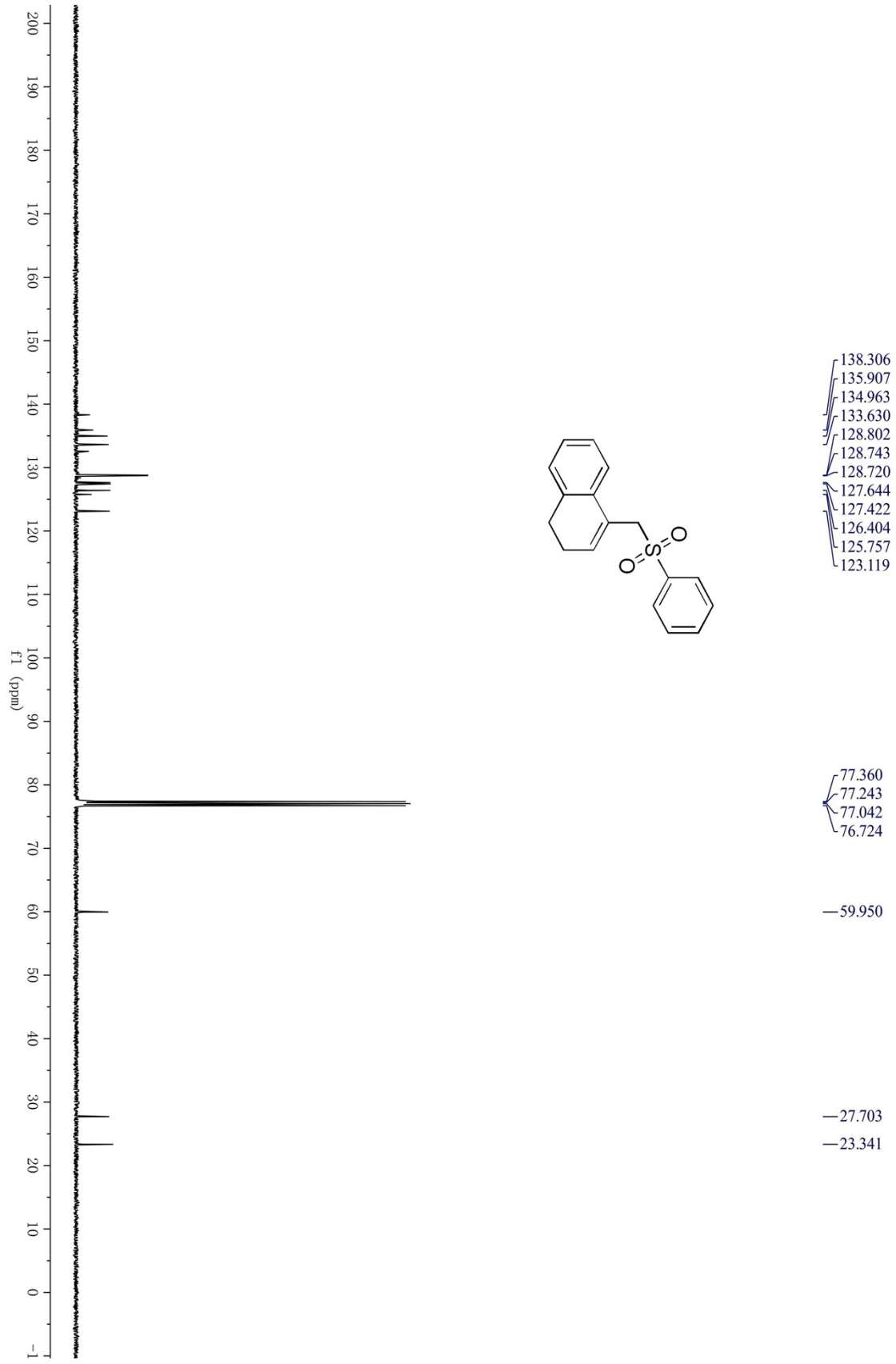
[2] Liu, Y.; Wang, Q. L.; Zhou, C. S.; Xiong, B. Q.; Zhang, P. L.; Yang, C. A.; Tang, K. W. *J. Org. Chem.* 2017, **82**, 7394.

[3] Liu, Y.; Wang, Q. L.; Zhou, C. S.; Xiong, B. Q.; Zhang, P. L.; Yang, C. A.; Tang, K. W. *J. Org. Chem.* 2018, **83**, 4657.

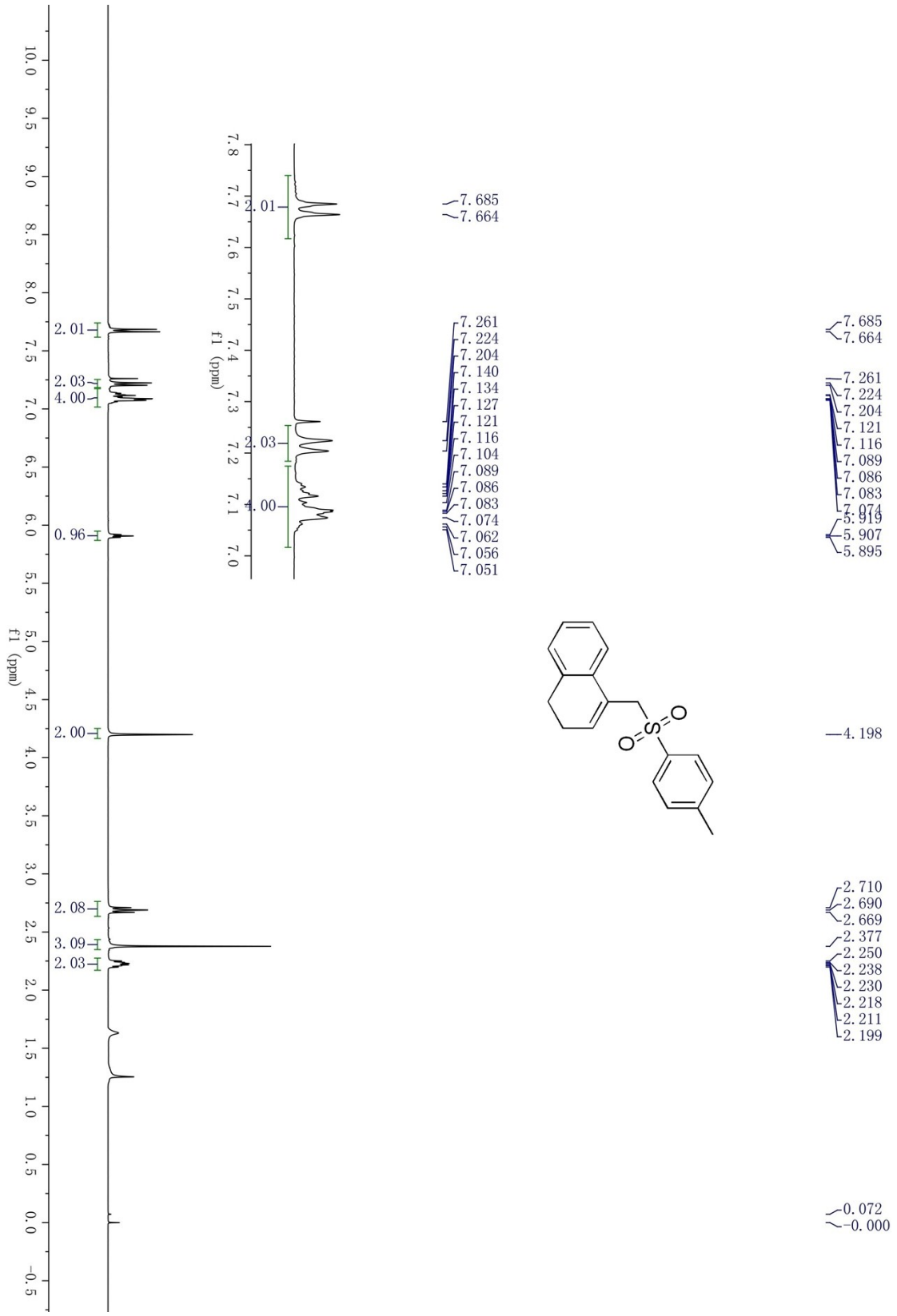
4. Spectra

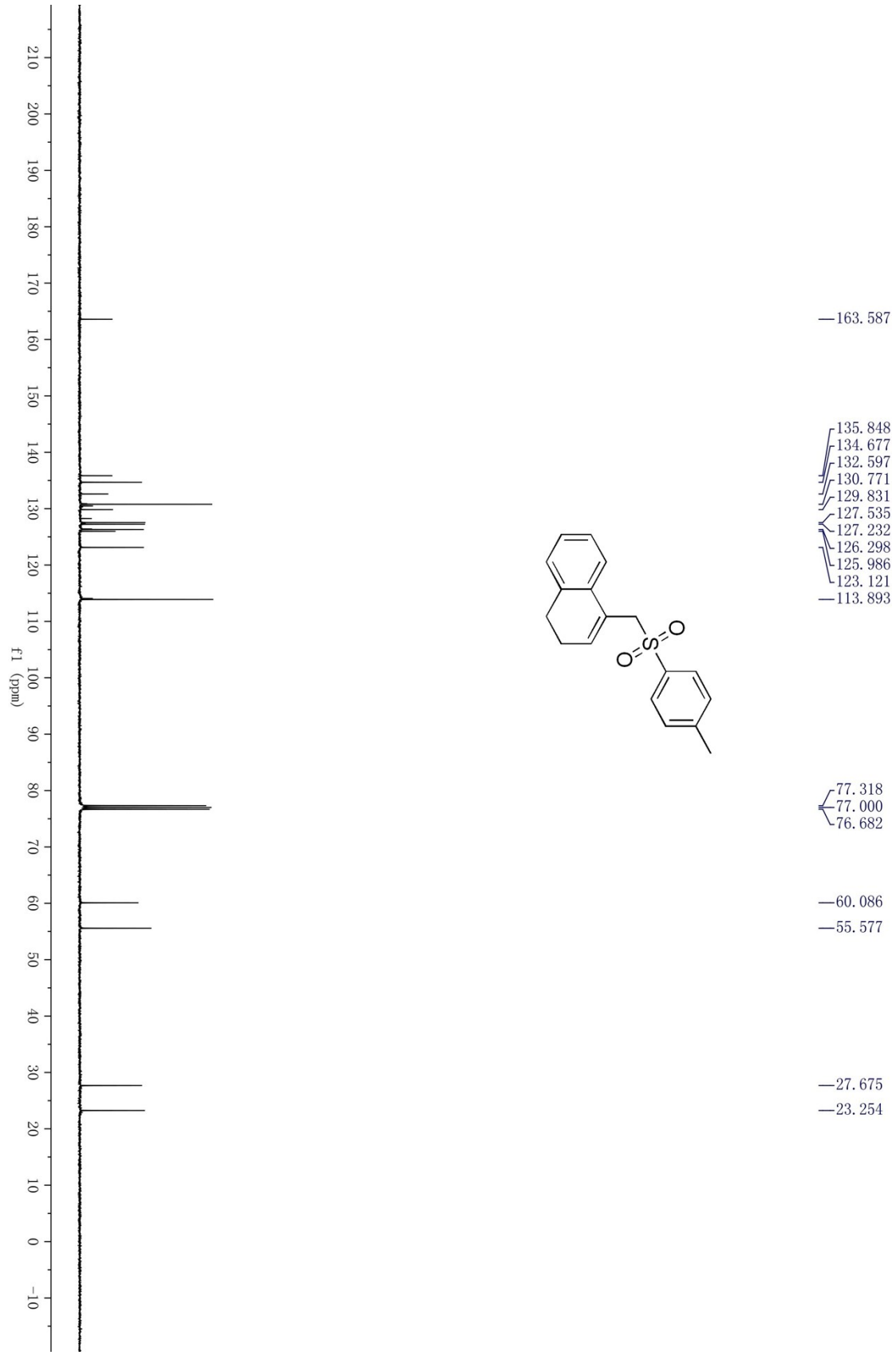
4-((Phenylsulfonyl)methyl)-1,2-dihydronaphthalene (3aa)



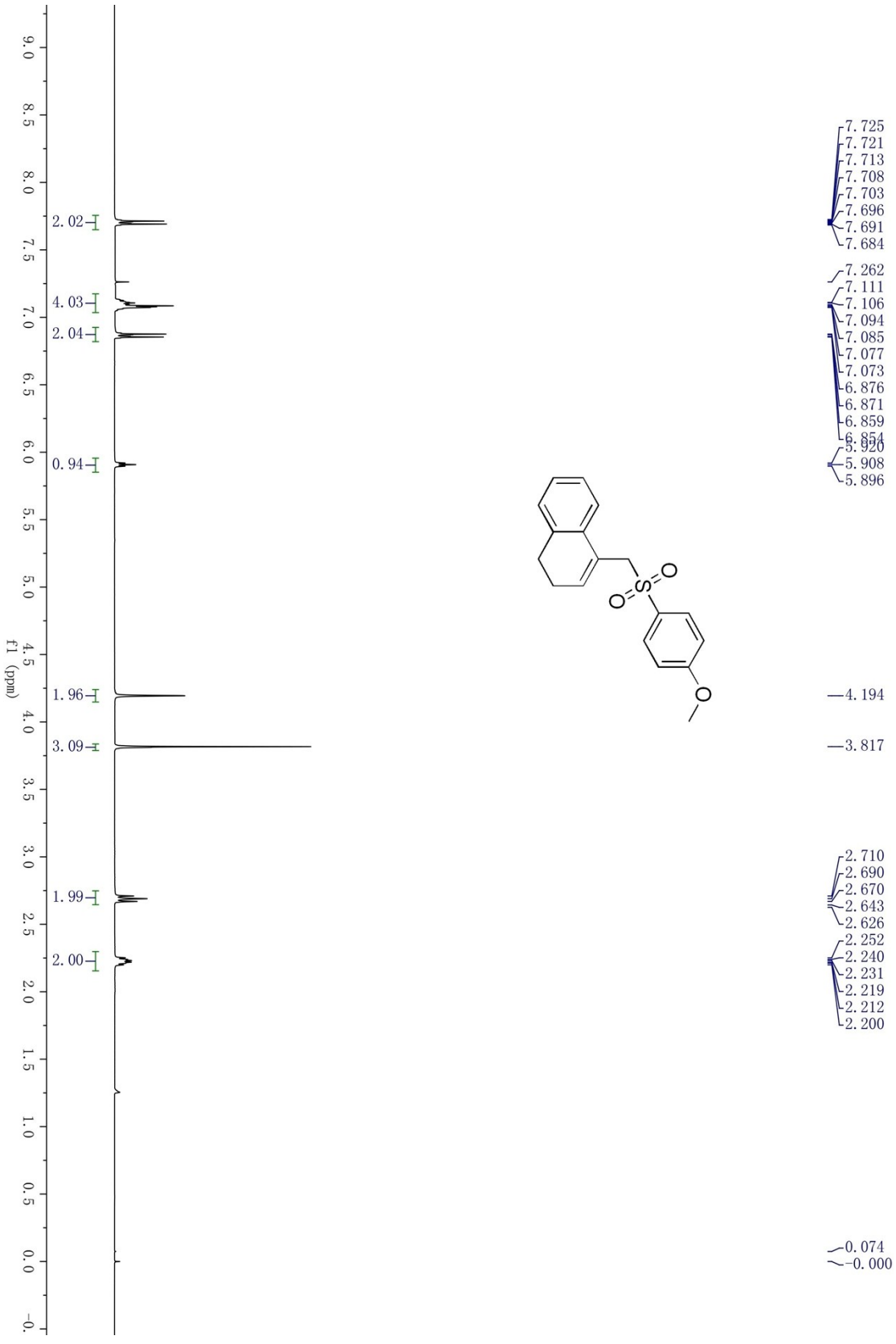

138.306
135.907
134.963
133.630
128.802
128.743
128.720
127.644
127.422
126.404
125.757
123.119
77.360
77.243
77.042
76.724
59.950
27.703
23.341
f1 (ppm)

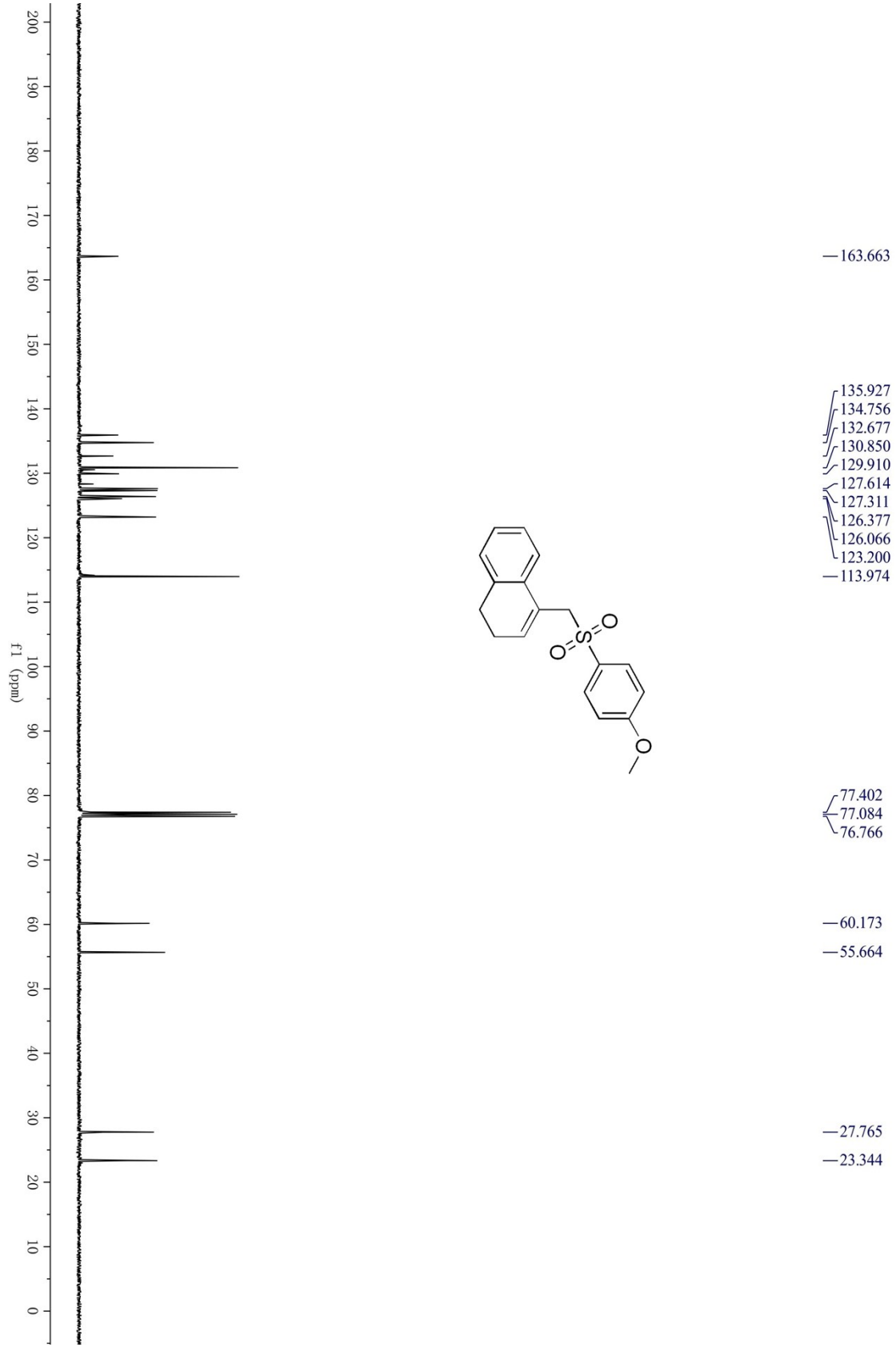
4-(Tosylmethyl)-1,2-dihydronaphthalene (3ab)



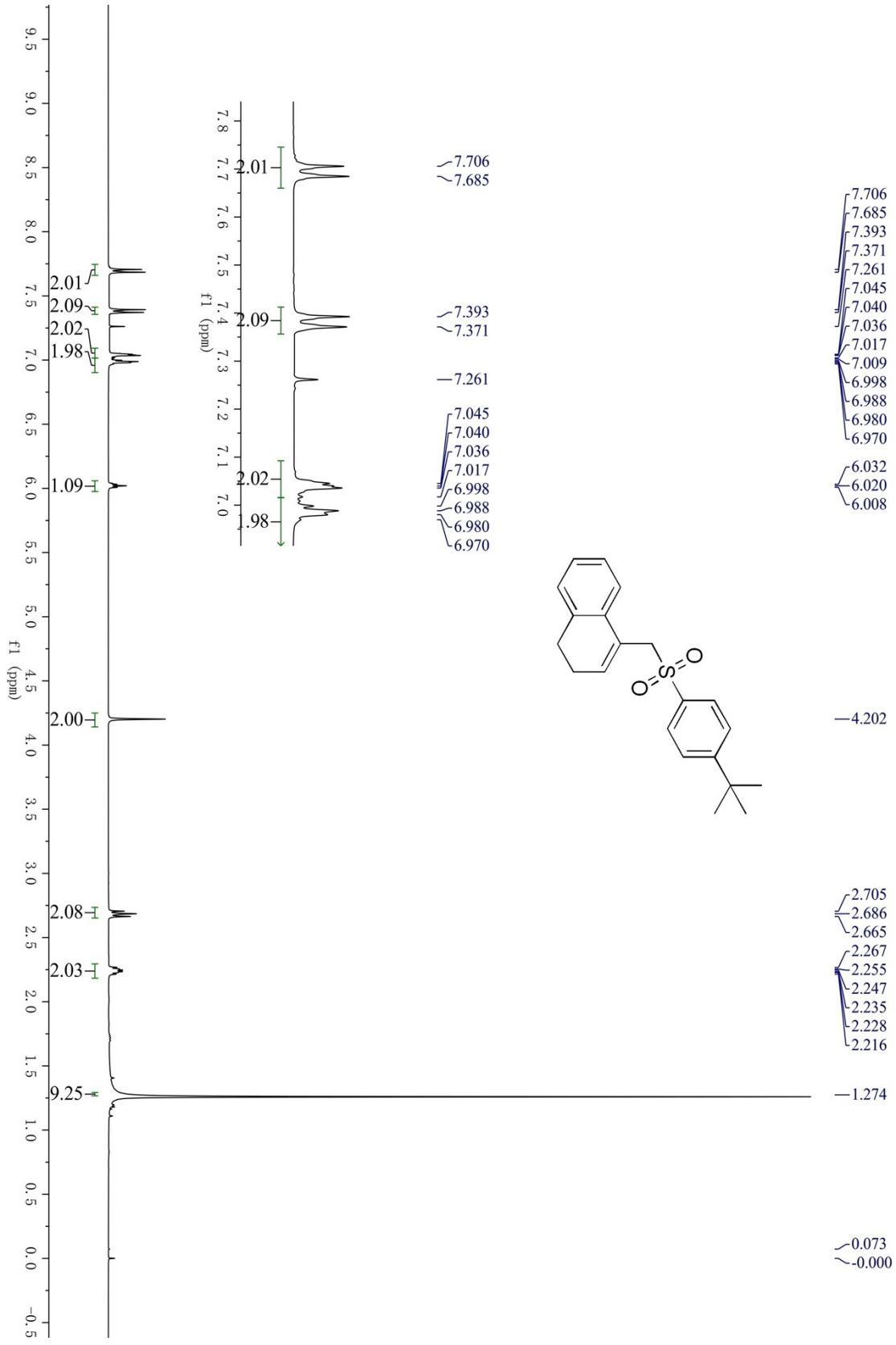

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
163.587
135.848
134.677
132.597
130.771
129.831
127.535
127.232
126.298
125.986
123.121
113.893
77.318
77.000
76.682
60.086
55.577
27.675
23.254
O
S
O

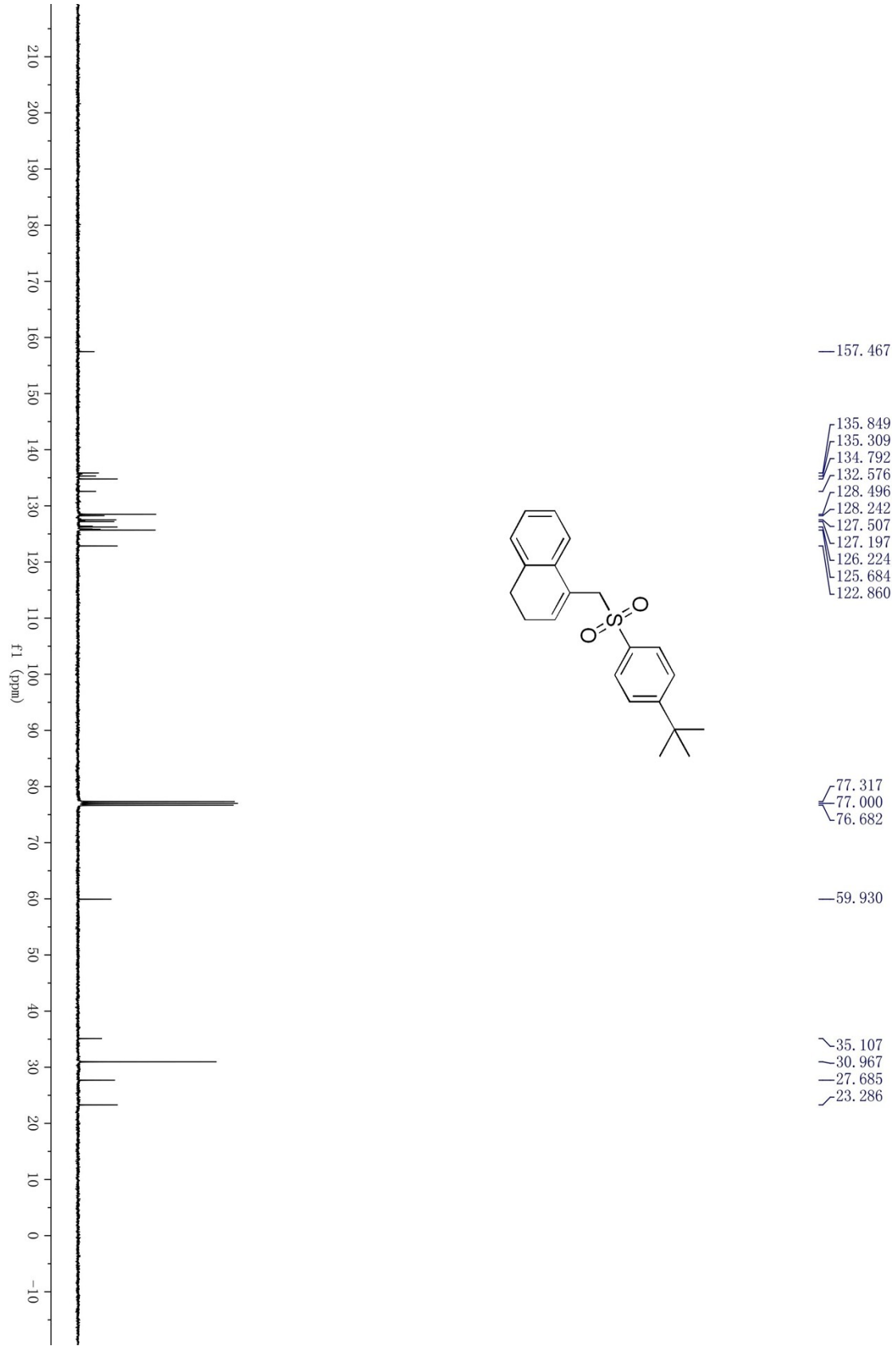
4-(((4-Methoxyphenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ac)



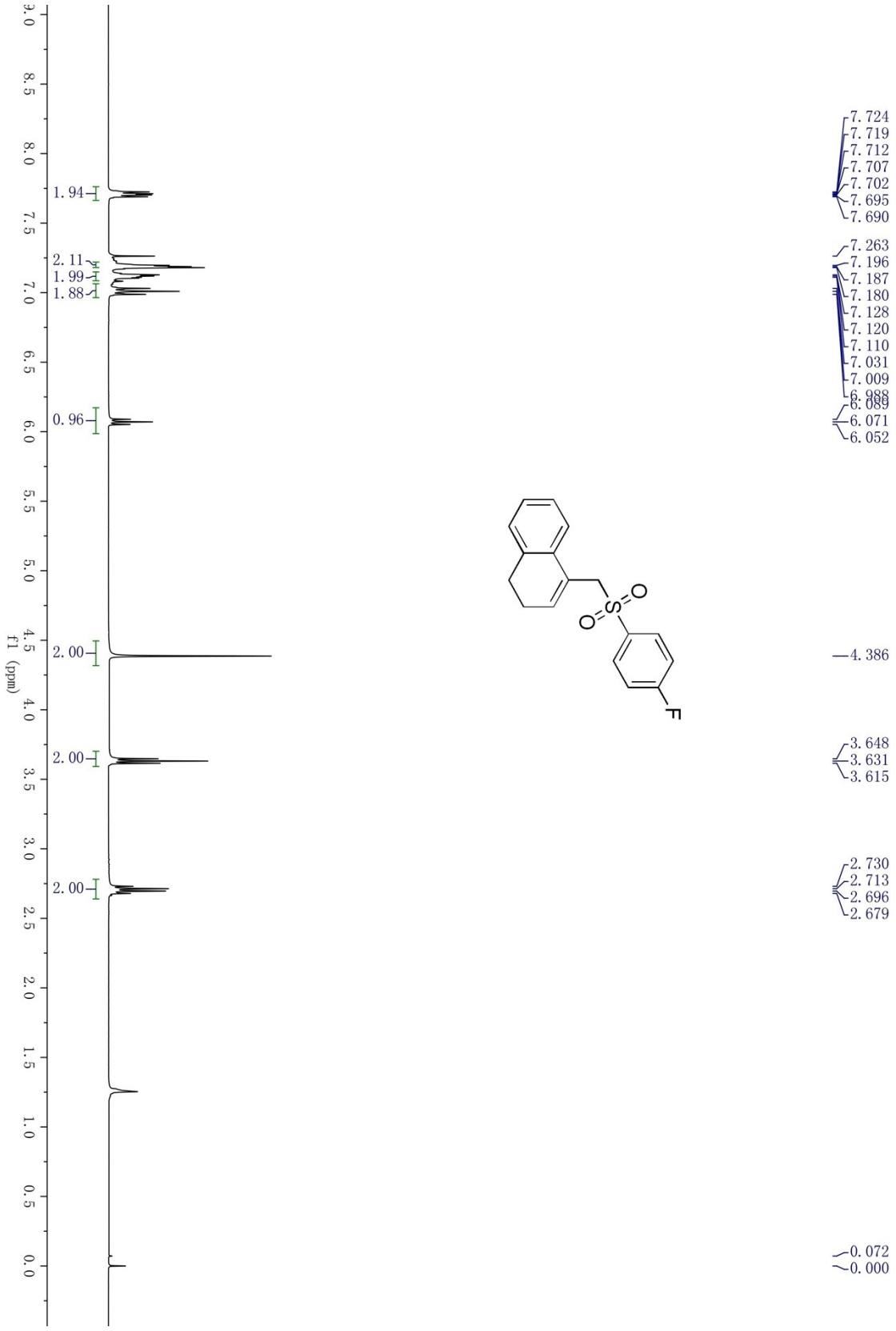

f1 (ppm)
163.663
135.927
134.756
132.677
130.850
129.910
127.614
127.311
126.377
126.066
123.200
113.974
77.402
77.084
76.766
60.173
55.664
27.765
23.344

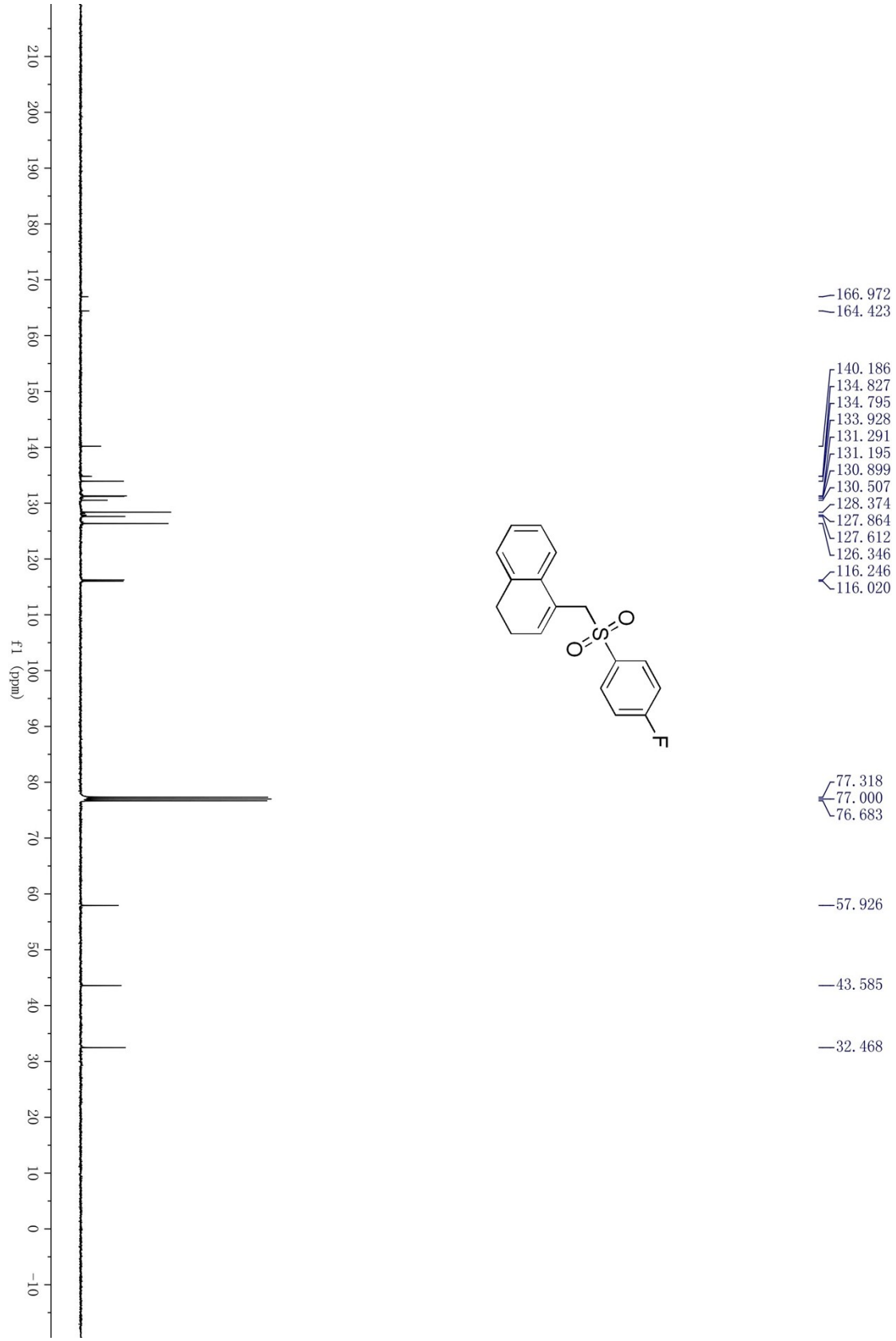
4-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ad)




157.467
135.849
135.309
134.792
132.576
128.496
128.242
127.507
127.197
126.224
125.684
122.860
77.317
77.000
76.682
59.930
35.107
30.967
27.685
23.286
f1 (ppm)

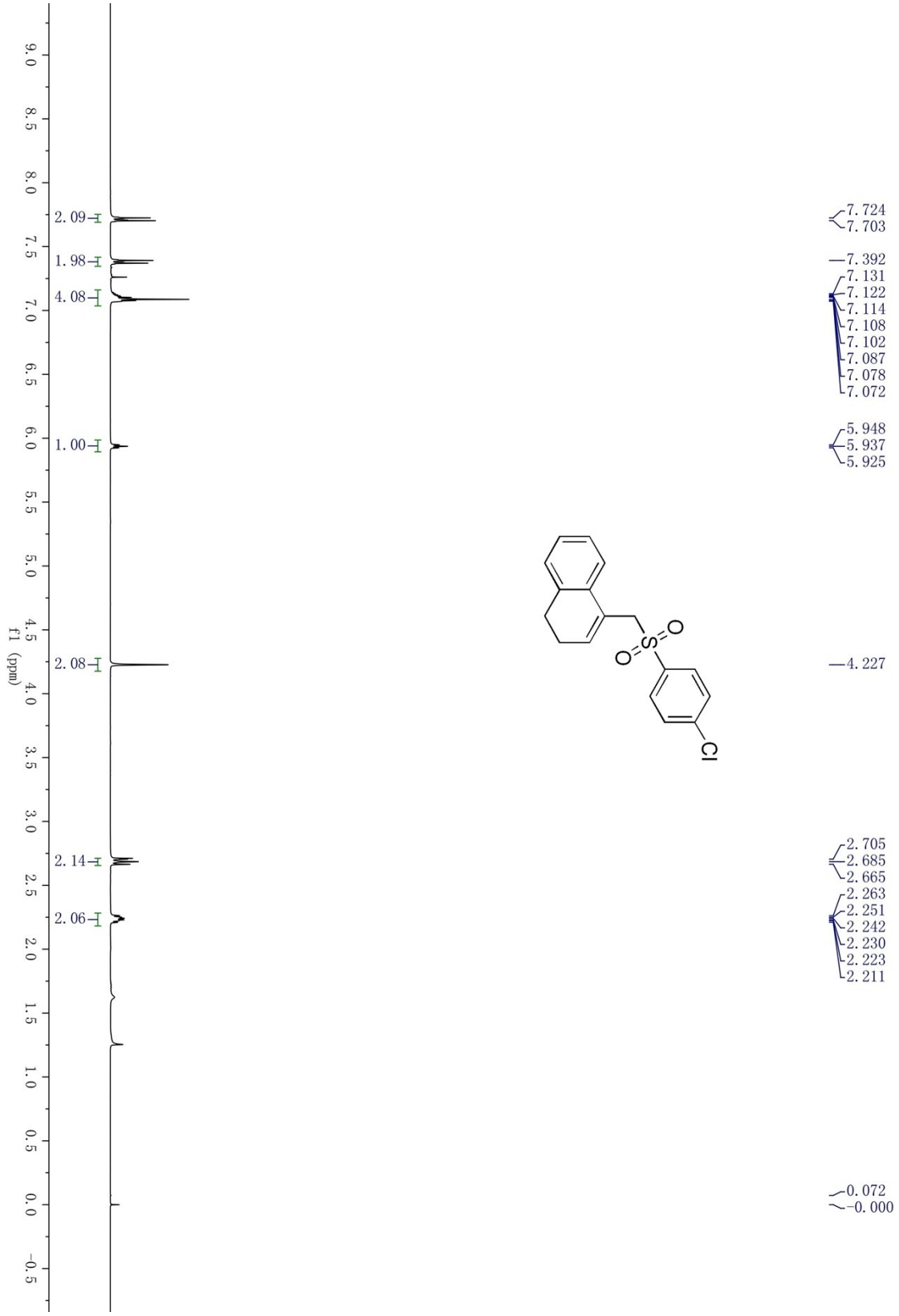
4-(((4-Fluorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ae)

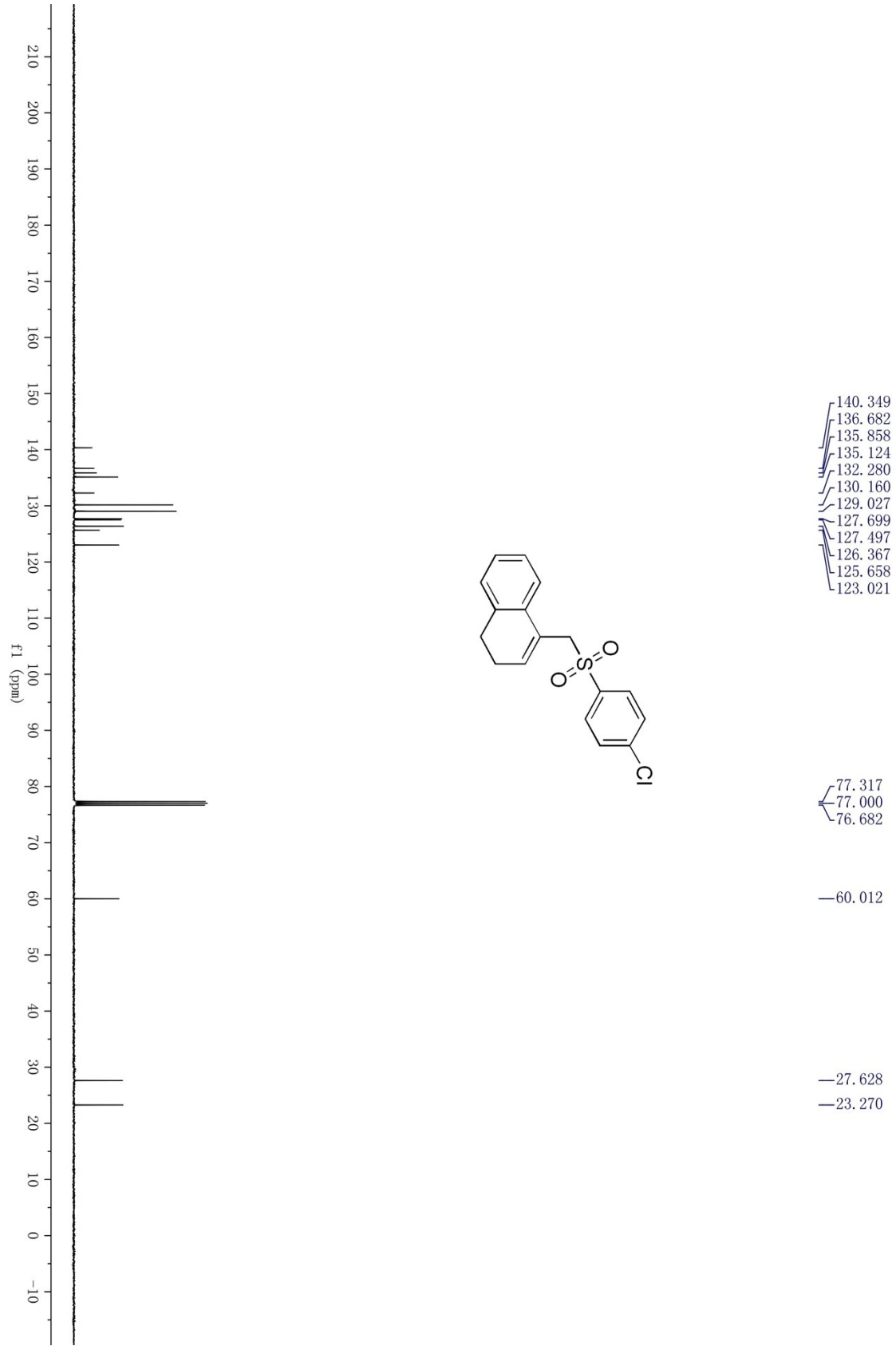



f1 (ppm)
166.972
164.423
140.186
134.827
134.795
133.928
131.291
131.195
130.899
130.507
128.374
127.864
127.612
126.346
116.246
116.020
77.318
77.000
76.683
57.926
43.585
32.468
O
S
O
F

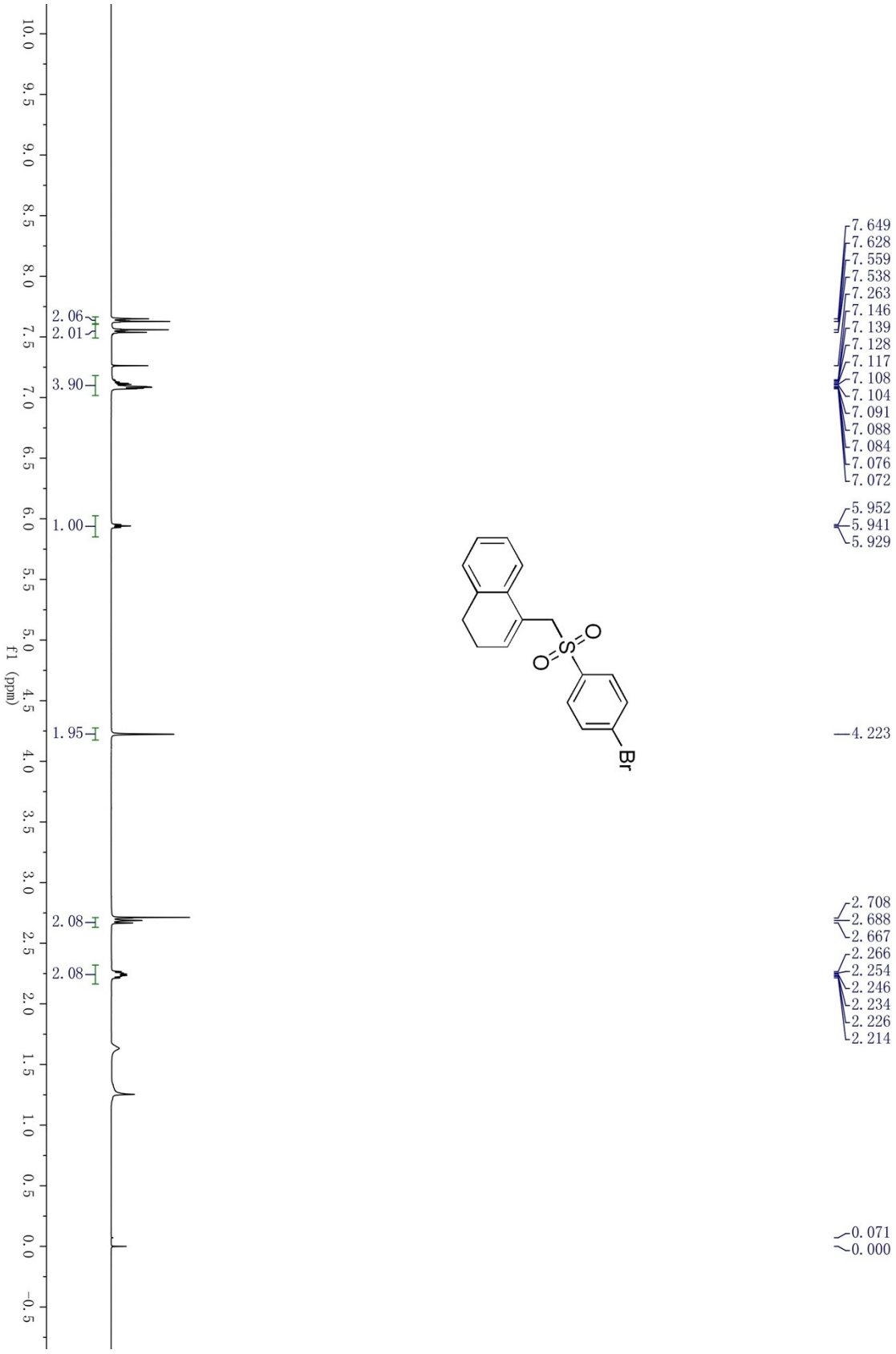
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)
O
O
S
F
−103.523

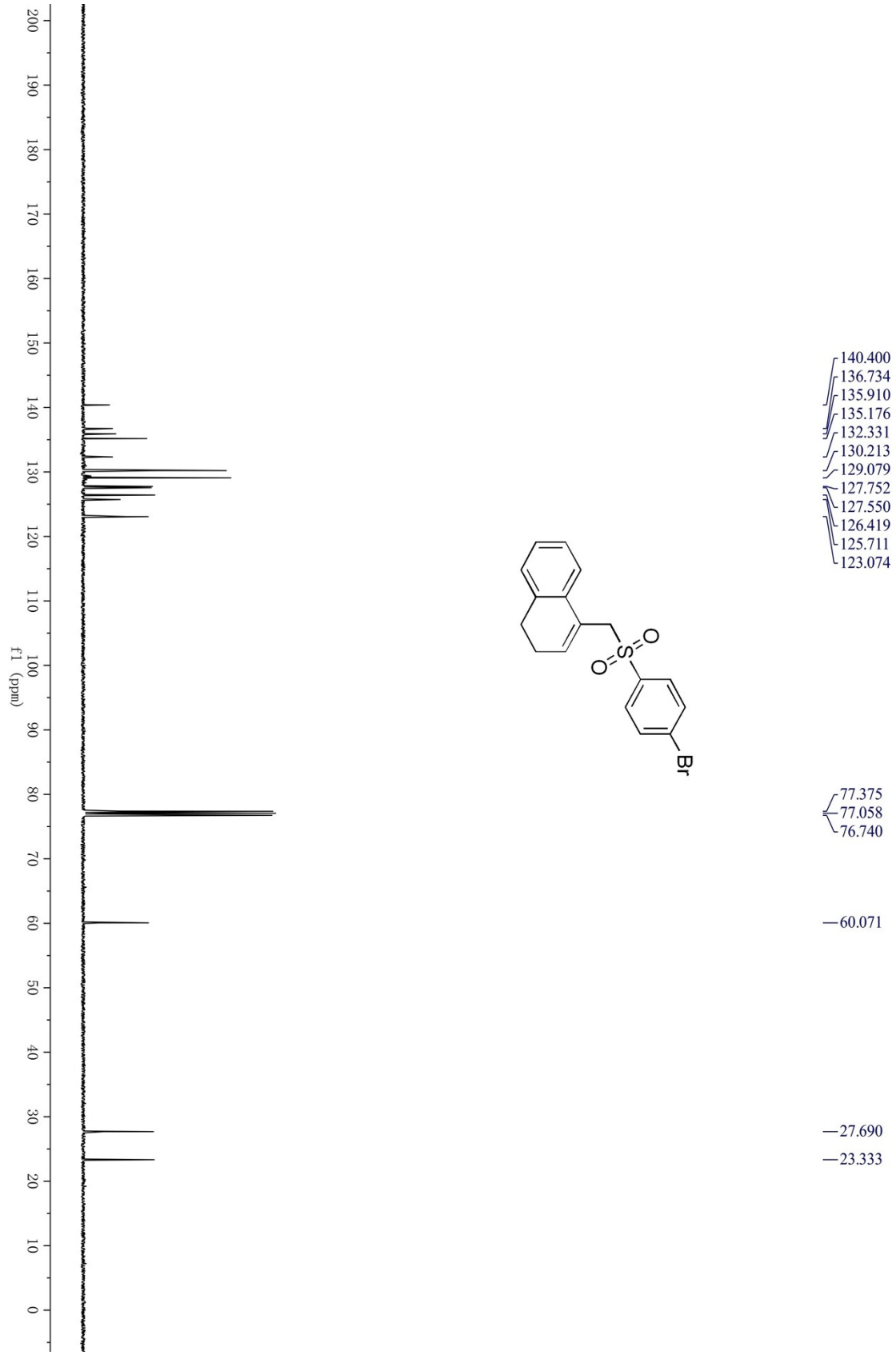
4-(((4-Chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene(3af)



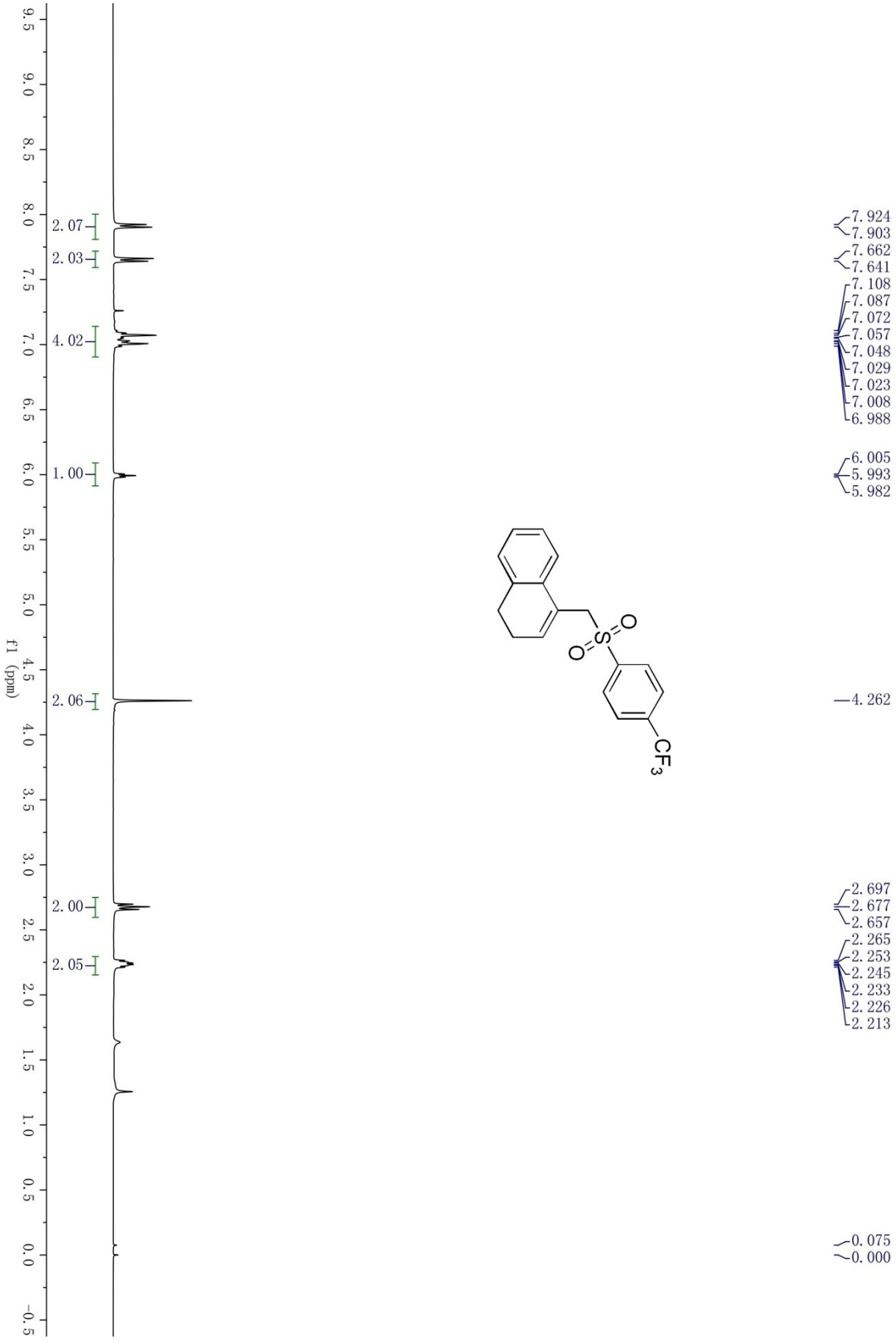

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
O
S
Cl
140.349
136.682
135.858
135.124
132.280
130.160
129.027
127.699
127.497
126.367
125.658
123.021
77.317
77.000
76.682
60.012
27.628
23.270

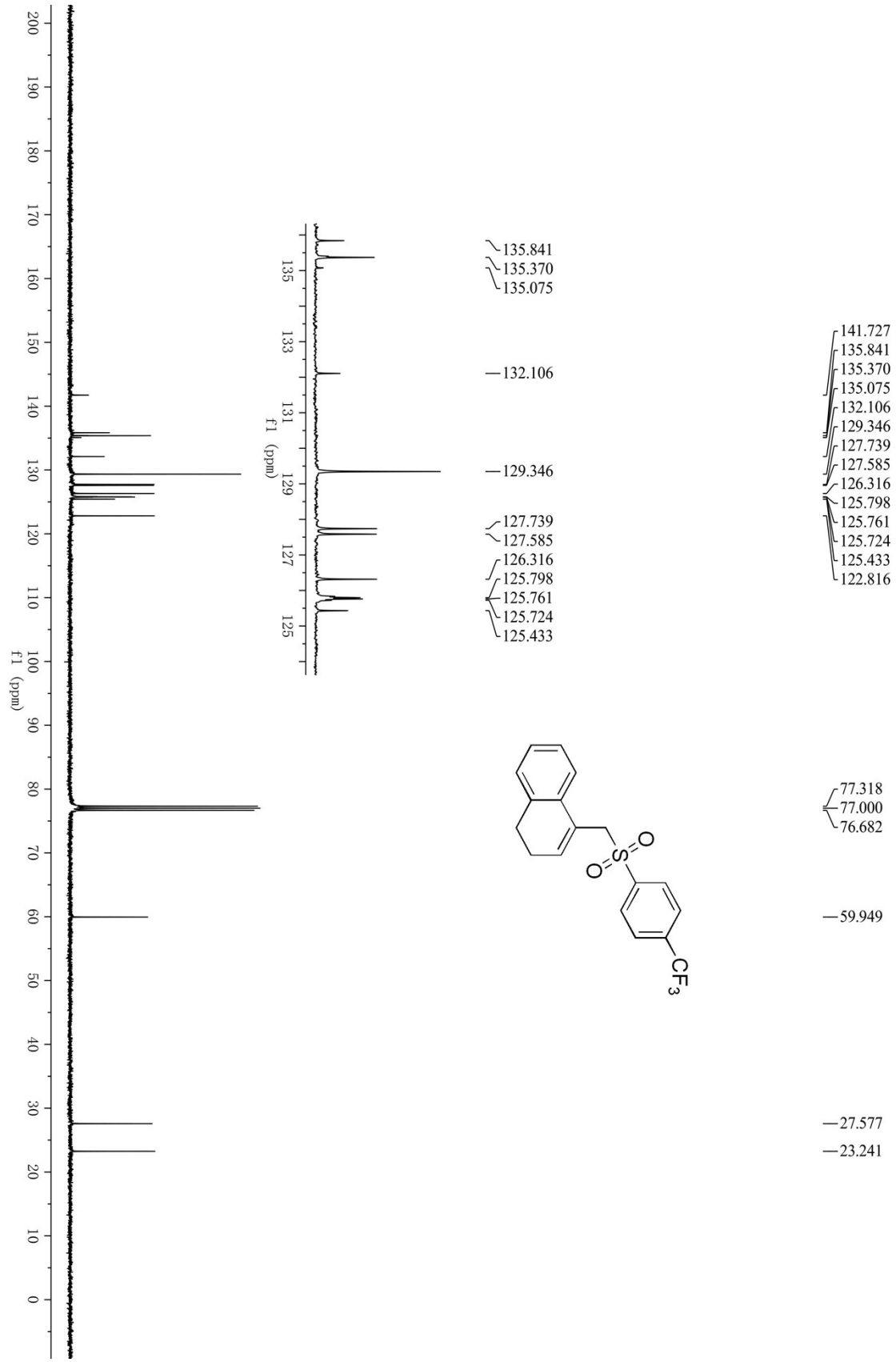
4-(((4-Bromophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ag)




200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
S
O
Br
140.400
136.734
135.910
135.176
132.331
130.213
129.079
127.752
127.550
126.419
125.711
123.074
77.375
77.058
76.740
60.071
27.690
23.333

4-(((4-(Trifluoromethyl)phenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ah)

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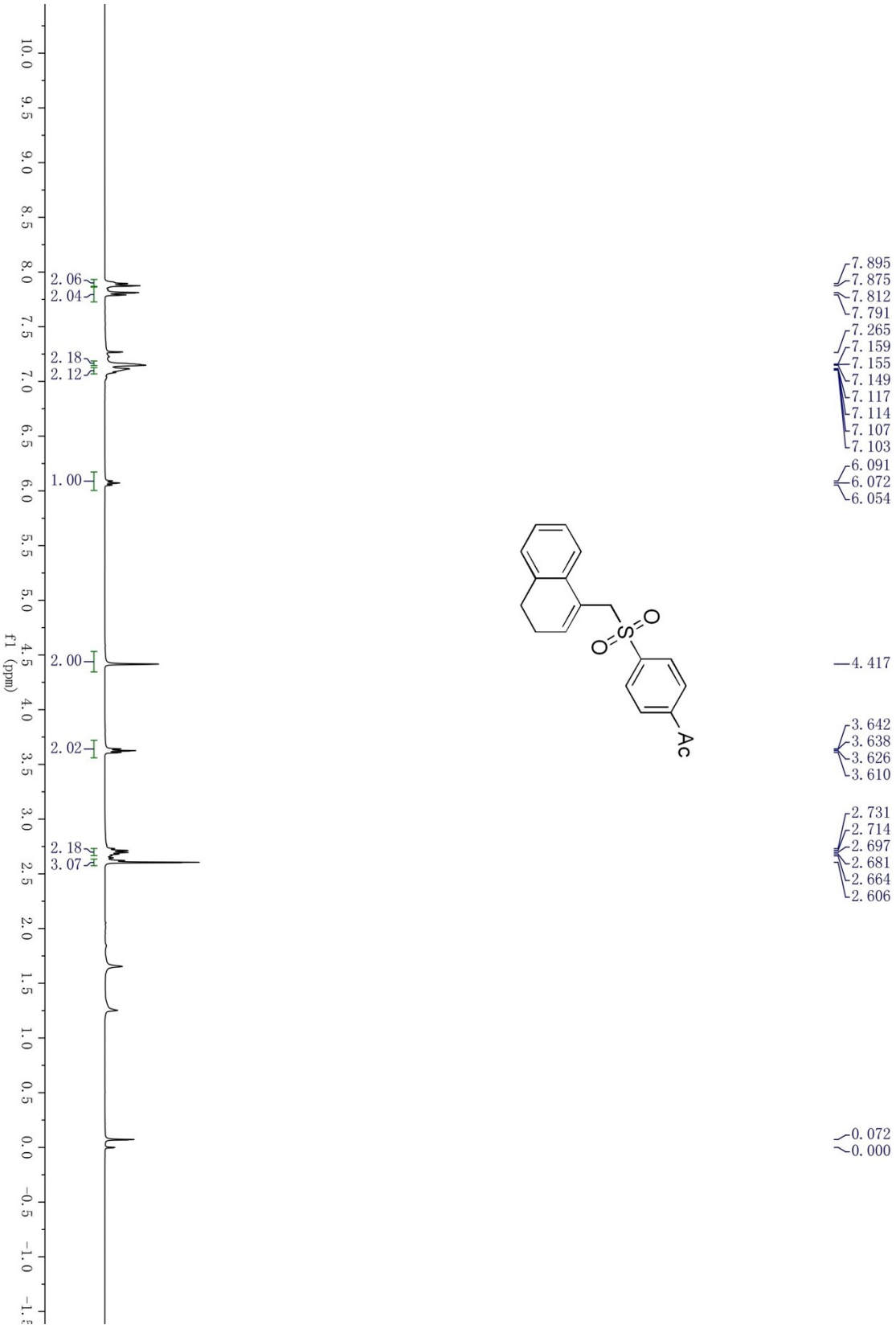
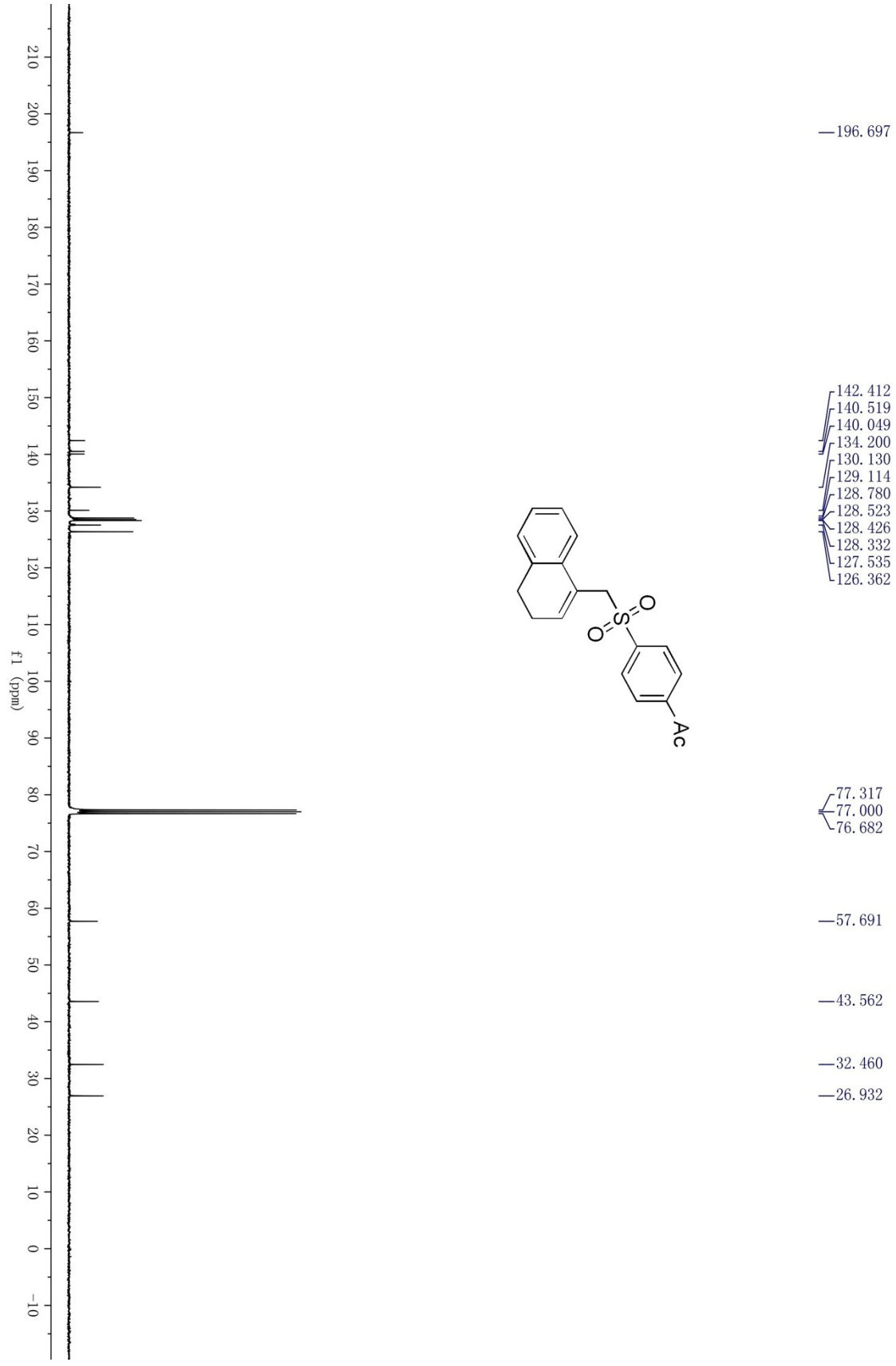
135.075
132.106
129.346
127.739
127.585
126.316
125.798
125.761
125.724
125.433
141.727
135.841
135.370
135.075
132.106
129.346
127.739
127.585
126.316
125.798
125.761
125.724
125.433
122.816
77.318
77.000
76.682
59.949
27.577
23.241
O
O
S
CF3

-63.282
f1 (ppm)

1-(4-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)phenyl)ethanone (3ai)

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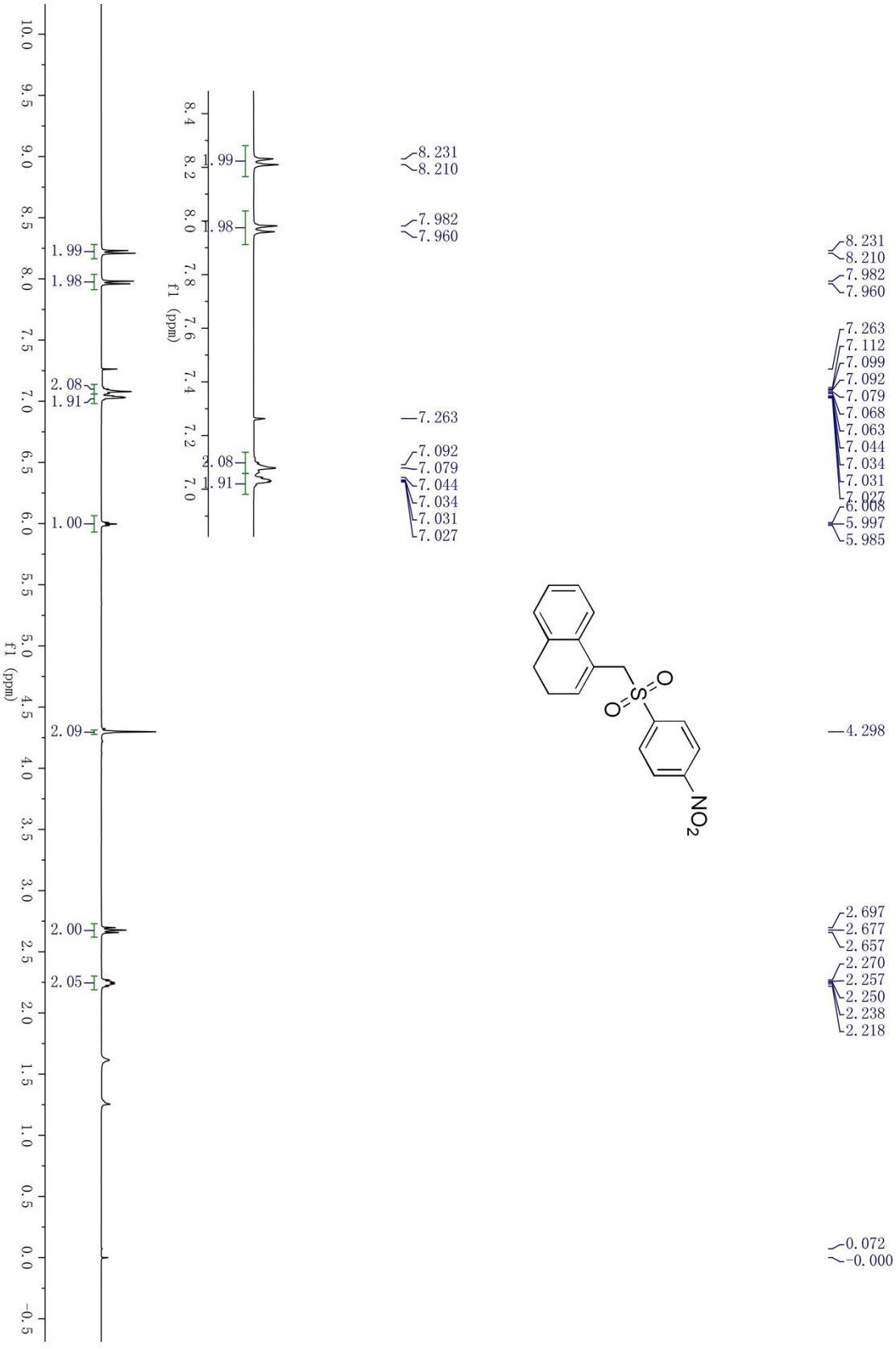
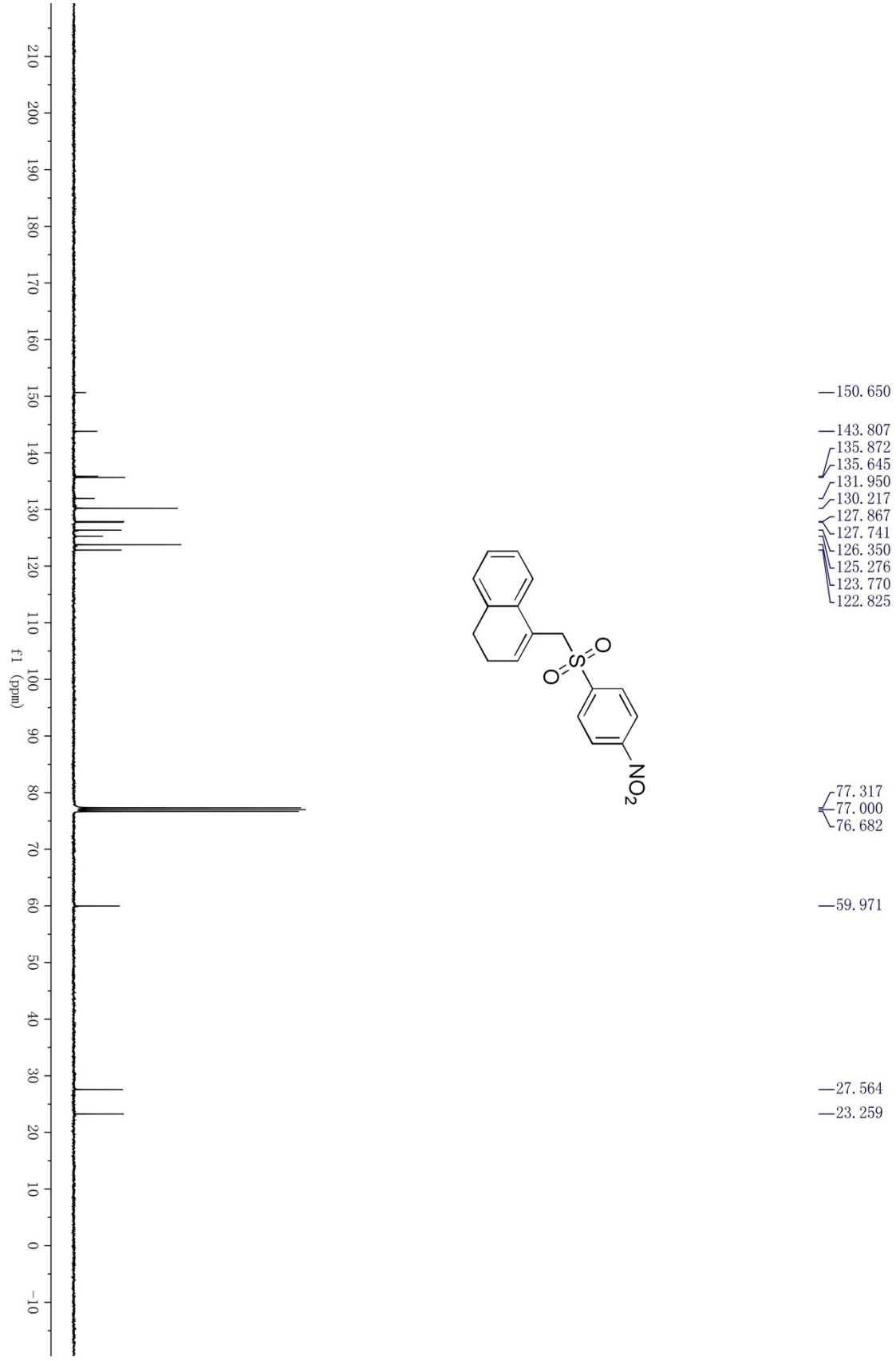
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
196.697
142.412
140.519
140.049
134.200
130.130
129.114
128.780
128.523
128.426
128.332
127.535
126.362
77.317
77.000
76.682
57.691
43.562
32.460
26.932
O
S
O
Ac

4-(((4-Nitrophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3aj)

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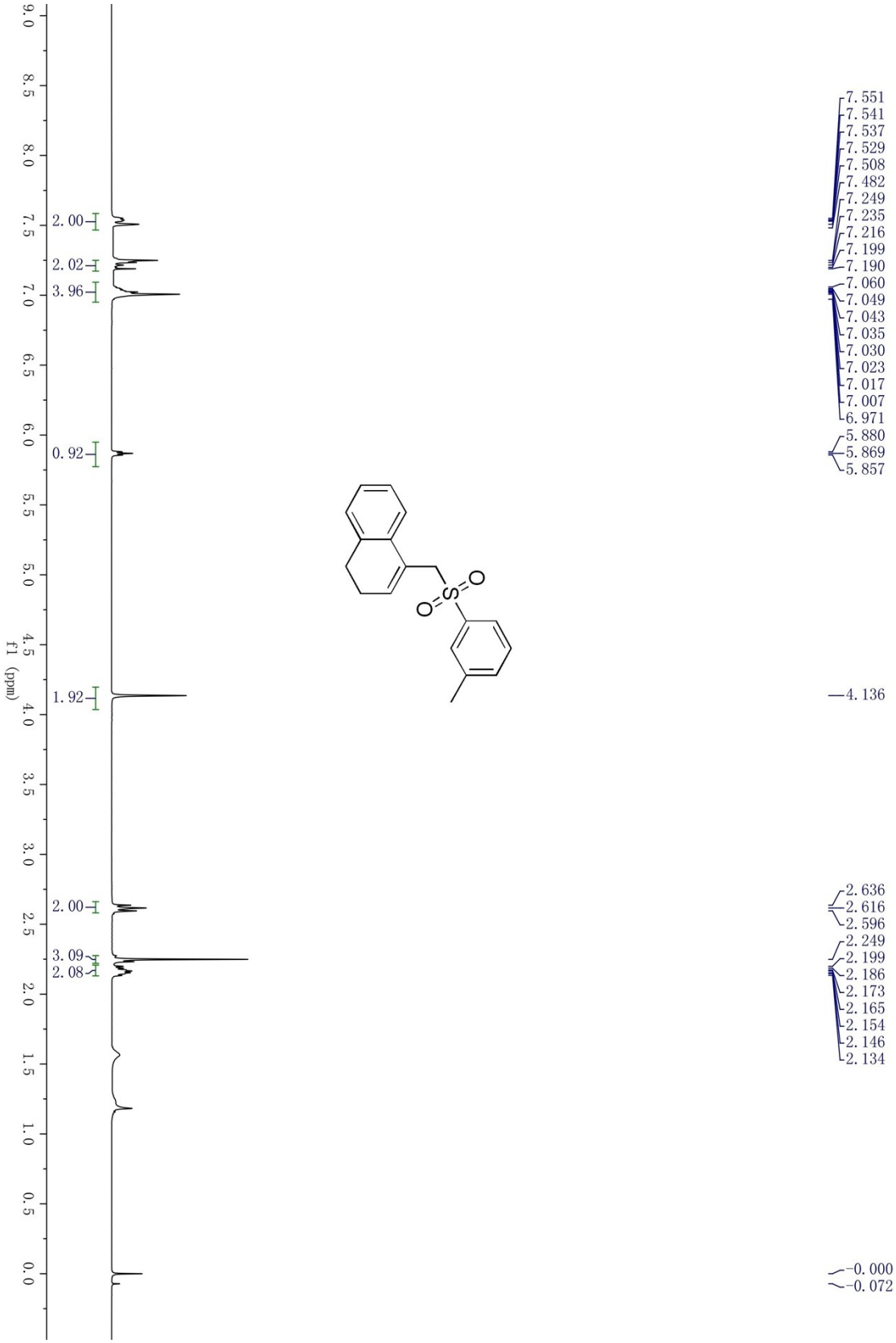
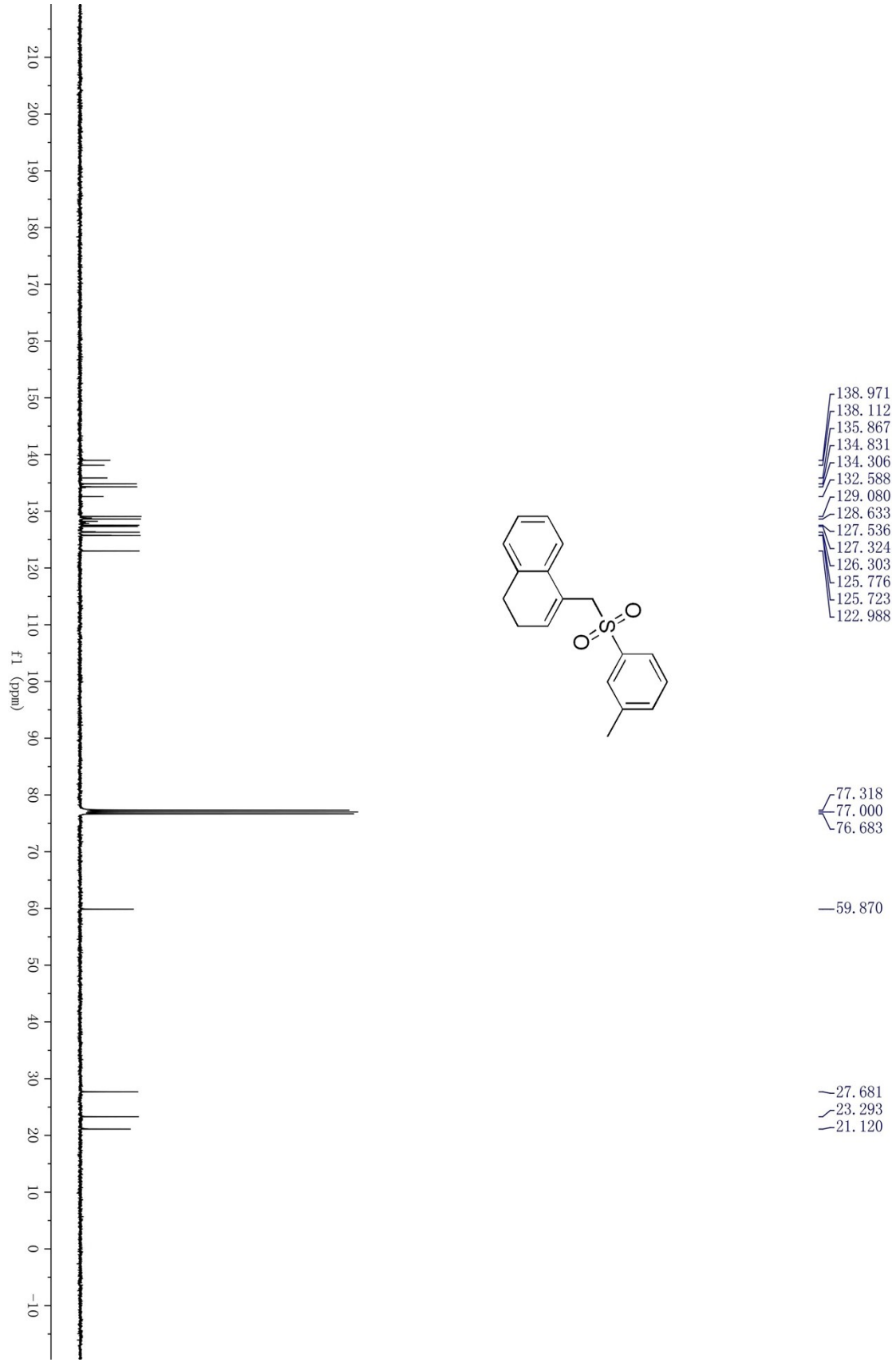
135.645
131.950
130.217
127.867
127.741
126.350
125.276
123.770
122.825
77.317
77.000
76.682
59.971
27.564
23.259
O
S
O
NO2

4-((*m*-Tolylsulfonyl)methyl)-1,2-dihydronaphthalene (3ak)




f1 (ppm)
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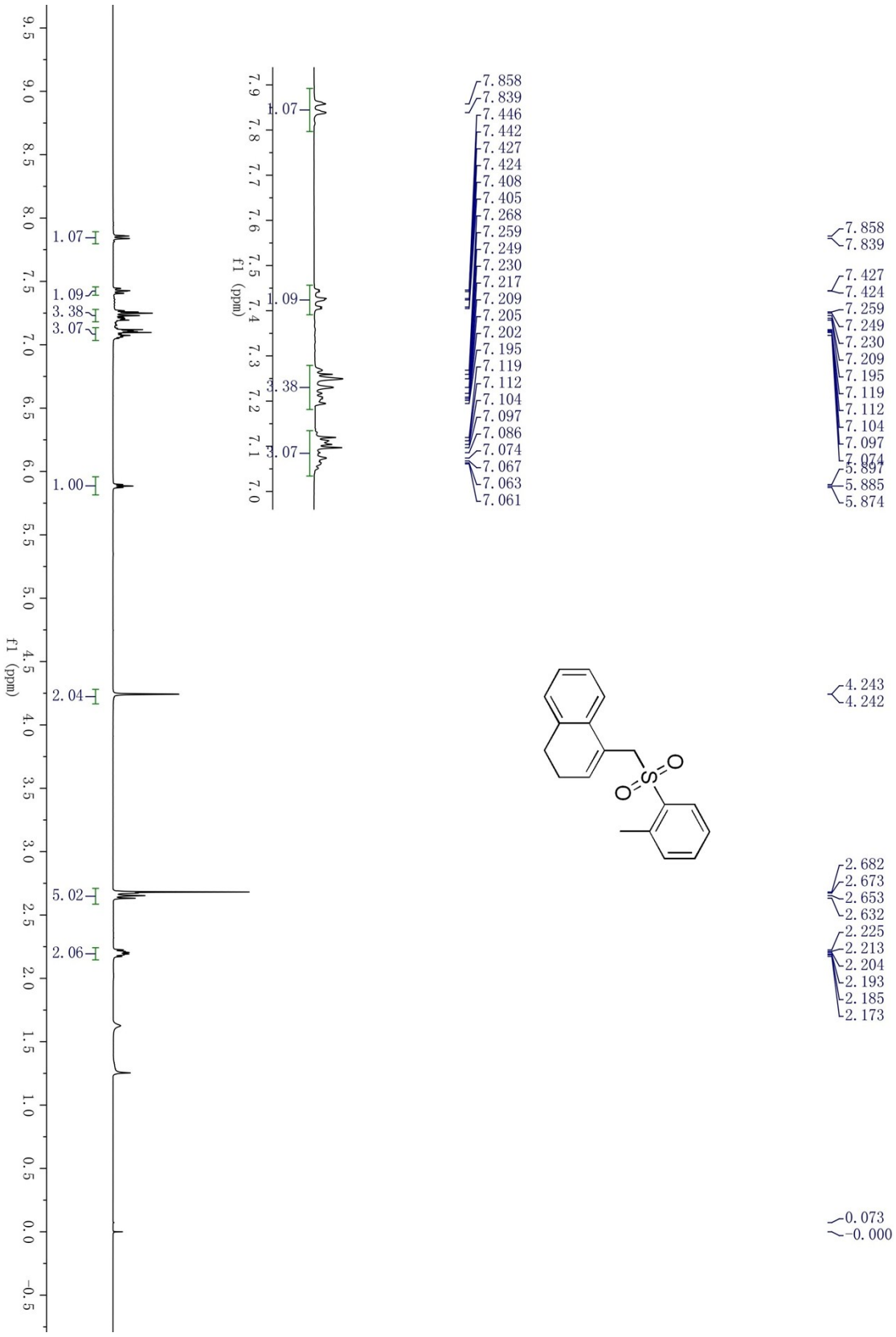
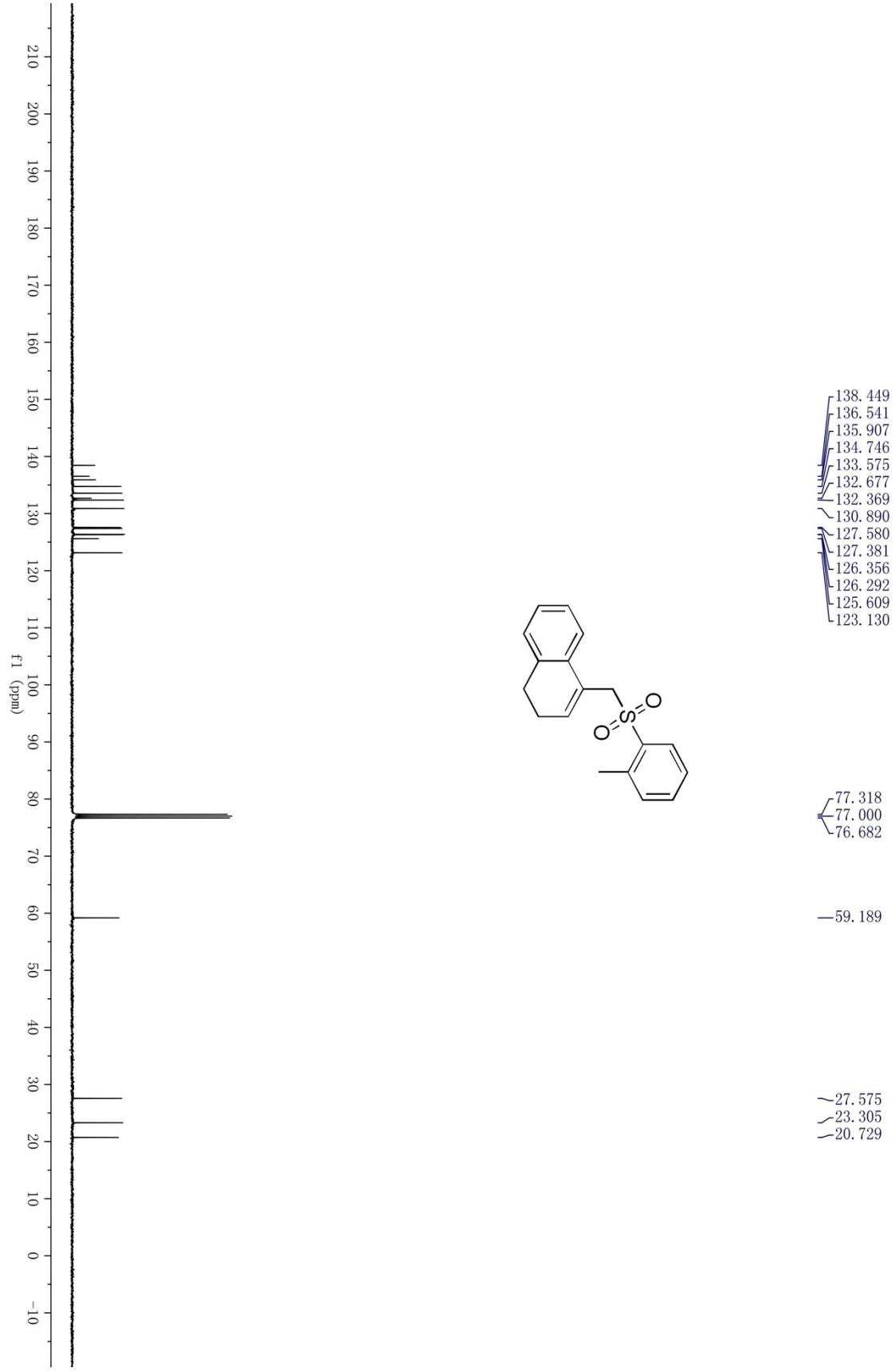
132.588
129.080
128.633
127.536
127.324
126.303
125.776
125.723
122.988
77.318
77.000
76.683
59.870
27.681
23.293
21.120

4-((*o*-Tolylsulfonyl)methyl)-1,2-dihydronaphthalene (3al)




f1 (ppm)
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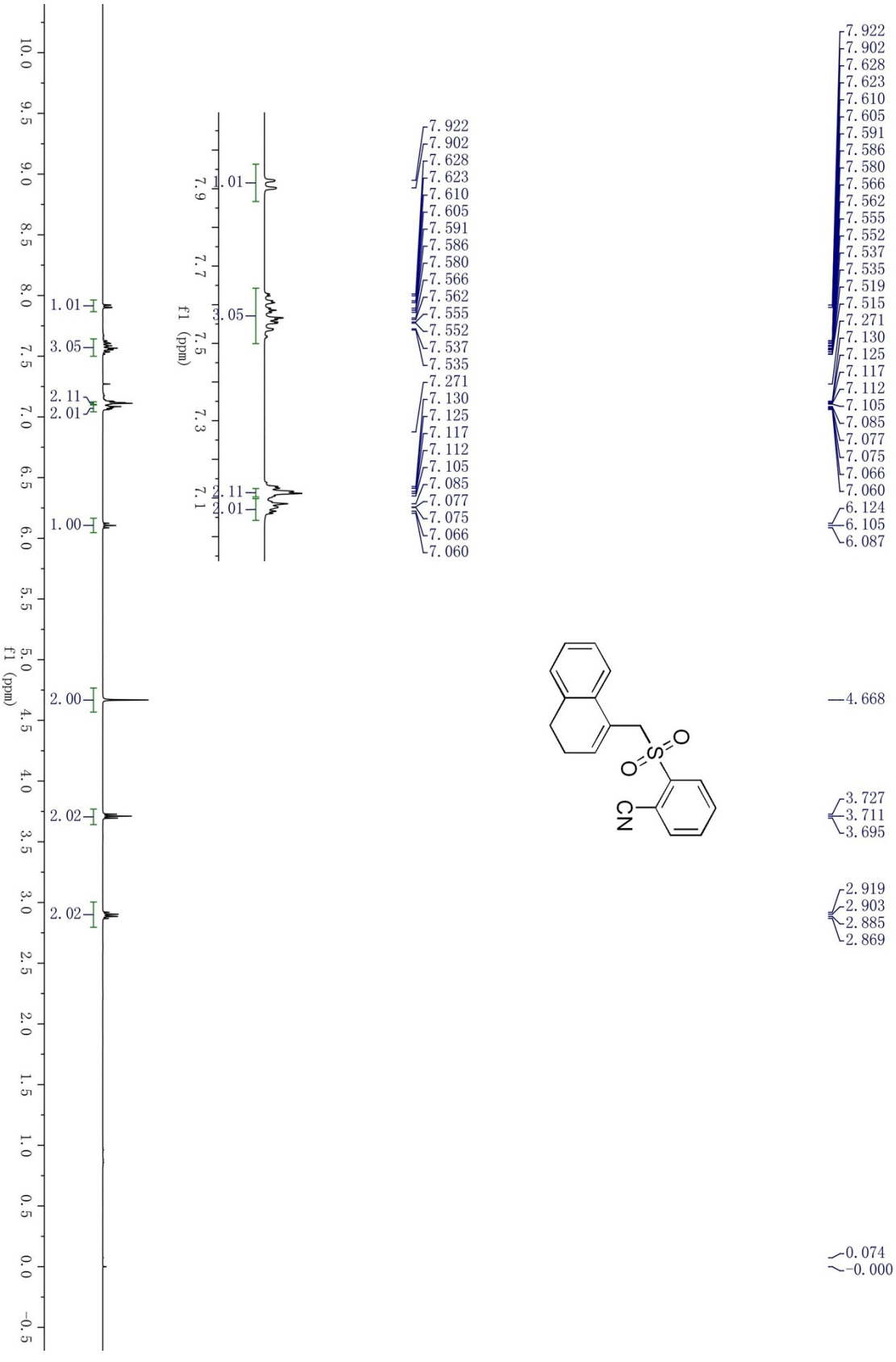
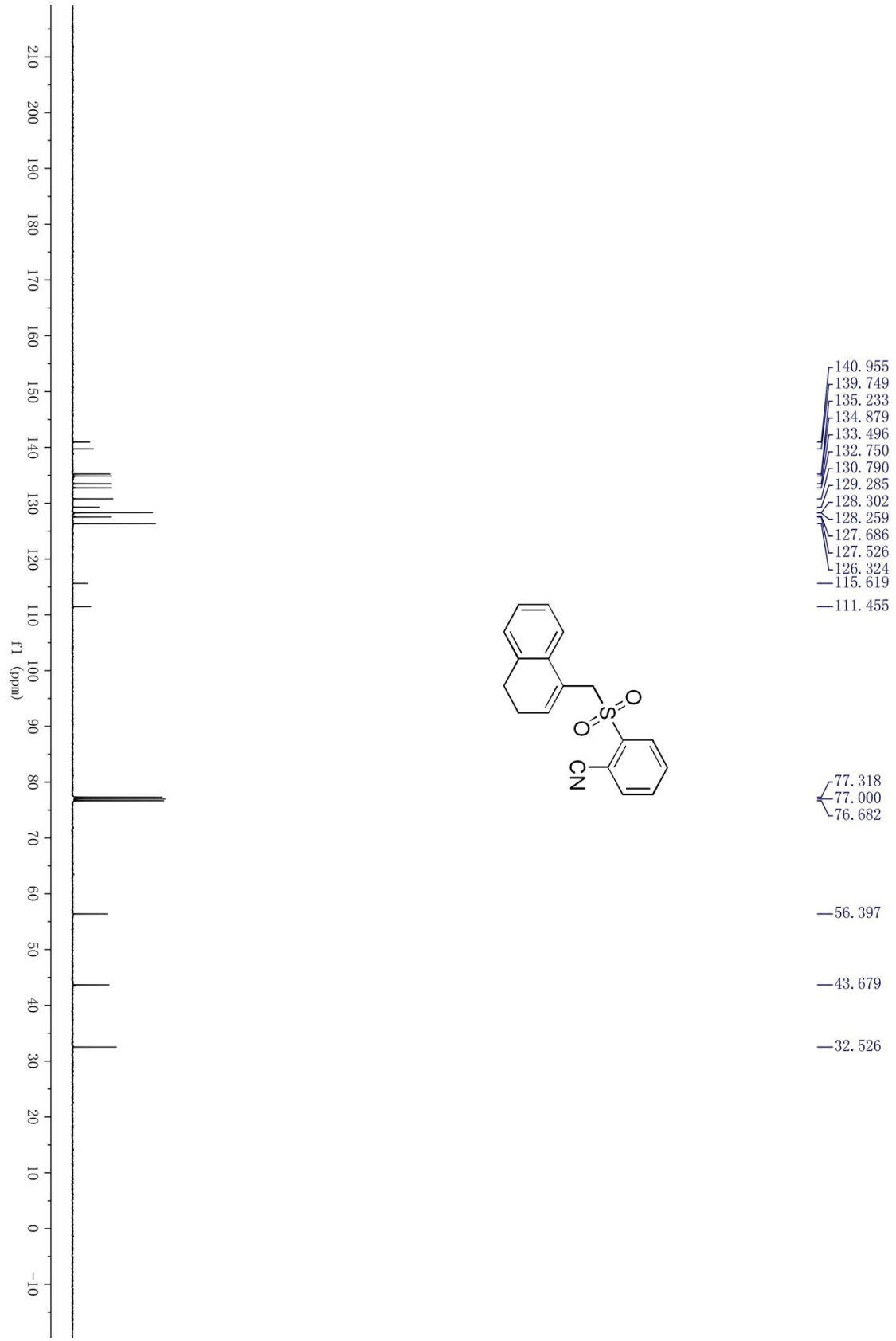
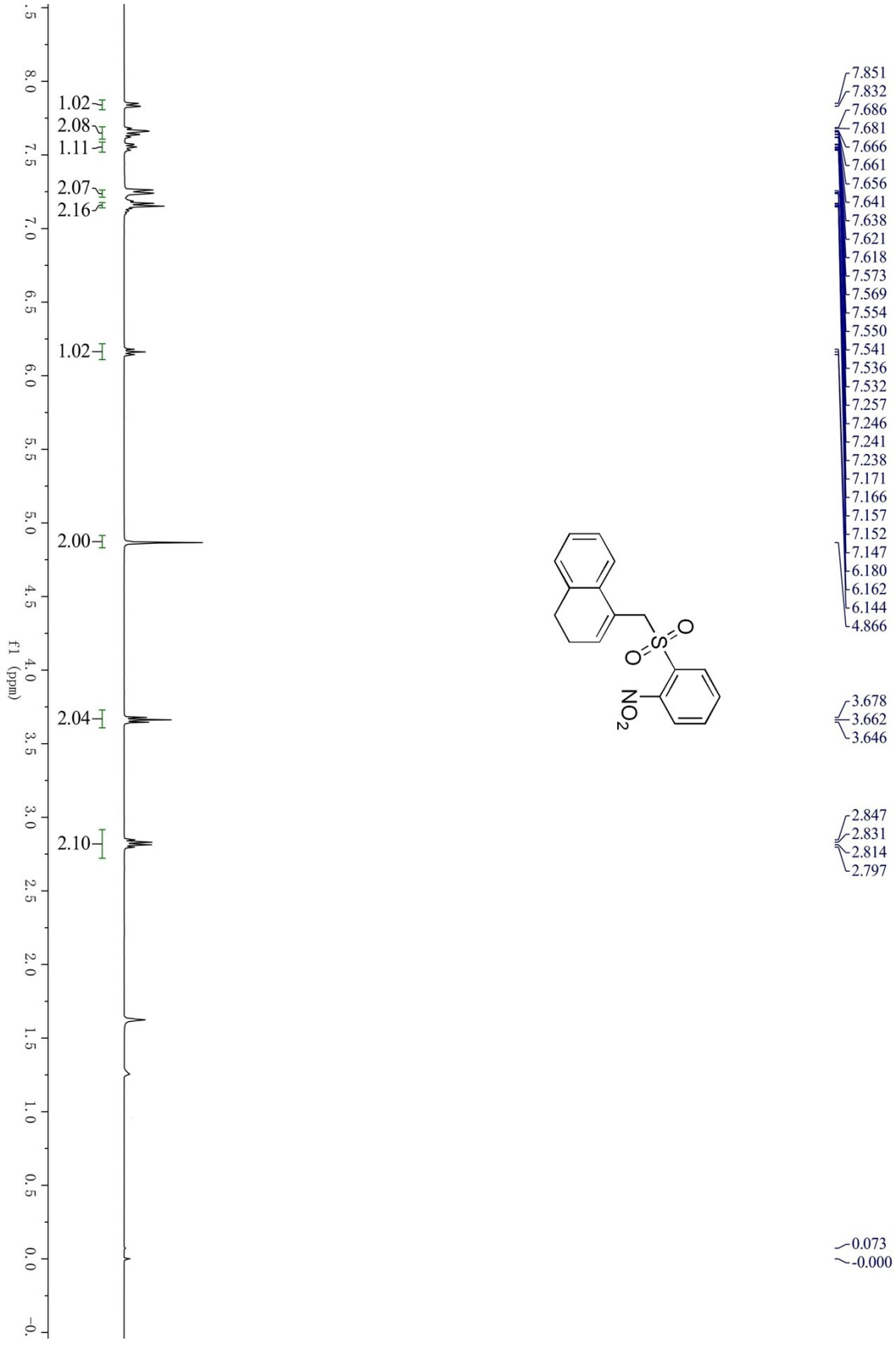
136.541
135.907
134.746
133.575
132.677
132.369
130.890
127.580
127.381
126.356
126.292
125.609
123.130
77.318
77.000
76.682
59.189
27.575
23.305
20.729

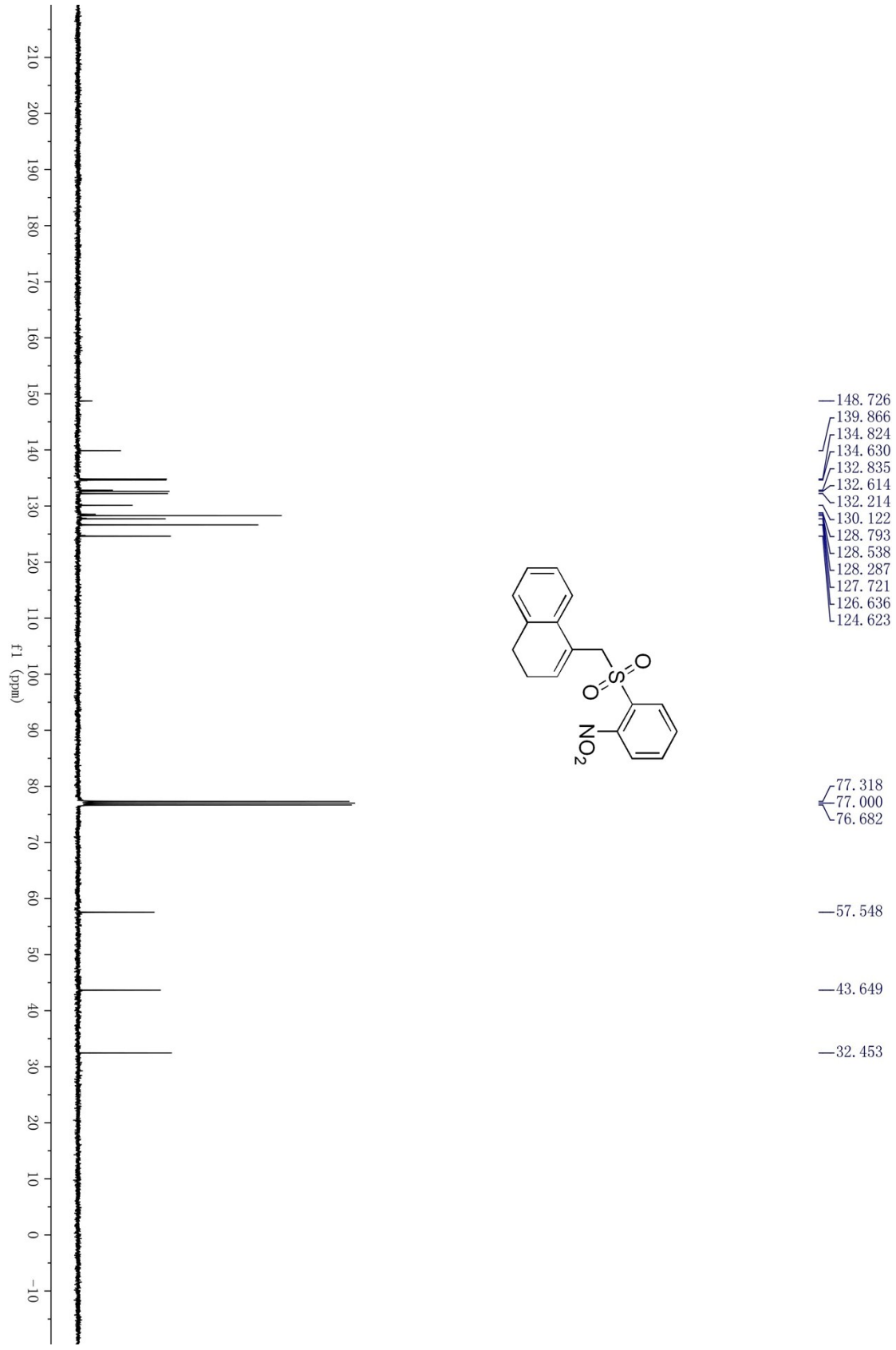
2-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)benzonitrile (3am)



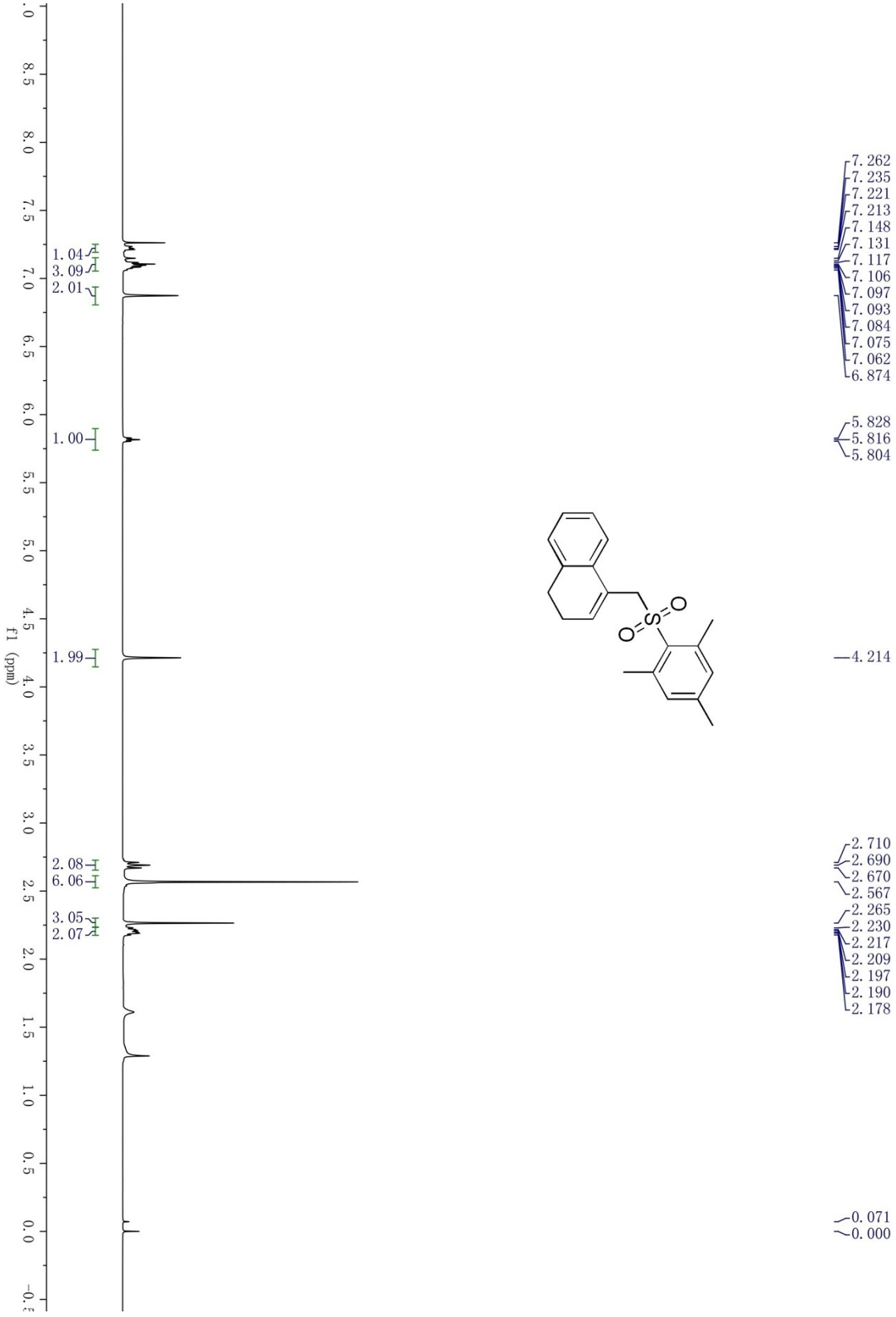

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
140.955
139.749
135.233
134.879
133.496
132.750
130.790
129.285
128.302
128.259
127.686
127.526
126.324
115.619
111.455
77.318
77.000
76.682
56.397
43.679
32.526
O
O
S
CN

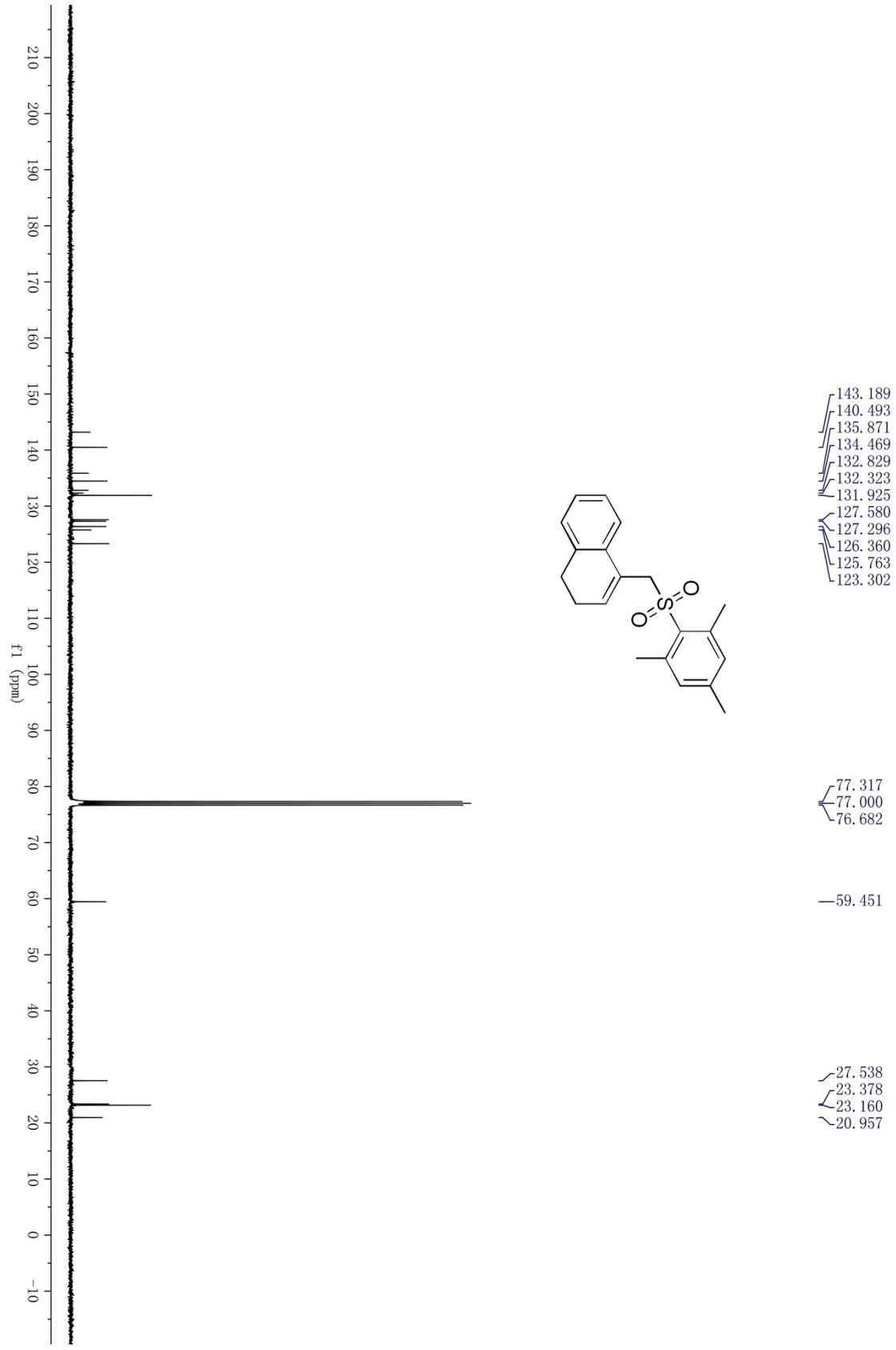
4-(((2-Nitrophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3an)



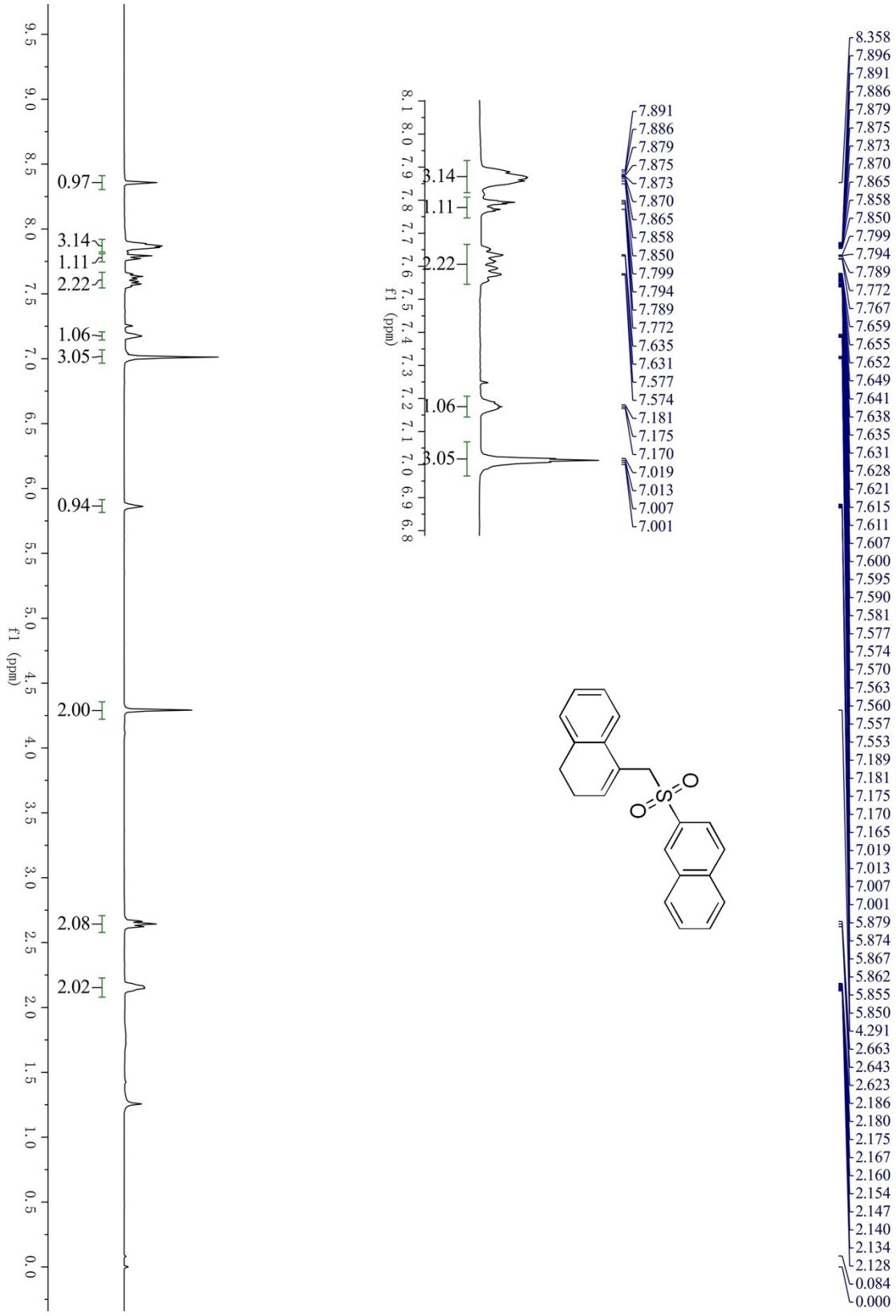

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
148.726
139.866
134.824
134.630
132.835
132.614
132.214
130.122
128.793
128.538
128.287
127.721
126.636
124.623
77.318
77.000
76.682
57.548
43.649
32.453
O
O
S
NO2

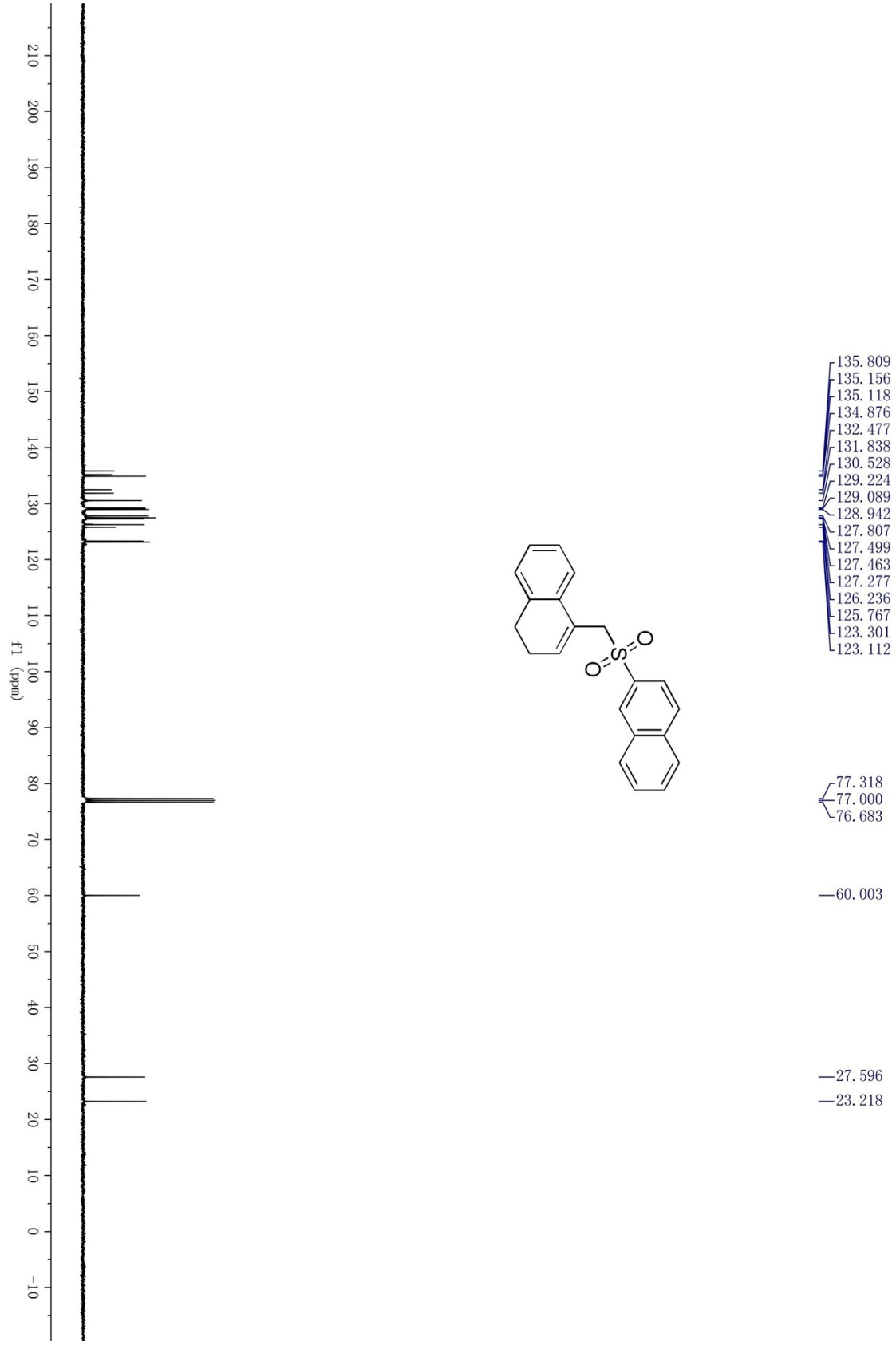
4-((Mesitylsulfonyl)methyl)-1,2-dihydronaphthalene (3ao)



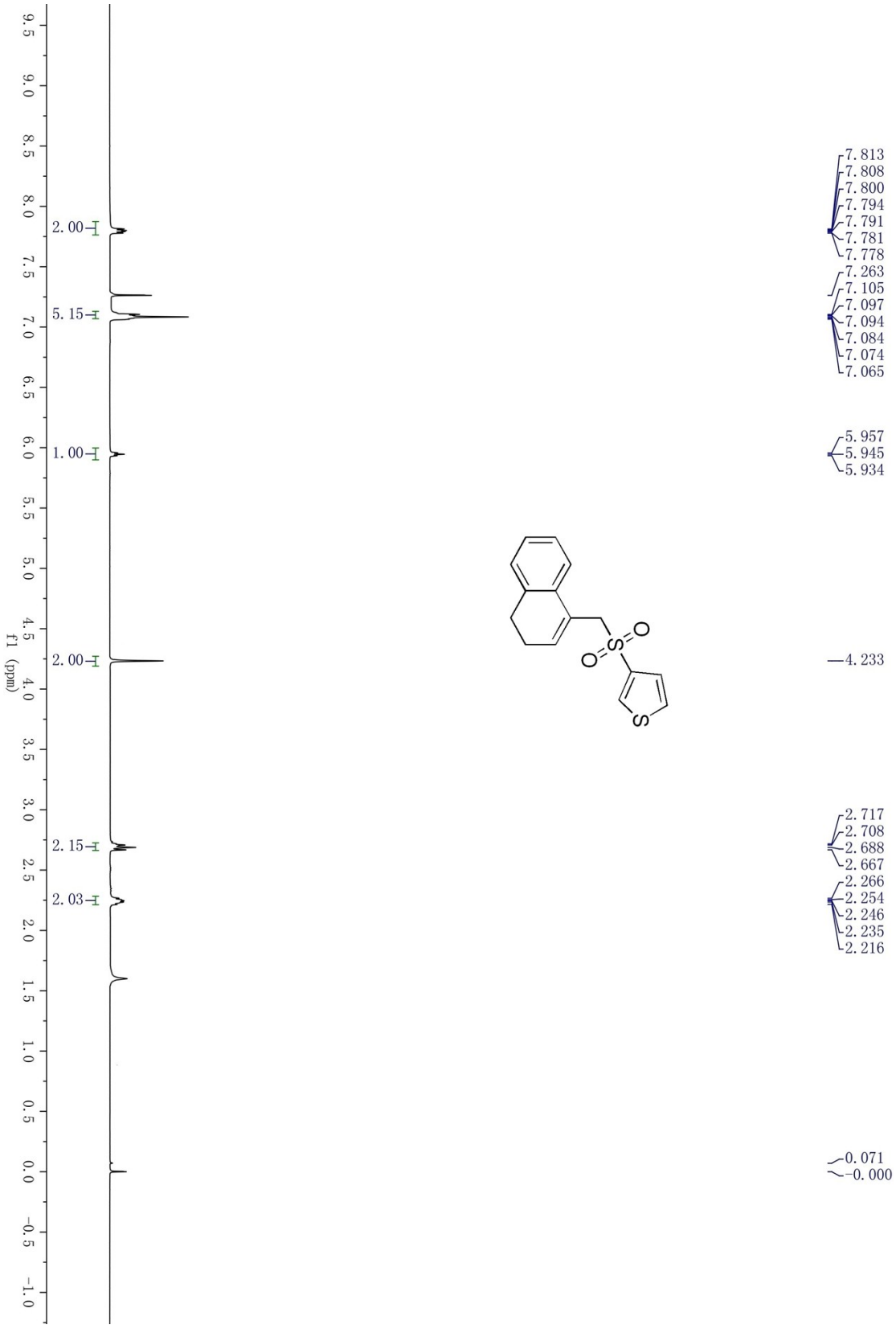

143.189
140.493
135.871
134.469
132.829
132.323
131.925
127.580
127.296
126.360
125.763
123.302
77.317
77.000
76.682
59.451
27.538
23.378
23.160
20.957
f1 (ppm)

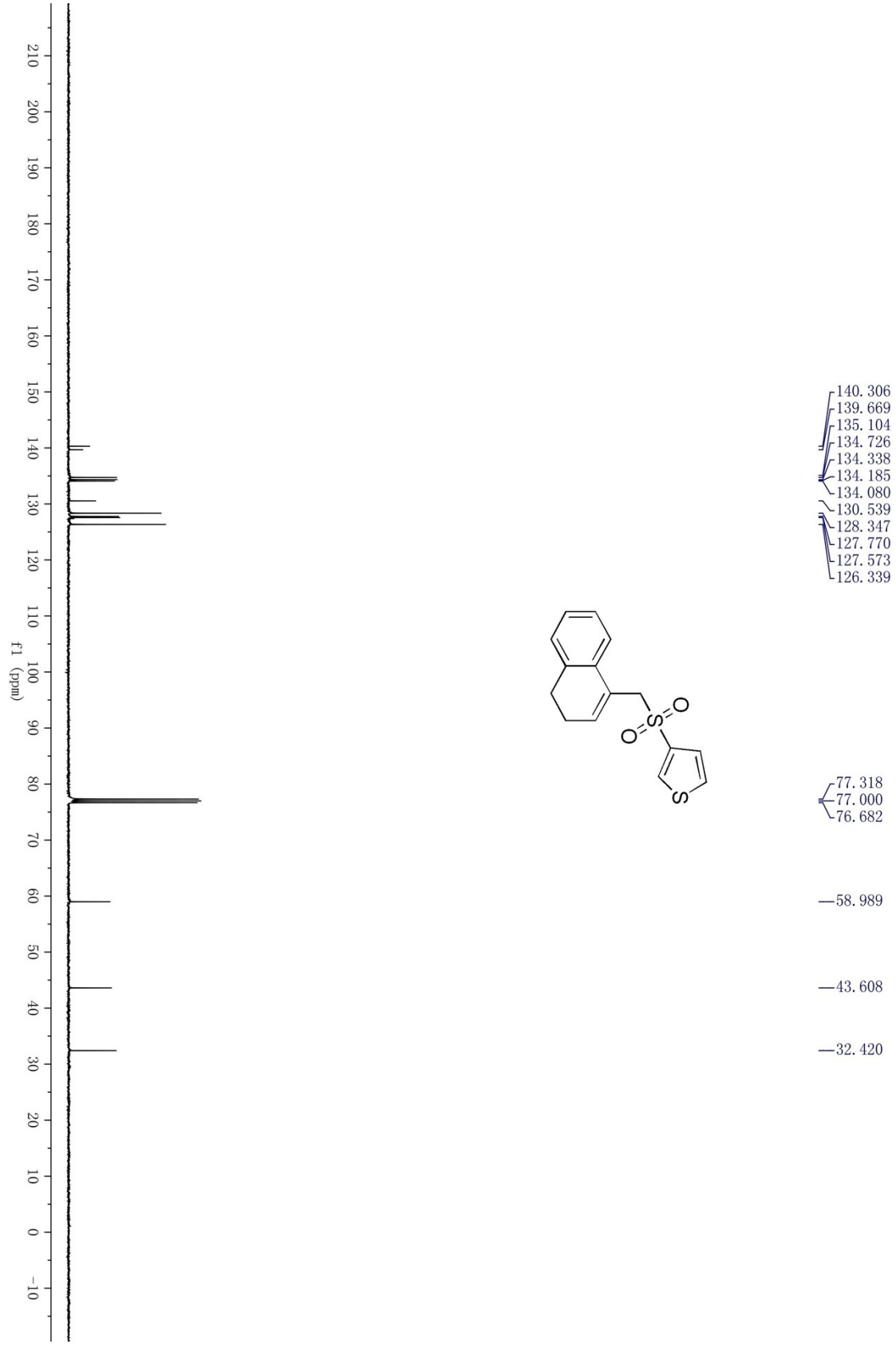
2-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)naphthalene (3ap)



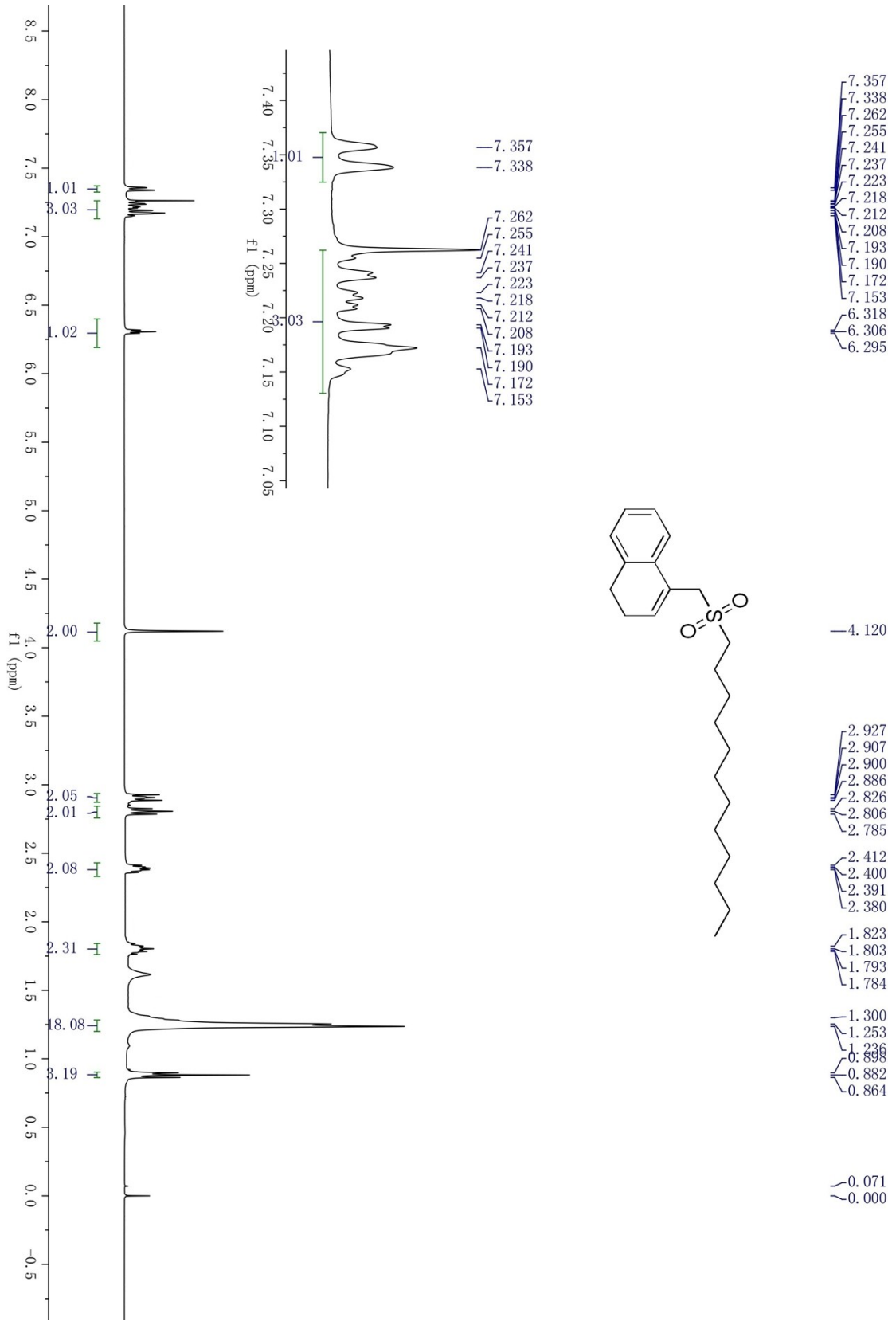

f1 (ppm)
135.809
135.156
135.118
134.876
132.477
131.838
130.528
129.224
129.089
128.942
127.807
127.499
127.463
127.277
126.236
125.767
123.301
123.112
77.318
77.000
76.683
60.003
27.596
23.218

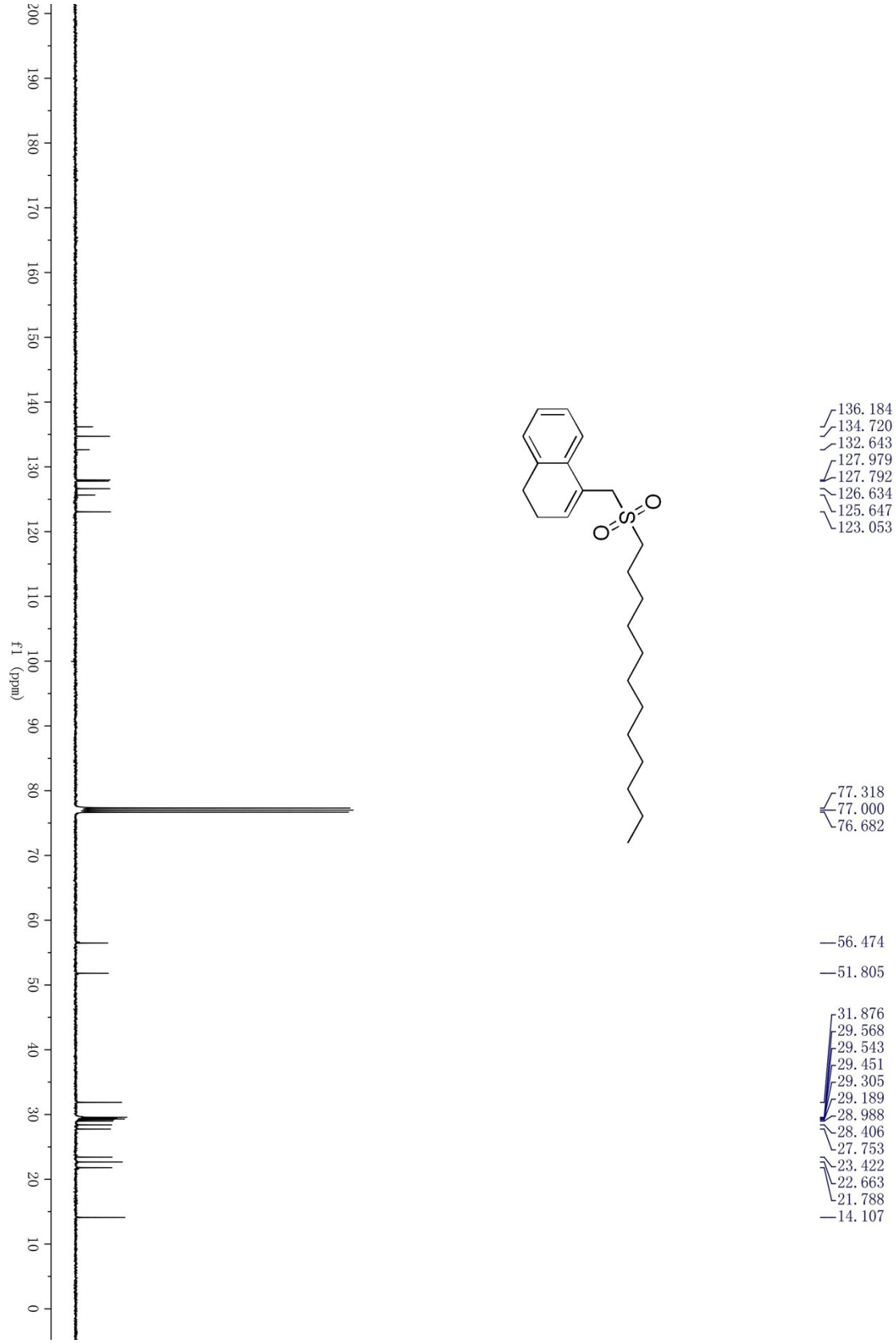
2-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)thiophene (3aq)



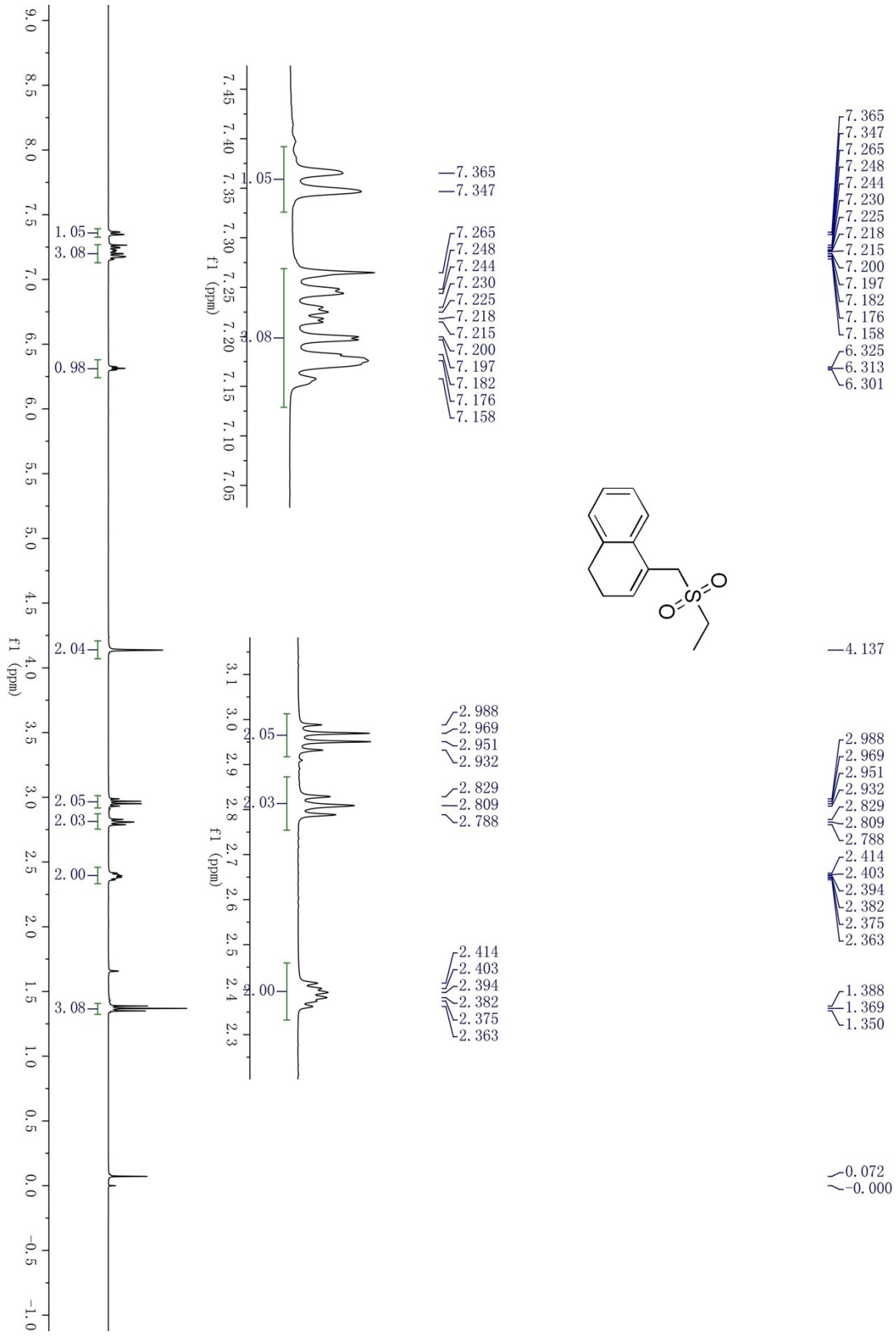

f1 (ppm)
140.306
139.669
135.104
134.726
134.338
134.185
134.080
130.539
128.347
127.770
127.573
126.339
77.318
77.000
76.682
58.989
43.608
32.420
O
S
O
S

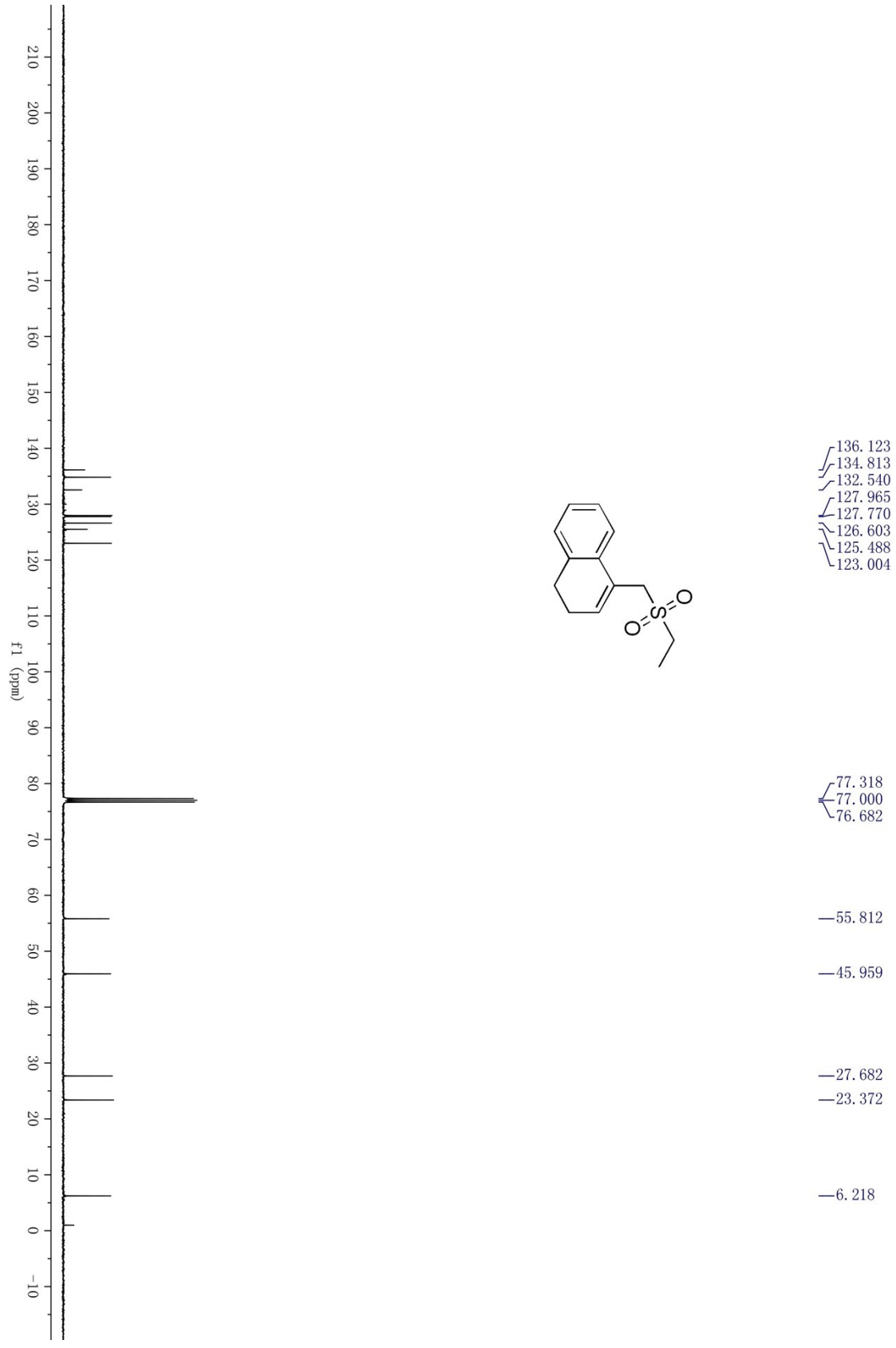
4-((Dodecylsulfonyl)methyl)-1,2-dihydronaphthalene (3at)



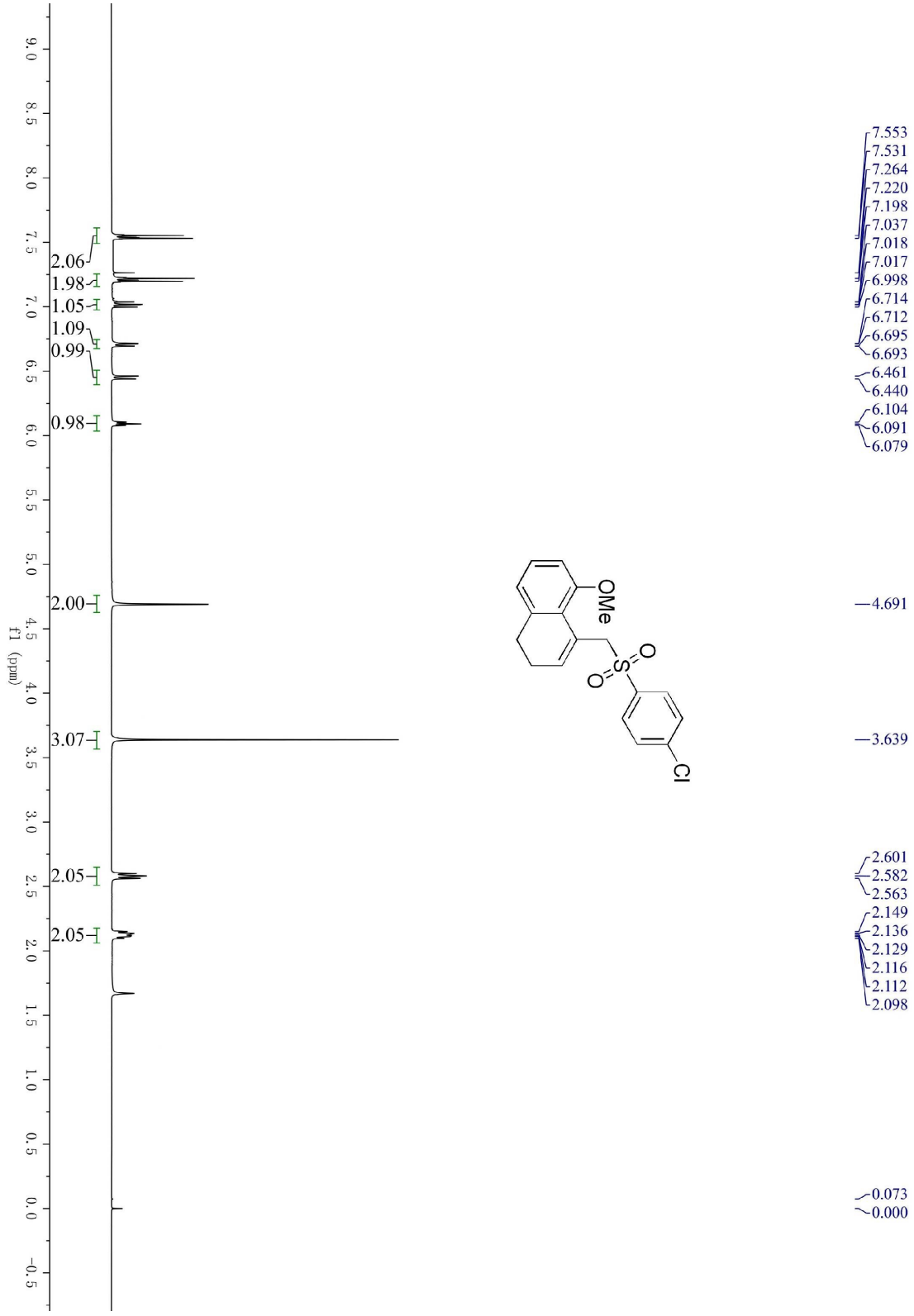

f1 (ppm)
136.184
134.720
132.643
127.979
127.792
126.634
125.647
123.053
77.318
77.000
76.682
56.474
51.805
31.876
29.568
29.543
29.451
29.305
29.189
28.988
28.406
27.753
23.422
22.663
21.788
14.107

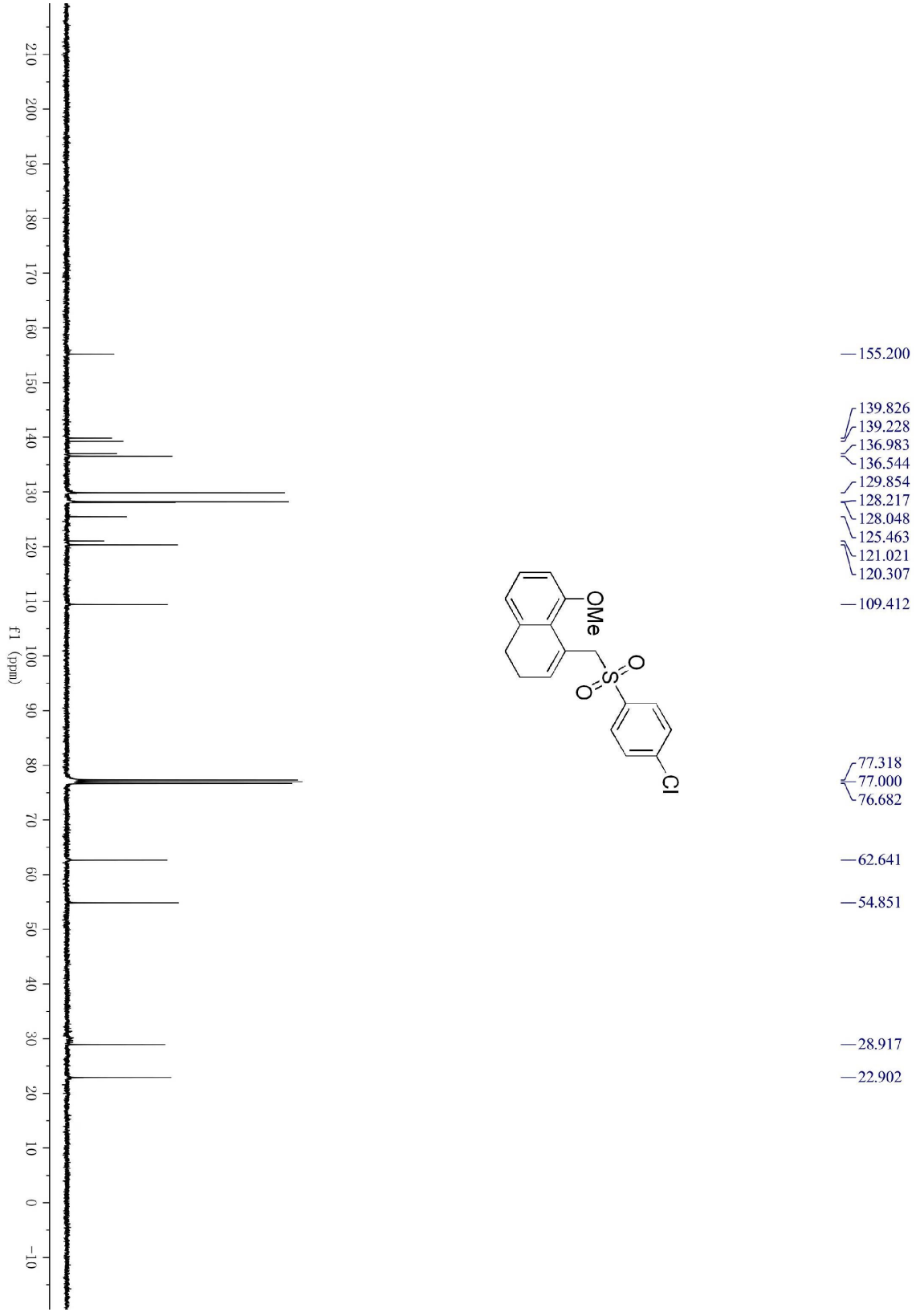
4-((Ethylsulfonyl)methyl)-1,2-dihydronaphthalene (3au)



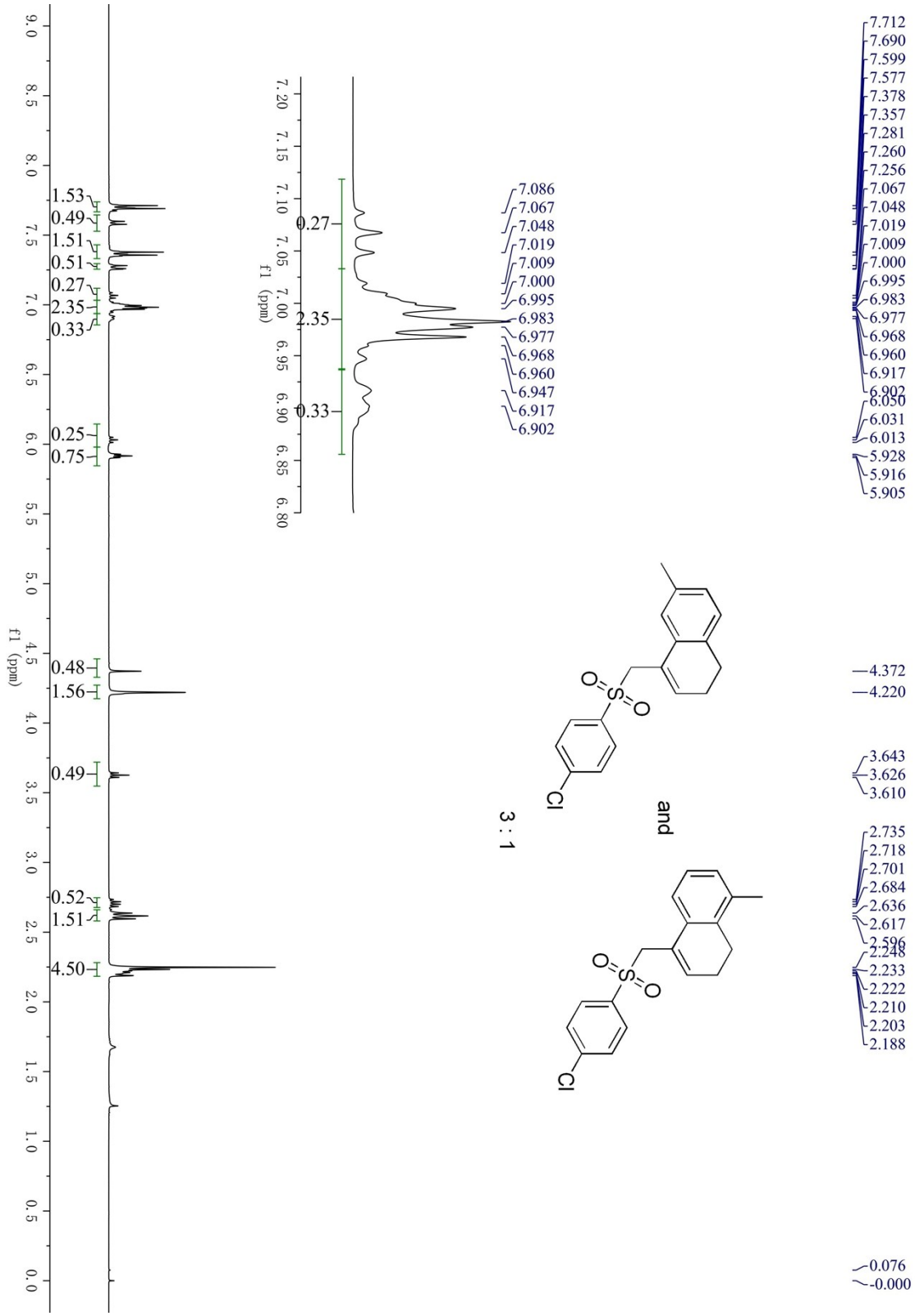

f1 (ppm)
136.123
134.813
132.540
127.965
127.770
126.603
125.488
123.004
77.318
77.000
76.682
55.812
45.959
27.682
23.372
6.218

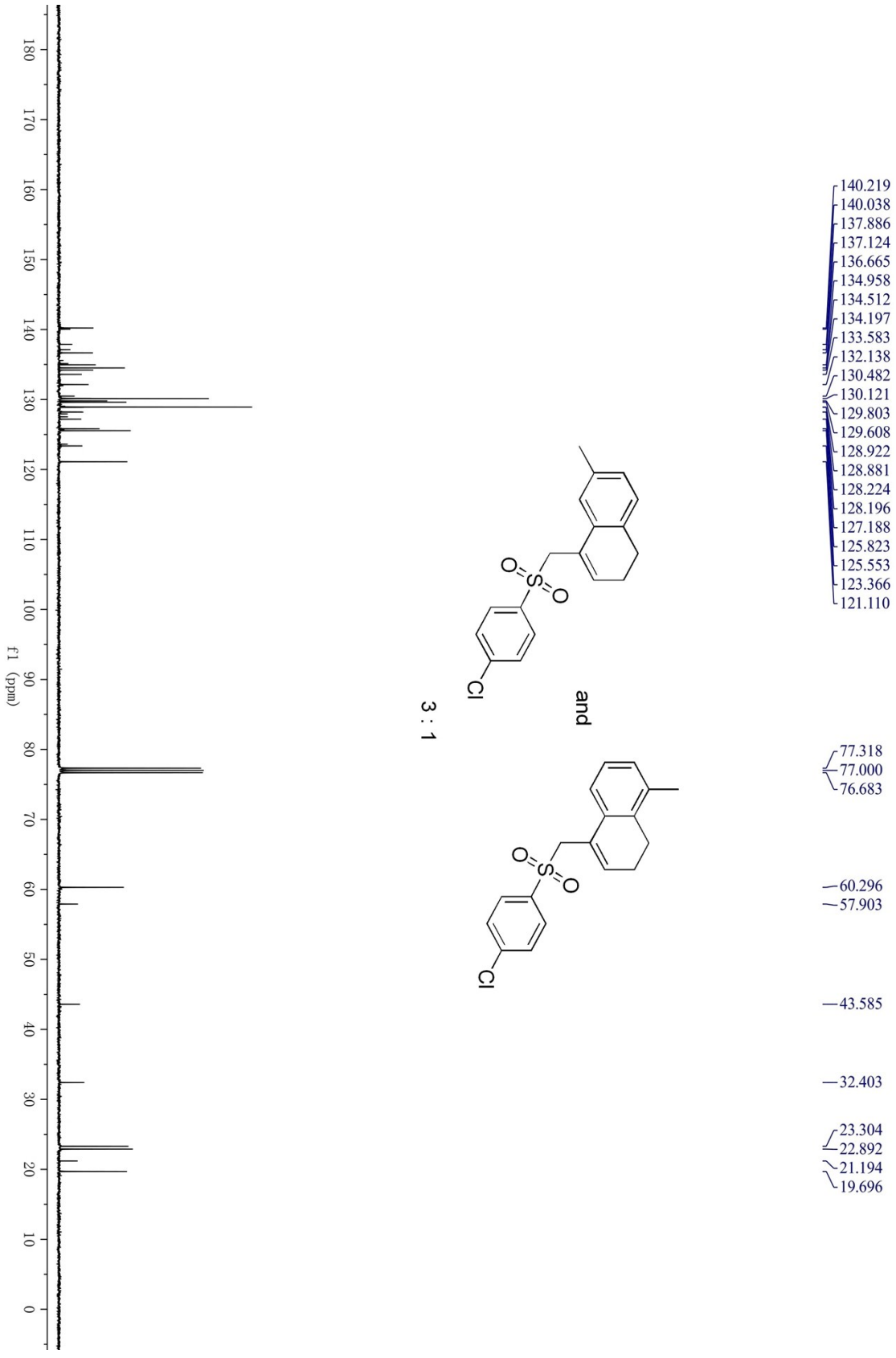
4-(((4-chlorophenyl)sulfonyl)methyl)-5-methoxy-1,2-dihydronaphthalene (3bf)



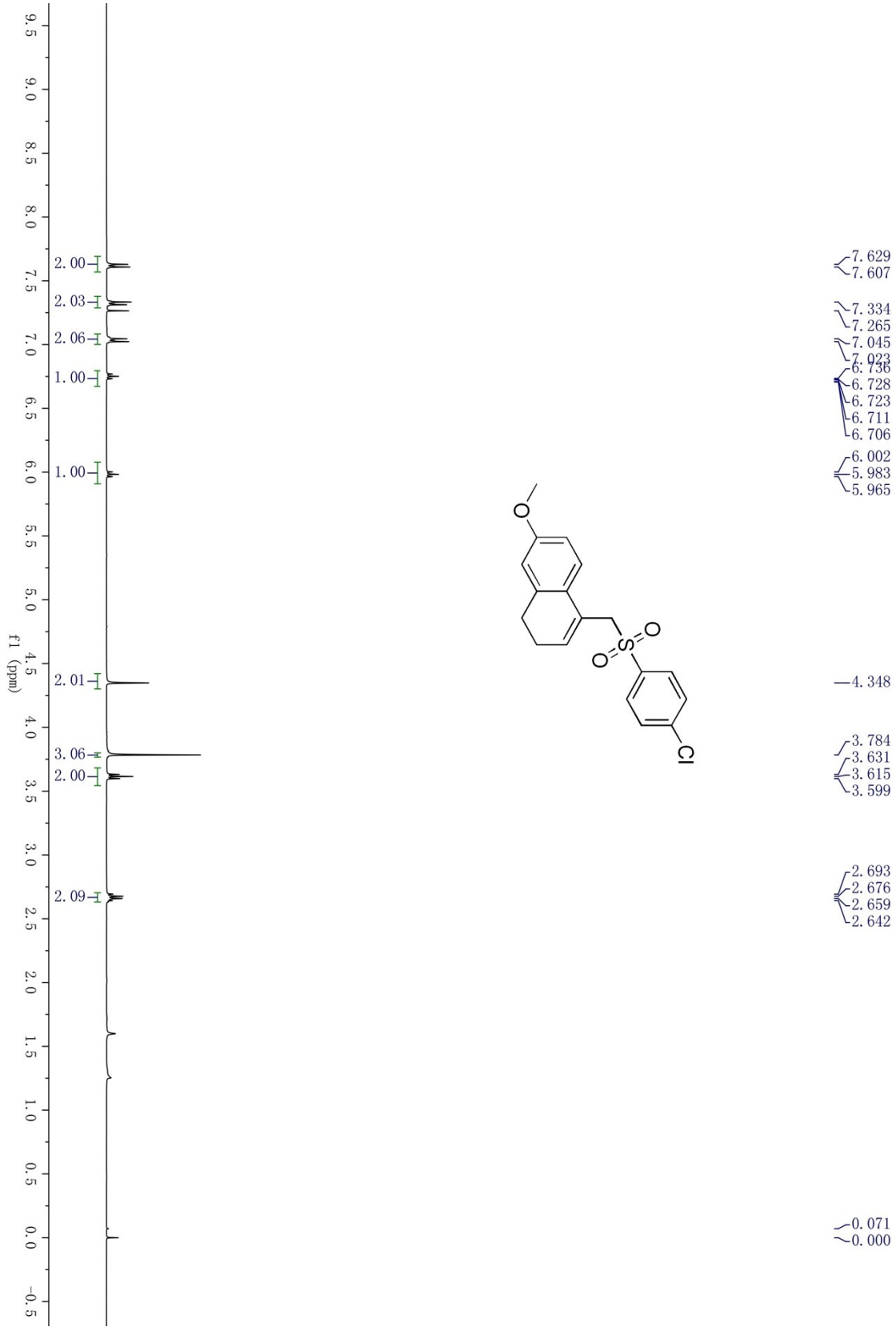

155.200
139.826
139.228
136.983
136.544
129.854
128.217
128.048
125.463
121.021
120.307
109.412
77.318
77.000
76.682
62.641
54.851
28.917
22.902
OMe
O
S
O
Cl
f1 (ppm)

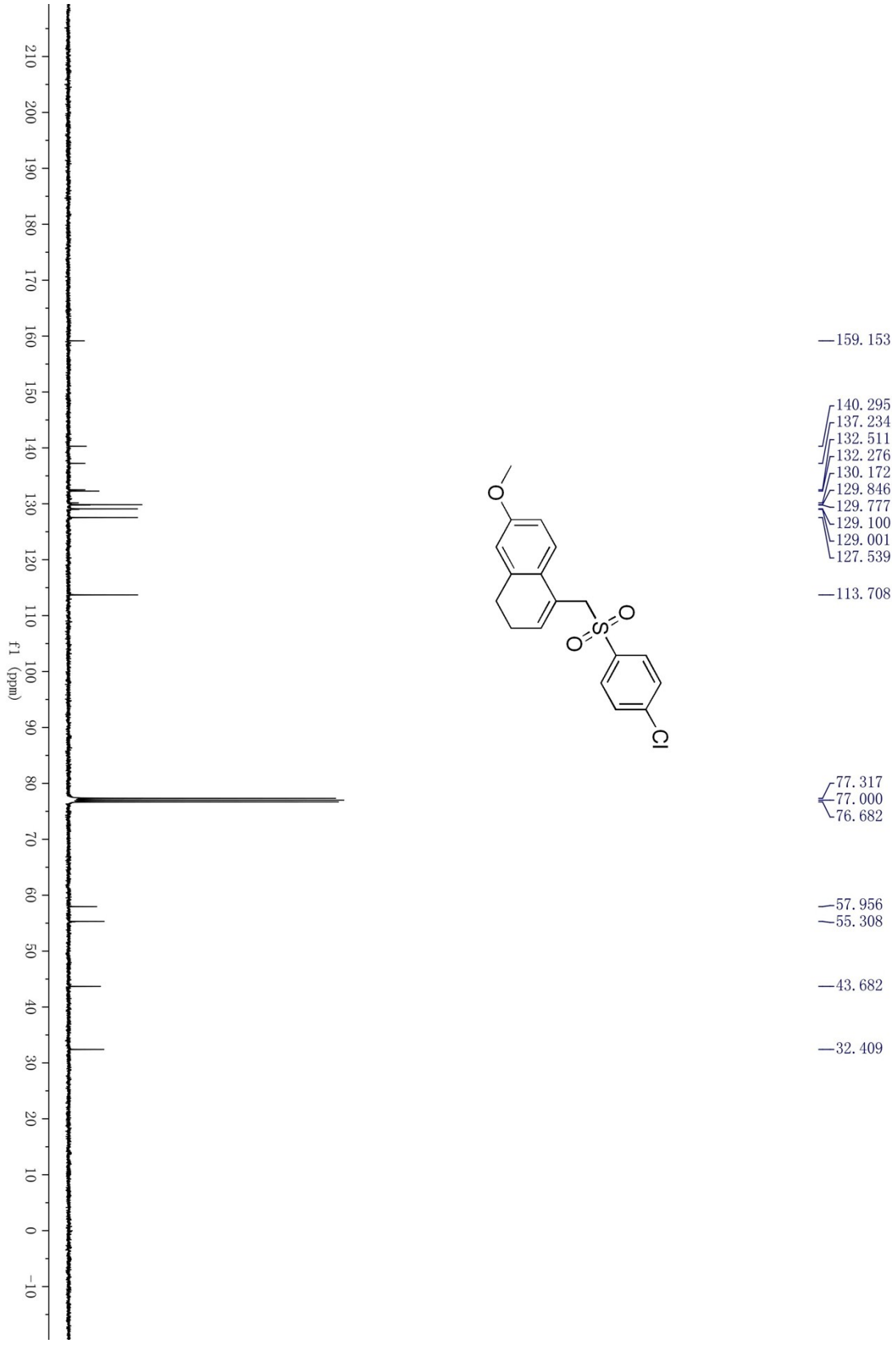
4-(((4-chlorophenyl)sulfonyl)methyl)-6-methyl-1,2-dihydronaphthalene (3cf) and **4-(((4-chlorophenyl)sulfonyl)methyl)-8-methyl-1,2-dihydronaphthalene (3cf')**



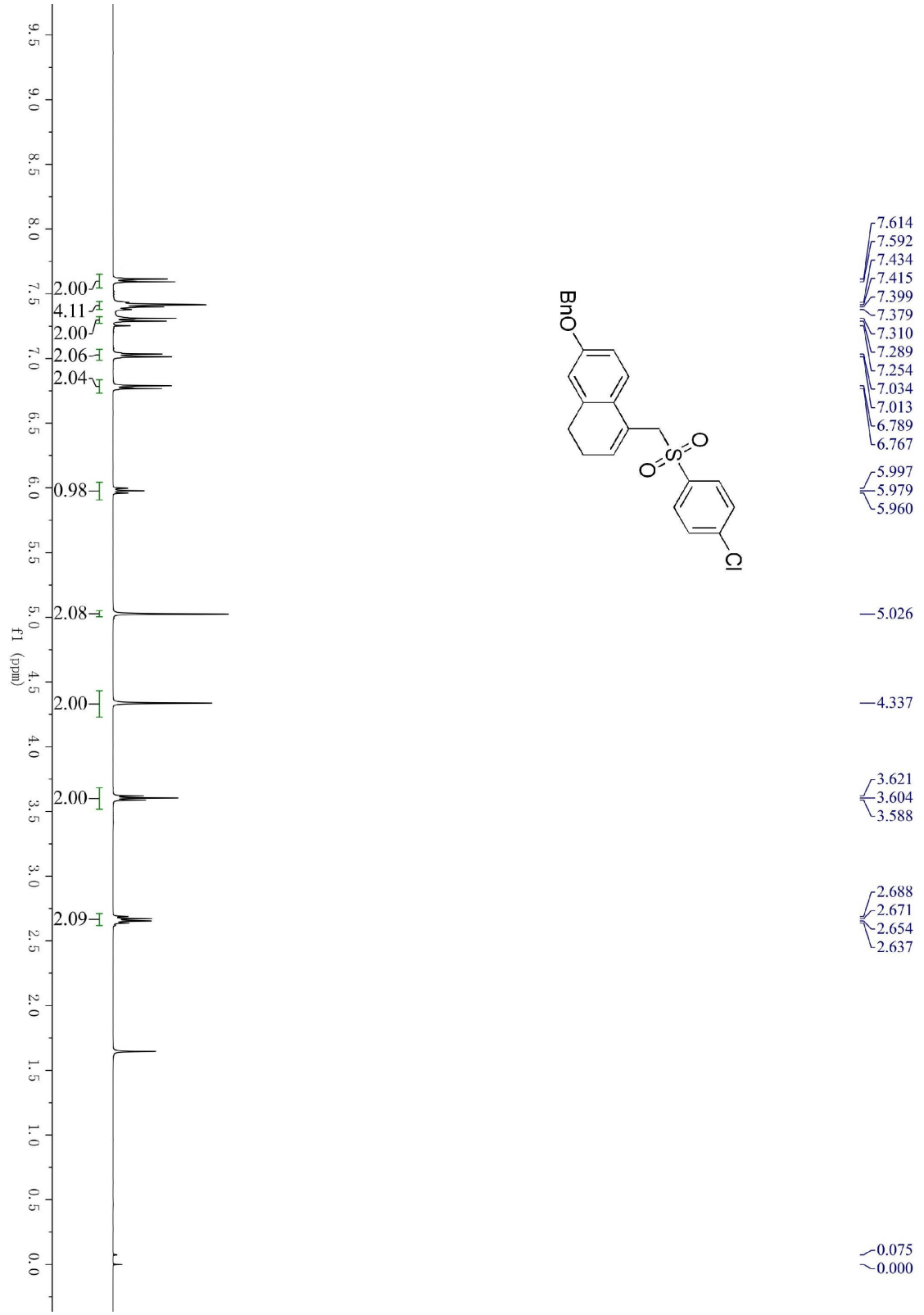

f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
140.219
140.038
137.886
137.124
136.665
134.958
134.512
134.197
133.583
132.138
130.482
130.121
129.803
129.608
128.922
128.881
128.224
128.196
127.188
125.823
125.553
123.366
121.110
77.318
77.000
76.683
60.296
57.903
43.585
32.403
23.304
22.892
21.194
19.696
3 : 1
and
Cl
Cl

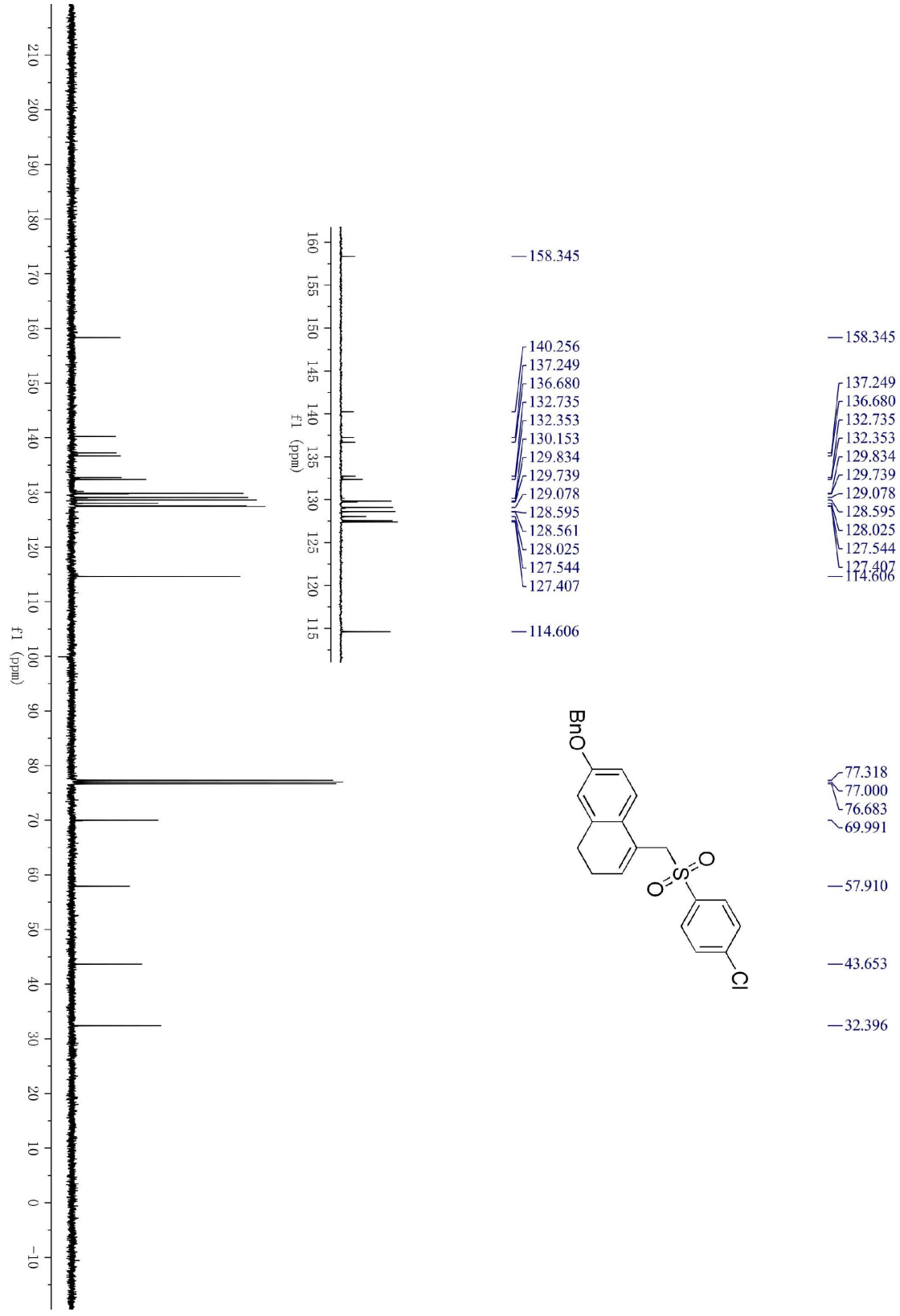
4-(((4-Chlorophenyl)sulfonyl)methyl)-7-methoxy-1,2-dihydronaphthalene (3df)



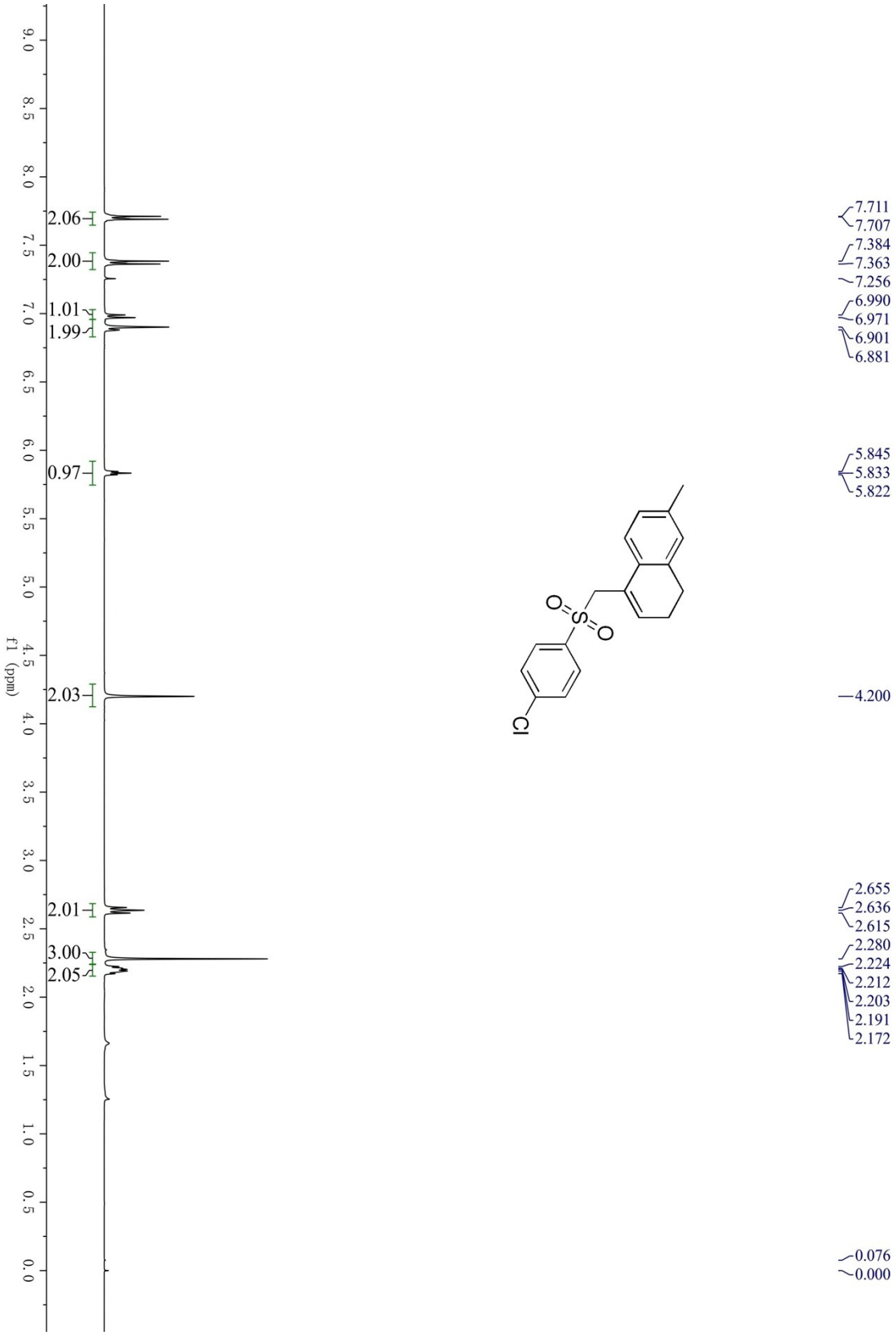

159.153
140.295
137.234
132.511
132.276
130.172
129.846
129.777
129.100
129.001
127.539
113.708
77.317
77.000
76.682
57.956
55.308
43.682
32.409
f1 (ppm)

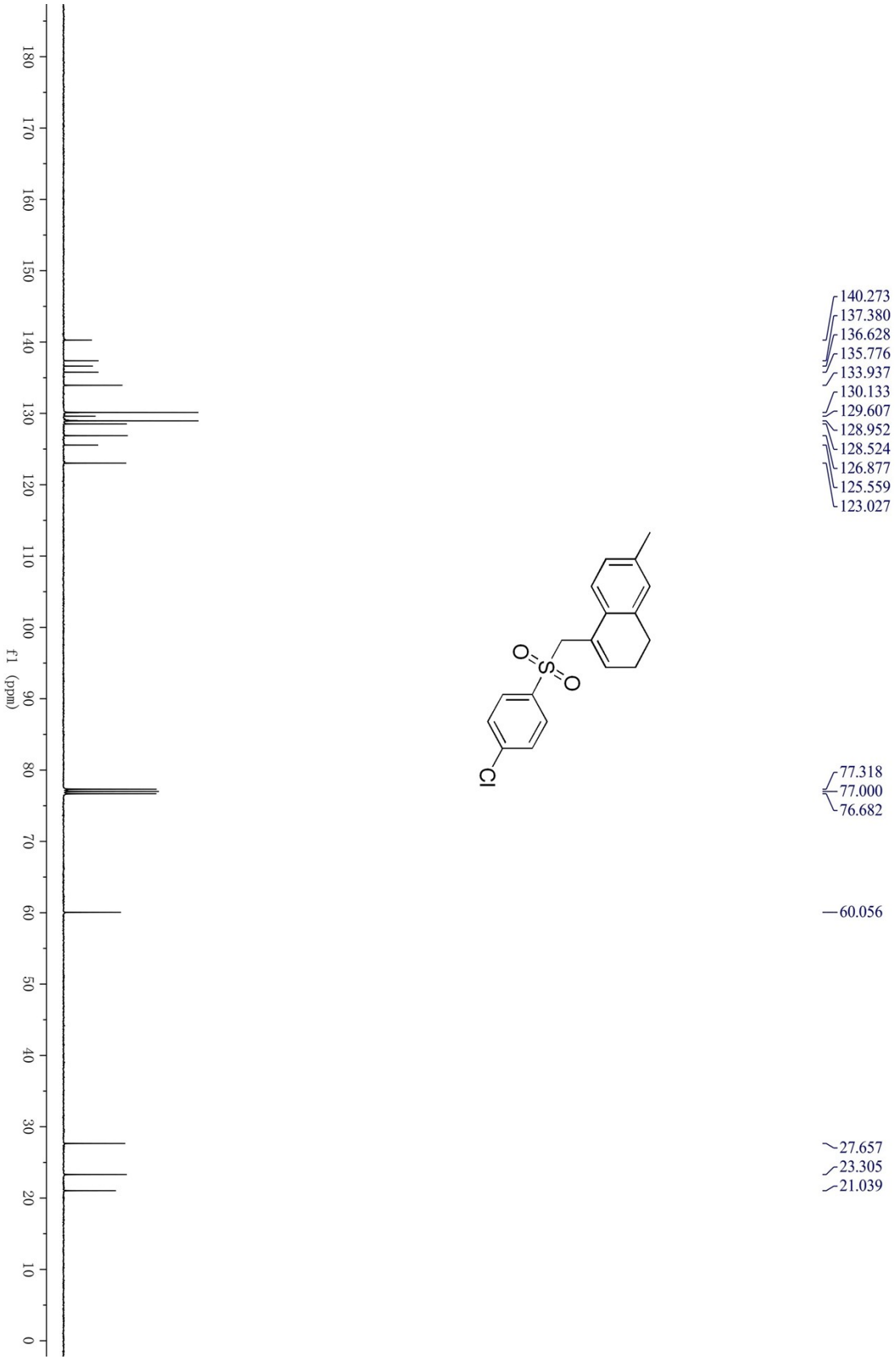
7-(benzyloxy)-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ef)



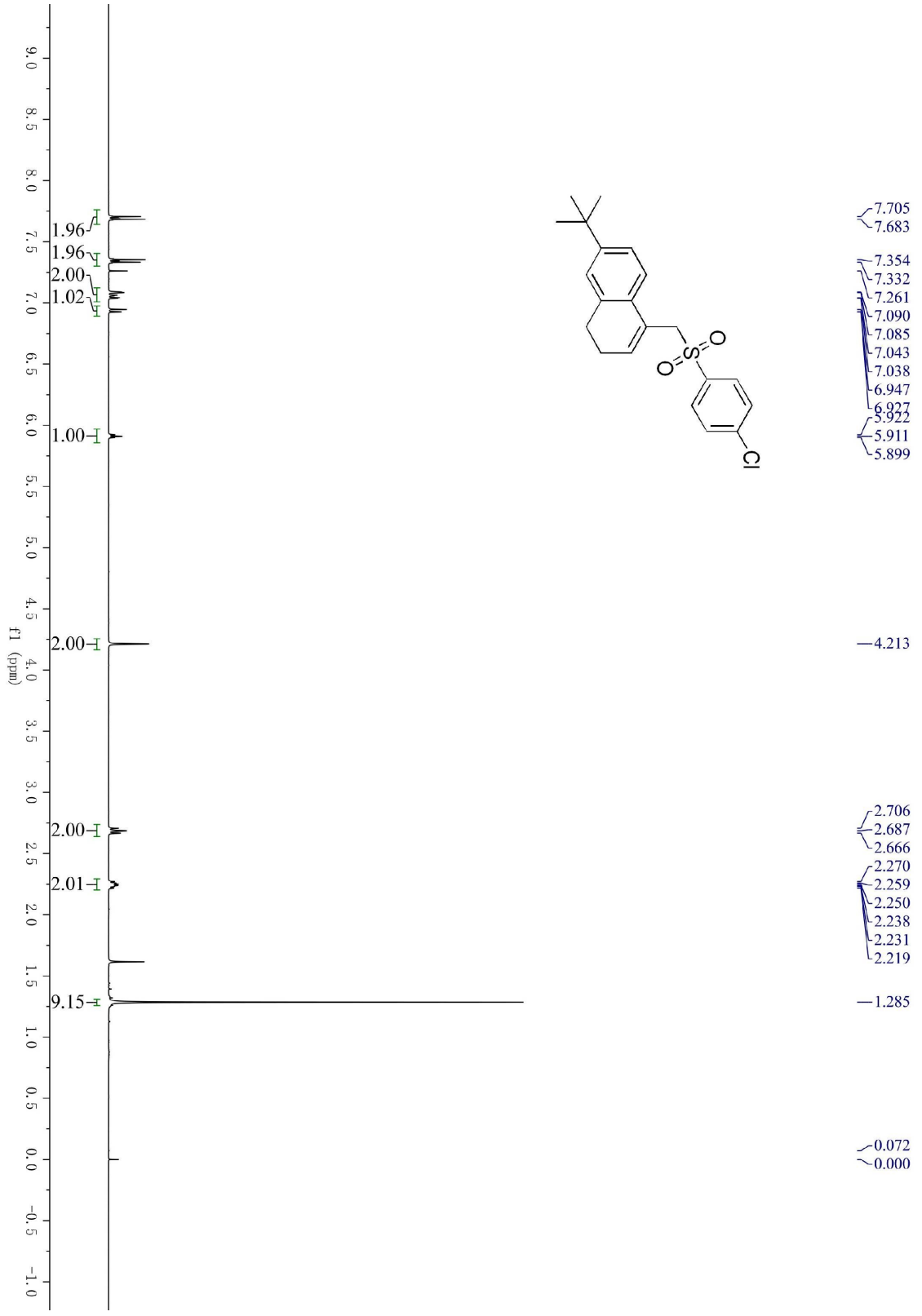

f1 (ppm)
158.345
140.256
137.249
136.680
132.735
132.353
130.153
129.834
129.739
129.078
128.595
128.561
128.025
127.544
127.407
114.606
BnO
O
S
O
Cl
77.318
77.000
76.683
69.991
57.910
43.653
32.396

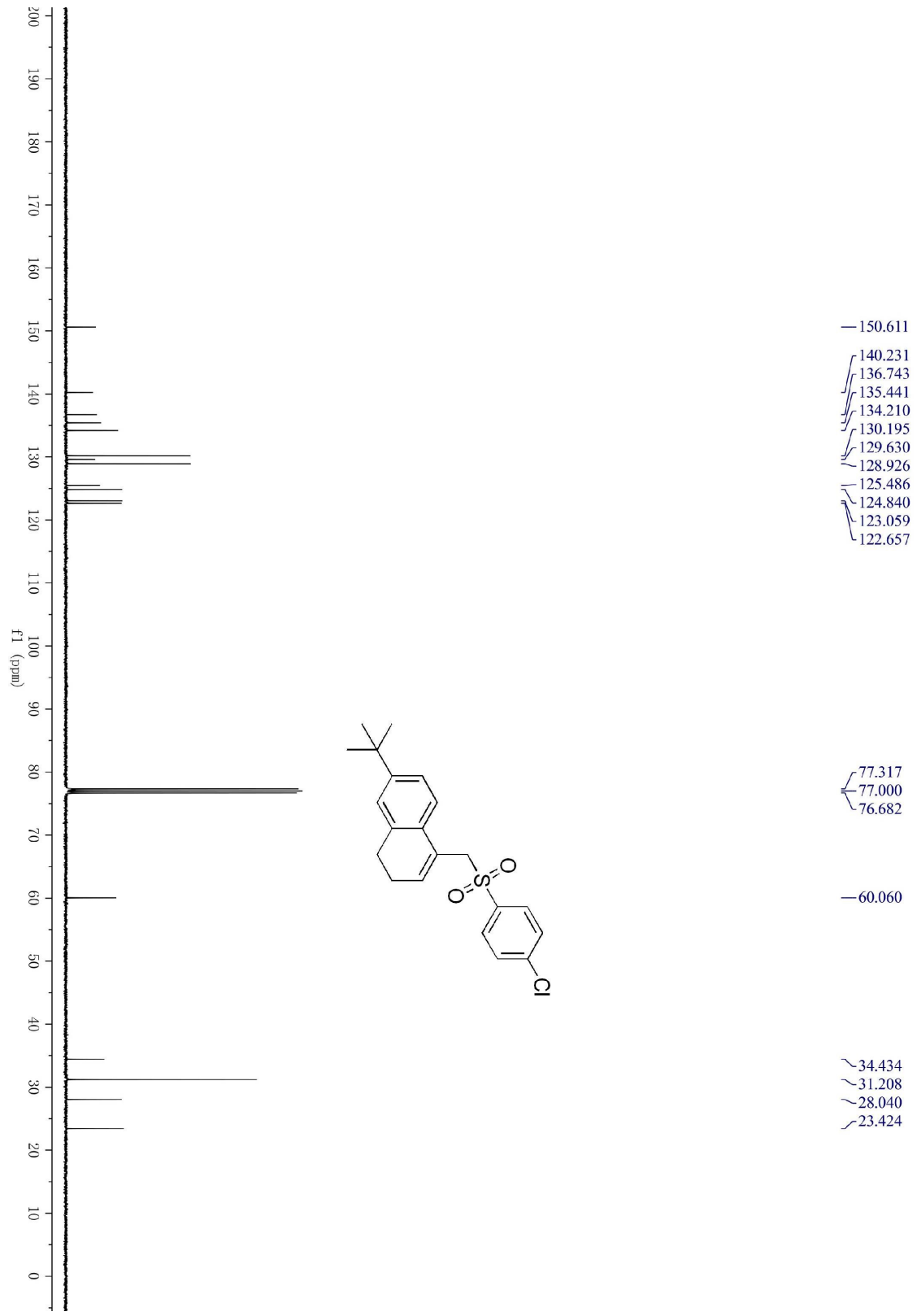
4-(((4-chlorophenyl)sulfonyl)methyl)-7-methyl-1,2-dihydronaphthalene (3ff)



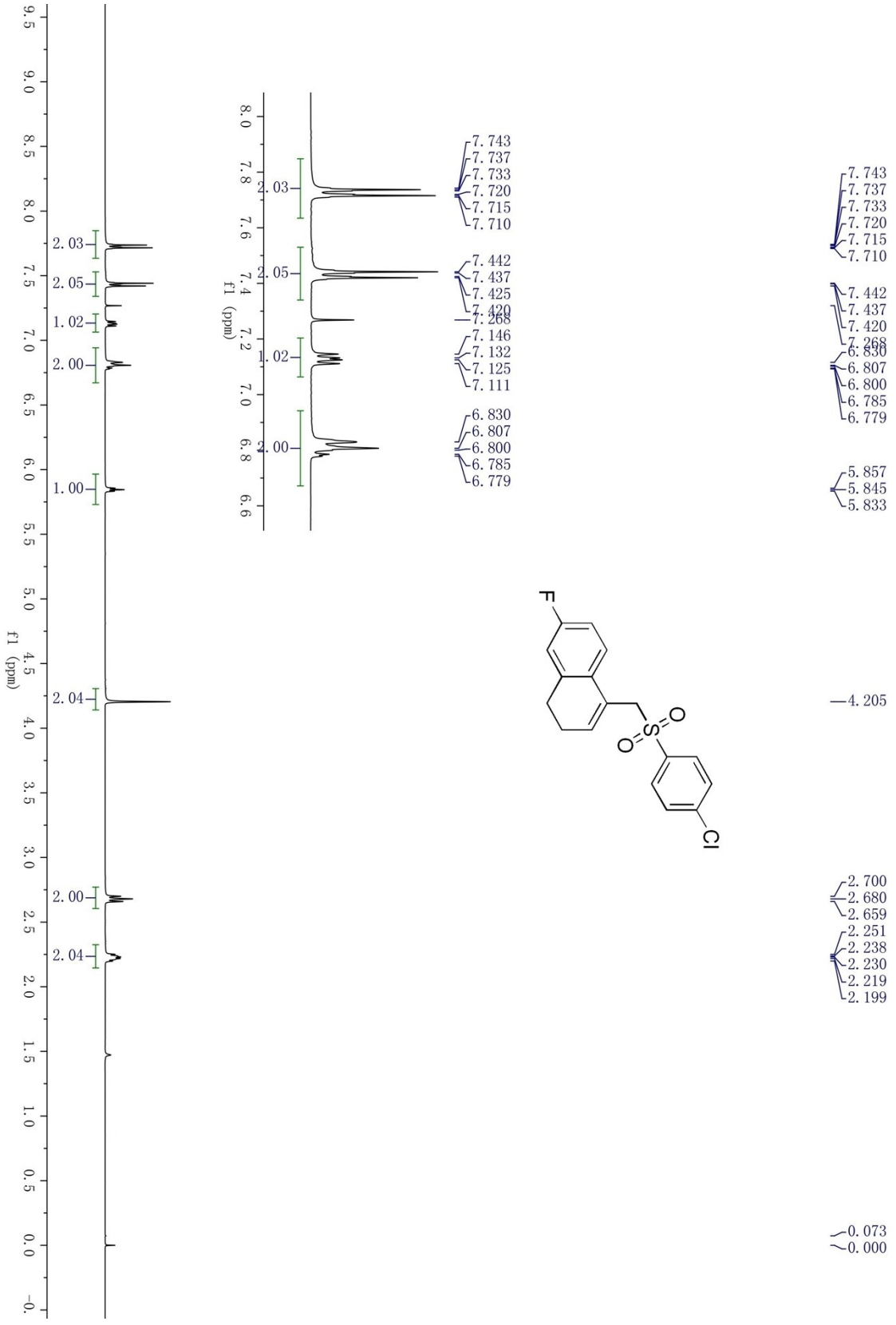

f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
O
S
O
Cl
140.273
137.380
136.628
135.776
133.937
130.133
129.607
128.952
128.524
126.877
125.559
123.027
77.318
77.000
76.682
60.056
27.657
23.305
21.039

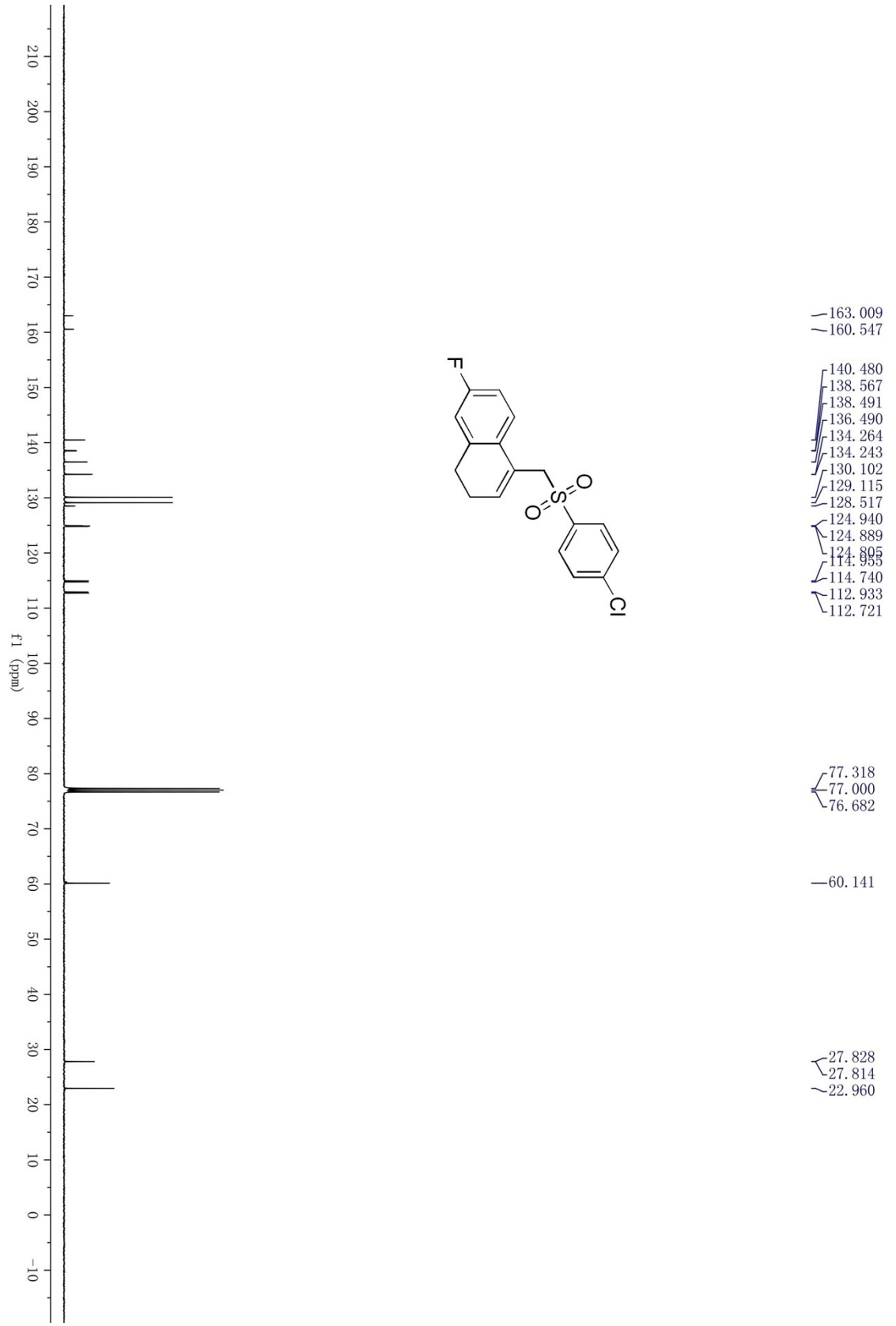
7-(*tert*-butyl)-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3gf)




f1 (ppm)
150.611
140.231
136.743
135.441
134.210
130.195
129.630
128.926
125.486
124.840
123.059
122.657
77.317
77.000
76.682
60.060
34.434
31.208
28.040
23.424
O
O
S
Cl

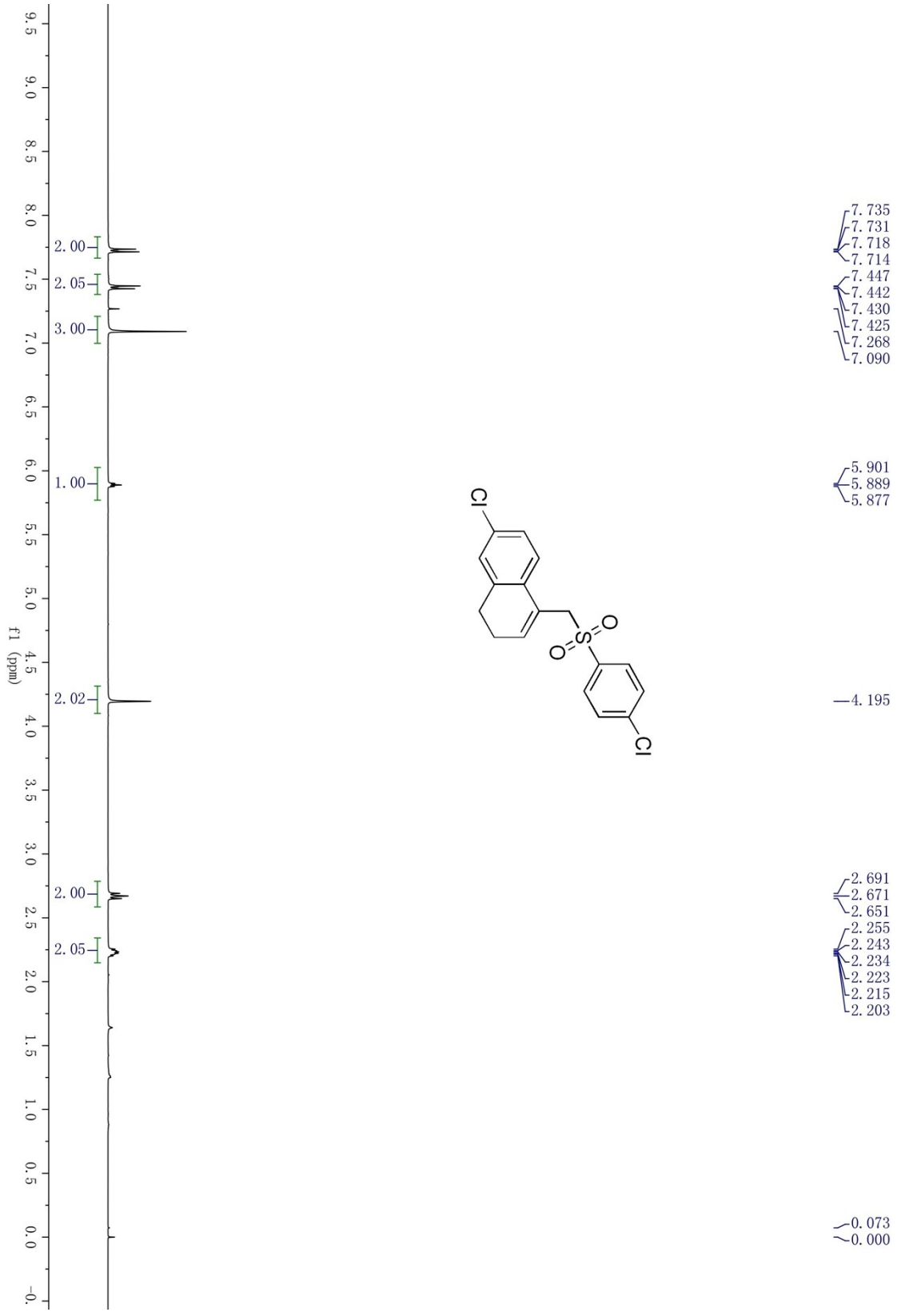
4-(((4-Chlorophenyl)sulfonyl)methyl)-7-fluoro-1,2-dihydronaphthalene (3hf)

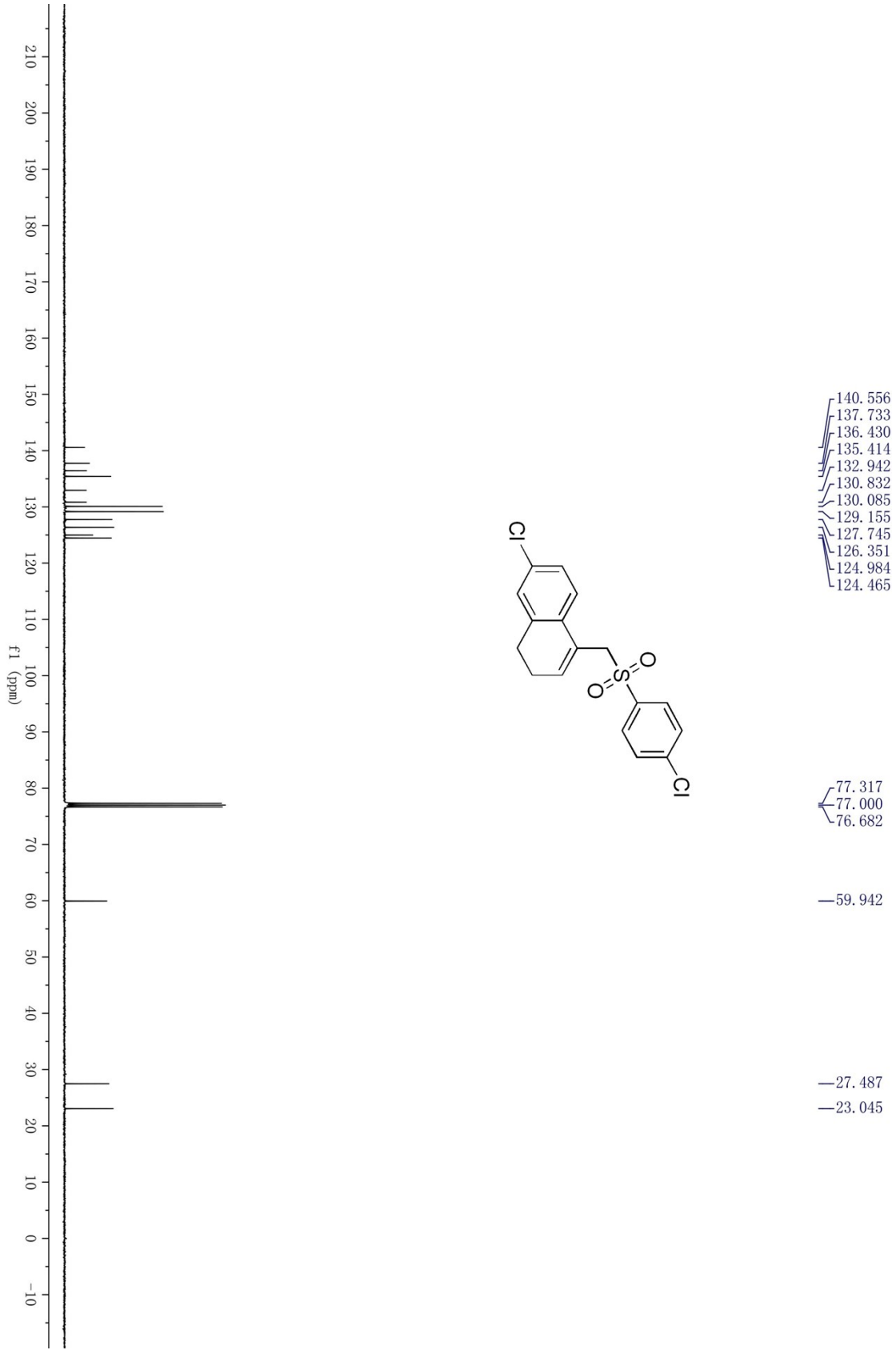



f1 (ppm)
F
O
O
S
Cl
163.009
160.547
140.480
138.567
138.491
136.490
134.264
134.243
130.102
129.115
128.517
124.940
124.889
124.805
114.955
114.740
112.933
112.721
77.318
77.000
76.682
60.141
27.828
27.814
22.960

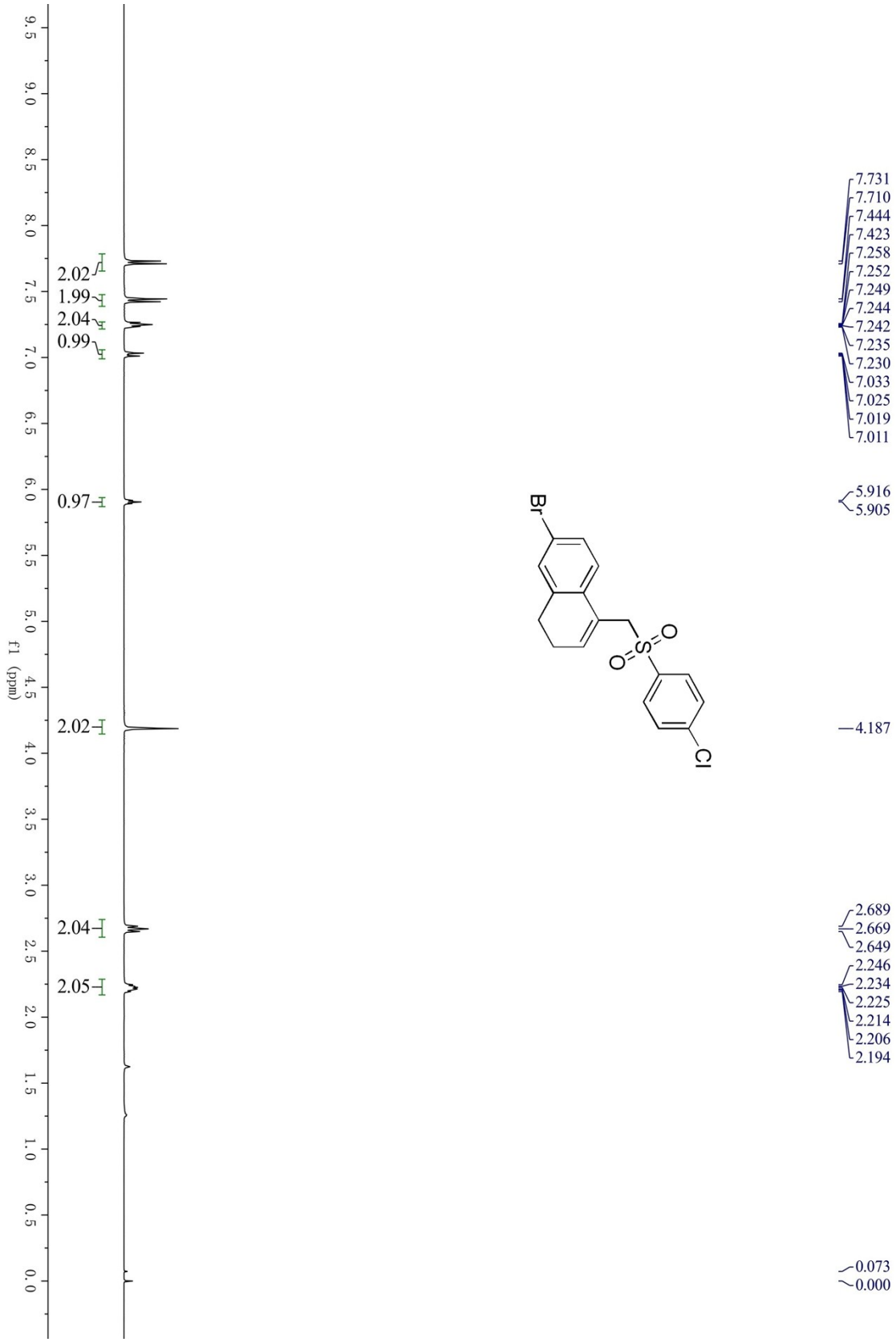
F
O
O
S
Cl
−114.101
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

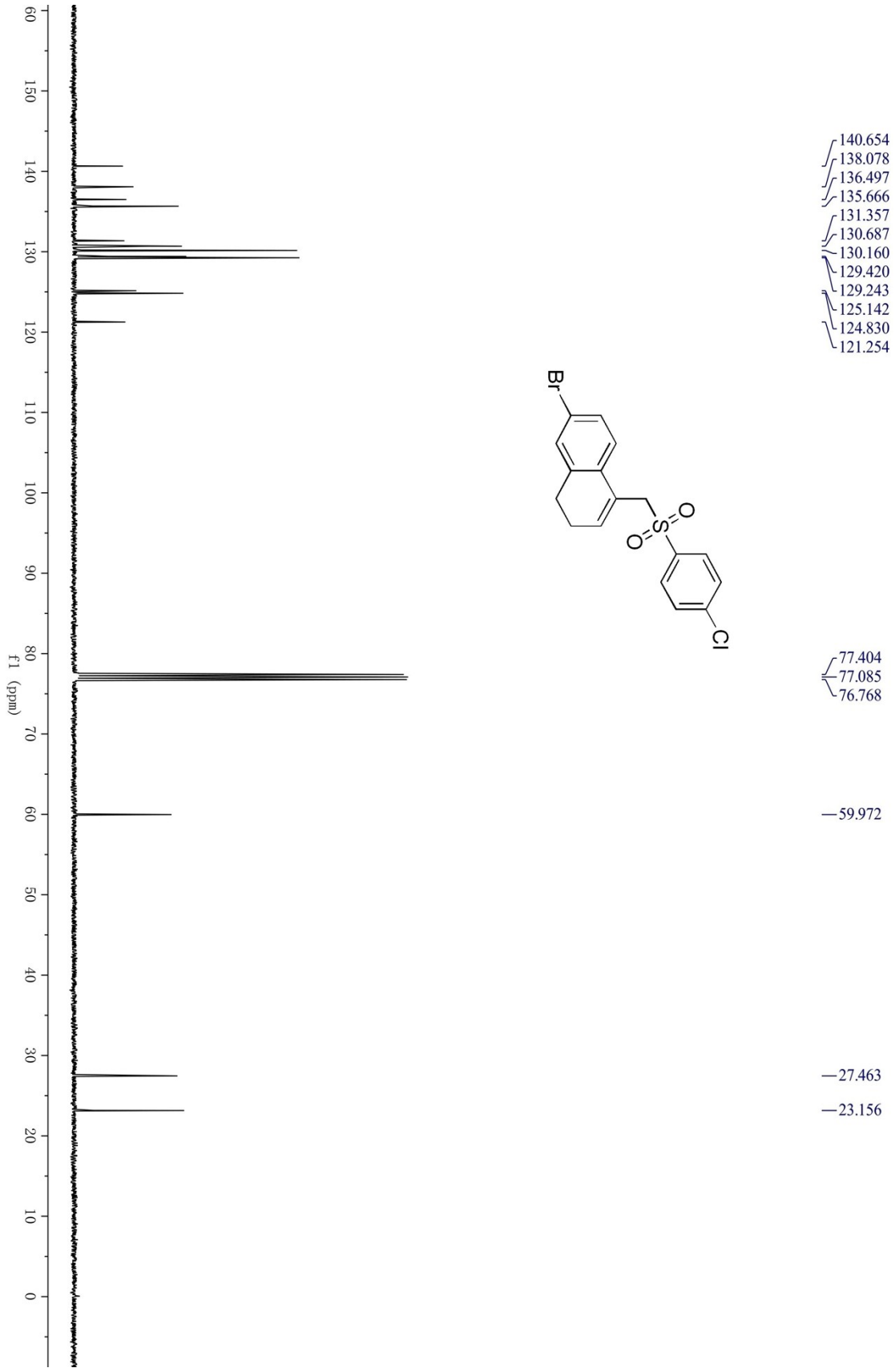
7-Chloro-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3if)



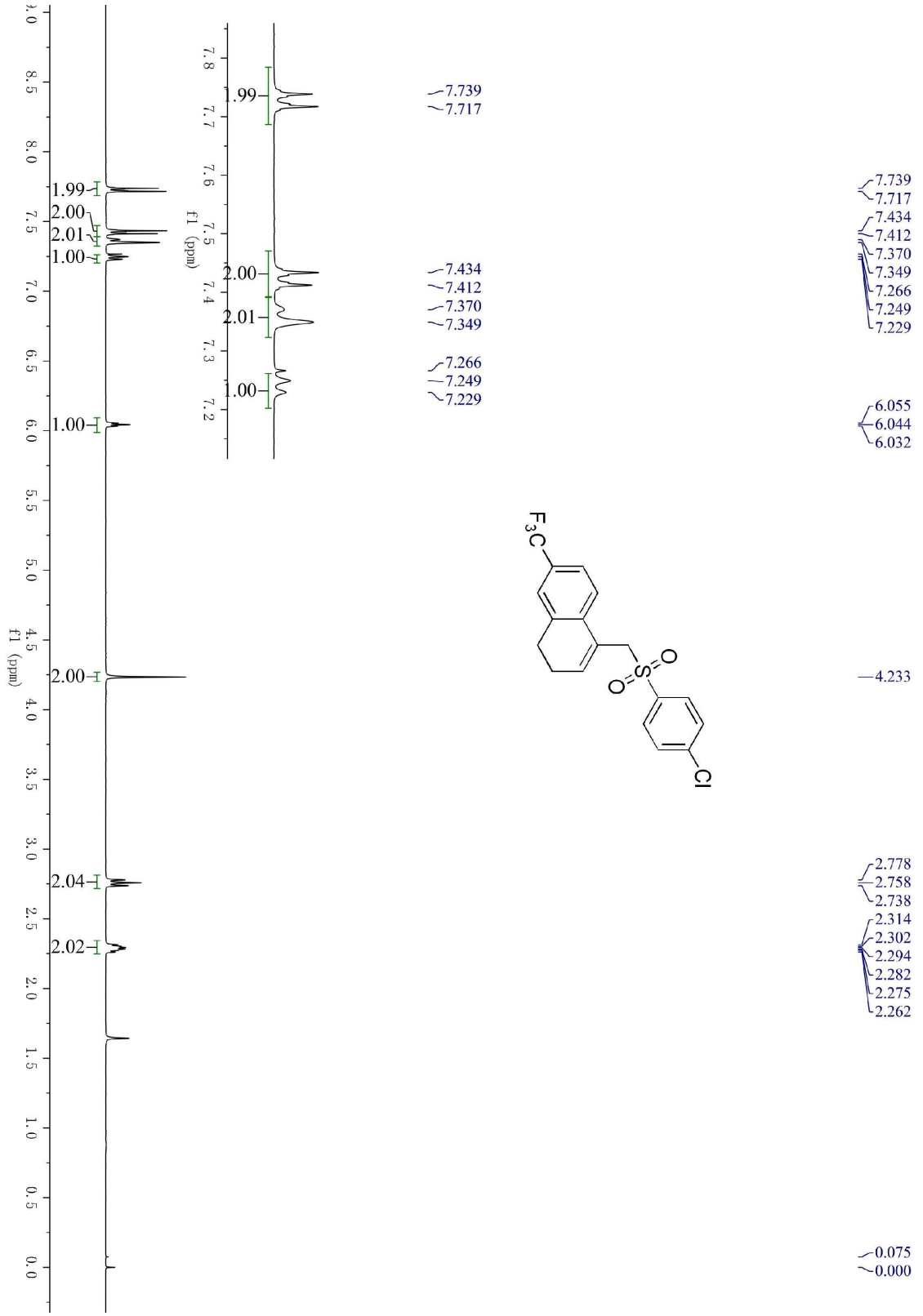

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Cl
O
O
S
Cl
140.556
137.733
136.430
135.414
132.942
130.832
130.085
129.155
127.745
126.351
124.984
124.465
77.317
77.000
76.682
59.942
27.487
23.045

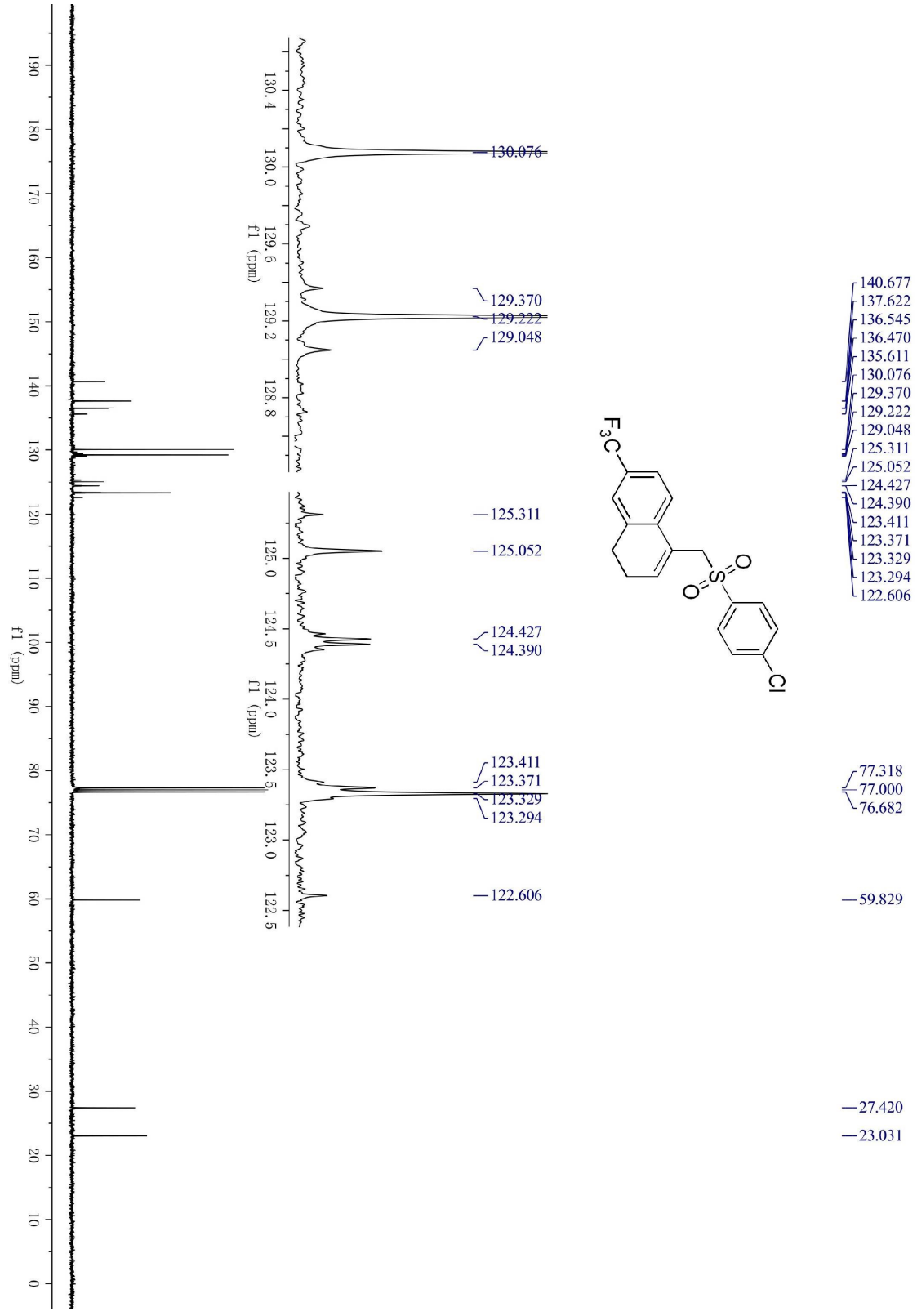
7-Bromo-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3jf)




140.654
138.078
136.497
135.666
131.357
130.687
130.160
129.420
129.243
125.142
124.830
121.254
Br
O
S
O
Cl
77.404
77.085
76.768
59.972
27.463
23.156
f1 (ppm)

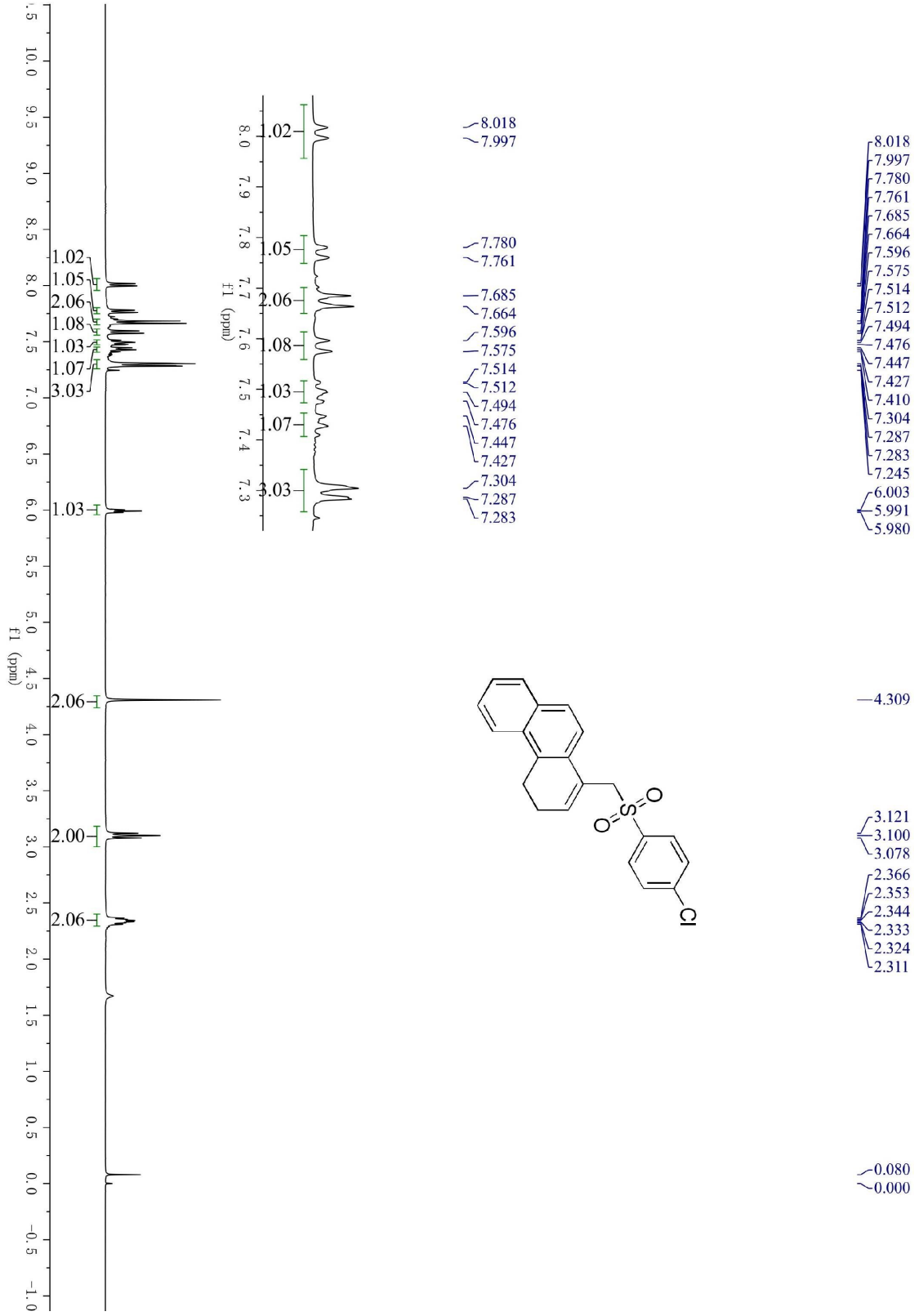
4-(((4-chlorophenyl)sulfonyl)methyl)-7-(trifluoromethyl)-1,2-dihydronaphthalene (3kf)

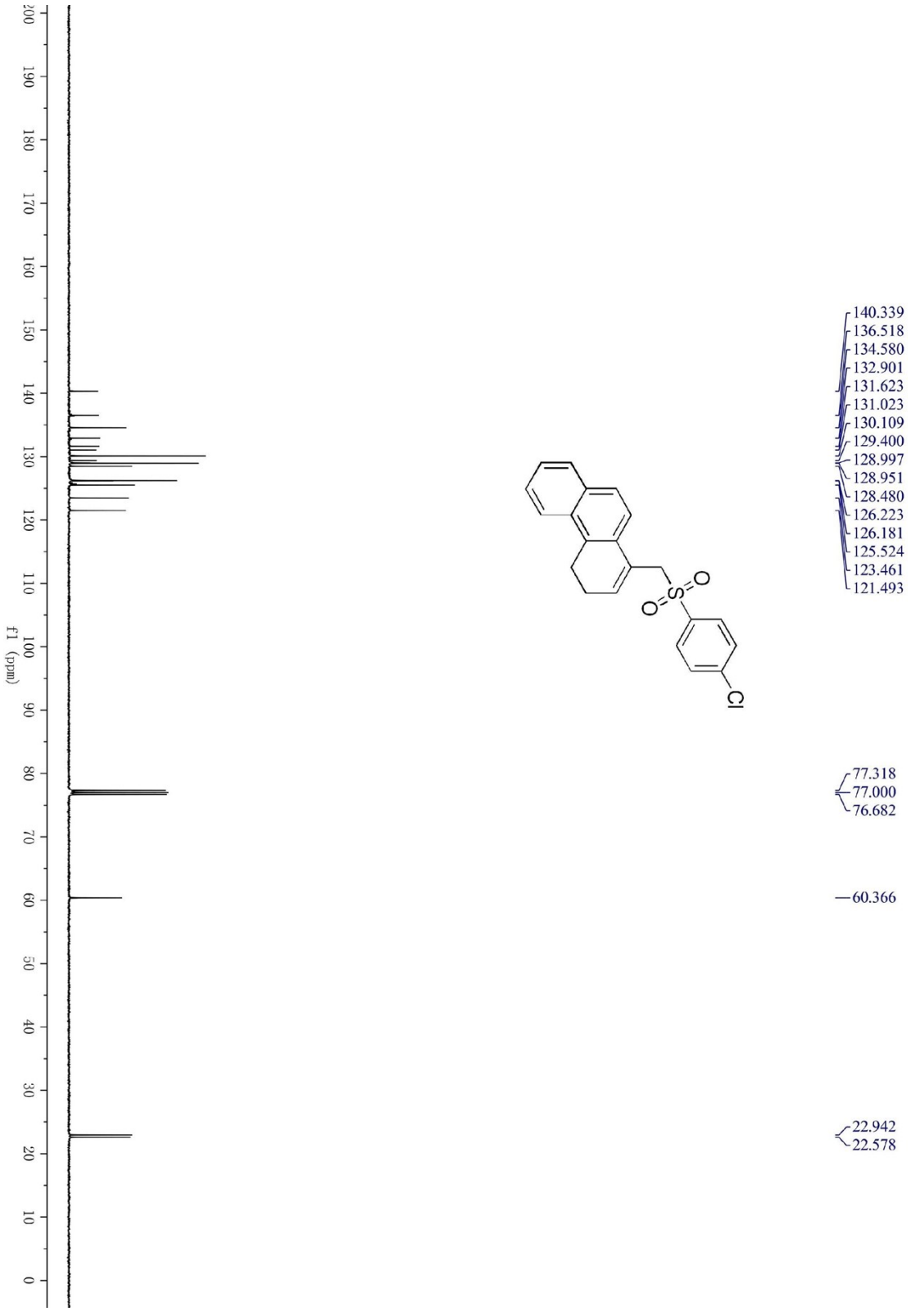



f1 (ppm)
130.076
129.370
129.222
129.048
125.311
125.052
124.427
124.390
123.411
123.371
123.329
123.294
122.606
F3C
Cl
O
O
S
140.677
137.622
136.545
136.470
135.611
130.076
129.370
129.222
129.048
125.311
125.052
124.427
124.390
123.411
123.371
123.329
123.294
122.606
77.318
77.000
76.682
59.829
27.420
23.031

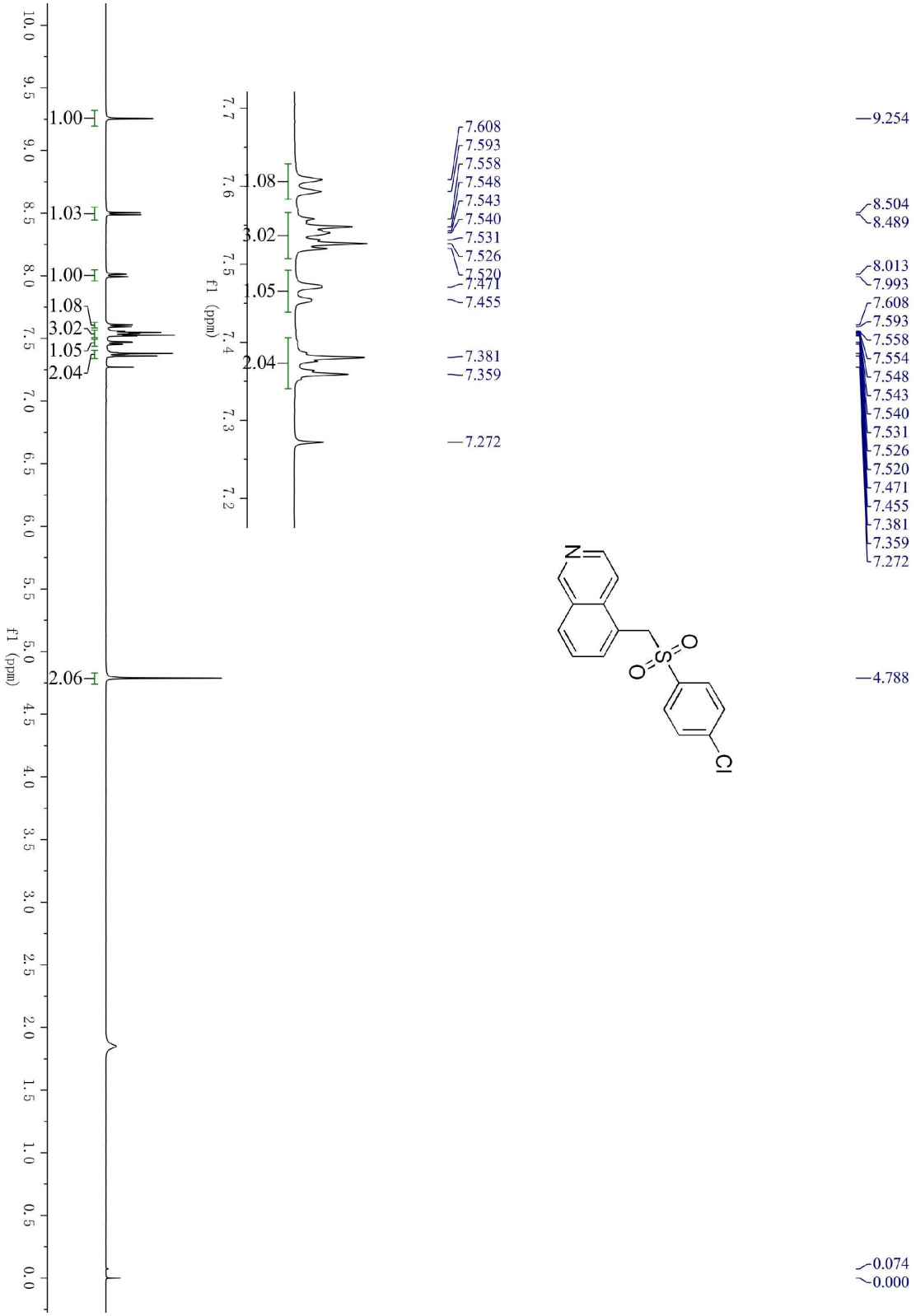
-62.610
F3C
O
S
O
Cl
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

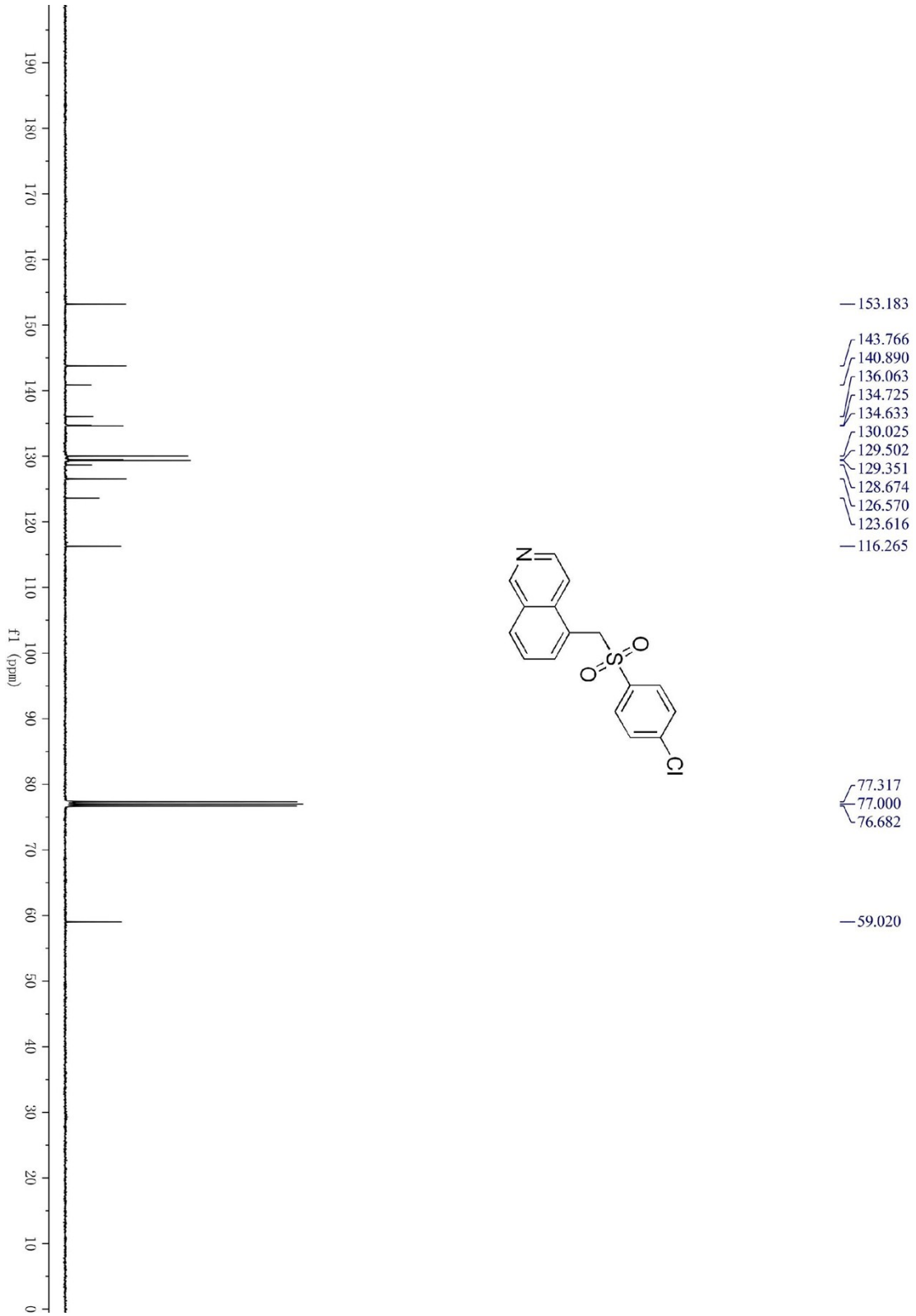
1-(((4-chlorophenyl)sulfonyl)methyl)-3,4-dihydrophenanthrene (3lf)



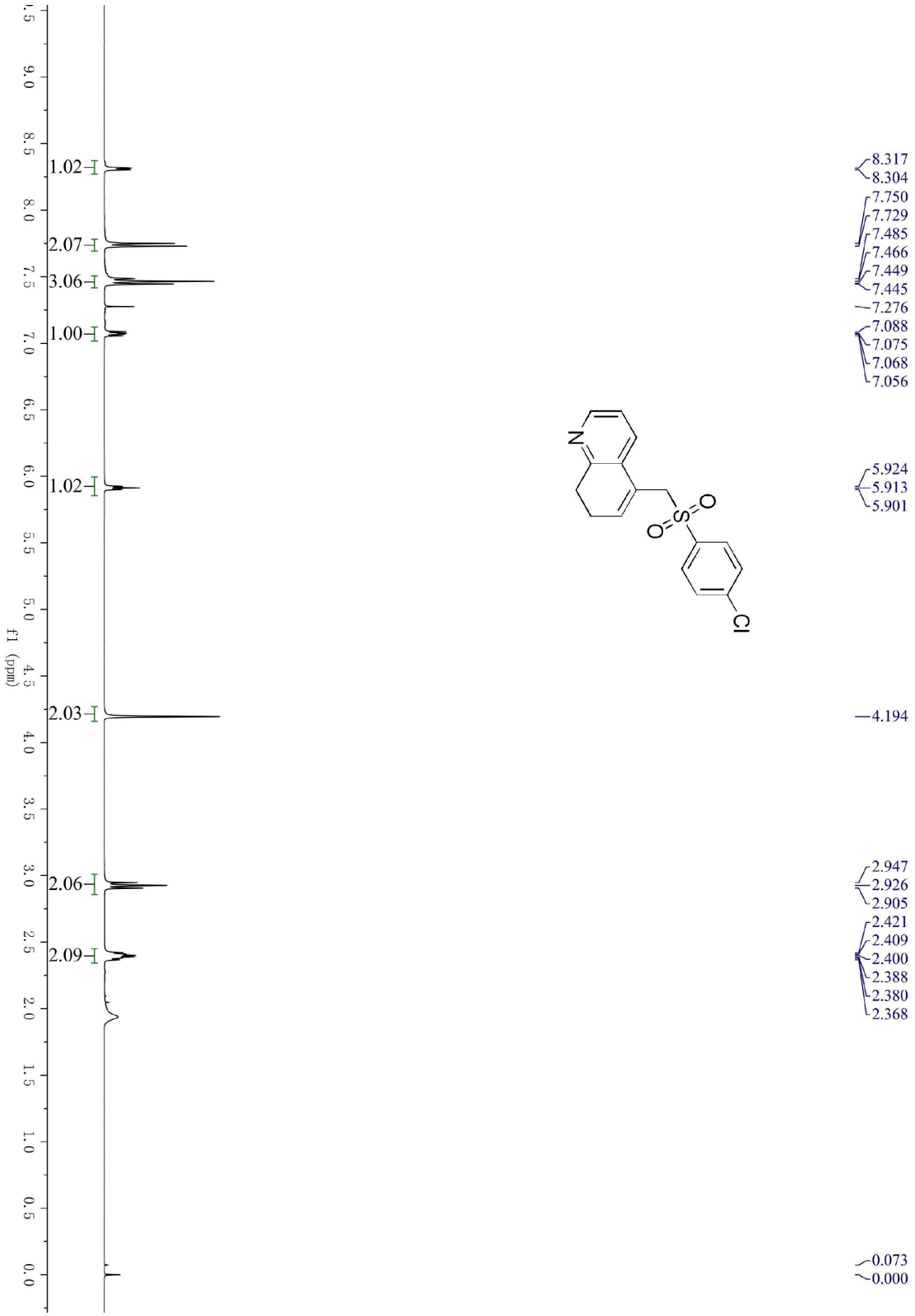

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
S
O
Cl
140.339
136.518
134.580
132.901
131.623
131.023
130.109
129.400
128.997
128.951
128.480
126.223
126.181
125.524
123.461
121.493
77.318
77.000
76.682
60.366
22.942
22.578

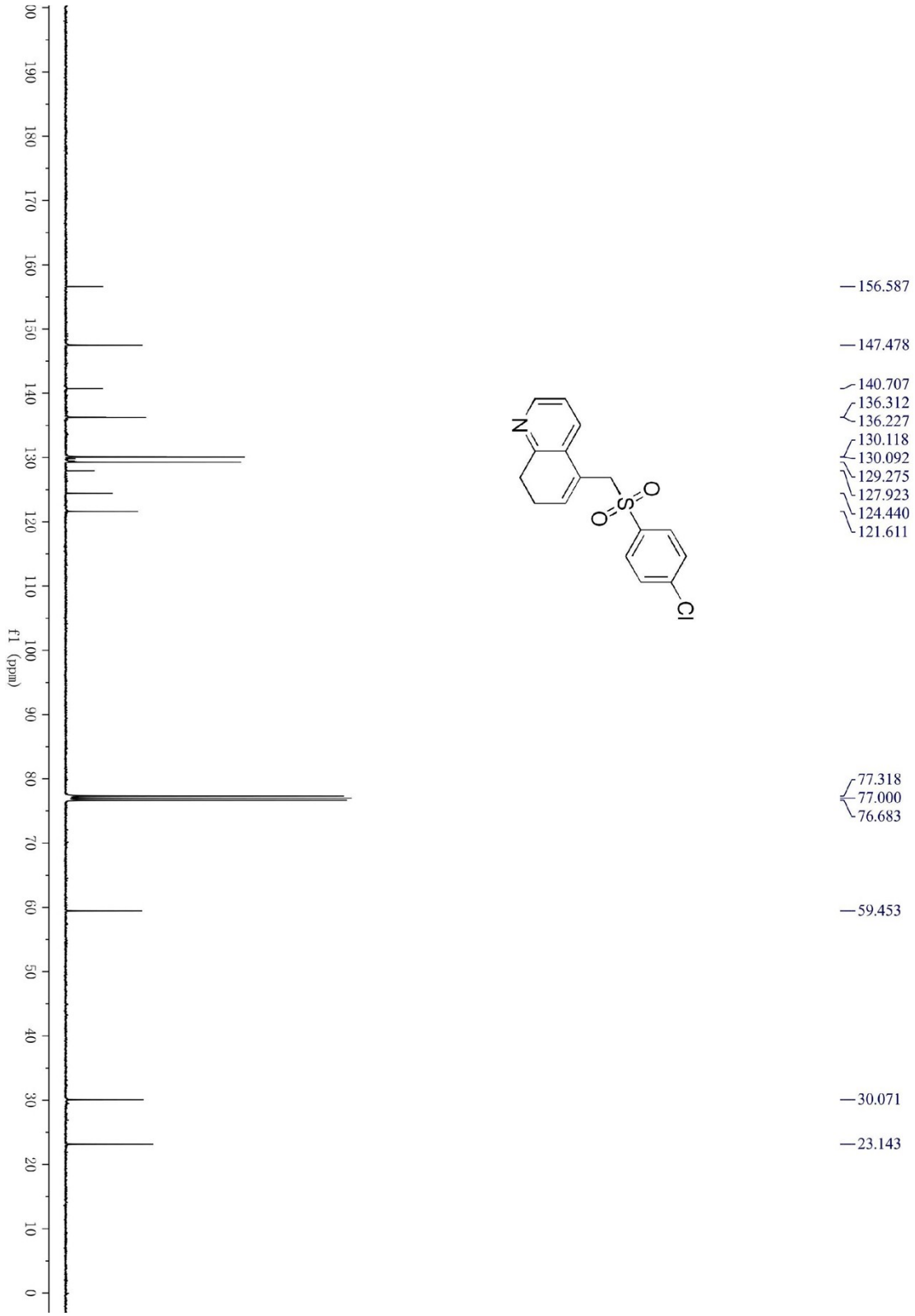
5-(((4-chlorophenyl)sulfonyl)methyl)isoquinoline (3mf)



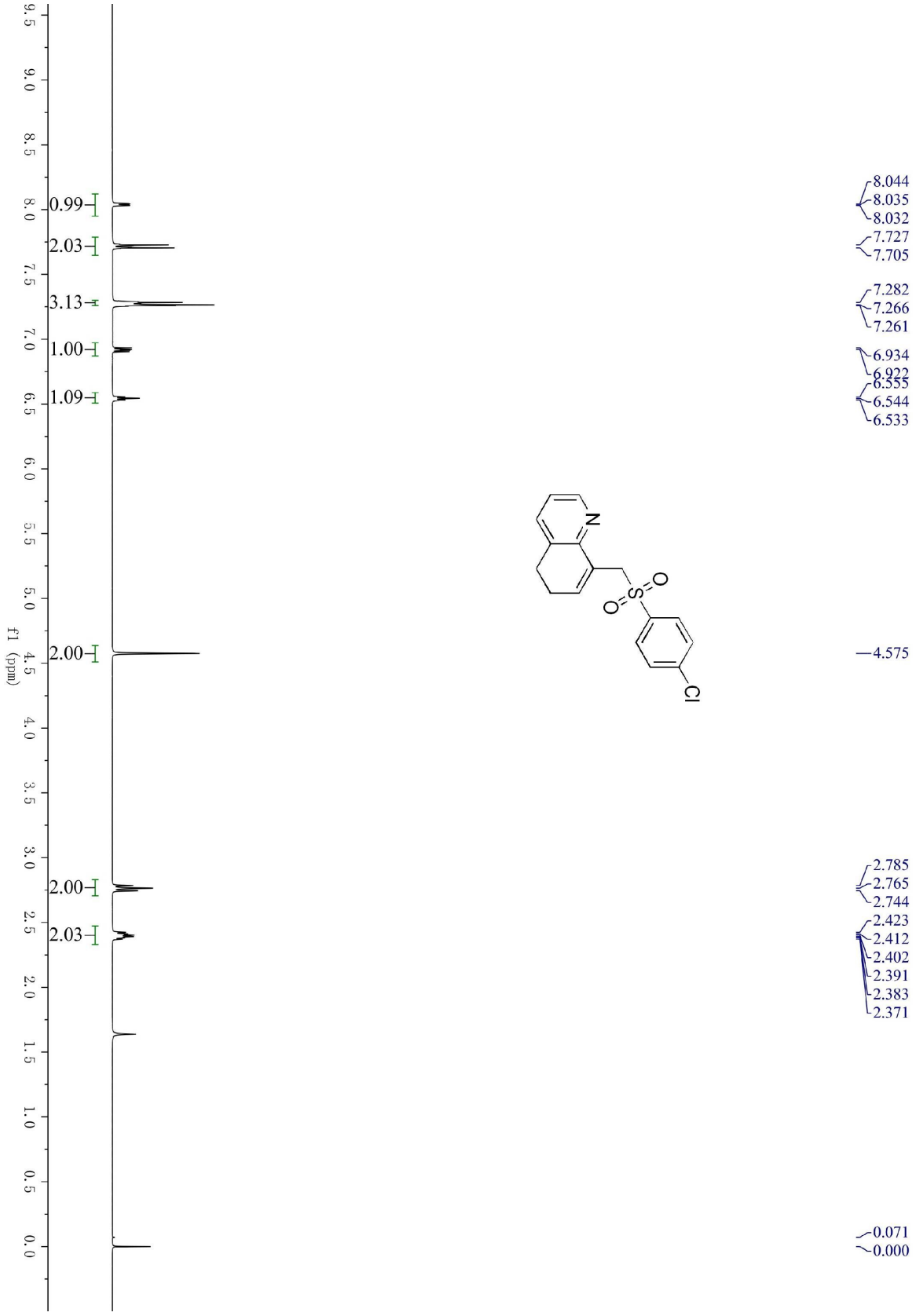

153.183
143.766
140.890
136.063
134.725
134.633
130.025
129.502
129.351
128.674
126.570
123.616
116.265
77.317
77.000
76.682
59.020
f1 (ppm)
N
O
O
S
Cl

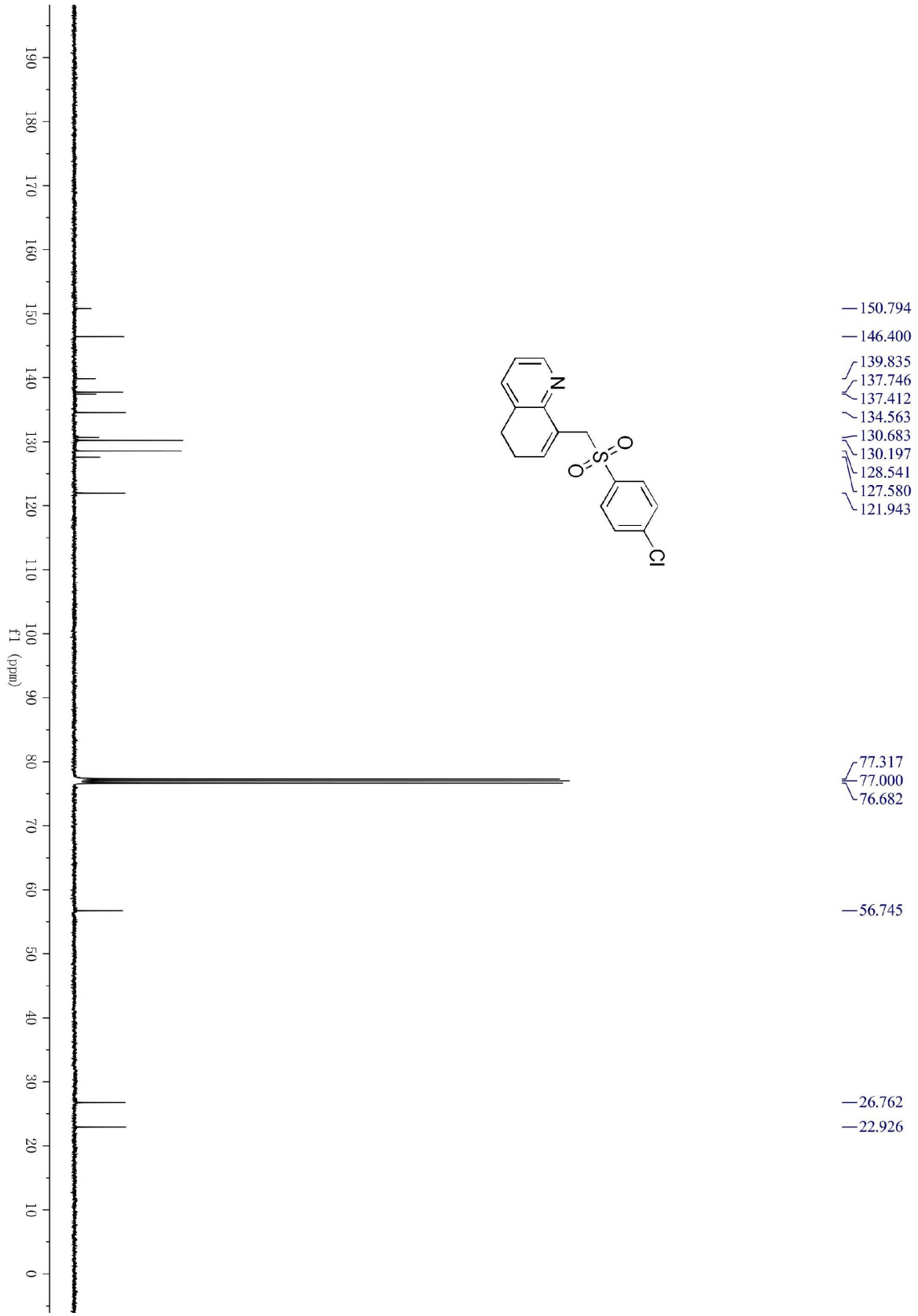
5-(((4-chlorophenyl)sulfonyl)methyl)-7,8-dihydroquinoline (3nf)



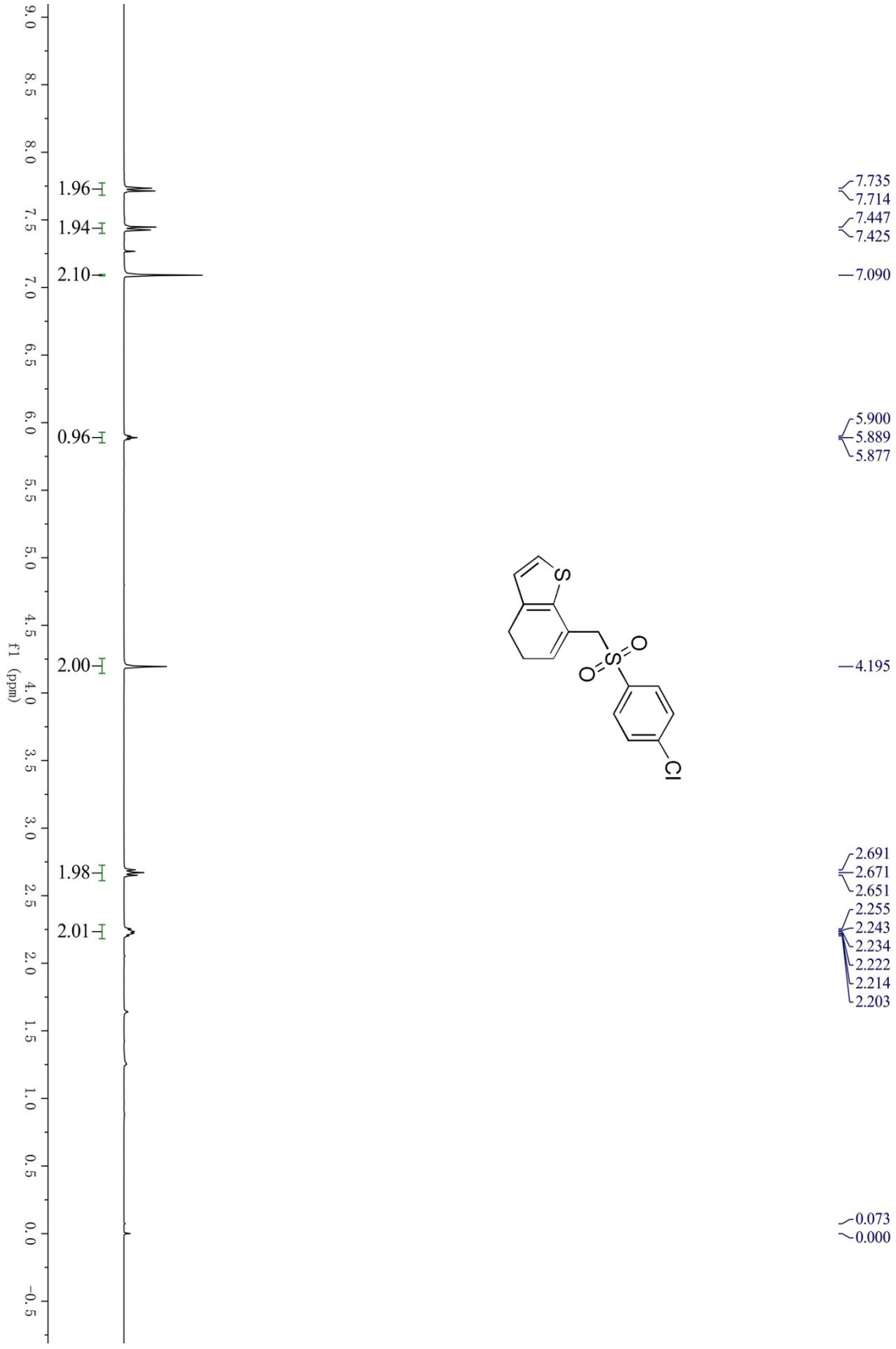

f1 (ppm)
156.587
147.478
140.707
136.312
136.227
130.118
130.092
129.275
127.923
124.440
121.611
77.318
77.000
76.683
59.453
30.071
23.143
N
O
O
S
Cl

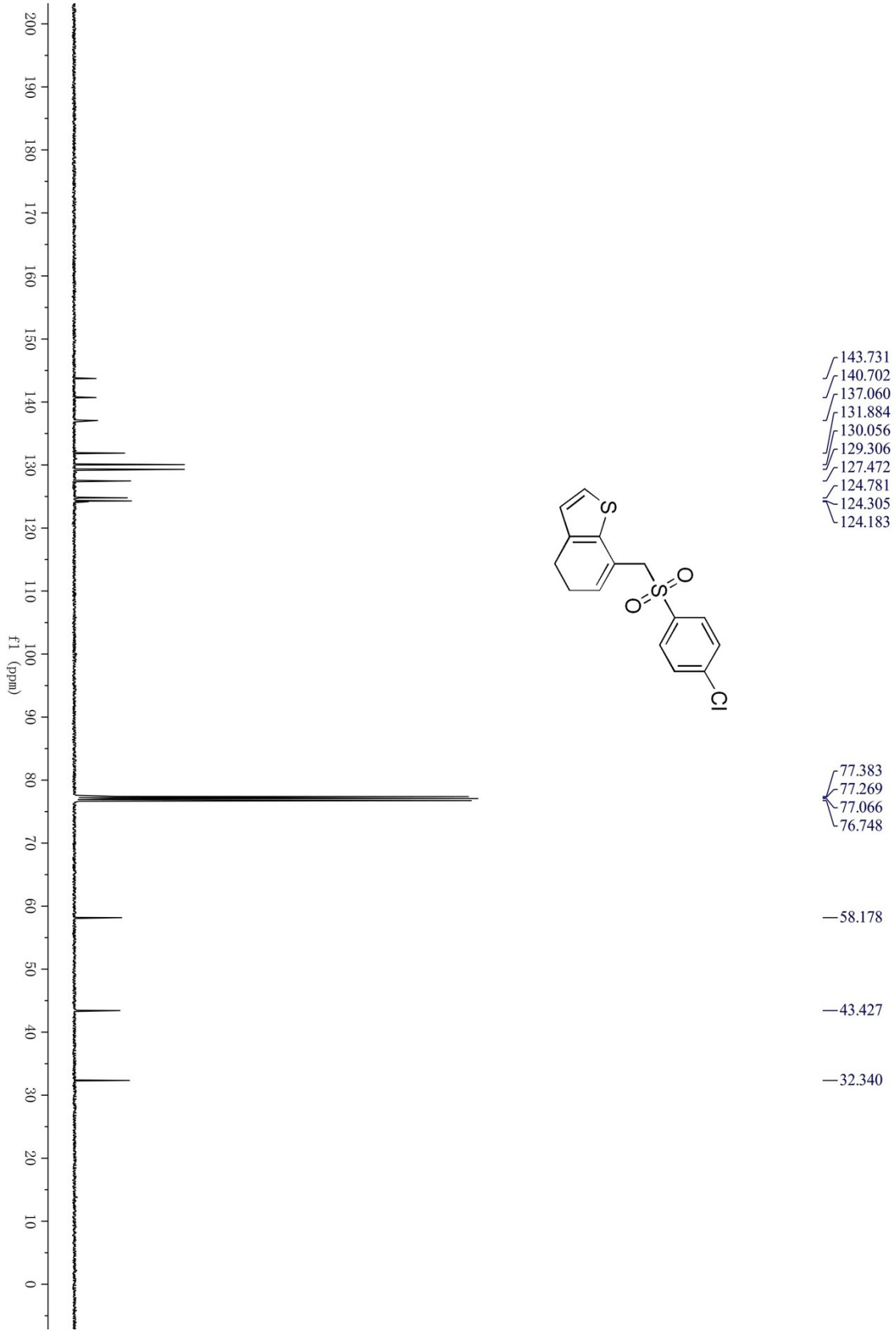
8-(((4-chlorophenyl)sulfonyl)methyl)-5,6-dihydroquinoline (3of)



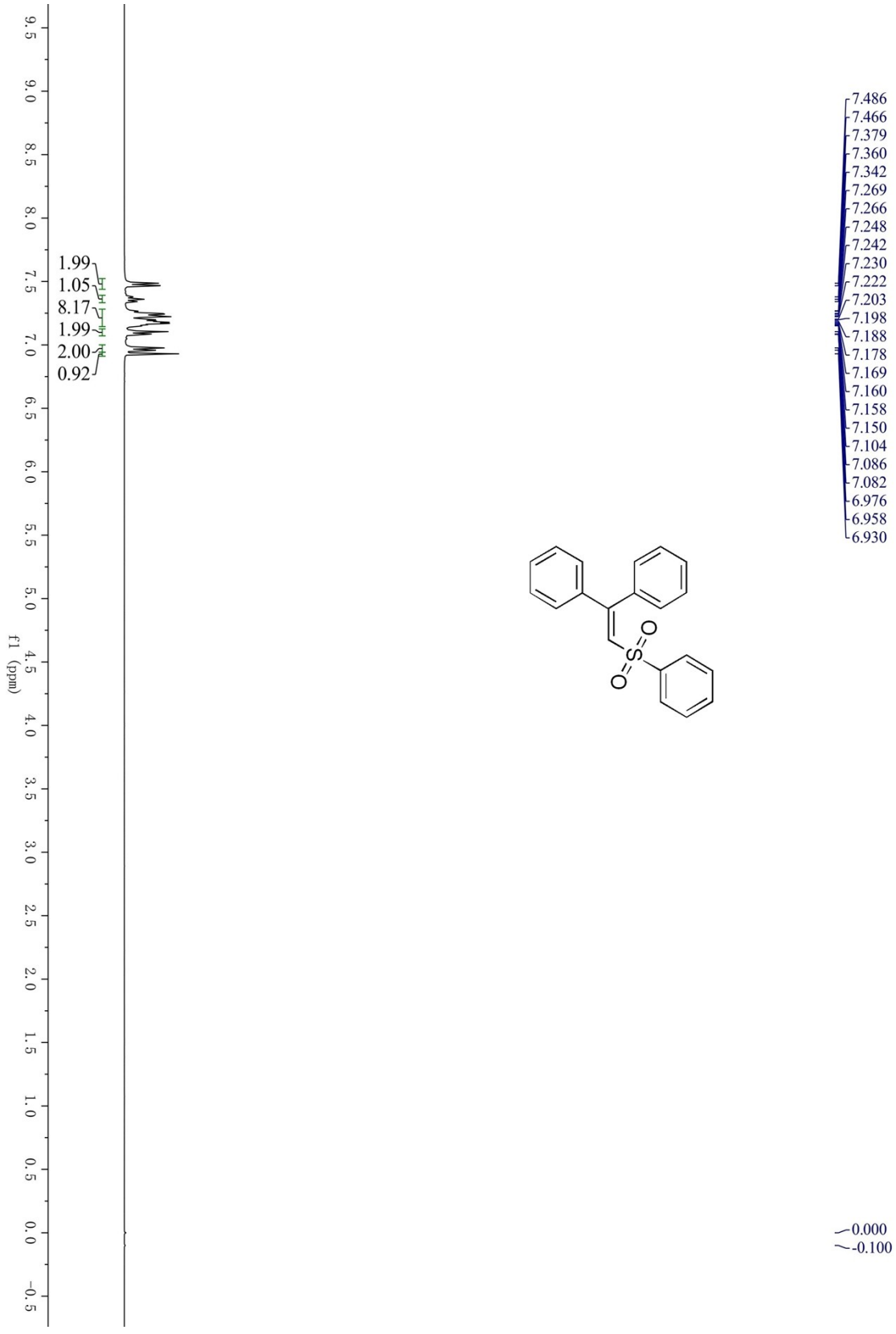

150.794
146.400
139.835
137.746
137.412
134.563
130.683
130.197
128.541
127.580
121.943
77.317
77.000
76.682
56.745
26.762
22.926
f1 (ppm)
N
O=S=O
Cl

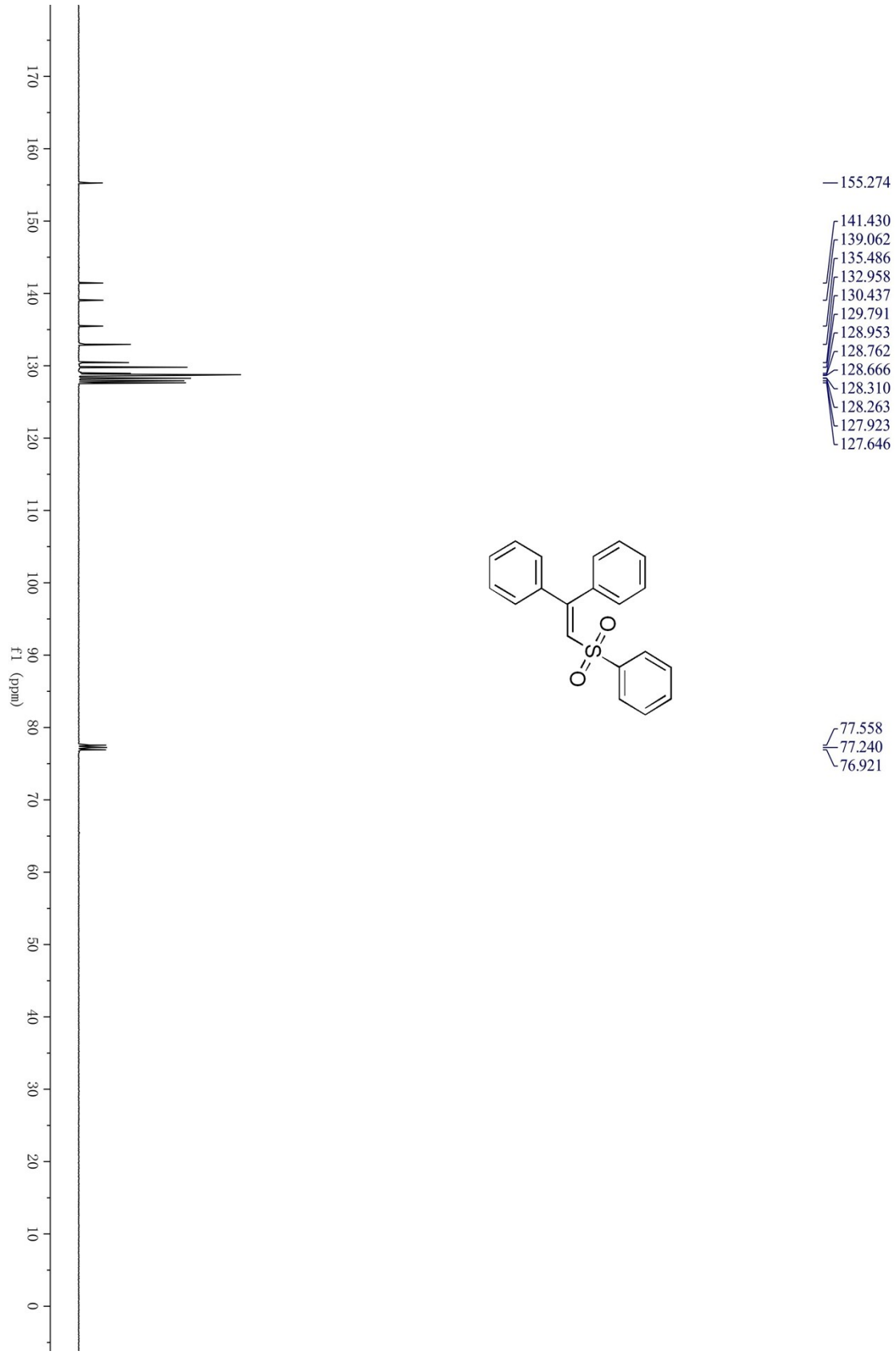
7-(((4-Chlorophenyl)sulfonyl)methyl)-4,5-dihydrobenzo[b]thiophene (3pf)




143.731
140.702
137.060
131.884
130.056
129.306
127.472
124.781
124.305
124.183
77.383
77.269
77.066
76.748
58.178
43.427
32.340
f1 (ppm)
S
O
O
S
Cl

(2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (4)




155.274
141.430
139.062
135.486
132.958
130.437
129.791
128.953
128.762
128.666
128.310
128.263
127.923
127.646
77.558
77.240
76.921
f1 (ppm)