A palladium-catalyzed coupling reaction of aryl nonaflates, sulfur dioxide and hydrazines

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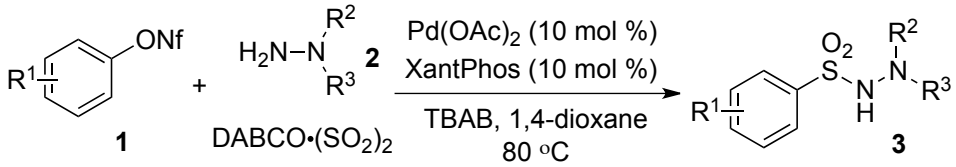
Supporting Information

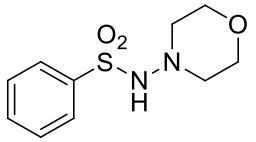
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the palladium-catalyzed coupling reaction of aryl nonaflates **1**, sulfur dioxide, and hydrazines **2***

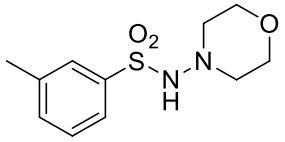


Aryl nonaflate **1** (0.3 mmol) and hydrazine **2** (0.6 mmol, 2 equiv.) was added to a solution of DABCO•$(SO_2)_2$ (0.3 mmol, 1 equiv.), $Pd(OAc)_2$ (0.03 mmol, 10 mol %), XantPhos (0.03 mmol, 10 mol %), and TBAB (0.6 mmol, 2 equiv.) in 1,4-dioxane (2.5 mL) under N_2 atmosphere. The mixture was stirred at 80 °C for 8-10 hours. After completion of the reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatograph (EaOAc/*n*-hexane, 1: 2) to give the desired *N*-aminosulfonamide **3**.



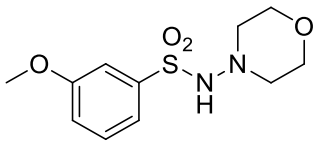
N-Morpholinobenzenesulfonamide (**3a**)[1]

Yield: 70%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, *J* = 4.6 Hz, 4H), 3.60 (t, *J* = 4.6 Hz, 4H), 3.84 (s, 1H), 7.53 (t, *J* = 7.5 Hz), 7.61 (t, *J* = 7.4 Hz), 7.99 (d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.6, 66.6, 128.1, 128.8, 133.1, 138.6.



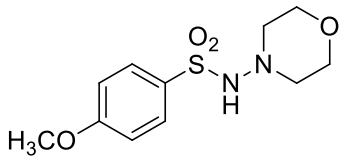
3-Methyl-*N*-morpholinobenzenesulfonamide (**3b**)[1]

Yield: 47%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.62 (t, *J* = 4.4 Hz, 4H), 3.61 (t, *J* = 4.4 Hz, 4H), 5.58 (s, 1H), 7.41(d, *J* = 4.8 Hz, 2H), 7.77-7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 56.7, 66.6, 125.2, 128.4, 128.7, 133.9, 138.4, 139.0; HRMS (ESI) calcd for $C_{11}H_{16}N_2O_3S$: 279.0774 (M + Na^+), found: 279.0775.



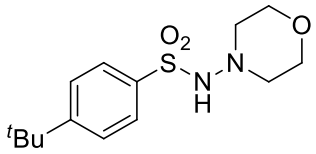
3-Methoxy-*N*-morpholinobenzenesulfonamide (**3c**)[1]

Yield: 72%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 4.6 Hz, 4H), 3.62 (t, *J* = 4.6 Hz, 4H), 3.87 (s, 3H), 5.86 (s, 1H), 7.12-7.15 (m, 1H), 7.43 (t, *J* = 8.0 Hz，1H), 7.49 (t, *J* = 2.0 Hz， 1H)，7.56 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 56.6, 66.6, 112.6, 119.6, 120.2, 129.9, 139.8, 159.7.



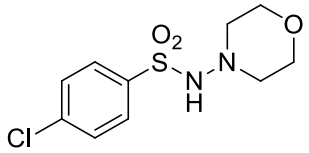
4-Methoxy-*N*-morpholinobenzenesulfonamide (**3d**)[1]

Yield: 63%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (t, *J* = 4.4 Hz, 4H), 3.62 (t, *J* = 4.3 Hz, 4H), 3.89 (s, 3H), 5.56 (s, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.7, 114.0, 128.8, 130.3, 163.2.



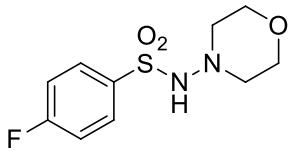
4-(*tert*-Butyl)-*N*-morpholinobenzenesulfonamide **(3e)**[1]

Yield: 67%, brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.64 (t, *J* = 4.6 Hz, 4H), 3.61 (t, *J* = 4.6 Hz, 4H), 5.75 (s, 1H), 7.53 (d, J = 8.6 Hz), 7.89 (d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0, 35.2, 56.7, 66.6, 125.8, 128.0, 135.6, 157.0.



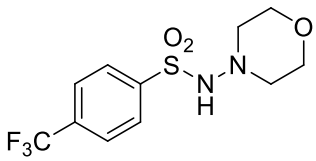
4-Chloro-*N*-morpholinobenzenesulfonamide (**3f**)[1]

Yield: 48%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (t, *J* = 4.5 Hz, 4H), 3.62 (t, *J* = 4.6 Hz, 4H), 5.53 (s, 1H), 7.50(d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.7, 66.6, 125.8, 127.9, 129.1, 129.6.



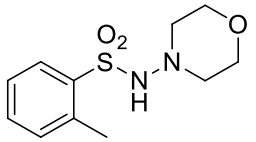
4-Fluoro-*N*-morpholinobenzenesulfonamide (**3g**)[1]

Yield: 36%, brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 4.5 Hz, 4H), 3.62 (t, *J* = 4.4 Hz, 4H), 5.52 (s, 1H), 7.21(t, *J* = 8.5 Hz, 2H), 7.98-8.01 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) *δ* 56.3, 66.4, 116.7 (d, J_F = 22.9 Hz), 131.1 (d, J_F = 9.5 Hz), 136.1, 164.9 (d, J_F = 250.7 Hz).



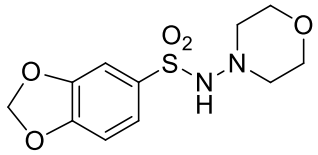
N-Morpholino-4-(trifluoromethyl)benzenesulfonamide (**3h**)[1]

Yield: 40%, brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (t, *J* = 4.5 Hz, 4H), 3.63 (t, *J* = 4.5 Hz, 4H), 5.61 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.3, 134.9 (q, *J* = 33.4 Hz), 128.6, 126.0 (d, *J* = 3.1 Hz), 124.5, 66.5, 56.8.



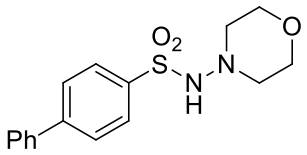
2-Methyl-*N*-morpholinobenzenesulfonamide (**3i**)[1]

Yield: 45%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (t, *J* = 4.6 Hz, 4H), 2.70 (s, 3H), 3.58 (t, *J* = 4.5 Hz, 4H), 5.52 (s, 1H), 7.30-7.36 (m, 2H), 7.47-7.50 (m, 1H), 8.07 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 56.7, 66.5, 126.1, 131.0, 132.3, 133.2, 136.4, 138.0.



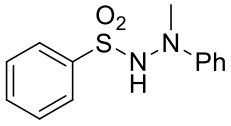
N-Morpholinobenzo[d][1,3]dioxole-5-sulfonamide (**3j**)

Yield: 40%, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (t, *J* = 4.6 Hz, 4H), 3.64 (t, *J* = 4.6 Hz, 4H), 5.42 (s, 1H), 6.10 (s, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.54 (dd, J_1 = 1.7 Hz, J_2 = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.8, 66.6, 102.3, 108.1, 108.3, 116.2, 124.0, 156.0, 156.6; HRMS (ESI) calcd for $C_{11}H_{14}N_2O_5S$: 287.0696 ($M + H^+$), found: 287.0694.



N-Morpholino-[1,1'-biphenyl]-4-sulfonamide (**3k**)[1]

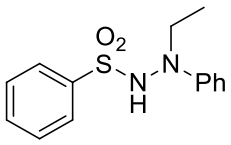
Yield: 40%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (t, *J* = 4.6 Hz, 4H), 3.63 (t, *J* = 4.6 Hz, 4H), 5.70 (s, 1H), 7.41-7.45 (m, 1H), 7.47-7.51 (m, 2H), 7.62-7.64 (m, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.8, 66.6, 127.3, 127.4, 128.6, 128.6, 129.1, 137.2, 139.1, 146.0.



N'-Methyl-*N'*-phenylbenzenesulfonohydrazide (**3l**)[1]

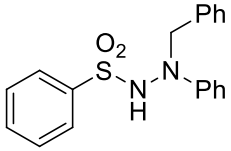
Yield: 50%, brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 3H), 6.36 (s, 1H), 6.84 (dd, J_1 = 8.0 Hz, J_2 = 11.0 Hz, 3H), 7.15 (t, *J* = 8.3 Hz, 2H)7.48 (t, *J* = 7.7 Hz,

2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.7, 114.4, 120.9, 128.1, 128.9, 129.1, 133.3, 138.5, 149.6.



N′-Ethyl-*N′*-phenylbenzenesulfonohydrazide (**3m**)[1]

Yield: 51%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.1 Hz, 3H), 3.41-3.49 (m, 2H), 6.67 (s, 1H), 6.80 (dd, J_1 = 7.6 Hz, J_2 = 12.6 Hz, 3H), 7.12 (t, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.5, 49.2, 113.6, 115.1, 120.8, 128.1, 128.9, 133.2, 138.7, 147.6.

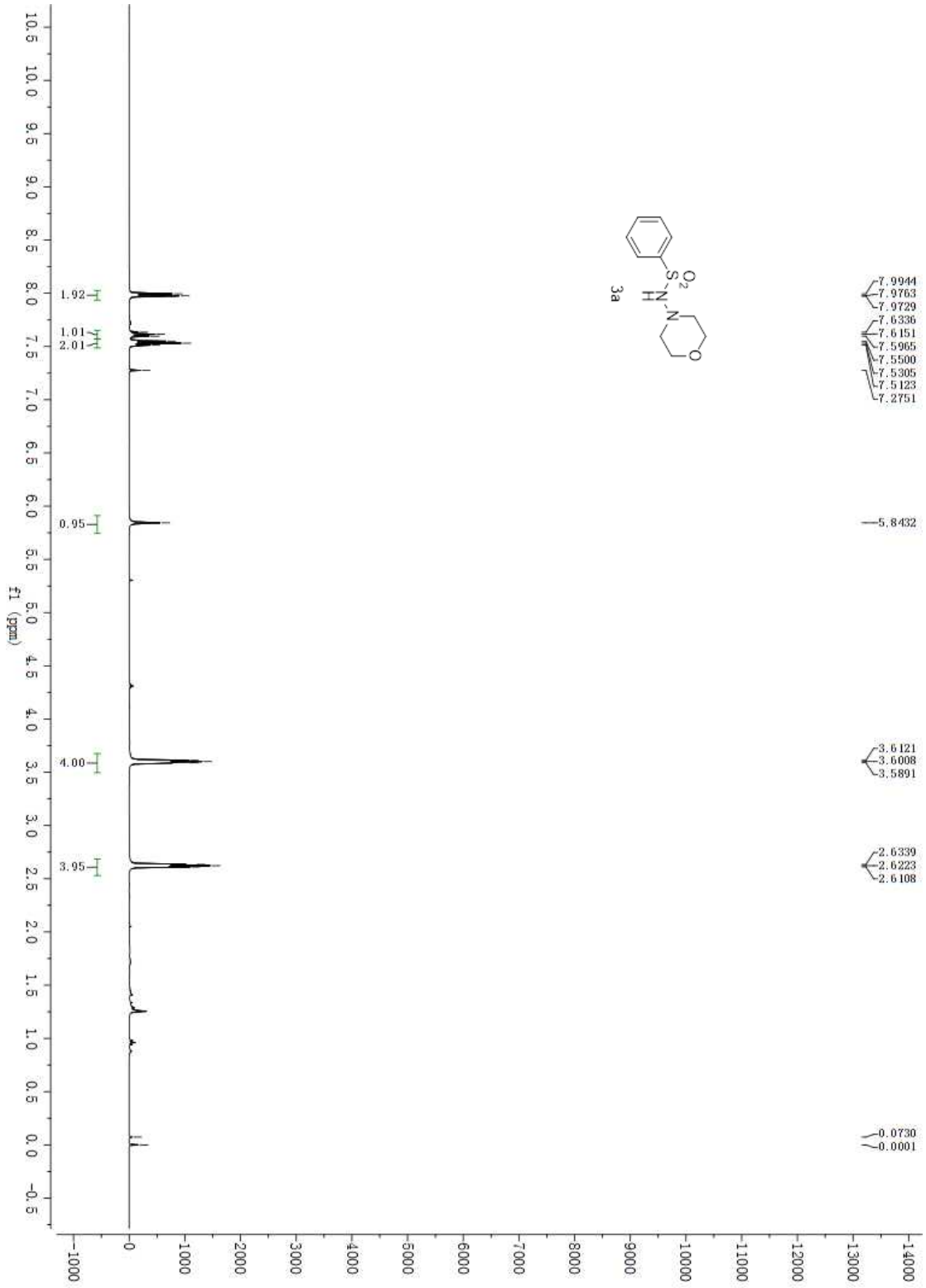


N′-Benzyl-*N′*-phenylbenzenesulfonohydrazide (**3n**)[1]

Yield: 45%, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (s, 2H), 6.36 (s, 1H), 6.85-6.93 (m, 3H), 7.04-7.06 (m, 2H), 7.16 (t, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 3.3 Hz, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.1, 115.3, 121.0, 128.0, 128.0, 128.3, 128.6, 128.8, 129.0, 133.3, 134.4, 138.8, 148.6.

References：

1. (a) Nguyen, B.; Emmett, E. J.; Willis, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 16372. (b) Zheng, D.; An, Y.; Li, Z.; Wu, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 2451. (c) Wang, X.; Xue, L.; Wang Z. *Org. Lett.*, **2014**, *16* ,4056.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3.5891
2.6339
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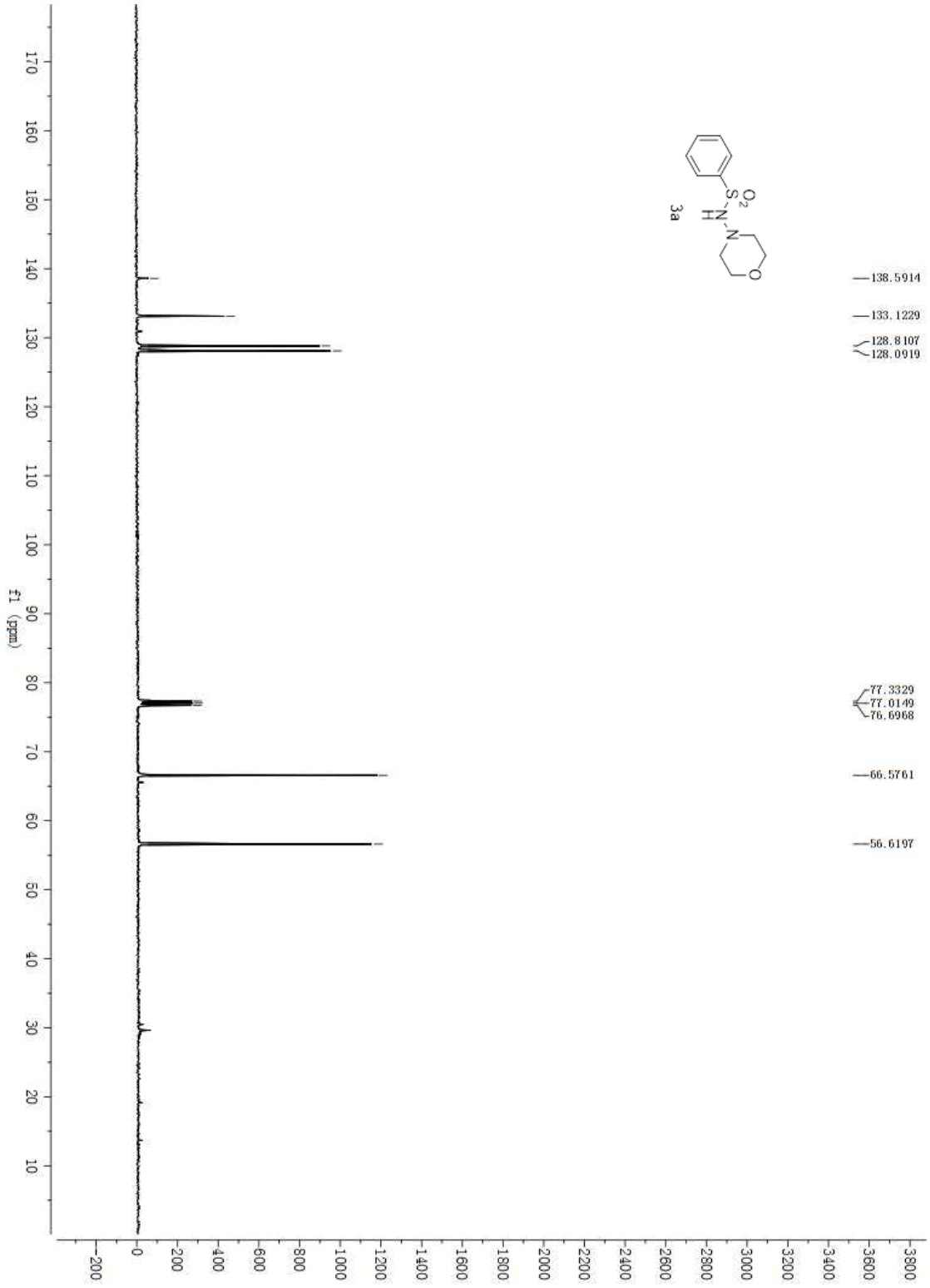
4.00
3.95
f1 (ppm)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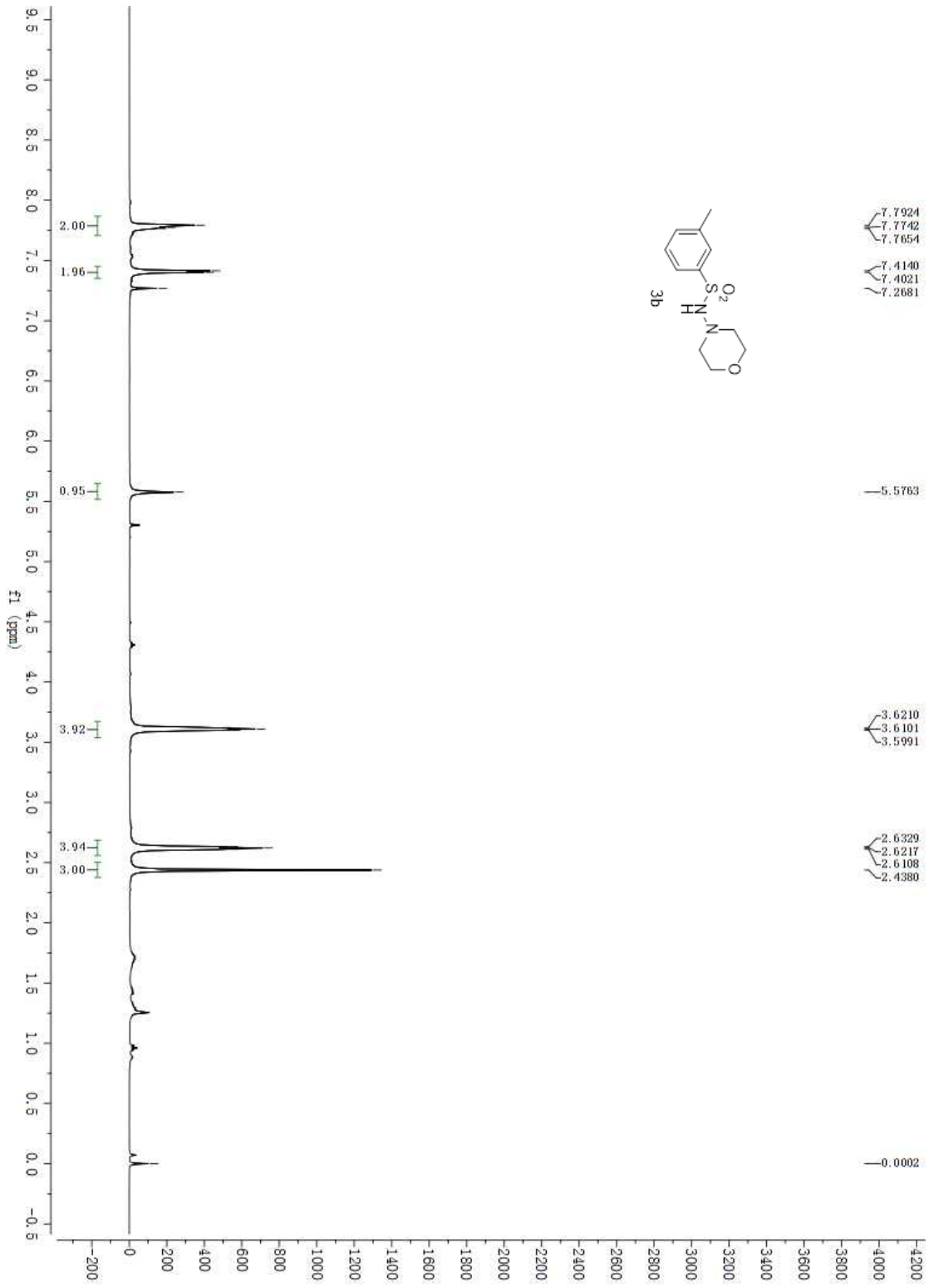
f1 (ppm)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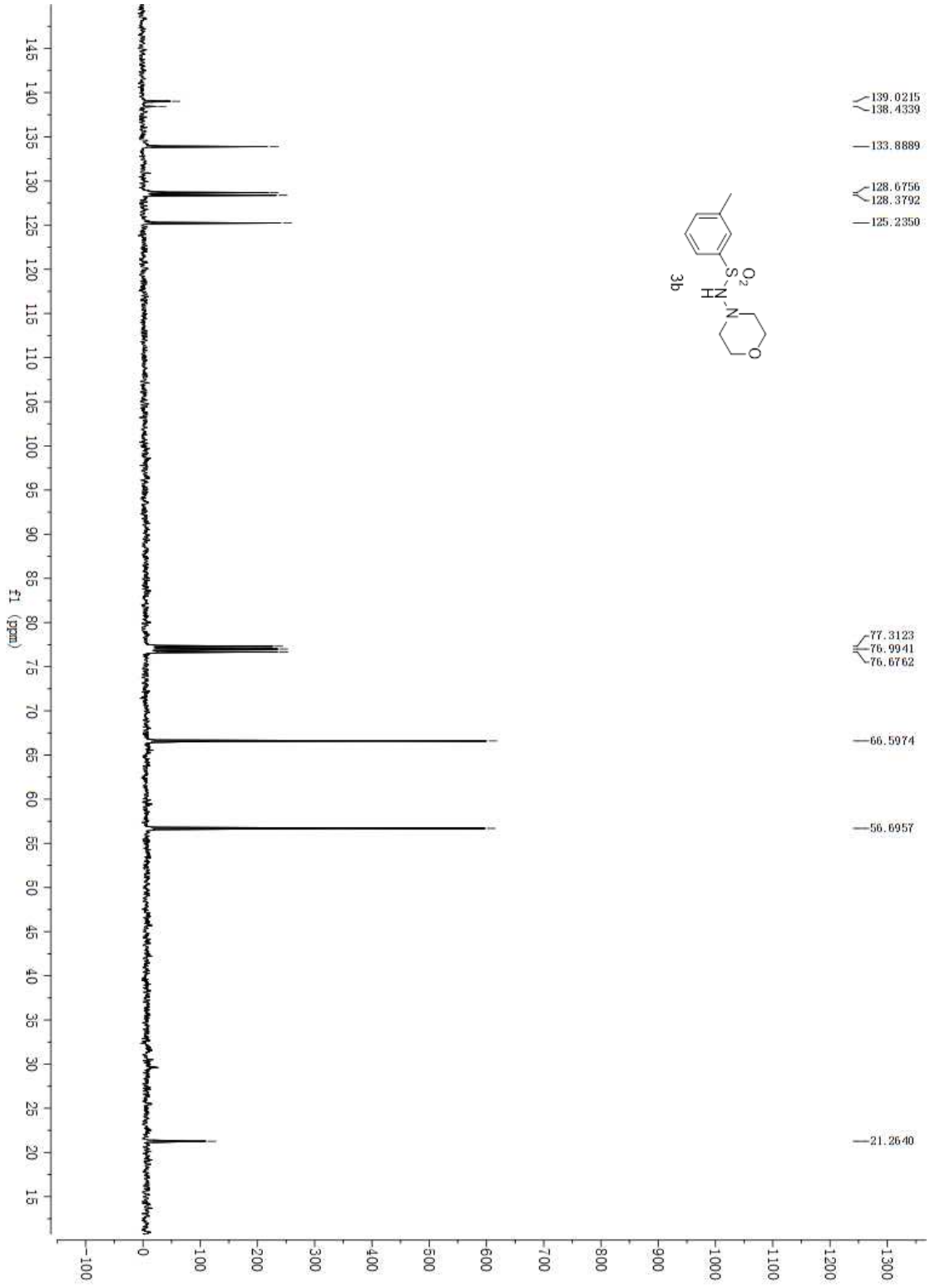
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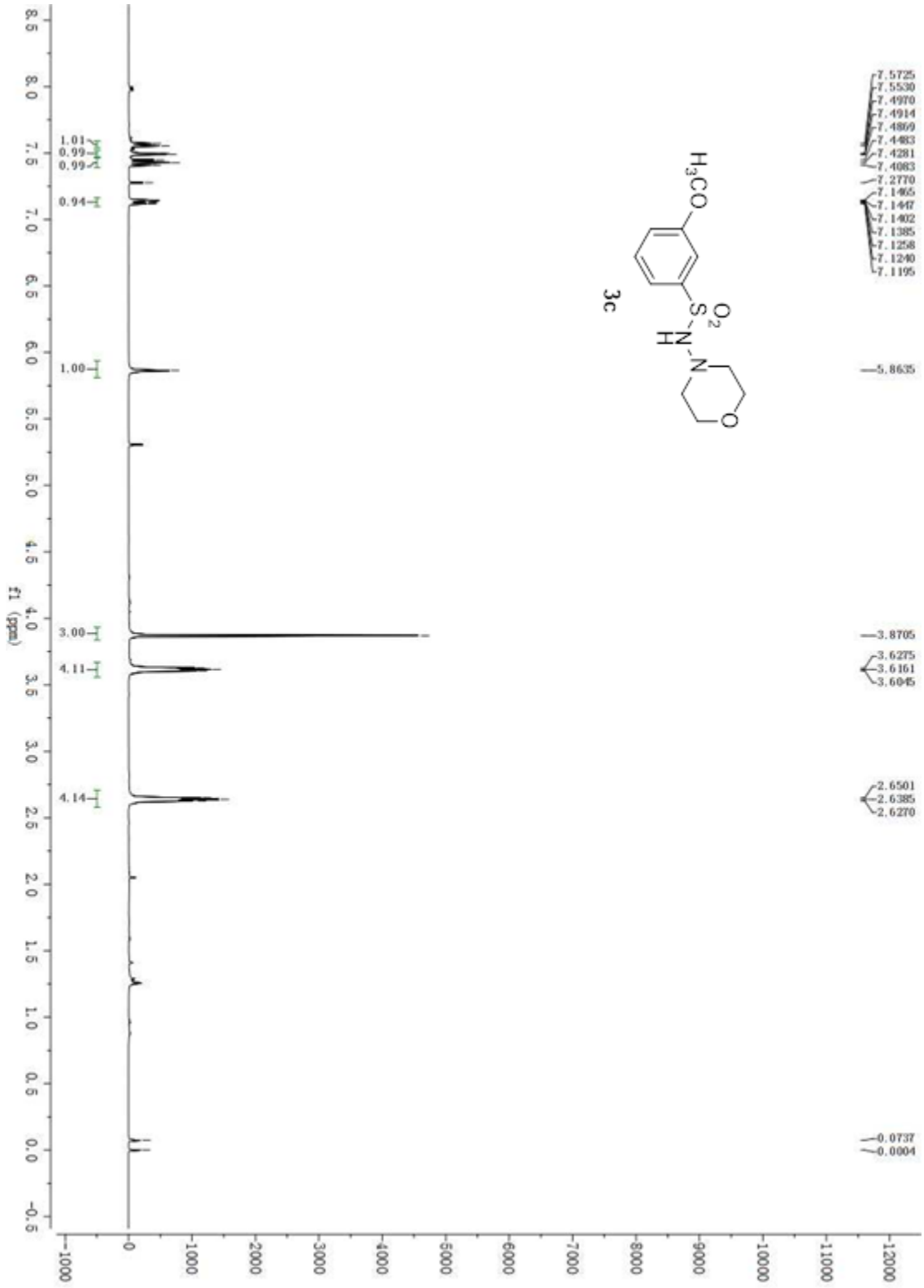
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0.99
0.99
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O2
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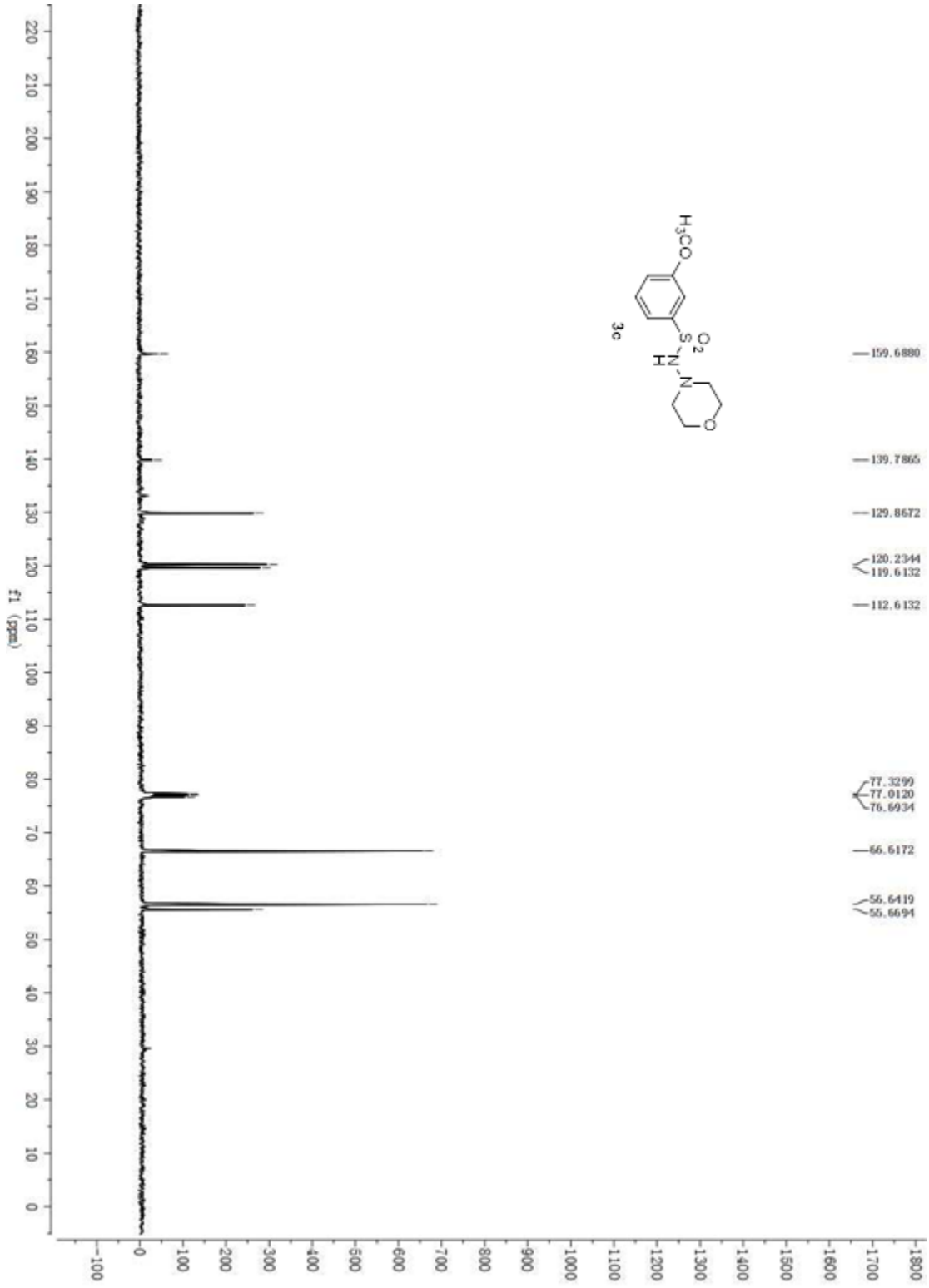
N
H
N
O
3c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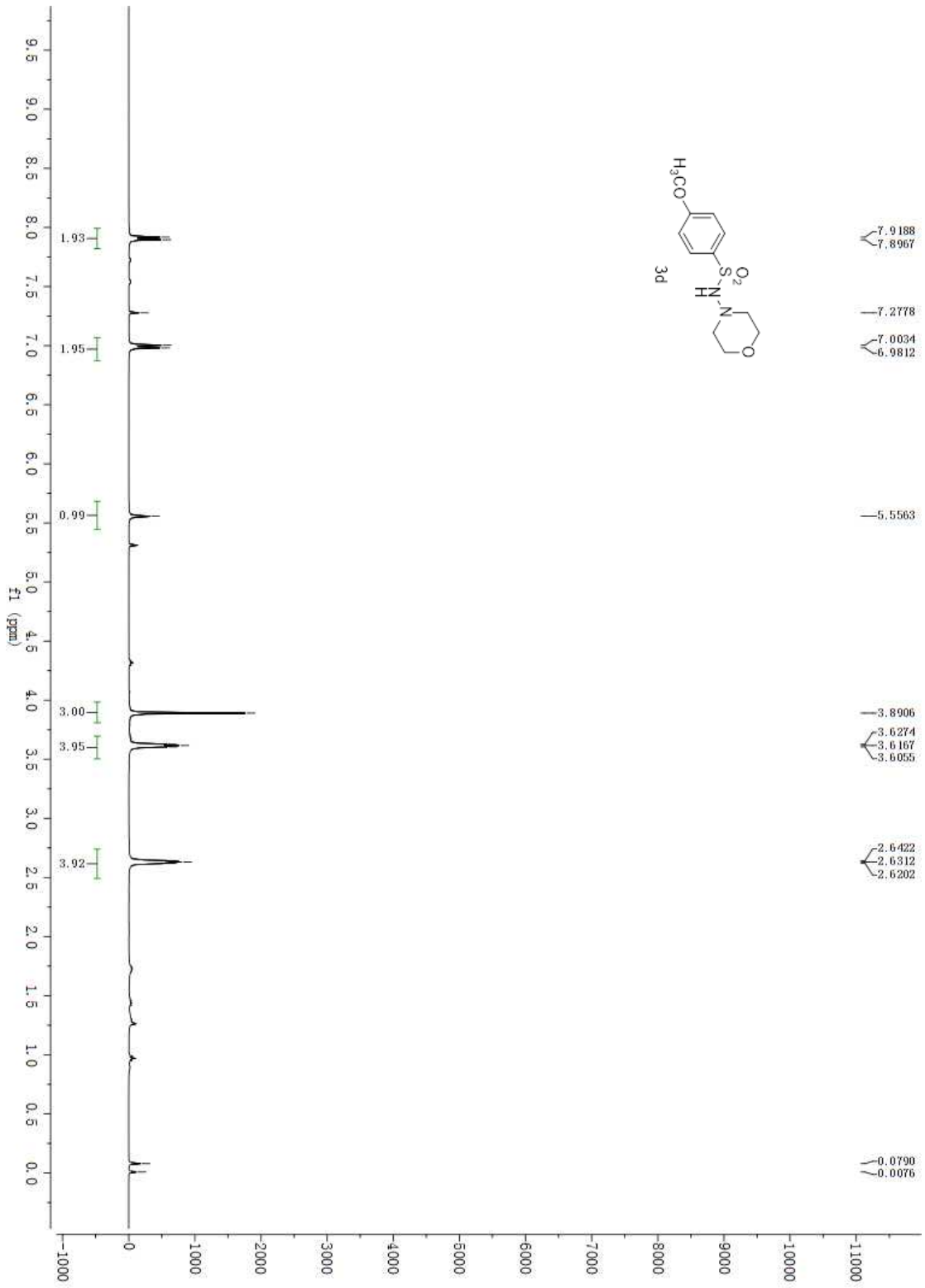
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2.6422
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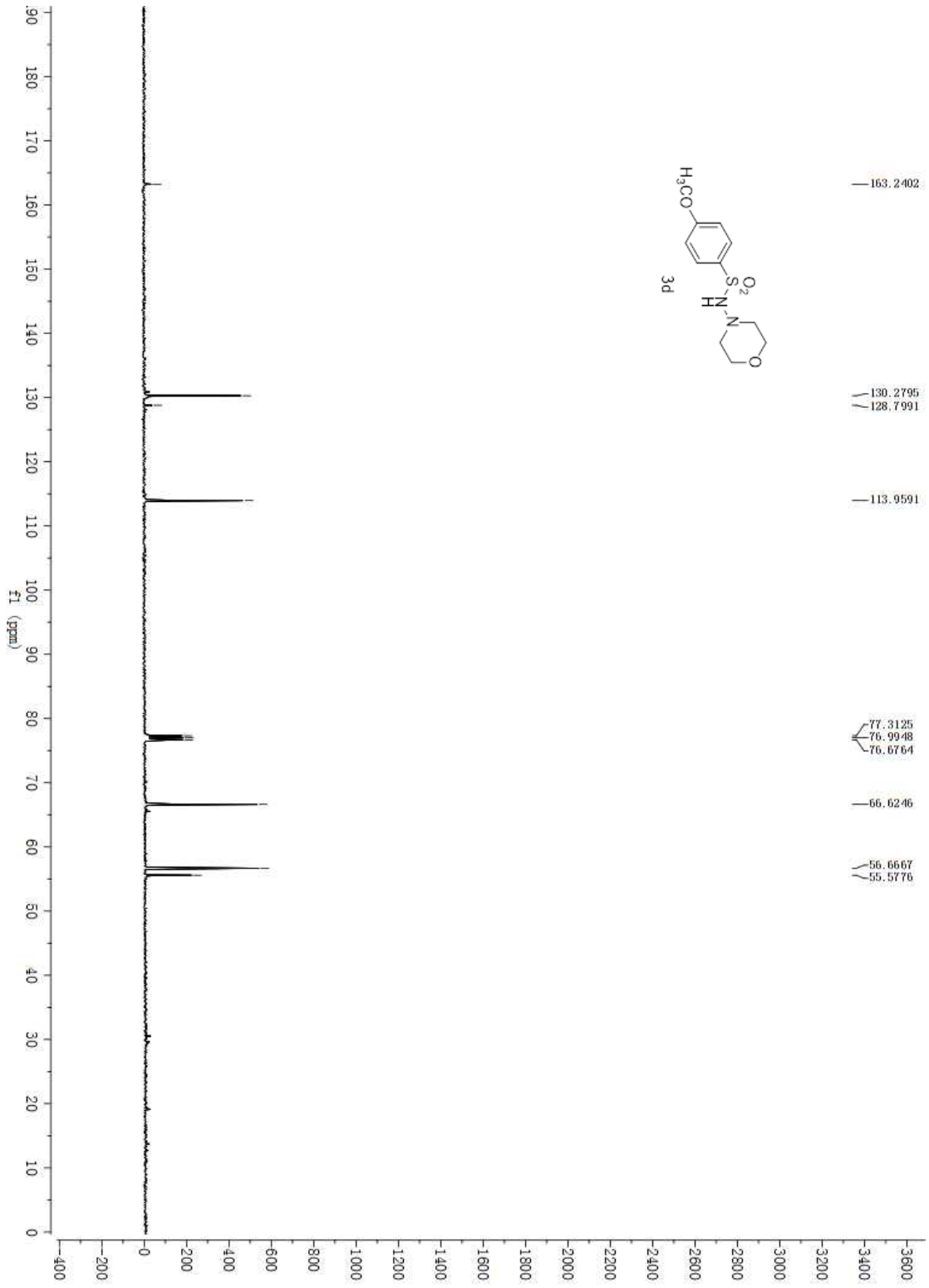
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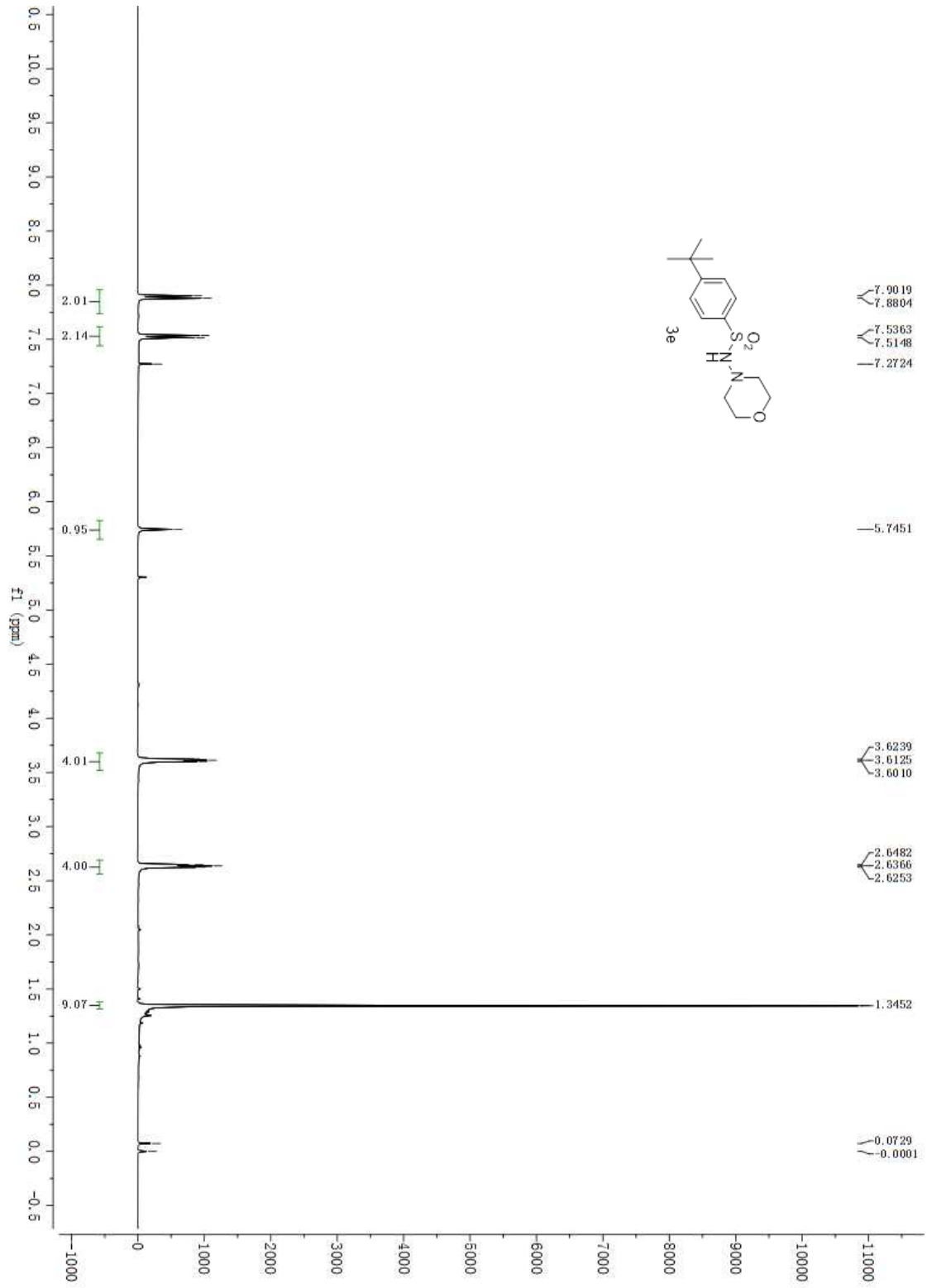
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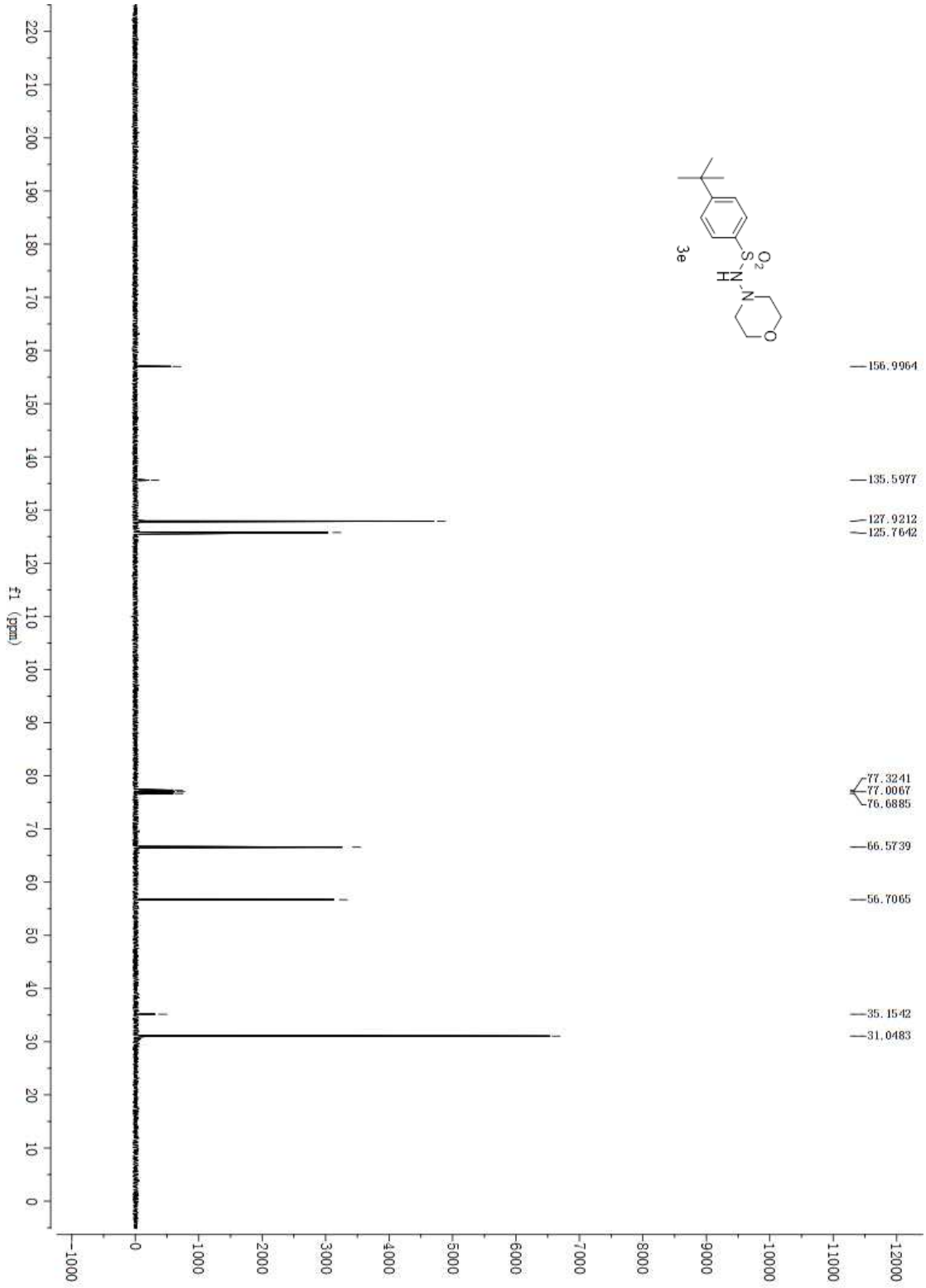
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127.9212
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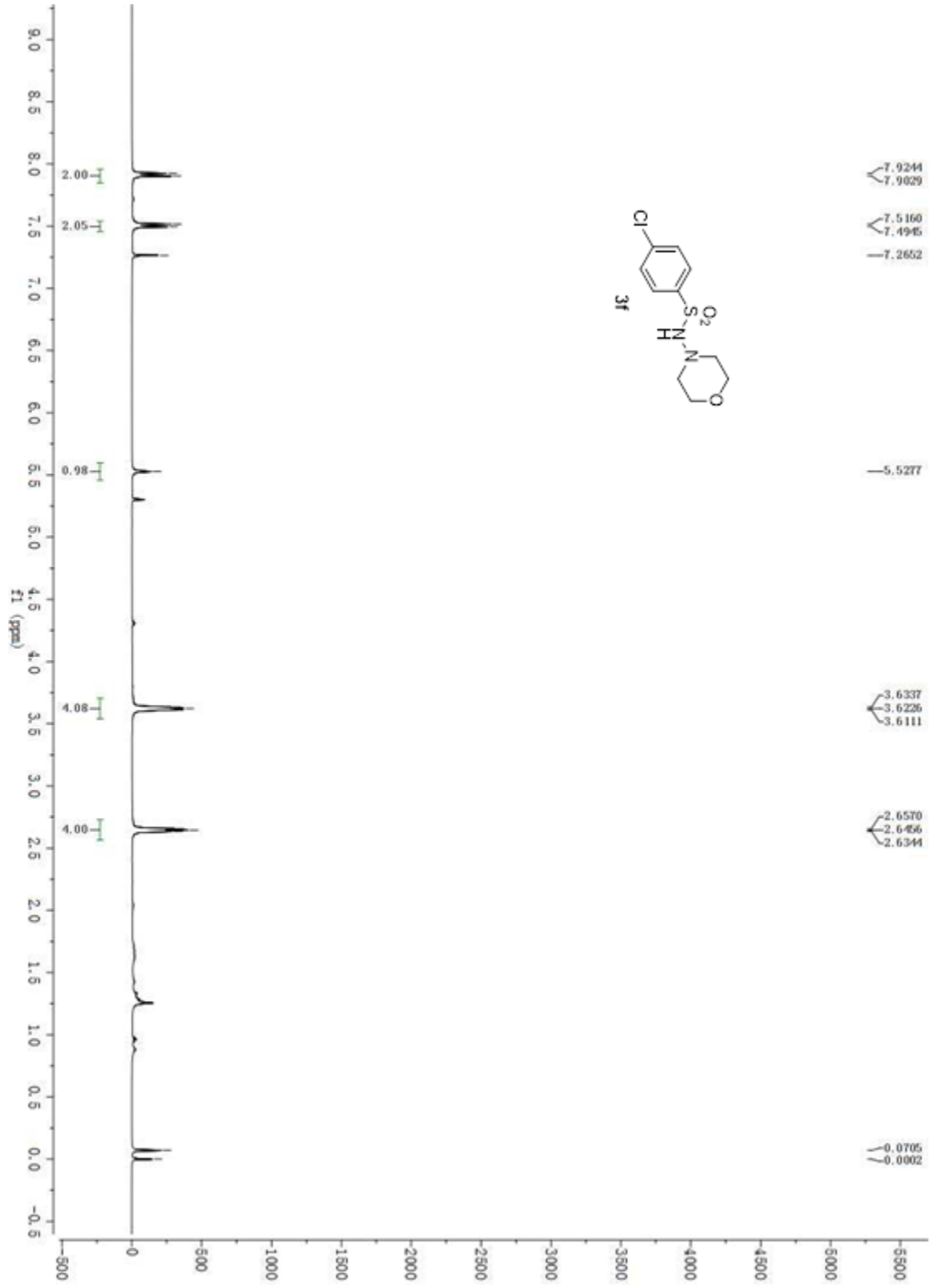
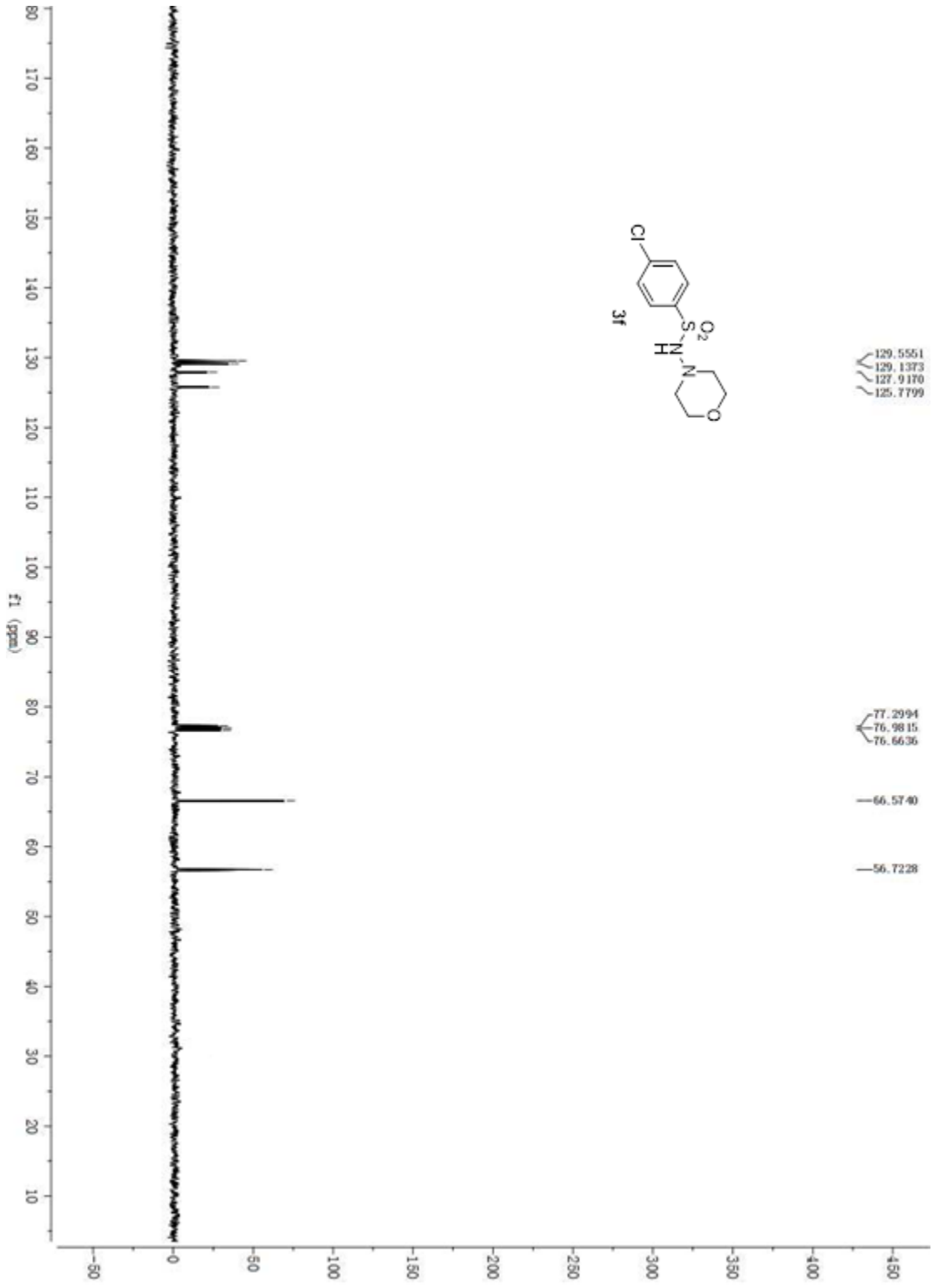
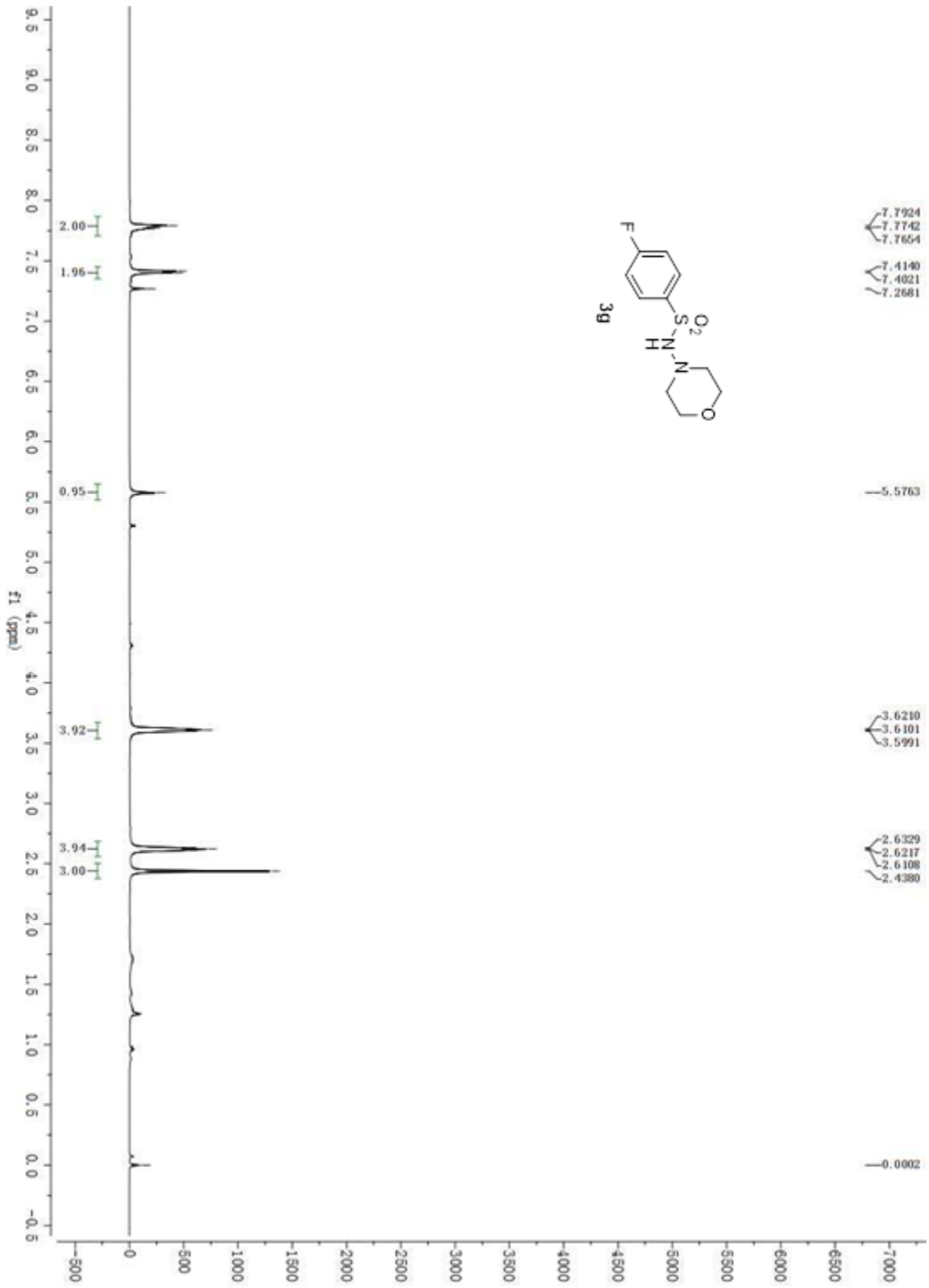
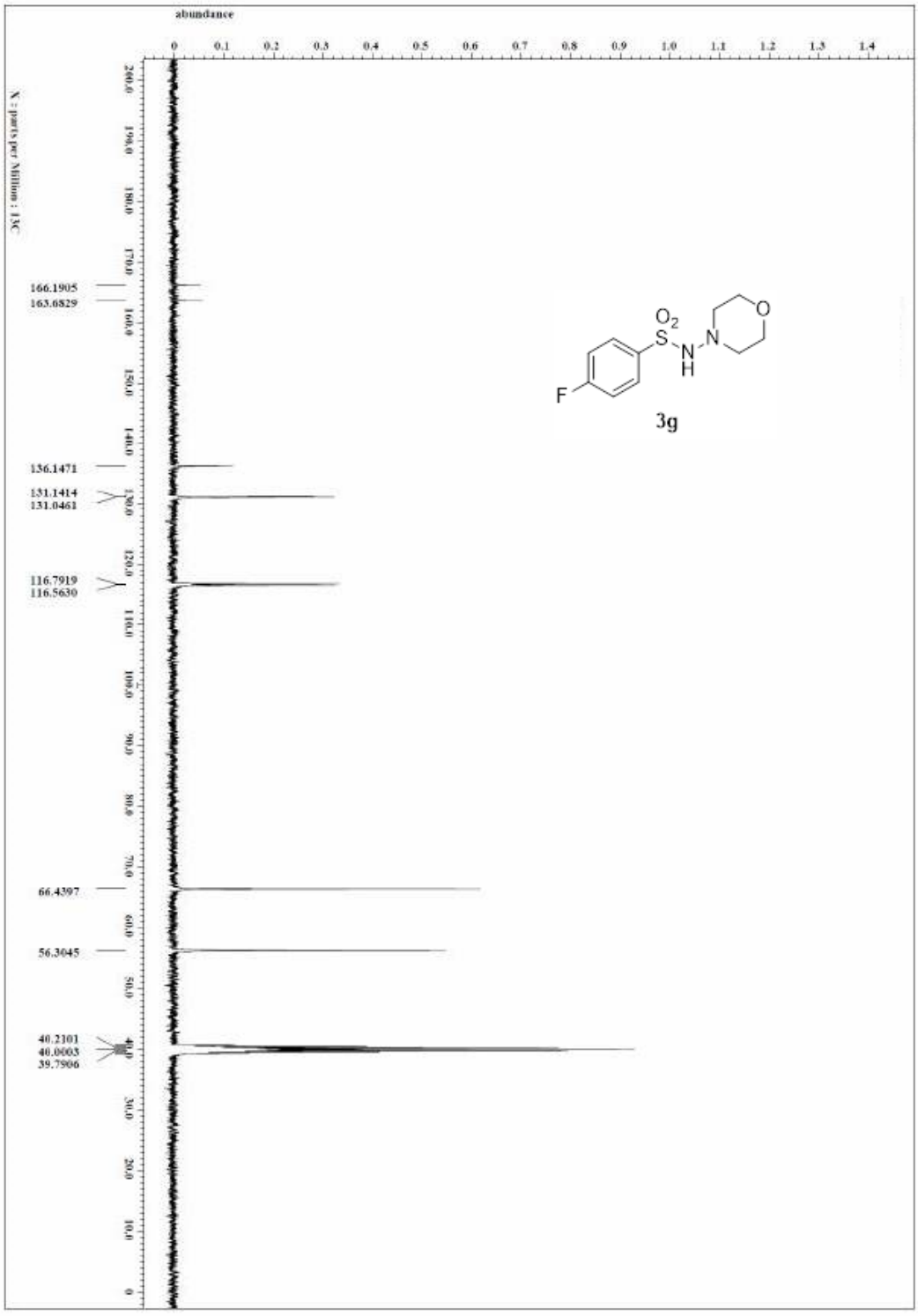
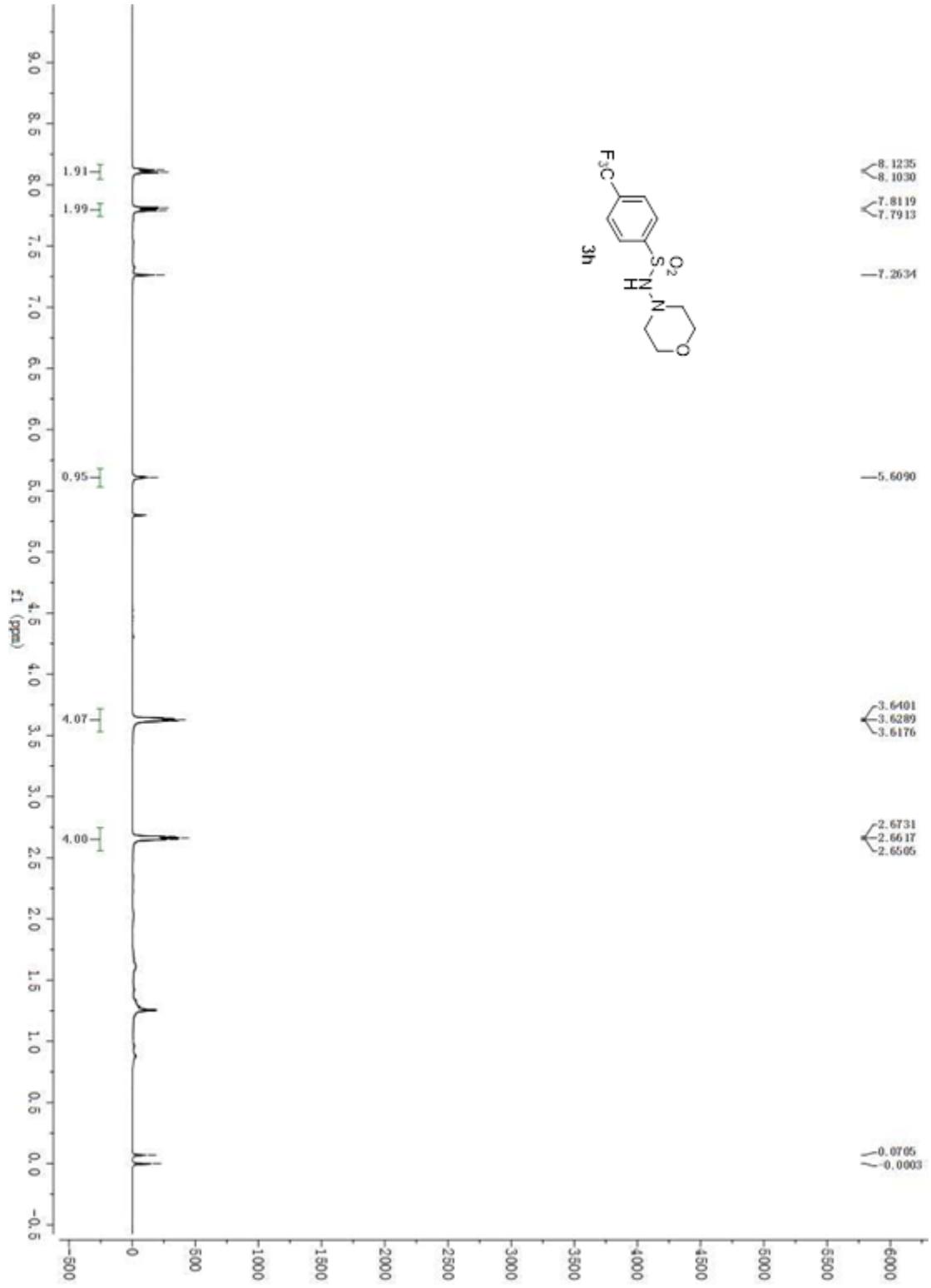
31.0483
f1 (ppm)

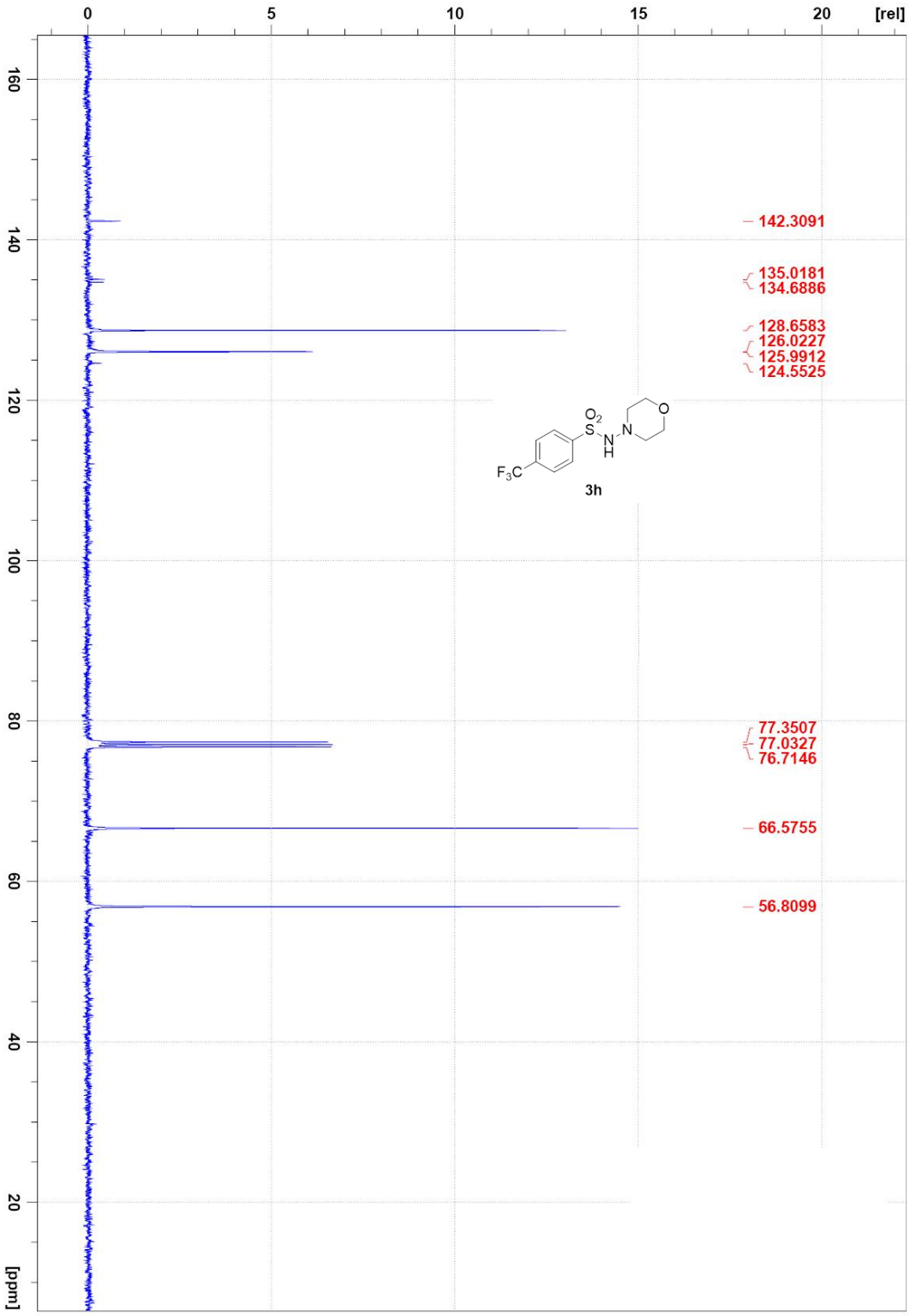

7.9244
7.9029
7.5160
7.4945
7.2652
5.5277
3.6337
3.6226
3.6111
2.6570
2.6456
2.6344
0.0705
0.0002
2.00
2.05
0.98
4.08
4.00
3f
f1 (ppm)

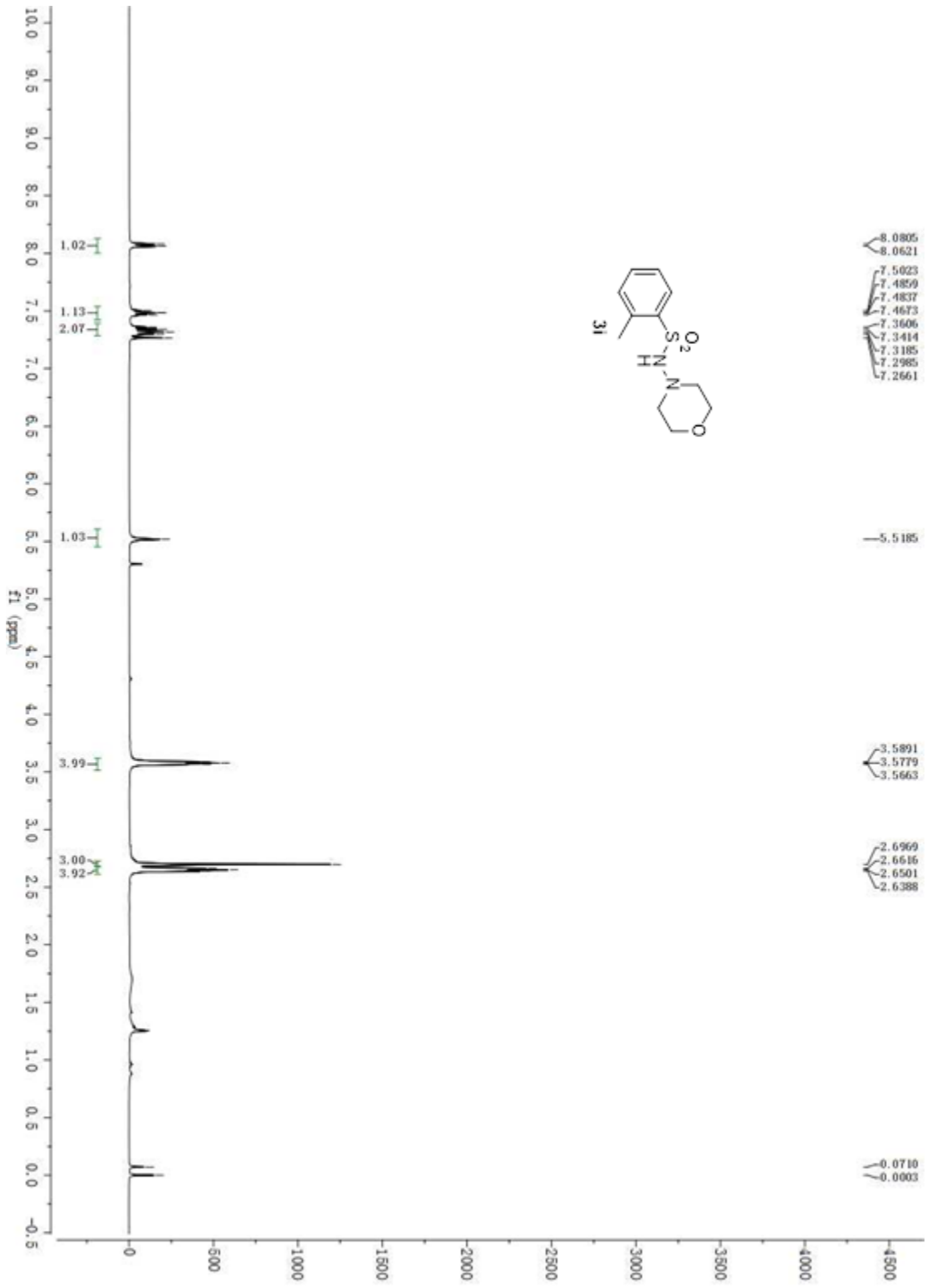

Cl
O2
S
H
N
N
O
3f
129.5551
129.1373
127.9170
125.7799
77.2994
76.9815
76.6636
66.5740
56.7228
f1 (ppm)

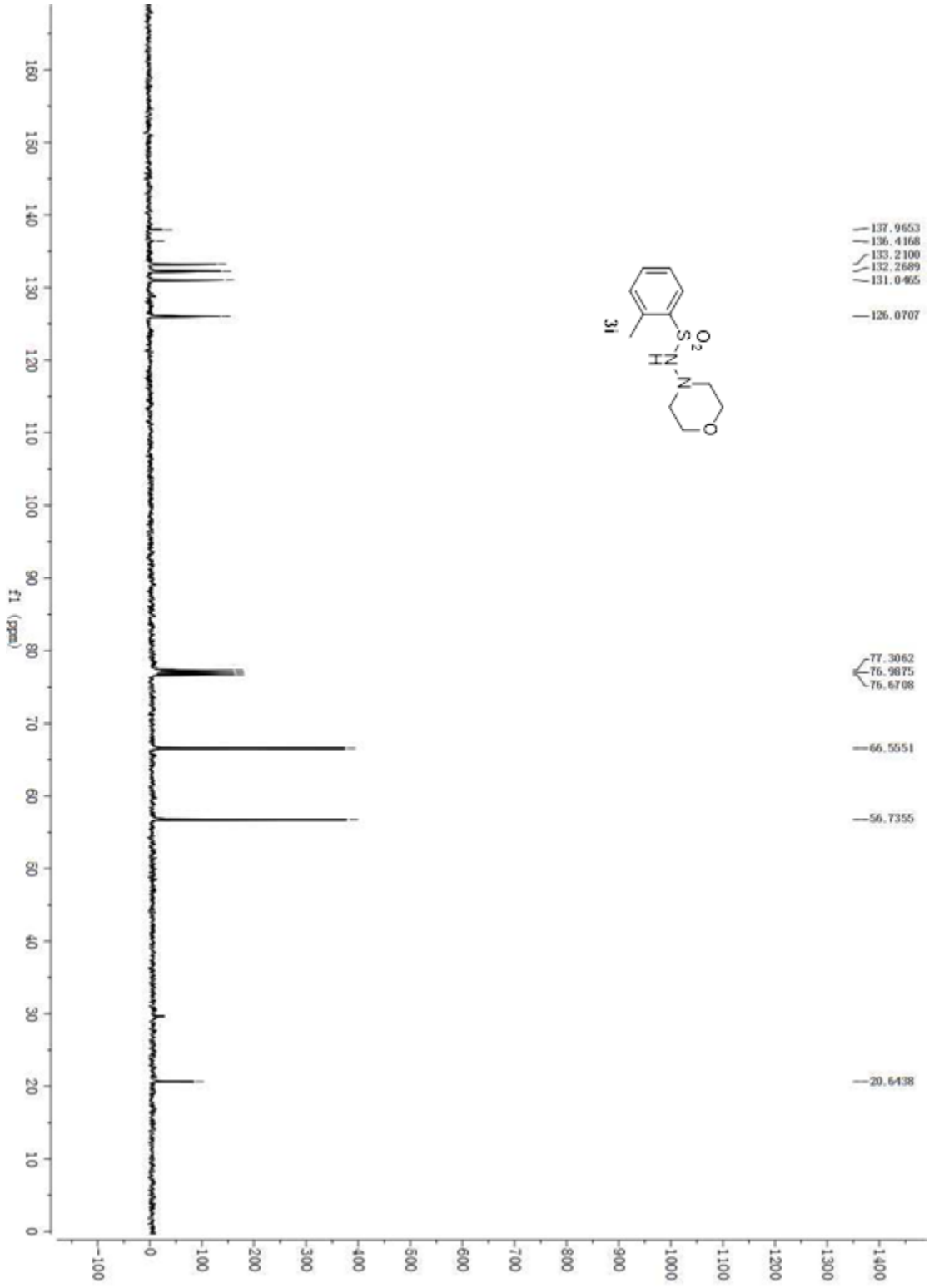

3g
7.7924
7.7742
7.7654
7.4140
7.4021
7.2681
5.5763
3.6210
3.6101
3.5991
2.6329
2.6217
2.6108
2.4380
0.0002
2.00
1.96
0.95
3.92
3.94
3.00
f1 (ppm)

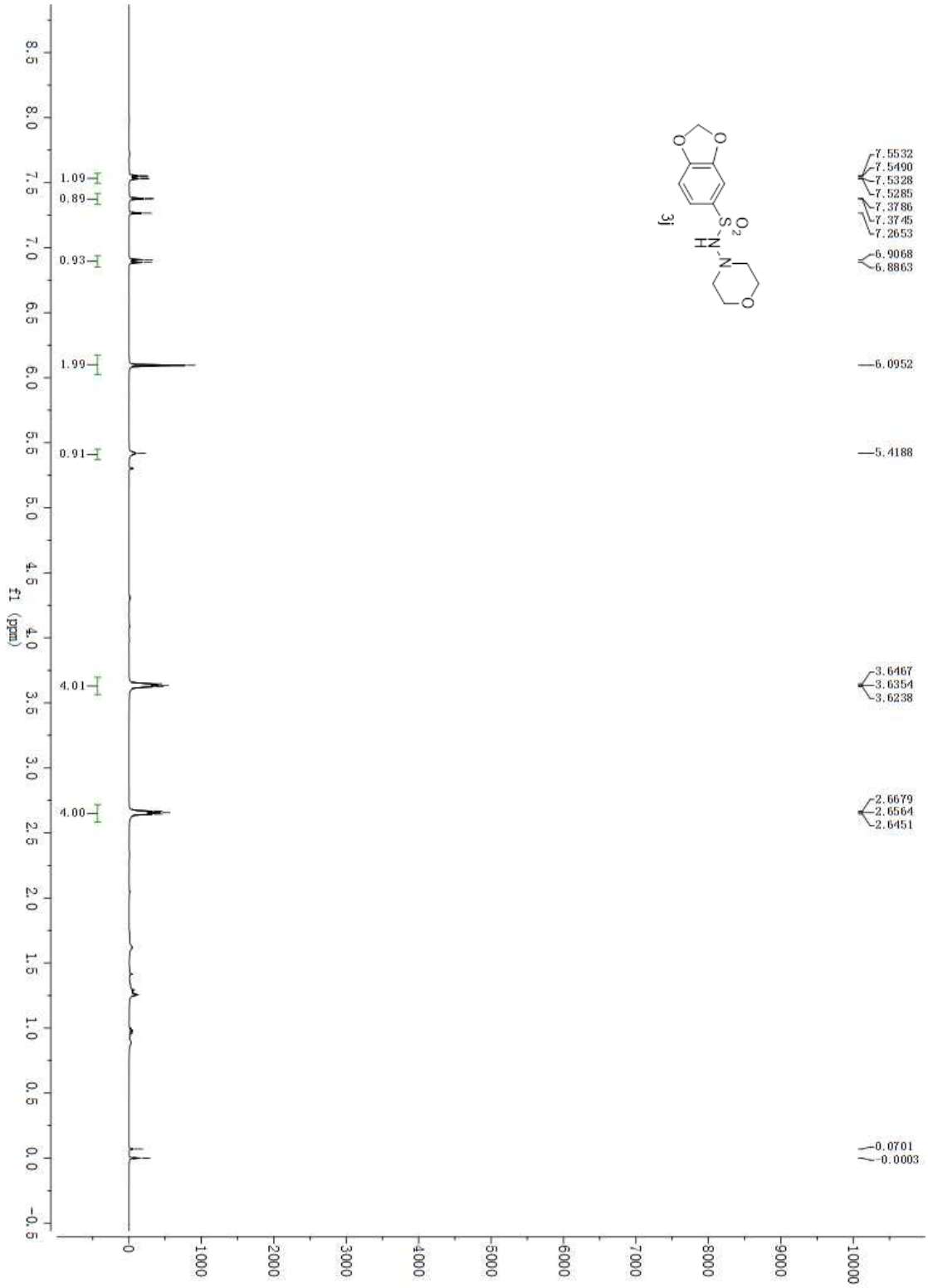

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4
X : parts per Million : 13C
240.0 230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
166.1905
163.0829
136.1471
131.1414
131.0461
116.7919
116.5630
66.4397
56.3045
40.2101
40.0003
39.7906
O2
S
N
H
N
O
F
3g

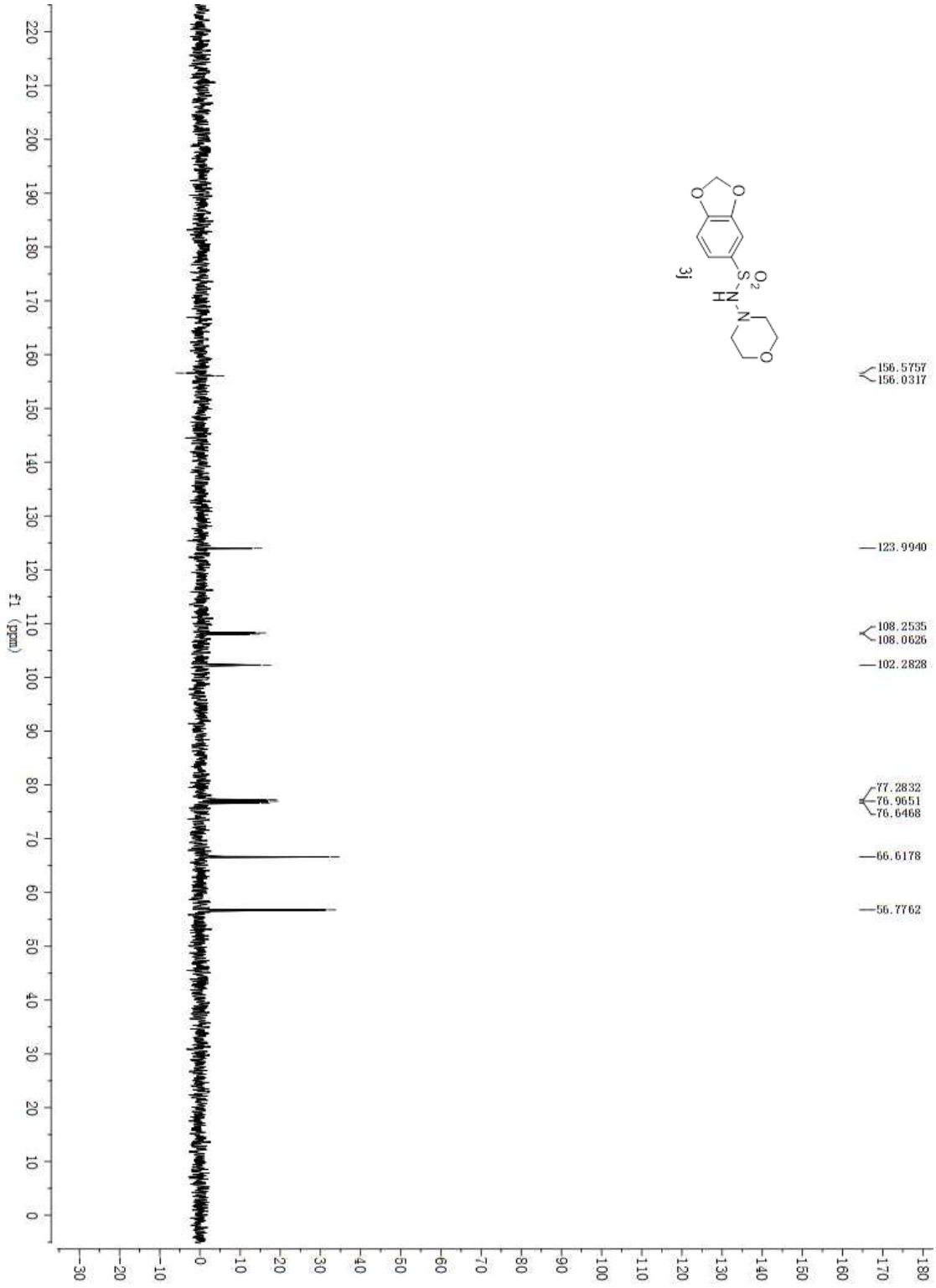

3h
8.1235
8.1030
7.8119
7.7913
7.2634
5.6090
3.6401
3.6289
3.6176
2.6731
2.6617
2.6505
0.0705
0.0003
1.91
1.99
0.95
4.07
4.00
f1 (ppm)

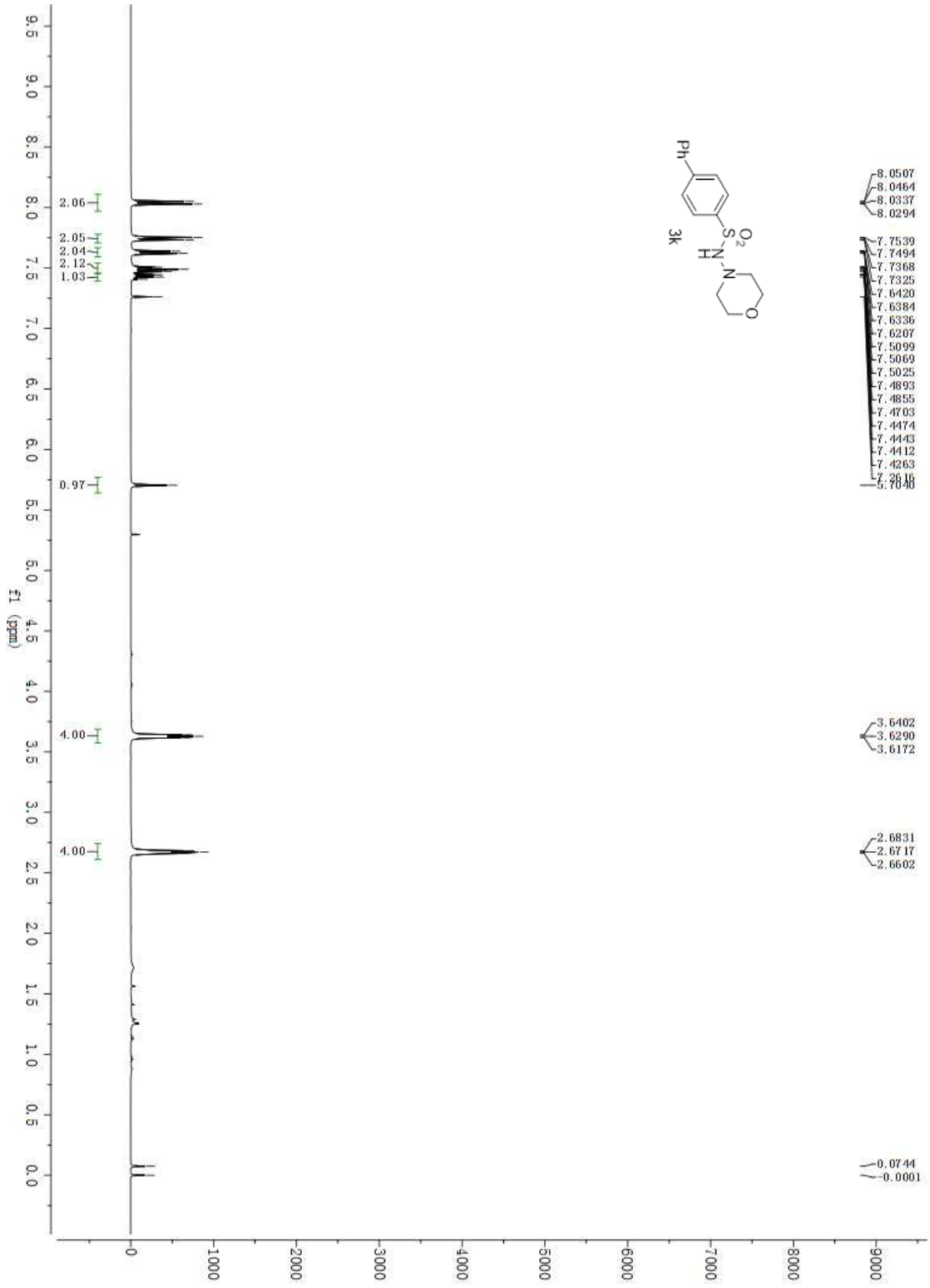

0
5
10
15
20
[rel]
160
140
120
100
80
60
40
20
[ppm]
142.3091
135.0181
134.6886
128.6583
126.0227
125.9912
124.5525
77.3507
77.0327
76.7146
66.5755
56.8099
O2
S
N
H
N
O
F3C
3h

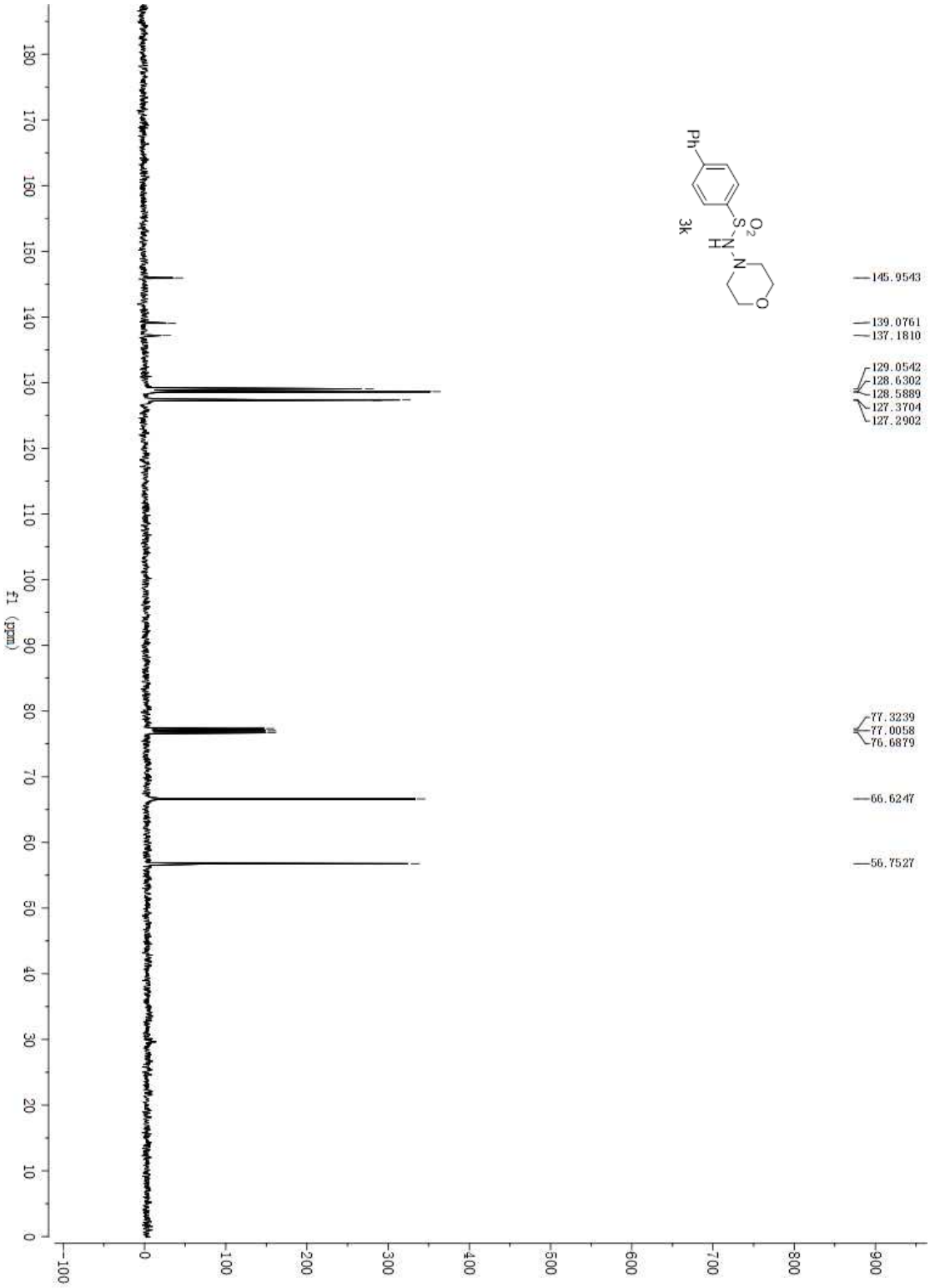

3i
8.0805
8.0621
7.5023
7.4859
7.4837
7.4673
7.3606
7.3414
7.3185
7.2985
7.2661
5.5185
3.5891
3.5779
3.5663
2.6969
2.6616
2.6501
2.6388
0.0710
0.0003
1.02
1.13
2.07
1.03
3.99
3.00
3.92
f1 (ppm)

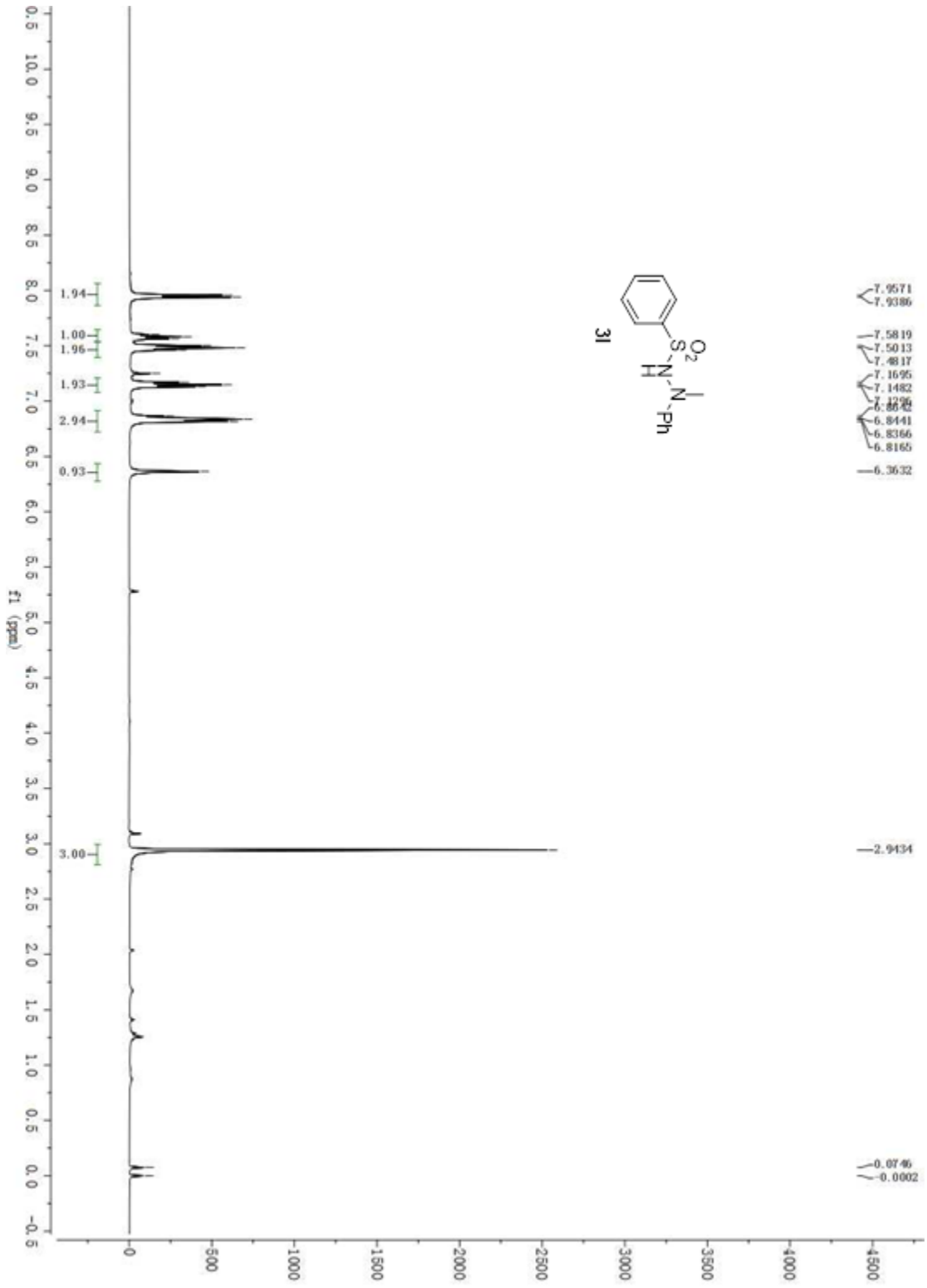

137.9653
136.4168
133.2100
132.2689
131.0465
126.0707
77.3062
76.9875
76.6708
66.5551
56.7355
20.6438
3i
f1 (ppm)

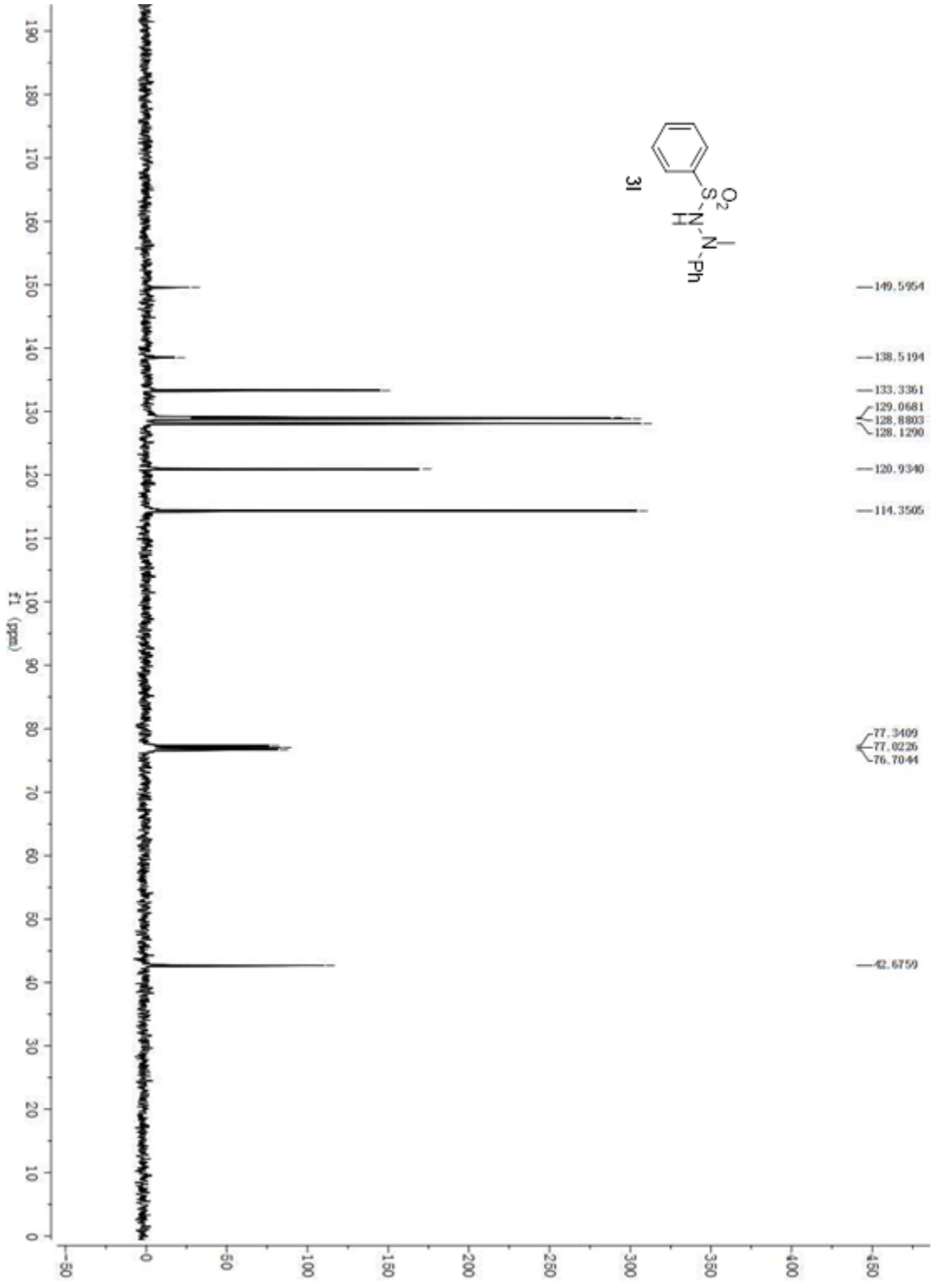

3j
7.5532
7.5490
7.5328
7.5285
7.3786
7.3745
7.2653
6.9068
6.8863
6.0952
5.4188
3.6467
3.6354
3.6238
2.6679
2.6564
2.6451
0.0701
-0.0003
1.09
0.89
0.93
1.99
0.91
4.01
4.00
f1 (ppm)

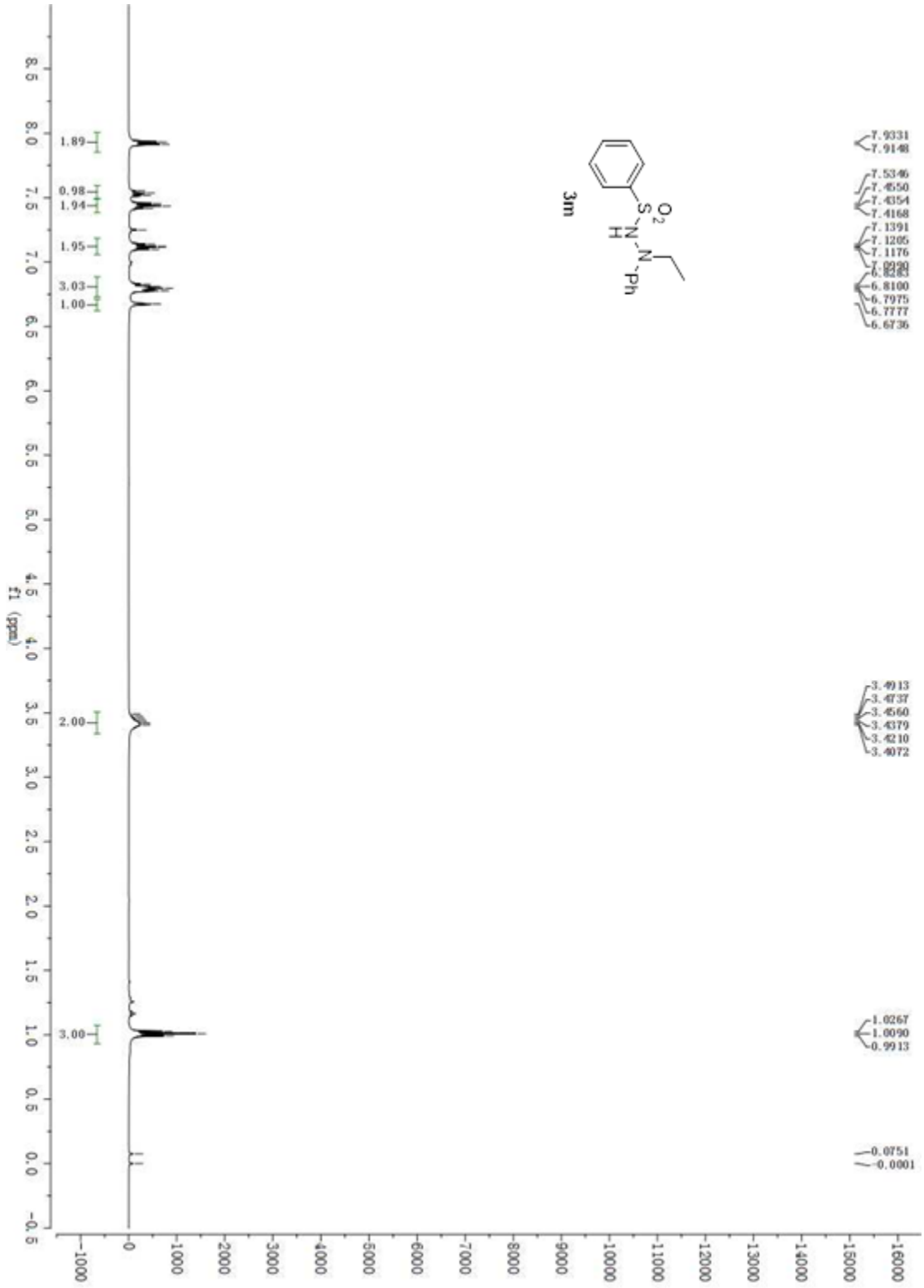

3j
156.5757
156.0317
123.9940
108.2535
108.0626
102.2828
77.2832
76.9651
76.6468
66.6178
56.7762
f1 (ppm)

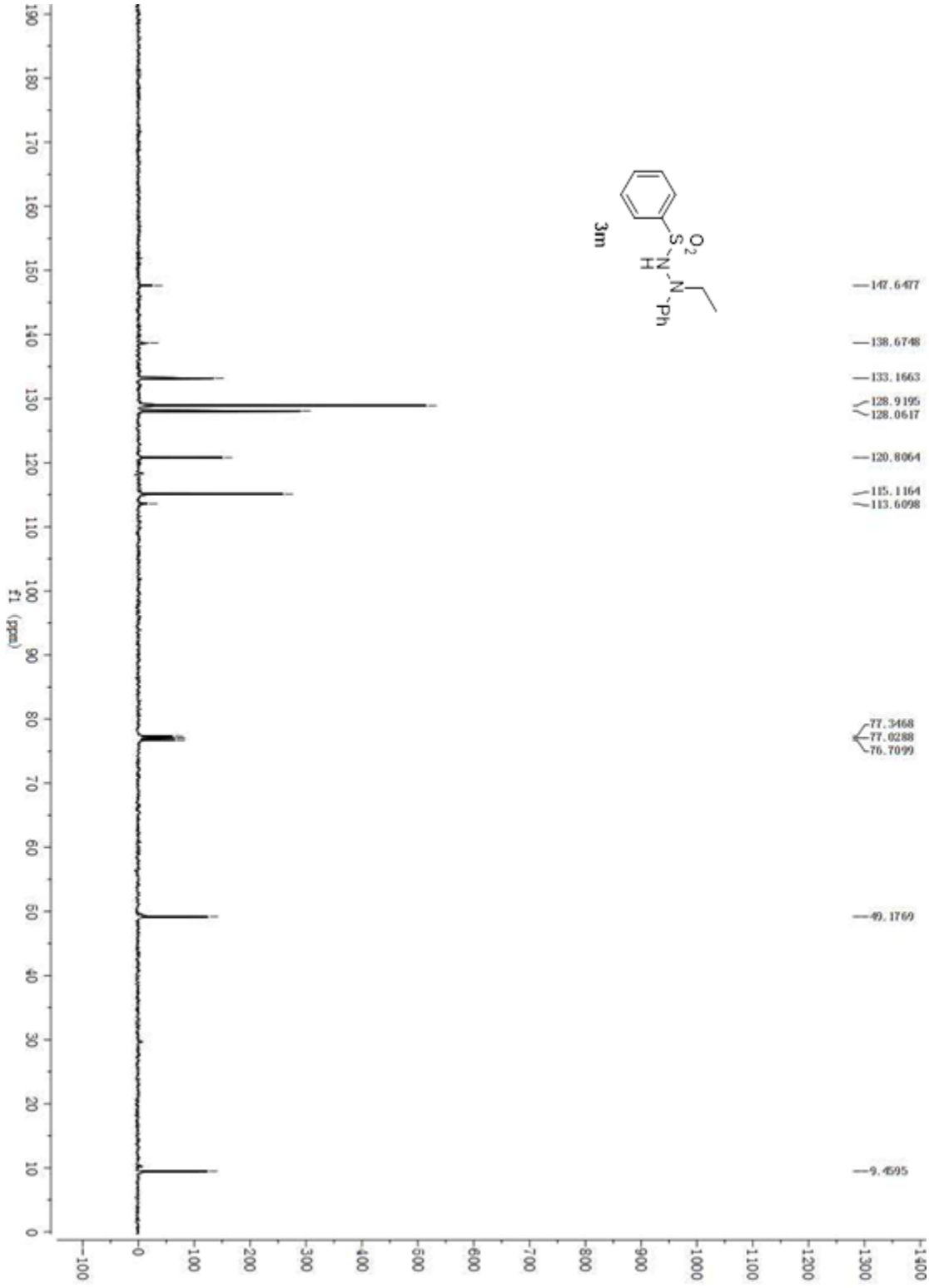

Ph
O2
S
N
H
N
O
3k
8.0507
8.0464
8.0337
8.0294
7.7539
7.7494
7.7368
7.7325
7.6420
7.6384
7.6336
7.6207
7.5099
7.5069
7.5025
7.4893
7.4855
7.4703
7.4474
7.4443
7.4412
7.4263
7.2616
5.7040
3.6402
3.6290
3.6172
2.6831
2.6717
2.6602
0.0744
-0.0001
2.06
2.05
2.04
2.12
1.03
0.97
4.00
4.00
f1 (ppm)

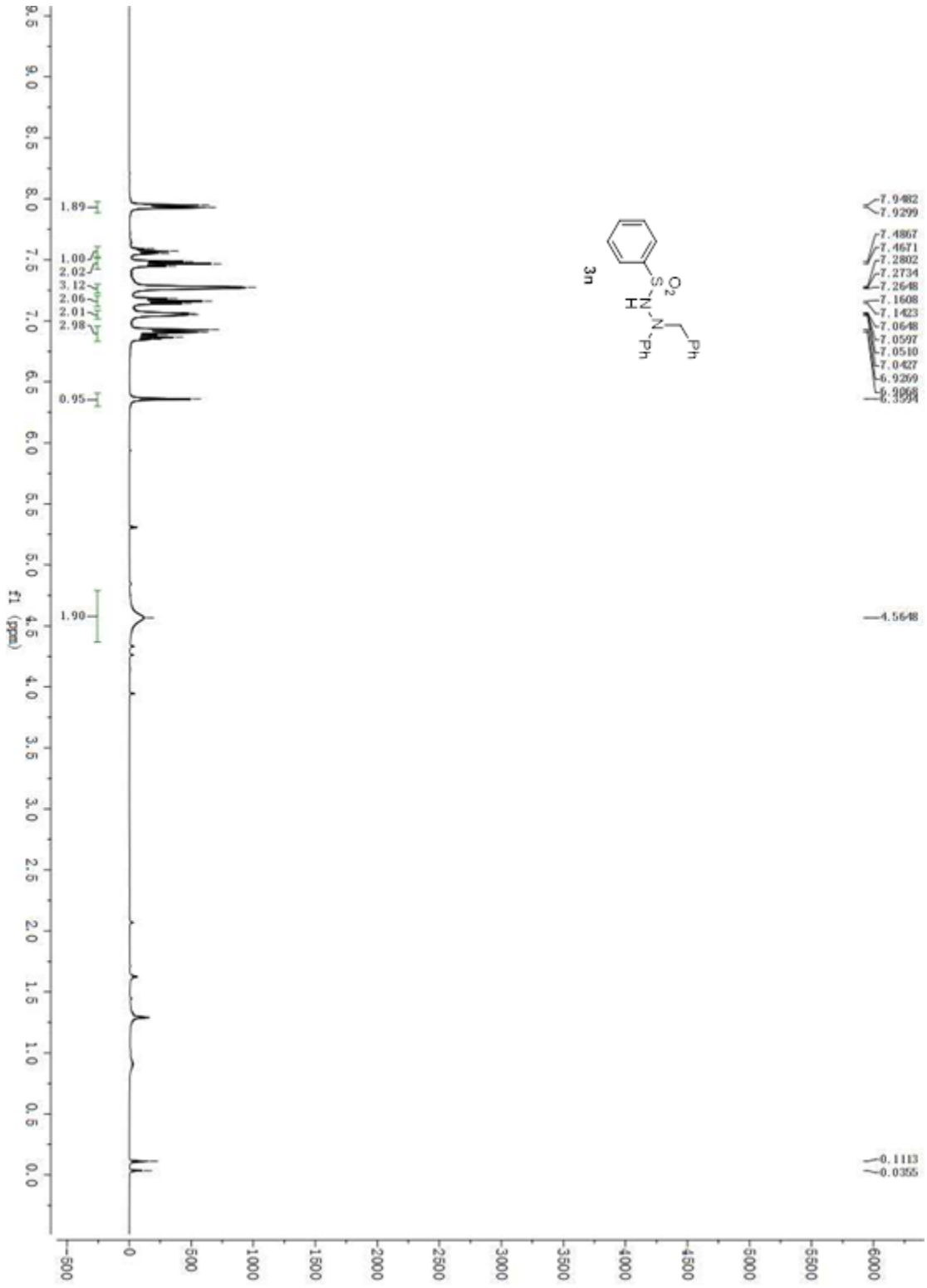

Ph
S
O2
H
N
N
O
3k
145.9543
139.0761
137.1810
129.0542
128.6302
128.5889
127.3704
127.2902
77.3239
77.0058
76.6879
66.6247
56.7527
f1 (ppm)

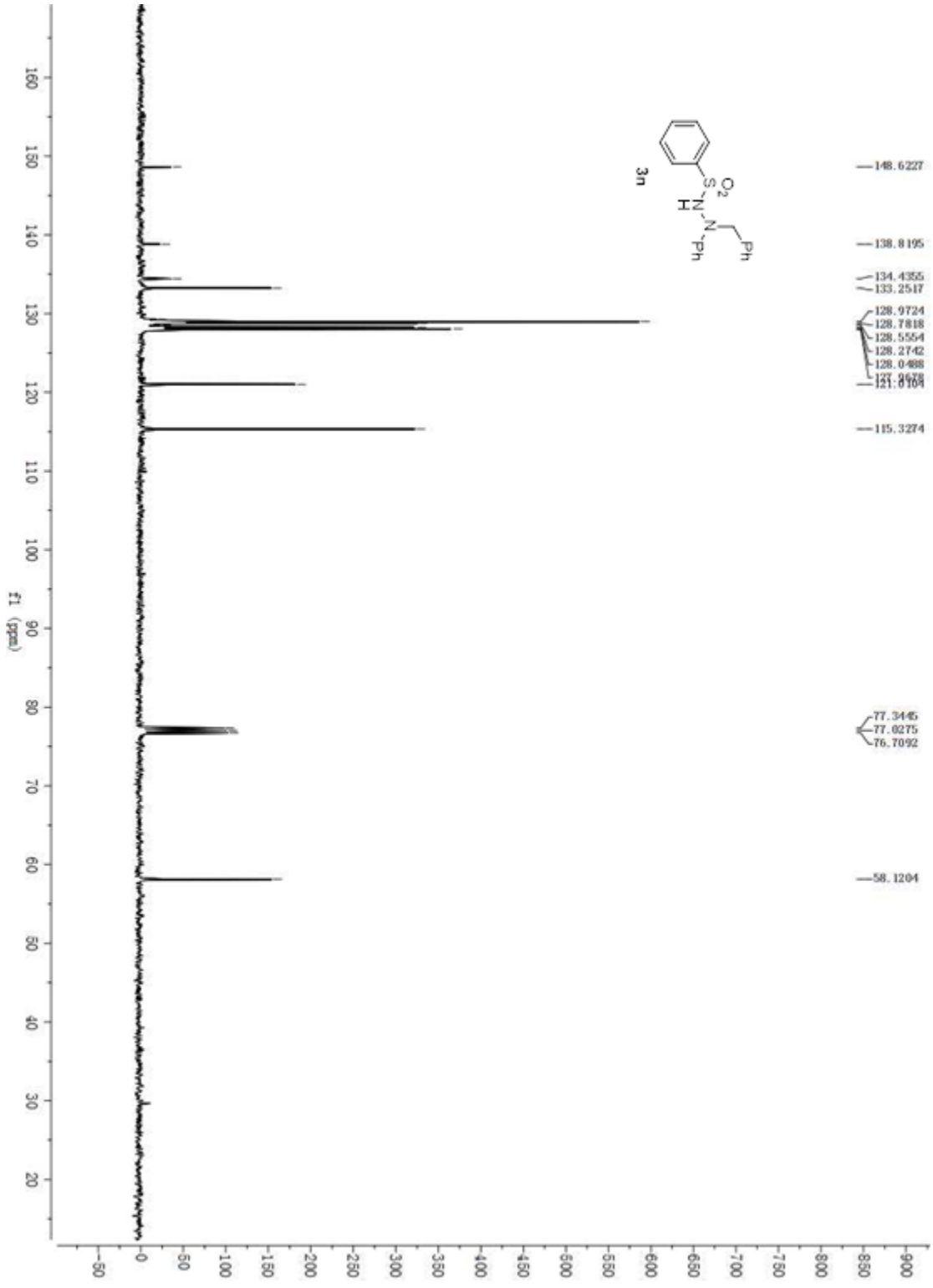

3l
7.9571
7.9386
7.5819
7.5013
7.4817
7.1695
7.1482
6.8441
6.8366
6.8165
6.3632
2.9434
0.0746
-0.0002
1.94
1.00
1.96
1.93
2.94
0.93
3.00
f1 (ppm)


3l
149.5954
138.5194
133.3361
129.0681
128.8803
128.1290
120.9340
114.3505
77.3409
77.0226
76.7044
42.6759
f1 (ppm)


3m
7.9331
7.9148
7.5346
7.4650
7.4354
7.4168
7.1391
7.1205
7.1176
6.8283
6.8100
6.7975
6.7777
6.6736
3.4913
3.4737
3.4560
3.4379
3.4210
3.4072
1.0267
1.0090
0.9913
0.0751
0.0001
1.89
0.98
1.94
1.95
3.03
1.00
2.00
3.00
f1 (ppm)


3m
147.6477
138.6748
133.1663
128.9195
128.0617
120.8064
115.1164
113.6098
77.3468
77.0288
76.7099
49.1769
9.4595
f1 (ppm)


3n
7.9482
7.9299
7.4867
7.4671
7.2802
7.2734
7.2648
7.1608
7.1423
7.0648
7.0597
7.0510
7.0427
6.9269
4.5648
0.1113
0.0355
1.89
1.00
2.02
3.12
2.06
2.01
2.98
0.95
1.90
f1 (ppm)


3n
148.6227
138.8195
134.4355
133.2517
128.9724
128.7818
128.5554
128.2742
128.0488
115.3274
77.3445
77.0275
76.7092
58.1204
f1 (ppm)