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Supporting Information

Molecular-iodine-catalyzed aerobic oxidative synthesis of β-hydroxy sulfones from alkenes

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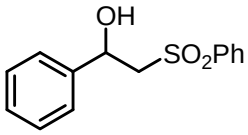
1. General Information.

All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Tokyo Kasei Kogyo Co., Ltd., Wako Pure Chemical Industries, Ltd., and Nacalai Tesque. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 and a JEOL AL 400 at room temperature in $CDCl_3$ or CD_3OD as a solvent (500 MHz and 400MHz for ^{1}H NMR and 125 MHz and 100MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for ^{1}H NMR and 77.0 ppm ($CDCl_3$) or 49.0 (CD_3OD) for ^{13}C NMR]. Flash column chromatography was performed with Silica Gel 60N (Kanto Chemical Co., Inc.,40−50 μm spherical, neutral).

2. General Procedure

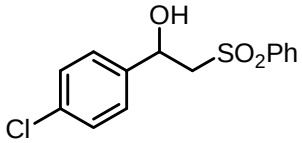
Synthesis of 1-phenyl-2-(phenylsulfonyl)ethanol (3aa) (Table 1, Entry 21): A solution of styrene (**1a**, 0.3 mmol), sodium benzenesulfinate dihydrate (**2a**, 0.6 mmol), I_2 (0.03 mmol) in MeCN (1 mL) and AcOH (0.4 mL) was stirred for 20 h. The reaction mixture was washed with aq. $Na_2S_2O_3$, dried over magnesium sulfate, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (hexane : ethyl acetate = 5 : 1) provided 1-phenyl-2-(phenylsulfonyl)ethanol (**3aa**) (73.2 mg, 93%).

Synthesis of 1-phenyl-2-(phenylsulfonyl)ethanol (3aa) [1] **(Table 2)**



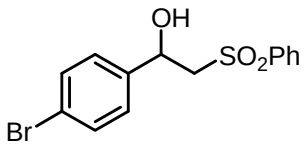
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.32-7.24 (m, 5H), 5.27 (d, J = 9.7 Hz, 1 H), 3.72 (br s, 1H), 3.50 (dd, J = 14.3 Hz, 9.7 Hz, 1H), 3.33 (dd, J = 14.3 Hz, 1.7 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 140.5, 139.0, 134.1, 129.4, 128.7, 128.3, 127.9, 125.6, 68.4, 63.8.

1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanol (3ba)[1] **(Table 2)**



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.5 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 5.26 (d, *J* = 10.1 Hz, 1 H), 3.83 (br s, 1H), 3.46 (dd, *J* = 14.4 Hz, 10.1 Hz, 1H), 3.29 (dd, *J* = 14.4 Hz, 1.7 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 139.1, 138.9, 134.2, 134.0, 129.5, 128.8, 127.9, 127.0, 67.7, 63.7.

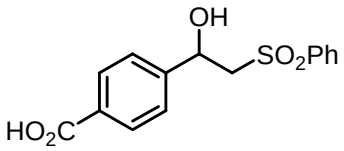
1-(4-bromophenyl)-2-(phenylsulfonyl)ethanol (3ca)[1] **(Table 2)**



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 5.23 (d, *J* = 9.8 Hz, 1 H), 3.87 (br s, 1H), 3.46 (dd, *J* = 14.3 Hz, 9.8 Hz, 1H), 3.29

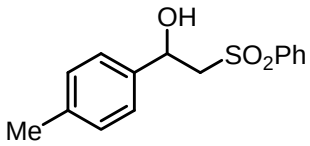
(dd, *J* = 14.3 Hz, 1.7 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 139.6, 138.9, 134.2, 131.8, 129.5, 127.9, 127.3, 122.2, 67.8, 63.6.

1-(4-carbonic acid phenyl)-2-(phenylsulfonyl)ethanol (3da) (Table 2)



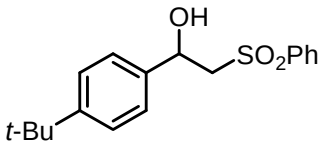
^{1}H-NMR (400 MHz, CD_3OD): δ = 7.95-7.91 (m, 4H), 7.70-7.60 (m, 1H), 7.59-7.56 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.21 (dd, *J* = 8.8 Hz, 3.7 Hz 1 H), 4.93 (br s, 1H), 3.68 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H), 3.55 (dd, *J* = 14.8 Hz, 3.7 Hz 1H). ^{13}C-NMR (100 MHz, CD_3OD): δ = 169.4, 148.8, 141.5, 134.8, 131.0, 130.2, 129.3, 127.2, 69.6, 64.3. Anal. Calcd for $C_{15}H_{14}O_5S$: C, 58.81; H, 4.61. Found: C, 58.67; H, 4.58.

2-(phenylsulfonyl)-1-*p*-tolylethanol (3ea)[1] (Table 2)



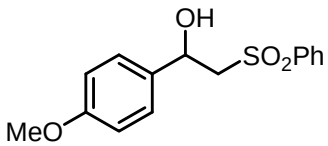
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 5.23 (d, *J* = 10.3 Hz, 1 H), 3.62 (br s, 1H), 3.49 (dd, *J* = 14.3 Hz, 10.3 Hz, 1H), 3.32 (dd, *J* = 14.3 Hz, 1.7 Hz, 1H), 2.31 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 139.1, 138.2, 137.6, 134.1, 129.4, 129.4, 127.9, 125.5, 68.3, 63.8, 21.1.

1-(4-*t*-Butylphenyl)-2-(phenylsulfonyl)ethanol (3fa) (Table 2)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.3 Hz, 2H), 7.66 (t, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 5.25 (d, *J* = 10.0 Hz, 1 H), 3.63 (br s, 1H), 3.52 (dd, *J* = 14.2 Hz, 10.0 Hz, 1H), 3.35 (dd, *J* = 14.2 Hz, 1.5 Hz, 1H), 1.27 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.4, 139.2, 137.6, 134.0, 129.4, 127.9, 125.6, 125.4, 68.2, 63.8, 34.5, 31.2. Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96. Found: C, 67.63; H, 6.99.

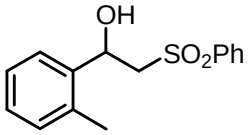
1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanol (3ga)[1](Table 2)



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.23 (d, *J* = 9.3 Hz, 1 H), 3.78 (s, 3H), 3.60 (br s, 1H), 3.50 (dd, *J* = 14.4 Hz, 9.3 Hz, 1H), 3.32 (dd, *J* = 14.4 Hz, 1.2 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 159.5, 139.1, 134.1, 132.7, 129.5, 128.0,

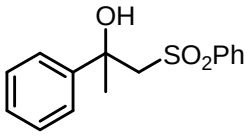
127.0, 114.1, 68.1, 63.9, 55.3.

2-(phenylsulfonyl)-1-o-tolylethanol (3ha)[1] (Table 2)



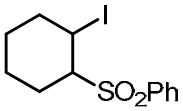
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.1 Hz, 2H), 7.68 (t, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.19-7.14 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 5.43 (d, *J* = 10.0 Hz, 1 H), 3.68 (br s, 1H), 3.43 (dd, *J* = 14.3 Hz, 10.0 Hz, 1H), 3.24 (d, *J* = 14.3 Hz, 1H), 2.07 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 138.9, 138.6, 134.1, 133.6, 130.5, 129.5, 128.0, 128.0, 126.6, 125.2, 64.9, 62.8, 18.5.

2-Hydroxy-2-phenylpropyl 4-methylphenyl sulfone (3ia)[2] (Table 2)



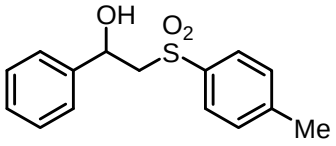
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59-7.51 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 3H), 4.64 (br s, 1H), 3.75 (d, *J* = 14.8 Hz, 1H), 3.62 (d, *J* = 14.8 Hz, 1H), 1.70 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 144.2, 140.1, 133.4, 129.0, 128.2, 127.4, 127.2, 124.6, 73.1, 66.5, 30.8.

1-Benzenesulphonyl-2-iodocyclohexane (4ja)[3](Table 2)



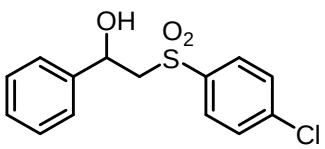
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.1 Hz, 2H), 7.70 (t, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 5.12 (d, *J* = 2.7 Hz, 1 H), 3.36 (dd, *J* = 2.7 Hz, 2.0 Hz, 1H), 2.28-2.19 (m, 2H), 2.05-1.95 (m, 3H), 1.75-1.67 (m, 2H), 1.57-1.53 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 138.0, 134.0, 129.4, 128.5, 67.4, 33.5, 25.1, 22.4, 21.7, 21.0.

2-Hydroxy-2-phenylethyl 4-methylphenyl sulfone (3ab)[2] (Table 2)



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32-7.24 (m, 5H), 5.24 (d, *J* = 9.3 Hz, 1 H), 3.79 (br s, 1H), 3.47 (dd, *J* = 14.3 Hz, 9.3 Hz, 1H), 3.31 (dd, *J* = 14.3 Hz, 1.8 Hz, 1H), 2.45 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 145.2, 140.6, 136.0, 130.1, 128.7, 128.2, 128.0, 125.6, 68.4, 63.9, 21.6.

2-Hydroxy-2-phenylethyl 4-chlorophenyl sulfone (3ac) (Table 2)



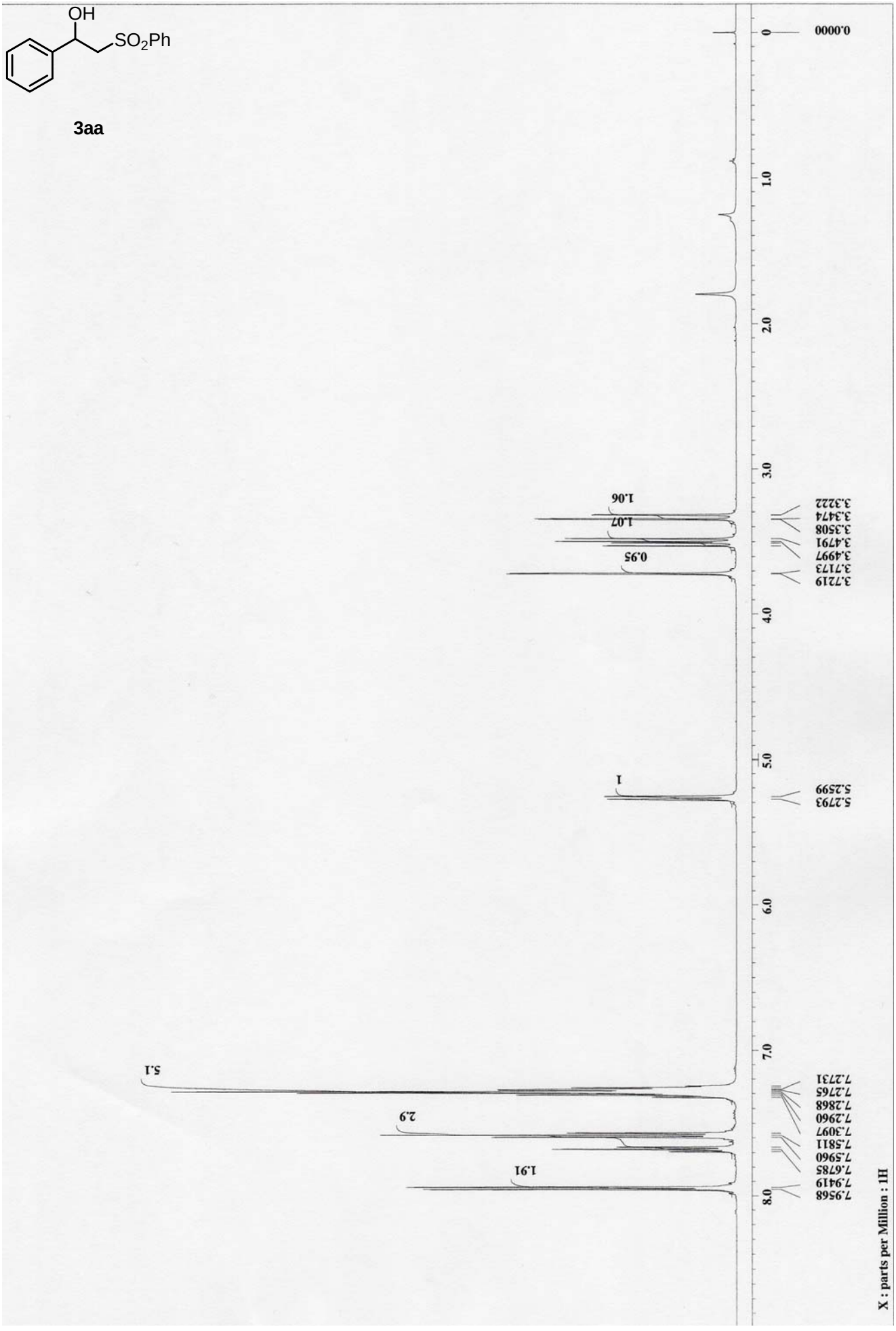
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (m, 2H), 7.53 (m, 2H), 7.35-7.26 (m, 5H), 5.27 (dd, *J* = 10.2 Hz, 2.0 Hz, 1 H), 3.52 (dd, *J* = 14.6 Hz, 10.2 Hz, 1H), 3.33 (dd, *J* = 14.6 Hz, 2.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 140.8, 140.5, 137.7, 129.7, 129.5, 128.8, 128.4, 125.6, 68.5, 63.9. Anal. Calcd for $C_{14}H_{13}ClO_3S$: C, 56.66; H, 4.42. Found: C, 56.46; H, 4.13.

3. References

(1) X. Wan, Q. Meng, H. Zhang, Y. Sun, W. Fan and Z. Zhang, *Org. Lett.*, 2007, **9**, 5613-5616.

(2) T. Taniguchi, A. Idota and H. Ishibashi, *Org. Biomol. Chem*., 2011, **9**, 3151–3153.

(3) L. M. Harwood, M. Julia and G. Le Thuillier, *Tetrahedron*, 1980, **36**, 2483-2487.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7.2731
5.2793
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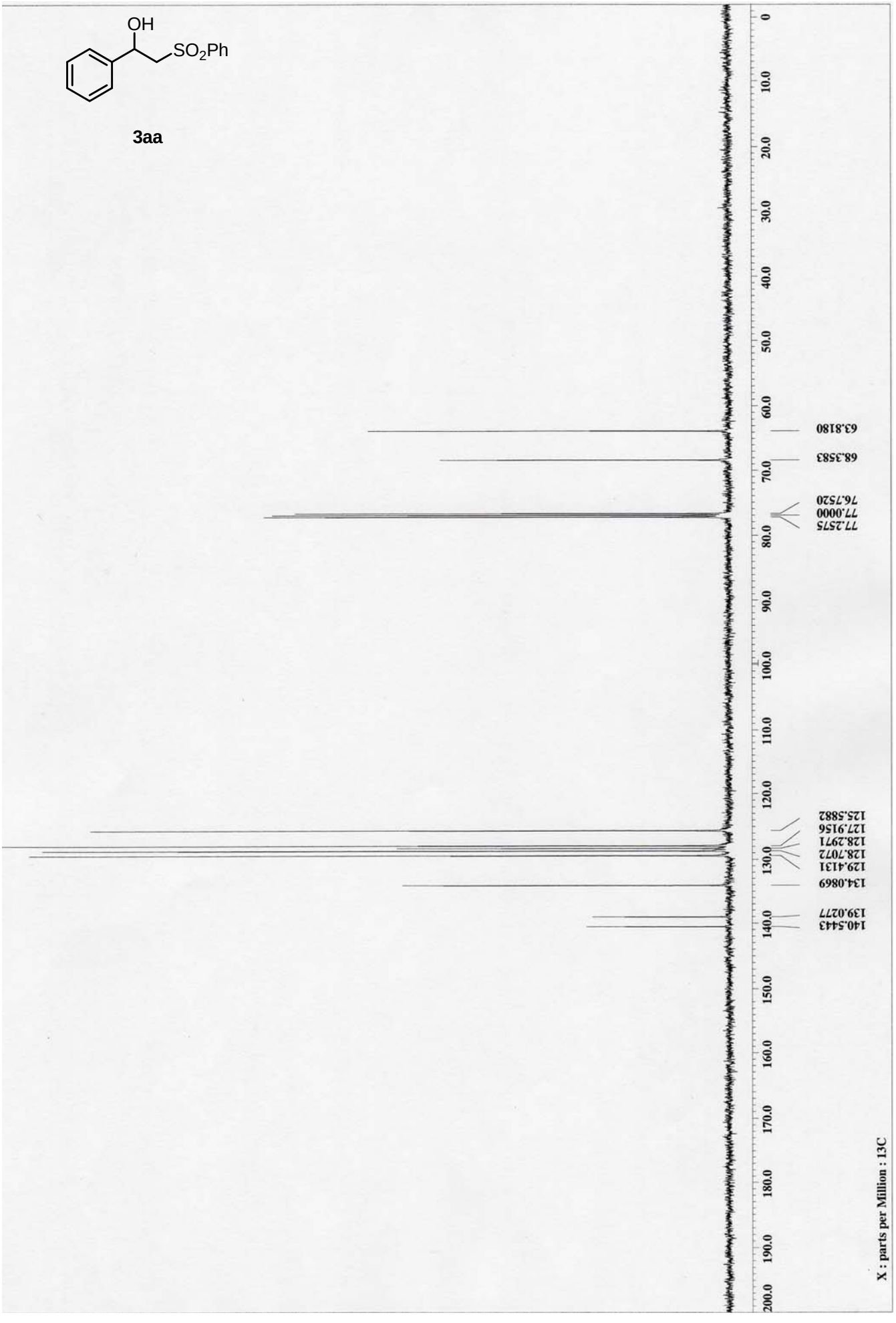
X : parts per Million : 1H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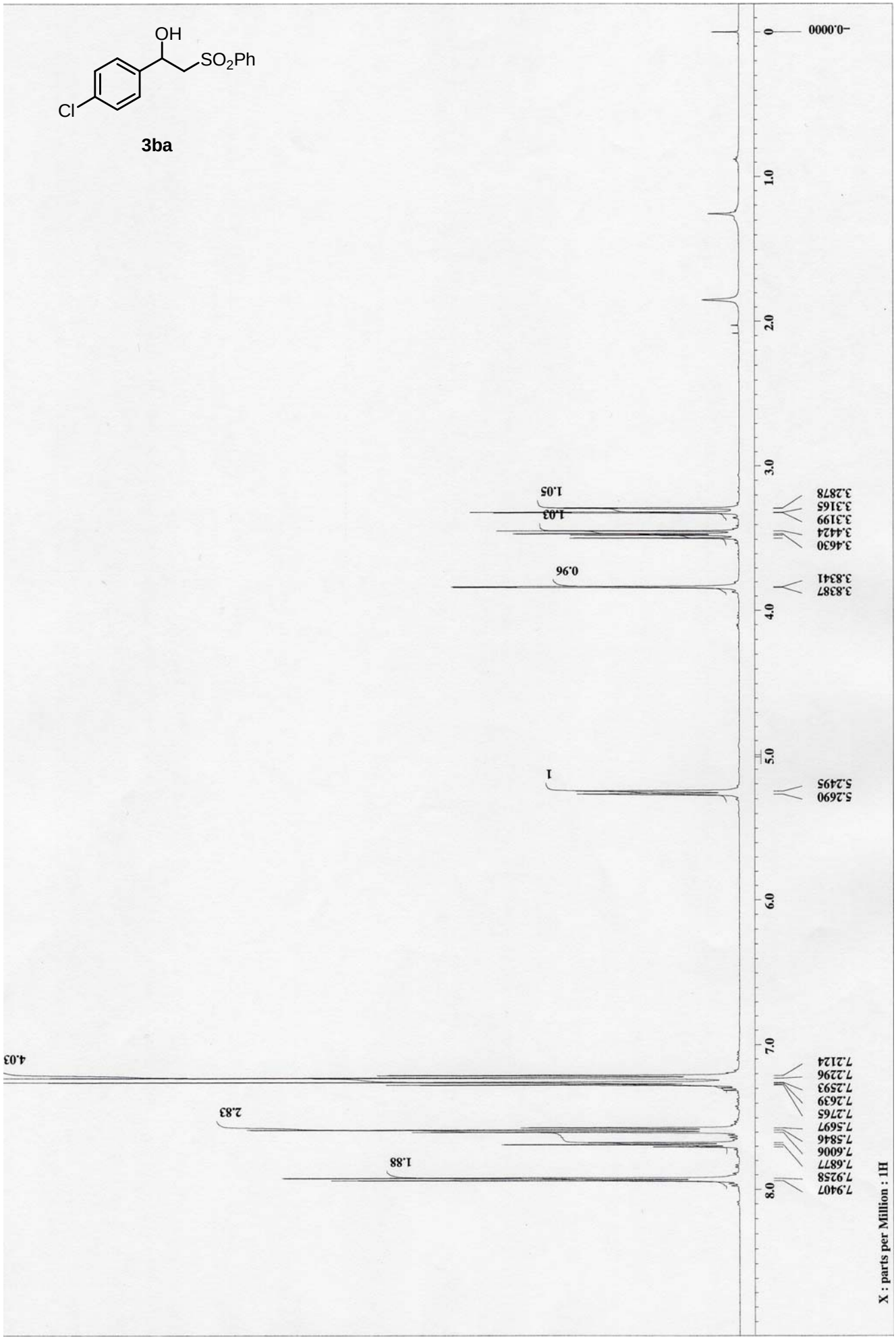
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3ba
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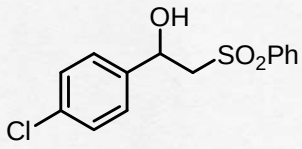
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Cl

3ba

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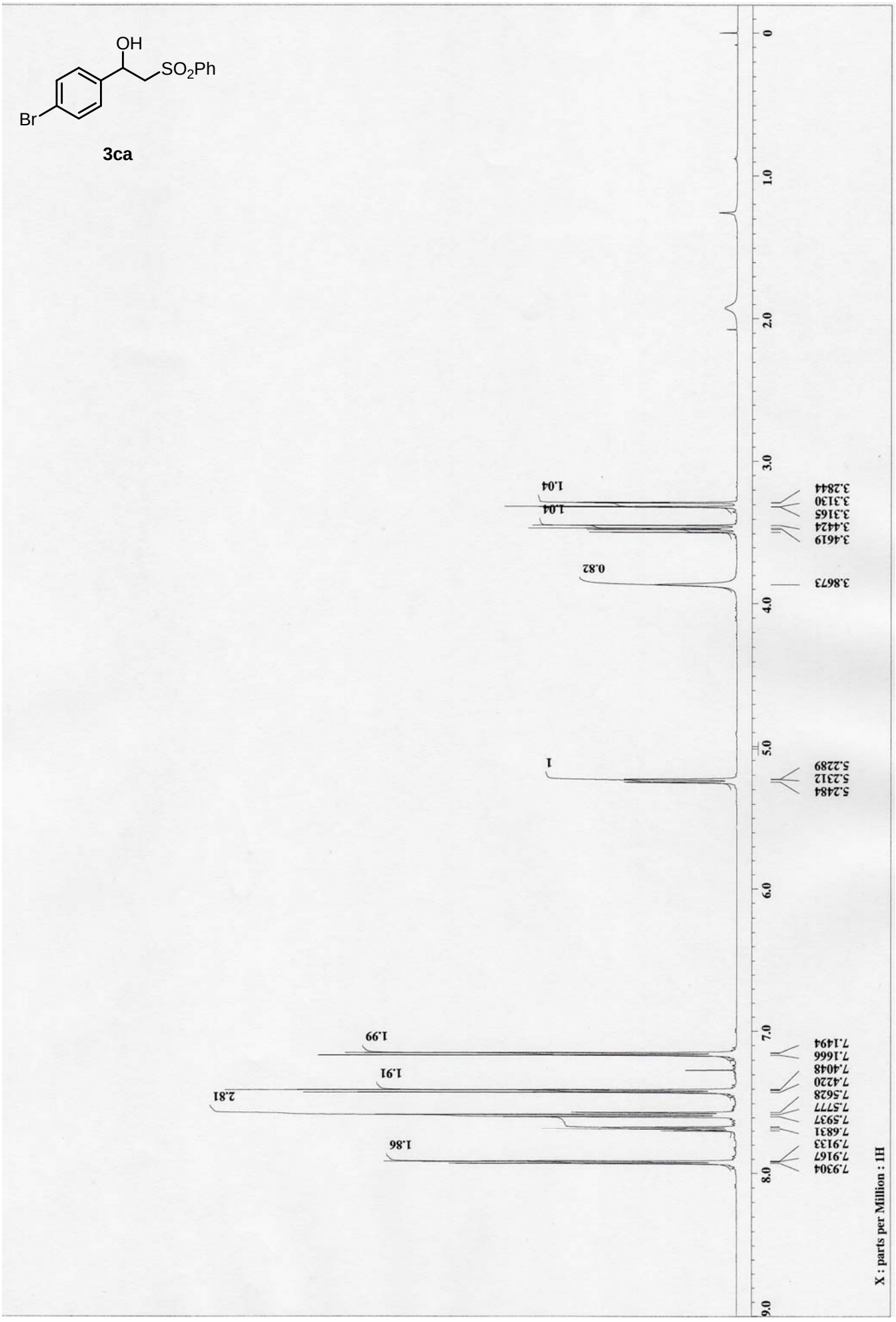
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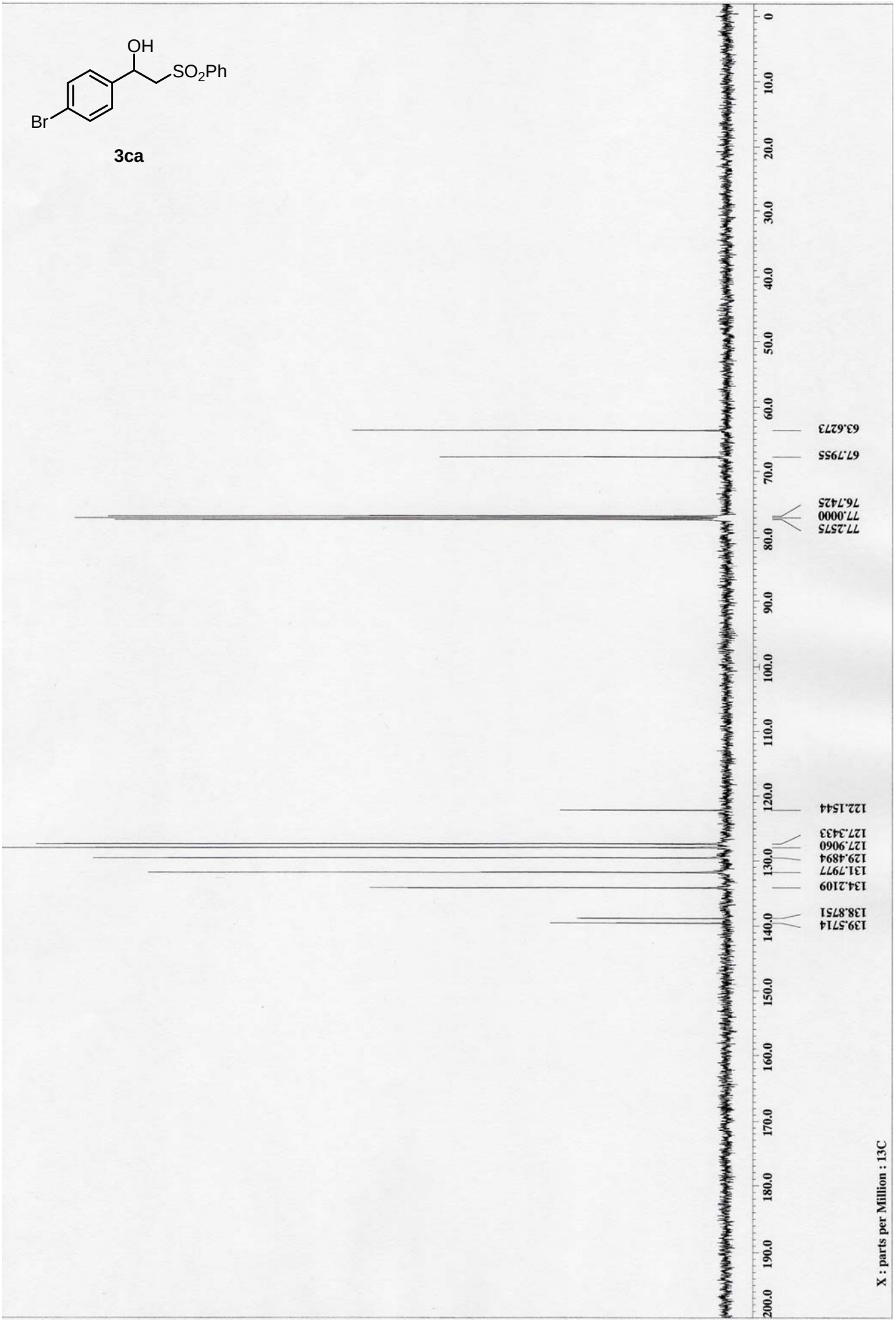
X : parts per Million : 1H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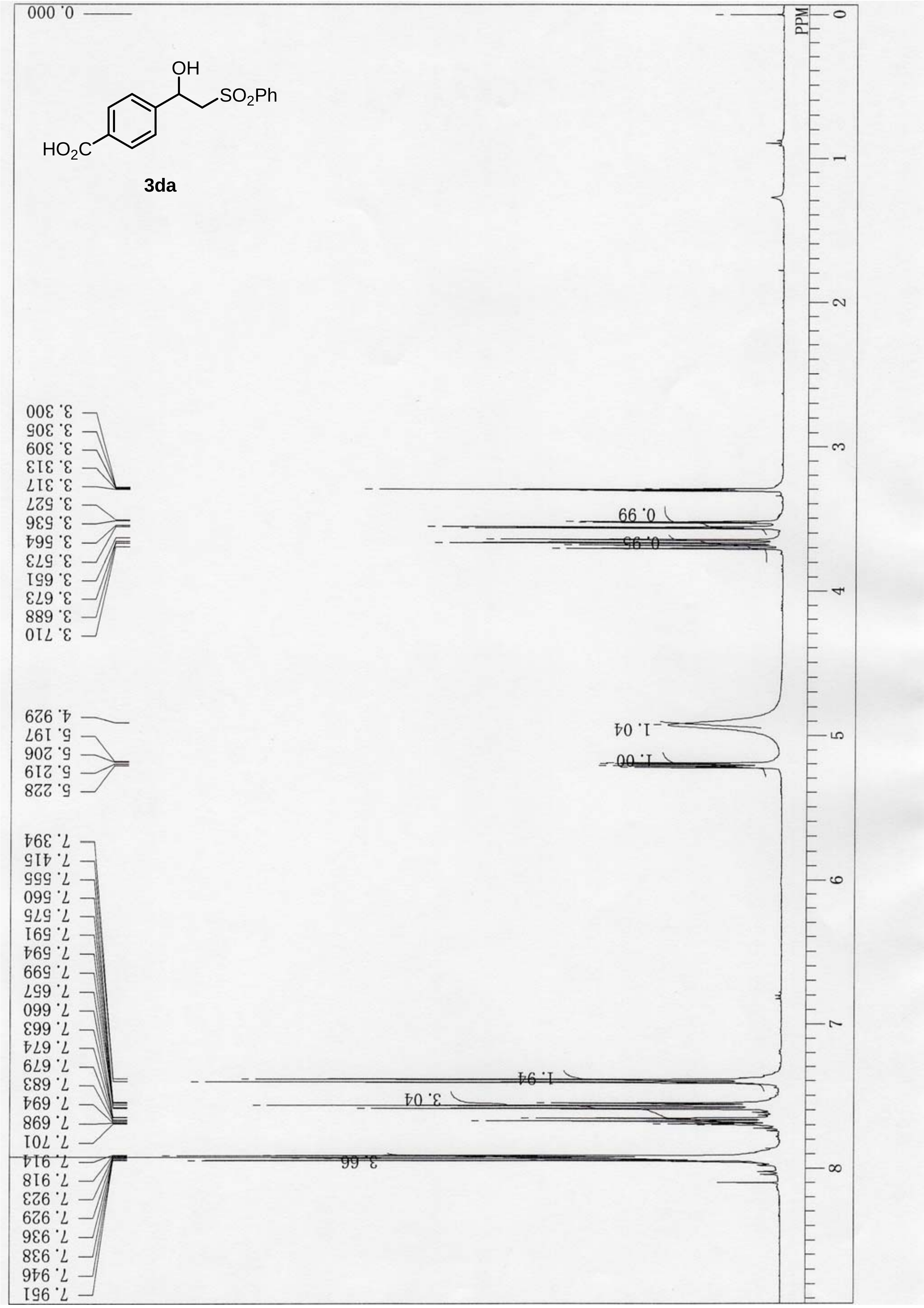
X : parts per Million : 13C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3.651
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7.575
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7.663
7.674
7.679
7.683
7.694
7.698
7.701
7.914
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7.923
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6
7
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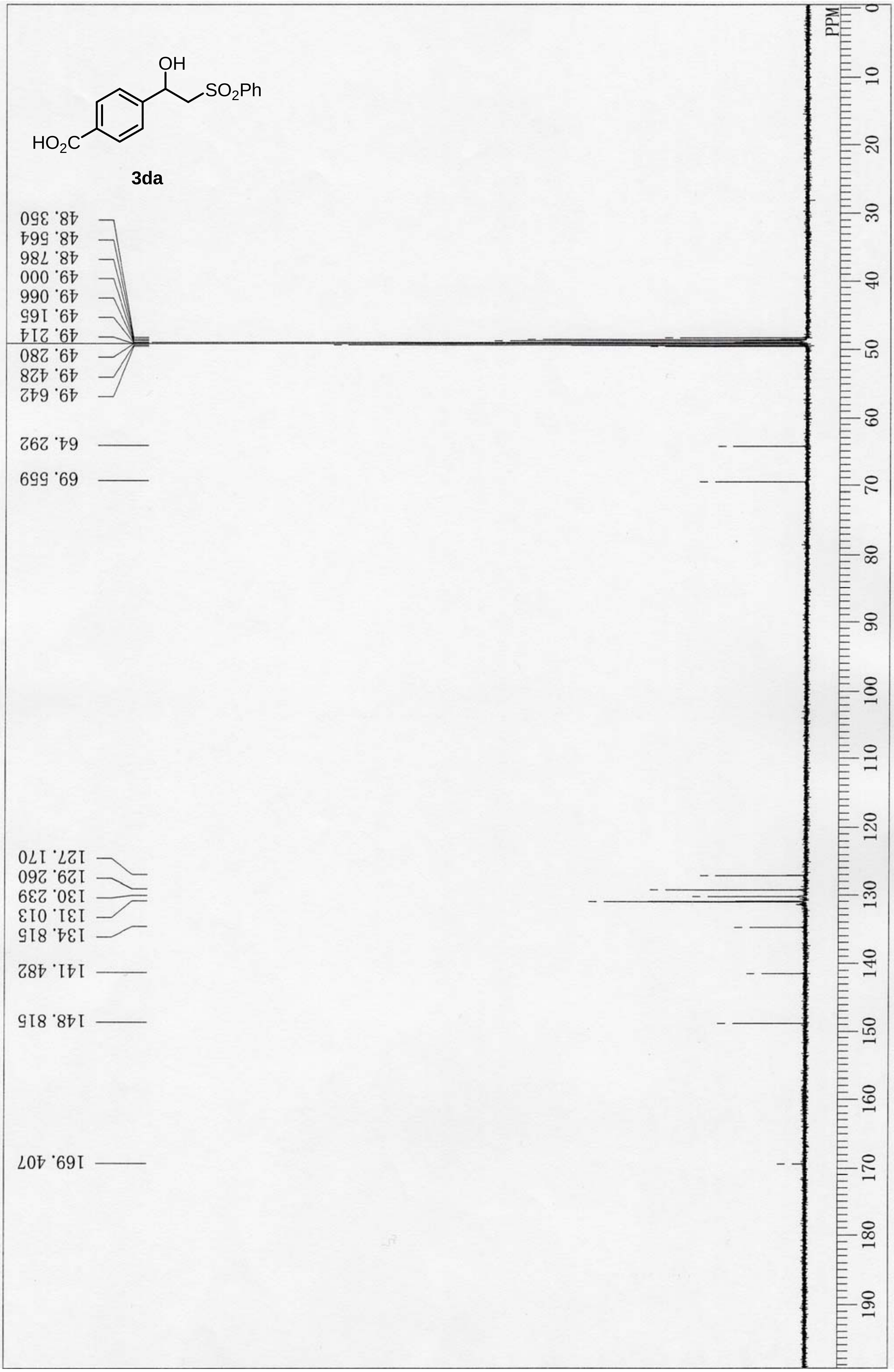
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130.239
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169.407
PPM
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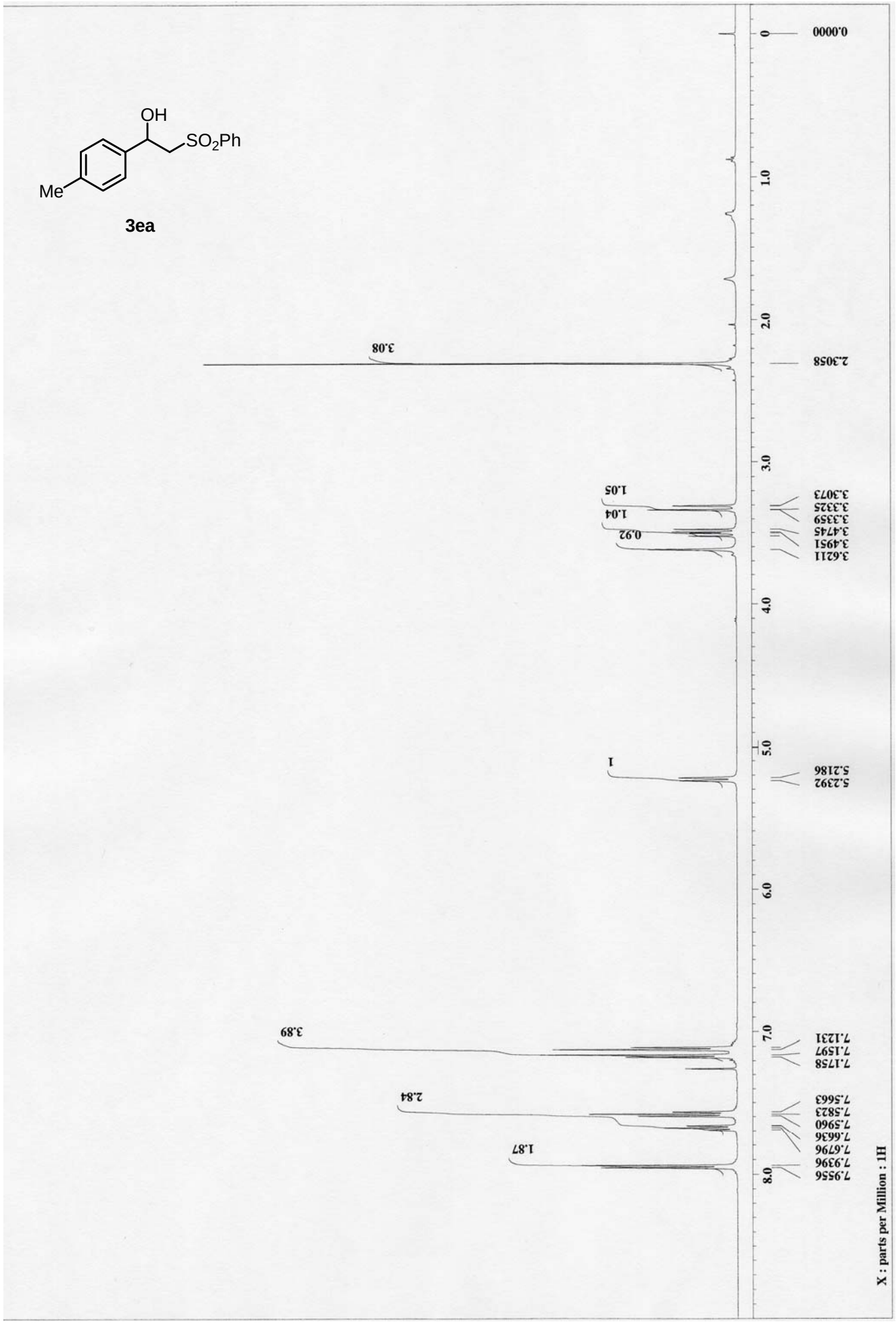
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SO2Ph
Me
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X : parts per Million : 1H
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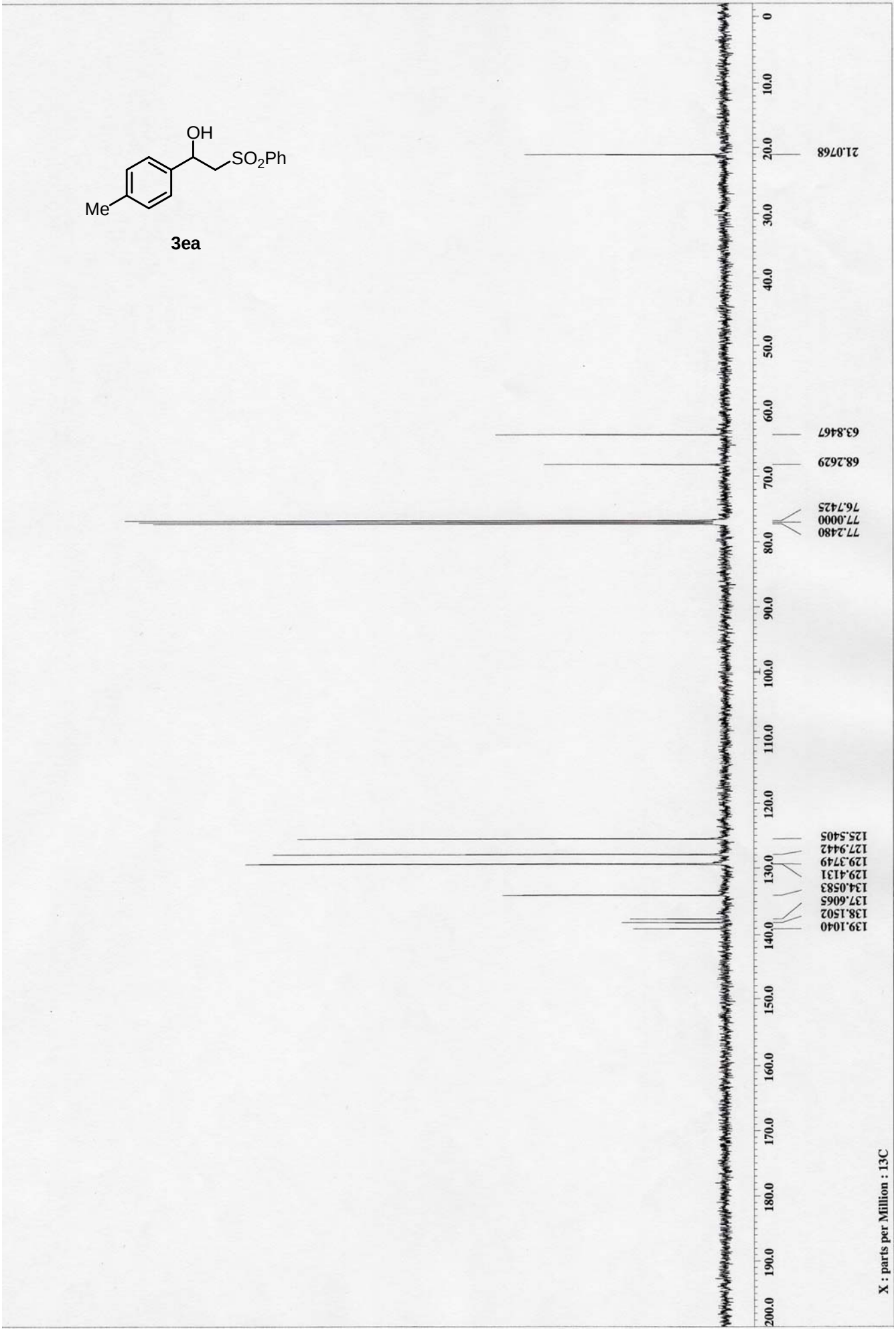
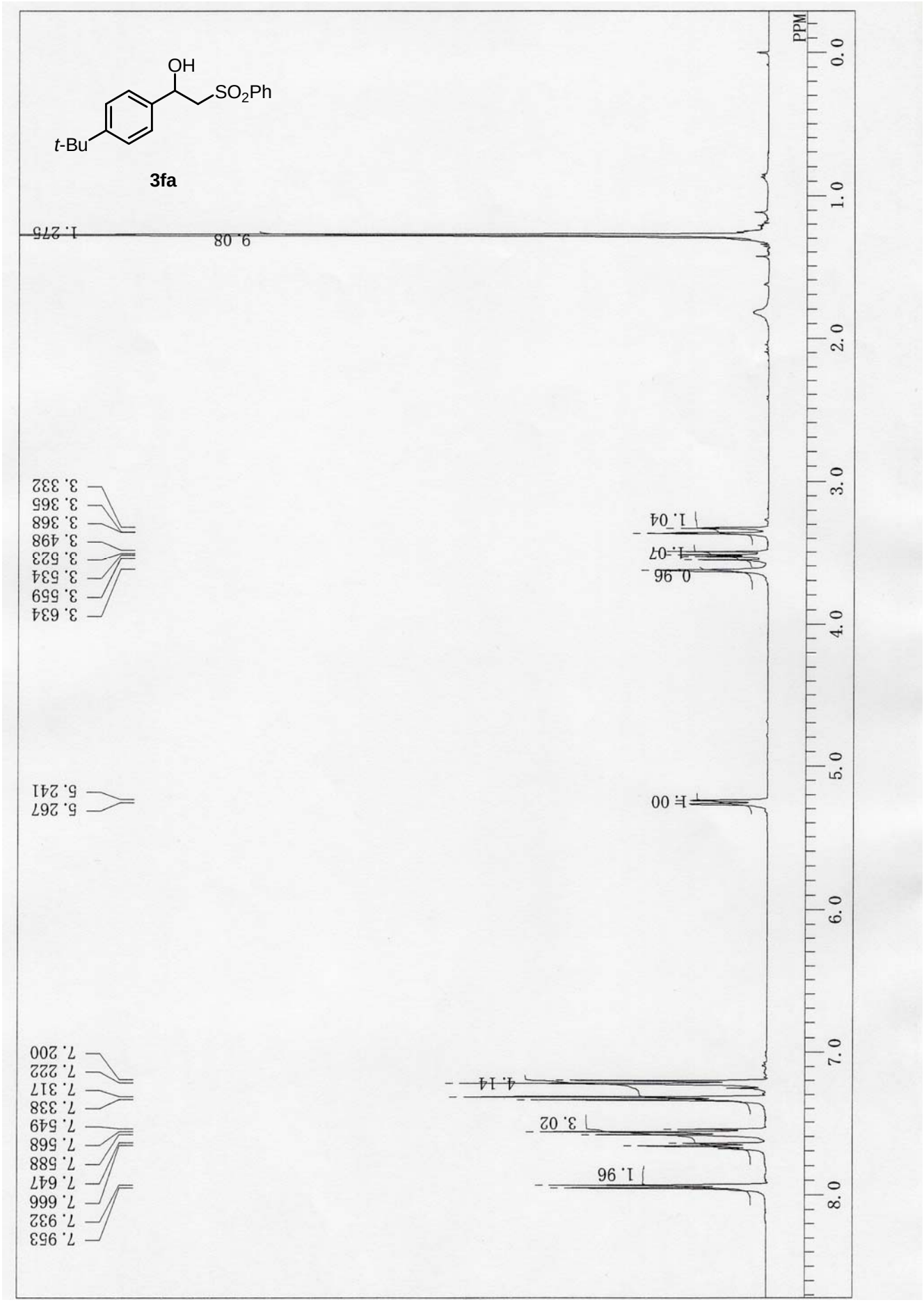
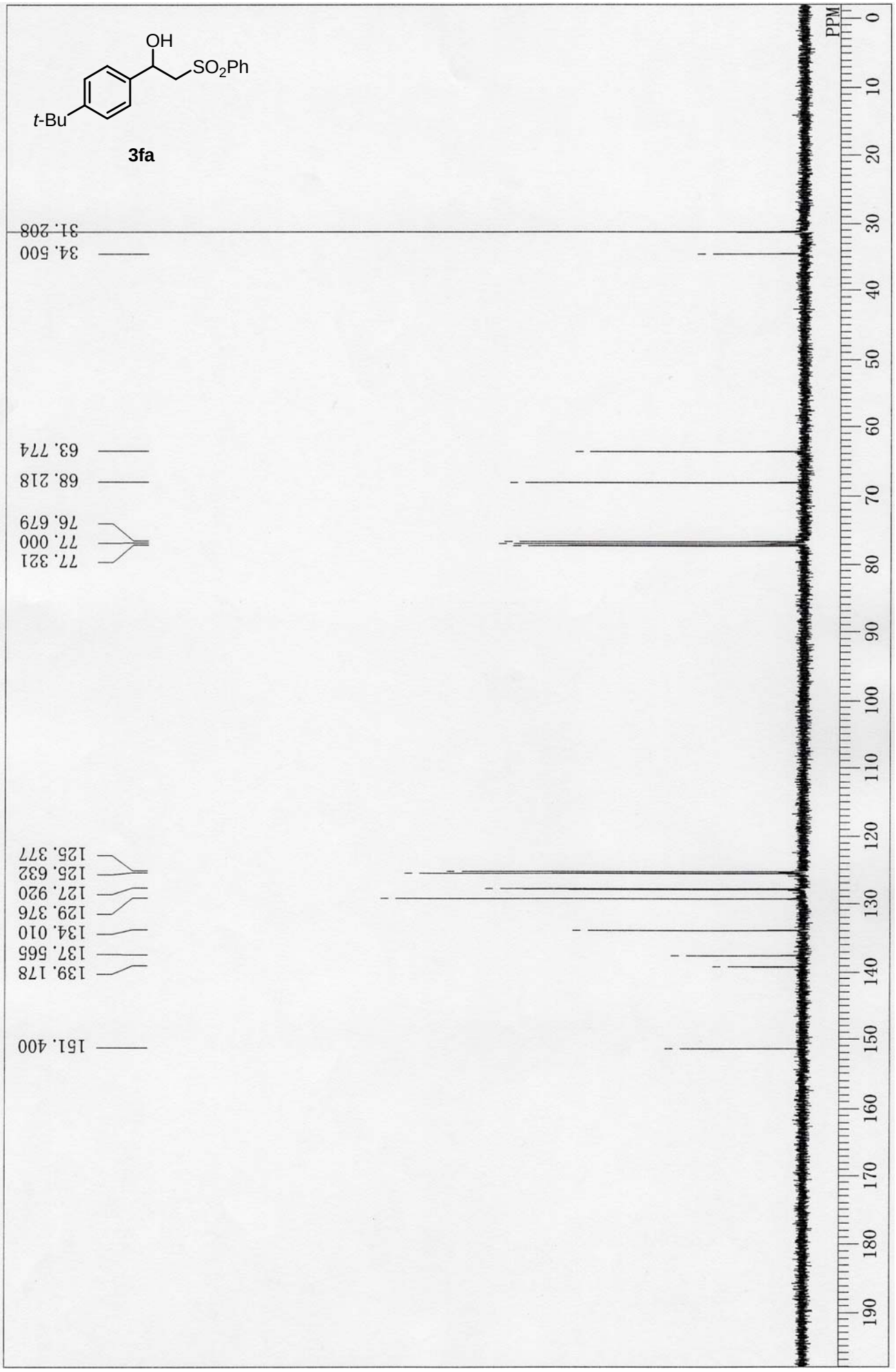
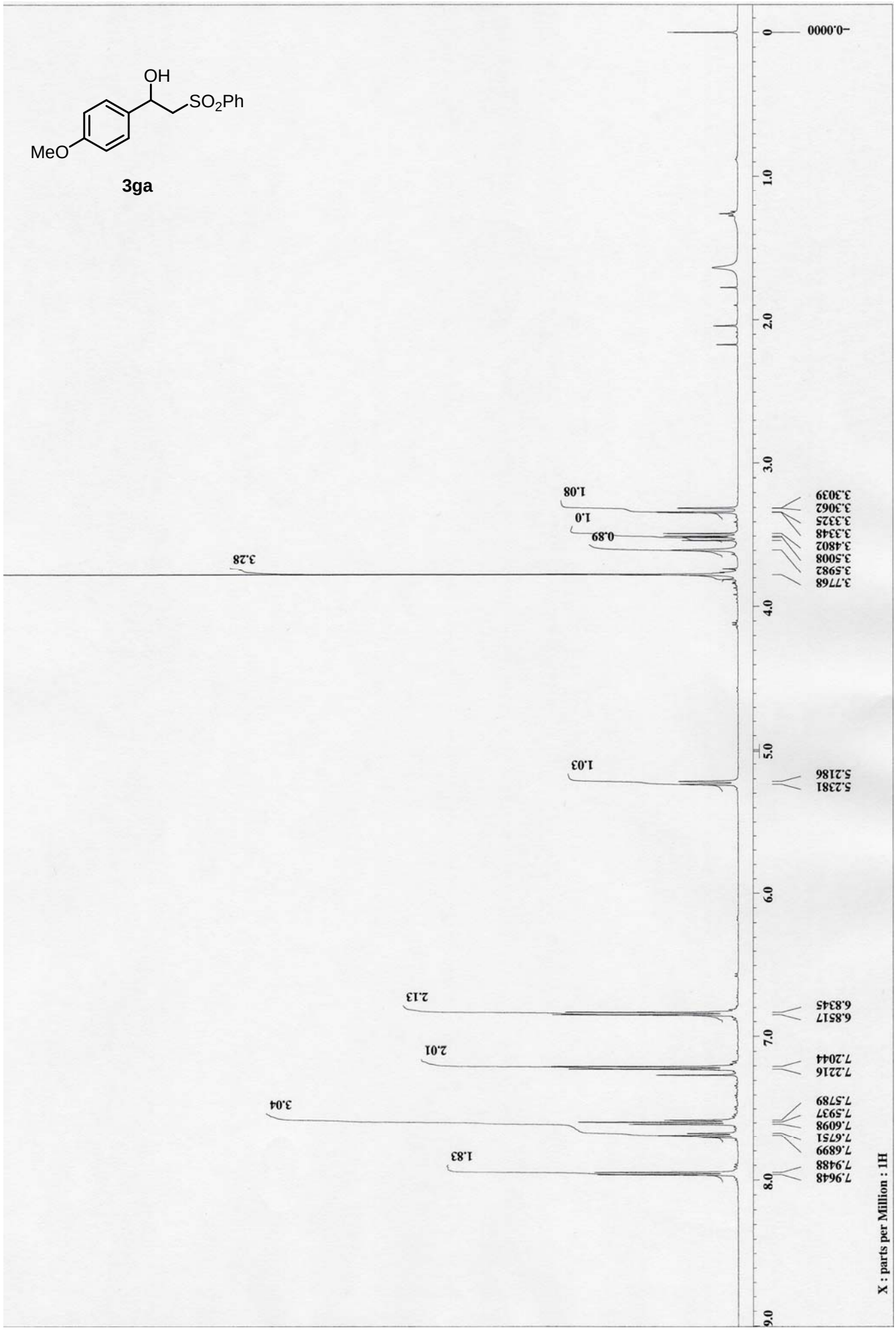
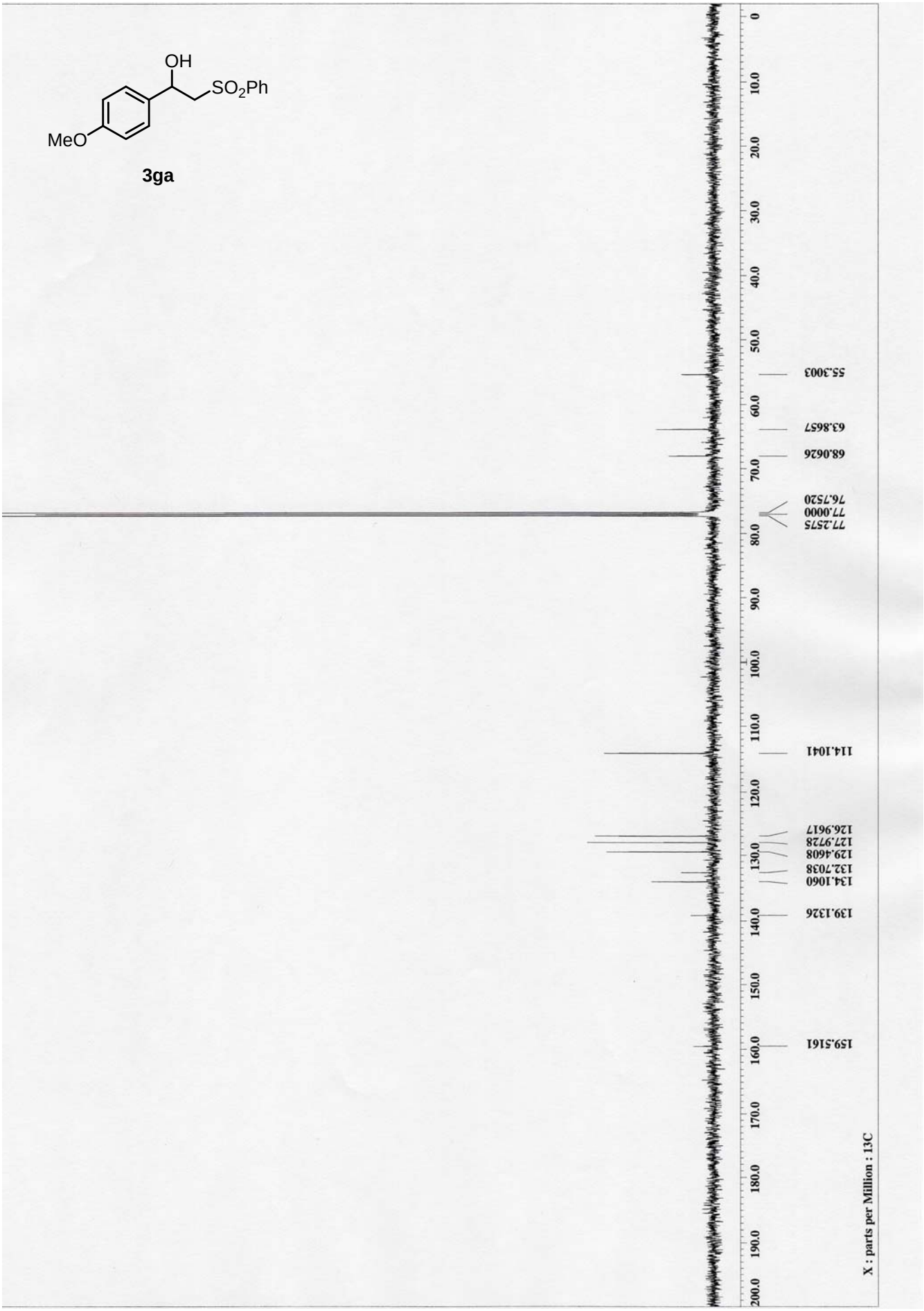
1.04
1.05

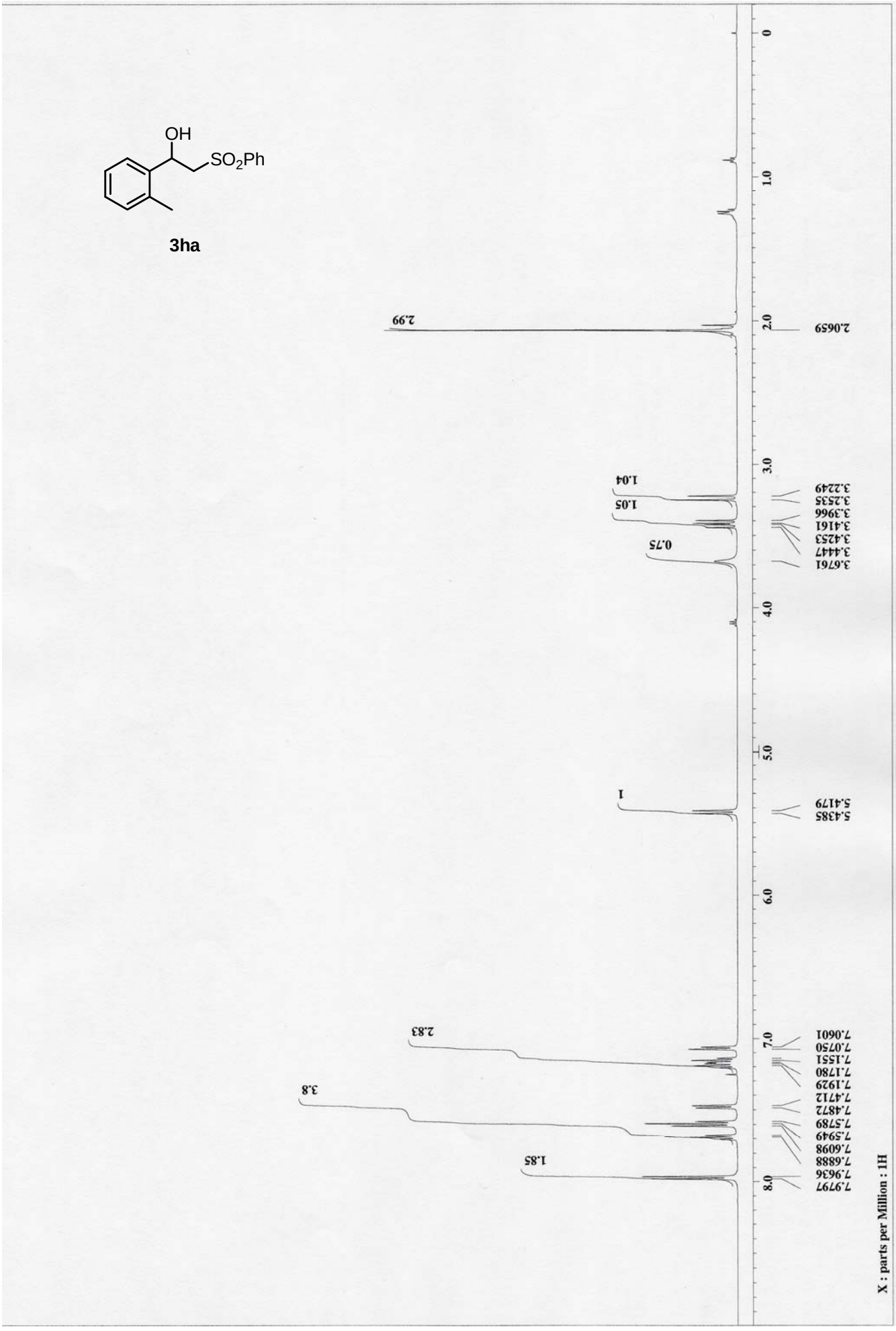

OH
SO2Ph
Me
3ea
21.0768
63.8467
68.2629
76.7425
77.0000
77.2480
125.5405
127.9442
129.3749
129.4131
134.0583
137.6065
138.1502
139.1040
X : parts per Million : 13C

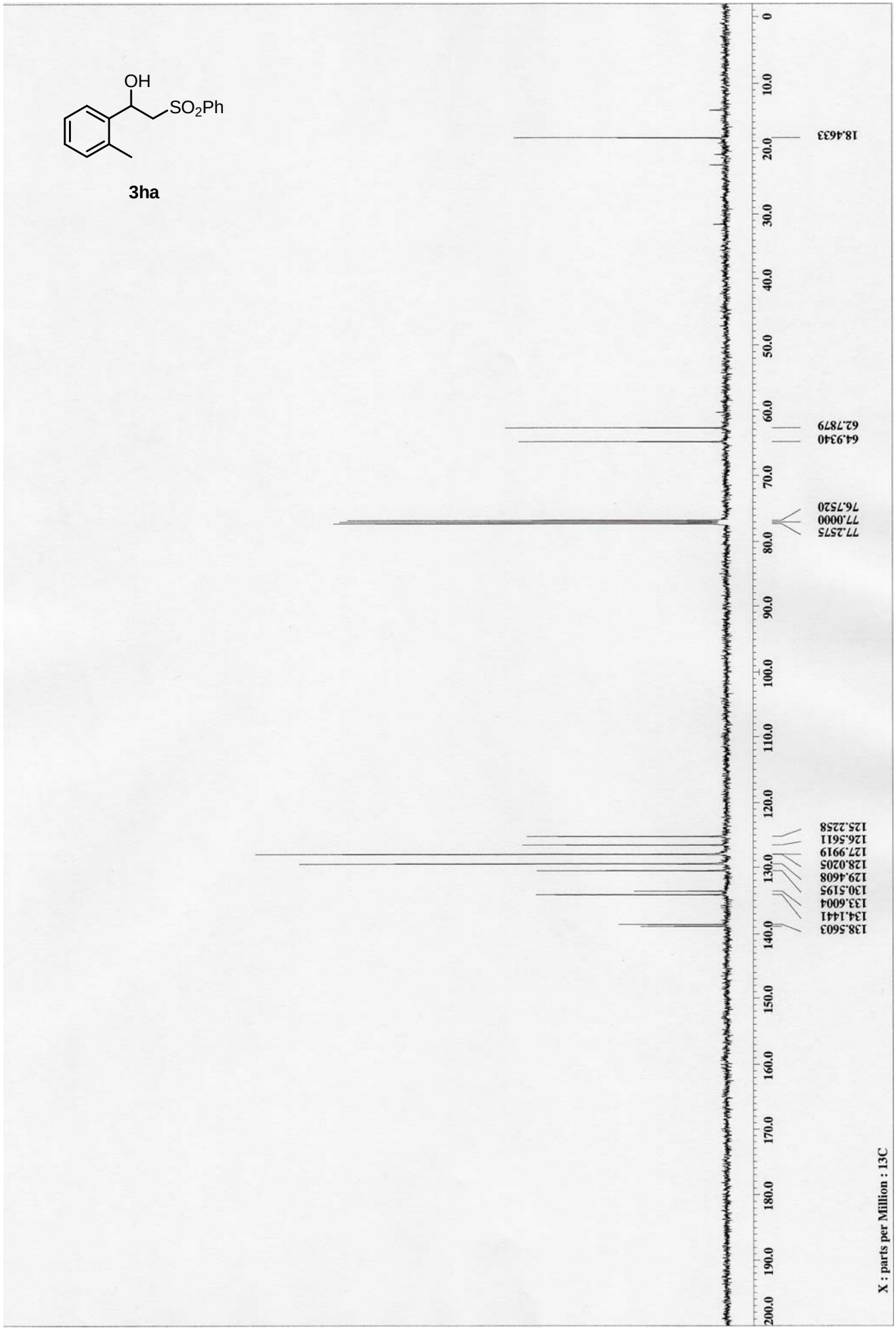

OH
SO2Ph
t-Bu
3fa
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
1.275
9.08
1.04
1.07
0.96
1.00
5.267
5.241
7.953
7.932
7.666
7.647
7.588
7.568
7.549
7.338
7.317
7.222
7.200
4.14
3.02
1.96

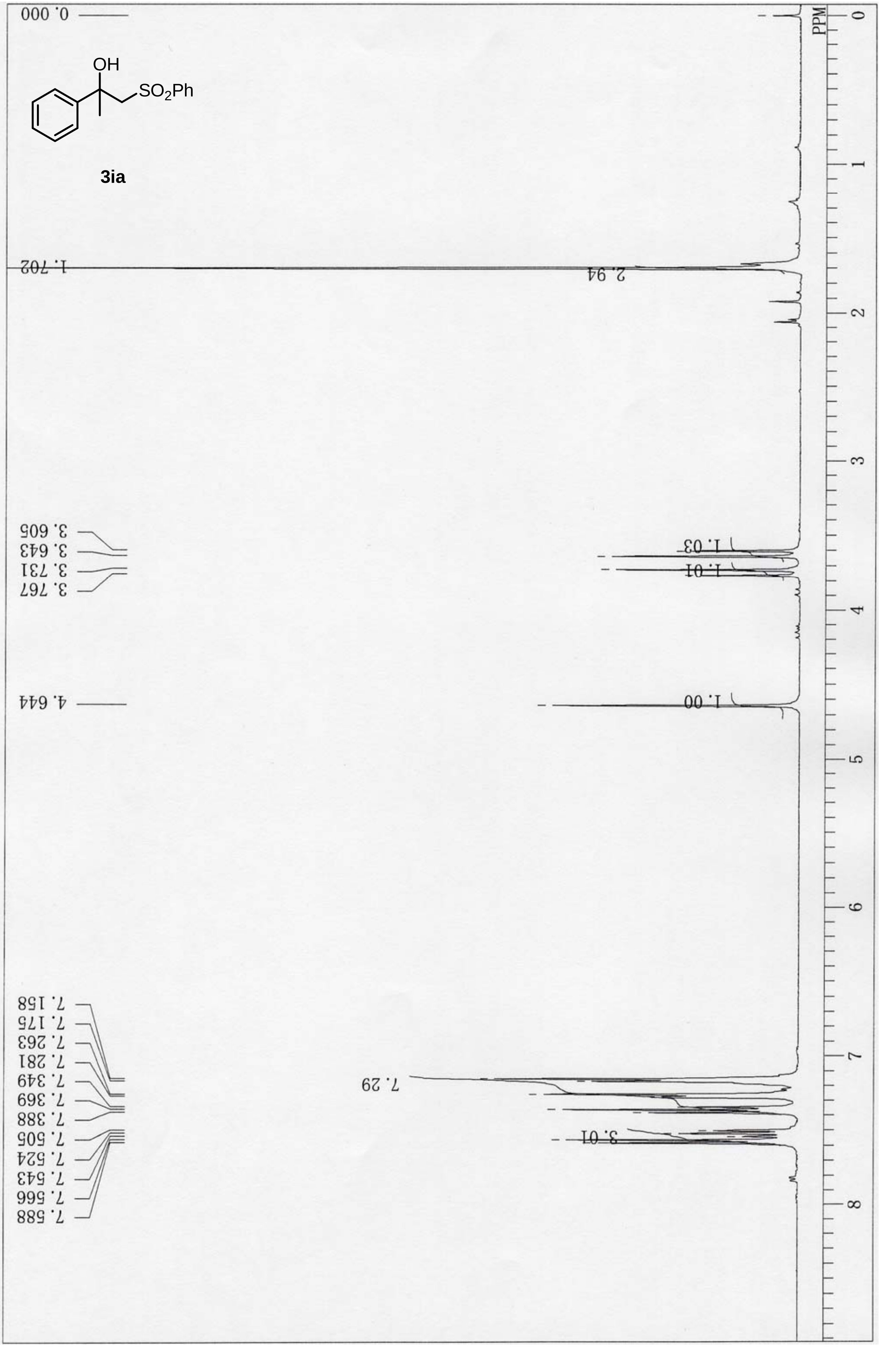

OH
SO2Ph
t-Bu
3fa
31.208
34.500
63.774
68.218
76.679
77.000
77.321
125.377
125.632
127.920
129.376
134.010
137.565
139.178
151.400
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


OH
SO2Ph
MeO
3ga
X : parts per Million : 1H
7.9648
7.9488
7.6899
7.6751
7.6098
7.5937
7.5789
7.2216
7.2044
6.8517
6.8345
5.2381
5.2186
3.7768
3.5982
3.5008
3.4802
3.3348
3.3325
3.3062
3.3039
3.28
1.83
3.04
2.01
2.13
1.03
0.89
1.0
1.08

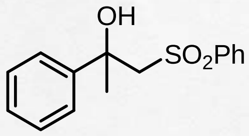

OH
SO2Ph
MeO
3ga
55.3003
63.8657
68.0626
76.7520
77.0000
77.2575
114.1041
126.9617
127.9728
129.4608
132.7038
134.1060
139.1326
159.5161
X : parts per Million : 13C


OH
SO2Ph
3ha
7.9797
7.9636
7.6888
7.6098
7.5949
7.5789
7.4872
7.4712
7.1929
7.1780
7.1551
7.0750
7.0601
5.4385
5.4179
3.6761
3.4447
3.4253
3.4161
3.3966
3.2535
3.2249
2.0659
1.85
3.8
2.83
1
0.75
1.05
1.04
2.99
X : parts per Million : 1H

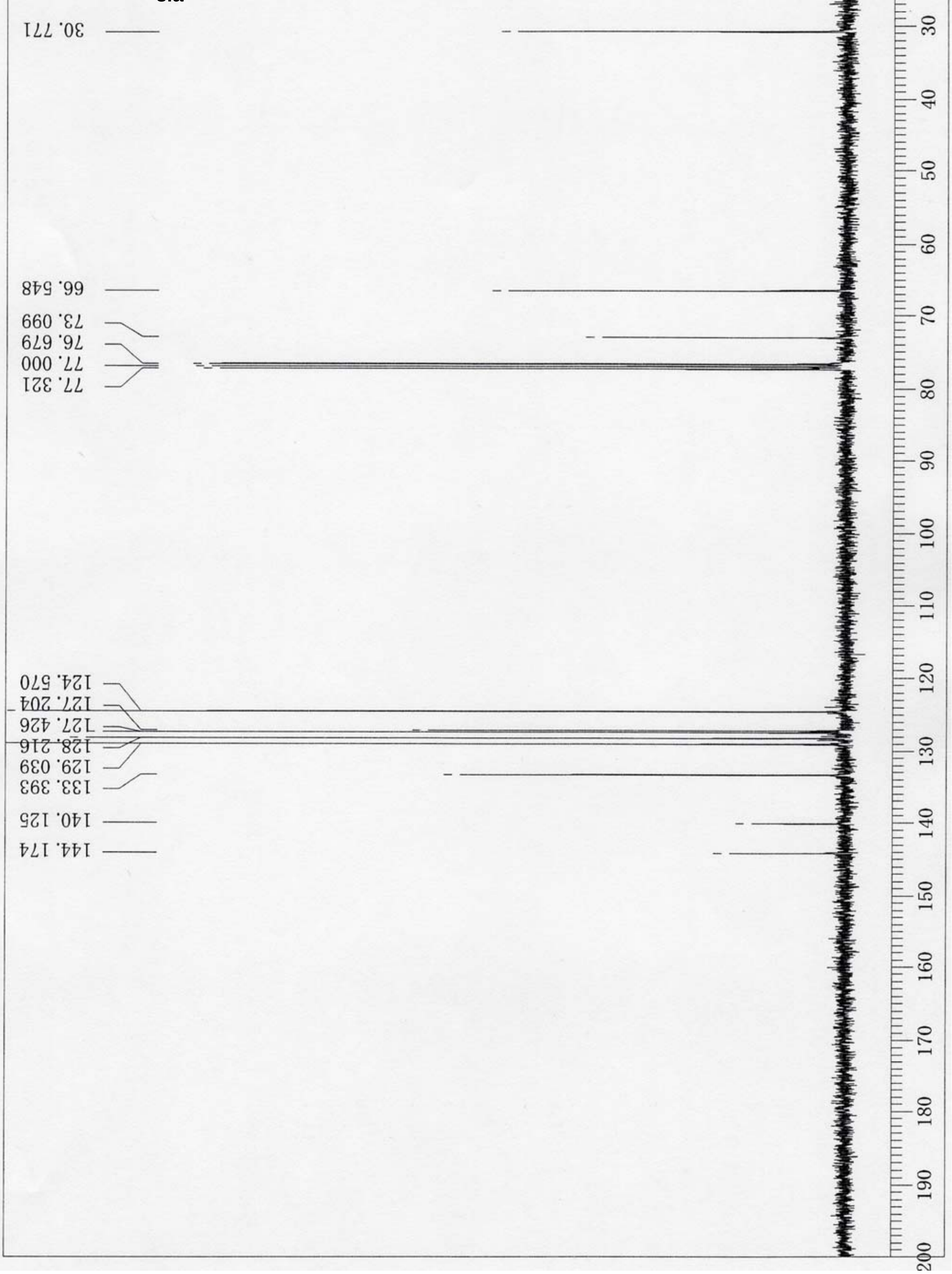

OH
SO2Ph
3ha
18.4633
62.7879
64.9340
76.7520
77.0000
77.2575
125.2258
126.5611
127.9919
128.0205
129.4608
130.5195
133.6004
134.1441
138.5603
X : parts per Million : 13C

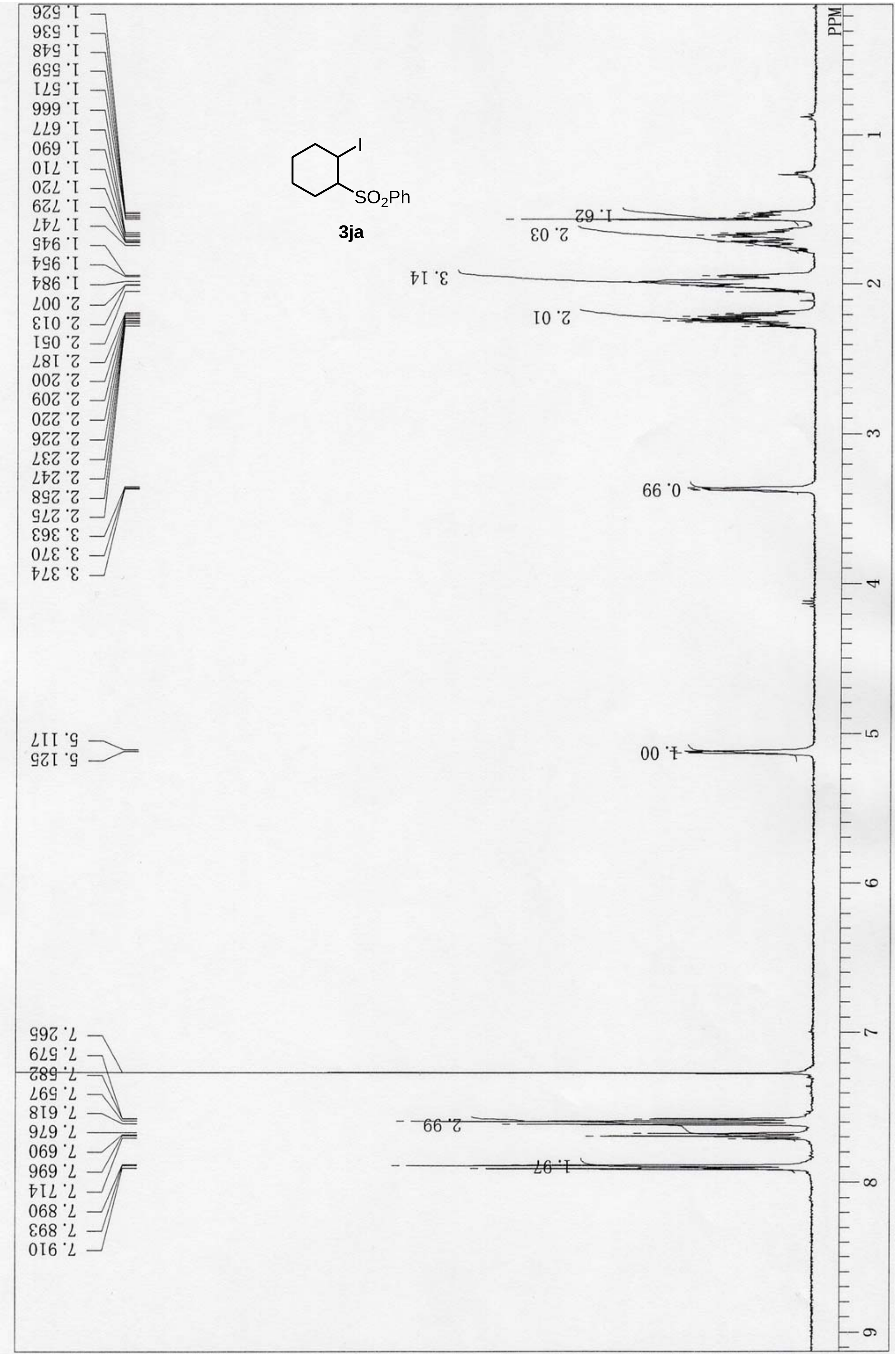


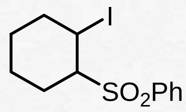
OH
SO2Ph
3ia
0.000
1.702
3.605
3.643
3.731
3.767
4.644
7.158
7.175
7.263
7.281
7.349
7.369
7.388
7.505
7.524
7.543
7.566
7.588
2.94
1.03
1.01
1.00
7.29
3.01
PPM
0
1
2
3
4
5
6
7
8


OH
SO2Ph

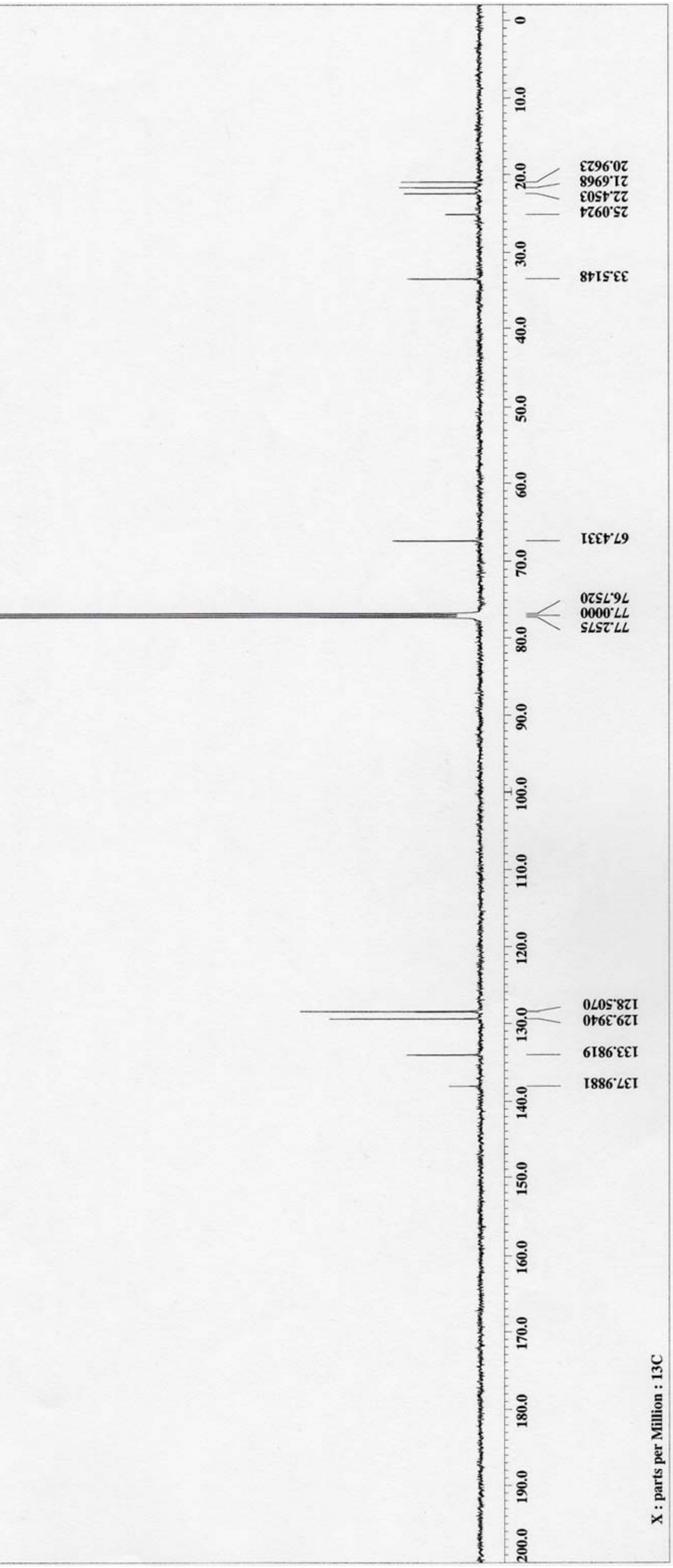
3ia

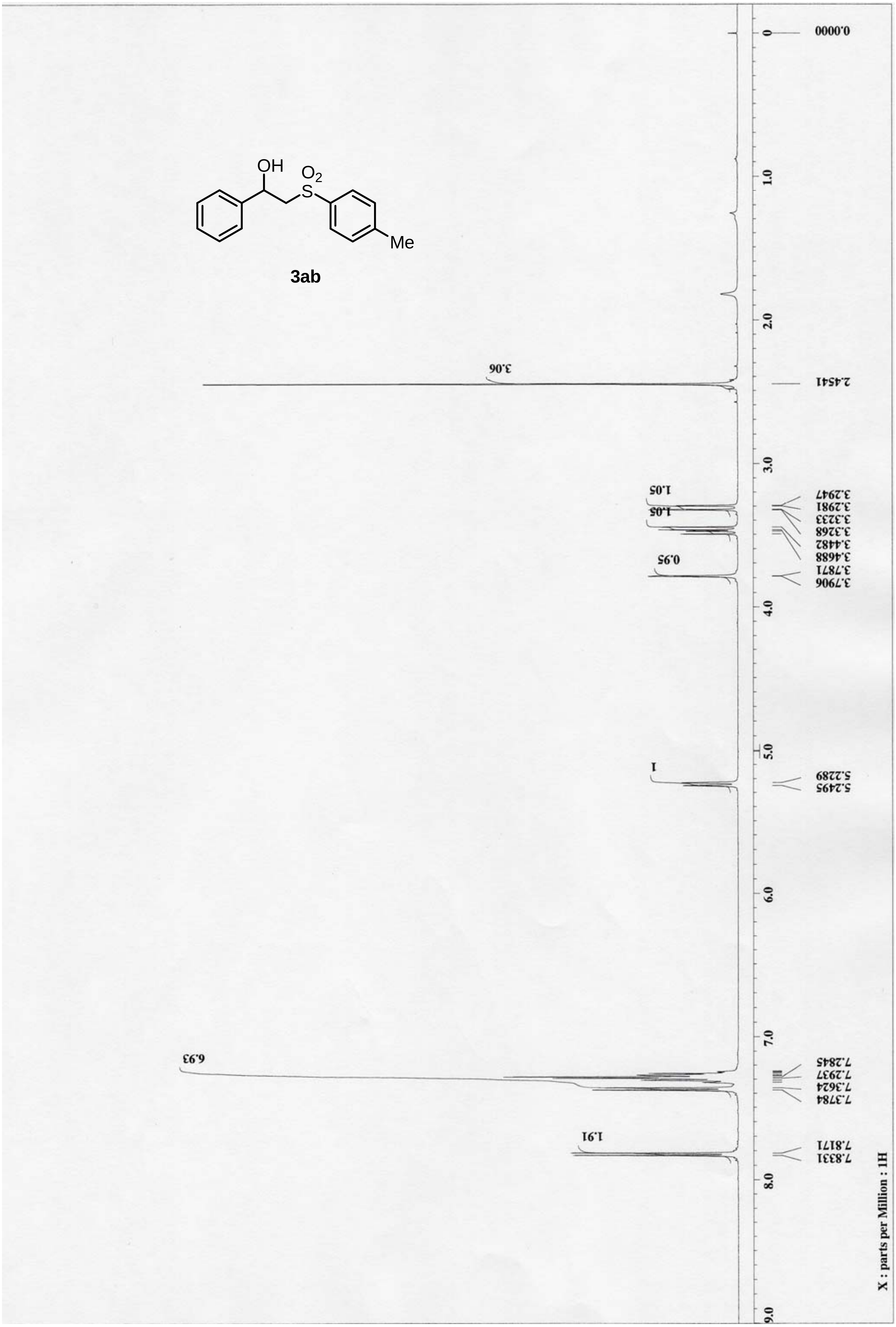

30.771
66.548
73.099
76.679
77.000
77.321
124.570
127.204
127.426
128.216
129.039
133.393
140.125
144.174
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

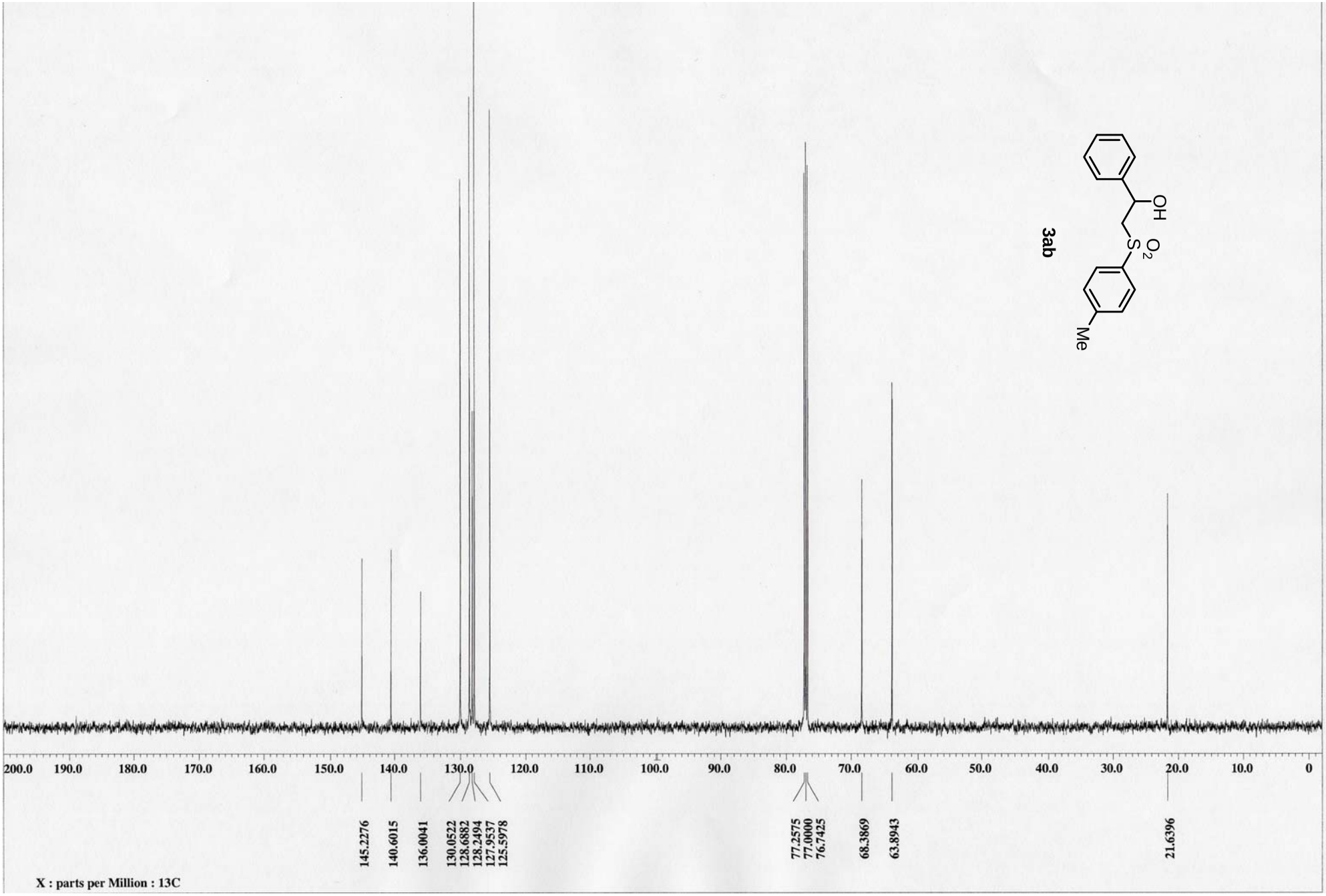

I
SO2Ph
3ja
1.526
1.536
1.548
1.559
1.571
1.666
1.677
1.690
1.710
1.720
1.729
1.747
1.945
1.954
1.984
2.007
2.013
2.051
2.187
2.200
2.209
2.220
2.226
2.237
2.247
2.258
2.275
3.363
3.370
3.374
5.117
5.125
7.265
7.579
7.582
7.597
7.618
7.676
7.690
7.696
7.714
7.890
7.893
7.910
1.62
2.03
3.14
2.01
0.99
1.00
2.99
1.97
PPM
1
2
3
4
5
6
7
8
9

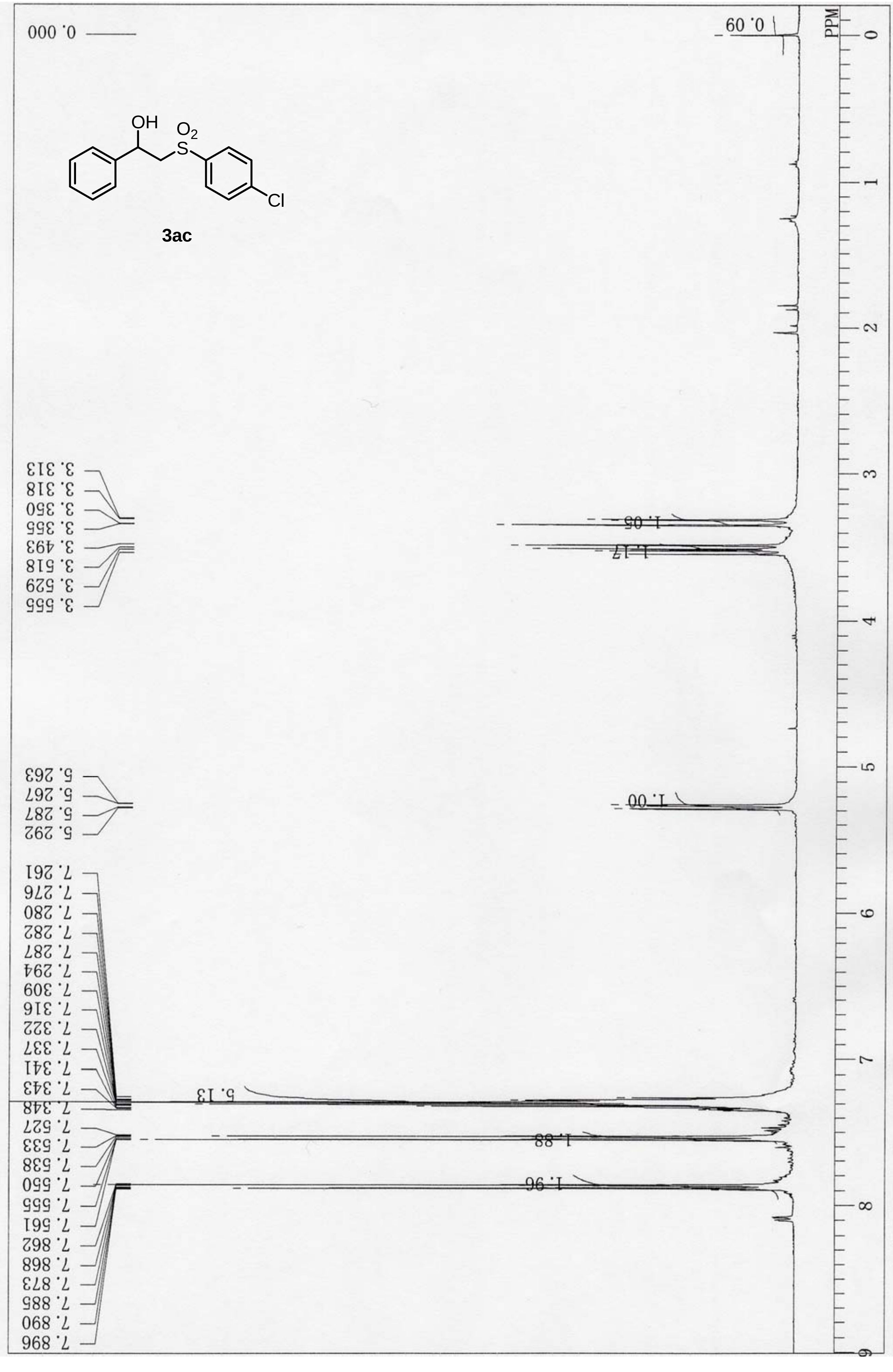

I
SO2Ph

3ja

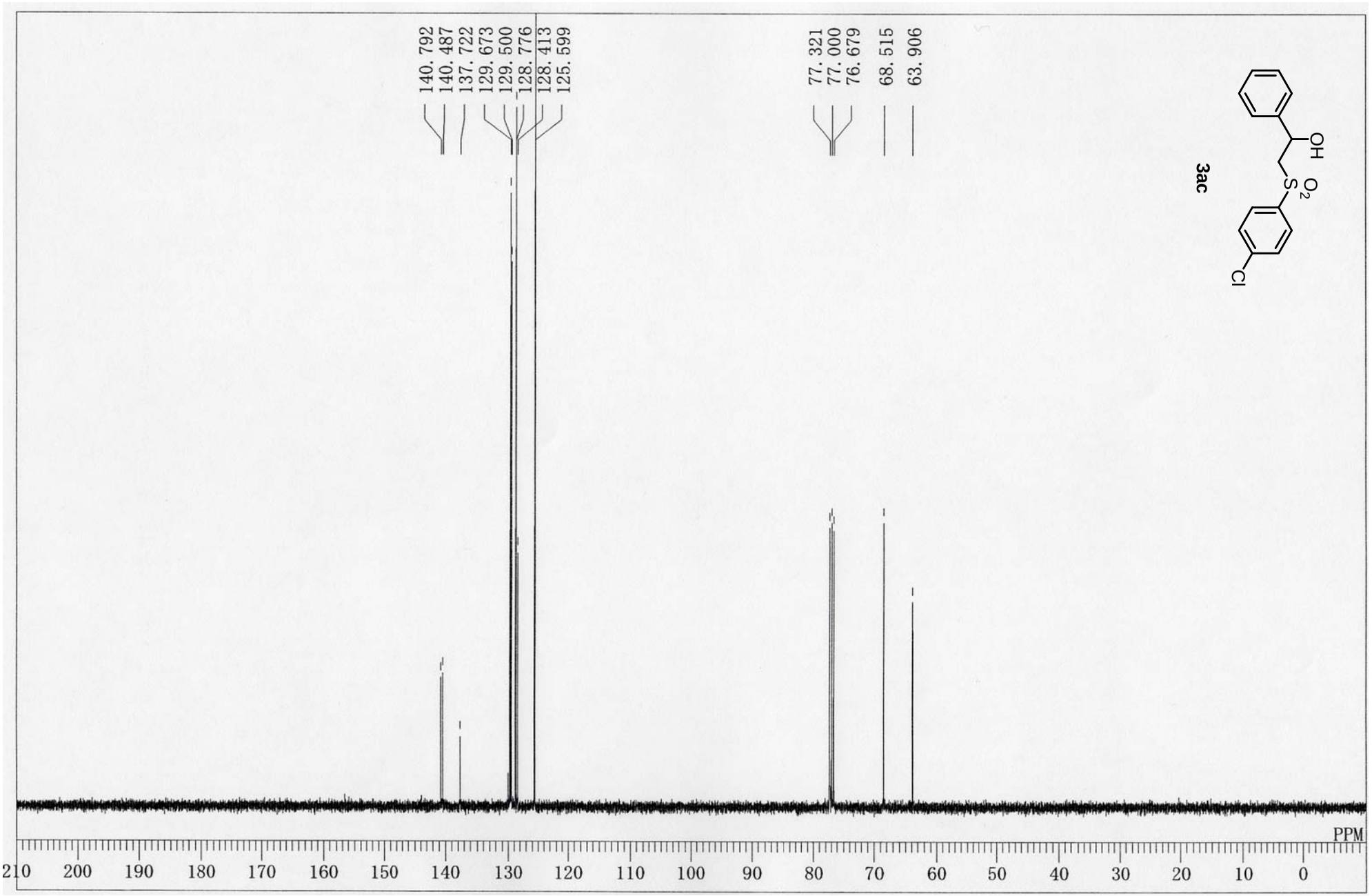

20.9623
21.6968
22.4503
25.0924
33.5148
67.4331
76.7520
77.0000
77.2575
128.5070
129.3940
133.9819
137.9881
X : parts per Million : 13C


OH
O2
S
Me
3ab
3.06
1.05
1.05
0.95
1
6.93
1.91
0.0000
2.4541
3.2947
3.2981
3.3233
3.3268
3.4482
3.4688
3.7871
3.7906
5.2289
5.2495
7.2845
7.2937
7.3624
7.3784
7.8171
7.8331
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H


OH
S
O2
Me
3ab
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
145.2276
140.6015
136.0041
130.0522
128.6882
128.2494
127.9537
125.5978
77.2575
77.0000
76.7425
68.3869
63.8943
21.6396
X : parts per Million : 13C



OH
O2
S
Cl
3ac
0.000
3.313
3.318
3.350
3.355
3.493
3.518
3.529
3.555
5.263
5.267
5.287
5.292
7.261
7.276
7.280
7.282
7.287
7.294
7.309
7.316
7.322
7.337
7.341
7.343
7.348
7.527
7.533
7.538
7.550
7.555
7.561
7.862
7.868
7.873
7.885
7.890
7.896
0.09
1.05
1.17
1.00
5.13
1.88
1.96
PPM
0
1
2
3
4
5
6
7
8
9


140.792
140.487
137.722
129.673
129.500
128.776
128.413
125.599
77.321
77.000
76.679
68.515
63.906
OH
O2
S
Cl
3ac
PPM
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0