Supporting Information

Copper-Catalyzed Synthesis of Benzimidazoles via Cascade Reactions of *o*-Haloacetanilide Derivatives with Amidine Hydrochlorides

Daoshan Yang,[†,‡] Hua Fu,[*,†] Liming Hu,[*,‡] Yuyang Jiang,[†,§] Yufen Zhao[†]

Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China, College of Life Sciences and Bioengineering, Beijing University of Technology, Beijing 100124, P. R. China, and Key Laboratory of Chemical Biology (Guangdong Province), Graduate School of Shenzhen, Tsinghua University, Shenzhen 518057, P. R. China

fuhua@mail.tsinghua.edu.cn; huliming@bjut.edu.cn

Table of contents

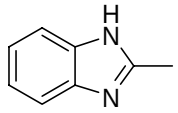
General experimental procedures

All reactions were carried out under nitrogen atmosphere. DMF and DMSO were dried over $MgSO_4$. Unless stated otherwise, all reagents were weighed and handled in air at room temperature. Flash chromatography was performed on silica gel (200 ~ 300 mesh). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.24 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of DMSO-d_6 as the internal standard (^{1}H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0 ppm).

General procedure for copper-catalyzed synthesis of 2-substituted *1H*-benzimidazoles (3a-k) and 1,2-disubstituted benzimidazoles (5a-i)

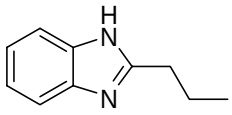
A flask was charged with CuBr (14 mg, 0.1 mmol), Cs_2CO_3 (977 mg, 3 mmol) (see Tables 2 and 3) in 2 mL of DMSO, and *o*-haloacetanilide (1 mmol) and amidine hydrochloride (1.2 mmol) (see Tables 2 and 3) were added to the flask at room temperature under nitrogen atmosphere. The mixture was stirred at 60 ~ 90 ^{o}C (see Tables 1 and 2) under nitrogen atmosphere. After the coupling reaction for a time as shown in Tables 2 and 3, the resulting solution was raised to 120 ^{o}C, and the reaction was maintained for 48 h. The reaction system was cooled to room temperature, and then the work-up was performed for synthesis of 2-substituted benzimidazoles in Table 2. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo, The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product. For synthesis of disubstituted benzimidazoles in Table 3, aryl iodide (2 mmol) and 3,4,7,8-tetramethyl-1,10-phenanthroline (47 mg, 0.2 mmol) were added to the resulting solution, and the reaction was carried out at 120 or 130 ^{o}C for 36 h under nitrogen atmosphere. The following work-up was similar to the former (2-substituted

benzimidazoles).



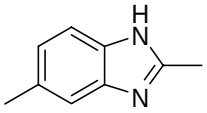
3a

2-Methylbenzimidazole (3a).[1] Eluent: ethyl acetate. Yield 80% (106 mg). White solid, mp 172-174 ^{o}C (lit.[1] 172-173 ^{o}C). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 9.86 (s, 1H), 7.57-7.54 (m, 2H), 7.23-7.21 (m, 2H), 2.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 151.6, 138.7, 122.2, 114.6, 15.0. ESI-MS M^+ m/z 132.0.



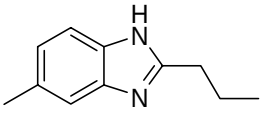
3b

2-Propylbenzimidazole (3b).[2] Eluent: petroleum ether/ethyl acetate (1:1). Yield 65% (103 mg). White solid, mp 155-157 ^{o}C (lit.[2] 156-157.5 ^{o}C). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ 12.7 (s, 1H), 7.56-7.55 (m, 2H), 7.30-7.19 (m, 2H), 3.00 (t, 2H, J = 7.6 Hz), 1.90 (dt, 2H, J = 7.6 Hz), 0.97 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 156.0, 138.7, 122.2, 114.7, 31.3, 22.0, 14.0. ESI-MS M^+ m/z 160.1.



3c

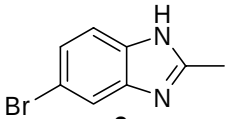
2,5-Dimethylbenzimidazole (3c).[3] Eluent: petroleum ether/ethyl acetate (3:1). Yield 75% (109 mg). Brown solid, mp 199-201 ^{o}C (lit.[3] 203-204 ^{o}C). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 9.93 (s, 1H), 7.44 (d, 1H, J = 8.3 Hz), 7.33 (s, 1H), 7.04 (d, 1H, J = 8.3 Hz), 2.62 (s, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 151.1, 138.5, 137.1, 132.0, 123.7, 114.4, 114.1, 21.7, 14.6. ESI-MS M^+ m/z 146.1.



3d

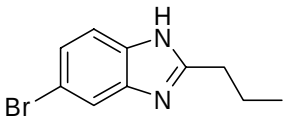
5-Methyl-2-propylbenzimidazole (3d). Eluent: petroleum ether/ethyl acetate (1:1). Yield 62% (107 mg). Yellow solid, mp 154-156 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ 11.6 (s, 1 H), 7.45-7.43 (d, 1H, J = 7.9 Hz), 7.33 (s, 1H), 7.05-7.02 (d, 1H, J

= 8.3 Hz), 2.92 (t, 2H, *J* = 7.6Hz), 2.44 (s, 3H), 1.88 (dt, 2H, *J* = 7.6 Hz), 0.97 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 155.3, 138.6, 137.2, 131.9, 123.5, 114.6, 114.2, 31.3, 21.9, 21.7, 13.9. ESI-MS M^+ m/z 174.3.



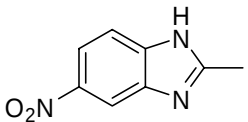
3e

5-Bromo-2-methylbenzimidazole (3e). Eluent: ethyl acetate. Yield 86% (180 mg). White solid, mp 232-233 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm), δ 7.65 (s, 1H), 7.43-7.40 (d, 1H, *J* = 9.0 Hz), 7.26-7.23 (d, 1H, *J* = 9.0 Hz), 2.50 (s, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 153.4, 141.3, 138.2, 124.4, 117.7, 116.1, 113.8, 15.1. ESI-MS M^+ 210.5, 212.4.



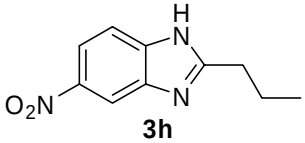
3f

5-Bromo-2-propylbenzimidazole (3f). Eluent: petroleum ether/ethyl acetate (2:1). Yield 65% (154 mg). White solid, 109-112 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ 12.0 (s, 1H), 7.68 (s, 1H), 7.42-7.39 (d, 1H, *J* = 8.6 Hz), 7.34-7.31 (d, 1H, *J* = 8.6 Hz), 2.95 (t, 2H, *J* = 7.6 Hz), 1.89 (dt, 2H, *J* = 7.2 Hz), 0.99 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 156.7, 139.8, 137.4, 125.5, 117.6, 115.8, 115.4, 31.3, 21.8, 13.9. ESI-MS M^+ m/z 238.9, 240.8.



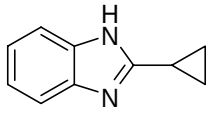
3g

2-Methyl-5-nitrobenzimidazole (3g).[4] Eluent: petroleum ether/ethyl acetate (1:1). Yield 74% (131 mg). Yellow solid, mp 218-220 ^{o}C (lit.[4] 218-220 ^{o}C). ^{1}H NMR (DMSO-d_6, 300 MHz, ppm), δ 12.95 (s, 1H), 8.37 (s, 1H), 8.07-8.04 (d, 2H, *J* = 9.0 Hz), 7.65(d, 2H, *J* = 9.0 Hz), 2.58 (s, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 142.6, 117.6, 15.4. ESI-MS M^+ m/z 176.1.



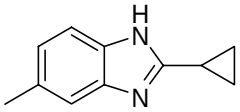
3h

5-Nitro-2-propylbenzimidazole (3h). Eluent: petroleum ether/ethyl acetate (1:1). Yield 80% (164 mg). Yellow solid, mp 135-137.5 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ 11.8 (s, 1H), 8.51 (s, 1H), 8.21-8.18 (d, 1H, J = 9.0Hz), 7.64-7.61 (d, 1H, J = 9.0 Hz), 3.06 (t, 2H, J = 7.2 Hz), 1.98 (dt, 2H, J = 7.2 Hz), 1.05(t, 3H, J = 7.2 Hz). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 160.4, 143.4, 142.8, 138.5, 118.6, 114.2, 111.8, 31.5, 21.6, 13.9. ESI-MS M^+ m/z 204.2.



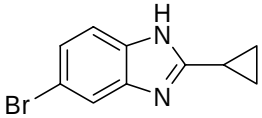
3i

2-Cyclopropylbenzimidazole (3i). Eluent: petroleum ether/ethyl acetate (3:1). Yield 65% (103 mg). White solid, mp 227-229 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 12.17 (s, 1H), 7.41 (m, 2H),7.09-7.07 (m, 2H), 2.12-2.05(m, 1H), 1.05-1.03 (dd, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 157.4, 121.4, 121.3, 109.1, 9.9, 9.2. ESI-MS M^+ m/z 158.1.



3j

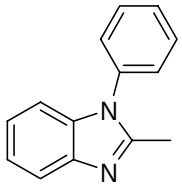
2-Cyclopropyl-5-methylbenzoimidazole (3j). Eluent: petroleum ether/ethyl acetate (4:1). Yield 70% (120 mg). Brown solid, mp 196-198 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.40-7.37 (d, 1H, J = 8.2 Hz), 7.27(s, 1H), 7.02-7.00 (d, 1H, J = 8.2 Hz), 2.43 (s, 3H), 1.20-1.18 (m, 2H), 1.09-1.00 (m, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 156.6, 138.1 136.2, 132.0, 123.6, 114.3, 113.9, 21.7, 9.8, 8.8. ESI-MS M^+ m/z 172.2.



3k

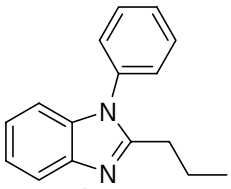
5-Bromo-2-cyclopropylbenzoimidazole (3k). Eluent: petroleum ether/ethyl acetate (5:1). Yield 62% (145 mg). Yellow solid, mp 199-202 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 12.42 (s, 1H), 7.60 (s, 1H), 7.38-7.36 (d, 1H, J = 8.3 Hz), 7.23-7.21 (d, 1H, J = 8.3 Hz), 2.51-2.09 (m, 1H), 1.08-1.03 (dd, 4H). ^{13}C NMR (DMSO-d_6, 75

MHz, ppm) δ 159.0, 124.2, 122.6, 121.3, 120.0, 118.7, 113.7, 9.9, 9.5. ESI-MS M^+ m/z 236.6，238.4.



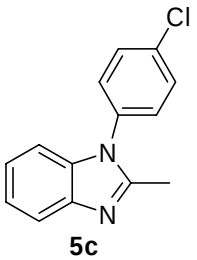
5a

2-Methyl-1-phenylbenzoimidazole (5a).[5] Eluent: petroleum ether/ethyl acetate (1:1). Yield 62% (129 mg). White solid, mp 70-72 ^{o}C (lit.[5] 49-51 ^{o}C). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.80-7.10 (m, 9H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 300 MHz, ppm) δ 151.6, 142.6, 136.5, 136.2, 130.0, 128.9, 127.2, 122.7, 122.5, 119.1, 110.0, 14.5. ESI-MS $[M+H]^+$ m/z 208.5.



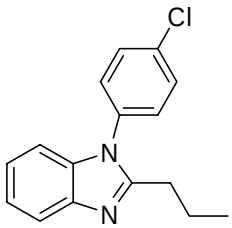
5b

1-Phenyl-2-propylbenzoimidazole (5b). Eluent: petroleum ether/ethyl acetate (6:1). Yield 65% (153 mg). Pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.80-7.10 (m, 9H), 2.77 (t, 2H, J = 7.6 Hz), 1.83 (dt, 2H, J = 7.6 Hz), 0.94 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 155.3, 136.6, 136.1, 130.0, 129.6, 129.0, 127.5, 122.6, 122.4, 119.2, 29.7, 21.3, 14.0. ESI-MS $[M+H]^+$ m/z 236.5.



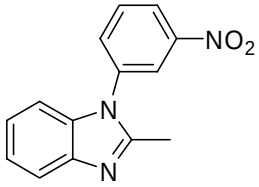
5c

1-(4-Chlorophenyl)-2-methylbenzoimidazole (5c). Eluent: petroleum ether/ethyl acetate (6:1). Yield 70% (169 mg). White solid, mp 99-101 ^{o}C . ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.75-7.10 (m, 8H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 142.6, 134.9, 134.7, 130.3, 128.5, 122.9, 122.7, 119.2, 109.8, 14.5. ESI-MS $[M+H]^+$ m/z 242.6，244.5.



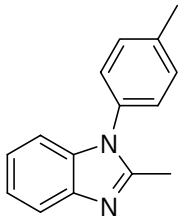
5d

1-(4-Chlorophenyl)-2-propylbenzoimidazole (5d). Eluent: petroleum ether/ethyl acetate (8:1). Yield 57% (154 mg). White solid, mp 71-73 ^{o}C . ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.85-7.05 (m, 8H), 2.75 (t, 2H, J = 7.2 Hz), 1.81 (dt, 2H, J = 7.6 Hz), 0.94 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 155.1, 142.6, 136.4, 135.0, 134.7, 130.3, 128.8, 122.8, 122.6, 119.3, 109.8, 29.7, 21.3, 14.0. ESI-MS $[M+H]^+$ m/z 270.7, 272.7.



5e

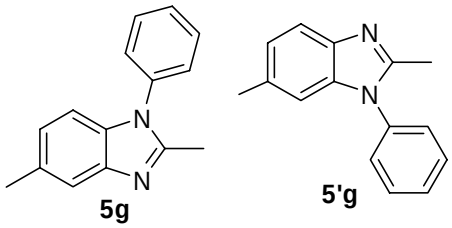
2-Methyl-1-(3-nitrophenyl)benzoimidazole (5e). Eluent: petroleum ether/ethyl acetate (3:1). Yield 49% (124 mg). Yellow solid, mp 172-174 ^{o}C . ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 8.42-8.30 (m, 2H), 7.85-7.76 (m, 3H), 7.35-7.12 (m, 3H), 2.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 149.3, 142.6, 137.4, 133.1, 131.1, 123.7, 123.4, 123.3, 122.3, 119.5, 109.5, 14.6. ESI-MS $[M+H]^+$ m/z 253.6.



5f

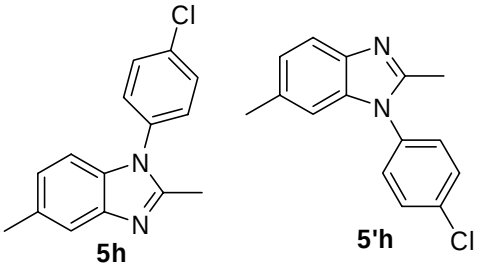
2-Methyl-1-p-tolylbenzoimidazole (5f).[6] Eluent: petroleum ether/ethyl acetate (4:1). Yield 62% (138 mg). Colorless needle crystal, mp 88-90 ^{o}C (lit.[6] 89-91 ^{o}C). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.75-7.73 (d, 1H, J = 6.0 Hz), 7.83-7.36 (d, 2H, J = 8.3 Hz), 7.28-7.10 (m, 5H), 2.50 (s, 3H), 2.48 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 151.8, 142.6, 139.0, 136.7, 133.5, 130.6, 126.9, 122.6, 122.4, 119.0, 21.3,

14.5. ESI-MS $[M+H]^+$ m/z 222.5.



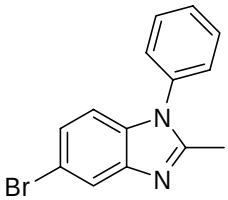
5g **5'g**

Compound 5g and 5g'. Eluent: petroleum ether/ethyl acetate (10:1 to 6:1). Yield 57% (127 mg). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.60-6.90 (m, 8H), 2.47-2.40 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 151.5, 151.0, 142.9, 140.7, 136.4, 136.3, 132.6, 132.1, 130.0, 128.8, 127.2, 127.1, 124.0, 123.9, 118.9, 118.6, 110.0, 109.5, 21.8, 21.6, 14.5. ESI-MS $[M+H]^+$ m/z 222.5.



5h **5'h**

Compound 5h and 5h'. Eluent: petroleum ether/ethyl acetate (6:1 to 1:1). Yield 60% (153mg). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.68-6.90 (m, 7H), 2.48-2.41 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 150.9, 150.8, 143.0, 140.7, 134.8, 134.7, 134.6, 134.5, 132.9, 132.4, 130.2, 128.5, 128.4, 124.2, 124.1, 119.1, 118.7, 109.8, 109.3, 21.8, 21.6, 14.5. ESI-MS $[M+H]^+$ m/z 256.8, 258.6.



5i

5-Bromo-2-methyl-1-phenylbenzoimidazole (5i). Eluent: petroleum ether/ethyl acetate (8:1). Yield 45% (129 mg). White solid, mp 125-127 ^{o}C . ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.87 (s, 1H), 7.62-7.53 (m, 3H), 7.36-7.27 (m, 3H), 7.0-6.97 (d, 1H), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 152.9, 143.9, 135.7, 135.5, 130.2, 129.2, 127.0, 125.7, 121.9, 115.4, 111.3, 14.5. ESI-MS $[M+H]^+$ m/z 286.8, 288.7.

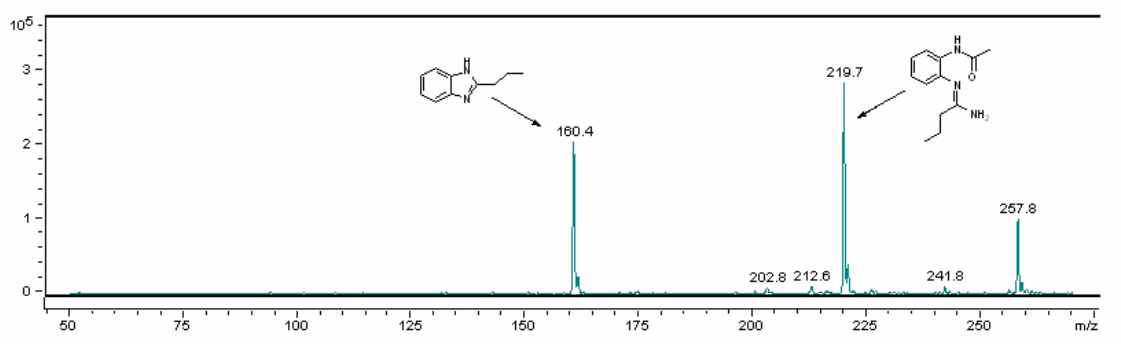


Figure 1. ESI mass spectrum of the reaction mixture after coupling of *o*-bromoacetoanilide with butyramidine hydrochloride for a time

References

(1) Valdez, J.; Cedillo, R.; Campos, A. H.; Yepez, L.; Luis, F. H.; Vazquez, G. N.; Tapia, A.; Cortes, R.; Hernandez, M.; Castillo, R. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2221–2224.

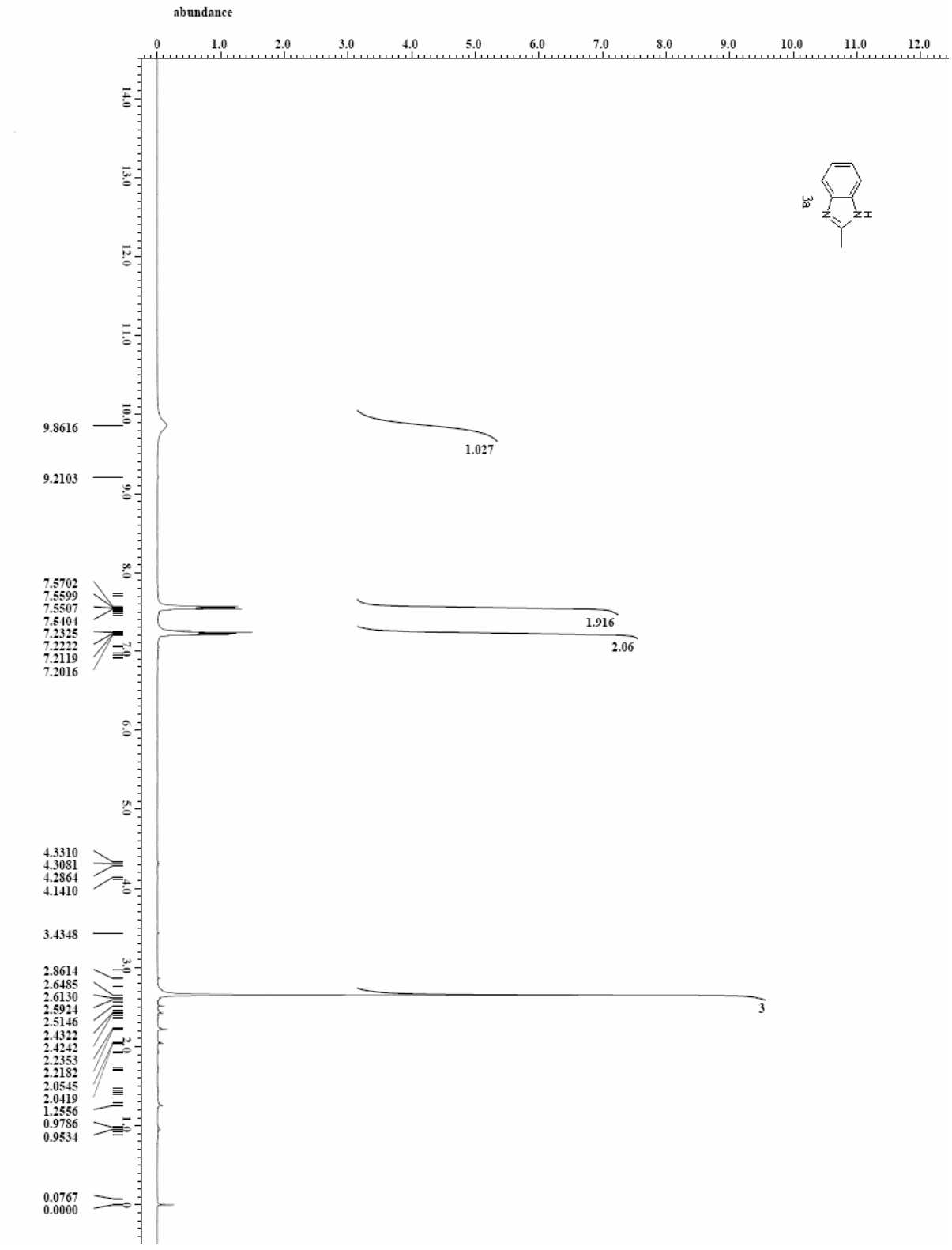
(2) Hay, J. V.; Portlock, D. E.; Wolfe, J. F. *J. Org. Chem.* **1973**, *38*, 4379-4382.

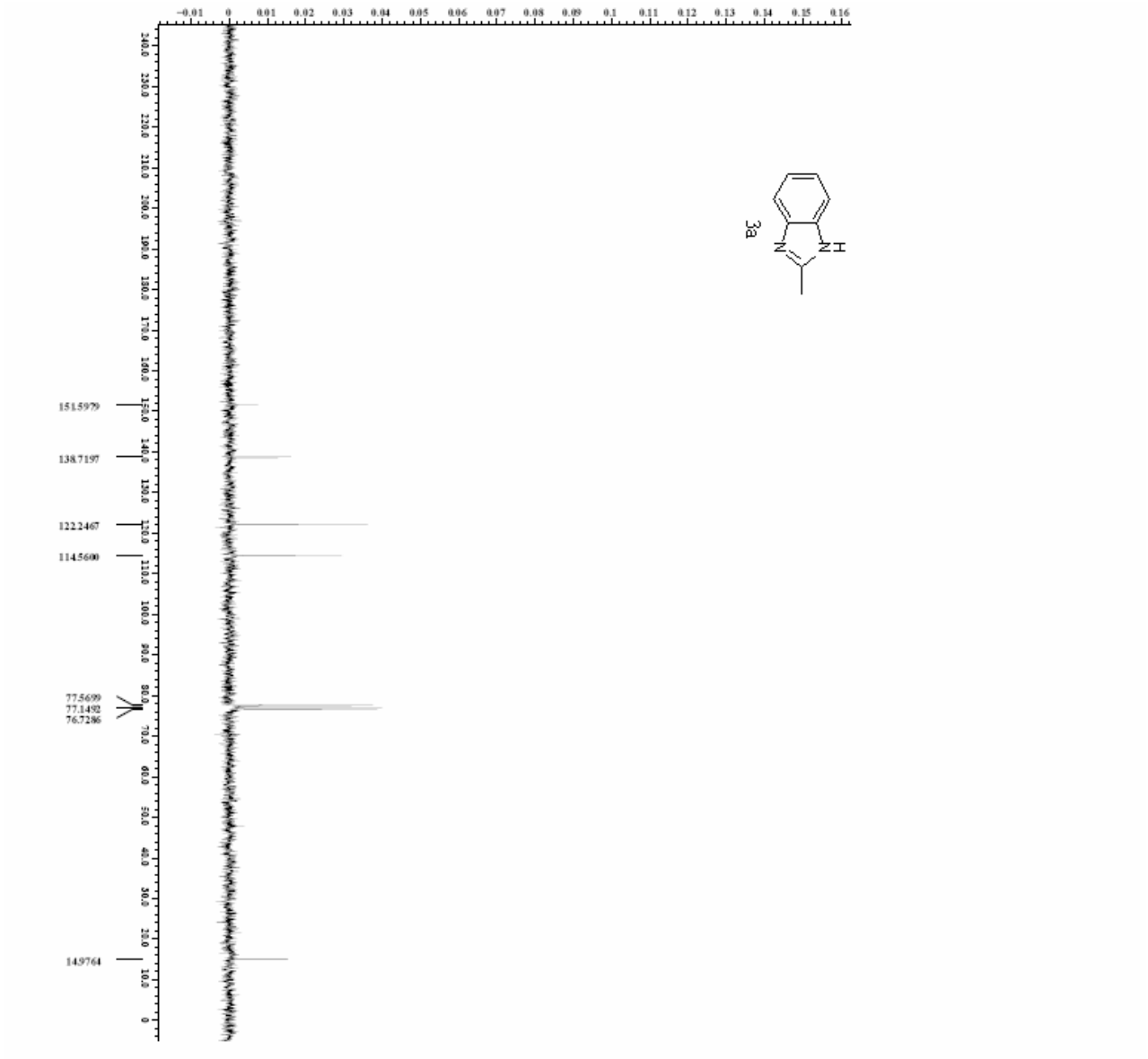
(3) Murray, M.; Ryan, A. J.; Little, P. J. *J. Med. Chem.* **1982**, *25*, 887–892.

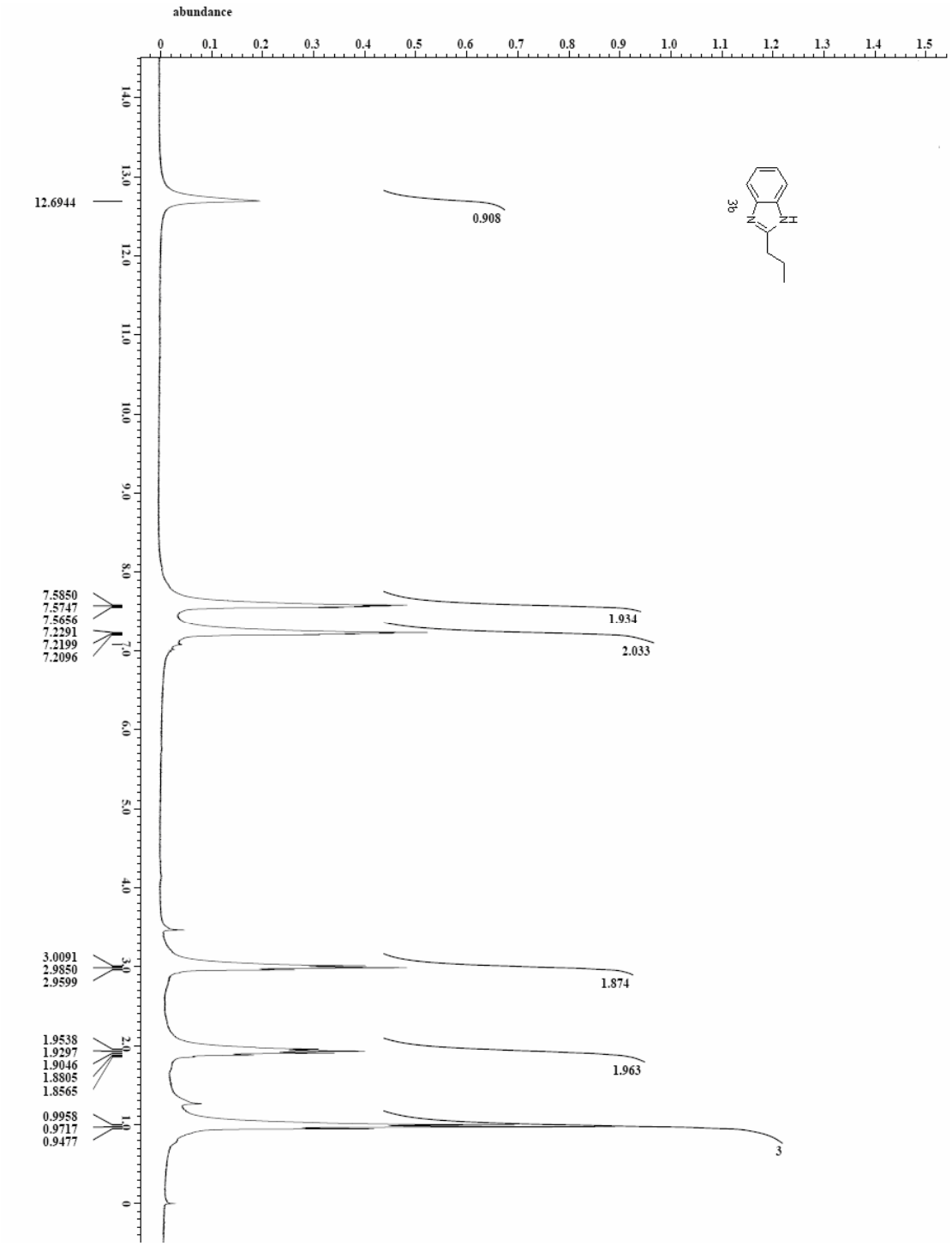
(4) Rabinowitz, J.L.; Wagner, E. C. *J. Am. Chem. Soc.* **1951**, *73*, 3030–3037.

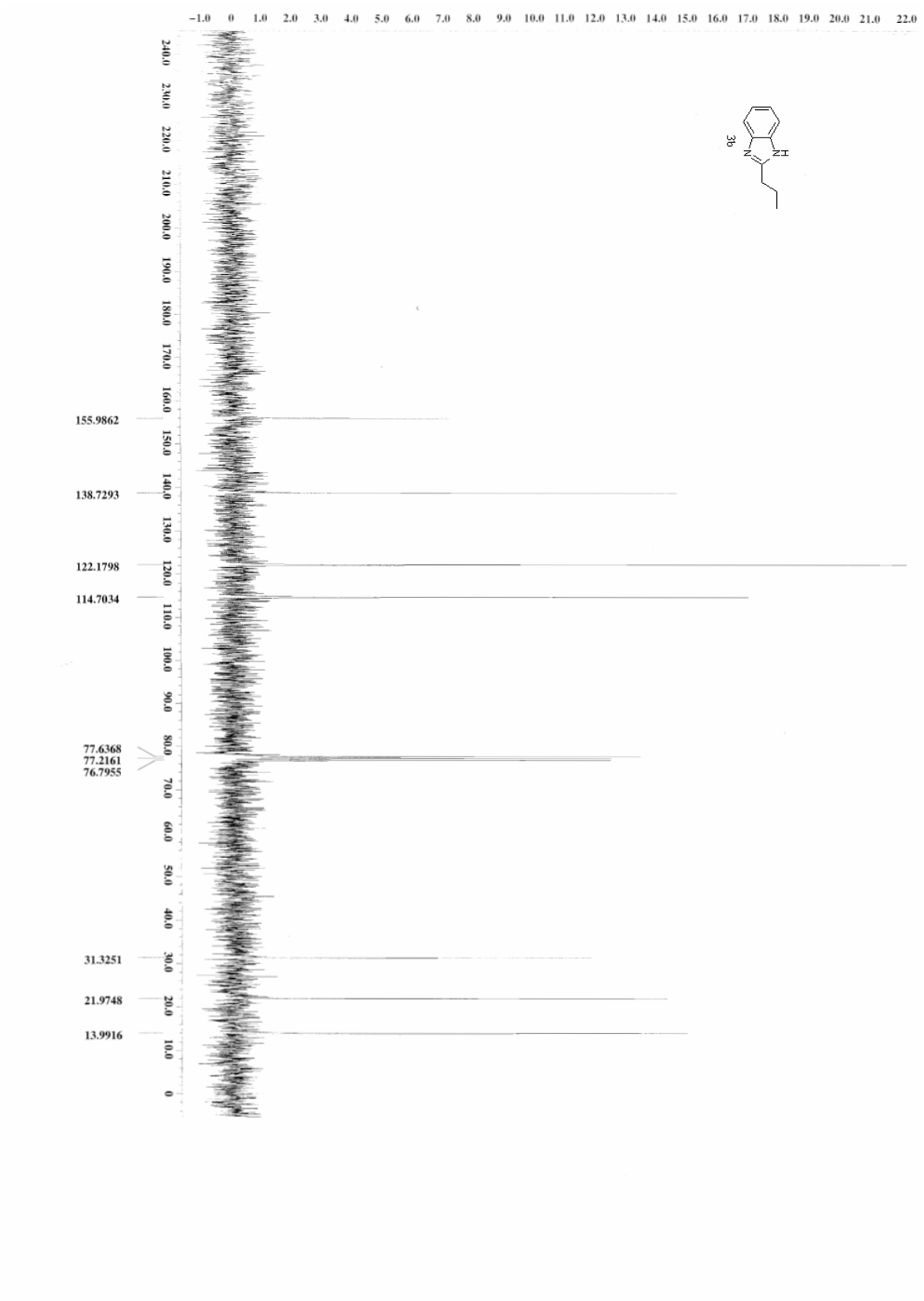
(5) Brain, C. T.; Steer, J. T. *J. Org. Chem.* **2003**, *68*, 6814-6816

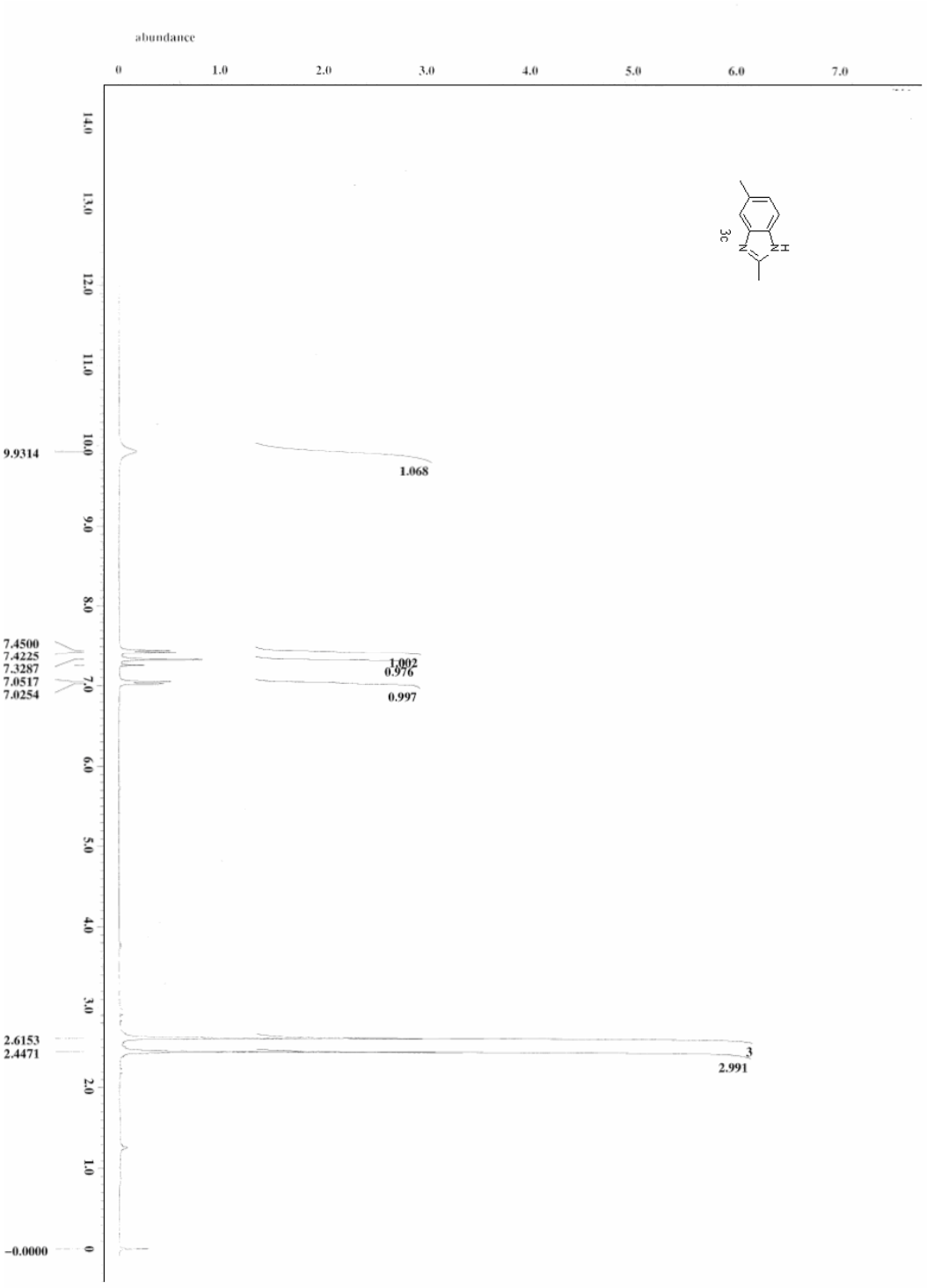
(6) Zheng, N.; Anderson, K. W.; Huang, X.; Nguyen, H. N. Buchwald, S. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 7509 –7512

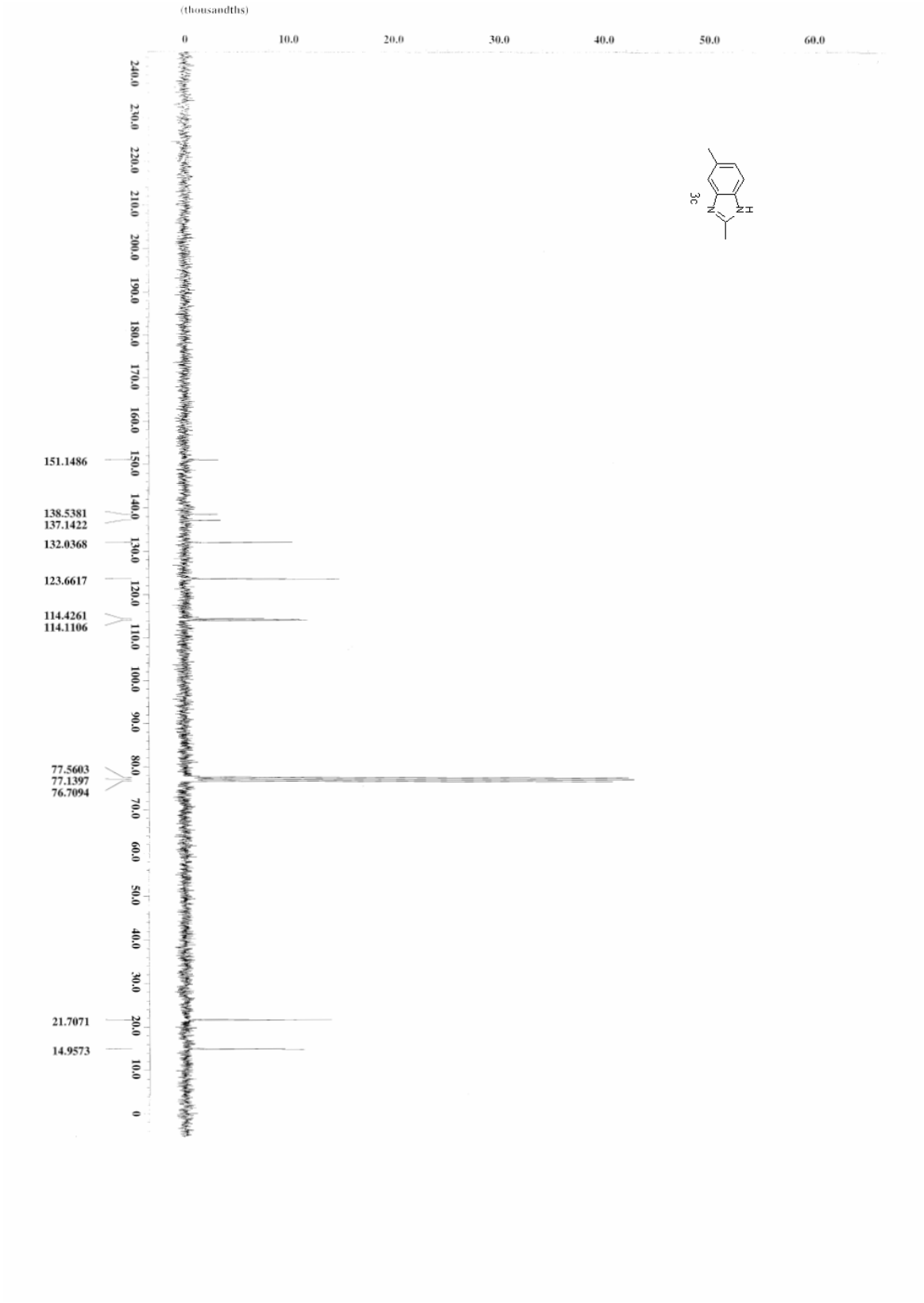

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
3a
9.8616
9.2103
7.5702
7.5599
7.5507
7.5404
7.2325
7.2222
7.2119
7.2016
4.3310
4.3081
4.2864
4.1410
3.4348
2.8614
2.6485
2.6130
2.5924
2.5146
2.4322
2.4242
2.2353
2.2182
2.0545
2.0419
1.2556
0.9786
0.9534
0.0767
0.0000
1.027
1.916
2.06
3

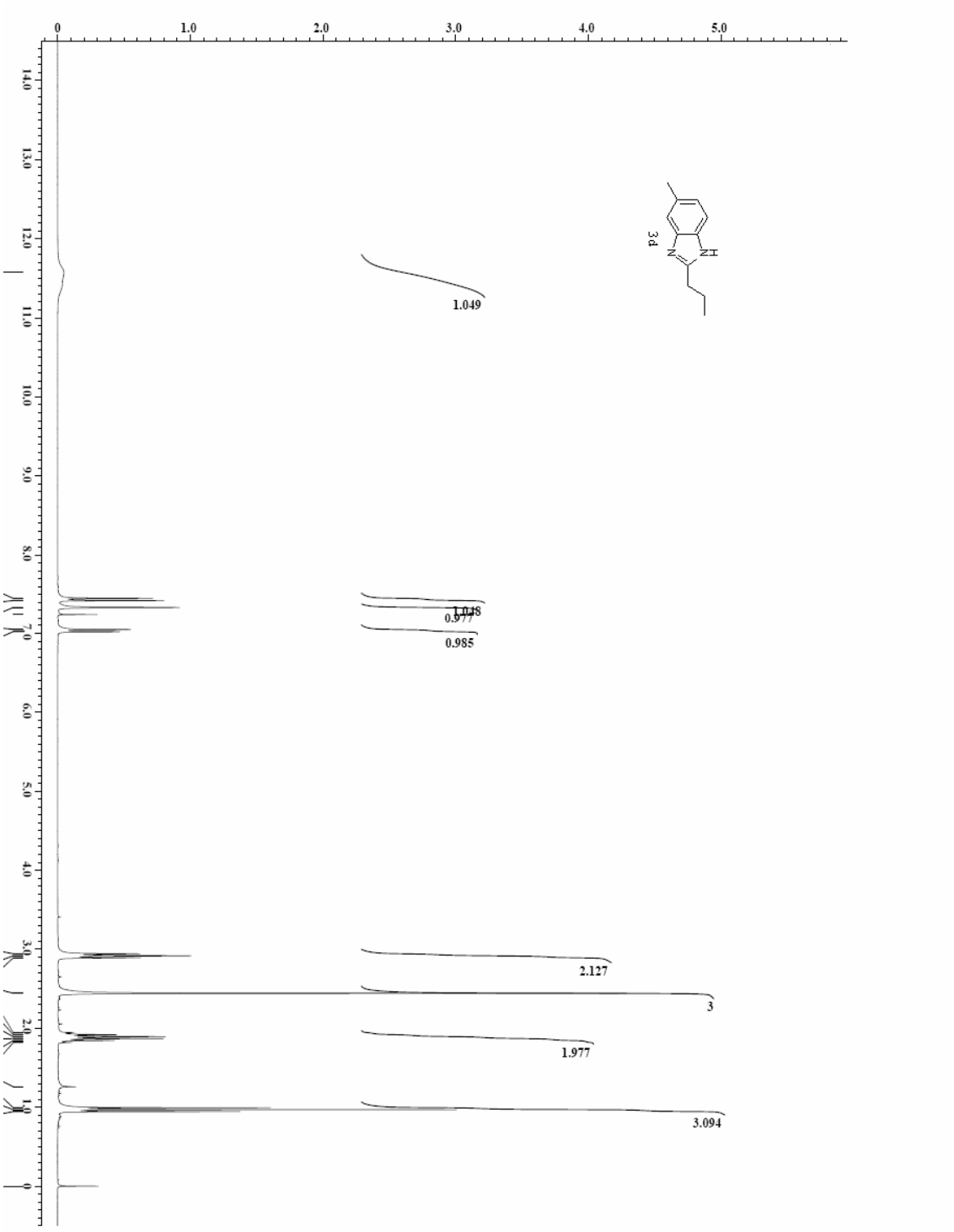

151.5979
138.7197
122.2467
114.5600
77.5699
77.1492
76.7286
14.9764
3a

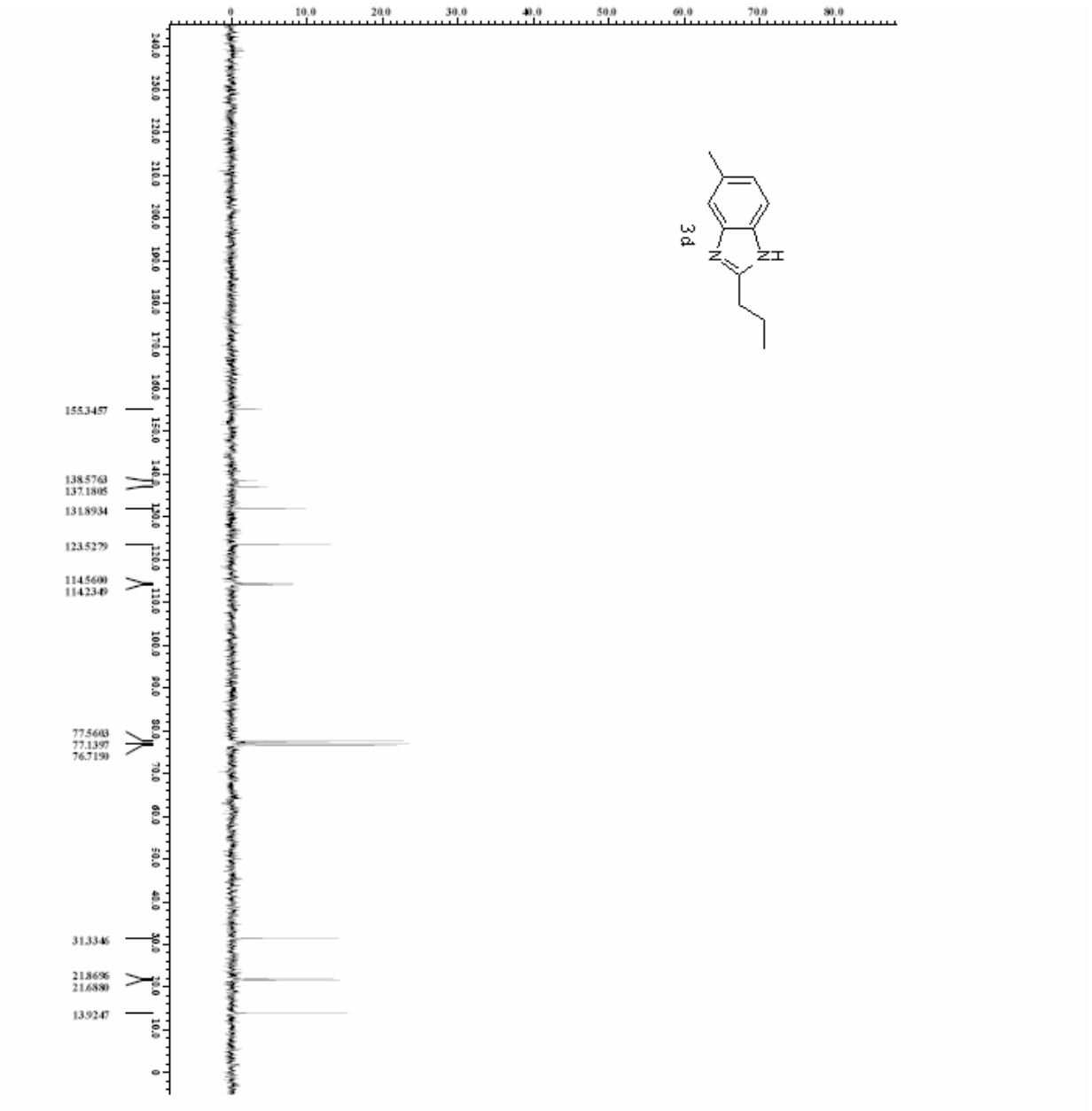

abundance
12.6944
7.5850
7.5747
7.5656
7.2291
7.2199
7.2096
3.0091
2.9850
2.9599
1.9538
1.9297
1.9046
1.8805
1.8565
0.9958
0.9717
0.9477
0.908
1.934
2.033
1.874
1.963
3
3b

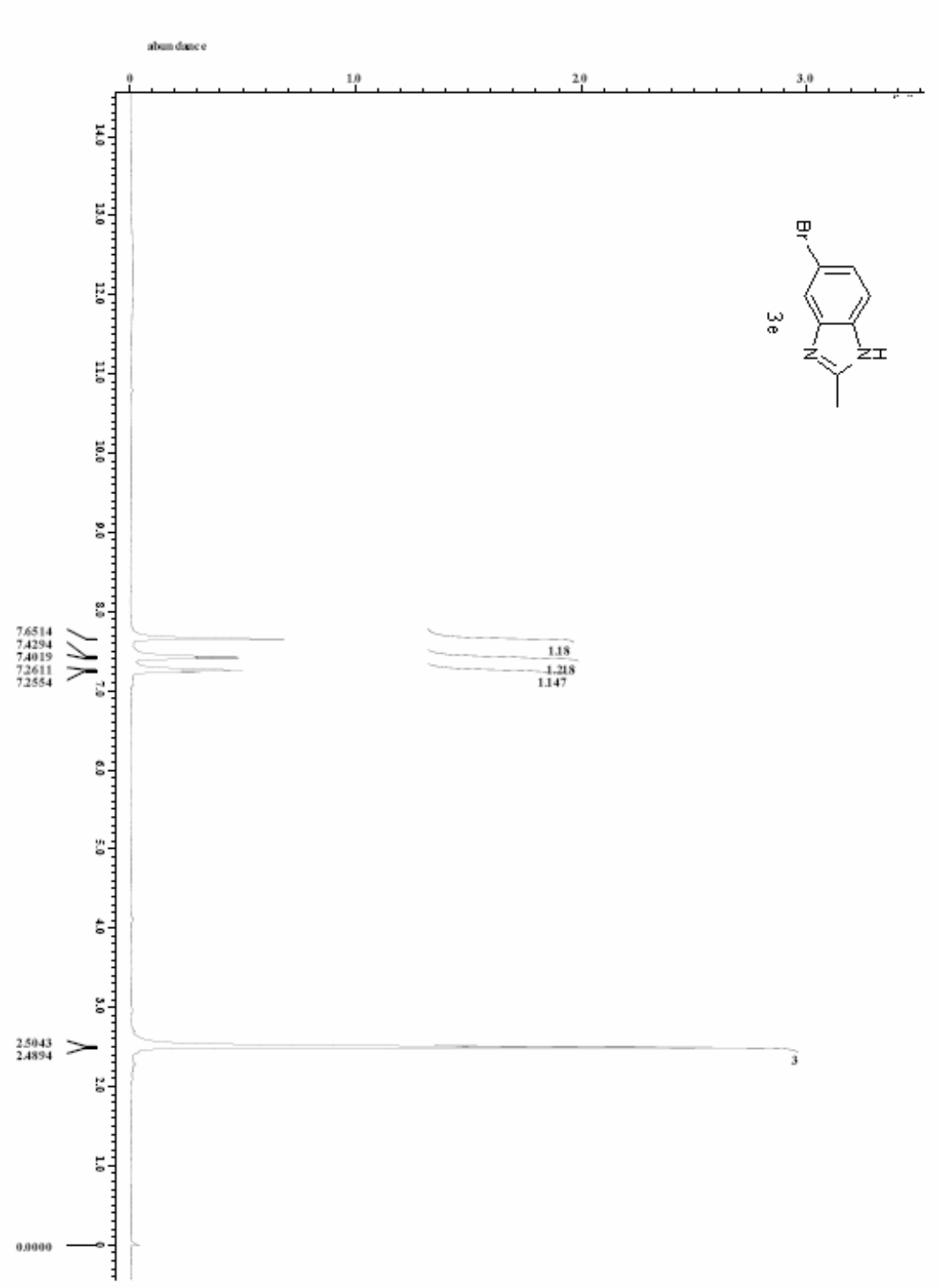

3b
155.9862
138.7293
122.1798
114.7034
77.6368
77.2161
76.7955
31.3251
21.9748
13.9916

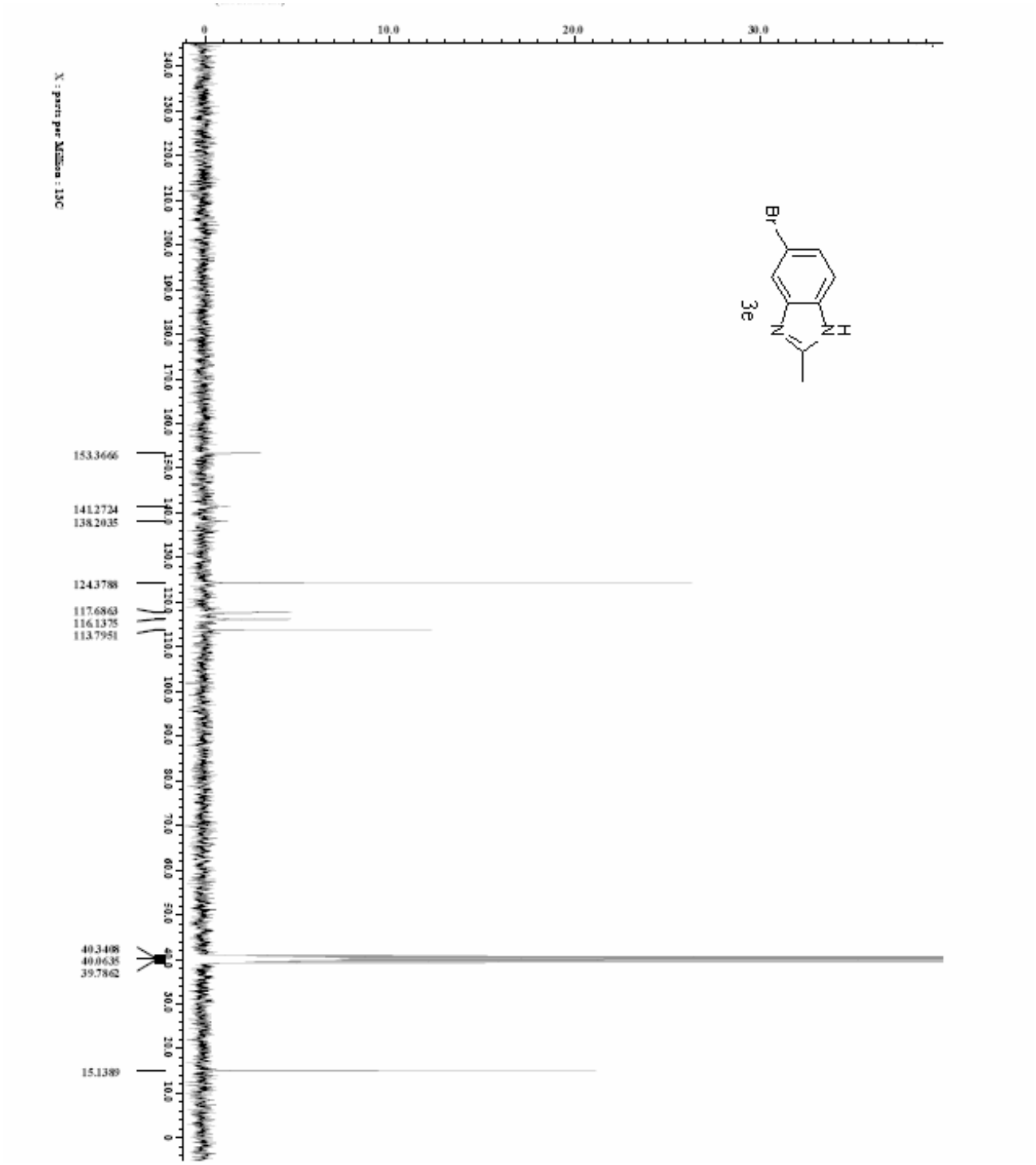

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.9314
1.068
7.4500
7.4225
7.3287
7.0517
7.0254
1.002
0.976
0.997
2.6153
2.4471
3
2.991
−0.0000
3c
N
H
N

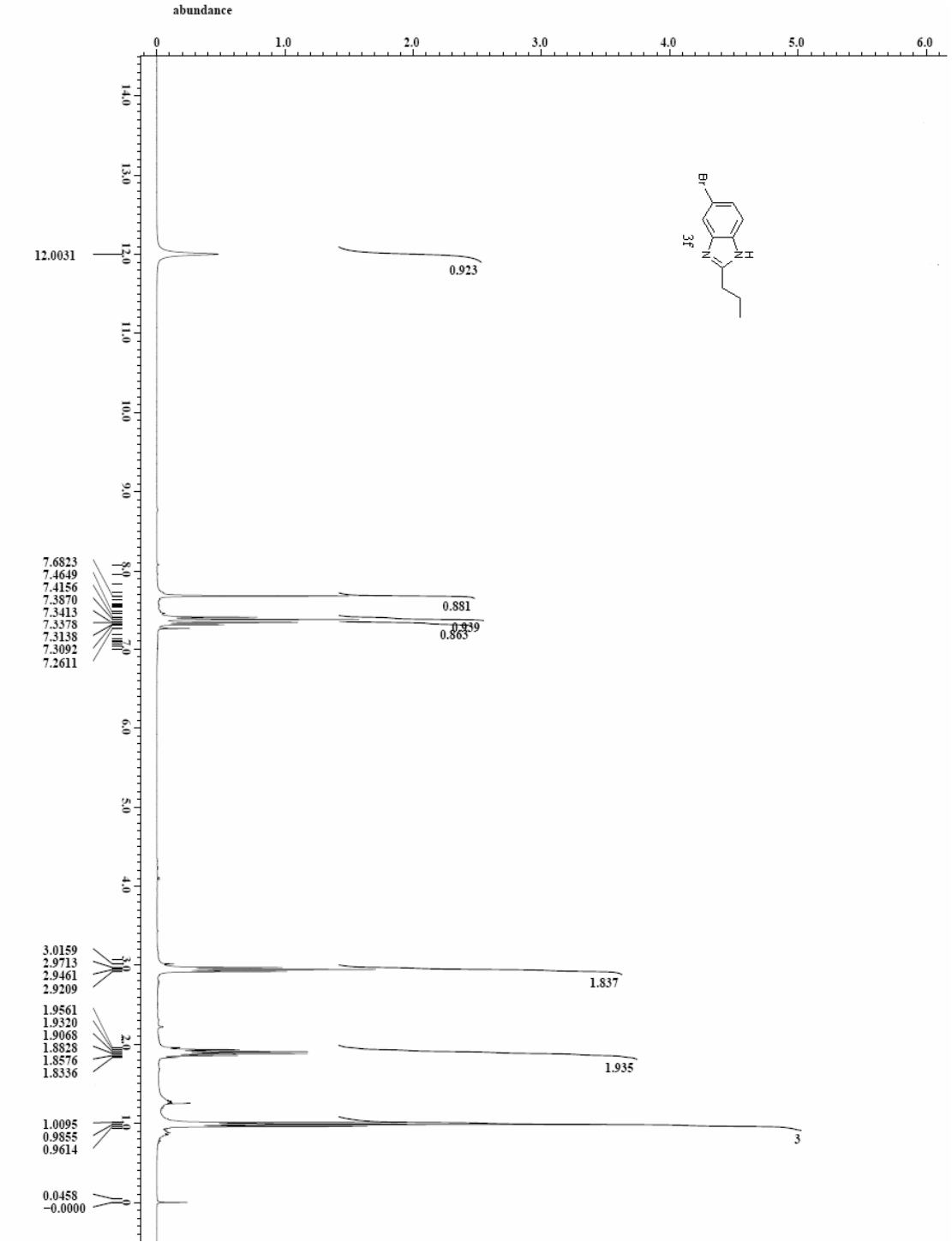

(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
240.0
230.0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.1486
138.5381
137.1422
132.0368
123.6617
114.4261
114.1106
77.5603
77.1397
76.7094
21.7071
14.9573
3c
N
H

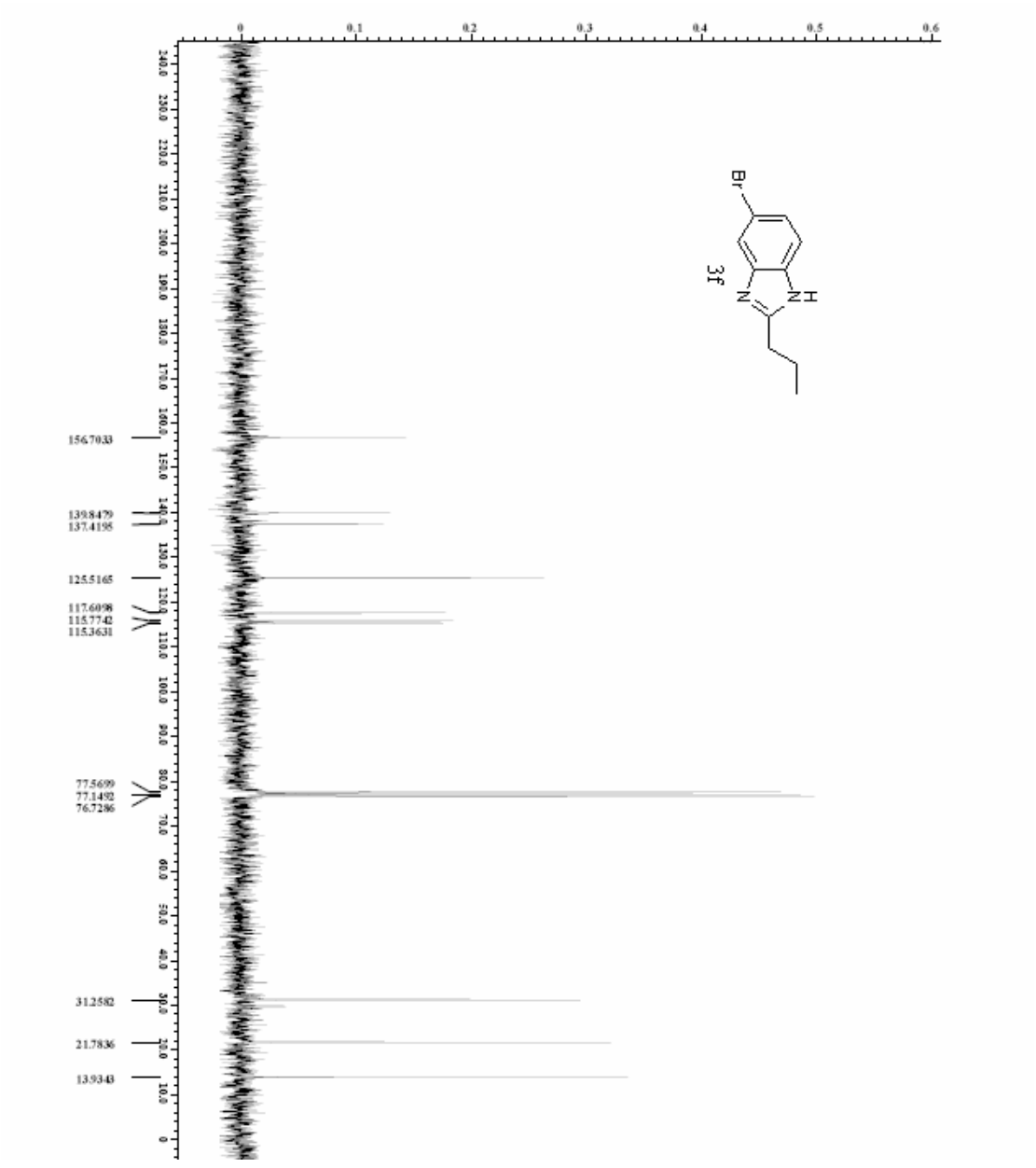

3d
1.049
1.018
0.977
0.985
2.127
3
1.977
3.094

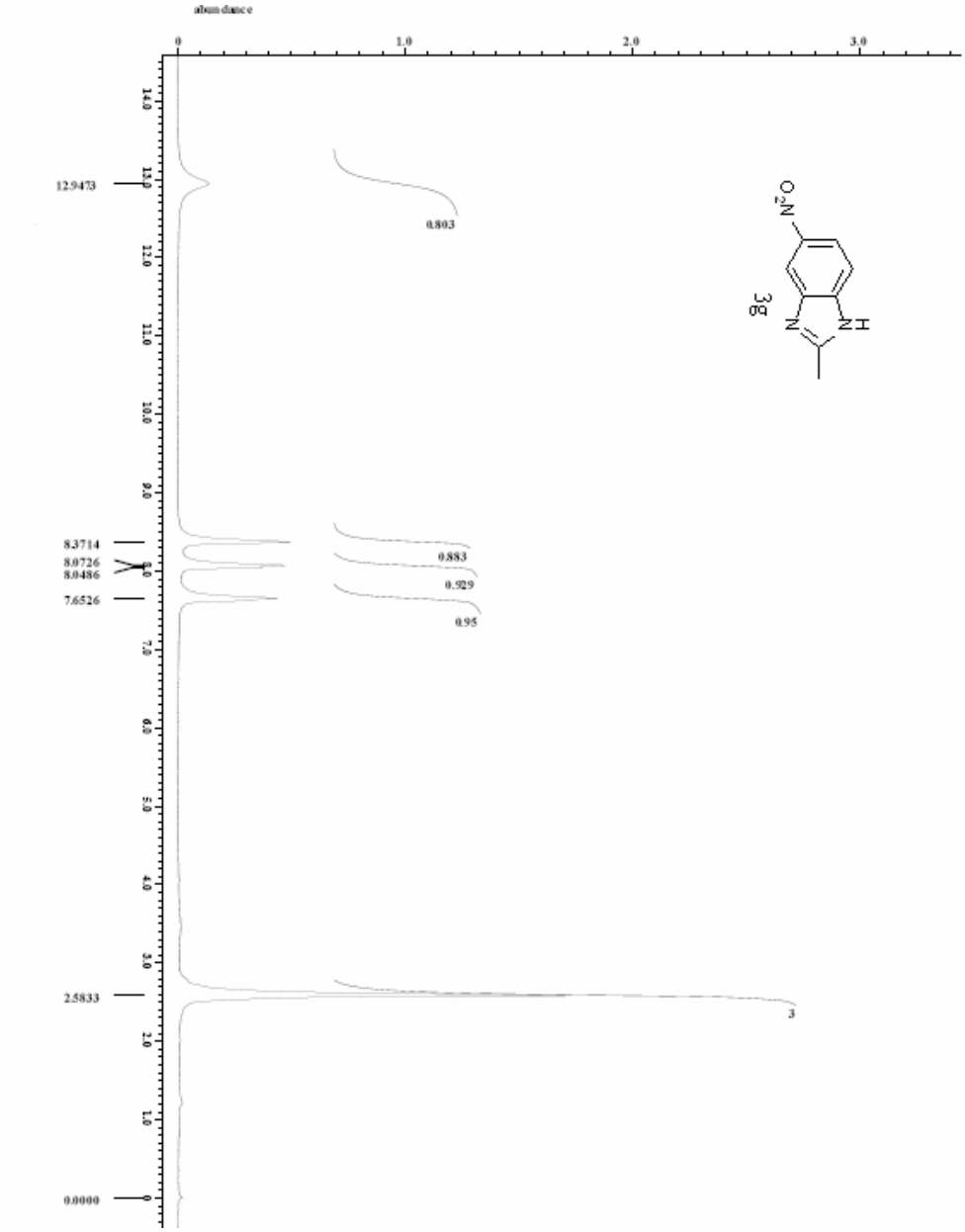

155.3457
138.5763
137.1805
131.8934
123.5279
114.5600
114.2349
77.5603
77.1397
76.7190
31.3346
21.8696
21.6880
13.9247
3a

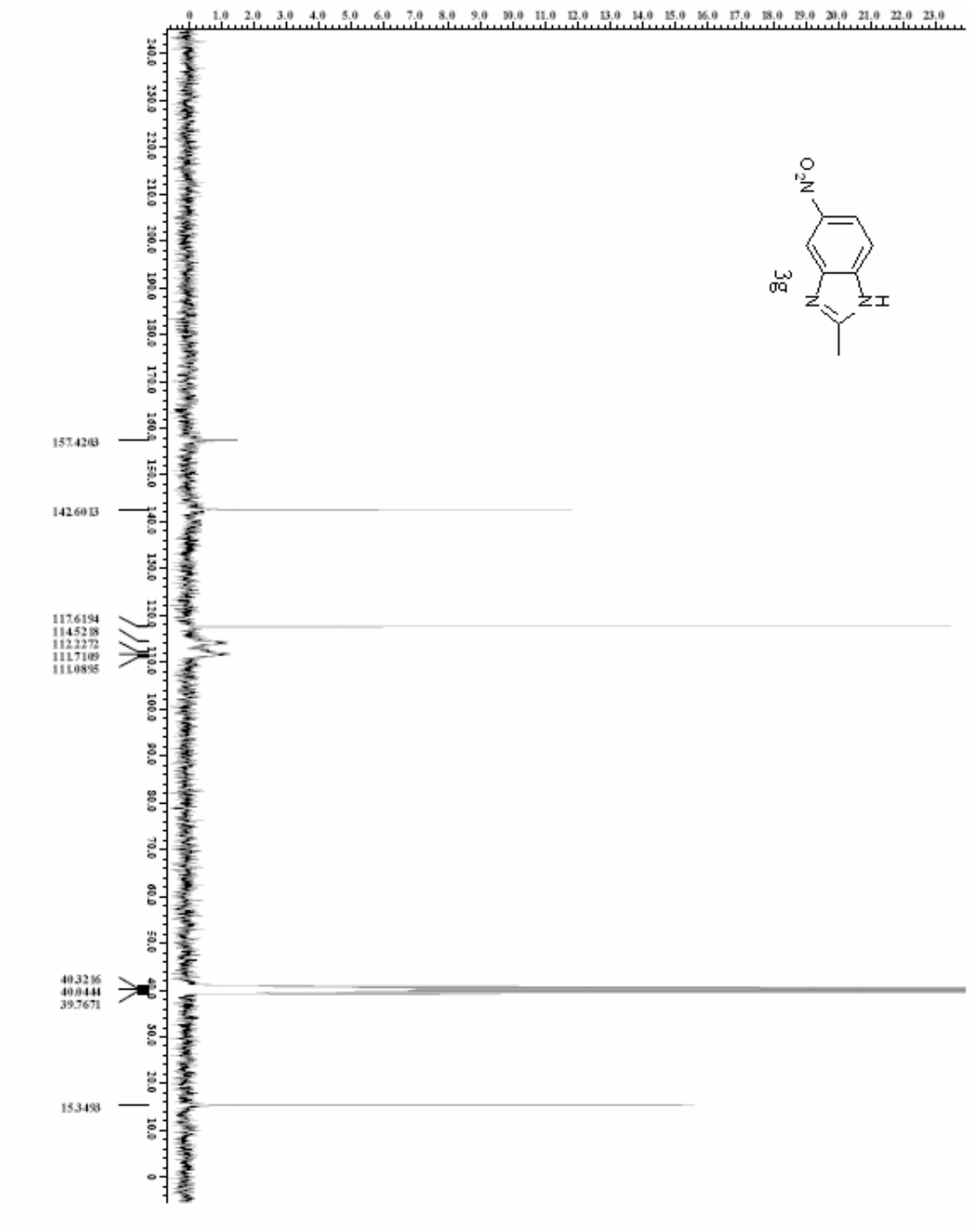

abundance
0
1.0
2.0
3.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6514
7.4294
7.4019
7.2611
7.2554
2.5043
2.4894
0.0000
1.18
1.218
1.147
3
Br
N
H
3e

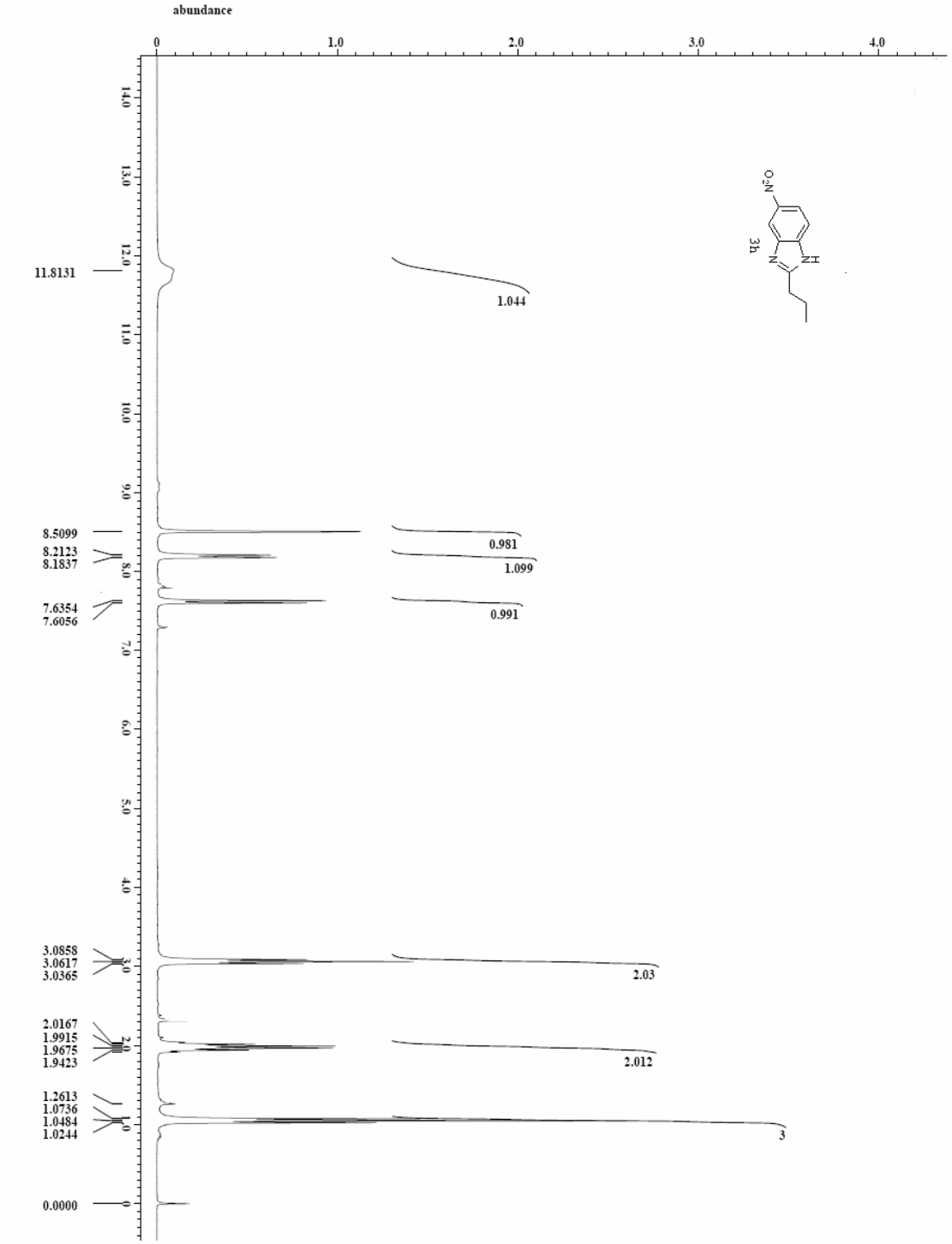

X : parts per Million : 13C
153.3666
141.2724
138.2035
124.3788
117.6863
116.1375
113.7951
40.3408
40.0635
39.7862
15.1389
Br
N
H
3e

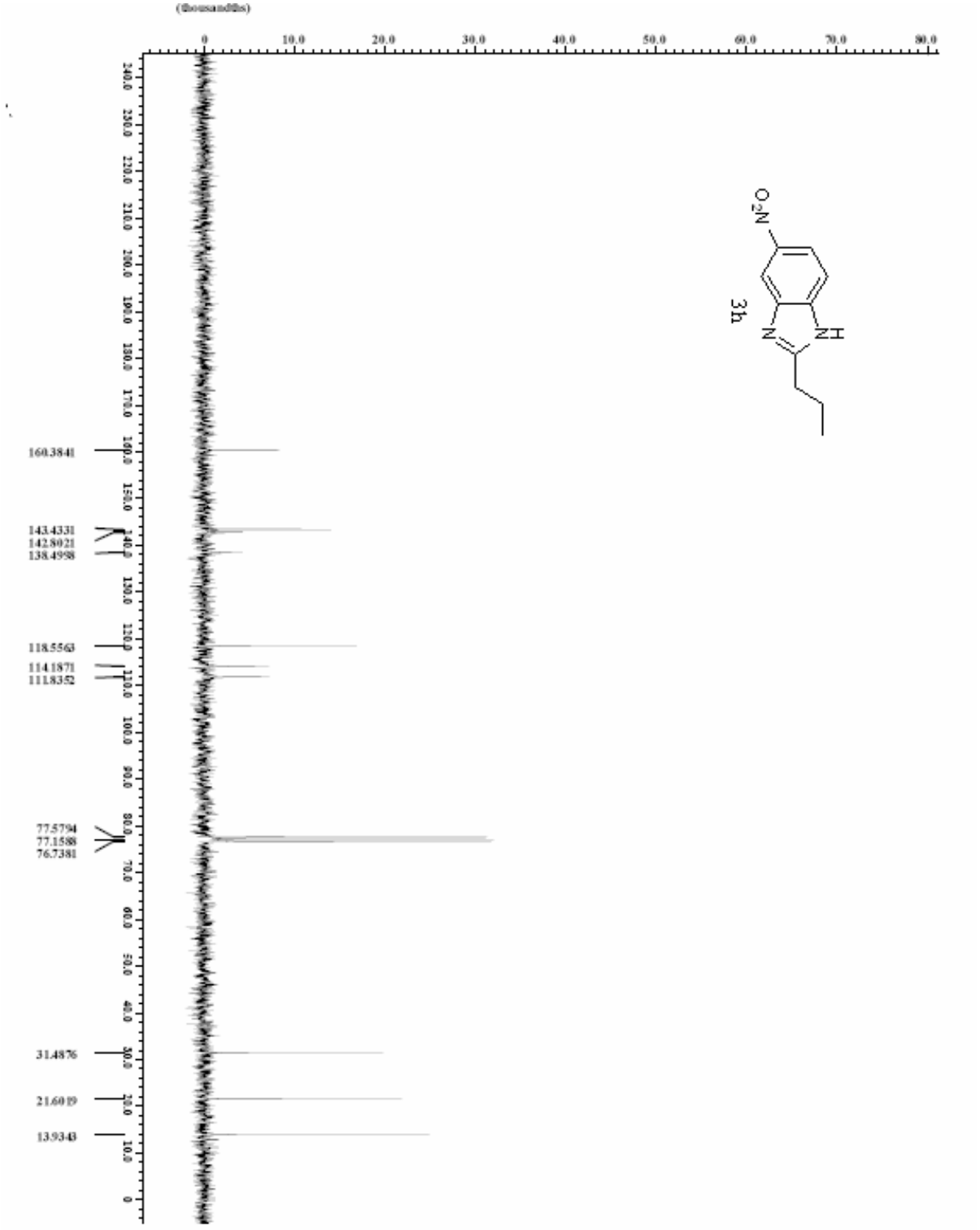

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
12.0031
0.923
7.6823
7.4649
7.4156
7.3870
7.3413
7.3378
7.3138
7.3092
7.2611
0.881
0.939
0.863
3.0159
2.9713
2.9461
2.9209
1.837
1.9561
1.9320
1.9068
1.8828
1.8576
1.8336
1.935
1.0095
0.9855
0.9614
3
0.0458
−0.0000
Br
3F
N
H
N

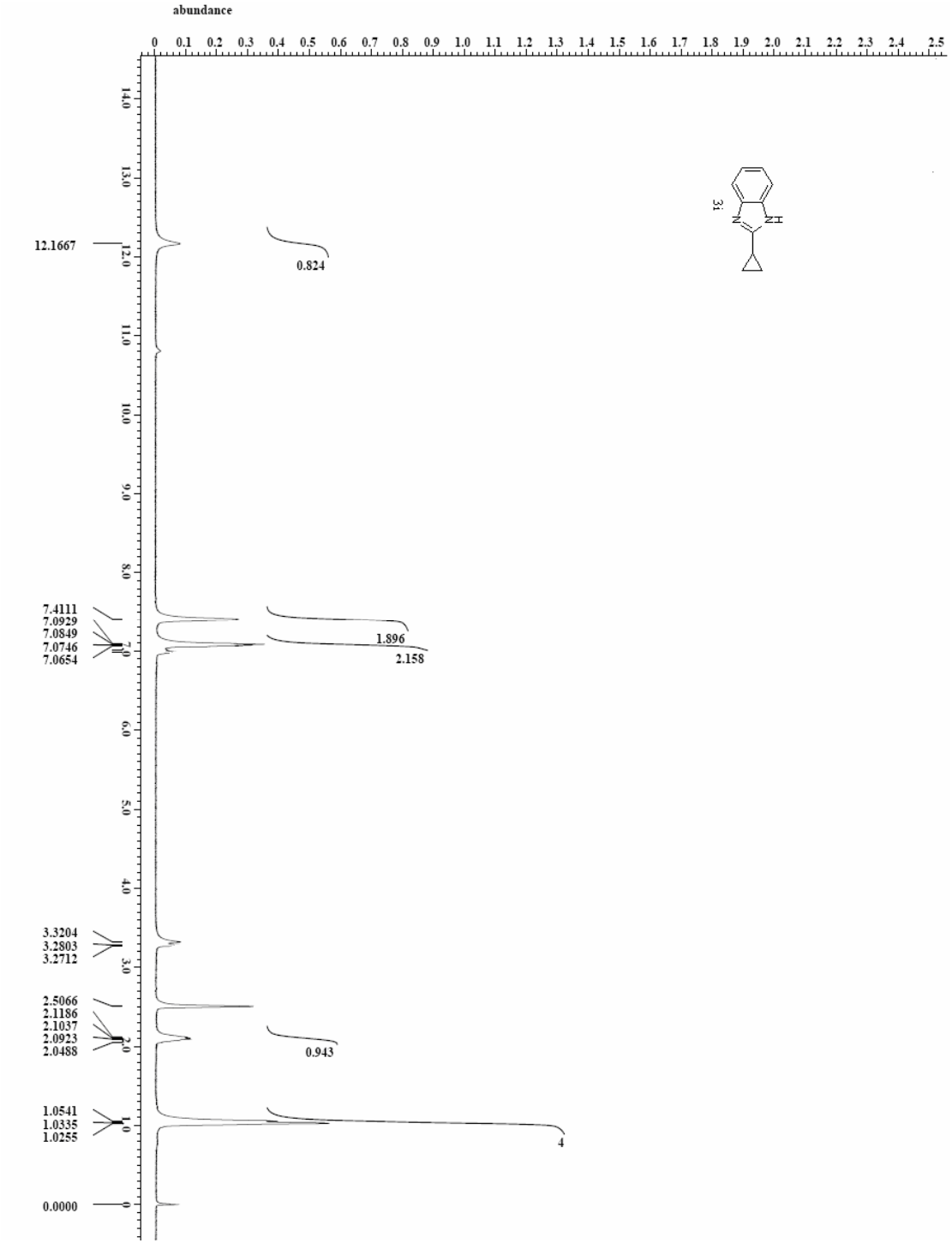

156.7033
139.8479
137.4195
125.5165
117.6098
115.7742
115.3631
77.5699
77.1492
76.7286
31.2582
21.7836
13.9343
Br
N
H
N
3f

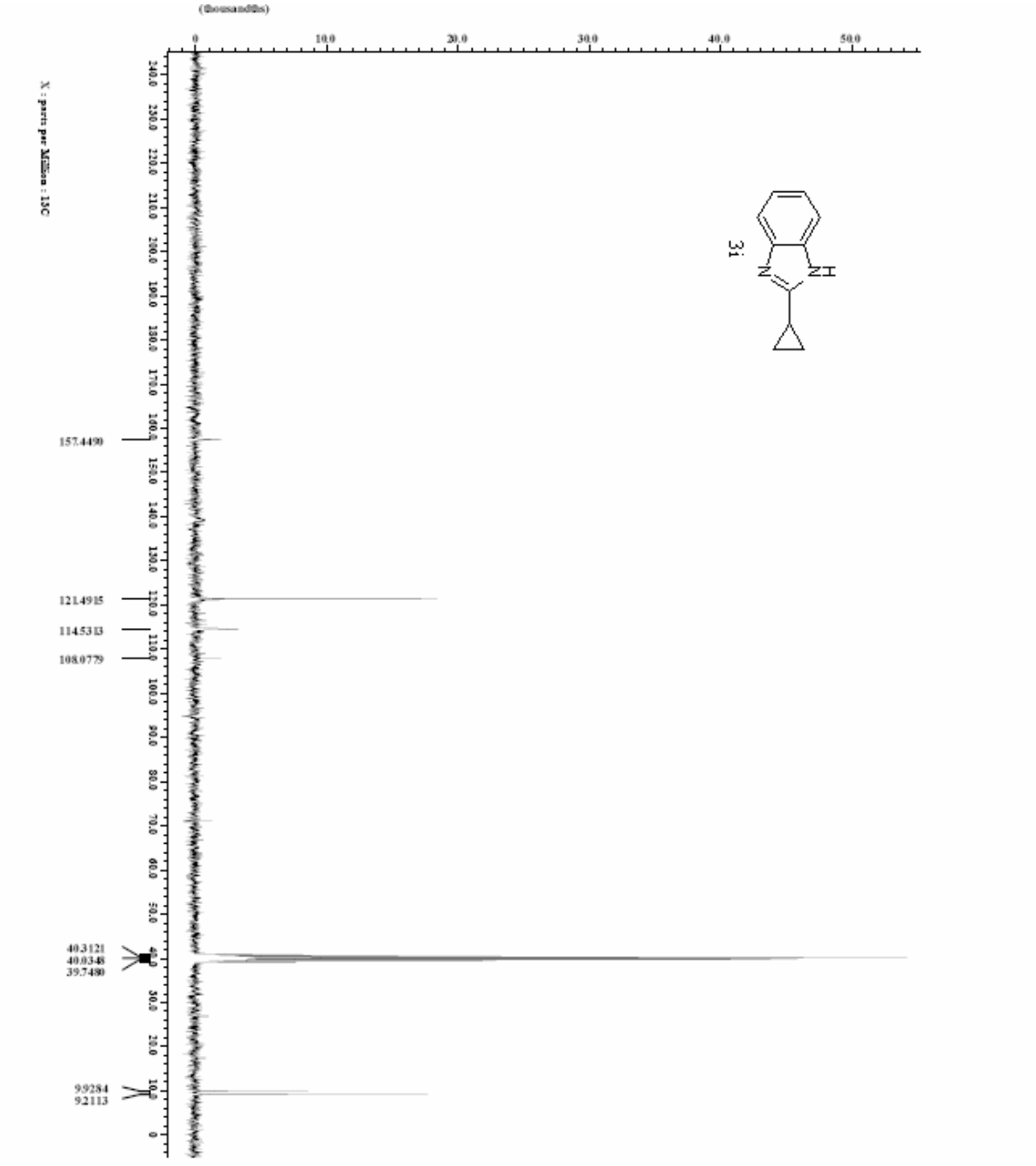

abundance
0
1.0
2.0
3.0
12.9473
8.3714
8.0726
8.0486
7.6526
2.5833
0.0000
0.803
0.883
0.929
0.95
3
O2N
3g
N
H
N

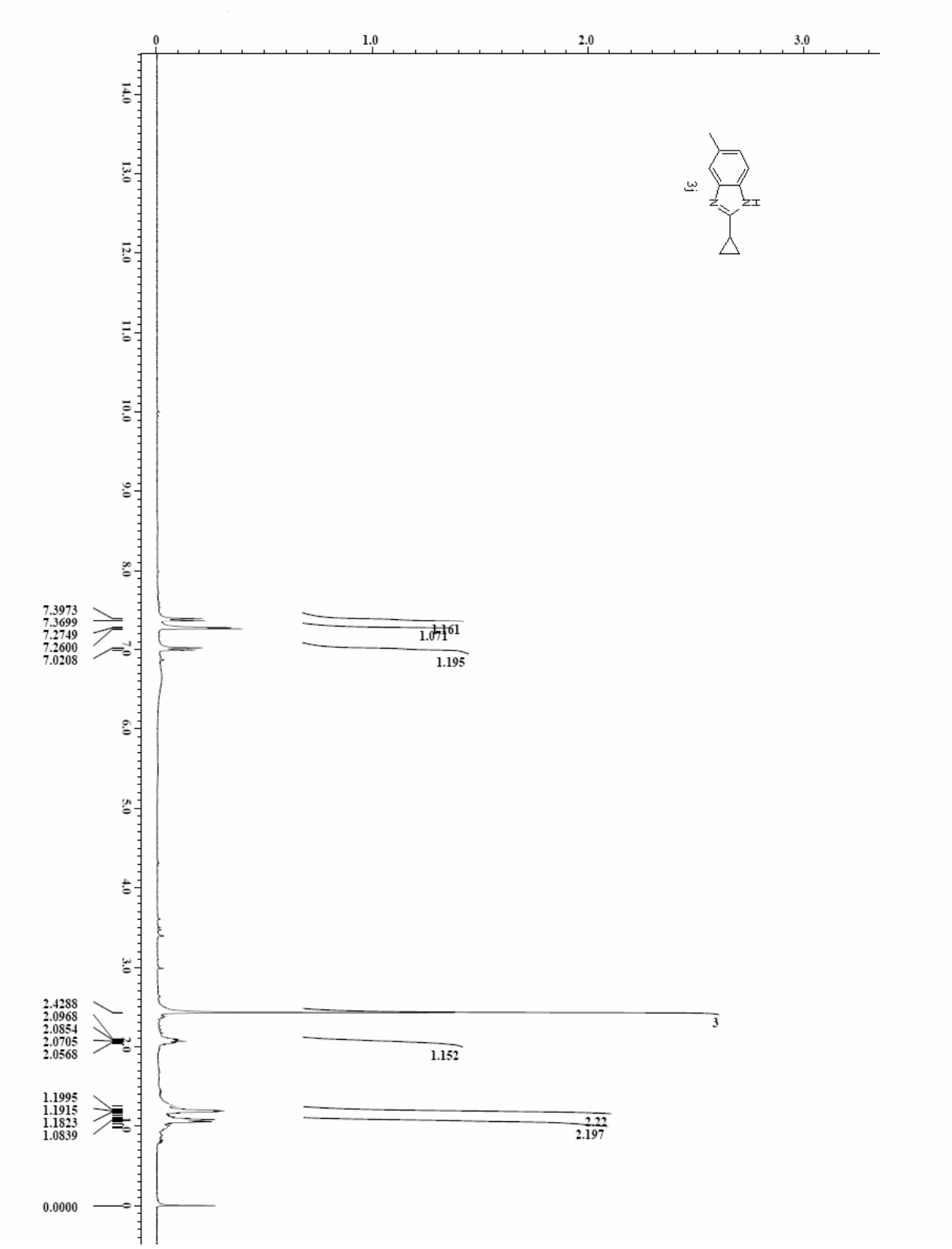

157.4203
142.6013
117.6194
114.5218
112.2272
111.7109
111.0895
40.3216
40.0444
39.7671
15.3493
3g

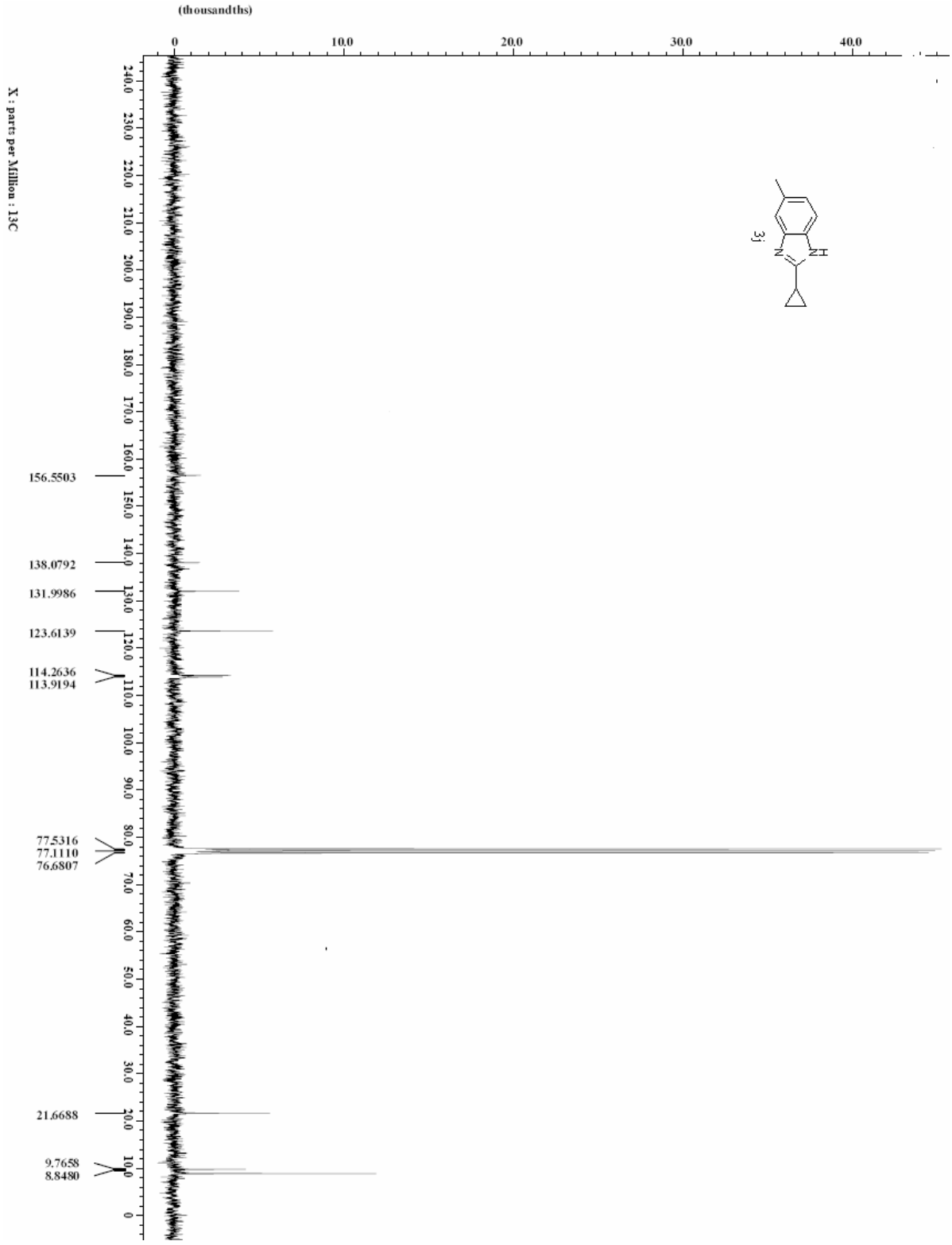

abundance
0
1.0
2.0
3.0
4.0
11.8131
1.044
8.5099
8.2123
8.1837
0.981
1.099
7.6354
7.6056
0.991
3.0858
3.0617
3.0365
2.03
2.0167
1.9915
1.9675
1.9423
2.012
1.2613
1.0736
1.0484
1.0244
3
0.0000
O2N
3h
N
H

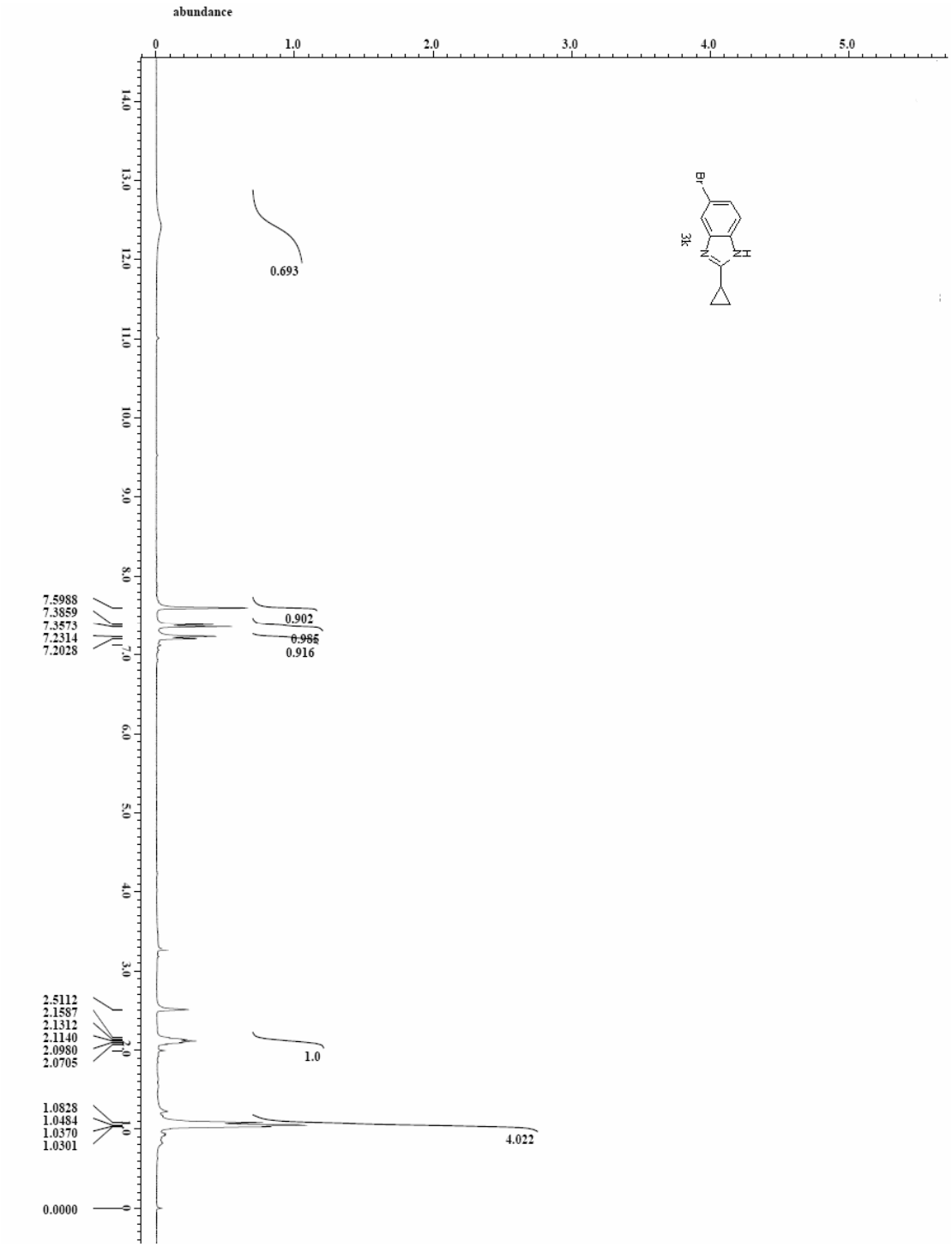

160.3841
143.4331
142.8021
138.4998
118.5563
114.1871
111.8352
77.5794
77.1588
76.7381
31.4876
21.6019
13.9343
3h

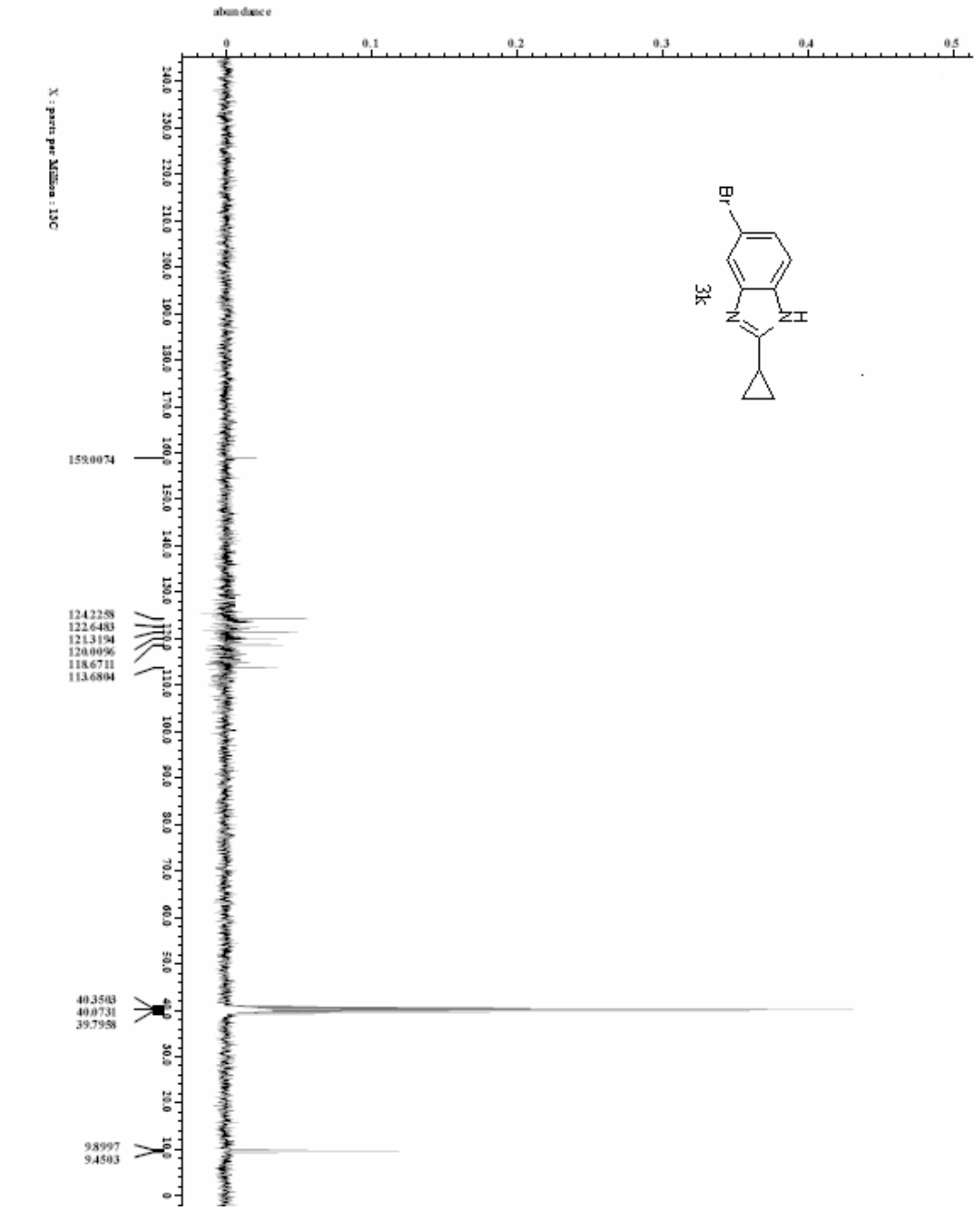

abundance
12.1667
7.4111
7.0929
7.0849
7.0746
7.0654
3.3204
3.2803
3.2712
2.5066
2.1186
2.1037
2.0923
2.0488
1.0541
1.0335
1.0255
0.0000
0.824
1.896
2.158
0.943
4
3i

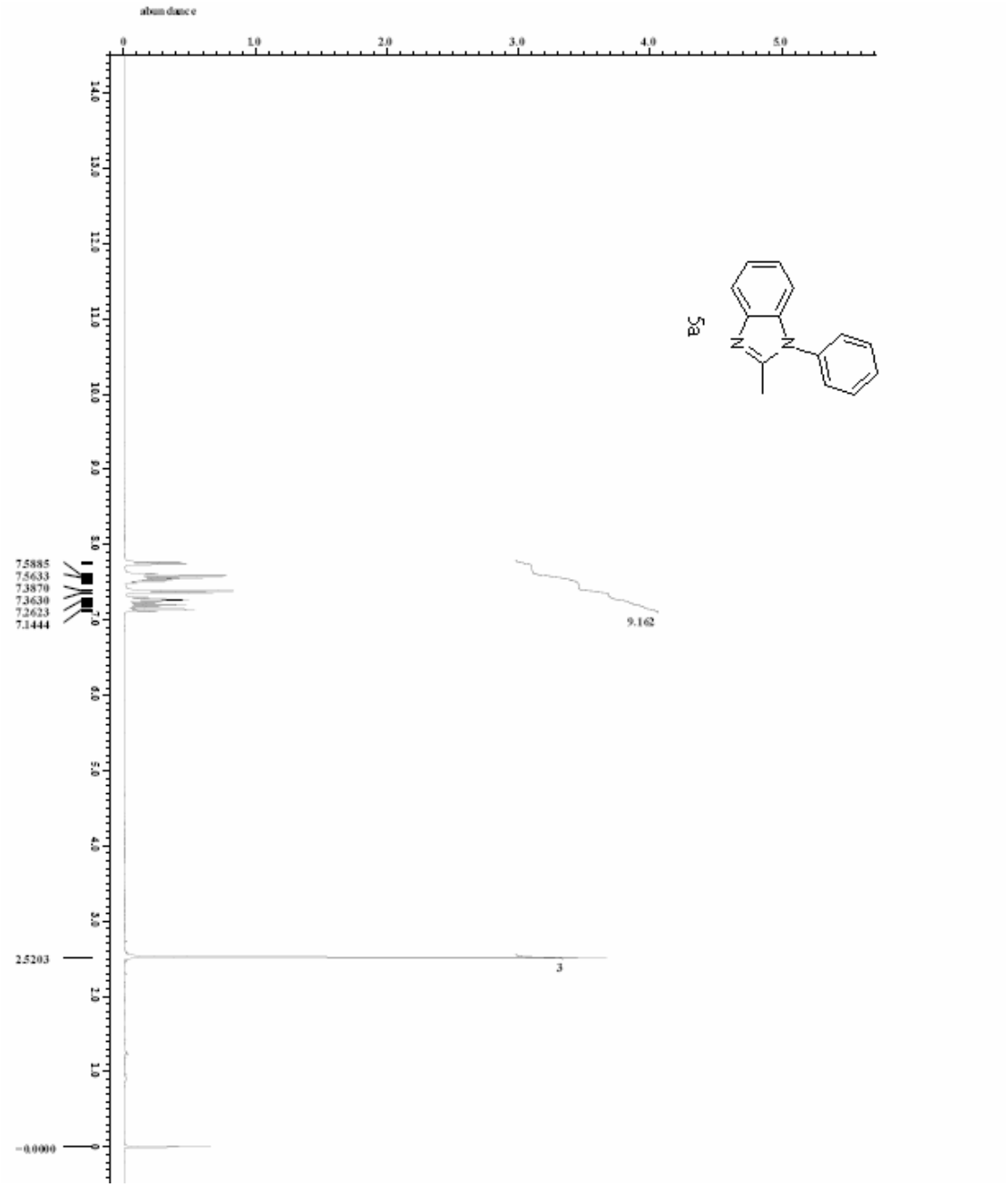

(thousandths)
0
10.0
20.0
30.0
40.0
50.0
X : parts per Million : 13C
157.4490
121.4915
114.5313
108.0779
40.3121
40.0348
39.7480
9.9284
9.2113
3i
N
H
N

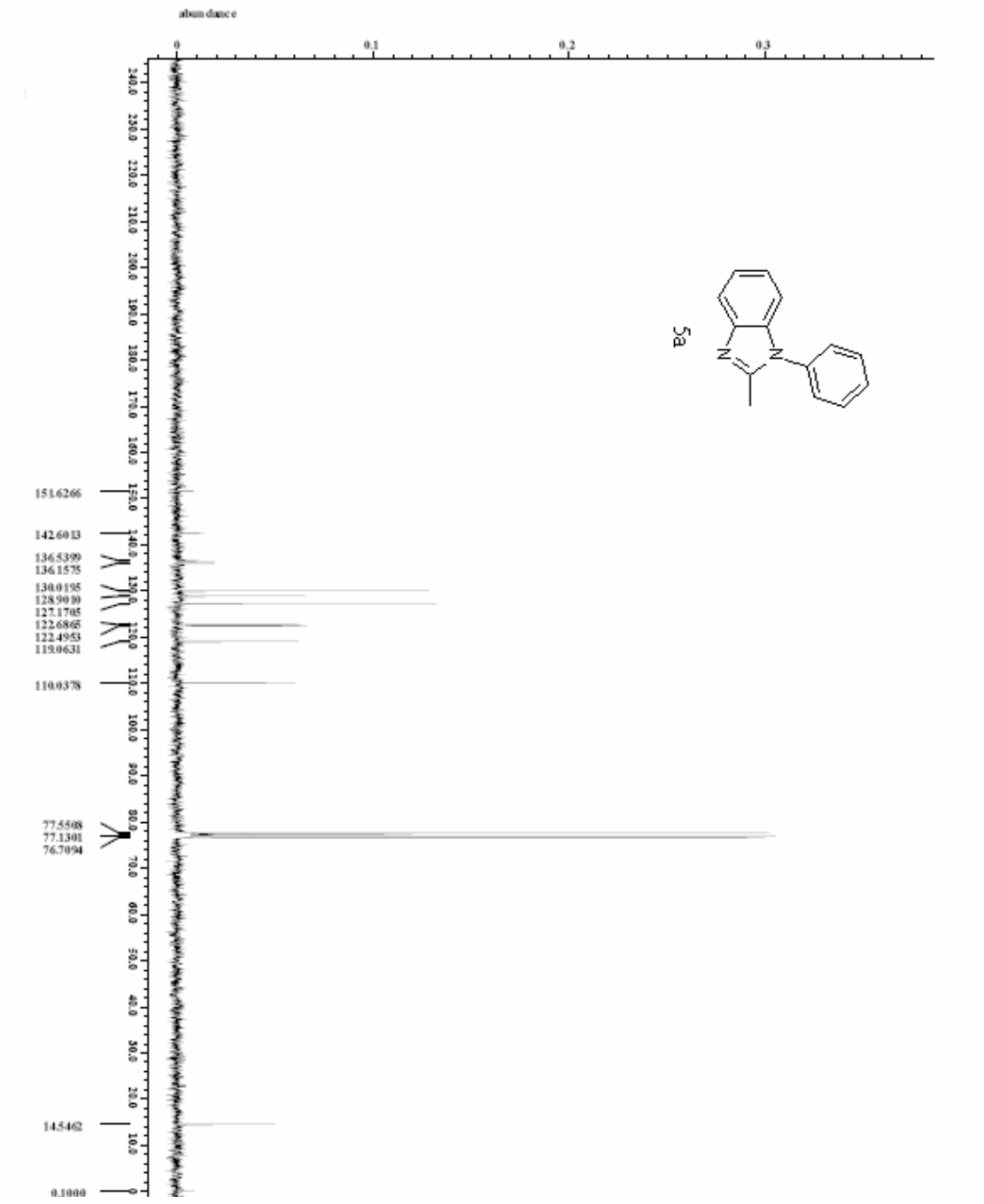

3j
7.3973
7.3699
7.2749
7.2600
7.0208
1.161
1.071
1.195
2.4288
2.0968
2.0854
2.0705
2.0568
3
1.152
1.1995
1.1915
1.1823
1.0839
2.22
2.197
0.0000

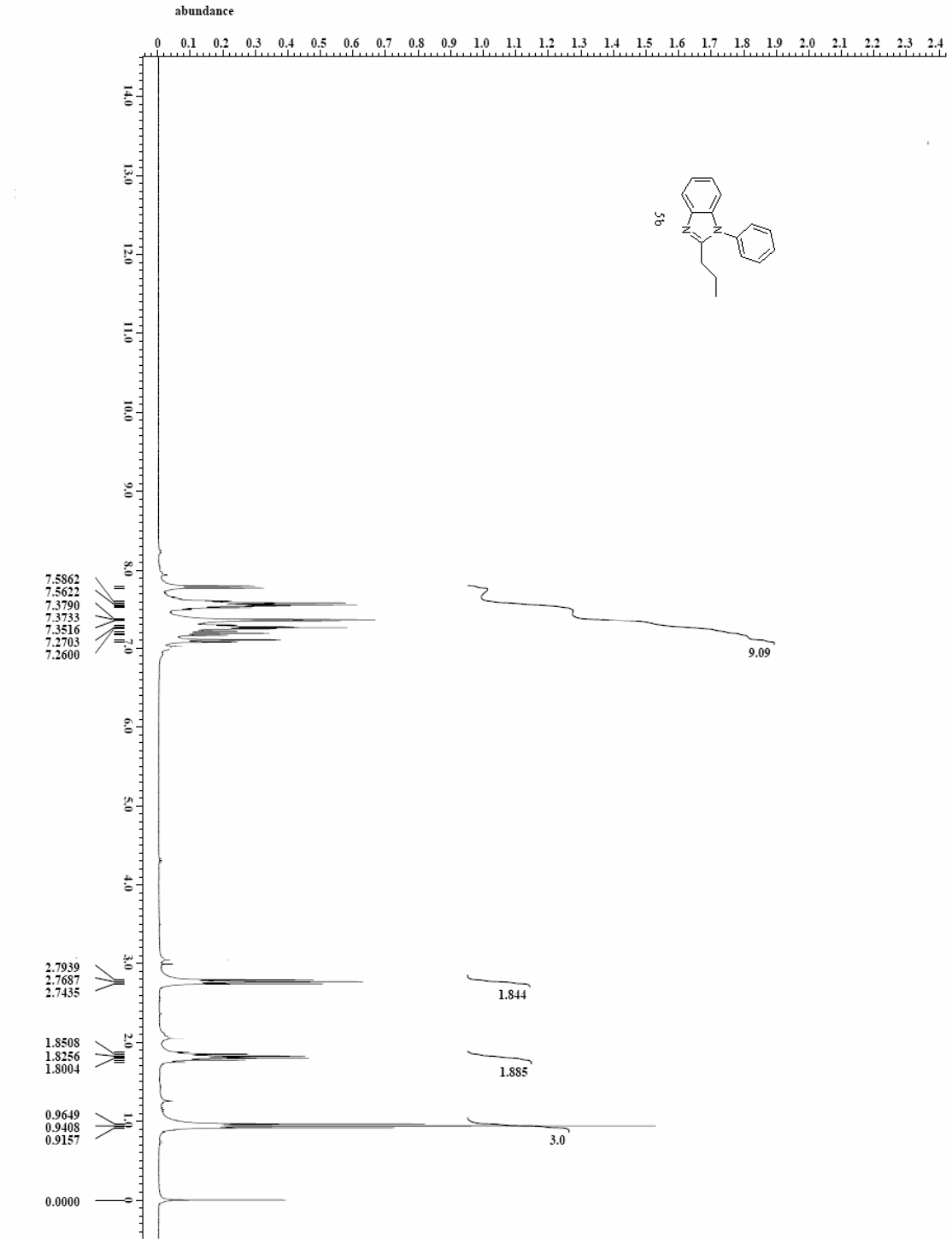

(thousandths)
X : parts per Million : 13C
156.5503
138.0792
131.9986
123.6139
114.2636
113.9194
77.5316
77.1110
76.6807
21.6688
9.7658
8.8480
31

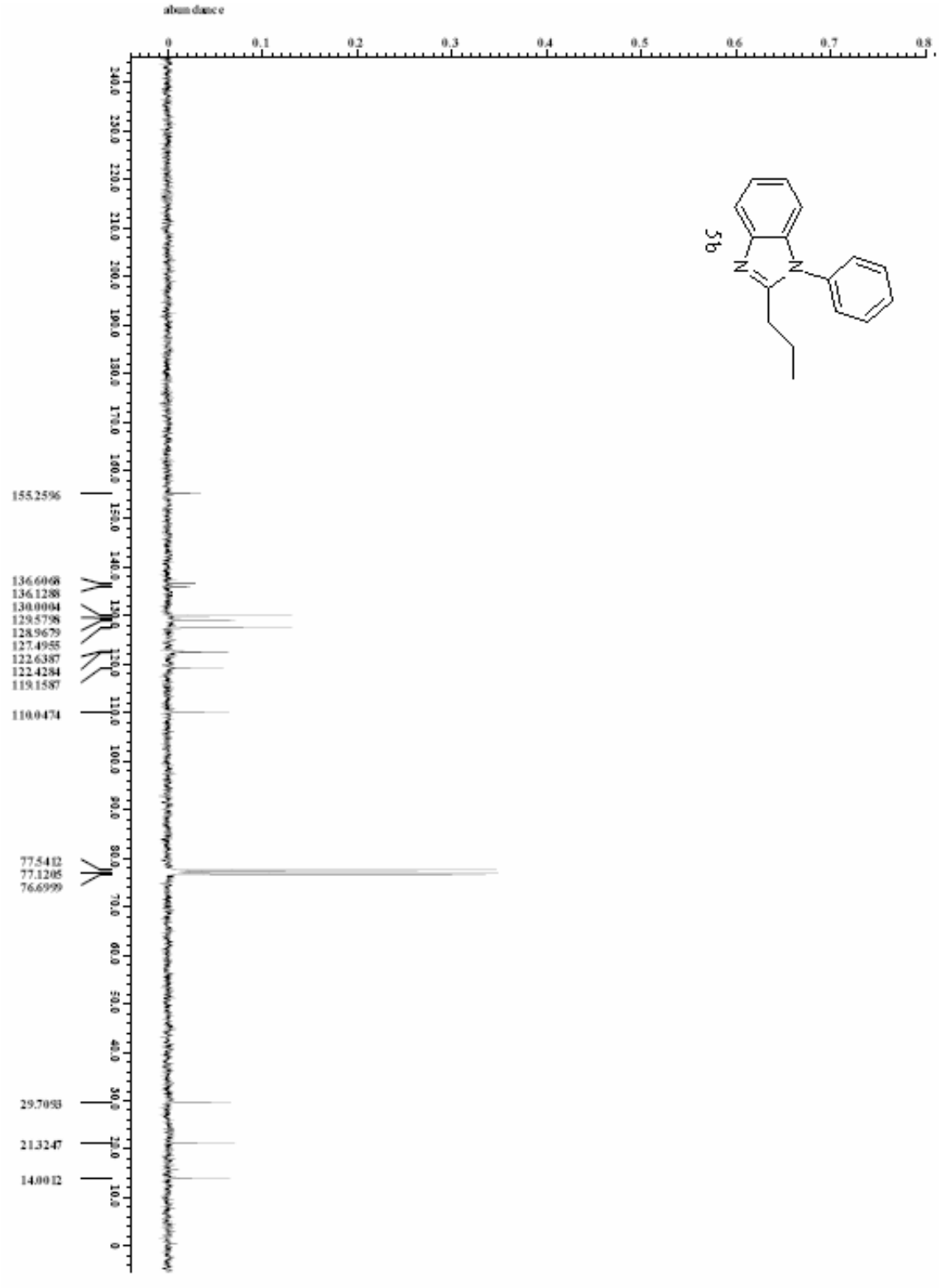

abundance
0
1.0
2.0
3.0
4.0
5.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.693
Br
3k
N
H
N
7.5988
7.3859
7.3573
7.2314
7.2028
0.902
0.985
0.916
2.5112
2.1587
2.1312
2.1140
2.0980
2.0705
1.0
1.0828
1.0484
1.0370
1.0301
4.022
0.0000

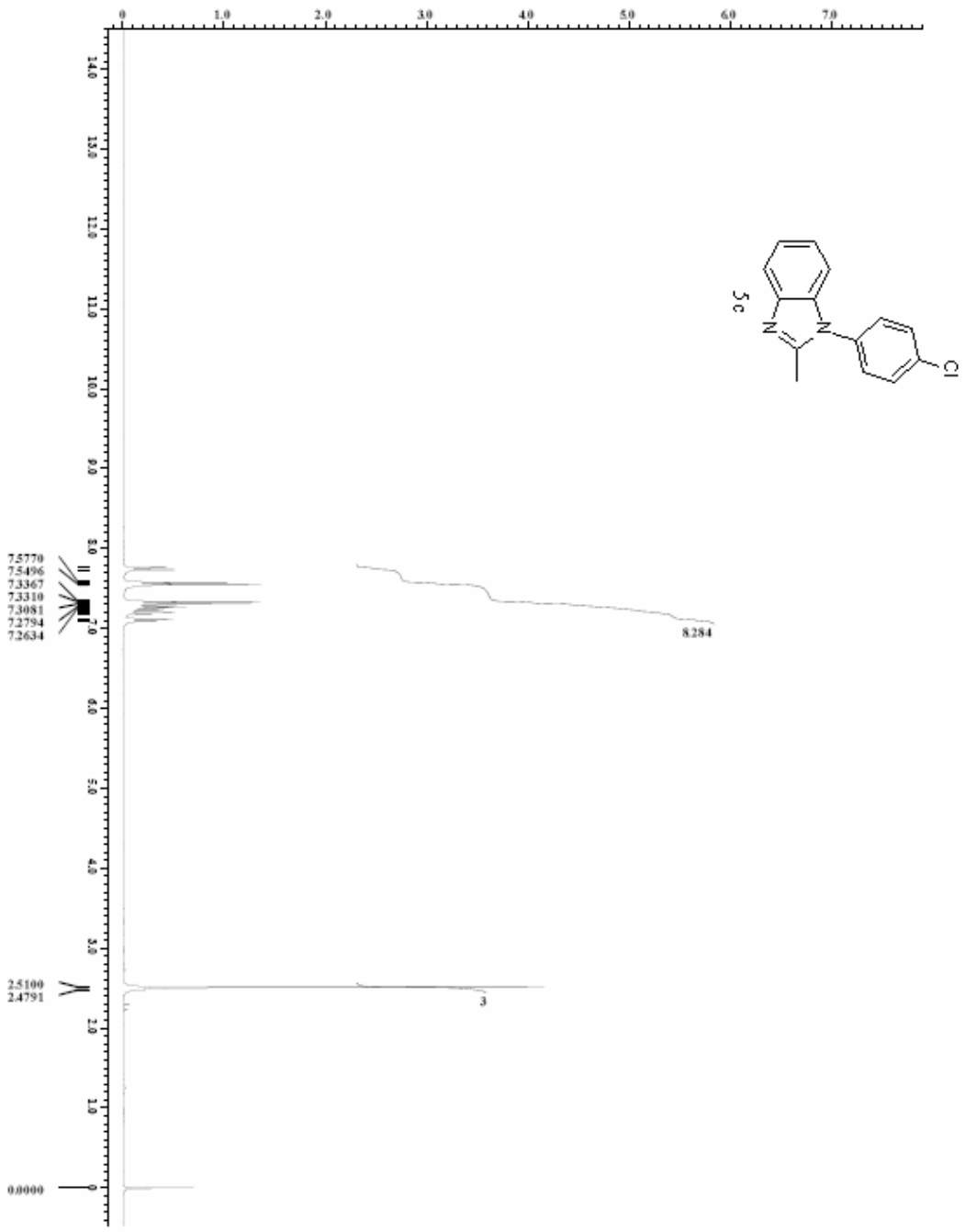

abundance
X : parts per Million : 13C
159.0074
124.2258
122.6483
121.3194
120.0096
118.6711
113.6804
40.3503
40.0731
39.7958
9.8997
9.4503
Br
N
H
N
3k

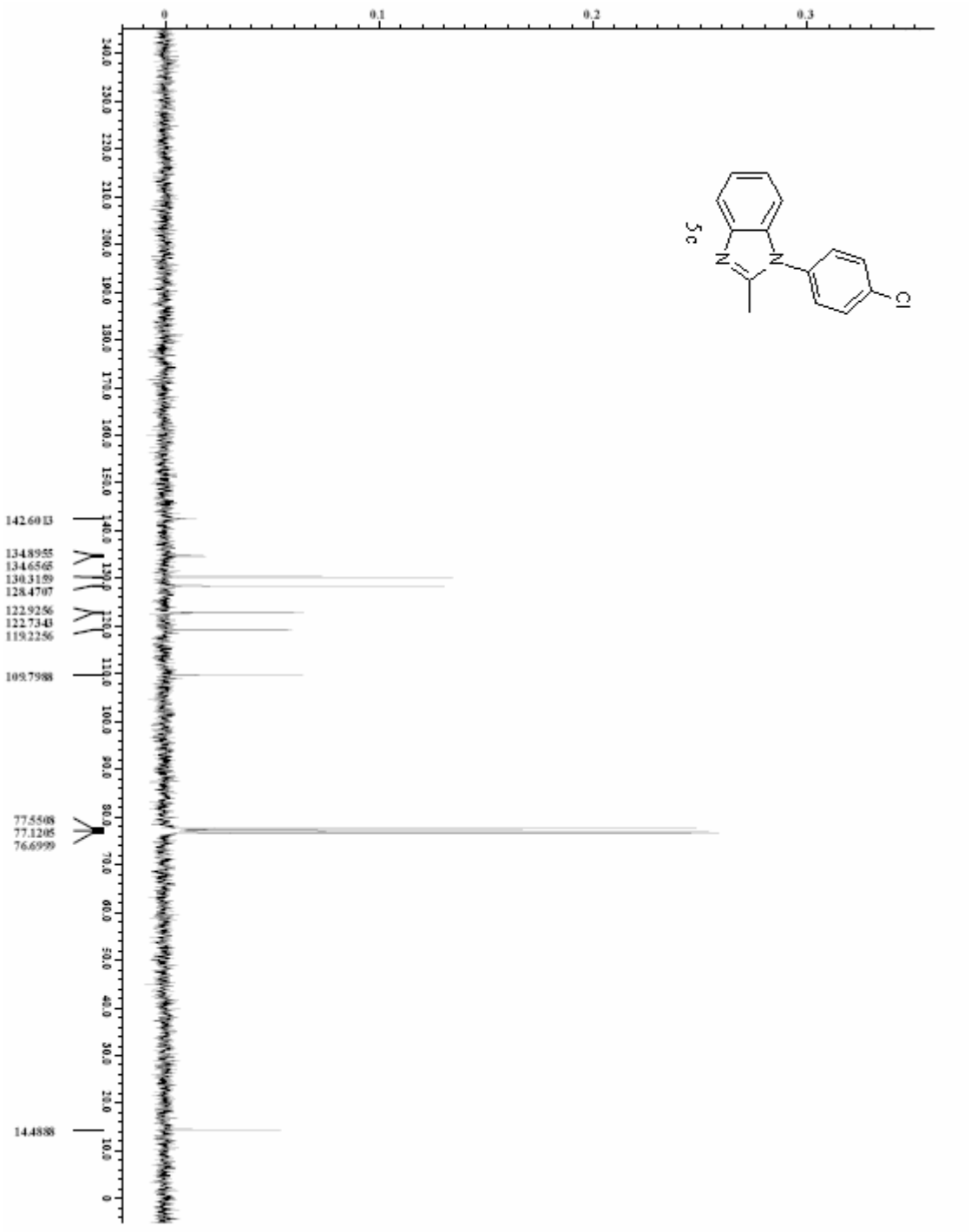

abundance
7.5885
7.5633
7.3870
7.3630
7.2623
7.1444
2.5203
-0.0000
9.162
3
5a

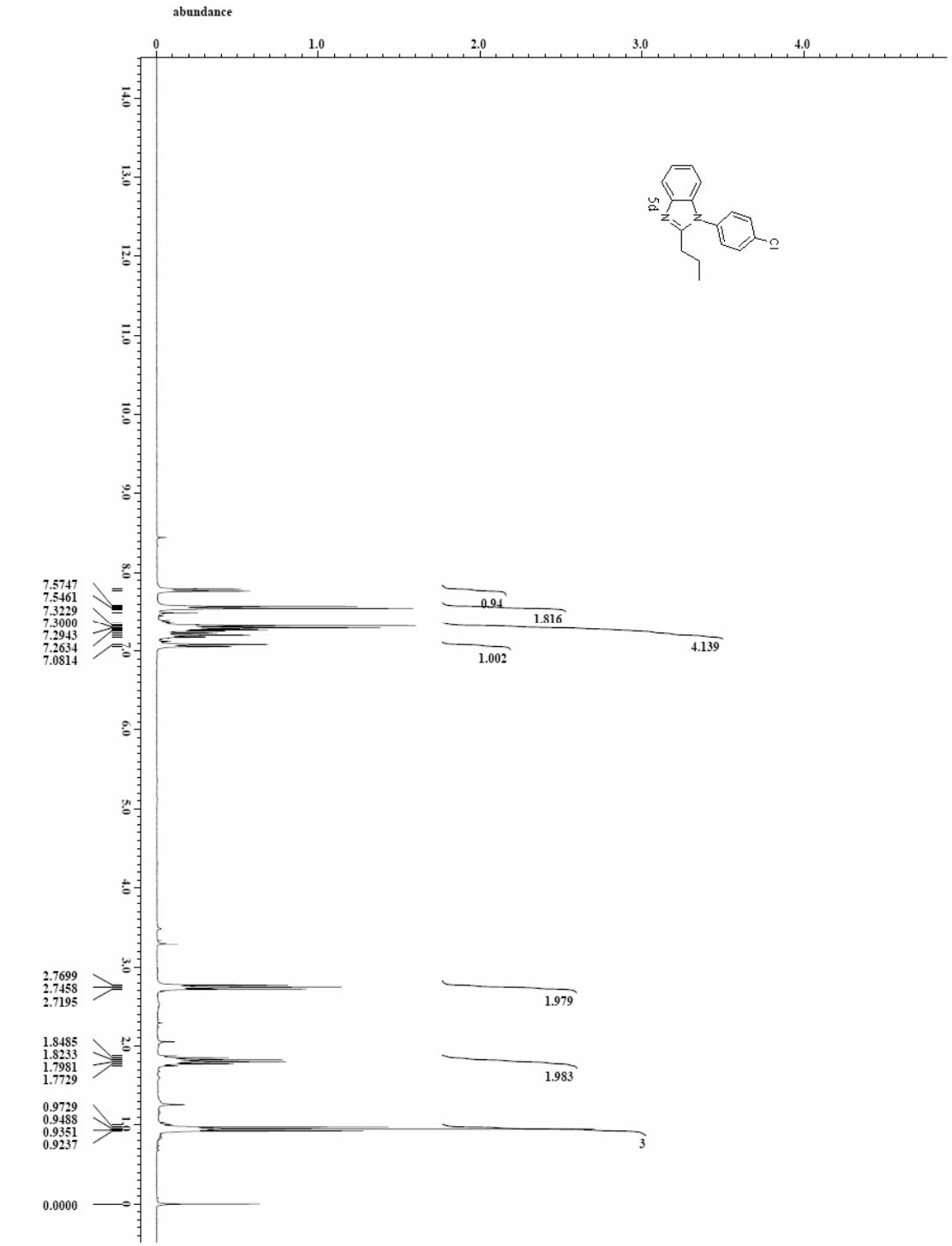

abundance
0
0.1
0.2
0.3
151.6266
142.6013
136.5399
136.1575
130.0195
128.9010
127.1705
122.6865
122.4953
119.0631
110.0378
77.5508
77.1301
76.7094
14.5462
0.1000
5a

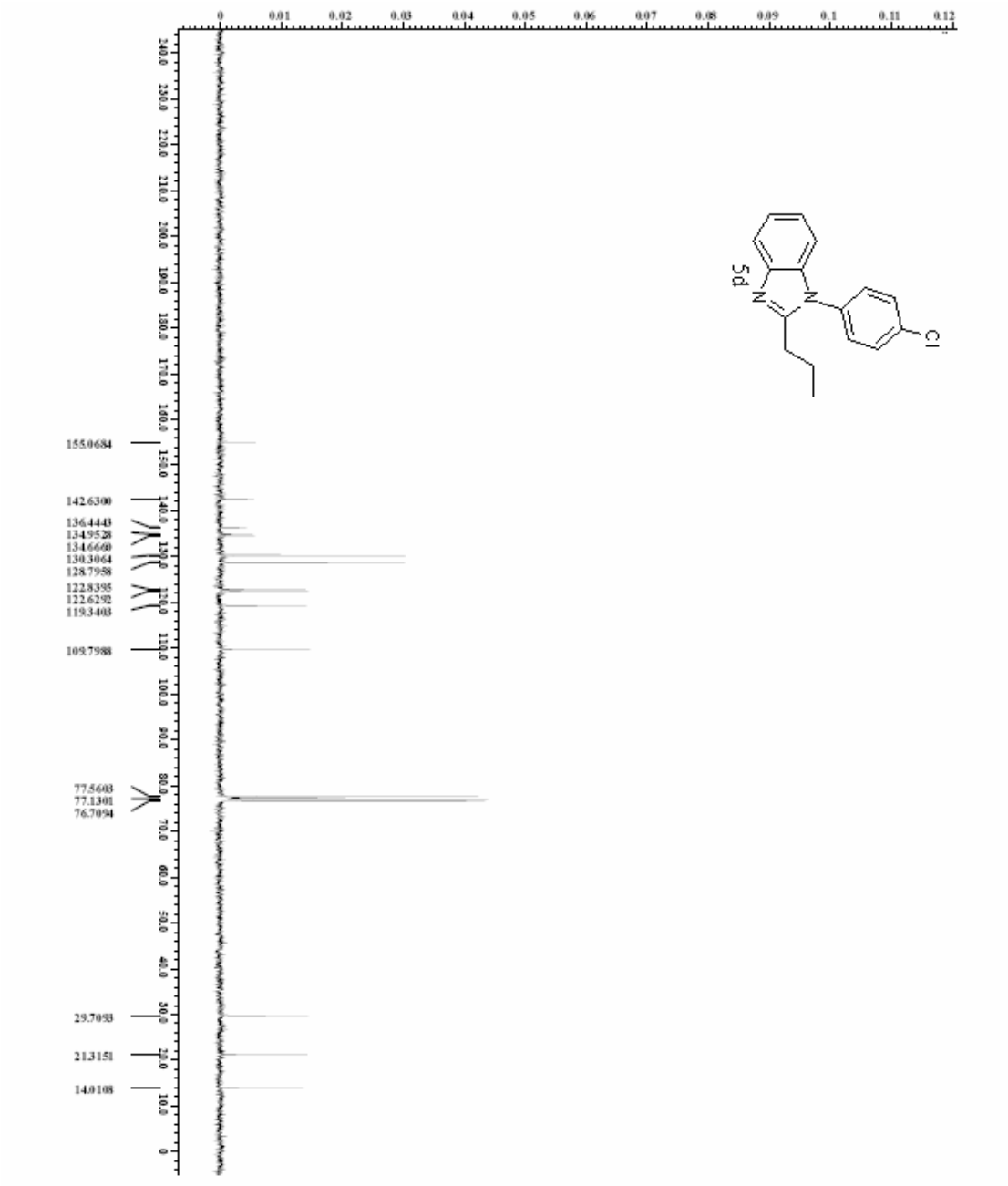

abundance
5b
7.5862
7.5622
7.3790
7.3733
7.3516
7.2703
7.2600
9.09
2.7939
2.7687
2.7435
1.844
1.8508
1.8256
1.8004
1.885
0.9649
0.9408
0.9157
3.0
0.0000

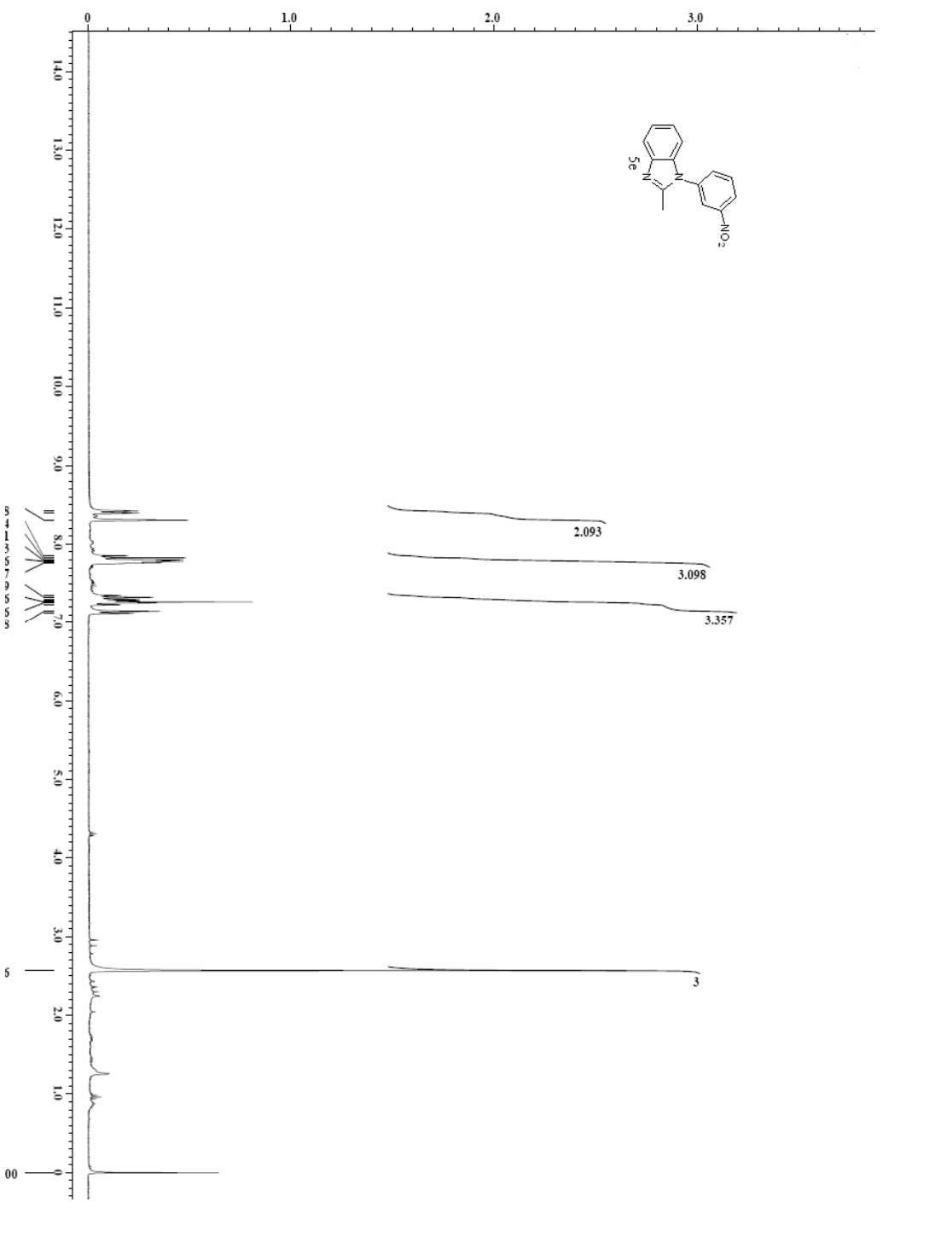

abundance
155.2596
136.6068
136.1288
130.0084
129.5798
128.9679
127.4955
122.6387
122.4284
119.1587
110.0474
77.5412
77.1205
76.6999
29.7053
21.3247
14.0012
5b

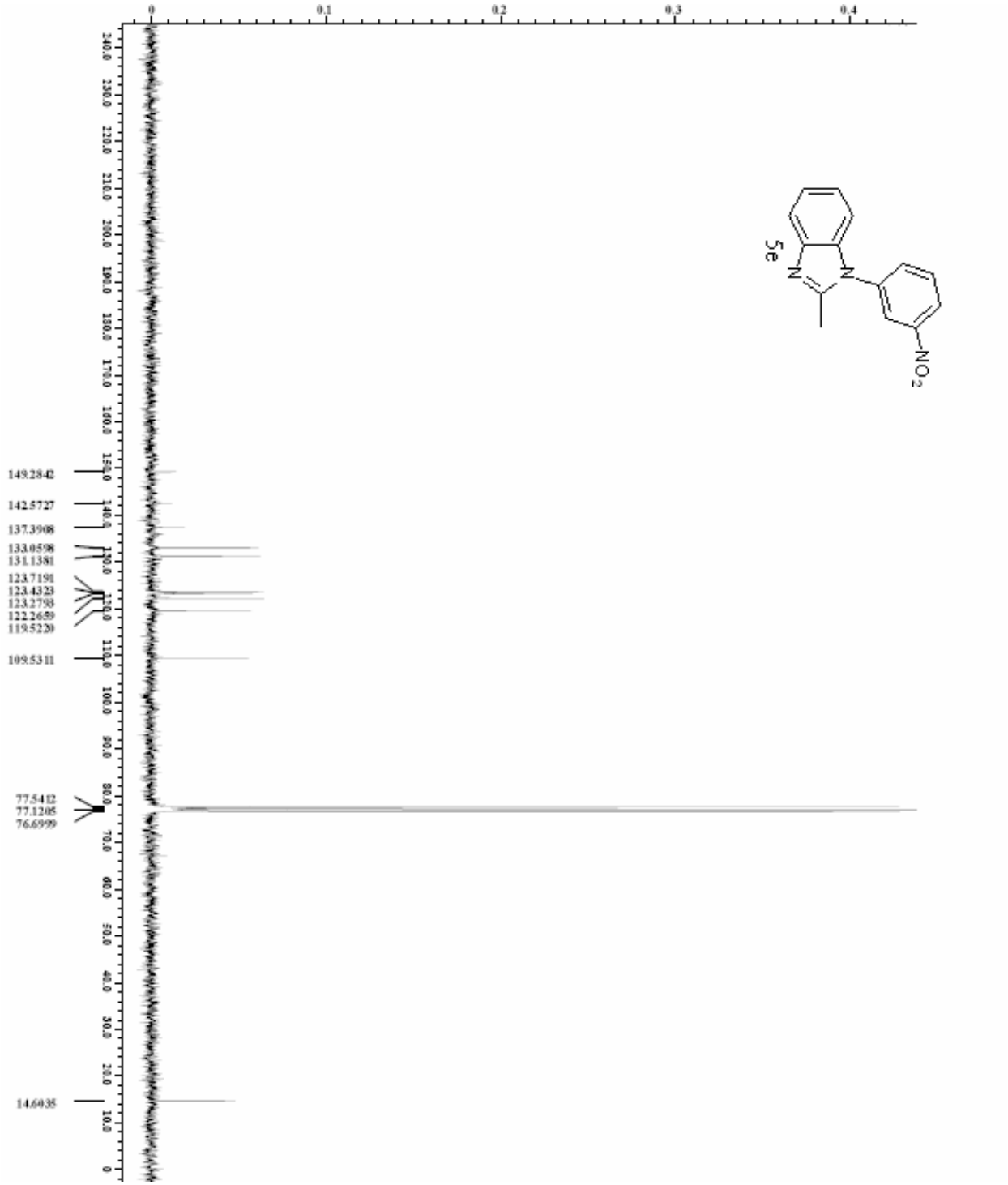

5c
Cl
7.5770
7.5496
7.3367
7.3310
7.3081
7.2794
7.2634
8.284
3
2.5100
2.4791
0.0000

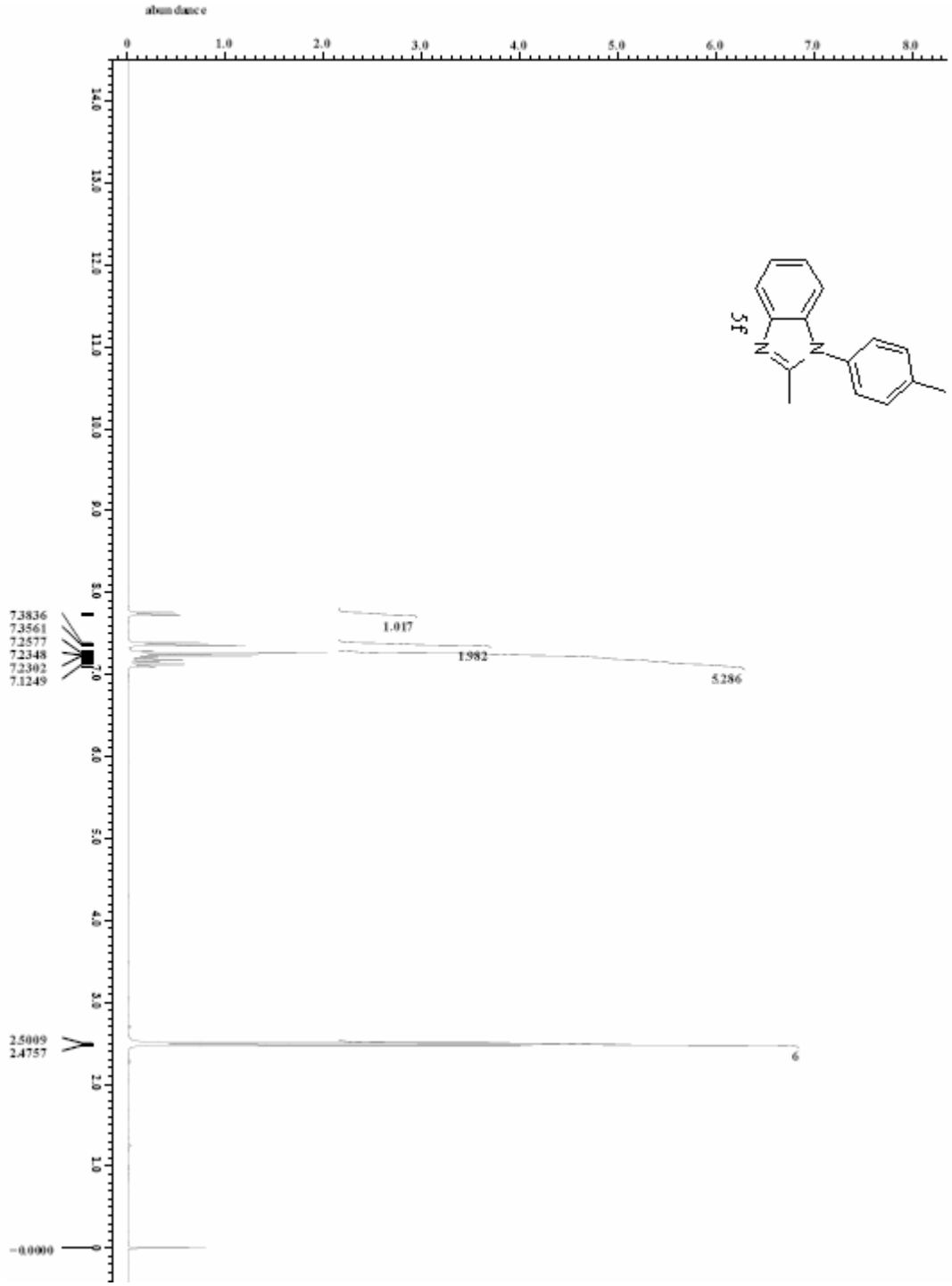

5c
N
N
Cl
142.6013
134.8935
134.6565
130.3159
128.4707
122.9256
122.7343
119.2256
109.7988
77.5508
77.1205
76.6999
14.4888

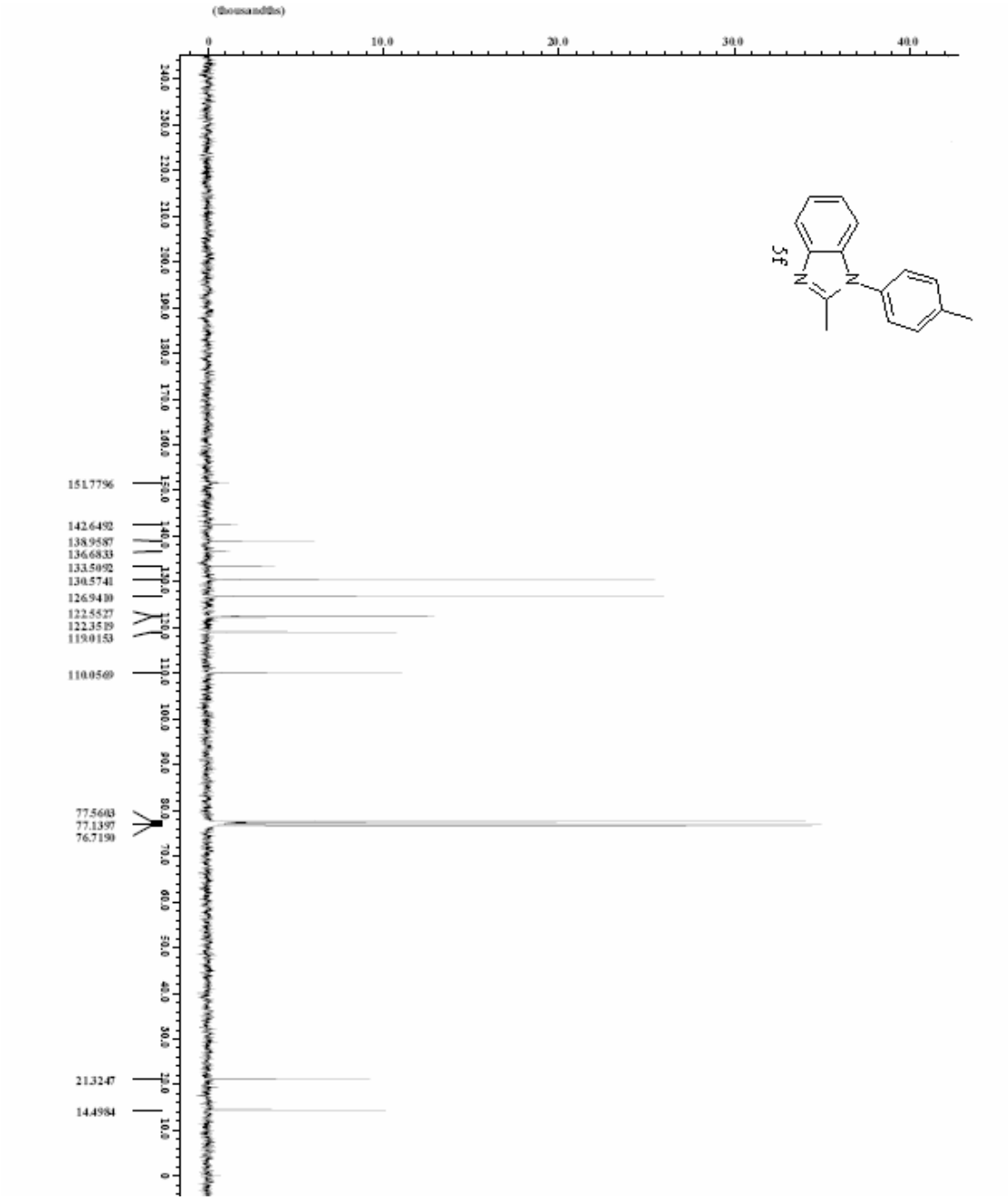

abundance
0
1.0
2.0
3.0
4.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5747
7.5461
7.3229
7.3000
7.2943
7.2634
7.0814
0.94
1.816
4.139
1.002
2.7699
2.7458
2.7195
1.979
1.8485
1.8233
1.7981
1.7729
1.983
0.9729
0.9488
0.9351
0.9237
3
0.0000
Cl

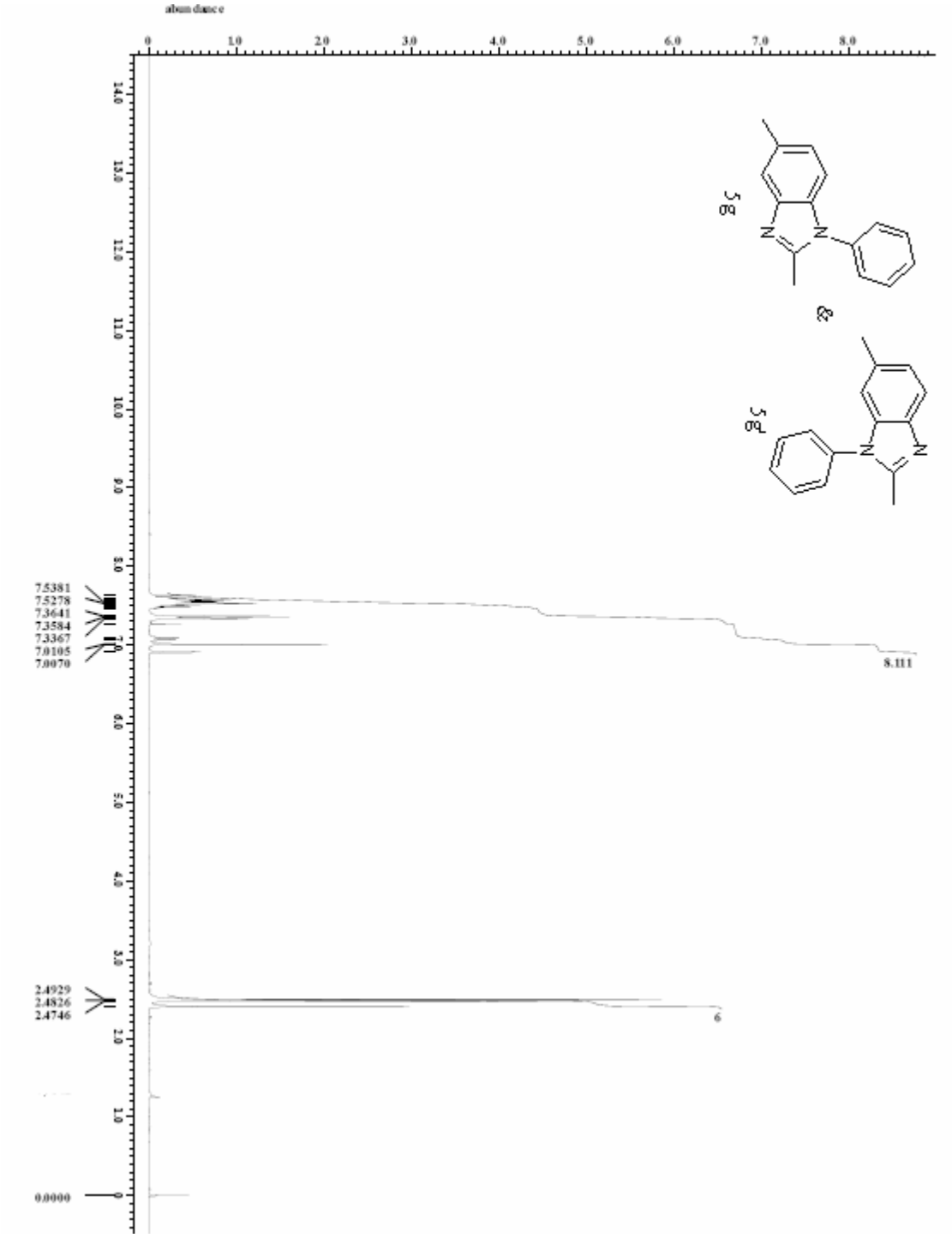

155.0684
142.6300
136.4443
134.9528
134.6660
130.3064
128.7958
122.8395
122.6292
119.3403
109.7988
77.5603
77.1301
76.7094
29.7093
21.3151
14.0108
5d
N
N
Cl

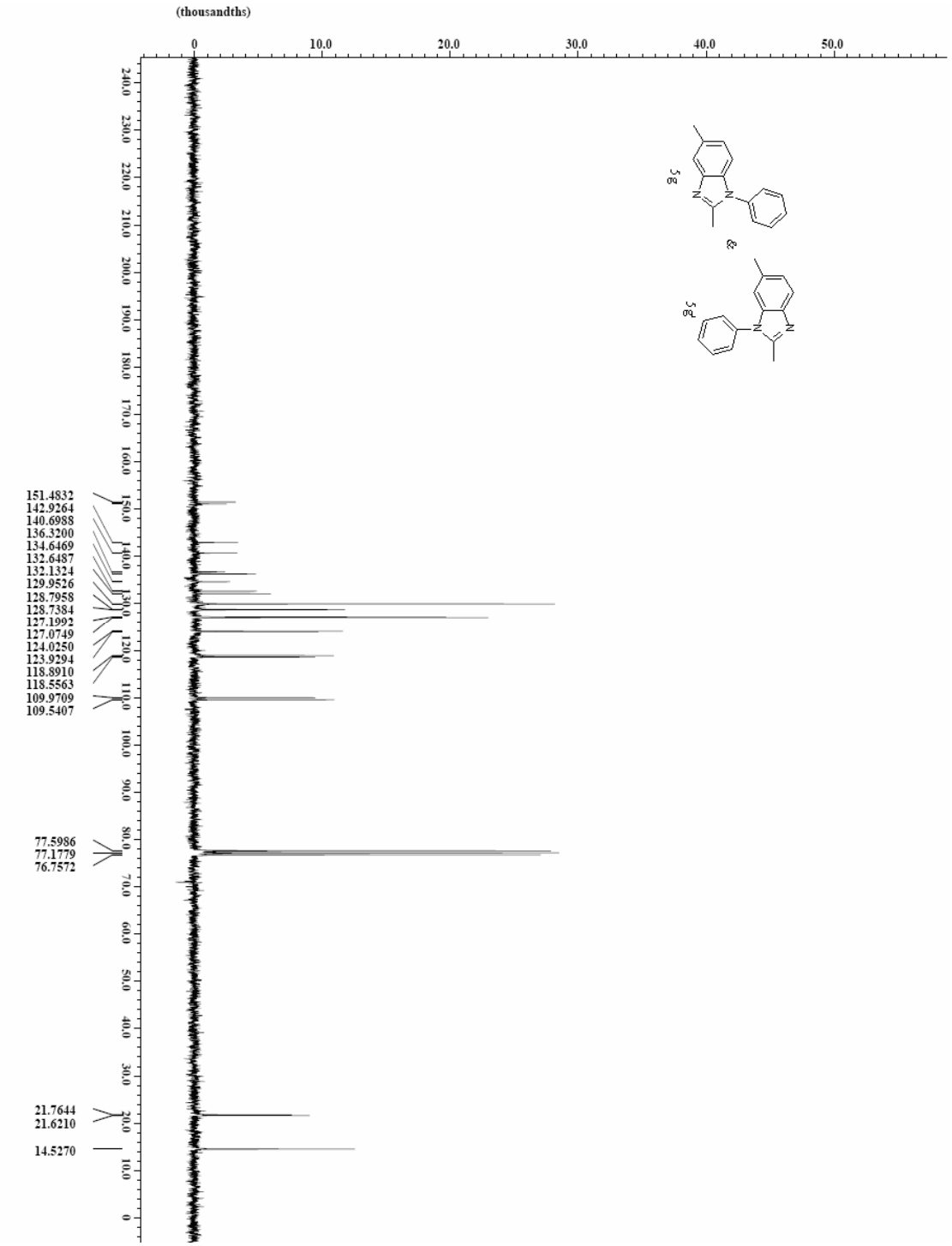

5e
NO2
2.093
3.098
3.357
3

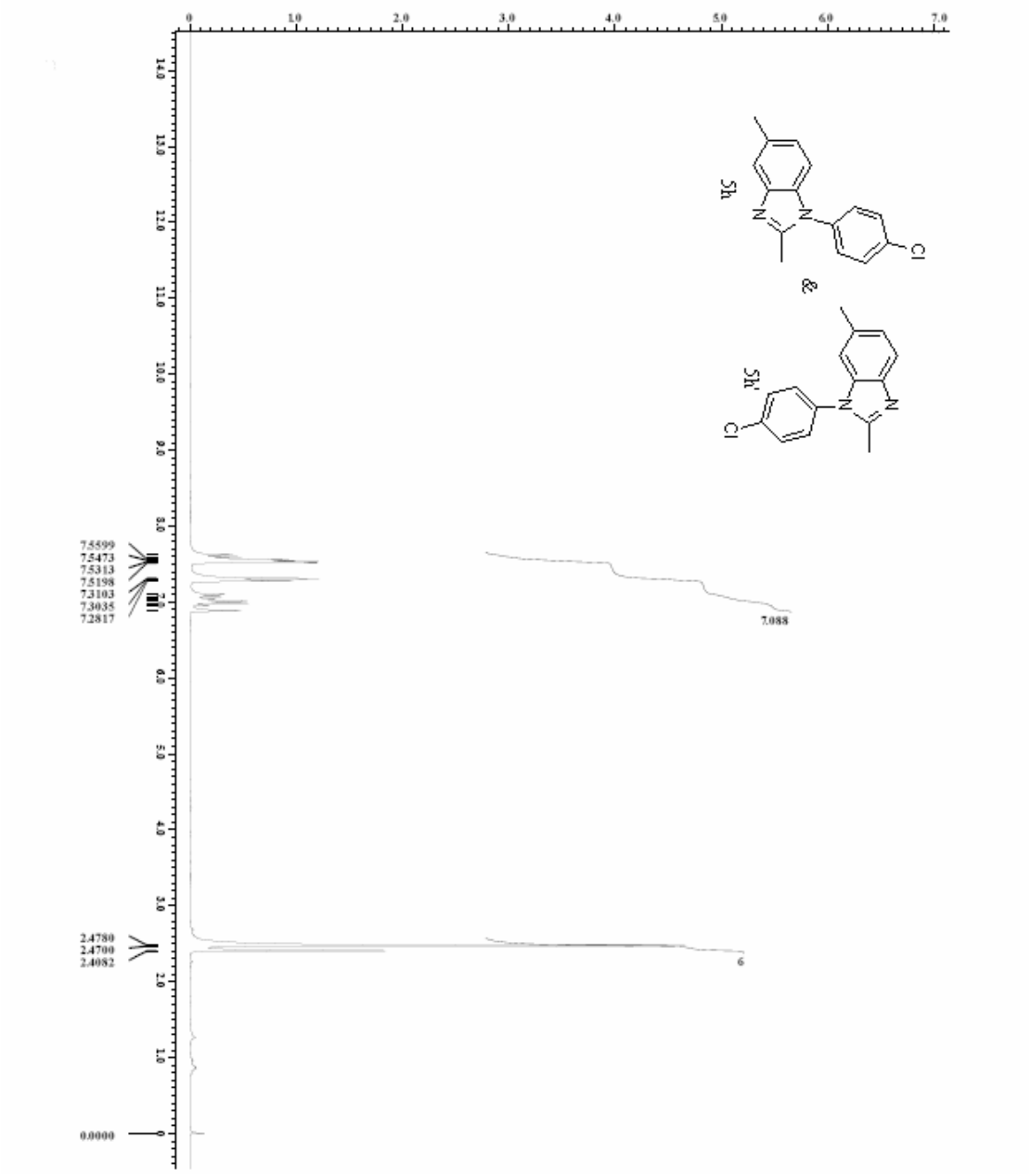

5e
NO2
149.2842
142.5727
137.3908
133.0598
131.1381
123.7191
123.4323
123.2798
122.2659
119.5220
109.5311
77.5412
77.1205
76.6999
14.6035

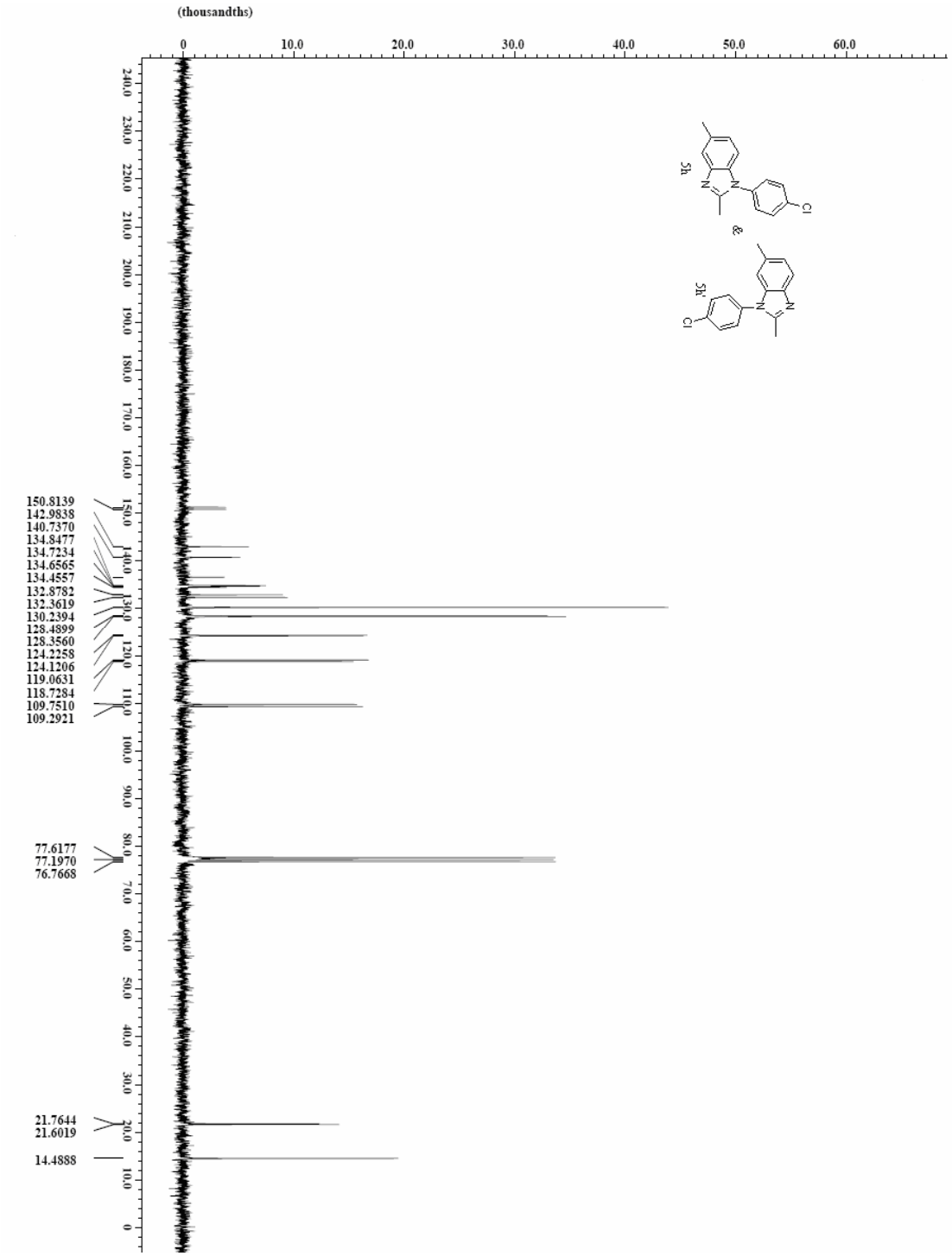

abundance
5f
7.3836
7.3561
7.2577
7.2348
7.2302
7.1249
1.017
1.982
5.286
2.5009
2.4757
6
-0.0000

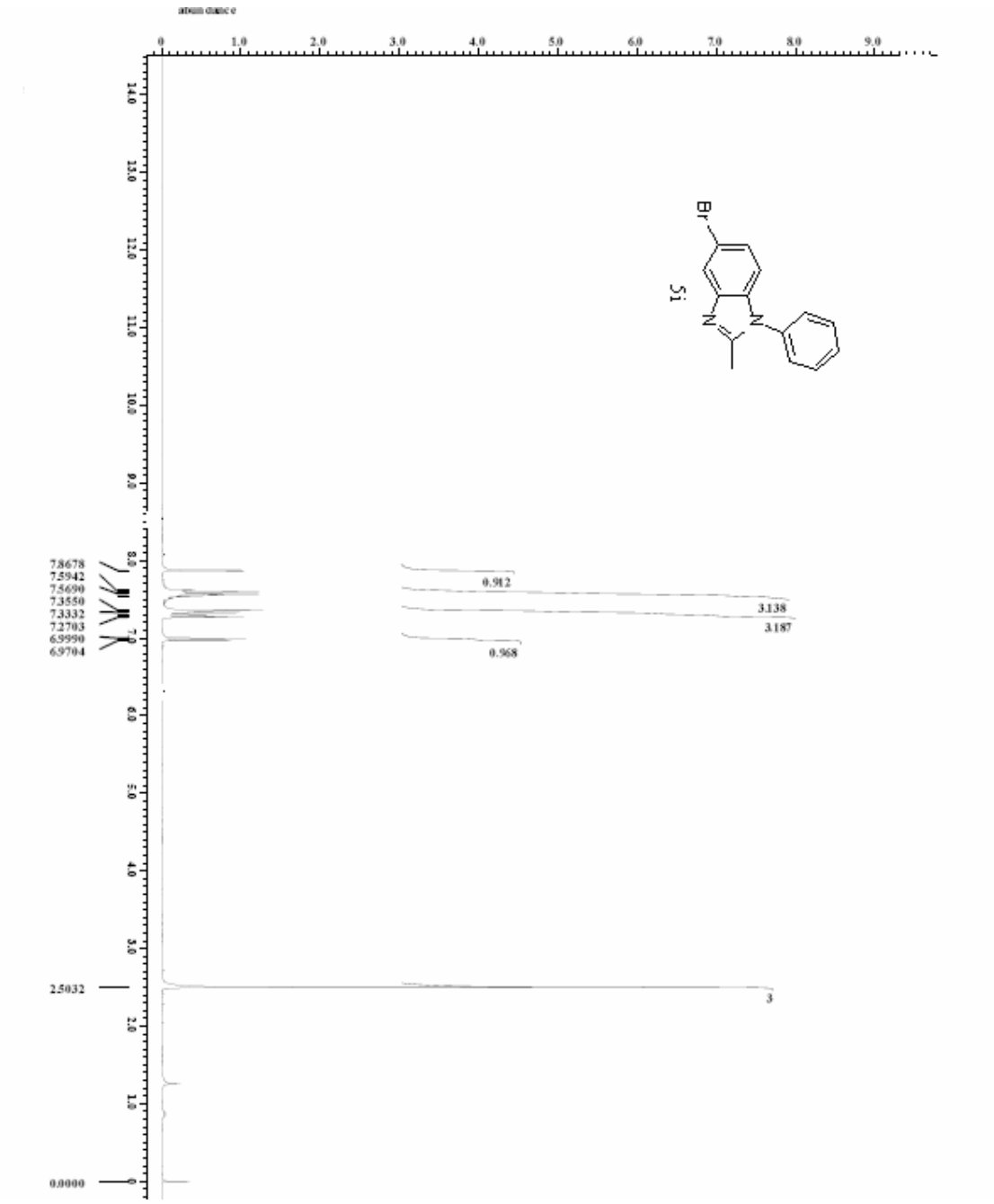

(thousandths)
0
10.0
20.0
30.0
40.0
5f
151.7796
142.6492
138.9587
136.6833
133.5092
130.5741
126.9439
122.5527
122.3519
119.0153
110.0569
77.5603
77.1397
76.7190
21.3247
14.4984

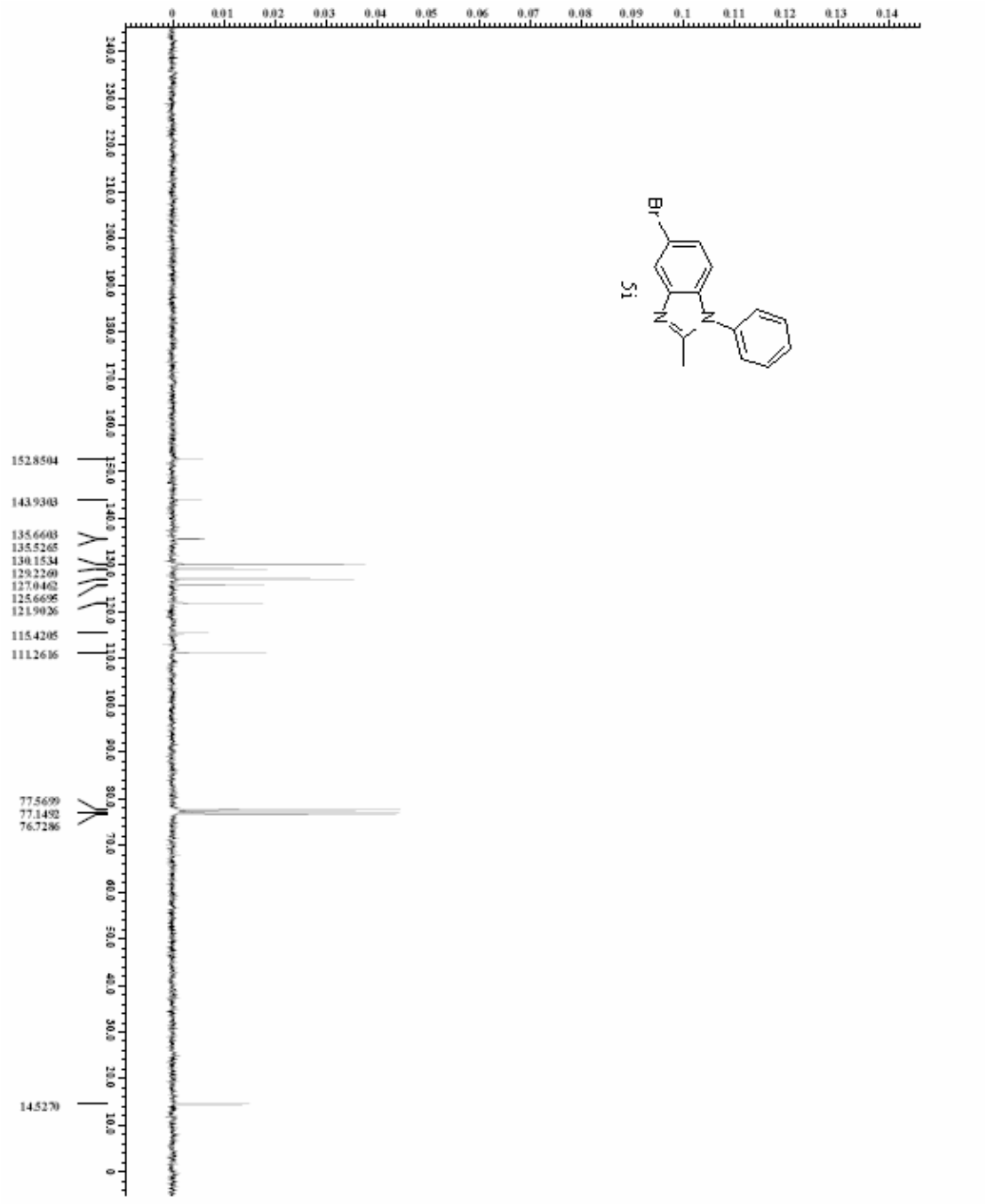

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
5g
&
5g'
7.5381
7.5278
7.3641
7.3584
7.3367
7.0105
7.0070
8.111
2.4929
2.4826
2.4746
6
0.0000


(thousandths)
0
10.0
20.0
30.0
40.0
50.0
151.4832
142.9264
140.6988
136.3200
134.6469
132.6487
132.1324
129.9526
128.7958
128.7384
127.1992
127.0749
124.0250
123.9294
118.8910
118.5563
109.9709
109.5407
77.5986
77.1779
76.7572
21.7644
21.6210
14.5270
5g
5g'


5h
Cl
&
5h'
Cl
7.5599
7.5473
7.5313
7.5198
7.3103
7.3035
7.2817
7.088
2.4780
2.4700
2.4082
6
0.0000


(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
5k
Cl
&
5k'
Cl
150.8139
142.9838
140.7370
134.8477
134.7234
134.6565
134.4557
132.8782
132.3619
130.2394
128.4899
128.3560
124.2258
124.1206
119.0631
118.7284
109.7510
109.2921
77.6177
77.1970
76.7668
21.7644
21.6019
14.4888


Br
N
N
5i
7.8678
7.5942
7.5690
7.3550
7.3332
7.2703
6.9990
6.9704
0.912
3.138
3.187
0.968
2.5032
3
0.0000


Br
Si
152.8504
143.9303
135.6603
135.5265
130.1534
129.2269
127.0462
125.6695
121.9026
115.4205
111.2616
77.5699
77.1492
76.7286
14.5270