Deprotonative Cadmation of Functionalized Aromatics

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General Methods

All reactions were performed under argon atmosphere. THF was distilled over sodium/benzophenone. Nuclear magnetic resonance spectra were acquired on Bruker ARX-200 (200 MHz and 50 MHz for ^{1}H and ^{13}C respectively) and Bruker AC-300 (300 MHz and 75 MHz for ^{1}H and ^{13}C respectively) spectrometers. Chemical shifts are given in ppm as δ values relative to tetramethylsilane (^{1}H, ^{13}C) and coupling constants are given in Hz. High resolution mass spectra measurements and elemental analyses were performed at the CRMPO in Rennes (Centre Régional de Mesures Physiques de l'Ouest) using respectively a Micromass MS/MS ZABSpec TOF instrument in EI mode and a Thermo-Finnigan Flash EA 1112 CHNS analyzer. Liquid chromatography separations were achieved on silica gel Merck Geduran Si 60 (40–63 mesh).

Typical Procedures

A. Deprotonative cadmation/Iodination. To a stirred, cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (847 mg, 6.0 mmol) in THF (5 mL) were successively added *n*-BuLi (1.6 M hexanes solution, 6.0 mmol) and $CdCl_2$·TMEDA (599 mg, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the aromatic substrate (4.0 mmol). After 2 h at room temperature, a solution of I_2 (1.52 g, 6.0 mmol) in THF (5 mL) was added. The mixture was stirred overnight before addition of an aqueous saturated solution of $Na_2S_2O_3$ (20 mL) and extraction with Et_2O (20 mL) and CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel gave the monoiodo derivative.

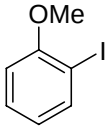
B. Deprotonative dicadmation/Diiodination. To a stirred, cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (1.69 g, 12.0 mmol) in THF (5 mL) were successively added *n*-BuLi (1.6 M

hexanes solution, 12.0 mmol) and $CdCl_2$·TMEDA (1.20 g, 4.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the aromatic substrate (4.0 mmol). After 2 h at room temperature, a solution of I_2 (3.05 g, 12.0 mmol) in THF (5 mL) was added. The mixture was stirred overnight before addition of an aqueous saturated solution of $Na_2S_2O_3$ (20 mL) and extraction with Et_2O (20 mL) and CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel gave the diiodo derivative.

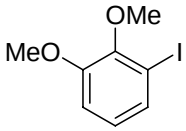
C. Deprotonative cadmation/Benzoylation. To a stirred, cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (847 mg, 6.0 mmol) in THF (5 mL) were successively added *n*-BuLi (1.6 M hexanes solution, 6.0 mmol) and $CdCl_2$·TMEDA (599 mg, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of furan (272 mg, 4.0 mmol). After 2 h at room temperature, a solution of benzoyl chloride (843 mg, 6.0 mmol) in THF (5 mL) was added at 0 °C. The mixture was stirred overnight before addition of an aqueous saturated solution of $NaHCO_3$ (20 mL) and extraction with Et_2O (20 mL) and CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel gave the benzoyl derivative.

D. Deprotonative cadmation/Cross coupling. To a stirred, cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (847 mg, 6.0 mmol) in THF (5 mL) were successively added *n*-BuLi (1.6 M hexanes solution, 6.0 mmol) and $CdCl_2$·TMEDA (599 mg, 2.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of furan (272 mg, 4.0 mmol). After 2 h at room temperature, the $Pd(OAc)_2$ (54 mg, 6 mol %), dppf (133 mg, 6 mol %) and 4-bromoanisole (748 mg, 4.0 mmol) were successively added. The solution was heated at reflux for 18 h before addition of water (1 mL) and AcOEt (20 mL). The reaction mixture was filtered on celite®, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel gave the cross-coupling product.

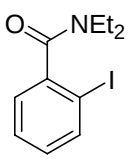
Compound Characterizations



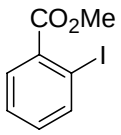
2-Iodoanisole (2a),[1] prepared using the general procedure **A**, 74% yield, orange oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.80 (s, 3H), 6.70 (dt, 1H, *J* = 1.3 and 7.6), 6.79 (dd, 1H, *J* = 1.3 and 8.3), 7.28 (ddd, 1H, *J* = 1.6, 7.4 and 8.3), 7.77 (dd, 1H, *J* = 1.6 and 7.6). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 56.0, 85.8, 110.7, 122.2, 129.3, 139.1, 157.6.



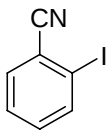
1-Iodo-2,3-dimethoxybenzene (2b),[2] prepared using the general procedure **A**, 79% yield, orange oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.83 (s, 3H), 3.85 (s, 3H), 6.83 (m, 2H), 7.34 (dd, 1H, *J* = 1.8 and 7.6). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 56.1, 60.5, 92.7, 112.9, 126.1, 130.7, 149.1, 153.0.



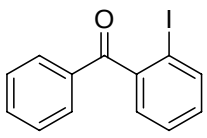
***N*,*N*-Diethyl-2-iodobenzamide (2c)**,[3] prepared using the general procedure **A**, 91% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.04 (t, 3H, *J* = 7.1), 1.27 (t, 3H, *J* = 7.1), 3.10 (m, 2H), 3.30 (m, 1H), 3.80 (m, 1H), 7.04 (dt, 1H, *J* = 1.8 and 7.5), 7.18 (dd, 1H, *J* = 1.8 and 7.5), 7.36 (dt, 1H, *J* = 1.0 and 7.5), 7.78 (dd, 1H, *J* = 1.0 and 7.5). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 12.0, 13.4, 38.4, 42.3, 92.3, 126.3, 127.7, 129.4, 138.5, 142.2, 169.3.



Methyl 2-iodobenzoate (2d),[4] prepared using the general procedure **A**, 62% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.94 (s, 3H), 7.15 (dt, 1H, *J* = 1.8 and 7.6), 7.40 (dt, 1H, *J* = 1.2 and 7.6), 7.81 (dd, 1H, *J* = 1.8 and 7.6), 7.99 (dd, 1H, *J* = 1.8 and 7.6). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 52.2, 93.9, 127.7, 130.7, 132.4, 134.7, 141.0, 166.5.



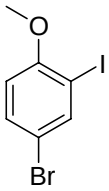
2-Iodobenzonitrile (2e),[1] prepared using the general procedure **A**, 68% yield, orange solid (mp 58-60 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.28 (dt, 1H, *J* = 1.7 and 7.6), 7.45 (dt, 1H, *J* = 1.1 and 7.6), 7.60 (dd, 1H, *J* = 1.7 and 7.6), 7.91 (dd, 1H, *J* = 1.1 and 7.6). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 98.4, 119.4, 120.6, 128.4, 133.8, 134.3, 139.6.



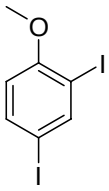
2-Iodobenzophenone (2f),[5] prepared using the general procedure **A**, 66% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.18 (dt, 1H, *J* = 1.8 and 7.4),

[1] Uchiyama, M.; Naka, H., Matsumoto, Y.; Ohwada, T. *J. Am. Chem. Soc.* **2004**, *126*, 10526-10527.
[2] Naka, H.; Uchiyama, M.; Matsumoto, Y.; Wheatley, A. E. H.; McPartlin, M.; Morey, J. V.; Kondo, Y. *J. Am. Chem. Soc.* **2007**, *129*, 1921-1930.
[3] Sapountzis, I., PhD Thesis, University of Munich, 2004.
[4] Dahl, B. J.; Branchaud, B. P. *Tetrahedron Lett.* **2004**, *45*, 9599-9602.
[5] Trybulski, E. J.; Reeder, E.; Blount, J. F.; Walser, A.; Fryer, R. I. *J. Org. Chem.* **1982**, *47*, 2441-2447.

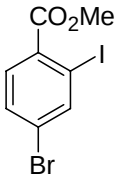
7.30 (dd, 1H, *J* = 1.8 and 7.6), 7.47 (m, 3H), 7.62 (m, 1H), 7.81 (m, 2H), 7.93 (dd, 1H, *J* = 0.9 and 7.9). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 92.3, 127.9, 128.6, 128.8 (2C), 130.6 (2C), 131.3, 133.9, 135.7, 139.8, 144.4, 197.4.



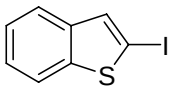
4-Bromo-2-iodoanisole (2g),[6] prepared using the general procedure **A**, 97% yield, yellow solid (mp 66-68 °C). ^{1}H NMR (CD_3COCD_3, 200 MHz): δ 3.87 (s, 3H), 6.90 (d, 1H, *J* = 8.8), 7.47 (dd, 1H, *J* = 2.4 and 8.8), 7.88 (d, 1H, *J* = 2.4). ^{13}C NMR (CD_3COCD_3, 50 MHz): δ 56.9, 87.1, 113.3, 113.4, 133.0, 141.4, 158.4.



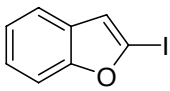
2,4-Diiodoanisole (2h),[7] prepared using the general procedure **A**, 83% yield, red solid (mp < 50 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.80 (s, 3H), 6.51 (d, 1H, *J* = 8.6), 7.51 (dd, 1H, *J* = 2.1 and 8.6), 8.00 (d, 1H, *J* = 2.1). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 56.4, 83.4, 87.5, 112.6, 138.0, 146.2, 157.8.



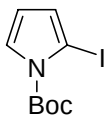
Methyl 4-bromo-2-iodobenzoate (2i), prepared using the general procedure **A**, 60% yield, orange solid (mp < 50 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.89 (s, 3H), 7.49 (dd, 1H, *J* = 1.9 and 8.4), 7.65 (d, 1H, *J* = 8.4), 8.12 (d, 1H, *J* = 1.9). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 52.7, 95.0, 126.7, 131.2, 132.0, 133.4, 143.5, 166.0. HRMS: calcd for $C_8H_6BrIO_2$: 339.8596, found: 339.8594.



2-Iodobenzo[*b*]thiophene (2j),[8] prepared using the general procedure **A**, 97% yield, yellow solid (mp 64 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.20-7.26 (m, 2H), 7.48 (s, 1H), 7.63-7.73 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 79.3, 121.3, 122.4, 124.5, 124.6, 133.9, 140.9, 144.5.



2-Iodobenzo[*b*]furan (2k),[9] prepared using the general procedure **A**, 84% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.98 (s, 1H), 7.21-7.29 (m, 2H), 7.47-7.57 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 96.0, 111.0, 117.4, 119.8, 123.3, 124.4, 129.3, 158.3.



***N*-Boc-2-iodopyrrole (2l)**,[10] prepared using the general procedure **A**, 68% yield, pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.62 (s, 9H), 6.17 (t, 1H, *J* = 3.4), 6.53 (dd, 1H, *J* = 3.4 and 1.8), 7.39 (dd, 1H, *J* = 3.6 and 2.0). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 27.9 (3C), 63.1, 84.6, 113.5, 124.8, 125.4, 147.9.

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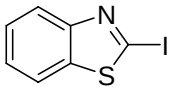
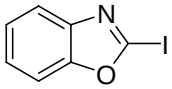
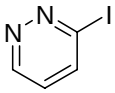
[6] Muraki, T.; Togo, H.; Yokoyama, M. *J. Org. Chem.* **1999**, *64*, 2883-2889.
[7] Hubig, S. M.; Jung, W.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 6233-6244.
[8] Vallgårda, J.; Appelberg, U.; Arvidsson, L.-E.; Hjorth, S.; Svensson, B. E.; Hacksell, U. *J. Med. Chem.* **1996**, *39*, 1485-1493.
[9] Mongin, F.; Bucher, A.; Bazureau, J. P.; Bayh, O.; Awad, H.; Trécourt, F. *Tetrahedron Lett.* **2005**, *46*, 7989-7992.
[10] Chen, W.; Cava, M. P. *Tetrahedron Lett.* **1987**, *28*, 6025-6026.



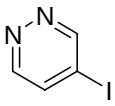
2-Iodobenzothiazole (2m),[11] prepared using the general procedure **A**, 97% yield, yellow solid (mp 80 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.34-7.49 (m, 2H), 7.82-7.87 (m, 1H), 8.00-8.06 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 105.8, 120.6, 122.7, 125.8, 126.5, 139.3, 154.4.



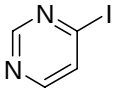
2-Iodobenzoxazole (2n),[12] prepared using the general procedure **A**, 63% yield, yellow solid (mp 90 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.21-7.26 (m, 2H), 7.44-7.50 (m, 1H), 7.60-7.65 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 109.2, 109.9, 118.9, 124.4, 125.1, 142.3, 153.7.



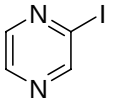
3-Iodopyridazine (2o),[13] prepared using the general procedure **A**, 55% yield, pale brown solid (mp 139 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.17 (dd, 1H, J = 4.8 and 8.6), 7.89 (dd, 1H, J = 1.5 and 8.6), 9.15 (dd, 1H, J = 1.5 and 4.8). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 125.8, 127.3, 137.3, 150.5.



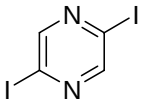
4-Iodopyridazine (2'o),[13] prepared using the general procedure **A**, 41% yield, pale brown solid (mp 117 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.89 (dd, 1H, J = 2.1 and 5.3), 8.82 (d, 1H, J = 5.3), 9.44 (br s, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 101.0, 135.5, 151.1, 158.4.



4-Iodopyrimidine (2p),[13] prepared using the general procedure **A**, 71% yield, yellow solid (mp 112 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.79 (dd, 1H, J = 1.3 and 5.3), 8.25 (d, 1H, J = 5.3), 8.89 (d, 1H, J = 1.3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 129.6, 133.2, 156.2, 158.8.

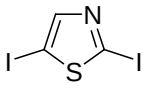


Iodopyrazine (2q),[13] prepared using the general procedure **A**, 59% yield, yellow solid (mp 90 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.38 (dd, 1H, J = 1.3 and 2.8), 8.50 (d, 1H, J = 2.8), 8.86 (d, 1H, J = 1.3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 118.5, 142.9, 145.8, 153.1.

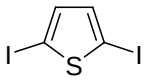


2,5-Diiodopyrazine (3q), prepared using the general procedure **B**, 58% yield, yellow solid (mp 141 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.63 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 116.6 (2C), 154.1 (2C). HRMS: calcd for $C_4H_2I_2N_2$: 331.8307, found: 331.8297. Anal. Calcd for $C_4H_2I_2N_2$: C, 14.48; H, 0.61; N, 8.44. Found: C, 14.31; H, 0.69; N, 8.48.

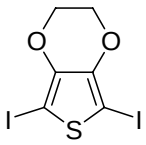
[11] Van den Hoven, B. G.; Alper, H. *J. Am. Chem. Soc.* **2001**, *123*, 1017-1022.
[12] Bayh, O.; Awad, H.; Mongin, F.; Hoarau, C.; Bischoff, L.; Trécourt, F.; Quéguiner, G.; Marsais, F.; Blanco, F.; Abarca, B.; Ballesteros, R. *J. Org. Chem.* **2005**, *70*, 5190-5196.
[13] Seggio, A.; Chevallier, F.; Vaultier, M.; Mongin, F. *J. Org. Chem.* **2007**, *72*, 6602-6605.



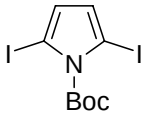
2,5-Diiodothiazole (3r),[14] prepared using the general procedure **B**, 50% yield, yellow solid (mp 110 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 74.8, 104.1, 152.8.



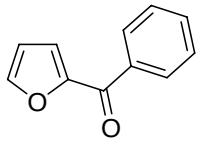
2,5-Diiodothiophene (3s),[15] prepared using the general procedure **B**, 74% yield, yellow solid (mp < 50 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.94 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 76.3 (2C), 138.9 (2C).



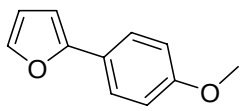
2,5-Diiodo-3,4-ethylenedioxythiophene (3t),[16] prepared using the general procedure **B**, 81% yield, yellow solid (mp 183 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.26 (s, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 51.9 (2C), 65.3 (2C), 143.9 (2C).



***N*-Boc-2,5-diiodopyrrole (3l)**, prepared using the general procedure **B**, 60% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.67 (s, 9H), 6.46 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.1 (3C), 64.8, 86.8 (2C), 126.6 (2C), 148.1. HRMS: calcd for $C_9H_{11}I_2NO_2$: 418.8879, found: 418.8879.



Furan-2-yl-phenylmethanone (4u),[17] prepared using the general procedure **C**, 76% yield, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.59 (dd, 1H, *J* = 1.7 and 3.6), 7.23 (dd, 1H, *J* = 0.7 and 3.6), 7.45-7.64 (m, 3H), 7.7 (dd, 1H, *J* = 0.7 and 1.7), 7.97 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 112.3, 120.7, 128.5 (2C), 129.4 (2C), 132.7, 137.4, 147.2, 152.4, 182.7.

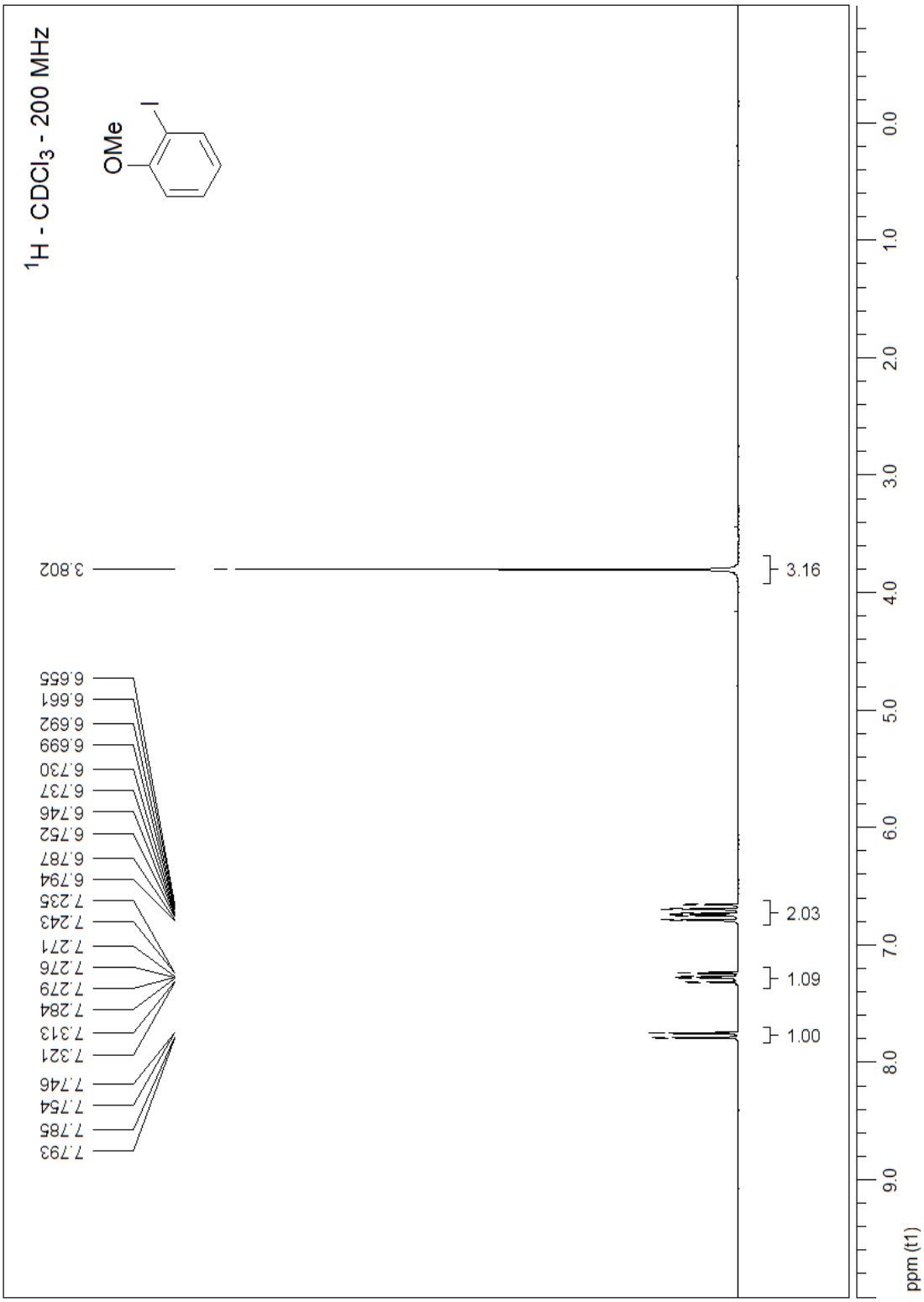


2-(4-Methoxyphenyl)furan (5u),[18] prepared using the general procedure **D**, 86% yield, yellow solid (mp 52-54 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.84 (s, 3H), 6.47 (dd, 1H, *J* = 1.8 and 3.5), 6.54 (d, 1H, *J* = 3.5), 6.95 (d, 2H, *J* = 8.9), 7.46 (d, 1H, *J* = 1.8), 7.64 (d, 2H, *J* = 8.9). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 55.3, 103.5, 111.6, 114.2 (2C), 124.1, 125.3 (2C), 141.5, 154.1, 159.1.

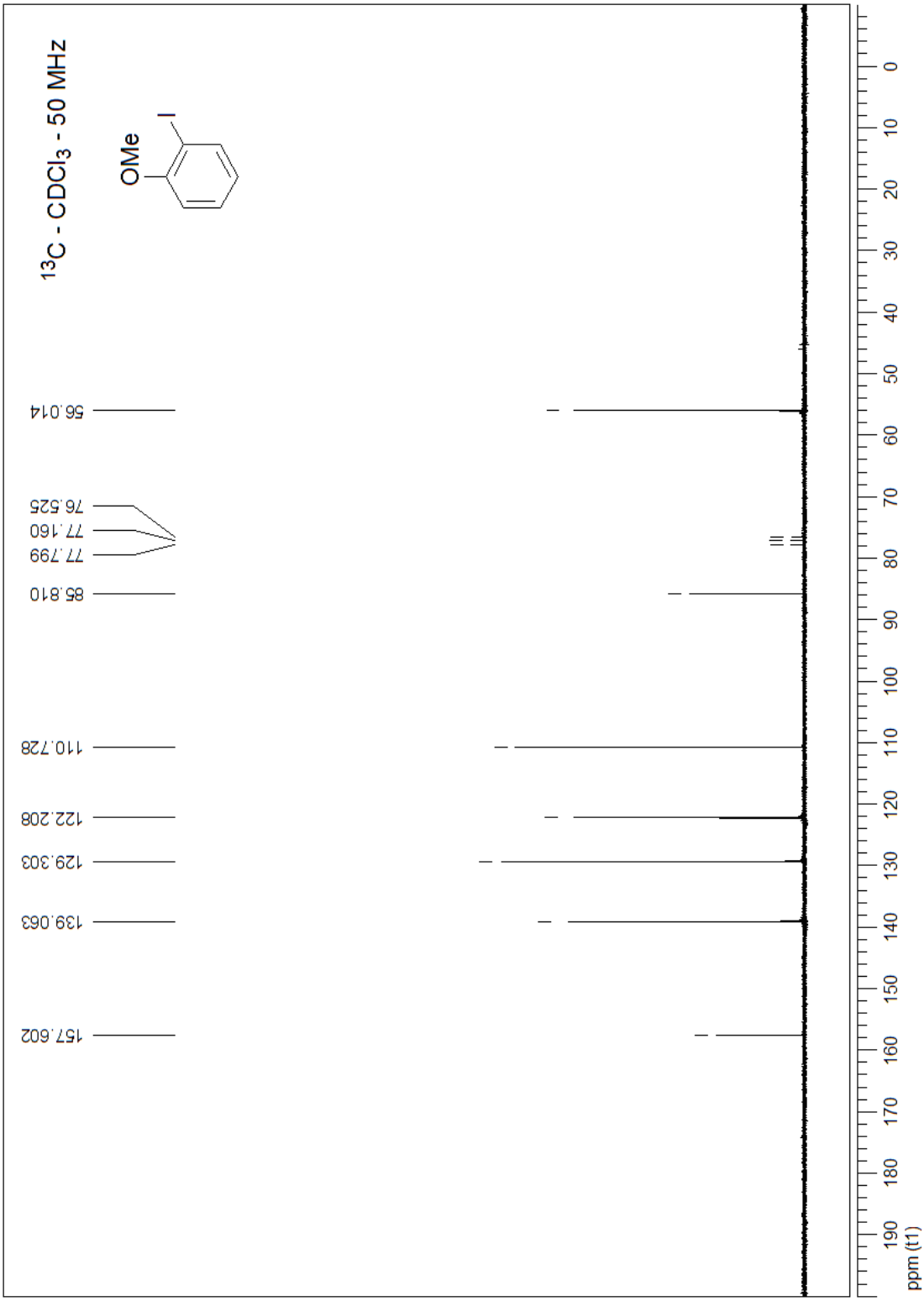
[14] Dondoni, A.; Mastellari, A. R.; Medici, A.; Negrini, E.; Pedrini, P. *Synthesis* **1986**, 757-760.
[15] Schanze, K. S.; Silverman, E. E.; Zhao, X. *J. Phys. Chem. B* **2005**, *109*, 18451-18459.
[16] Meng, H.; Perepichka, D. F.; Bendikov, M.; Wudl, F.; Pan, G. Z.; Yu, W.; Dong, W.; Brown, B. *J. Am. Chem. Soc.* **2003**, *125*, 15151-15162.
[17] Crawford, J. J.; Henderson, K. W.; Kerr, W. J. *Org. Lett.* **2006**, *8*, 5073-5076.
[18] Tanis, S. T.; Deaton, M. V.; Dixon, L. A.; Mcwilliams, M. C.; Raggon, J. W., Collins, M. A. *J. Org. Chem.* **1998**, *63*, 6914-6928.

^{1}H and ^{13}C NMR spectra

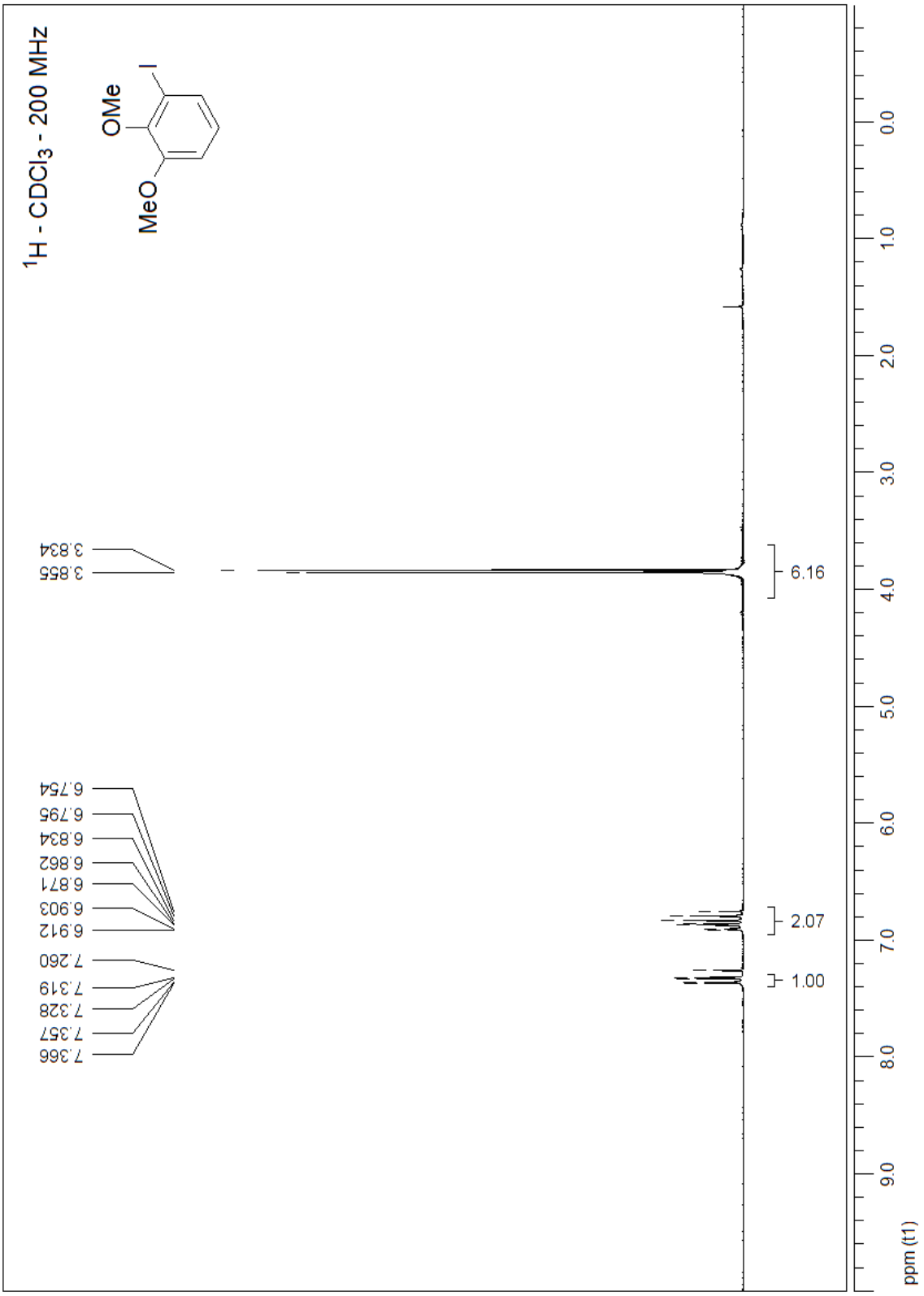
2-Iodoanisole (2a).



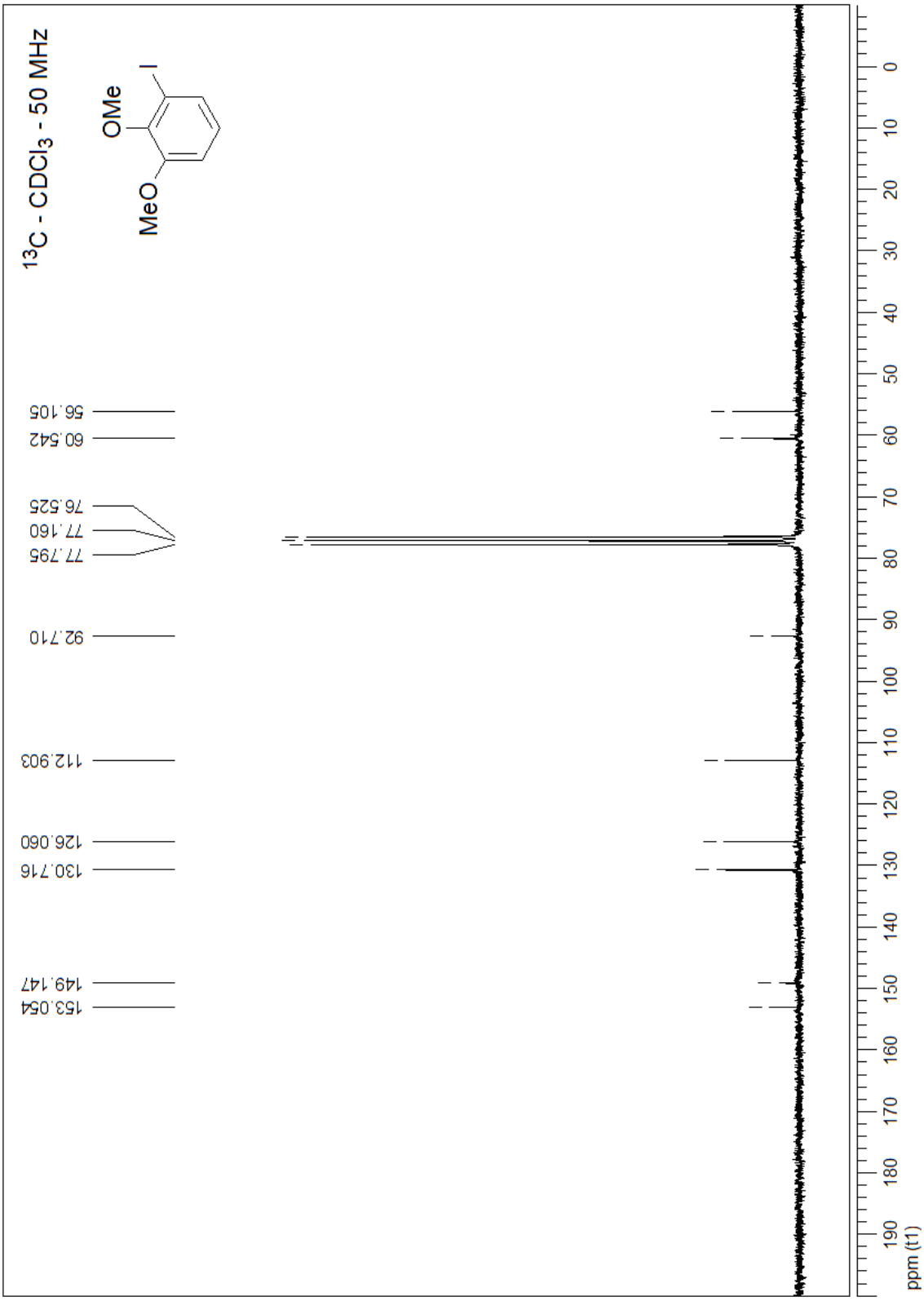
2-Iodoanisole (2a).



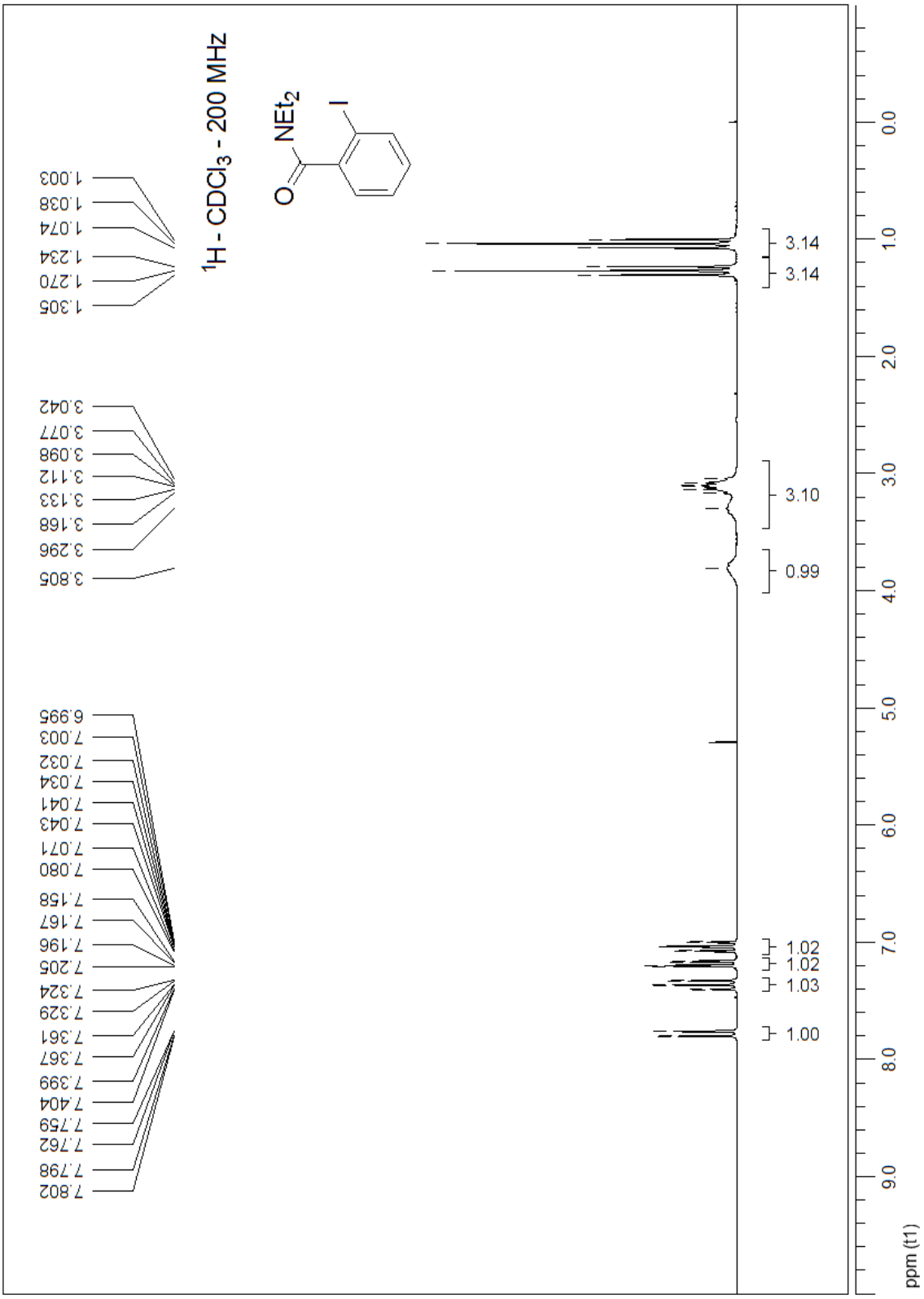
1-Iodo-2,3-dimethoxybenzene (2b).



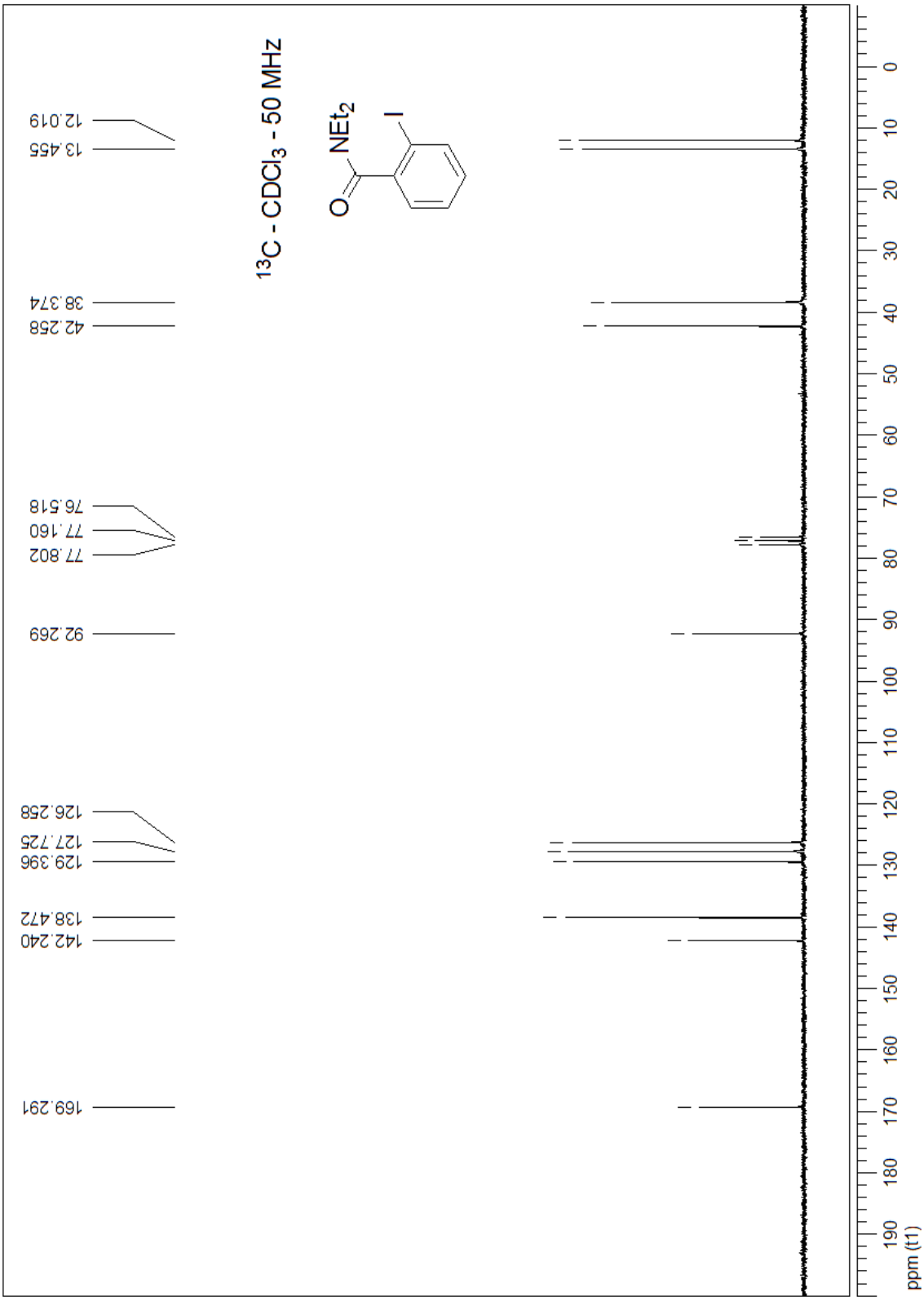
1-Iodo-2,3-dimethoxybenzene (2b).



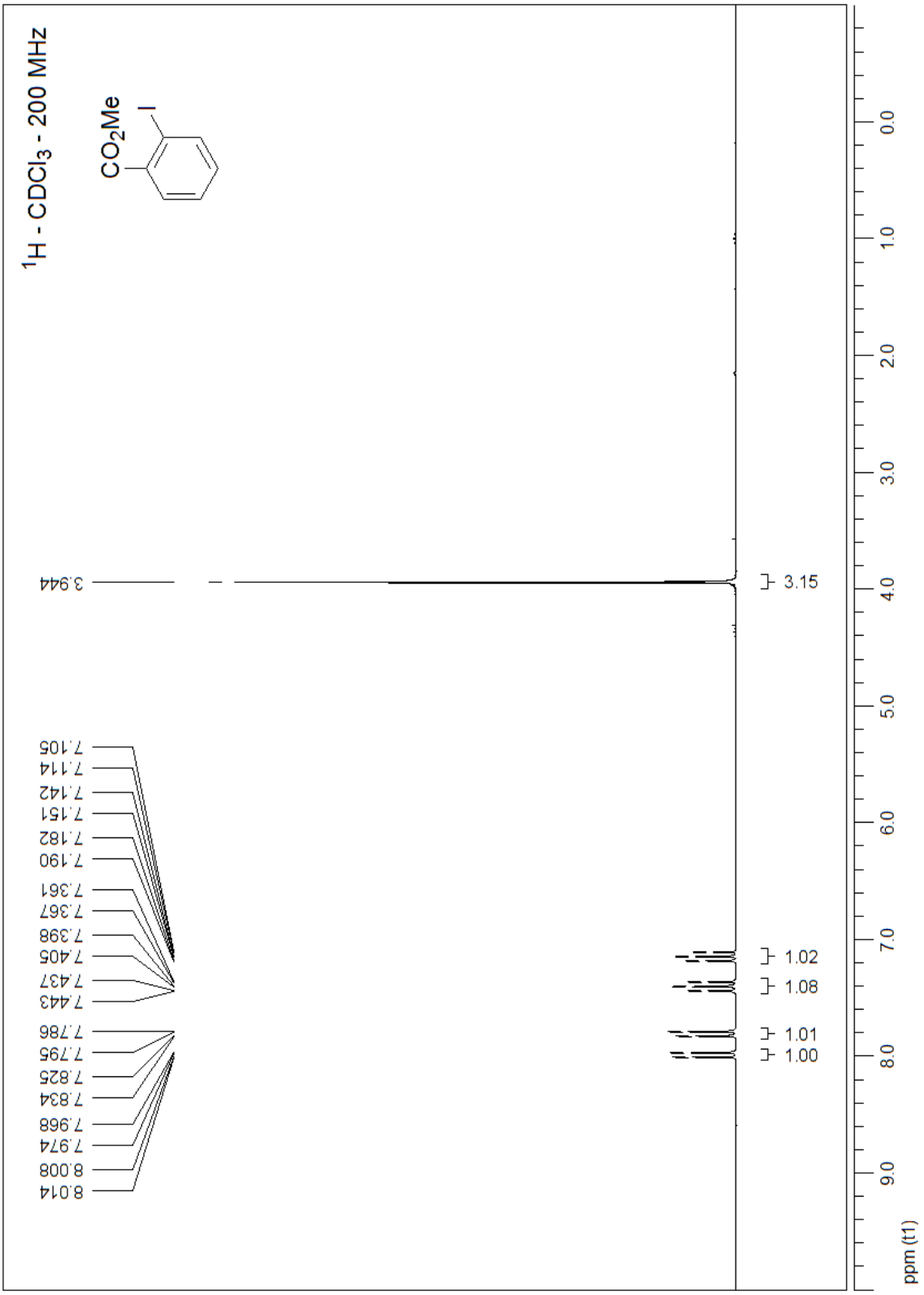
_N_,_N_-Diethyl-2-iodobenzamide (2c).



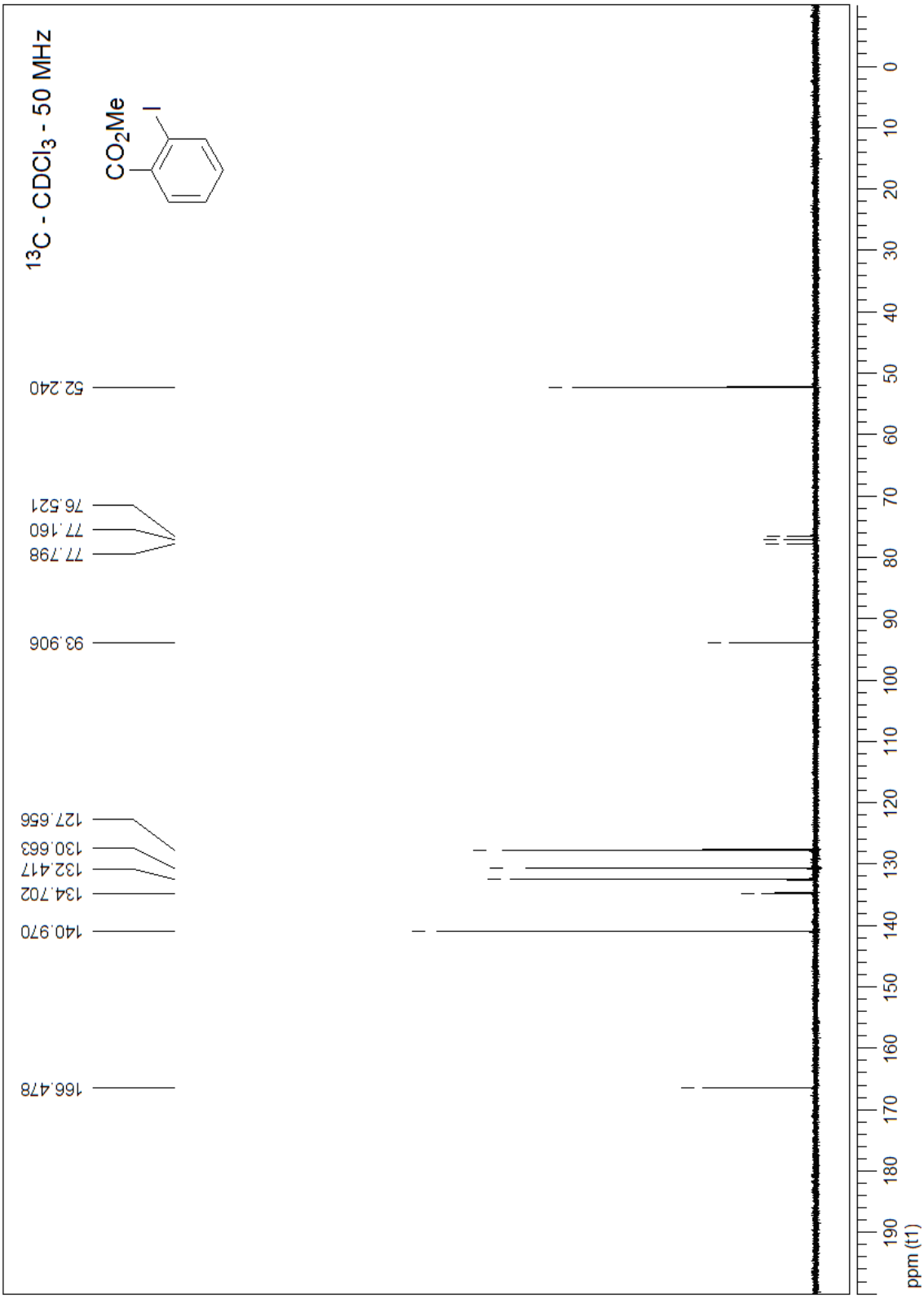
***N*,*N*-Diethyl-2-iodobenzamide (2c).**



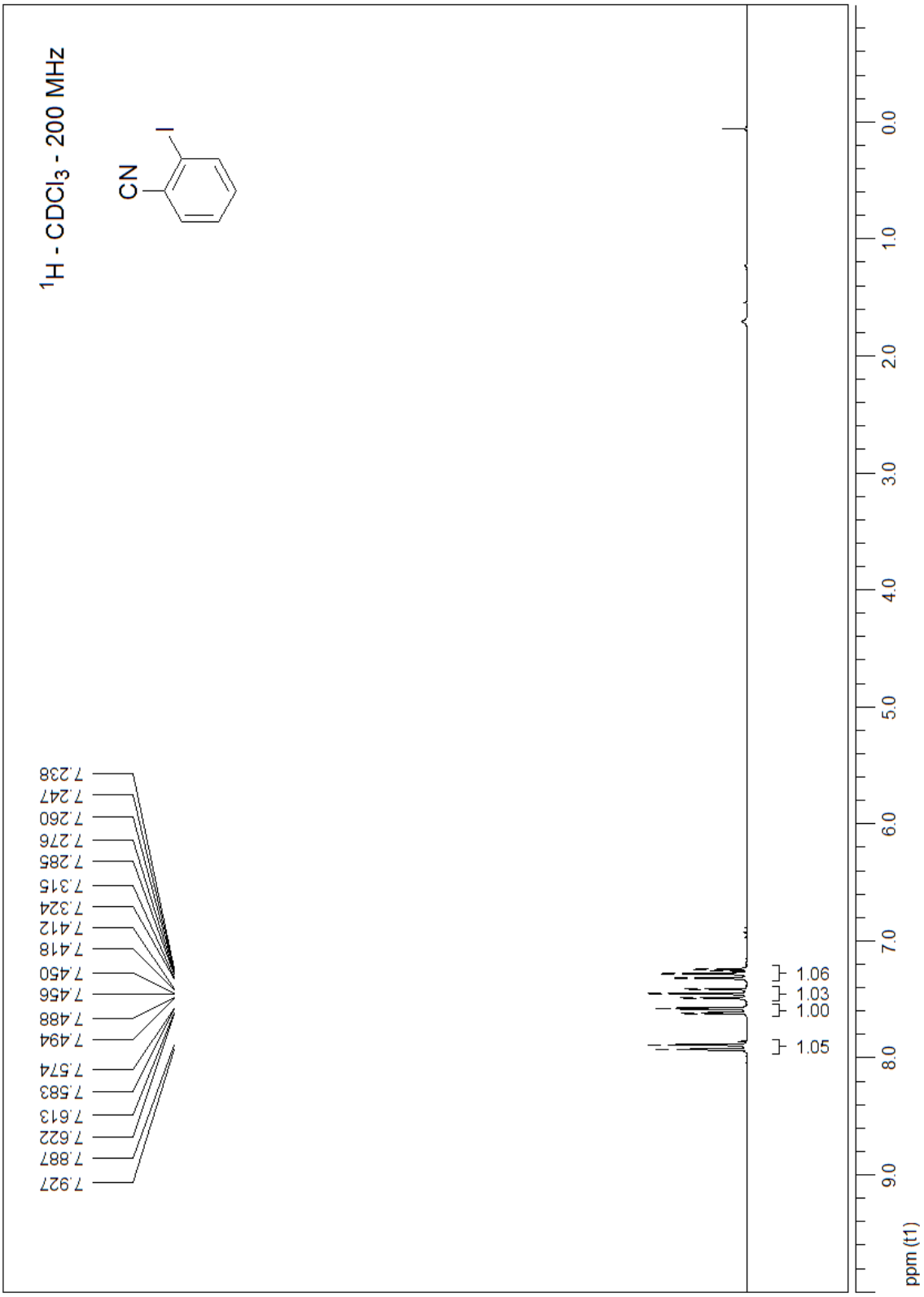
Methyl 2-iodobenzoate (2d).



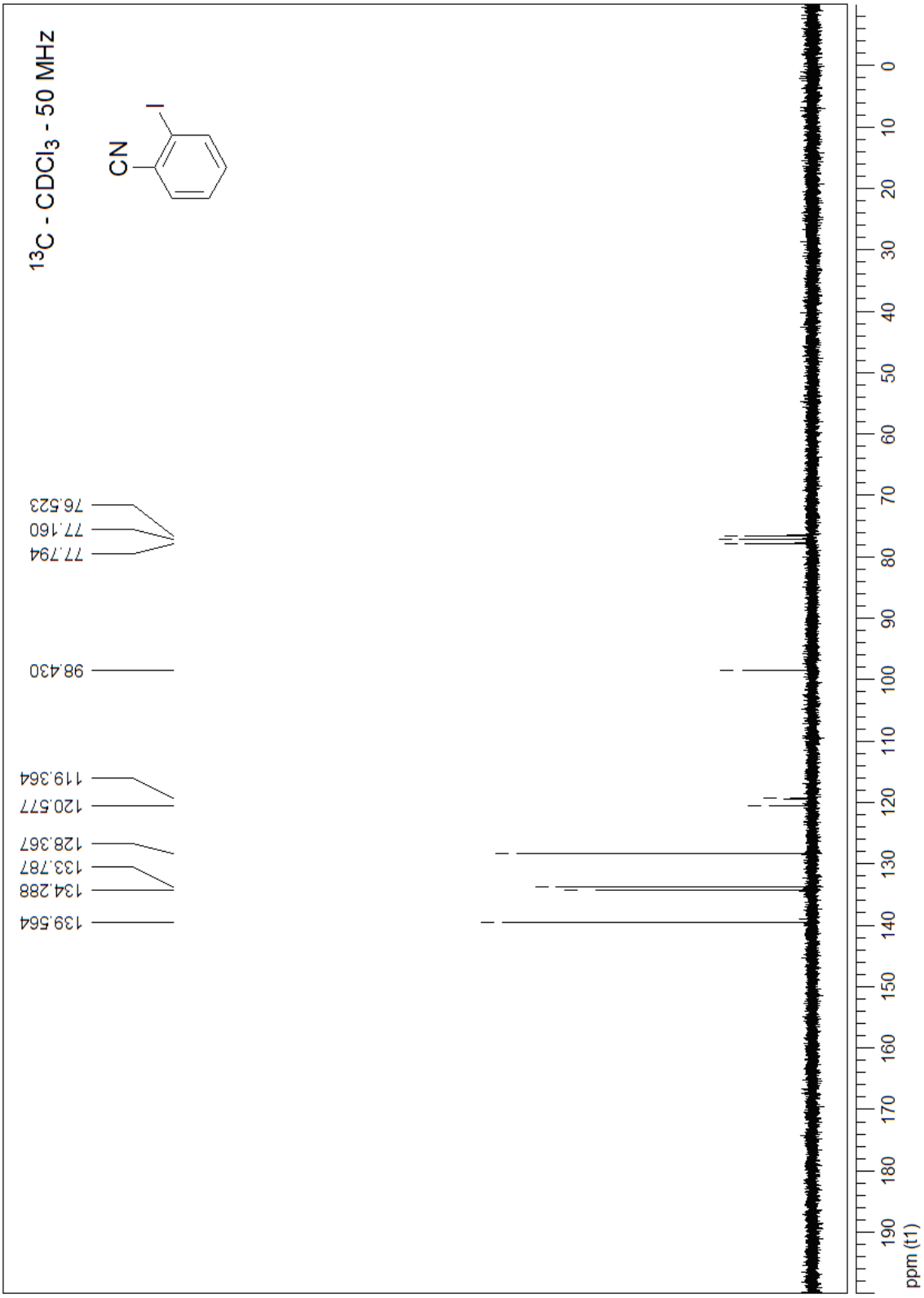
Methyl 2-iodobenzoate (2d).



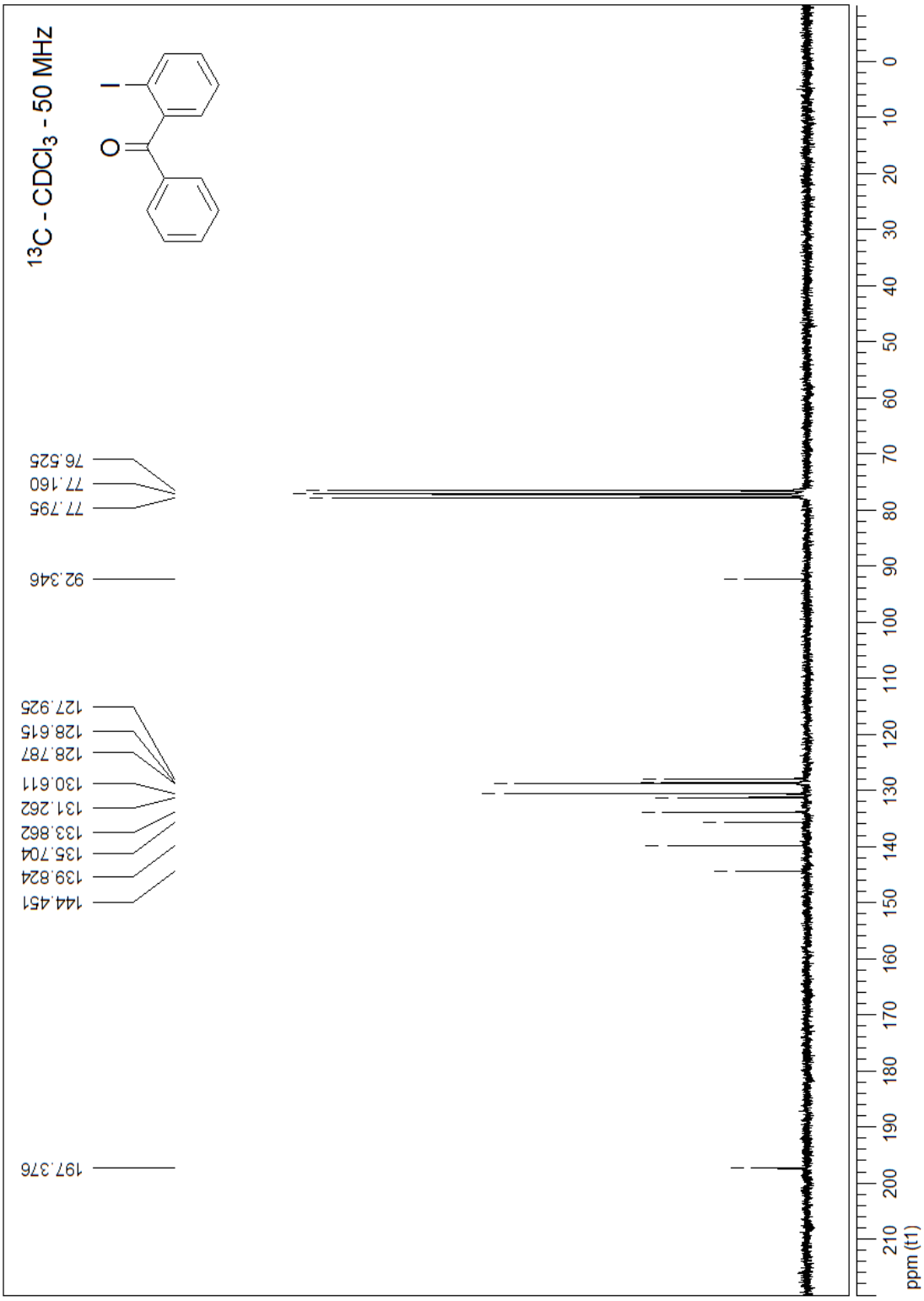
2-Iodobenzonitrile (2e).



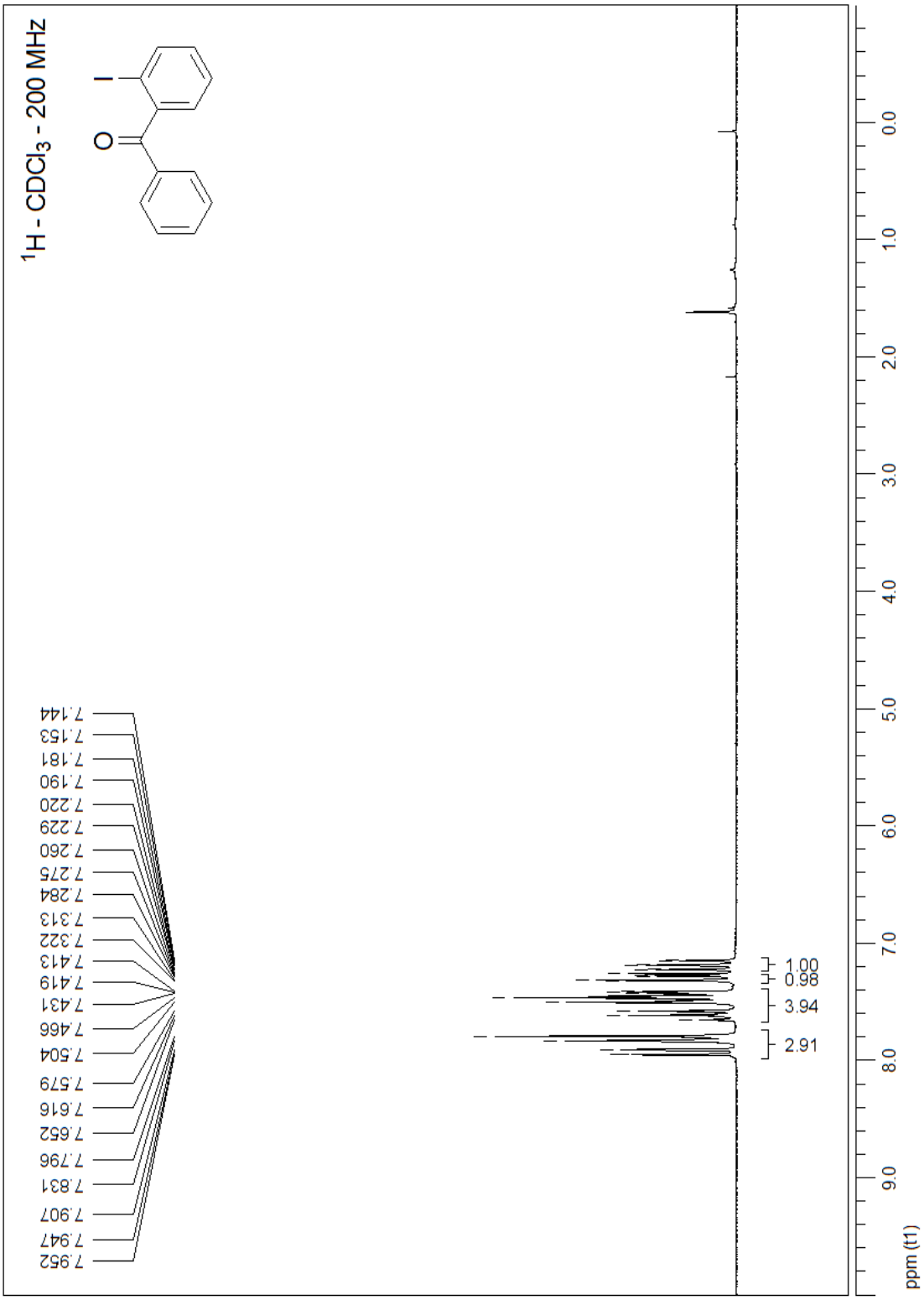
2-Iodobenzonitrile (2e).



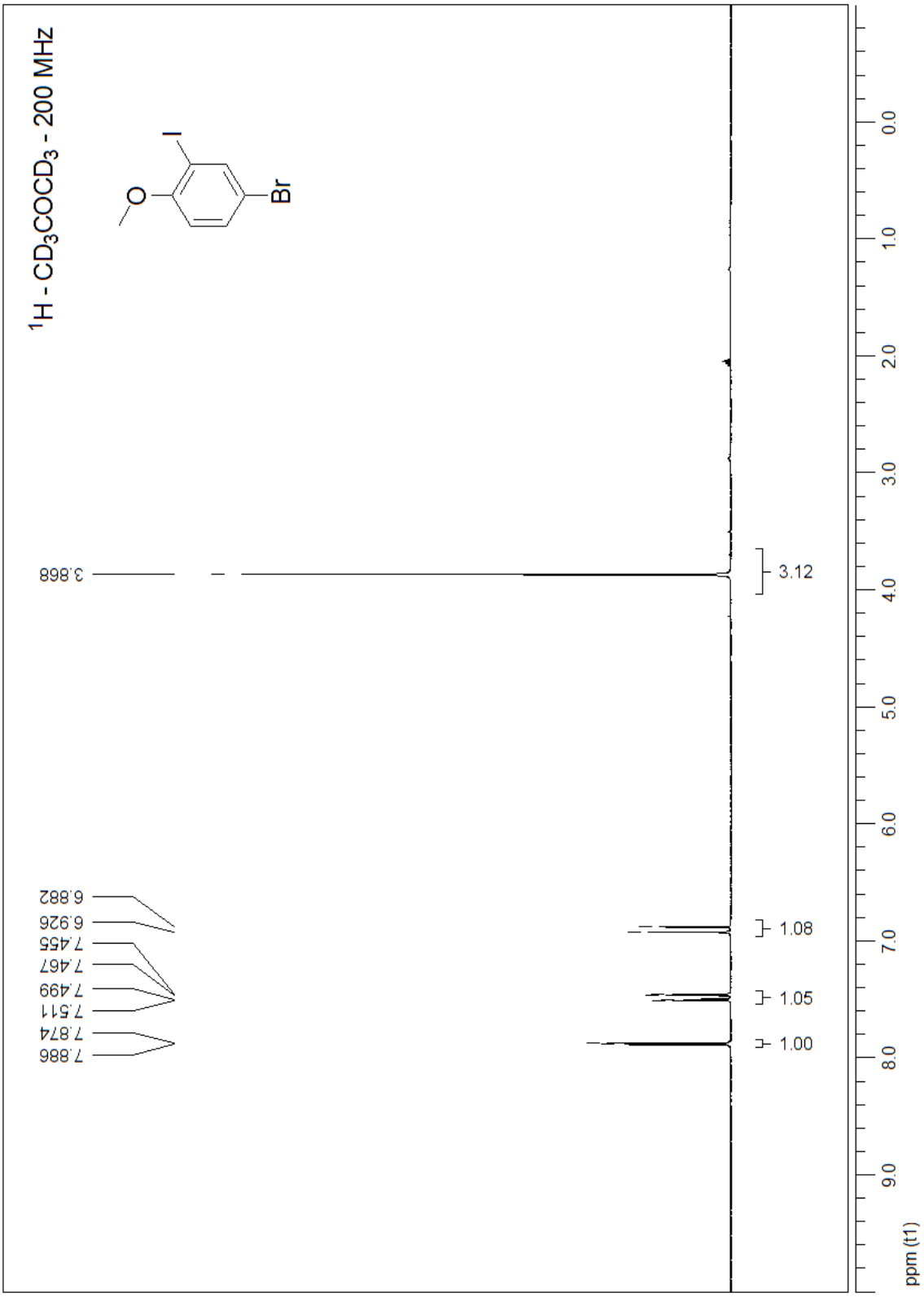
2-Iodobenzophenone (2f).



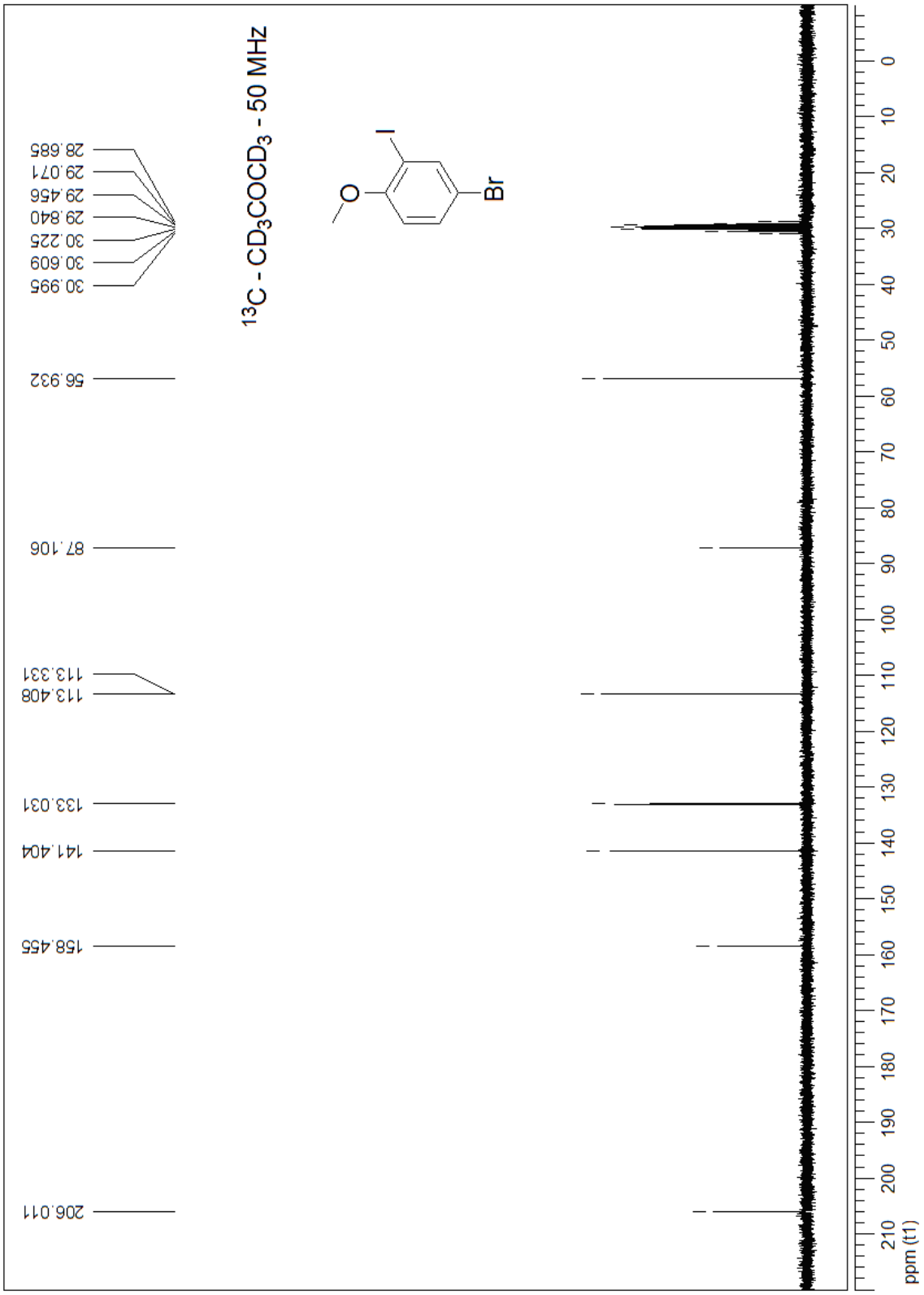
2-Iodobenzophenone (2f).



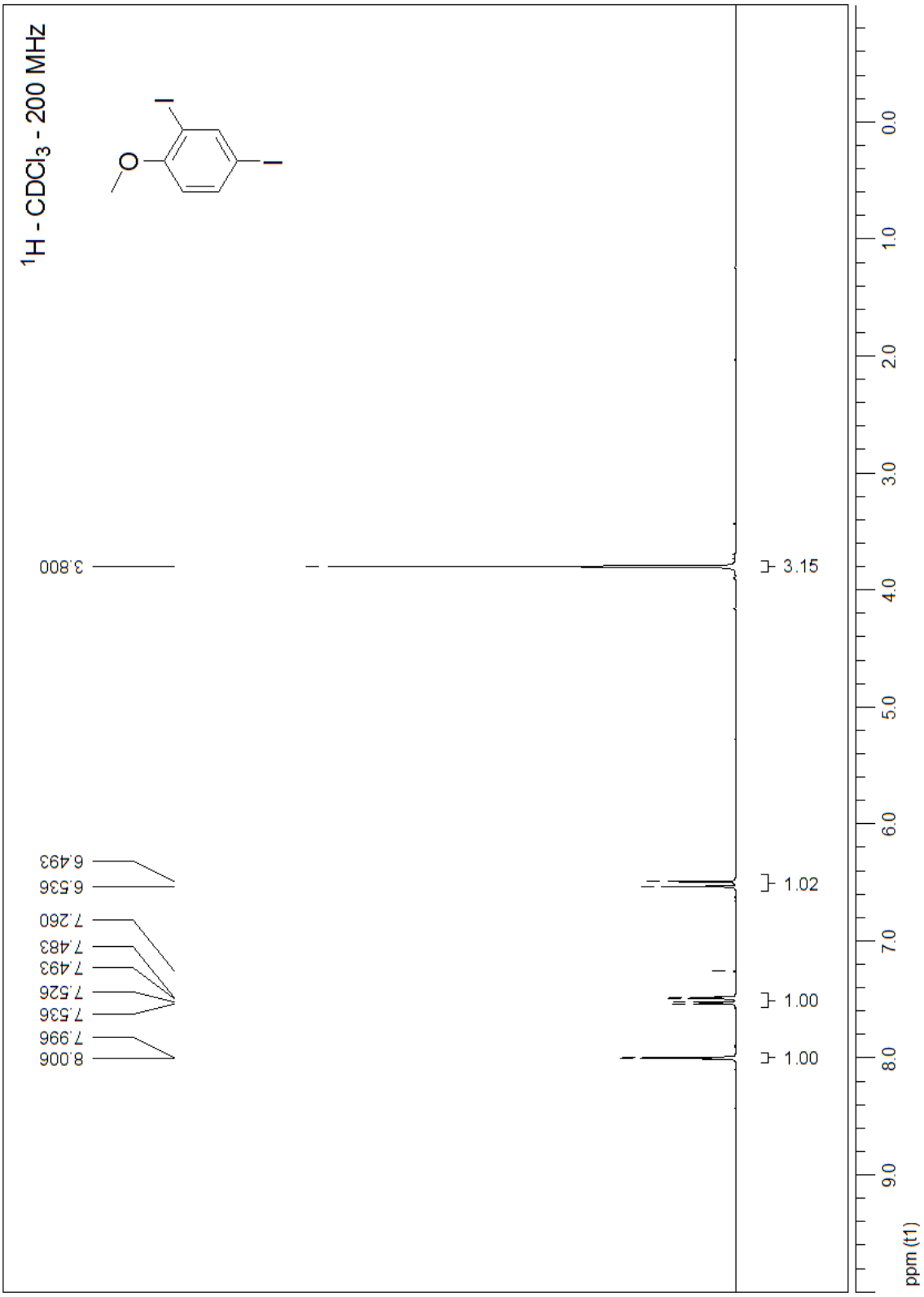
4-Bromo-2-iodoanisole (2g).



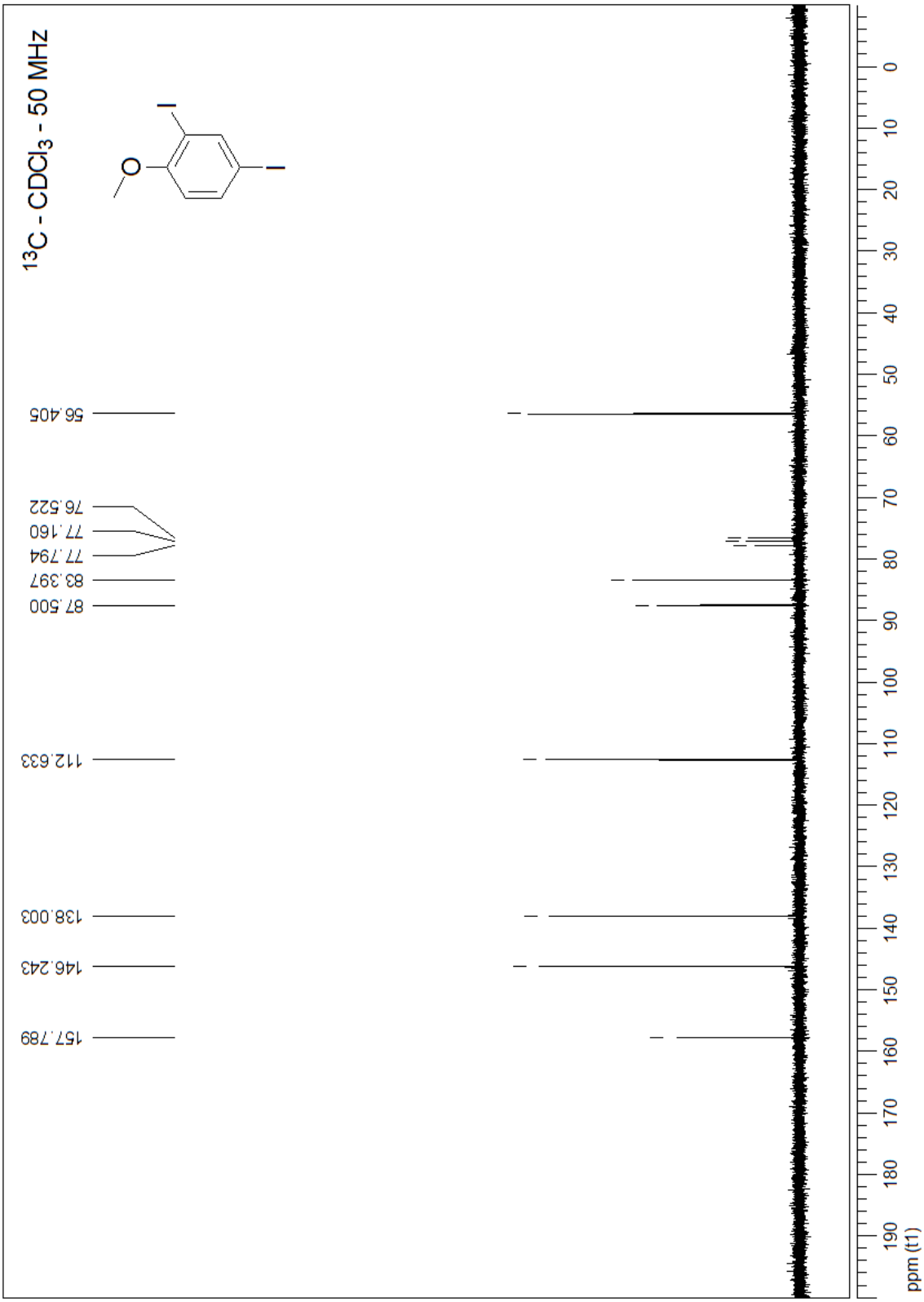
4-Bromo-2-iodoanisole (2g).



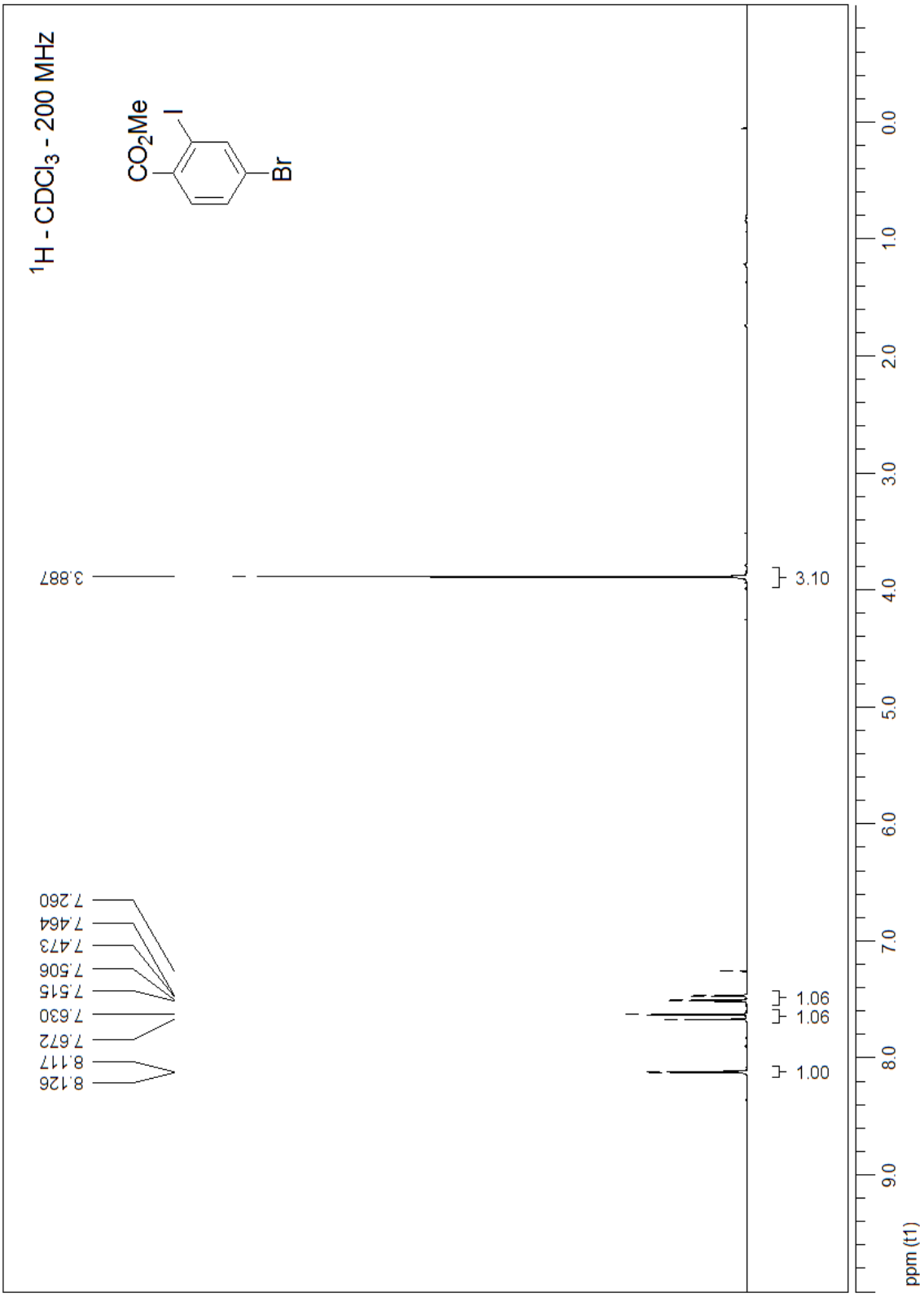
2,4-Diiodoanisole (2h).



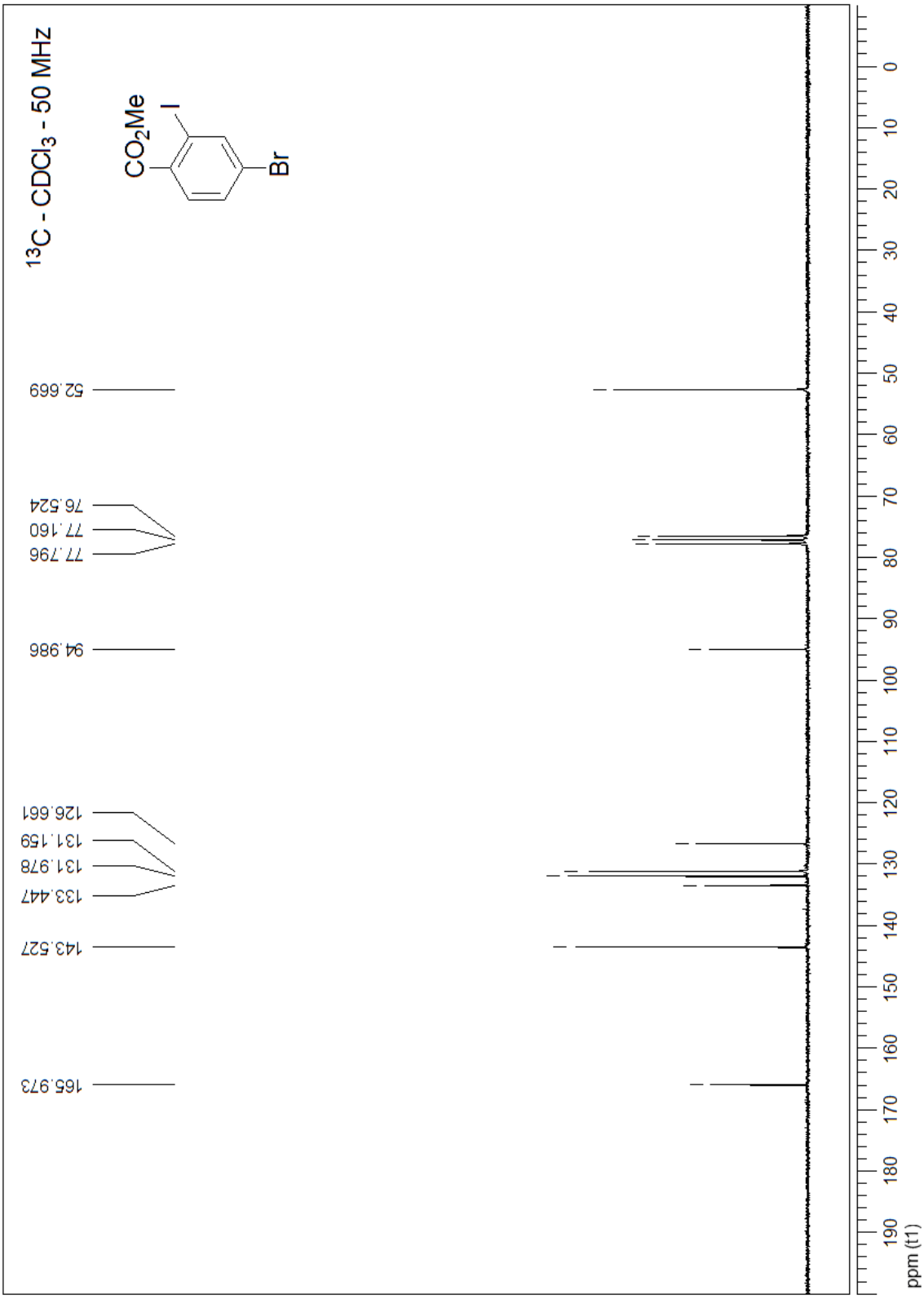
2,4-Diiodoanisole (2h).



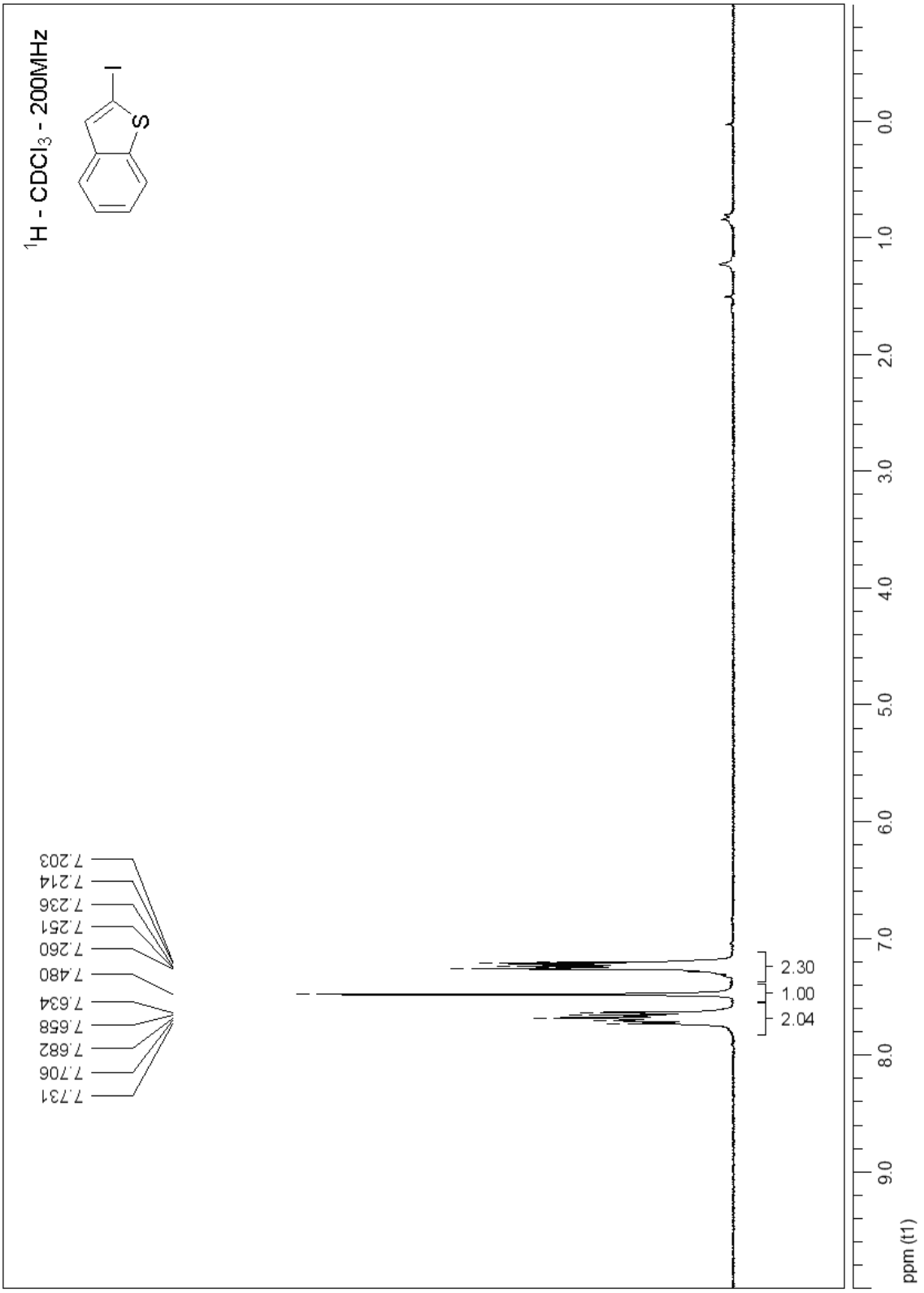
Methyl 4-bromo-2-iodobenzoate (2i).



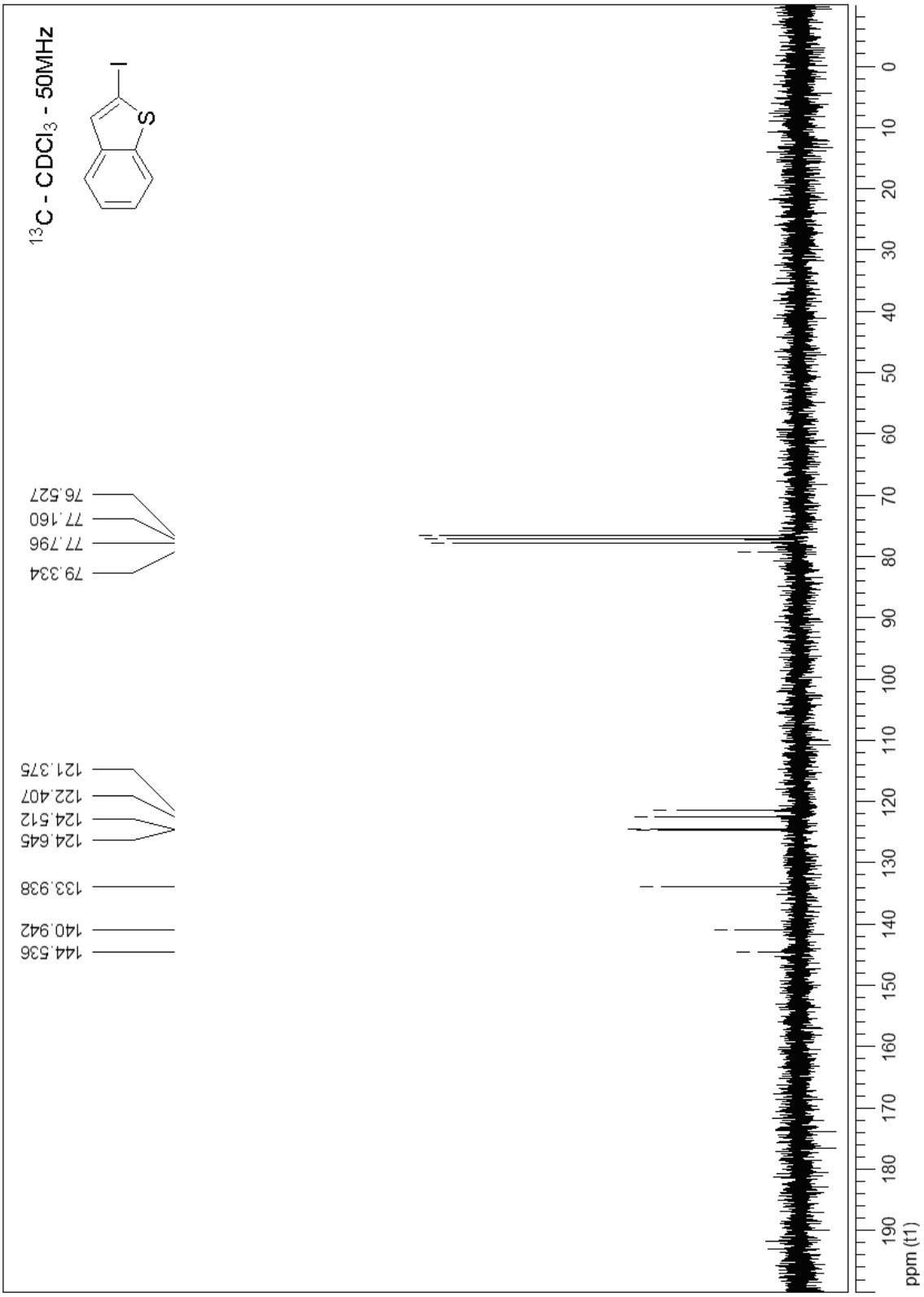
Methyl 4-bromo-2-iodobenzoate (2i).



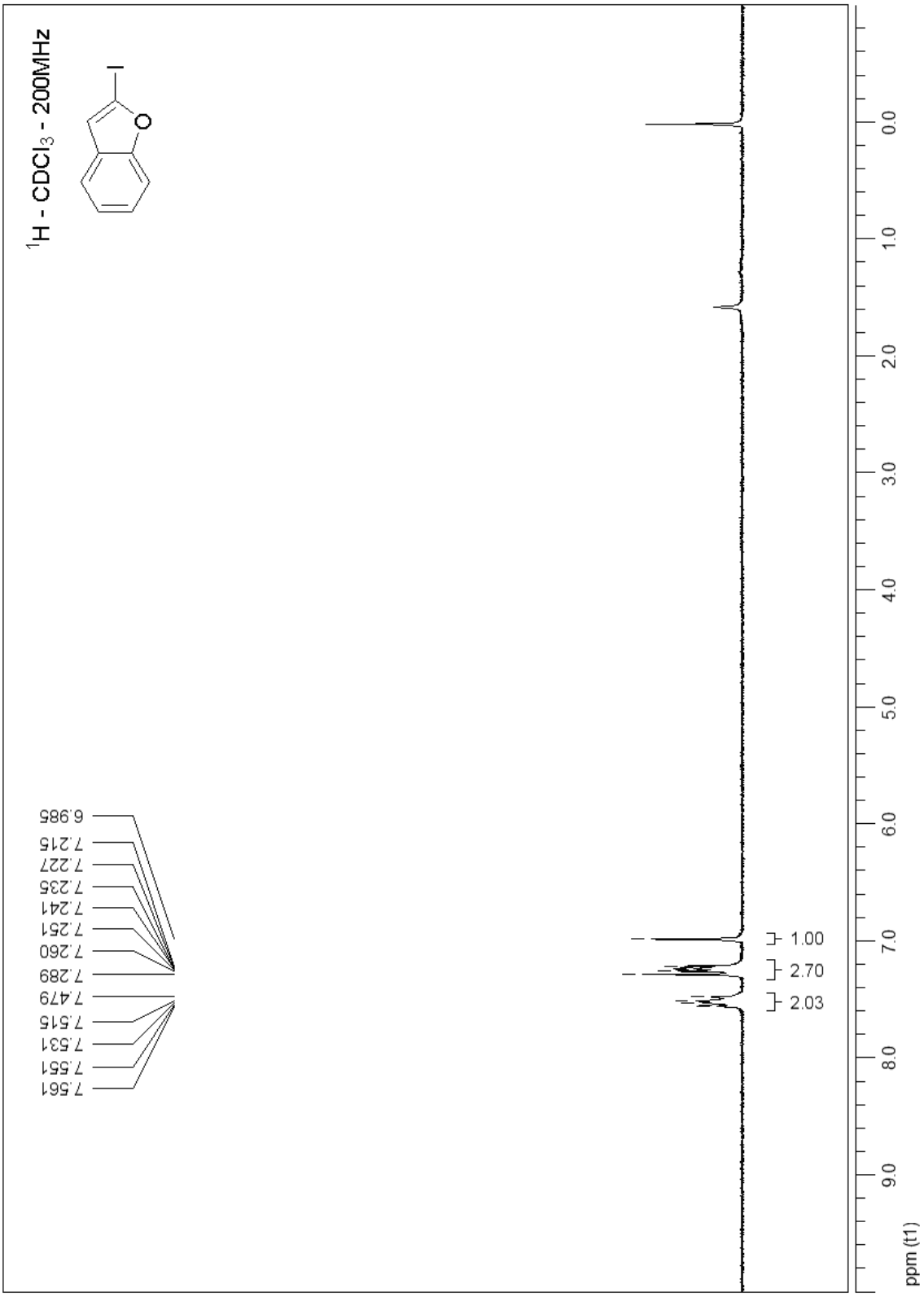
2-Iodobenzo[*b*]thiophene (2j).



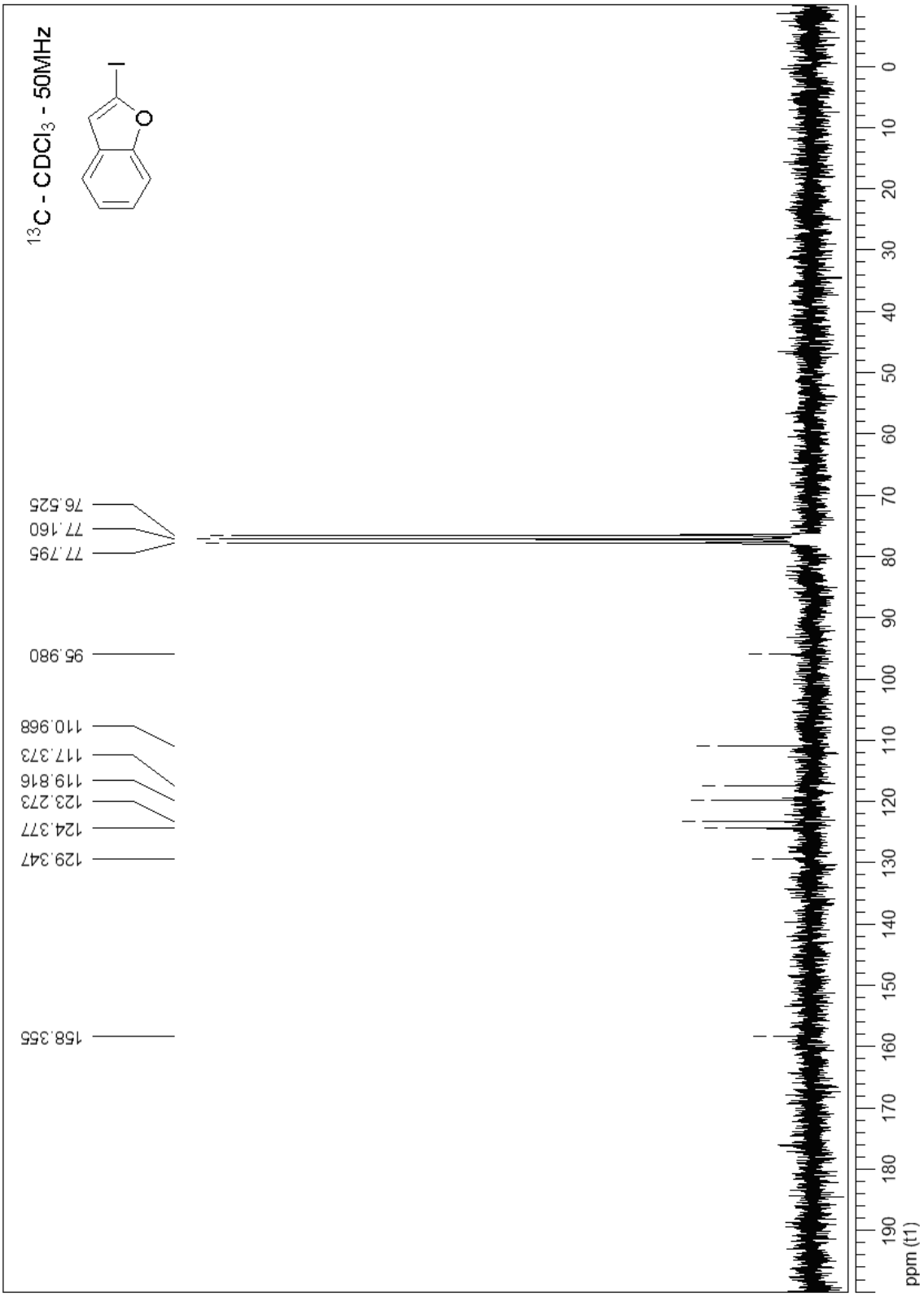
2-Iodobenzo[*b*]thiophene (2j).



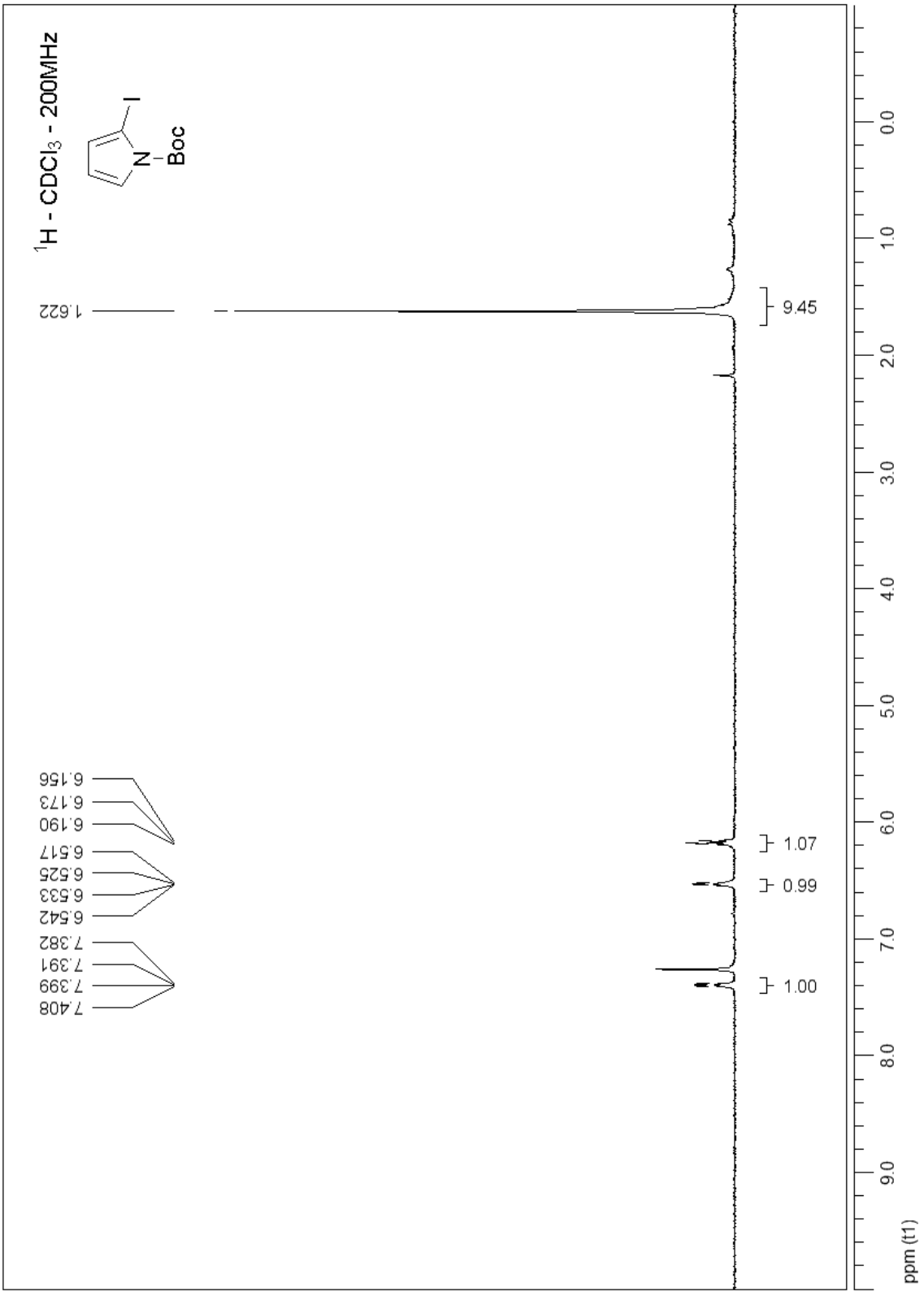
2-Iodobenzo[*b*]furan (2k).



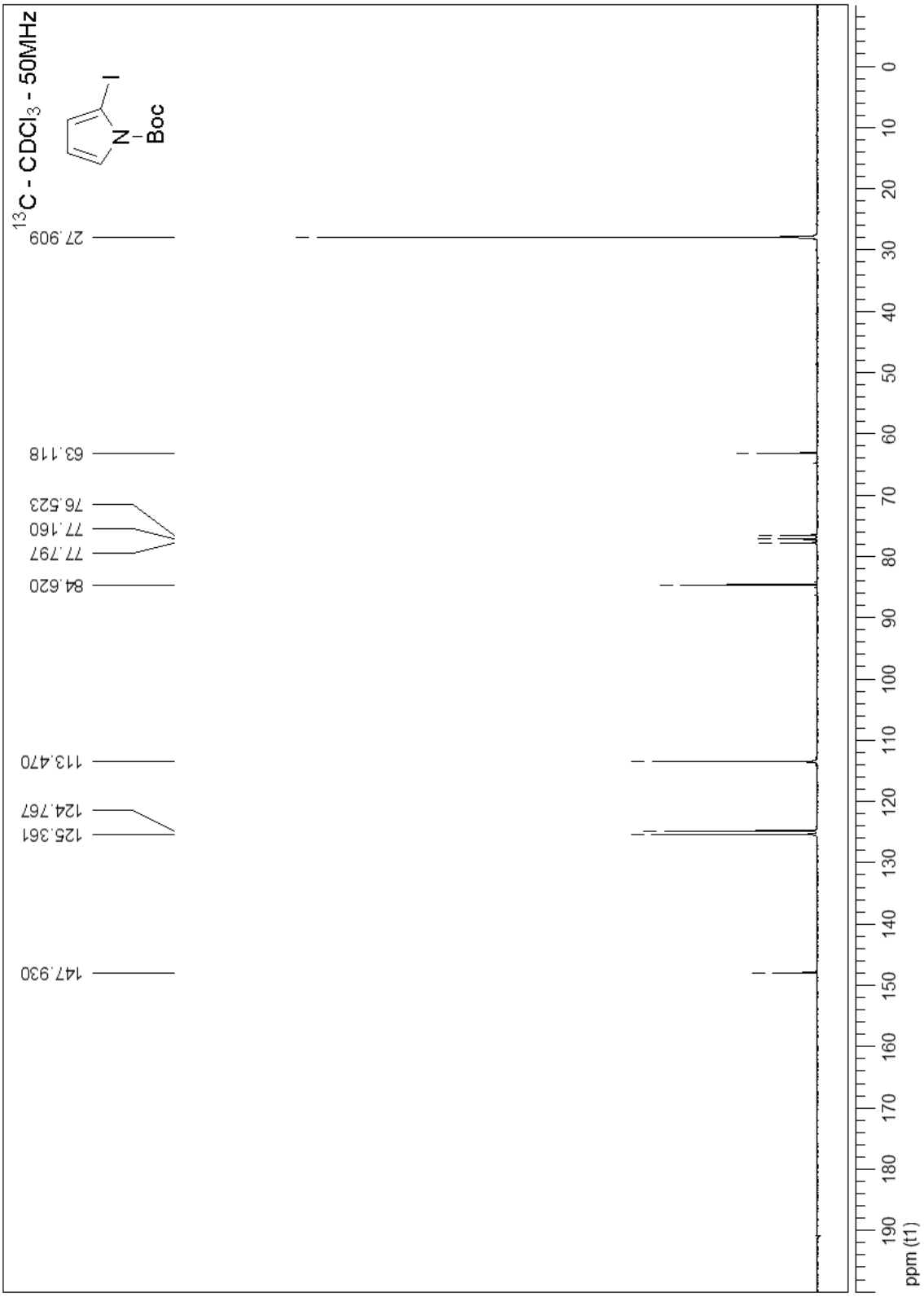
2-Iodobenzo[*b*]furan (2k).



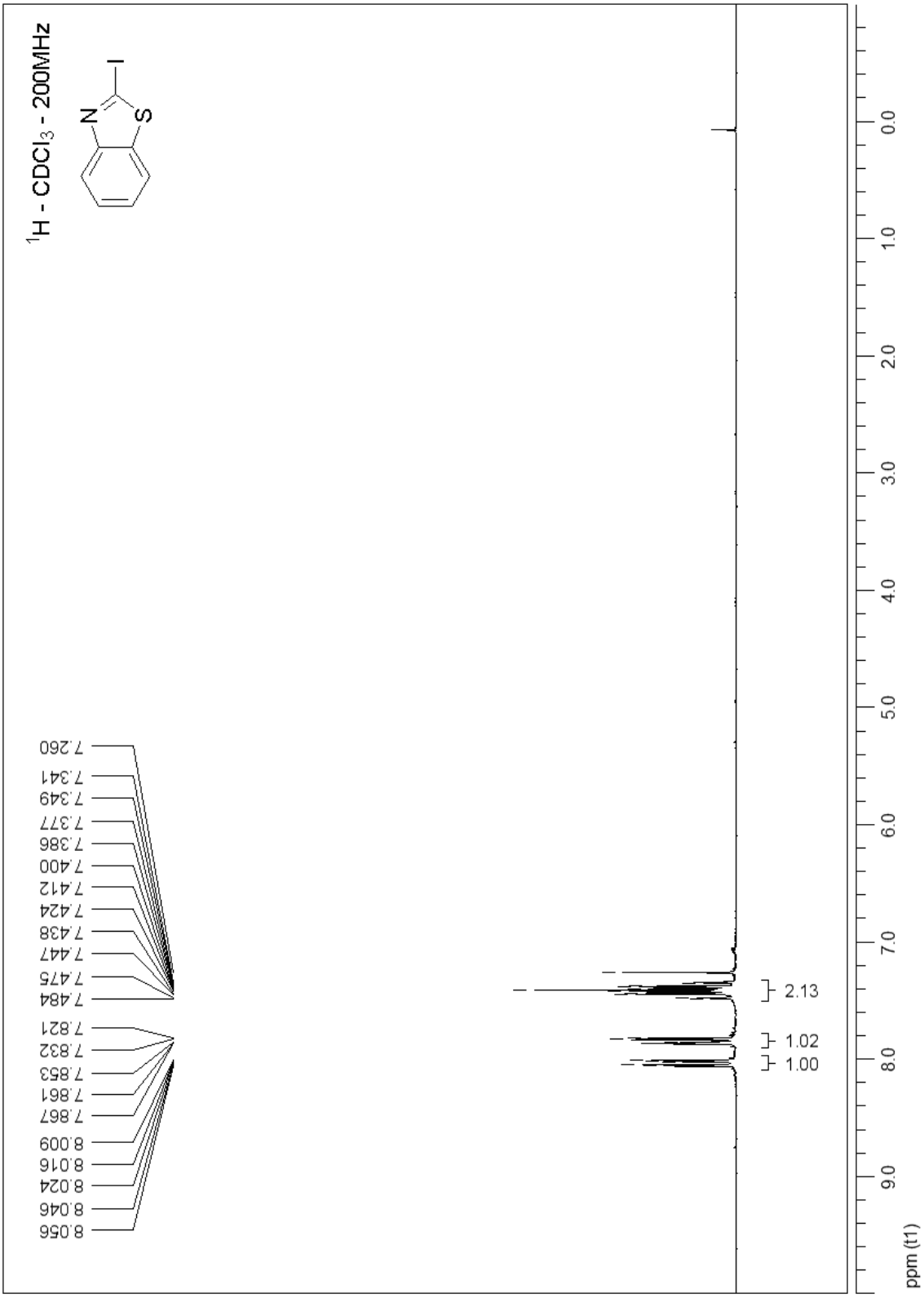
_N_-Boc-2-iodopyrrole (2l).



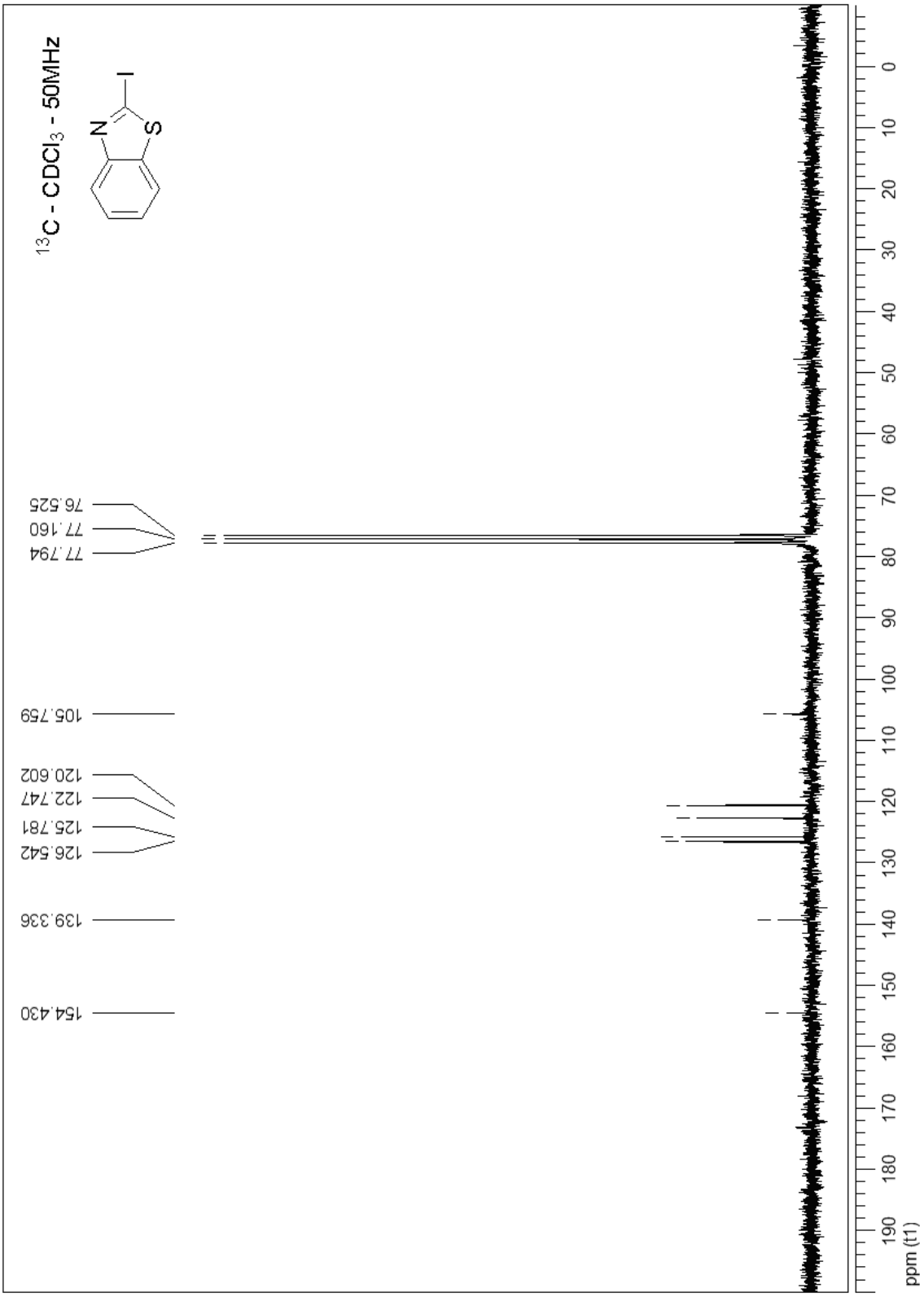
***N*-Boc-2-iodopyrrole (2l).**



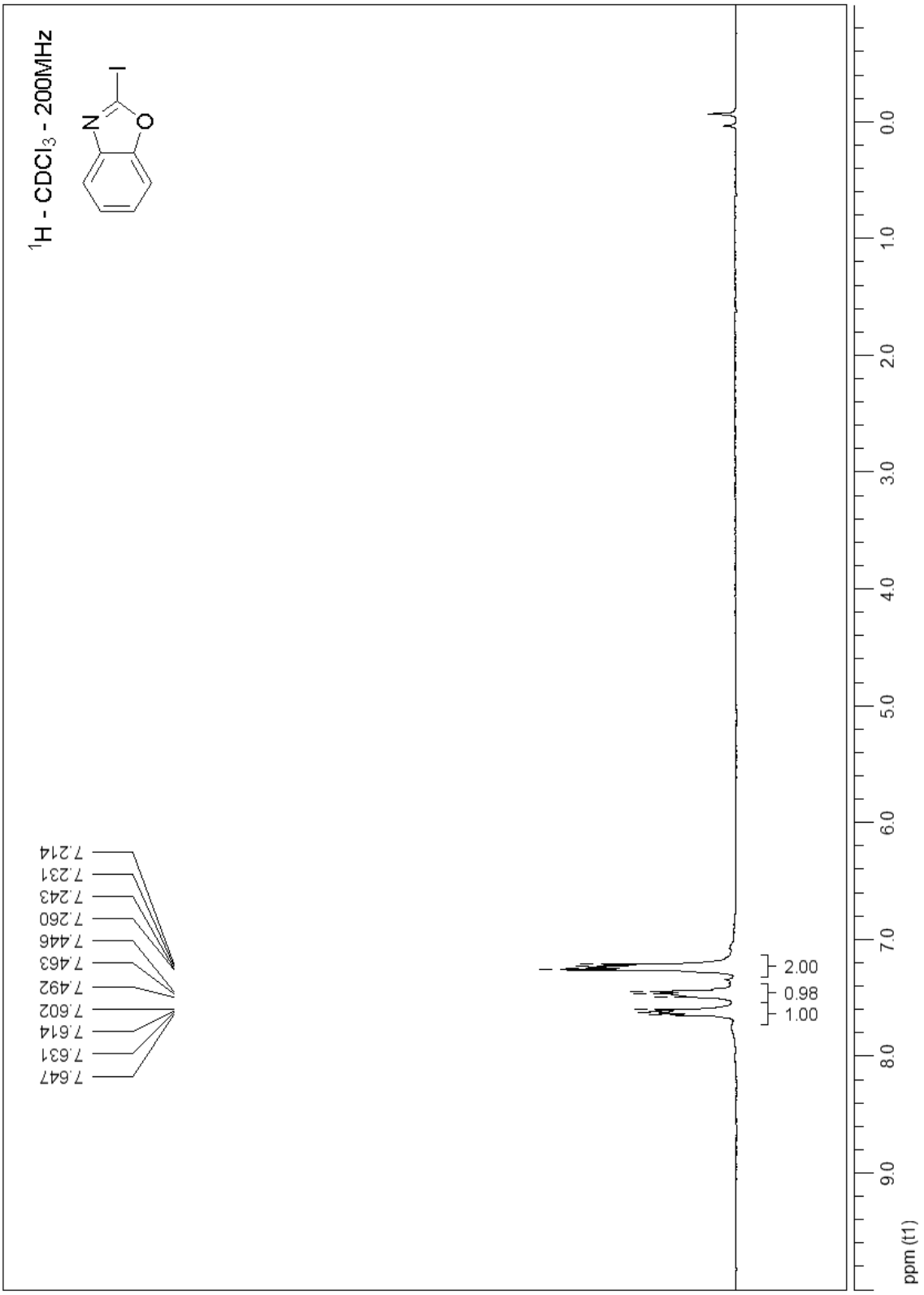
2-Iodobenzothiazole (2m).



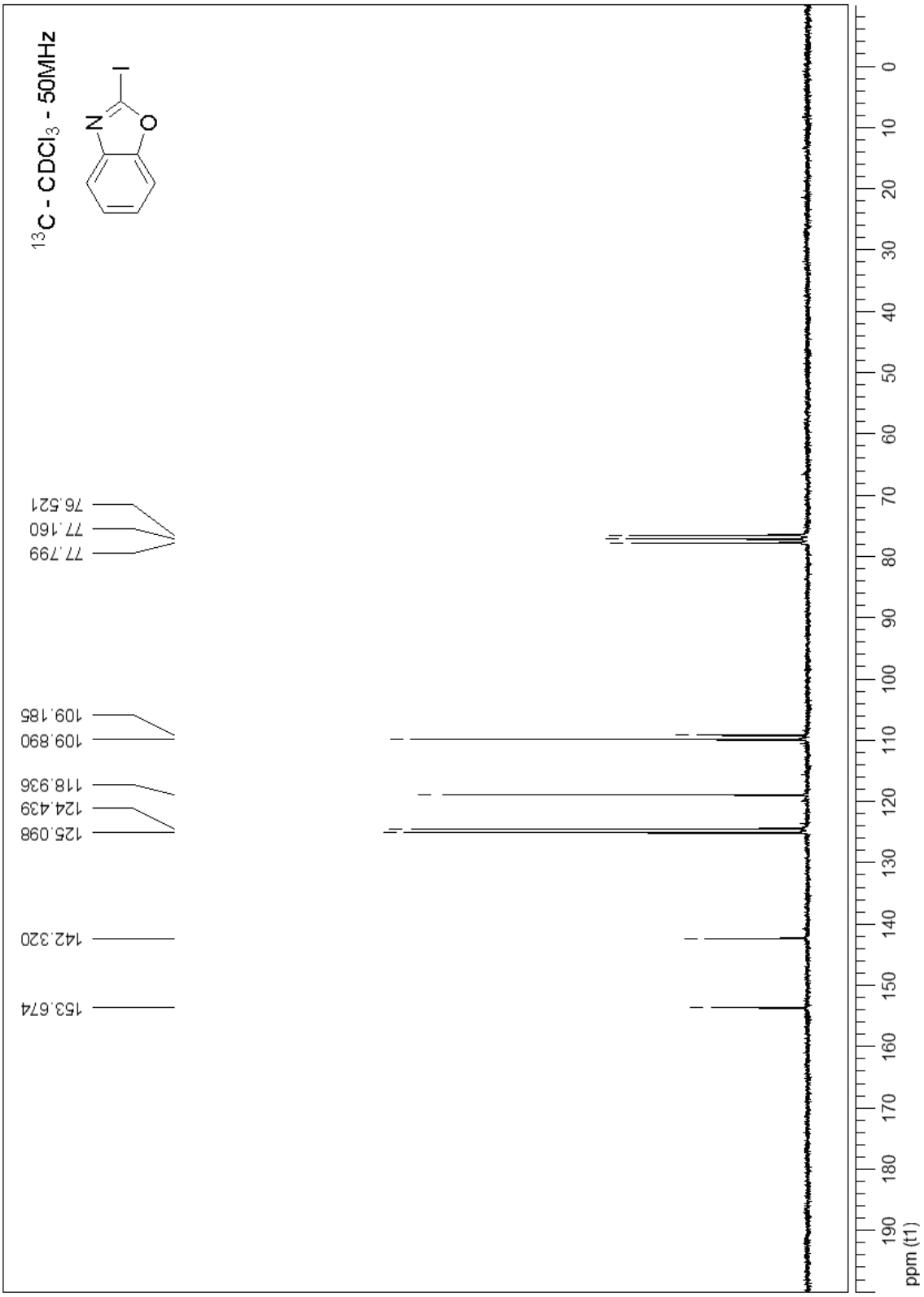
2-Iodobenzothiazole (2m).



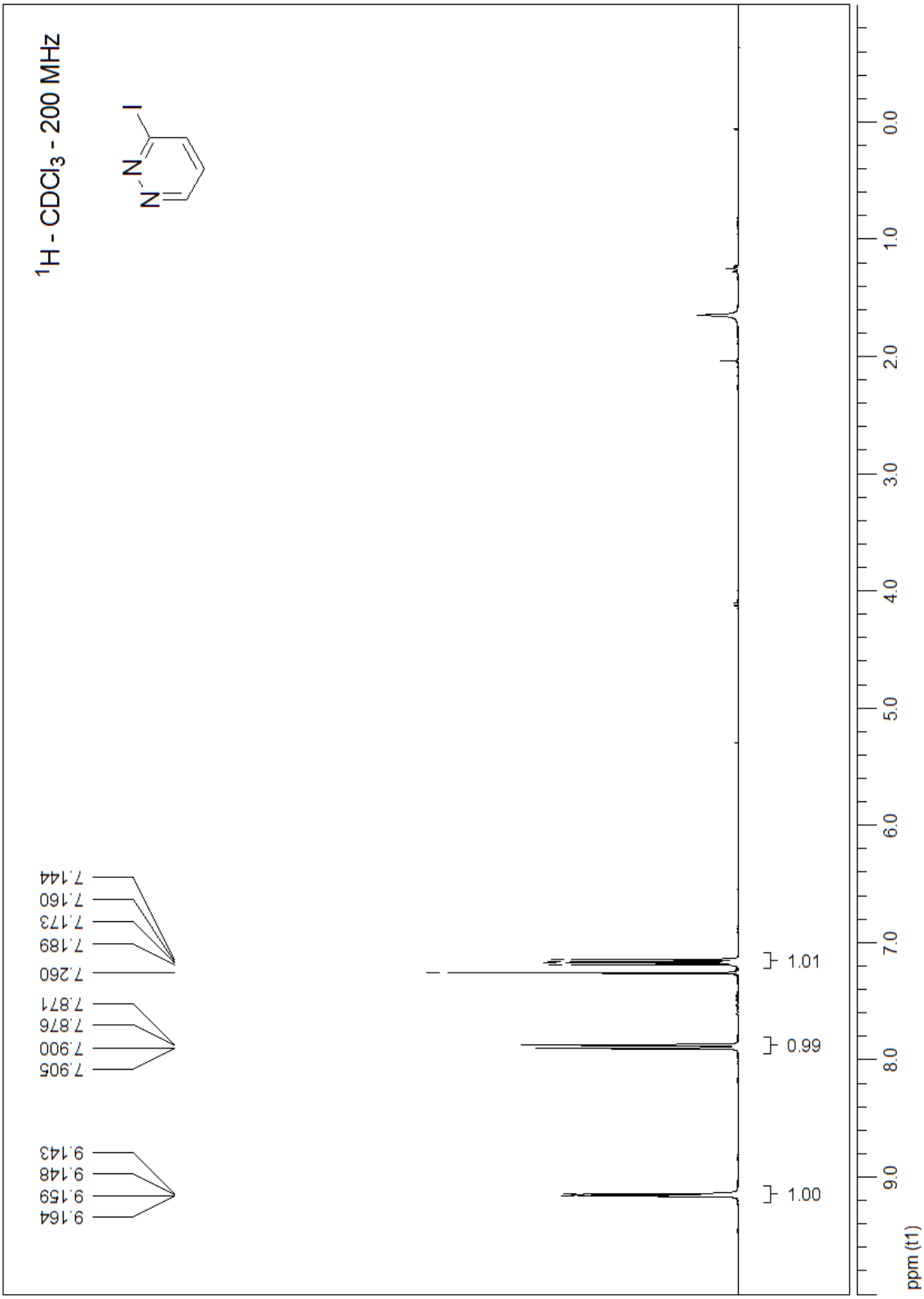
2-Iodobenzoxazole (2n).



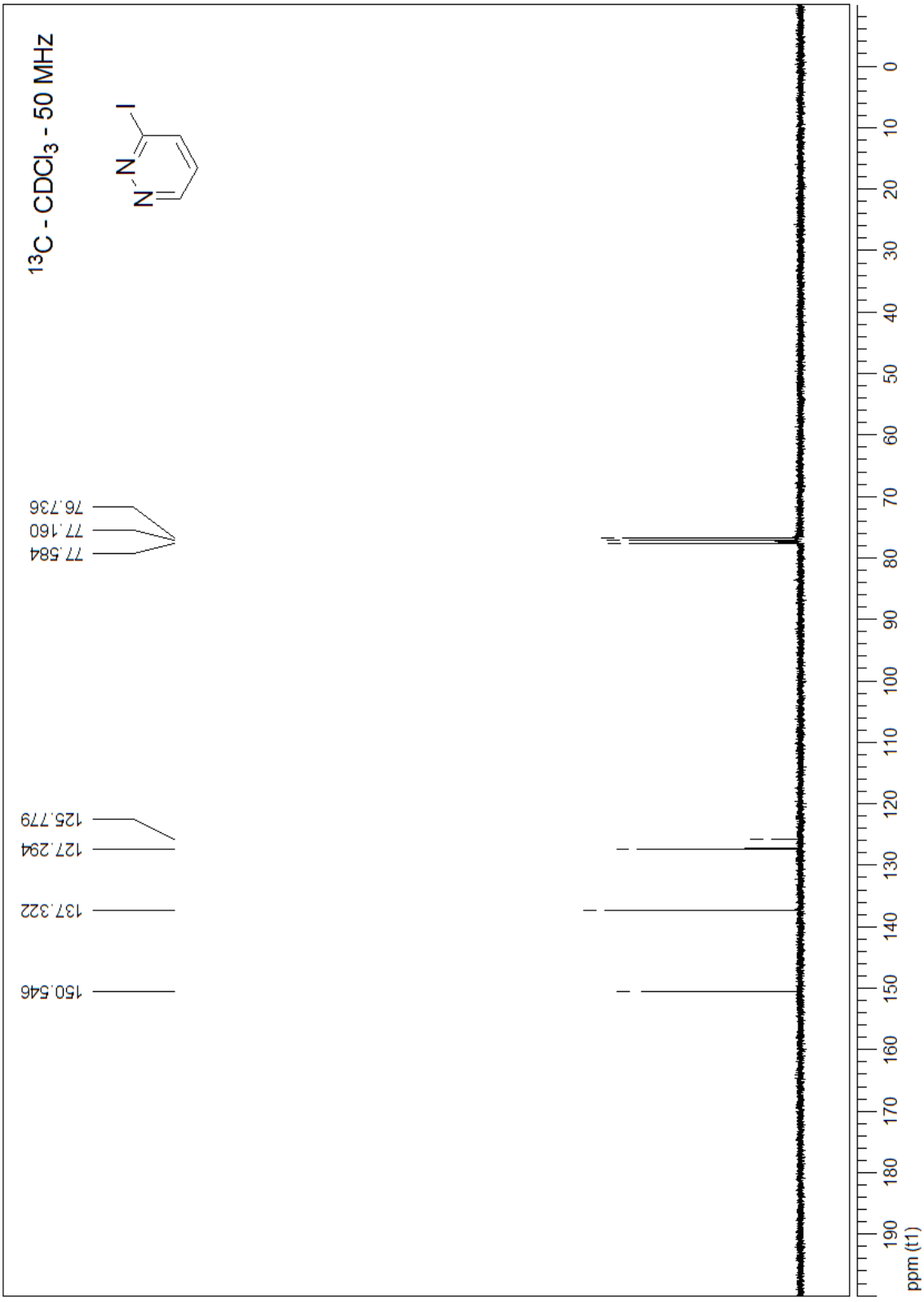
2-Iodobenzoxazole (2n).



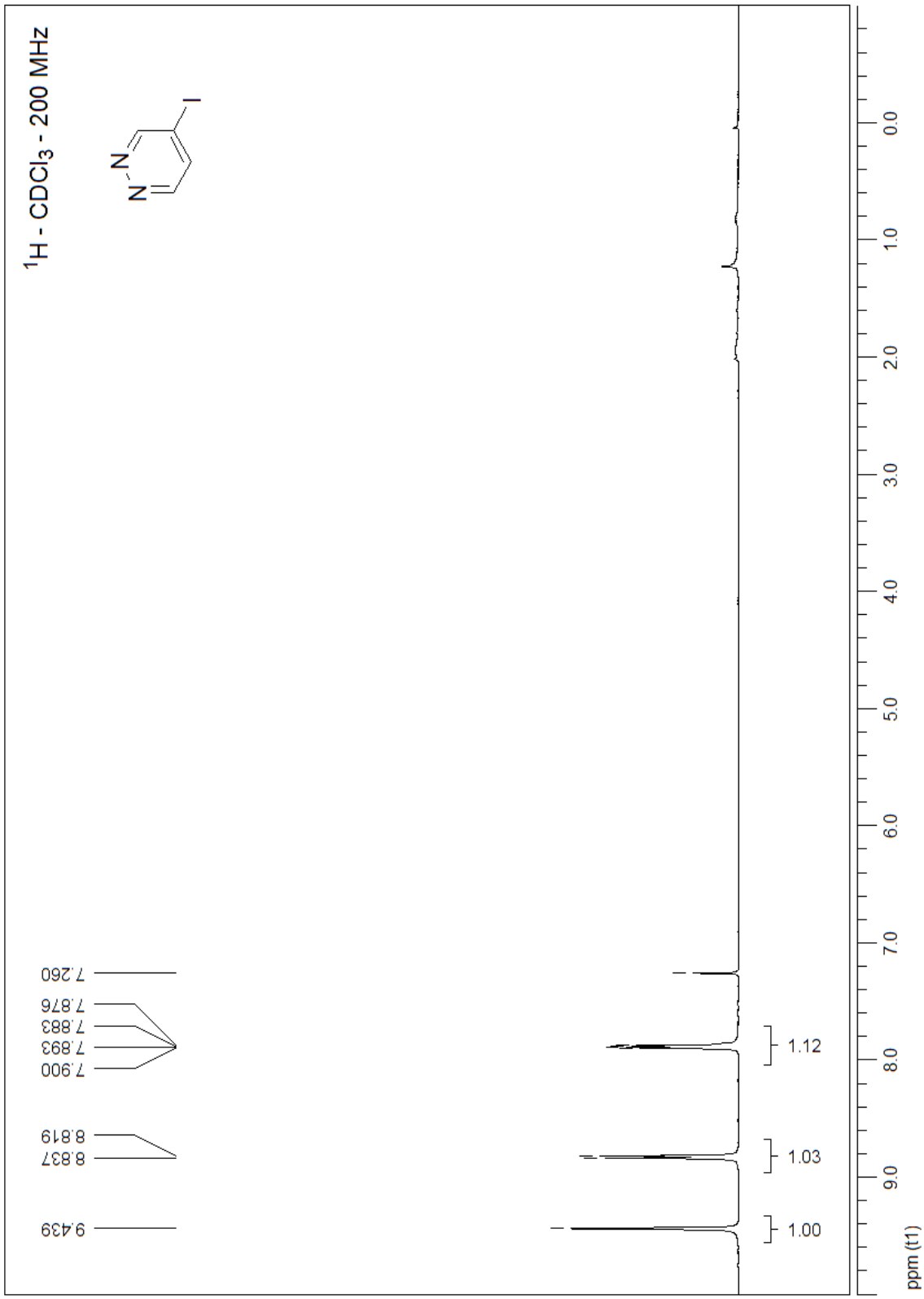
3-Iodopyridazine (2o).



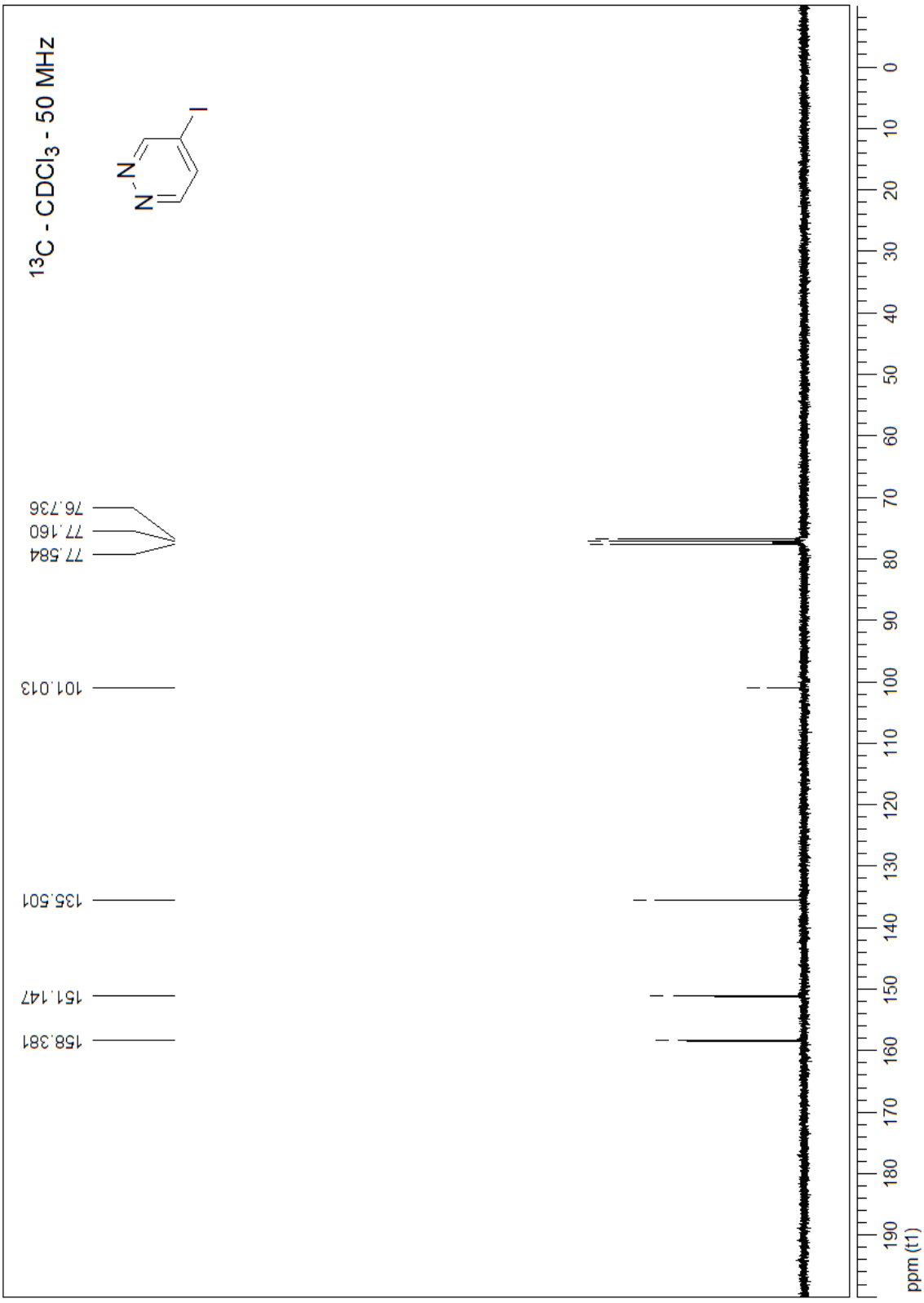
3-Iodopyridazine (2o).



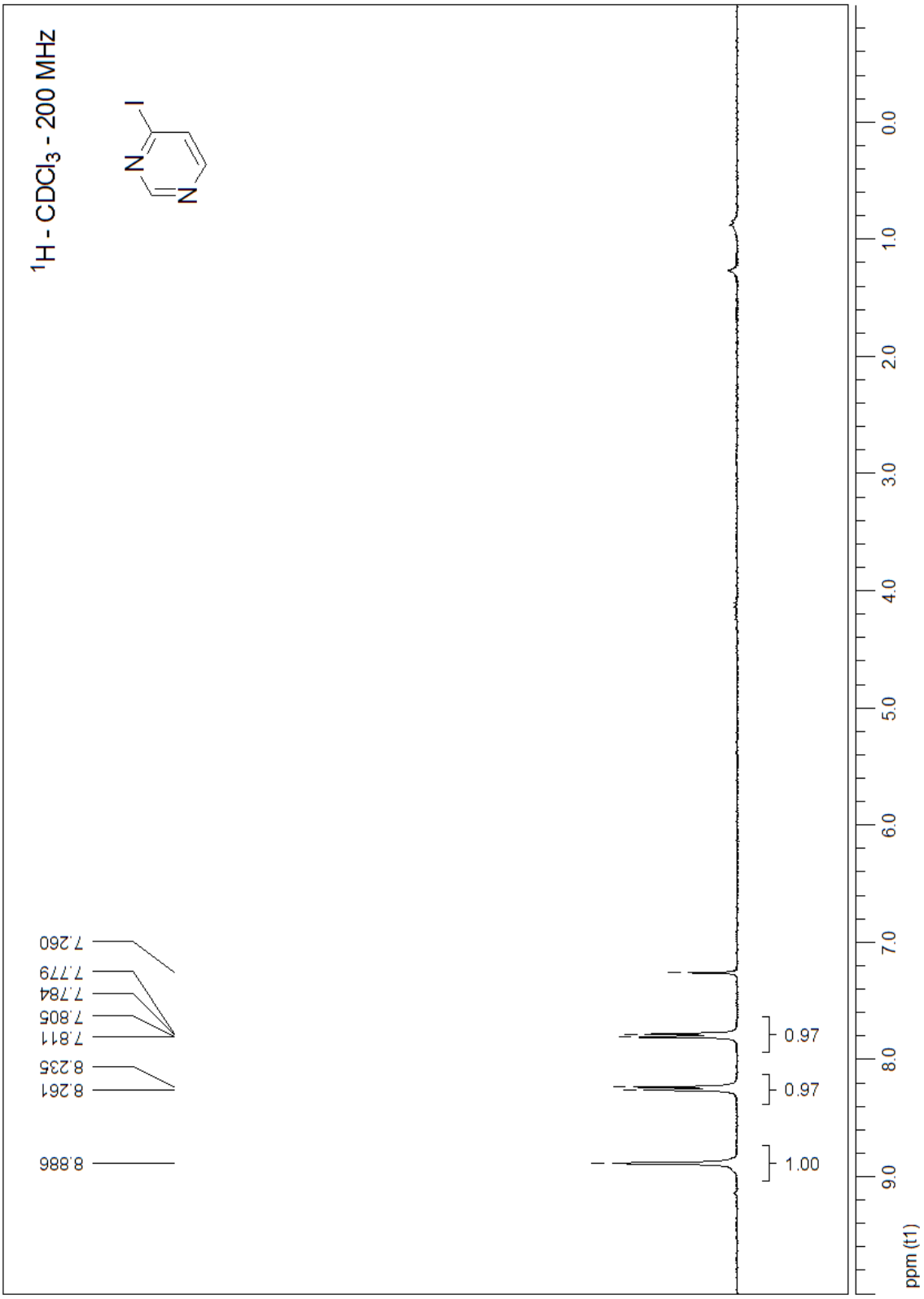
4-Iodopyridazine (2'o).



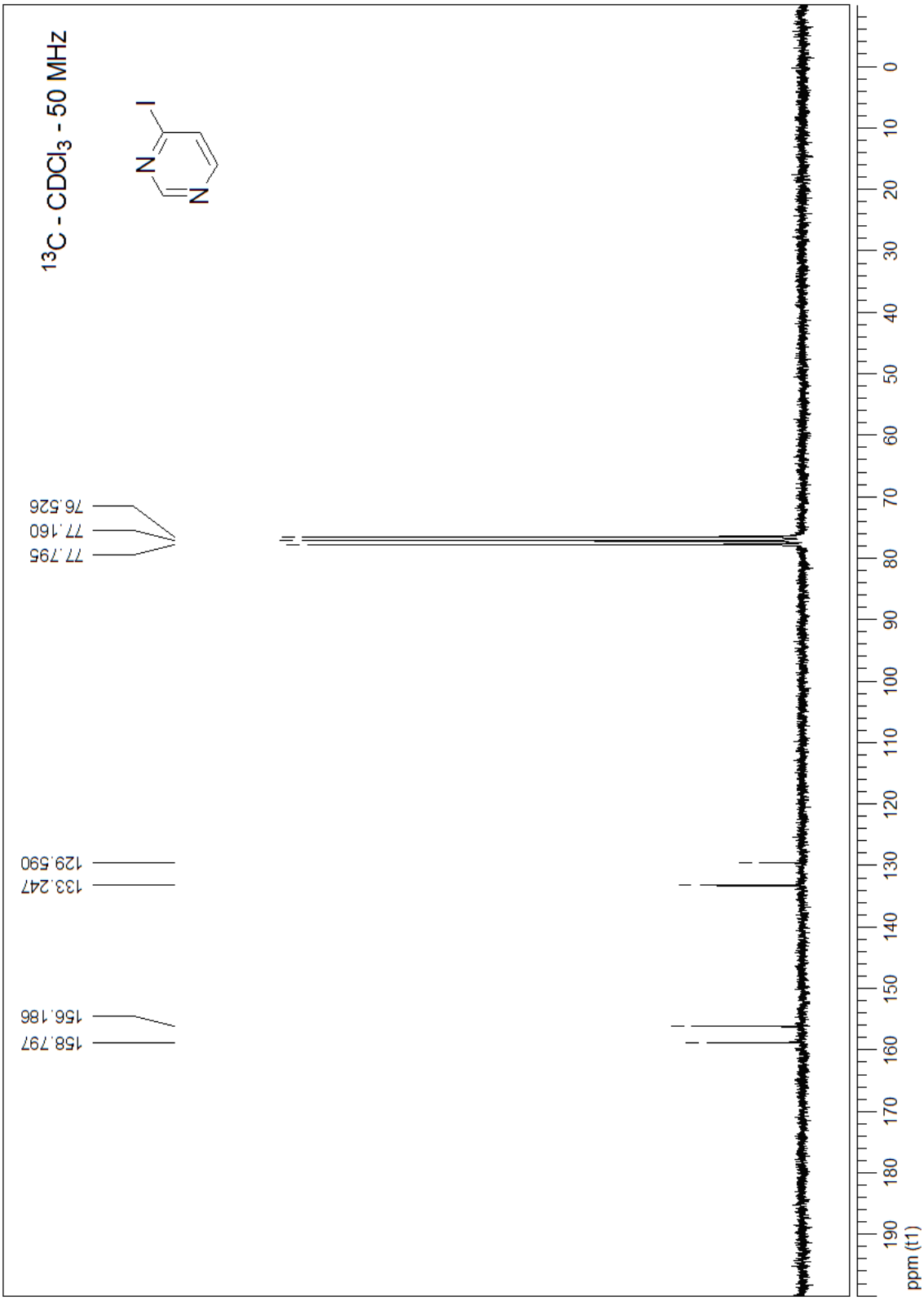
4-Iodopyridazine (2'o).



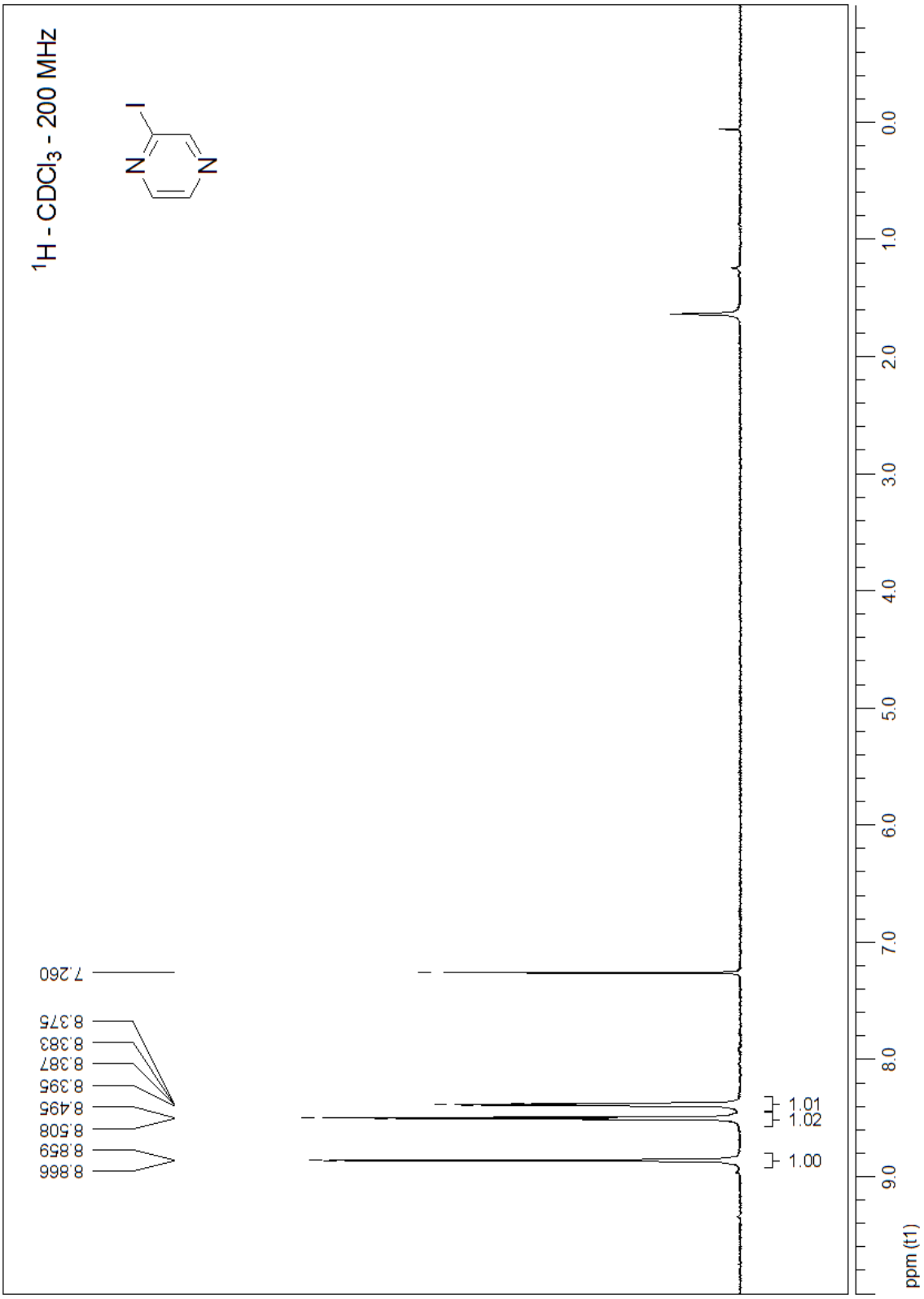
4-Iodopyrimidine (2p).



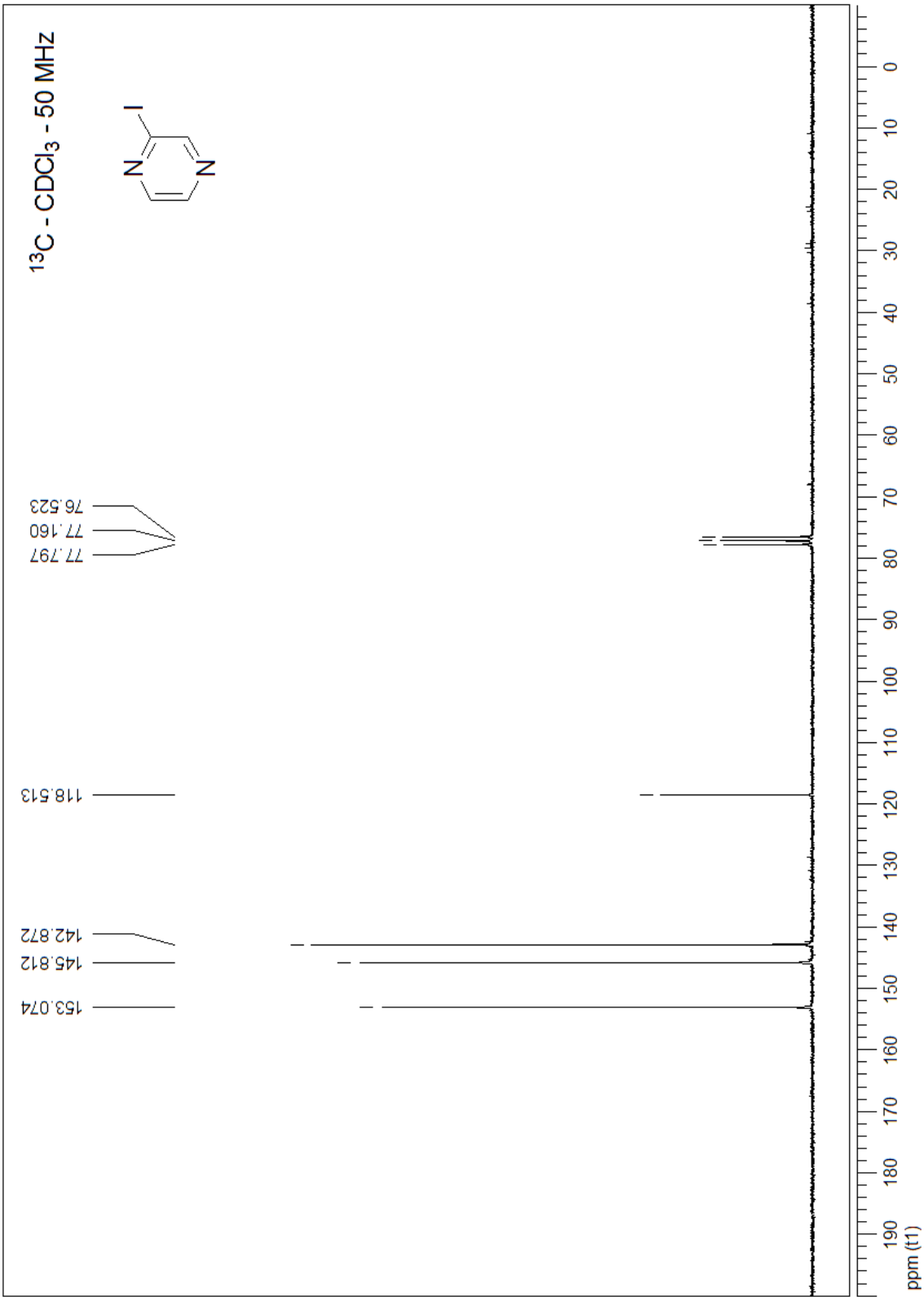
4-Iodopyrimidine (2p).



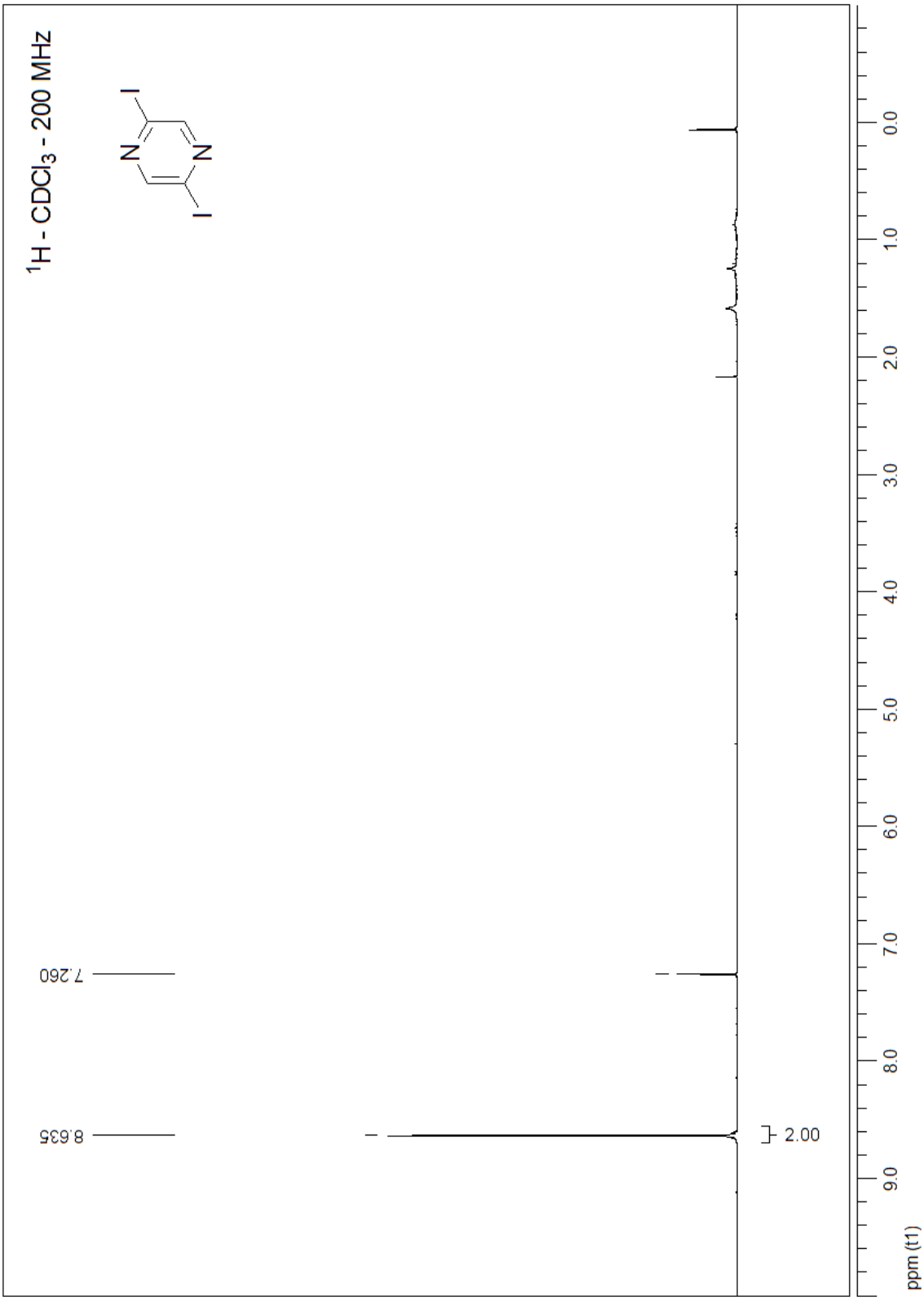
2-Iodopyrazine (2q).



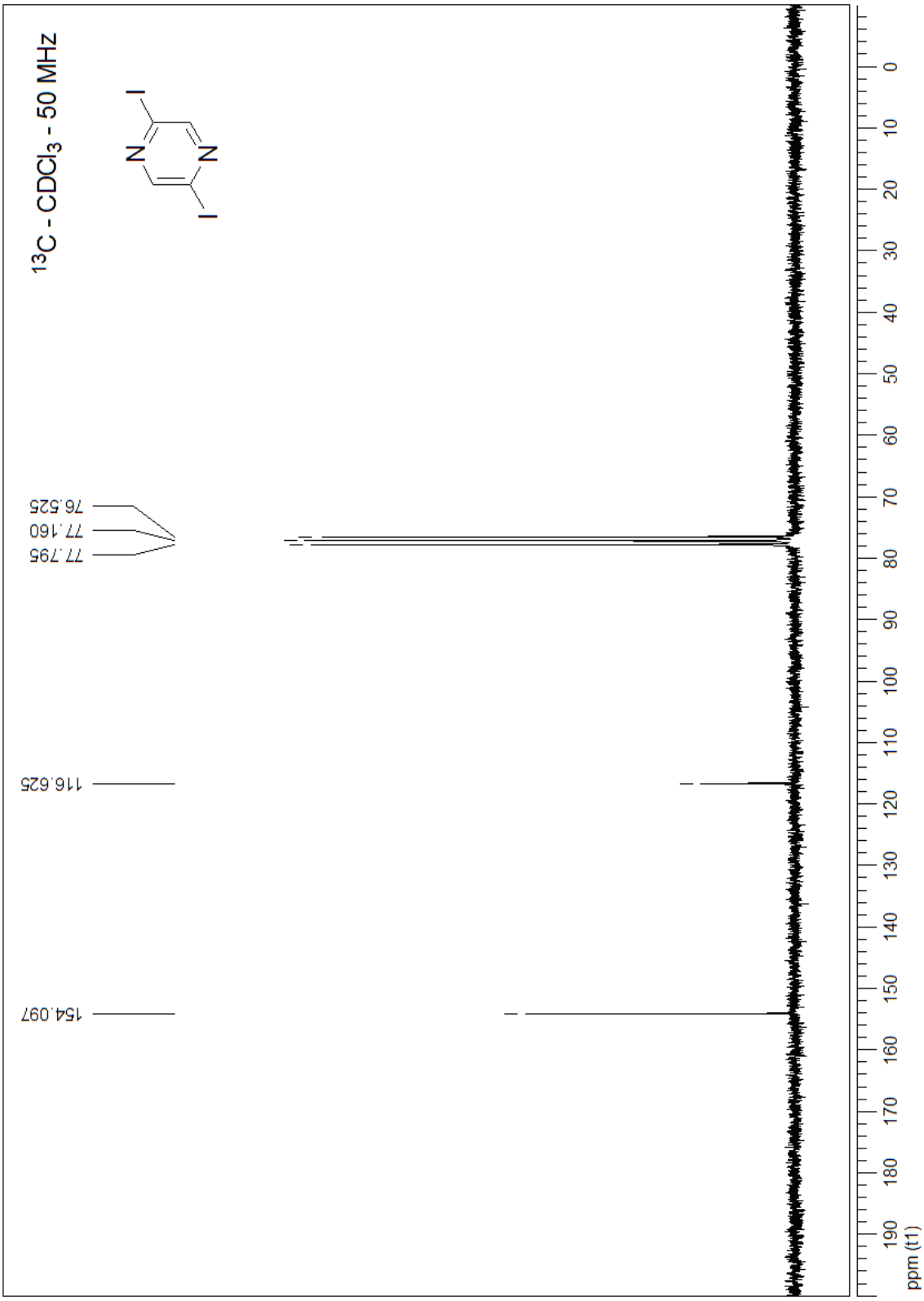
2-Iodopyrazine (2q).



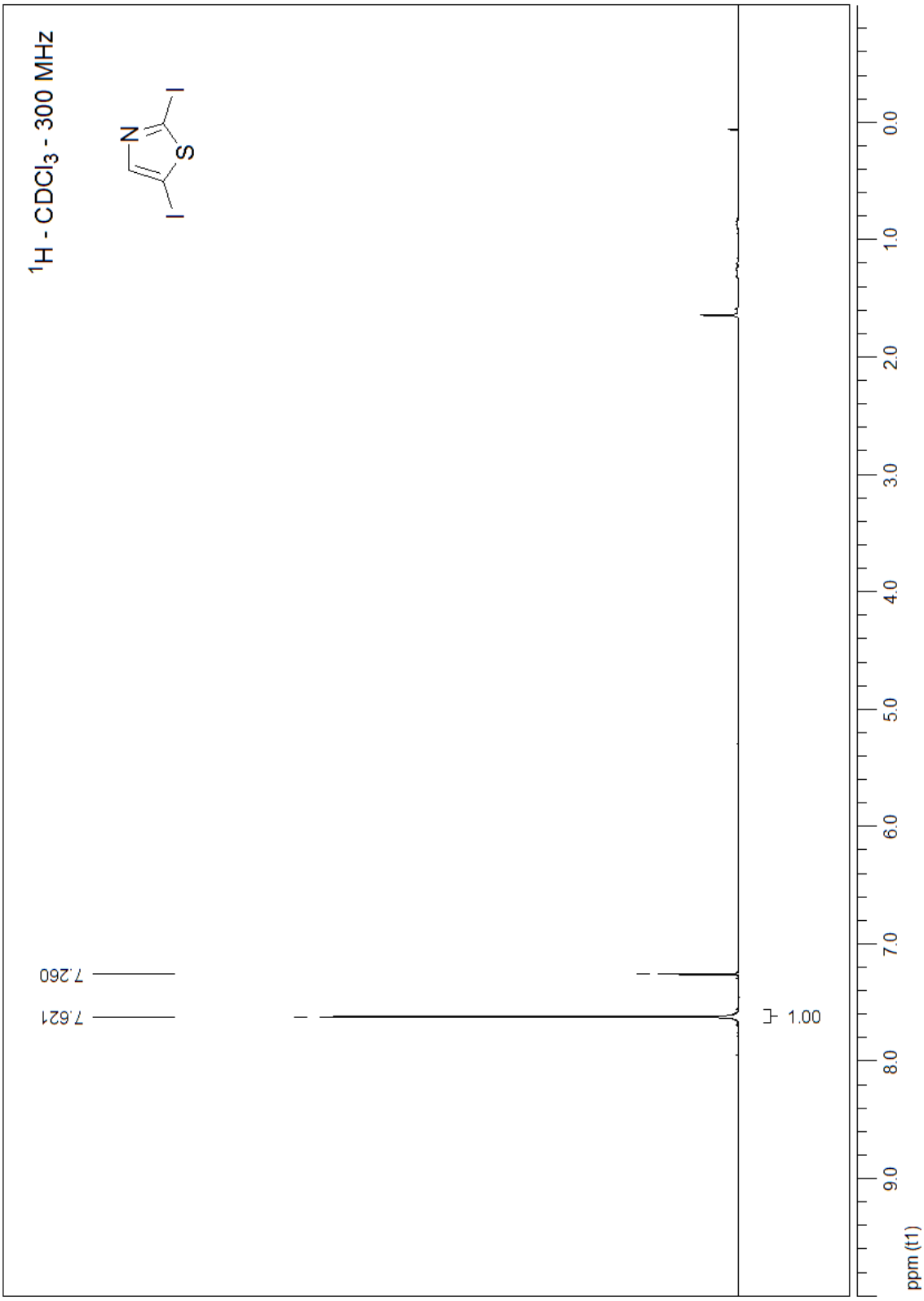
2,5-Diiodopyrazine (3q).



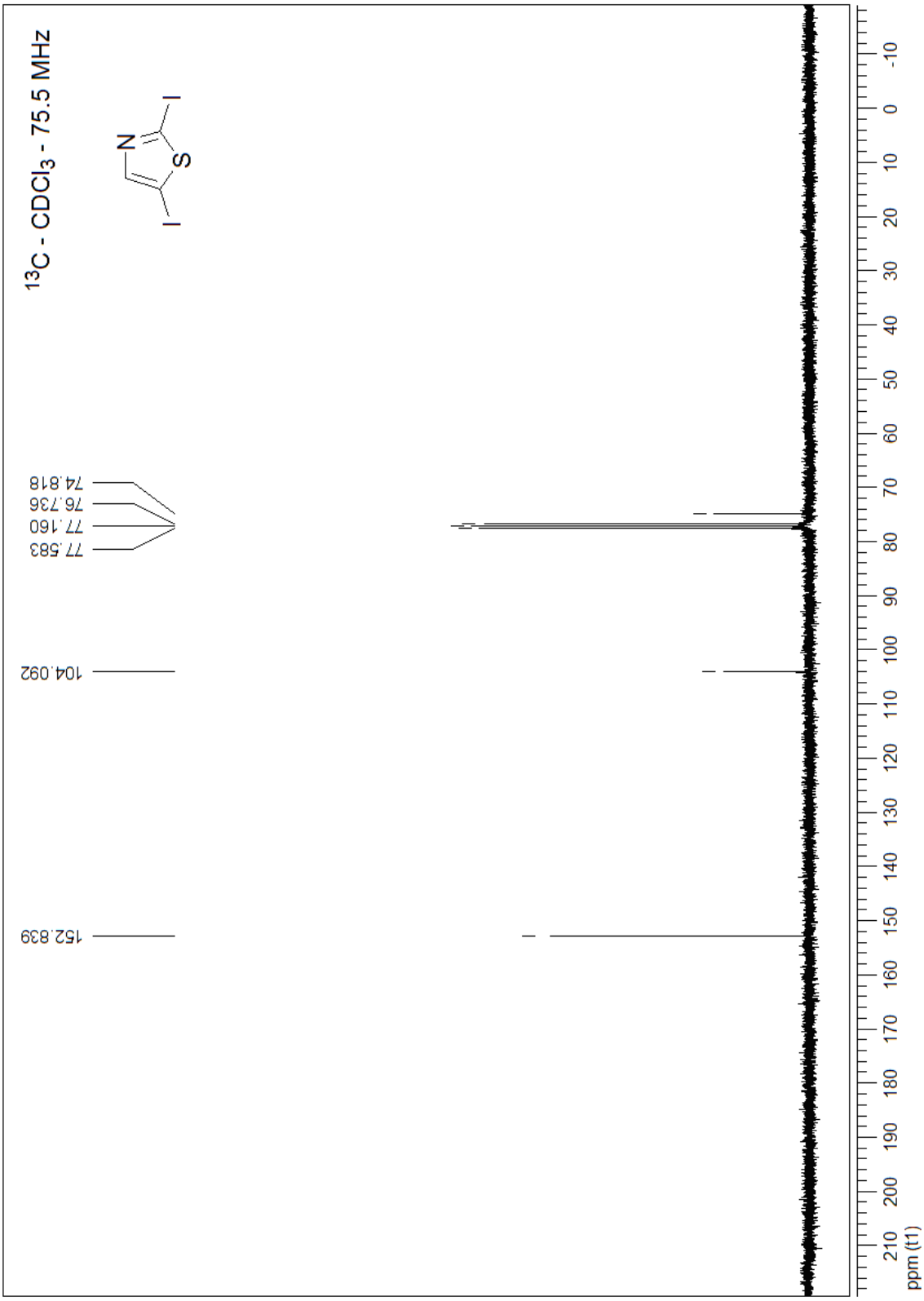
2,5-Diiodopyrazine (3q).



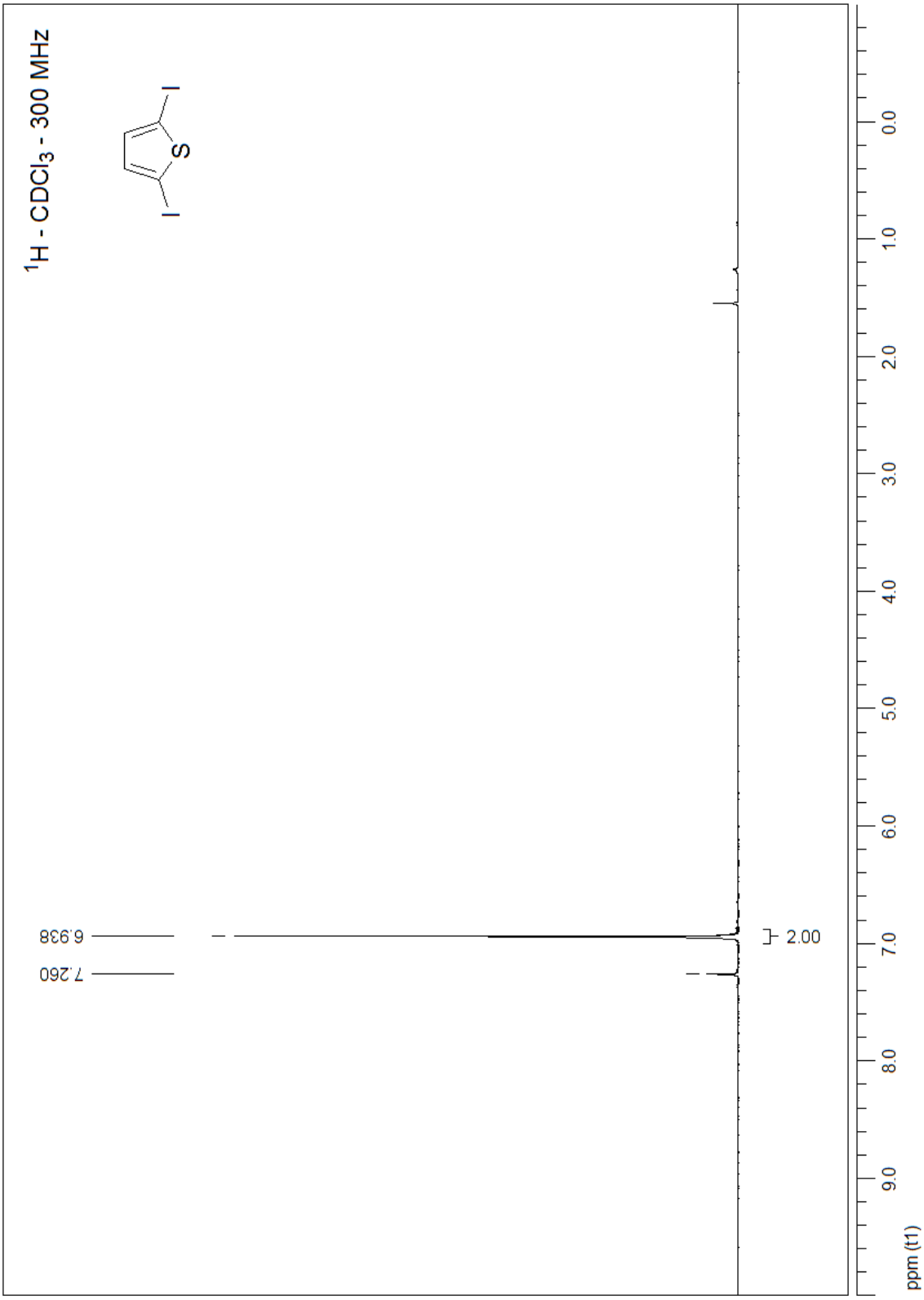
2,5-Diiodothiazole (3r).



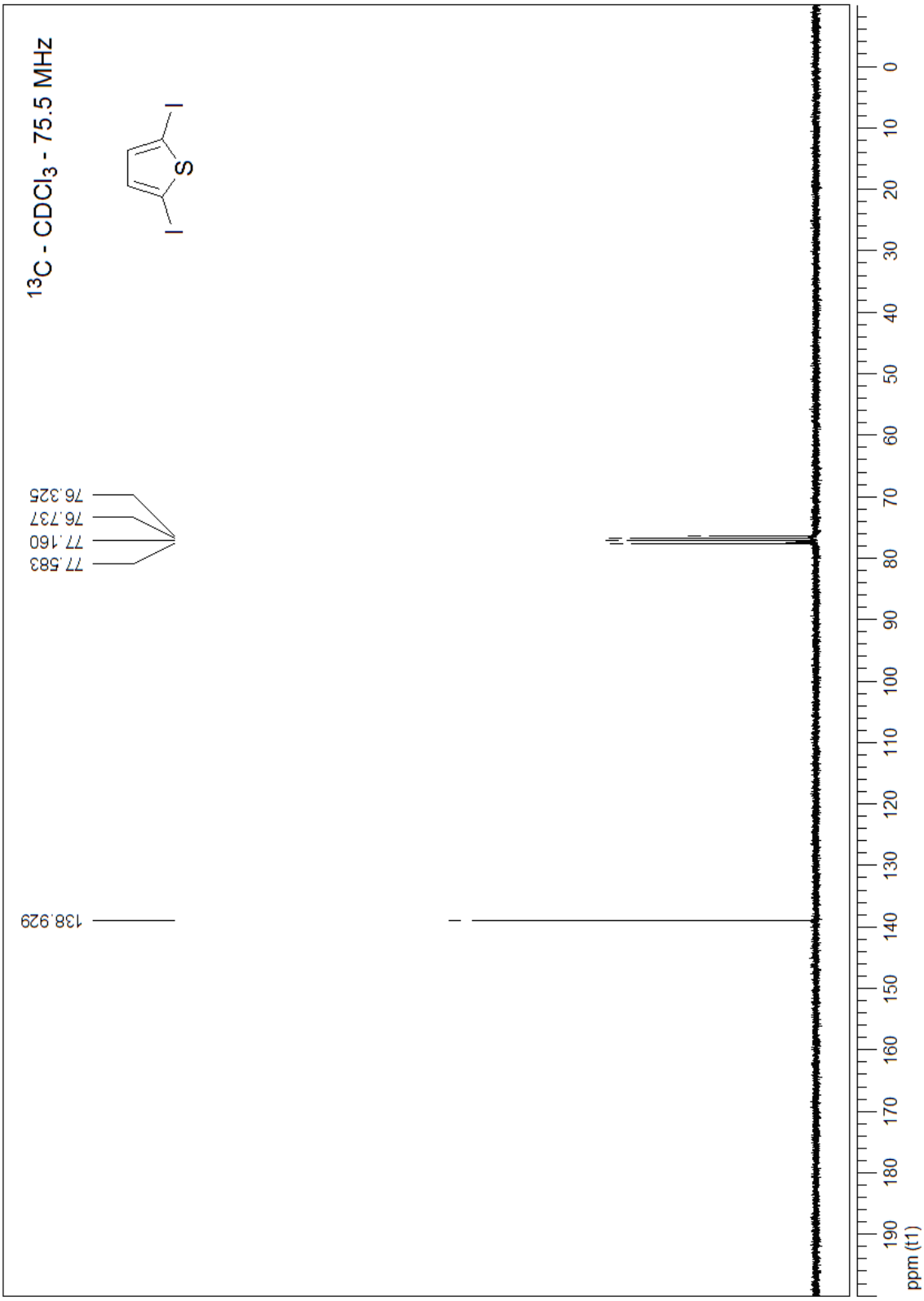
2,5-Diiodothiazole (3r).



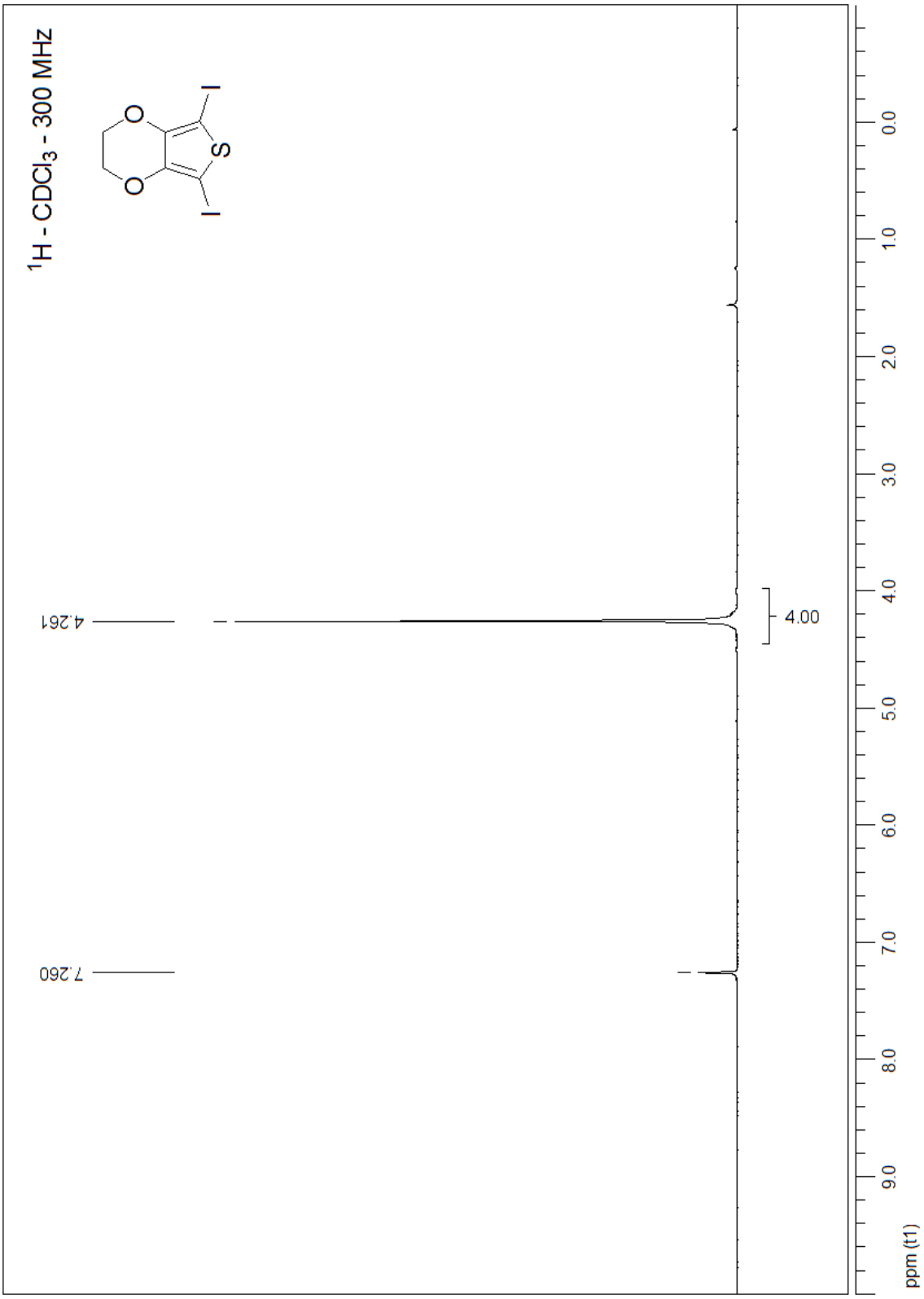
2,5-Diiodothiophene (3s).



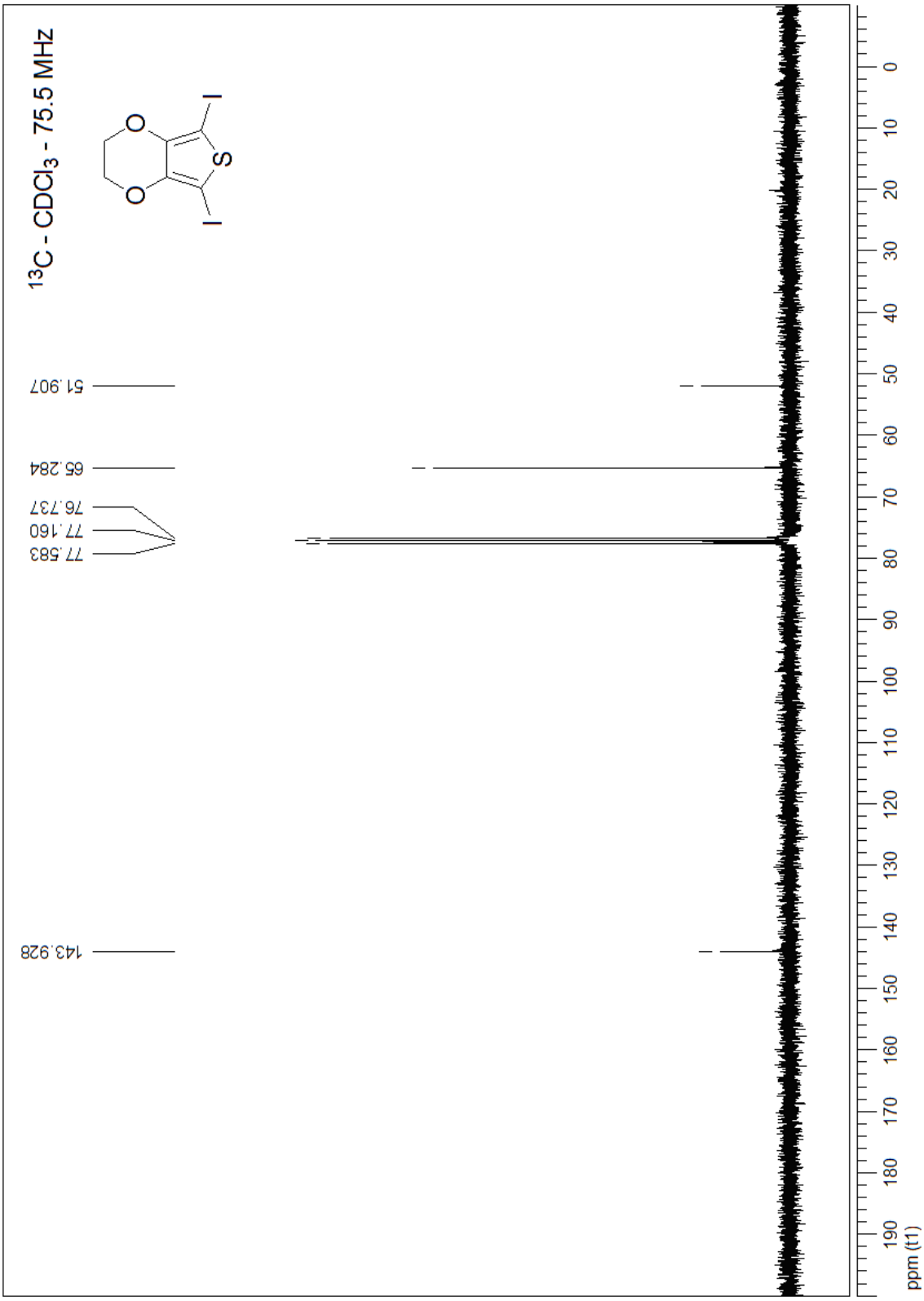
2,5-Diiodothiophene (3s).



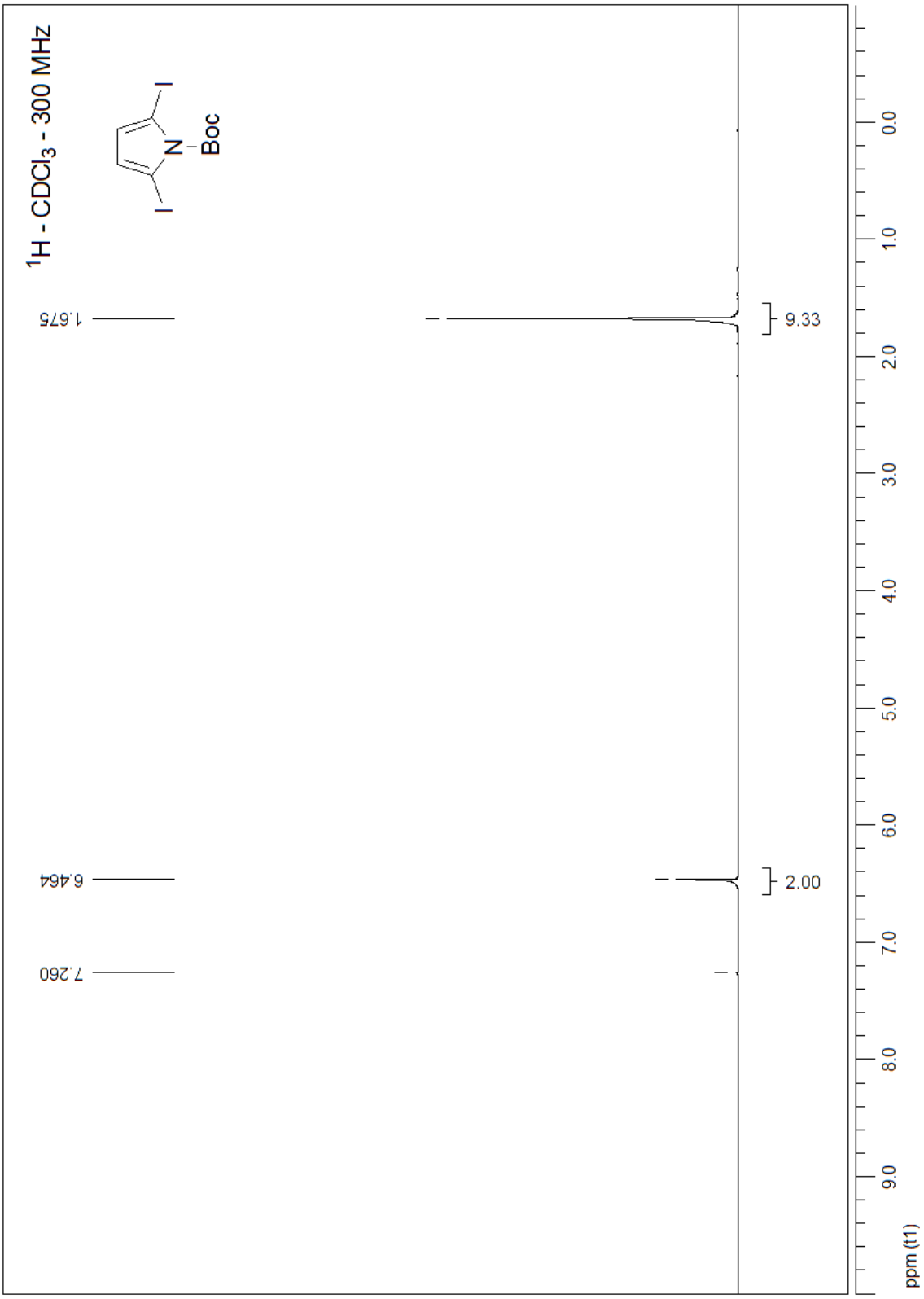
2,5-Diiodo-3,4-ethylenedioxythiophene (3t).



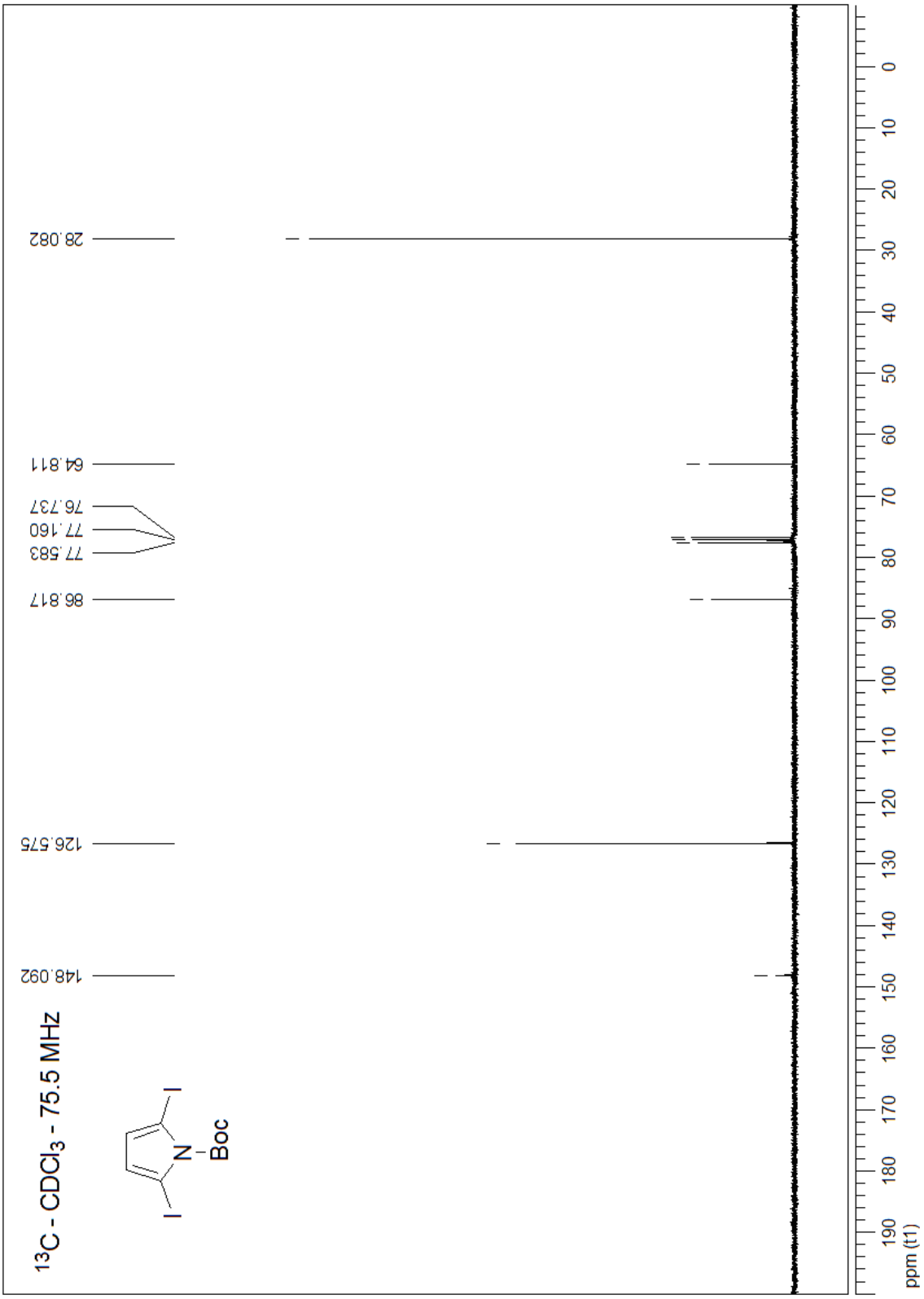
2,5-Diiodo-3,4-ethylenedioxythiophene (3t).



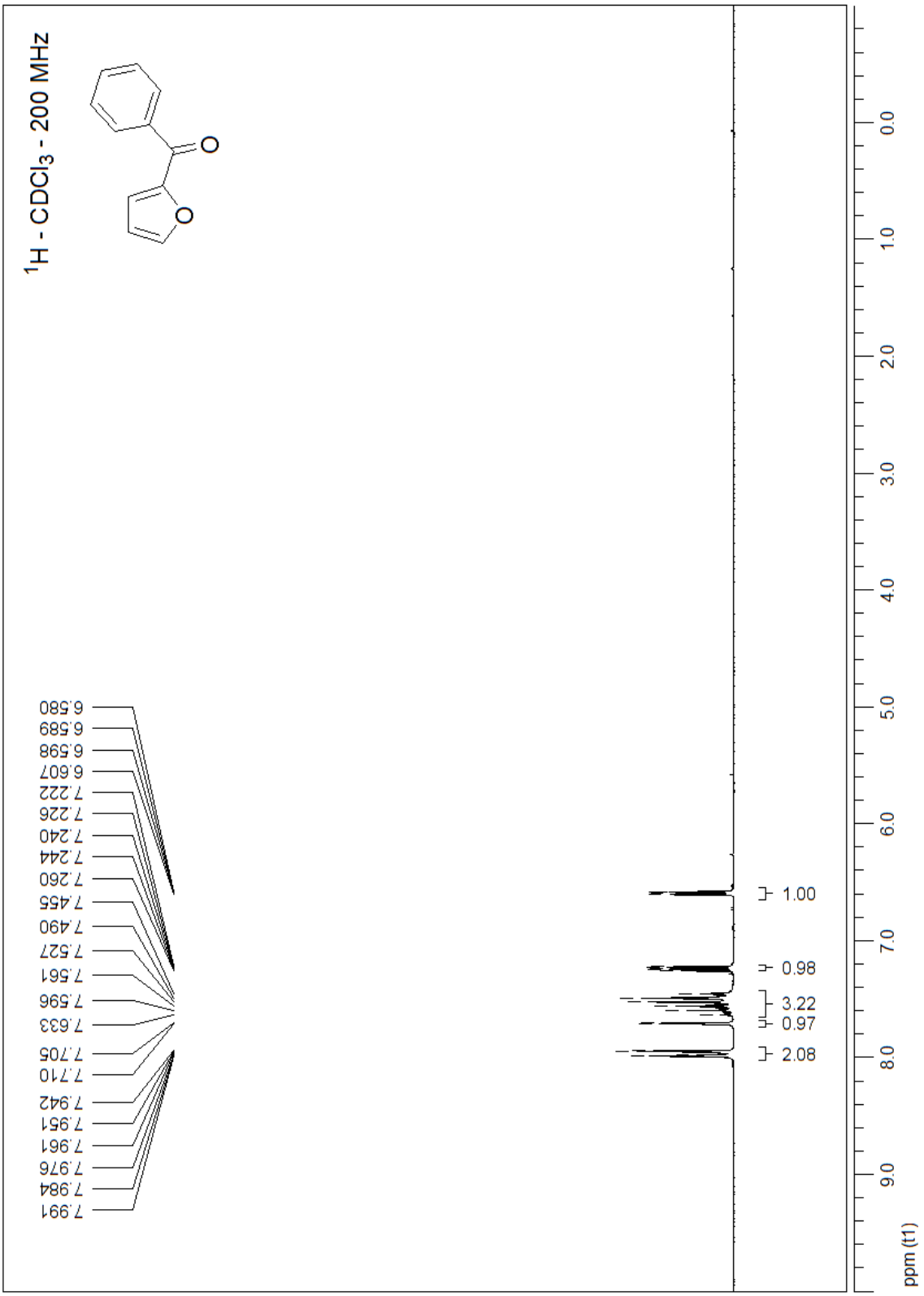
***N*-Boc-2,5-diiodopyrrole (3l).**



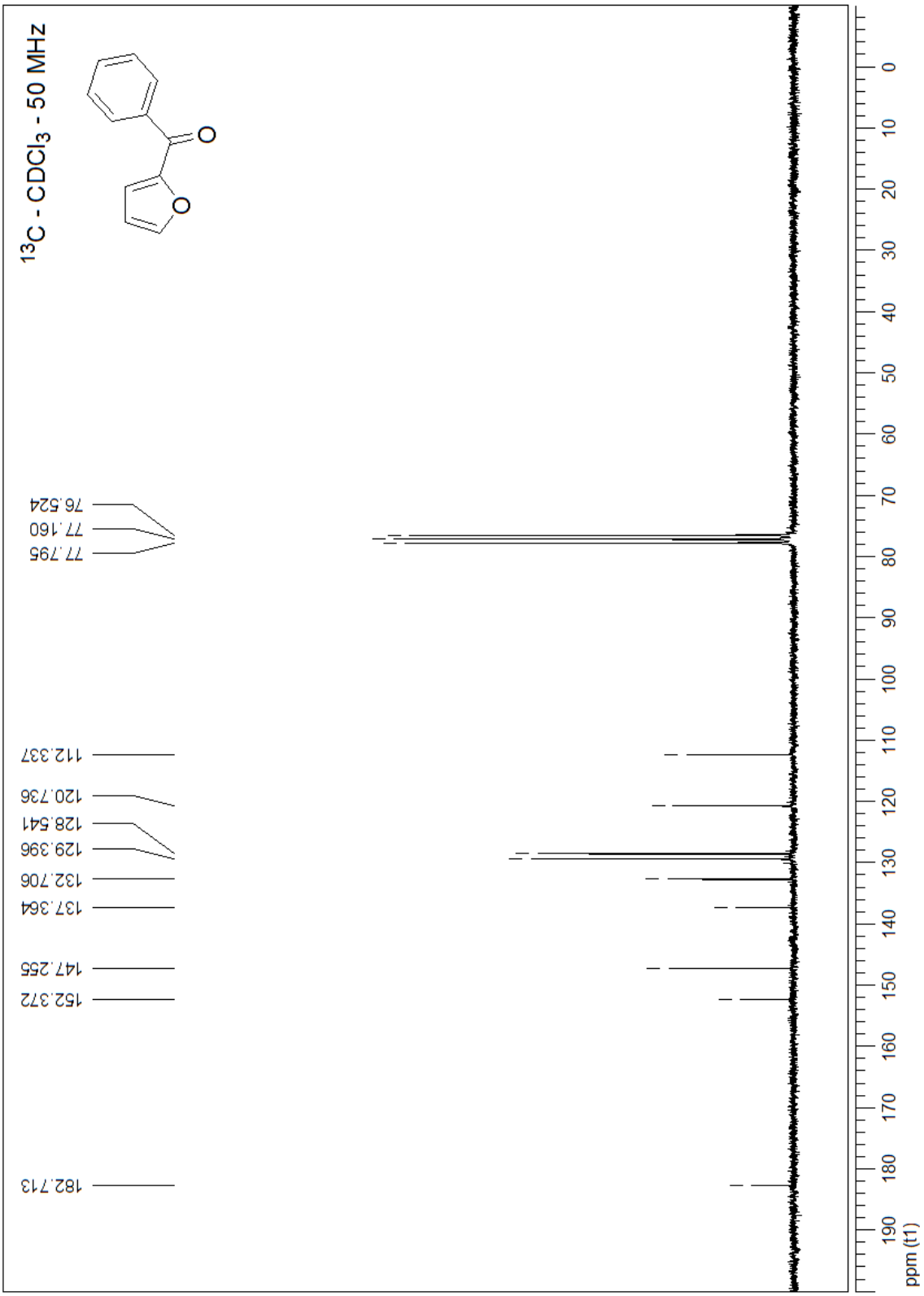
_N_-Boc-2,5-diiodopyrrole (3l).



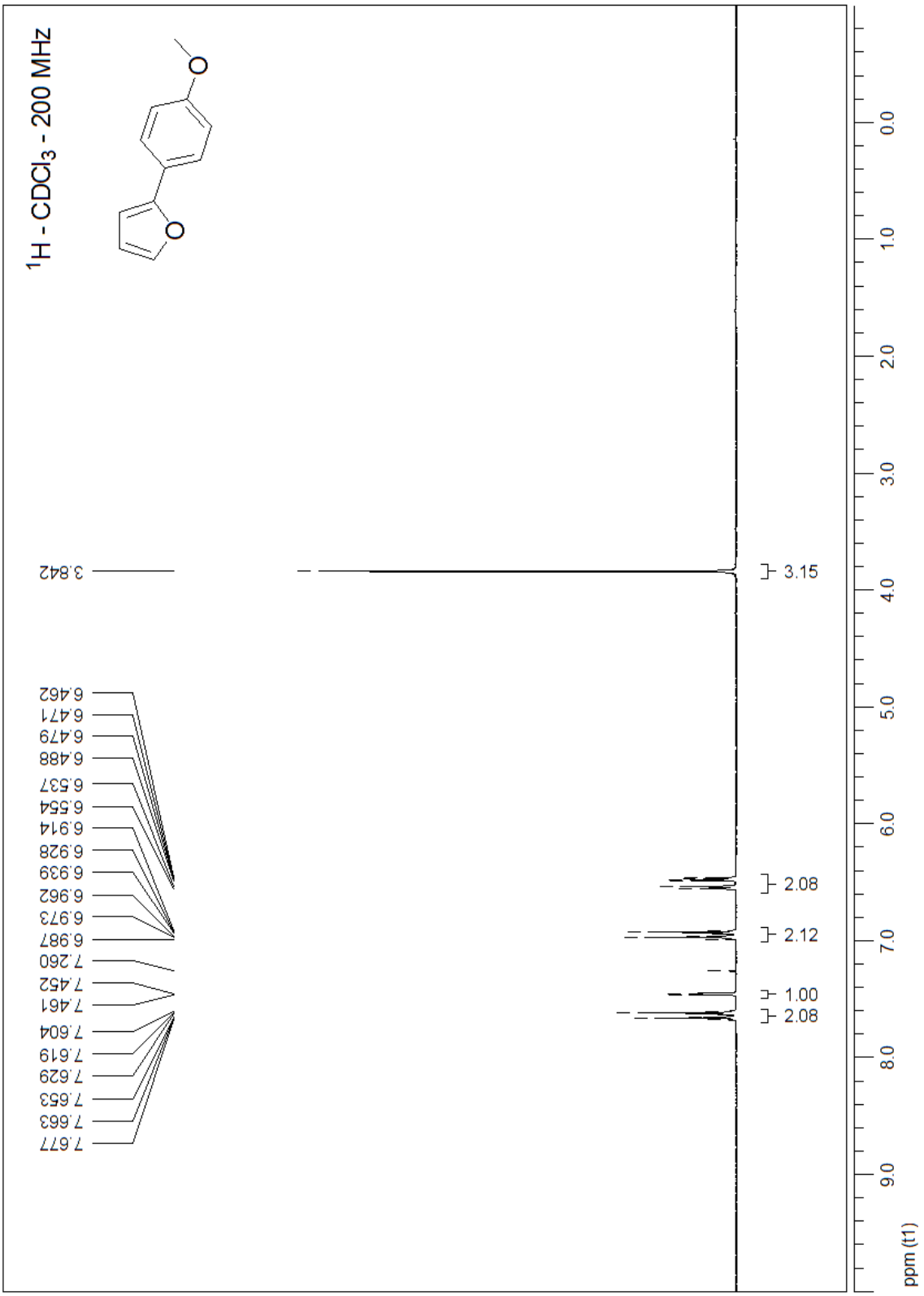
2-(Benzoyl)furan (4u).



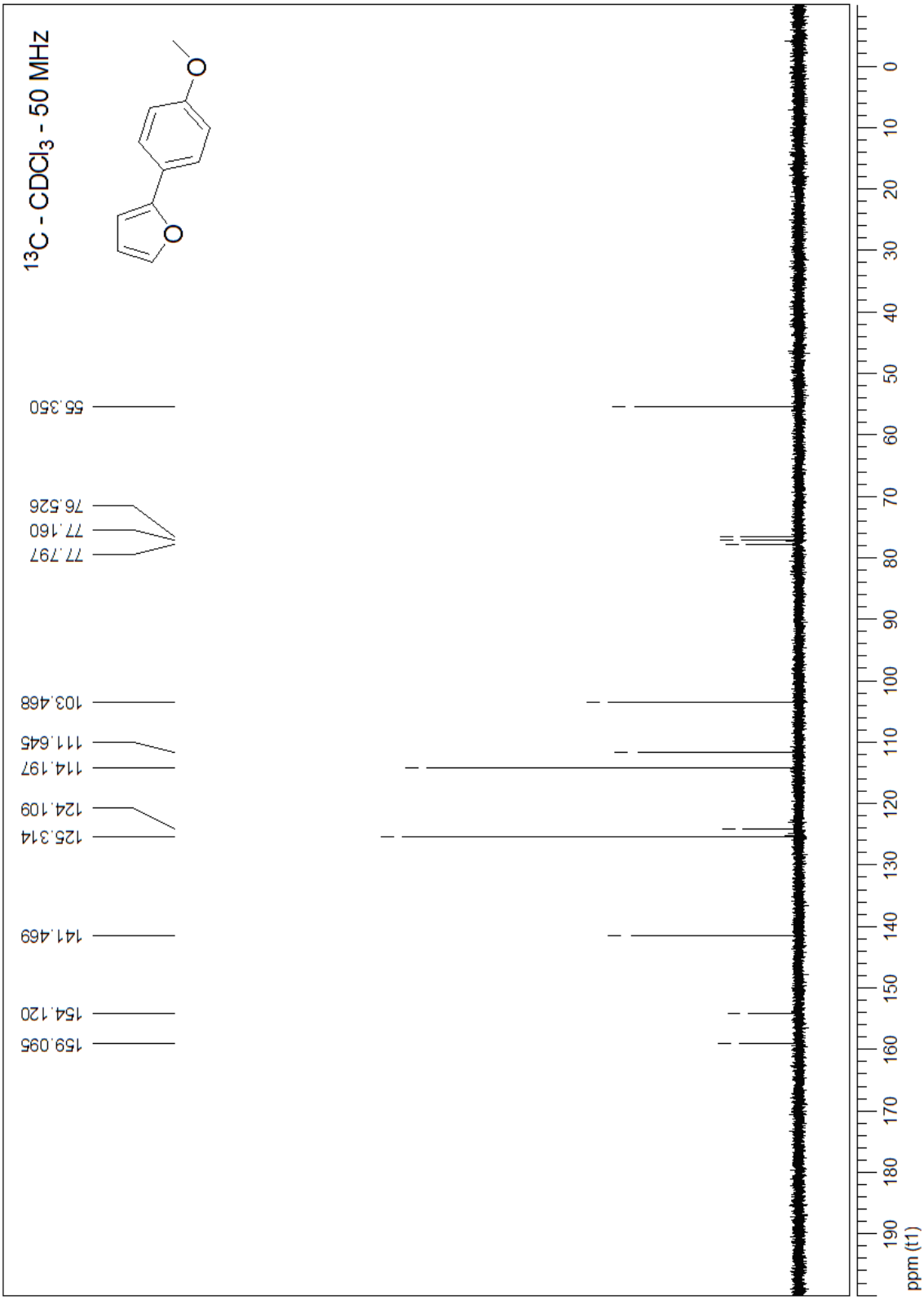
2-(Benzoyl)furan (4u).



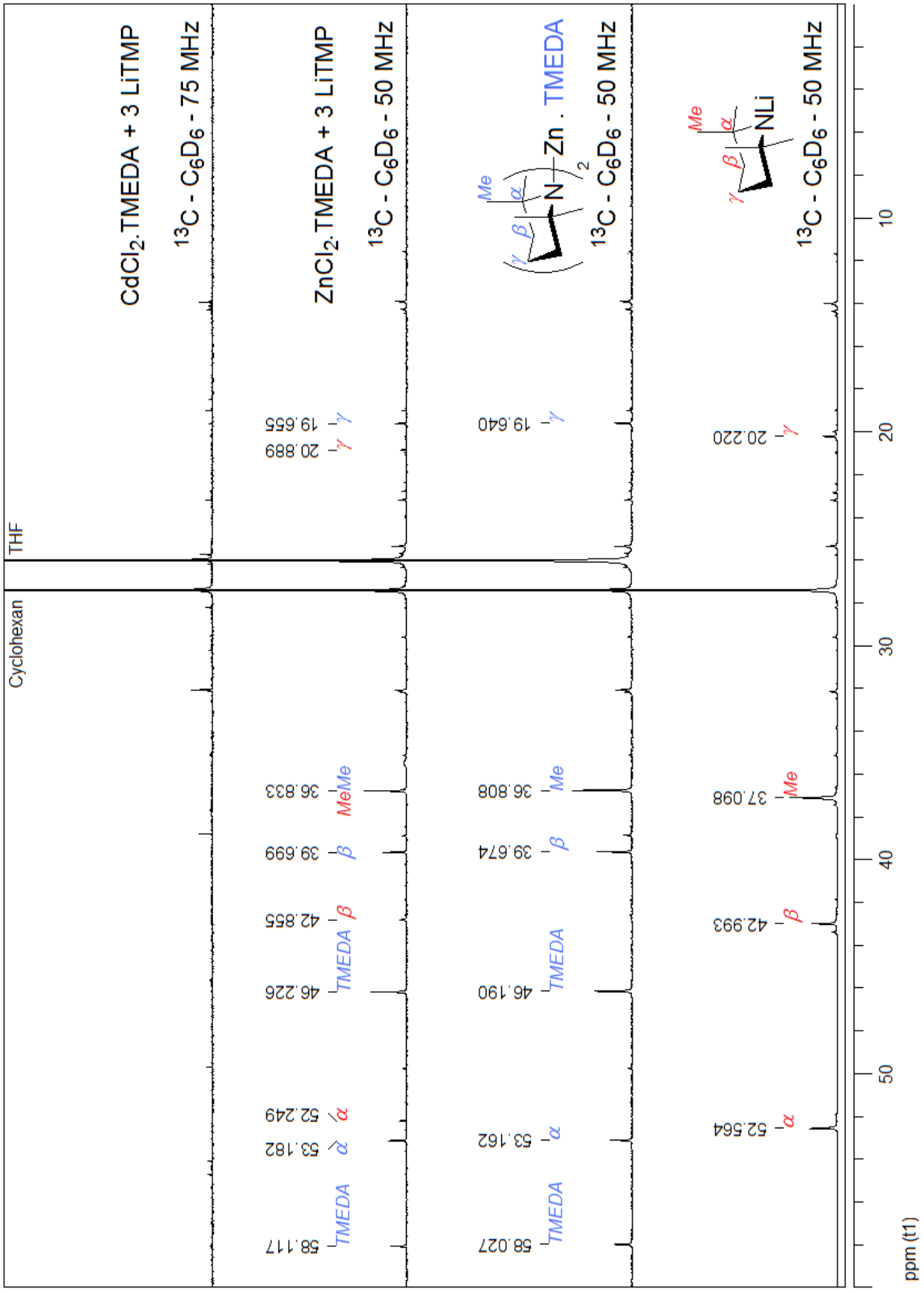
2-(4-Methoxyphenyl)furan (5u).



2-(4-Methoxyphenyl)furan (5u).



Comparison between the NMR spectra of the basic mixtures



Computational Methods

All calculations were carried out with the Gaussian 03 program package.[19] The molecular structures and harmonic vibrational frequencies were obtained at the B3LYP[20] level with the basis set of Ahlrichs' SVP all–electron basis set for Zn[21] and Cd,[22] and 6–31G* for the other atoms. Geometry optimization and vibrational analysis were performed at the same level. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0 for minima).

[19] *Gaussian 03*, revision B.04; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 2003.

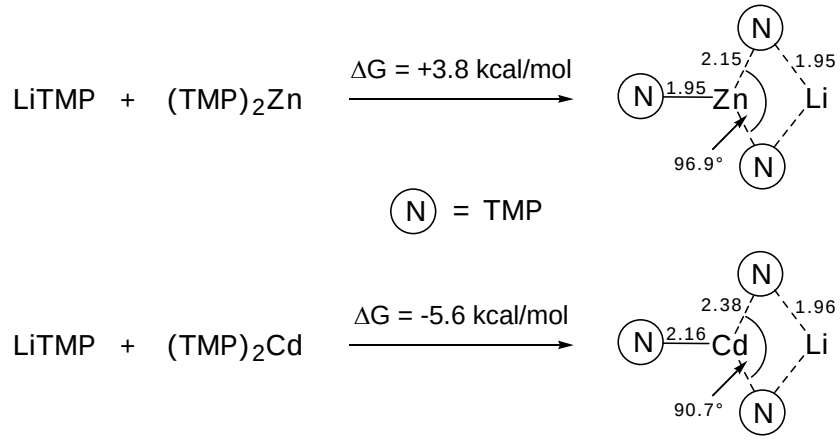
[20] (a) Becke, A. D. *Phys. Rev.* **1988,** *A38*, 3098-3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372-1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988,** *B37*, 785-788.

[21] Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys*. **1992**, *97*, 2571-2577.

[22] Ahlrichs, R.; May, K. *Phys. Chem. Chem. Phys.* **2000**, *2*, 943-945.

Cartesian Coordinates and Total Electron Energies

Scheme 1.



LiTMP

HF= -416.0754217

Sum of electronic and thermal Free Energies= -415.853417

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.243946	1.189283	-0.683129
2	6	0	1.257433	-0.183899	0.043321
3	7	0	0.002698	-0.910813	-0.151539
4	6	0	-1.264782	-0.207992	0.038263
5	6	0	-1.269458	1.167591	-0.684701
6	6	0	-0.020000	1.995967	-0.363326
7	6	0	1.662237	0.015568	1.532939
8	6	0	2.365421	-1.054358	-0.591465
9	6	0	-1.674202	-0.017484	1.527711
10	6	0	-2.355939	-1.092305	-0.602130
11	3	0	0.136746	-2.546438	-0.837924
12	1	0	1.271799	1.005605	-1.767346
13	1	0	2.145334	1.766746	-0.431897

14	1	0	-2.180160	1.730121	-0.433555
15	1	0	-1.293867	0.985643	-1.769247
16	1	0	-0.027070	2.928852	-0.943015
17	1	0	-0.022752	2.296111	0.693334
18	1	0	1.601301	-0.941333	2.064143
19	1	0	1.009197	0.721491	2.051814
20	1	0	2.688836	0.397336	1.621213
21	1	0	2.408469	-2.040632	-0.095457
22	1	0	3.363221	-0.611718	-0.487472
23	1	0	2.176602	-1.197750	-1.665944
24	1	0	-2.709315	0.340600	1.614407
25	1	0	-1.038648	0.703270	2.048588
26	1	0	-1.593285	-0.973320	2.057952
27	1	0	-3.357563	-0.654964	-0.508346
28	1	0	-2.387217	-2.076834	-0.107152
29	1	0	-2.151942	-1.238440	-1.672380

$(TMP)_2Zn$

HF= -2596.2999701

Sum of electronic and thermal Free Energies= -2595.832486

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.901060	-1.402829	0.358045
2	6	0	2.550450	-0.886849	0.918009
3	7	0	1.851541	-0.073388	-0.097408
4	6	0	2.575963	0.954160	-0.873807
5	6	0	3.924284	0.387591	-1.387438
6	6	0	4.738637	-0.294623	-0.285395
7	6	0	1.667335	-2.112493	1.221739
8	6	0	2.782010	-0.145581	2.262158
9	6	0	1.712221	1.303428	-2.101013
10	6	0	2.818016	2.273910	-0.093200

11	6	0	-3.900306	1.403547	0.358865
12	6	0	-2.549710	0.886892	0.918259
13	7	0	-1.851541	0.073357	-0.097648
14	6	0	-2.576697	-0.953845	-0.873821
15	6	0	-3.924957	-0.386632	-1.386864
16	6	0	-4.738600	0.295799	-0.284442
17	6	0	-1.665962	2.112103	1.221866
18	6	0	-2.781097	0.145472	2.262332
19	6	0	-1.713566	-1.303325	-2.101407
20	6	0	-2.819014	-2.273598	-0.093299
21	30	0	-0.000016	-0.000811	-0.049125
22	1	0	3.688615	-2.164881	-0.404711
23	1	0	4.462417	-1.899721	1.160465
24	1	0	4.503263	1.193670	-1.857470
25	1	0	3.710497	-0.353246	-2.170403
26	1	0	5.660263	-0.717014	-0.706073
27	1	0	5.054679	0.437088	0.469724
28	1	0	0.713739	-1.813328	1.683542
29	1	0	2.160860	-2.792782	1.925454
30	1	0	1.447867	-2.665940	0.301778
31	1	0	1.837712	0.279356	2.623214
32	1	0	3.498705	0.674155	2.171213
33	1	0	3.162402	-0.831735	3.030021
34	1	0	2.222876	2.020883	-2.753720
35	1	0	0.760012	1.767518	-1.801463
36	1	0	1.489775	0.402803	-2.683799
37	1	0	3.218567	3.053488	-0.754231
38	1	0	3.523904	2.151035	0.731849
39	1	0	1.874796	2.638776	0.330139
40	1	0	-3.687795	2.165637	-0.403833
41	1	0	-4.461149	1.900541	1.161579
42	1	0	-4.504468	-1.192395	-1.856779
43	1	0	-3.711154	0.354217	-2.169809
44	1	0	-5.660185	0.718660	-0.704740
45	1	0	-5.054717	-0.435849	0.470711
46	1	0	-0.712300	1.812477	1.683224
47	1	0	-2.158935	2.792453	1.925915

48	1	0	-1.446637	2.665633	0.301925
49	1	0	-1.836850	-0.279957	2.622948
50	1	0	-3.498193	-0.673928	2.171494
51	1	0	-3.160885	0.831649	3.030474
52	1	0	-2.224805	-2.020394	-2.754078
53	1	0	-0.761495	-1.767966	-1.802261
54	1	0	-1.490842	-0.402691	-2.684064
55	1	0	-3.220041	-3.052959	-0.754299
56	1	0	-3.524619	-2.150603	0.731977
57	1	0	-1.875798	-2.638869	0.329717

$(TMP)_3ZnLi$

HF= -3012.3973692

Sum of electronic and thermal Free Energies= -3011.679792

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.242381	1.619748	-0.120870
2	7	0	-2.116813	-0.013461	-0.021306
3	7	0	1.282099	-1.592846	0.127215
4	30	0	-0.165397	-0.005422	-0.006970
5	6	0	1.182325	-2.468045	1.346168
6	6	0	0.778460	-3.931589	1.017337
7	6	0	1.617129	-4.564603	-0.089937
8	6	0	1.528408	-3.683525	-1.332772
9	6	0	1.951367	-2.214563	-1.067652
10	6	0	-2.887113	-0.963678	-0.861475
11	6	0	-4.259213	-1.315400	-0.231167
12	6	0	-5.154434	-0.098327	0.061243
13	6	0	-4.318888	1.175001	0.273796
14	6	0	-2.896647	0.918248	0.833671
15	6	0	1.877272	2.258069	1.083826
16	6	0	1.430483	3.723221	1.333159

17	6	0	1.518315	4.598179	0.086003
18	6	0	0.704467	3.943759	-1.027454
19	6	0	1.143186	2.487834	-1.344835
20	6	0	3.512165	-2.169058	-0.972826
21	6	0	1.592945	-1.417814	-2.334972
22	6	0	0.081854	-1.926773	2.277994
23	6	0	2.495782	-2.500858	2.181908
24	6	0	3.440427	2.233483	1.021740
25	6	0	1.499393	1.463930	2.347078
26	6	0	0.068049	1.919836	-2.291188
27	6	0	2.468766	2.547282	-2.159691
28	6	0	-2.133180	-2.296837	-0.992975
29	6	0	-3.093862	-0.417601	-2.303242
30	6	0	-2.211899	2.294317	0.890055
31	6	0	-3.006198	0.393682	2.292836
32	3	0	2.357790	0.028406	0.012046
33	1	0	0.837606	-4.528942	1.936929
34	1	0	-0.272557	-3.940708	0.703097
35	1	0	1.250639	-5.574351	-0.315046
36	1	0	2.661393	-4.683889	0.229064
37	1	0	0.490868	-3.685719	-1.689857
38	1	0	2.142839	-4.090424	-2.147594
39	1	0	-4.060962	-1.858284	0.700795
40	1	0	-4.782286	-2.022260	-0.888497
41	1	0	-5.768762	-0.306467	0.945912
42	1	0	-5.860231	0.067681	-0.762097
43	1	0	-4.843749	1.865584	0.946818
44	1	0	-4.208288	1.707610	-0.677709
45	1	0	2.030959	4.144016	2.151295
46	1	0	0.389786	3.714318	1.680814
47	1	0	2.564019	4.734800	-0.221151
48	1	0	1.130970	5.602326	0.301048
49	1	0	0.762386	4.538354	-1.948884
50	1	0	-0.349975	3.932194	-0.725551
51	1	0	3.971506	-2.529716	-1.901509
52	1	0	3.907652	-2.768431	-0.152393
53	1	0	3.895031	-1.142320	-0.832071

54	1	0	1.946768	-0.382065	-2.288311
55	1	0	0.512390	-1.399597	-2.506457
56	1	0	2.061142	-1.870556	-3.216985
57	1	0	-0.874618	-1.840835	1.755630
58	1	0	-0.057570	-2.602675	3.130340
59	1	0	0.333480	-0.946133	2.691951
60	1	0	2.320744	-2.974952	3.156008
61	1	0	2.865220	-1.486062	2.375325
62	1	0	3.300674	-3.059607	1.697614
63	1	0	3.841604	1.211483	0.896702
64	1	0	3.875851	2.606414	1.957108
65	1	0	3.843416	2.833411	0.205117
66	1	0	1.932629	1.932506	3.238702
67	1	0	1.875394	0.435287	2.318784
68	1	0	0.414305	1.426401	2.485973
69	1	0	-0.074756	2.591809	-3.146136
70	1	0	-0.893251	1.812309	-1.781691
71	1	0	0.347437	0.944875	-2.701337
72	1	0	2.300116	3.019802	-3.135710
73	1	0	2.861891	1.540852	-2.349218
74	1	0	3.254477	3.120714	-1.661299
75	1	0	-1.118202	-2.147372	-1.369551
76	1	0	-2.649603	-2.973149	-1.685892
77	1	0	-2.055054	-2.795948	-0.022443
78	1	0	-3.617436	0.542369	-2.309461
79	1	0	-3.667256	-1.119742	-2.924397
80	1	0	-2.122462	-0.259708	-2.787133
81	1	0	-2.713248	2.956328	1.607796
82	1	0	-2.233931	2.777312	-0.092488
83	1	0	-1.164444	2.207013	1.187901
84	1	0	-3.580275	1.080577	2.930075
85	1	0	-2.007804	0.285504	2.733333
86	1	0	-3.487756	-0.587611	2.334685

$(TMP)_2Cd$

HF= -6283.9768305

Sum of electronic and thermal Free Energies= -6283.512388

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.177969	-1.366686	0.355633
2	6	0	2.805100	-0.891753	0.903485
3	7	0	2.091662	-0.110267	-0.122381
4	6	0	2.786672	0.948188	-0.878269
5	6	0	4.158089	0.427609	-1.385711
6	6	0	4.985177	-0.232926	-0.280480
7	6	0	1.966690	-2.148867	1.204951
8	6	0	3.005949	-0.147500	2.252295
9	6	0	1.929821	1.282154	-2.114763
10	6	0	2.984602	2.274031	-0.093107
11	6	0	-4.177396	1.367765	0.353827
12	6	0	-2.804695	0.893160	0.902395
13	7	0	-2.091556	0.109908	-0.122396
14	6	0	-2.787065	-0.949216	-0.876923
15	6	0	-4.158301	-0.428802	-1.385013
16	6	0	-4.985040	0.233325	-0.280518
17	6	0	-1.965918	2.150426	1.202067
18	6	0	-3.005922	0.150983	2.252305
19	6	0	-1.930414	-1.285249	-2.112993
20	6	0	-2.985561	-2.273907	-0.090015
21	48	0	0.000046	-0.000440	-0.005782
22	1	0	3.995555	-2.135341	-0.408018
23	1	0	4.748132	-1.844768	1.163272
24	1	0	4.714909	1.253883	-1.847446
25	1	0	3.972376	-0.315444	-2.173450
26	1	0	5.921841	-0.626331	-0.696244
27	1	0	5.274256	0.506357	0.477945
28	1	0	1.006022	-1.883297	1.674713

29	1	0	2.483781	-2.814084	1.906217
30	1	0	1.761620	-2.706402	0.284287
31	1	0	2.045065	0.240905	2.612709
32	1	0	3.692500	0.698281	2.167976
33	1	0	3.408025	-0.821818	3.019731
34	1	0	2.432123	2.010468	-2.761901
35	1	0	0.967383	1.733573	-1.824682
36	1	0	1.727855	0.378702	-2.700721
37	1	0	3.375161	3.064995	-0.746672
38	1	0	3.679732	2.168499	0.743174
39	1	0	2.025476	2.616449	0.315177
40	1	0	-3.994646	2.135154	-0.411005
41	1	0	-4.747394	1.847316	1.160720
42	1	0	-4.715412	-1.255501	-1.845642
43	1	0	-3.972466	0.313205	-2.173715
44	1	0	-5.921696	0.626355	-0.696653
45	1	0	-5.274088	-0.504881	0.478974
46	1	0	-1.005409	1.885245	1.672377
47	1	0	-2.482884	2.816880	1.902243
48	1	0	-1.760546	2.706451	0.280561
49	1	0	-2.045371	-0.237845	2.613146
50	1	0	-3.693306	-0.694238	2.169306
51	1	0	-3.407237	0.826746	3.018865
52	1	0	-2.433231	-2.013904	-2.759346
53	1	0	-0.968382	-1.737165	-1.822298
54	1	0	-1.727574	-0.382649	-2.699950
55	1	0	-3.375412	-3.065878	-0.742782
56	1	0	-3.681499	-2.167162	0.745440
57	1	0	-2.026751	-2.615542	0.319678

$(TMP)_3CdLi$

HF= -6700.0888456

Sum of electronic and thermal Free Energies= -6699.374671

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.444922	1.704716	0.132696
2	7	0	2.369779	-0.016983	0.020075
3	7	0	-1.488027	-1.671821	-0.134464
4	48	0	0.205722	-0.009195	0.004959
5	6	0	-1.403518	-2.520143	-1.368476
6	6	0	-0.931899	-3.973021	-1.084576
7	6	0	-1.679854	-4.650759	0.060353
8	6	0	-1.550617	-3.780661	1.307879
9	6	0	-2.057497	-2.333232	1.084592
10	6	0	3.119286	-1.019707	0.799739
11	6	0	4.490943	-1.334902	0.150440
12	6	0	5.380293	-0.094811	-0.064361
13	6	0	4.548842	1.193466	-0.213871
14	6	0	3.125448	0.964062	-0.782650
15	6	0	-1.991478	2.380472	-1.089089
16	6	0	-1.448789	3.815017	-1.309853
17	6	0	-1.559641	4.687898	-0.062554
18	6	0	-0.831088	3.991248	1.083495
19	6	0	-1.341354	2.551263	1.366631
20	6	0	-3.618706	-2.349861	1.080601
21	6	0	-1.656336	-1.524902	2.331109
22	6	0	-0.358365	-1.929093	-2.336058
23	6	0	-2.747653	-2.567198	-2.150061
24	6	0	-3.551867	2.435886	-1.093951
25	6	0	-1.601909	1.562641	-2.333176
26	6	0	-0.313945	1.933273	2.336454
27	6	0	-2.685747	2.633620	2.144465
28	6	0	2.336646	-2.344489	0.840599

29	6	0	3.323896	-0.567373	2.274228
30	6	0	2.413785	2.329457	-0.748335
31	6	0	3.223192	0.530165	-2.272760
32	3	0	-2.460610	0.031238	-0.005589
33	1	0	-1.017631	-4.561966	-2.007451
34	1	0	0.135219	-3.944172	-0.827100
35	1	0	-1.262429	-5.648248	0.248321
36	1	0	-2.735822	-4.805829	-0.198714
37	1	0	-0.491584	-3.736886	1.595718
38	1	0	-2.090498	-4.225173	2.155165
39	1	0	4.292967	-1.817874	-0.814154
40	1	0	5.020066	-2.078127	0.761367
41	1	0	6.005476	-0.250935	-0.952076
42	1	0	6.076673	0.025290	0.774810
43	1	0	5.079396	1.913920	-0.850116
44	1	0	4.437883	1.676077	0.764185
45	1	0	-1.974793	4.272847	-2.158800
46	1	0	-0.390343	3.745146	-1.594539
47	1	0	-2.612050	4.869765	0.194043
48	1	0	-1.116802	5.674543	-0.249698
49	1	0	-0.902721	4.582334	2.006198
50	1	0	0.235207	3.934467	0.827319
51	1	0	-4.012402	-2.710556	2.039388
52	1	0	-4.036521	-2.980866	0.294945
53	1	0	-4.032523	-1.338191	0.934099
54	1	0	-2.063378	-0.506186	2.311827
55	1	0	-0.566722	-1.458468	2.430448
56	1	0	-2.041778	-1.997866	3.241974
57	1	0	0.638850	-1.906160	-1.882443
58	1	0	-0.285700	-2.544004	-3.241276
59	1	0	-0.619291	-0.918719	-2.663689
60	1	0	-2.620704	-3.059610	-3.122703
61	1	0	-3.116969	-1.551195	-2.341024
62	1	0	-3.531980	-3.109169	-1.616316
63	1	0	-3.992602	1.435647	-0.947032
64	1	0	-3.930972	2.803992	-2.055831
65	1	0	-3.957832	3.079478	-0.312175

66	1	0	-1.965988	2.046513	-3.247091
67	1	0	-2.036642	0.555279	-2.318873
68	1	0	-0.513506	1.466953	-2.421597
69	1	0	-0.229726	2.544194	3.243407
70	1	0	0.683483	1.887279	1.885555
71	1	0	-0.600731	0.928832	2.661086
72	1	0	-2.550691	3.132261	3.112830
73	1	0	-3.077016	1.627581	2.344204
74	1	0	-3.457340	3.186537	1.603545
75	1	0	1.338834	-2.205387	1.276029
76	1	0	2.853433	-3.095429	1.451604
77	1	0	2.207831	-2.749717	-0.168703
78	1	0	3.888820	0.366680	2.339613
79	1	0	3.854262	-1.325791	2.867281
80	1	0	2.348969	-0.391535	2.746210
81	1	0	2.924446	3.064067	-1.384206
82	1	0	2.381069	2.721187	0.274232
83	1	0	1.379826	2.252033	-1.106621
84	1	0	3.754472	1.272457	-2.884985
85	1	0	2.216373	0.407387	-2.692245
86	1	0	3.739065	-0.428295	-2.380240
