Electronic Supplementary Material (ESI) for ChemComm.

Copper-catalyzed Aerobic Oxidative Cleavage of C-C Bonds in Epoxides Leading to Aryl Nitriles and Aryl Aldehydes

Lijun Gu, *[a] and Cheng Jin [b]

[a] Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission & Ministry of Education, Yunnan Minzu University, Kunming, Yunnan, 650500, China

[b] New United Group Company Limited, Changzhou, Jiangsu, 213166, China

Supporting Information

List of Contents

(A) Materials and equipment

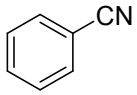
Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. ^{1}H NMR spectra were recorded on a Bruker-400 NMR spectrometer using TMS as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (J) were measured in Hz. GC-MS analyses were performed on a SHIMADZU QP2010. High Resolution mass spectrometer (HRMS) spectra were recorded on a Bruker micrOTOF-Q II analyzer. 200-300 mesh silica gel was used for column chromatography.

(B) Typical experimental procedure

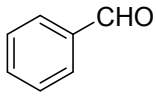
Typical Experimental Procedure for the Synthesis of ketones

An oven-dried Schlenk tube was charged with a magnetic stir-bar, 2,3-diaryloxiranes **1** (0.3 mmol), NaN_3 (0.40 mmol), $CuCl_2 \cdot 2H_2O$ (10 mol%), DMF (2.0 mL), The tube was sealed, and oxygen was purged through syringe. Reaction was stirred at 100 ˚C for 10 h. After the reaction was finished, the reaction mixture was diluted in 30 mL ethyl acetate, filtered on celite pad. The organic portion was washed with a saturated solution of brine (8 mL×3), dried (Na_2SO_4) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **2** and **3**.

(C) Analytical data

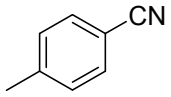


Benzonitrile 2a. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.65 (d, J = 5.2 Hz, 2H), 7.60 (t, J = 5.2 Hz, 1H), 7.60 (t, J = 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 132.6, 132.0, 129.0, 118.5, 112.4; LRMS (EI 70 ev): *m/z* (%): 103 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_6N $(M+H)^+$ 104.0523, found 104.0520; Known compound.[1]

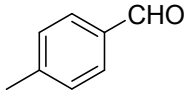


Benzaldehyde 3a. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 10.01 (s, 1H), 7.89 (dd, J = 1.2 Hz, J = 1.6 Hz, 2H), 7.65-7.61 (m, 1H), 7.55 (t, J = 7.6 Hz, 2H); ^{13}C NMR

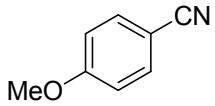
(100 MHz, $CDCl_3$, ppm): δ 192.4, 136.3, 134.4, 129.7, 128.9; LRMS (EI 70 ev) *m/z* (%): 106 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_7O $(M+H)^+$ 107.0491, found 107.0486; Known compound.[2]



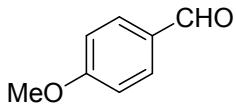
4-Methylbenzonitrile 2b. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.56 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.2, 131.6, 129.6, 119.0, 109.5, 21.6; LRMS (EI 70 ev) *m/z* (%): 117 (M^+, 100); HRMS *m/z* (ESI) calcd for C_8H_8N $(M+H)^+$ 118.0679, found 118.0686; Known compound.[1]



4-Methylbenzaldehyde 3b. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.94 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.4, 145.1, 134.1, 129.9, 129.7, 21.5; LRMS (EI 70 ev) *m/z* (%): 120 (M^+, 100); HRMS *m/z* (ESI) calcd for C_8H_9O $(M+H)^+$ 121.0647, found 121.0649; Known compound.[3]

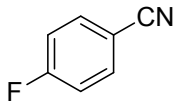


4-Methoxybenzonitrile 2c. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.60 (d, J = 9.2 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H); 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.7, 133.9, 119.2, 114.6, 103.8, 55.5; LRMS (EI 70 ev) *m/z* (%): 133 (M^+, 100); HRMS *m/z* (ESI) calcd for C_8H_8NO $(M+H)^+$ 134.0629, found 134.0621; Known compound.[1]

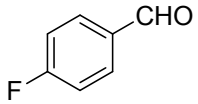


4-Methoxybenzaldehyde 3c. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.89 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H); 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.1, 164.0, 131.6, 129.3, 114.3, 55.3; LRMS (EI 70 ev) *m/z* (%): 136 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_8H_9O_2$ $(M+H)^+$ 137.0597, found 137.0590;

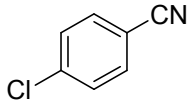
Known compound.[3]



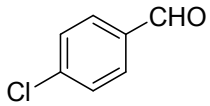
4-Fluorobenzonitrile 2d. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.71-7.68 (m, 2H), 7.21 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.8 (d, J = 253.4 Hz), 134.4 (d, J = 9.5 Hz), 118.1, 117.0 (d, J = 21.4 Hz), 108.5 (d, J = 4.7 Hz), LRMS (EI 70 ev) *m/z* (%): 121 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_5FN $(M+H)^+$ 122.0429, found 122.0422; Known compound.[1]



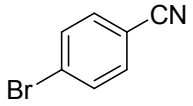
4-Fluorobenzaldehyde 3d. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.95 (s, 1H), 7.91-7.88 (m, 2H), 7.22-7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.5, 167.7 (d, J = 255.1 Hz), 132.8 (d, J = 2.6 Hz), 132.2 (d, J = 9.6 Hz), 116.4 (d, J = 22.2 Hz); LRMS (EI 70 ev) *m/z* (%): 124 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_6FO $(M+H)^+$ 125.0397, found 125.0395; Known compound.[3]



4-Chlorobenzonitrile 2e. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.63 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.5, 133.5, 130.0, 118.2, 110.6; LRMS (EI 70 ev) *m/z* (%): 137 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_5ClN $(M+H)^+$ 138.0133, found 138.0141; Known compound.[1]

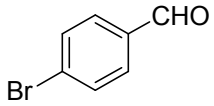


4-Chlorobenzaldehyde 3e. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.98 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.8, 140.9, 134.6, 130.9, 129.4; LRMS (EI 70 ev) *m/z* (%): 140 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_6ClO $(M+H)^+$ 141.0101, found 141.0110; Known compound.[3]

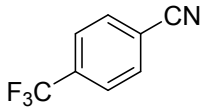


4-Bromobenzonitrile 2f. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.65-7.62 (m,

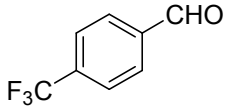
2H), 7.54-7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 133.3, 132.6, 128.0, 118.0, 111.1; LRMS (EI 70 ev) *m/z* (%): 183 $[M+1]^+$ (45), 181 (53); HRMS *m/z* (ESI) calcd for C_7H_5BrN $(M+H)^+$ 181.9629, found 181.9644; Known compound.[1]



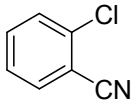
4-Bromobenzaldehyde 3f. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.99 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.6, 134.6, 132.1, 130.6, 129.4; LRMS (EI 70 ev) *m/z* (%): 186 $[M+1]^+$ (41), 183 (57); HRMS *m/z* (ESI) calcd for C_7H_6BrO $(M+H)^+$ 184.9597, found 184.9611; Known compound.[4]



4-(Trifluoromethyl)benzonitrile 2g. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.82 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 134.6, 134.3, 132.6, 126.2, 126.18, 126.15, 126.11, 124.3, 121.6, 117.4, 115.9; LRMS (EI 70 ev) *m/z* (%): 171 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_8H_5F_3N$ $(M+H)^+$ 172.0391, found 172.0399; Known compound.[1]

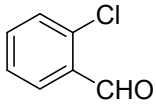


4-(Trifluoromethyl)benzaldehyde 3g. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 10.04 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 6.4 Hz, 2H), 7.74 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.0, 138.5, 135.8, 135.5, 135., 134.8, 129.7, 127.4, 125.95, 125.92, 124.7, 122.0, 119.2; LRMS (EI 70 ev) *m/z* (%): 174 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_8H_6F_3O$ $(M+H)^+$ 175.0359, found 175.0366; Known compound.[5]

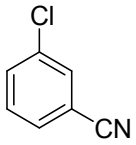


2-Chlorobenzonitrile 2h. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.69-7.66 (m, 1H), 7.57-7.50 (m, 2H), 7.40-7.36 (m, 1H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.8, 133.9, 133.8, 130.0, 127.1, 115.9, 113.3; LRMS (EI 70 ev) *m/z* (%): 137 (M^+,

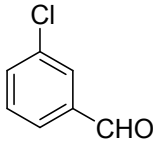
100); HRMS *m/z* (ESI) calcd for C_7H_5ClN $(M+H)^+$ 138.0133, found 138.0139; Known compound[1].



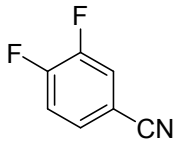
2-Chlorobenzaldehyde 3h. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 10.30 (s, 1H), 7.87 (dd, J = 3.6 Hz, J = 7.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.40-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 189.9, 137.6, 134.9, 132.6, 130.6, 129.1, 127.4; LRMS (EI 70 ev) *m/z* (%): 140 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_6ClO $(M+H)^+$ 141.0101, found 141.0112; Known compound[3].



3-Chlorobenzonitrile 2i. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.54 (s, 1H), 7.50-7.46 (m, 2H), 7.35 (t, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.6, 133.0, 131.5, 130.0, 129.8, 117.5, 114.1; LRMS (EI 70 ev) *m/z* (%): 137 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_5ClN $(M+H)^+$ 138.0133, found 138.0143; Known compound[1].

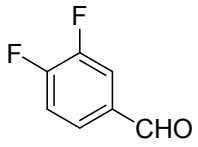


3-Chlorobenzaldehyde 3i. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.96 (s, 1H), 7.85-7.82 (m, 1H), 7.75-7.71 (m, 1H), 7.61-7.57 (m, 1H), 7.52 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.9, 137.6, 135.1, 134.0, 130.2, 129.2, 128.1; LRMS (EI 70 ev) *m/z* (%): 140 (M^+, 100); HRMS *m/z* (ESI) calcd for C_7H_6ClO $(M+H)^+$ 141.0101, found 141.0108; Known compound[3].

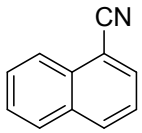


3,4-Difluorobenzonitrile 2j. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.53-7.50 (m, 1H), 7.49-7.45 (m, 1H), 7.33-7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.7, 154.6, 152.1, 152.0, 151.5, 151.4, 149.0. 148.9, 129.66, 129.62, 129.58, 129.54,

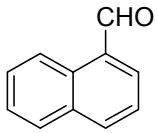
121.6, 121.48, 121.47, 118.9, 118.7, 116.8, 108.94, 108.90, 108.8; LRMS (EI 70 ev) *m/z* (%): 139 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_7H_4F_2N$ $(M+H)^+$ 140.0335, found 140.0343; Known compound.[7]



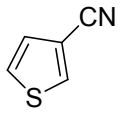
3,4-Difluorobenzaldehyde 3j. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.87 (s, 1H), 7.65-7.62 (m, 2H), 7.33-7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 189.4, 155.6, 155.5, 153.0, 152.9, 152.1, 151.9, 149.6, 149.4, 133.4, 133.37, 133.33, 127.29, 127.26, 127.22, 127.1, 118.0, 117.8, 117.4, 117.2; LRMS (EI 70 ev) *m/z* (%): 142 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_7H_5F_2O$ $(M+H)^+$ 143.0303, found 143.0311; Known compound.[6]



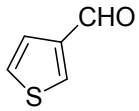
1-Naphthonitrile 2k. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 8.21 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.91-7.88 (m, 2H), 7.69-7.65 (m, 1H), 7.62-7.58 (m, 1H), 7.52 (dd, J = 3.6 Hz, J = 4.4 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 133.3, 132.8, 132.4, 132.3, 128.5, 128.4, 127.5, 124.9, 124.6, 117.5, 110.0; LRMS (EI 70 ev) *m/z* (%): 153 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_{11}H_8N$ $(M+H)^+$ 154.0680, found 154.0684; Known compound.[1]



1-Naphthaldehyde 3k. ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 10.32 (s, 1H), 9.13 (d, J = 6.4 Hz, 1H), 8.23 (d, J = 6.4 Hz, 1H), 8.15 (dd, J = 0.8 Hz, J = 5.2 Hz, 1H), 8.03 (d, J = 6.4 Hz, 1H), 7.73-7.66 (m, 2H), 7.63-7.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.9, 137.0, 135.4, 133.7, 131.3, 130.2, 129.4, 129.1, 127.6, 125.4, 124.3; LRMS (EI 70 ev) *m/z* (%): 156 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_{11}H_9O$ $(M+H)^+$ 157.0648, found 157.0645; Known compound.[5]



Thiophene-3-carbonitrile 2l. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 7.93-7.92 (m, 1H), 7.42-7.39 (m, 1H), 7.27-7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.2, 128.3, 127.1, 114.9, 110.1; LRMS (EI 70 ev) *m/z* (%): 109 (M^+, 100); HRMS *m/z* (ESI) calcd for C_5H_4NS $(M+H)^+$ 110.0086, found 110.0082; Known compound.[8]



Thiophene-3-carbaldehyde 3l. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ 9.91 (s, 1H), 8.12 (dd, J = 1.2 Hz, J = 1.2 Hz, 1H), 7.54 (dd, J = 0.8 Hz, J = 0.8 Hz, 1H), 7.37-7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 184.9, 142.9, 136.7, 127.3, 125.2; LRMS (EI 70 ev) *m/z* (%): 112 (M^+, 100); HRMS *m/z* (ESI) calcd for C_5H_4NS $(M+H)^+$ 113.0054, found 113.0056; Known compound.[4]

(D) References

1. Yu, L.; Li, H.; Zhang, X.; Ye, J.; Liu, J.; Xu, Q.; Lautens, M. *Org. lett*. **2014**, *16*, 1346-1349.

2. Yuan, Y.; Shi, X.; Liu, W. *Synlett*. **2011**, 559-564.

3. Wang, X.; Liu, R.; Jin, Y.; Liang, X. *Chem*. *Eur*. *J*. **2008**, *14*, 2679-2685.

4. Yu B.; Zhao Y.; Zhang H.; Xu J.; Hao L.; Gao X.; Liu Z. *Chem*. *Commun*. **2014**, *50*, 2330-2333.

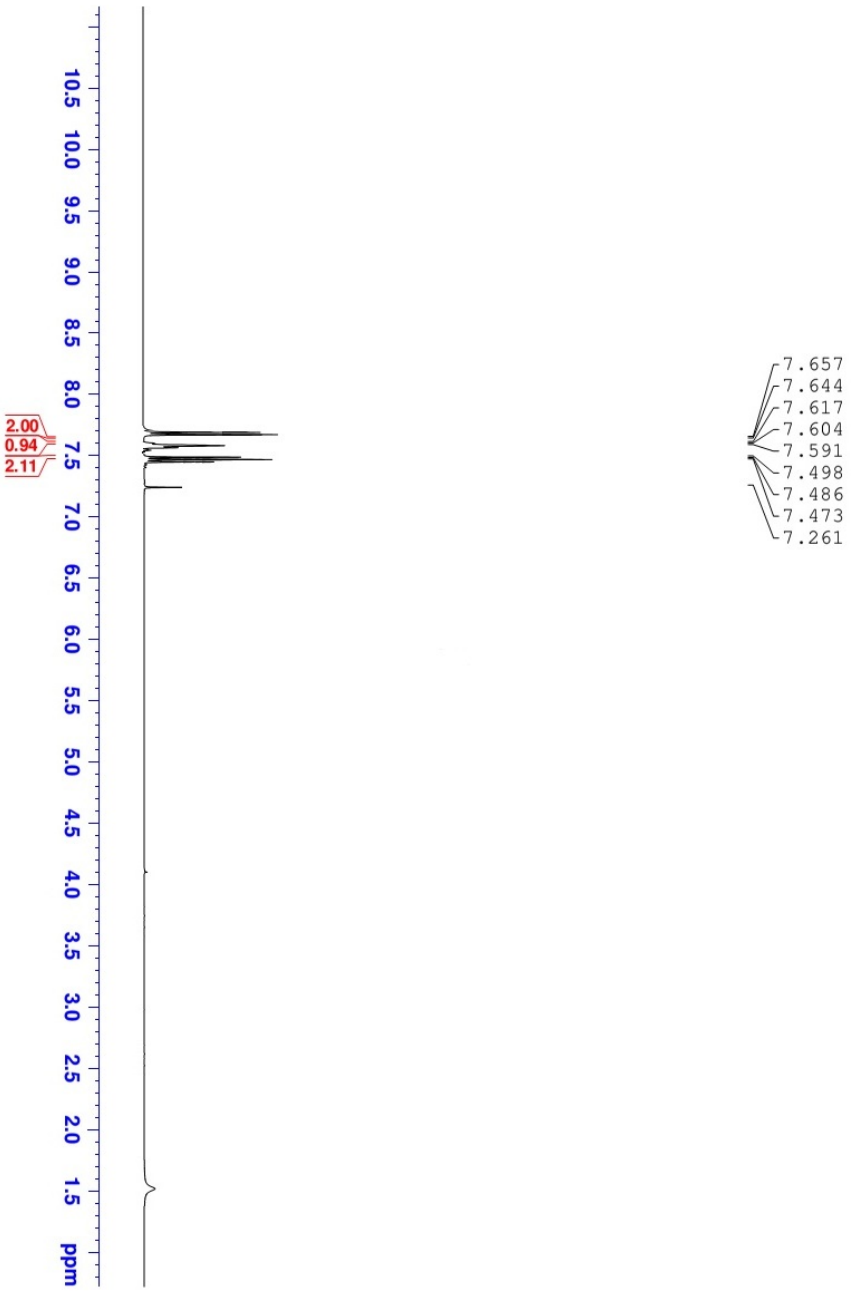
5. Shaikh, T. M. A.; Emmanuvel, L.; Sudalai, A. *J*. *Org*. *Chem*. **2006**, *71*, 5043-5046.

6. Lee, S. H.; Nikonov, G. I. *Dalton Trans*. **2014**, *43*, 8888-8893.

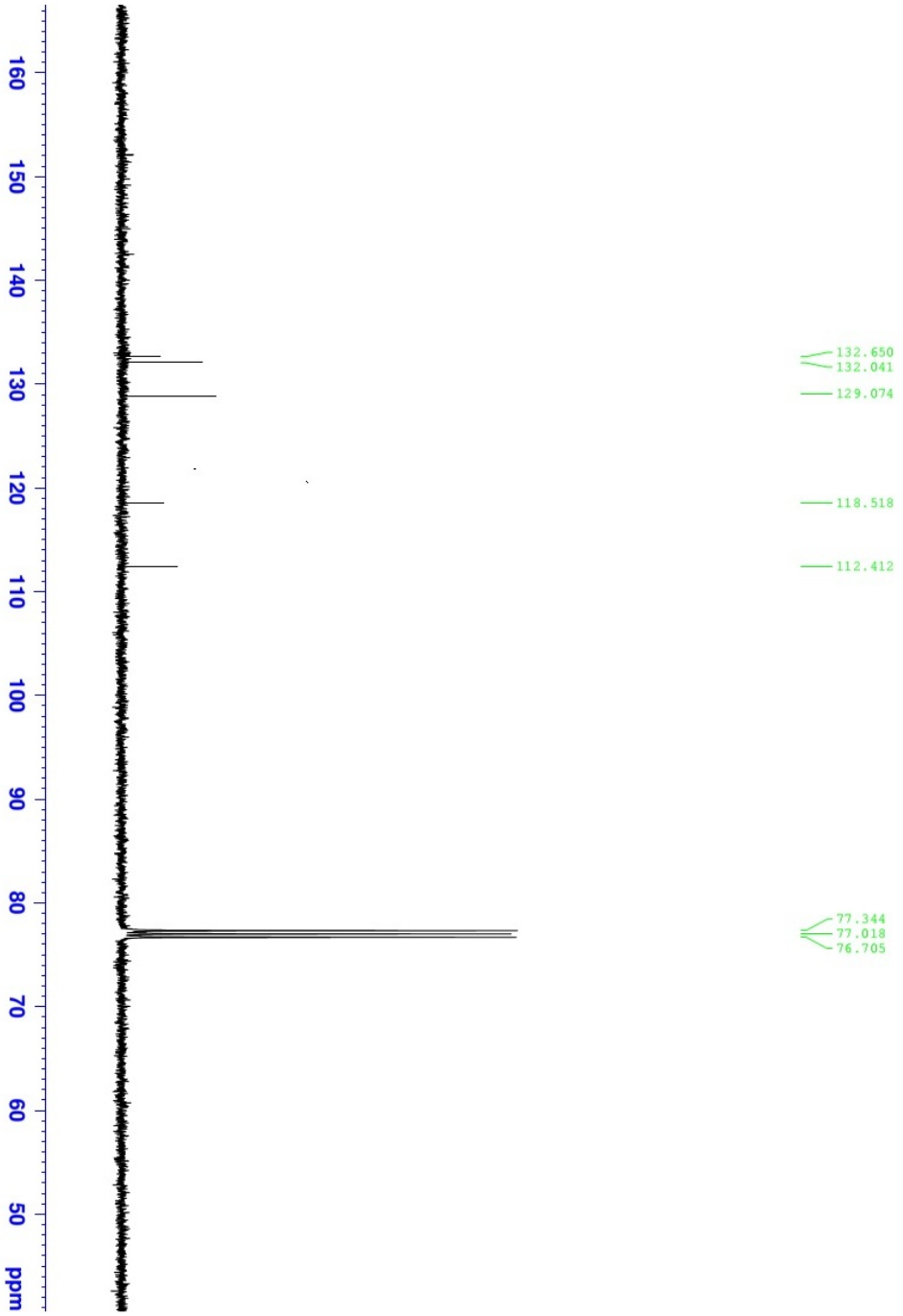
7. Liu, J.; Xu, J.; Ren, J.; Zeng, B. *Chem*. *Lett*. **2014**, *43*, 190-192.

8. Zhang, Z.; Liebeskind, L. S. Org. lett. **2006**, *8*, 4331-4333.

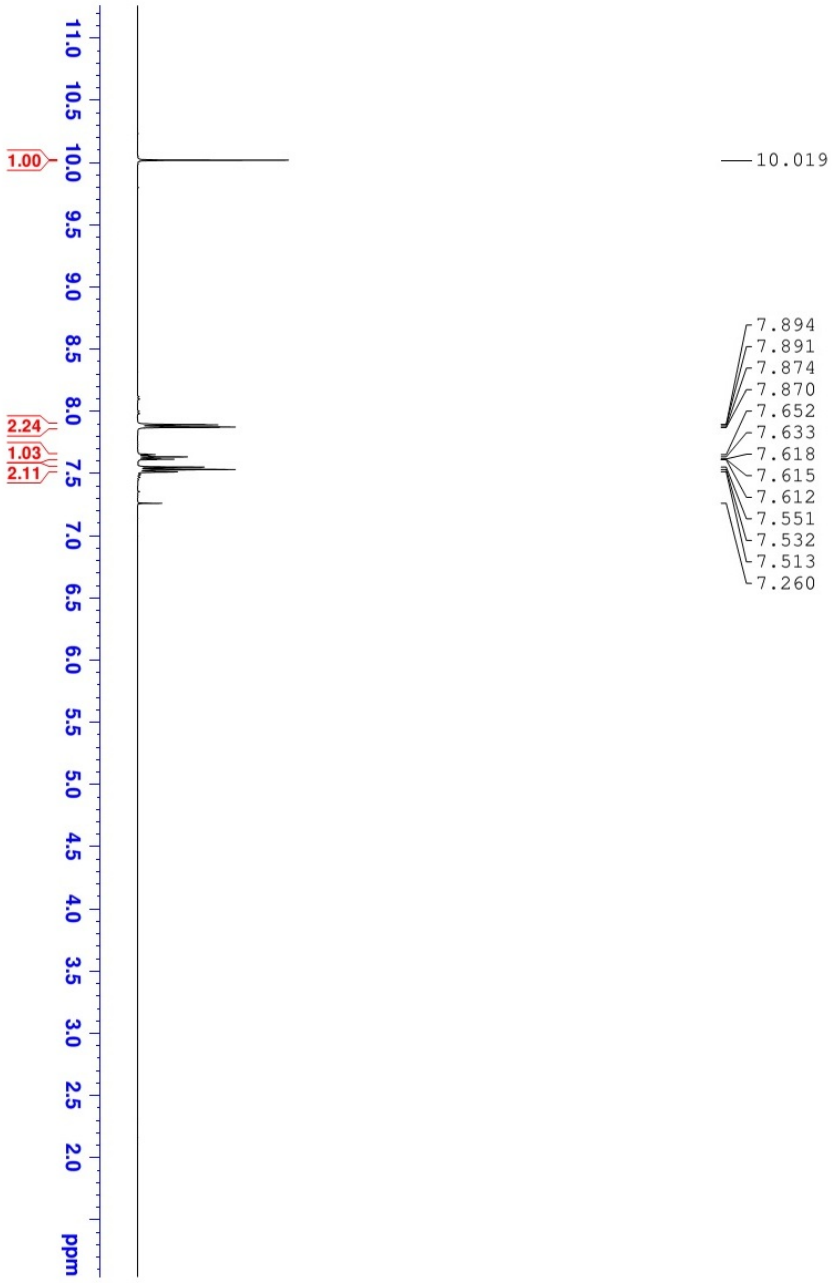
(E) Spectra



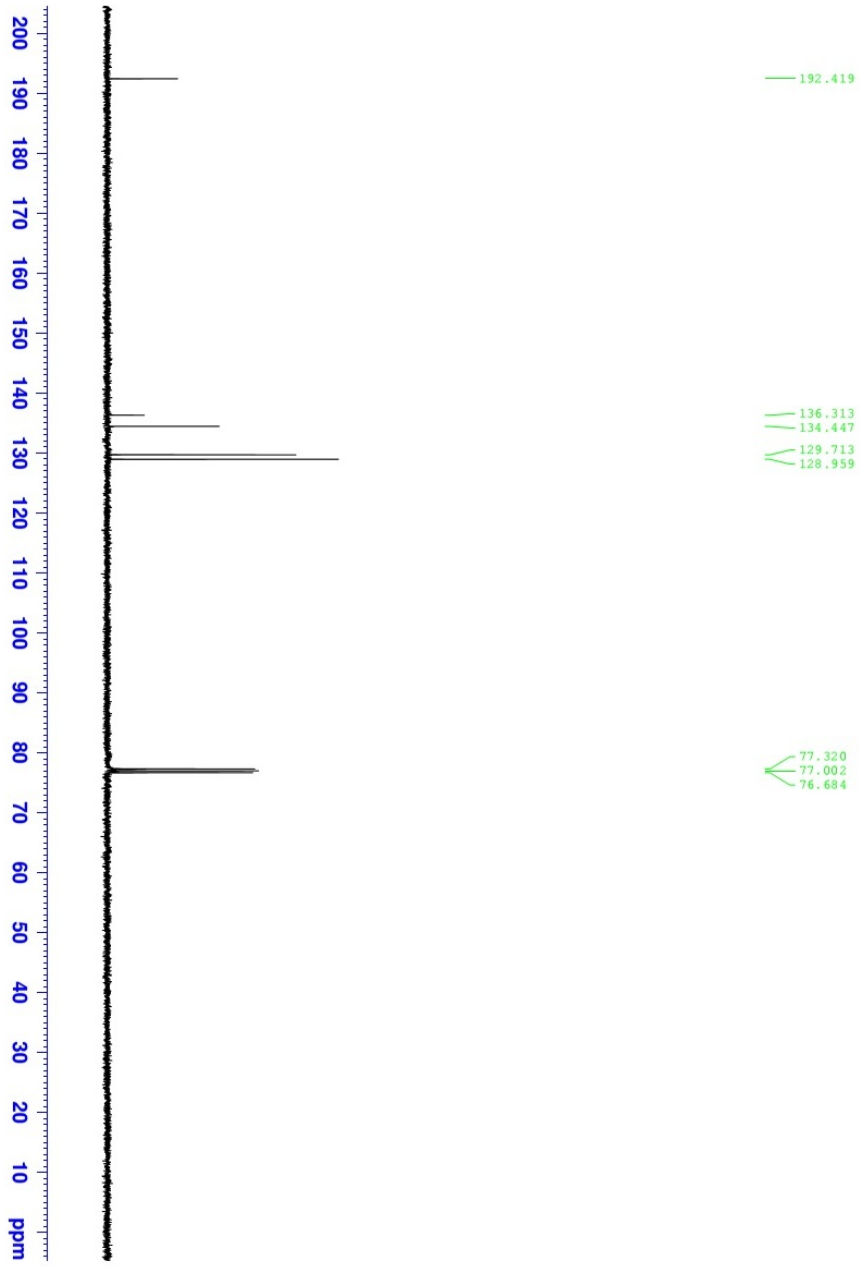
^{1}H NMR of Compound 2a



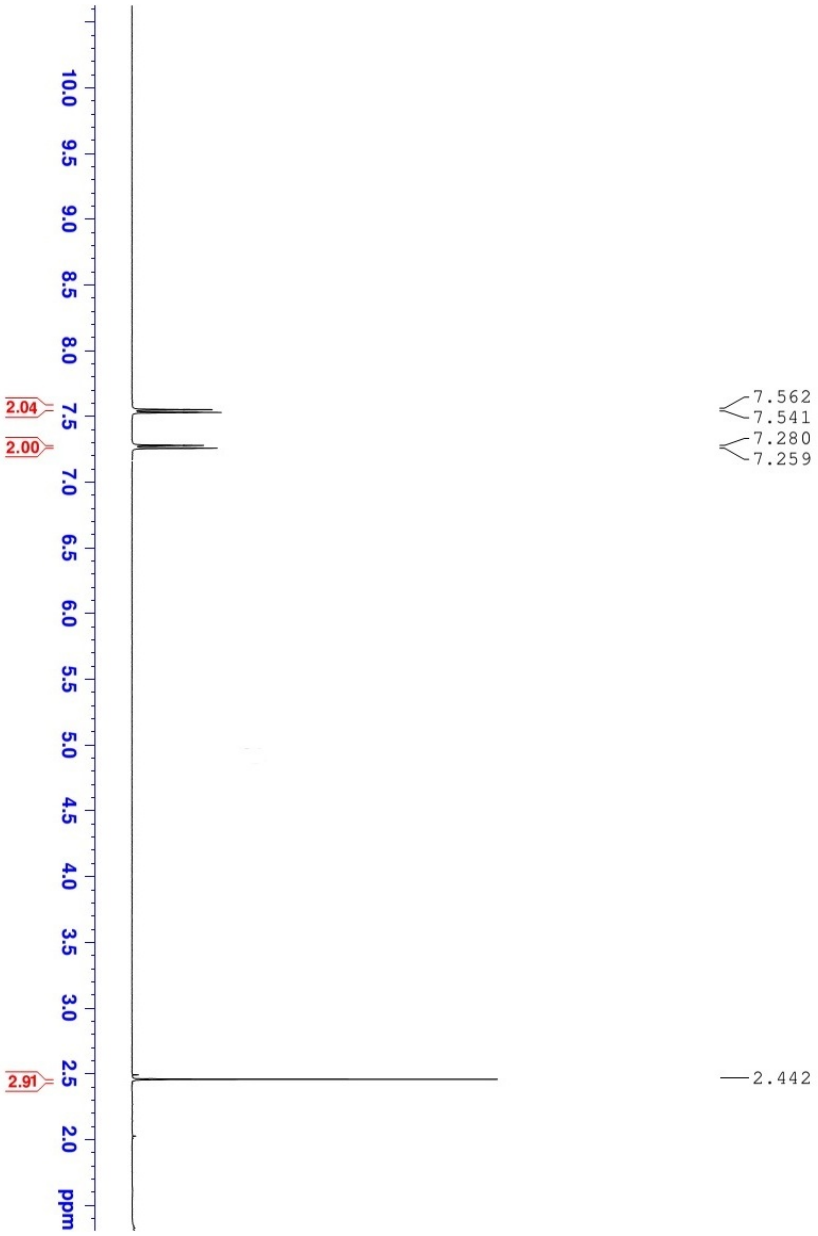
^{13}C NMR of Compound 2a



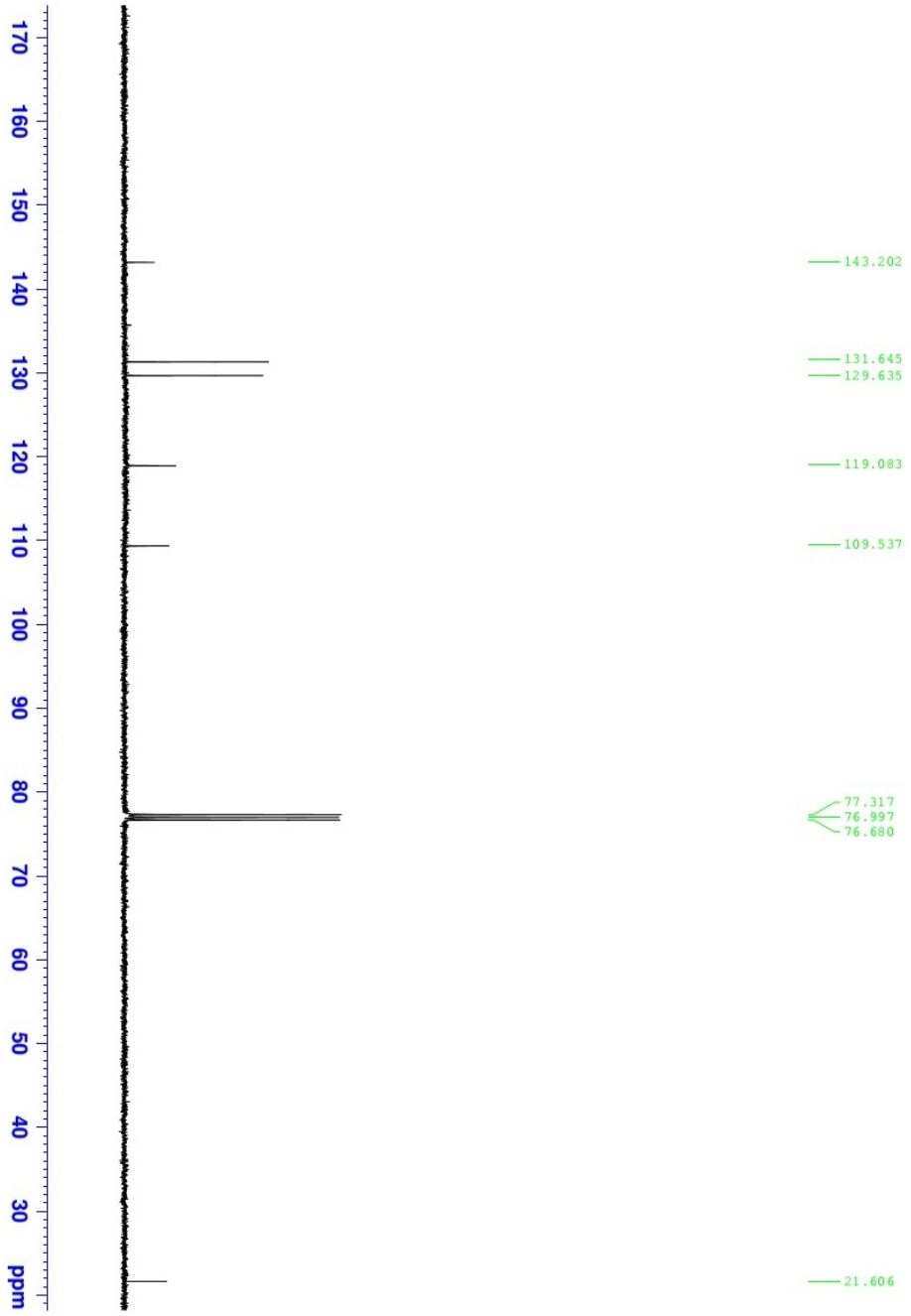
^{1}H NMR of Compound 3a



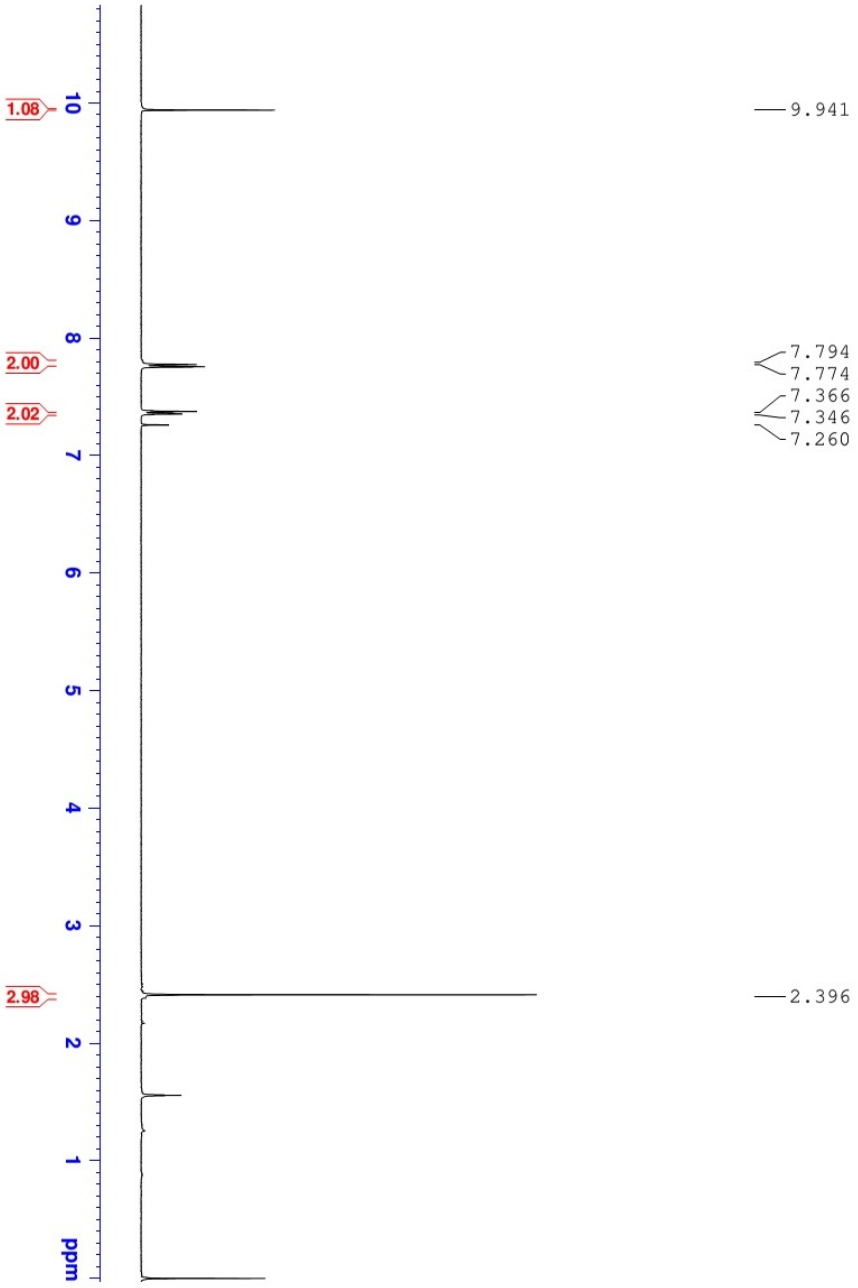
^{13}C NMR of Compound 3a



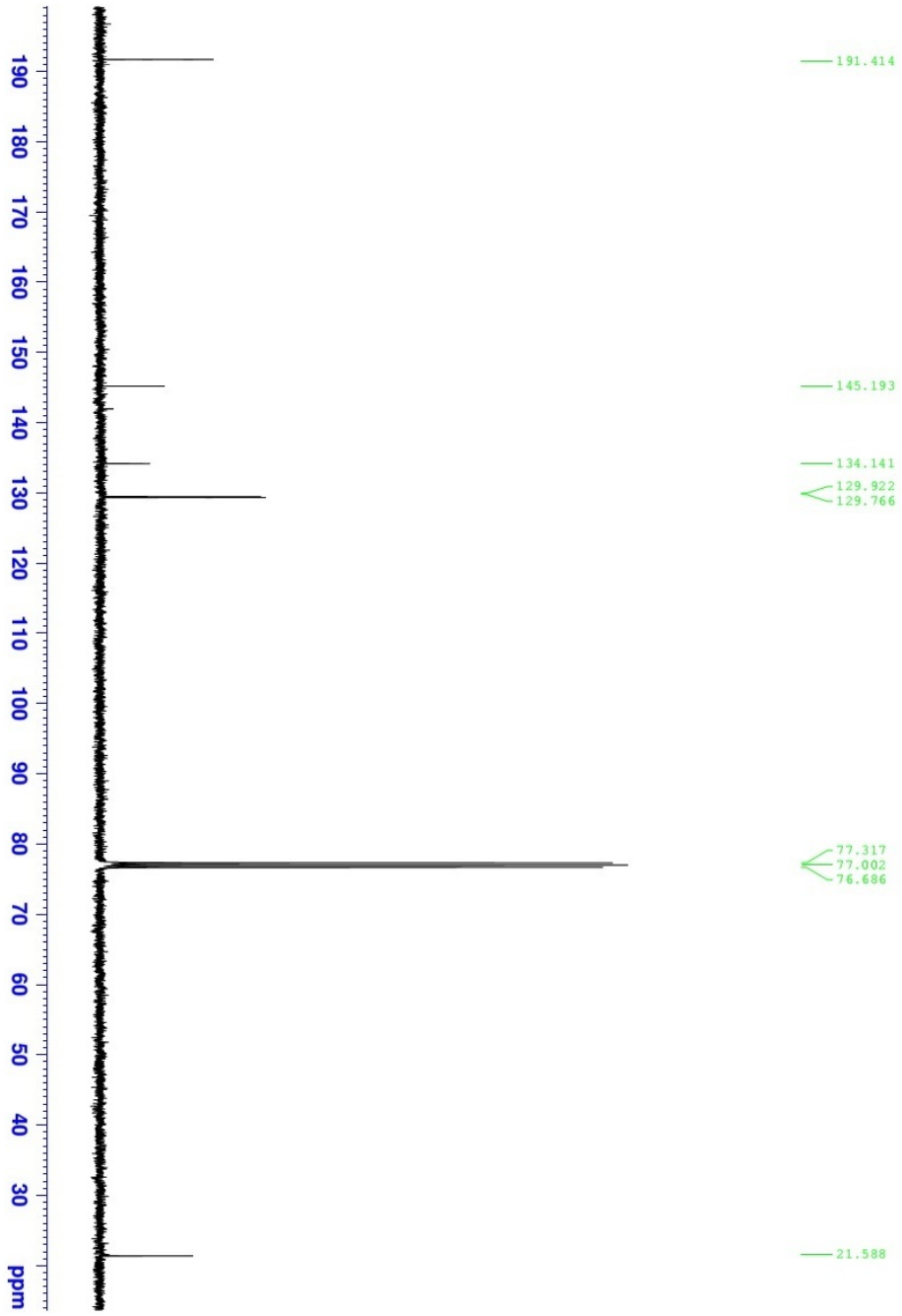
[1]H NMR of Compound 2b



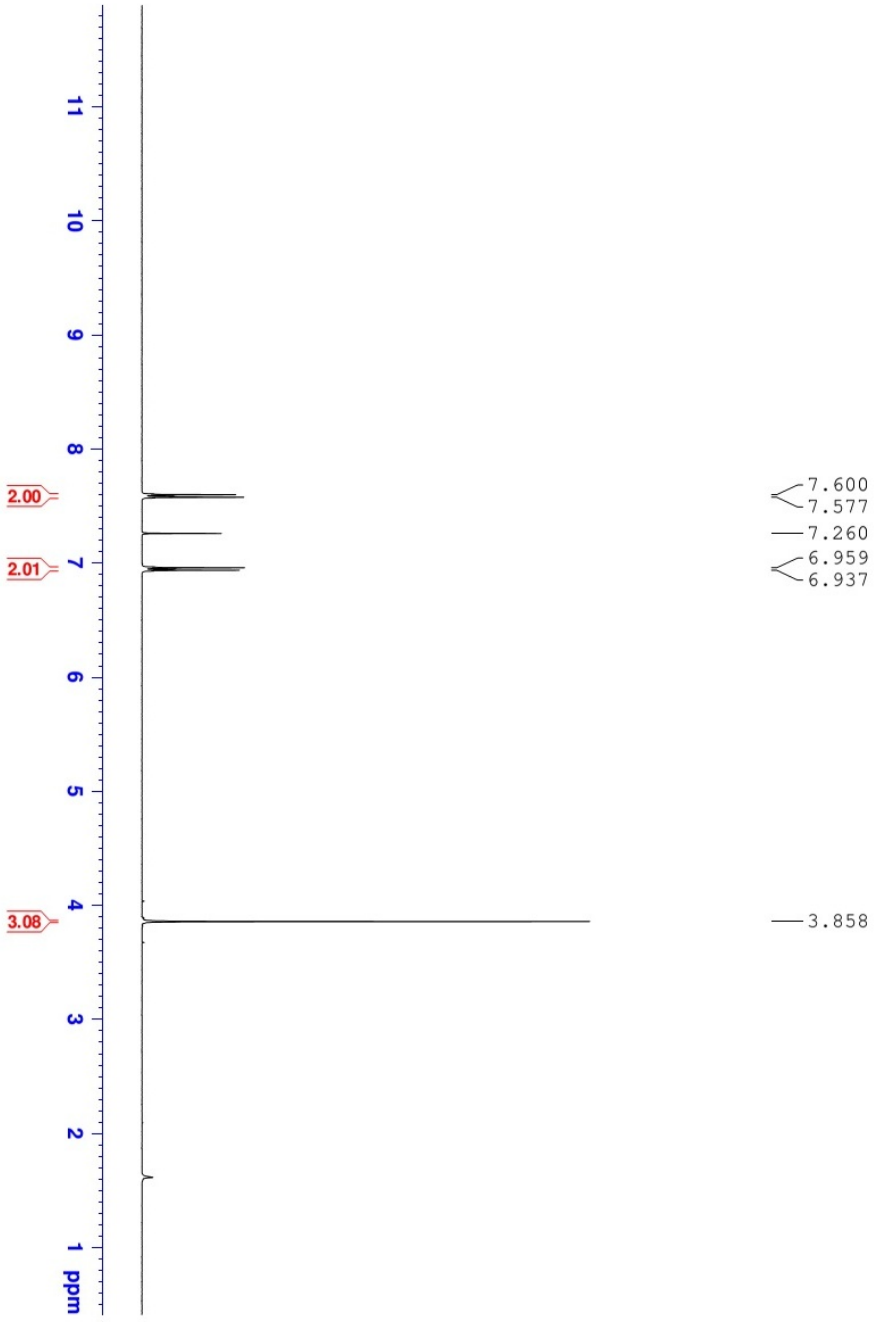
^{13}C NMR of Compound 2b



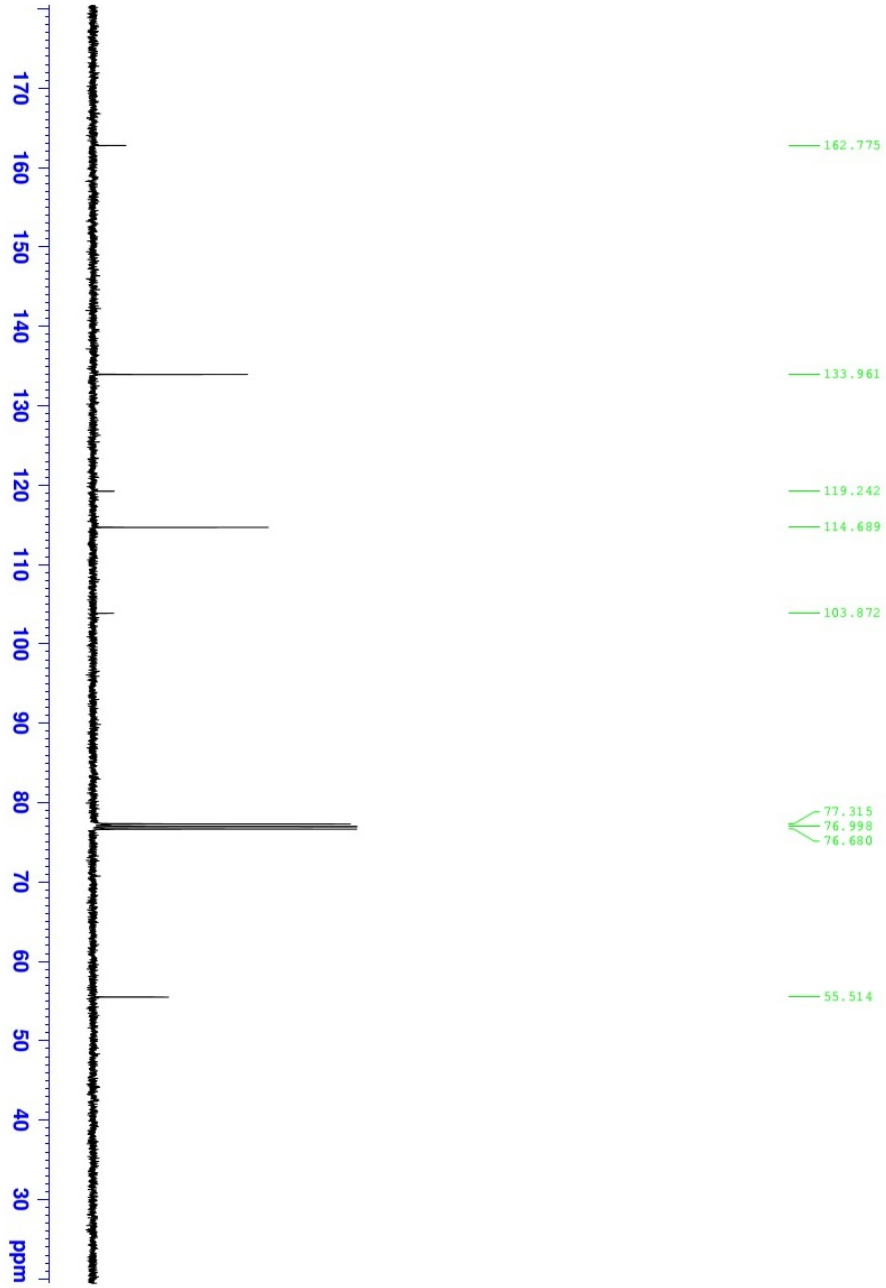
^{1}H NMR of Compound 3b



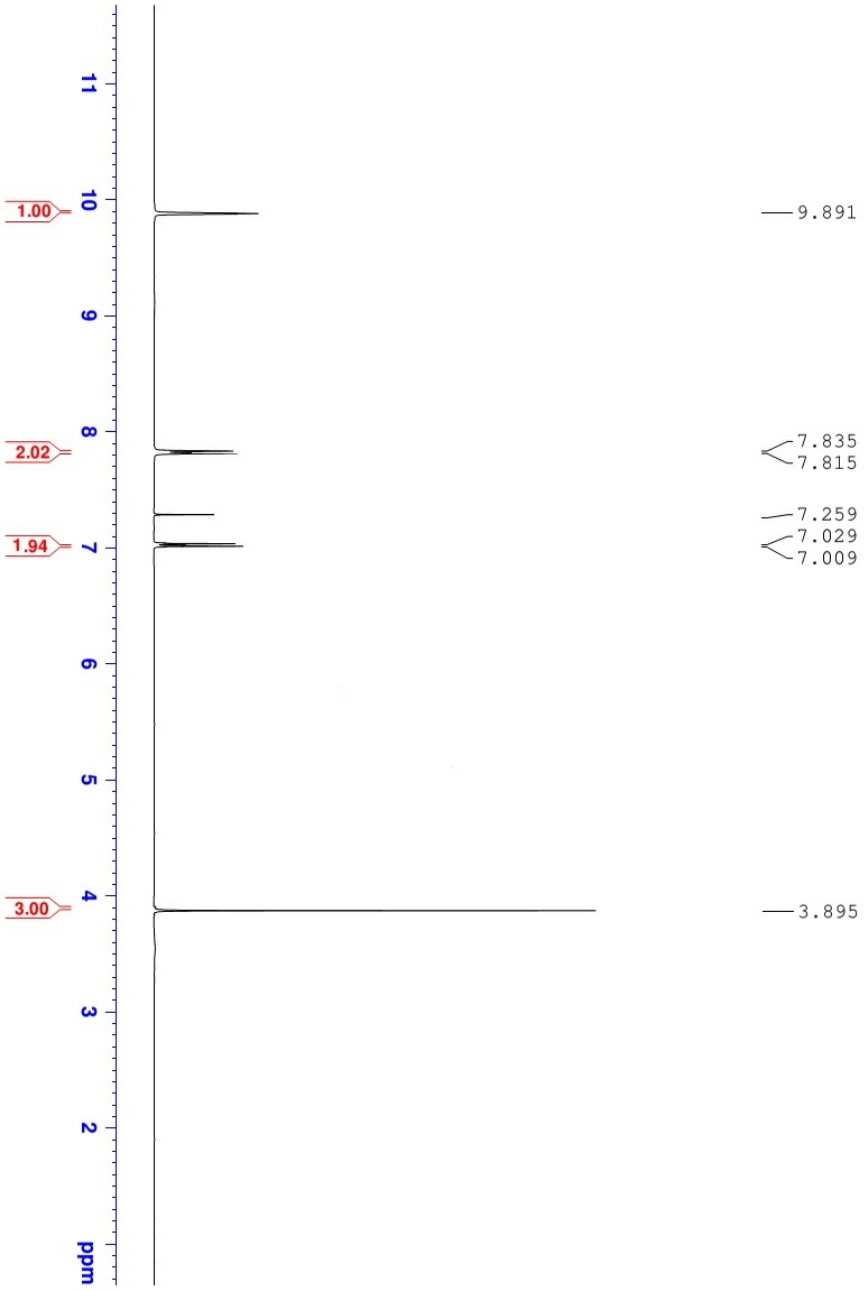
^{13}C NMR of Compound 3b



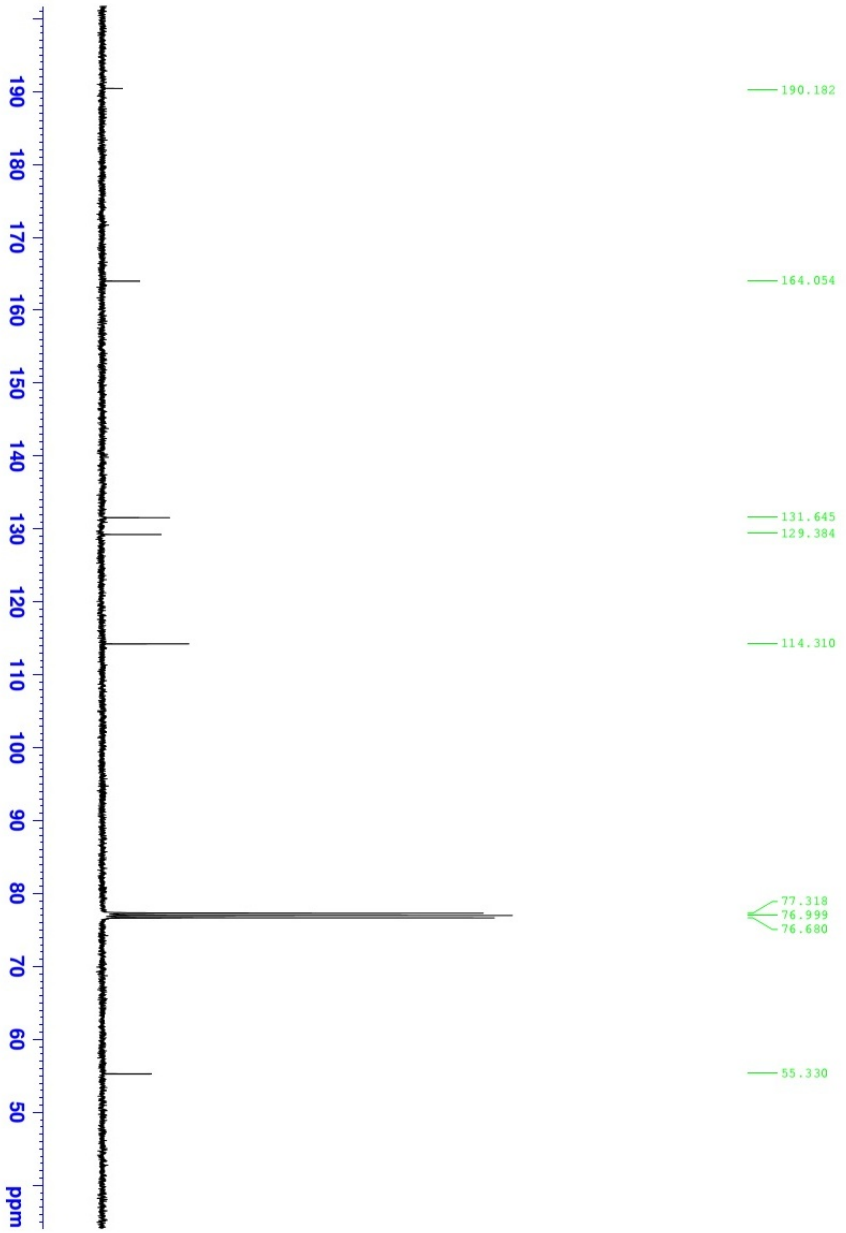
^{1}H NMR of Compound 2c



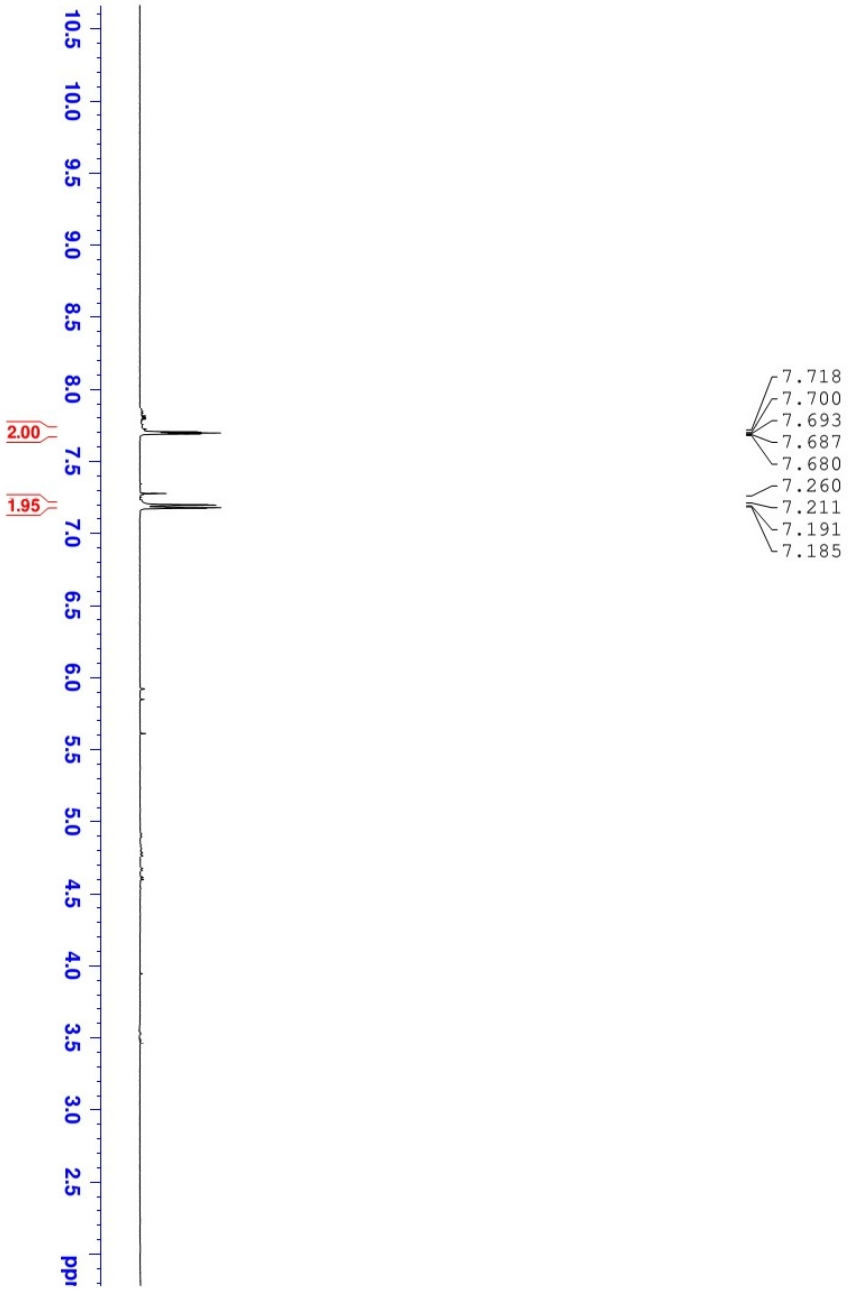
^{13}C NMR of Compound 2c



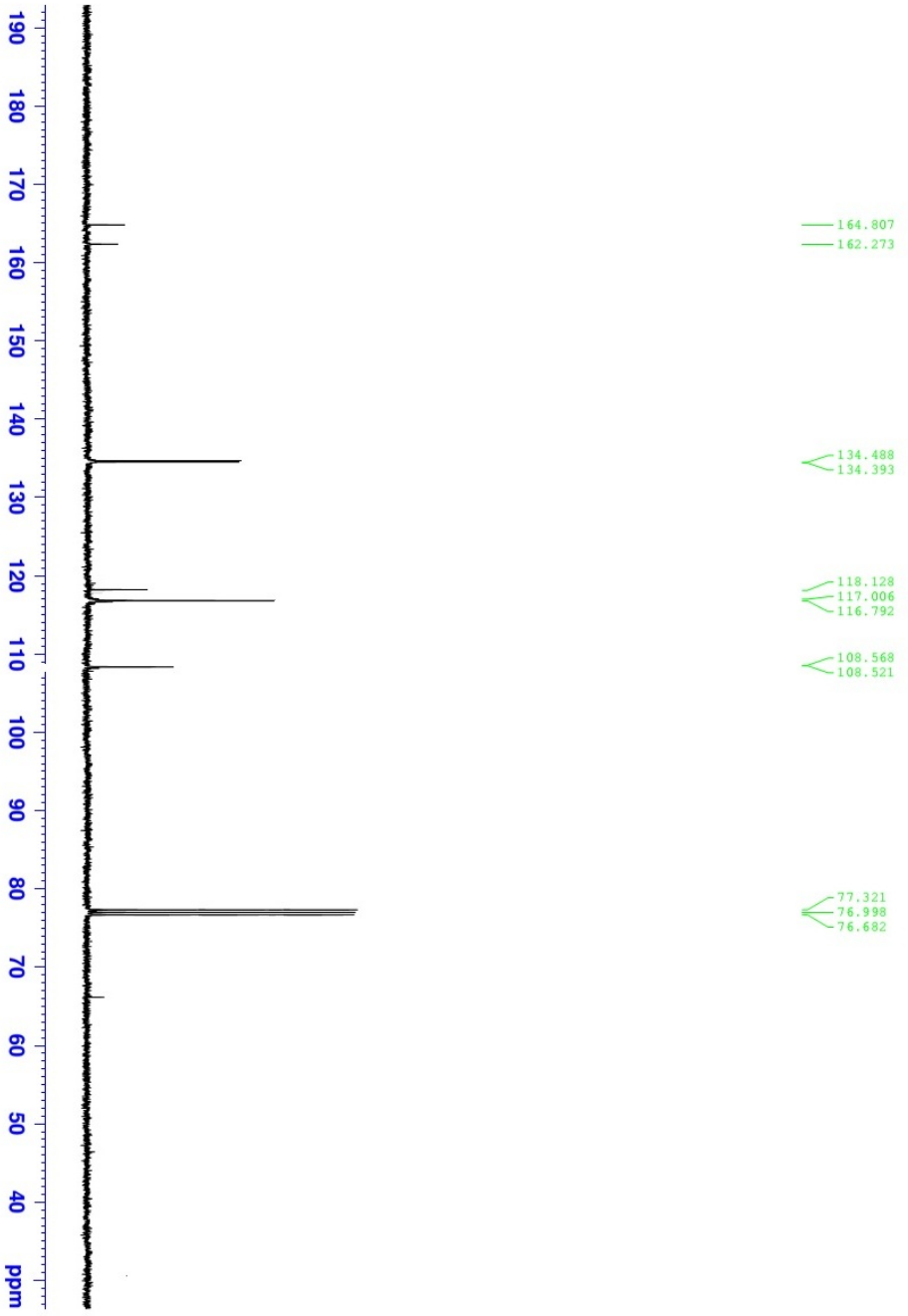
^{1}H NMR of Compound 3c



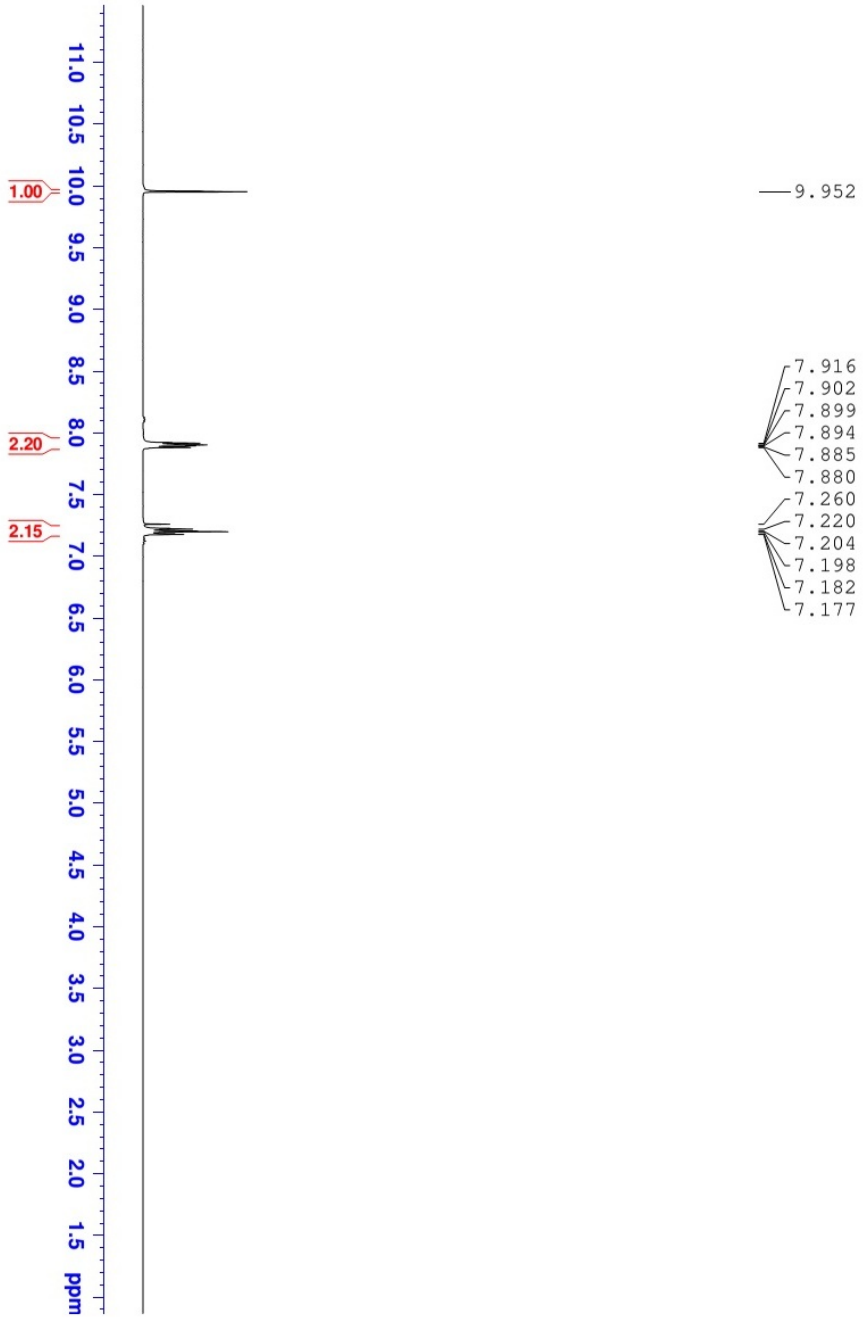
^{13}C NMR of Compound 3c



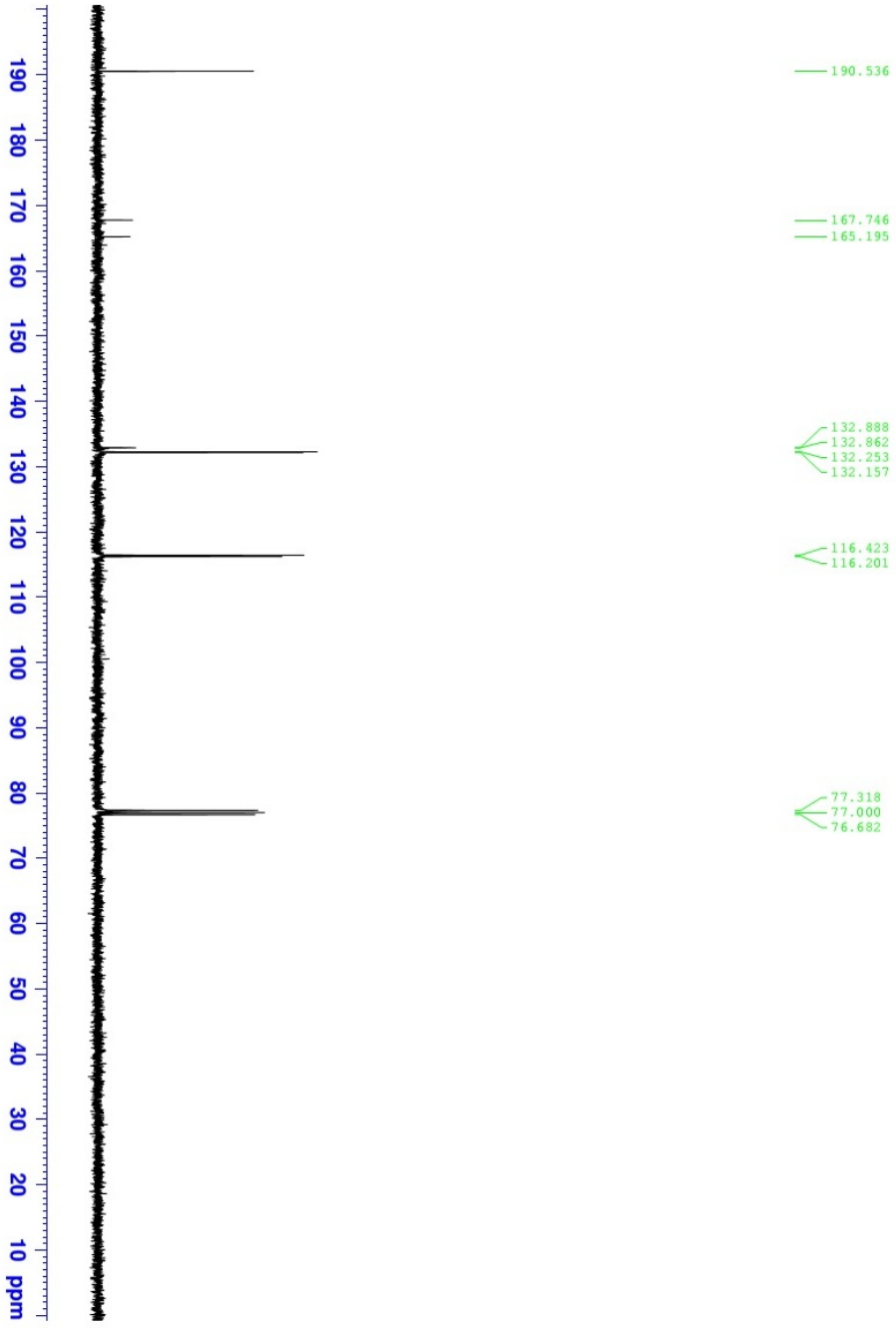
^{1}H NMR of Compound 2d



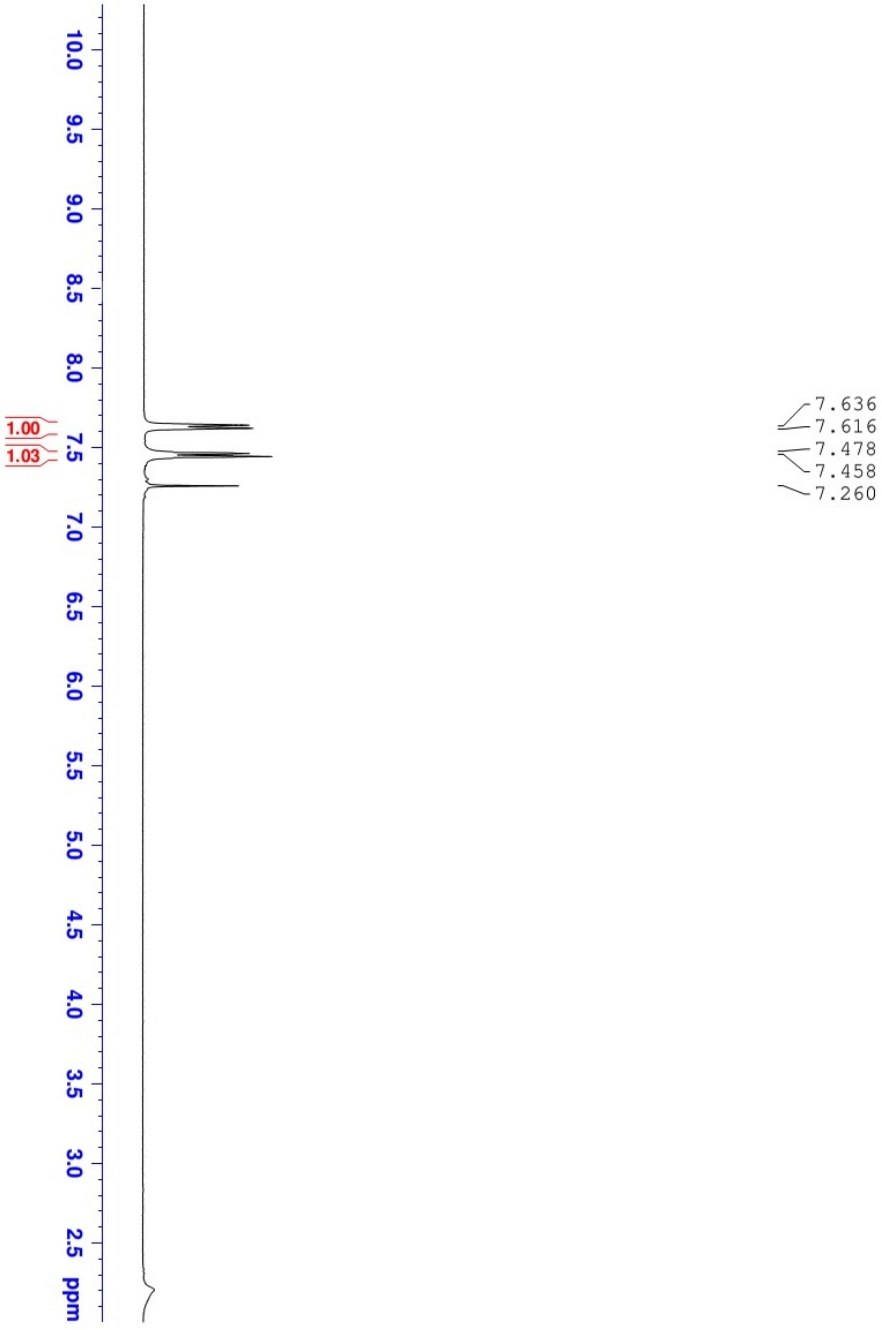
^{13}C NMR of Compound 2d



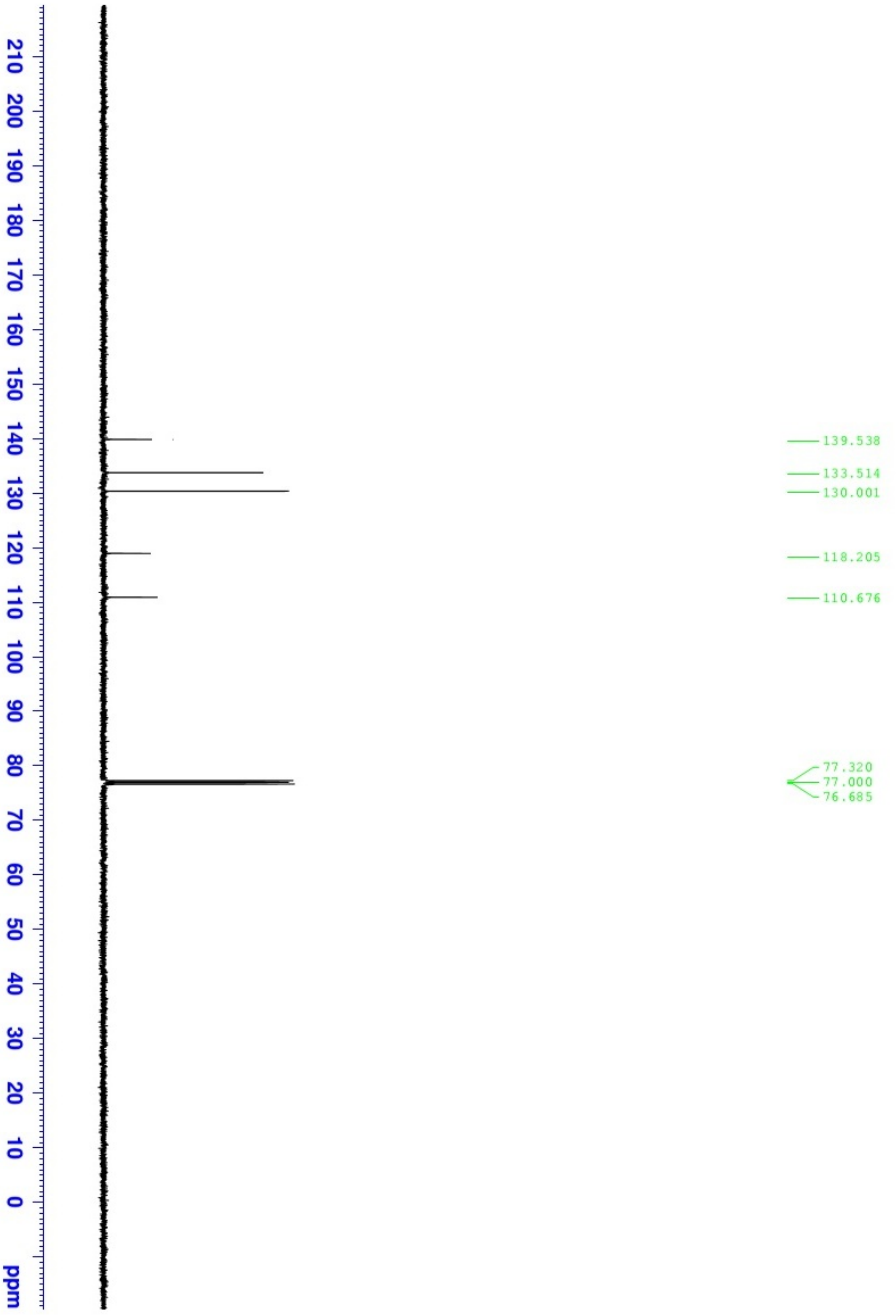
^{1}H NMR of Compound 3d



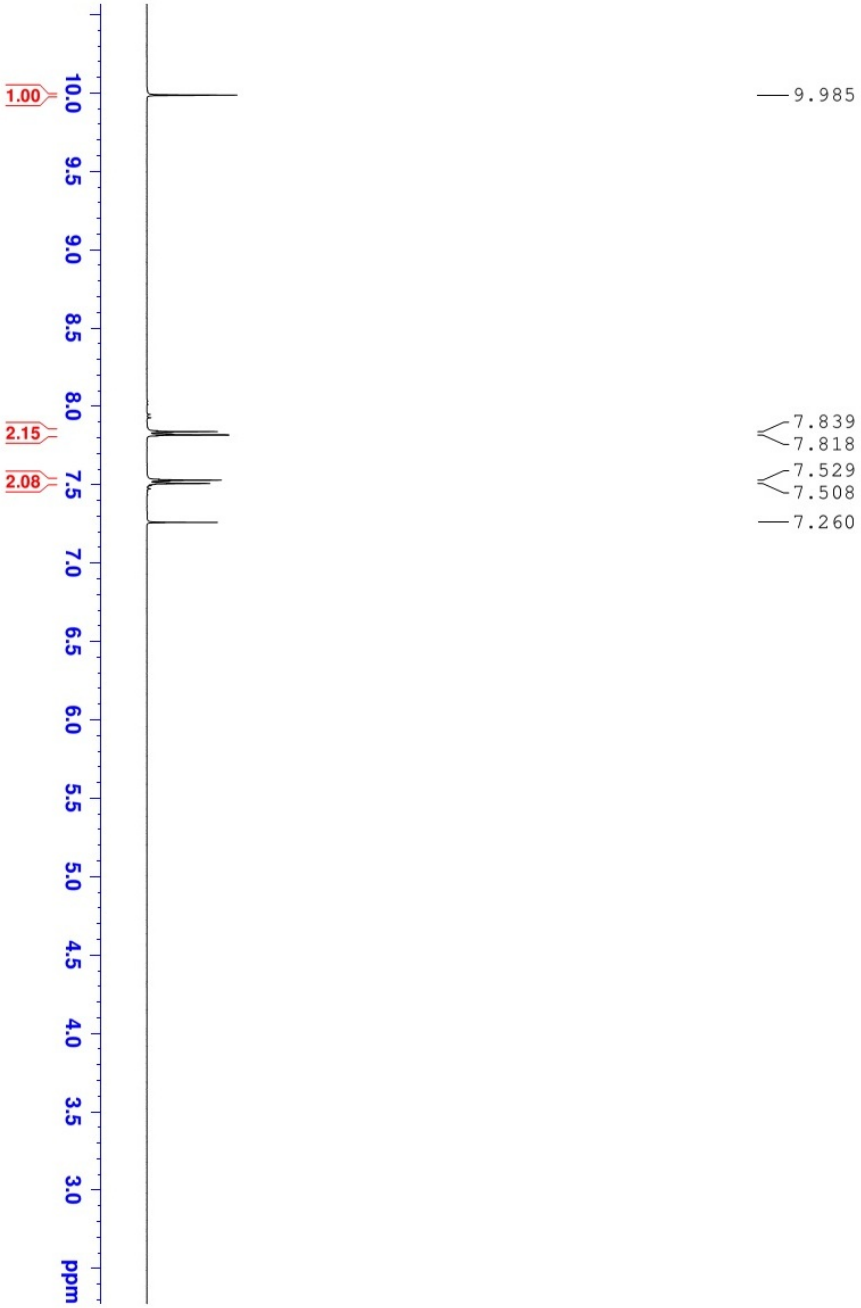
^{13}C NMR of Compound 3d



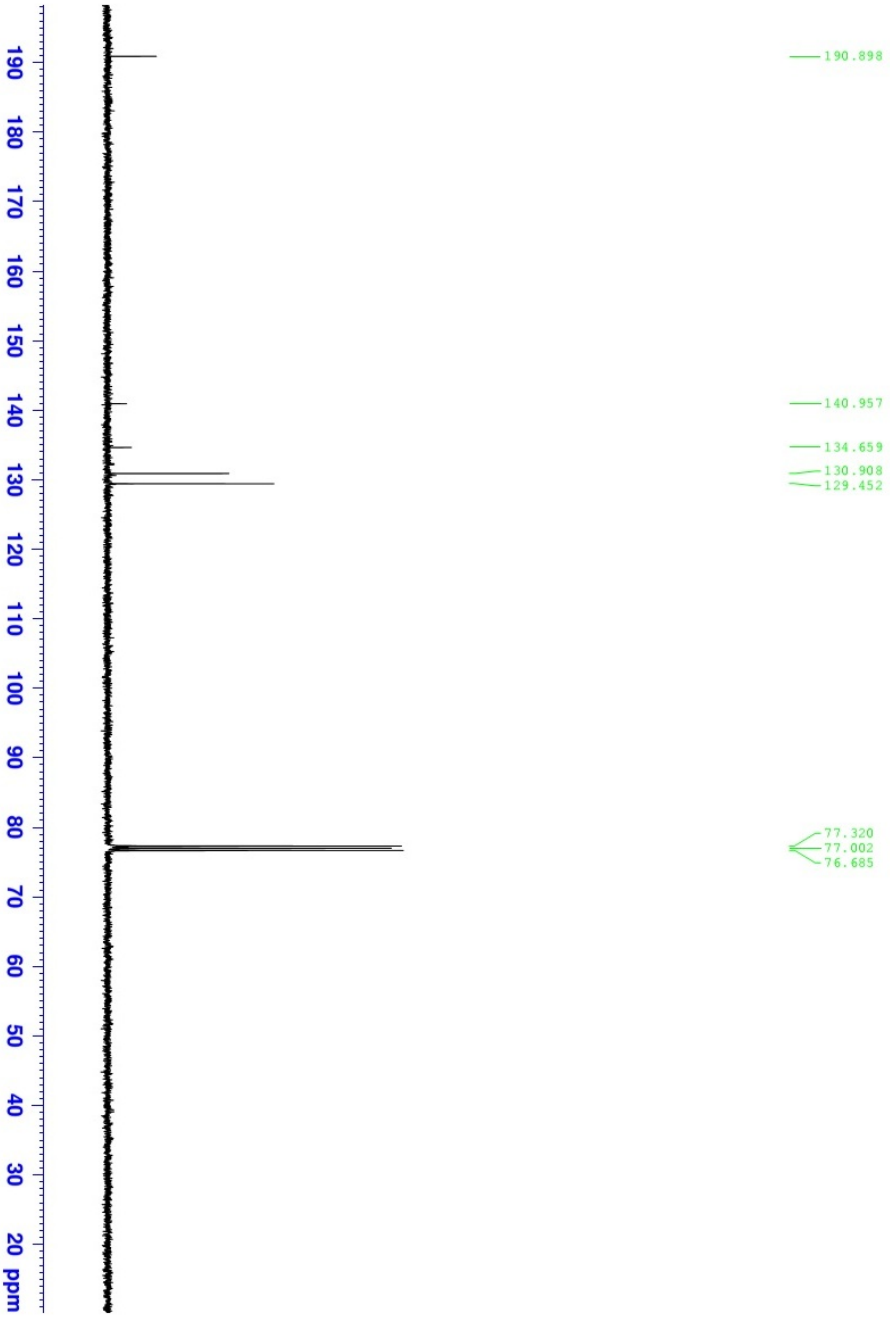
^{1}H NMR of Compound 2e



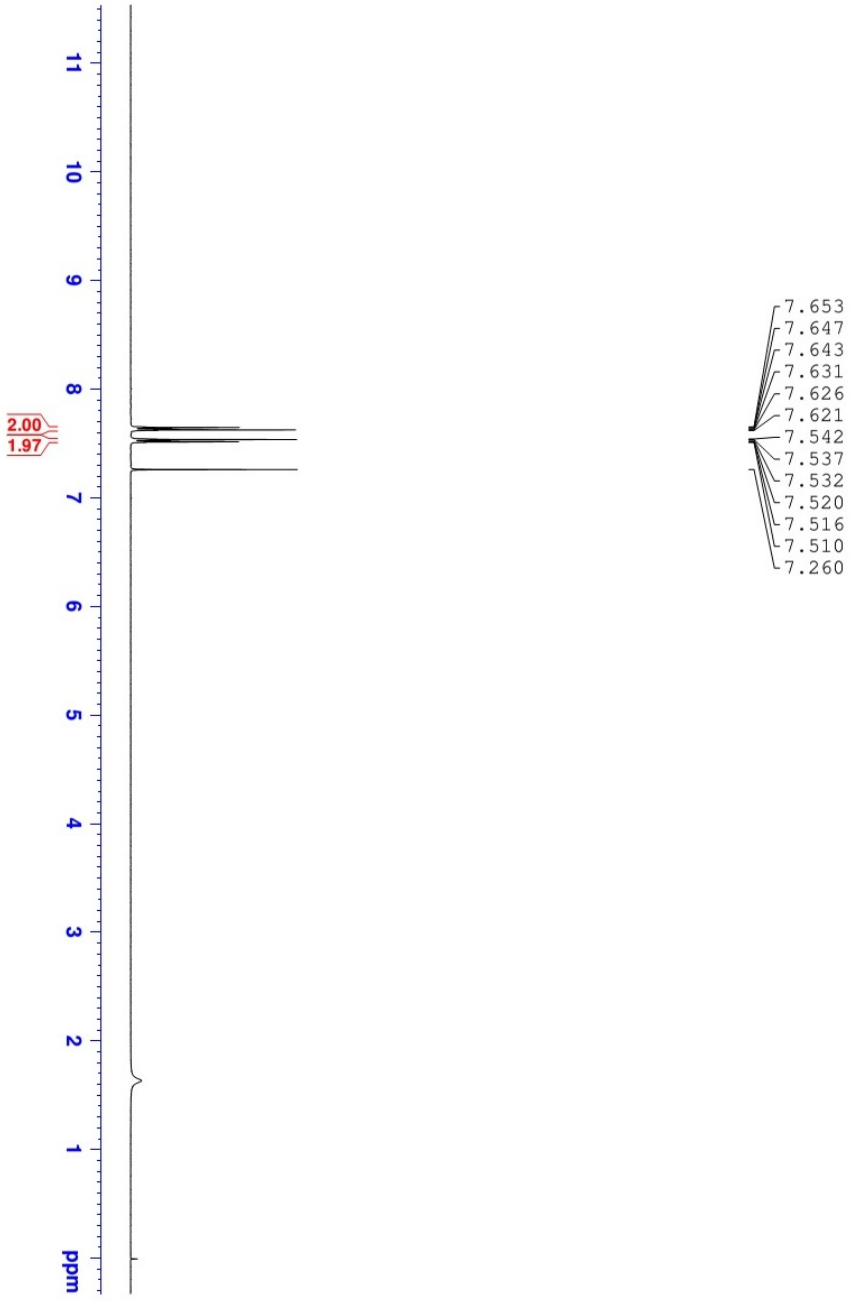
^{13}C NMR of Compound 2e



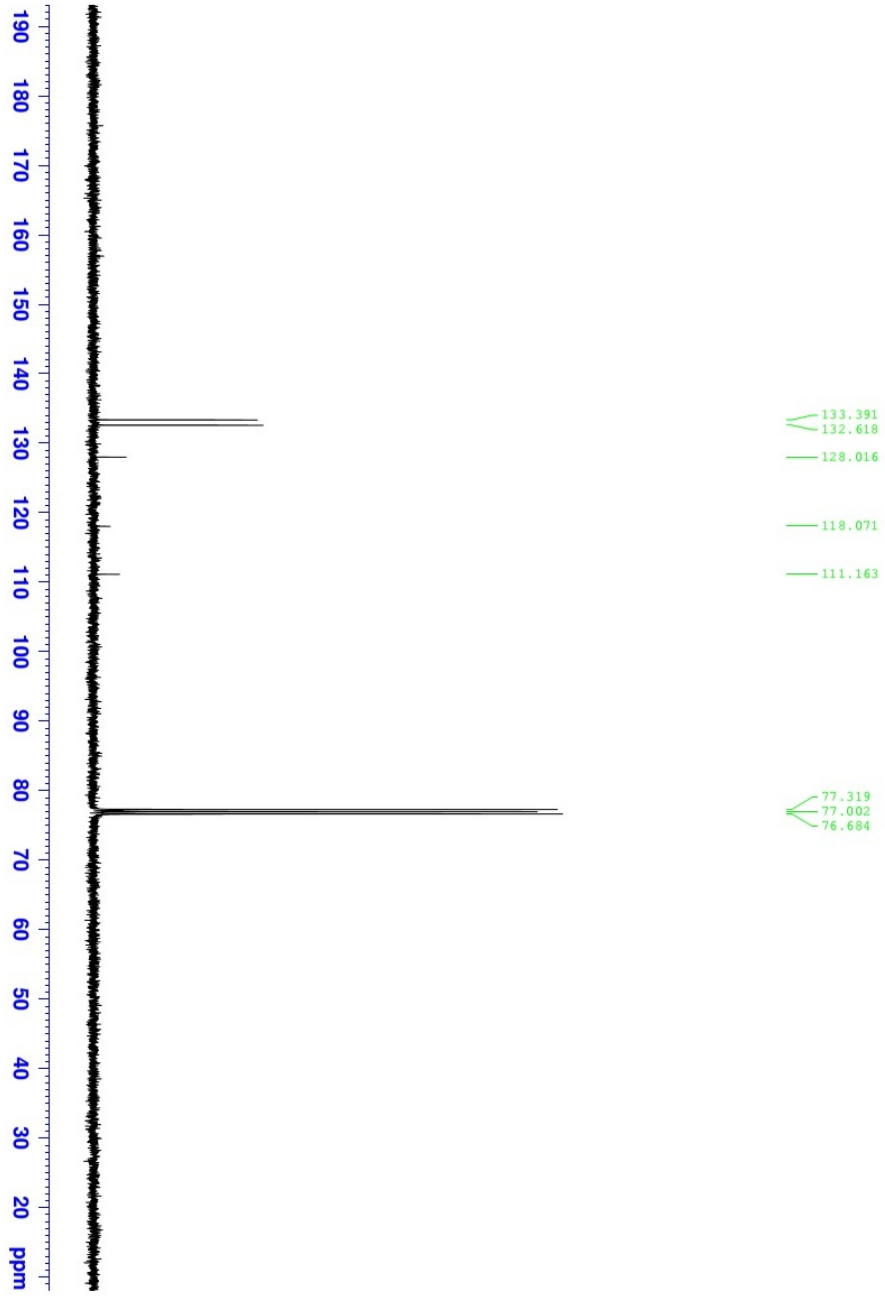
^{1}H NMR of Compound 3e



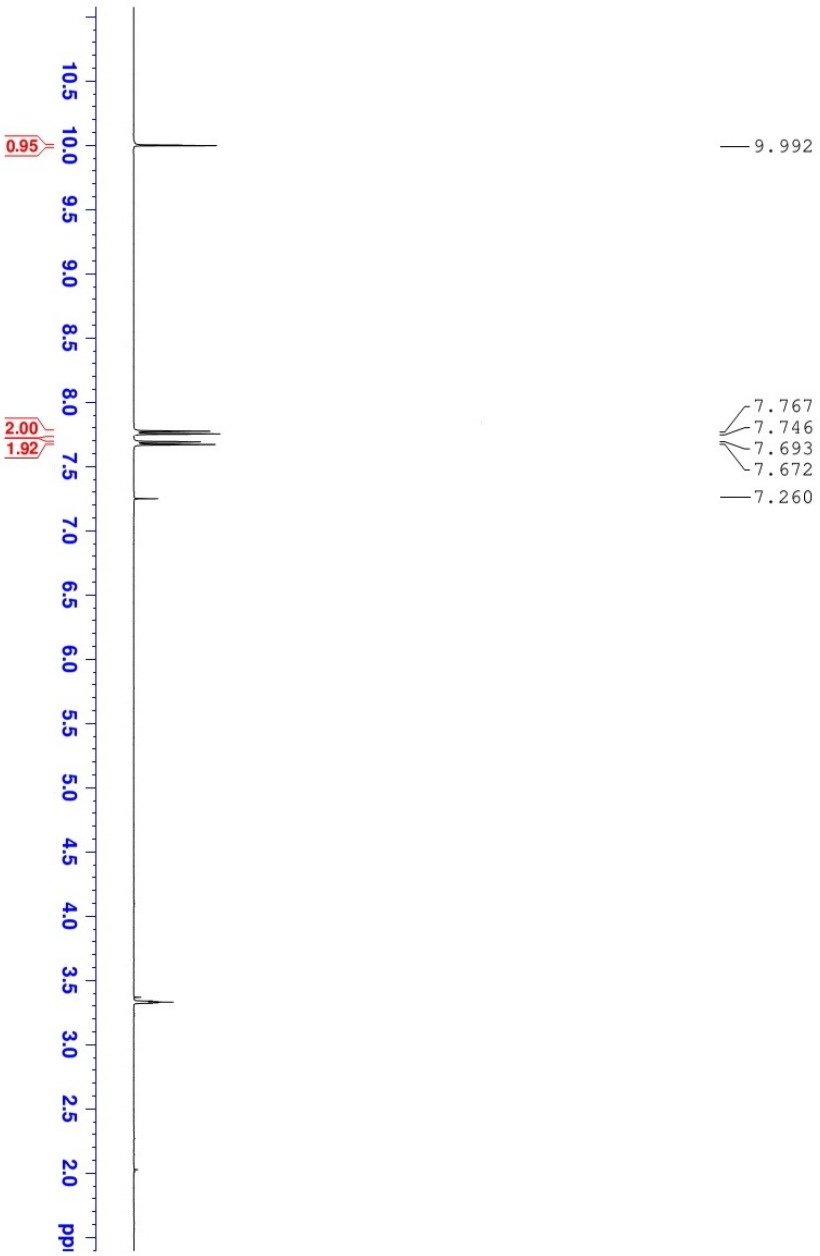
^{13}C NMR of Compound 3e



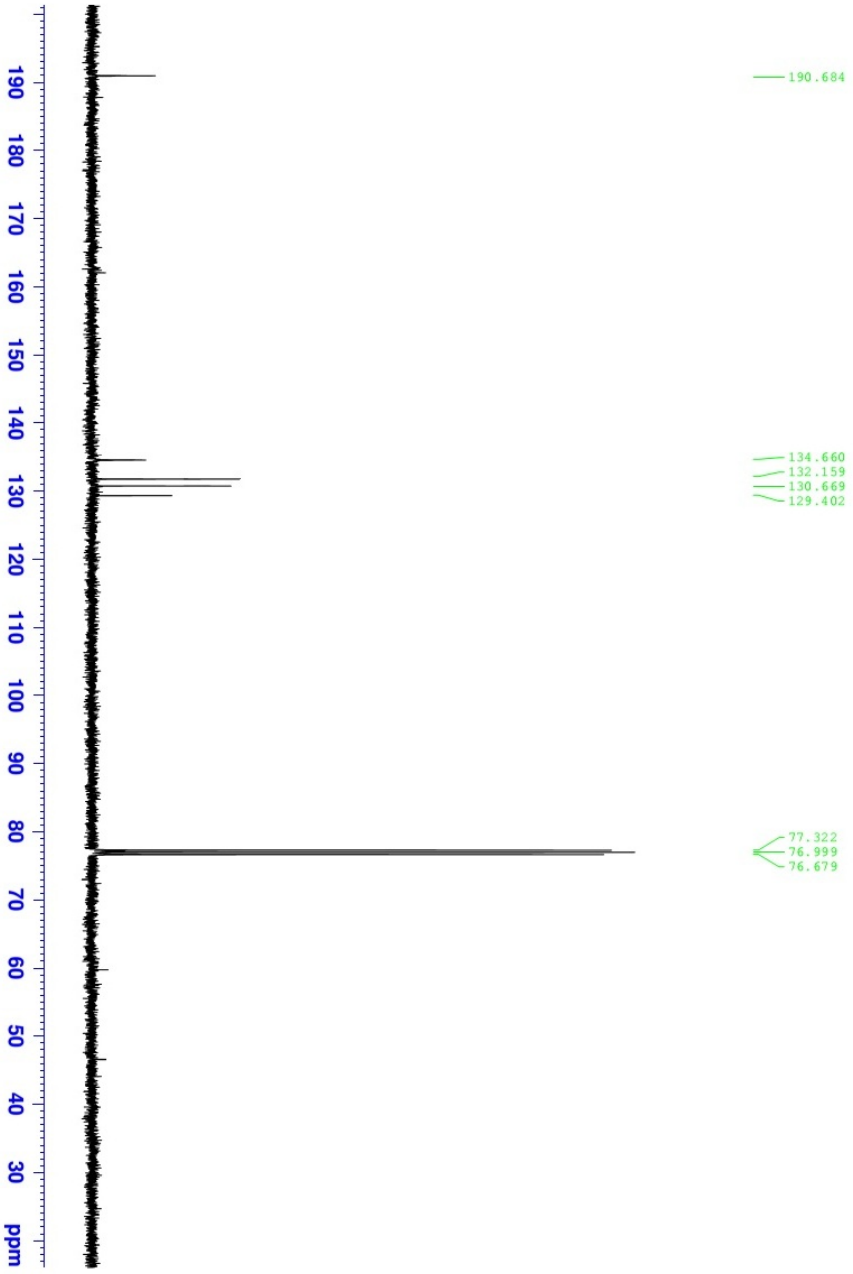
^{1}H NMR of Compound 2f



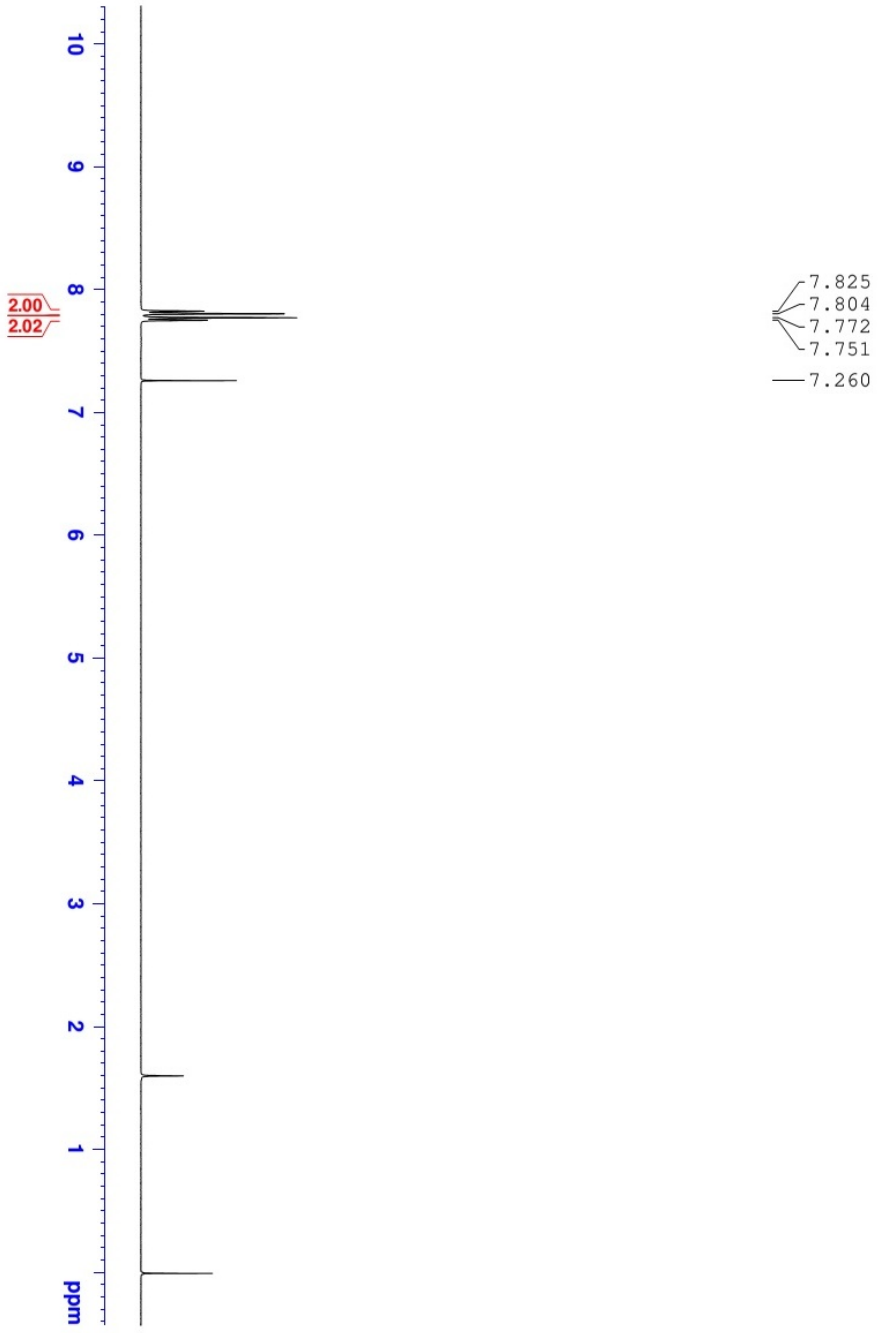
^{13}C NMR of Compound 2f



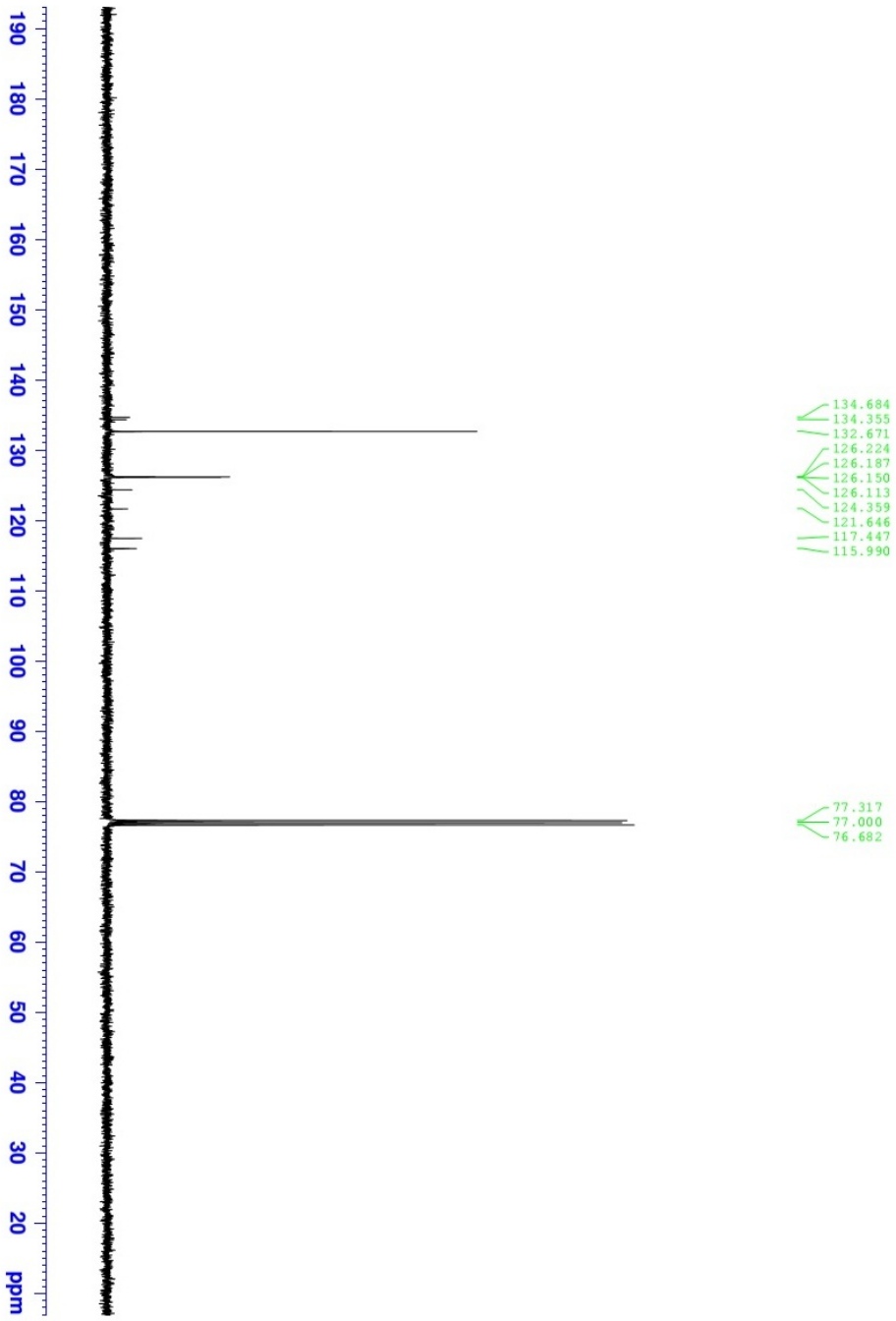
^{1}H NMR of Compound 3f



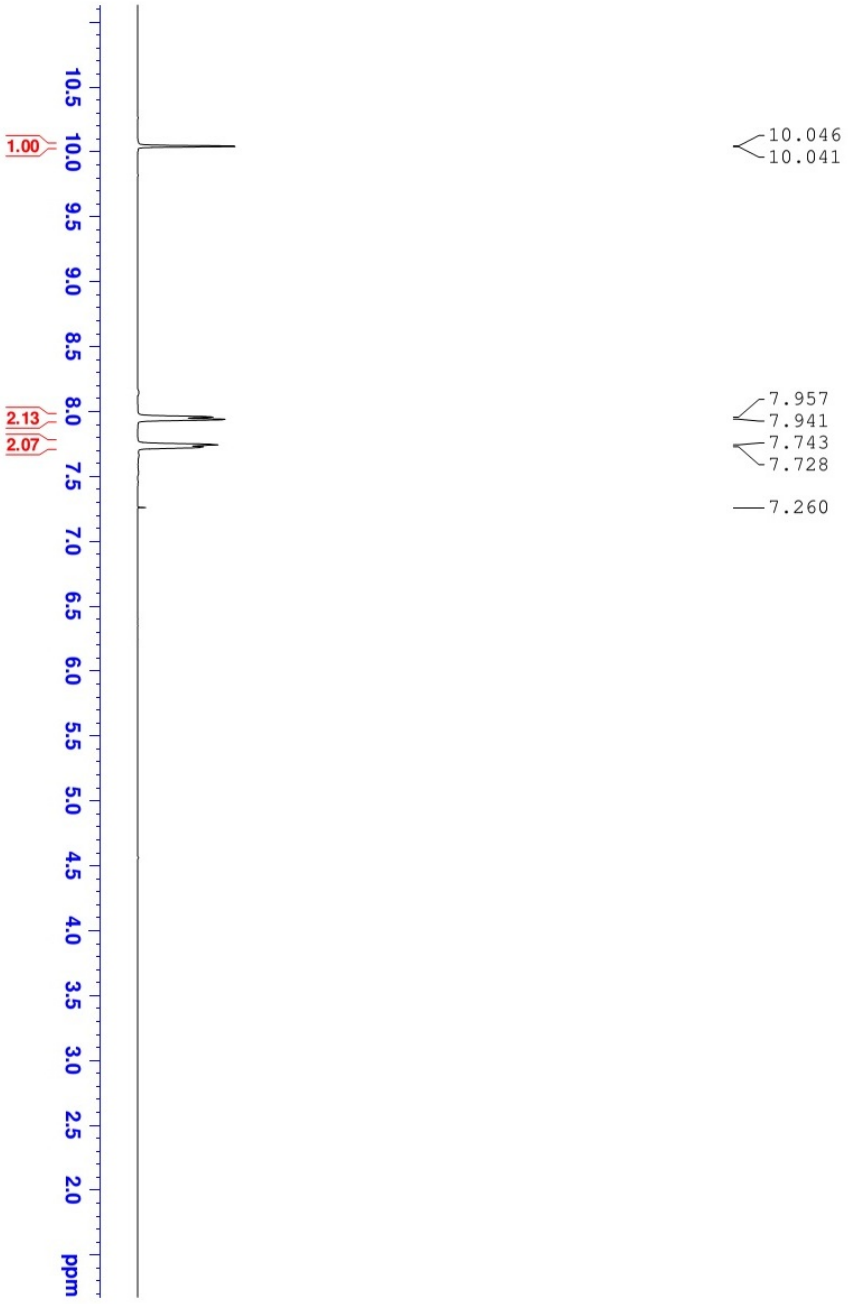
^{13}C NMR of Compound 3f



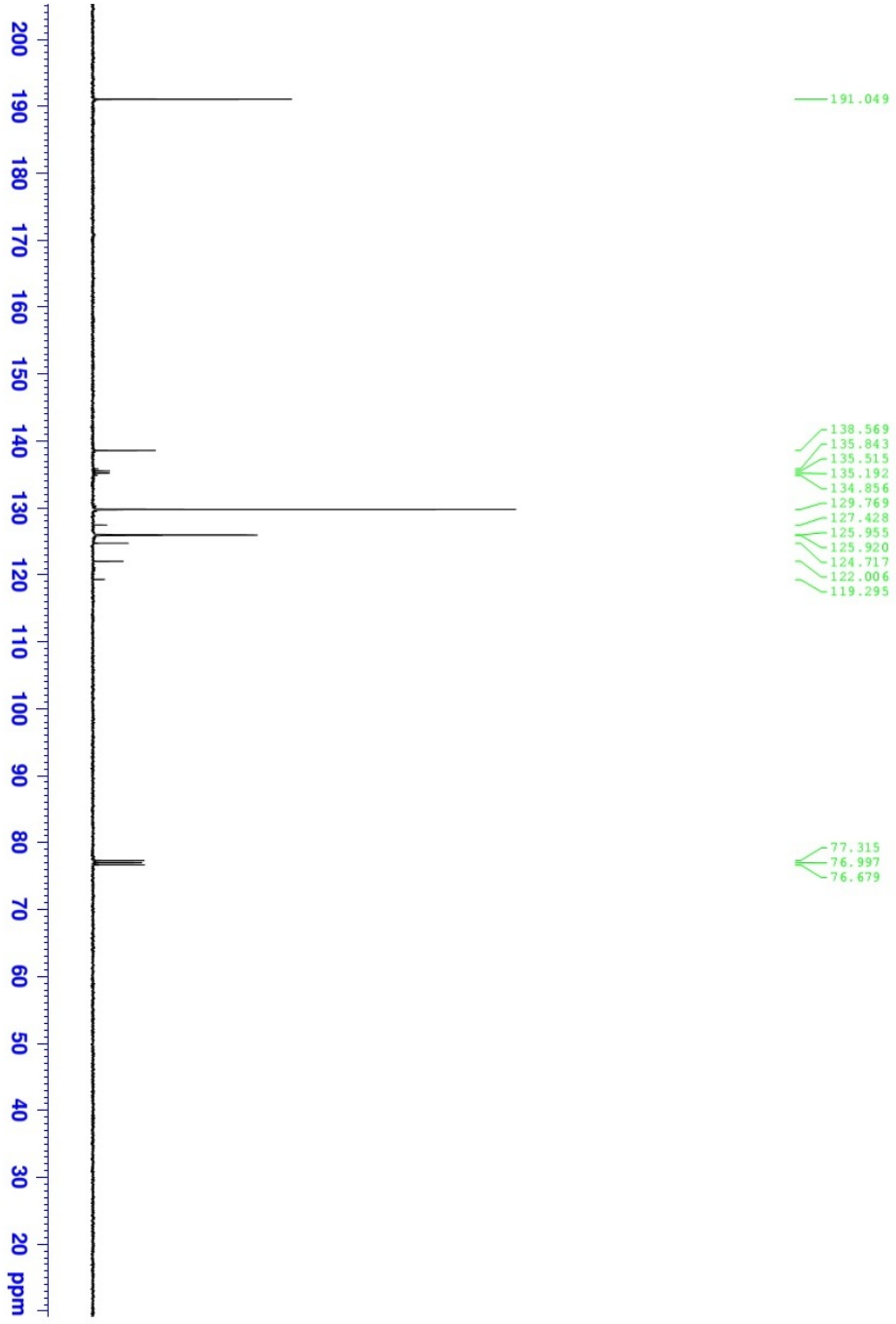
^{1}H NMR of Compound 2g



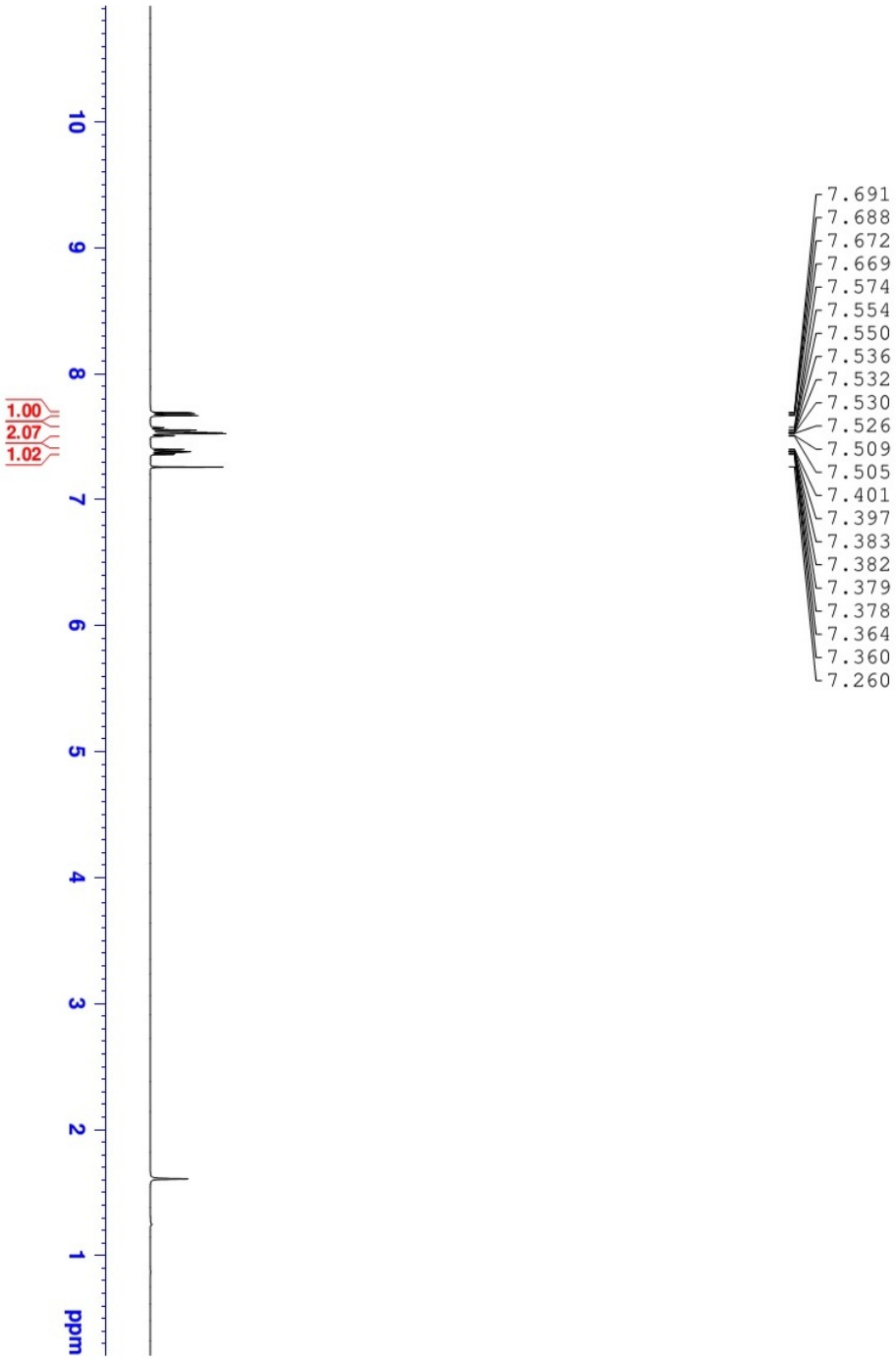
^{13}C NMR of Compound 2g



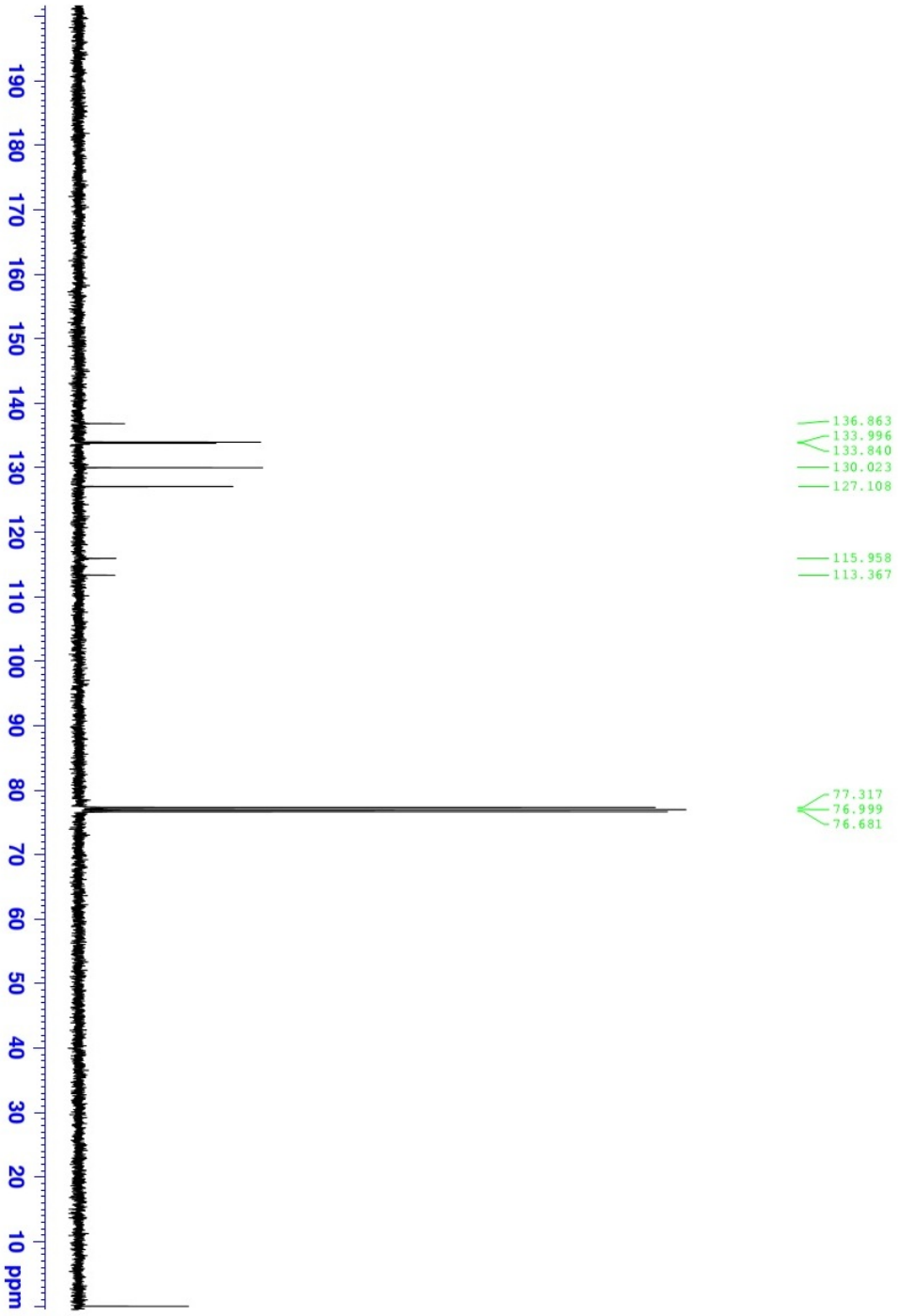
^{1}H NMR of Compound 3g



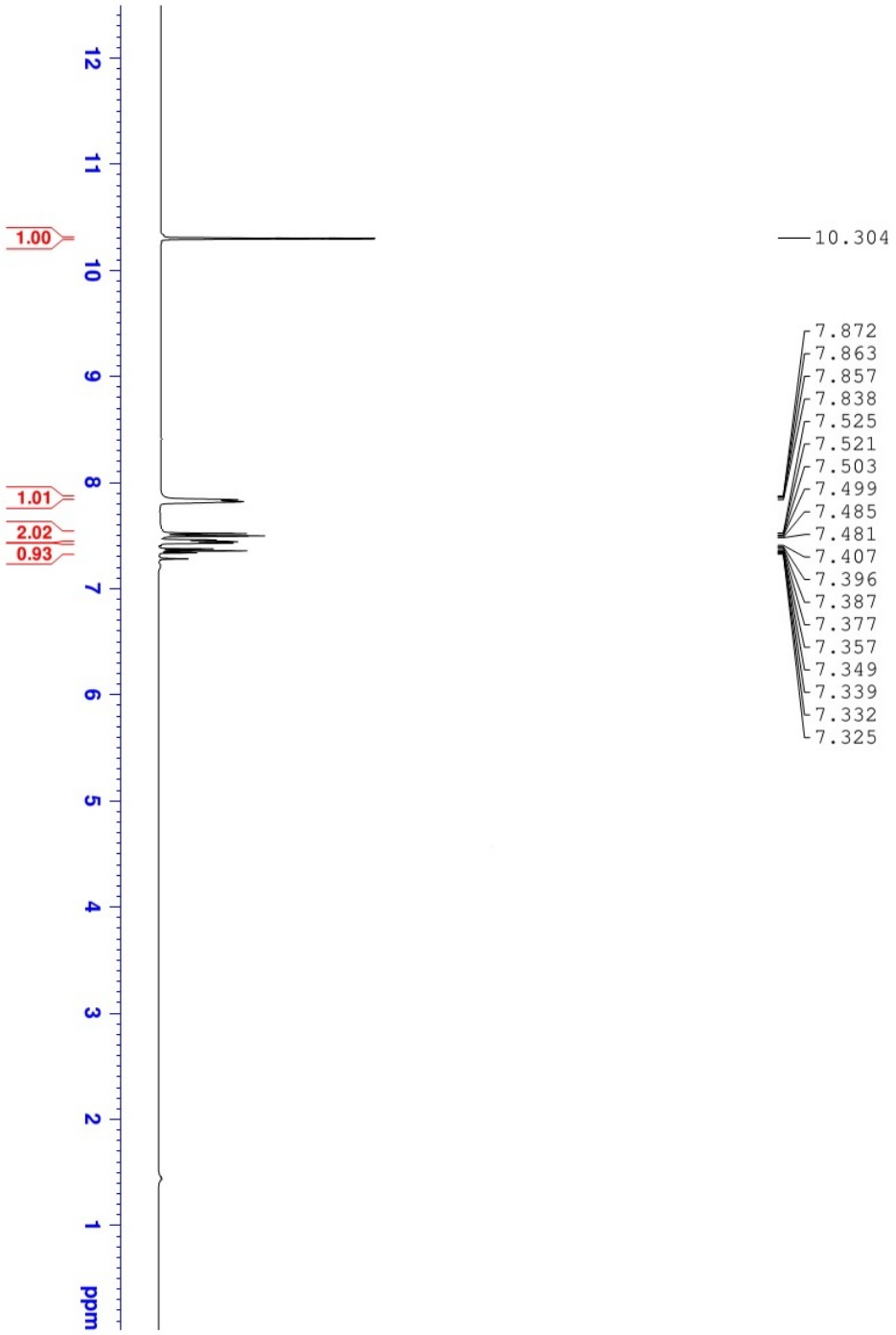
^{13}C NMR of Compound 3g



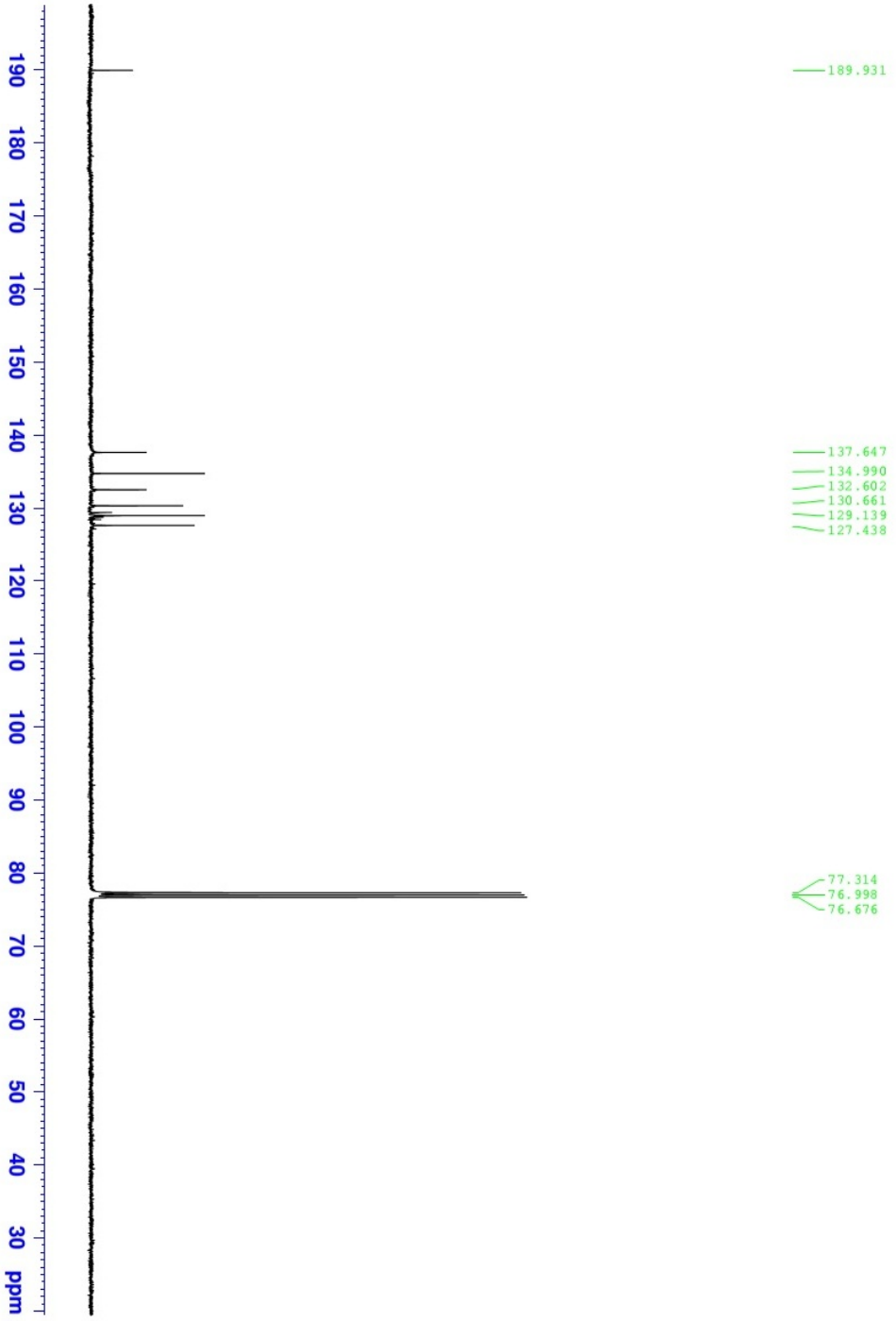
^{1}H NMR of Compound 2h



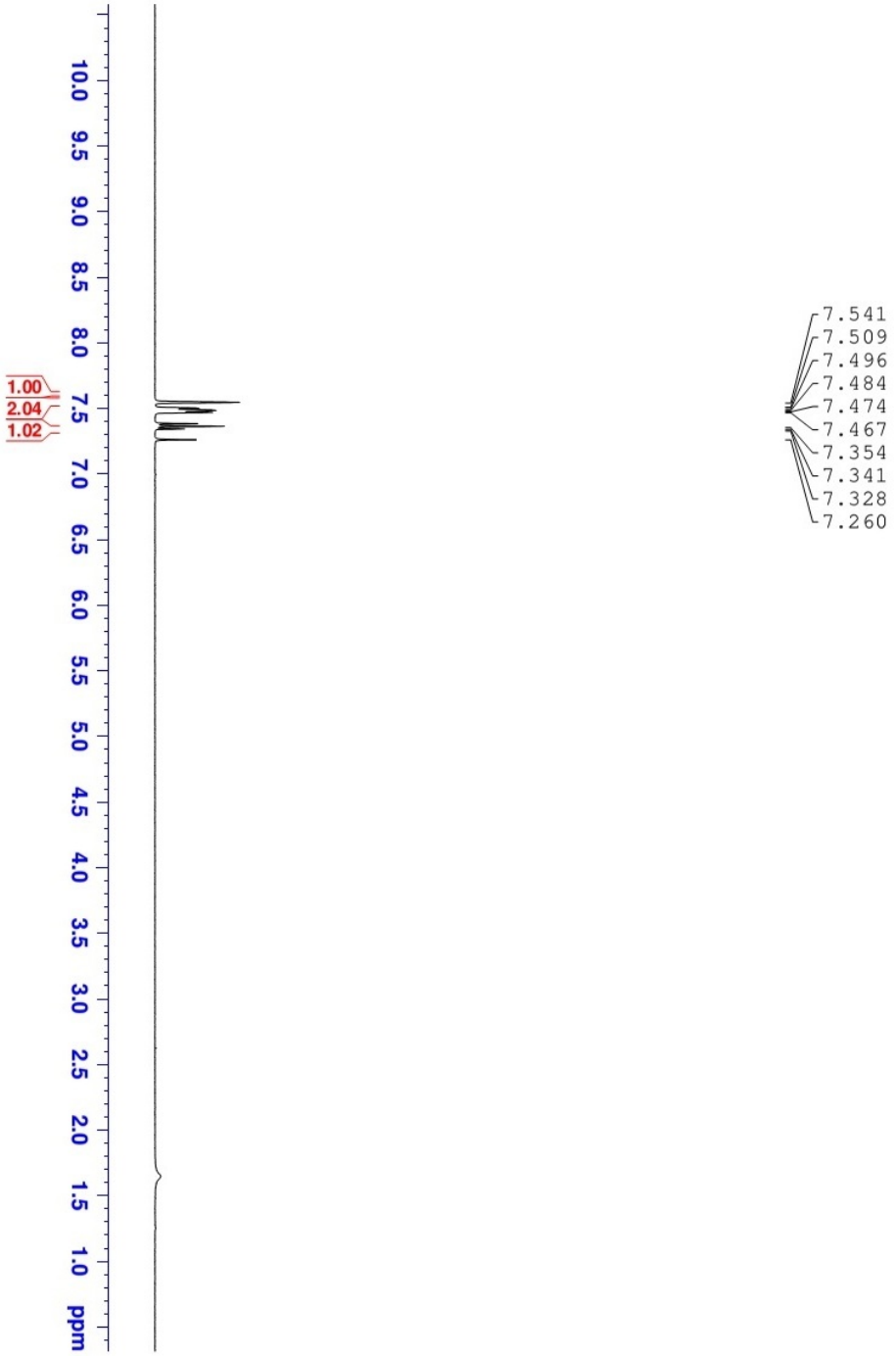
^{13}C NMR of Compound 2h



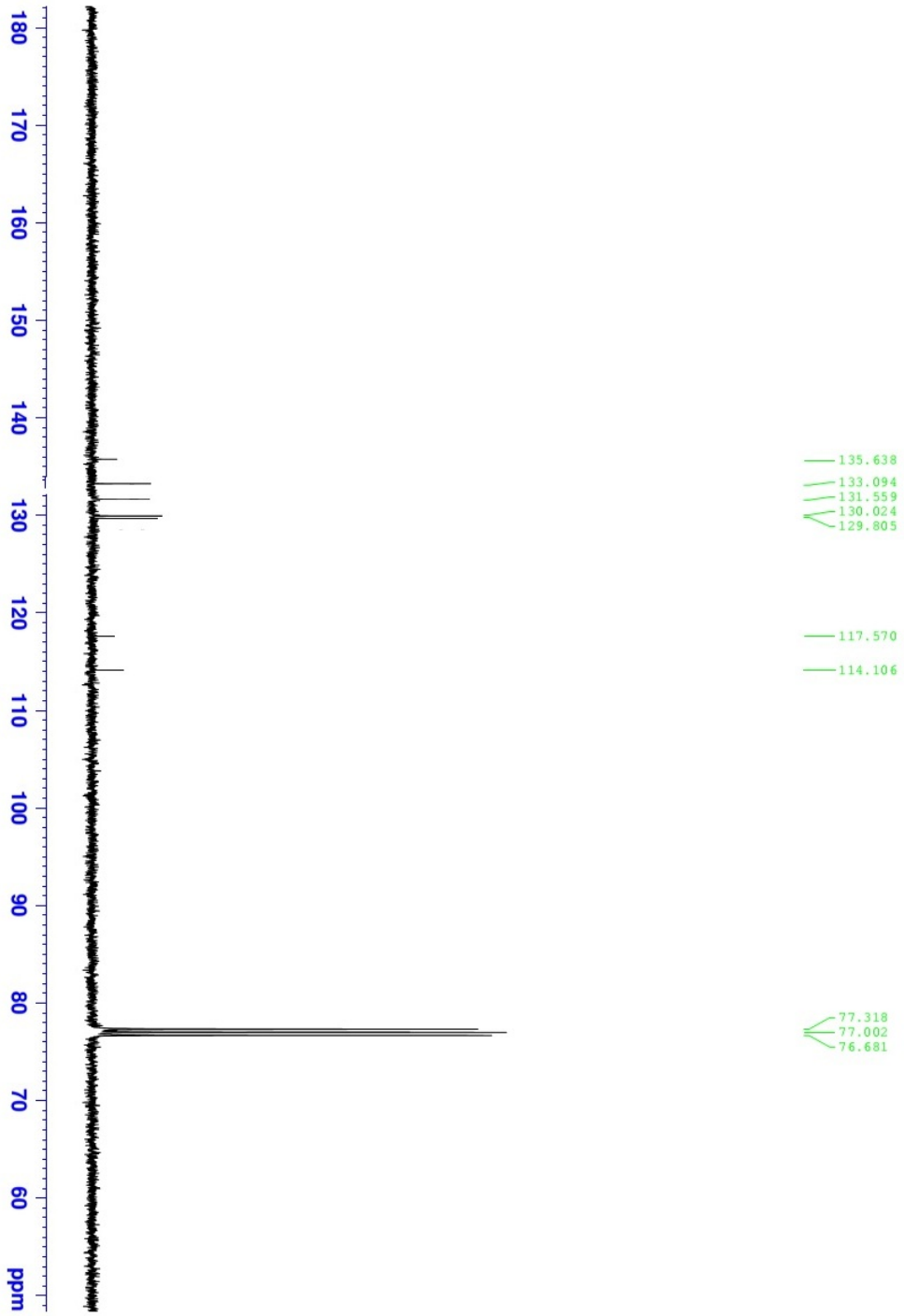
^{1}H NMR of Compound 3h



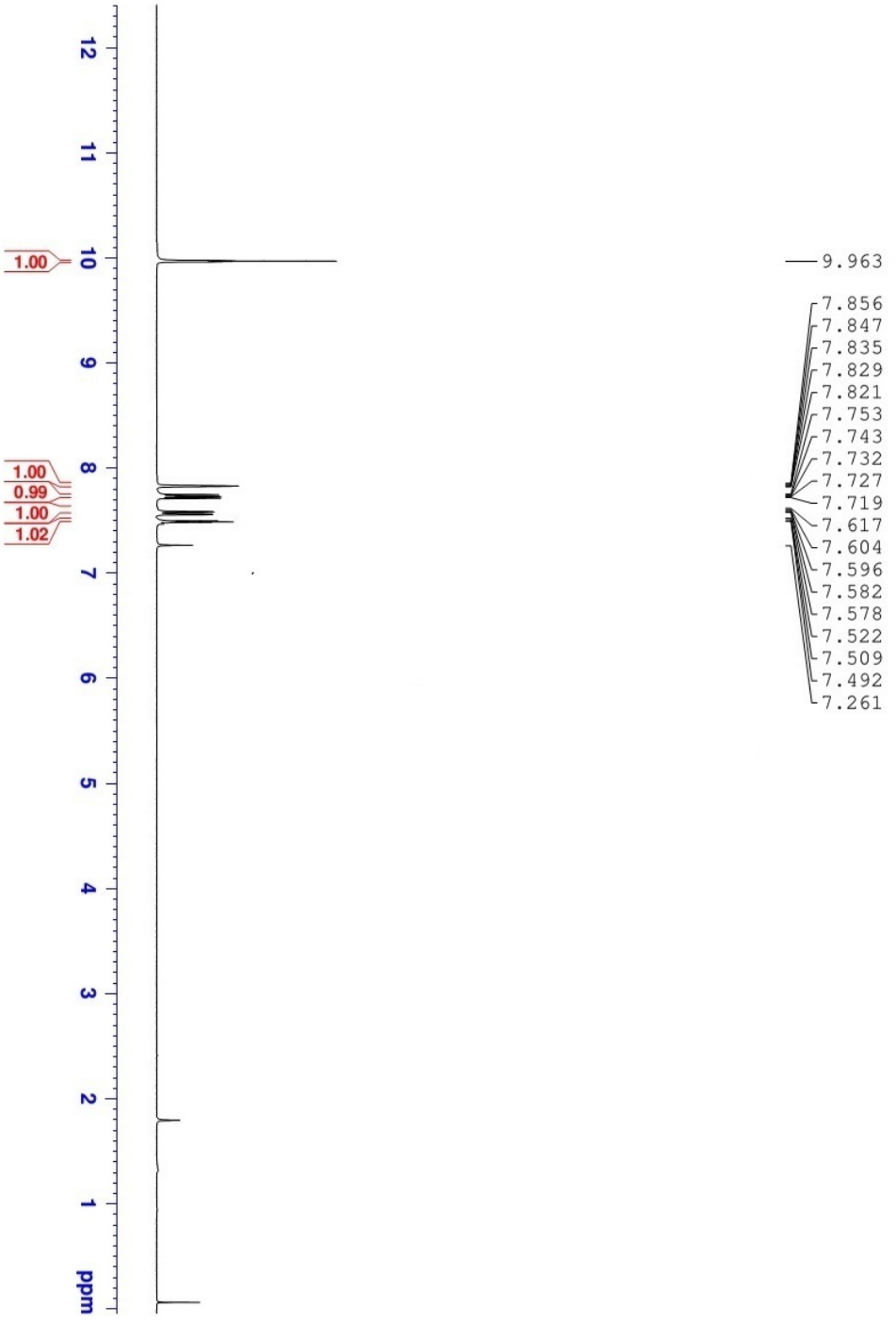
^{13}C NMR of Compound 3h



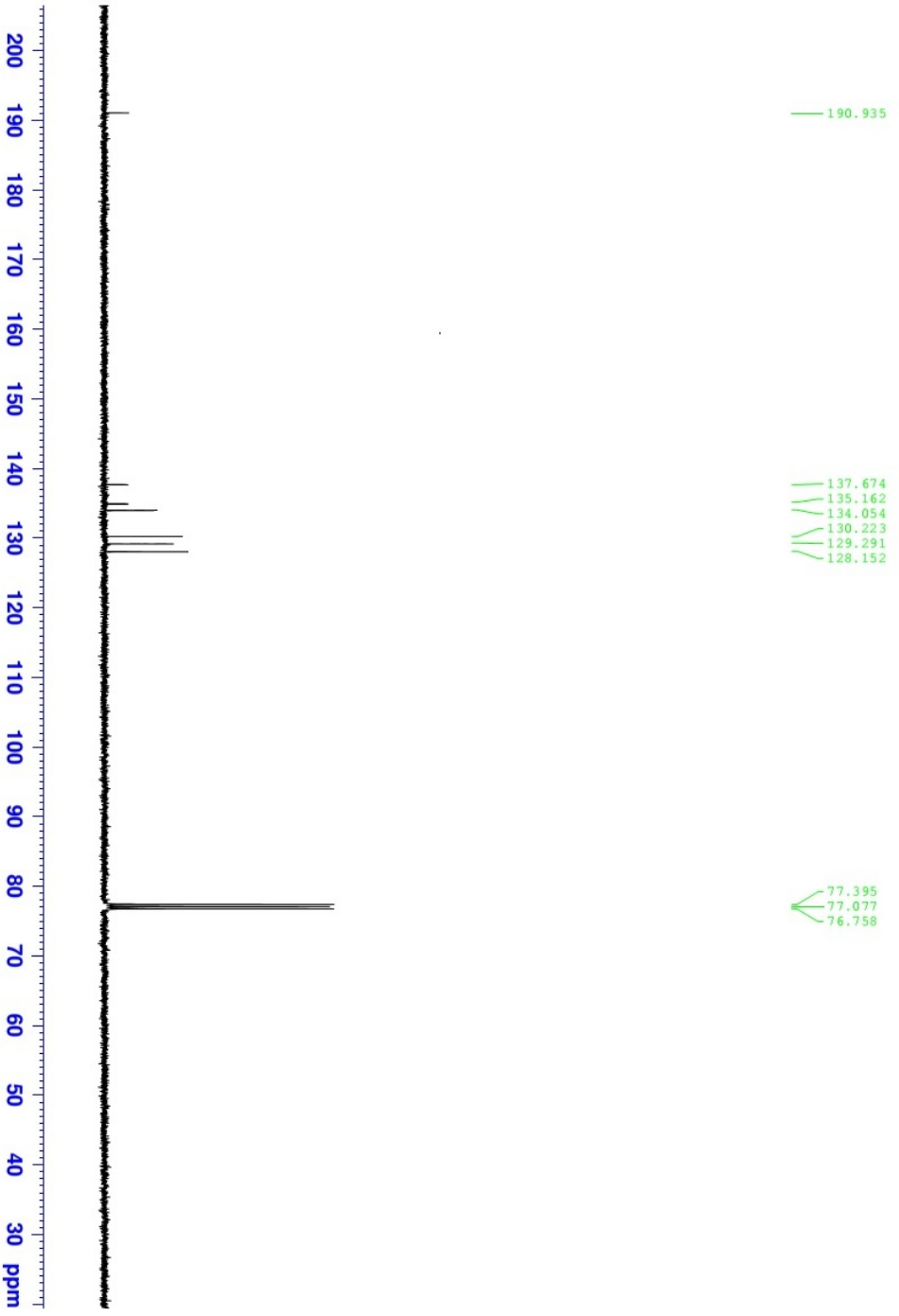
^{1}H NMR of Compound 2i



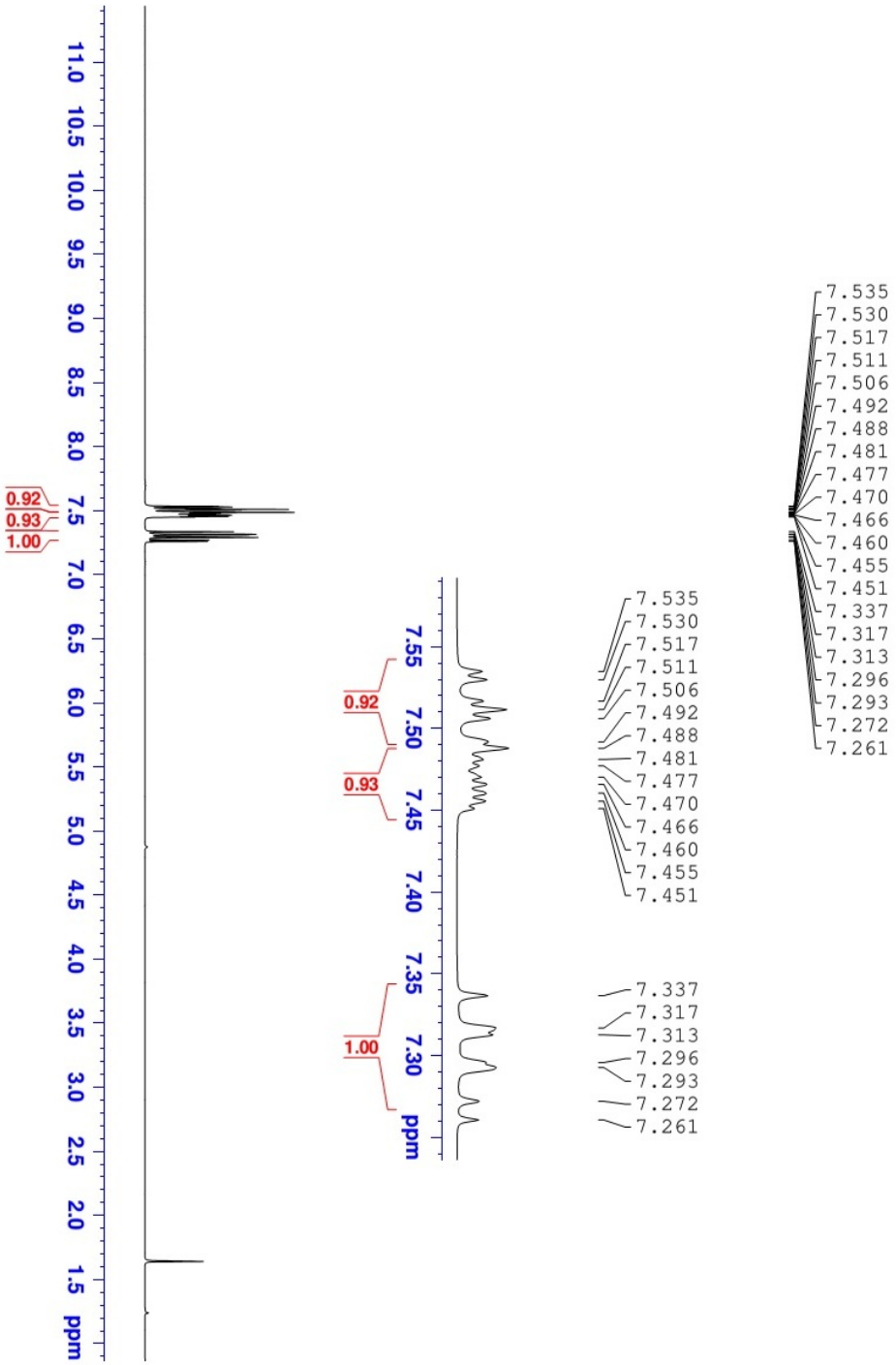
^{13}C NMR of Compound 2i



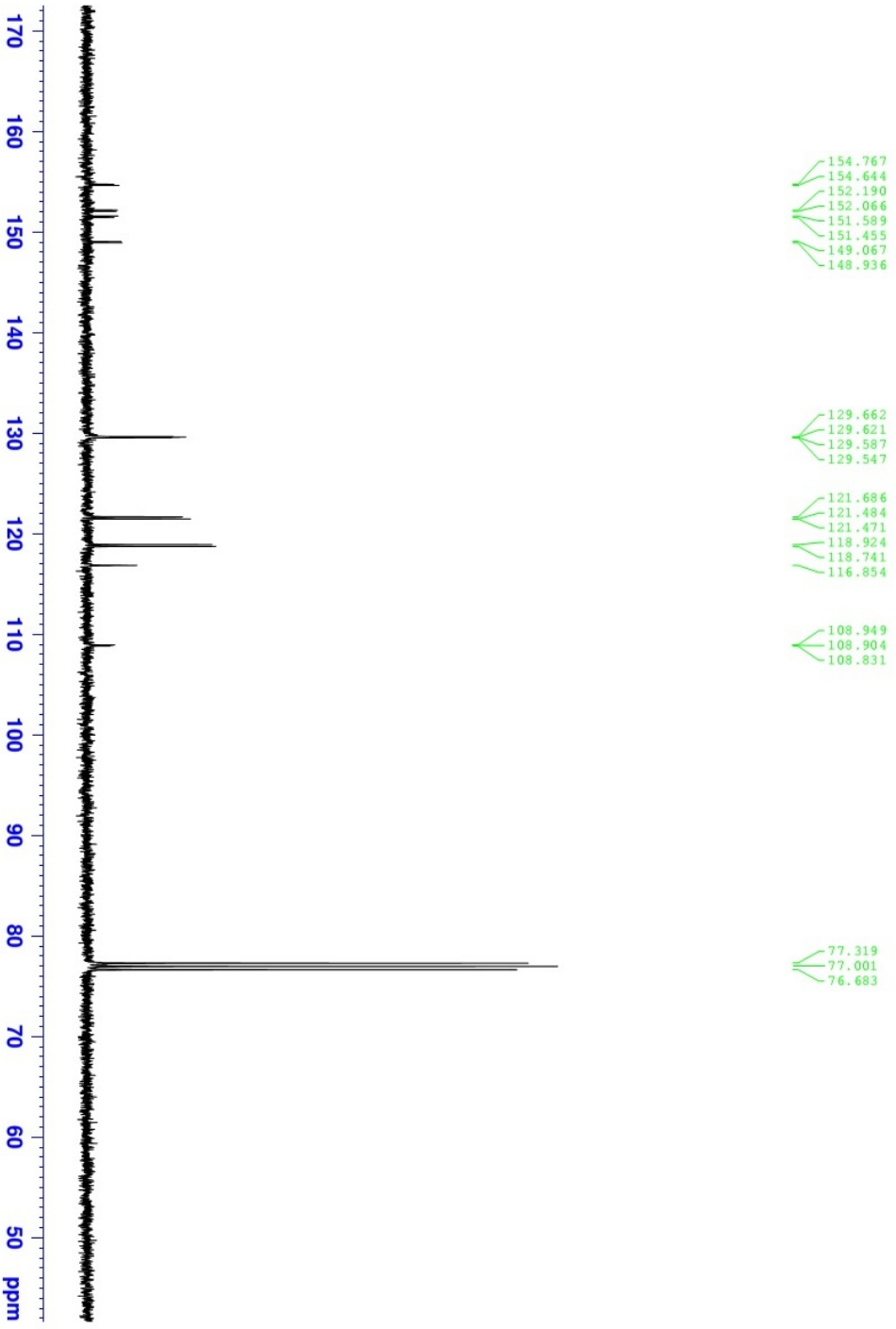
^{1}H NMR of Compound 3i



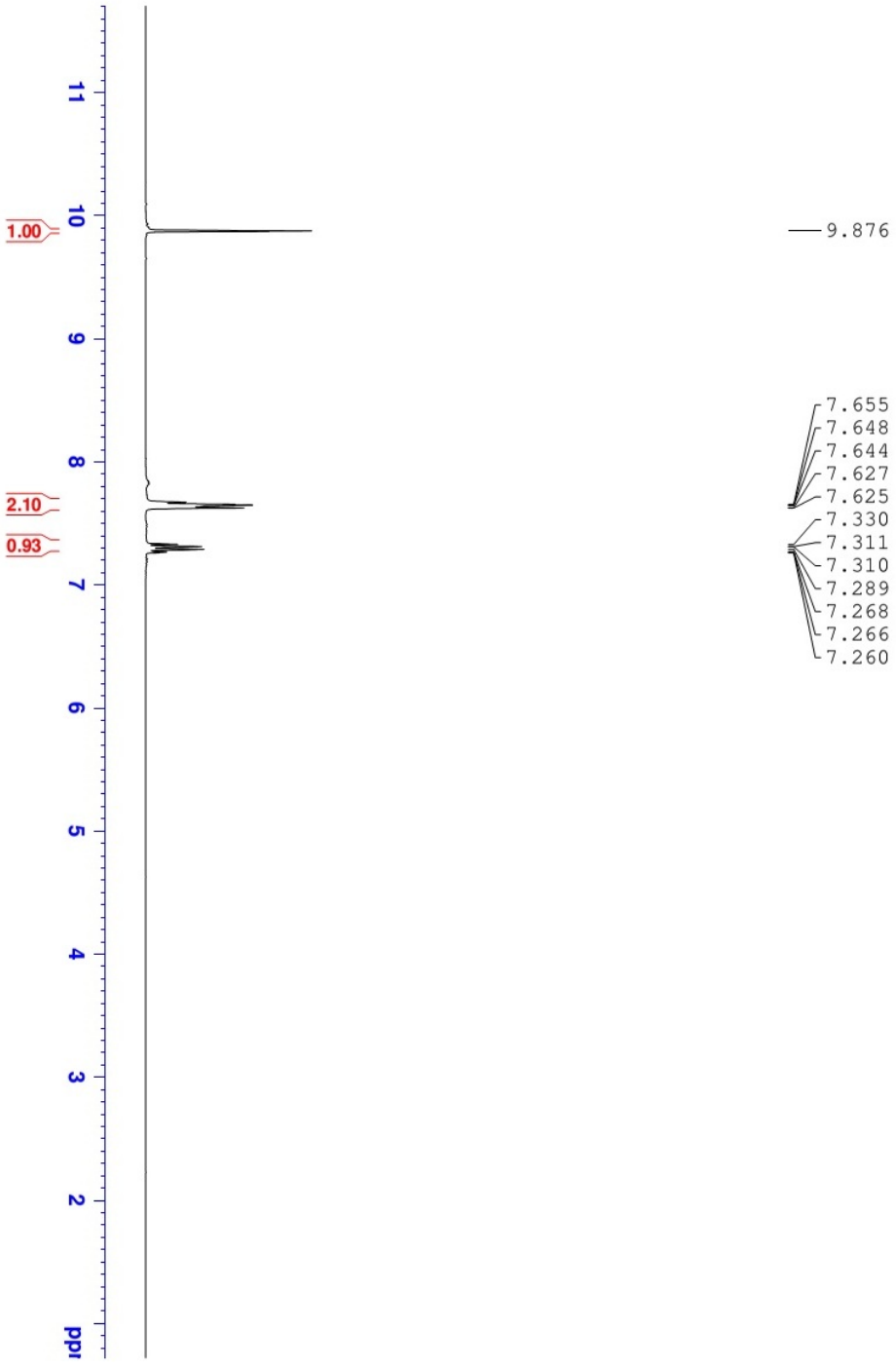
^{13}C NMR of Compound 3i



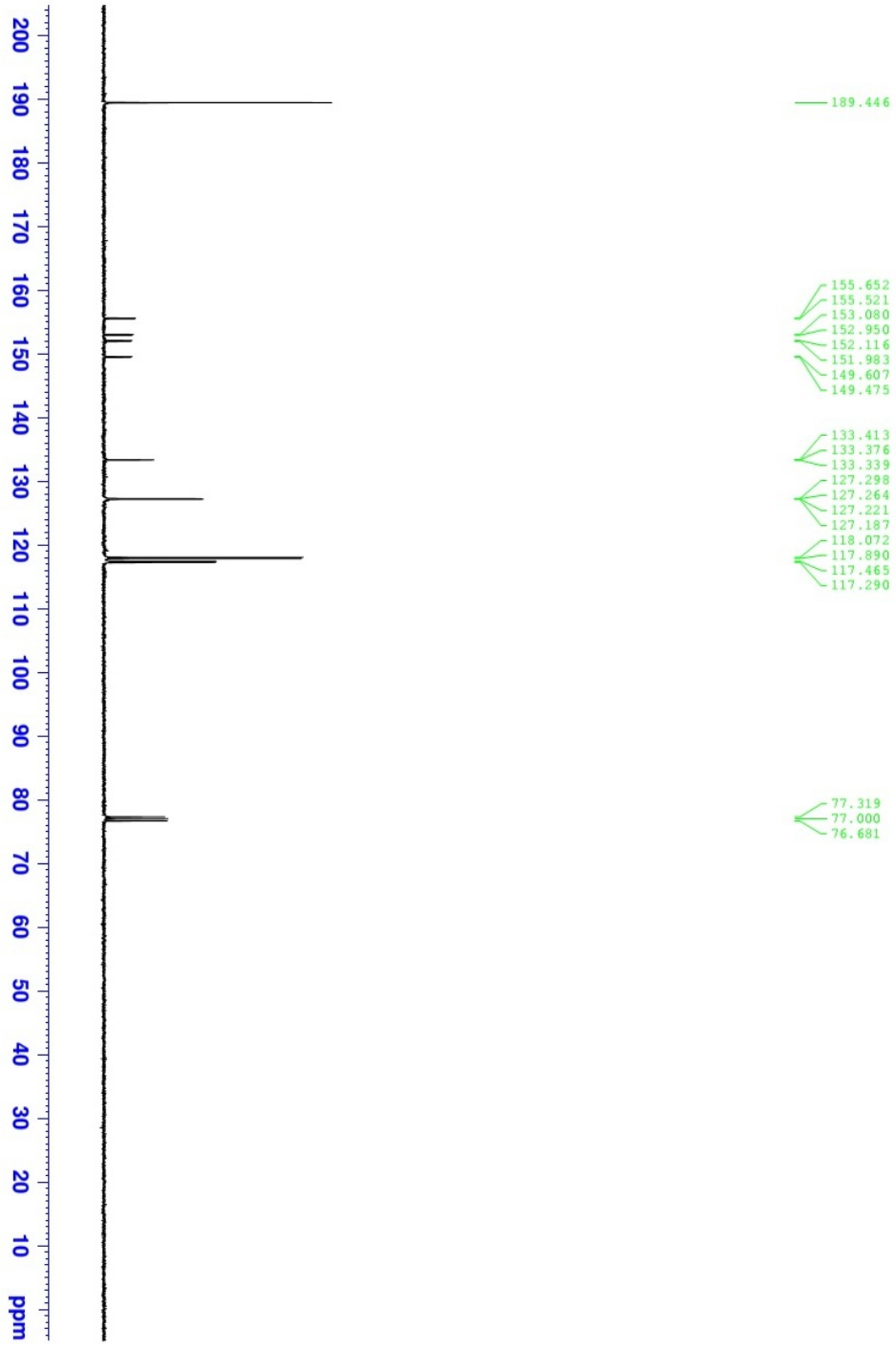
^{1}H NMR of Compound 2j



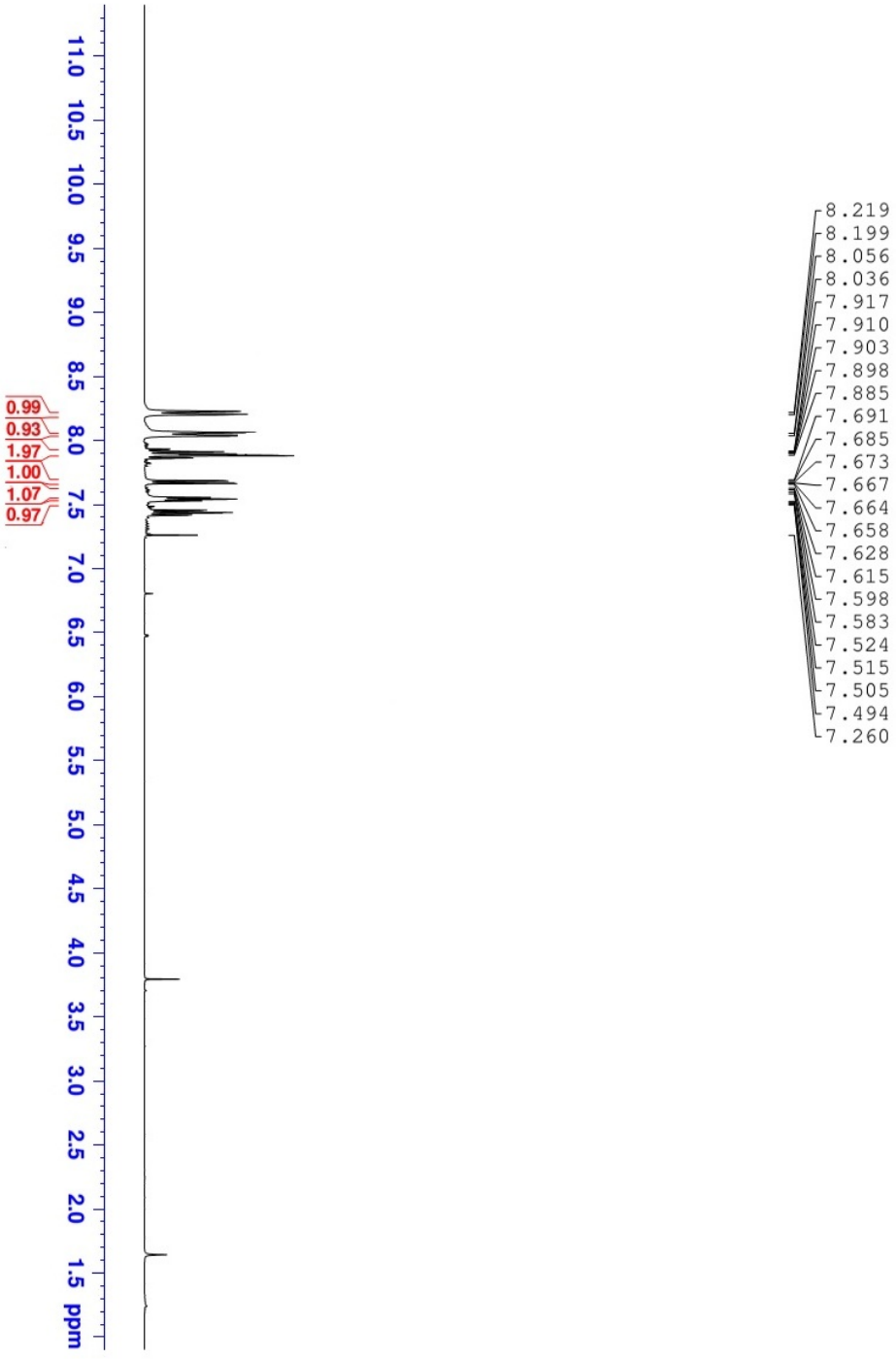
^{13}C NMR of Compound 2j



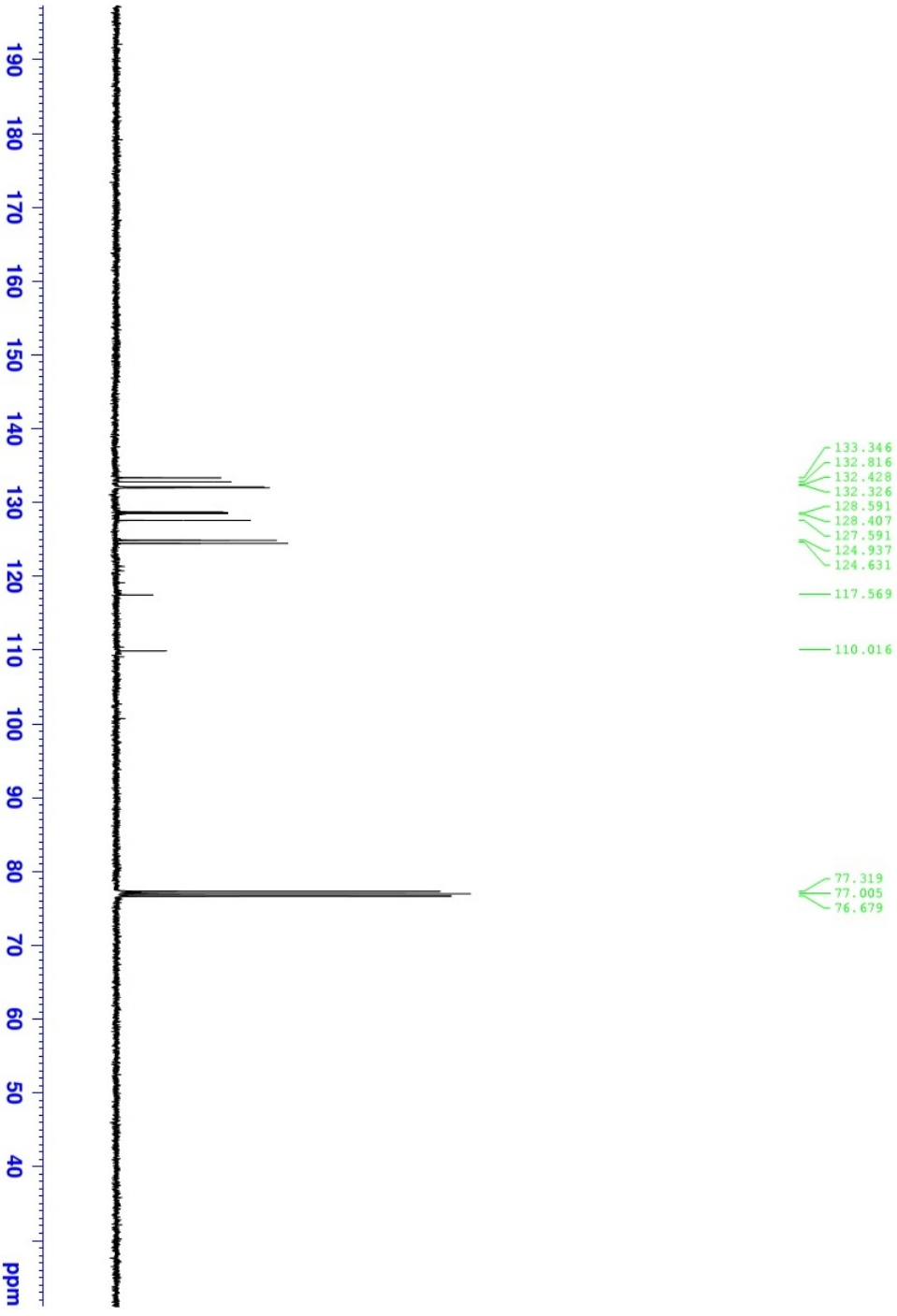
^{1}H NMR of Compound 3j



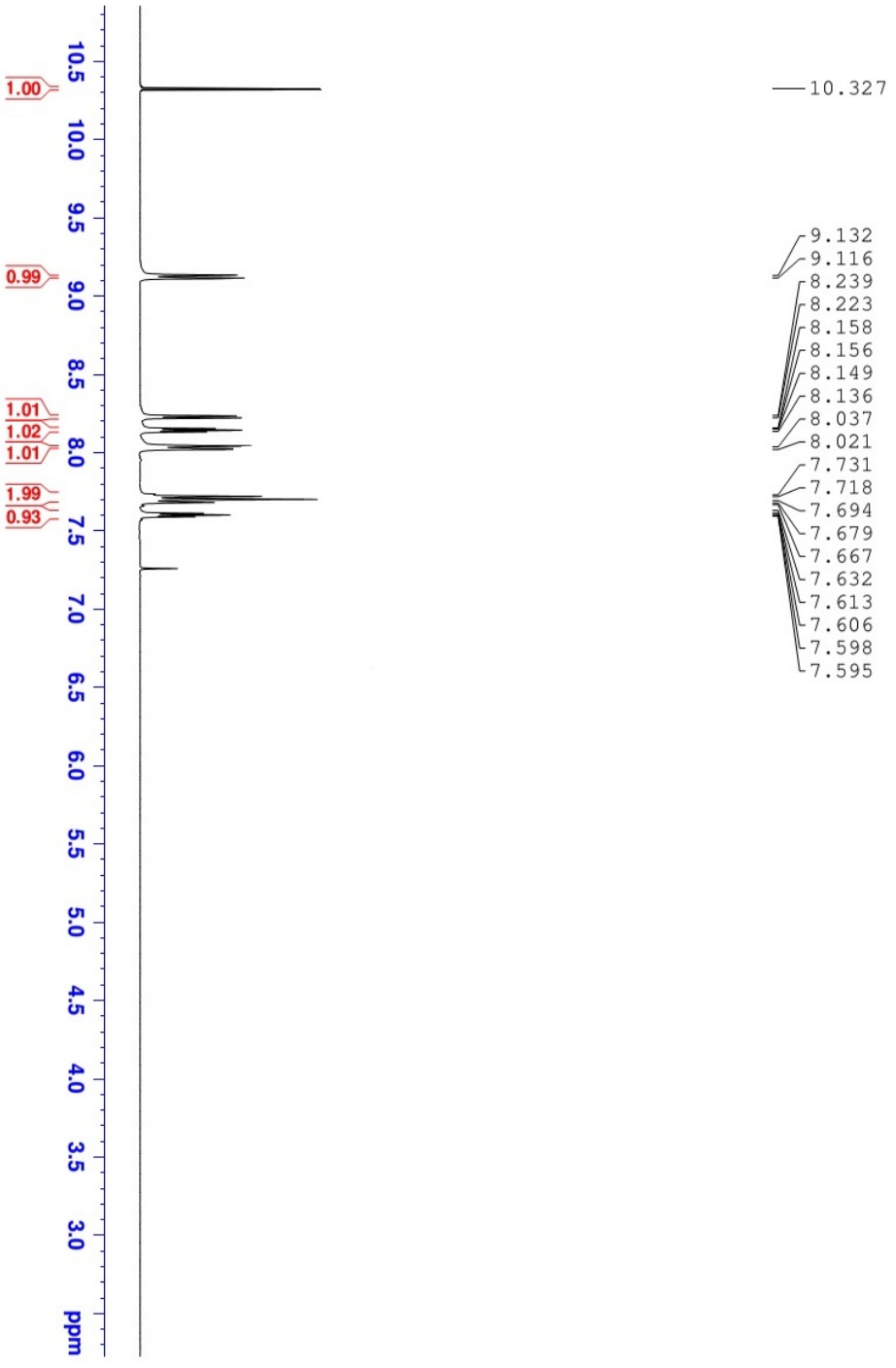
^{13}C NMR of Compound 3j



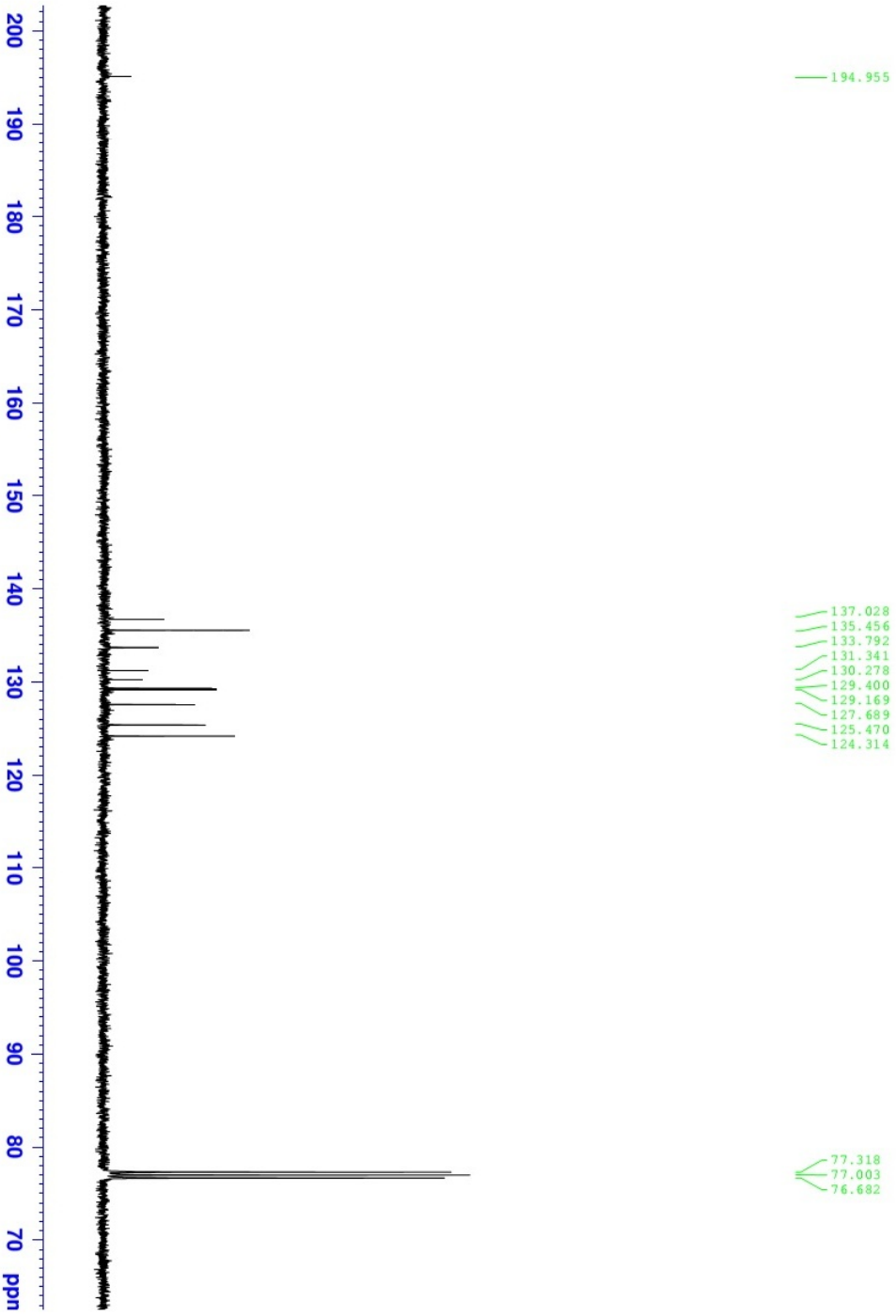
^{1}H NMR of Compound 2k



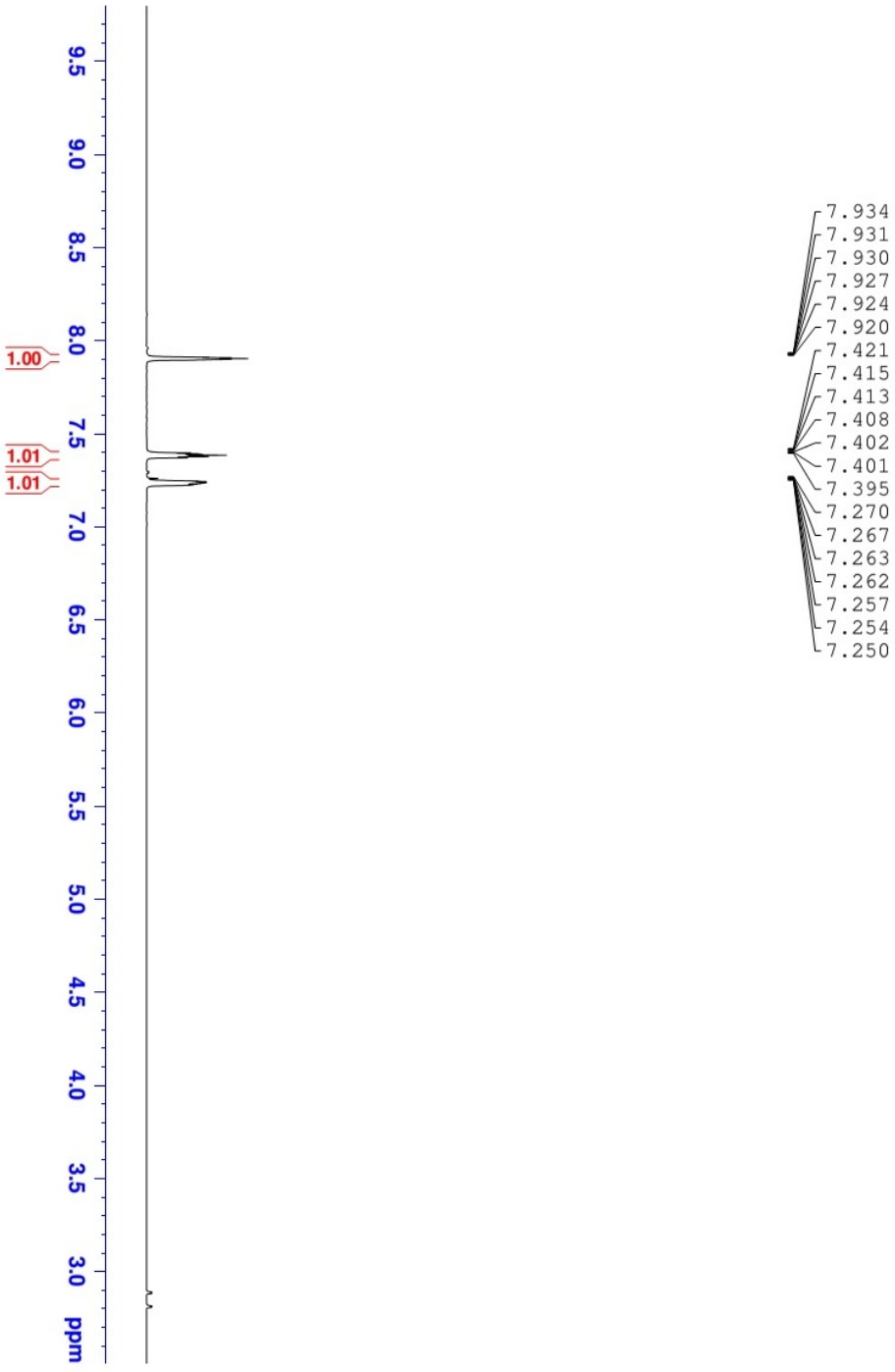
^{13}C NMR of Compound 2k



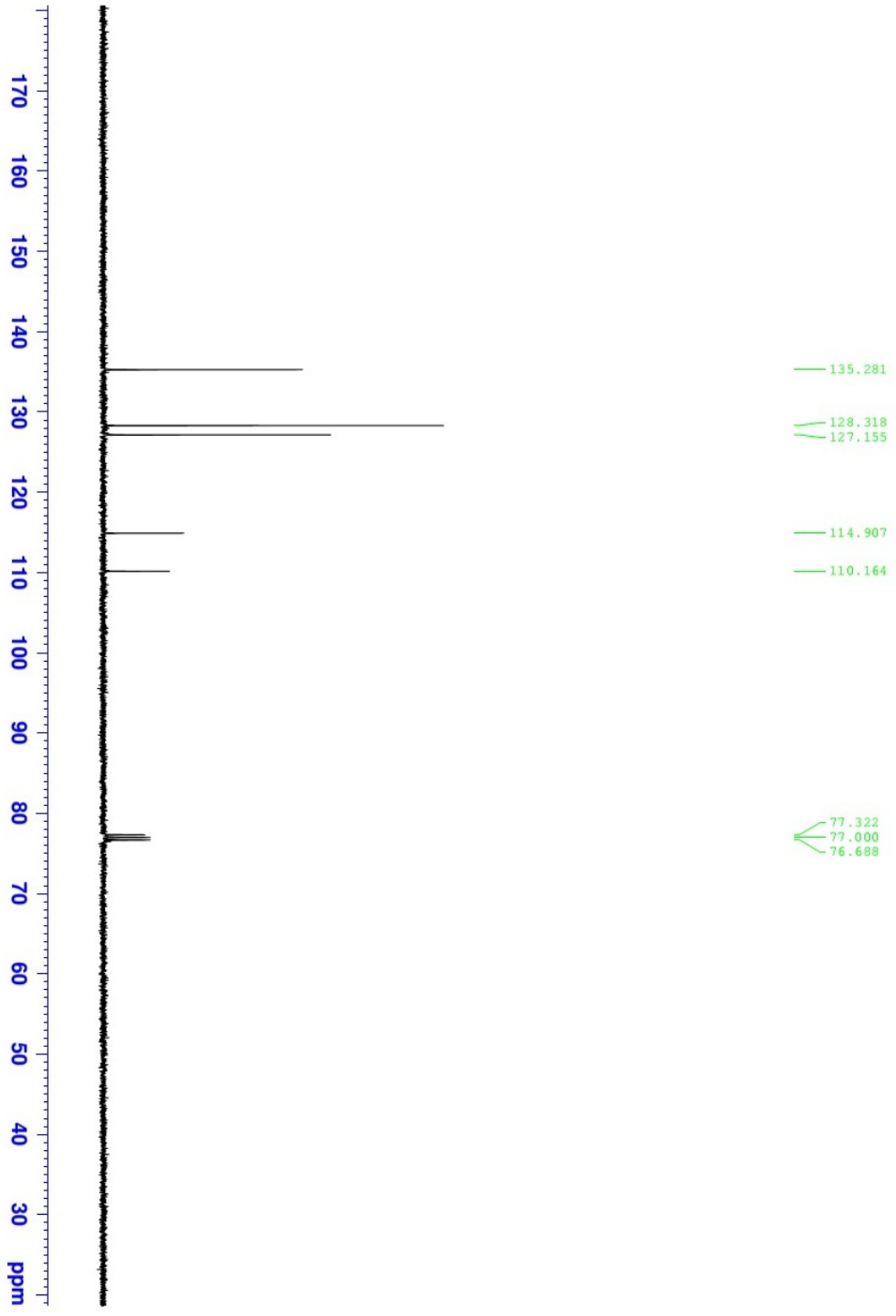
^{1}H NMR of Compound 3k



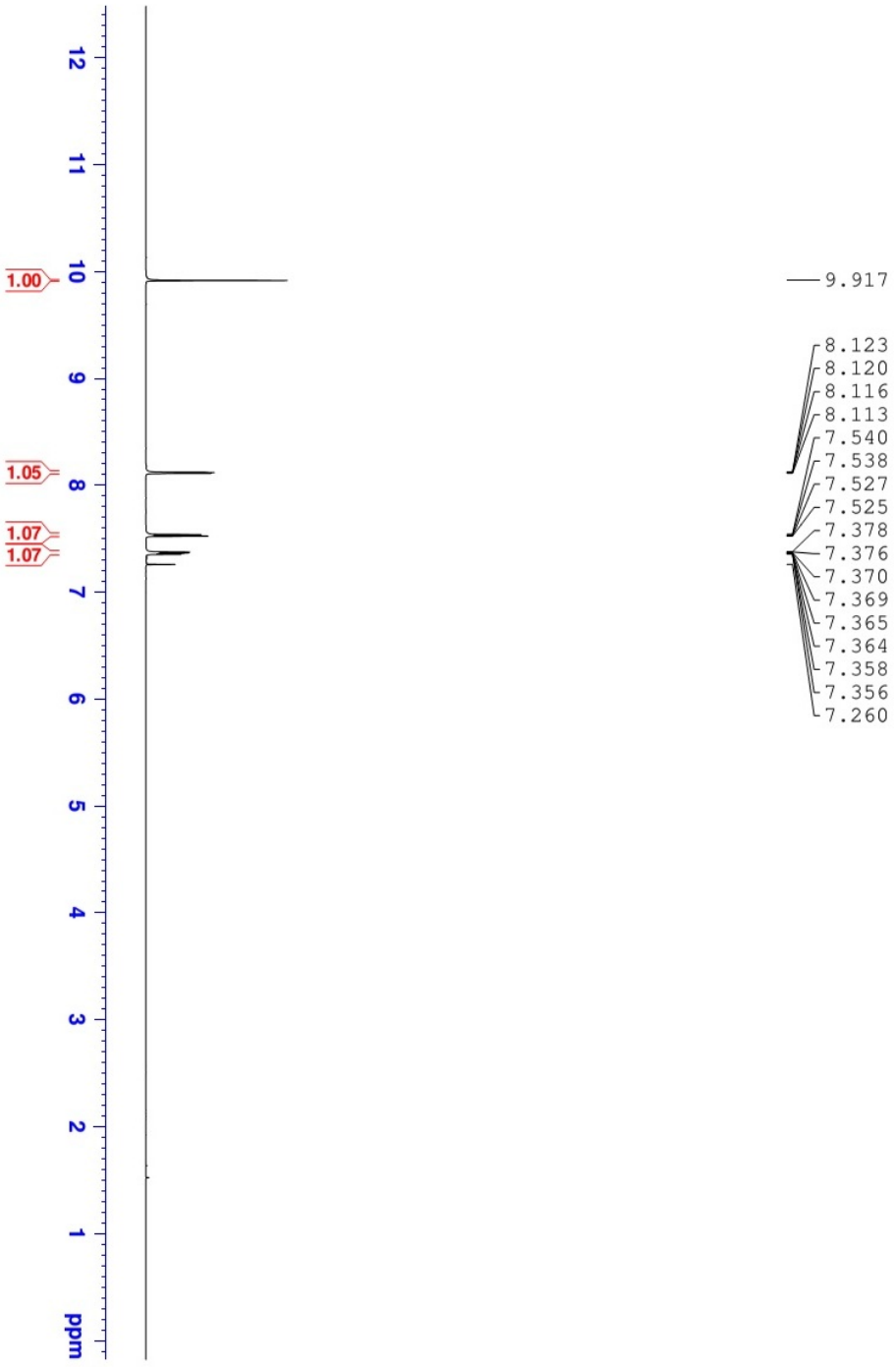
^{13}C NMR of Compound 3k



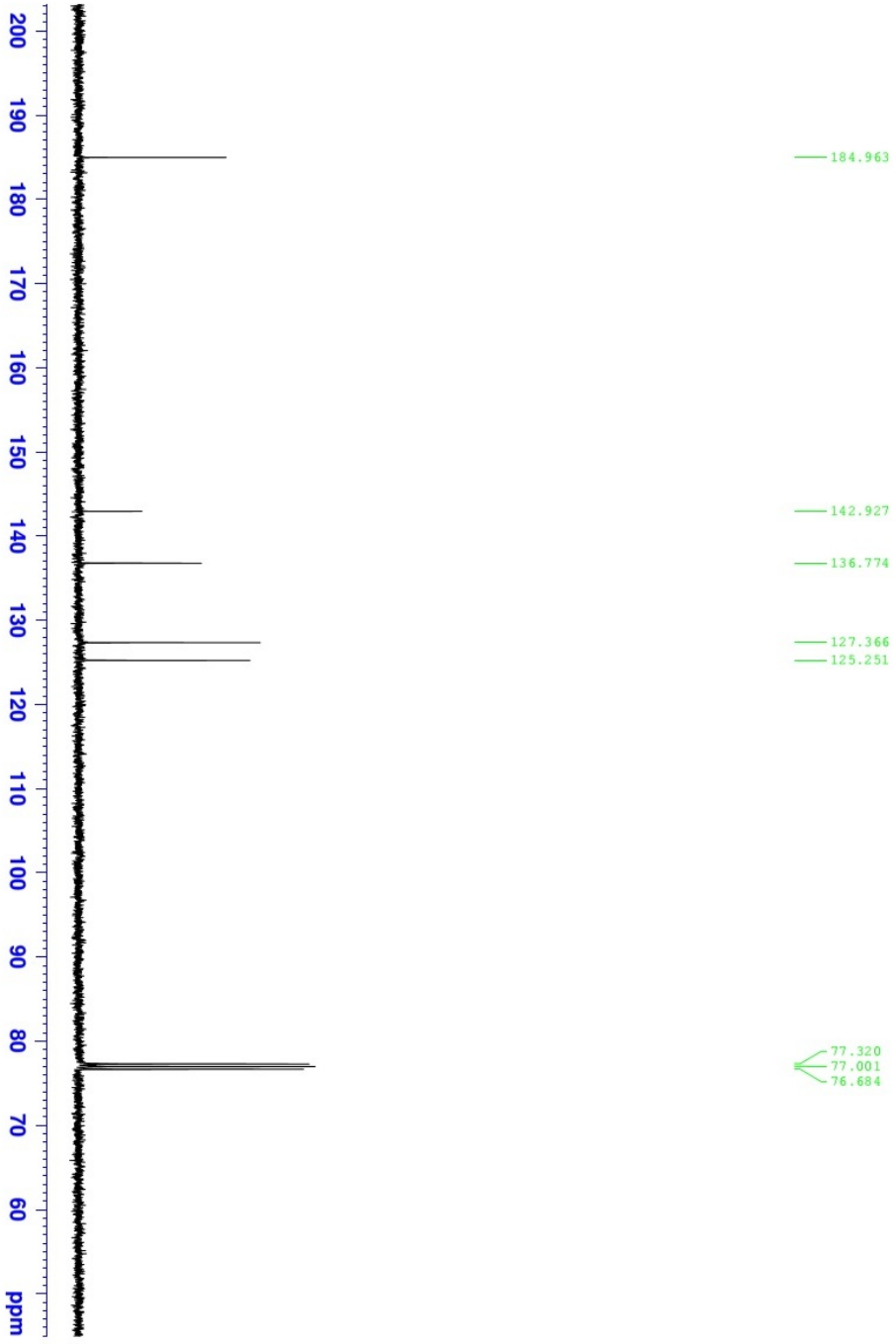
^{1}H NMR of Compound 2l



^{13}C NMR of Compound 2l



^{1}H NMR of Compound 3l



^{13}C NMR of Compound 3l