Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

List of Contents

(A) Materials and equipment

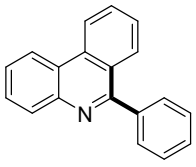
Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. For substrates **2** were prepared according the literature methods.[1] ^{1}H NMR spectra were recorded on a Bruker-400 NMR spectrometer using TMS as an internal standard. Chemical shift values (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 substituted benzoxazoles (3):

To a Schlenk tube were added arylsulfonyl chlorides **1** (0.45 mmol), 2-isocyanobiphenyls **2** (0.30 mmol), MeCN (2.0 mL), Eosin Y (5 mol%), K_2HPO_4 (0.45 mmol), Then the tube was charged with argon, and was stirred at room temperature with the irradiation of a 5 W blue LED for about 10-12 h. After the reaction was finished, the reaction mixture was diluted in 35 mL ethyl acetate, washed with a saturated solution of brine (8 mL), saturated $NaHCO_3$ (10 mL), a saturated solution of brine (8 mL), 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 substituted phenanthridines **3**.

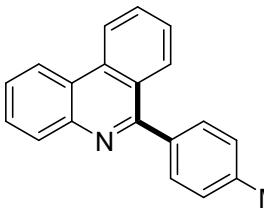
(C) Analytical data



3aa

6-phenylphenanthridine (3aa): [2]

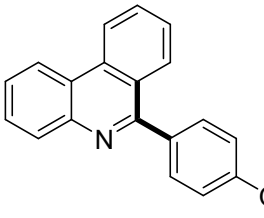
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, J = 8.4 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.30-8.27 (m, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.89-7.84 (m, 1H), 7.81-7.68 (m, 4H), 7.64-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.1, 143.7, 139.8, 133.3, 130.5, 130.4, 129.6, 128.9, 128.7, 128.6, 128.3, 127.0, 126.7, 125.0, 123.2, 122.0, 121.6; LRMS (EI 70 ev) *m/z* (%):255 (M^+); HRMS m/z (ESI) calcd for $C_{19}H_{14}N$ $(M+H)^+$ 256.1127, found 256.1123.



3ab

6-*p*-tolylphenanthridine (3ab): [2]

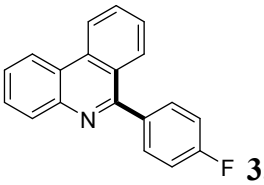
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (d, J = 8.4 Hz, 1H), 8.59-8.57 (m, 1H), 8.23 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 8.12 (dd, J = 8.4 Hz, J = 0.8 Hz, 1H), 7.82-7.80 (m, 1H), 7.76-7.59 (m, 5H), 7.39-7.35 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4, 143.4, 138.1, 136.5, 133.0, 130.4, 130.1, 129.6, 129.1, 129.0, 128.9, 128.8, 127.2, 126.5, 123.4, 122.1, 121.6, 21.4; LRMS (EI 70 ev) *m/z* (%):269 (M^+); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1287.



3ac

6-(4-methoxyphenyl)phenanthridine (3ac): [2]

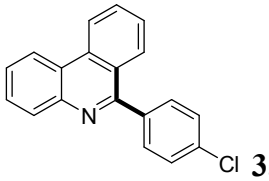
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, J = 8.4 Hz, 1H), 8.59 (d, J = 7.2 Hz, 1H), 8.27-8.22 (m, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.85-7.80 (m, 1H), 7.75-7.56 (m, 5H), 7.08 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 160.0, 143.1, 133.4, 132.2, 131.0, 130.4, 130.1, 129.0, 128.6, 127.1, 126.6, 125.4, 123.3, 122.1, 121.8, 113.6, 55.2; LRMS (EI 70 ev) *m/z* (%):285 (M^+); HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M+H)^+$ 286.1232, found 286.1226.



3ad

6-(4-fluorophenyl)phenanthridine (3ad): [3]

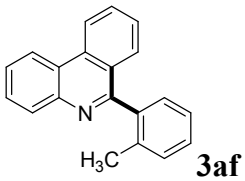
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (d, J = 8.4 Hz, 1H), 8.71-8.67 (m, 1H), 8.26 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 8.10 (d, J = 7.2 Hz, 1H), 7.91-7.86 (m, 1H), 7.82-7.68 (m, 4H), 7.64-7.60 (m, 1H), 7.37-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3 (d, J = 245.7 Hz), 160.1, 143.3, 135.2 (d, J = 3.4 Hz), 133.3, 131.4 (d, J = 8.2 Hz), 130.6, 130.0, 128.8, 128.5, 127.2, 127.0, 125.4, 123.5, 122.3, 122.0, 116.2 (d, J = 22.3 Hz); LRMS (EI 70 ev) *m/z* (%):273 (M^+); HRMS m/z (ESI) calcd for $C_{19}H_{13}FN$ $(M+H)^+$ 274.1033, found 274.1031.



3ae

6-(4-chlorophenyl)phenanthridine (3ae): [4]

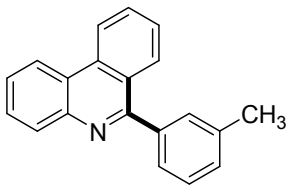
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.88-7.81 (m, 1H), 7.75-7.68 (m, 4H), 7.62 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.2, 143.6, 138.1, 135.2, 133.4, 131.1, 130.5, 130.1, 129.2, 128.4, 128.0, 127.3, 126.6, 125.1, 123.4, 122.2, 122.0; LRMS (EI 70 ev) *m/z* (%):289 (M^+), 288; HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0740.



3af

6-*o*-tolylphenanthridine (3af): [4]

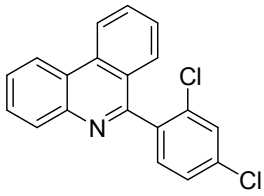
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, J = 8.0 Hz, 1H), 8.63 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 8.22 (d, J = 7.6 Hz, 1H), 7.85-7.81 (m, 1H), 7.77-7.72 (m, 1H), 7.69-7.64 (m, 2H), 7.60-7.55 (m, 1H), 7.41-7.34 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.3, 143.7, 138.9, 136.6, 133.1, 130.8, 130.2, 129.8, 129.2, 128.7, 128.3, 128.0, 127.2, 127.1, 126.3, 125.5, 123.8, 122.3, 122.0; LRMS (EI 70 ev) *m/z* (%): 269 (M^+); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1281.



3ag

6-*m*-tolylphenanthridine (3ag): [2]

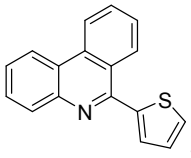
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.21 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.86-7.82 (m, 1H), 7.77-7.73 (m, 1H), 7.70-7.65 (m, 1H), 7.62-7.58 (m, 1H), 7.55 (s, 1H), 7.49-7.41 (m, 2H), 7.31 (d, J = 6.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1, 143.3, 139.5, 138.1, 133.3, 130.6, 130.1, 129.9, 129.3, 129.0, 128.7, 128.1, 127.1, 126.8, 126.4, 125.3, 123.6, 121.9, 121.7, 21.7; LRMS (EI 70 ev) *m/z* (%): 269 (M^+); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1277.



3ah

6-(2,4-dichlorophenyl)phenanthridine (3ah): [5]

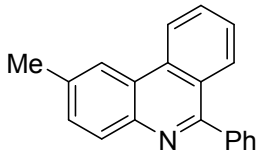
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (d, J = 8.4 Hz, 1H), 8.68 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 8.30-8.25 (m, 1H), 7.93-7.88 (m, 1H), 7.83-7.76 (m, 2H), 7.70-7.62 (m, 3H), 7.52-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 143.6, 137.2, 135.3, 134.4, 133.1, 132.0, 131.0, 130.3, 129.4, 129.0, 128.1, 127.6, 127.4, 127.2, 125.2, 124.1, 122.2, 122.0; LRMS (EI 70 ev) *m/z* (%): 325 (M^++1), 324 (M^+), 323; HRMS m/z (ESI) calcd for $C_{19}H_{12}Cl_2N$ $(M+H)^+$ 324.0347, found 324.0352.



3ai

6-(thiophen-2-yl)phenanthridine (3ai): [4]

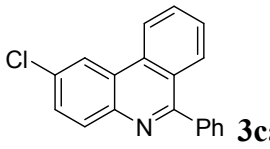
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, J = 8.4 Hz, 1H), 8.60-8.55 (m, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.86-7.81 (m, 1H), 7.74-7.63 (m, 4H), 7.55 (d, J = 4.8 Hz, 1H), 7.25-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.6, 143.4, 142.3, 133.2, 130.7, 130.2, 129.1, 128.8, 128.0, 127.8, 127.4, 127.1, 126.8, 124.7, 123.5, 122.2, 121.8; LRMS (EI 70 ev) *m/z* (%): 261 (M^+); HRMS m/z (ESI) calcd for $C_{17}H_{12}NS$ $(M+H)^+$ 262.0690, found 262.0694.



3ba

2-methyl-6-phenylphenanthridine (3ba): [1]

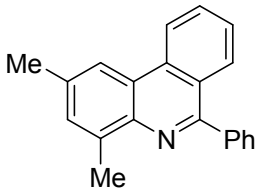
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (d, J = 8.0 Hz, 1H), 8.34 (s, 1H), 8.11, (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.79-7.75 (m, 1H), 7.70-7.67 (m, 2H), 7.53-7.44 (m, 5H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 142.1, 139.6, 136.4, 133.1, 130.5, 130.1, 129.8, 129.5, 128.7, 128.4, 128.3, 126.8, 125.2, 123.2, 122.1, 121.2; 269 (M^+); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1285.



3ca

2-chloro-6-phenylphenanthridine (3ca): [1]

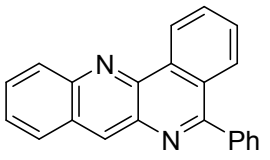
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 3.6 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.90-7.87 (m, 1H), 7.71-7.61 (m, 4H), 7.57-7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.2, 142.0, 139.3, 133.1, 132.4, 131.7, 131.2, 129.8, 129.4, 129.1, 129.0, 128.6, 127.9, 125.3, 124.8, 122.4, 122.0; LRMS (EI 70 ev) *m/z* (%):289 (M^+); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0742.



3da

2,4-dimethyl-6-phenylphenanthridine (3da): [1]

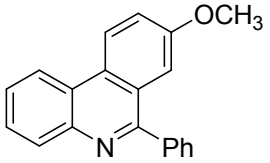
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 8.13 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.79-7.75 (m, 3H), 7.56-7.46 (m, 4H), 7.41 (s, 1H); 2.81 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 140.7, 140.0, 137.2, 136.1, 133.5, 131.2, 130.0, 129.9, 128.4, 128.3, 128.2, 126.5, 124.7, 123.4, 122.2, 119.1, 22.3, 18.4; LRMS (EI 70 ev) *m/z* (%):283 (M^+); HRMS m/z (ESI) calcd for $C_{21}H_{18}N$ $(M+H)^+$ 284.1439, found 284.1437.



3ea

5-phenyldibenzo[b,h][1,5]naphthyridine (3ea): [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (d, J = 7.6 Hz, 1H), 8.98 (s, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.12 (dd, J = 3.2 Hz, J = 2.0 Hz, 2H), 7.99-7.96 (m, 1H), 7.87-7.74 (m, 4H), 7.64-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.1, 148.2, 143.0, 139.4, 136.5, 136.1, 134.2, 131.4, 130.3, 129.8, 129.7, 129.7, 129.3, 128.8, 128.7, 128.6, 128.5, 127.4, 126.5, 124.6; LRMS (EI 70 ev) *m/z* (%):306 (M^+); HRMS m/z (ESI) calcd for $C_{22}H_{14}N_2$ $(M+H)^+$ 307.1235, found 307.1229.

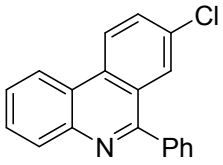


3fa

8-methoxy-6-phenylphenanthridine (3fa): [5]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (d, J = 8.4 Hz, 1H), 8.51-8.47 (m, 1H), 8.17 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.74-7.67 (m, 2H), 7.63-7.58 (m, 2H), 7.55-7.48 (m, 3H), 7.44-7.40 (m, 2H), 3.87 (s,

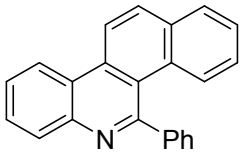
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 158.3, 143.1, 139.2, 130.3, 130.0, 129.3, 128.4, 128.0, 127.8, 127.1, 124.1, 121.5, 121.1, 116.1, 114.5, 110.0, 56.1; LRMS (EI 70 ev) *m/z* (%):285 (M^+); HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M+H)^+$ 286.1232, found 286.1231.



3ga

8-chloro-6-phenylphenanthridine (3ga): [2]

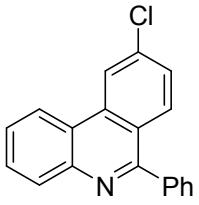
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 7.6 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 2.8 Hz, 1H), 7.79-7.74 (m, 2H), 7.70-7.63 (m, 3H), 7.58-7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 143.1, 139.2, 133.0, 131.6, 131.2, 130.2, 129.5, 129.2, 128.9, 128.4, 127.7, 127.0, 126.1, 124.3, 123.0, 121.8; LRMS (EI 70 ev) *m/z* (%): 290 $(M+1)^+$, 289 (M^+); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0744.



3ha

5-phenylbenzo[i]phenanthridine (3ha): [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67-8.63 (m, 2H), 8.31 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.80-7.76 (m, 2H), 7.72-7.69 (m, 1H), 7.62-7.59 (m, 2H), 7.51-7.46 (m, 4H), 7.23-7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 144.2, 143.6, 134.4, 133.2, 132.6, 130.4, 129.7, 129.3, 129.1, 129.0, 128.6, 128.5, 128.2, 127.0, 126.5, 126.1, 123.7, 122.4, 121.5, 120.2; LRMS (EI 70 ev) *m/z* (%): 305(M^+); HRMS m/z (ESI) calcd for $C_{23}H_{16}N$ $(M+H)^+$ 306.1282, found 306.1279.

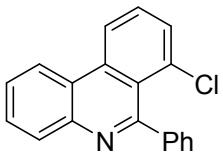


3ia

9-chloro-6-phenylphenanthridine (3ia): [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (s, 1H), 8.52 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.70-7.67 (m, 3H), 7.55-7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6, 144.0, 139.4, 137.1, 134.5, 130.6, 130.1, 129.4, 129.0, 128.8, 128.4, 127.6, 127.2, 123.5, 122.7, 122.0, 121.8; LRMS (EI 70 ev) *m/z* (%): 290 $(M+1)^+$, 289 (M^+), 288; HRMS m/z

(ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0731.



3ja

7-chloro-6-phenylphenanthridine (3ja):

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (d, J = 8.0 Hz, 1H), 8.58 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.07 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.82-7.78 (m, 1H), 7.70-7.64 (m, 4H), 7.59-7.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 143.6, 139.0, 136.1, 133.7, 131.4, 130.2, 129.9, 129.1, 128.6, 128.3, 127.4, 127.1, 125.6, 123.4, 122.5, 122.0; LRMS (EI 70 ev) *m/z* (%): 290 $(M+1)^+$, 289 (M^+), 288, 161; HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0734.

(D) References

1 M. Tobisu, K. Koh, T. Furukawa and N. Chatani, *Angew. Chem. Int. Ed.*, 2012, **51**, 11363.

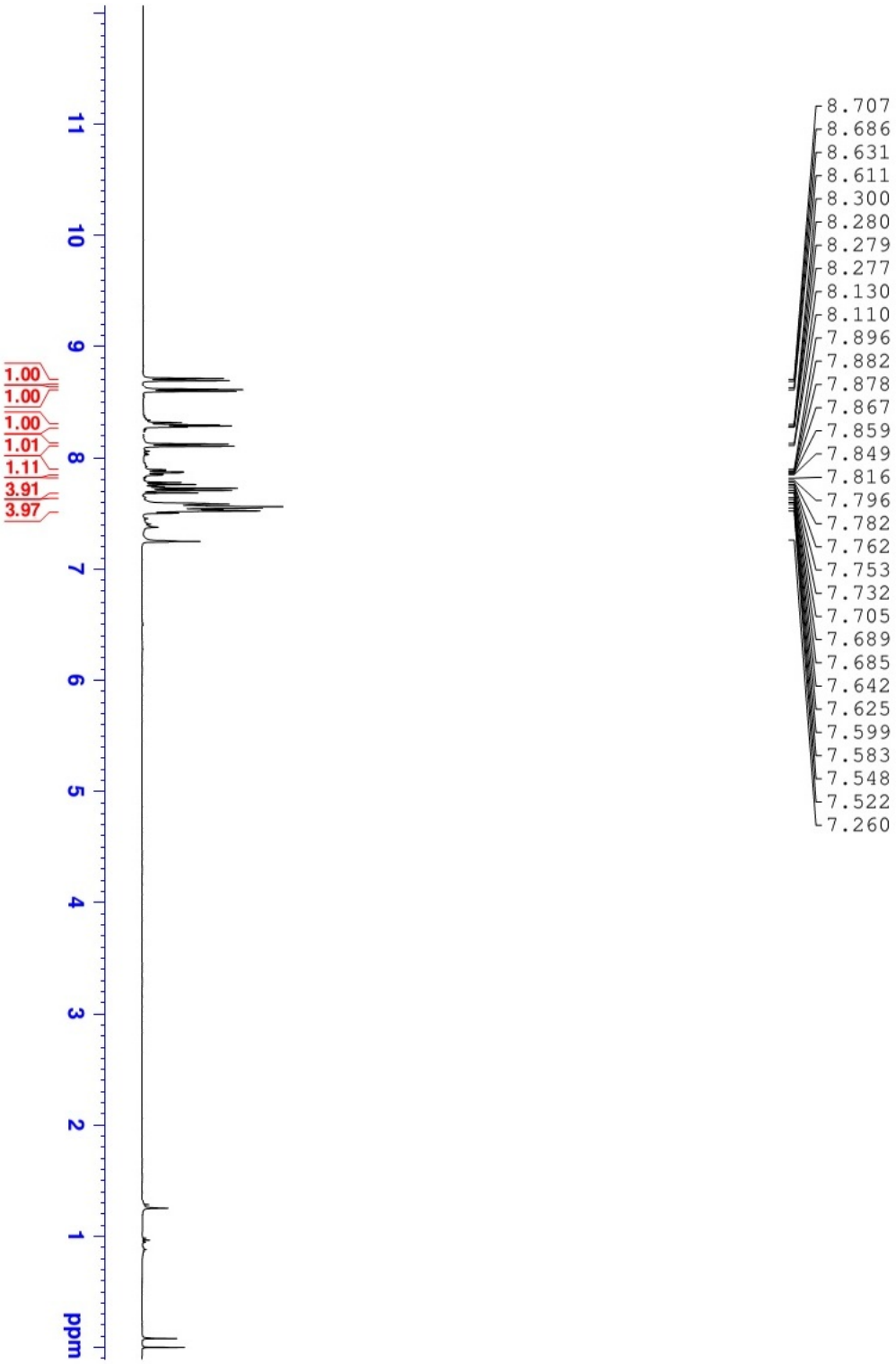
2 J. Peng, T. Chen, C. Chen and B. Li, *J. Org. Chem.*, 2011, **76**, 9507.

3 Y. Su, H. Huang, C. Li, C. Chien, Y. Tao, P. Chou, S. Datta and R. Liu, *Adv. Mater.*, 2003, **15**, 884.

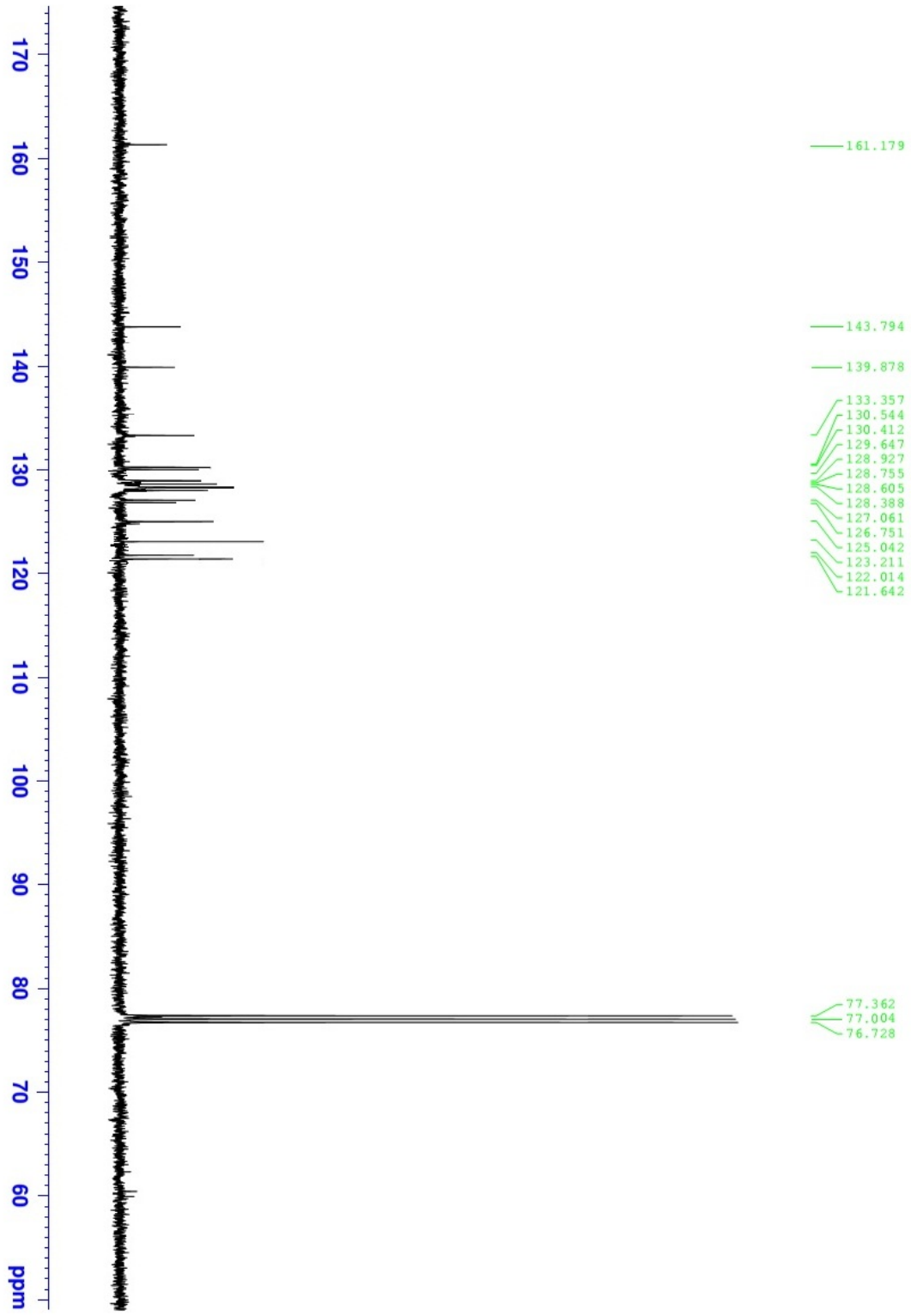
4 L. Zhang, G. Y. Ang and S. Chiba, *Org. Lett.*, 2010, **12**, 3682.

5 T. Xiao, L. Li, G. Lin, Q. Wang, P. Zhang, Z. Mao and L. Zhou, *Green Chem.*, 2014, **DOI:** 10.1039/C3GC42517G.

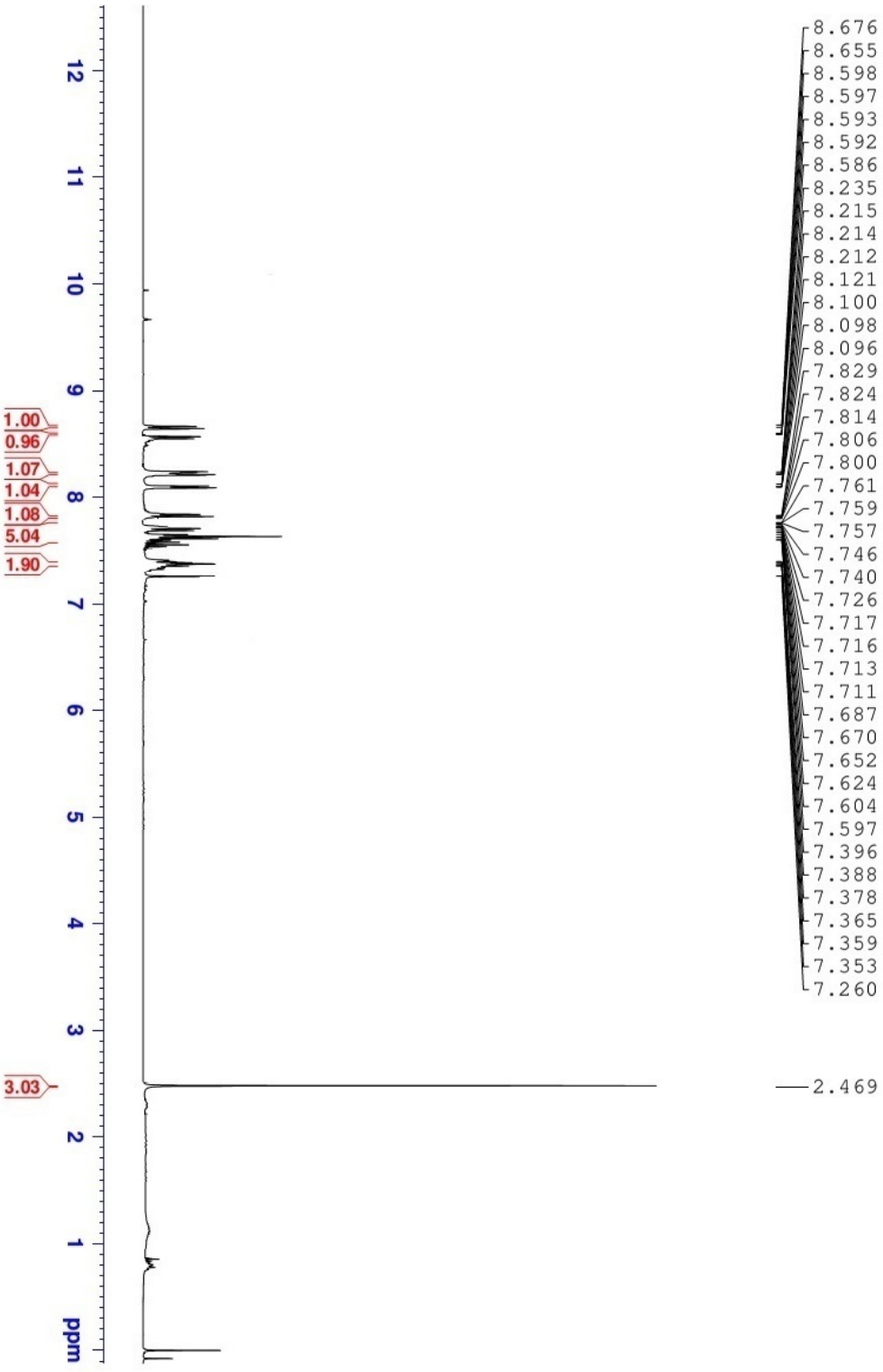
(E) Spectra



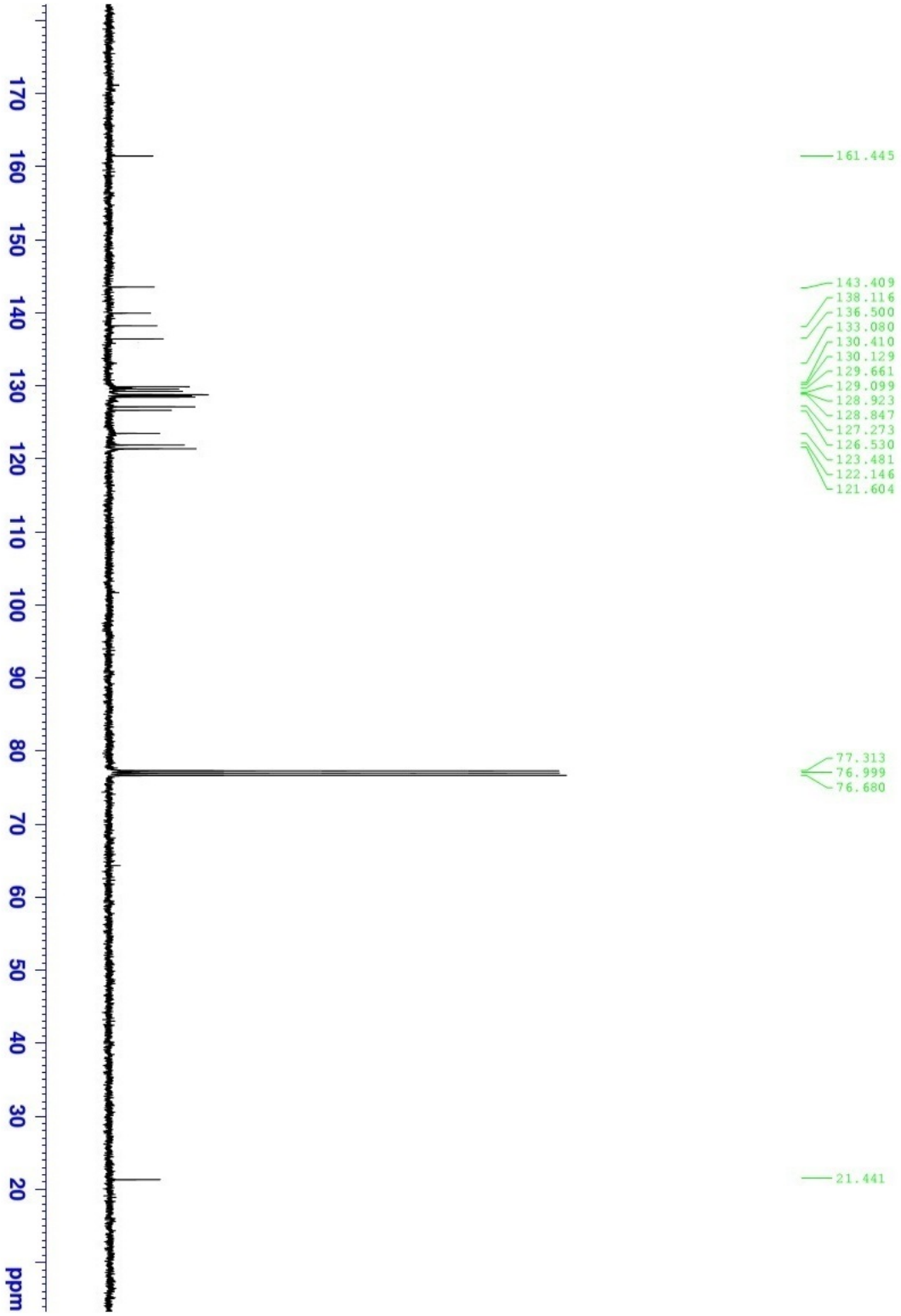
^{1}H NMR of Compound 3aa



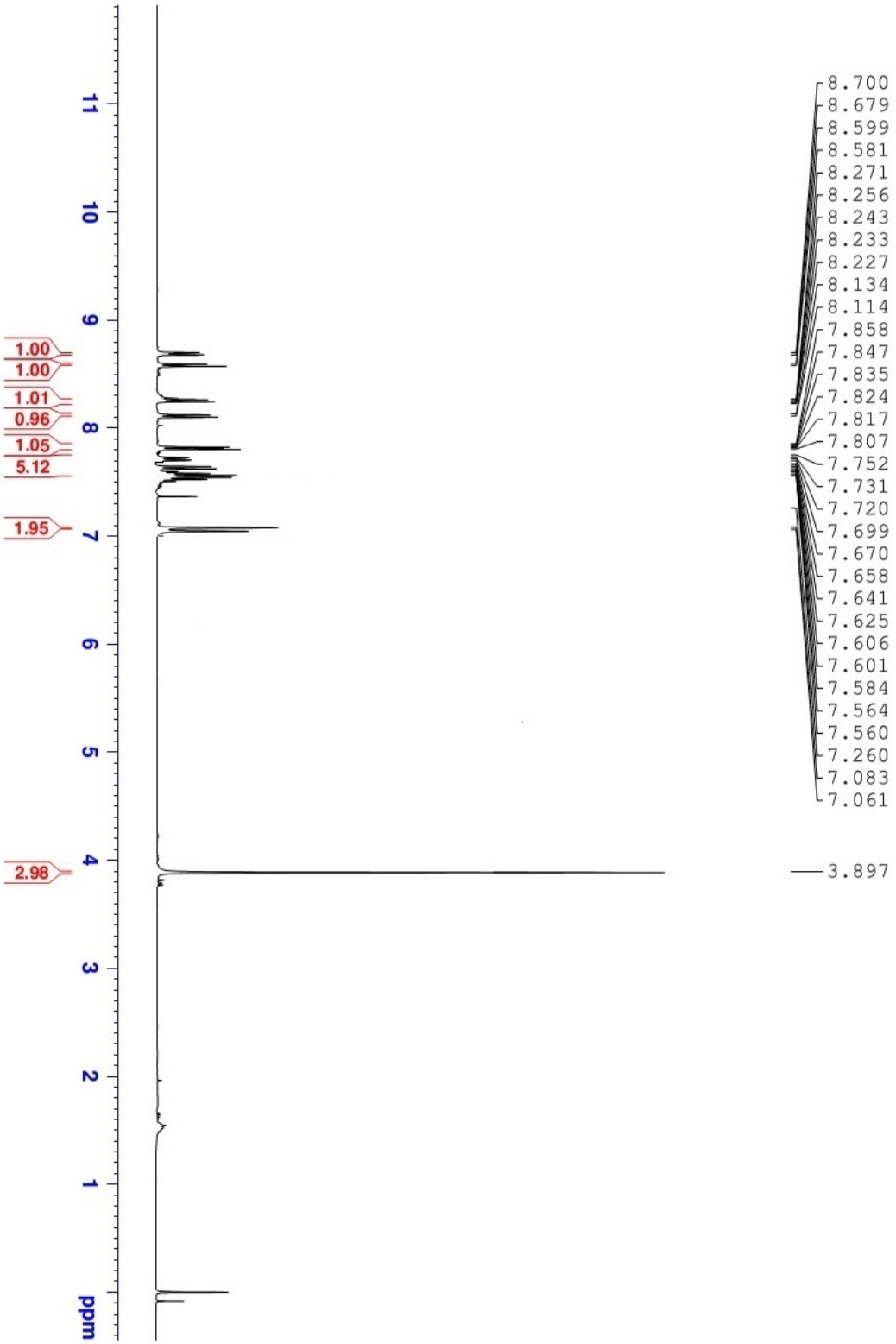
^{13}C NMR of Compound 3aa



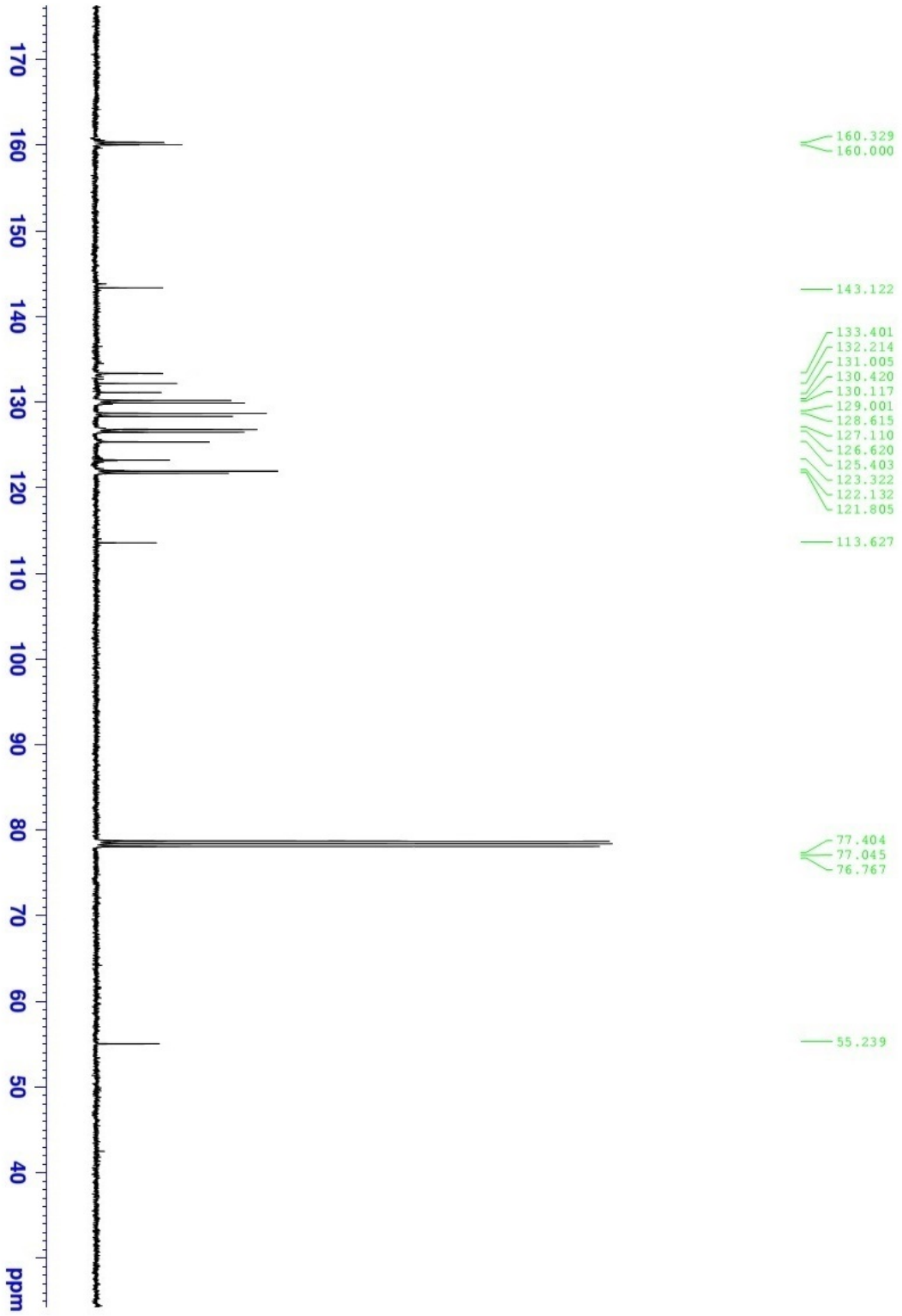
^{1}H NMR of Compound 3ab



^{13}C NMR of Compound 3ab



^{1}H NMR of Compound 3ac



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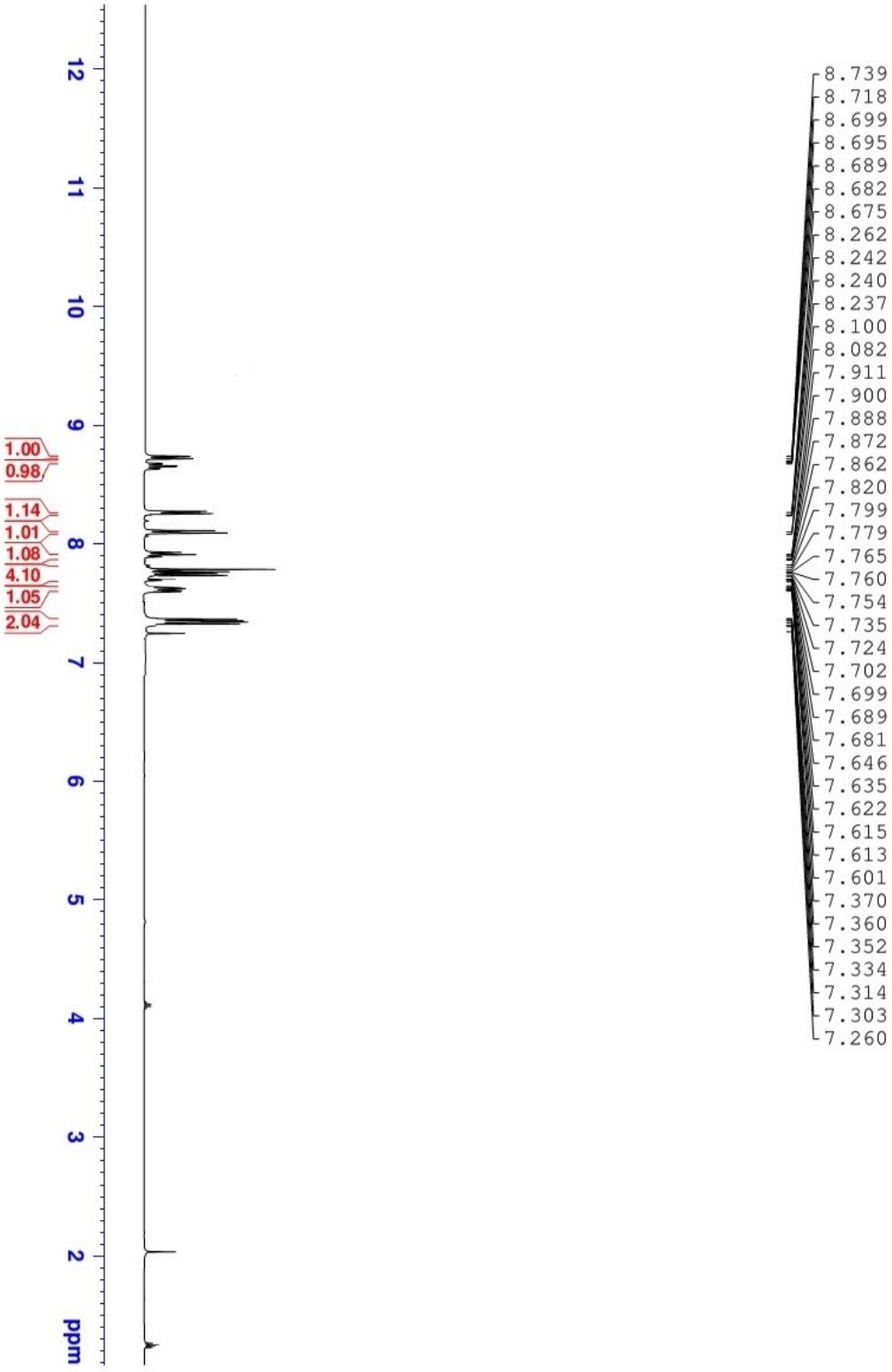
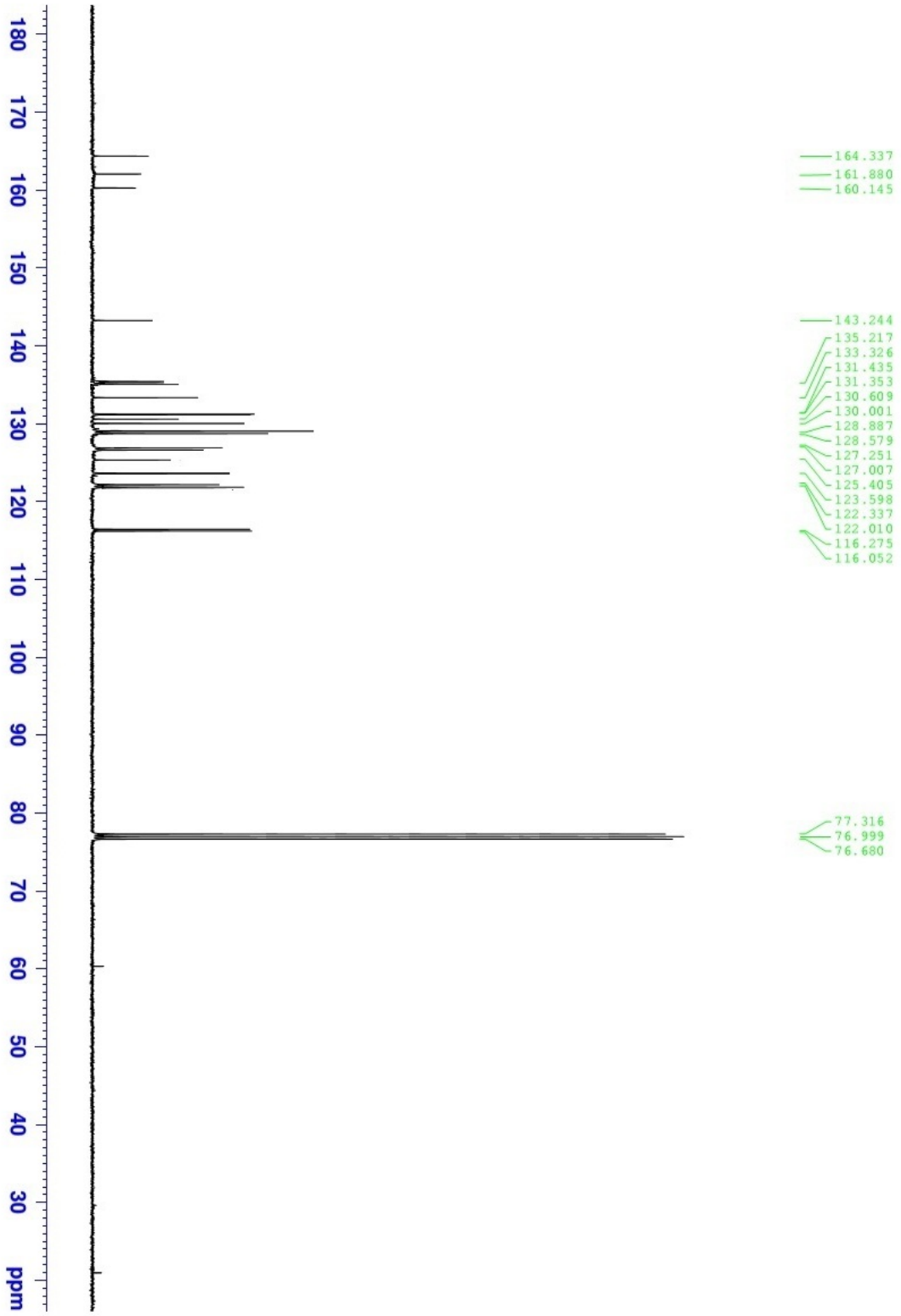
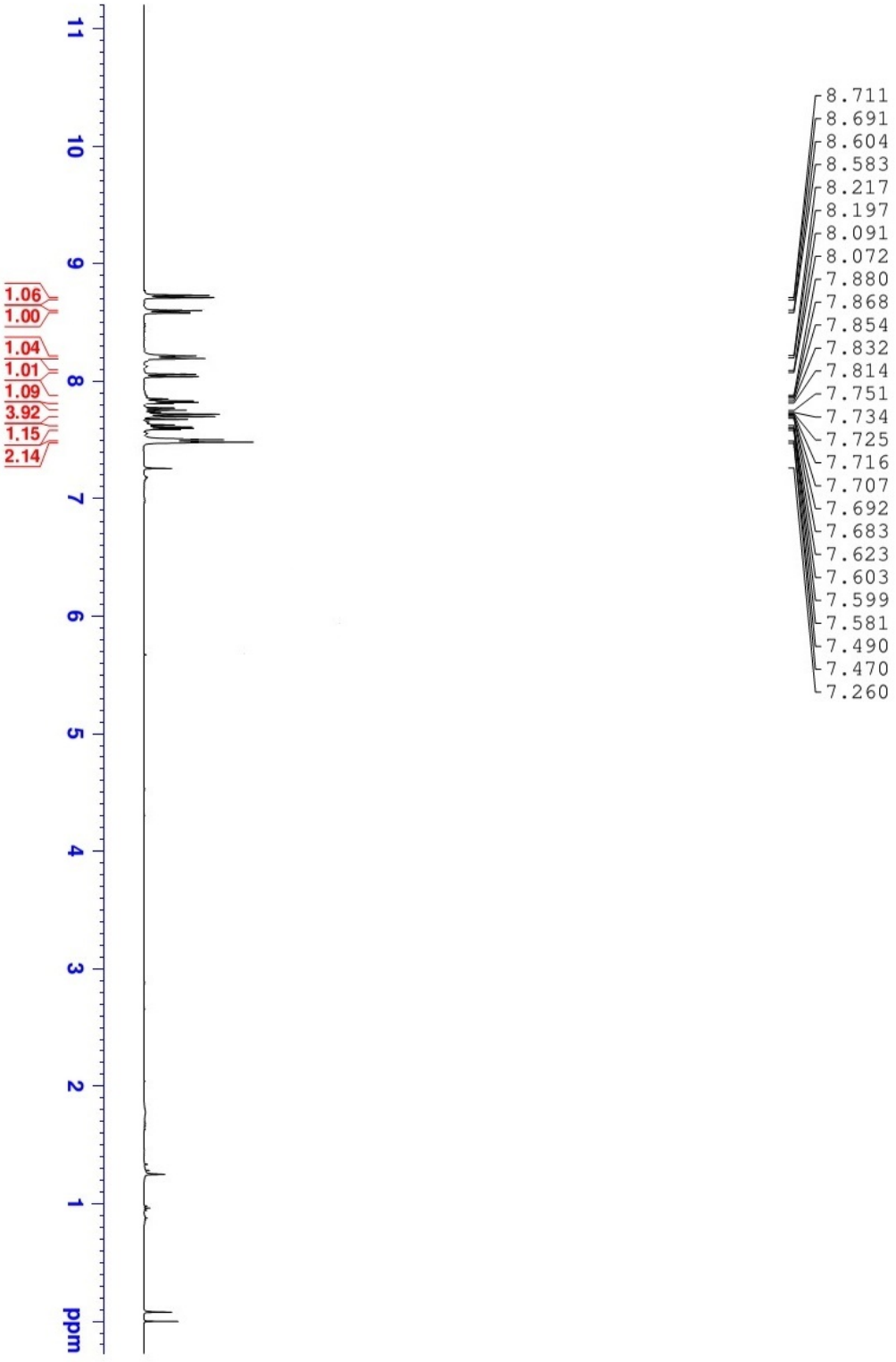


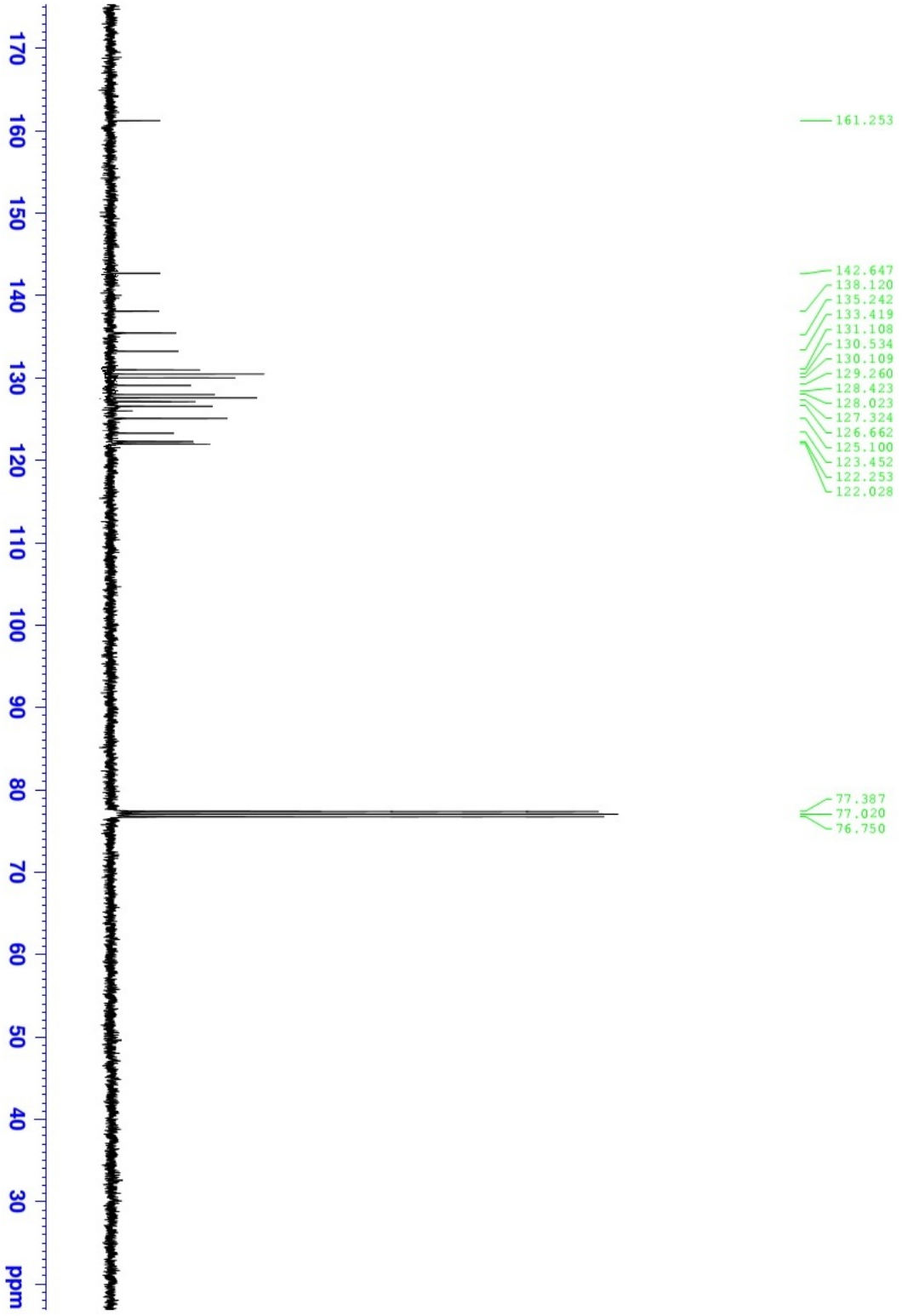
^{1}H NMR of Compound 3ad



^{13}C NMR of Compound 3ad



^{1}H NMR of Compound 3ae



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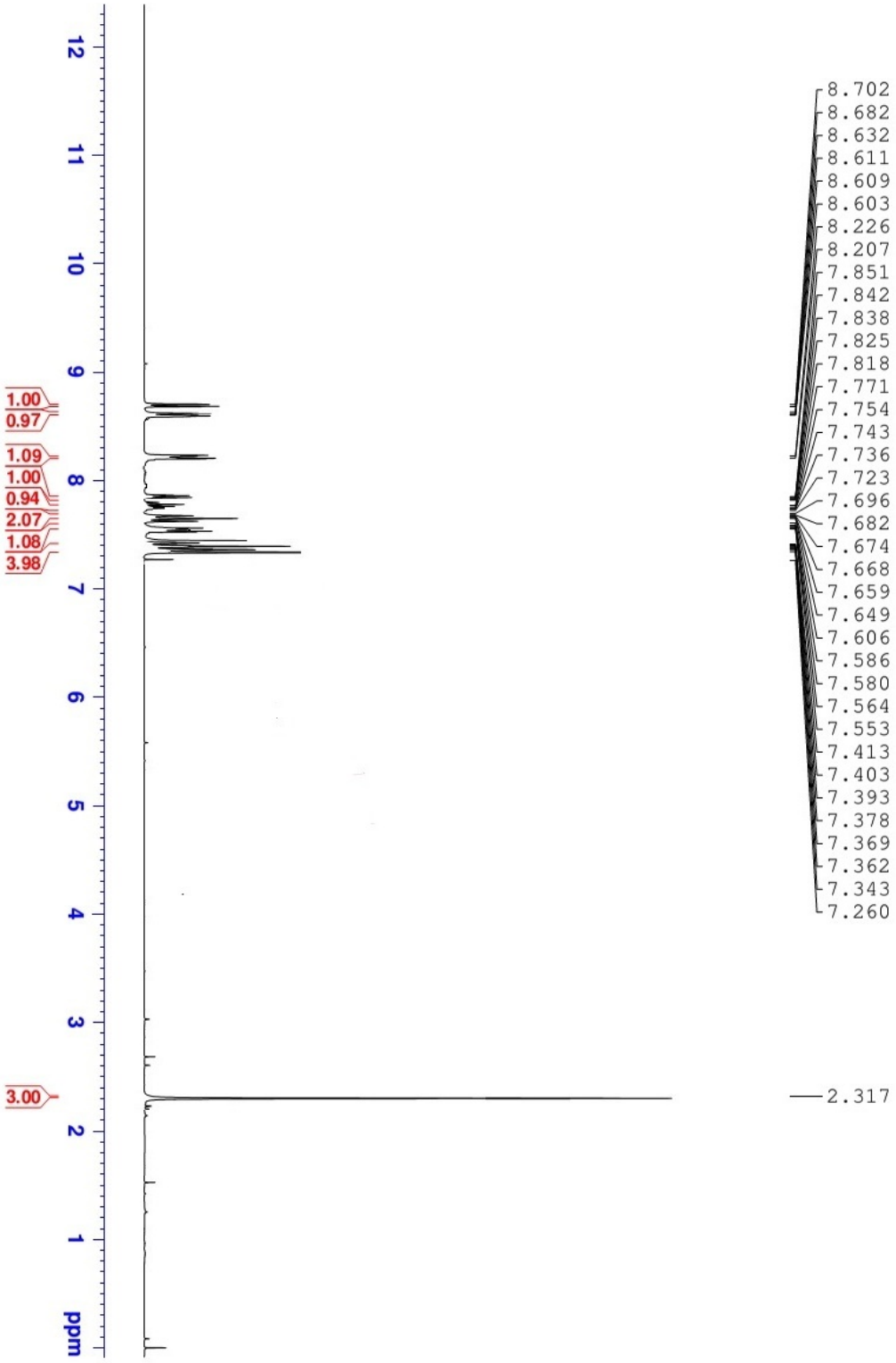
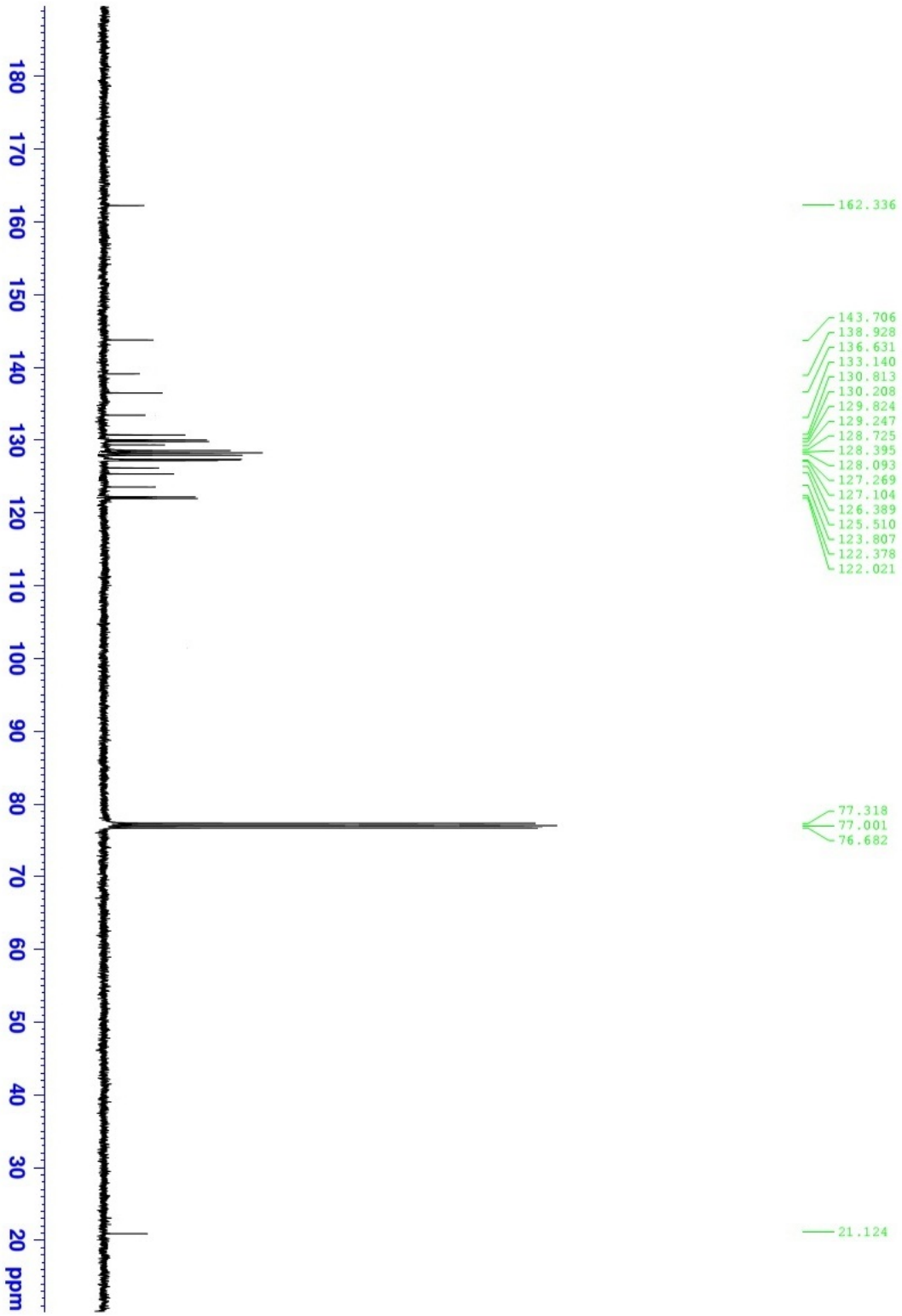
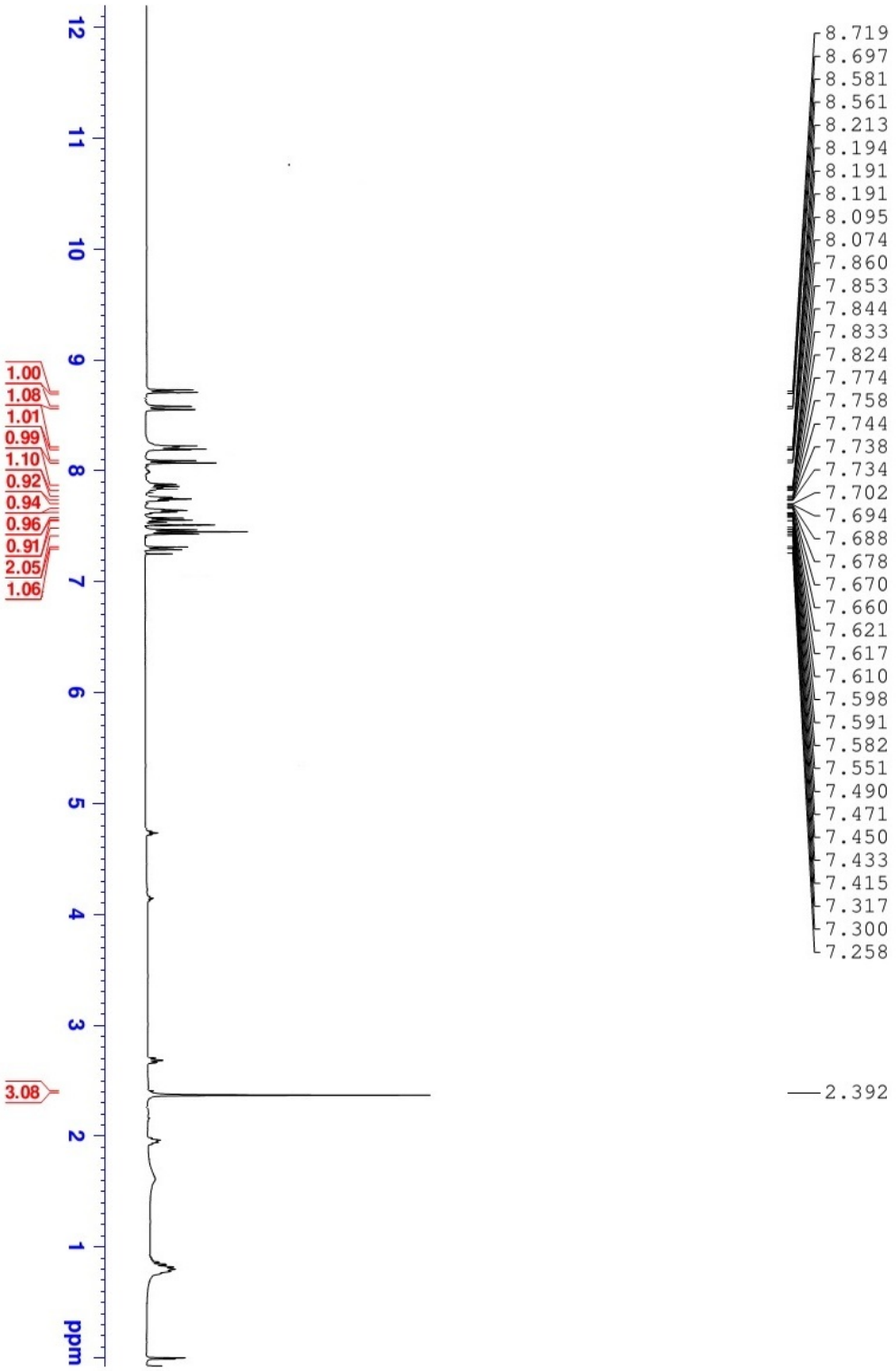


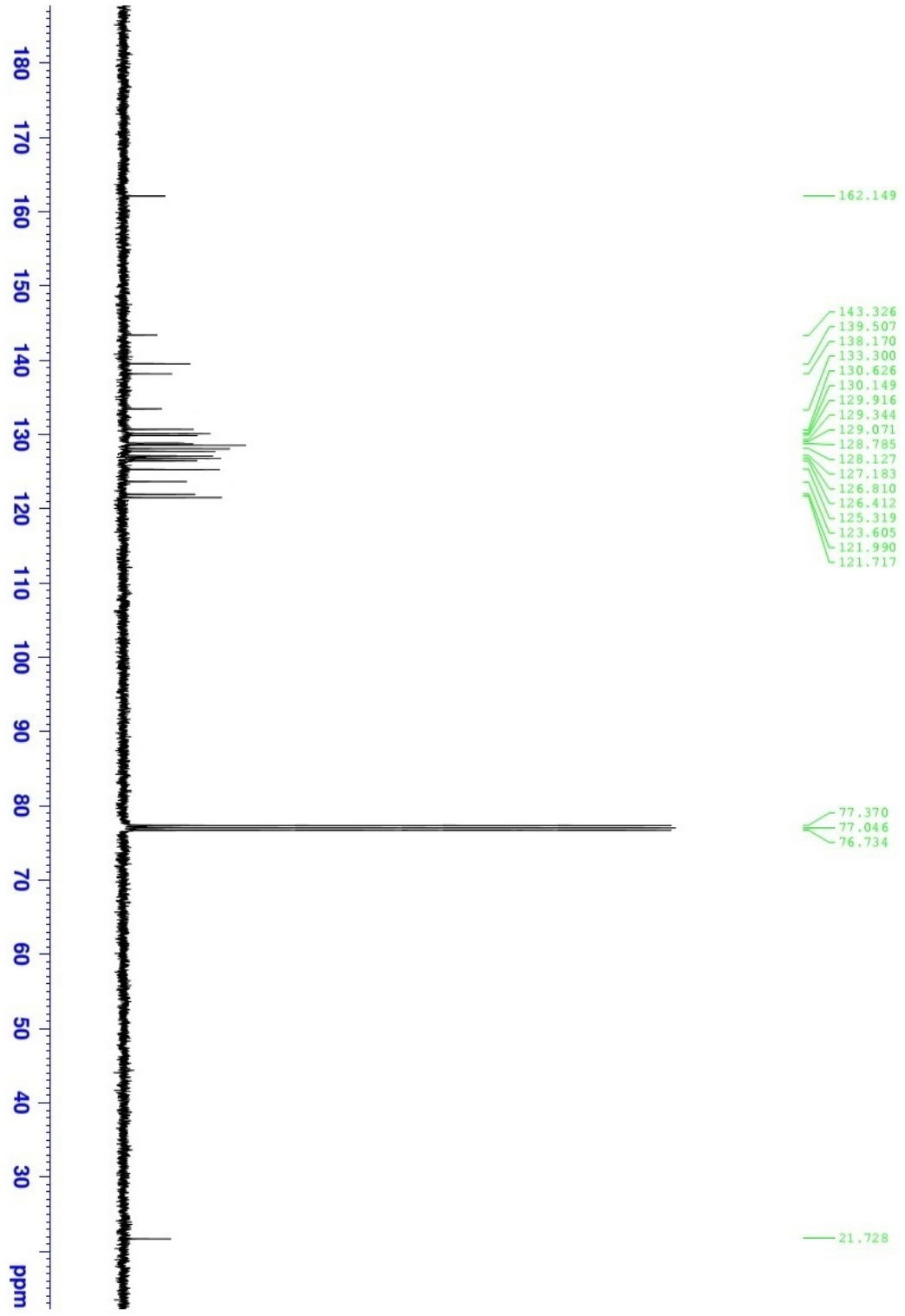
^{1}H NMR of Compound 3af



^{13}C NMR of Compound 3af



^{1}H NMR of Compound 3ag



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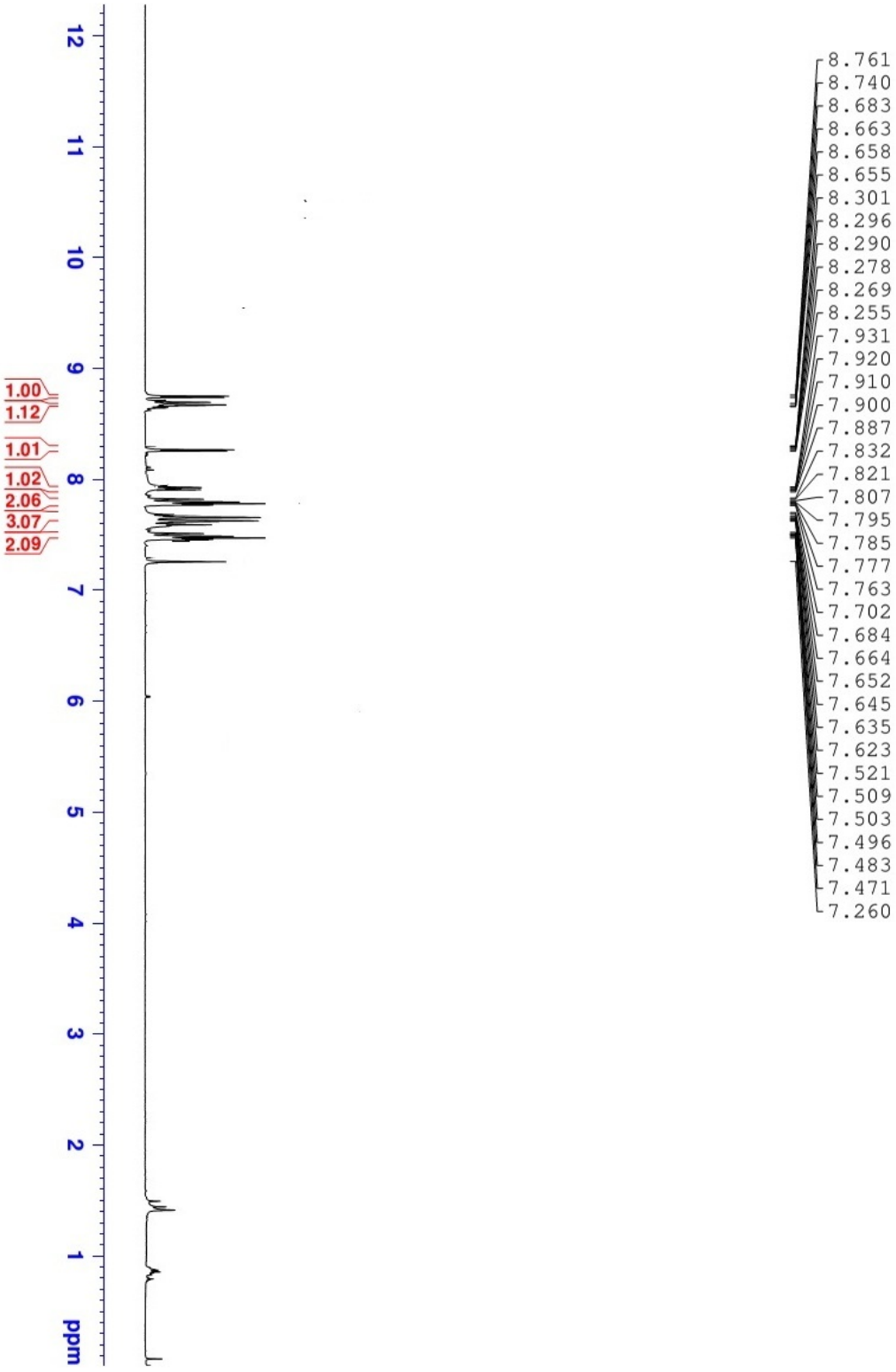
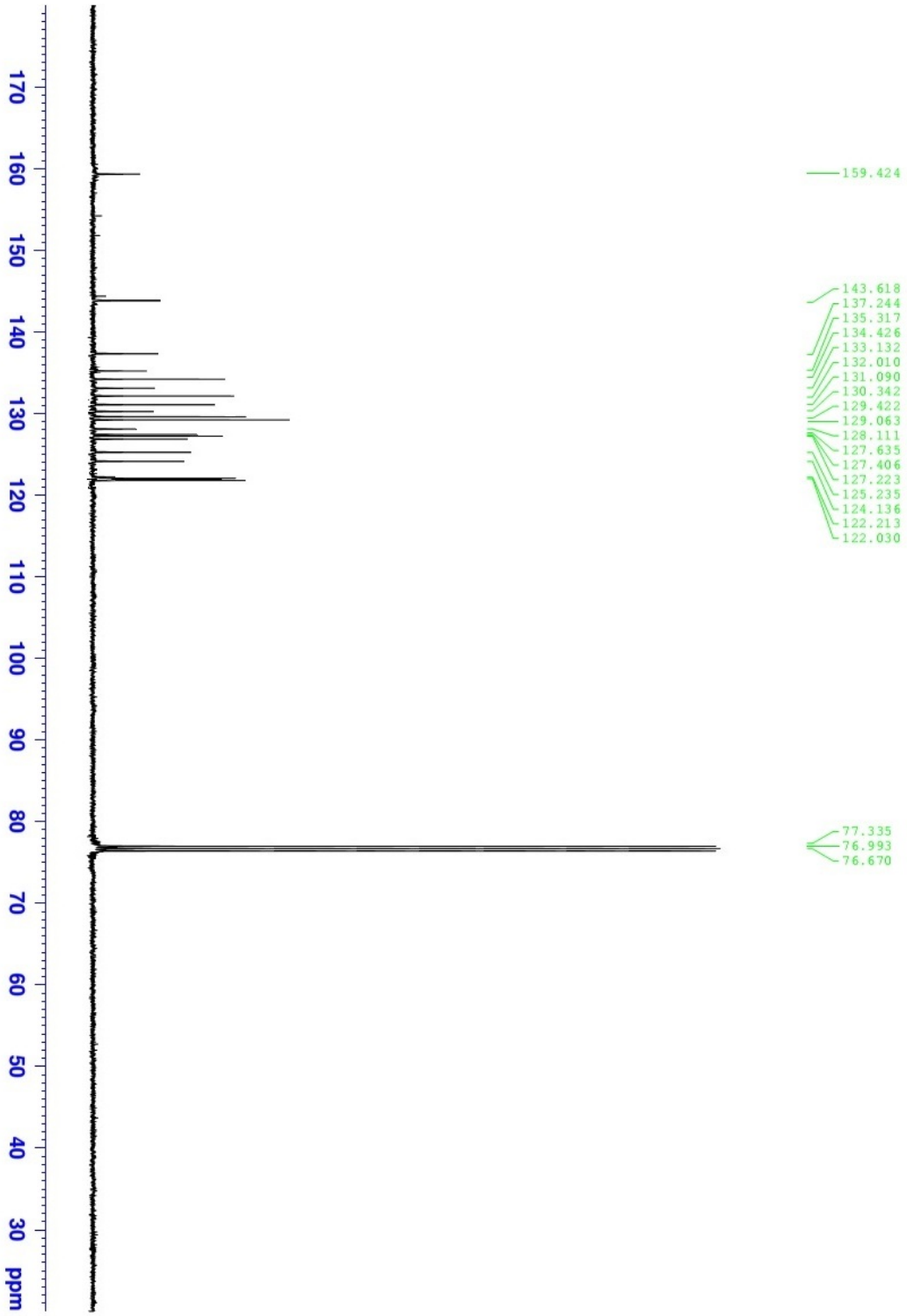
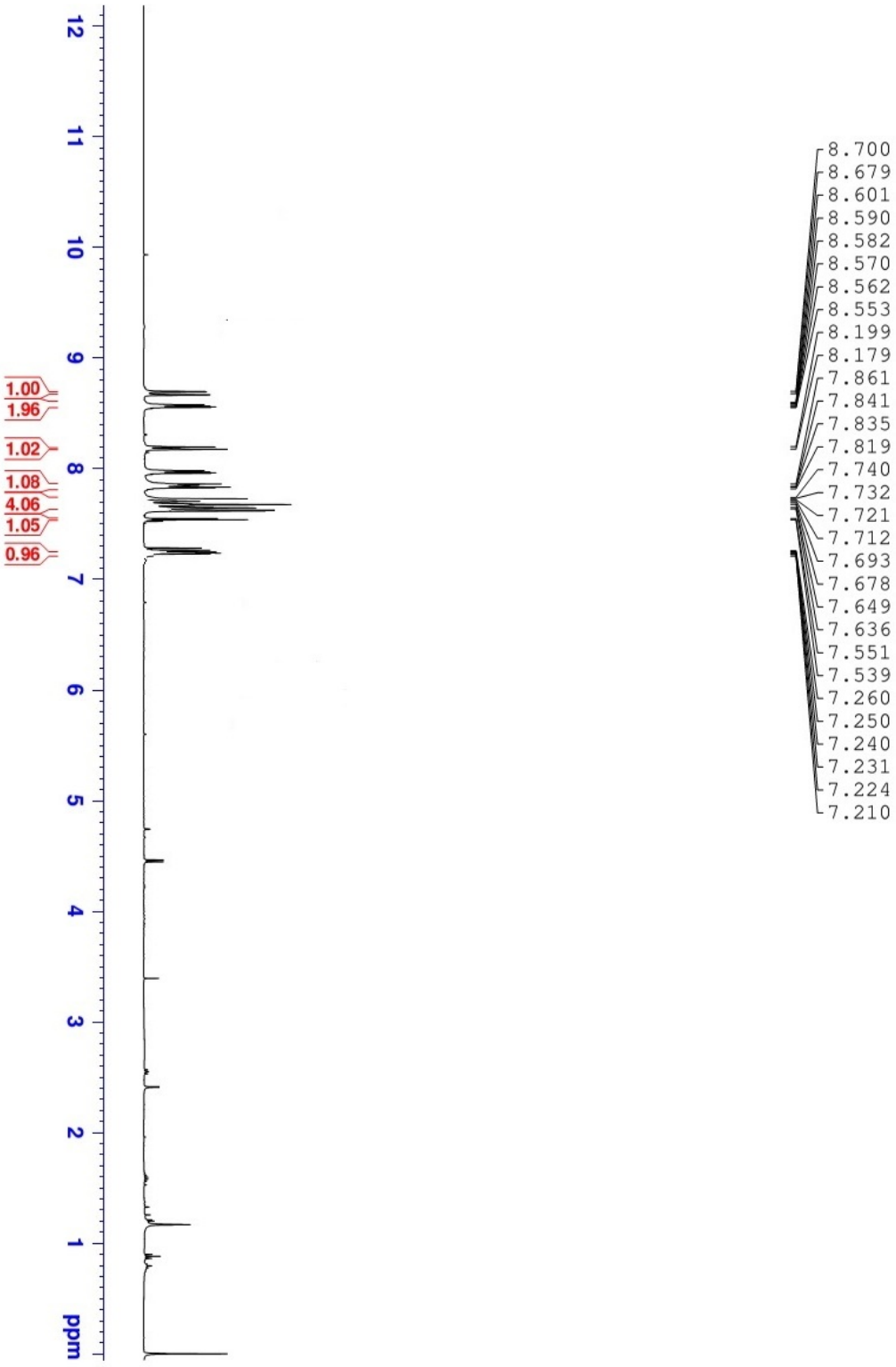


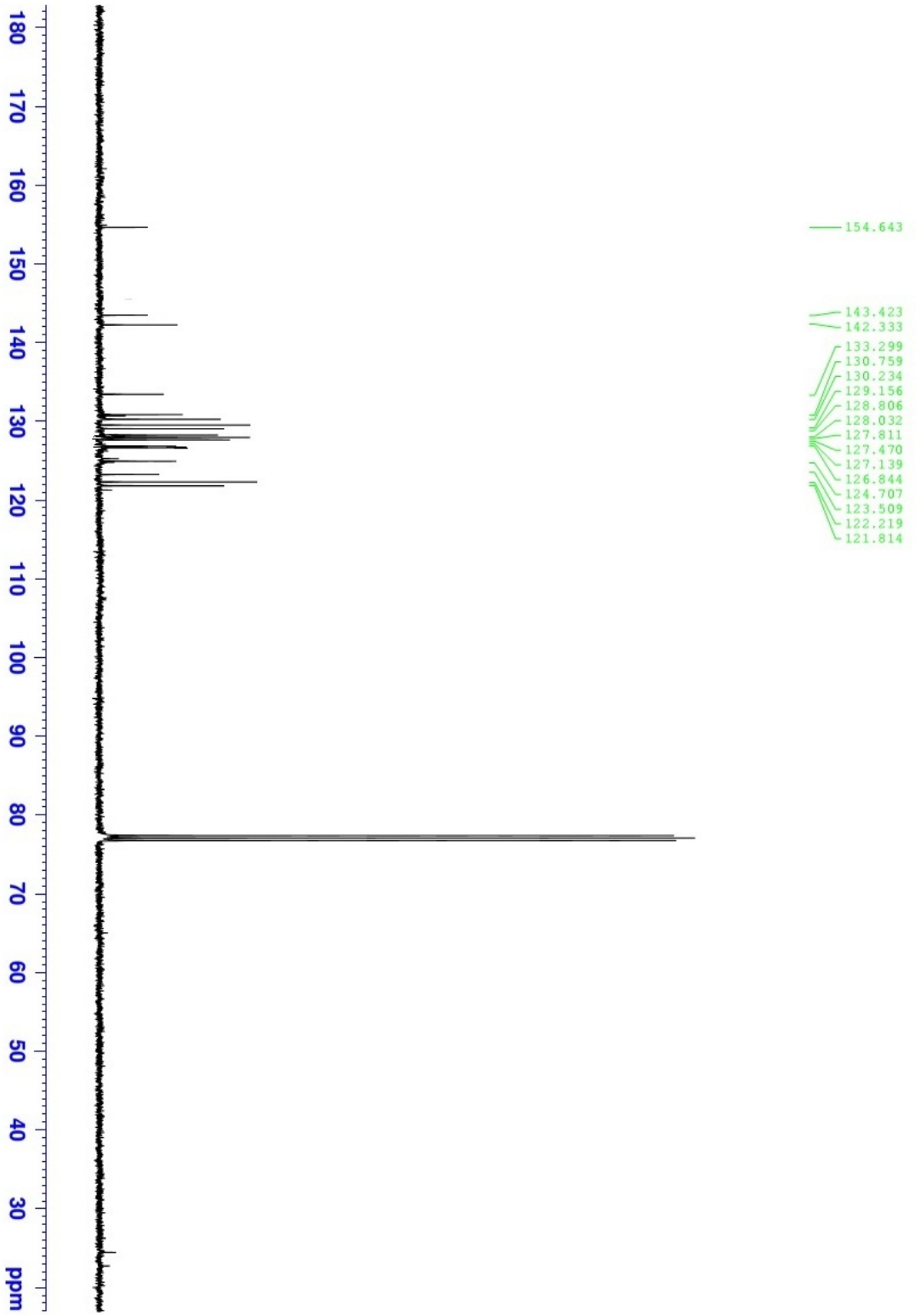
^{1}H NMR of Compound 3ah



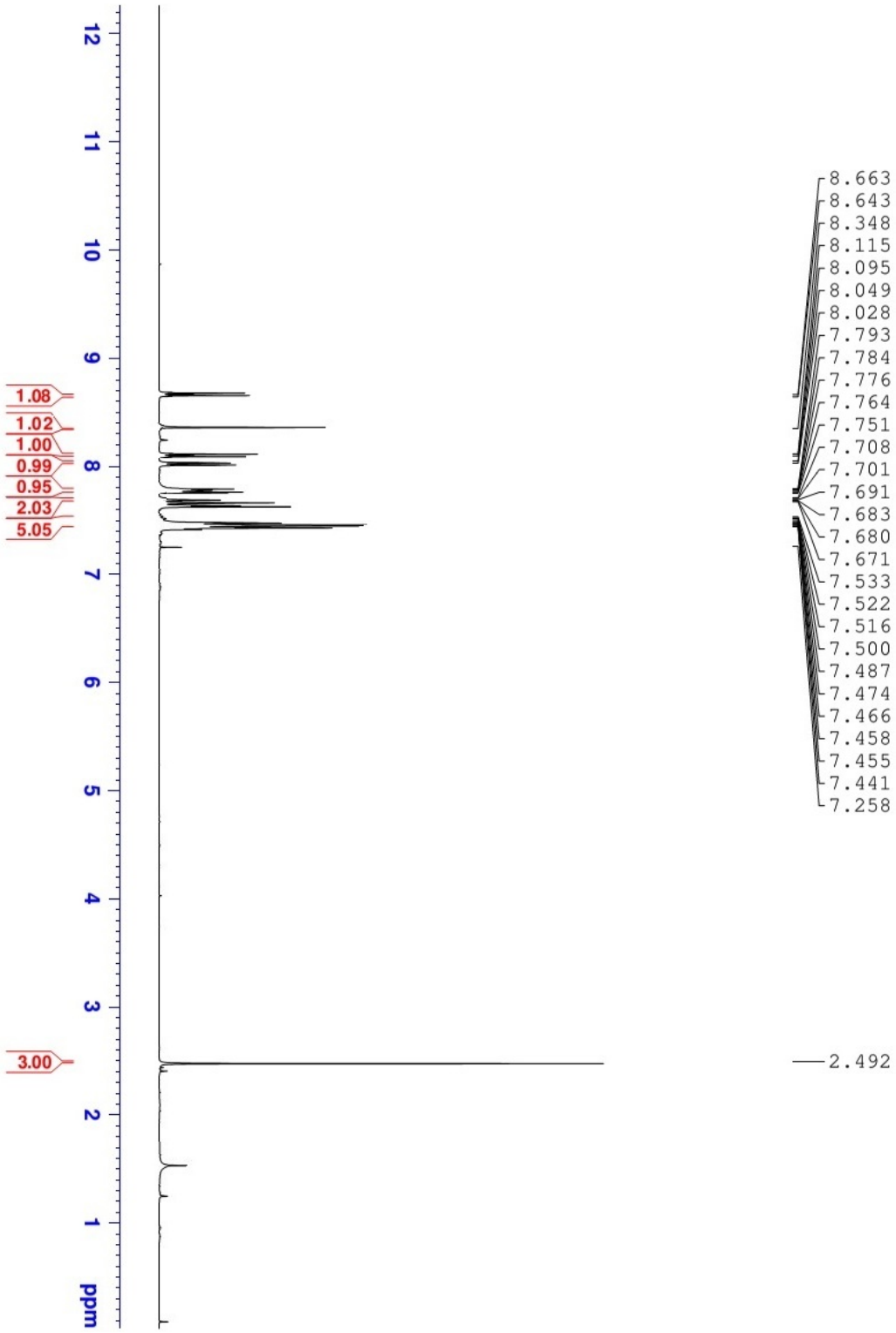
^{13}C NMR of Compound 3ah



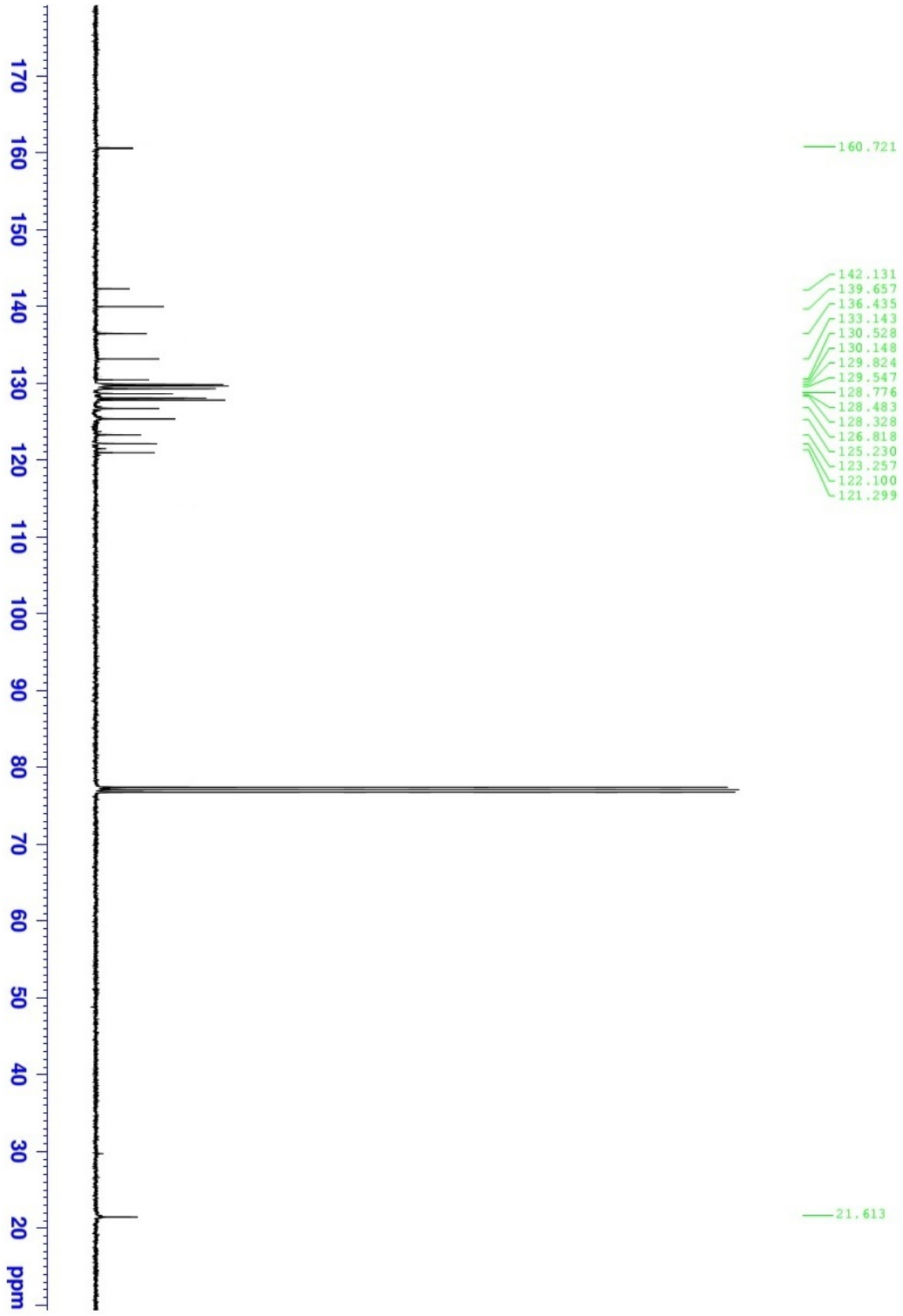
^{1}H NMR of Compound 3ai



^{13}C NMR of Compound 3ai



^{1}H NMR of Compound 3ba



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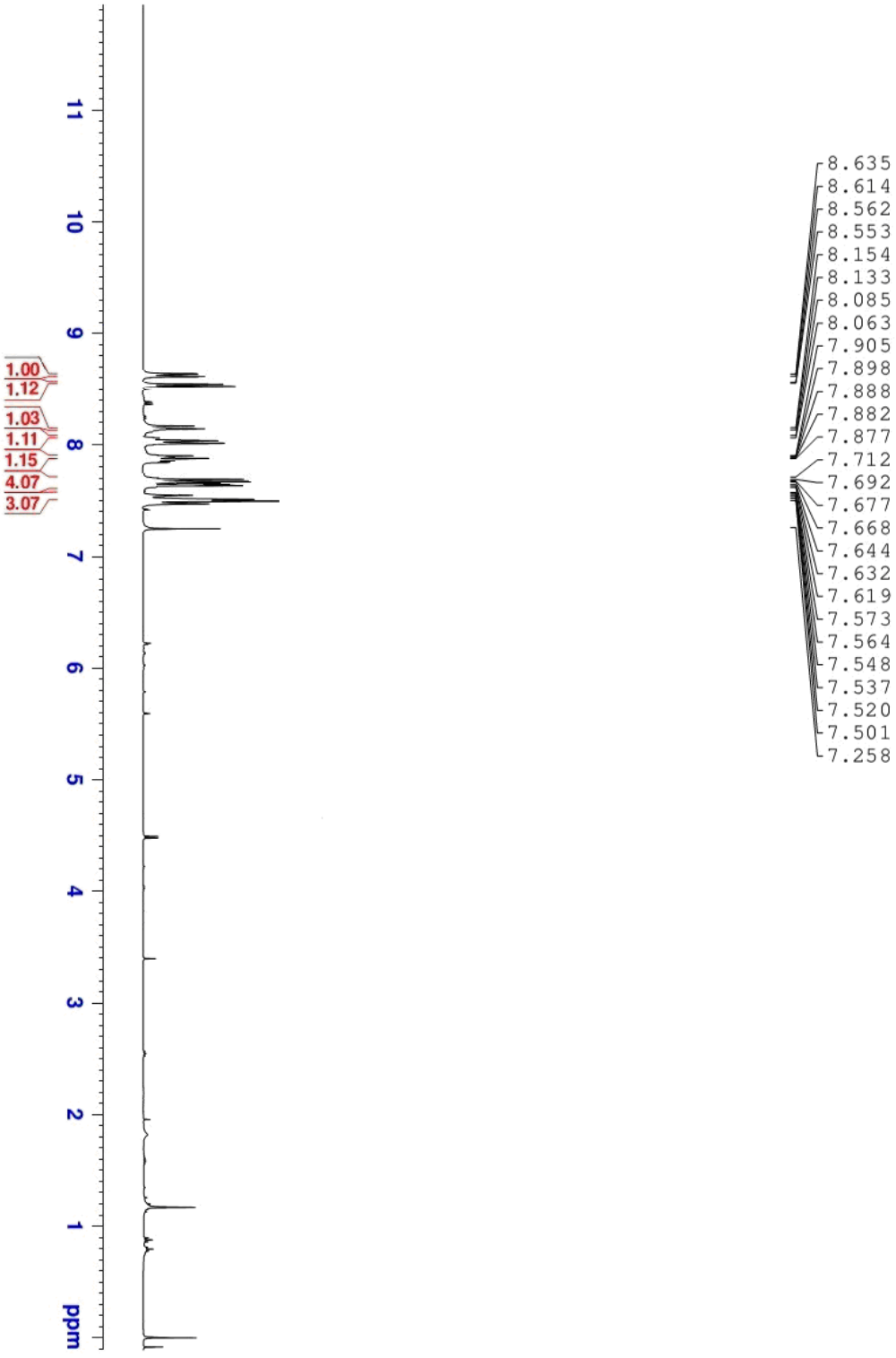

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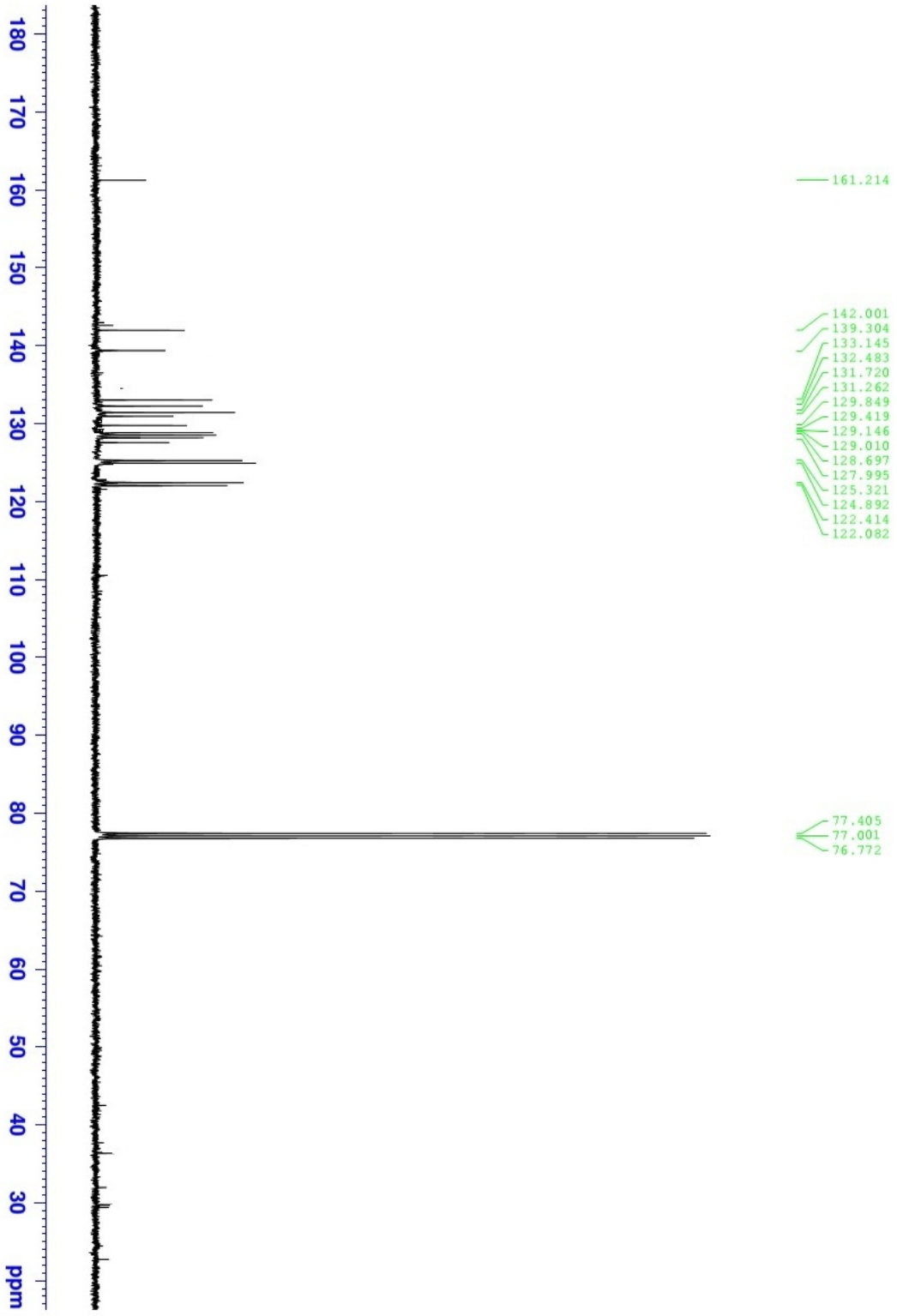
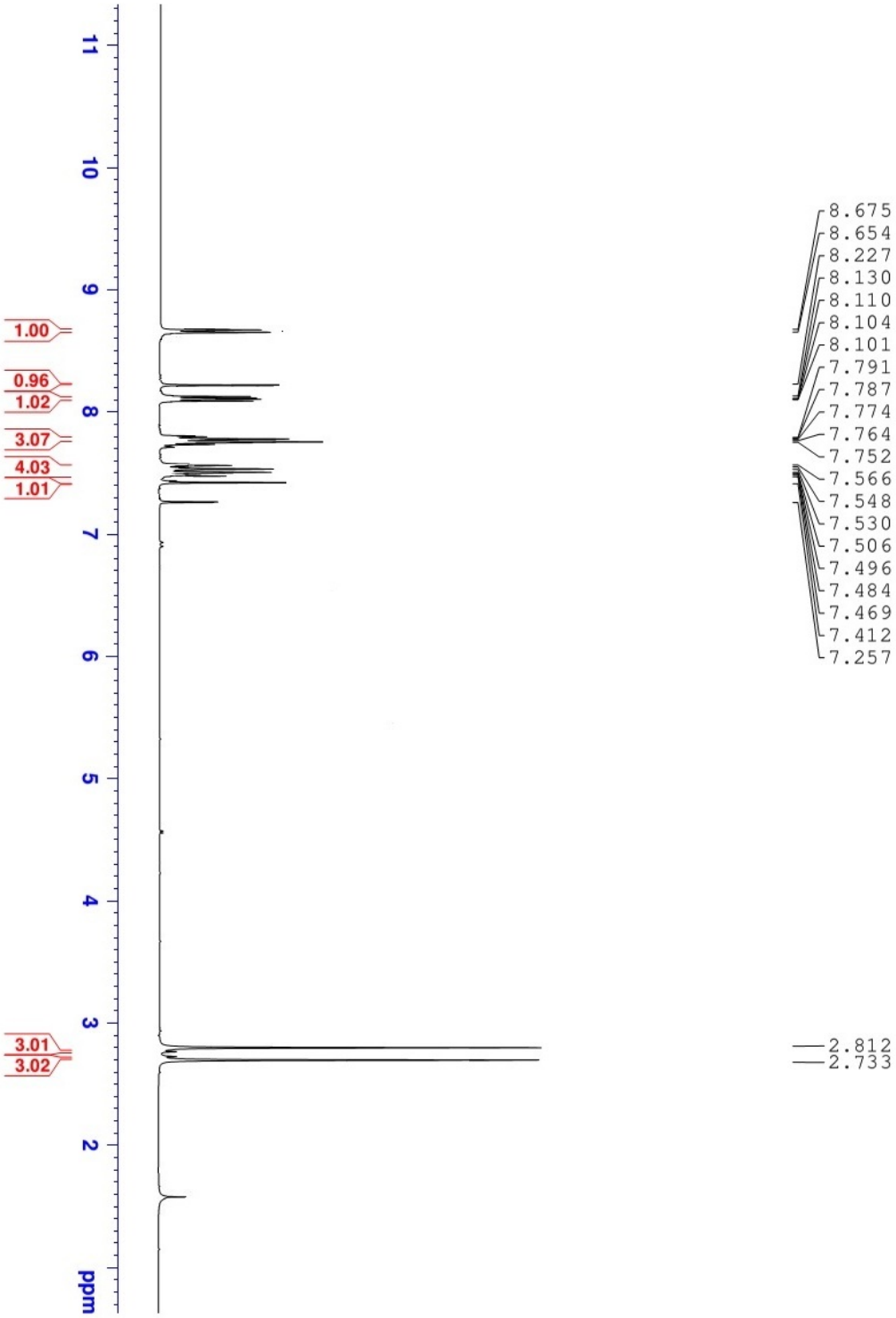


^{13}C NMR of Compound 3ca



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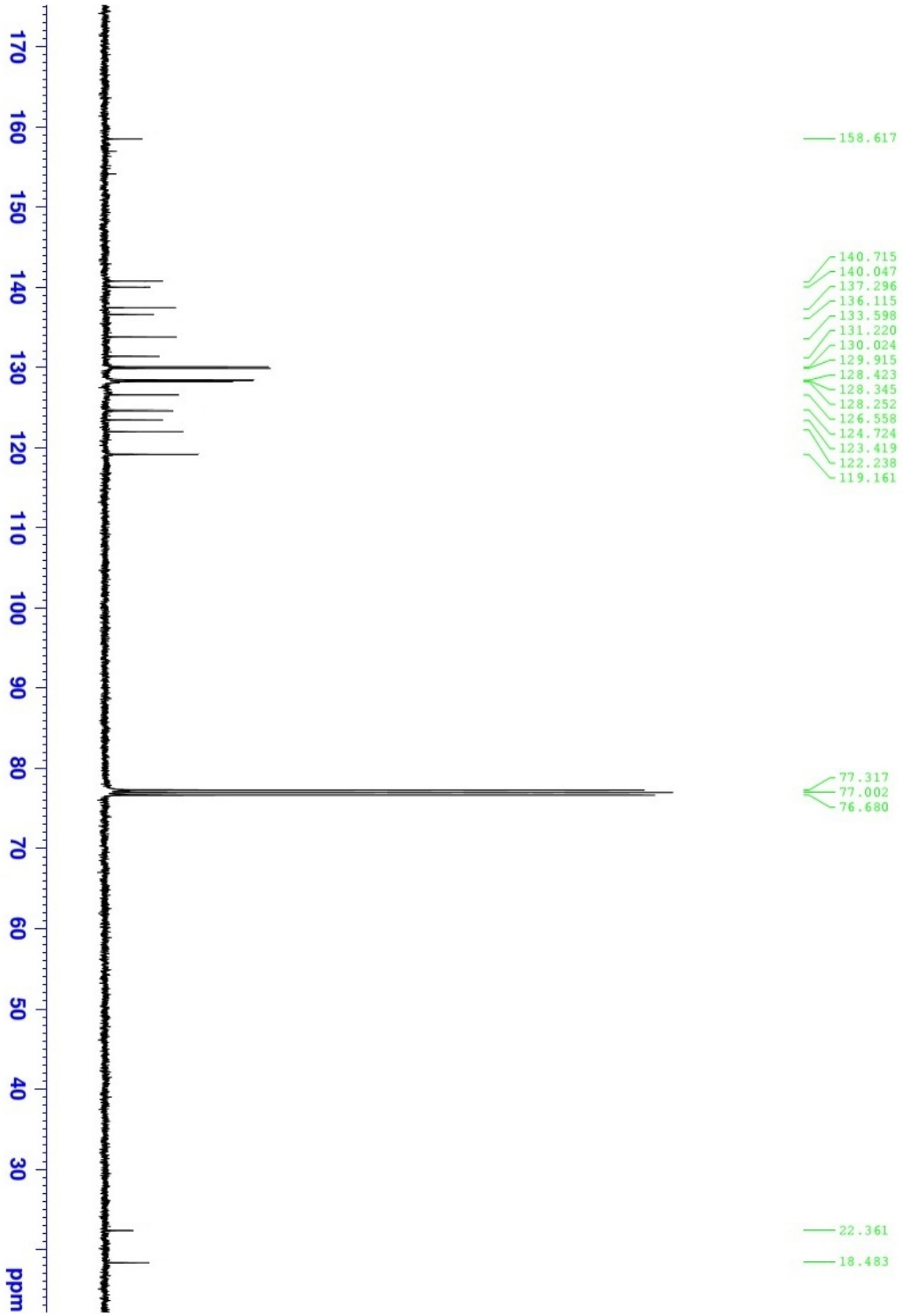

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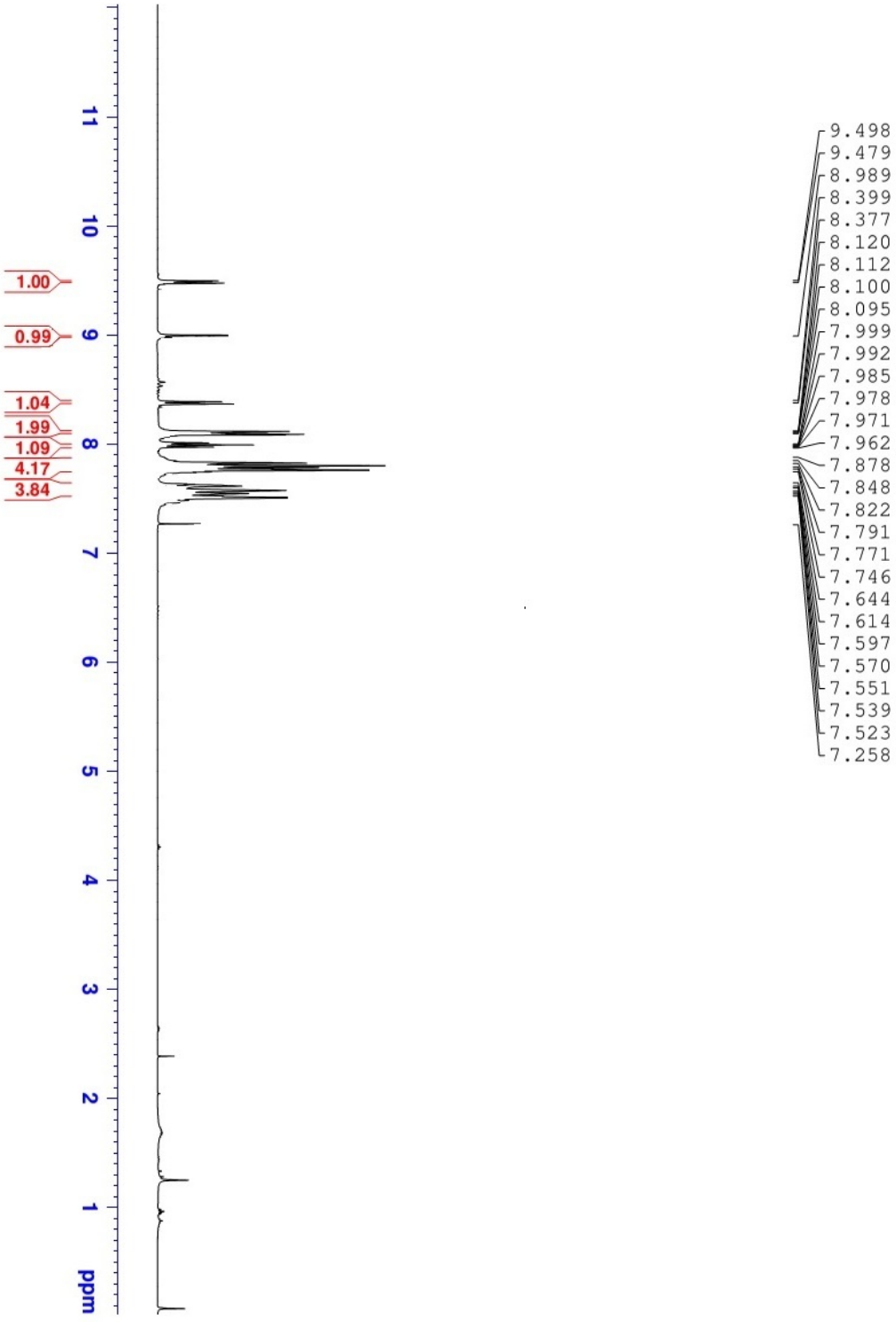

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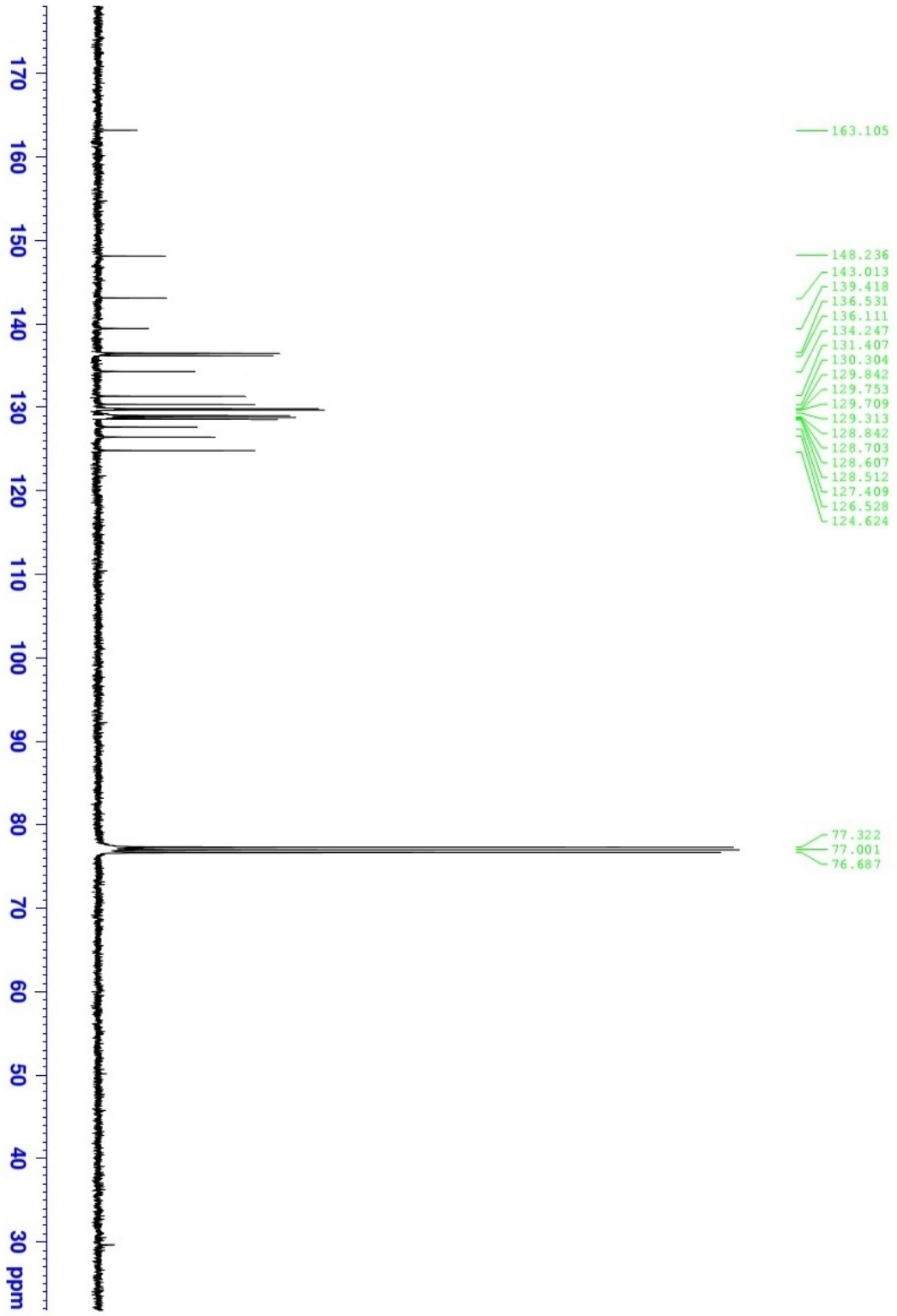

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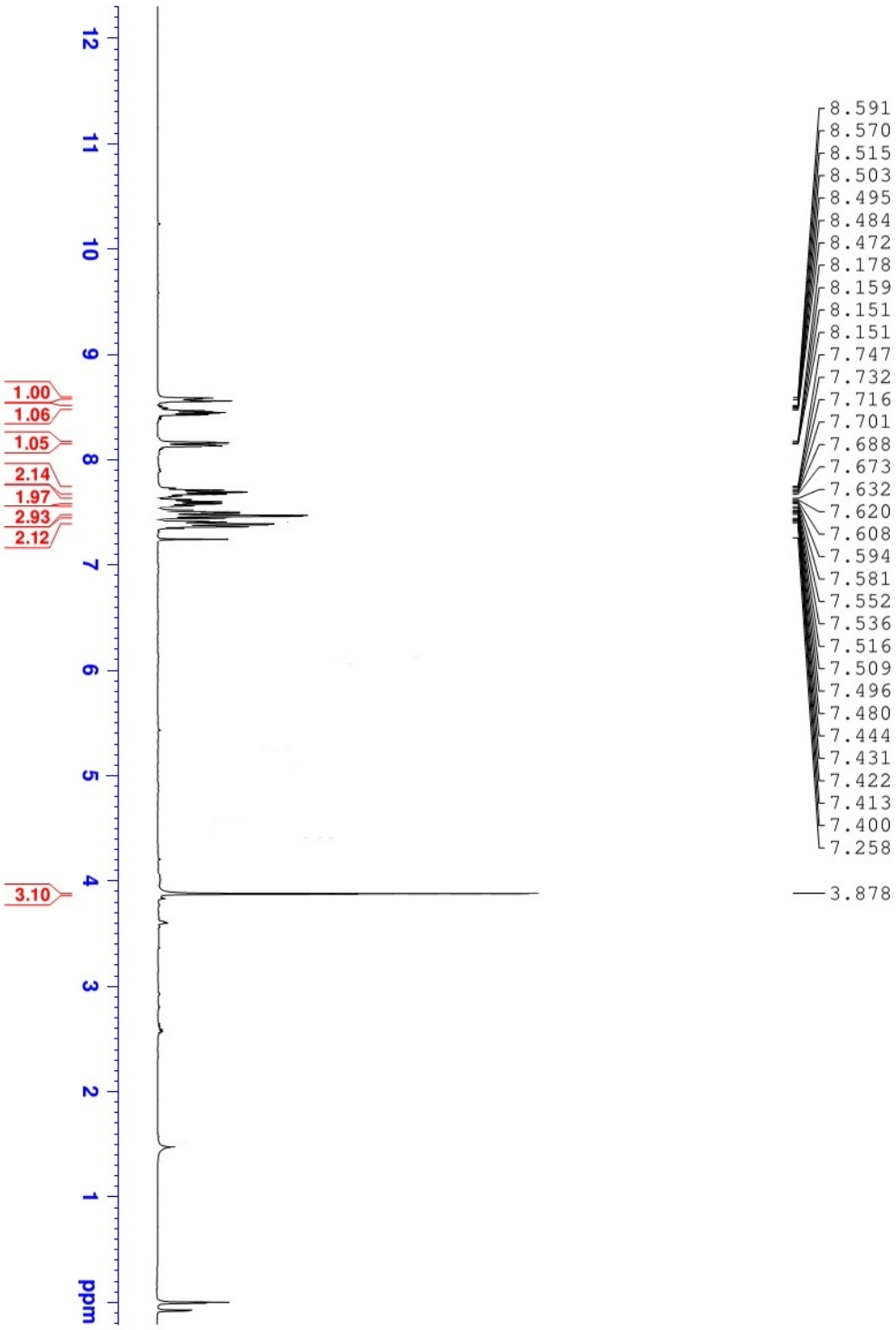
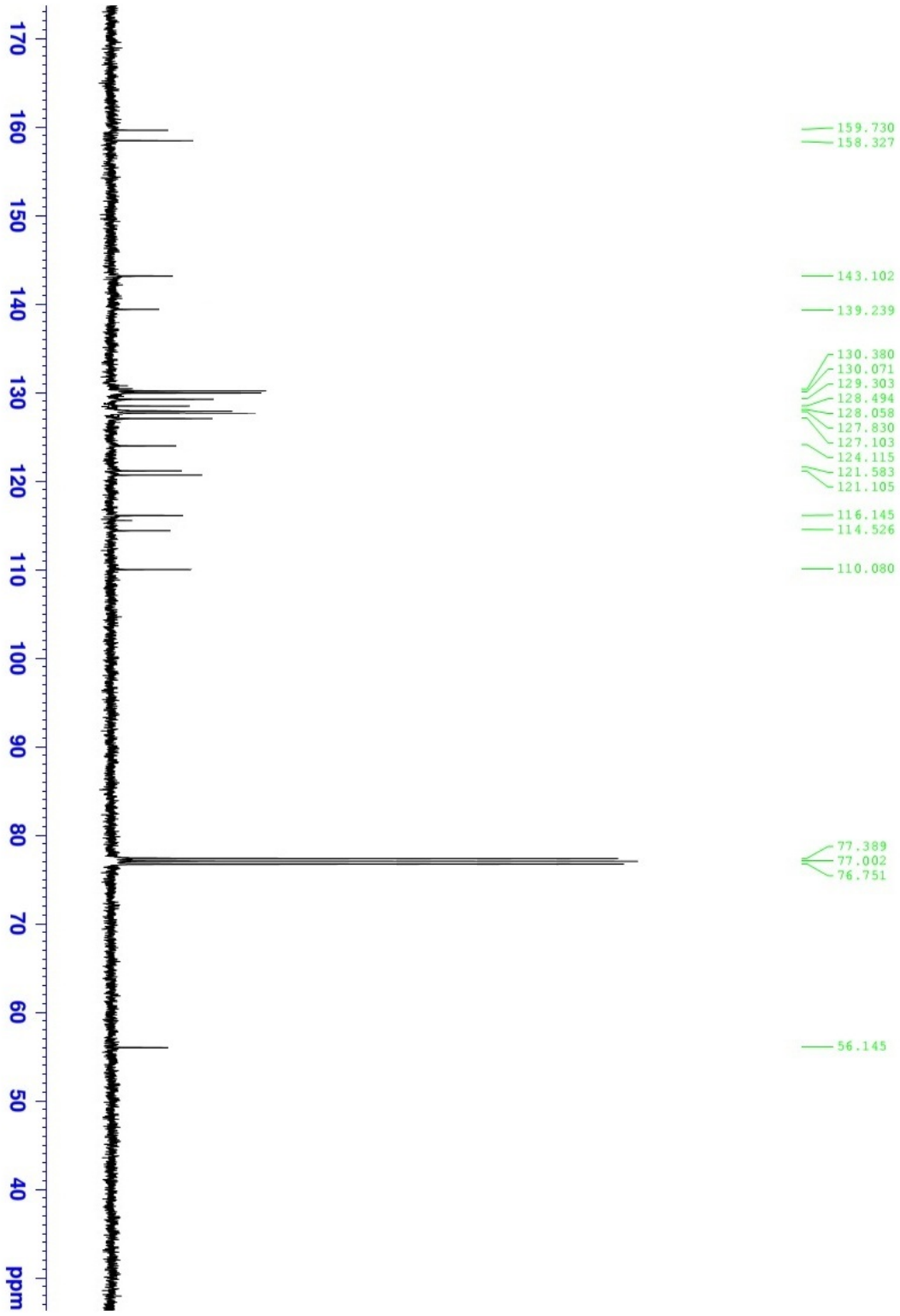


^{1}H NMR of Compound 3fa



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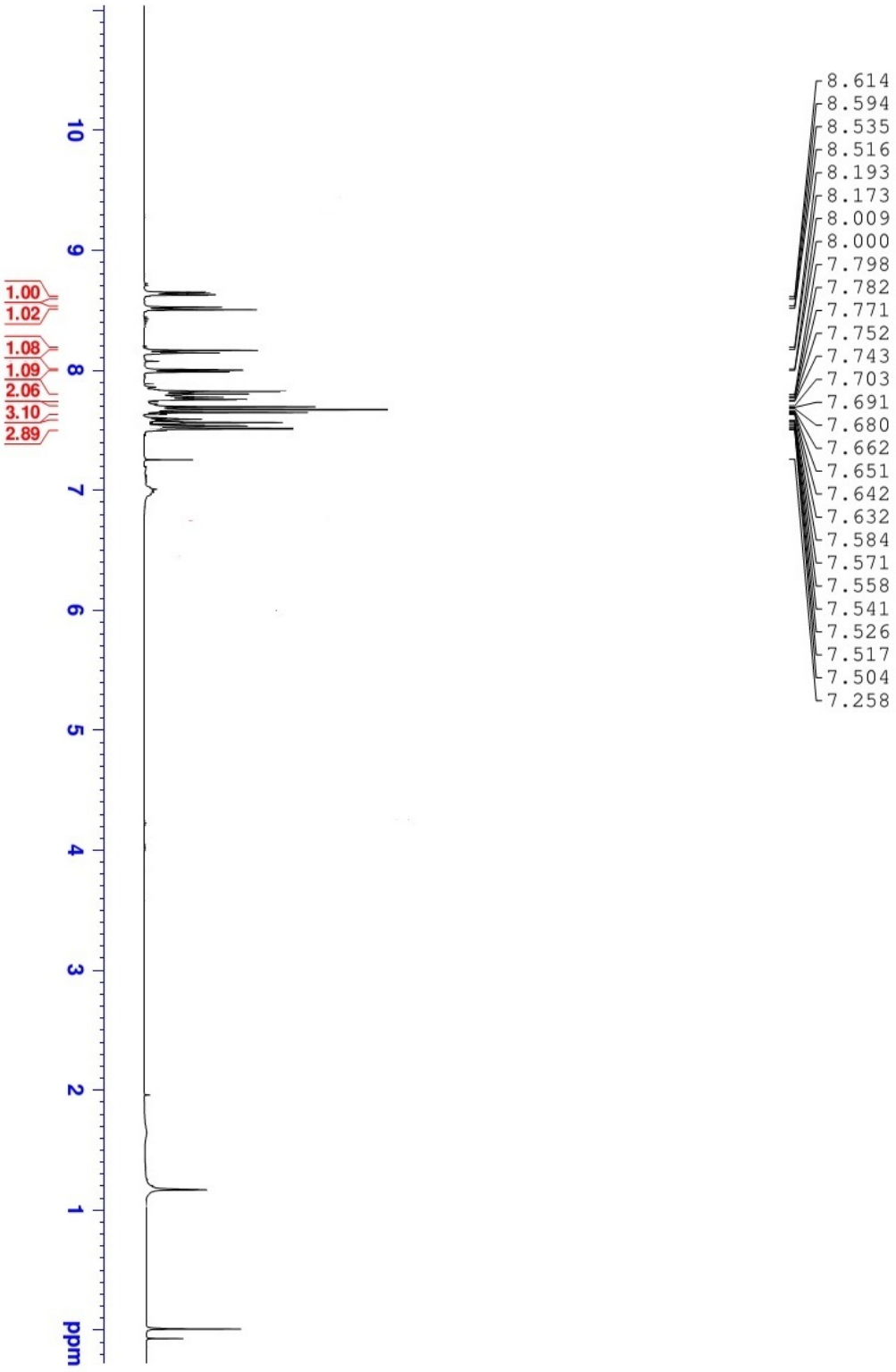
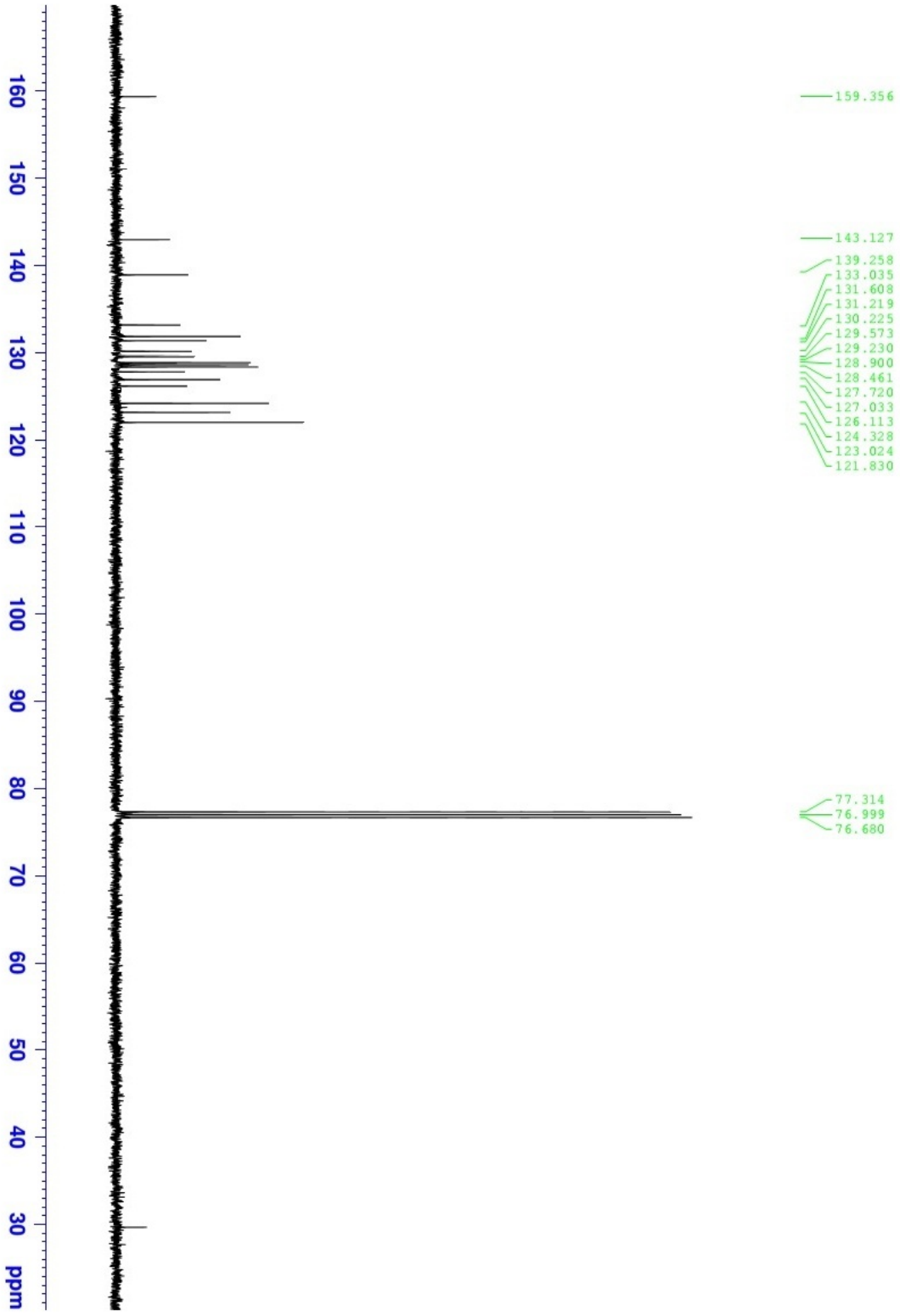


^{1}H NMR of Compound 3ga



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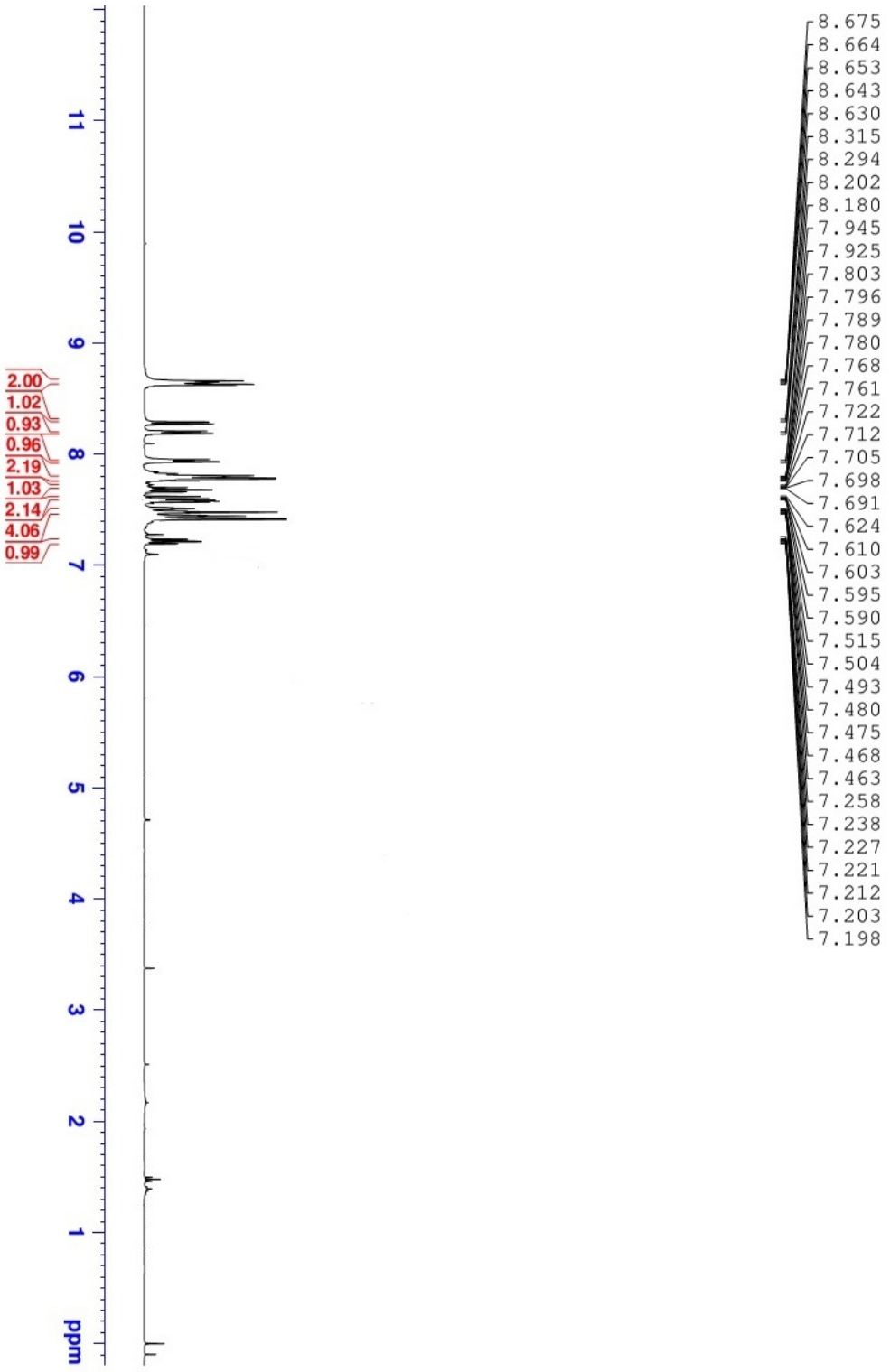
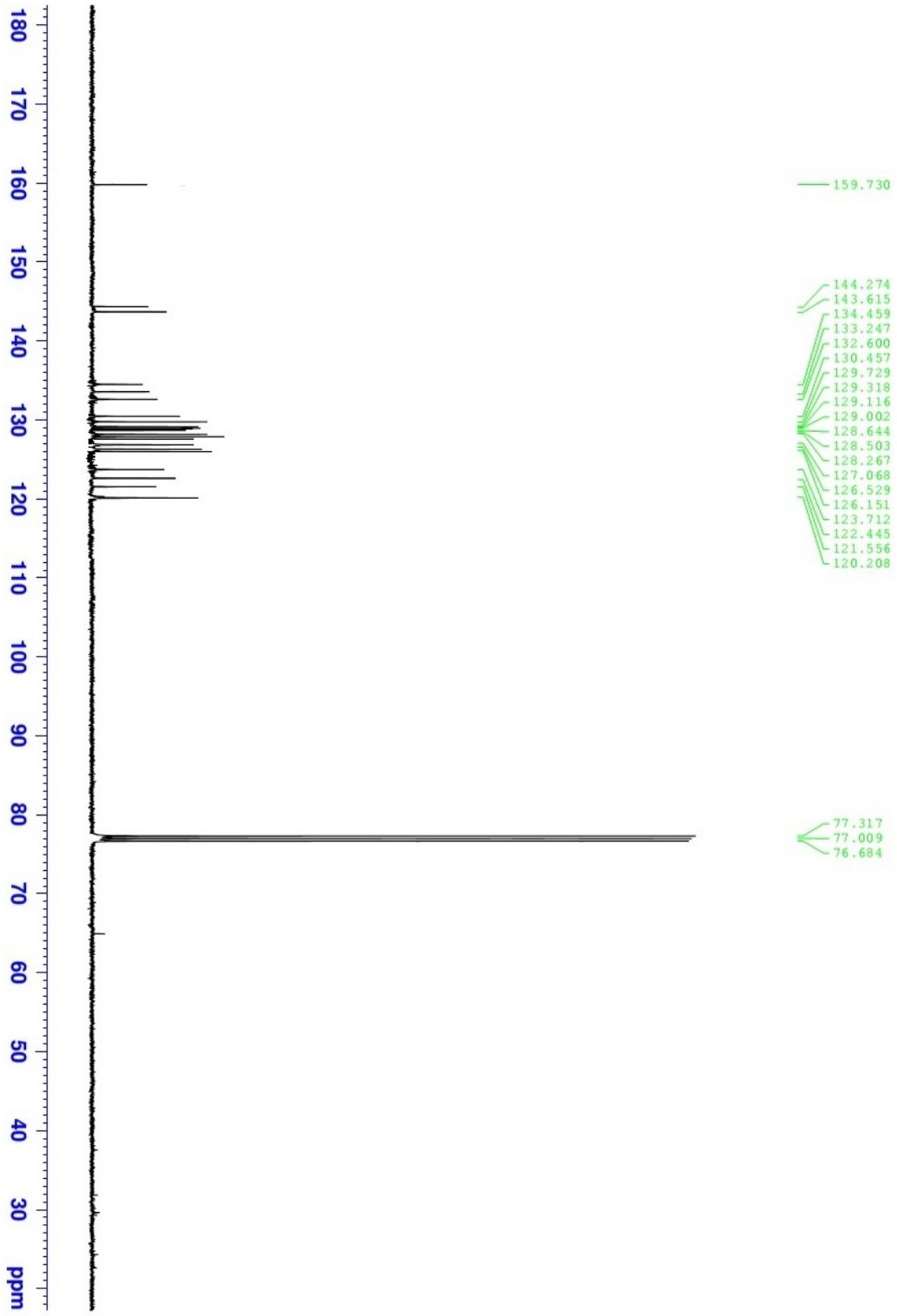


^{1}H NMR of Compound 3ha



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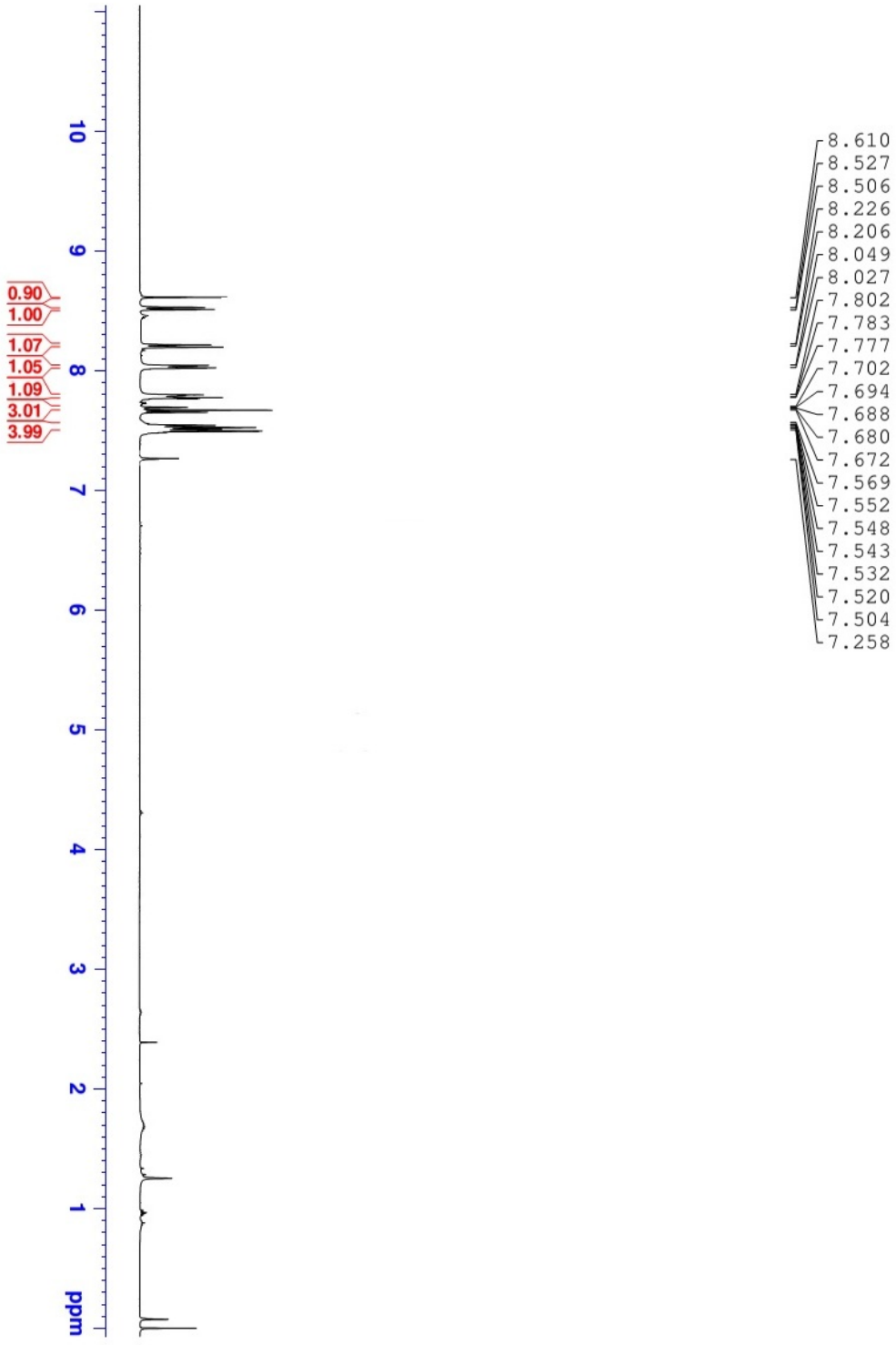
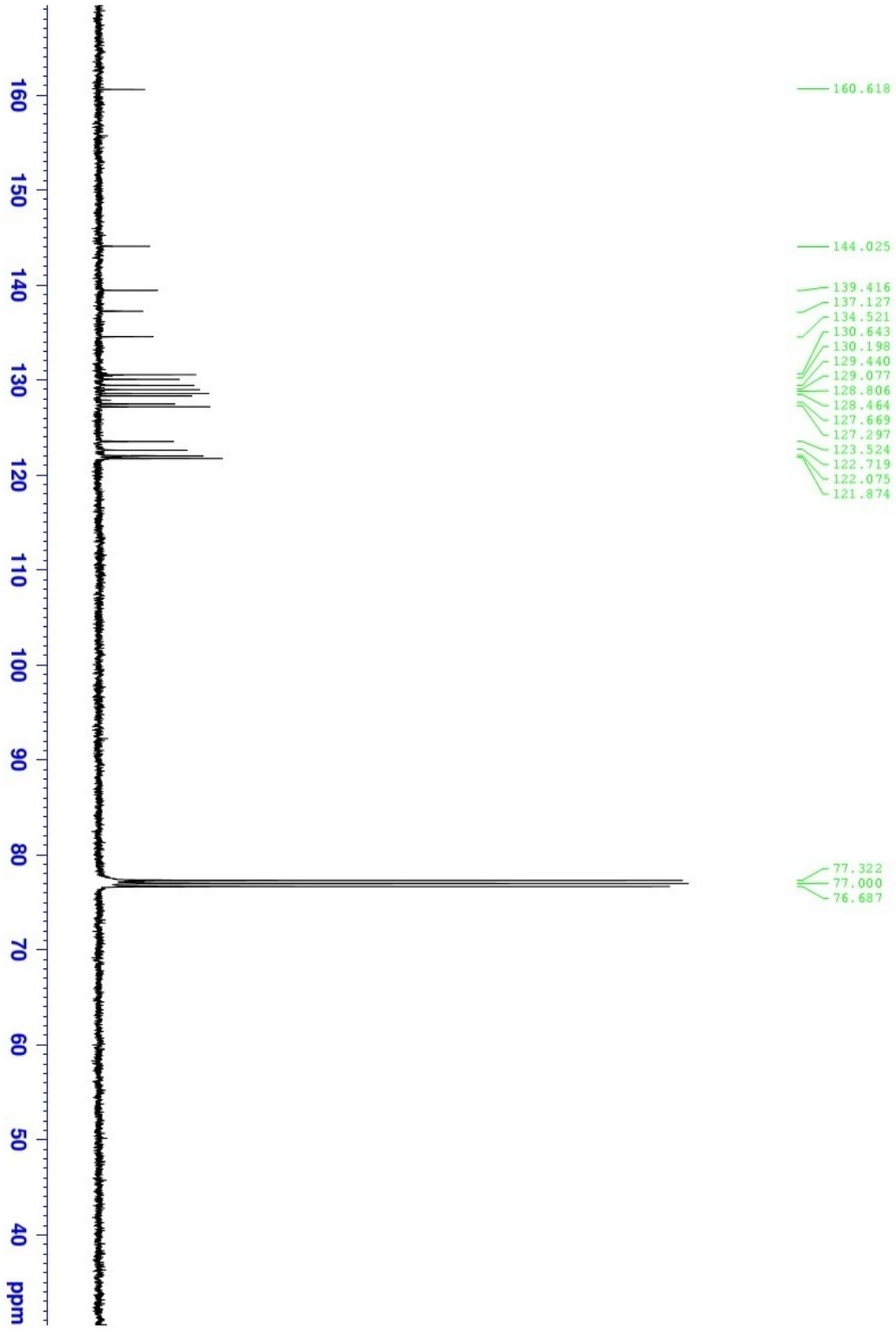


^{1}H NMR of Compound 3ia



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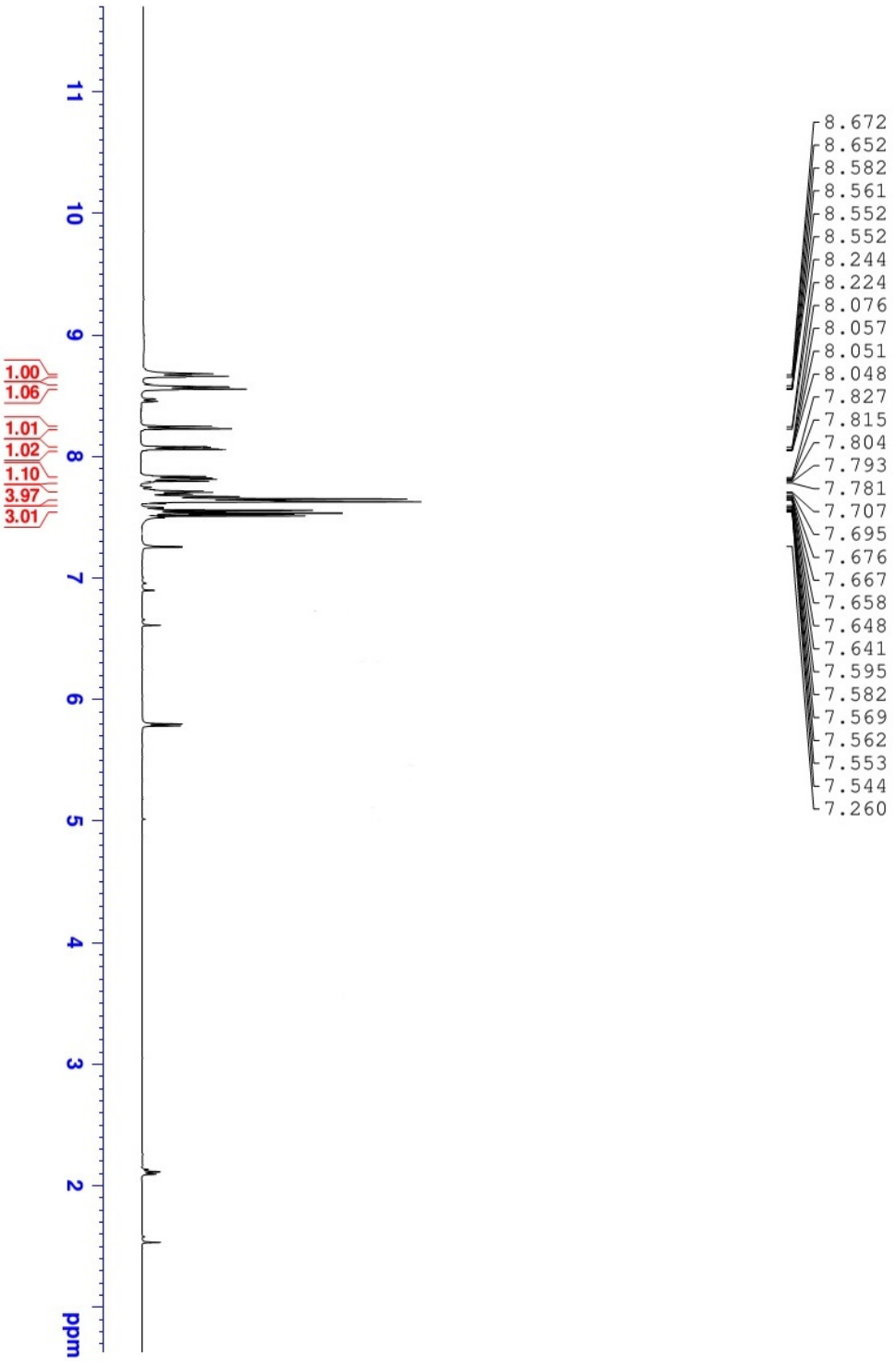

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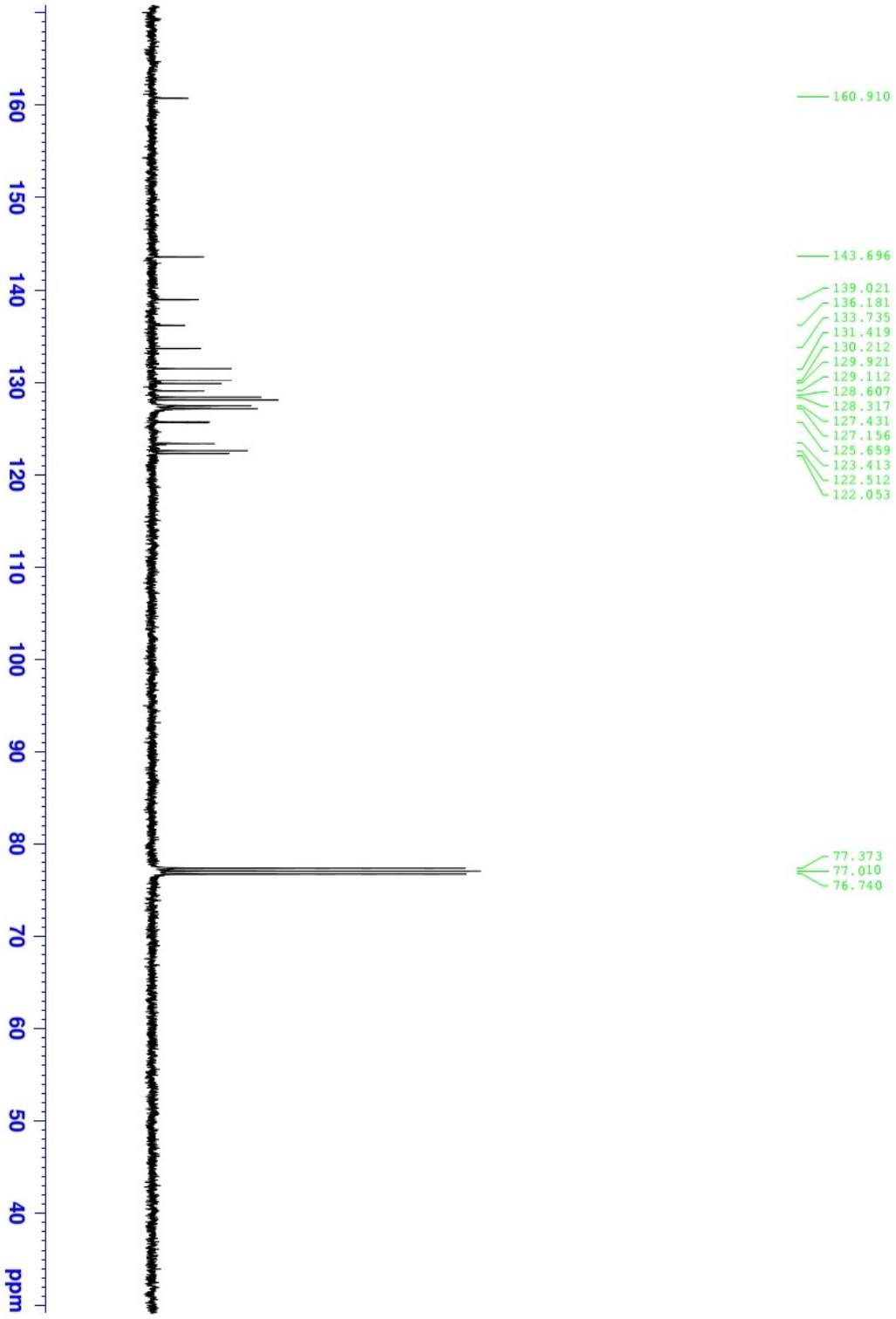

^{13}C NMR of Compound 3ja