Metal-Free, Visible-Light-Mediated transformation of aryl diazonium salts and (hetero)arenes: An Efficient Route to Aryl Ketone

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Supporting Information

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(G) Spectra

(A) Materials and equipment

Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. The supplier of the autoclave irradiation set up is YanZheng Co. Ltd., China. For substrates **1** were prepared according the literature methods.[1] All title products were characterized by Infrared (IR), MS, ^{1}H NMR, ^{13}C NMR and High Resolution mass spectrometer (HRMS). IR spectra were reported in frequency of the absorption (cm^{-1}). ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (*J*) were measured in Hz. Mass spectra were obtained with ionization voltages of 70 eV. HRMS spectra were obtained by ESI on a TOF mass. 200-300 mesh silica gel was used for column chromatography.

(B) Typical experimental procedure

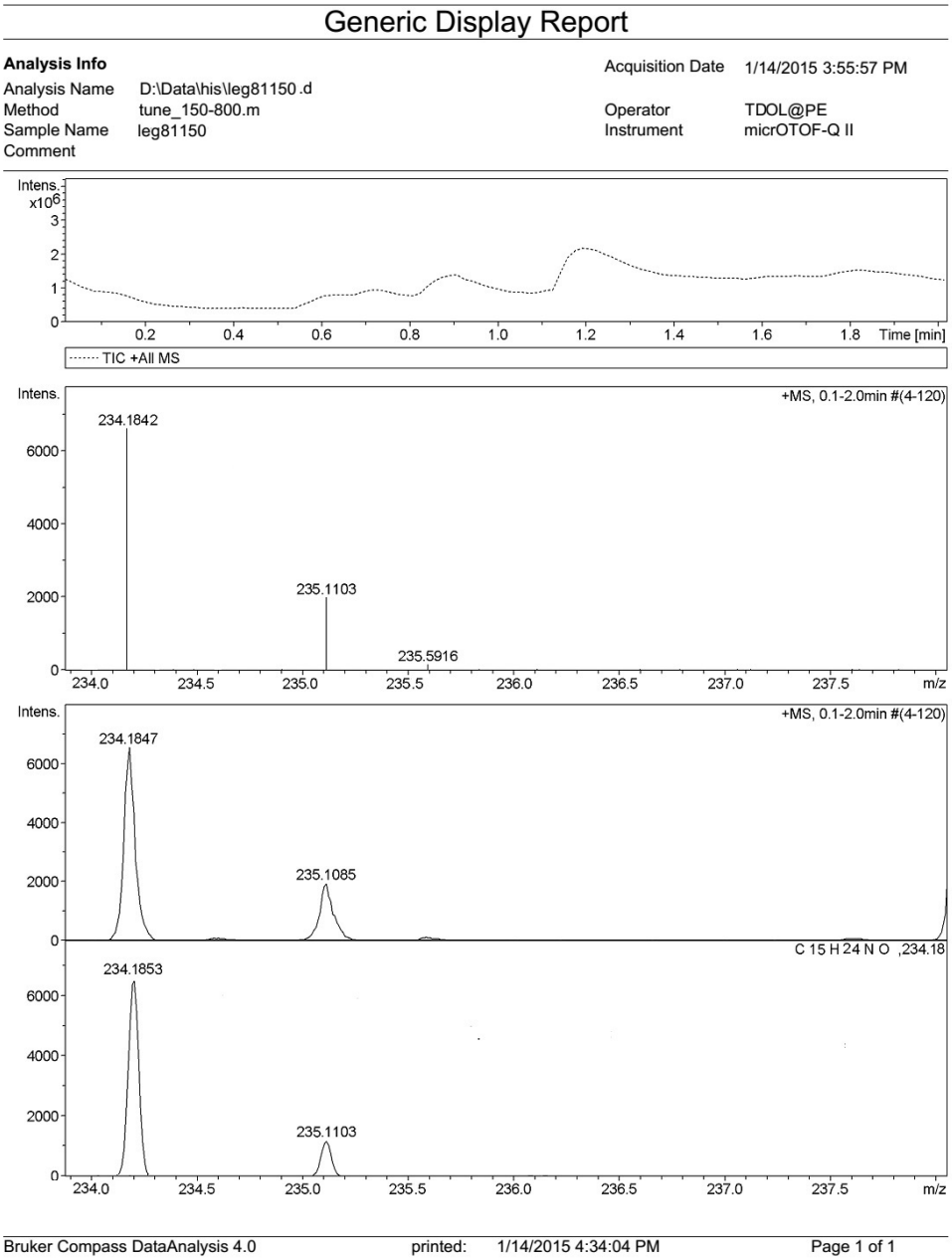
Typical Experimental Procedure for the Synthesis of compounds 3:

To an 8 mL vial equipped with a magnetic stir bar was charged with **1** (0.3 mmol), **2** (0.3 mmol), Eosin Y (3 mol%), dry MeCN (2.0 mL), The vial was purged with N_2 in the dark and transferred into an autoclave with a Quartz window bottom. The autoclave was flushed three times and slowly filled with 70 atm of CO. The reaction was irradiated with external LEDs at room temperature for 16 h. After the reaction was finished, the gas was carefully released and the vial retrieved, the reaction mixture was diluted with 5 mL H_2O, extracted with ethyl acetate (10 mL×3). The organic portion was washed with a saturated solution of brine, dried (Na_2SO_4) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to provide the desired products **3**.

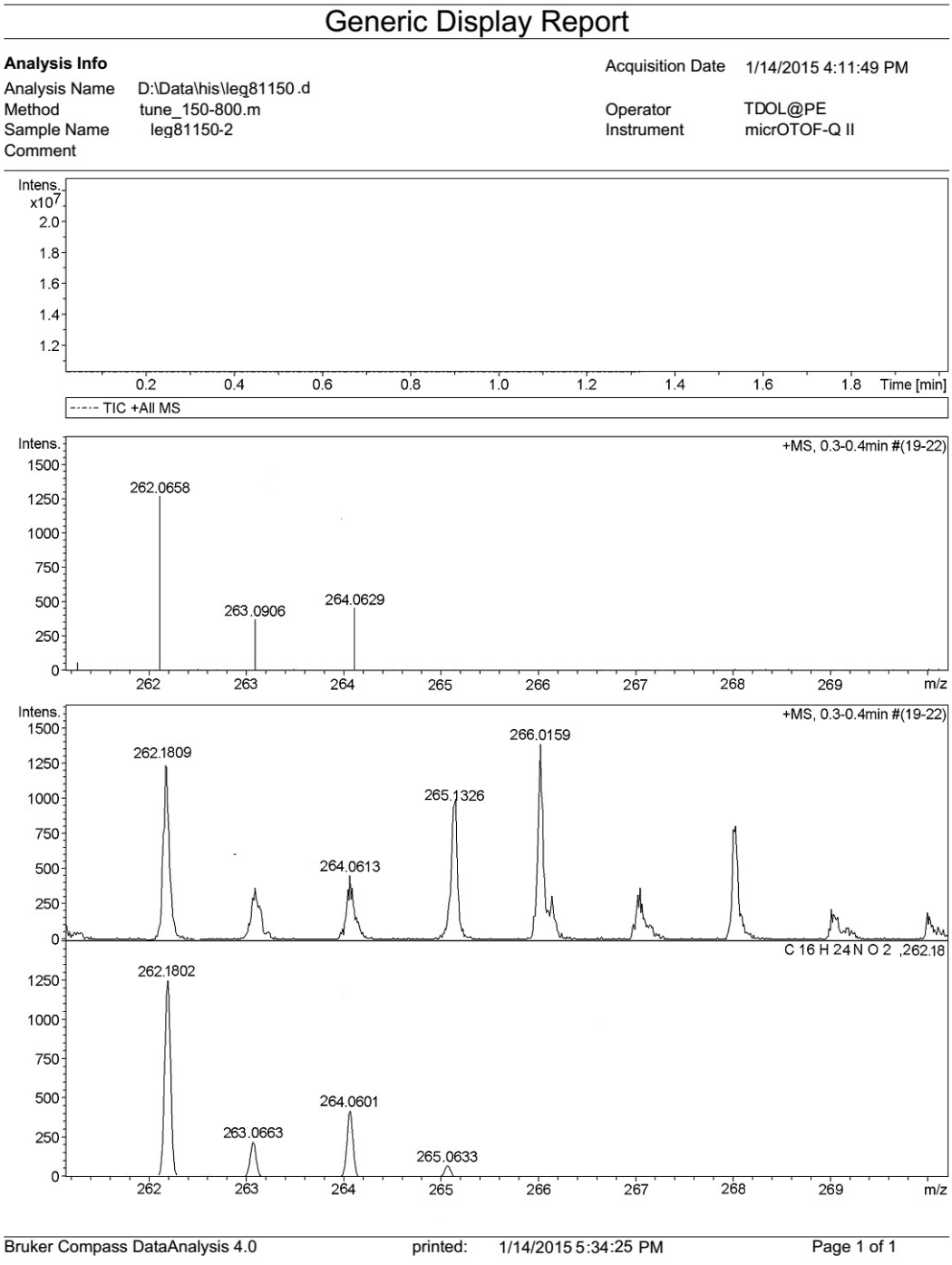
(D) Radical trapping experiments

See standard procedure above, but with addition of TEMPO (1 equiv.)

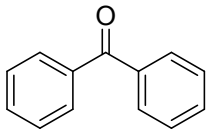
The HRMS spectra of **4**



The HRMS spectra of **5**



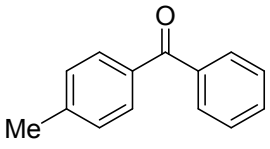
(E) Analytical data



3aa

Benzophenone (3aa): [2]

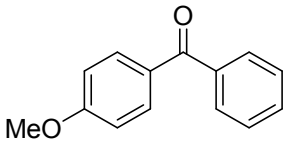
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (dd, J = 8.0 Hz, J = 1.6 Hz, 4H), 7.61-7,56 (m, 2H), 7.51-7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.7, 137.8, 132.5, 130.2, 128.4; IR (neat cm^{-1}): 1660 (C=O); LRMS (EI 70 ev) *m/z* (%): 182 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{11}O$ $(M+H)^+$ 183.0804, found 183.0801.



3ab

Phenyl(p-tolyl)methanone (3ab): [2]

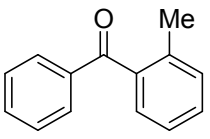
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 143.2, 137.9, 134.8, 132.1, 130.2, 129.8, 128.9, 128.1, 21.6; IR (neat cm^{-1}): 1658 (C=O); LRMS (EI 70 ev) *m/z* (%): 196 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $(M+H)^+$ 197.0960, found 197.0963.



3ac

(4-Methoxyphenyl)(phenyl)methanone (3ac): [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.51-7.45 (m, 3H), 6.96 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.1, 163.2, 138.2, 132.4, 131.7, 130.0, 129.5, 128.2, 113.6, 55.8; IR (neat cm^{-1}): 1652 (C=O); LRMS (EI 70 ev) *m/z* (%): 212 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O_2$ $(M+H)^+$ 213.0909, found 213.0913.

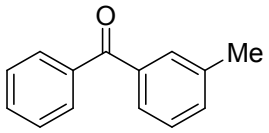


3ad

Phenyl(o-tolyl)methanone (3ad): [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 7.2 Hz, 2H), 7.54-7.50 (m, 1H), 7.43-7.36 (m, 2H),

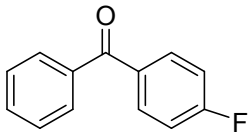
7.33-7.26 (m, 1H), 7.25-7.20 (m, 3H); 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.5, 138.8, 138.1, 137.0, 133.5, 131.7, 130.6, 130.3, 129.0, 128.8, 125.4, 20.4; IR (neat cm^{-1}): 1647 (C=O); LRMS (EI 70 ev) *m/z* (%): 196 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $(M+H)^+$ 197.0960, found 197.0961.



3ae

Phenyl(m-tolyl)methanone (3ae): [3]

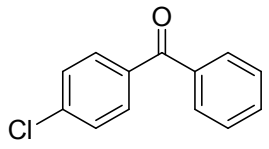
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (dd, J = 1.2 Hz, J = 8.4 Hz, 2H), 7.62-7.57 (m, 3H), 7.46-7.40 (m, 2H), 7.38 (dd, J = 4.4 Hz, J = 4.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.8, 138.1, 137.4, 137.1, 133.0, 132.1, 130.6, 130.1, 128.4, 128.0, 127.2, 21.3; IR (neat cm^{-1}): 1663 (C=O); LRMS (EI 70 ev) *m/z* (%): 196 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $(M+H)^+$ 197.0960, found 197.0954.



3af

(4-Florophenyl)(phenyl)methanone (3af): [2]

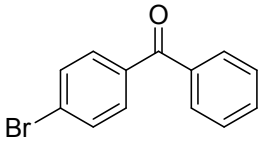
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.83 (m, 2H), 7.78 (d, J = 4.2 Hz, 2H), 7.62 (dd, J = 7.2 Hz, J = 1.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.5, 165.5 (J = 252.9 Hz), 137.6, 132.7 (J = 2.5 Hz), 132.6 (J = 14.8 Hz), 132.0, 129.8, 128.3, 115.5 (J = 21.8 Hz); IR (neat cm^{-1}): 1661 (C=O); LRMS (EI 70 ev) *m/z* (%): 200 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{10}FO$ $(M+H)^+$ 201.0710, found 201.0719.



3ag

(4-Chlorophenyl)(phenyl)methanone (3ag): [2]

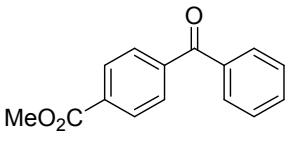
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (t, J = 7.2 Hz, 4H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (dd, J = 7.6 Hz, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.4, 138.8, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.3; IR (neat cm^{-1}): 1664 (C=O); LRMS (EI 70 ev) *m/z* (%): 218 (41), 216 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{10}ClO$ $(M+H)^+$ 217.0415, found 217.0410.



3ah

(4-Bromophenyl)(phenyl)methanone (3ah):[2]

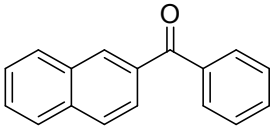
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (t, J = 4.2 Hz, 2H), 7.69 (dd, J = 2.0 Hz, J = 2.0 Hz, 2H), 7.64-7.58 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.6, 137.1, 136.3, 132.6, 131.6, 131.5, 129.9, 128.4, 127.5; IR (neat cm^{-1}): 1659 (C=O); LRMS (EI 70 ev) *m/z* (%): 260 (M^+, 100), 258 (81); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}BrO$ $(M + H)^+$ 260.9909, found 260.9913.



3ai

Methyl 4-Benzoylbenzoate (3ai): [4]

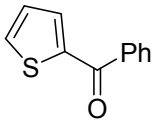
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.78-7.76 (m, 2H), 7.60-7.56 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.1, 166.2, 141.0, 137.0, 133.1, 132.8, 130.0, 129.6, 129.3, 128.2, 52.1; IR (neat cm^{-1}): 1731 (C=O), 1652 (C=O); LRMS (EI 70 ev) *m/z* (%): 240 (M^+, 100); HRMS m/z (ESI) calcd for $C_{15}H_{13}O_3$ $(M+H)^+$ 241.0861, found 241.0855.



3aj

(Naphthalen-6-yl)(phenyl)methanone (3aj): [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.98-7.84 (m, 6H), 7.63-7.56 (m, 2H), 7.52-7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.1, 137.8, 135.1, 134.6, 132.4, 32.1, 131.7, 130.0, 129.4, 128.5, 128.3, 128.1, 127.7, 126.7, 125.6; 1660 (C=O); LRMS (EI 70 ev) *m/z* (%): 232 (M^+, 100); HRMS m/z (ESI) calcd for $C_{17}H_{13}O$ $(M+H)^+$ 233.0959, found 233.0961.

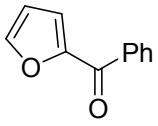


3ba

Phenyl(thiophen-2-yl)methanone (3ba):[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 4.8 Hz, 1H), 7.65 (d, J = 3.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz,

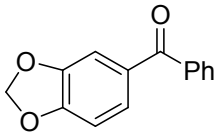
$CDCl_3$) δ: 188.2, 143.6, 138.1, 134.8, 134.1, 132.2, 129.1, 128.3, 127.9; IR (neat cm^{-1}): 1638 (C=O); LRMS (EI 70 ev) *m/z* (%): 188 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_{11}H_9OS$ $(M + H)^+$ 189.0368, found 189.0361.



3ca

(Furan-2-yl)(phenyl)methanone (3ca): [7]

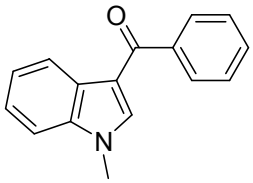
^1H NMR (400 MHz, $CDCl_3$) δ: 7.99-7.94 (m, 2H), 7.72 (dd, J = 2.4 Hz, J = 1.2 Hz, 1H), 7.64-7.57 (m, 1H), 7.51-7.44 (m, 2H), 7.24 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H), 6.61 (dd, J = 4.8 Hz, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 182.8, 152.2, 147.2, 137.1, 132.2, 129.2, 128.4, 120.7, 112.5; IR (neat cm^{-1}): 1630 (C=O); LRMS (EI 70 ev) *m/z* (%): 172 (M^+, 100); HRMS m/z (ESI) calcd for $C_{11}H_9O_2$ $(M+H)^+$ 173.0637, found 173.0648.



3da

(3,4-Methylenedioxyphenyl)phenylmethanone (3da): [8]

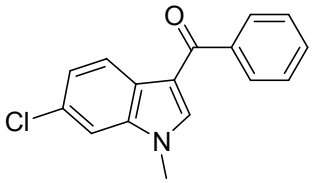
^1H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.70 (m, 2H), 7.57-7.51 (m, 1H), 7.47-7.42 (m, 2H), 7.37-7.32 (m, 2H), 6.85 (d, J = 8.4 Hz, 1H), 6.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.2, 151.7, 148.3, 138.4, 132.3, 132.1, 129.9, 128.1, 127.3, 110.2, 108.0, 102.1; IR (neat cm^{-1}): 1663 (C=O); LRMS (EI 70 ev) *m/z* (%): 226 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{11}O_3$ $(M+H)^+$ 227.0703, found 227.0698.



3ea

(1-Methyl-1H-indol-3-yl)(phenyl)methanone **(3ea):** [9]

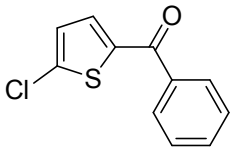
^1H NMR (400 MHz, $CDCl_3$) δ: 8.37-8.34 (m, 1H), 7.73 (d, J = 6.8 Hz, 2H), 7.73-7.38 (m, 4H), 7.29 (dd, J = 3.6 Hz, J = 4.0 Hz, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.9, 140.9, 137.9, 137.5, 131.1, 128.6, 128.3, 127.1, 123.6, 122.74, 122.73, 115.5, 109.6, 33.6, IR (neat cm^{-1}): 1657 (C=O); LRMS (EI 70 ev) *m/z* (%): 235 (M^+, 100); HRMS m/z (ESI) calcd for $C_{16}H_{13}NNaO$ $(M+Na)^+$ 258.0889, found 258.0897.



3fa

(6-Chloro-1-methyl-1H-indol-3-yl)(phenyl)methanone (3fa): [10]

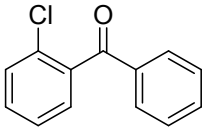
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 6.8 Hz, 1H), 7.47 (s, 2H), 7.31-7.27 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.4, 140.2, 138.0, 137.8, 131.2, 129.3, 128.5, 128.1, 125.4, 123.5, 123.1, 115.2, 109.6, 33.2; IR (neat cm^{-1}): 1671 (C=O); LRMS (EI 70 ev) *m/z* (%): 269 (M^+, 71); HRMS m/z (ESI) calcd for $C_{16}H_{13}ClNNaO$ $(M+Na)^+$ 292.0500, found 292.0494



3ga

(5-Chlorothiophen-2-yl)(phenyl)methanone (3ga): [11]

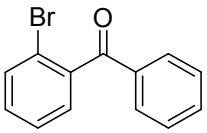
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75-7.71 (m, 2H), 7.53-7.44 (m, 3H), 7.38 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.8, 144.0, 141.3, 137.6, 136.0, 133.4, 129.8, 128.2, 127.4; IR (neat cm^{-1}): 1643 (C=O); LRMS (EI 70 ev) *m/z* (%): 221 (M^+, 81); HRMS m/z (ESI) calcd for $C_{11}H_8ClOS$ $(M+H)^+$ 222.9979, found 222.9985. HRMS m/z (ESI) calcd for $C_{15}H_{13}O_3$ $(M+H)^+$ 241.0861, found 241.0855



3ia

(2-Chlorophenyl)(phenyl)methanone (3ia): [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.80 (m, 2H), 7.62-7.59 (m, 1H), 7.49-7.44 (m, 4H), 7.39-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.2, 138.7, 136.1, 133.6, 131.4, 130.9, 130.0, 129.0, 128.6, 128.3, 126.6; IR (neat cm^{-1}): 1652 (C=O); LRMS (EI 70 ev) *m/z* (%): 218 (36), 216 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{10}ClO$ $(M+H)^+$ 217.0415, found 217.0419.

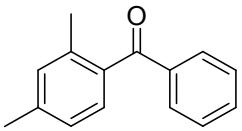


3ja

(2-Bromophenyl)(phenyl)methanone (3ja): [12]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J = 7.6 Hz, 2H), 7.64-7.57 (m, 2H), 7.47-7.39 (m, 3H),

7.35 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.7, 140.4, 135.9, 133.6, 133.0, 131.0, 130.0, 128.8, 128.5, 127.1, 119.3; IR (neat cm^{-1}): 1666 (C=O); LRMS (EI 70 ev) *m/z* (%): 260 (M^+, 76), 258 (72); HRMS *m/z* (ESI) calcd for $C_{13}H_{10}BrO$ $(M + H)^+$ 260.9909, found 260.9917.



3ka

(2,4-Dimethylphenyl)(phenyl)methanone (3ka): [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (dd, J = 0.8 Hz, J = 6.8 Hz, 2H), 7.59-7.46 (m, 1H), 7.47 (t, J = 6.2 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 7.12 (s, 1H), 7.04 (d, J = 7.2 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.2, 140.3, 138.0, 137.2, 135.4, 133.0, 131.9, 130.2, 129.4, 128.5, 125.8, 21.1, 20.0; IR (neat cm^{-1}): 1667 (C=O); LRMS (EI 70 ev) *m/z* (%):210 (M^+, 100); HRMS *m/z* (ESI) calcd for $C_{15}H_{15}O$ $(M + H)^+$ 211.1116, found 211.1119.

(F) References

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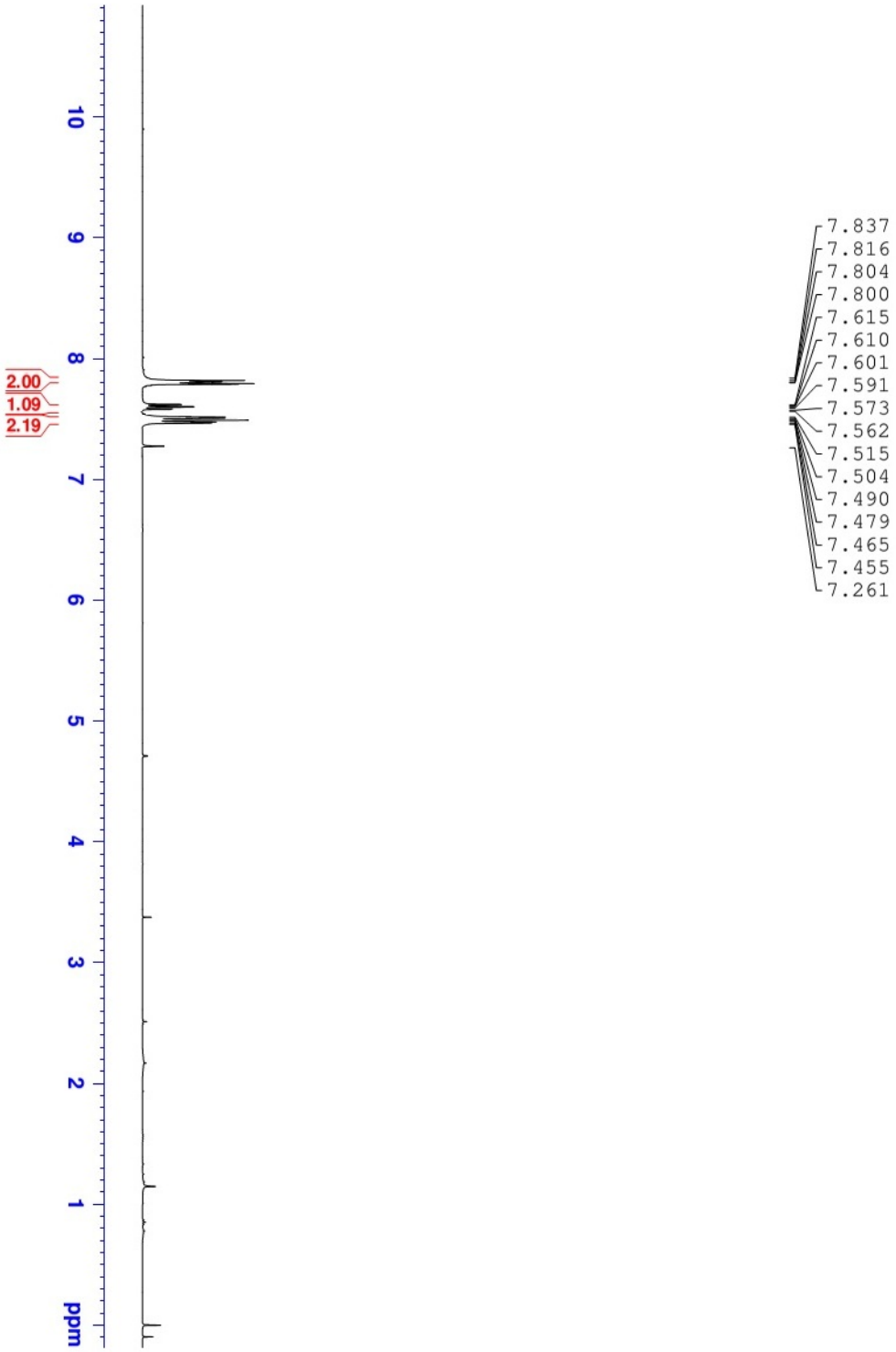
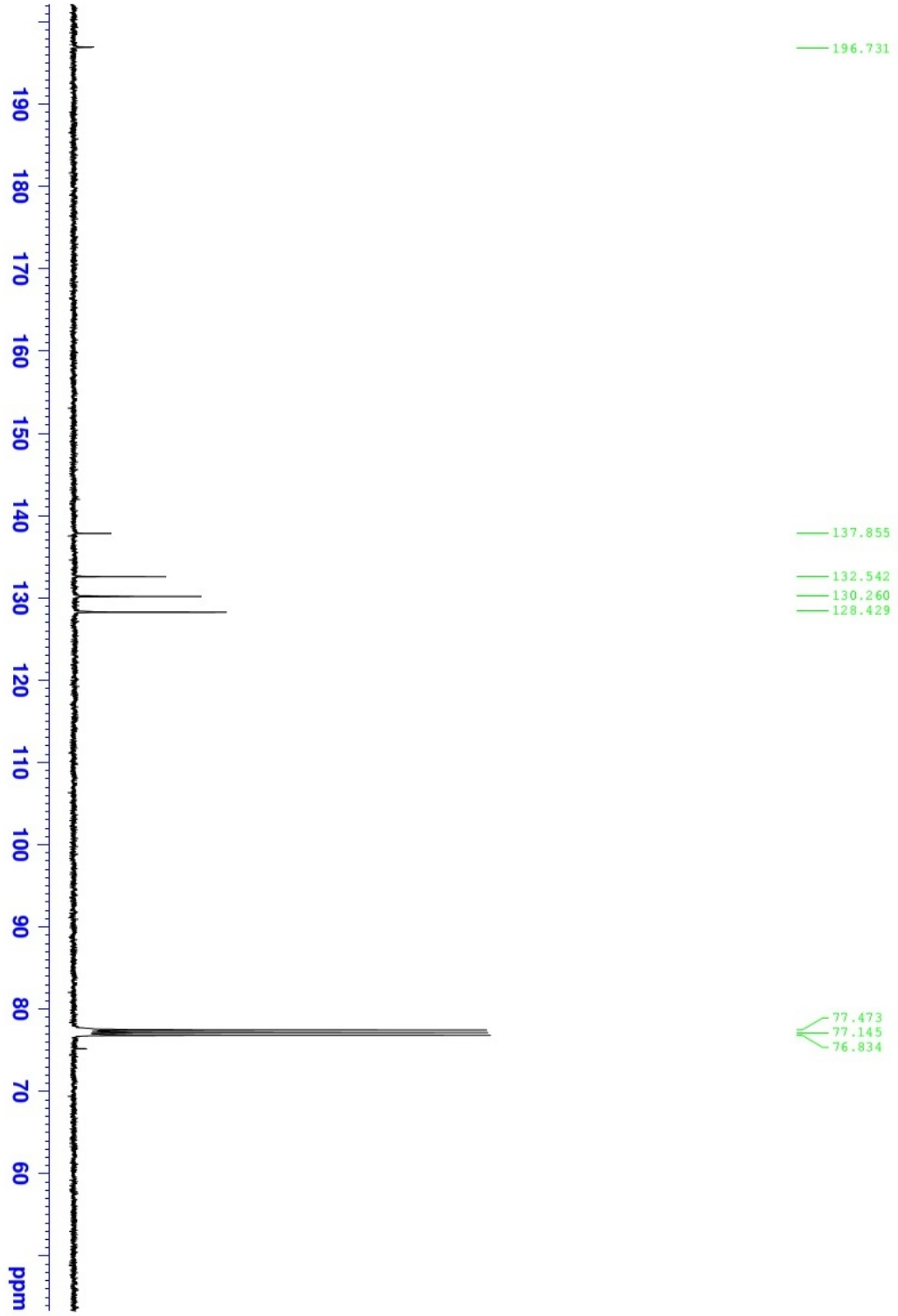
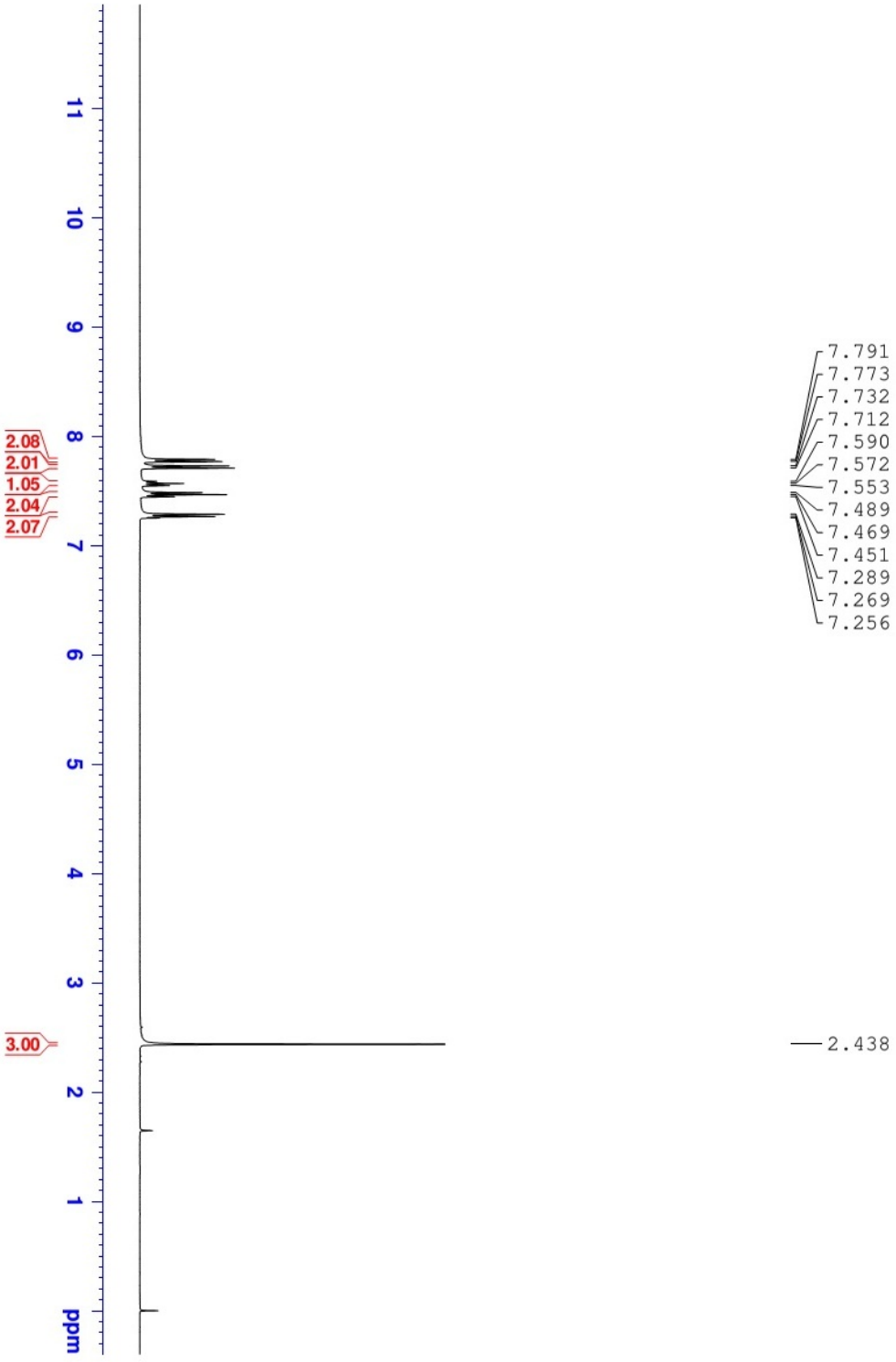
(G) **Spectra**



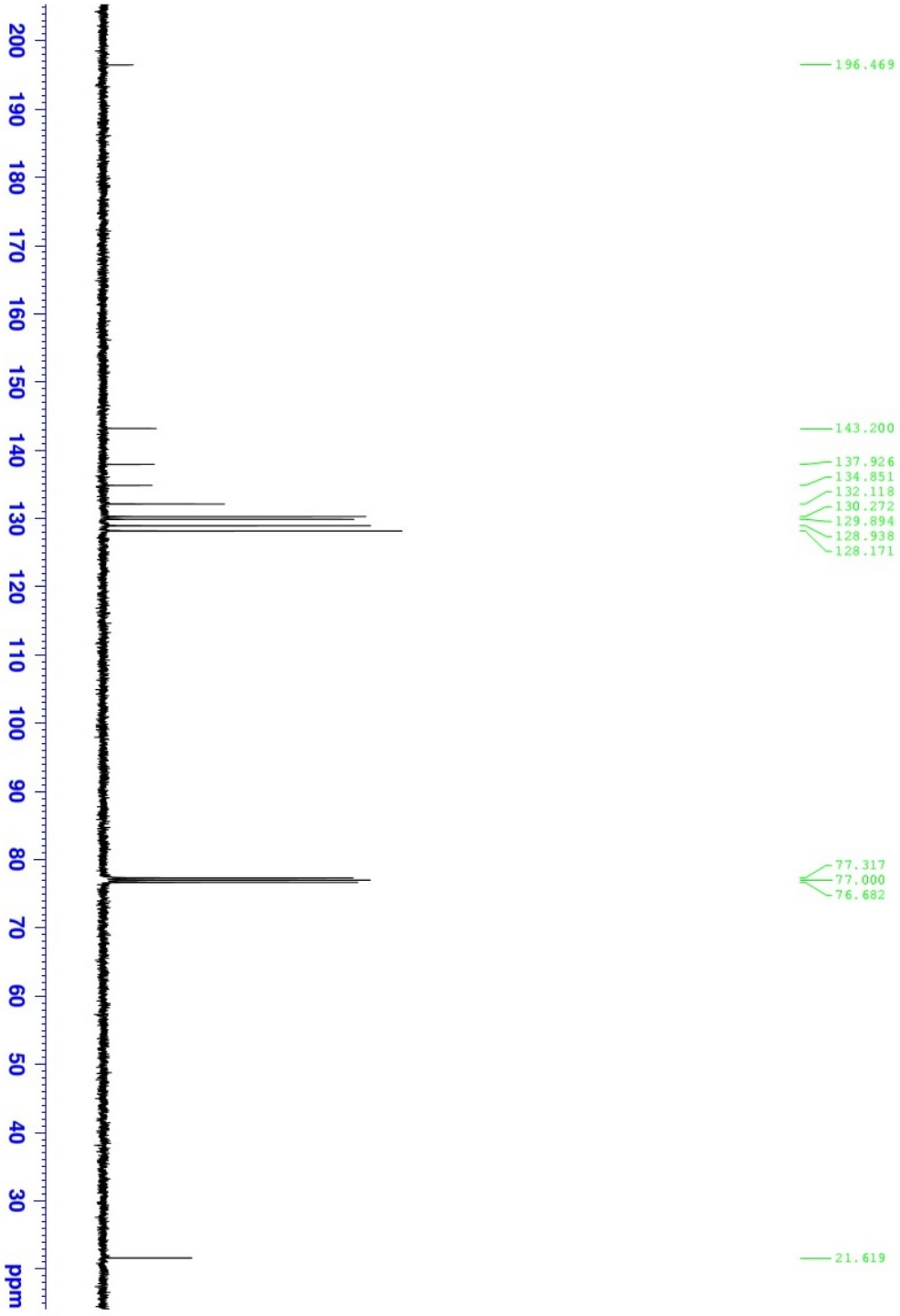
^{1}H NMR of Compound 3aa



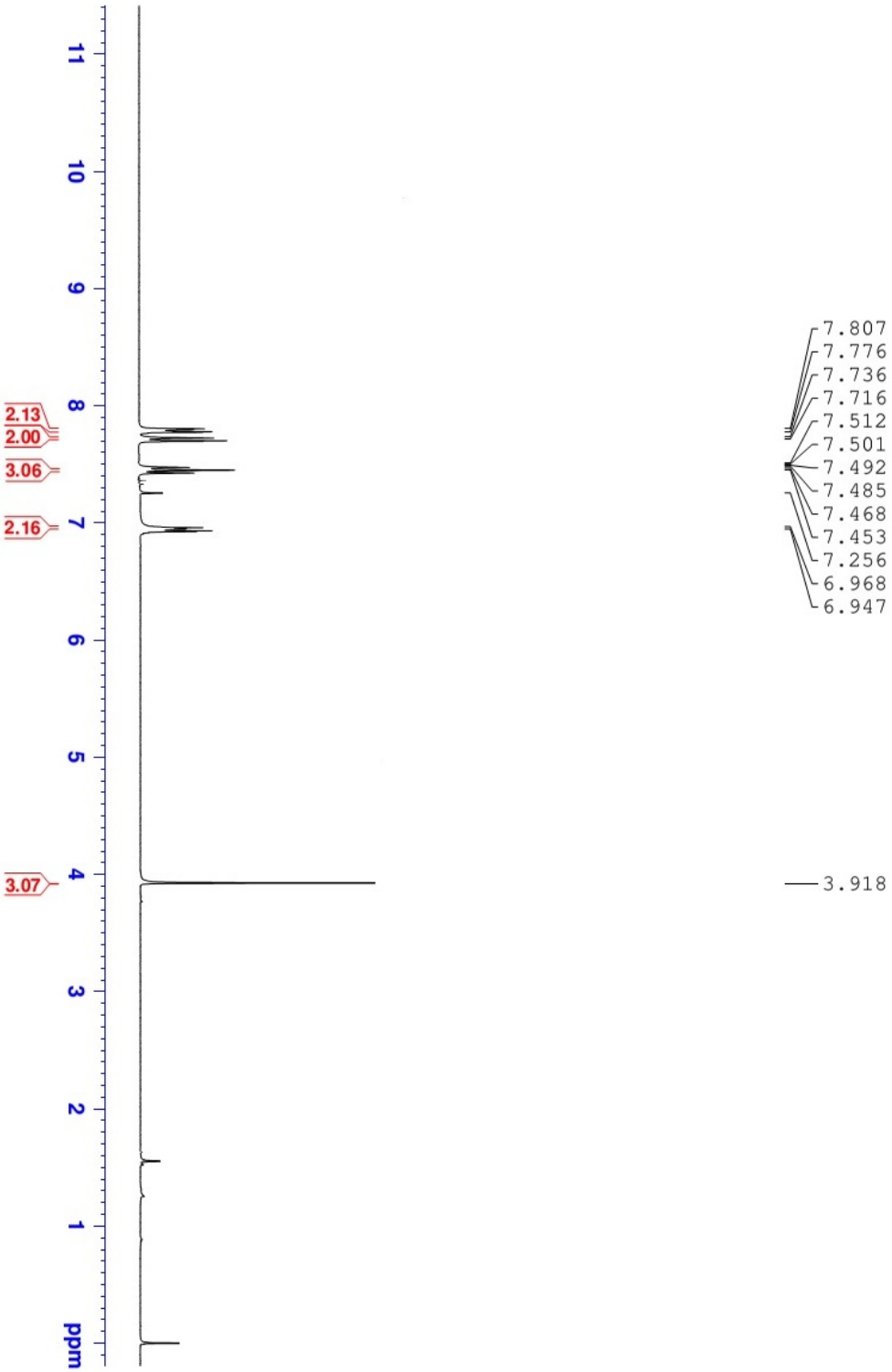
^{13}C NMR of Compound 3aa



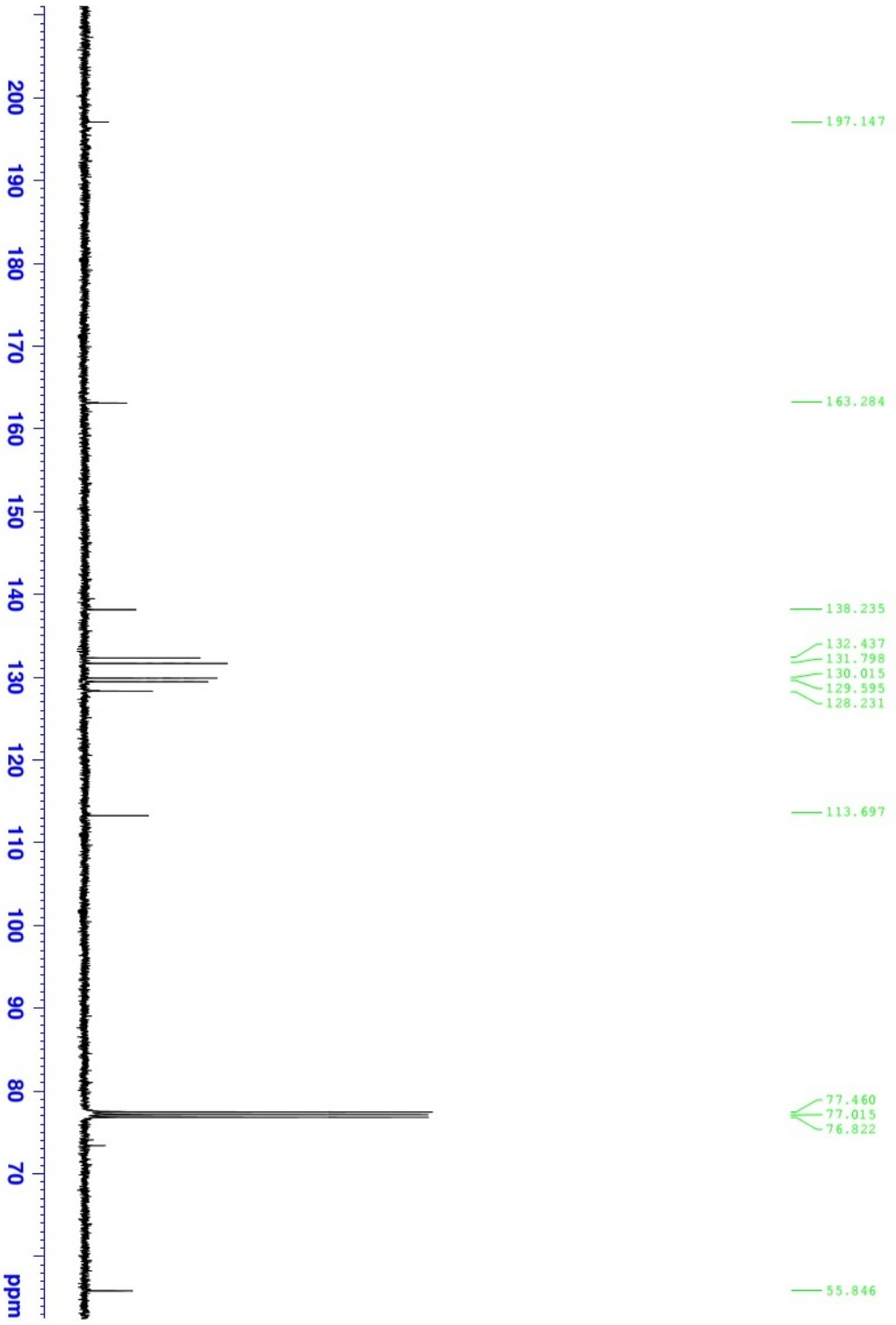
^{1}H NMR of Compound 3ab



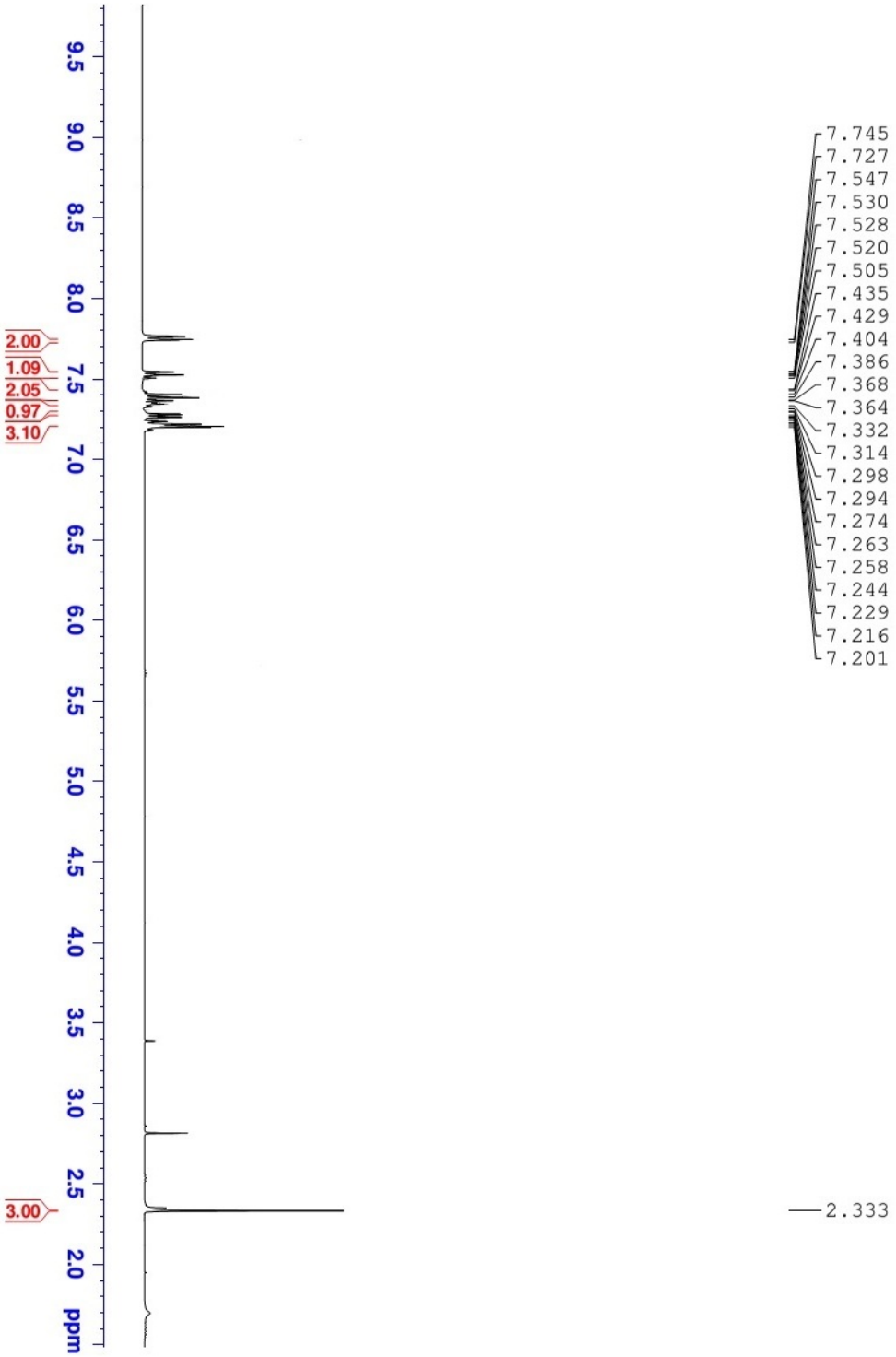
^{13}C NMR of Compound 3ab



^{1}H NMR of Compound 3ac



^{13}C NMR of Compound 3ac



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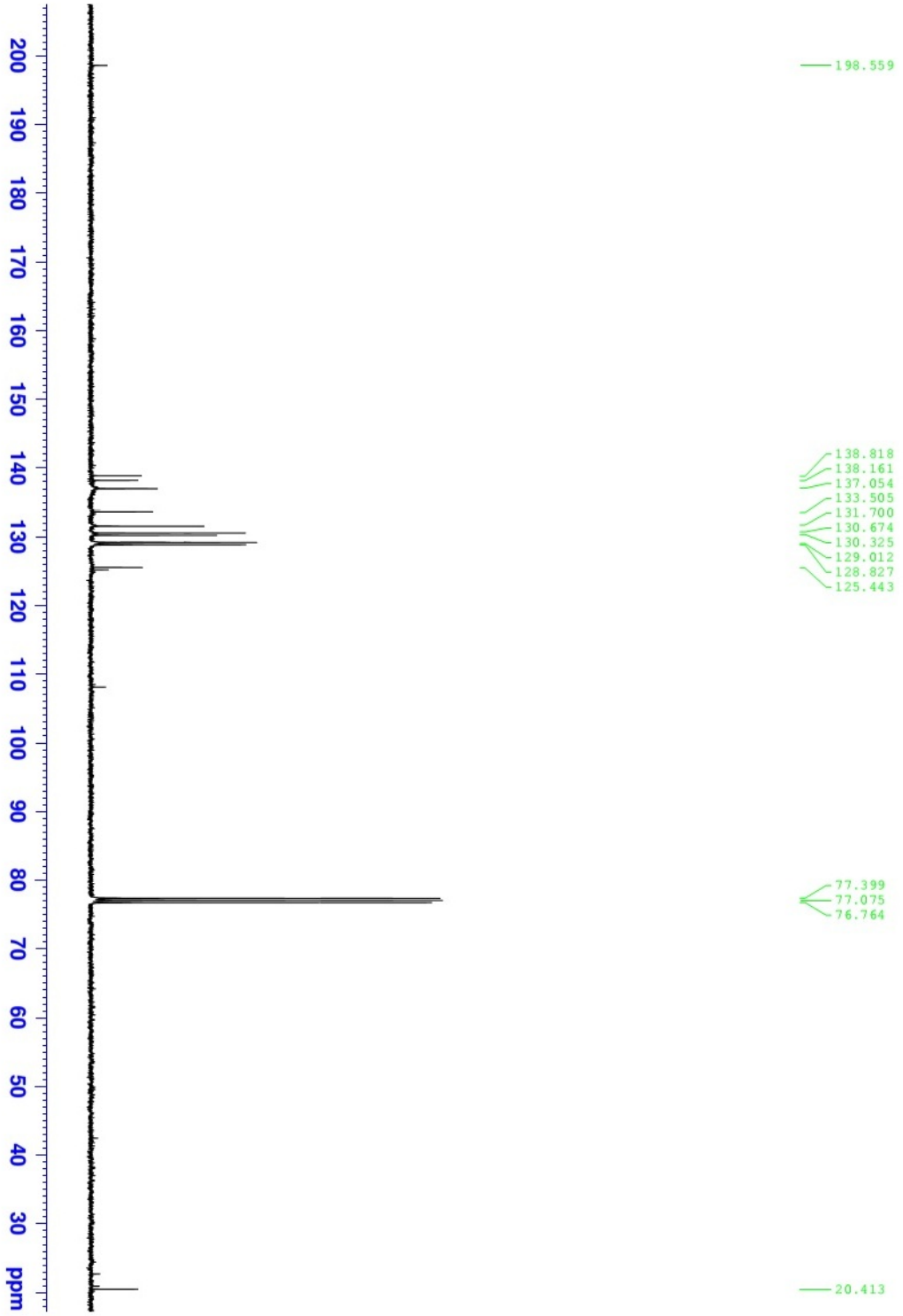
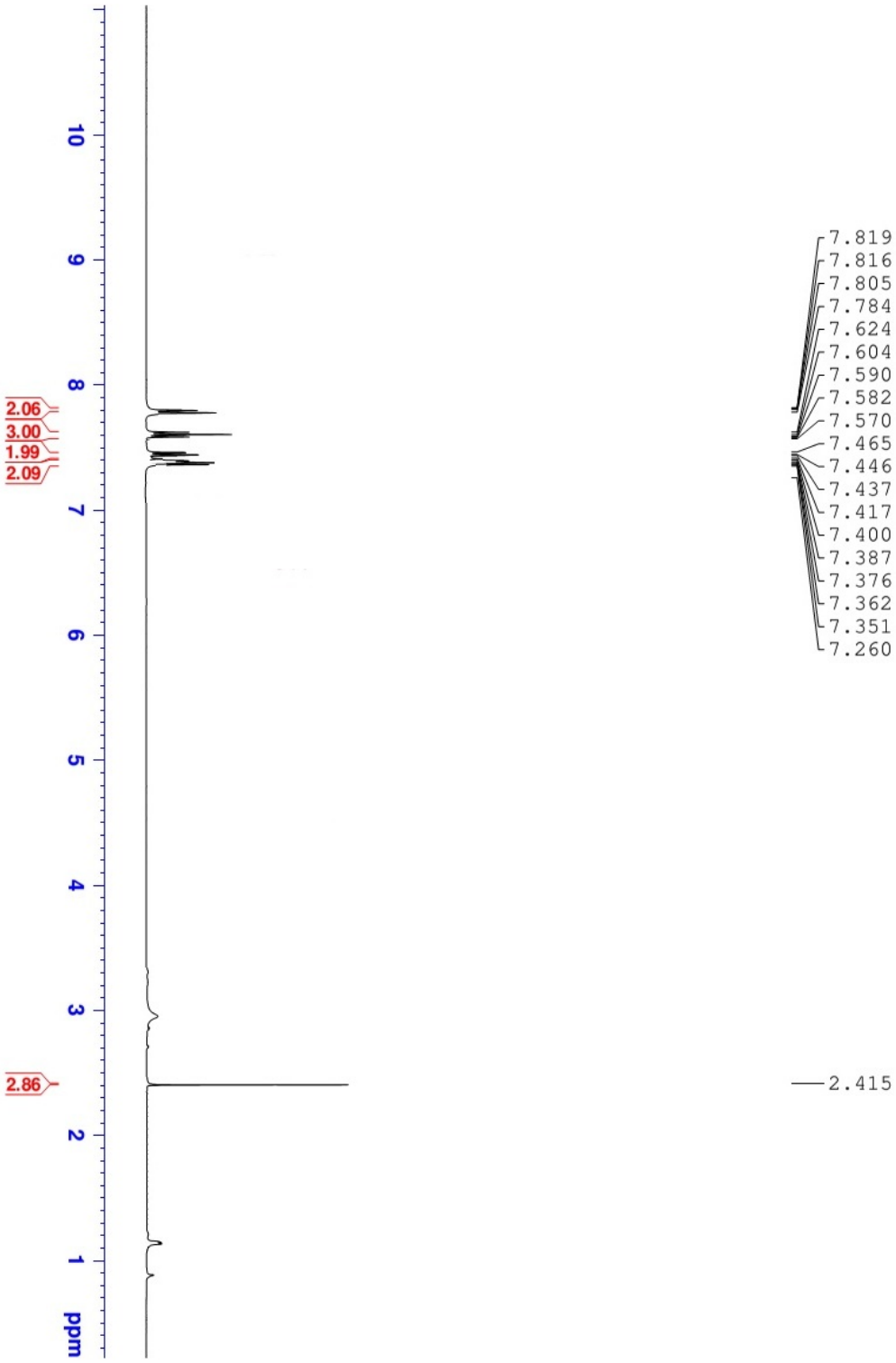
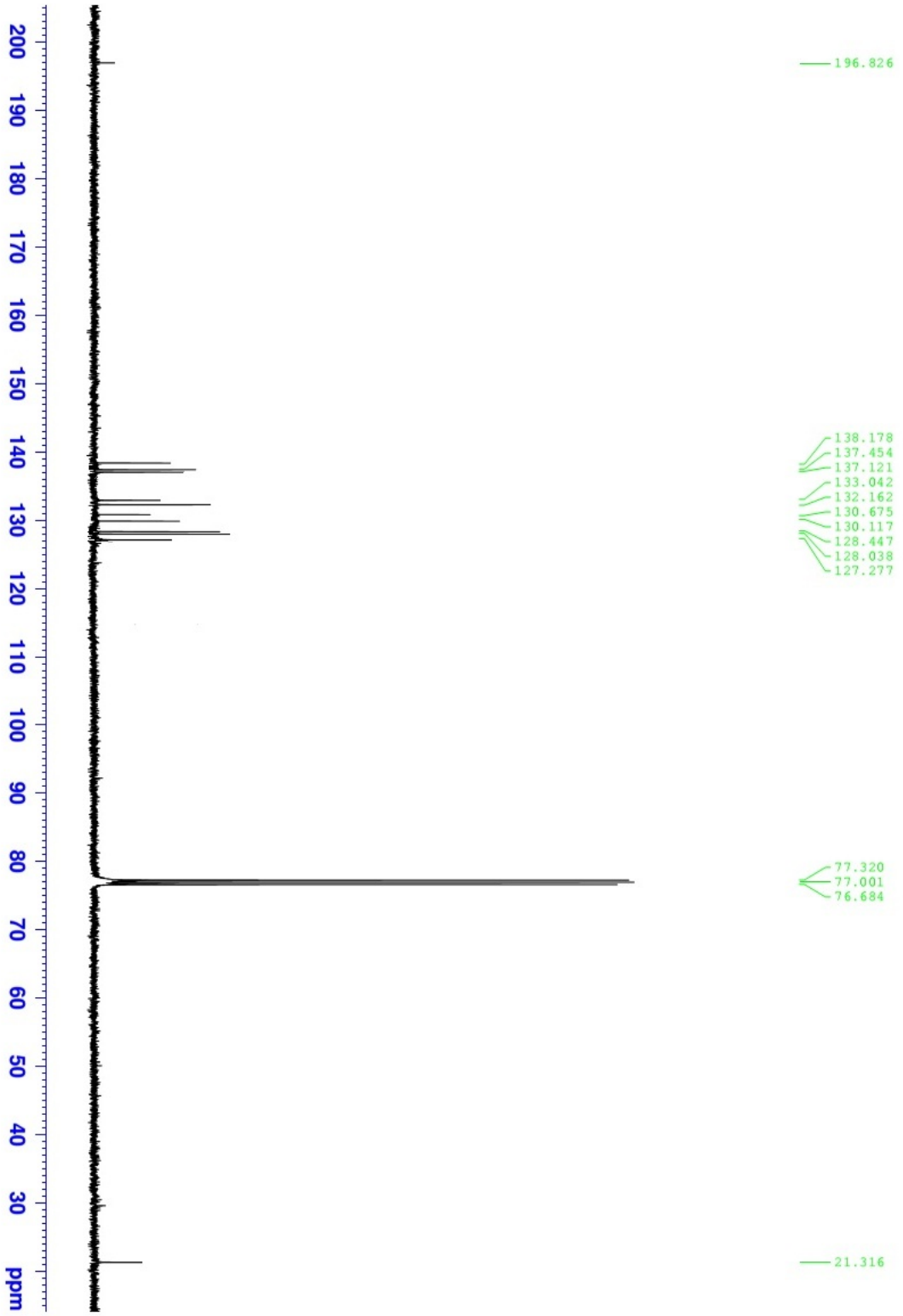


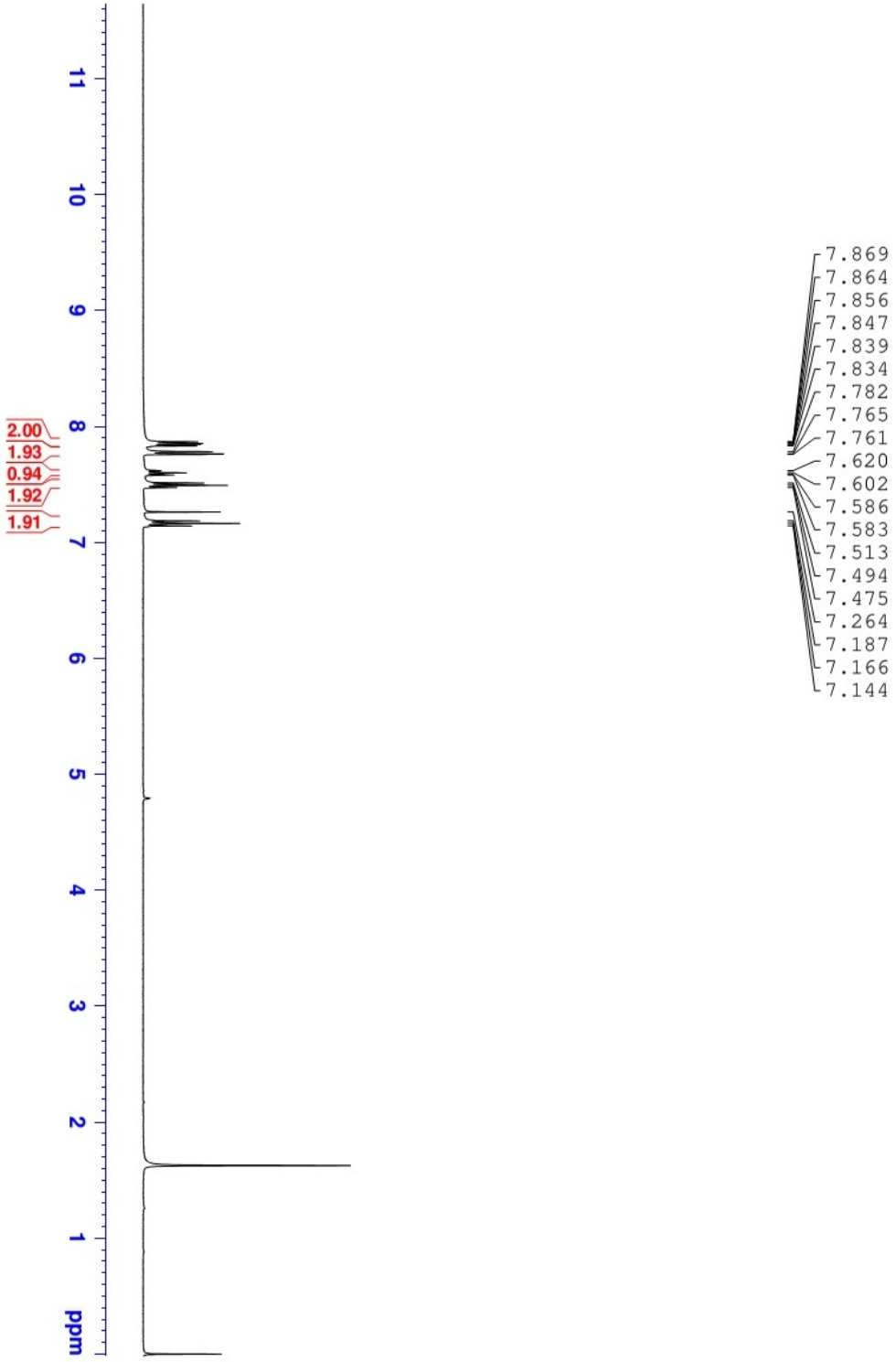
^{13}C NMR of Compound 3ad



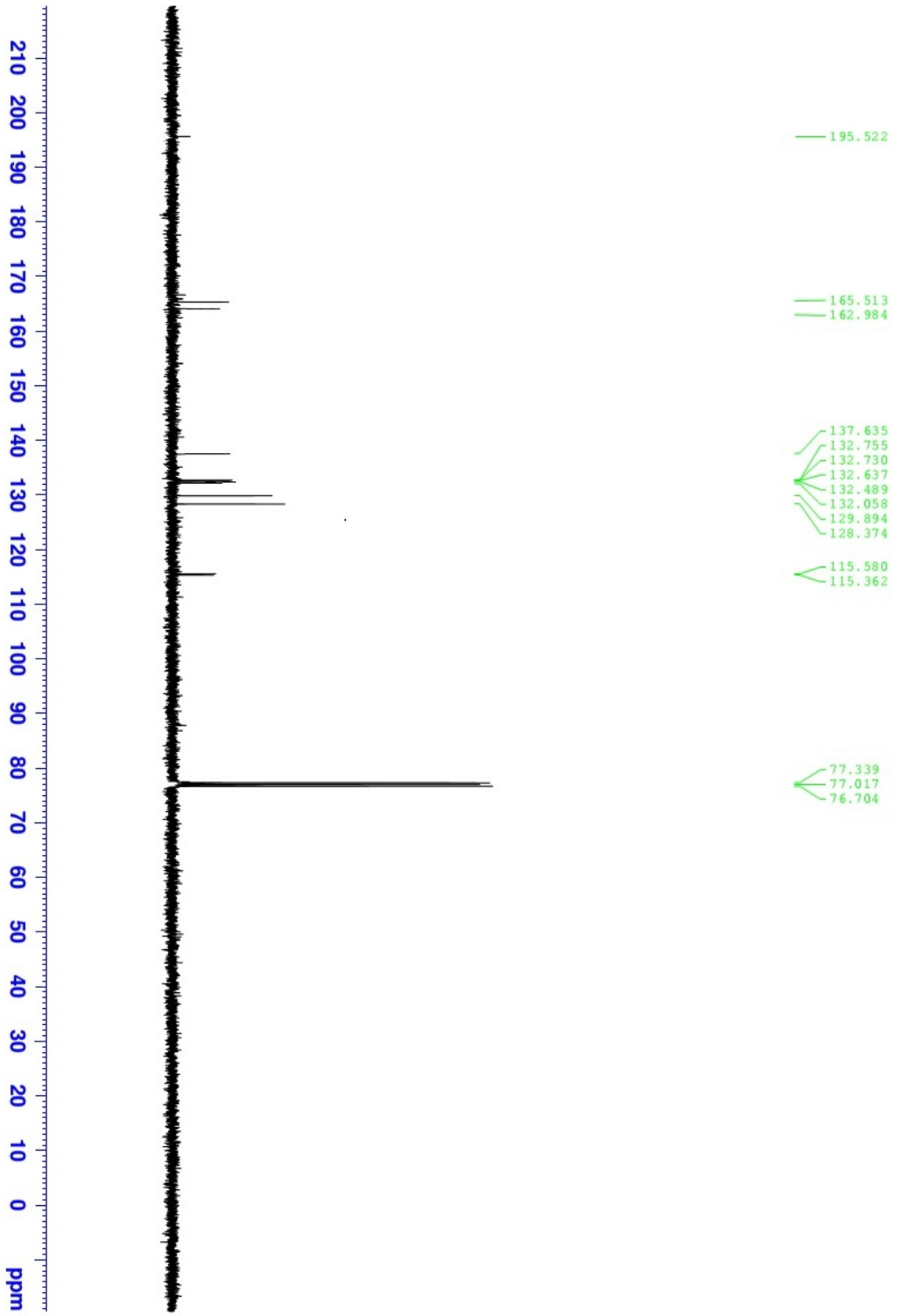
[1]H NMR of Compound 3ae



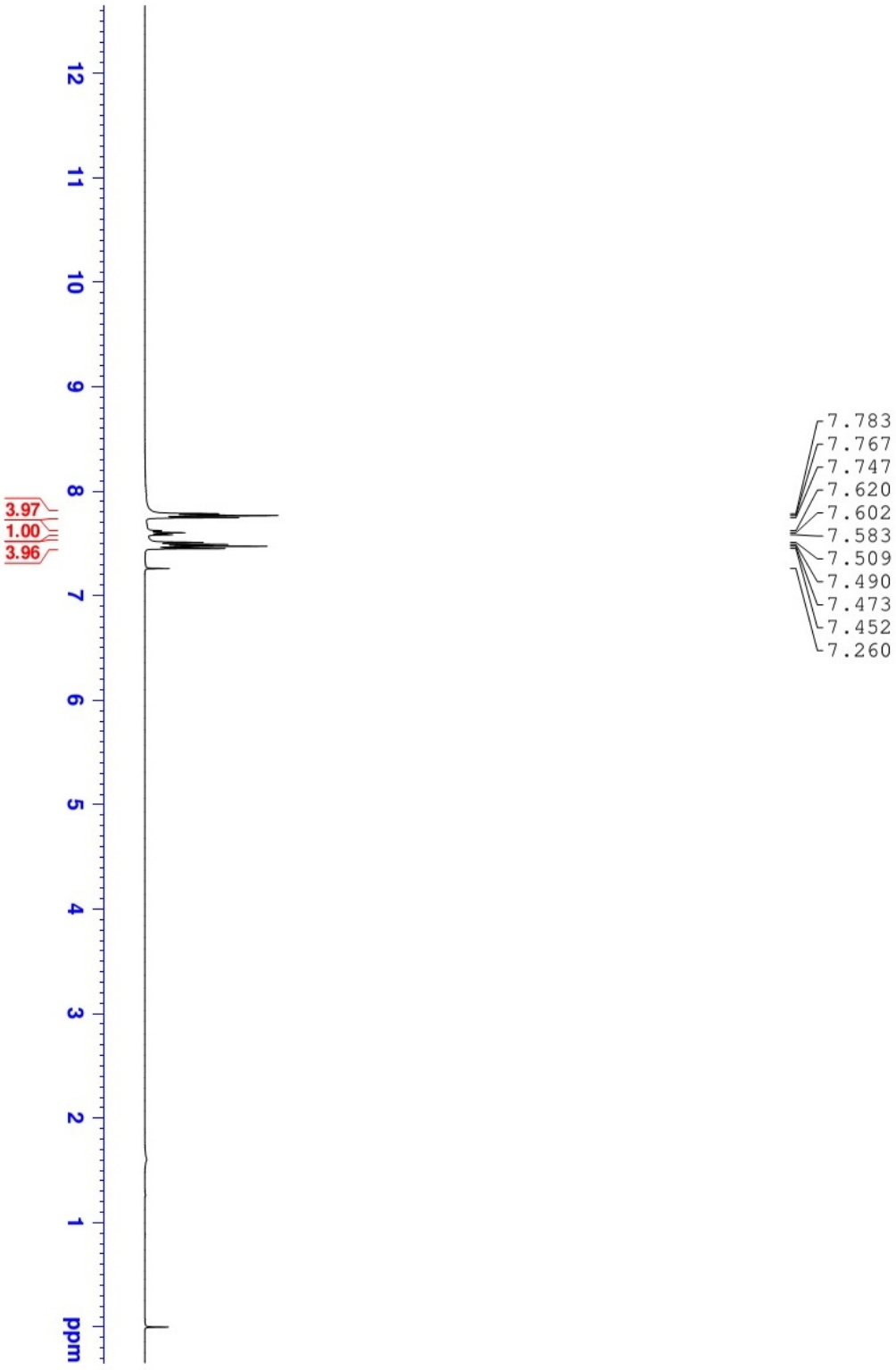
^{13}C NMR of Compound 3ae



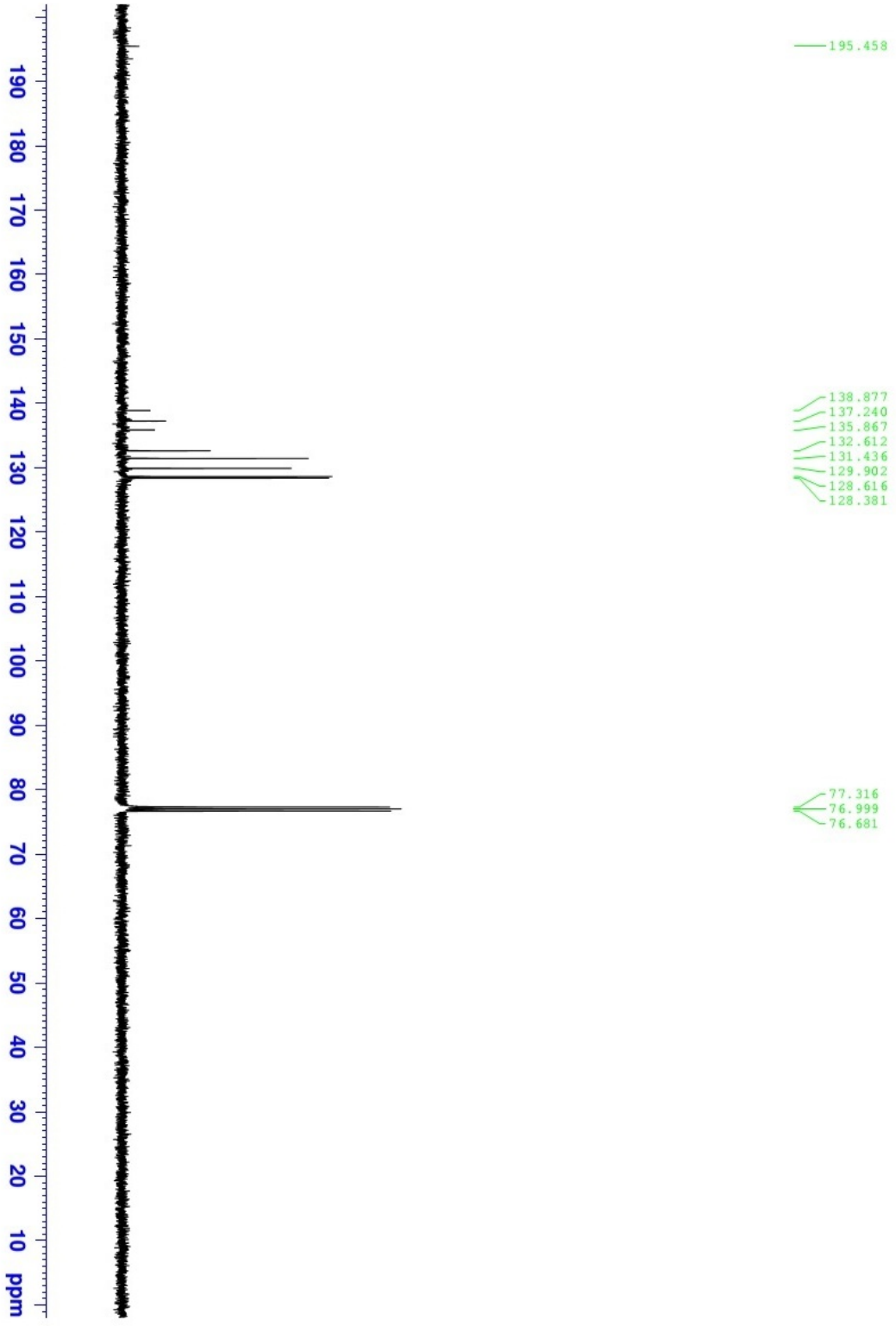
^{1}H NMR of Compound 3af



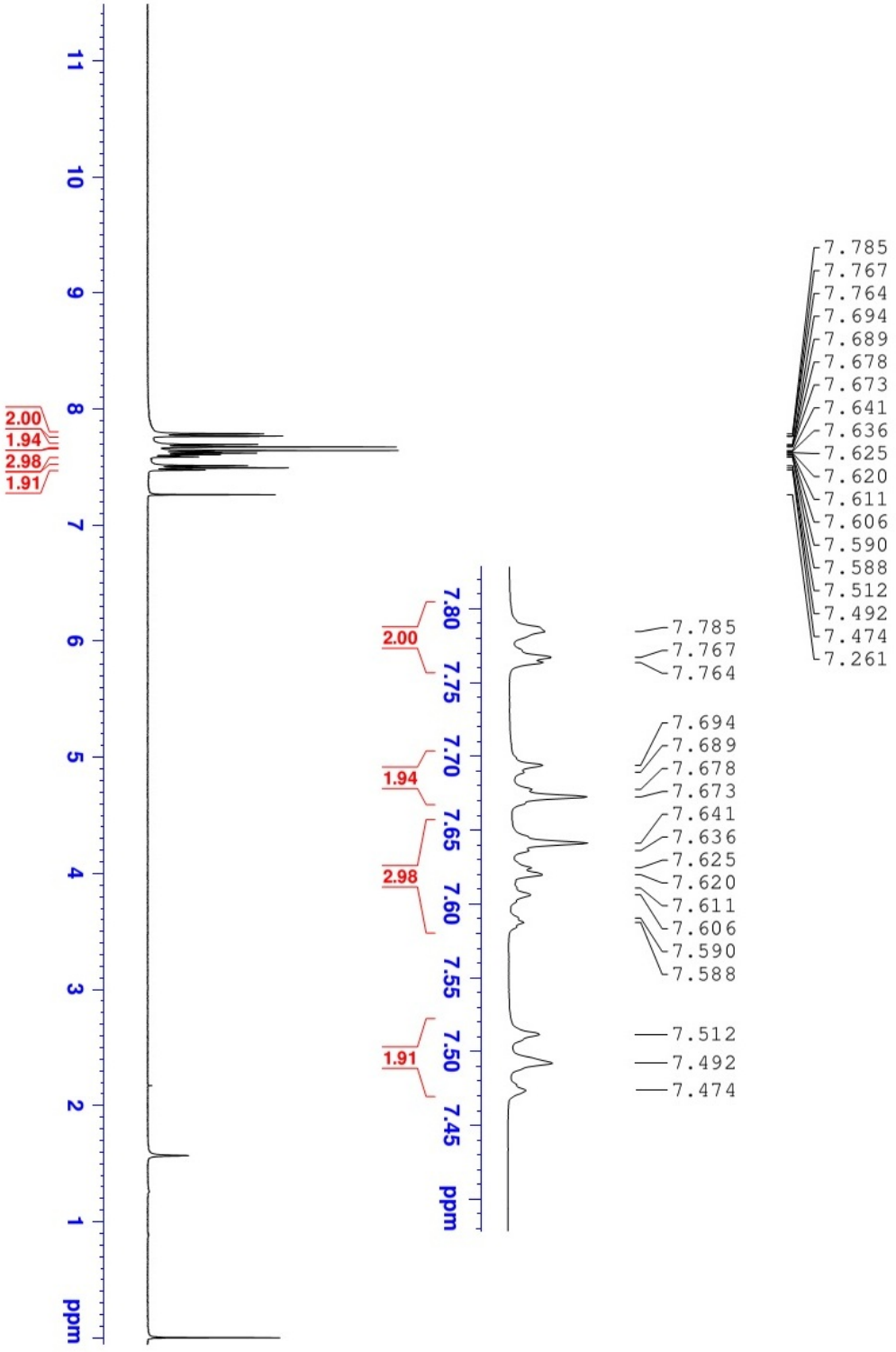
^{13}C NMR of Compound 3af



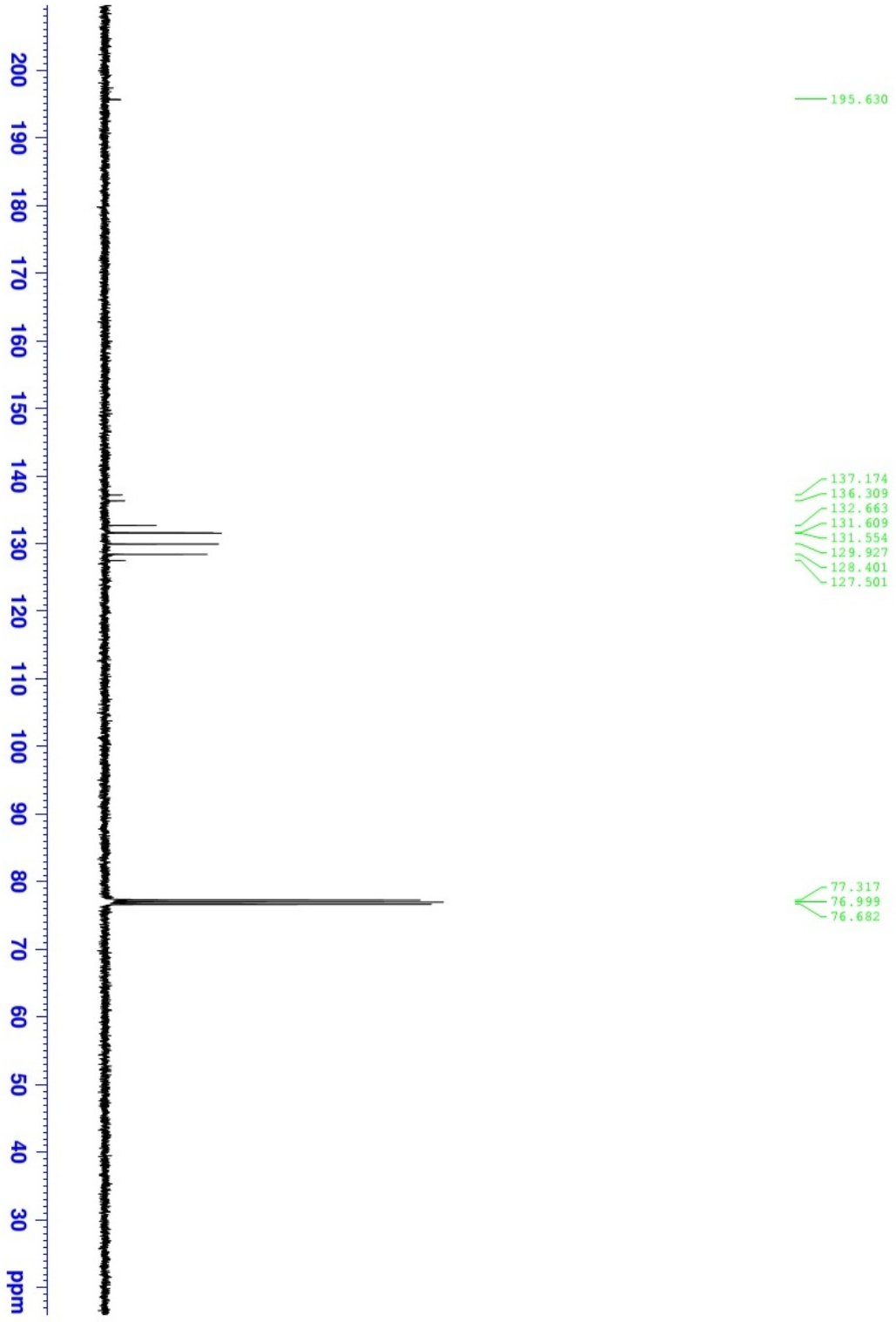
^{1}H NMR of Compound 3ag



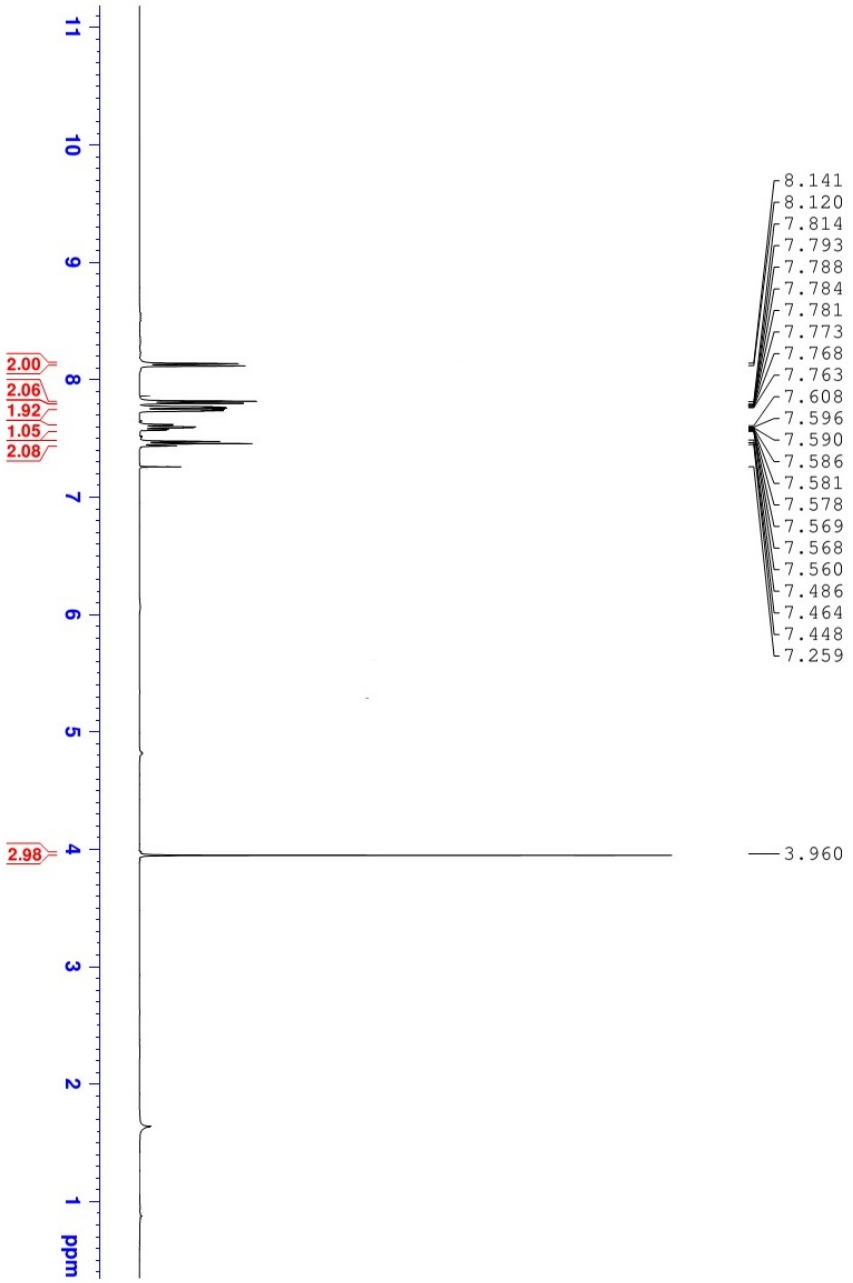
^{13}C NMR of Compound 3ag



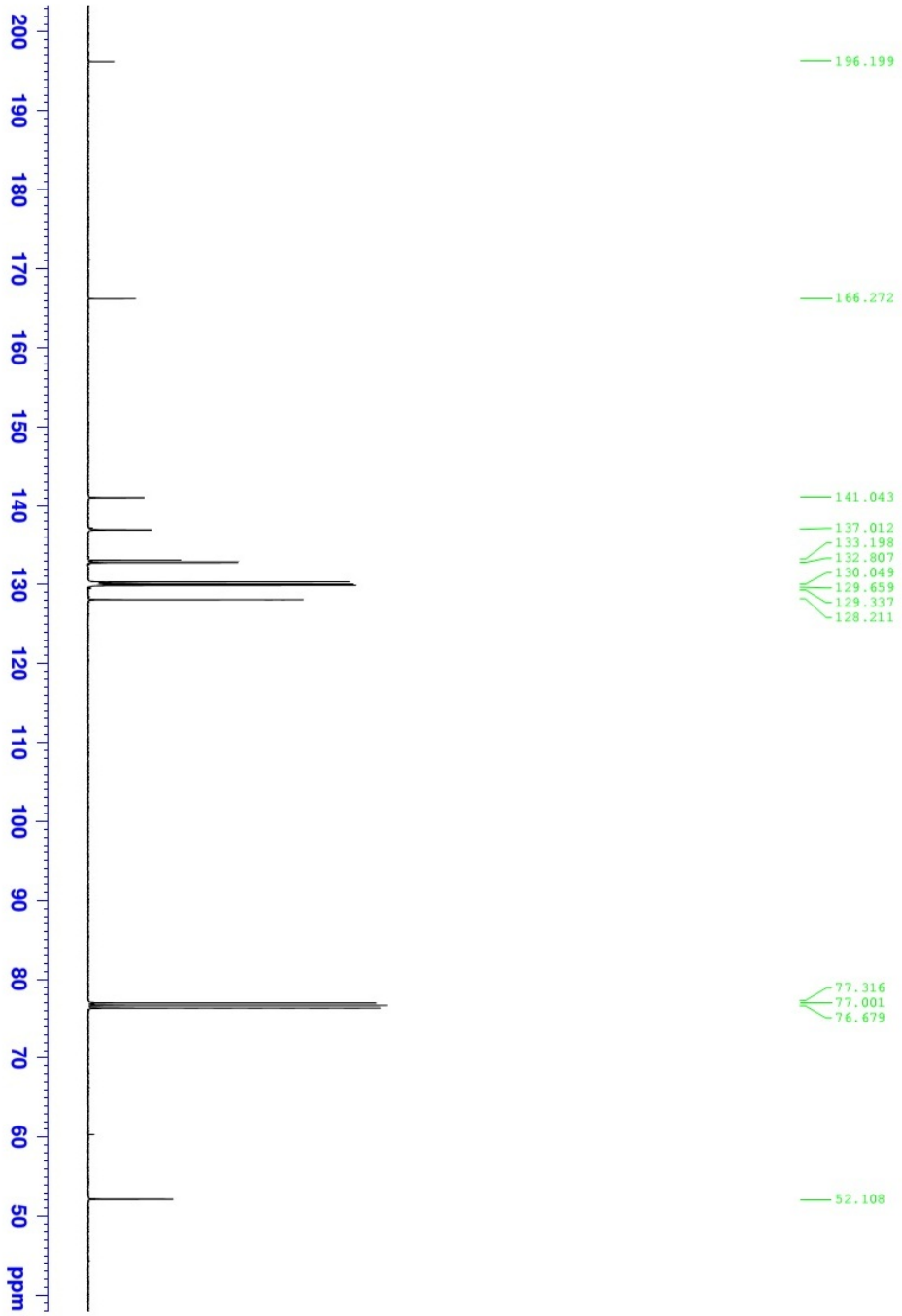
[1]H NMR of Compound 3ah



^{13}C NMR of Compound 3ah



^{1}H NMR of Compound 3ai



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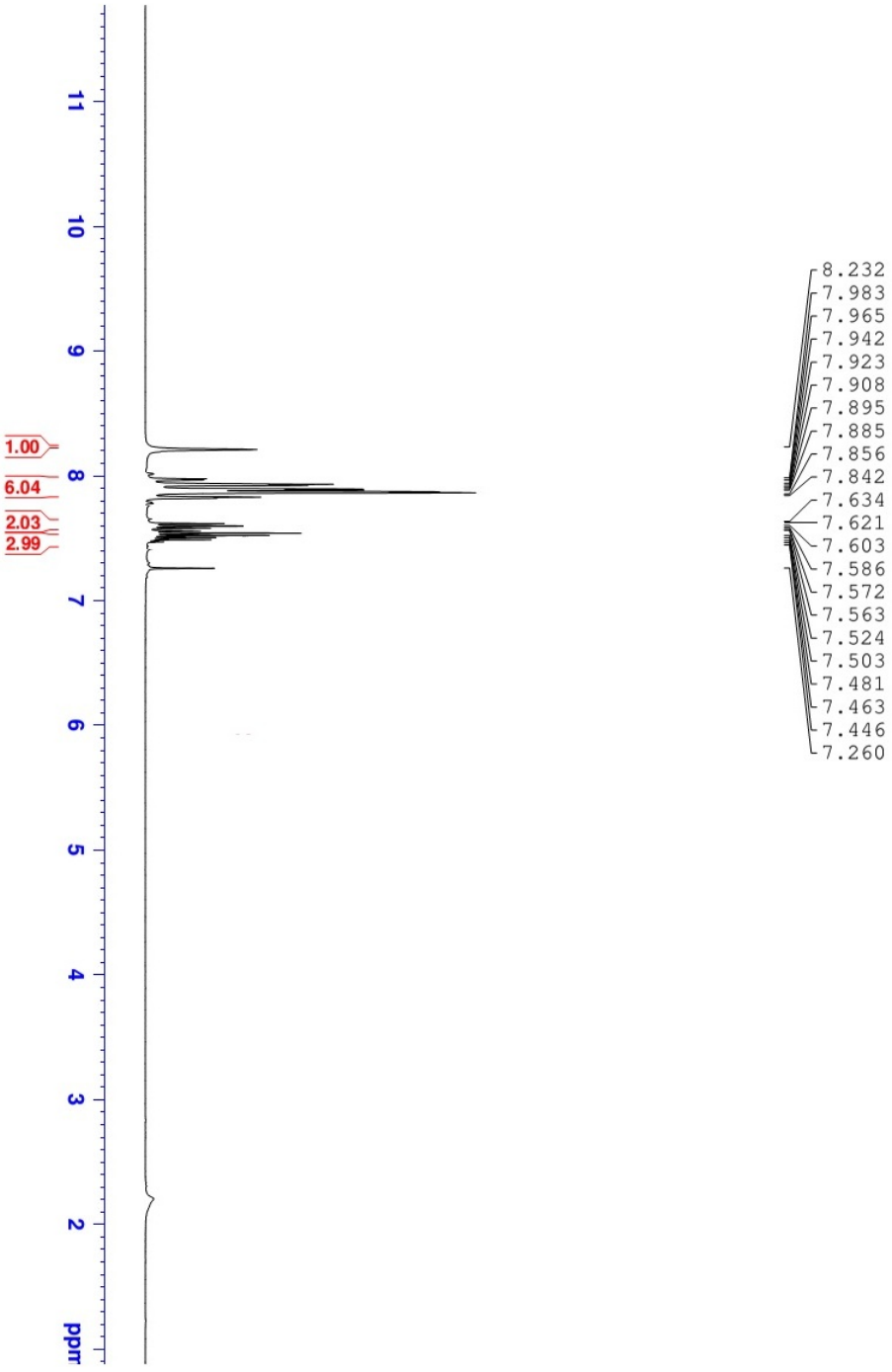

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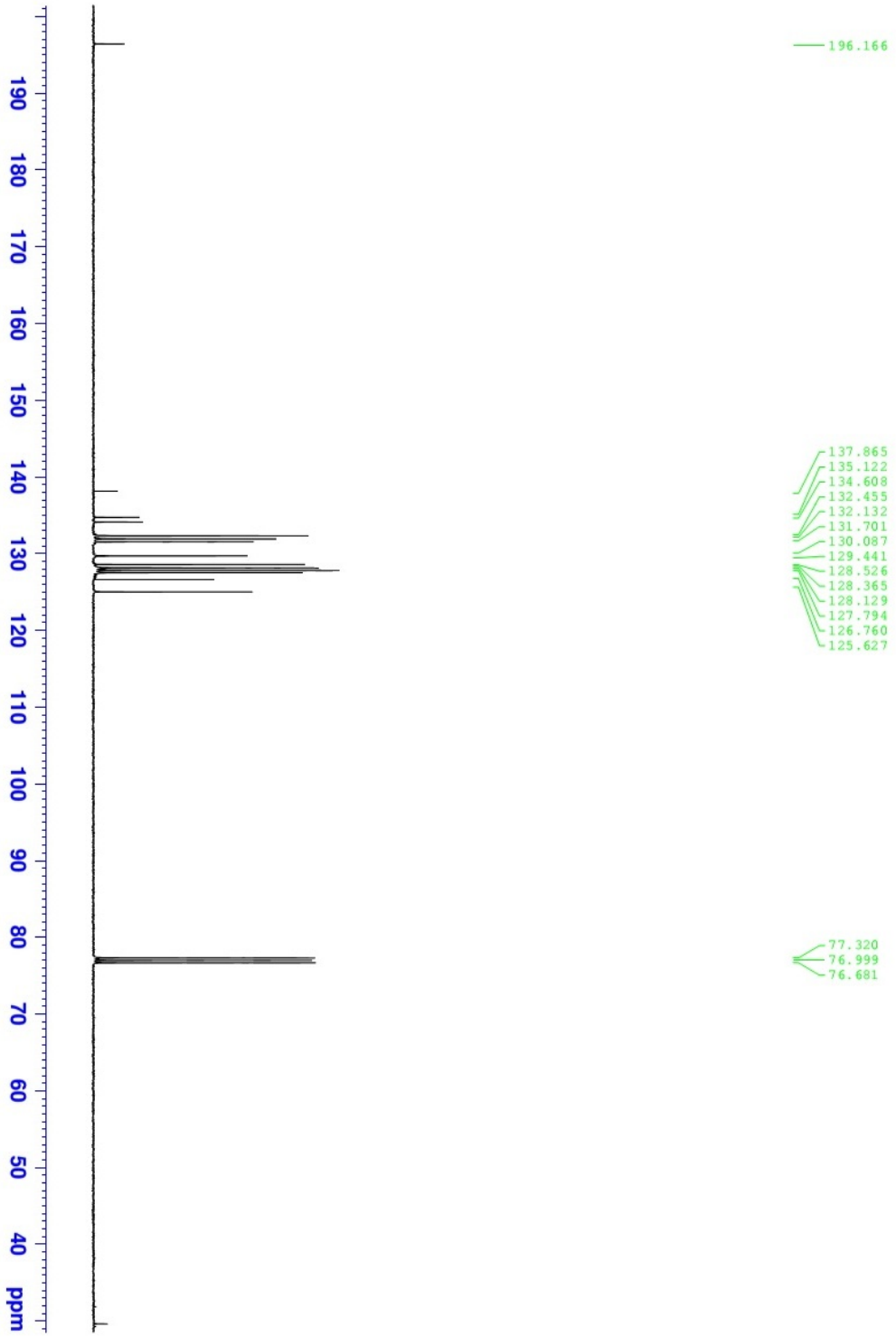

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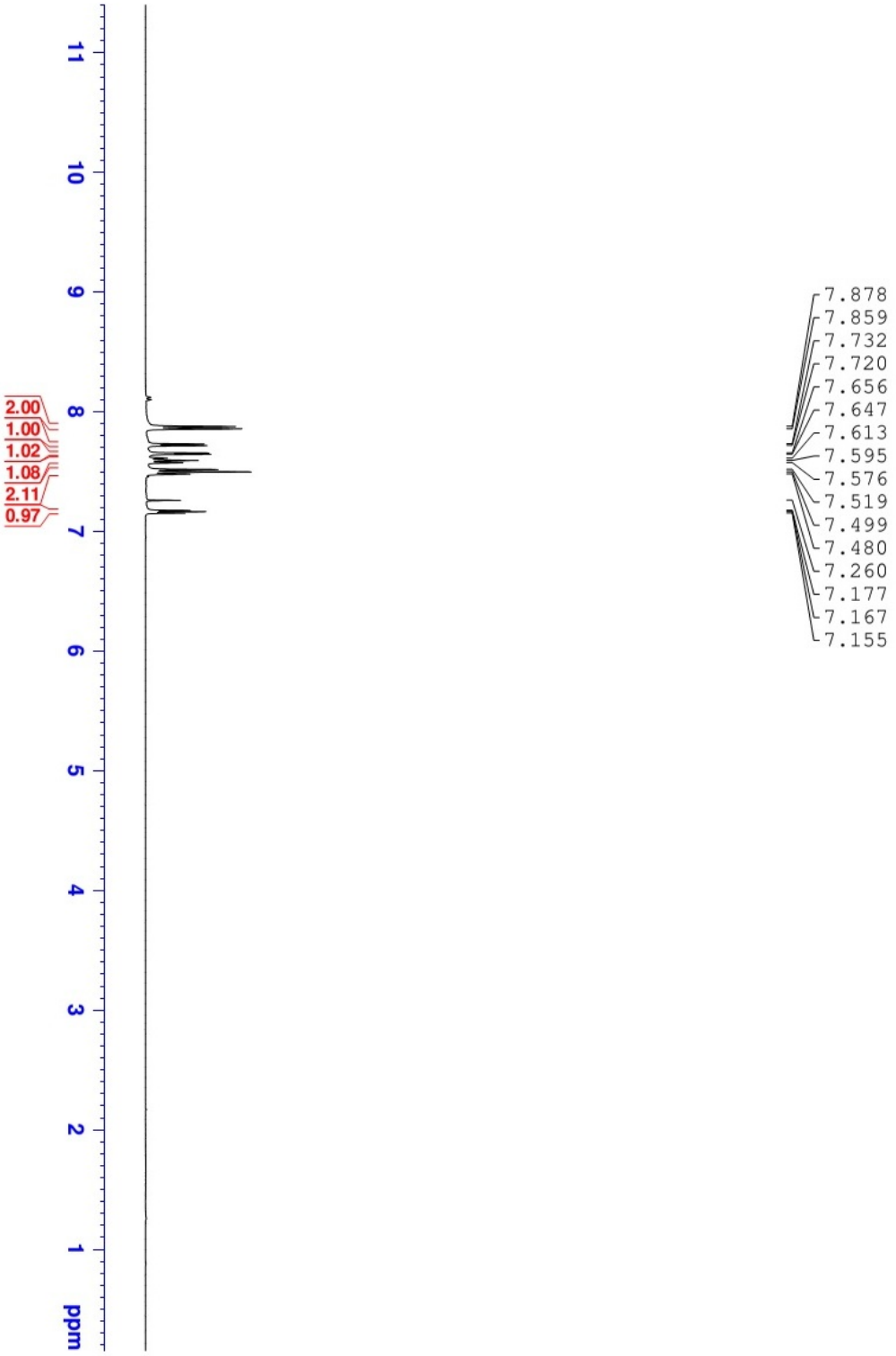

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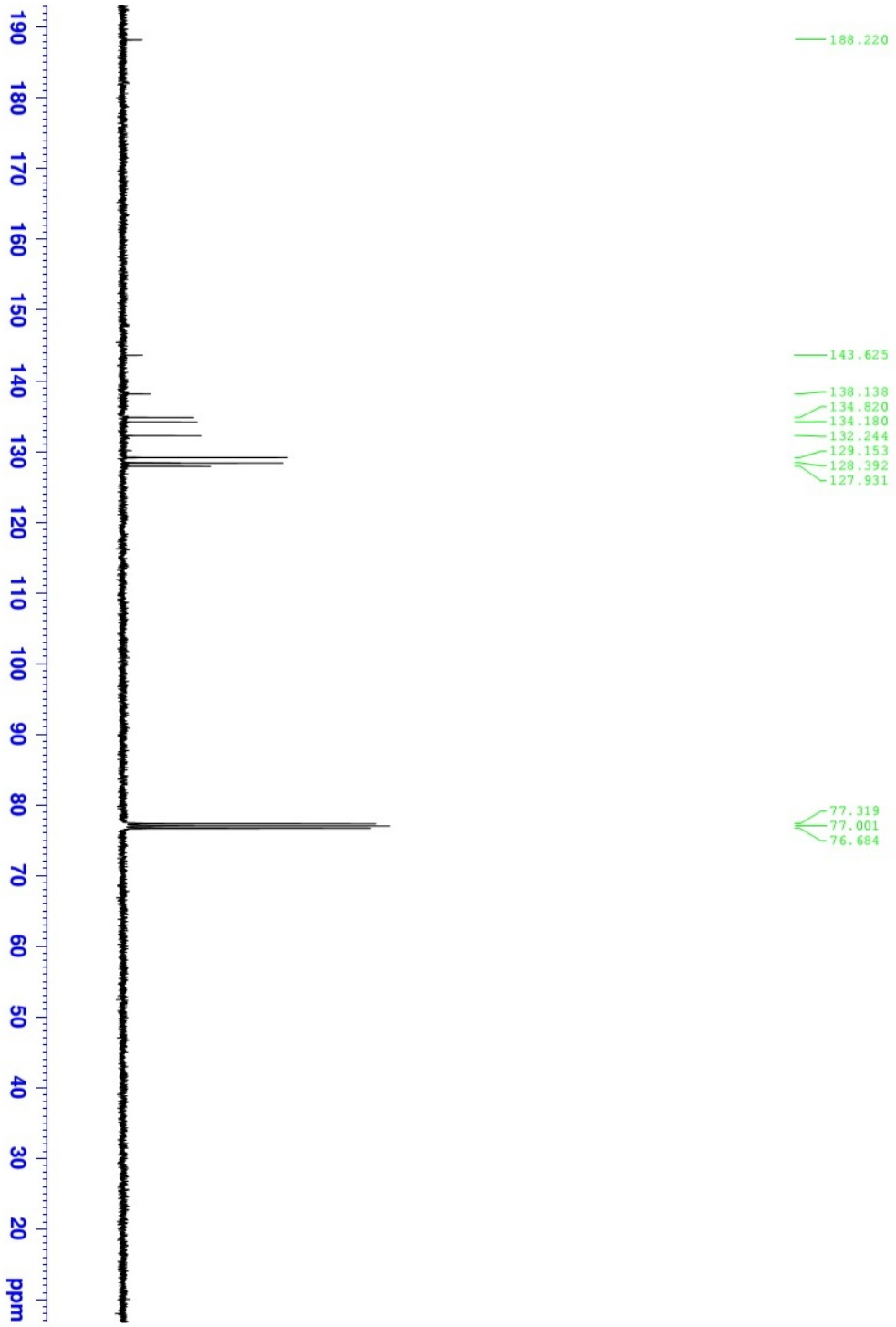

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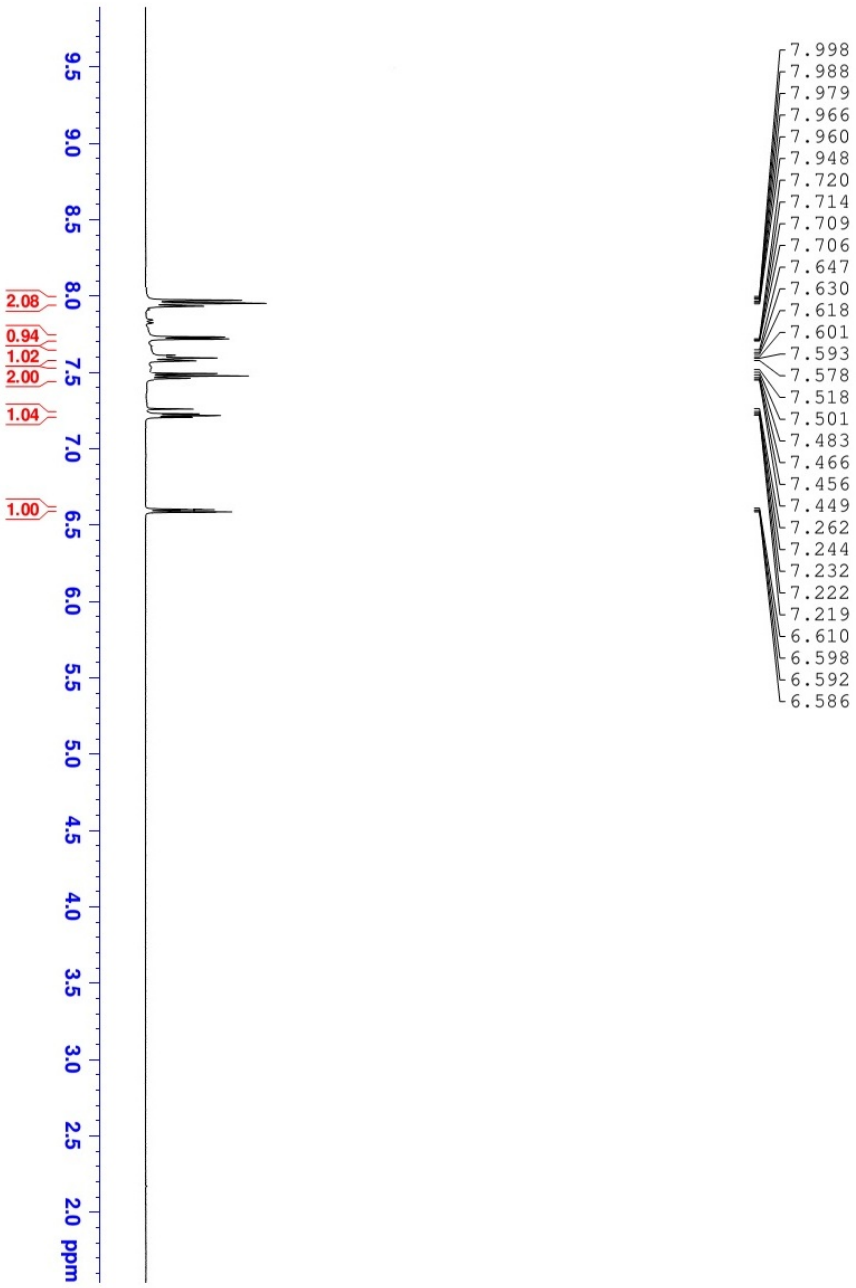

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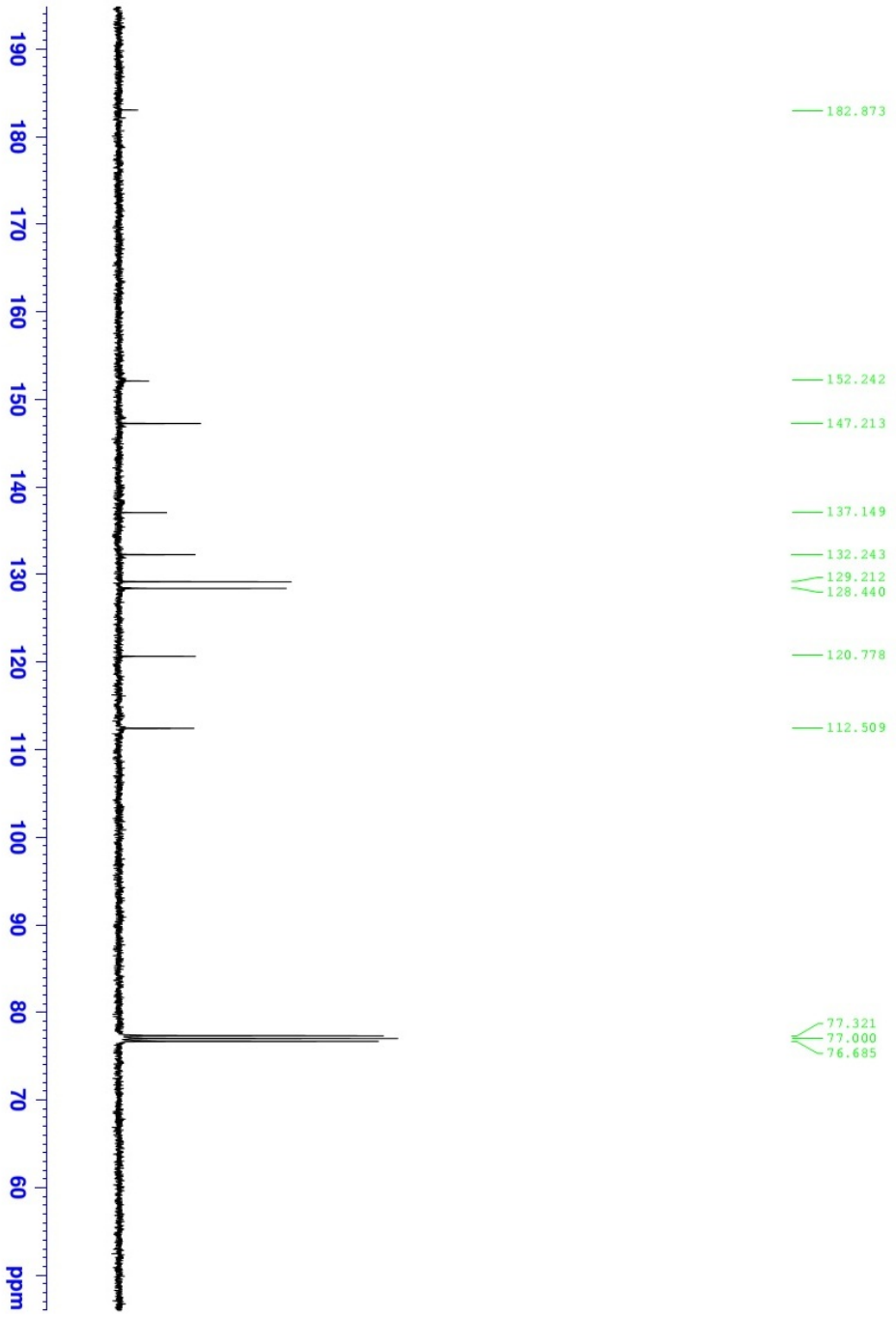

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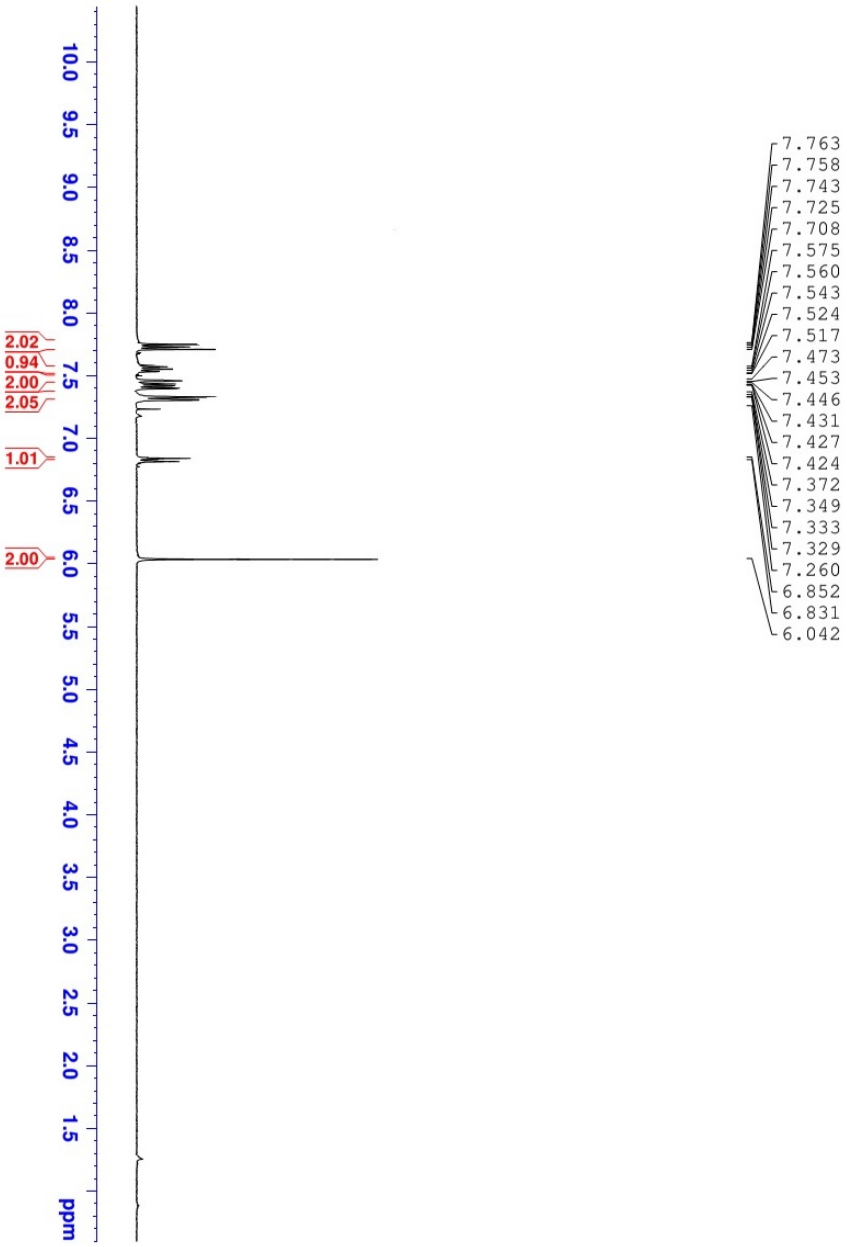

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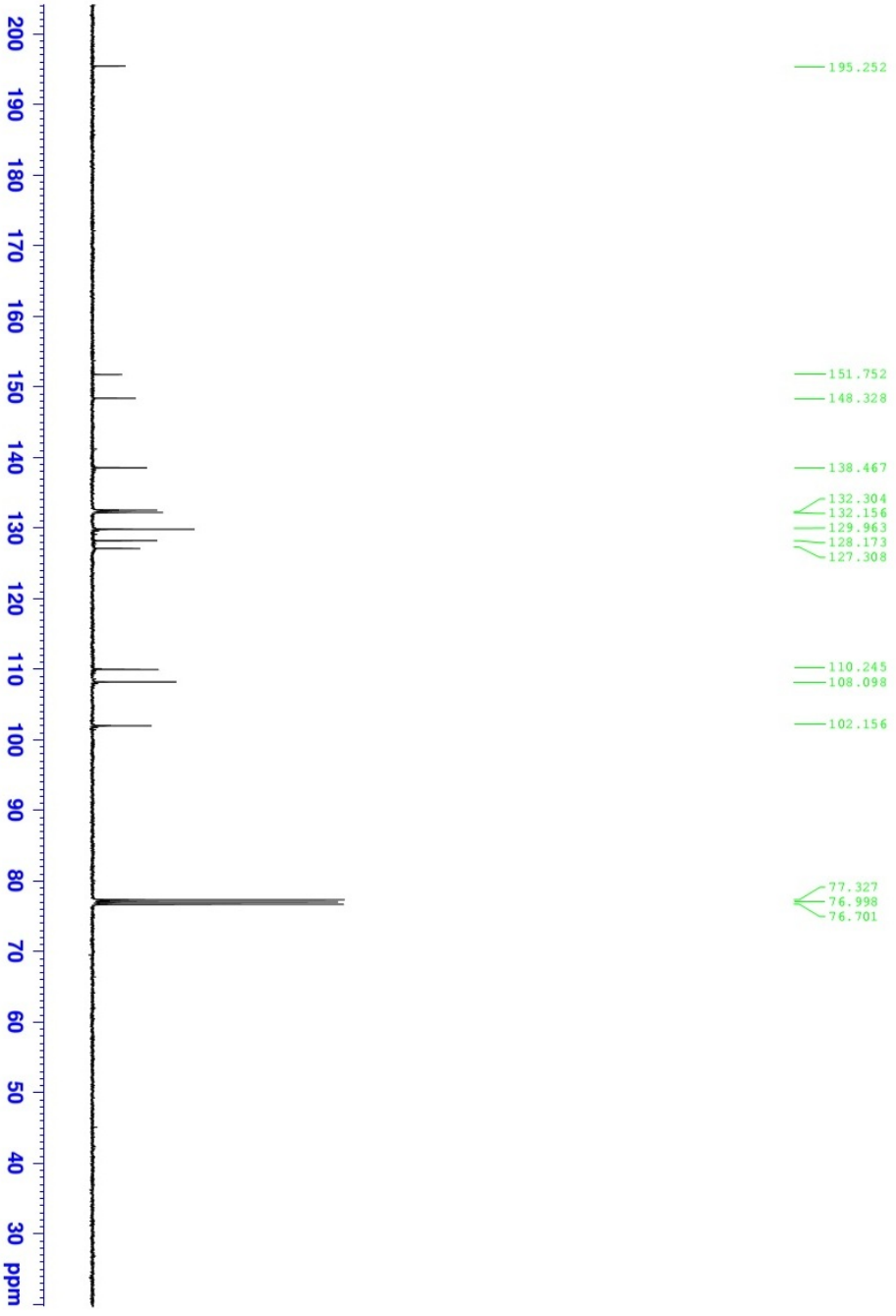

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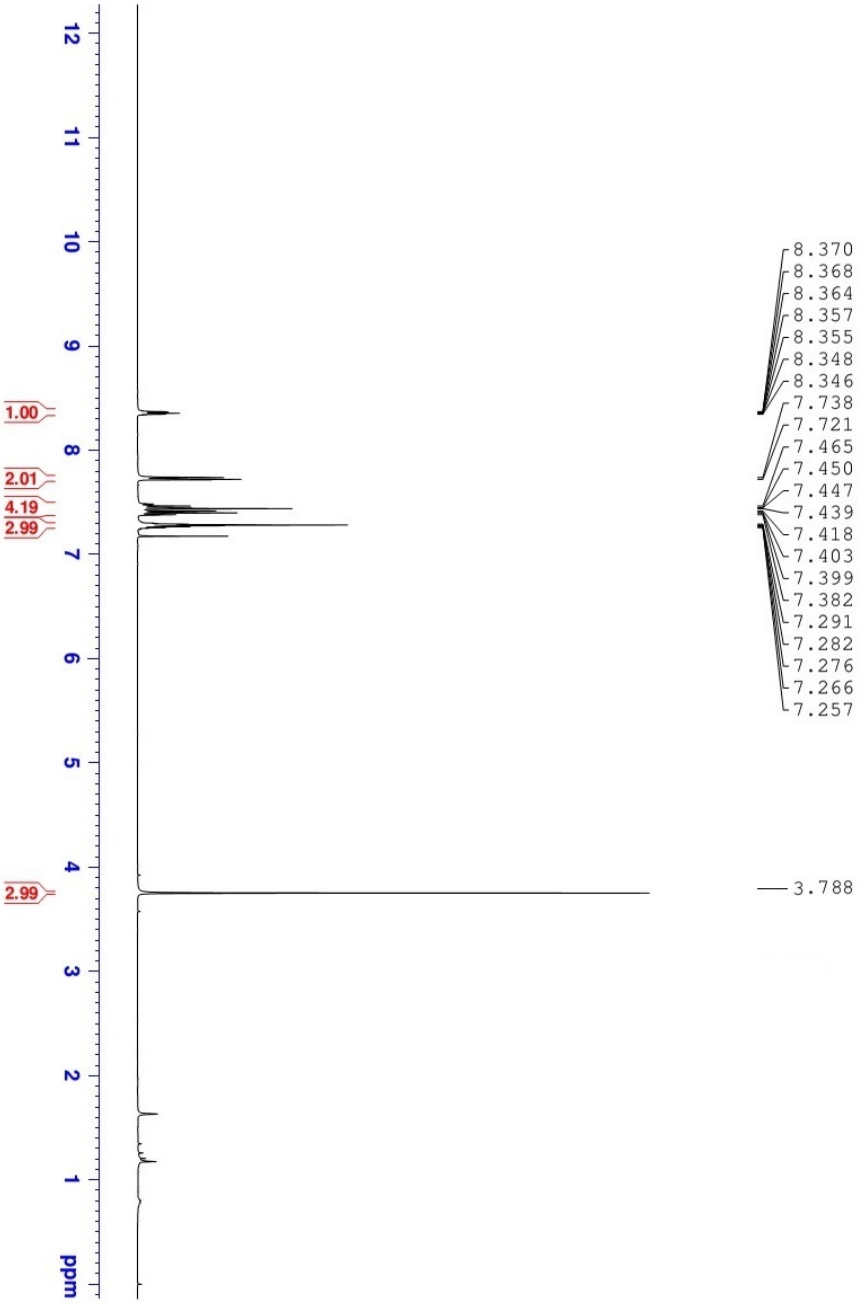

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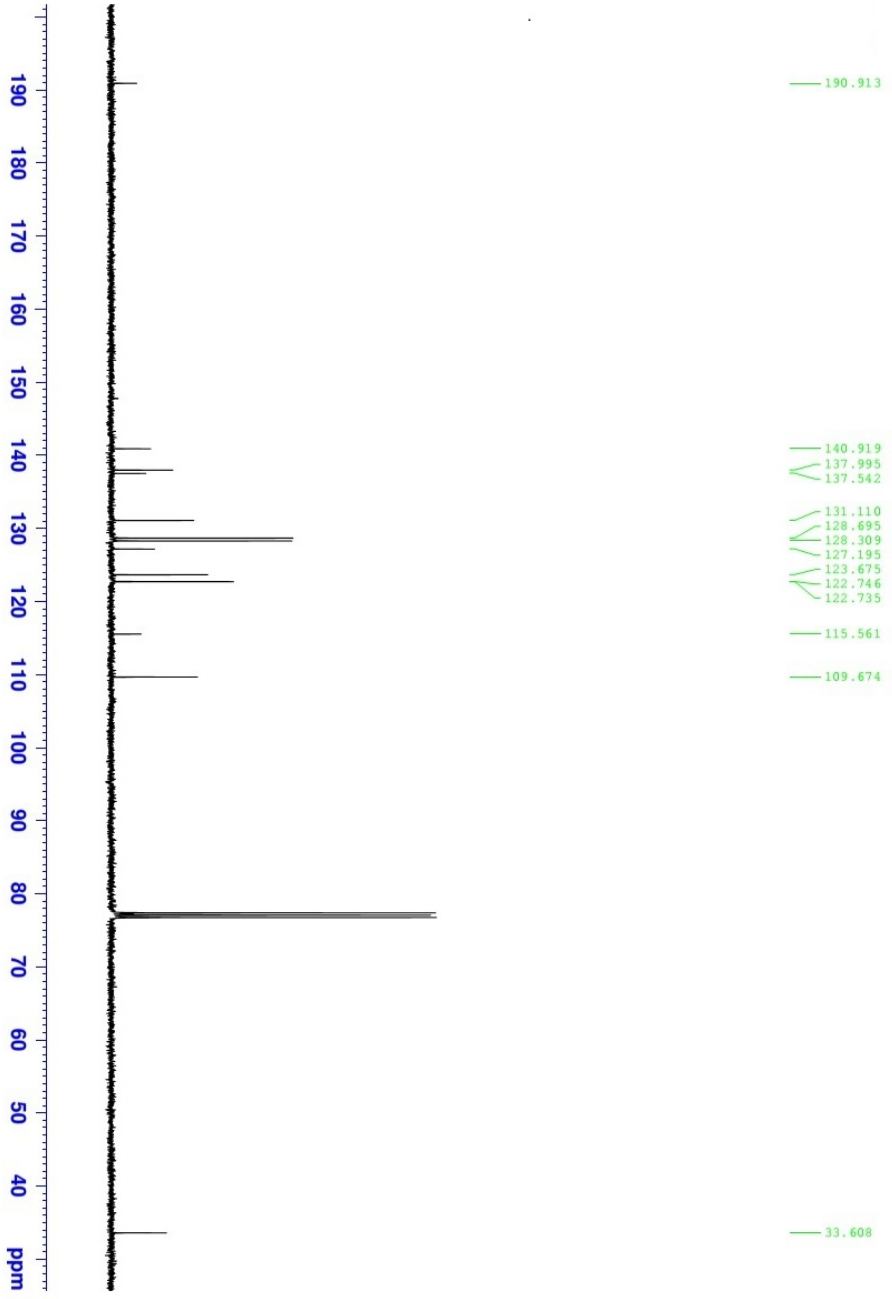

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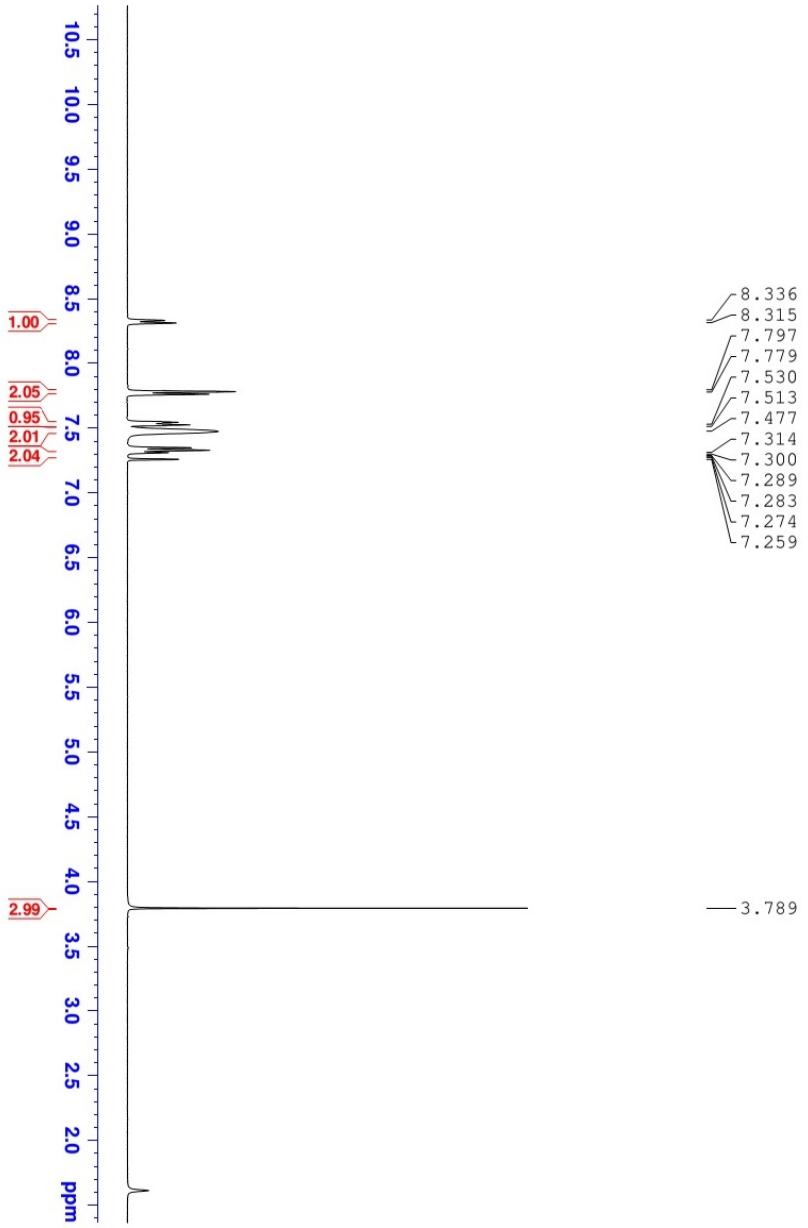
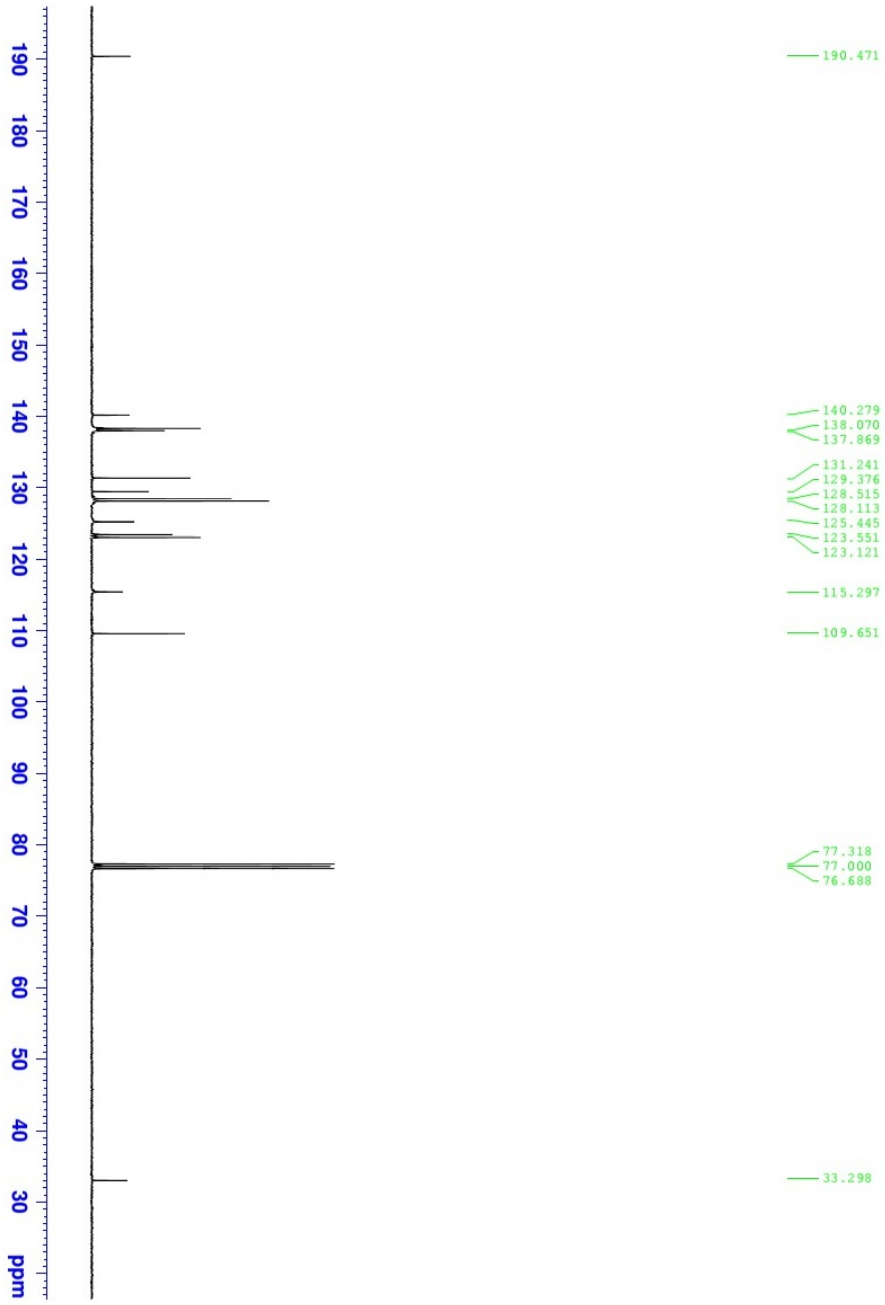


^{1}H NMR of Compound 3fa



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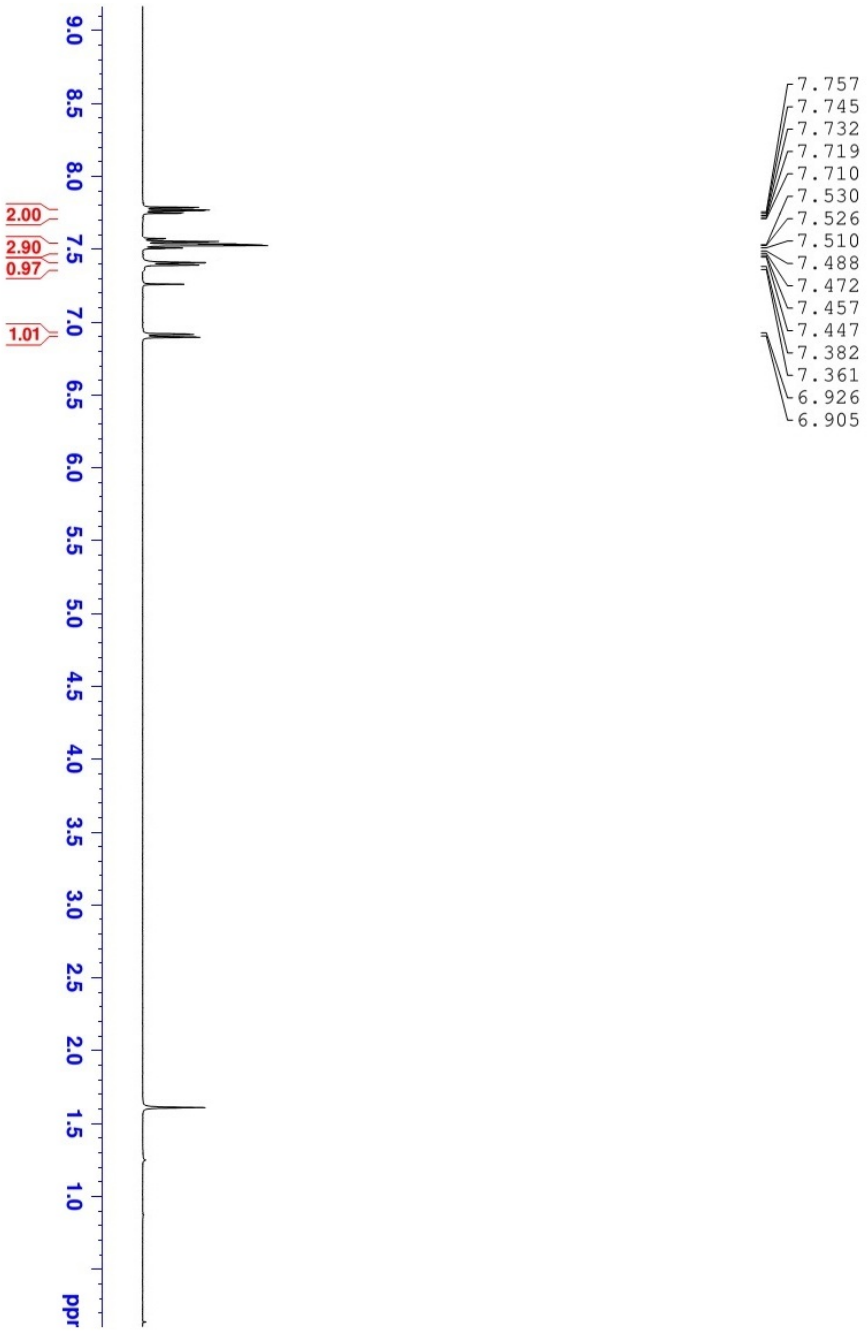
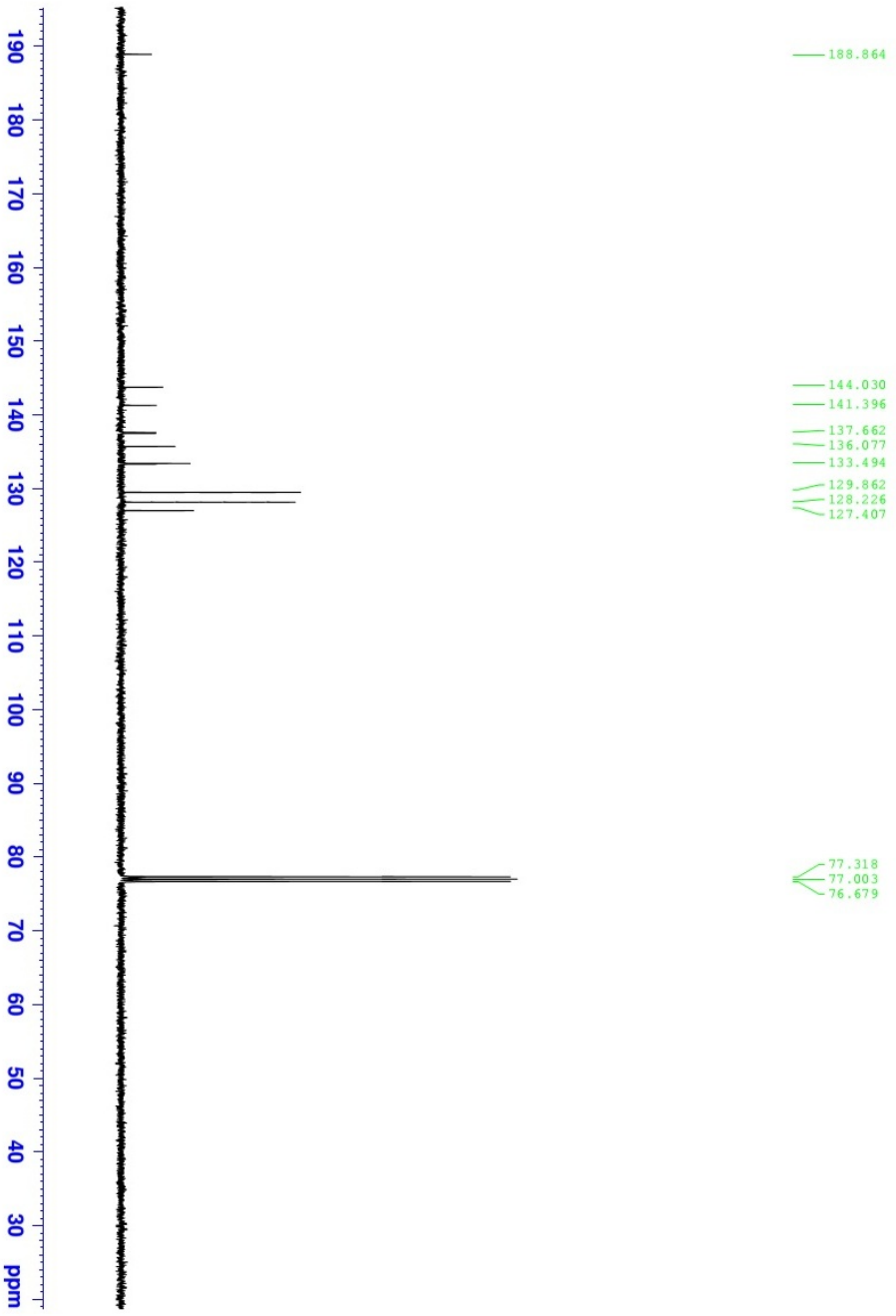
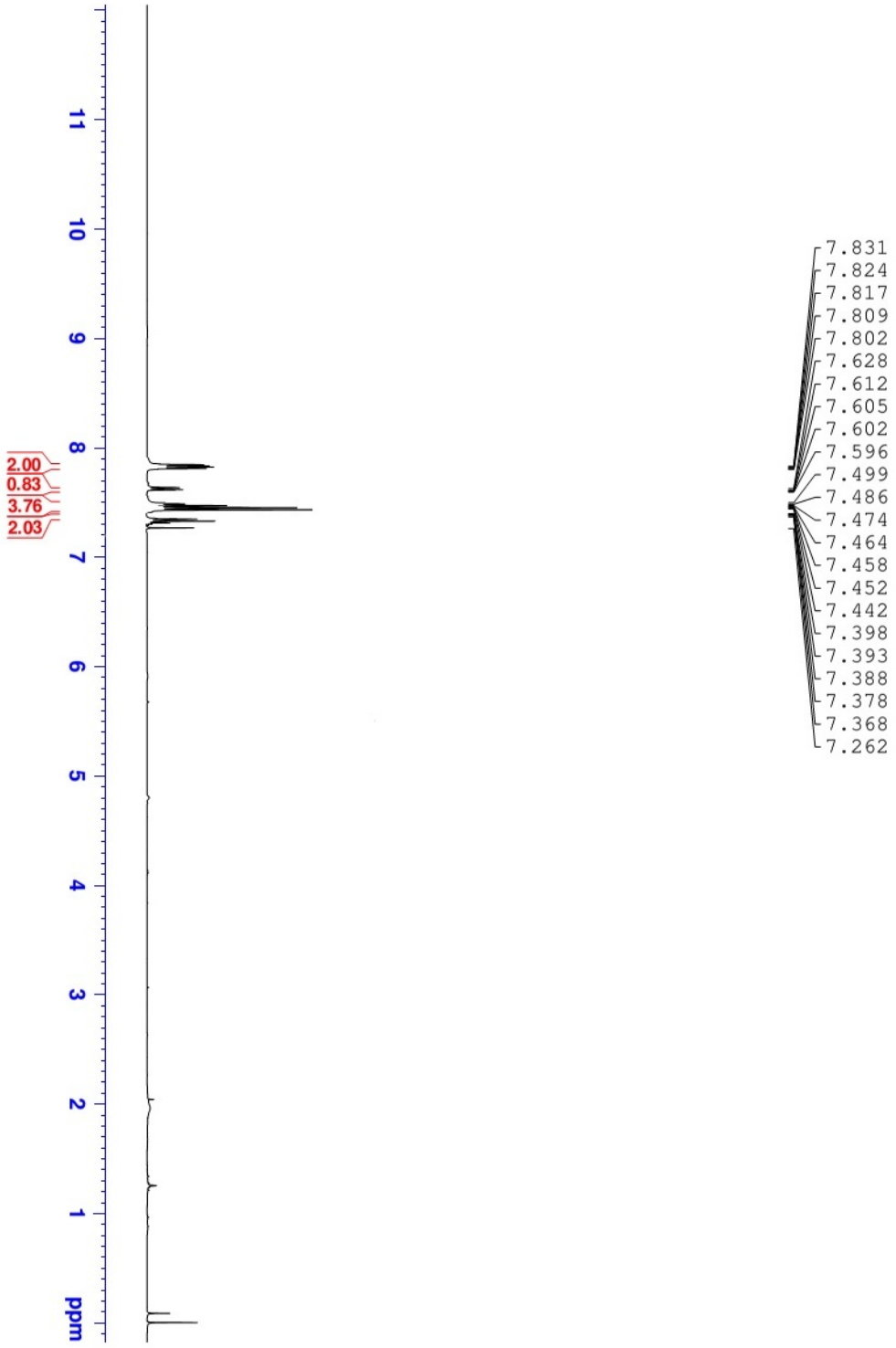


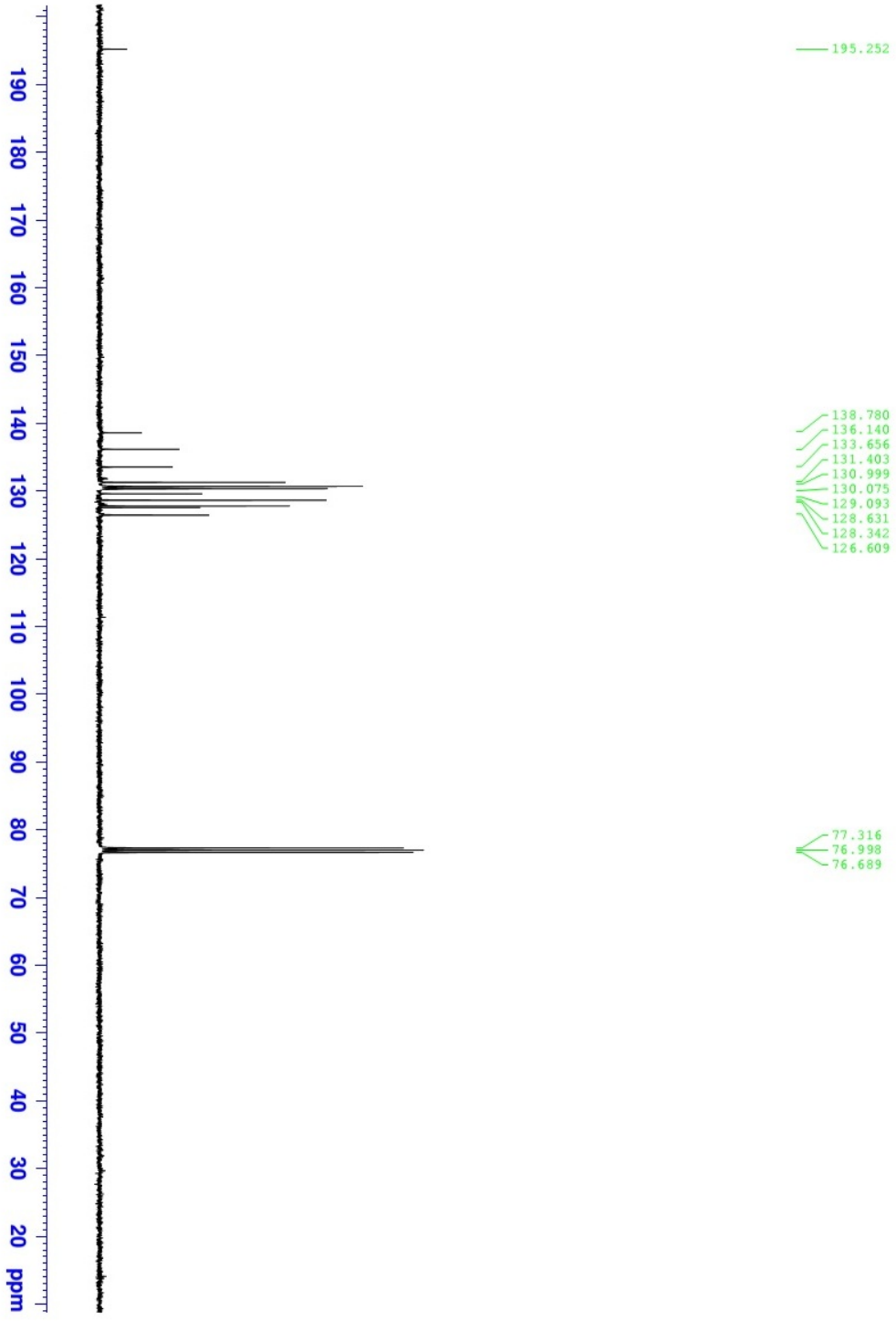
^{1}H NMR of Compound 3ga



^{13}C NMR of Compound 3ga



^{1}H NMR of Compound 3ia



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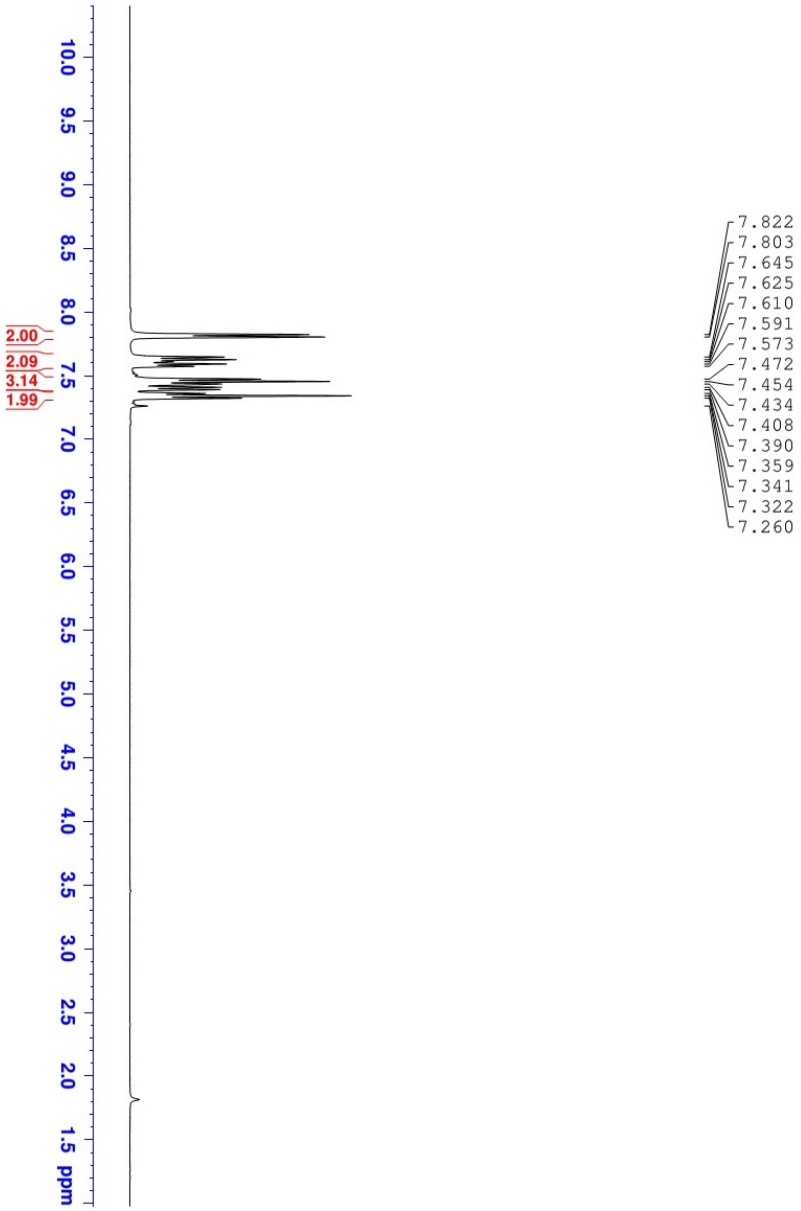

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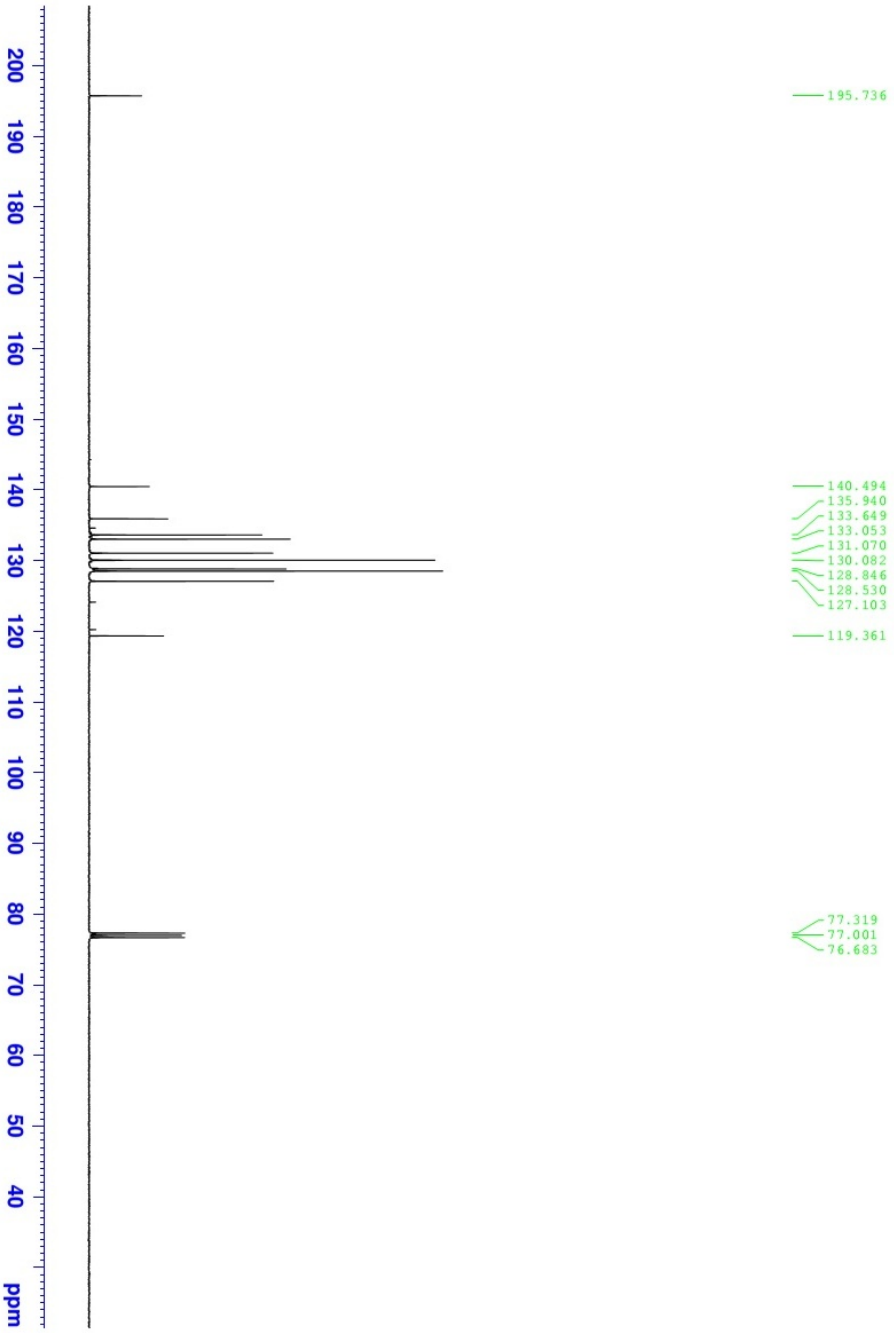

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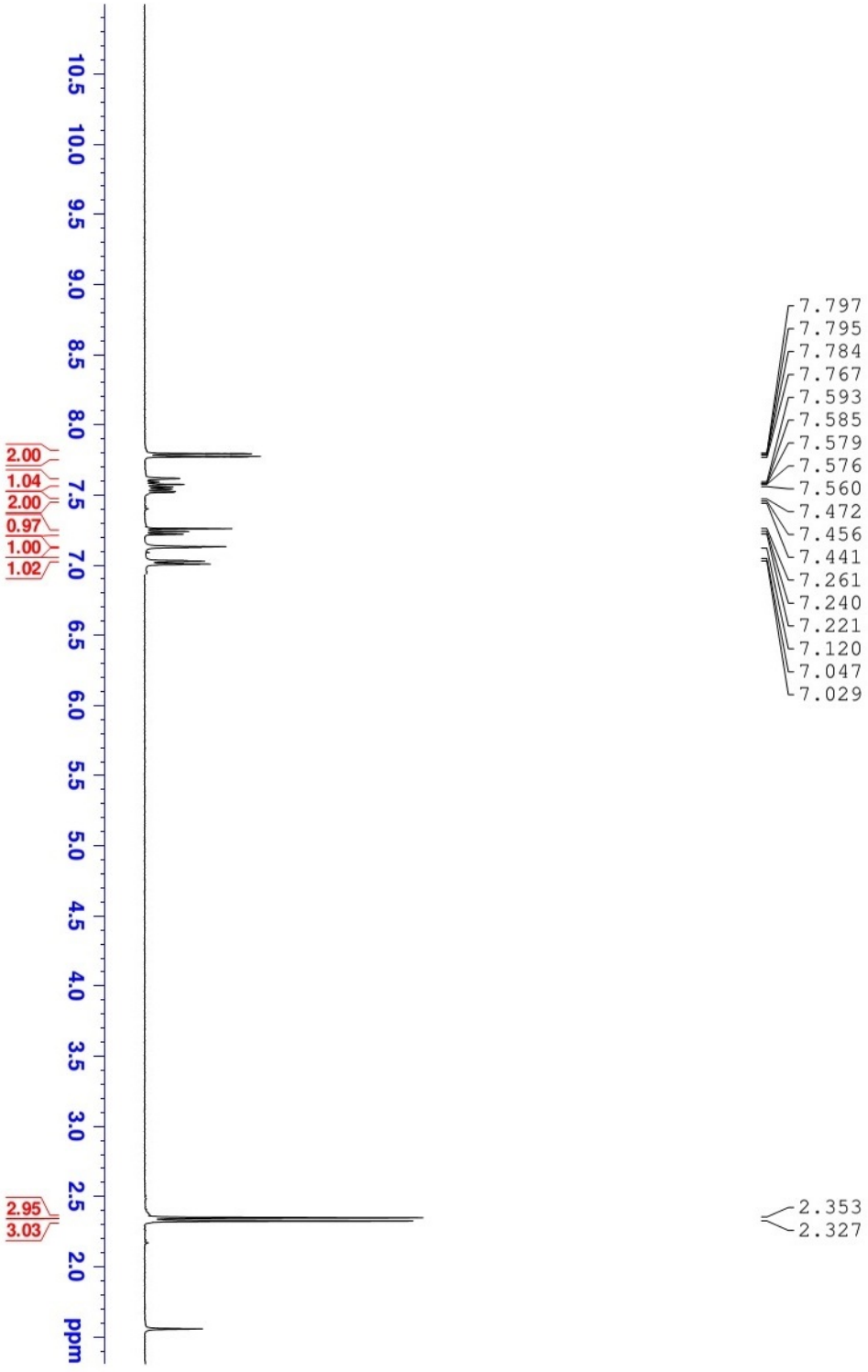

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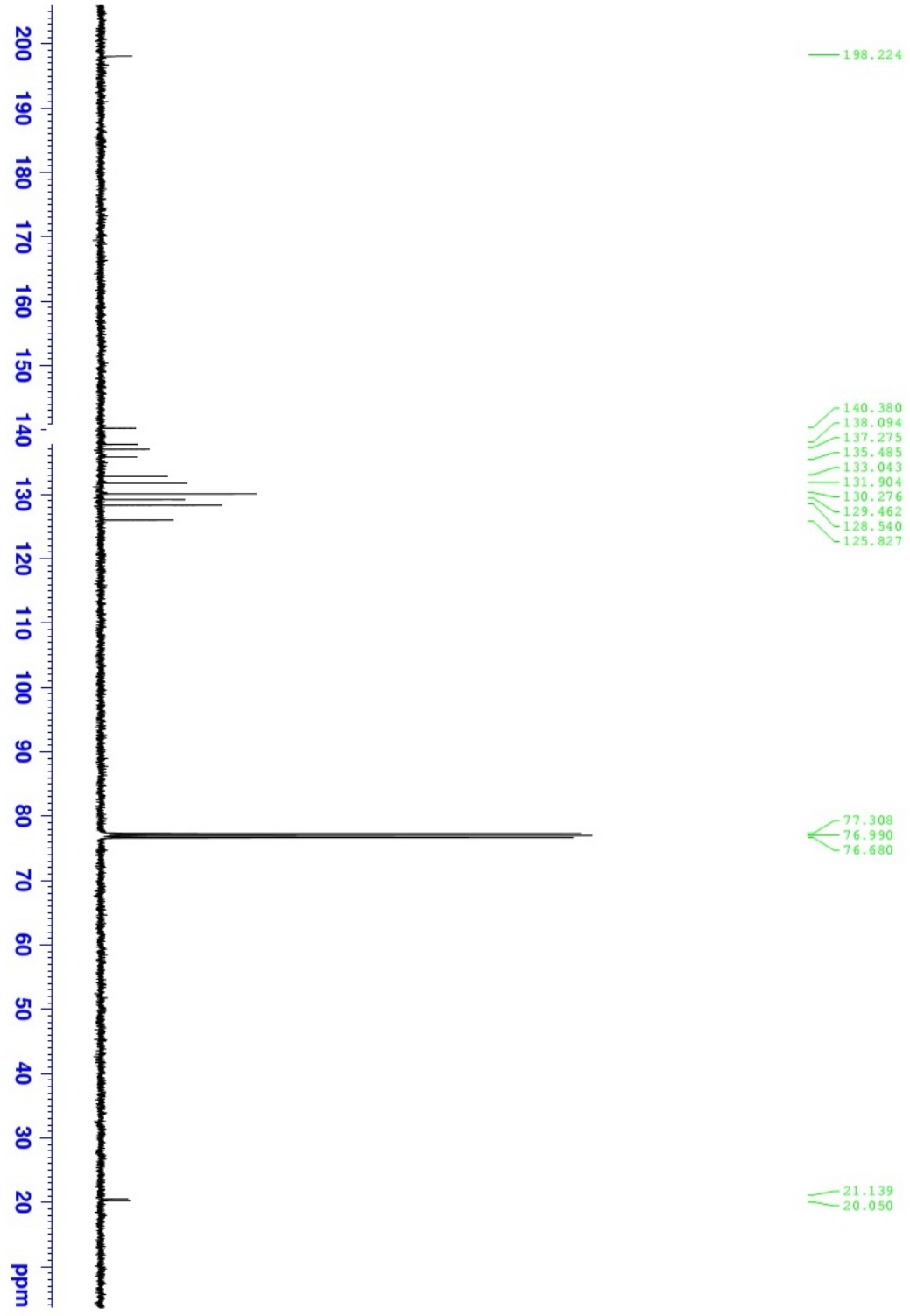

^{13}C NMR of Compound 3ka