Supplementary Information

Photocatalytic Redox-Neutral Minisci Hydoxyalkylation of N-Heteroaromatics with Aldehydes

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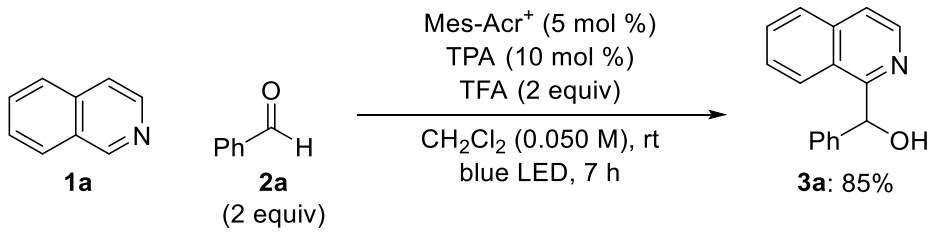
1. General Method

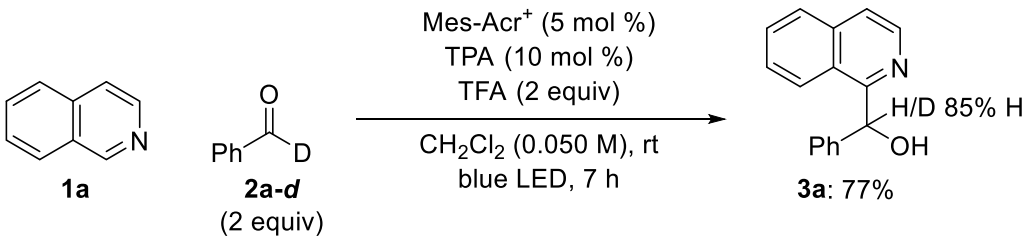
^{1}H NMR spectra were recorded on JEOL ECX500 (500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR), and JEOL ECS400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 370 MHz for ^{19}F NMR) spectrometer. For ^{1}H NMR and ^{13}C NMR, chemical shifts were reported in the scale relative to $CHCl_3$ (δ = 7.24 for ^{1}H NMR) or $CDCl_3$ (δ = 77.0 for ^{13}C NMR), used as an internal reference. For ^{19}F NMR, chemical shifts were reported relative to hexafluorobenzene (δ = -164.90 ppm) as an external reference. Electrospray ionization (ESI)-mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer for HRMS. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM), Biotage Isolera One and Biotage SNAP Ultra, or Yamazen Smart Flash and Universal Column Premium. All non-commercially available compounds were prepared and characterized as described in Section 6 of this SI. Other reagents were purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd., and were used as received. A Valore VBP-L24-C2 with 38W LED lamp (VBL-SE150-BBB(430)) was used as the blue LED light source. Emission Spectroscopy and Stern-Volmer Analysis (section 6) were conducted at ambient temperature, 20 ºC, under an Ar atmosphere. Emission spectra were recorded on a SHIMADZU RF-5300PC with a conventional quartz cuvette (path length, l = 1 cm). UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer.

2. General Procedure for C–H hydroxyalkylation of *N*-heteroaromatics



Isoquinoline (**1a**) (12.9 mg, 0.10 mmol), benzaldehyde (**2a**) (20.4 μL, 0.20 mmol), Mes-Acr$^+$ (2.0 mg, 0.005 mmol), TPA (3.6 mg, 0.010 mmol), and TFA (15.3 μL, 0.20 mmol) were dissolved in degassed CH_2Cl_2 (2.0 mL) in a screw-capped vial under argon atmosphere. The vial was subjected to blue LED irradiation for 7 hours under temperature control (ca. 27–29 ºC). Then, the reaction mixture was passed through a pad of alumina eluting with CH_2Cl_2 and EtOAc. The crude material was purified by a SiO_2 flash column chromatography with EtOAc and *n*-hexane to afford **3a** (20.0 mg, 0.085 mmol) in 85% yield as white solids.

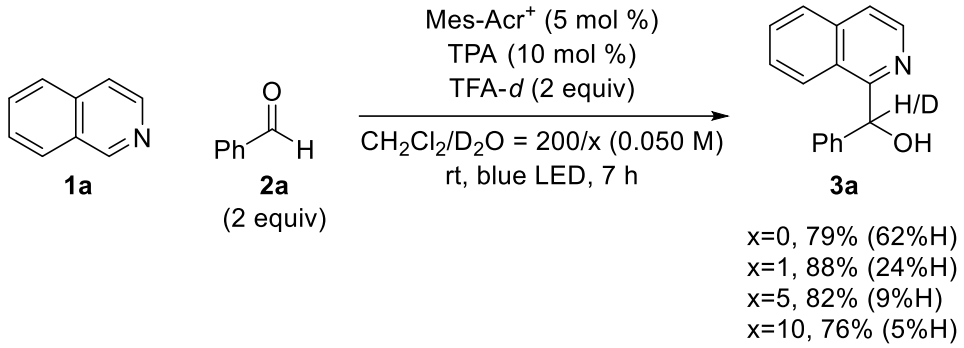
3. Procedure for Deuterium Labeling Experiments (for Aldehyde)



Isoquinoline (**1a**) (12.9 mg, 0.10 mmol), benzaldehyde-α-d (**2a-*d***) (20.3 μL, 0.20 mmol), Mes-Acr$^+$ (2.0 mg, 0.005 mmol), TPA (3.6 mg, 0.010 mmol), and TFA (15.3 μL, 0.20 mmol) were dissolved in degassed CH_2Cl_2 (2.0 mL)

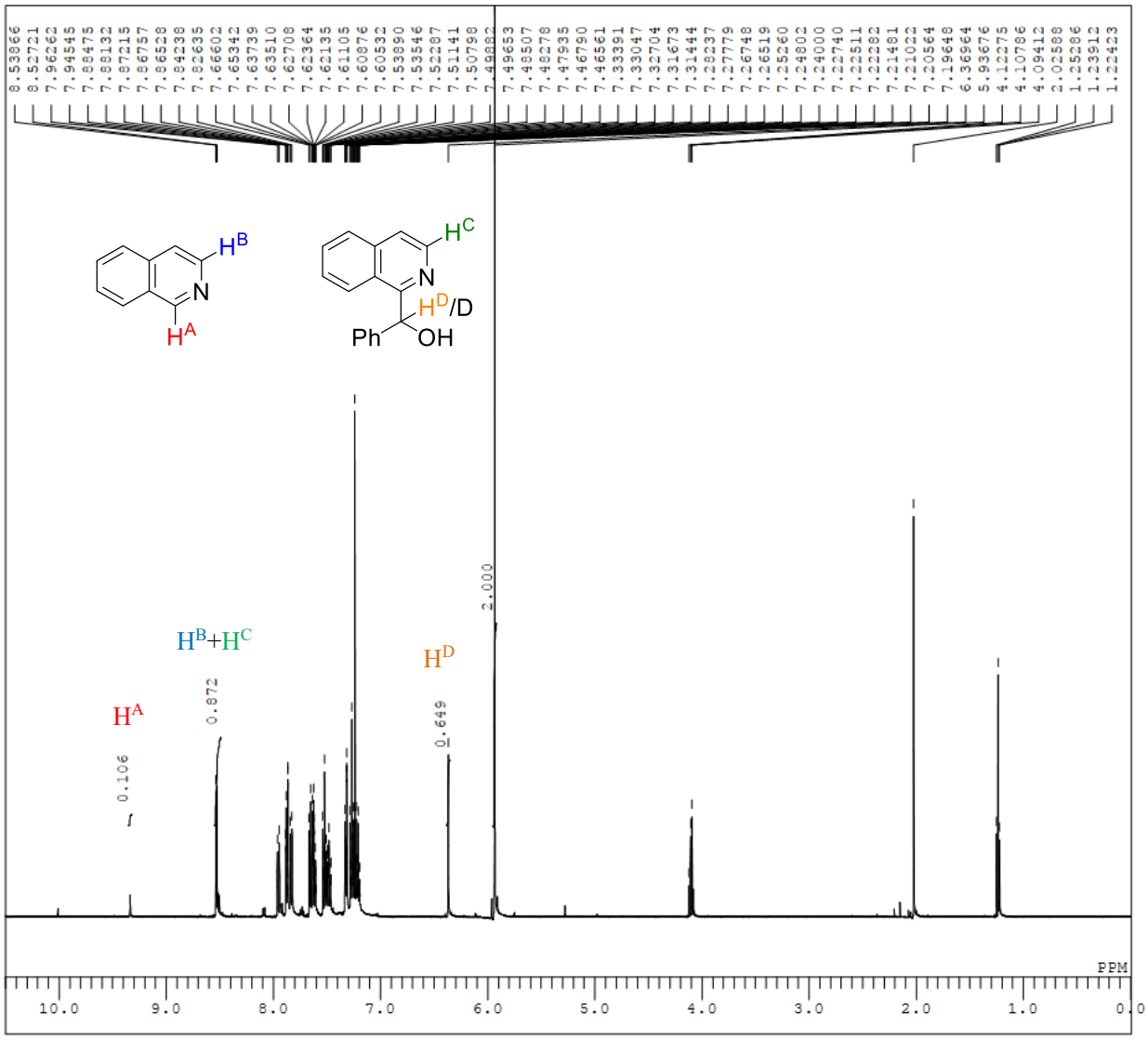
in a screw-capped vial under argon atmosphere. The vial was subjected to blue LED irradiation for 7 hours under temperature control (ca. 27–29 ºC). Then, the reaction mixture was passed through a pad of alumina eluting with CH_2Cl_2 and EtOAc. Then, the solvent was removed under reduced pressure, and 1,1,2,2-tetrachloroethane was added to the crude mixture as an internal standard. Yield of **3a** was determined to be 77% based on the ^1H NMR analysis. The incorporation ratio of benzylic proton was determined by the relative integration value of the H (see the NMR chart below).

4. Procedure for Deuterium Labeling Experiments (for TFA)

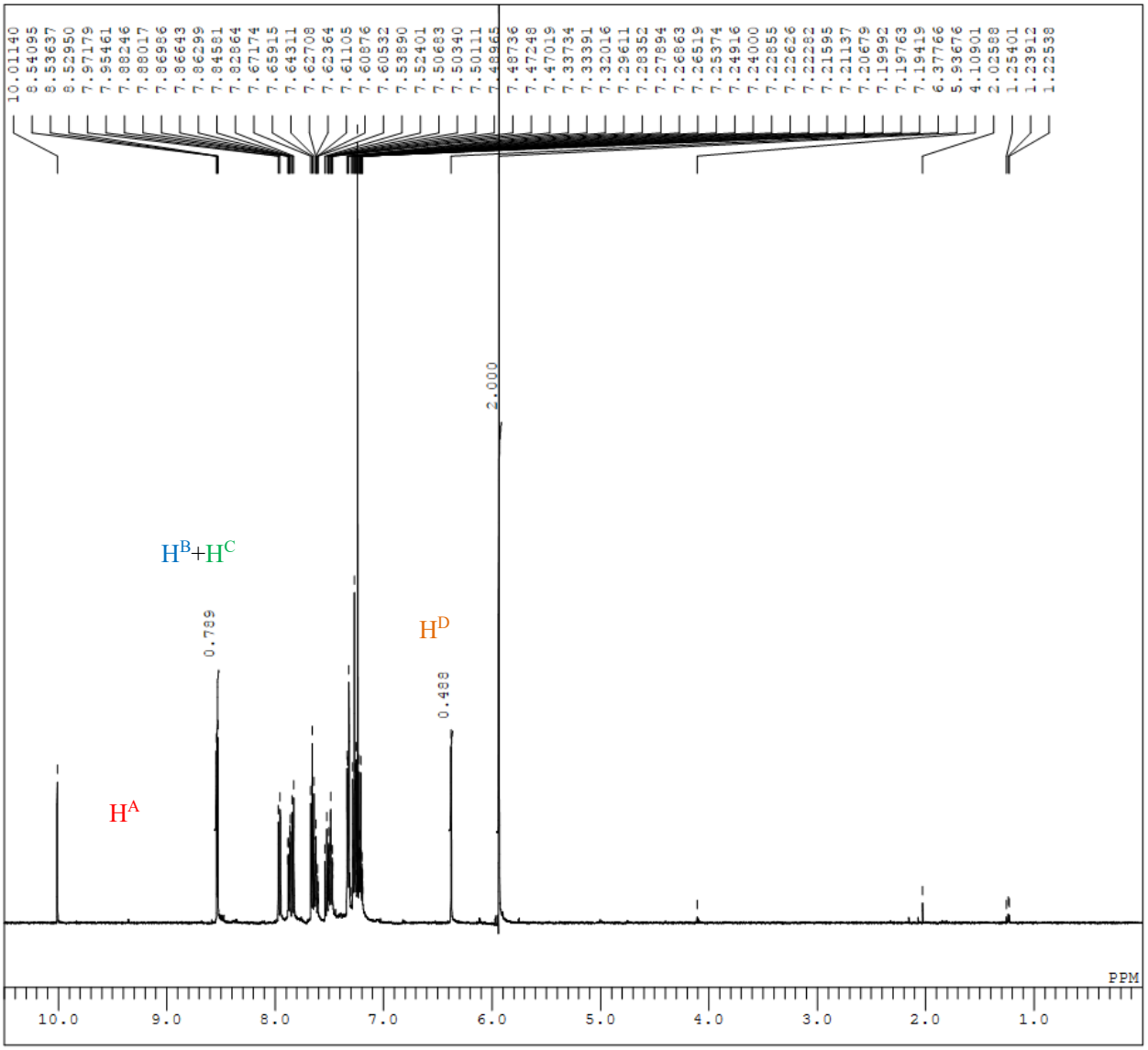


Isoquinoline (**1a**) (12.9 mg, 0.10 mmol), benzaldehyde (**2a**) (20.4 μL, 0.20 mmol), Mes-Acr$^+$ (2.0 mg, 0.005 mmol), TPA (3.6 mg, 0.010 mmol), and TFA-*d* (15.3 μL, 0.20 mmol) were dissolved in degassed CH_2Cl_2 (2.0 mL) in a screw-capped vial under argon atmosphere. D_2O (10 μL, 50 μL, 100 μL, (x=1, 5, 10, respectively)) was added and argon was flashed to the reaction mixture. The vial was subjected to blue LED irradiation for 7 hours under temperature control (ca. 27–29 ºC). Then, the reaction mixture was passed through a pad of alumina eluting with CH_2Cl_2 and EtOAc. Then, the solvent was removed under reduced pressure, and 1,1,2,2-tetrachloroethane was added to the crude mixture as an internal standard. Yield of **3a** was determined to be 79%, 88%, 82%, 76% (x=0, 1, 5, 10 respectively) based on the ^1H NMR analysis. The incorporation ratio of benzylic proton was determined by the relative integration value of the H (see the NMR chart below).

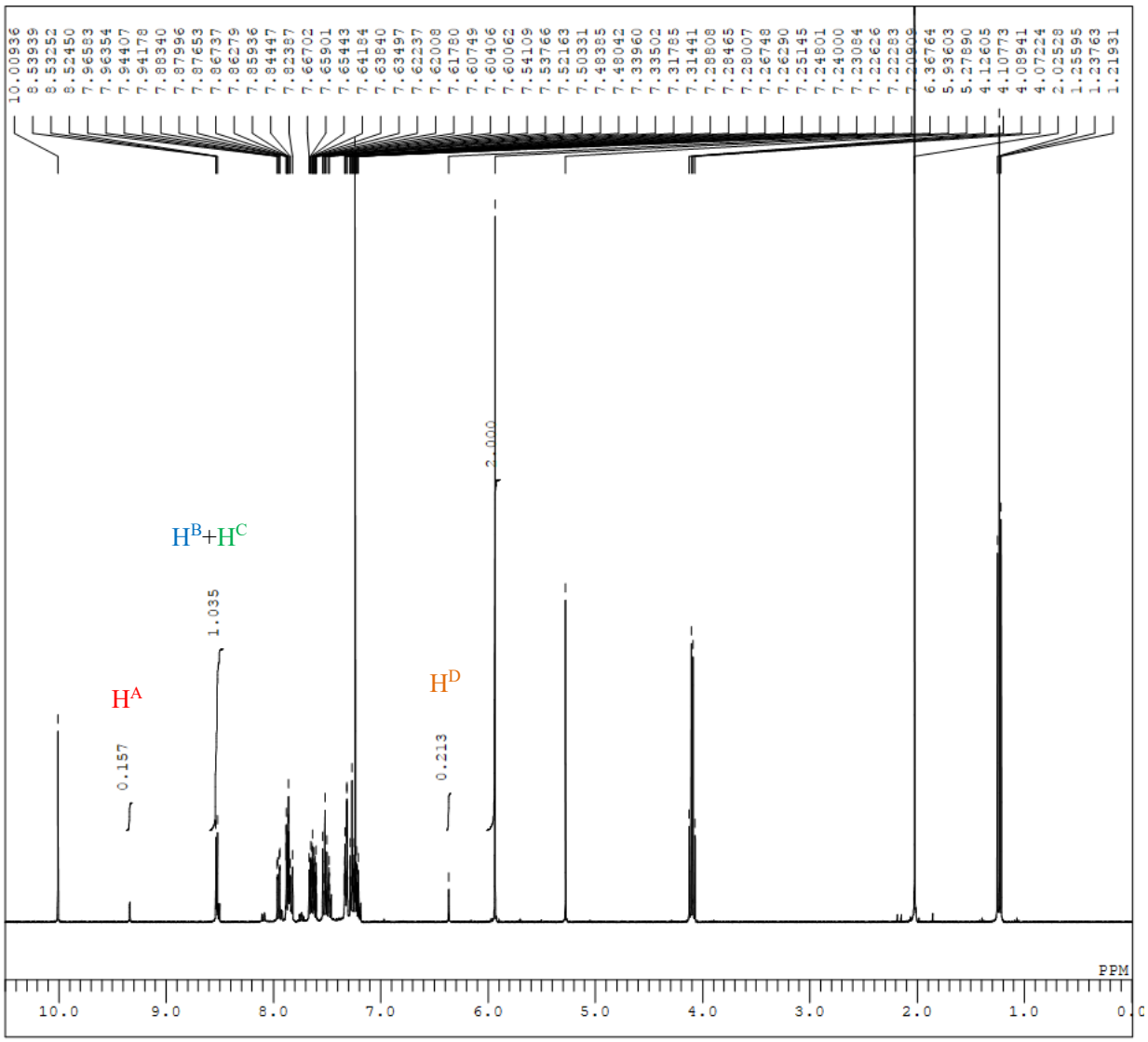
Benzaldehyde-α-*d* as an aldehyde



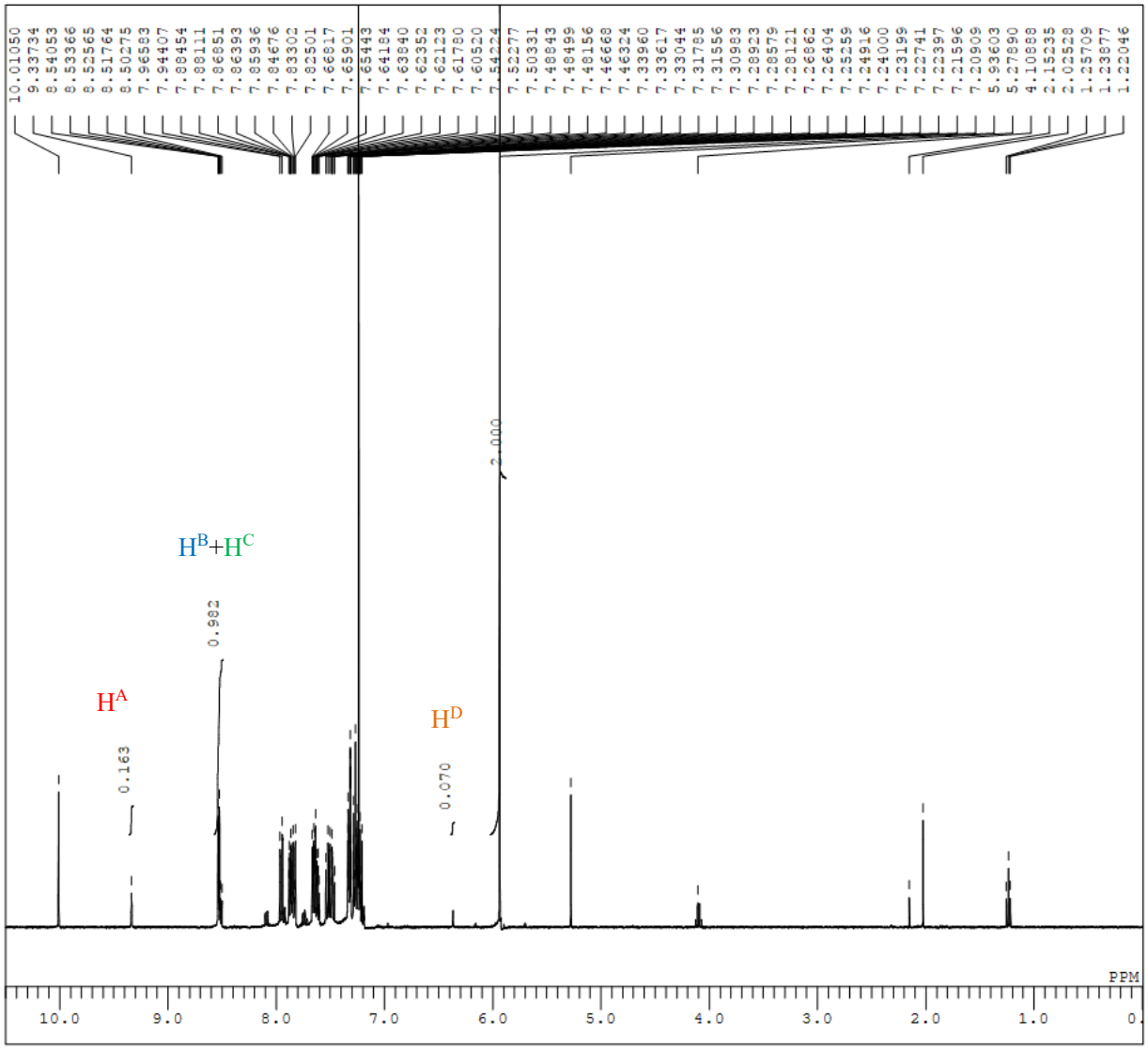
TFA-*d* as a proton source



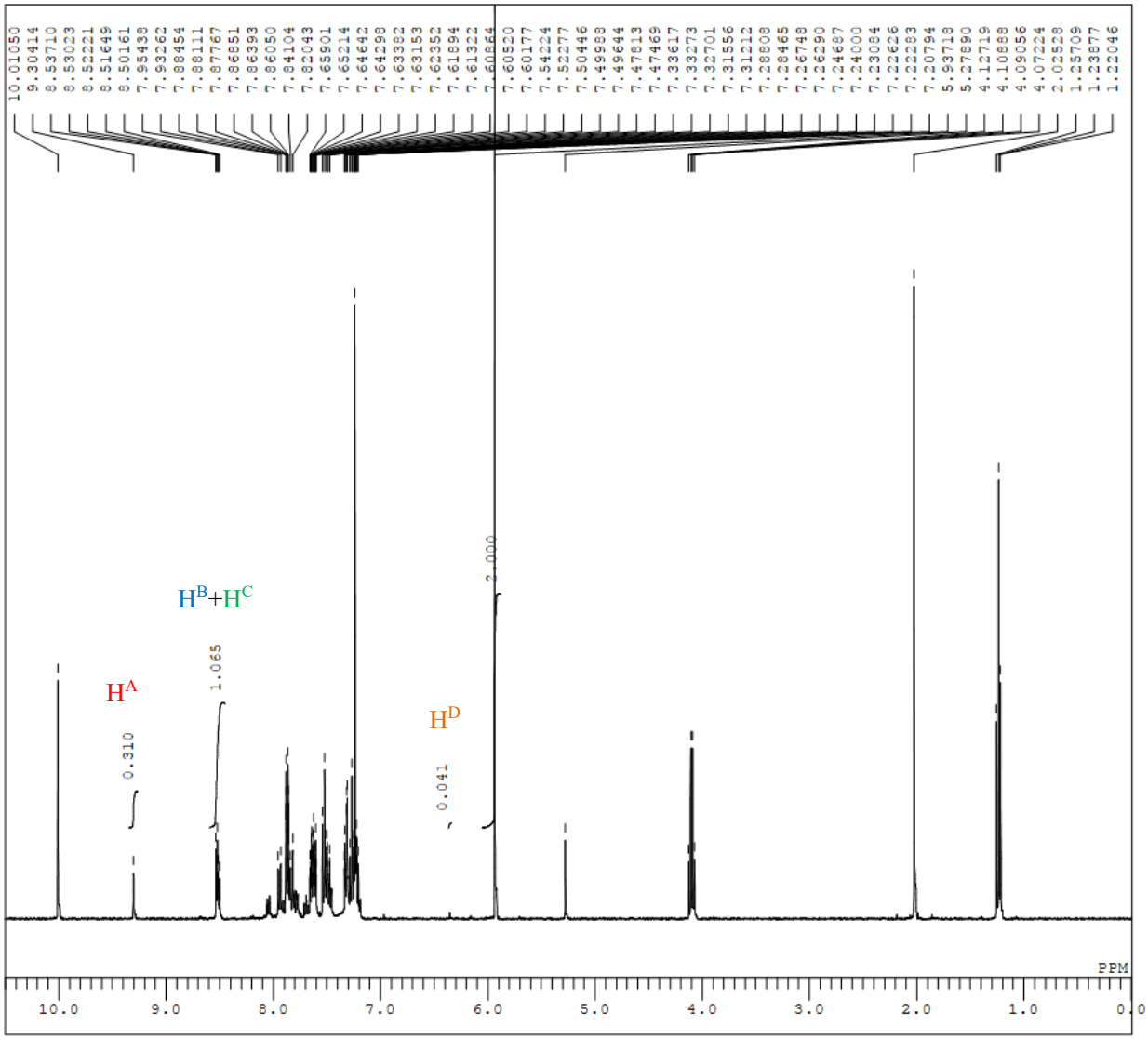
TFA-*d* and D_2O (10 μL) as a proton source



TFA-*d* and D_2O (50 μL) as a proton source



TFA-*d* and D_2O (100 μL) as a proton source

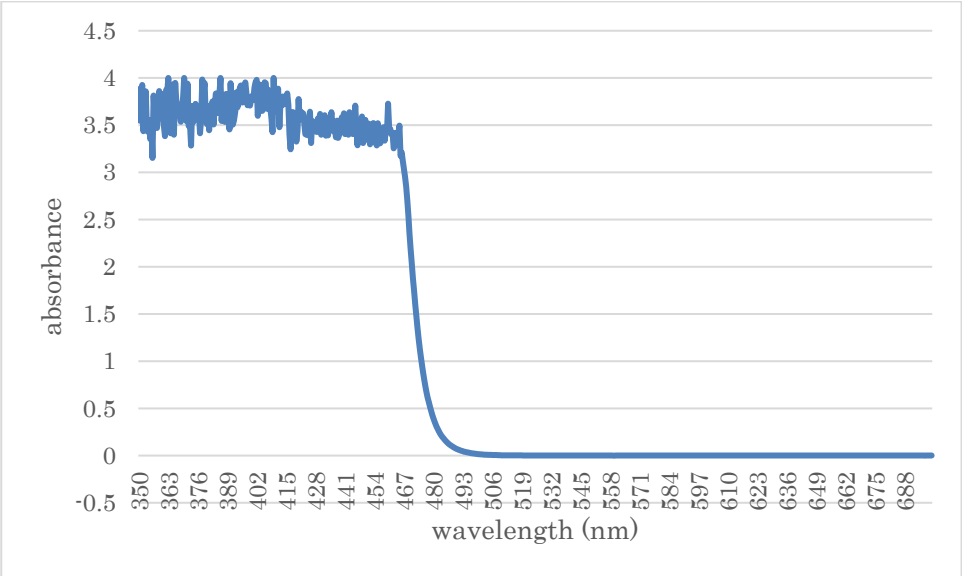


5. Quantum yield analysis

According to the procedure of Shang and Fu (*Science*, **2019**, *363*, 1429.) and Yoon (*Chem. Sci.* **2015**, *6*, 5426.), the quantum yield of the reaction was measured by chemical actinometry using potassium ferrioxalate.

(5-A) UV-vis Absorption Spectroscopy

The absorbance of Mes-Acr^{+} was measured at the reaction concentration (2.5×10^{-3} M). The absorbance at 430 nm is >3 indicating the fraction of light (f_R) absorbed is >0.999.



(5-B) photon flux

The actinometer solution was prepared by dissolving 0.737 g of potassium ferrioxalate trihydrate in 10 mL H_2SO_4 (0.05 M) and stored in the dark. The buffer solution was prepared by dissolving 2.5 g of sodium acetate and 0.5 mL of H_2SO_4 (95%) in 50 mL of distilled water.

To a screw-capped vial, 1 mL of the actinometer solution was added. After 430 nm blue LED irradiation for 60 sec, 50 µL of this solution was added to a 5 mL volumetric flask containing 15 mg of 1,10-phenanthroline in 3 mL of the buffer solution. Then, the flask was filled with distilled H_2O. The absorbance at 510 nm of this solution was measured by UV-vis absorption spectroscopy. This procedure is repeated for the non-irradiated sample. According to Lambert-Beer law, the conversion to Fe^{2+} was determined using the equation described below where v_1 is the volume of the irradiated sample (1 mL), v_2 is the volume of the solution taken from irradiated samples for determination about Fe^{2+} (0.050 mL), v_3 is the volume of the solution after complexation with 1,10-phenanthroline (5 mL), ΔA(510 nm) is the difference about the absorbance between irradiated and non-irradiated samples (2.802), l is the optical path-length (1 cm), and ε(510 nm) is molar extinction coefficient of $[Fe(phen)_3]^{2+}$ (11100 L mol^{-1} cm^{-1}).

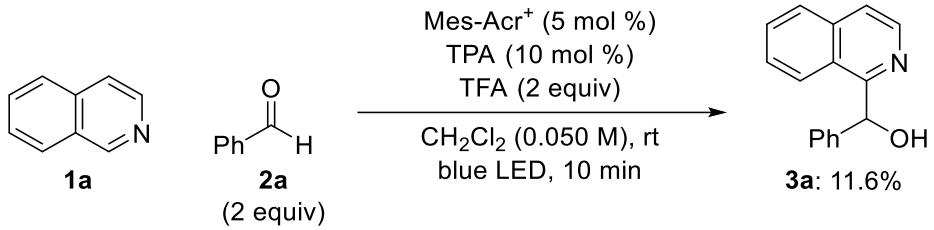
$$Fe^{2+} = \frac{v_1 \cdot v_3 \cdot \Delta A(510\ nm)}{10^3 \cdot v_2 \cdot l \cdot \varepsilon(510\ nm)}$$

The photon flux (Φ_q) was determined using the equation described below where Φ(430 nm) is the quantum yield for the ferrioxalate actinometer at 430 nm (1.01), t is irradiation time (60 sec), f is the fraction of absorbed light (f

= 1-10$^{-A(430\ nm)}$ > 0.999 where A(430 nm) was observed as 3.057). The photon flux (Φ_q) was determined as 4.17×10^{-7} einstein sec^{-1}.

$$\Phi_q = \frac{\mathrm{Fe}^{2+}}{\Phi(430\ nm) \cdot \mathrm{t} \cdot f}$$

(5-C) reaction quantum yield



Isoquinoline (**1a**) (12.9 mg, 0.10 mmol), benzaldehyde (**2a**) (20.4 µL, 0.20 mmol), Mes-Acr^{+} (2.0 mg, 0.005 mmol), TPA (3.6 mg, 0.010 mmol), and TFA (15.3 µL, 0.20 mmol) were dissolved in degassed CH_2Cl_2 (2.0 mL) in a screw-capped vial under argon atmosphere. The vial was subjected to 430 nm blue LED irradiation for 10 minutes under temperature control (ca. 27–29 ºC). Then, the reaction mixture was passed through a pad of alumina eluting with CH_2Cl_2 and EtOAc. Then, the solvent was removed under reduced pressure, and 1,1,2,2-tetrachloroethane was added to the crude mixture as an internal standard. Yield of **3a** was determined to be 11.6% (1.16 × 10^{-5} mol) based on the ^{1}H NMR analysis.

The reaction quantum yield (Φ_R) was determined using the equation described below where the photon flux (Φ_q) is 4.17 × 10^{-7} (einsteins sec^{-1}) (determined by actinometry), *n* (*product*) is the yield of the product (1.16 × 10^{-5} mol), *t* is the reaction time (600 sec) and the fraction of incident light absorbed by the photocatalyst (f_R) is >0.999. The reaction quantum yield (Φ_R) was determined as 0.046, which suggests the closed catalytic cycle.

$$\Phi_R = \frac{n\ (product)}{\Phi_q \cdot t\ \cdot\ f_R}$$

6. Emission Spectroscopy and Stern-Volmer Analysis

Emission spectra of deaerated 1,2-dichloroethane (DCE) solutions of Mes-Acr$^+$ (0.05 mM) in the presence of organocatalyst TPA (0.25-1.0 mM) were measured with the excitation wavelength of 430 nm (Figure S1). Note that UV-Vis absorption spectra measured before and after the measurement of emission spectroscopy were identical in all cases, suggesting that no degradation of Mes-Acr$^+$ occurred during the measurements. In the presence of TPA, the decrease in emission intensity was observed.

We also conducted Stern-Volmer analysis of the obtained emission spectra according to the following equation:

$$\boldsymbol{I^0/I = 1 + K_{SV}[Q] = 1 + k_q I^0[Q]}$$

where I^0 and I are the fluorescence intensity in the absence and presence of the quencher (Q), K_{SV} is the Stern-Volmer constant, k_q is the bimolecular quenching constant, and [Q] is the concentration of the quencher. K_{SV} was estimated from the slope of a plot of I^0/I against [Q] (Figure S2). The decay of the emission intensity depended on the concentration of quencher TPA, and we observed the significant Stern-Volmer constant of 0.14 along with quencher rate constant k_q of 0.028 (Figure S2).

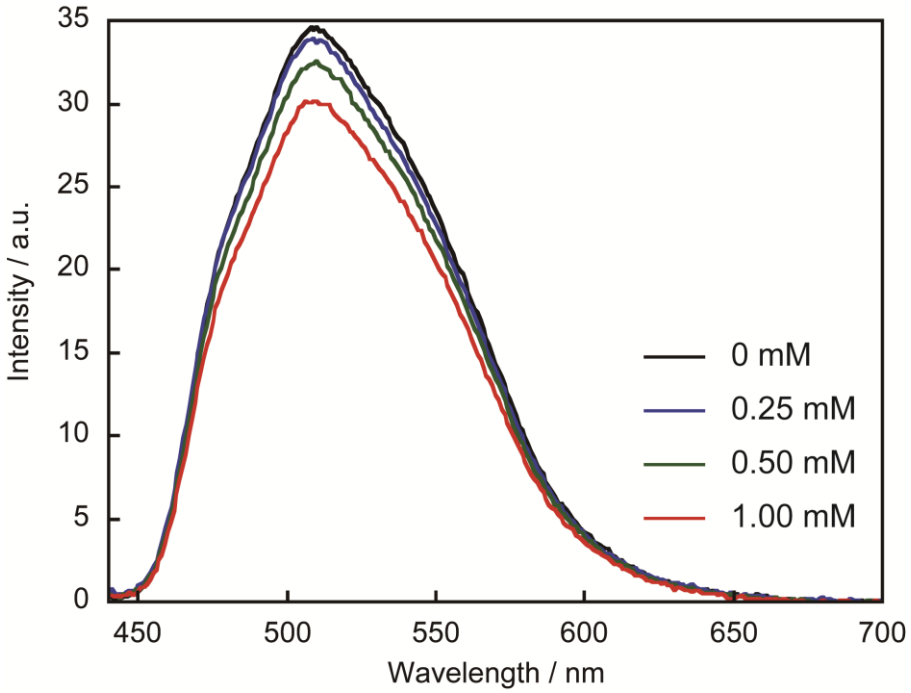


Figure S1. The emission spectra of photoredox catalyst Mes-Acr$^+$ (0.05 mM) in DCE in the presence of organocatalyst TPA (0, 0.25, 0.50, and 1.00 mM) at the excitation wavelength of 430 nm.

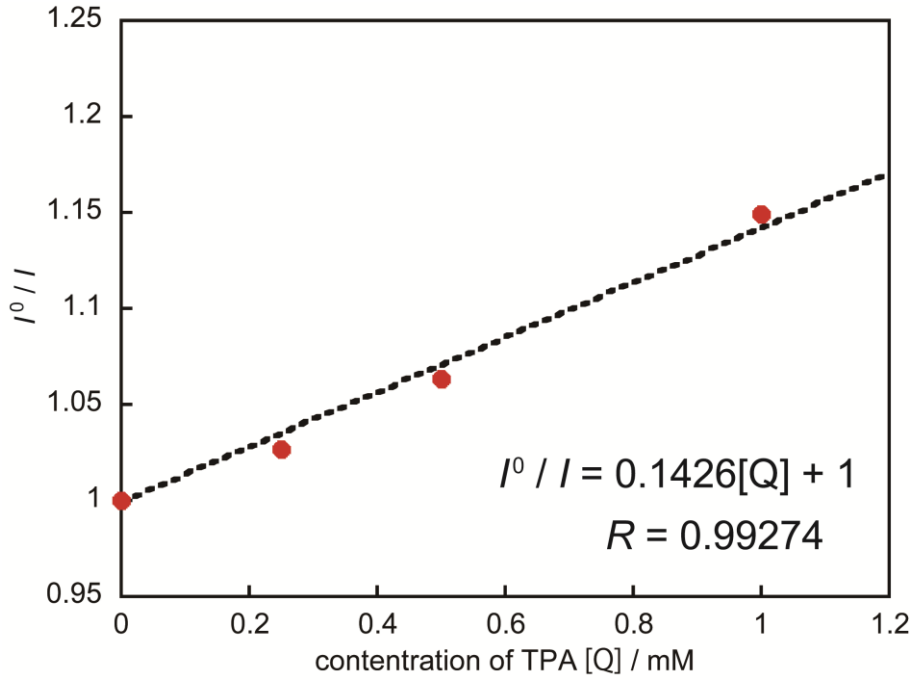


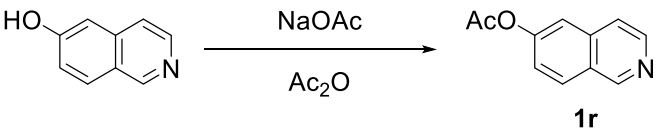
Figure S2. A Stern-Volmer plot of Mes-Acr$^+$ (0.05 mM) in DCE in the presence of the quencher (Q), organocatalyst TPA. The Stern-Volmer quenching constant, K_{SV}, was determined from the slope of the linear fitting function, where the bimolecular quenching constant, k_q, is equal to K_{SV}/I^0.

In addition, Glorius and co-workers already reported that there was no reaction between 4-fluorobenzaldehyde and the excited state of Mes-Acr$^+$ by Stern-Volmer analysis (*J. Am. Chem. Soc.* **2017**, *139*, 13652.). Therefore, the thiyl radical (RS•) was assumed to be generated from the organocatalyst TPA through a single electron oxidation by the excited state of Mes-Acr$^+$.

7. Syntheses of Substrates

Compounds **1af**[1] and **2i**–**2l**[2] were prepared as reported previously.

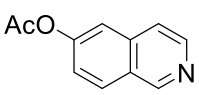
(7-A) Synthesis of 1r



1r

A solution of isoquinolin-6-ol (290 mg, 2 mmol) and sodium acetate (15 mg, 0.18 mmol) in acetic anhydride (1.21 mL, 2.9 mmol) was stirred at room temperature. After 17 hours of stirring, the reaction was quenched with water. The water phase was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/3 to 3/1, v/v) to afford **1r** (186 mg, 0.99 mmol) in 50% yield as white sold.

isoquinolin-6-yl acetate (1r)

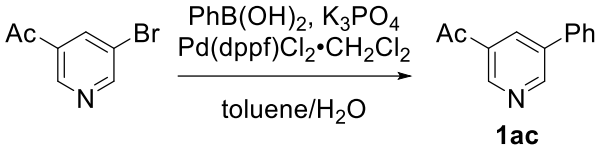


1r

^{1}H NMR ($CDCl_3$): δ = 9.23 (1H, s), 8.50 (1H, d, J = 5.7 Hz), 7.99 (1H, d, J = 8.6 Hz), 7.62 (1H, d, J = 5.7 Hz), 7.55 (1H, d, J = 2.3 Hz), 7.34 (1H, d, J = 8.6, 2.3 Hz), 2.35 (3H, s);

^{13}C NMR ($CDCl_3$): δ = 169.05, 151.88, 151.82, 143.12, 136.68, 129.55, 126.58, 122.89, 120.45, 117.32, 21.17.; HRMS (ESI): *m/z* calcd for $C_{11}H_9NO_2Na$ $[M+Na]^+$ 210.0525. Found 210.0526; IR (neat): 2931, 1755, 1372, 1208, 822 cm^{-1}.

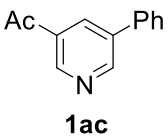
(7-B) Synthesis of 1ac



1ac

A solution of 1-(5-bromopyridin-3-yl)ethan-1-one (400 mg, 2 mmol), $PhB(OH)_2$ (488 mg, 4 mmol) and $Pd(dppf)Cl_2•CH_2Cl_2$ (49.0 mg, 0.06 mmol) in toluene (36 mL) was heated at 100 °C. To the mixture, a solution of K_3PO_4 (1.70 g, 8 mmol) in H_2O (4 ml) was added. The reaction mixture was stirred at 100 °C for 14 hours. After cooled to room temperature, the reaction was quenched with 1 M HCl aqueous solution. The water phase was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/9 to 1/2, v/v) to afford **1ac** (322 mg, 1.63 mmol) in 82% yield as pale brown sold.

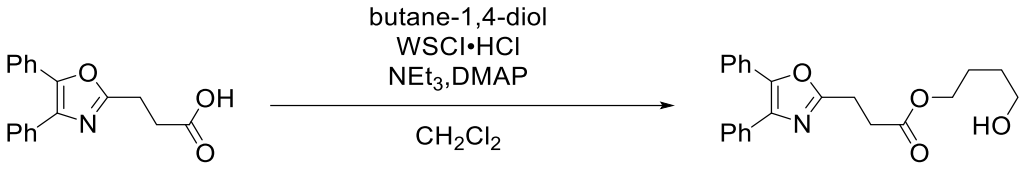
1-(5-phenylpyridin-3-yl)ethan-1-one (1ac)



1ac

^{1}H NMR ($CDCl_3$): δ = 9.10 (1H, d, *J* = 2.0 Hz), 8.99 (1H, d, *J* = 2.3 Hz), 8.39 (1H, dd, *J* = 2.3, 2.0 Hz), 7.62-7.57 (2H, m), 7.52-7.45 (2H, m), 7.45-7.39 (1H, m), 2.67 (3H, s); ^{13}C NMR ($CDCl_3$): δ = 196.71, 151.94, 148.45, 136.77, 136.65, 133.53, 132.17, 129.21, 128.62, 127.18, 26.89.; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NONa$ $[M+Na]^+$ 220.0733. Found 220.0744; IR (neat): 1690, 1434, 1239, 763 cm^{-1}.

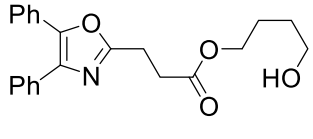
(7-C) Synthesis of 2ag



S1

To a solution of butane-1,4-diol (2.39 mL, 27 mmol), WSCI•HCl (3.45 g, 18 mmol), oxaprozin (2.64 g, 9.0 mmol), and DMAP (222 mg, 1.8 mmol) in CH_2Cl_2 (30 mL), NEt_3 (3.78 mL, 27 mmol) was added. After 19 hours of stirring at room temperature, 1 M HCl aqueous solution was added and the water phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed by saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/19 to 3/2, v/v) as an eluent twice to afford **S1** (2.51 g, 6.87 mmol) in 76% yield as white solid.

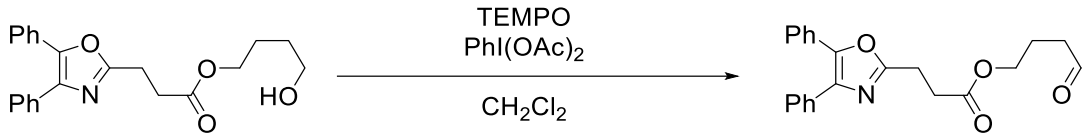
4-hydroxybutyl 3-(4,5-diphenyloxazol-2-yl)propanoate (S1)



S1

^{1}H NMR ($CDCl_3$): δ = 7.66-7.50 (4H, m), 7.38-7.25 (6H, m), 4.13 (2H, t, *J* = 6.6

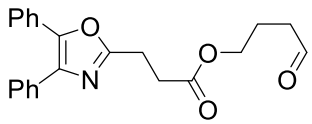
Hz), 3.56 (2H, t, *J* = 6.3 Hz), 3.16 (2H, t, *J* = 7.4 Hz), 2.89 (2H, t, *J* = 7.4 Hz), 2.09 (1H, s), 1.74-1.61 (2H, m), 1.61-1.46 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 171.95, 161.74, 145.34, 134.93, 132.23, 128.77, 128.55, 128.47, 128.40, 128.02, 127.80, 126.34, 64.59, 62.00, 31.04, 28.95, 24.98, 23.44.; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}NO_4Na$ $[M+Na]^+$ 388.1519. Found 388.1508; IR (Neat): 3395, 2945, 1734, 1571, 1445, 1177, 765 cm^{-1}



S1 **2ag**

To a solution of **S1** (731 mg, 2.0 mmol) and TEMPO (32 mg, 0.20 mmol) in CH_2Cl_2 (2.0 mL), $PhI(OAc)_2$ (708 mg, 2.2 mmol) was added. After 5 hours of stirring, the reaction was quenched with saturated $Na_2S_2O_3$ aqueous solution. The water phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed by saturated $NaHCO_3$ aqueous solution and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/19 to 2/3, v/v) to afford **2ag** (549 mg, 1.51 mmol) in 76% yield as colorless oil.

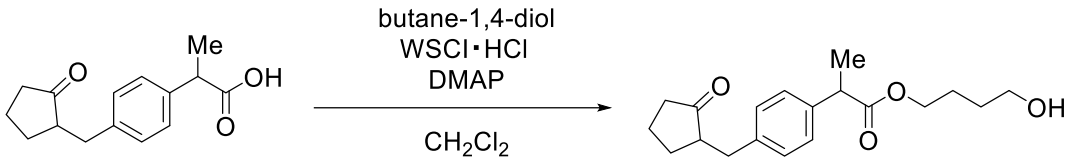
4-oxobutyl 3-(4,5-diphenyloxazol-2-yl)propanoate (2ag)



2ag

^{1}H NMR ($CDCl_3$): δ = 9.66 (1H, s), 7.67-7.48 (4H, m), 7.39-7.25 (6H, m), 4.15 (2H, t, *J* = 6.3 Hz), 3.17 (2H, t, *J* = 7.3 Hz), 2.89 (2H, t, *J* = 7.3 Hz), 2.49 (2H, dt, *J* = 7.2, 1.1 Hz), 1.95 (2H, dt, *J* = 7.2, 6.3 Hz); ^{13}C NMR ($CDCl_3$): δ = 201.10, 171.89, 161.69, 145.44, 135.01, 132.30, 128.86, 128.64, 128.55, 128.50, 128.10, 127.85, 126.44, 63.69, 40.37, 31.00, 23.45, 21.23.; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}NO_4Na$ $[M+Na]^+$ 386.1363. Found 386.1354; IR (Neat): 2960, 1735, 1571, 1444, 1168, 765 cm^{-1}

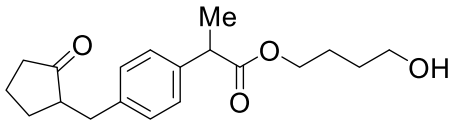
(7-D) Synthesis of 2ah



S2

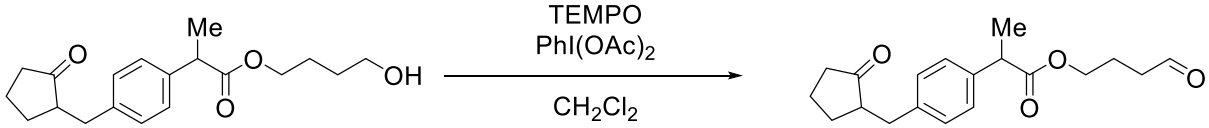
To a solution of butane-1.4-diol (542 μL, 6.09 mmol), WSCI·HCl (467 mg, 2.44 mmol), and DMAP (24.8 mg, 0.23 mmol) in CH_2Cl_2 (6 mL), loxoprofen was added (500 mg, 2.03 mmol). After overnight of stirring at room temperature, 1 M HCl aqueous solution was added and the water phase was extracted with CH_2Cl_2 three times. The combined organic layers were washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography (EtOAc/*n*-hexane = 1/3, v/v) to afford **S2** (555 mg, 1.74 mmol) in 86% yield as colorless oil.

4-hydroxybutyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (S2)



S2

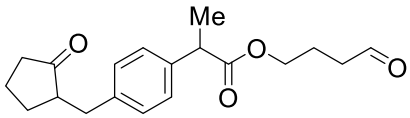
^{1}H NMR ($CDCl_3$): δ = 7.18 (2H, d, *J* = 8.0 Hz), 7.08 (2H, d, *J* = 8.0 Hz), 4.05 (2H, t, *J* = 6.6 Hz), 3.65 (1H, q, *J* = 7.3 Hz), 3.56 (2H, t, *J* = 6.4 Hz), 3.07 (1H, dd, *J* = 14.0, 4.4 Hz), 2.56-2.41 (1H, m), 2.37-2.21 (2H, m), 2.12-2.00 (2H, m), 1.98-1.86 (1H, m), 1.79-1.59 (4H, m), 1.57-1.40 (5H, m); ^{13}C NMR ($CDCl_3$): δ = 220.21, 174.58, 160.79, 140.30, 138.72, 138.33, 136.42, 130.30, 128.99, 127.57, 127.44, 127.38, 124.62, 123.92, 120.57, 77.26, 76.74, 68.92, 64.50, 50.93, 45.10, 45.07, 38.13, 35.26, 35.20, 35.13, 29.16, 24.68, 20.48, 18.43, 18.35.; HRMS (ESI): *m/z* calcd for $C_{19}H_{26}O_4Na$ $[M+Na]^+$ 341.1723. Found 341.1709; IR (Neat): 3449, 2938, 1732, 1512, 1453, 1203, 1164, 860 cm^{-1}



S2 **2ah**

To a solution of **S2** (352 mg, 1.1 mmol) and TEMPO (17.3 mg, 0.11 mmol) in CH_2Cl_2 (1.0 mL), $PhI(OAc)_2$ (392 mg, 1.22 mmol) was added. After 19 hours of stirring, the reaction was quenched with saturated $Na_2S_2O_3$ aqueous solution. The water phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed by saturated $NaHCO_3$ aqueous solution and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography (EtOAc/*n*-hexane = 1/3, v/v) to afford **2ah** (157 mg, 0.98 mmol) in 45% yield as colorless oil.

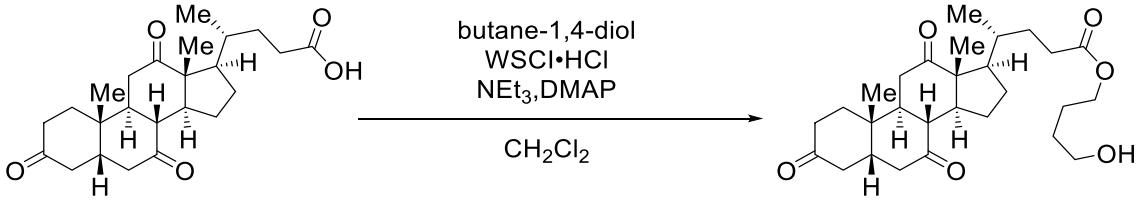
4-oxobutyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (2ah)



2ah

^{1}H NMR ($CDCl_3$): δ = 9.67-9.60 (1H, m), 7.17 (2H, d, *J* = 8.0 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 4.13-3.88 (2H, m), 3.71-3.56 (1H, m), 3.09 (1H, dd, *J* = 14.0, 4.3 Hz), 2.54-2.39 (1H, m), 2.38-2.20 (4H, m), 2.16-1.96 (2H, m), 1.96-1.78 (3H, m), 1.77-1.57 (1H, m), 1.56-1.35 (4H, m); ^{13}C NMR ($CDCl_3$): δ = 220.15, 201.12, 174.41, 138.86, 138.18, 129.04, 127.40, 77.32, 77.68, 63.49, 50.88, 44.98, 40.19, 38.09, 35.08, 29.13, 21.16, 20.44, 18.23.; HRMS (ESI): *m/z* calcd for $C_{19}H_{24}O_4Na$ $[M+Na]^+$ 339.1567. Found 339.1563; IR (Neat): 2964, 2726, 1733, 1512, 1162, 860 cm^{-1}

(7-E) Synthesis of 2ai

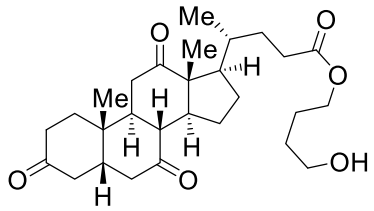


S3

To a solution of butane-1,4-diol (2.39 mL, 27 mmol), WSCI•HCl (3.45 g, 18 mmol), dehydrocholic acid (3.63 g,

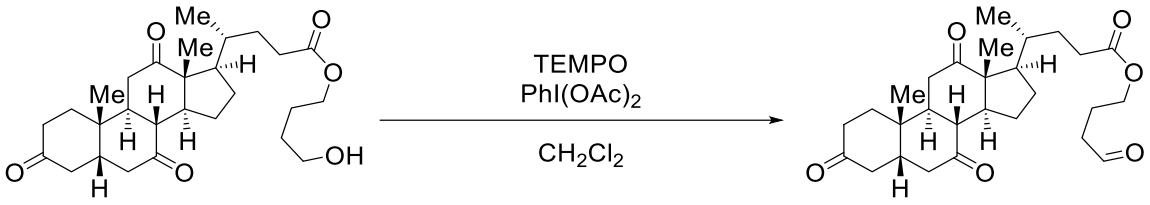
9.0 mmol), and DMAP (222 mg, 1.8 mmol) in CH_2Cl_2 (30 mL), NEt_3 (3.78 mL, 27 mmol) was added. After 16 hours of stirring at room temperature, 1 M HCl aqueous solution was added and the water phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed by saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/9 to 1/0, v/v) as an eluent twice to afford **S3** (984 mg, 2.07 mmol) in 23% yield as white solid.

4-hydroxybutyl (*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (S3)



S3

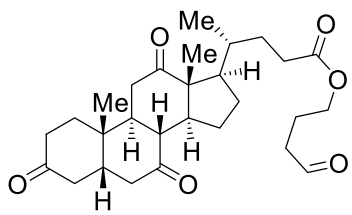
^{1}H NMR ($CDCl_3$): δ = 4.06 (2H, t, *J* = 6.6 Hz), 3.63 (2H, t, *J* = 6.3 Hz), 2.94-2.72 (3H, m), 2.42-1.49 (22H, m), 1.42-1.14 (7H, m), 1.03 (3H, s), 0.80 (3H, d, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$): δ = 212.00, 209.10, 208.71, 174.12, 64.04, 62.25, 56.82, 51.68, 48.91, 46.76, 45.54, 45.46, 44.90, 42.71, 38.56, 36.40, 35.94, 35.40, 35.18, 31.41, 30.35, 29.08, 29.08, 27.52, 25.05, 21.83, 18.57, 11.78.; HRMS (ESI): *m/z* calcd for $C_{28}H_{42}O_6Na$ $[M+Na]^+$ 497.2874. Found 497.2866; IR (Neat): 3398, 2958, 1720, 1706, 1173, 734 cm^{-1}



S3 **2ai**

To a solution of **S3** (474 mg, 1.0 mmol) and TEMPO (32 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL), $PhI(OAc)_2$ (354 mg, 1.1 mmol) was added. After 14 hours of stirring, the reaction was quenched with saturated $Na_2S_2O_3$ aqueous solution. The water phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed by saturated $NaHCO_3$ aqueous solution and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/10 to 2/1, v/v) to afford **2ai** (254 mg, 0.54 mmol) in 54% yield as white solid.

4-oxobutyl (*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (2ai)

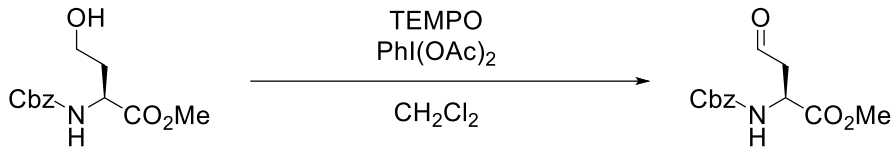


2ai

^{1}H NMR ($CDCl_3$): δ = 9.76 (1H, s), 4.07 (2H, t, *J* = 6.3 Hz), 2.96-2.72 (3H, m), 2.56-2.46 (2H, m), 2.41-1.70 (18H, m), 1.64-1.52 (1H, m), 1.42-1.15 (7H, m), 1.04 (3H, s), 0.82 (3H, d, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$): δ = 211.92, 209.04, 208.69, 201.18, 173.94, 63.19, 56.85, 51.70, 48.95, 46.80, 45.56, 45.49, 44.94, 42.75, 40.46, 38.60, 36.45, 35.98, 35.44, 35.23, 31.33, 30.34, 27.58, 25.09, 21.87, 21.32, 18.59, 11.81.; HRMS (ESI): *m/z* calcd for $C_{28}H_{40}O_6Na$ $[M+Na]^+$

495.2717. Found 495.2713; IR (Neat): 2961, 1708, 1387, 1172, 913, 744 cm^{-1}

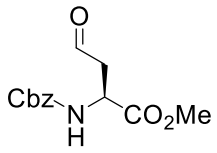
(7-F) Synthesis of 2aj



2aj

To a solution of *N*-(Benzyloxycarbonyl)-homoserine methyl ester[3] (401 mg, 1.5 mmol) and TEMPO (23 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL), $PhI(OAc)_2$ (531 mg, 1.65 mmol) was added. After 1.5 hours of stirring, the reaction was quenched with saturated $Na_2S_2O_3$ aqueous solution. The water phase was extracted with CH_2Cl_2 three times. The combined organic layer was washed by saturated $NaHCO_3$ aqueous solution and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc/*n*-hexane (1/19 to 1/1, v/v) twice to afford **2aj** (150 mg, 0.57 mmol) in 38% yield as colorless oil.

methyl (*S*)-2-(((benzyloxy)carbonyl)amino)-4-oxobutanoate (2aj)

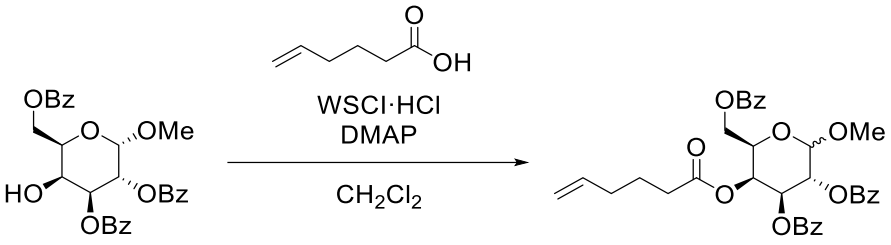


2aj

NMR spectra of the obtained product were consistent with the reported one.[4]

^{1}H NMR ($CDCl_3$): δ = 9.76 (1H, s), 7.39-7.26 (5H, m), 5.64 (1H, t, *J* = 7.4 Hz), 5.10 (2H, s), 4.68-4.54 (1H, m), 3.73 (3H, s), 3.22-2.93 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 199.17, 171.08, 155.88, 136.00, 128.55, 128.27, 128.11, 67.19, 52.89, 49.00, 45.83.

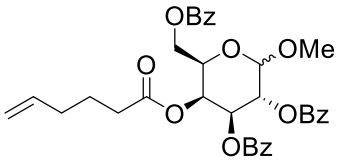
(7-G) Synthesis of 2ak



S4

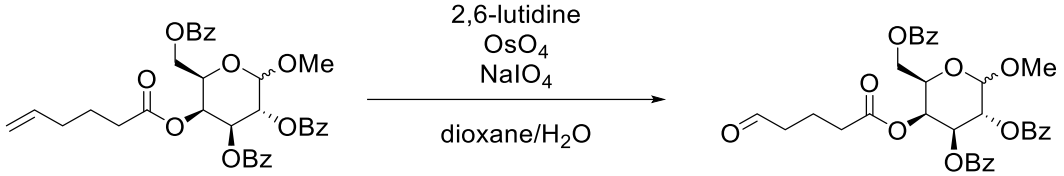
To a solution of hex-5-enoic acid (153 μL, 1.29 mmol), WSCI·HCl (248 mg, 1.29 mmol), and DMAP (22.4 mg, 0.18 mmol) in CH_2Cl_2 (6 mL), protected sugar (500 mg 1.08 mmol) was added. After overnight of stirring at room temperature, 1 M HCl aqueous solution was added and the water phase was extracted with CH_2Cl_2 three times. The combined organic layers were washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography (EtOAc/*n*-hexane = 1/3, v/v) to afford **S4** (599 mg, 1.07 mmol) in 99% yield as colorless oil.

(3*R*,4S,5S,6*R*)-6-((benzoyloxy)methyl)-5-(hex-5-enoyloxy)-2-methoxytetrahydro-2H-pyran-3,4-diyl dibenzoate (S4)



S4

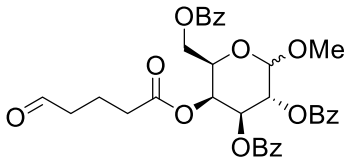
^{1}H NMR ($CDCl_3$): δ = 8.08-7.95 (4H, m), 7.92-7.83 (2H, m), 7.60-7.26 (9H, m), 5.84-5.79 (2H, m), 5.76-5.64 (1H, m), 5.62-5.46 (1H, m), 5.24-5.15 (1H, m), 5.03-4.83 (2H, m), 4.57-4.45 (2H, m), 4.37-4.23 (1H, m), 3.44 (3H, m), 2.51-2.36 (2H, m), 2.08-1.87 (2H, m), 1.73-1.61 (2H, m).; ^{13}C NMR ($CDCl_3$): δ = 172.52, 166.02, 166.00, 165.47, 137.34, 133.35, 133.24, 133.21, 129.83, 129.67, 129.58, 129.46, 129.22, 129.18, 128.46, 128.40, 128.34, 115.53, 97.55, 77.26, 76.74, 68.99, 68.30, 66.55, 66.23, 55.63, 33.23, 32.88, 23.97.; HRMS (ESI): *m/z* calcd for $C_{34}H_{34}O_{10}Na$ $[M+Na]^+$625.2044. Found 625.2017; IR (Neat): 3069, 2937, 1734, 1601, 1278, 1110, 1070, 1050, 1028, 711 cm^{-1}



S4 **2ak**

To a solution of **S4** (143 mg, 0.25 mmol) in 3:1 dioxane/H_2O (1.2 mL), 2,6-lutidine (58.9 μL, 0.51 mmol), OsO_4 (2.5 % wt. % in tert-butanol, 59.0 μL, 0.02 mmol) and $NaIO_4$ (217 mg, 1.02 mmol) were added. After overnight of stirring at room temperature, the reaction mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography (EtOAc/*n*-hexane = 1/3, v/v) to afford **2ak** (103 mg, 0.18 mmol) in 72% yield as a colorless oil.

(3*R*,4S,5S,6*R*)-6-((benzoyloxy)methyl)-2-methoxy-5-((5-oxopentanoyl)oxy)tetrahydro-2H-pyran-3,4-diyl dibenzoate (2ak)

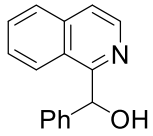


2ak

^{1}H NMR ($CDCl_3$): δ = 9.61 (1H, s), 8.12-7.93 (4H, m), 7.86 (2H, d, *J* = 8.2 Hz), 7.62-7.29 (9H, m), 5.86-5.75 (2H, m), 5.66-5.51 (1H, m), 5.19 (1H, d, *J* = 3.7 Hz), 4.57-4.41 (2H, m), 4.39-4.27 (1H, m), 3.45 (3H, s), 2.48 (2H, t, *J* = 8.0 Hz), 2.37 (2H, t, *J* = 7.6 Hz), 1.95-1.79 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 201.12, 171.96, 166.00, 165.44, 133.39, 133.31, 133.29, 129.83, 129.66, 129.53, 129.40, 129.19, 128.48, 128.41, 97.57, 77.26, 76.74, 68.80, 68.46, 68.40, 66.21, 55.68, 42.59, 32.75, 17.12.; HRMS (ESI): *m/z* calcd for $C_{33}H_{32}O_{11}Na$ $[M+Na]^+$ 627.1837. Found 627.1819; IR (Neat): 3504, 2938, 2724, 1724, 1451, 1271, 1110, 1070, 1049, 1029, 711 cm^{-1}

8. Characterization of Target Compounds

isoquinolin-1-yl(phenyl)methanol (3a)

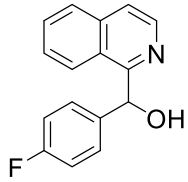


3a

NMR spectra of the obtained product were consistent with the reported one.[5]

20.0 mg, 85% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.50 (1H, d, *J* = 6.0 Hz), 7.91 (1H, d, *J* = 8.2 Hz), 7.80 (1H, d, *J* = 8.2 Hz), 7.65-7.55 (2H, m), 7.50-7.39 (1H, m), 7.34-7.11 (5H, m), 6.33 (1H, s); ^{13}C NMR ($CDCl_3$): δ = 159.12, 143.21, 139.82, 136.57, 130.33, 128.71, 127.86, 127.63, 127.50, 127.38, 125.15, 124.80, 121.13, 72.52.

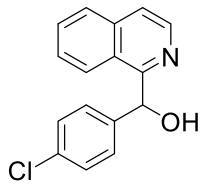
(4-fluorophenyl)(isoquinolin-1-yl)methanol (3b)



3b

19.7 mg, 78% yield; white solid; ^{1}H NMR ($CDCl_3$): 8.52 (1H, d, *J* = 5.5 Hz), 7.95-7.78 (2H, m), 7.69-7.60 (2H, m), 7.52-7.43 (1H, m), 7.34-7.21 (2H, m), 7.03-6.98 (2H, m), 6.46-6.05 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 162.28 (d, *J* = 250.8 Hz), 158.82, 139.97, 139.24 (d, *J* = 2.9 Hz), 136.58, 130.34, 129.36 (d, *J* = 8.6 Hz), 127.53, 127.46, 125.03, 124.59, 121.22, 115.58 (d, *J* = 21.9 Hz), 71.75.; ^{19}F NMR ($CDCl_3$): δ = -113.87.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}FNONa$ $[M+Na]^+$ 276.0795. Found 276.0807; IR (Neat): 3378, 2925, 1506, 1071, 747 cm^{-1}.

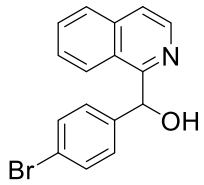
(4-chlorophenyl)(isoquinolin-1-yl)methanol (3c)



3c

18.9 mg, 70% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.52 (1H, d, *J* = 4.8 Hz), 7.93-7.75 (2H, m), 7.69-7.58 (2H, m), 7.54-7.43 (1H, m), 7.29-7.17 (4H, m), 6.47-5.93 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 158.62, 141.80, 139.98, 136.61, 133.69, 130.41, 129.02, 128.89, 127.61, 127.50, 125.04, 124.53, 121.30, 71.77.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}ClNONa$ $[M+Na]^+$ 292.0500. Found 292.0510; IR (Neat): 3357, 2925, 1490, 1090, 747 cm^{-1}.

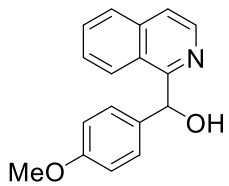
(4-bromophenyl)(isoquinolin-1-yl)methanol (3d)



3d

21.7 mg, 69% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.52 (1H, d, *J* = 5.2 Hz), 7.91-7.80 (2H, m), 7.69-7.61 (2H, m), 7.52-7.45 (1H, m), 7.42-7.36 (2H, m), 7.21-7.17 (2H, m), 6.31 (1H, s); ^{13}C NMR ($CDCl_3$): δ = 158.56, 142.26, 139.90, 136.63, 131.84, 130.47, 129.35, 127.66, 127.51, 125.03, 124.55, 121.89, 121.33, 71.83.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}BrNONa$ $[M+Na]^+$ 335.9994. Found 336.0010; IR (Neat): 3357, 2921, 1486, 1071, 746 cm^{-1}.

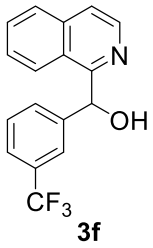
isoquinolin-1-yl(4-methoxyphenyl)methanol (3e)



3e

22.0 mg, 83% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.51 (1H, d, *J* = 6.0 Hz), 7.92 (1H, d, *J* = 8.2 Hz), 7.82 (1H, d, *J* = 8.7 Hz), 7.66-7.57 (2H, m), 7.51-7.42 (1H, m), 7.29-7.16 (2H, m), 6.86-6.74 (2H, m), 6.31 (1H, s), 3.72 (3H, s); ^{13}C NMR ($CDCl_3$): δ = 159.33, 159.14, 139.89, 136.53, 135.70, 130.22, 128.86, 127.40, 127.35, 125.12, 124.85, 121.00, 114.06, 71.99, 55.19.; HRMS (ESI): *m/z* calcd for $C_{17}H_{15}NO_2Na$ $[M+Na]^+$ 288.0995. Found 288.1002; IR (Neat): 3344, 3003, 1509, 1024, 1000, 742 cm^{-1}.

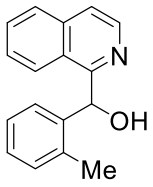
isoquinolin-1-yl(3-(trifluoromethyl)phenyl)methanol (3f)



3f

18.6 mg, 61% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.54 (1H, d, *J* = 6.0 Hz), 7.95-7.81 (2H, m), 7.71-7.60 (3H, m), 7.55-7.44 (3H, m), 7.42-7.31 (1H, m), 6.65-5.92 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 158.22, 141.18, 140.06, 136.66, 131.00 (q, *J* = 31.6 Hz), 130.87, 130.49, 129.16, 127.74, 127.57, 125.01, 124.75 (q, *J* = 4.0 Hz), 124.45 (q, *J* = 4.0 Hz), 124.31, 123.93 (q, *J* = 270.6 Hz), 121.46, 71.90.; ^{19}F NMR ($CDCl_3$): δ = -62.13.; HRMS (ESI): *m/z* calcd for $C_{17}H_{12}F_3NONa$ $[M+Na]^+$ 326.0763. Found 326.0759; IR (Neat): 3371, 2927, 1329, 1123, 704 cm^{-1}.

isoquinolin-1-yl(*o*-tolyl)methanol (3g)

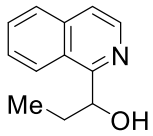


3g

NMR spectra of the obtained product were consistent with the reported one.[6]

20.8 mg, 83% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.55 (1H, d, *J* = 5.7 Hz), 7.84 (1H, d, *J* = 8.0 Hz), 7.67 (1H, d, *J* = 5.7 Hz), 7.64-7.58 (2H, m), 7.44-7.37 (1H, m), 7.22 (1H, d, *J* = 7.4 Hz), 7.15-7.09 (1H, m), 6.97-6.91 (1H, m), 6.62 (1H, d, *J* = 7.4 Hz), 6.53 (1H, s), 6.19 (1H, brs), 2.63 (3H, s); ^{13}C NMR ($CDCl_3$): δ = 159.42, 141.31, 139.78, 136.60, 136.44, 130.99, 130.26, 127.94, 127.84, 127.47, 127.36, 126.29, 125.32, 124.77, 121.02, 69.88, 19.46.

1-(isoquinolin-1-yl)propan-1-ol (3h)

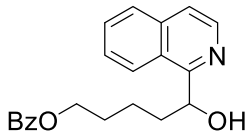


3h

NMR spectra of the obtained product were consistent with the reported one.[7]

13.6 mg, 73% yield; pale yellow oil; ^{1}H NMR ($CDCl_3$): δ = 8.43 (1H, d, *J* = 5.7 Hz), 8.03 (1H, d, *J* = 8.6 Hz), 7.85 (1H, d, *J* = 8.6 Hz), 7.72-7.66 (1H, m), 7.63-7.54 (2H, m), 5.41 (1H, dd, *J* = 7.4, 3.4 Hz), 5.12 (1H, brs), 2.12-1.98 (1H, m), 1.76-1.62 (1H, m), 0.99 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ =161.24, 140.21, 136.42, 130.25, 127.52, 127.28, 124.84, 124.18, 120.42, 70.61, 31.98, 9.70.

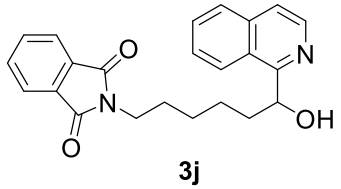
5-hydroxy-5-(isoquinolin-1-yl)pentyl benzoate (3i)



3i

28.7 mg, 86% yield; pale yellow oil; ^{1}H NMR ($CDCl_3$): δ = 8.38 (1H, d, *J* = 5.5 Hz), 8.04-7.89 (3H, m), 7.80 (1H, d, *J* = 8.7 Hz), 7.69-7.60 (1H, m), 7.59-7.40 (3H, m), 7.40-7.29 (2H, m), 5.56-5.35 (1H, m), 5.14 (1H, brs), 4.40-4.13 (2H, m), 2.14-1.91 (1H, m), 1.90-1.43 (5H, m); ^{13}C NMR ($CDCl_3$): δ = 166.60, 161.18, 139.79, 136.50, 132.78, 130.57, 130.36, 129.51, 128.27, 127.59, 127.57, 124.67, 124.12, 120.67, 69.42, 64.82, 38.65, 28.60, 22.12.; HRMS (ESI): *m/z* calcd for $C_{21}H_{21}NO_3Na$ $[M+Na]^+$ 358.1414. Found 358.1398; IR (Neat): 3403, 2950, 1715, 1118, 713 cm^{-1}.

2-(6-hydroxy-6-(isoquinolin-1-yl)hexyl)isoindoline-1,3-dione (3j)

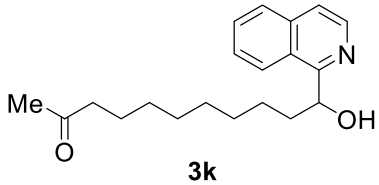


3j

31.7 mg, 85% yield; white solid; ^{1}H NMR ($CDCl_3$): δ = 8.40 (1H, d, *J* = 6.0 Hz), 8.00 (1H, d, *J* = 8.2 Hz), 7.86-7.74 (3H, m), 7.74-7.52 (5H, m), 5.54-5.34 (1H, m), 5.12 (1H, brs), 3.63 (2H, t, *J* = 7.3 Hz), 2.05-1.82 (1H, m), 1.74-1.16 (7H, m); ^{13}C NMR ($CDCl_3$): δ = 168.39, 161.30, 140.03, 136.42, 133.80, 132.11, 130.36, 127.52, 127.42, 124.68, 124.12, 123.10, 120.49, 69.47, 39.00, 37.96, 28.55, 26.83,

25.18.; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N_2O_3Na$ $[M+Na]^+$ 397.1523. Found 397.1524; IR (Neat): 3462, 2939, 1770, 1710, 1056, 751 cm^{-1}.

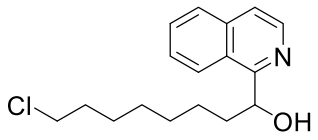
11-hydroxy-11-(isoquinolin-1-yl)undecan-2-one (3k)



3k

25.7 mg, 82% yield; white solid; ^1H NMR ($CDCl_3$): δ = 8.42 (1H, d, *J* = 5.7 Hz), 8.00 (1H, d, *J* = 8.0 Hz), 7.84 (1H, d, *J* = 8.0 Hz), 7.71-7.65 (1H, m), 7.64-7.53 (2H, m), 5.43 (1H, d, *J* = 7.7, 2.6 Hz), 5.10 (1H, brs), 2.37 (2H, t, *J* = 7.4 Hz), 2.10 (3H, s), 1.99-1.88 (1H, m), 1.69-1.37 (5H, m), 1.38-1.14 (8H, m); ^{13}C NMR ($CDCl_3$): δ = 209.38, 161.49, 140.26, 136.39, 130.22, 127.51, 127.28, 124.73, 124.09, 120.37, 69.60, 43.75, 39.27, 29.82, 29.47, 29.35, 29.26, 29.09, 25.55, 23.78.; HRMS (ESI): *m/z* calcd for $C_{20}H_{27}NO_2Na$ $[M+Na]^+$ 336.1934. Found 336.1931; IR (Neat): 3402, 2928, 2853, 1714, 1075, 749 cm^{-1}

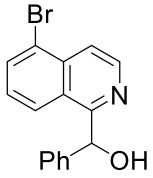
8-chloro-1-(isoquinolin-1-yl)octan-1-ol (3l)



3l

15.9 mg, 54% yield; colorless oil; ^1H NMR ($CDCl_3$): δ = 8.43 (1H, d, *J* = 6.0 Hz), 8.06-7.97 (1H, m), 7.86 (1H, d, *J* = 8.2 Hz), 7.74-7.66 (1H, m), 7.66-7.54 (2H, m), 5.52-5.39 (1H, m), 5.13 (1H, brs), 3.49 (2H, t, *J* = 6.9 Hz), 2.02-1.86 (1H, m), 1.82-1.16 (11H, m); ^{13}C NMR ($CDCl_3$): δ = 161.46, 140.10, 136.45, 130.36, 127.56, 127.38, 124.73, 124.12, 120.48, 69.58, 45.14, 39.19, 32.56, 29.36, 28.79, 26.77, 25.48.; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}ClNONa$ $[M+Na]^+$ 314.1282. Found 314.1269; IR (Neat): 3393, 2932, 1506, 1068, 747 cm^{-1}

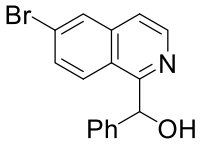
(5-bromoisoquinolin-1-yl)(phenyl)methanol (3m)



3m

27.4 mg, 87% yield; white solid; ^1H NMR ($CDCl_3$): δ = 8.60 (1H, d, *J* = 6.4 Hz), 8.00 (1H, d, *J* = 6.0 Hz), 7.94-7.81 (2H, m), 7.36-7.11 (6H, m), 6.32 (1H, s); ^{13}C NMR ($CDCl_3$): δ = 159.67, 142.85, 141.01, 135.81, 134.23, 128.82, 128.05, 127.92, 127.58, 126.29, 124.57, 122.46, 120.20, 72.59.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}BrNONa$ $[M+Na]^+$ 335.9994. Found 335.9992; IR (Neat): 3364, 2927, 1489, 1067, 750 cm^{-1}

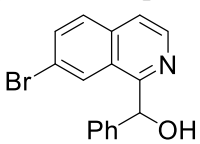
(6-bromoisoquinolin-1-yl)(phenyl)methanol (3n)



3n

29.9 mg, 95% yield; white solid; ^1H NMR ($CDCl_3$): δ = 8.52 (1H, d, *J* = 5.7 Hz), 7.97 (1H, d, *J* = 1.7 Hz), 7.77 (1H, d, *J* = 9.2 Hz), 7.55-7.45 (2H, m), 7.29-7.15 (5H, m), 6.28 (1H, s); ^{13}C NMR ($CDCl_3$): δ = 159.51, 142.84, 140.79, 137.76, 131.12, 129.54, 128.81, 128.06, 127.56, 126.57, 125.37, 123.58, 120.11, 72.59.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}BrNONa$ $[M+Na]^+$ 335.9994. Found 335.9983; IR (Neat): 3363, 2925, 1490, 1063, 758 cm^{-1}

(7-bromoisoquinolin-1-yl)(phenyl)methanol (3o)

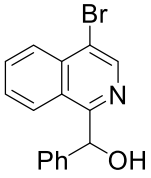


3o

23.1 mg, 74% yield; white solid; ^1H NMR ($CDCl_3$): δ = 8.55 (1H, d, *J* = 6.0 Hz), 8.10 (1H, s), 7.70 (1H, s), 7.61 (1H, d, *J* = 5.5 Hz), 7.40-7.15 (5H, m), 6.27 (1H, s), 6.09 (1H, brs); ^{13}C NMR ($CDCl_3$): δ = 158.42, 142.73, 140.41, 135.02, 133.90, 129.05, 128.86, 128.10, 127.52,

127.23, 126.15, 121.36, 120.82, 72.52.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}BrNONa$ $[M+Na]^+$ 335.9994. Found 335.9988; IR (Neat): 3365, 2924, 1492, 1066, 757 cm^{-1}

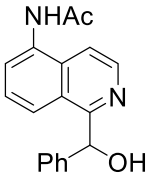
(4-bromoisoquinolin-1-yl)(phenyl)methanol (3p)



3p

19.7 mg, 63% yield; white solid; ^1H NMR ($CDCl_3$): δ = 8.73 (1H, s), 8.19 (1H, d, *J* = 8.7 Hz), 7.96 (1H, d, *J* = 8.2 Hz), 7.78-7.68 (1H, m), 7.60-7.49 (1H, m), 7.34-7.16 (5H, m), 6.33 (1H, s); ^{13}C NMR ($CDCl_3$): δ = 158.82, 142.72, 141.65, 135.14, 131.61, 128.80, 128.46, 128.05, 127.54, 126.82, 126.22, 125.16, 119.63, 72.52.; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}BrNONa$ $[M+Na]^+$ 335.9994. Found 335.9992; IR (Neat): 3345, 2926, 1496, 1063, 759 cm^{-1}

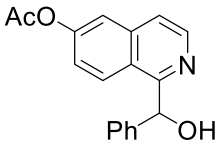
***N*-(1-(hydroxy(phenyl)methyl)isoquinolin-5-yl)acetamide (3q)**



3q

21.0 mg, 72% yield; brown solid; ^1H NMR ($CDCl_3$): δ = 8.47 (1H, d, *J* = 6.0 Hz), 7.92-7.68 (3H, m), 7.60 (1H, d, *J* = 6.0 Hz), 7.42-7.31 (1H, m), 7.31-7.11 (5H, m), 6.29 (1H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$): δ = 169.18, 159.56, 142.88, 140.14, 132.30, 130.94, 128.73, 128.53, 127.97, 127.55, 127.27, 125.52, 122.45, 114.62, 72.61, 24.10.; HRMS (ESI): *m/z* calcd for $C_{18}H_{16}N_2O_2Na$ $[M+Na]^+$ 315.1104. Found 315.1108; IR (Neat): 3263, 3008, 1668, 1541, 1044, 753 cm^{-1}

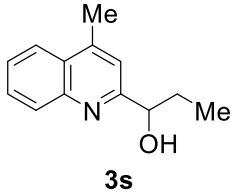
1-(hydroxy(phenyl)methyl)isoquinolin-6-yl acetate (3r)



3r

27.5 mg, 94% yield; pale yellow solid; ^1H NMR ($CDCl_3$): δ = 8.52 (1H, d, *J* = 5.7 Hz), 7.96 (1H, d, *J* = 9.2 Hz), 7.61 (1H, d, *J* = 5.7 Hz), 7.56 (1H, d, *J* = 2.3 Hz), 7.34-7.16 (6H, m), 6.31 (1H, s), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$): δ = 168.96, 159.08, 151.51, 143.01, 140.61, 137.66, 128.78, 127.98, 127.62, 126.76, 123.16, 122.77, 120.94, 118.13, 72.63, 21.15.; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}NO_3Na$ $[M+Na]^+$ 316.0944. Found 316.0944; IR (Neat): 3412, 2929, 1763, 1495, 1144, 706 cm^{-1}

1-(4-methylquinolin-2-yl)propan-1-ol (3s)

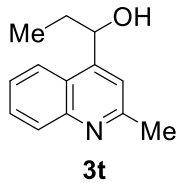


3s

NMR spectra of the obtained product were consistent with the reported one.[8]

15.6 mg, 78% yield; white solid; ^1H NMR ($CDCl_3$): δ = 8.05 (1H, d, *J* = 8.0 Hz), 7.96 (1H, d, *J* = 8.6 Hz), 7.72-7.64 (1H, m), 7.56-7.50 (1H, m), 7.15 (1H, s), 4.97 (1H, brs), 4.81 (1H, dd, *J* = 6.9, 4.0 Hz), 2.69 (3H, s), 2.08-1.89 (1H, m), 1.80-1.67 (1H, m), 0.96 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ = 161.48, 146.16, 145.05, 129.37, 129.31, 127.49, 126.07, 123.73, 118.90, 73.28, 30.86, 18.94, 9.27.

1-(2-methylquinolin-4-yl)propan-1-ol (3t)

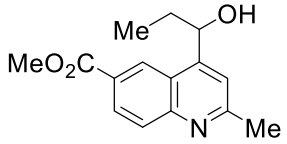


3t

14.0 mg, 70% yield; colorless oil; ^1H NMR ($CDCl_3$): δ = 8.02 (1H, d, *J* = 8.0 Hz), 7.93-7.87 (1H, m), 7.67-7.59 (1H, m), 7.48-7.42 (1H, m), 7.41 (1H, s), 5.35 (1H, dd, *J* = 7.7, 4.3 Hz), 2.68 (3H, s), 2.01-1.90 (1H, m), 1.87-1.76 (1H, m), 1.02 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ = 158.72, 150.65, 147.42, 129.15, 128.94, 125.62, 123.81, 122.83, 118.35, 71.08, 31.22,

25.10, 10.27; HRMS (ESI): *m/z* calcd for $C_{13}H_{15}NONa$ $[M+Na]^+$ 224.1046. Found 224.1056; IR (Neat): 3363, 2965, 1602, 1508, 1093, 759 cm^{-1}

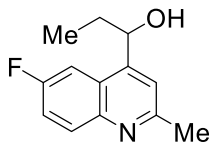
methyl 4-(1-hydroxypropyl)-2-methylquinoline-6-carboxylate (3u)



3u

16.5 mg, 64% yield; pale brown solid; ^1H NMR ($CDCl_3$): δ = 8.62 (1H, d, *J* = 1.9 Hz), 8.19 (1H, dd, *J* = 9.1, 1.9 Hz), 8.03 (1H, d, *J* = 9.1 Hz), 7.49 (1H, s), 5.41 (1H, dd, *J* = 7.7, 4.3 Hz), 3.96 (3H, s), 2.71 (3H, s), 2.02-1.88 (1H, m), 1.88-1.74 (1H, m), 1.02 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (CD_3OD): δ = 167.93, 162.93, 155.11, 150.25, 129.91, 129.33, 128.47, 127.59, 124.72, 120.93, 71.82, 53.01, 32.55, 24.95, 10.57.; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}NO_3Na$ $[M+Na]^+$ 282.1101. Found 282.1114; IR (Neat): 3214, 2963, 1718, 1458, 1276, 1103, 761 cm^{-1}

1-(6-fluoro-2-methylquinolin-4-yl)propan-1-ol (3v)

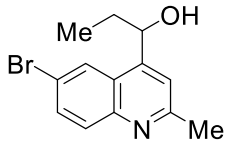


3v

NMR spectra of the obtained product were consistent with the reported one.[9]

15.7 mg, 72% yield; yellow oil; ^1H NMR ($CDCl_3$): δ = 8.00 (1H, dd, *J* = 9.5, 4.0 Hz), 7.55 (1H, dd, *J* = 9.5, 4.0 Hz), 7.43-7.39 (2H, m), 5.23-5.21 (1H, m), 2.70 (3H, s), 2.18 (1H, brs) 1.98-1.91 (1H, m), 1.84-1.78 (1H. m), 1.03 (3H, t, *J* = 7.4 Hz).; ^{13}C NMR ($CDCl_3$): δ = 158.80 (d, *J* = 244.4 Hz), 158.13 (d, *J* = 2.4 Hz), 149.52, 149.48, 144.98, 131.57 (d, *J* = 9.1Hz), 124.45 (d, *J* = 9.1 Hz), 119.54 (d, *J* = 23.3Hz), 106.86 (d, *J* = 23.3Hz), 71.53, 30.98, 25.17, 10.21.; ^{19}F NMR ($CDCl_3$): δ = –113.64.

1-(6-bromo-2-methylquinolin-4-yl)propan-1-ol (3w)

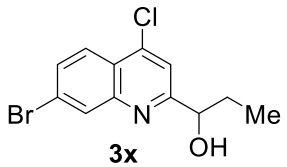


3w

NMR spectra of the obtained product were consistent with the reported one.[9]

13.8 mg, 49% yield; colorless oil; ^1H NMR ($CDCl_3$): δ = 8.09 (1H, s), 7.88 (1H, d, *J* = 9.0 Hz), 7.71 (1H, dd, *J* = 9.0, 1.3 Hz), 7.43 (1H, s), 5.26 (1H, br), 2.70 (3H, s) 2.12 (1H, brs), 1.96-1.92 (1H, m), 1.87-1.79 (1H, m), 1.03 (3H, t, *J* = 7.4 Hz).; ^{13}C NMR ($CDCl_3$): δ = 159.34, 149.19, 146.47, 132.40, 130.94, 125.40, 125.08, 119.56, 119.25, 71.28, 31.10, 25.32, 10.17.

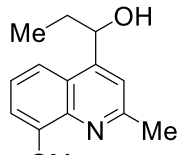
1-(7-bromo-4-chloroquinolin-2-yl)propan-1-ol (3x)



3x

16.5 mg, 58% yield; pale colorless oil; ^1H NMR ($CDCl_3$): δ = 8.26 (1H, d, *J* = 1.7 Hz), 8.05 (1H, d, *J* = 9.1 Hz), 7.69 (1H, dd, *J* = 1.7, 9.1 Hz), 7.45 (1H, s), 4.83-4.80 (1H, m), 4.38 (1H, d, *J* = 5.2 Hz), 2.02-1.93 (1H, m), 1.78-1.69 (1H, m), 0.95 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ = 163.61, 147.85, 143.33, 131.44, 130.84, 125.52, 125.11, 124.36, 118.83, 73.62, 30.80, 9.22.; HRMS (ESI): *m/z* calcd for $C_{12}H_{11}BrClNONa$ $[M+Na]^+$ 321.9605. Found 321.9594; IR (Neat): 3390, 2965, 1603, 1487, 1276, 1112, 709 cm^{-1}

1-(8-methoxy-2-methylquinolin-4-yl)propan-1-ol (3y)

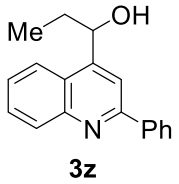


3y

9.7 mg, 42% yield; brown oil; ^1H NMR ($CDCl_3$): δ = 7.48-7.46 (2H, m), 7.39 (1H, dd, *J* = 8.2, 7.7 Hz), 7.02 (1H, d, *J* = 8.0 Hz), 5.35 (1H, dd, *J* = 8.4, 5.5 Hz), 4.05 (3H, s), 2.78 (3H, s),

2.02-1.93 (1H, m), 1.96-1.74 (1H, m), 1.02 (3H, J = 7.6 Hz) ; ^{13}C NMR ($CDCl_3$): δ = 157.11, 150.64, 148.31, 139.57, 130.49, 129.33, 128.76, 127.51, 126.08, 122.77, 115.25, 71.52, 31.12, 10.01.; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NO_2$ $[M+H]^+$ 232.1332. Found 232.1328; IR (Neat): 3373, 2931, 1725, 1261, 1094, 709 cm^{-1}

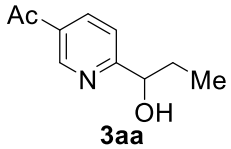
1-(2-phenylquinolin-4-yl)propan-1-ol (3z)



3z

19.8 mg, 75% yield; yellow oil; ^{1}H NMR ($CDCl_3$): δ = 8.18 (1H, d, J = 8.3 Hz), 8.12 (2H, d, J = 7.4 Hz), 7.97 (1H, s), 7.93 (1H, d, J = 8.3 Hz), 7.69 (1H, dd, J =7.7, 6.9 Hz), 7.50-7.42 (4H, m), 5.39 (1H, dd, J = 7.4, 4.6 Hz), 2.34 (1H, brs), 2.04-1.96 (1H, m), 1.90-1.82 (1H, m), 1,05 (3H, t, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$): δ = 157.11, 150.64, 148.31, 139.57, 130.49, 129.33, 129.21, 128.76, 127.51, 126.08, 124.48, 122.77, 115.25, 71.52, 31.12, 10.01.; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383. Found 264.1380; IR (Neat): 3392, 2963, 1596, 1081, 769 cm^{-1}

1-(6-(1-hydroxypropyl)pyridin-3-yl)ethan-1-one (3aa)



3aa

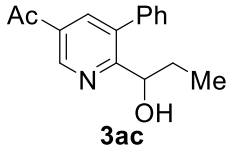
10.1 mg, 56% yield; colorless oil; ^{1}H NMR ($CDCl_3$): δ = 9.07 (1H, d, J = 1.8 Hz), 8.22 (1H, dd, J = 8.4, 1.8 Hz), 7.38 (1H, d, J = 8.4 Hz), 4.75 (1H, dd, J = 7.3, 4.6 Hz), 3.62 (1H, brs), 2.62 (3H, s), 1.97-1.81 (1H, m), 1.79-1.63 (1H, m), 0.93 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$): δ = 196.26, 166.52, 148.56, 136.33, 131.26, 120.41, 73.91, 31.17, 26.74, 9.30.; HRMS (ESI): *m/z* calcd for $C_{10}H_{12}NO_2Na$ $[M+Na]^+$ 202.0838. Found 202.0848; IR (Neat): 3393, 2967, 1686 1595, 1113, 858 cm^{-1}

1-(5-bromo-6-(1-hydroxypropyl)pyridin-3-yl)ethan-1-one (3ab)

3ab

14.7 mg, 57% yield; pale yellow oil; ^{1}H NMR ($CDCl_3$): δ = 9.00 (1H, d, J = 1.7 Hz), 8.36 (1H, d, J = 1.7 Hz), 5.00-4.91 (1H, m), 4.06 (1H, d, J = 8.6 Hz), 2.62 (3H, s), 1.97-1.86 (1H, m), 1.63-1.51 (1H, m), 0.99 (3H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ = 194.90, 164.45, 146.76, 140.13, 132.53, 119.18, 72.79, 29.91, 26.81, 9.63.; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}BrNO_2Na$ $[M+Na]^+$ 279.9944. Found 279.9949; IR (Neat): 3451, 2966, 1693 1583, 1112, 854 cm^{-1}

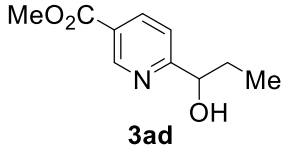
1-(6-(1-hydroxypropyl)-5-phenylpyridin-3-yl)ethan-1-one (3ac)



3ac

13.1 mg, 51% yield; pale yellow oil; ^{1}H NMR ($CDCl_3$): δ = 9.09 (1H, d, J = 2.0 Hz), 8.06 (1H, d, J = 2.0 Hz), 7.48-7.40 (3H, m), 7.32-7.26 (2H, m), 4.94-4.82 (1H, m), 4.20 (1H, d, J = 8.6 Hz), 2.64 (3H, s), 1.58-1.49 (1H, m), 1.41-1.30 (1H, m), 0.71 (3H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ = 196.35, 163.69, 147.31, 137.45, 137.38, 135.51, 131.04, 128.81, 128.79, 128.32, 71.15, 30.52, 26.83, 9.40.; HRMS (ESI): *m/z* calcd for $C_{16}H_{17}NO_2Na$ $[M+Na]^+$ 278.1151. Found 278.1155; IR (Neat): 3421, 2965, 1688, 1591, 1235, 704 cm^{-1}

methyl 6-(1-hydroxypropyl)nicotinate (3ad)

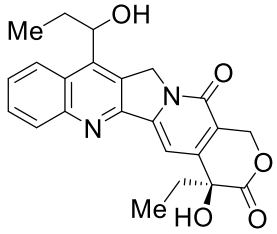


3ad

14.5 mg, 74% yield (inseparable mixture of regioisomers (C_6:C_2+C_4=3.9:1)); pale brown oil; Only the NMR spectrum of the major regioisomer is described. ^{1}H NMR ($CDCl_3$): δ = 9.12 (1H, d, J = 1.9 Hz), 8.27 (1H, dd, J = 8.4, 1.9 Hz), 7.35 (1H, d, J =

8.4 Hz), 5.41 (1H, dd, *J* = 7.2, 4.3 Hz), 3.93 (3H, s), 1.97-1.78 (1H, m), 1.79-1.65 (1H, m), 0.93 (3H, t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$): δ = 166.36, 165.52, 149.42, 137.86, 124.87, 120.09, 73.90, 52.42, 31.20, 9.30.; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}NO_3Na$ $[M+Na]^+$ 218.0788. Found 218.0792; IR (Neat): 3393, 2965, 1731, 1600, 1121, 766 cm^{-1}

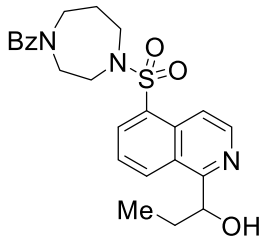
(*4S*)-4-ethyl-4-hydroxy-11-(1-hydroxypropyl)-1,12-dihydro-14H-pyrano[3',4':6,7]indolizino[1,2-b]quinoline-3,14(4H)-dione (3ae)



3ae

17.2 mg, 42% yield (inseparable mixture of diastereomers (A:B=1:1)); yellow solid; ^{1}H NMR (DMSO-d_6): δ = 8.35-8.21 (1H, m, A+B), 8.20-8.10 (1H, m, A+B), 7.90-7.76 (1H, m, A+B), 7.73-7.60 (1H, m, A+B), 7.33 (1H, s, A+B), 6.52 (1H, s, A), 5.92 (1H, s, B), 5.64-5.52 (1H, m, A+B), 5.51-5.29 (4H, m, A+B), 3.41-3.19 (1H, m, A+B), 1.97-1.56 (4H, m, A+B), 0.99 (3H, t, *J* = 7.2 Hz, A+B), 0.93-0.78 (3H, m, A+B); ^{13}C NMR (DMSO-d_6): δ = 172.53, 172.47, 156.80, 152.68, 152.65, 149.95, 148.32, 148.30, 147.21, 145.29, 129.90, 129.84, 127.45, 126.33, 125.14, 124.46, 124.40, 118.94, 96.42, 72.40, 72.31, 69.77, 69.72, 65.27, 51.20, 51.17, 30.24, 30.16, 30.10, 10.18, 10.16, 7.79, 7.74.; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N_2O_5Na$ $[M+Na]^+$ 429.1421. Found 429.1434; IR (Neat): 3420, 2962, 2852, 1748, 1654, 1260, 1026, 799 cm^{-1}

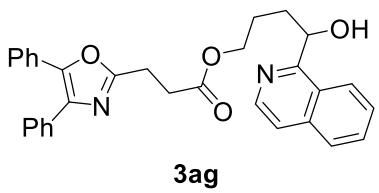
(4-((1-(1-hydroxypropyl)isoquinolin-5-yl)sulfonyl)-1,4-diazepan-1-yl)(phenyl)methanone (3af)



3af

44.9 mg, 99% yield; brown oil; ^{1}H NMR (CD_3OD): δ = 8.78 (1H, dd, *J* = 16.6, 8.6 Hz), 8.58 (1H, dd, *J* = 14.9, 6.3 Hz), 8.50-8.26 (2H, m), 7.87-7.71 (1H, m), 7.49-7.18 (5H, m), 5.49-5.34 (1H, m), 3.92-3.70 (2H, m), 3.68-3.40 (6H, m), 2.08-1.62 (4H, m), 1.02-0.92 (3H, m).; ^{13}C NMR ($CDCl_3$): δ = 171.76, 171.65, 162.43, 142.23, 135.91, 135.06, 132.96, 132.87, 132.25, 129.86, 129.68, 128.54, 126.45, 126.28, 125.87, 125.60, 117.01, 70.91, 51.76, 50.55, 48.58, 48.31, 48.19, 47.96, 46.59, 44.92, 32.25, 29.74, 27.58, 9.74.; HRMS (ESI): *m/z* calcd for $C_{24}H_{27}N_3O_4SNa$ $[M+Na]^+$ 476.1614. Found 476.1619; IR (Neat): 3393, 2965, 1626, 1422, 1327, 1150, 731 cm^{-1}

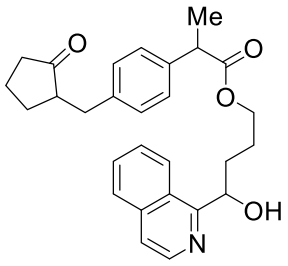
4-hydroxy-4-(isoquinolin-1-yl)butyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3ag)



3ag

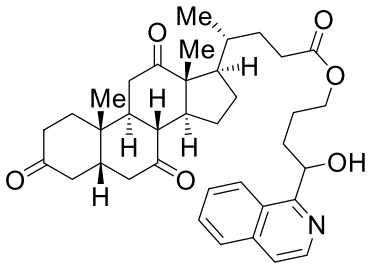
36.5 mg, 74% yield; colorless oil; ^{1}H NMR ($CDCl_3$): δ = 8.41 (1H, d, *J* = 5.7 Hz), 7.98 (1H, d, *J* = 8.6 Hz), 7.84 (1H, d, *J* = 8.0 Hz), 7.71-7.63 (1H, m), 7.63-7.49 (6H, m), 7.36-7.25 (6H, m), 5.53-5.38 (1H, m), 5.16 (1H, brs), 4.26-4.05 (2H, m), 3.13 (2H, t, *J* = 7.6 Hz), 2.85 (2H, t, *J* = 7.6 Hz), 2.16-1.52 (4H, m); ^{13}C NMR ($CDCl_3$): δ = 171.97, 161.69, 160.76, 145.35, 140.30, 136.42, 135.07, 132.41, 130.30, 128.93, 128.58, 128.49, 128.39, 127.99, 127.84, 127.55, 127.43, 126.41, 124.65, 123.91, 120.58, 68.89, 64.61, 35.21, 31.09, 24.59, 23.49.; HRMS (ESI): *m/z* calcd for $C_{31}H_{28}N_2O_4Na$ $[M+Na]^+$ 515.1941. Found 515.1926; IR (Neat): 3419, 2923, 1733, 1504, 1175, 764 cm^{-1}

4-hydroxy-4-(isoquinolin-1-yl)butyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (3ah)



3ah

24.9 mg, 56% yield; yellow oil; ^{1}H NMR ($CDCl_3$): δ = 8.42 (1H, d, *J* = 6.3 Hz), 7.94 (1H, d, *J* = 8.6 Hz), 7.87 (1H, d, *J* = 8.6 Hz), 7.72-7.67 (1H, m), 7.63-7.50 (2H, m), 7.13 (2H, d, *J* = 6.9 Hz), 7.05-6.95 (2H, m), 5.45-5.36 (1H, m), 4.23-3.94 (2H, m), 3.70-3.47 (1H, m), 3.13-2.89 (1H, m), 2.48-2.34 (1H, m), 2.35-2.17 (2H, m), 2.08-1.80 (5H, m), 1.44-1.36 (3H, m); ^{13}C NMR ($CDCl_3$): δ = 220.21, 174.59, 160.79, 140.30, 138.72, 138.33, 136.42, 130.30, 128.99, 127.57, 127.45, 127.38, 124.63, 123.92, 120.57, 77.26, 76.74, 68.92, 64.50, 50.93, 45.10, 45.07, 38.13, 35.26, 35.20, 35.13, 29.16, 24.68, 20.48, 18.43, 18.35.; HRMS (ESI): *m/z* calcd for $C_{28}H_{31}NO_4Na$ $[M+Na]^+$ 468.2145. Found 468.2130; IR (Neat): 3436, 2960, 1731, 1512, 1337, 1163, 749 cm^{-1}

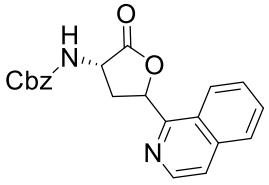


3ai

4-hydroxy-4-(isoquinolin-1-yl)butyl (4*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (3ai)

40.4 mg, 67% yield; pale yellow solid; ^{1}H NMR ($CDCl_3$): δ = 8.43 (1H, d, *J* = 5.7 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 7.91-7.81 (1H, m), 7.75-7.68 (1H, m), 7.66-7.56 (2H, m), 5.55-5.40 (1H, m), 5.20 (1H, brs), 4.17-4.01 (2H, m), 2.94-2.73 (3H, m), 2.39-1.51 (21H, m), 1.44-1.11 (7H, m), 1.02-0.98 (3H, m), 0.85-0.71 (3H, m); ^{13}C NMR ($CDCl_3$): δ = 211.94, 211.92, 209.05, 208.71, 174.03, 174.00, 161.06, 161.04, 139.15, 136.67, 131.00, 127.81, 127.68, 127.65, 124.62, 124.25, 120.96, 68.92, 63.96, 56.82, 51.69, 48.92, 46.77, 45.57, 45.49, 44.92, 42.73, 38.57, 36.42, 35.95, 35.39, 35.23, 35.20, 31.45, 31.43, 30.39, 27.55, 27.52, 25.05, 25.04, 24.74, 21.85, 18.57, 11.77, 11.75.; HRMS (ESI): *m/z* calcd for $C_{37}H_{47}NO_6Na$ $[M+Na]^+$ 624.3296. Found 624.3272; IR (Neat): 3398, 2960, 1710, 1383, 1173, 913, 732 cm^{-1}

benzyl ((3*S*)-5-(isoquinolin-1-yl)-2-oxotetrahydrofuran-3-yl)carbamate (3aj')



3aj'

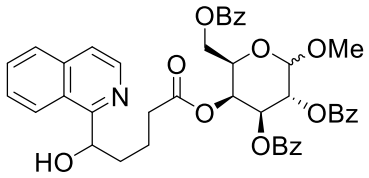
Due to instability of **3aj** for SiO_2, **3aj** was isolated as the lactone (**3aj'**). The procedure is as follows. Isoquinoline (**1a**) (12.9 mg, 0.10 mmol), methyl (*S*)-2-(((benzyloxy)carbonyl)amino)-4-oxobutanoate (**2aj**) (31.8 mg, 0.12 mmol), Mes-Acr$^+$ (2.0 mg, 0.005 mmol), TPA (3.6 mg, 0.010 mmol), and TFA (15.3 μL, 0.20 mmol) were dissolved in degassed CH_2Cl_2 (2.0 mL) in a screw-capped vial under argon atmosphere. The vial was subjected to blue LED irradiation for 3 hours under temperature control (ca. 27–29 ºC). Then, the reaction mixture was passed through a pad of alumina eluting with CH_2Cl_2 and EtOAc. Then, the solvent was removed under reduced pressure. To a solution of the residue in CH_2Cl_2 (2.0 mL), SiO_2 (1.0 g) was added. After 4 hours of stirring, the solvent was removed under reduced pressure. The crude material was purified by a SiO_2 flash column chromatography with EtOAc and *n*-hexane to afford **3aj'** (18.4 mg, 0.051 mmol) in 51% yield (dr=1.1/1) as white solid.

major isomer: ^{1}H NMR ($CDCl_3$): δ = 8.48 (1H, d, *J* = 5.7 Hz), 8.17 (1H, d, *J* = 8.0 Hz), 7.86 (1H, d, *J* = 8.0 Hz), 7.74-7.68 (1H, m), 7.67-7.61 (2H, m), 7.42-7.27 (5H, m), 6.46 (1H, d, *J* = 8.6 Hz), 5.33 (1H, brs), 5.13 (2H, s), 5.01-4.86 (1H, m), 3.51-3.36 (1H, m), 2.80-2.64 (1H, m); ^{13}C NMR ($CDCl_3$): δ = 175.24, 155.93, 154.95, 141.62, 136.57, 135.97, 130.41, 128.58, 128.31, 128.25, 128.02, 127.59, 126.23, 124.05, 121.84, 75.23, 67.35, 50.33,

33.23.; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}N_2O_4Na$ $[M+Na]^+$ 385.1159. Found 385.1164; IR (Neat): 3334, 1784, 1716, 1523, 1261, 829 cm^{-1}

minor isomer: ^1H NMR ($CDCl_3$): δ = 8.51 (1H, d, *J* = 5.2 Hz), 8.24 (1H, d, *J* = 8.6 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 7.77-7.59 (3H, m), 7.41-7.26 (5H, m), 6.27 (1H, t, *J* = 7.4 Hz), 5.78 (1H, d, *J* = 6.9 Hz), 5.24-5.04 (2H, m), 4.94-4.80 (1H, m), 3.22-2.92 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 174.17, 156.07, 153.83, 141.51, 136.62, 136.01, 130.55, 128.56, 128.27, 128.16, 128.16, 127.51, 126.98, 124.32, 122.27, 75.91, 67.34, 51.04, 33.54.; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}N_2O_4Na$ $[M+Na]^+$ 385.1159. Found 385.1160; IR (Neat): 3288, 1780, 1685, 1541, 1338, 913 cm^{-1}

(*3R*,*4S*,*5S*,*6R*)-6-((benzoyloxy)methyl)-5-((5-hydroxy-5-(isoquinolin-1-yl)pentanoyl)oxy)-2-methoxytetrahydro-2H-pyran-3,4-diyl dibenzoate (3ak)



3ak

The reaction was conducted at 0.035 mmol scale. 19.0 mg, 79% yield (inseparable mixture of diastereomers (A:B=1.1:1)); colorless oil; ^1H NMR ($CDCl_3$): δ = 8.40 (1H, d, *J* = 5.7 Hz, A), 8.33 (1H, d, *J* = 5.7 Hz, B), 8.05-7.80 (7H, m, A+B), 7.71 (1H, d, *J* = 8.6 Hz, A+B), 7.69-7.62 (1H, m, A+B), 7.60-7.48 (4H, m, A+B), 7.44-7.30 (5H, m, A+B), 7.29-7.21 (1H, m, A+B) 7.10-7.04 (1H, m, A+B), 5.85-5.73 (2H, m, A+B), 5.64-5.49 (1H, m, A+B), 5.44-5.32 (1H, m, A+B), 5.26-5.18 (1H, m, A+B), 5.11 (1H, brs, A+B), 4.55-4.43 (2H, m), 4.36-4.23 (1H, m, A+B), 3.42 (3H, m, A+B), 2.58-2.44 (2H, m, A+B), 2.06-1.71 (3H, m, A+B), 1.70-1.45 (1H, m, A+B).; ^{13}C NMR ($CDCl_3$): δ =172.42, 165.99, 165.46, 160.89, 160.75, 140.31, 136.39, 133.32, 133.20, 132.97, 130.26, 129.85, 129.69, 129.67, 129.59, 129.51, 129.44, 129.23, 128.45, 128.43, 128.41, 128.29, 128.10, 127.43, 124.68, 124.02, 123.96, 120.50, 120.43, 97.54, 97.51, 77.32, 77.20, 76.68, 69.21, 69.11, 68.33, 68.27, 66.59, 66.54, 62.28, 55.64, 53.40, 38.23, 38.14, 33.76, 21.22, 21.03.; HRMS (ESI): *m/z* calcd for $C_{42}H_{39}NO_{11}Na$ $[M+Na]^+$ 756.2415. Found 756.2379; IR (Neat):3421, 2933, 1725, 1451, 1270, 1070, 710 cm^{-1}

9. References

1. Hu, X.; Li, G.-X.; He, G.; Chen, G. *Org. Chem. Front.* **2019**, *6*, 3205-3209.

2. Fuse, H.; Mitsunuma, H.; Kanai, M. *J. Am. Chem. Soc.* **2020**, *142*, 4493-4499.

3. Lang, C. S.; Wong, S. H.; Chow, S.; Challinor, V. L.; Yong, K. W.; Fletcher, M. T.; Arthur, D. M.; Ng, J. C.; De Voss, J. J. *Org. Biomol. Chem.* **2016**, *14*, 6826-6832.

4. Ottersbach, P. A.; Schmitz, J.; Schnakenburg, G.; Gütschow, M. *Org. Lett.* **2013**, *15*, 448– 451.

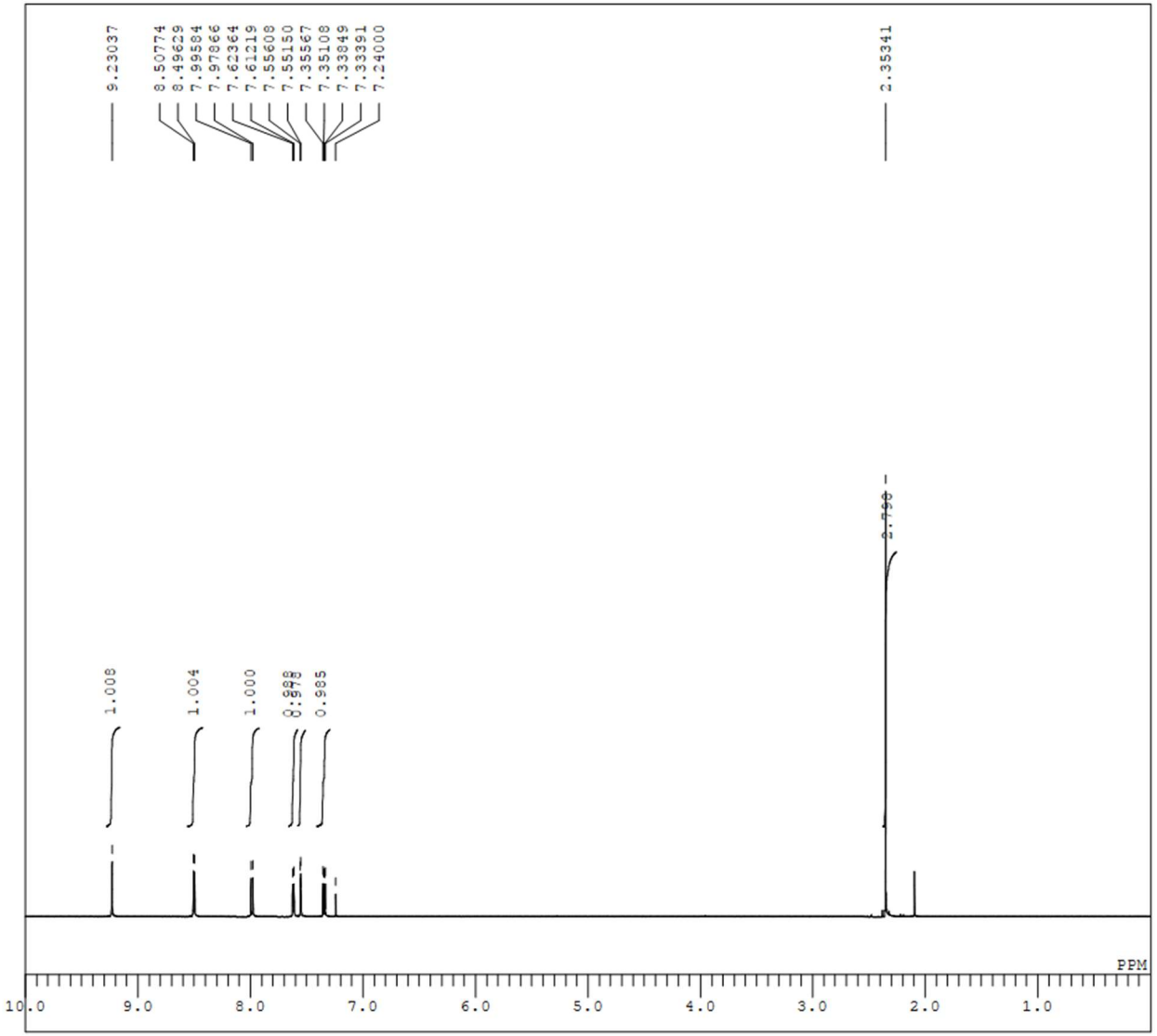
5. Bieszczad, B.; Perego, L. A.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2019**, *58*, 16878-16883.

6. Wang, B.; Zhou, H.; Lu, G.; Liu, Q.; Jiang, X. *Org. Lett.* **2017**, *19*, 2094-2097.

7. Niu, L.; Jiamei Liu, J.; Liang, X.-A.; Wang, S.; Lei, A. *Nat. Commun.* **2019**, *10*, 467.

8. Zhao, H.; Li, Z.; Jin, J. *New J. Chem.* **2019**, *43*, 12533-12537.

9. Wang, S.; Xing, S.; Zhang, Y.; Fan, Y.; Zhao, H.; Wang, J.; Zhang, S.; Wang, W. *RSC Adv.*, **2019**, *9*, 41847-41850.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1.000
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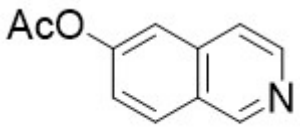
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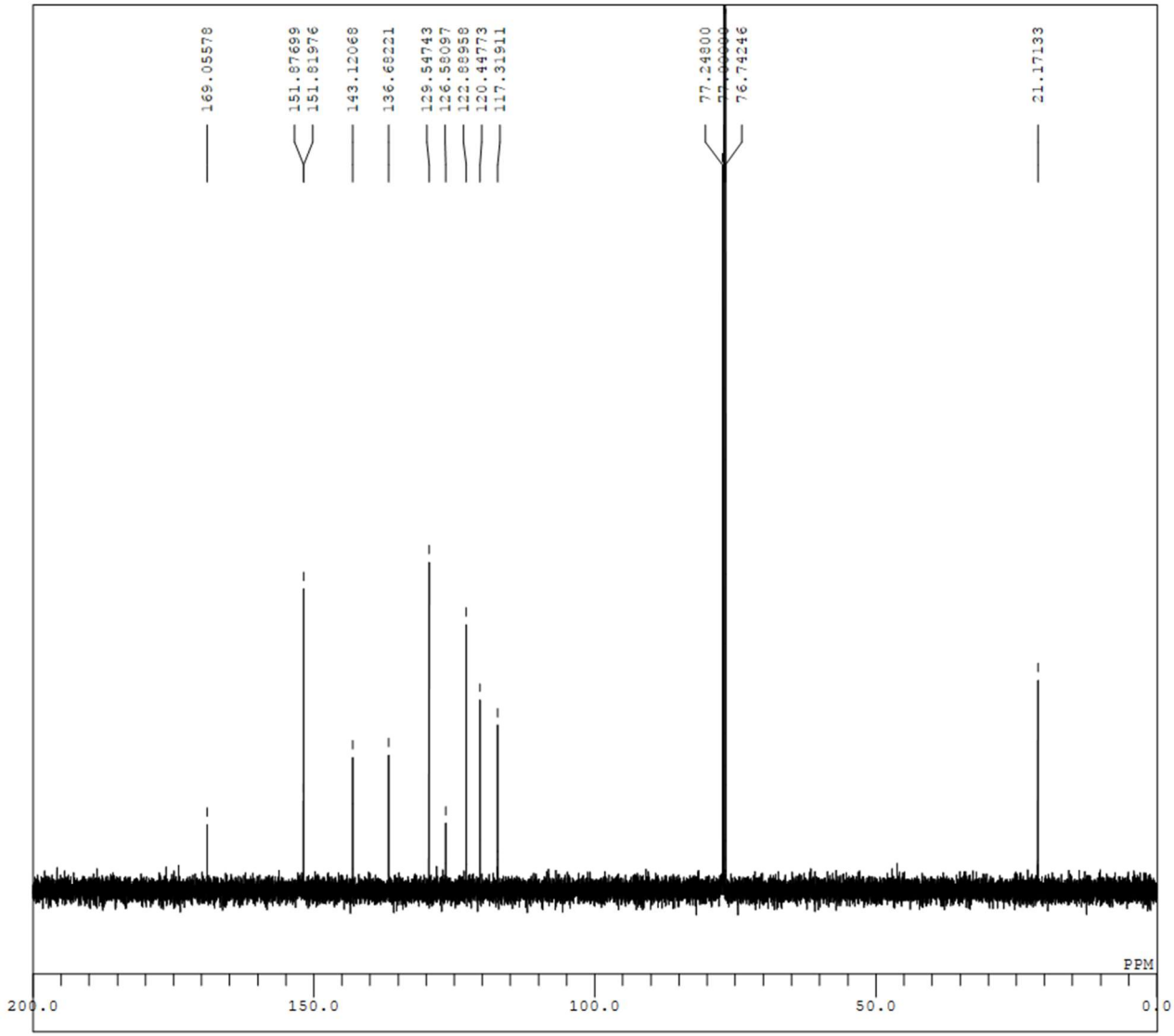
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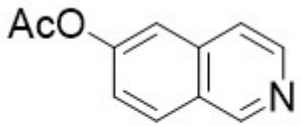
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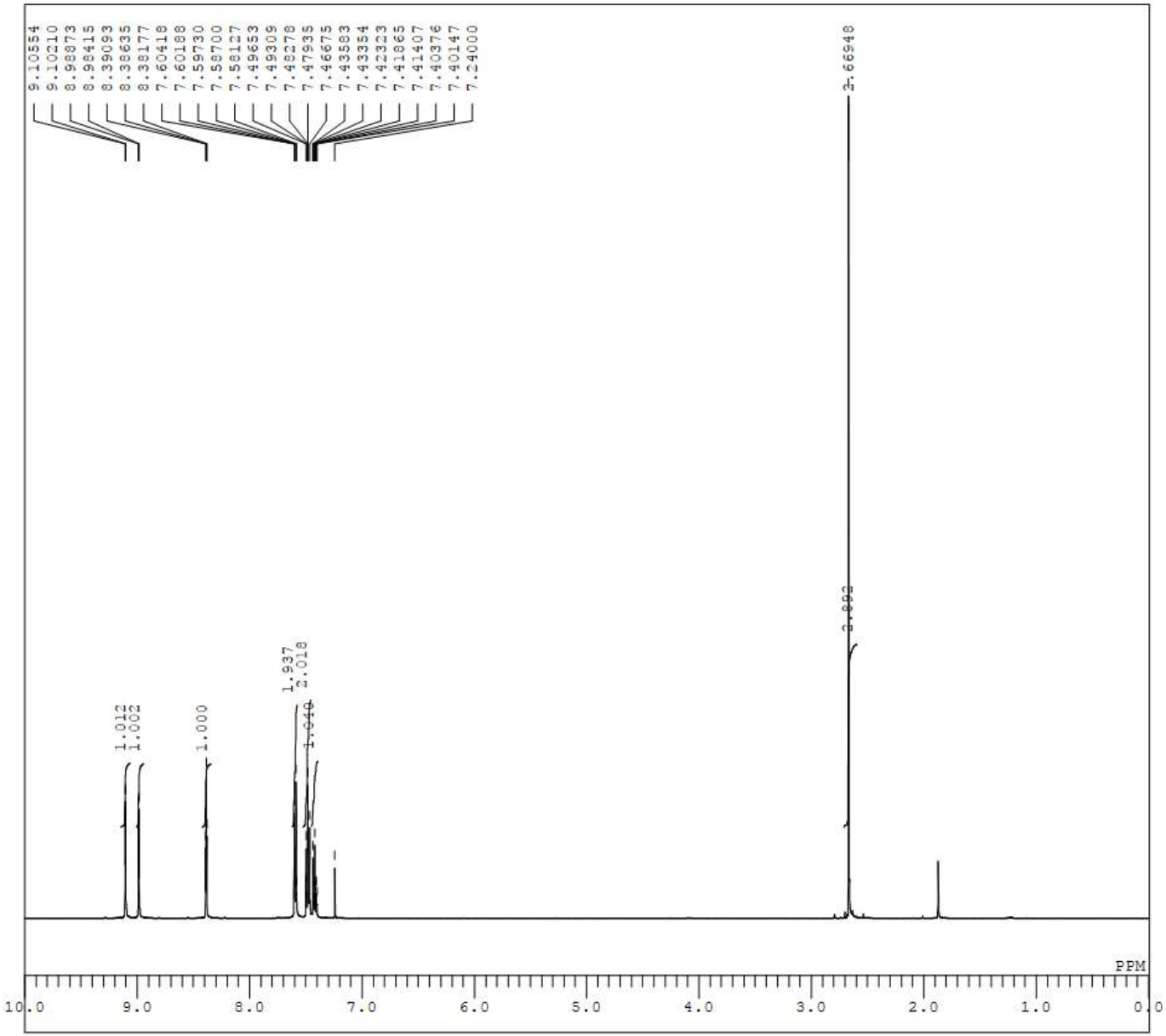
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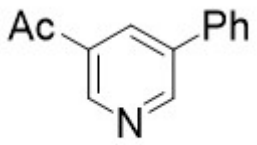
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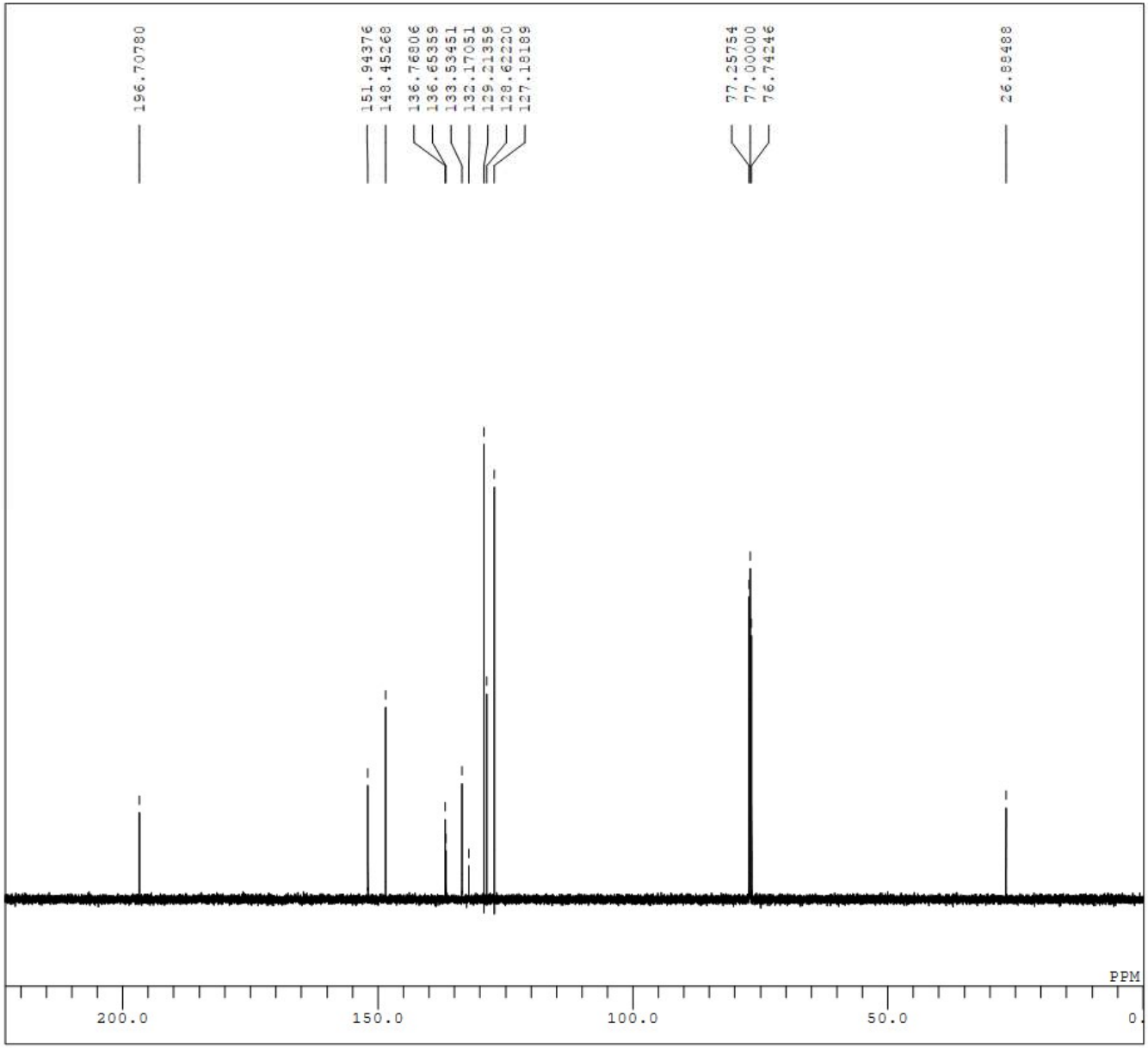
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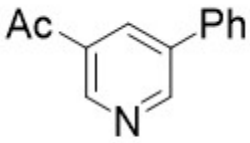
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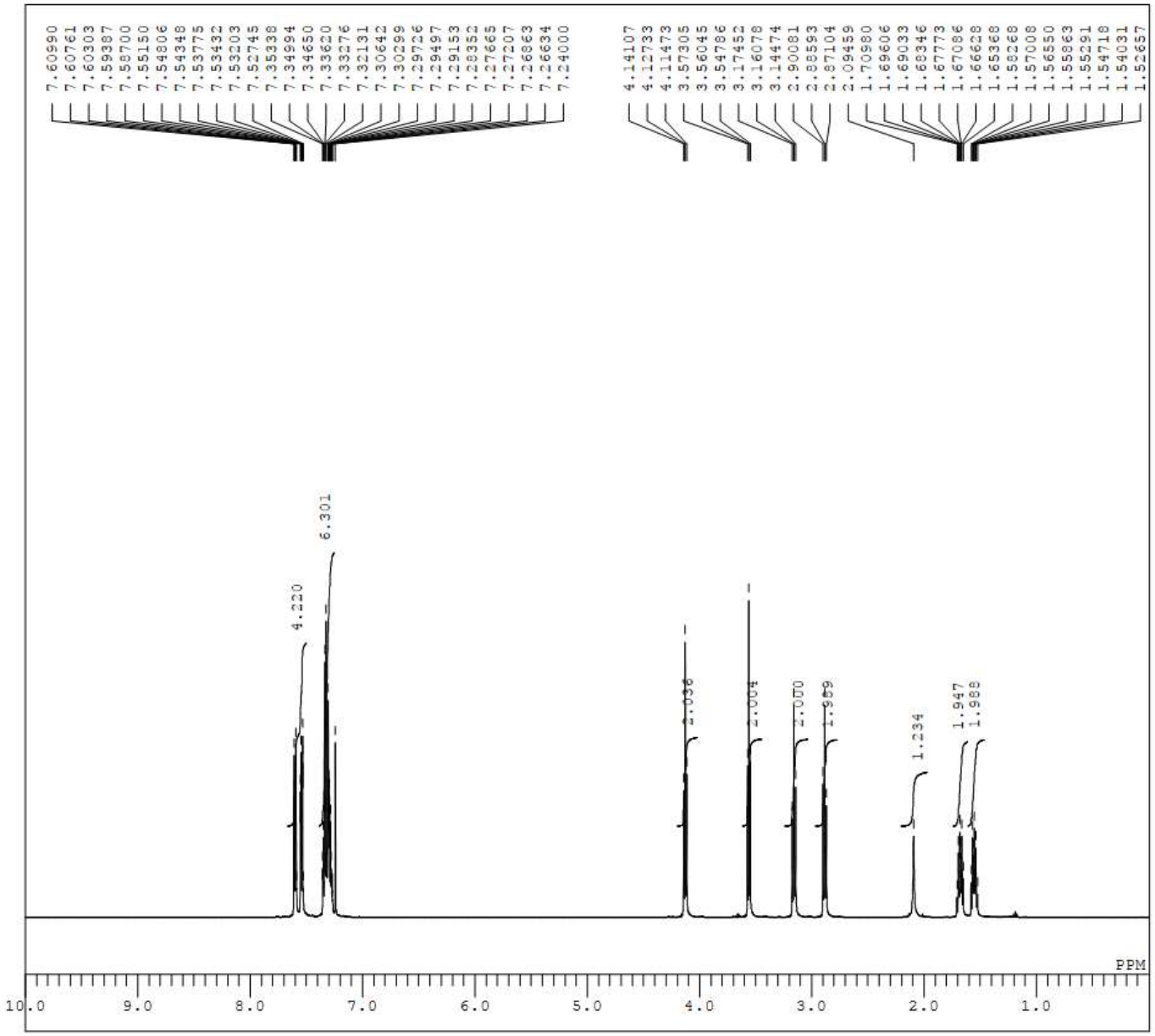
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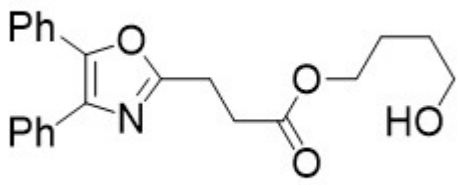
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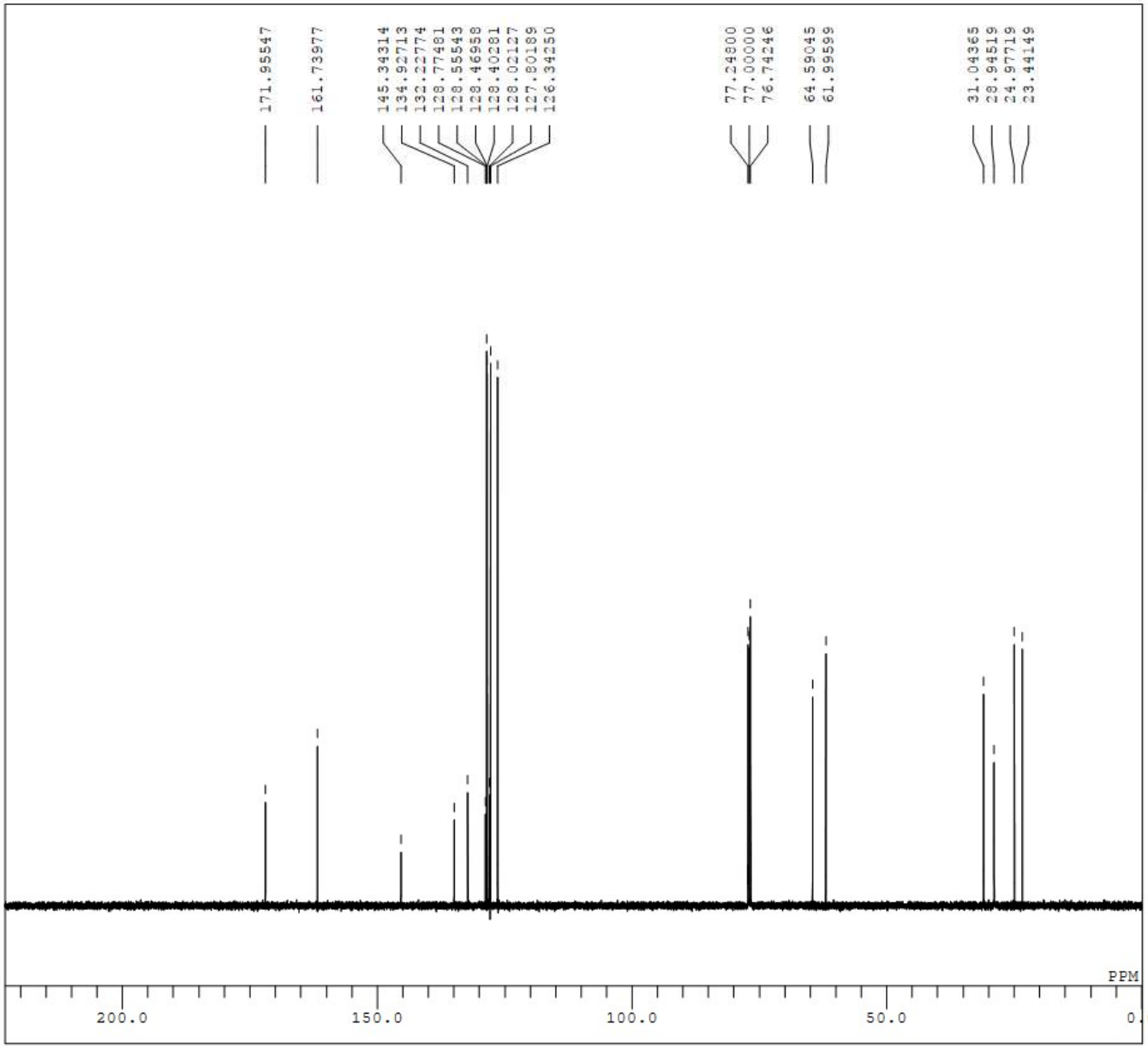
S1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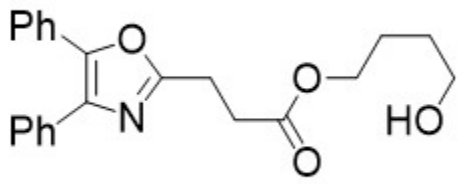
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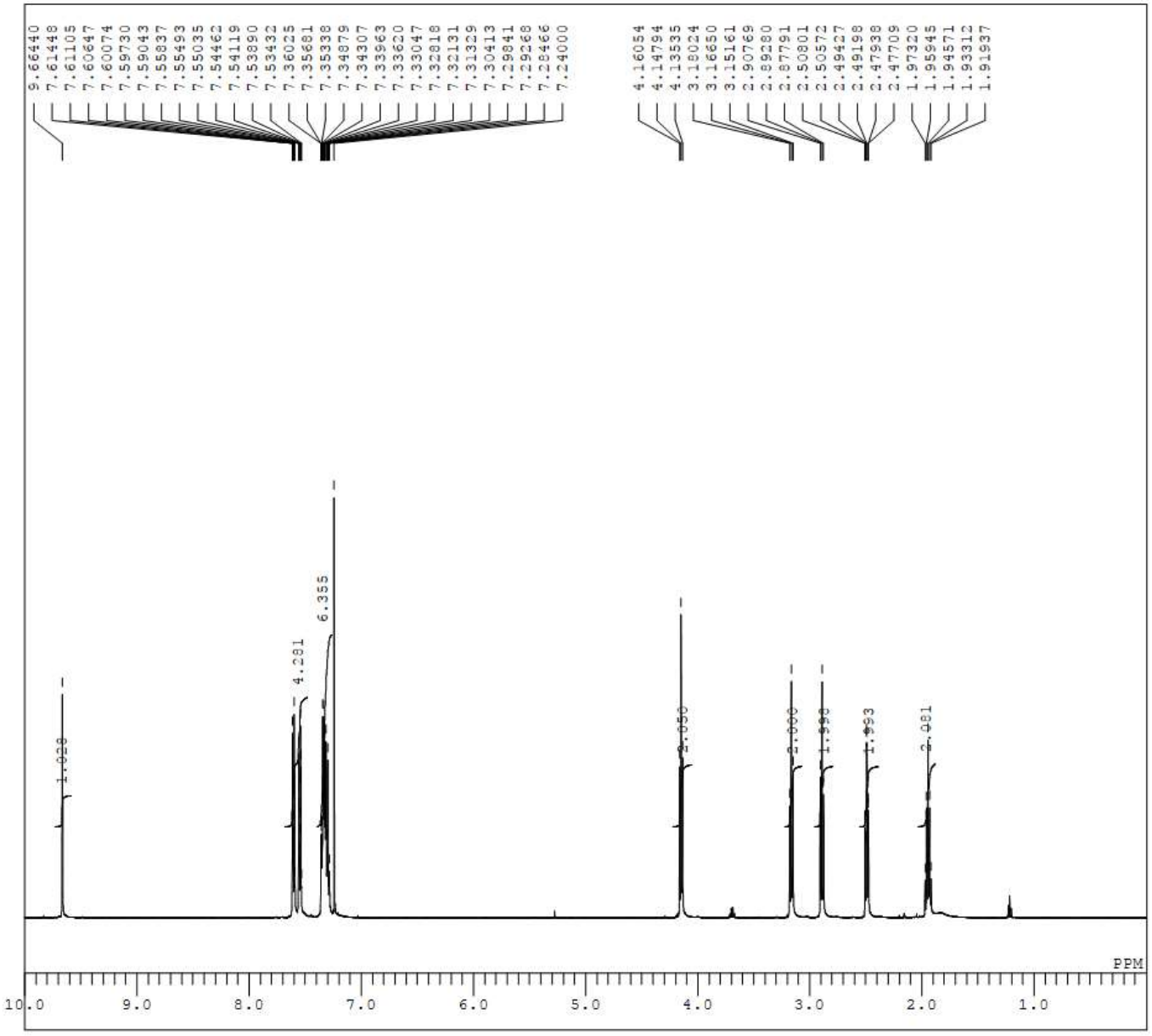
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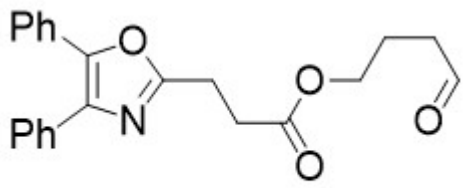
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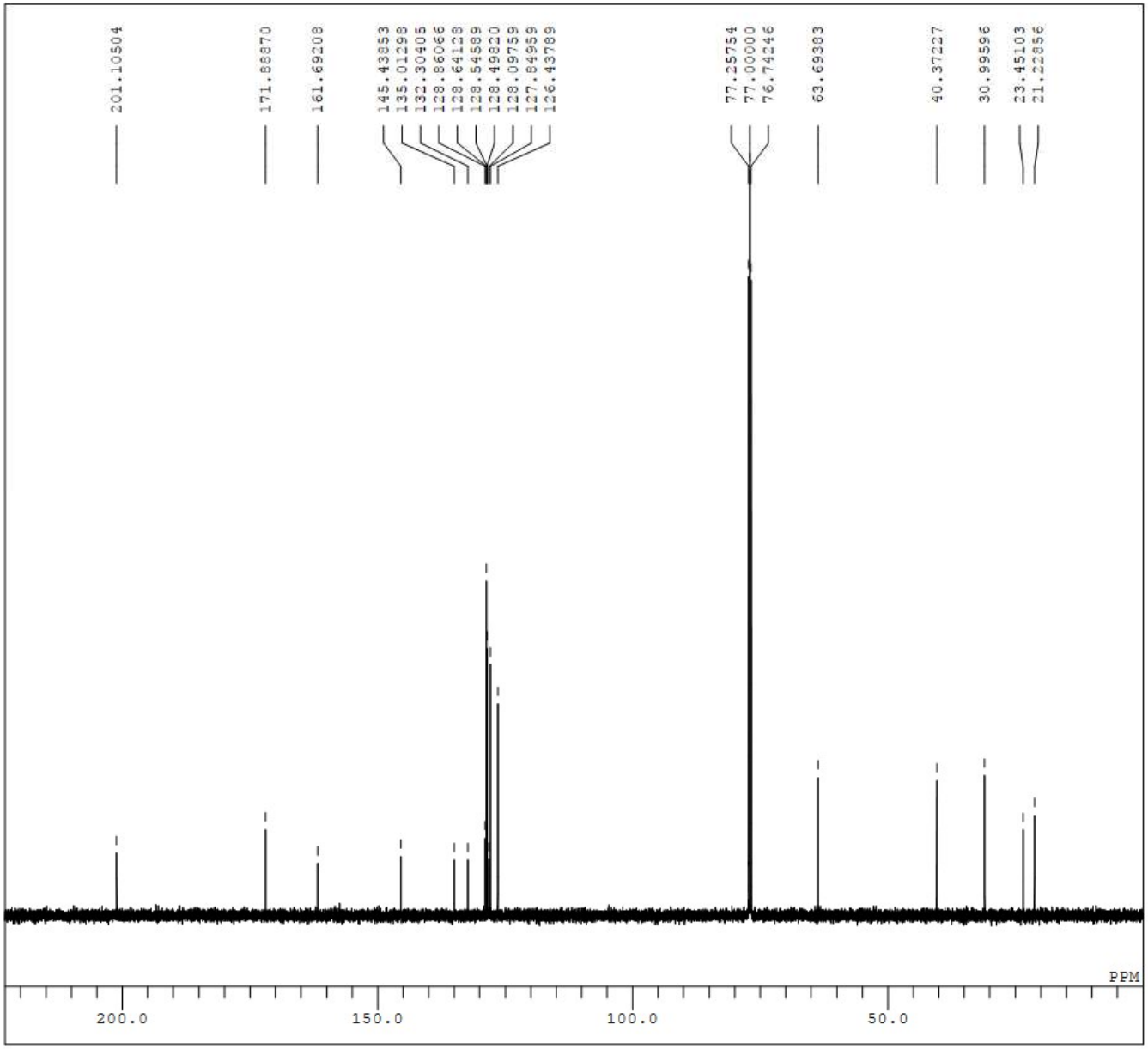
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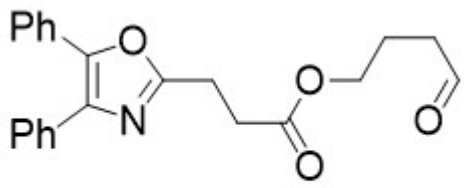
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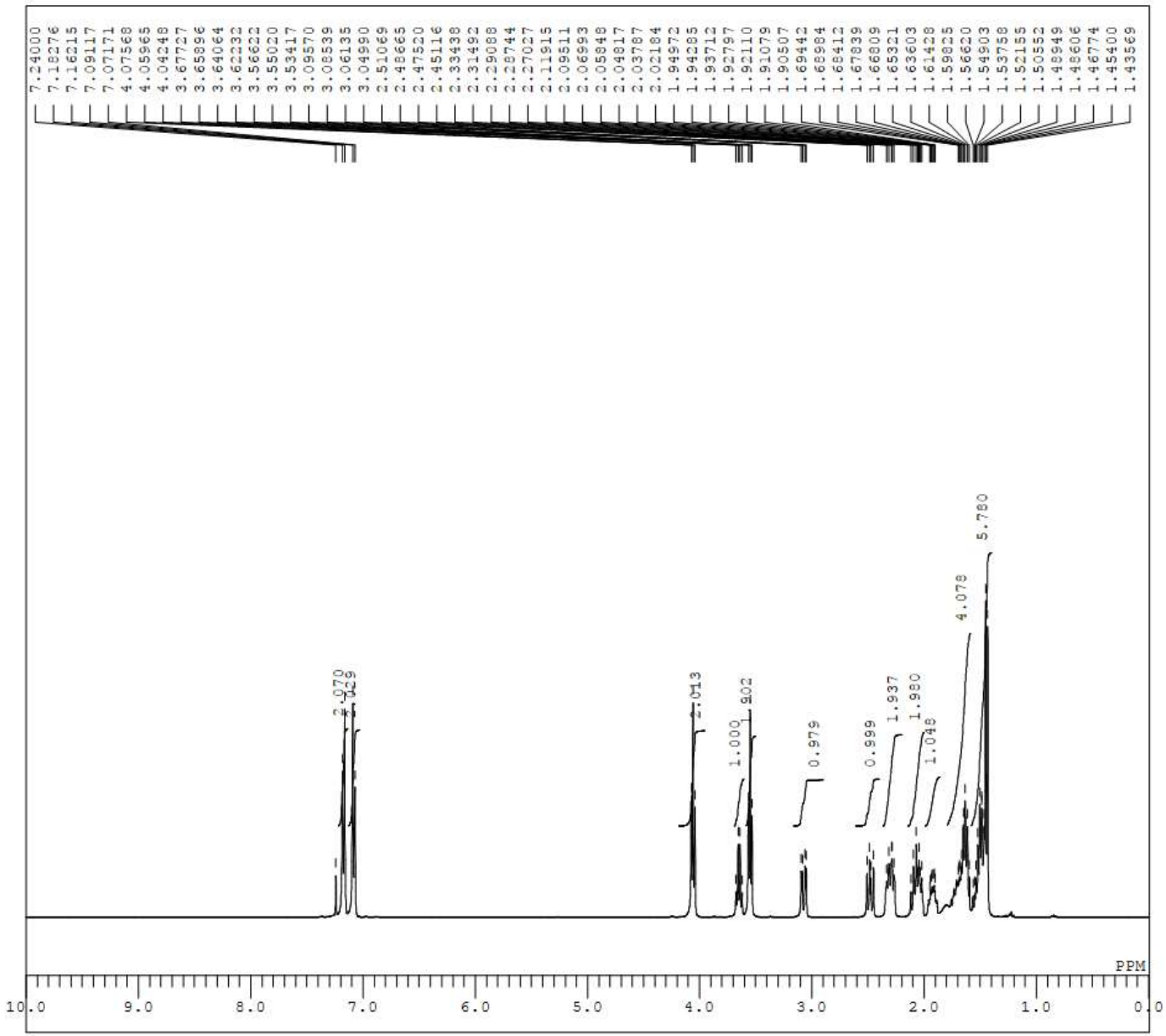
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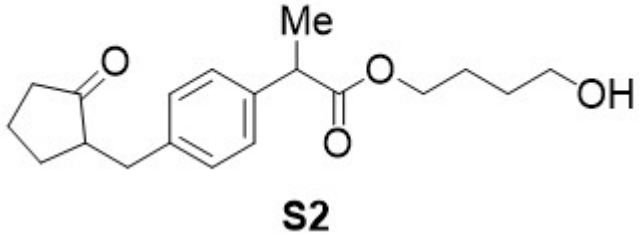
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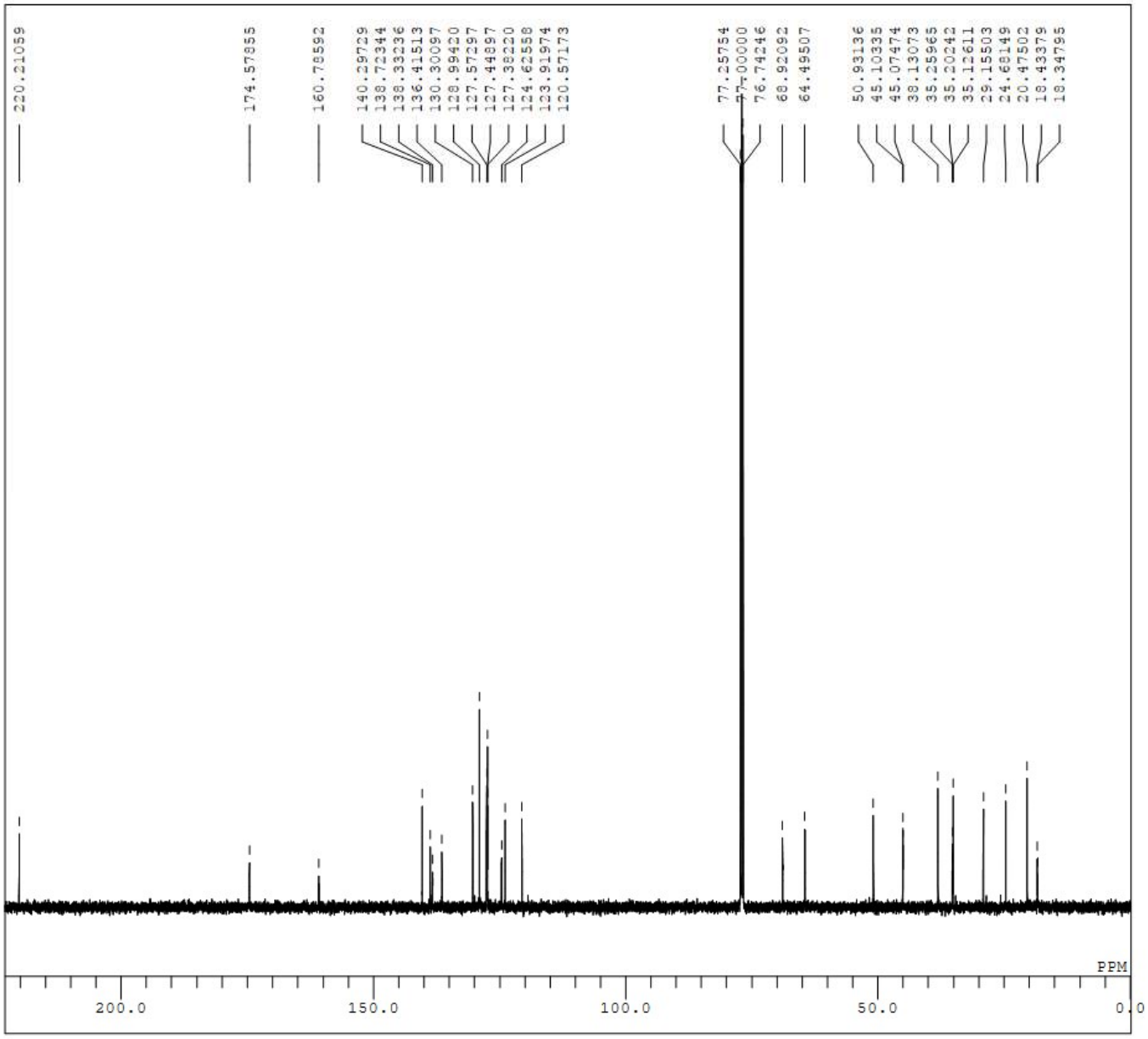
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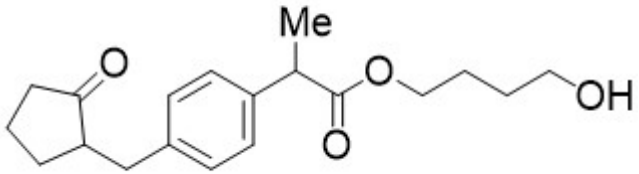
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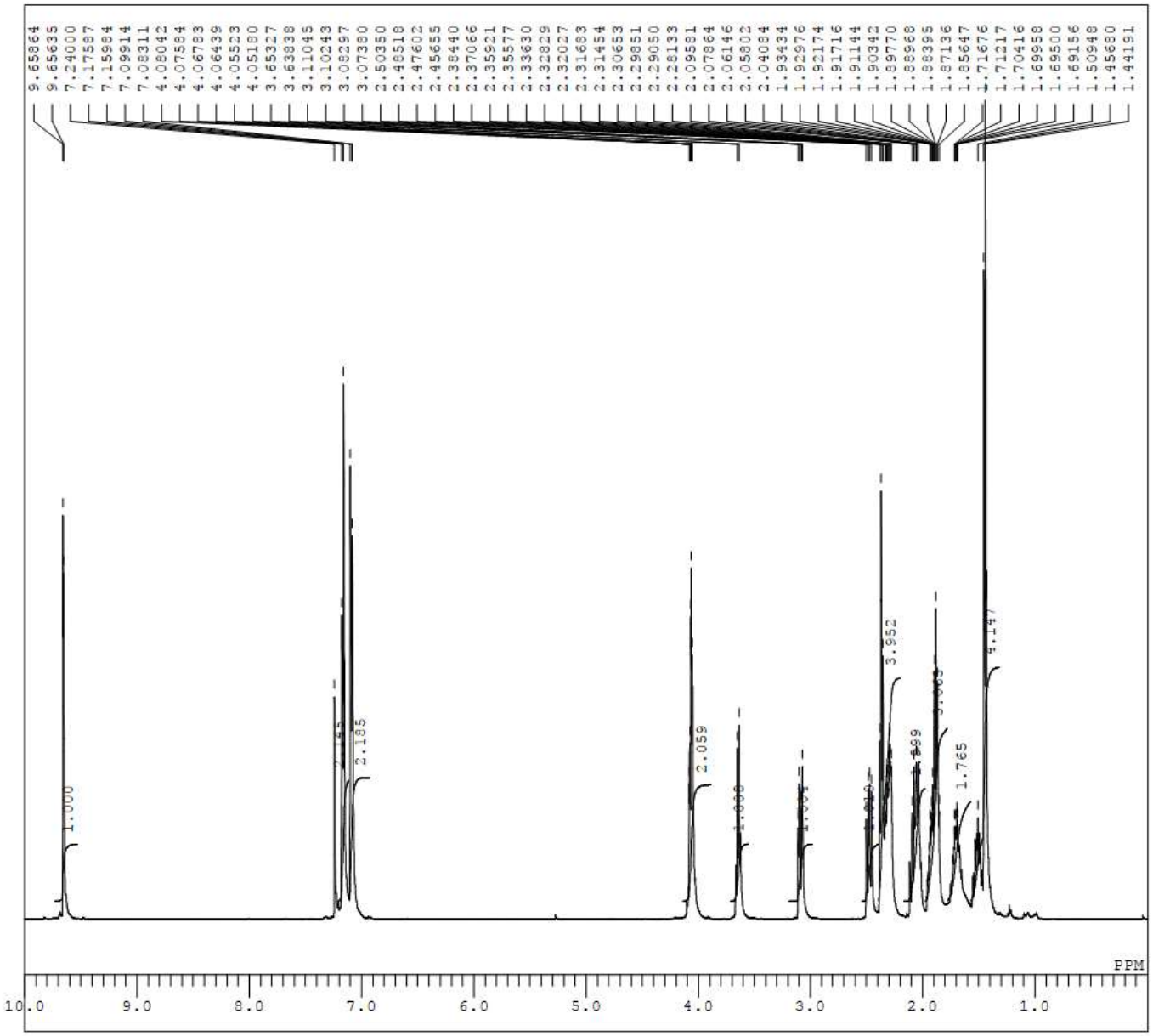
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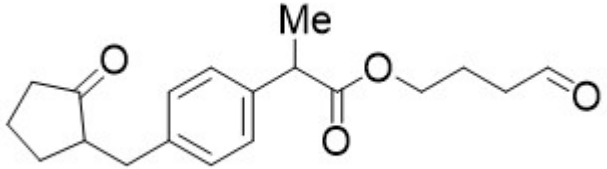
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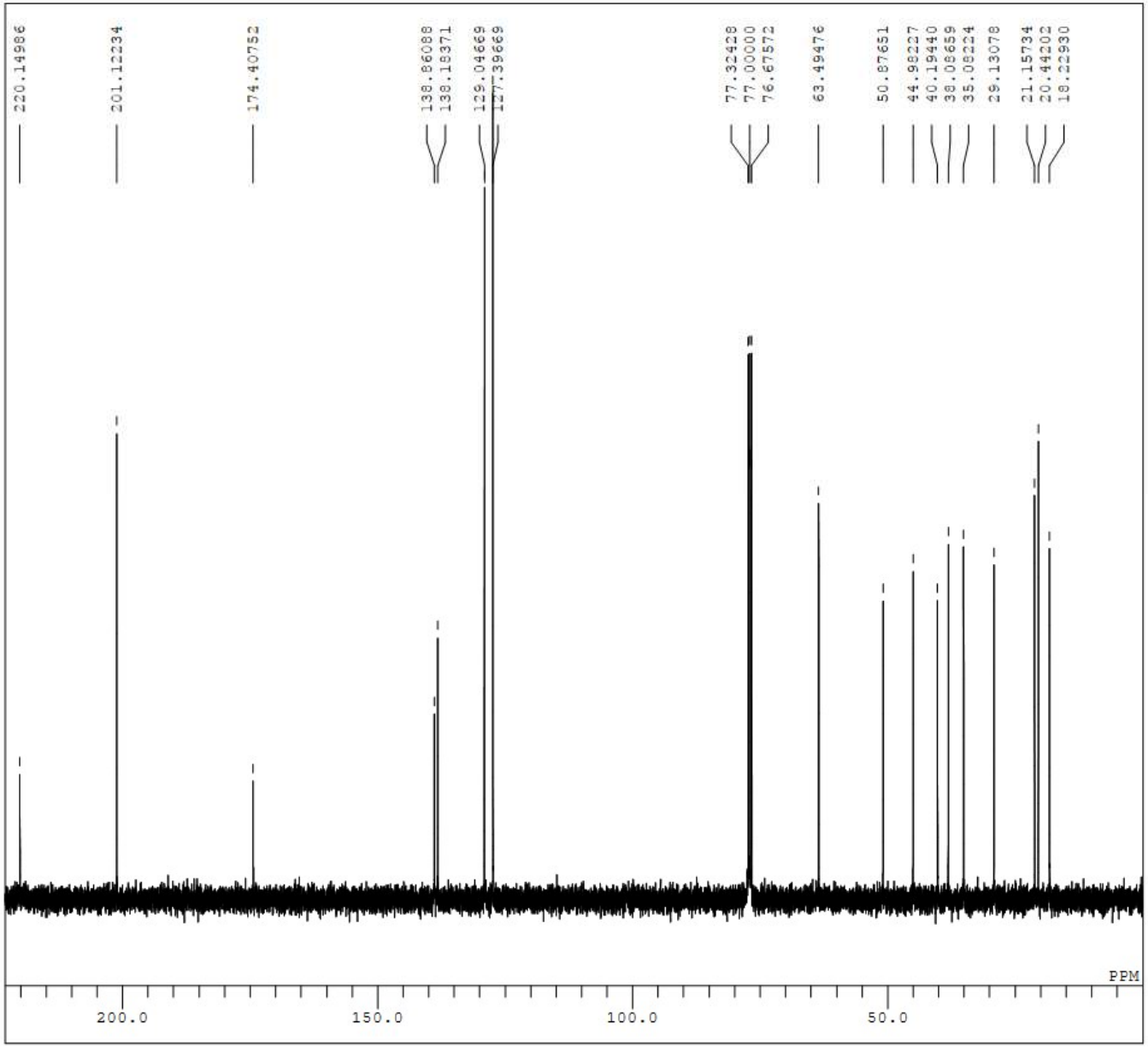
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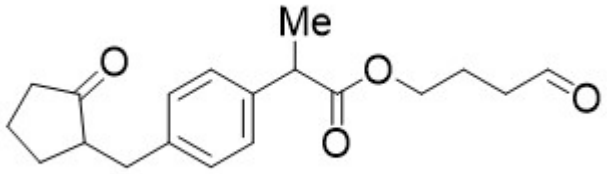
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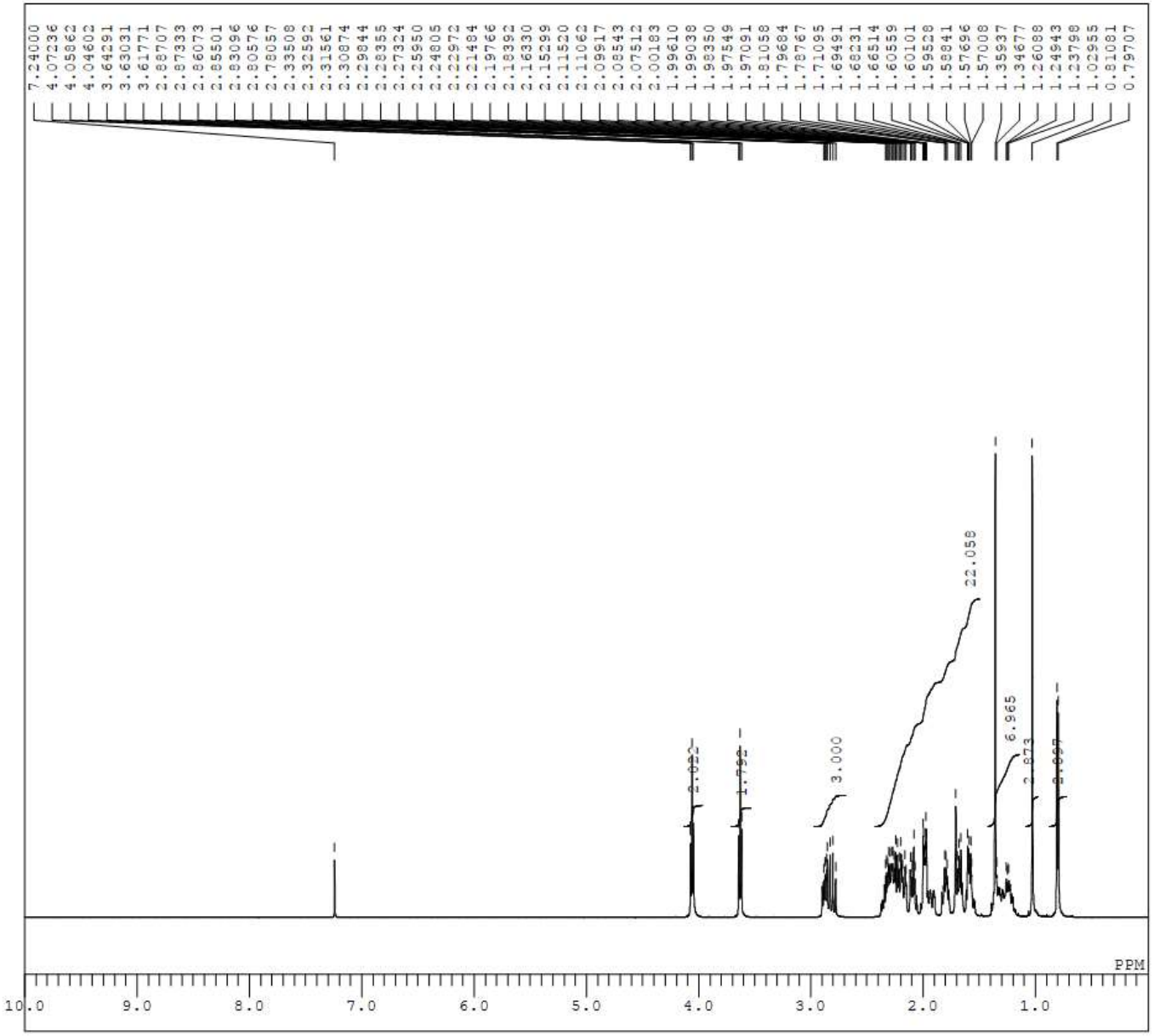
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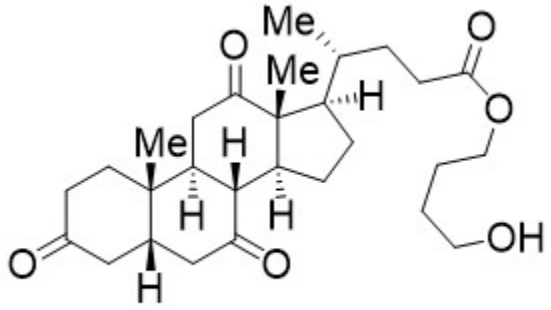
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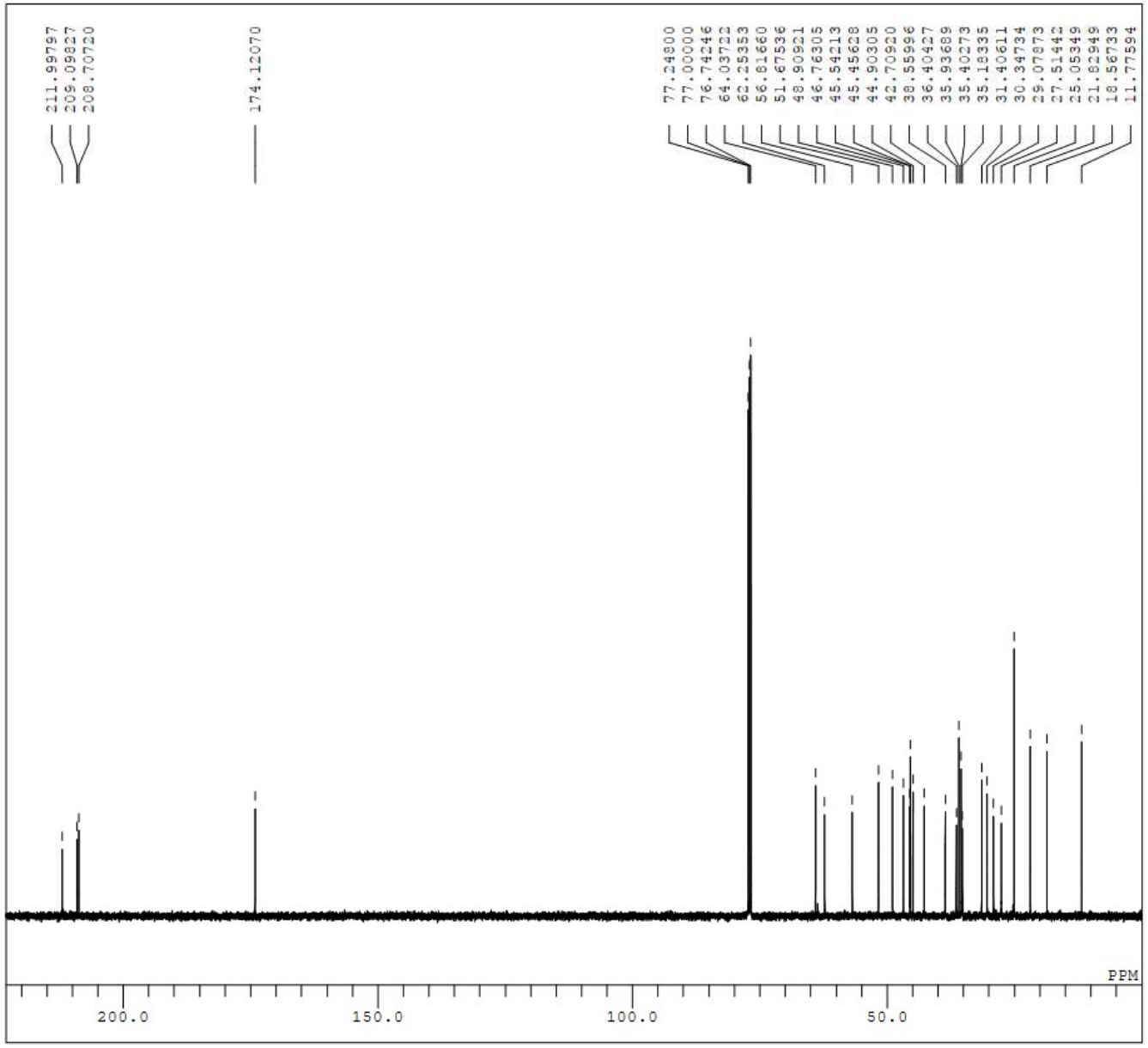
OH

S3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35.93689
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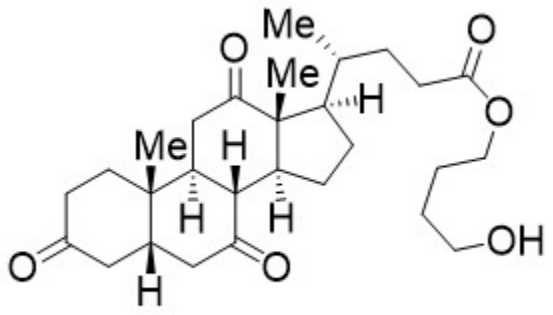
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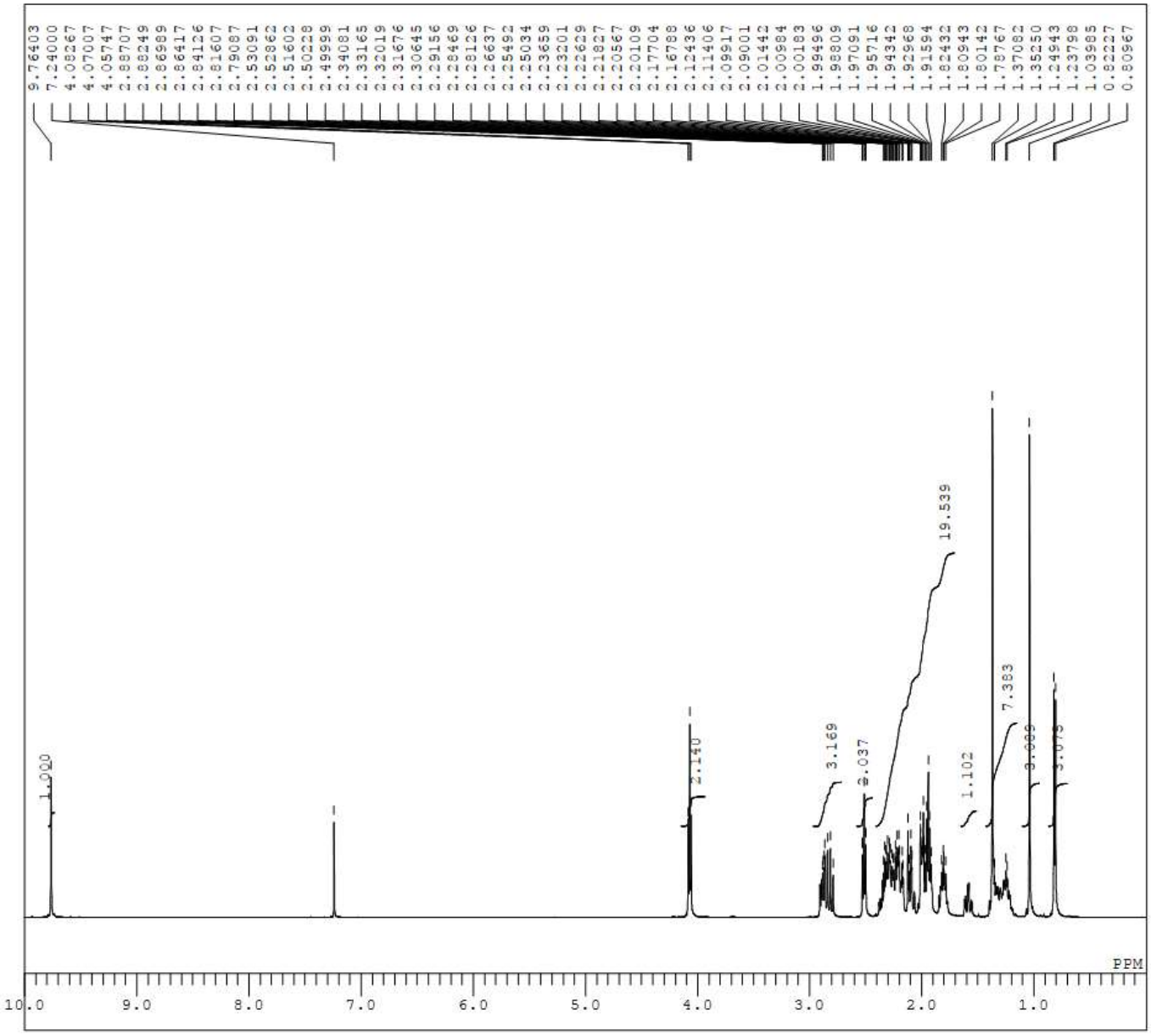
O
O
H
OH

S3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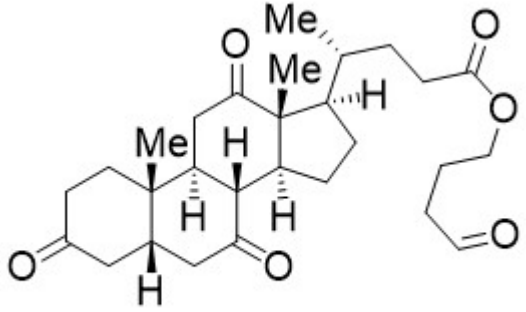
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O
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Me
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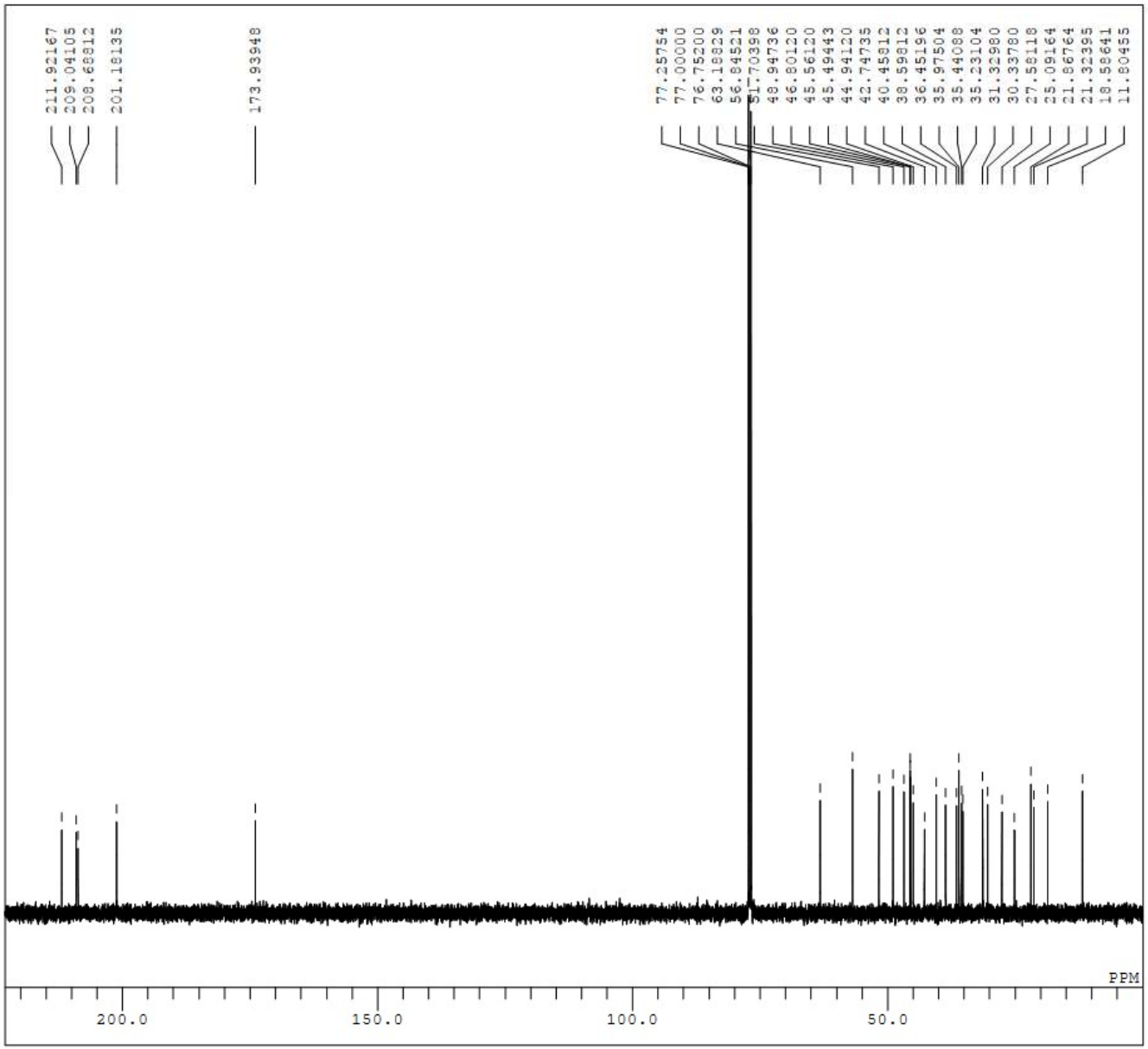
O
O
H

2ai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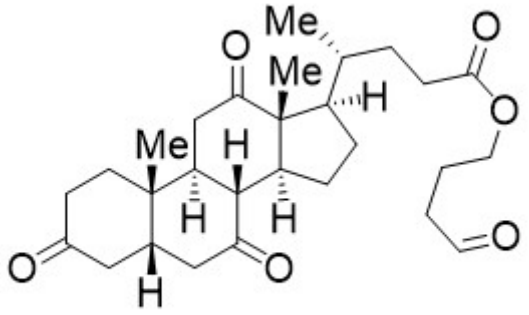
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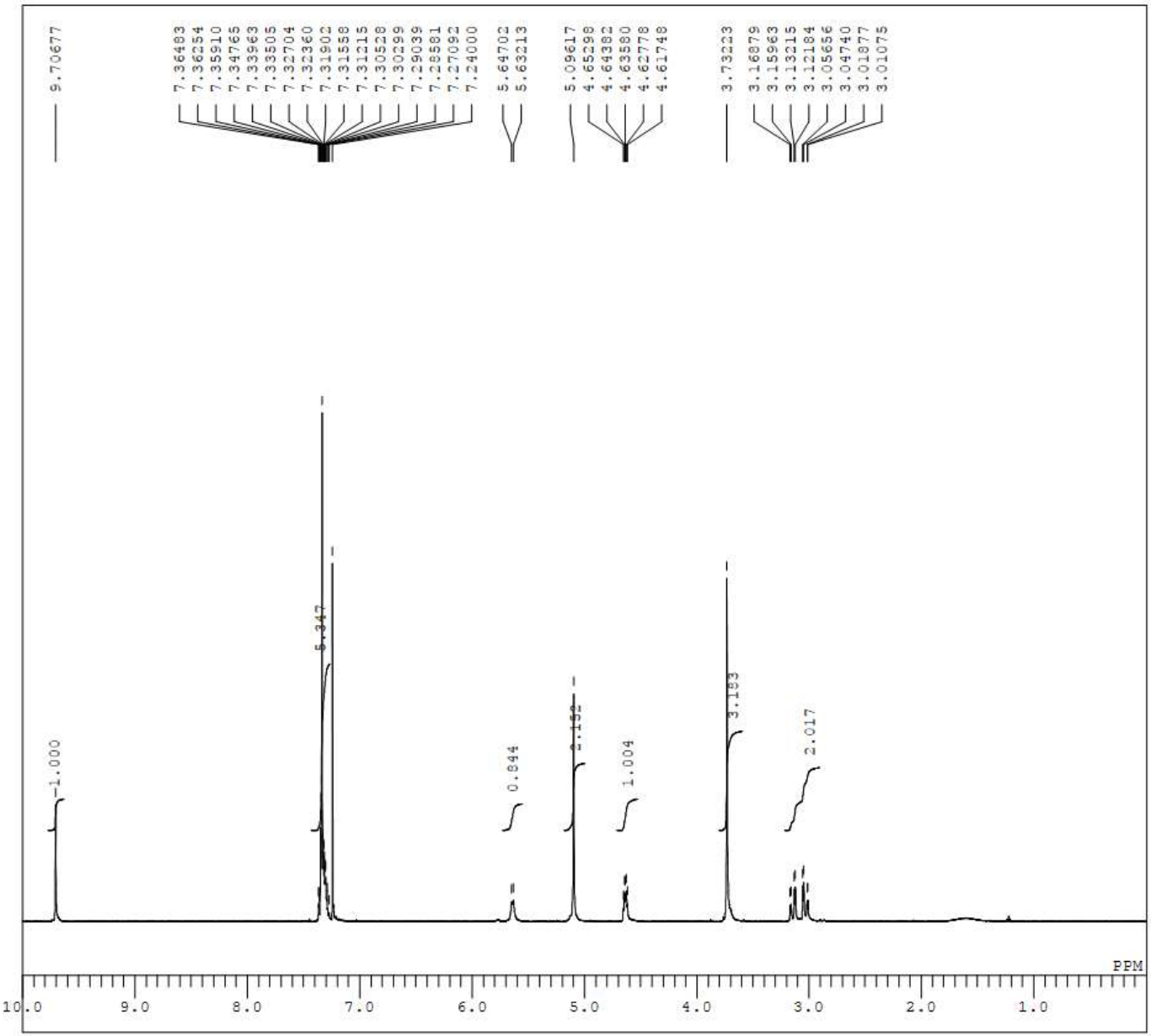
H
O
O

2ai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4.62778
4.61748
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3.13215
3.12184
3.05656
3.04740
3.01877
3.01075
5.347
1.000
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2.152
1.004
3.183
2.017
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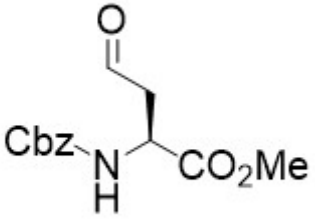
7.0
6.0
5.0
4.0
3.0
2.0
1.0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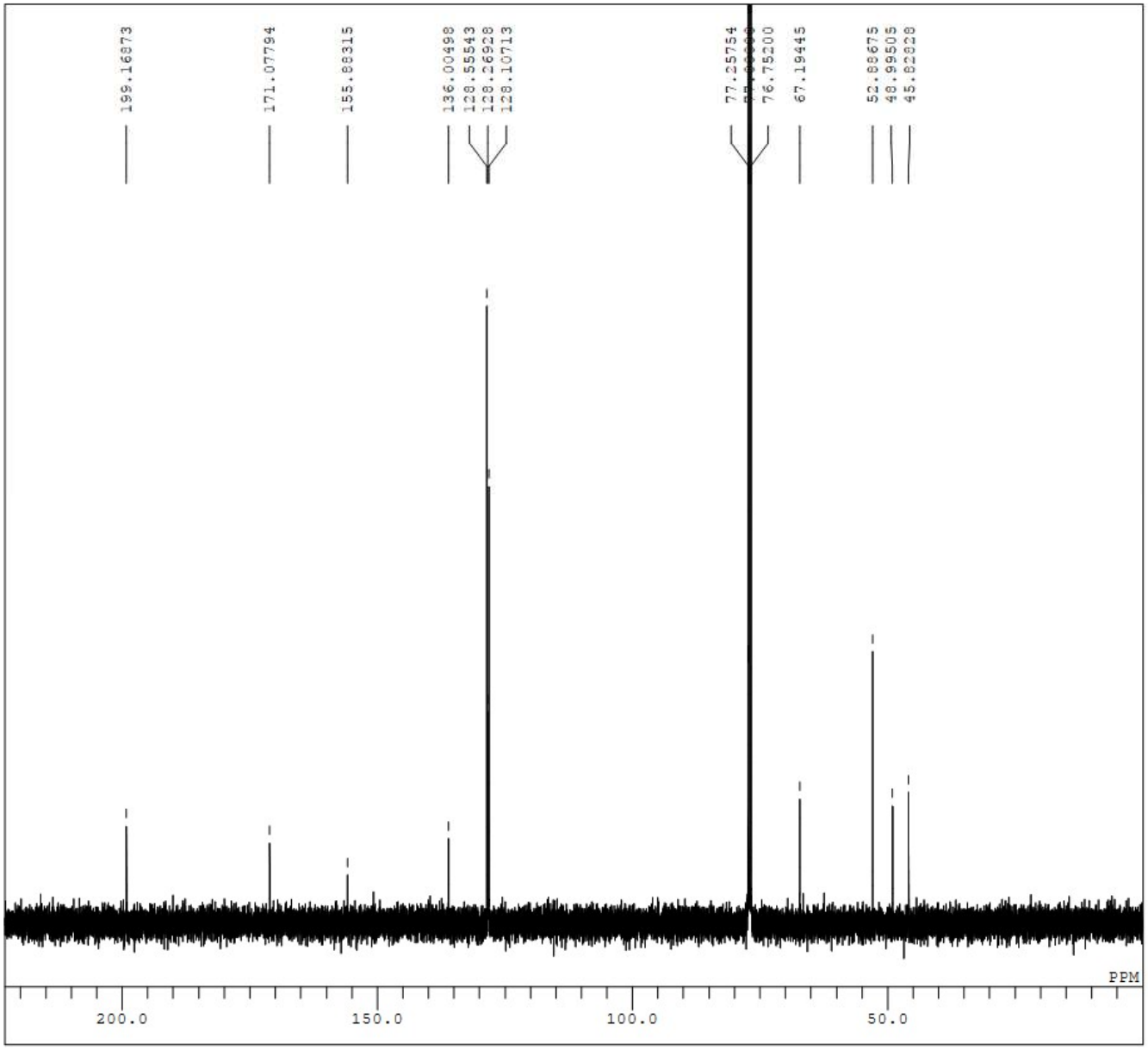
Cbz
N
H
CO2Me

2aj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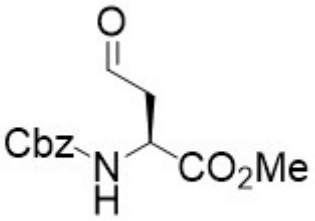
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Cbz
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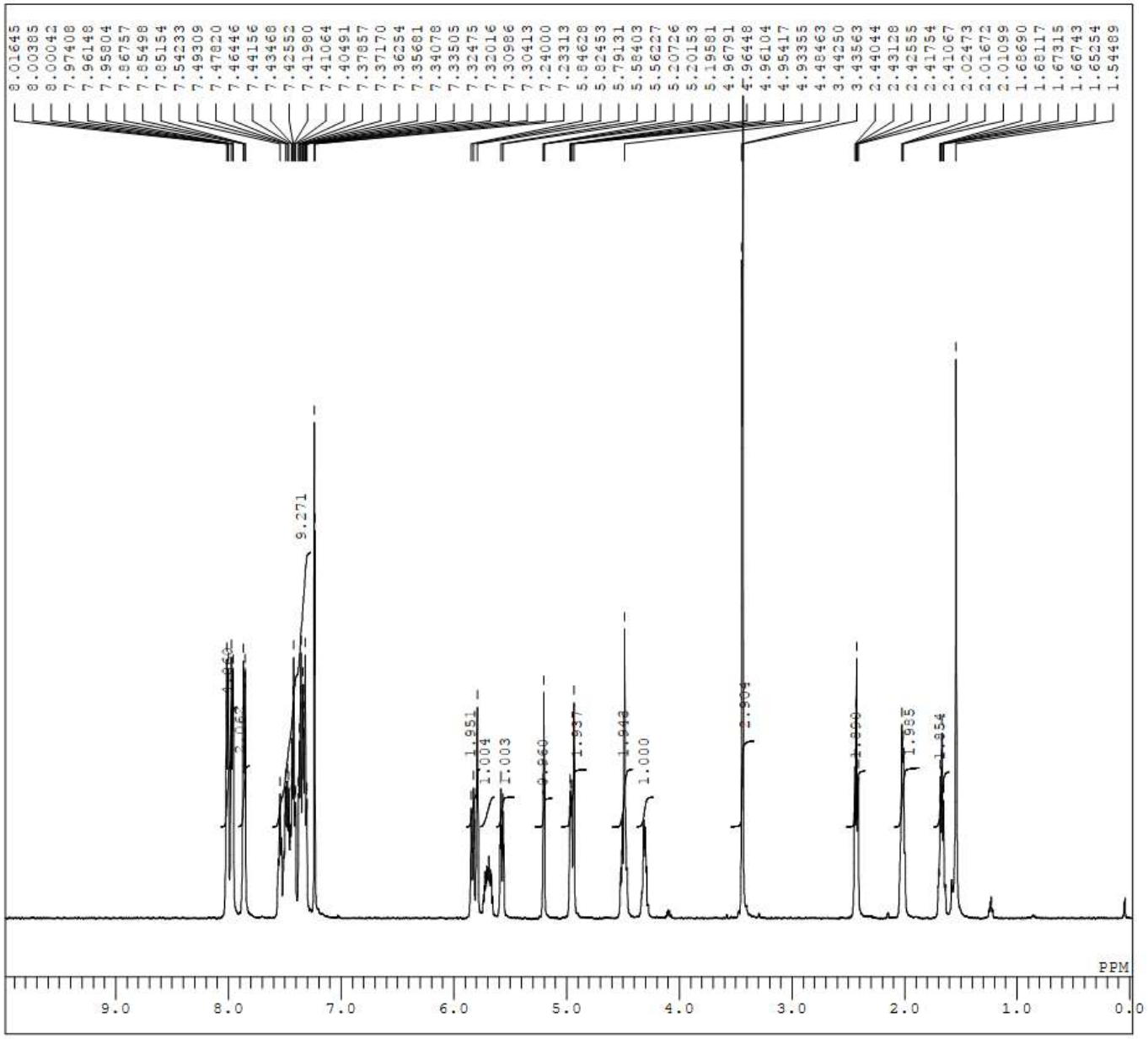
2aj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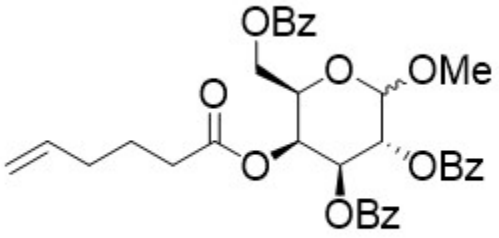
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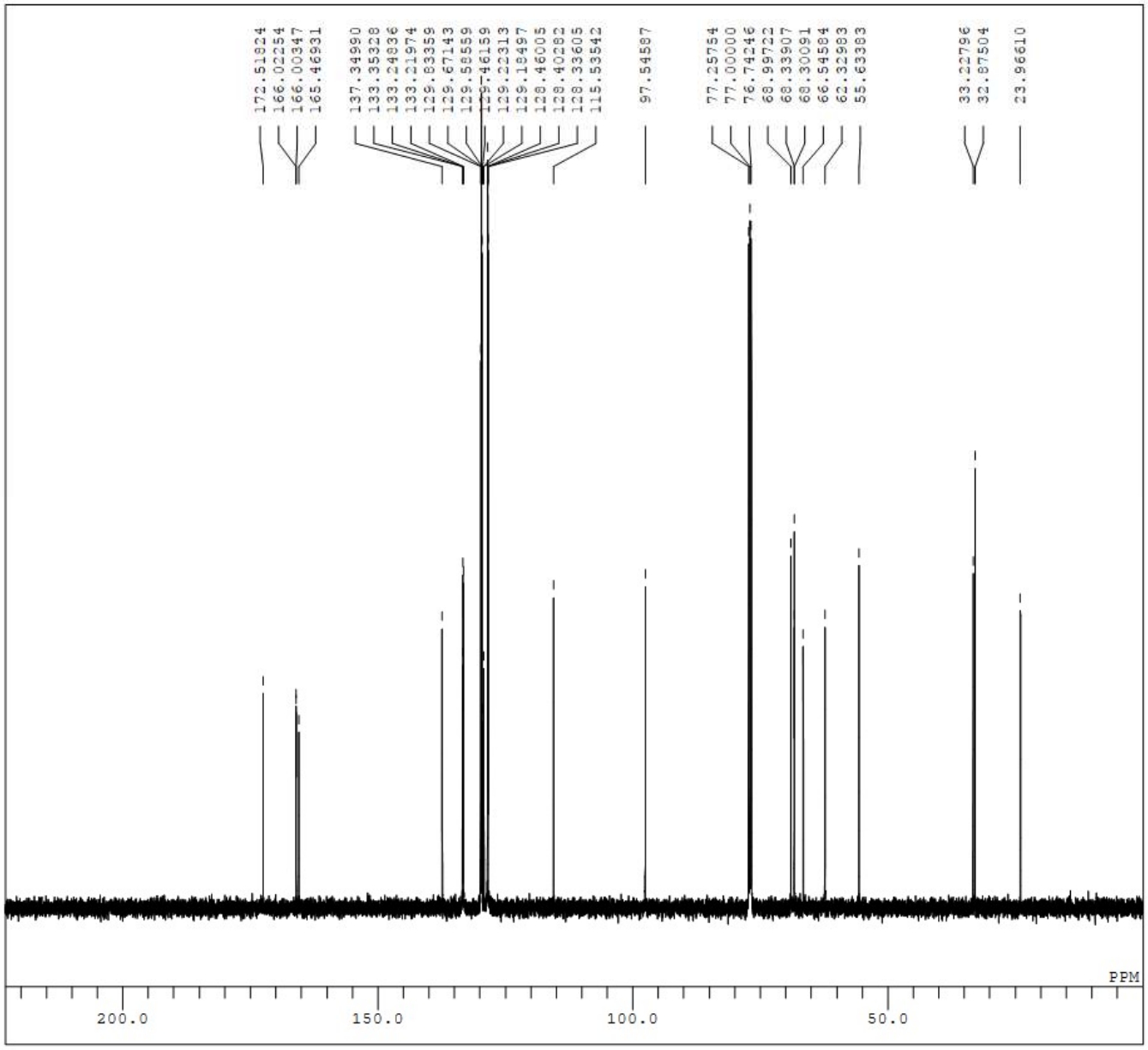
OMe
O
O
OBz
OBz

S4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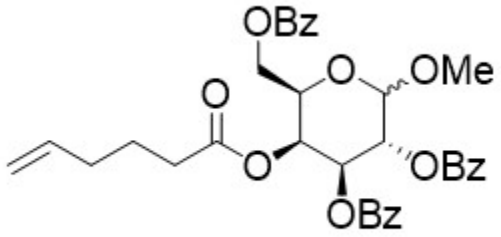
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OMe
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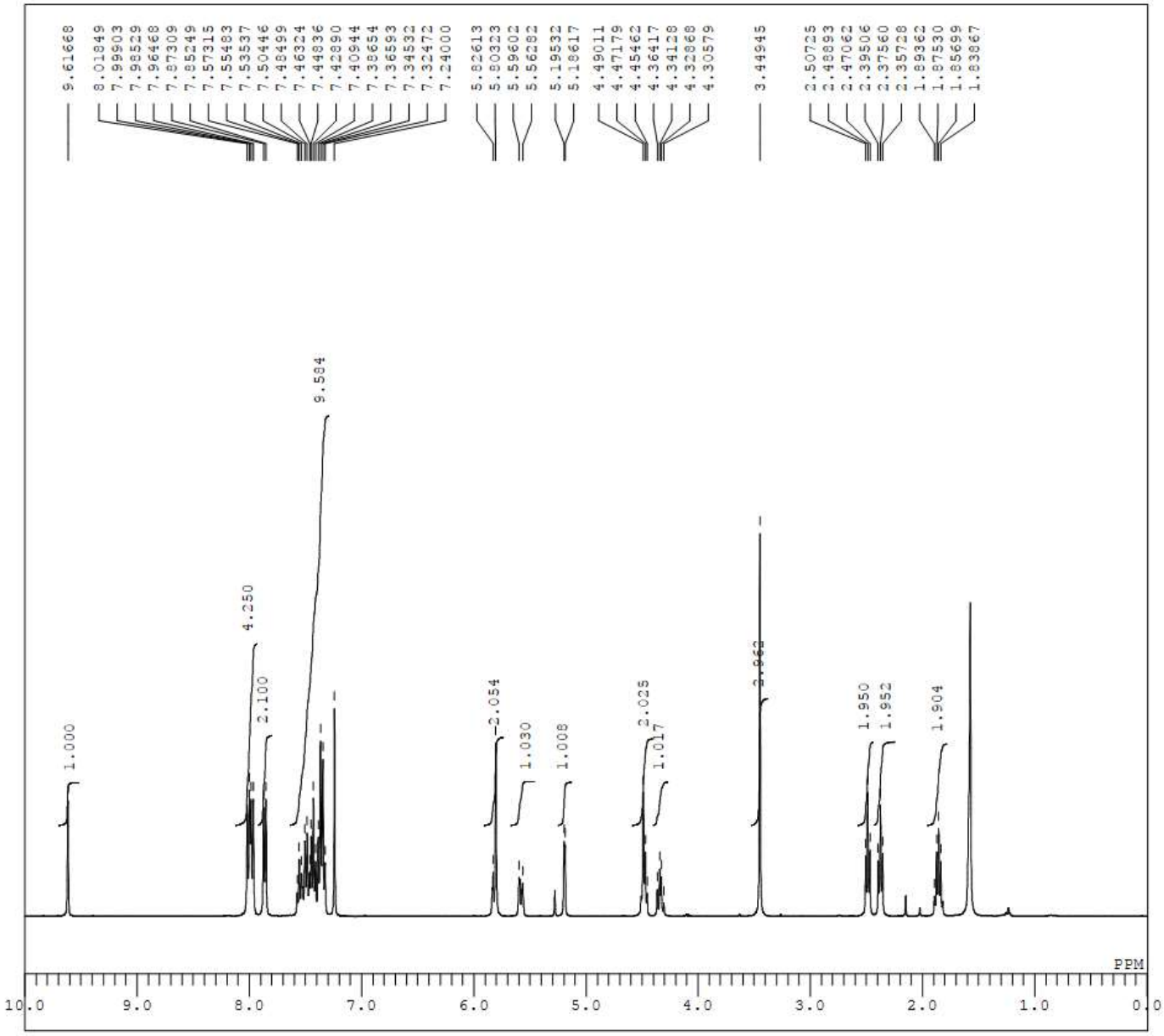
O
OBz
OBz

S4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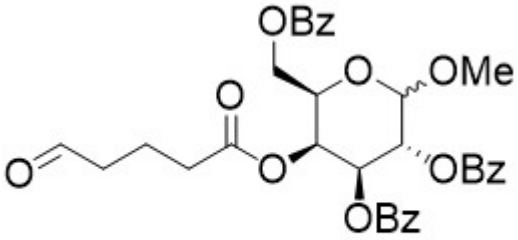
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OMe
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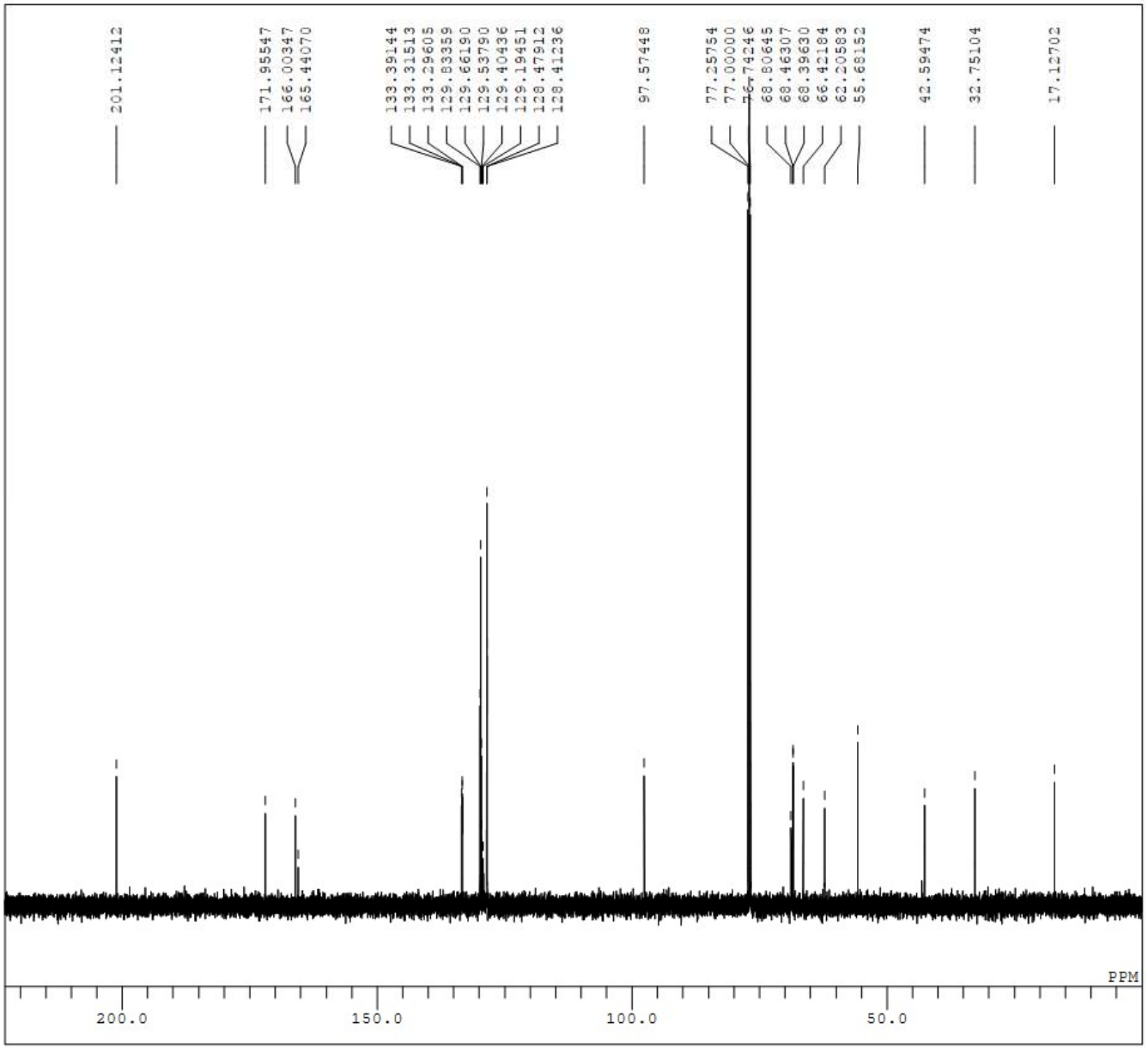
O
OBz
O
OBz

2ak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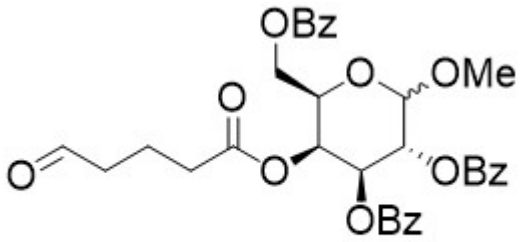
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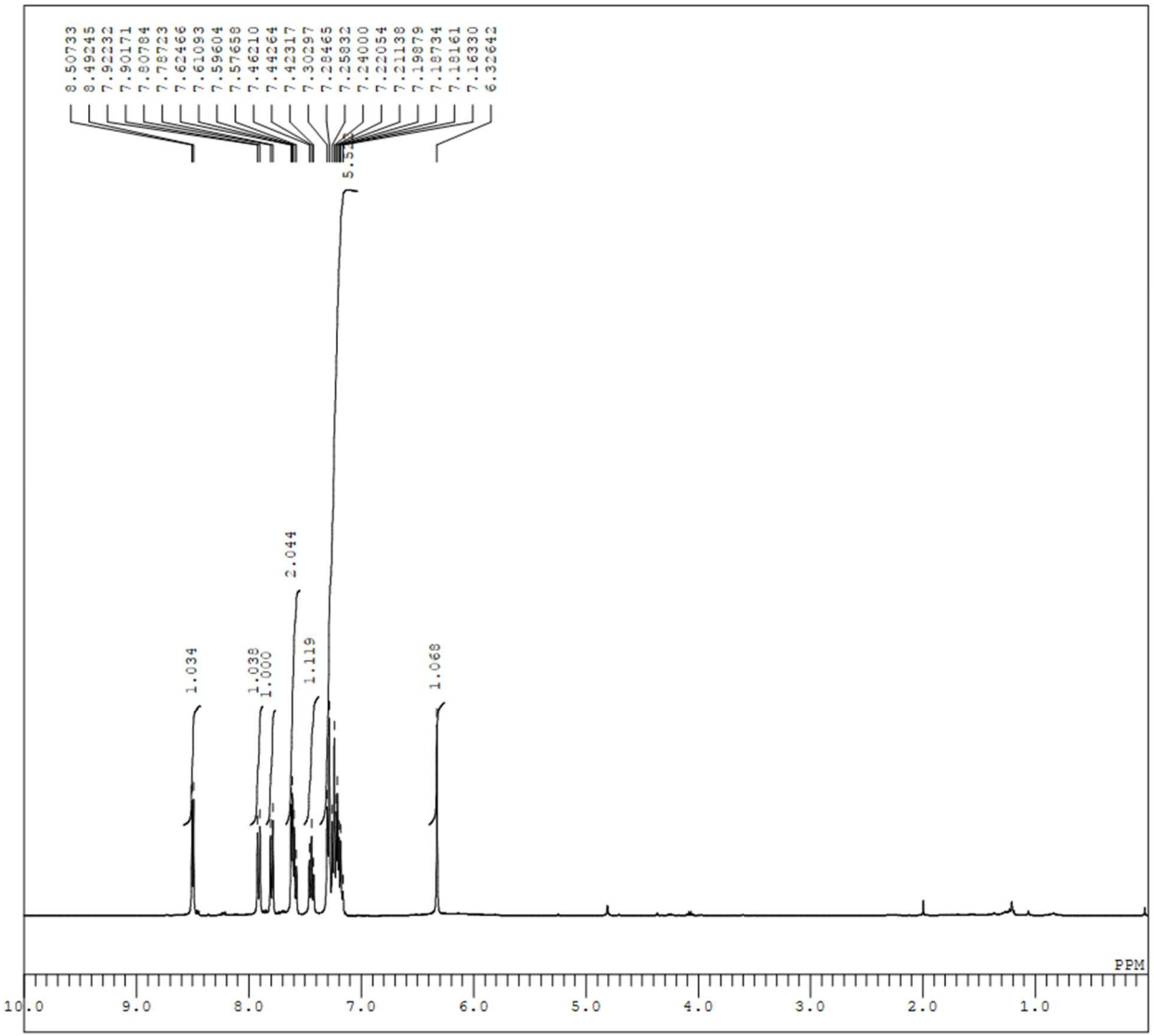
OBz
OBz

2ak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7.16330
6.32642
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1.039
1.000
2.044
1.119
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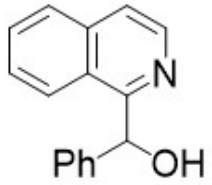
1.0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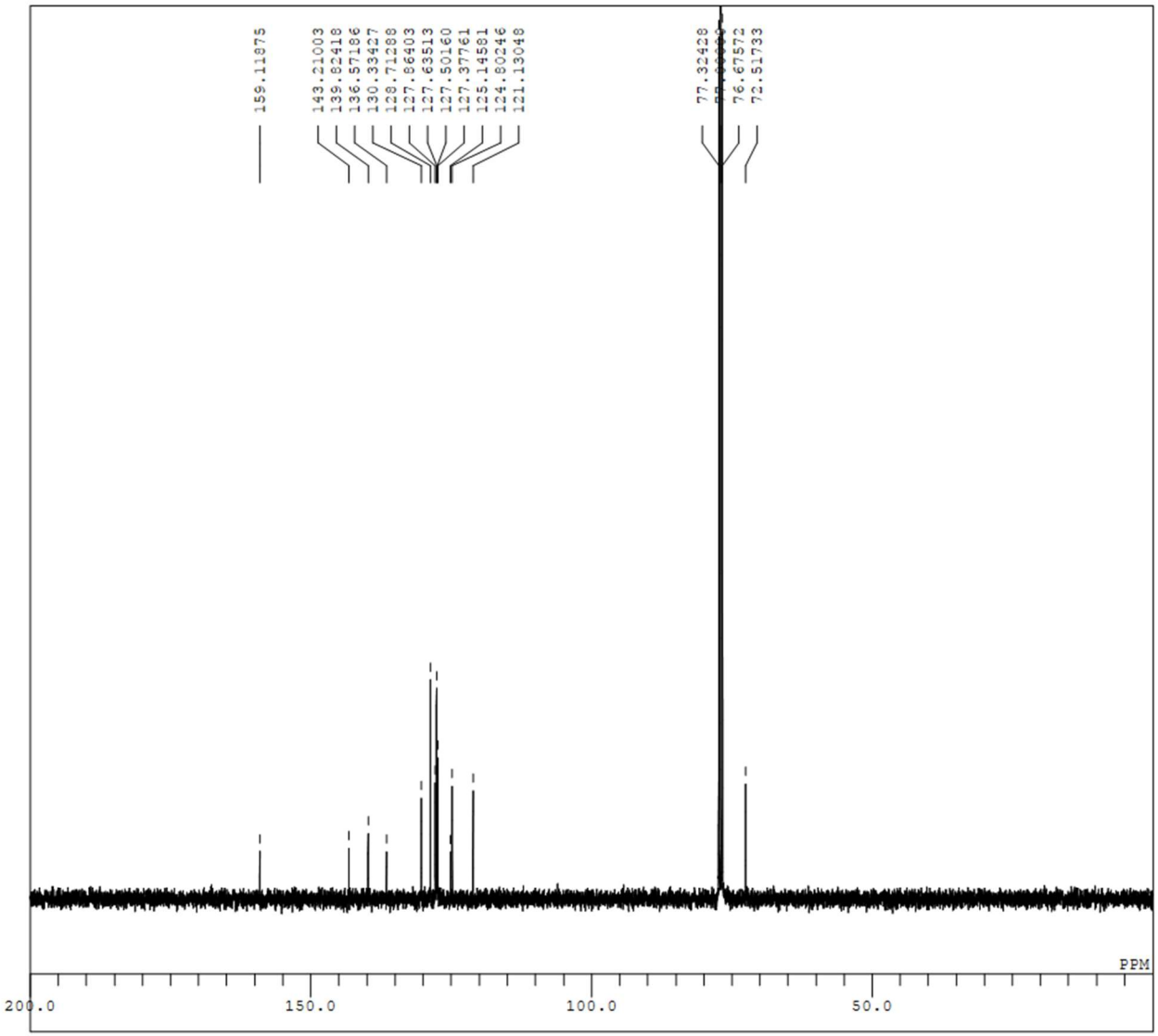
Ph
OH

3a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PPM
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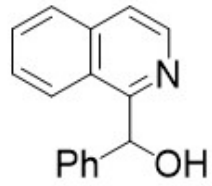
150.0
100.0
50.0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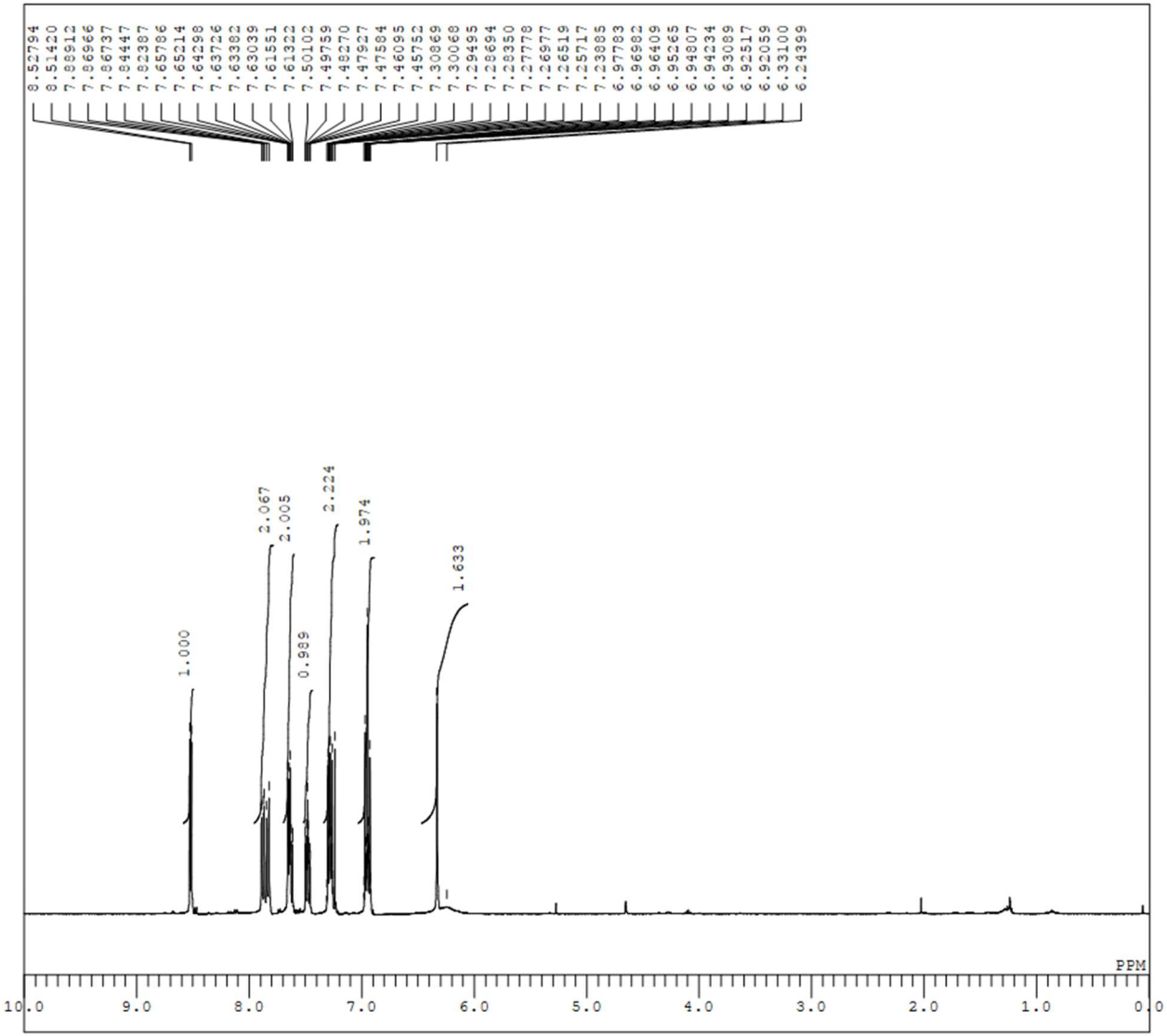
Ph
OH

3a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1.633
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6.0
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4.0
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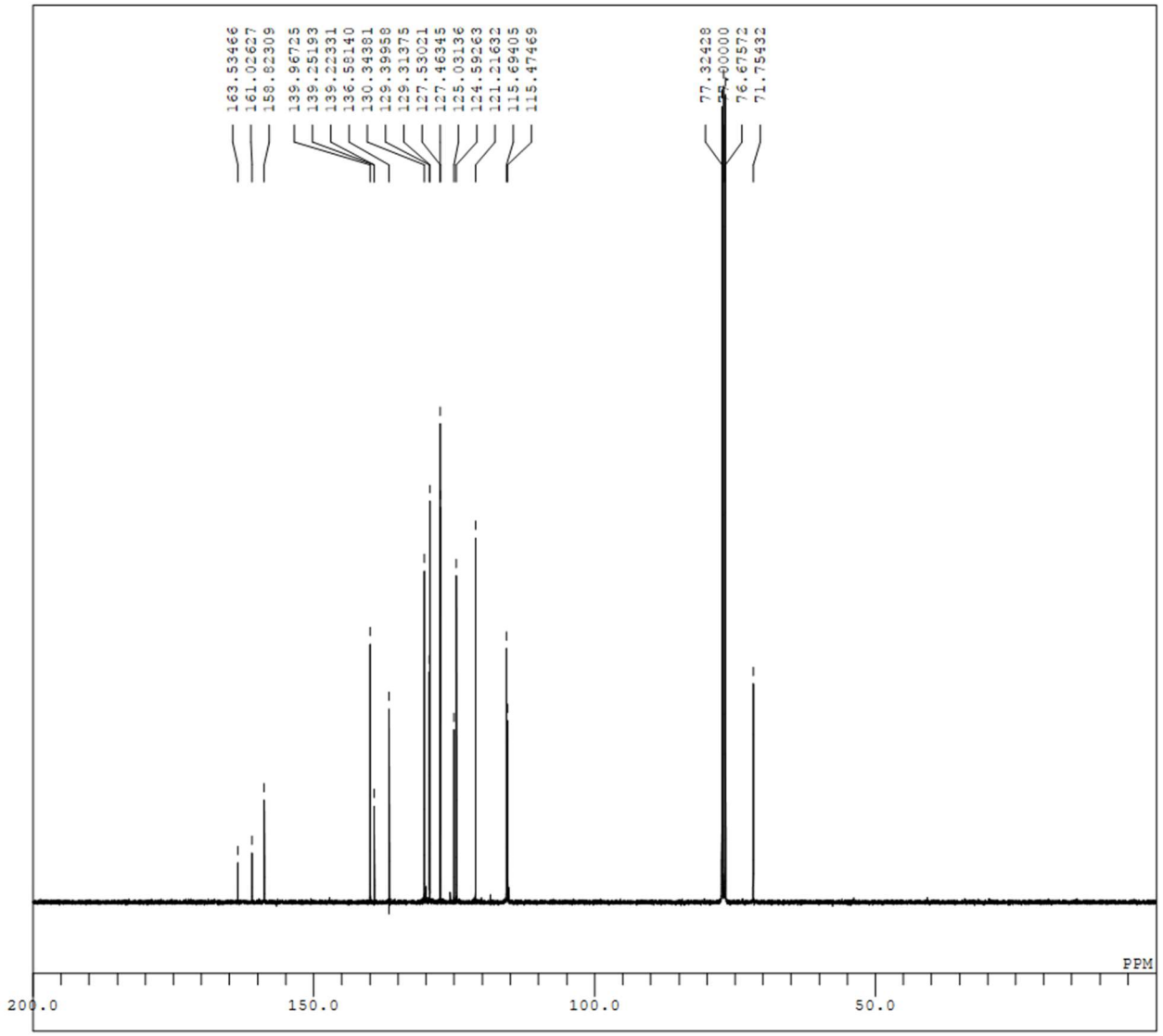
1.0
0.0


N
OH
F

3b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127.46345
125.03136
124.59263
121.21632
115.69405
115.47469
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76.67572
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PPM
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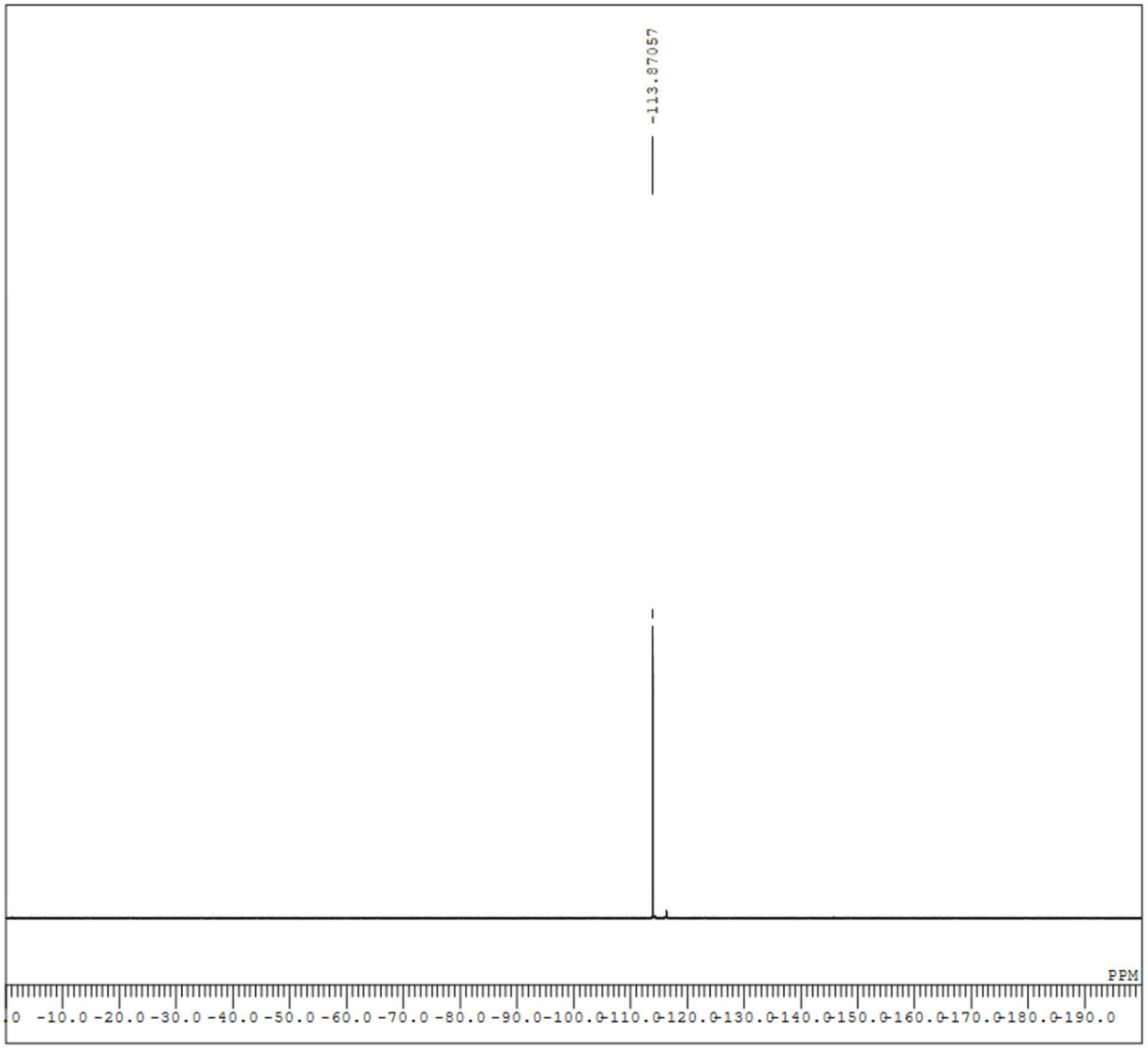
150.0
100.0
50.0


N
OH
F

3b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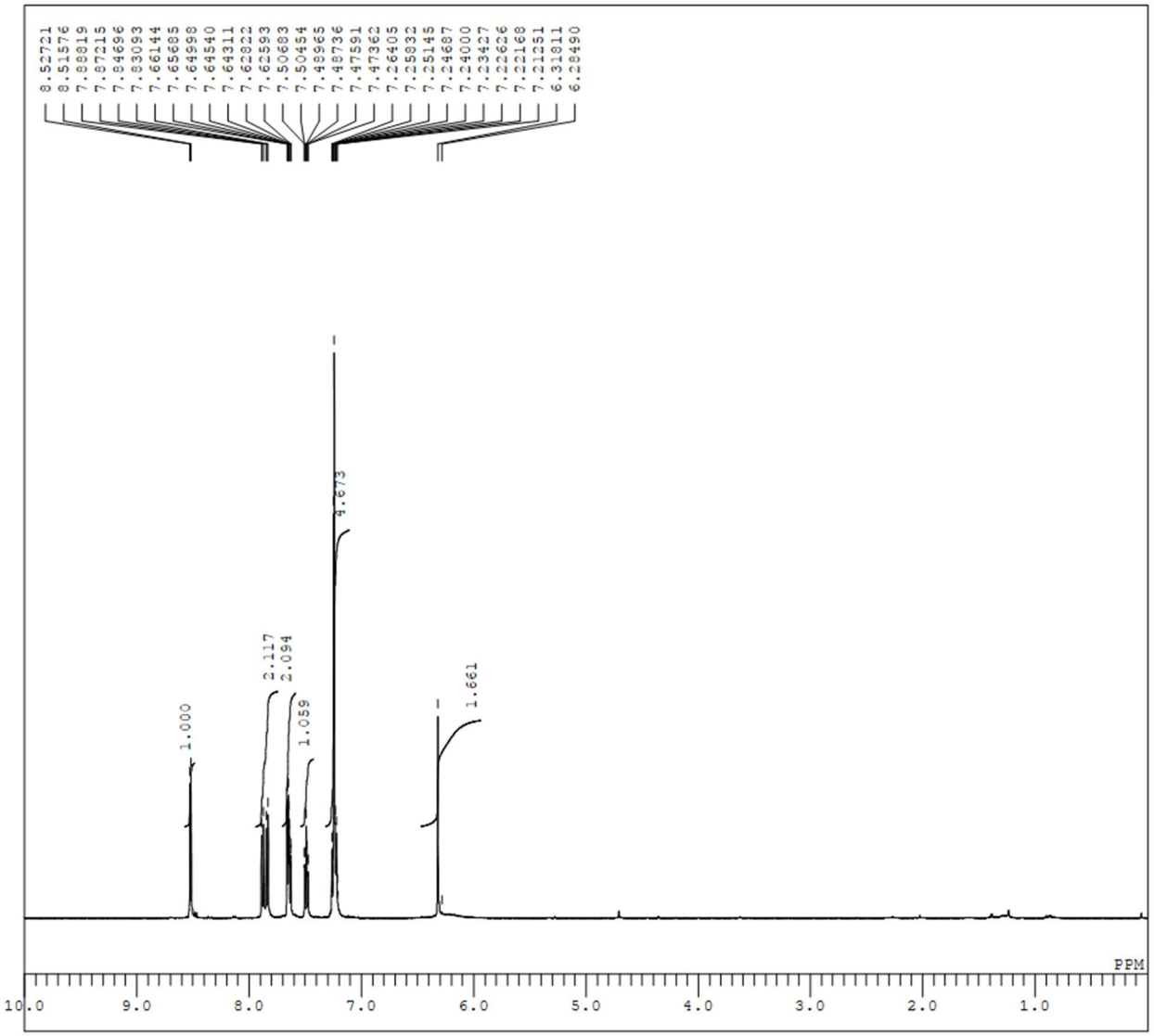
PPM
0.0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0


N
OH
F

3b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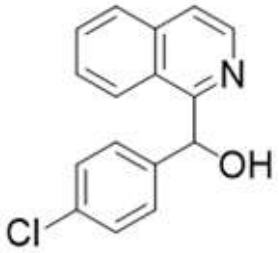
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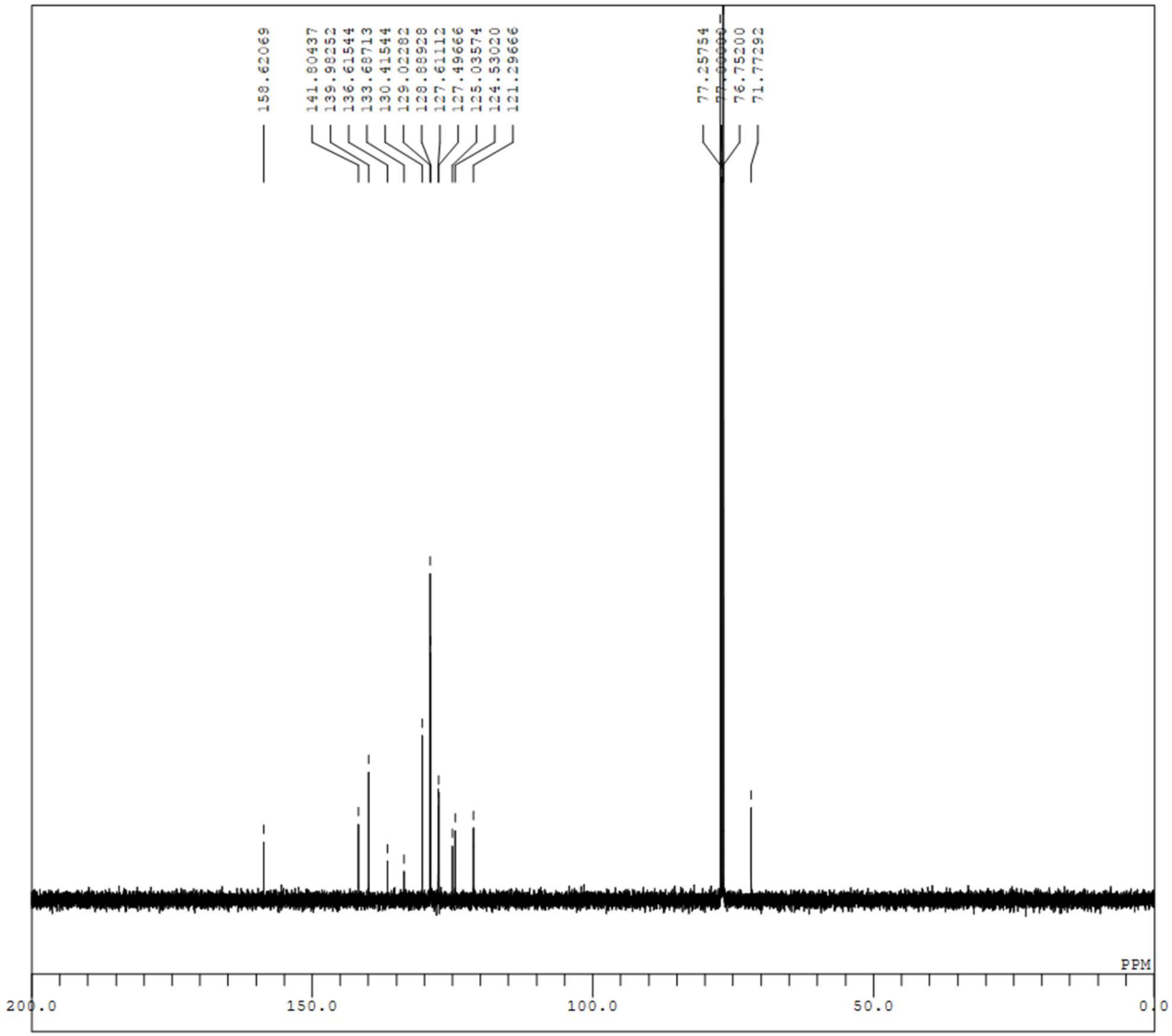
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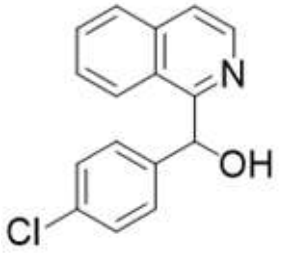
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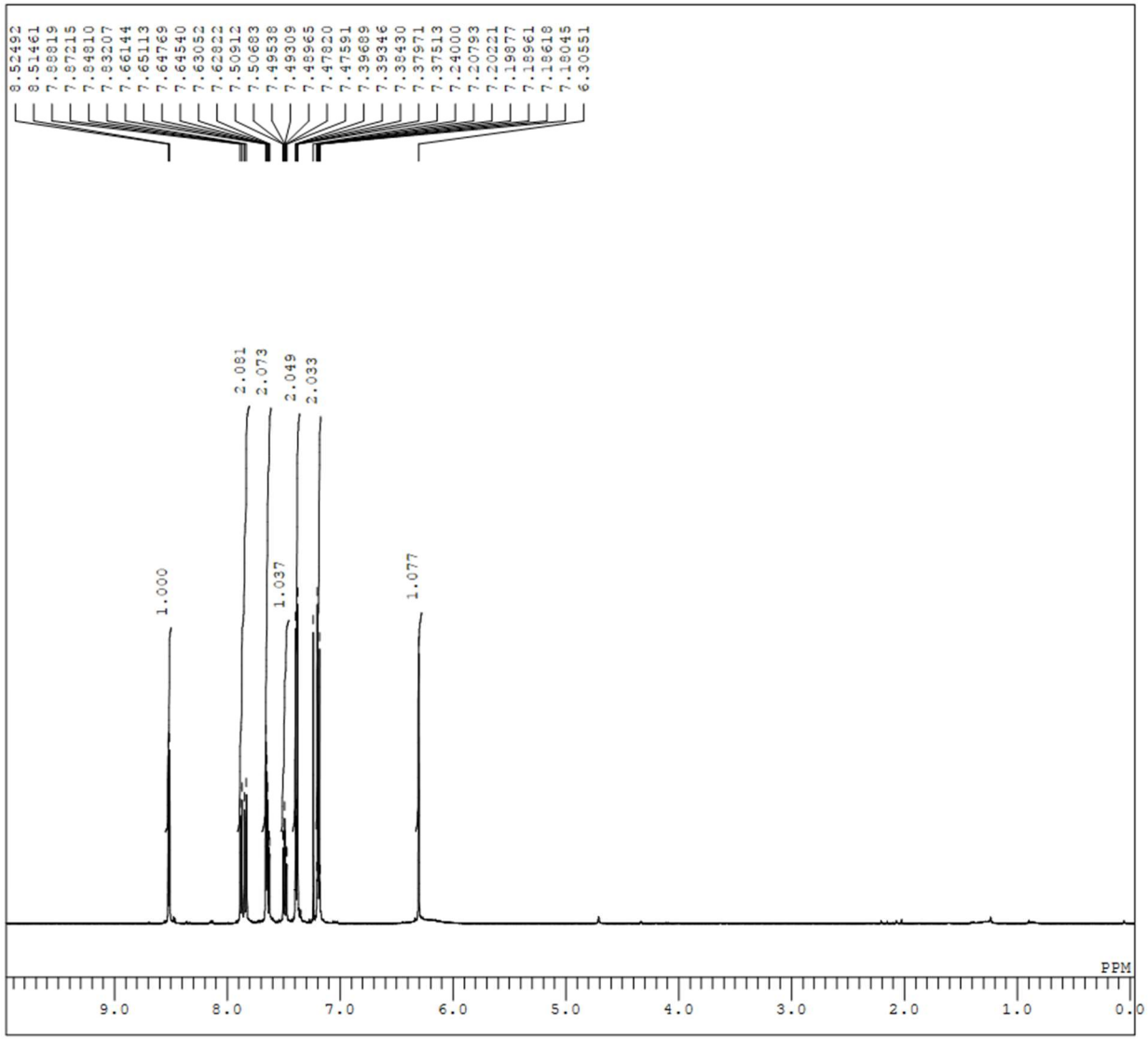
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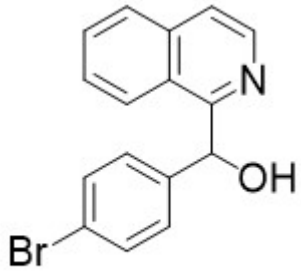
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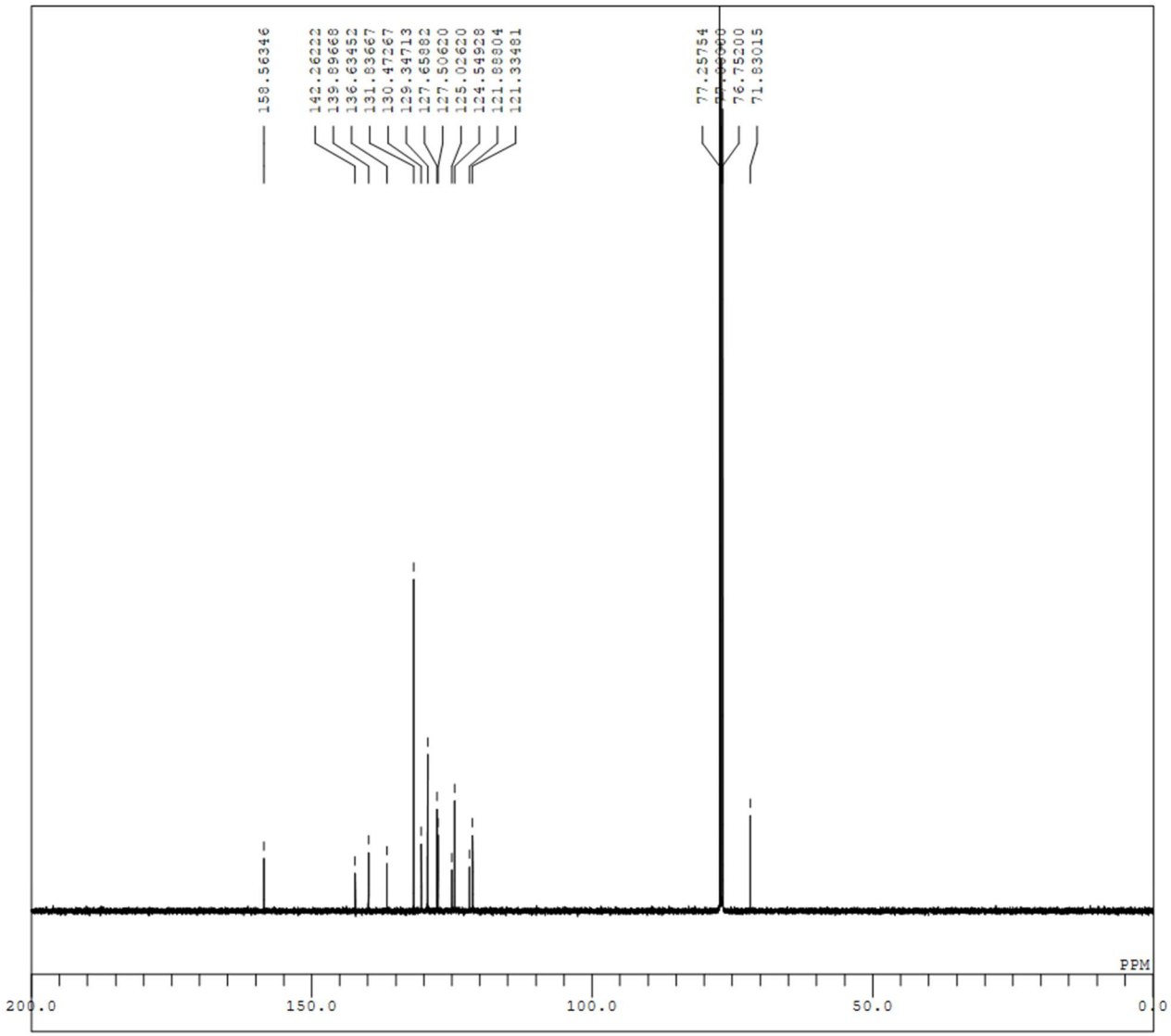
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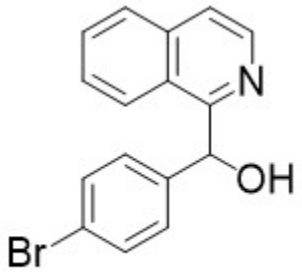
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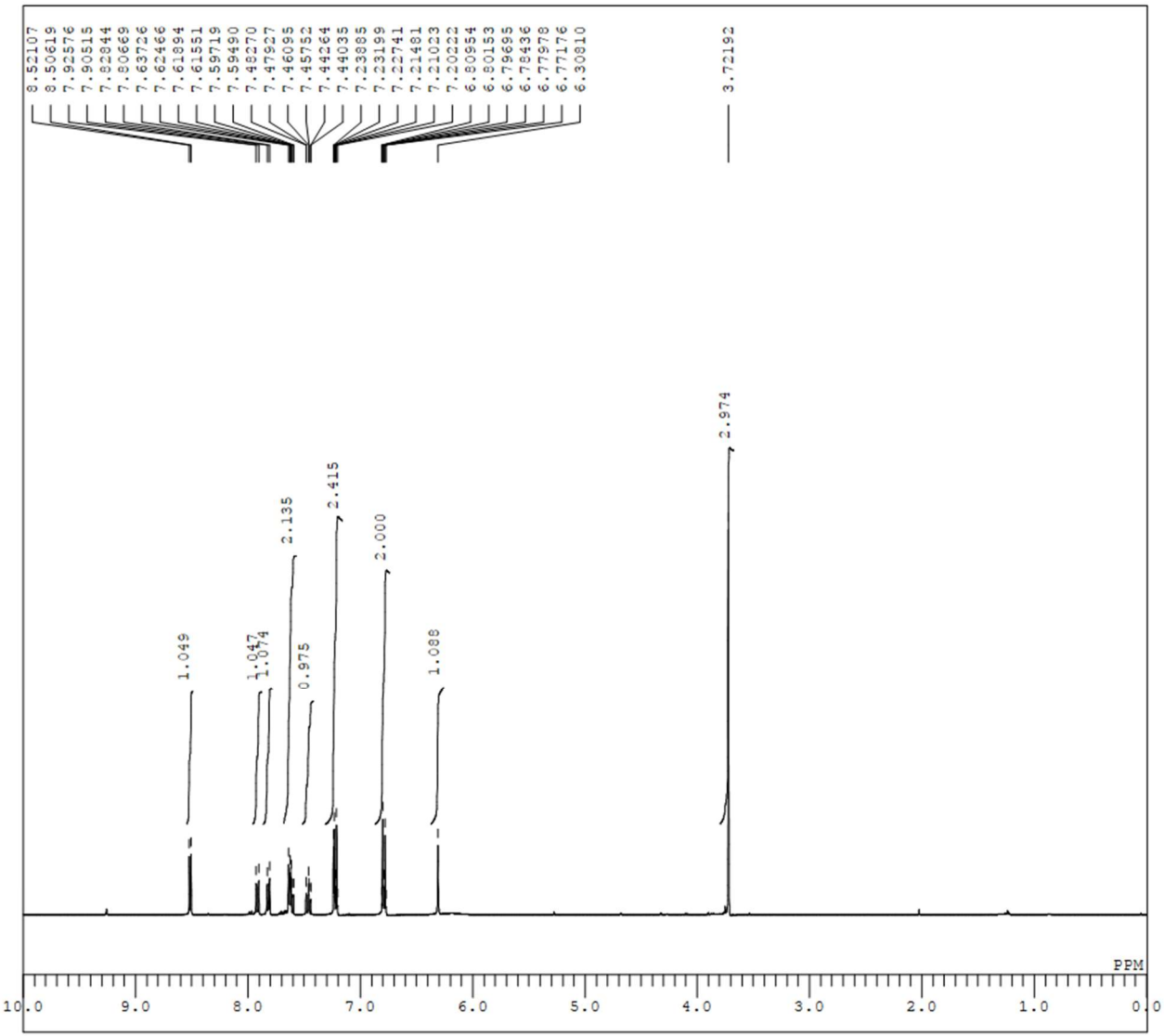
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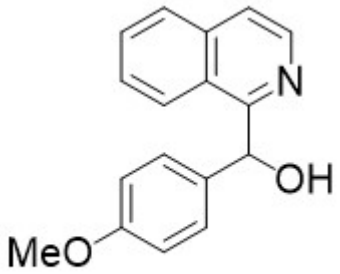
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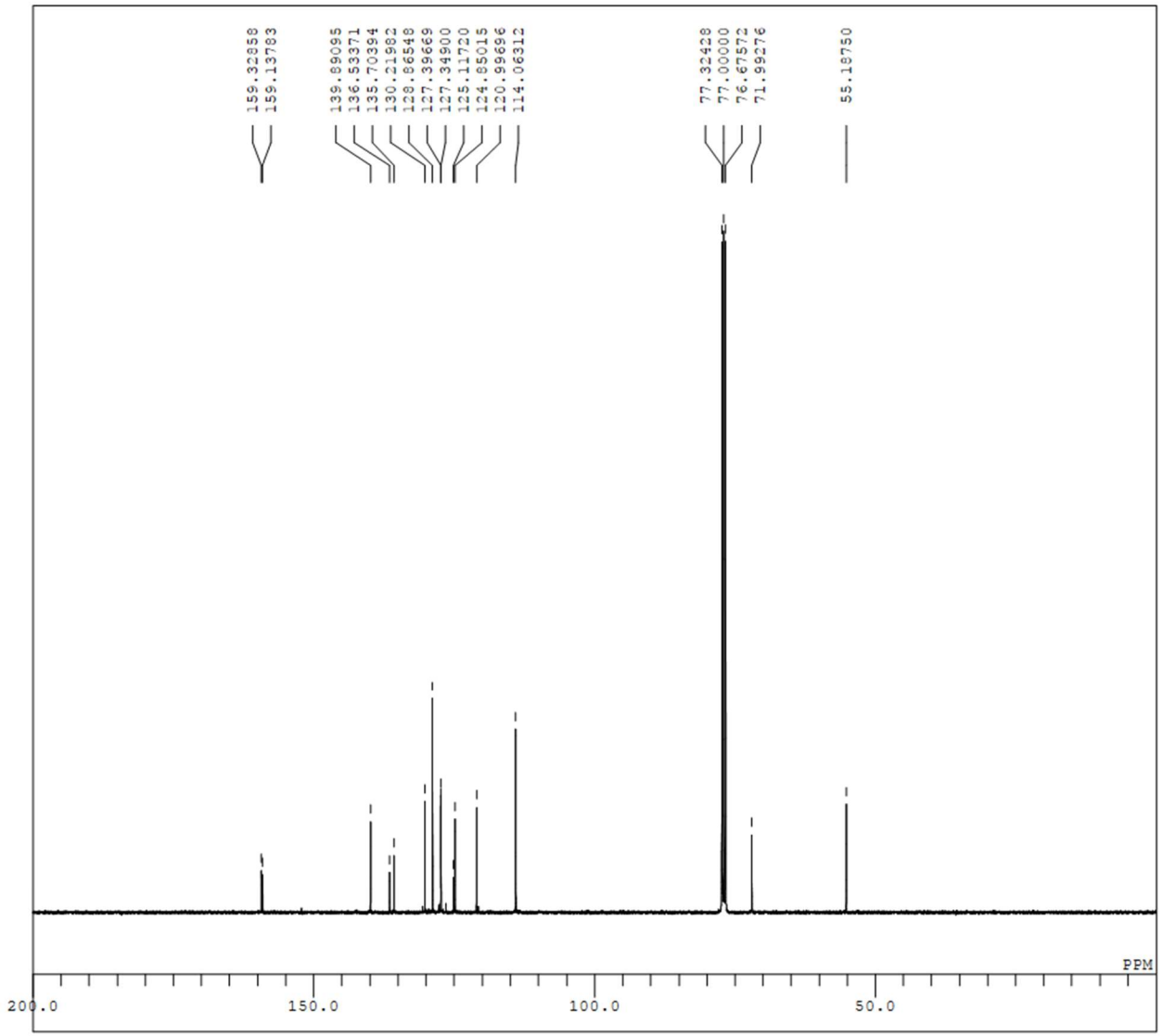
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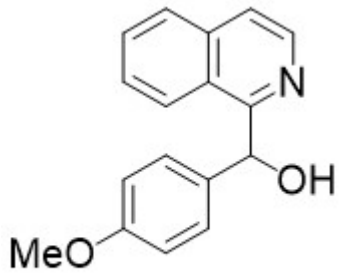
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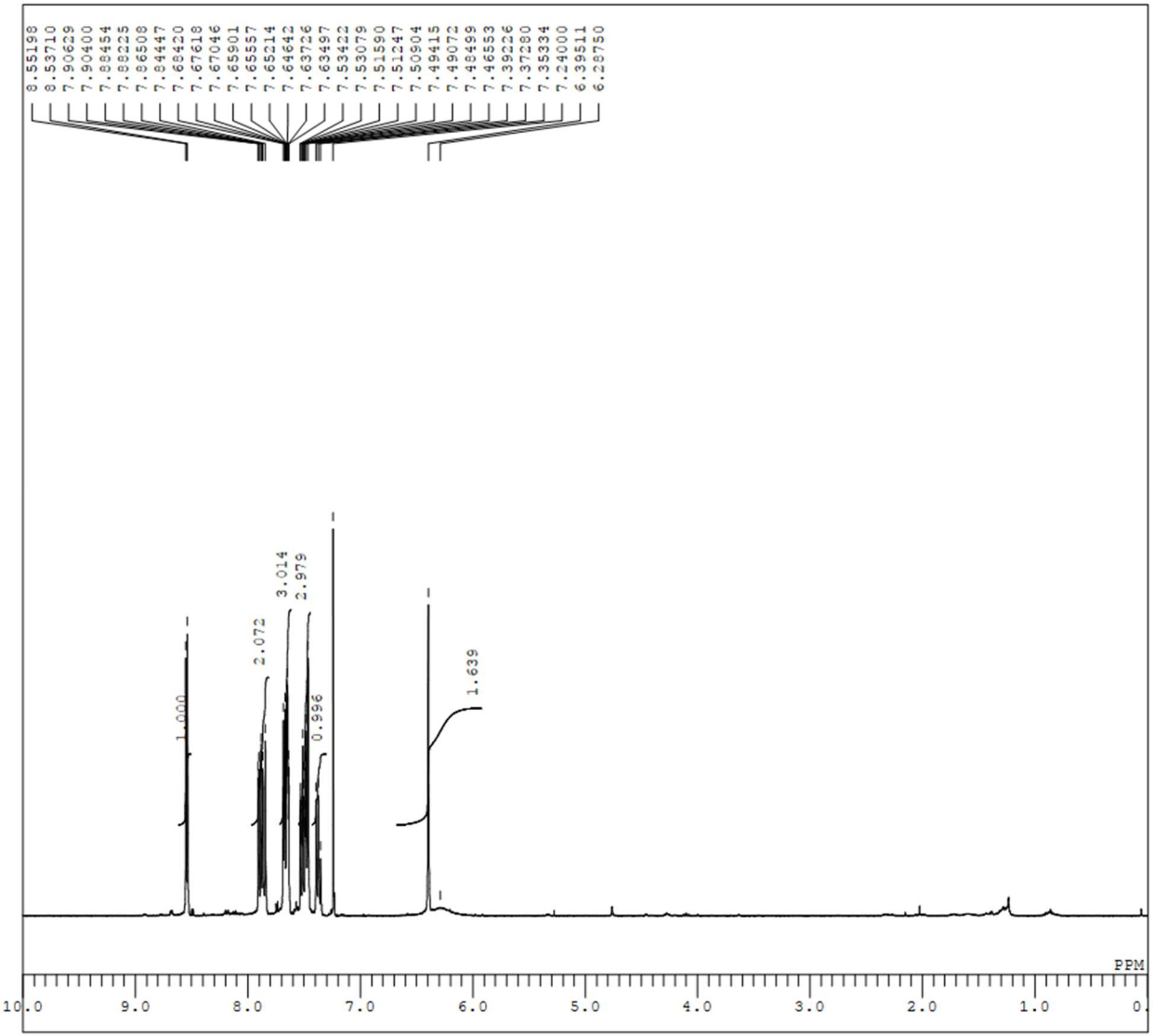
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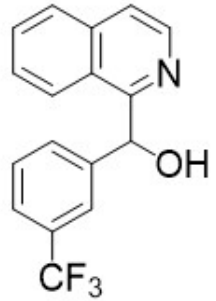
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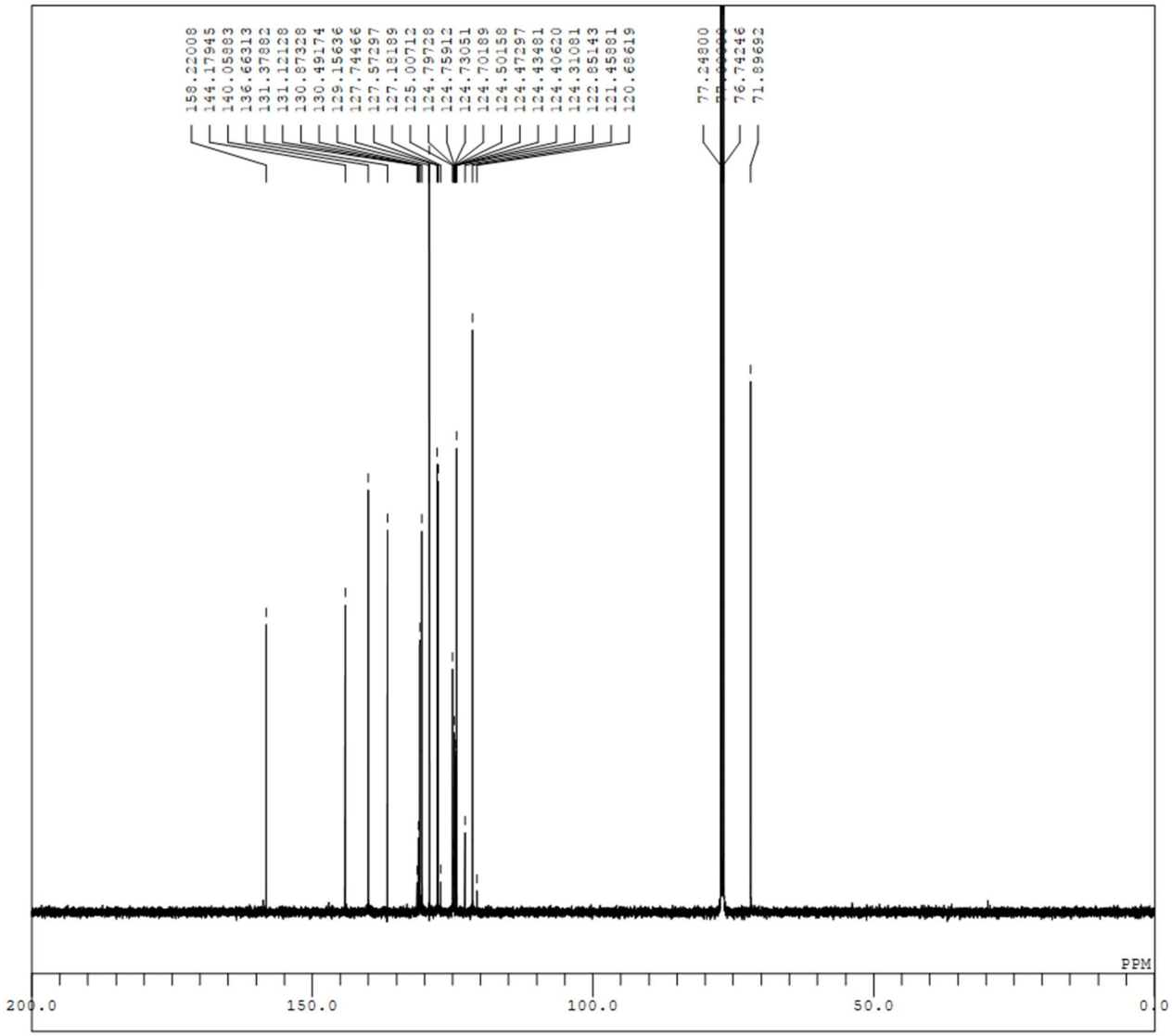
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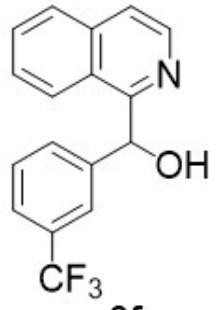
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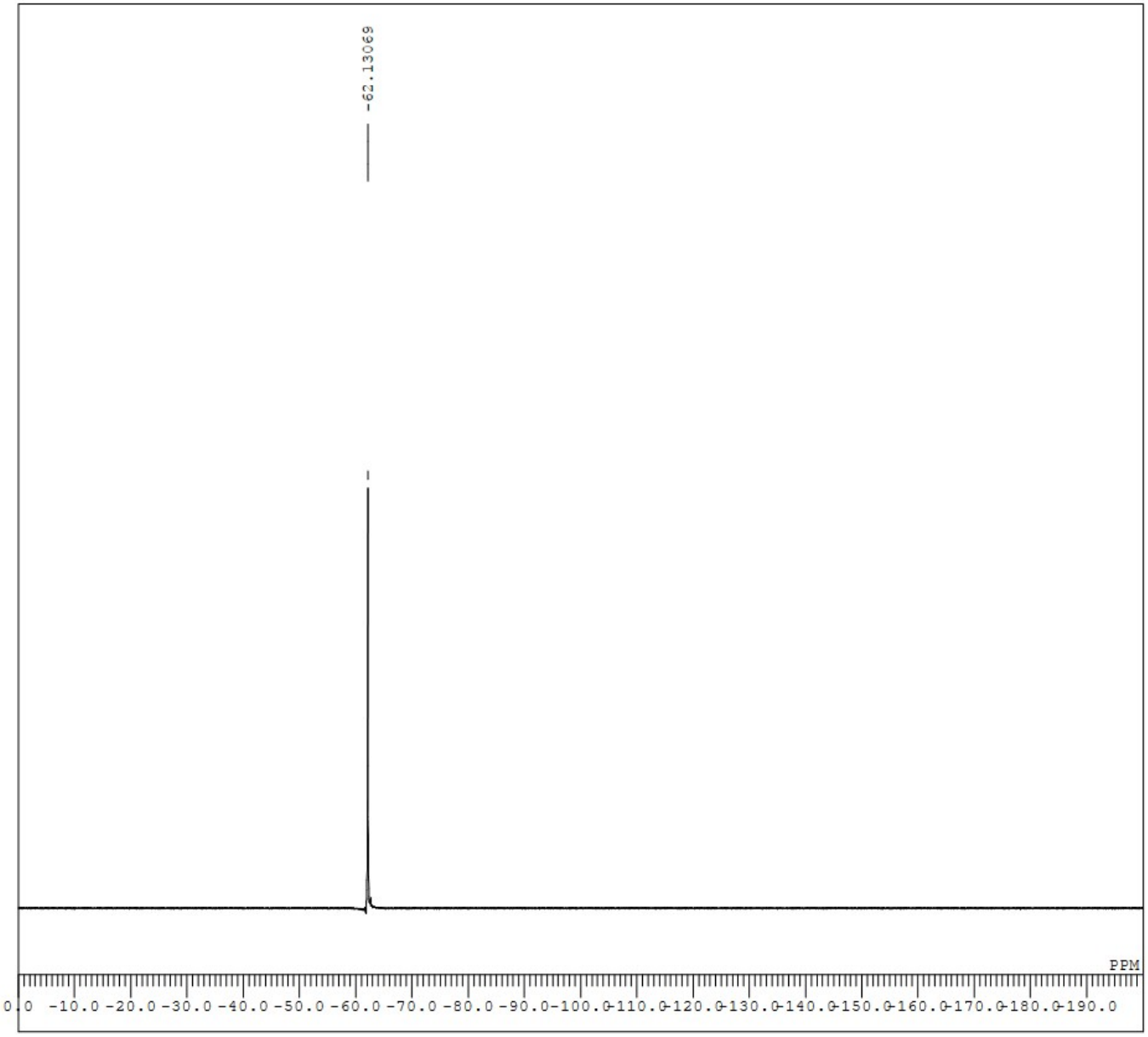
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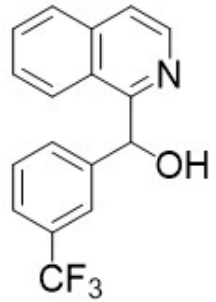
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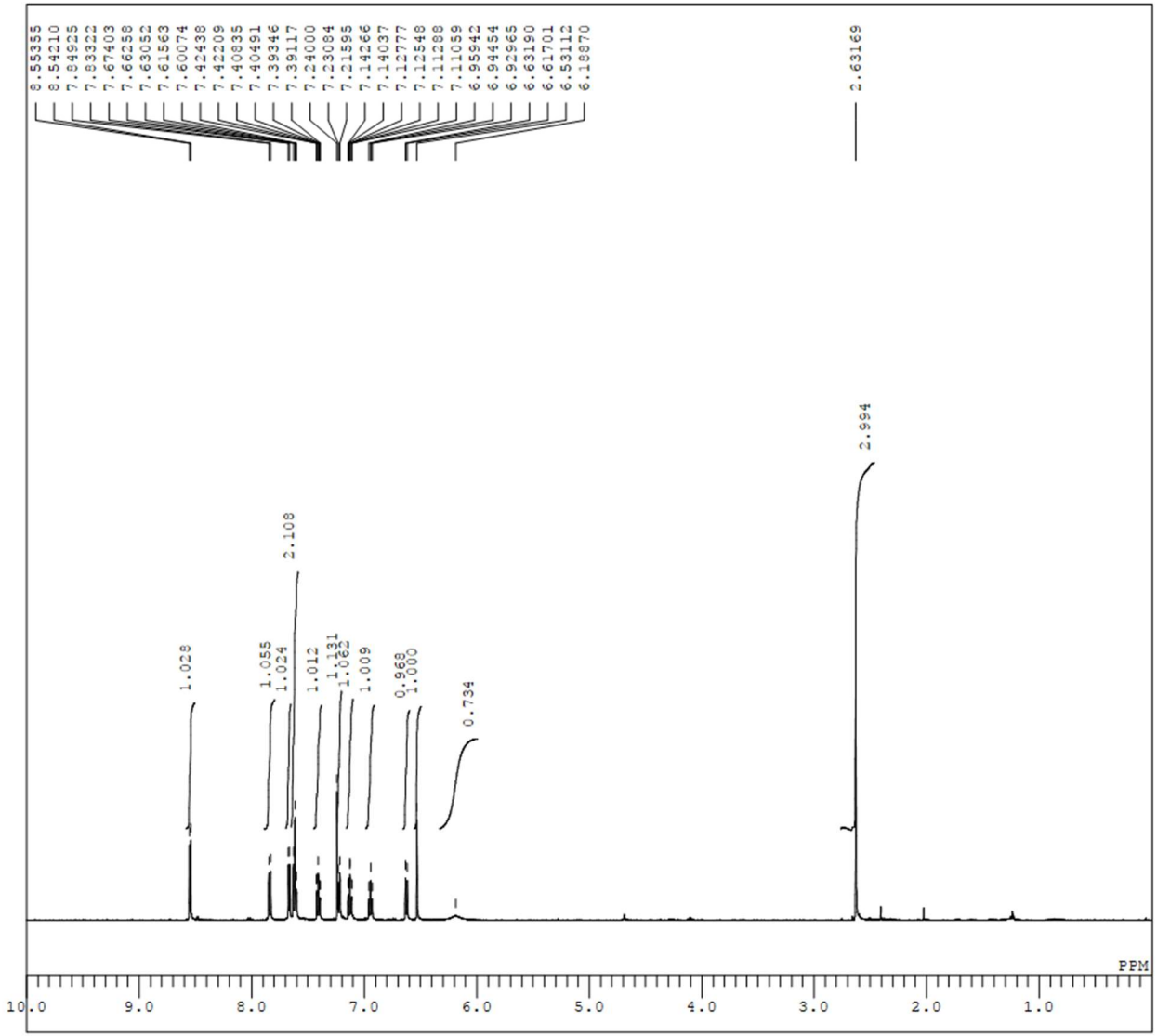
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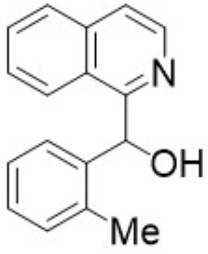
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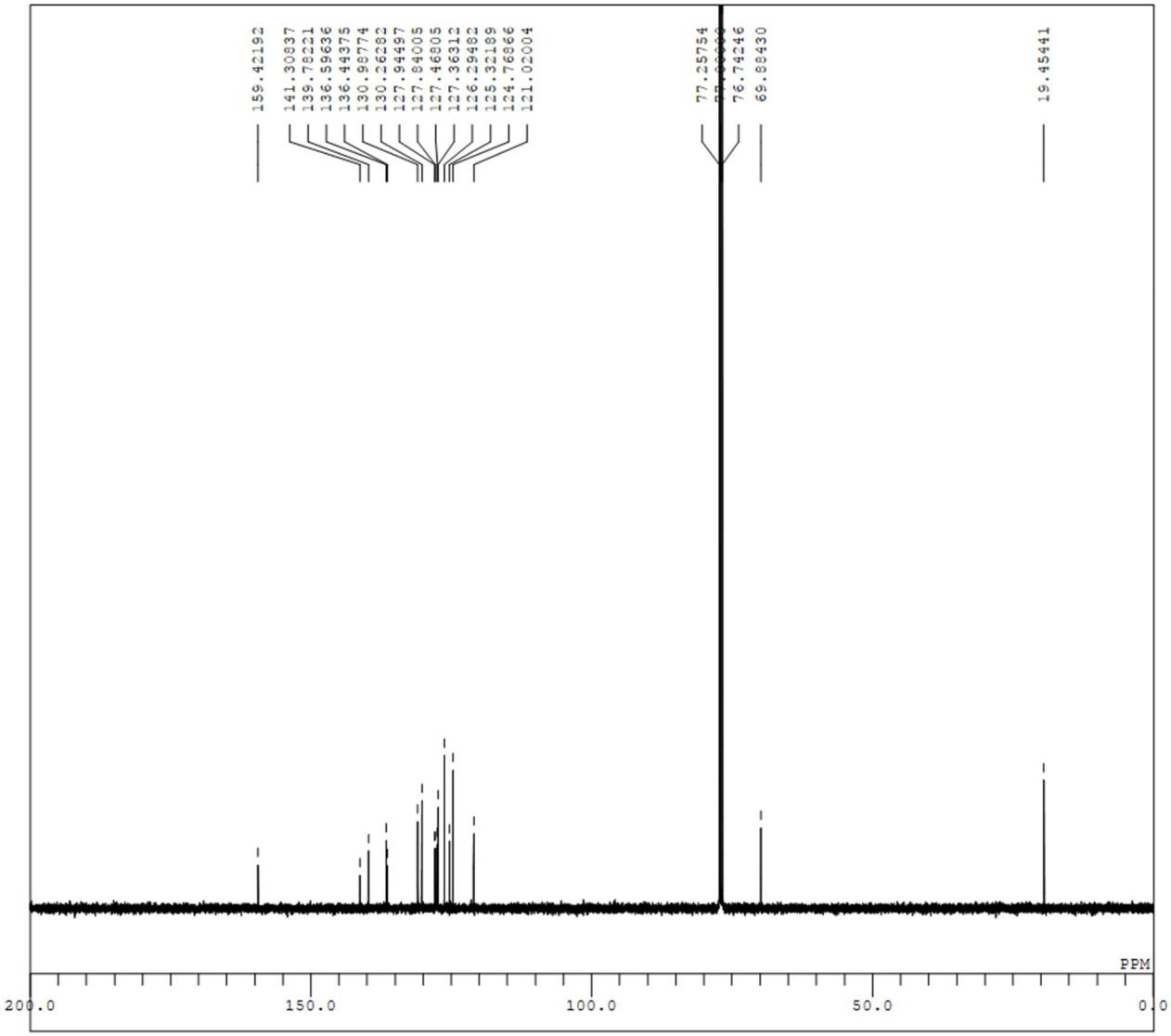
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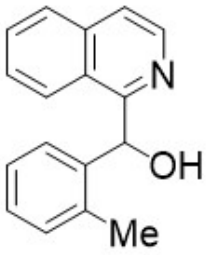
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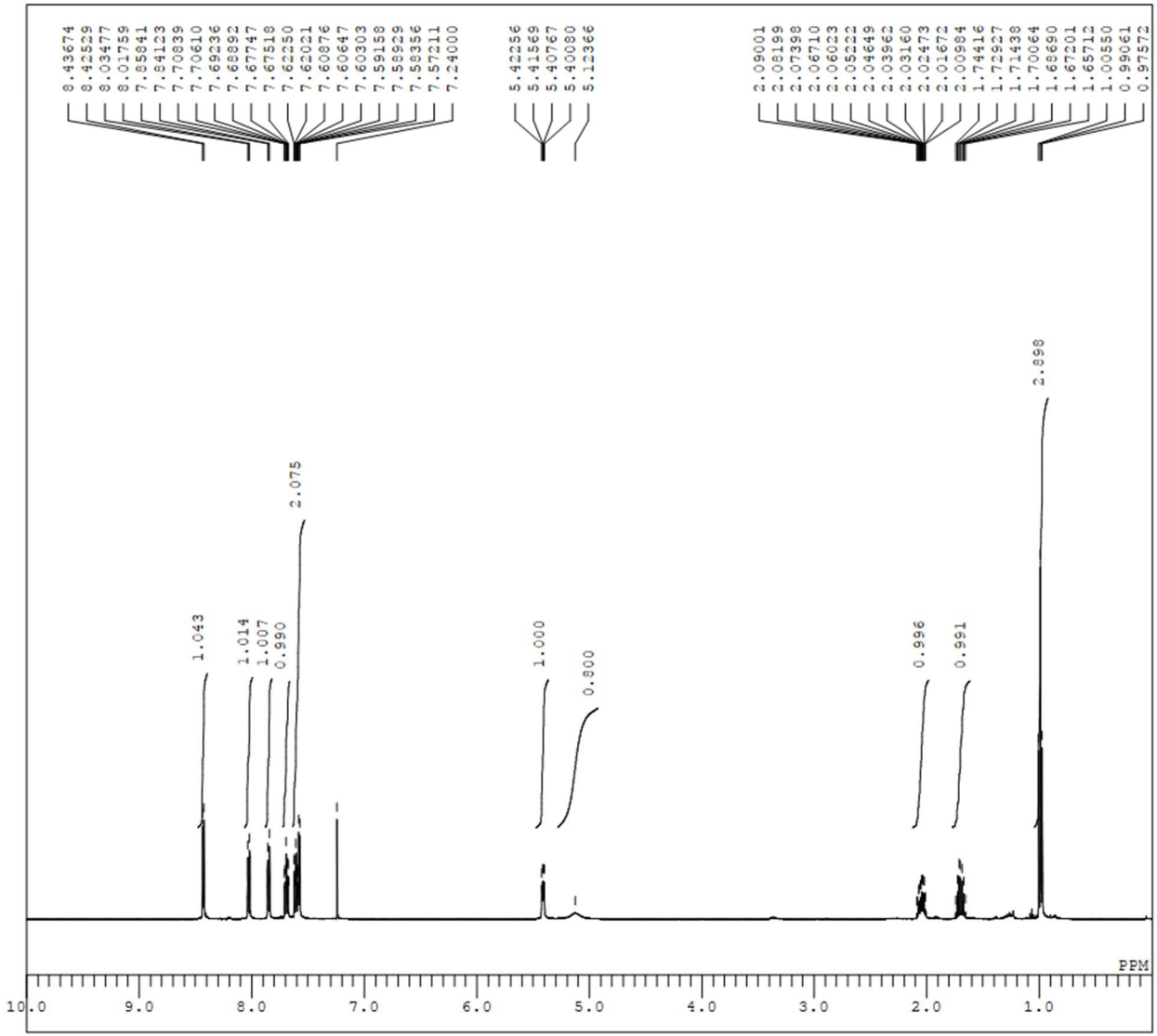
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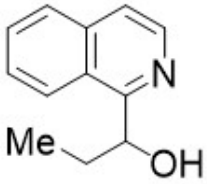
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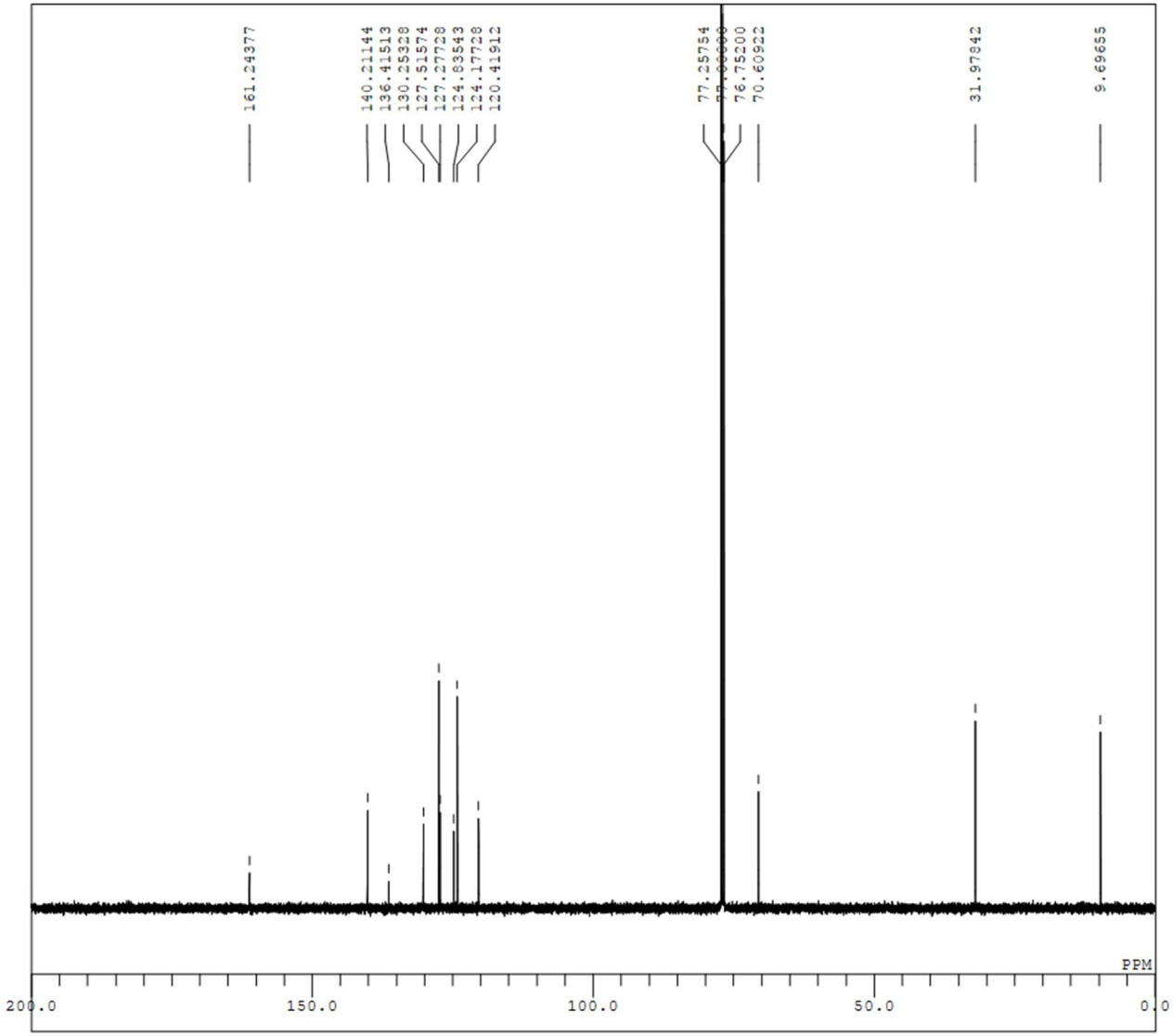
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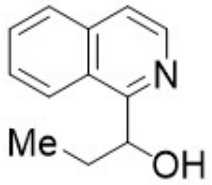
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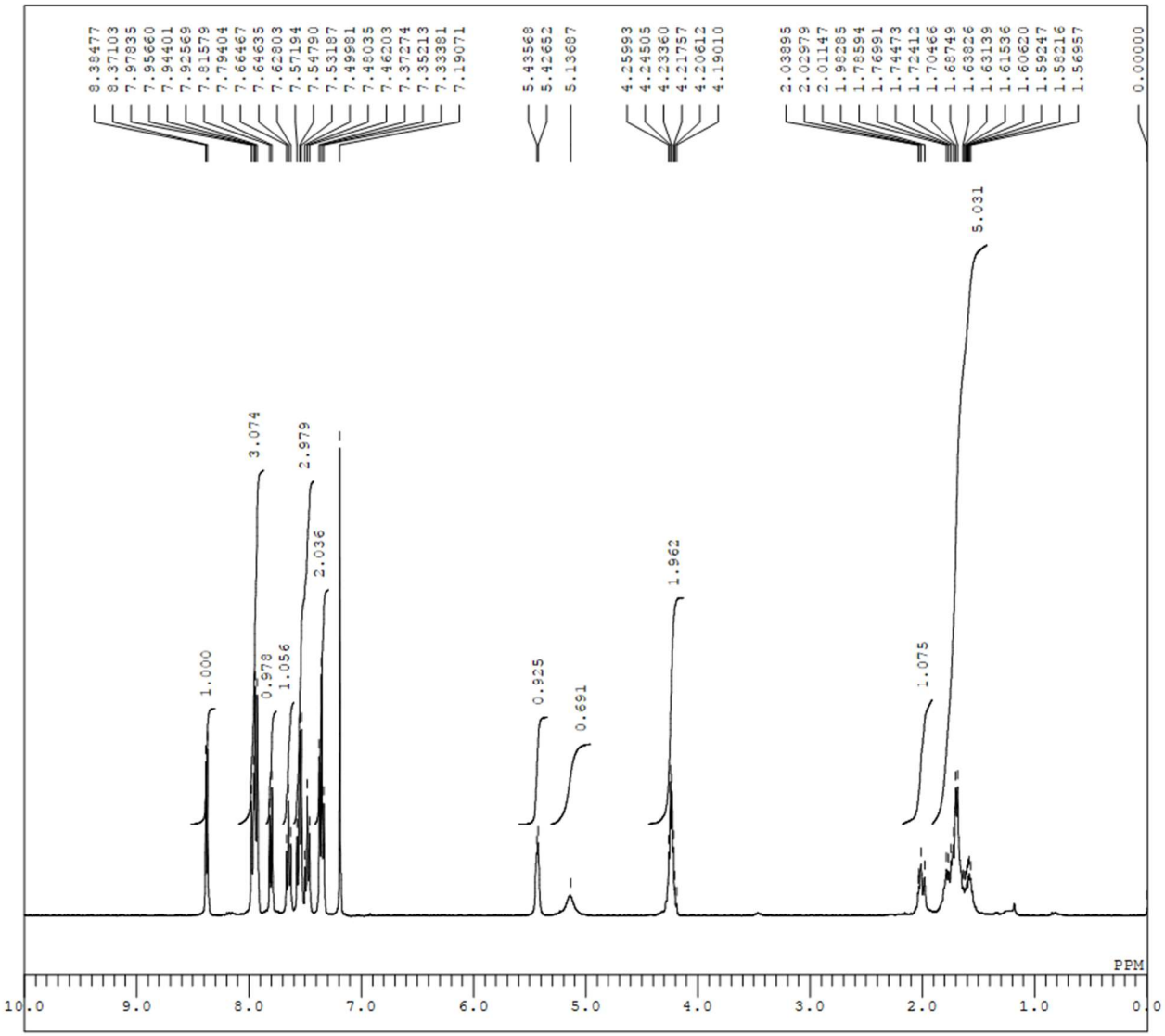
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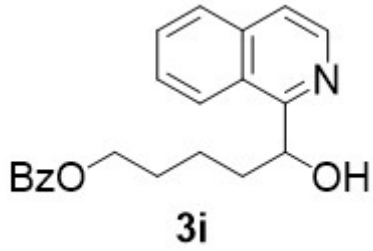
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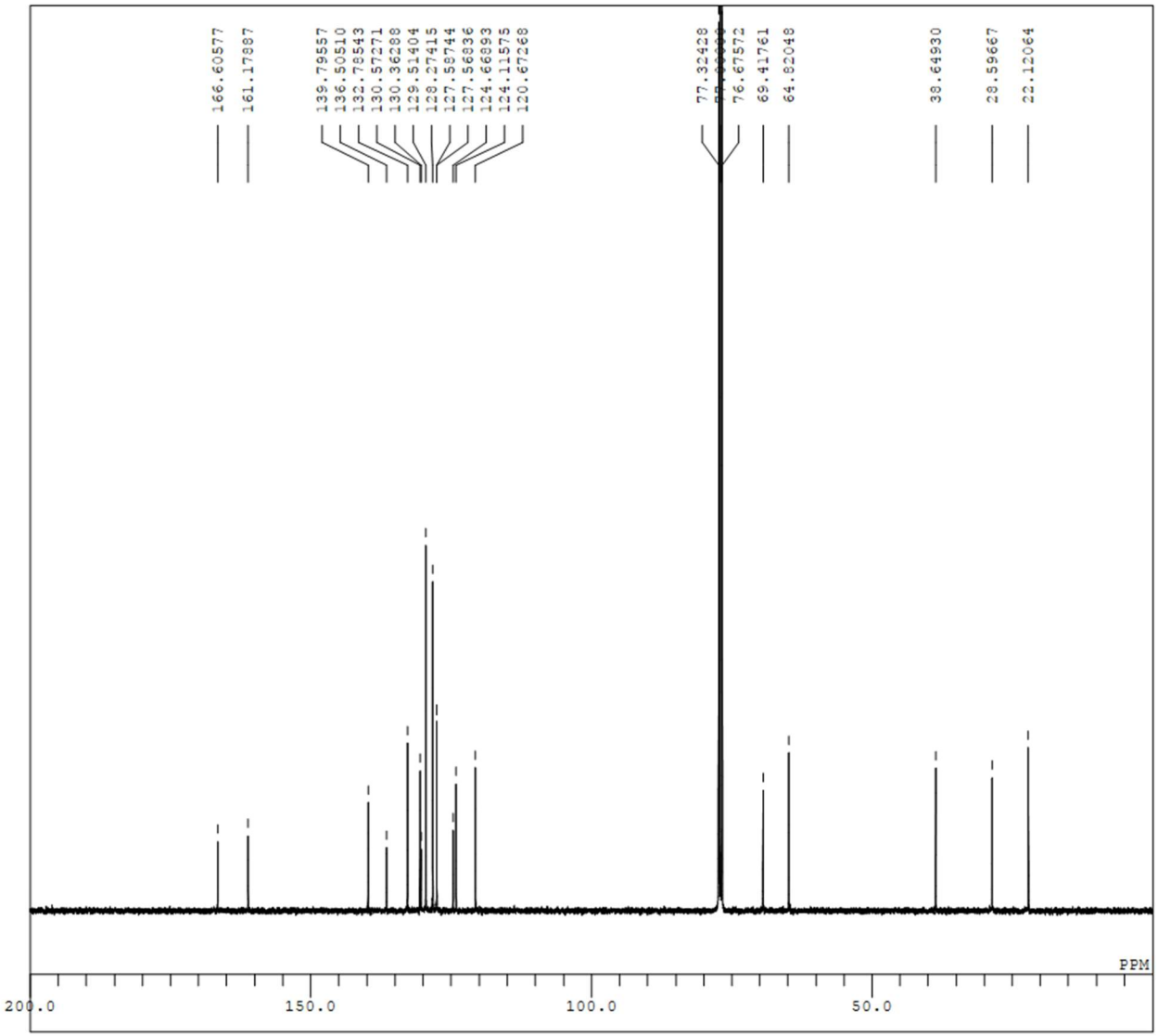
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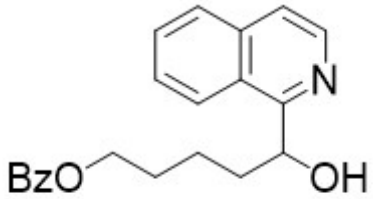
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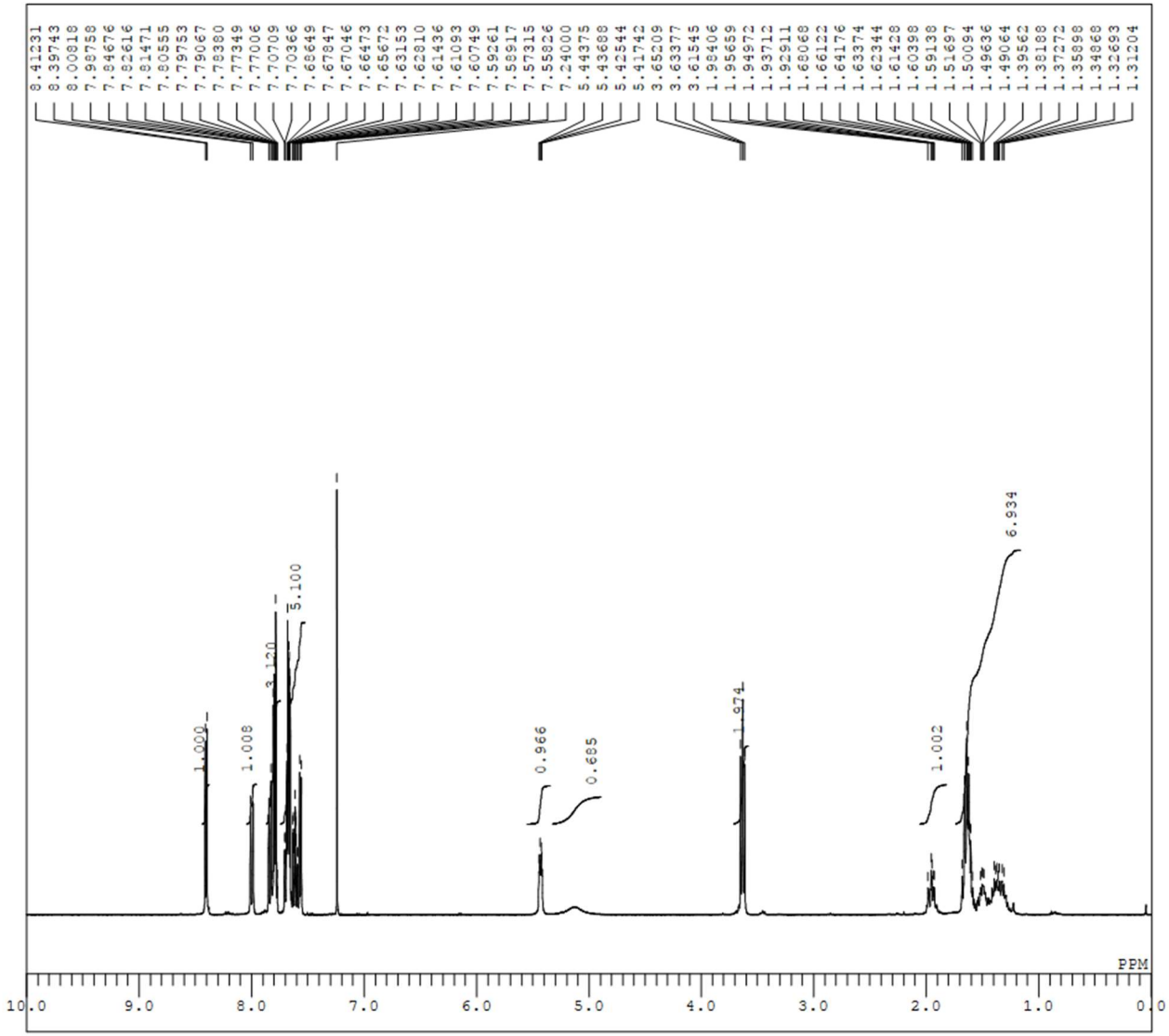
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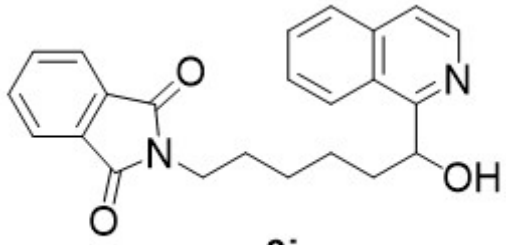
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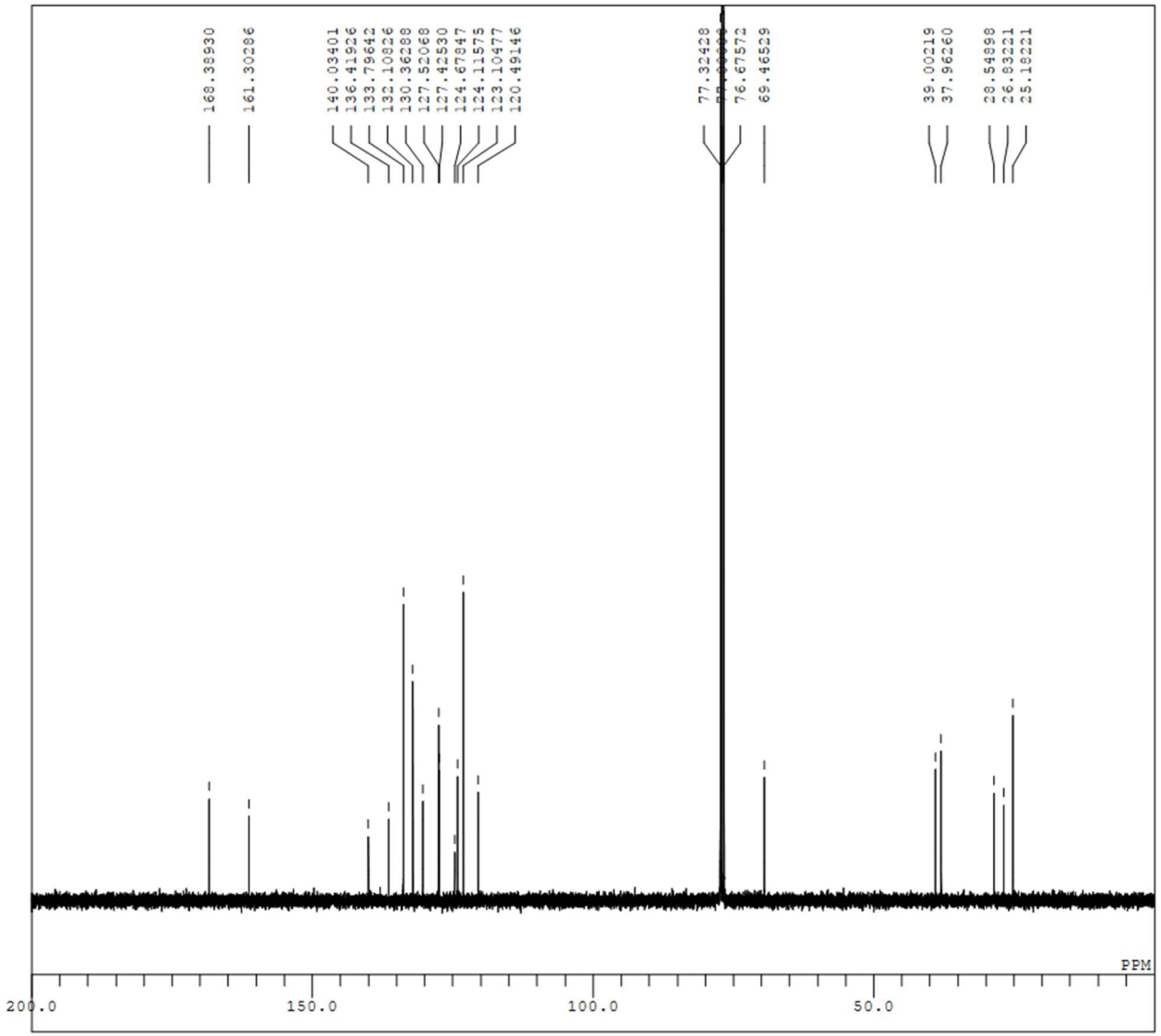
3j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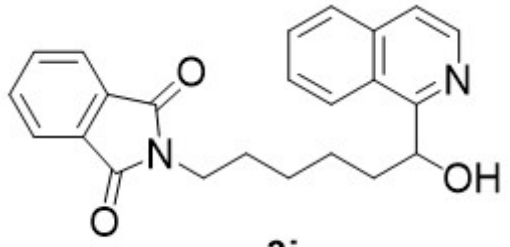
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OH

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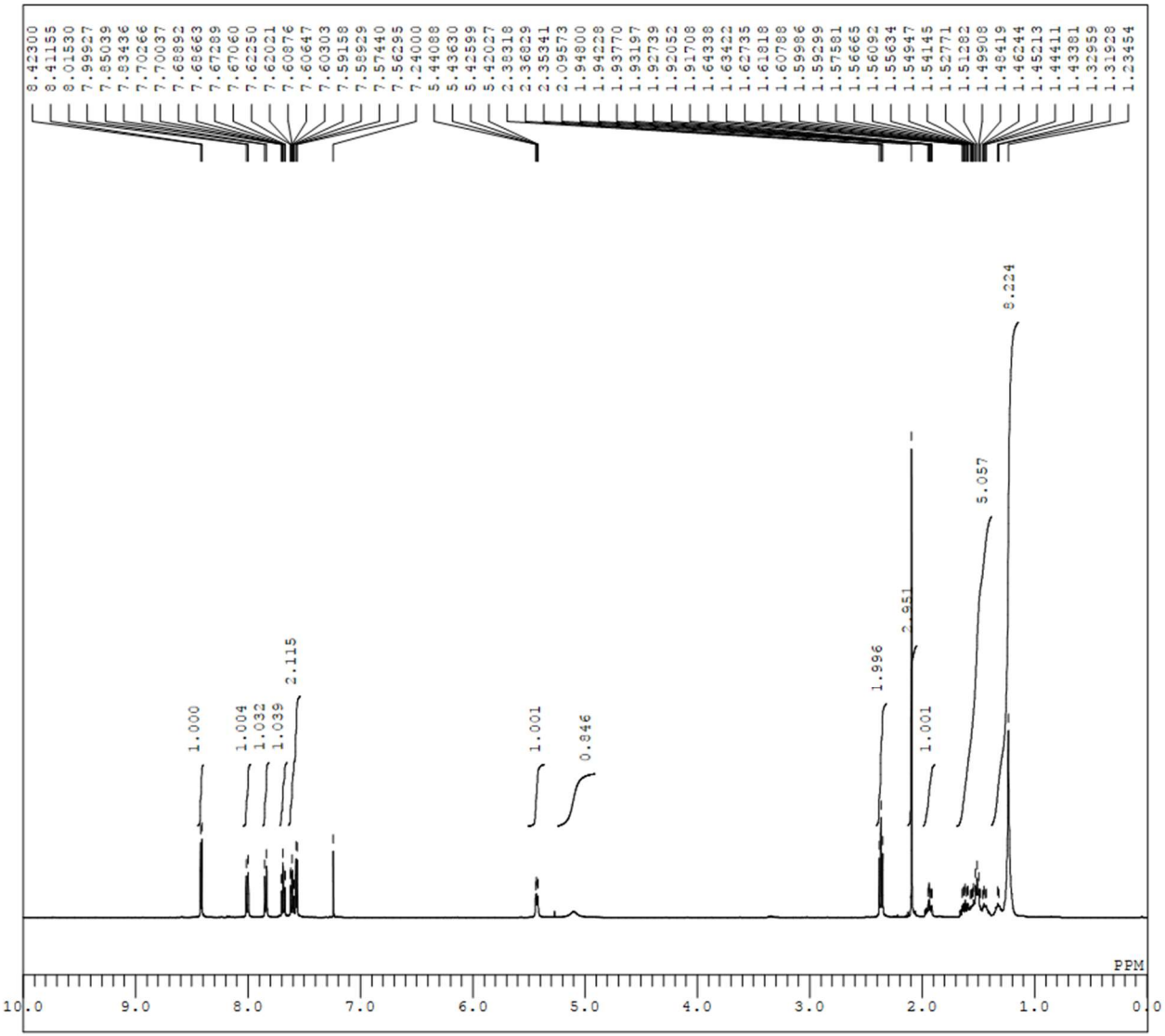
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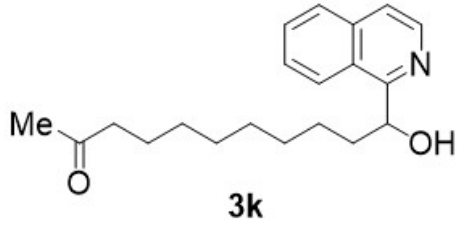
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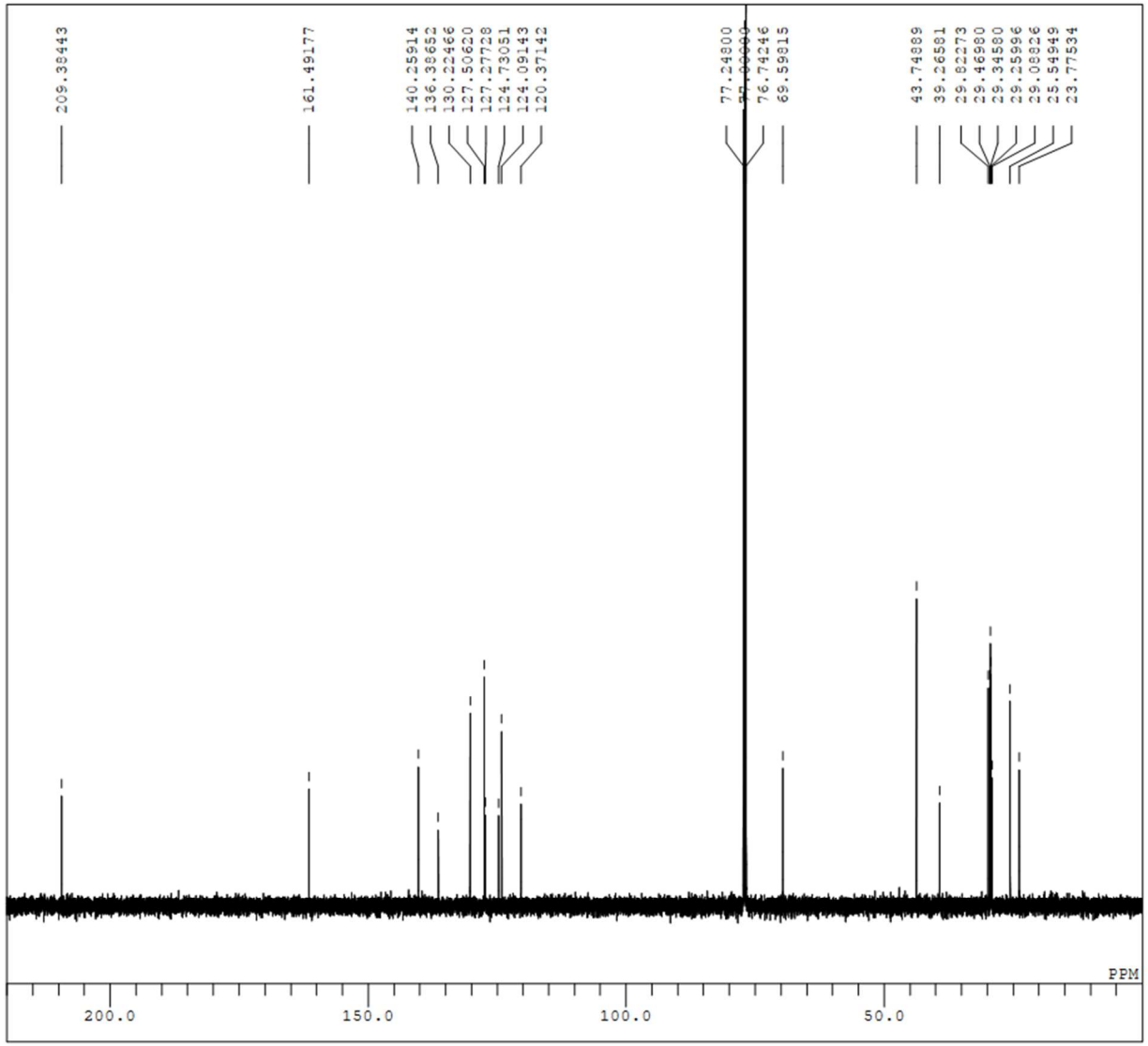
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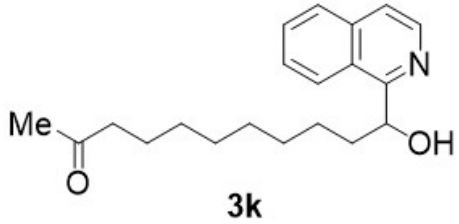
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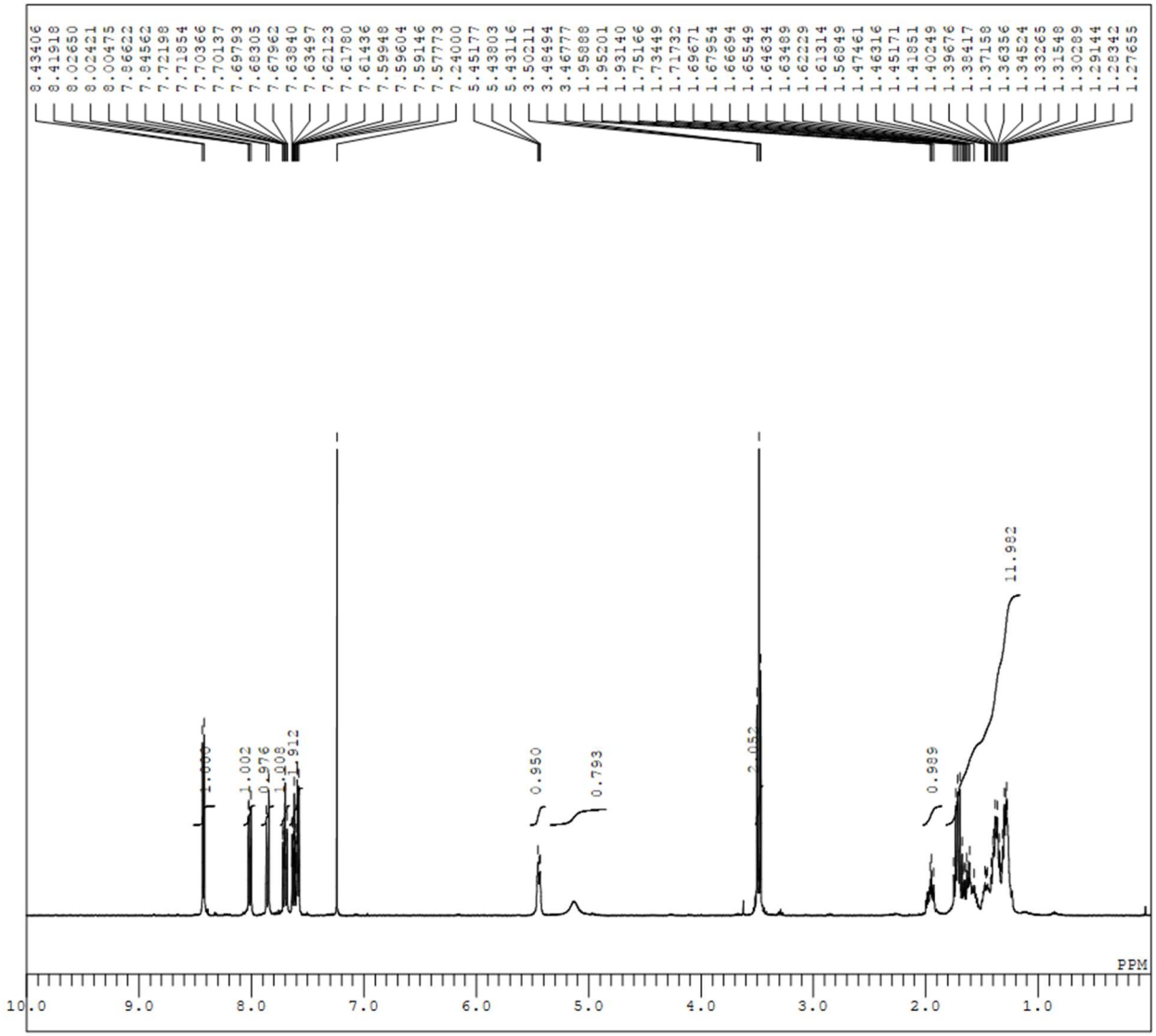
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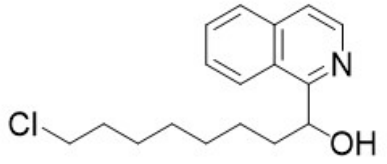
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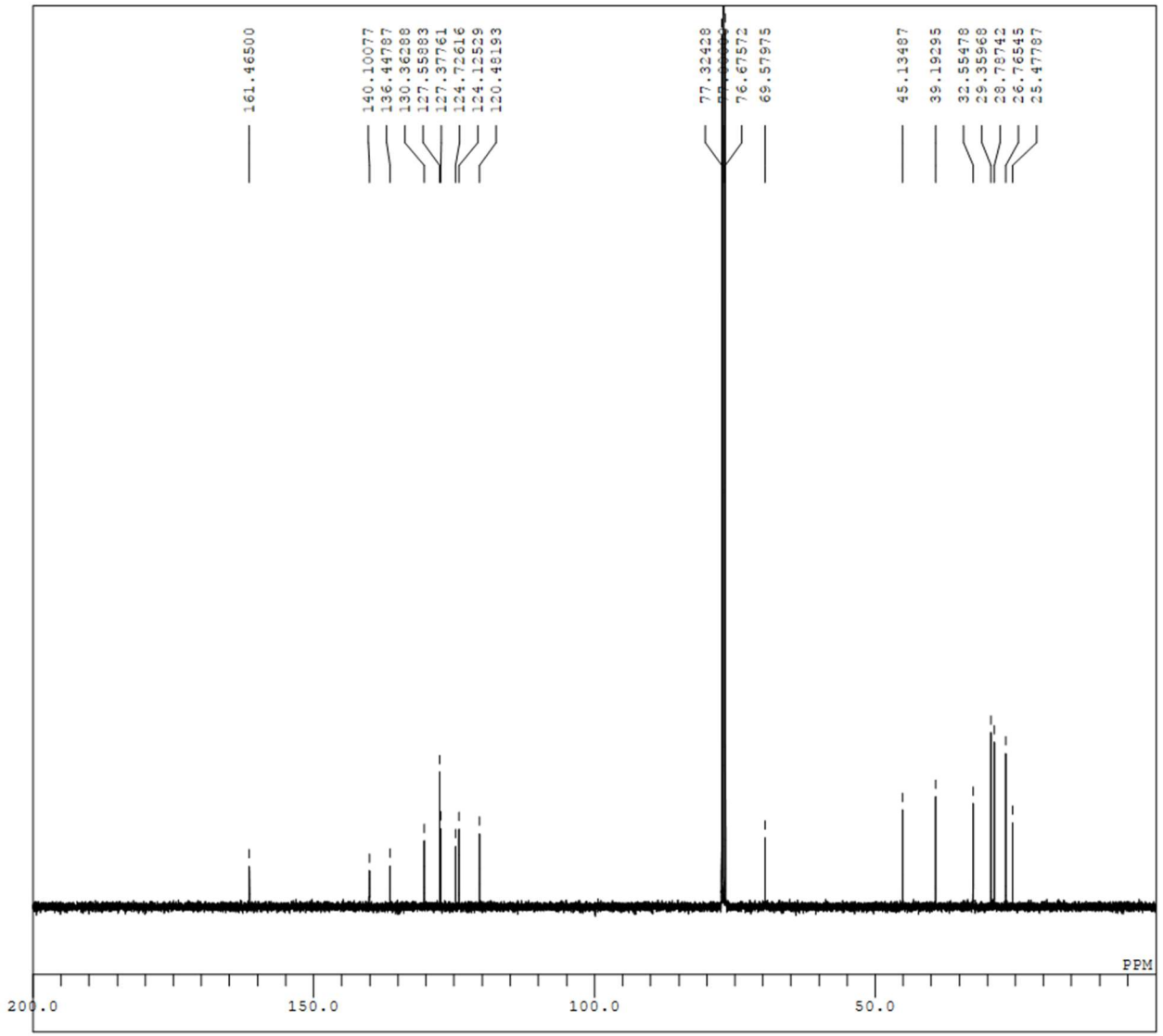
OH

3l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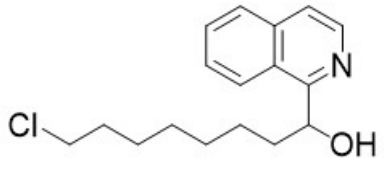
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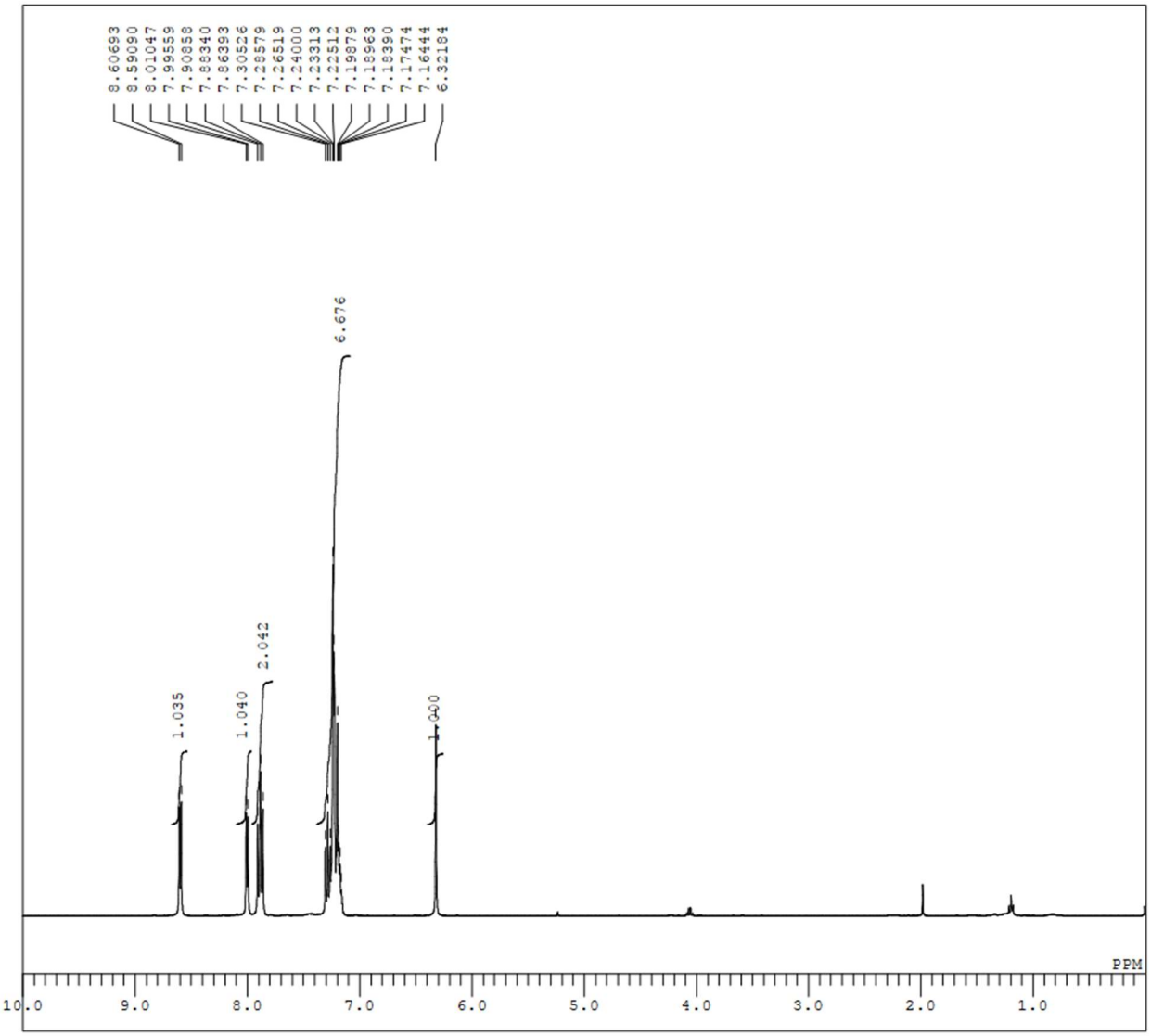
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1.040
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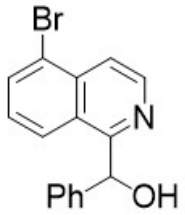
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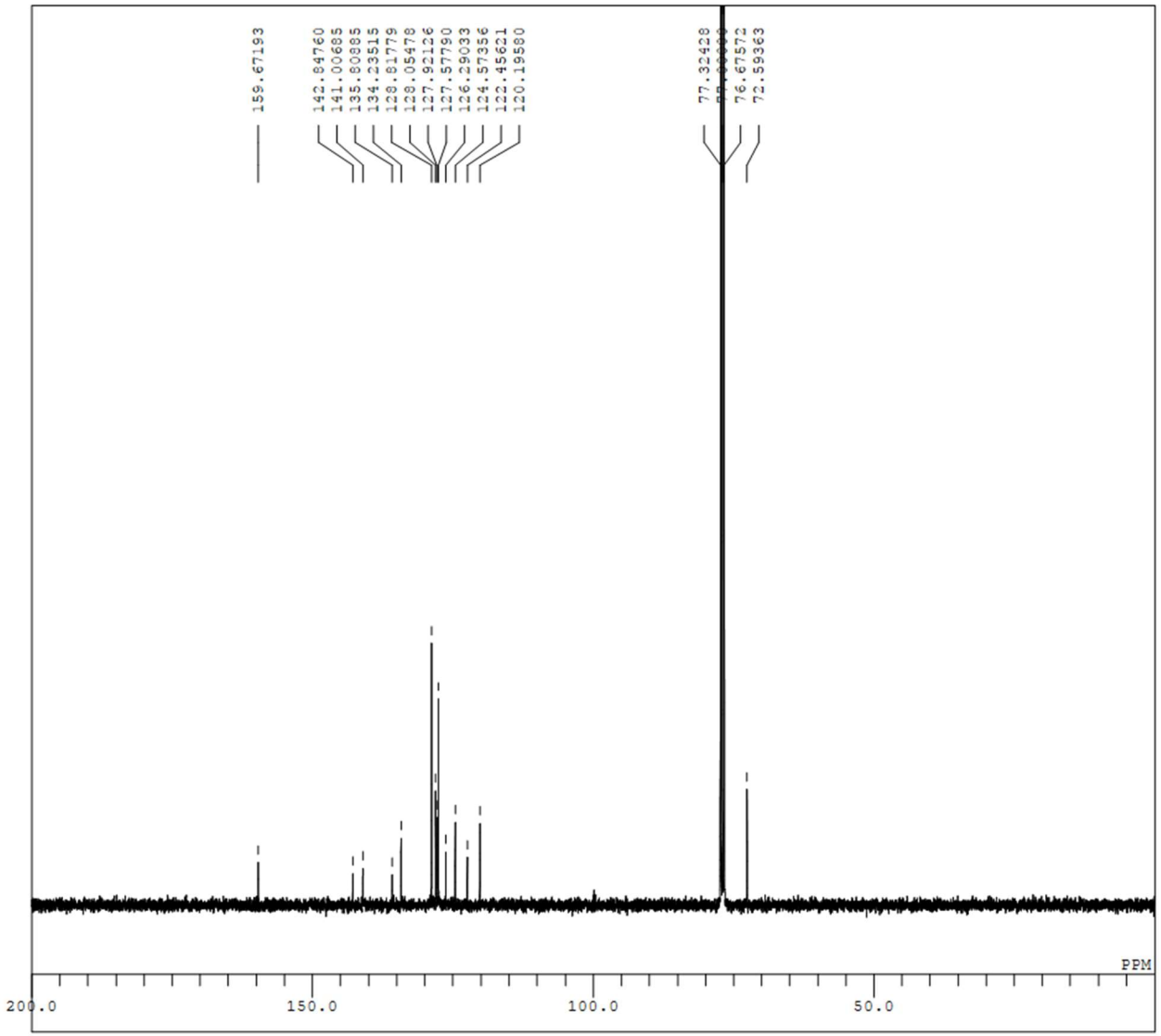
Ph
OH

3m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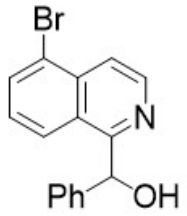
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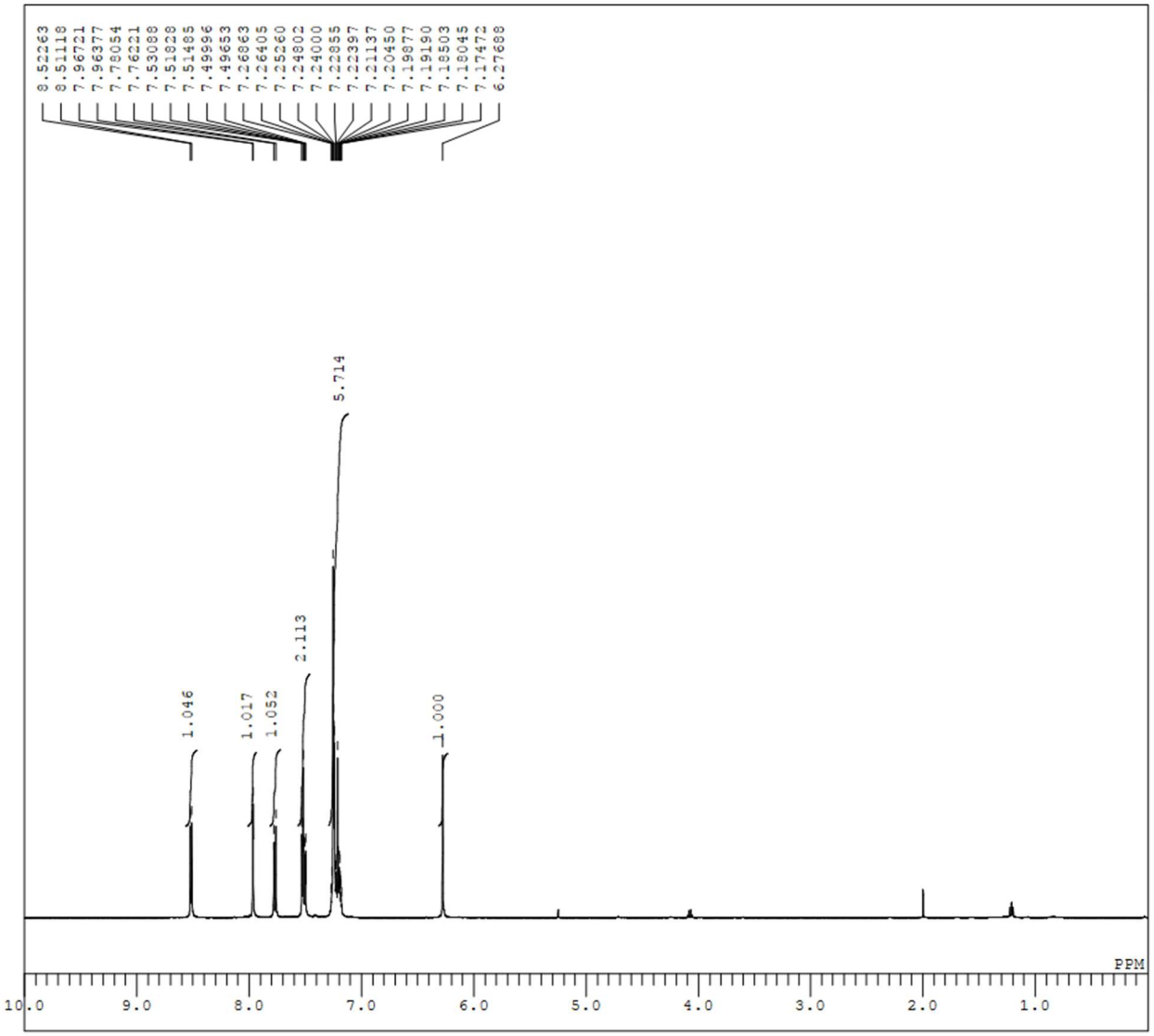
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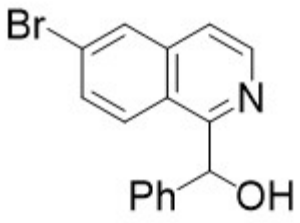
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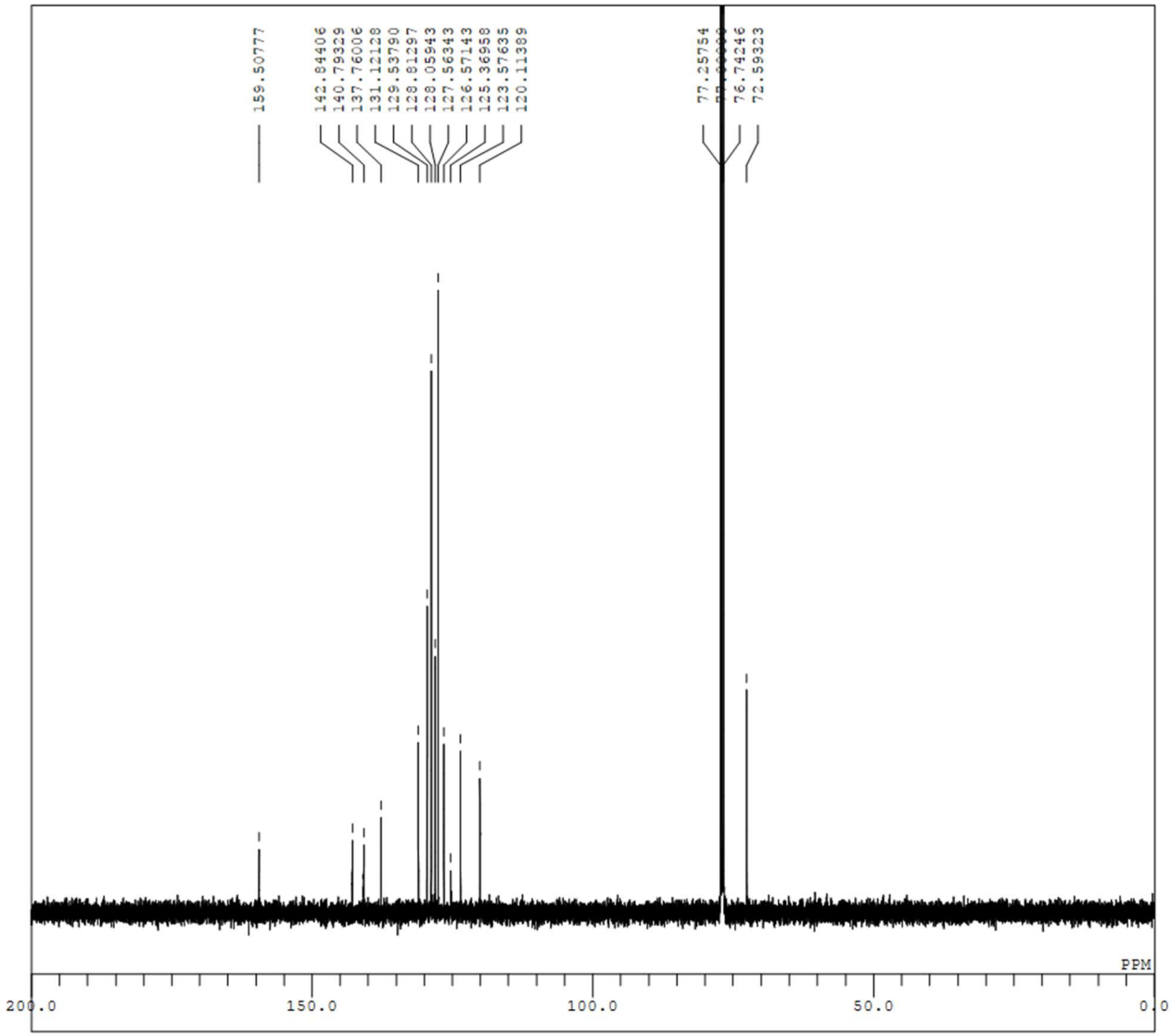
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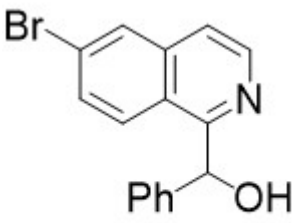
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Ph
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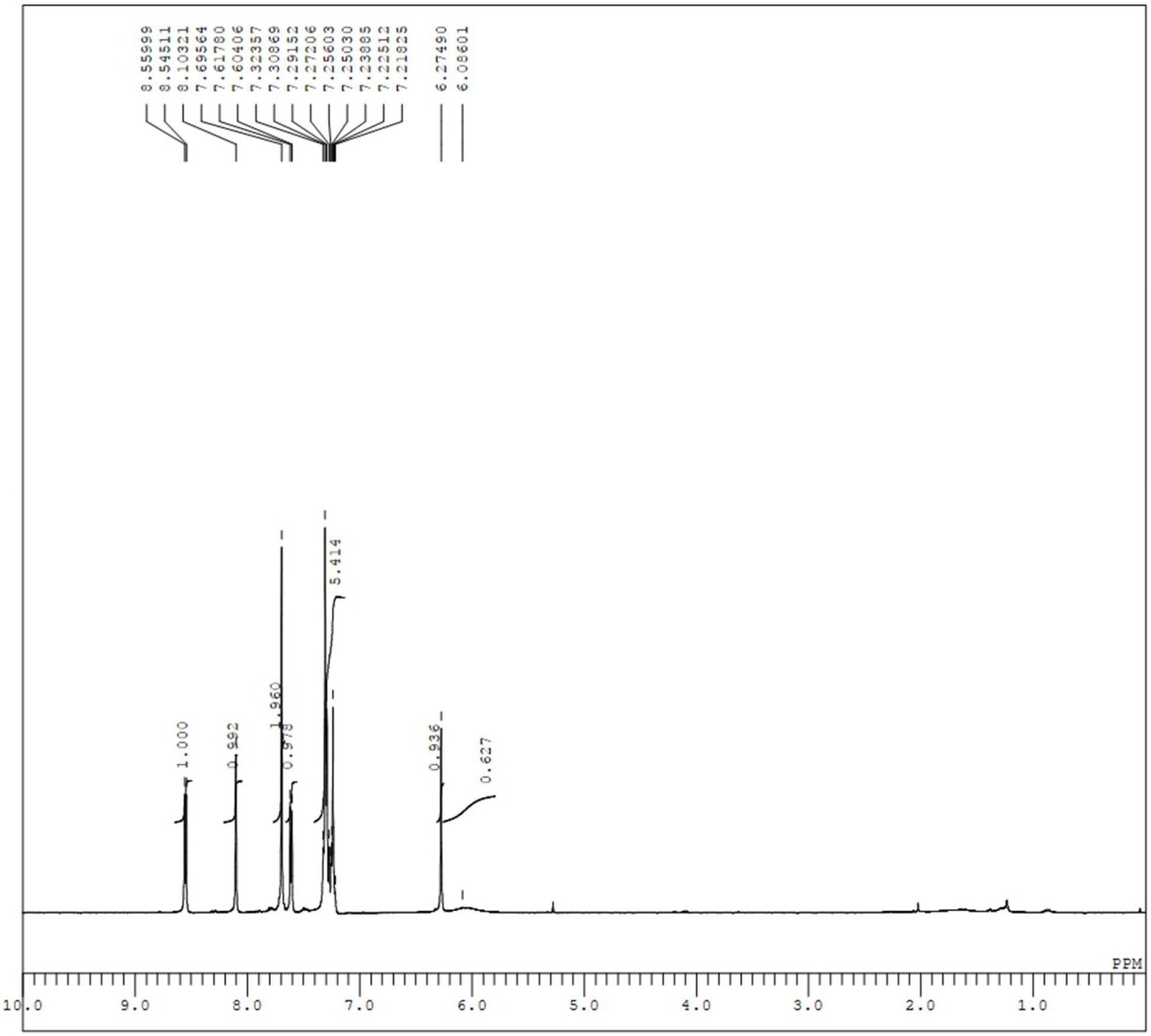
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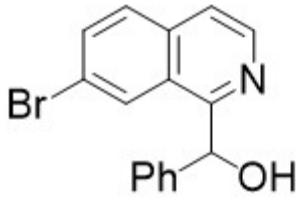
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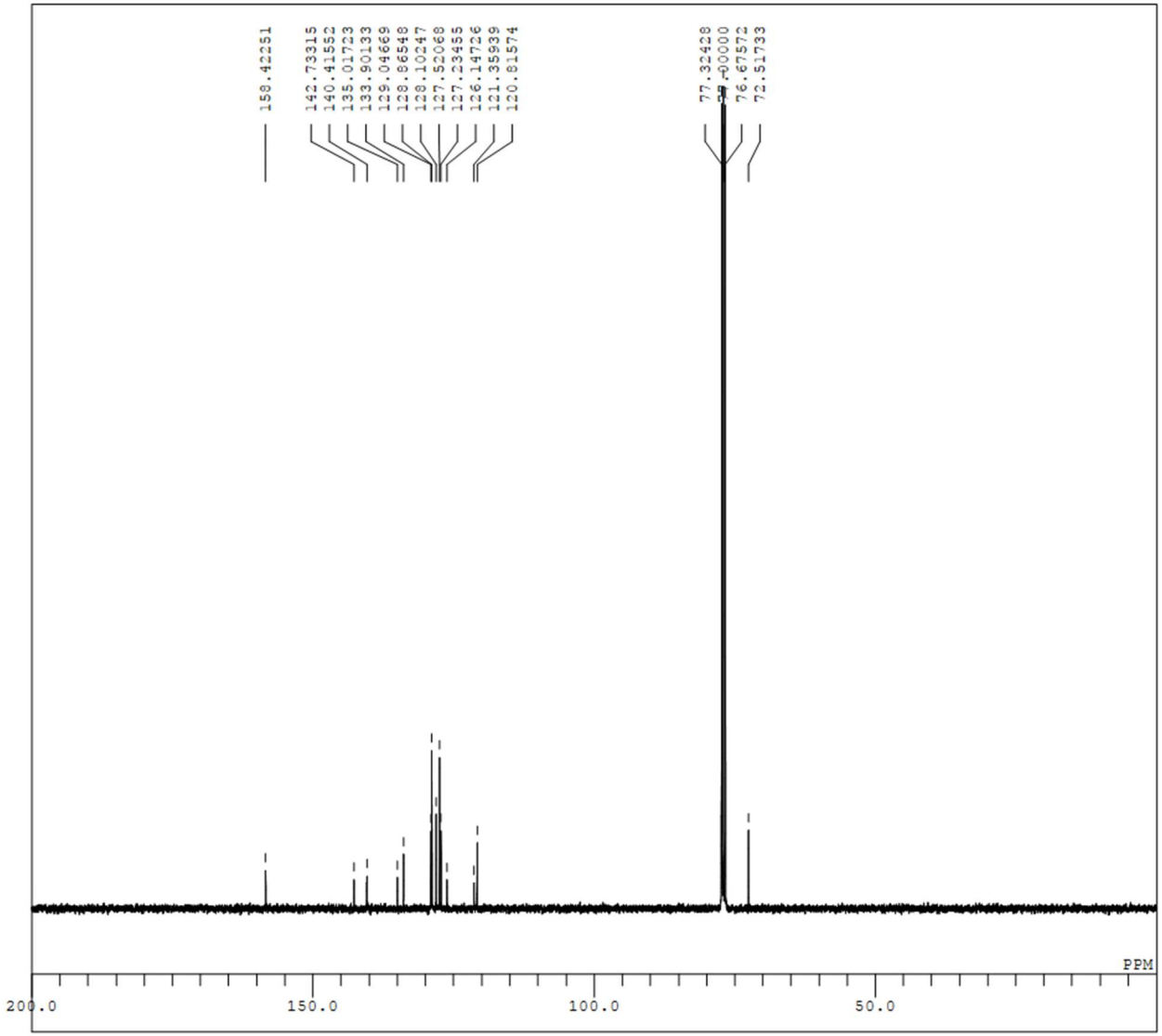
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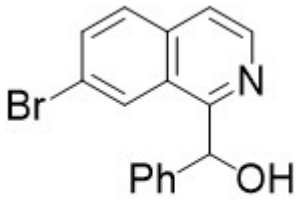
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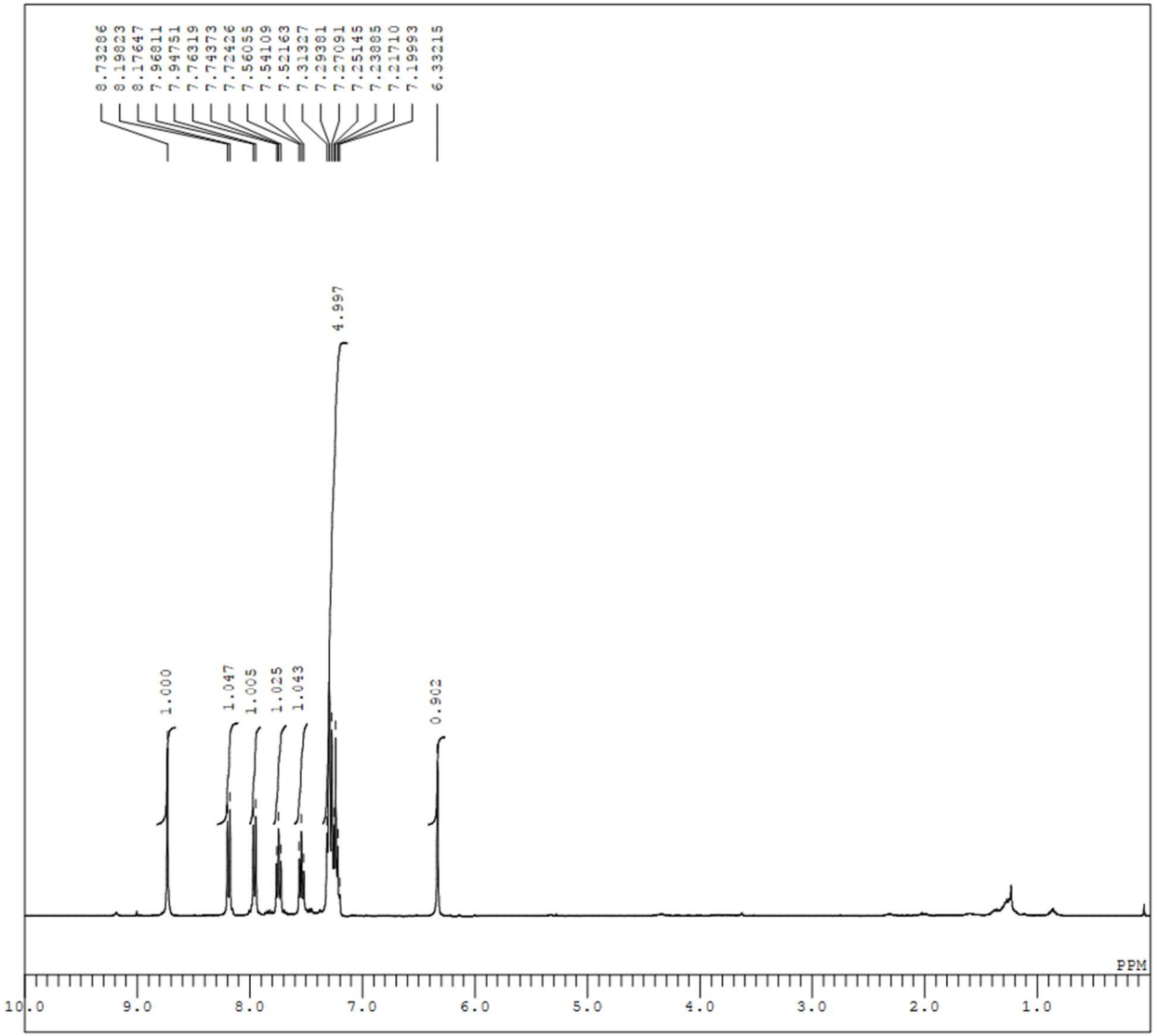
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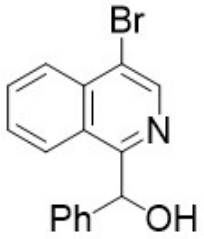
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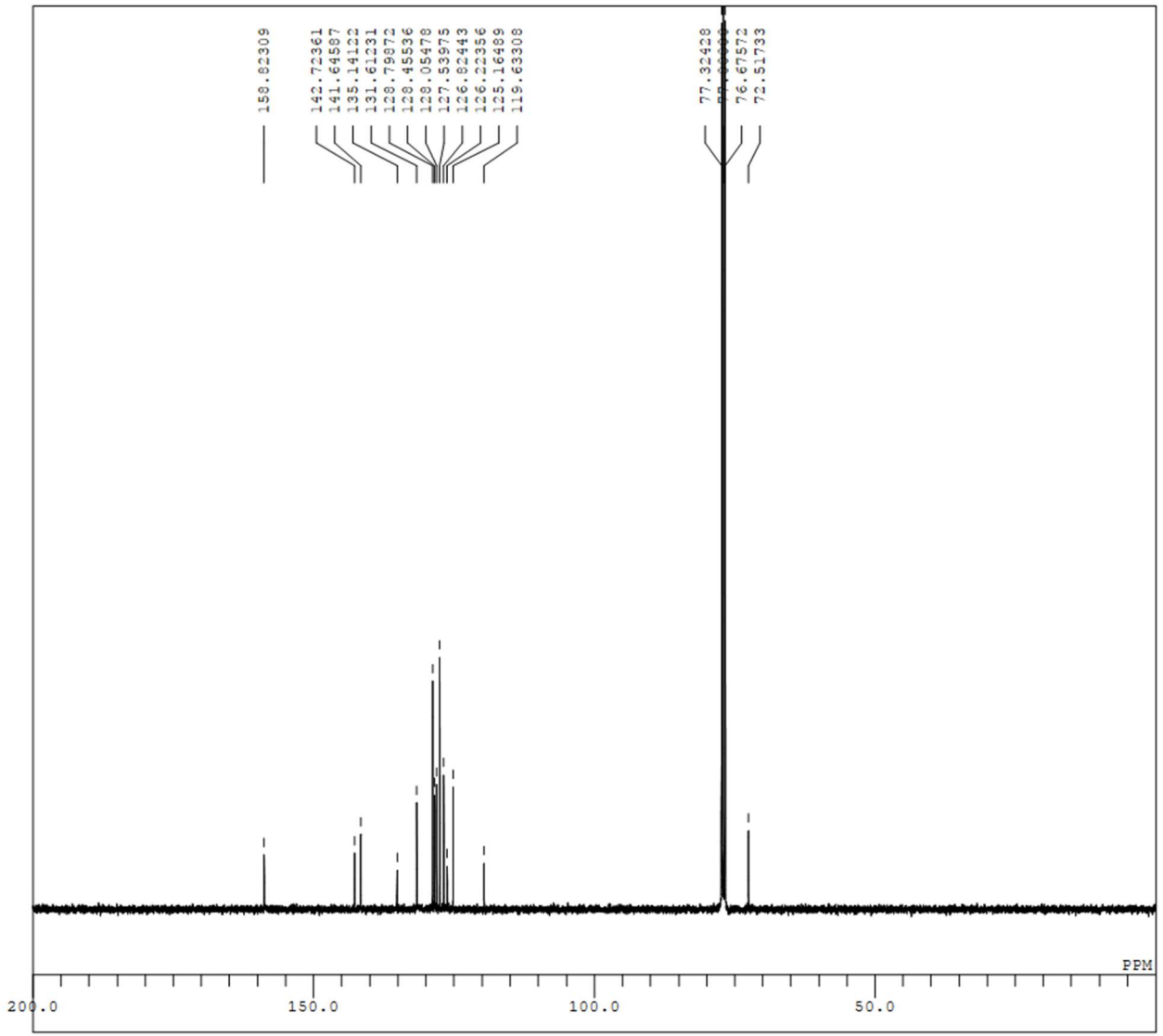
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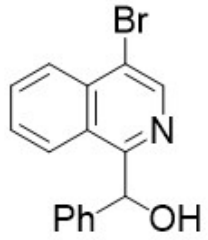
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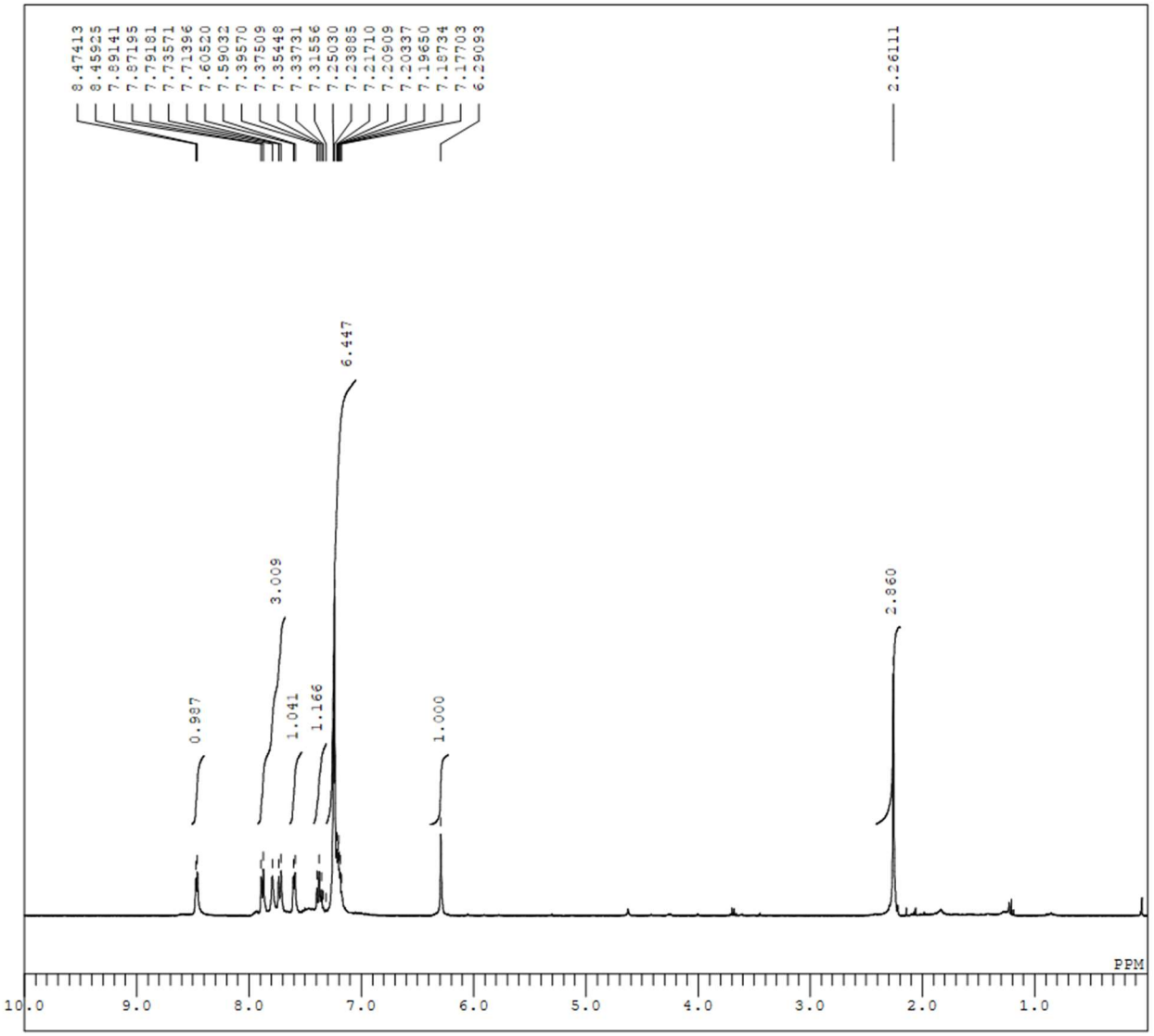
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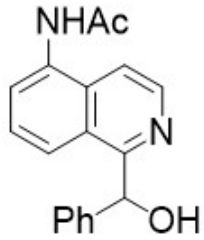
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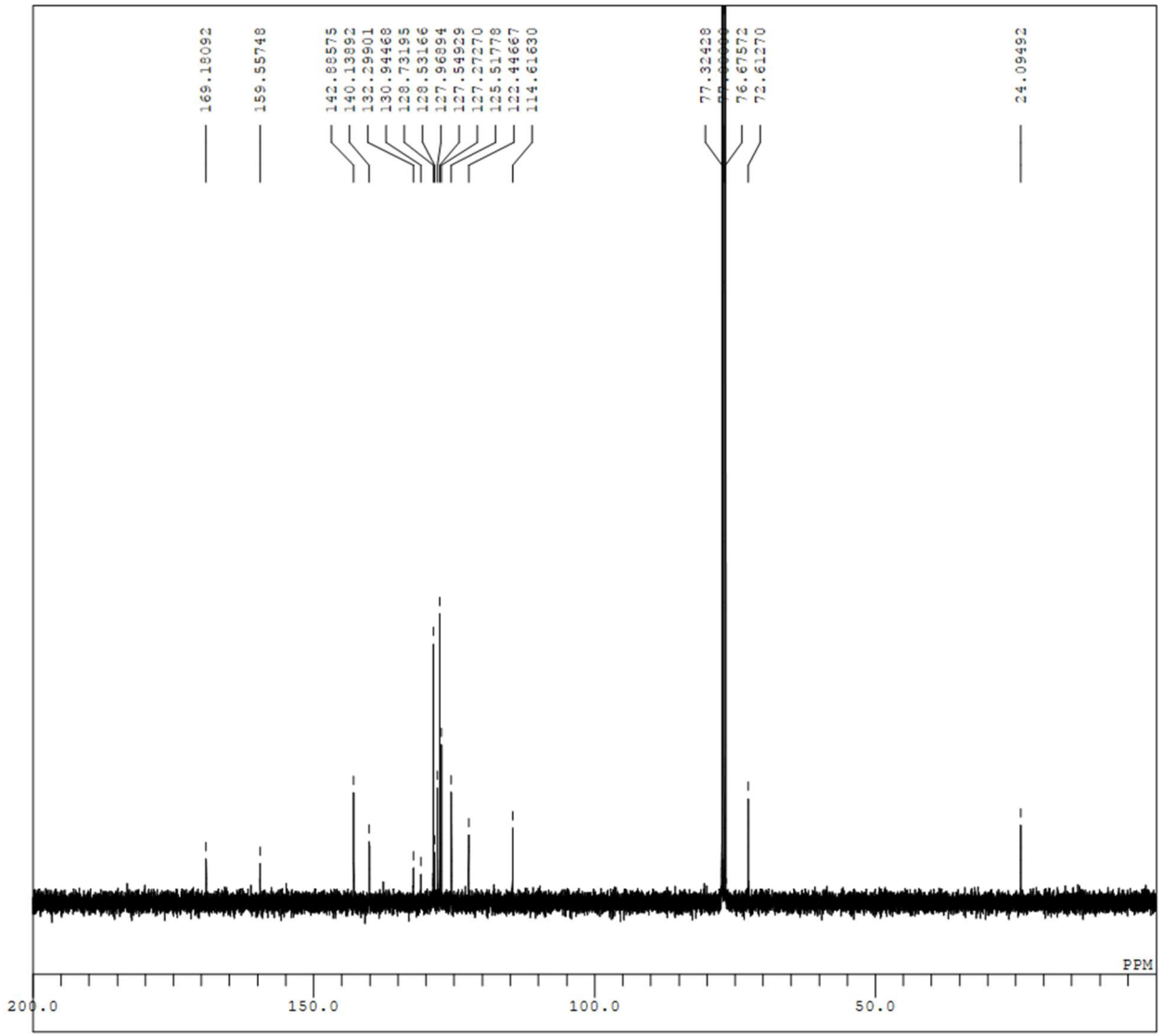
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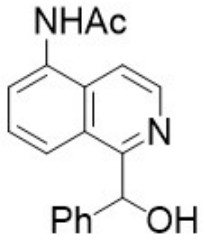
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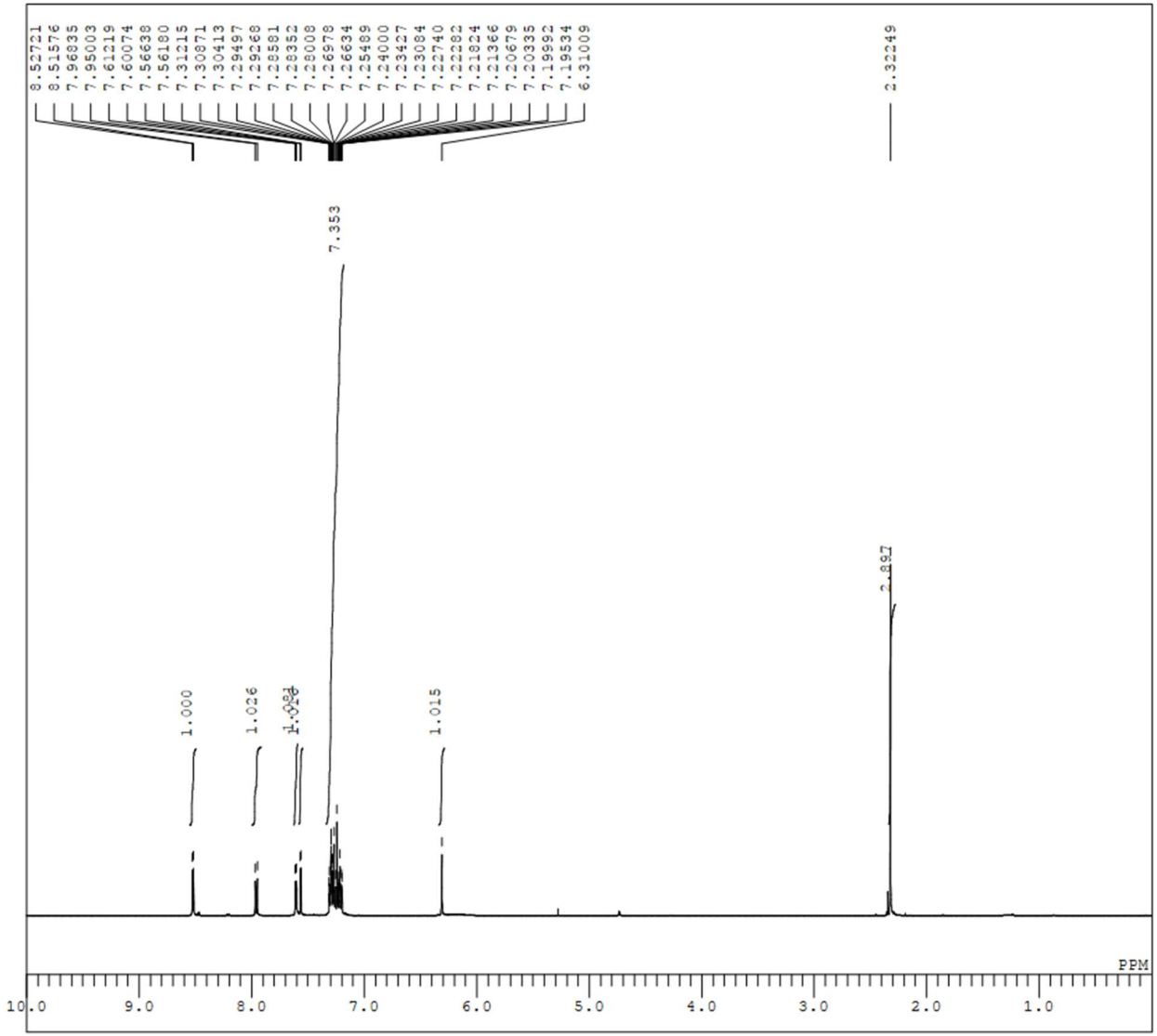
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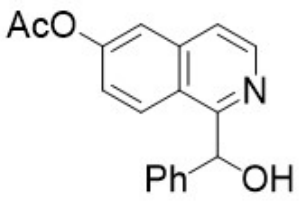
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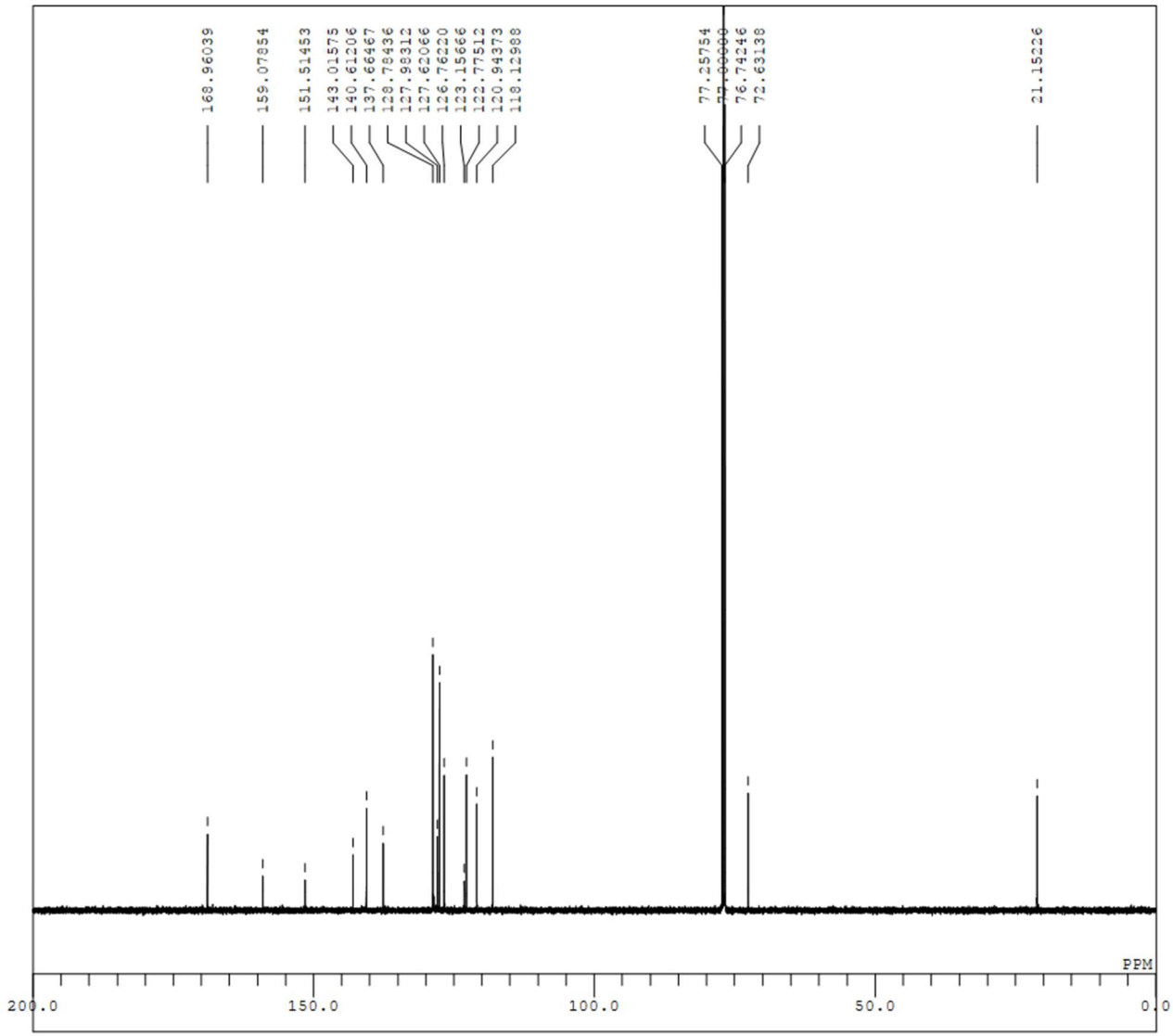
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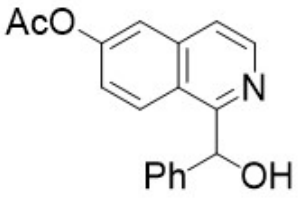
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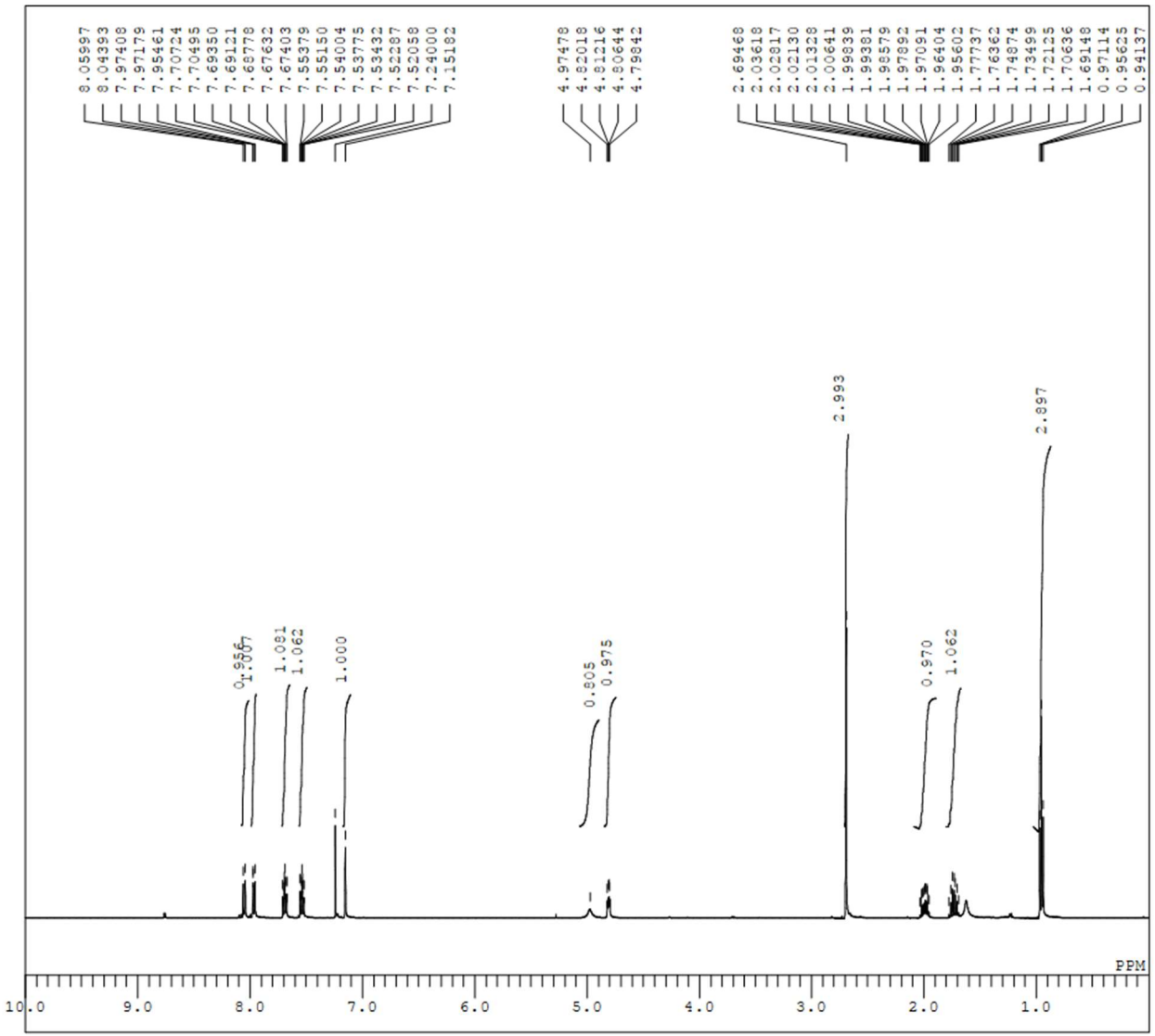
OH

3r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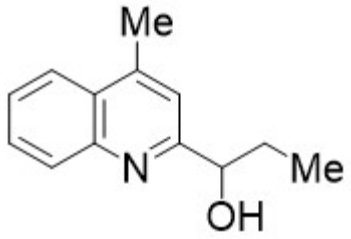
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Me
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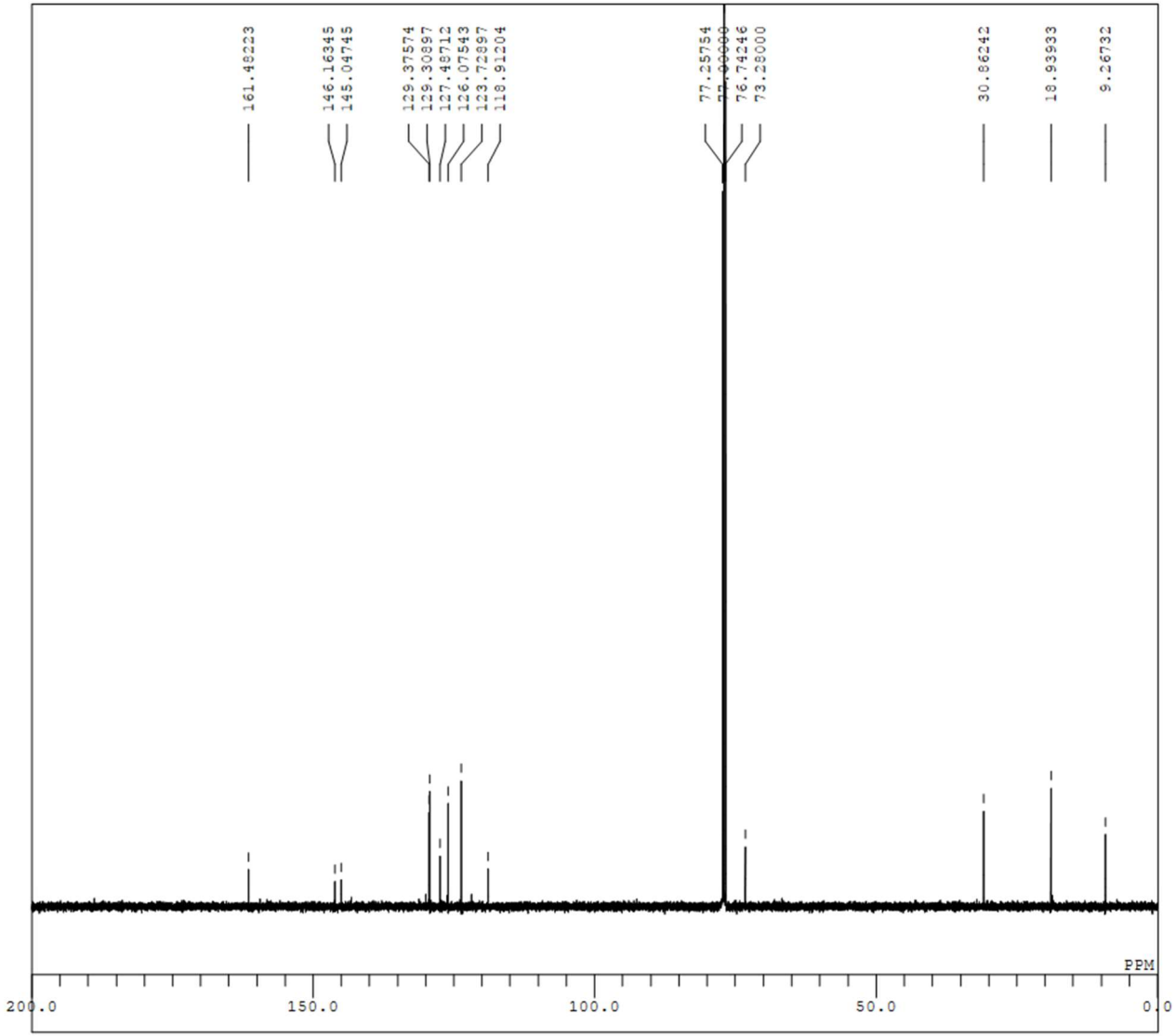
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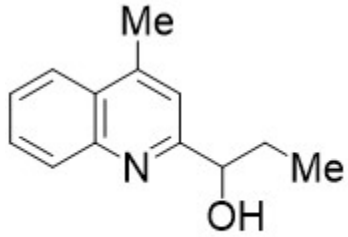
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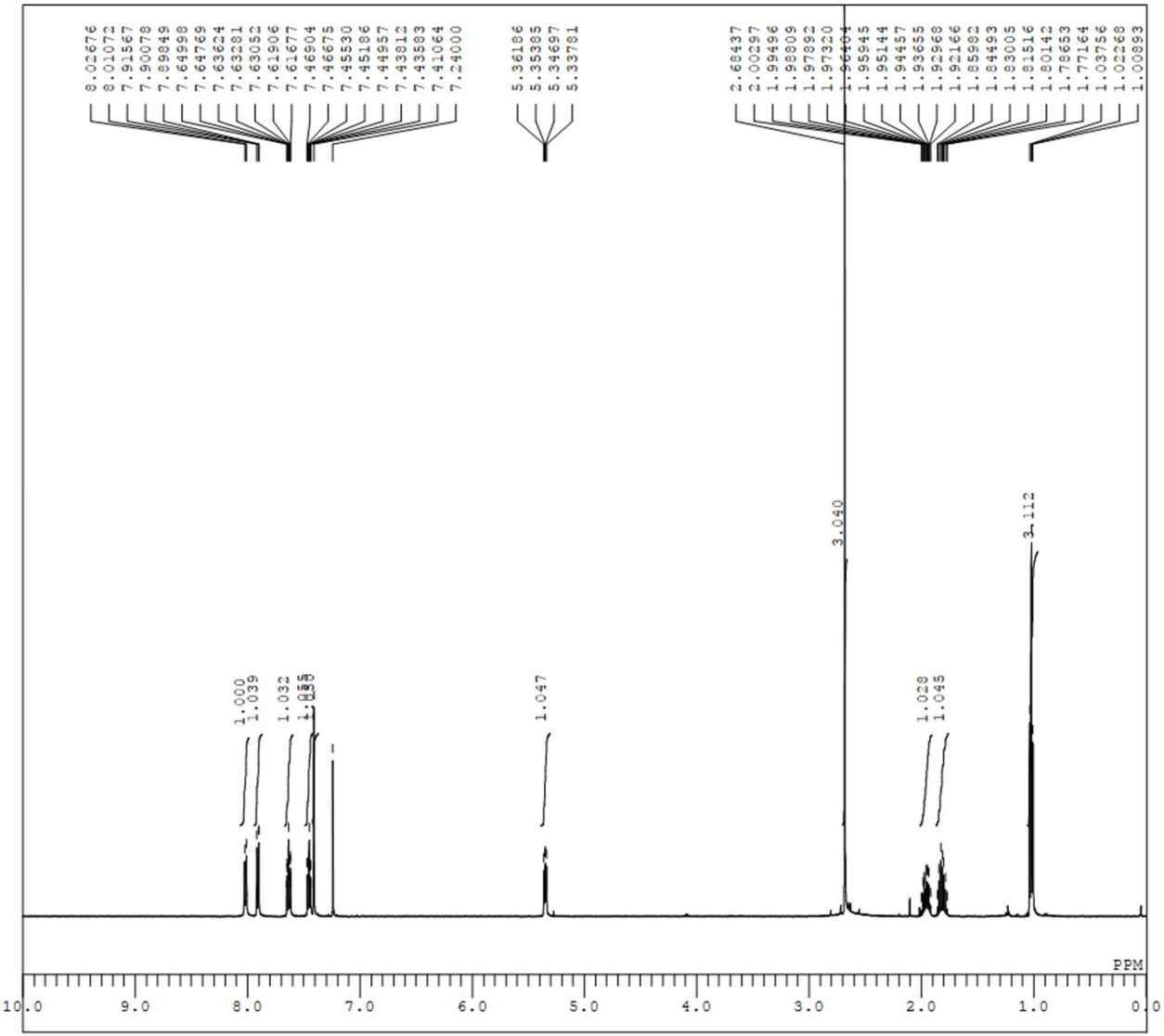
3s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1.00893
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3.112
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1.028
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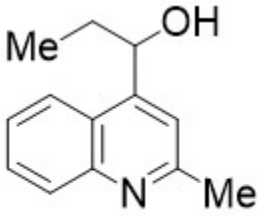
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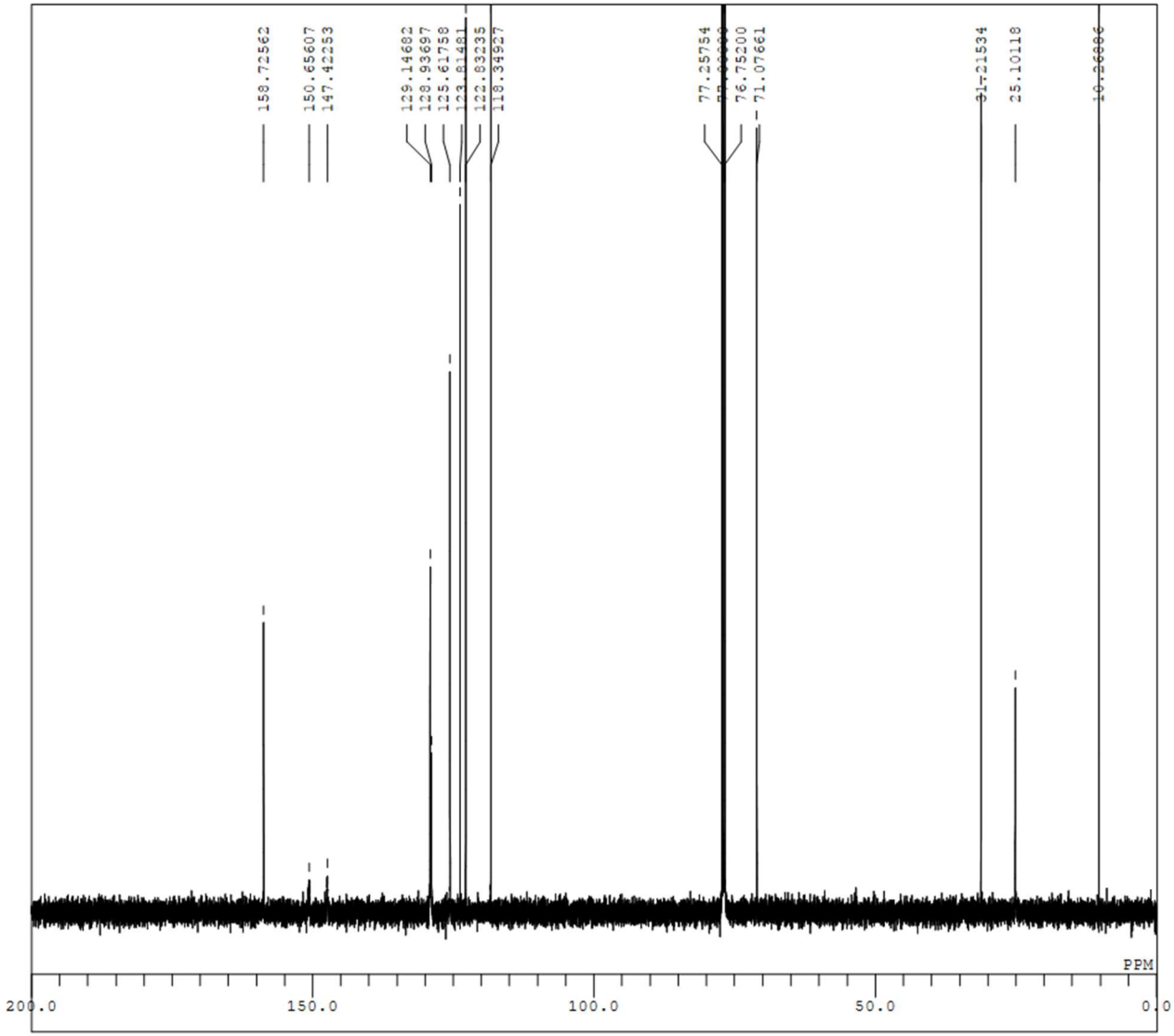
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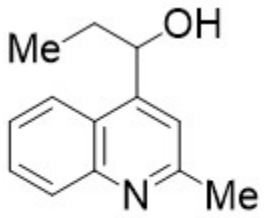
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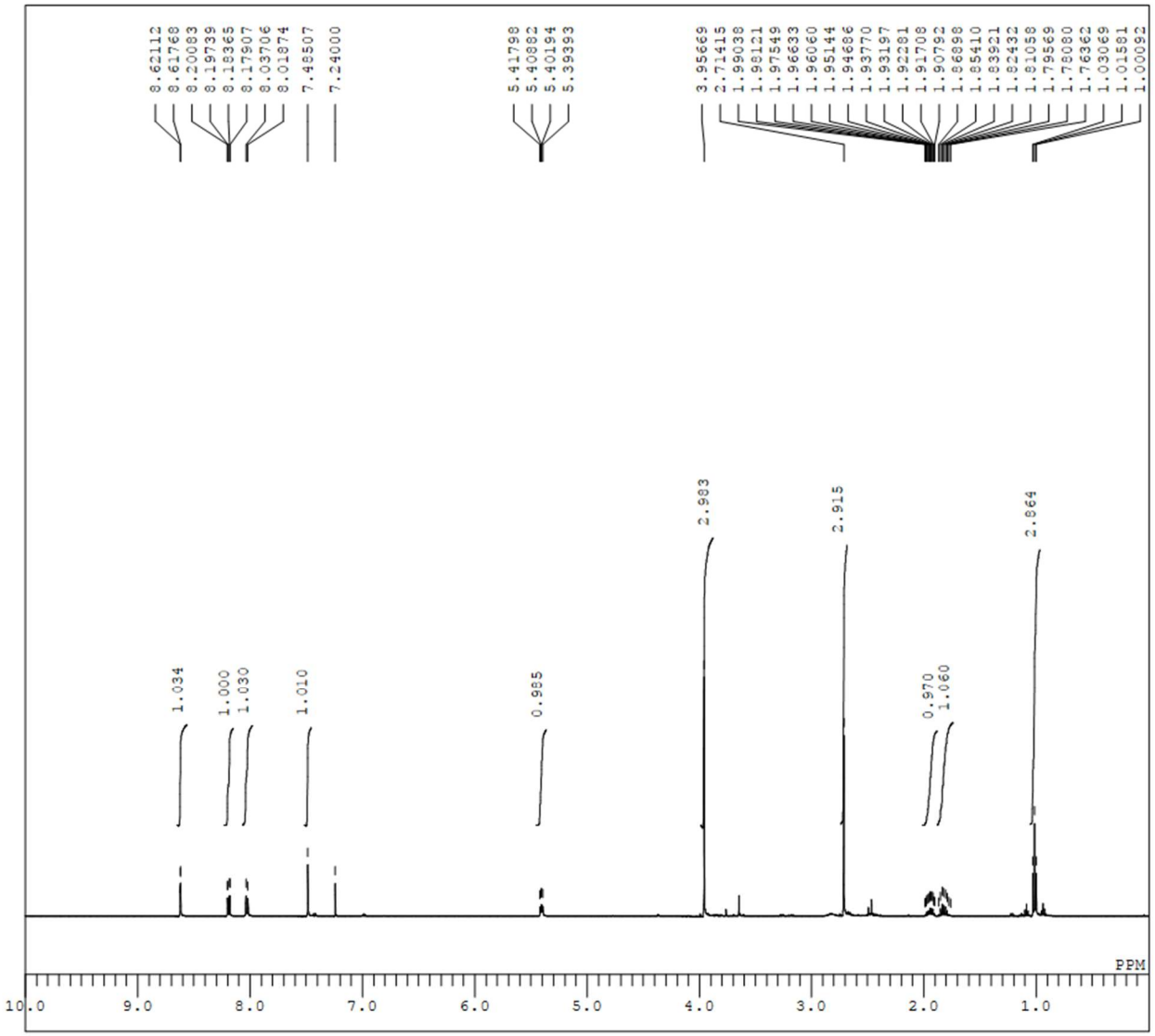
3t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5.40882
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5.39393
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1.97549
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1.034
1.000
1.030
1.010
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2.915
0.970
1.060
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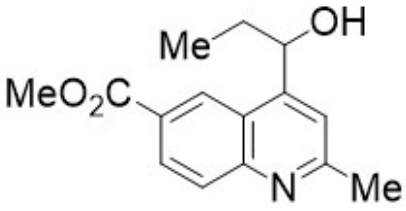
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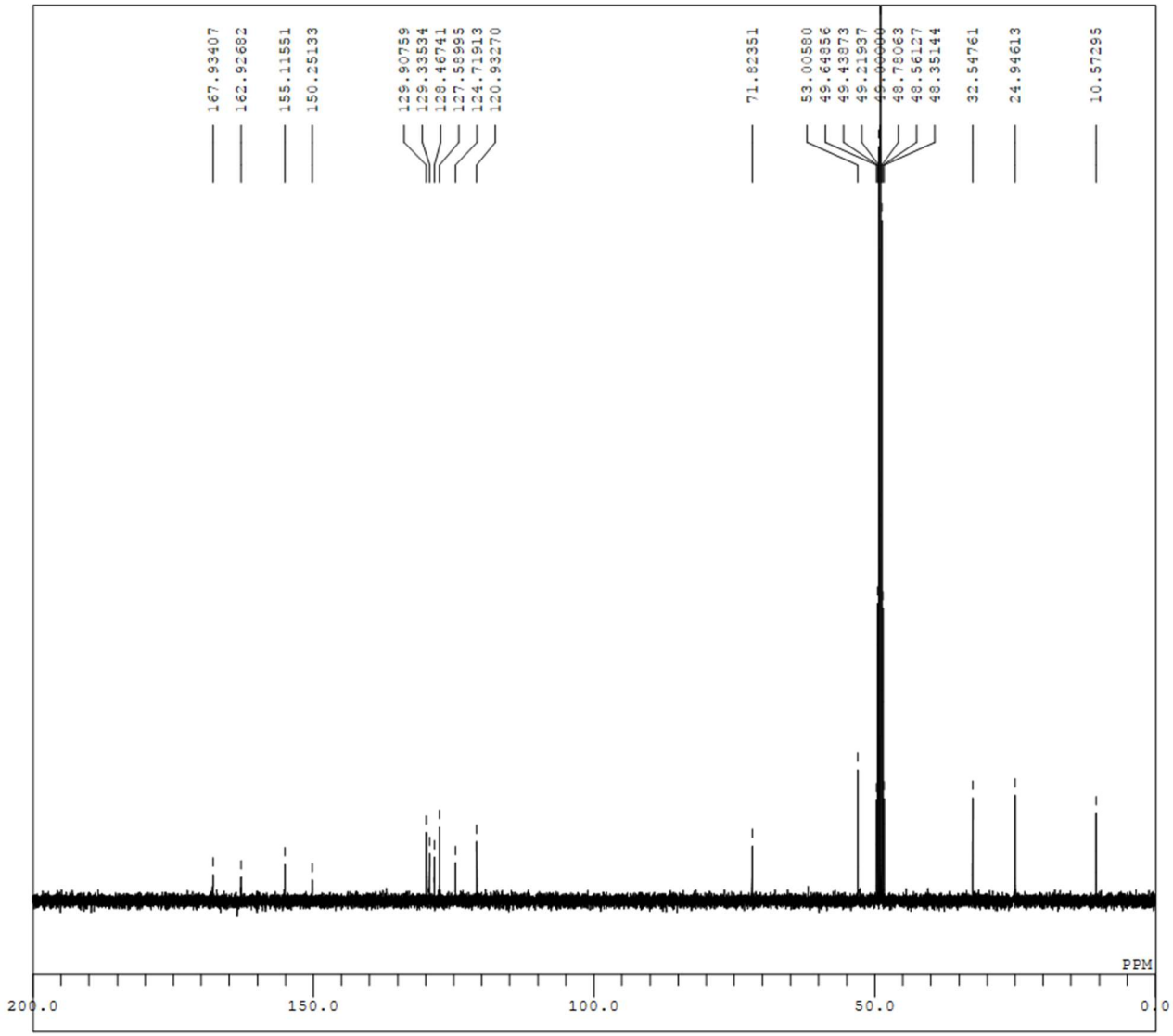
N
Me

3u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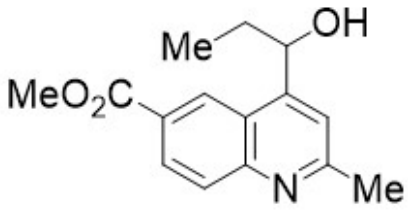
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N
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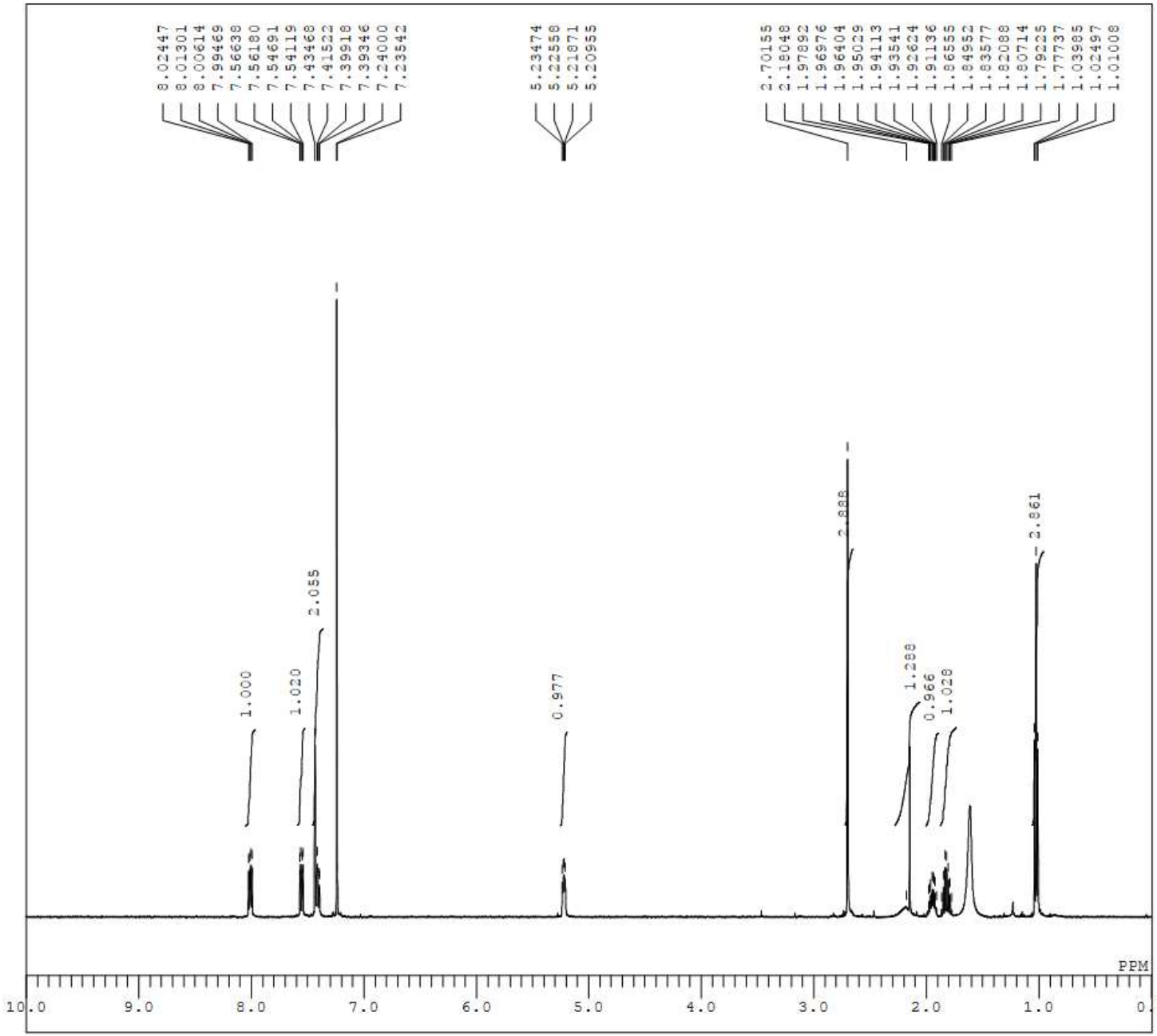
3u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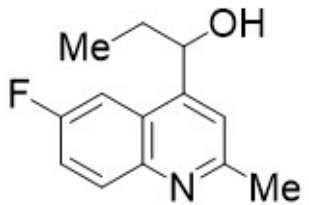
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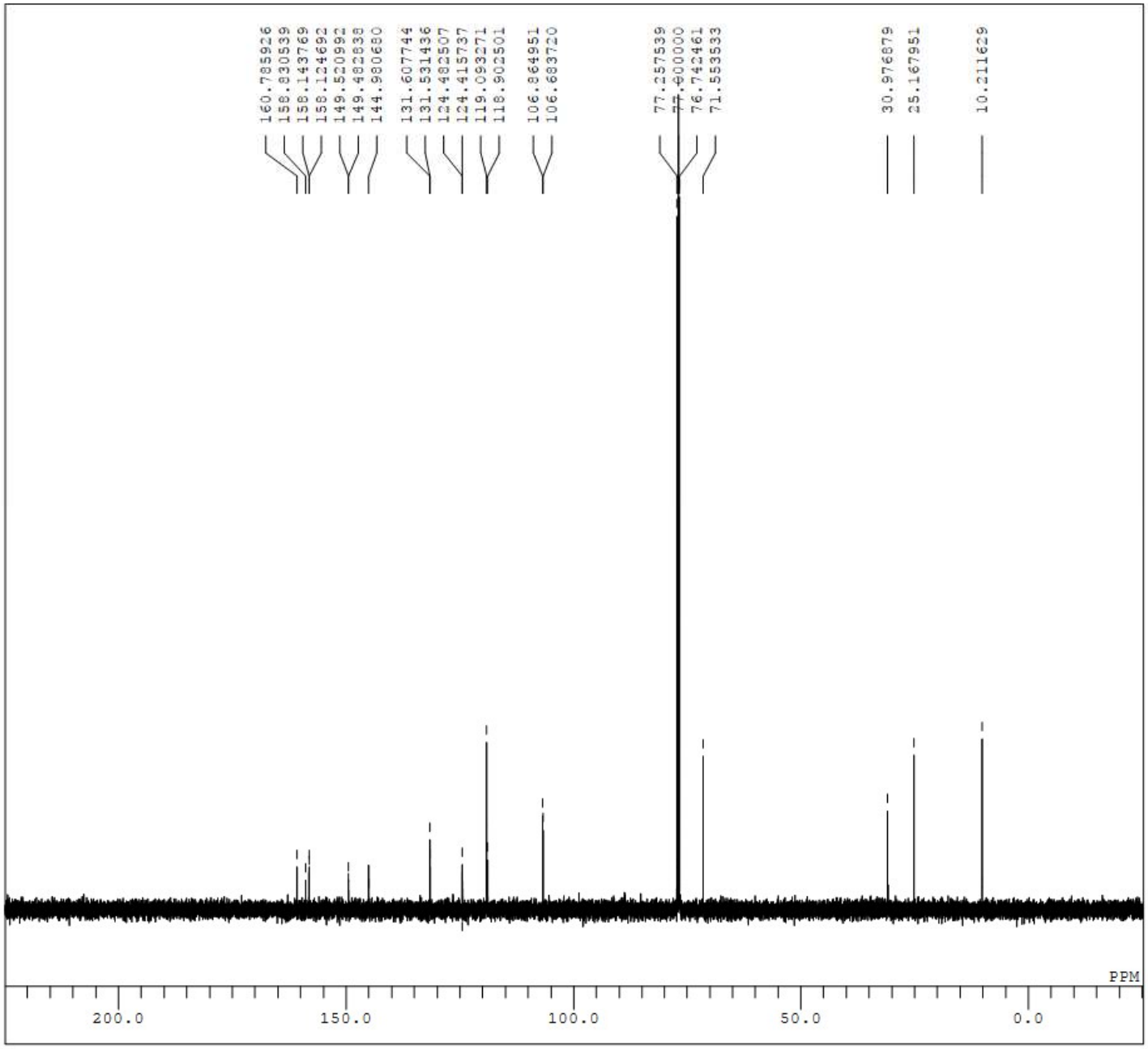
F
N
Me

3v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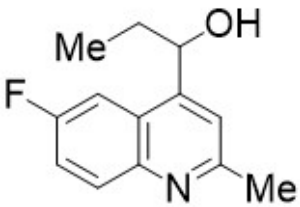
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OH
F
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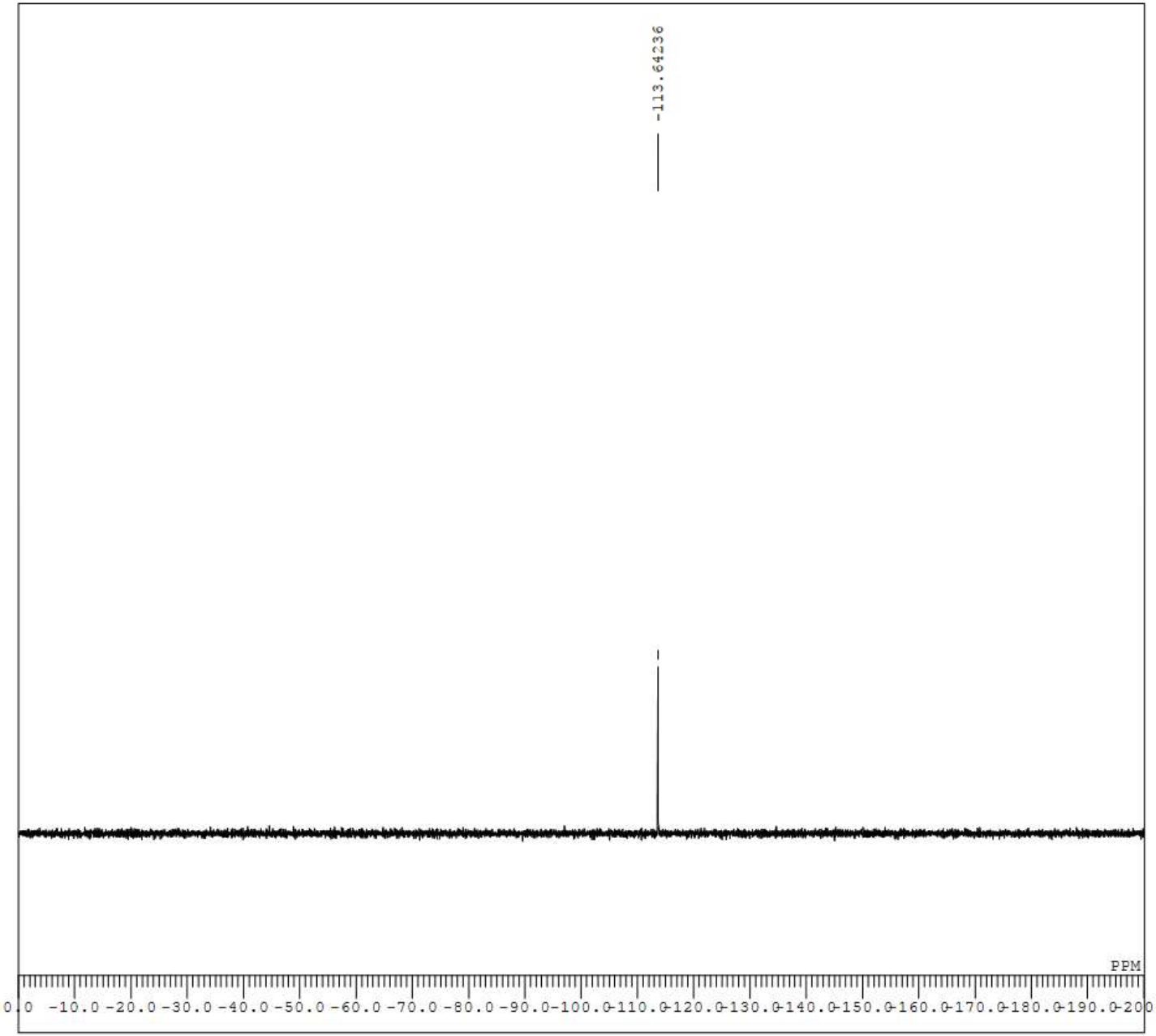
Me

3v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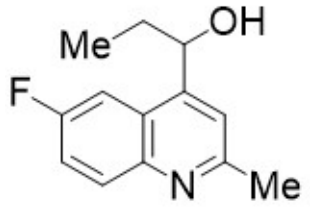
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F
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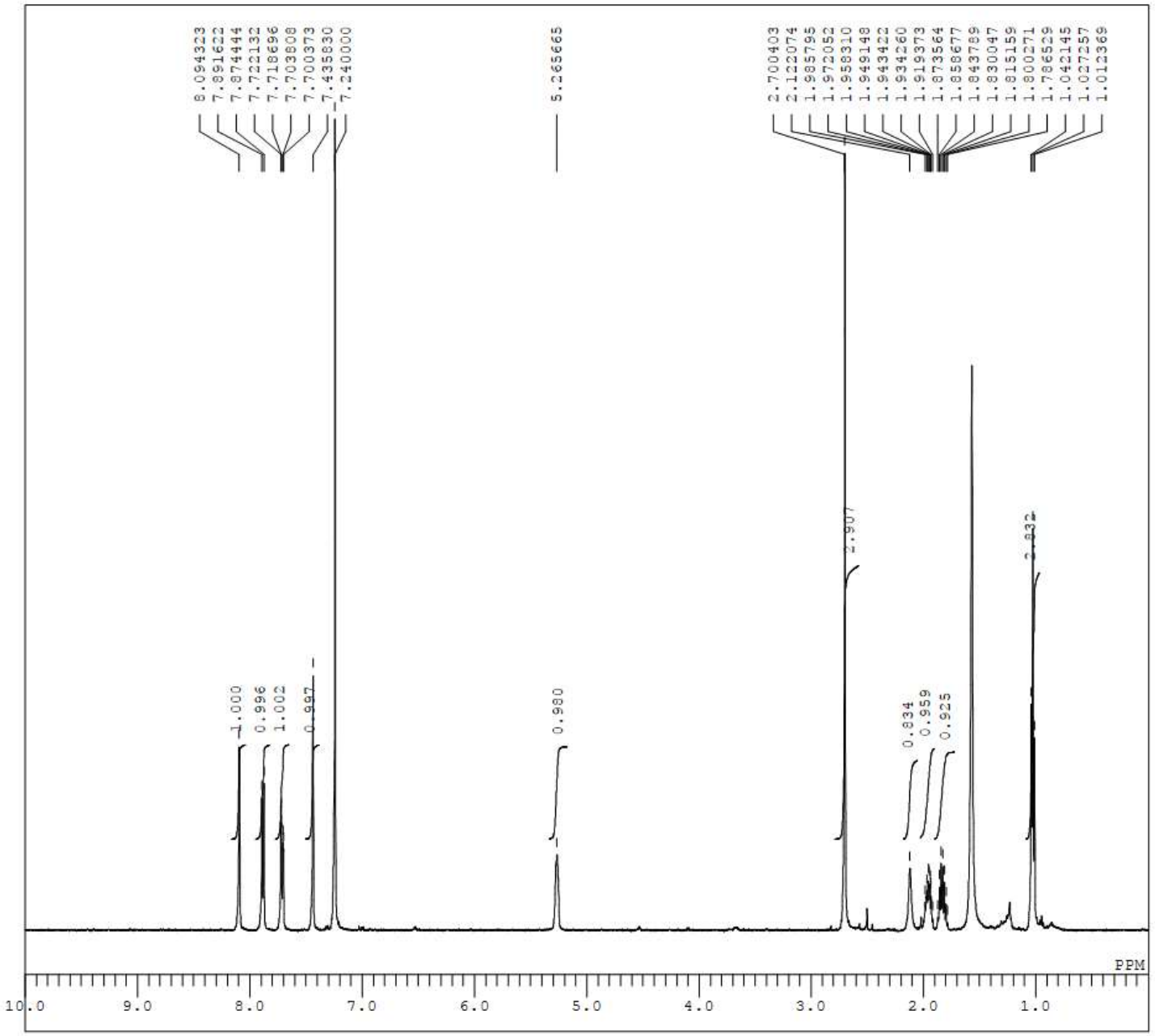
Me

3v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1.934260
1.919373
1.873564
1.858677
1.843789
1.830047
1.815159
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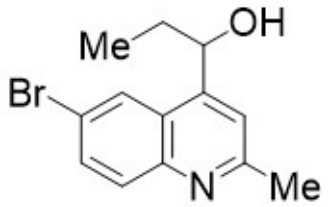
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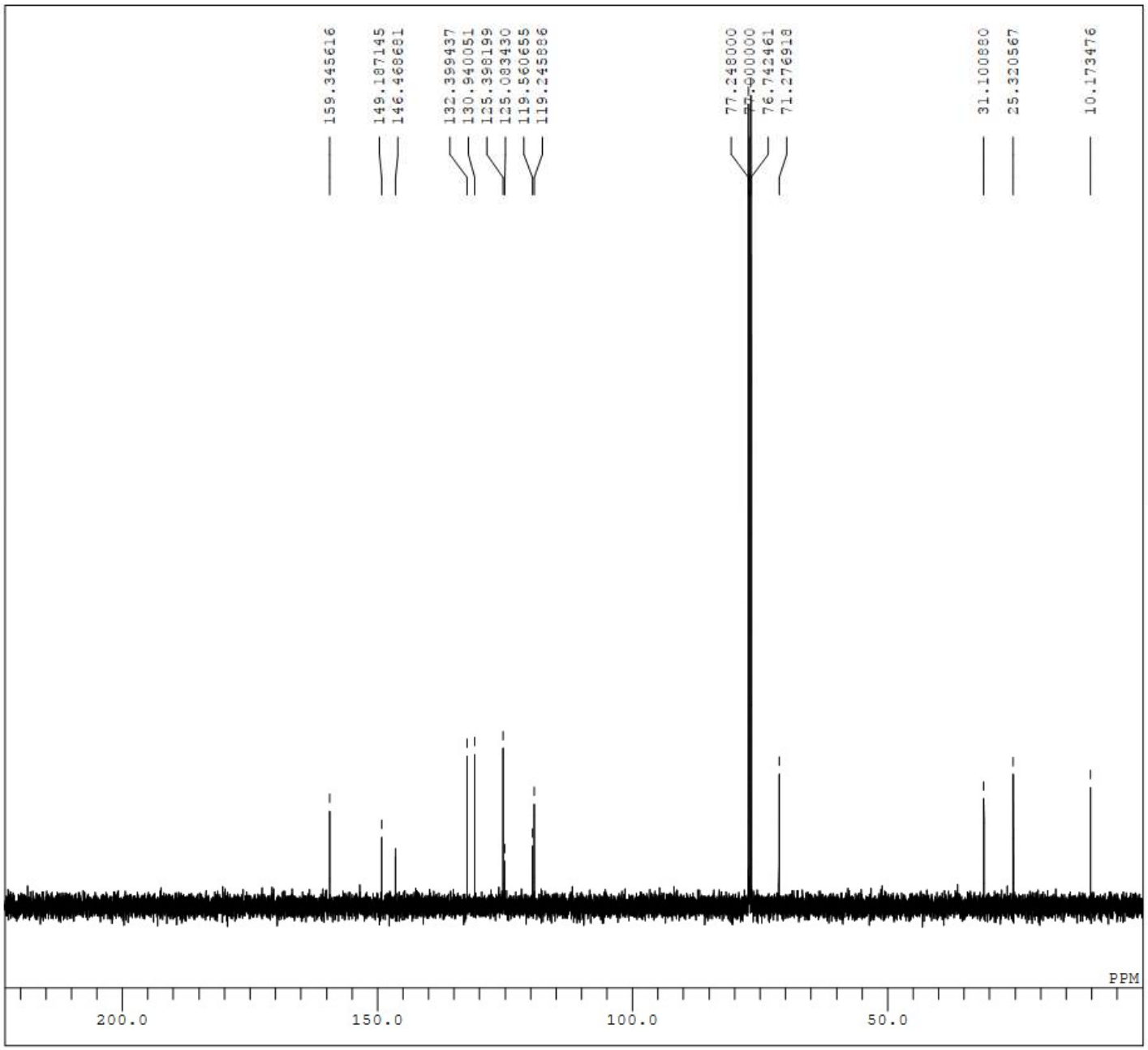
3w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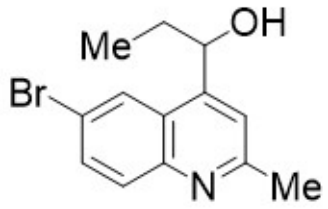
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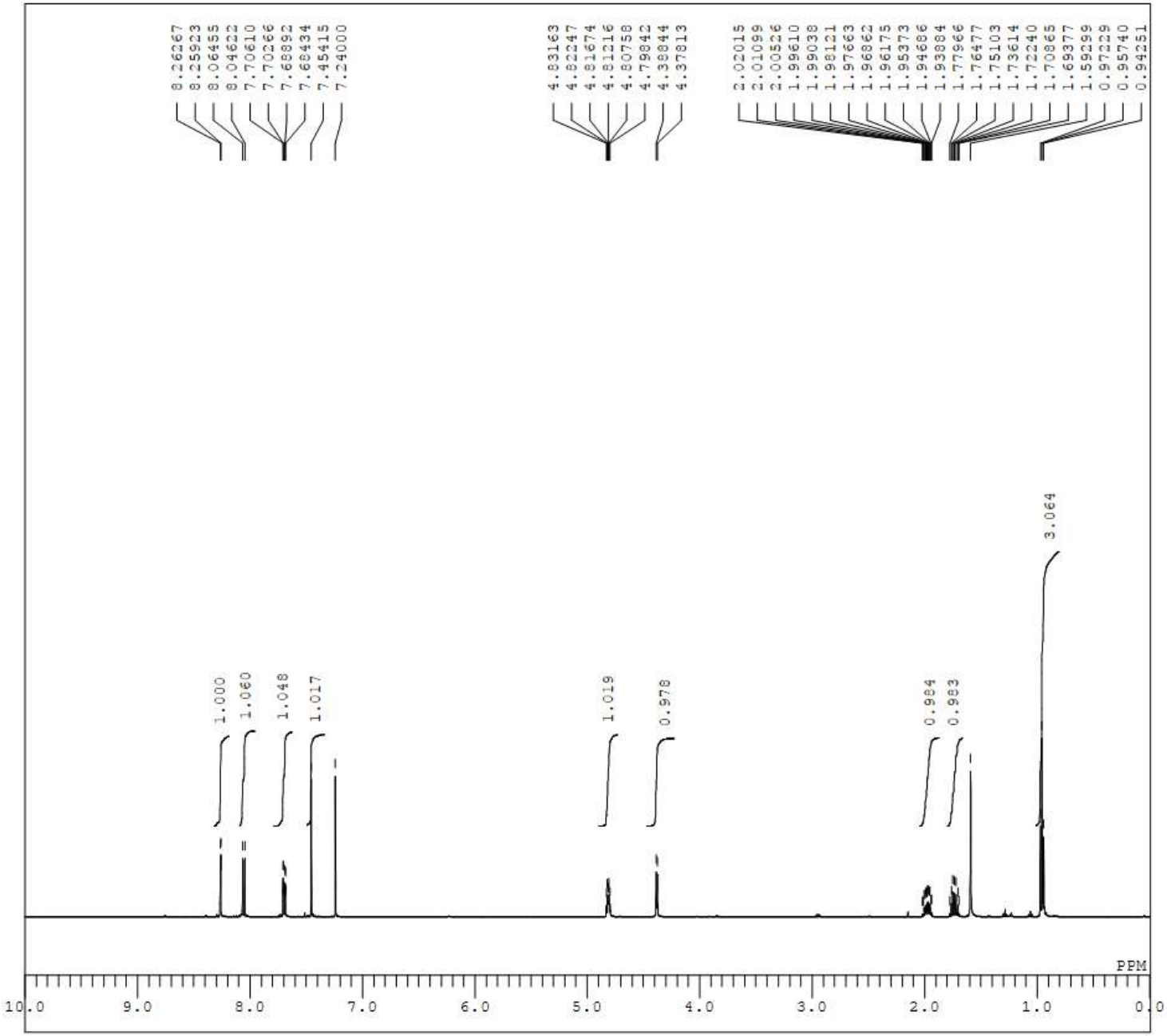
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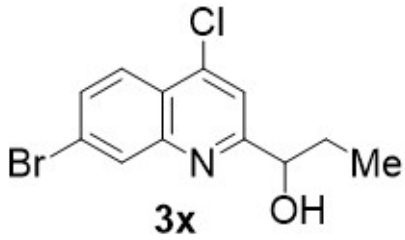
Cl
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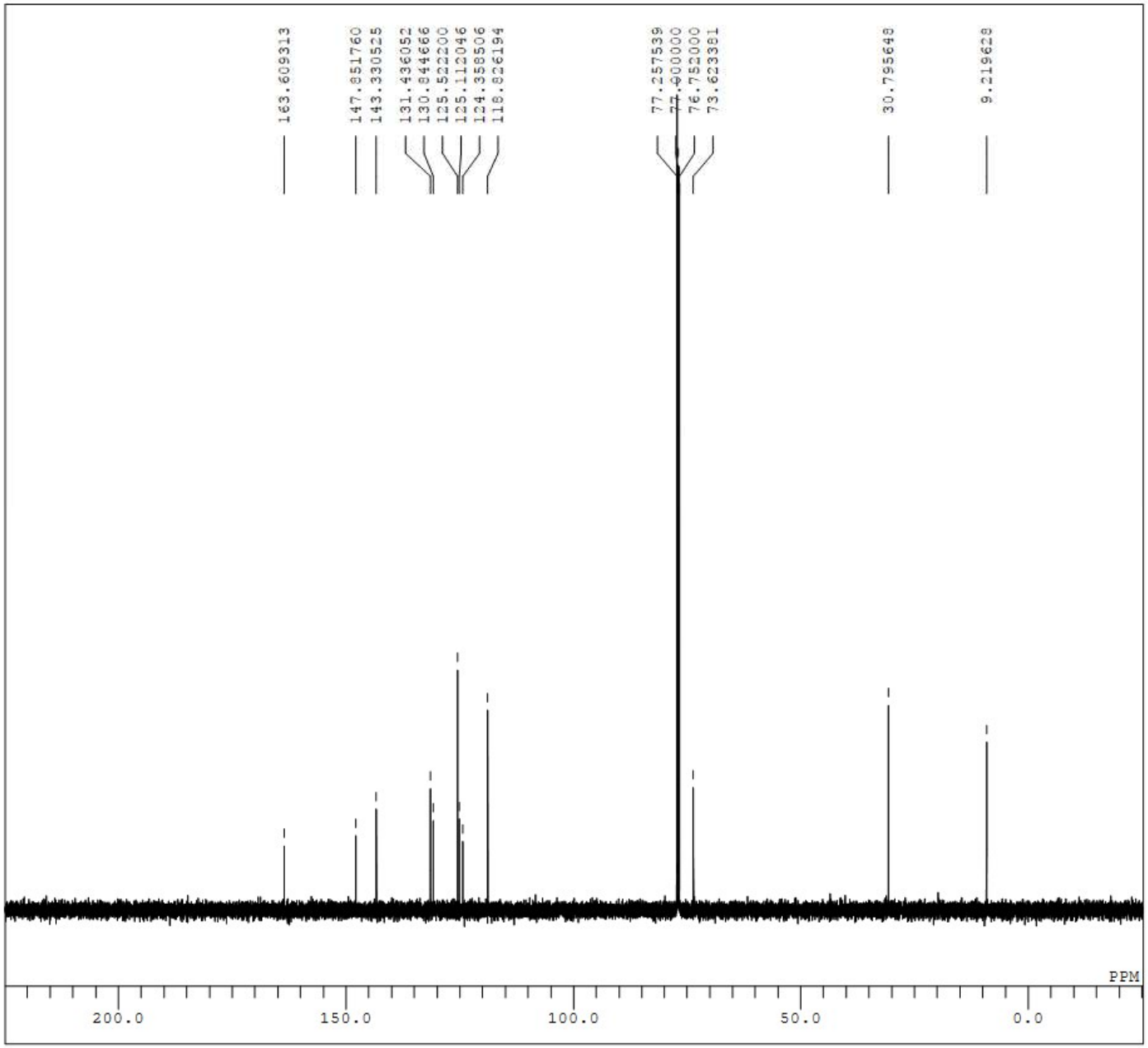
Me
OH

3x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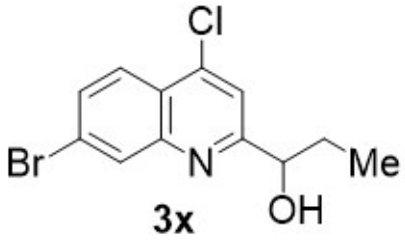
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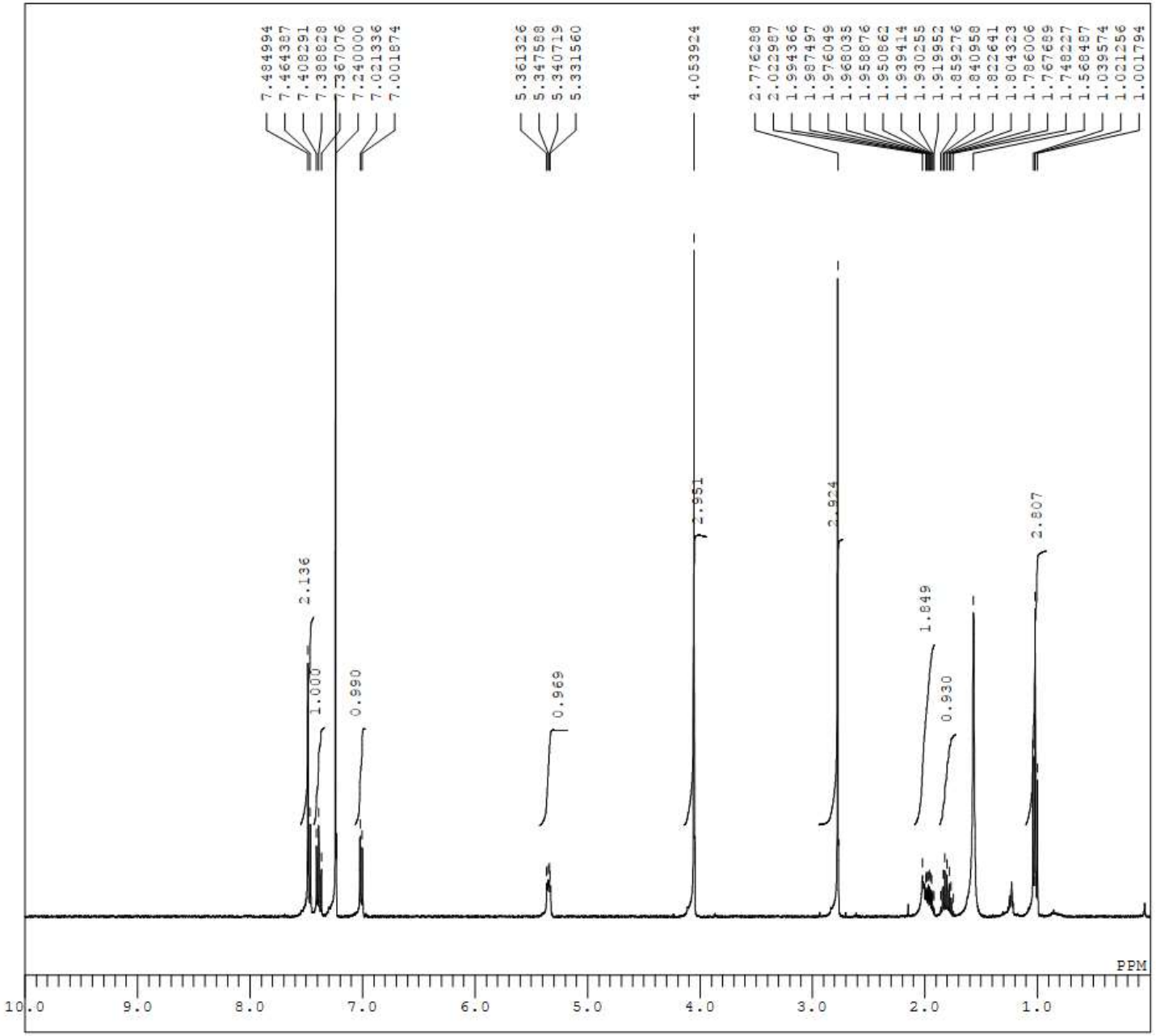
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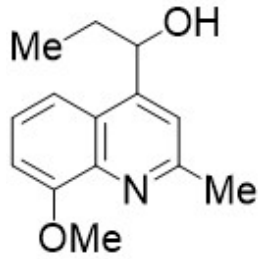
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OMe

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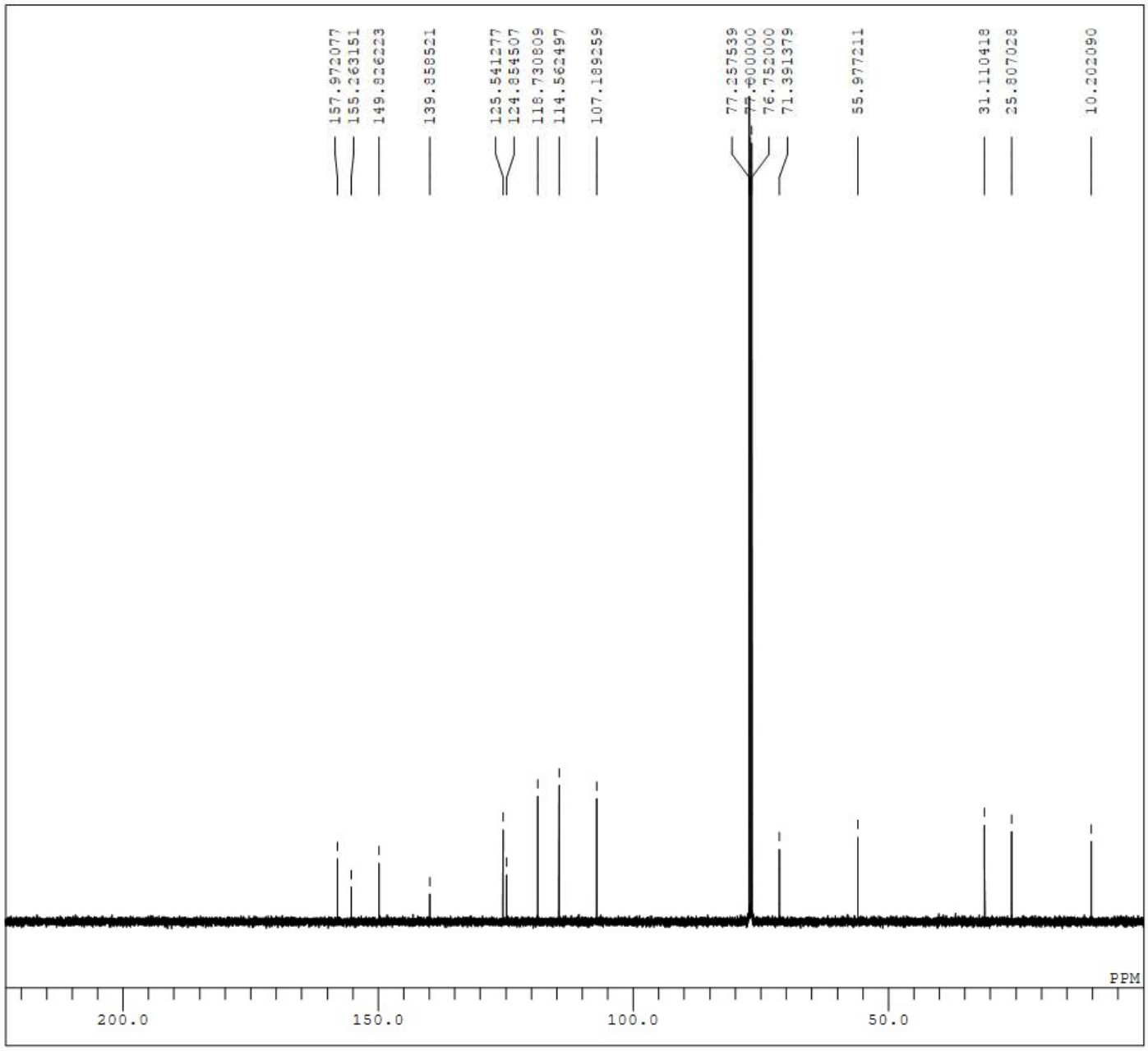
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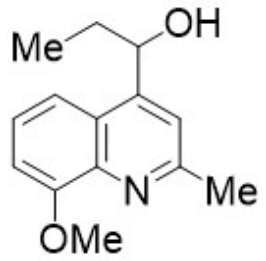
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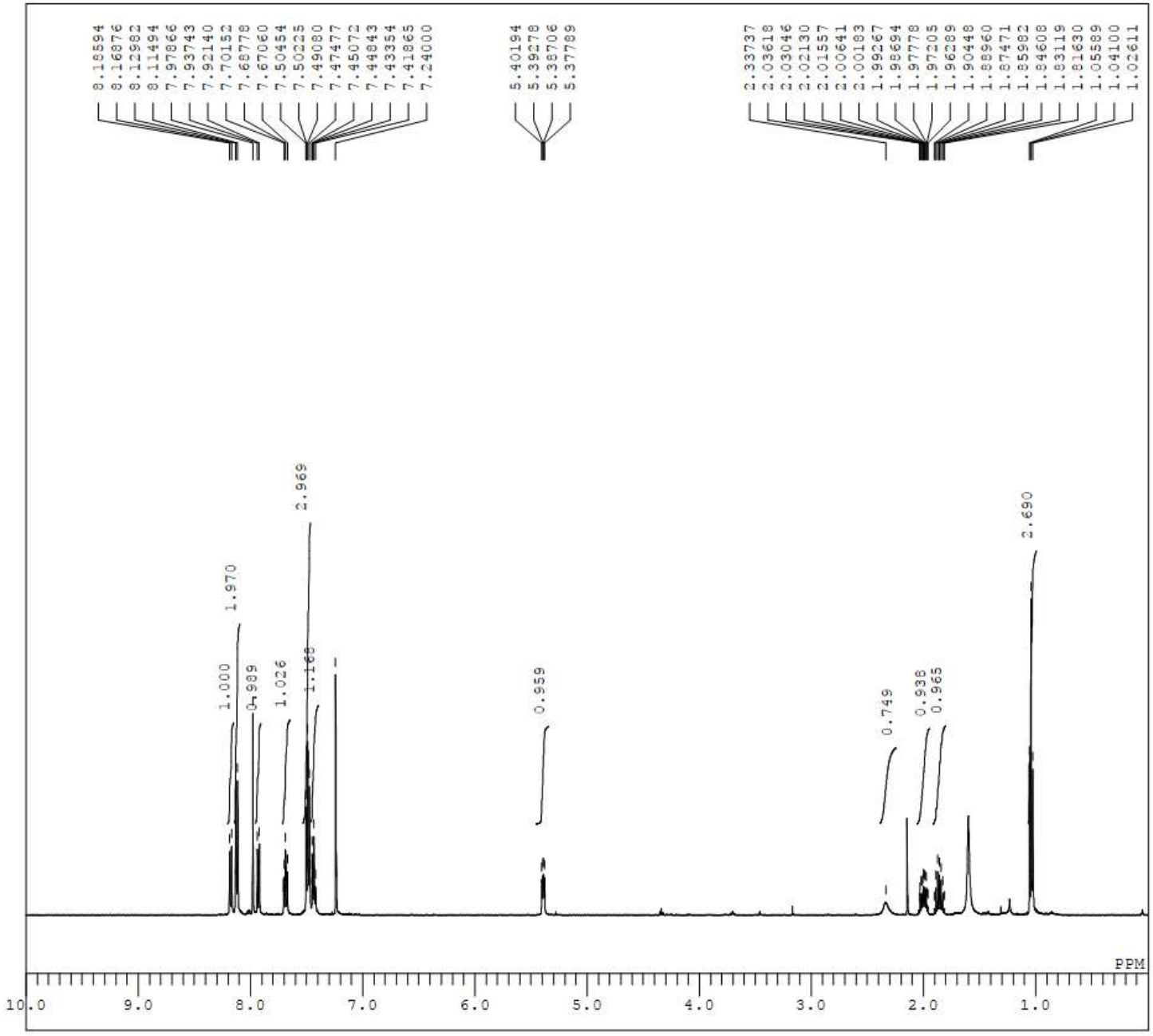
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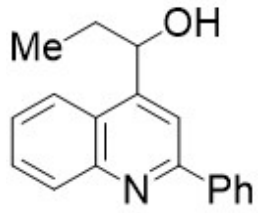
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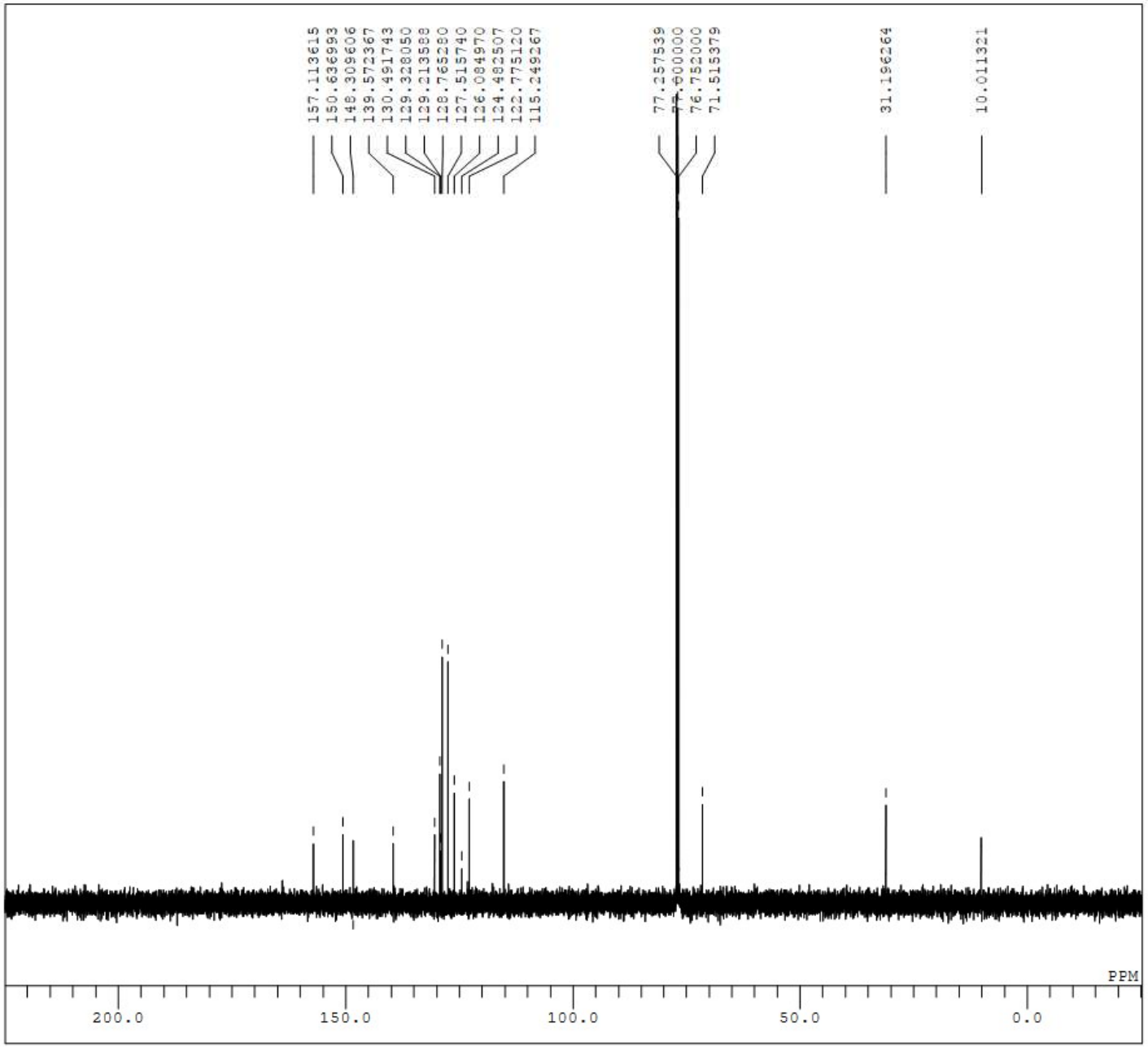
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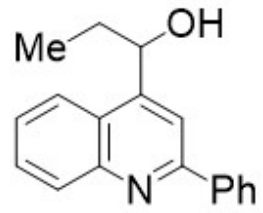
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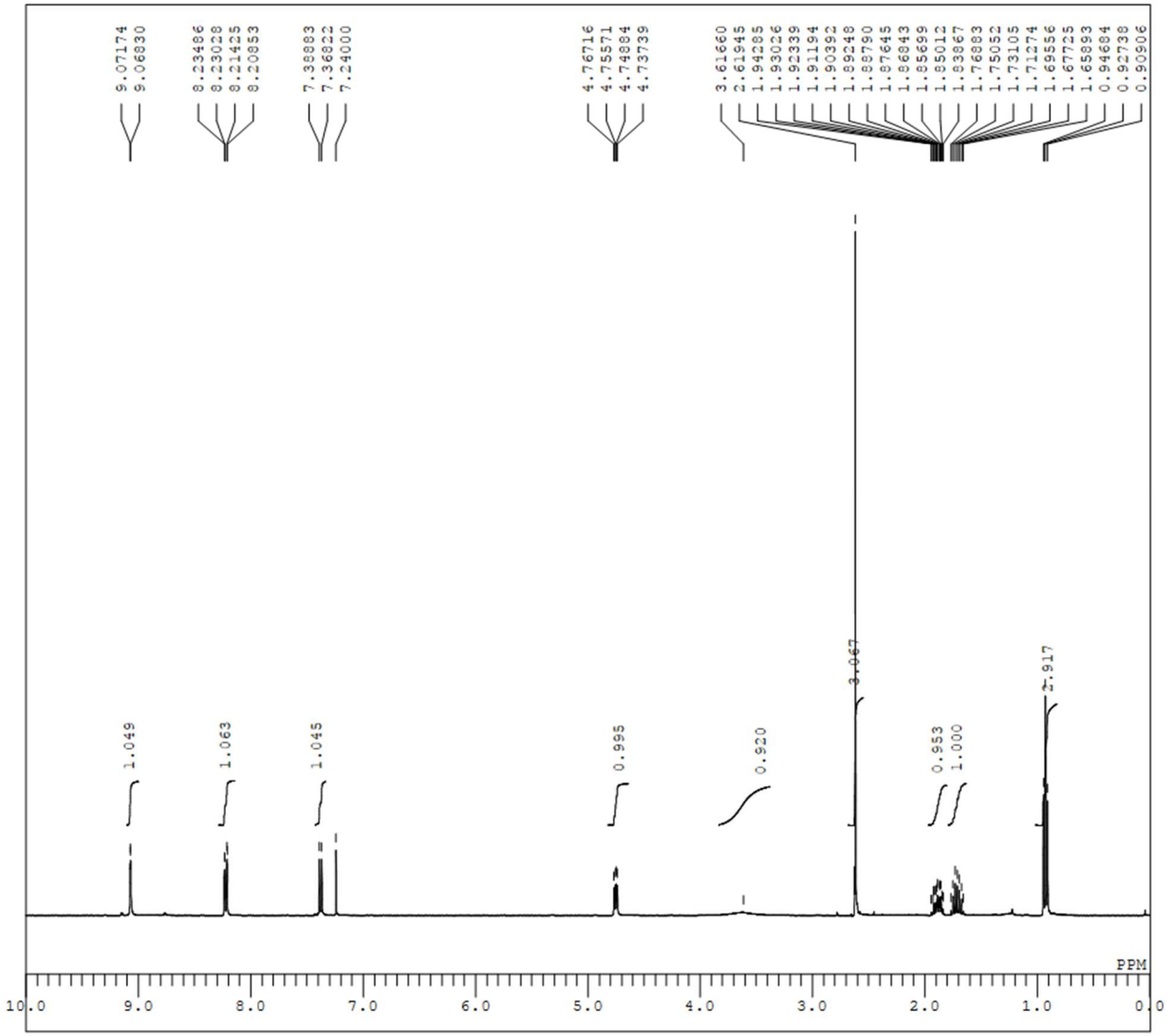
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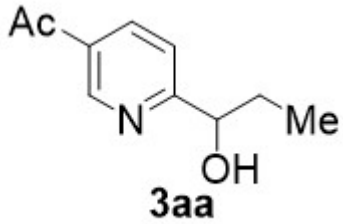
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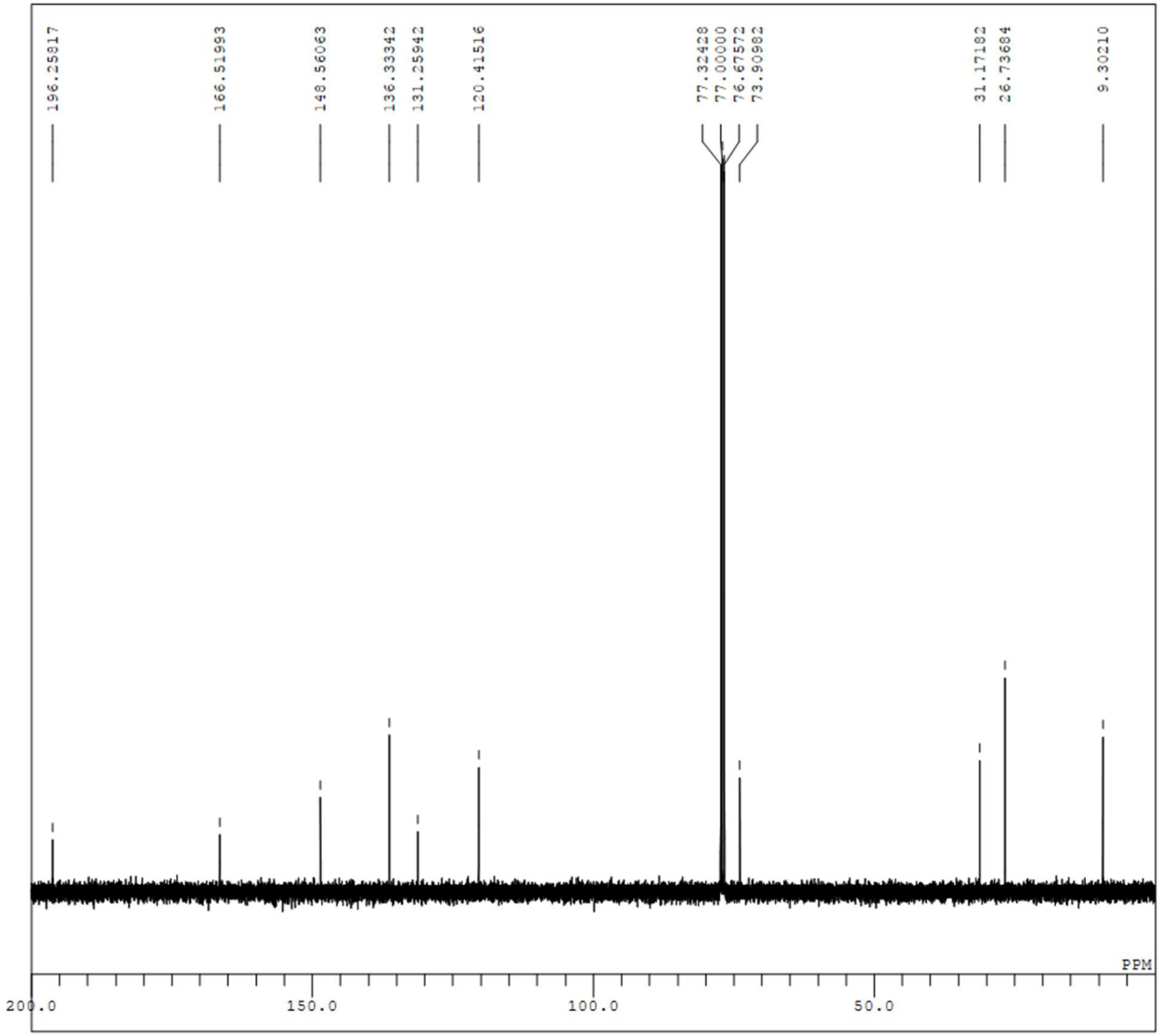
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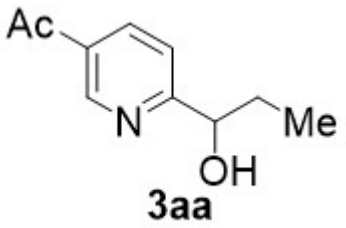
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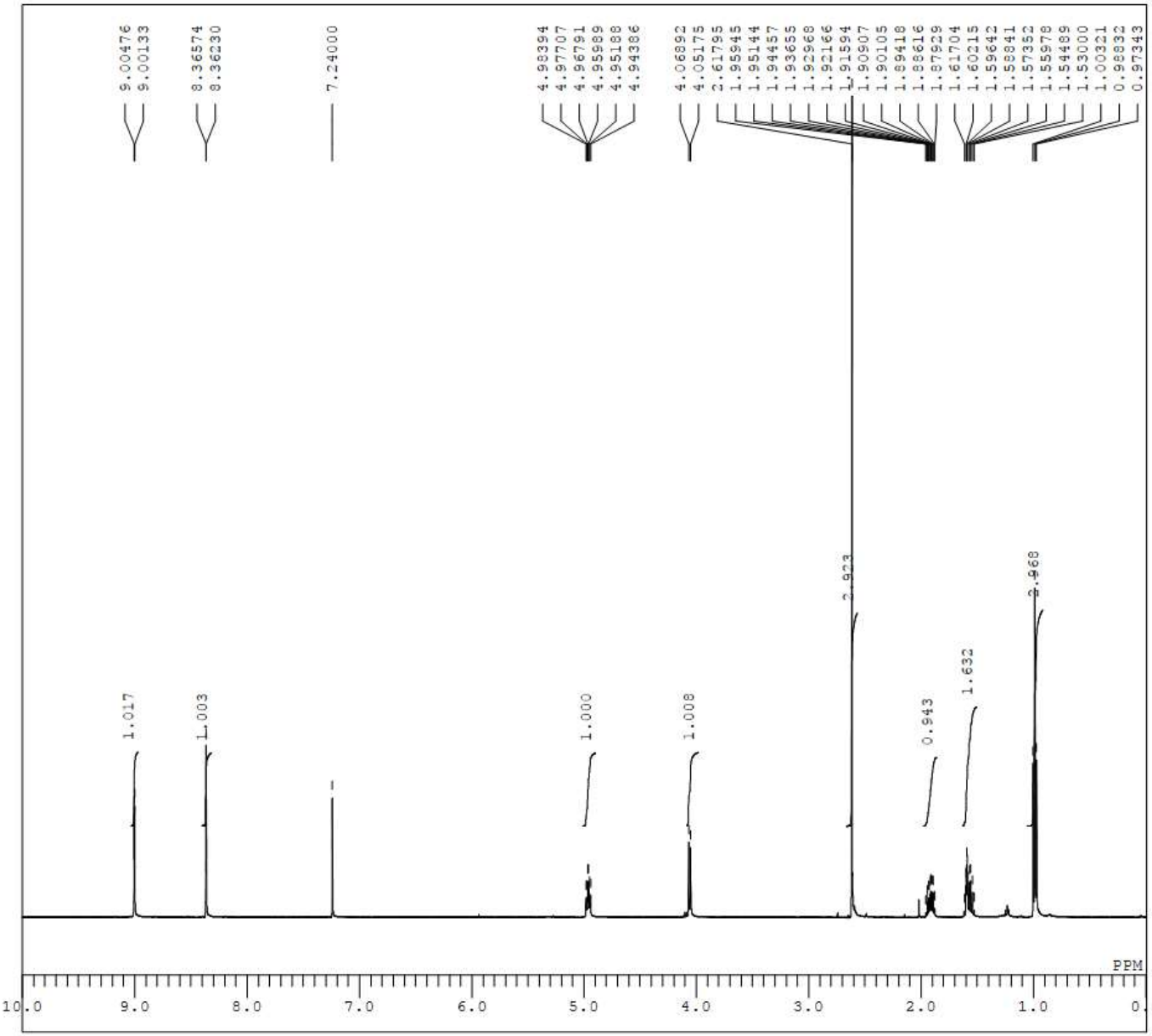
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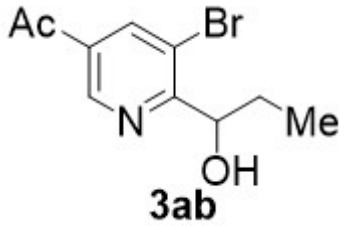
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Me
OH

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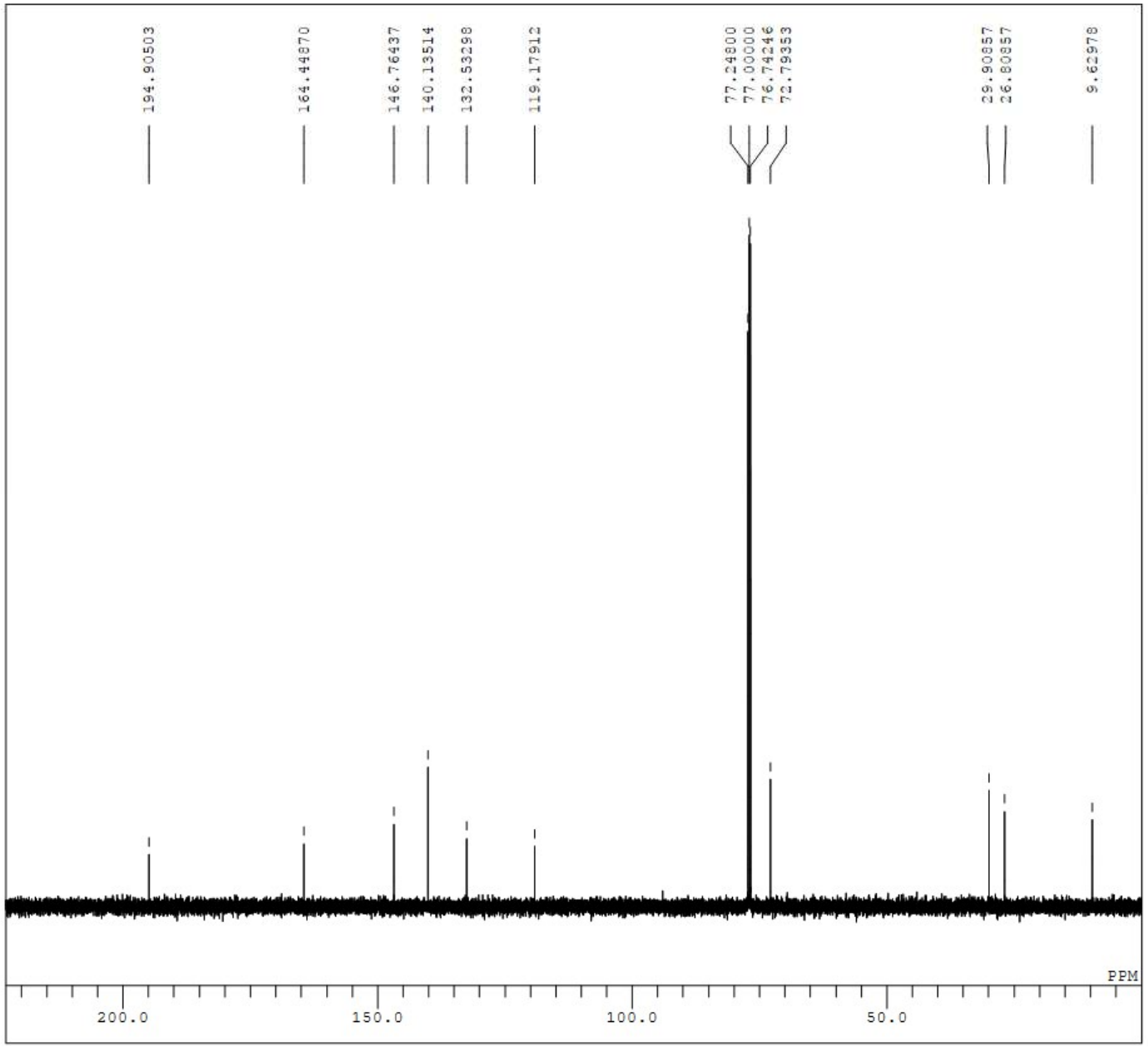
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Ac
Br
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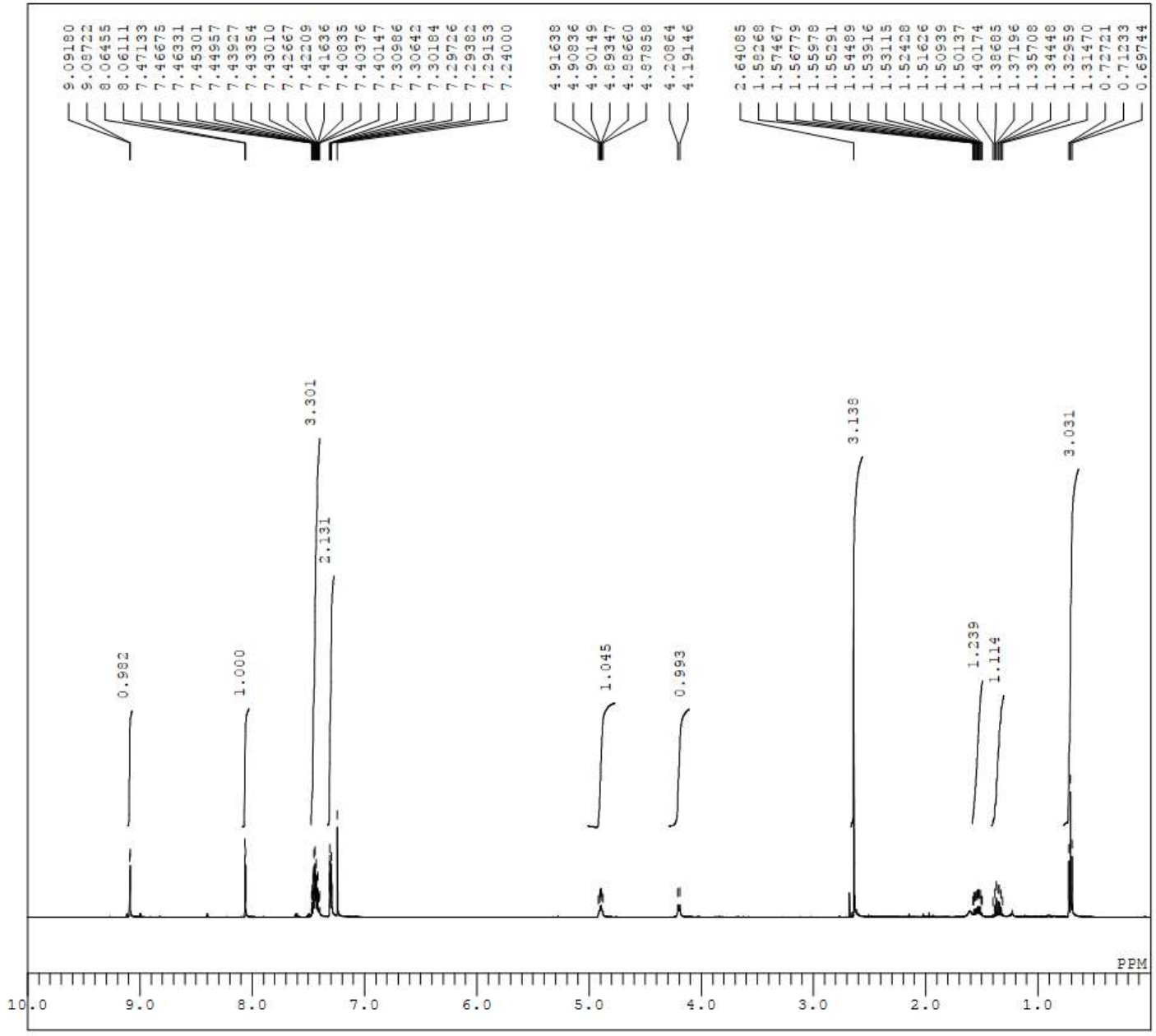
Me
OH

3ab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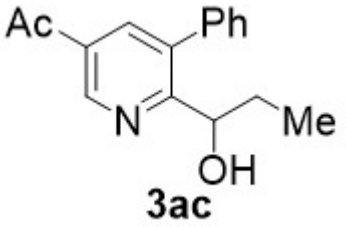
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Me
OH

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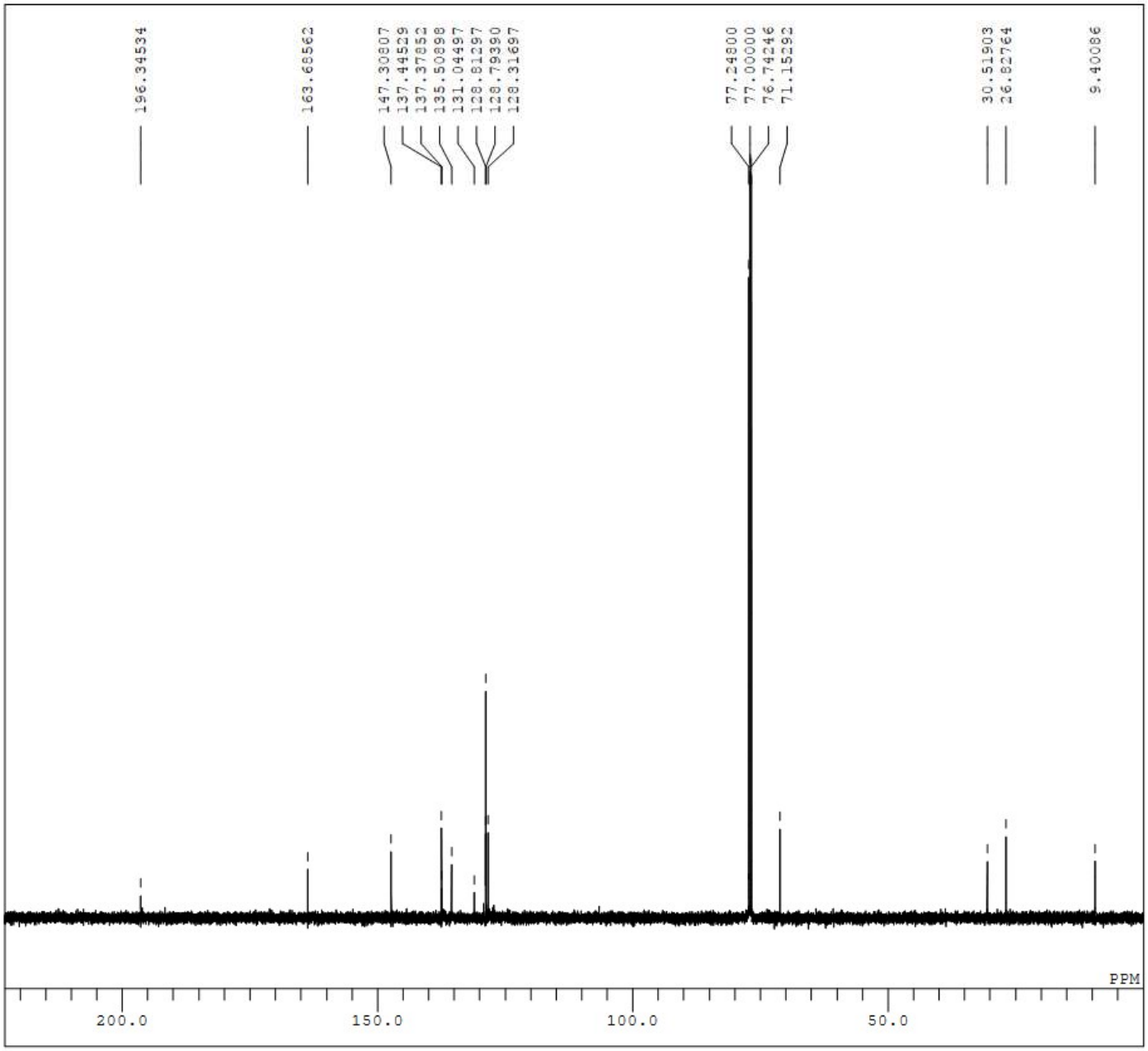
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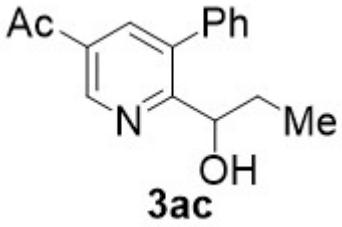
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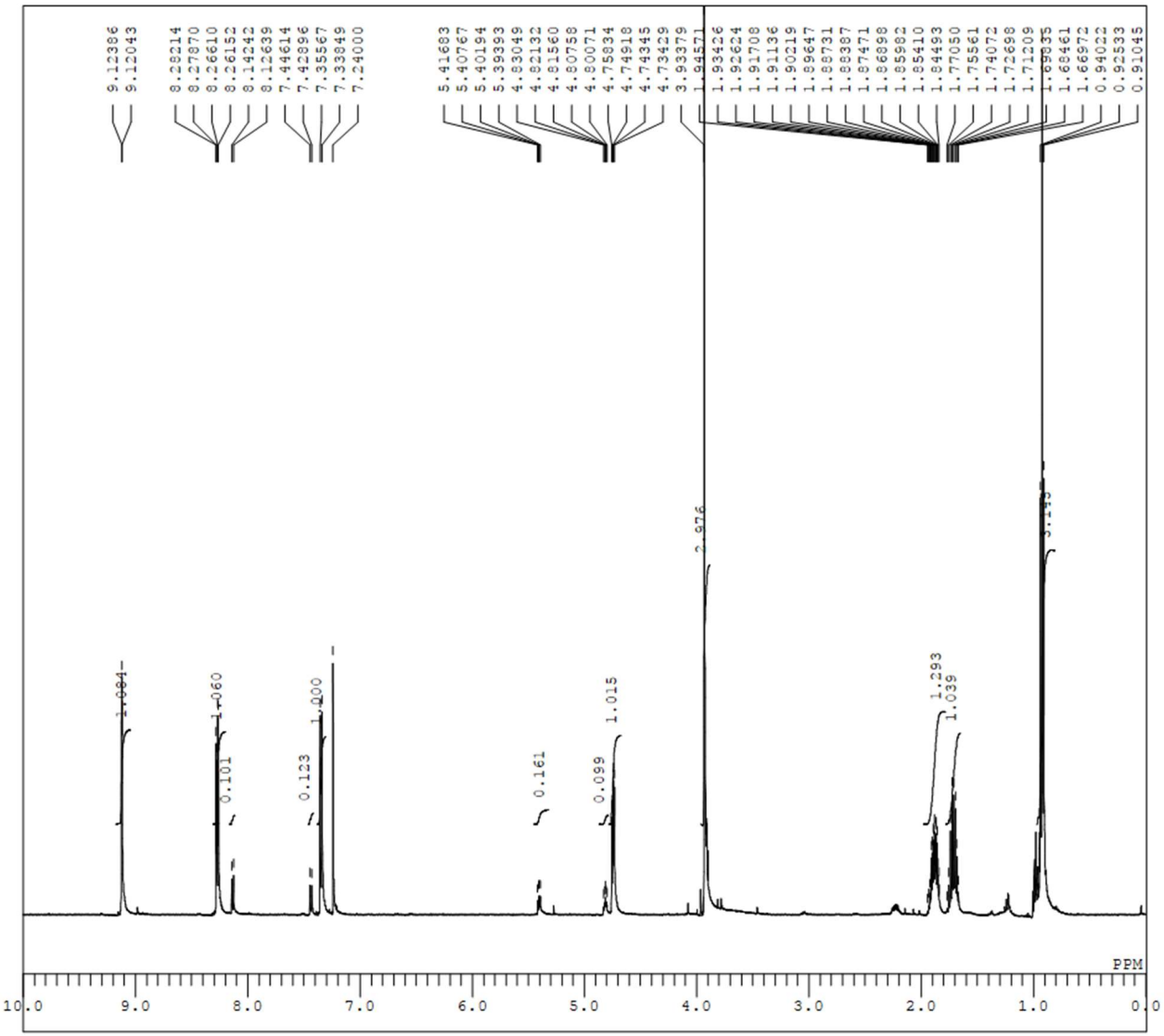
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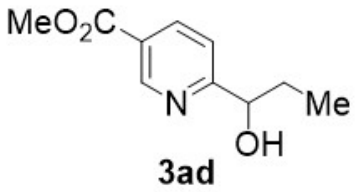
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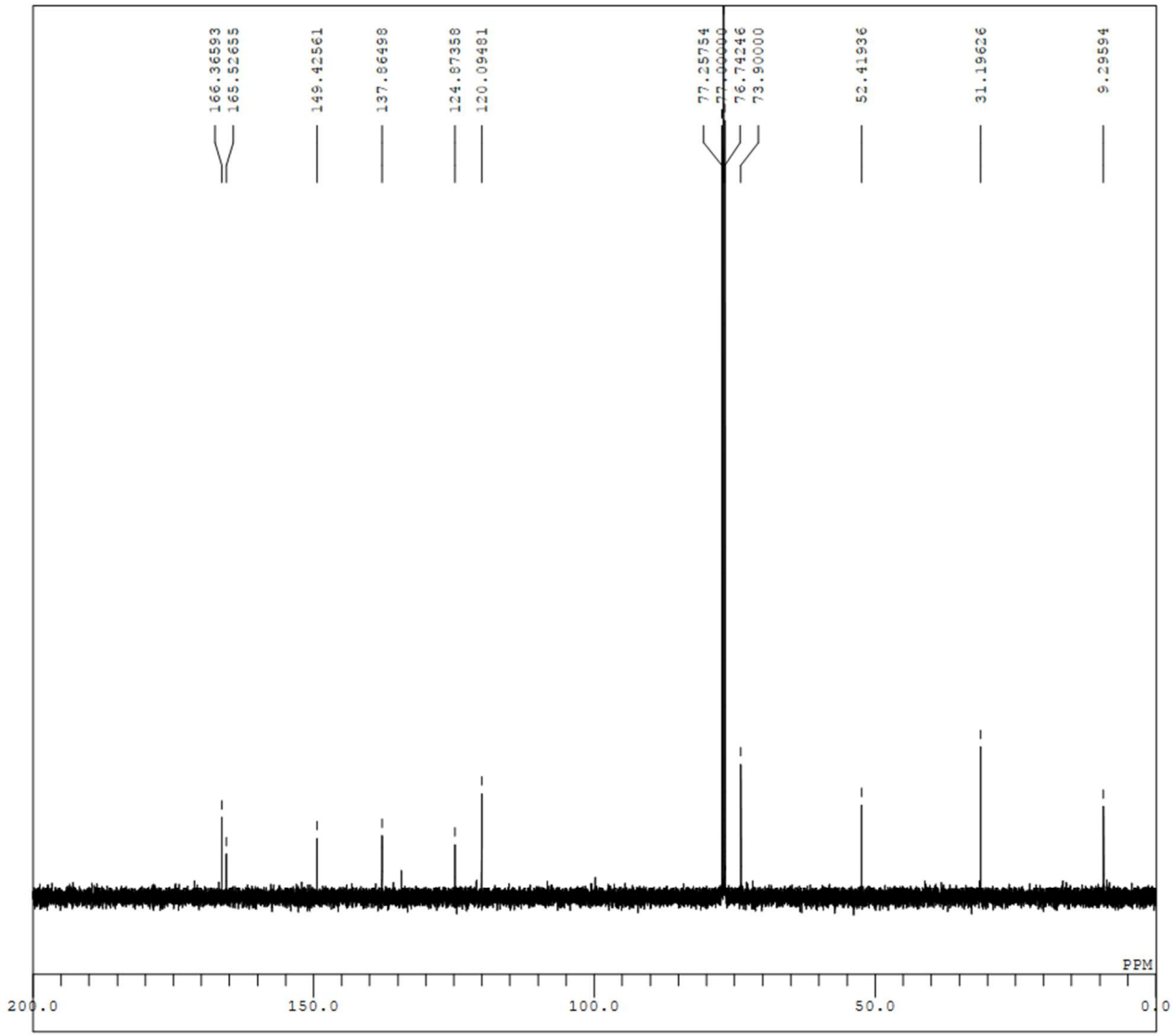
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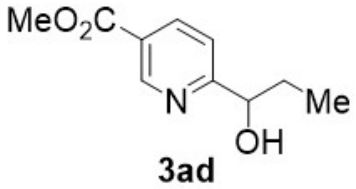
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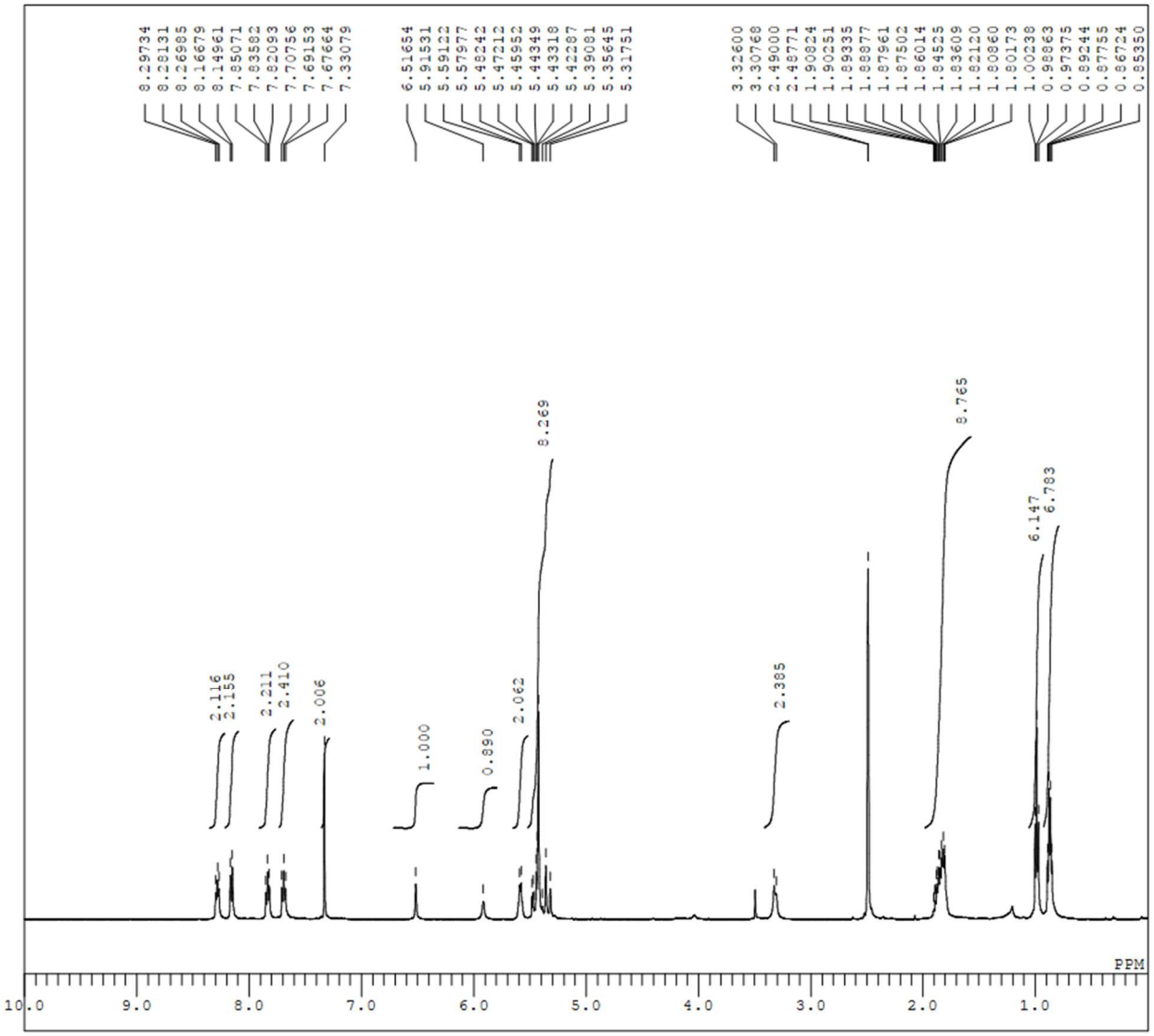
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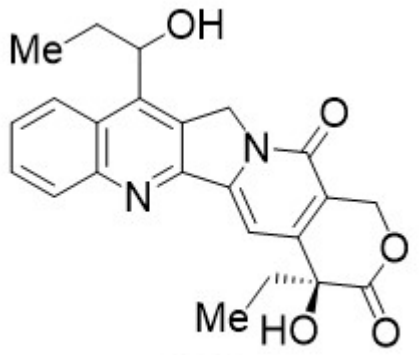
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O
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O

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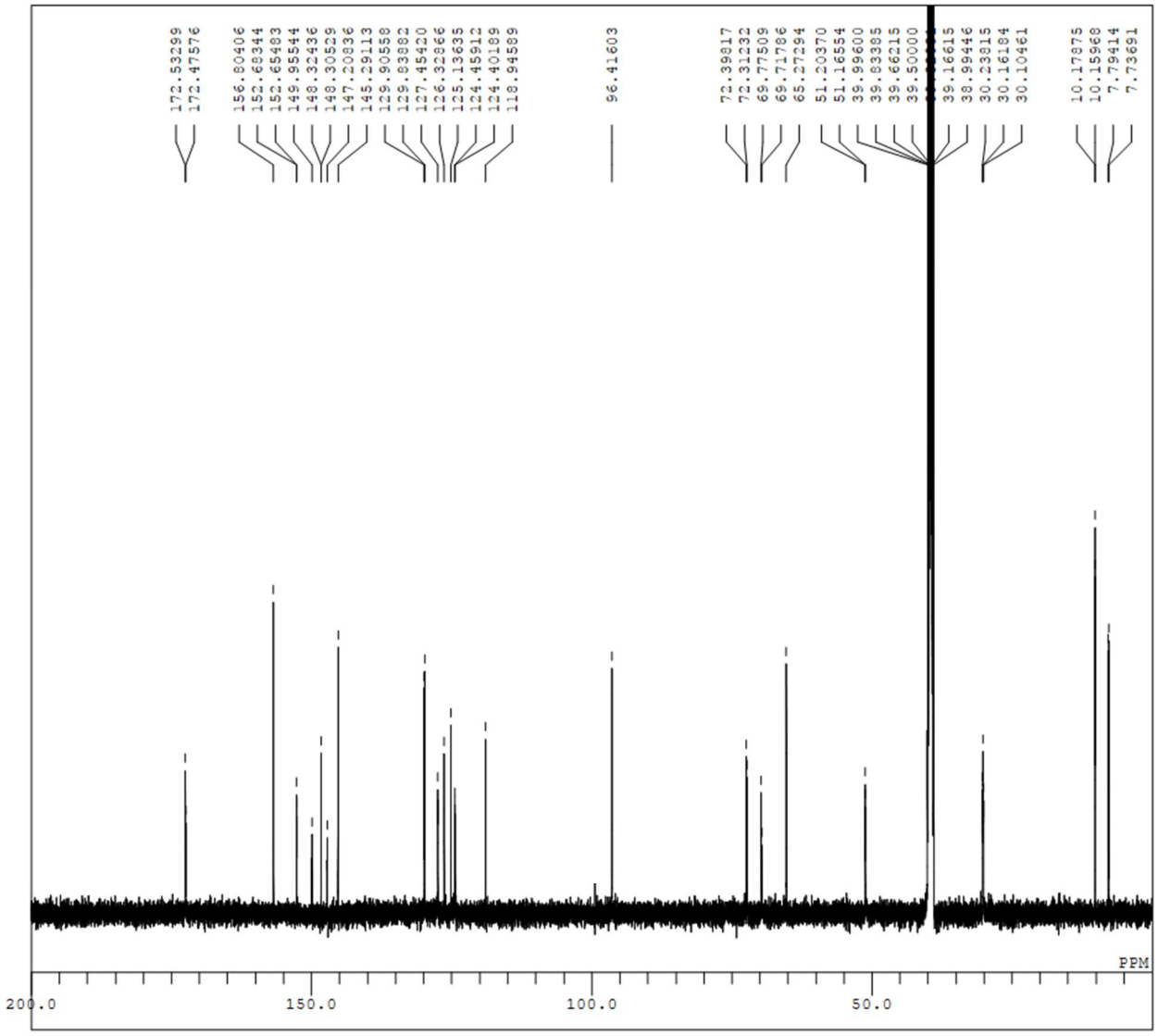
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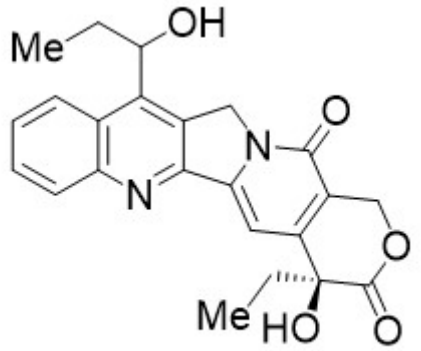
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HO

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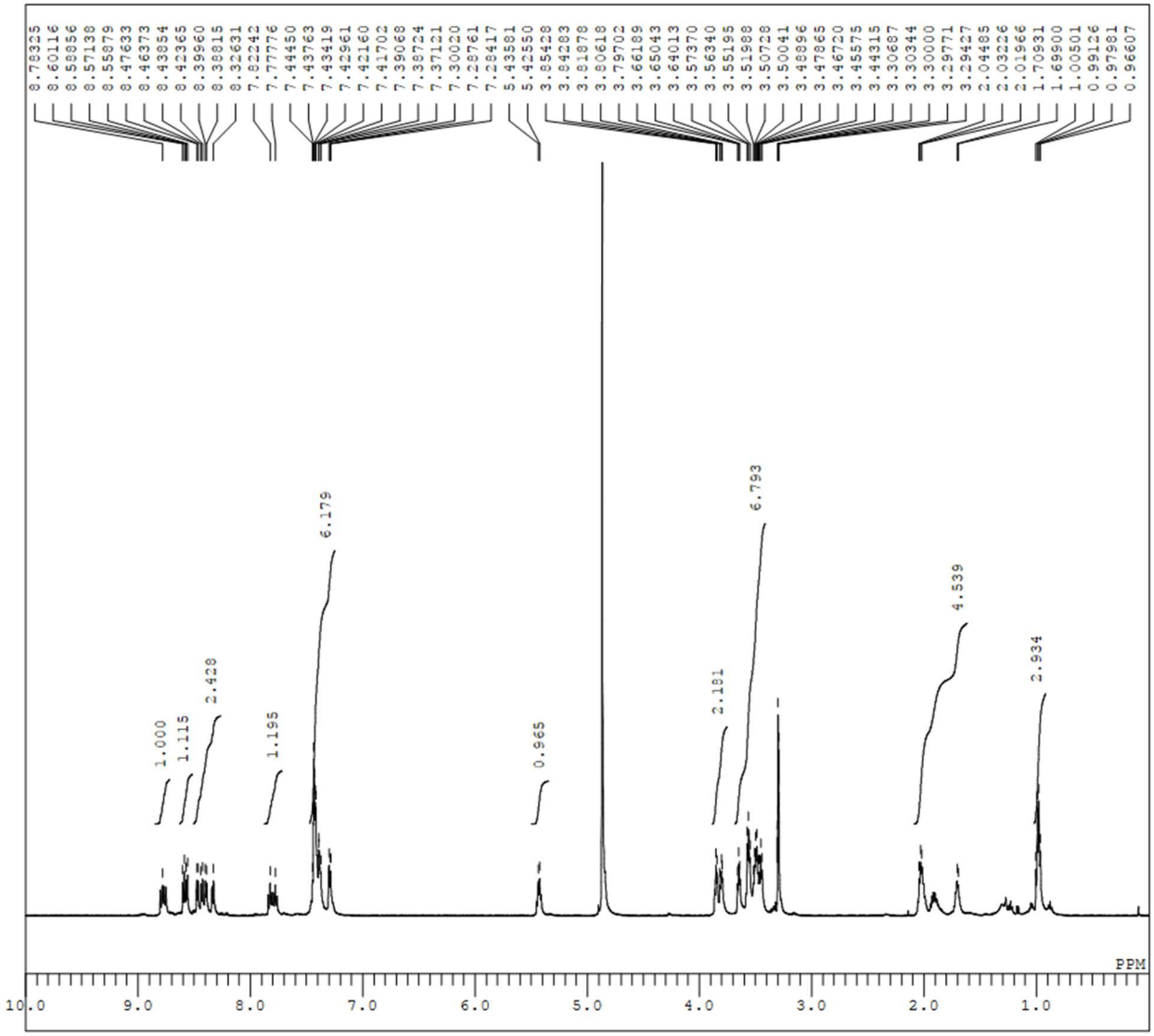
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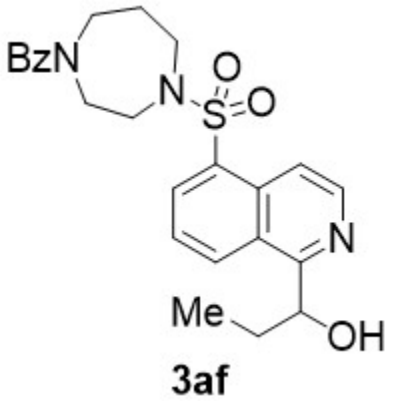
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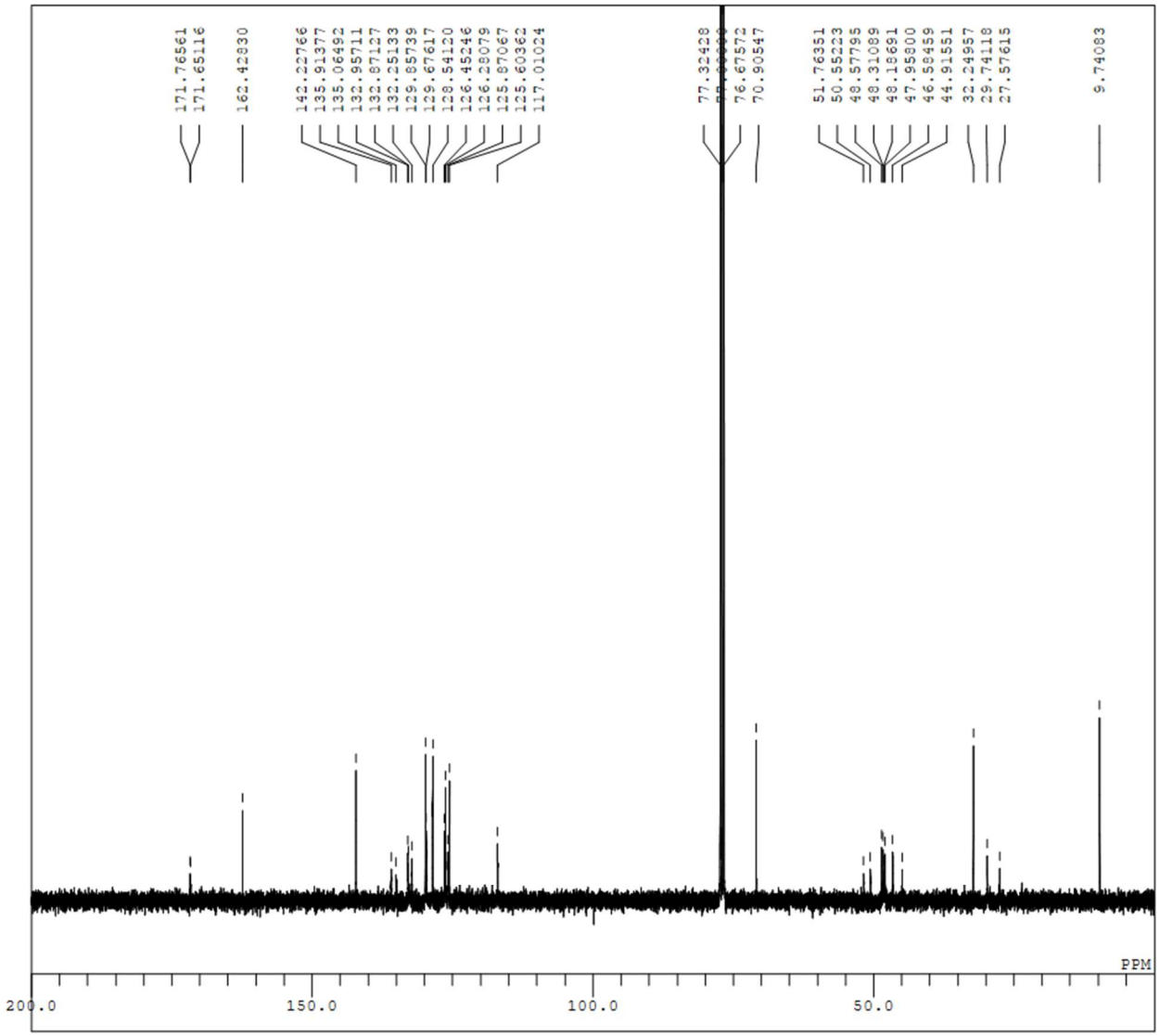
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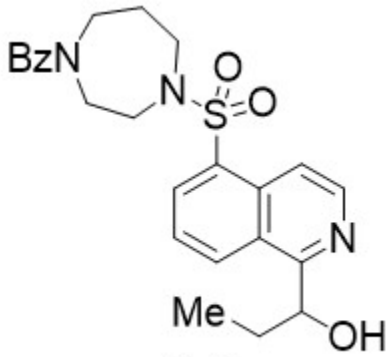
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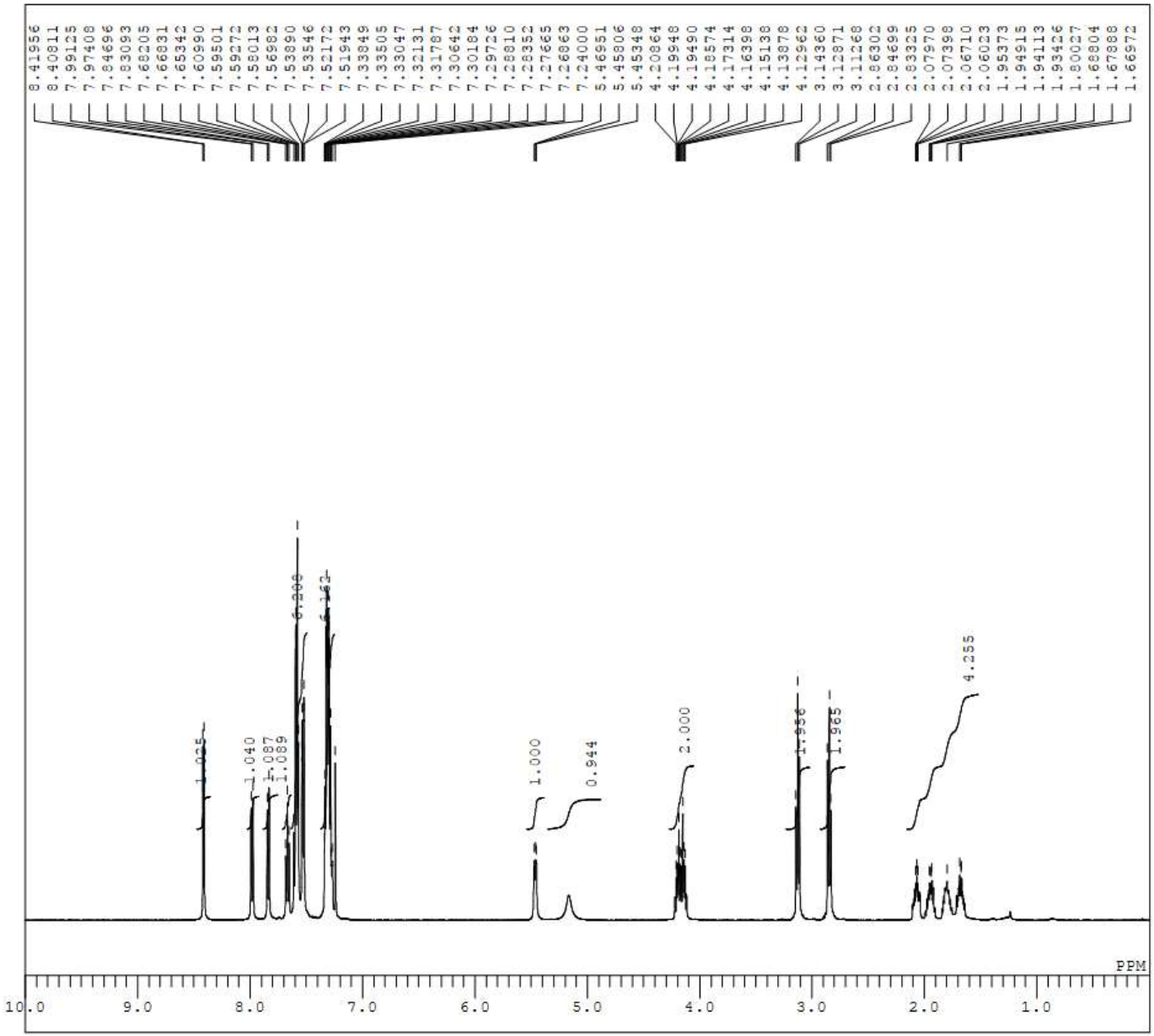
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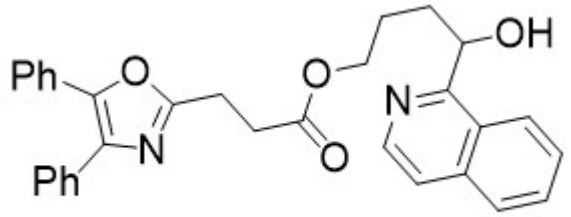
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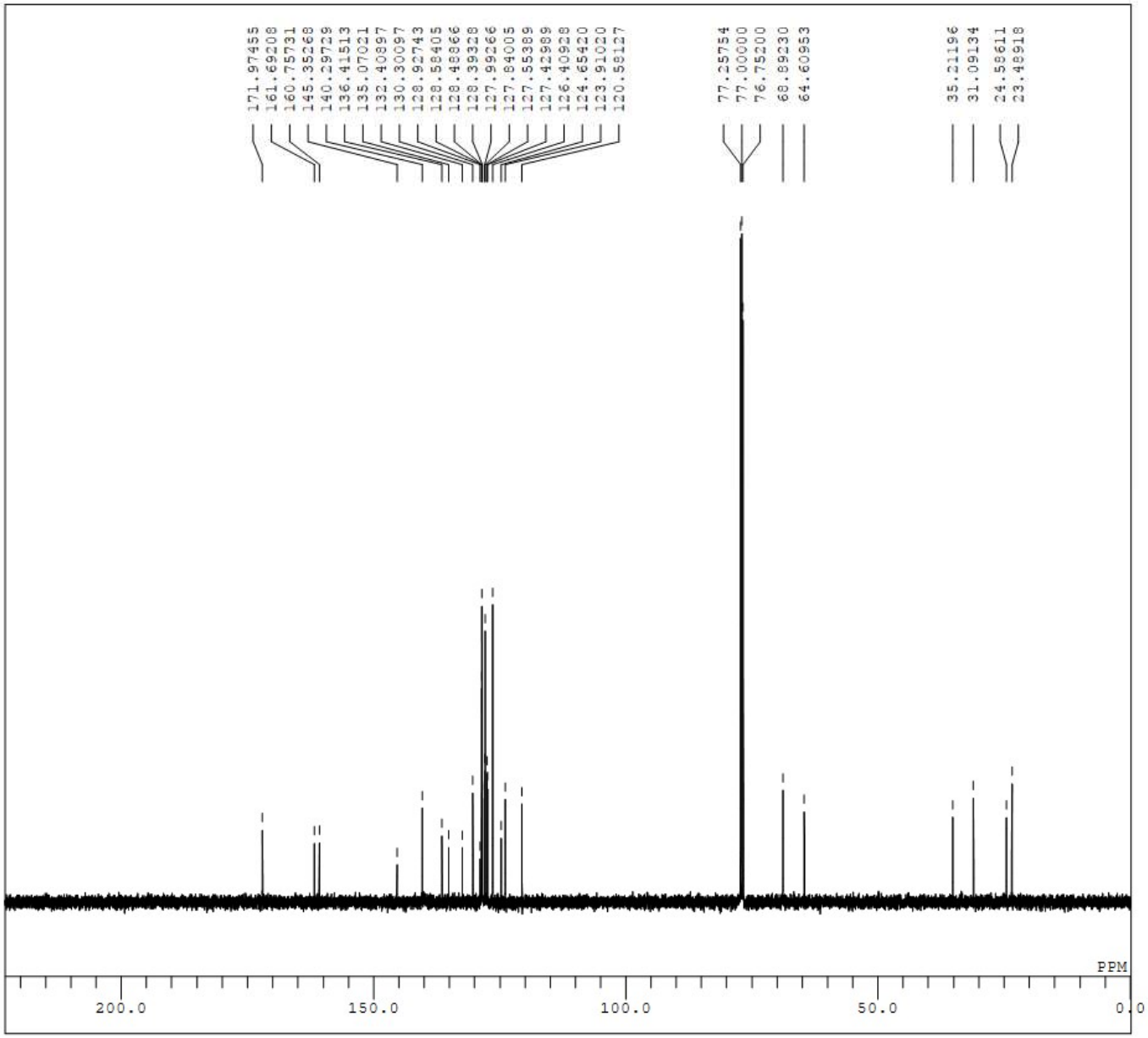
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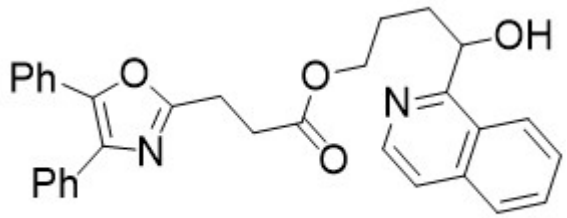
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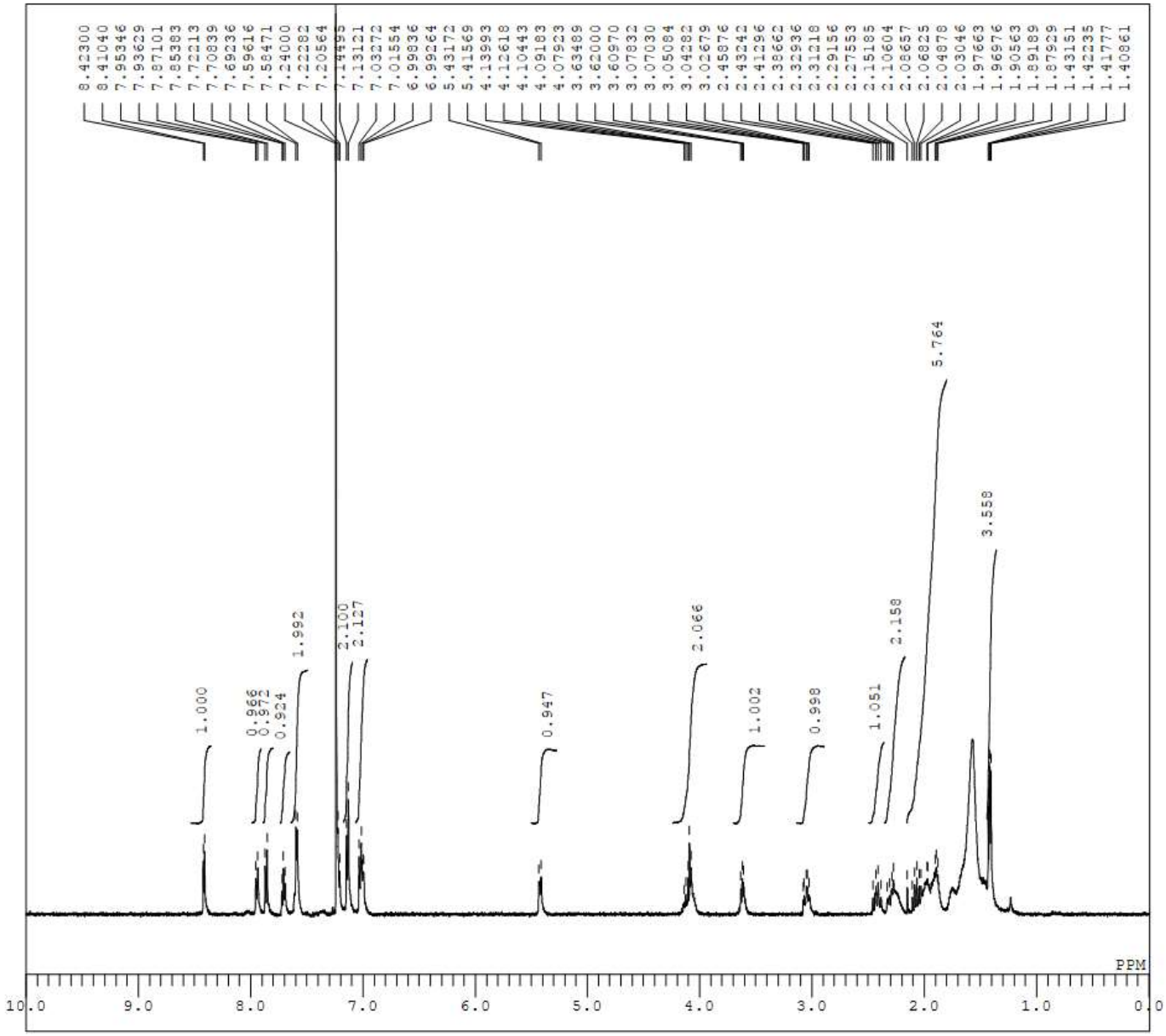
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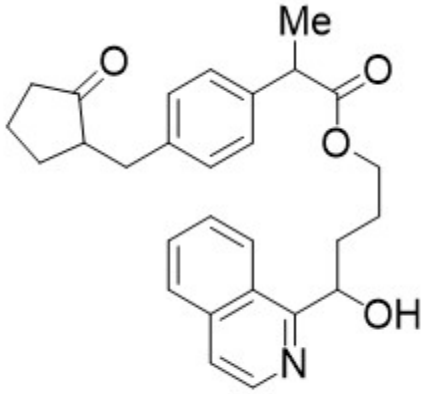
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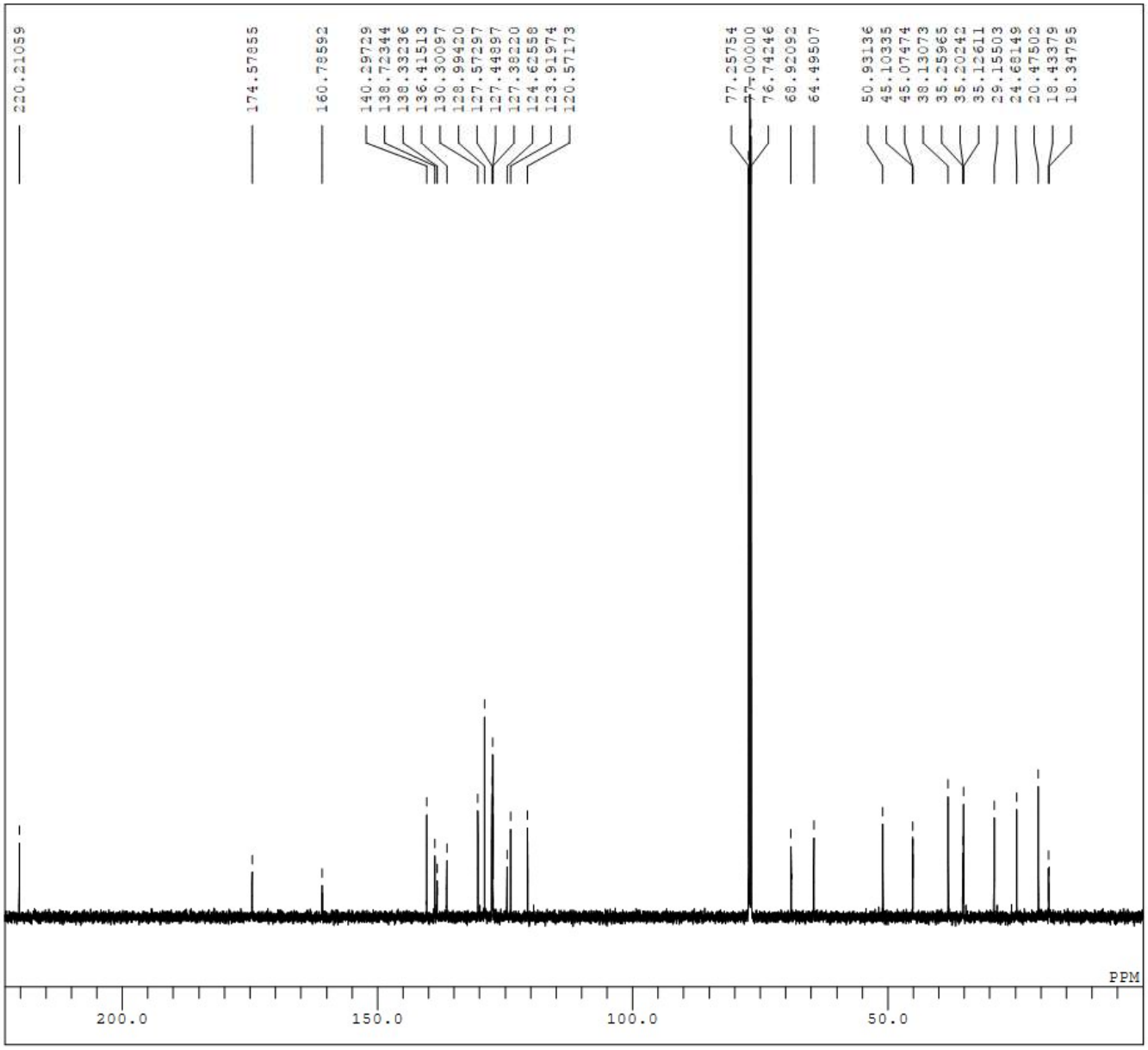
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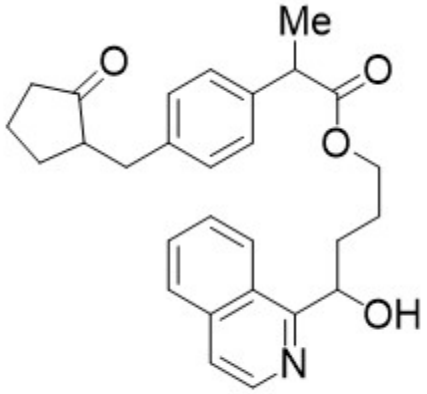
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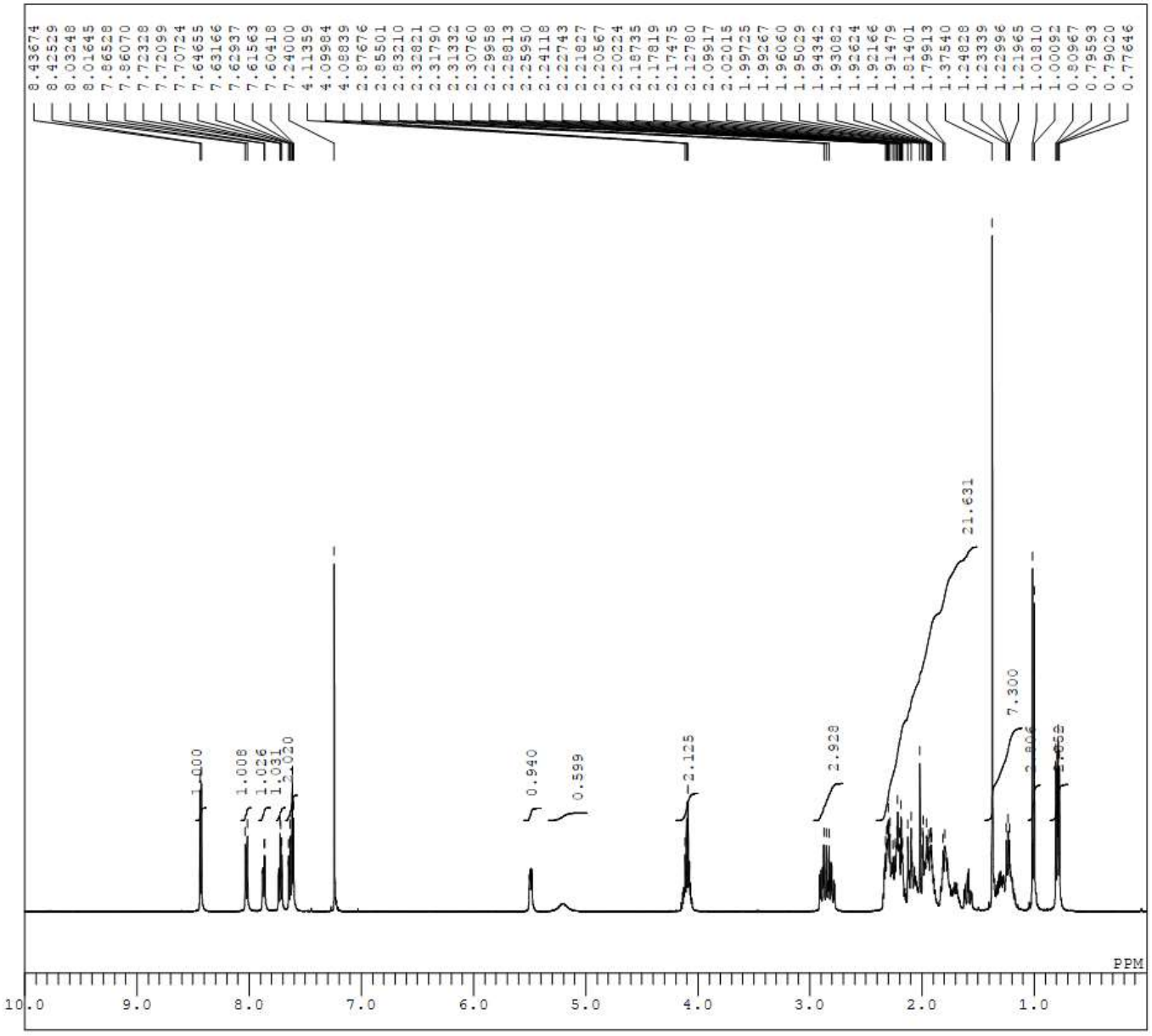
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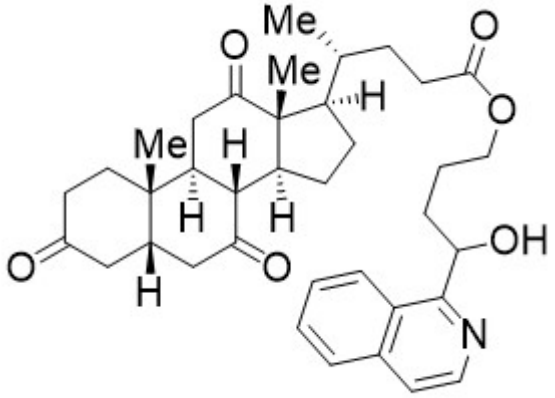
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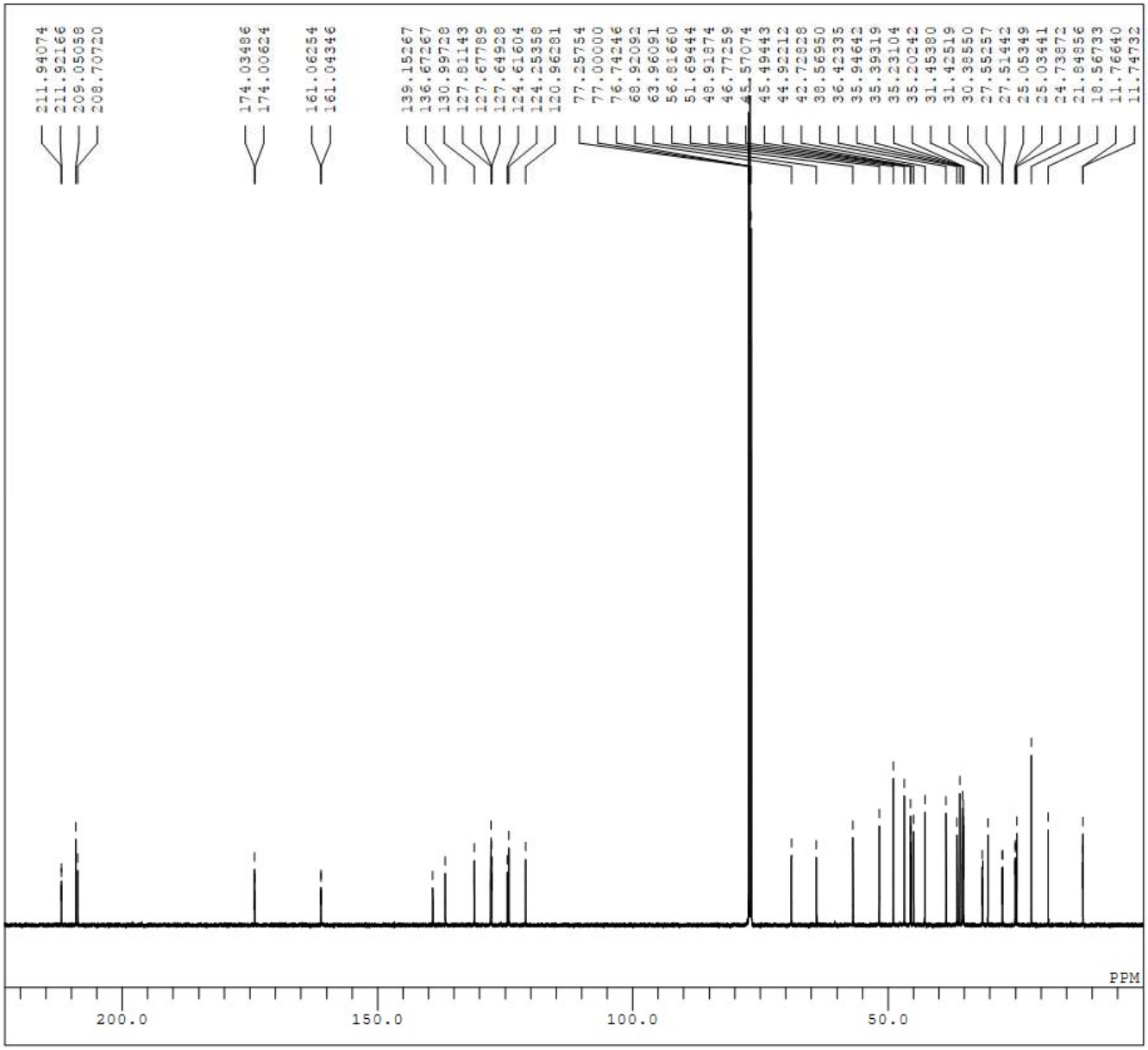
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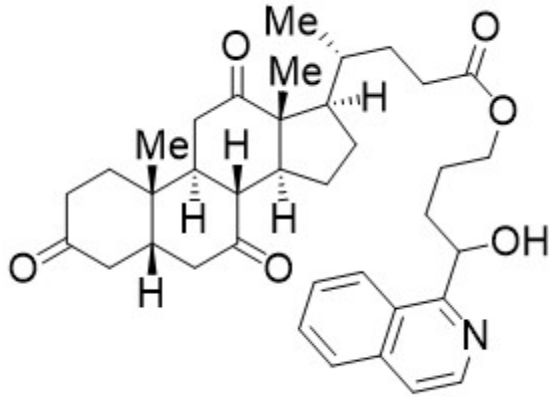
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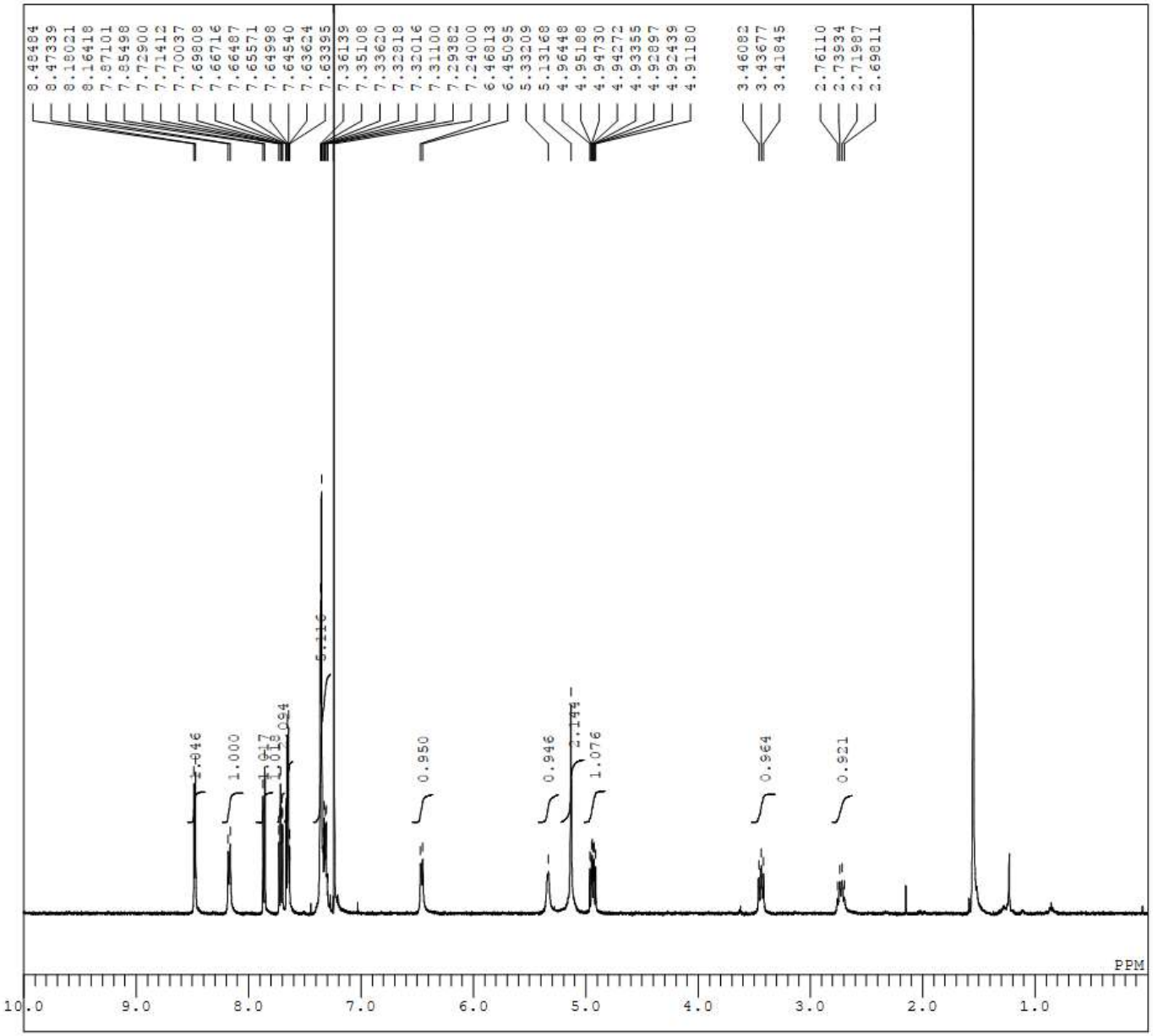

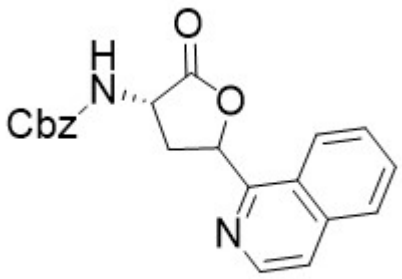

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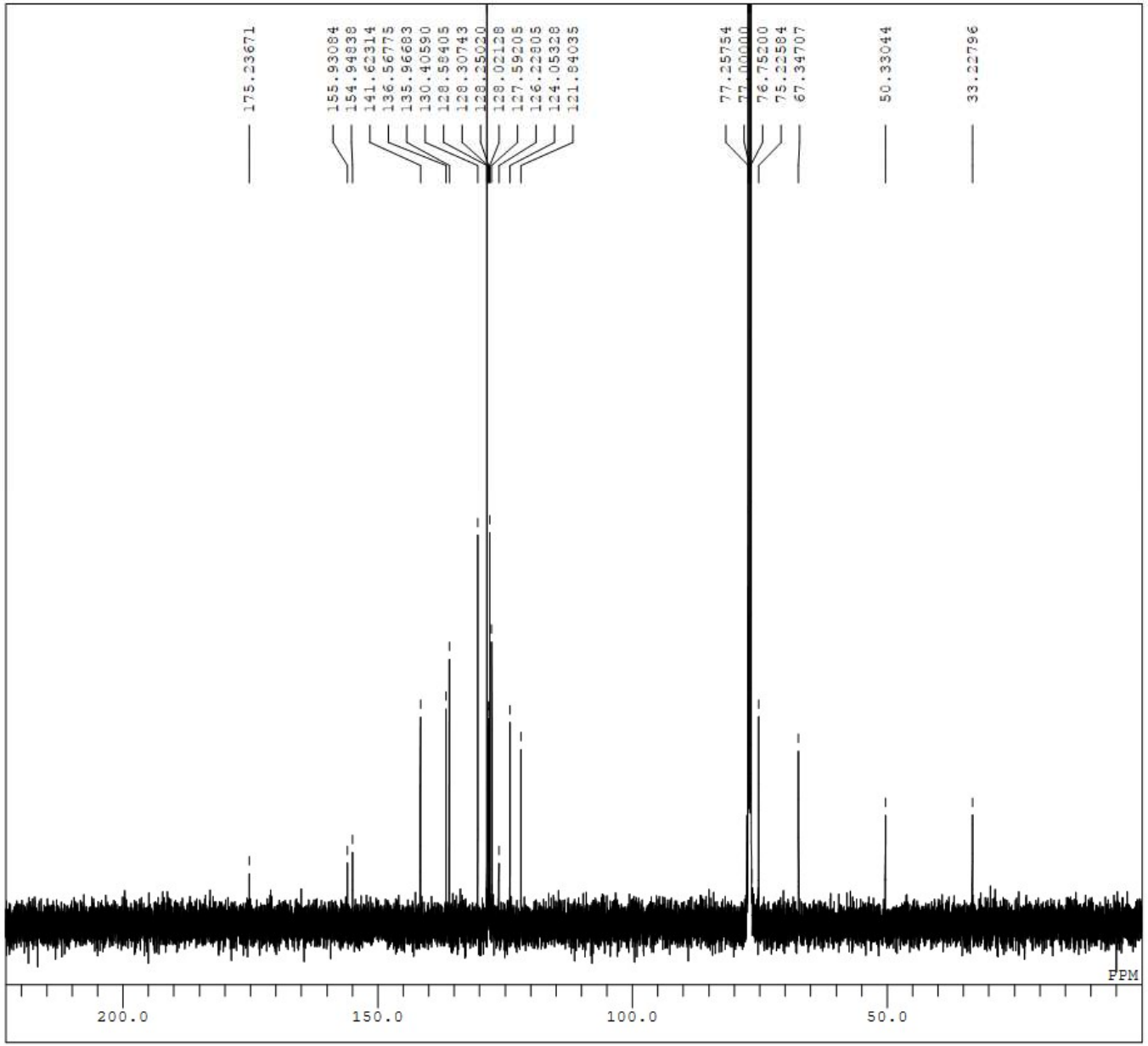

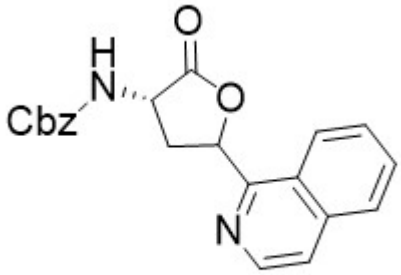

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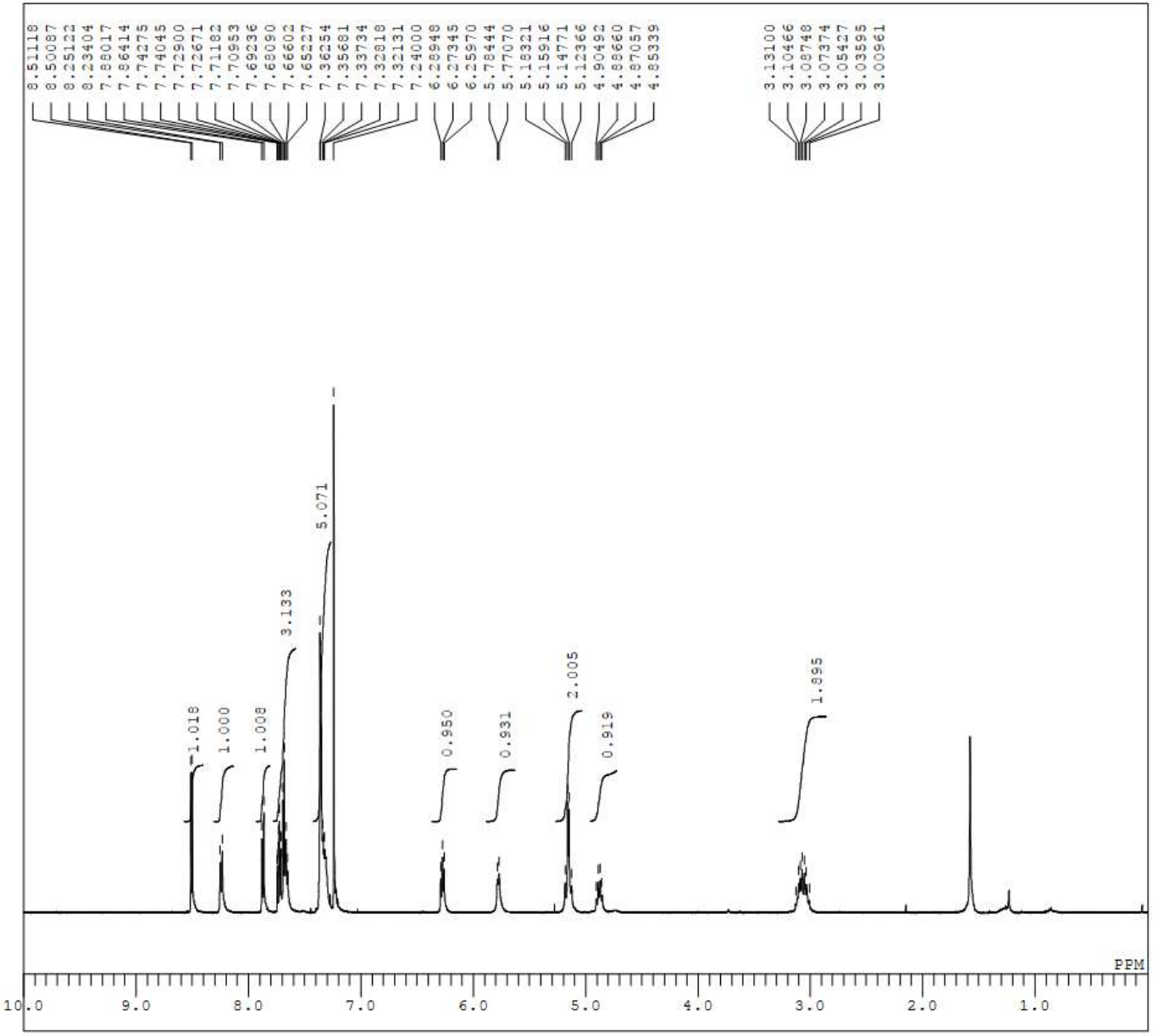
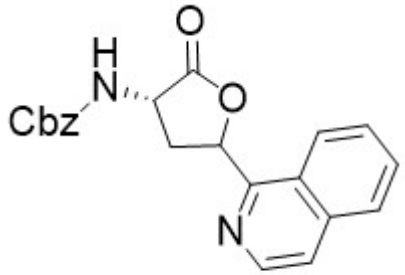
major isomer





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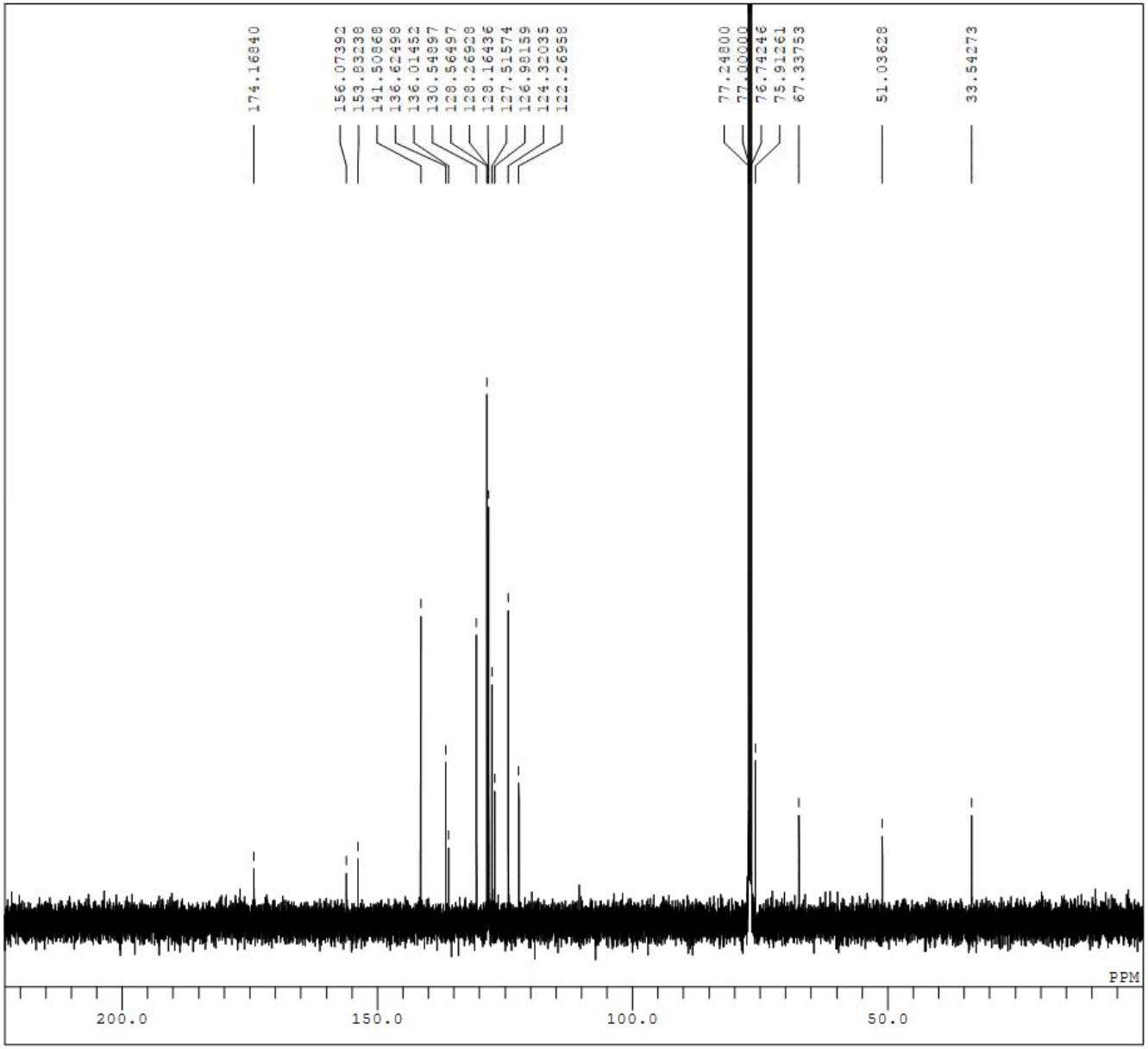

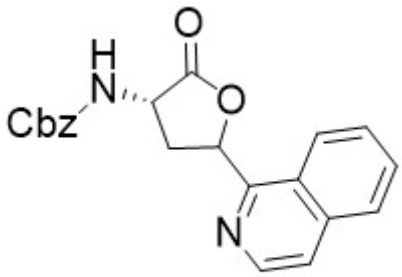

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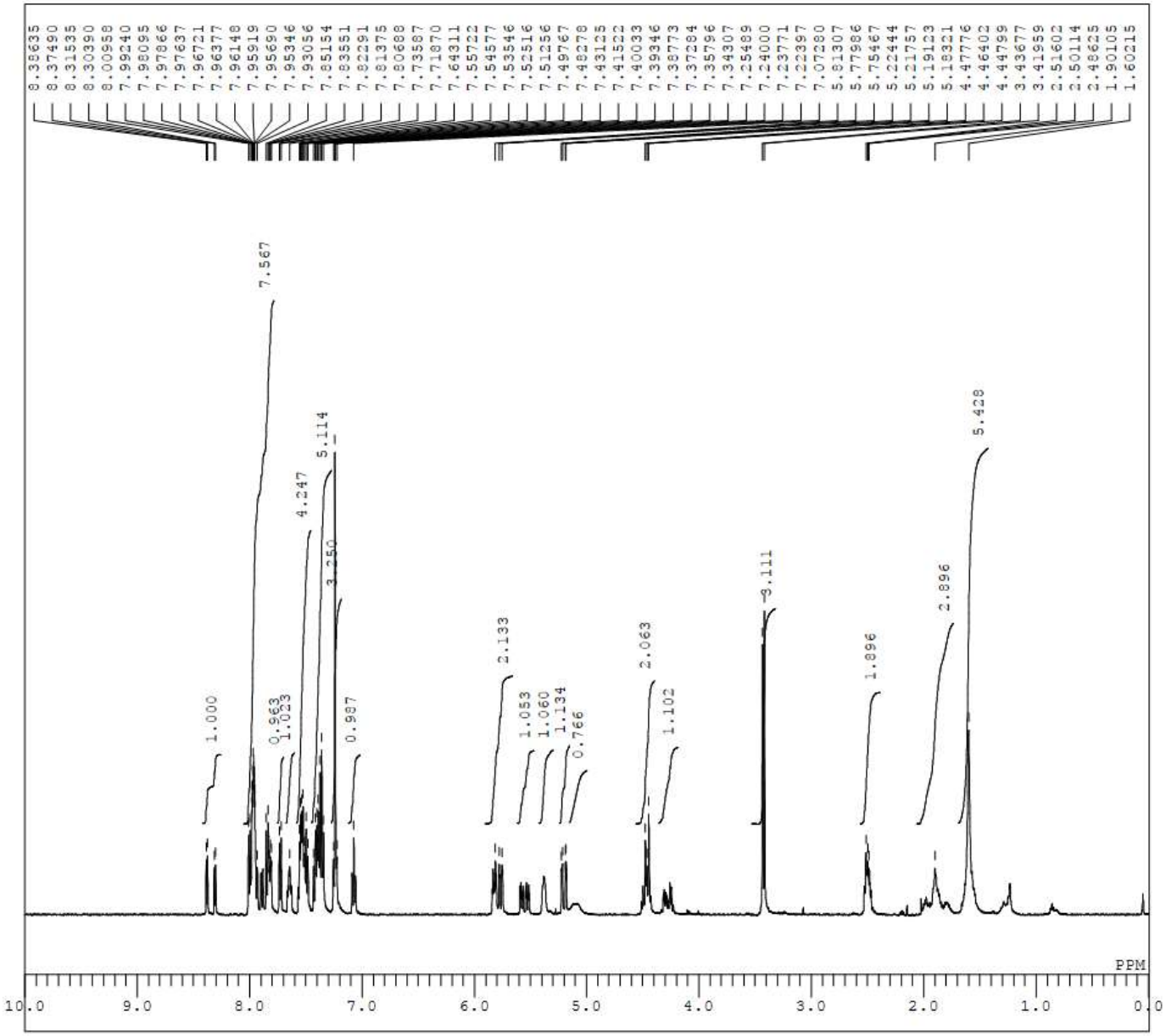
minor isomer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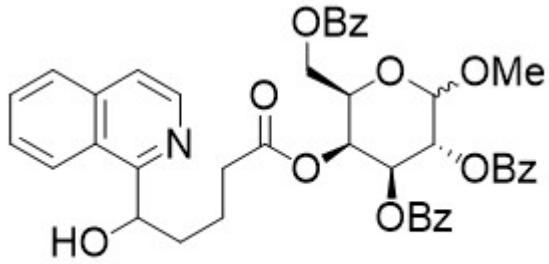
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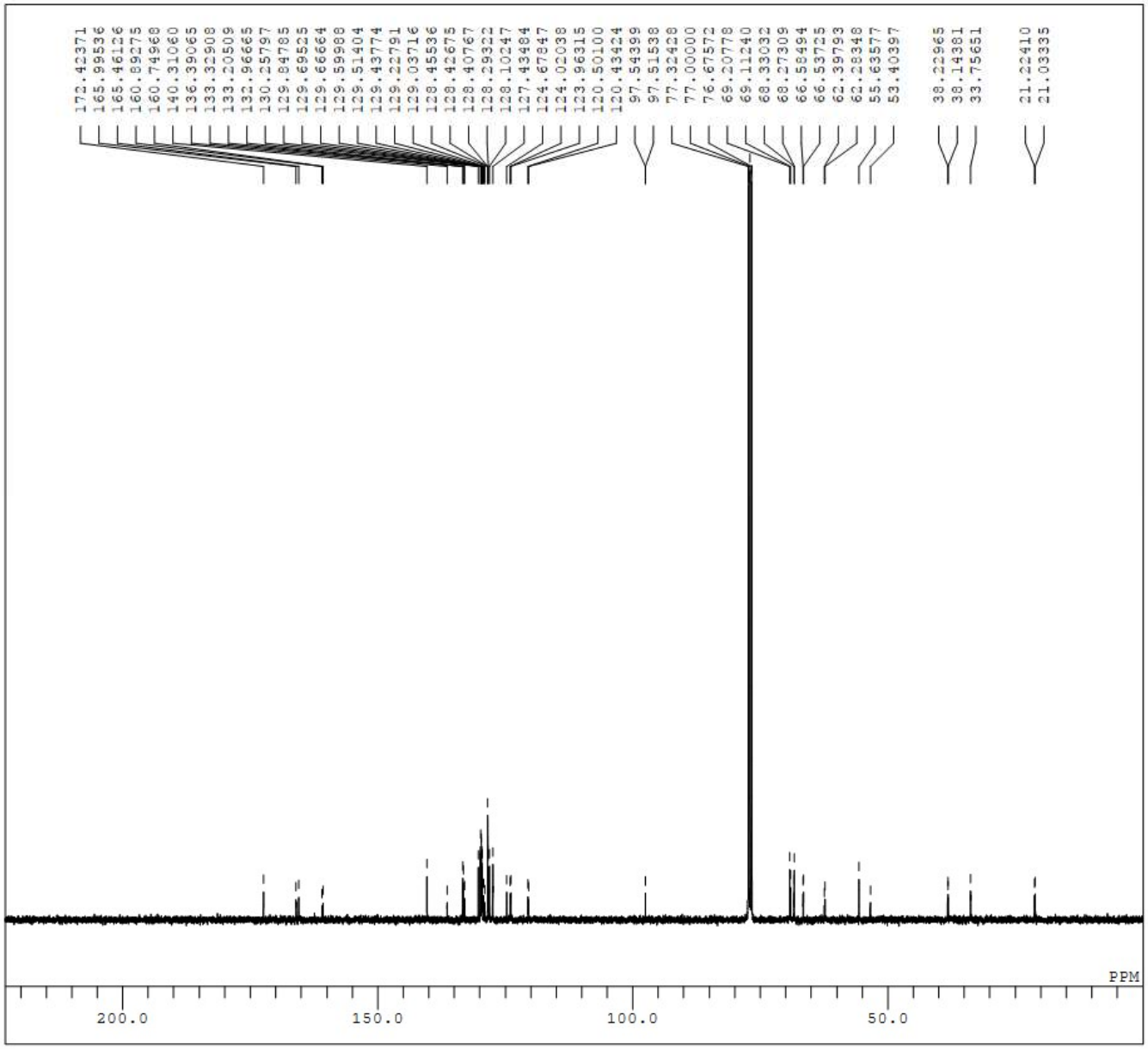
O
OBz
HO
OBz

3ak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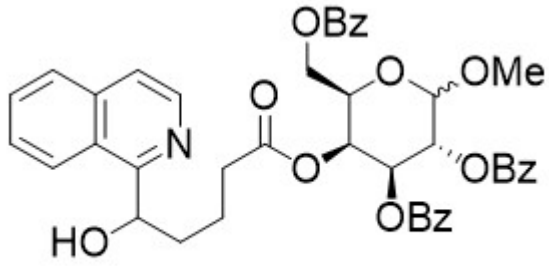
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OBz
OBz
HO

3ak