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Supporting information

Palladium supported on magnesium hydroxyl fluoride: an effective acid catalyst for the hydrogenation of imines and *N*-heterocycles

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I) General Remarks.

All solvents were dried using standard methods and stored over molecular sieves (4 Å). All reactions were carried out under a dry nitrogen atmosphere and were repeated at least twice. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV_{254} plates. Flash chromatography was carried out with Macherey silica gel (Kielselgel 60). ^{1}H (300 MHz), ^{13}C (75 MHz), ^{19}F (282 MHz) NMR spectra were acquired on Bruker Avance I and II spectrometers. Coupling constants are expressed in Hz. ^{1}H NMR shifts are given relative to the residual solvent resonances at 7.26 ppm, and ^{13}C NMR shifts are given relative to the residual solvent peak of $CDCl_3$ (77.16 ppm). 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed Gas chromatography analyses were done on GC Shimadzu 2010+with FID detectors using Supelco SPB-5 column (30 m, 0.25 mm,0.25 μm) and with nitrogen as gas carrier. GC-MS analyses were performed on a Shimadzu QP2010+ (EI mode) using Supelco column SLBTM-5ms (30m, 0.25mm, 0.25μm). All commercial reagents and solvents were used as received unless otherwise stated. Imine reagents **1a**,[S1] **1b**,[S2] **1c**,[S3] **1d**,[S4] **1e**,[S3] **1f**,[S4] **1g**,[S3] **3a**,[S1] **3b**,[S5] **3c**,[S6] **3d**,[S1] **3e**,[S1] **3f**,[S1] **3g**,[S1] **3h**[S7] were prepared as reported.

II) General Procedure for catalysts synthesis, characterizations and the catalyzed hydrogenation reactions.

Catalysts synthesis

CAUTION: HF is a highly toxic acid which causes severe burns when in contact with skin!

Synthesis of catalyst (1PMF-ppt) by coprecipitation method[S8]

Under a well ventilated fume hood, a slurry of magnesium oxide (3.193 g) in 50 mL methanol and 10 mL distilled water was prepared in a 250 mL polypropylene beaker. Under stirring, a sub-stoichiometric amount of hydrofluoric acid (1.2 equivalents, 7 mL 40% aq.) was added dropwise. After dissolution of MgO in aqueous HF, palladium acetate (1 wt %) dissolved in methanol (10 mL) was then added under stirring over a period of 45 min. The reaction mixture was subsequently stirred for an additional 3 h and further heated in a water bath at 80 °C until complete evaporation of solvent and formation of a powder. Finally, the prepared catalyst (1PMF-ppt) was heated at 250 °C in air for 5 h.

Synthesis of catalyst (1PMF-imp) by impregnation method

Under a well ventilated fume hood, a slurry of magnesium oxide (3.193 g) in 50 mL methanol and 10 mL distilled water was prepared in a 250 mL polypropylene beaker. Under stirring, a sub-stoichiometric amount of hydrofluoric acid (1.2 equivalents, 7 mL 40% aq.) was added dropwise. After dissolution of MgO in aqueous HF, the slow precipitation of $MgF_{2-x}(OH)_x$ took place and the reaction mixture was stirred for an additional 1 h. Afterwards, the resulting slurry was further heated in a water bath at 80 °C until complete evaporation of solvent and formation of a powder of $MgF_{2-x}(OH)_x$ which was dried in an oven at 100 °C. The resulting

support was then dispersed in methanol and a solution of palladium acetate (1 wt %) in methanol (10 mL) was added dropwise to the support slurry. The solution was stirred for 1 h, and then the excess solvent was removed by heating the solution at 80 °C in a water bath until formation of a powder. The prepared catalyst (1PMF-imp) was then dried in an oven at 100 °C for 1 h and subsequently heated at 250 °C in air for 5 h.

Catalyst characterizations

Powder X-ray diffraction (P-XRD) analysis

The prepared catalysts were characterized by X-ray diffraction using PAN analytical X'Pert Pro Dual Goniometer diffractometer. The diffractometer consist of X'celerator solid state detector with CuKα (λ=1.5406Å, 40kV, 30mA) radiation and a Ni filter. The X-ray diffraction pattern of sample was collected in the range of 2θ = 20-80° with a step size of 0.02° and scan rate of 4° min^{-1}.

BET surface area measurements

The BET surface area of the catalysts was determined by the N_2 sorption at -196 °C, using Autosorb Quanta Chrome equipment. Prior to N_2 adsorption, the sample was evacuated at 200 °C under vacuum. The specific surface area was determined according to the BET equation.

Fourier transformed infrared spectroscopic studies (FTIR)

The Fourier Transform Infrared (FT-IR) spectra of the samples were recorded on a Thermo Nicolet Nexus 670 IR instrument using DTGS detector. KBr pellets technique was used to prepare the samples and the spectra were recorded with a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1} averaged over 100 scans.

Electron microscopy

The morphology of samples were determined using scanning electron microscopy (SEM) on a FEI quanta 200 3D dual beam ESEM instrument having thermionic emission tungsten filament in the 3 nm range at 30 kV. The particle size and d-spacing value was determined using Transmission electron microscopy and analysis was done on a Tecnai G2-20 FEI instrument operating at an accelerating voltage of 300 kV. Before analysis, the powder samples were ultrasonically dispersed in isopropanol, and two drops of isopropanol containing the solid were deposited on a carbon coated copper grid.

Catalysis

General procedure for catalytic hydrogenations of imines

Imine reagents (0.055 mmol, around 0.1 g depending the substrate) and catalyst (1PMF-ppt) (0.005 g, 5wt.%, 0.013 mol% of Pd) were introduced in a Schlenk tube. After a vacuum purge, methanol (5 mL) was added under nitrogen and the flask connected to a balloon filled with hydrogen. After 3 vacuum-hydrogen purges, the reaction mixture was heated at the given temperature under stirring for specific time. In order to follow the progress of the reaction,

aliquots (0.1 mL) were taken at defined times, filtered through a pad of Celite, and washed with CH_2Cl_2 (3 mL). The combined solvents were evaporated under reduced pressure and products were analysed by ^1H NMR. At the end of the reaction, solvent was evaporated under vacuum and the crude product was directly purified by flash chromatography or by preparative TLC.

General procedure for catalytic hydrogenations of *N*-heterocycles

A 50 mL stainless-steel autoclave equipped with a magnetic stir bar was charged with the *N*-heterocycle reagent (0.055 mmol, around 0.1 g depending the substrate), catalyst (1PMF-ppt) or (1PMF-imp) (0.005 g, 5wt.%, 0.013 mol% of Pd) and methanol (5 mL). The autoclave was then filled with hydrogen at a pressure of 20 bar after 3 purges. The reaction mixture was heated at 90 ºC under stirring for defined time. At the end of the reaction, after cooling and depressurization, the solvent was evaporated under vacuum and the crude product was directly isolated by flash chromatography or preparative TLC.

Procedure for catalyst recycling

The catalyst recycling study was carried out by using catalyst (1PMF-ppt) and imine **1a** under optimized reaction conditions: 0.5 g imine **1a**, 0.05 g catalyst (1PMF-ppt) (10 wt % catalyst with respect to substrate, 0.027 mol% of Pd), 15.0 mL methanol solvent, balloon H_2, 27 ºC, 2 h. At the end of the reaction, the catalyst was separated from the reaction mixture by centrifugation and the separated catalyst was washed with methanol for 2-3 times. Afterwards, the resulting solid was dried in an oven at 80 °C and subsequently used as catalyst for the next reaction under identical experimental conditions. The same procedure was repeated for the next three recycle assays.

Pd leaching test

The leaching test was carried out to check any Pd leaching in the reaction mixture under optimized reaction conditions. A mixture of imine **1a** (0.5 g) and catalyst (1PMF-ppt) (0.05 g catalyst, 10 wt.% with respect to substrate, 0.027 mol%) was stirred in methanol (15 mL) by bubbling H_2 at 27 ºC for 2 h. The catalyst was then separated from the reaction mixture by centrifugation and the supernatant was further allowed to react under identical reaction conditions without the catalyst.

Procedure for preparation of ICP samples

ICP-AES analysis of prepared catalyst was done by using Spectro Arcos spectrometer. The samples were prepared by dissolving the catalyst into a minimum amount of freshly prepared aqua regia solution (1:3, nitric acid and hydrochloric acid), if necessary the solutions were heated up to 80 °C. After dissolution and cooling of the samples, the prepared solutions were diluted in 100 mL volumetric flasks using ultrapure water (Millipore^{TM}), which were subjected to the ICP analysis. Metal leaching of the catalyst was studied by ICP-AES analysis before and after the catalytic reactions.

The BET surface area measurements of fresh and used catalysts (1PMF-ppt) showed close values (105 vs 106 m^2/g, respectively) with similar pore size and pore volume (Figure S1, Table S1).

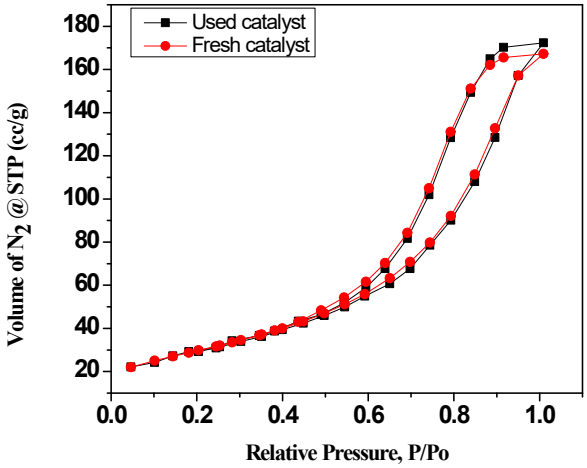


Figure S1. BET surface area analysis of pattern of fresh and used catalyst (1PMF-ppt).

Table S1. Surface characterization of fresh and used catalyst

Catalyst	Surface area (m^2/g)	Pore size (nm)	Pore volume (cc/g)
Fresh- (1PMF-ppt)	106	4.8	0.25
Used- (1PMF-ppt)	105	4.9	0.25

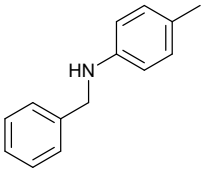
III) Characterization of compounds.

Hydrogenation of aldimines

_N_-benzylaniline 2a[S1]

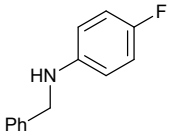
^{1}H NMR (300 MHz, $CDCl_3$): δ= 4.03 (bs, 1H, NH), 4.35 (s, 2H, CH_2), 6.65 (d, ^3J= 8.2 Hz, 2H, H_{Ar}), 6.75 (t, ^3J= 7.3 Hz, 1H, H_{Ar}), 7.17 (t, ^3J= 7.4 Hz, 2H, H_{Ar}), 7.35 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 48.4 (CH_2), 112.9 (2CH), 117.7 (1CH), 127.3 (1CH), 127.6 (2CH), 128.7 (2CH), 129.3 (2CH), 139.5 (C), 148.3 (C, CN).

N-benzyl-4-methylaniline 2b[S9]



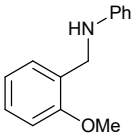
^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.16 (s, 3H, CH_3), 4.23 (s, 2H, CH_2), 6.50 (d, ^3J = 8.4 Hz, 2H, CH), 6.90 (d, ^3J = 8.0 Hz, 2H, CH), 7.29 (m, 5H, CH).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 20.5 (CH_3), 48.9 (CH_2), 113.3 (CH), 127.1 (C), 127.3 (CH), 127.7 (CH), 128.7 (CH), 129.9 (CH), 139.6 (C), 145.7 (C).

_N_-(4-Fluorophenyl)benzenemethanamine 2c[S10]



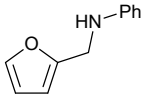
^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.83 (br s, 1H, NH), 4.31 (s, 2H, CH_2), 6.66 (m, 2H, H_{Ar}), 6.89 (m, 2H, H_{Ar}), 7.33 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 49.1 (CH_2), 113.8 (d, $2CH_{meta}$, $J_{C\text{-}F}$= 7.5 Hz), 115.8 (d, $2CH_{ortho}$, $J_{C\text{-}F}$= 22.5 Hz), 127.5 (CH), 127.6 (2CH), 128.8 (2CH), 139.3(C, CN), 144.5 (d, C_{para}, $J_{C\text{-}F}$= 2.3 Hz), 156.0 (d, C_{ipso}, $J_{C\text{-}F}$= 234.0 Hz).

_N_-(2-methoxybenzyl)aniline 2d[S11]



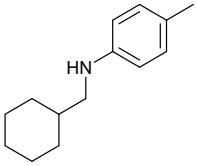
^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.88 (s, 3H, OCH_3), 4.36 (s, 2H, CH_2), 6.71 (m, 3H, H_{Ar}), 6.93 (m, 2H, H_{Ar}), 7.19 (m, 1H, H_{Ar}), 7.27 (m, 1H, H_{Ar}), 7.33 (dd, ^3J= 7.3 Hz, 1H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 43.7 (CH_2), 55.4 (OCH_3), 110.4 (CH), 113.4 (2CH), 117.6 (CH), 120.7 (CH), 127.4 (C), 128.5 (CH), 129.1 (CH), 129.3 (2CH), 148.4 (C), 157.6 (C).

***N*-(furan-2-ylmethyl)aniline 2e[S12]**



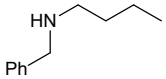
^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.83 (bs, 1H), 4.34 (d, ^3J = 0.8 Hz, 2H, CH_2), 6.26 (qd, ^3J =3.2 Hz, 1H, H_{fur}), 6.34 (dd, ^3J = 3.3 Hz, 1 H, H_{fur}), 6.70 (m, 2H, H_{Ar}), 6.78 (m, 1H, H_{Ar}), 7.21 (m, 2H, H_{Ar}), 7.39 (dd, ^3J = 1.9 Hz, 1H, H_{fur}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 41.5 (CH_2), 107.1 (CH), 110.5 (CH), 113.3 (2CH), 118.2 (CH), 129.4 (2CH), 142.1 (CH), 147.6 (C), 152.8 (C).

N-(cyclohexylmethyl)-4-methylaniline 2f[S13]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.98 (m, 2H, CH_2), 1.25 (m, 3H, CH_2), 1.59 (m, 1H), 1.77 (m, 5H, 3CH_2), 2.25 (s, 3H, CH_3), 2.95 (d, ^3J = 6.6 Hz, 2H, CH_2), 3.60 (bs, 1H, NH), 6.55 (d, ^3J = 8.4 Hz, 2H, CH), 6.99 (d, ^3J = 8.4 Hz, 2H, CH).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 20.5 (CH_3), 26.1 (CH_2), 26.8 (CH_2), 31.4 (CH_2), 37.7 (CH), 51.2 (CH_2), 113.1 (CH), 126.3 (C), 129.8 (CH), 146.4 (C).

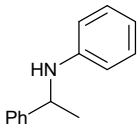
***N*-Benzyl-butyl-amine 2g[S14]**



^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.94 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.36 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 2.66 (t, ^3J = 7.2 Hz, 2H, CH_2), 3.82 (s, 2H, N-CH_2), 7.31 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 14.1 (CH_3), 20.6 (CH_2), 32.2 (CH_2), 49.3 (CH_2), 54.1 (CH_2), 127.0 (CH), 128.3 (2CH), 128.5 (2CH), 140.5 (C).

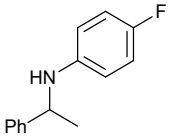
Hydrogenation of ketimines

***N*-(1-phenylethyl)aniline 4a[S1]**



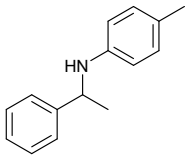
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.51 (d, ^3J = 6.3 Hz, 3H, CH_3), 4.10 (1s, 1H, NH), 4.49 (q, ^3J= 6.69 Hz, 1H, CH), 6.51 (d, ^3J= 8.64 Hz, 2H, H_{Ar}), 6.64 (t, ^3J= 7.2 Hz, 1H, H_{Ar}), 7.09 (m, 2H, H_{Ar}), 7.24 (m, 1H, H_{Ar}), 7.34 (m, 4H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.1 (CH_3), 53.7 (CH), 113.5 (2CH), 117.4 (CH), 125.9 (2CH), 127.0 (CH), 128.8 (2CH), 129.2 (2CH), 145.3 (C), 147.4 (C, CN).

4-fluoro-*N*-(1-phenylethyl)aniline 4b[S5]



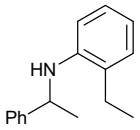
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.50 (d, ^3J= 6.7 Hz, 3H, CH_3), 4.41 (q, ^3J= 6.7 Hz, 1H, CH), 6.44 (m, 2H, H_{Ar}), 6.78 (m, 2H, H_{Ar}), 7.31 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.2 (CH_3), 54.3 (CH), 114.3 (d, $2CH_{meta}$, $J_{C\text{-}F}$= 7.3 Hz), 115.5 (d, $2CH_{ortho}$, $J_{C\text{-}F}$= 22.2 Hz), 125.9 (2CH), 127.1 (CH), 128.8 (2CH), 143.6 (d, C_{para}, $J_{C\text{-}F}$= 1.1 Hz), 145.1 (C, CN), 156.0 (d, C_{ipso}, $J_{C\text{-}F}$= 233.4 Hz).

4-methyl-N-(1-phenylethyl)aniline 4c[S15]



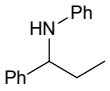
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.53 (d, ^3J= 6.7 Hz, 3H, CH_3), 2.22 (s, 3H, CH_3), 4.48 (q, ^3J = 6.7 Hz, 1H, CH), 6.46 (d, ^3J= 7.9 Hz, 1H, CH), 6.93 (d, ^3J= 8.0 Hz, 1H, CH), 7.24 (m, 1H), 7.37 (m, 4H, CH).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 20.5 (CH_3), 25.2 (CH_3), 53.8 (CH), 113.5 (CH), 125.9 (CH), 126.5 (C), 126.9 (CH), 128.7 (CH), 129.7 (CH), 145.1 (C), 145.5 (C).

2-ethyl-*N*-(1-phenylethyl)aniline 4d[S16]



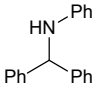
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.37 (s, 3H, $CH_{3\ Et}$), 1.61 (d, J = 6.59 Hz, 3H, CH_3), 2.63 (q, ^3J = 7.54 Hz, 2H, CH_2), 4.0 (bs, 1H, NH), 4.58 (q, ^3J = 6.59 Hz, 1H), 6.44 (dd, ^3J = 1.00 Hz, 1H, H_{Ar}), 6.70 (td, ^3J= 7.39 Hz, 1H, H_{Ar}), 7.0 (m, 1H, H_{Ar}), 7.12 (m, 1H, H_{Ar}), 7.27 (m, 1H, H_{Ar}), 7.38 (m, 4H, H_{Ar}).^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0 (CH_3), 24.1 (CH_2), 25.4 (CH_3), 53.4 (CH), 111.5 (CH), 117.1 (CH), 125.9 (2CH), 126.9 (2CH), 127.3 (C), 127.8 (CH), 128.7 (2CH), 144.5 (C), 145.4 (C). HRMS (EI): calculated for $C_{16}H_{20}N$ (M+), 226.3407; found, 226.15903.

***N*-(1-phenylpropyl)aniline 4e[S1]**



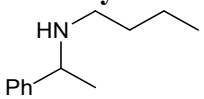
^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.96 (t, ^3J= 7.4 Hz, 3H, CH_3), 1.83 (m, 2H, CH_2), 4.06 (bs, 1H, NH), 4.23 (t, ^3J= 6.7 Hz, 1H, CH), 6.52 (d, ^3J= 7.7 Hz, 2H, H_{Ar}), 6.63 (t, ^3J= 7.3 Hz, 1H, H_{Ar}), 7.08 (t, ^3J= 7.9 Hz, 2H, H_{Ar}), 7.21 (m, 1H, H_{Ar}), 7.31 (m, 4H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 10.9 (CH_3), 31.8 (CH_2), 59.9 (CH), 113.4 (2CH), 117.3 (CH), 126.6 (2CH), 127.1 (CH), 128.6 (2CH), 129.2 (2CH), 144.0 (C), 147.6 (C, CN).

***N*-benzhydrylaniline 4f[S1]**



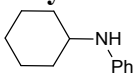
^{1}H NMR (300 MHz, $CDCl_3$): δ= 5.50 (s, 1H, CH), 6.57 (d, ^3J= 7.7 Hz, 2H, H_{Ar}), 6.71 (t, ^3J=7.3 Hz, 1H, H_{Ar}), 7.12 (t, ^3J= 7.5 Hz, 2H, H_{Ar}), 7.29 (m, 10H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 63.2 (CH), 113.7 (2CH), 117.9 (CH), 127.5 (2CH), 127.7 (4CH), 128.9 (4CH), 129.3 (2CH), 143.1 (2C), 147.6 (C, CN).

***N*-Benzylbutan-1-amine 4g[S17]**



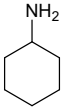
^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.87 (t, ^3J = 1.0 Hz, 3H, CH_3 $_{n\text{-Bu}}$), 1.29 (m, 2H, CH_2), 1.37 (d, ^3J = 6.6 Hz, 3H, CH_3), 1.46 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 3.76 (q, ^3J = 6.6 Hz, 1H, CH), 7.23 (m, 2H, H_{Ar}), 7.33 (m, 3H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 14.1 (CH_3), 20.6 (CH_2), 24.4 (CH_3), 32.4(CH_2), 47.5(CH_2), 58.6 (CH), 126.7 (2CH), 127.0 (CH), 128.5 (2CH), 145.4(C).

***N*-cyclohexylaniline 4h[S18]**



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.25 (m, 6H), 1.75 (m, 2H), 2.06 (m, 2H), 3.25 (non, ^3J= 3.7 Hz, 1H), 6.59 (d, ^3J= 7.6 Hz, 2H_{Ar}), 6.67 (t, ^3J= 7.3 Hz, 1H_{Ar}), 7.16 (t, ^3J= 7.9 Hz, 2H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.2 (2CH_2), 26.1 (CH_2), 33.5 (2CH_2), 51.9 (CH), 113.4 (2CH), 117.1 (CH), 129.5 (2CH), 147.4 (C).

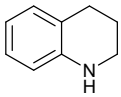
Cyclohexanamine 4i CAS [108-91-8][S19]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.03 (m, 2H), 1.21 (m, 3H), 1.62 (m, 1H), 1.72 (m, 2H), 1.85 (m, 2H), 2.54 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.5 (2CH_2), 26.4 (CH_2), 34.5 (2CH_2), 53.2 (CH).

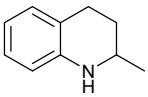
Hydrogenation of heterocycles

1,2,3,4-tetrahydroquinoline 6a[S20]



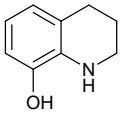
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.95 (m, 2H, CH_2), 2.77 (t, ^{3}J= 6.4 Hz, 2H, CH_2), 3.25 (t, ^{3}J = 5.5 Hz, 2H, CH_2), 6.48 (d, ^{3}J= 7.8 Hz, 1H, CH), 6.61 (t, ^{3}J= 7.3 Hz, 1H, CH), 6.88 (m, 2H, CH).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 22.3 (CH_2), 27.1 (CH_2), 42.1 (CH_2), 114.4 (CH), 117.1 (CH), 121.6 (C), 126.9 (CH), 129.6 (CH), 144.8 (C).

2-methyl-1,2,3,4-tetrahydroquinoline 6b[S21]



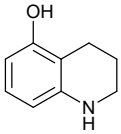
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.27 (d, ^{3}J= 6.3 Hz, 3H, CH_3), 1.65 (m, 1H), 1.94 (m, 1H), 2.79 (m, 2H), 3.43 (m, 1H), 6.62 (d, ^{3}J= 7.9 Hz, 1H), 6.69 (t, ^{3}J= 7.4 Hz, 1H), 7.05 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 22.6 (CH_3), 26.6 (CH_2), 30.2 (CH_2), 47.2 (CH), 114.1 (CH), 117.0 (CH), 121.1 (C), 126.7 (CH), 129.3 (CH), 144.8 (C).

1,2,3,4-tetrahydroquinolin-8-ol 6c[S22]



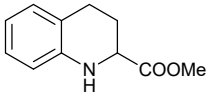
^{1}H NMR (300 MHz, acetone-d_6): δ= 1.88 (m, 2H), 2.71 (m, 2H), 3.31 (m, 2H), 6.33 (t, ^{3}J= 7.6 Hz, 1H), 6.43 (d, ^{3}J= 7.6 Hz, 1H), 6.53 (d, ^{3}J= 7.7 Hz, 1H).
^{13}C NMR (75 MHz, acetone-d_6): δ= 23.1 (CH_2), 27.6 (CH_2), 42.2 (CH_2), 112.4 (CH), 116.2 (CH), 121.4 (CH), 121.9 (C), 134.9 (C), 144.2 (C).

1,2,3,4-tetrahydroquinolin-5-ol 6d[S23]



^{1}H NMR (300 MHz, acetone-d_6): δ= 1.84 (m, 2H), 2.61 (t, ^{3}J= 6.5 Hz, 2H), 3.19 (t, ^{3}J= 5.4 Hz, 2H), 6.01 (d, ^{3}J= 8.0 Hz, 1H), 6.07 (d, ^{3}J= 6.1 Hz, 1H), 6.65 (t, ^{3}J= 7.9 Hz, 1H), 7.85 (bs, 1H, OH).
^{13}C NMR (75 MHz, acetone-d_6): δ= 21.5 (CH_2), 22.8 (CH_2), 42.0 (CH_2), 103.8 (CH), 106.9 (CH), 108.6 (C), 127.2 (CH), 147.4 (C), 156.2 (C).

Methyl 1,2,3,4-tetrahydroquinoline-2-carboxylate 6g[S24]

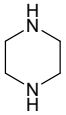


^{1}H NMR (300 MHz, $CDCl_3$) δ= 2.04 (m, 1H), 2.30 (m, 1H), 2.79 (m, 2H), 3.79 (s, 3H, CH_3), 3.90 (dd, ^{3}J= 3.8 Hz, 1H), 4.10 (bs, 1H, NH), 6.61 (d, ^{3}J= 8.0 Hz, 1H), 6.67 (t, ^{3}J= 7.6 Hz, 1H), 7.01 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ= 24.7, 25.8, 52.4, 53.9, 114.6, 117.7, 120.6, 127.1, 129.1, 142.9, 173.8.

Piperidine CAS [110-89-4] 8a[S25]

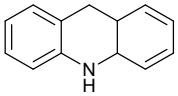
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.41 (bs, 6H), 2.67 (bs, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.0 (CH_2), 27.1 ($2CH_2$), 47.3 ($2CH_2$).

Piperazine CAS [110-85-0] 8b[S25]



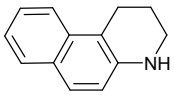
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.42 (bs, 1H, 2NH), 2.65 (bs, 8H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 47.1 (CH_2).

4a,9,9a,10-tetrahydroacridine 8c[S26]



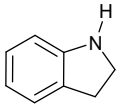
^{1}H NMR (300 MHz, $CDCl_3$): δ= 4.06 (s, 2H, CH_2), 5.96 (bs, 1H, NH), 6.67 (d, ^3J= 3.1 Hz, 2H), 6.87 (t, ^3J= 2.9 Hz, 2H), 7.09 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 31.5 (CH_2), 113.5 (CH), 120.1 (C), 120.8 (CH), 127.1 (CH), 128.7 (CH), 140.2 (C).

1,2,3,4-tetrahydrobenzo[f]quinoline 8d[S27]



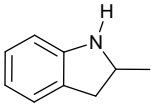
^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.16 (m, 2H), 3.09 (t, ^3J= 6.5 Hz, 2H), 3.39 (t, ^3J= 5.5 Hz, 2H), 3.94 (bs, 1H, NH), 6.82 (d, ^3J= 8.7 Hz, 1H), 7.28 (t, ^3J= 7.0 Hz, 1H), 7.49 (t, ^3J= 7.0 Hz, 1H), 7.57 (d, ^3J= 8.7 Hz, 1H), 7.74 (d, ^3J= 8.0 Hz, 1H), 7.80 (d, ^3J= 8.5 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 22.4 (CH_2), 22.8 (CH_2), 41.8 (CH_2), 111.9 (C), 118.4 (CH), 121.3 (CH), 121.7 (CH), 126.4 (CH), 127.5 (CH), 127.9 (C), 128.5 (CH), 133.6 (C), 142.0 (C).

Indoline CAS [496-15-1] 8e[S28]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.06 (t, ^3J= 8.2 Hz, 2H), 3.59 (t, ^3J= 8.3 Hz, 2H), 6.75 (m, 2H), 7.05 (t, ^3J= 7.5 Hz, 1H), 7.14 (d, ^3J= 7.3 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 29.9 (CH_2), 47.4 (CH_2), 109.7 (CH), 118.9 (CH), 124.8 (CH), 127.3 (CH), 129.5 (C), 151.4 (C).

2-Methyl-indoline CAS [6872-06-6] 8f[S29]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.30 (d, 2H), 2.66 (dd, ^3J= 7.7 Hz, 1H), 3.15 (dd, ^3J= 8.5 Hz, 1H), 3.65 (bs, 1H), 4.02 (m, 1H), 6.62 (d, ^3J= 7.7 Hz, 1H), 6.71 (t, ^3J= 7.4 Hz, 1H), 7.03 (t, ^3J= 7.6 Hz, 1H), 7.08 (d, ^3J= 7.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ= 22.3 (CH_3), 37.8 (CH_2), 55.3 (CH), 109.4 (CH), 118.7 (CH), 124.8 (CH), 127.3 (CH), 129.1 (C), 150.9 (C).

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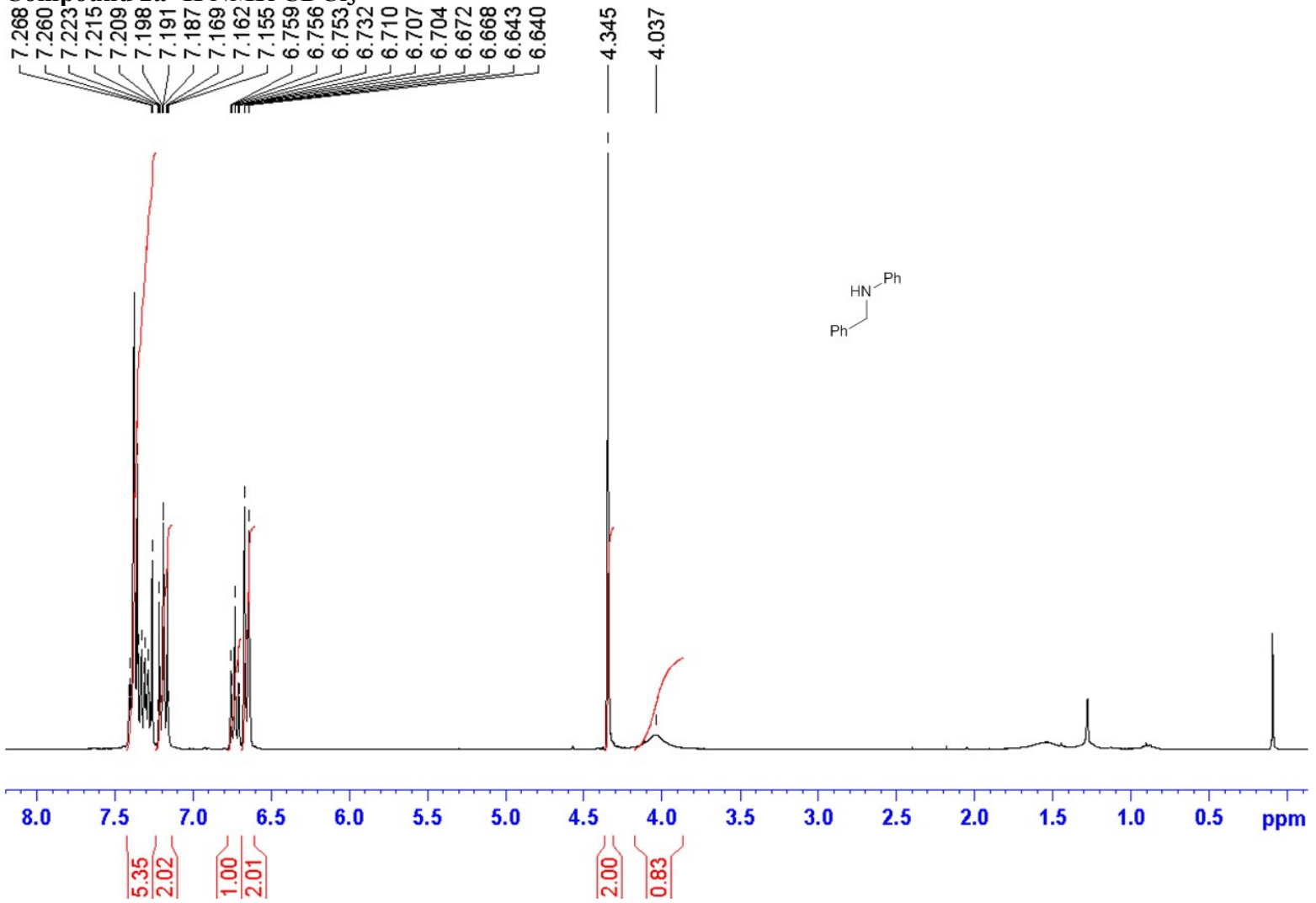
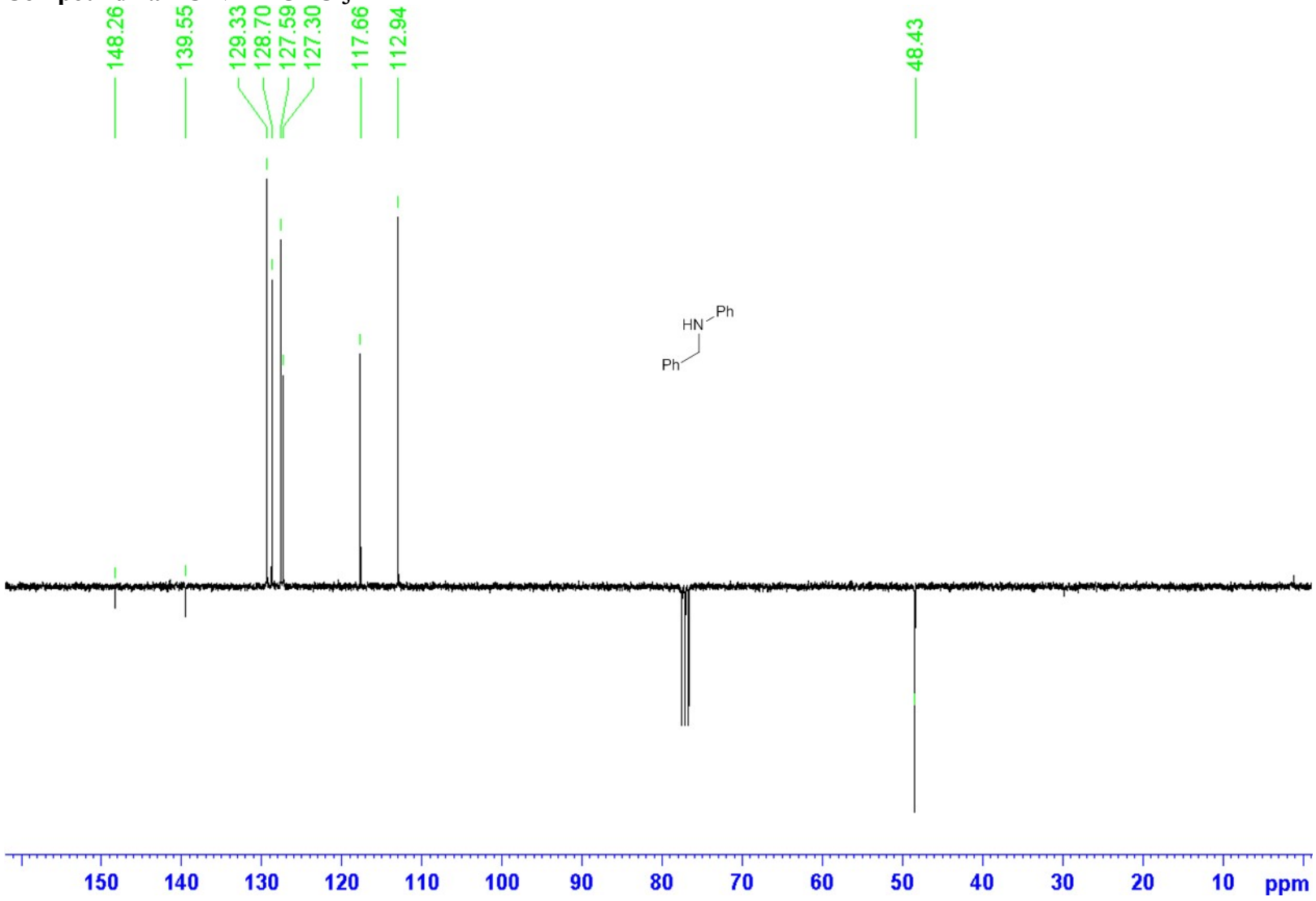
V) ^{1}H, ^{13}C NMR spectra of isolated compounds.

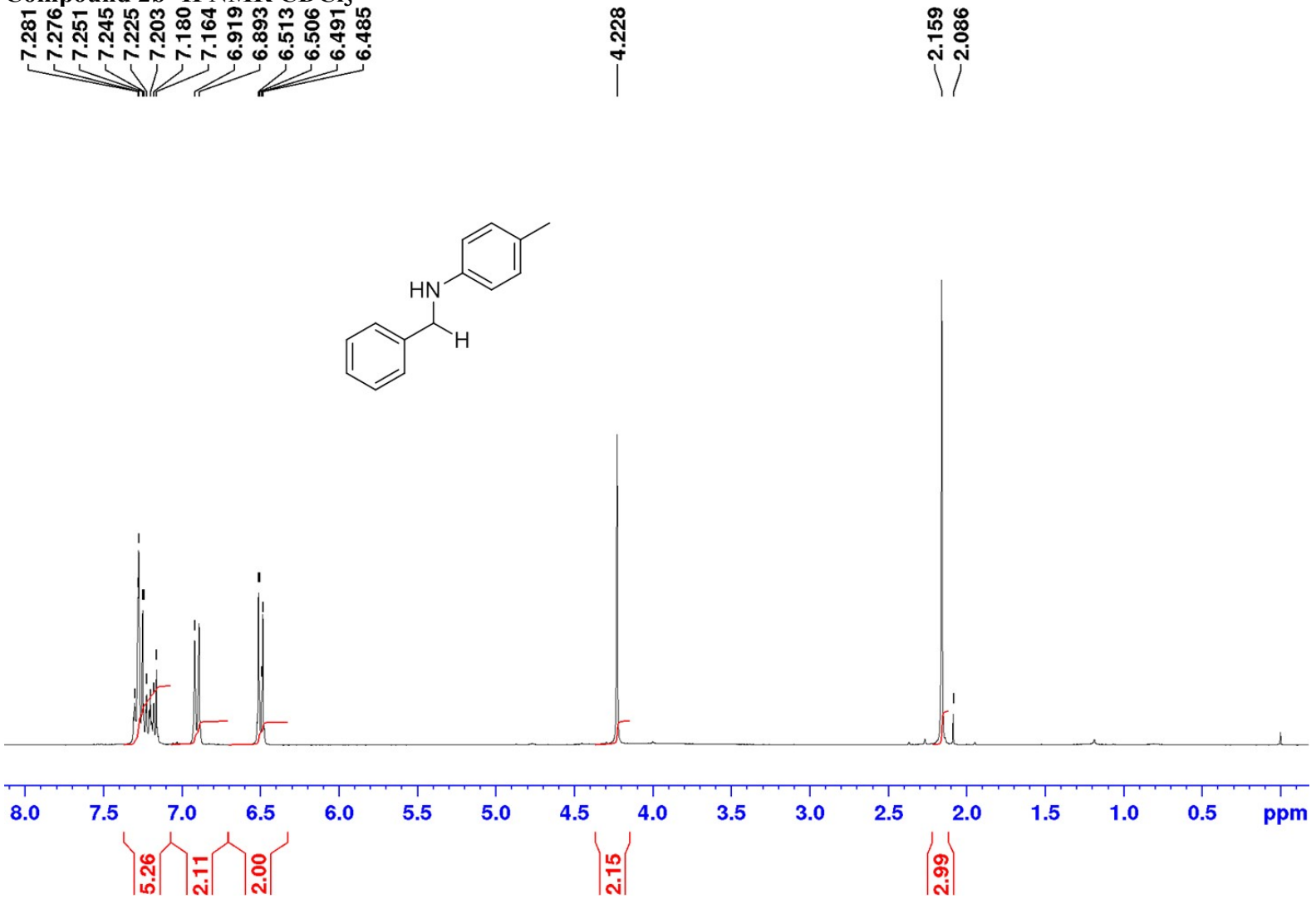
Compound 2a ^{1}H NMR $CDCl_3$



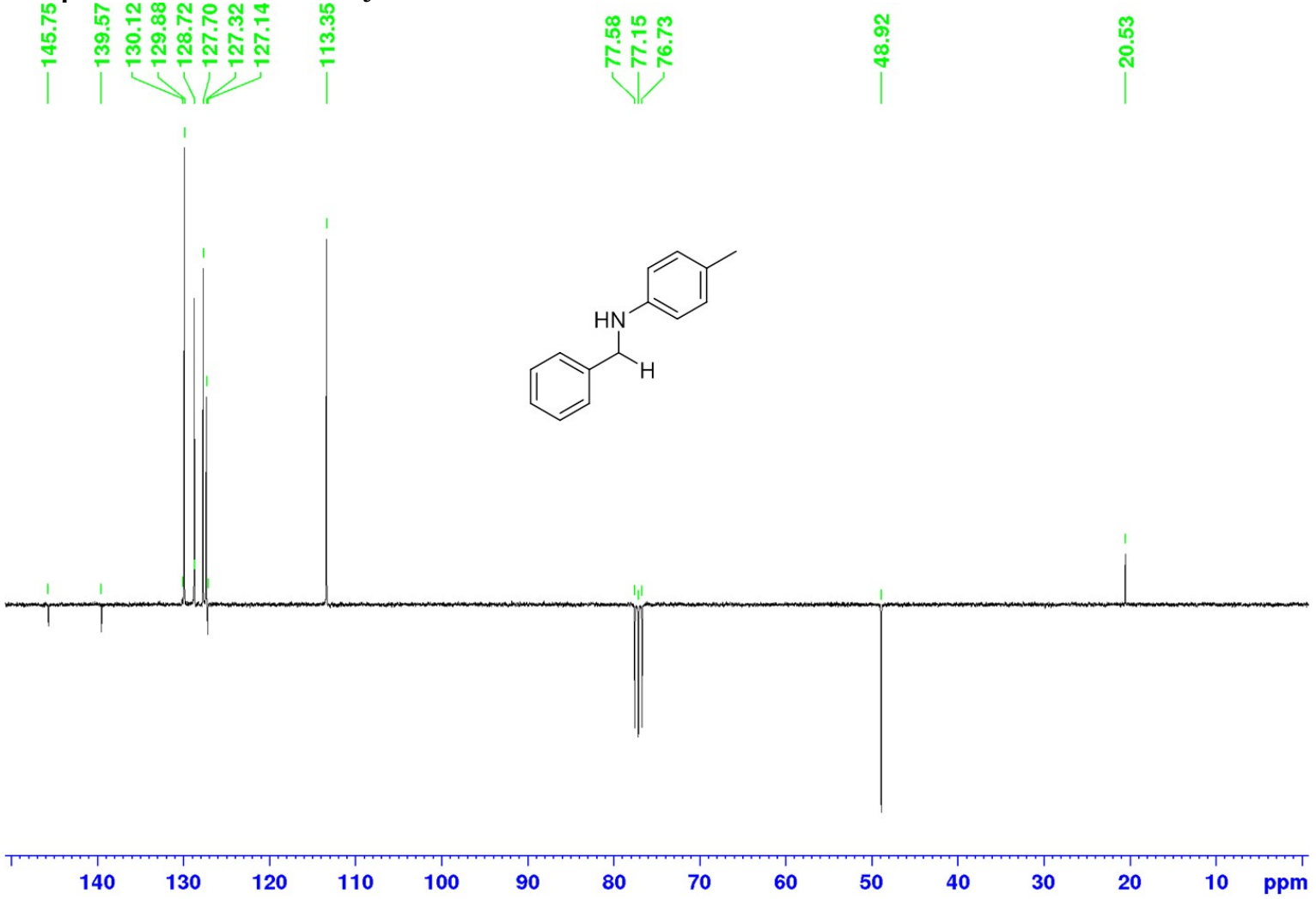
Compound 2a ^{13}C NMR $CDCl_3$



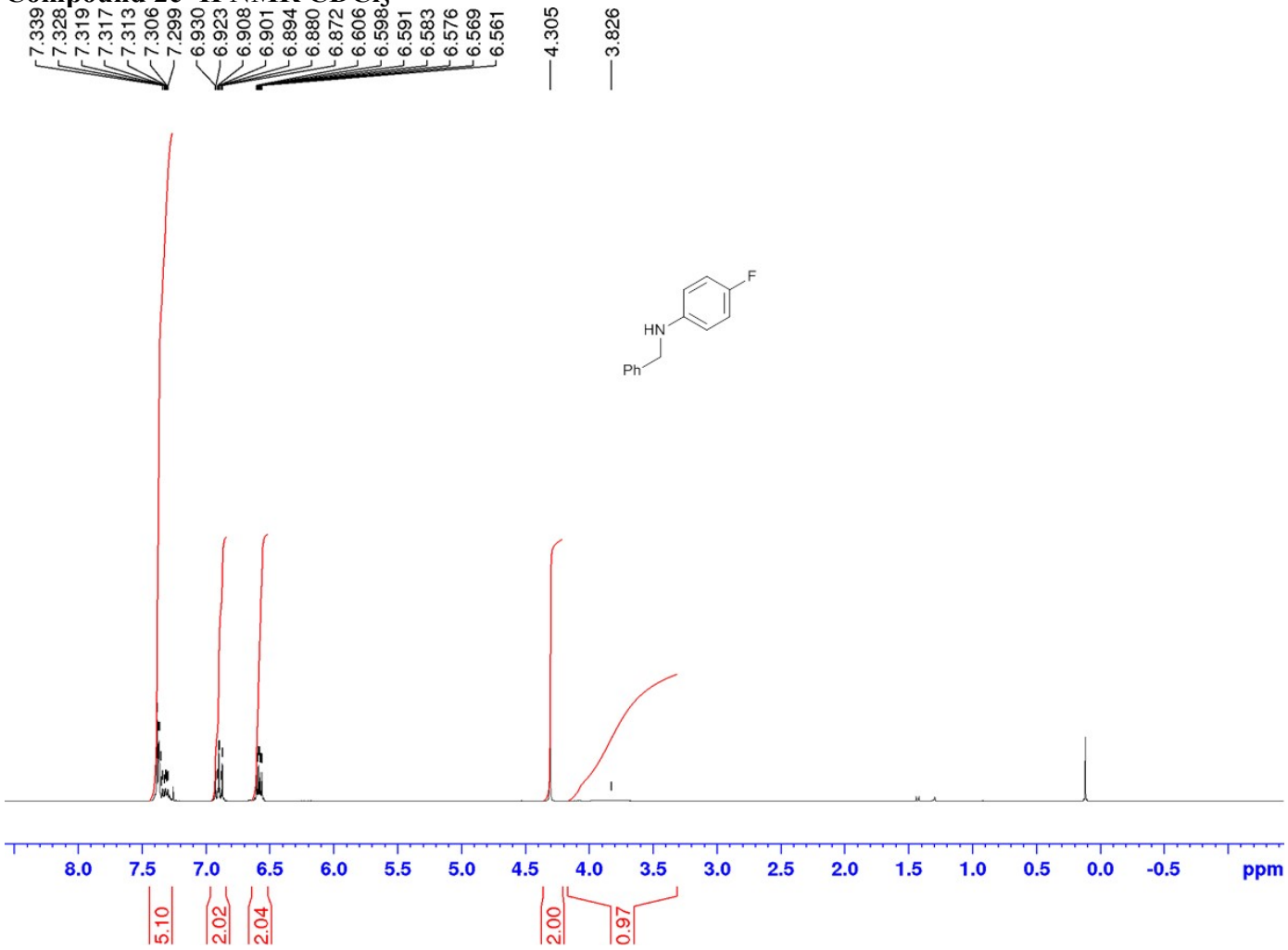
Compound 2b ^{1}H NMR $CDCl_3$



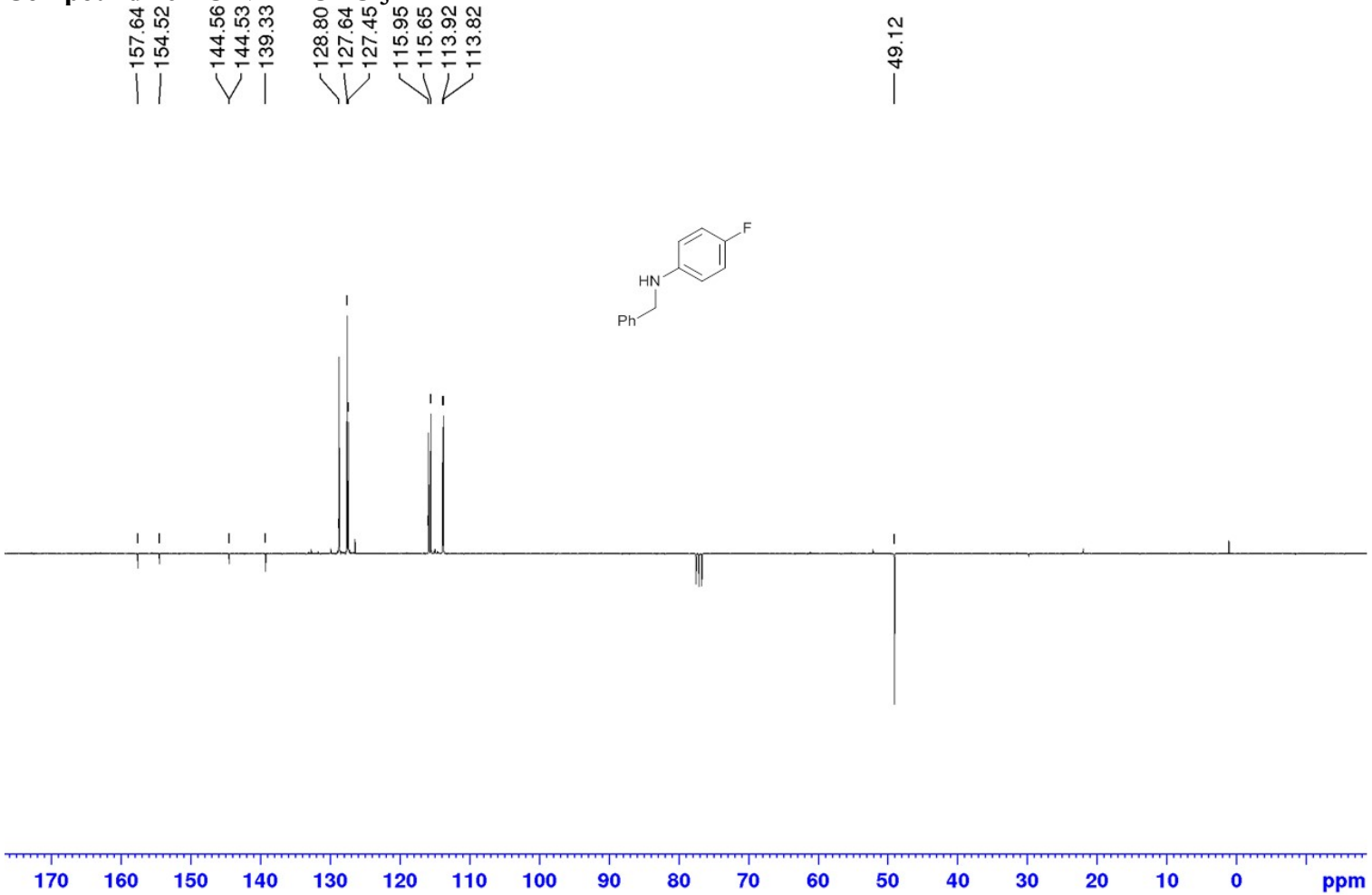
Compound 2b ^{13}C NMR $CDCl_3$



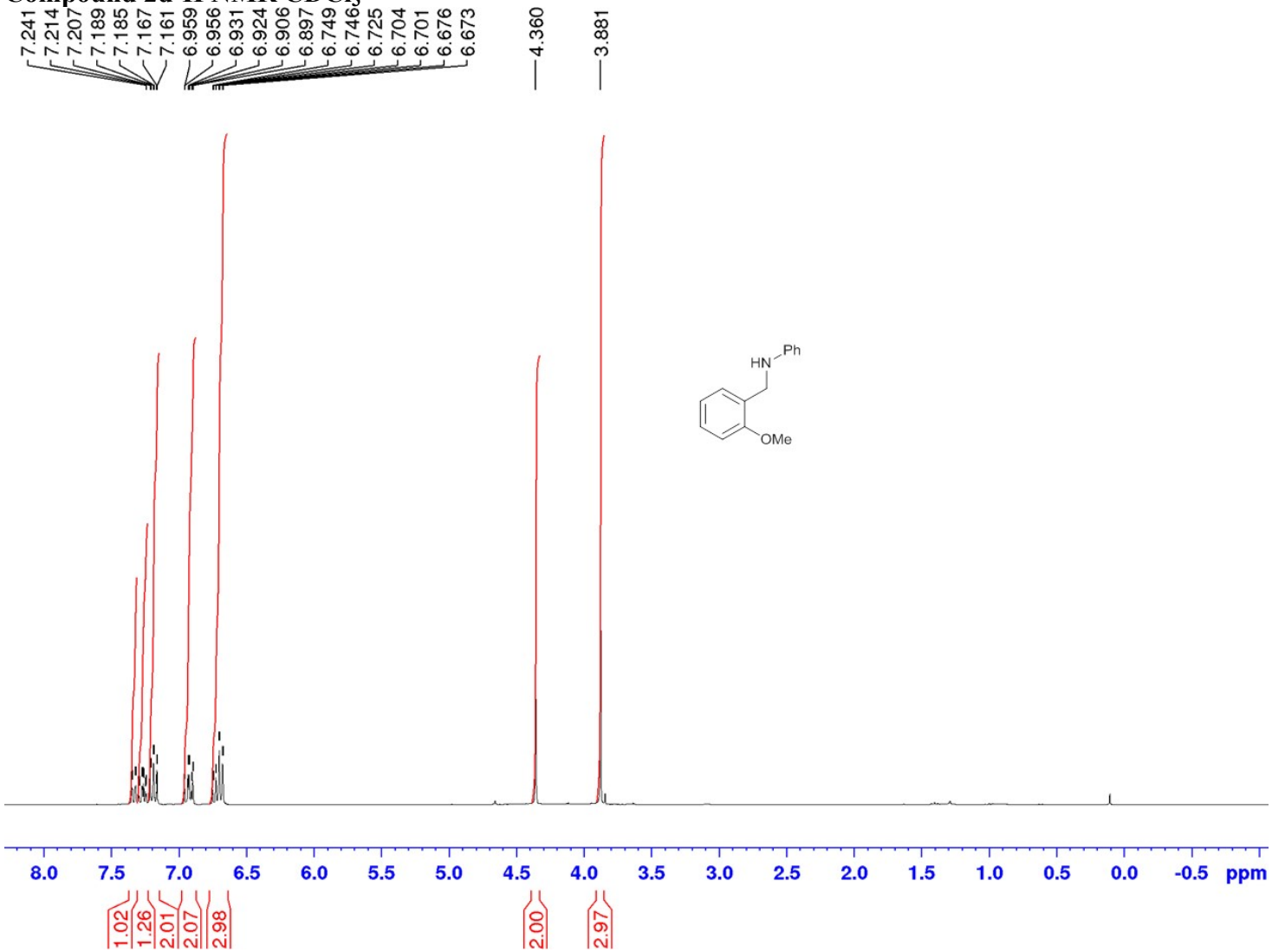
Compound 2c ^{1}H NMR $CDCl_3$



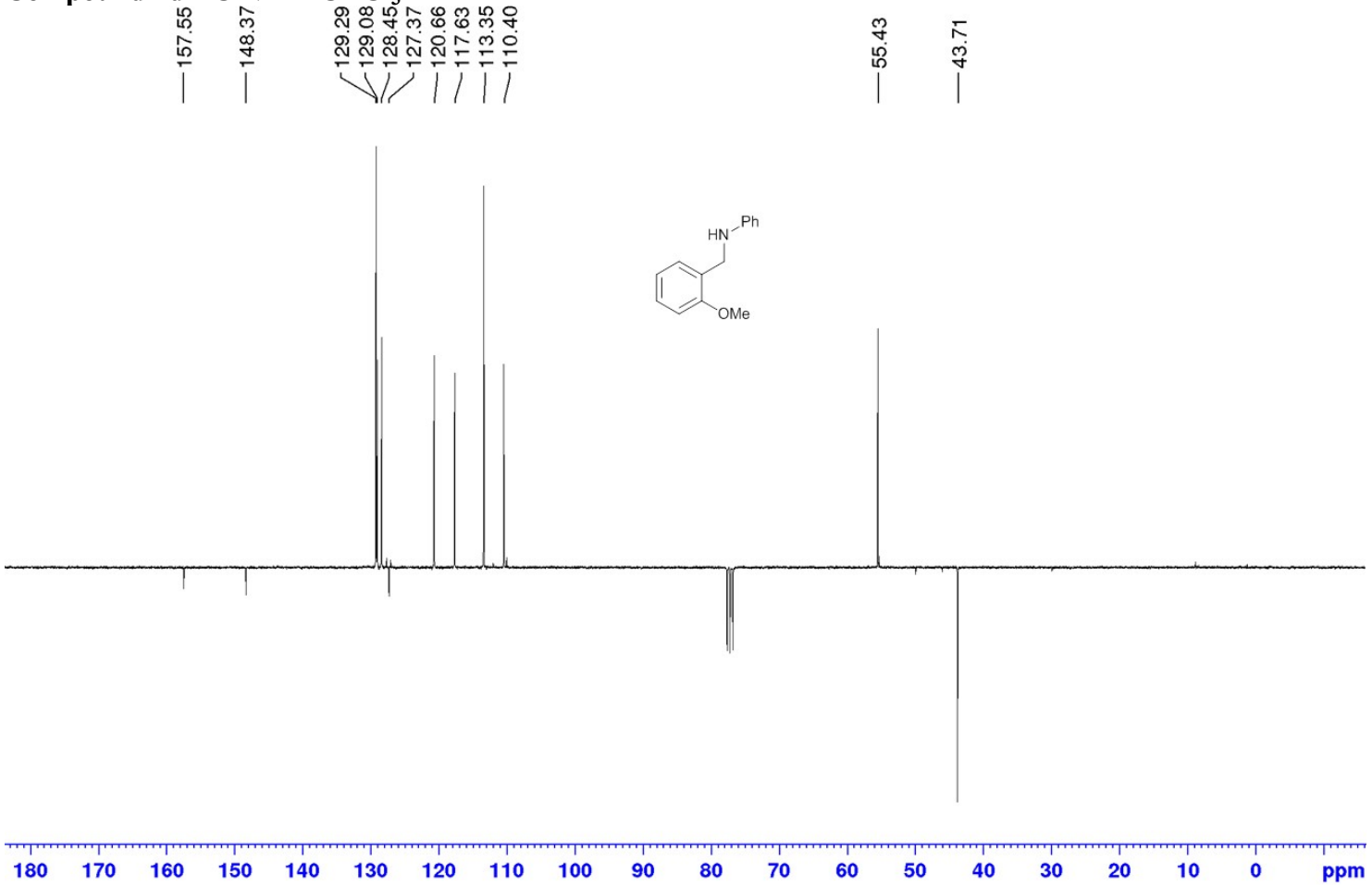
Compound 2c ^{13}C NMR $CDCl_3$



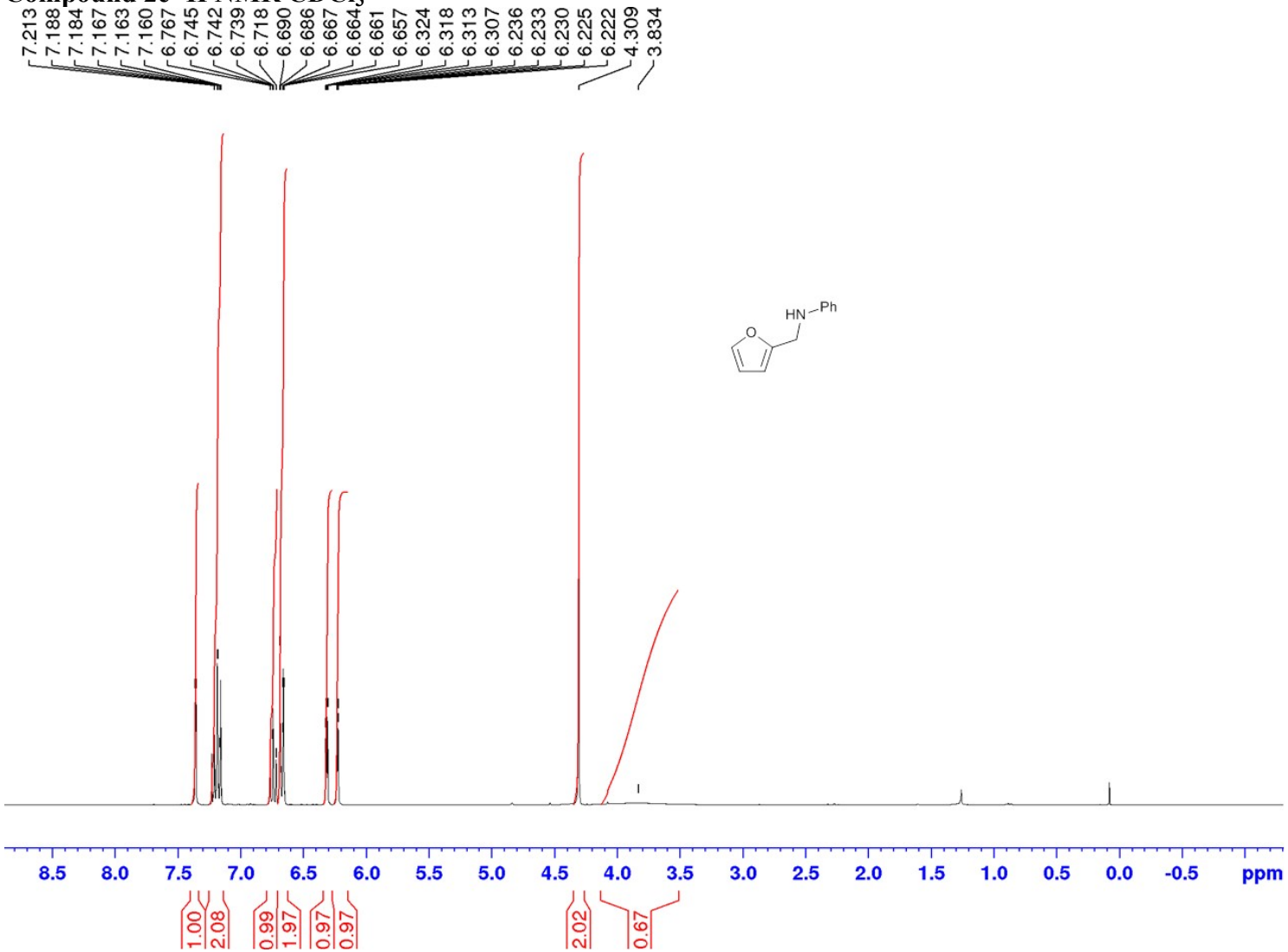
Compound 2d ^{1}H NMR $CDCl_3$



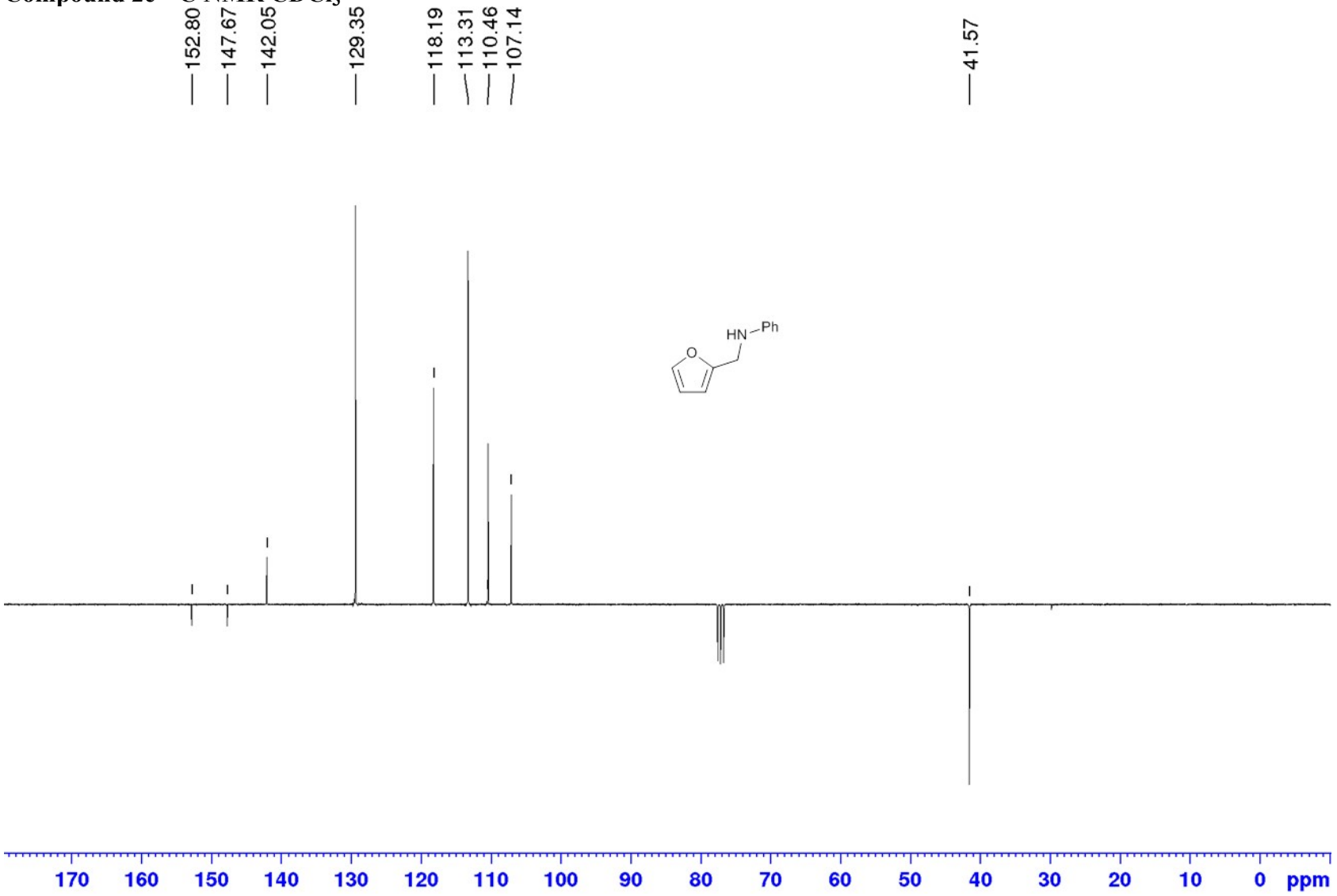
Compound 2d ^{13}C NMR $CDCl_3$



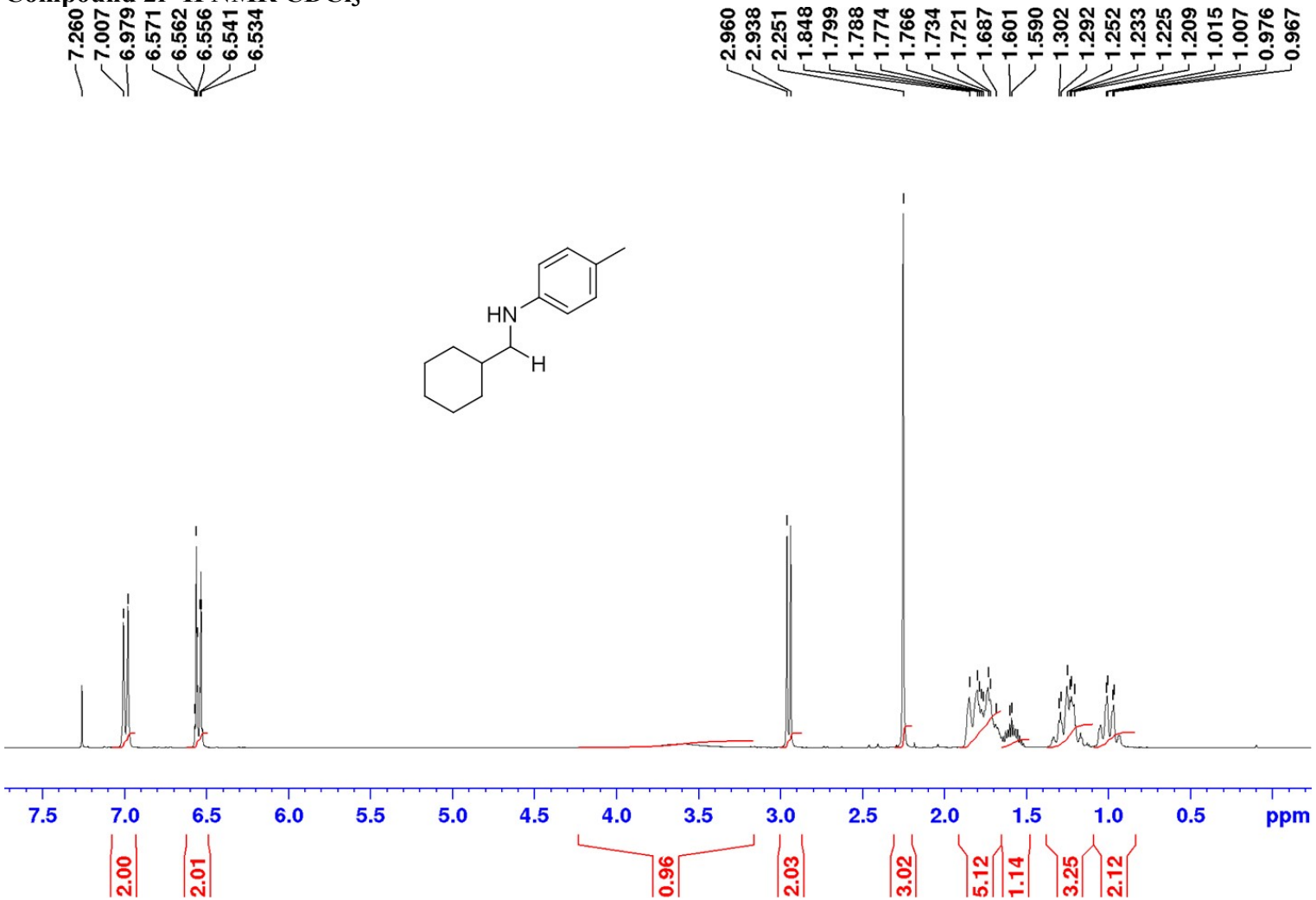
Compound 2e ^{1}H NMR $CDCl_3$



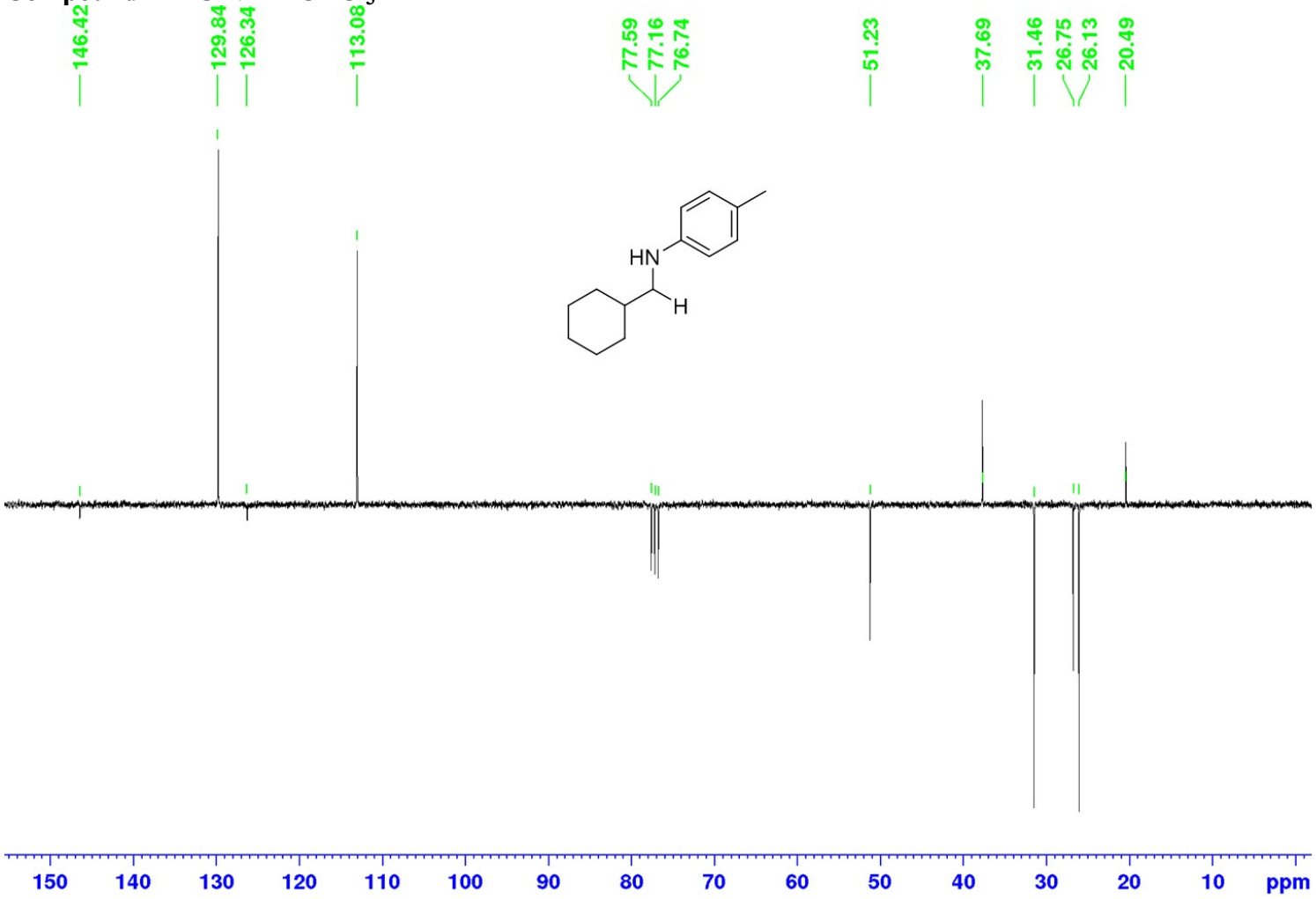
Compound 2e ^{13}C NMR $CDCl_3$



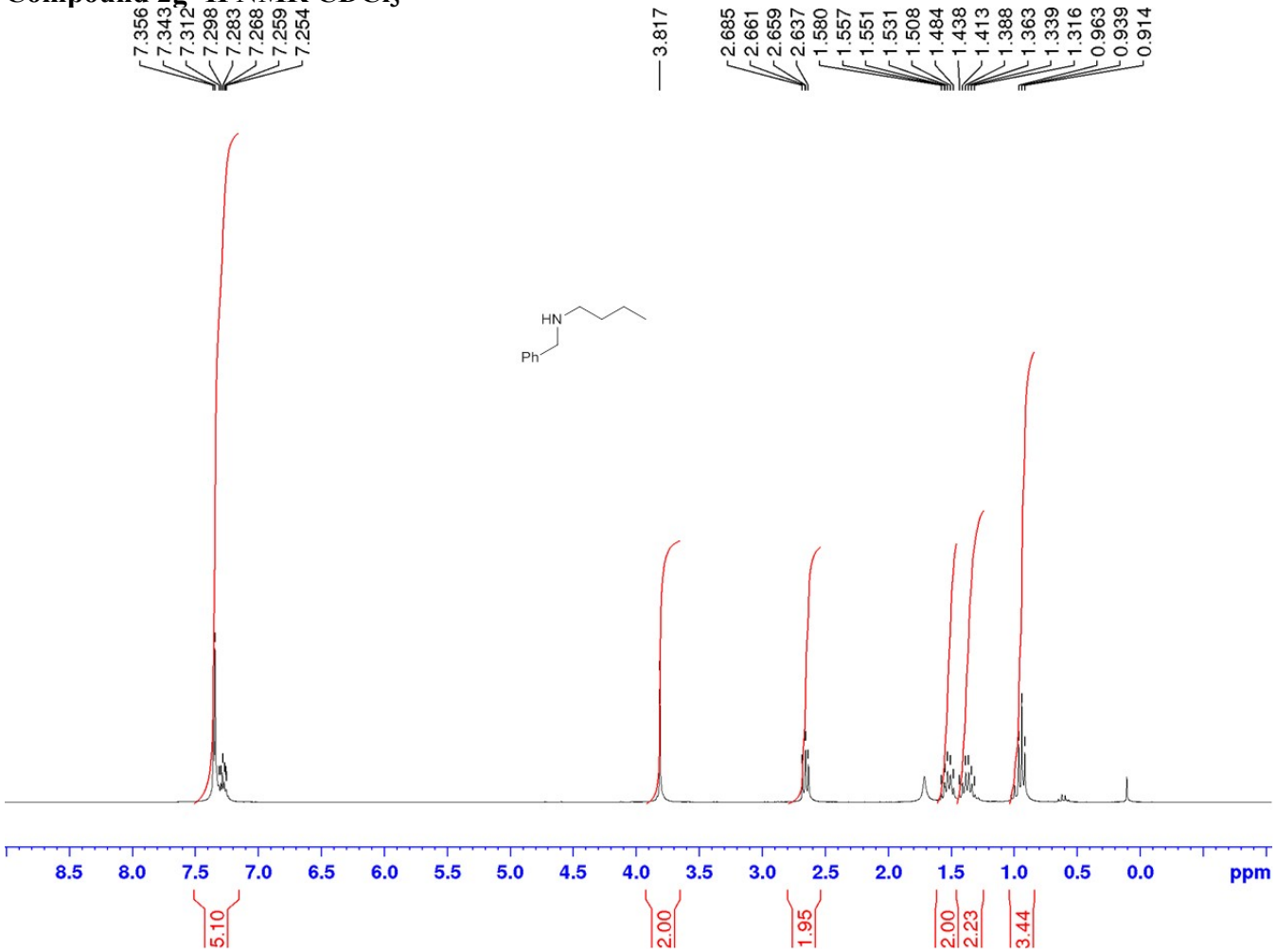
Compound 2f ^{1}H NMR $CDCl_3$



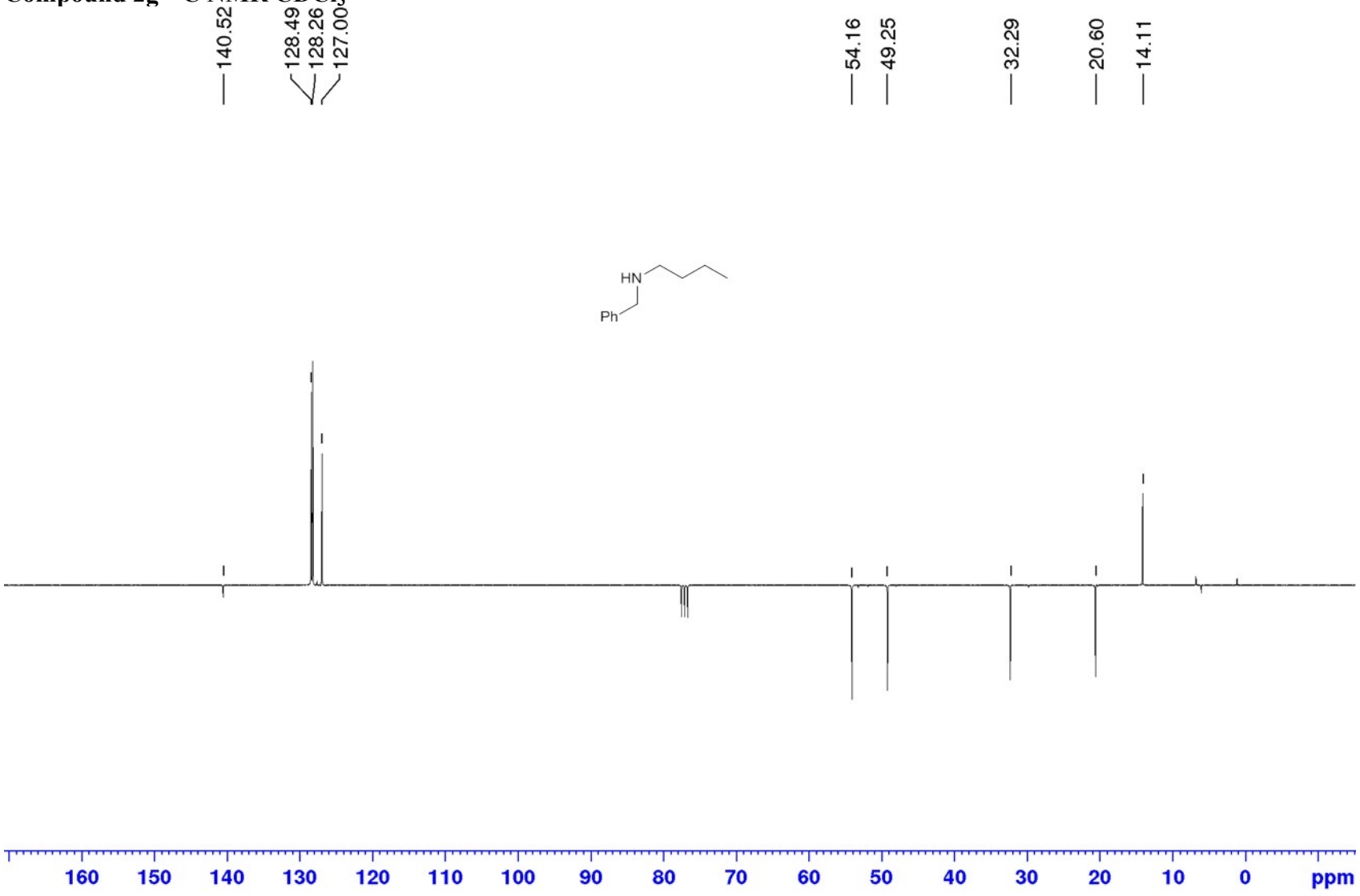
Compound 2f ^{13}C NMR $CDCl_3$



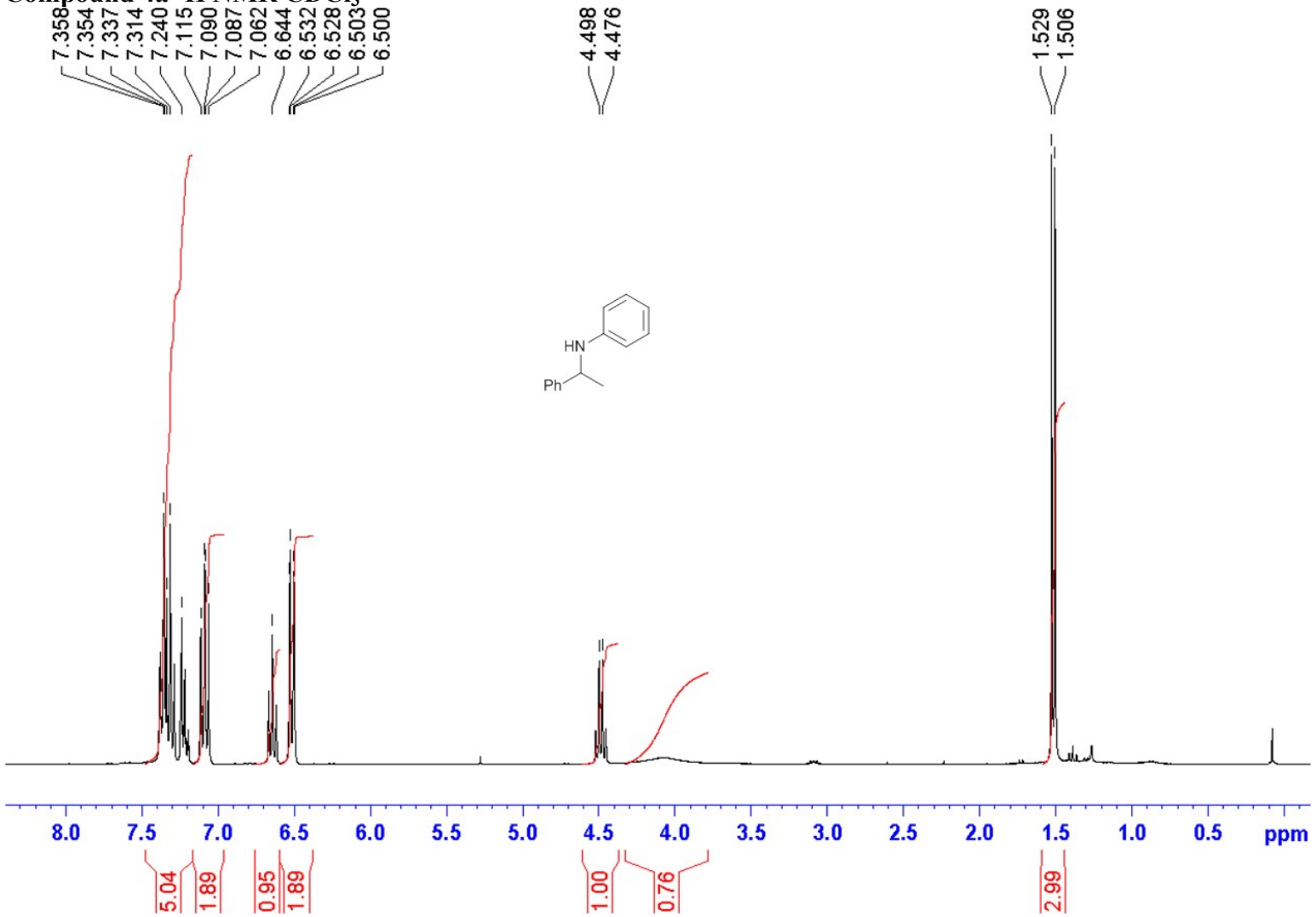
Compound 2g ^{1}H NMR $CDCl_3$



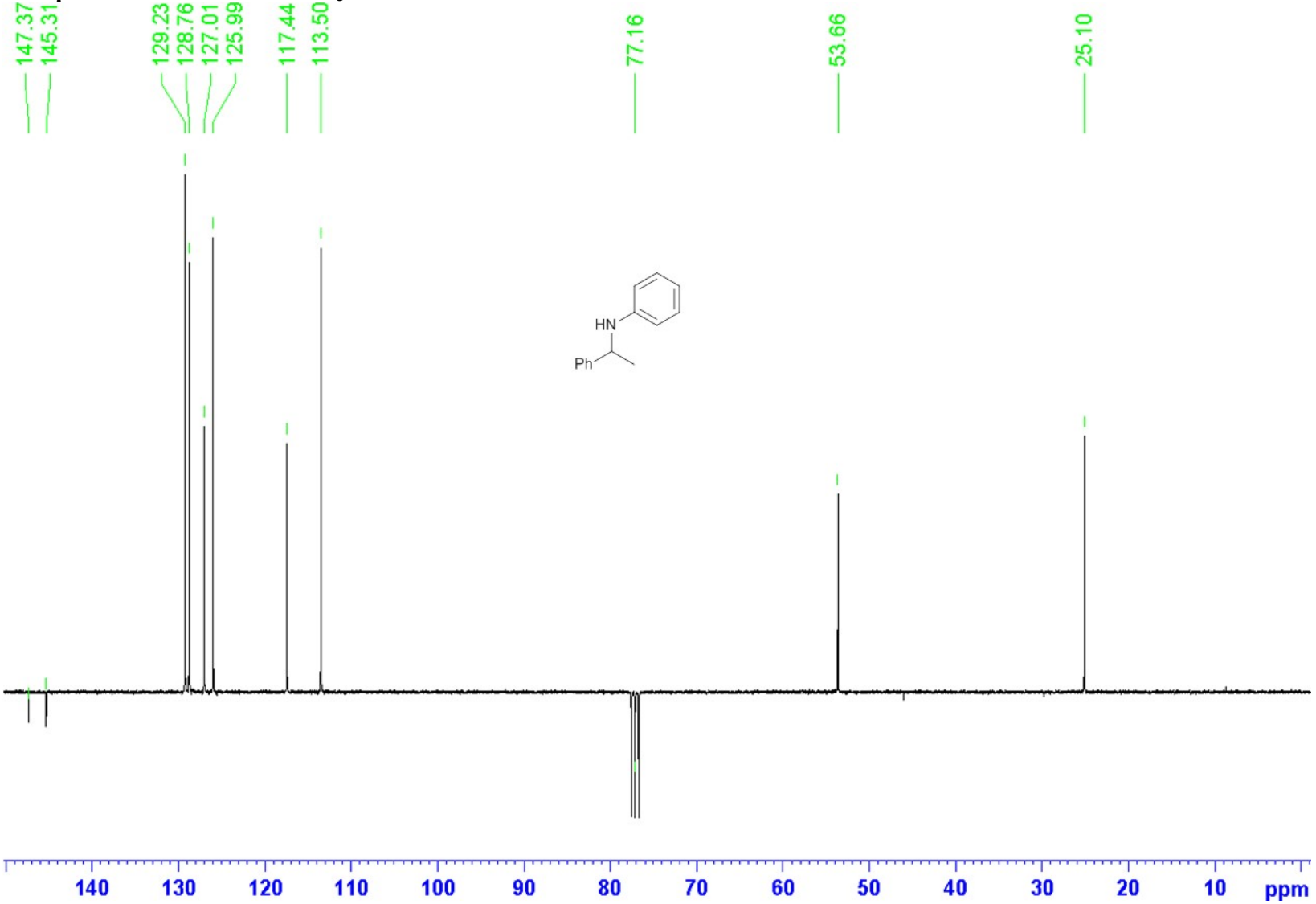
Compound 2g ^{13}C NMR $CDCl_3$



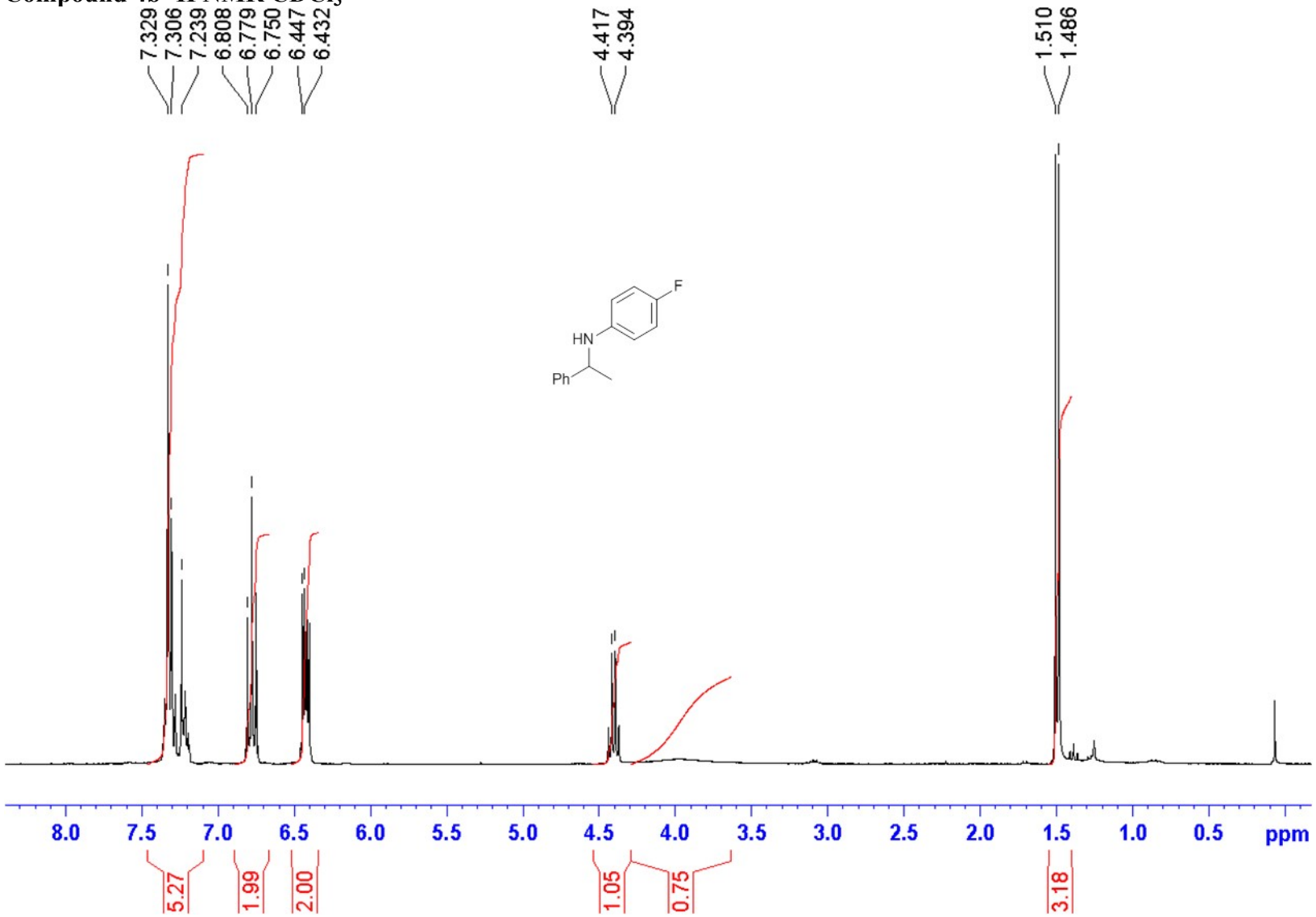
Compound 4a ^{1}H NMR $CDCl_3$



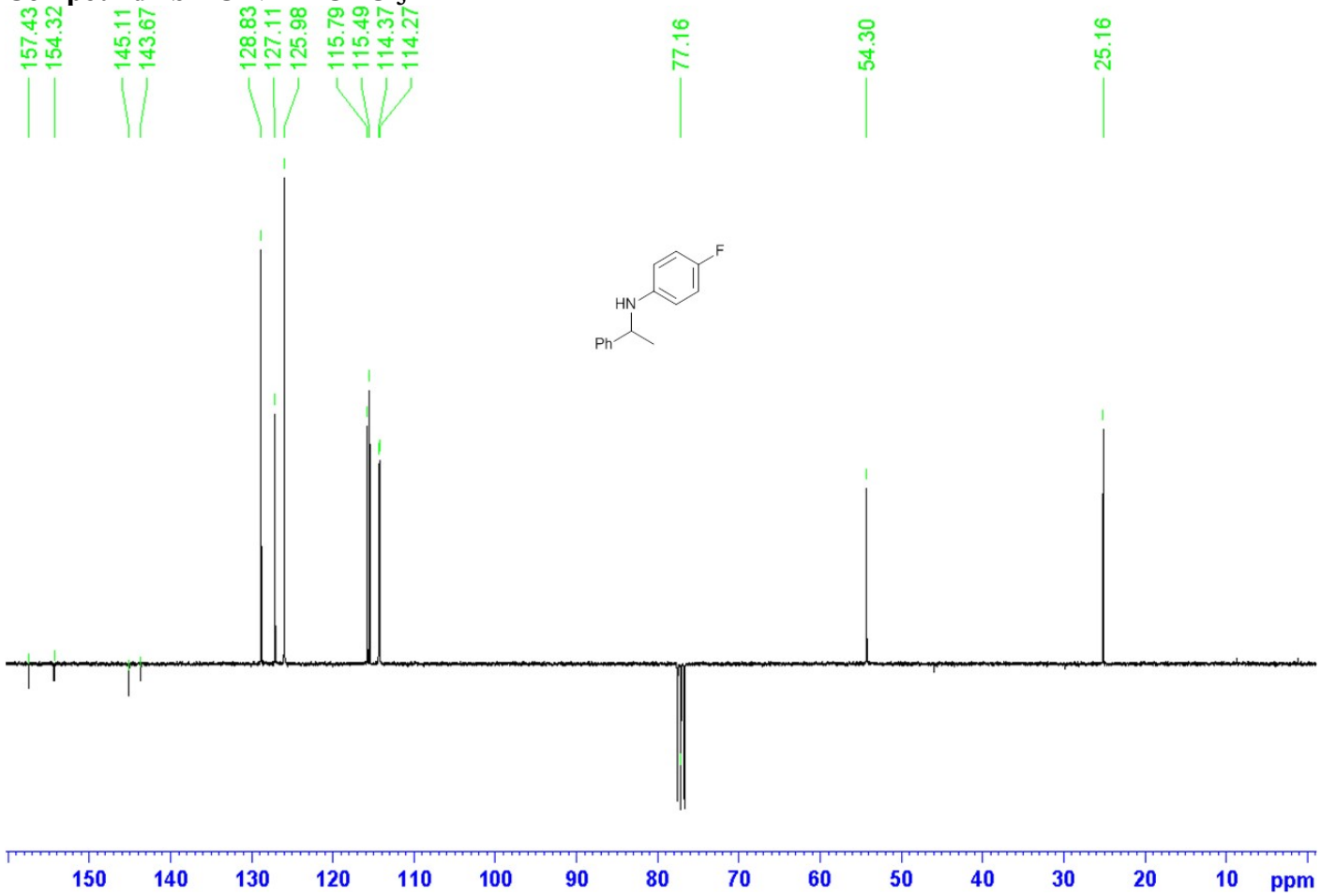
Compound 4a ^{13}C NMR $CDCl_3$



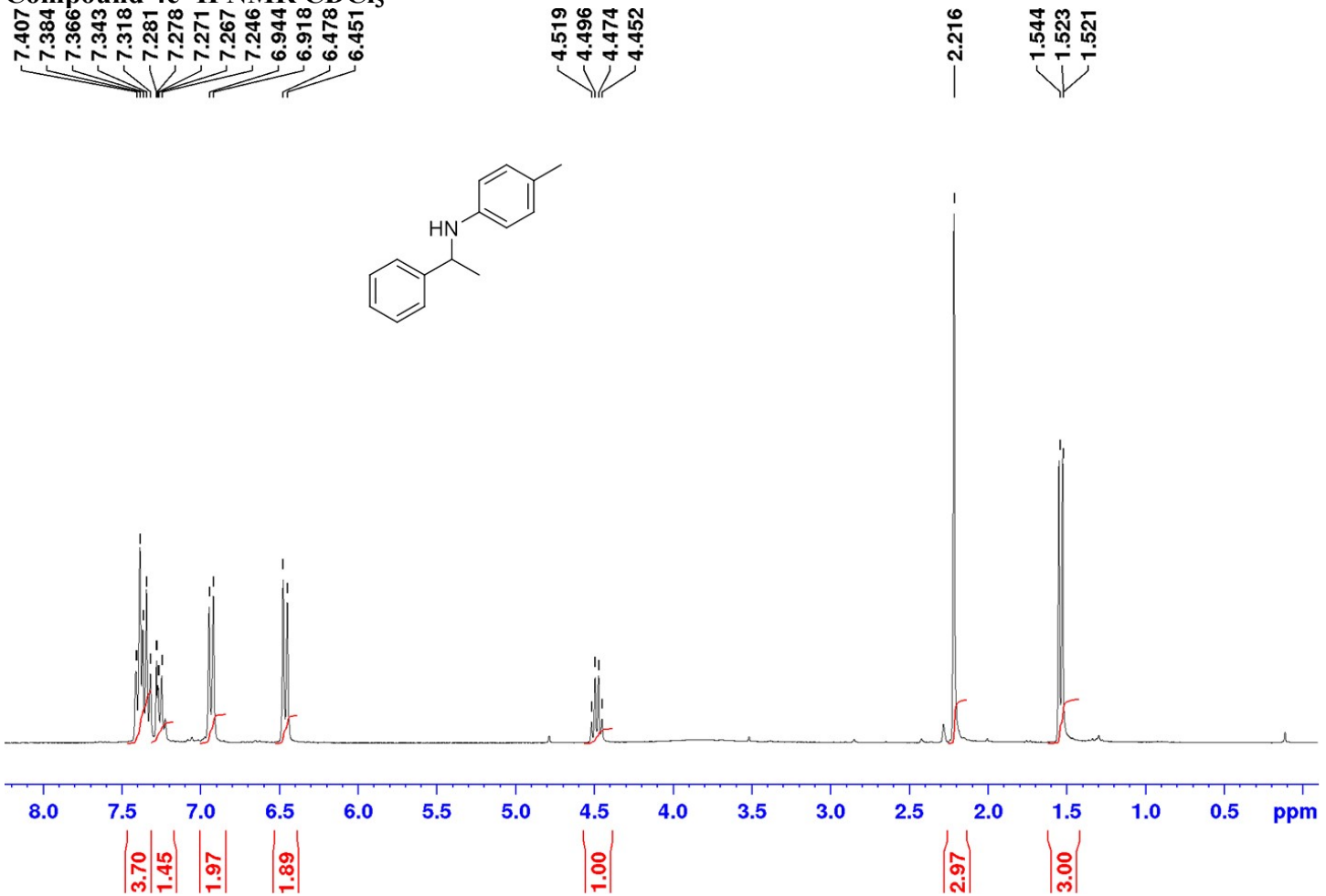
Compound 4b ^{1}H NMR $CDCl_3$



Compound 4b ^{13}C NMR $CDCl_3$



Compound 4c ^{1}H NMR $CDCl_3$



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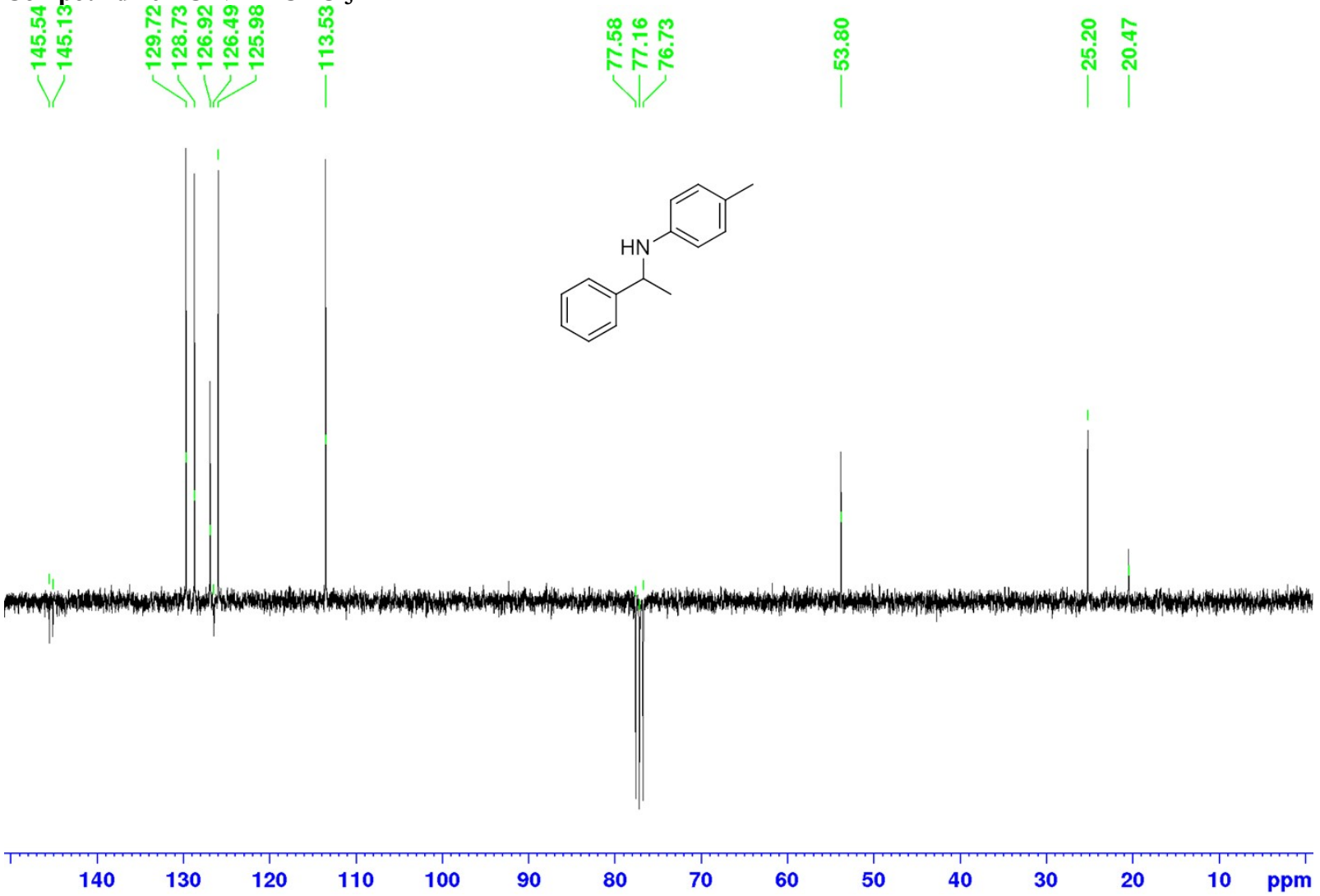
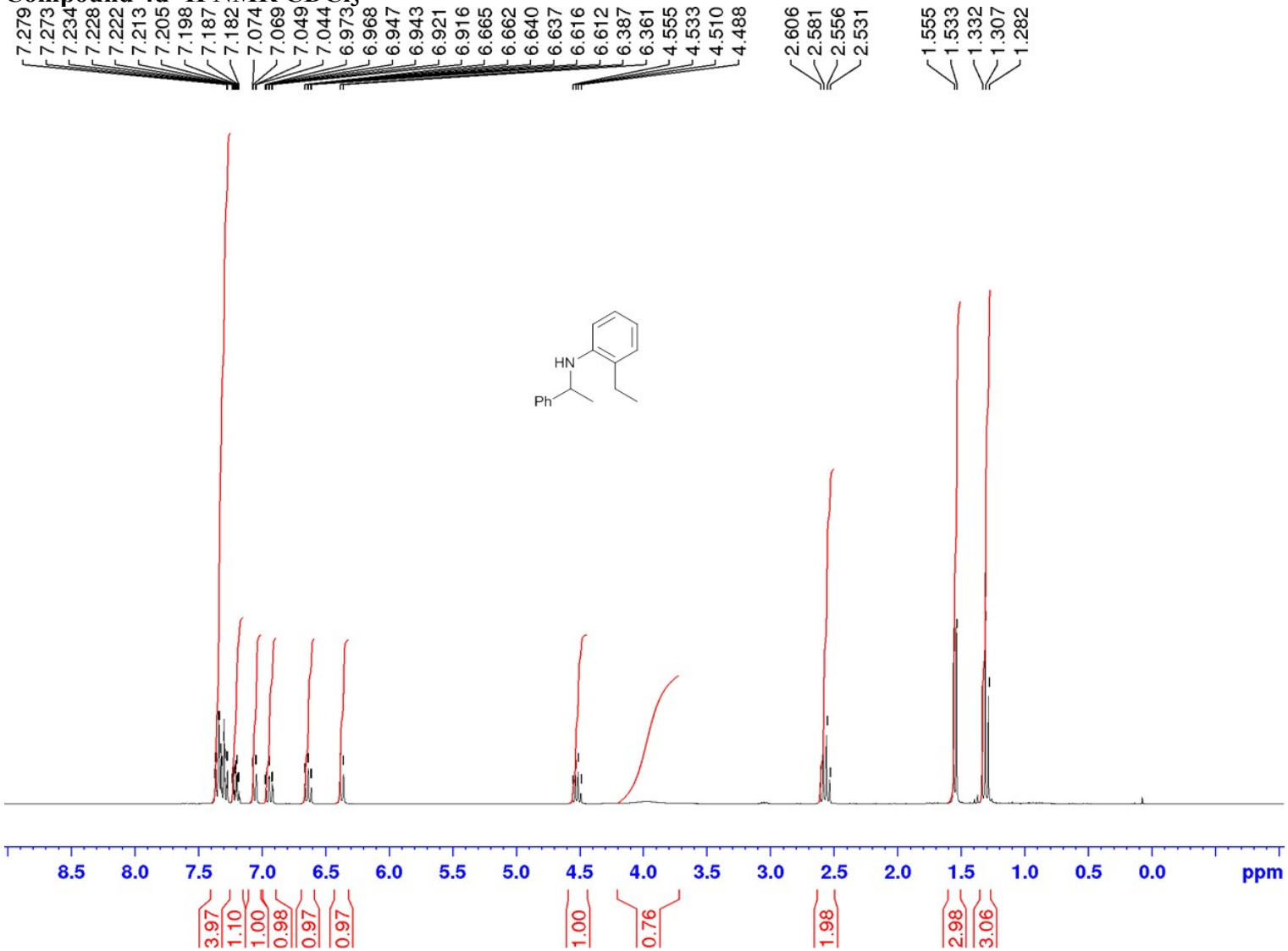
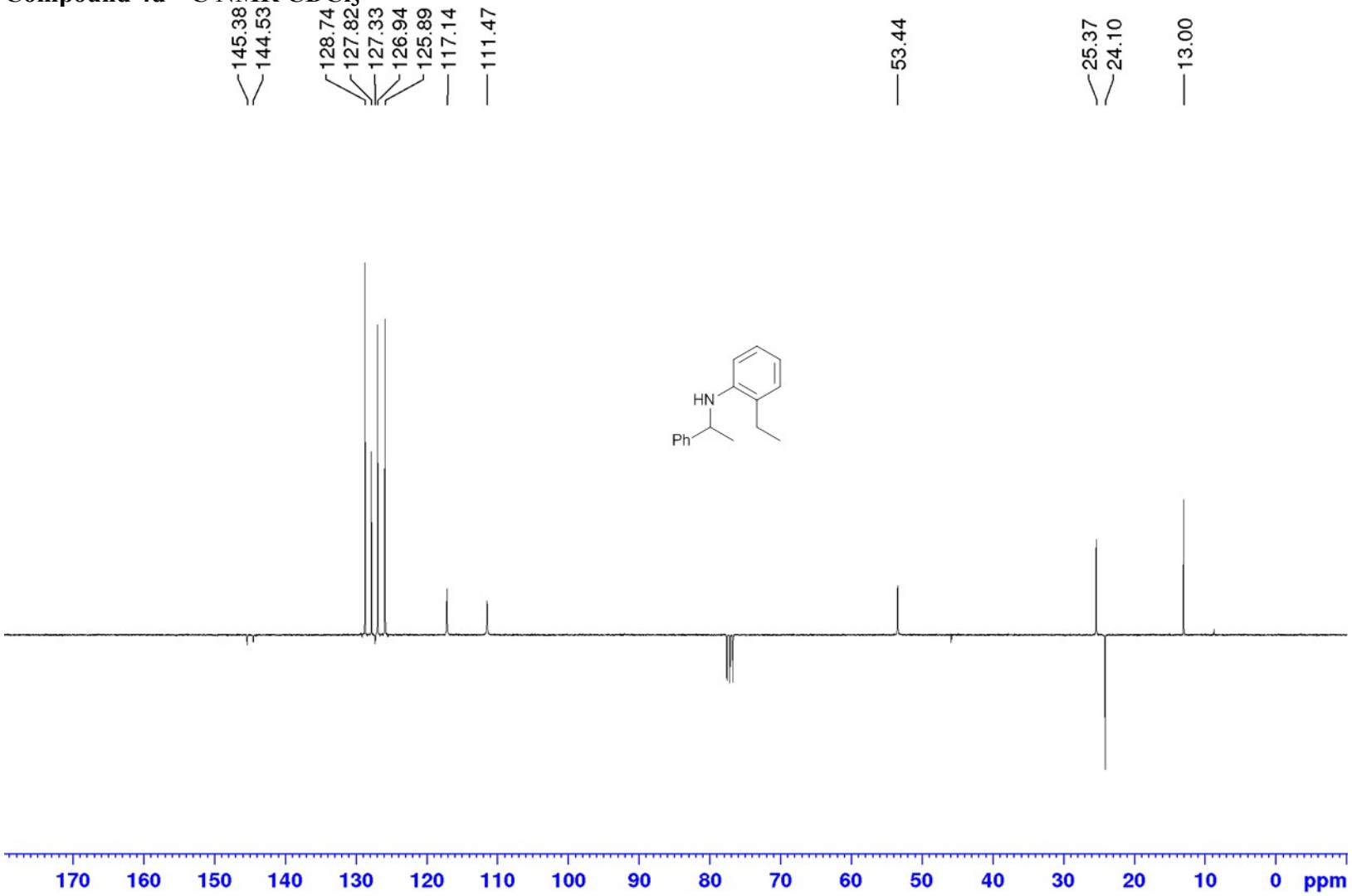


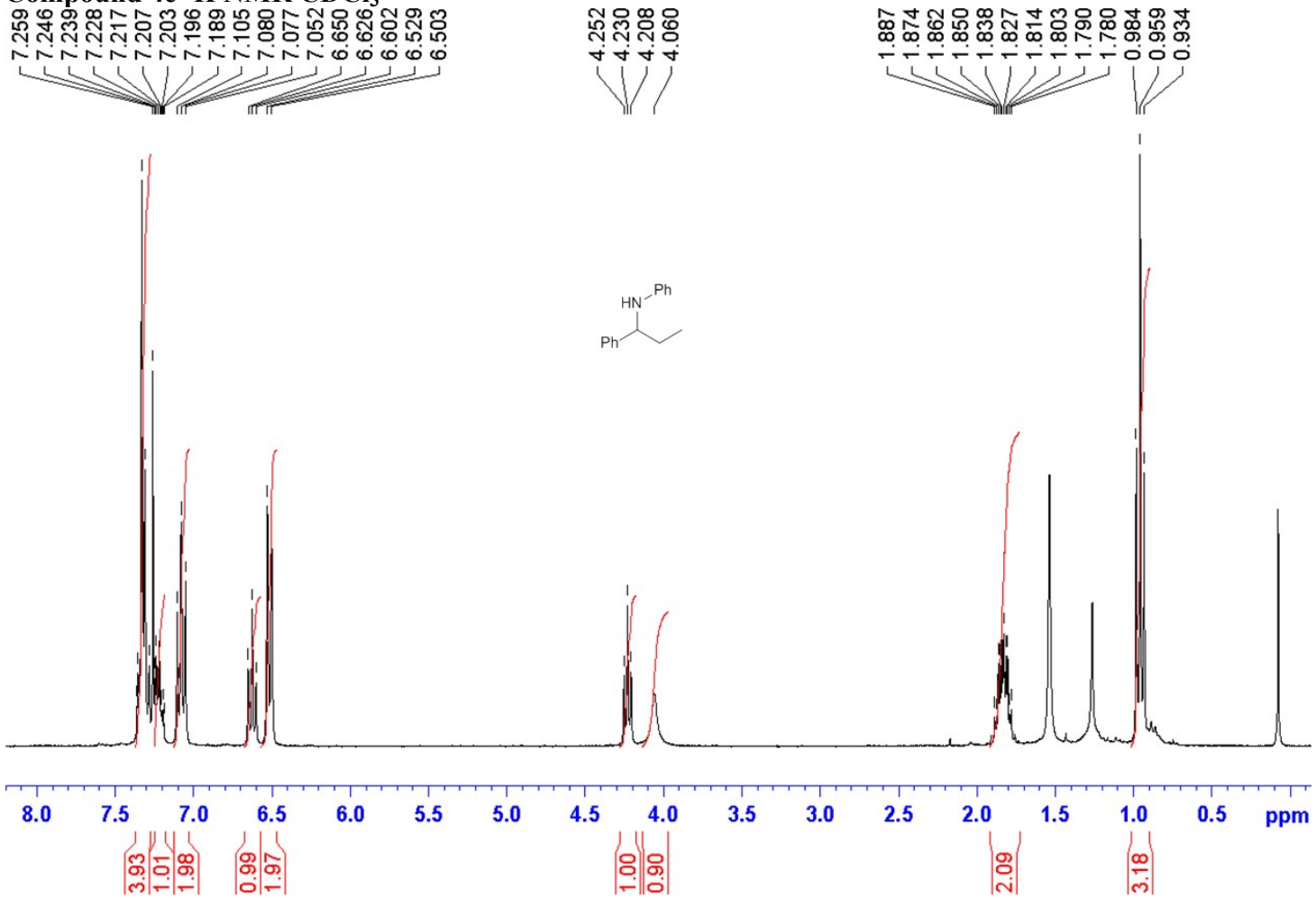
Compound 4d ^{1}H NMR $CDCl_3$



Compound 4d ^{13}C NMR $CDCl_3$



Compound 4e ^{1}H NMR $CDCl_3$



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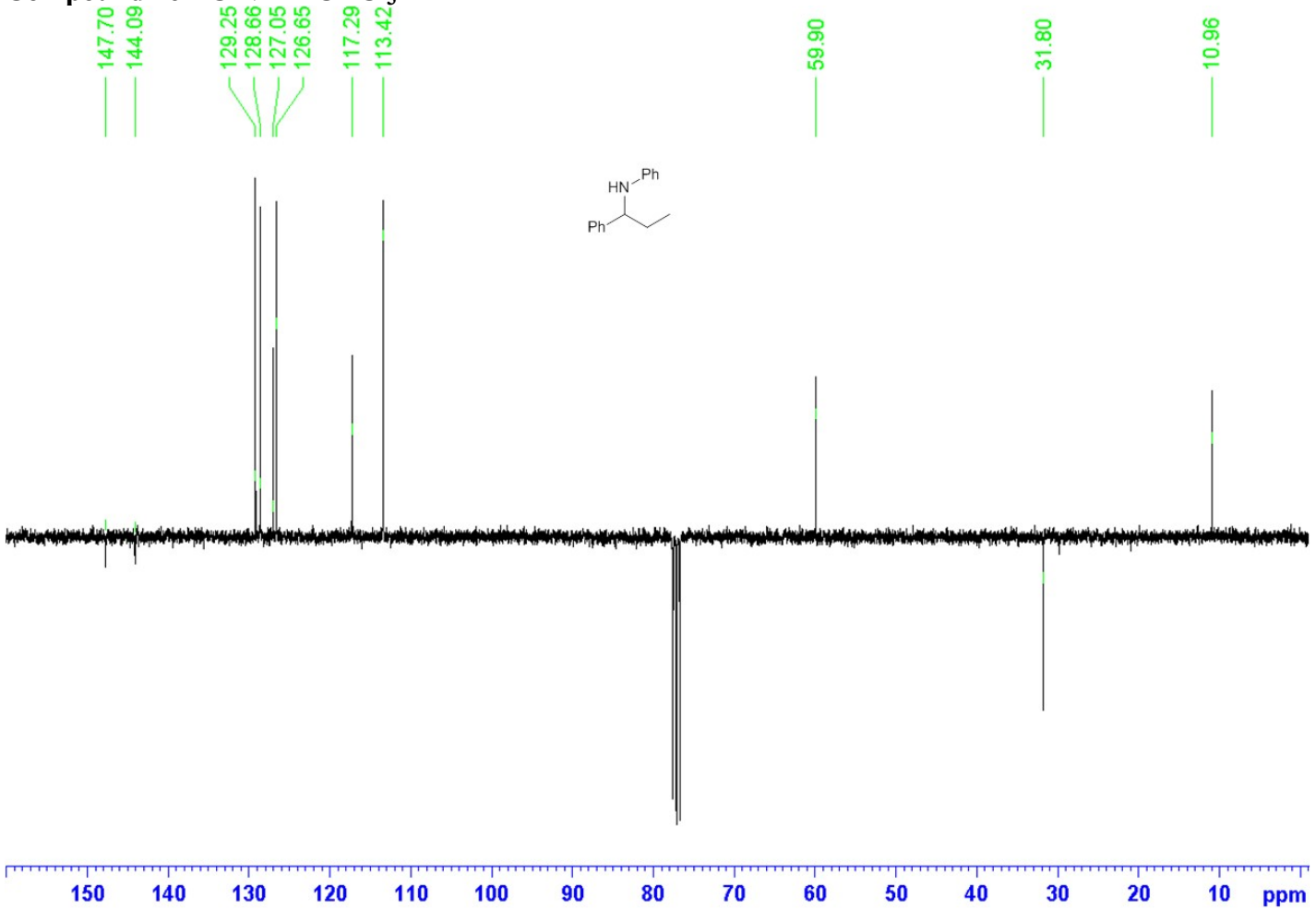
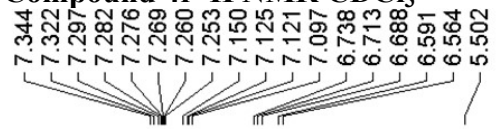
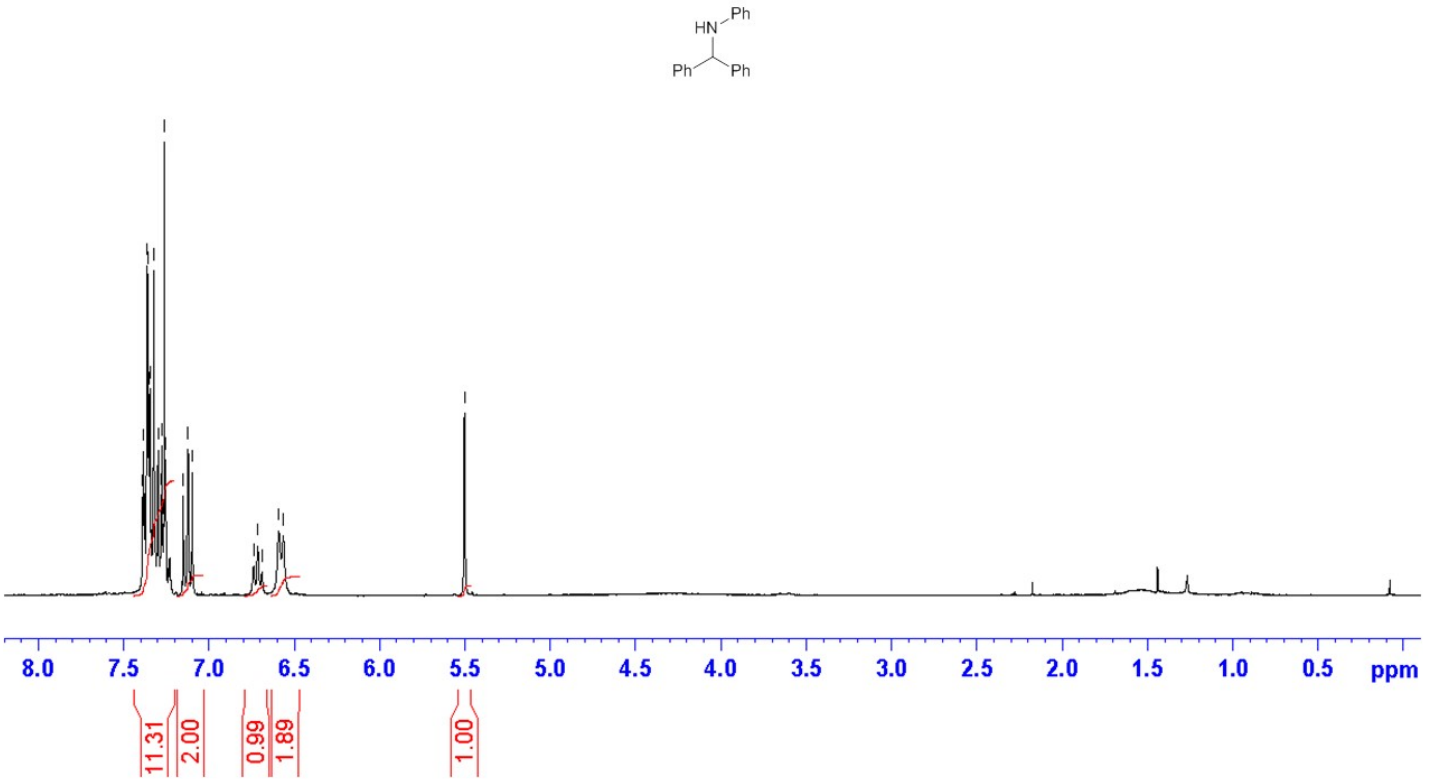
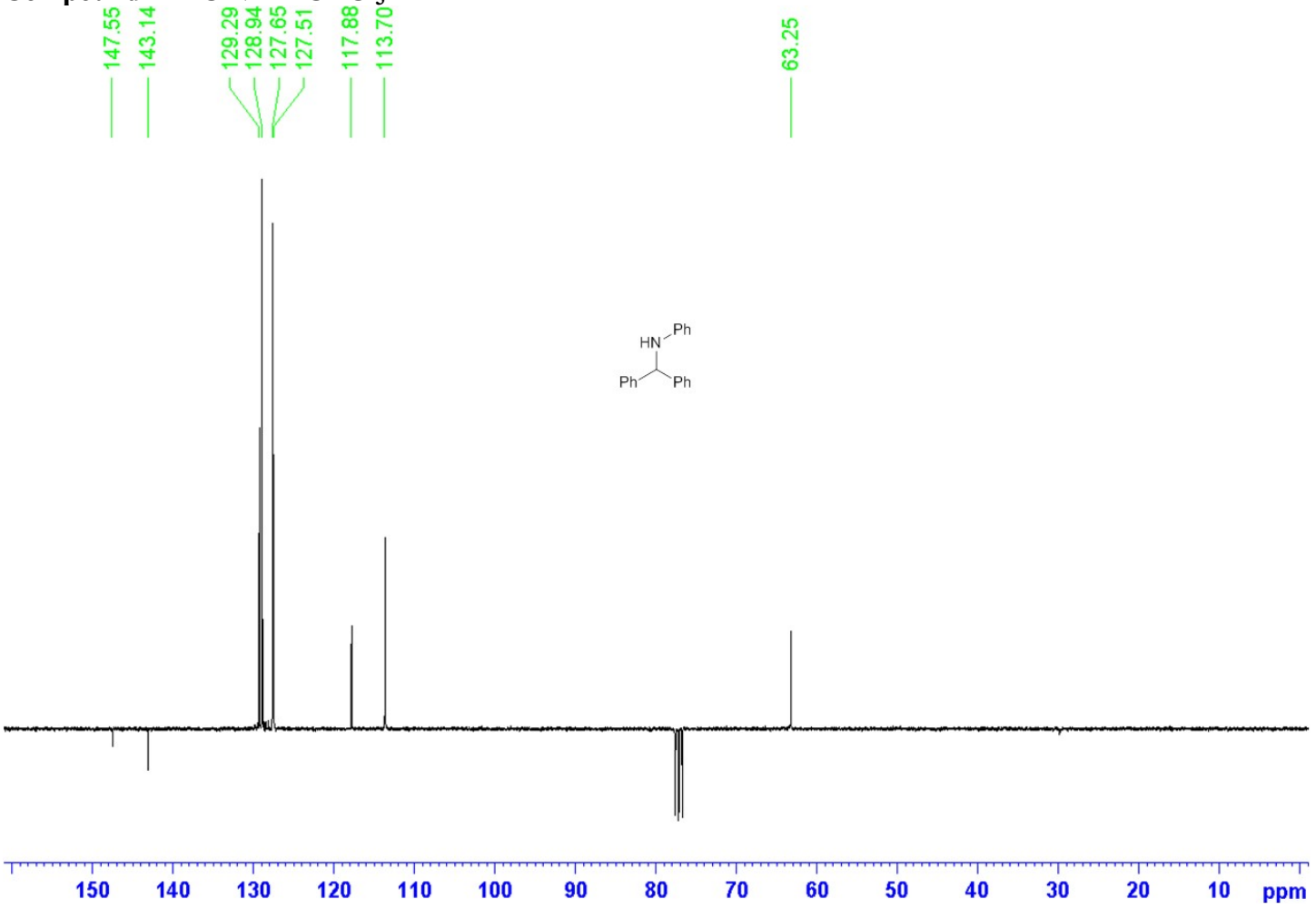


Compound 4f ^{1}H NMR $CDCl_3$

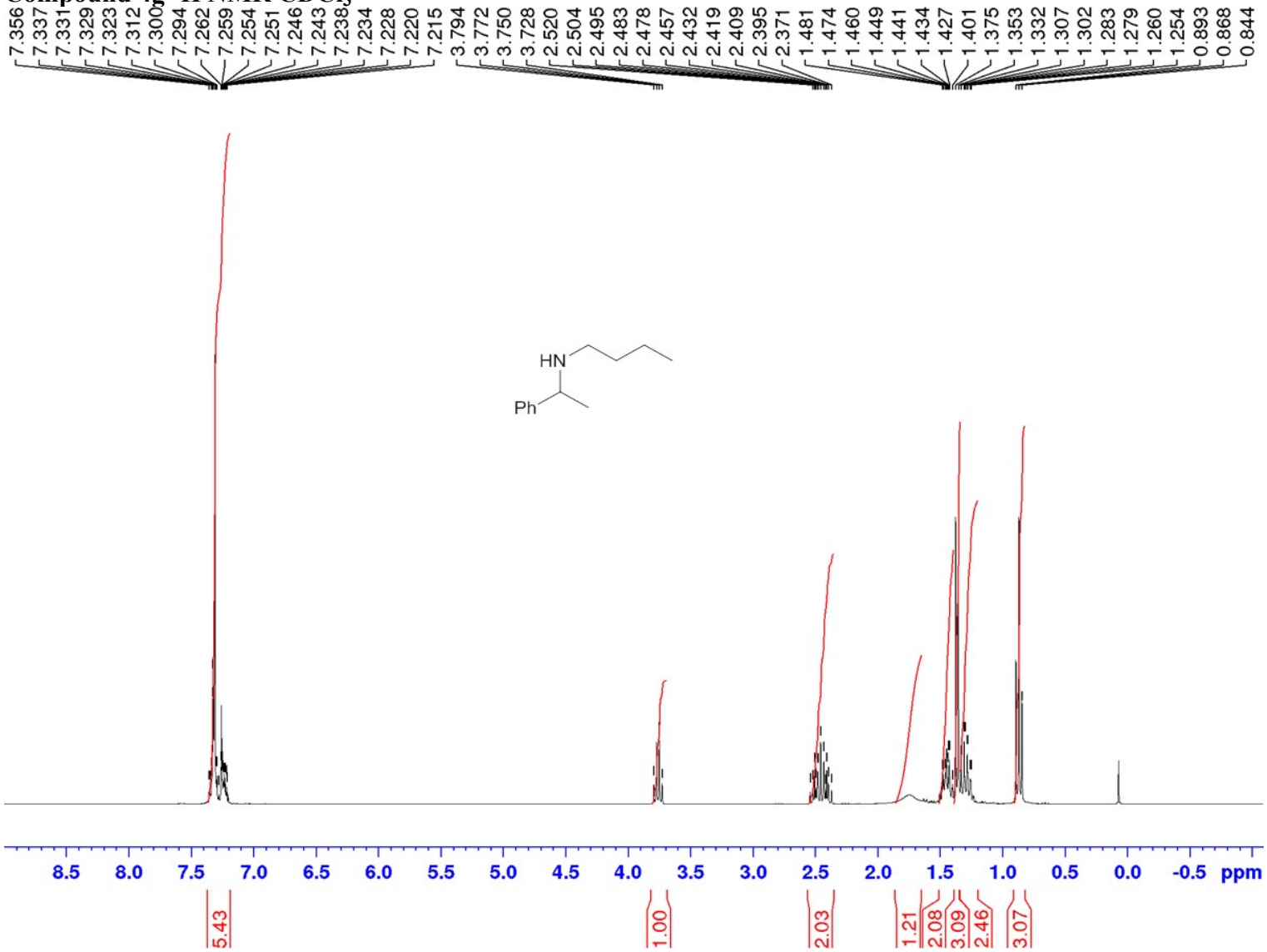




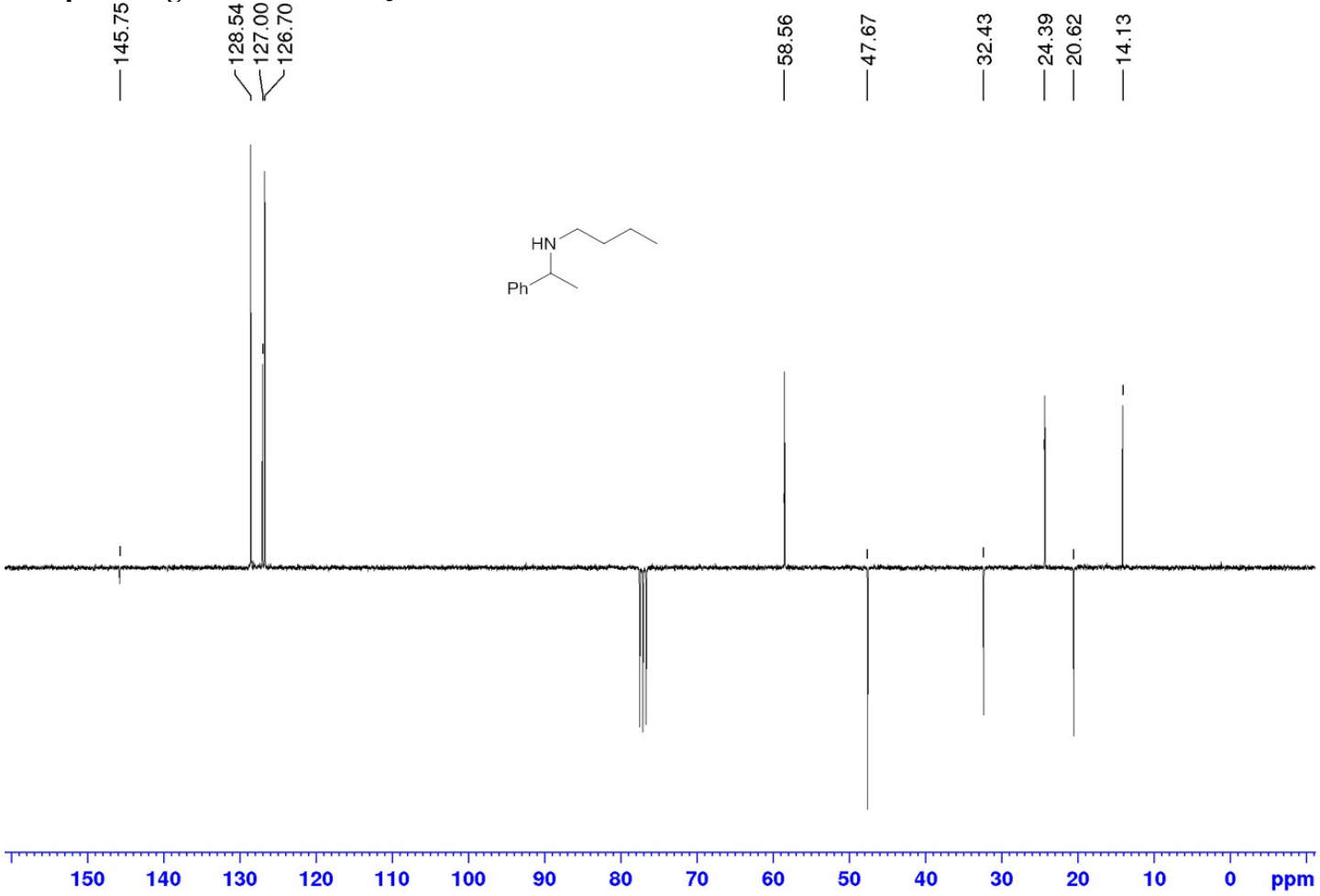
Compound 4f ^{13}C NMR $CDCl_3$



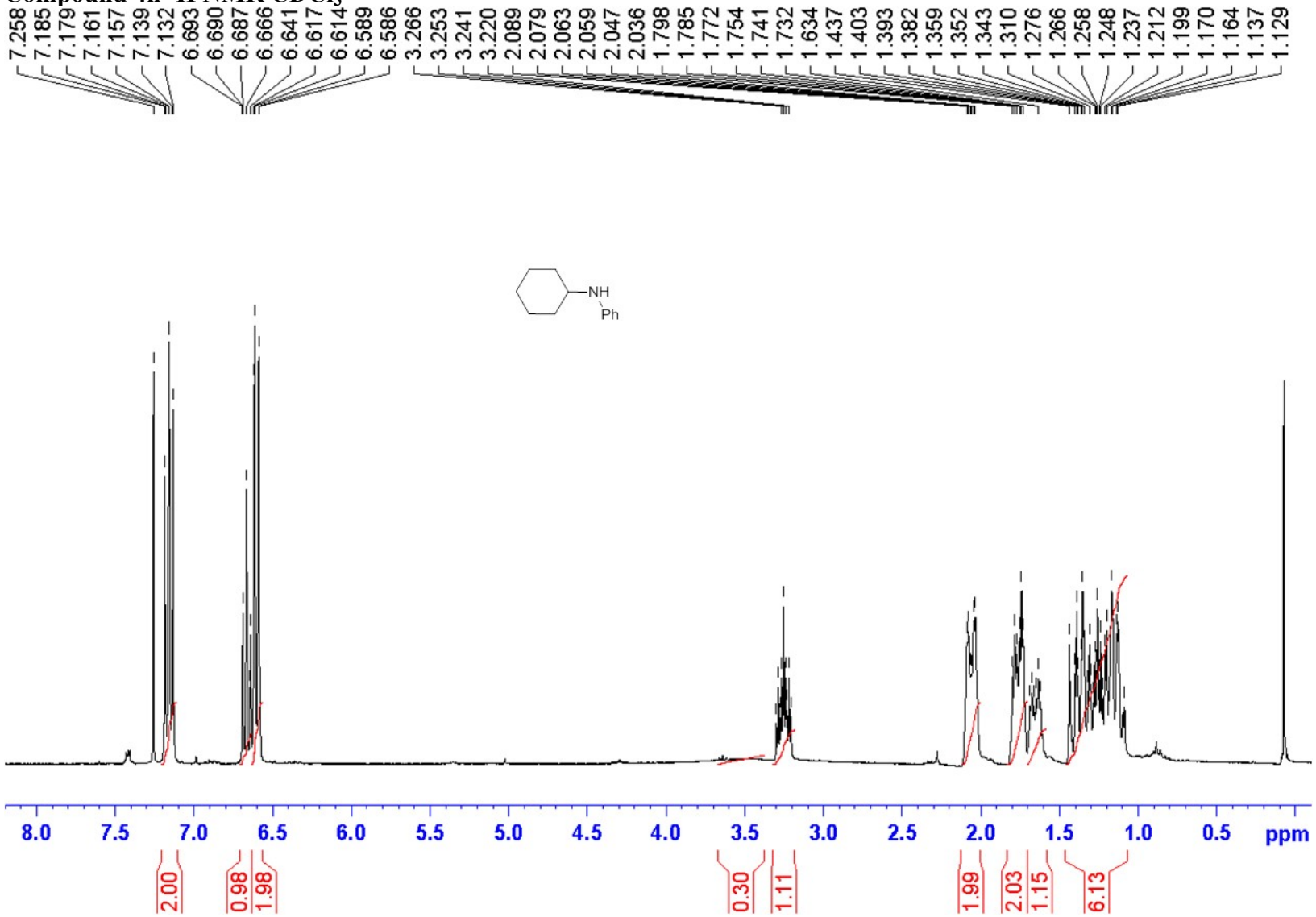
Compound 4g ^{1}H NMR $CDCl_3$



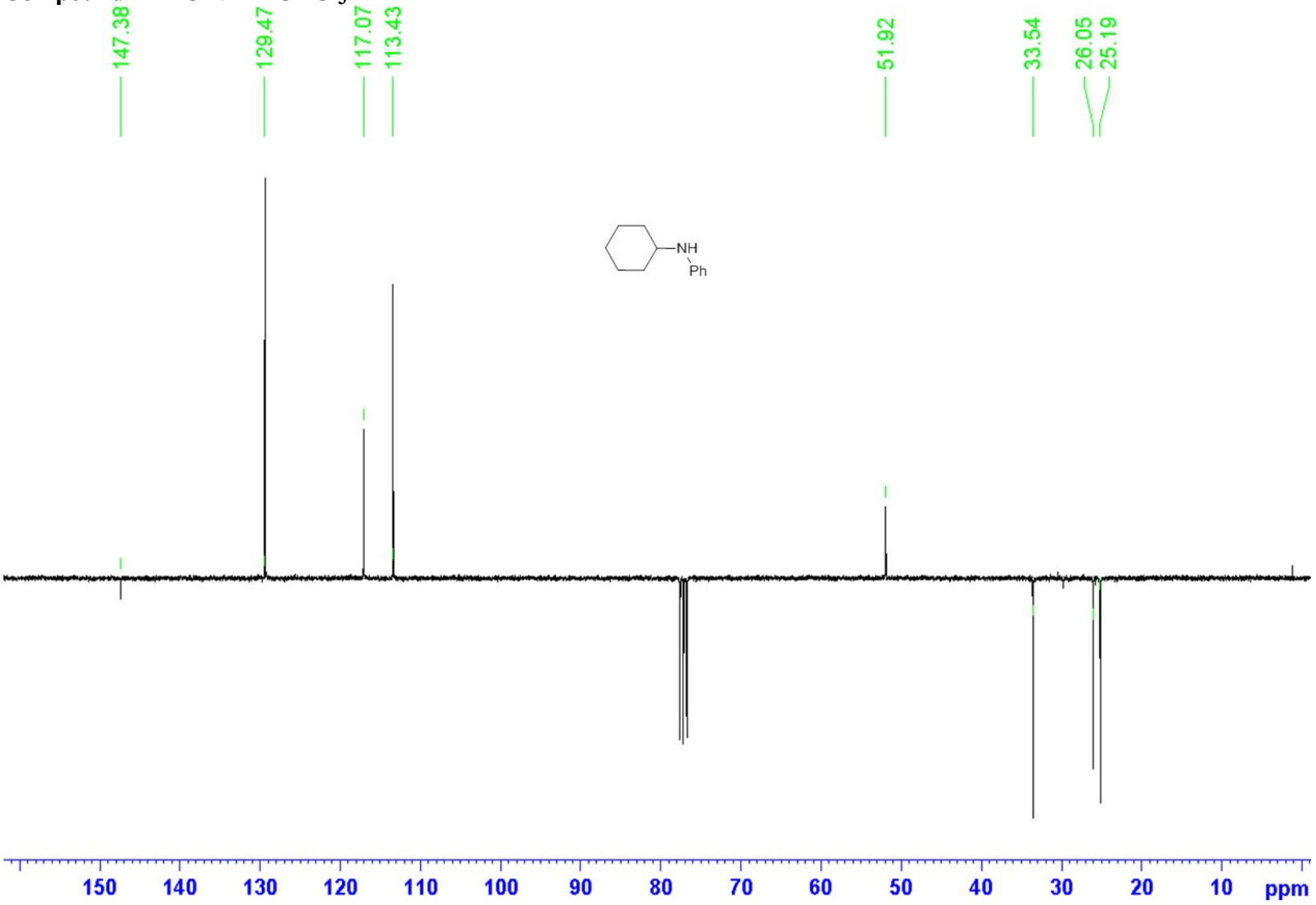
Compound 4g ^{13}C NMR $CDCl_3$



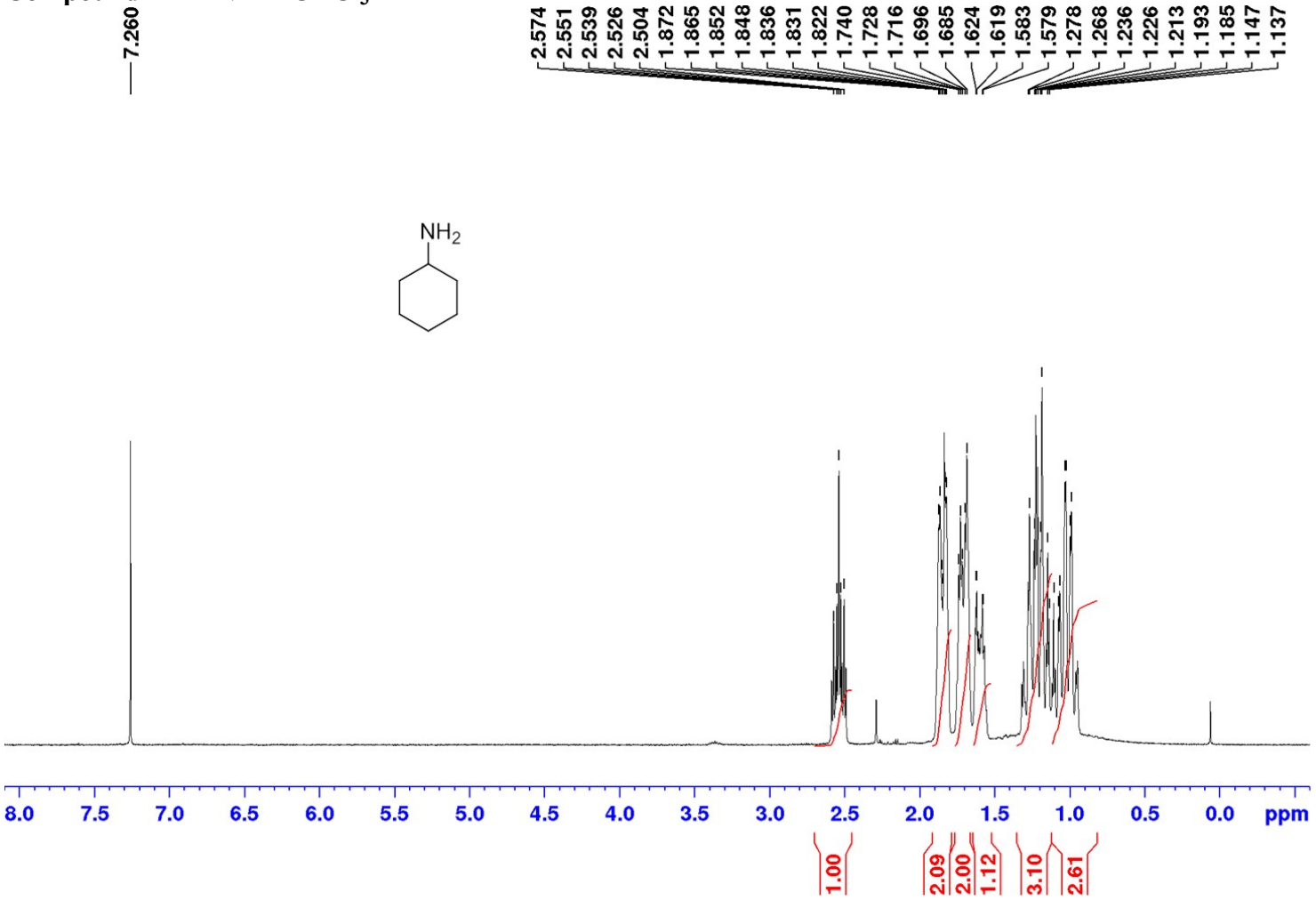
Compound 4h ^{1}H NMR $CDCl_3$



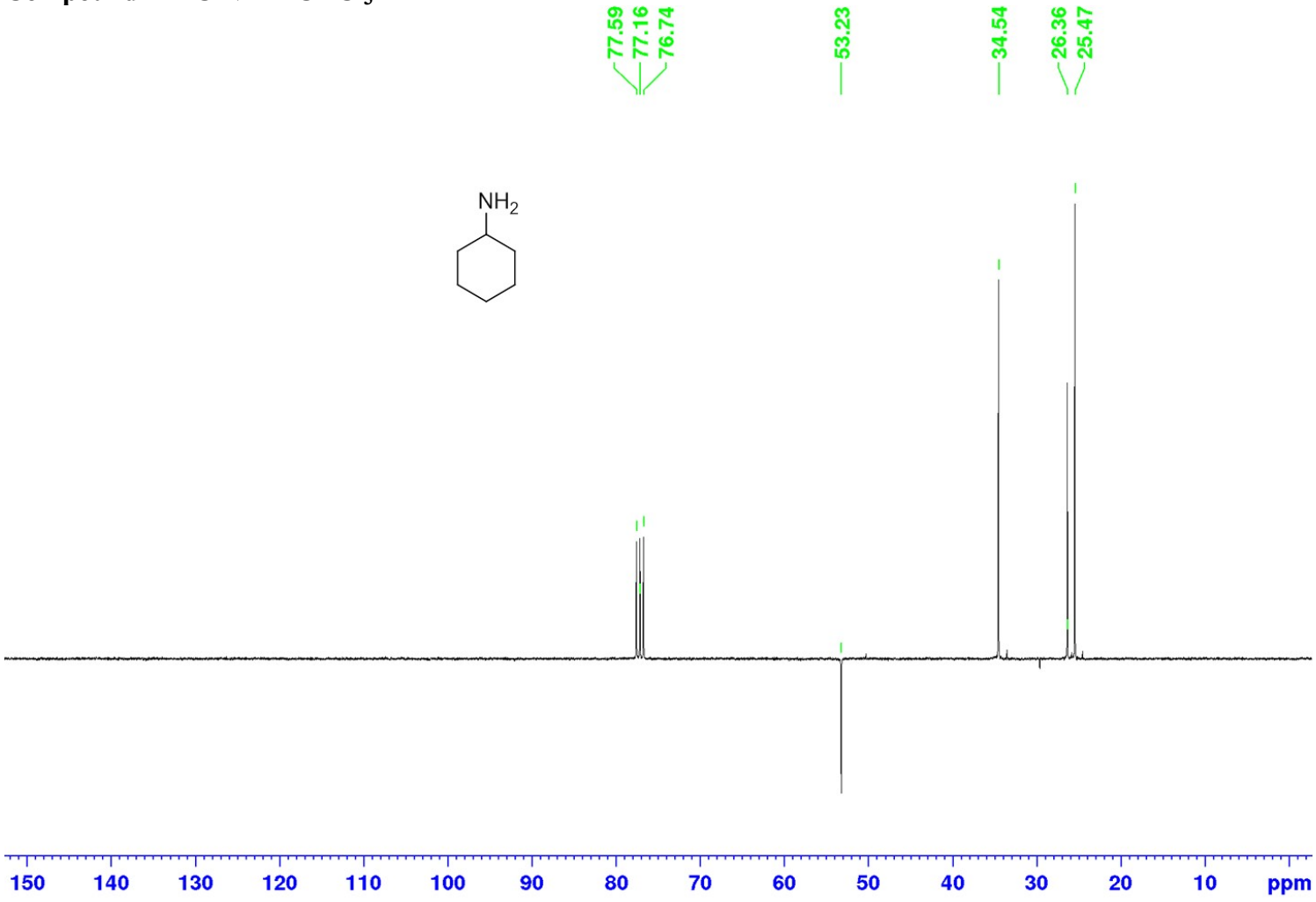
Compound 4h ^{13}C NMR $CDCl_3$



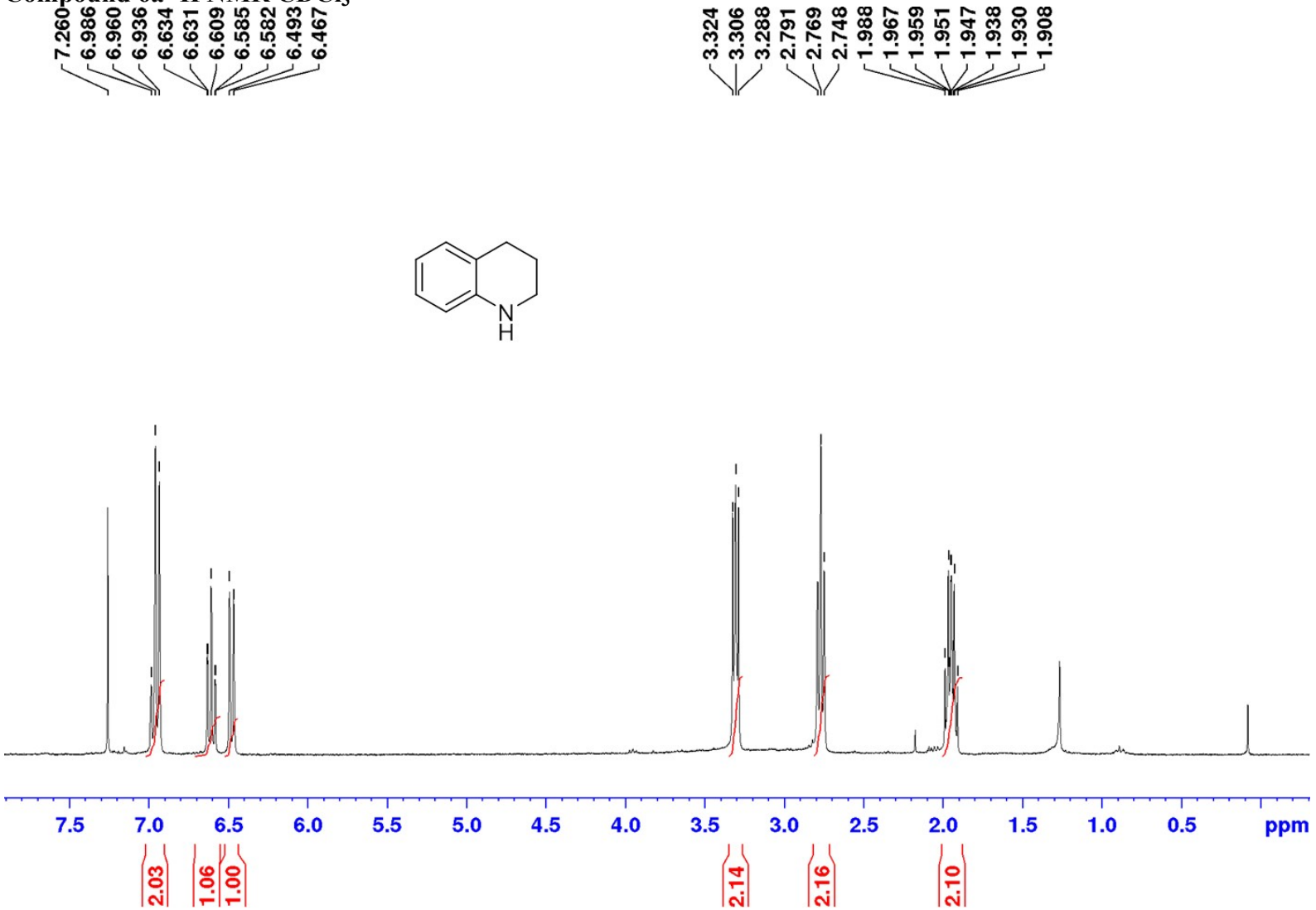
Compound 4i ^{1}H NMR $CDCl_3$



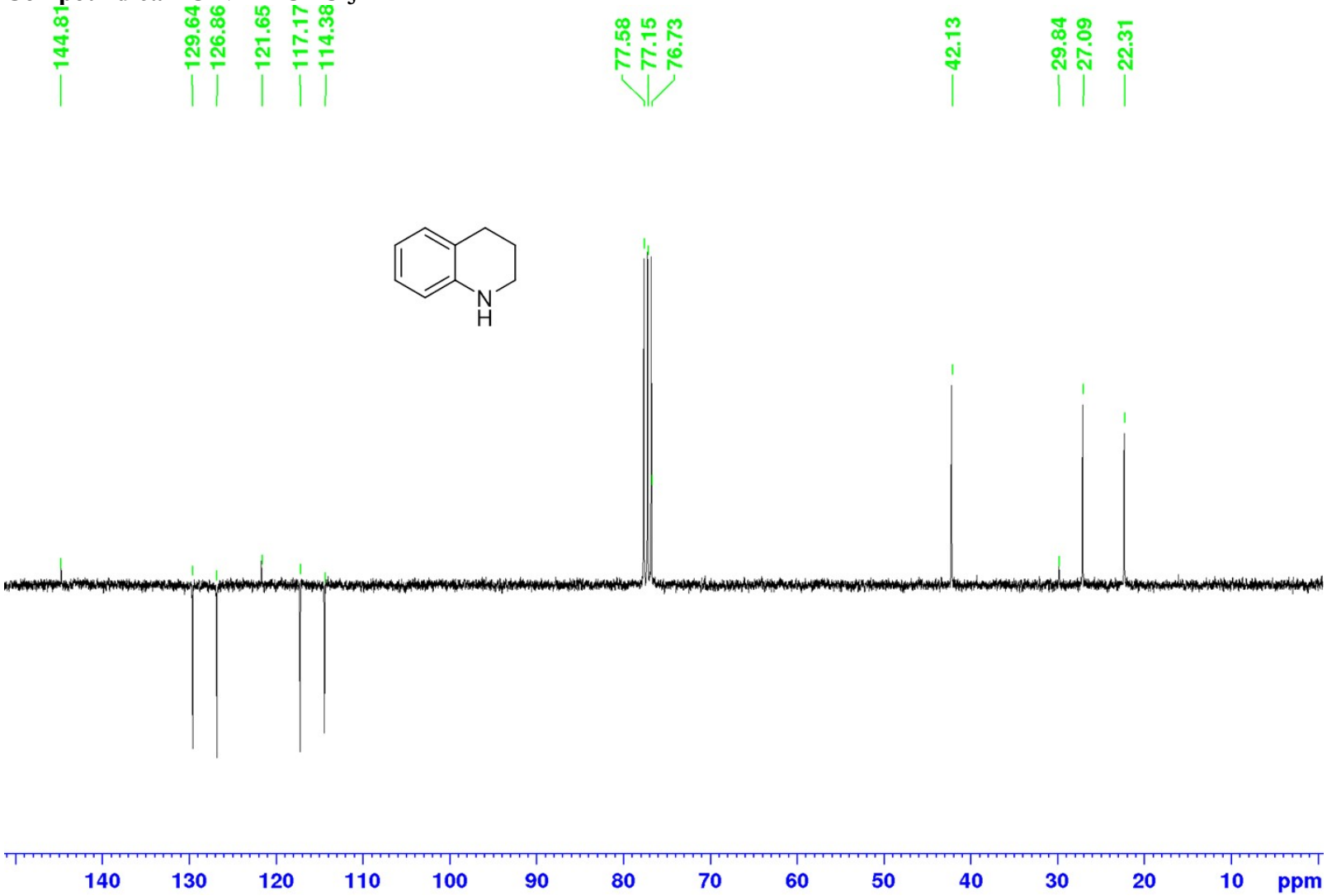
Compound 4i ^{13}C NMR $CDCl_3$



Compound 6a ^{1}H NMR $CDCl_3$



Compound 6a ^{13}C NMR $CDCl_3$



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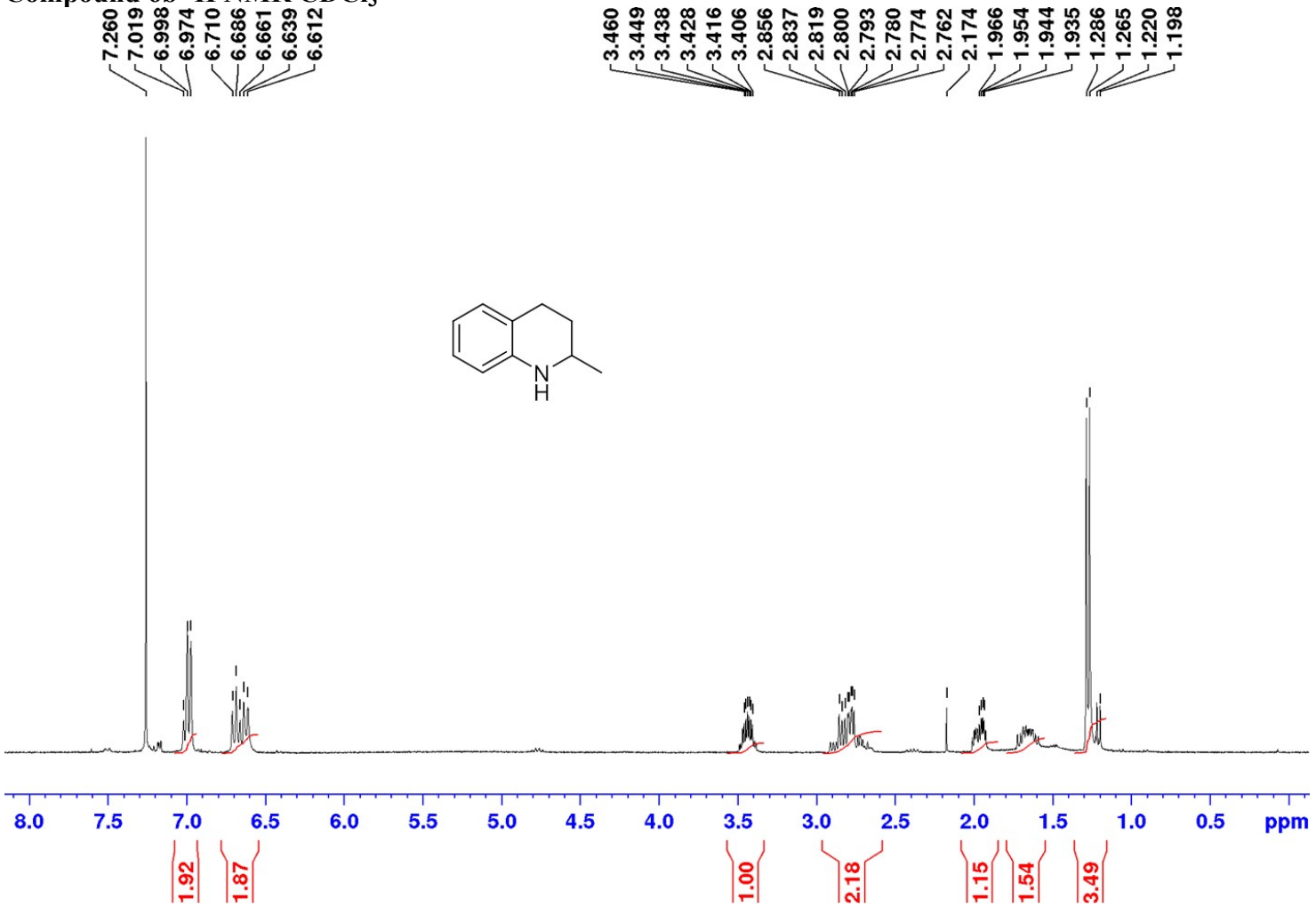

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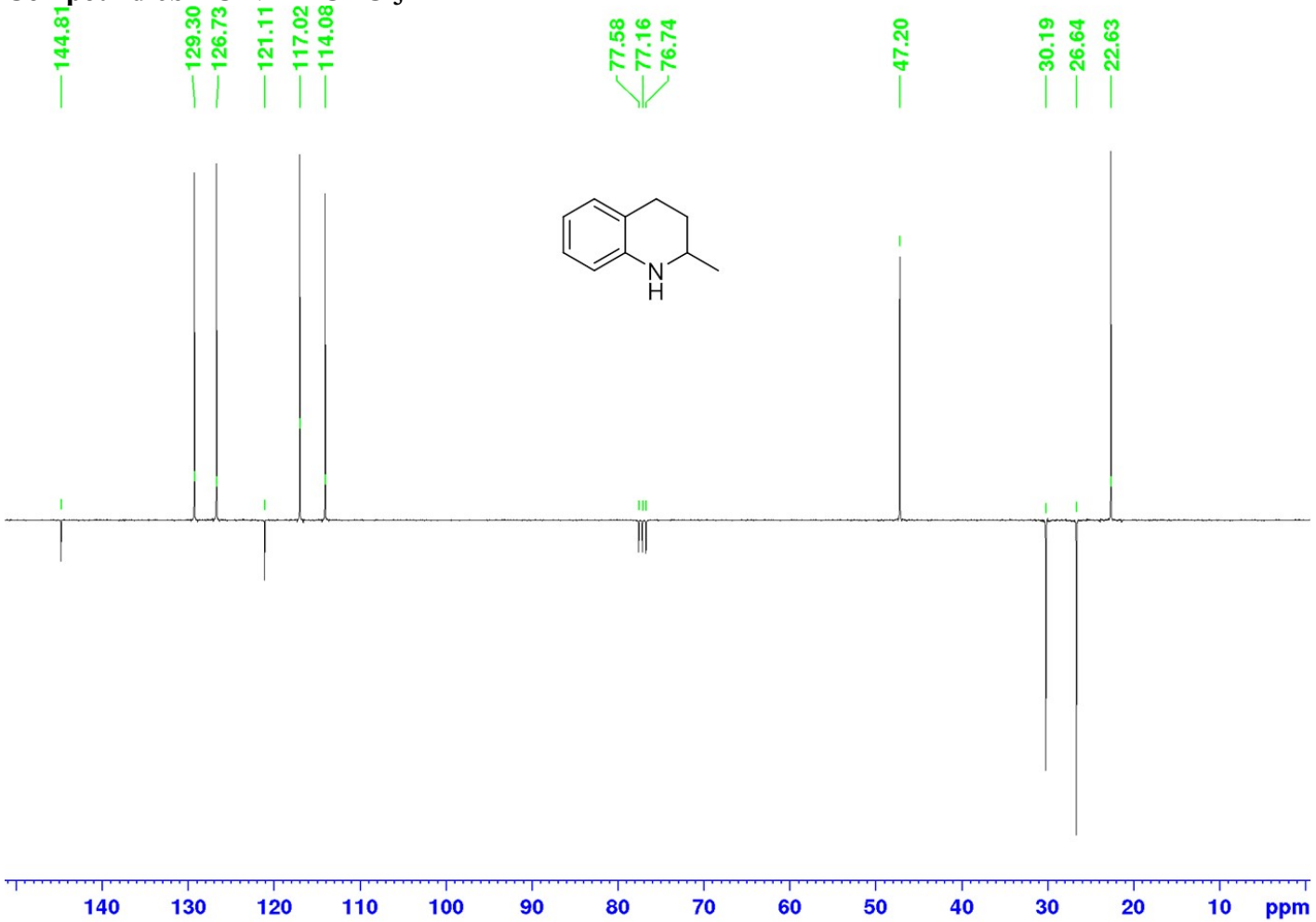
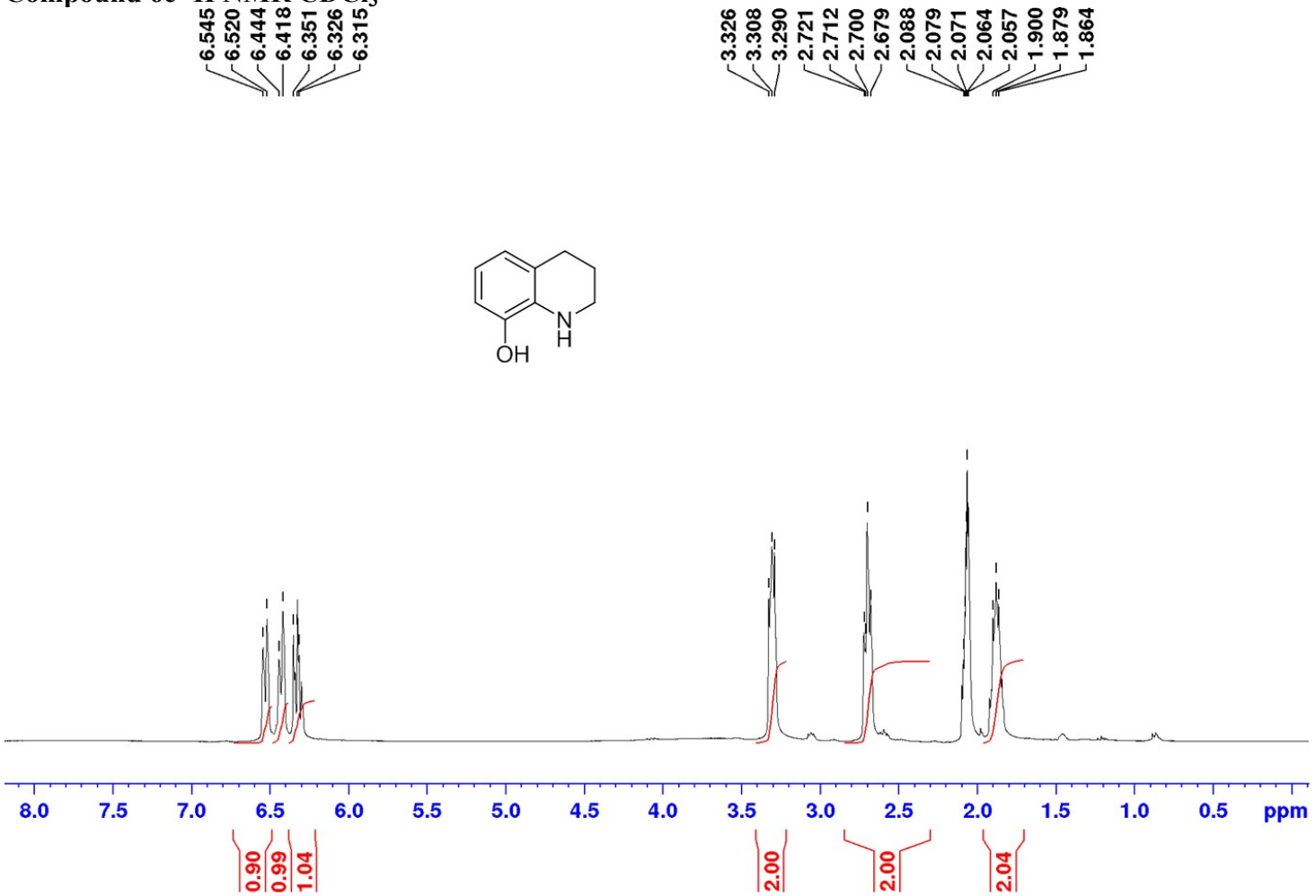


Compound 6c ^{1}H NMR $CDCl_3$



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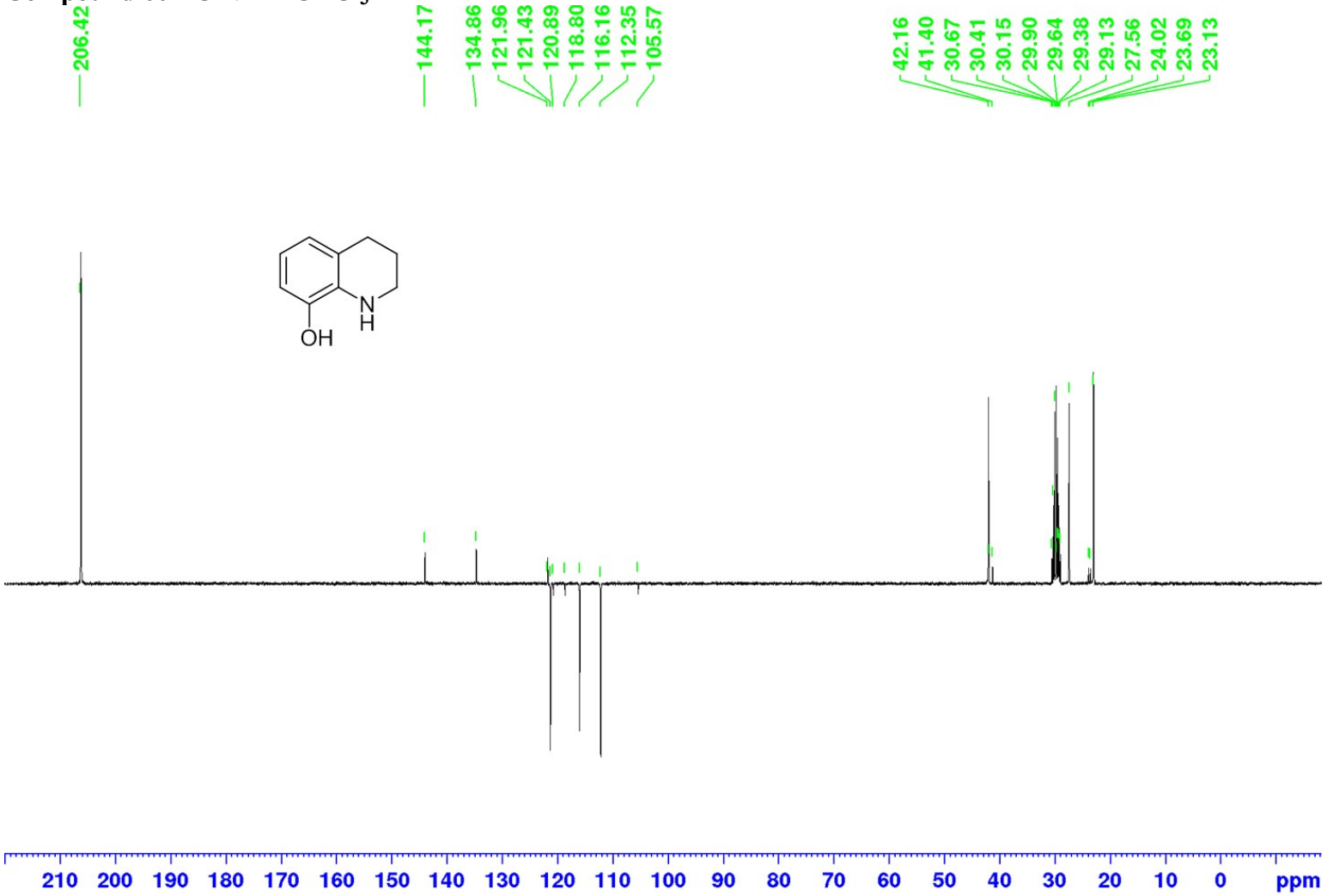

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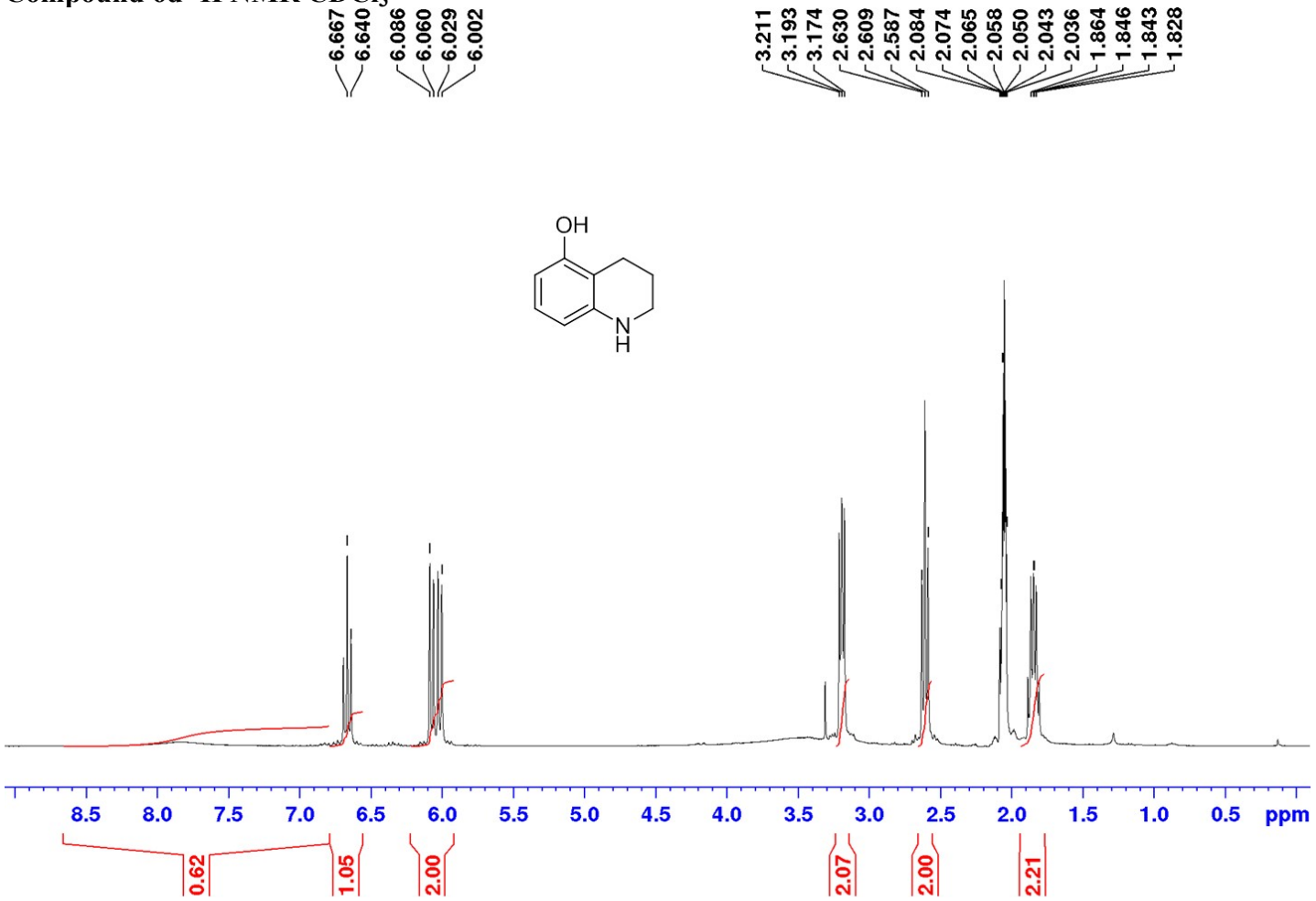
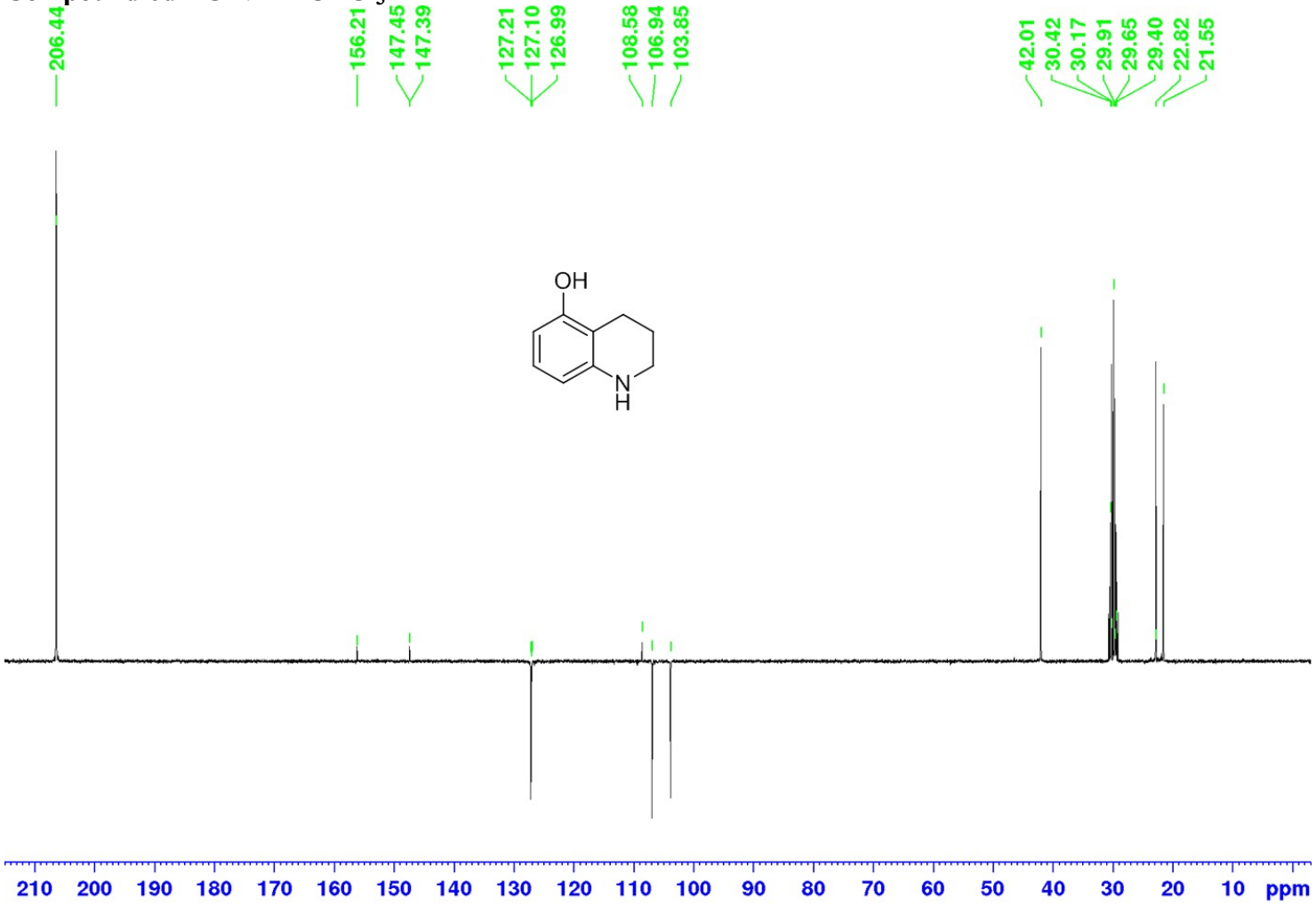
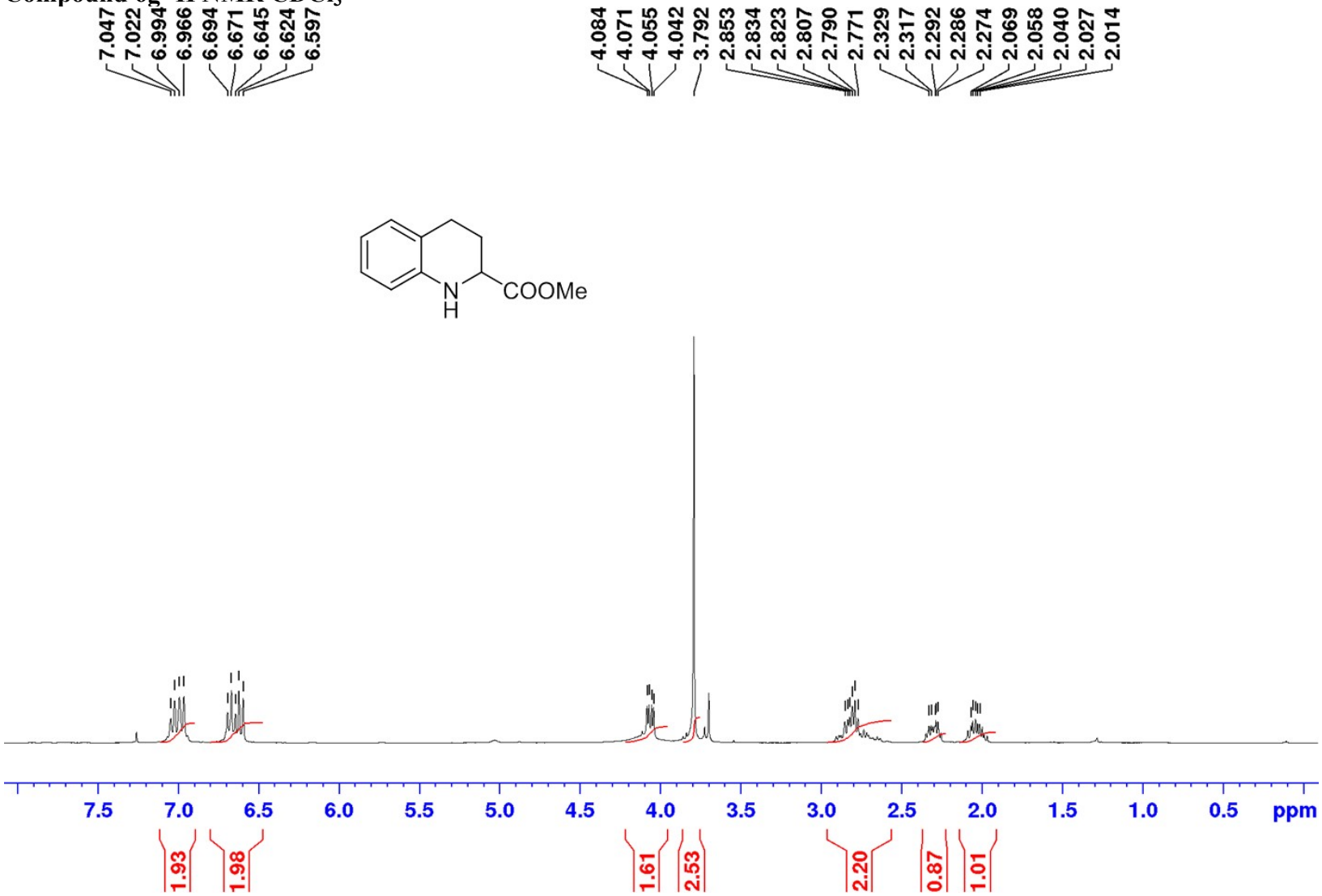


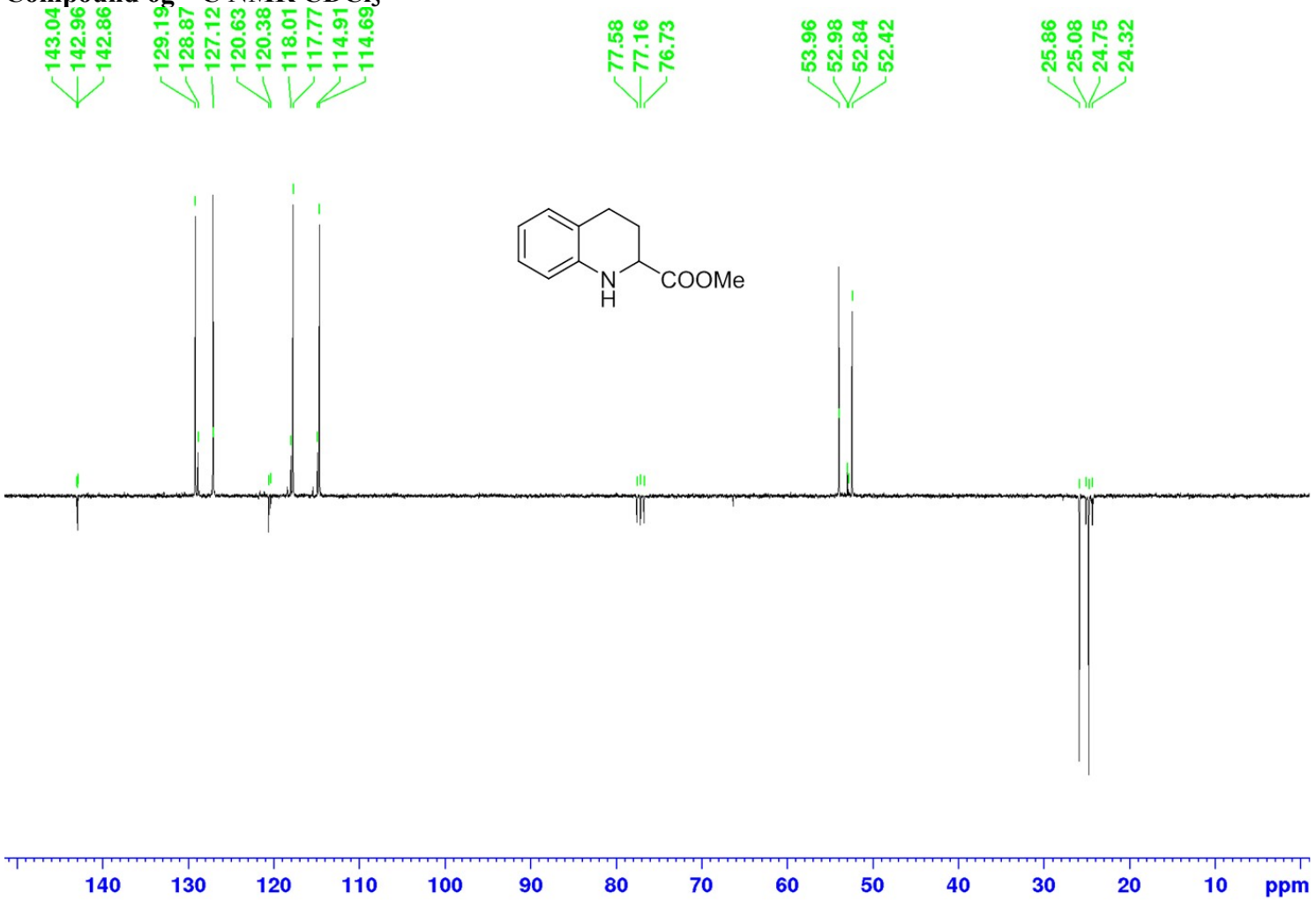
Compound 6d ^{13}C NMR $CDCl_3$



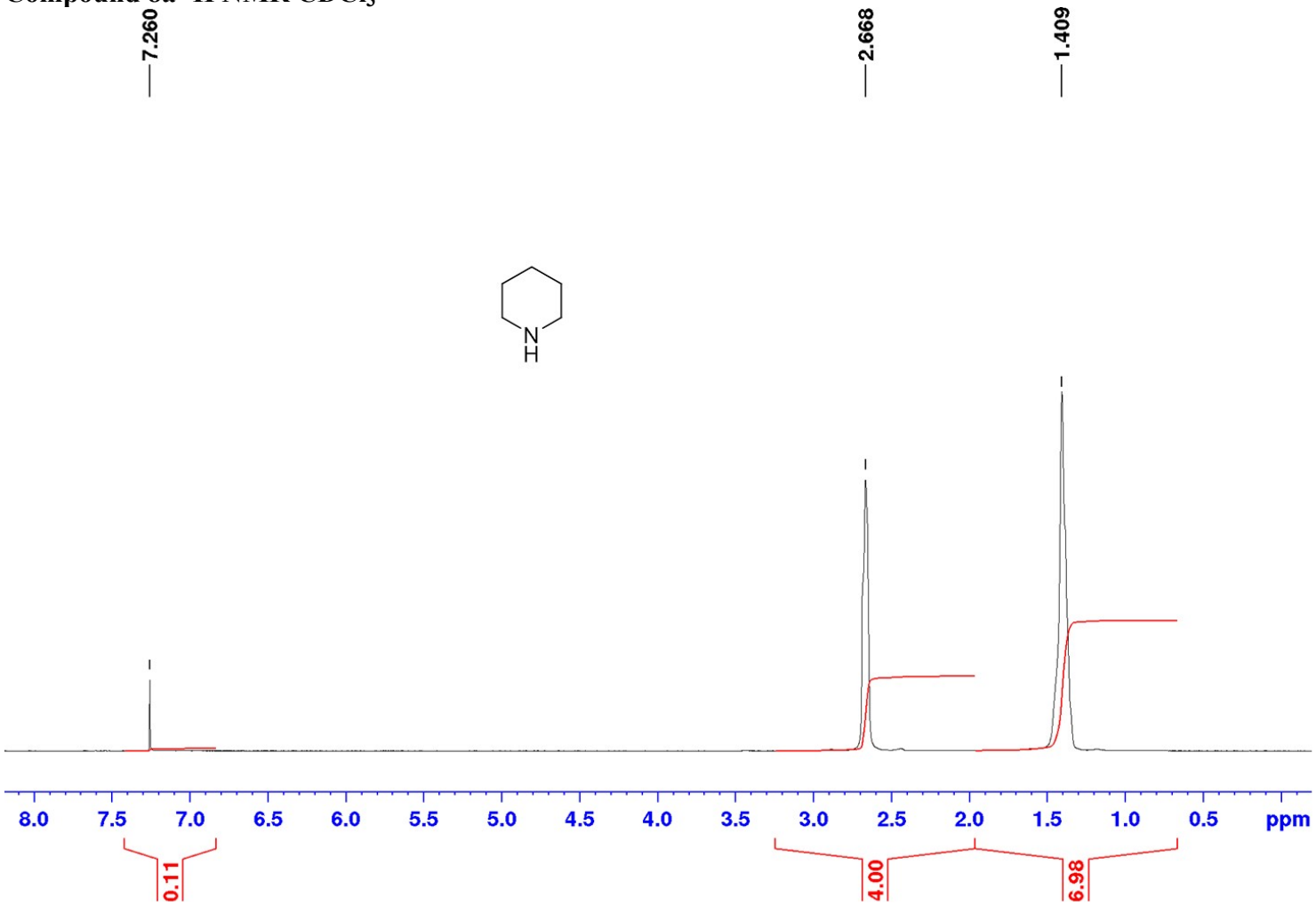
Compound 6g ^{1}H NMR $CDCl_3$



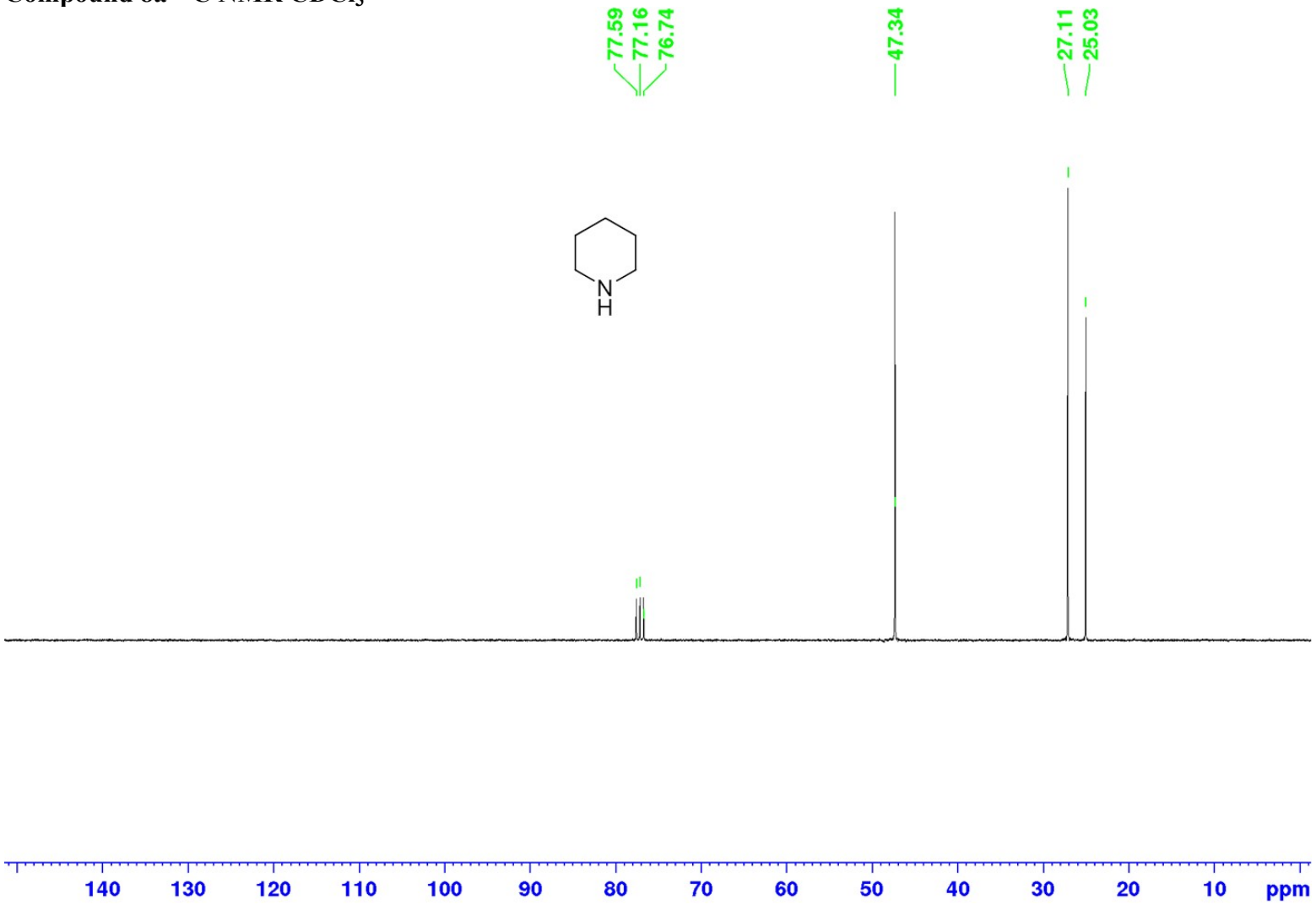
Compound 6g ^{13}C NMR $CDCl_3$



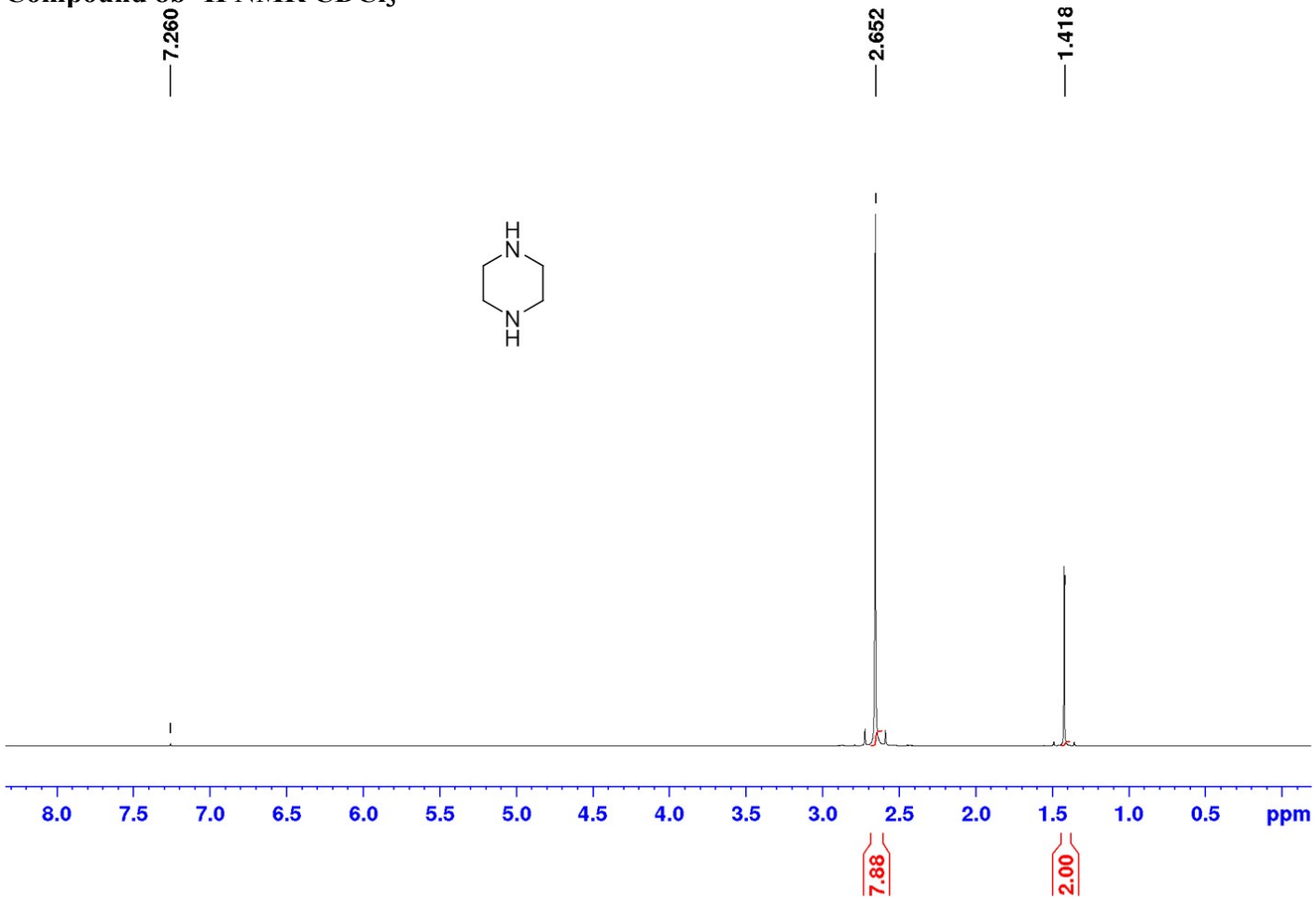
Compound 8a ^{1}H NMR $CDCl_3$



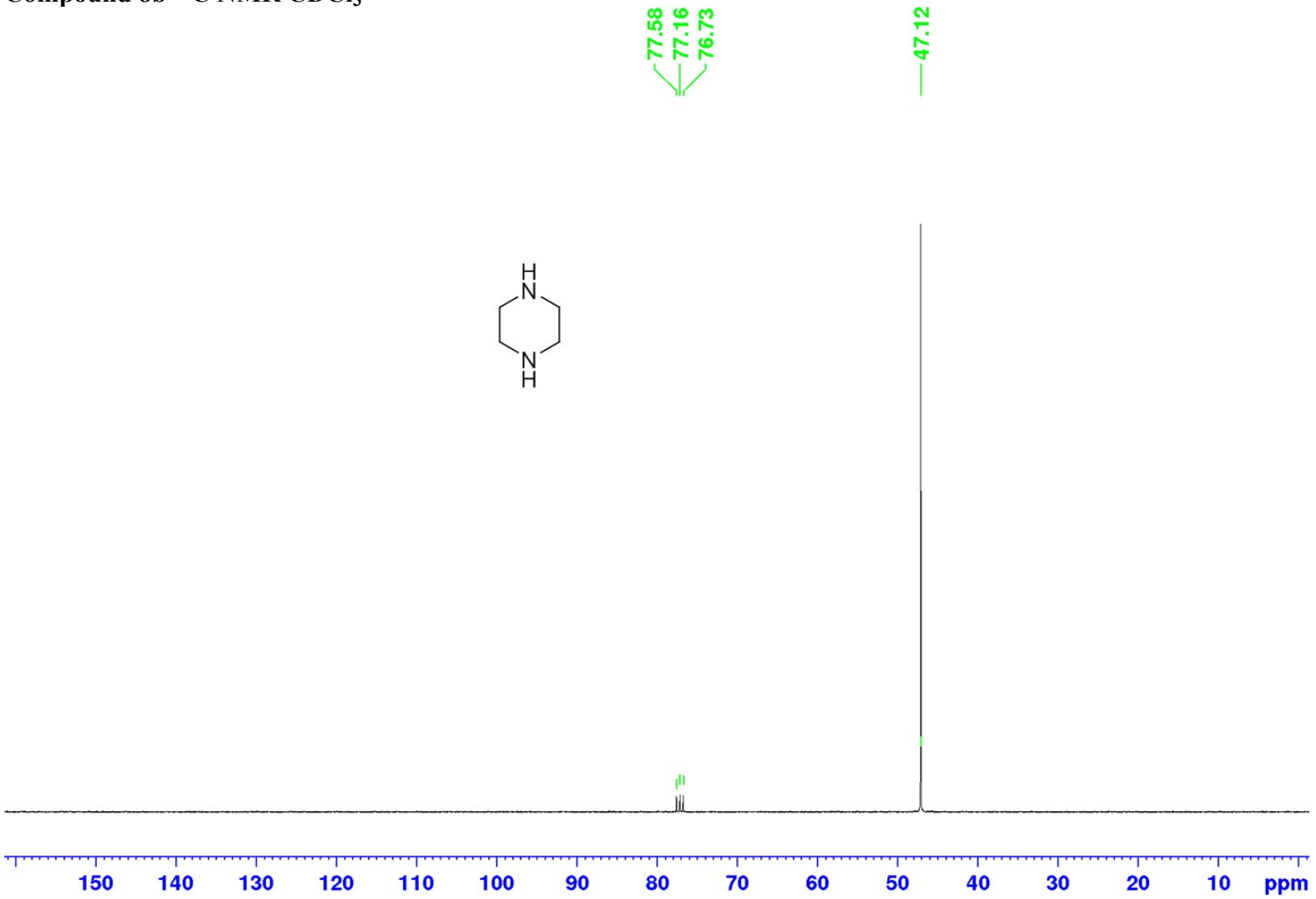
Compound 8a ^{13}C NMR $CDCl_3$



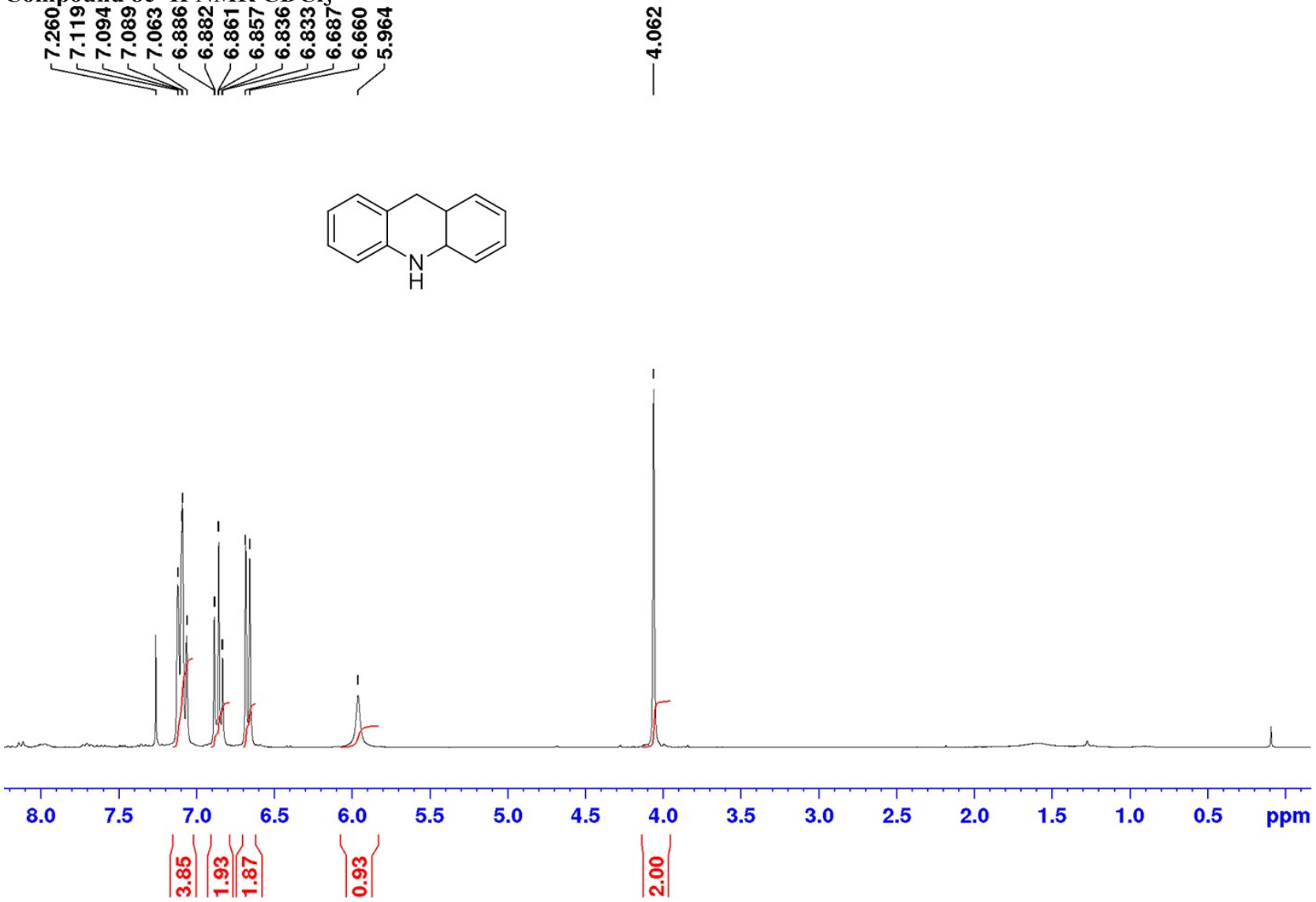
Compound 8b ^{1}H NMR $CDCl_3$



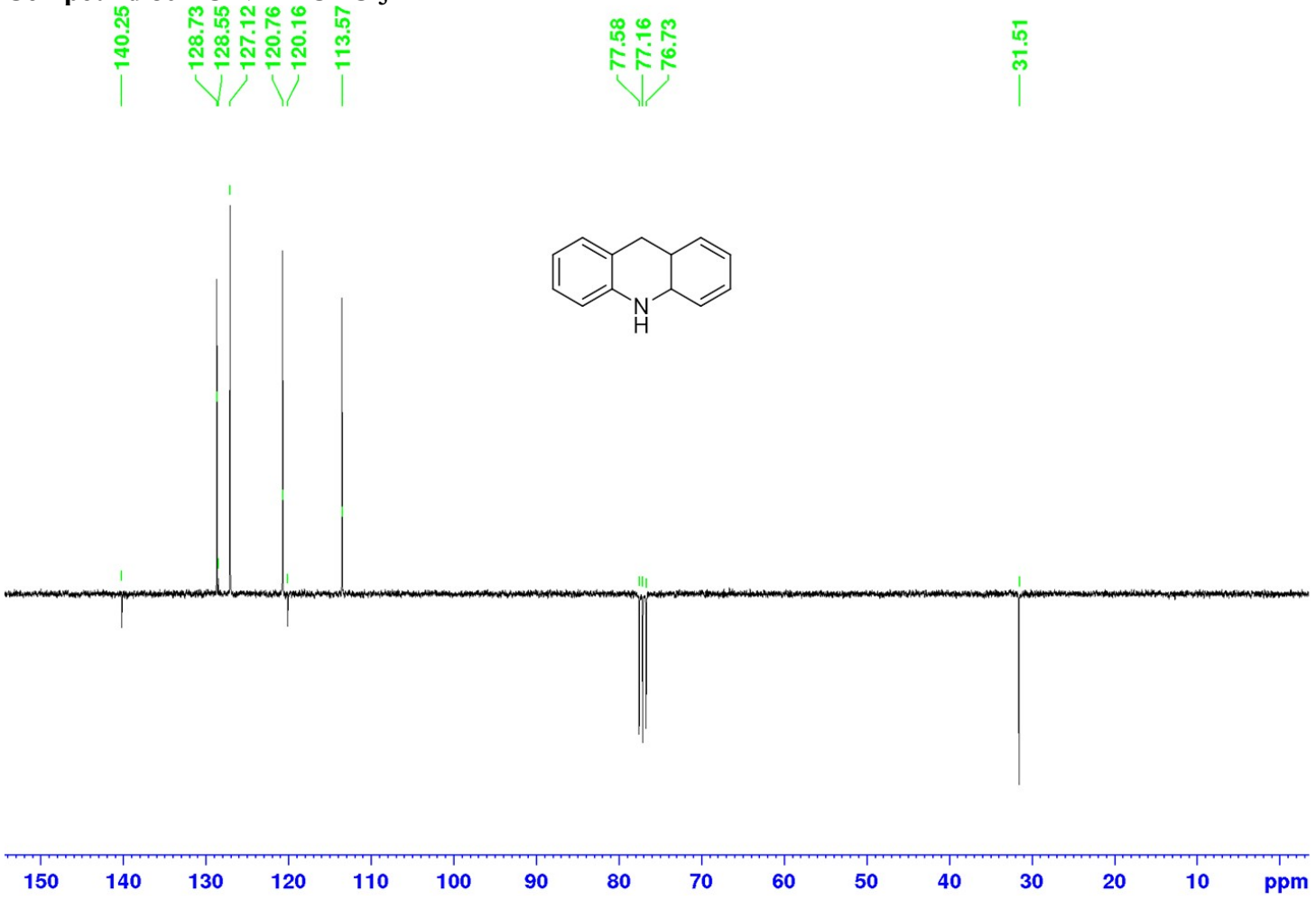
Compound 8b ^{13}C NMR $CDCl_3$



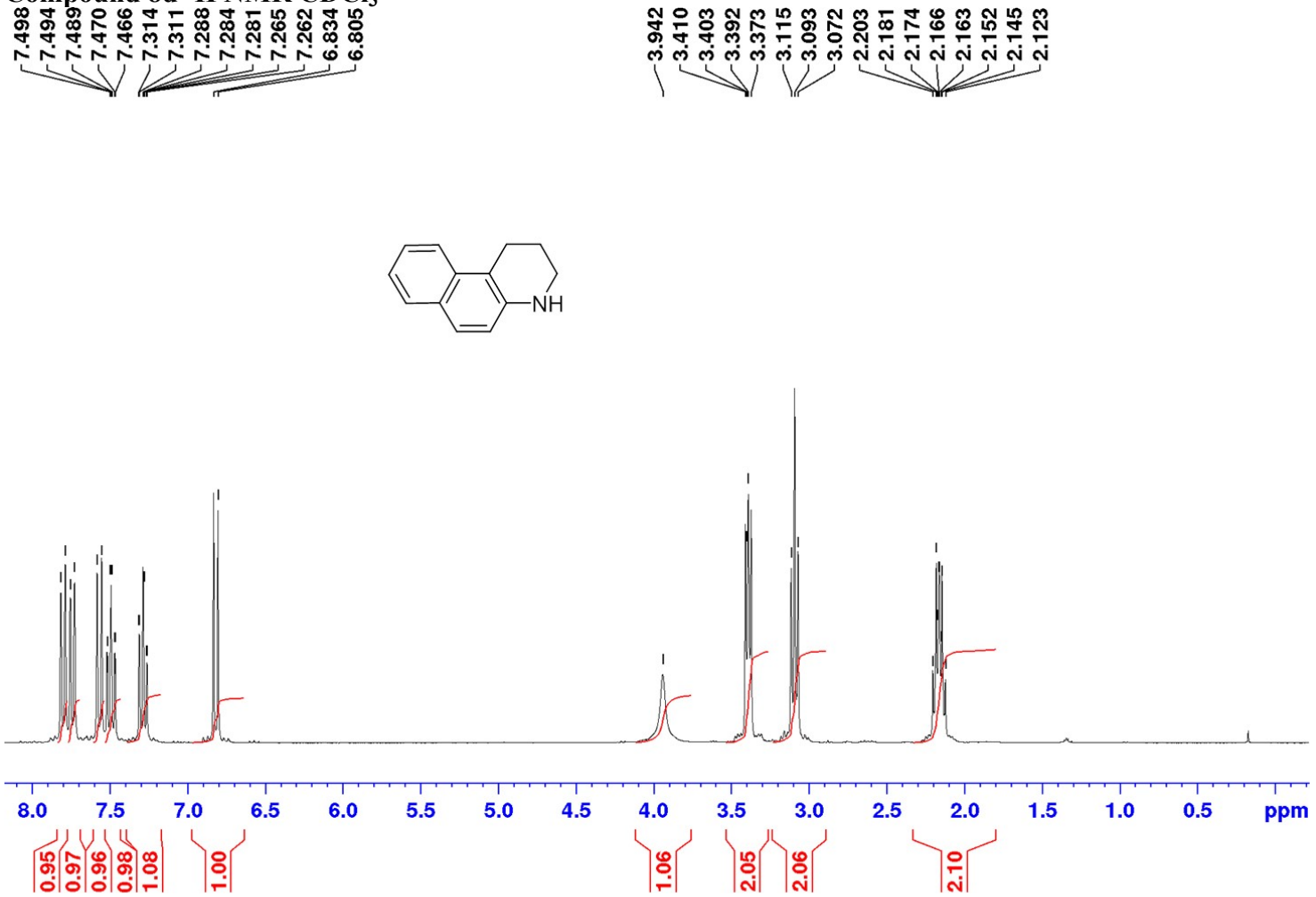
Compound 8c ^{1}H NMR $CDCl_3$



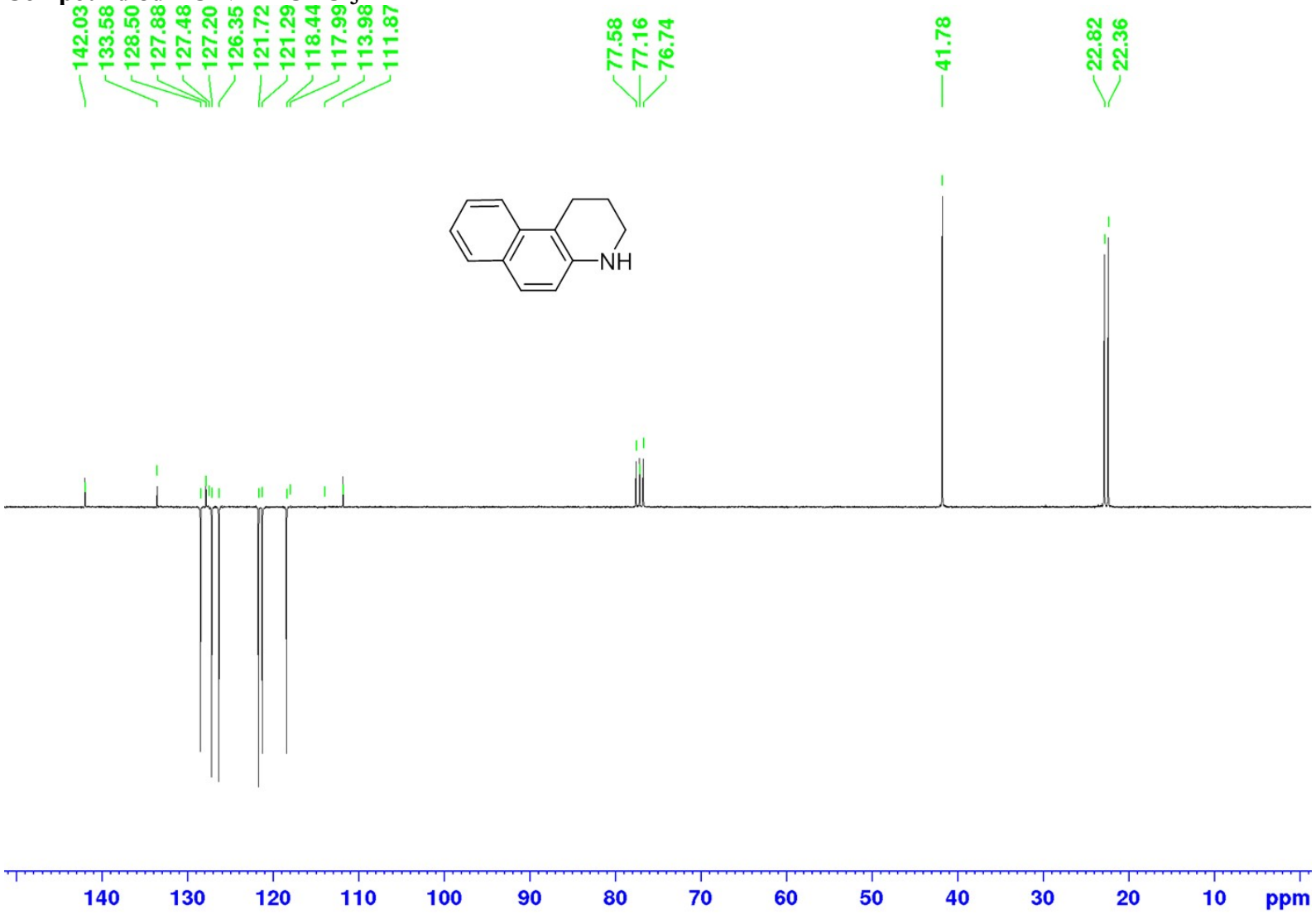
Compound 8c ^{13}C NMR $CDCl_3$



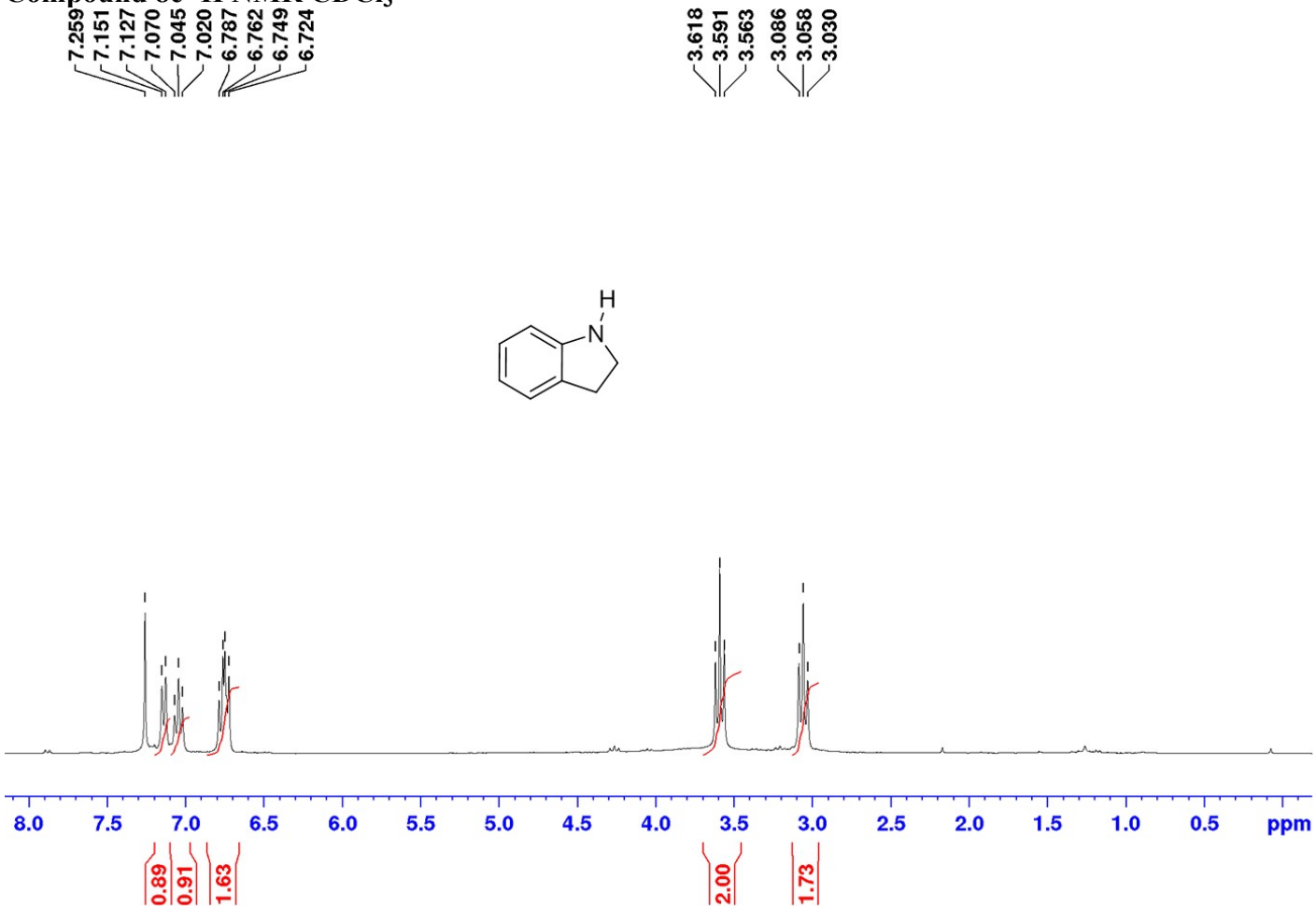
Compound 8d ^{1}H NMR $CDCl_3$



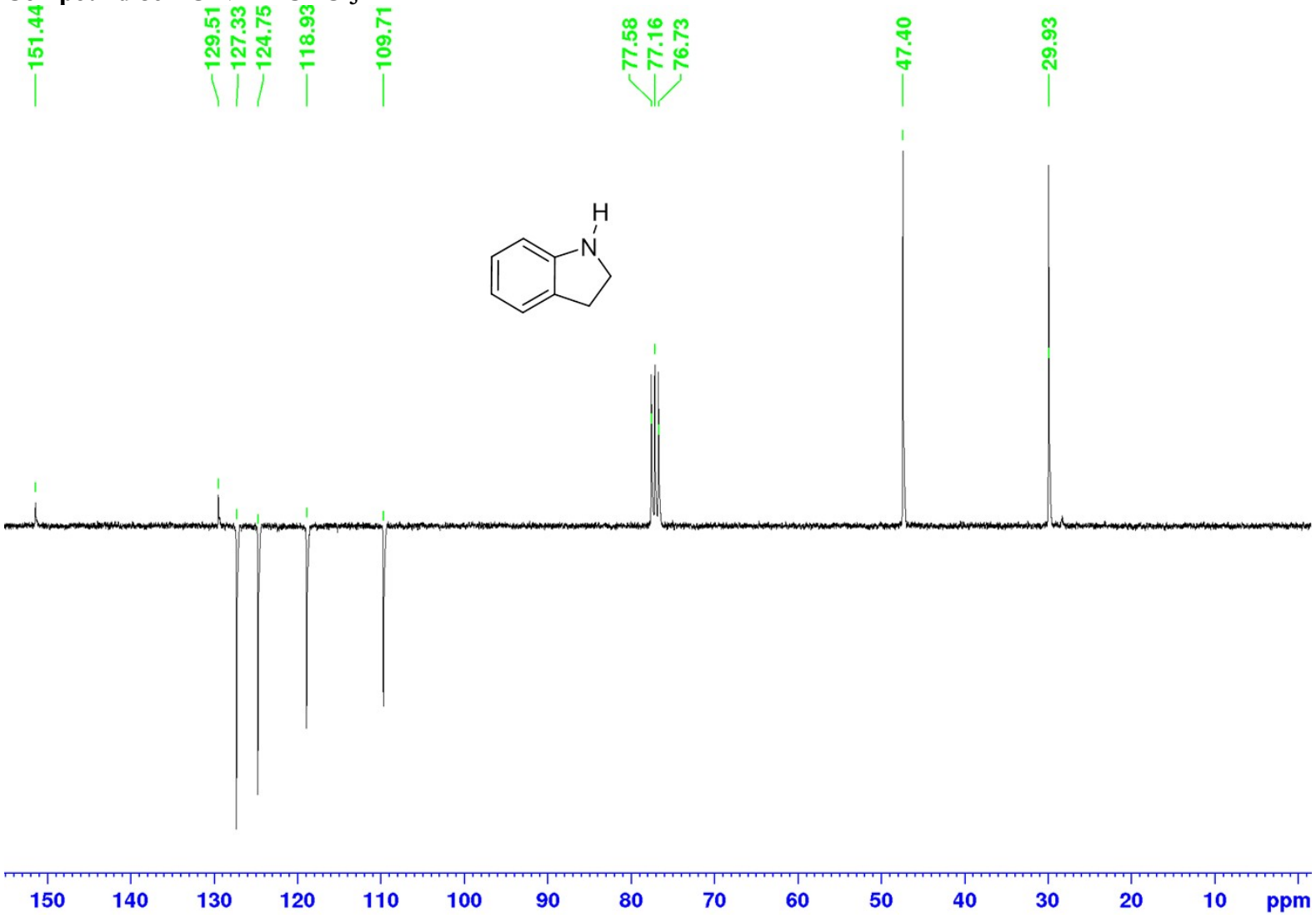
Compound 8d ^{13}C NMR $CDCl_3$



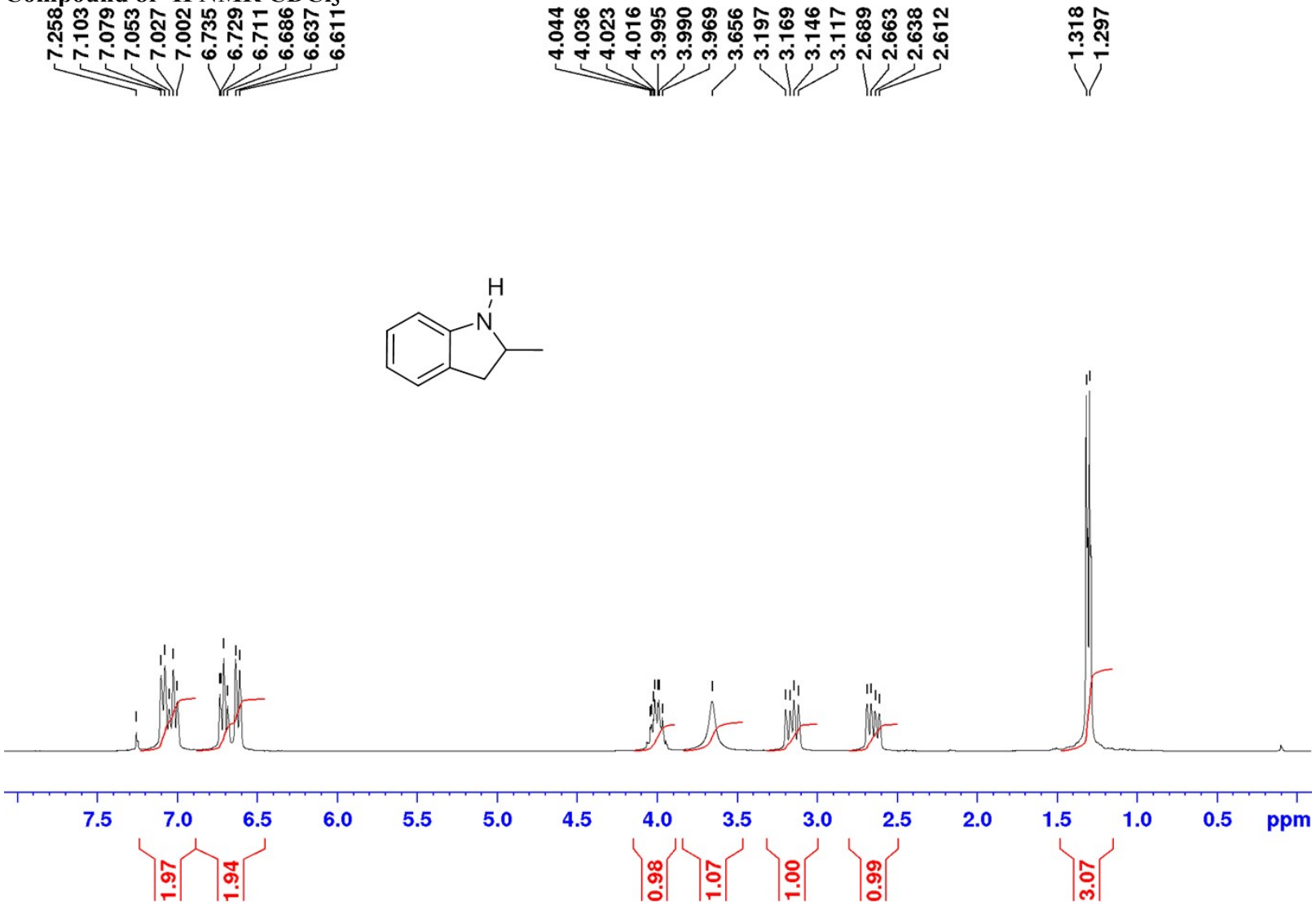
Compound 8e ^{1}H NMR $CDCl_3$



Compound 8e ^{13}C NMR $CDCl_3$



Compound 8f ^{1}H NMR $CDCl_3$



Compound 8f ^{13}C NMR $CDCl_3$