Electronic Supplementary Information

Electrostatically Tuned Phenols: A Scalable Catalyst for Room Temperature Hydrogenation and Tandem Reductive Alkylation

Brijesh Patel[a,b], Shilpa Dabas[a,b], Parth Patel[a,b] and Saravanan Subramanian[*a,b]

[a] Inorganic Materials and Catalysis Discipline, CSIR- Central salt and Marine Chemical Research institute, Bhavnagar – 364002 Gujarat, India.

[b] Academy of Scientific and Innovative Research(AcSIR), Gaziabad-201002, India

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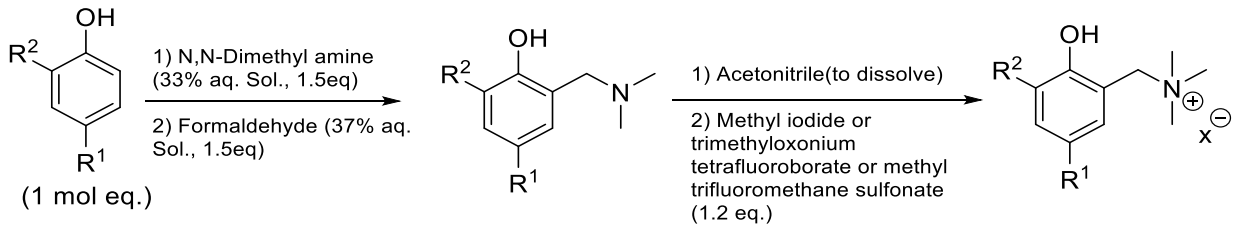
1. General Methods

Reagents and solvents were obtained from commercial sources and used as received. Air- and moisture-sensitive liquids were transferred via a syringe and a stainless-steel needle. Reactions were magnetically stirred and monitored by thin layer chromatography. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. For separation of products column chromatography was carried out using Finar 100-200 mess silica as stationary phase.

Nuclear magnetic resonance (NMR) spectra were acquired on a 500 MHz Bruker Avance III spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm and referenced to tetramethylsilane or residual solvent peaks as internal standards (for $CDCl_3$, tetramethylsilane) ppm for ^{1}H and $CDCl_3$ 77.16 ppm for ^{13}C; for DMSO-d6, 2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C. NMR data are reported as follows: chemical shifts, multiplicity (s, singlet; d, doublet; dd, doublet of doublet; t, triplet; td, triplet of doublet; q, quartet; m, multiplet; br, broad signal), coupling constants (Hz), and integration. The reduced products were identified with a gas chromatography (Bruker 450-GC; equipped with a capillary column HP-5, 30m × 0.25 mm) using a flame ionization detector.

2. General procedure for catalyst synthesis

General synthesis



Scheme S1: General scheme for synthesis of ETP catalysts

The phenol-alkylammonium salt was prepared by modifying the literature procedure.[1] Appropriate phenol (1 eq.) was taken in a round bottom flask and aqueous solutions of dimethylamine (1.5 equiv., 33%) and formaldehyde (1.5 eq. 37%) were added. The reaction

mixture was stirred overnight at room temperature. Then the reaction mixture is extracted by ethyl acetate / water workup. Subsequently, the solvent is evaporated under reduced pressure. The obtained crude product is dissolved in the acetonitrile and add the methyl iodide or trimethyloxonium tetrafluoroborate or methyltrifluoromethane sulfonate (1.5 eq.). Allow the reaction mixture to stir for 24 h at room temperature. The precipitated product was filtered and washed with diethyl ether to yield pure product of ETPs.

3. Gram scale synthesis of ETP-2 catalyst

Appropriate 2,4-*tert*-butylphenol (10 g) was taken in a round bottom flask and aqueous solutions of dimethylamine (1.5 eq. 33%) and formaldehyde (1.5 eq. 37%) were added. The reaction mixture was stirred overnight at room temperature. Then the reaction mixture is extracted by ethyl acetate / water workup. Subsequently, the solvent is evaporated under reduced pressure. The obtained crude product is dissolved in the acetonitrile and add the methyl iodide (1.5 eq.). Allow the reaction mixture to stir for 24 h at room temperature. The precipitated product was filtered and washed with diethyl ether to yield pure product of ETP-2. Yield: 15.8 gm (80.42%)

Fig. S1: Gram scale synthesised ETP-2

4. Cost estimation of catalyst

The ETP catalyst was synthesized from the commercially available and relatively cheap starting materials. Thus, we are intended to estimate the total cost involved in the process of making catalyst.

The details are summarized as follows and by the calculation we found ETP-2 cost ~$ 0.73/g and ETP-6 cost ~$ 3.3/g.

2,4-*tert*-Butylphenol 99% (Sigma Aldrich)- $48.80/500gm

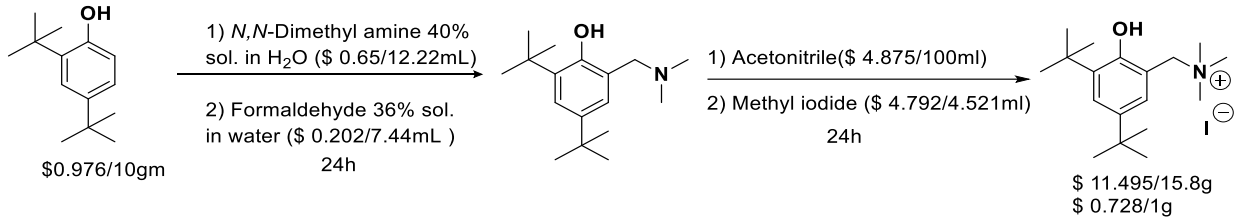
Dimethylamine solution 40 wt. % in H2O (Sigma Aldrich): - $107.00/2L

Formaldehyde Solution 36% Supelco (Millipore Sigma) - $543.00/20 L

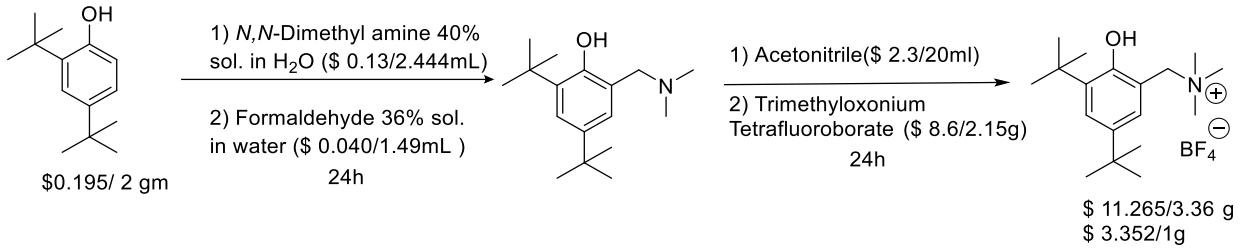
Acetonitrile, ACS, 99.5+ %, Thermo Scientific- $195/4L

Iodomethane purum, ≥99.0% (GC) (Sigma Aldrich)- $530/500 ml

Trimethyloxonium Tetrafluoroborate >95.0% (TCI chemicals)- $100/25 g

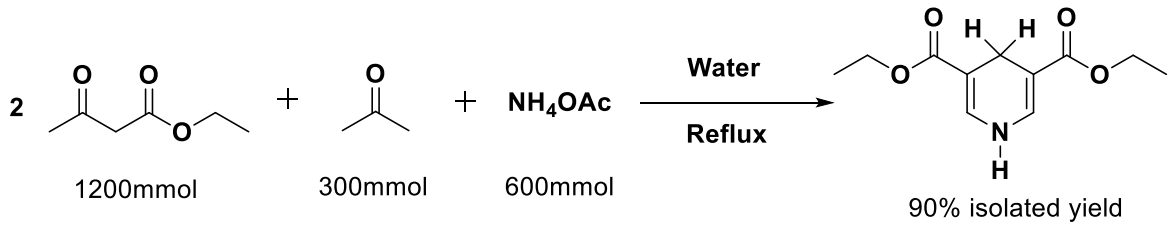


Scheme S2: Cost estimate of ETP-2



Scheme S3: Cost estimate of ETP-6

5. Synthesis of Hantzsch ester

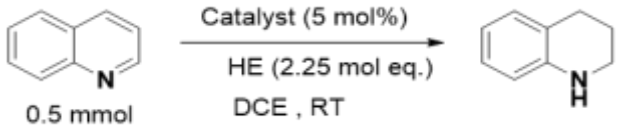


Scheme S4: Synthesis of Hantzsch ester

Ethyl Hantzsch ester (HEH) was synthesized according to the literature procedure.[2] Briefly, paraformaldehyde (300 mmol), ethyl acetoacetate (1200 mmol), and ammonium acetate (600 mmol) were mixed in 500 mL of water. The reaction was stirred at refluxing temperature for 2 h. The reaction was monitored for completion and then cooled to room temperature. The product was filtrated and washed with 30 mL of water (twice). The obtained yellow solid product was dried and used without further purification (yield: 90%).

6. General procedure for transfer hydrogenation reaction

At Room Temperature

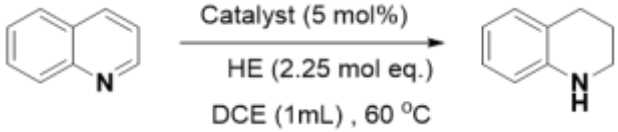


Scheme S5: General procedure for transfer hydrogenation reaction at RT

In a pyrex tube (15 mL), substituted quinoline (0.5 mmol), Hantzsch ester (2.5 equiv.), ETP catalyst (5 mol%) and solvent (1 mL) were charged. The reaction tube was closed immediately and allowed to stir at room temperature. The reaction was monitored for completion by TLC in *n*-hexane and ethyl acetate as eluent. After completion of the reaction, the crude compound was purified by column chromatography on silica gel to obtain pure compound.

Note: 1,2,3,4-THQ's are highly iodine active and easily identified in a reaction mixture.

At 60°C



Scheme S6: General procedure for transfer hydrogenation reaction at 60°C

In a pyrex tube (15 mL), substituted quinoline (0.5 mmol), Hantzsch ester (2.5 equiv.), ETP catalyst (5 mol%) and solvent (1 mL) were charged. The reaction tube was closed immediately and placed in a preheated oil bath (60 °C) with continuous stirring. The reaction was monitored

for completion by TLC in *n*-hexane and ethyl acetate as mobile phase eluent. After completion of the reaction, the crude compound was purified by column chromatography on silica gel to yield pure compound.

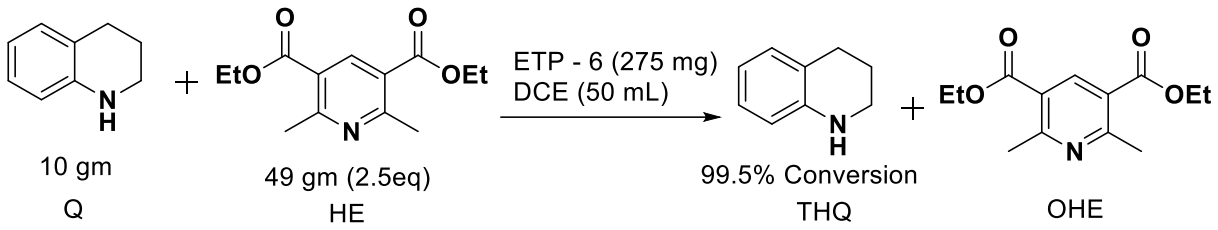
7. Multigram scale synthesis of 1,2,3,4-tetrahydroquinoline

In a 250 mL round bottom flask, quinoline (10 g, 77.4 mmol), Hantzsch ester (49 g, 387 mmol, 2.5 equiv.), catalyst ETP-6 (1 mol%, 0.774 mmol, 275 mg) and solvent (50 mL) were charged. The reaction mixture was closed immediately and placed in a preheated oil bath (60 ^{o}C) with continuous stirring. The reaction was monitored by TLC for its completion using n-hexane and ethyl acetate as solvent system. The reaction gets completed at 8 h and resulted the conversion of THQ in 99.5%. After the completion of reaction the solvent was removed (~90%) under reduced pressure leaving behind the crude reaction mixture in minimum amount of solvent and proceeded further in the following ways.

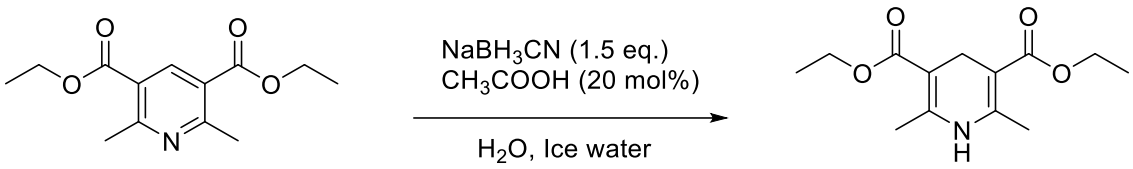
In step 1, diethyl ether (2 x 100 mL) was added to the crude reaction mixture to precipitate out the catalyst. The catalyst was filtered and dried at 60 ^{o}C using air oven. The filtrate containing diethyl ether and minimum amount of reaction solvent was allowed to remove completely under reduced pressure.

In step 2, to the obtained residual solid, water was added (5 x 20 mL) and subsequently filtered off slowly under vacuum condition. The recovered OHE (off-white residue) was treated in step 2' using the below regeneration procedure (mentioned in ESI -8).

On the other hand, the aqueous filtrate contains the product (THQ) and residual OHE (~5-8%). The step 3 involves the removal of the left over OHE from the product, KOH (10 g) was added and allowed to stir for 15 minutes, this base treatment process allows the conversion of OHE into the water soluble potassium salt of hydrolysed HE.[3] Furthermore, upon the addition of dichloromethane (3 x 100 mL) will extract the product from the aqueous layer. The organic layer was collected and added anhydrous sodium sulphate. Upon filtration followed by the removal of organic solvent under reduced pressure results the desired THQ with 81% yield. The product was treated with charcoal and obtained the final yield as 78%.



8. Procedure for the regeneration of Hantzsch-1,4-dihydropyridine (HE)



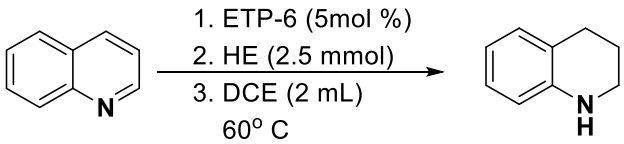
Scheme S5: Process for the regeneration of HE

The OHE and unutilized HE obtained in step 2 (as shown in figure 6) was used as such for the regeneration of HE by adopting the literature procedure.[4] In a 500 mL round bottom flask, the solid residue obtained in the step 2 (46.86 g, 0.184 mol), water (200 mL) and acetic acid (2.5 mL, 20 mol%) were charged and placed in an ice bath. To the reaction mixture $NaBH_3CN$ (13.91 gm, 1.2 mol. eq.) was slowly added and allowed to stir for 24 h. The reaction was monitored by TLC for its completion using hexane and ethyl acetate as solvent system. Once the reaction gets complete, the obtained solid precipitate was filtered, washed thoroughly with water and ice-cold acetone. The obtained yellow powder was dried using vacuum desiccator. Isolated yield: 45.20 g, 92%.

9. General procedure for reductive alkylation

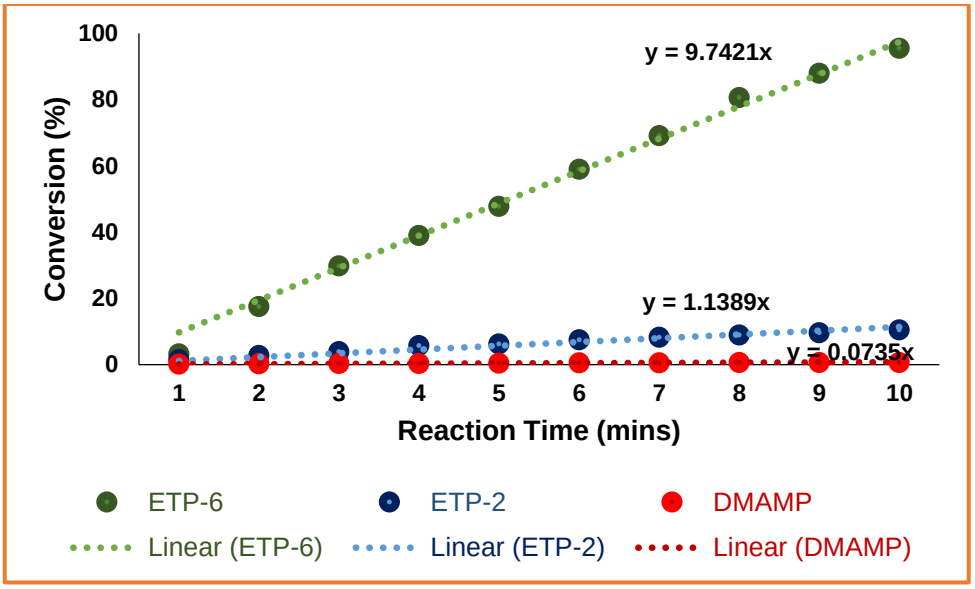
In a reaction tube (15 mL), quinoline (0.5 mmol), substituted aldehyde (0.5 mmol), Hantzsch ester (1.75 mmol), ETP-6 (5 mol%) and DCE (2 mL) were taken. Then the reaction tube was properly closed and placed in a preheated oil bath at 60 ^{o}C for 3 h with continuous stirring. The reaction was monitored by TLC using petroleum ether and ethyl acetate as solvent system. After completion of the reaction, the reaction tube was brought to room temperature and the crude compound was purified through silica gel column chromatography.

10. Percentage recovery of HE and its corresponding reusability



No. of Cycle	Quinoline (concentration)	HE used (mg)	Conversion of Quinoline (%)	HE Recovered (mg)	HE Recovered (%)
1	64.58 mg (59.08 µL)	317.5 mg	99.50	287.9 mg	90.67
2	58.55 mg (53.57 µL)	287.9 mg	99.08	255.23 mg	88.65
3	51.91 mg (47.50 µL)	255.23 mg	98.46	217.49 mg	85.21
4	44.23 mg (40.47 µL)	217.49 mg	95.85	179.02 mg	82.31

11. Kinetics profile of the transfer hydrogenation of quinoline[a]



[a]Normalized rate constant (k_{rel}) relative to DMAMP (uncharged system) as standard

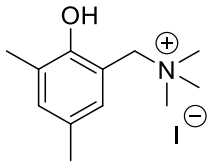
Fig. S2: Kinetic profile of ETP catalyst

Table S1: Relative rate constant for selected catalyst[5]

Catalyst	Time (min.)	Yield (%)	Slope = $(\Delta y/\Delta x)$	K_{rel}
DMAMP	10	0.634	0.0735	1
ETP-2	10	10.483	1.1389	15.495
ETP-6	10	95.521	9.7421	132.55

12. Characterization data of catalysts

1. 1-(2-hydroxy-3,5-dimethylphenyl)-*N*,*N*,*N*-trimethylmethanaminium iodide (ETP-1)

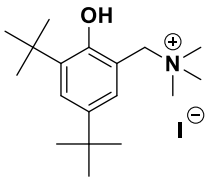


Yield : 48%

^{1}H NMR (500 MHz, DMSO) δ 8.73 (s, 1H), 7.12 (s, 3H), 4.38 (s, 3H), 3.13 (s, 6H), 2.19 (s, 9H).

^{13}C NMR (126 MHz, CDCl3) δ 154.30, 132.41, 123.82, 117.48, 66.16, 53.78, 53.74, 46.98, 15.96.

2. 1-(2-hydroxy-3,5-dimethylphenyl)-N,N,N-trimethylmethanaminium iodide (ETP-2)

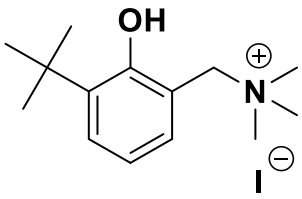


Yield : 85%

^{1}H NMR (500 MHz, DMSO) δ 8.66 (s, 1H), 7.39 (s, 1H), 7.32 (s, 1H), 4.68 (s, 2H), 3.12 (s, 6H), 2.76 (s, 3H), 1.40 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (500 MHz, DMSO) δ 153.23, 142.06, 138.82, 129.55, 125.90, 116.86, 63.40, 54.39, 48.06, 34.83, 33.99, 31.28, 29.79.

3. 1-(3-(tert-butyl)-2-hydroxyphenyl)-*N*,*N*,*N*-trimethylmethanaminium iodide (ETP-3)

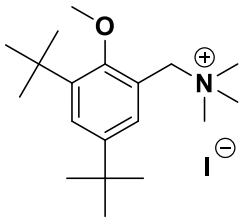


Yield : 78%

^{1}H NMR (500 MHz, DMSO) δ 8.96 (s, 1H), 7.39 (d, *J* = 9.7 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 4.64 (s, 2H), 3.02 (s, 9H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 155.66, 139.25, 132.46, 129.29, 120.22, 116.85, 63.47, 54.51, 51.86, 34.71, 29.66

4. 1-(3,5-di-tert-butyl-2-methoxyphenyl)-*N,N,N*-trimethylmethanaminium iodide (ETP-4)

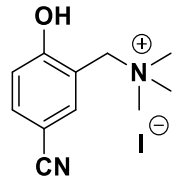


Yield : 46%

^{1}H NMR (500 MHz, DMSO) δ 7.48 (d, *J* = 2.6 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 4.51 (s, 2H), 3.78 (s, 3H), 2.97 (s, 9H), 1.38 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 140.02, 136.23, 88.29, 73.70, 61.41, 44.50, 43.74, 9.61

5. 1-(5-cyano-2-hydroxyphenyl)-*N,N,N*-trimethylmethanaminium iodide (ETP-5)

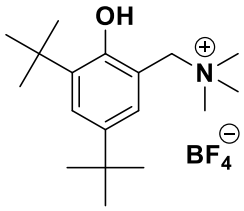


Yield: 89%

^{1}H NMR (500 MHz, DMSO) δ 11.59 (s, 1H), 7.91 (d, J = 2.2 Hz, 1H), 7.82 (dd, J = 8.5, 2.1 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 4.48 (s, 2H), 3.06 (s, 9H).

^{13}C NMR (126 MHz, DMSO) δ 161.57, 139.22, 136.09, 118.92, 117.29, 116.31, 101.54, 61.93, 52.28.

6. 1-(2-hydroxy-3,5-dimethylphenyl)-*N,N,N*-trimethylmethanaminium tetrafluoroborate (ETP-6)

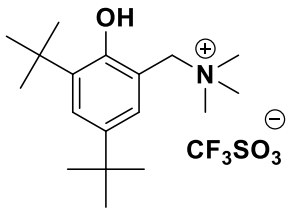


Yield: 87%

^{1}H NMR (500 MHz, CD_3CN) δ 7.72 (d, *J* = 2.5 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 6.51 (s, 1H), 4.51 (d, *J* = 5.7 Hz, 2H), 3.04 (d, *J* = 5.1 Hz, 6H), 2.36 (s, 3H), 1.68 (s, 9H), 1.56 (s, 9H).

^{13}C NMR (500 MHz, CD_3CN) δ 151.87, 145.21, 139.23, 127.86, 127.11, 120.16, 59.26, 43.52, 35.23, 34.97, 31.66, 31.50, 30.80, 30.16, 29.65.

7. 1-(3,5-di-tert-butyl-2-hydroxyphenyl)-*N,N,N*-trimethylmethanaminium trifluoromethanesulfonate (ETP-7)

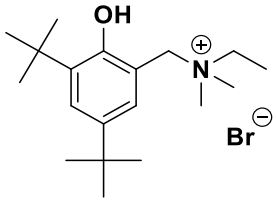


Yield : 83%

^{1}H NMR (500 MHz, CD_3CN) δ 7.50 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 6.50 (s, 1H), 4.46 (s, 2H), 2.99 (s, 9H), 1.41 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.33, 144.66, 139.91, 130.13, 127.96, 65.85, 53.49, 53.45, 53.42, 35.55, 34.99, 31.56, 30.21.

8. *N*-(3,5-di-tert-butyl-2-hydroxybenzyl)-*N,N*-dimethylethanaminium bromide (ETP-8)

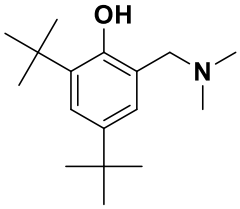


Yield : 24%

^{1}H NMR (500 MHz, DMSO) δ 8.69 (s, 1H), 7.39 (d, J = 2.6 Hz, 1H), 7.32 (d, J = 2.6 Hz, 1H), 4.72 (s, 2H), 3.31 (q, J = 7.3 Hz, 2H), 2.96 (s, 3H), 2.76 (s, 3H), 1.39 (s, 9H), 1.28 (s, 9H), 1.25 – 1.19 (t, 3H).

^{13}C NMR (126 MHz, DMSO) δ 153.33, 142.07, 138.84, 129.62, 125.94, 116.89, 63.45, 57.89, 48.90, 48.02, 34.88, 34.03, 31.33, 29.82, 7.79.

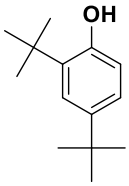
9. 2,4-di-tert-butyl-6-((dimethylamino)methyl)phenol (DMAMP)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 2.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 3.60 (s, 2H), 2.31 (s, 6H), 1.42 (s, 9H), 1.28 (s, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.61, 140.41, 135.51, 123.24, 122.91, 121.44, 63.74, 44.45, 34.97, 34.26, 31.84, 29.74

10. 2,4-di-tert-butylphenol (DTBP)

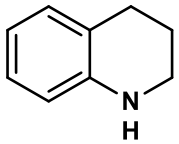


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 4.61 (s, 1H), 1.42 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (500 MHz, DMSO) δ 151.89, 143.12, 135.31, 124.24, 123.68, 116.06, 34.87, 34.42, 31.77, 29.81.

13. Characterization data of tetrahydroquinoline products

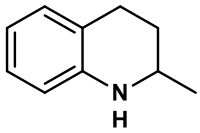
1. 1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 – 6.87 (m, 2H), 6.59 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.50 – 6.40 (m, 1H), 3.77 (s, 1H), 3.38 – 3.16 (m, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 1.91 (dt, *J* = 7.0, 3.5 Hz, 2H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 144.86, 129.58, 126.78, 121.48, 116.98, 114.25, 42.05, 27.05, 22.25.

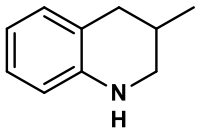
2. 2-methyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (t, *J* = 6.6 Hz, 2H), 6.60 (t, *J* = 7.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.39 (ddp, *J* = 15.3, 6.3, 3.1 Hz, 1H), 2.83 (ddd, *J* = 17.3, 11.6, 5.7 Hz, 1H), 2.72 (ddd, *J* = 16.4, 5.3, 3.4 Hz, 1H), 1.92 (ddt, *J* = 12.4, 6.0, 3.2 Hz, 1H), 1.58 (dddd, *J* = 12.8, 11.5, 9.9, 5.3 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (500 MHz, MeOD) δ 147.66, 132.16, 129.58, 123.99, 119.86, 116.89, 80.18, 79.92, 79.67, 50.04, 33.02, 29.49, 25.50.

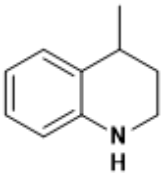
3. 3-methyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 14.6, 7.8 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 3.61 (s, 1H), 3.25 (ddd, *J* = 10.9, 3.7, 2.0 Hz, 1H), 2.97 – 2.83 (m, 1H), 2.77 (dd, *J* = 15.2, 3.8 Hz, 1H), 2.42 (dd, *J* = 15.9, 10.3 Hz, 1H), 2.05 (ddddd, *J* = 11.5, 10.2, 8.5, 4.3, 1.9 Hz, 1H), 1.04 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 144.40, 129.64, 126.81, 121.23, 117.04, 113.98, 48.96, 35.58, 27.30, 19.16.

4. 3-methyl-1,2,3,4-tetrahydroquinoline

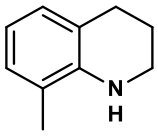


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.01 – 6.92 (m, 1H), 6.63 (td, *J* = 7.4, 1.3 Hz, 1H), 6.47 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.40 – 3.18 (m, 2H), 2.91 (d, *J* = 6.5 Hz, 1H), 1.98 (d, *J* = 5.4 Hz, 1H), 1.68 (dt, *J* = 6.6, 3.3 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 144.38, 128.58, 126.86, 126.75,

117.09, 114.30, 39.14, 30.35, 30.00, 29.85, 29.34, 22.78.

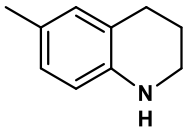
5. 8-methyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 13.5, 7.4 Hz, 2H), 6.55 (t, *J* = 7.4 Hz, 1H), 3.42 – 3.31 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.07 (s, 3H), 1.98 – 1.89 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 127.96, 127.49, 121.30, 120.99, 116.51, 42.47, 27.41, 22.28, 17.28.

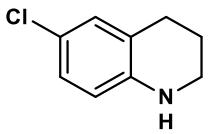
6. 8-methyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 – 6.80 (m, 2H), 6.55 (t, *J* = 7.4 Hz, 1H), 3.40 – 3.32 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.07 (s, 3H), 2.00 – 1.87 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 127.96, 127.49, 121.30, 120.99, 116.51, 42.47, 27.41, 22.28, 17.28.

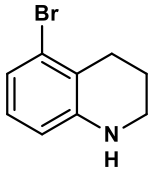
7. 6-chloro-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 – 6.86 (m, 2H), 6.36 (d, *J* = 8.1 Hz, 1H), 3.70 (s, 1H), 3.31 – 3.23 (m, 2H), 2.71 (t, *J* = 6.4 Hz, 2H), 1.94 – 1.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.39, 129.11, 126.59, 122.96, 121.22, 115.18, 41.94, 26.96, 21.83.

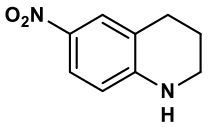
8. 5-bromo-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 – 6.84 (m, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.40 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.30 – 3.20 (m, 2H), 2.76 (t, *J* = 6.6 Hz, 2H), 2.01 – 1.89 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.63, 127.68, 126.11, 120.84, 113.28, 41.60, 29.85, 27.77, 22.34.

9. 6-Nitro-1,2,3,4-tetrahydroquinoline

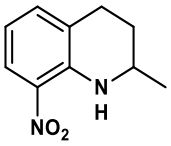


^{1}H NMR (500 MHz, CDCl3) δ 7.97 – 7.75 (m, 2H), 6.36 (d, *J* = 9.6 Hz, 1H), 4.78 (s, 1H), 3.42 (s, 2H), 2.79 (s, 2H), 1.95 (s, 2H).

^{13}C NMR (126 MHz, MeOD) δ 126.03, 124.40, 119.94, 112.26,

41.84, 27.00, 20.91.

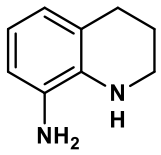
10. 8-Nitro-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 6.46 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.64 (td, *J* = 6.6, 3.3 Hz, 1H), 2.82 (dd, *J* = 7.7, 4.6 Hz, 2H), 2.00 (dq, *J* = 13.0, 4.4 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 1H), 1.33 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.08, 134.78, 130.51, 124.72, 124.46, 114.29, 47.20, 28.01, 26.94, 22.40.

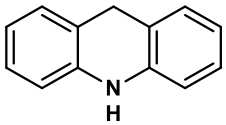
11. 8-amino-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, CDCl3) δ 6.66 – 6.45 (m, 3H), 3.33 – 3.30 (m, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 1.90 (dt, *J* = 10.9, 6.2 Hz, 2H).

^{13}C NMR (126 MHz, DMSO) δ 133.95, 123.32, 121.19, 118.10, 114.14, 77.41, 77.16, 76.91, 42.64, 27.10, 22.46.

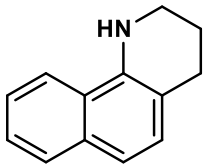
12. 9,10-dihydroacridine



^{1}H NMR (500 MHz, CDCl3) δ 7.16 – 6.98 (m, 4H), 6.85 (td, *J* = 7.4, 1.2 Hz, 2H), 6.66 (dd, *J* = 7.9, 1.2 Hz, 2H), 5.95 (s, 1H), 4.05 (s, 2H).

^{13}C NMR (126 MHz, MeOD) δ 140.26, 128.74, 127.13, 120.77, 120.18, 113.57, 31.52, 1.17.

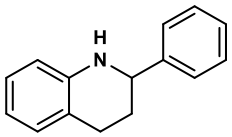
13. 1,2,3,4-tetrahydrobenzo[h]quinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 1H), 7.70 – 7.63 (m, 1H), 7.38 (dq, *J* = 6.1, 3.6, 2.4 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 4.11 (d, *J* = 7.1 Hz, 1H), 3.51 – 3.45 (m, 2H), 2.90 (t, *J* = 6.4 Hz, 2H), 2.06 – 2.00 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.10, 133.15, 128.70, 128.64, 125.04, 124.85, 123.37, 119.53, 117.06, 115.94, 42.55, 27.57, 22.26.

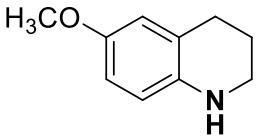
14. 2-phenyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.30 – 7.24 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.68 – 6.60 (m, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 4.42 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.01 (s, 1H), 2.91 (ddd, *J* = 16.2, 10.7, 5.4 Hz, 1H), 2.72 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.15 – 2.05 (m, 1H), 2.04 – 1.92 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.93, 144.84, 129.41, 128.69, 127.55, 127.01, 126.66, 120.98, 117.27, 114.09, 56.36, 31.09, 26.49.

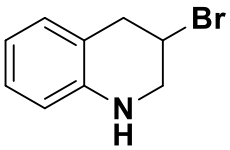
15. 8-Methoxy-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.82 (d, J = 7.5 Hz, 1H), 6.42 (dd, J = 7.7, 1.7 Hz, 1H), 6.28 (d, J = 1.7 Hz, 1H), 3.32 – 3.20 (m, 2H), 2.71 (t, J = 6.5 Hz, 2H), 2.25 – 2.17 (m, 3H), 1.95 – 1.85 (m, 2H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 144.74, 136.46, 129.50, 118.67, 118.04, 114.90, 42.15, 26.72, 22.53, 21.23

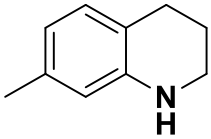
16. 3-Bromo-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.99 (td, J = 7.7, 1.5 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 6.67 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 4.48 (tdd, J = 7.8, 4.8, 3.1 Hz, 1H), 3.64 (ddd, J = 12.1, 3.3, 1.7 Hz, 1H), 3.45 (dd, J = 12.1, 7.6 Hz, 1H), 3.35 (dd, J = 16.4, 4.8 Hz, 1H), 3.14 (dd, J = 16.5, 7.7 Hz, 1H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 141.69, 137.62, 129.55, 127.08, 119.33, 118.88, 115.30, 49.31, 43.86, 37.78.

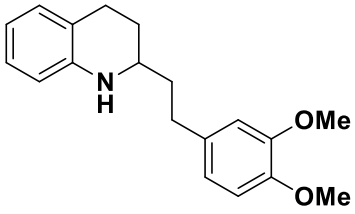
17. 7-Methyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.82 (d, J = 7.5 Hz, 1H), 6.42 (dd, J = 7.7, 1.7 Hz, 1H), 6.28 (d, J = 1.7 Hz, 1H), 3.32 – 3.20 (m, 2H), 2.71 (t, J = 6.5 Hz, 2H), 2.25 – 2.17 (m, 3H), 1.95 – 1.85 (m, 2H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 144.74, 136.46, 129.50, 118.67, 118.04, 114.90, 42.15, 26.72, 22.53, 21.23.

18. 2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline

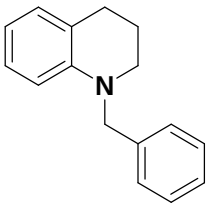


^{1}H NMR (600 MHz, ACETONITRILE-D3) δ 7.05 – 6.95 (m, 3H), 6.92 (d, J = 2.8 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.60 (t, J = 8.0 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.34 – 3.26 (m, 1H), 2.83 – 2.73 (m, 4H), 2.06 – 1.99 (m, 1H), 1.84 (dt, J = 14.9, 6.9 Hz, 2H), 1.65 (dt, J = 16.2, 5.6 Hz, 1H).

^{13}C NMR (600 MHz, ACETONITRILE-D3) δ 150.06, 148.32, 146.08, 136.00, 129.90, 127.42, 121.77, 121.10, 117.11, 114.73, 113.24, 112.84, 56.34, 56.24, 51.80, 39.18, 32.08, 28.54, 26.89.

14. Characterisation Data of Reductive Alkylated Product

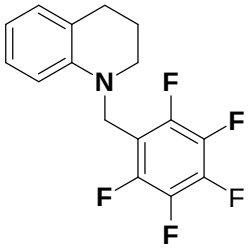
1. 1-benzyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 5H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.57 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.47 (s, 2H), 3.36 (t, *J* = 5.7 Hz, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.07 – 1.95 (m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 145.72, 139.07, 129.10, 128.68, 127.28, 126.85, 126.69, 122.34, 115.94, 111.08, 55.29, 50.00, 28.33, 22.49.

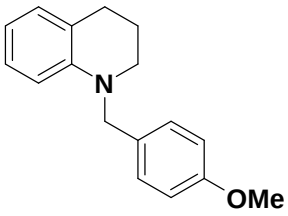
2. 1-((pentafluorophenyl)methyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.02 (m, 1H), 6.96 (dq, *J* = 7.4, 1.2 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.63 (td, *J* = 7.3, 1.1 Hz, 1H), 4.53 (s, 2H), 3.33 (t, *J* = 5.7 Hz, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 1.98 – 1.89 (m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 144.53, 129.55, 127.27, 123.46, 117.19, 111.28, 49.92, 44.13, 28.17, 22.15.

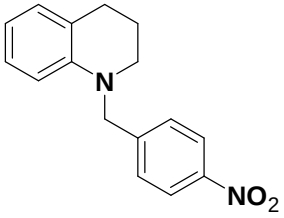
3. 1-(4-methoxybenzyl)-1,2,3,4-tetrahydroquinoline



1H NMR (500 MHz, CDCl3) δ 7.25 – 7.12 (m, 2H), 6.97 (t, J = 7.4 Hz, 2H), 6.90 – 6.76 (m, 2H), 6.62 – 6.46 (m, 2H), 4.40 (s, 2H), 3.77 (s, 3H), 3.36 – 3.29 (m, 2H), 2.80 (t, J = 6.3 Hz, 2H), 2.02 – 1.94 (m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 158.60, 145.75, 130.90, 129.10, 127.86, 127.27, 122.35, 115.86, 114.07, 111.07, 55.37, 54.63, 49.78, 28.34, 22.48.

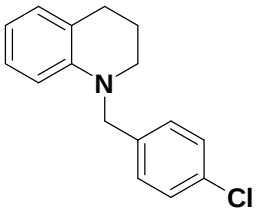
4. 1-(4-nitrobenzyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.78 (m, 2H), 6.50 (t, *J* = 7.3 Hz, 1H), 6.24 (d, *J* = 8.2 Hz, 1H), 4.43 (s, 2H), 3.28 (t, *J* = 5.7 Hz, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 2.01 – 1.86 (m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 146.29, 146.05, 144.00, 128.31, 126.30, 126.27, 122.94, 121.59, 115.67, 109.91, 54.16, 49.37, 27.10, 21.44.

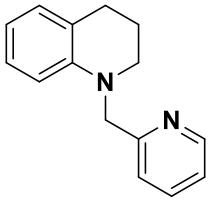
5. 1-(4-chlorobenzyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.58 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 4.41 (s, 2H), 3.35 – 3.30 (m, 2H), 2.80 (s, 1H), 2.80 (d, *J* = 12.8 Hz, 1H), 2.00 (p, *J* = 6.1 Hz, 2H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 145.49, 137.62, 132.54, 129.22, 128.84, 128.09, 127.32, 122.49, 116.29, 111.07, 54.84, 50.08, 28.27, 22.51.

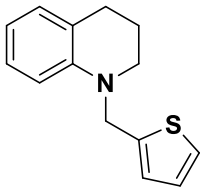
6. 1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 7.26 (d, *J* = 2.5 Hz, 1H), 7.18 – 7.02 (m, 4H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.86 (td, *J* = 7.3, 1.4 Hz, 1H), 4.42 (s, 2H), 3.08 – 2.95 (m, 2H), 2.83 (t, *J* = 6.6 Hz, 2H), 2.03 – 1.87 (m, 2H).

13C NMR (600 MHz, CHLOROFORM-D) δ 146.36, 141.40, 135.89, 129.69, 127.03, 123.52, 123.18, 121.45, 120.67, 116.49, 57.72, 48.38, 31.80, 29.80.

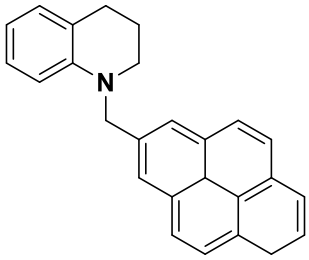
7. 1-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 7.15 – 7.11 (m, 1H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.63 – 6.53 (m, 1H), 4.59 (s, 2H), 3.33 (t, *J* = 5.7 Hz, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 1.96 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 145.04, 142.53, 129.29, 127.17, 126.83, 124.77, 124.23, 122.92, 116.58, 111.53, 50.63, 49.57, 28.20, 22.39.

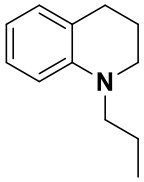
8. 1-((3a1,6-dihydropyren-2-yl)methyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.23 (d, J = 9.1 Hz, 1H), 8.17 (dd, J = 9.1, 7.7 Hz, 2H), 8.09 (dd, J = 18.5, 8.5 Hz, 2H), 8.01 (d, J = 0.9 Hz, 2H), 7.99 (td, J = 7.5, 1.0 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.04 (dd, J = 7.3, 1.6 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.61 (td, J = 7.3, 1.2 Hz, 1H), 6.53 (d, J = 8.2 Hz, 1H), 5.15 (s, 2H), 3.40 (t, J = 5.7 Hz, 2H), 2.88 (t, J = 6.3 Hz, 2H), 2.05 (p, J = 6.1 Hz, 2H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 145.93, 131.57, 131.47, 130.90, 130.61, 129.17, 128.51, 127.69, 127.65, 127.42, 127.03, 126.04, 125.28, 125.23, 125.04, 124.98, 124.66, 122.76, 122.36, 116.22, 111.21, 53.63, 49.73, 28.39, 22.68, 1.16.

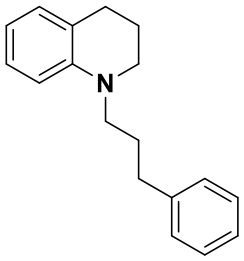
9. 1-propyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 7.08 – 6.98 (m, 1H), 6.92 (dq, *J* = 7.3, 1.5 Hz, 1H), 6.57 – 6.49 (m, 2H), 3.26 (td, *J* = 5.7, 2.5 Hz, 2H), 3.22 – 3.14 (m, 2H), 2.74 (td, *J* = 6.5, 2.4 Hz, 2H), 1.93 (tdd, *J* = 6.7, 4.8, 2.8 Hz, 2H), 1.65 – 1.55 (m, 2H), 0.95 – 0.88 (m, 3H).

^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.08 – 6.98 (m, 1H), 6.92 (dq, J = 7.3, 1.5 Hz, 1H), 6.57 – 6.49 (m, 2H), 3.26 (td, J = 5.7, 2.5 Hz, 2H), 3.22 – 3.14 (m, 2H), 2.74 (td, J = 6.5, 2.4 Hz, 2H), 1.93 (tdd, J = 6.7, 4.8, 2.8 Hz, 2H), 1.65 – 1.55 (m, 2H), 0.95 – 0.88 (m, 3H).

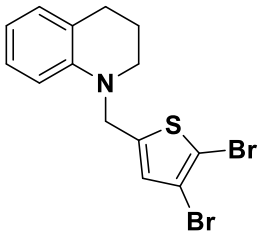
10. 1-(3-phenylpropyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.28 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 7.9 Hz, 3H), 7.00 (t, J = 7.7 Hz, 1H), 6.92 (d, J = 7.4 Hz, 1H), 6.53 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.3 Hz, 1H), 3.30 – 3.19 (m, 4H), 2.70 (dt, J = 44.6, 7.1 Hz, 5H), 1.99 – 1.85 (m, 5H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 145.39, 141.98, 129.25, 128.46, 127.16, 125.97, 122.39, 115.48, 110.61, 51.06, 49.55, 33.54, 28.28, 27.82, 22.36.

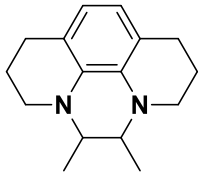
11. 1-((4,5-dibromothiophen-2-yl)methyl)-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.03 (dddd, J = 8.1, 7.3, 1.7, 0.8 Hz, 1H), 6.97 (ddd, J = 7.5, 1.8, 0.9 Hz, 1H), 6.76 (q, J = 1.0 Hz, 1H), 6.66 – 6.62 (m, 1H), 6.59 (d, J = 8.2 Hz, 1H), 4.49 (d, J = 1.0 Hz, 2H), 3.35 – 3.27 (m, 2H), 2.77 (t, J = 6.4 Hz, 2H), 2.01 – 1.97 (m, 2H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 180.95, 138.00, 129.48, 127.27, 126.91, 123.76, 123.18, 117.34, 115.80, 111.52, 51.28, 50.01, 28.01, 22.36.

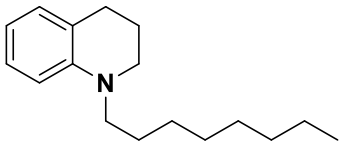
12. 5,6-dimethyl-1,2,3,5,6,8,9,10-octahydropyrazino[1,2,3,4-lmn][1,10]phenanthroline



^{1}H NMR (600 MHz, CHLOROFORM-D) δ 6.29 (s, 2H), 3.30 (ddd, J = 10.8, 6.5, 4.7 Hz, 2H), 3.23 – 3.14 (m, 2H), 2.86 (ddd, J = 11.0, 6.9, 4.8 Hz, 2H), 2.72 – 2.66 (m, 4H), 1.97 – 1.92 (m, 4H), 1.08 (d, J = 6.1 Hz, 6H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 131.58, 119.43, 117.96, 55.63, 46.64, 27.74, 22.49, 14.19.

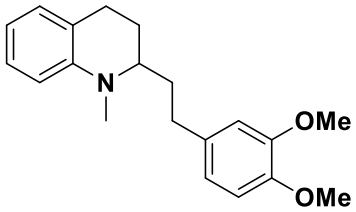
13. 1-octyl-1,2,3,4-tetrahydroquinoline



^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 6.15 (t, *J* = 7.7 Hz, 1H), 6.04 (d, *J* = 7.3 Hz, 1H), 5.70 – 5.63 (m, 2H), 2.41 – 2.37 (m, 2H), 2.36 – 2.31 (m, 2H), 1.86 (t, *J* = 6.4 Hz, 2H), 1.06 (p, *J* = 6.2 Hz, 2H), 0.46 – 0.36 (m, 15H).

^{13}C NMR (600 MHz, CHLOROFORM-D) δ 145.50, 129.24, 127.17, 122.27, 115.28, 110.58, 51.67, 49.57, 31.99, 29.68, 29.48, 28.36, 27.43, 26.33, 22.80, 22.40, 14.23.

14. 2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (Cuspareine)

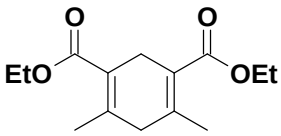


^{1}H NMR (600 MHz, CHLOROFORM-*D*) δ 7.08 (td, *J* = 7.8, 1.6 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.69 (m, 2H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.29 (dq, *J* = 8.5, 4.4 Hz, 1H), 2.91 (s, 3H), 2.89 – 2.85 (m, 1H), 2.68 (ddt, *J* = 19.0, 10.2, 4.8 Hz, 2H), 2.53 (ddd, *J* = 13.8, 10.1, 6.4 Hz, 1H), 1.93 (dtt, *J* = 20.9, 8.3, 4.2 Hz, 4H), 1.73 (ddd, *J* = 13.7, 8.9, 4.3 Hz, 1H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 148.96, 147.28, 145.34, 134.69, 128.73, 127.16, 121.76, 120.11, 115.45, 111.66, 111.37, 110.66, 58.44, 55.97, 55.90, 38.12, 33.12, 31.96, 24.46, 23.64.

15. Characterisation Data of HE and OHE

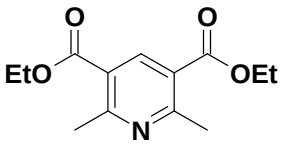
Hantzsch Ester



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (s, 1H), 4.17 (qd, J = 7.1, 1.1 Hz, 4H), 3.26 (s, 2H), 2.85 (s, 1H), 2.19 (s, 6H), 1.29 (td, J = 7.1, 1.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.11, 144.94, 99.41, 59.67, 30.96, 24.78, 19.15, 14.47.

Oxidised Hantzsch Ester



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 4.40 (q, J = 7.1 Hz, 4H), 2.85 (s, 6H), 1.42 (t, J = 7.1 Hz, 6H).

^{13}C NMR (500 MHz, CDCl3) δ 166.11, 162.37, 141.06, 123.19, 61.55, 25.12, 14.41.

16. ^{1}H and ^{13}C NMR of Catalyst

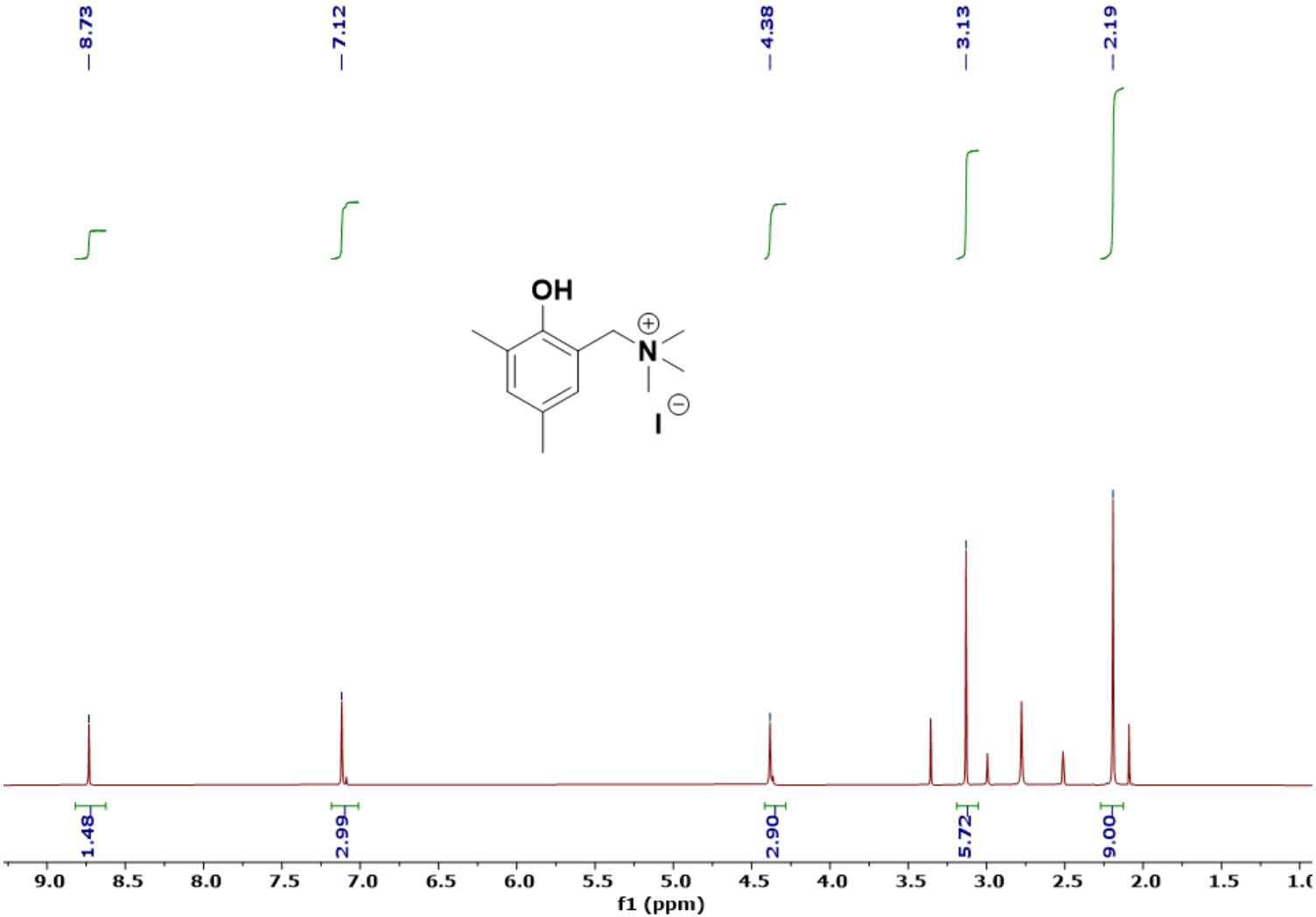


Fig. S3 ^{1}H NMR Spectrum of ETP-1 (DMSO, 500 MHz, 298K)

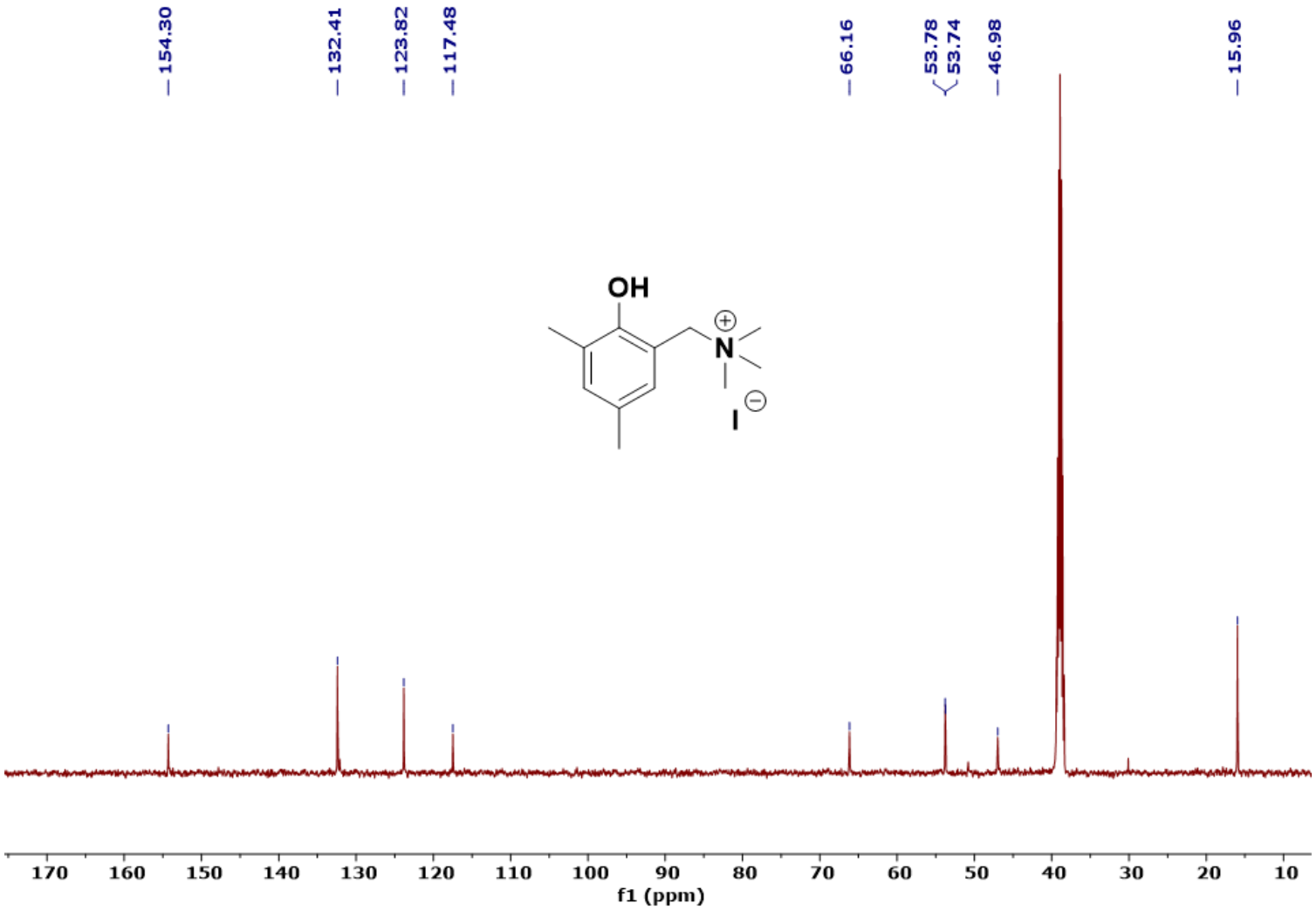


Fig. S4 ^{13}C NMR Spectrum of ETP-1 (DMSO, 500 MHz, 298K)

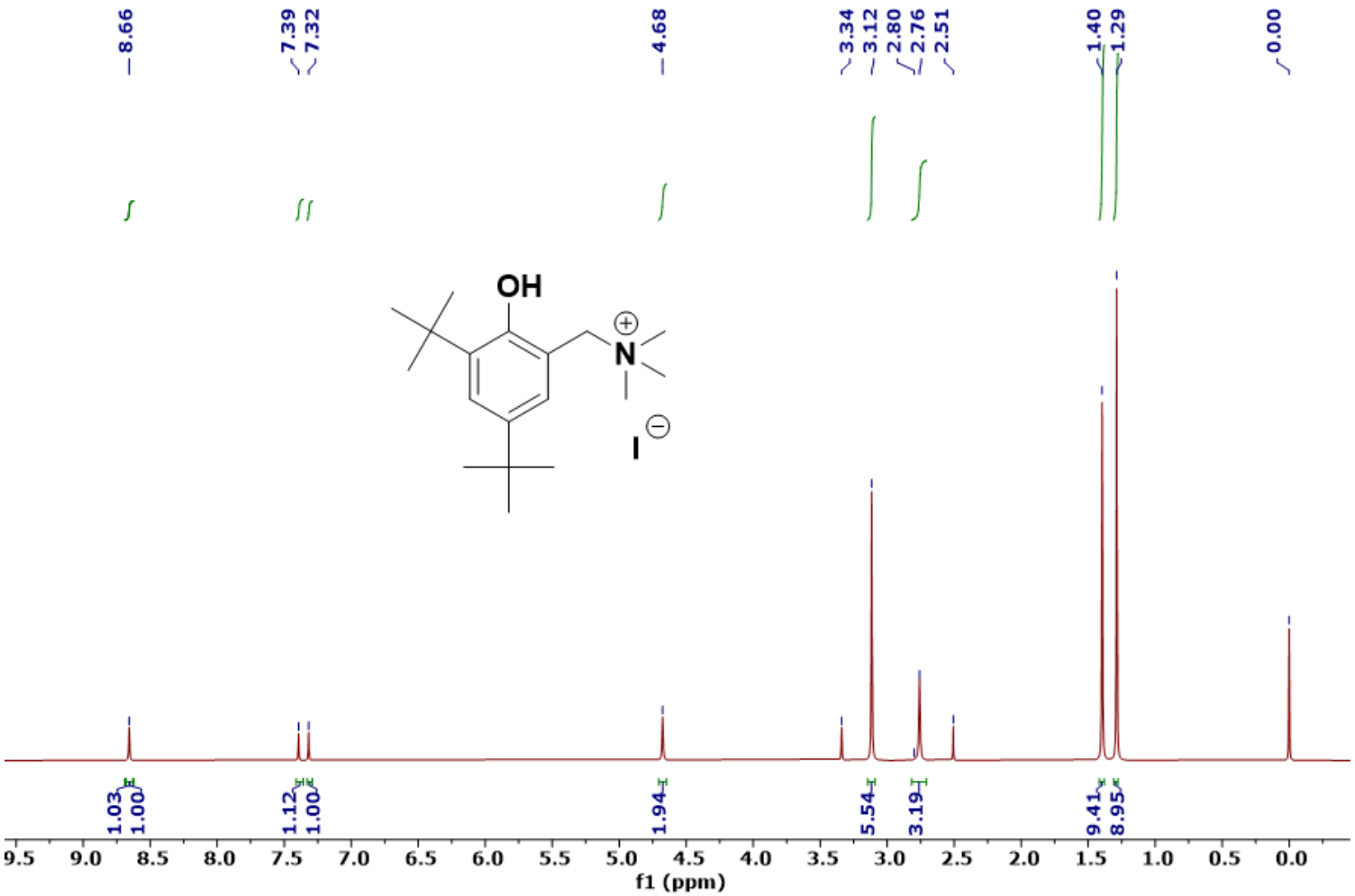


Fig. S5 ^{1}H NMR Spectrum of ETP-2 (DMSO, 500 MHz, 298K)

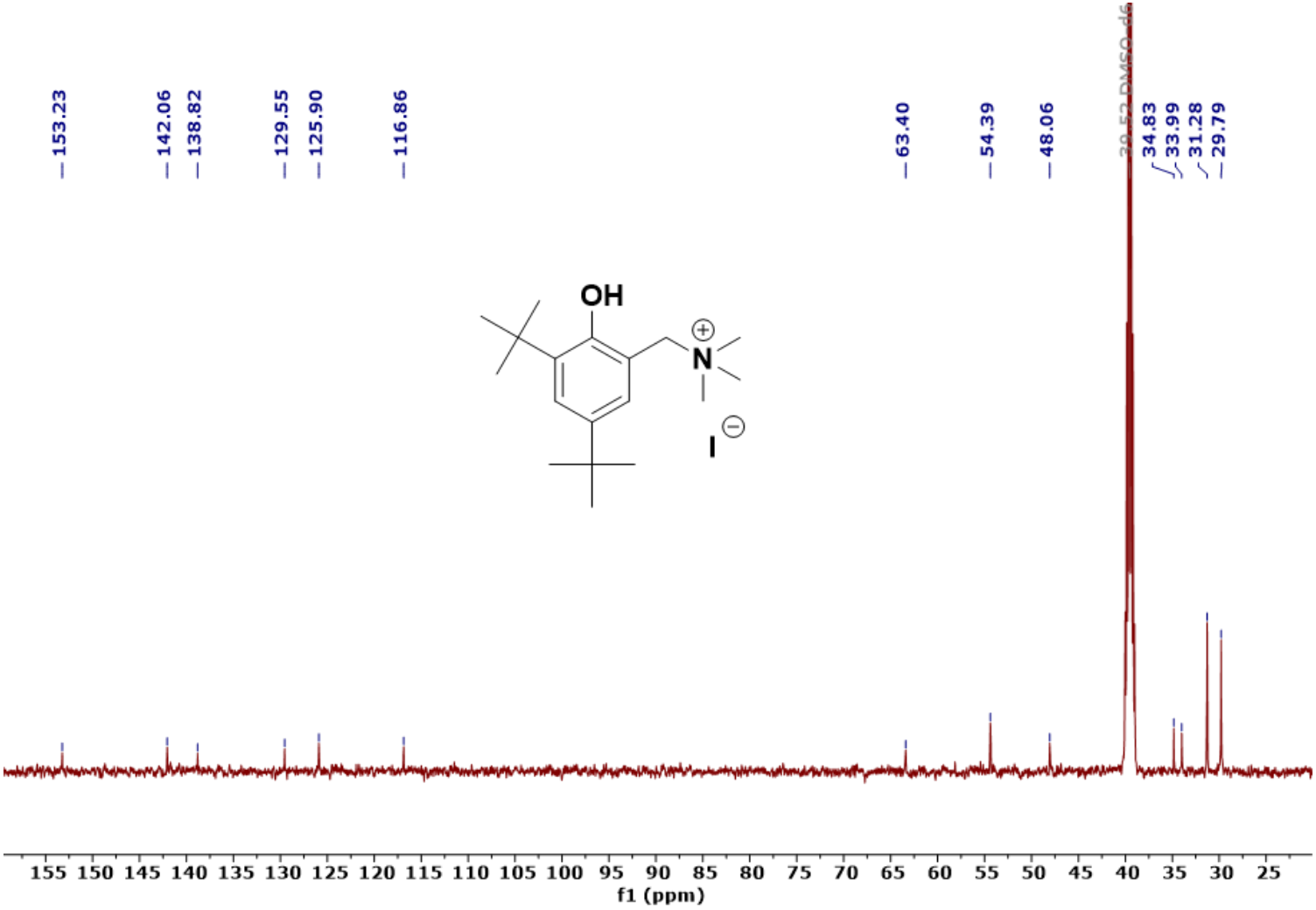


Fig. S6 ^{13}C NMR Spectrum of ETP-2 (DMSO, 500 MHz, 298K)

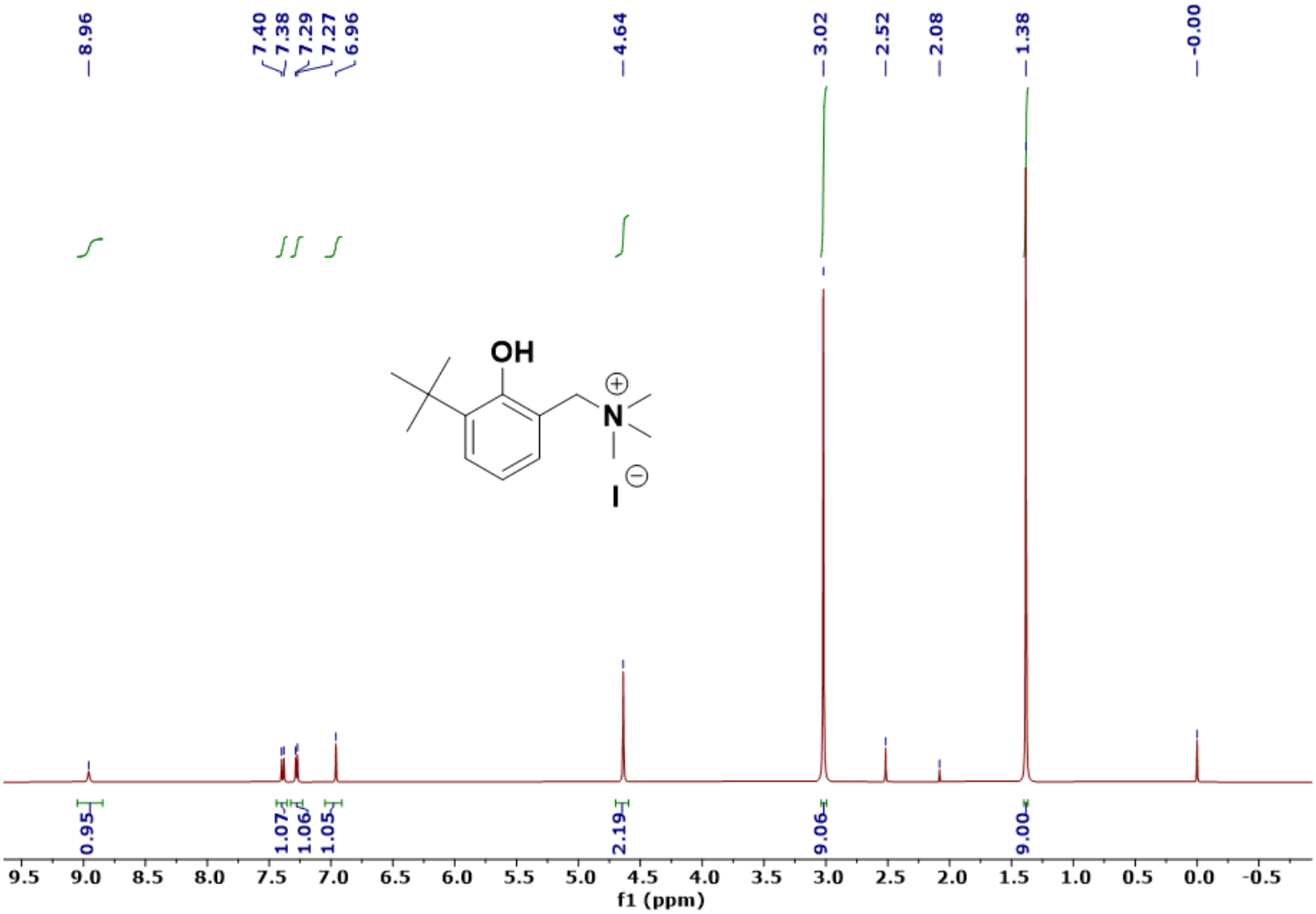


Fig. S7 ^{1}H NMR Spectrum of ETP-3 (DMSO, 500 MHz, 298K)

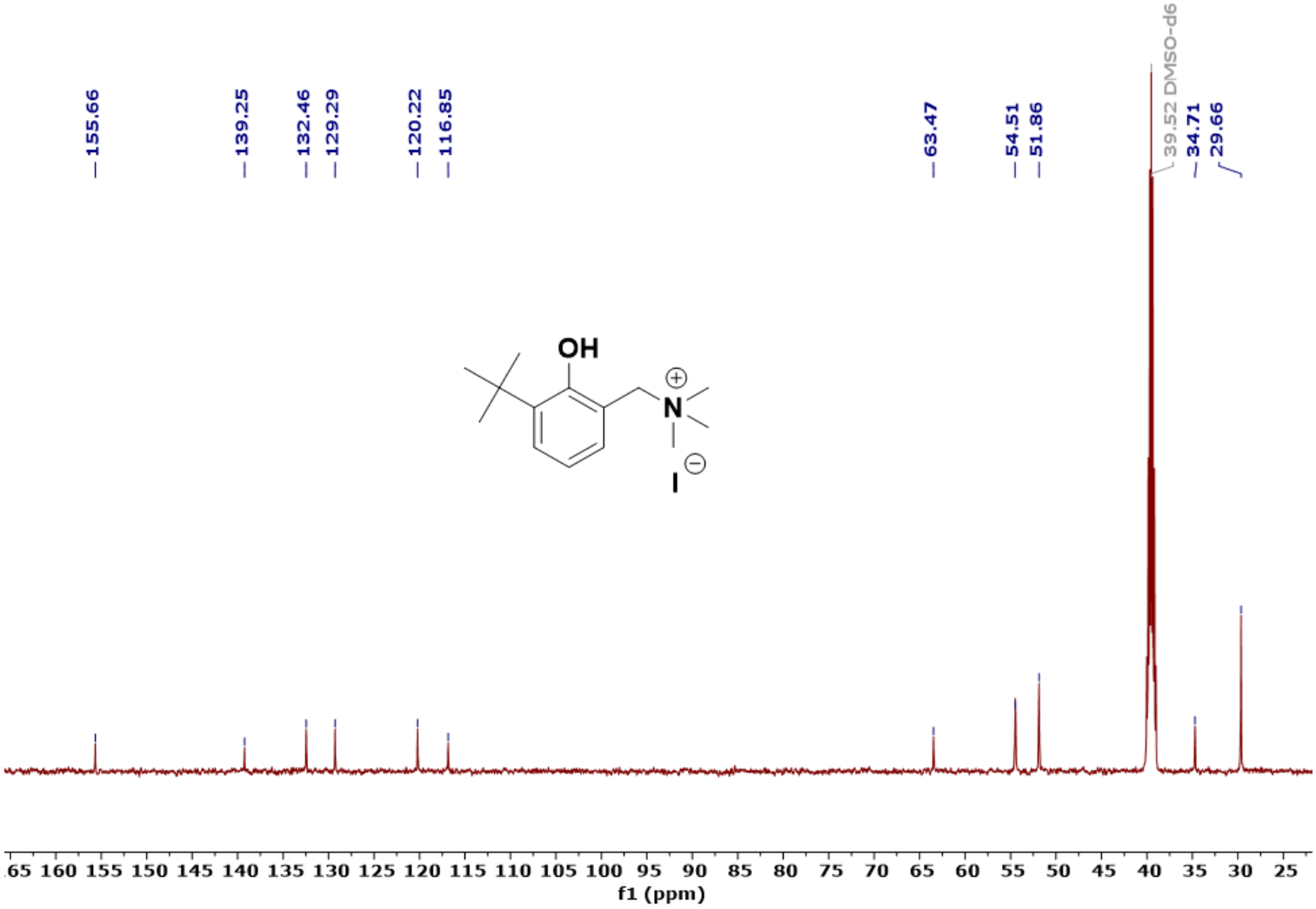


Fig. S8 ^{13}C NMR Spectrum of ETP-3 (DMSO, 500 MHz, 298K)

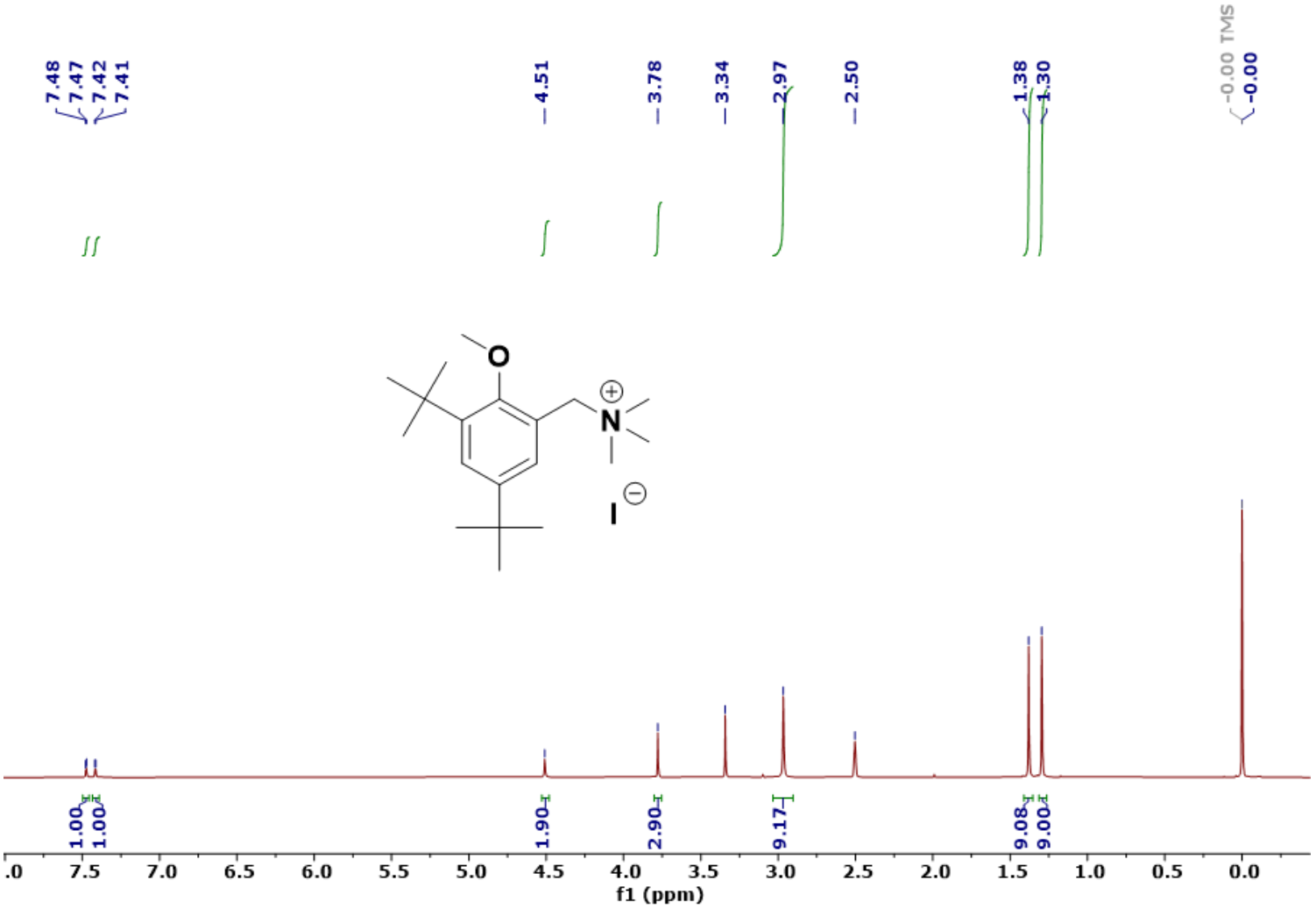


Fig. S9 ^{1}H NMR Spectrum of ETP-4 (DMSO, 500 MHz, 298K)

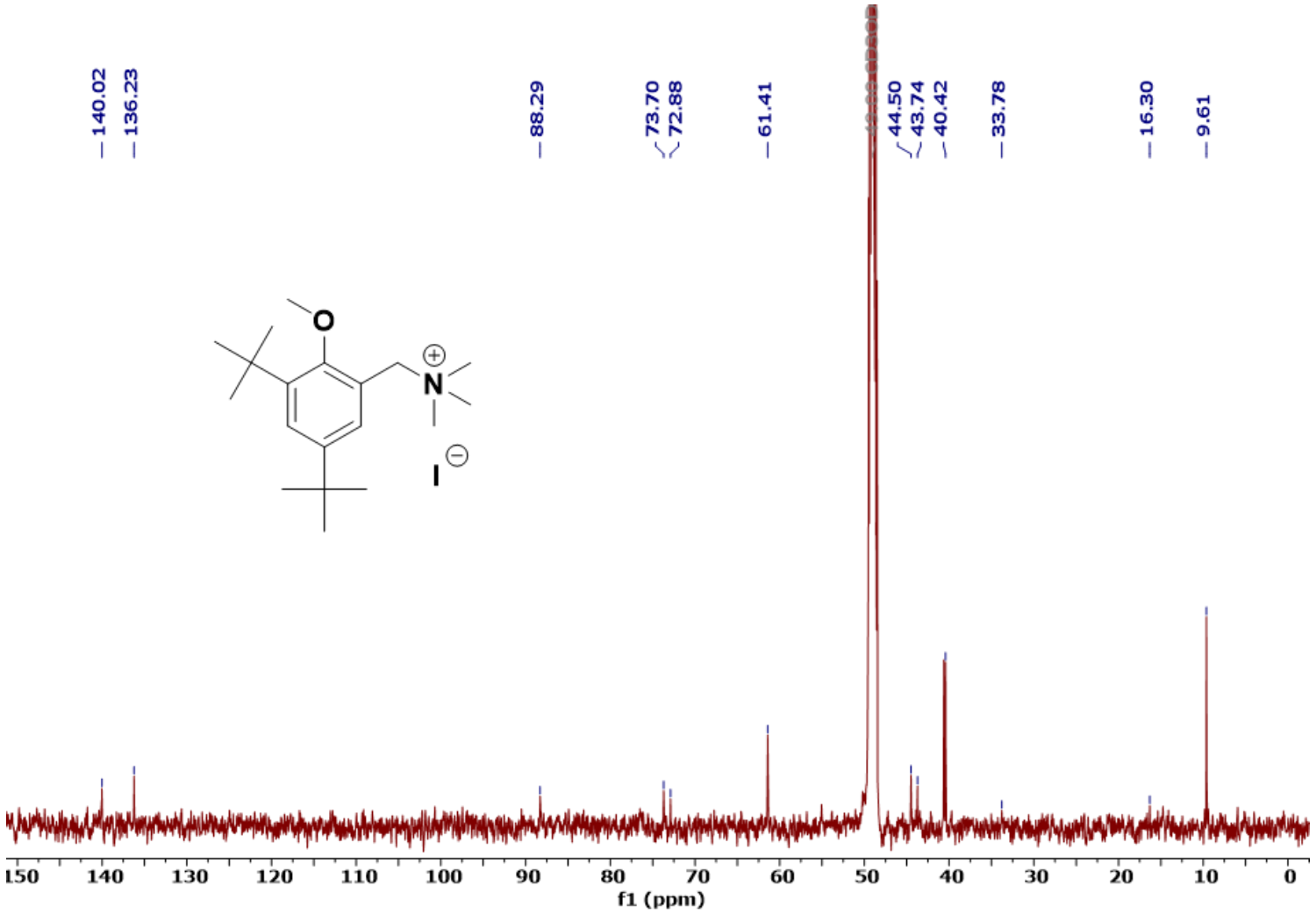


Fig. S10 ^{13}C NMR Spectrum of ETP-4 (DMSO, 500 MHz, 298K)

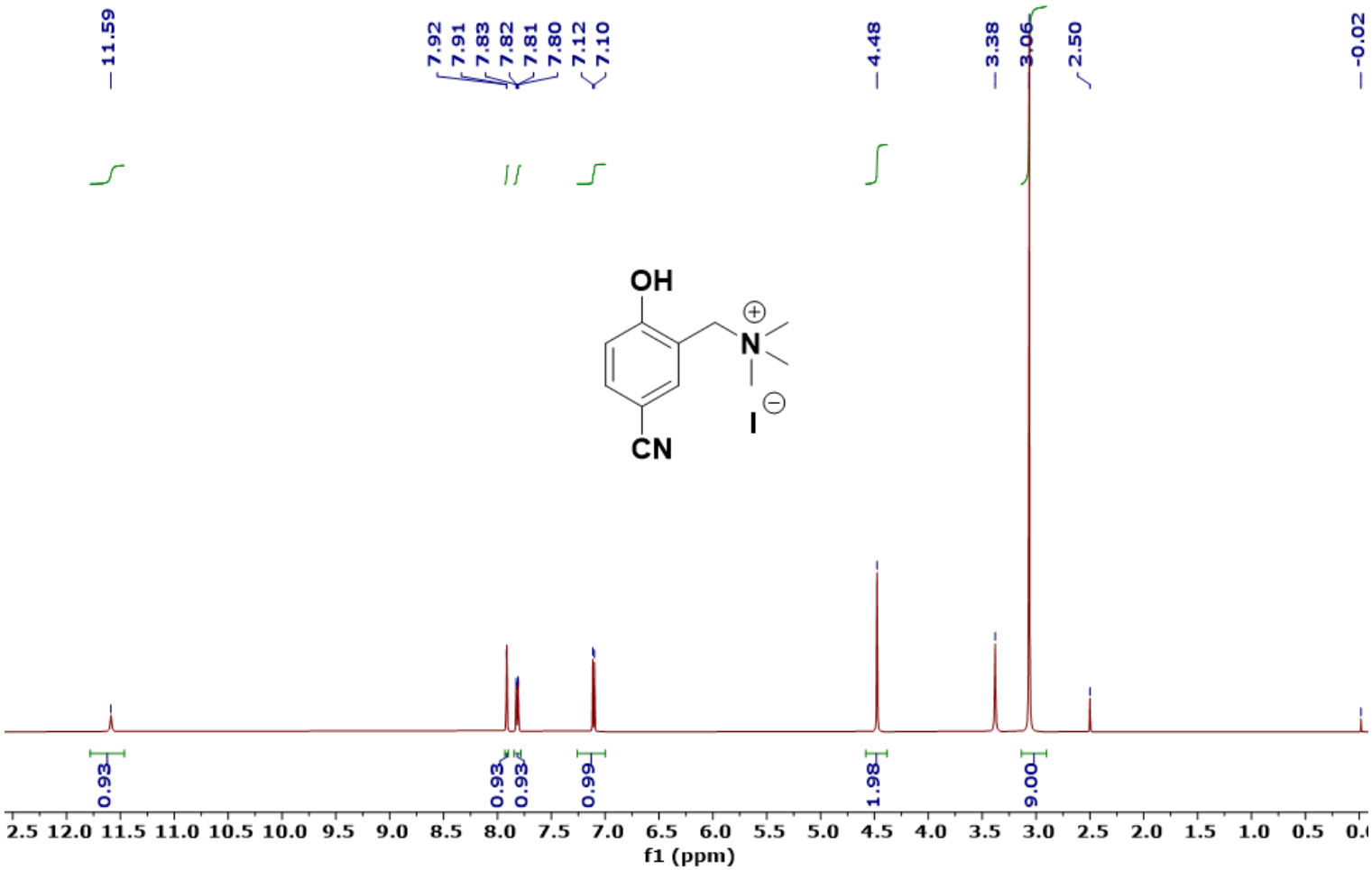


Fig. S11 ^{1}H NMR Spectrum of ETP-5 (DMSO, 500 MHz, 298K)

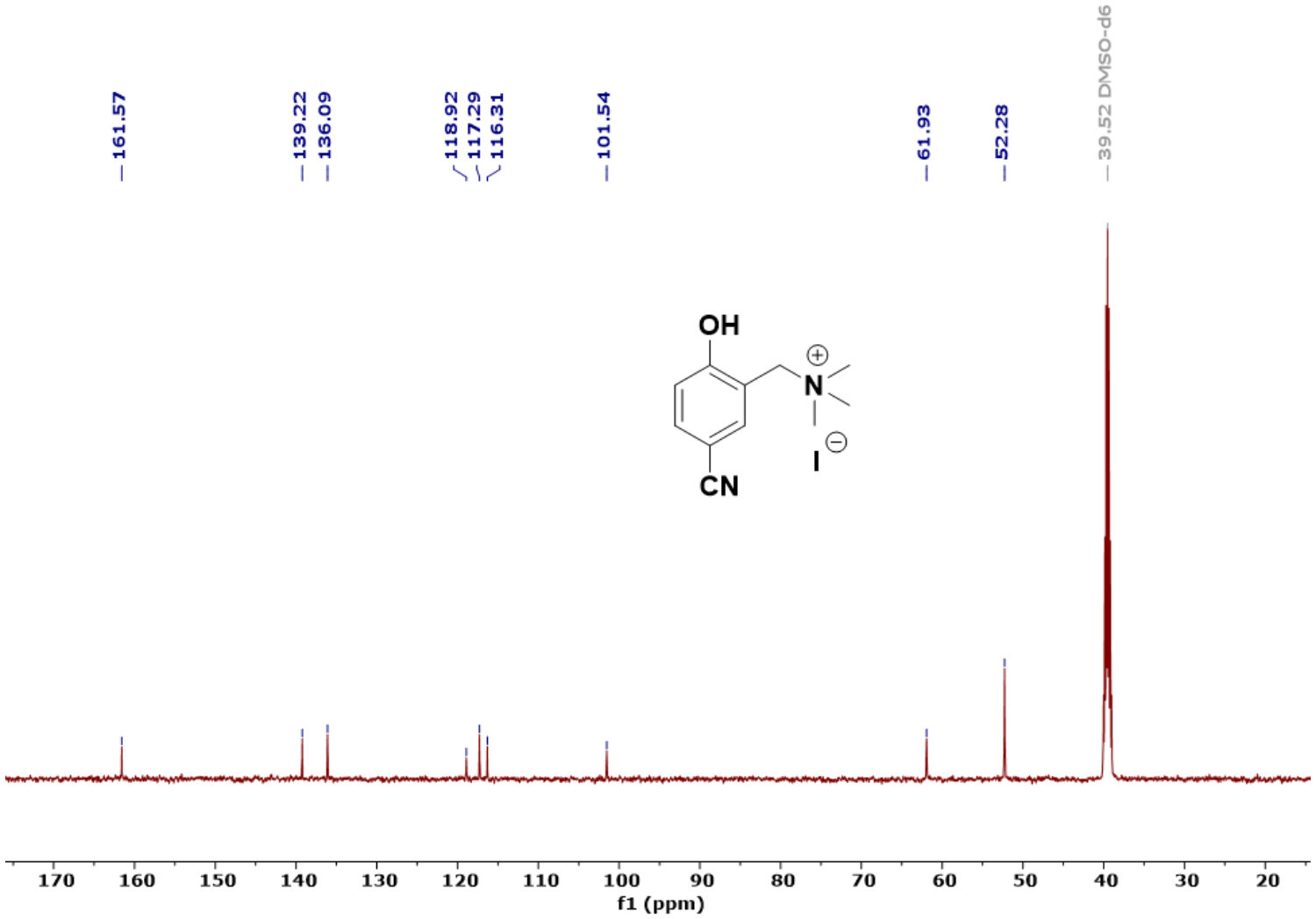


Fig. S12 ^{13}C NMR Spectrum of ETP-5(DMSO, 500 MHz, 298K)

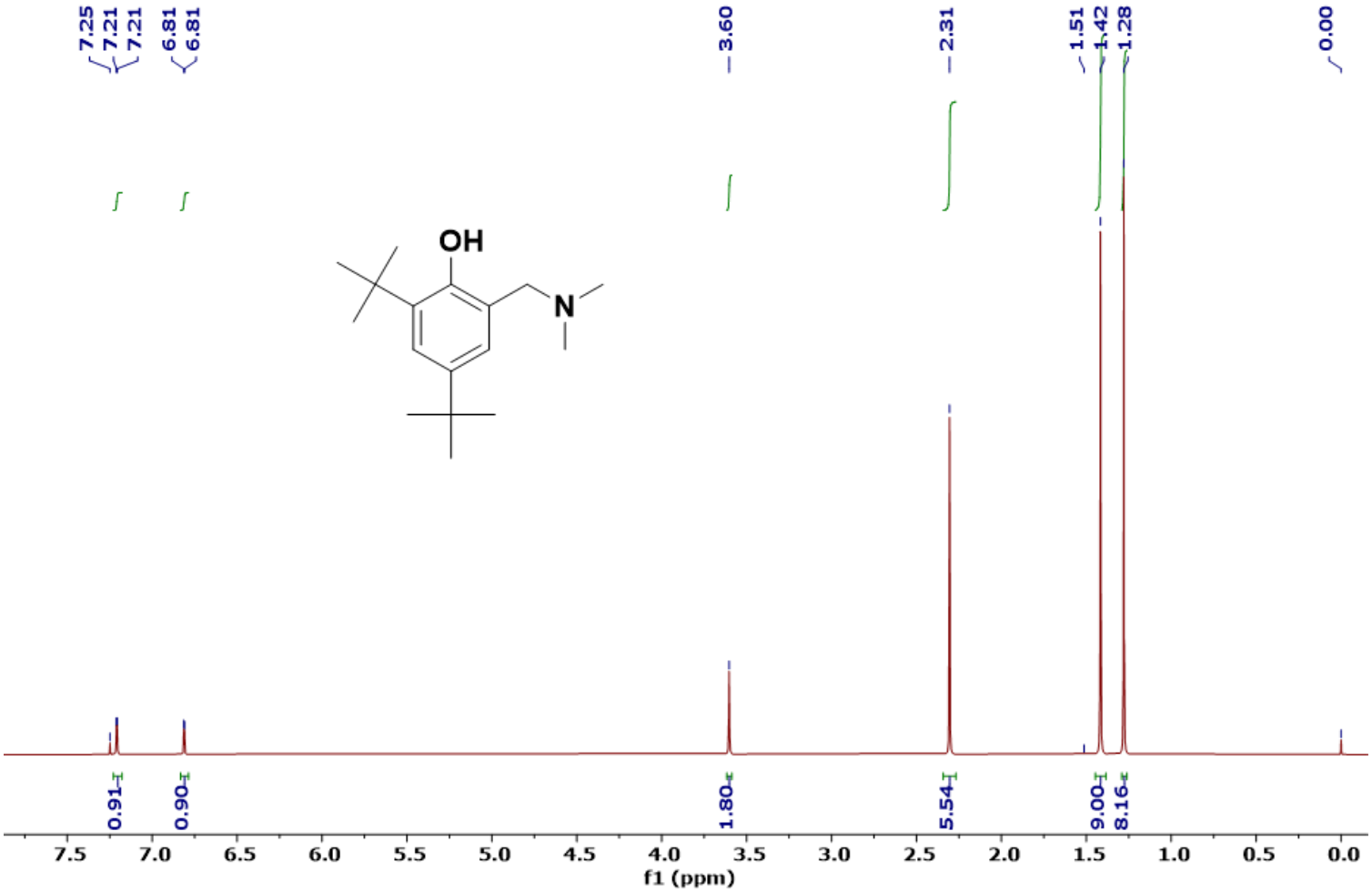


Fig. S13 ^{1}H NMR Spectrum of DMAMP (DMSO, 500 MHz, 298K)

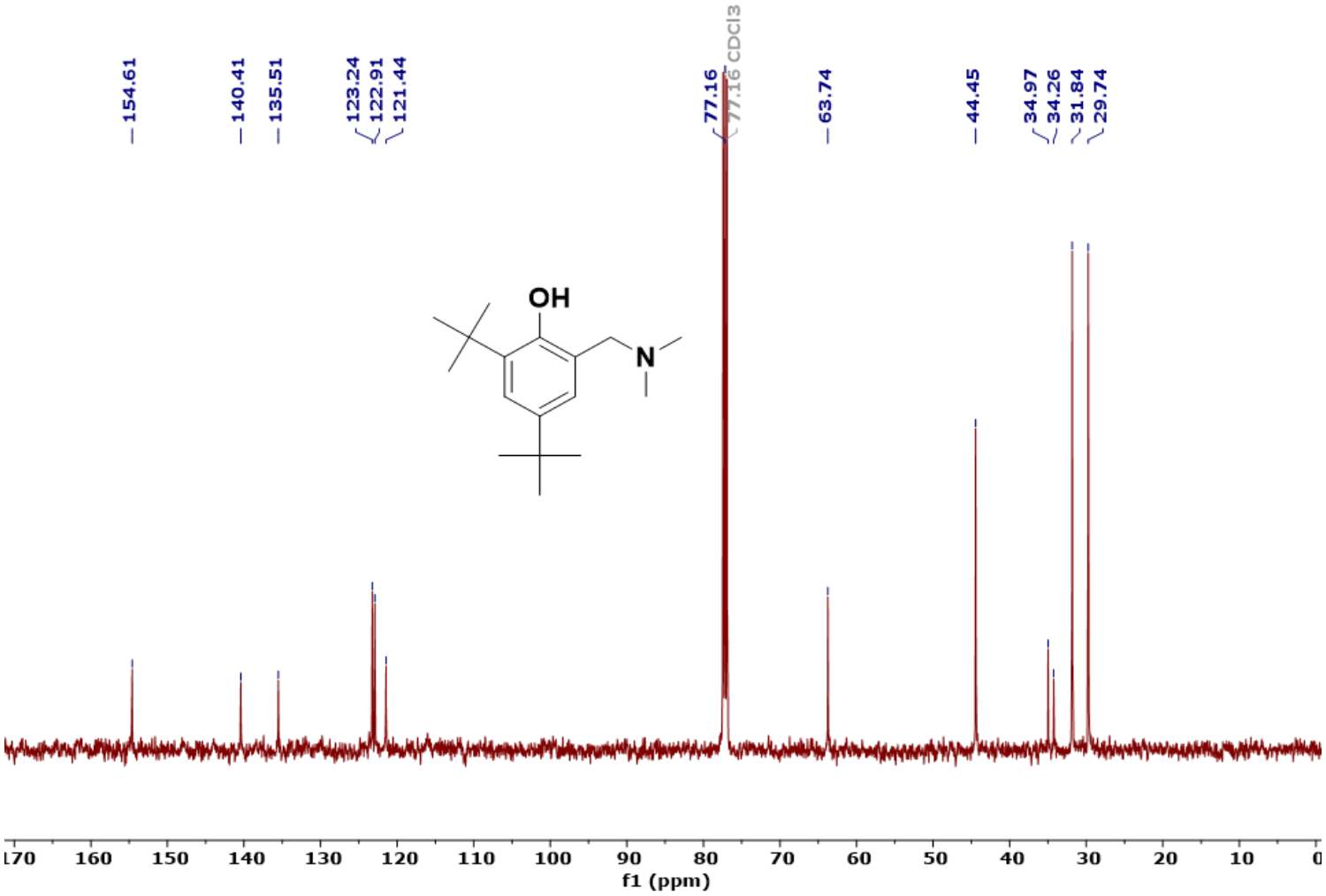


Fig. S14 ^{13}C NMR Spectrum of DMAMP(DMSO, 500 MHz, 298K)

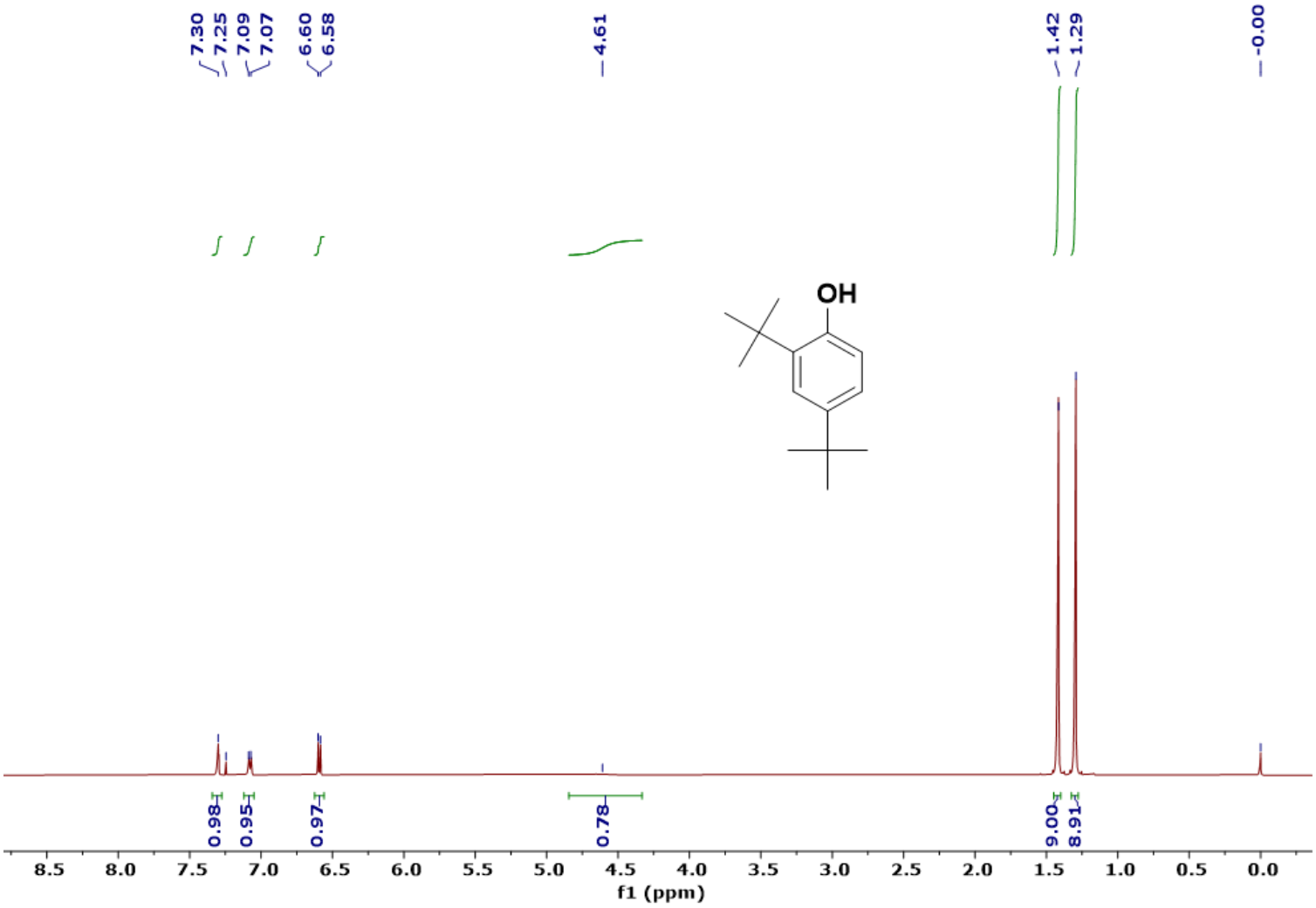


Fig. S15 ^{1}H NMR Spectrum of DTBP (DMSO, 500 MHz, 298K)

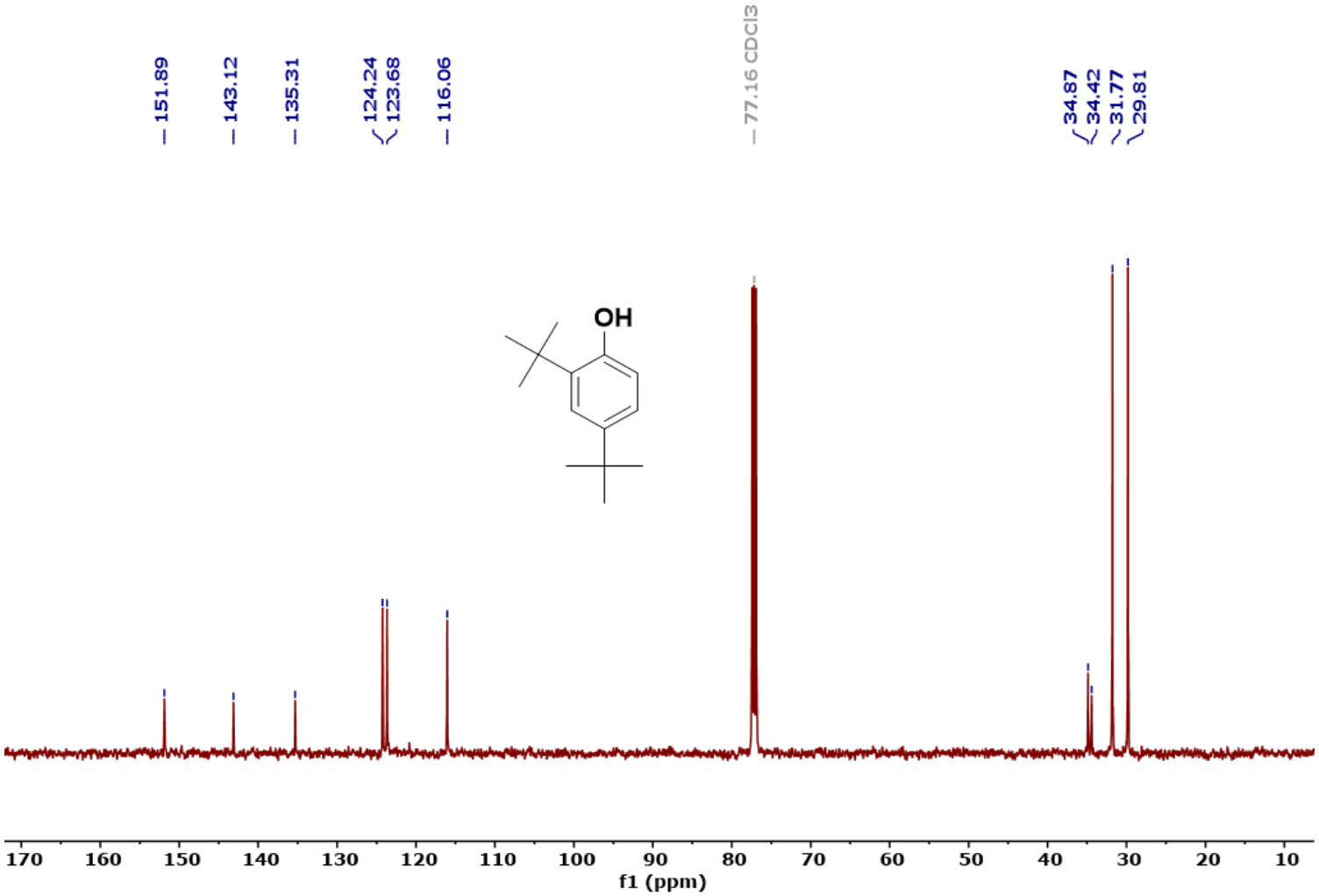


Fig. S16 ^{13}C NMR Spectrum of DTBP(DMSO, 500 MHz, 298K)

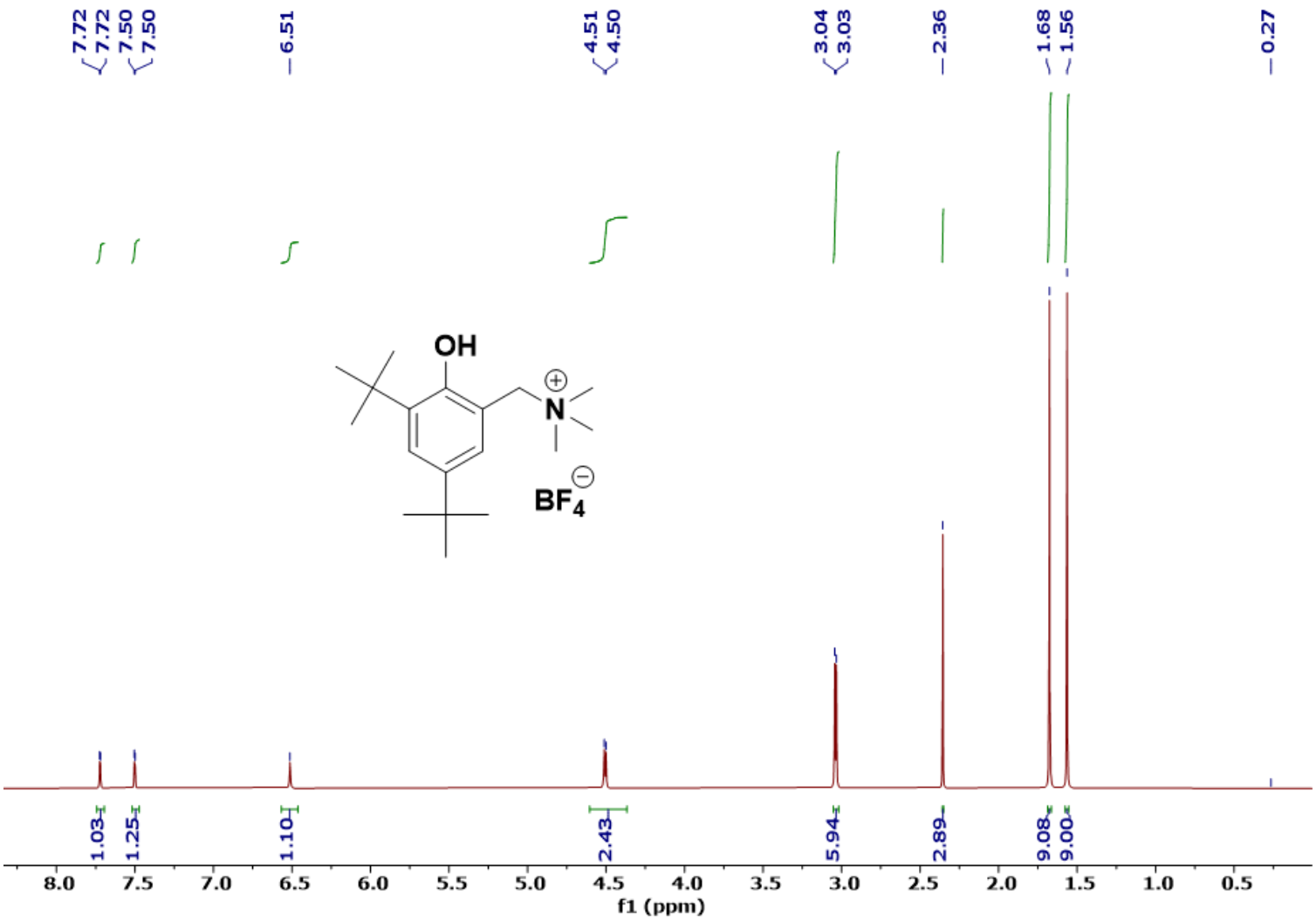


Fig. S17 ^{1}H NMR Spectrum of ETP-6(DMSO, 500 MHz, 298K)

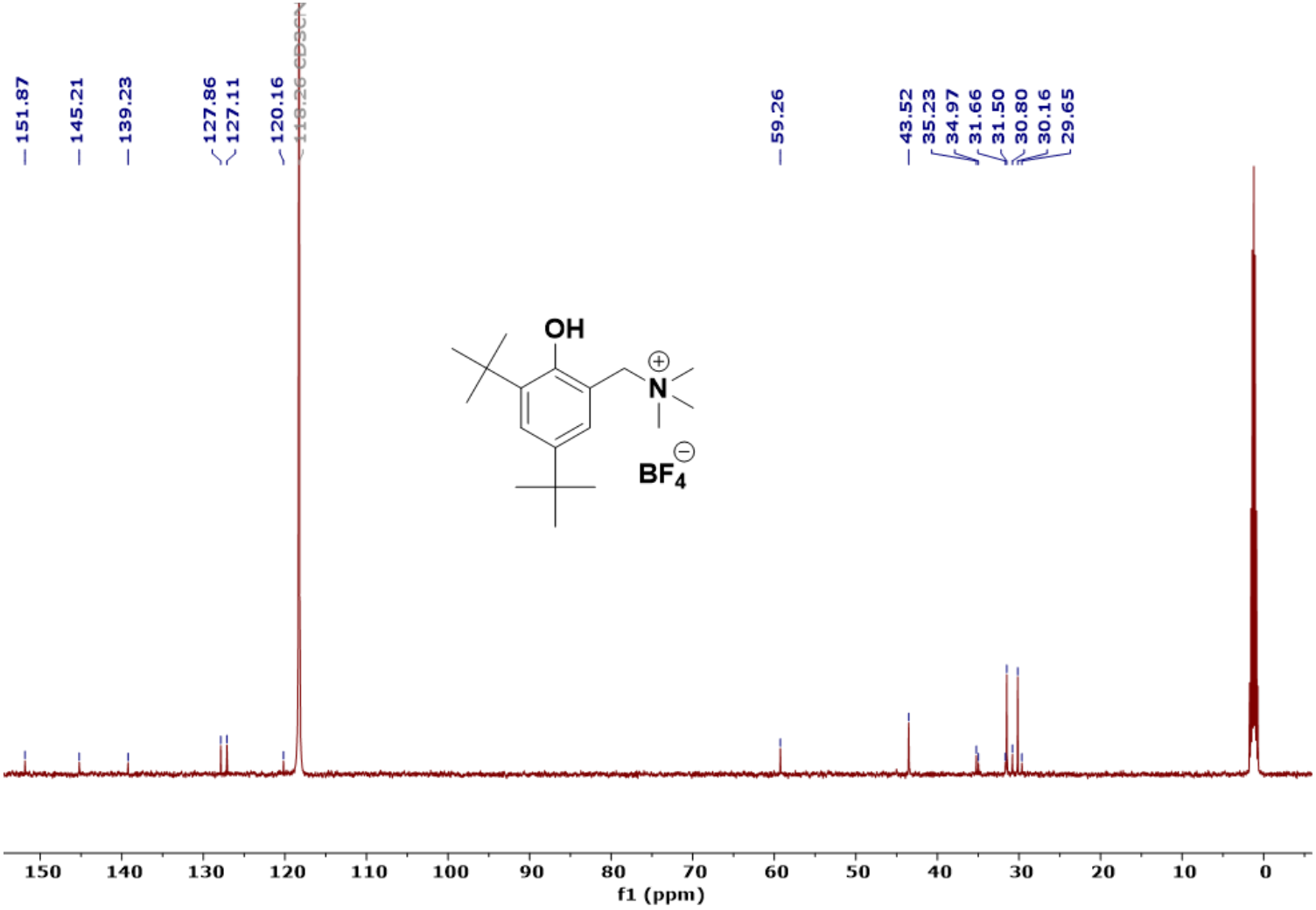


Fig. S18 ^{13}C NMR Spectrum of ETP-6 (DMSO, 500 MHz, 298K)

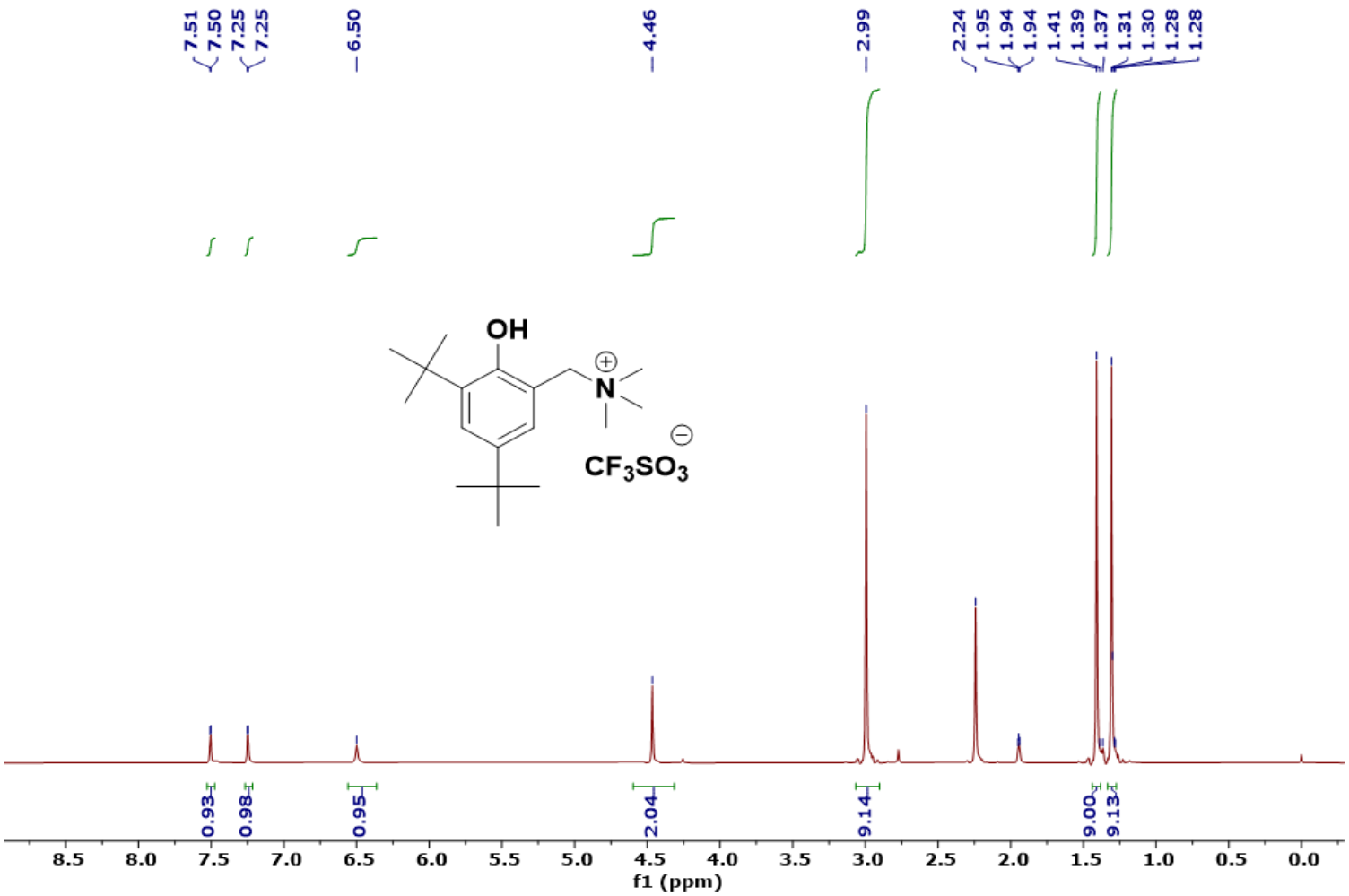


Fig. S19 ^{1}H NMR Spectrum of ETP-7 (DMSO, 500 MHz, 298K)

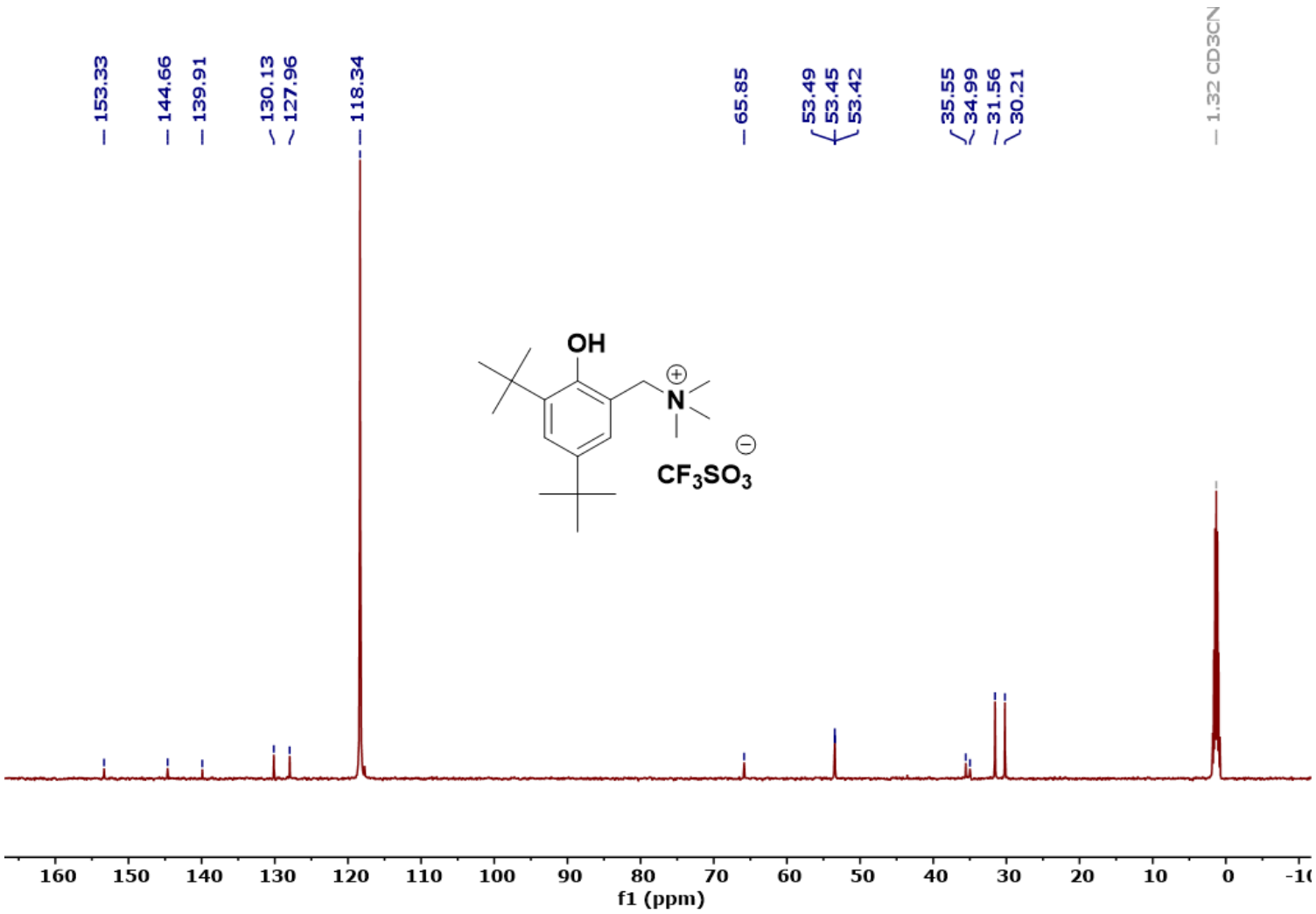


Fig. S20 ^{13}C NMR Spectrum of ETP-7 (DMSO, 500 MHz, 298K)

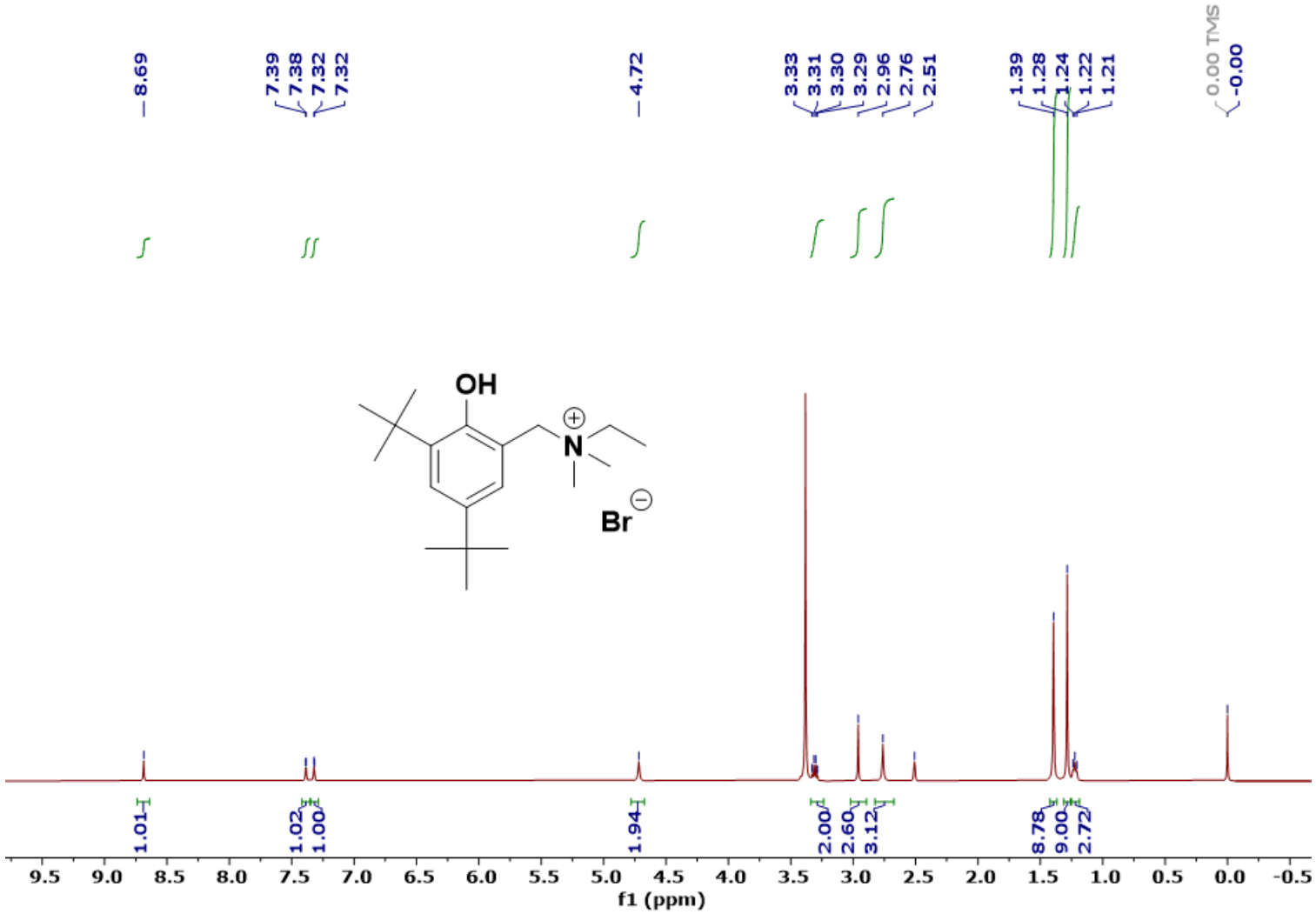


Fig. S21 ^{1}H NMR Spectrum of ETP-8 (DMSO, 500 MHz, 298K)

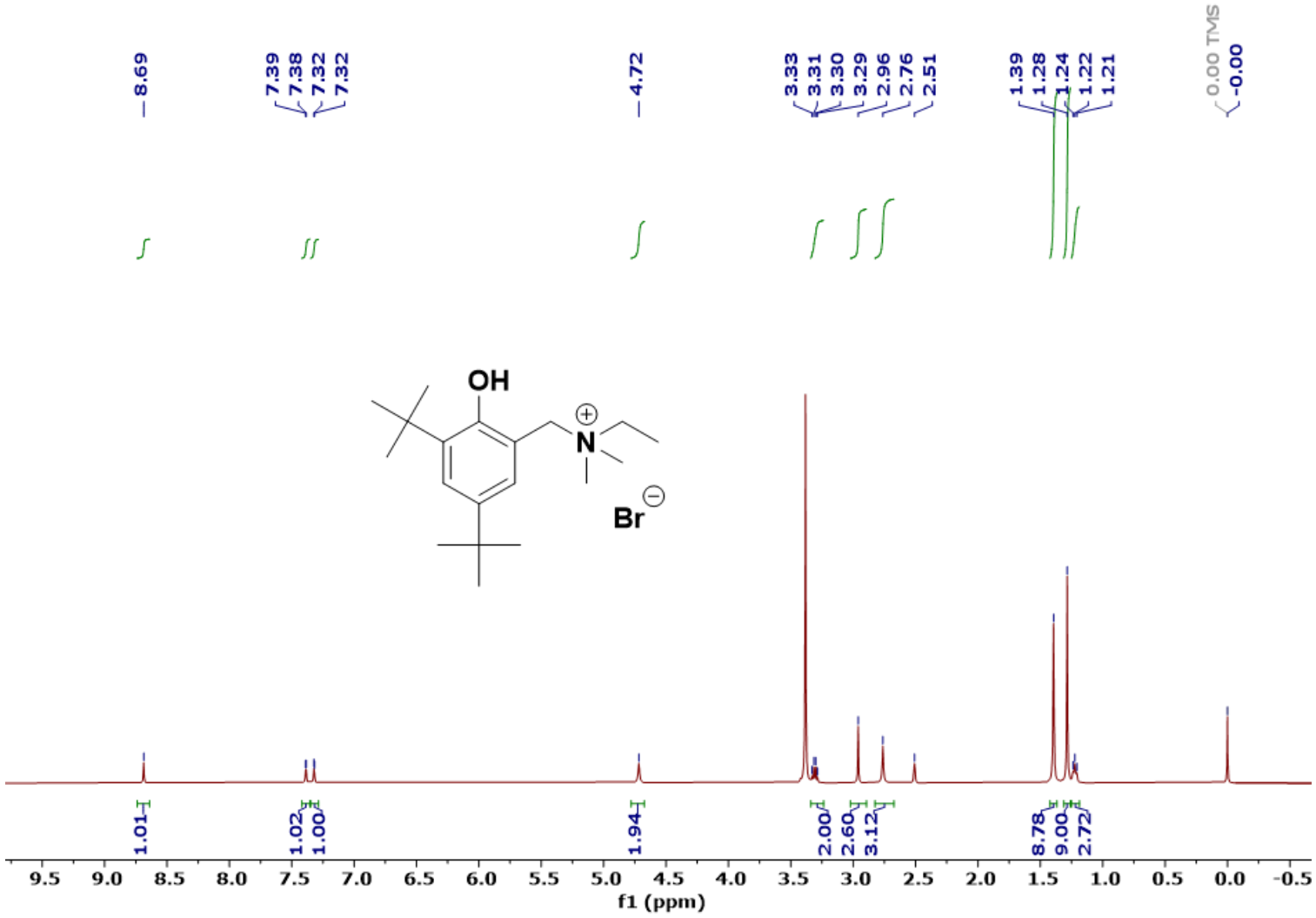


Fig. S22 ^{13}C NMR Spectrum of ETP-8 (DMSO, 500 MHz, 298K)

17. ^{1}H and ^{13}C NMR of Product

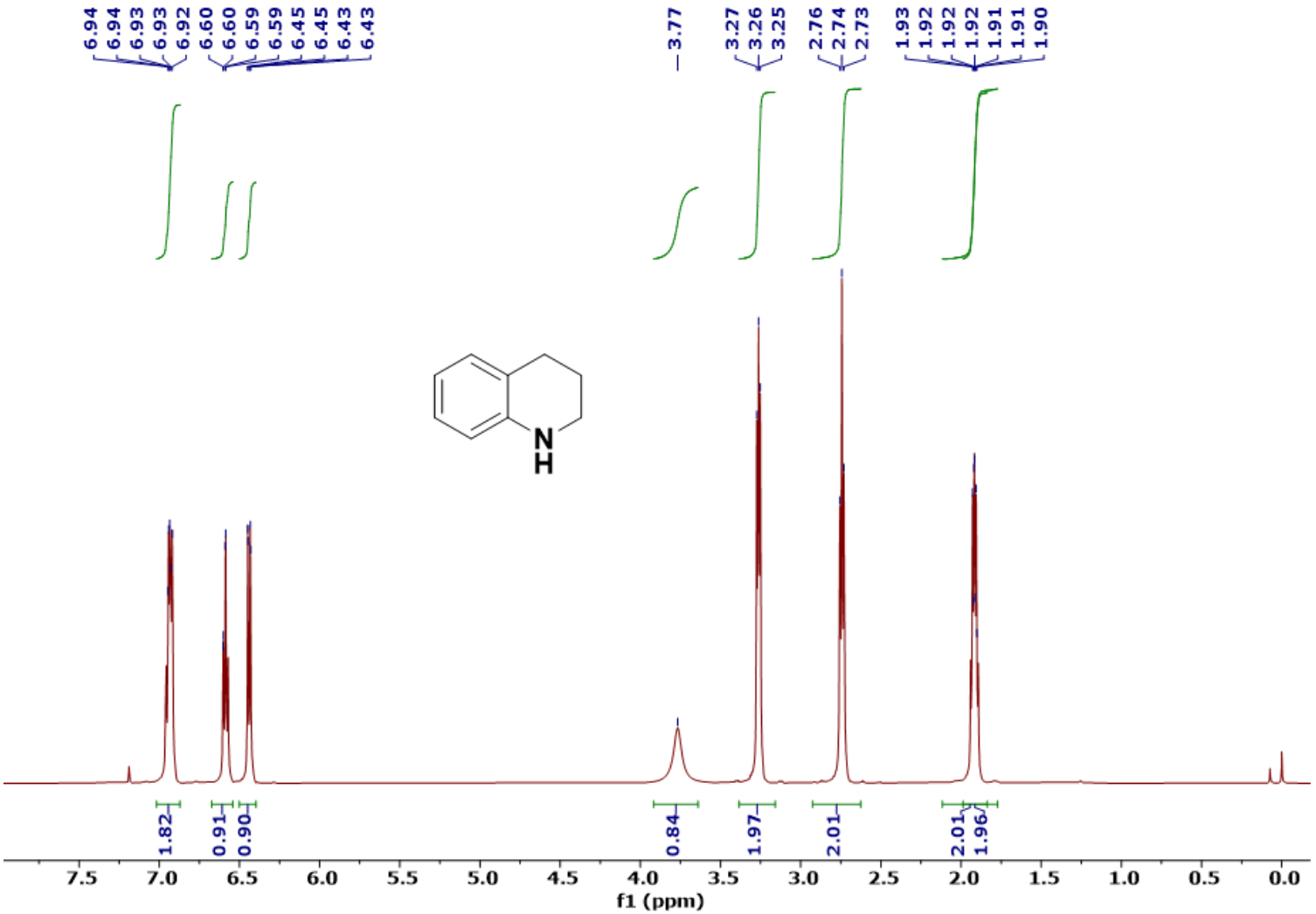


Fig. S23 ^{1}H NMR Spectrum of 1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

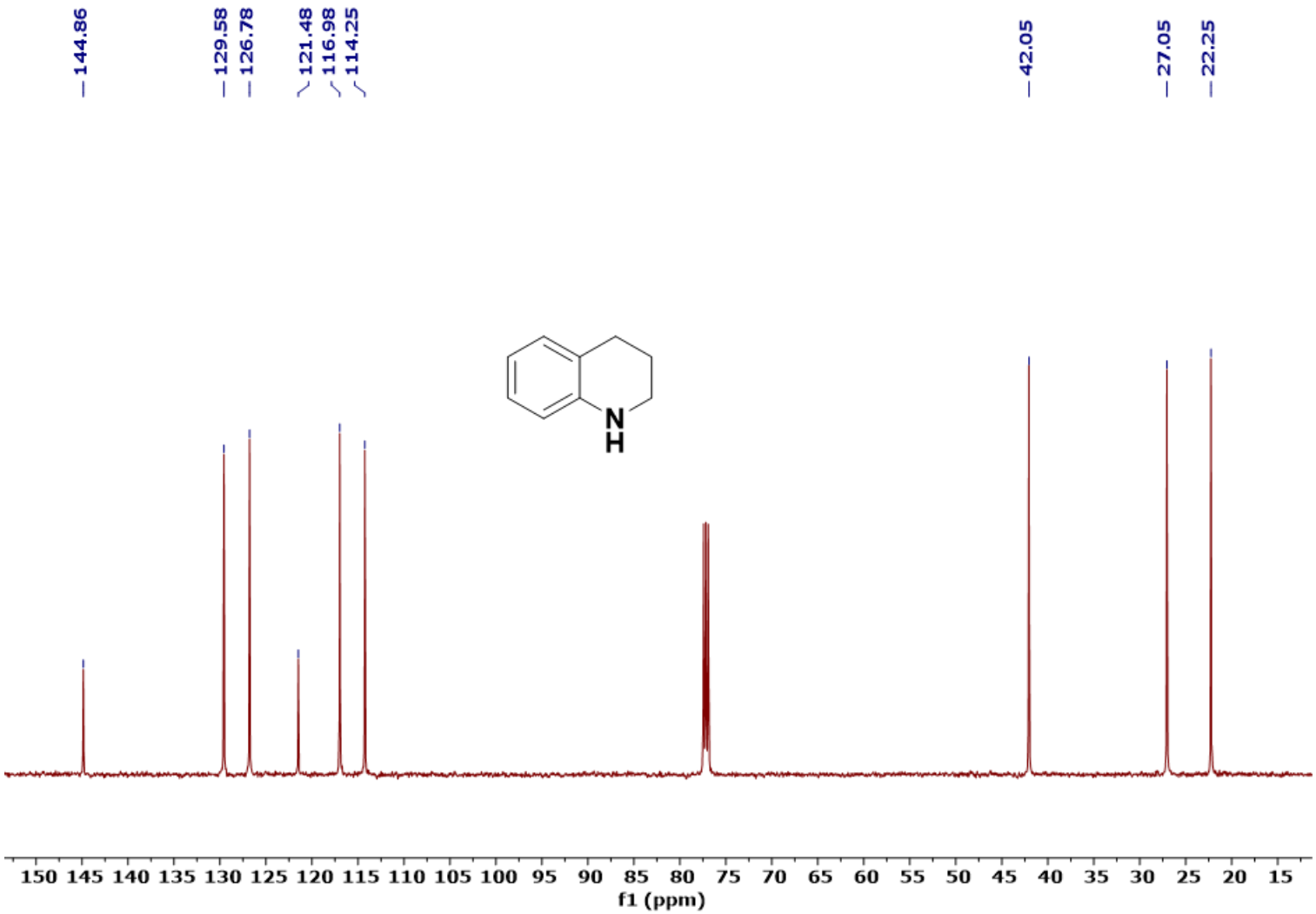


Fig. S24 ^{13}C NMR Spectrum of 1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

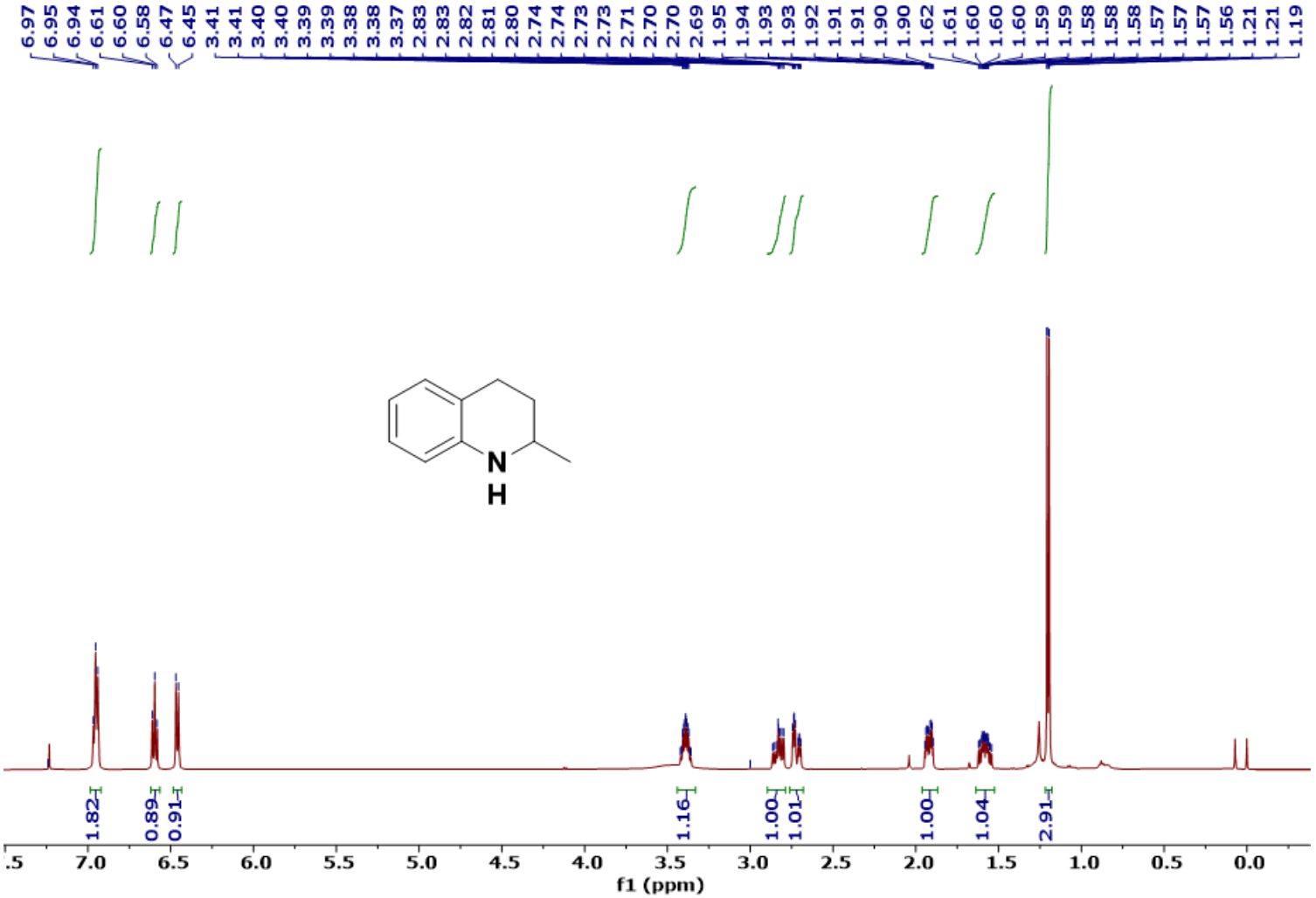


Fig. S25 ^{1}H NMR Spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

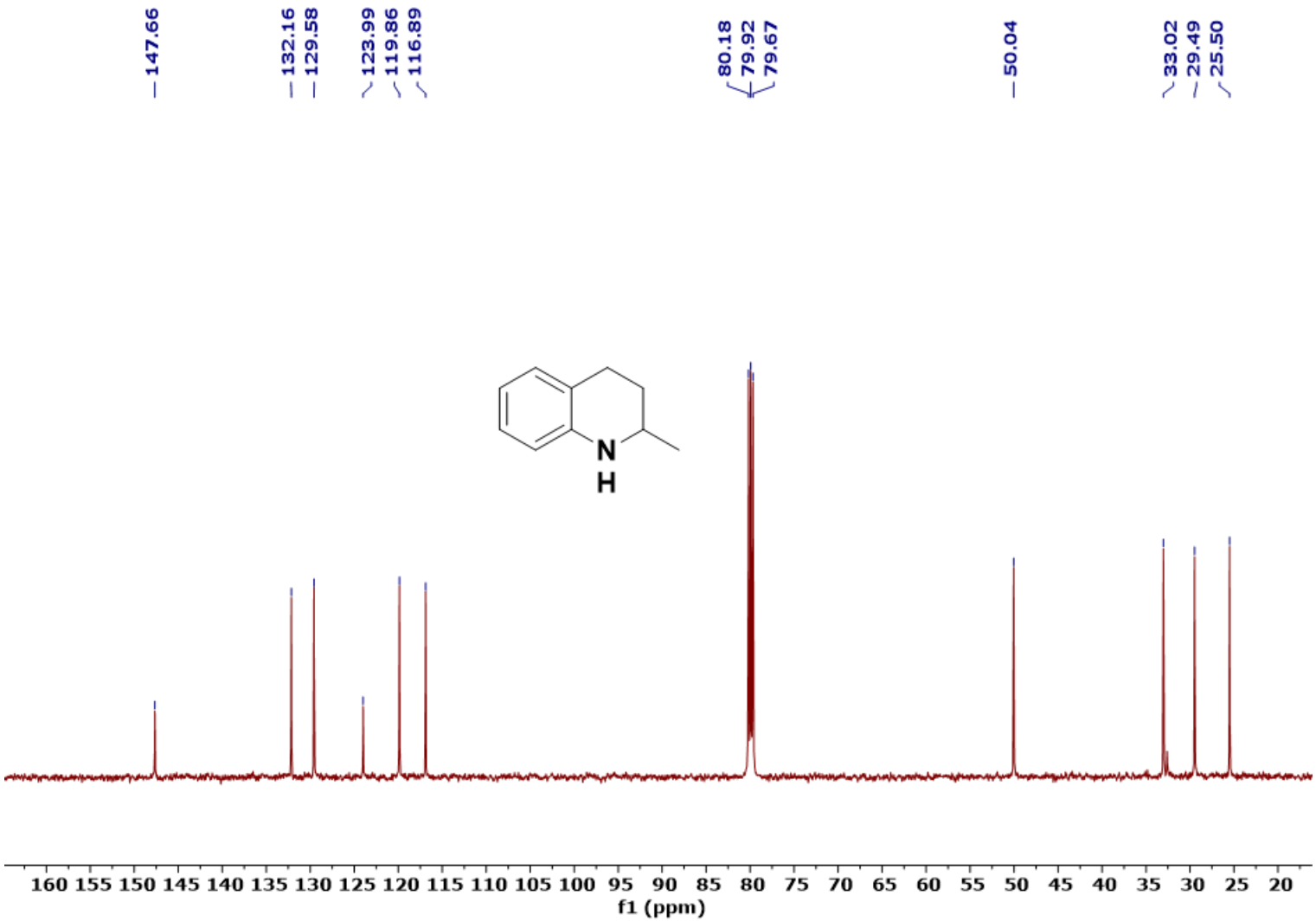


Fig. S26 ^{13}C NMR Spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

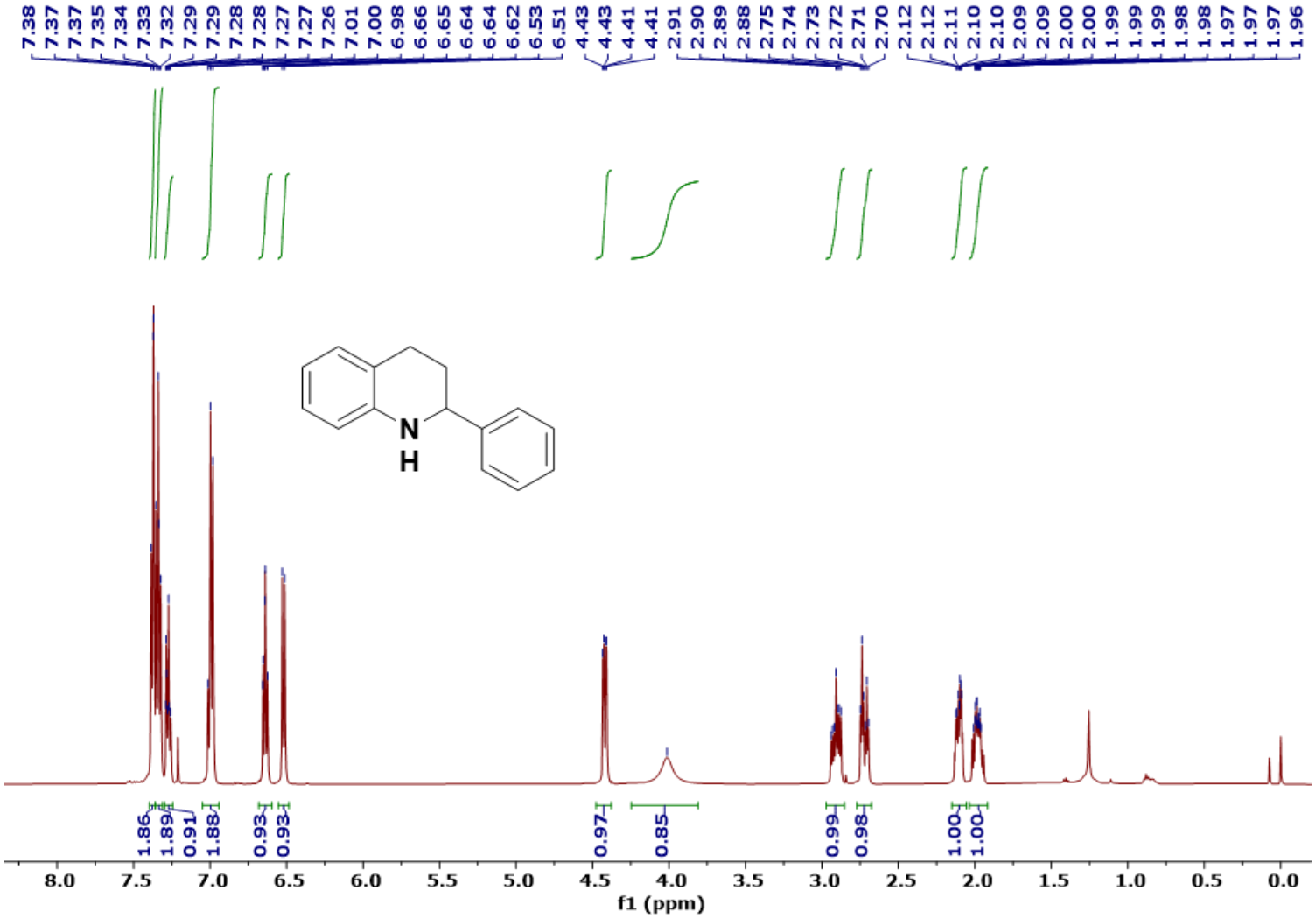


Fig. S27 ^{1}H NMR Spectrum of 2-phenyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

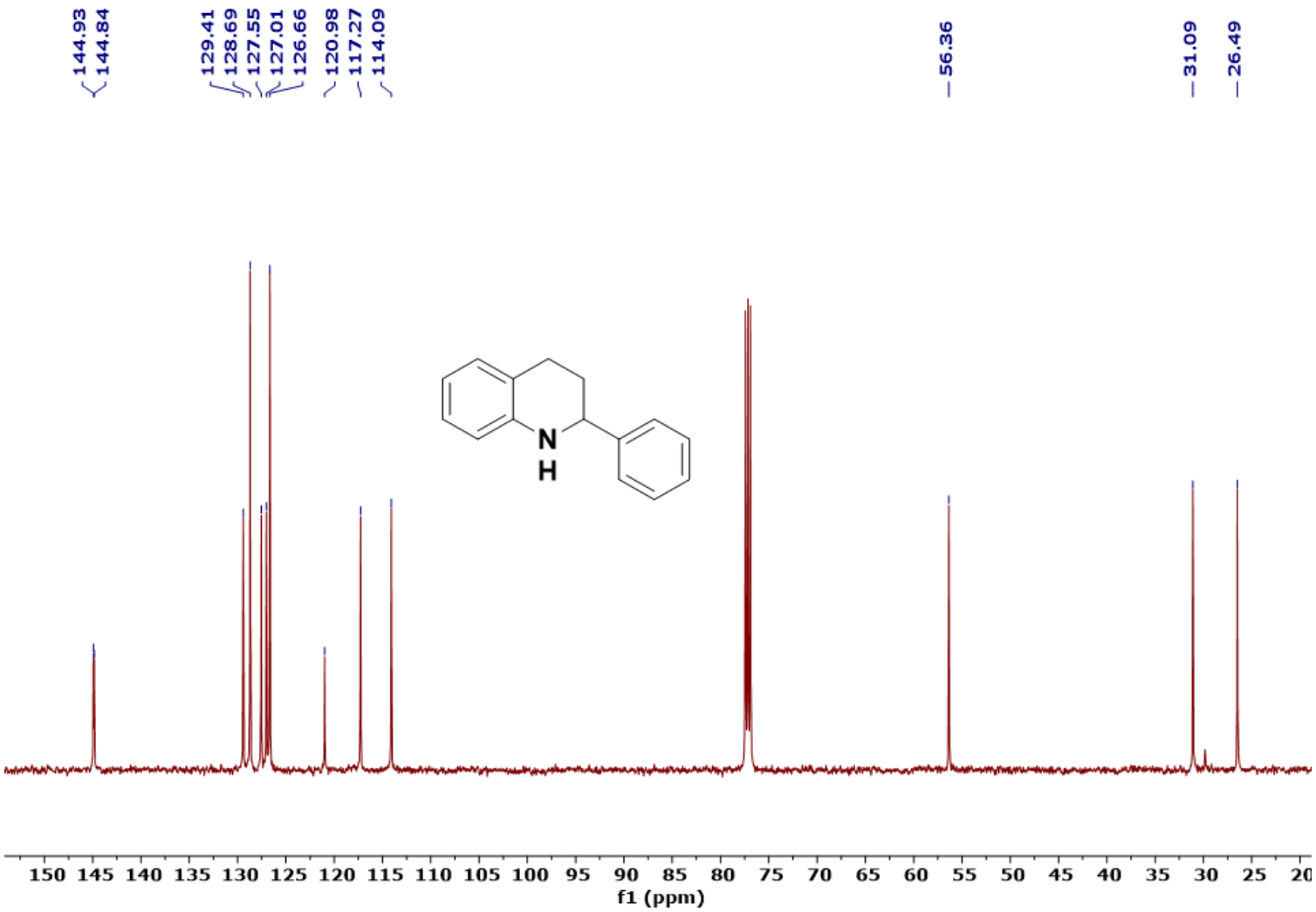


Fig. S28 ^{13}C NMR Spectrum of 2-phenyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

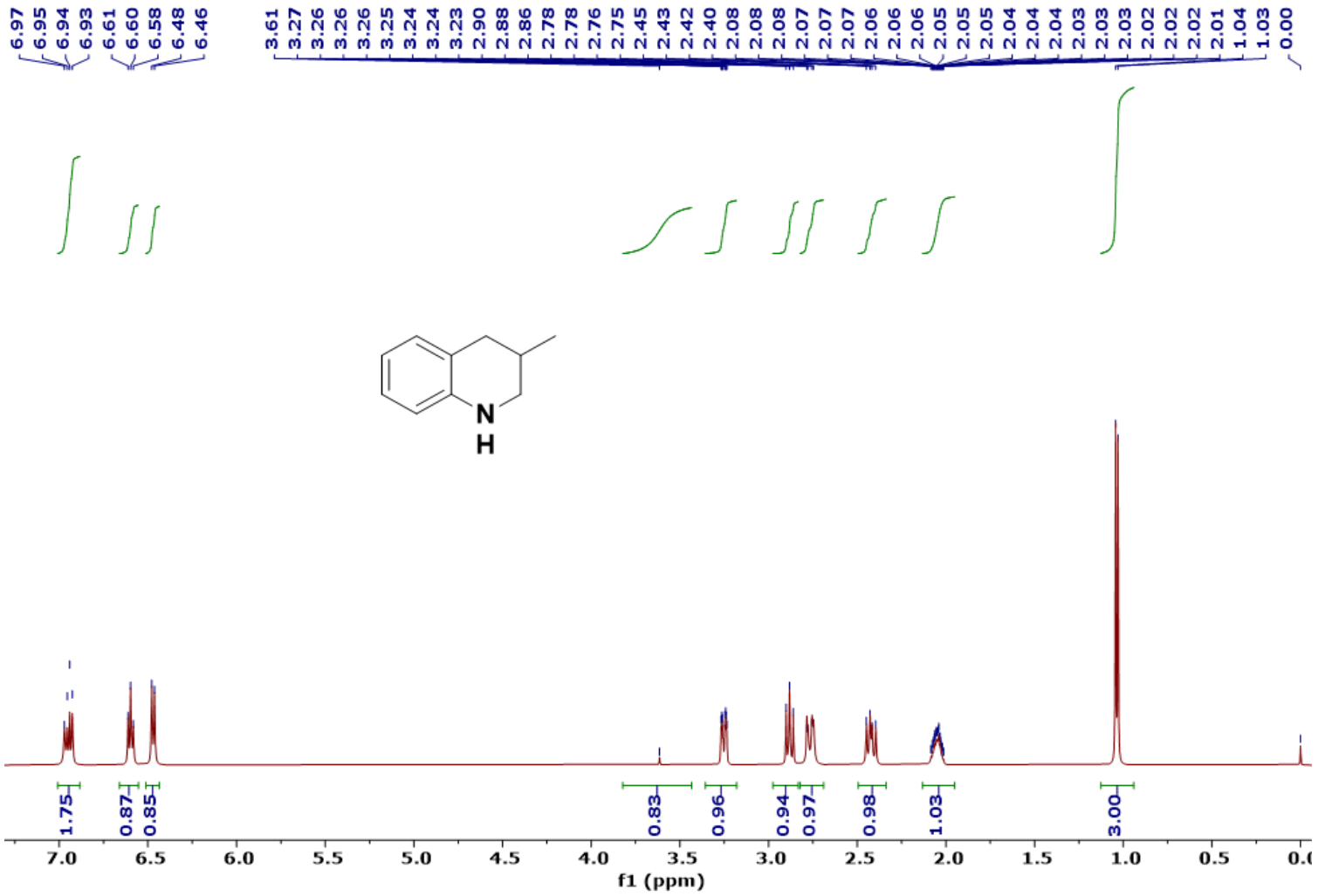


Fig. S29 ^{1}H NMR Spectrum of 3-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

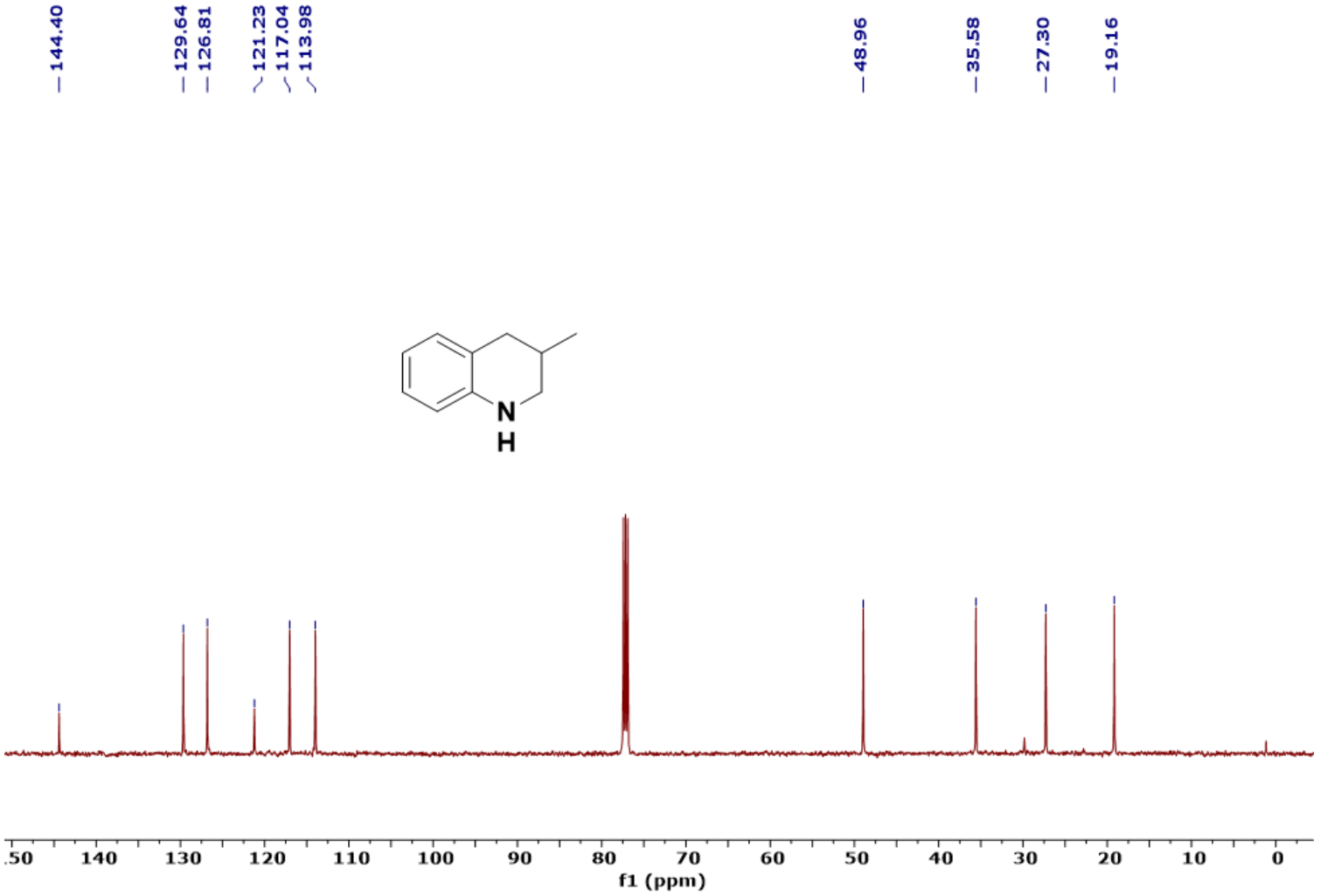


Fig. S30 ^{13}C NMR Spectrum of 3-methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

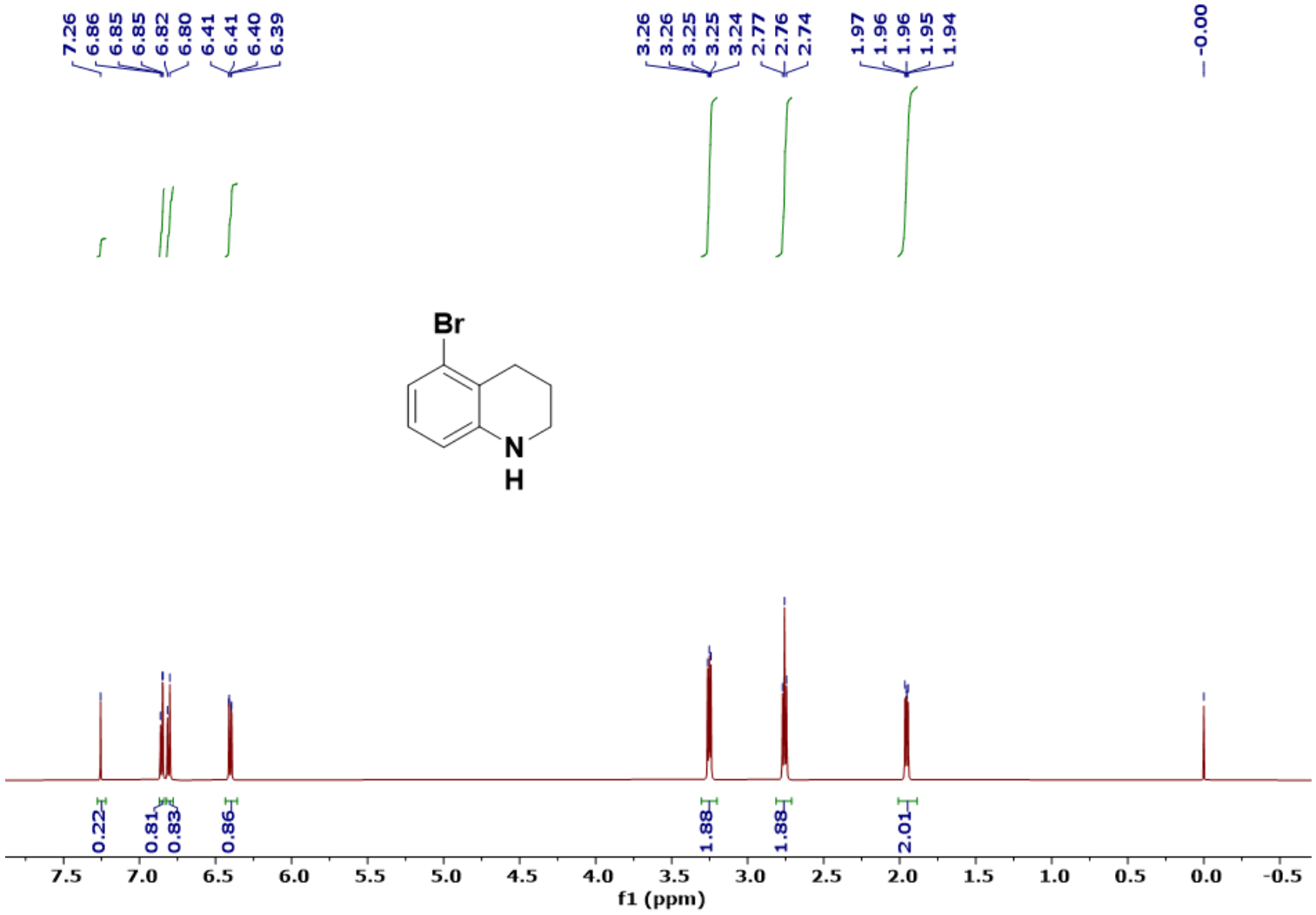


Fig. S31 ^{1}H NMR Spectrum of 5-bromo-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

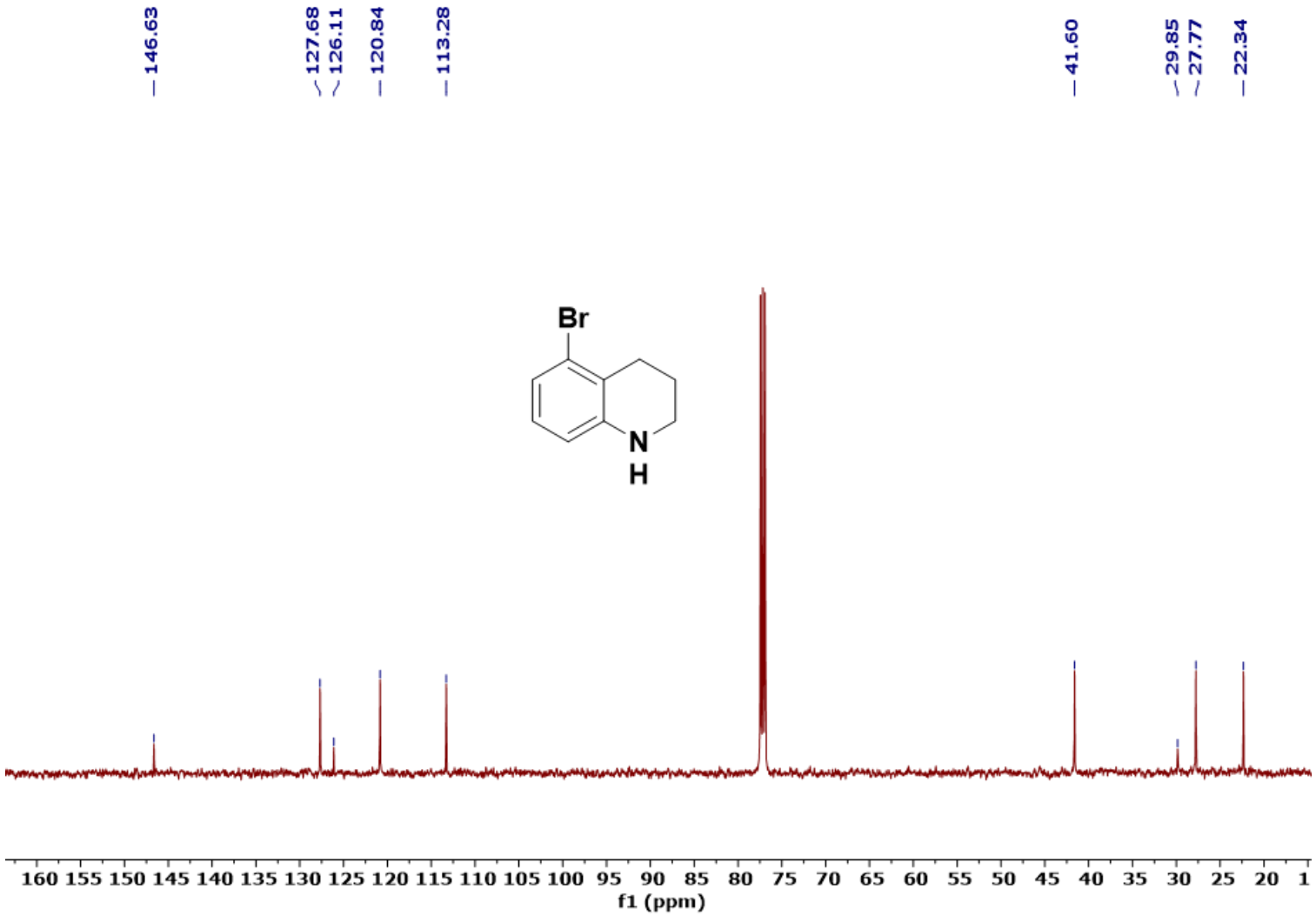


Fig. S32 ^{13}C NMR Spectrum of 5-bromo-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

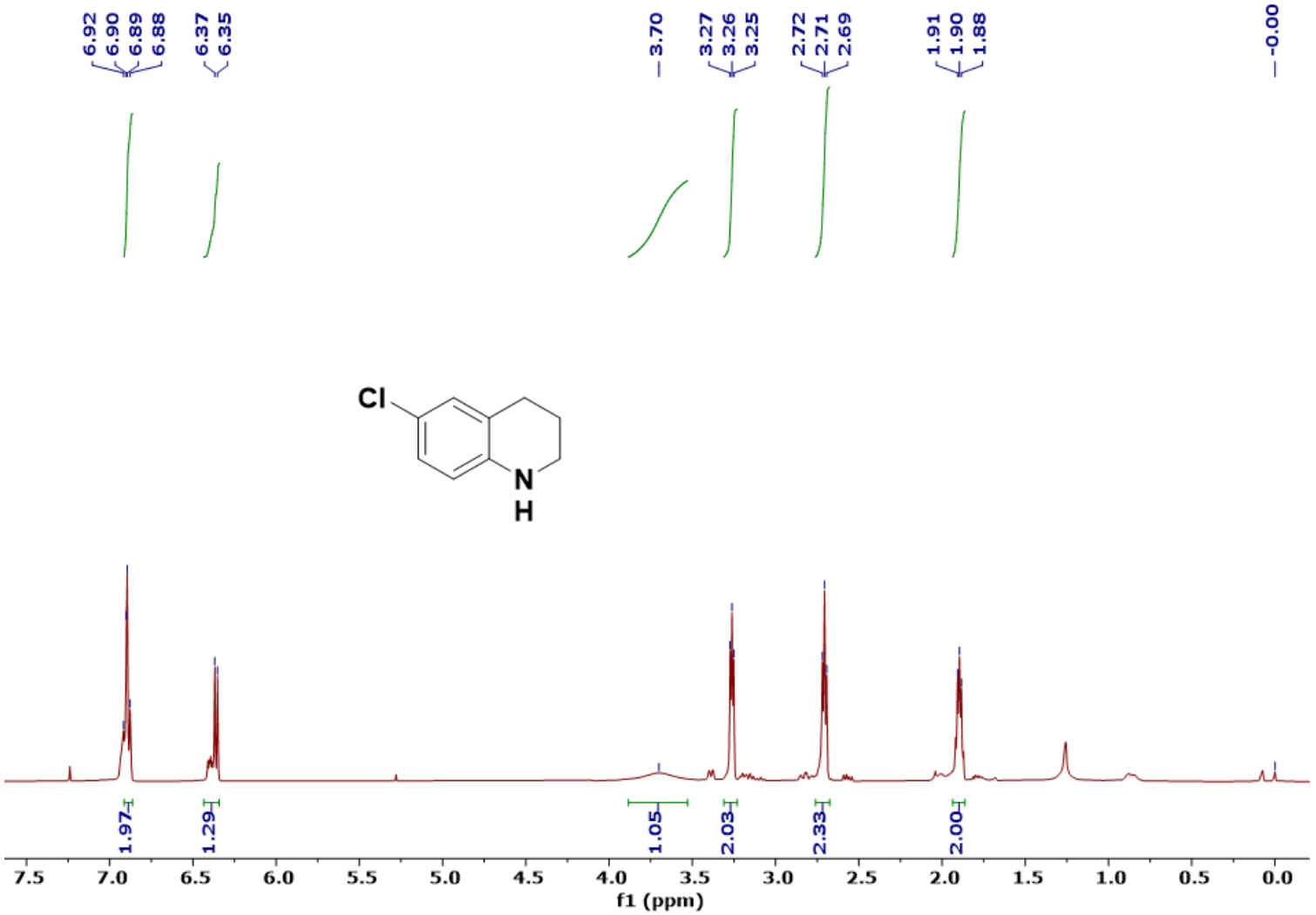


Fig. S33 ^{1}H NMR Spectrum of 6-chloro-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

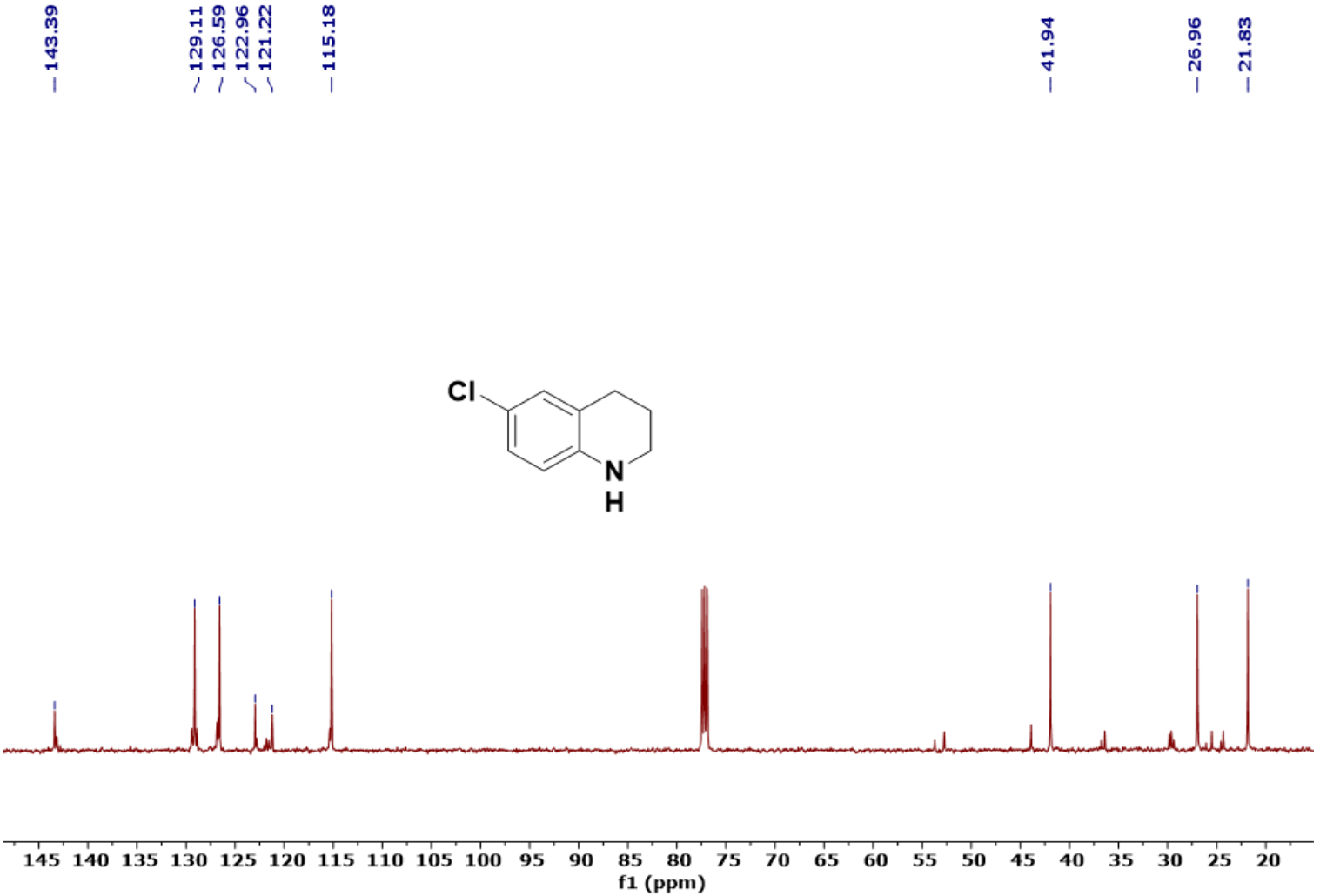


Fig. S34 ^{13}C NMR Spectrum of 6-chloro-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

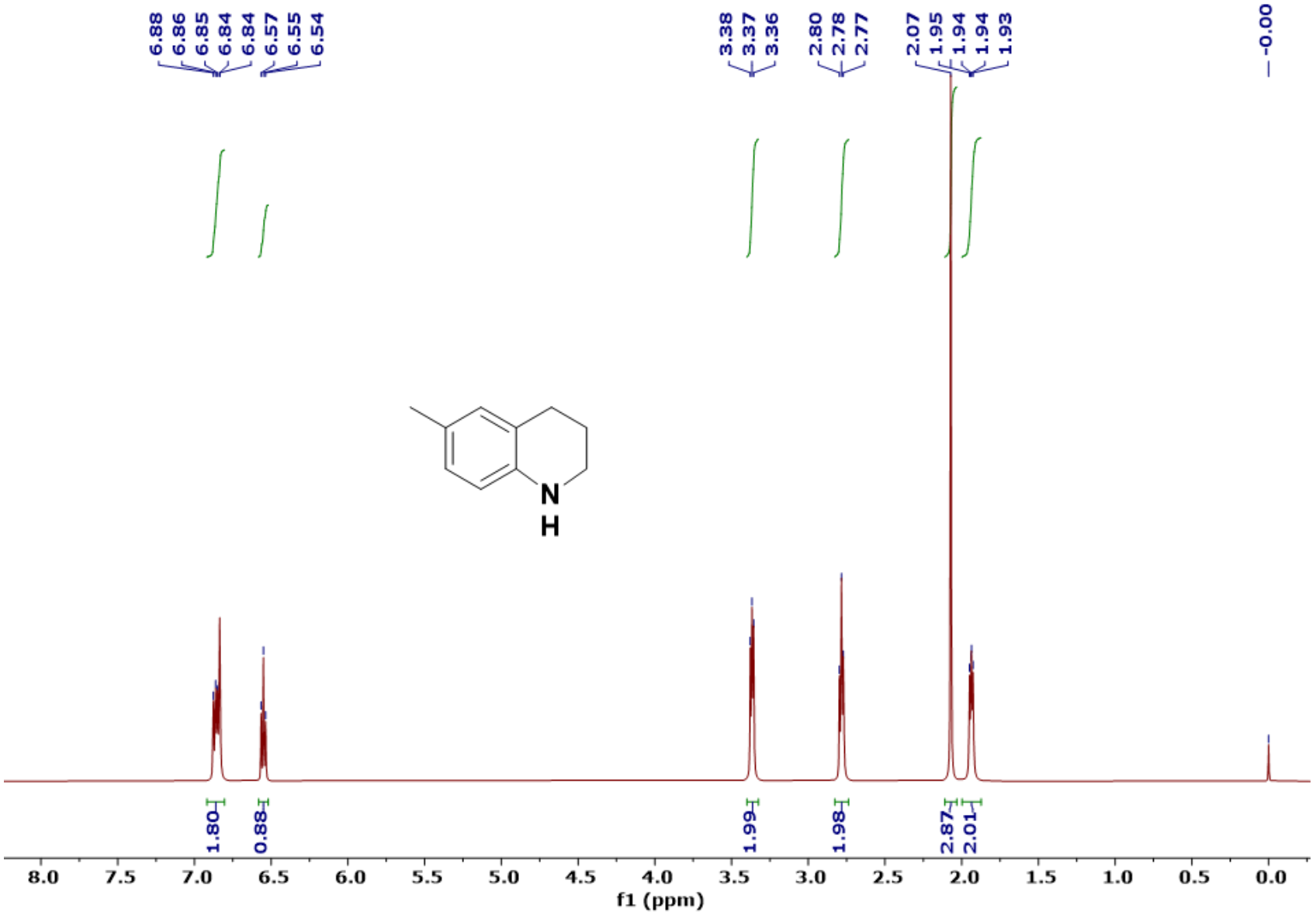


Fig. S35 ^{1}H NMR Spectrum of 6-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

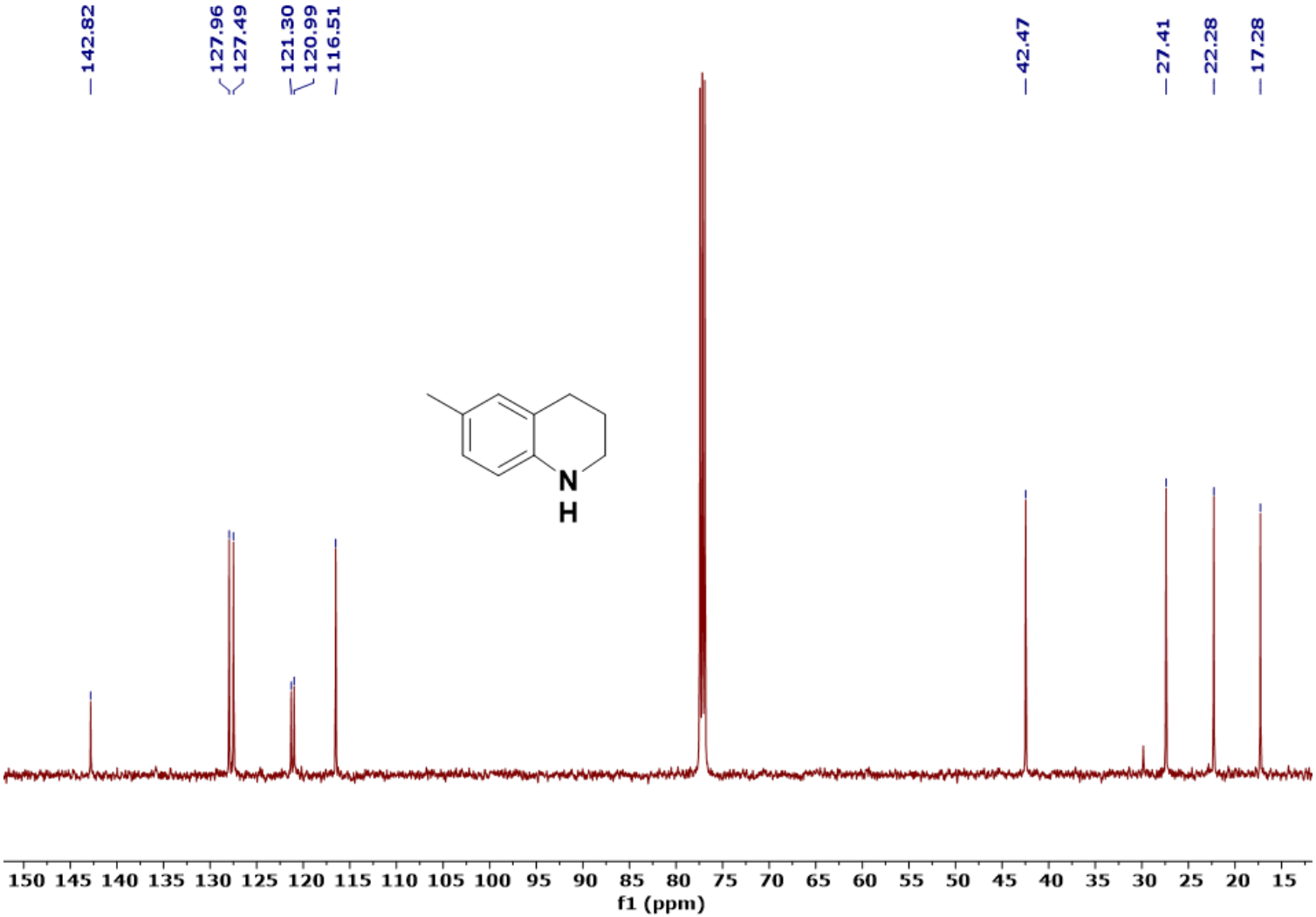


Fig. S36 ^{13}C NMR Spectrum of 6-methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

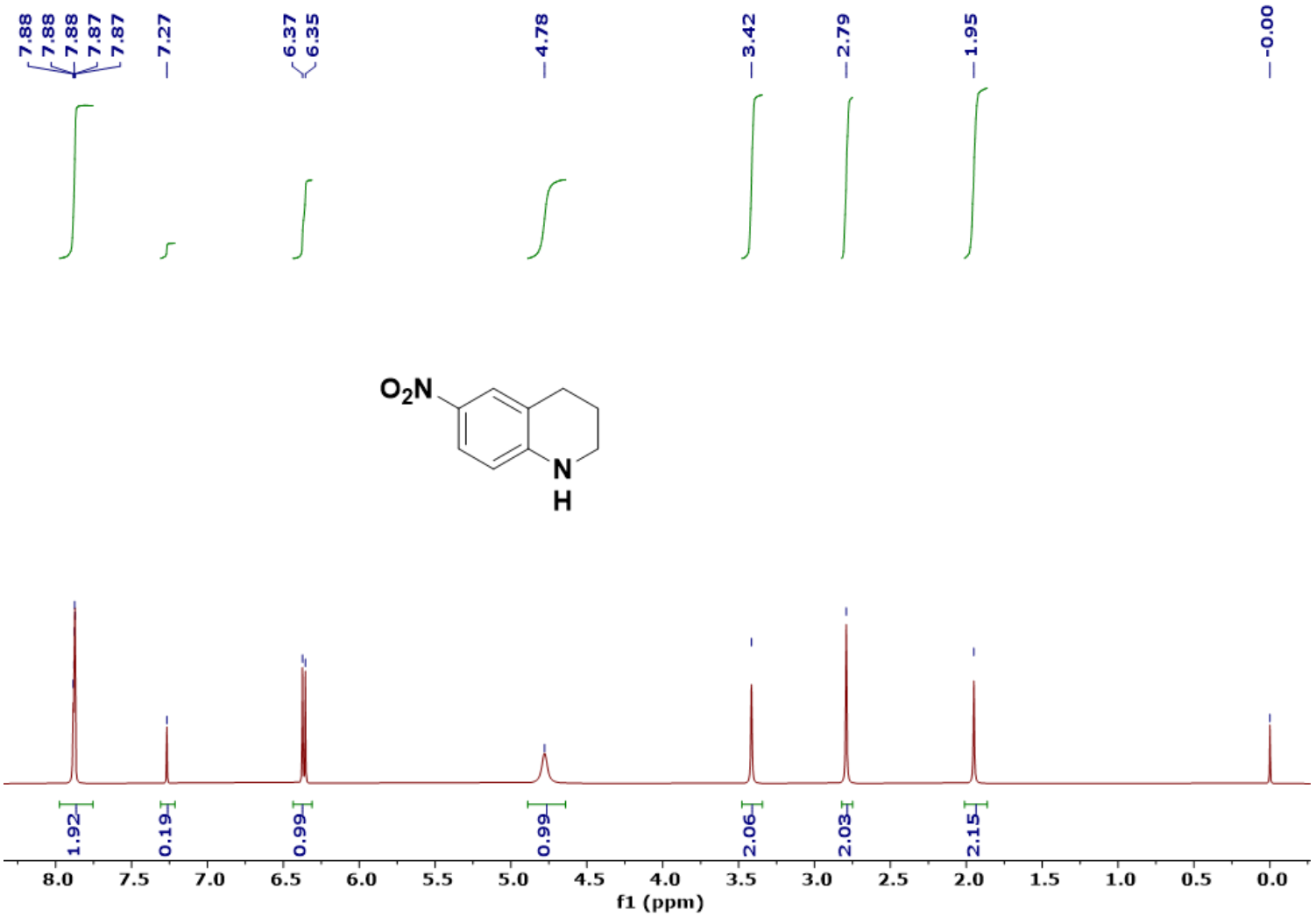


Fig. S37 ^{1}H NMR Spectrum of 6-nitro-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

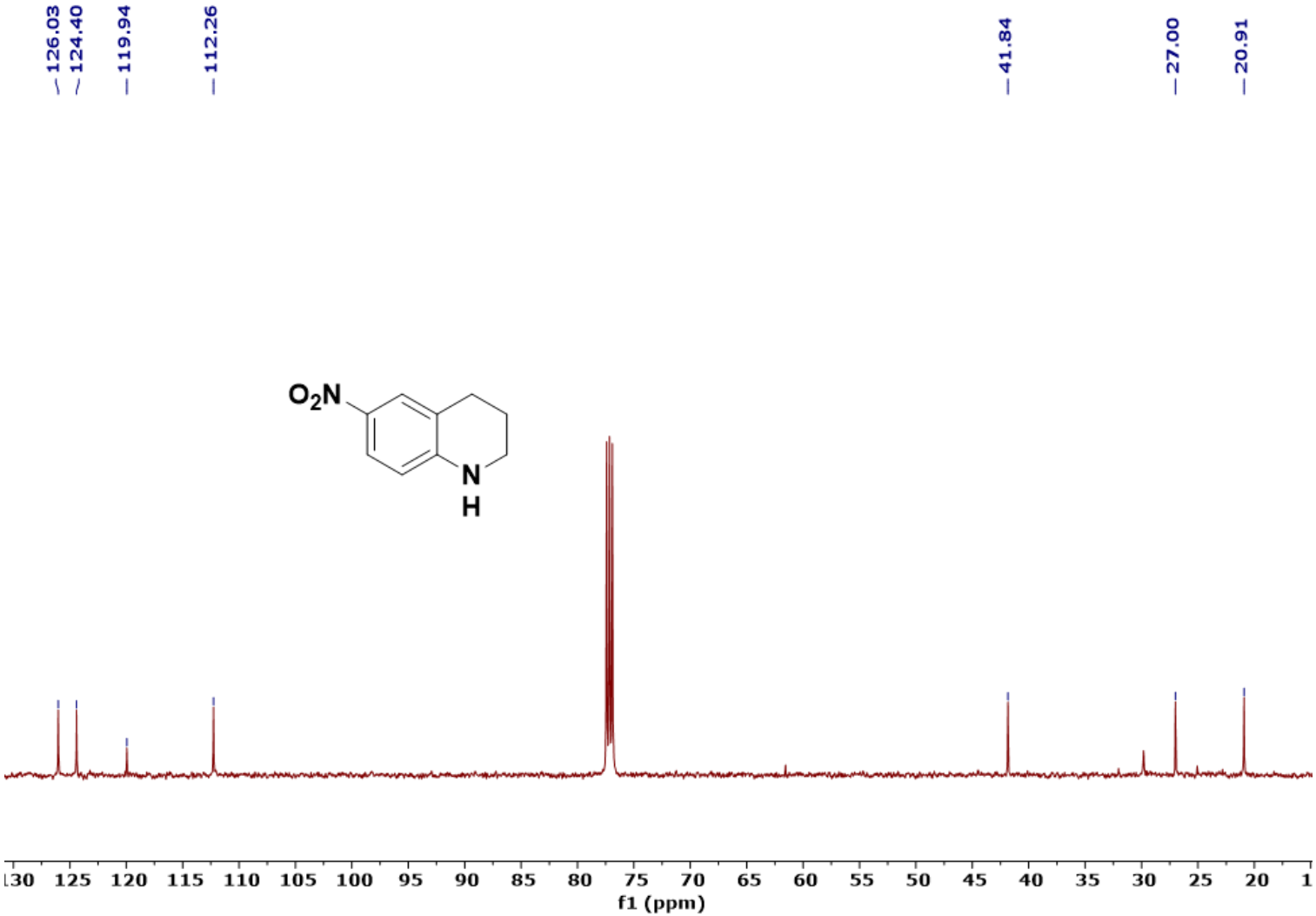


Fig. S38 ^{13}C NMR Spectrum of 6-nitro-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

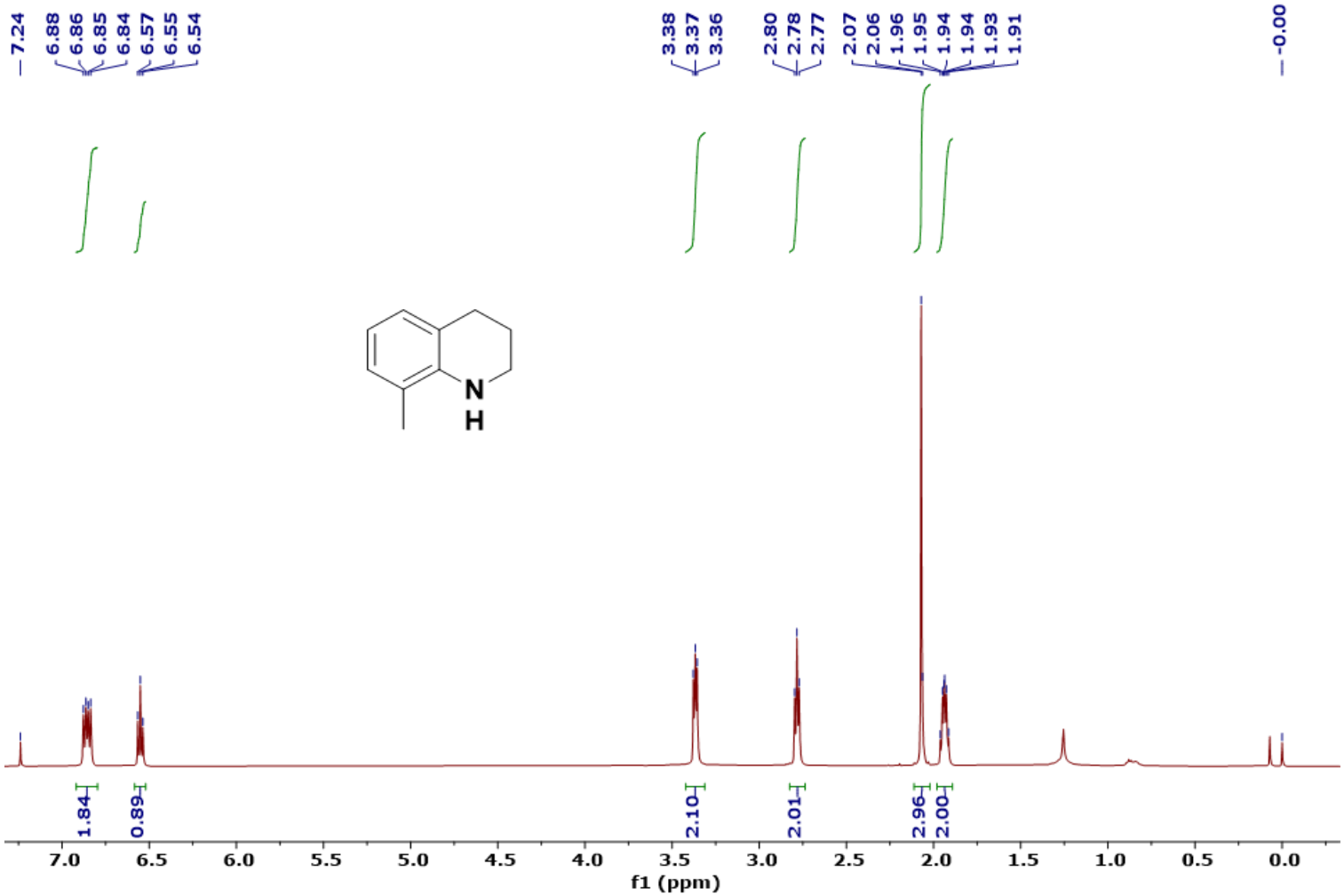


Fig. S39 ^{1}H NMR Spectrum of 8-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

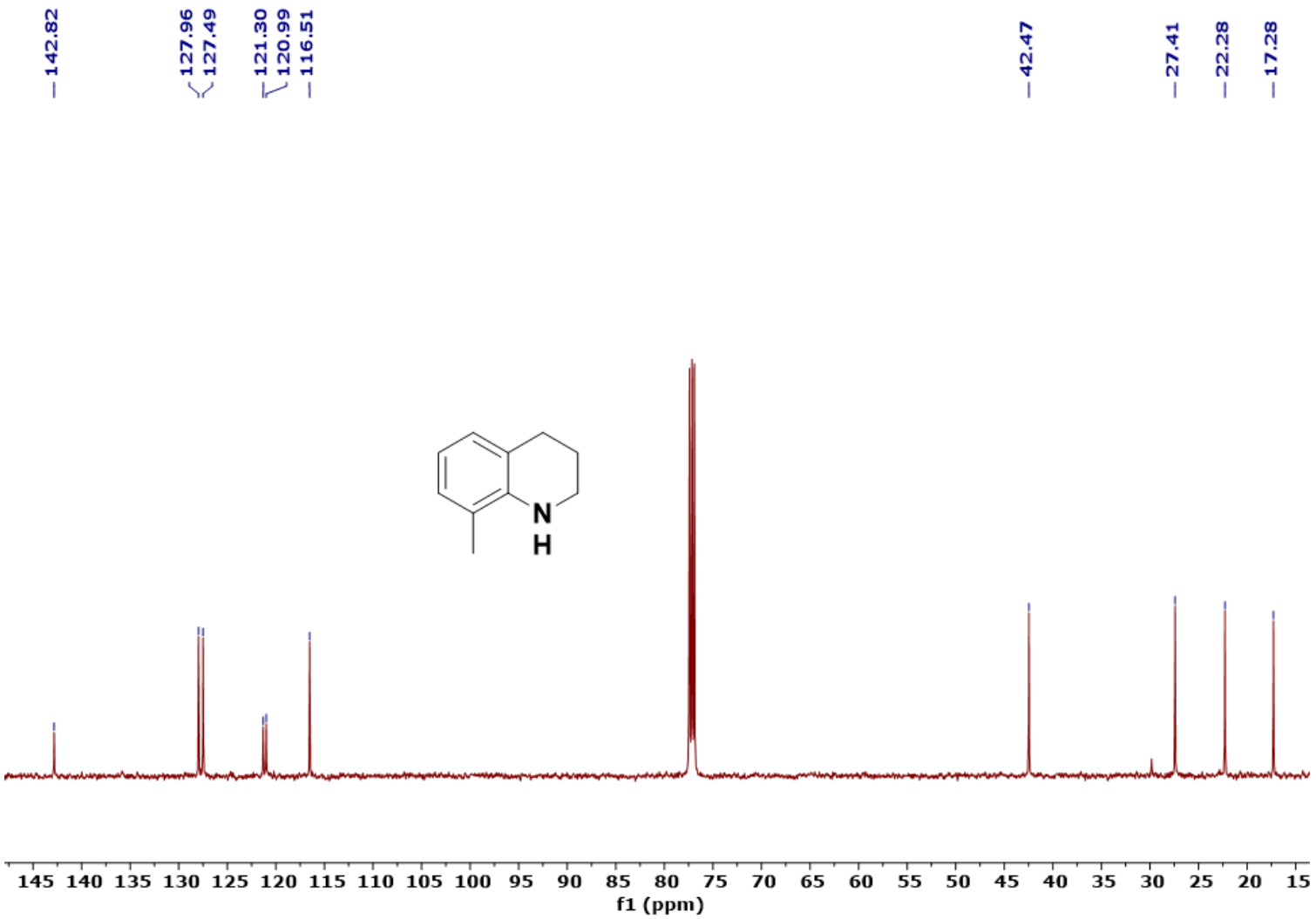


Fig. S40 ^{13}C NMR Spectrum of 8-methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

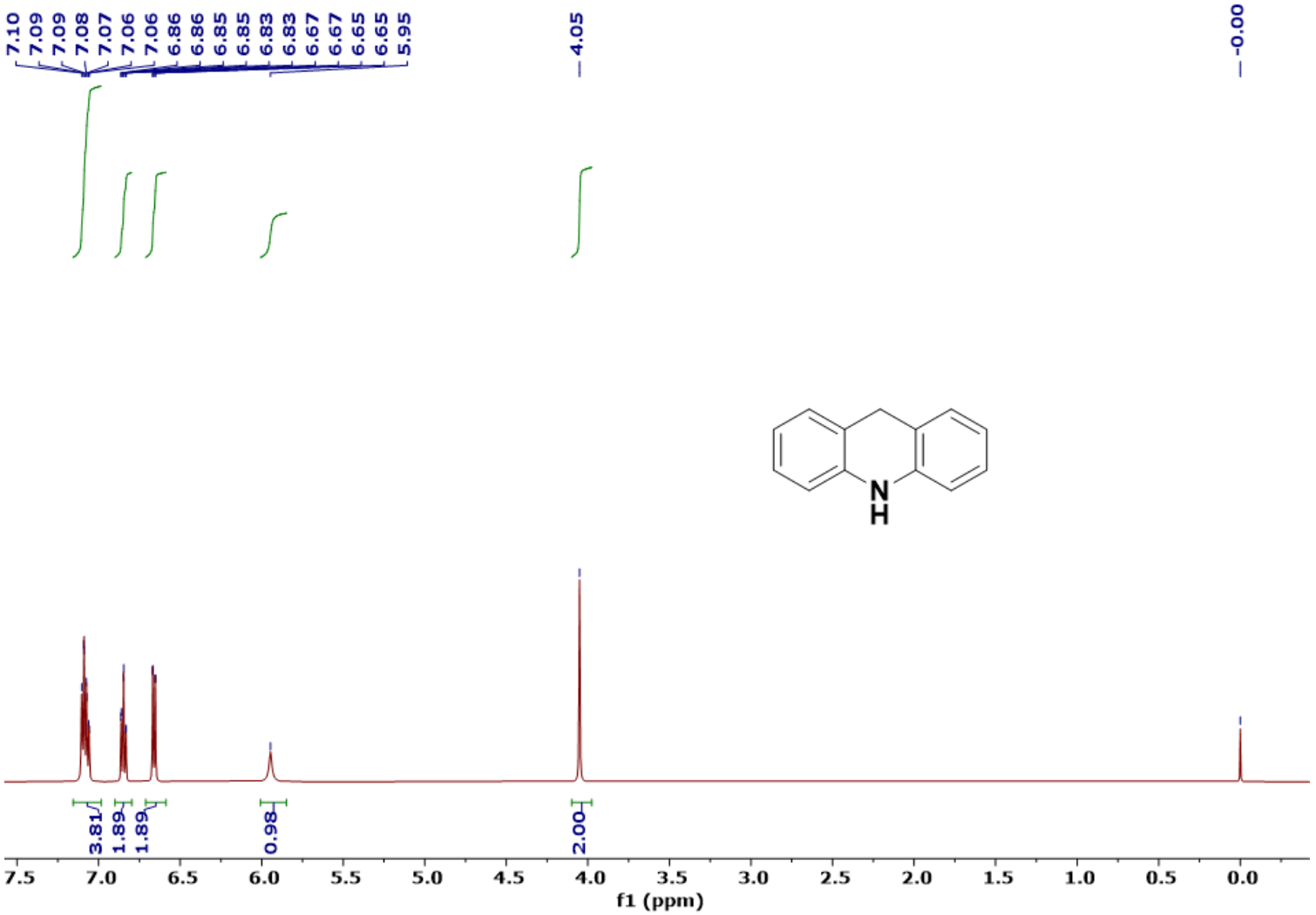


Fig. S41 ^{1}H NMR Spectrum of 9,10-dihydroacridine ($CDCl_3$, 500 MHz, 298K)

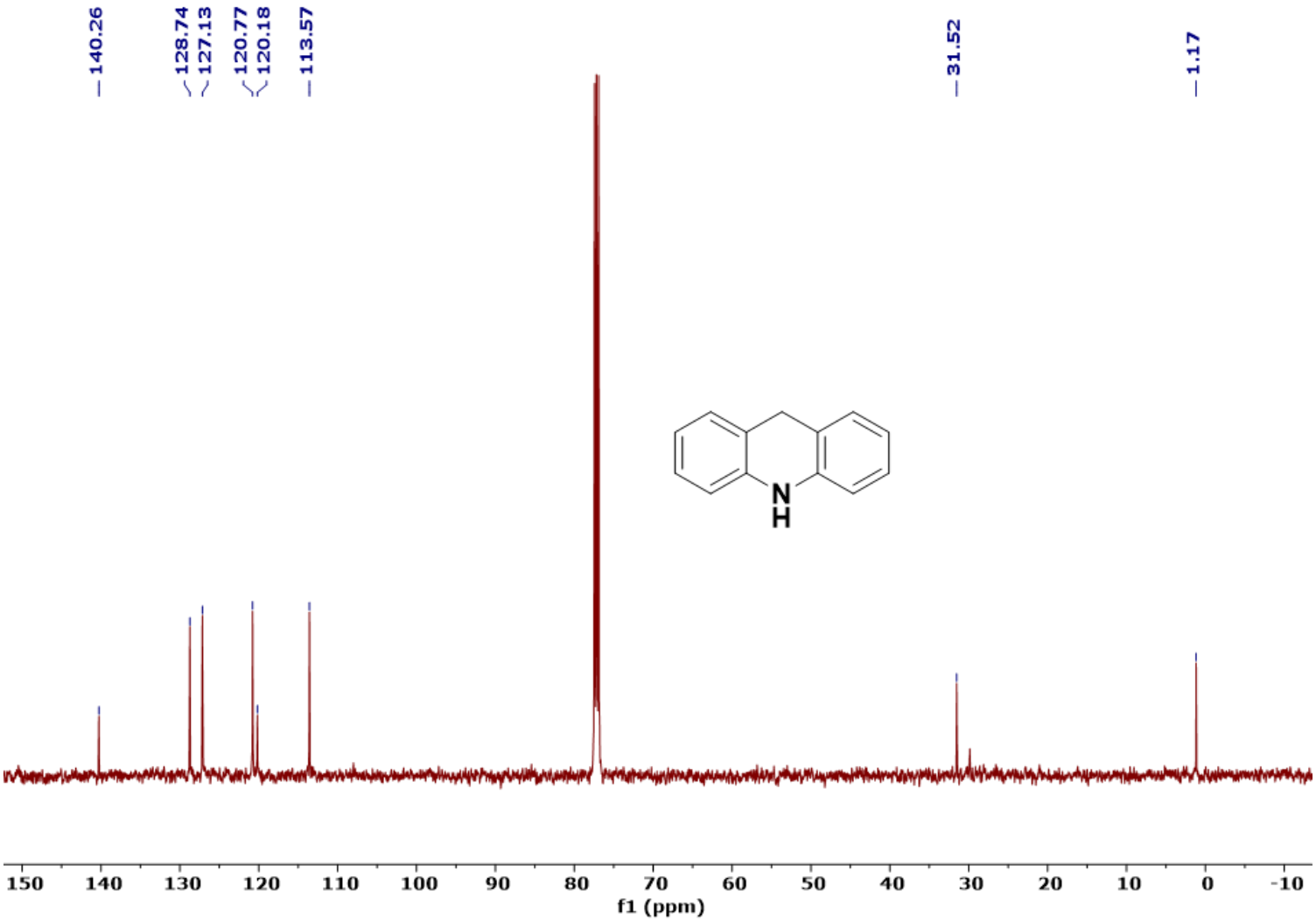


Fig. S42 ^{13}C NMR Spectrum of 9,10-dihydroacridine (CDCl3, 500 MHz, 298K)

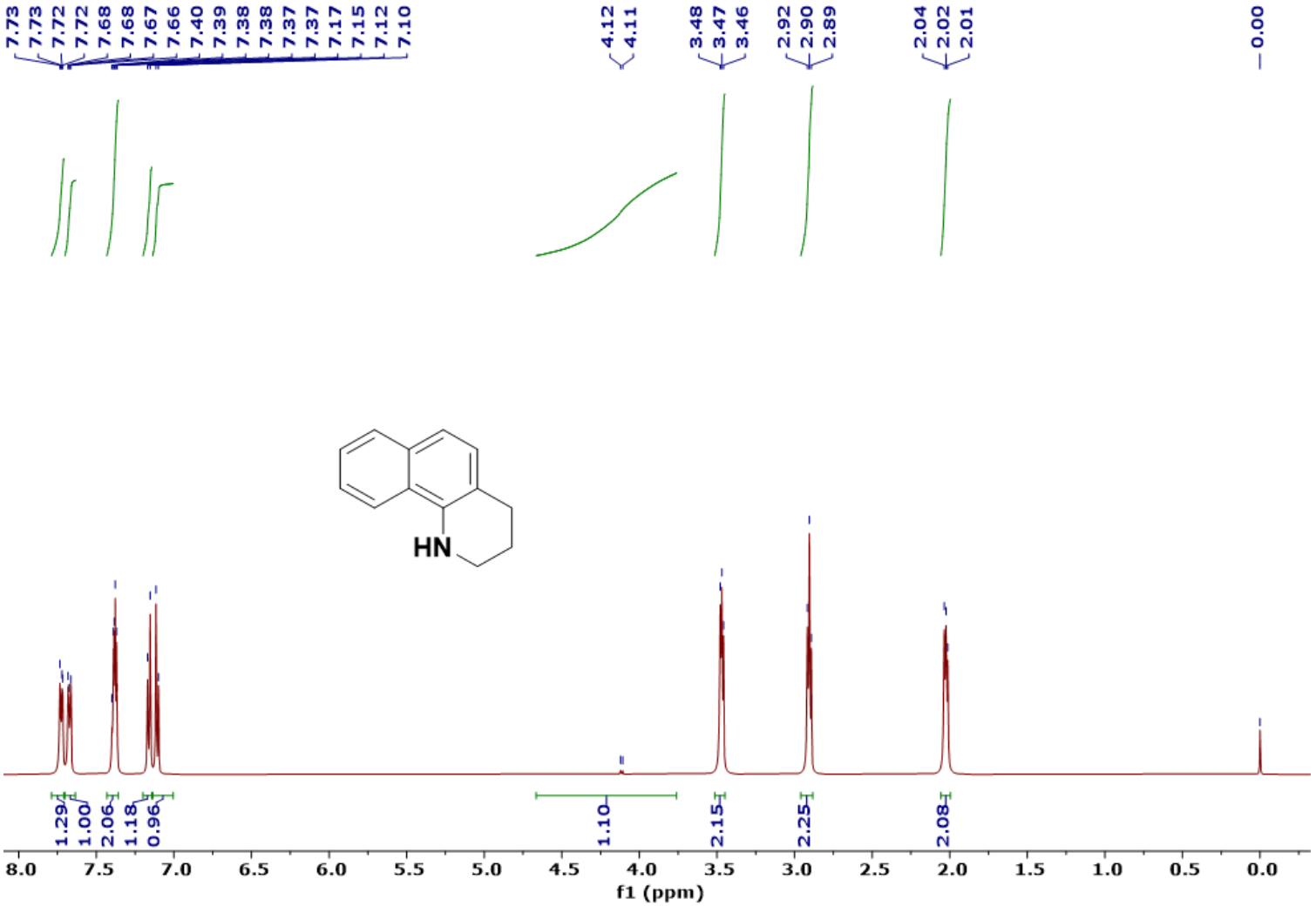


Fig. S43 ^{1}H NMR Spectrum of 1,2,3,4-tetrahydrobenzo[h]quinoline ($CDCl_3$, 500 MHz, 298K)

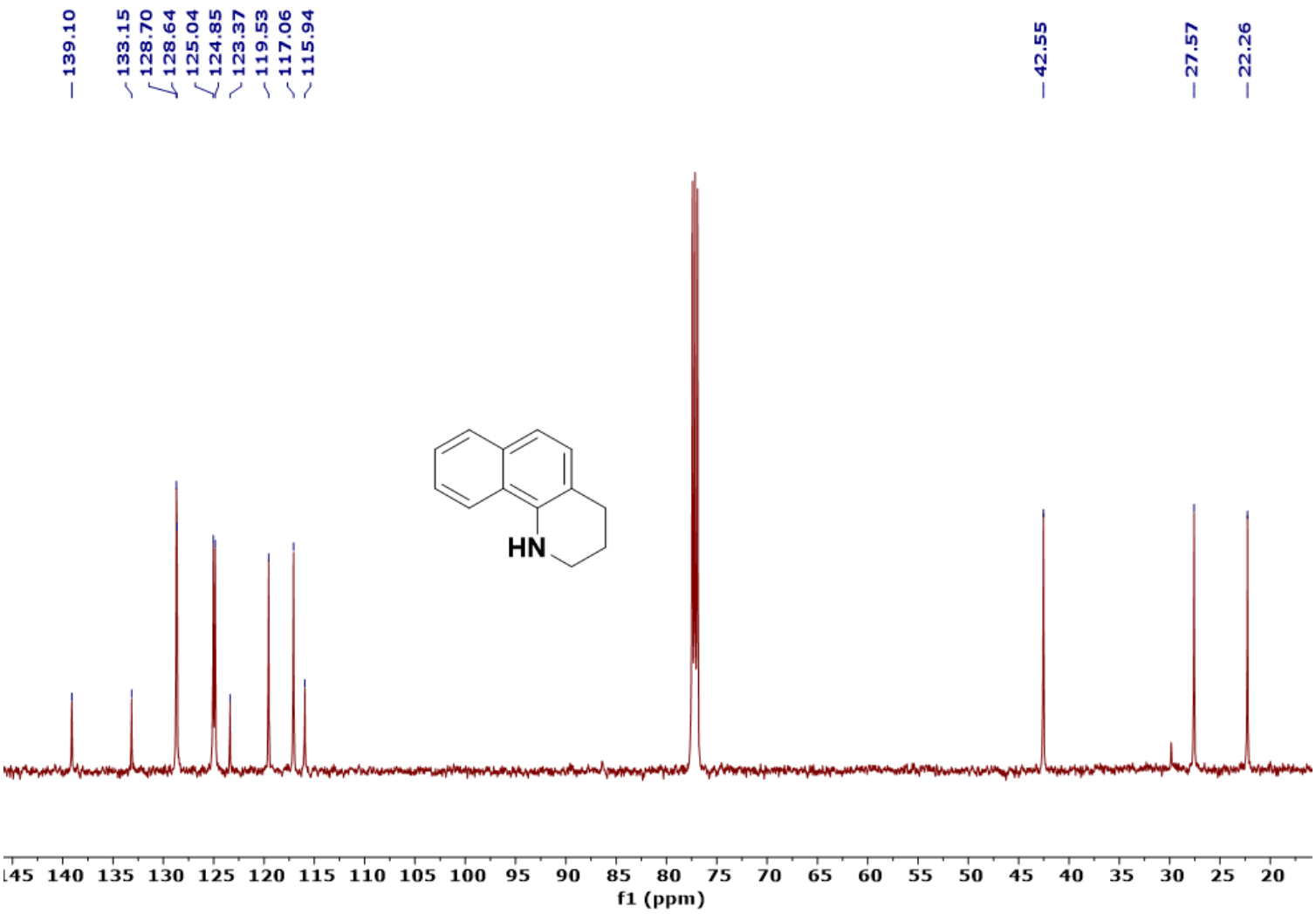


Fig. S44 ^{13}C NMR Spectrum of 1,2,3,4-tetrahydrobenzo[h]quinoline (CDCl3, 500 MHz, 298K)

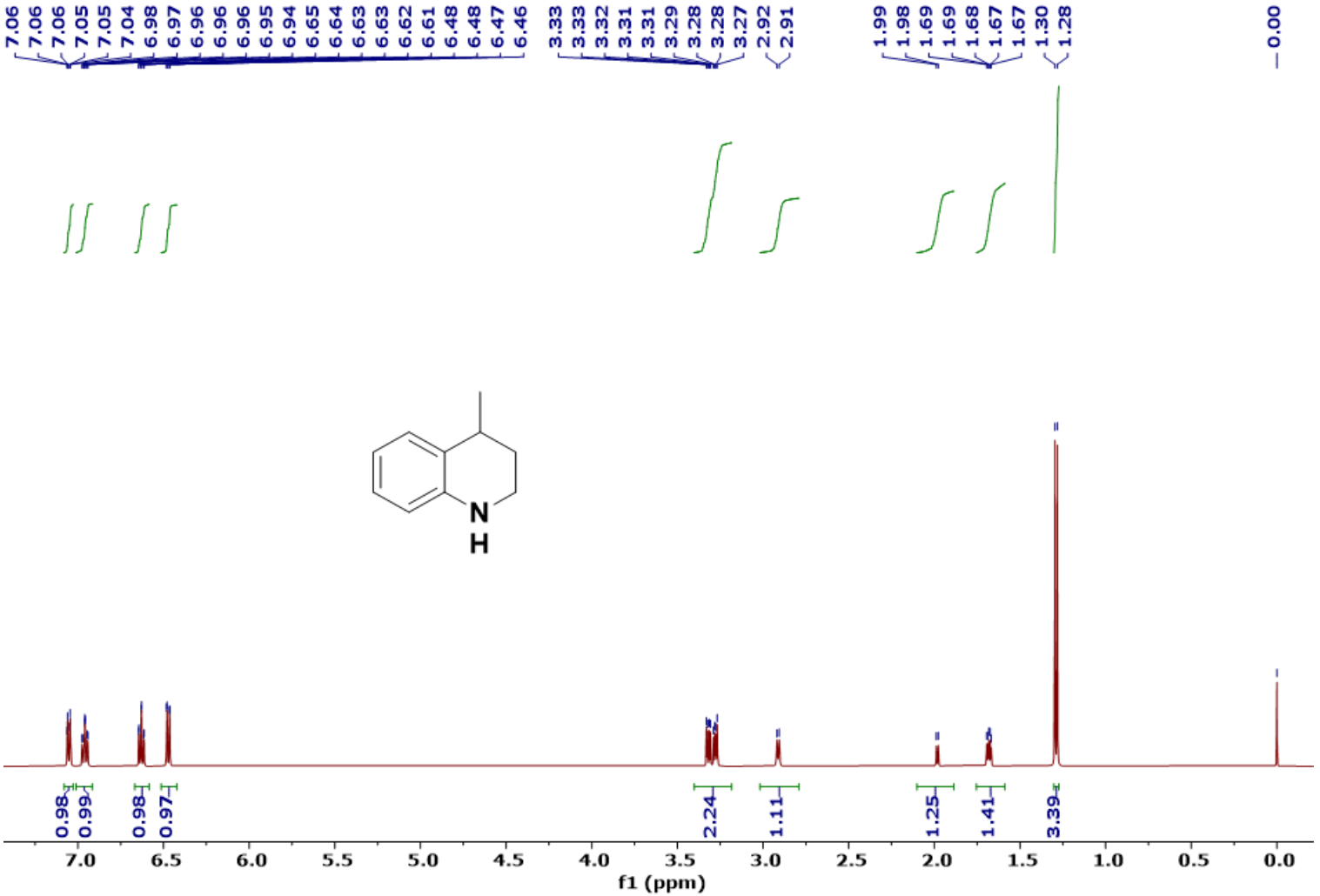


Fig. S45 ^{1}H NMR Spectrum of 4-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

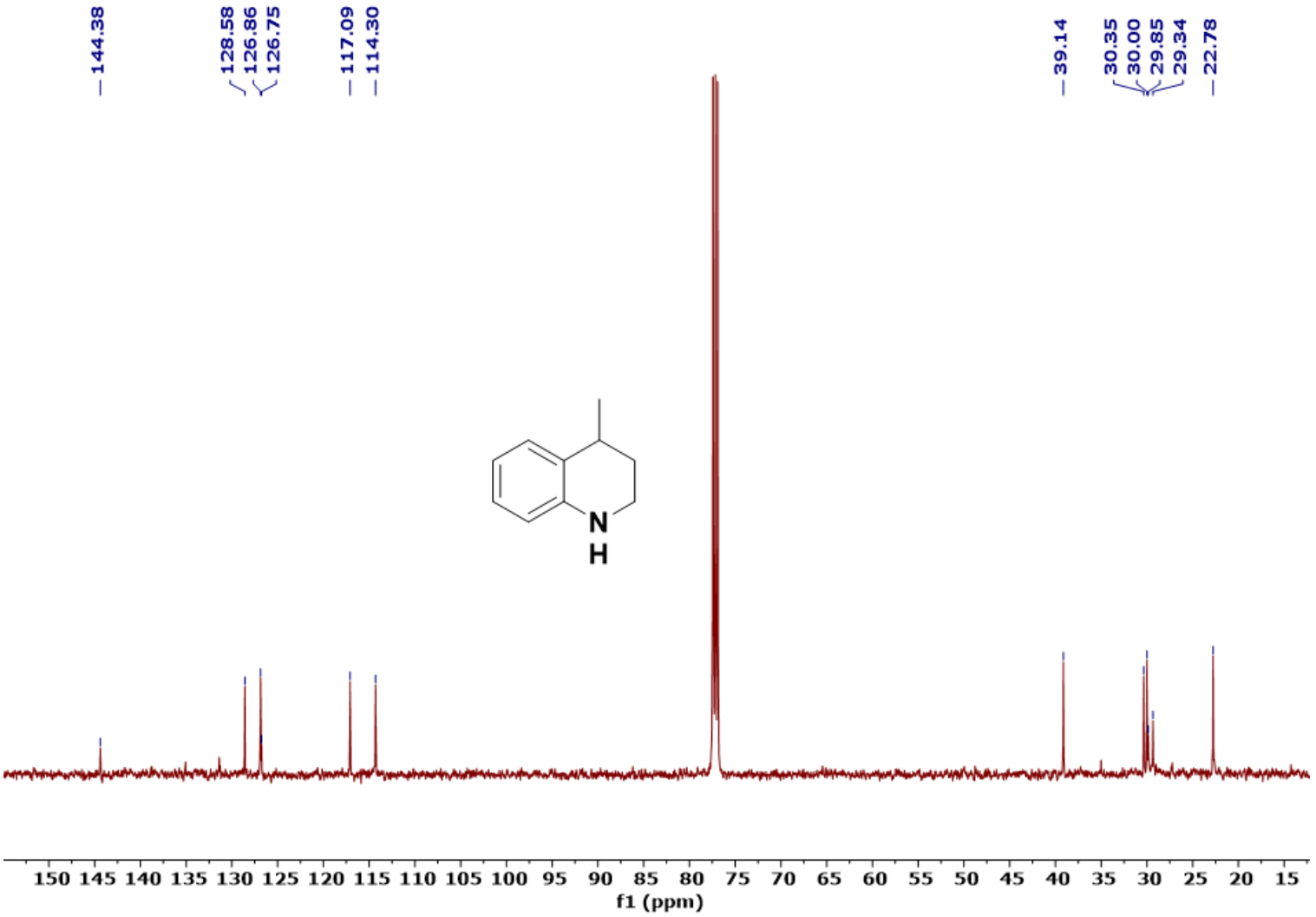


Fig. S46 ^{13}C NMR Spectrum of 4-methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

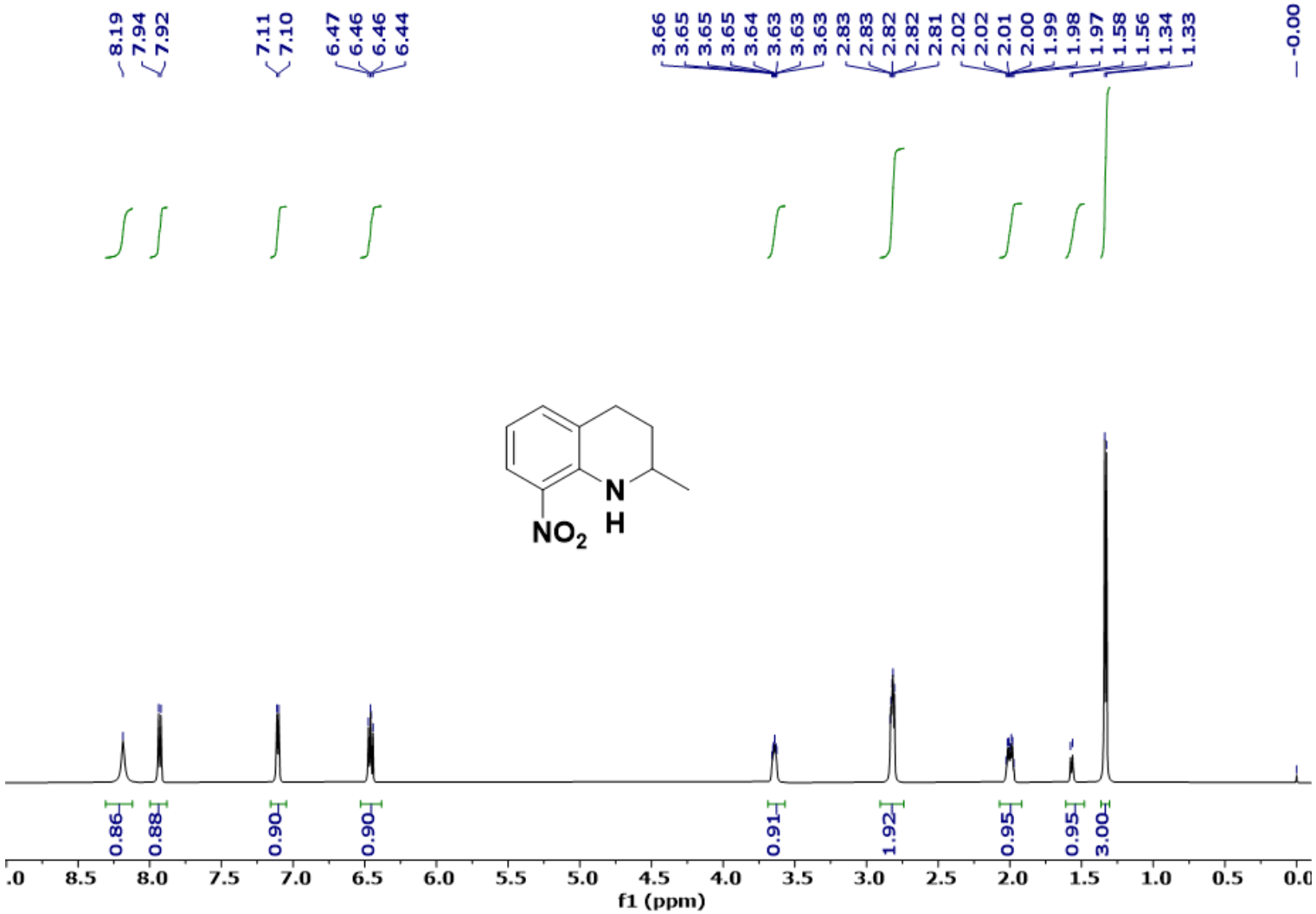


Fig. S47 ^{1}H NMR Spectrum of 8-nitro-2-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

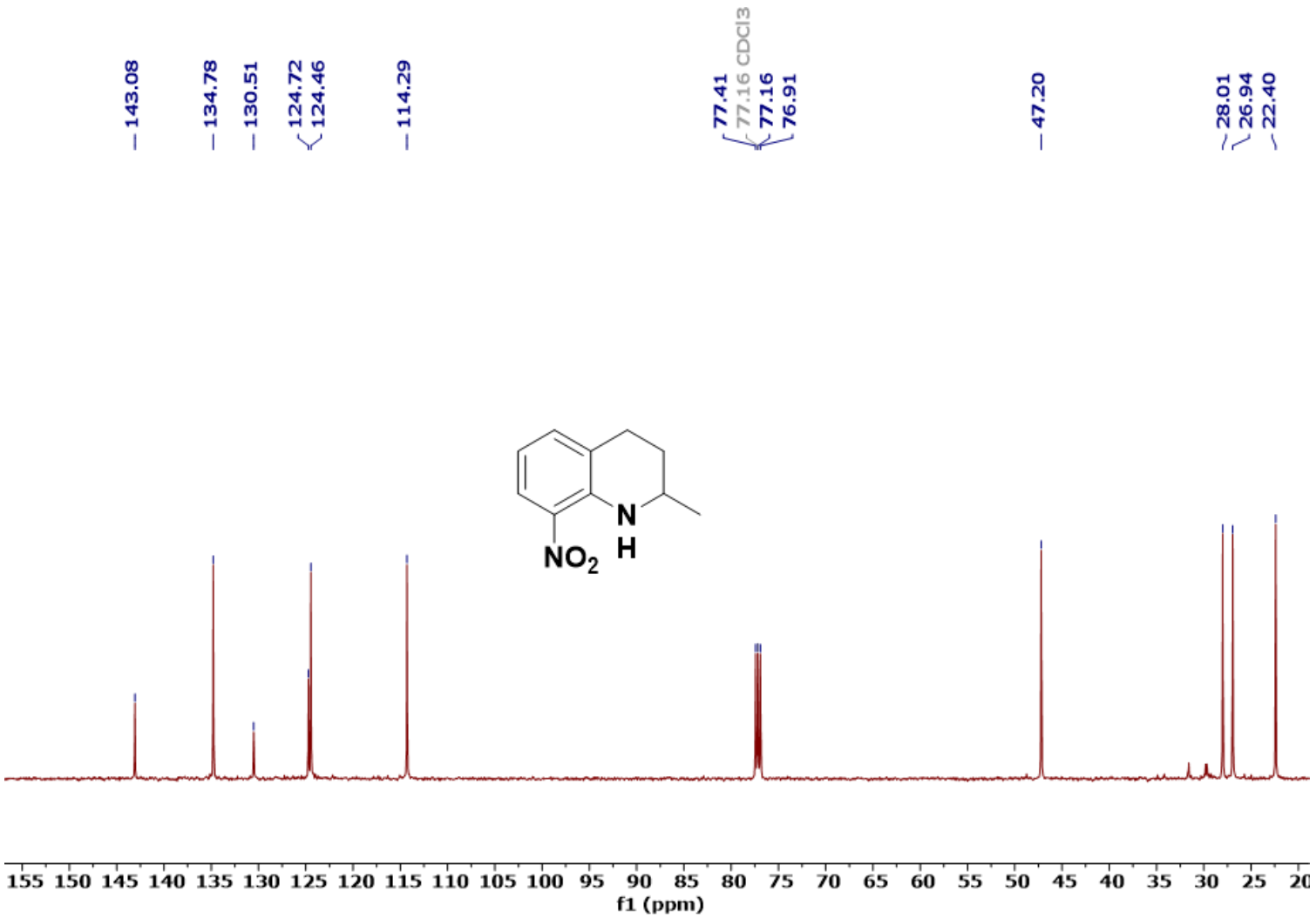


Fig. S48 ^{13}C NMR Spectrum of 8-nitro-2-methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

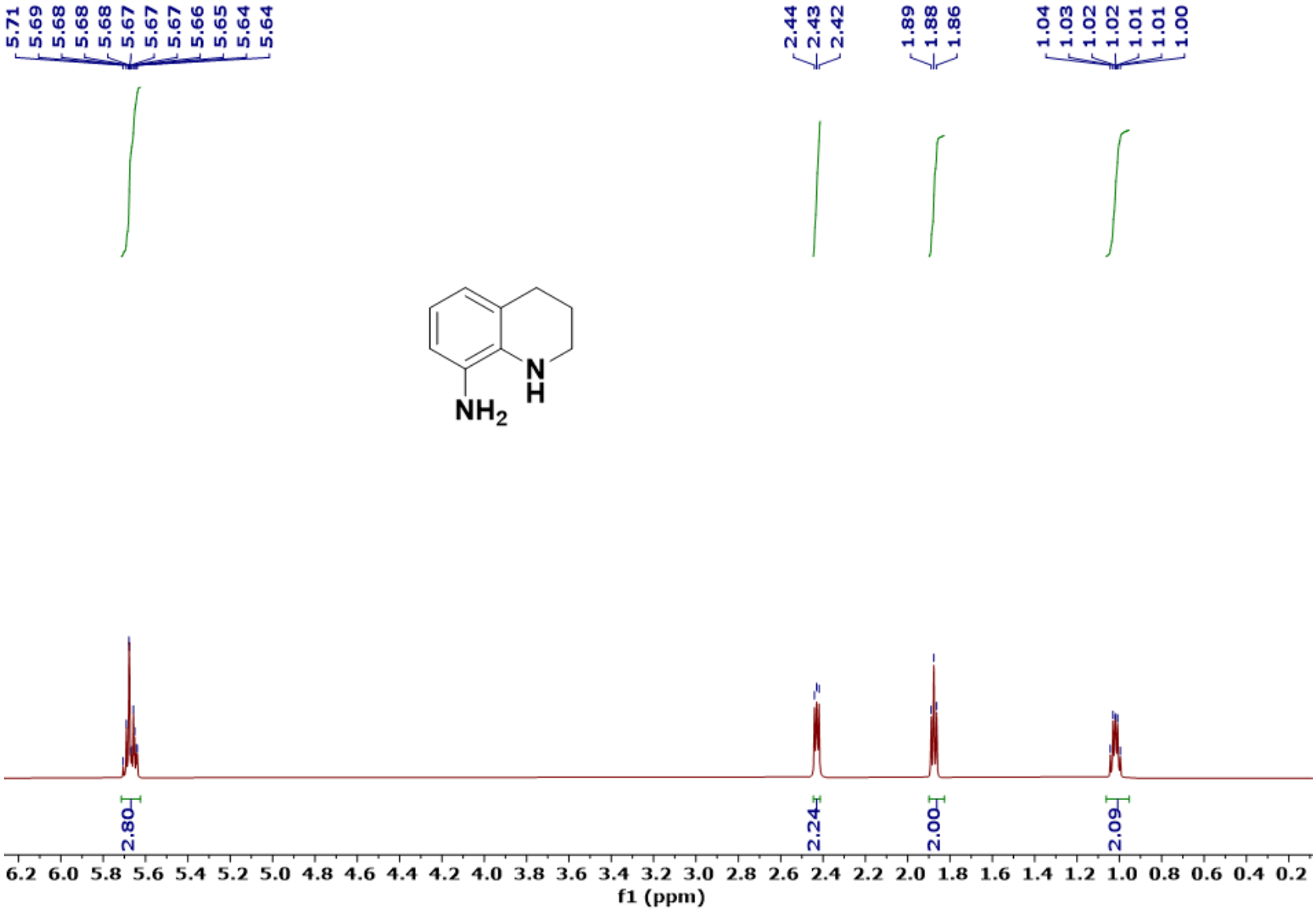


Fig. S49 ^{1}H NMR Spectrum of 8-amino -1,2,3,4-tetrahydroquinoline ($CDCl_3$, 600 MHz, 298K)

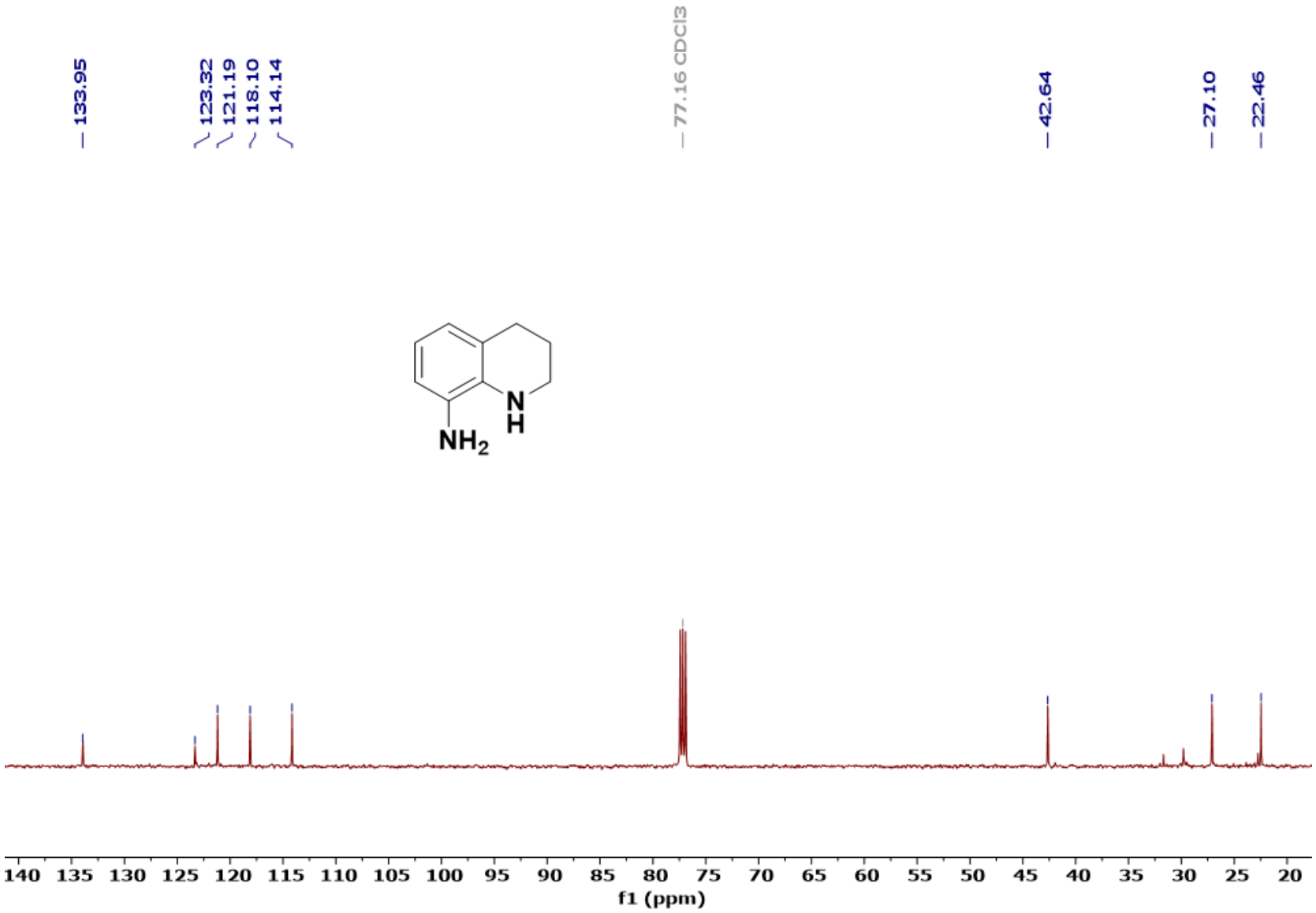


Fig. S50 ^{13}C NMR Spectrum of 8-amino-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

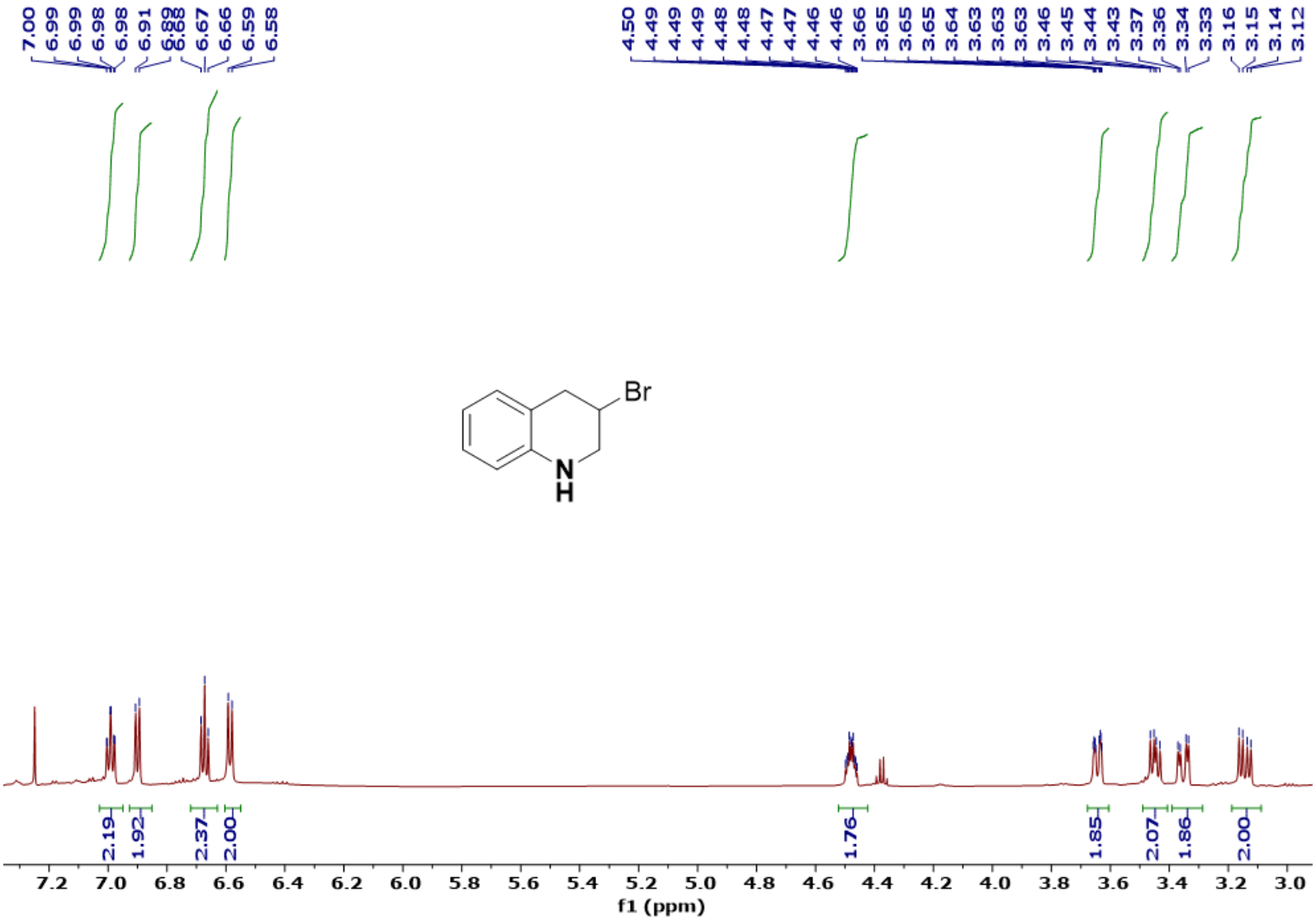


Fig. S51 ^{1}H NMR Spectrum of 3-Bromo-1,2,3,4-tetrahydroquinoline (CDCl3, 600 MHz, 298K)

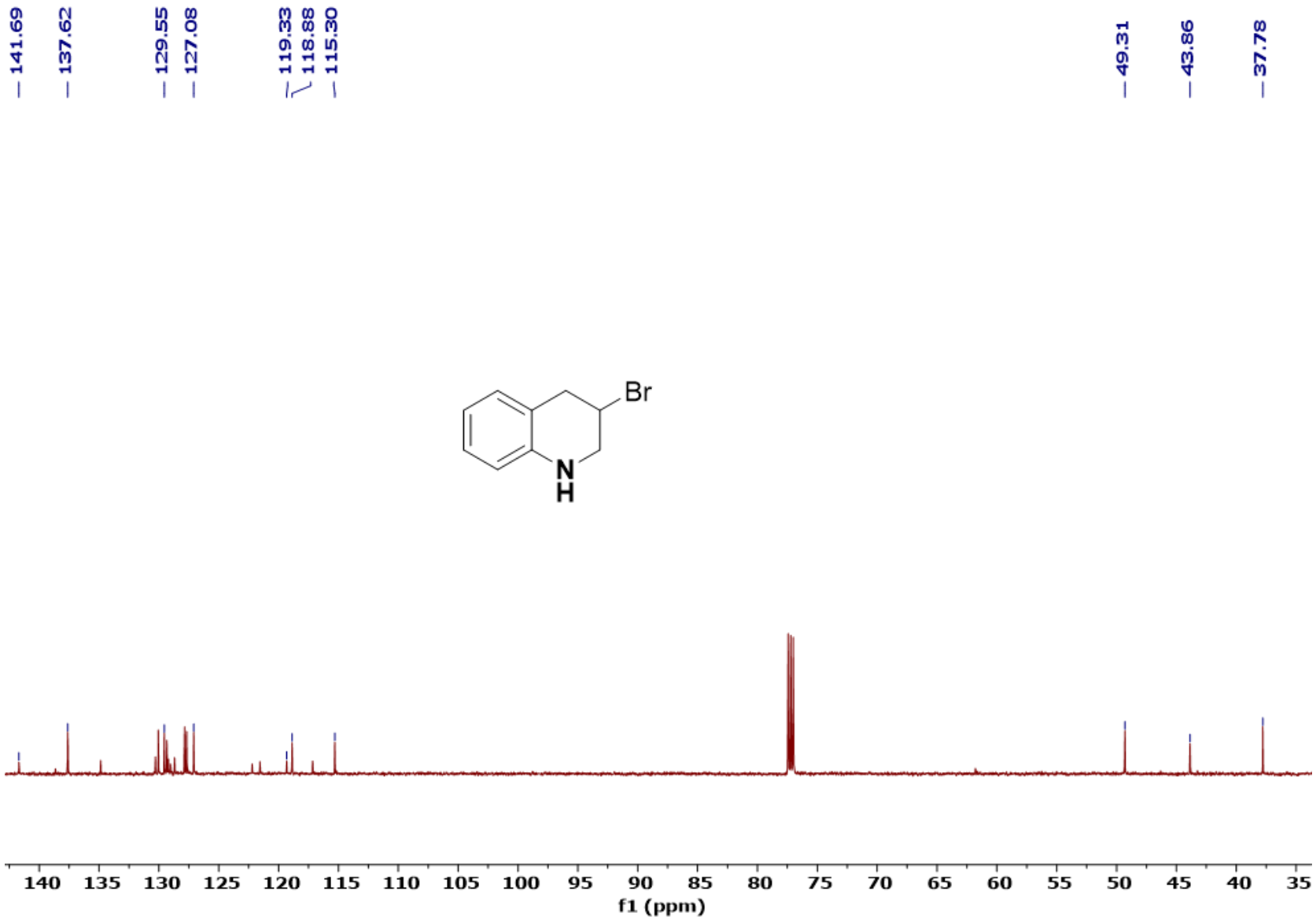


Fig. S52 ^{13}C NMR Spectrum of 3-Bromo-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

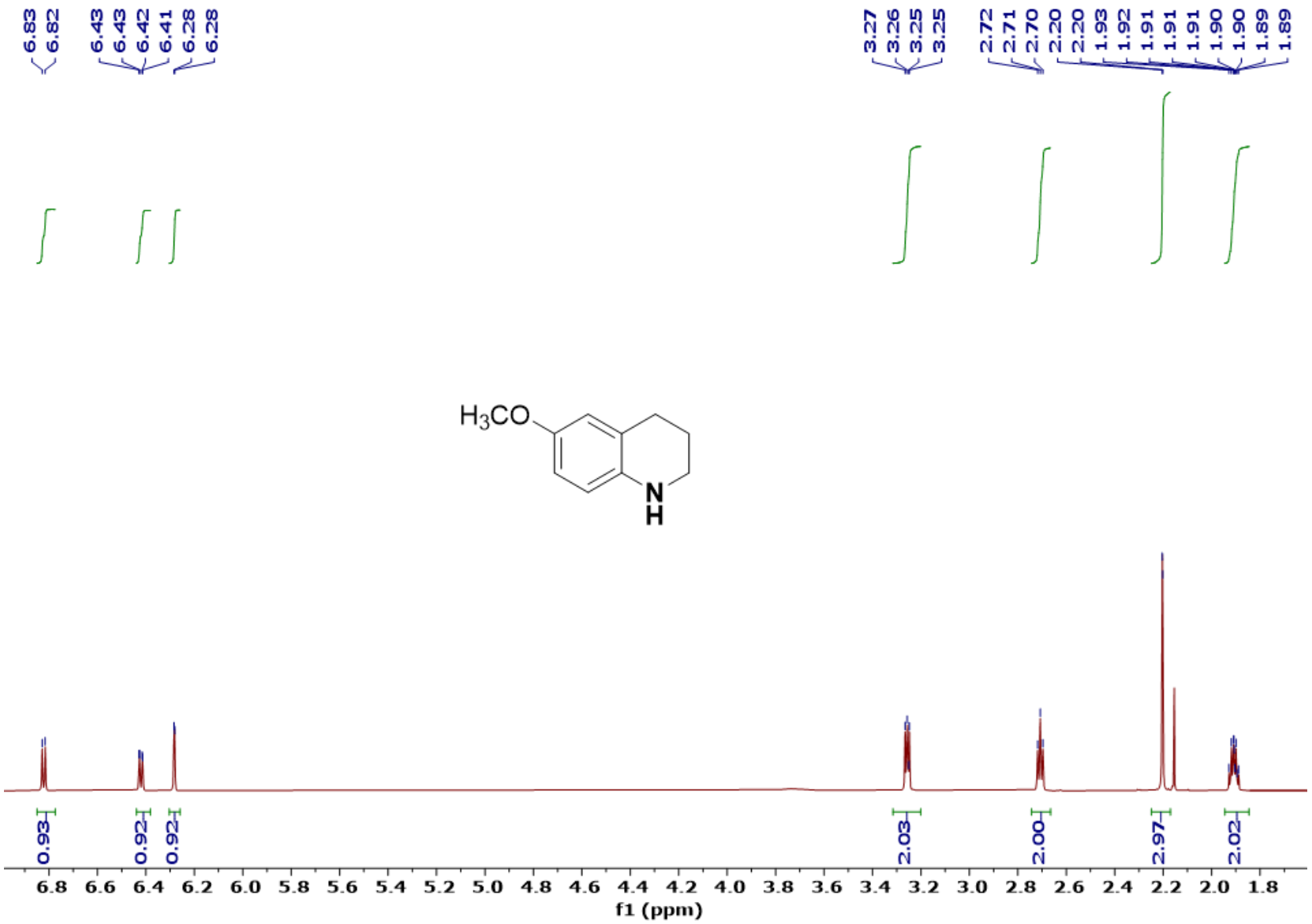


Fig. S53 ^{1}H NMR Spectrum of 6-Methoxy-1,2,3,4-tetrahydroquinoline (CDCl3, 600 MHz, 298K)

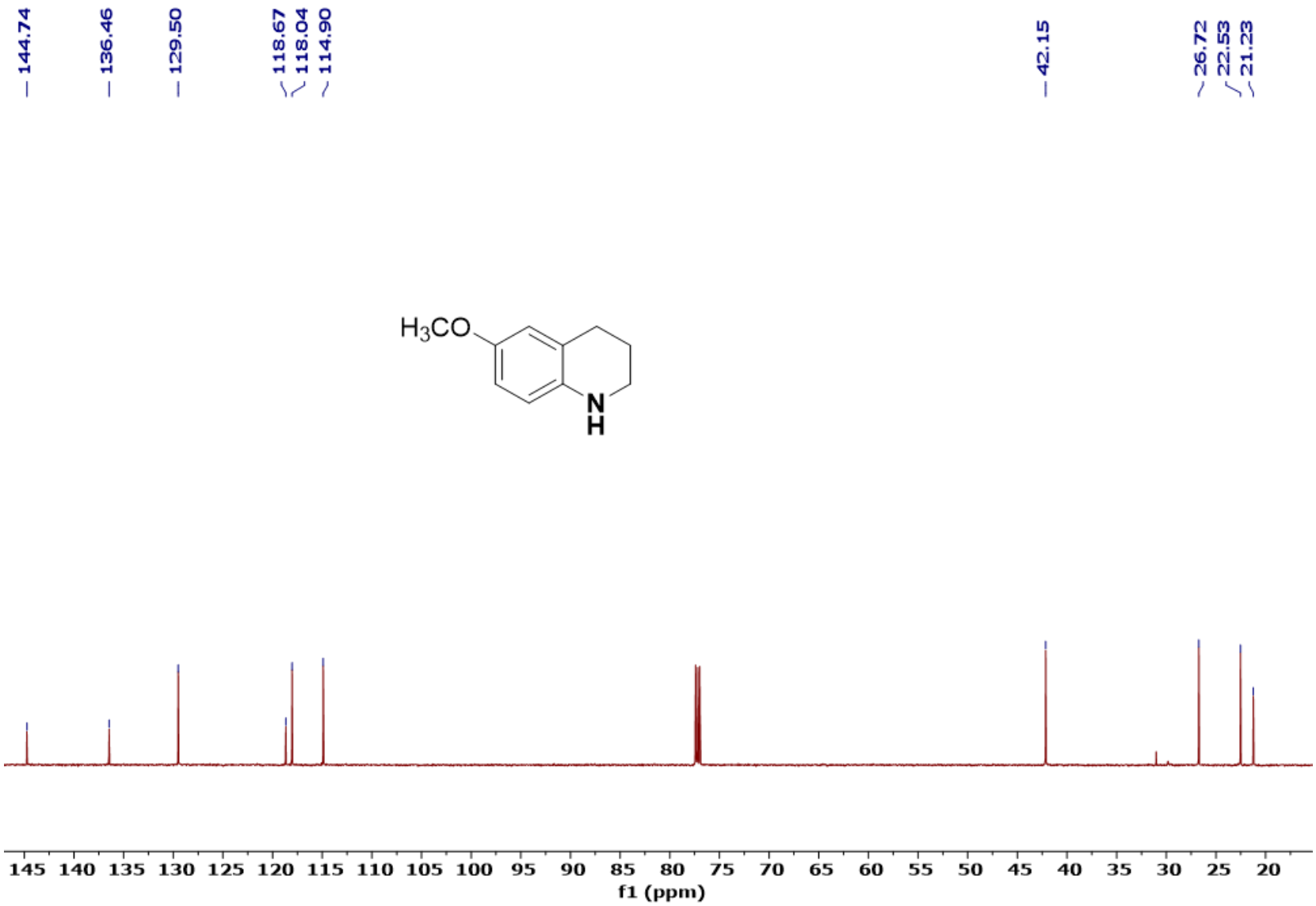


Fig. S54 ^{13}C NMR Spectrum of 6-Methoxy-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

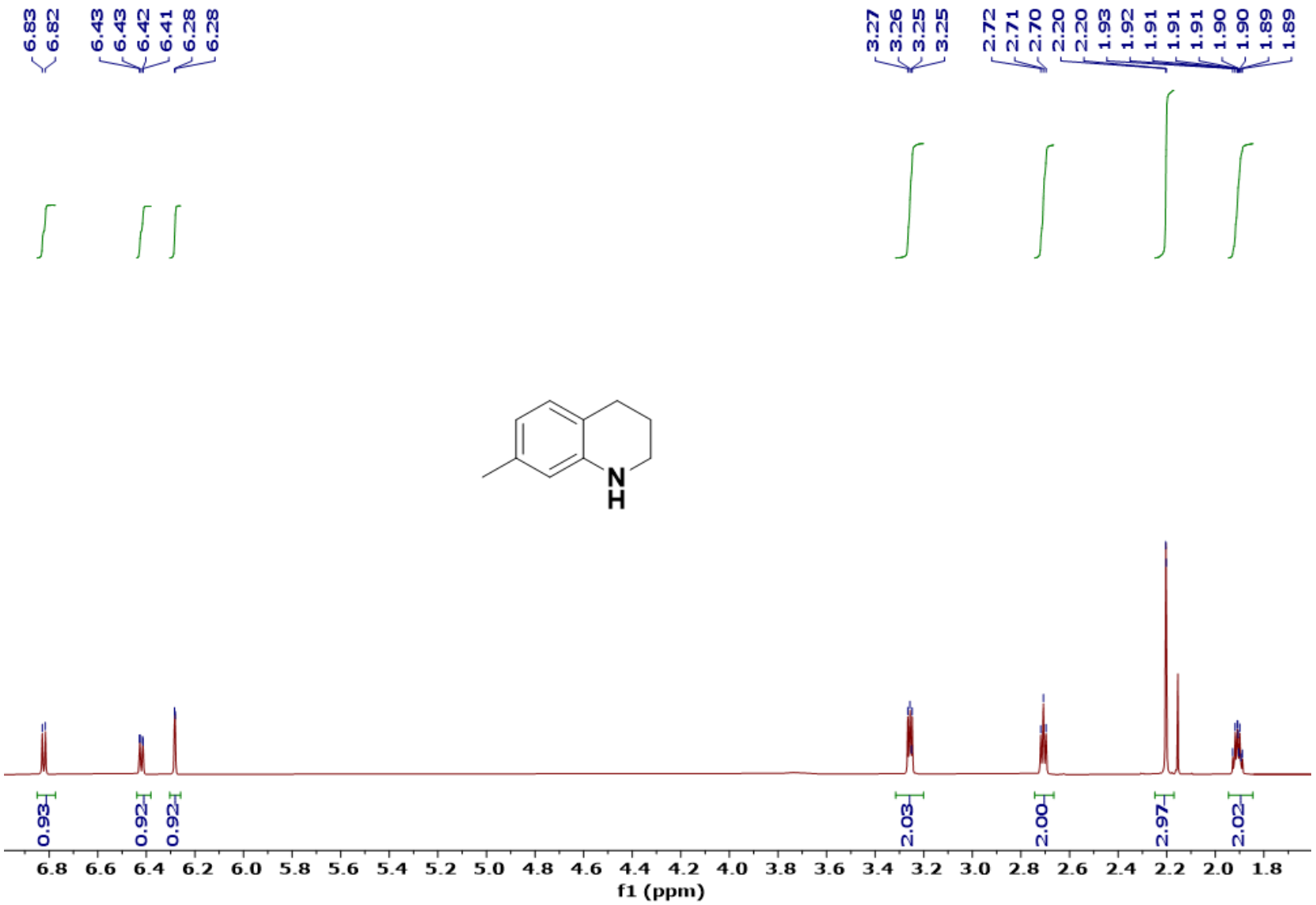


Fig. S55 ^{1}H NMR Spectrum of 7-Methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 600 MHz, 298K)

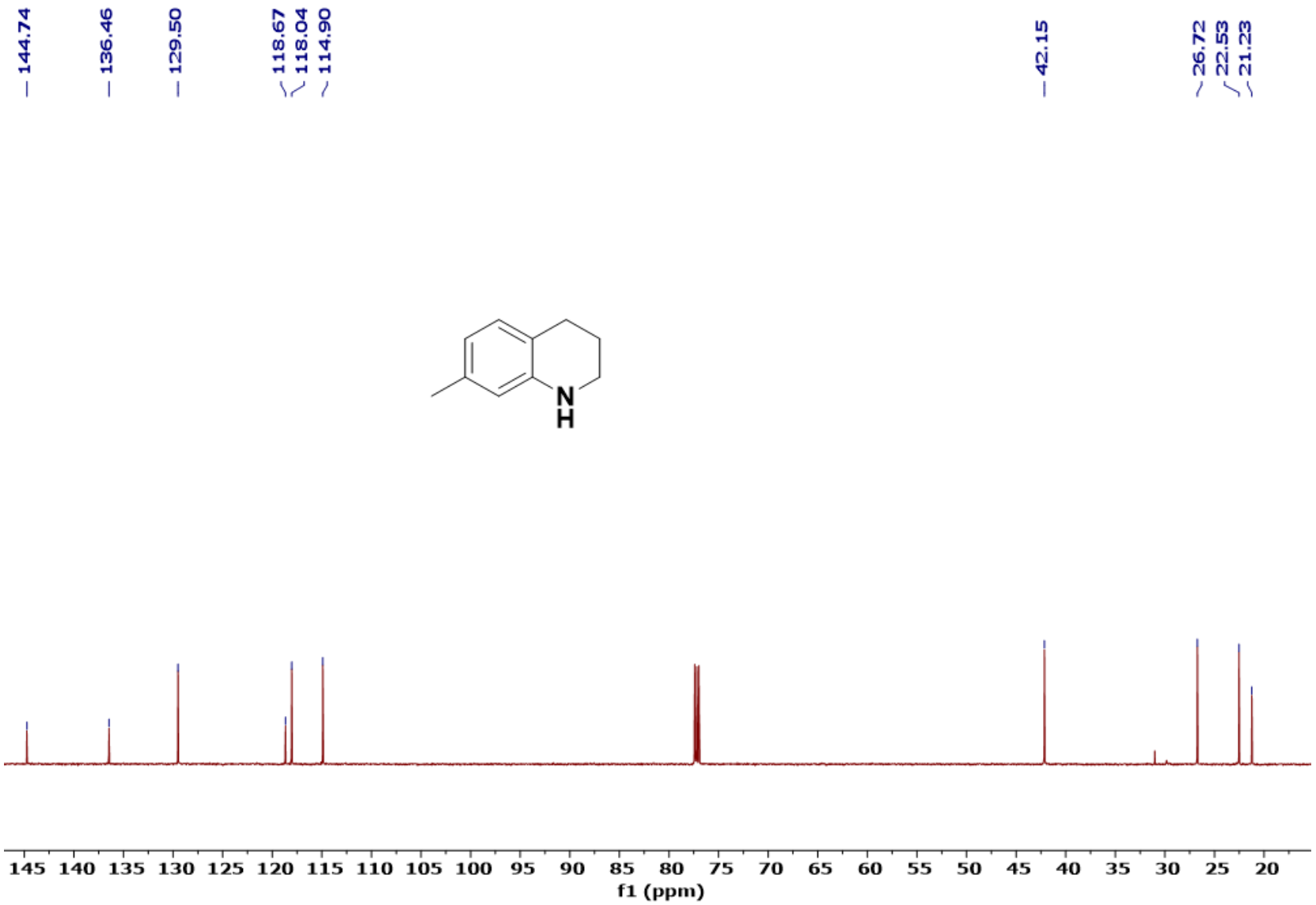


Fig. S56 ^{13}C NMR Spectrum of 7-Methyl-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

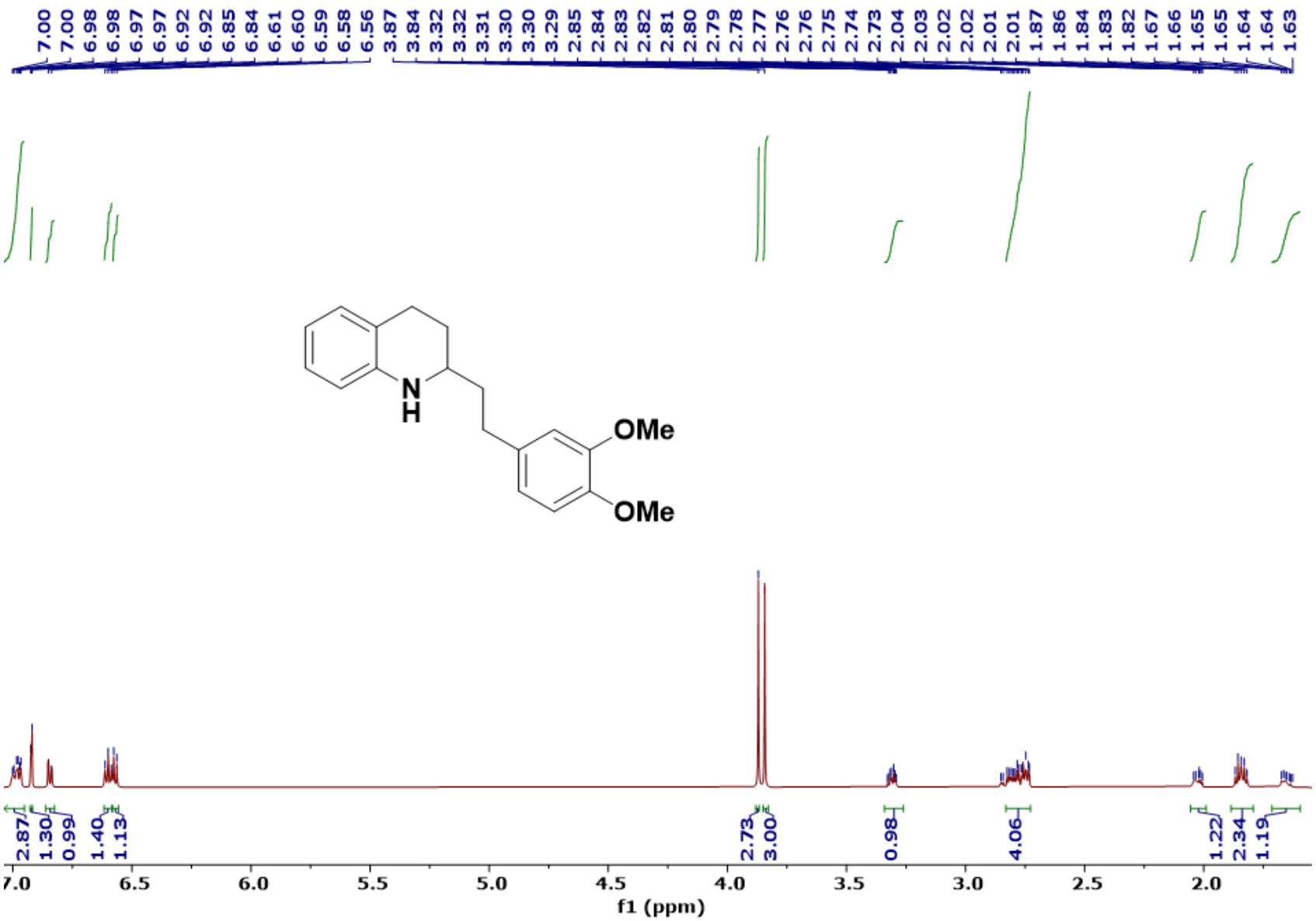


Fig. S57 1H NMR Spectrum of 2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (CD_3CN, 600 MHz, 298K)

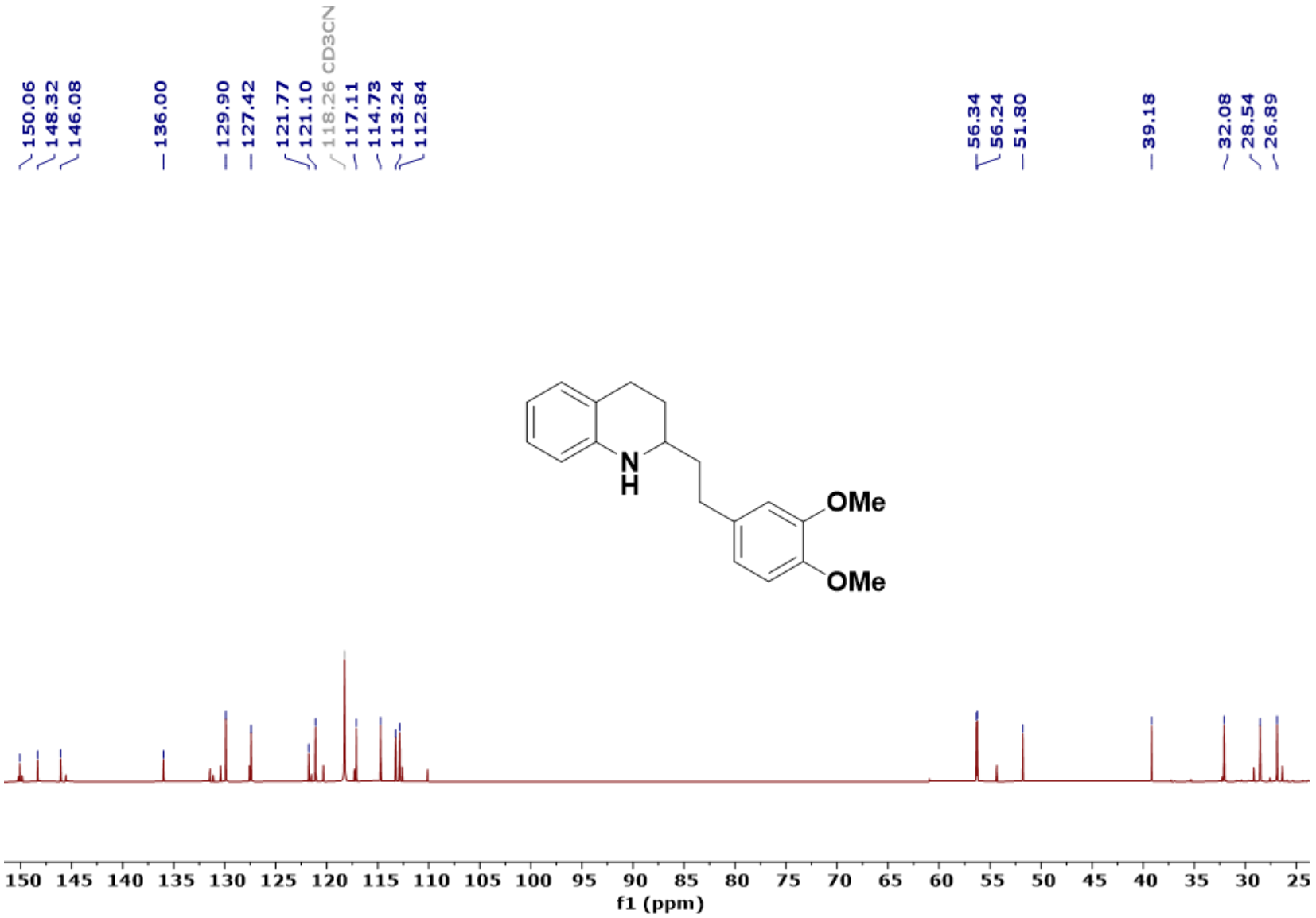


Fig. S58 ^{13}C NMR Spectrum of 2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (CD_3CN, 500 MHz, 298K)

18. ^{1}H and ^{13}C NMR of Reductive alkylated Product

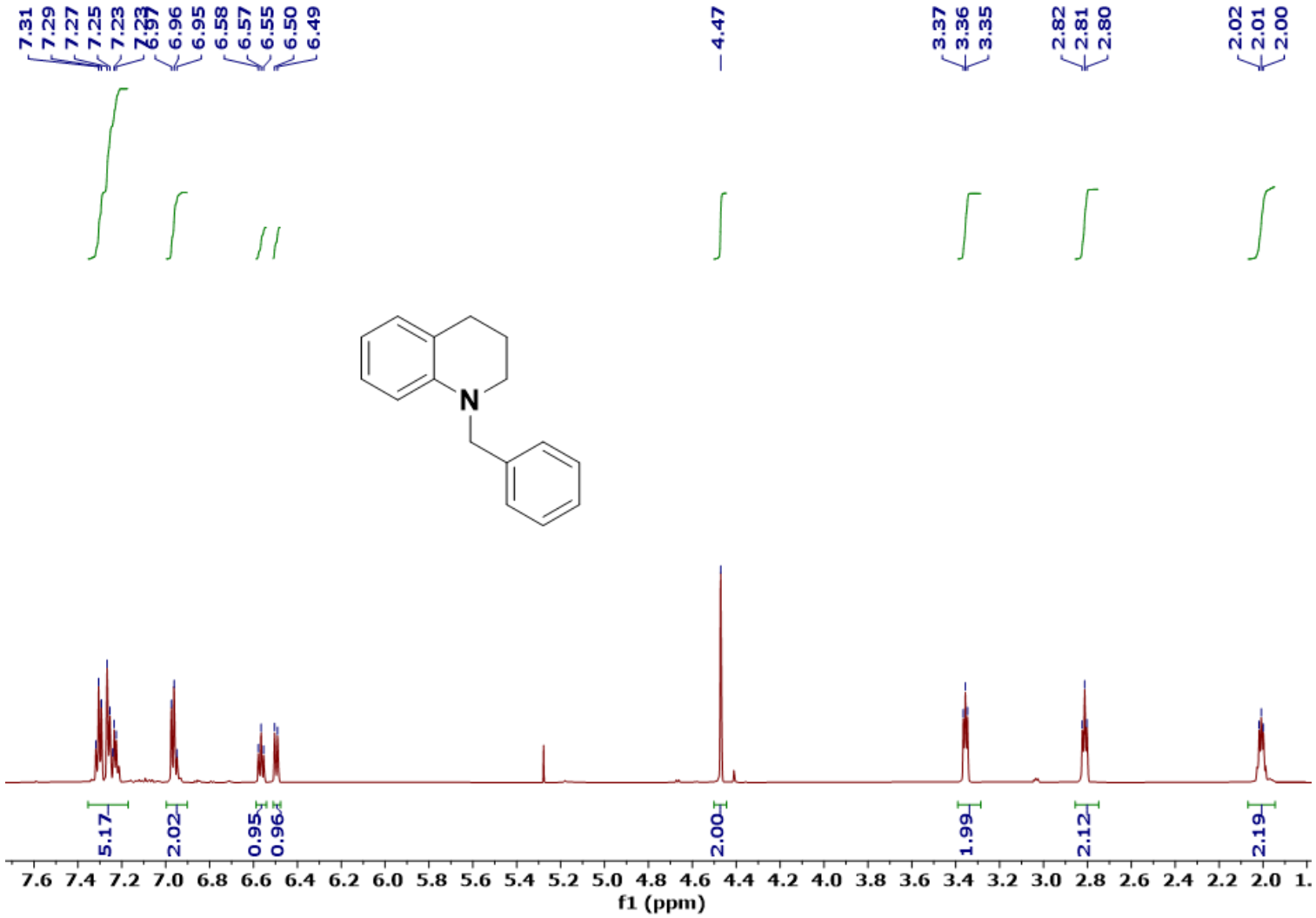


Fig. S59 ^{1}H NMR Spectrum of 1-benzyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

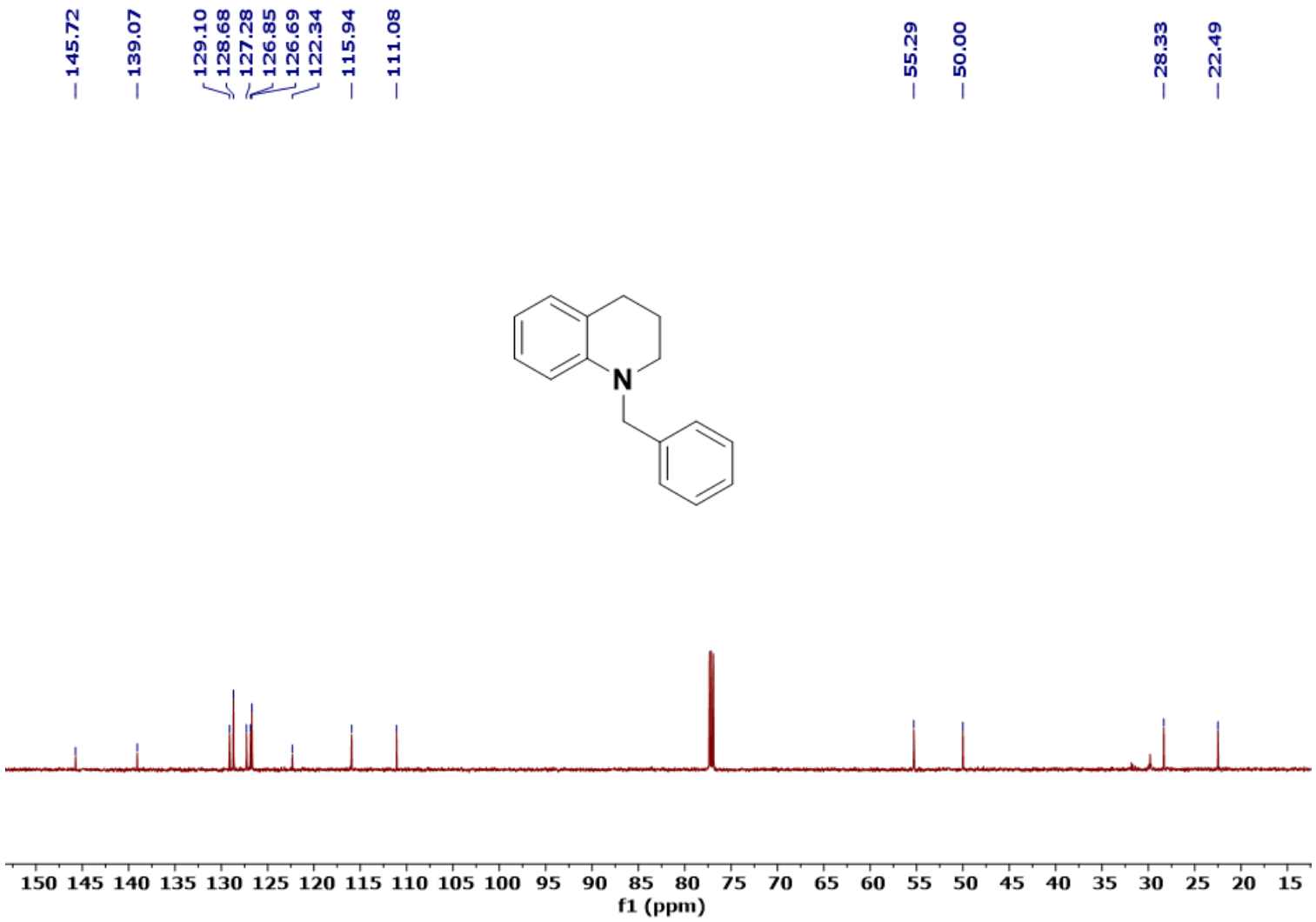


Fig. S60 ^{13}C NMR Spectrum of 1-benzyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

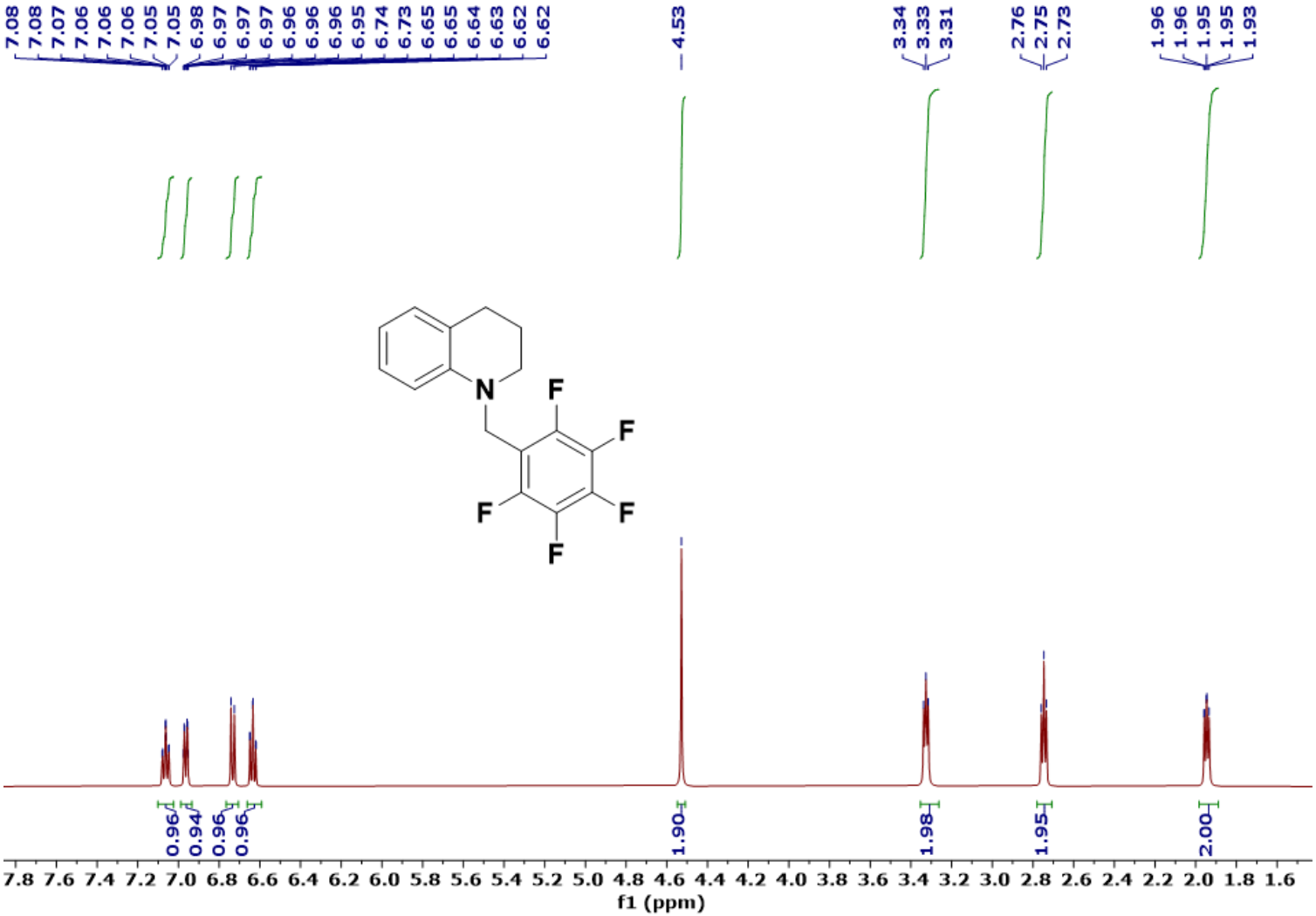


Fig. S61 ^{1}H NMR Spectrum of 1-((pentafluorophenyl)methyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

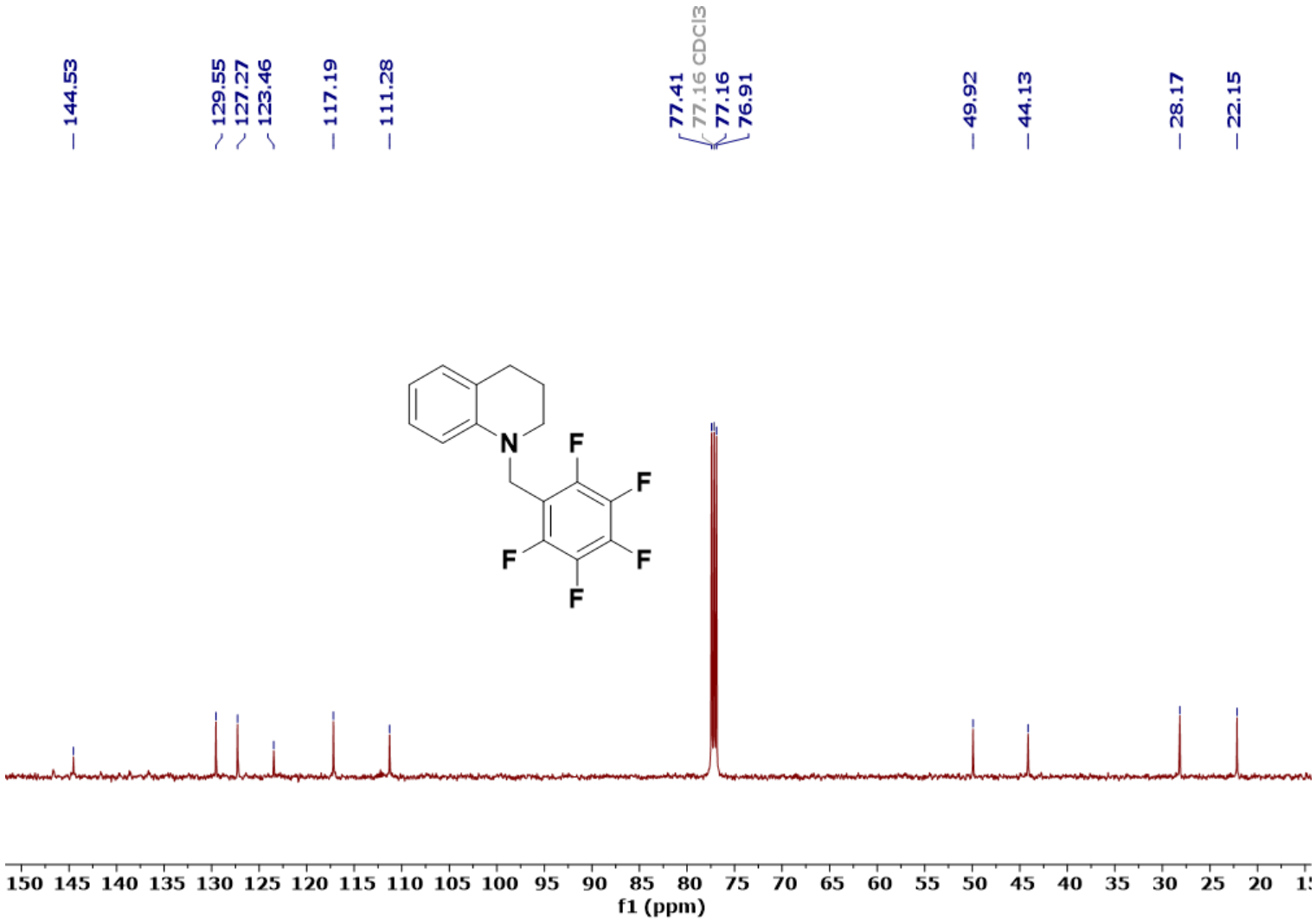


Fig. S62 ^{13}C NMR Spectrum of 1-((pentafluorophenyl)methyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

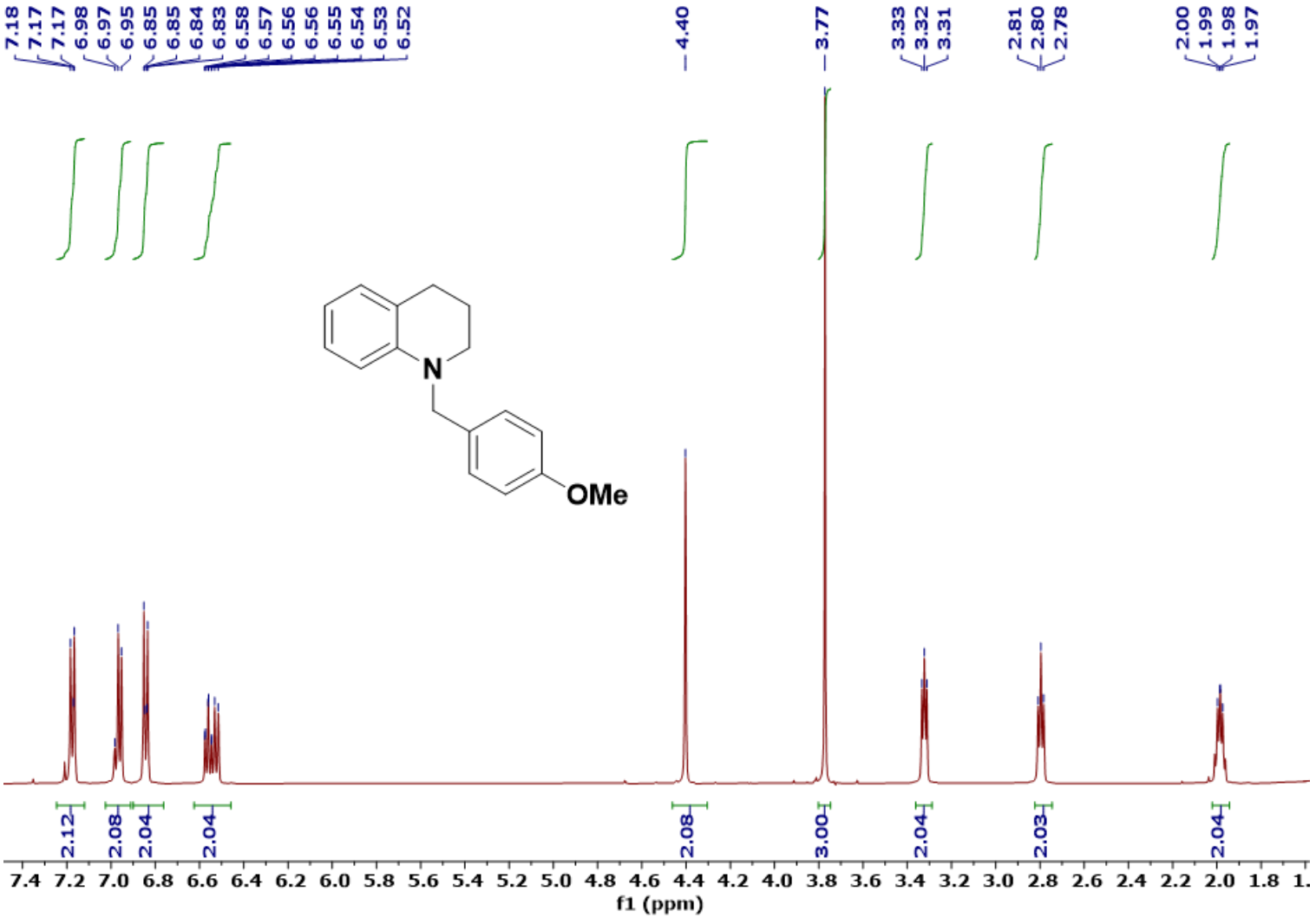


Fig. S63 ^{1}H NMR Spectrum of 1-(4-methoxybenzyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

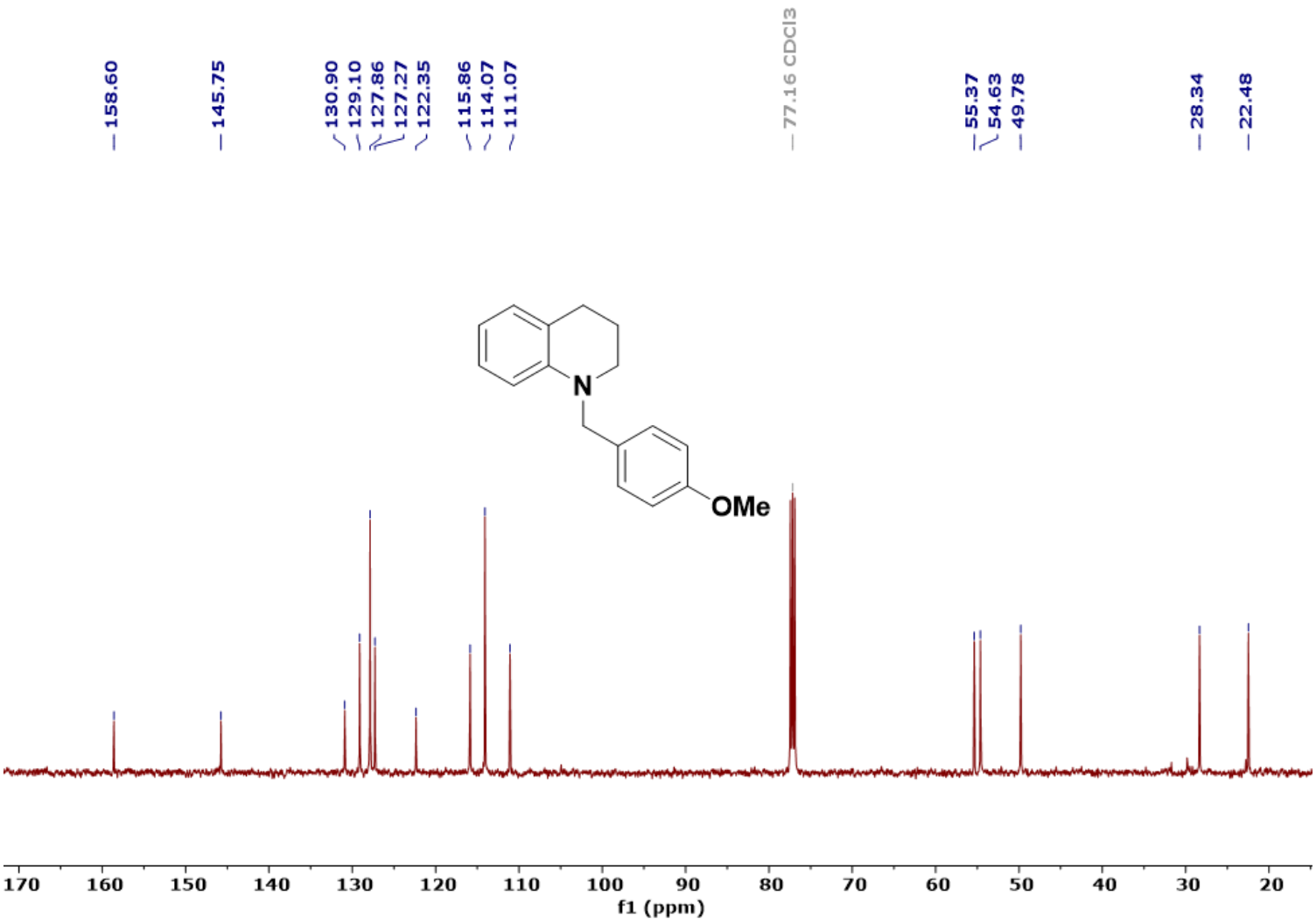


Fig. S64 ^{13}C NMR Spectrum of 1-(4-methoxybenzyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

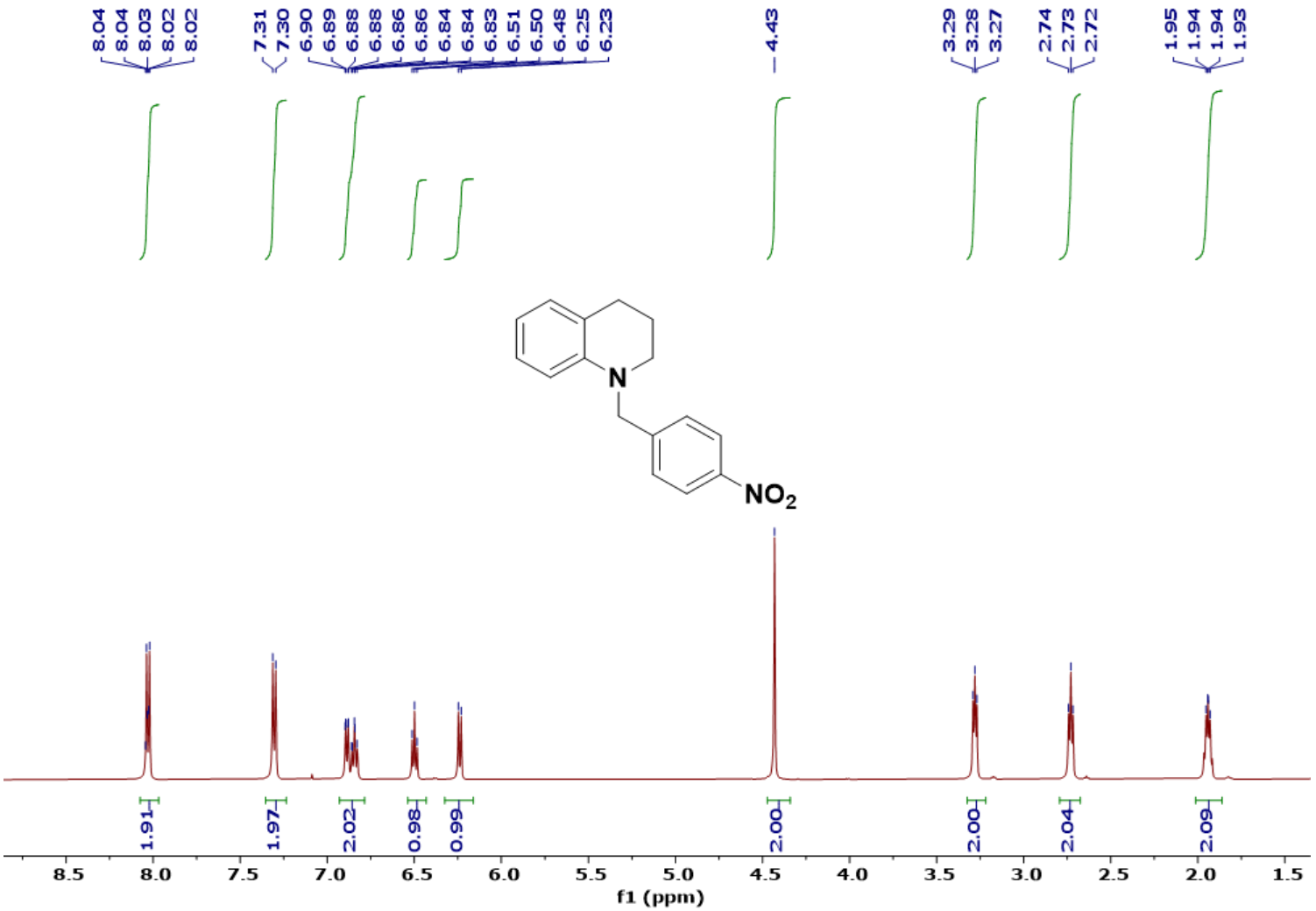


Fig. S65 ^{1}H NMR Spectrum of 1-(4-nitrobenzyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

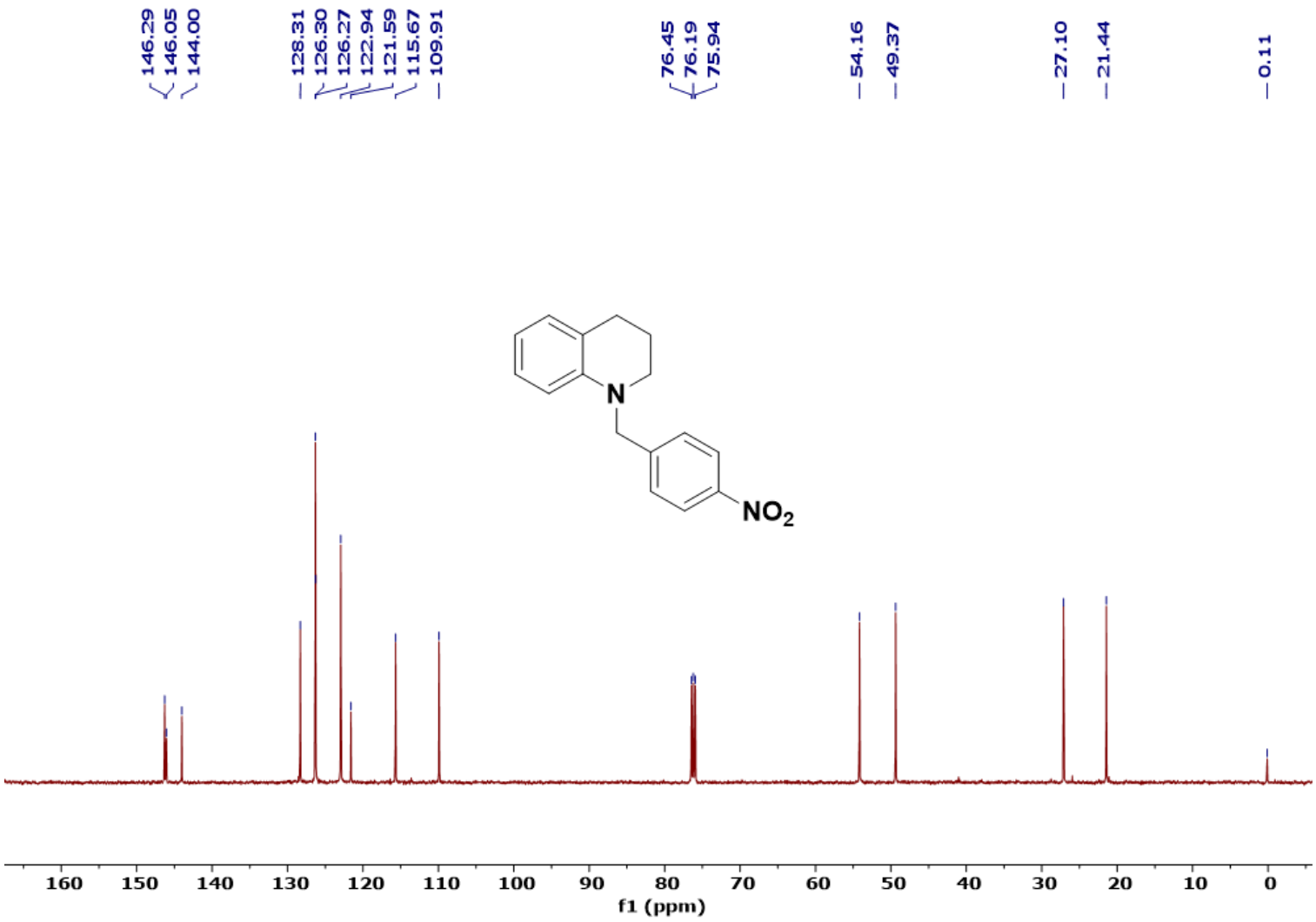


Fig. S66 ^{13}C NMR Spectrum of 1-(4-nitrobenzyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

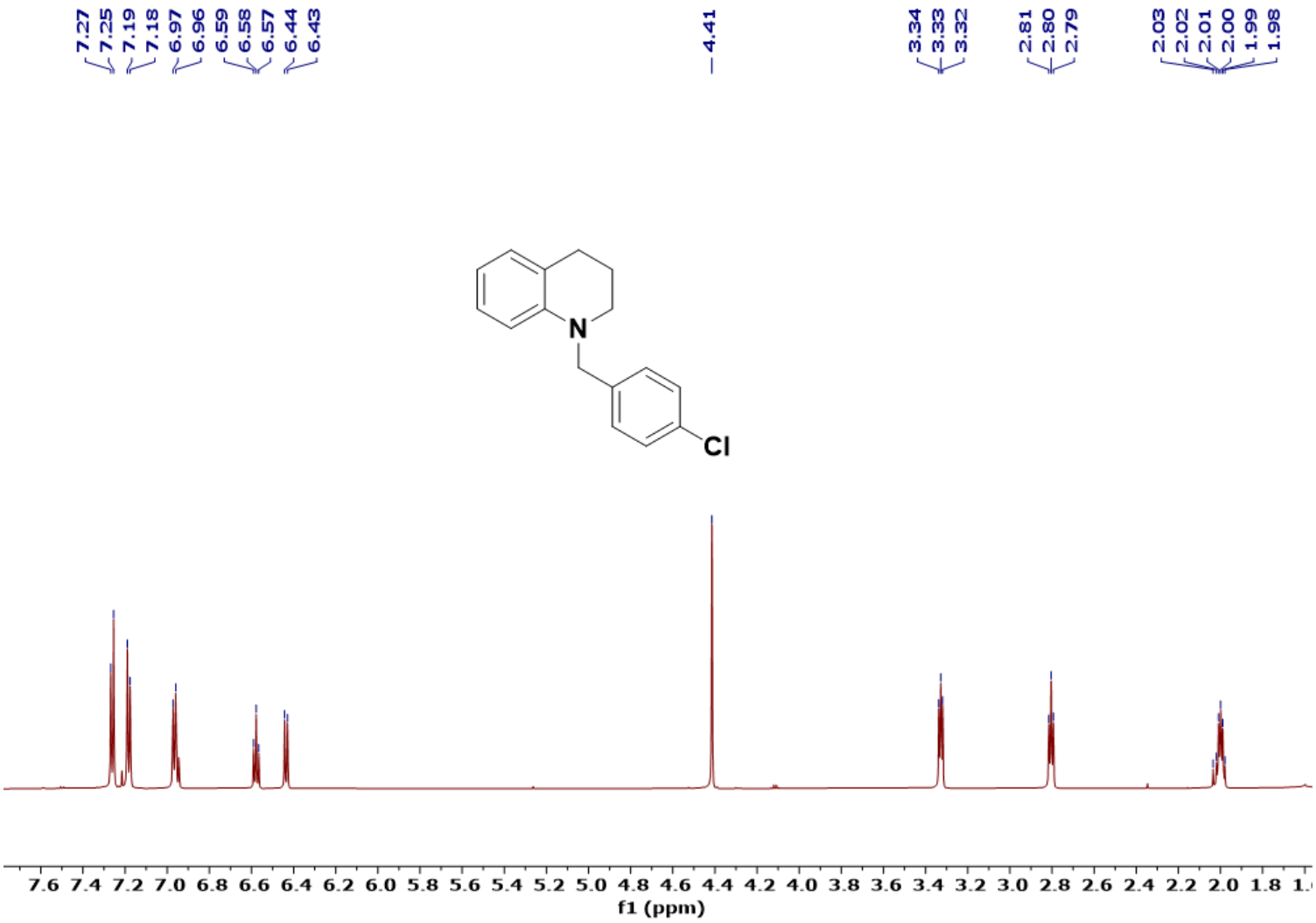


Fig. S67 ^{1}H NMR Spectrum of 1-(4-chlorobenzyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

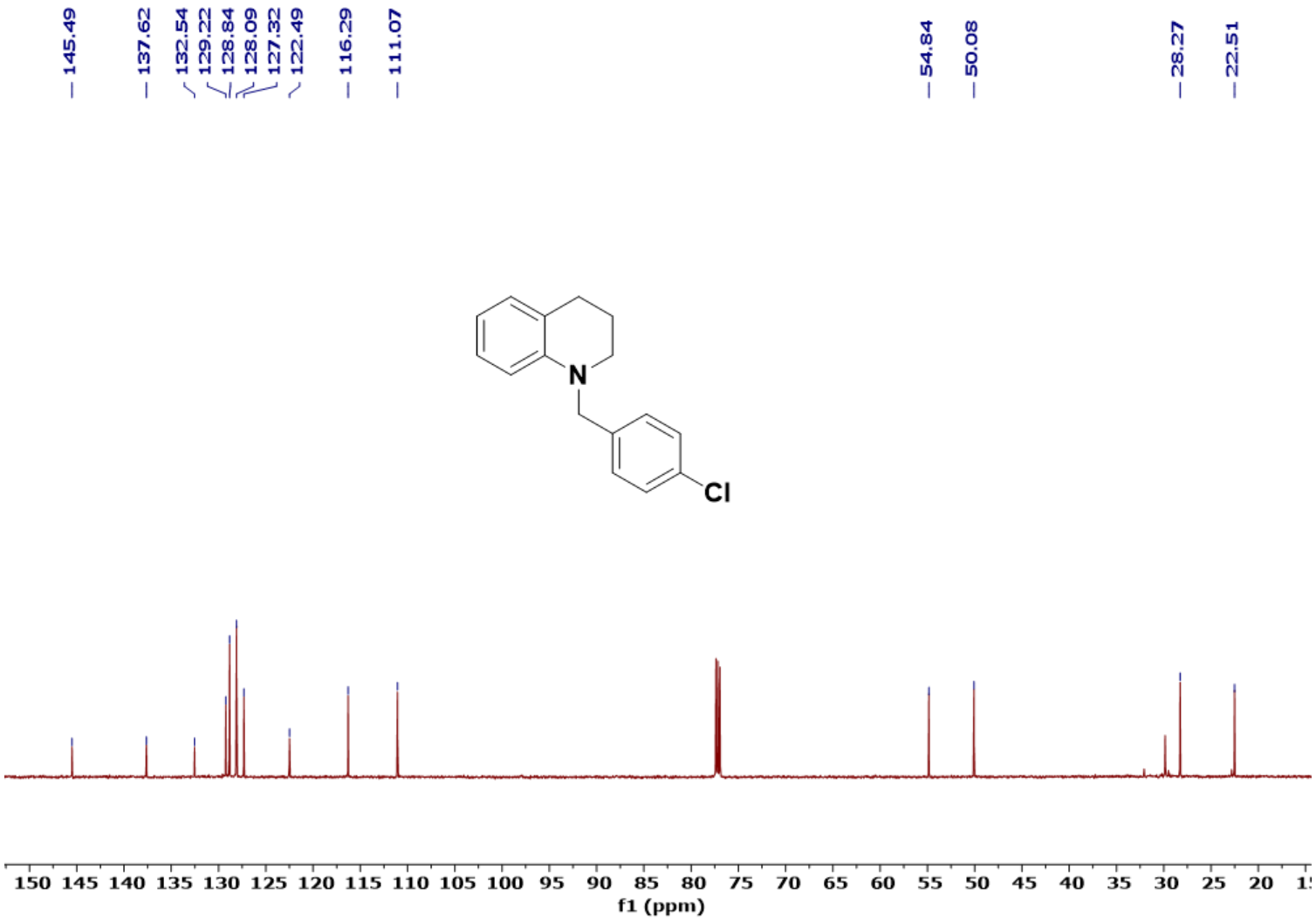


Fig. S68 ^{13}C NMR Spectrum of 1-(4-chlorobenzyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

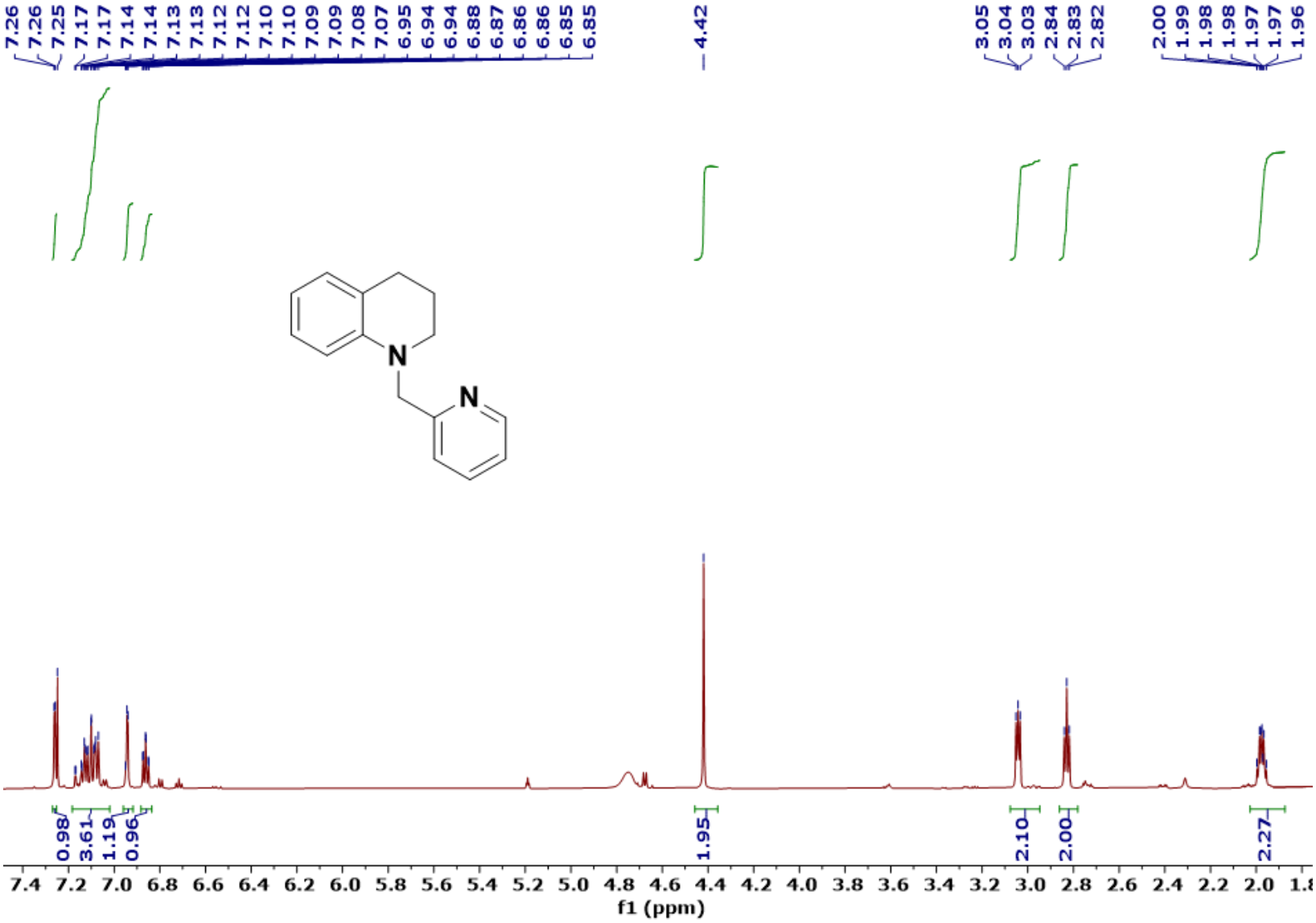


Fig. S69 ^{1}H NMR Spectrum of 1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

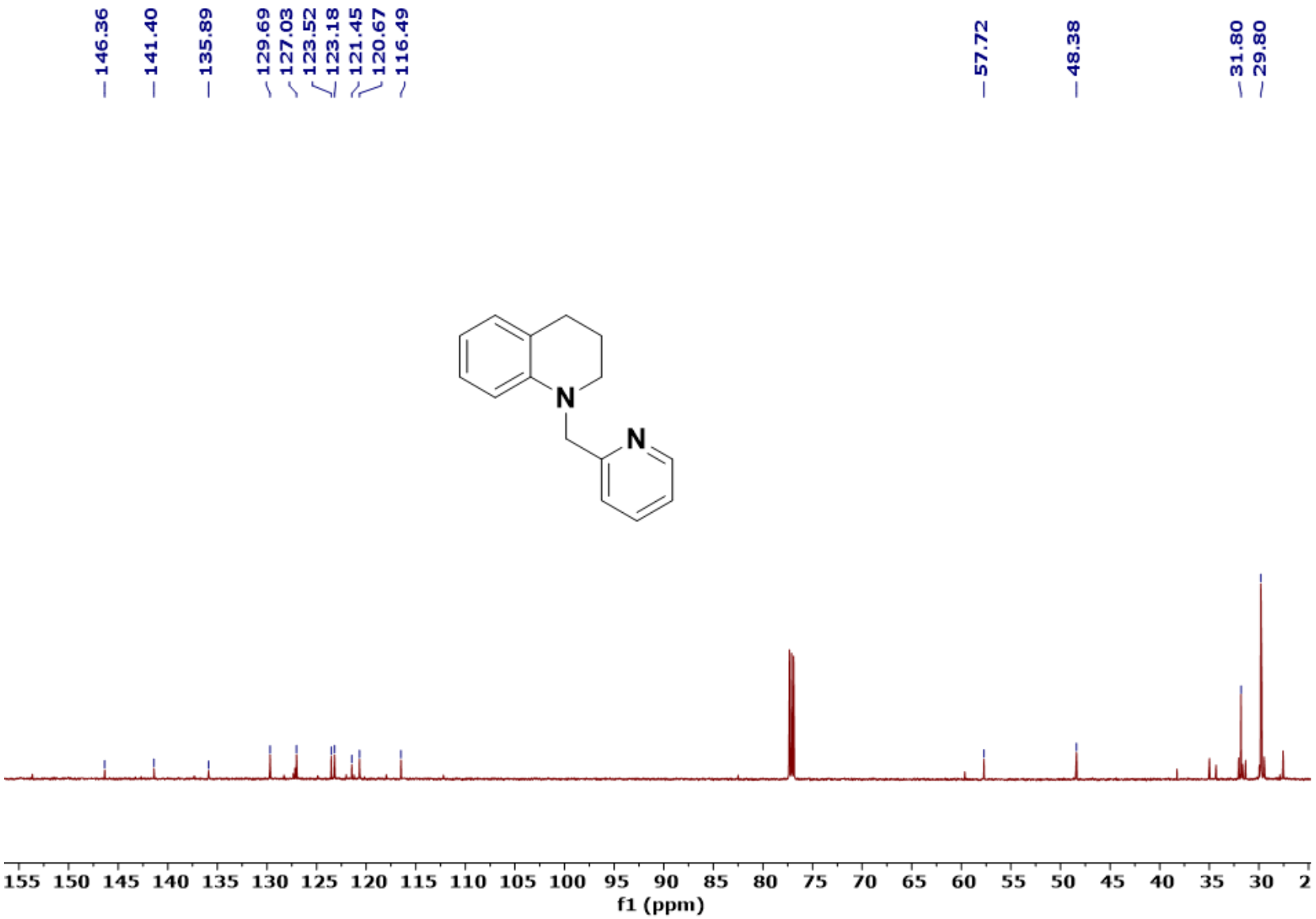


Fig. S70 ^{13}C NMR Spectrum of 1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

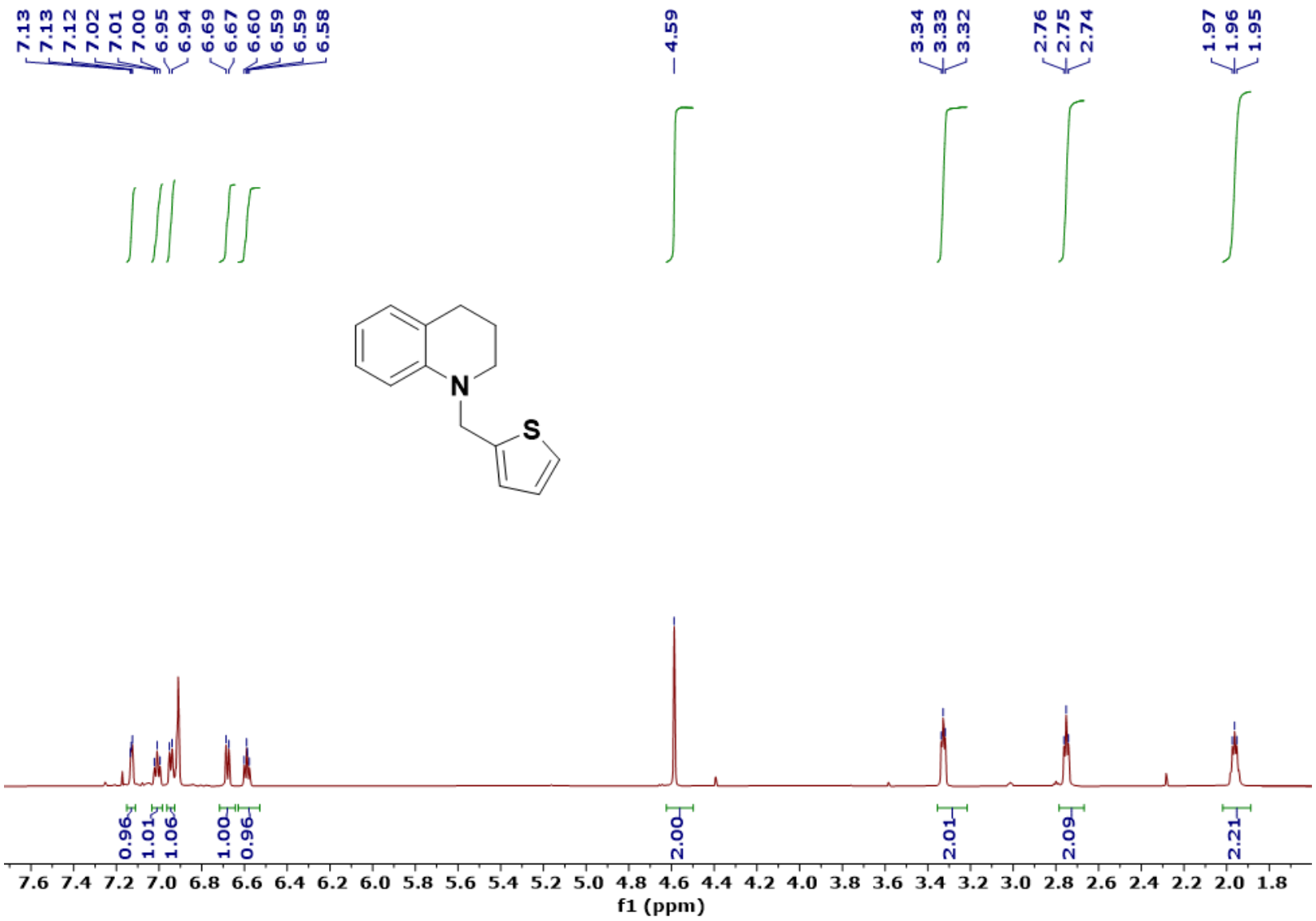


Fig. S71 ^{1}H NMR Spectrum of 1-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

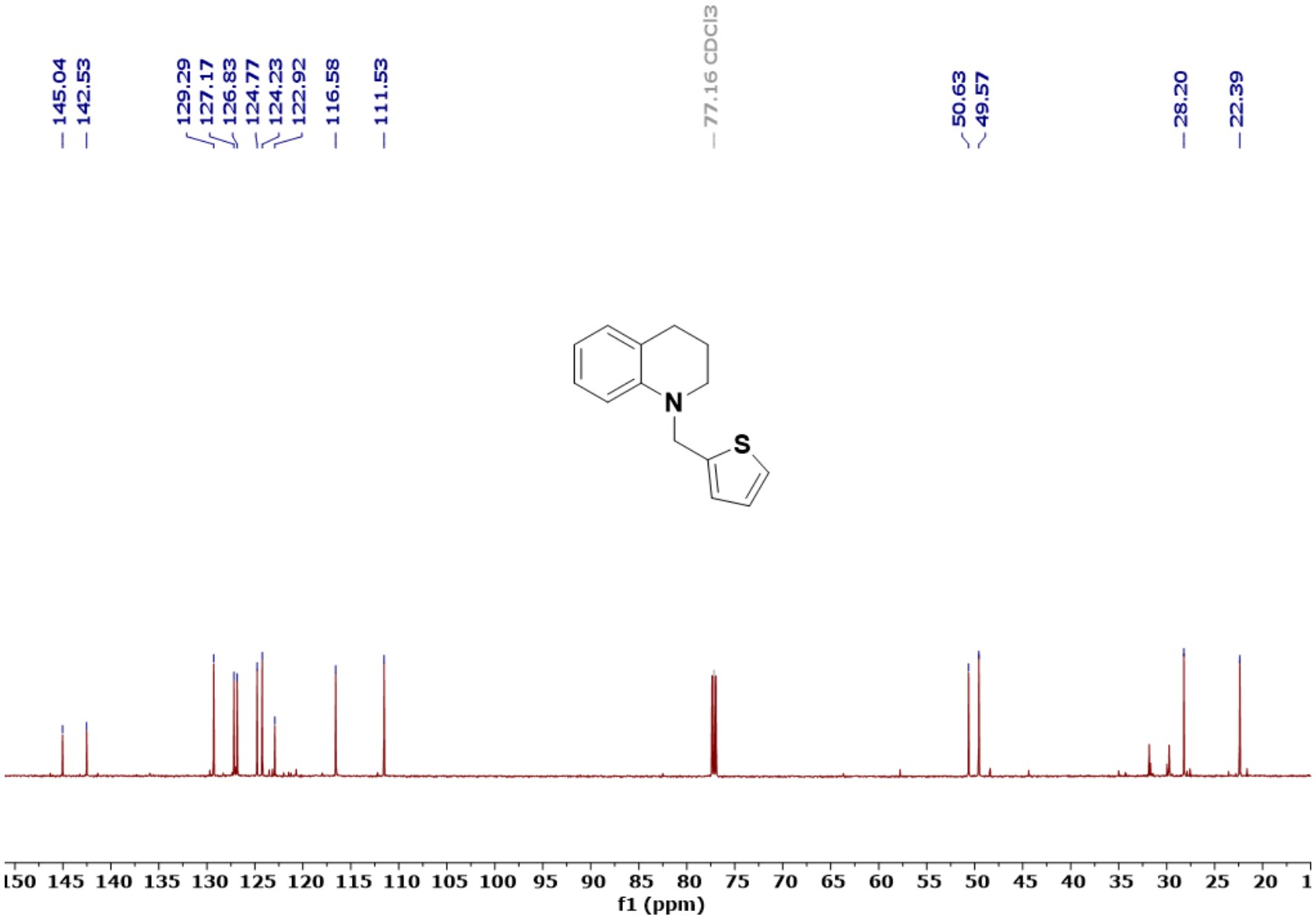


Fig. S72 ^{13}C NMR Spectrum of 1-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroquinoline (CDCl3, 500 MHz, 298K)

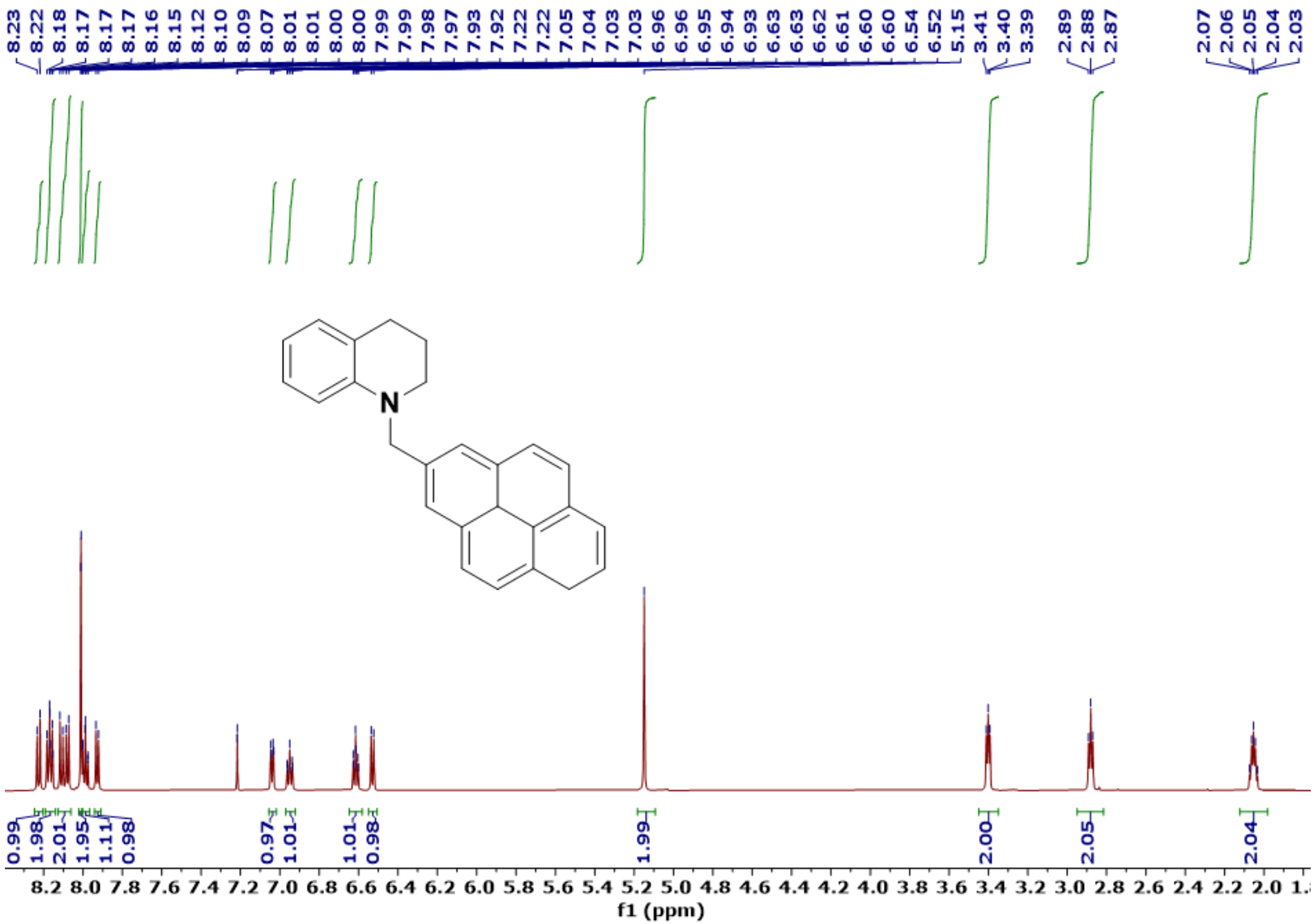


Fig. S73 ^{1}H NMR Spectrum of 1-((3a1,6-dihydropyren-2-yl)methyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

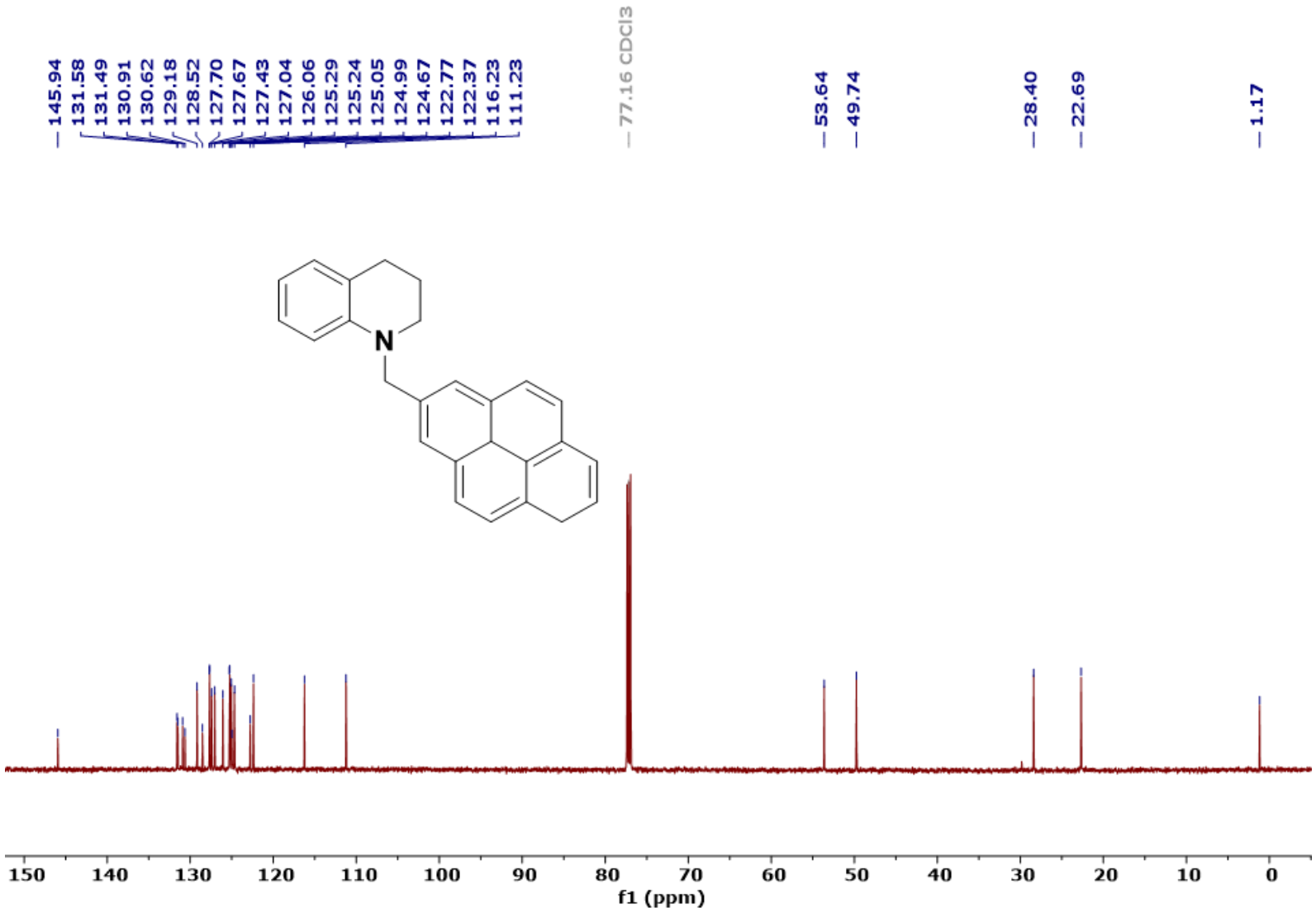


Fig. S74 ^{13}C NMR Spectrum of 1-((3a1,6-dihydropyren-2-yl)methyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

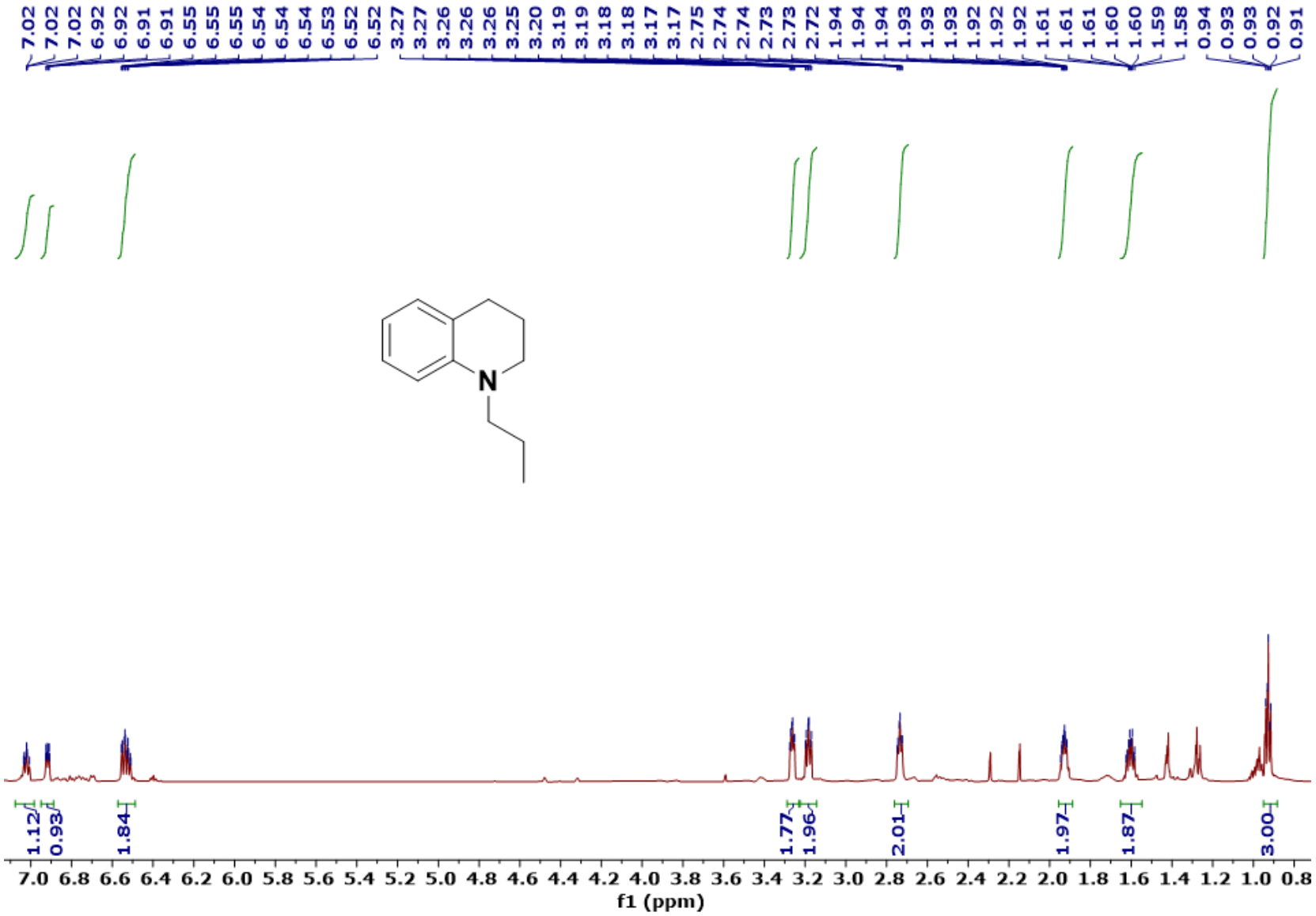


Fig. S75 ^{1}H NMR Spectrum of 1-propyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

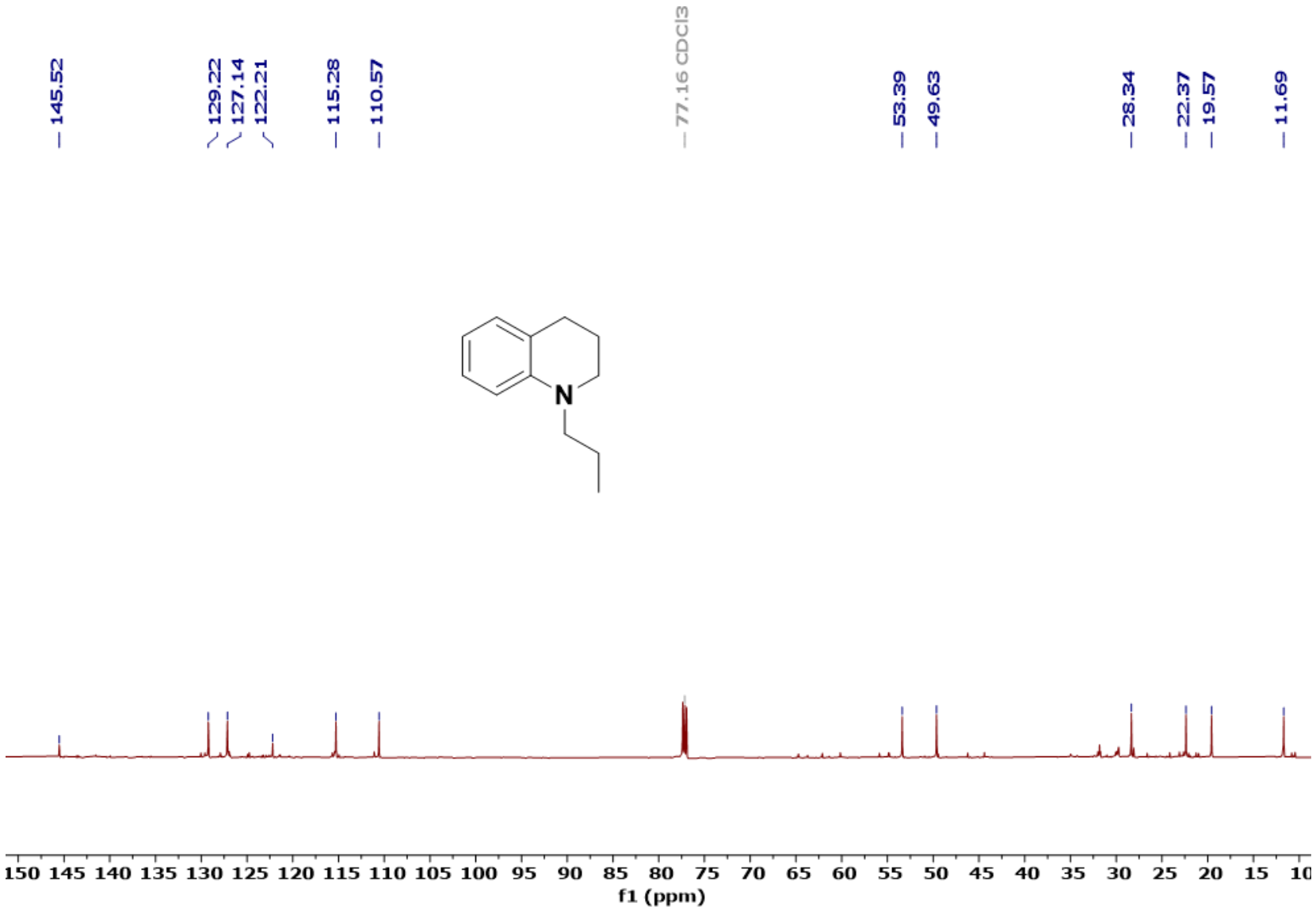


Fig. S76 ^{13}C NMR Spectrum of 1-propyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

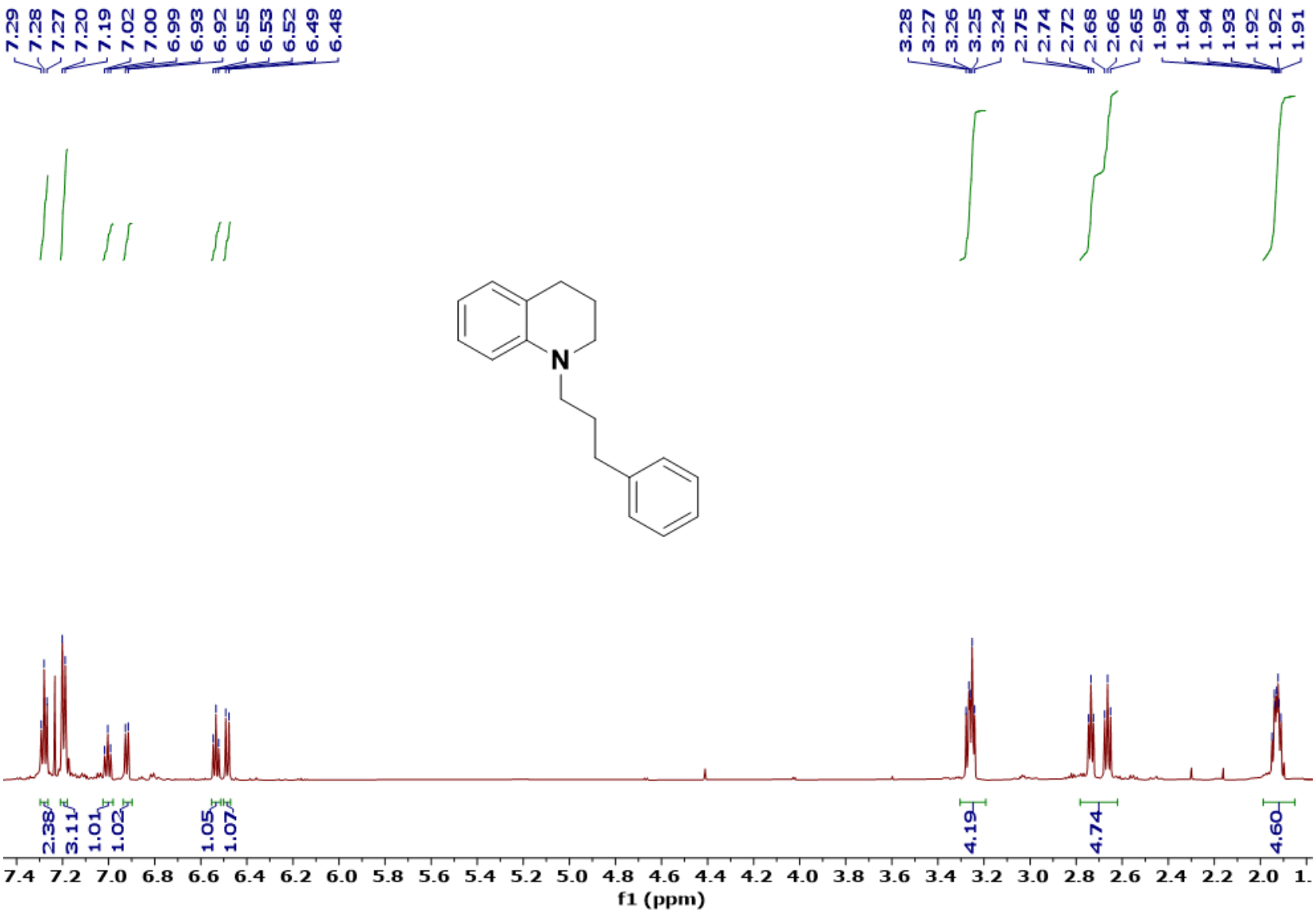


Fig. S77 ^{1}H NMR Spectrum of 1-(3-phenylpropyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

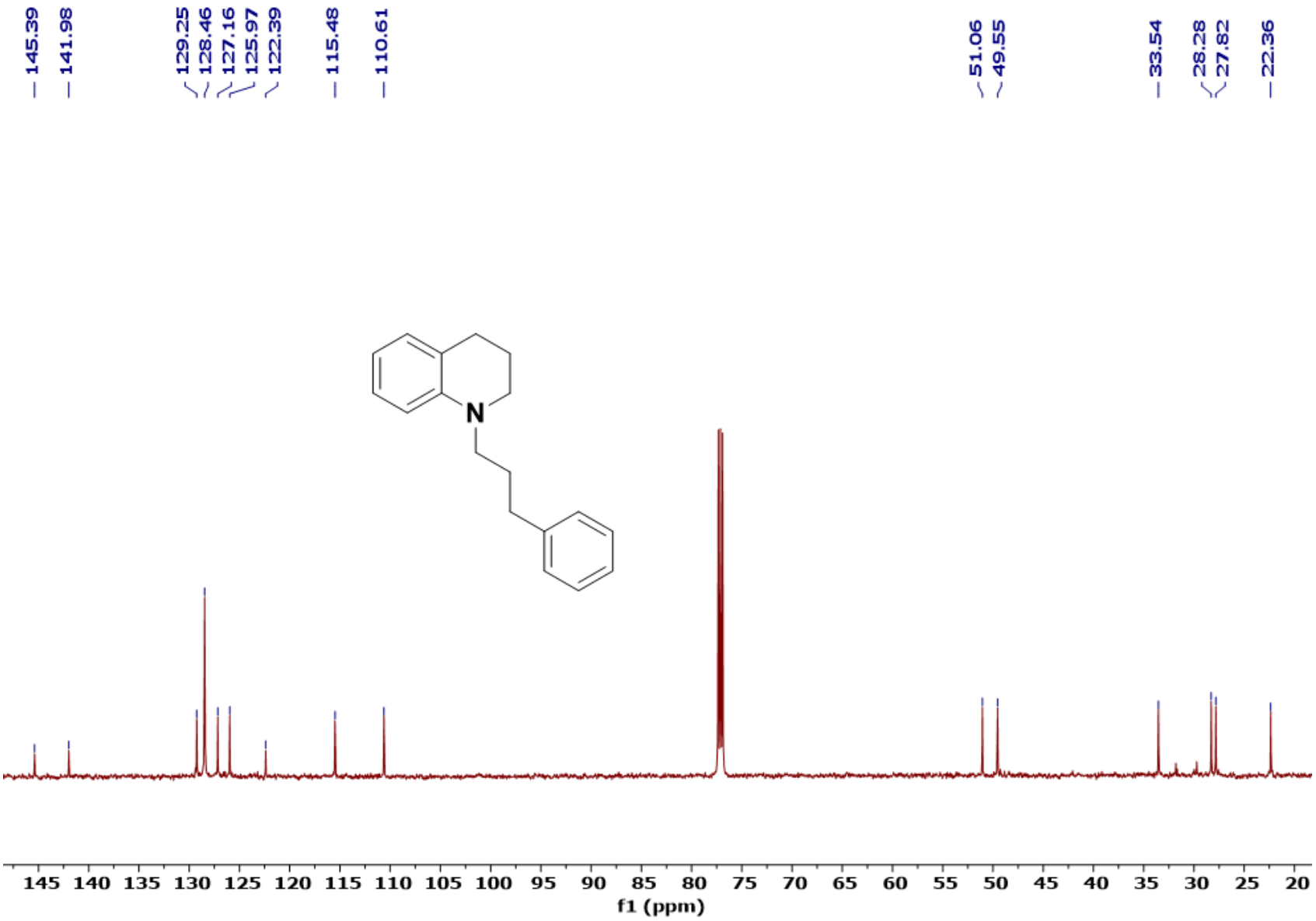


Fig. S78 ^{13}C NMR Spectrum of 1-(3-phenylpropyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

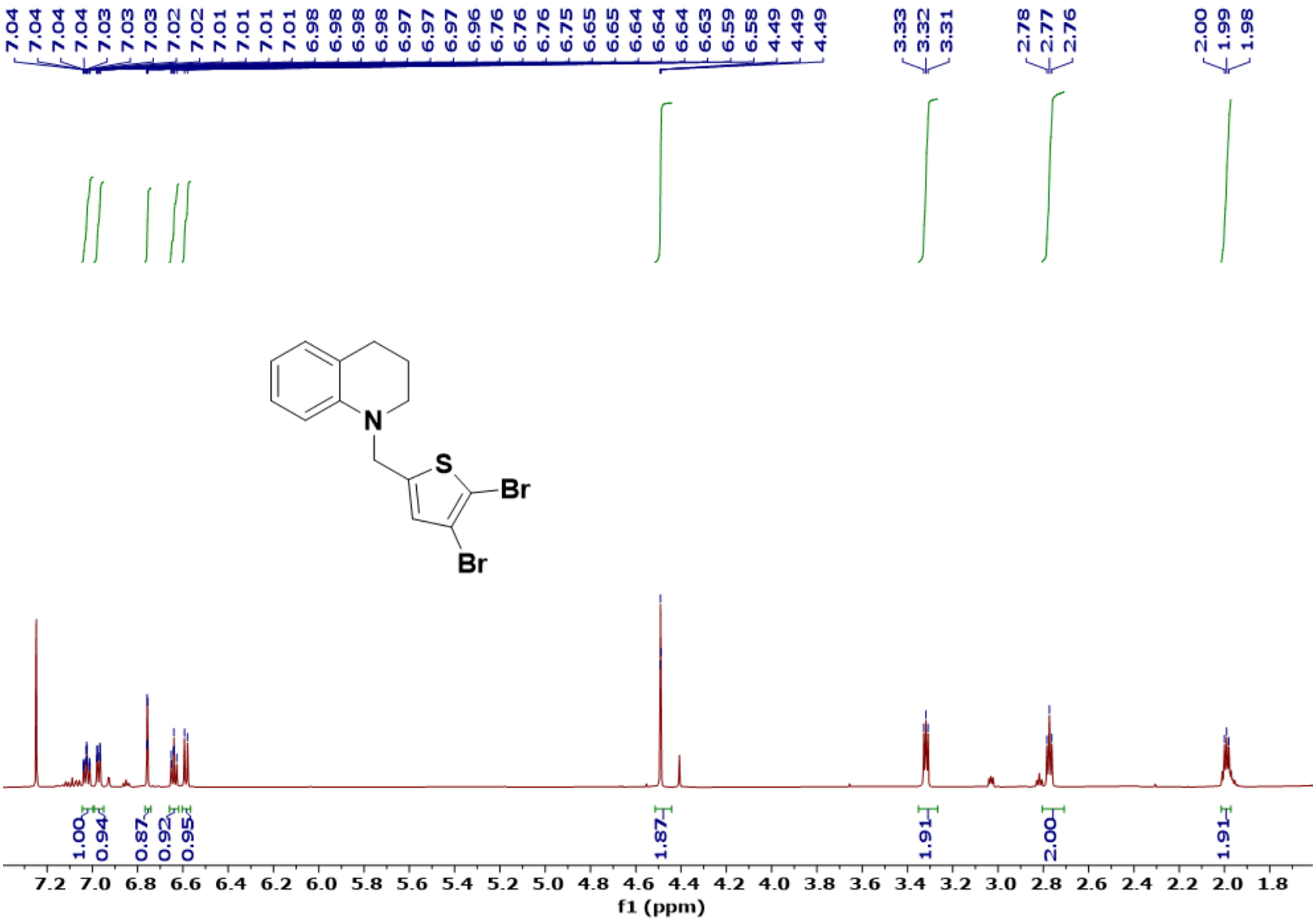


Fig. S79 ^{1}H NMR Spectrum of 1-((4,5-dibromothiophen-2-yl)methyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

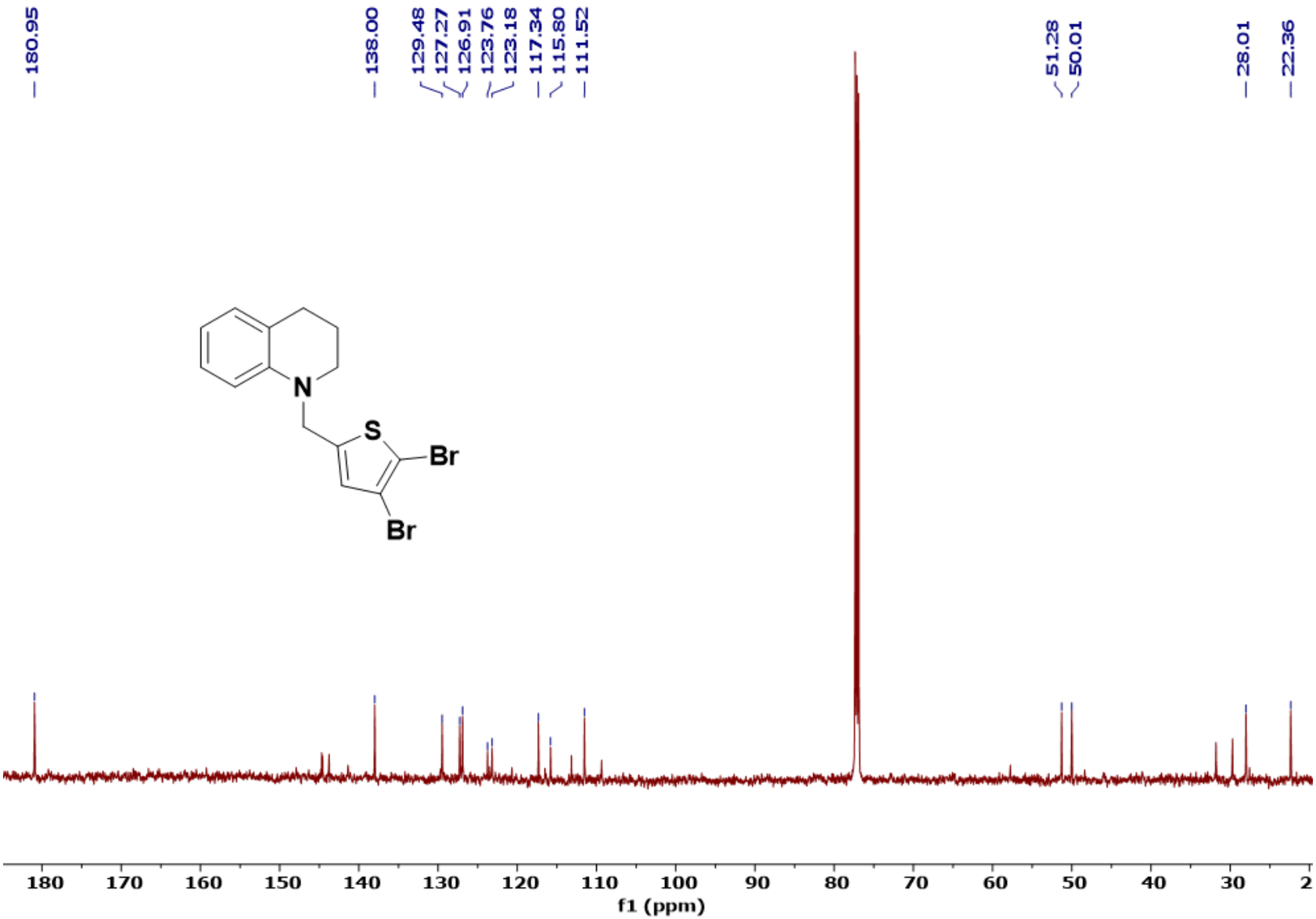


Fig. S80 ^{13}C NMR Spectrum of 1-((4,5-dibromothiophen-2-yl)methyl)-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

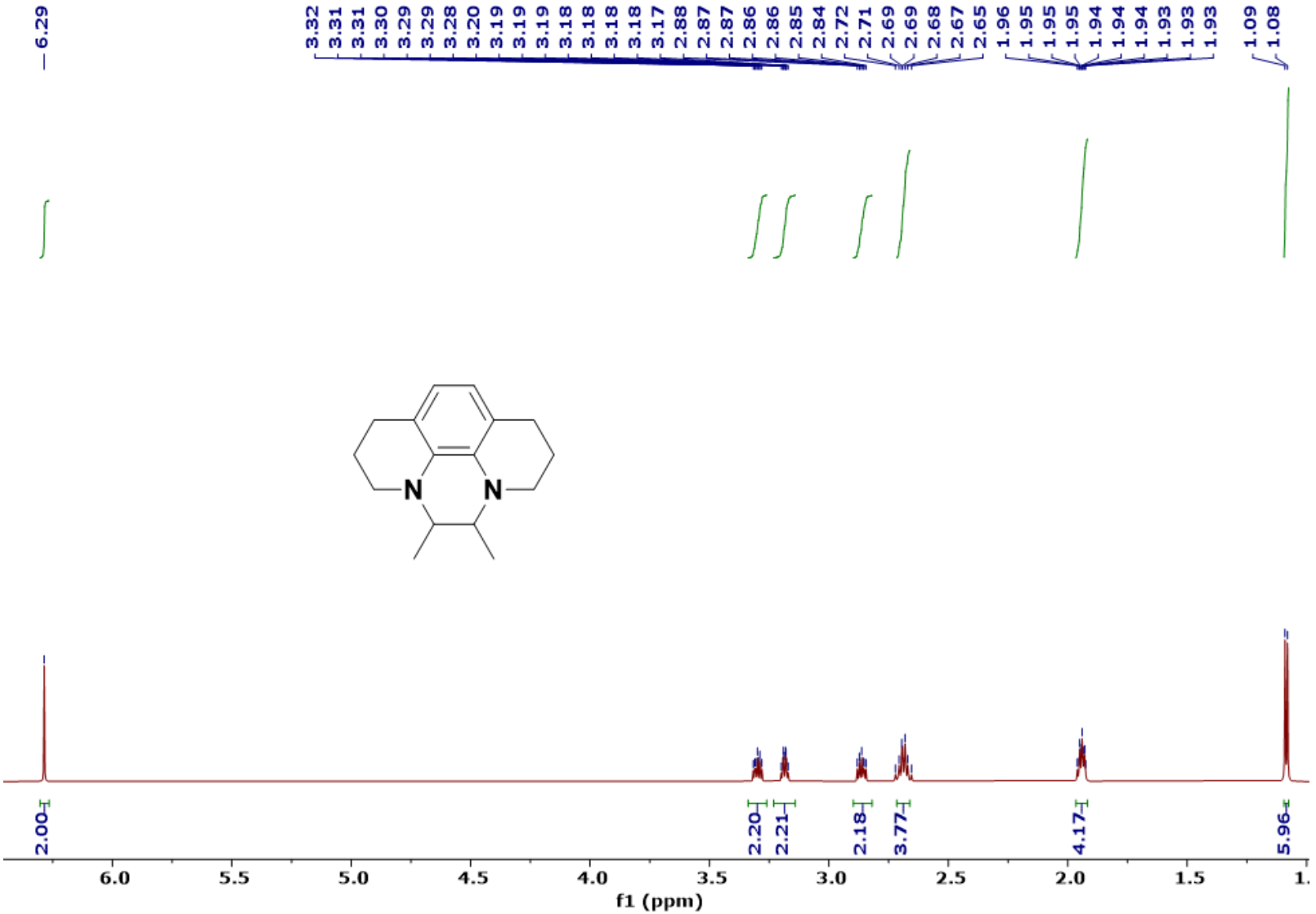


Fig. S81 ^{1}H NMR Spectrum of 5,6-dimethyl-1,2,3,5,6,8,9,10-octahydropyrazino[1,2,3,4-lmn][1,10]phenanthroline ($CDCl_3$, 500 MHz, 298K)

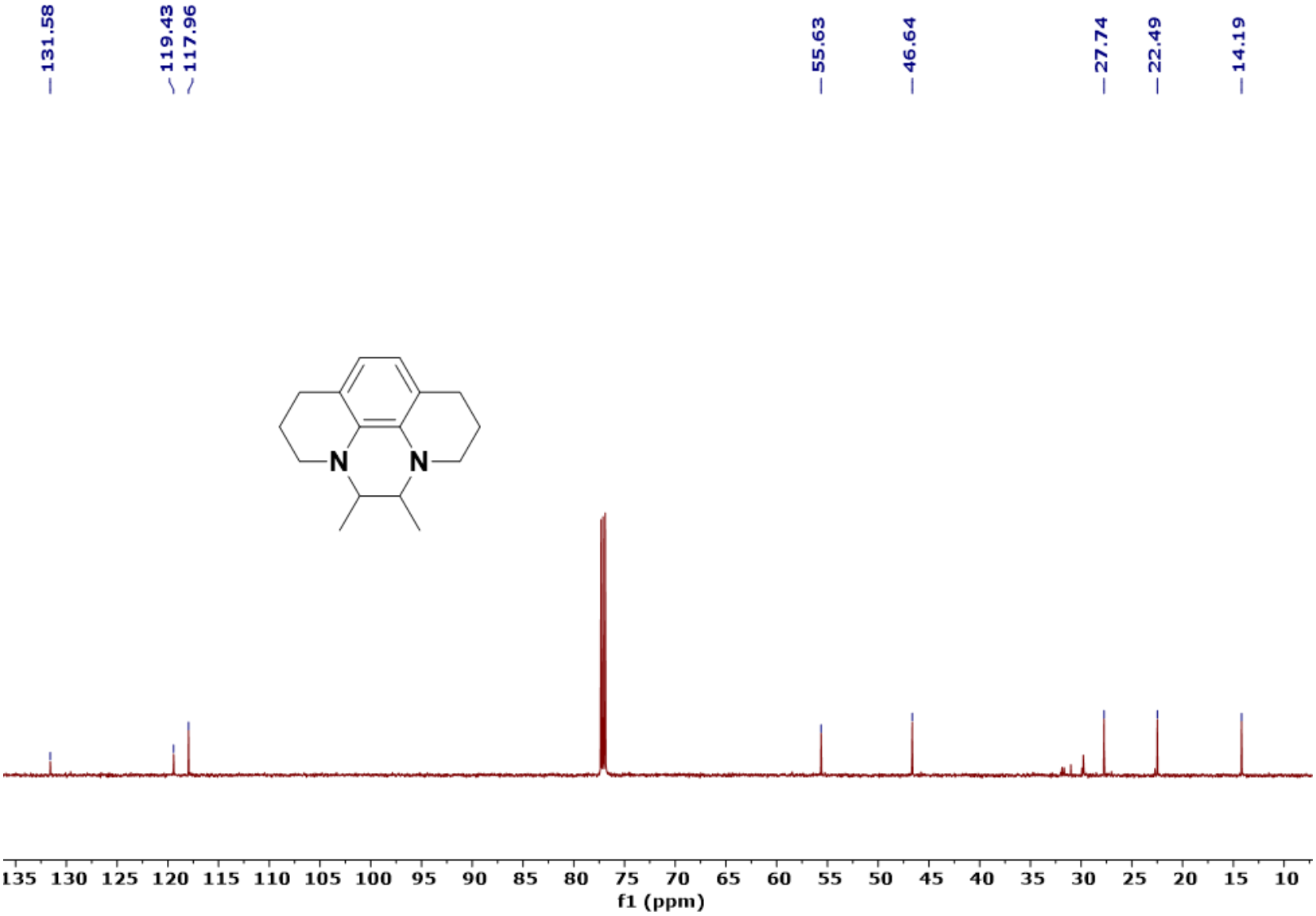


Fig. S82 ^{13}C NMR Spectrum of 5,6-dimethyl-1,2,3,5,6,8,9,10-octahydropyrazino[1,2,3,4-lmn][1,10]phenanthroline ($CDCl_3$, 500 MHz, 298K)

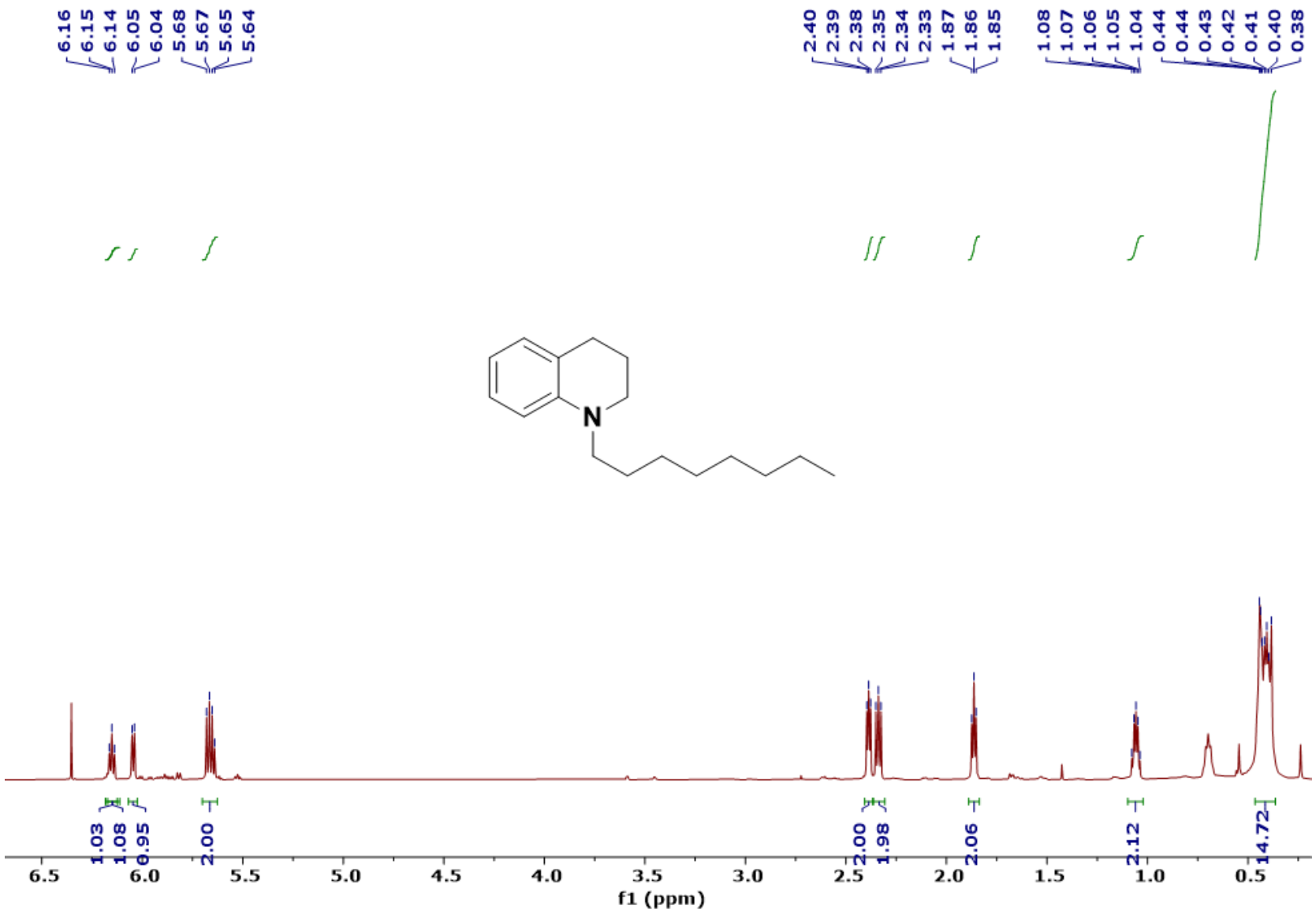


Fig. S83 ^{1}H NMR Spectrum of 1-octyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

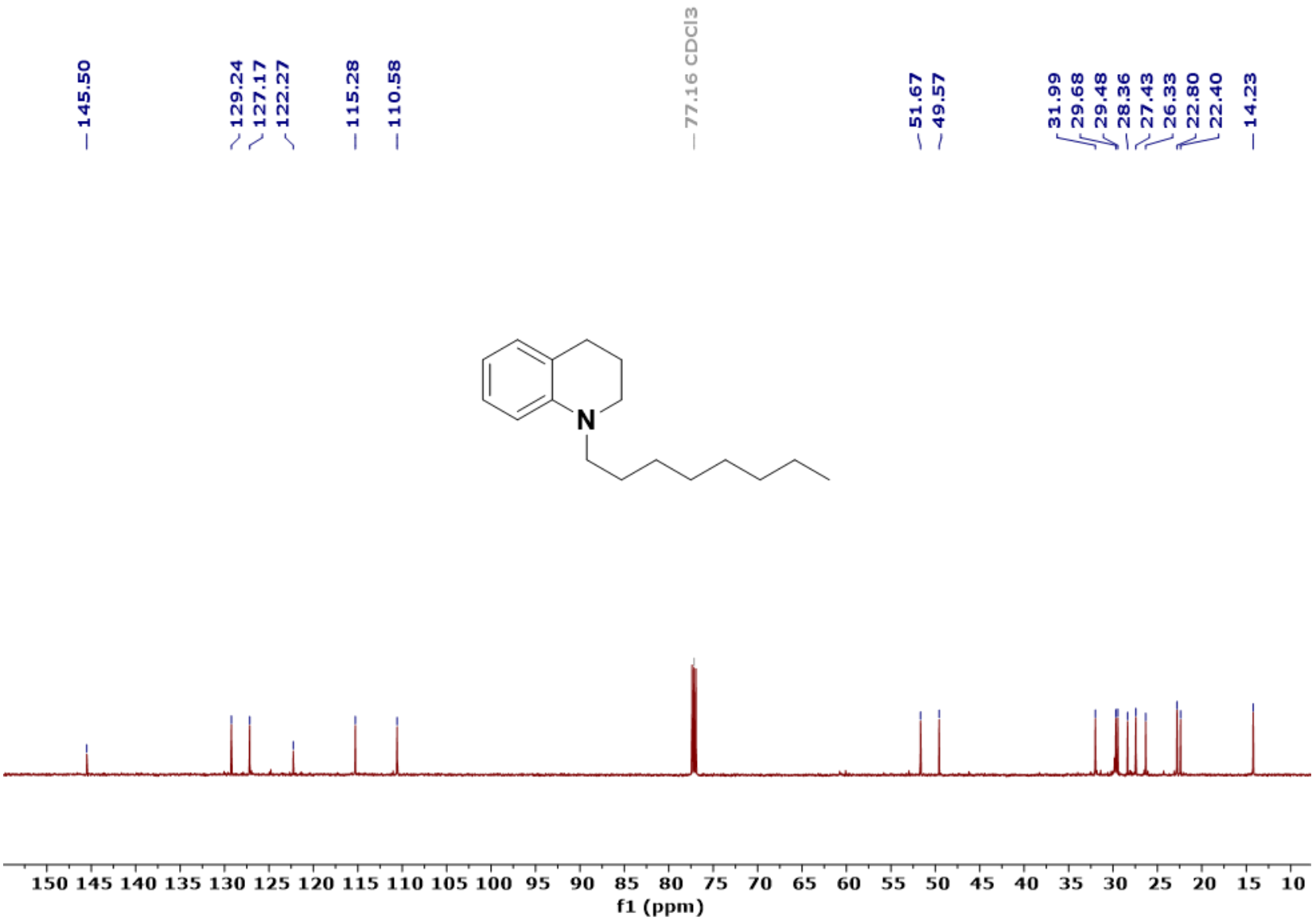


Fig. S84 ^{13}C NMR Spectrum of 1-octyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz, 298K)

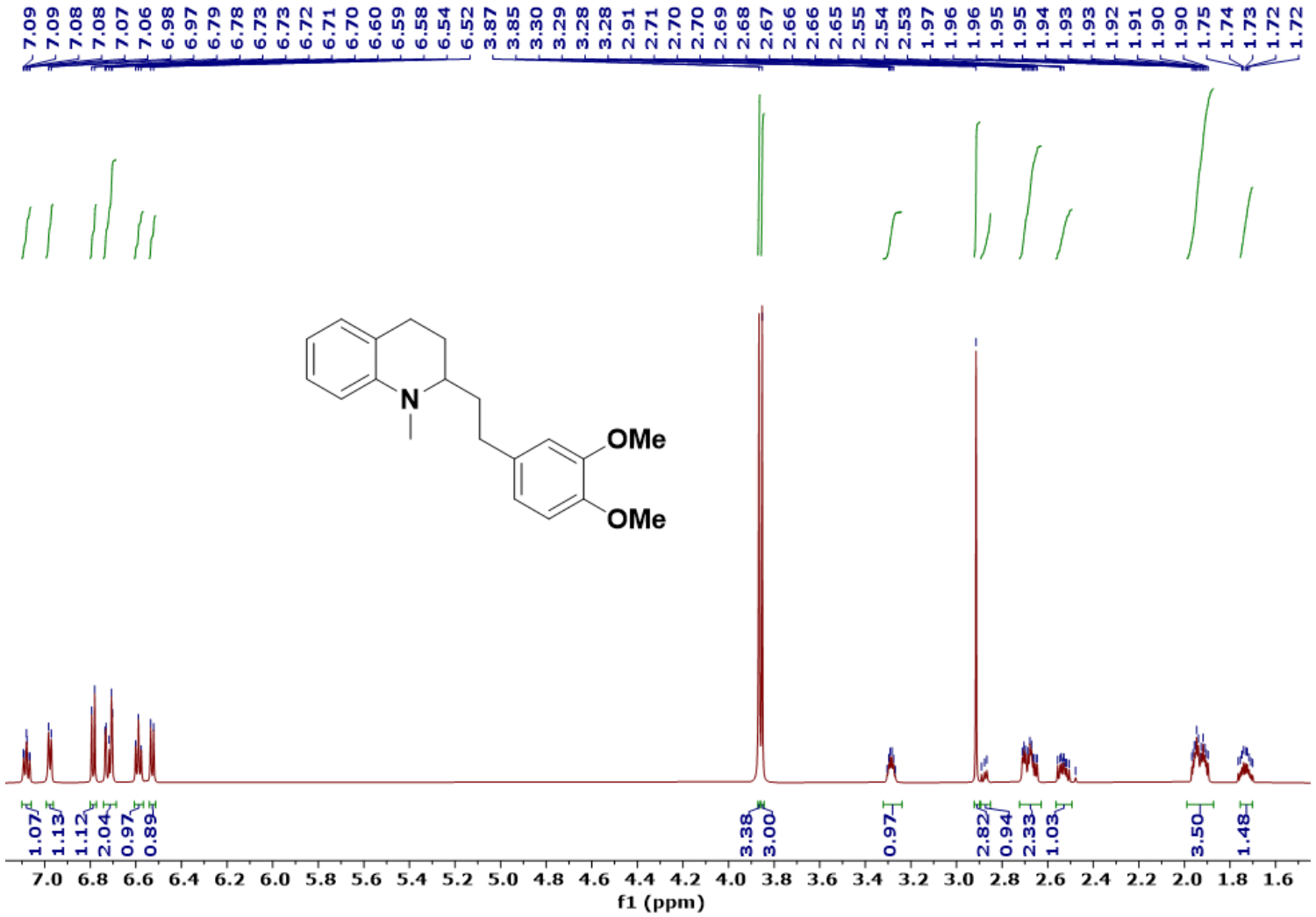


Fig. S85 ^{1}H NMR Spectrum of 2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (Cuspareine) ($CDCl_3$, 500 MHz, 298K)

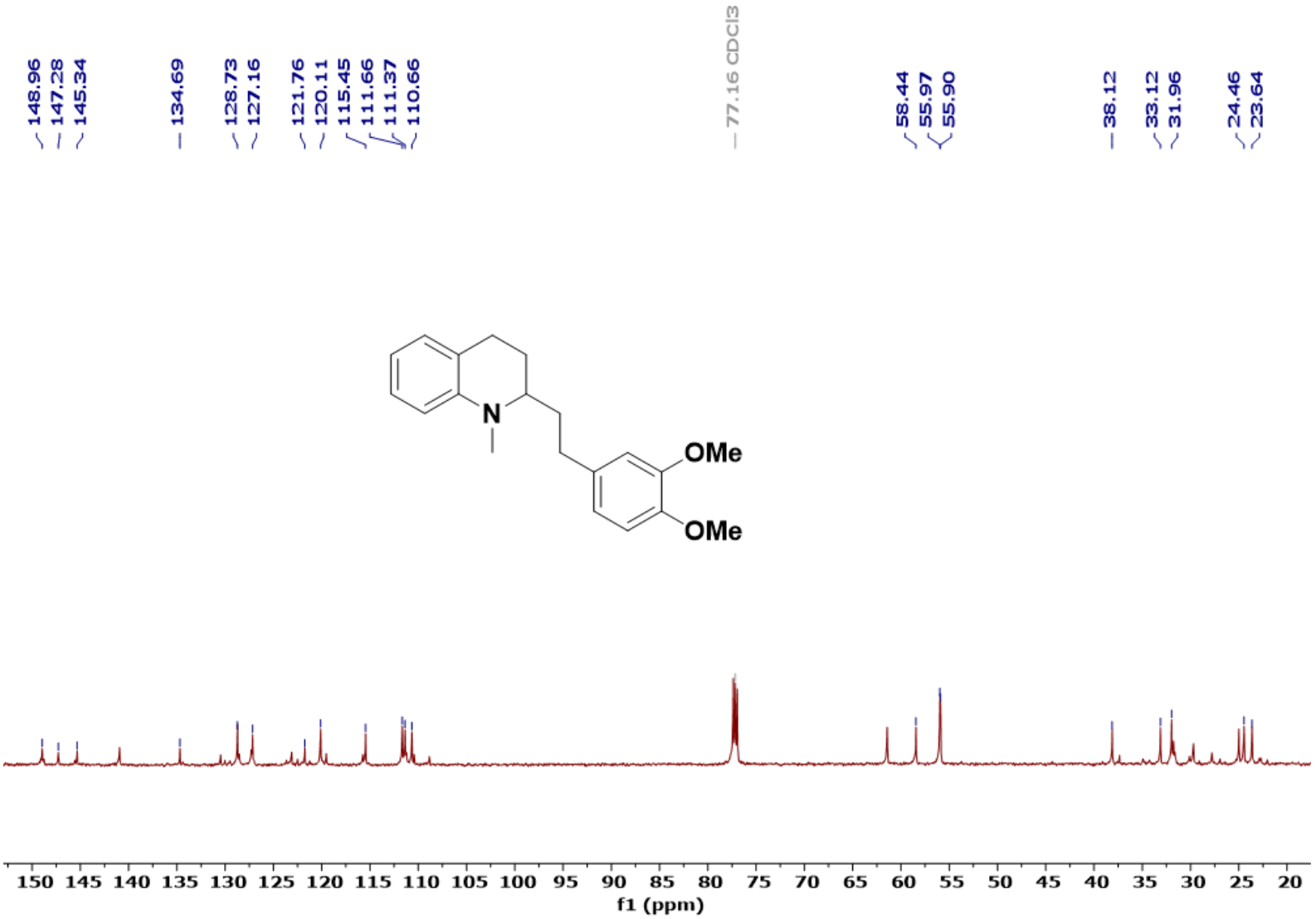


Fig. S86 ^{1}H NMR Spectrum of 2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (Cuspareine) ($CDCl_3$, 500 MHz, 298K)

19. ^{1}H and ^{13}C NMR of HE and OHE

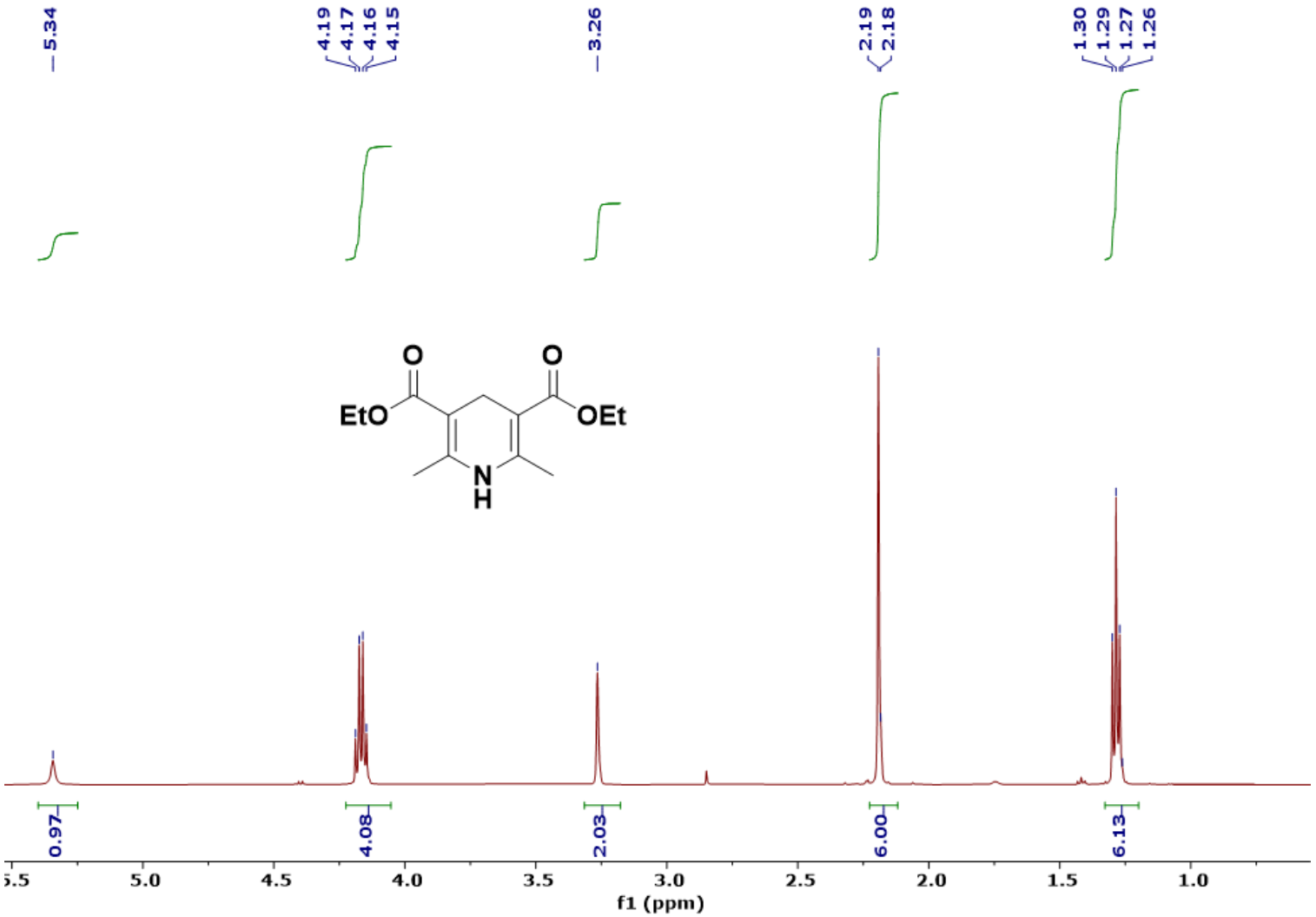


Fig. S87 ^{1}H NMR Spectrum of HE

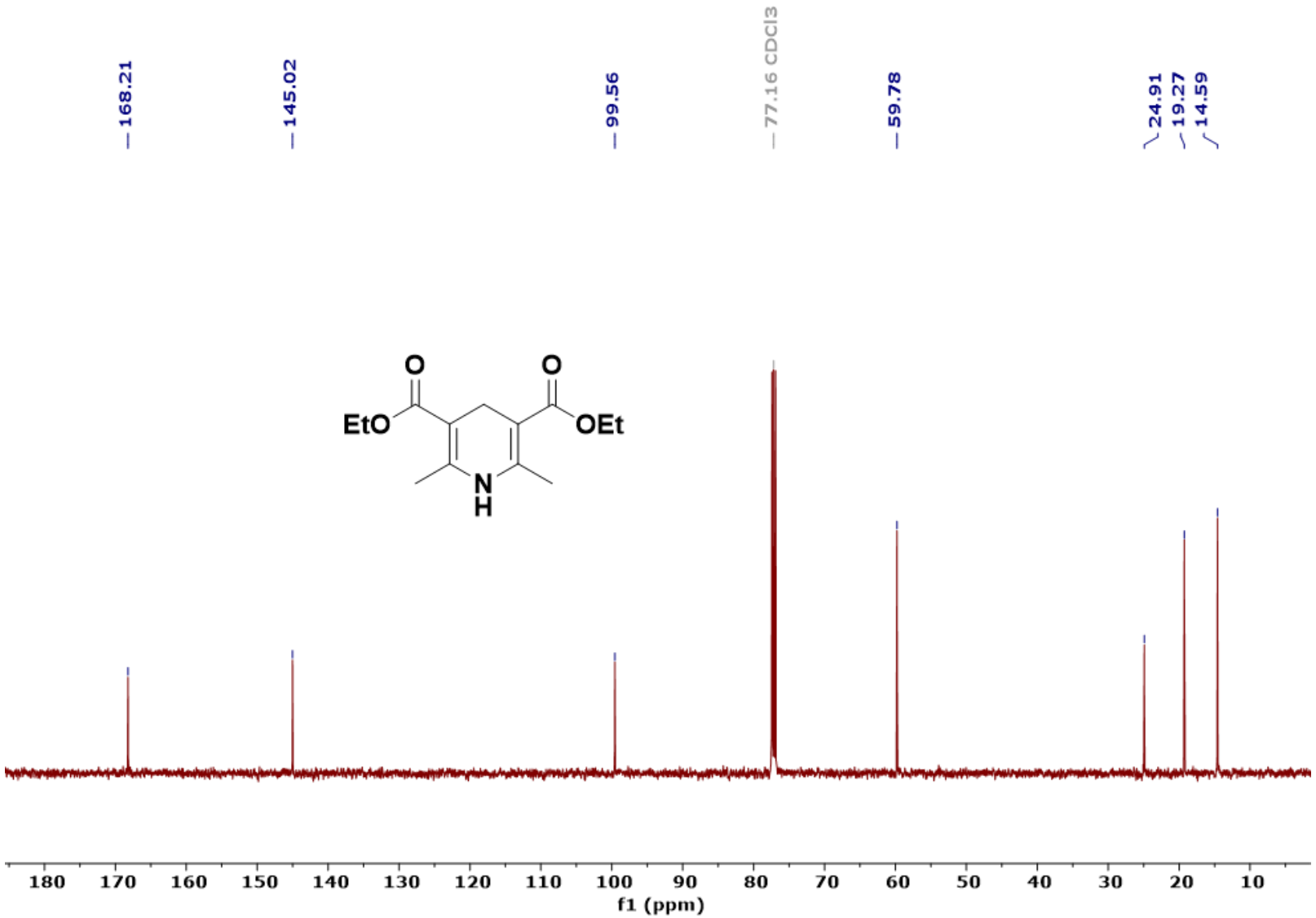


Fig. S88 ^{13}C NMR Spectrum of HE

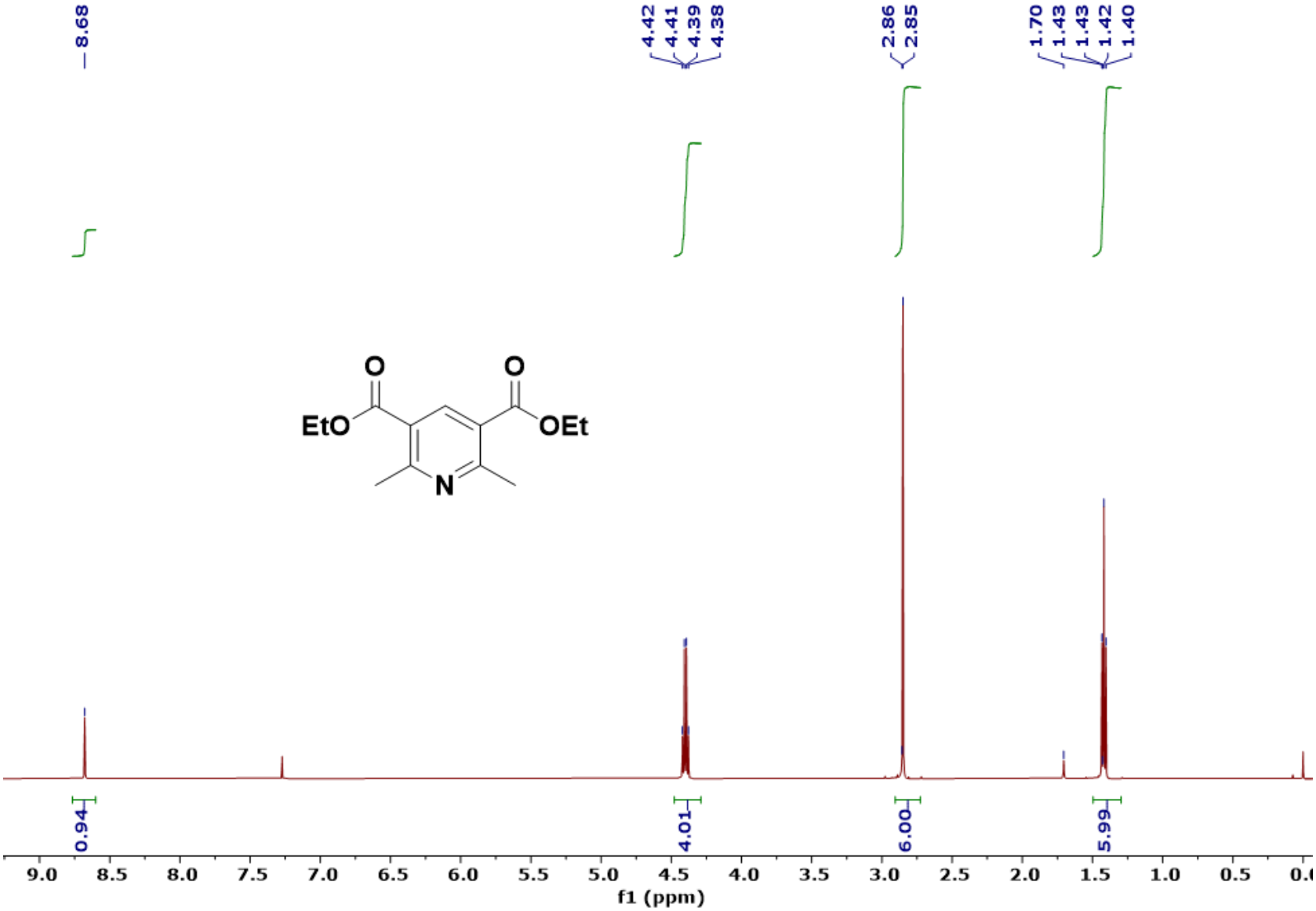


Fig. S89 ^{1}H NMR Spectrum of Oxidised HE

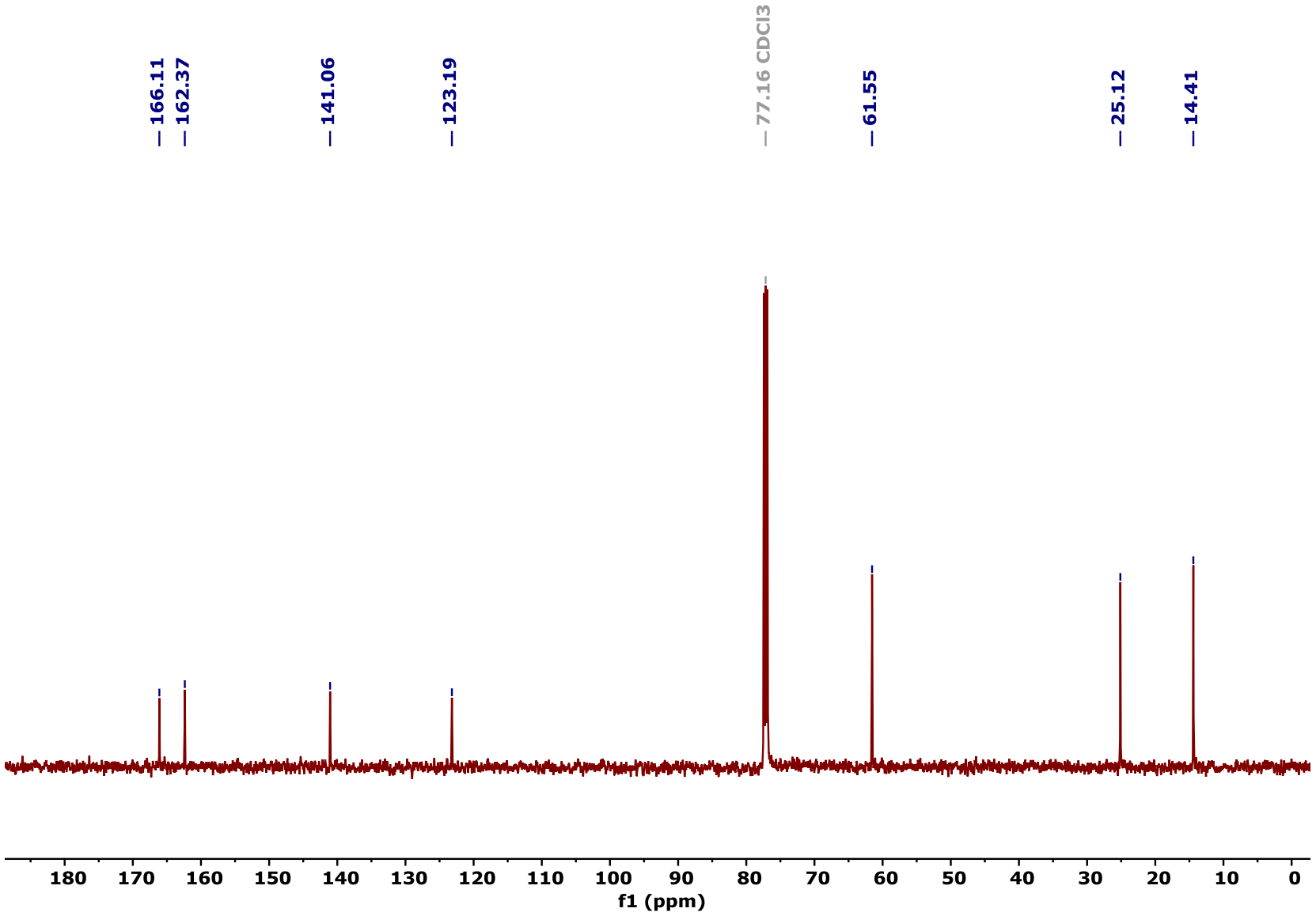


Fig. S90 ^{13}C NMR Spectrum of Oxidised HE

20. References:

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