Supporting Information

Boric acid catalyzed chemoselective reduction of quinolines

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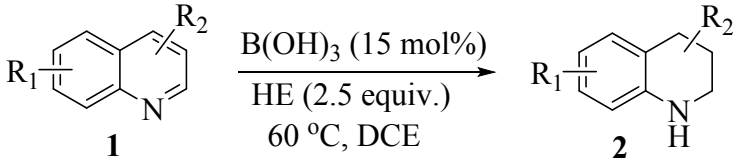
1. General Information

All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd. and directly used as received without any further purification unless otherwise mentioned. 2-pentylquinoline,[1] quinolin-2-ylmethanol,[2] 2-styrylquinoline,[3] (*E*)-2-(3,4-dimethoxystyryl)quinoline,[3] 3-methyl-2-phenylquinoline,[1] methyl quinoline-2-carboxylate,[4] 3-cyanoquinoline,[5] 8-(benzyloxy)quinoline,[6] quinolin-8-yl-4-methylbenzenesulfonate,[7] *N*-(quinolin-8-yl)acetamide,[8] quinolin-8-ylacetate,[9] 2-(2-benzimidazolyl)quinolone[10] and 2-(quinolin-2-yl)benzo[*d*]thiazole[10] were prepared according to the reported literature. Boric acid, phenyl boronic acid, and 4-methoxy phenyl boronic acid were purchased from Avra Synthesis Private Ltd and used without further purification. Hantzsch ester was prepared according to the reported literature.[11] All the transfer hydrogenation reactions were performed in a pyrex tube and were carried out under air. ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of the compounds were measured in $CDCl_3$ and DMSO-d_6 as a solvent by using TMS as an internal standard. Chemical shifts, δ (in ppm), are reported relative to TMS δ (^{1}H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^{1}H) 7.26 ppm, δ (^{13}C) 77.16 ppm; DMSO-d_6, (^{1}H) 2.50 ppm, δ (^{13}C) 39.52 ppm) were used for calibration. Bruker Avance III 600 and 400 spectrometers were used to record the NMR spectra. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (*J*) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, sext = sextet, br = broad, and brs = broad singlet. IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520. Merck or Spectrochem silica gel 60-120 was used for column chromatography.

2. General procedure for transfer hydrogenation reaction



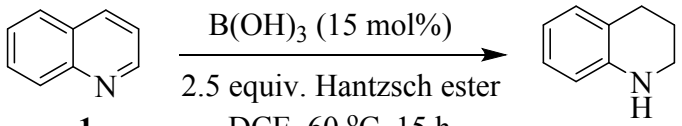
1 **2**

Scheme S1: Transfer hydrogenation of substituted quinolines.

In a pyrex tube (15 mL), substituted quinoline (0.5 mmol), Hantzsch ester (2.5 equiv.), $B(OH)_3$ (15 mol%) and solvent (2 mL) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath (60 °C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in *n*-hexane and ethyl acetate solvent system. After completion of the reaction, the crude compound was purified by column chromatography on silica gel for pure compound.

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

3. Procedure for gram scale transfer hydrogenation reaction



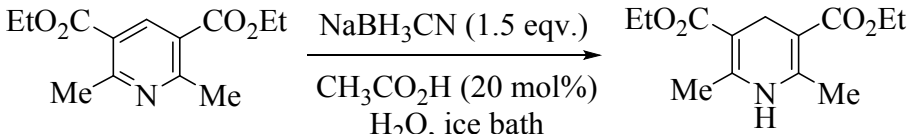
1
1 g scale

2a,
95%

Scheme S2: Gram scale transfer hydrogenation of quinoline.

In a pyrex tube (100 mL), quinoline (1.09 gm, 8.46 mmol), Hantzsch ester (5.35 gm, 2.5 eqv.), $B(OH)_3$ (79 mg, 15 mol%) and DCE (15 mL) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath (60 °C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in hexane and ethyl acetate solvent system. Once the reaction was complete, reaction tube was brought to room temperature and purified by column chromatography for pure product. The final product was then analysed by ^{1}H and ^{13}C NMR. Isolated yield: 1.07 gm, 95%.

4. Procedure for Hantzsch pyridine (HE') to Hantzsch-1,4-dihydropyridine (HE) recovery



HE'

HE, 91%

Scheme S3: Reduction of Hantzsch pyridine ester to Hantzsch-1,4-dihydropyridine ester.

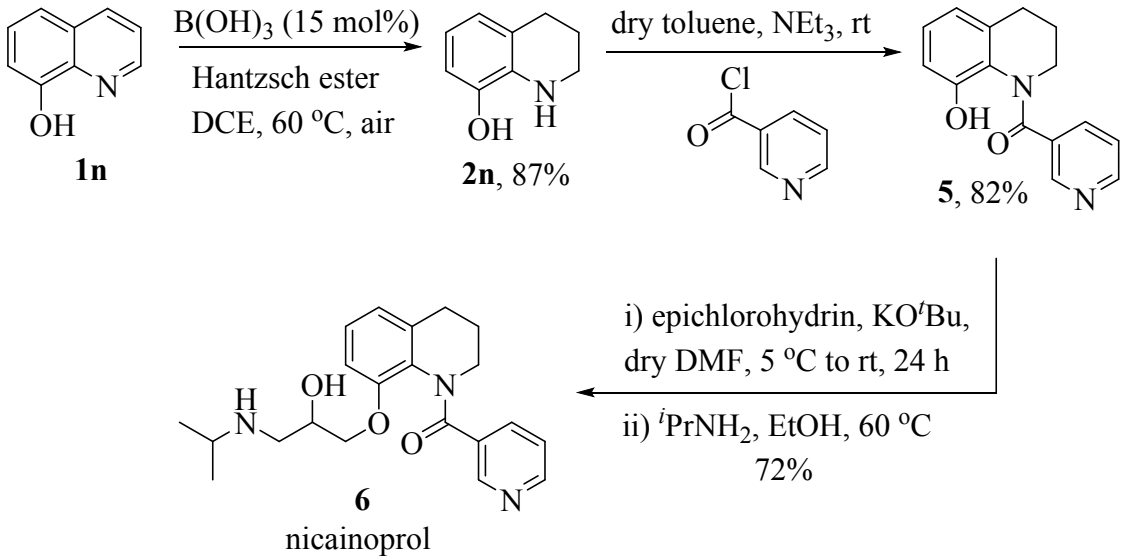
In a 50 mL round bottom flask, Hantzsch pyridine (1 gm, 3.9 mmol), water (10 mL) and acetic acid (45 µL, 20 mol%) were charged and placed in an ice bath. In the reaction mixture $NaBH_3CN$ (294 mg, 1.2 eqv.) was slowly added and stirred for overnight. The reaction was monitored by thin layered chromatography (TLC) in hexane and ethyl acetate solvent system. Once the reaction was completed, solid precipitate was filtered, washed thoroughly by water and ice cold acetone and dried on vacuum desiccator. Isolated yield: 0.9 g, 91%.

5. Applications of synthesized 1,2,3,4-tetrahydroquinoline derivatives

5.1 Synthesis of nicainoprol

Transfer hydrogenation of 8-hydroxyquinoline to 8-hydroxy-1,2,3,4-tetrahydroquinoline

In a pyrex tube (100 mL), 8-hydroxyquinoline (1 g, 6.8 mmol, 1 eqv.), Hantzsch ester (4.3 g, 17 mmol, 2.5 eqv.), $B(OH)_3$ (15 mol%) and DCE (15 mL) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath (60 °C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in *n*-hexane and ethyl acetate solvent system. Once the reaction was completed, reaction tube was brought to room temperature and purified by silica column chromatography using CH_2Cl_2/ MeOH mixture to get the pure 8-hydroxy-1,2,3,4-tetrahydroquinoline (**2n**). Isolated yield: 0.882 g, 87%, colourless oil.



Scheme S4: Synthesis of nicainoprol.

Synthesis of compound 5

In a 50 mL schlenk flask, 8-hydroxy-1,2,3,4-tetrahydroquinoline (0.6 g, 4.02 mmol,1 eqv.), nicotinoyl chloride (0.681 g, 4.83 mmol, 1.2 eqv.), triethyl amine (0.611 g, 6.04 mmol, 1.5 eqv.) and dry toluene (20 mL) were charged and stirred overnight in argon atmosphere at room temperature. Once the reaction was complete, toluene was evaporated by using rotary evaporator. The solid reaction crude was purified by liquid-liquid separation method (water/ ethyl acetate), the organic layer was added with Na_2SO_4 to remove the excess water and concentrated in a rotary evaporator. Afterwards, the solid crude was purified by silica column chromatography using CH_2Cl_2 : MeOH (5-10% MeOH mixture) solvent system to obtain pure product as white solid (838 mg, 82%); m.p: 121~122 °C.

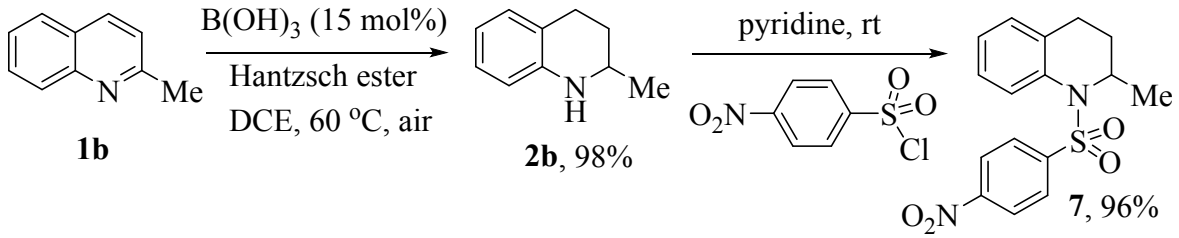
Synthesis of compound 6

In a 50 mL schlenk flask, compound **5** (0.125 g, 0.49 mmol, 1 eqv.) was dissolved in dry DMF (0.5 mL) and potassium *tert*-butoxide (0.066 g, 0.59 mmol, 1.2 eqv.) was charged onto it. The entire solution was stirred in ice cold bath (~0-5 °C) for 30 min followed by the dropwise addition of epichlorohydrin (0.068 g, 0.735 mmol, 1.5 eqv.). After complete addition the reaction mixture was continue to stir at ice cold bath for next 30 minutes and then allowed warm to room temperature and stirred for another 24 h. The reaction was monitored by thin layered chromatography (TLC) in CH_2Cl_2 and methanol solvent system. After completion of the reaction, crude reaction was concentrated in rotary evaporator and purified by using liquid-liquid separation method (water/ ethyl acetate). The organic layer (ethyl acetate fraction) was added with Na_2SO_4 to remove the excess water and concentrated in a rotary evaporator. Afterwards, the solid crude (0.118 g, 78%) was directly proceeded for the next step without any further purification. The compound was sensitive towards air and moisture, recommendable to store under argon at -20 °C.

In a 50 mL pyrex tube, above crude compound (0.118 g, 0.38 mmol, 1 eqv.) was dissolved in dry ethanol (2 mL) and isopropylamine (0.045 g, 0.76 mmol, 2 eqv.) was charged onto it. The

tube was closed under argon flow and the entire solution was stirred at 60 °C for 12 hours. The reaction was monitored using thin layered chromatography (TLC). Upon complete consumption of the starting material, the reaction mixture is concentrated in rotary evaporator to remove ethanol and unreacted isopropylamine. Pure compound **6** was obtained by neutral alumina column chromatography using CH_2Cl_2 : MeOH (4% MeOH mixture) solvent system to obtain pure product as white solid (130 mg, 93%); m.p: 120~122 ℃ . Overall yield in the last step: 75%.

5.2 Synthesis of antitrypanasomal active compound (7)



Scheme S5: Synthesis of antitrypanasomal active compound.

Step 1: Transfer hydrogenation of 2-methylquinoline to 2-methyl-1,2,3,4-tetrahydroquinoline

In a pyrex tube (15 mL), 6-methoxyquinoline (159 mg, 1 mmol), Hantzsch ester (633 mg, 2.5 eqv.), $B(OH)_3$ (10 mg, 15 mol%) and dichloroethane (5 mL) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath (60 °C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in hexane and ethyl acetate solvent system. Once the reaction was completed, reaction tube was brought to room temperature and purified by column chromatography for pure product. Isolated yield- 144 mg, 98%, colourless oil.

Step 2: Synthesis of 2-methyl-1-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (7)[12]

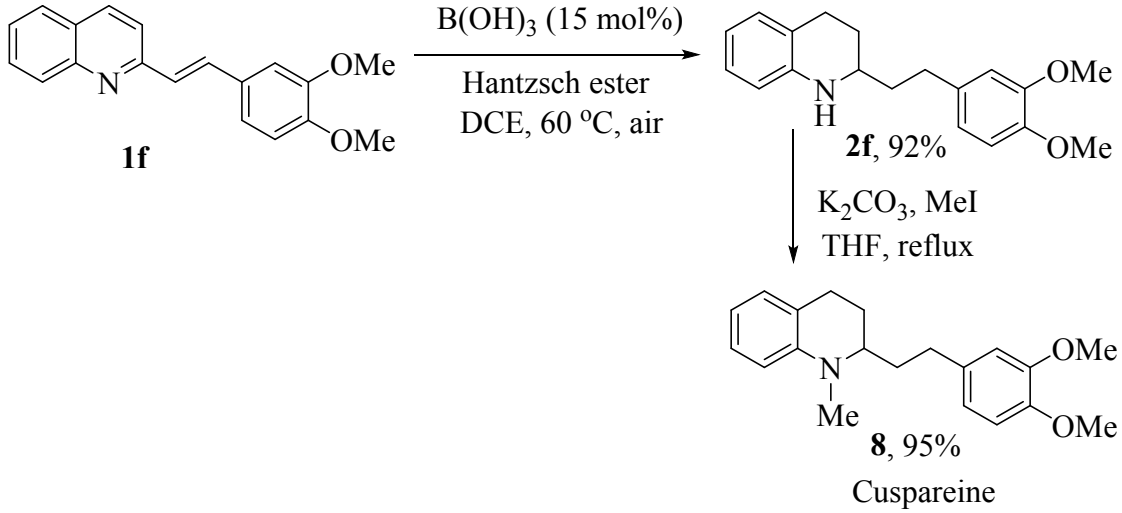
In a 25 mL round bottom flask, 2-methyl-1,2,3,4-tetrahydroquinoline (100 mg, 0.68 mmol), 4-nitrobenzenesulfonyl chloride (150 mg, 1 eqv.) and pyridine (3 mL) were charged and allowed to stir at room temperature for 20 h. After consuming the substrates, water was added to the reaction mixture and extracted by using ethyl acetate. The organic layer was further washed with diluted HCl solution to remove the pyridine in traces. Afterwards, in the organic layer Na_2SO_4 was added to remove excess water and finally organic solvent was evaporated by using rotary evaporator. The product was further purified by column chromatography using hexane and ethyl acetate solvent system to obtain the pure product as pale yellow solid (217 mg, 96%); m.p: 160~162 ℃.

5.3 Synthesis of cuspareine (8)

Step 1: Transfer hydrogenation of (*E*)-2-(3,4-dimethoxystyryl)quinolone (1f) to 2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (2f)

In a pyrex tube (15 mL), (*E*)-2-(3,4-dimethoxystyryl)quinoline (100 mg, 0.34 mmol), Hantzsch ester (217 mg, 2.5 eqv.), $B(OH)_3$ (4 mg, 15 mol%) and dichloroethane (3 mL) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath

(60 °C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in hexane and ethyl acetate solvent system. Once the reaction was complete, reaction tube was brought to room temperature (30 °C) and purified by column chromatography for pure product. Isolated yield- 93 mg, 92%.

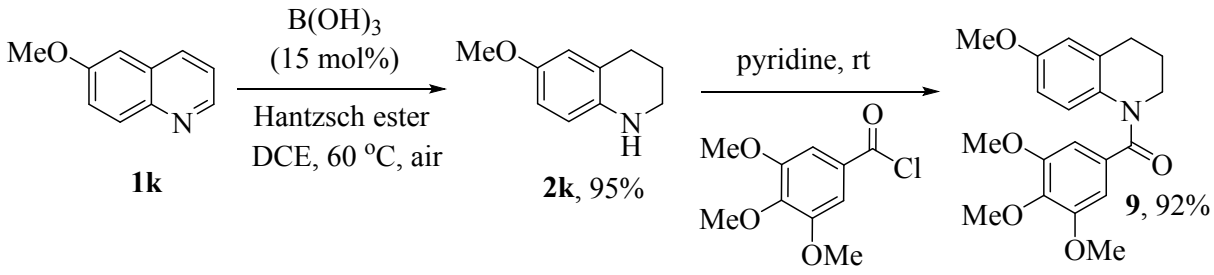


Scheme S6: Synthesis of (±) cuspareine.

Step 2: Synthesis of 2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (8)[13]

In a pyrex tube (15 mL), 2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (50 mg, .17 mmol), methyl iodide (32 µL, 3 eqv.), potassium carbonate (1 eqv.) and dry THF (3 mL) were charged. The reaction mixture was allowed to reflux in a pre-heated oil bath for 20 h. Once the substrates were consumed, THF was evaporated using rotary evaporator and directly purified by column chromatography (*n*-hexane/ ethyl acetate) to afford the pure product as yellow oil (50 mg, 95%).

5.4 Synthesis of tubulin polymerization inhibitor (9)



Scheme S7: Synthesis of tubulin polymerization inhibitor.

Step 1: Transfer hydrogenation of 6-methoxyquinoline to 6-methoxy-1,2,3,4-tetrahydroquinoline

In a pyrex tube (15 mL), 6-methoxyquinoline (159 mg, 1 mmol), Hantzsch ester (633 mg, 2.5 eqv.), $B(OH)_3$ (10 mg, 15 mol%) and dichloroethane (5 mL) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath (60 °C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in

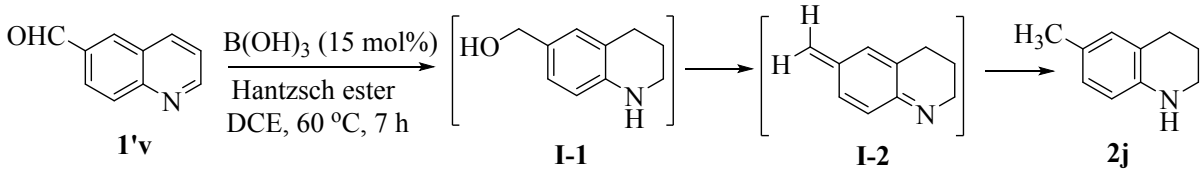
hexane and ethyl acetate solvent system. Once the reaction was complete, reaction tube was brought to room temperature and purified by column chromatography for pure product **2k**. Isolated yield: 155 mg, 95%.

Step 2: Synthesis of compound 9[14]

In a 50 mL schlenk flask, 6-methoxy-1,2,3,4-tetrahydroquinoline (100 mg, 0.61 mmol), was dissolved in pyridine (2 mL). Next, 3,4,5-trimethoxybenzoyl chloride (0.92 mmol, 1.5 eqv.) was added to the above solution and resulting mixture was allowed to stir at room temperature for overnight. Once the reaction was completed, water was added to the reaction mixture and extracted by using ethyl acetate. The organic layer was further washed with diluted HCl solution to remove the pyridine in traces. Afterwards, in the organic layer Na_2SO_4 was added to remove excess water and finally organic solvent was evaporated by using rotary evaporator. The product was further purified by column chromatography using hexane and ethyl acetate solvent system to obtain the pure product as light yellow viscous liquid (200 mg, 92%).

6. Proposed pathway for the reduction of quinoline-6-carbaldehyde

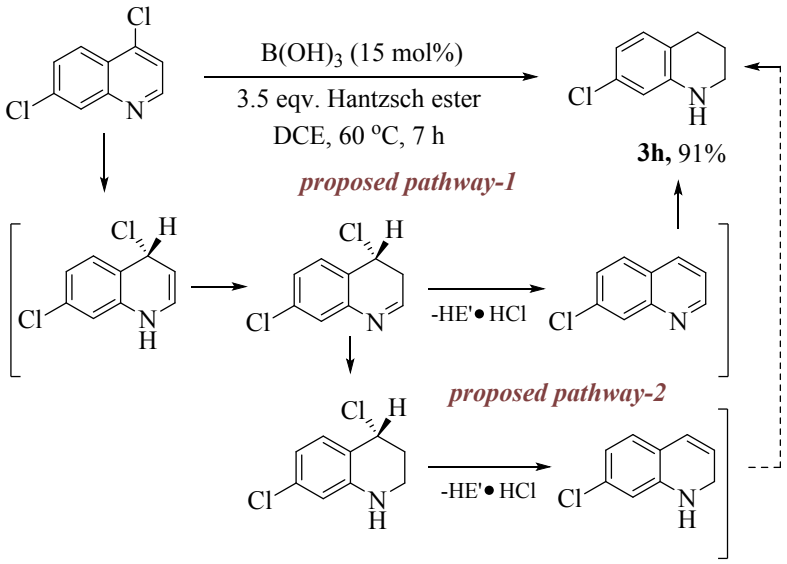
The reduction of quinoline-6-carbaldehyde possibly possesses in stepwise manner, first, both quinoline ring and carbaldehyde unit were reduced to give intermediate **I-1**, then converted to 6-methylene-2,3,4,6-tetrahydroquinoline (**I-2**) *via* hydroxo-group liberation by the activation of boric acid, subsequently further reduction leads to 6-methyl-1,2,3,4-tetrahydroquinoline **2j**.



Scheme S8: Proposed pathway for the reduction of quinoline-6-carbaldehyde

7. Proposed pathway for the reduction of 4,7-dichloroquinoline

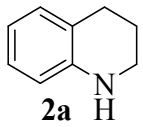
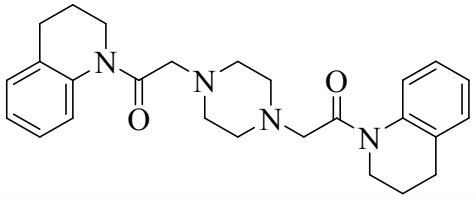
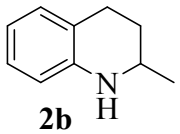
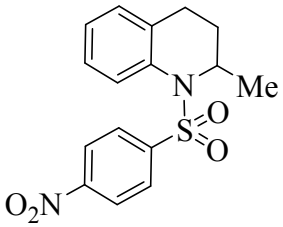
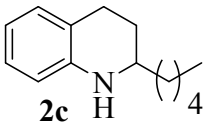
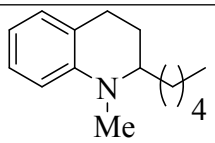
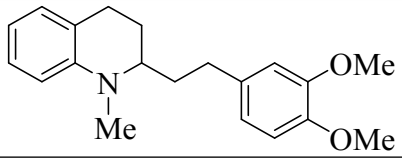
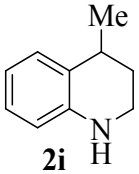
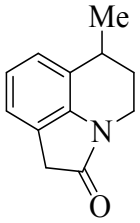
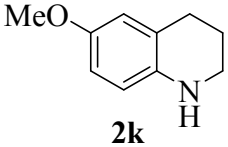
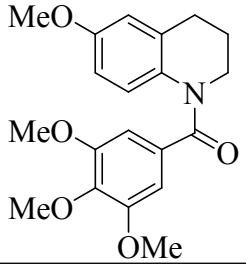
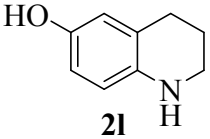
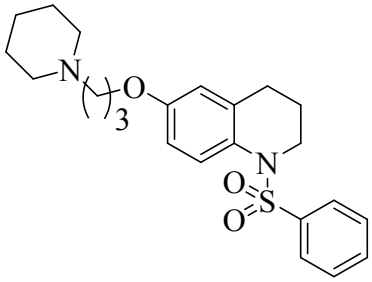
The proposed pathway for the reduction of 4,7-dichloroquinoline is given below.

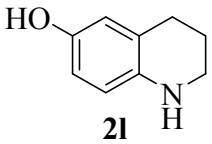
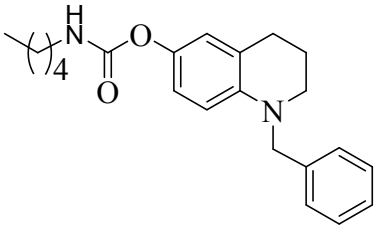
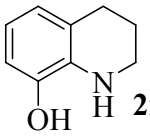
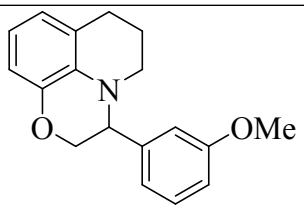
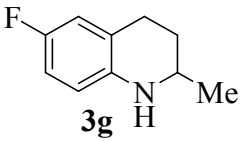
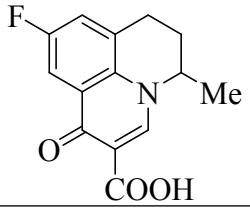


Scheme S9: Proposed pathway for the reduction of 4,7-dichloroquinoline

8. Synthesized precursors for bioactive molecules

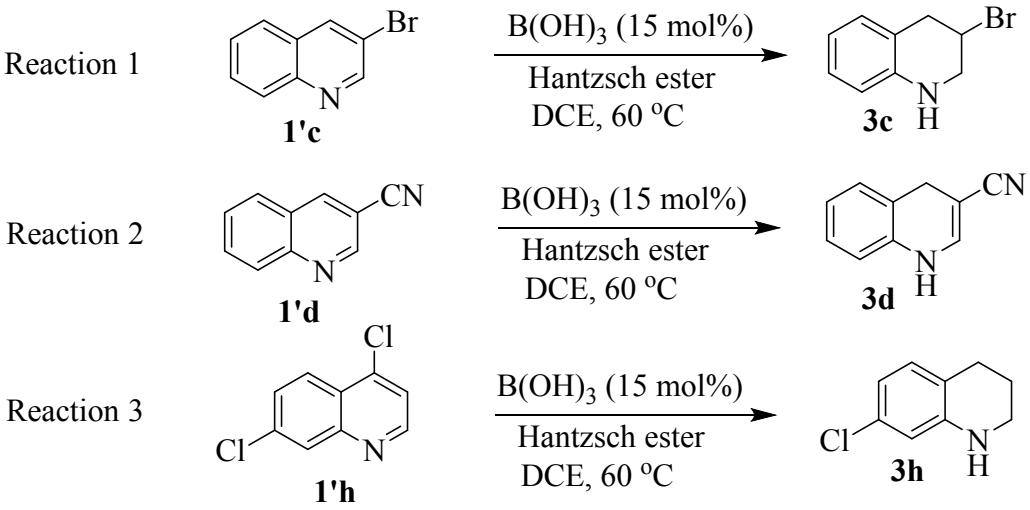
Table S1: Some reduced quinoline compound as an active intermediate for the synthesis of biological active molecules.

Entry	1,2,3,4-THQ derivative	Bioactive compound	Application	Ref.
1	 **2a**		Aspernigerin, Natural alkaloid	15
2	 **2b**		Anti trypanasomal activity	12
3	 **2c**		(±)Angustureine Natural alkaloid	16
4	**2f**		Cuspareine (natural alkaloids)	13
5	 **2i**		CNS depressant agent	17
6	 **2k**		Tubulin polymerization Inhibitor	14
7	 **2l**		Histanime H3-Receptor antagonist	18

8	 **2l**		AChE inhibitor	19
9	 **2n**		Oxygen radical scavenger	20
10	 **3g**		Flumequine antibiotic	21

9. Reaction mechanism studies

9.1 Observations from substrate scope studies



Scheme S10: Transfer hydrogenation of 3-bromo, 3-cyano and 4,7-dichloroquinoline with Hantzsch ester.

While conducting the substrate scope studies, few substrates like 3-bromo, 3-cyano and 4,7-dichloroquinolines surprises us because 4,7-dicholoroquinoline ends with 7-chloro-1,2,3,4-tetrahydroquinoline, whereas 3-bromo quinoline gives 3-bromo-1,2,3,4-tetrahydro quinoline and no dehalogenated product. However, the reaction of 3-cyanoquinoline experiment ends with 3-cyano-1,4-dihydroquinoline which might be due to stabilization of conjugation of π electrons. These results suggest, the reaction might proceed via 1,4 addition of hydride into quinoline moiety.

9.2 ^{1}H NMR spectrum of crude reaction mixture

Further, with close inspection of ^{1}H NMR spectrum of reaction mixture, we found two of the interesting peaks at δ = 4.65 and 3.43 ppm (H3 and H4 respectively). The chemical shifts are well matched with the previous report[22] and probably due to the presence of 1,4-dihydroquinoline as an intermediate on the crude reaction.

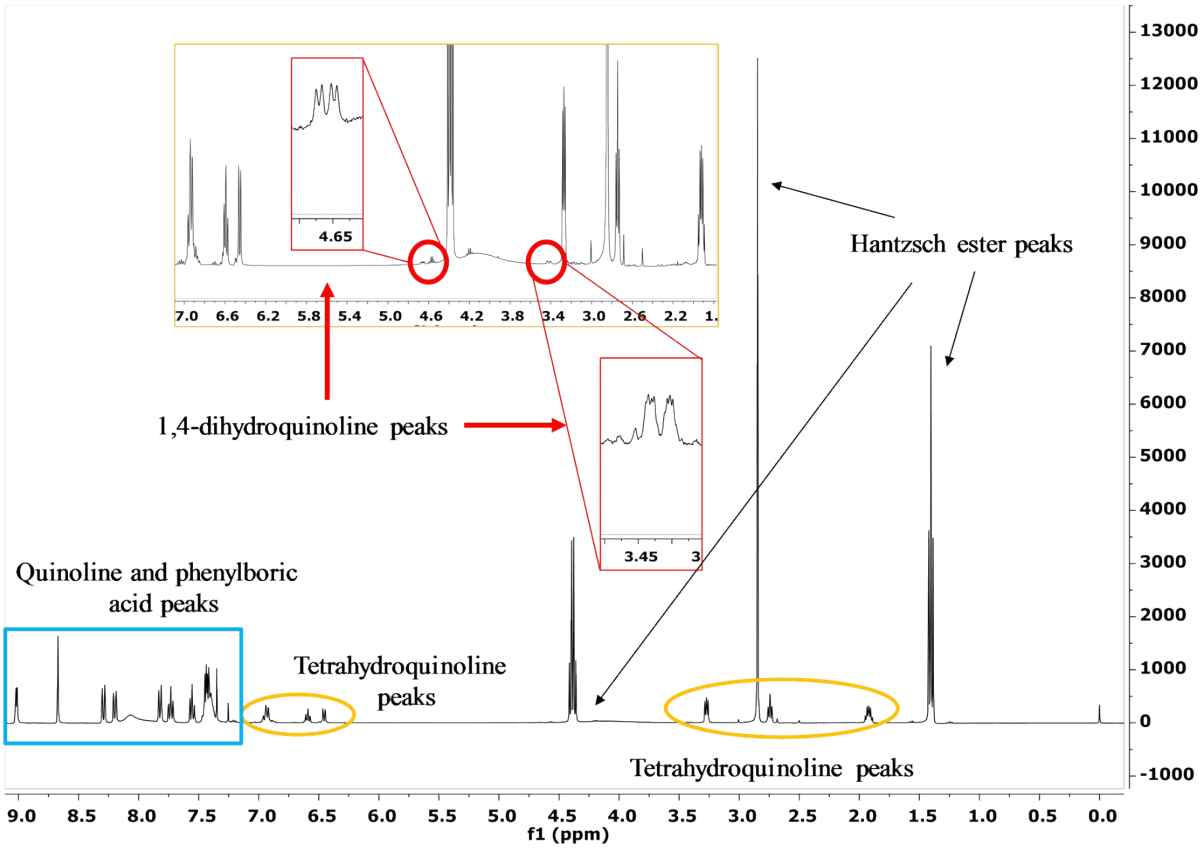


Figure S1: ^{1}H NMR spectra of quinoline reduction crude. NMR experiment and reaction conditions: In a quartz NMR tube, quinoline (54 mg, 0.42 mmol), Hantzsch ester (2.5 eqv.), $B(OH)_3$ (15 mol%), $CDCl_3$ (600 µL) were charged. The NMR tube was properly closed and placed in a preheated oil bath (50 °C) for 1 h. Then, the reaction crude was analysed by ^{1}H NMR at 50 °C in 400 MHz Bruker NMR instrument.

9.3 Interactions between quinoline, catalyst and Hantzsch ester (^{1}H and ^{11}B NMR)

9.3A. The reaction conditions for the ^{1}H and ^{11}B NMR experiment of quinolines, phenyl boronic acid and Hantzsch ester

The reaction conditions for the ^{1}H NMR experiment of quinolines and phenyl boronic acid: In a quartz NMR tube, quinoline (26 mg, 0.2 mmol), $PhB(OH)_2$ (24 mg, 0.2 mmol), $CDCl_3$ (600 µL) were charged. The NMR tube was properly closed and placed in a preheated oil bath (50 °C) for 1 h. Then, the reaction crude was analysed by ^{1}H NMR at 50 °C in 400 MHz Bruker NMR instrument.

The reaction conditions for the ^{11}B NMR experiment of phenyl boronic acid and Hantzsch ester: In a quartz NMR tube, Hantzsch ester (86 mg, 0.34 mmol), $PhB(OH)_2$ (12 mg, 0.1 mmol), $CDCl_3$ (600 µL) were charged. The NMR tube was properly closed and placed in a preheated oil bath (50 °C) for 1 h. Then, the reaction crude was analysed by ^{1}H NMR at 50 °C in 400 MHz Bruker NMR instrument.

The reaction conditions for the ^{11}B NMR experiment of phenyl boronic acid and quinolines: In a quartz NMR tube, quinoline (44 mg, 0.34 mmol), $PhB(OH)_2$ (12 mg, 0.1 mmol), $CDCl_3$ (600 µL) were charged. The NMR tube was properly closed and placed in a preheated oil bath (50 °C) for 1 h. Then, the reaction crude was analysed by ^{1}H NMR at 50 °C in 400 MHz Bruker NMR instrument.

9.3B. [1]H NMR experiment of phenyl boronic acid and Hantzsch ester

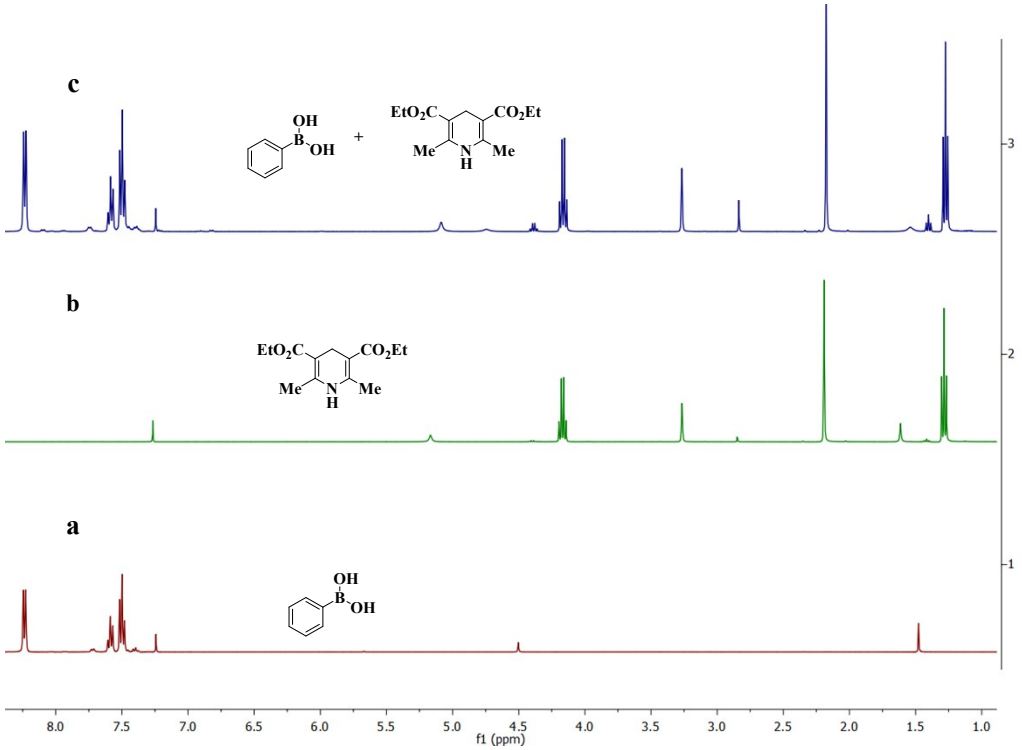
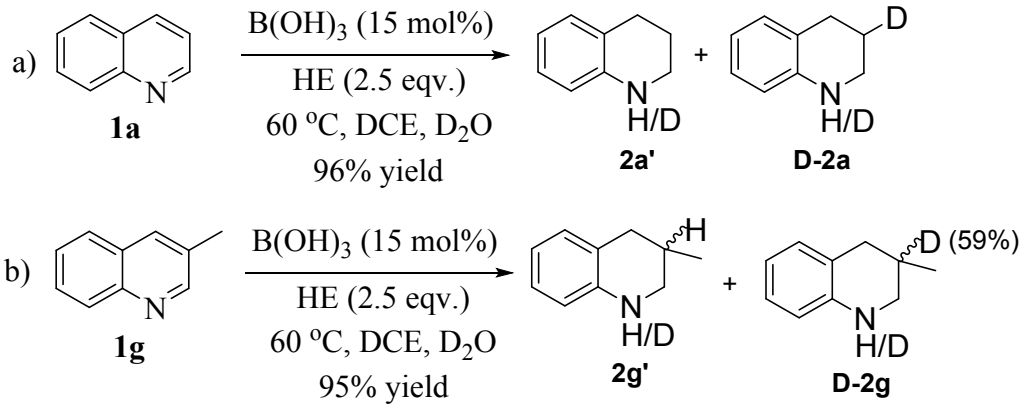


Figure S2: Comparative ^{1}H NMR spectra of (a) phenylboronic acid; (b) Hantzsch ester; and (c) combination of phenylboronic acid with Hantzsch ester (NMR experiment and reaction conditions: In a quartz NMR tube, Hantzsch ester (50 mg, 0.2 mmol), $PhB(OH)_2$ (24 mg, 0.2 mmol), $CDCl_3$ (600 µL) were charged. The NMR tube was properly closed and placed in a preheated oil bath (50 ^{o}C) for 1 h. Then, the reaction crude was analysed by ^{1}H NMR at 50 ^{o}C in 400 MHz Bruker NMR instrument).

9.4 Deuterium-labelling experiment

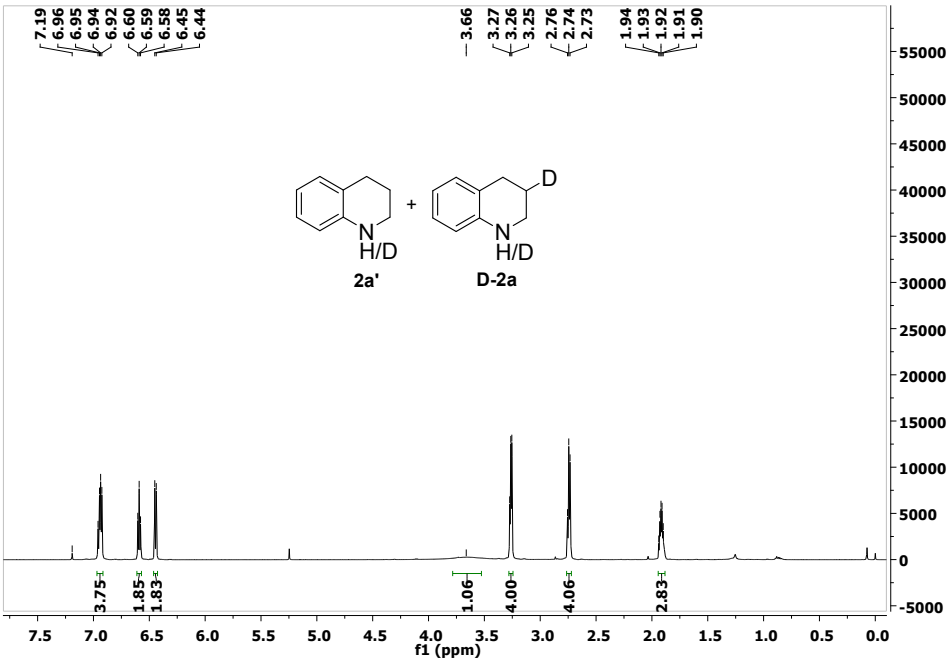
Reaction conditions: In a pyrex tube (15 mL), substituted quinoline (1 mmol), Hantzsch ester (2.5 eqv.), $B(OH)_3$ (15 mol%), dichloroethane (3 mL) and D_2O (0.60 mmol) were charged. The reaction tube was closed, without the exclusion of air and placed in a preheated oil bath (60 ^{o}C) with continuous stirring. The reaction was monitored by thin layered chromatography (TLC) in *n*-hexane and ethyl acetate solvent system. Once the reaction complete, reaction tube was brought to room temperature and purified by column chromatography for pure compound. The final product was then analysed by ^{1}H and ^{13}C NMR.



Scheme S10: Deuterium labelled experiment for quinoline (a) and 3-methyl quinolone (b).

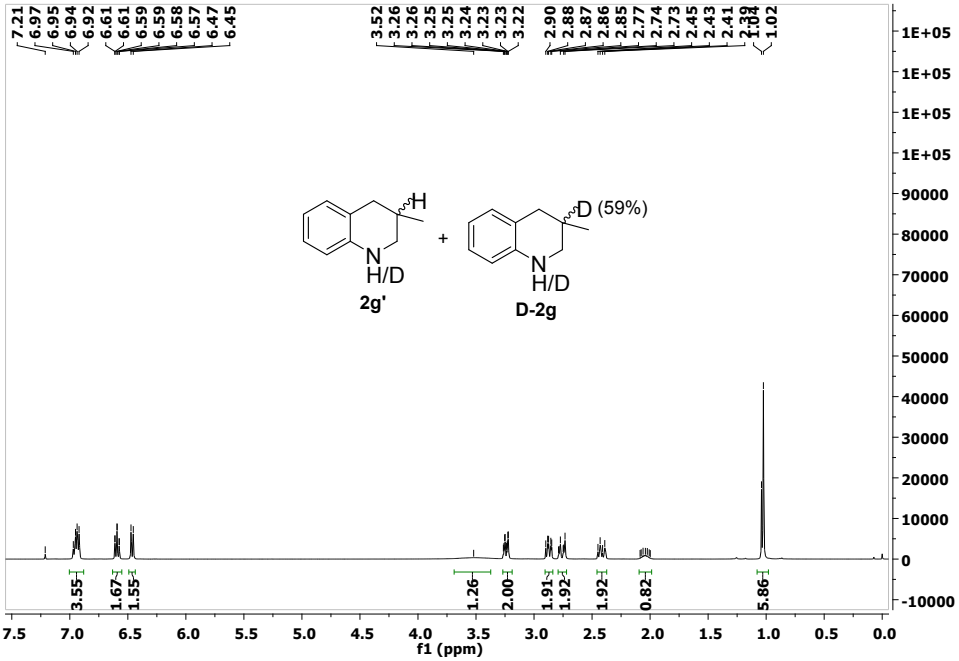
^{1}H NMR spectrum of deuterated 1,2,3,4-tetrahydroquinoline (2a' + D-2a):

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.96–6.92 (m, 4H, **2a'** + **D-2a**), 6.60–6.58 (t, J = 7.3 Hz, 2H, **2a'** + **D-2a**), 6.45–6.44 (d, J = 7.9 Hz, 2H, **2a'** + **D-2a**), 3.66 (br, 2H, **2a'** + **D-2a**), 3.27–3.25 (m, 4H, **2a'** + **D-2a**), 2.76–2.73 (t, J = 6.8 Hz, 2H, **2a'** + **D-2a**), 1.94–1.90 (m, 3H, **2a'** + **D-2a**)



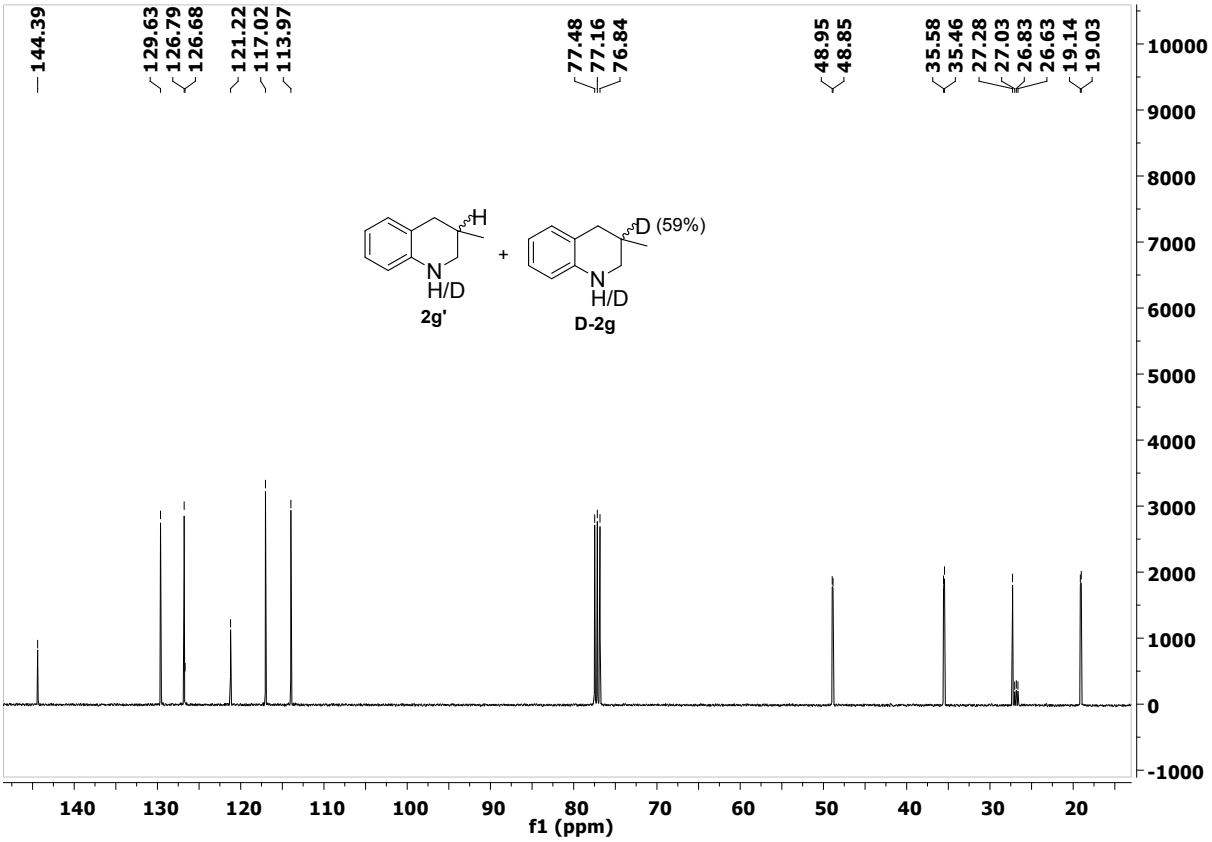
^{1}H NMR spectrum of deuterated 3-methyl-1,2,3,4-tetrahydroquinoline (2g' + D-2g):

^{1}H NMR (400 MHz, Chloroform-d): δ 6.97-6.92 (dd, J = 12.6, 7.1 Hz, 4H, **2g'** + **D-2g**), 6.61–6.57 (m, 2H, **2g'** + **D-2g**), 6.47–6.45 (d, J = 7.9 Hz, 2H, **2g'** + **D-2g**), 3.52 (br, 2H, **2g'** + **D-2g**), 3.26-3.22 (m, 2H, **2g'** + **D-2g**), 2.90–2.85 (m, 2H, **2g'** + **D-2g**), 2.79–2.73 (m, 2H, **2g'** + **D-2g**), 2.45–2.39 (m, 2H, **2g'** + **D-2g**), 2.07–2.02 (m, 1H, **2g'**) 1.04 (s, 6H, **2g'** + **D-2g**).



^{13}C NMR spectrum of deuterated 3-methyl-1,2,3,4-tetrahydroquinoline (2g' + D-2g):

^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.39, 129.63, 126.79, 126.68, 121.22, 117.02, 113.97, 48.95, 48.85, 35.58, 35.46, 27.28, 27.03, 26.83, 26.63, 19.14, 19.03.



10. Crystallographic study of compound 3f

The crystal was obtained by crystallisation of compound **3f** in the presence of chloroform as solvent at room temperature using slow evaporation technique. X-ray crystallographic data were collected using Supernova, single source at offset, Eos diffractometer. Data refinement and cell reduction were carried out by *CrysAlisPro*. Structures were solved by direct methods using SHELXL-2014/7 and WinGX and refined by a full-matrix least-squares method using SHELXL-2014/7. All of the non-H atoms were refined anisotropically. The ORTEP diagram was obtained with the help of ORTEP software with 40% thermal ellipsoid (see in below, Figure S5). The crystallographic parameters and refinement data were listed in Table S2.

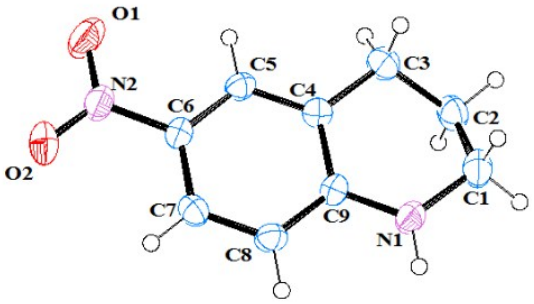


Figure S3: Molecular structure of compound **3f** (thermal ellipsoid 40% probability level).

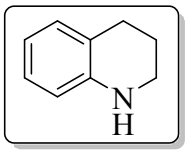
Selected bond lengths (in Å): O(2)-N(2) 1.236(2), O(1)-N(2) 1.237(2), N(1)-C(9) 1.354(2), N(1)-C(1) 1.450(2), C(4)-C(5) 1.377(3), C(4)-C(9) 1.426(3), C(4)-C(3) 1.505(2), C(9)-C(8) 1.402(2), C(5)-C(6) 1.386(3), C(6)-C(7) 1.396(3), C(8)-C(7) 1.365(3), C(1)-C(2) 1.508(3), C(3)-C(2) 1.520(3).

Table S2. Crystal data and structure refinement for **3f**

Identification code	shelx	
CCDC:	1946184	
Empirical formula	$C_9H_{10}N_2O_2$	
Formula weight	178.19	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.5569(7) Å	α = 90°.
	b = 7.5729(6) Å	β = 101.729(9)°.
	c = 15.4076(14) Å	γ = 90°.
Volume	863.33(13) $Å^3$	
Z		
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	376	
Crystal size	0.35 × 0.32 × 0.30 mm^3	
Theta range for data collection	2.700 to 24.982°.	
Index ranges	-8<=h<=5, -5<=k<=9, -12<=l<=18	
Reflections collected	2994	
Independent reflections	1513 [R(int) = 0.0277]	
Completeness to theta = 25.242°	97.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1513 / 0 / 120	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1192	
R indices (all data)	R1 = 0.0690, wR2 = 0.1387	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.185 and -0.244 $e.Å^{-3}$	

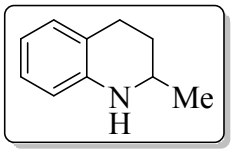
11. Analytical data of the products

1,2,3,4-tetrahydroquinoline (2a)



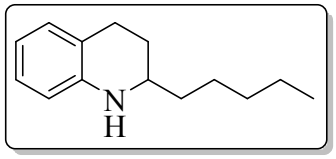
Colourless oil (65 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 – 6.93 (m, 2H), 6.59 (t, J = 7.4 Hz, 1H), 6.46 (d, J = 7.9 Hz, 1H), 3.30 – 3.28 (m, 2H), 2.76 (t, J = 6.4 Hz, 2H), 1.96 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.89, 129.64, 126.84, 121.59, 117.08, 114.32, 42.12, 27.09, 22.31. Spectral data is in accordance with the literature.[14]

2-methyl-1,2,3,4-tetrahydroquinoline (2b)



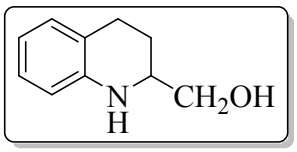
Colourless oil (72 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 – 6.93 (m, 2H), 6.61 – 6.57 (m, 1H), 6.46 – 6.44 (m, 1H), 3.64 (brs, 1H), 3.42 – 3.34 (m, 1H), 2.87-2.79 (m, 1H), 2.74 – 2.68 (m, 1H), 1.94 – 1.88 (m, 1H), 1.62 – 1.53 (m, 1H), 1.20 (d, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.79, 129.26, 126.68, 121.05, 116.95, 114.02, 47.14, 30.14, 26.61, 22.60. Spectral data is in accordance with the literature.[14]

2-pentyl-1,2,3,4-tetrahydroquinoline (2c)



Colourless oil (92 mg, 91%). Isolated yield: 91%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 – 6.93 (m, 2H), 6.59 (td, J = 7.4, 1.2 Hz, 1H), 6.47 (dd, J = 8.4, 1.3 Hz, 1H), 3.76 (brs, 1H), 3.23 (dtd, J = 9.5, 6.3, 2.9 Hz, 1H), 2.87 – 2.66 (m, 2H), 1.99 – 1.93 (m, 1H), 1.49-1.26 (m, 8H), 1.59 – 1.49 (m, 1H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.77, 129.39, 126.84, 121.63, 117.12, 114.25, 51.78, 36.79, 32.10, 28.25, 26.57, 25.55, 22.79, 14.19. Spectral data is in accordance to the reported literature.[23]

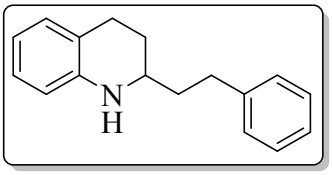
(1,2,3,4-tetrahydroquinolin-2-yl) methanol (2d)



Pale yellow oil (70 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.00 – 6.95 (m, 2H), 6.63 (td, J = 7.4, 1.2 Hz, 1H), 6.54 (dd, J = 7.9, 1.2 Hz, 1H), 3.75 (dd, J = 10.4, 3.8 Hz, 1H), 3.56 (dd, J = 10.4, 7.7 Hz, 1H), 3.47 – 3.44 (m, 1H), 2.84 (ddd, J = 16.4, 10.8, 5.6 Hz, 1H), 2.74 (dt, J = 16.3, 4.9 Hz, 1H), 1.90 (dddd, J = 13.1, 5.6, 4.3, 3.2 Hz, 1H), 1.71 (dddd, J = 12.9, 10.8,

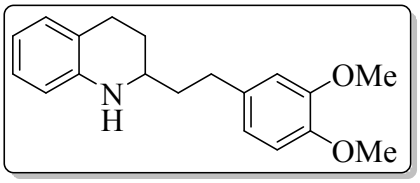
9.4, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.27, 129.37, 127.02, 121.58, 117.61, 114.68, 66.90, 52.90, 26.03, 24.46. Spectral data is in accordance to the reported literature.[24]

2-phenethyl-1,2,3,4-tetrahydroquinoline (2e)



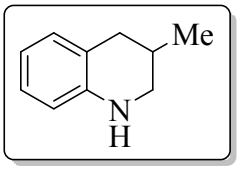
Started with a conjugated double bond containing substrate 2-styrylquinoline. For this, 3.5 equiv. of Hantzsch ester was used. White sticky liquid (105 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 6.97-6.93 (m, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 7.8 Hz, 1H), 3.74 (brs, 1H), 3.31-3.28 (m, 1H), 2.79 – 2.72 (m, 4H), 1.99 (ddd, J = 16.0, 8.3, 4.6 Hz, 1H), 1.86 – 1.80 (m, 2H), 1.69 –1.65 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.65, 141.98, 129.38, 128.62, 128.49, 126.87, 126.10, 121.42, 117.16, 114.27, 51.25, 38.39, 32.31, 28.12, 26.35. Spectral data is in accordance with the literature.[25]

2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (2f)



Started with a conjugated double bond containing substrate (*E*)-2-(3,4-dimethoxy styryl)quinoline. For this, 3.5 equiv. of Hantzsch ester was used. Yellow sticky solid (136 mg, 92%); m.p: 52~54 ^{o}C. ^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.96 – 6.94 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 1.6 Hz, 1H), 6.60 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 7.7 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.29 (td, J = 9.2, 6.4 Hz, 1H), 2.79 (dd, J = 10.6, 5.5 Hz, 1H), 2.76 – 2.72 (m, 1H), 2.68 (t, J = 8.0 Hz, 2H), 1.99 (dd, J = 8.7, 3.4 Hz, 1H), 1.80 (td, J = 8.9, 7.4, 3.4 Hz, 2H), 1.69 (dd, J = 10.5, 5.3 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.94, 147.30, 144.57, 134.51, 129.32, 126.80, 121.34, 120.16, 117.08, 114.20, 111.62, 111.30, 55.99, 55.89, 51.25, 38.49, 31.88, 28.06, 26.26. Spectral data is in accordance with the literature.[13]

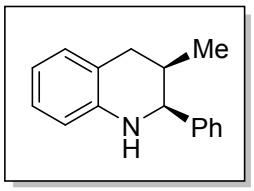
3-methyl-1,2,3,4-tetrahydroquinoline (2g)



Colourless oil (71 mg, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.96-6.93 (m, 2H), 6.60 (t, J = 6.9 Hz, 1H), 6.48 (d, J = 7.9 Hz, 1H), 3.84 (brs, 1H), 3.26 (ddd, J = 11.0, 3.6, 2.0 Hz, 1H), 2.91 – 2.86 (m, 1H), 2.77 (ddd, J = 16.0, 4.8, 1.6 Hz, 1H), 2.43 (dd, J = 16.0, 10.3 Hz,

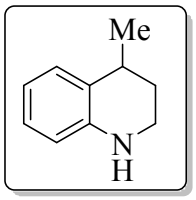
1H), 2.07 – 1.98 (m, 1H), 1.04 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.39, 129.62, 126.78, 121.19, 117.00, 113.96, 48.94, 35.57, 27.28, 19.14. Spectral data is in accordance with the literature.[14]

3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2h)



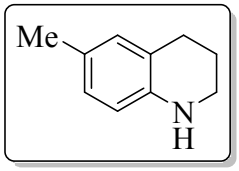
White solid (99 mg, 89%); m.p: 84~86 ^{o}C. *cis* : *trans* = 10:1. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.32 – 7.22 (m, 5H, major + minor), 7.04 – 6.98 (m, 2H, major + minor), 6.65 (td, J = 7.4, 1.2 Hz, 1H, major + minor), 6.54 (dd, J = 8.0, 1.2 Hz, 1H, minor major + minor), 4.50 (d, J = 3.6 Hz, 1H, major, 90%), 4.39 (d, J = 3.6 Hz, 1H, minor, 10%), 4.11 (brs, 1H, major, 90%), 3.94 (d, J = 12.4 Hz, 1H, minor, 10%), 3.38 (d, J = 12.4 Hz, 1H, minor, 10%), 2.96 (dd, J = 16.1, 5.0 Hz, 1H, major, 90%), 2.49 (dd, J = 16.1, 6.8 Hz, 2H, major 90% + minor 10%), 2.44-2.39 (m, 1H, minor, 10%), 2.31-2.28 (m, 1H, major, 90%), 0.88 (d, J = 6.4 Hz, 3H, minor, 10%), 0.81 (d, J = 6.9 Hz, 3H, major, 90%). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.28, 143.05, 129.83, 128.24, 127.29, 127.23, 127.00, 120.14, 117.19, 113.79, 59.48, 33.50, 32.01, 15.27 (for major 90%). HRMS (ESI) *m/z*: calculated for $C_{16}H_{18}N$ ($M+H^+$): 224.1434; found: 224.1446. Spectral data is in accordance to the literature.[26] The relative *cis*- configuration was tentatively assigned by comparison with literature data.[26]

4-methyl-1,2,3,4-tetrahydroquinoline (2i)



Colourless oil (69 mg, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.05 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H), 6.63 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 7.9 Hz, 1H), 3.36-3.27 (m, 2H), 2.94 – 2.89 (m, 1H), 2.02 – 1.95 (m, 1H), 1.71 – 1.65 (m, 1H), 1.29 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.39, 128.58, 126.87, 126.78, 117.11, 114.31, 39.17, 30.38, 30.04, 22.76. Spectral data is in accordance to the reported literature.[14]

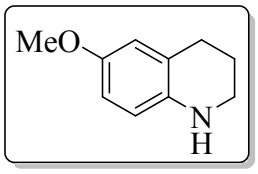
6-methyl-1,2,3,4-tetrahydroquinoline (2j)



Colourless oil (71 mg, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.78 – 6.76 (m, 2H), 6.39 (d, J = 8.6 Hz, 1H), 3.43 (brs, 1H), 3.31 – 3.20 (m, 2H), 2.72 (t, J = 6.5 Hz, 2H), 2.19 (s, 3H), 1.94 – 1.88 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.52, 130.16, 127.34, 126.33,

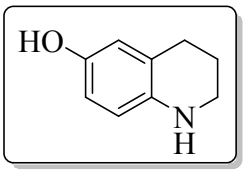
121.69, 114.56, 42.29, 27.02, 22.55, 20.50. Spectral data is in accordance to the reported literature.[27]

6-methoxy-1,2,3,4-tetrahydroquinoline (2k)



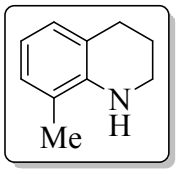
Colourless oil (77 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.60 – 6.55 (m, 2H), 6.45 – 6.43 (d, J = 8.5 Hz, 1H), 3.72 (s, 3H), 3.26 – 3.23 (m, 2H), 3.14 (brs, 1H), 2.75 (t, J = 6.5 Hz, 2H), 1.95-1.89 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 151.97, 138.97, 123.03, 115.71, 115.02, 113.03, 55.94, 42.46, 27.28, 22.56. Spectral data is in accordance to the reported literature.[27]

6-hydroxy-1,2,3,4-tetrahydroquinoline (2l)



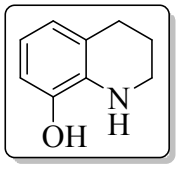
White solid (65 mg, 88%); m.p: 160~162 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (s, 1H), 6.47 – 6.34 (m, 3H), 3.10 – 3.07 (m, 2H), 2.58 (t, J = 6.4 Hz, 2H), 1.79 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 149.30, 135.57, 123.05, 116.33, 115.66, 113.69, 41.43, 26.43, 21.64. Spectral data is in accordance to the reported literature.[28]

8-methyl-1,2,3,4-tetrahydroquinoline (2m)



Colourless oil (70 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.88 – 6.84 (m, 2H), 6.55 (t, J = 7.4 Hz, 1H), 3.65 (brs, 1H), 3.38 – 3.36 (m, 2H), 2.79 (t, J = 6.4 Hz, 2H), 2.07 (s, 3H), 1.97-1.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.81, 127.95, 127.49, 121.29, 120.98, 116.50, 42.46, 27.40, 22.27, 17.27. Spectral data is in accordance to the reported literature.[14]

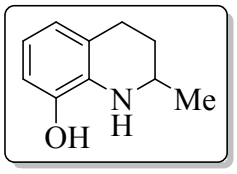
8-hydroxy-1,2,3,4-tetrahydroquinoline (2n)



White solid (65 mg, 87%); m.p: 120~122 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (s, 1H), 6.45 – 6.26 (m, 3H), 4.60 (s, 1H), 3.20 (brs, 2H), 2.63 (brs, 2H), 1.78 (brs, 2H). ^{13}C NMR (101

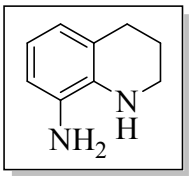
MHz, DMSO-d_6): δ 143.18, 133.73, 120.37, 119.86, 114.71, 111.39, 40.80, 26.43, 21.79. Spectral data is in accordance to the reported literature.[28]

2-methyl-1,2,3,4-tetrahydroquinolin-8-ol (2o)



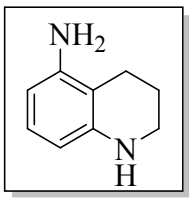
White solid (69 mg, 85%); m.p: 75~77 °C. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.60 – 6. 46 (m, 3H), 4.61 (s, 1H), 3.33 (s, 1H), 2.86 – 2.71 (m, 2H), 1.94 – 1.90 (m, 1H), 1.62 – 1.57 (m, 1H), 1.23 – 1.22 (d, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.96, 133.69, 123.28, 121.72, 117.29, 112.75, 47.27, 30.19, 26.44, 22.41. Spectral data is in accordance to the reported literature.[29]

8-amino-1,2,3,4-tetrahydroquinoline (2p)



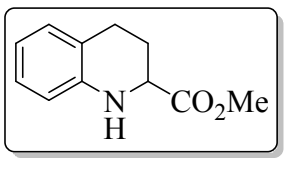
Brown oil (65 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.59 – 6.51 (m, 3H), 3.32 – 3.29 (m, 2H), 2.76 (t, J = 6.4 Hz, 2H), 1.93 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 133.99, 133.93, 123.31, 121.19, 118.09, 114.15, 42.65, 27.11, 22.48. HRMS (ESI) *m/z*: calculated for $C_9H_{13}N_2$ ($M+H^+$): 149.1073; found: 149.1086. Spectral data is in accordance to the reported literature.[30]

1,2,3,4-tetrahydroquinolin-5-amine (2q)



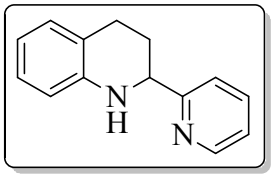
Yellow solid (62 mg, 83%); m.p: 96~98 °C. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.81 (t, J = 8.0 Hz, 1H), 6.09 (d, J = 7.9 Hz, 1H), 6.01 (d, J = 8.0 Hz, 1H), 3.26 – 3.23 (m, 2H), 2.85 (s, 1H), 2.48 (t, J = 6.7 Hz, 2H), 2.06 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.89, 145.05, 127.15, 106.95, 105.71, 104.82, 41.52, 22.48, 21.66. Spectral data is in accordance with literature.[31]

Methyl 1,2,3,4-tetrahydroquinoline-2-carboxylate (3a)



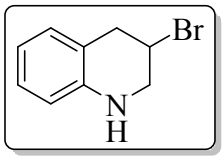
Pale yellow oil (85 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.02 – 6.94 (m, 2H), 6.65 (td, J = 7.4, 1.2 Hz, 1H), 6.59 (dd, J = 8.0, 1.2 Hz, 1H), 4.05 (dd, J = 8.8, 3.8 Hz, 1H), 3.78 (s, 3H), 2.83 – 2.73 (m, 2H), 2.28 (dtd, J = 13.0, 5.6, 3.8 Hz, 1H), 2.01 (dtd, J = 12.9, 9.0, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 173.86, 143.08, 129.27, 127.20, 120.69, 117.83, 114.73, 54.06, 52.50, 25.95, 24.85. Spectral data is in accordance to the reported literature.[32]

2-(pyridin-2-yl)-1,2,3,4-tetrahydroquinoline (3b)



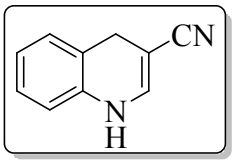
Brown oil (86 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.58 (d, J = 4.9 Hz, 1H), 7.70 – 7.66 (td, J = 7.7, 1.8 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.05 – 6.99 (m, 2H), 6.68 – 6.62 (m, 2H), 4.59 (dd, J = 8.8, 3.5 Hz, 1H), 2.92-2.89 (m, 1H), 2.70 (dt, J = 16.3, 5.2 Hz, 1H), 2.29 – 2.24 (m, 1H), 2.06 – 2.02 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.22, 149.25, 144.28, 136.91, 129.38, 127.10, 122.32, 121.24, 120.74, 117.43, 114.60, 57.00, 28.90, 26.12. HRMS (ESI) *m/z*: calculated for $C_{14}H_{15}N_2$ ($M+H^+$): 211.1235; found: 211.1244. Spectral data is in accordance to the reported literature.[25]

3-bromo-1,2,3,4-tetrahydroquinoline (3c)



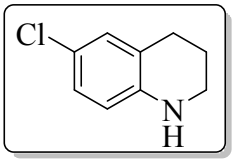
Brown oil (97 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.05 – 7.00 (m, 1H), 6.93 (d, J = 7.4 Hz, 1H), 6.67 (td, J = 7.5, 0.9 Hz, 1H), 6.53 (d, J = 7.9 Hz, 1H), 4.52 – 4.46 (m, 1H), 3.65 (ddd, J = 12.1, 3.2, 1.8 Hz, 1H), 3.48 (ddd, J = 12.1, 7.6, 0.9 Hz, 1H), 3.39 (dd, J = 16.5, 4.7 Hz, 1H), 3.19 (dd, J = 16.4, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.73, 129.58, 127.68, 118.71, 118.20, 114.66, 49.52, 44.32, 37.96. HRMS (ESI) *m/z*: calculated for $C_9H_{11}BrN$ ($M+H^+$): 212.0069; found: 212.0081.

1,4-dihydroquinoline-3-carbonitrile (3d)



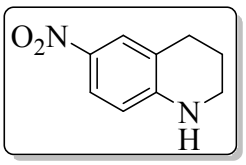
White solid (71 mg, 91%); m.p: 106~107 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.10 – 7.06 (m, 1H), 6.98 – 6.92 (m, 2H), 6.82 (d, J = 5.9 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.14 (brs, 1H), 3.72 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 139.43, 135.82, 129.48, 127.81, 123.93, 121.24, 118.59, 115.30, 78.06, 27.03. HRMS (ESI) *m/z*: calculated for $C_{10}H_9N_2$ ($M+H^+$): 157.0765; found: 157.0778.

6-chloro-1,2,3,4-tetrahydroquinoline (3e)



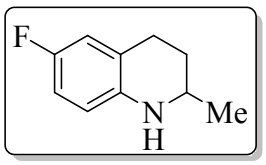
Pale yellow sticky liquid (77 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.89 (s, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.35(d, J = 8.0 Hz, 1H), 3.76 (brs, 1H), 3.27 – 3.24 (m, 2H), 2.70 (t, J = 6.4 Hz, 2H), 1.92 – 1.86 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 143.40, 129.10, 126.58, 122.95, 121.20, 115.17, 41.94, 26.96, 21.83. Spectral data is in accordance to the reported literature.[27]

6-nitro-1,2,3,4-tetrahydroquinoline (3f)



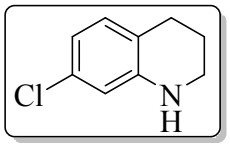
White solid (77 mg, 87%); m.p: 160~162 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.90 – 7.87 (m, 2H), 6.36 (m, J = 9.6 Hz,1H), 4.75 (brs, 1H), 3.42 (td, J = 6.0, 2.0 Hz, 2H), 2.79 (t, J = 6.3 Hz, 2H), 1.95 (dt, J = 12.4, 6.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 150.52, 137.32, 126.04, 124.41, 119.95, 112.27, 41.85, 27.00, 20.92. Spectral data is in accordance to the reported literature. [33]

6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (3g)



Colourless sticky liquid (73 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.70-6.65 (m, 2H), 6.41 – 6.38 (m, 1H), 3.72 (brs, 1H), 3.36 – 3.32 (m, 1H), 2.85 – 2.81 (m, 1H), 2.79-2.71 (m, 1H), 1.94 – 1.89 (m, 1H), 1.58 – 1.56 (m, 1H), 1.20 (d, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 155.63 (d, J = 235.3 Hz), 141.1 (d, J = 1.8 Hz), 122.61 (d, J = 6.6 Hz), 115.51 (d, J = 21.6 Hz), 114.84 (d, J = 7.7 Hz), 113.28 (d, J = 22.5 Hz), 47.44, 30.02, 26.84, 22.63. Spectral data is in accordance to the reported literature.[27]

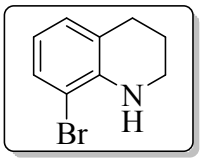
7-chloro-1,2,3,4-tetrahydroquinoline (3h)



4,7-dichloroquinoline was used as the substrate. Colourless oil (76 mg, 91%). For this, 3.5 equiv. of Hantzsch ester was used. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.83 (d, J = 8 Hz, 1H), 6.53 (dd, J = 8.0, 2.1 Hz, 1H), 6.42 (d, J = 2.1 Hz, 1H), 3.84 (brs, 1H), 3.29 – 3.26 (m, 2H), 2.70 (t, J = 6.4 Hz, 2H), 1.93 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ

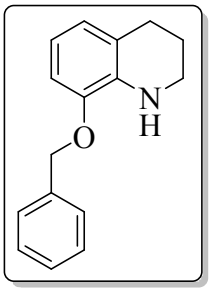
145.80, 132.03, 130.51, 119.72, 116.63, 113.49, 41.79, 26.66, 21.92. Spectral data is in accordance to the reported literature.[34]

8-bromo-1,2,3,4-tetrahydroquinoline (3i)



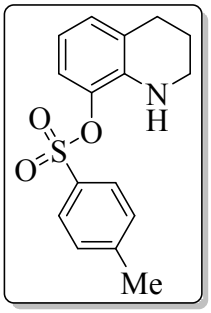
Colourless oil (90 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.22 (d, J = 8.0 Hz, 1H), 6.88 (dd, J = 7.4, 0.7 Hz, 1H), 6.44 (t, J = 7.7 Hz, 1H), 4.42 (brs, 1H), 3.39 – 3.37 (m, 2H), 2.77 (t, J = 6.3 Hz, 2H), 1.95 – 1.89 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.85, 130.15, 128.52, 122.97, 117.03, 108.84, 42.18, 27.57, 21.83. Spectral data is in accordance to the reported literature.[14]

8-(benzyloxy)-1,2,3,4-tetrahydroquinoline (3j)



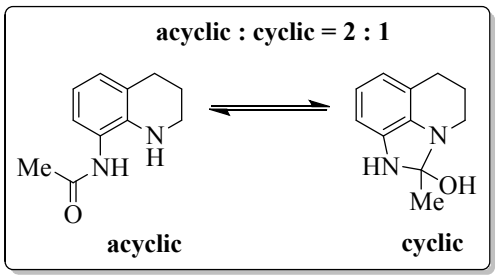
Colourless oil (110 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.43 – 7.22 (m, 5H), 6.65 (dd, J = 16.2, 7.7 Hz, 2H), 6.54 (t, J = 7.7 Hz, 1H), 5.03 (s, 2H), 4.29 (brs, 1H), 3.32 – 3.29 (m, 2H), 2.78 (t, J = 6.4 Hz, 2H), 1.98 – 1.92 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.53, 137.42, 134.89, 128.64, 128.05, 127.77, 122.12, 121.62, 115.66, 108.88, 70.36, 41.56, 26.82, 22.17. Spectral data is in accordance to the reported literature.[14]

1,2,3,4-tetrahydroquinolin-8-yl-4′-methylbenzenesulfonate (3k)



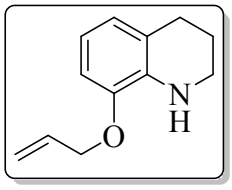
White solid (130 mg, 86%); m.p: 62~64 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.77 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H)), 6.80 (d, J = 7.2 Hz, 2H), 6.59 (dd, J = 8.2, 1.4 Hz, 1H), 6.39 (t, J = 7.8 Hz, 1H), 4.18 (brs, 1H), 3.20-3.16 (m, 2H), 2.72 – 2.68 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 1.85 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.45, 137.95, 136.07, 133.04, 129.79, 128.66, 127.87, 123.65, 120.16, 115.22, 41.36, 27.01, 21.85, 21.50. HRMS (ESI) *m/z*: calculated for $C_{16}H_{18}NO_3S$ ($M+H^+$): 304.1007; found: 304.1037.

***N*-(1,2,3,4-tetrahydroquinolin-8-yl)acetamide (3l)**



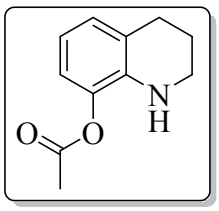
White solid (80 mg, 84%); m.p: 113~115 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.11 (brs, 1H, acyclic, 67%), 7.01 (d, J = 7.8 Hz, 1H, acyclic, 67%), 6.93 (d, J = 7.2 Hz, 1H, cyclic, 33%), 6.87 (d, J = 7.2 Hz, 1H, acyclic, 67%), 6.83 (d, J = 7.2 Hz, 1H, cyclic, 33%), 6.68 (brs, 1H, cyclic, 33%), 6.63 (t, J = 7.6 Hz, 1H, acyclic, 67%), 6.55 (t, J = 7.2 Hz, 1H, cyclic, 33%), 4.14 (brs, 1H, acyclic, 67%), 3.32-3.29 [(m, 2H, acyclic, 67%) + (m, 2H, cyclic, 33%)], 2.78 [(t, 2H, acyclic, 67%) + (t, 2H, cyclic, 33%)], 2.17 (s, 3H, acyclic 67%), 1.91-1.87 [(m, 2H, acyclic, 67%) + (m, 2H, cyclic, 33%) + (s, 3H, cyclic, 33%)]. ^{13}C NMR (101 MHz, Chloroform-*d*): δ 169.25, 139.36, 129.29, 127.87, 126.61, 124.34, 123.42, 123.33, 117.41, 115.95, 42.30, 41.76, 27.45, 27.15, 23.88, 22.00, 21.76, 20.51. HRMS (ESI) *m/z*: calculated for $C_{11}H_{14}N_2O$ (M^+): 190.1106; found: 190.1185.

8-(allyloxy)-1,2,3,4-tetrahydroquinoline (3m)



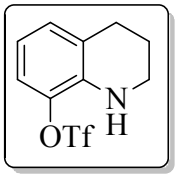
Colourless oil (80 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.66-6.62 (m, 2H), 6.58 – 6.54 (m, 1H), 6.10-6.05 (m, 1H), 5.42 (dd, J = 17.3, 1.6 Hz, 1H), 5.30 (dd, J = 10.5, 1.5 Hz, 1H), 4.55 (dt, J = 5.4, 1.6 Hz, 2H), 3.37– 3.35 (m, 2H), 2.80 (t, J = 6.4 Hz, 2H), 1.97 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.29, 134.88, 133.82, 122.03, 121.64, 117.45, 115.68, 108.94, 69.21, 41.59, 26.82, 22.19. Spectral data is in accordance to the reported literature.[14]

1,2,3,4-tetrahydroquinolin-8-yl acetate (3n)



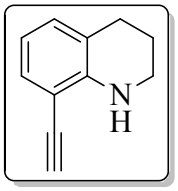
Yellow oil (84 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.80 (s, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 7.4 Hz, 1H), 3.72 – 3.69 (m, 2H), 2.85 (t, J = 7.0 Hz, 2H), 2.38 (s, 3H), 2.10 – 2.04 (p, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 171.66, 150.52, 133.24, 128.94, 127.43, 121.04, 118.38, 47.87, 26.52, 24.24, 23.36. HRMS (ESI) *m/z*: calculated for $C_{11}H_{14}NO_2$ ($M+H^+$): 192.1024; found: 192.1016.

1,2,3,4-tetrahydroquinolin-8-yl trifluoromethanesulfonate (3o)



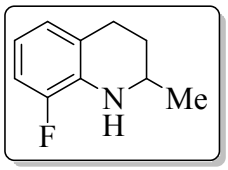
Yellow oil (151 mg, 85%). ^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.95 (dd, J = 19.0, 7.9 Hz, 2H), 6.55 (t, J = 7.8 Hz, 1H), 4.17 (brs, 1H), 3.38-3.36 (m, 2H), 2.79 (t, J = 6.3 Hz, 2H), 1.96-1.92 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 137.25, 136.39, 128.99, 124.58, 120.31, 119.22, 115.73, 41.56, 27.01, 21.35. ^{19}F NMR (377 MHz, Chloroform-*d*): δ -73.98. HRMS (ESI) *m/z*: calculated for $C_{10}H_{11}F_3NO_3S$ ($M+H^+$): 282.0406; found: 282.0425.

8-ethynyl-1,2,3,4-tetrahydroquinoline (3p)



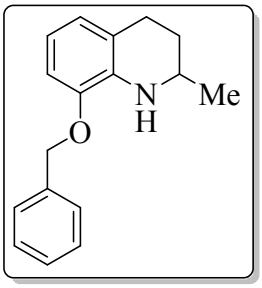
Colourless oil (69 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.15 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.3 Hz, 1H), 6.49 (t, J = 7.5 Hz, 1H), 4.74 (brs, 1H), 3.41-3.38 (m, 2H), 3.37 (s, 1H), 2.76-2.75 (t, J = 6.4 Hz, 2H), 1.96 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.56, 130.48, 130.22, 120.84, 115.61, 104.80, 82.42, 81.20, 41.89, 27.26, 21.74. HRMS (ESI) *m/z*: calculated for $C_{11}H_{12}N$ ($M+H^+$): 158.0969; found: 158.0975.

8-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (3q)



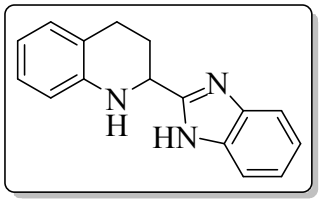
Colourless sticky liquid (71 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.81 – 6.73 (m, 2H), 6.52 – 6.47 (m, 1H), 3.88 (brs, 1H), 3.45-3.37 (m, 1H), 2.88 – 2.72 (m, 2H), 1.95 – 1.92 (m, 1H), 1.64 –1.61 (m, 1H), 1.25 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 150.83 (d, J = 238.3 Hz), 133.35 (d, J = 12.2 Hz), 124.4 (d, J = 2.8 Hz), 123.5 (d, J = 3.8 Hz), 115.74 (d, J = 7.5 Hz), 112.25 (d, J = 18.4 Hz), 46.8, 29.86, 26.35 (d, J = 3 Hz), 22.64. HRMS (ESI) *m/z*: calculated for $C_{10}H_{13}FN$ ($M+H^+$): 166.1027; found: 166.1037.

8-(benzyloxy)-2-methyl-1,2,3,4-tetrahydroquinoline (3r)



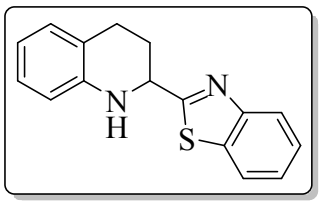
Colourless oil (112 mg, 89%).[1]H NMR (400 MHz, Chloroform-*d*): δ 7.43-7.30 (m, 5H), 6.65 (t, J = 8.6 Hz, 2H), 6.53 (t, J = 7.8 Hz, 1H), 5.07 – 5.01 (m, 2H), 4.18 (brs, 1H), 3.40 – 3.35 (m, 1H), 2.85 (ddd, J = 16.8, 11.2, 5.7 Hz, 1H), 2.77 – 2.71 (m, 1H), 1.94 – 1.90 (m, 1H), 1.63 – 1.56 (m, 1H), 1.22 – 1.21 (d, J = 6.3 Hz, 3H). [13]C NMR (101 MHz, Chloroform-*d*): δ 145.33, 137.52, 134.93, 128.64, 128.01, 127.73, 121.95, 121.40, 115.76, 109.11, 70.50, 46.79, 30.15, 26.48, 22.69. HRMS (ESI) *m/z*: calculated for $C_{17}H_{20}NO$ ($M+H^+$): 254.1544; found: 254.1538.

2-(1H-benzo[*d*]imidazol-2-yl)-1,2,3,4-tetrahydroquinoline (3s)



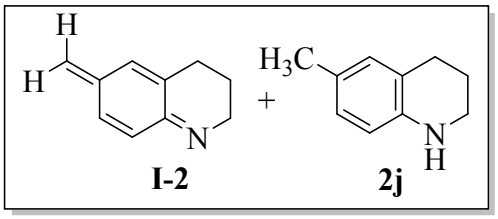
Pale yellow solid (103 mg, 83%); m.p: 156~157 ℃. [1]H NMR (400 MHz, Chloroform-*d*): δ 7.56 (brs, 2H), 7.25-7.23 (m, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.9 Hz, 1H), 4.88 (t, J = 4 Hz, 1H), 2.86 – 2.79 (m, 1H), 2.63-2.56 (m, 1H), 2.36 (dd, J = 13.0, 6.6 Hz, 1H), 2.22 (d, J = 4.6 Hz, 1H). [13]C NMR (101 MHz, Chloroform-*d*): δ 157.18, 142.79, 129.63, 127.32, 122.68, 121.67, 118.59, 114.98, 50.93, 27.80, 25.07. HRMS (ESI) *m/z*: calculated for $C_{16}H_{16}N_3$ ($M+H^+$): 250.1344; found: 250.1338.

2-(1,2,3,4-tetrahydroquinolin-2-yl)benzo[*d*]thiazole (3t)



Yellow oil (113 mg, 85%). [1]H NMR (400 MHz, Chloroform-*d*): δ 7.99 (dd, J = 8.2, 1.1 Hz, 1H), 7.86 (dt, J = 8.0, 0.9 Hz, 1H), 7.48 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.37 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.07 (td, J = 7.7, 1.6 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.74 – 6.67 (m, 2H), 4.97 (ddd, J = 6.2, 4.9, 3.1 Hz, 1H), 4.61 (brs, 1H), 2.95 – 2.82 (m, 1H), 2.78-2.71 (m, 1H), 2.38-2.33 (m, 2H). [13]C NMR (101 MHz, Chloroform-*d*): δ 177.39, 153.78, 142.86, 135.08, 129.43, 127.30, 126.19, 125.01, 122.99, 121.97, 121.34, 118.45, 114.85, 54.60, 29.09, 25.22. HRMS (ESI) *m/z*: calculated for $C_{16}H_{15}N_2S$ ($M+H^+$): 267.0955; found: 267.0981.

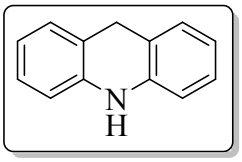
6-methylene-2,3,4,6-tetrahydroquinoline (I-2) + 6-methyl-1,2,3,4-tetrahydroquinoline (2j)



I-2 **2j**

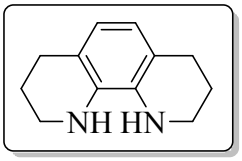
Yellow oil (**I-2** + **2j**): (53 mg, 73%), I-**2**:**2j** = 1:3 ratio; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.18-7.21 (m, 2H, minor, 25%), 6.77-6.79 [(m, 2H, major, 75%) + (m, 1H, minor, 25%)], 6.40-6.42 (m, 1H, major, 75%), 6.37-3.39 (m, 2H, minor, 25%), 4.28-4.42 (m, 1H, major, 75%), 3.35-3.37 (m, 2H, minor, 25%), 3.25-3.28 (m, 2H, major, 75%), 2.71-2.75 [(m, 2H, major, 75%) + (m, 2H, minor, 25%)], 2.2 (s, 3H, major, 75%), 1.90-1.96 [(m, 2H, major, 75%) + (m, 2H, minor, 25%)]. ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.01, 142.53, 133.39, 131.43, 130.22, 127.39, 126.45, 121.78, 114.63, 113.39, 42.34, 41.74, 27.05, 26.87, 22.59, 21.13, 20.54. HRMS (ESI) *m/z*: calculated for $C_{10}H_{12}N$ ($M+H^+$) for **I-2**: 146.0970; found: 146.0963. calculated for $C_{10}H_{14}N$ ($M+H^+$) for **2j**: 148.1126; found: 148.1127.

9,10-dihydroacridine (4a)



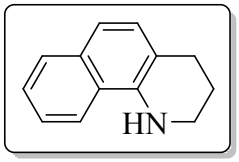
White solid (89 mg, 98%); m.p: 171~173 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.10 – 7.05 (m, 4H), 6.84 (td, *J* = 7.4, 1.2 Hz, 2H), 6.65 (dd, *J* = 7.8, 1.2 Hz, 2H), 5.93 (brs, 1H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.25, 128.73, 127.12, 120.76, 120.16, 113.57, 31.51. Spectral data is in accordance to the reported literature.[14]

1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (4b)



For this, 5 eqv. of Hantzsch ester was used. Yellow solid (81 mg, 86%); m.p: 69~71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.45 (s, 2H), 3.31 – 3.28 (m, 4H), 2.73 (t, *J* = 6.3 Hz, 4H), 1.89 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 132.88, 120.51, 119.20, 42.69, 26.99, 22.59. spectral data is matched with the literature.[30]

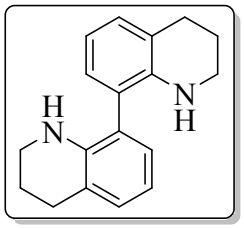
1,2,3,4-tetrahydrobenzo[*h*]quinoline (4c)



Light brown oil (89 mg, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.73 – 7.71 (m, 1H), 7.67 – 7.65 (m, 1H), 7.40 – 7.34 (m, 2H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H),

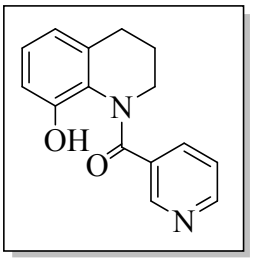
4.23 (brs, 1H), 3.46 – 3.44 (m, 2H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.04 – 1.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): *δ* 139.03, 133.13, 128.68, 128.62, 125.02, 124.83, 123.37, 119.54, 117.08, 115.96, 42.52, 27.55, 22.22. Spectral data is in accordance to the reported literature.[27]

1,1',2,2',3,3',4,4'-octahydro-8,8'-biquinoline (4d)



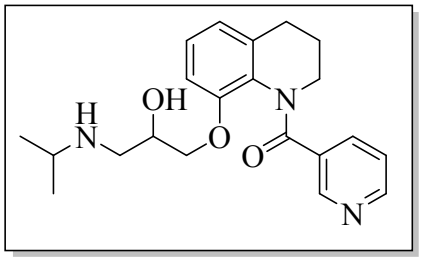
For this, 5 eqv. of Hantzsch ester was used. Isolated yield: 92%. Yellow oil (121 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*): *δ* 6.97 (d, *J* = 7.3 Hz, 2H), 6.91 (d, *J* = 7.3 Hz, 2H), 6.66 (t, *J* = 7.4 Hz, 2H), 3.29 – 3.22 (m, 4H), 2.83 (t, *J* = 6.4 Hz, 4H), 1.98 – 1.89 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*): *δ* 142.49, 128.98, 128.83, 123.4, 121.59, 116.63, 42.10, 27.58, 22.07. HRMS (ESI) *m/z*: calculated for $C_{18}H_{21}N_2$ ($M+H^+$): 265.1704; found: 265.1709.

(8-hydroxy-3,4-dihydroquinolin-1(2H)-yl)(pyridin-3-yl)methanone (5)



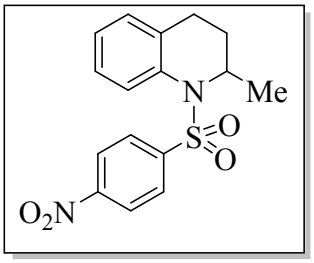
Isolated yield: 82%. ^{1}H NMR (400 MHz, DMSO-d_6): *δ* 9.43 (s, 1H), 8.46 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.38 (d, *J* = 2.2 Hz, 1H), 7.58 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.23 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.72 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.42 (dd, *J* = 8.1, 1.3 Hz, 1H), 3.4 (brs, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 1.91 (brs, 2H). ^{1}H NMR (400 MHz, CD_3CN): *δ* 8.48 (br, 2H), 7.68 – 7.66 (m, 1H), 7.23 – 7.21 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.53 – 6.51 (m, 1H), 3.64 (brs, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 1.91 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): *δ* 167.62, 150.20, 149.24, 148.17, 136.31, 134.96, 133.27, 127.11, 126.56, 122.63, 118.22, 114.24, 42.86, 26.28, 24.47. HRMS (ESI) *m/z*: calculated for $C_{15}H_{15}N_2O_2$ ($M+H^+$): 255.1133; found: 255.1132.

(8-(2-hydroxy-3-(isopropylamino)propoxy)-3,4-dihydroquinolin-1(2H)-yl)(pyridin-3-yl)methanone (6)



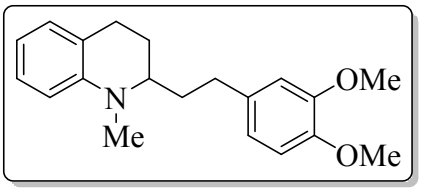
Isolated yield: 75%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.62 – 8.55 (m, 2H), 7.73 (br, 1H), 7.20 – 7.17 (m, 1H), 7.08 (t, J = 7.9 Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.64 – 6.61 (m, 1H), 4.22 (br, 1H), 3.80 – 3.76 (m, 2H), 3.58 – 3.48 (m, 2H), 2.86 – 2.66 (m, 4H), 2.56 – 2.51 (m, 1H), 2.22 (br, 2H), 1.89 – 1.80 (m, 2H), 1.05 (d, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 168.57, 151.13, 151.07, 149.09, 135.67, 132.44, 128.64, 127.04, 122.87, 122.79, 120.79, 111.32, 71.92, 70.98, 68.68, 68.06, 49.10, 26.75, 24.82, 23.07, 22.98. HRMS (ESI) *m/z*: calculated for $C_{21}H_{28}N_3O_3$ ($M+H^+$): 370.2125; found: 370.2141.

2-methyl-1-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (7)



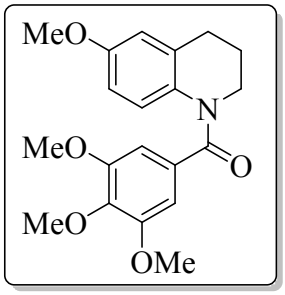
Isolated yield: 96%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.21 (d, J = 8.9 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.16 (t, J = 7.9 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 4.43 – 4.35 (hext, J = 6.4 Hz, 1H), 2.44 – 2.37 (m, 1H), 1.89 – 1.81 (m, 1H), 1.71 – 1.64 (m, 1H), 1.41 – 1.36 (m, 1H), 1.34 – 1.32 (d, J = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*): δ 144.85, 134.40, 133.80, 128.36, 128.28, 127.62, 127.28, 126.55, 124.17, 53.43, 30.61, 25.02, 22.03. Spectral data is in accordance to the reported literature.[12]

2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (8)



Isolated yield: 95%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.10-7.06 (m, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.80 – 6.78 (m, 1H), 6.74 – 6.70 (m, 2H), 6.58 (t, J = 7.3, 1.1 Hz, 1H), 6.52 (d, J = 8.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.30 – 3.27 (dq, J = 8.6, 4.3 Hz, 1H), 2.91 (s, 3H), 2.82 – 2.87 (m, 1H), 2.72-2.66 (m, 2H), 2.55 – 2.53 (m, 1H), 1.96 – 1.92 (m, 3H), 1.74 – 1.73 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 149.08, 147.40, 145.47, 134.82, 128.83, 127.27, 121.90, 120.22, 115.55, 111.79, 111.49, 110.78, 58.58, 56.11, 56.04, 38.24, 33.25, 32.08, 24.58, 23.74. The obtained spectroscopic data were in agreement with the reported data for this compound.[16]

(6-methoxy-3,4-dihydroquinolin-1(2H)-yl)(3,4,5-trimethoxyphenyl)methanone (9)



Isolated yield: 92%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.66 (d, J = 2.4 Hz, 1H), 6.55 (d, J = 1.7 Hz, 2H), 6.45 (dd, J = 7.0, 4.3 Hz, 1H), 3.83 (td, J = 6.5, 2.1 Hz, 2H), 3.79 (s, J = 2.1 Hz, 3H), 3.70 (d, J = 2.3 Hz, 3H), 3.65 (d, J = 2.1 Hz, 6H), 2.76 (td, J = 6.7, 2.1 Hz, 2H), 2.02 – 1.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 169.37, 156.60, 152.71, 139.56, 132.99, 132.57, 131.24, 126.27, 113.12, 111.44, 106.25, 60.86, 56.04, 55.40, 44.58, 27.18, 24.15. Spectra data is in accordance to the reported literature.[14]

12. ^{1}H, ^{13}C, and ^{19}F NMR spectra of the products

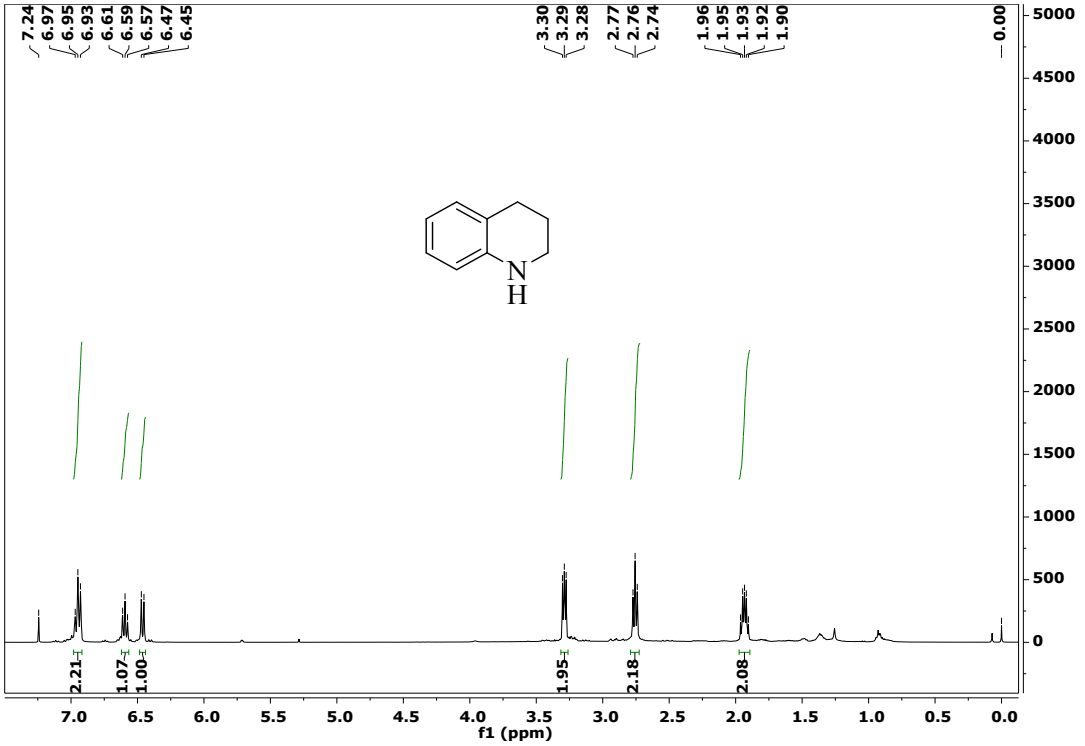


Figure S4: ^{1}H NMR Spectrum of **2a** ($CDCl_3$, 400 MHz, 298 K)

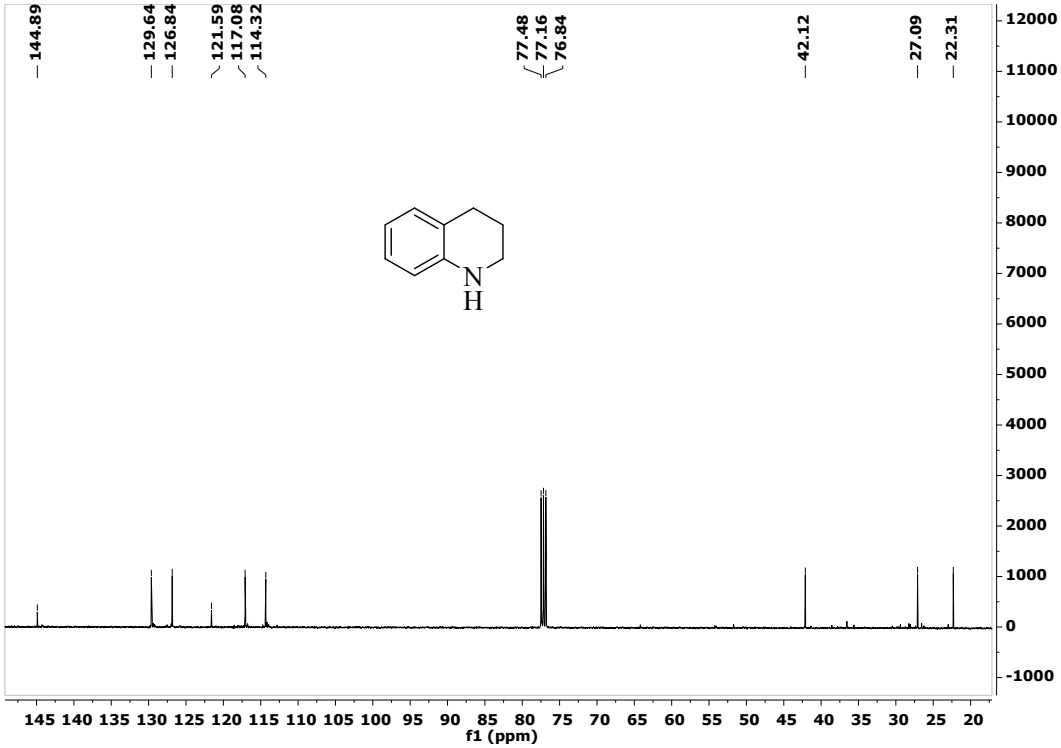


Figure S5: ^{13}C NMR Spectrum of **2a** ($CDCl_3$, 101 MHz, 298 K)

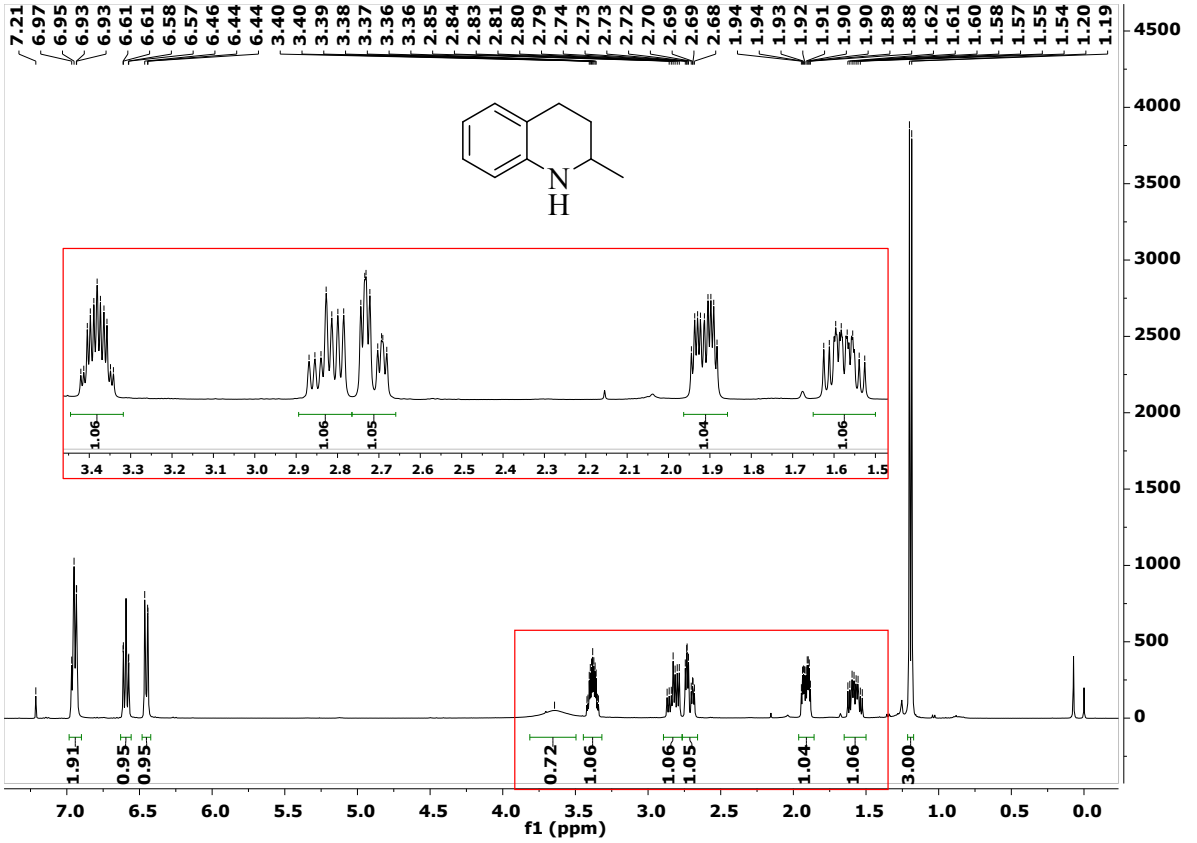


Figure S6: ^{1}H NMR Spectrum of **2b** ($CDCl_3$, 400 MHz, 298 K)

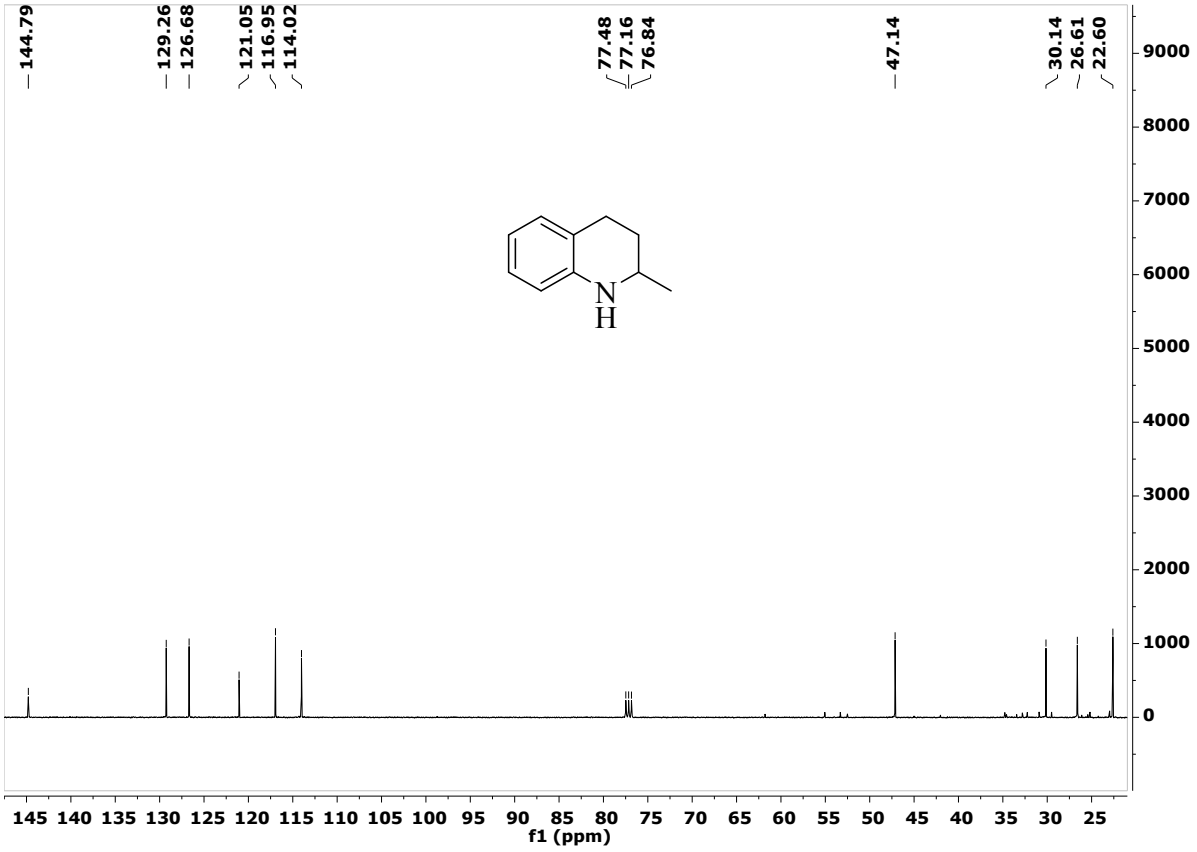


Figure S7: ^{13}C NMR Spectrum of **2b** ($CDCl_3$, 101 MHz, 298 K)

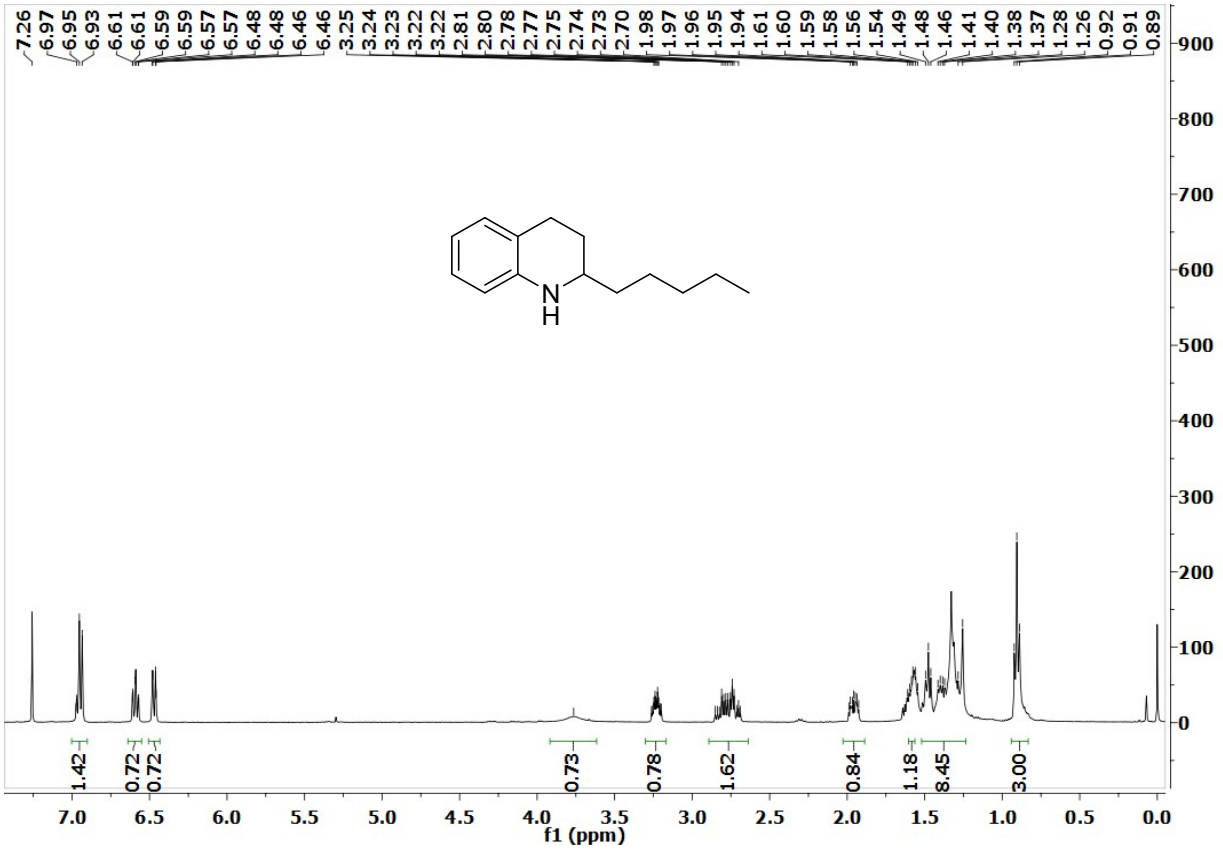


Figure S8: ^{1}H NMR Spectrum of **2c** ($CDCl_3$, 400 MHz, 298 K)

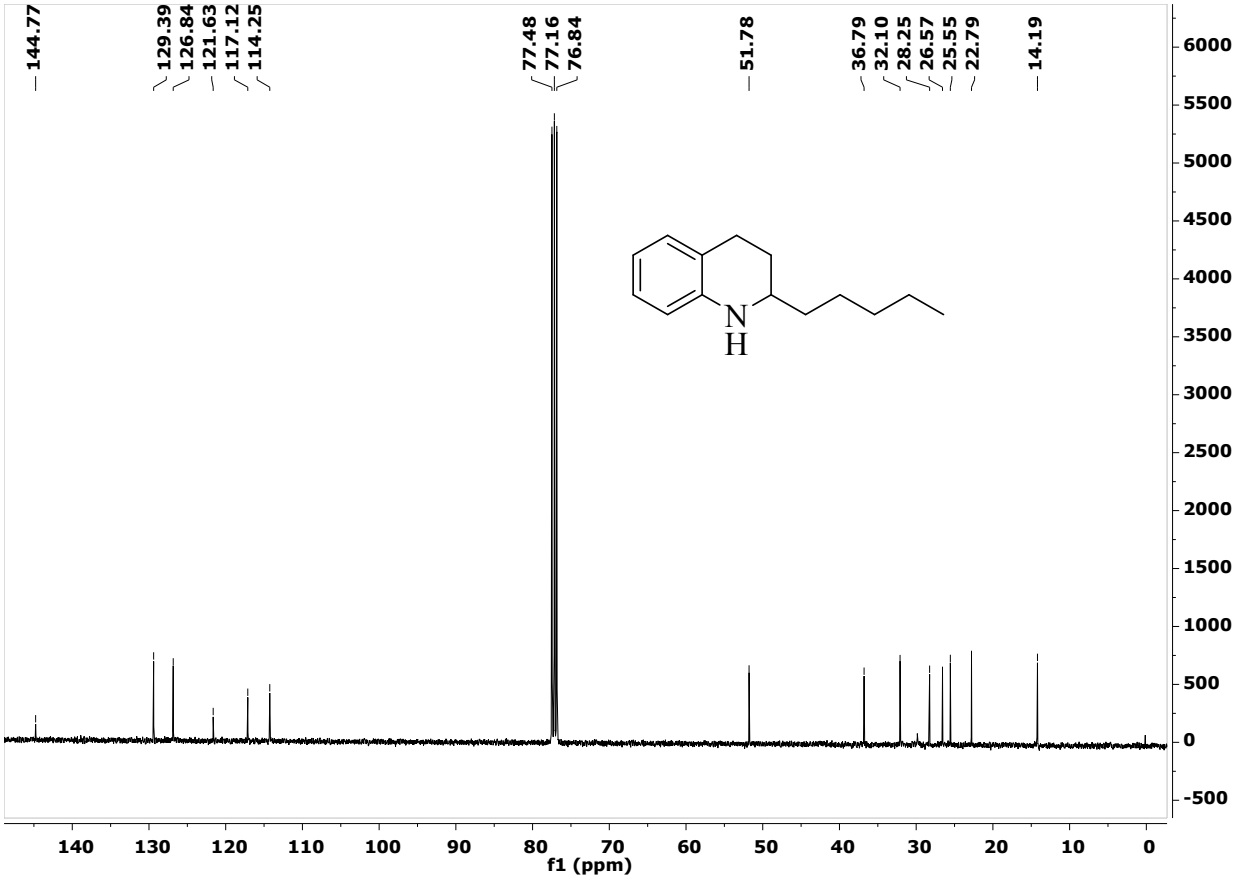


Figure S9: ^{13}C NMR Spectrum of **2c** ($CDCl_3$, 101 MHz, 298 K)

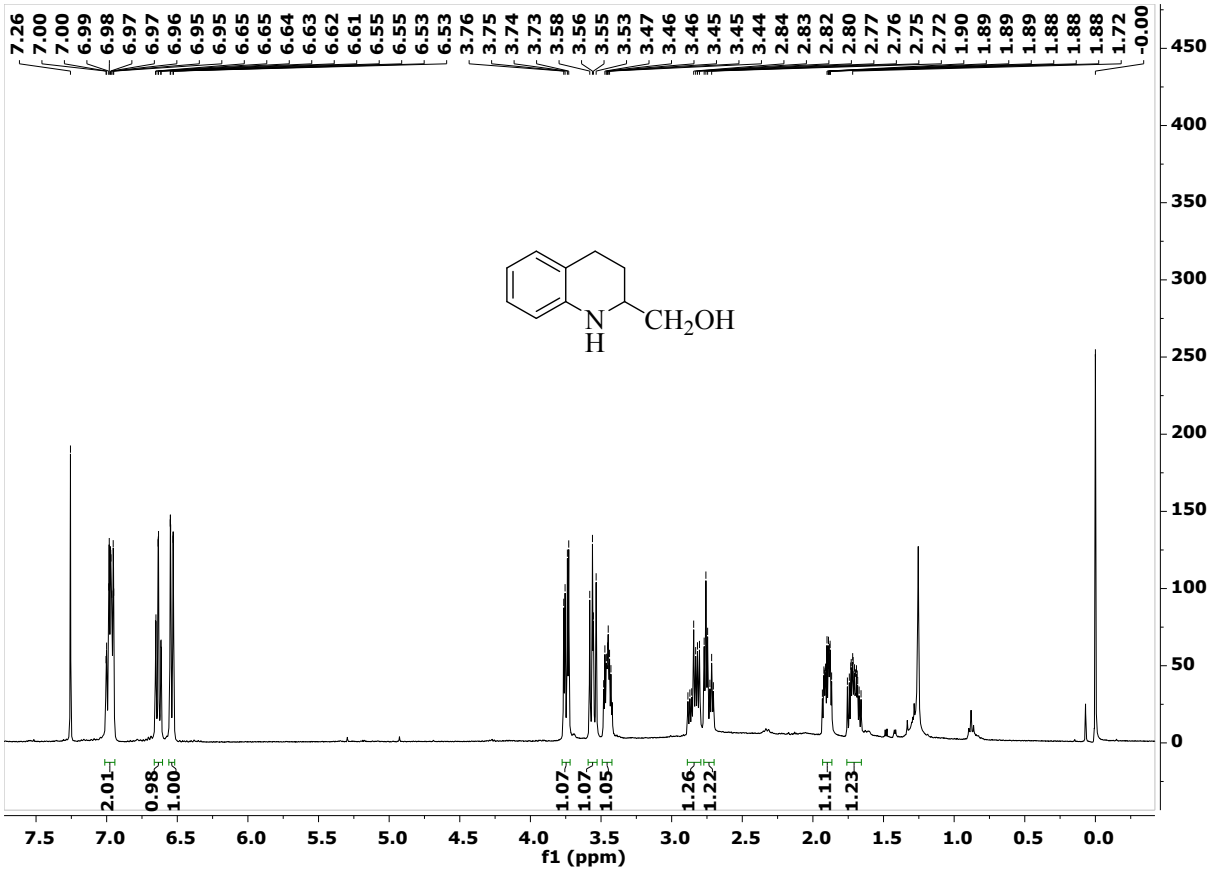


Figure S10: ^{1}H NMR Spectrum of **2d** ($CDCl_3$, 400 MHz, 298 K)

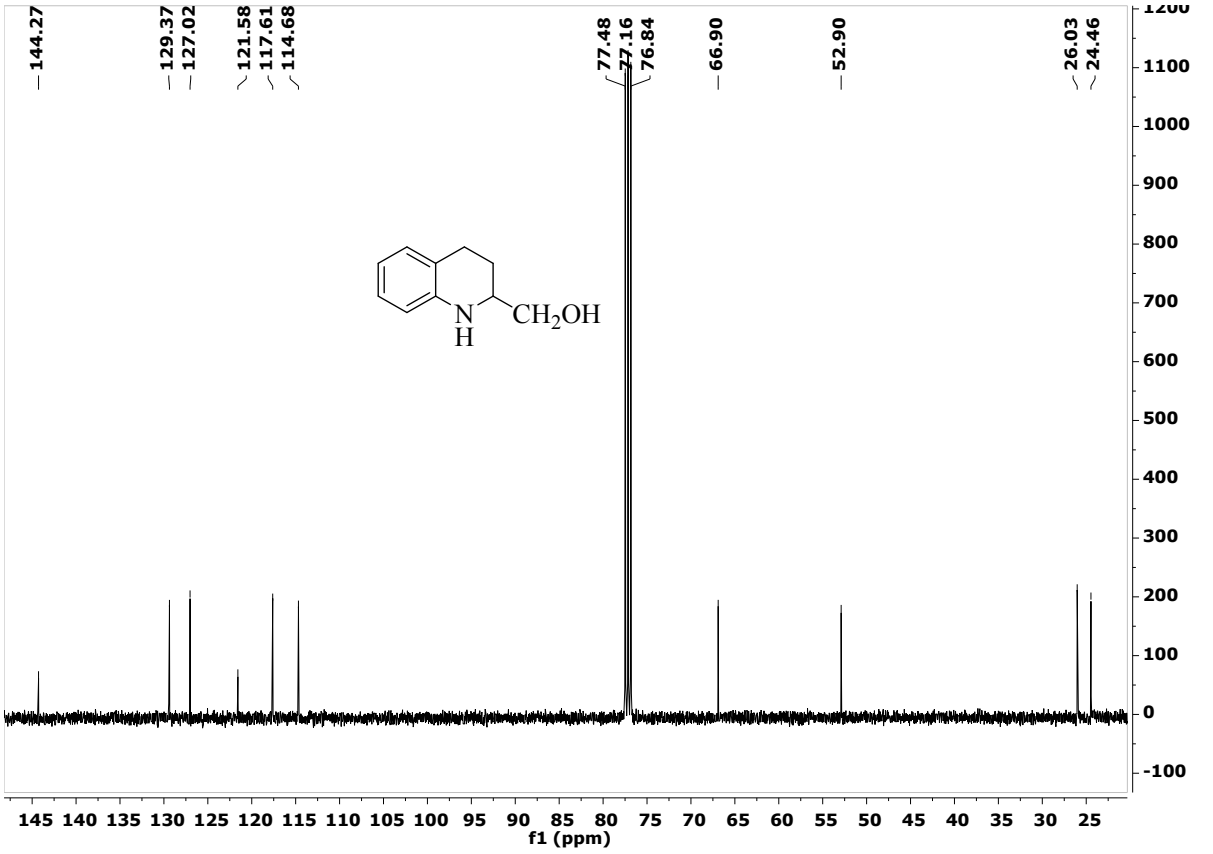


Figure S11: ^{13}C NMR Spectrum of **2d** ($CDCl_3$, 101 MHz, 298 K)

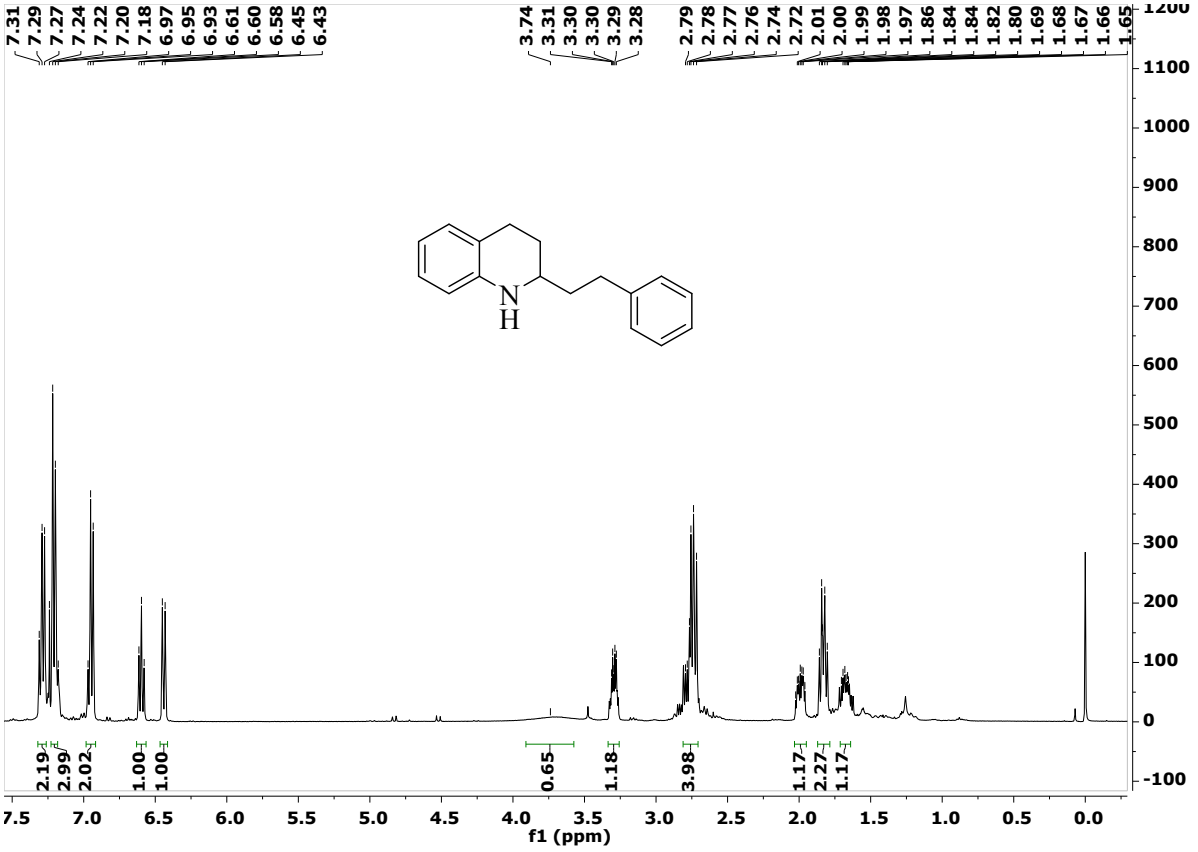


Figure S12: ^{1}H NMR Spectrum of **2e** ($CDCl_3$, 400 MHz, 298 K)

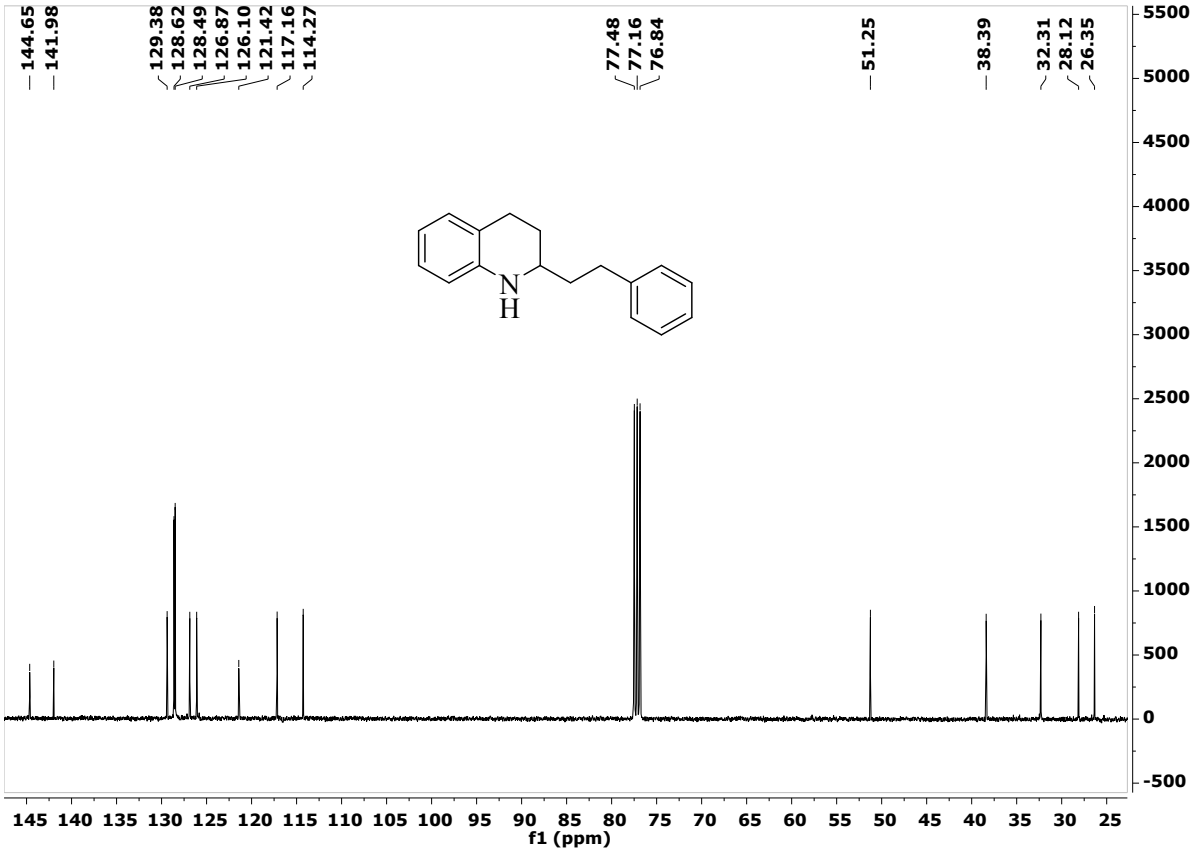


Figure S13: ^{13}C NMR Spectrum of **2e** ($CDCl_3$, 101 MHz, 298 K)

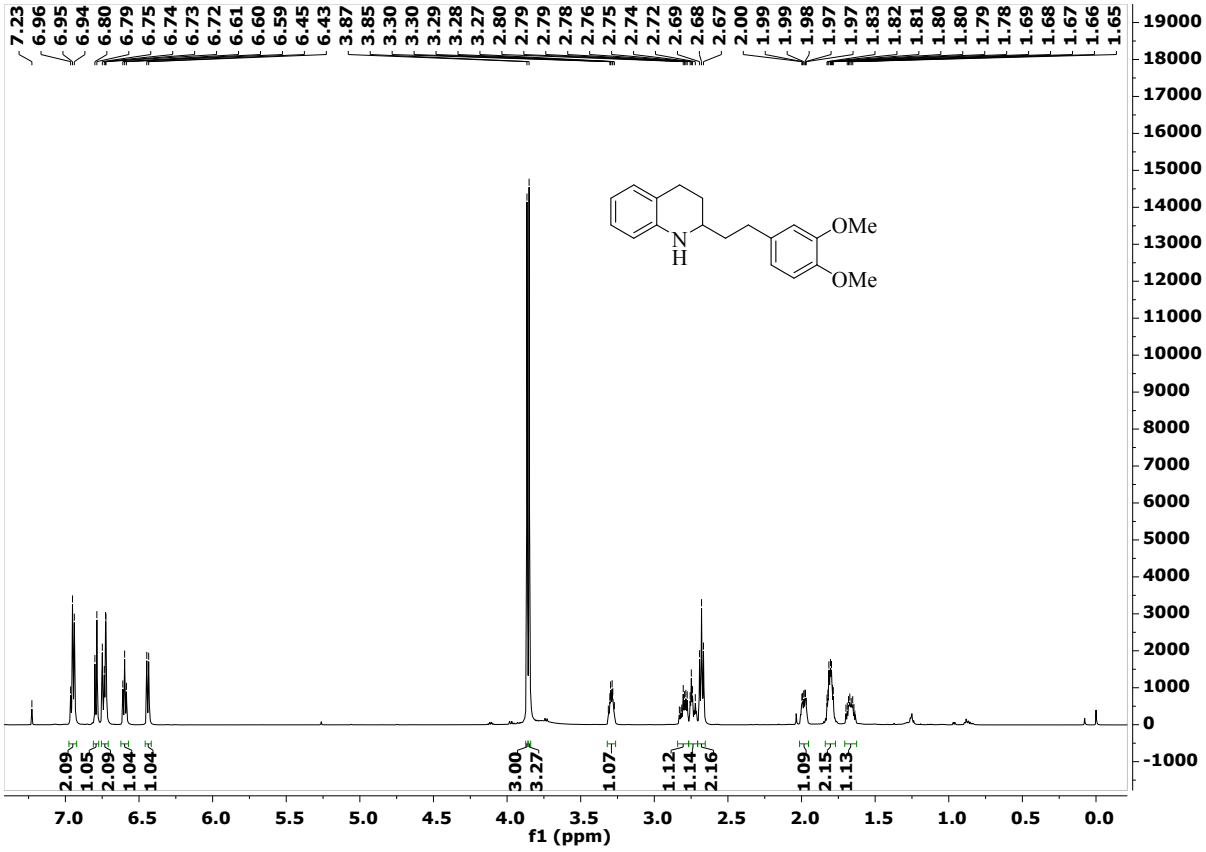


Figure S14: ^{1}H NMR Spectrum of **2f** ($CDCl_3$, 600 MHz, 298 K)

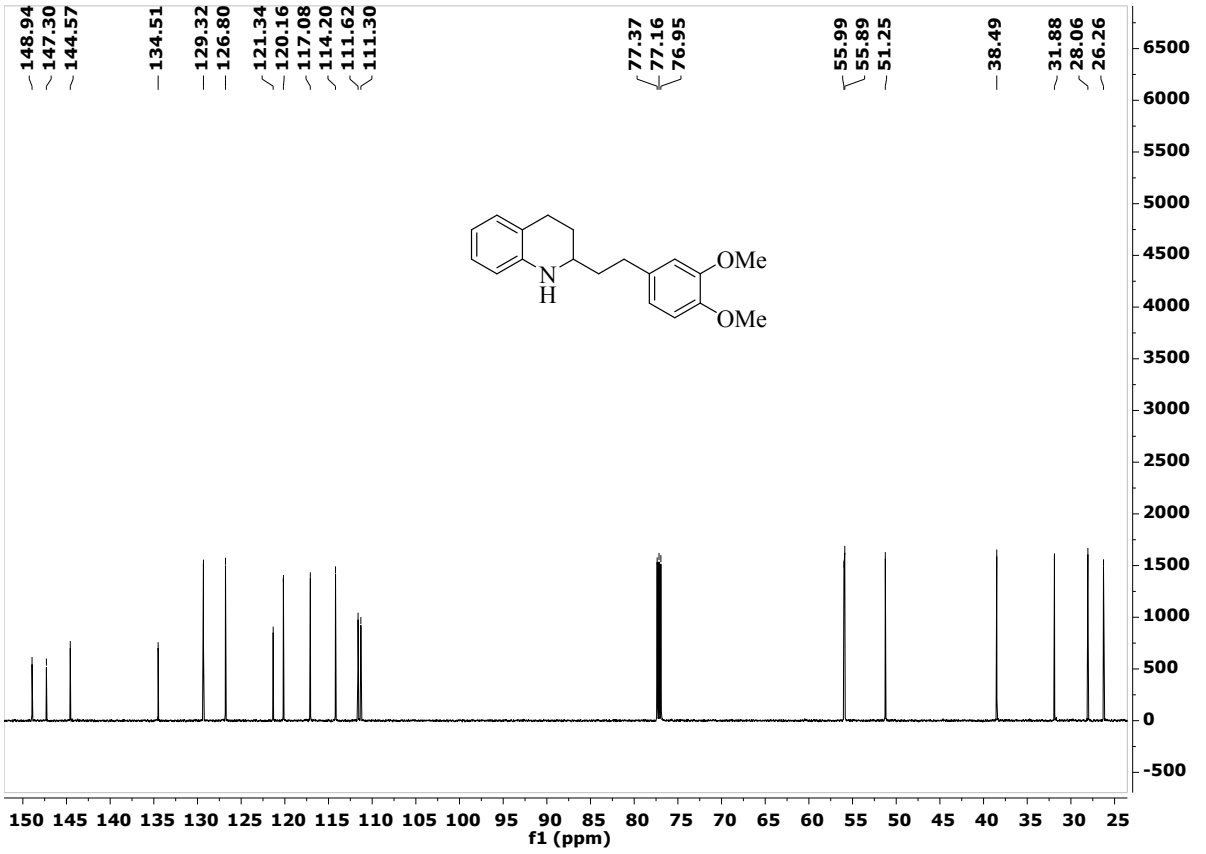


Figure S15: ^{13}C NMR Spectrum of **2f** ($CDCl_3$, 151 MHz, 298 K)

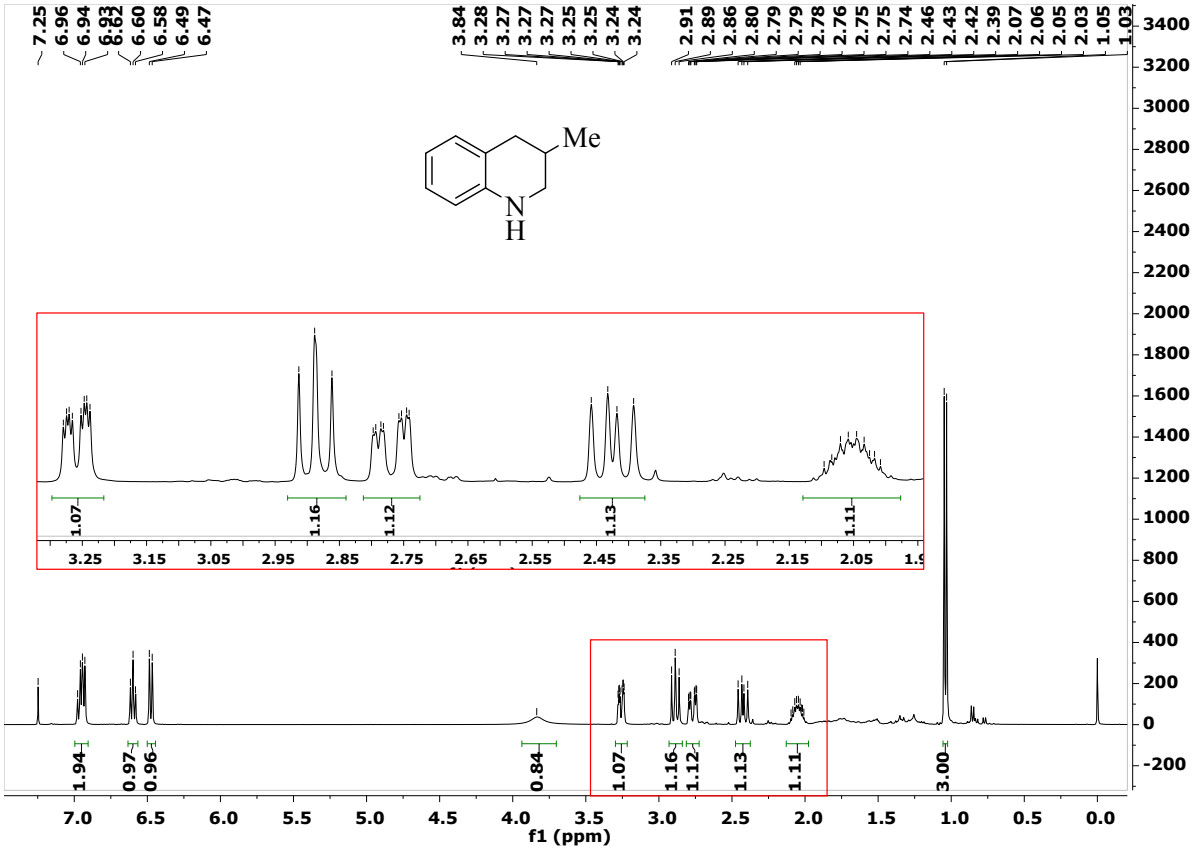


Figure S16: ^{1}H NMR Spectrum of **2g** ($CDCl_3$, 400 MHz, 298 K)

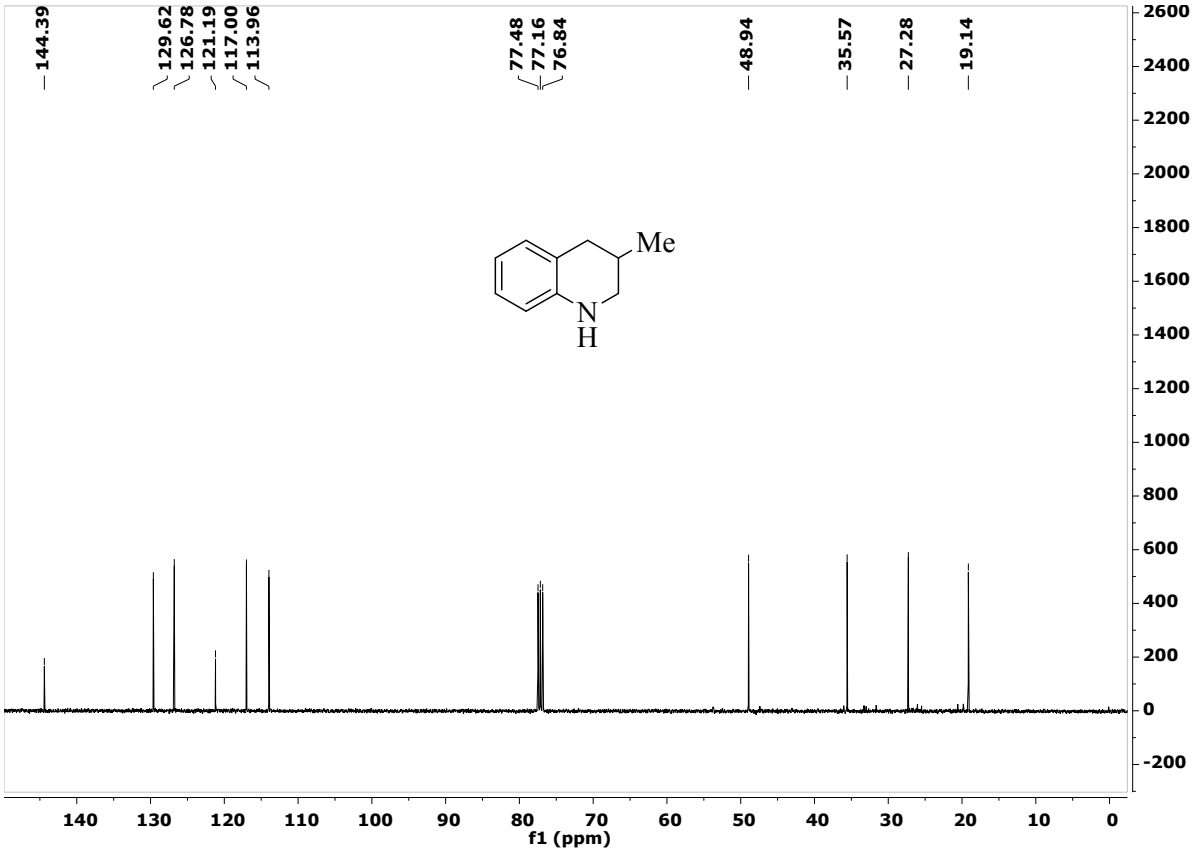


Figure S17: ^{13}C NMR Spectrum of **2g** ($CDCl_3$, 101 MHz, 298 K)

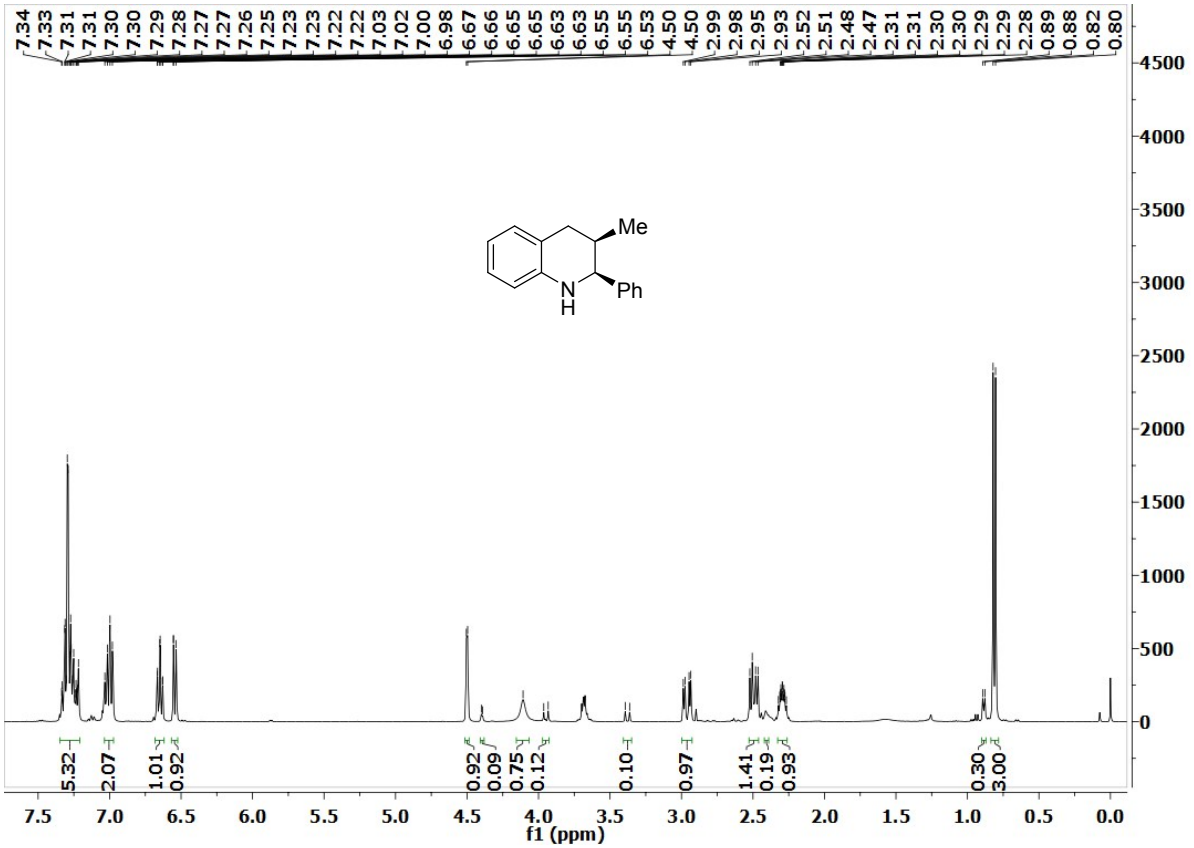


Figure S18: ^{1}H NMR Spectrum of **2h** ($CDCl_3$, 400 MHz, 298 K)

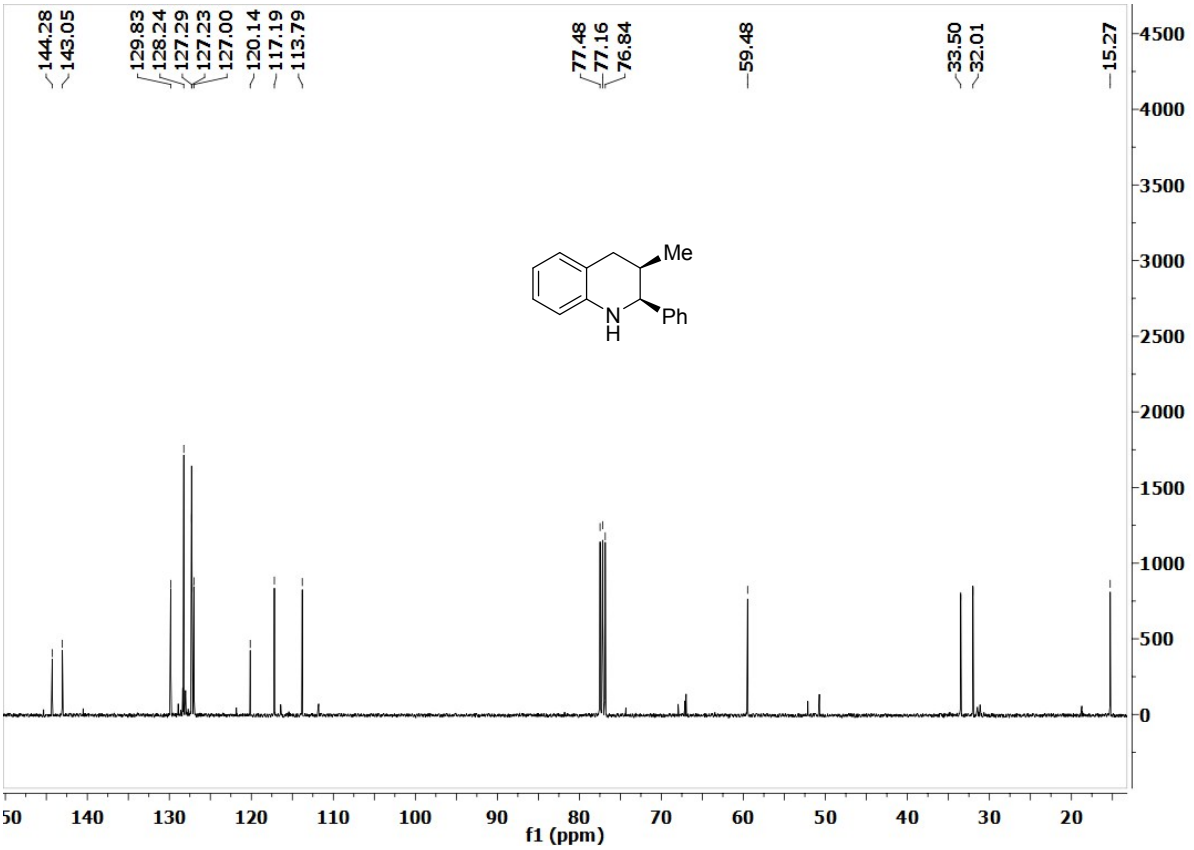


Figure S19: ^{13}C NMR Spectrum of **2h** ($CDCl_3$, 101 MHz, 298 K)

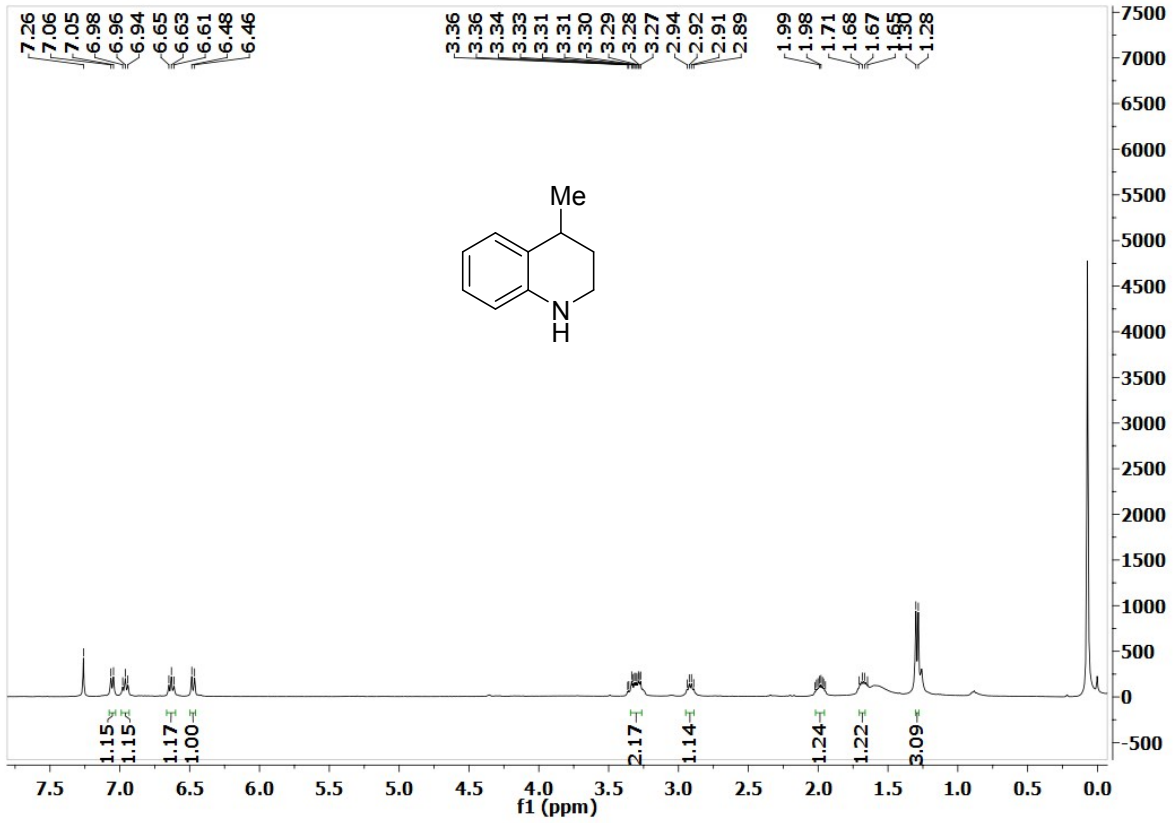


Figure S20: ^{1}H NMR Spectrum of **2i** ($CDCl_3$, 400 MHz, 298 K)

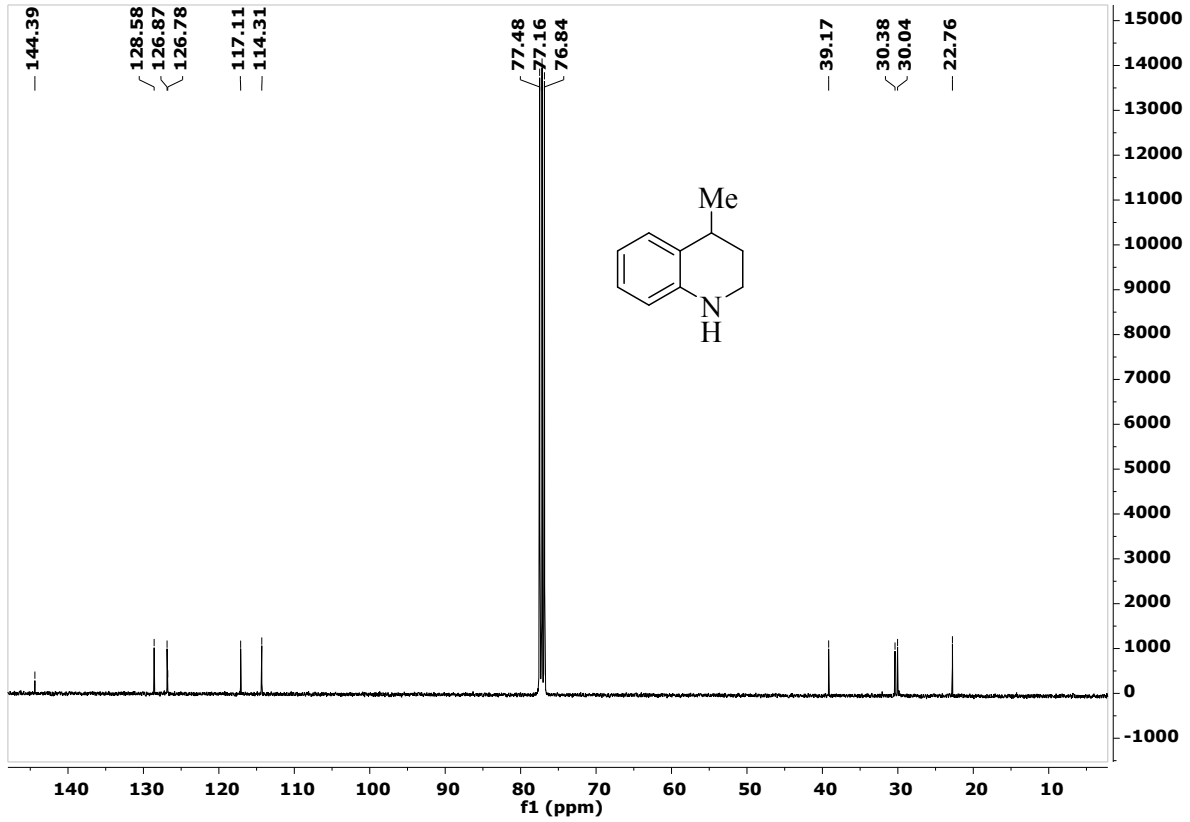


Figure S21: ^{13}C NMR Spectrum of **2i** ($CDCl_3$, 101 MHz, 298 K)

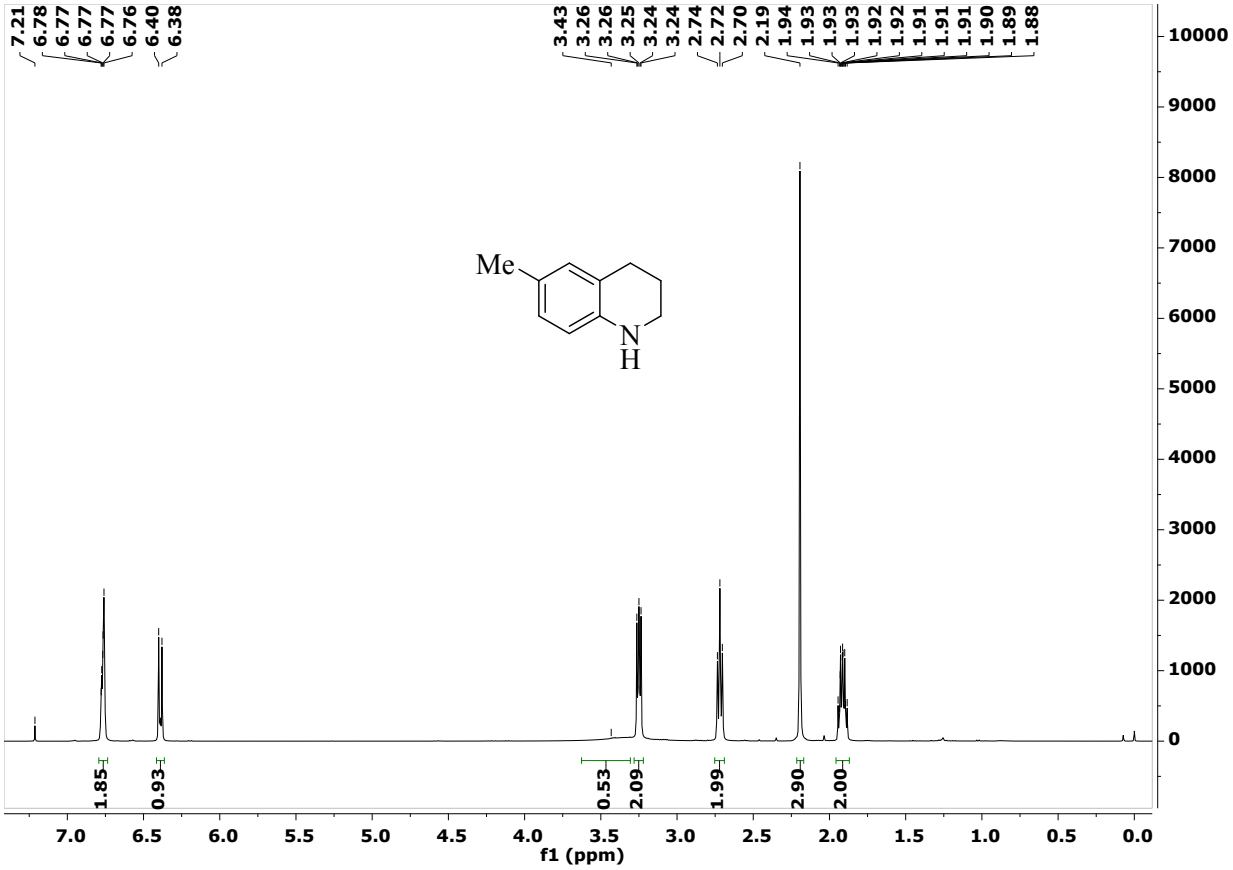


Figure S22: ^{1}H NMR Spectrum of **2j** ($CDCl_3$, 400 MHz, 298 K)

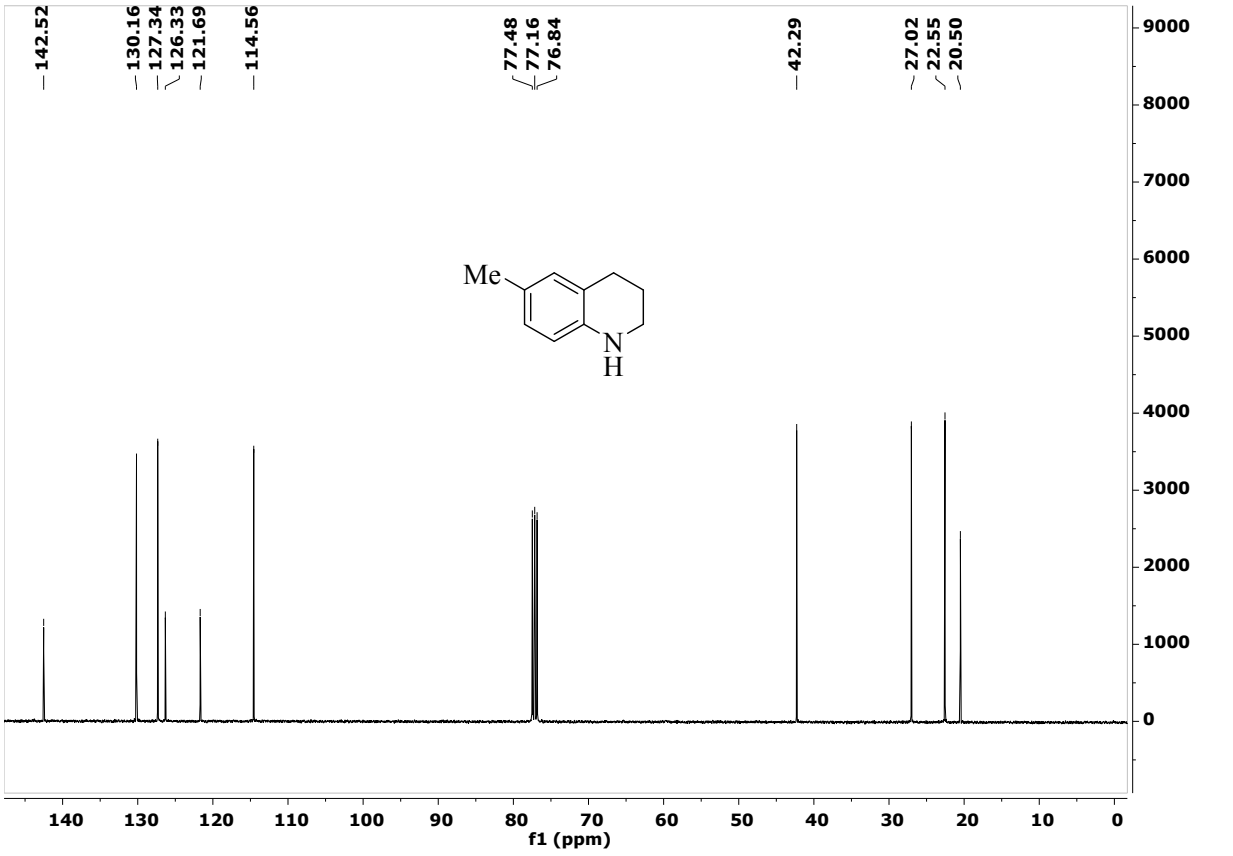


Figure S23: ^{13}C NMR Spectrum of **2j** ($CDCl_3$, 101 MHz, 298 K)

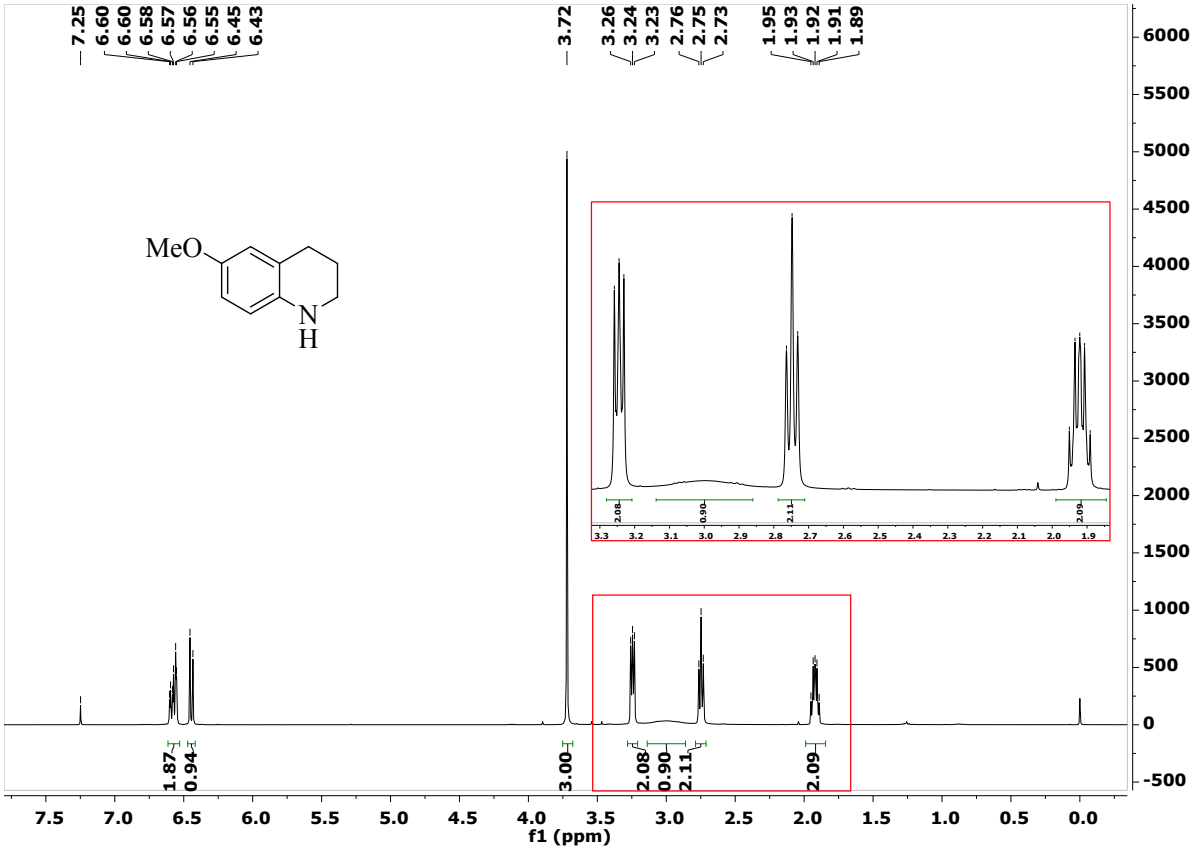


Figure S24: ^{1}H NMR Spectrum of **2k** ($CDCl_3$, 400 MHz, 298 K)

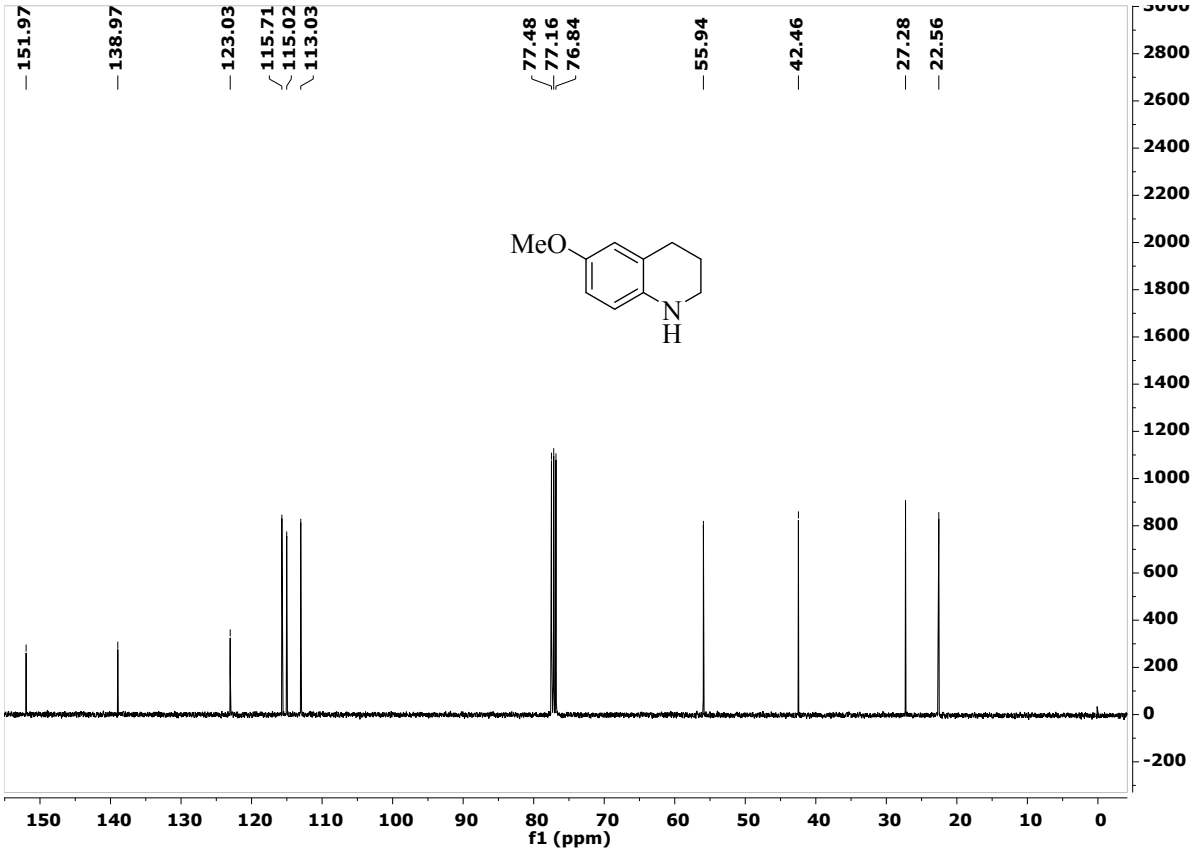


Figure S25: ^{13}C NMR Spectrum of **2k** ($CDCl_3$, 101 MHz, 298 K)

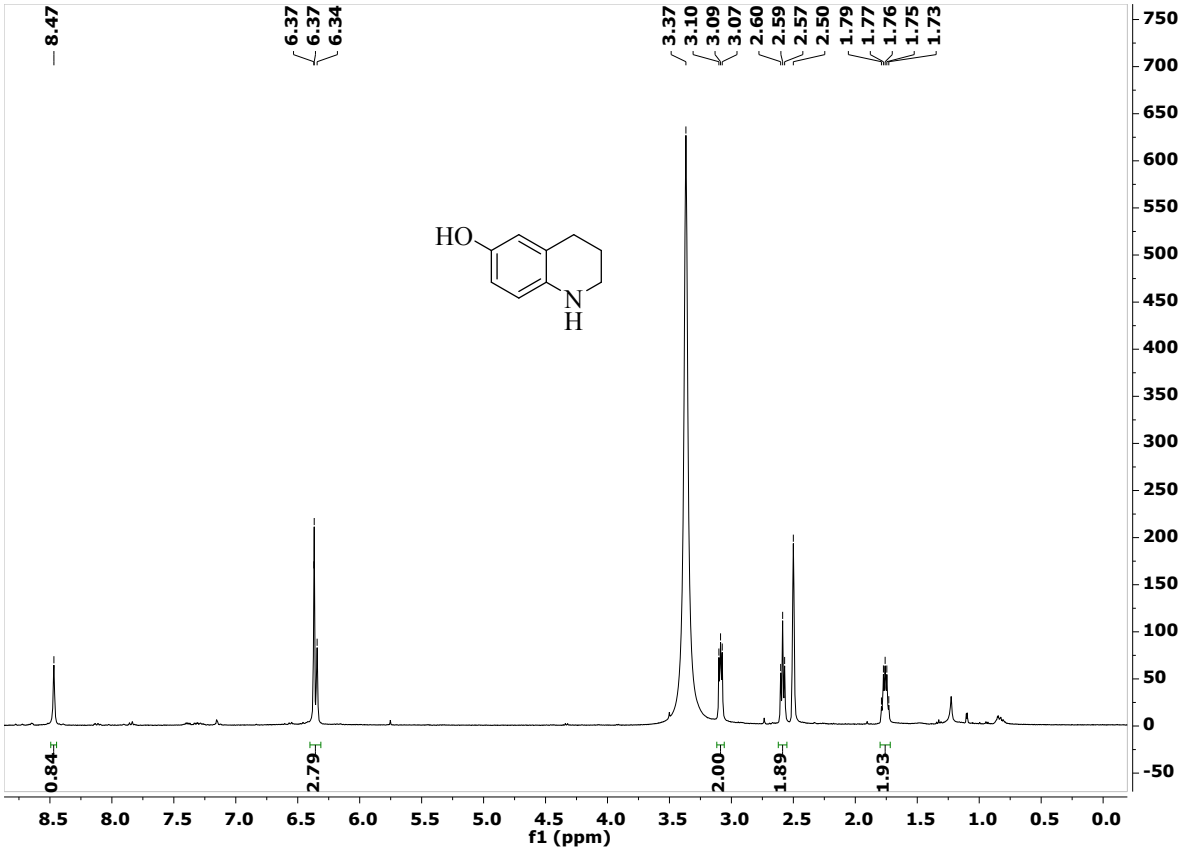


Figure S26: [1]H NMR Spectrum of **2l** (DMSO-d_6, 400 MHz, 298 K)

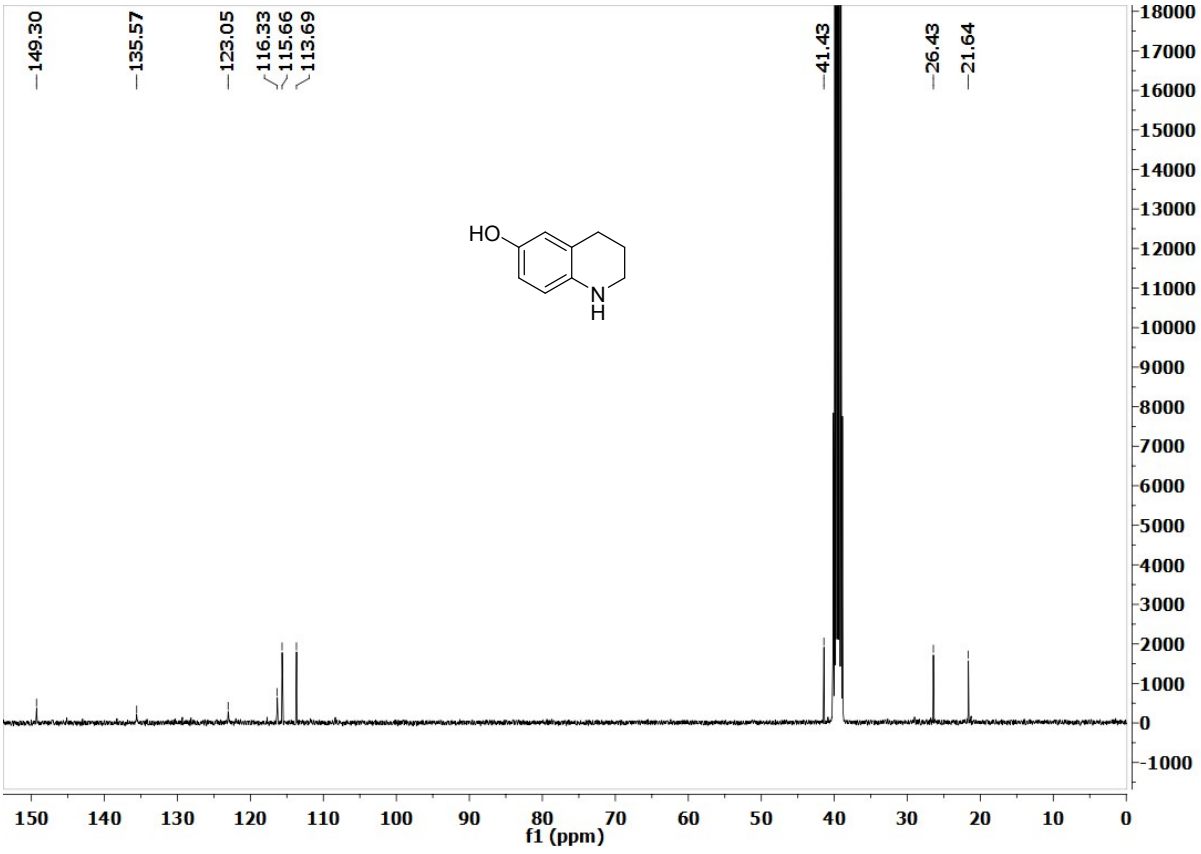


Figure S27: [13]C NMR Spectrum of **2l** (DMSO-d_6, 101 MHz, 298 K)

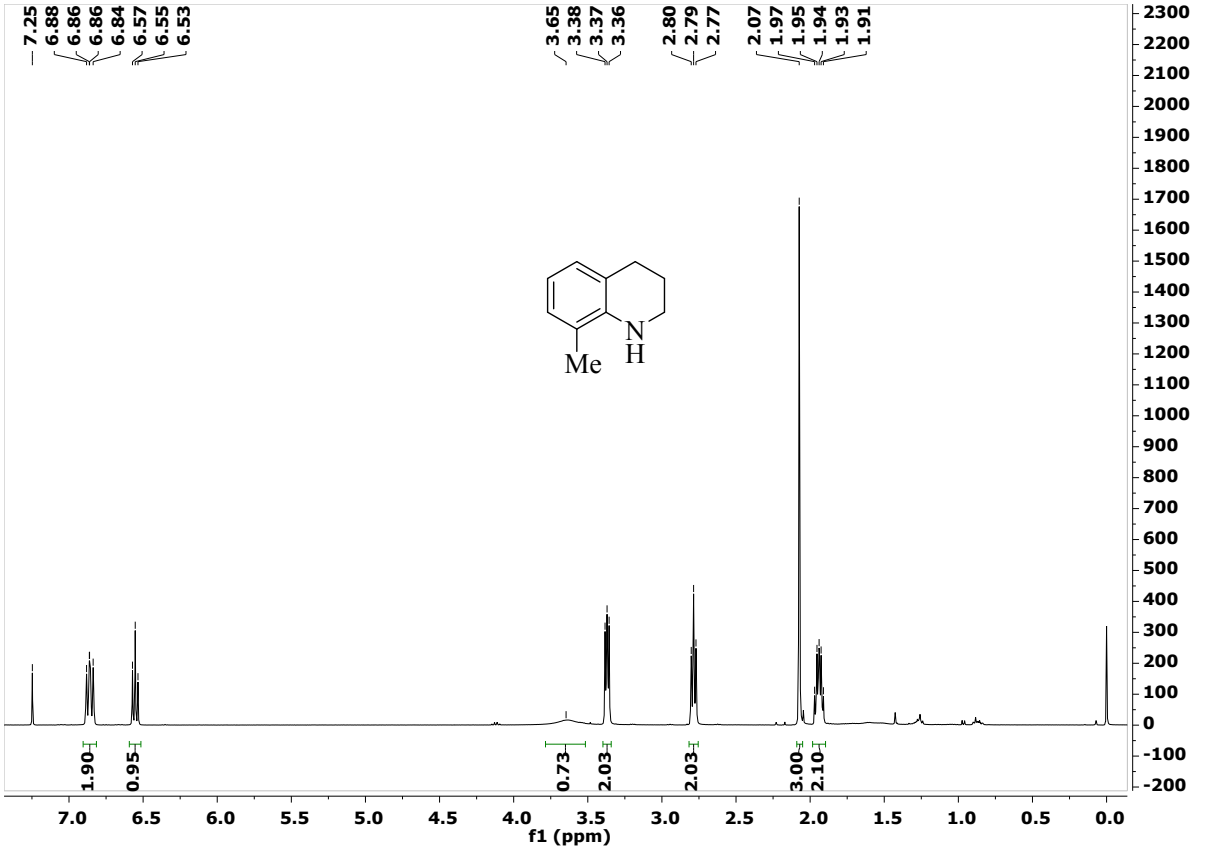


Figure S28: ^{1}H NMR Spectrum of **2m** ($CDCl_3$, 400 MHz, 298 K)

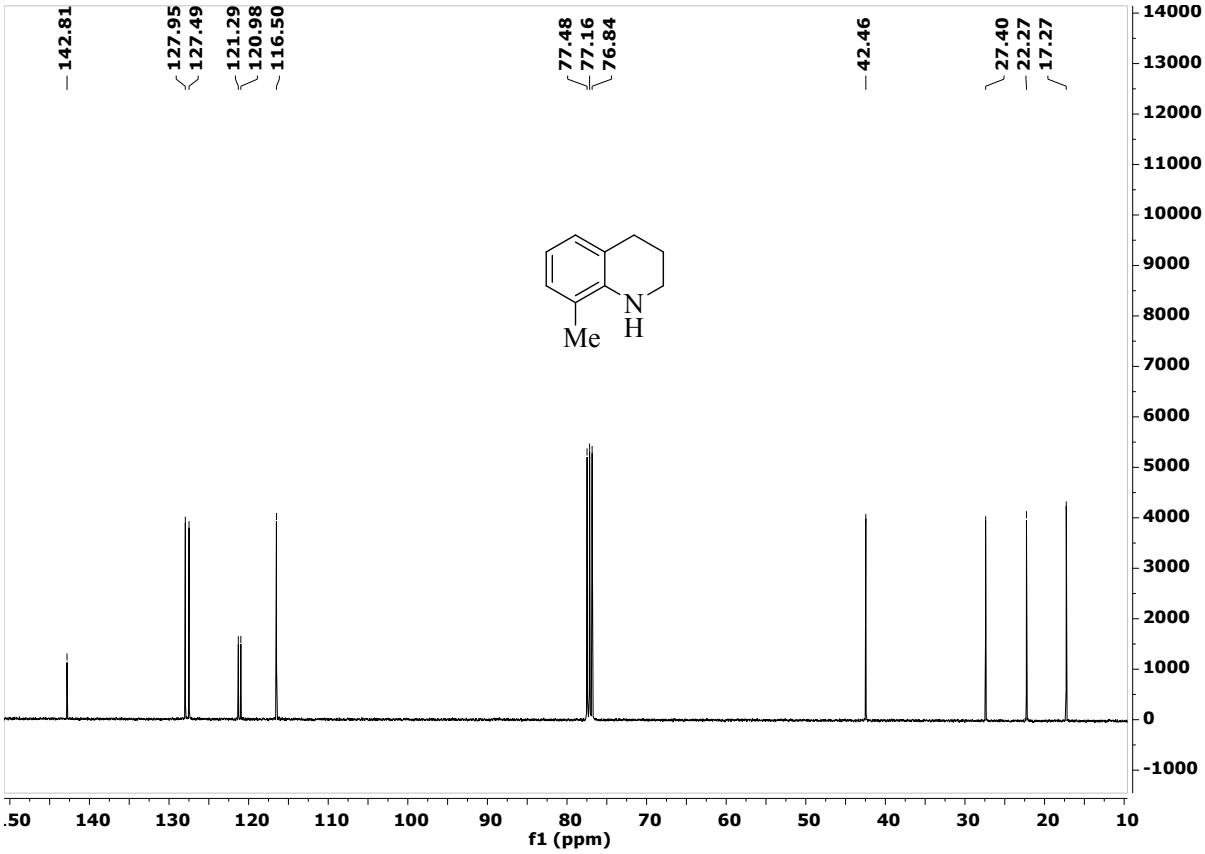


Figure S29: ^{13}C NMR Spectrum of **2m** ($CDCl_3$, 101 MHz, 298 K)

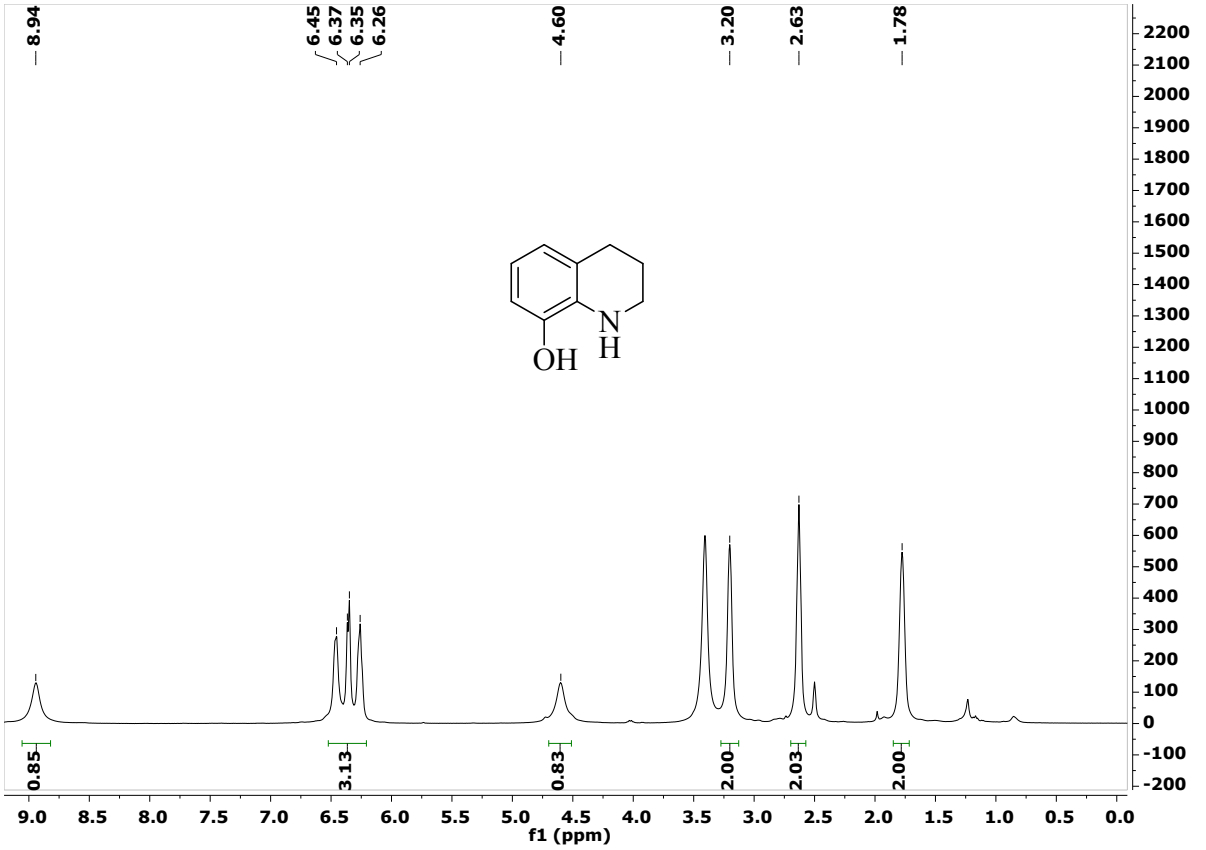


Figure S30: [1]H NMR Spectrum of **2n** (DMSO-d_6, 400 MHz, 298 K)

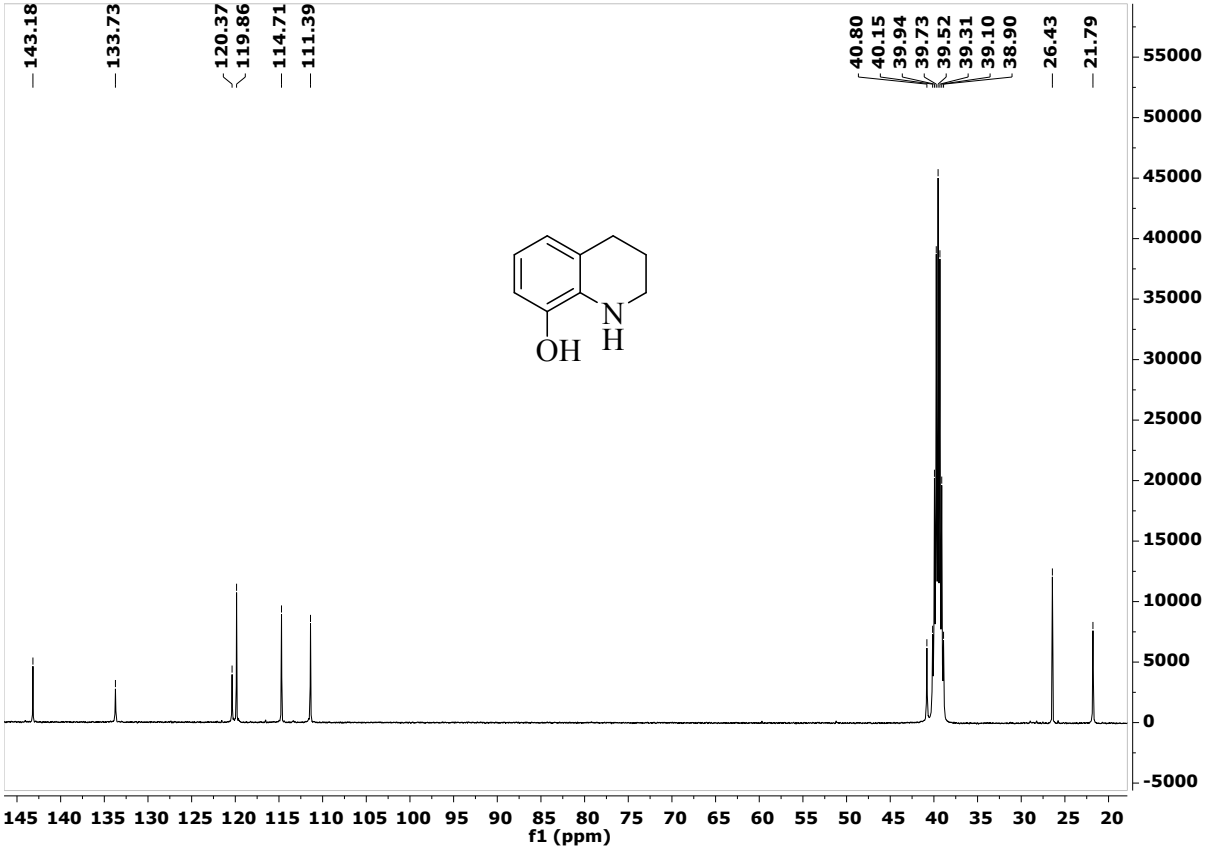


Figure S31: [13]C NMR Spectrum of **2n** (DMSO-d_6, 101 MHz, 298 K)

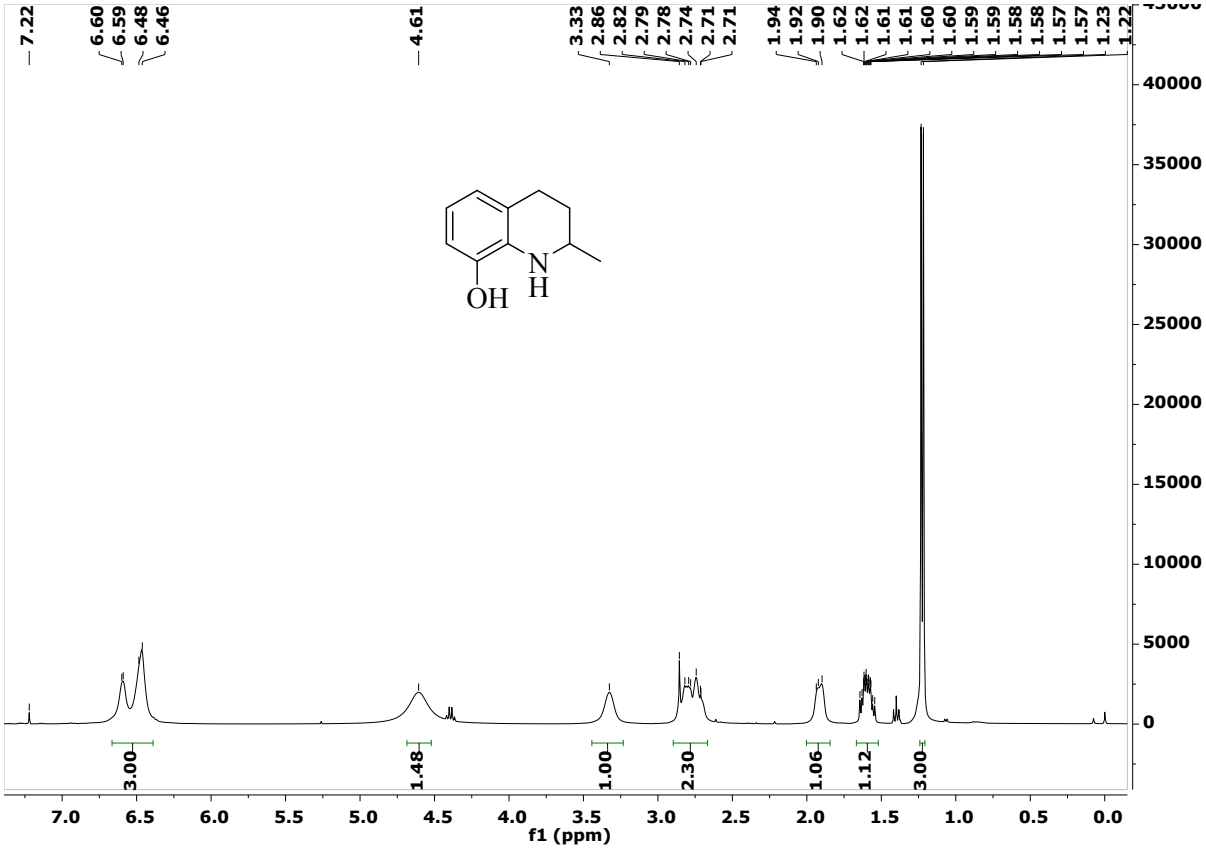


Figure S32: [1]H NMR Spectrum of **2o** ($CDCl_3$, 400 MHz, 298 K)

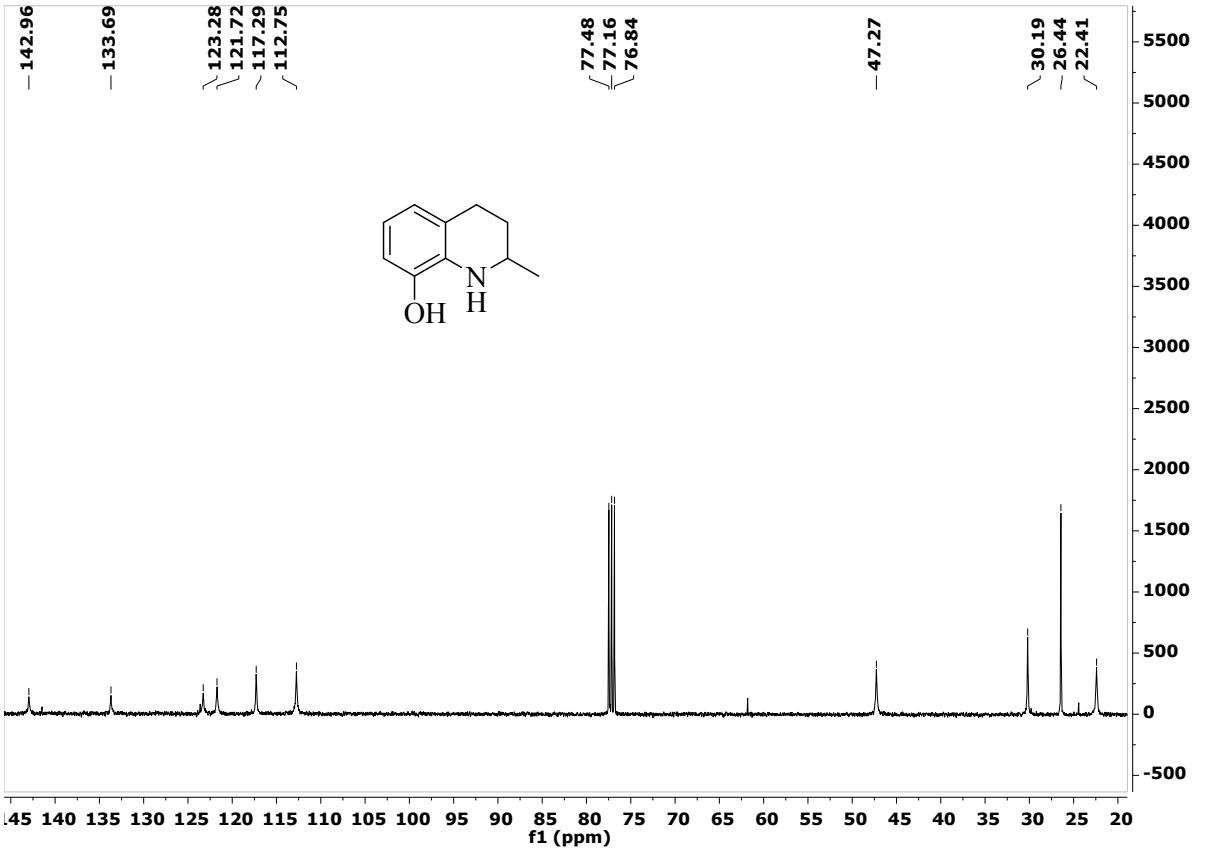


Figure S33: [13]C NMR Spectrum of **2o** ($CDCl_3$, 101 MHz, 298 K)

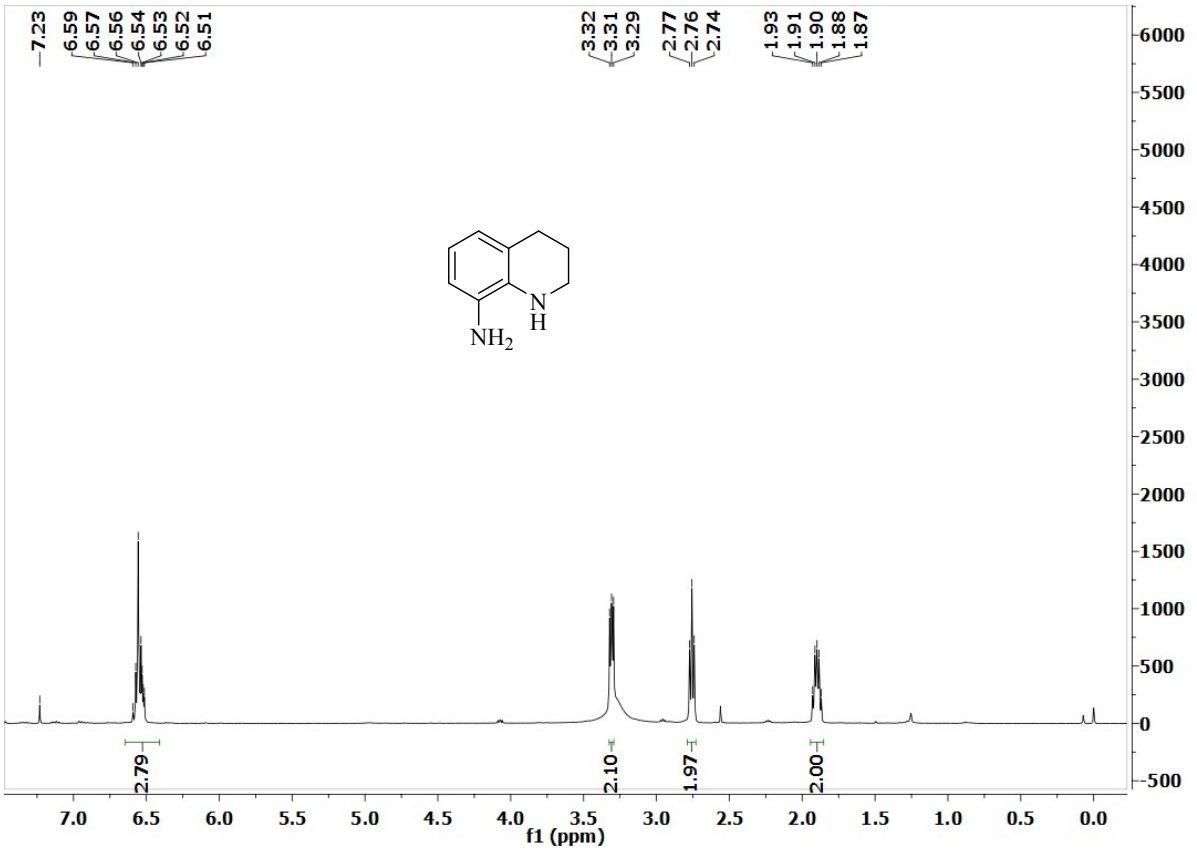


Figure S34: ^{1}H NMR Spectrum of **2p** ($CDCl_3$, 400 MHz, 298 K)

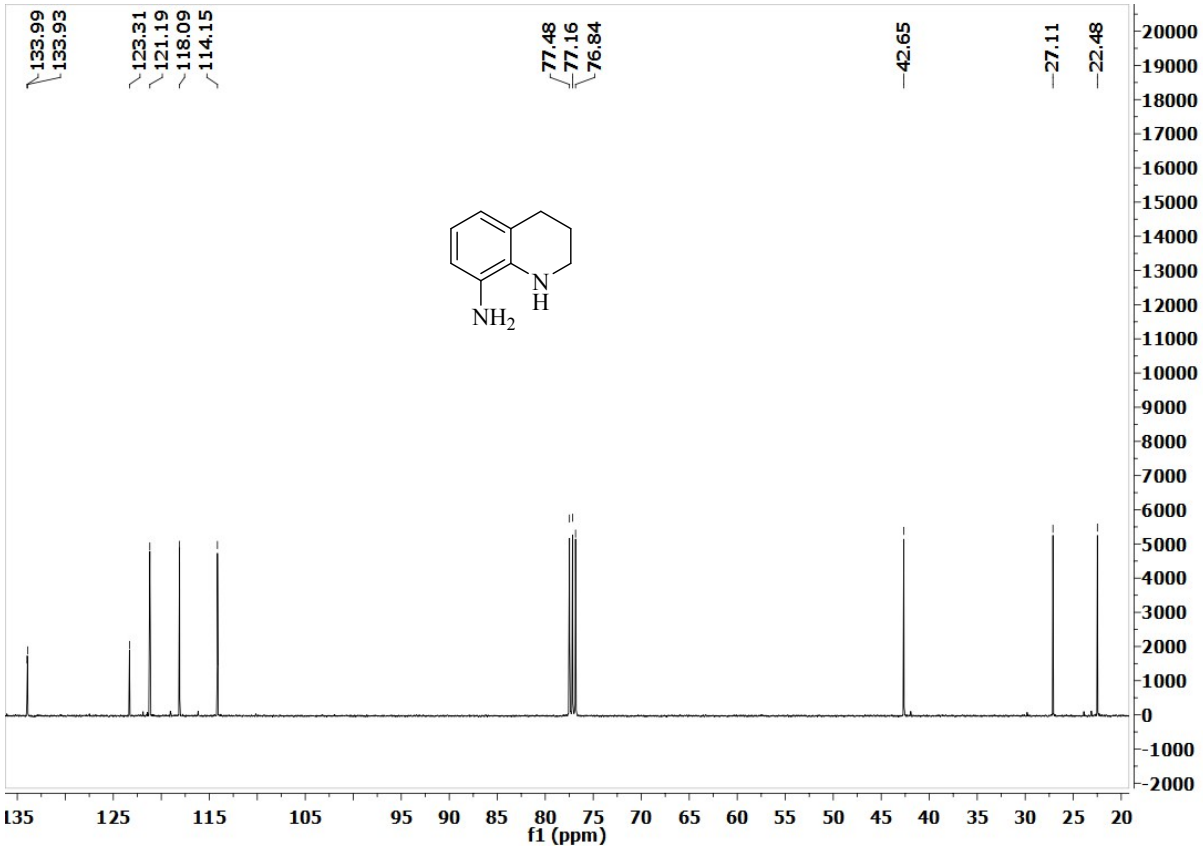


Figure S35: ^{13}C NMR Spectrum of **2p** ($CDCl_3$, 101 MHz, 298 K)

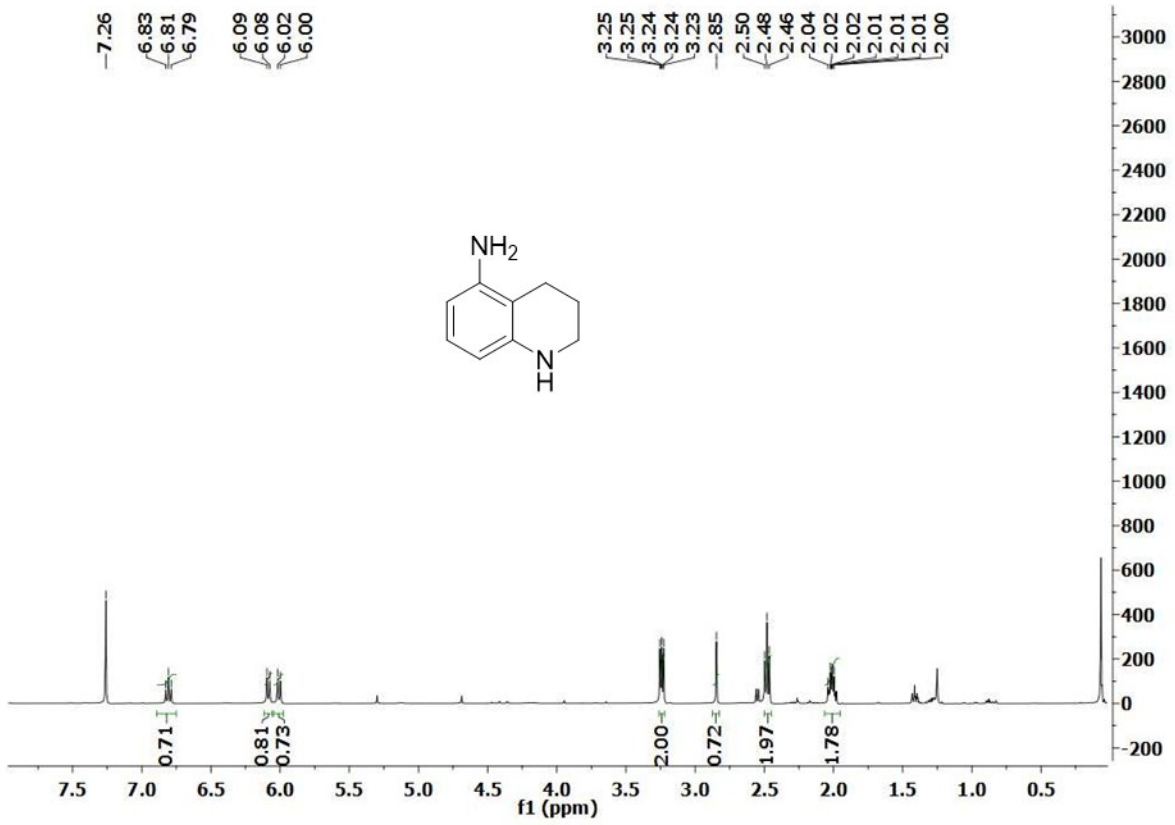


Figure S36: [1]H NMR Spectrum of **2q** ($CDCl_3$, 400 MHz, 298 K)

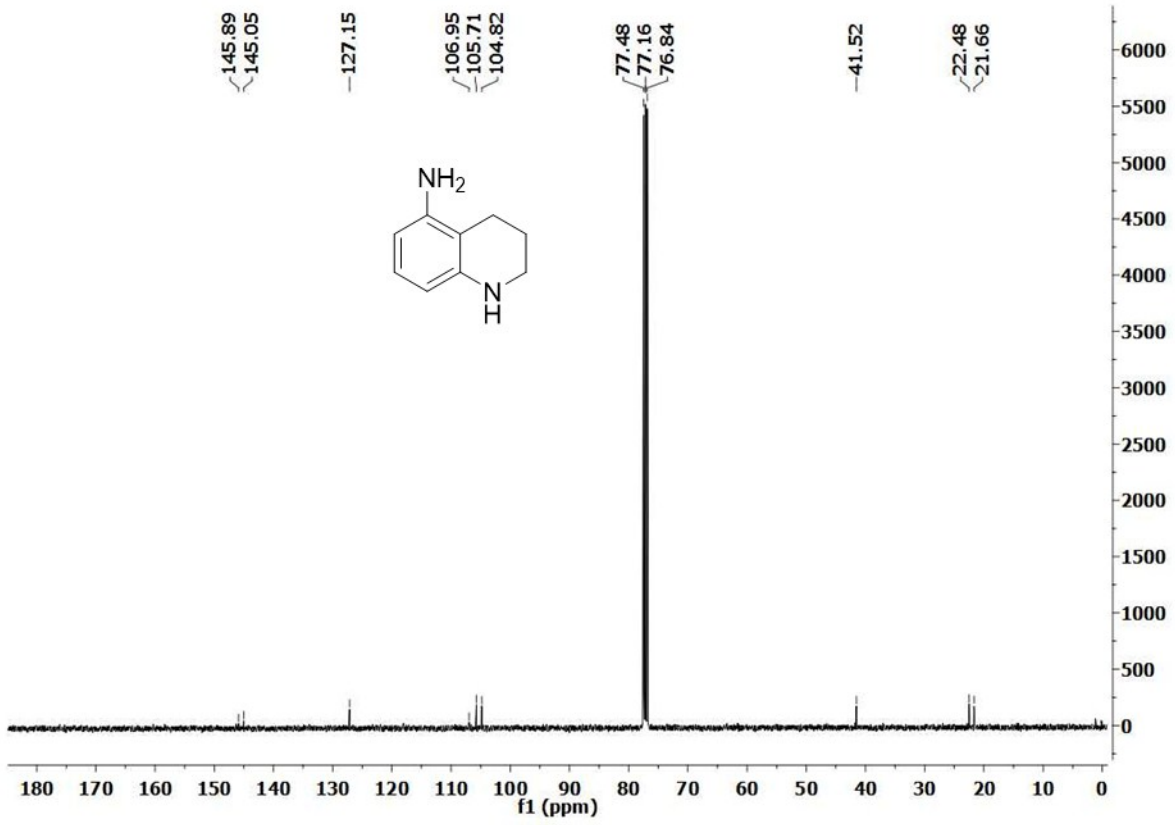


Figure S37: [13]C NMR Spectrum of **2q** ($CDCl_3$, 101 MHz, 298 K)

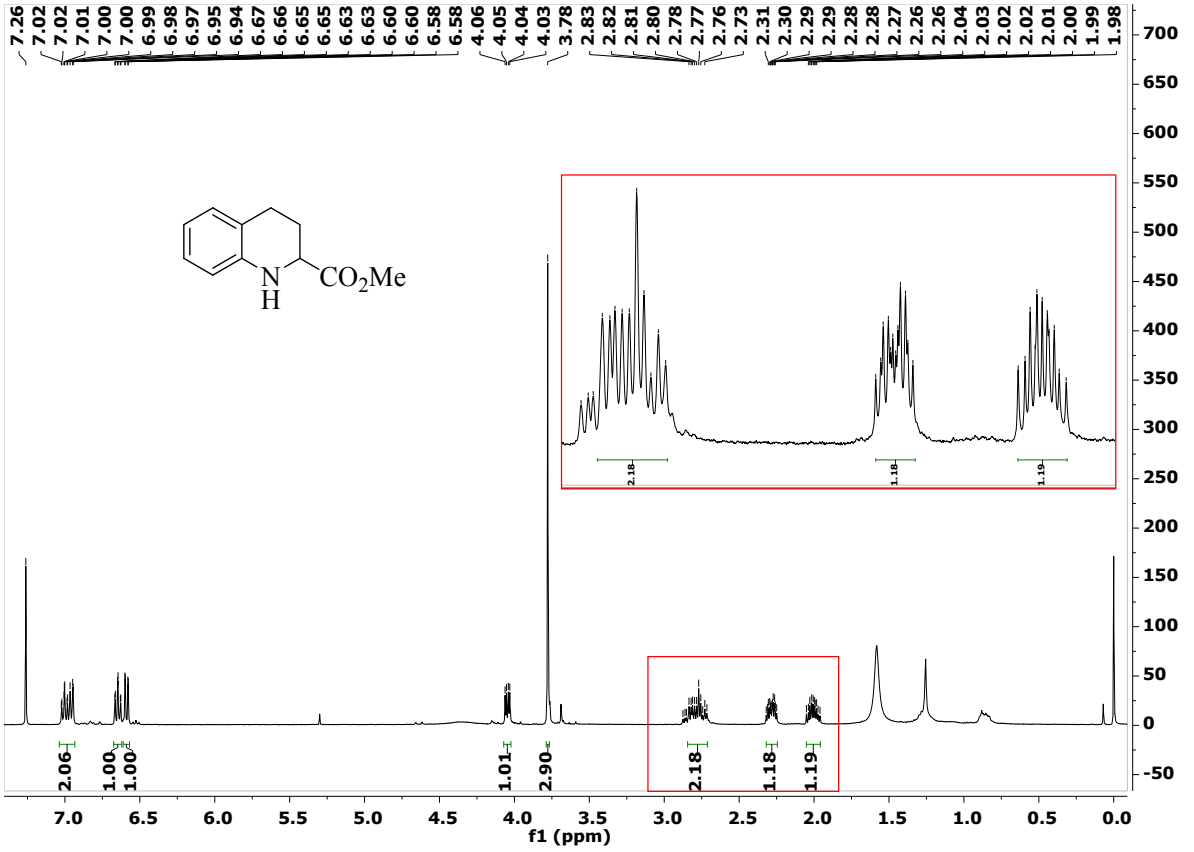


Figure S38: ^{1}H NMR Spectrum of **3a** ($CDCl_3$, 400 MHz, 298 K)

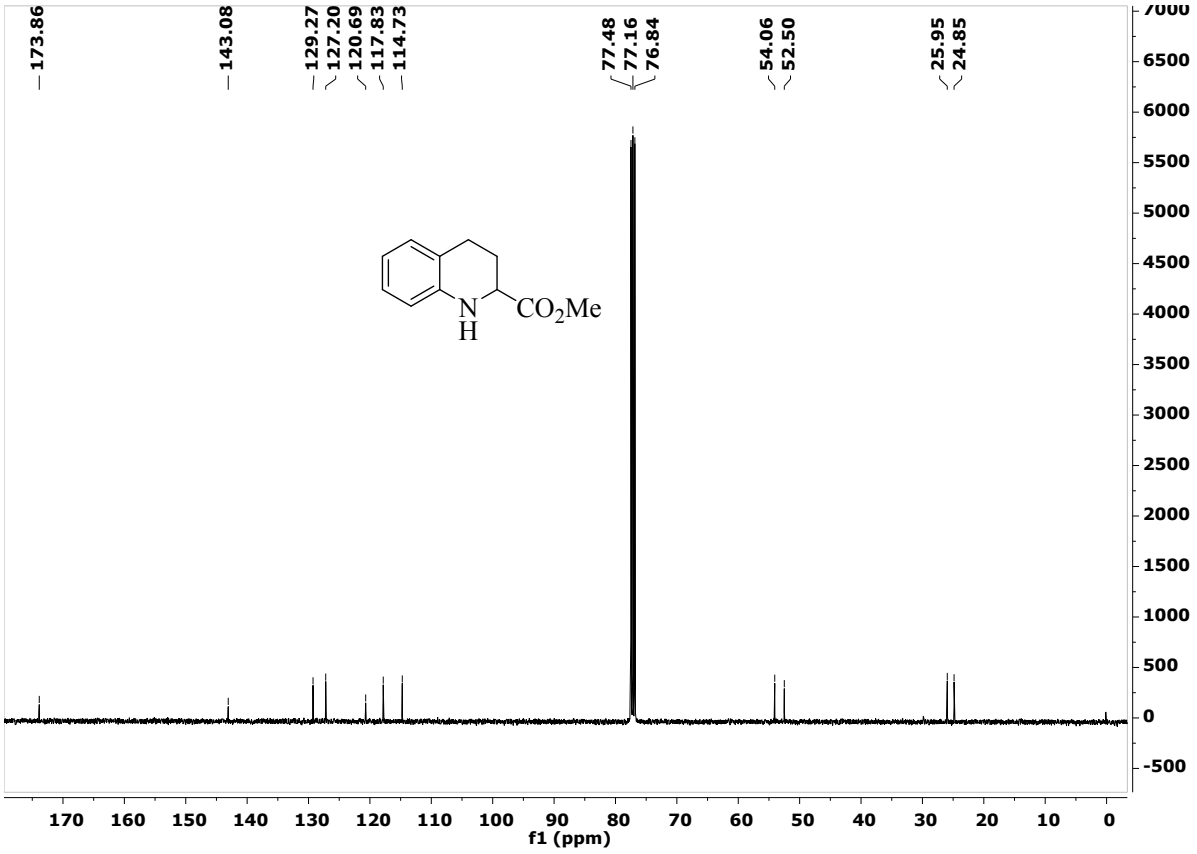


Figure S39: ^{13}C NMR Spectrum of **3a** ($CDCl_3$, 101 MHz, 298 K)

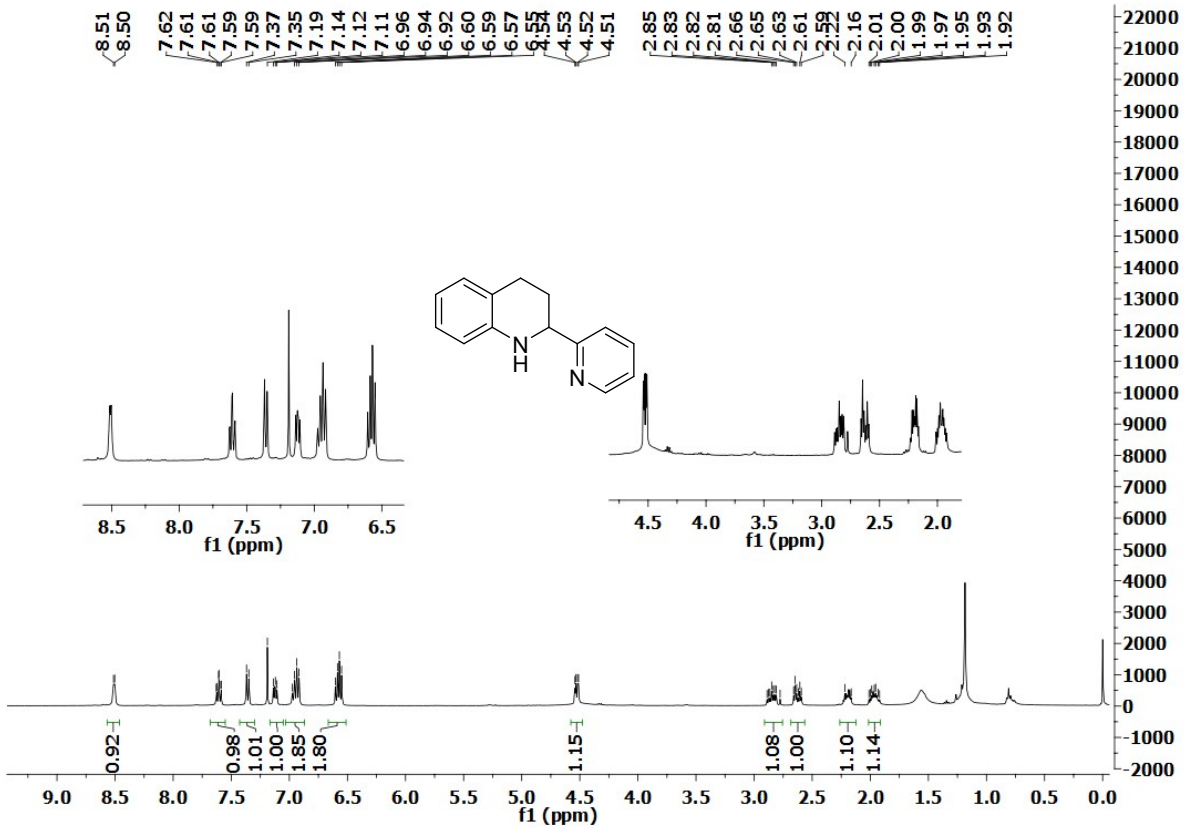


Figure S40: ^{1}H NMR Spectrum of **3b** ($CDCl_3$, 400 MHz, 298 K)

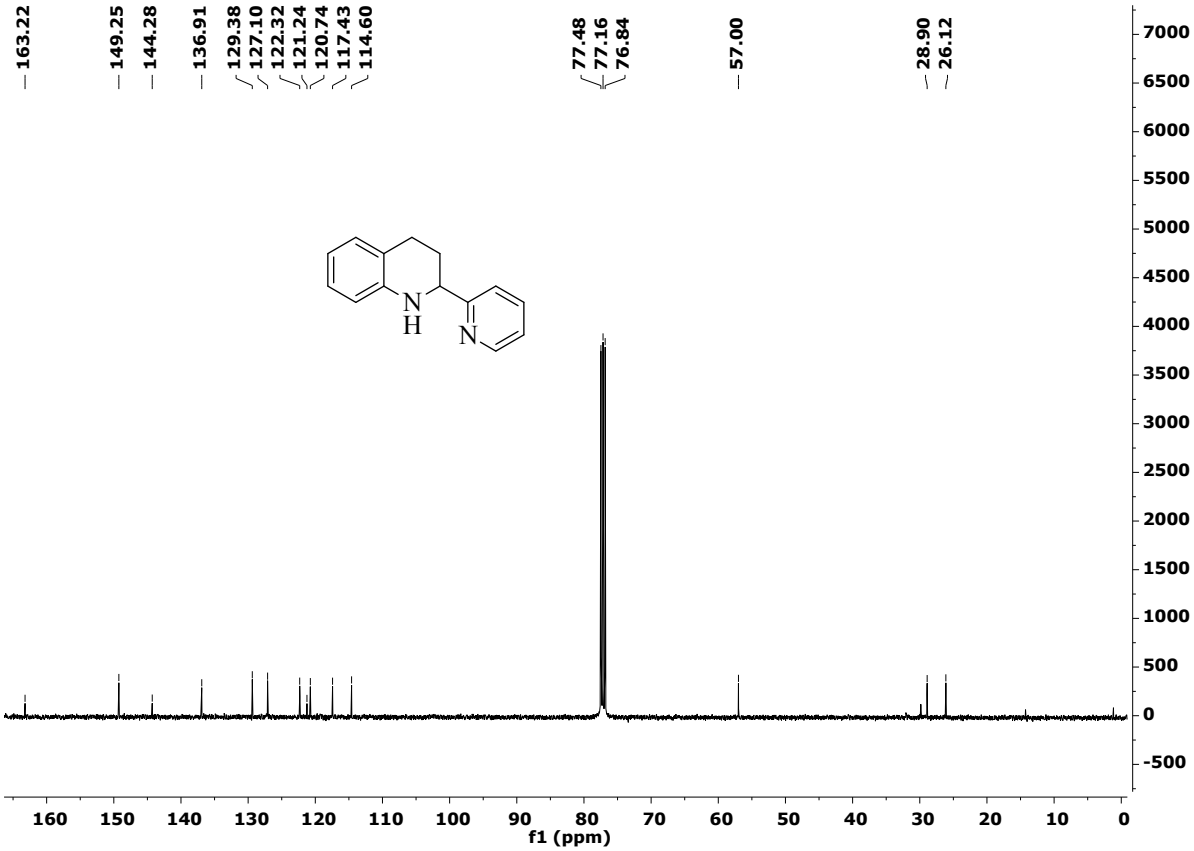


Figure S41: ^{13}C NMR Spectrum of **3b** ($CDCl_3$, 101 MHz, 298 K)

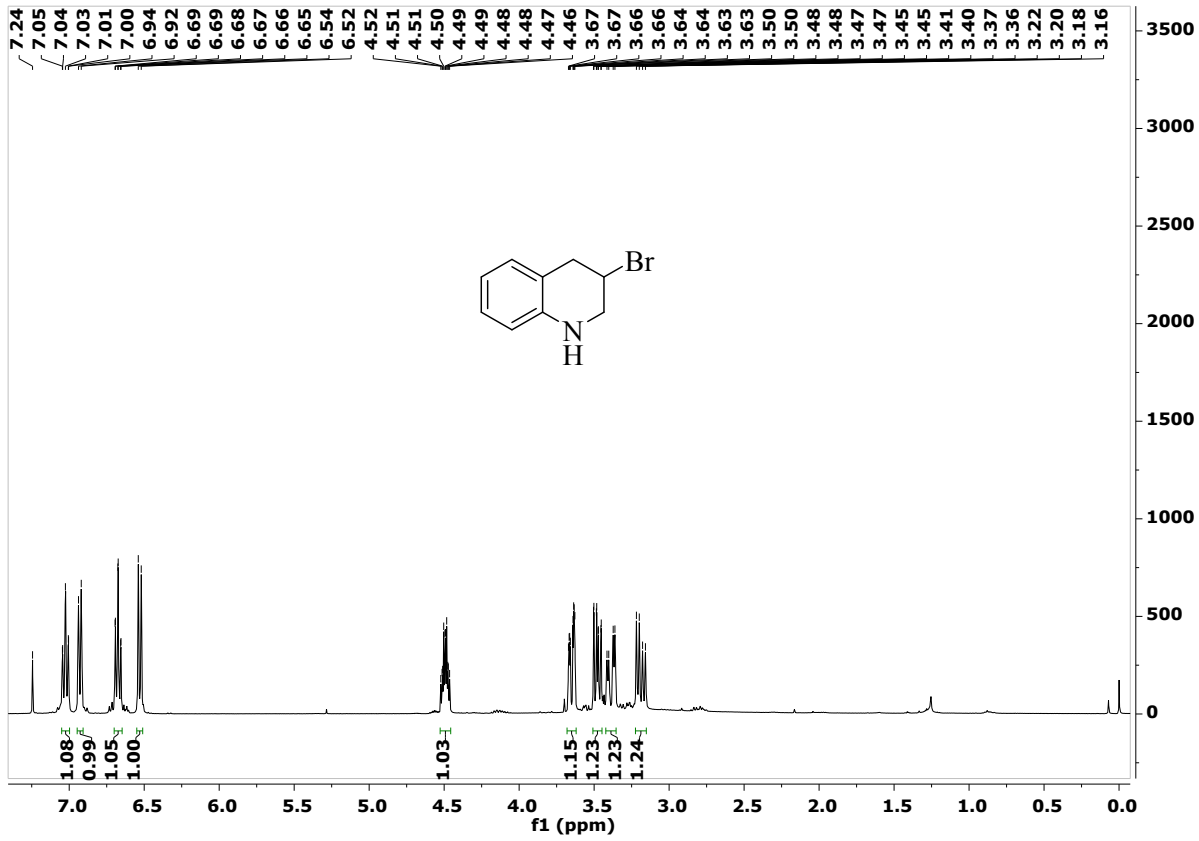


Figure S42: ^{1}H NMR Spectrum of **3c** ($CDCl_3$, 400 MHz, 298 K)

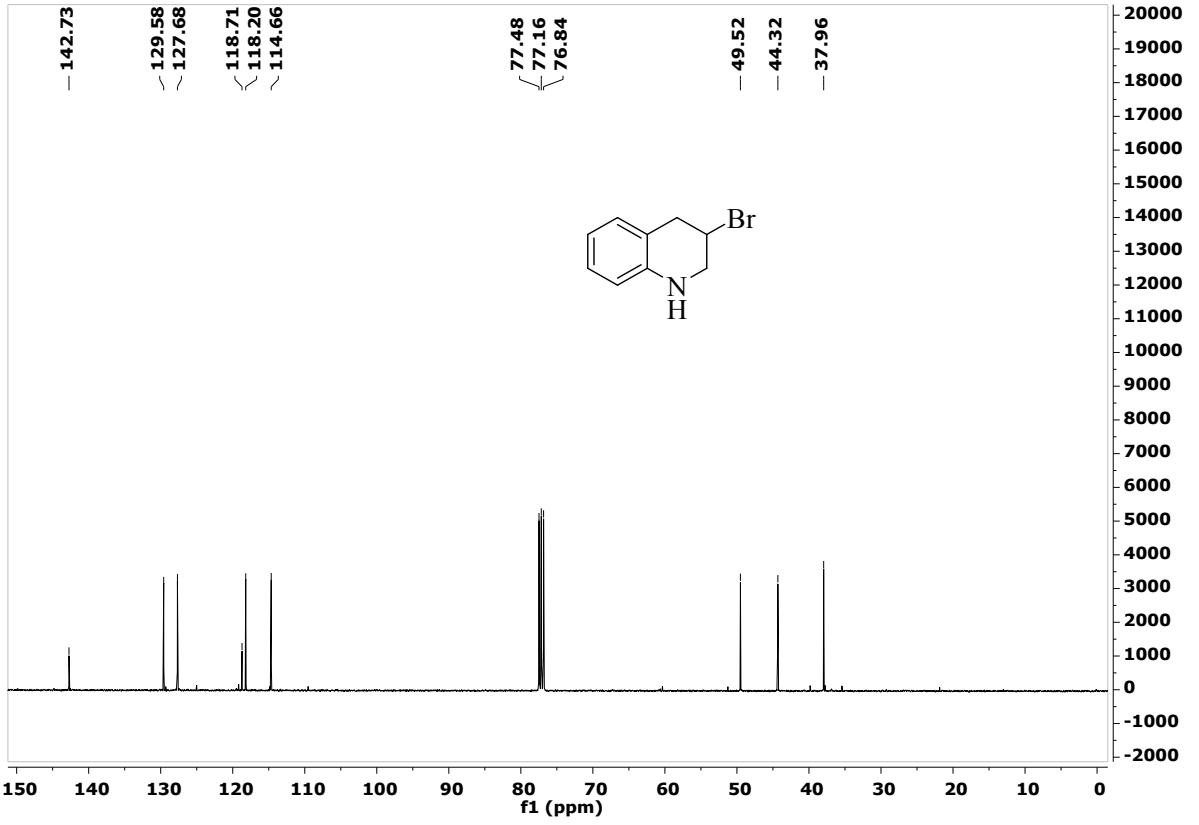


Figure S43: ^{13}C NMR Spectrum of **3c** ($CDCl_3$, 101 MHz, 298 K)

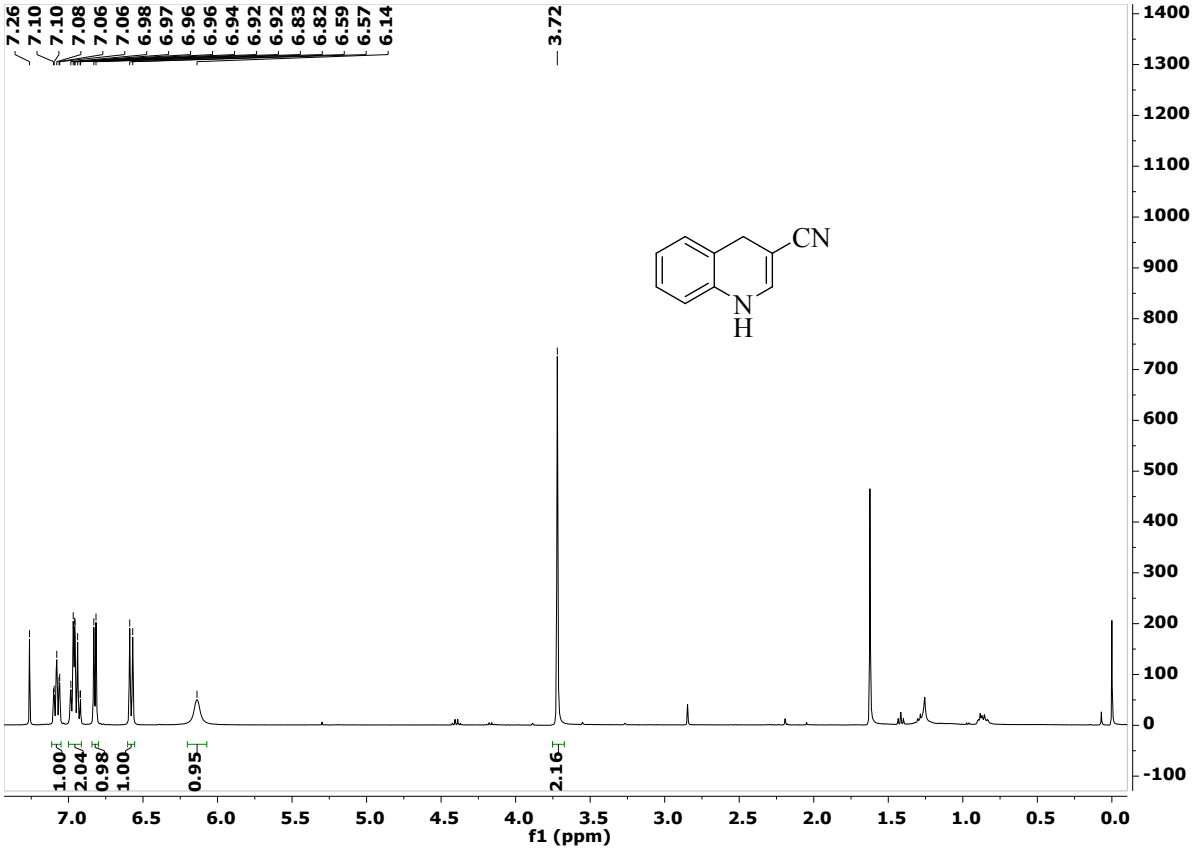


Figure S44: ^{1}H NMR Spectrum of **3d** ($CDCl_3$, 400 MHz, 298 K)

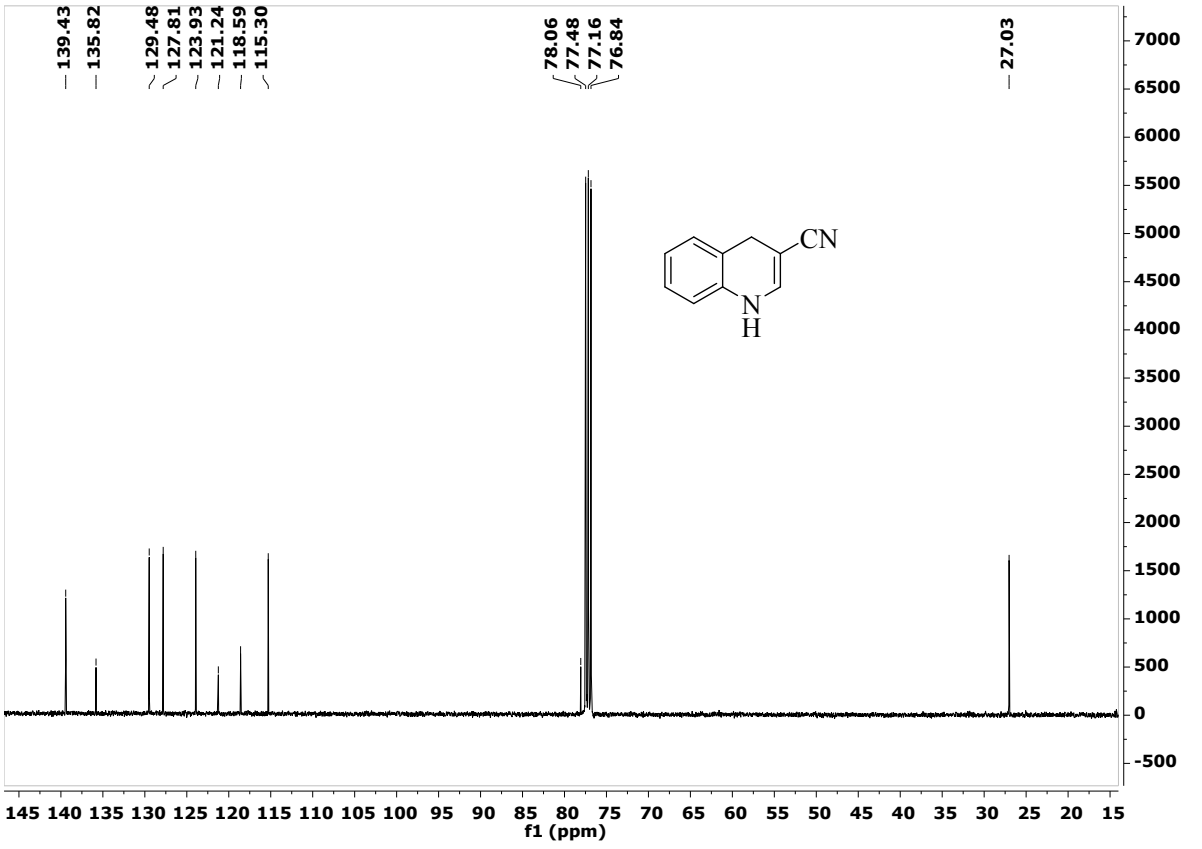


Figure S45: ^{13}C NMR Spectrum of **3d** ($CDCl_3$, 101 MHz, 298 K)

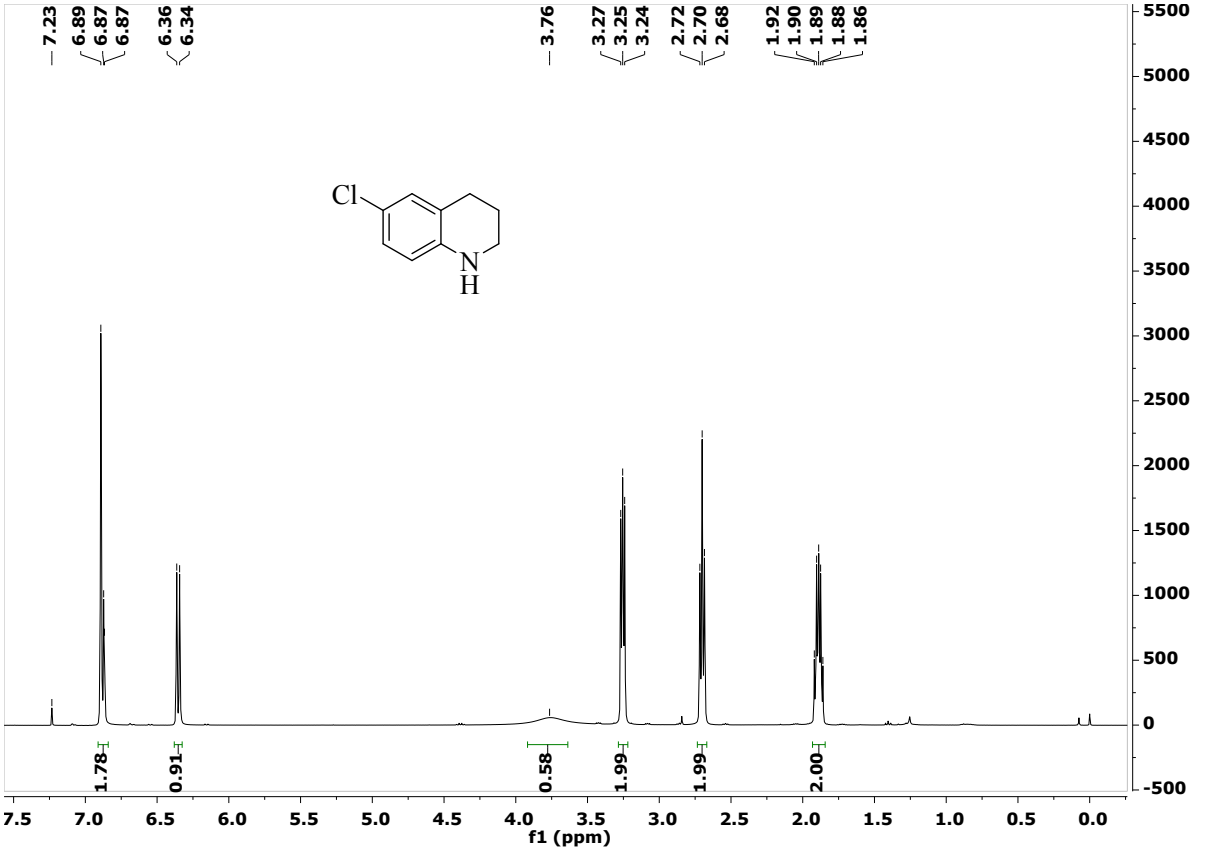


Figure S46: ^{1}H NMR Spectrum of **3e** ($CDCl_3$, 400 MHz, 298 K)

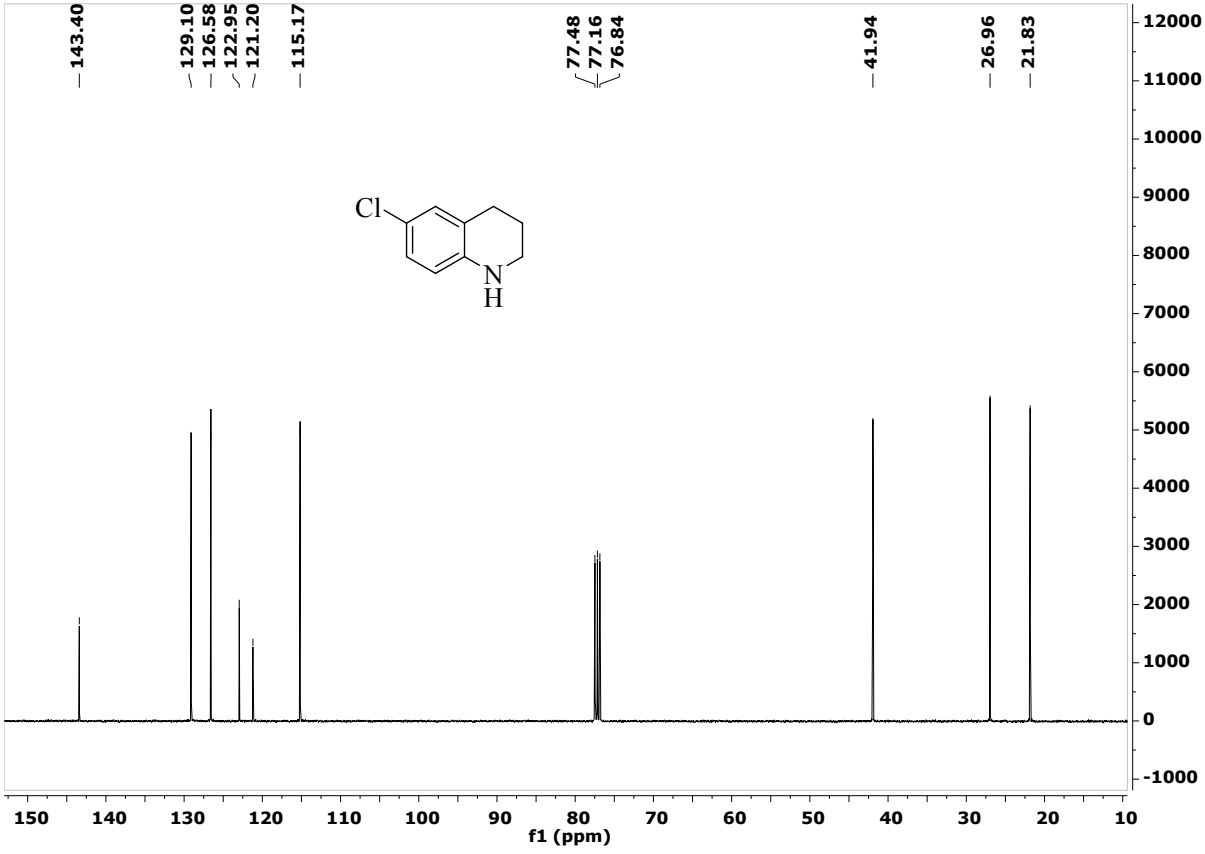


Figure S47: ^{13}C NMR Spectrum of **3e** ($CDCl_3$, 101 MHz, 298 K)

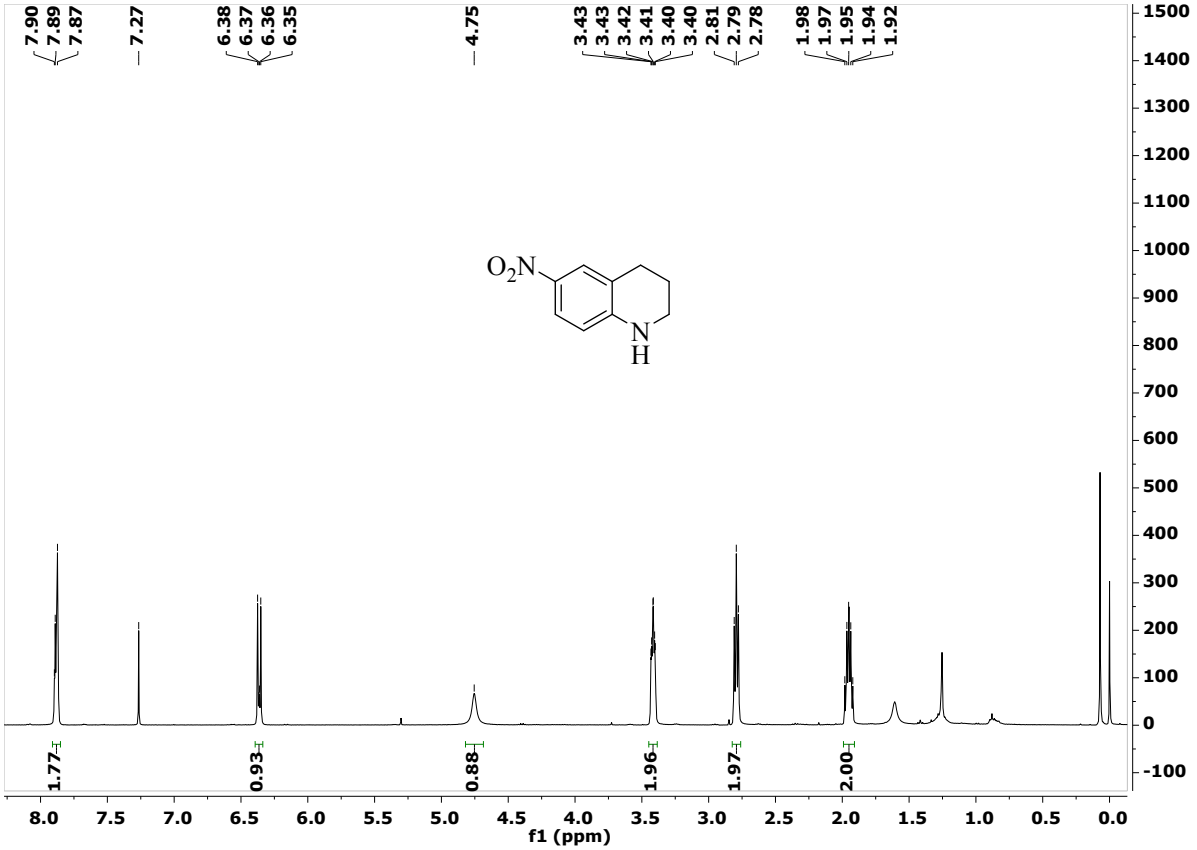


Figure S48: ^{1}H NMR Spectrum of **3f** ($CDCl_3$, 400 MHz, 298 K)

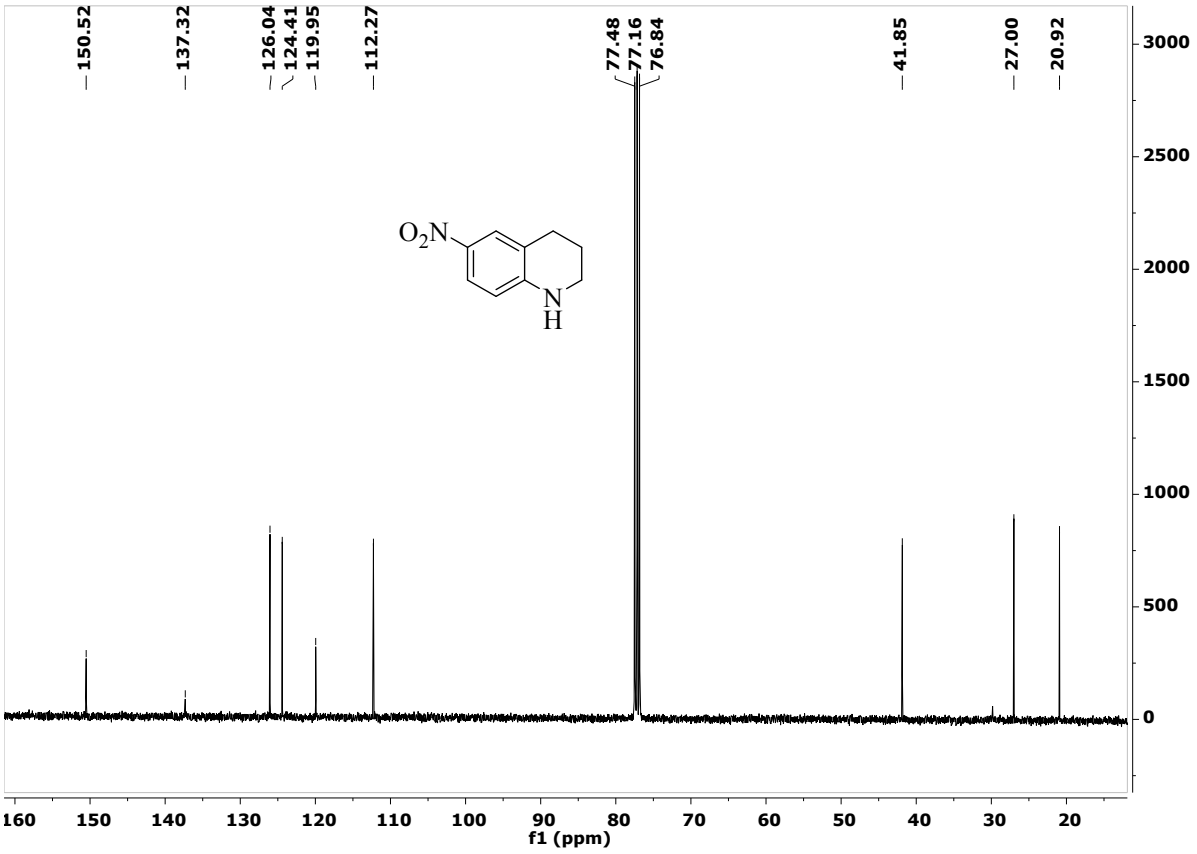


Figure S49: ^{13}C NMR Spectrum of **3f** ($CDCl_3$, 101 MHz, 298 K)

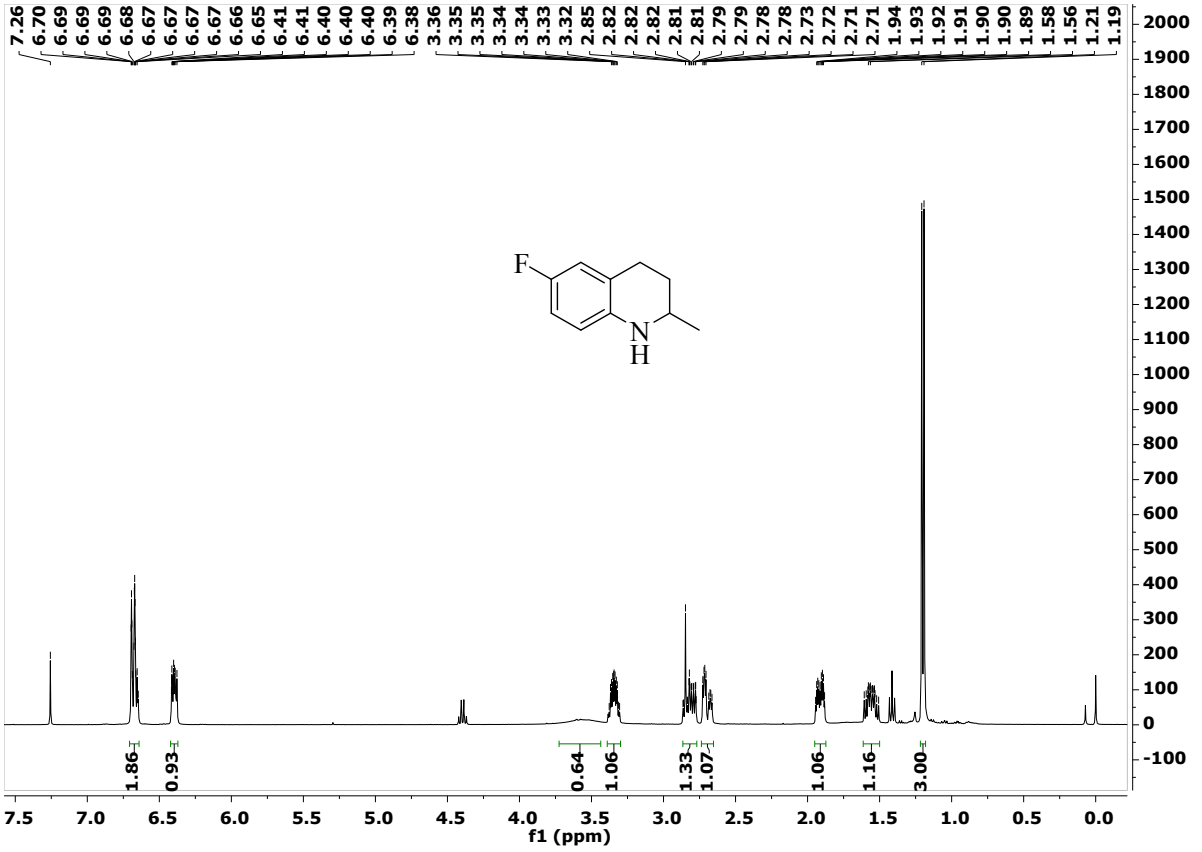


Figure S50: ^{1}H NMR Spectrum of **3g** ($CDCl_3$, 400 MHz, 298 K)

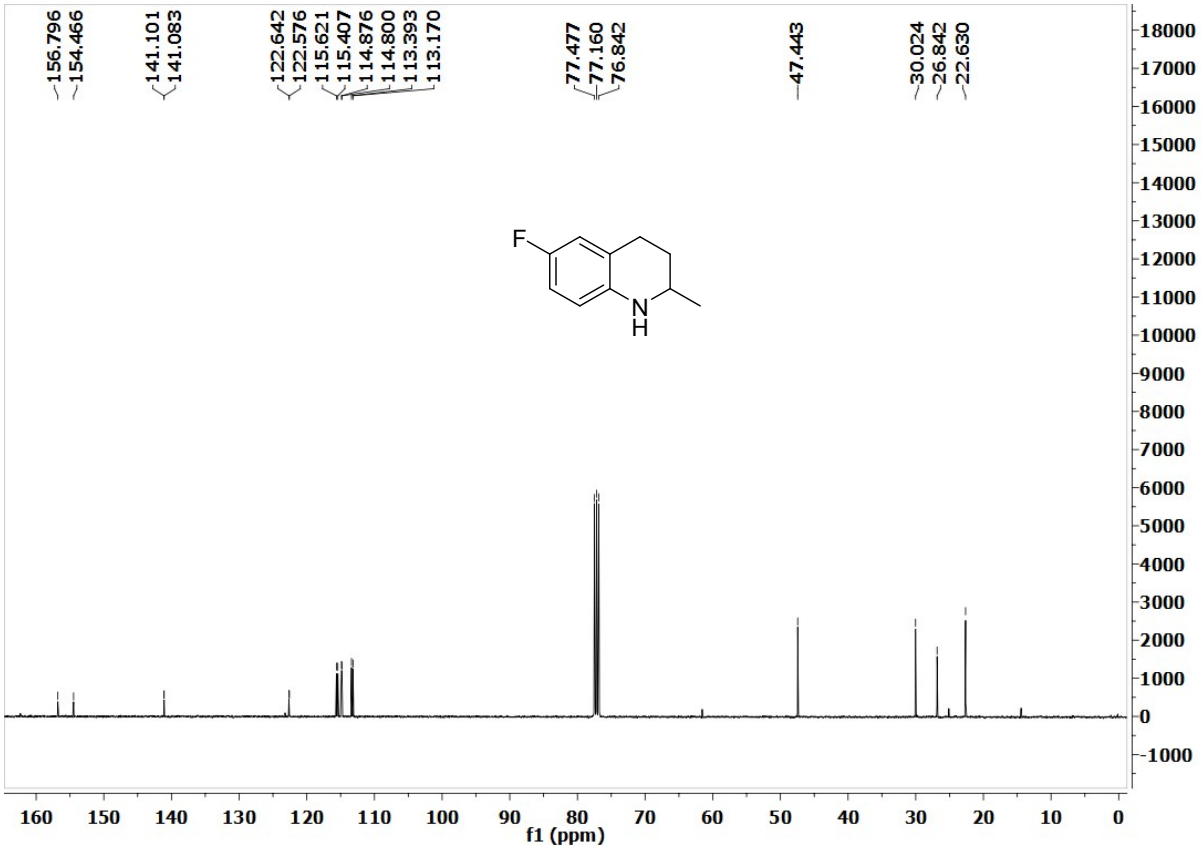


Figure S51: ^{13}C NMR Spectrum of **3g** ($CDCl_3$, 101 MHz, 298 K)

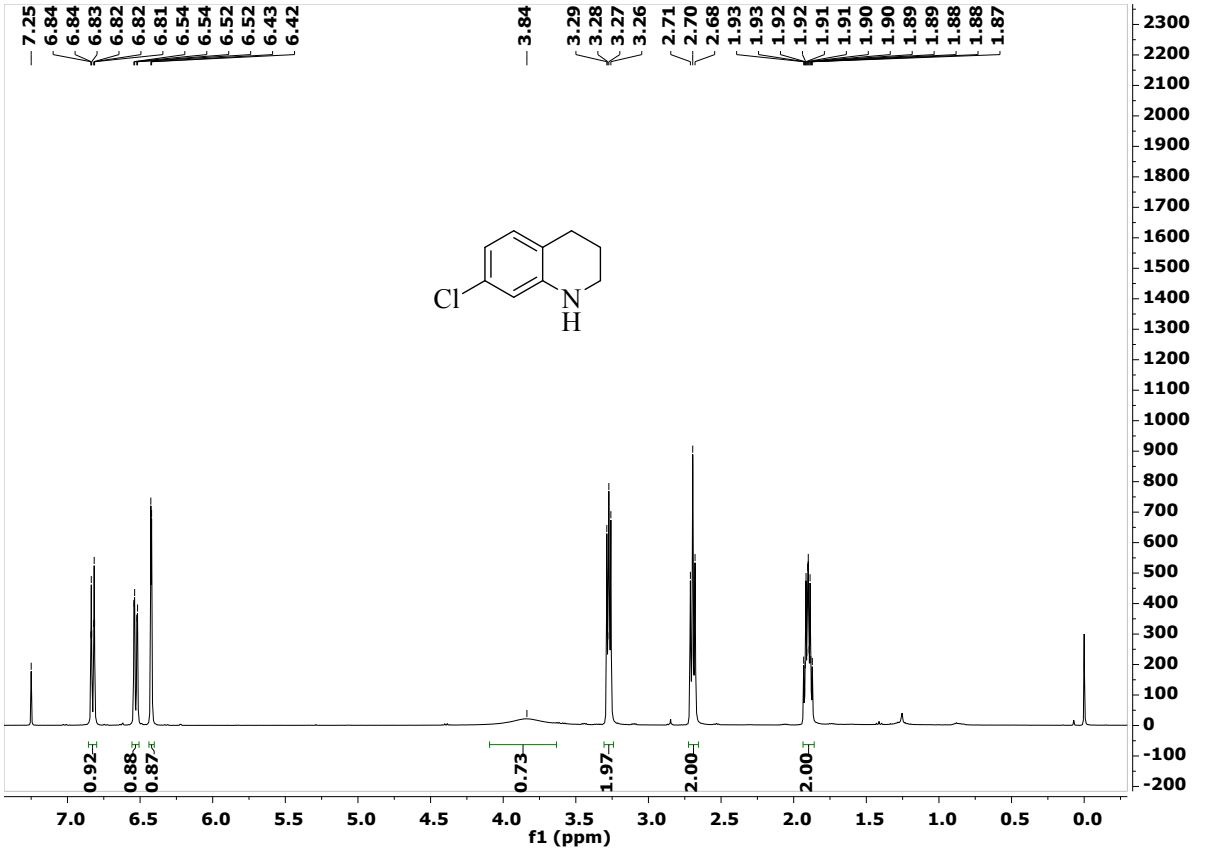


Figure S52: ^{1}H NMR Spectrum of **3h** ($CDCl_3$, 400 MHz, 298 K)

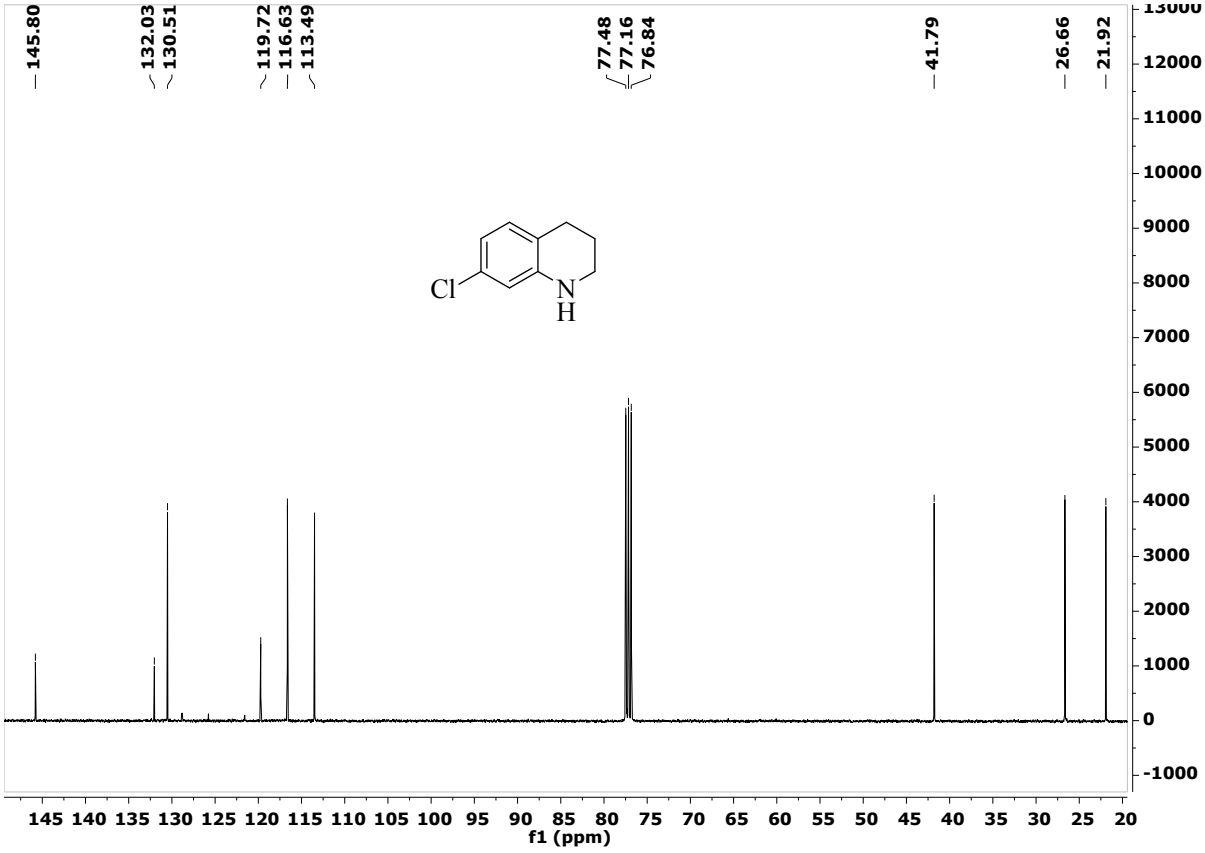


Figure S53: ^{13}C NMR Spectrum of **3h** ($CDCl_3$, 101 MHz, 298 K)

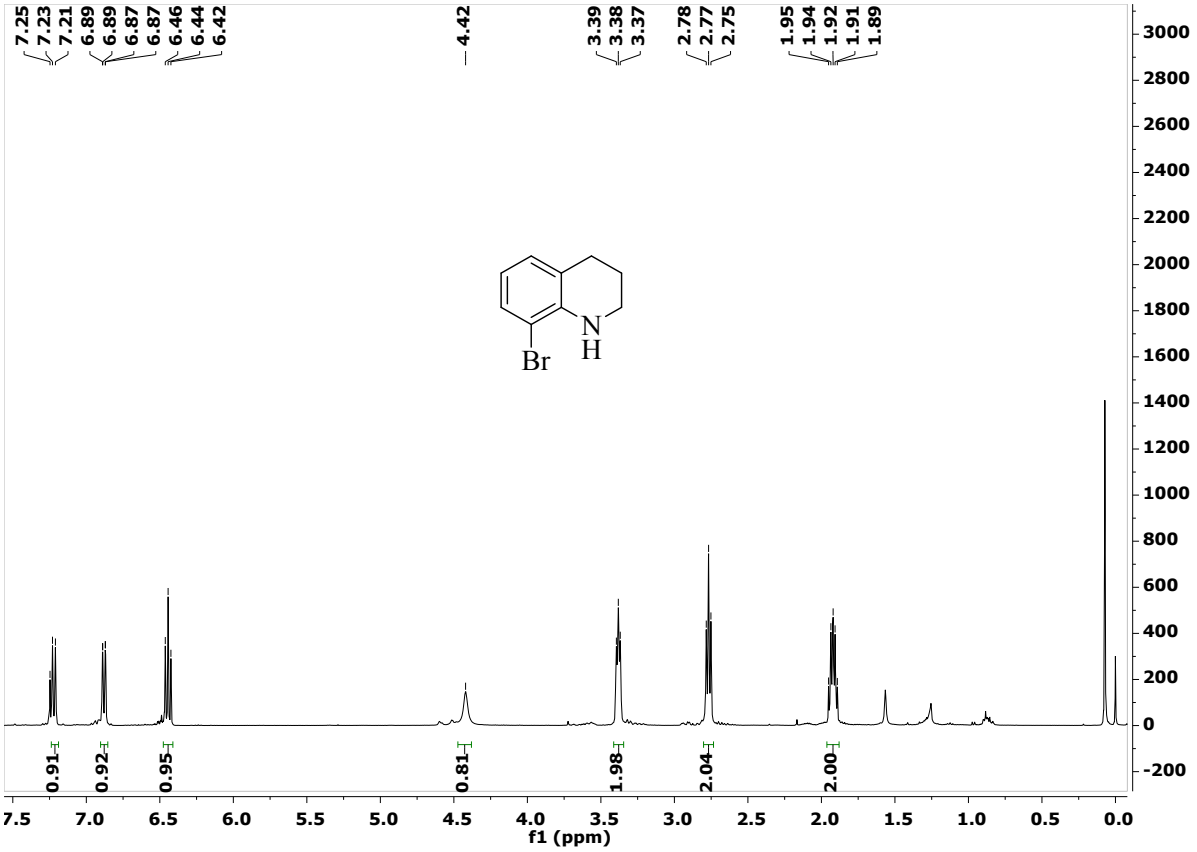


Figure S54: ^{1}H NMR Spectrum of **3i** ($CDCl_3$, 400 MHz, 298 K)

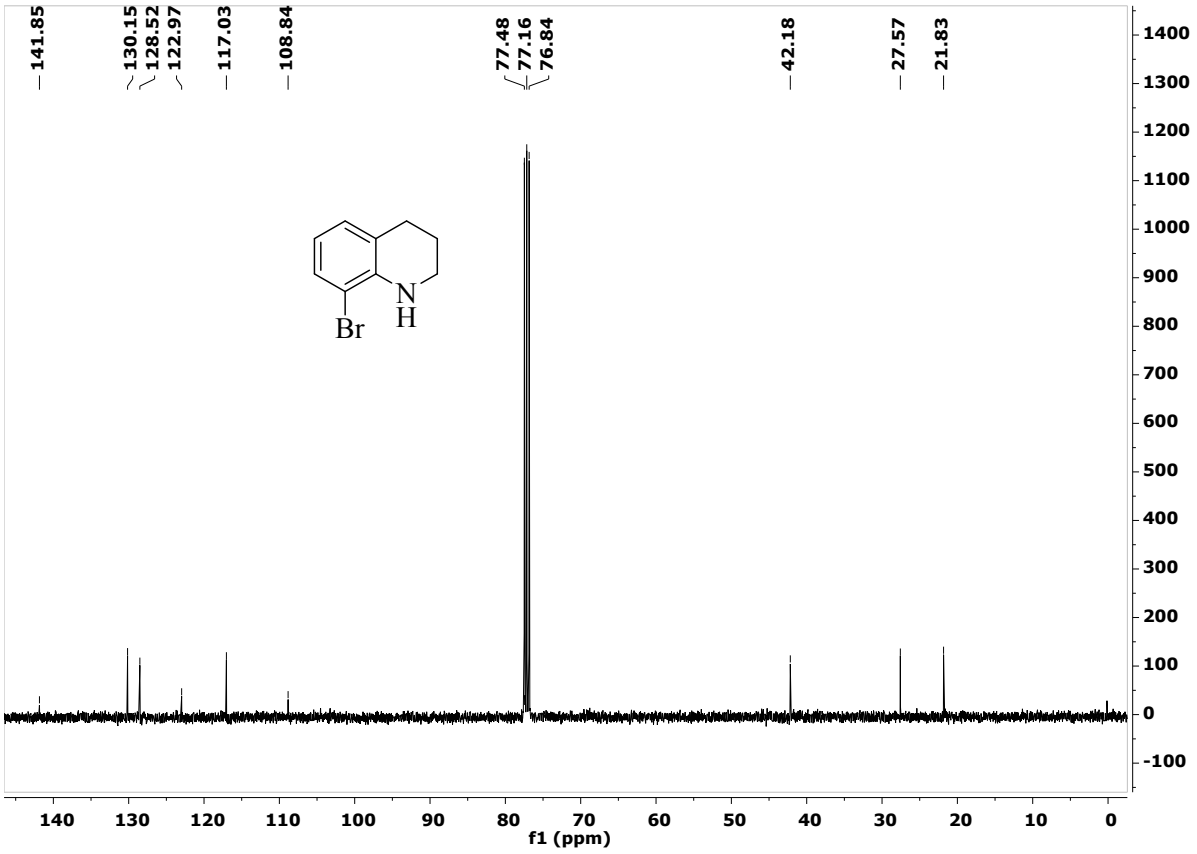


Figure S55: ^{13}C NMR Spectrum of **3i** ($CDCl_3$, 101 MHz, 298 K)

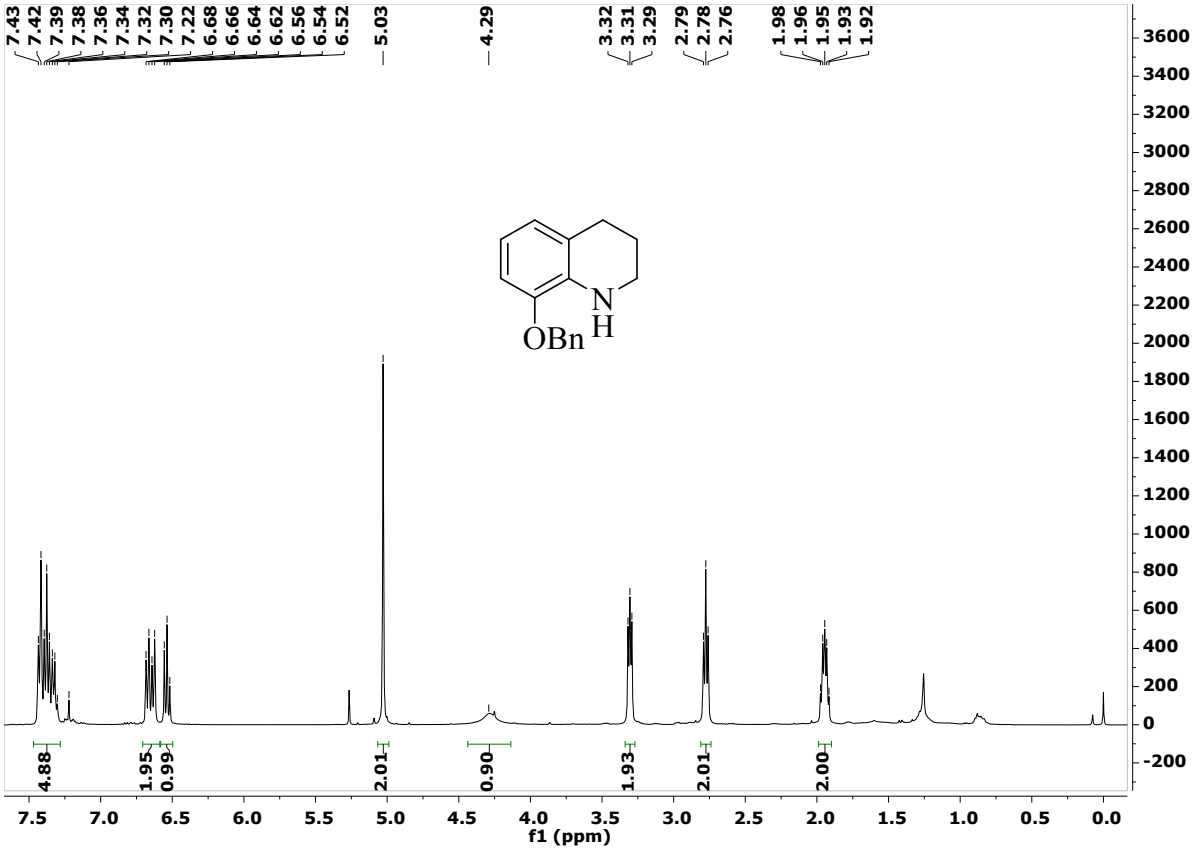


Figure S56: ^{1}H NMR Spectrum of **3j** ($CDCl_3$, 400 MHz, 298 K)

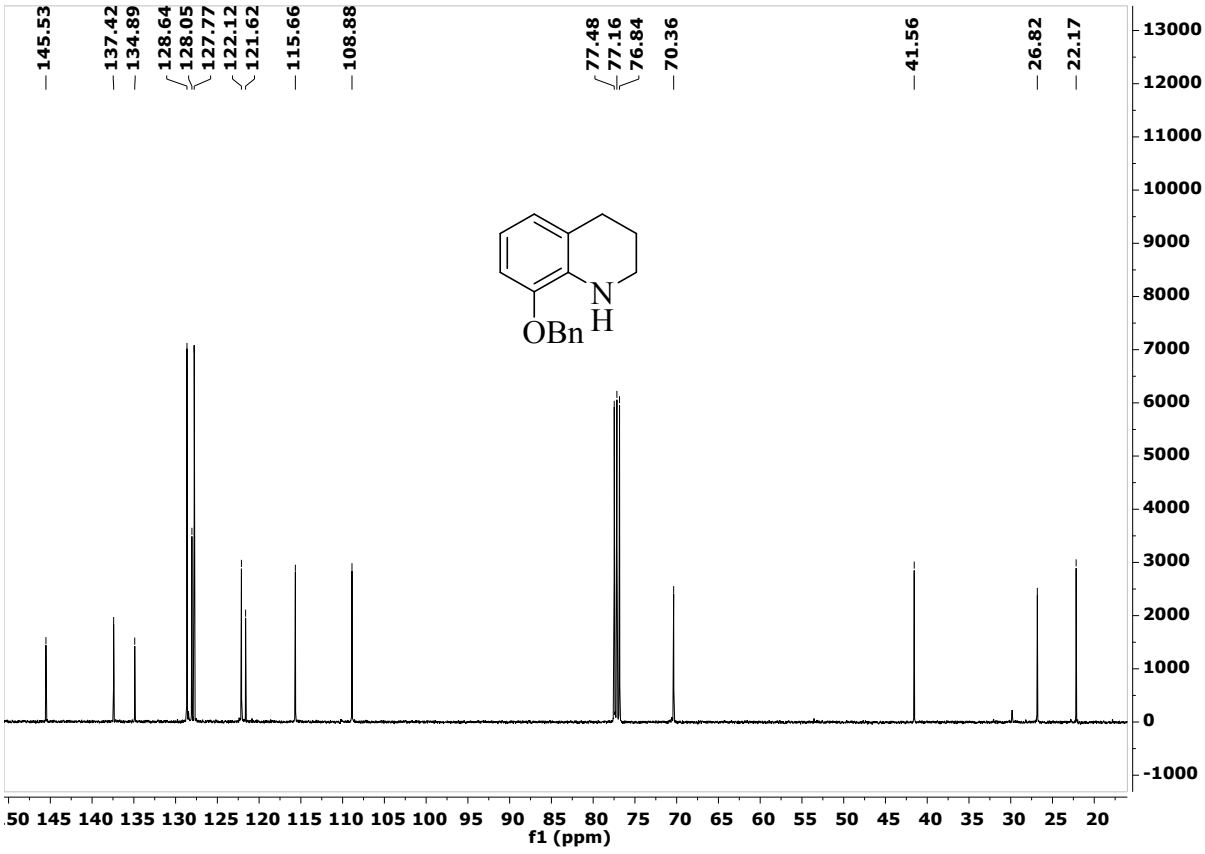


Figure S57: ^{13}C NMR Spectrum of **3j** ($CDCl_3$, 101 MHz, 298 K)

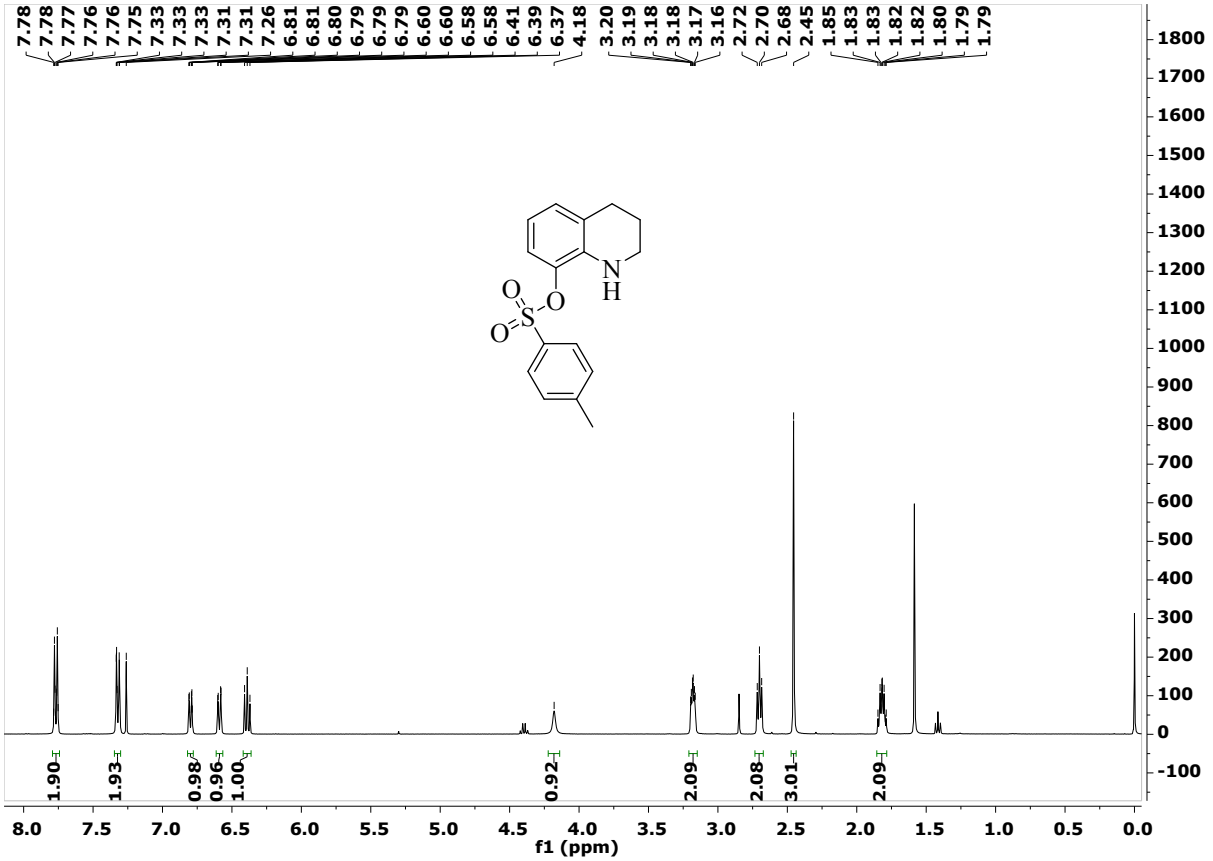


Figure S58: ^{1}H NMR Spectrum of **3k** ($CDCl_3$, 400 MHz, 298 K)

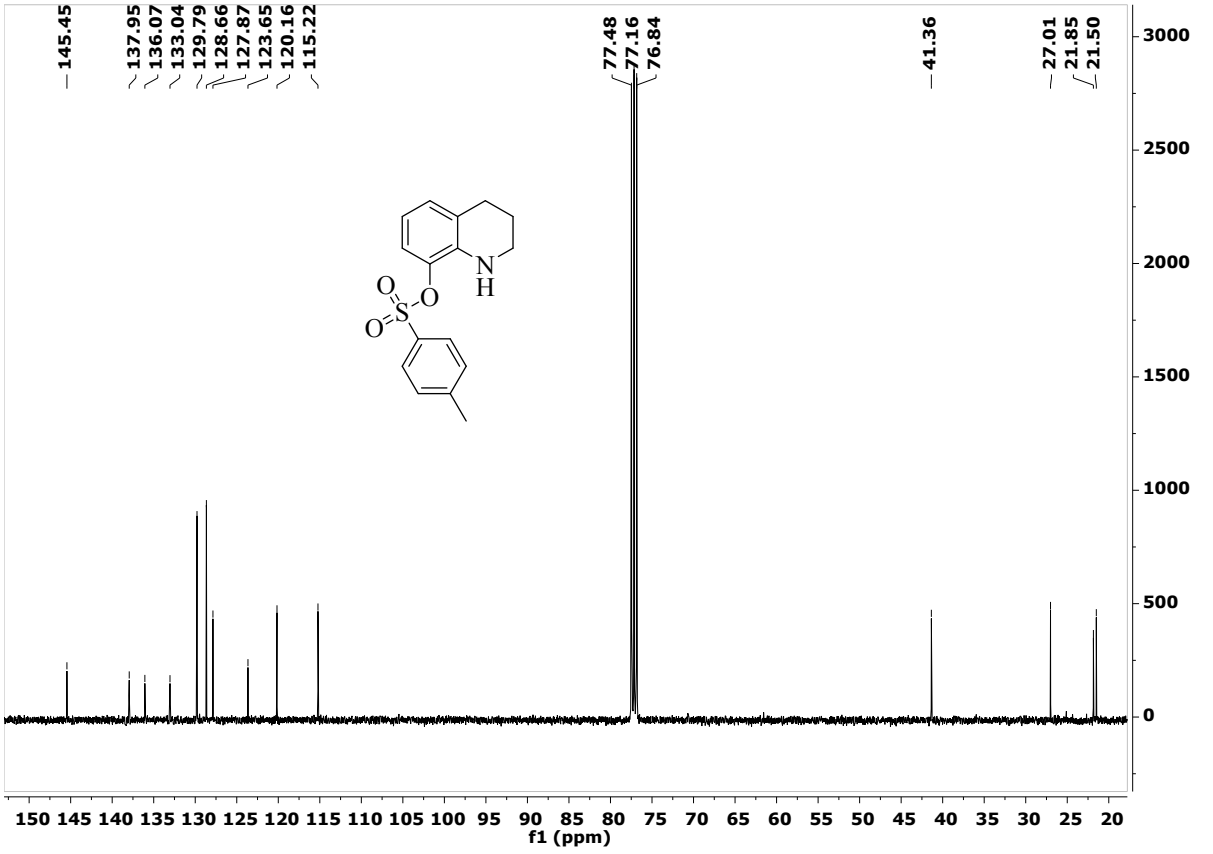


Figure S59: ^{13}C NMR Spectrum of **3k** ($CDCl_3$, 101 MHz, 298 K)

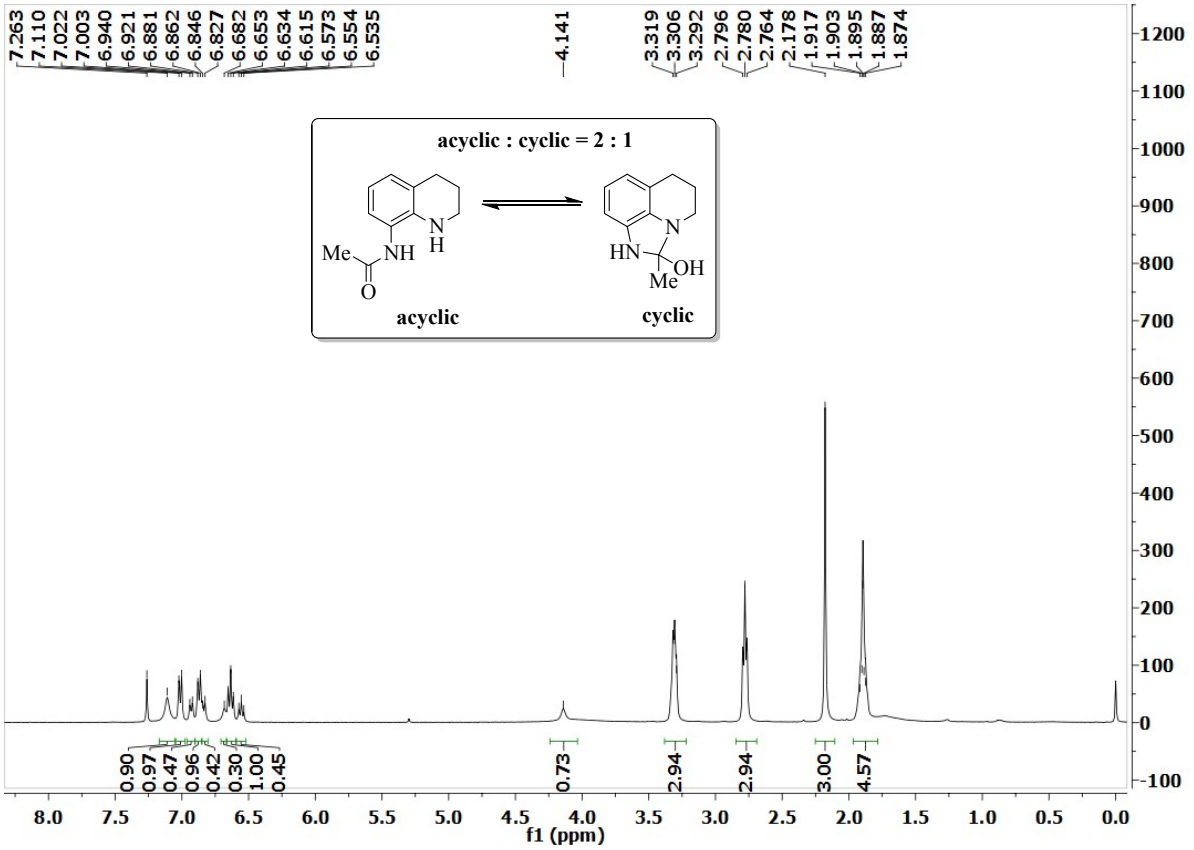


Figure S60: ^{1}H NMR Spectrum of **3l** ($CDCl_3$, 400 MHz, 298 K)

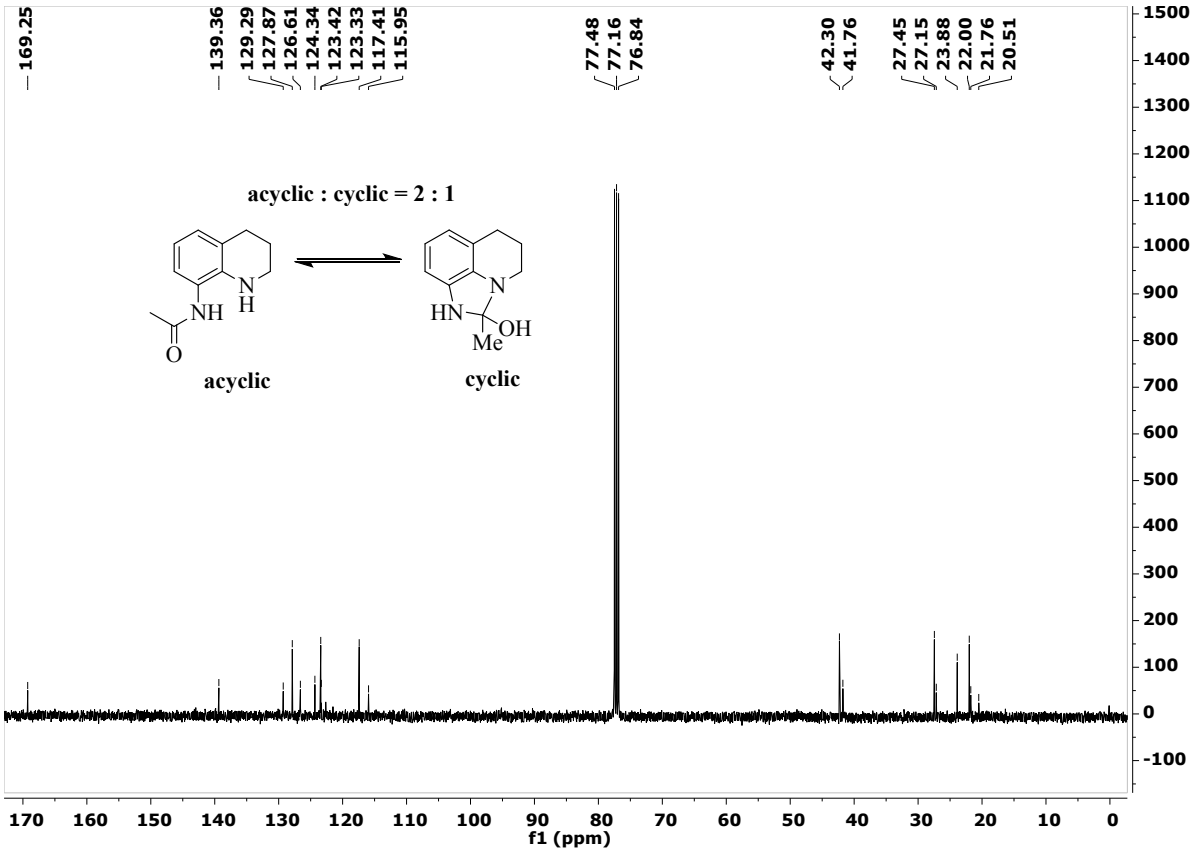


Figure S61: ^{13}C NMR Spectrum of **3l** ($CDCl_3$, 101 MHz, 298 K)

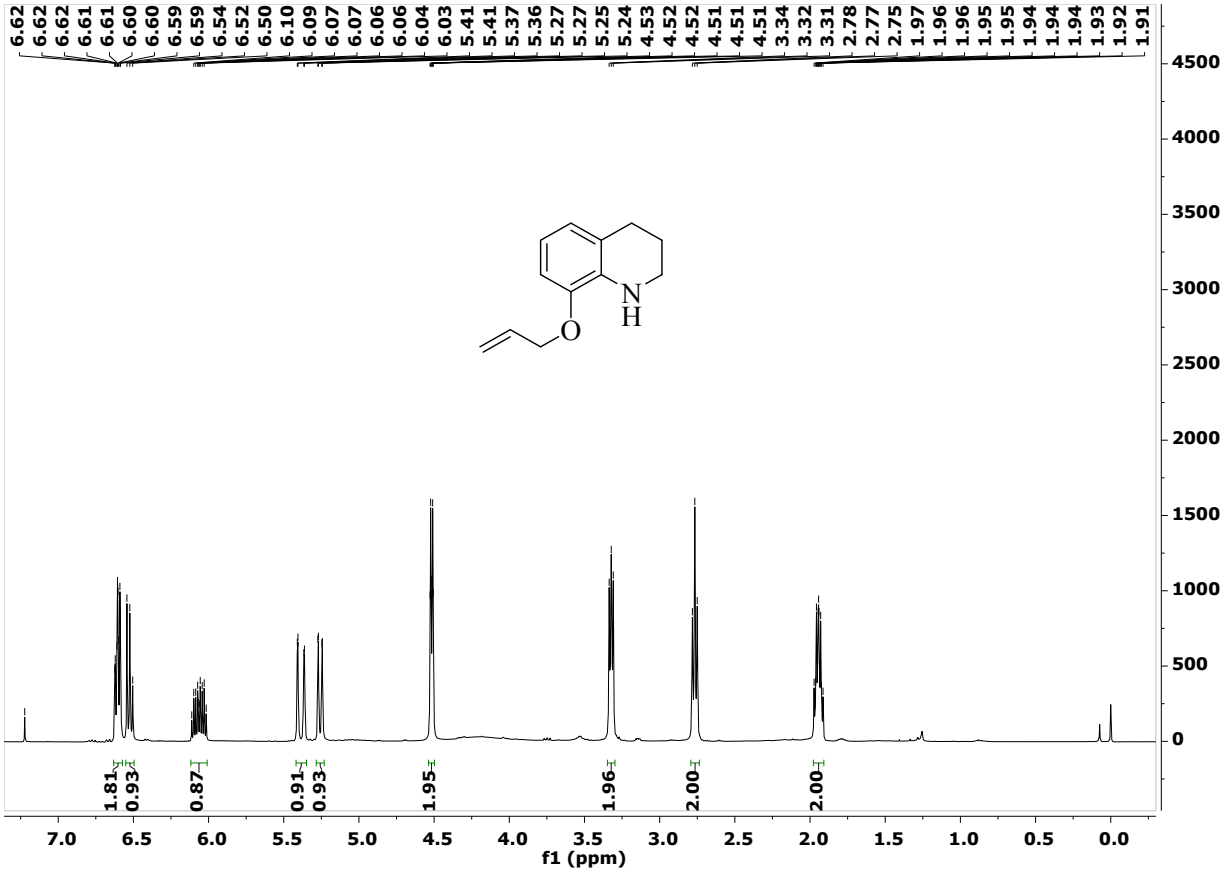


Figure S62: ^{1}H NMR Spectrum of **3m** ($CDCl_3$, 400 MHz, 298 K)

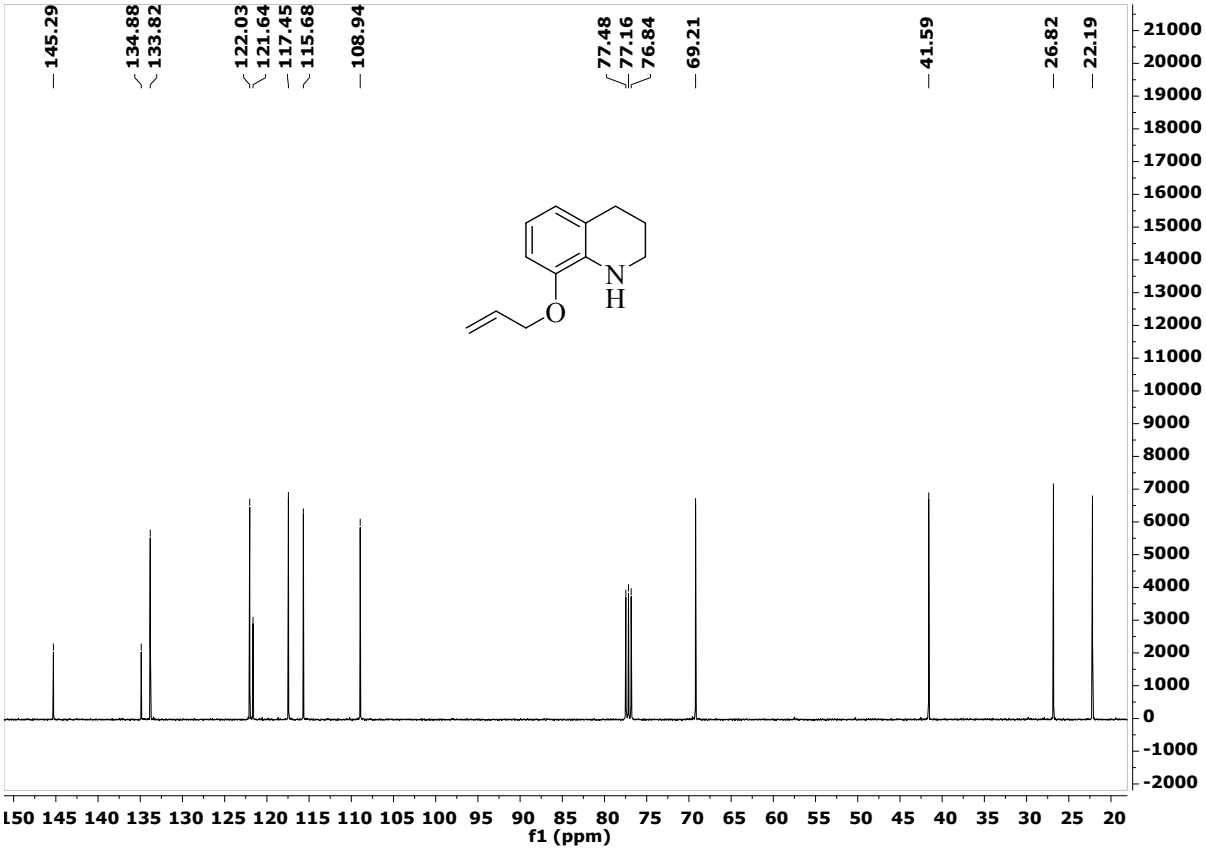


Figure S63: ^{13}C NMR Spectrum of **3m** ($CDCl_3$, 101 MHz, 298 K)

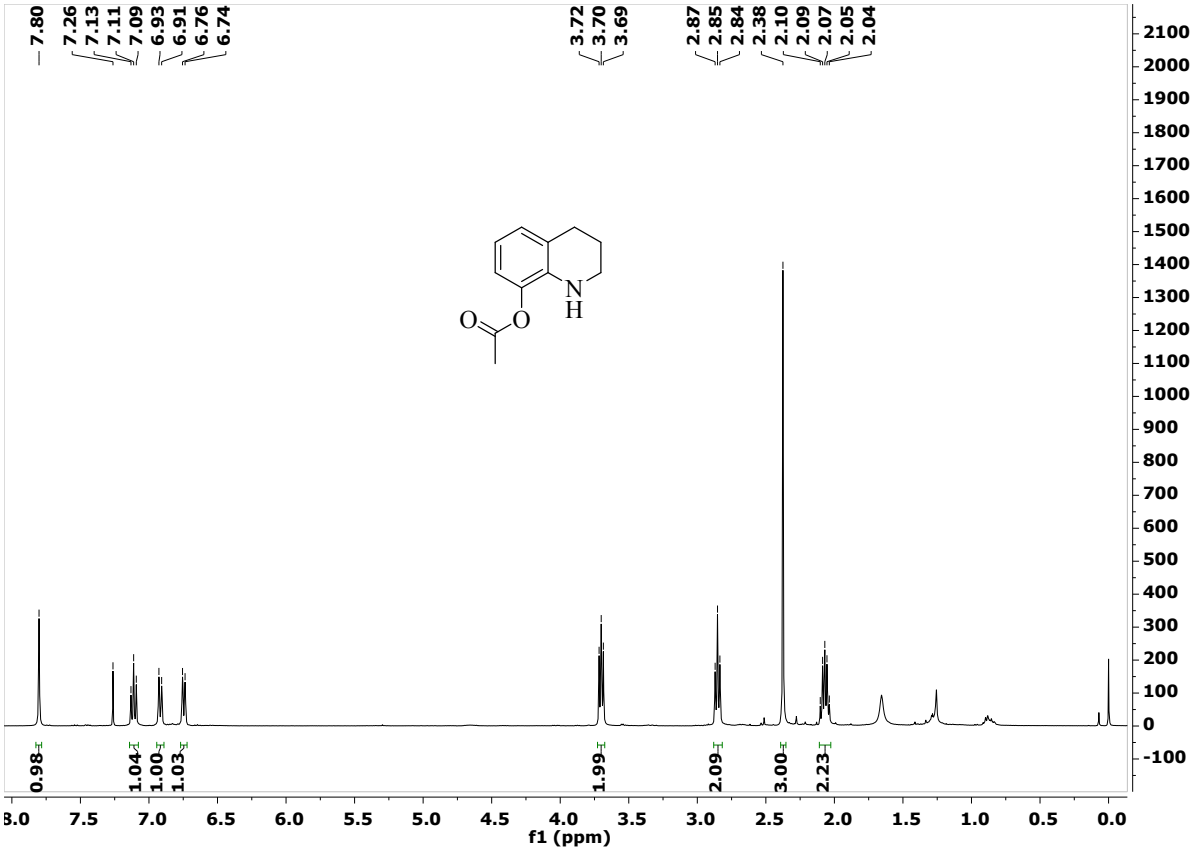


Figure S64: ^{1}H NMR Spectrum of **3n** ($CDCl_3$, 400 MHz, 298 K)

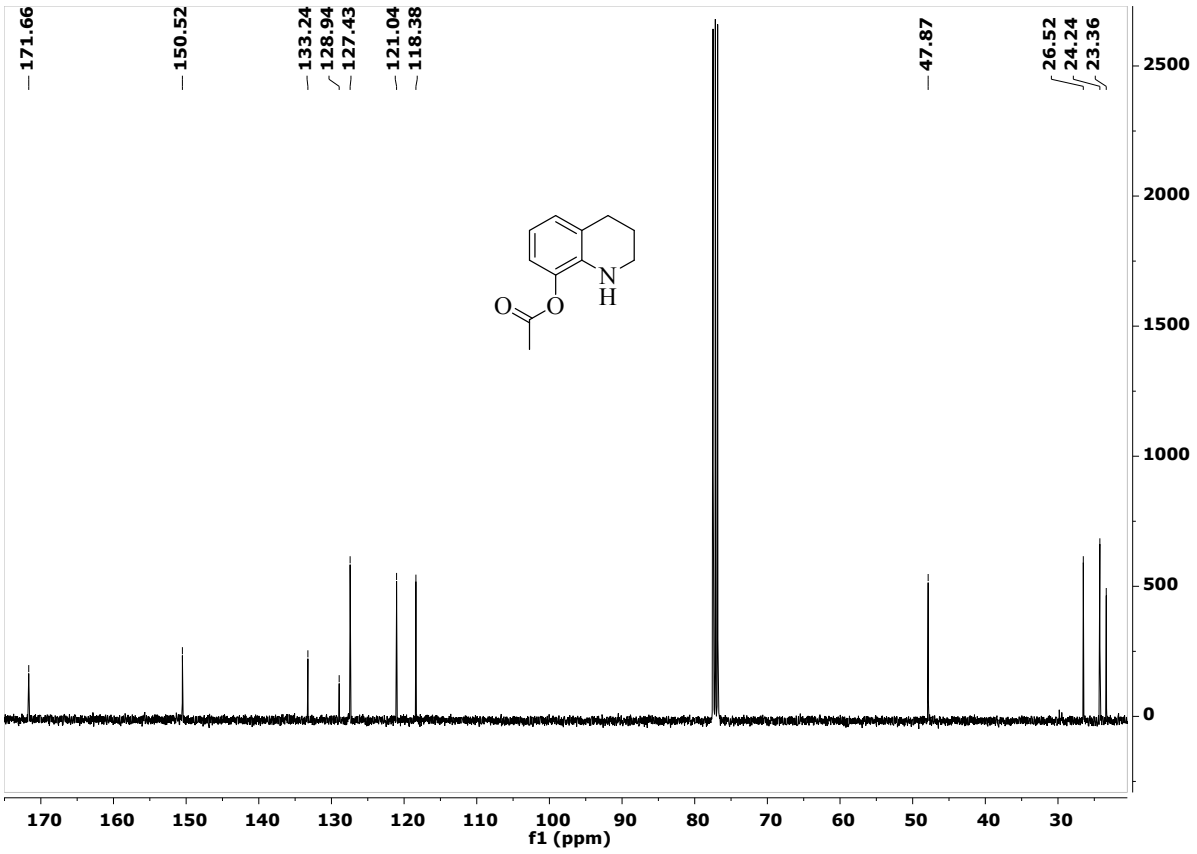


Figure S65: ^{13}C NMR Spectrum of **3n** ($CDCl_3$, 101 MHz, 298 K)

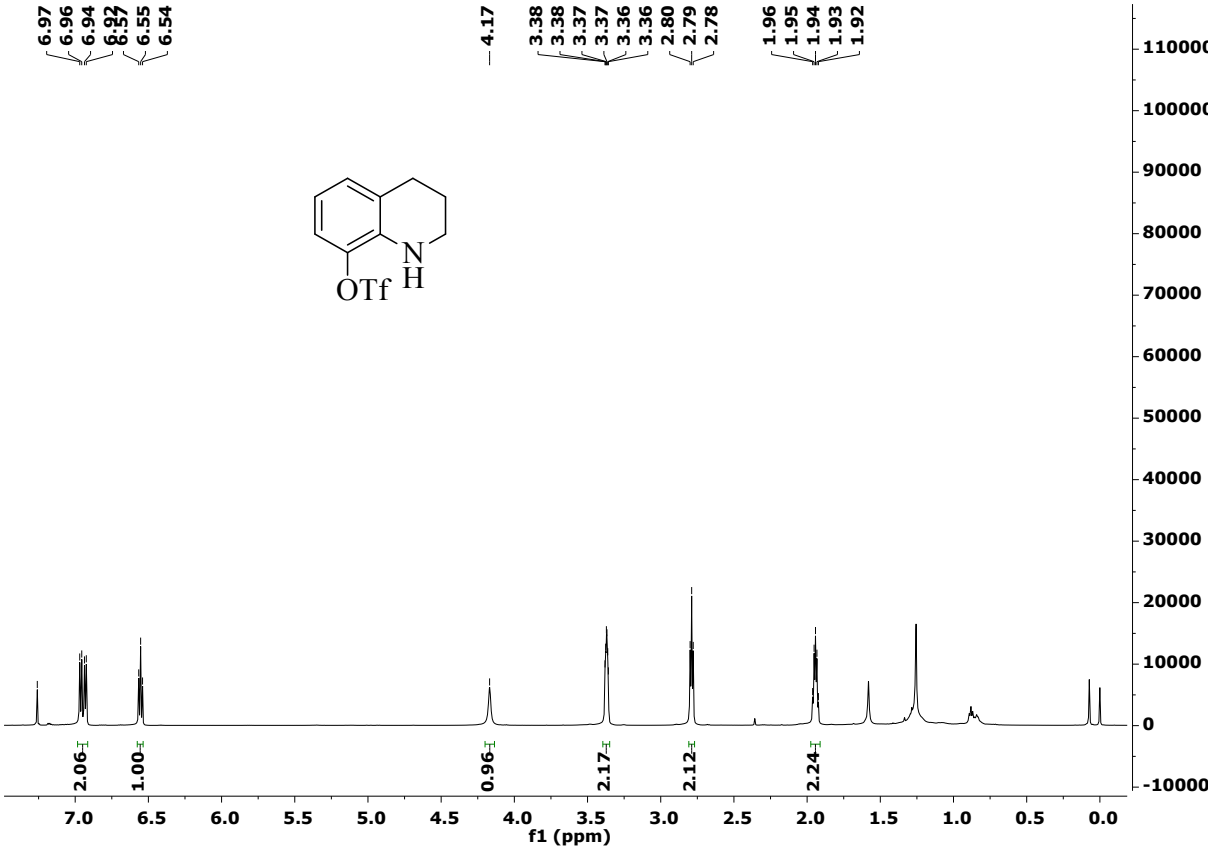


Figure S66: ^{1}H NMR Spectrum of **3o** ($CDCl_3$, 600 MHz, 298 K)

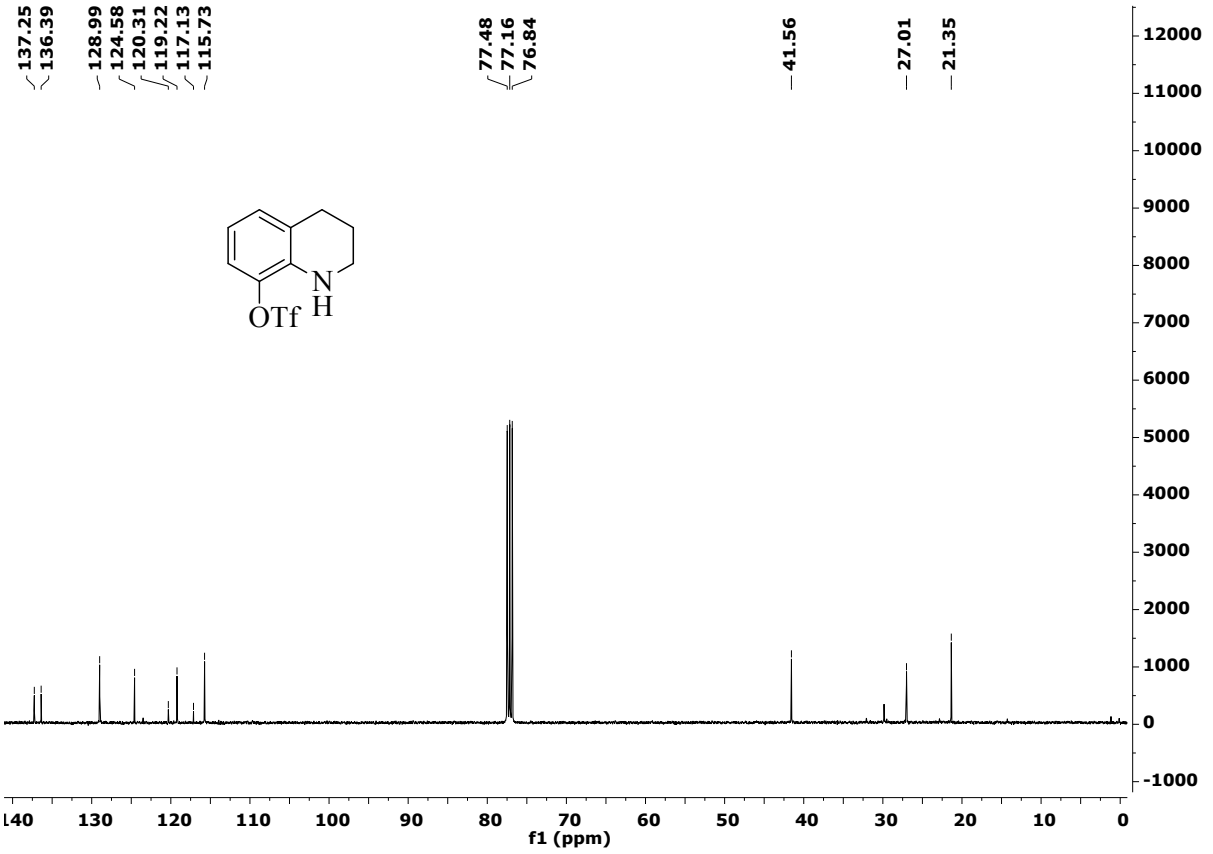


Figure S67: ^{13}C NMR Spectrum of **3o** ($CDCl_3$, 101 MHz, 298 K)

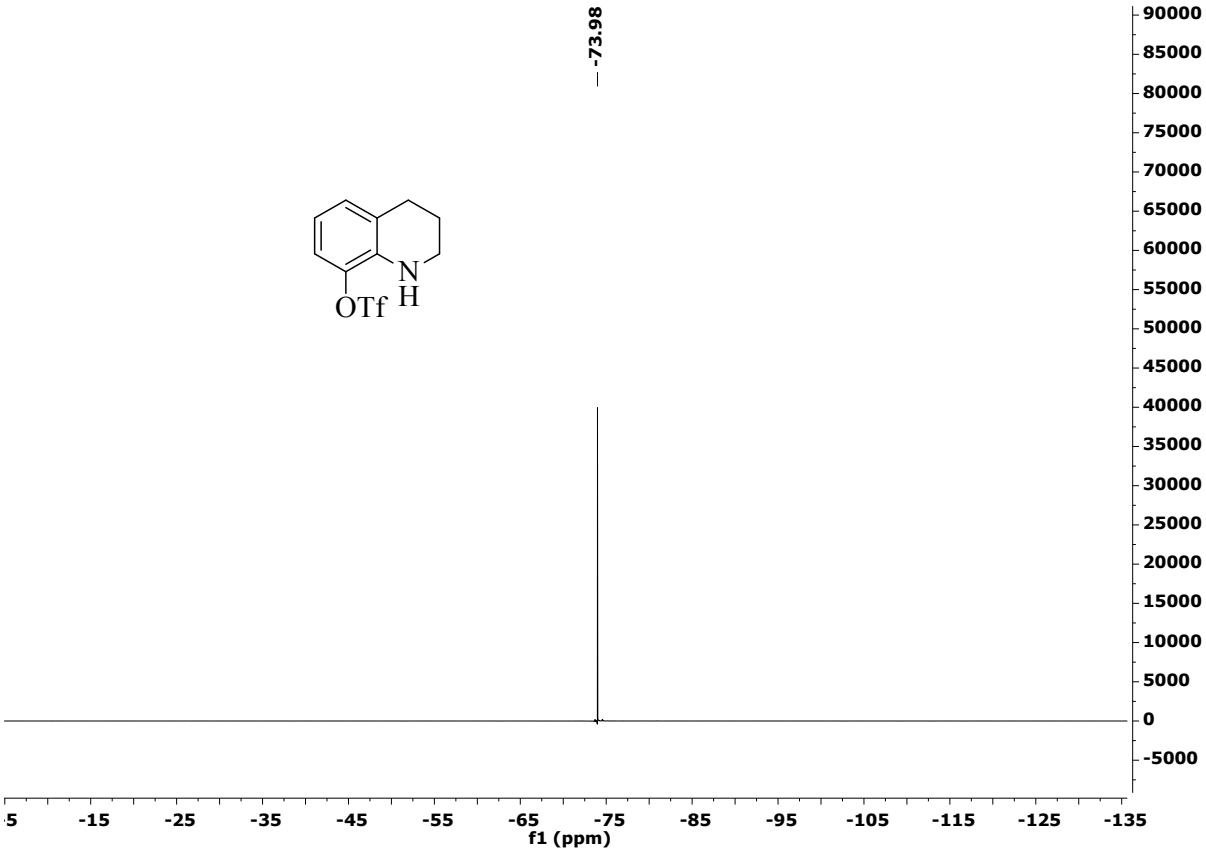


Figure S68: ^{19}F NMR Spectrum of **3o** ($CDCl_3$, 377 MHz, 298 K)

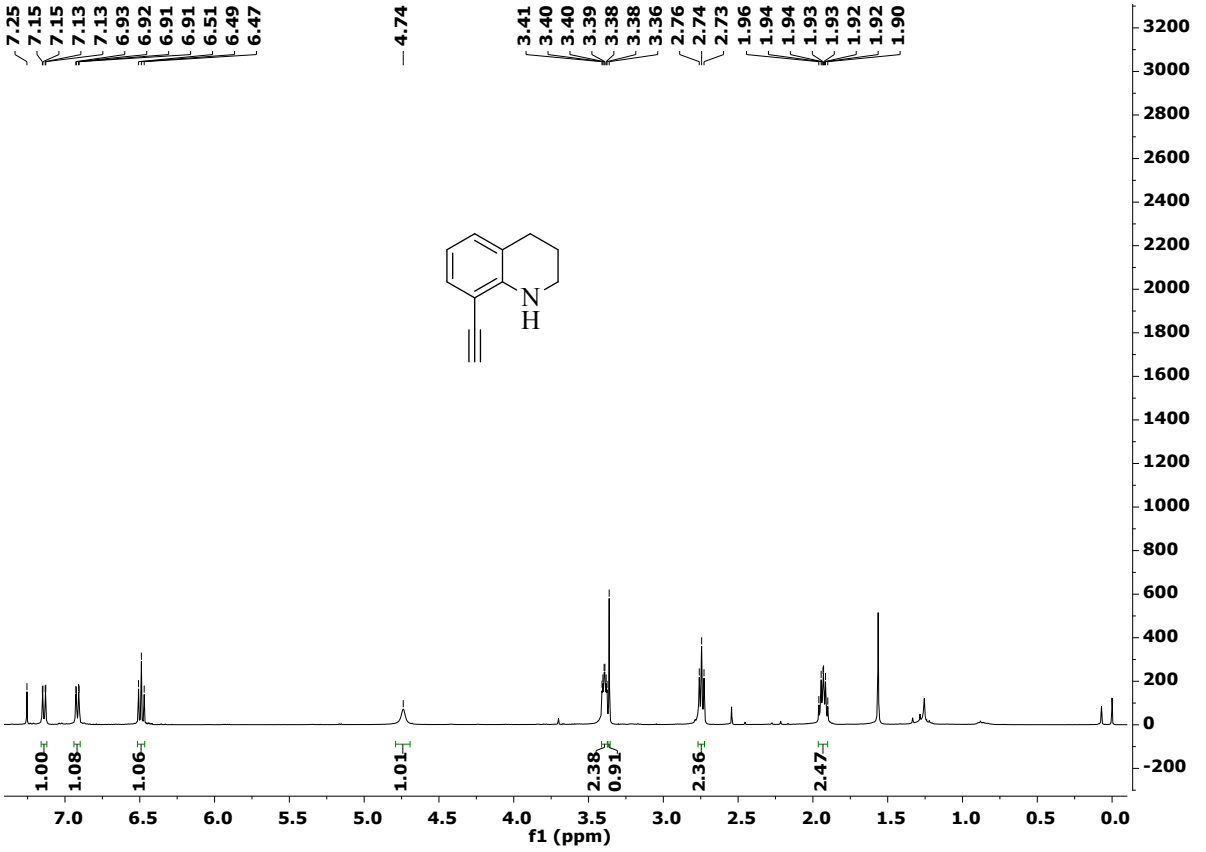


Figure S69: ^{1}H NMR Spectrum of **3p** ($CDCl_3$, 400 MHz, 298 K)

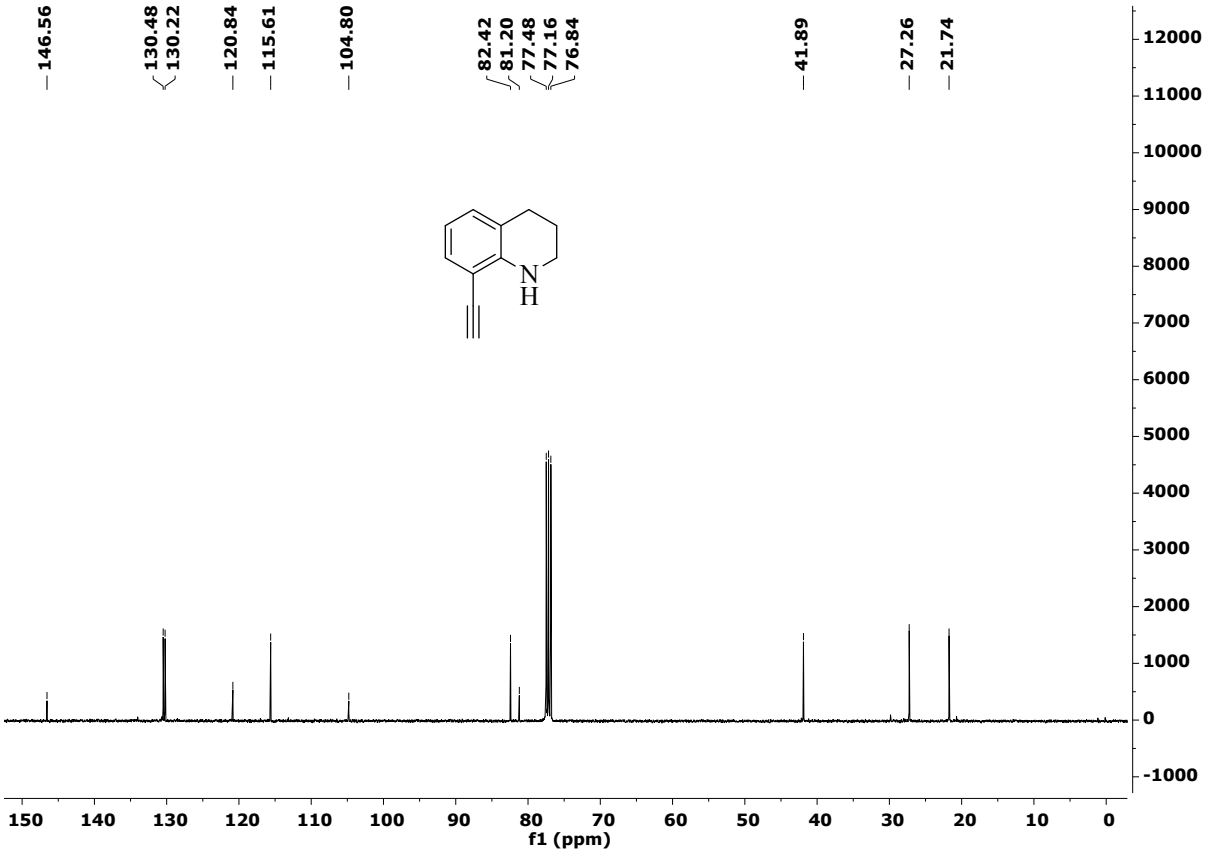


Figure S70: ^{13}C NMR Spectrum of **3p** ($CDCl_3$, 101 MHz, 298 K)

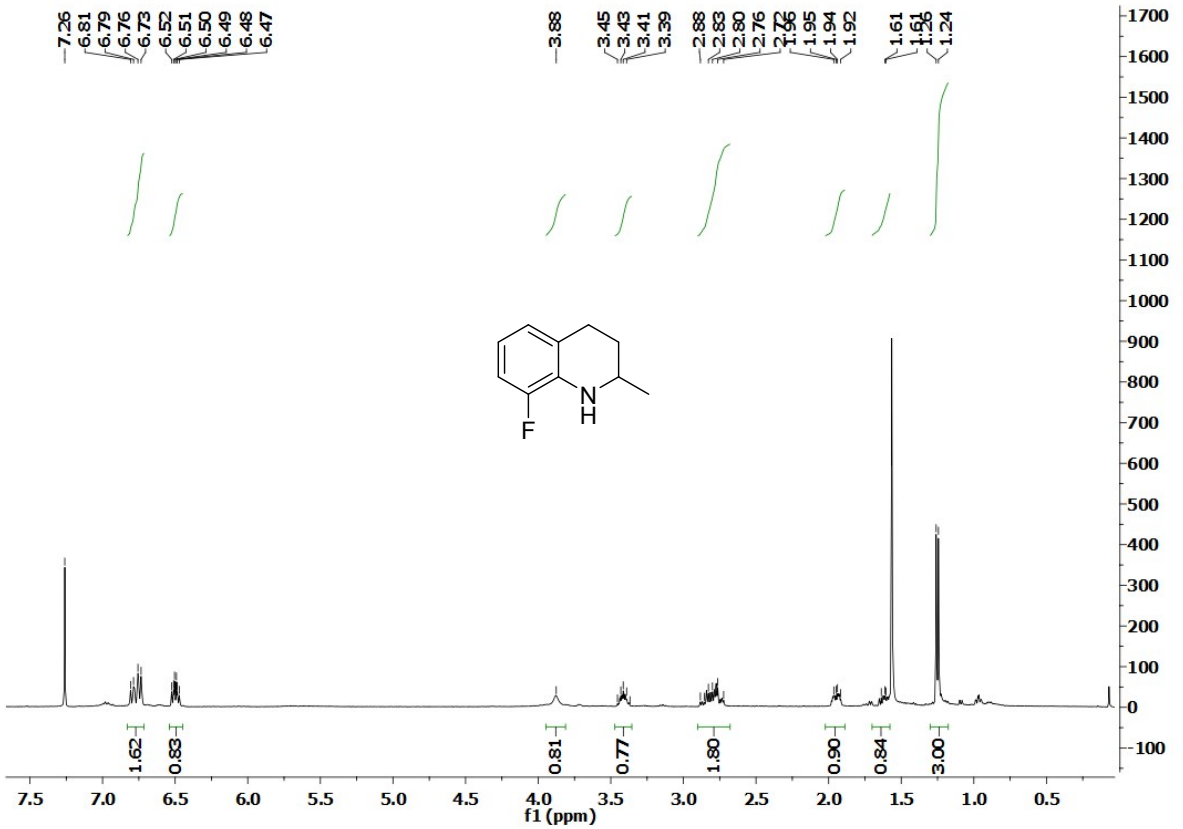


Figure S71: ^{1}H NMR Spectrum of **3q** ($CDCl_3$, 400 MHz, 298 K)

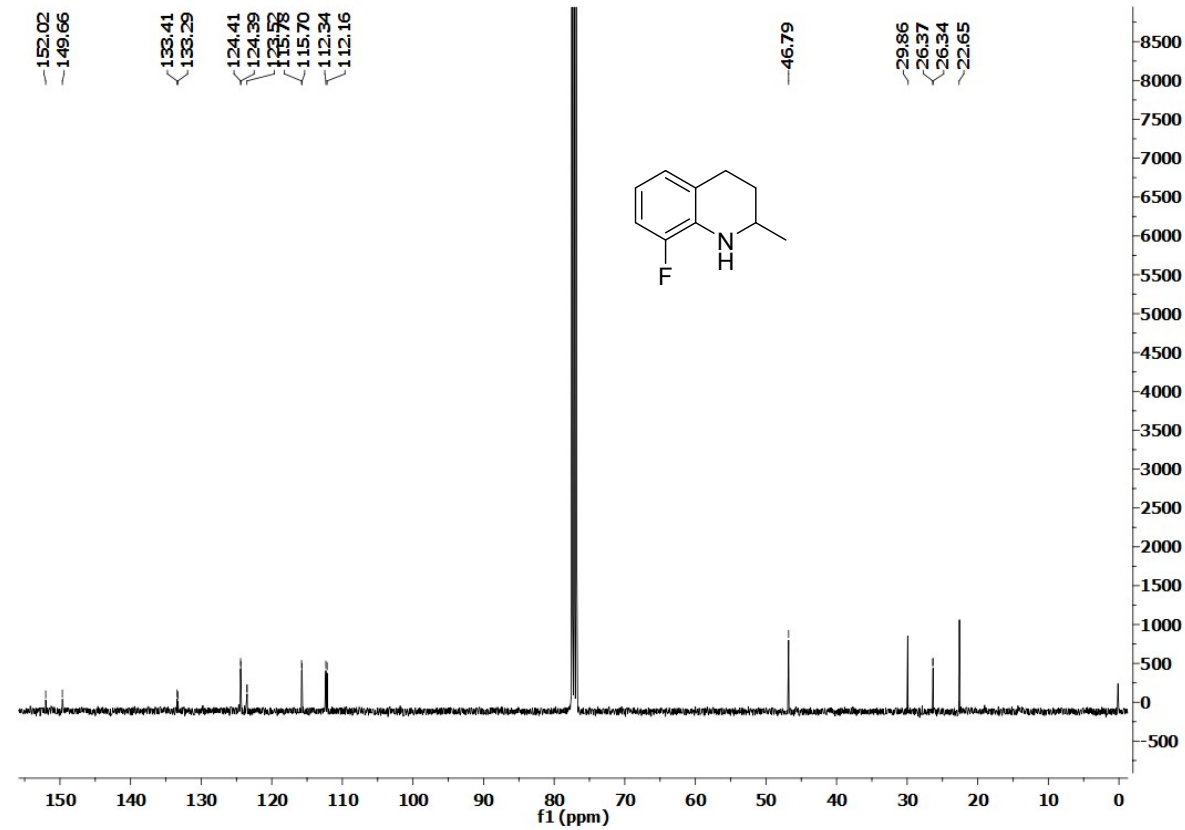


Figure S72: ^{13}C NMR Spectrum of **3q** ($CDCl_3$, 101 MHz, 298 K)

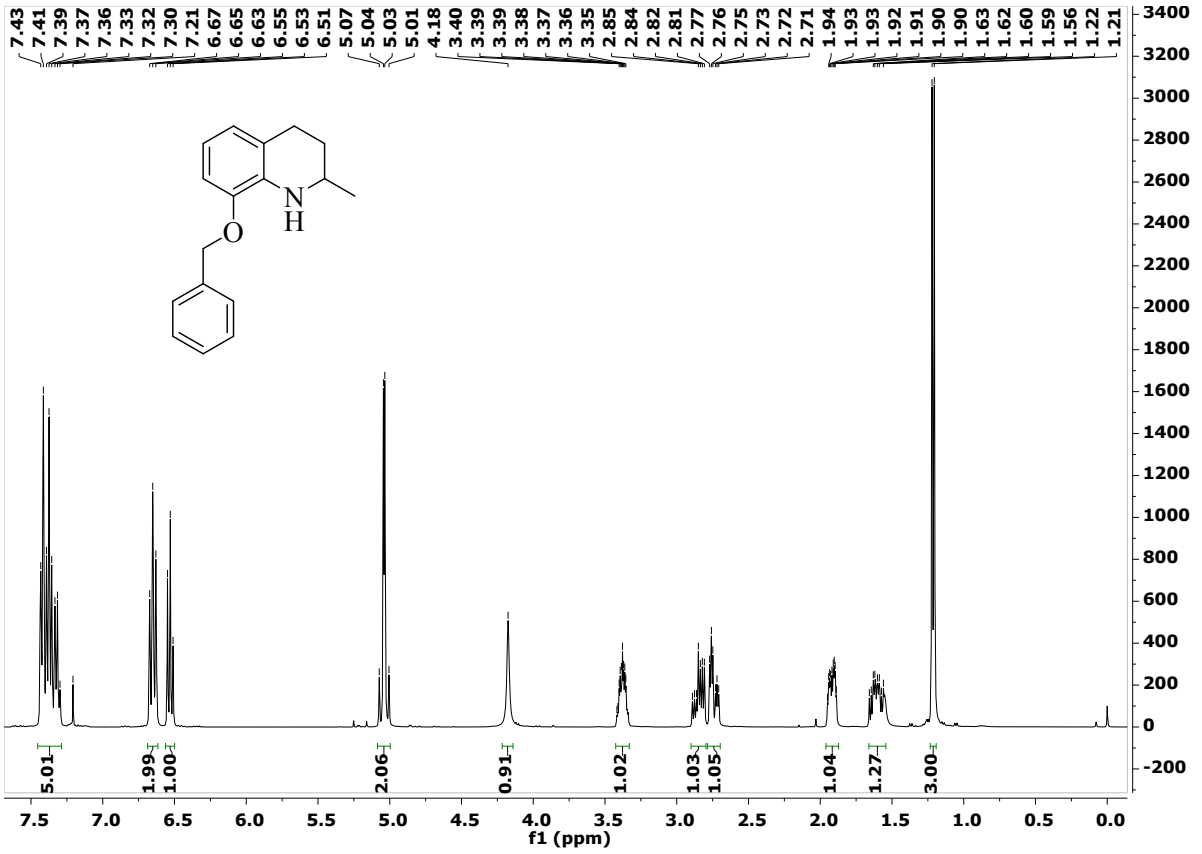


Figure S73: ^{1}H NMR Spectrum of **3r** ($CDCl_3$, 400 MHz, 298 K)

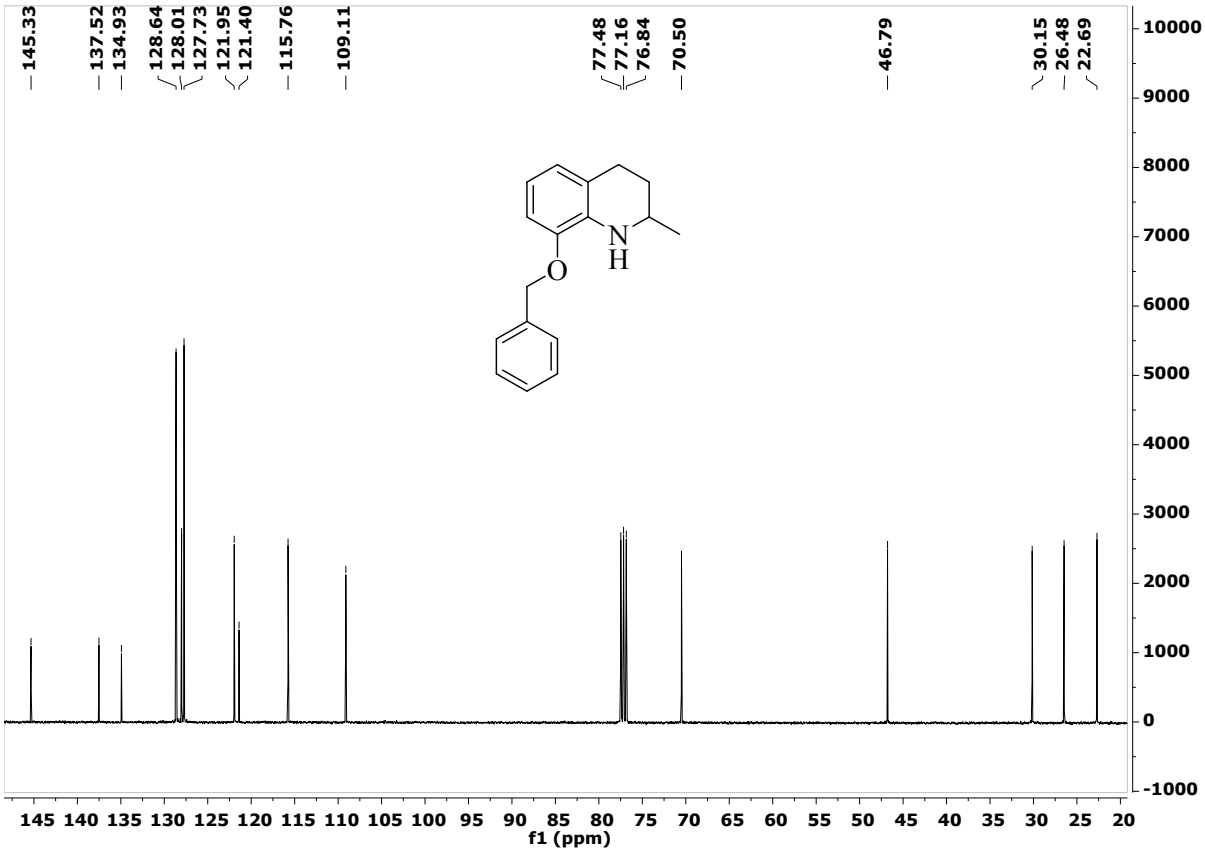


Figure S74: ^{13}C NMR Spectrum of **3r** ($CDCl_3$, 101 MHz, 298 K)

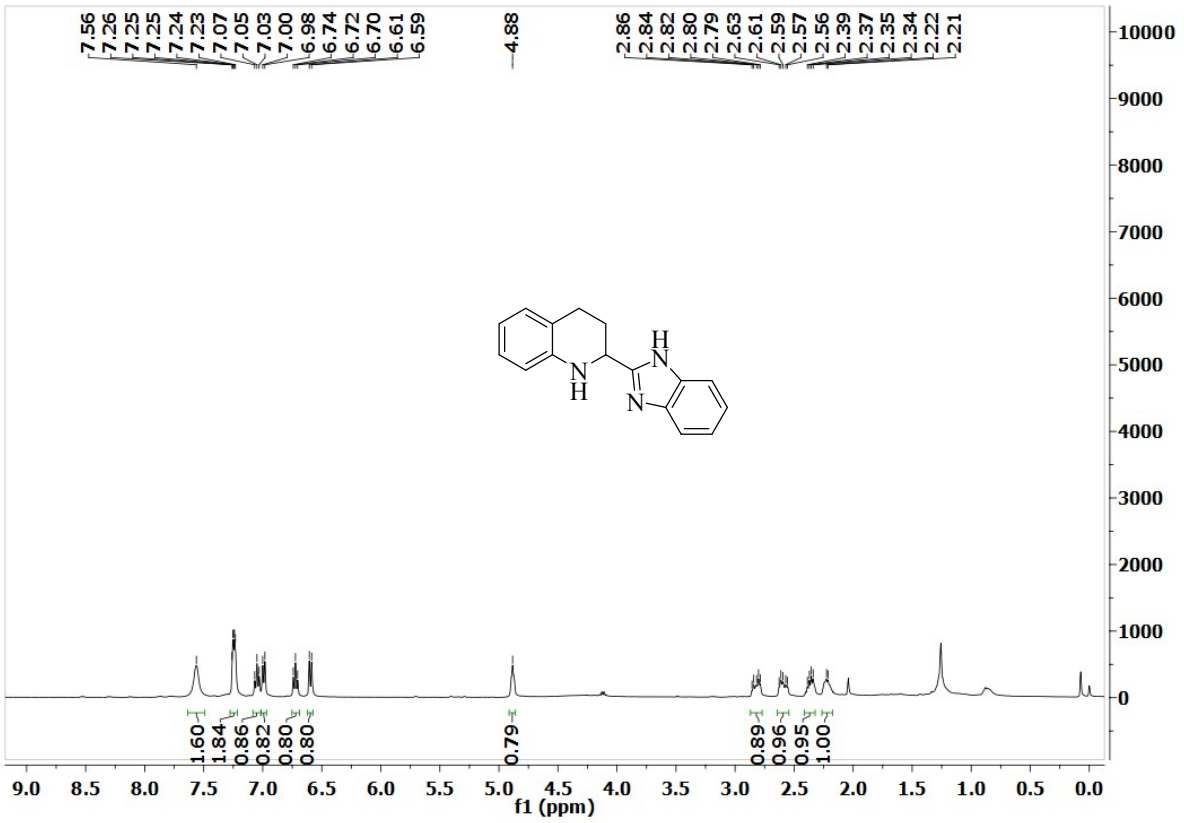


Figure S75: ^{1}H NMR Spectrum of **3s** ($CDCl_3$, 400 MHz, 298 K)

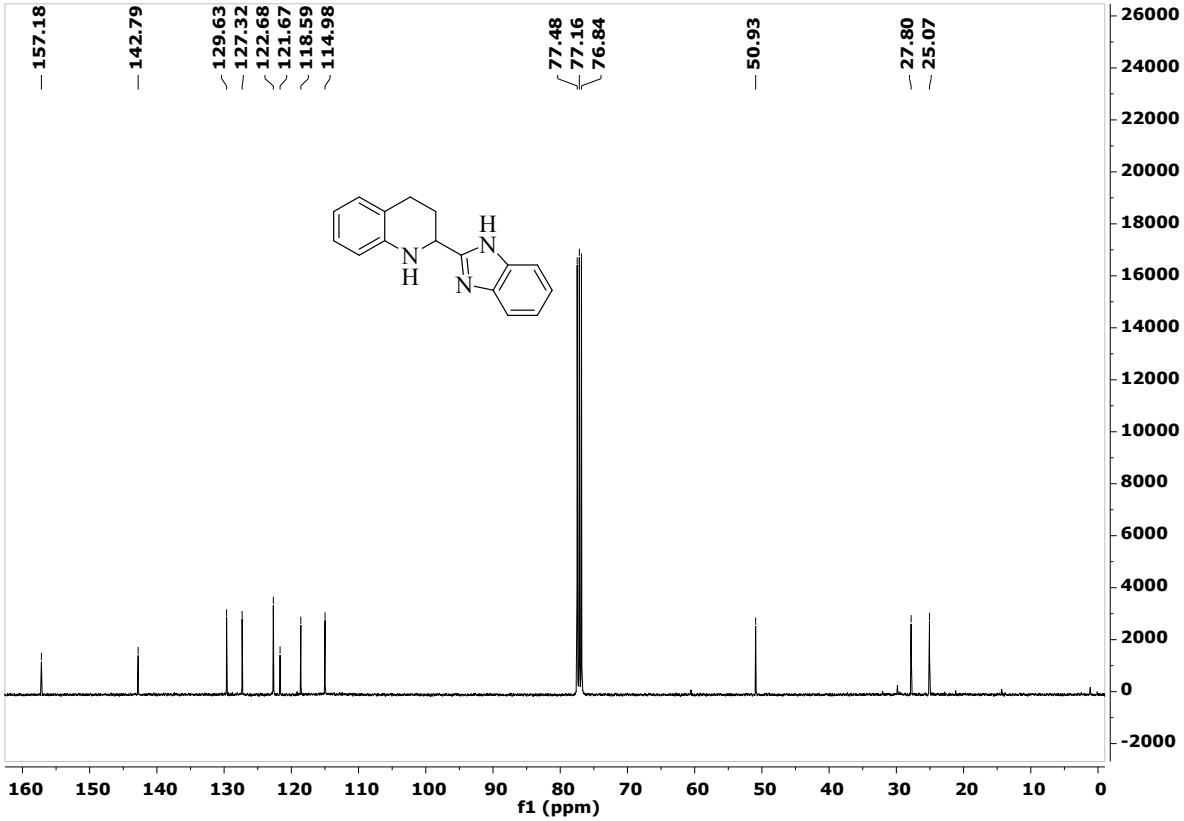


Figure S76: ^{13}C NMR Spectrum of **3s** ($CDCl_3$, 101 MHz, 298 K)

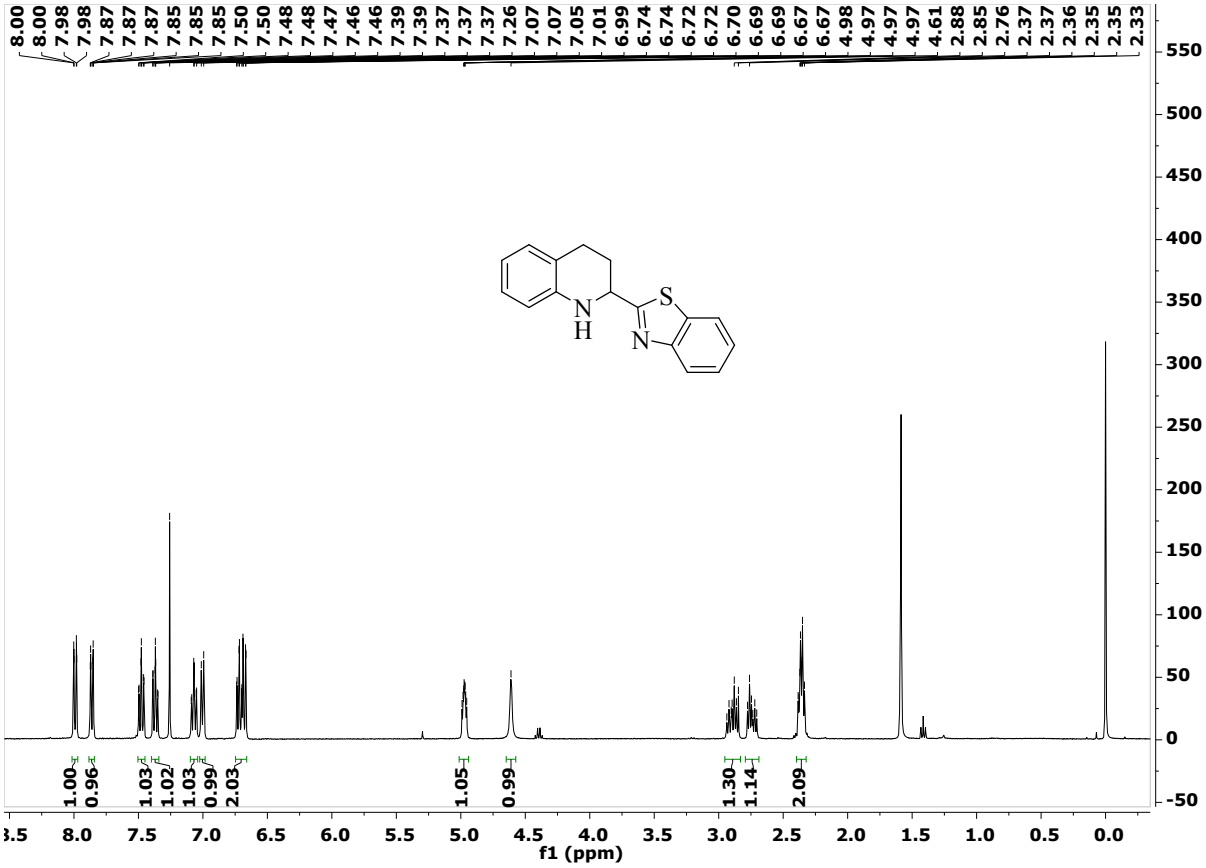


Figure S77: ^{1}H NMR Spectrum of **3t** ($CDCl_3$, 400 MHz, 298 K)

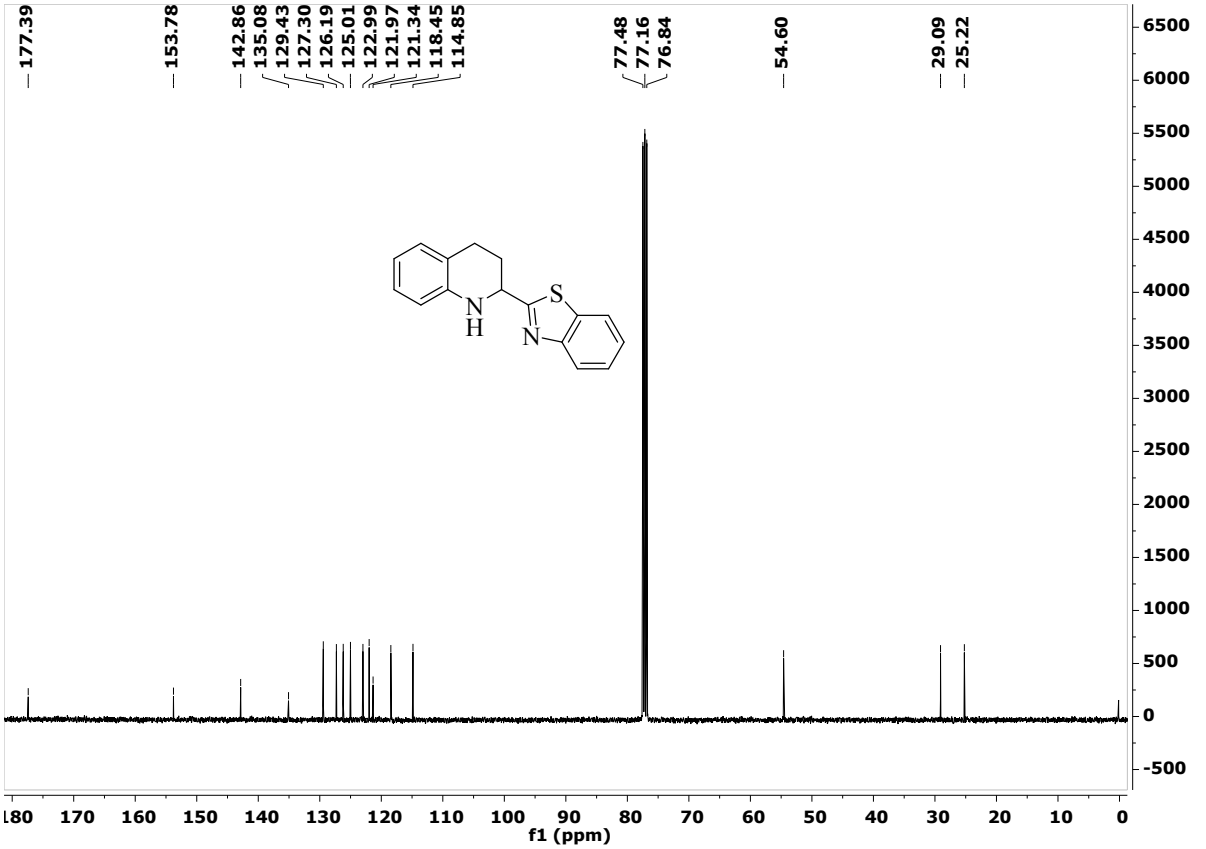


Figure S78: ^{13}C NMR Spectrum of **3t** ($CDCl_3$, 101 MHz, 298 K)

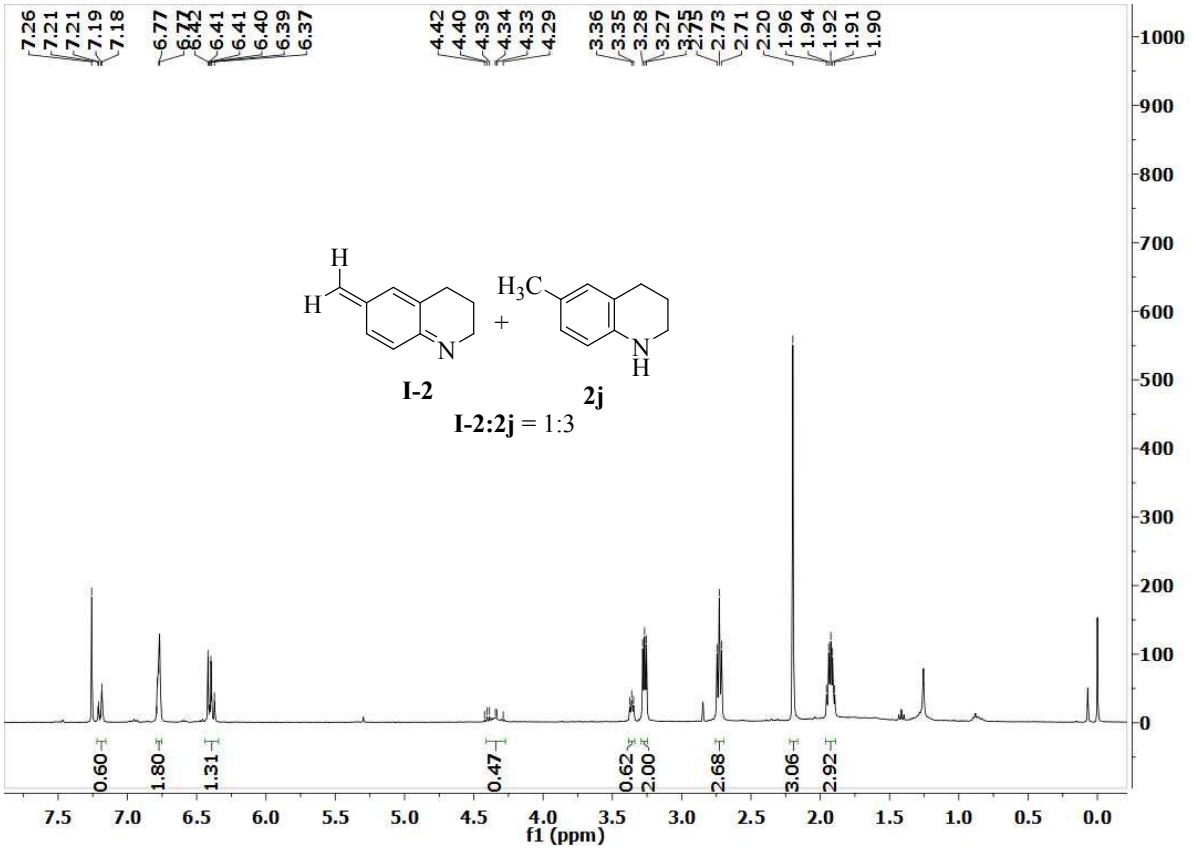


Figure S79: ^{1}H NMR Spectrum of **I-2+2j** ($CDCl_3$, 400 MHz, 298 K)

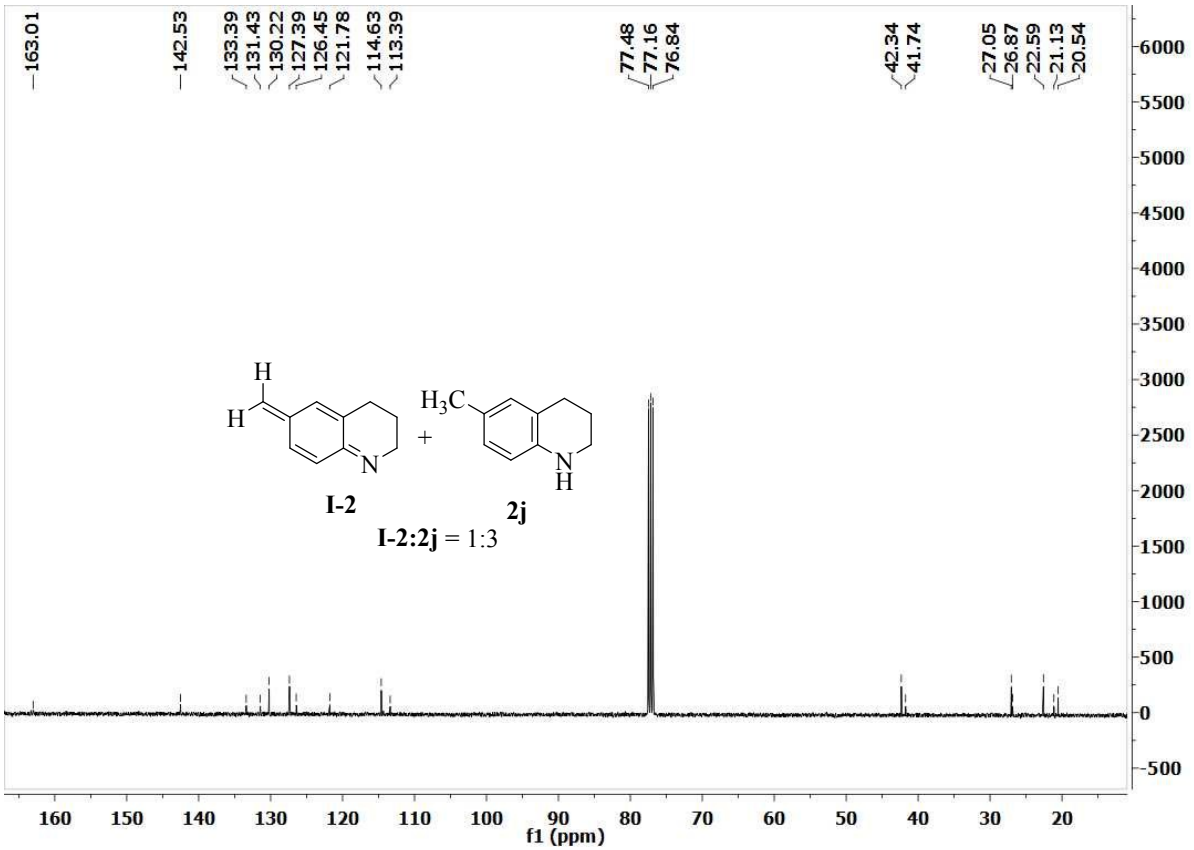


Figure S80: ^{1}H NMR Spectrum of **I-2+2j** ($CDCl_3$, 101 MHz, 298 K)

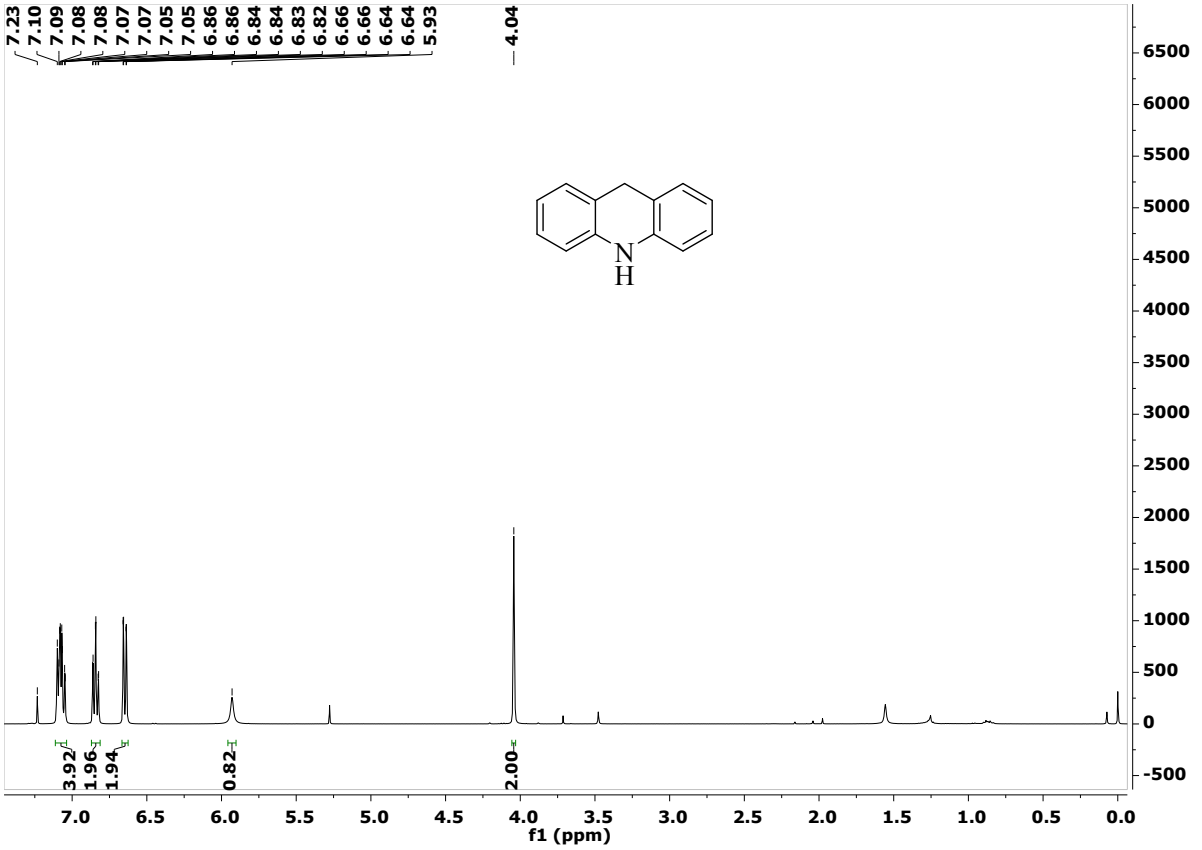


Figure S81: ^{1}H NMR Spectrum of **4a** ($CDCl_3$, 400 MHz, 298 K)

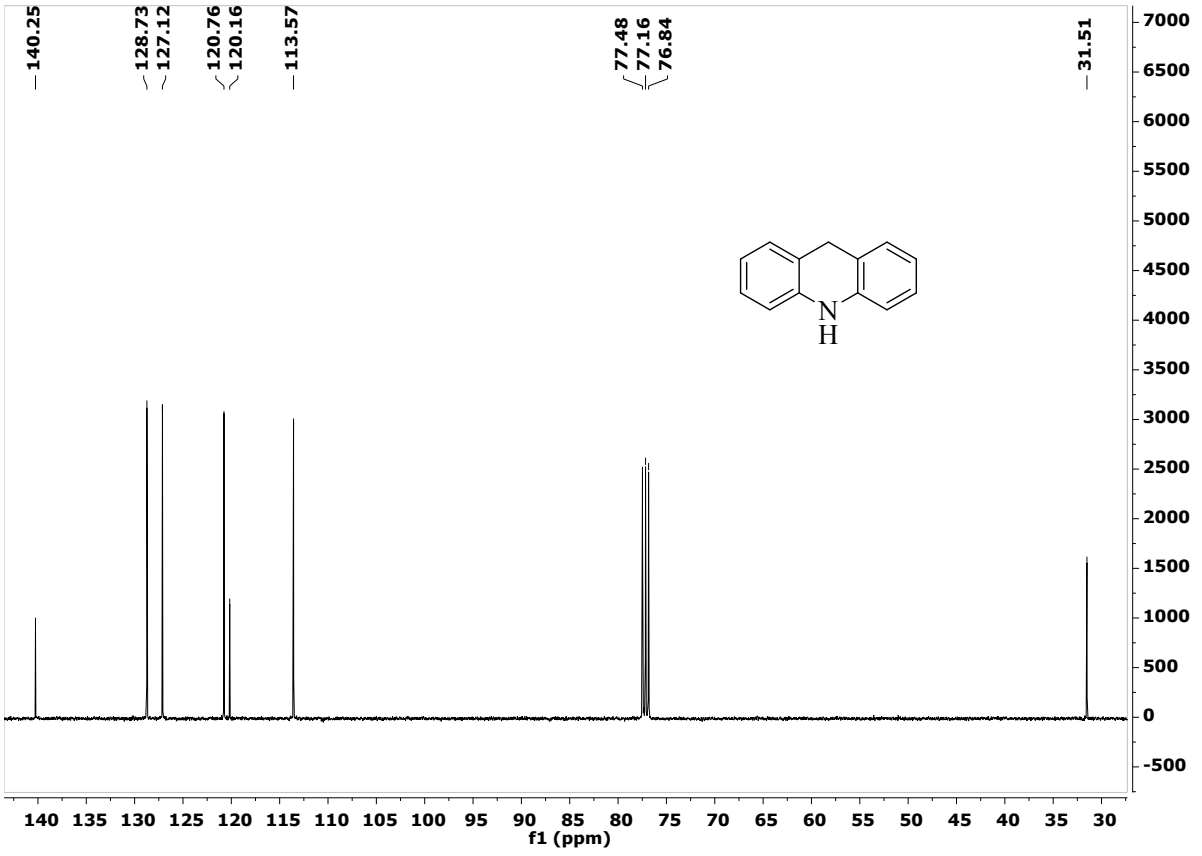


Figure S82: ^{13}C NMR Spectrum of **4a** ($CDCl_3$, 101 MHz, 298 K)

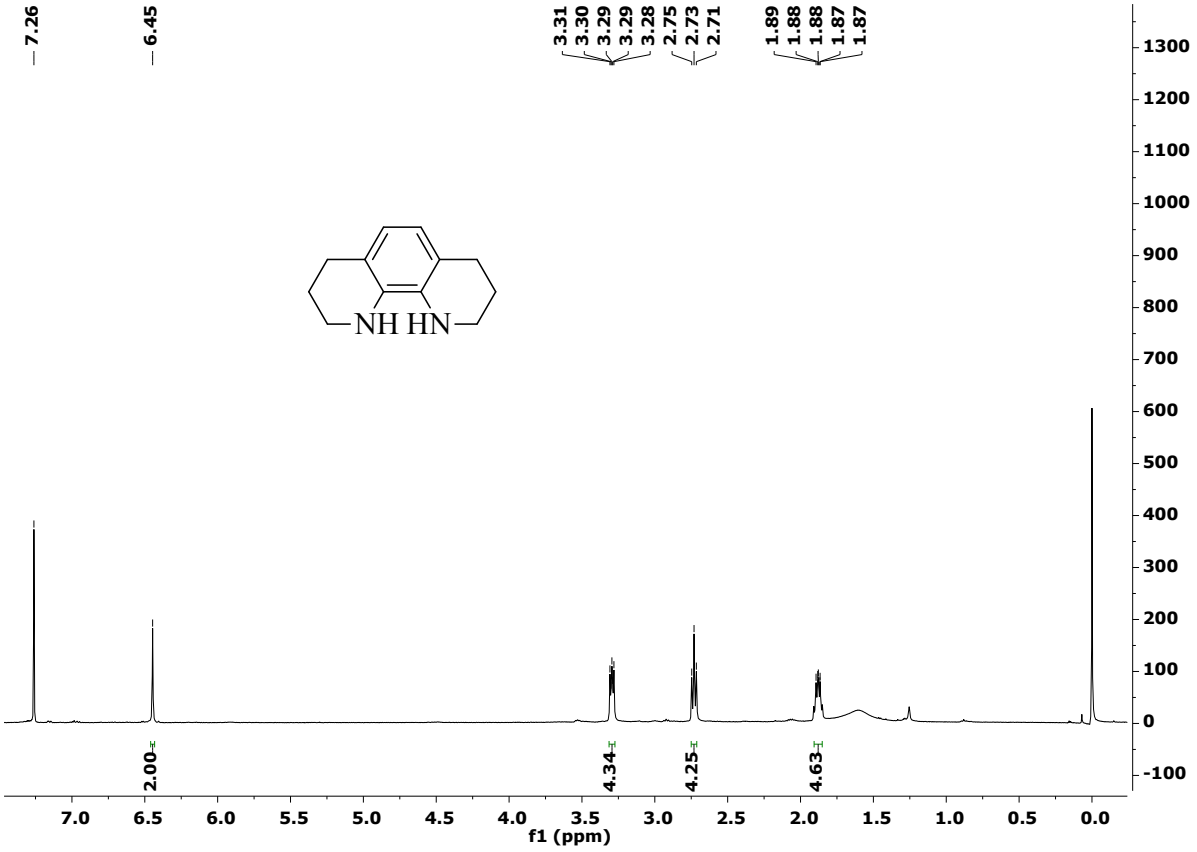


Figure S83: ^{1}H NMR Spectrum of **4b** ($CDCl_3$, 400 MHz, 298 K)

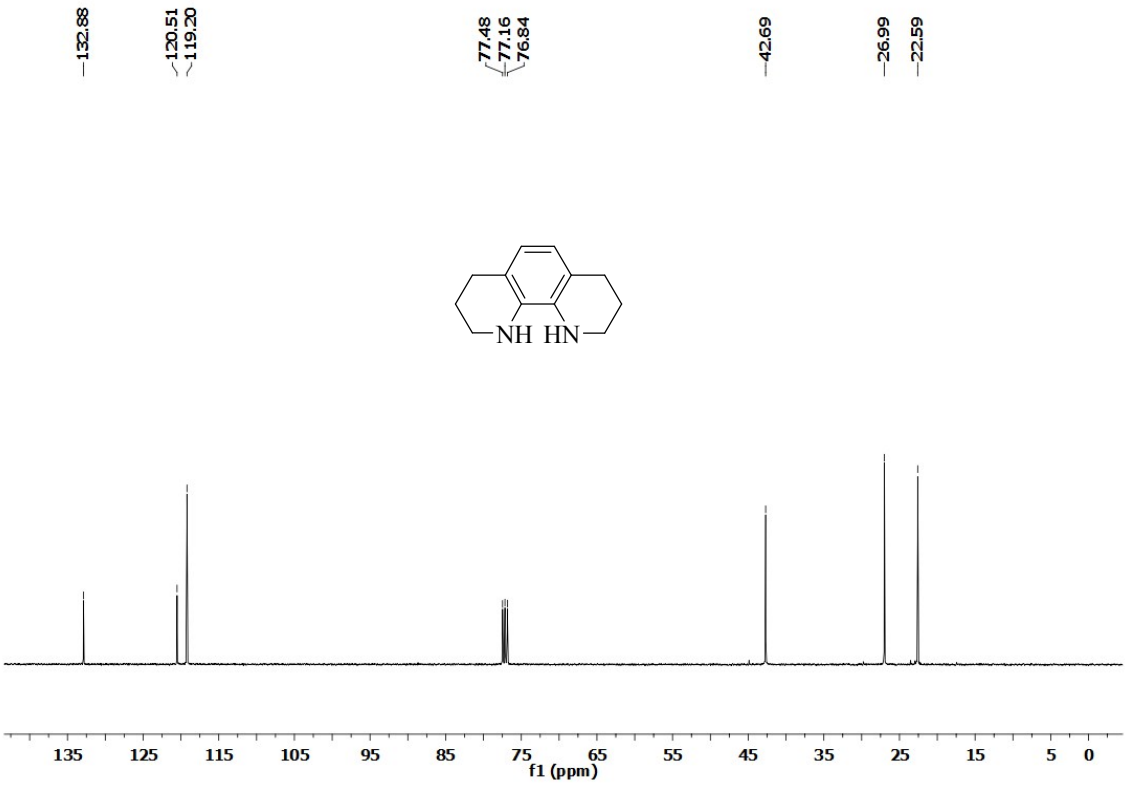


Figure S84: ^{13}C NMR Spectrum of **4b** ($CDCl_3$, 101 MHz, 298 K)

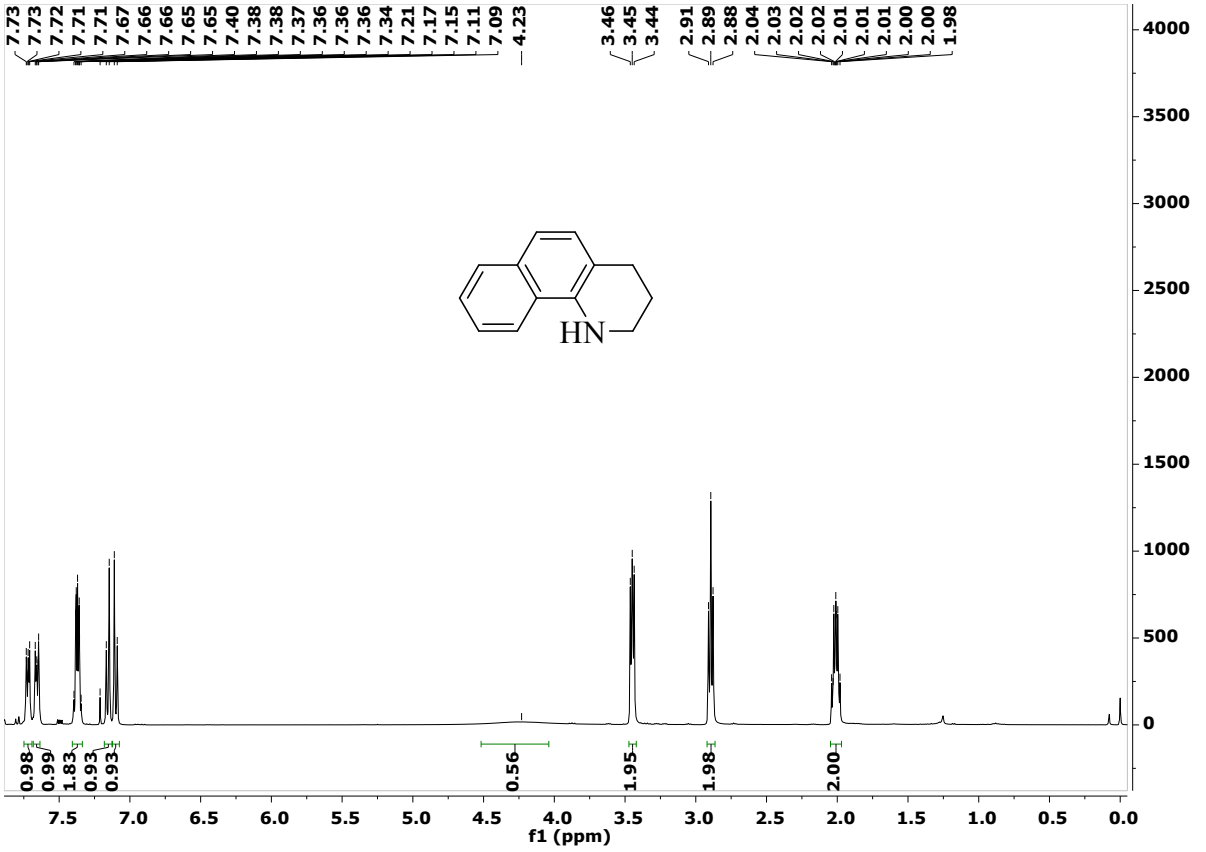


Figure S85: ^{1}H NMR Spectrum of **4c** ($CDCl_3$, 400 MHz, 298 K)

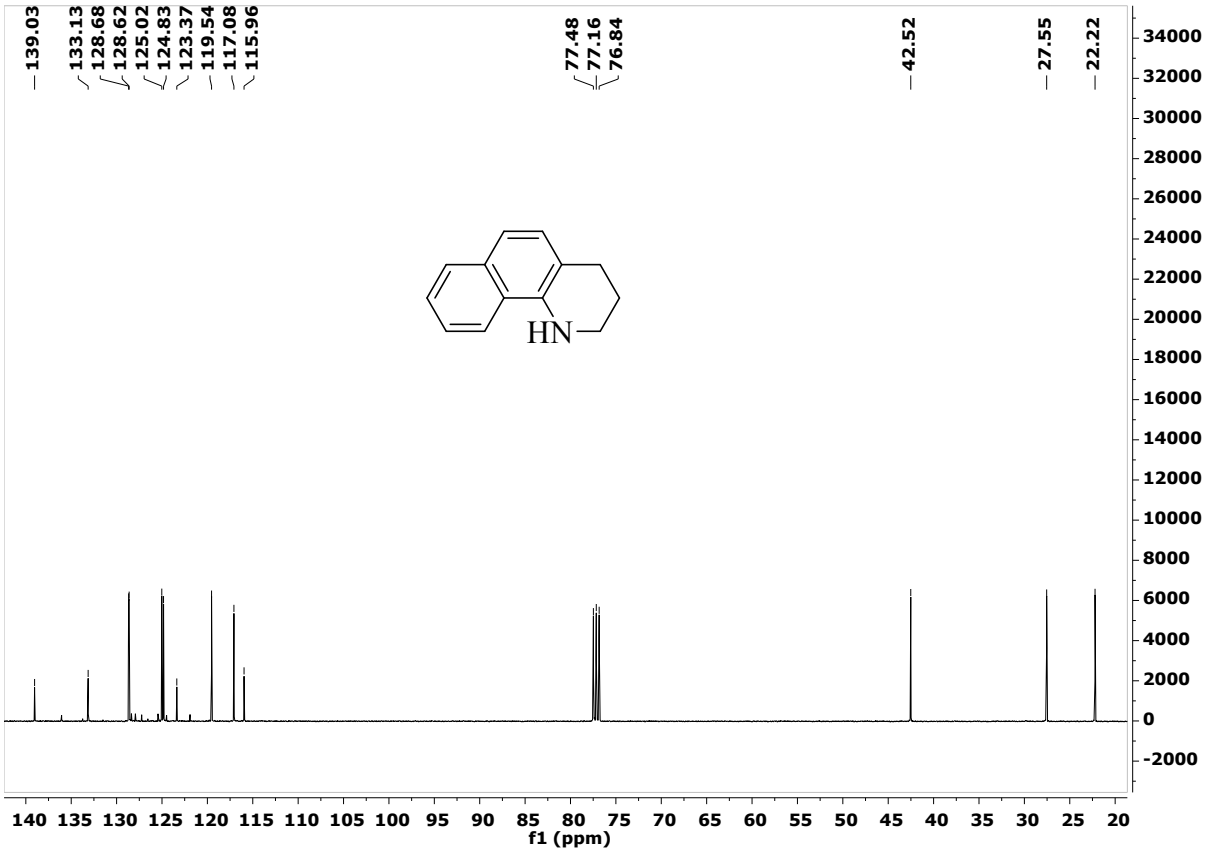


Figure S86: ^{13}C NMR Spectrum of **4c** ($CDCl_3$, 101 MHz, 298 K)

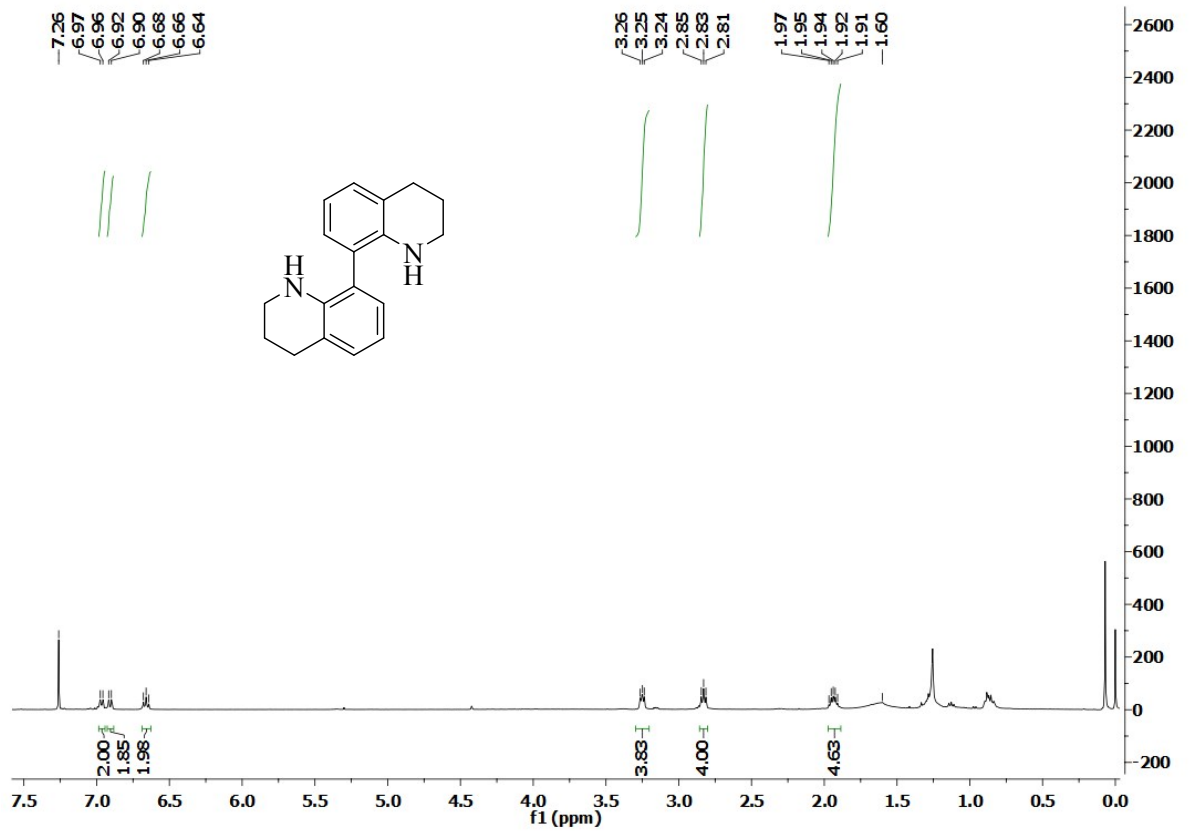


Figure S87: ^{1}H NMR Spectrum of **4d** ($CDCl_3$, 400 MHz, 298 K)

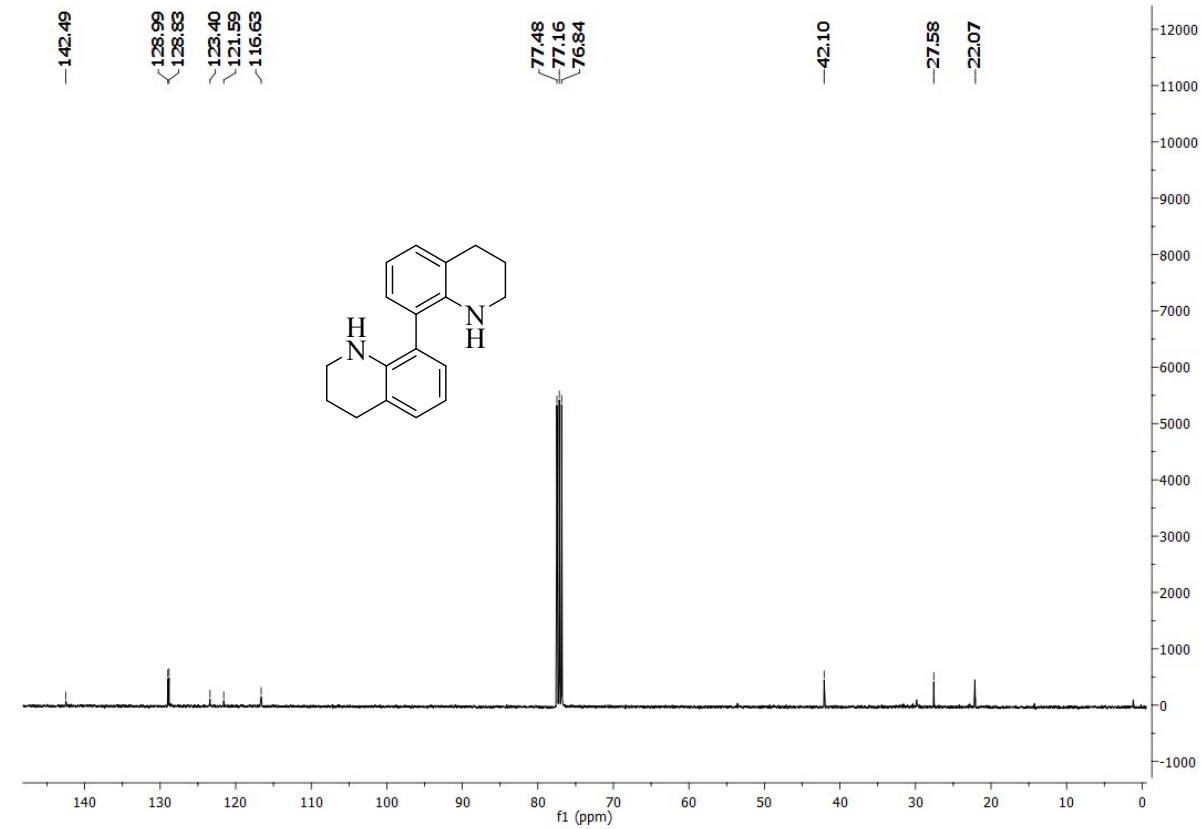


Figure S88: ^{13}C NMR Spectrum of **4d** ($CDCl_3$, 101 MHz, 298 K)

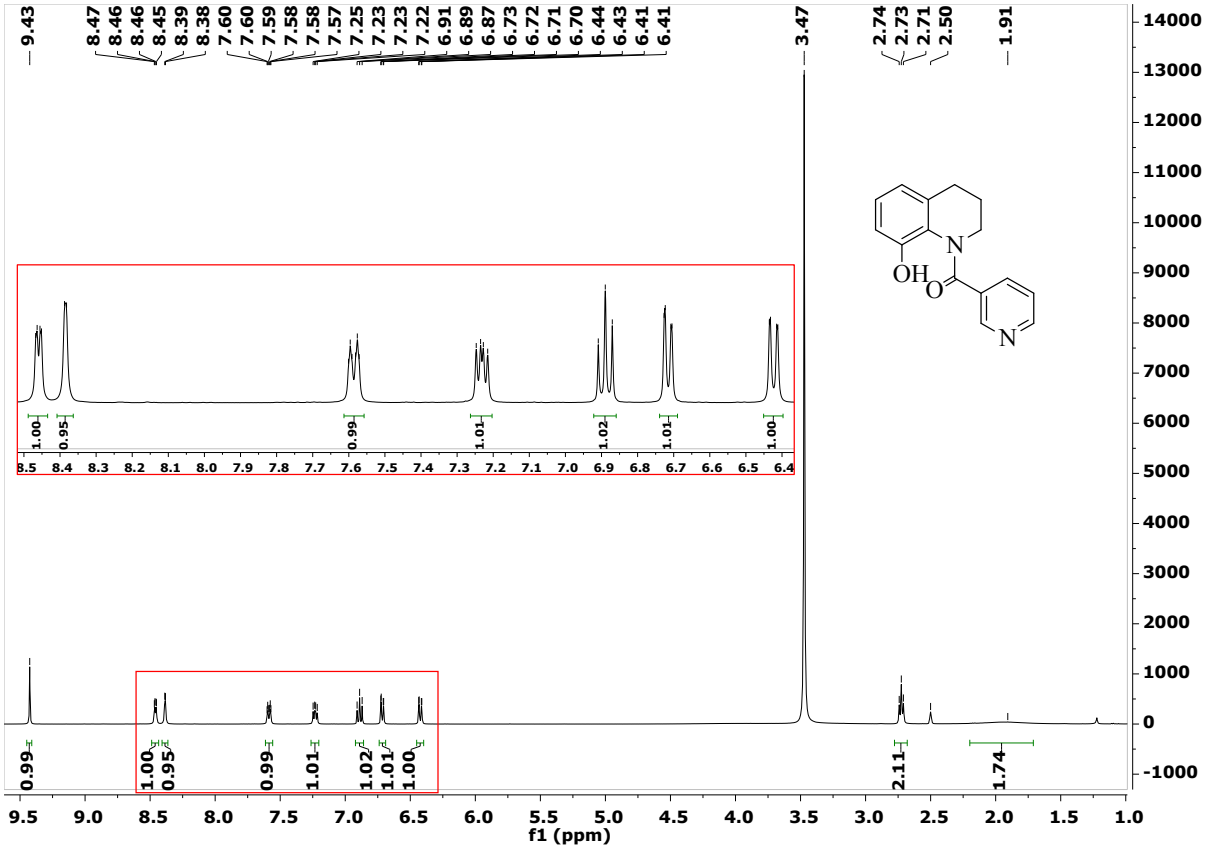


Figure S89: [1]H NMR Spectrum of **5** (DMSO-d_6, 400 MHz, 298 K)

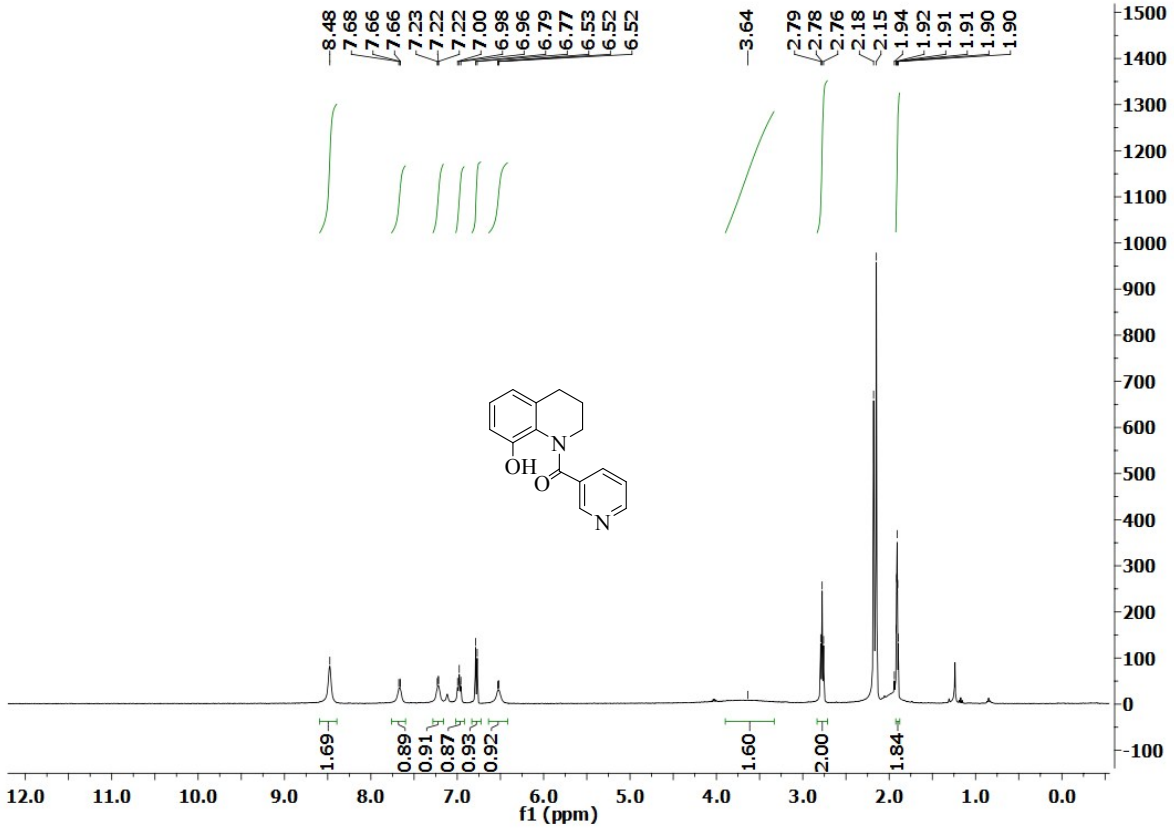


Figure S90: [1]H NMR Spectrum of **5** (CD_3CN, 400 MHz, 298 K)

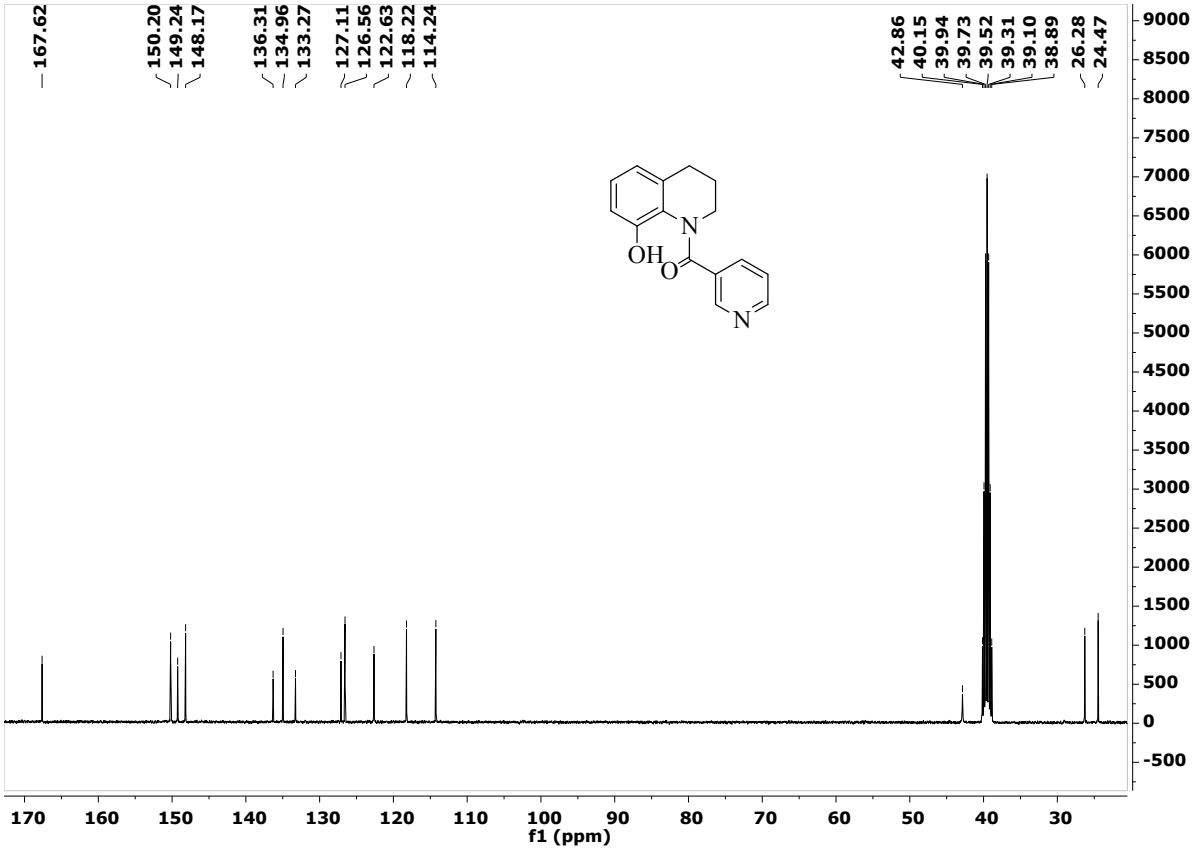


Figure S91: ^{13}C NMR Spectrum of **5** (DMSO-d_6, 101 MHz, 298 K)

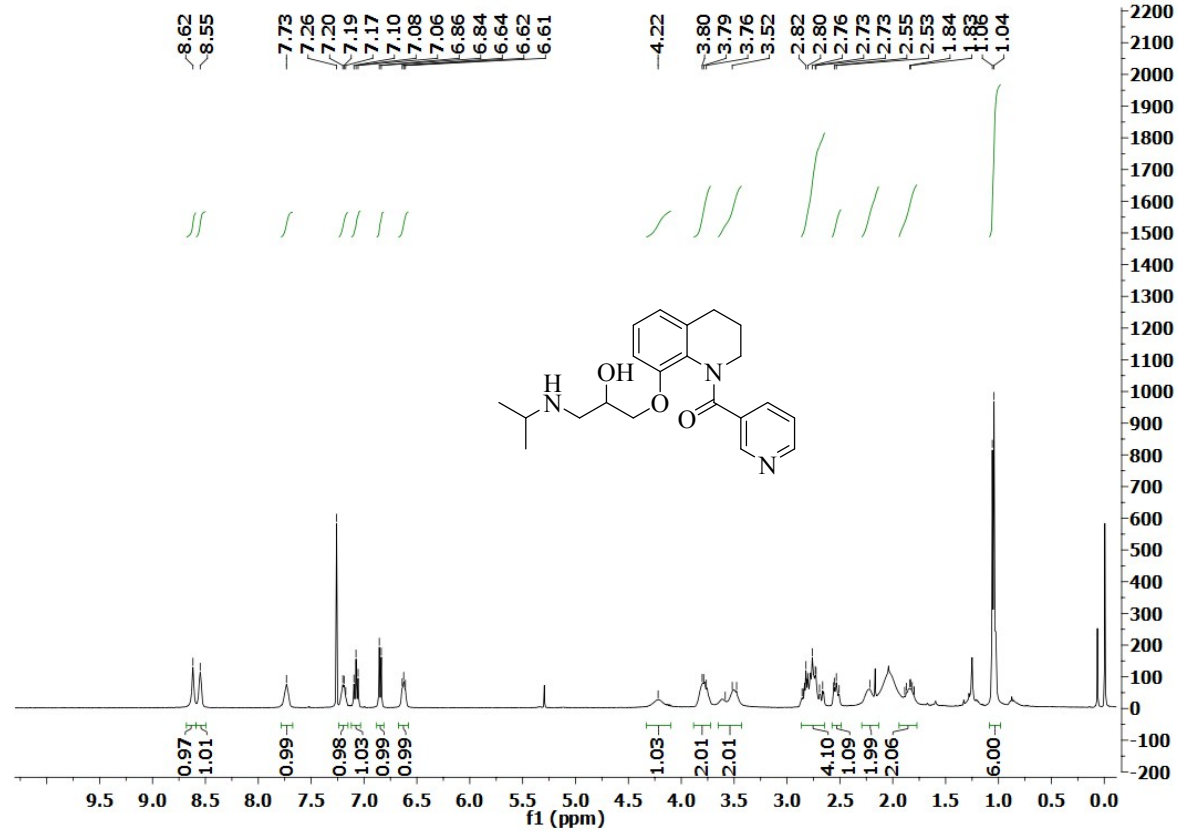


Figure S92: ^{1}H NMR Spectrum of **6** ($CDCl_3$, 400 MHz, 298 K)

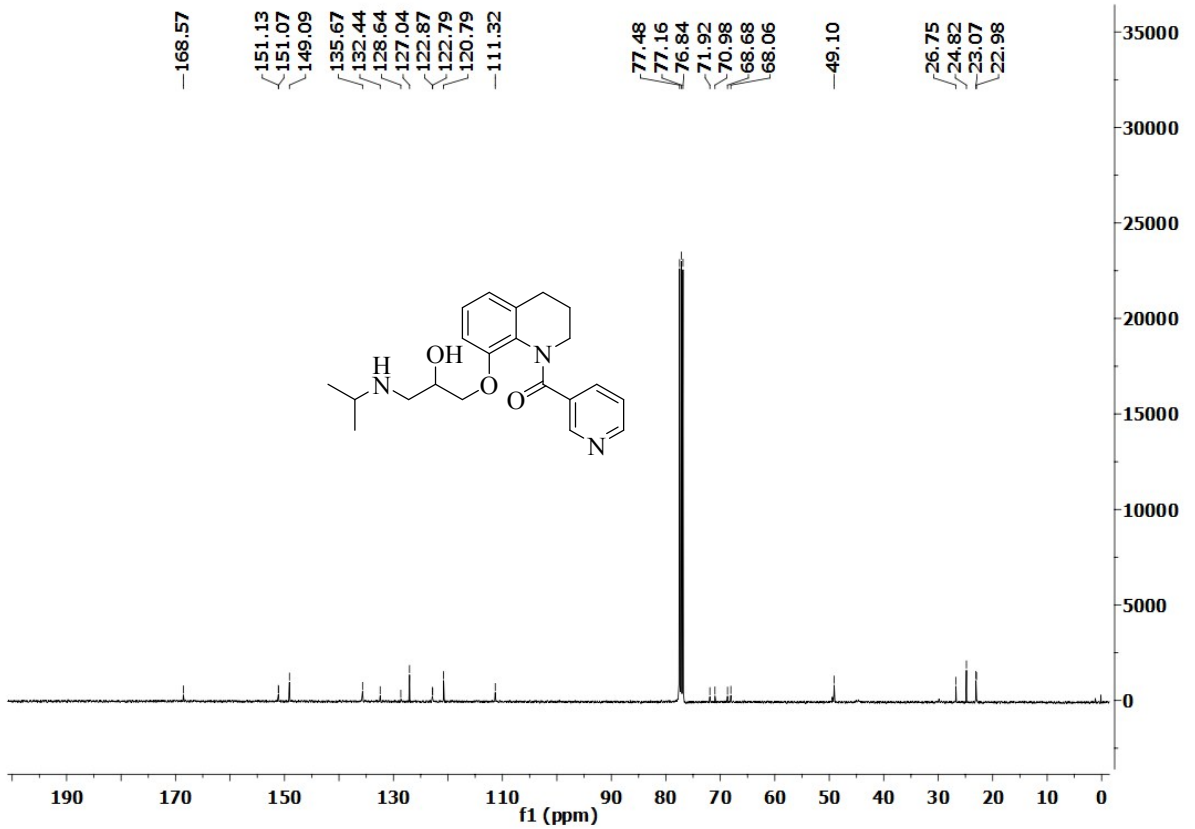


Figure S93: ^{13}C NMR Spectrum of **6** ($CDCl_3$, 101 MHz, 298 K)

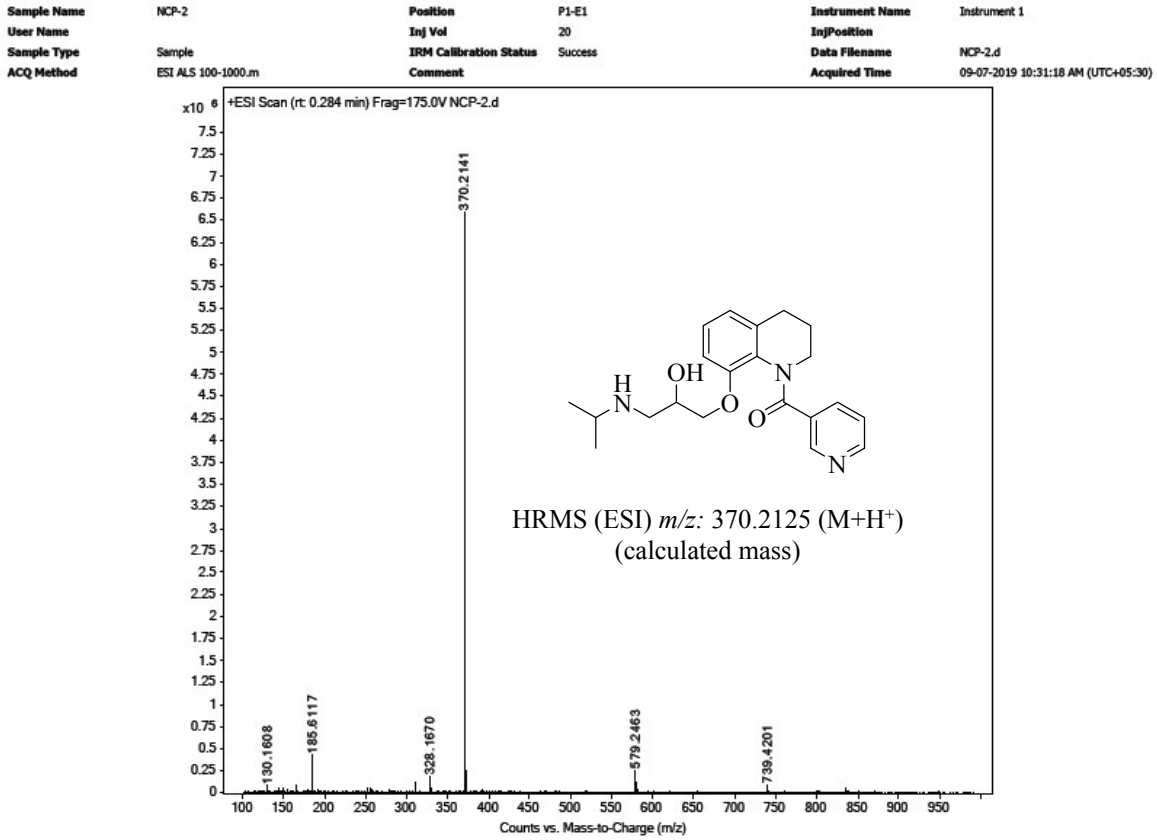


Figure S94: HRMS Spectrum of **6**

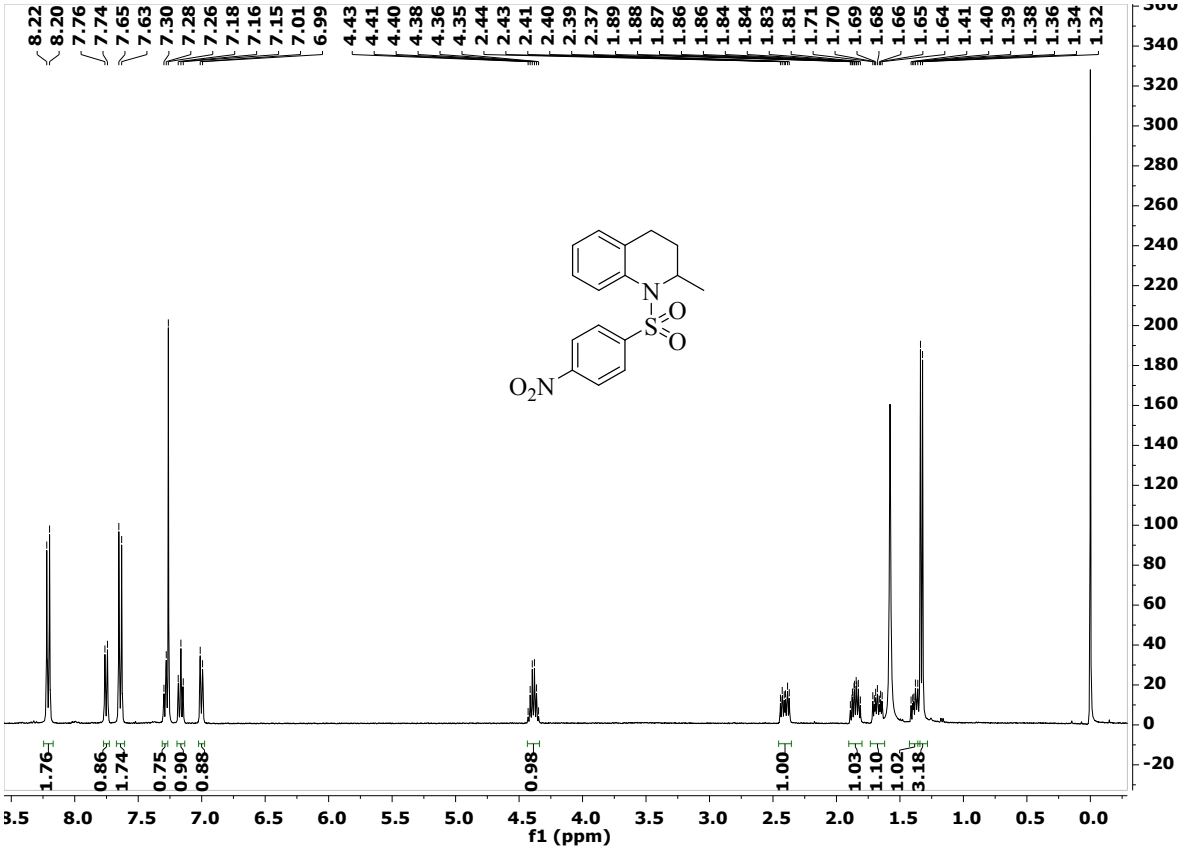


Figure S95: ^{1}H NMR Spectrum of **7** ($CDCl_3$, 400 MHz, 298 K)

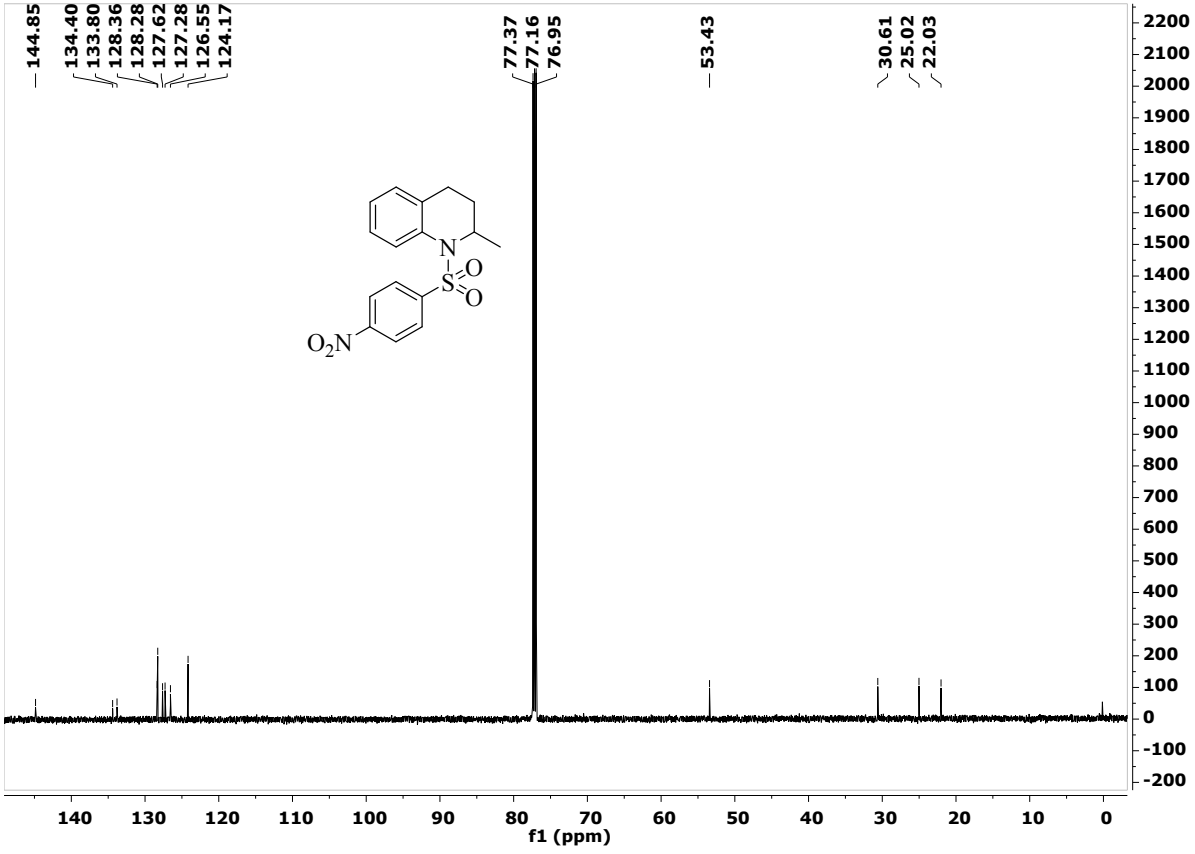


Figure S96: ^{13}C NMR Spectrum of **7** ($CDCl_3$, 151 MHz, 298 K)

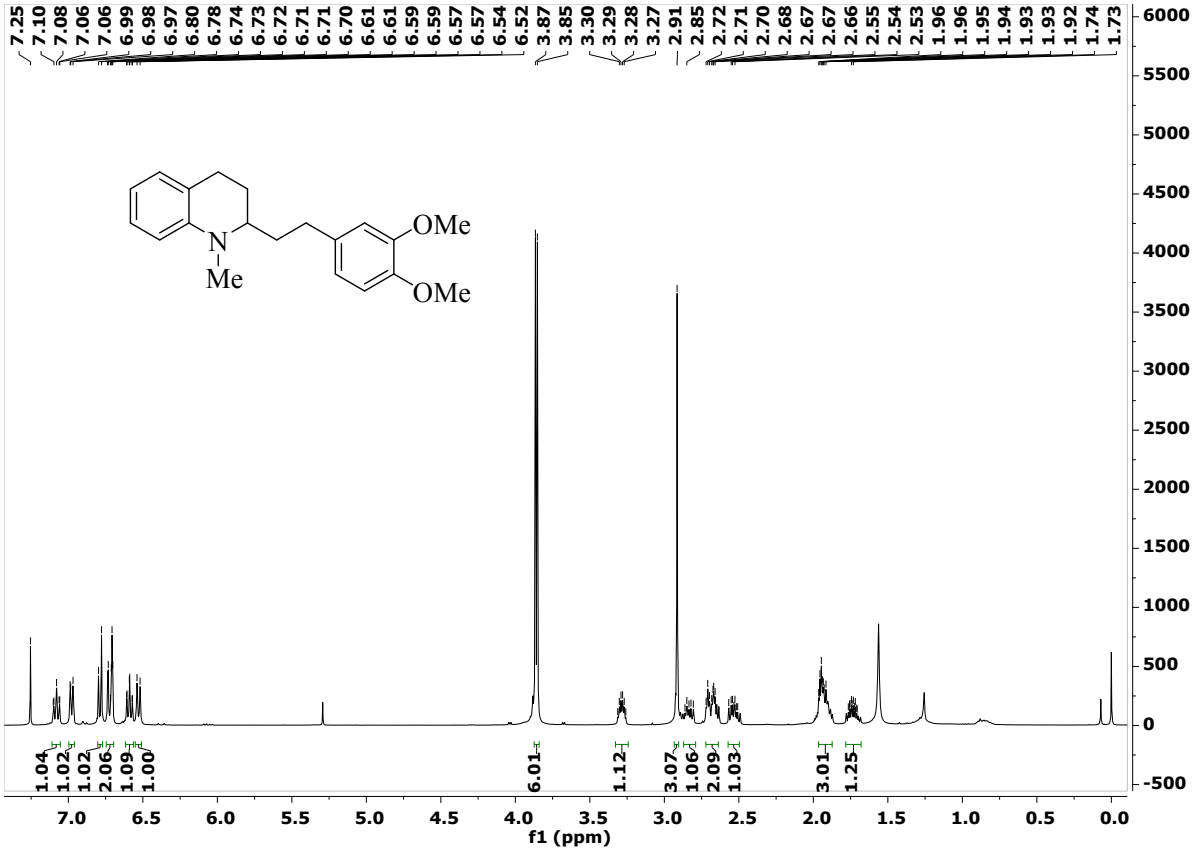


Figure S97: ^{1}H NMR Spectrum of **8** ($CDCl_3$, 400 MHz, 298 K)

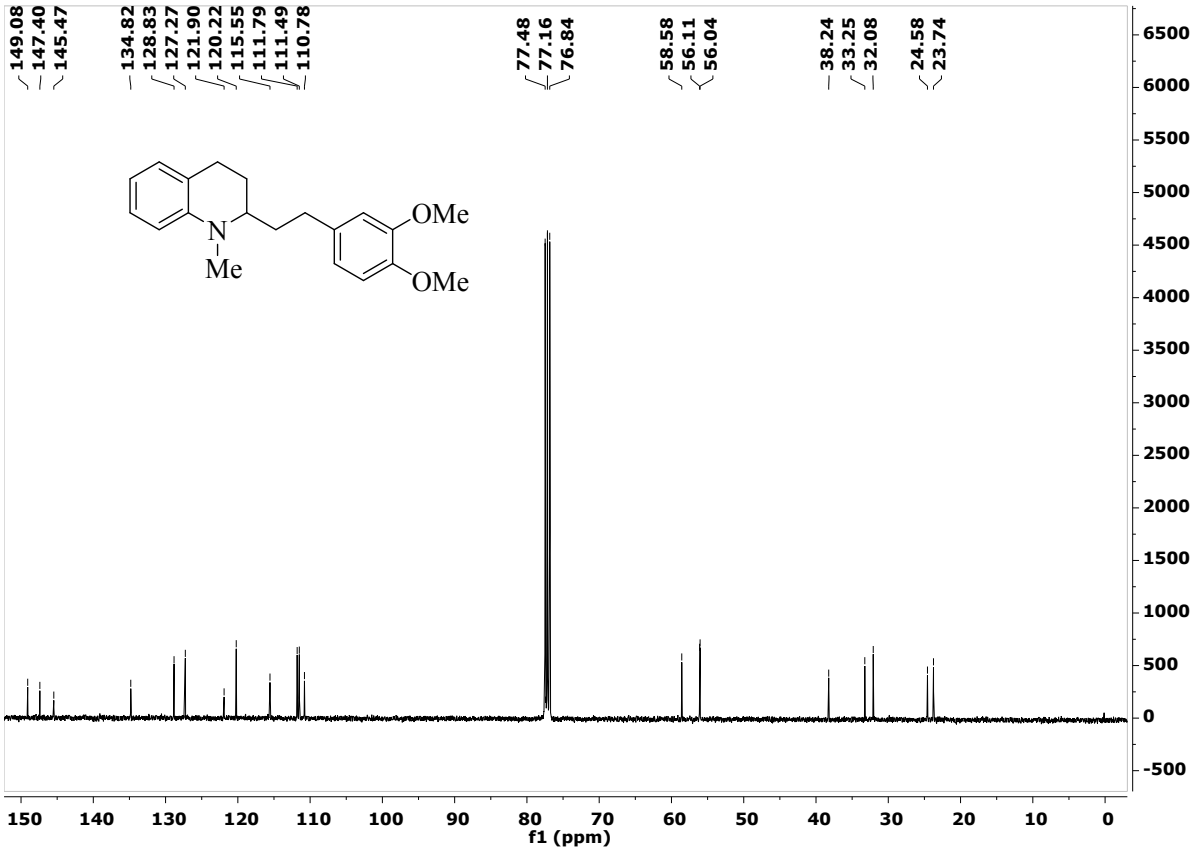


Figure S98: ^{13}C NMR Spectrum of **8** ($CDCl_3$, 101 MHz, 298 K)

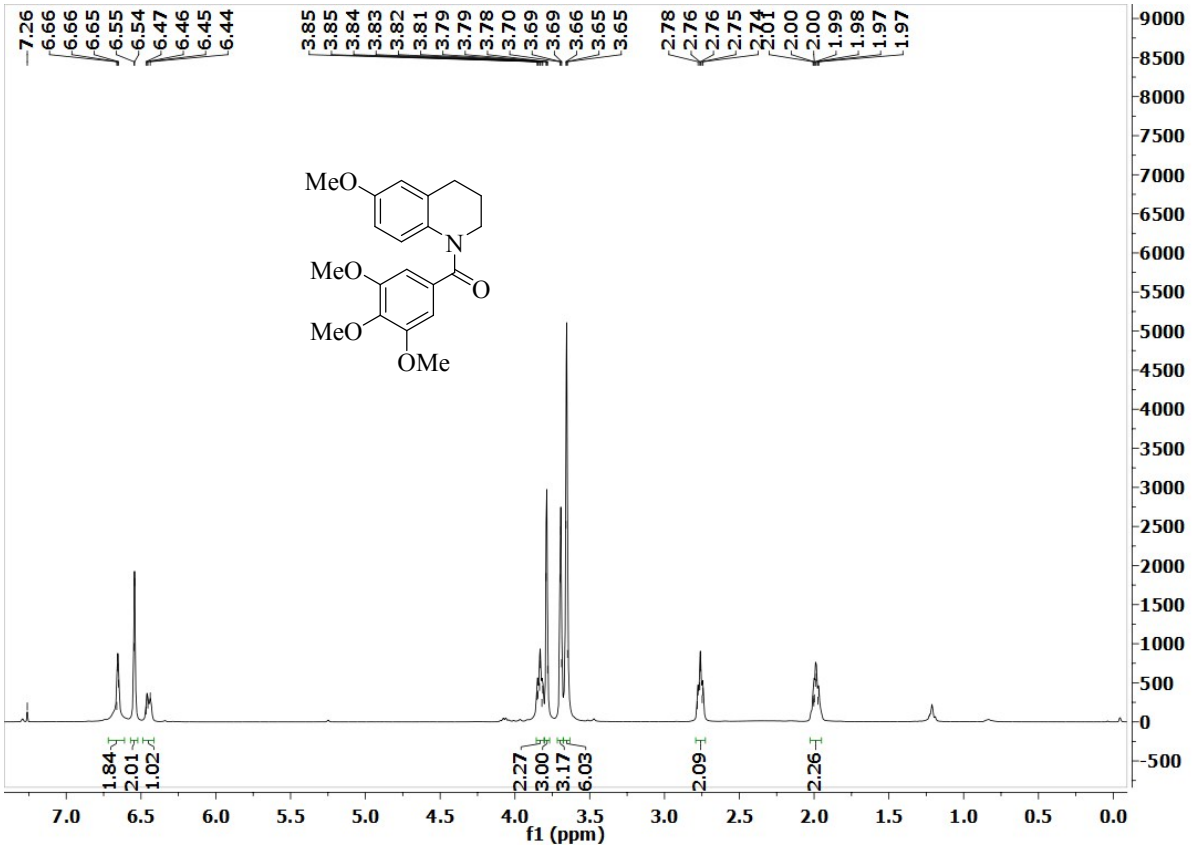


Figure S99: ^{1}H NMR Spectrum of **9** ($CDCl_3$, 400 MHz, 298 K)

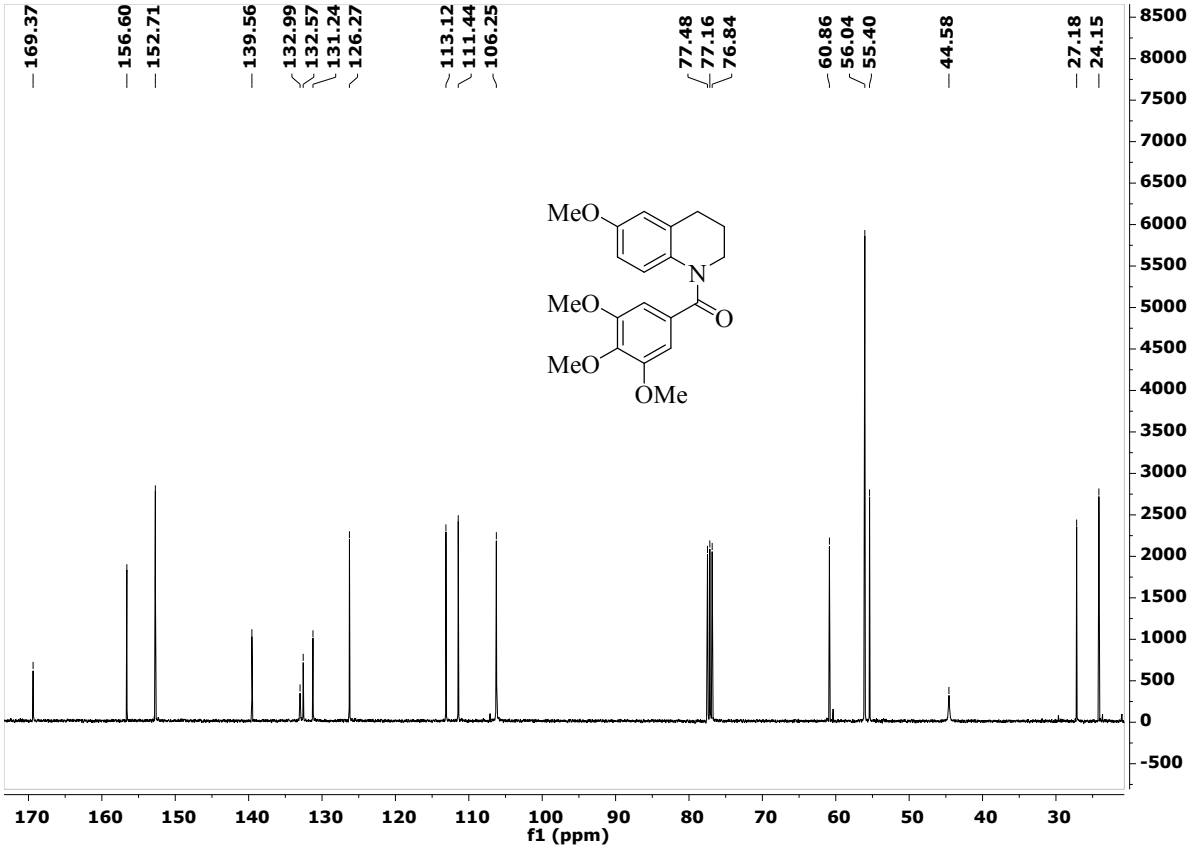


Figure S100: ^{13}C NMR Spectrum of **9** ($CDCl_3$, 101 MHz, 298 K)

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