Supporting Information

Tandem reductive alkylation of quinolines to functionalized tetrahydroquinolines enabled by HFIP

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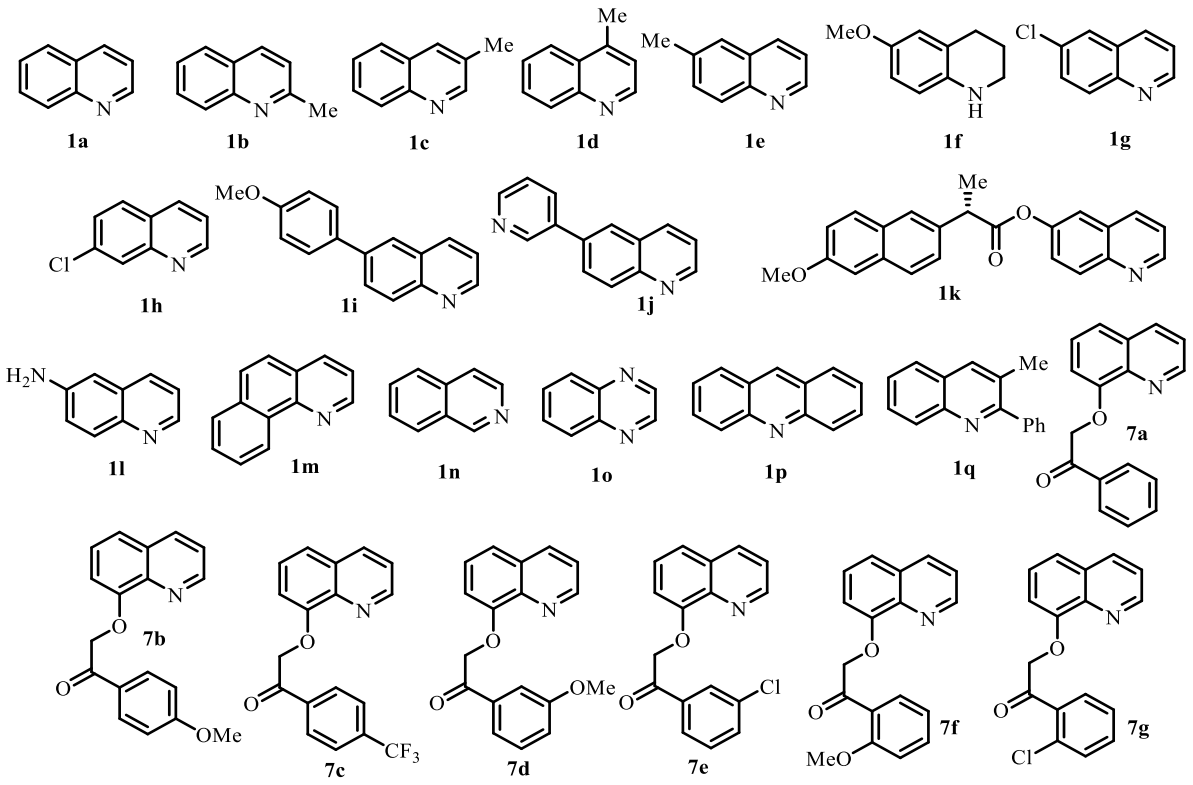
1. General Information

All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd., Finar Chemicals, and BLD Pharma directly used as received without any further purification unless otherwise mentioned. Hantzsch ester was synthesized according to the reported literature.[1] ^{1}H, ^{13}C, and ^{19}F NMR spectra of the compounds were measured in $CDCl_3$, 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 internal reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^{1}H) 7.26 ppm, δ (^{13}C) 77.16 ppm), were also used for calibration. Bruker Avance III 600, 500 and 400 spectrometers were used to record the NMR spectra. Chemical shifts (δ) values were reported in ppm and spin-spin coupling constant (J) were expressed in Hz, and other data were reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, p = pentate, sext = sextet, hept = heptane, 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 (UHPLC - Q-TOF - HRMS). Merck silica gel 60 - 120 was used for column chromatography. otherwise stated. All the final reactions were carried out under air and in preheated oil baths unless otherwise mentioned. Completion of reactions was examined by thin layer chromatography carried out on pre-coated Merck silica gel-60 F_{254} aluminium plates with ultraviolet light (UV) or iodine as visualizing agents.

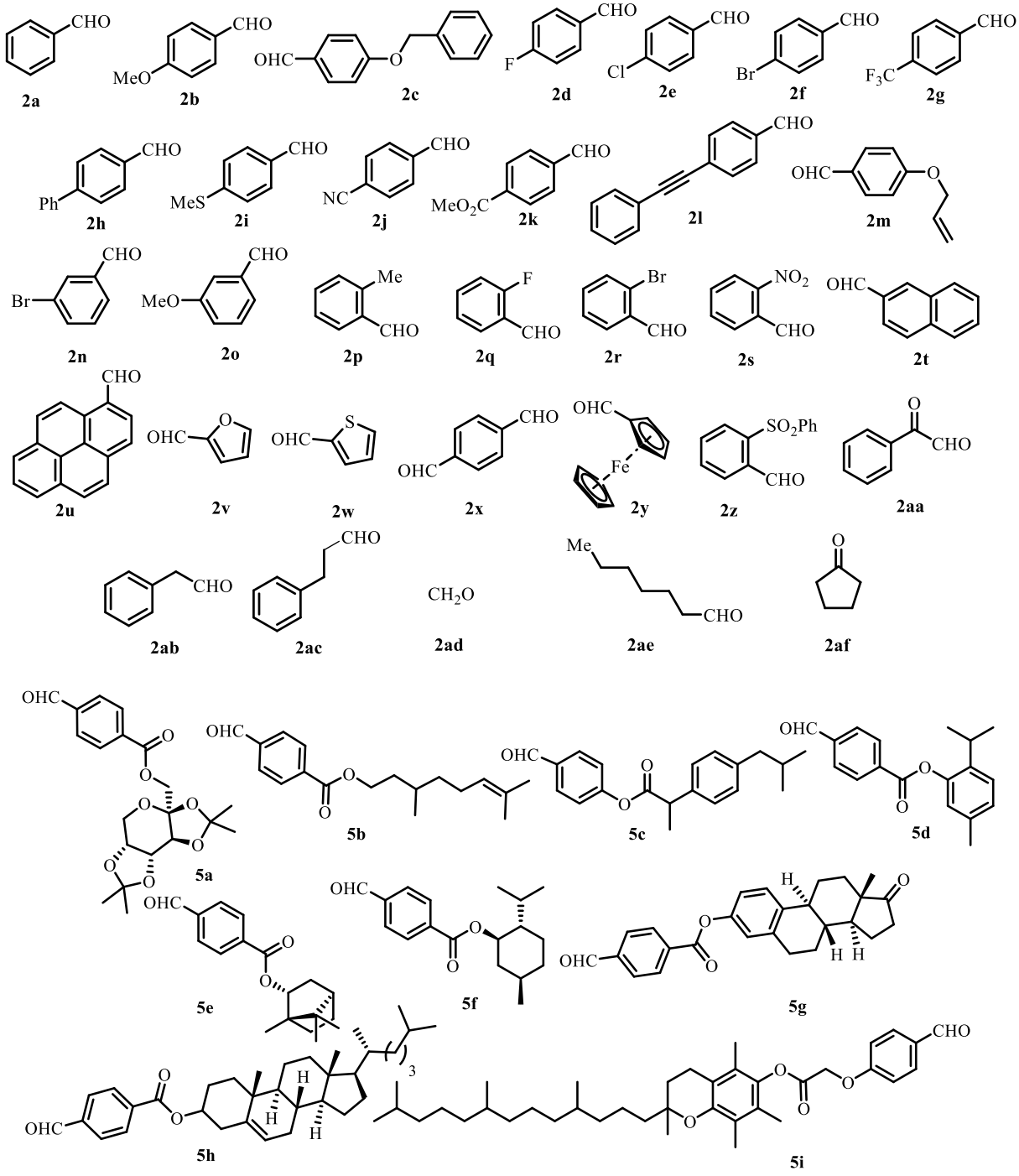
2. Synthesis of starting material

2.1 *N*-heteroarenes employed in the reaction:



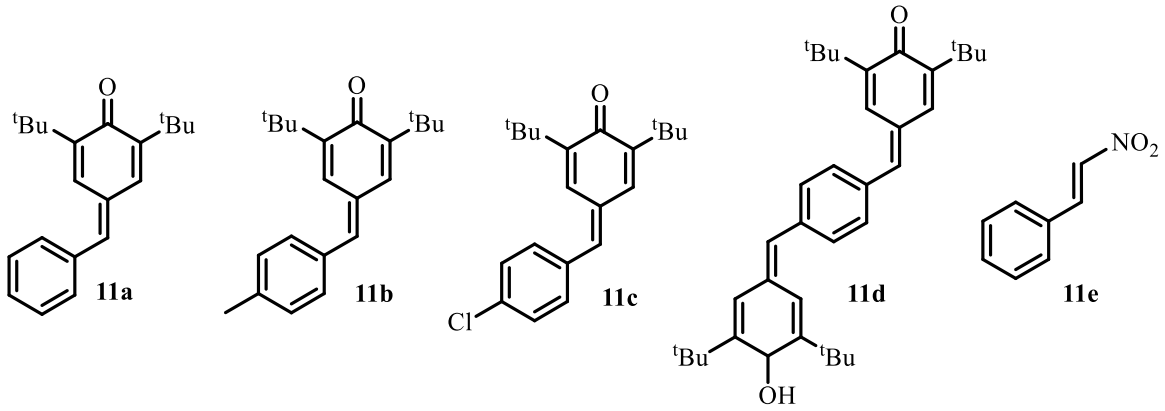
Compounds **1i**[2], **1j**[3], **1k**[4], **7a-7b**[5], **7d**[5], **7f**[5] are synthesized by known procedures.

2.2 Aldehydes and ketone employed in the reaction:



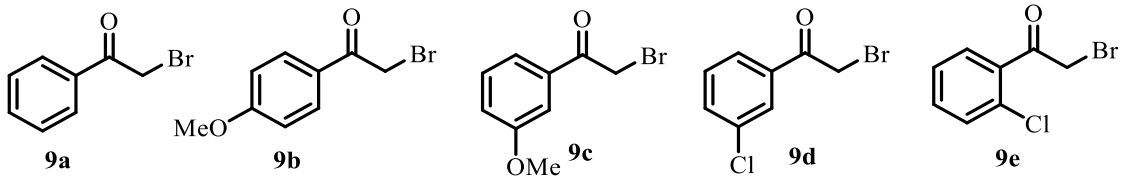
Compounds **2c**,[6] **2l**,[7] **2m**,[8] are synthesized by known procedure. The biologically relevant motifs containing aldehyde derivatives **5a**,[9] **5b,**[10] **5c,**[11] **5e**,[12] **5f**,[13] **5g**,[14] **5h**,[13], **5i**[15] were synthesized by the known procedure.

2.3 Alkylating precursors employed in the reaction:

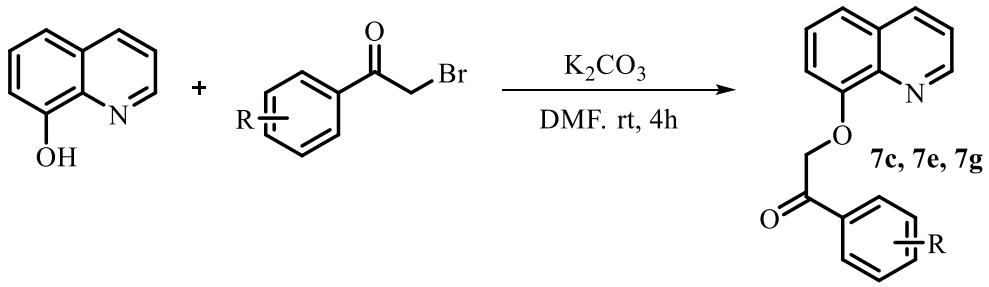


Compounds **11b-11c**[16]**, 11d**[17] are synthesized by known procedures.

2.4 α-bromoacetophenone employed in the reaction:



General procedure for the synthesis of 1-aryl-2-(quinolin-8-yloxy) ethanone



Scheme S1: Synthesis of 1-aryl-2-(quinolin-8-yloxy) ethenone derivatives

Experimental procedure: To a stirred solution of substituted Quinolin-8-o1 (1.7 mmol), K_2CO_3 (1.7 mmol) in dry DMF (5 mL) were stirred at room temperature for 10-15 mins. To this solution desired substituted 2-bromoacetophenone (1.7 mmol) in dry DMF (5 mL) was added in one portion. The resulting mixture was stirred at rt for 4 h (TLC monitoring) and then poured into ice-water (40 mL). The filtrate was concentrated and purified on a silica gel column (petroleum ether/ethyl acetate) to yield the 1-aryl-2-(quinolin-8-yloxy) ethanone **(7c, 7e, 7g)**. Compound **7c, 7e, 7g** was prepared for the first time following a known procedure.[5]

2-(quinolin-8-yloxy)-1-(4-(trifluoromethyl) phenyl) ethan-1-one (7c)

(Pale yellow solid, 78%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.93 (dd, J = 4.2, 1.7 Hz, 1H), 8.22 (d, J = 8.2 Hz, 2H), 8.13 (dd, J = 8.3, 1.6 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.45 – 7.43 (m,

2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.00 – 6.99 (m, 1H), 5.60 (s, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): *δ* 194.4, 153.7, 149.6, 140.3, 137.3, 136.2, 135.1 (q, *J* = 32.7 Hz), 129.8, 128.9, 126.5, 126.0 (q, *J* = 3.6 Hz), 124.5, 122.7, 122.0, 121.4, 72.5. $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$): *δ* -63.24. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{18}H_{13}F_3NO_2$:332.0893; found: 332.0892.

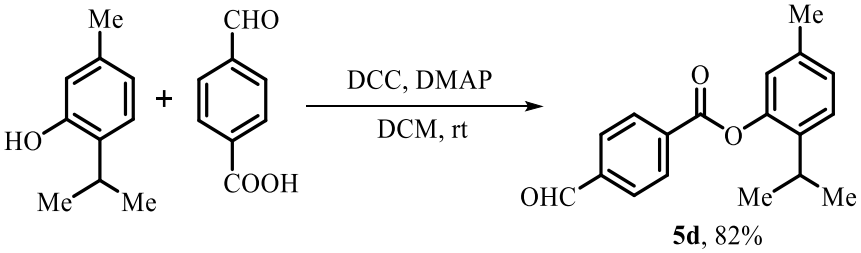
1-(3-chlorophenyl)-2-(quinolin-8-yloxy) ethan-1-one (7e)

(Pale yellow solid, 86%) ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 7.99 – 7.97 (m, 1H), 7.56 – 7.54 (m, 1H), 7.44 – 7.42 (m, 3H), 7.41 – 7.37 (m, 1H), 6.98 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.58 (s, 2H).$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): *δ* 193.7, 153.8, 149.6, 140.3, 136.14, 136.11, 135.3, 133.9, 130.3, 129.8, 128.5, 126.5, 121.9, 121.2, 110.5, 72.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{13}ClNO_2$:298.0630; found: 298.0629.

1-(2-chlorophenyl)-2-(quinolin-8-yloxy) ethan-1-one (7g)

(Pale yellow solid, 82%) ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.67 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.42 – 7.38 (m, 5H), 7.34 – 7.31 (m, 1H), 6.99 (dd, *J* = 6.6, 2.3 Hz, 1H), 5.56 (s, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): *δ* 197.2, 153.6, 149.4, 140.1, 136.1, 135.9, 132.7, 131.5, 130.6, 130.0, 129.6, 127.1, 126.4, 121.7, 120.9, 110.1, 73.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{13}ClNO_2$:298.0630; found: 298.0628.

Synthesis of 2-isopropyl-5-methylphenyl 4-formylbenzoate (5d)



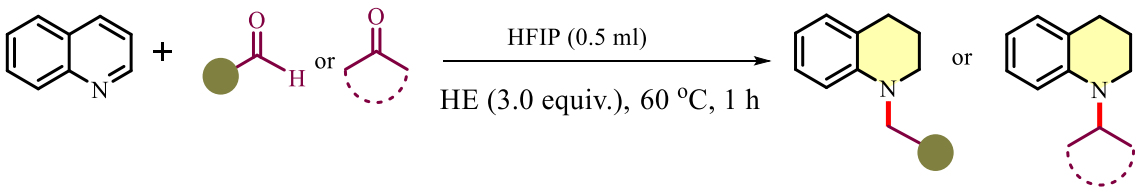
Scheme S2: Synthesis of 2-isopropyl-5-methylphenyl 4-formylbenzoate

Reaction conditions: To a 100 mL round-bottom flask were added 4-formylbenzoic acid (0.225 g, 1.5 mmol, 0.5 equiv), 2-isopropyl-5-methylphenol (0.225 g, 1.5 mmol, 0.5 equiv), *N*, *N*'-dicyclohexylcarbodiimide (0.340 g, 1.65 mmol, 0.55 equiv) and DMAP (0.018 g, 0.15 mmol, 0.05 equiv). DCM (15 mL) was then added at room temperature. The mixture was stirred at room temperature until the acid was consumed as monitored by TLC. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 10:1, v/v) to yield the desired compound **5d** as yellow oil (0.347 g, 82%). Compound **5d** was prepared for the first time following a known procedure.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.28 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.9 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.86 (s, 1H), 2.98 – 2.91 (m, 1H), 2.25 (s, 3H), 1.13 (d, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 191.6, 164.5, 148.0, 139.7, 137.1, 136.9, 134.6, 130.8, 129.8, 127.6, 126.7, 122.7, 27.4, 23.1, 20.9. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{18}H_{18}NaO_3$: 305.1149; found: 305.1163.

3. General procedure for synthesis of *N*-alkyl tetrahydroquinolines

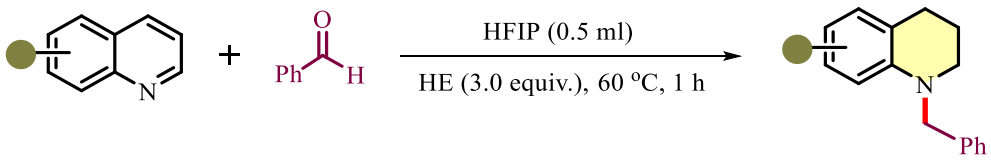
3.1. General procedure for synthesis of *N*- alkyl tetrahydroquinolines with different carbonyls (GP-1)



Scheme S3. Synthesis of *N*-alkyl tetrahydroquinolines

Reaction condition: A mixture of quinoline **1a** (0.5 mmol), aldehyde or cyclic ketone (0.5 mmol), HE (1.5 mmol) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 1 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

3.2. General procedure for synthesis of *N*-alkyl tetrahydroquinolines with substituted quinolines (GP-2)

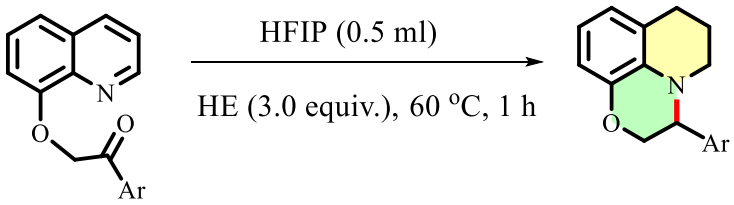


Scheme S4. Synthesis of *N*-alkyl tetrahydroquinolines

Reaction condition: A mixture of substituted quinolines (0.5 mmol), benzaldehyde (0.5 mmol), HE (3.0 equiv) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 1 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction,

all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

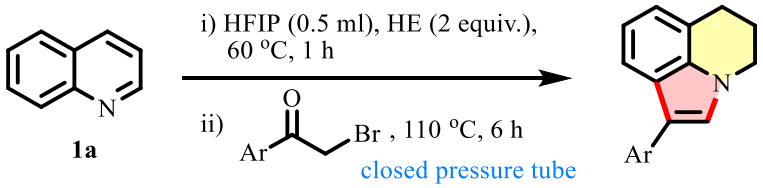
4. General procedure for synthesis of benzoxazine derivative (GP-3)



Scheme S5. Synthesis of benzoxazine derivatives

Reaction condition: A mixture of 1-aryl-2-(8-quinolinyloxy) ethanone (0.5 mmol), HE (3.0 equiv.) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 1 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

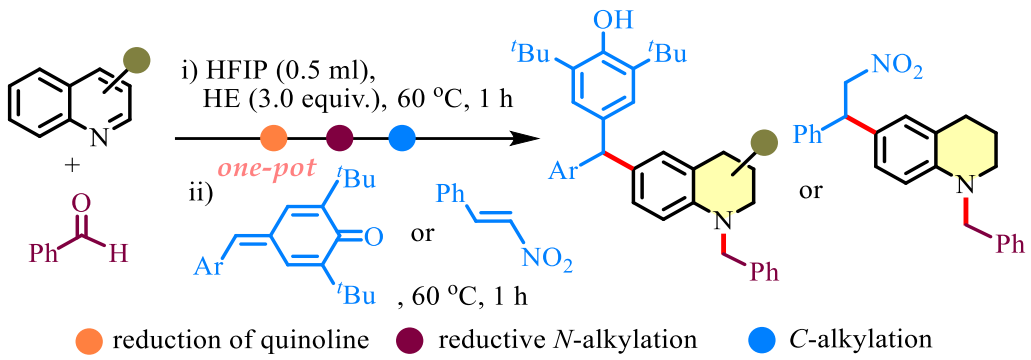
5. General procedure for synthesis of lilolidine derivative (GP-4)



Scheme S6. Synthesis of lilolidine derivative

Reaction condition: In the first step, a mixture of quinoline (0.5 mmol), HE (2.0 equiv.) and HFIP (0.5 ml) were added into a closed pressure tube (15 mL) equipped with stirring bar. The pressure tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 1 h. Then in the same pressure tube, substituted α-bromoacetophenone (0.5 mmol) were added and placed in a preheated oil bath at 110 °C with continuous stirring for 6 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

6. General procedure for synthesis of *C*-functionalized THQ derivatives (GP-5)



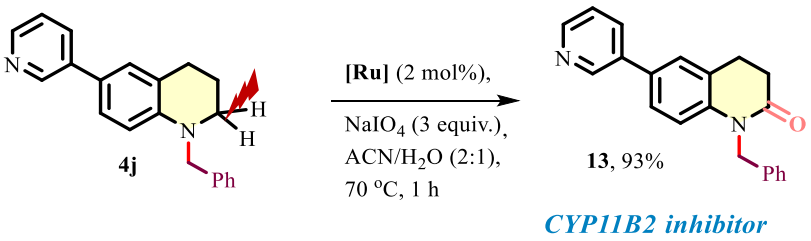
Scheme S7. Synthesis of *C*-functionalized THQ derivatives

Reaction condition: A mixture of substituted quinolines (0.5 mmol), benzaldehyde (0.5 mmol), HE (1.5 mmol) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 1 h. Then *p*-QMs or nitroolefins (0.5 mmol) was added in the same reaction tube at 60 °C with continuous stirring for 1 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

7. Post synthetic modification

(a) selective α-methylene oxidation of *N*-alkylated tetrahydroquinolines

Synthesis of CYP11B2 inhibitor (13)

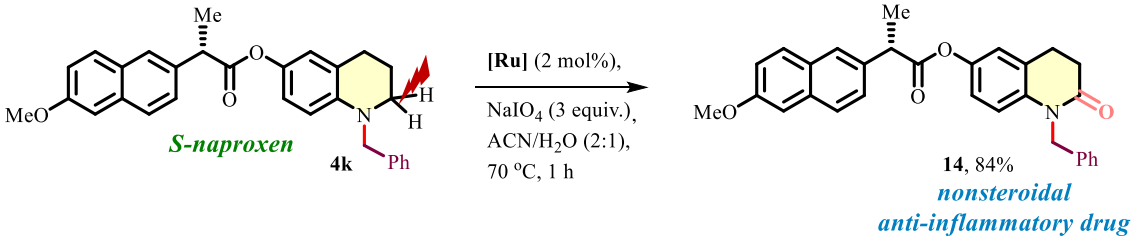


Scheme S8. Synthesis of CYP11B2 inhibitor (13)

Reaction condition: $NaIO_4$ (1.5 mmol, 3 equiv.) was taken in a screw-capped reaction tube and dissolved it in water (1 mL). Then **4j** (0.5 mmol, 1 equiv.), **[Ru-2]**[3] (2 mol%), and acetonitrile (2 mL) were added to the reaction tube and stirred the reaction mixture at 70 °C for 1 hour. After the completion of the reaction as confirmed by TLC, the reaction mixture was worked up with CH_2Cl_2 and water. The organic layer was separated and the aqueous layer was again extracted with CH_2Cl_2 (two times, 5 mL). The combined organic layer was washed with brine solution (8 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated under a vacuum. The crude product was purified through silica-gel column chromatography to get the pure product **13** as white solid (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, J = 2.4 Hz, 1H), 8.55 (d, J = 6.4 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.40 – 7.39 (m, 1H), 7.35 – 7.30 (m, 4H), 7.26 – 7.23 (m, 3H), 6.98 (d, J = 8.4 Hz, 1H), 5.22 (s, 2H), 3.09 – 3.05 (m, 2H), 2.86 – 2.83 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 170.5, 148.4, 148.0, 140.0, 136.9, 135.8, 134.0, 132.5, 128.9, 127.3, 127.2, 126.6, 126.5, 126.2, 123.7, 116.3, 46.2, 31.9, 25.8. Spectral data is in accordance to the reported literature. [3]

Synthesis of nonsteroidal anti-inflammatory drug (14)



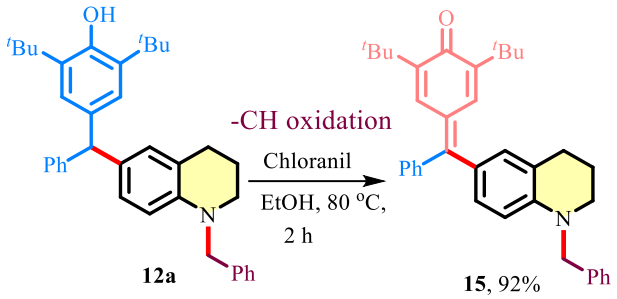
Scheme S9. Synthesis of nonsteroidal anti-inflammatory drug (14)

Reaction condition: $NaIO_4$ (1.5 mmol, 3 equiv.) was taken in a screw-capped reaction tube and dissolved it in water (1 mL). Then **4k** (0.5 mmol, 1 equiv.), **[Ru-2]**[3] (2 mol%), and acetonitrile (2 mL) were added to the reaction tube and stirred the reaction mixture at 70 °C for 1 hour. After the completion of the reaction as confirmed by TLC, the reaction mixture was worked up with CH_2Cl_2 and water. The organic layer was separated and the aqueous layer was again extracted with CH_2Cl_2 (two times, 5 mL). The combined organic layer was washed with brine solution (8 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated under a vacuum. The crude product was purified through silica-gel column chromatography to get the pure product **14** as pale-yellow oil (84%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 – 7.71 (m, 3H), 7.47 – 7.46 (m, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 7.17 – 7.13 (m, 4H), 6.81 – 6.78 (m, 2H), 6.71 (dd, J = 8.8, 2.6 Hz, 1H), 5.13 (s, 2H), 4.06 (q, J = 7.1 Hz, 1H), 3.92 (s, 3H), 2.92 – 2.90 (m, 2H), 2.77 – 2.74 (m, 2H), 1.67 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 173.5, 170.4, 157.9, 146.1, 137.7, 136.8, 135.1, 133.9, 129.4, 129.1, 128.9, 127.6, 127.5, 127.3, 126.5, 126.24, 126.16, 121.0, 120.1, 119.3, 116.4, 105.7, 55.5, 46.4, 45.6, 31.6, 25.6, 18.6. Spectral data is in accordance to the reported literature. [3]

(b) Functionalization of (12a)

Synthesis of 4-((1-benzyl-1,2,3,4-tetrahydroquinolin-6-yl) (phenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (15)

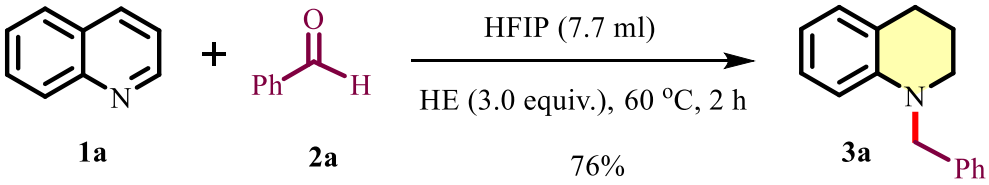


Scheme S10. Functionalization of (12a)

Experimental procedure: A mixture of **12a** (0.193 mmol, 1.0 equiv), chloranil (1.5 equiv), EtOH (5 mL) were added into a round bottom flask (50 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 80 ºC with continuous stirring for 2 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography to yield the desired compound **15** as orange solid (92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.37 (m, 4H), 7.31 (d, J = 8.2 Hz, 2H), 7.27 – 7.26 (s, 3H), 7.19 (d, J = 8.1 Hz, 2H), 7.01 (s, 1H), 6.91 (s, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.46 (d, J = 8.6 Hz, 1H), 4.52 (s, 2H), 3.44 – 3.42 (m, 2H), 2.78 (t, J = 6.1 Hz, 2H), 2.06 – 2.01 (m, 2H), 1.30 (s, 9H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 186.0, 158.1, 146.1, 136.6, 134.2, 133.1, 132.9, 132.8, 132.5, 129.2, 129.1, 128.4, 128.1, 128.0, 127.9, 121.6, 110.1, 54.6, 50.2, 35.4, 35.3, 29.8, 29.6, 28.1, 22.2. Spectral data is in accordance to the reported literature. [3]

8. Gram scale reaction



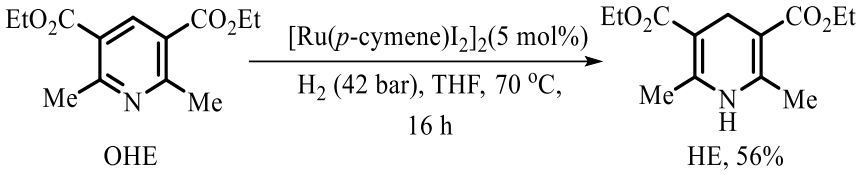
Scheme S11: Gram scale reaction

Experimental procedure: A mixture of **1a** (1.0 g, 7.7 mmol), **2a** (1.0 equiv), HE (3.0 equiv) and HFIP (7.7 mL) were added into a round bottom flak (100 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 ºC with continuous stirring for 2 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified

through silica gel column chromatography to get pure compound as yellow oil of **3a** (1.309 g, 76%).

9. Recovery of Hantzsch-1,4-dihydropyridine (HE)

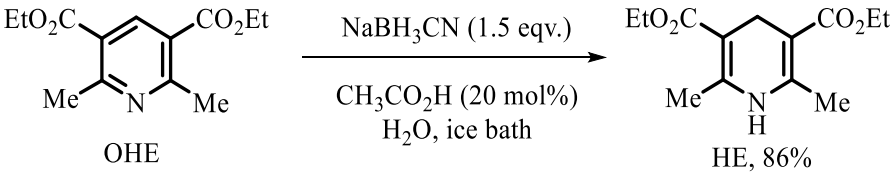
Route-A:



Scheme S12: Hydrogenation of oxidised Hantzsch ester

Experimental procedure:[18] A mixture of [Ru(*p*-cymene)I_2]$_2$ (10 mg, 0.01 mmol) and OHE (50.0 mg, 0.2 mmol) in THF (10 mL) was stirred at room temperature for 10 min in glove box, then the mixture was loaded to an autoclave. The hydrogenation was performed at 70 °C under H_2 (42 bar) for 16 h. After carefully release of the hydrogen, the autoclave was opened. Isolated yield (yellow solid, 27 mg, 56%).

Route-B



Scheme S13: Reduction of oxidised Hantzsch ester to Hantzsch-1,4-dihydropyridine ester

Experimental procedure:[19] In a 50 mL round bottom flask, OHE (1.0 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 $NaBH_3CN$ (0.294 gm, 1.2 equiv.) 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: (0.830 g, 86%).

10. Mechanistic and Kinetic studies

10.1 Interaction of HFIP with quinoline

To probe the nature of binding interaction with HFIP and quinoline, the combination of quinoline and HFIP (molar ratio 1:5) in $CDCl_3$ at rt has been examined. The study was initiated with 1:5 mixture of quinoline **1a**: HFIP in $CDCl_3$, and record the ^{1}H NMR (Figure S1 and Figure S2). A notable deshielded shift of the hydroxyl group signal in HFIP from 3.22 to 5.91

ppm upon mixing with **1a** was observed, indicating a strong hydrogen bonding between the -OH of HFIP and *N*-atom of quinoline moiety.

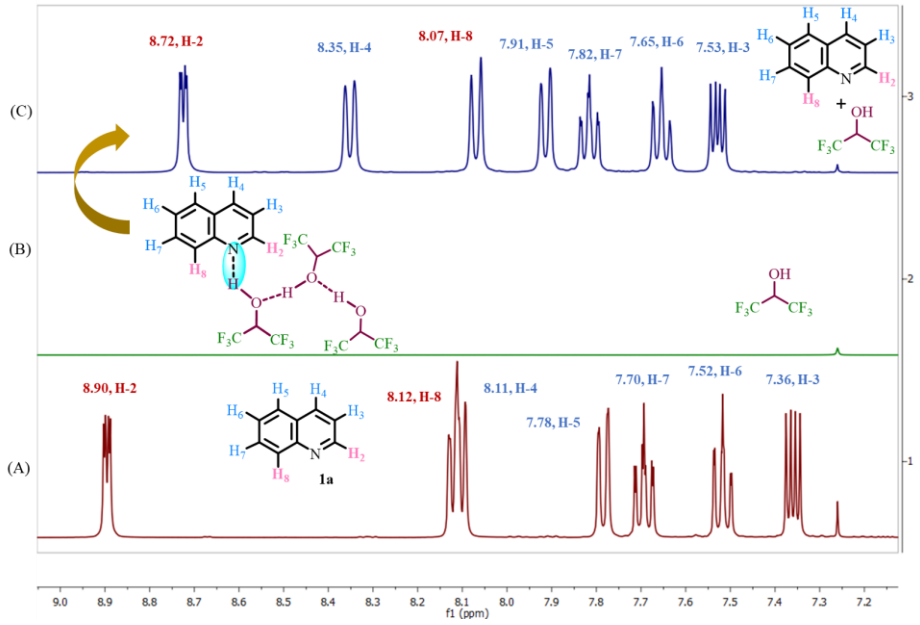


Figure S1: H-bonding between the substrate **1a** and HFIP (zoom-in region of the aromatic protons). (A) ^{1}H NMR of **1a** (10 mg, 0.077 mmol), (B) ^{1}H NMR of HFIP, (C) after addition of HFIP into the solution of **1a** in $CDCl_3$ (molar ratio 1:5) at 298 K.

Furthermore, the chemical shift of the aromatic proton H_2 and H_8 of **1a** adjacent to the quinyl nitrogen shifted significantly from 8.90 to 8.72 ppm, and 8.12 to 8.07 ppm, respectively, upon addition of HFIP, while the chemical shifts of the aromatic protons H_3, H_4, H_5, H_6, and H_7 of the **1a** shifted from 7.36, 8.11, 7.78, 7.52 and 7.70 ppm to 7.53, 8.35, 7.91, 7.65 and 7.82 ppm, respectively. Such a noteworthy change in the ^{1}H NMR pattern of the quinyl region is consistent with the existence of a strong hydrogen bonding between **1a** and HFIP.

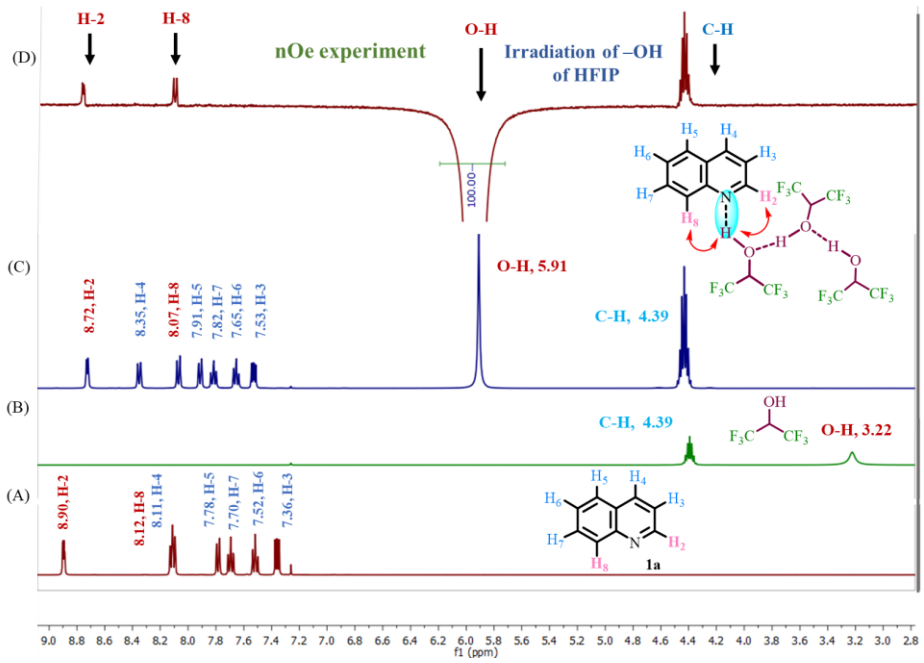


Figure S2: H-bonding between the substrate **1a** and HFIP. (A) ^{1}H NMR of **1a**, (B) ^{1}H NMR of HFIP, (C) after addition of HFIP into the solution of **1a** in $CDCl_3$ (molar ratio 1:5) and (D) 1D NOE of (C) at 298 K.

Then 1D Nuclear Overhauser effect (NOE) experiment was carried out in order to gain insight the dipolar spatial interactions between protons nuclei spatially close to each other. Upon irradiating the hydroxyl proton signal of a 1:5 mixture of **1a**: HFIP at 5.91 ppm, clear interaction of the hydroxyl peak of HFIP with the neighbouring protons was observed with the aromatic proton H_2 signal at 8.72 ppm and H_8 signal at 8.07 ppm. These correlation study further suggests that strong indication of the presence of a strong hydrogen bonding between **1a** and HFIP.

10.2 Interaction of HFIP with aldehyde

In order to illustrate the interaction of HFIP and aldehyde, we performed the ^{1}H, ^{13}C NMR, and IR spectroscopic experiments by using HFIP and freshly distilled 4-trifluoromethyl benzaldehyde, respectively. While two equivalents of HFIP was added to 4-trifluoromethyl benzaldehyde in $CDCl_3$, a downfield shift of nearly 0.52 ppm for hydroxyl peak of HFIP in ^{1}H NMR and 2.76 ppm for carbonyl signal of aldehyde in ^{13}C NMR were observed (Figure S3, S4).

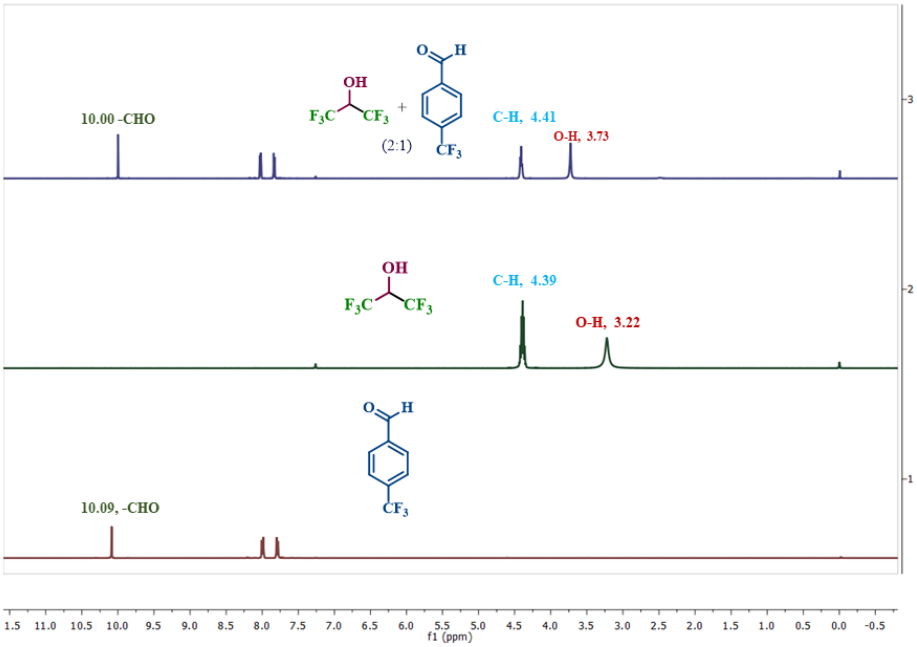


Figure S3: ^{1}H NMR spectra of freshly distilled 4-trifluoromethylbenzaldehyde (10 mg, 0.077 mmol), HFIP (19 mg, 0.114 mmol), and the mixture of 4-trifluoromethylbenzaldehyde and HFIP (molar ratio 1:2) in $CDCl_3$ at 298 K.

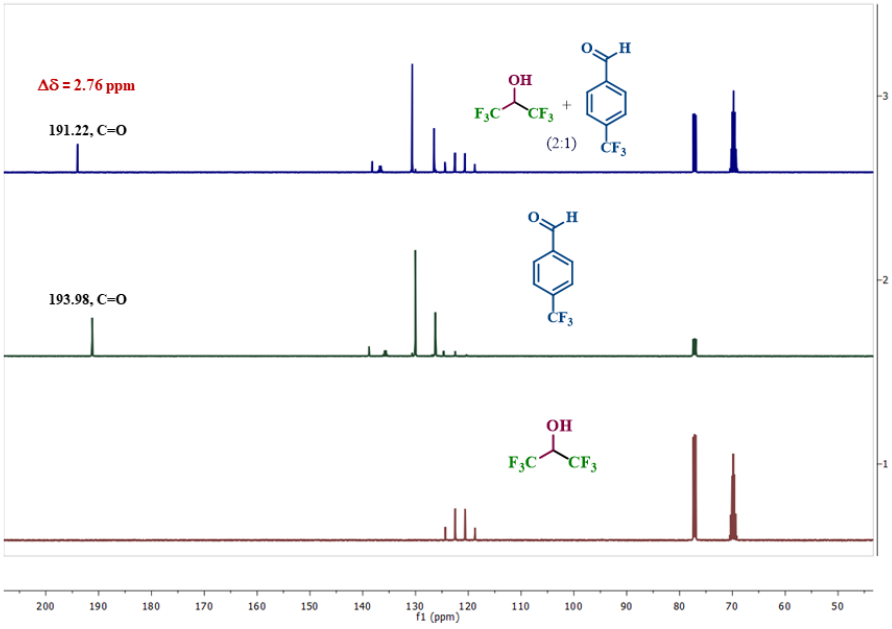


Figure S4: ^{13}C NMR spectra of 4-trifluoromethylbenzaldehyde (10 mg, 0.077 mmol), HFIP (19 mg, 0.114 mmol), and the mixture of 4-trifluoromethylbenzaldehyde and HFIP (molar ratio 1:2) in $CDCl_3$ at 298 K.

In IR, the carbonyl value shifted to a lower wave number from 1708.03 cm^{-1} to 1694.12 cm^{-1} after mixing with HFIP at room temperature (Figure S5). Approximately 14 cm^{-1} lower wave number has been observed for the carbonyl group in a mixture compared to free aldehyde, which supports hydrogen bonding interaction between aldehyde and HFIP (Figure S5). A

downfield shift for hydroxyl peak of HFIP in ^{1}H NMR and ensuing downfield shift for carbonyl in aldehyde in ^{13}C NMR supports weak hydrogen bonding interaction with aldehyde and HFIP. It has been further reinforced by using IR spectroscopic experiments in the solid-state.

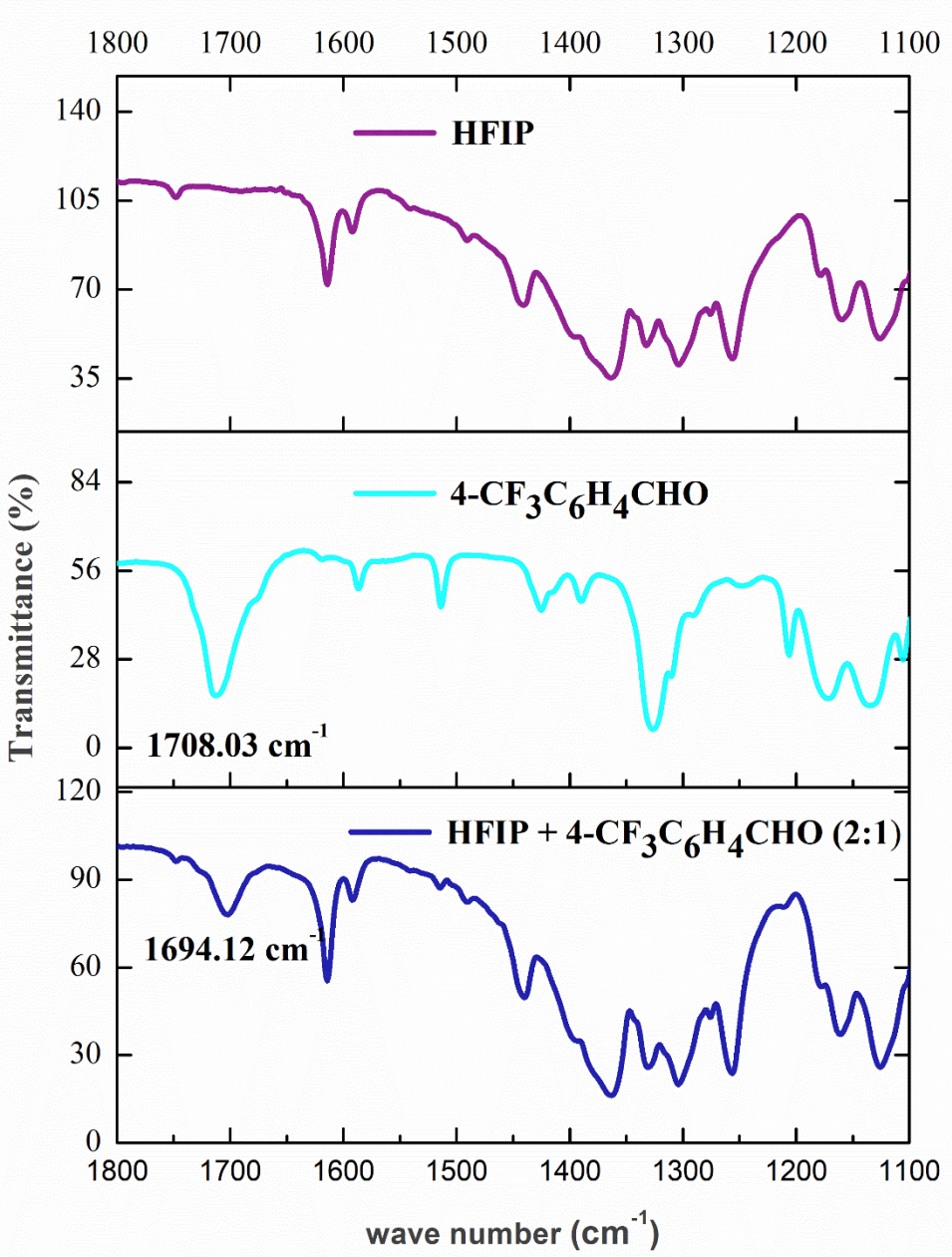


Figure S5: IR spectroscopy to support the interaction of 4-trifluoromethyl benzaldehyde and HFIP.

10.3 Interaction of HFIP with Hantzsch ester

To examine the interaction of HFIP and Hantzsch ester, we have checked the ^{1}H NMR with the combination of Hantzsch ester and HFIP (molar ratio 1:2) in $CDCl_3$ at rt. whereas no characteristic –OH proton signal was shifted while mixing with HFIP (Figure S6).

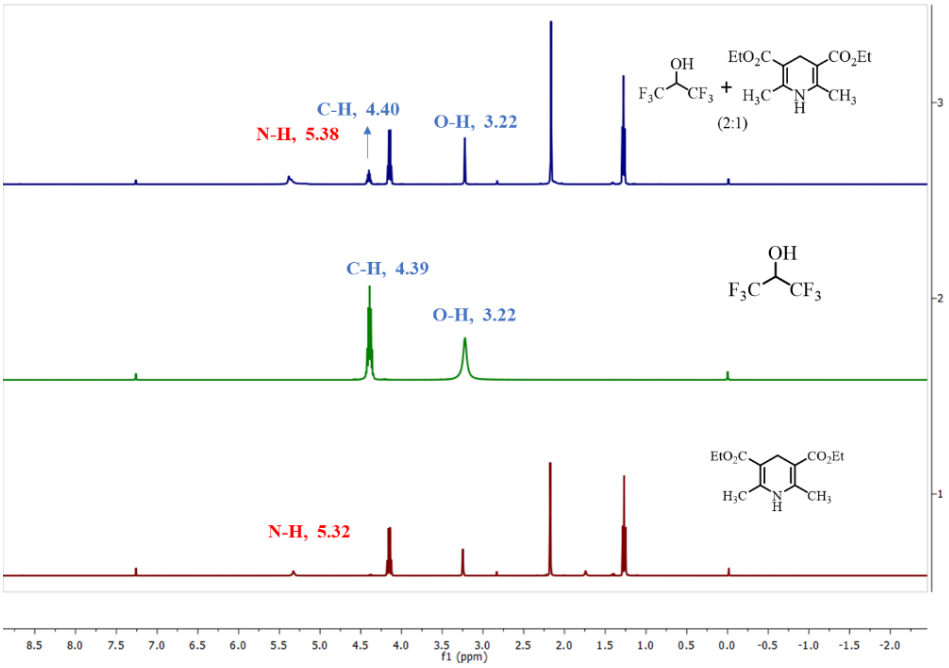


Figure S6: ^{1}H NMR spectra of HFIP (26.4 mg, 0.158 mmol), Hantzsch ester (20 mg, 0.079 mmol), and the mixture of HFIP and Hantzsch ester (molar ratio 2:1) in $CDCl_3$ at 298 K.

However, in ^{13}C NMR, the carbonyl value in Hantzsch ester was shifted downfield from 168.22 to 168.91 ppm ($\Delta\delta$ = 0.7 ppm). A weak hydrogen bonding interaction may exist between Hantzsch ester and –OH of HFIP. (Figure S7).

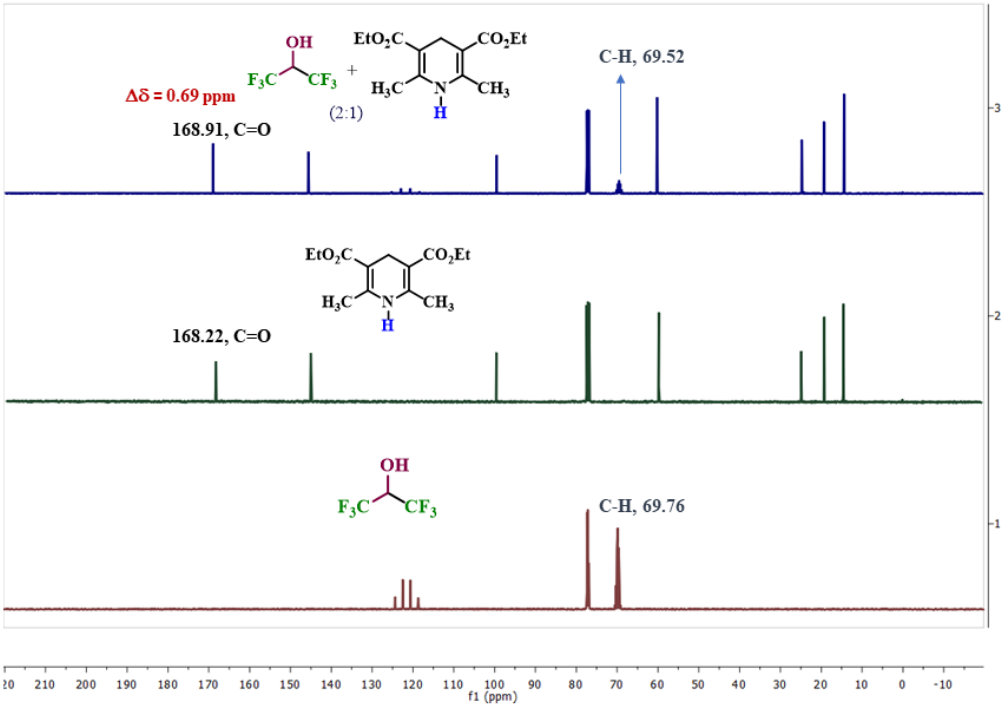


Figure S7. ^{13}C spectra of HFIP (26.4 mg, 0.158 mmol), Hantzsch ester (20 mg, 0.079 mmol), and the mixture of HFIP and Hantzsch ester (molar ratio 2:1) in $CDCl_3$ at 298 K.

10.4 Interaction of THQ with Hantzsch ester

To examine the interaction of THQ and Hantzsch ester, we have checked the ^{1}H NMR with the combination of Hantzsch ester and HFIP (molar ratio 1:1) in $CDCl_3$ at rt. It was found that there is no hydrogen-bonding interaction exist between Hantzsch ester and THQ (Figure S8).

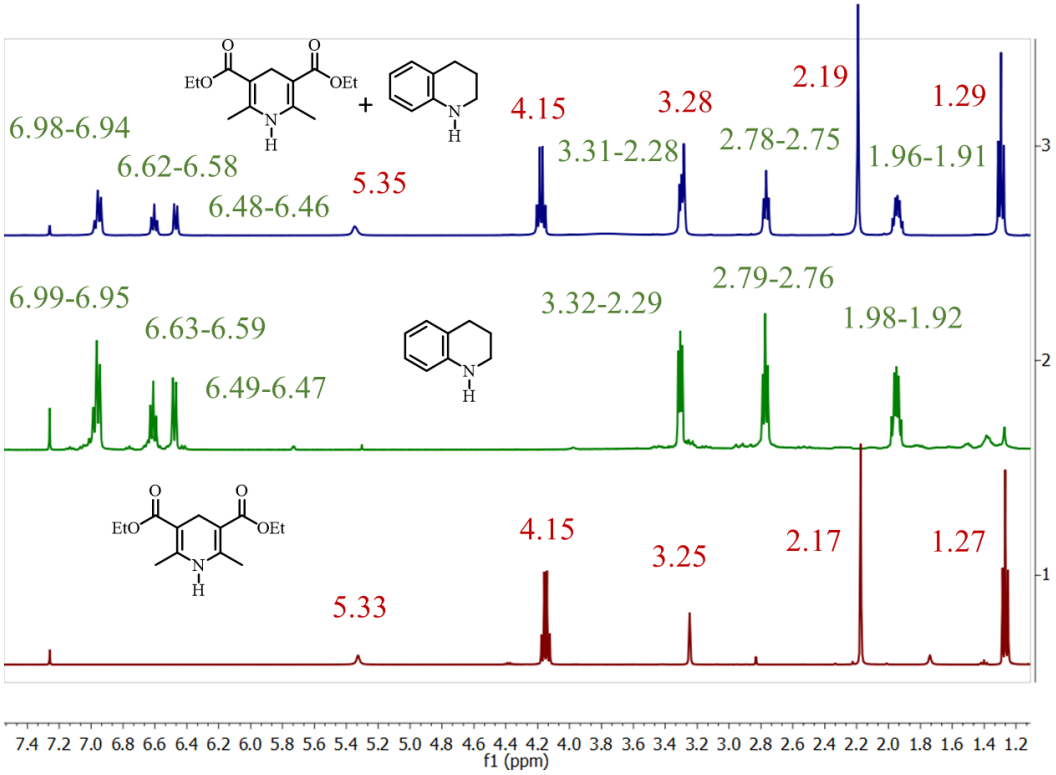
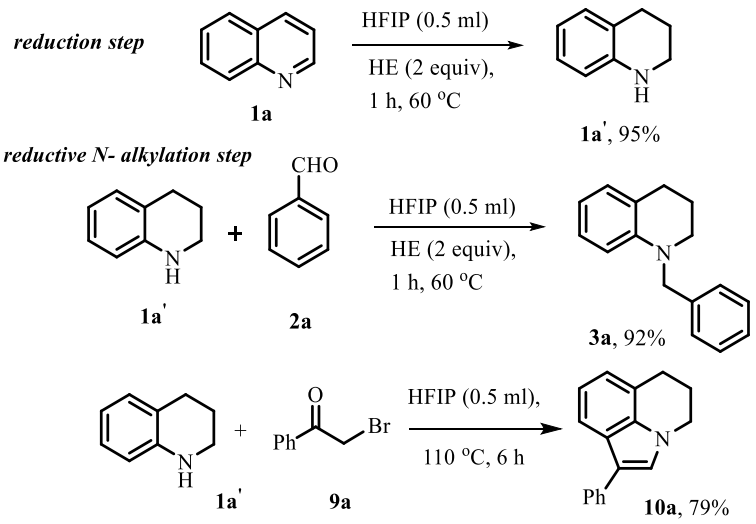


Figure S8. Interaction between the HE and THQ (1:1) in $CDCl_3$ (^{1}H NMR).

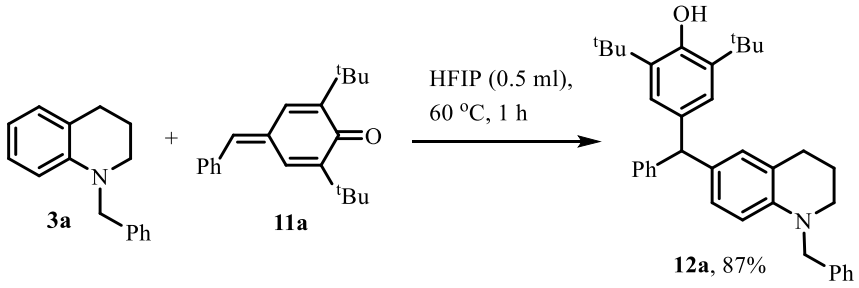
10.4 Proof of 1,2,3,4-tetrahydroquinoline as the intermediate

To gain more insight into the reaction pathway, we performed the reaction with quinoline **1a** (0.065 g, 0.5 mmol, 1.0 equiv.), HE (0.253 g, 1.0 mmol, 2.0 equiv.), and HFIP (0.5 mL) at 60 °C for 1 h. As expected tetrahydroquinoline **1a'** obtained in 95% yield (0.063 g). For the subsequent step the reaction was conducted with the formed **1a'** (0.063 g, 0.47 mmol, 1.0 equiv.), and aldehyde **2a** (0.050 g, 0.47 mmol, 1.0 equiv), HE (0.119 g, 0.47 mmol, 1.0 equiv), and HFIP (0.5 mL) at 60 °C for 1 h under identical conditions the desired product **3a** was obtained in 92% yield (0.098 g). From the following experimental observation, one can infer that the reaction is involved in two steps i) reduction of quinoline to THQ and ii) then reductive *N*-alkylation with the aldehyde. Then the reaction was examined with the THQ **1a'** (0.047 mmol, 1.0 equiv.), α-bromoacetophenone **9a** (0.094 g, 0.047 mmol, 1.0 equiv.), and HFIP (0.5 mL) at 110 °C for 6 h, the desired product **10a** was obtained in 79% yield (0.087 g). It suggests that THQs **1a'** is as an intermediate in the process (Scheme S14).



Scheme S14: Proof of 1,2,3,4-tetrahydroquinoline as the intermediate

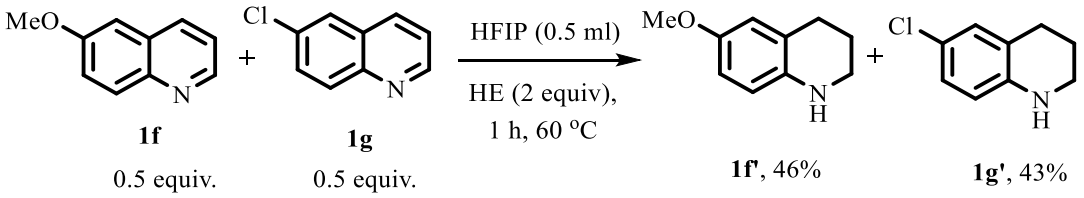
Likewise, when the reaction was performed with **3a** (0.104 g, 0.47 mmol, 1.0 equiv), *p*-QM **11a** (0.138 g, 0.47 mmol, 1.0 equiv.) at 60 °C for 1 h under standard conditions, the desired product **12a** was obtained in 87% yield (0.212 g) (Scheme S15). This indicates that compound **3a** is an intermediate for the *C*-functionalized *N*-alkylated THQ **12a**.



Scheme S15: Proof of 1,2,3,4-tetrahydroquinoline as the intermediate

10.5 Electronic effect for the 1st step

To know the electronic effect of the substrate in the 1st step, we performed the reaction with **1f** (0.040 g, 0.25 mmol, 0.5 equiv.), **1g** (0.041 g, 0.25 mmol, 0.5 equiv.), HE (0.253 g, 1.0 mmol, 2.0 equiv.), and HFIP (0.5 mL) at 60 °C for 1 h. As expected, the desired hydrogenated product **1f'** and **1g'** was obtained in 46% yield and 43% yield, respectively. Since a comparable yield was obtained in both the cases, one can infer that there is no considerable electronic effect in the reduction step (Scheme S16).

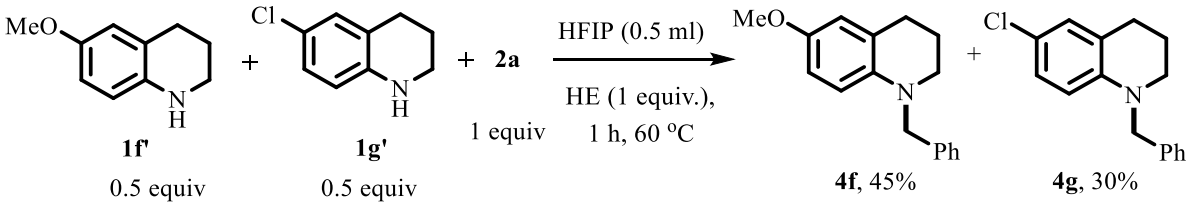


Scheme S16: Electronic effect of the quinoline hydrogenation step

10.6 Electronic effect for the 2nd step

To know the electronic effect in the 2nd step, the reaction was initiated with equal ratio of C6-substituted THQ **1f'** and **1g'**, respectively, in the presence of **2a** under identical conditions. A competitive reaction suggested that the electron-donating group (-OMe) on the THQ enhanced the rate of the reaction with respect to an electron-withdrawing group (-Cl) (Scheme S17).

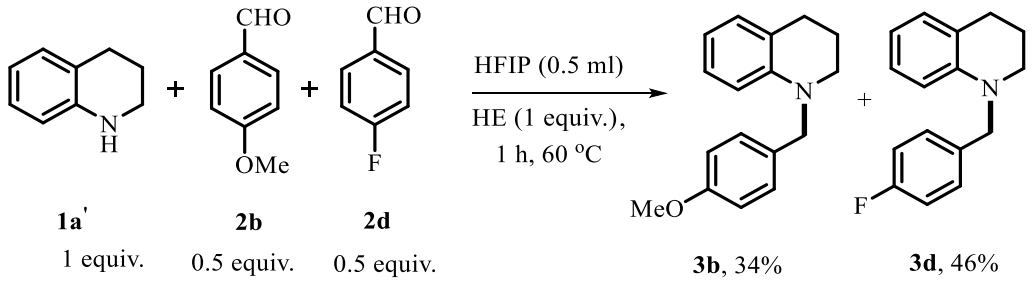
Reaction conditions: The 6-methoxy tetrahydroquinoline **1f'** (0.041 g, 0.25 mmol, 0.5 equiv), 6-chloro tetrahydroquinoline **1g'** (0.042 g, 0.25 mmol, 0.5 equiv), aldehyde **2a** (0.053 g, 0.5 mmol, 1.0 equiv.), HE (0.127 g, 0.5 mmol, 1.0 equiv), and HFIP (0.5 mL) at 60 °C for 1 h, the product **4f** and **4g** was obtained in 45% yield (0.057 g) and 30% yield (0.039 g), respectively.



Scheme S17: Competitive reaction with substituted quinoline.

Likewise, the reaction was examined with equal ratio of 4-methoxy benzaldehyde **2b** and 4-fluoro benzaldehyde **2d** in the presence of THQ **1a'** under identical conditions. A competitive reaction suggested that electron-withdrawing group (*p*-F) on the benzaldehyde enhanced the rate of the reaction with respect to an electron-donating group (*p*-OMe) (Scheme S18).

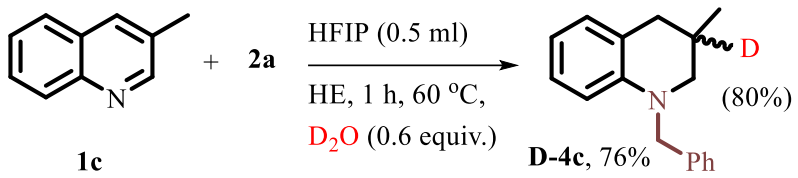
Reaction conditions: Tetrahydroquinoline **1a'** (0.067 g, 0.5 mmol, 1.0 equiv.), 4-methoxy benzaldehyde **2b** (0.034 g, 0.25 mmol, 0.5 equiv), 4-fluoro benzaldehyde **2d** (0.031 g, 0.25 mmol, 0.5 equiv), HE (0.127 g, 0.5 mmol, 1.0 equiv), and HFIP (0.5 mL) at 60 °C for 1 h, the product **3b** and **3d** was obtained in 34% yield (0.043 g) and 46% yield (0.056 g), respectively.



Scheme S18. Competitive reaction with aldehyde

10.7 Deuterium-labelling experiment

In order to locate the hydridic proton and acidic proton in the *N*-alkyl-THQ product, we have performed the catalytic experiment with 3-methyl quinoline **1c** in the presence of D_2O. The outcome demonstrated that the deuterium atom was incorporated at the C3 position of *N*-alkyl-THQ derivative **4c** (Scheme S19).



Scheme S19: Deuterium-labelled experiment with 3-methyl quinoline

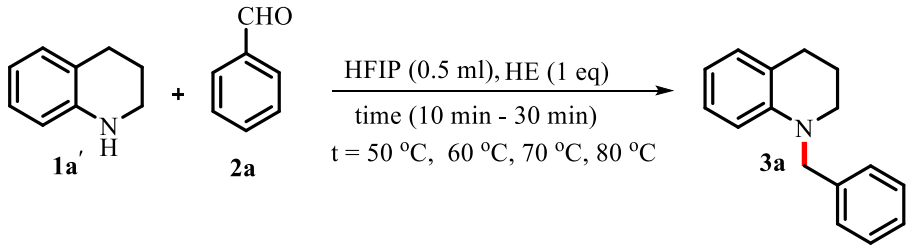
Reaction conditions: In a reaction tube (15 mL), 3-methyl quinoline **1c** (0.071 g, 0.5 mmol), **2a** (0.053 g, 0.5 mmol), HE (0.76 g, 1.5 mmol, 3 equiv.), HFIP (0.5 ml), and D_2O (0.6 equiv.) were charged, then sealed with screw-cap, the resulting solution was heated at 60 °C for 1 h under standard conditions, the desired product **D-4c** was obtained in 76% yield.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 10H, **4c + D-4c**), 6.98 – 6.95 (m, 4H, **4c + D-4c**), 6.57 (t, J = 7.3 Hz, 2H, **4c + D-4c**), 6.50 (d, J = 8.5 Hz, 2H, **4c + D-4c**), 4.47 (s, 4H, **4c + D-4c**), 3.30 – 3.26 (m, 2H, **4c + D-4c**), 3.05 – 3.00 (m, 2H, **4c + D-4c**), 2.84 – 2.79 (m, 2H, **4c + D-4c**), 2.53 – 2.47 (m, 2H, **4c+ D-4c**), 2.23–2.12 (m, 1H, **3ca**) 1.05 (s, 6H, **4c + D-4c**).

10.8 Eyring Studies

An oven dried reaction tube, **1a'** (0.066 g, 0.5 mmol, 1.0 equiv.), aldehyde **2a** (0.053 g, 0.5 mmol, 1.0 equiv.), and HE (0.126 g, 0.5 mmol, 1 equiv.) in HFIP (0.5 mL) were taken. The reaction tube was properly closed and placed in a pre-heated oil bath at respective temperature for the specified times. The measure yield of product was plotted against to obtain the slope which gave the rate constant for each case.



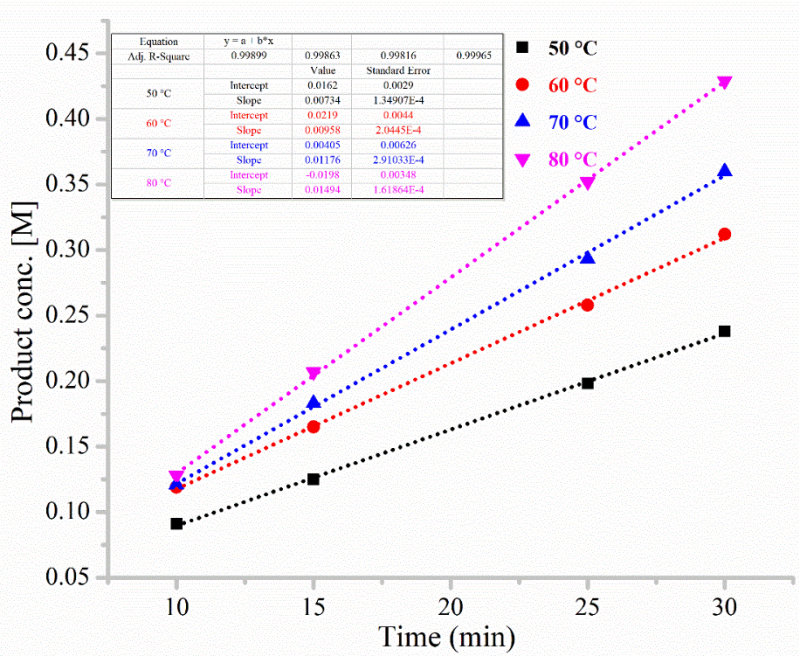


Figure S9: Concentration [Product] *vs* time plot at different temperatures.

Temp	1/T	*k*	ln(*k*/T)
323 K (50 °C)	0.003095	7.34×10^{-3}	-10.69
333 K (60 °C)	0.003003	9.58×10^{-3}	-10.45
343 K (70 °C)	0.002915	11.76×10^{-3}	-10.28
353 K (80 °C)	0.002832	14.94×10^{-3}	-10.07

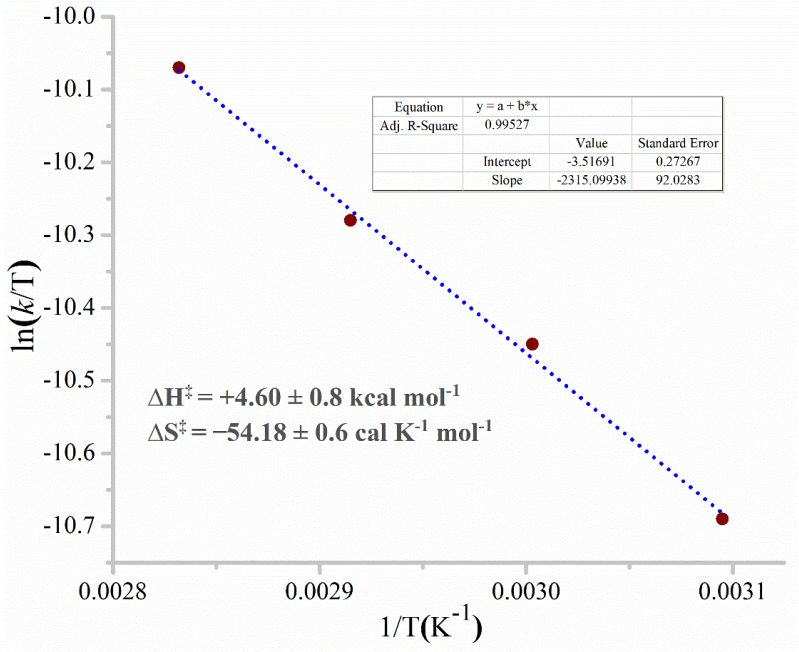


Figure S9: Arrhenius-Eyring plot

Activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$) values were obtained from the slope and intercept of plots of ln(*k*/*T*) vs 1/*T* (Figure S12) using the following equation:

$$\mathbf{\ln(k/T) = -\Delta H^{\#}/R.(1/T) + \ln k_B/h + \Delta S^{\#}/R}$$

where k_B = Boltzmann constant, R = universal gas constant, and h = Planck's constant.

From the plot of ln(*k*/*T*) vs 1/*T*,

$$\text{Slope} = -2315.1$$

$$\textit{Or}, -\Delta H^{\ddagger}/R = -2315.1$$

$$\textit{Or}, \Delta H^{\ddagger} = -(-2315.1) \times (1.987 \text{ cal } K^{-1}mol^{-1})$$

$$= 4600.1 \text{ cal } mol^{-1}$$

$$= 4.60 \text{ kcal } mol^{-1}$$

And,

$$\text{Intercept} = -3.51$$

$$\textit{Or}, \ln (k_B/h) + \Delta S^{\#}/R = -3.51$$

$$\textit{Or}, \ln (1.38 \times 10^{-23} \text{ J } K^{-1}/6.626 \times 10^{-34} \text{ J s}) + \Delta S^{\#}/1.987 \text{ cal } K^{-1} \text{ mol}^{-1} = -3.51$$

$$\textit{Or}, \ln (2.083 \times 10^{10} \text{ } K^{-1} \text{ } s^{-1}) + \Delta S^{\#}/1.987 \text{ cal } K^{-1} \text{ mol}^{-1} = -3.51$$

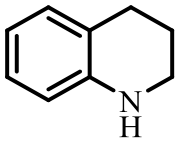
$$\textit{Or}, 23.76 + \Delta S^{\#}/1.987 \text{ cal } K^{-1} \text{ mol}^{-1} = -3.51$$

$$\textit{Or}, \Delta S^{\#}/1.987 \text{ cal } K^{-1} \text{ mol}^{-1} = -27.27$$

$$\textit{Or}, \Delta S^{\#} = -54.18 \text{ cal } K^{-1} \text{ mol}^{-1}$$

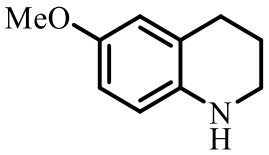
11. Analytical data of the products

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



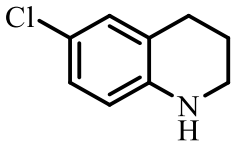
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 – 6.95 (m, 2H), 6.61 (t, J = 8.1 Hz, 1H), 6.48 (d, J = 7.9 Hz, 1H), 3.32 – 3.29 (m, 2H), 2.77 (t, J = 6.4 Hz, 2H), 1.98 – 1.92 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.9, 129.6, 126.8, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3. Spectral data is in accordance with the literature. [19]

6-methoxy-1,2,3,4-tetrahydroquinoline (1f')



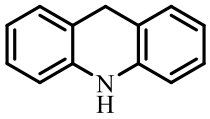
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.61 – 6.56 (m, 2H), 6.46 (d, J = 8.5 Hz, 1H), 3.73 (s, 3H), 3.01 (brs, 1H), 3.27 – 3.24 (m, 2H), 2.76 (t, J = 6.5 Hz, 2H), 1.96-1.90 (m, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.0, 139.0, 123.0, 115.7, 115.0, 113.0, 55.9, 42.5, 27.3, 22.6. Spectral data is in accordance to the reported literature. [19]

6-chloro-1,2,3,4-tetrahydroquinoline (1g')



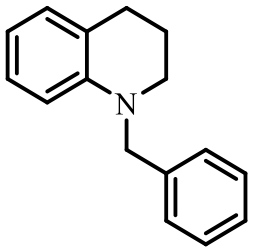
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1H), 6.38 (d, J = 8.0 Hz, 1H), 3.76 (brs, 1H), 3.30 – 3.27 (m, 2H), 2.73 (t, J = 6.4 Hz, 2H), 1.95 – 1.89 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 143.4, 129.1, 126.6, 122.9, 121.2, 115.2, 41.9, 27.0, 21.8 Spectral data is in accordance to the reported literature. [19]

9,10-dihydroacridine (1p')



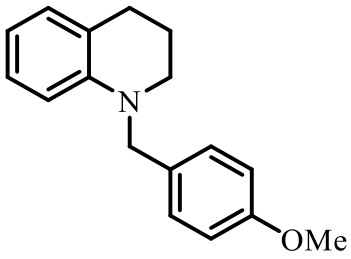
White solid (0.087 g, 96%); M.p: 171~173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 – 7.05 (m, 4H), 6.86 – 6.82 (M, 2H), 6.65 (dd, J = 7.8, 1.2 Hz, 2H), 5.93 (brs, 1H), 4.04 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 140.3, 128.7, 127.1, 120.8, 120.2, 113.6, 31.5. Spectral data is in accordance to the reported literature. [20]

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



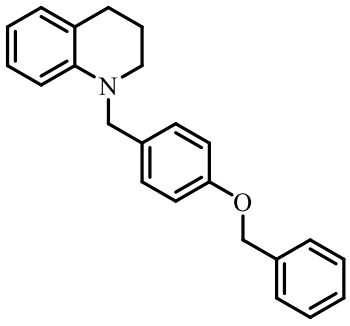
By following the **GP-1**, the title compound **3a** was isolated as light-yellow oil (0.104 g, 93%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.21 (m, 5H), 6.98 – 6.95 (m, 2H), 6.57 (t, J = 7.3 Hz, 1H), 6.50 (d, J = 8.3 Hz, 1H), 4.47 (s, 2H), 3.37 – 3.35 (m, 2H), 2.82 (t, J = 6.2 Hz, 2H), 2.03 – 1.99 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 145.8, 139.1, 129.1, 128.7, 127.3, 126.9, 126.7, 122.4, 116.0, 111.1, 55.3, 50.0, 28.4, 22.5. Spectral data is in accordance to the reported literature. [15]

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



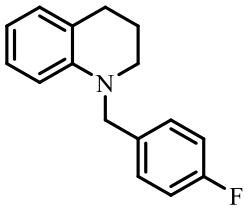
By following the **GP -1**, the title compound **3b** was isolated as light-yellow oil (0.109 g, 86%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, J = 8.5 Hz, 2H), 7.00 – 6.97 (m, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.59 – 6.54 (m, 2H), 4.42 (s, 2H), 3.80 (s, 3H), 3.34 (t, J = 5.6 Hz, 2H), 2.82 (t, J = 6.3 Hz, 2H), 2.03 – 1.98 (m, 2H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.7, 145.8, 131.0, 129.1, 127.9, 127.3, 122.4, 115.9, 114.1, 111.1, 55.4, 54.7, 49.8, 28.4, 22.5. Spectral data is in accordance to the reported literature. [15]

1-(4-(benzyloxy) benzyl)-1,2,3,4-tetrahydroquinoline (3c)



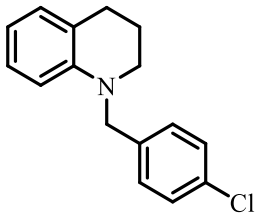
By following the **GP -1**, the title compound **3c** was isolated as light-yellow oil (0.137 g, 83%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.28 (m, 5H), 7.16 – 7.14 (m, 2H), 6.97 – 6.89 (m, 4H), 6.57 – 6.50 (m, 2H), 4.99 (s, 2H), 4.37 (s, 2H), 3.30 – 3.28 (m, 2H), 2.77 (t, J = 6.3 Hz, 2H), 1.98 – 1.93 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 157.8, 145.7, 137.2, 131.2, 129.1, 128.6, 128.0, 127.9, 127.5, 127.2, 122.3, 115.9, 115.0, 111.1, 70.1, 54.6, 49.7, 28.3, 22.4. Spectral data is in accordance to the reported literature. [15]

1-(4-fluorobenzyl)-1, 2, 3, 4-tetrahydroquinoline (3d)



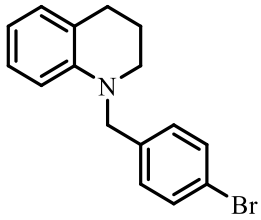
By following the **GP-1**, the title compound **3d** was isolated as light-yellow oil (0.115 g, 95%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 2H), 7.01 – 6.96 (m, 4H), 6.58 (t, J = 7.3 Hz, 1H), 6.47 (d, J = 8.5 Hz, 1H), 4.43 (s, 2H), 3.34 (t, J = 5.6 Hz 2H), 2.81 (t, J = 6.3 Hz, 2H), 2.03 – 1.98 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.9 – 161.0 (C-F, $^1J_{C\text{-}F}$ = 244.5 Hz), 145.6, 134.6 (C-F, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.2, 128.2 (C-F, $^3J_{C\text{-}F}$ = 7.9 Hz), 127.3, 122.5, 116.2, 115.6 - 115.4 (C-F, $^2J_{C\text{-}F}$ = 21.5 Hz, 111.1, 54.8, 50.0, 28.3, 22.5. ^{19}F NMR (471 MHz, $CDCl_3$): δ -116.46. Spectral data is in accordance to the reported literature. [15]

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



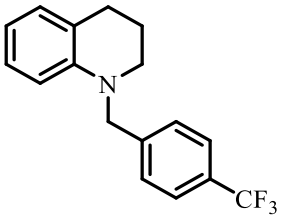
By following the **GP-1**, the title compound **3e** was isolated as light-yellow oil (0.120 g, 93%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.00 – 6.97 (m, 2H), 6.60 (d, J = 7.3 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 4.44 (s, 2H), 3.36 (t, J = 5.6 Hz, 2H), 2.83 (t, J = 6.3 Hz, 2H), 2.05 – 2.01 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.5, 137.6, 132.5, 129.2, 128.8, 128.1, 127.3, 122.5, 116.3, 111.1, 54.8, 50.1, 28.3, 22.5. Spectral data is in accordance to the reported literature. [15]

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



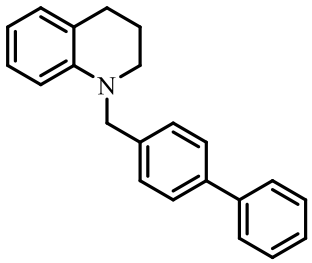
By following the **GP-1**, the title compound **3f** was isolated as light-yellow oil (0.134 g, 89%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 6.99 – 6.95 (m, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 8.1 Hz, 1H), 4.41 (s, 2H), 3.34 (t, J = 5.6 Hz, 2H), 2.82 (t, J = 6.2 Hz, 2H), 2.04 – 1.99 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 145.5, 138.2, 131.8, 129.2, 128.5, 127.3, 122.5, 120.6, 116.3, 111.1, 54.9, 50.1, 28.3, 22.5. Spectral data is in accordance to the reported literature. [15]

1-(4-(trifluoromethyl) benzyl)-1,2,3,4-tetrahydroquinoline (3g)



By following the **GP-1**, the title compound **3g** was isolated as light-yellow oil (0.138 g, 95%) solid using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.04 – 6.99 (m, 2H), 6.64 (t, J = 7.2 Hz, 1H), 6.45 (d, J = 8.2 Hz, 1H), 4.55 (s, 2H), 3.42 – 3.40 (m, 2H), 2.87 (t, J = 6.2 Hz, 2H), 2.07 (p, J = 6.1 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.3, 143.5, 129.2, 127.3, 126.9, 125.6 (q, J = 3.7 Hz), 122.5, 116.4, 111.0, 55.1, 50.2, 28.2, 22.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.28. Spectral data is in accordance to the reported literature. [15]

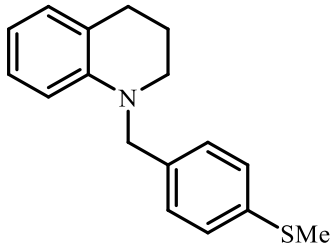
1-([1,1'-biphenyl]-4-ylmethyl)-1,2,3,4-tetrahydroquinolines (3h)



By following the **GP -1**, the title compound **3h** was isolated as light-yellow oil (0.130 g, 87 %) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 – 7.56 (m, 4H), 7.46 – 7.43 (s, 2H), 7.37 – 7.35 (s, 3H), 7.02 – 7.01 (m, 2H), 6.62 – 6.56 (m, 2H), 4.54 (s, 2H), 3.42 – 3.41 (m, 2H), 2.87 – 2.85 (m, 2H),

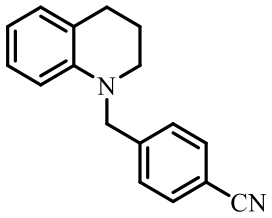
2.08 – 2.05 (m, 2H).$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 145.7, 141.1, 139.9, 138.2, 129.2, 128.9, 127.5, 127.35, 127.28, 127.2, 122.4, 116.0, 111.1, 55.1, 50.1, 28.4, 22.5. Spectral data is in accordance to the reported literature. [15]

1-(4-(methylthio) benzyl)-1,2,3,4-tetrahydroquinoline (3i)



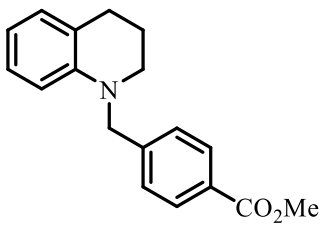
By following the **GP-1**, the title compound **3i** was isolated as light-yellow oil (0.110 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 – 7.17 (m, 4H), 6.97 – 6.94 (m, 2H), 6.56 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.6 Hz, 1H), 4.41 (s, 2H), 3.33 (t, J = 5.7 Hz, 2H), 2.80 (t, J = 6.3 Hz, 2H), 2.45 (s, 3H), 2.02 – 1.97 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 145.6, 136.6, 136.1, 129.1, 127.32, 127.28, 127.26, 122.4, 116.0, 111.1, 54.9, 50.0, 28.3, 22.5, 16.3. Spectral data is in accordance to the reported literature. [15]

4-((3,4-dihydroquinolin-1(2H)-yl) methyl) benzonitrile (3j)



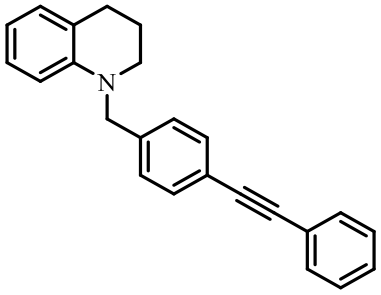
By following the **GP-1**, the title compound **3j** was isolated as white solid (0.119 g, 96%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80).m.p. 62-64°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.37 (d, J = 8.2 Hz, 1H), 4.52 (s, 2H), 3.38 (t, J = 5.6 Hz 2H), 2.85 (t, J = 6.3 Hz, 2H), 2.05 (p, J = 6.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 145.1, 132.6, 129.3, 127.34, 127.33, 122.6, 119.0, 116.7, 111.0, 110.8, 55.4, 50.4, 28.2, 22.5. Spectral data is in accordance to the reported literature. [15]

Methyl 4-((3, 4-dihydroquinolin-1(2H)-yl) methyl) benzoate (3k)



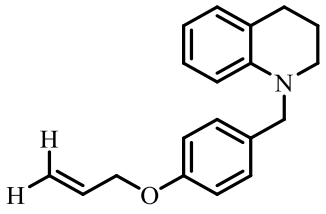
By following the **GP -1**, the title compound **3k** was isolated as light-yellow oil (0.131 g, 93%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.00 – 6.95 (m, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.41 (d, J = 8.2 Hz, 1H), 4.52 (s, 2H), 3.90 (s, 3H), 3.39 – 3.37 (m, 2H), 2.83 (t, J = 6.2 Hz, 2H), 2.06 – 2.01 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.2, 145.4, 144.8, 130.1, 129.2, 128.9, 127.3, 126.6, 122.5, 116.3, 111.0, 55.4, 52.2, 50.3, 28.3, 22.5. IR (KBr, selected band): 1722.60 cm^{-1}. Spectral data is in accordance to the reported literature. [15]

1-(4-(phenylethynyl) benzyl)-1,2,3,4-tetrahydroquinoline (3l)



By following the **GP -1**, the title compound **3l** was isolated as yellow oil (0.142 g, 88%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.51 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.35 – 7.31 (m, 3H), 7.25 – 7.23 (m, 2H), 6.99 – 6.96 (m, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 4.47 (s, 2H), 3.37 – 3.35 (m, 2H), 2.82 (t, J = 6.2 Hz, 2H), 2.02 (p, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.6, 139.6, 132.0, 131.7, 129.2, 128.5, 128.3, 127.3, 126.7, 123.4, 122.4, 121.8, 116.2, 111.1, 89.5, 89.2, 55.3, 50.1, 28.3, 22.5. IR (KBr, selected band): 2217.5 cm^{-1}. Spectral data is in accordance to the reported literature. [15]

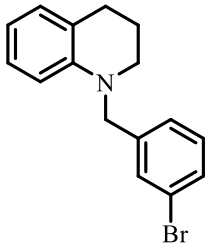
1-(4-(allyloxy) benzyl)-1, 2, 3, 4-tetrahydroquinoline (3m)



By following the **GP -1**, the title compound **3m** was isolated as light-yellow oil (0.117 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.59 – 6.53 (m, 2H), 6.09 – 6.02 (m, 1H), 5.41 (d, J = 17.2 Hz, 1H), 5.29 (m, 1H), 4.52 (d, J = 5.2 Hz, 2H), 4.41 (s, 2H), 3.35 – 3.32 (m, 2H), 2.81 (t, J = 5.8 Hz, 2H), 2.02 – 1.98 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.7, 145.8, 133.5, 131.2, 129.1, 127.9, 127.3,

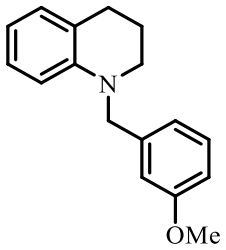
122.4, 117.8, 115.9, 115.0, 111.1, 69.0, 54.7, 49.8, 28.4, 22.5. Spectral data is in accordance to the reported literature. [15]

1-(3-bromobenzyl)-1,2,3,4-tetrahydroquinoline (3n)



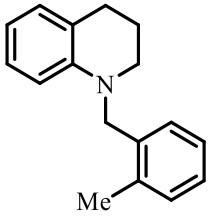
By following the **GP -1**, The title compound **3n** was isolated as light-yellow oil (0.134 g, 89%,) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.36 – 7.33 (m, 1H), 7.18 – 7.12 (m, 2H), 6.98 – 6.94 (m, 2H), 6.58 (t, J = 7.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 4.40 (s, 2H), 3.34 – 3.31 (m, 2H), 2.80 (t, J = 6.2 Hz, 2H), 2.00 (p, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.4, 141.8, 130.3, 130.0, 129.6, 129.2, 127.3, 125.2, 122.9, 122.5, 116.3, 111.1, 55.1, 50.2, 28.2, 22.5. Spectral data is in accordance to the reported literature. [15]

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



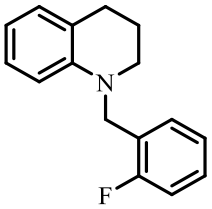
By following the **GP -1**, the title compound **3o** was isolated as light-yellow oil (0.111 g, 88 %) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (t, J = 7.8 Hz, 1H), 6.96 – 6.94 (m, 2H), 6.84 (d, J = 7.6 Hz, 1H), 6.81 (s, 1H), 6.76 – 6.74 (m, 1H), 6.55 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.6 Hz, 1H), 4.41 (s, 2H), 3.73 (s, 3H), 3.34 – 3.32 (m, 2H), 2.79 (t, J = 6.3 Hz, 2H), 1.98 (p, J = 6.1 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 160.0, 145.7, 140.9, 129.7, 129.0, 127.2, 122.3, 118.9, 116.0, 112.4, 112.0, 111.1, 55.3, 55.2, 50.0, 28.3, 22.5. Spectral data is in accordance to the reported literature. [3]

1-(2-methylbenzyl)-1,2,3,4-tetrahydroquinoline (3p)



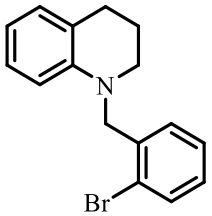
By following the **GP -1**, the title compound **3p** was isolated as light-yellow oil (0.103 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.12 (m, 4H), 7.01 – 6.95 (m, 2H), 6.61 – 6.57 (m, 1H), 6.39 (d, J = 8.2 Hz, 1H), 4.41 (s, 2H), 3.38 – 3.35 (m, 2H), 2.86 (t, J = 6.2 Hz, 2H), 2.34 (s, 3H), 2.08 – 2.02 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.8, 136.1, 135.7, 130.4, 129.0, 127.3, 126.8, 126.21, 126.15, 122.4, 115.9, 111.0, 53.6, 49.9, 28.4, 22.6, 19.1. Spectral data is in accordance to the reported literature. [15]

1-(2-fluorobenzyl)-1,2,3,4-tetrahydroquinoline (3q)



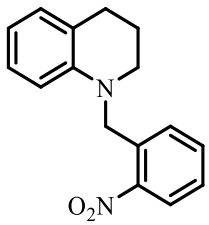
By following the **GP -1**, the title compound **3q** was isolated as white solid (0.113 g, 94%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). m.p. 61-63 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.20 (m, 2H), 7.07 – 7.03 (m, 2H), 6.99 – 6.96 (m, 2H), 6.58 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 4.52 (s, 2H), 3.39 – 3.37 (m, 2H), 2.83 – 2.81 (m, 2H), 2.02 (p, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 161.9 – 160.2 (C-F, $^1J_{C\text{-}F}$ = 245.1 Hz), 145.5, 129.2, 128.42, 128.38, 128.4 – 124.3 (C-F, $^3J_{C\text{-}F}$ = 2.31 Hz), 127.4, 125.7 – 125.6 (C-F, $^2J_{C\text{-}F}$ = 14.61 Hz), 124.2 (C-F, $^3J_{C\text{-}F}$ = 3.55 Hz), 122.4, 116.1, 115.4 – 115.3 (C-F, $^2J_{C\text{-}F}$ = 21.1 Hz), 110.9, 50.1, 49.30, 49.27, 28.3, 22.5. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$): δ -118.61. Spectral data is in accordance to the reported literature. [15]

1-(2-bromobenzyl)-1,2,3,4-tetrahydroquinoline (3r)



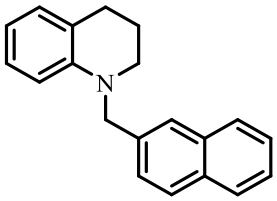
By following the **GP -1**, the title compound **3r** was isolated as light-yellow oil (0.133 g, 88%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 7.7 Hz, 1H), 7.21 – 7.20 (m, 2H), 7.12 – 7.09 (m, 1H), 6.98 (d, J = 7.3 Hz, 1H), 6.96 – 6.93 (m, 1H), 6.59 – 6.57 (m, 1H), 6.29 (d, J = 8.2 Hz, 1H), 4.45 (s, 2H), 3.41 – 3.39 (m, 2H), 2.84 (t, J = 5.8 Hz, 2H), 2.07 – 2.03 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.2, 137.1, 132.9, 129.1, 128.4, 127.8, 127.6, 127.4, 123.0, 122.2, 116.2, 110.9, 56.3, 50.3, 28.3, 22.6. Spectral data is in accordance to the reported literature. [15]

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



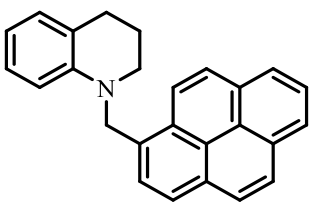
By following the **GP -1**, the title compound **3s** was isolated as light-red solid (0.130 g, 97%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.1Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.3 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.62 (t, J = 7.3 Hz, 1H), 6.27 (d, J = 8.2 Hz, 1H), 4.85 (s, 2H), 3.41 – 3.39 (m, 2H), 2.87 (t, J = 6.2 Hz, 2H), 2.10 – 2.05 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.3, 145.1, 135.3, 134.1, 129.2, 128.6, 127.9, 127.4, 125.6, 122.5, 116.6, 110.9, 54.0, 50.4, 28.2, 22.5. Spectral data is in accordance to the reported literature. [15]

1-(naphthalen-2-ylmethyl)-1,2,3,4-tetrahydroquinoline (3t)



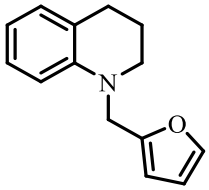
By following the **GP -1**, the title compound **3t** was isolated as white solid (0.120 g, 88%,) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). m.p. 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 8.01 (m, 1H), 7.93 – 7.91 (m, 1H), 7.79 – 7.77 (m, 1H), 7.58 – 7.52 (m, 2H), 7.41 (d, J = 5.5 Hz, 2H), 7.04 (d, J = 7.9 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.63 – 6.59 (m, 1H), 6.46 (d, J = 8.2 Hz, 1H), 4.93 (s, 2H), 3.43 – 3.40 (m, 2H), 2.89 (t, J = 6.2 Hz, 2H), 2.10 – 2.04 (m, 2H).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.8, 134.0, 132.9, 131.4, 129.1, 129.0, 127.5, 127.4, 126.1, 125.81, 125.79, 123.7, 122.8, 122.5, 116.0, 111.1, 53.4, 49.8, 28.4, 22.6. Spectral data is in accordance to the reported literature. [15]

1-(pyren-1-ylmethyl)-1,2,3,4-tetrahydroquinoline (3u)



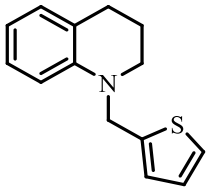
By following the **GP -1**, the title compound **3u** was isolated as light-green solid (0.149 g, 86%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). m.p. 175-177 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.27 (d, J = 9.1 Hz, 1H), 8.22 – 8.19 (m, 2H), 8.15 (d, J = 9.1 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.04 (s, 2H), 8.03 – 8.01 (m, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.06 (d, J = 7.3 Hz, 1H), 6.97 (t, J = 7.7 Hz, 1H), 6.63 (t, J = 7.1 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 5.20 (s, 2H), 3.45 – 3.43 (m, 2H), 2.91 (t, J = 5.8 Hz, 2H), 2.11 – 2.07 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.9, 131.6, 131.5, 130.9, 130.6, 129.2, 128.5, 127.73, 127.68, 127.4, 127.1, 126.1, 125.31, 125.26, 125.1, 125.0, 124.7, 122.8, 122.4, 116.2, 111.2, 53.7, 49.8, 28.4, 22.7. Spectral data is in accordance to the reported literature. [15]

1-(furan-2-ylmethyl)-1,2,3,4-tetrahydroquinoline (3v)



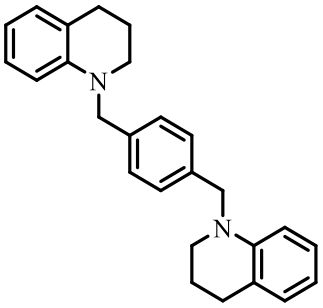
By following the **GP -1**, the title compound **3v** was isolated as light-yellow oil (0.090 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 1.2 Hz, 1H), 7.04 (t, J = 8.8 Hz, 1H), 6.96 (d, J = 7.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 6.62 – 6.59 (m, 1H), 6.30 – 6.29 (m, 1H), 6.17 – 6.16 (m, 1H), 4.42 (s, 2H), 3.38 – 3.35 (m, 2H), 2.76 (t, J = 6.4 Hz, 2H), 2.01 – 1.95 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.5, 145.1, 141.9, 129.2, 127.1, 122.9, 116.4, 111.4, 110.3, 107.2, 49.7, 48.5, 28.2, 22.4. Spectral data is in accordance to the reported literature. [15]

1-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroquinoline (3w)



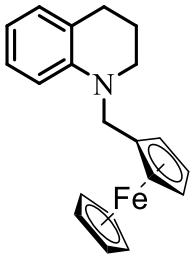
By following the **GP -1**, the title compound **3w** was isolated as light-yellow oil (0.095 g, 83%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.17 (m, 1H), 7.05 (t, J = 8.0 Hz, 1H), 7.00 – 6.95 (m, 3H), 6.72 (d, J = 8.2 Hz, 1H), 6.63 (t, J = 7.3 Hz, 1H), 4.64 (s, 2H), 3.39 – 3.36 (m, 2H), 2.79 (t, J = 6.3 Hz, 2H), 2.04 – 1.98 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.1, 142.6, 129.3, 127.2, 126.9, 124.8, 124.3, 123.0, 116.6, 111.6, 50.7, 49.6, 28.2, 22.4. Spectral data is in accordance to the reported literature. [15]

1,4-bis((3,4-dihydroquinolin-1(2H)-yl) methyl) benzene (3x)



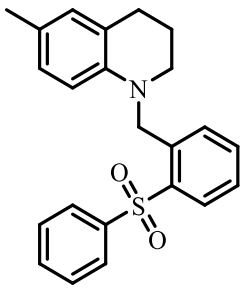
By following the **GP -1**, the title compound **3x** was isolated as yellow oil (0.136 g, 74%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (s, 4H), 7.00– 6.96 (m, 4H), 6.58 (t, J = 7.3 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 4.46 (s, 4H), 3.38 – 3.35 (m, 4H), 2.81 (t, J = 6.2 Hz, 4H), 2.04 – 1.99 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 145.7, 137.6, 129.1, 127.3, 127.0, 122.4, 115.9, 111.1, 55.1, 50.0, 28.4, 22.5. Spectral data is in accordance to the reported literature. [15]

Cyclopenta-2,4-dien-1-yl(2-((3,4-dihydroquinolin-1(2H)-yl) methyl) cyclopenta-2,4-dien-1-yl) iron (3y)



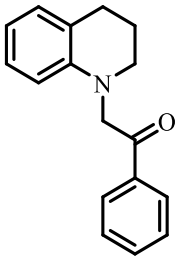
By following the **GP -1**, the title compound **3y** was isolated as light-yellow oil (0.109 g, 66%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.04 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 7.3 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.55 (t, J = 7.2 Hz, 1H), 4.22 (s, 2H), 4.20 (t, J = 1.9 Hz, 2H), 4.16 (s, 5H), 4.08 (t, J = 1.9 Hz, 2H), 3.27 – 3.25 (m, 2H), 2.71 (t, J = 6.4 Hz, 2H), 1.94 – 1.90 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.5, 129.3, 127.0, 122.7, 115.9, 111.4, 69.1, 68.7, 67.9, 50.7, 49.0, 28.3, 22.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{22}FeN$:332.1097; found: 332.1057.

6-methyl-1-(2-(phenylsulfonyl) benzyl)-1,2,3,4-tetrahydroquinoline (3z)



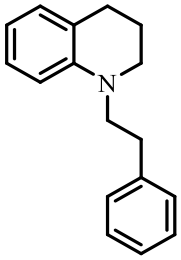
By following the **GP -1**, the title compound **3z** was isolated as white solid (0.164 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). m.p. 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (dd, J = 7.6, 1.6 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.64 – 7.60 (m, 1H), 7.55 – 7.41 (m, 5H), 6.77 (s, 1H), 6.47 – 6.44 (m, 1H), 5.44 (d, J = 8.2 Hz, 1H), 4.57 (s, 2H), 3.28 – 3.25 (m, 2H), 2.76 (t, J = 6.3 Hz, 2H), 2.13 (s, 3H), 2.01 – 1.96 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 142.6, 141.2, 139.0, 137.8, 134.3, 133.4, 130.0, 129.9, 129.4, 128.0, 127.8, 127.5, 127.4, 125.3, 122.2, 110.5, 53.2, 50.5, 28.1, 22.6, 20.2. Spectral data is in accordance to the reported literature. [15]

2-(3,4-dihydroquinolin-1(2H)-yl)-1-phenylethan-1-one (3aa)



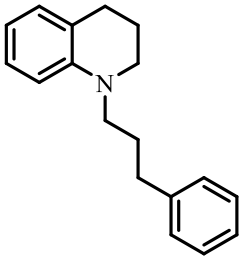
By following the **GP -1**, the title compound **3aa** was isolated a light-yellow oil (0.087 g, 69%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.52). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.5 Hz, 2H), 7.59 – 7.56 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 6.97 – 6.92 (m, 2H), 6.58 (t, J = 7.2 Hz, 1H), 6.29 (d, J = 8.1 Hz, 1H), 4.67 (s, 2H), 3.38 – 3.35 (m, 2H), 2.81 (t, J = 6.2 Hz, 2H), 2.04 – 1.98 (m, 2H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 196.5, 145.1, 135.7, 133.5, 129.2, 128.8, 127.1, 122.8, 116.6, 110.4, 57.7, 50.6, 28.1, 22.4. Spectral data is in accordance to the reported literature. [3]

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



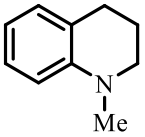
By following the **GP -1**, the title compound **3ab** was isolated as yellow oil (0.087 g, 73%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 7.08 (t, J = 7.8 Hz, 2H), 6.95 (d, J = 7.3 Hz, 1H), 6.66 (d, J = 8.2 Hz, 1H), 6.57 (t, J = 7.3 Hz, 1H), 3.50 – 3.47 (m, 2H), 3.22 – 3.20 (m, 2H), 2.88 – 2.85 (m, 2H), 2.74 (t, J = 6.3 Hz, 2H), 1.90 (p, J = 6.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 144.9, 140.1, 129.4, 129.0, 128.6, 127.3, 126.3, 122.5, 115.7, 110.5, 53.5, 49.7, 32.6, 28.3, 22.3. Spectral data is in accordance to the reported literature. [15]

1-(3-phenylpropyl)-1,2,3,4-tetrahydroquinoline (3ac)



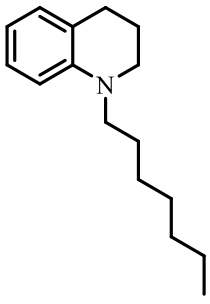
By following the **GP -1**, The title compound **3ac** was isolated as light-yellow oil (0.108 g, 86%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, J = 7.8 Hz, 2H), 7.21 – 7.19 (m, 3H), 7.02 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 7.1 Hz, 1H), 6.55 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 8.2 Hz, 1H), 3.29 – 3.25 (m, 4H), 2.75 (t, J = 6.3 Hz, 2H), 2.69 – 2.66 (m, 2H), 1.96 – 1.91 (m, 4H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.4, 142.0, 129.3, 128.50, 128.48, 127.2, 126.0, 122.4, 115.5, 110.6, 51.1, 49.6, 33.6, 28.3, 27.8, 22.4. Spectral data is in accordance to the reported literature. [15]

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



By following the **GP -1**, the title compound **3ad** was isolated as colourless oil (0.047 g, 64%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (t, J = 7.7 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.66 – 6.63 (m, 2H), 3.27 – 3.24 (m, 2H), 2.92 (s, 3H), 2.81 (t, J = 6.4 Hz, 2H), 2.05 – 1.99 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.9, 128.9, 127.2, 123.0, 116.3, 111.1, 51.4, 39.2, 27.9, 22.6. Spectral data is in accordance to the reported literature. [15]

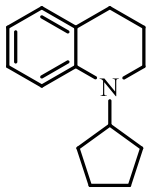
1-heptyl-1,2,3,4-tetrahydroquinoline (3ae)



By following the **GP -1**, The title compound **3ae** was isolated as light-green oil (0.082 g, 71%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H

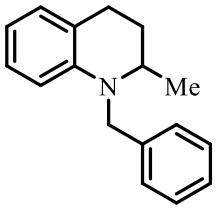
NMR (400 MHz, $CDCl_3$): δ 7.06 – 7.02 (m, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.59 – 6.52 (m, 2H), 3.29 – 3.21 (m, 4H), 2.75 (t, J = 6.3 Hz, 2H), 1.98 – 1.92 (m, 2H), 1.62 – 1.55 (m, 2H), 1.34 – 1.30 (m, 8H), 0.91 – 0.88 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.5, 129.2, 127.2, 122.3, 115.3, 110.6, 51.7, 49.6, 32.0, 29.4, 28.4, 27.4, 26.3, 22.8, 22.4, 14.2. Spectral data is in accordance to the reported literature. [15]

1-cyclopentyl-1,2,3,4-tetrahydroquinoline (3af)



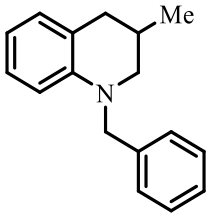
By following the **GP -1**, The title compound **3af** was isolated as light-yellow oil (0.082 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^1H NMR (400 MHz, $CDCl_3$): 7.08 – 7.06 (m, 1H), 6.95 (d, J = 7.3 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 6.56 (t, J = 7.1 Hz, 1H), 4.20 (p, J = 7.9 Hz, 1H), 3.21 – 3.18 (m, 2H), 2.75 (t, J = 6.4 Hz, 2H), 1.95 – 1.86 (m, 4H), 1.77 – 1.59 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 146.4, 129.1, 127.1, 123.5, 115.4, 111.2, 58.7, 42.1, 28.6, 28.1, 24.3, 22.8. Spectral data is in accordance to the reported literature. [15]

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



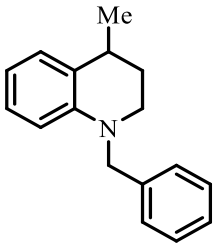
By following the **GP -2**, the title compound **4b** was isolated as light-yellow oil (0.096 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.19 (m, 5H), 7.00 (d, J = 7.3 Hz, 1H), 6.94 (t, J = 6.8 Hz, 1H), 6.58 – 6.54 (m, 1H), 6.39 (d, J = 8.2 Hz, 1H), 4.57 – 4.43 (m, 2H), 3.61 – 3.54 (m, 1H), 2.96 – 2.88 (m, 1H), 2.78 – 2.72 (m, 1H), 2.08 – 2.00 (m, 1H), 1.86 – 1.80 (m, 1H), 1.18 (d, J = 6.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.9, 139.6, 128.9, 128.7, 127.2, 126.7, 126.4, 121.9, 115.6, 111.5, 53.5, 53.1, 28.3, 24.2, 19.1. Spectral data is in accordance to the reported literature. [15]

1-benzyl-3-methyl-1,2,3,4-tetrahydroquinoline (4c)



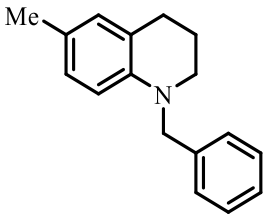
By following the **GP -2**, the title compound **4c** was isolated as light-yellow oil (0.100 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 5H), 6.98 – 6.95 (m, 2H), 6.57 (t, J = 7.2 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 4.48 (s, 2H), 3.30 – 3.26 (m, 1H), 3.06 – 3.01 (m, 1H), 2.84 – 2.79 (m, 1H), 2.54 – 2.47 (m, 1H), 2.23 – 2.12 (m, 1H), 1.05 (d, J = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.3, 139.1, 129.2, 128.7, 127.3, 126.9, 126.7, 122.0, 116.0, 110.8, 57.0, 55.3, 36.6, 27.4, 19.2. Spectral data is in accordance to the reported literature. [15]

1-benzyl-4-methyl-1,2,3,4-tetrahydroquinoline (4d)



By following the **GP -2**, the title compound **4d** was isolated as light-yellow oil (0.103 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.22 (m, 5H), 7.07 (d, J = 7.2 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.62 – 6.59 (m, 1H), 6.50 (d, J = 8.2 Hz, 1H), 4.49 (s, 2H), 3.45 – 3.39 (m, 1H), 3.34 – 3.29 (m, 1H), 2.96 – 2.95 (m, 1H), 2.09 – 2.02 (m, 1H), 1.77 – 1.72 (m, 1H), 1.33 – 1.31 (m, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.0, 139.0, 128.7, 128.0, 127.4, 127.2, 126.9, 126.7, 115.9, 111.1, 55.3, 46.7, 31.2, 29.8, 22.4. Spectral data is in accordance to the reported literature. [15]

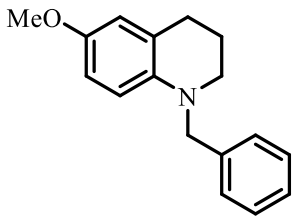
1-benzyl-6-methyl-1,2,3,4-tetrahydroquinoline (4e)



By following the **GP -2**, the title compound **4e** was isolated as colorless oil (0.106 g, 89%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H

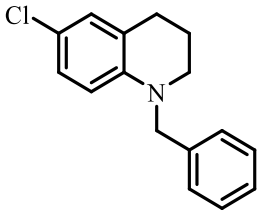
NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.21 (m, 5H), 6.81 (s, 1H), 6.78 (d, J = 8.2 Hz, 1H), 6.42 (d, J = 8.2 Hz, 1H), 4.44 (s, 2H), 3.33 (t, J = 5.6 Hz, 2H), 2.79 (t, J = 6.3 Hz, 2H), 2.19 (s, 3H), 2.00 (p, J = 6.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 143.6, 139.3, 129.9, 128.7, 127.6, 126.81, 126.76, 125.1, 122.4, 111.3, 55.5, 50.0, 28.3, 22.7, 20.3. Spectral data is in accordance to the reported literature. [15]

1-benzyl-6-methoxy-1,2,3,4-tetrahydroquinoline (4f)



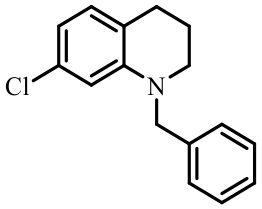
By following the **GP -2**, the title compound **4f** was isolated as yellow oil (0.116 g, 92%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 25/1, R_f = 0.70). ^1H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 5H), 6.61 – 6.56 (m, 2H), 6.45 (d, J = 8.8 Hz, 1H), 4.41 (s, 2H), 3.71 (s, 3H), 3.30 – 3.28 (m, 2H), 2.81 – 2.79 (m, 2H), 2.02 – 1.97 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 151.0, 140.5, 139.5, 128.7, 126.9, 126.8, 123.9, 115.4, 112.5, 112.4, 56.1, 55.9, 50.1, 28.5, 22.7. Spectral data is in accordance to the reported literature. [15]

1-benzyl-6-chloro-1,2,3,4-tetrahydroquinoline (4g)



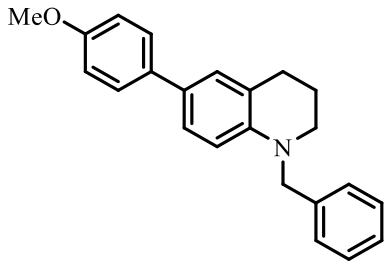
By following the **GP -2**, the title compound **4g** was isolated as yellow oil (0.106 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^1H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.31 (m, 2H), 7.24 – 7.22 (m, 3H), 6.93 (s, 1H), 6.90 – 6.88 (m, 1H), 6.39 – 6.37 (d, J = 8.8 Hz, 1H), 4.46 (s, 2H), 3.37 – 3.35 (m, 2H), 2.78 (t, J = 6.3 Hz, 2H), 2.02 – 1.98 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 144.2, 138.5, 128.8, 128.7, 127.0, 126.9, 126.6, 123.9, 120.4, 112.1, 55.3, 50.0, 28.2, 22.3. Spectral data is in accordance to the reported literature. [15]

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



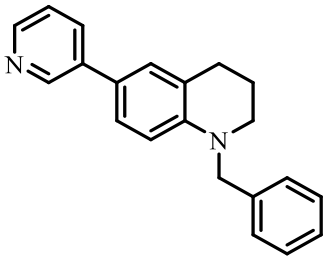
By following the **GP -2**, the title compound **4h** was isolated as light-yellow oil (0.107 g, 83%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 6.86 (d, J = 7.9 Hz, 1H), 6.53 – 6.50 (m, 1H), 6.47 – 6.46 (m, 1H), 4.44 (s, 2H), 3.35 – 3.32 (m, 2H), 2.75 (t, J = 6.2 Hz, 2H), 1.97 (p, J = 6.1 Hz, 2H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.6, 138.1, 132.7, 129.9, 128.8, 127.1, 126.6, 120.7, 115.6, 110.6, 55.0, 49.6, 27.8, 22.2. Spectral data is in accordance to the reported literature. [15]

1-benzyl-6-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (4i)



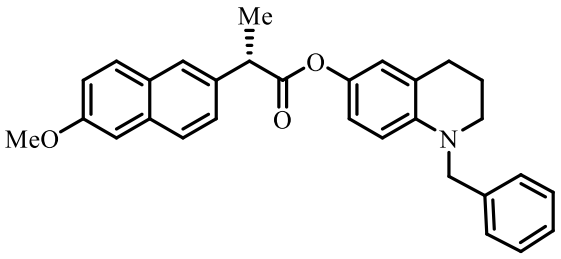
By following the **GP -2**, the title compound **4i** was isolated as colorless oil (0.145 g, 88%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.41 (m, 2H), 7.32 – 7.28 (m, 4H), 7.25 – 7.22 (m, 1H), 7.18 – 7.16 (m, 2H), 6.91 – 6.90 (m, 2H), 6.56 – 6.54 (m, 1H), 4.50 (s, 2H), 3.80 (s, 3H), 3.39 – 3.37 (m, 2H), 2.88 – 2.85 (m, 2H), 2.05 – 2.03 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.2, 144.8, 139.0, 134.2, 128.7, 128.6, 127.5, 127.3, 126.9, 126.7, 125.5, 122.6, 114.2, 111.4, 55.43, 55.37, 50.1, 28.5, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{23}H_{24}NO$:330.1853; found: 330.1855.

1-benzyl-6-(pyridin-3-yl)-1,2,3,4-tetrahydroquinoline (4j)



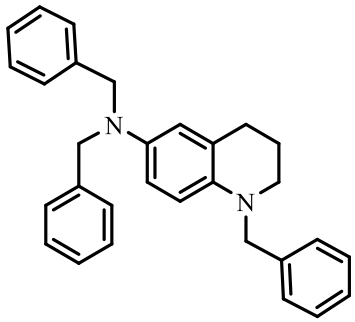
By following the **GP -2**, the title compound **4j** was isolated as yellow solid (0.125 g, 83%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, J = 2.4 Hz, 1H), 8.45 (d, J = 3.9 Hz, 1H), 7.79 (dt, J = 8.0, 2.0 Hz, 1H), 7.35 – 7.21 (m, 8H), 6.59 (d, J = 8.3 Hz, 1H), 4.54 (s, 2H), 3.43 (t, J = 5.7 Hz, 2H), 2.90 (t, J = 6.3 Hz, 2H), 2.09 – 2.03 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 147.5, 146.9, 145.8, 138.6, 136.9, 133.4, 128.8, 127.7, 127.1, 126.6, 126.0, 124.9, 123.6, 122.9, 111.5, 55.2, 50.1, 28.5, 22.4. Spectral data is in accordance to the reported literature. [3]

1-benzyl-1,2,3,4-tetrahydroquinolin-6-yl (S)-2-(6-methoxynaphthalen-2-yl) propanoate (4k)



By following the **GP -2**, the title compound **4k** was isolated as colourless oil (0.178 g, 79%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.70 (m, 3H), 7.49 – 7.47 (m, 1H), 7.30 – 7.27 (m, 2H), 7.22 – 7.21 (m, 3H), 7.15 – 7.11 (m, 2H), 6.61 – 6.60 (m, 1H), 6.58 – 6.56 (m, 1H), 6.38 – 6.36 (m, 1H), 4.40 (s, 2H), 4.05 – 4.01 (m, 1H), 3.90 (s, 3H), 3.31 – 3.29 (m, 2H), 2.73 (t, J = 6.2 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.65 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 174.0, 157.8, 143.6, 141.0, 138.8, 135.6, 133.9, 129.4, 129.1, 128.7, 127.3, 126.9, 126.7, 126.4, 126.2, 123.0, 121.6, 119.5, 119.1, 111.3, 105.7, 55.6, 55.4, 49.9, 45.6, 28.3, 22.3, 18.7. Spectral data is in accordance to the reported literature. [3]

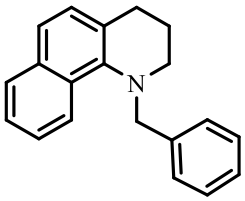
***N, N*,1-tribenzyl-1,2,3,4-tetrahydroquinolin-6-amine (4l)**



By following the **GP -2**, the title compound **4l** was isolated as purple-oil (0.146 g, 70%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.20 (m, 15H), 6.52 – 6.40 (m, 3H), 4.47 (s, 4H), 4.34 (s, 2H), 3.24 – 3.22 (m, 2H), 2.72 (t, J = 6.1 Hz, 2H), 1.98 – 1.95 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz,

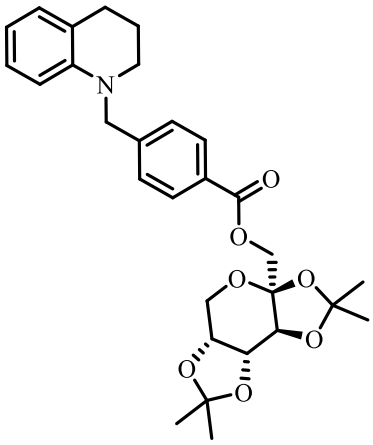
$CDCl_3$): δ 141.2, 140.0, 139.7, 138.6, 128.6, 128.5, 127.2, 127.0, 126.8, 123.8, 115.4, 113.2, 112.9, 56.4, 55.1, 50.1, 28.6, 22.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{30}H_{31}N_2$:419.2482; found: 419.2485.

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



By following the **GP -2**, the title compound **4m** was isolated as colourless oil (0.093 g, 68%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.13 (m, 1H), 7.78 – 7.76 (m, 1H), 7.64 (d, J = 7.2 Hz, 2H), 7.47 – 7.43 (m, 3H), 7.40 – 7.33 (m, 3H), 7.18 (d, J = 8.4 Hz, 1H), 4.35 (s, 2H), 3.18 – 3.15 (m, 2H), 2.97 – 2.94 (m, 2H), 1.93 – 1.86 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.3, 139.9, 133.6, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 127.5, 127.1, 127.0, 125.45, 125.38, 125.1, 123.0, 122.2, 59.2, 47.0, 28.1, 16.6. Spectral data is in accordance to the reported literature. [15]

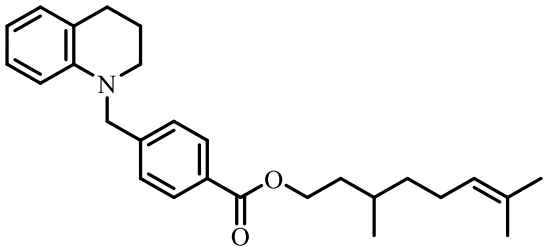
((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 4-((3,4-dihydroquinolin-1(2H)-yl)methyl)benzoate (6a)



By following the **GP -1**, the title compound **6a** was isolated as light-yellow oil (0.209 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.42). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.00 – 6.95 (m, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.42 (d, J = 8.2 Hz, 1H), 4.67 – 4.64 (m, 2H), 4.52 (s, 2H), 4.47 (d, J = 2.5 Hz, 1H), 4.34 (d, J = 11.8 Hz, 1H), 4.26 (d, J = 7.9 Hz, 1H), 3.98 – 3.95 (m, 1H), 3.81 (d, J = 13.0 Hz, 1H), 3.39 – 3.35 (m, 2H), 2.84 (t, J = 6.2 Hz, 2H), 2.04 (p, J = 6.2 Hz, 2H), 1.56 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.9, 145.4, 145.1, 130.3, 129.2, 128.7, 127.3, 126.6, 122.5, 116.4, 111.1, 109.3, 108.9, 101.8,

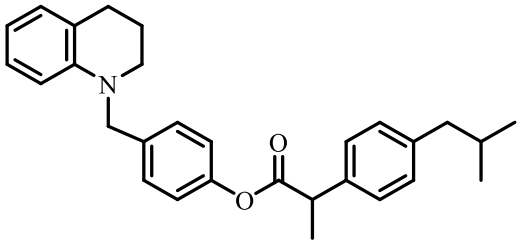
70.9, 70.6, 70.2, 65.4, 61.5, 55.4, 50.3, 28.2, 26.7, 26.0, 25.7, 24.2, 22.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{29}H_{36}NO_{7:}$ 510.2487; found: 510.2488.

3,7-dimethyloct-6-en-1-yl 4-((3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (6b)



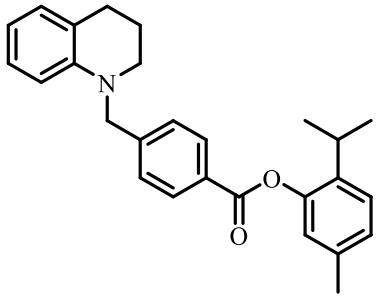
By following the **GP -1**, the title compound **6b** was isolated as light-yellow oil (0.160 g, 79%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.42 (d, J = 8.2 Hz, 1H), 5.09 (t, J = 6.6 Hz, 1H), 4.51 (s, 2H), 4.37 – 4.30 (m, 2H), 3.38 – 3.36 (m, 2H), 2.83 (t, J = 6.2 Hz, 2H), 2.06 – 1.95 (m, 4H), 1.84 – 1.77 (m, 1H), 1.67 (s, 3H), 1.64 – 1.63 (m, 1H), 1.60 (s, 3H), 1.57 – 1.53 (m, 1H), 1.43 – 1.36 (m, 1H), 1.24 – 1.19 (m, 1H), 0.96 (d, J = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.7, 145.5, 144.7, 131.5, 130.1, 129.4, 129.2, 127.3, 126.6, 124.7, 122.5, 116.4, 111.1, 63.6, 55.4, 50.3, 37.1, 35.7, 29.7, 28.3, 25.8, 25.6, 22.5, 19.6, 17.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{27}H_{36}NO_2$**:** 406.2741; found: 406.2741.

4-((3,4-dihydroquinolin-1(2H)-yl) methyl) phenyl 2-(4-isobutylphenyl) propanoate (6c)



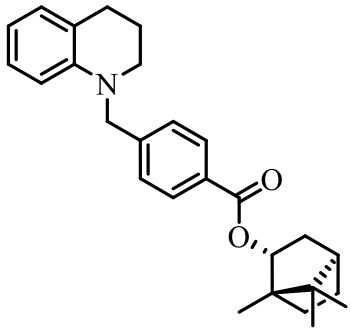
By following the **GP-1**, the title compound **6c** was isolated as light-yellow oil (0.186 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 7.9 Hz, 2H), 7.24 – 7.20 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.96 – 6.92 (m, 4H), 6.56 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 4.42 (s, 2H), 3.92 (q, J = 7.1 Hz, 1H), 3.32 – 3.30 (m, 2H), 2.79 (t, J = 6.2 Hz, 2H), 2.46 (d, J = 7.2 Hz, 2H), 1.98 (p, J = 6.1 Hz, 2H), 1.90 – 1.82 (m, 1H), 1.59 (d, J = 7.1 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 173.5, 149.8, 145.6, 140.9, 137.4, 136.5, 129.6, 129.1, 127.6, 127.34, 127.32, 122.4, 121.6, 116.1, 111.1, 54.9, 50.0, 45.4, 45.2, 30.3, 28.3, 22.53, 22.50, 18.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{29}H_{34}NO_2$: 428.2585; found: 428.2584.

2-isopropyl-5-methylphenyl 4-((3, 4-dihydroquinolin-1(2H)-yl) methyl) benzoate (6d)



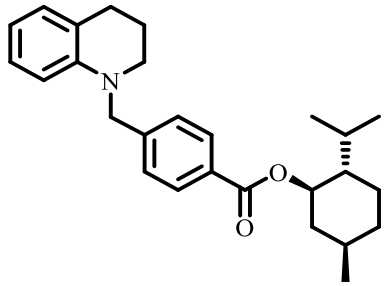
By following the **GP** -1, the title compound **6d** was isolated as light-yellow oil (0.184 g, 92%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.93 (s, 1H), 6.62 – 6.59 (m, 1H), 6.45 (d, J = 8.1 Hz, 1H), 4.56 (s, 2H), 3.42 – 3.40 (m, 2H), 3.07 – 3.01 (m, 1H), 2.85 (t, J = 6.3 Hz, 2H), 2.34 (s, 3H), 2.08 – 2.03 (m, 2H), 1.20 (d, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.4, 148.3, 145.6, 145.4, 137.3, 136.8, 130.7, 129.3, 128.4, 127.4, 127.3, 126.9, 126.6, 123.0, 122.6, 116.4, 111.1, 55.5, 50.4, 28.3, 27.4, 23.2, 22.5, 21.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{27}H_{30}NO_2$: 400.2272; found: 400.2271.

(1S,2R,4R)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 4-((3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (6e)



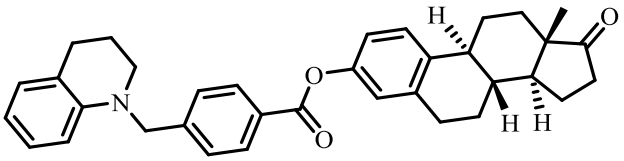
By following the **GP -1**, the title compound **6e** was isolated as light-yellow oil (0.170 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.60 (t, J = 7.2 Hz, 1H), 6.43 (d, J = 8.1 Hz, 1H), 4.93 – 4.91 (m, 1H), 4.53 (s, 2H), 3.40 – 3.38 (m, 2H), 2.84 (t, J = 6.2 Hz, 2H), 2.05 (p, J = 6.2 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.81 – 1.80 (m, 1H), 1.77 – 1.72 (m, 1H), 1.65 – 1.58 (m, 1H), 1.28 – 1.15 (m, 2H), 1.12 (s, 3H), 0.94 (s, 3H), 0.90 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.0, 145.4, 144.5, 130.0, 129.7, 129.2, 127.3, 126.6, 122.5, 116.3, 111.0, 81.6, 55.3, 50.3, 49.1, 47.1, 45.2, 39.1, 33.9, 28.3, 27.2, 22.5, 20.3, 20.2, 11.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{27}H_{34}NO_2$: 404.2585; found: 404.2584.

(1R, 2S, 5R)-2-isopropyl-5-methylcyclohexyl 4-((3, 4-dihydroquinolin-1(2H)-yl) methyl) benzoate (6f)



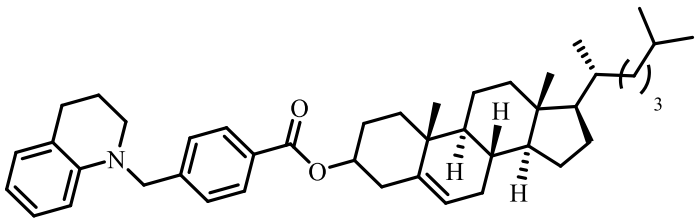
By following the **GP-1**, the title compound **6f** was isolated as light-yellow oil (0.172 g, 85%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.00 – 6.95 (m, 2H), 6.60 (t, J = 7.3, 1H), 6.47 (d, J = 8.2 Hz, 1H), 4.95 – 4.90 (m, 1H), 4.52 (s, 2H), 3.39 – 3.37 (m, 2H), 2.84 (t, J = 6.3 Hz, 2H), 2.14 – 2.12 (m, 1H), 2.06 – 2.01 (m, 2H), 1.99 – 1.94 (m, 1H), 1.74 – 1.72 (m, 2H), 1.57 – 1.53 (m, 2H), 1.18 – 1.06 (m, 2H), 0.94 – 0.91 (m, 7H), 0.80 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.1, 145.4, 144.5, 130.1, 129.7, 129.2, 127.3, 126.6, 122.5, 116.3, 111.1, 74.9, 55.4, 50.2, 47.4, 41.1, 34.5, 31.6, 28.3, 26.6, 23.8, 22.5, 22.2, 20.9, 16.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{27}H_{36}NO_2$: 406.2741; found: 406.2741.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-((3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (6g)



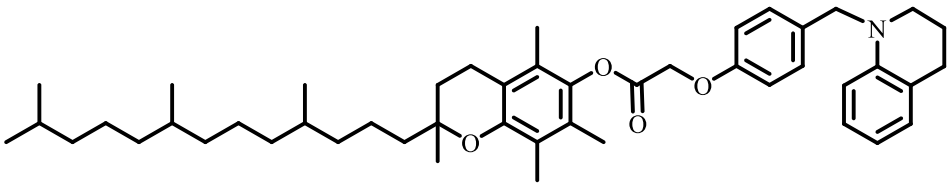
By following the **GP** -1, the title compound **6g** was isolated as light-yellow oil (0.208 g, 77%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/5, R_f = 0.42). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.5 Hz, 1H), 6.99 – 6.94 (m, 4H), 6.61 (t, J = 7.3 Hz, 1H), 6.43 (d, J = 8.2 Hz, 1H), 4.55 (s, 2H), 3.41 – 3.39 (m, 2H), 2.95 – 2.93 (m, 2H), 2.85 (t, J = 6.2 Hz, 2H), 2.55 – 2.49 (m, 1H), 2.45 – 2.42 (m, 1H), 2.34 – 2.30 (m, 1H), 2.19 – 2.14 (m, 1H), 2.10 – 2.04 (m, 3H), 1.99 – 1.97 (m, 1H), 1.68 – 1.59 (m, 3H), 1.56 – 1.43 (m, 4H), 0.93 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 221.0, 165.4, 149.0, 145.6, 145.4, 138.2, 137.5, 130.7, 129.3, 128.4, 127.3, 126.8, 126.6, 122.6, 121.9, 119.0, 116.4, 111.1, 55.5, 50.6, 50.4, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 28.3, 26.5, 25.9, 22.5, 21.7, 14.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{35}H_{38}NO_3$: 520.2847; found: 520.2849.

(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (6h)



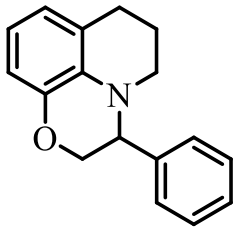
By following the **GP** -1, the title compound **6h** was isolated as white solid (0.257 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.00 – 6.95 (m, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.43 (d, J = 8.2 Hz, 1H), 5.41 (d, J = 4.1 Hz, 1H), 4.89 – 4.83 (m, 1H), 4.52 (s, 2H), 3.39 – 3.37 (m, 2H), 2.84 (t, J = 6.2 Hz, 2H), 2.46 (d, J = 7.8 Hz, 2H), 2.05 – 1.99 (m, 5H), 1.93 – 1.88 (m, 1H), 1.88 – 1.82 (m, 1H), 1.78 – 1.69 (m, 1H), 1.61 – 1.47 (m, 6H), 1.42 – 1.35 (m, 3H), 1.25 – 1.11 (m, 7H), 1.08 (s, 3H), 1.05 – 0.99 (m, 4H), 0.94 (d, J = 6.5 Hz, 3H), 0.89 – 0.88 (m, 6H), 0.71 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.0, 145.5, 144.5, 139.8, 130.1, 129.7, 129.2, 127.3, 126.6, 122.9, 122.5, 116.3, 111.1, 74.6, 56.8, 56.3, 55.4, 50.23, 50.19, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.3, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 22.5, 21.2, 19.5, 18.9, 12.0. Spectral data is in accordance to the reported literature. [15]

2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl) chroman-6-yl 2-(4-((3,4-dihydroquinolin-1(2H)-yl) methyl) phenoxy) acetate (6i)



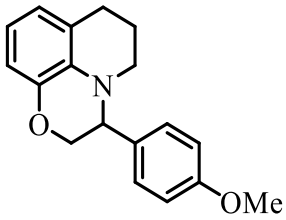
By following the **GP** -1, the title compound **6i** was isolated as light-yellow oil (0.277 g, 78%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 (d, J = 7.9 Hz, 2H), 7.00 – 6.96 (m, 4H), 6.59 (t, J = 7.2 Hz, 1H), 6.53 (d, J = 8.1 Hz, 1H), 4.91 (s, 2H), 4.43 (s, 2H), 3.35 – 3.33 (m, 2H), 2.82 (t, J = 6.1 Hz, 2H), 2.60 – 2.58 (m, 2H), 2.09 (s, 3H), 2.03 – 2.00 (m, 5H), 1.95 (s, 3H), 1.84 – 1.73 (m, 3H), 1.56 – 1.51 (m, 3H), 1.45 – 1.35 (m, 7H), 1.32 – 1.26 (m, 8H), 1.16 – 1.07 (m, 6H), 0.88 – 0.85 (m, 12H).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.9, 157.0, 149.8, 145.7, 140.1, 132.4, 129.2, 128.0, 127.3, 126.7, 125.0, 123.4, 122.5, 117.7, 116.0, 115.1, 111.2, 75.3, 65.5, 54.7, 49.9, 39.5, 37.6, 37.5, 37.4, 32.9, 32.8, 28.3, 28.1, 25.0, 24.9, 24.6, 22.9, 22.8, 22.5, 21.2, 20.7, 19.9, 19.8, 19.7, 13.1, 12.3, 12.0. Spectral data is in accordance to the reported literature. [15]

3-phenyl-2,3,6,7-tetrahydro-5H- [1,4] oxazino[2,3,4-ij] quinoline (8a)



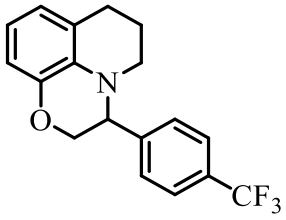
By following the **GP -3**, the title compound **8a** was isolated as white solid (0.117 g, 93%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). m.p.102-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.25 (m, 5H), 6.67 – 6.64 (m, 2H), 6.59 – 6.56 (m, 1H), 4.25 – 4.19 (m, 2H), 4.16 – 4.11 (m, 1H), 3.09 – 3.04 (m, 1H), 2.84 – 2.76 (m, 3H), 2.04 – 1.88 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.6, 139.0, 133.0, 128.9, 128.1, 127.6, 123.5, 122.2, 117.3, 114.0, 70.3, 60.3, 46.2, 27.1, 22.3. Spectral data is in accordance to the reported literature. [5]

3-(4-methoxyphenyl)-2,3,6,7-tetrahydro-5H- [1,4] oxazino[2,3,4-ij] quinoline (8b)



By following the **GP -3**, the title compound **8b** was isolated as white solid (0.129 g, 92%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.60). m.p. 84 -86 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.66 (t, J = 7.8, 2H), 6.58 (t, J = 7.7 Hz, 1H), 4.22 – 4.09 (m, 3H), 3.81 (s, 3H), 3.07 – 3.04 (m, 1H), 2.87 – 2.74 (m, 3H), 2.01 – 1.88 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 159.5, 143.6, 133.1, 130.9, 128.7, 123.6, 122.1, 117.3, 114.3, 113.9, 70.4, 59.6, 55.4, 46.0, 27.2, 22.3. Spectral data is in accordance to the reported literature. [5]

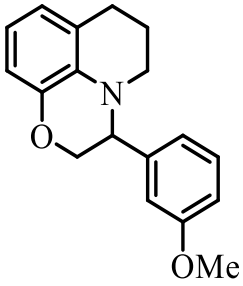
3-(4-(trifluoromethyl) phenyl)-2,3,6,7-tetrahydro-5H-[1,4] oxazino[2,3,4-ij] quinoline (8c)



By following the **GP -3**, the title compound **8c** was isolated as white solid (0.153 g, 96%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). m.p. 92 -94 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 6.68 (d, J = 7.6 Hz, 2H), 6.61 – 6.58 (m, 1H), 4.31 – 4.29 (m, 1H), 4.26 – 4.24 (m, 1H), 4.14 – 4.11 (m, 1H), 3.06 – 3.02 (m, 1H), 2.89 – 2.81 (m, 3H), 2.05 – 1.93 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 143.6, 143.4, 139.4, 132.4, 127.9, 127.0, 125.9 (CF_3, J_{C-F}, = 3.7 Hz), 124.04,

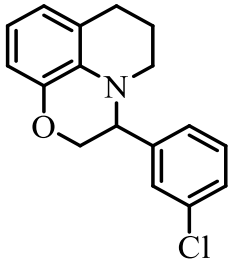
124.02, 123.4, 122.4, 117.4, 114.2, 69.7, 60.2, 46.6, 27.1, 22.2. $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$): δ -62.53. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{18}H_{17}F_3NO$: 320.1257; found: 320.1253.

3-(3-methoxyphenyl)-2,3,6,7-tetrahydro-5H- [1,4] oxazino[2,3,4-ij] quinoline (8d)



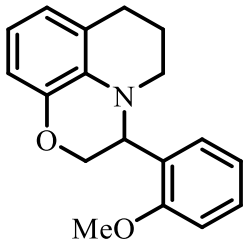
By following the **GP -3**, the title compound **8d** was isolated as white solid (0.127 g, 90%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.60). m.p. 90 -91 ºC ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 1H), 6.89 (d, J = 7.3 Hz, 1H), 6.85 – 6.84 (m, 2H), 6.66 – 6.64 (m, 2H), 6.59 – 6.56 (m, 1H), 4.24 – 4.22 (m, 1H), 4.18– 4.11 (m, 2H), 3.79 (s, 3H), 3.10 – 3.08 (m, 1H), 2.84 – 2.76 (m, 3H), 2.05 – 1.89 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 160.2, 143.6, 140.7, 133.0, 130.0, 123.6, 122.2, 120.0, 117.4, 114.0, 113.4, 113.2, 70.3, 60.3, 55.4, 46.2, 27.1, 22.3. Spectral data is in accordance to the reported literature. [5]

3-(3-chlorophenyl)-2,3,6,7-tetrahydro-5H- [1,4] oxazino[2,3,4-ij] quinoline (8e)



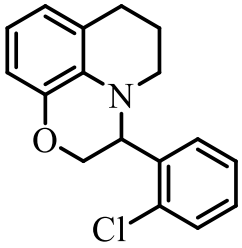
By following the **GP -3**, the title compound **8e** was isolated as white solid (0.134 g, 94%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). m.p. 93 -94 ºC ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.29 (m, 3H), 7.20 – 7.17 (m, 1H), 6.68 – 6.66 (m, 2H), 6.61 – 6.58 (m, 1H), 4.25 – 4.19 (m, 2H), 4.15 – 4.09 (m, 1H), 3.09 – 3.04 (m, 1H), 2.87 – 2.79 (m, 3H), 2.07 – 1.90 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 143.4, 141.4, 134.8, 132.6, 130.3, 128.3, 127.7, 125.7, 123.5, 122.3, 117.4, 114.1, 69.9, 60.1, 46.4, 27.1, 22.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{17}ClNO$: 286.0994; found: 286.0997.

3-(2-methoxyphenyl)-2,3,6,7-tetrahydro-5H- [1,4] oxazino[2,3,4-ij] quinoline (8f)



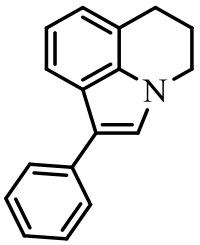
By following the **GP -3**, the title compound **8f** was isolated as white solid (0.124 g, 88%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.60). m.p. 101 -103 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.23 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 6.92 – 6.89 (m, 2H), 6.65 – 6.63 (m, 2H), 6.53 – 6.50 (m, 1H), 4.76 (m, 1H), 4.23 – 4.17 (m, 2H), 3.85 (s, 3H), 3.20 – 3.18 (m, 1H), 2.97 – 2.93 (m, 1H), 2.85 – 2.82 (m, 2H), 2.01 – 1.95 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.1, 143.2, 133.0, 128.6, 127.7, 127.2, 122.5, 122.1, 120.9, 116.1, 114.1, 110.6, 68.3, 55.4, 53.9, 46.8, 27.3, 22.2. Spectral data is in accordance to the reported literature. [5]

3-(2-chlorophenyl)-2,3,6,7-tetrahydro-5H- [1,4] oxazino[2,3,4-ij] quinoline (8g)



By following the **GP -3**, the title compound **8g** was isolated as white solid (0.133 g, 93%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). m.p. 97 -99 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.37 (m, 1H), 7.28 – 7.25 (m, 1H), 7.23 – 7.20 (m, 2H), 6.67 – 6.66 (m, 2H), 6.55 (t, J = 7.7 Hz, 1H), 4.81 (t, J = 3.8 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.15 – 3.11 (m, 1H), 2.85 – 2.82 (m, 1H), 2.84 (t, J = 5.6 Hz, 2H), 1.98 (p, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 143.1, 136.7, 133.1, 132.5, 130.0, 128.9, 128.6, 127.4, 122.6, 122.3, 116.6, 114.2, 67.8, 57.1, 46.9, 27.2, 22.1. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{17}ClNO$: 286.0994; found: 286.0996.

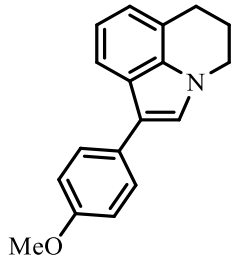
1-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij] quinoline (10a)



By following the **GP -4**, the title compound **10a** was isolated as pale-yellow oil (0.094 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70).^{1}H

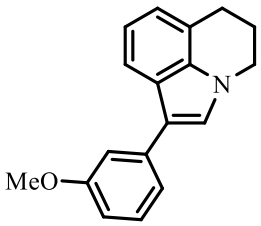
NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.28 (s, 1H), 7.25 – 7.22 (m, 1H), 7.09 (t, J = 7.3 Hz, 1H), 6.96 (d, J = 7.0 Hz, 1H), 4.19 (t, J = 5.7 Hz, 2H), 3.02 (t, J = 6.2 Hz, 2H), 2.27 (p, J = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 136.3, 135.1, 128.9, 127.0, 125.6, 123.9, 123.8, 122.2, 120.5, 119.1, 117.7, 116.7, 44.4, 24.9, 22.9. Spectral data is in accordance to the reported literature. [20]

1-(4-methoxyphenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij] quinoline (10b)



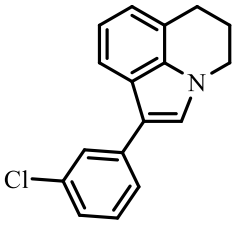
By following the **GP -4**, the title compound **10b** was isolated as white solid (0.111 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.60). m.p. 126 -128 ºC ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.21 (s, 1H), 7.09 (t, J = 7.2 Hz, 1H), 7.00 – 6.95 (m, 3H), 4.20 (t, J = 5.5 Hz, 2H), 3.86 (s, 3H), 3.03 (t, J = 5.9 Hz, 2H), 2.28 (p, J = 5.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 157.9, 135.0, 129.0, 128.1, 123.9, 123.2, 122.1, 120.3, 119.0, 117.6, 116.4, 114.4, 55.5, 44.3, 24.9, 23.0. Spectral data is in accordance to the reported literature. [20]

1-(3-methoxyphenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij] quinoline (10c)



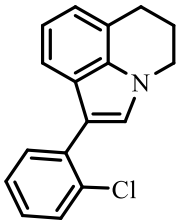
By following the **GP -4**, the title compound **10c** was isolated as pale-yellow solid (0.108 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.60). m.p. 128 -130 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.24 (s, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.0 Hz, 1H), 6.81 – 6.79 (s, 1H), 4.20 – 4.18 (m, 2H), 3.87 (s, 3H), 3.01 (t, J = 6.0 Hz, 2H), 2.26 (p, J = 5.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.1, 137.7, 135.1, 129.8, 124.0, 123.8, 122.2, 120.5, 119.6, 119.1, 117.7, 116.6, 112.6, 111.0, 55.4, 44.4, 24.9, 22.9. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{18}H_{18}NO$: 264.1383; found: 264.1384.

1-(3-chlorophenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij] quinoline (10d)



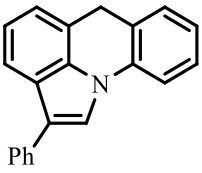
By following the **GP -4**, the title compound **10d** was isolated as light-yellow oil (0.111 g, 83%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 1H), 7.65 (m, 1H), 7.56 – 7.54 (m, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.27 (s, 1H), 7.20 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 6.97 (d, J = 7.6 Hz, 1H), 4.19 – 4.16 (m, 2H), 3.00 (t, J = 6.1 Hz, 2H), 2.25 (p, J = 6.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 138.2, 135.1, 134.6, 130.1, 126.7, 125.4, 124.9, 124.3, 123.6, 122.3, 120.8, 119.4, 117.4, 115.3, 44.4, 24.8, 22.9. Spectral data is in accordance to the reported literature. [20]

1-(2-chlorophenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij] quinoline (10e)



By following the **GP -4**, the title compound **10e** was isolated as light-yellow oil (0.078 g, 58%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (s, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 7.0 Hz, 1H), 4.25 – 4.23 (m, 2H), 3.04 (t, J = 6.1 Hz, 2H), 2.31 (t, J = 6.1 Hz, 2H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 134.5, 134.3, 132.8, 131.7, 130.3, 127.1, 126.8, 126.4, 124.8, 122.1, 120.4, 119.0, 117.9, 113.1, 44.4, 24.9, 23.0. Spectral data is in accordance to the reported literature. [21]

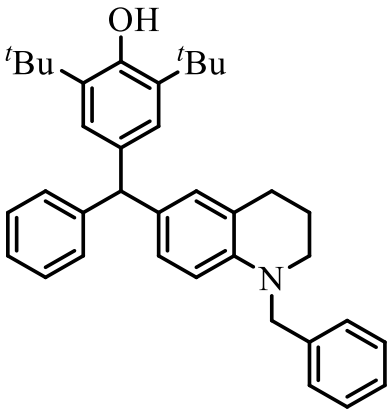
2-phenyl-6H-pyrrolo[3,2,1-de]acridine (10f):



By following the **GP-4**, the title compound **10f** was isolated as white solid (0.123 g, 88%); M.p: 131-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.46 (t, J = 7.3 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.07 – 7.04 (m, 2H), 4.46 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 135.4, 135.3, 134.6, 130.4, 129.0, 127.7, 127.2, 126.4, 125.4, 124.2, 123.9,

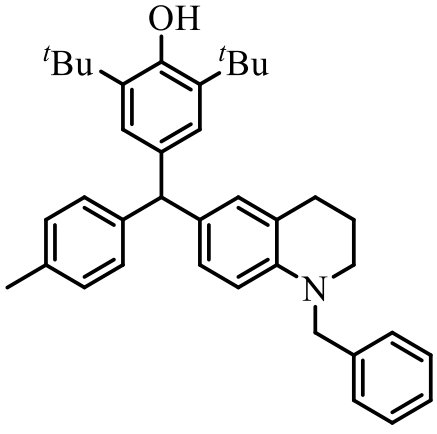
122.9, 120.5, 120.4, 120.2, 118.0, 117.7, 113.3, 29.9. HRMS (ESI) *m/z*: $[M-H]^+$ calculated for $C_{21}H_{14}N$: 280.1121; found: 280.1117.

4-((1-benzyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-*tert*-butylphenol (12a)



By following the **GP -5**, the title compound **12a** was isolated as dark-red liquid using (0.228 g, 88%) silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.18 (m, 7H), 7.13 (t, J = 7.6 Hz, 3H), 6.92 (s, 2H), 6.75 (s, 1H), 6.66 (d, J = 8.3 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 5.26 (s, 1H), 5.01 (brs, 1H), 4.42 (s, 2H), 3.32 – 3.29 (m, 2H), 2.72 (t, J = 6.2 Hz, 2H), 1.96 (p, J = 6.1 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0, 146.0, 144.0, 139.3, 135.4, 135.0, 132.3, 130.1, 129.5, 128.6, 128.1, 128.0, 126.85, 126.83, 126.1, 125.8, 122.1, 110.9, 56.2, 55.5, 50.0, 34.5, 30.5, 28.4, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{44}NO$: 518.3418; found: 518.3419.

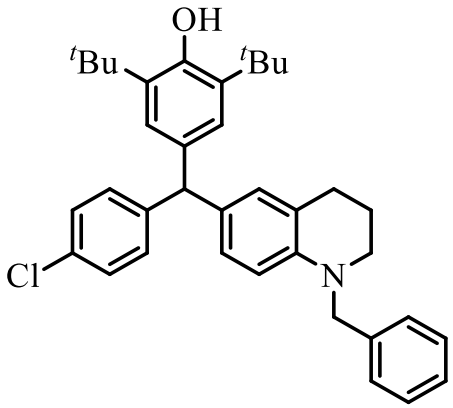
4-((1-benzyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (*p*-tolyl) methyl)-2, 6-di-*tert*-butylphenol (12b)



By following the **GP -5**, the title compound **12b** was isolated as dark-red liquid (0.223 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.20 (m, 5H), 7.05 – 6.99 (m, 2H), 6.92 (s, 2H), 6.75 (s, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 5.21 (s, 1H), 5.00 (s, 1H), 4.43 (s, 2H), 3.32 – 3.30 (m, 2H), 2.73 (t, J = 6.3 Hz, 2H), 2.29 (s, 3H), 1.97 (p, J = 6.0 Hz, 2H), 1.36 (s,

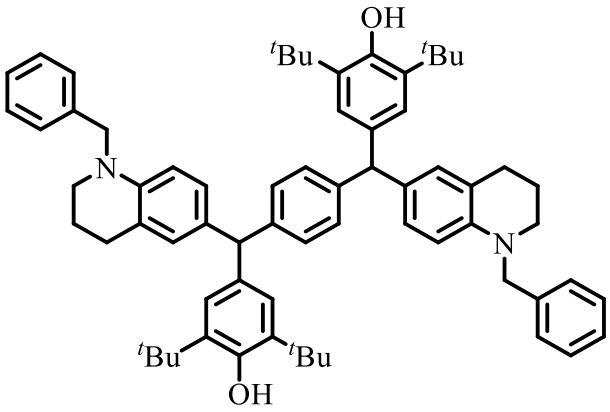
18H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 152.0, 144.0, 143.0, 139.4, 135.4, 135.2, 135.1, 132.6, 130.1, 129.3, 128.8, 128.6, 127.9, 126.9, 126.8, 126.1, 122.1, 111.0, 55.9, 55.6, 50.0, 34.5, 30.5, 28.4, 22.7, 21.1. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{46}NO$: 532.3574; found: 532.3574.

4-((1-benzyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (4-chlorophenyl) methyl)-2, 6-di-*tert*-butyl phenol (12c)



By following the **GP -5**, the title compound **12c** was isolated as dark-red liquid (0.248 g, 90%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 7.20 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.88 (s, 2H), 6.71 (s, 1H), 6.62 (d, J = 8.5 Hz, 1H), 6.41 (d, J = 8.3 Hz, 1H), 5.22 (s, 1H), 5.04 (s, 1H), 4.44 (s, 2H), 3.34 – 3.32 (m, 2H), 2.73 (t, J = 6.4 Hz, 2H), 1.98 (p, J = 6.4 Hz, 2H), 1.36 (s, 18H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.1, 144.6, 144.1, 139.2, 135.5, 134.5, 131.6, 131.5, 130.8, 130.0, 128.7, 128.2, 127.9, 126.9, 126.8, 126.0, 122.2, 110.9, 55.54, 55.47, 50.0, 34.5, 30.5, 28.4, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}ClNO$: 552.3028; found: 552.3025.

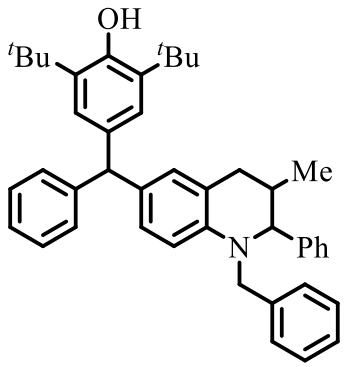
4,4'-(1,4-phenylenebis((1-benzyl-1,2,3,4-tetrahydroquinolin-6-yl) methylene)) bis(2,6-di-*tert*-butylphenol) (12d)



By following the **GP -5**, the title compound **12d** was isolated as dark-red liquid (0.340 g, 71%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 5H), 7.25 – 7.20 (m, 5H), 6.99 (s, 4H), 6.91 (s,

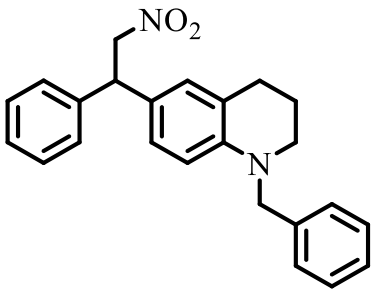
4H), 6.74 (s, 2H), 6.66 – 6.63 (m, 2H), 6.40 (d, J = 8.4 Hz, 2H), 5.22 (s, 2H), 5.00 (brs, 2H), 4.43 (s, 4H), 3.32 – 3.30 (m, 4H), 2.72 (t, J = 6.1 Hz, 4H), 1.97 (p, J = 6.1 Hz, 4H), 1.35 (s, 36H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 151.9, 143.9, 143.14, 143.08, 139.4, 135.4, 135.3, 135.2, 132.5, 130.1, 129.0, 128.6, 128.0, 126.85, 126.81, 126.1, 122.00, 121.99, 110.87, 110.85, 55.8, 55.5, 50.0, 34.5, 30.5, 28.4, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{68}H_{81}N_2O_2$: 957.6293; found: 957.6284.

4-((1-benzyl-3-methyl-2-phenyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-tert-butylphenol (12e)



By following the **GP -5**, the title compound **12e** was isolated as dark-red liquid (0.240 g, 79%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). cis: trans = 1:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 14H), 7.22 – 7.21 (m, 6H), 7.18 – 7.14 (m, 6H), 7.12 – 7.10 (m, 4H), 6.92 (s, 4H), 6.81 (s, 1H), 6.76 – 6.73 (m, 2H), 6.65 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 8.4 Hz, 2H), 5.31 (d, J = 5.7 Hz, 2H), 5.04 (d, J = 3.2 Hz, 2H), 4.50 (dd, J = 17.3, 5.9 Hz, 2H), 4.39 (s, 2H), 4.17 (d, J = 17.4 Hz, 2H), 2.52 – 2.48 (m, 6H), 1.37 (s, 36H), 0.86 (d, J = 6.5 Hz, 3H), 0.84 (d, J = 5.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 152.0, 146.1, 145.9, 143.5, 140.81, 140.79, 139.32, 139.28, 135.3, 135.1, 131.8, 131.7, 130.0, 129.8, 129.6, 129.5, 128.72, 128.68, 128.3, 128.2, 128.11, 128.09, 128.0, 127.3, 126.8, 126.4, 126.22, 126.17, 125.8, 121.27, 121.25, 109.78, 109.75, 67.2, 56.14, 56.06, 53.4, 34.5, 31.72, 31.68, 30.51, 30.5, 18.7, 18.6. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{44}H_{50}NO$: 608.3887; found: 608.3895.

(R)-1-benzyl-6-(2-nitro-1-phenylethyl)-1, 2, 3, 4-tetrahydroquinoline (12f)



By following the **GP -5**, the title compound **12f** was isolated as pale-yellow oil (0.158 g, 85%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.52). ^1H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 4H), 7.22 – 7.18 (m, 6H), 6.79 – 6.76 (m, 2H), 6.40 (d, J = 8.4 Hz, 1H), 4.90 – 4.82 (m, 2H), 4.72 – 4.69 (m, 1H), 4.40 (s, 2H), 3.32 – 3.30

(m, 2H), 2.73 (t, J = 6.2 Hz, 2H), 1.95 (p, J = 6.1 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 145.0, 140.2, 138.8, 128.9, 128.7, 128.4, 127.7, 127.3, 126.9, 126.6, 126.3, 126.2, 122.7, 111.2, 79.7, 55.3, 49.9, 48.4, 28.3, 22.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{24}H_{25}N_2O_2$:373.1911; found: 373.1912.

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

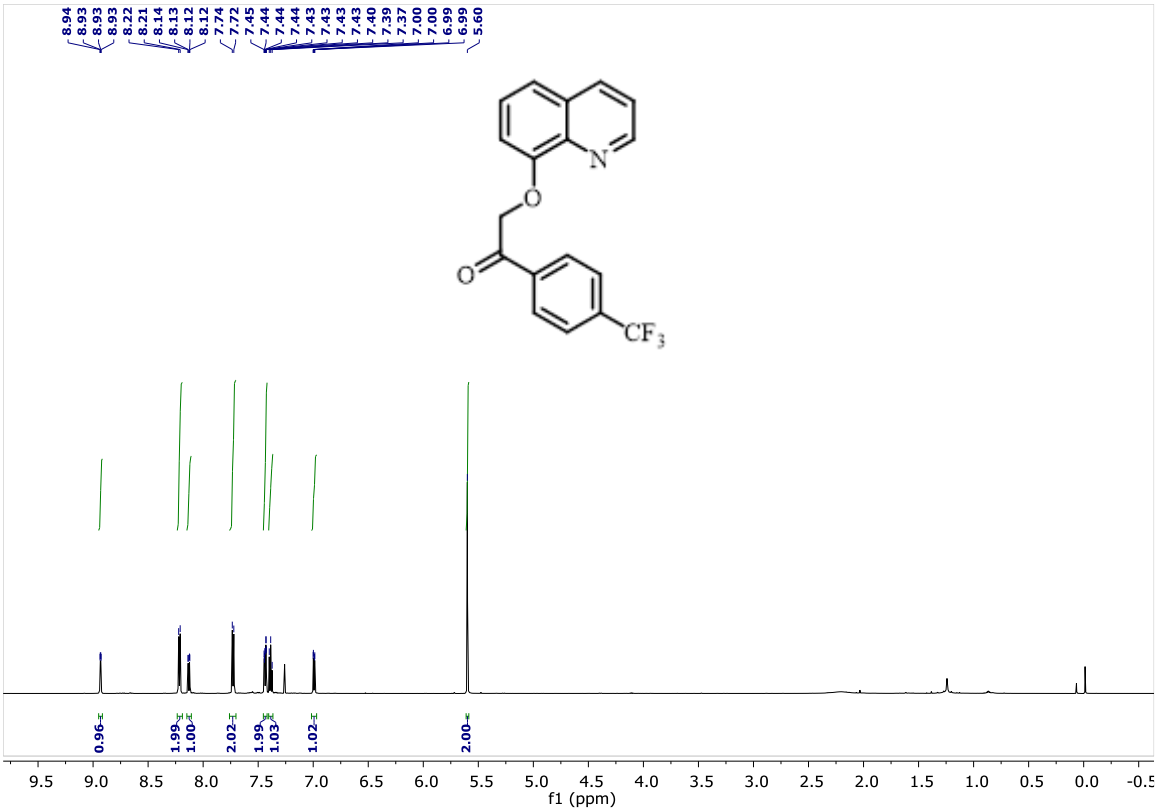


Figure S10: ^{1}H NMR Spectrum of **7c** ($CDCl_3$, 600 MHz, 298 K)

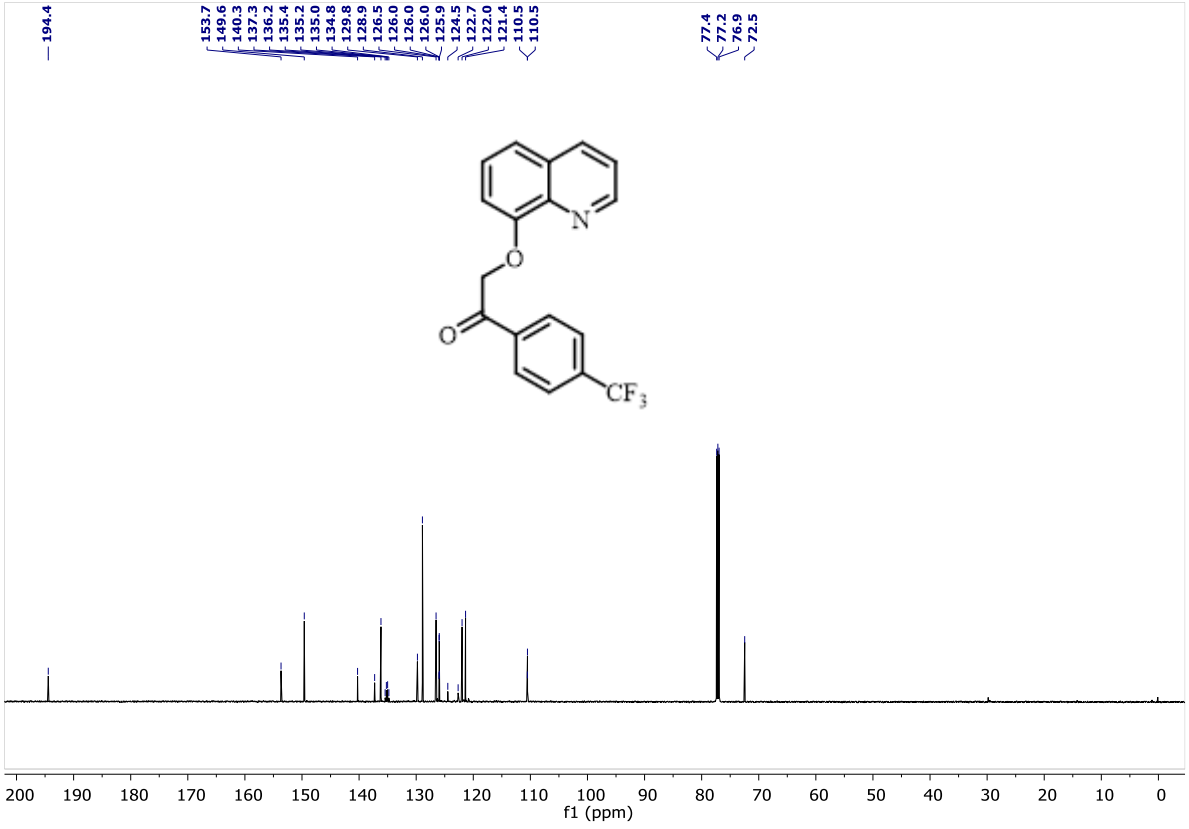


Figure S11: $^{13}C\{^{1}H\}$ NMR Spectrum of **7c** ($CDCl_3$, 151 MHz, 298 K)

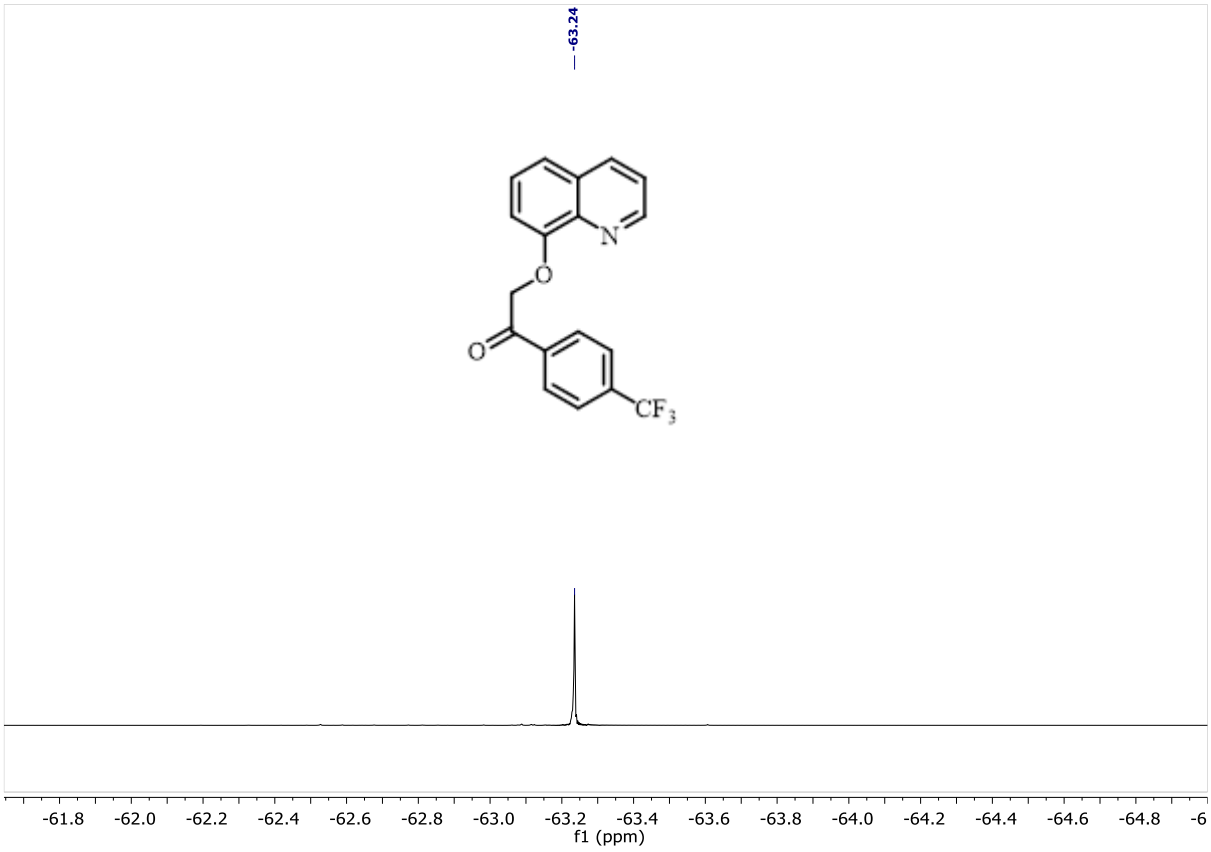


Figure S12: $^{19}F\{^{1}H\}$ NMR Spectrum of **7c** ($CDCl_3$, 565 MHz, 298 K)

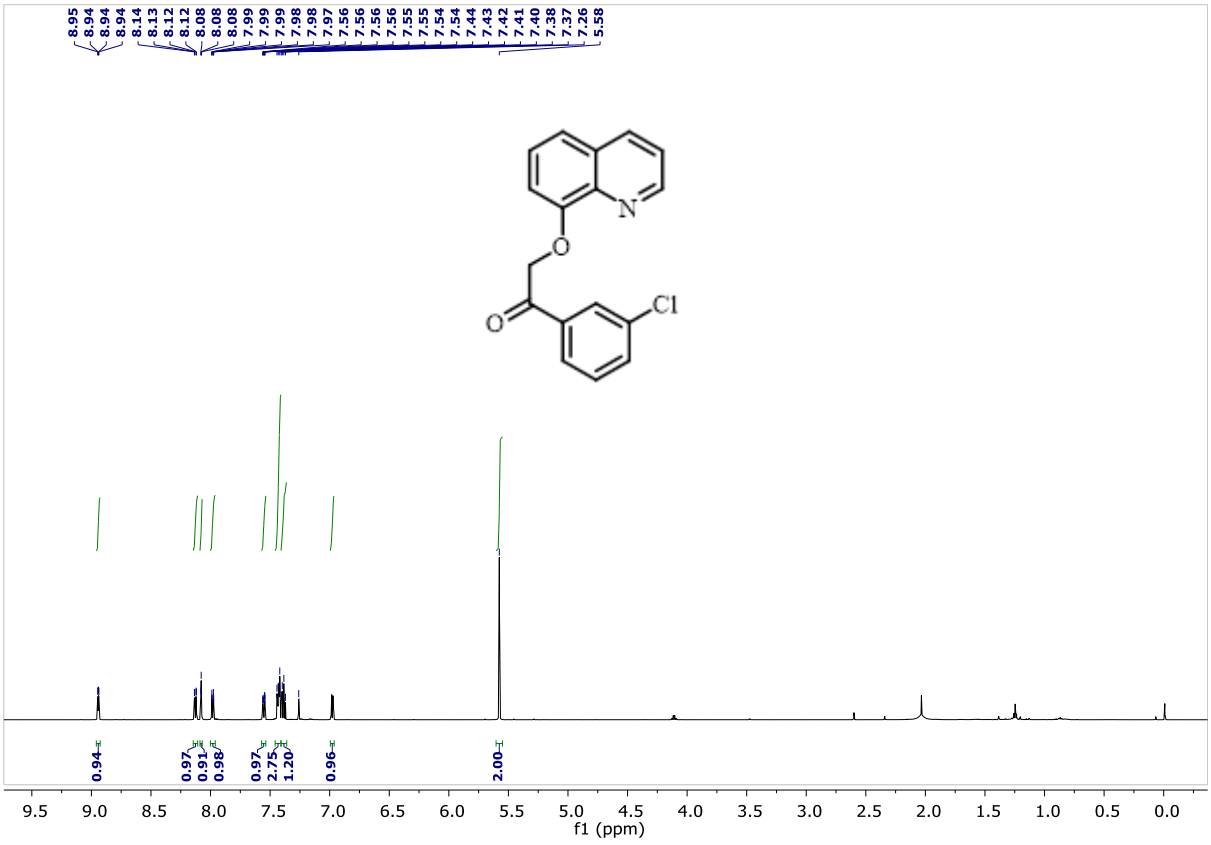


Figure S13: ^{1}H NMR Spectrum of **7e** ($CDCl_3$, 600 MHz, 298 K)

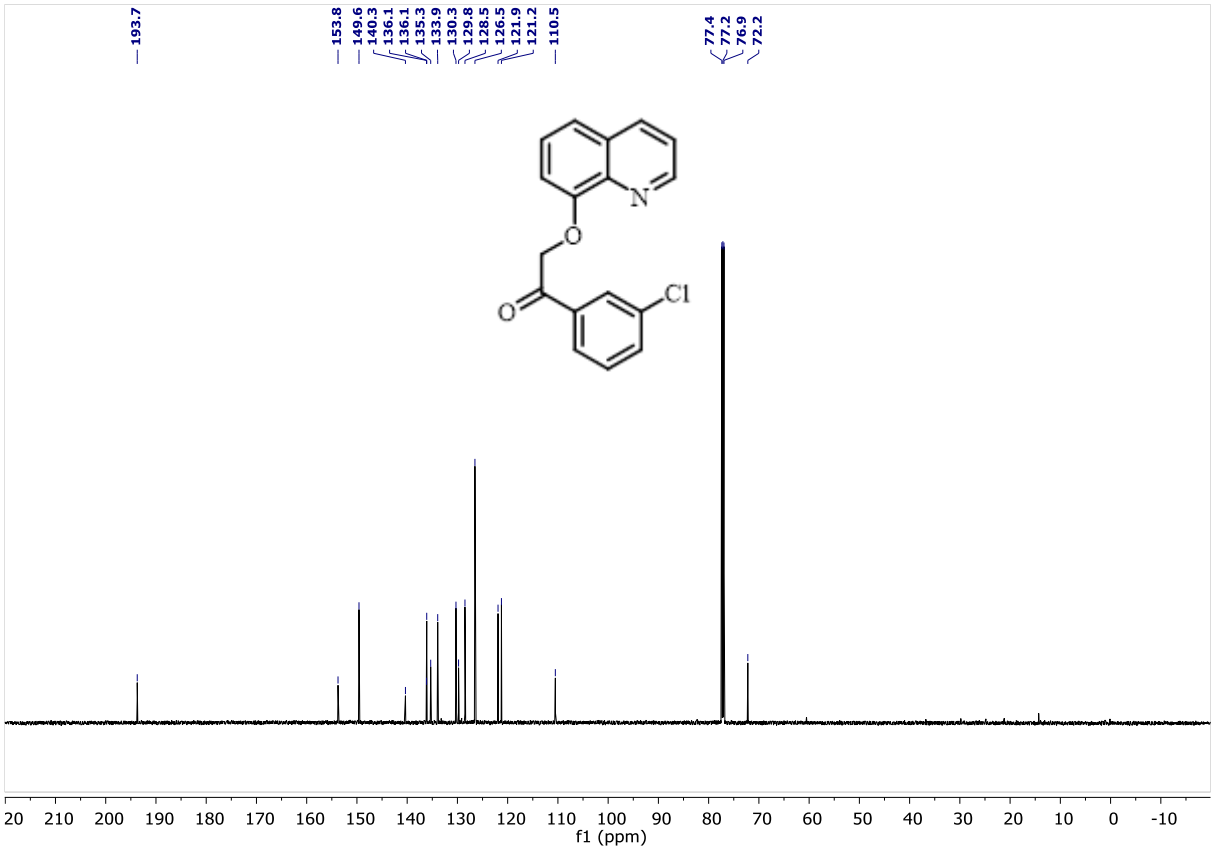


Figure S14: $^{13}C\{^{1}H\}$ NMR Spectrum of **7e** ($CDCl_3$, 151 MHz, 298 K)

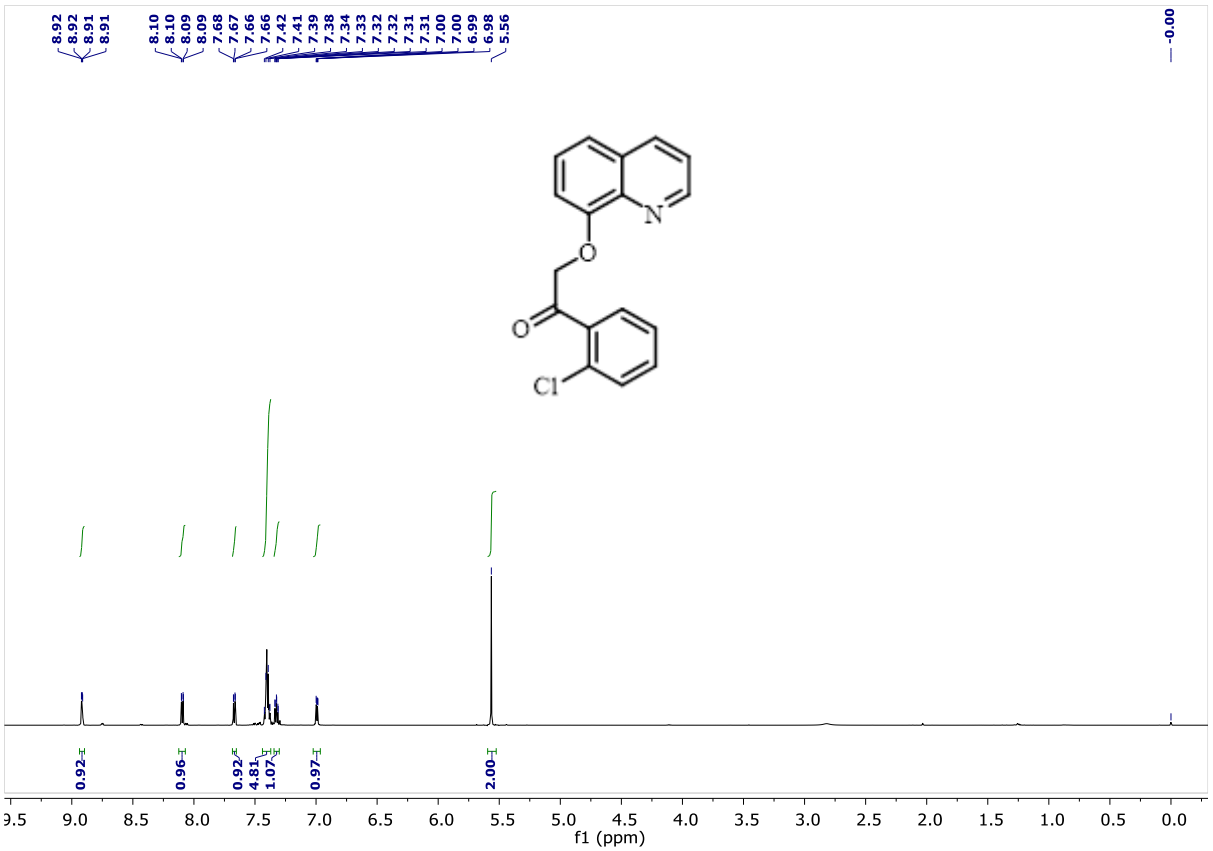


Figure S15: ^{1}H NMR Spectrum of **7g** ($CDCl_3$, 600 MHz, 298 K)

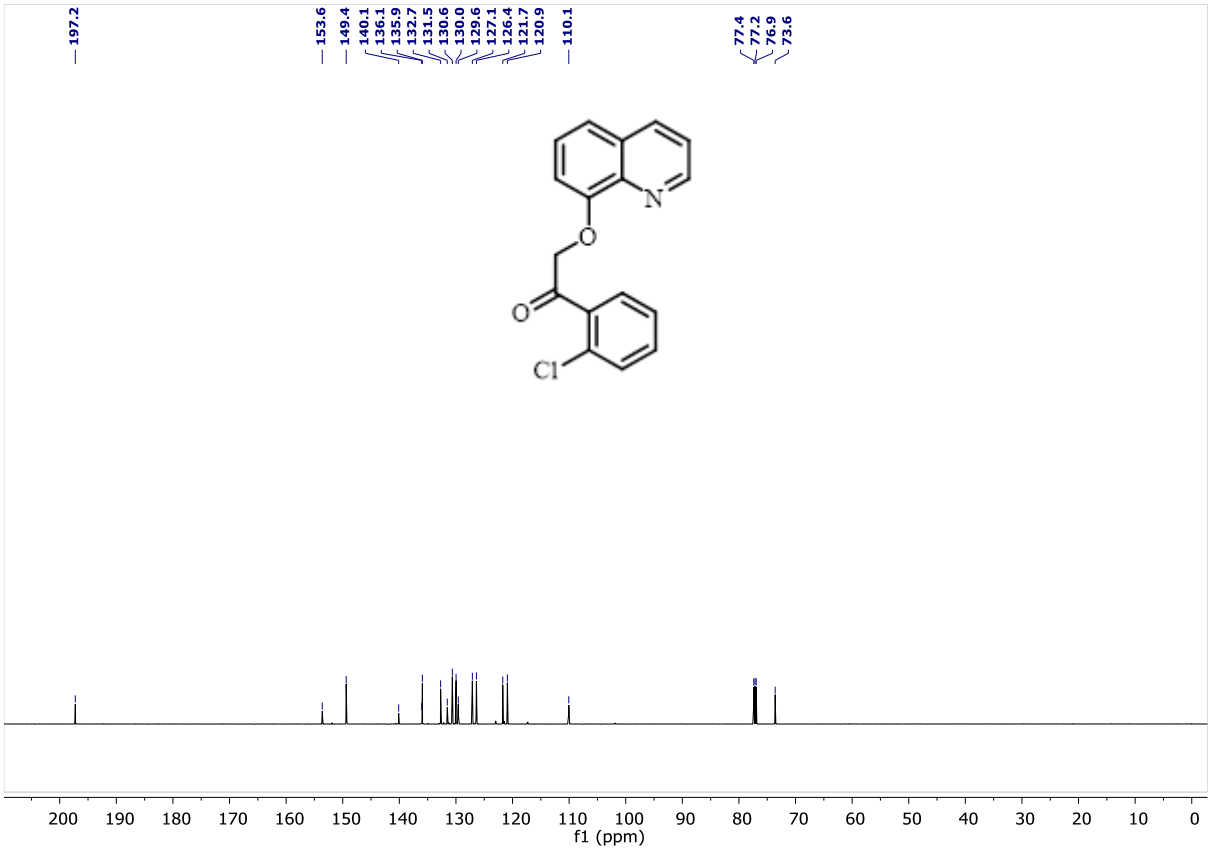


Figure S16: $^{13}C\{^{1}H\}$ NMR Spectrum of **7e** ($CDCl_3$, 151 MHz, 298 K)

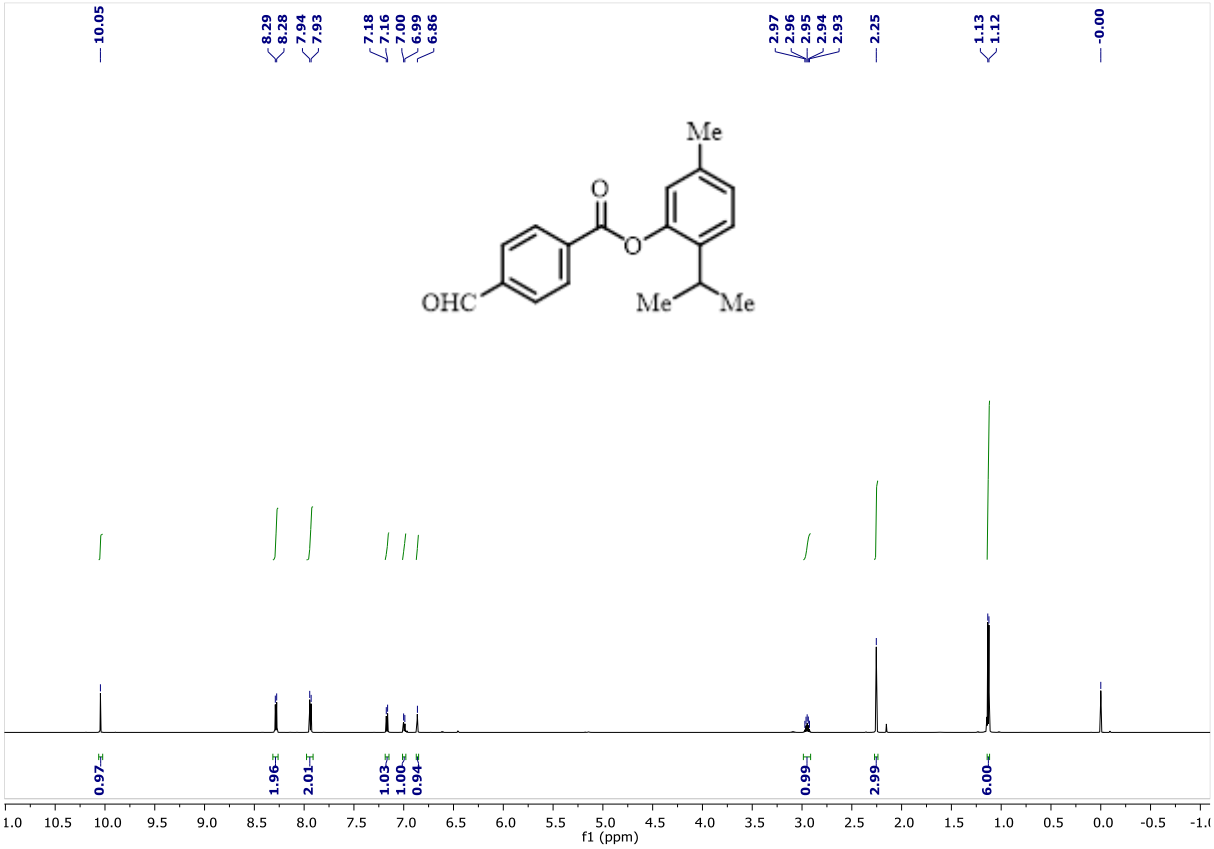


Figure S17: ^{1}H NMR Spectrum of **5d** ($CDCl_3$, 600 MHz, 298 K)

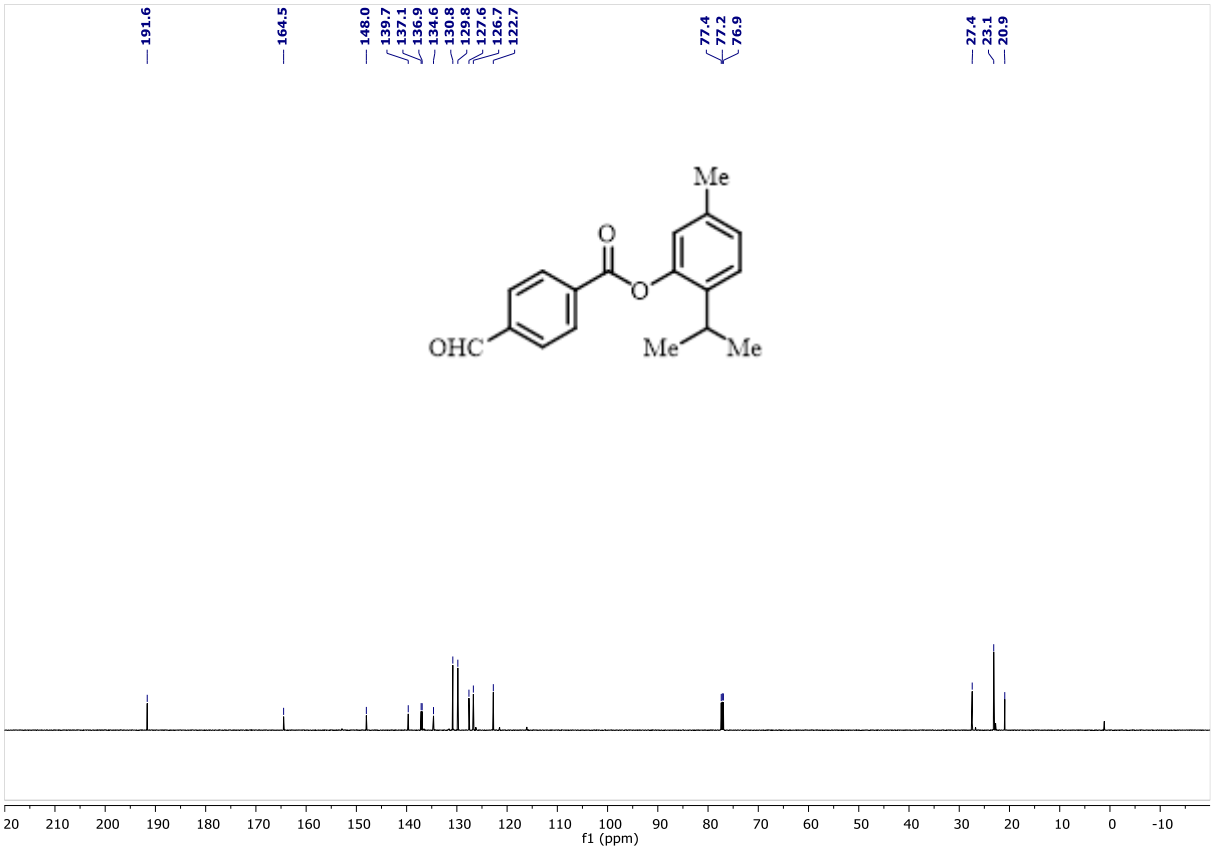


Figure S18: $^{13}C\{^{1}H\}$ NMR Spectrum of **5d** ($CDCl_3$, 151 MHz, 298 K)

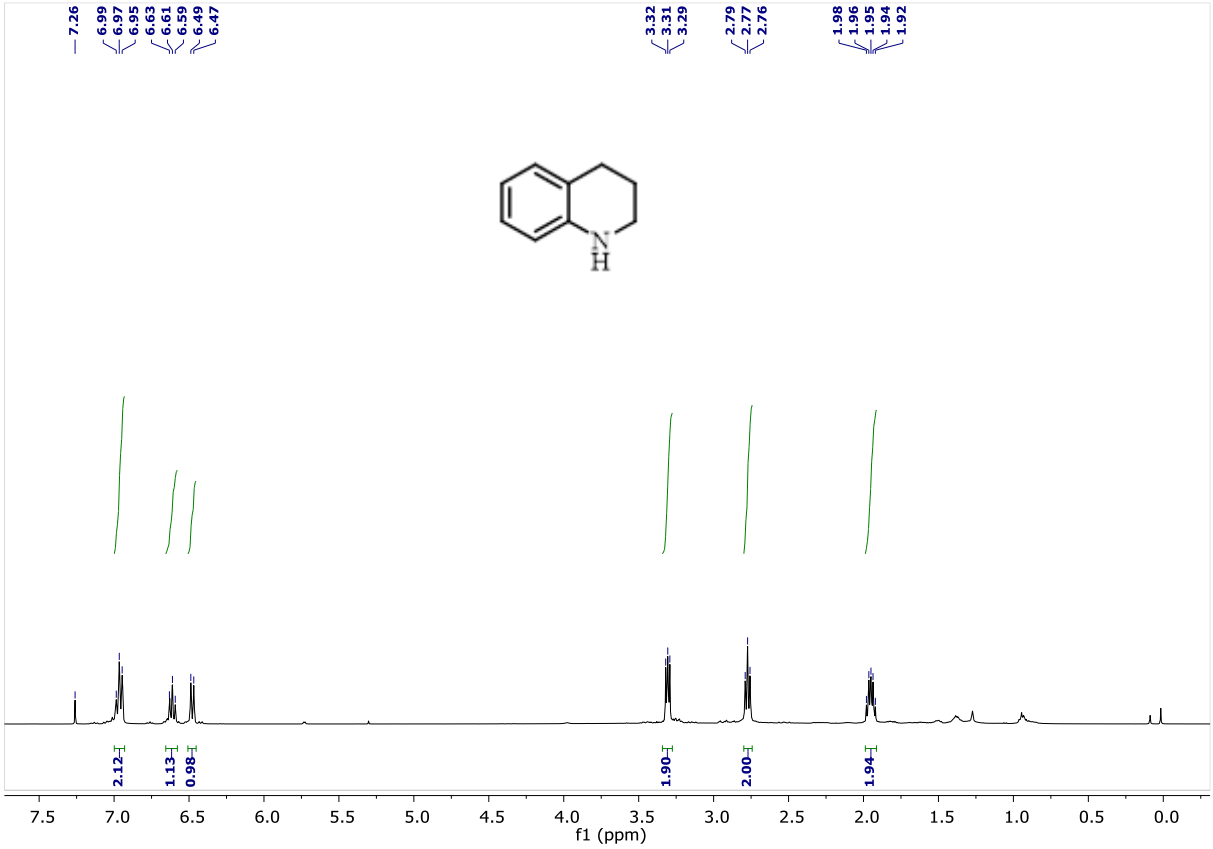


Figure S19: ^{1}H NMR Spectrum of **1a'** ($CDCl_3$, 400 MHz, 298 K)

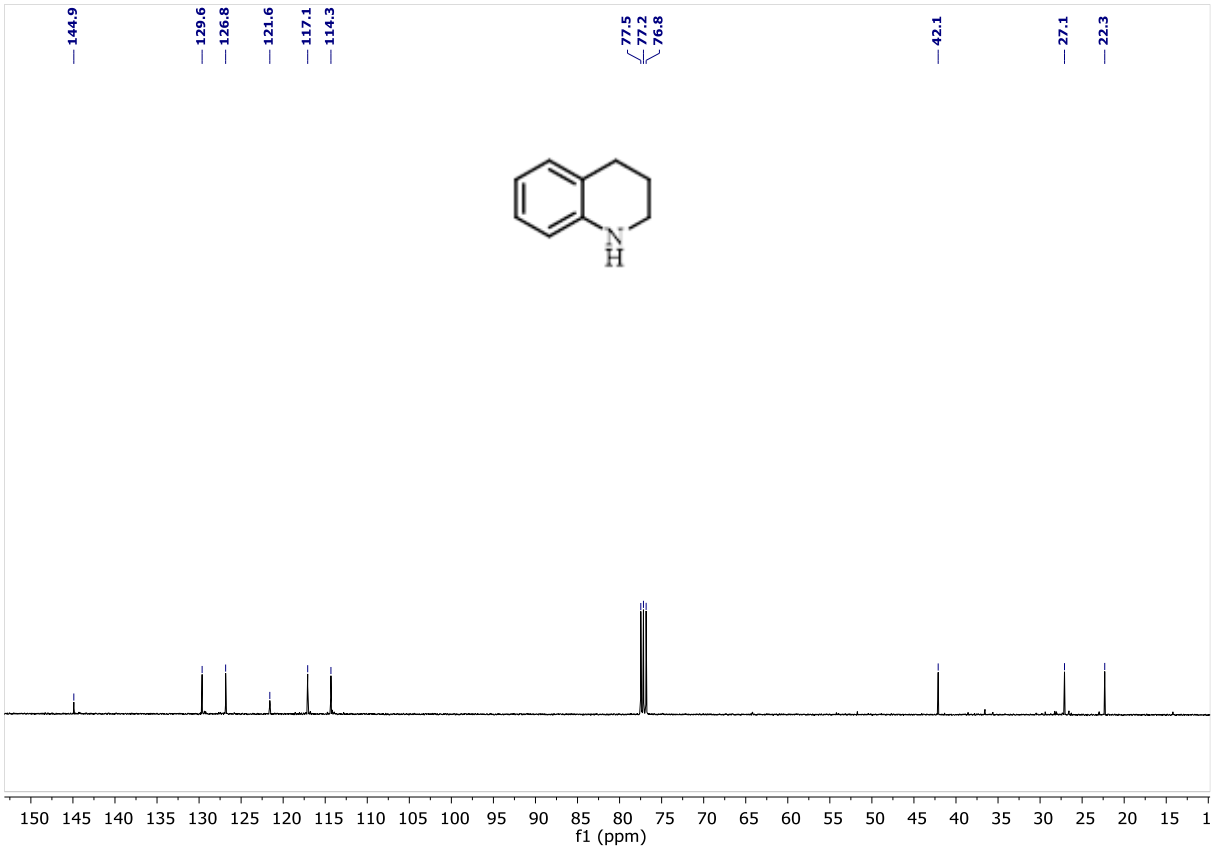


Figure S20: $^{13}C\{^{1}H\}$ NMR Spectrum of **1a'** ($CDCl_3$, 101 MHz, 298 K)

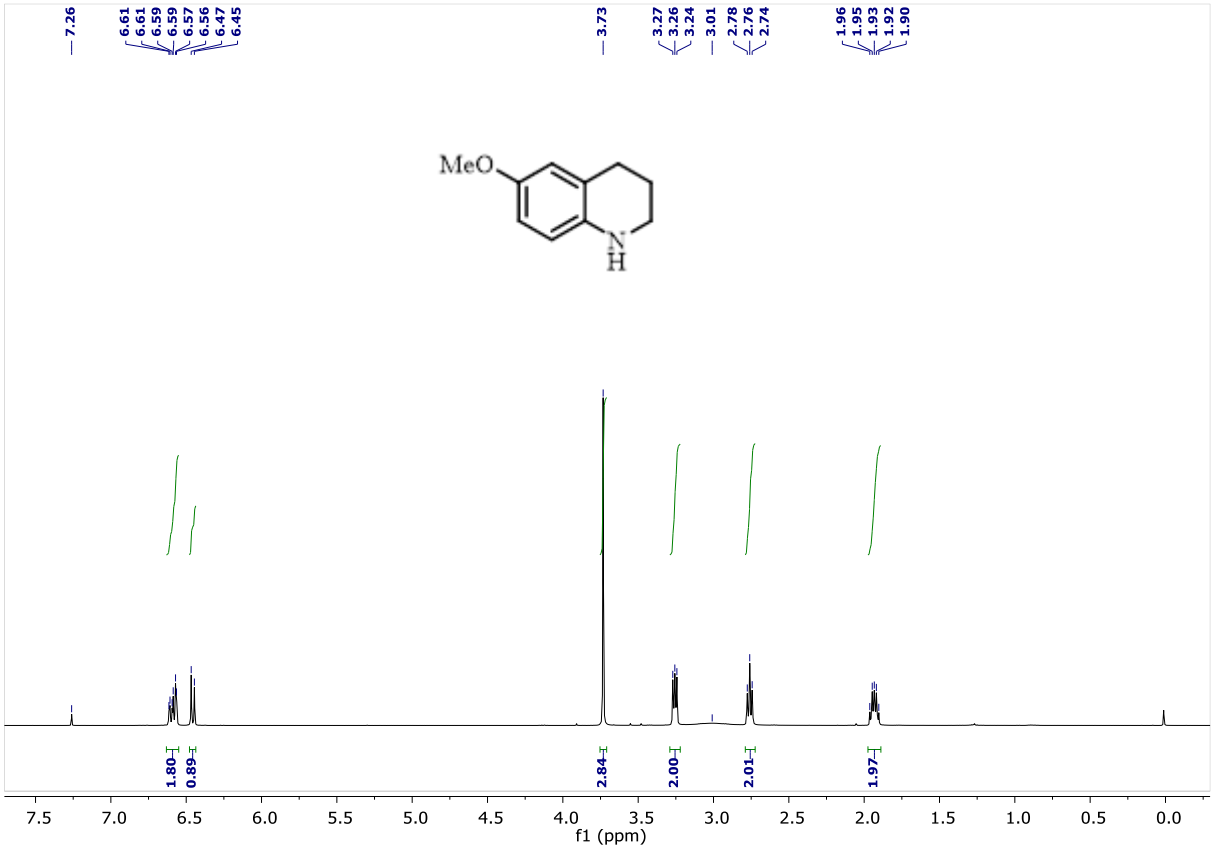


Figure S21: ^{1}H NMR Spectrum of **1f'** ($CDCl_3$, 400 MHz, 298 K)

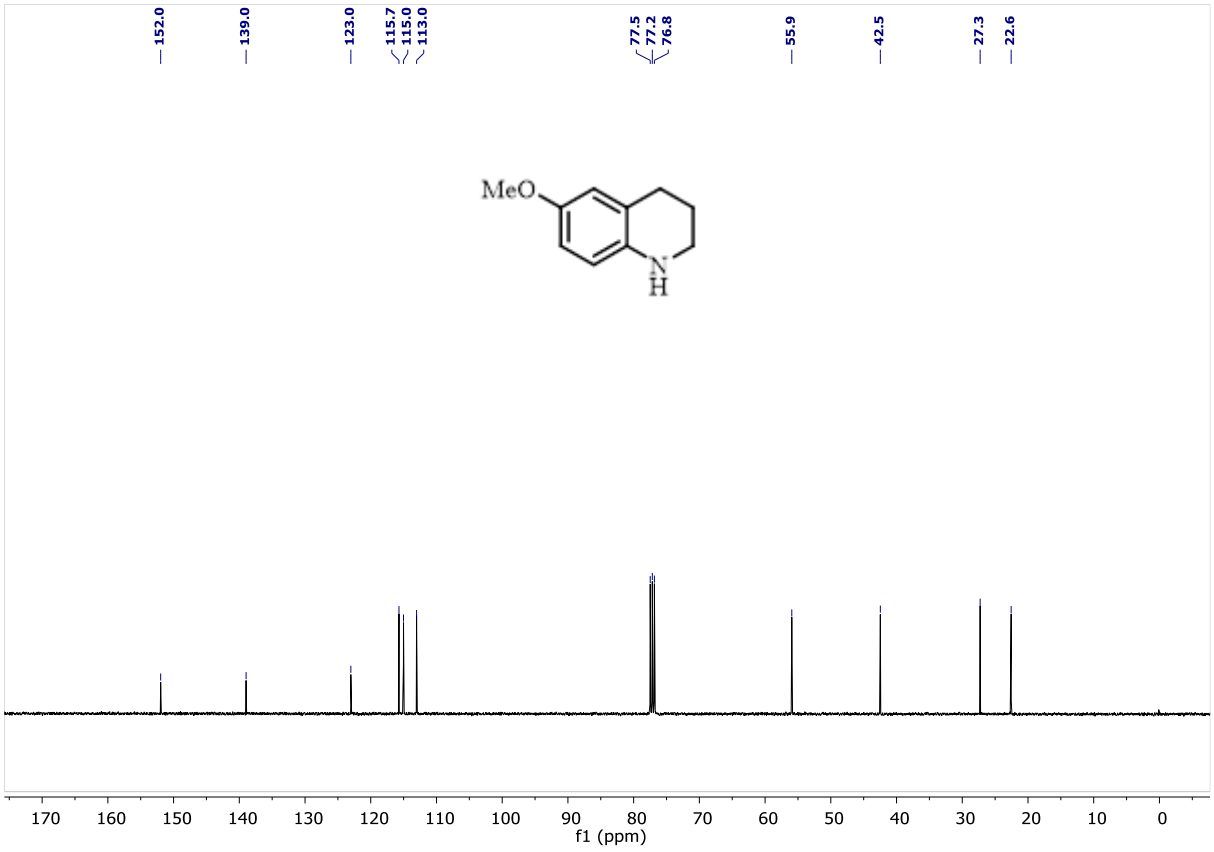


Figure S22: $^{13}C\{^{1}H\}$ NMR Spectrum of **1f** ($CDCl_3$, 101 MHz, 298 K)

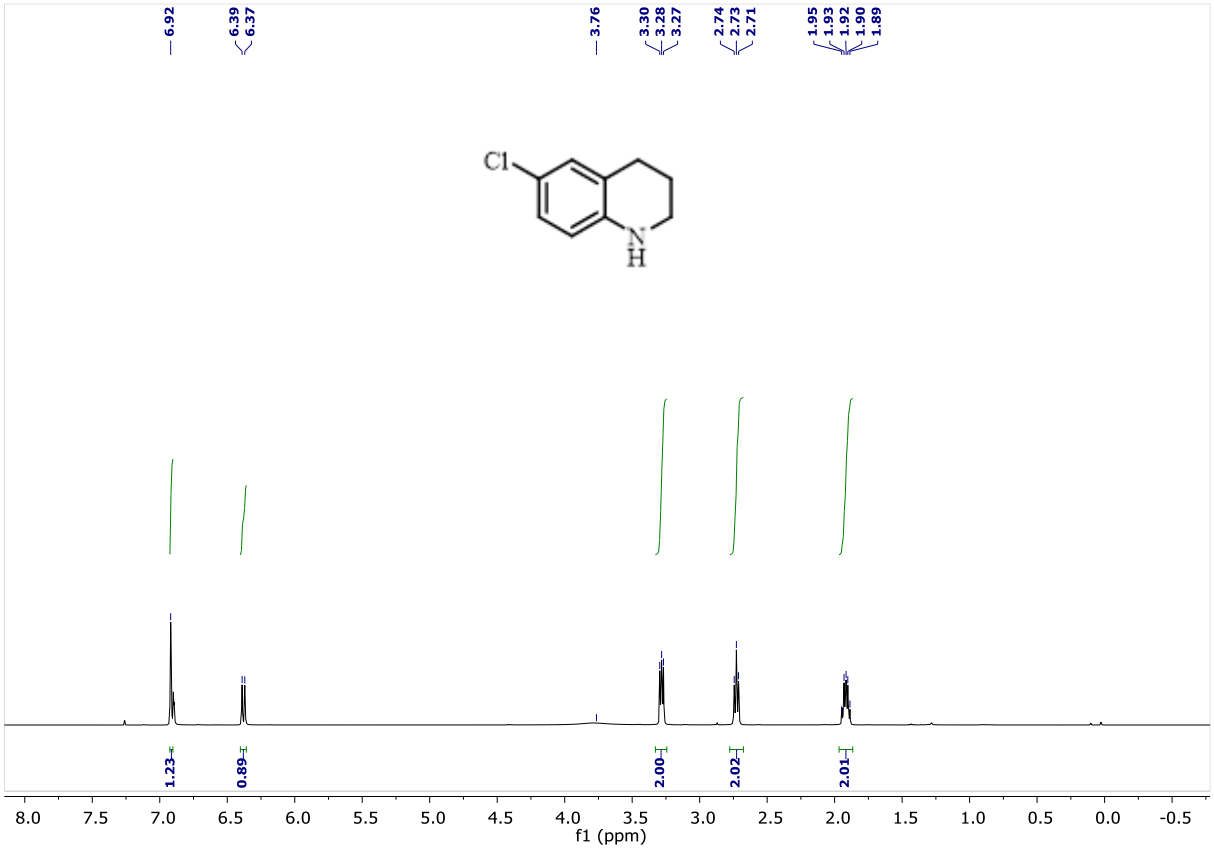


Figure S23: ^{1}H NMR Spectrum of **1g'** ($CDCl_3$, 400 MHz, 298 K)

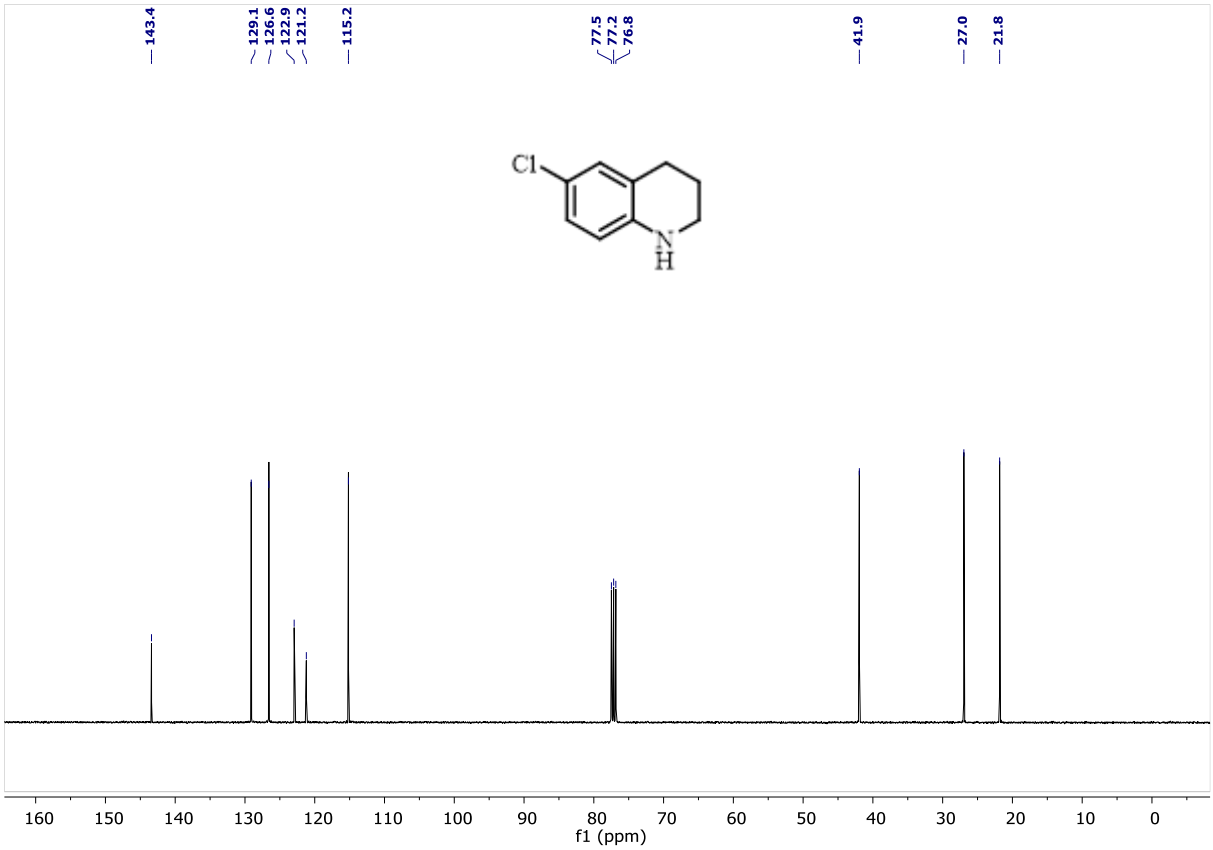


Figure S24: $^{13}C\{^{1}H\}$ NMR Spectrum of **1g'** ($CDCl_3$, 101 MHz, 298 K).

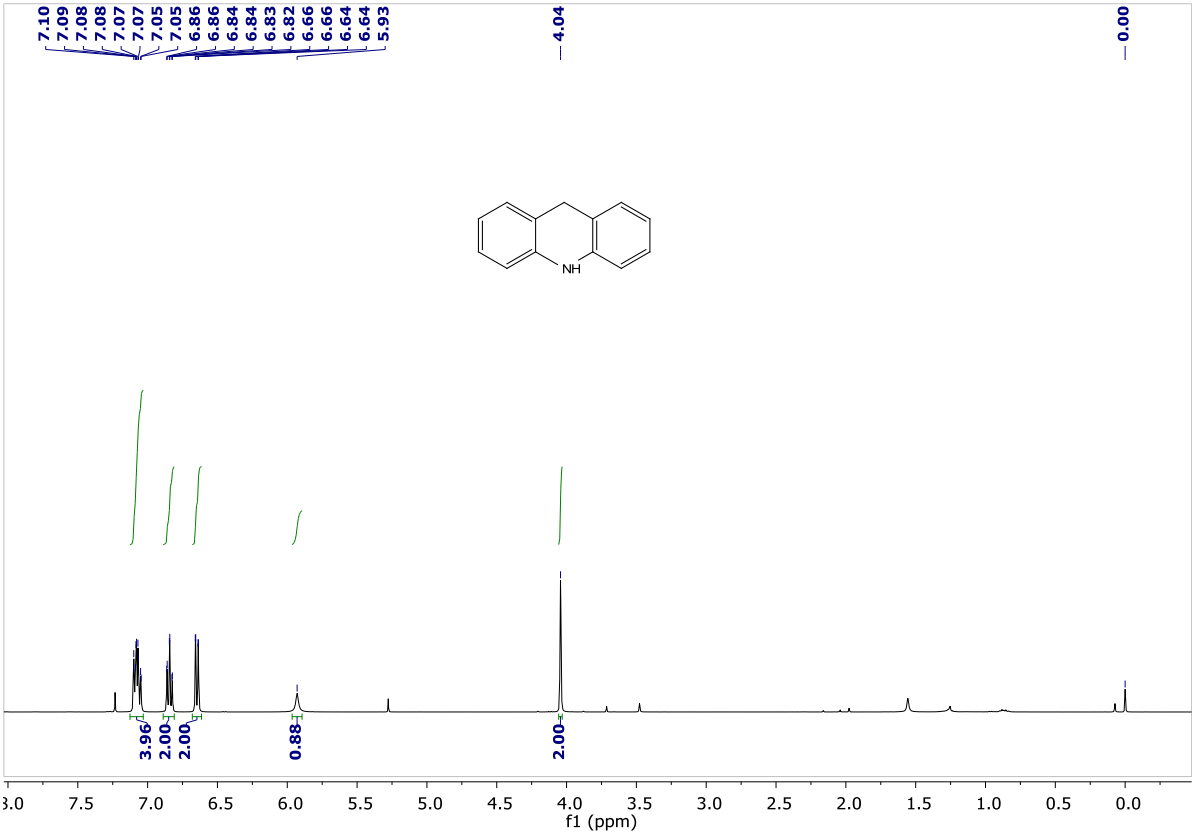


Figure S25: ^{1}H NMR Spectrum of **1p'** ($CDCl_3$, 400 MHz, 298 K).

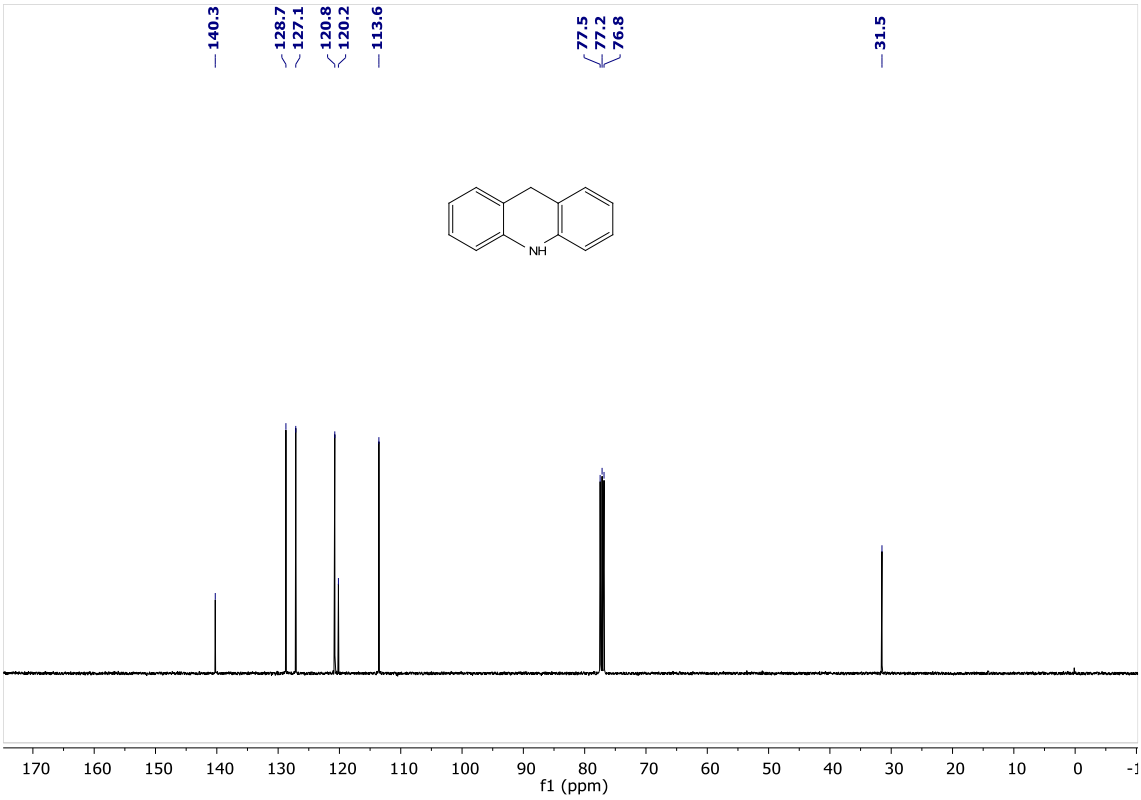


Figure S26: ^{13}C {^{1}H} NMR Spectrum of **1p'** ($CDCl_3$, 101 MHz, 298 K).

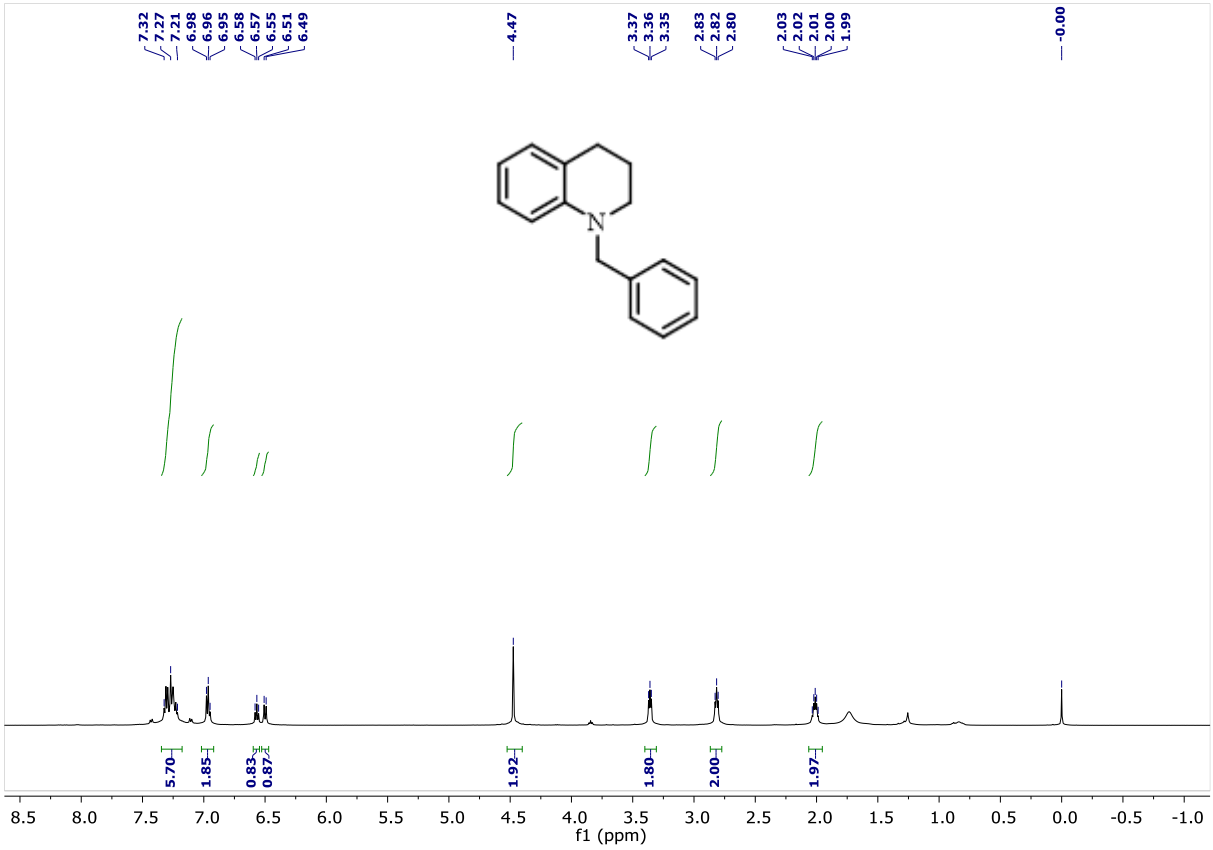


Figure S27: ^{1}H NMR Spectrum of **3a** ($CDCl_3$, 500 MHz, 298 K)

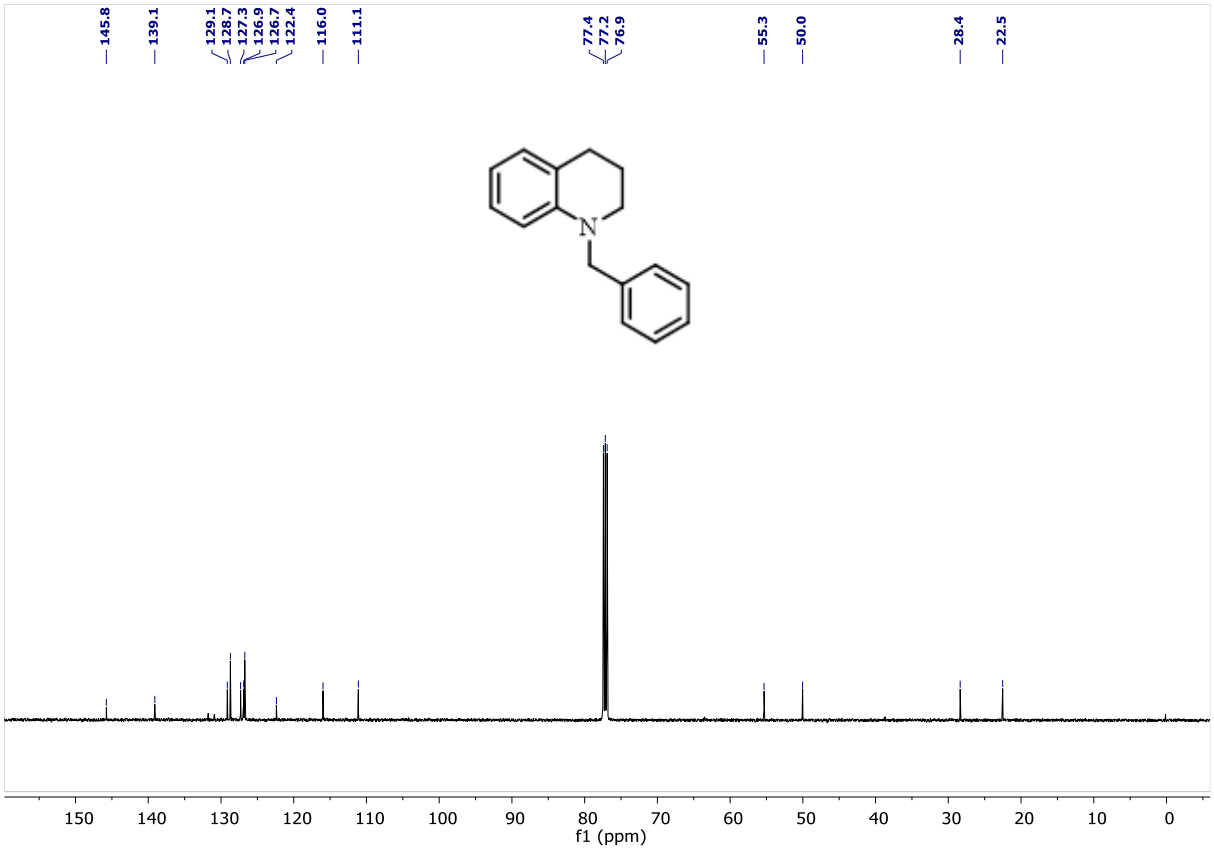


Figure S28: $^{13}C\{^{1}H\}$ NMR Spectrum of **3a** ($CDCl_3$, 126 MHz, 298 K)

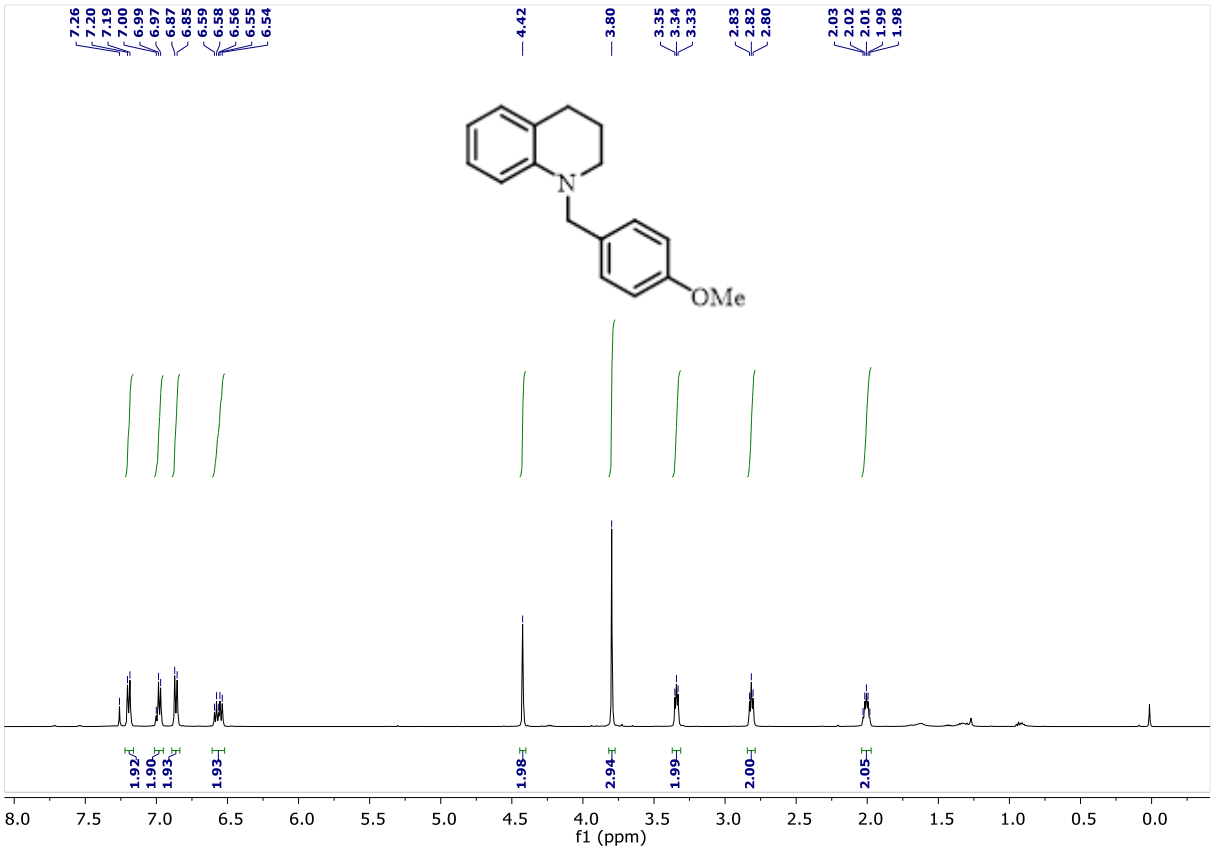


Figure S29: ^{1}H NMR Spectrum of **3b** ($CDCl_3$, 500 MHz, 298 K)

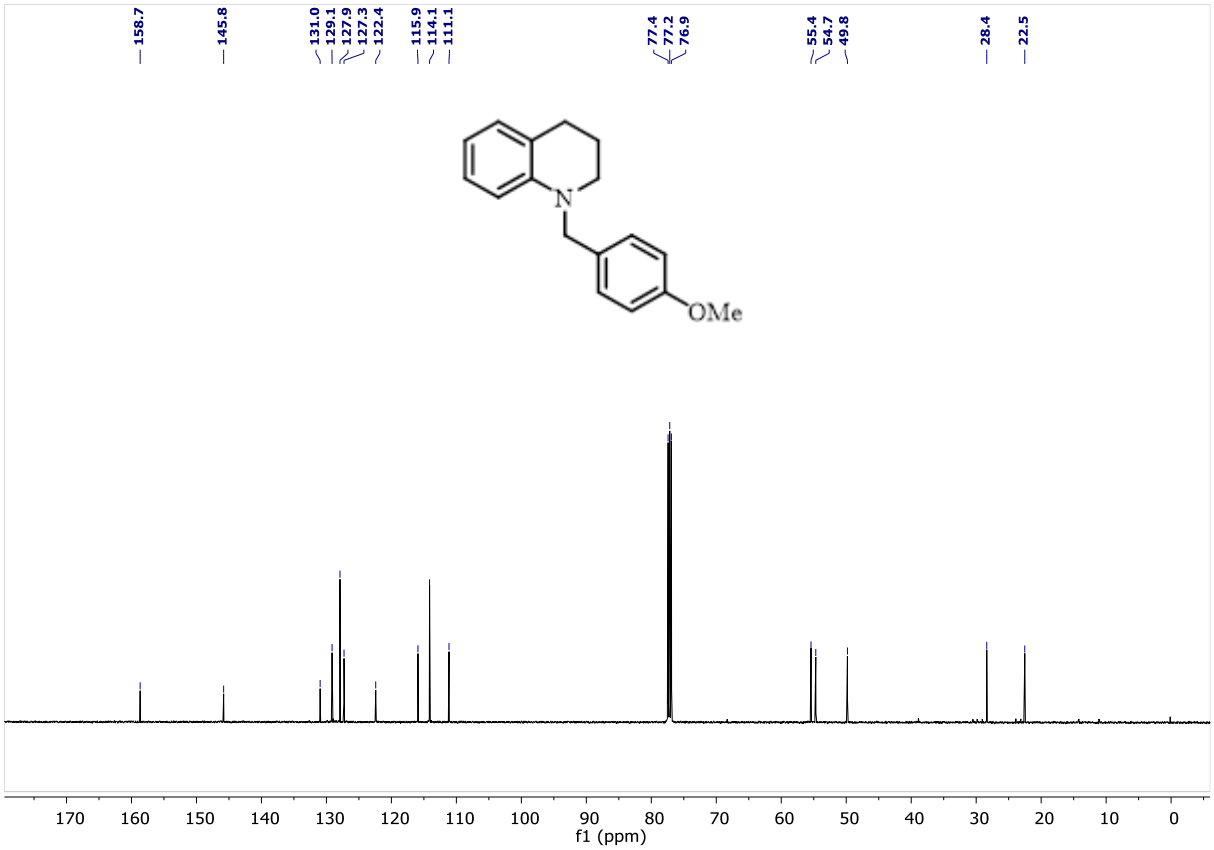


Figure S30: $^{13}C\{^{1}H\}$ NMR Spectrum of **3b** ($CDCl_3$, 126 MHz, 298 K)

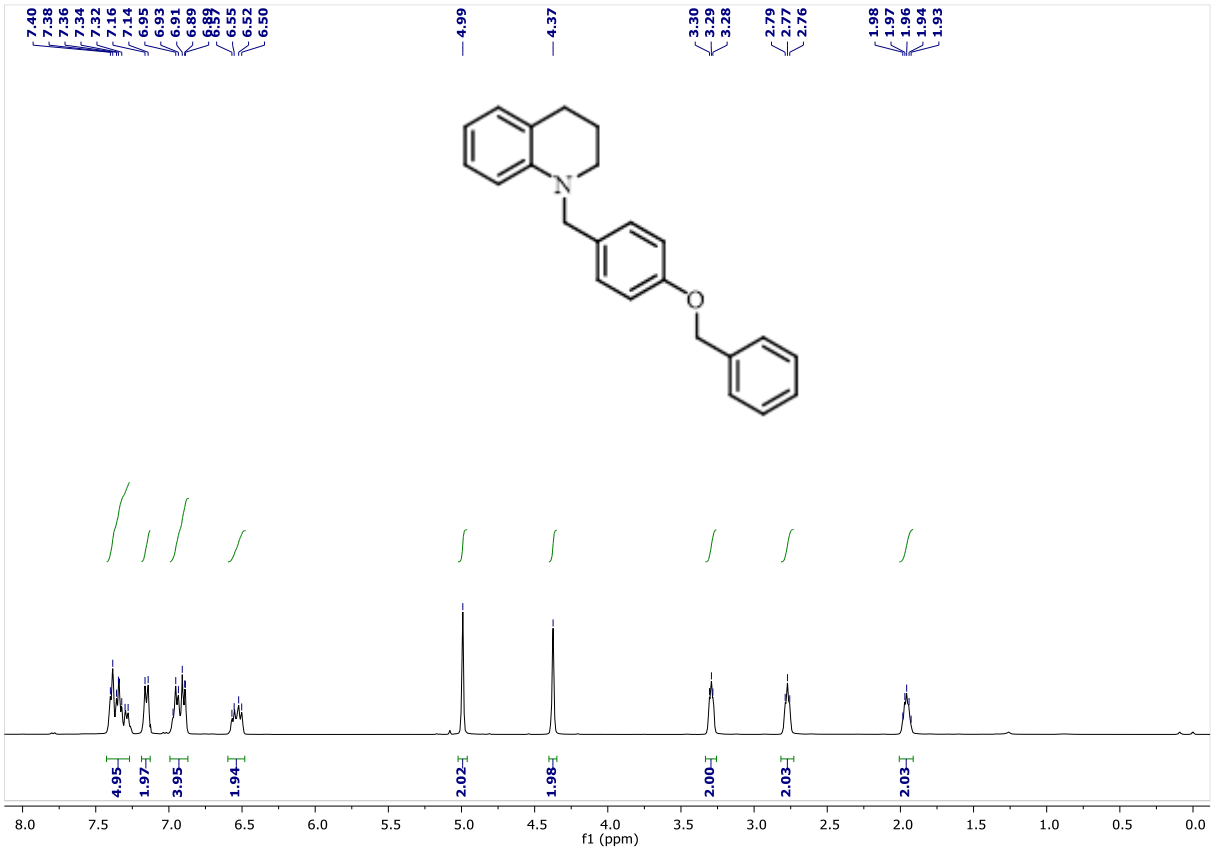


Figure S31: ^{1}H NMR Spectrum of **3c** ($CDCl_3$, 400 MHz, 298 K)

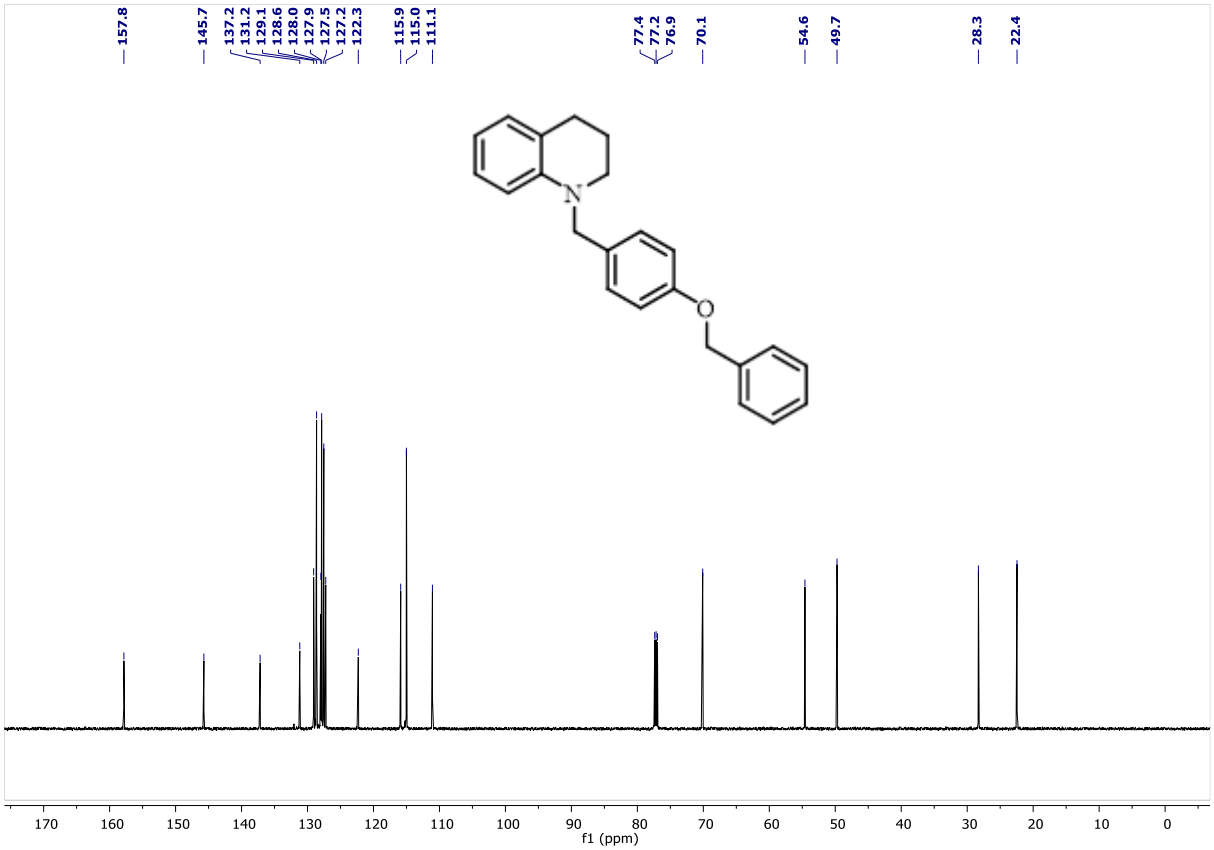


Figure S32: $^{13}C\{^{1}H\}$ NMR Spectrum of **3c** ($CDCl_3$, 151 MHz, 298 K)

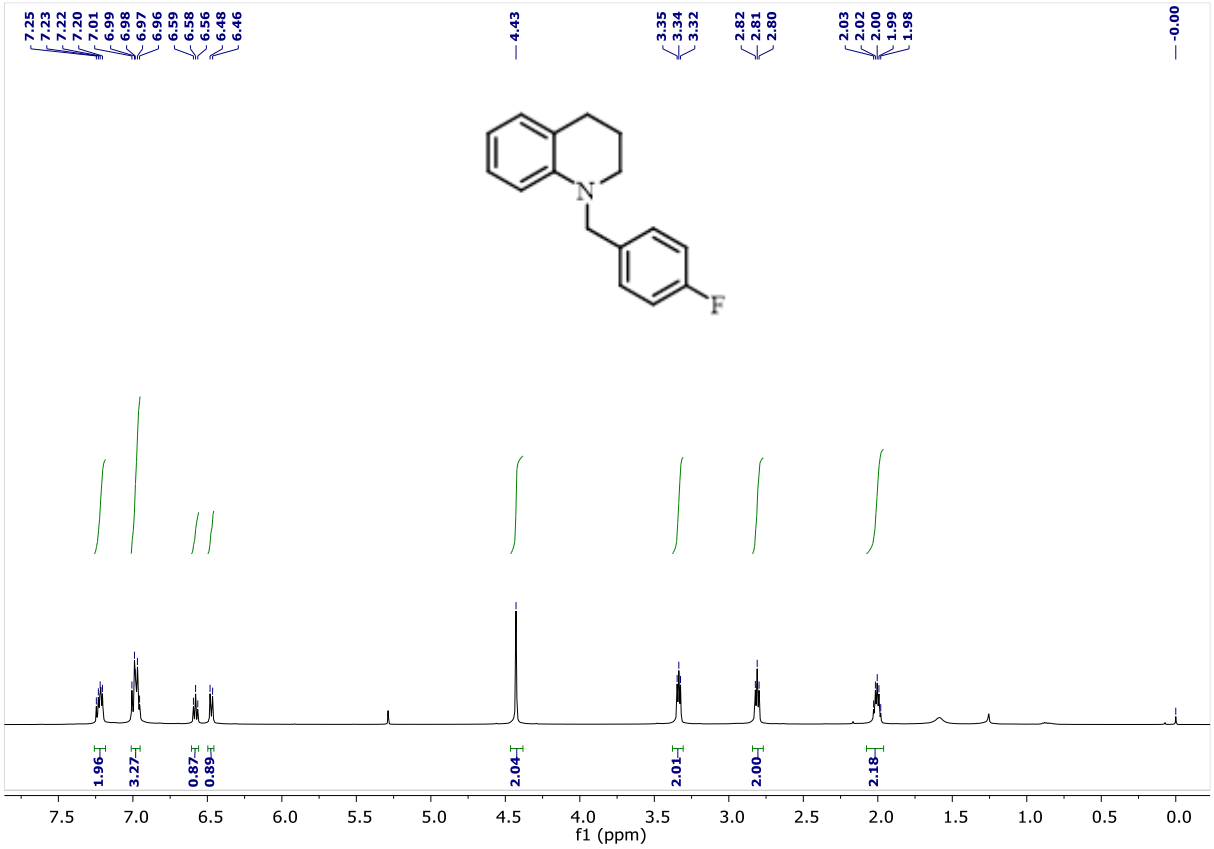


Figure S33: ^{1}H NMR Spectrum of **3d** ($CDCl_3$, 500 MHz, 298 K)

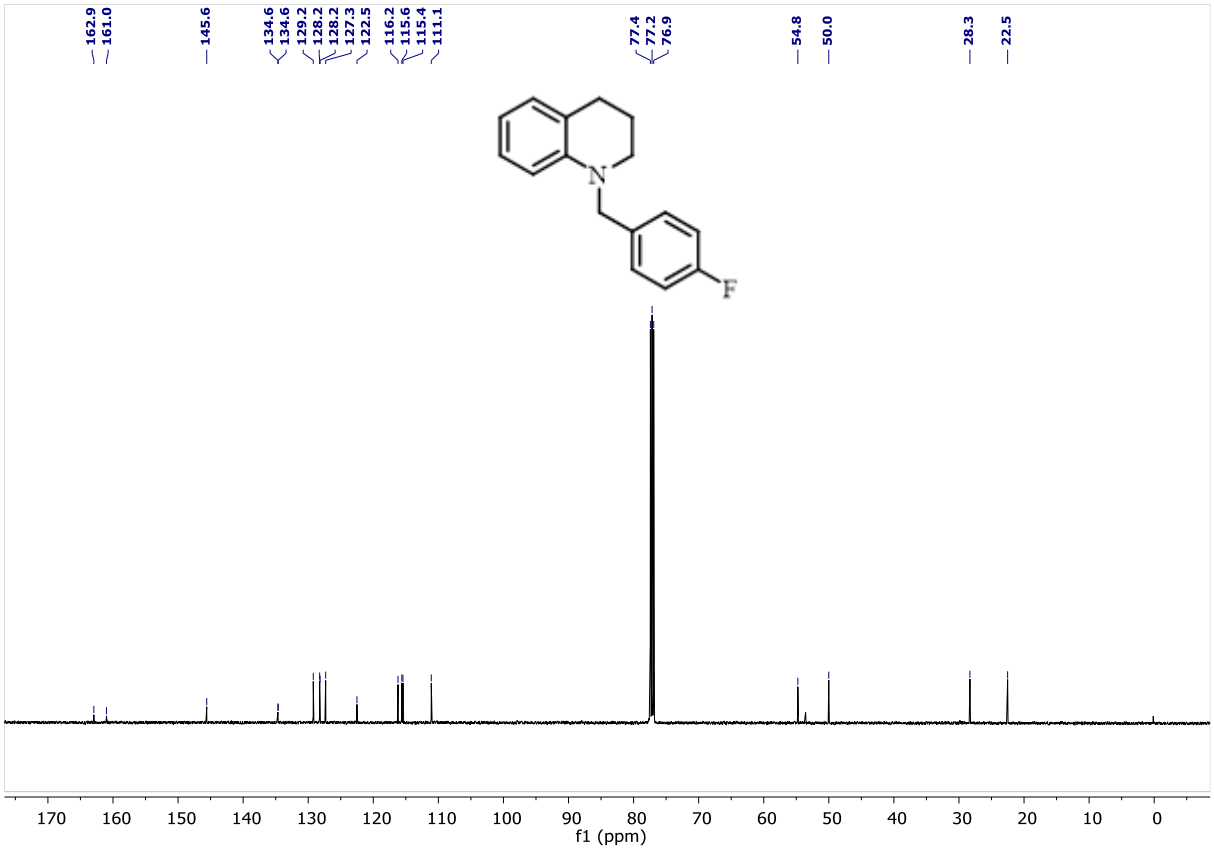


Figure S34: $^{13}C\{^{1}H\}$ NMR Spectrum of **3d** ($CDCl_3$, 126 MHz, 298 K)

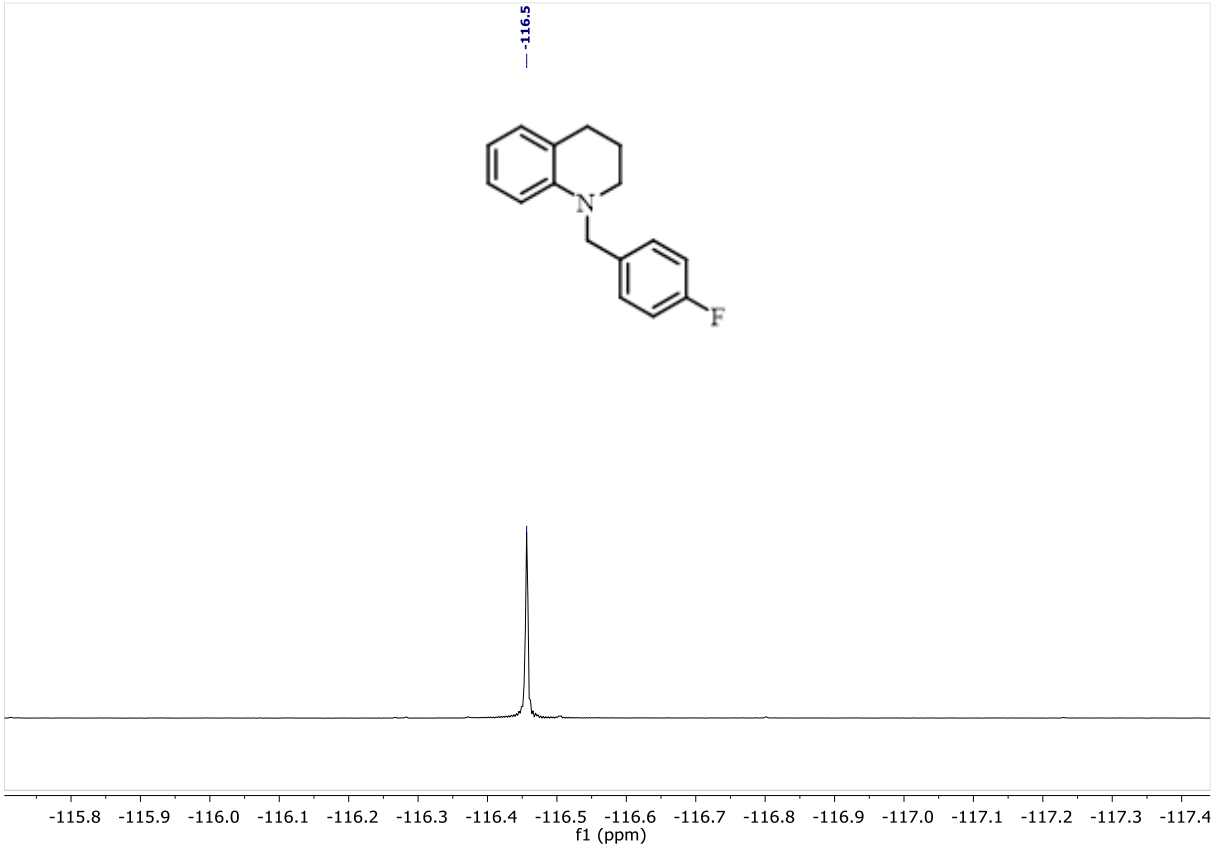


Figure S35: $^{19}F\{^{1}H\}$ NMR Spectrum of **3d** ($CDCl_3$, 471 MHz, 298 K)

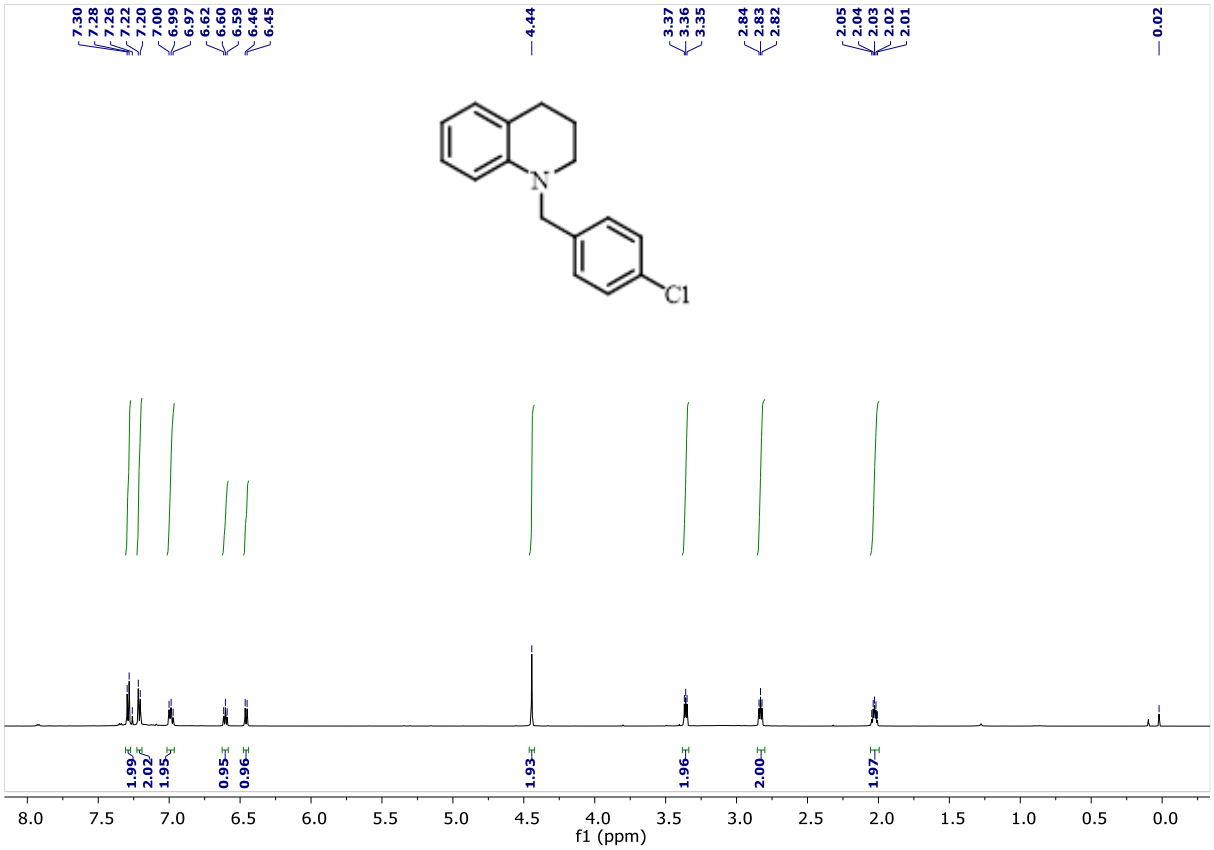


Figure S36: ^{1}H NMR Spectrum of **3e** ($CDCl_3$, 600 MHz, 298 K)

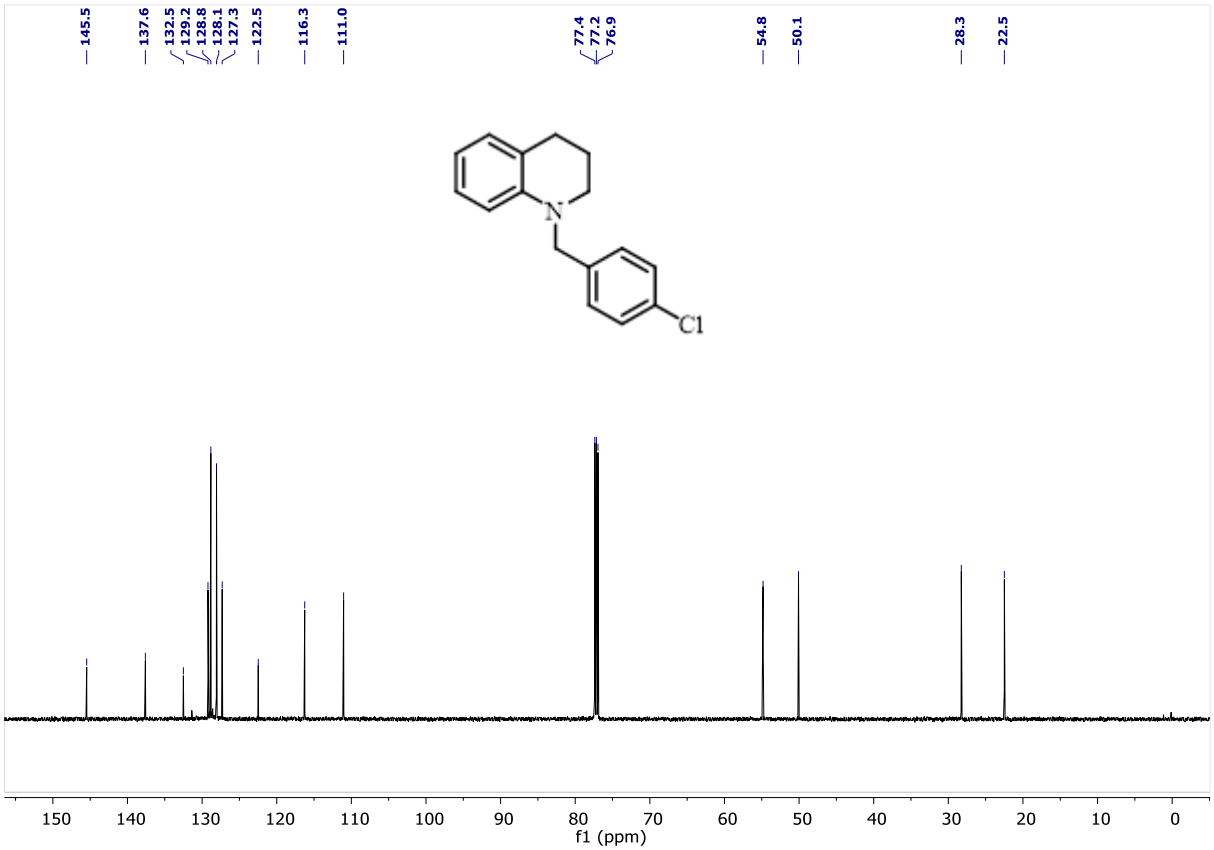


Figure S37: $^{13}C\{^{1}H\}$ NMR Spectrum of **3e** ($CDCl_3$, 151 MHz, 298 K)

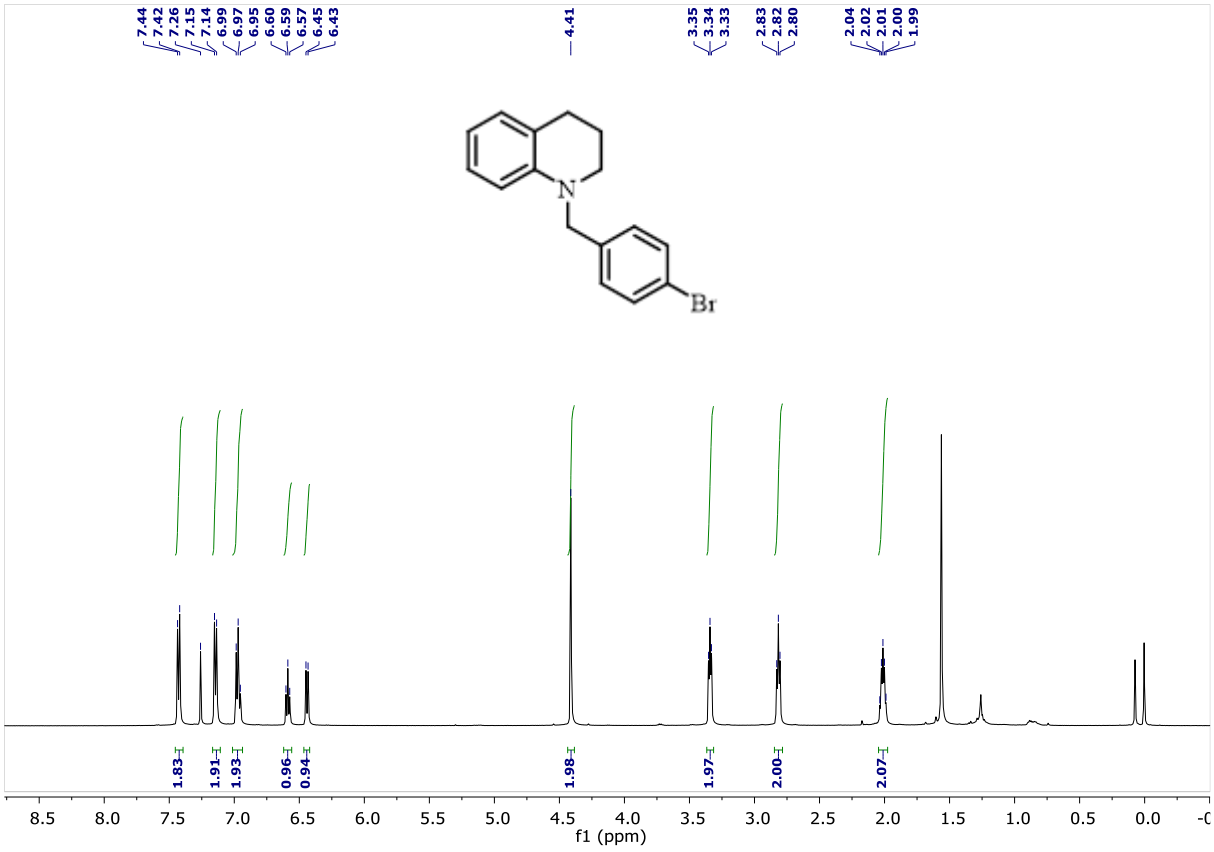


Figure S38: ^{1}H NMR Spectrum of **3f** ($CDCl_3$, 500 MHz, 298 K)

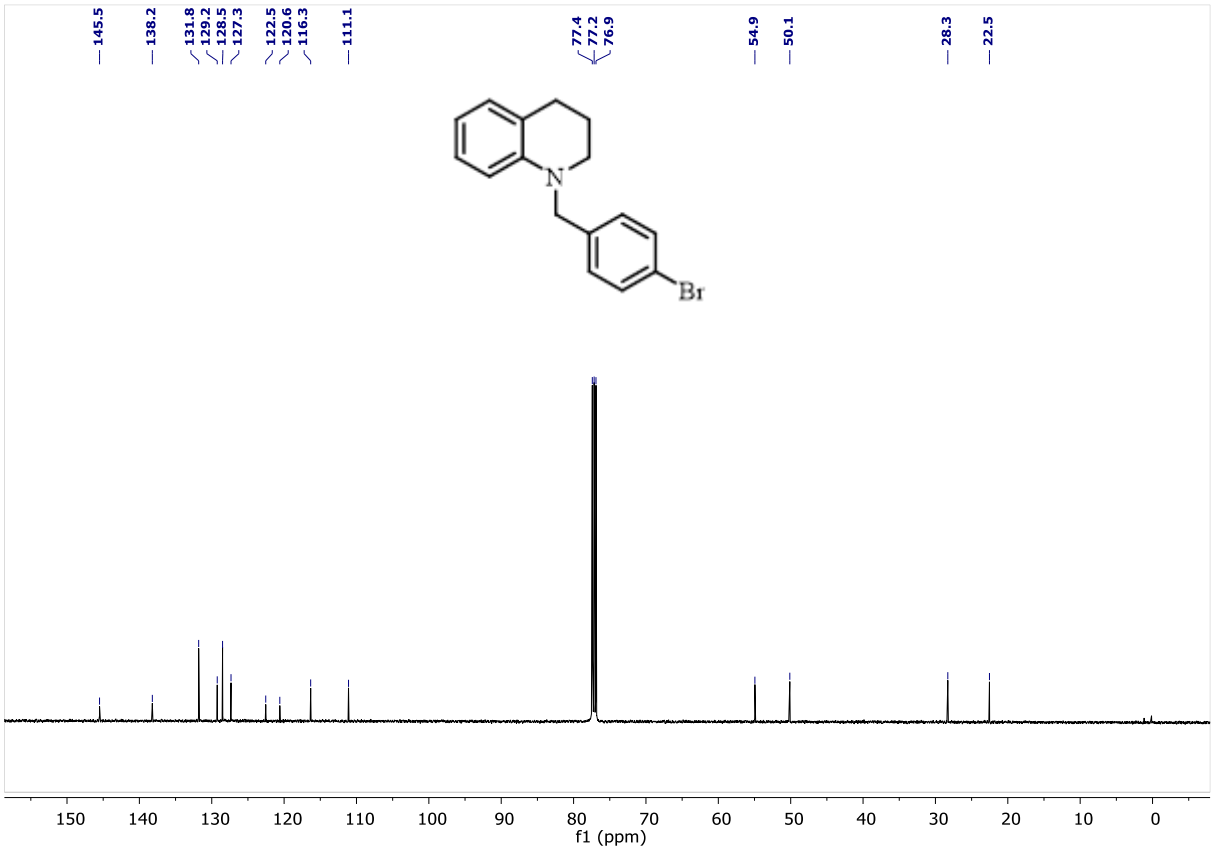


Figure S39: $^{13}C\{^{1}H\}$ NMR Spectrum of **3f** ($CDCl_3$, 126 MHz, 298 K)

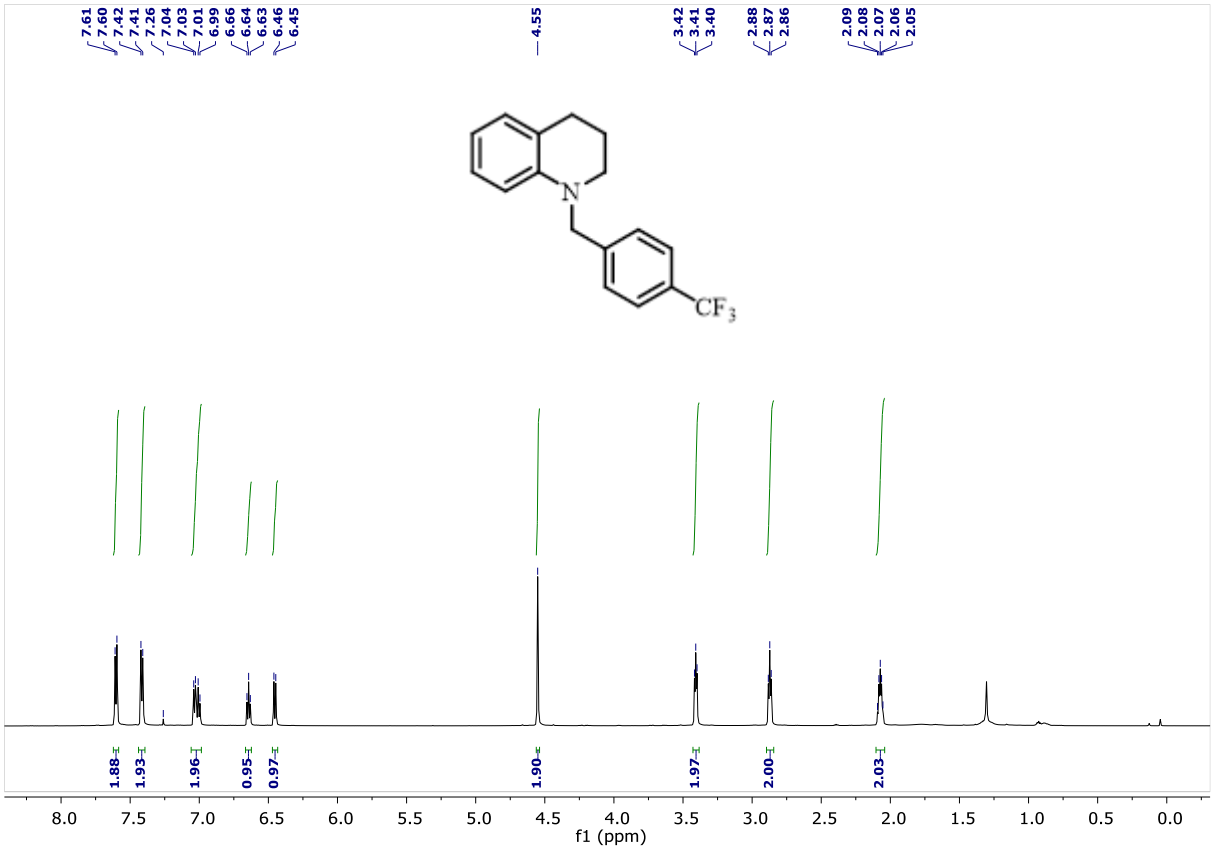


Figure S40: ^{1}H NMR Spectrum of **3g** ($CDCl_3$, 600 MHz, 298 K)

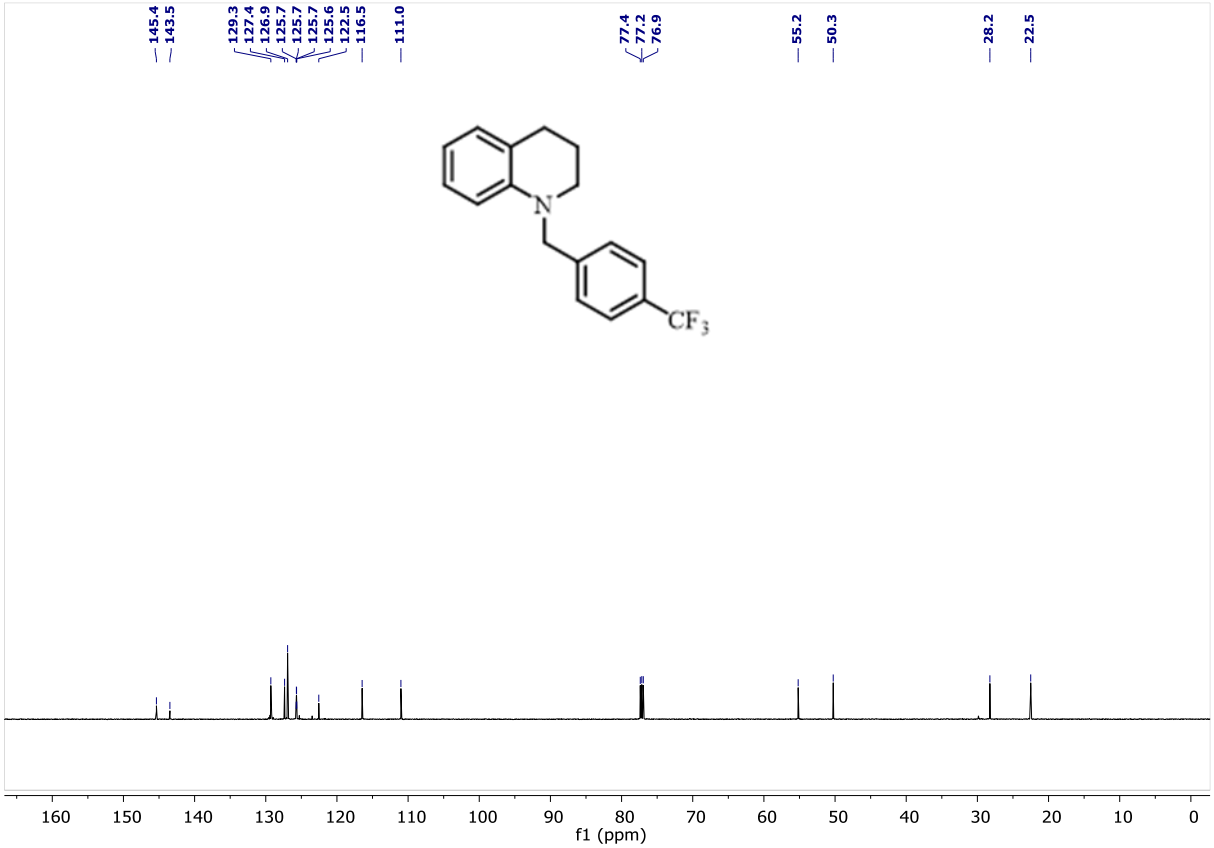


Figure S41: $^{13}C\{^{1}H\}$ NMR Spectrum of **3g** ($CDCl_3$, 151 MHz, 298 K)

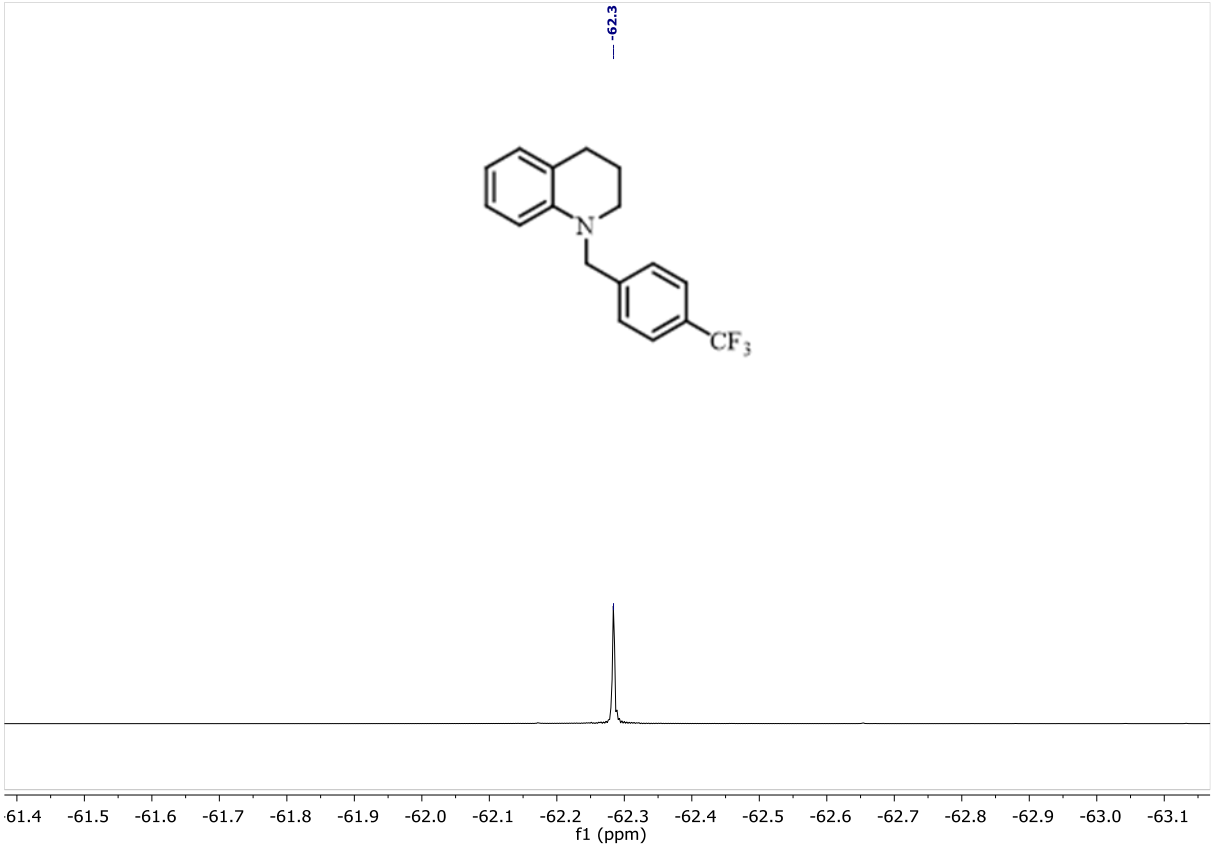


Figure S42: $^{19}F\{^{1}H\}$ NMR Spectrum of **3g** ($CDCl_3$, 565 MHz, 298 K)

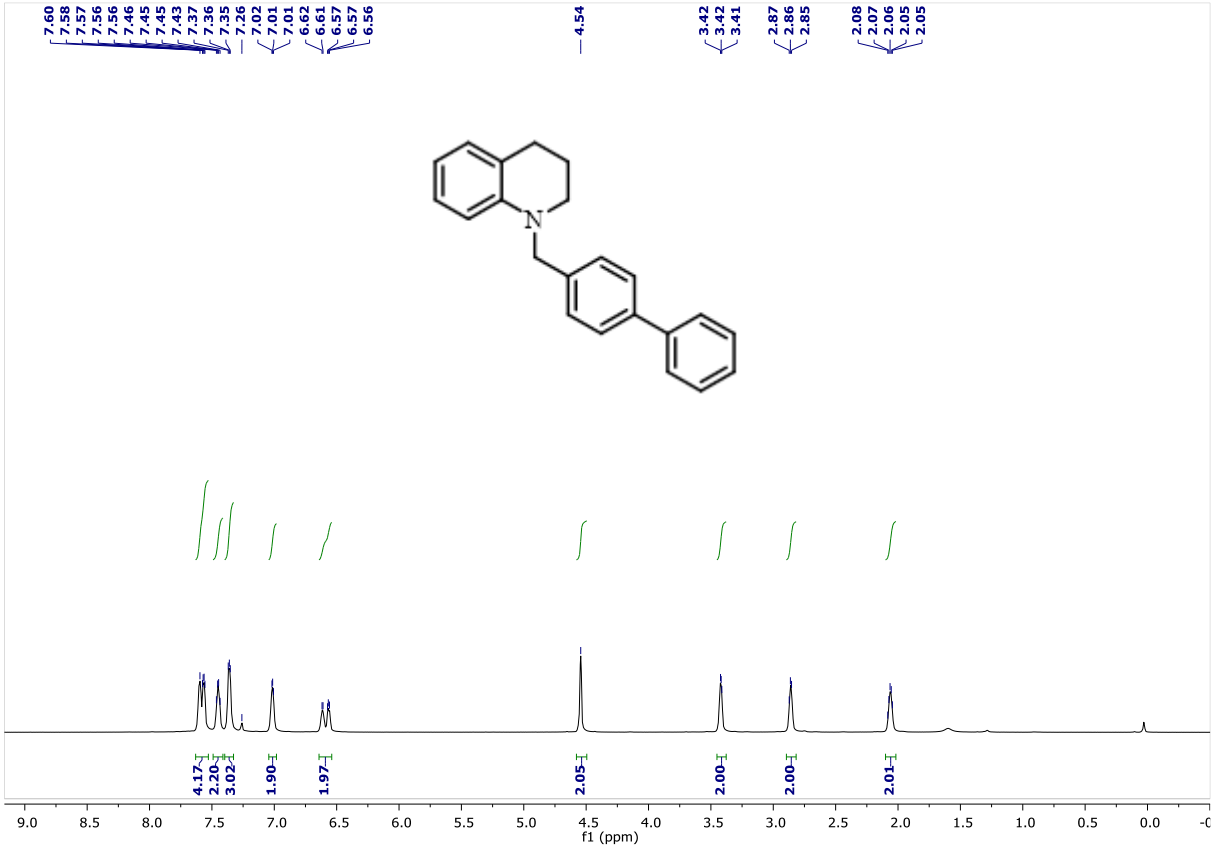


Figure S43: ^{1}H NMR Spectrum of **3h** ($CDCl_3$, 600 MHz, 298 K)

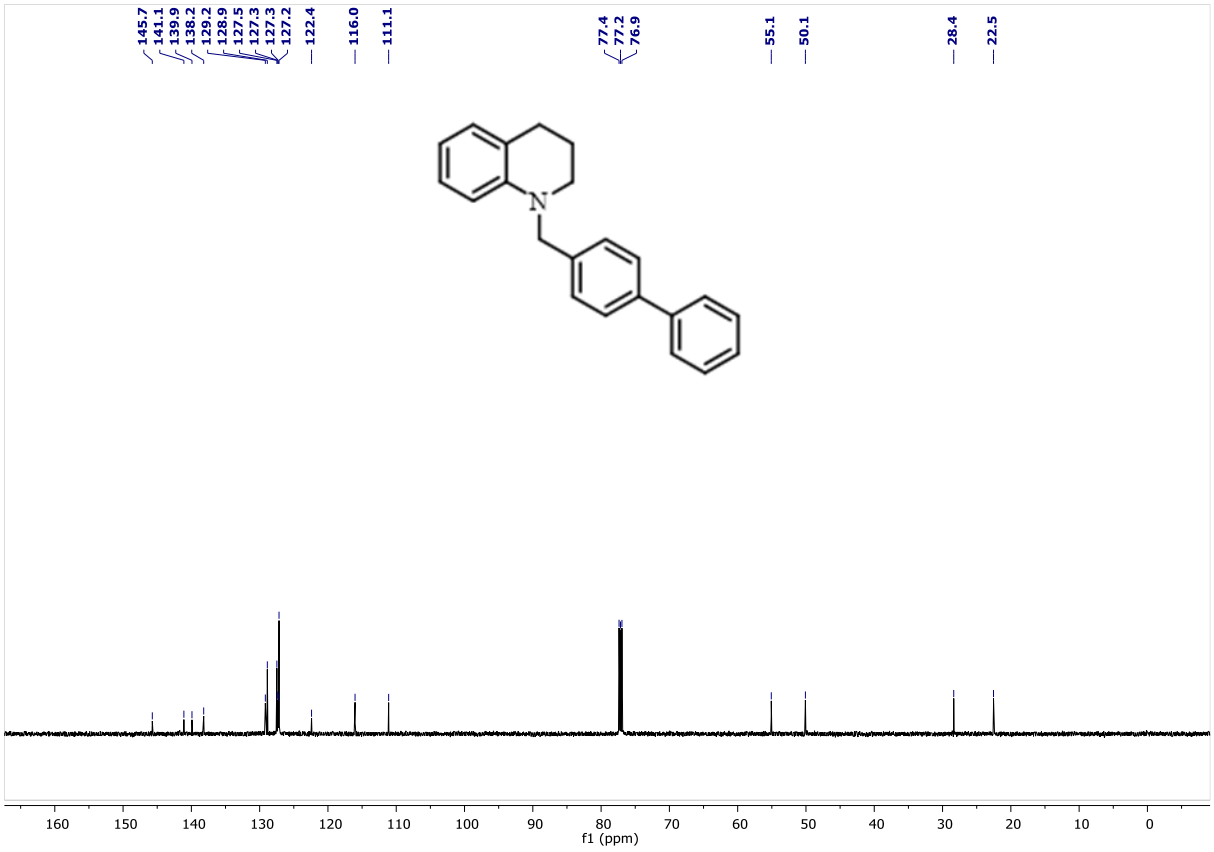


Figure S44: $^{13}C\{^{1}H\}$ NMR Spectrum of **3h** ($CDCl_3$, 151 MHz, 298 K)

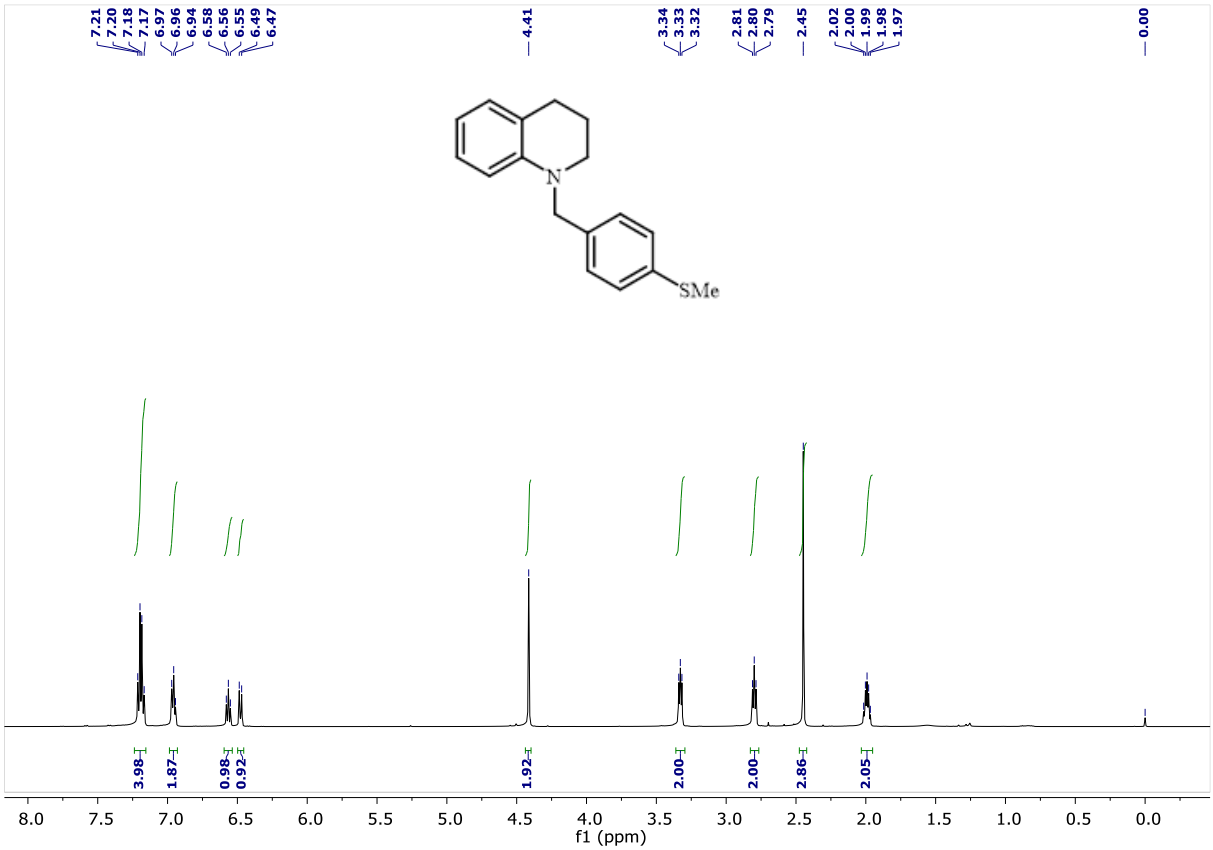


Figure S45: ^{1}H NMR Spectrum of **3i** ($CDCl_3$, 500 MHz, 298 K)

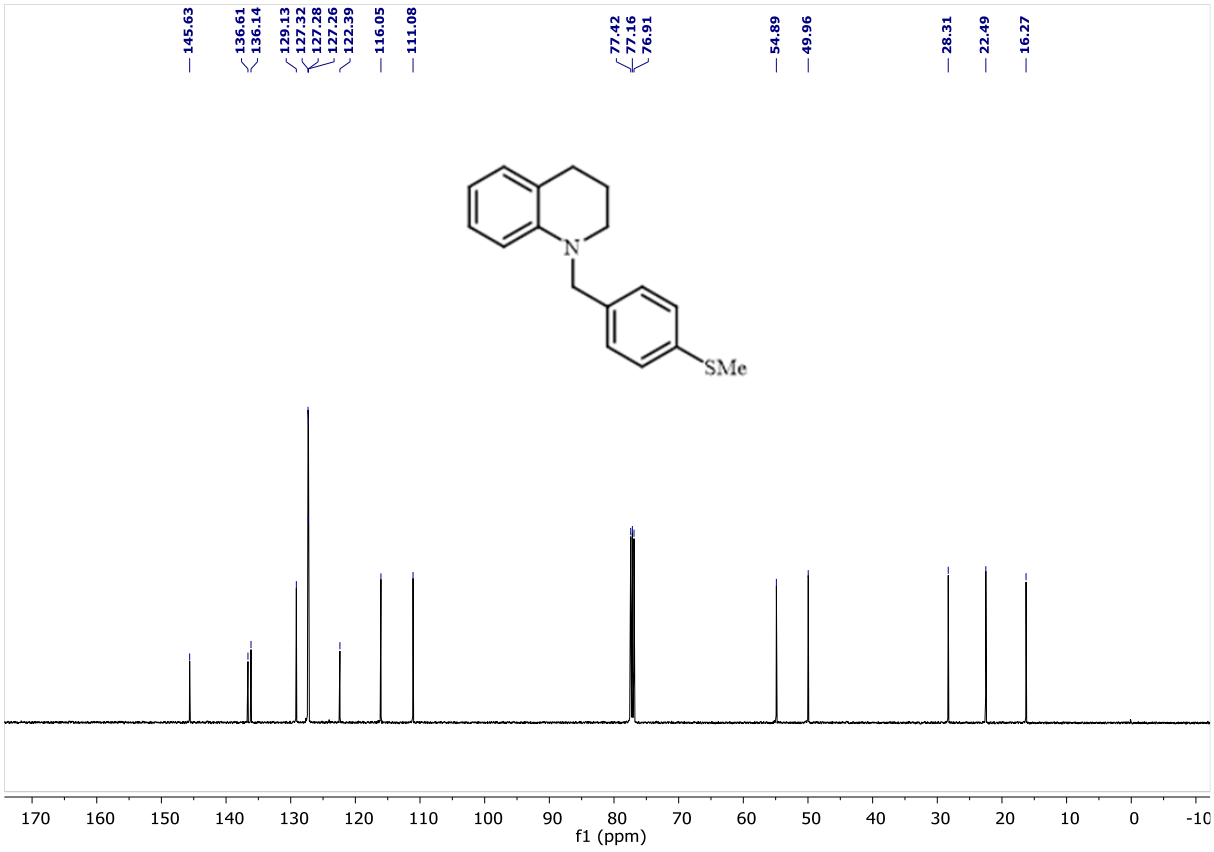


Figure S46: $^{13}C\{^{1}H\}$ NMR Spectrum of **3i** ($CDCl_3$, 126 MHz, 298 K)

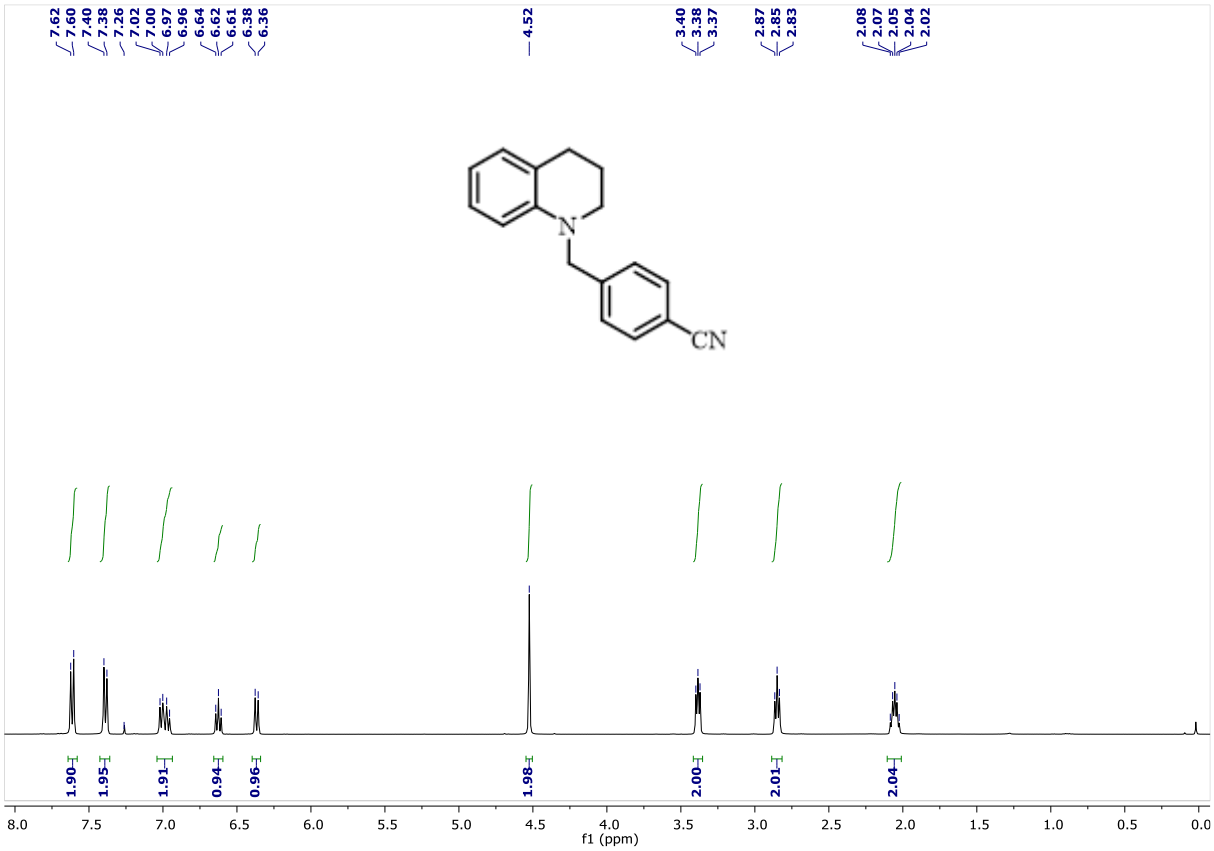


Figure S47: ^{1}H NMR Spectrum of **3j** ($CDCl_3$, 400 MHz, 298 K)

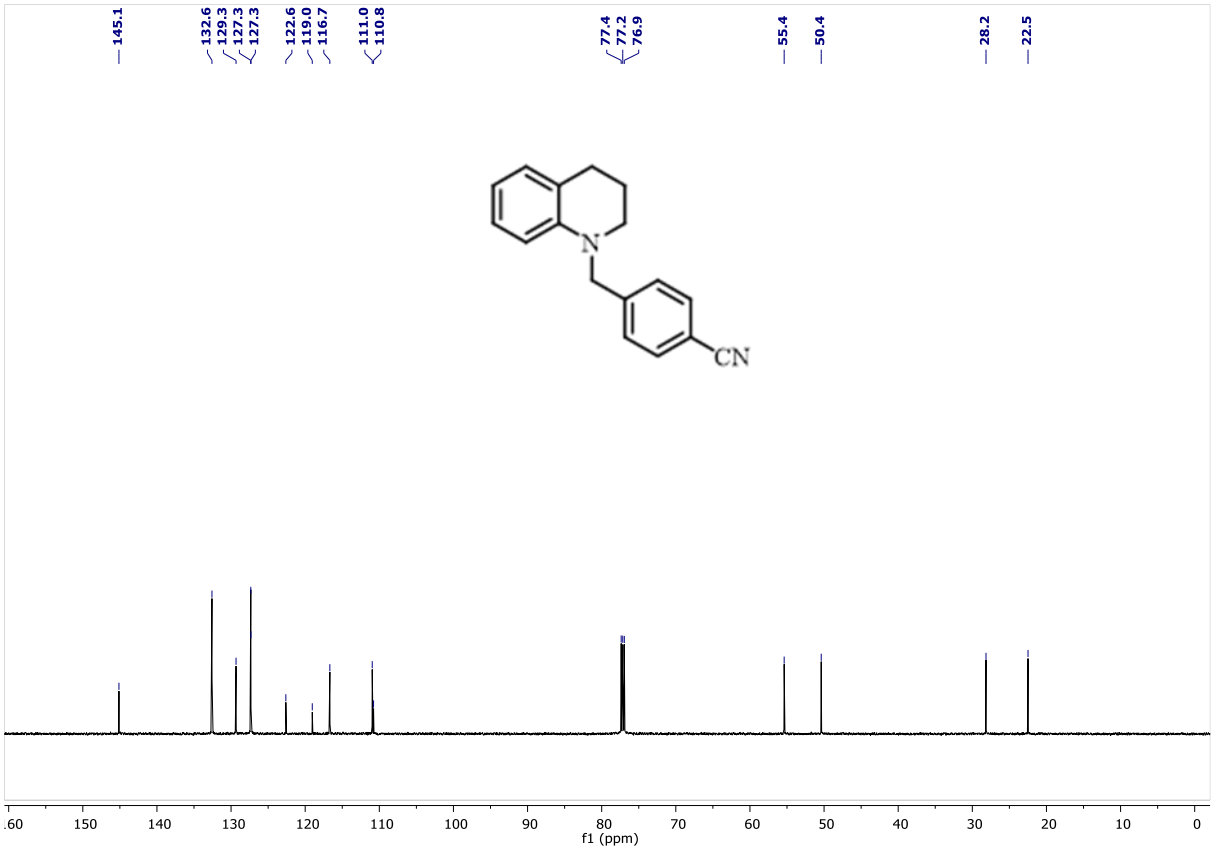


Figure S48: $^{13}C\{^{1}H\}$ NMR Spectrum of **3j** ($CDCl_3$, 151 MHz, 298 K)

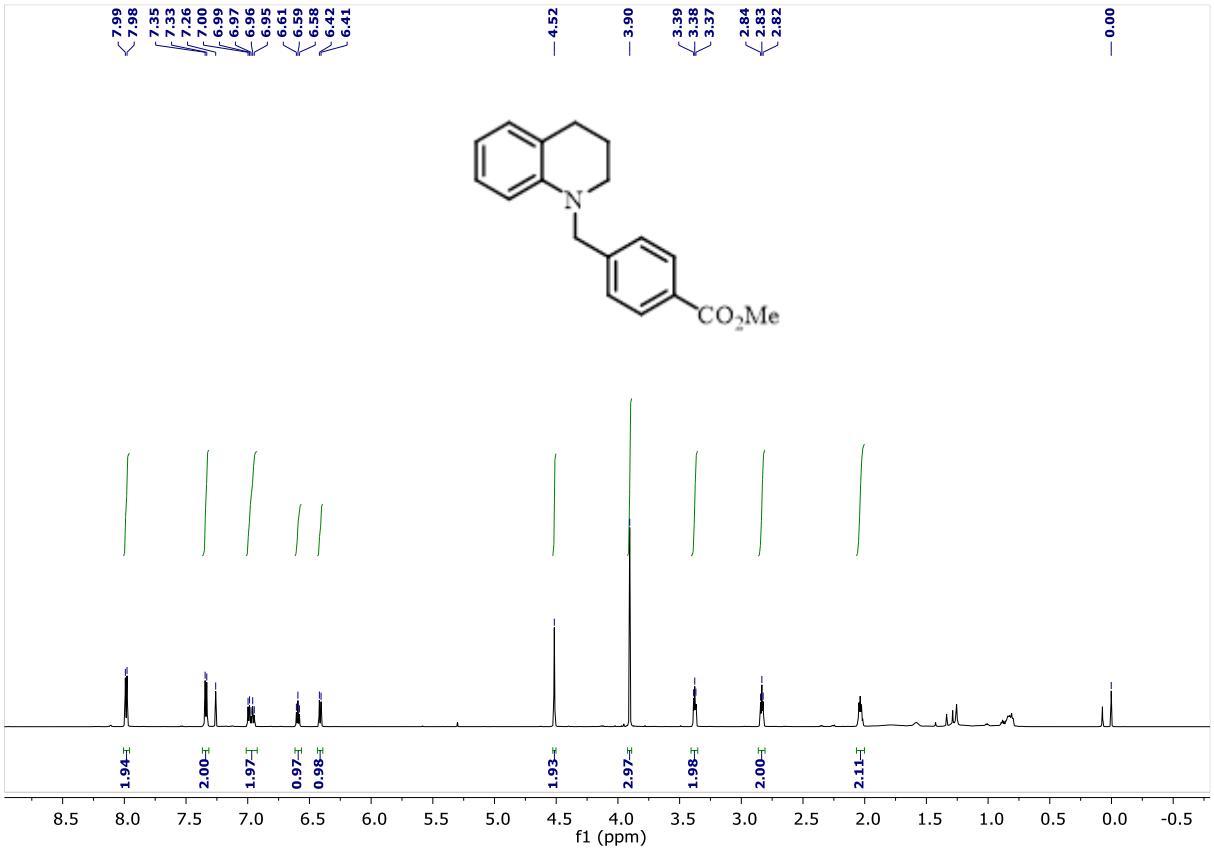


Figure S49: ^{1}H NMR Spectrum of **3k** ($CDCl_3$, 600 MHz, 298 K)

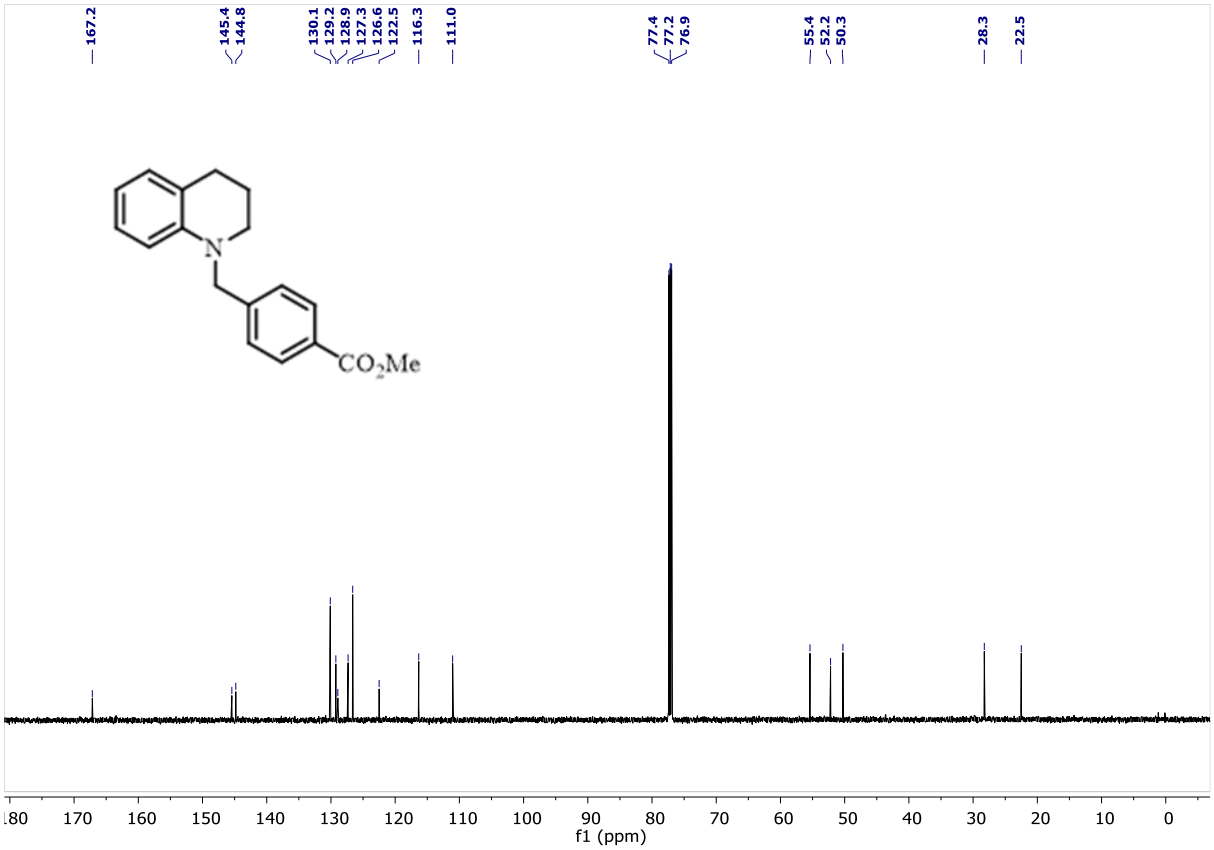


Figure S50: $^{13}C\{^{1}H\}$ NMR Spectrum of **3k** ($CDCl_3$, 151 MHz, 298 K)

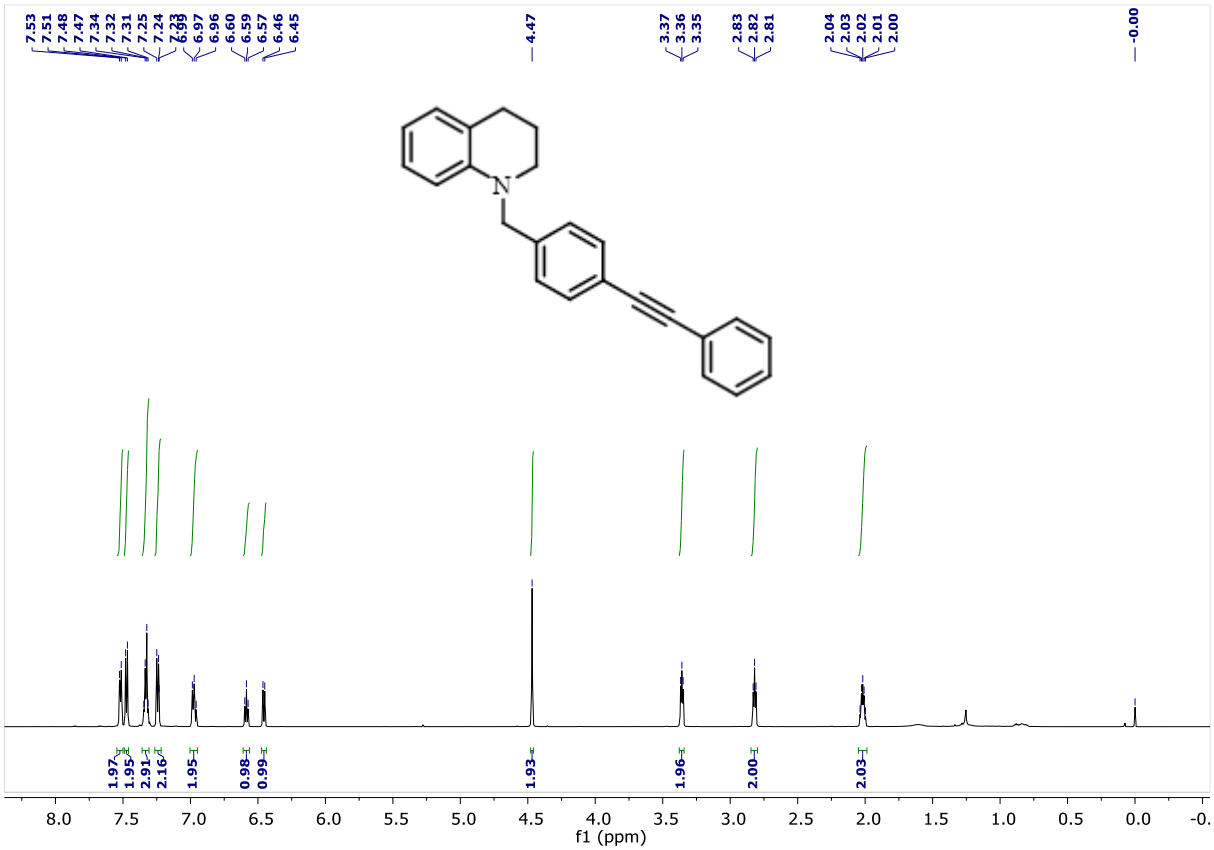


Figure S51: ^{1}H NMR Spectrum of **3l** ($CDCl_3$, 600 MHz, 298 K)

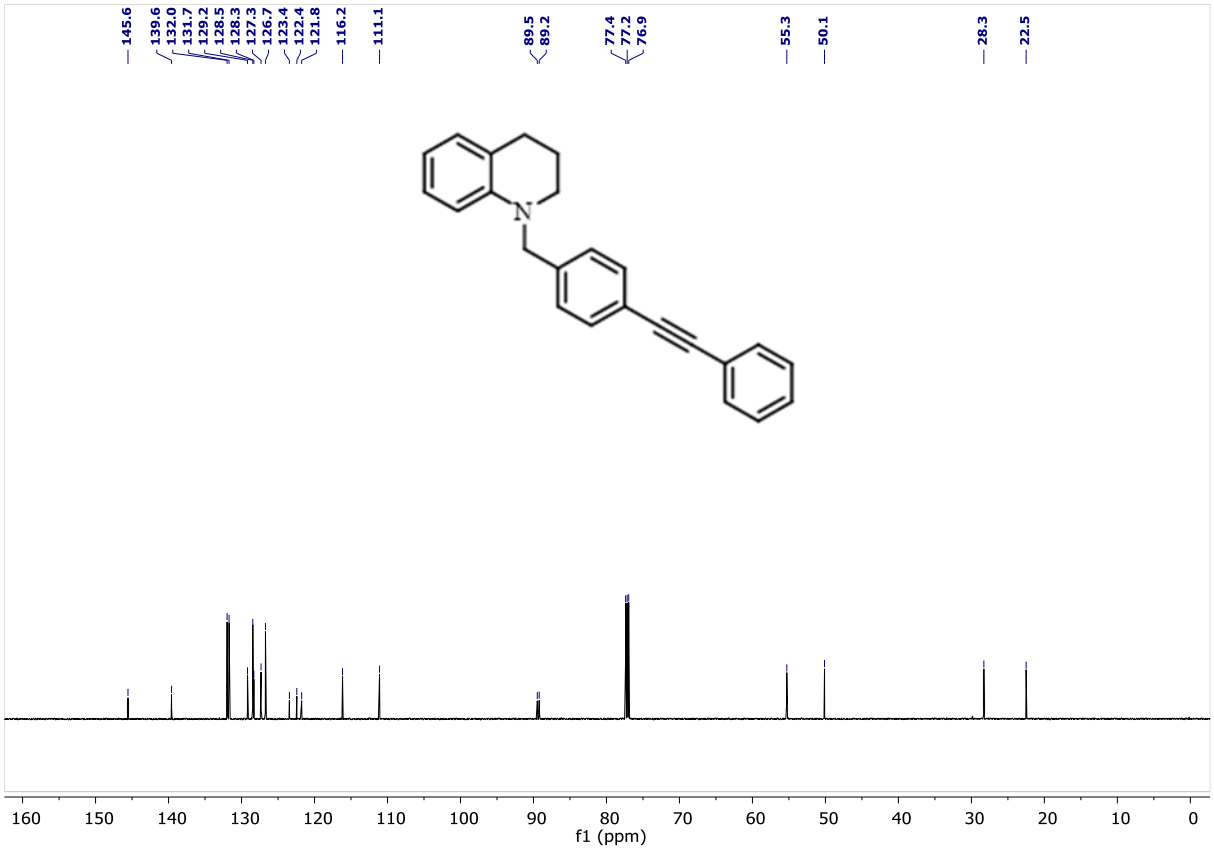


Figure S52: $^{13}C\{^{1}H\}$ NMR Spectrum of **3l** ($CDCl_3$, 151 MHz, 298 K)

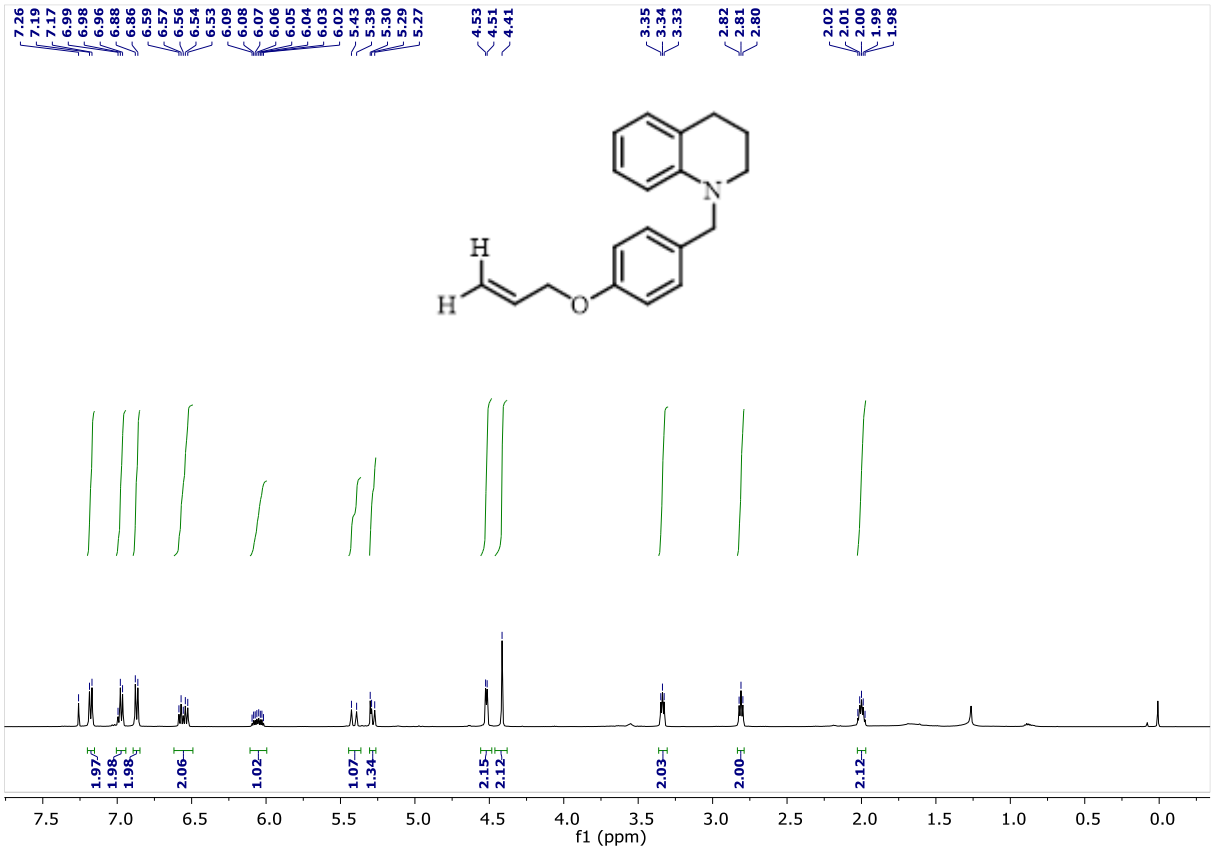


Figure S53: ^{1}H NMR Spectrum of **3m** ($CDCl_3$, 500 MHz, 298 K)

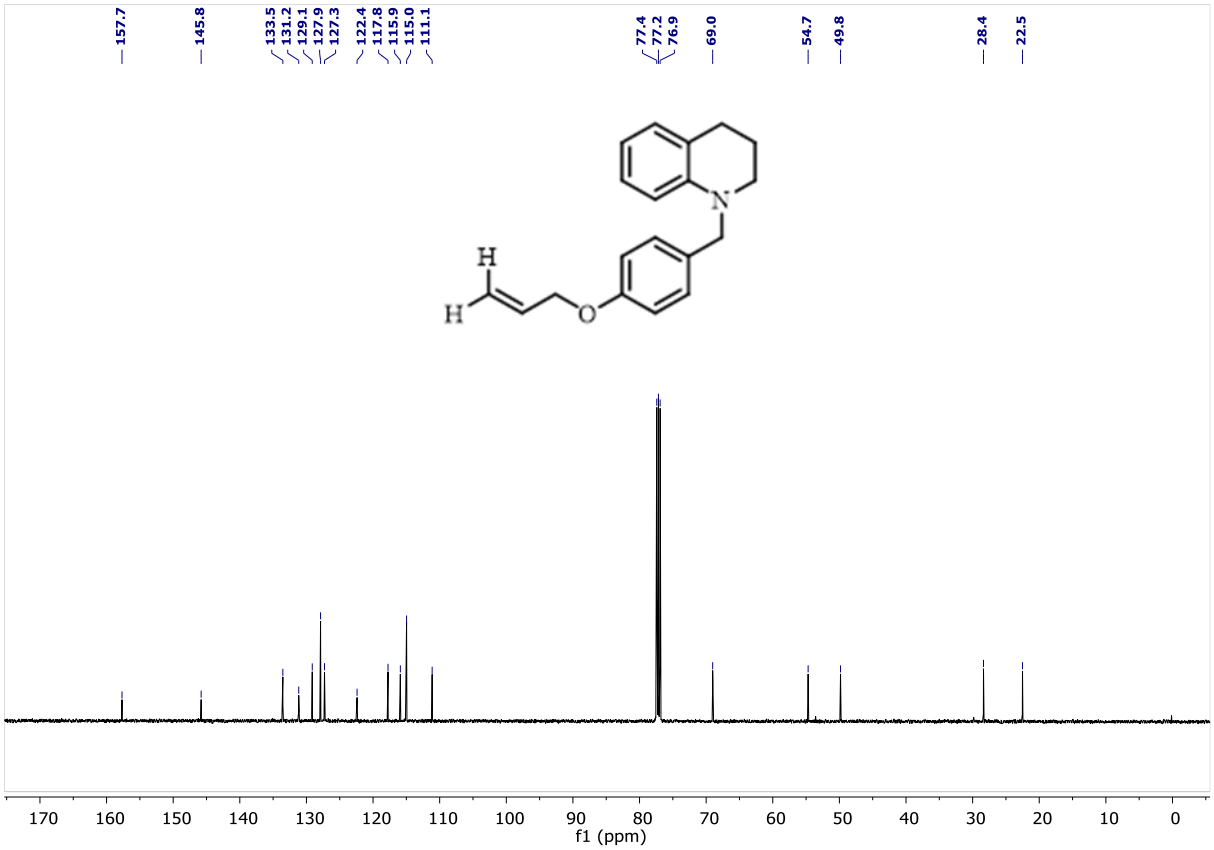


Figure S54: $^{13}C\{^{1}H\}$ NMR Spectrum of **3m** ($CDCl_3$, 126 MHz, 298 K)

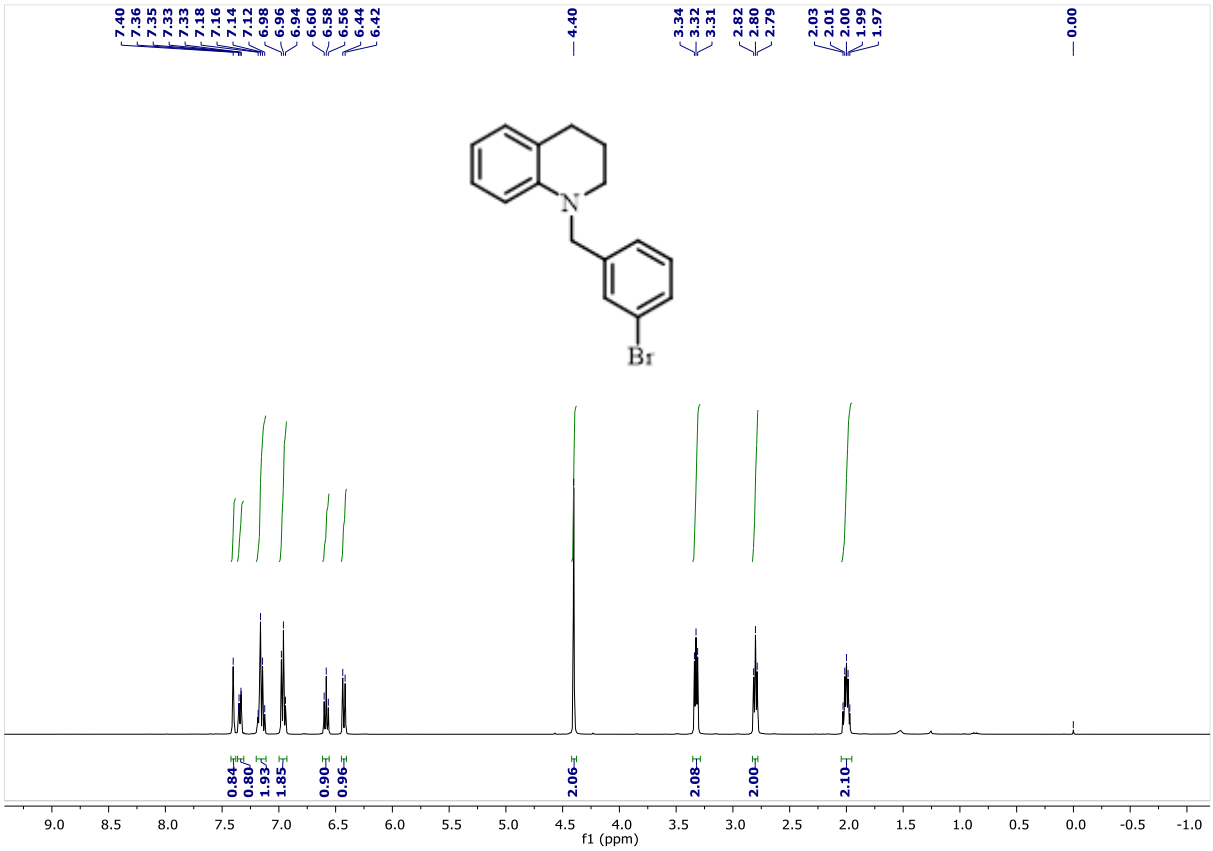


Figure S55: ^{1}H NMR Spectrum of **3n** ($CDCl_3$, 400 MHz, 298 K)

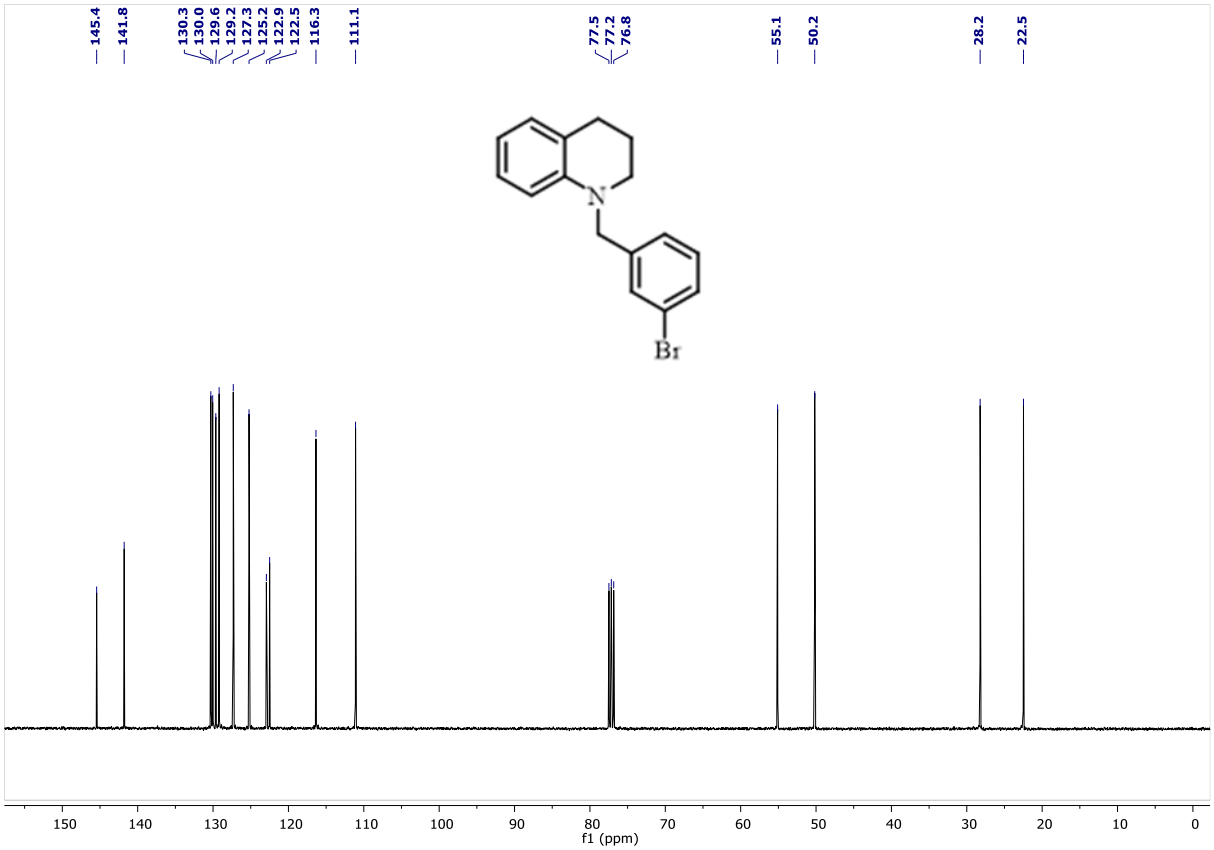


Figure S56: $^{13}C\{^{1}H\}$ NMR Spectrum of **3n** ($CDCl_3$, 101 MHz, 298 K)

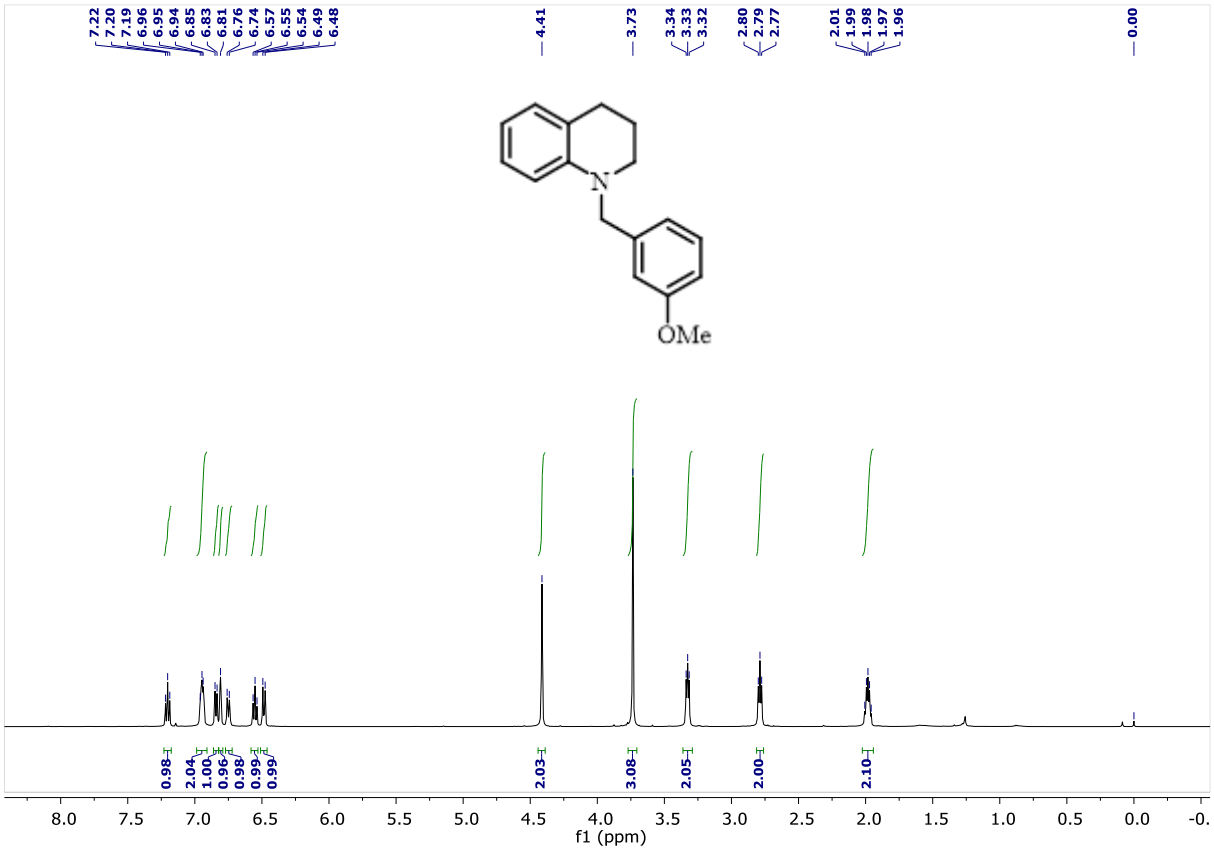


Figure S57: ^{1}H NMR Spectrum of **3o** ($CDCl_3$, 500 MHz, 298 K)

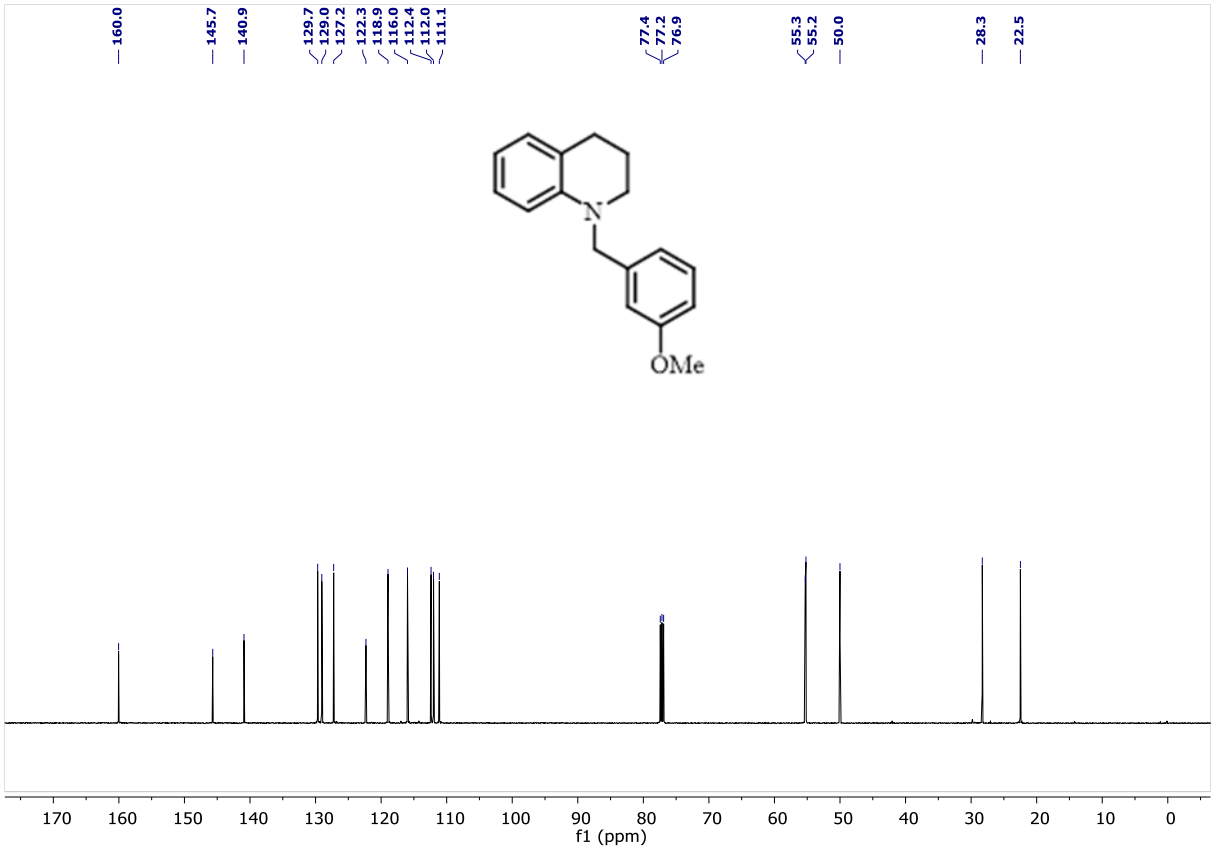


Figure S58: $^{13}C\{^{1}H\}$ NMR Spectrum of **3o** ($CDCl_3$, 126 MHz, 298 K)

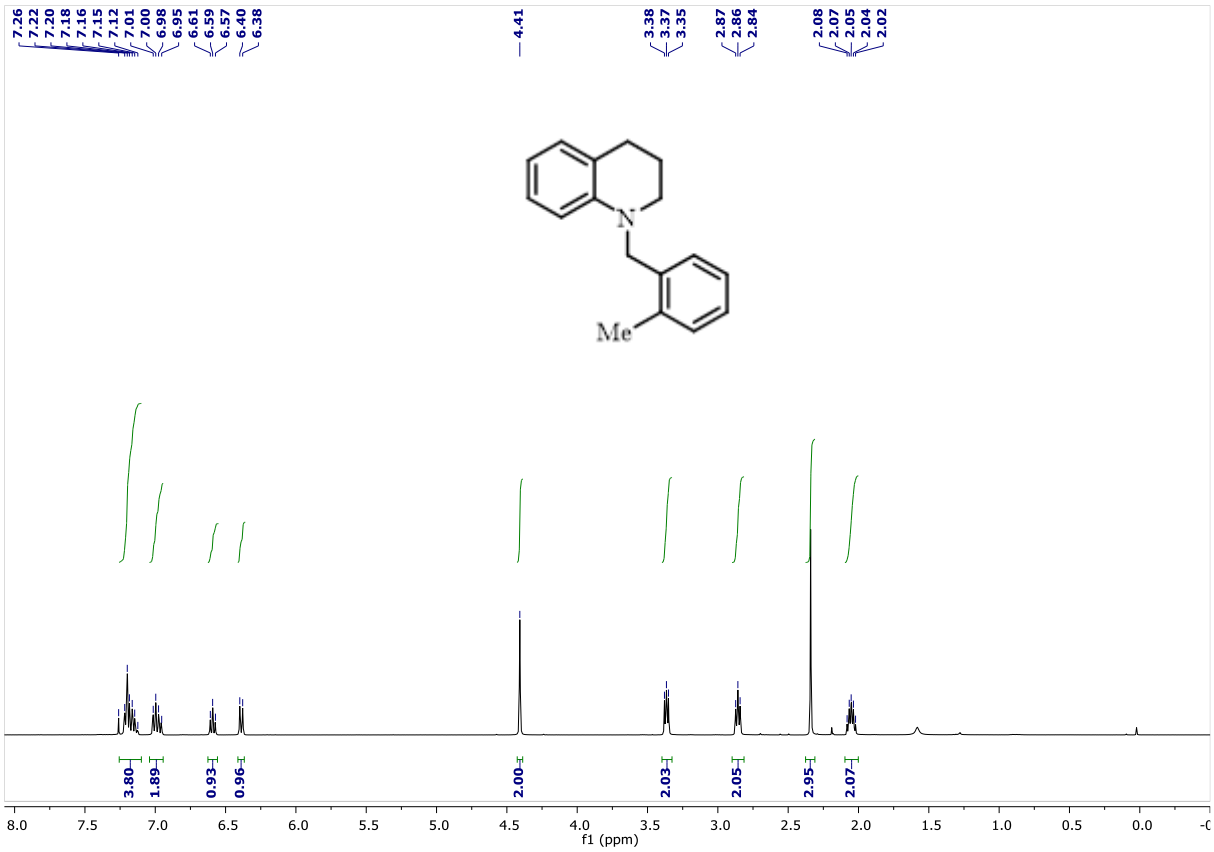


Figure S59: ^{1}H NMR Spectrum of **3p** ($CDCl_3$, 400 MHz, 298 K)

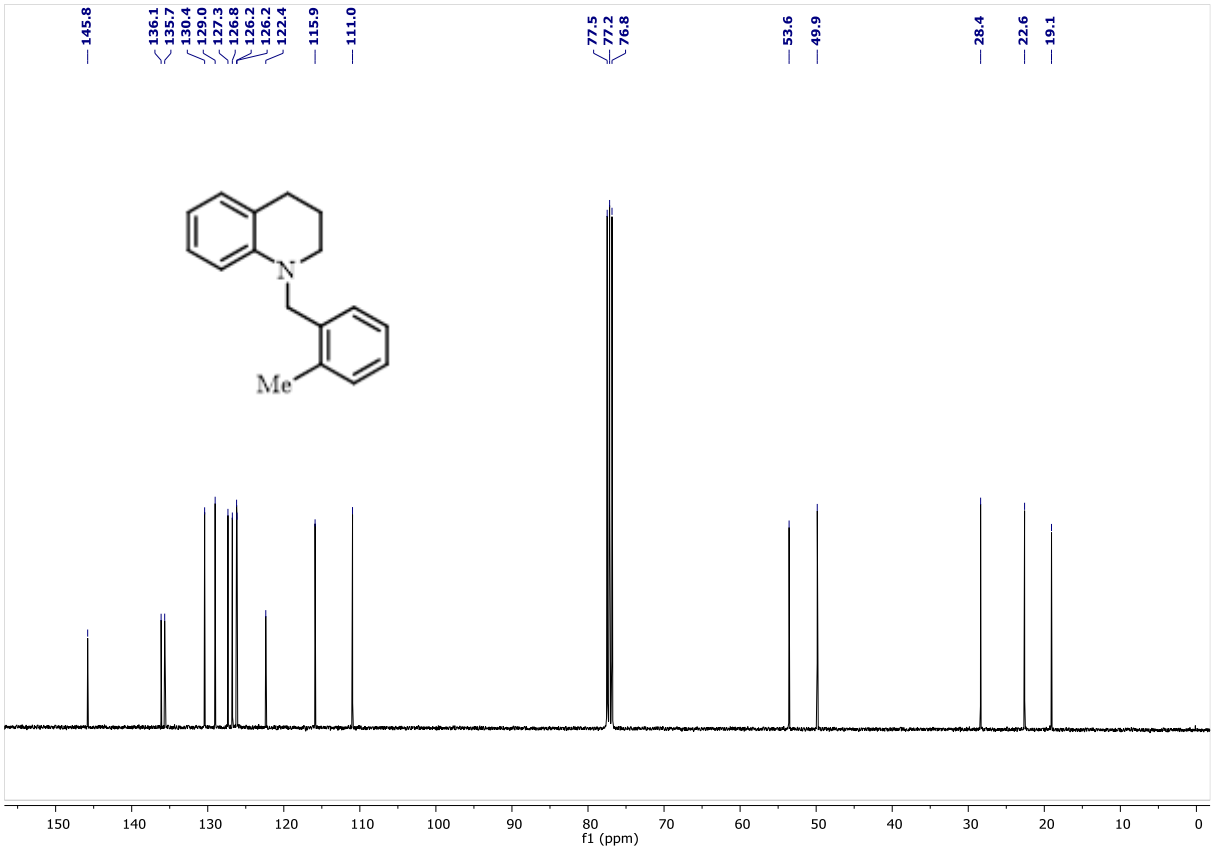


Figure S60: $^{13}C\{^{1}H\}$ NMR Spectrum of **3p** ($CDCl_3$, 101 MHz, 298 K)

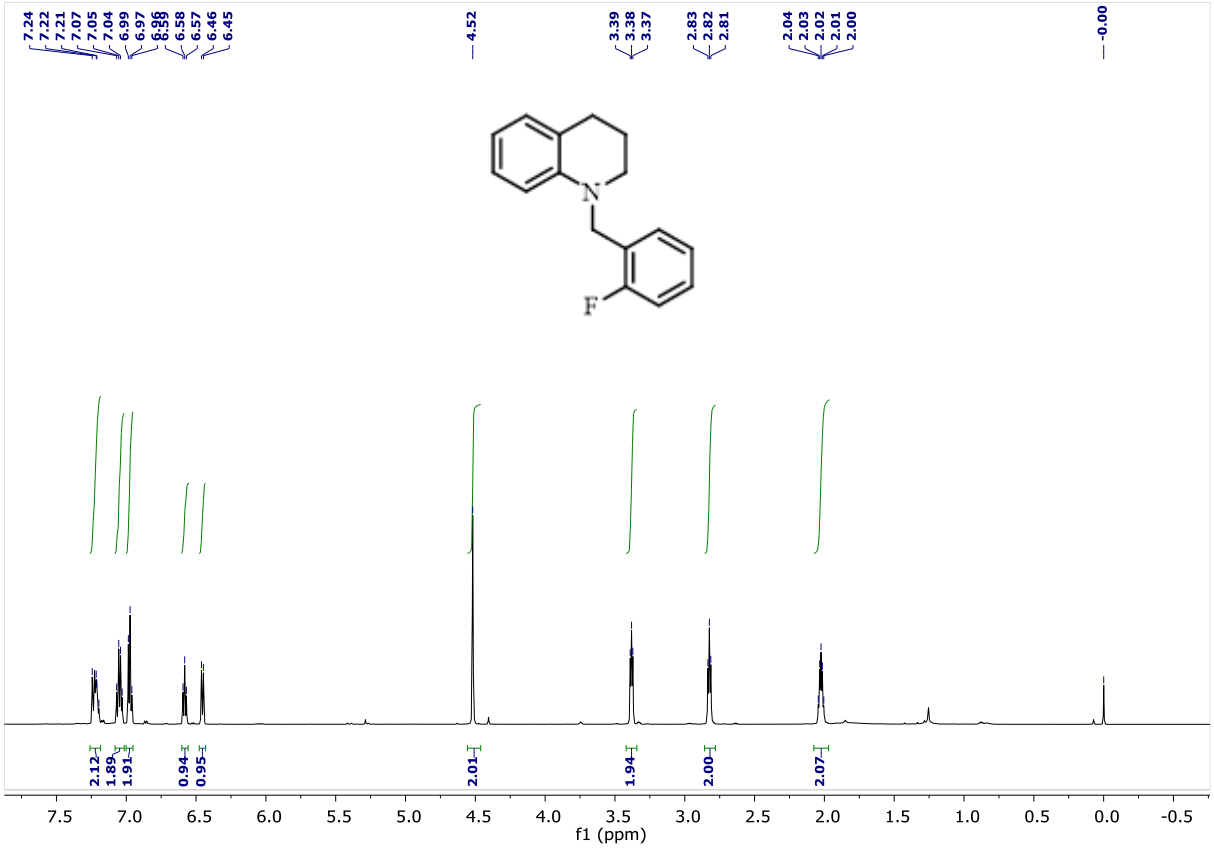


Figure S61: ^{1}H NMR Spectrum of **3q** ($CDCl_3$, 600 MHz, 298 K)

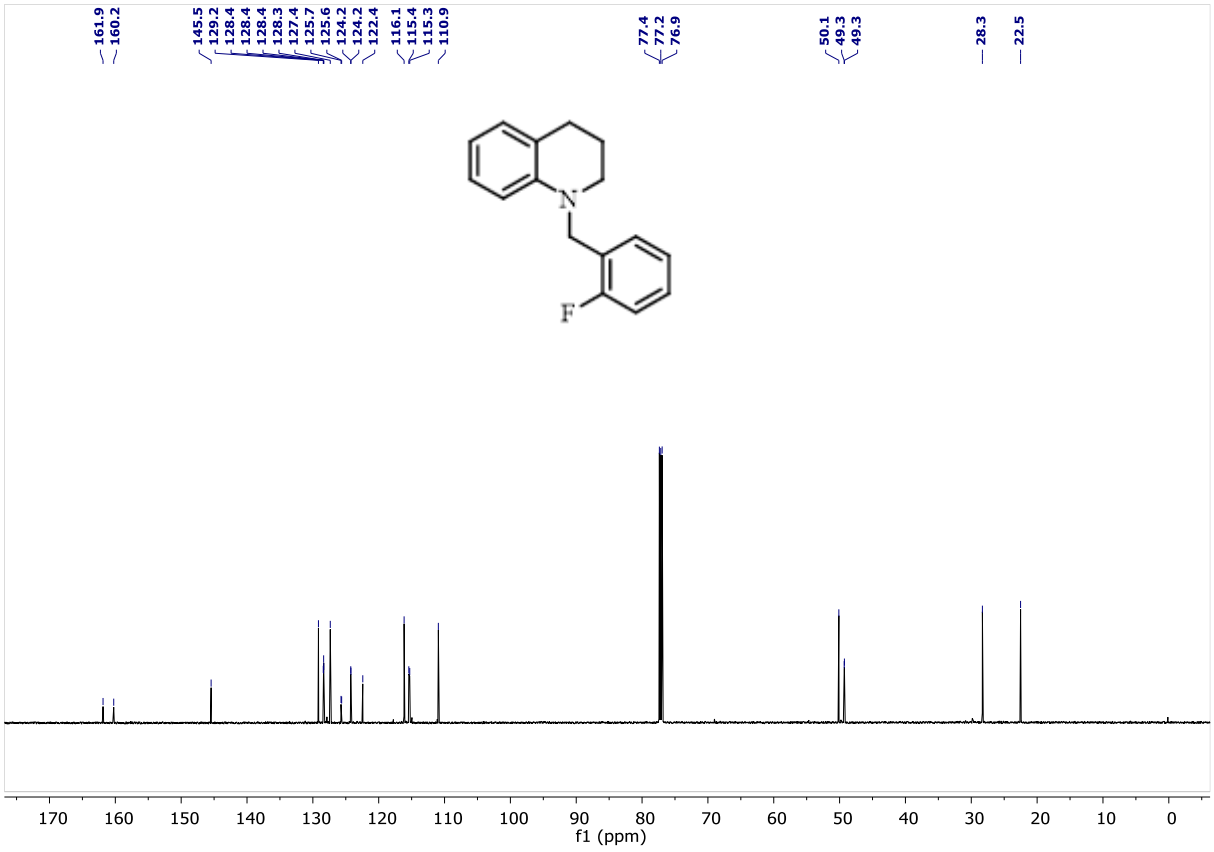


Figure S62: $^{13}C\{^{1}H\}$ NMR Spectrum of **3q** ($CDCl_3$, 151 MHz, 298 K)

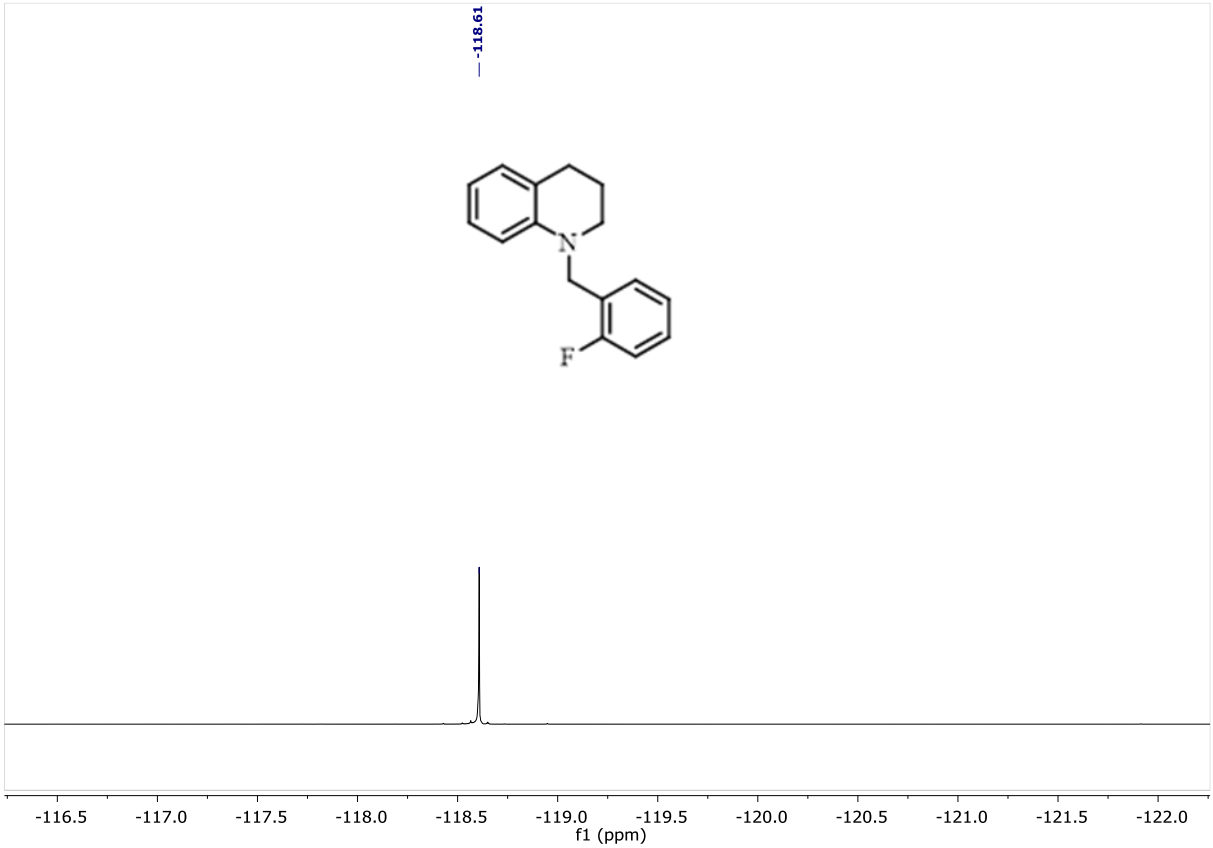


Figure S63: $^{19}F\{^{1}H\}$ NMR Spectrum of **3q** ($CDCl_3$, 471 MHz, 298 K)

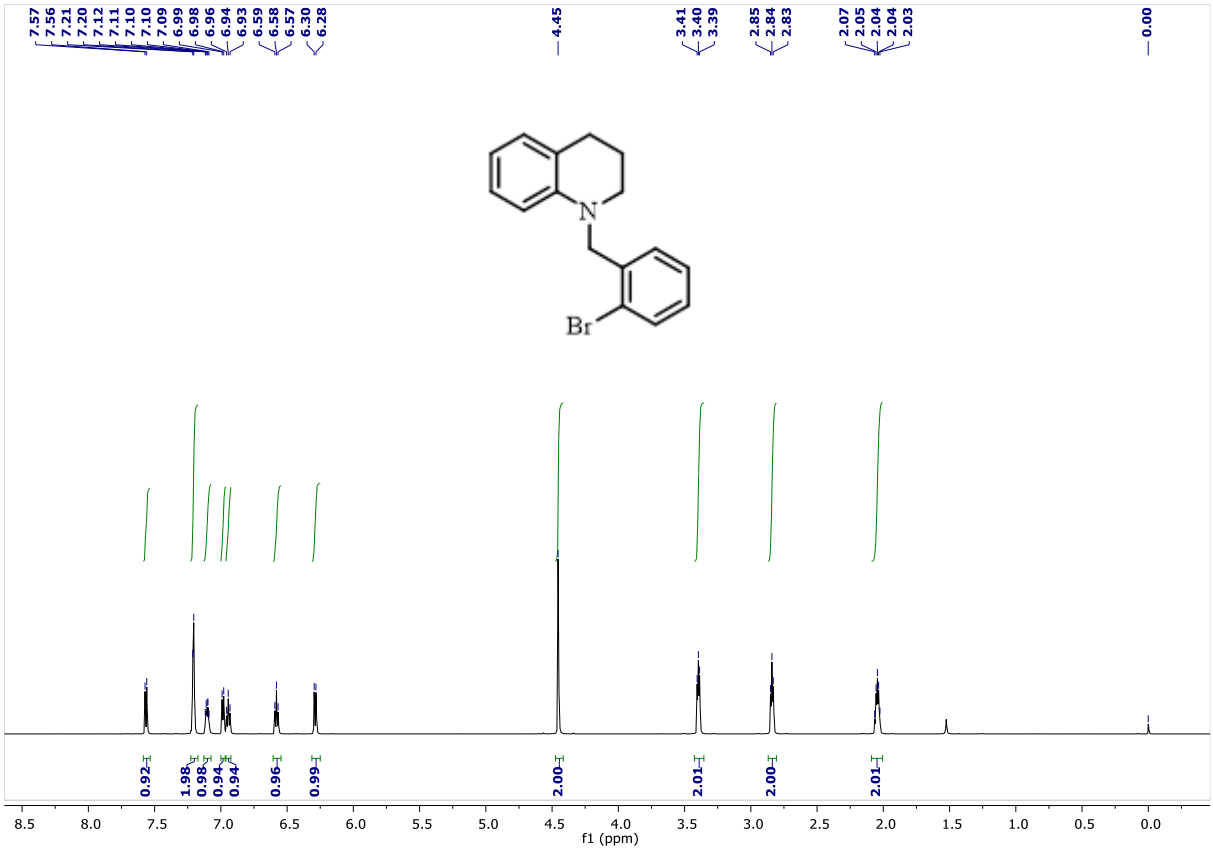


Figure S64: ^{1}H NMR Spectrum of **3r** ($CDCl_3$, 600 MHz, 298 K)

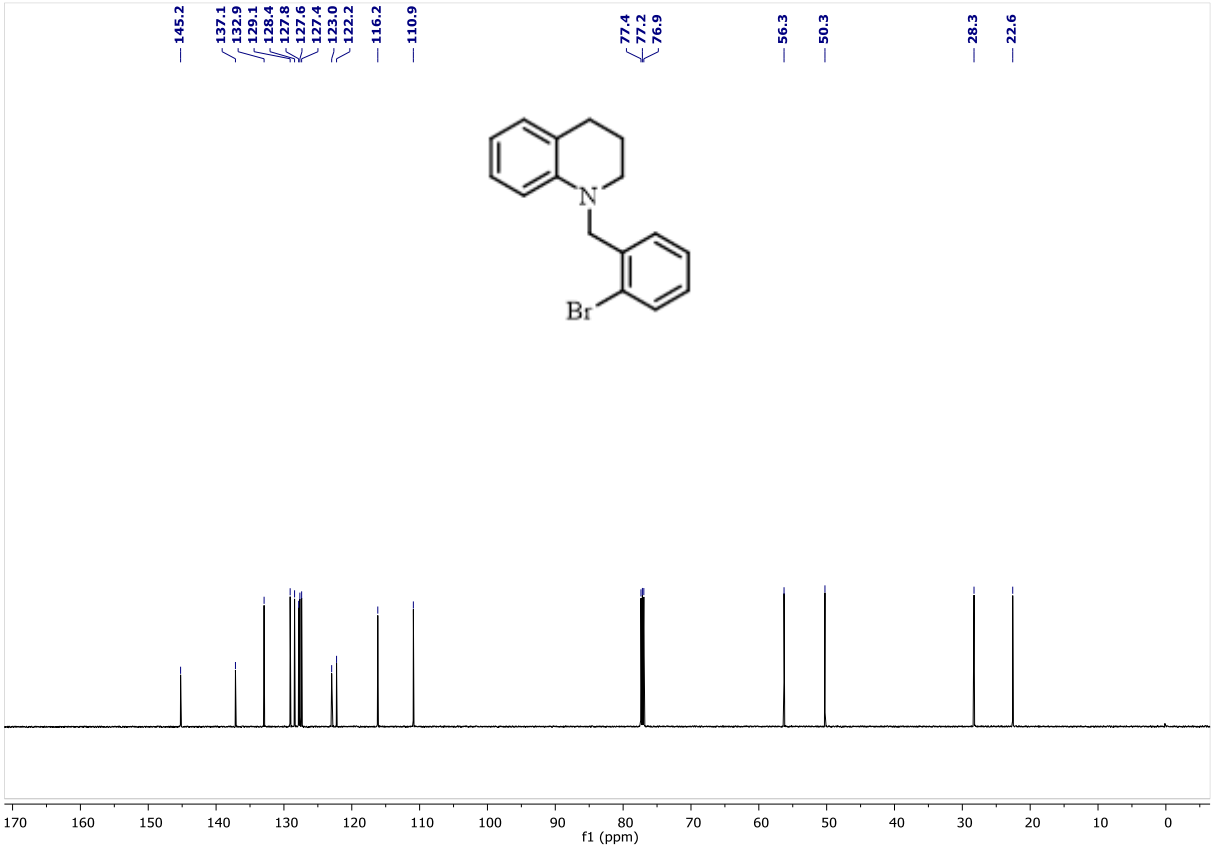


Figure S65: $^{13}C\{^{1}H\}$ NMR Spectrum of **3r** ($CDCl_3$, 151 MHz, 298 K)

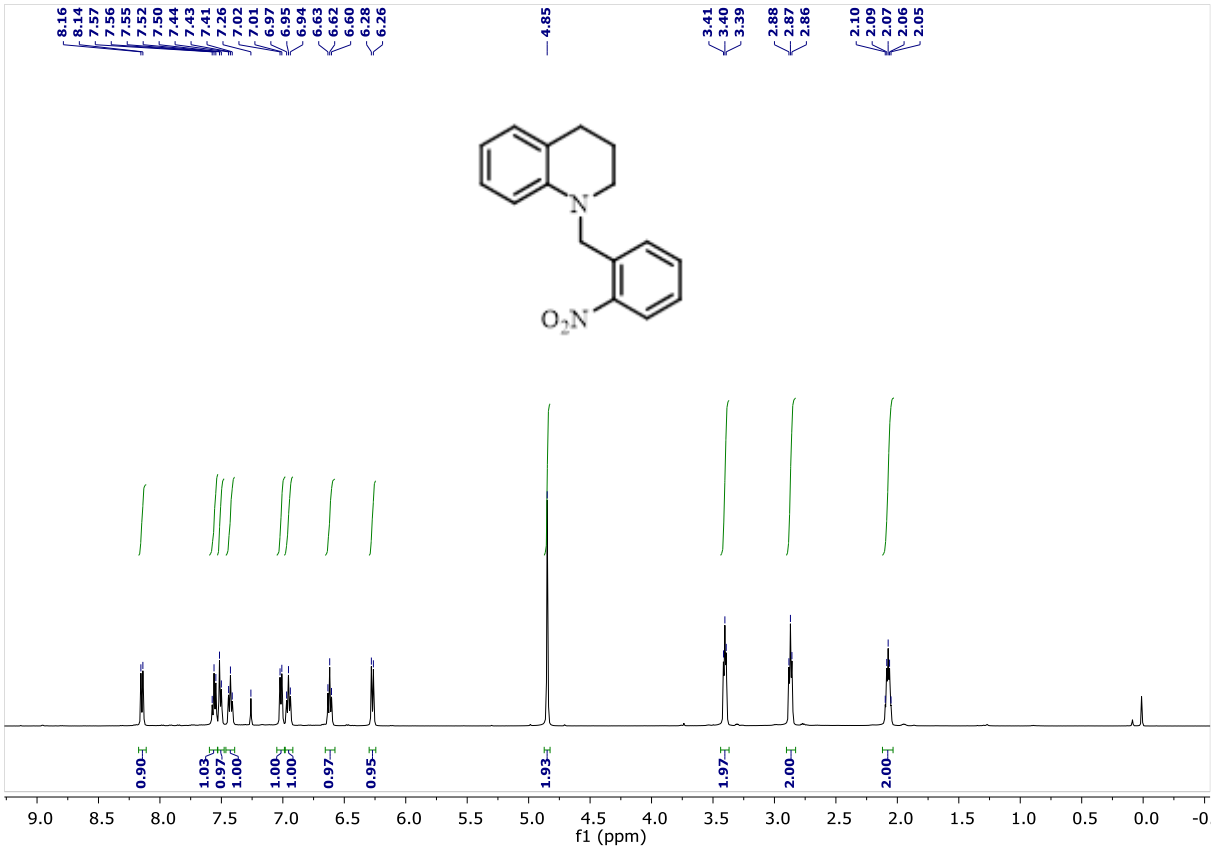


Figure S66: ^{1}H NMR Spectrum of **3s** ($CDCl_3$, 500 MHz, 298 K)

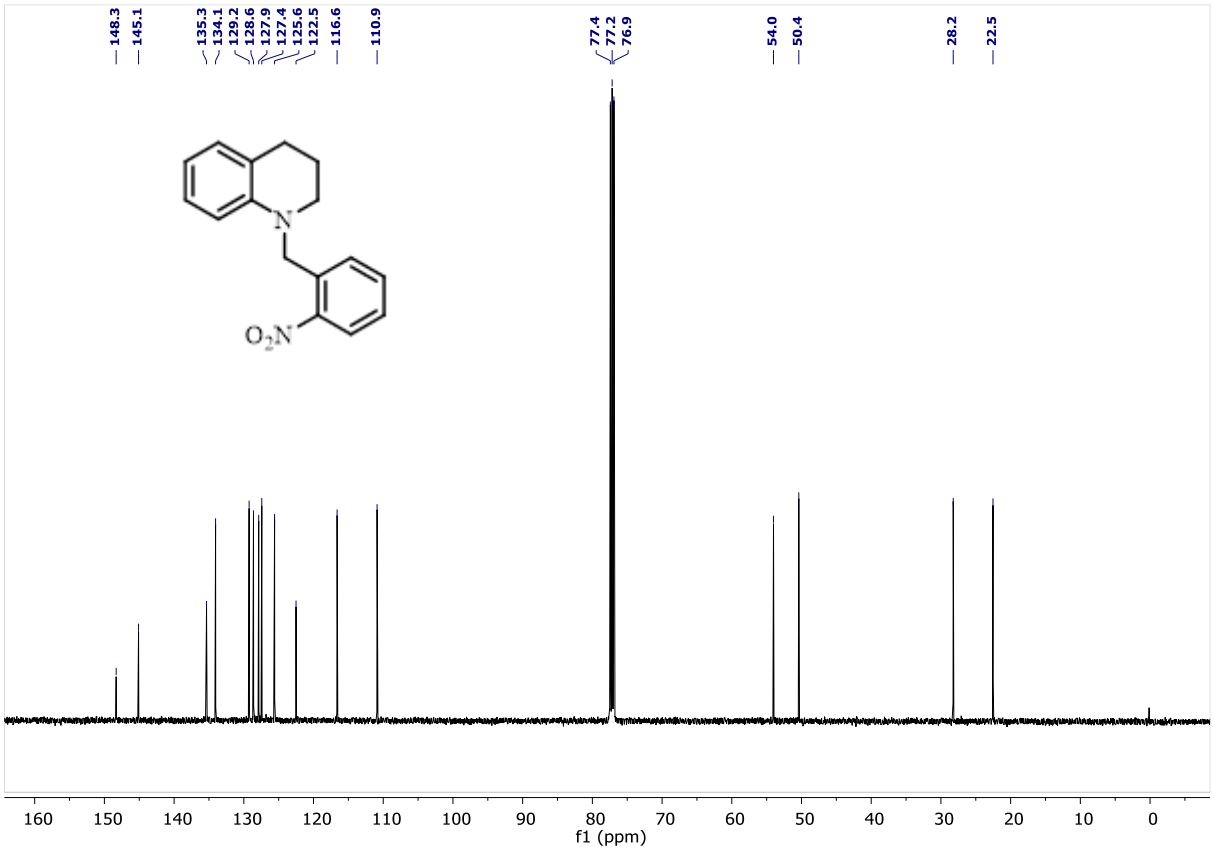


Figure S67: $^{13}C\{^{1}H\}$ NMR Spectrum of **3s** ($CDCl_3$, 126 MHz, 298 K)

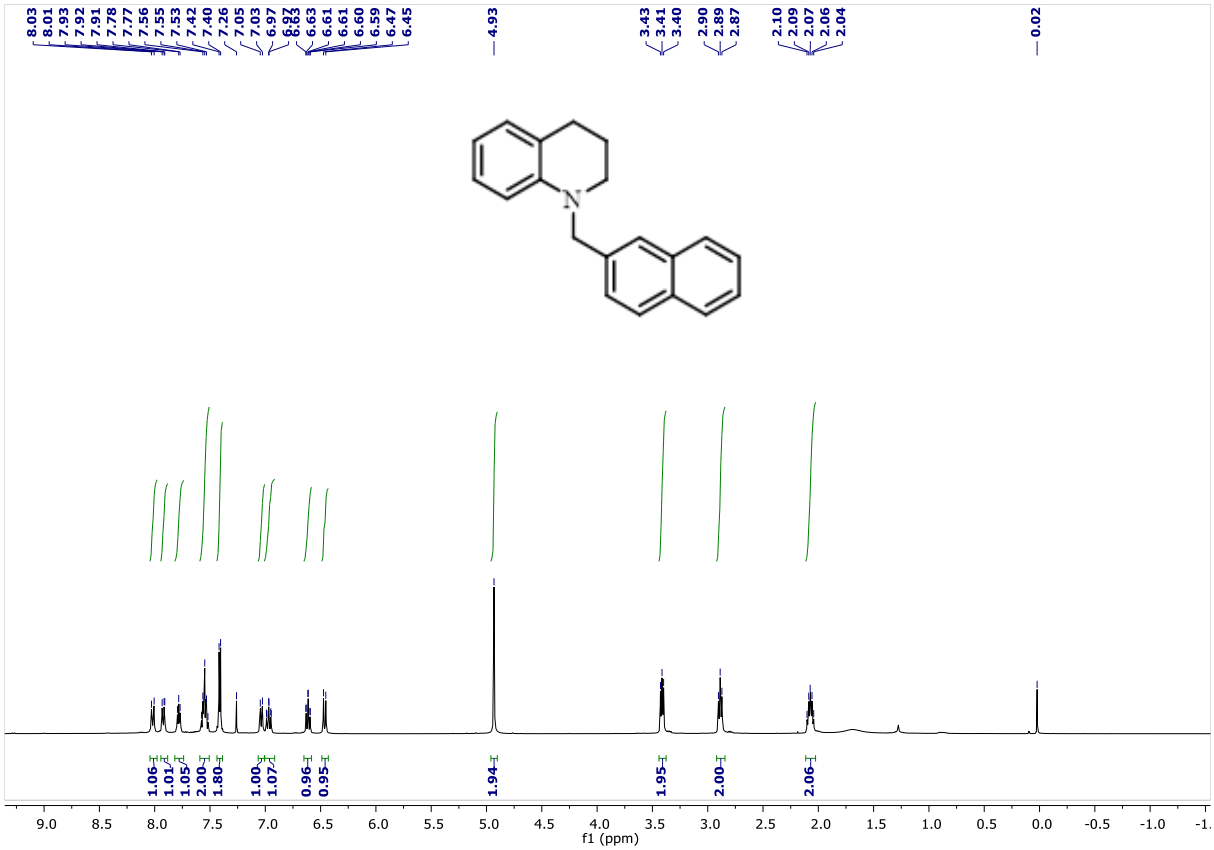


Figure S68: ^{1}H NMR Spectrum of **3t** ($CDCl_3$, 400 MHz, 298 K)

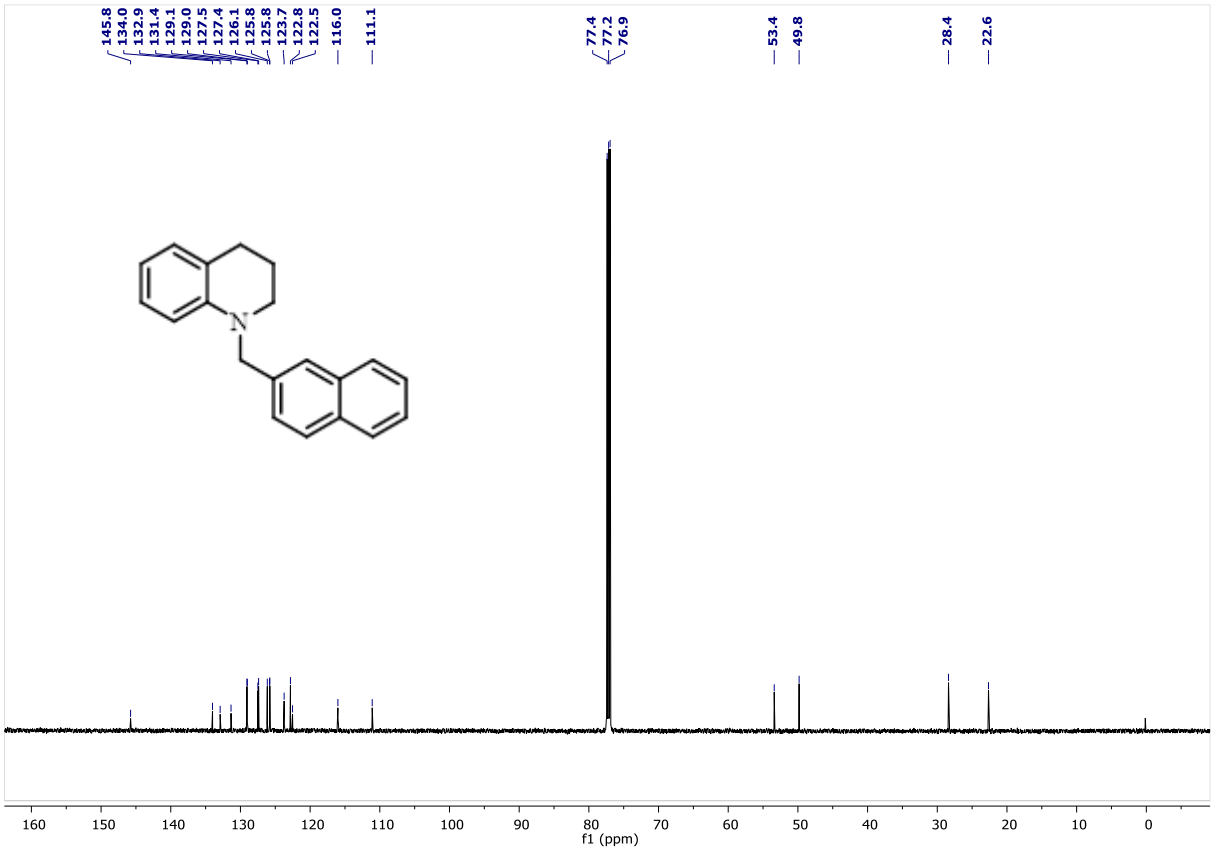


Figure S69: $^{13}C\{^{1}H\}$ NMR Spectrum of **3t** ($CDCl_3$, 151 MHz, 298 K)

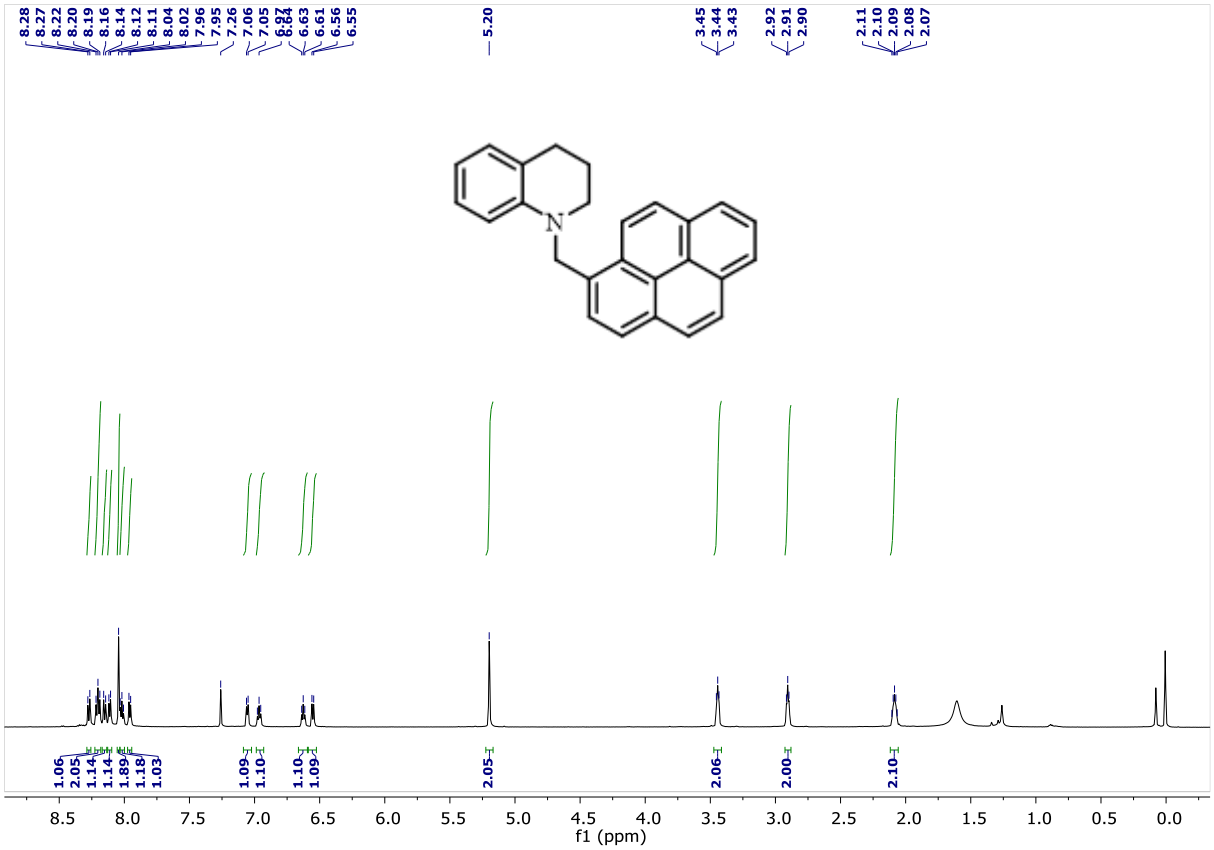


Figure S70: ^{1}H NMR Spectrum of **3u** ($CDCl_3$, 600 MHz, 298 K)

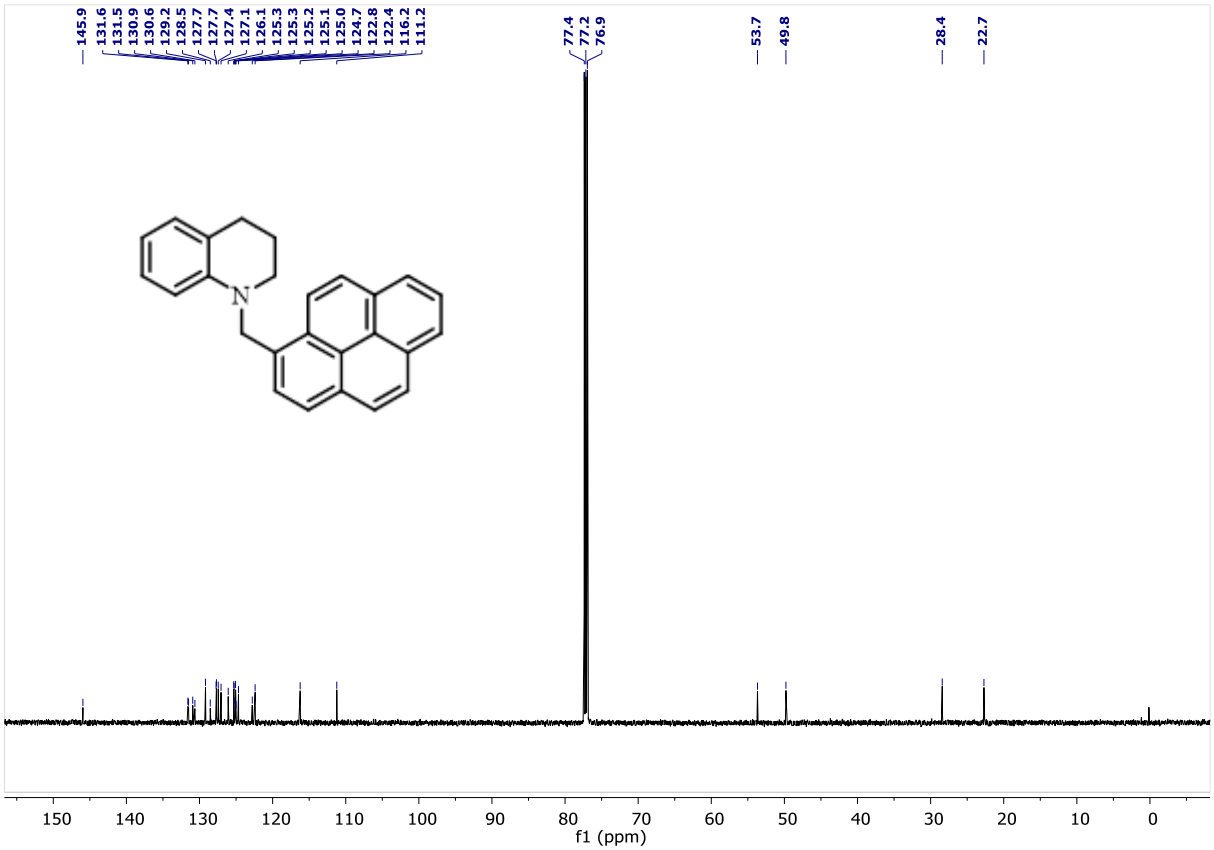


Figure S71: $^{13}C\{^{1}H\}$ NMR Spectrum of **3u** ($CDCl_3$, 151 MHz, 298 K)

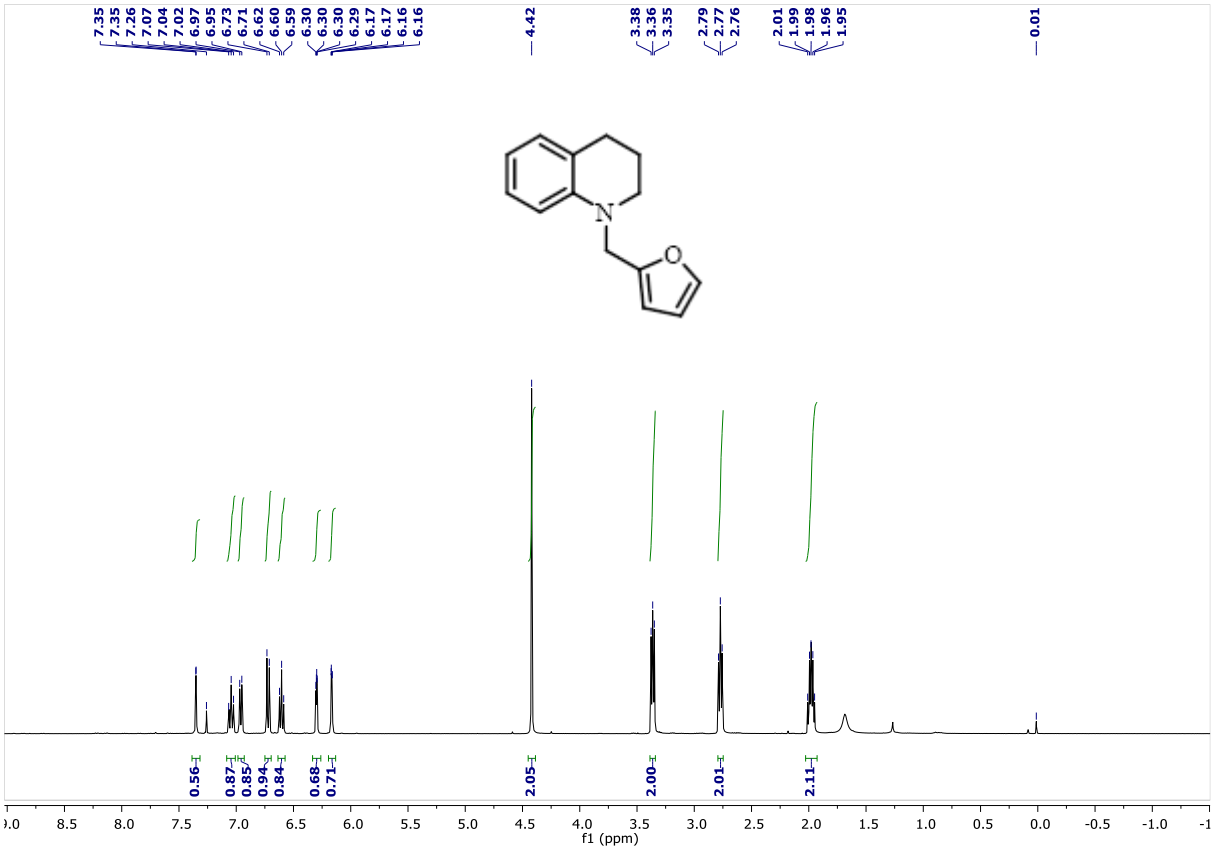


Figure S72: ^{1}H NMR Spectrum of **3v** ($CDCl_3$, 400 MHz, 298 K)

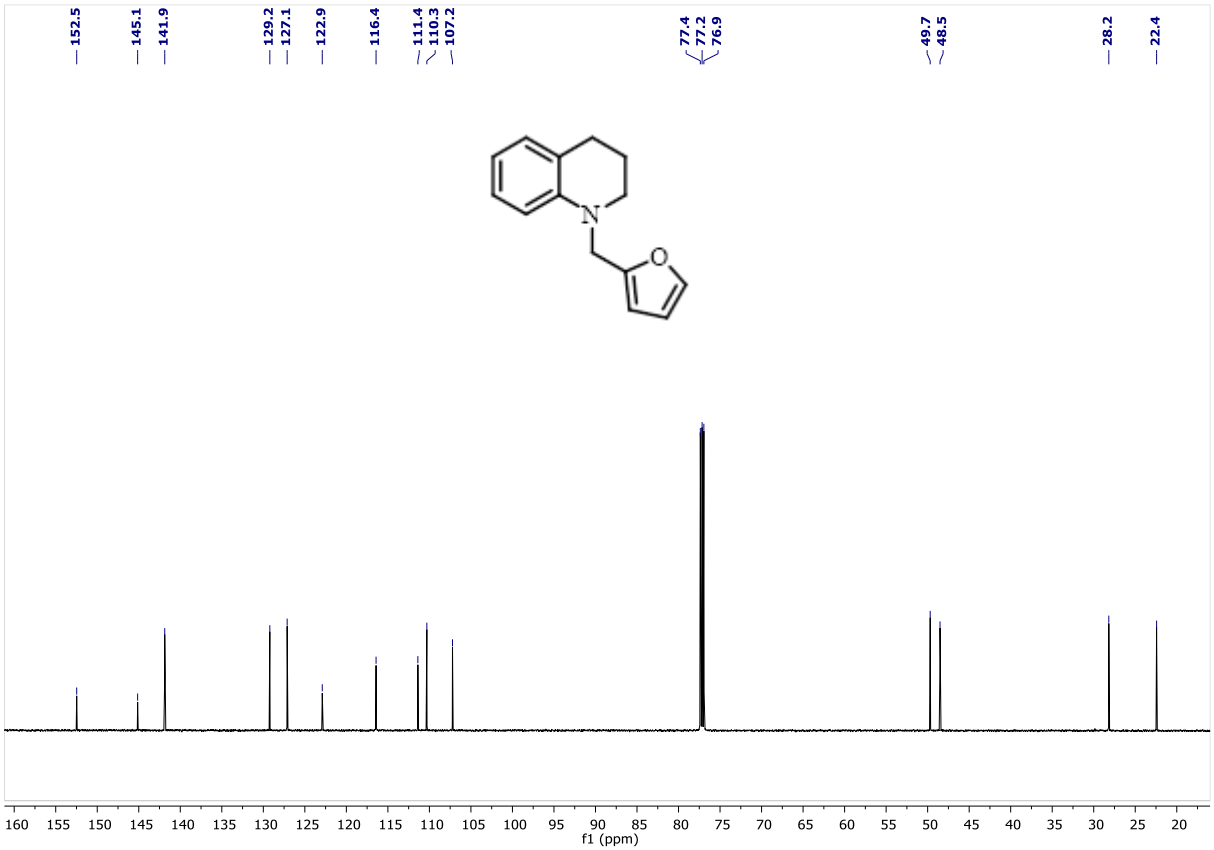


Figure S73: $^{13}C\{^{1}H\}$ NMR Spectrum of **3v** ($CDCl_3$, 151 MHz, 298 K)

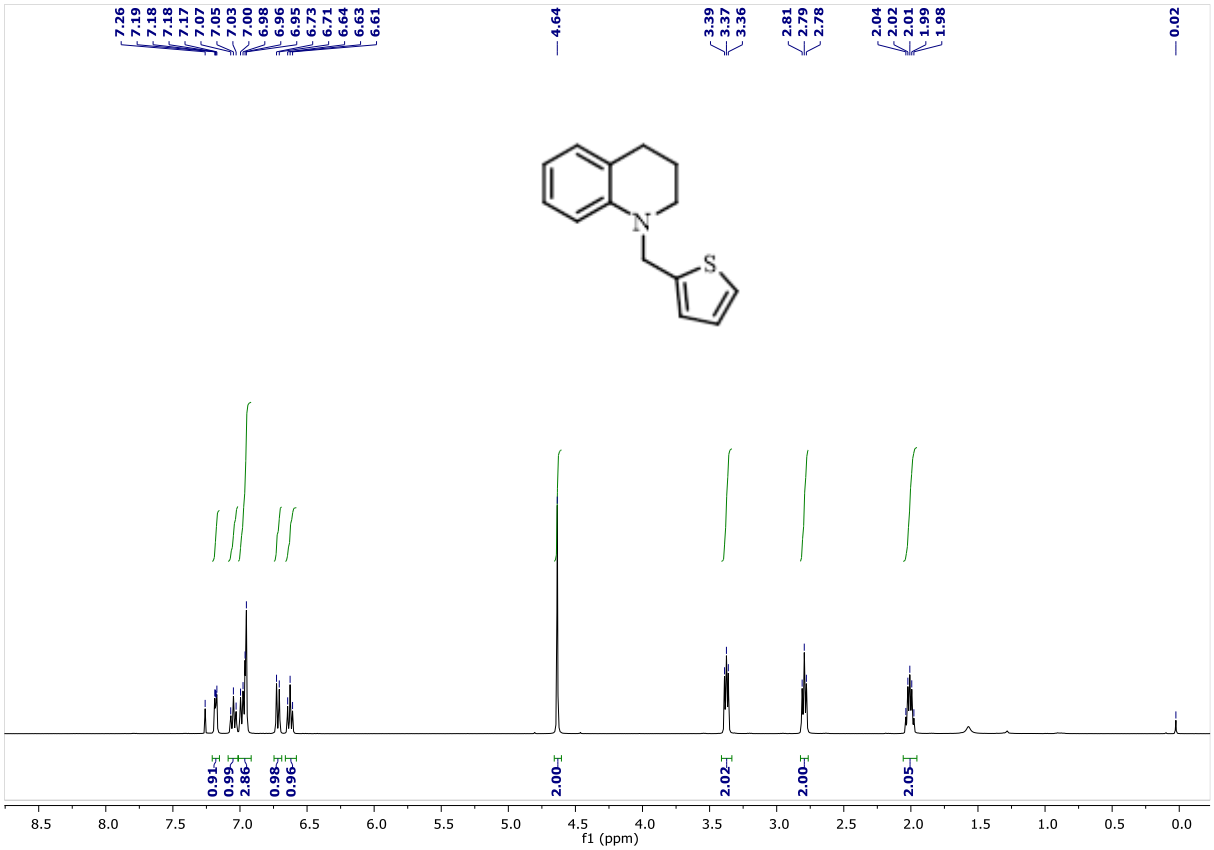


Figure S74: ^{1}H NMR Spectrum of **3w** ($CDCl_3$, 400 MHz, 298 K)

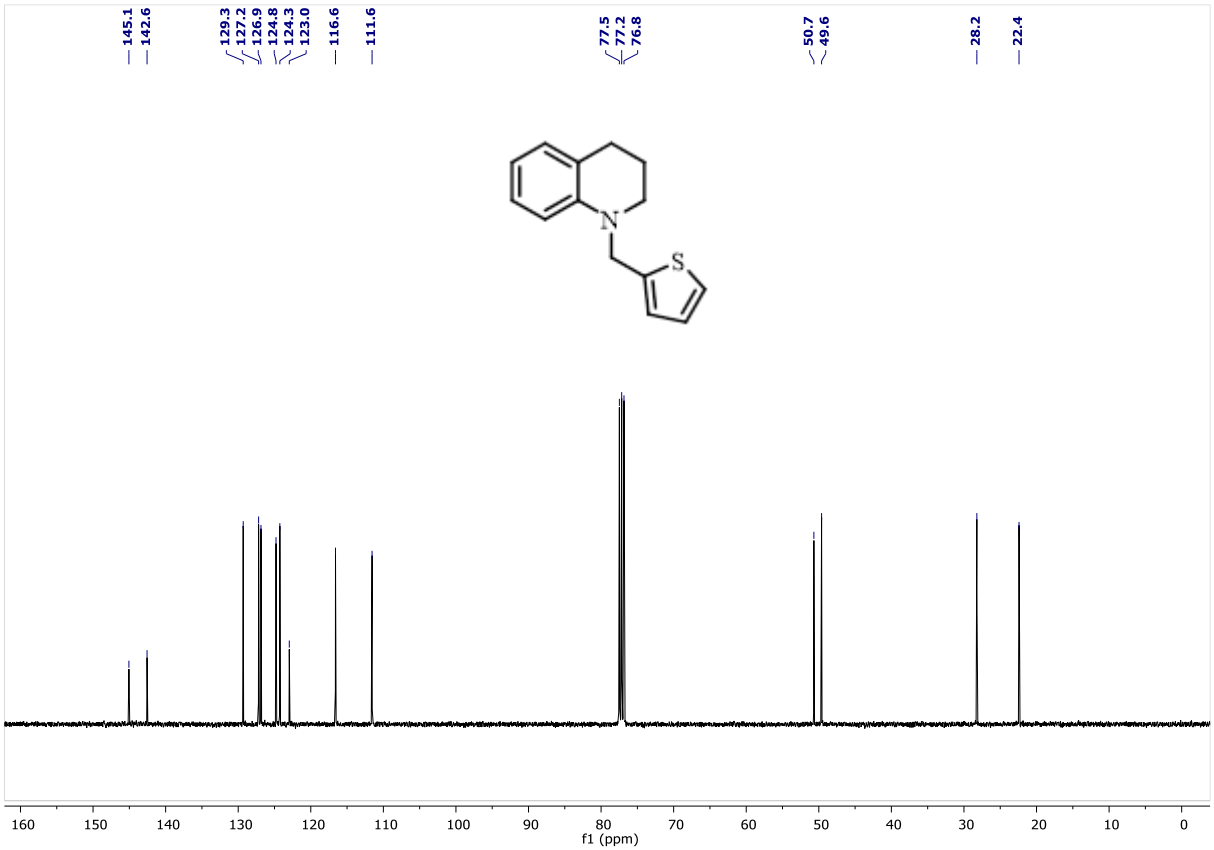


Figure S75: $^{13}C\{^{1}H\}$ NMR Spectrum of **3w** ($CDCl_3$, 101 MHz, 298 K)

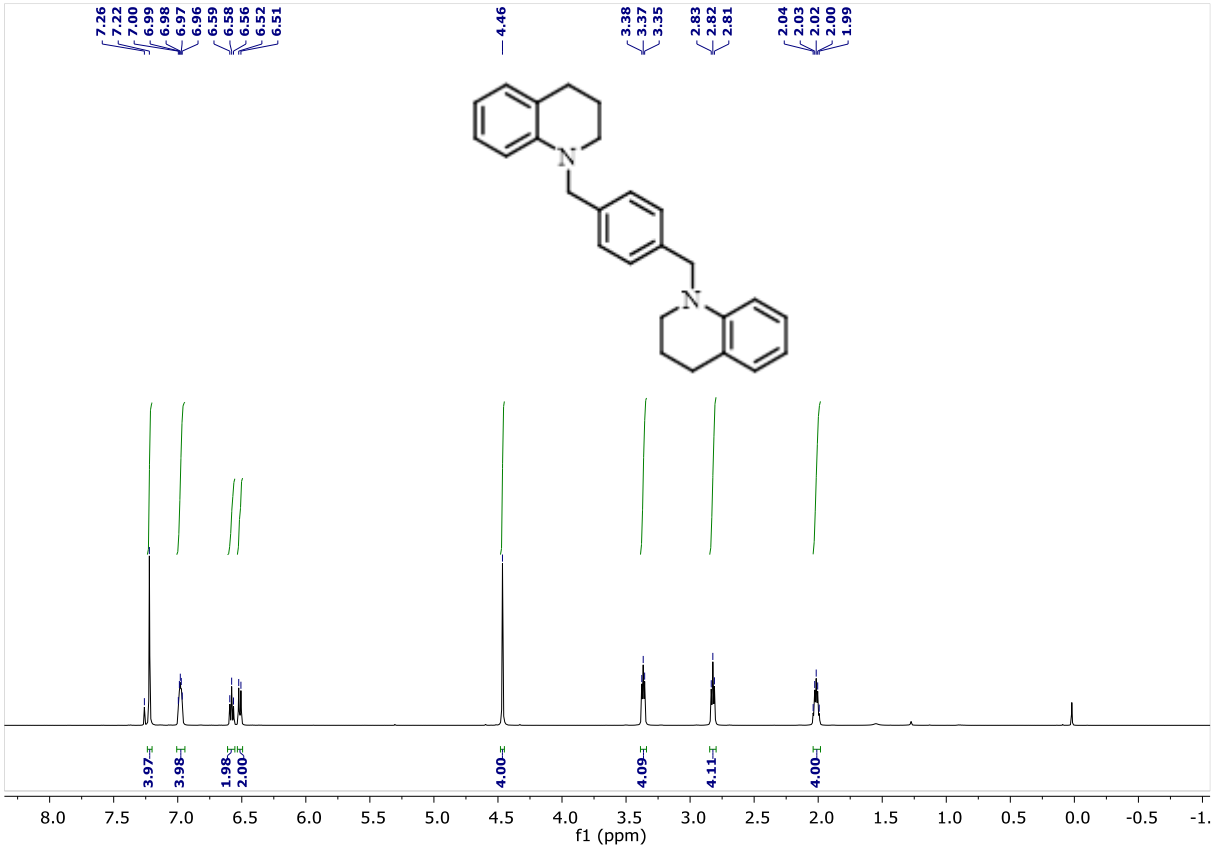


Figure S76: ^{1}H NMR Spectrum of **3x** ($CDCl_3$, 500 MHz, 298 K)

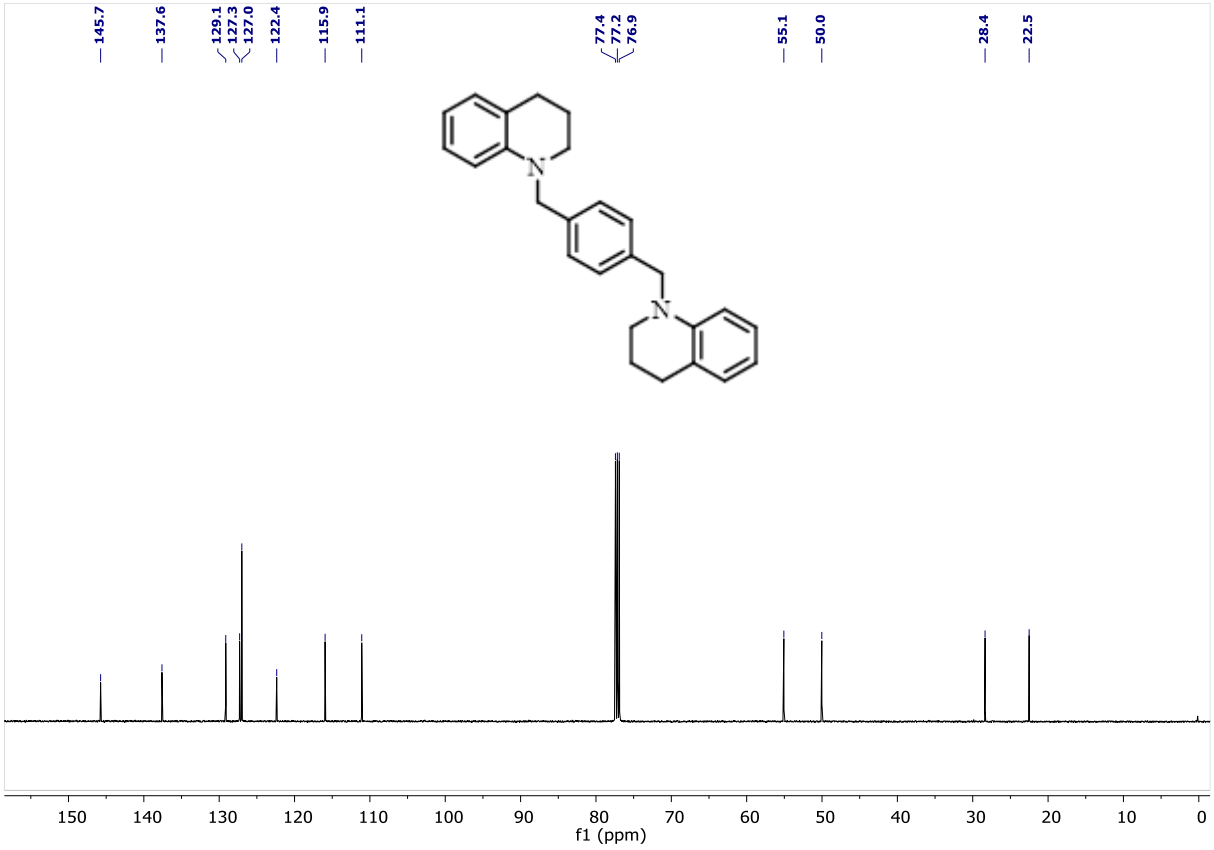


Figure S77: $^{13}C\{^{1}H\}$ NMR Spectrum of **3x** ($CDCl_3$, 126 MHz, 298 K)

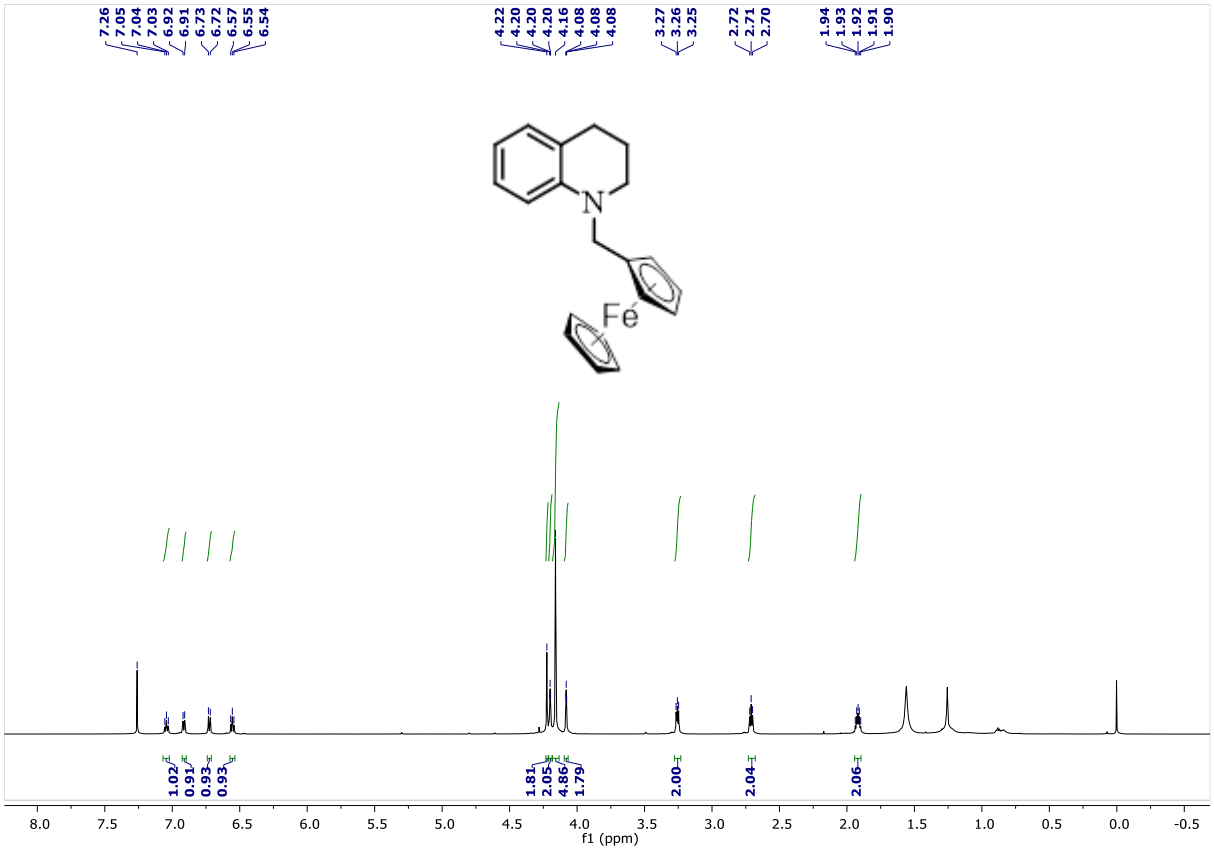


Figure S78: ^{1}H NMR Spectrum of **3y** ($CDCl_3$, 600 MHz, 298 K)

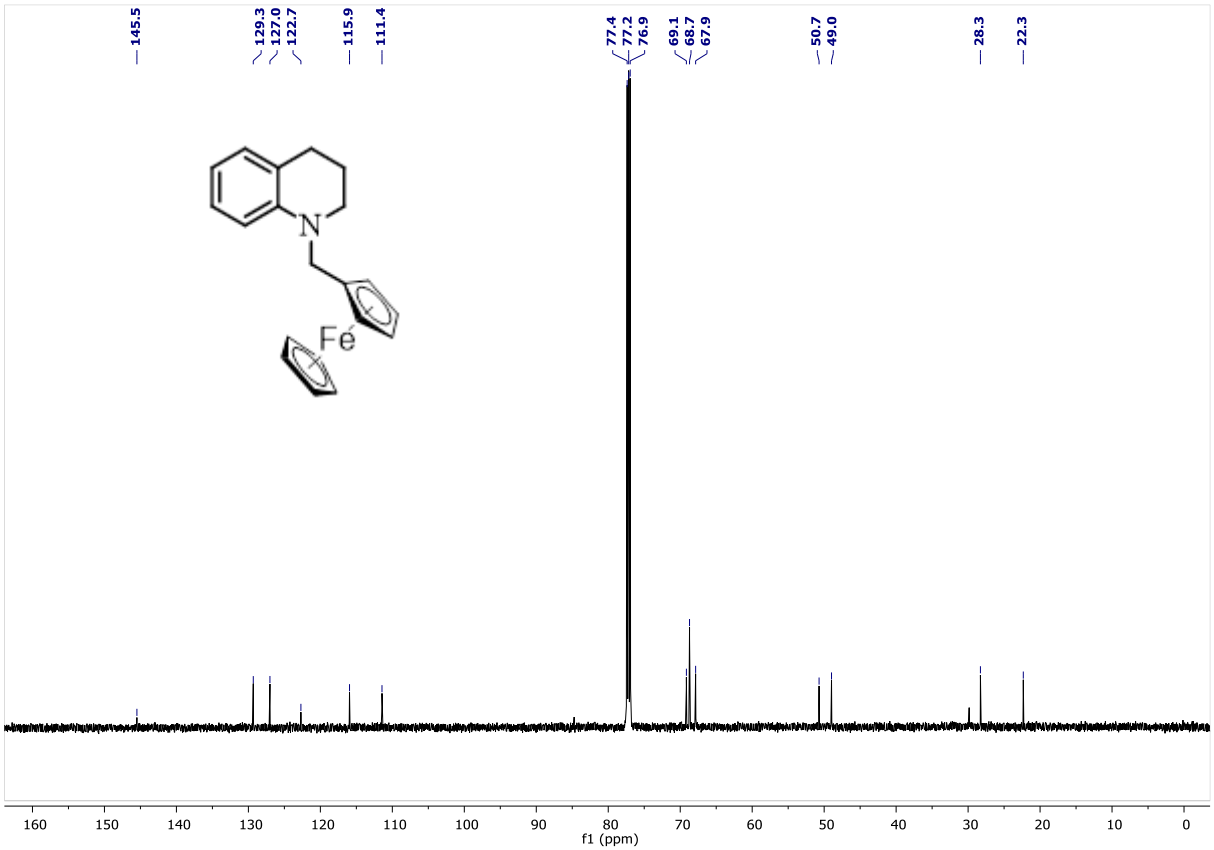


Figure S79: $^{13}C\{^{1}H\}$ NMR Spectrum of **3y** ($CDCl_3$, 151 MHz, 298 K)

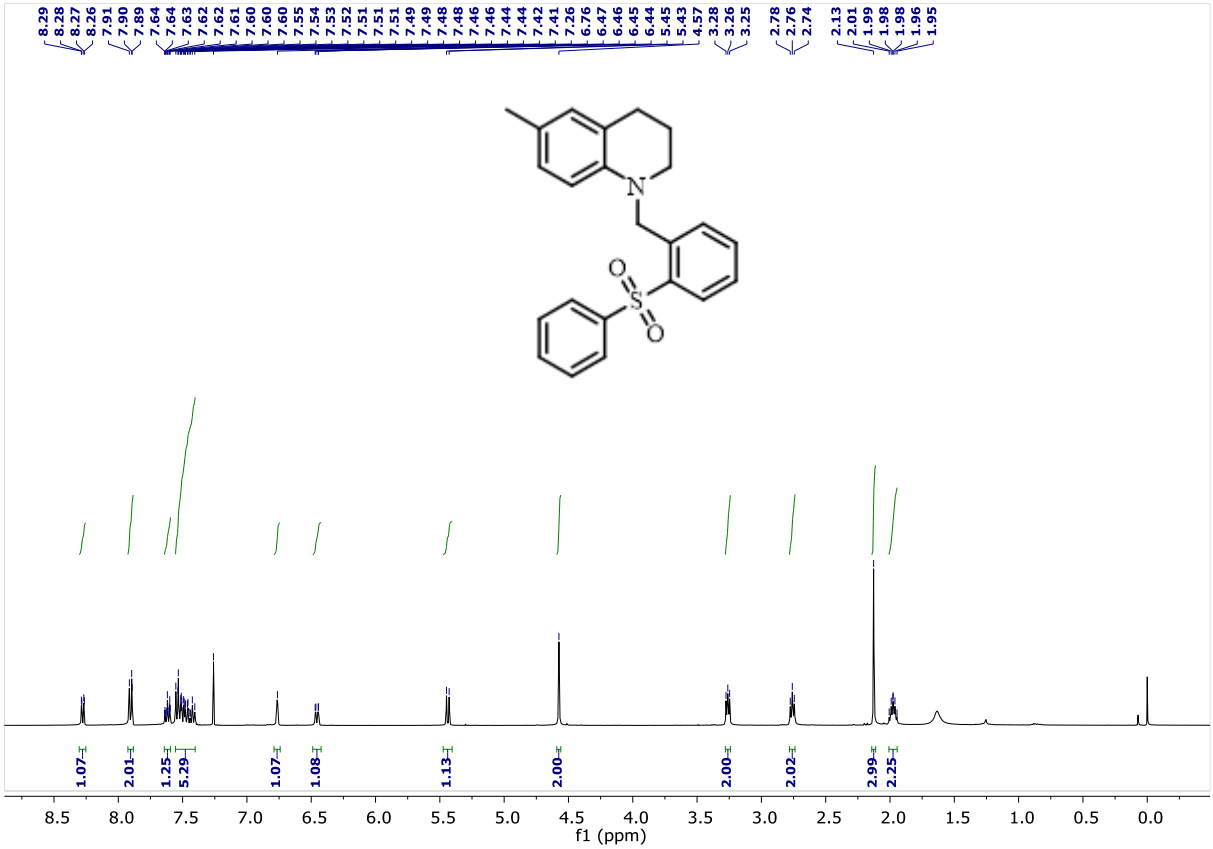


Figure S80: ^{1}H NMR Spectrum of **3z** ($CDCl_3$, 400 MHz, 298 K)

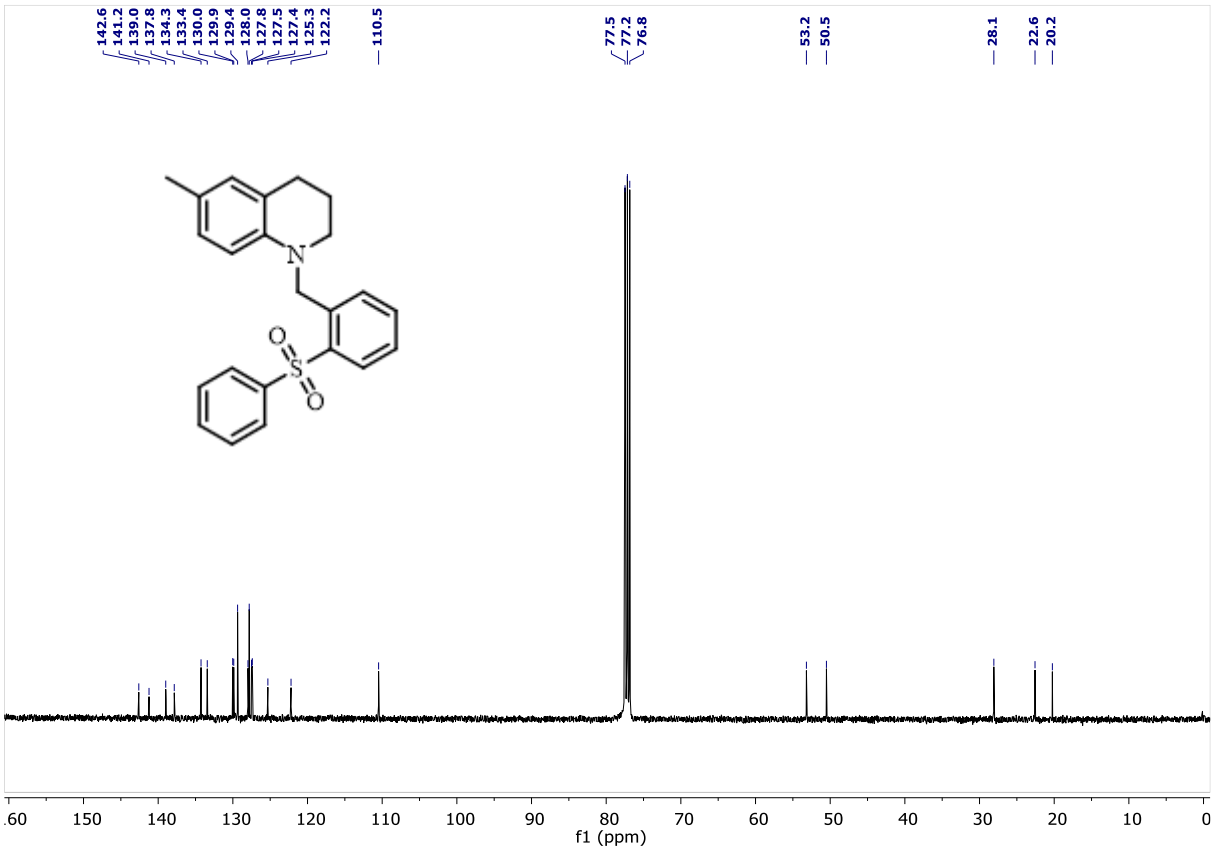


Figure S81: $^{13}C\{^{1}H\}$ NMR Spectrum of **3z** ($CDCl_3$, 101 MHz, 298 K)

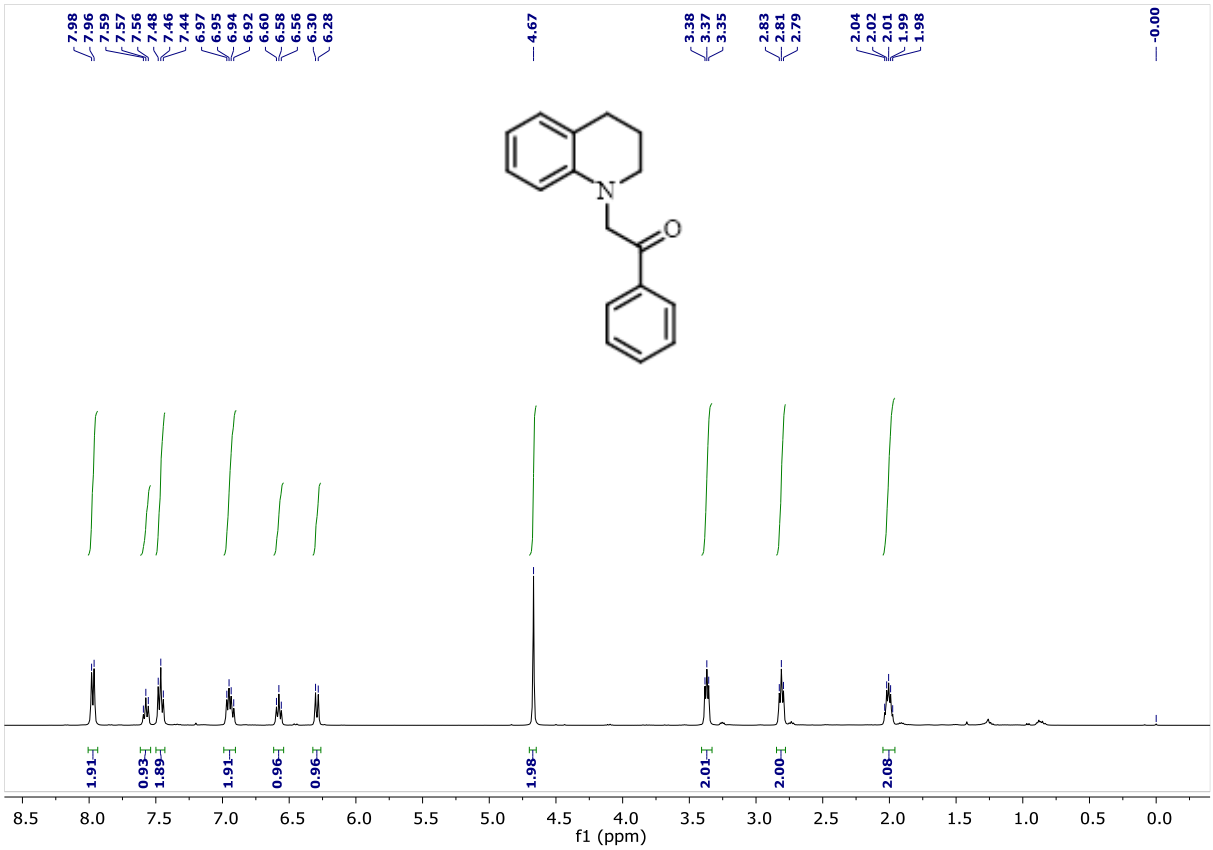


Figure S82: ^{1}H NMR Spectrum of **3aa** ($CDCl_3$, 400 MHz, 298 K)

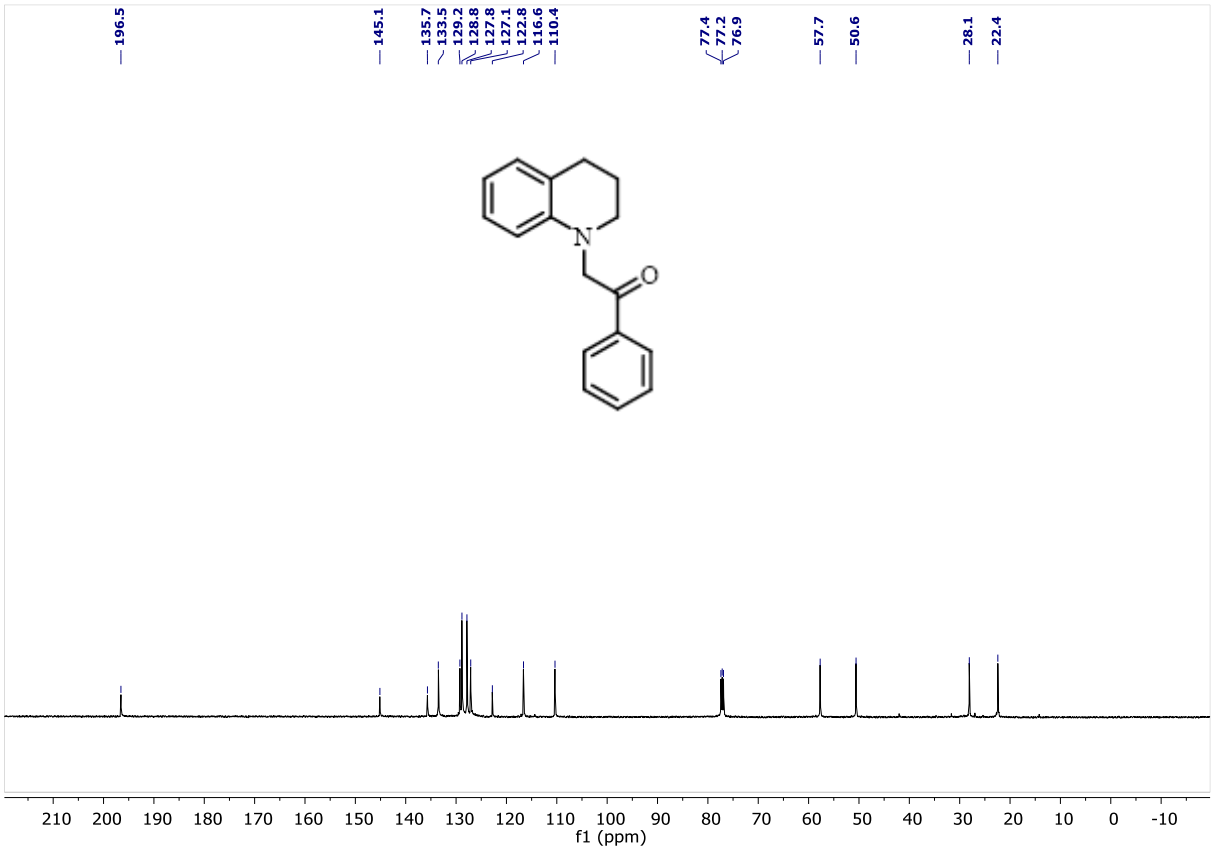


Figure S83: $^{13}C\{^{1}H\}$ NMR Spectrum of **3aa** ($CDCl_3$, 126 MHz, 298 K)

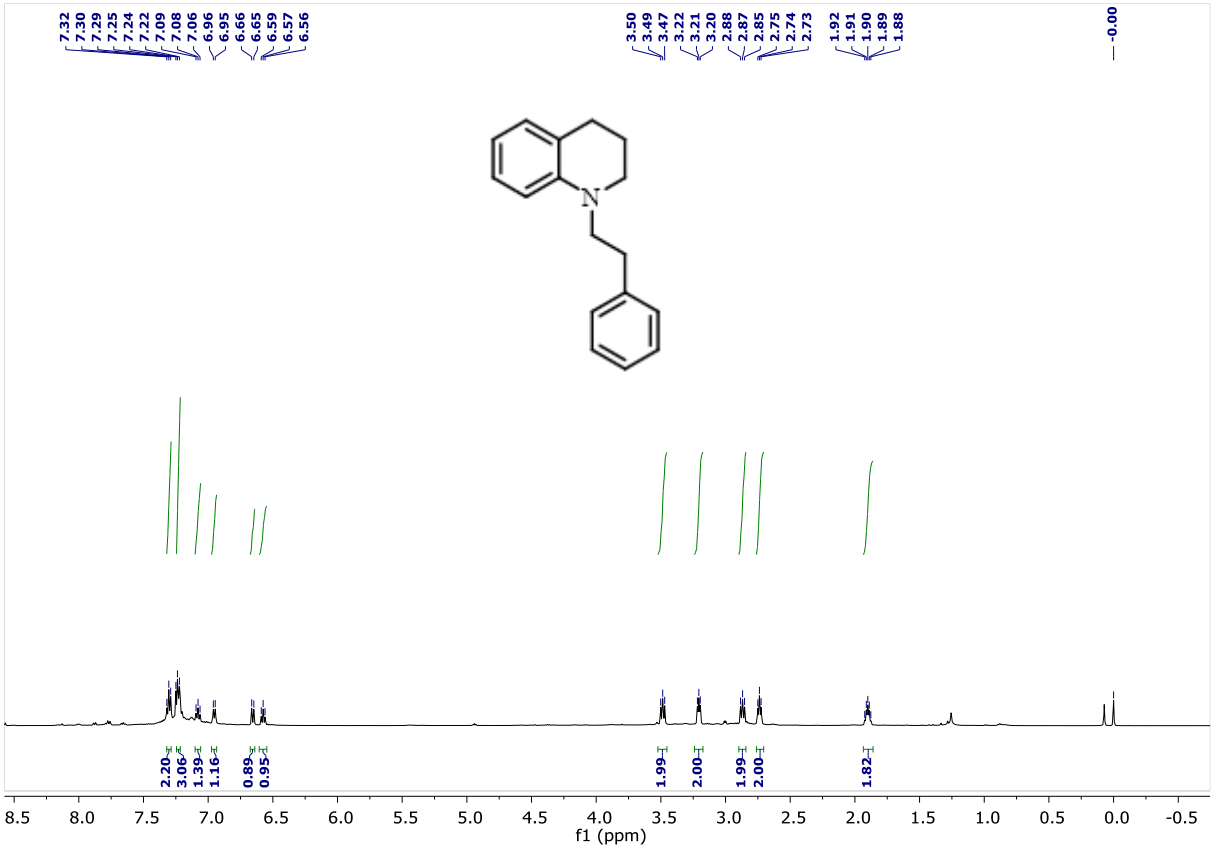


Figure S84: ^{1}H NMR Spectrum of **3ab** ($CDCl_3$, 500 MHz, 298 K)

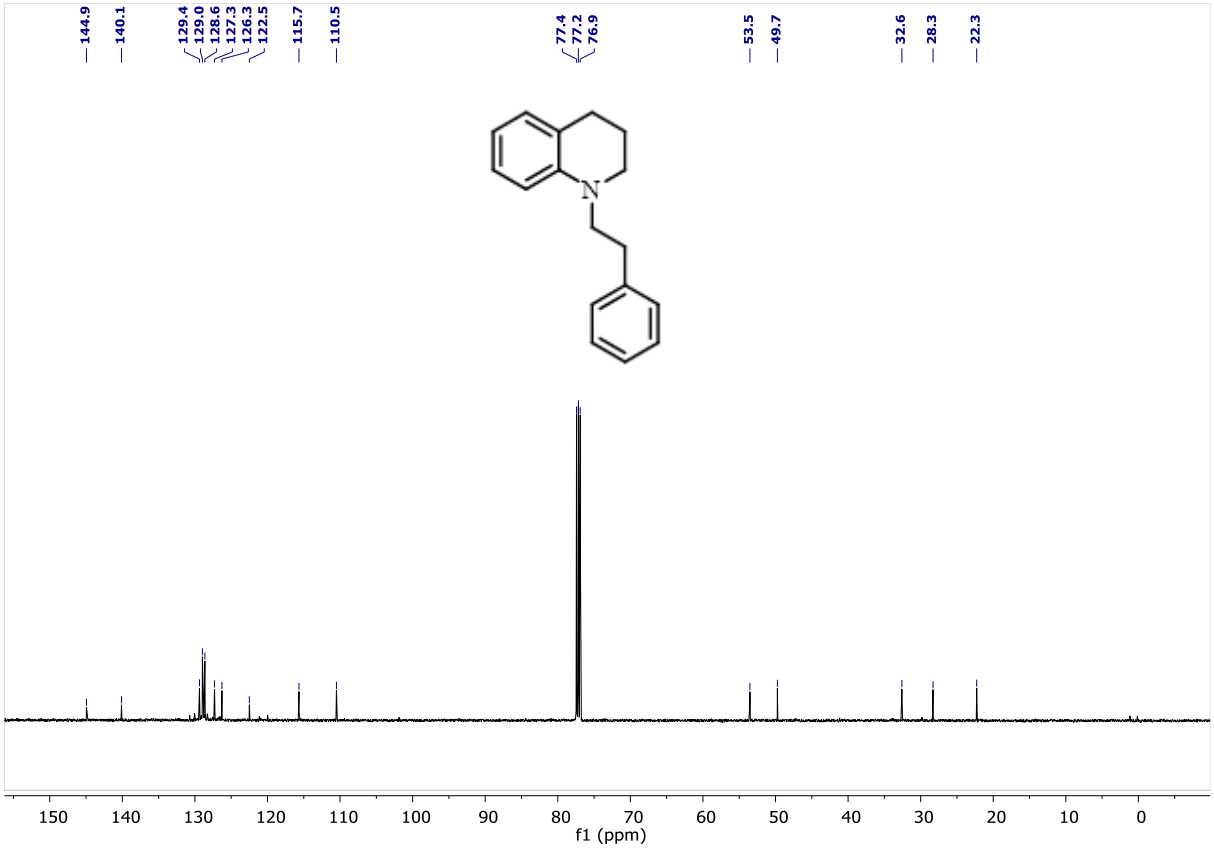


Figure S85: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ab** ($CDCl_3$, 126 MHz, 298 K)

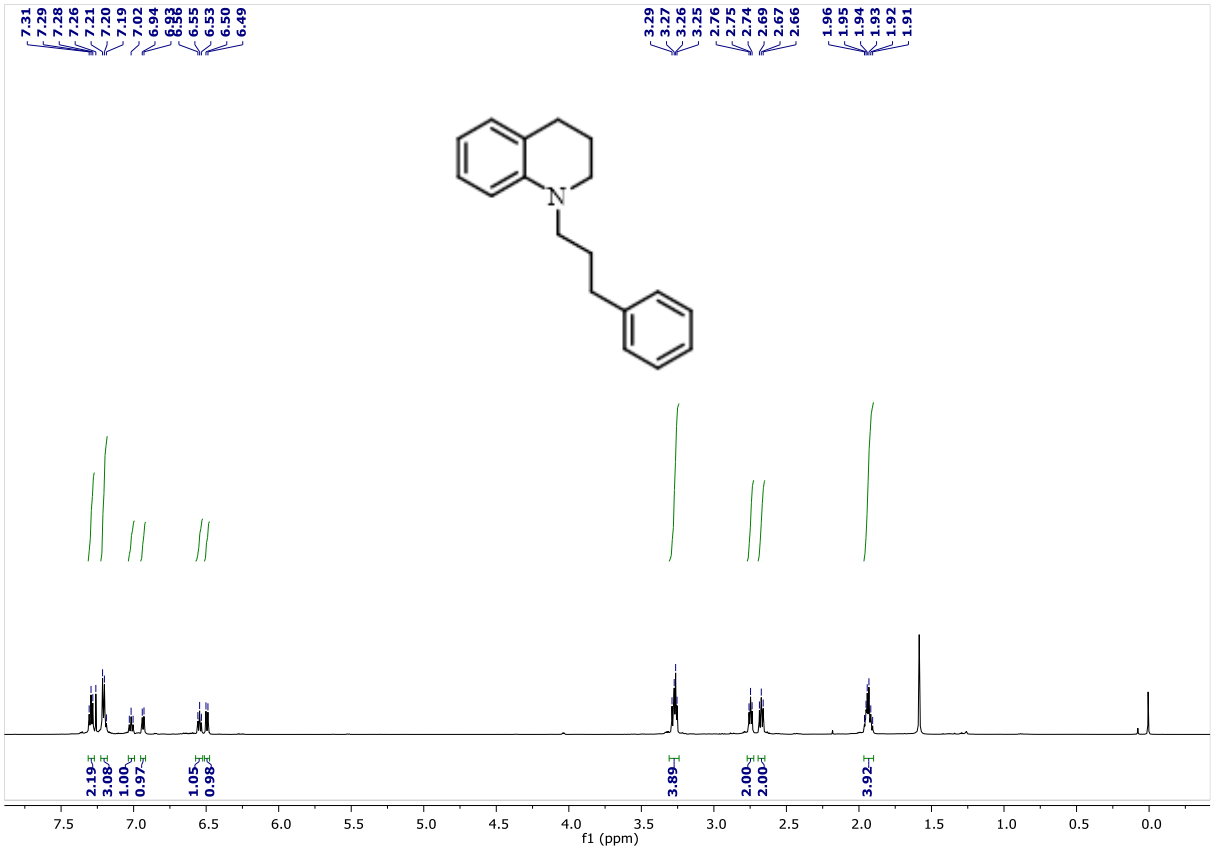


Figure S86: ^{1}H NMR Spectrum of **3ac** ($CDCl_3$, 600 MHz, 298 K)

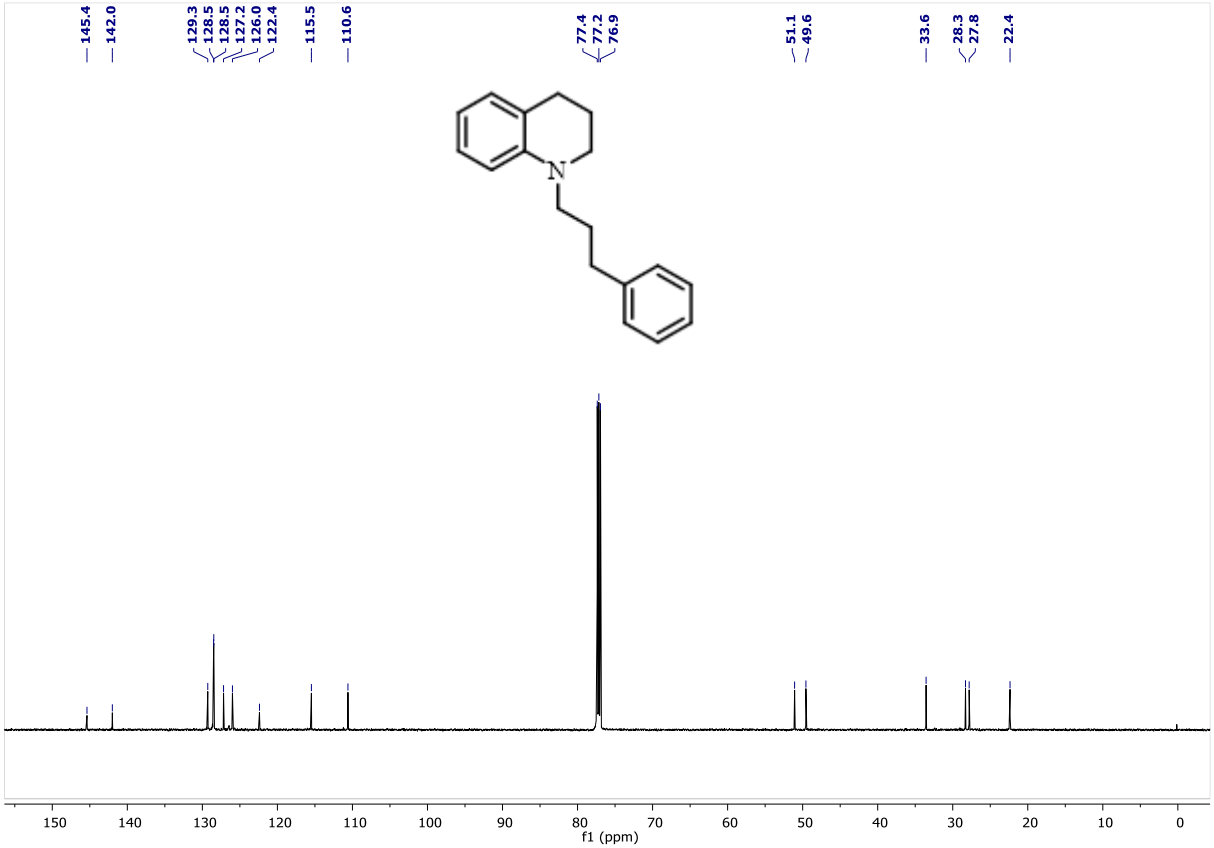


Figure S87: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ac** ($CDCl_3$, 151 MHz, 298 K)

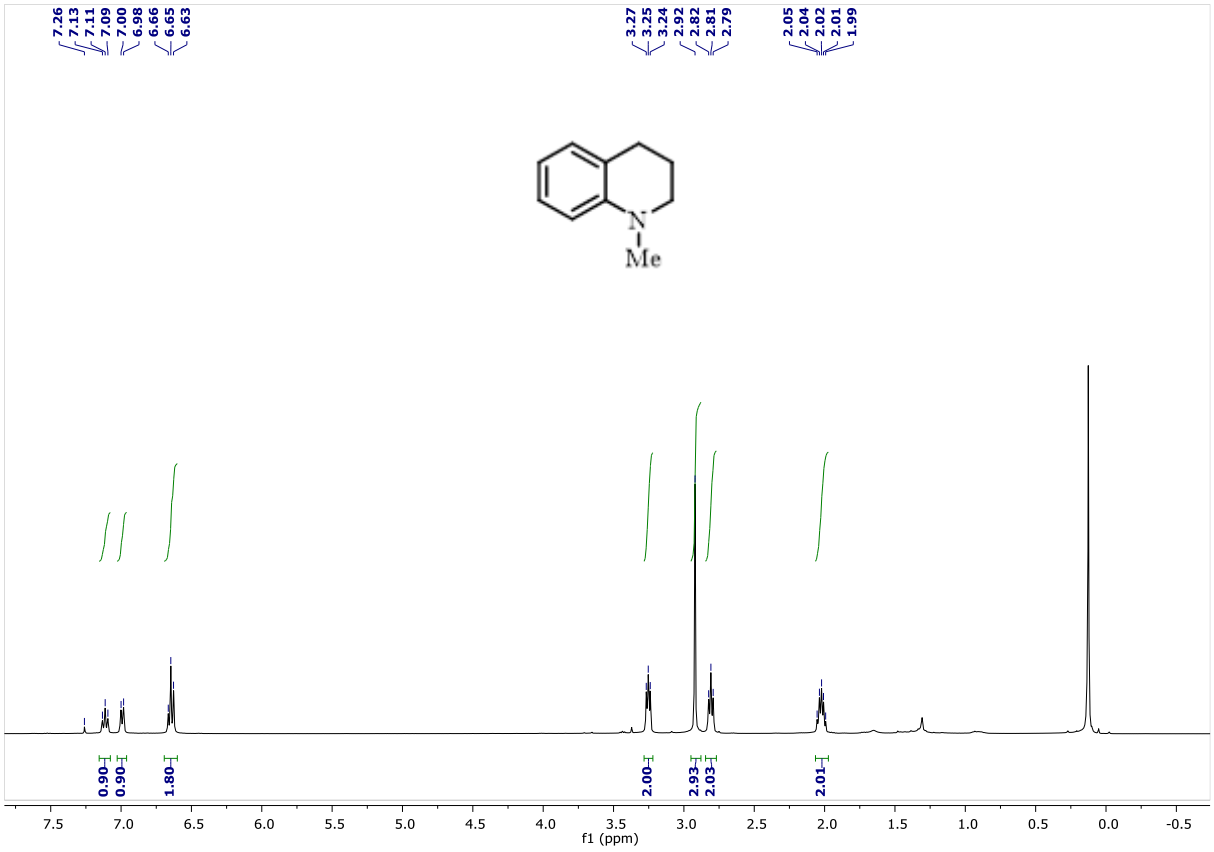


Figure S88: ^{1}H NMR Spectrum of **3ad** ($CDCl_3$, 400 MHz, 298 K)

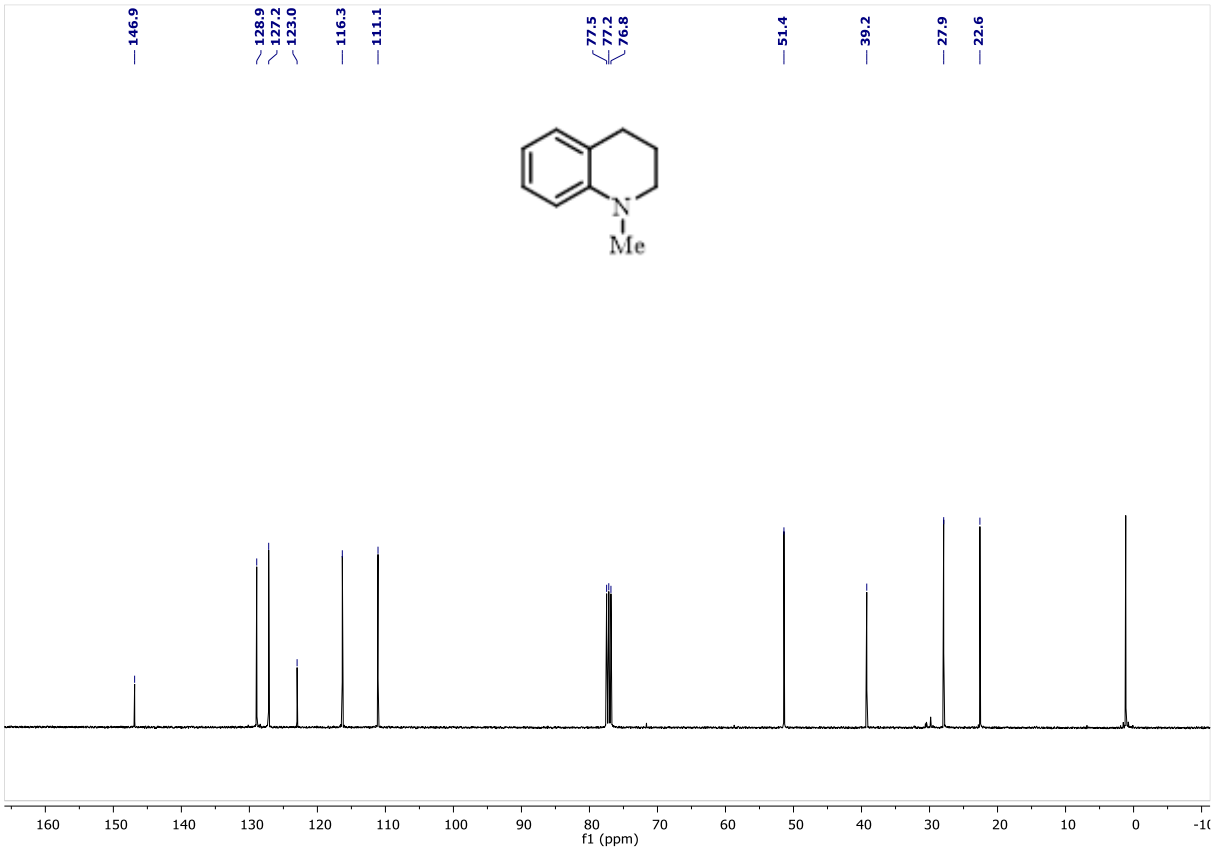


Figure S89: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ad** ($CDCl_3$, 101 MHz, 298 K)

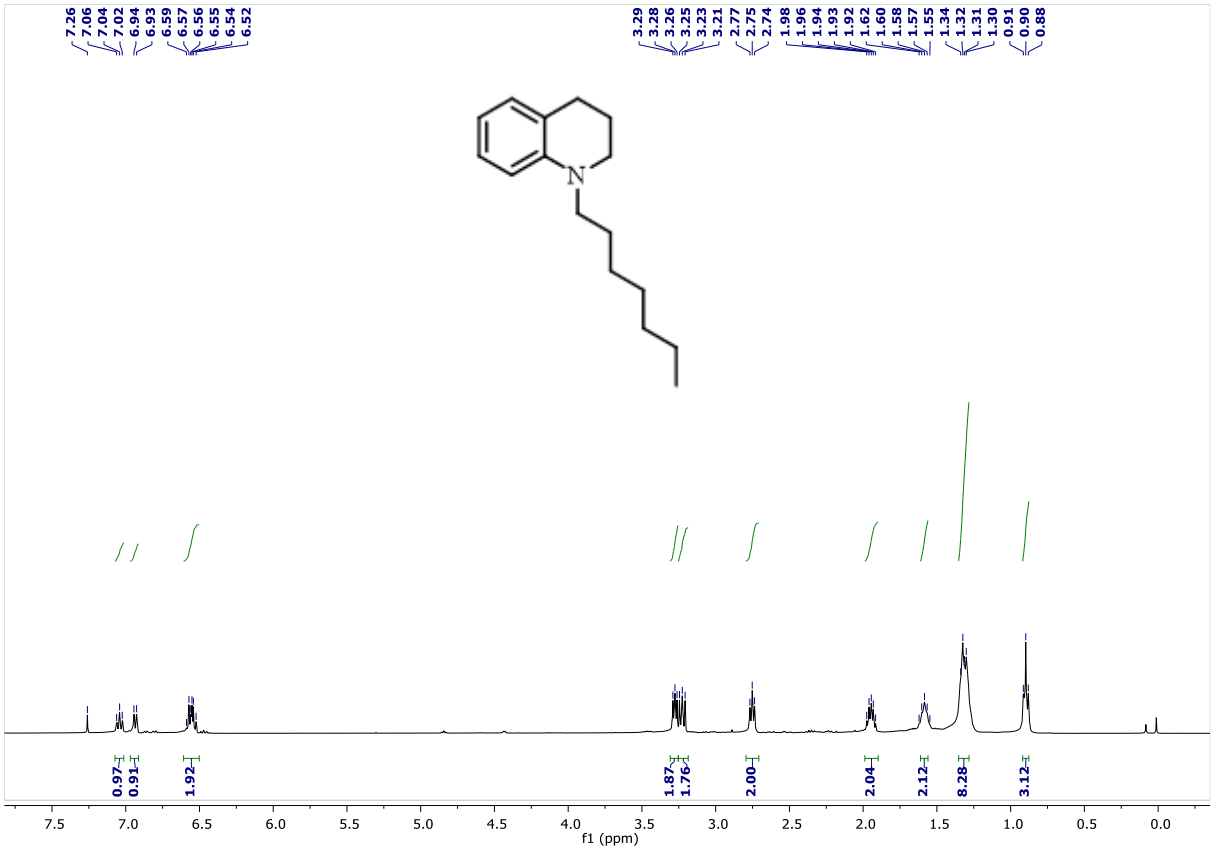


Figure S90: ^{1}H NMR Spectrum of **3ae** ($CDCl_3$, 400 MHz, 298 K)

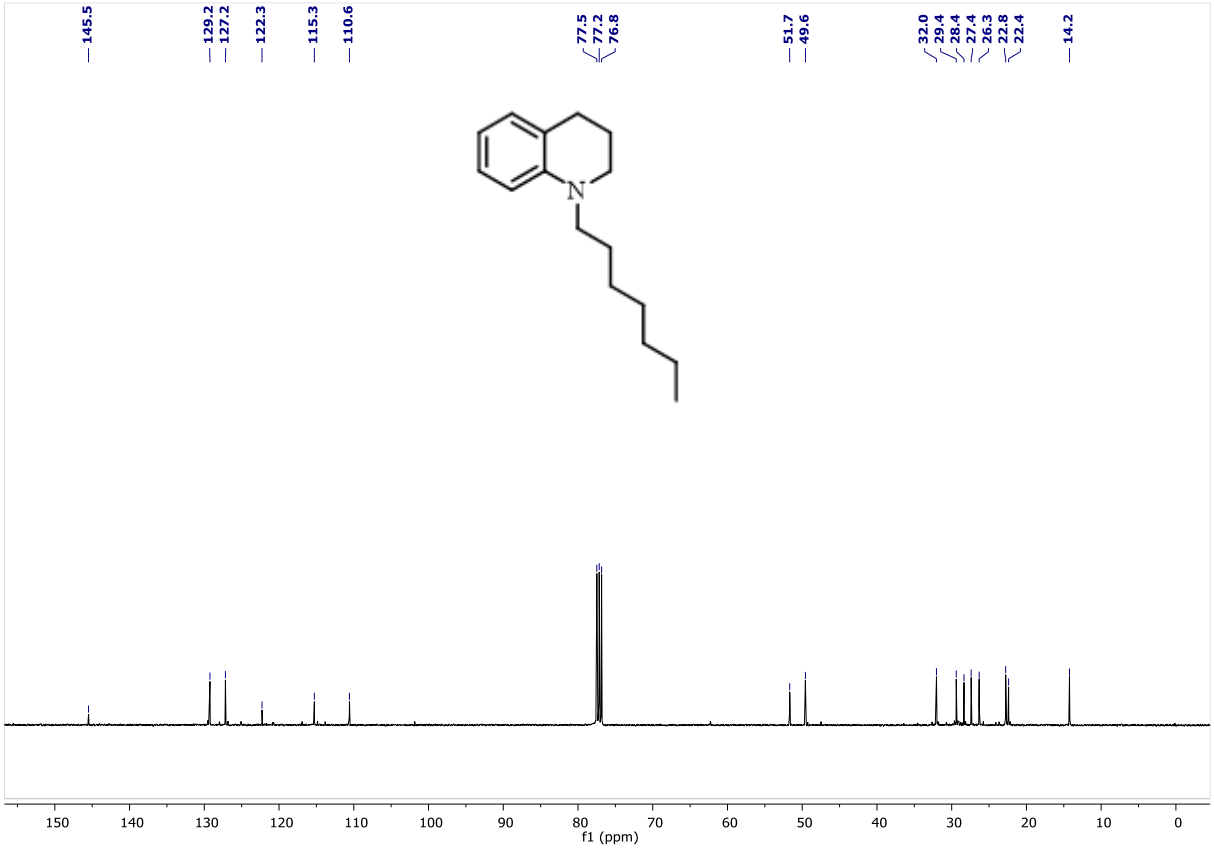


Figure S91: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ae** ($CDCl_3$, 101 MHz, 298 K)

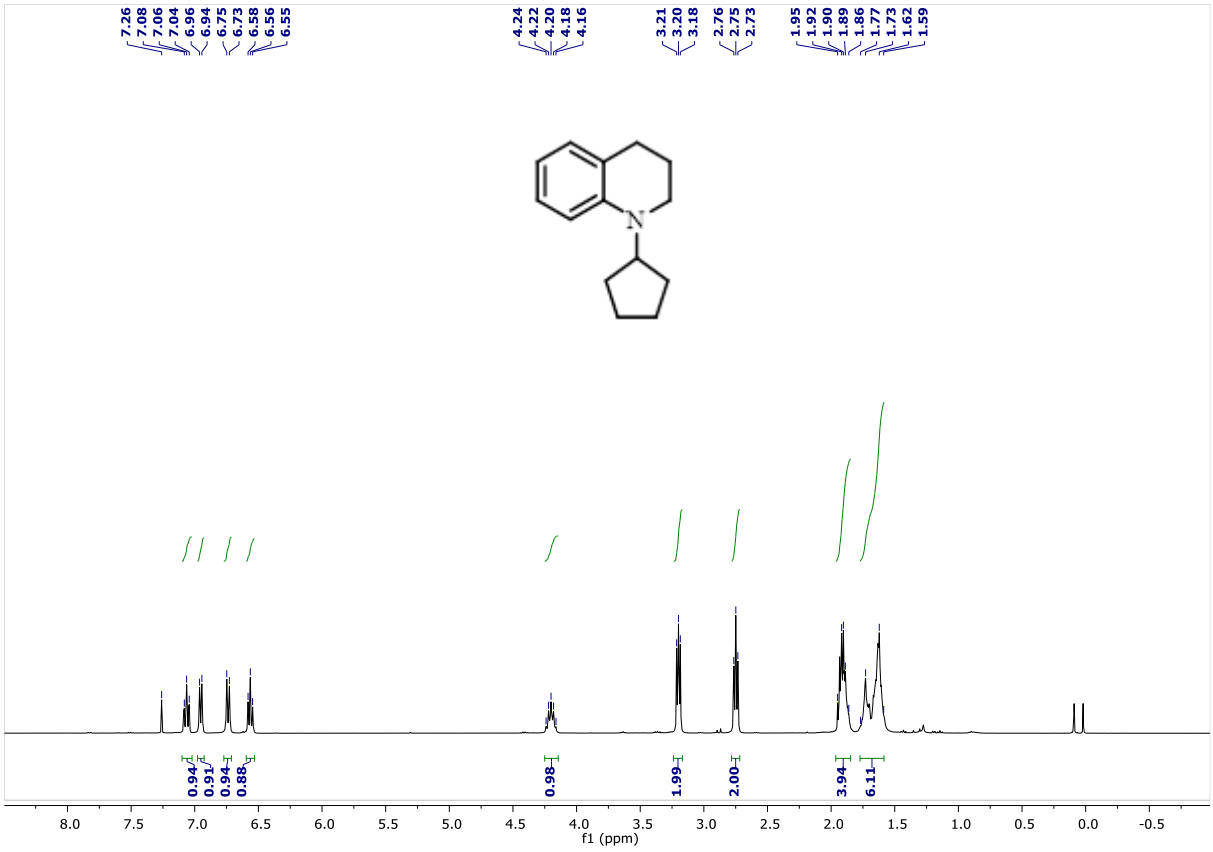


Figure S92: ^{1}H NMR Spectrum of **3af** ($CDCl_3$, 400 MHz, 298 K)

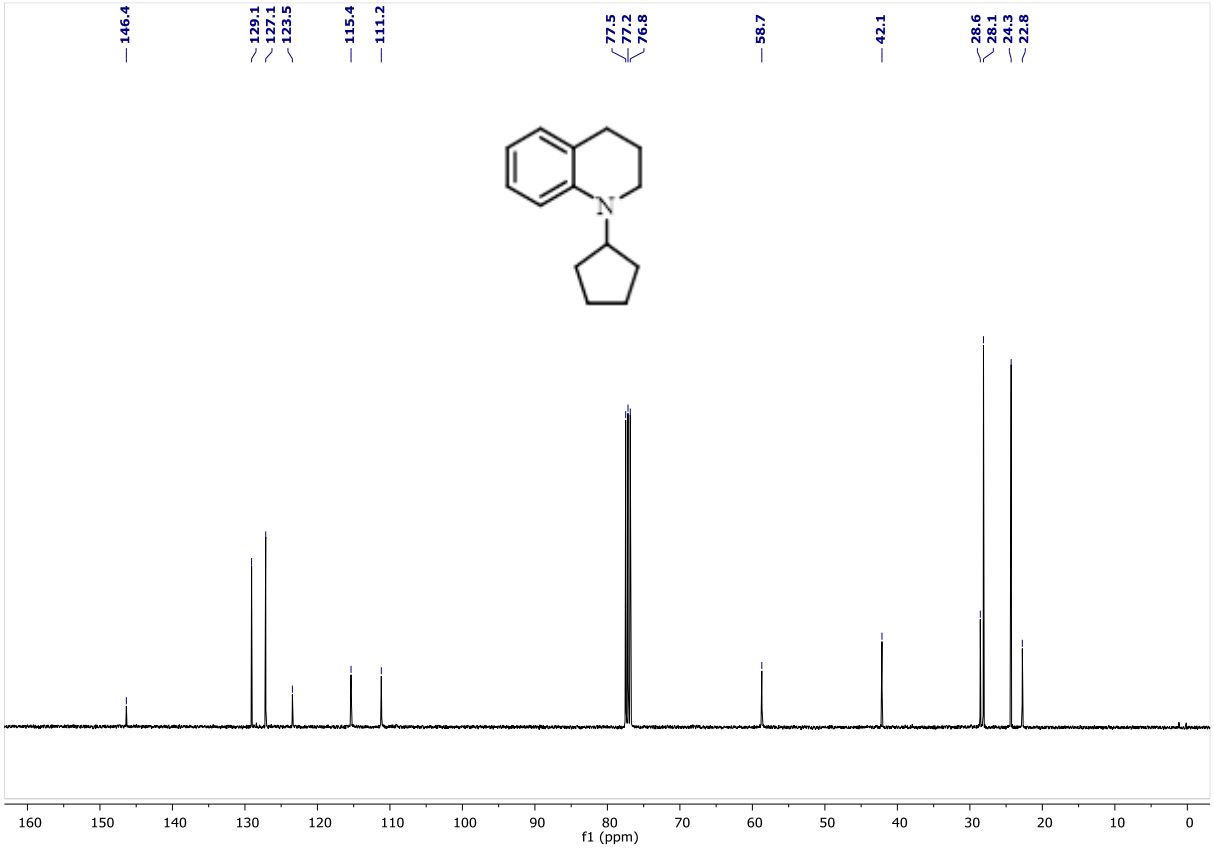


Figure S93: $^{13}C\{^{1}H\}$ NMR Spectrum of **3af** ($CDCl_3$, 101 MHz, 298 K)

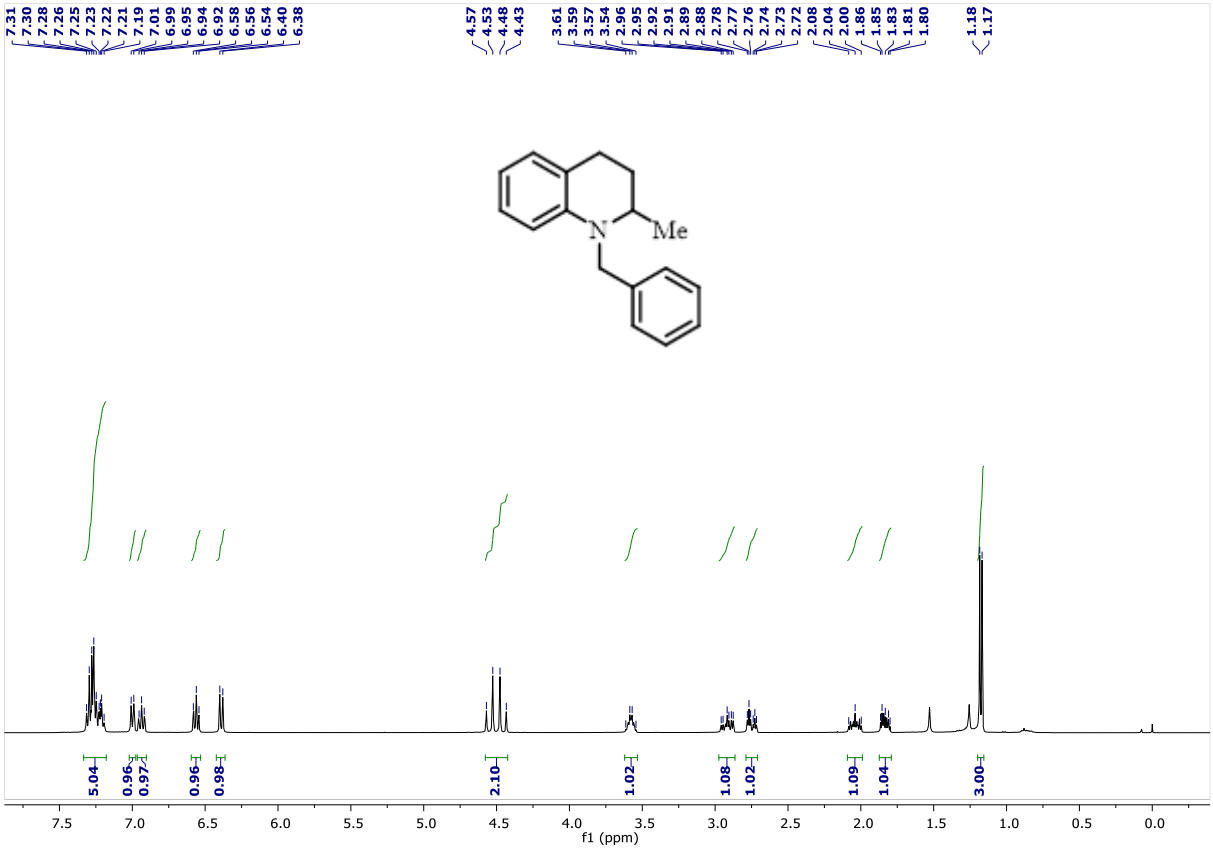


Figure S94: ^{1}H NMR Spectrum of **4b** ($CDCl_3$, 400 MHz, 298 K)

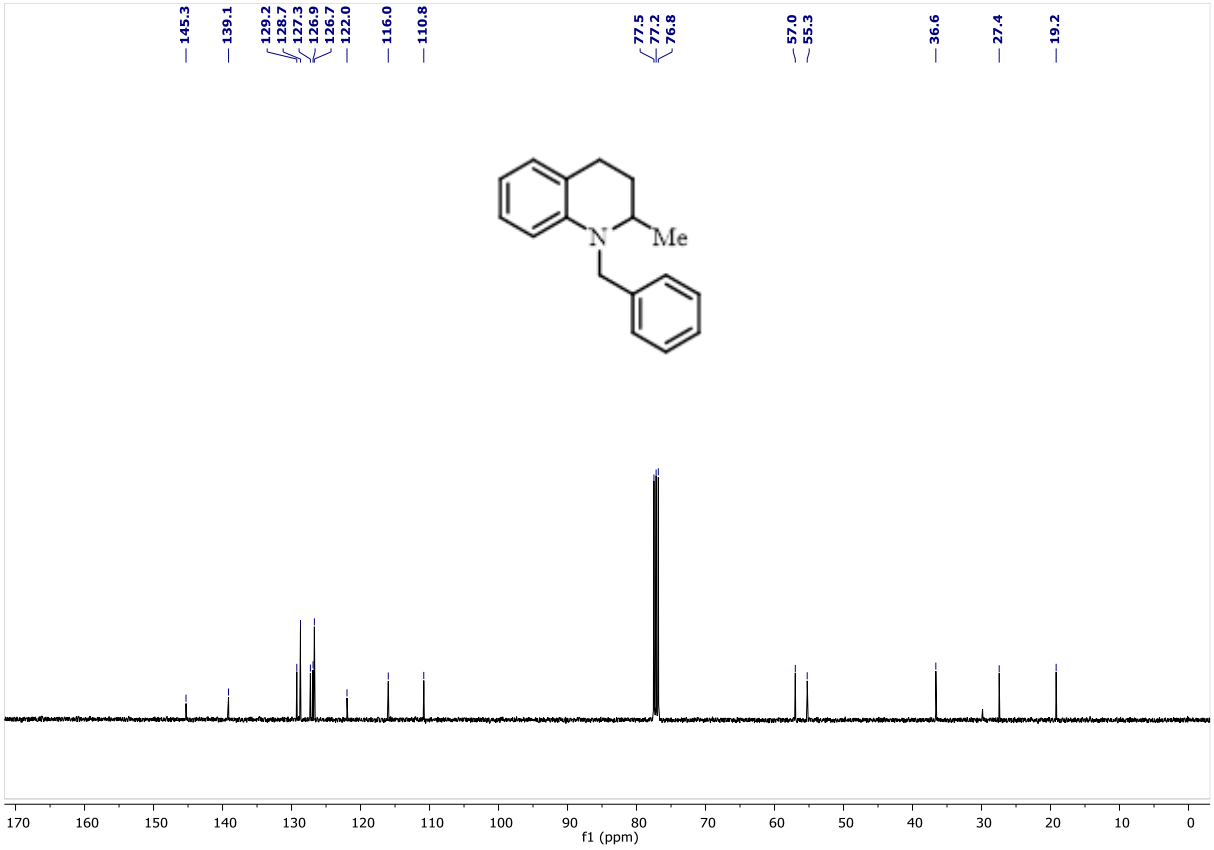


Figure S95: ^{13}C{^{1}H} NMR Spectrum of **4b** ($CDCl_3$, 101 MHz, 298 K)

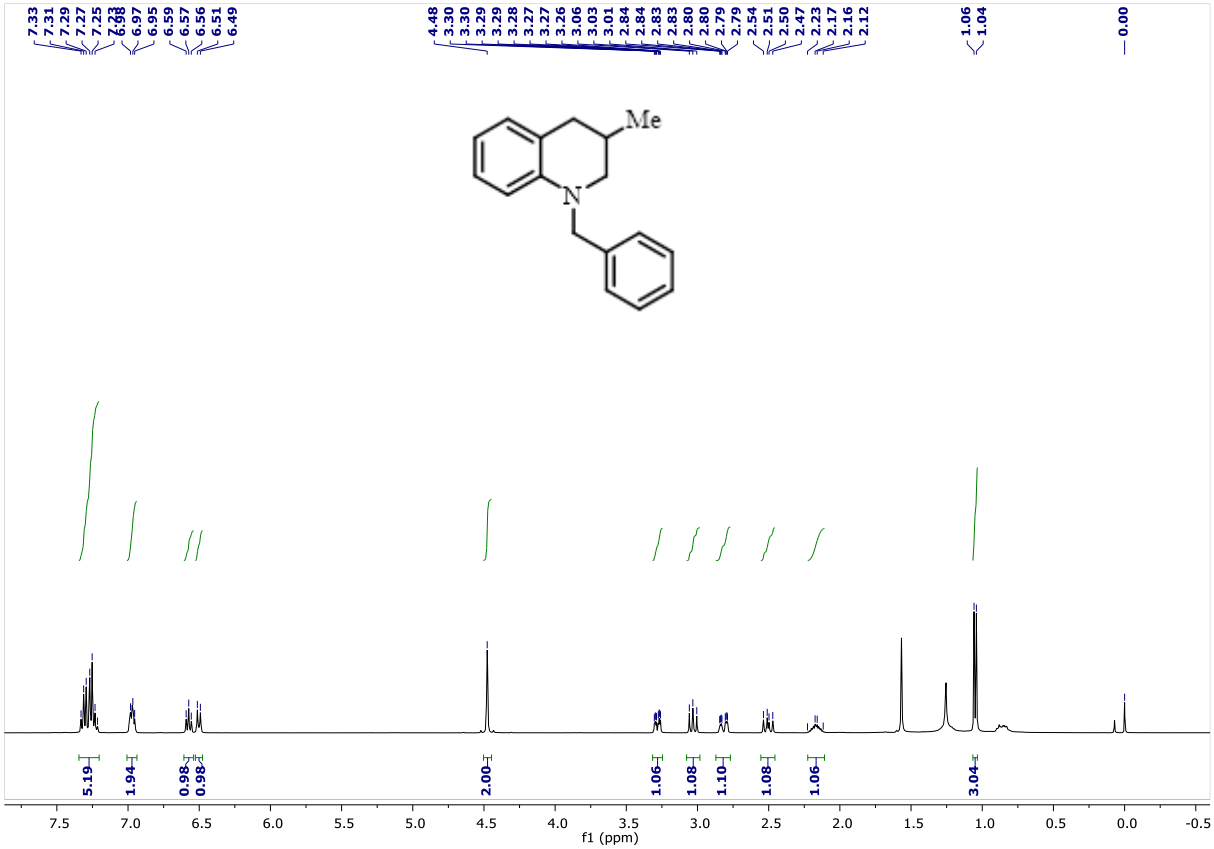


Figure S96: ^{1}H NMR Spectrum of **4c** ($CDCl_3$, 400 MHz, 298 K)

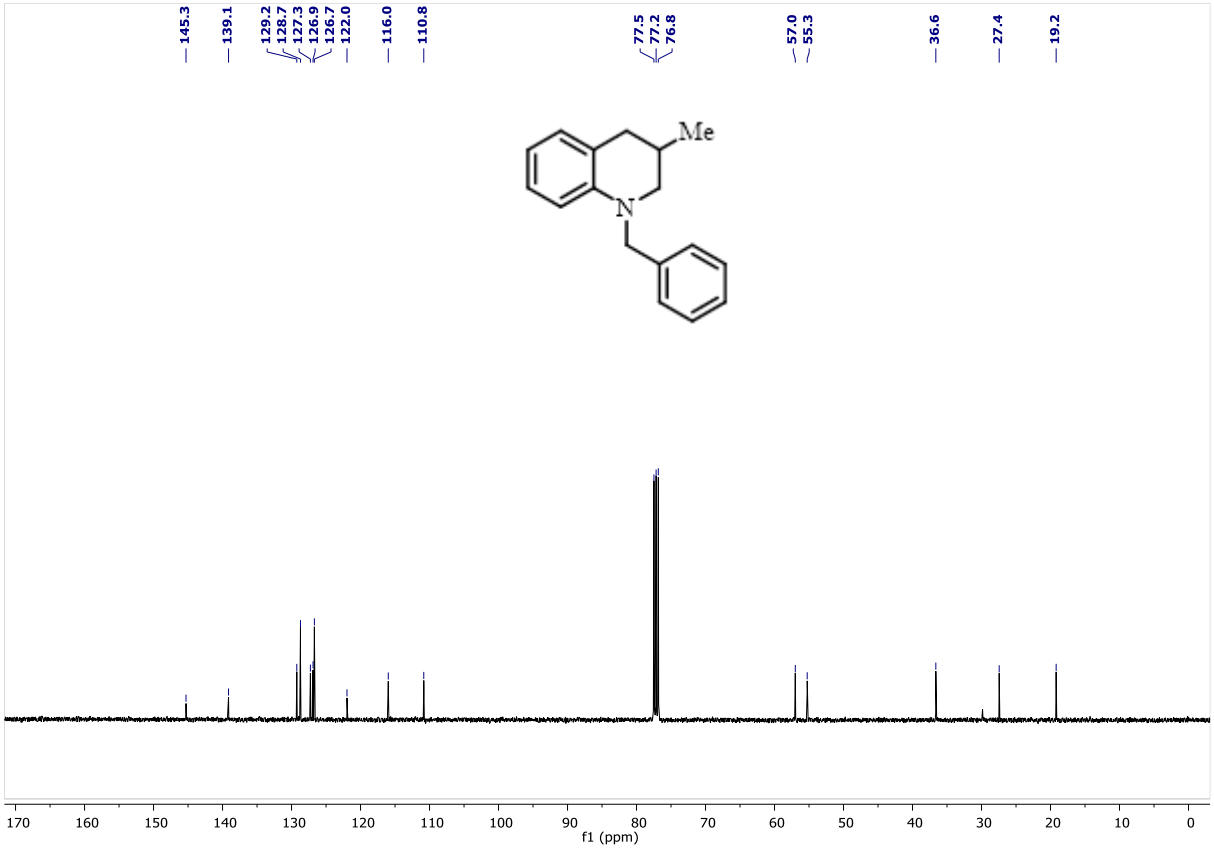


Figure S97: $^{13}C\{^{1}H\}$ NMR Spectrum of **4c** ($CDCl_3$, 101 MHz, 298 K)

Figure S98: ^{1}H NMR Spectrum of **4d** ($CDCl_3$, 400 MHz, 298 K)

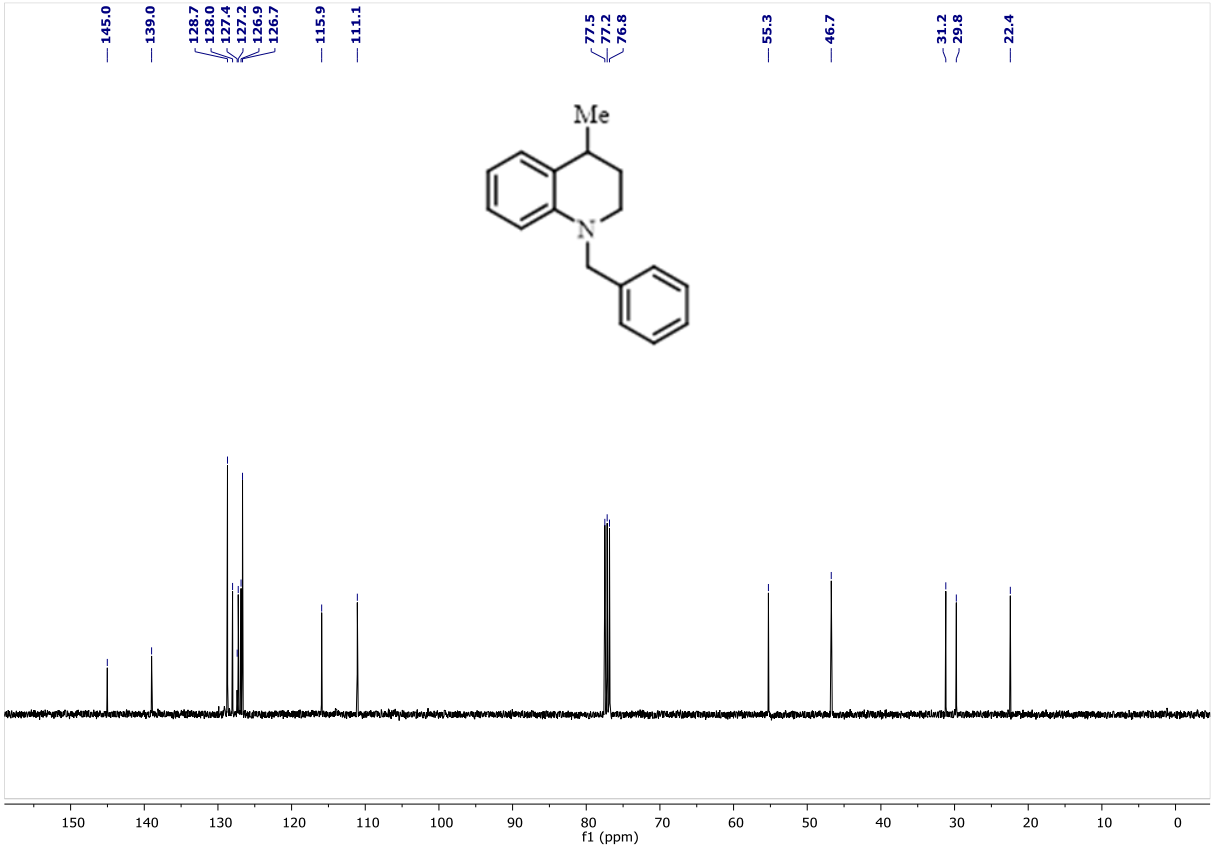


Figure S99: $^{13}C\{^{1}H\}$ NMR Spectrum of **4d** ($CDCl_3$, 101 MHz, 298 K)

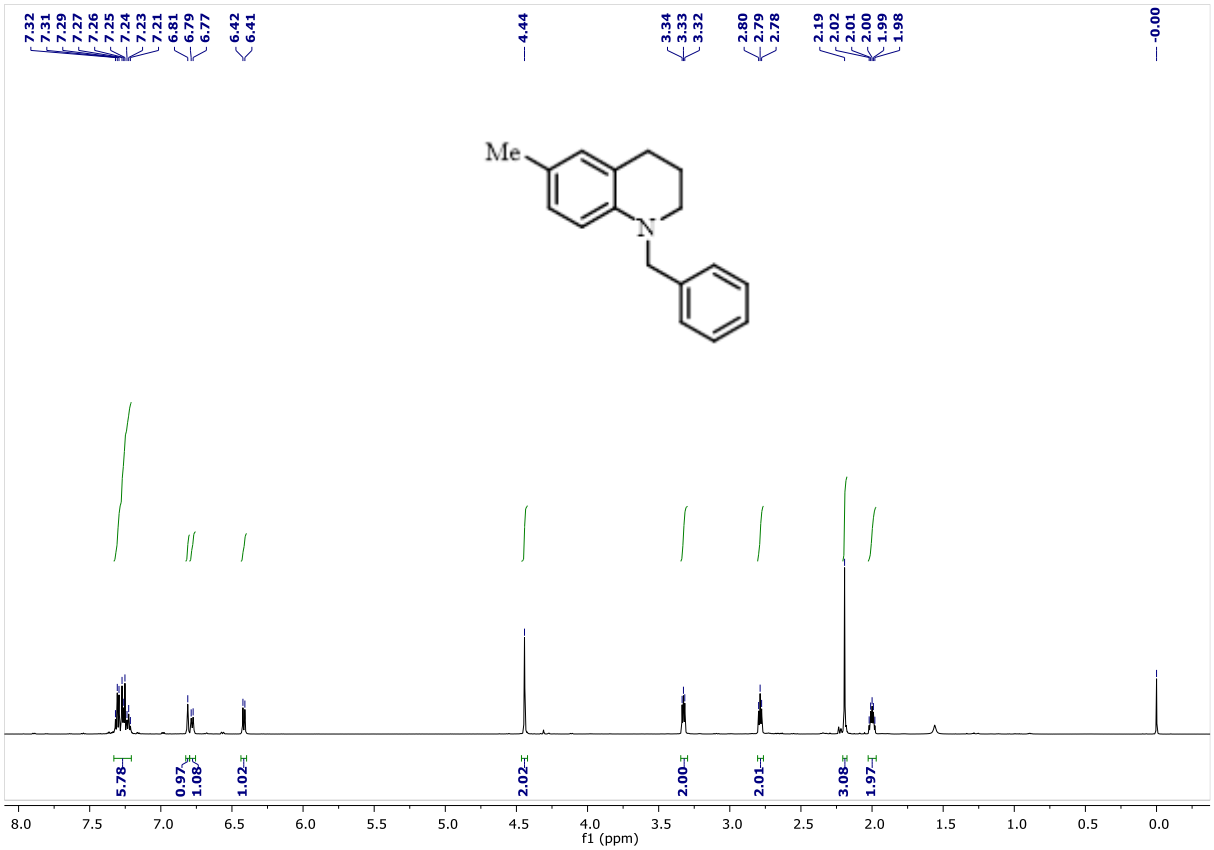


Figure S100: ^{1}H NMR Spectrum of **4e** ($CDCl_3$, 600 MHz, 298 K)

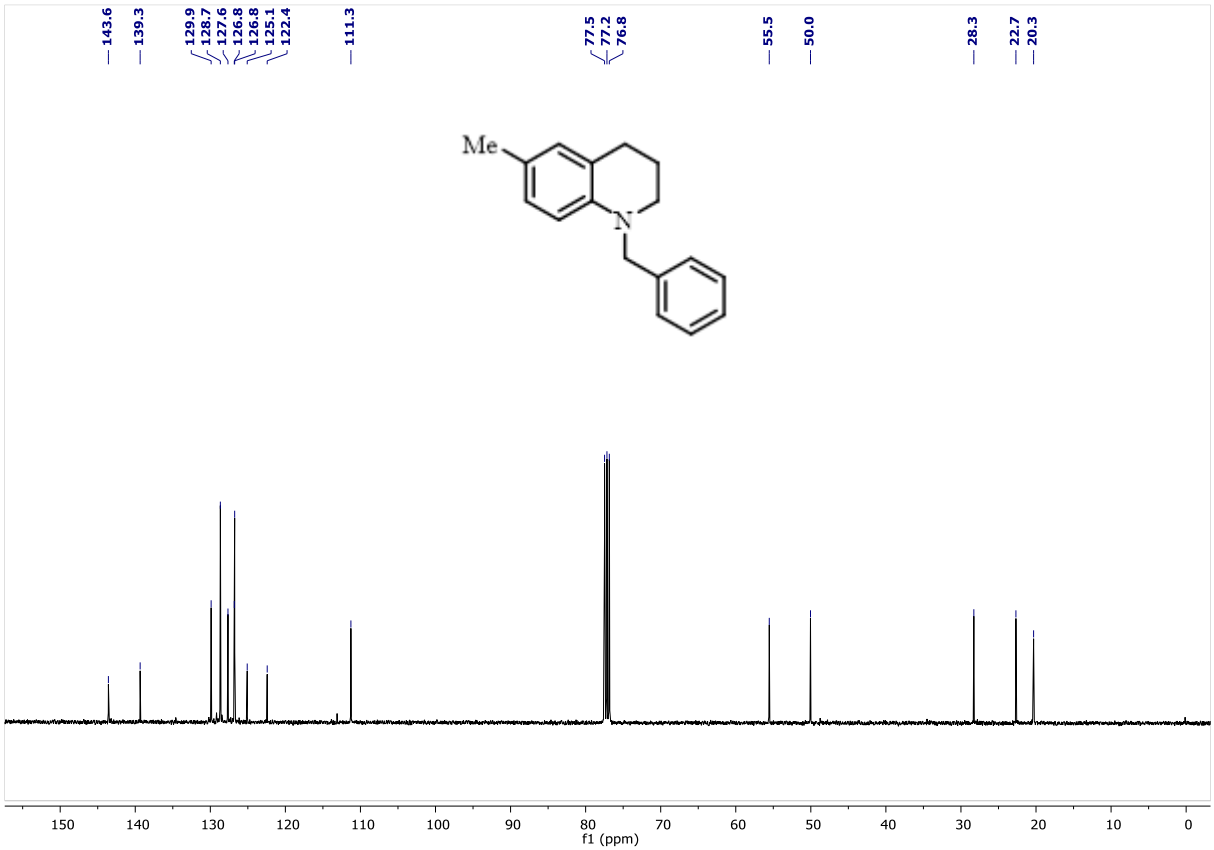


Figure S101: $^{13}C\{^{1}H\}$ NMR Spectrum of **4e** ($CDCl_3$, 101 MHz, 298 K)

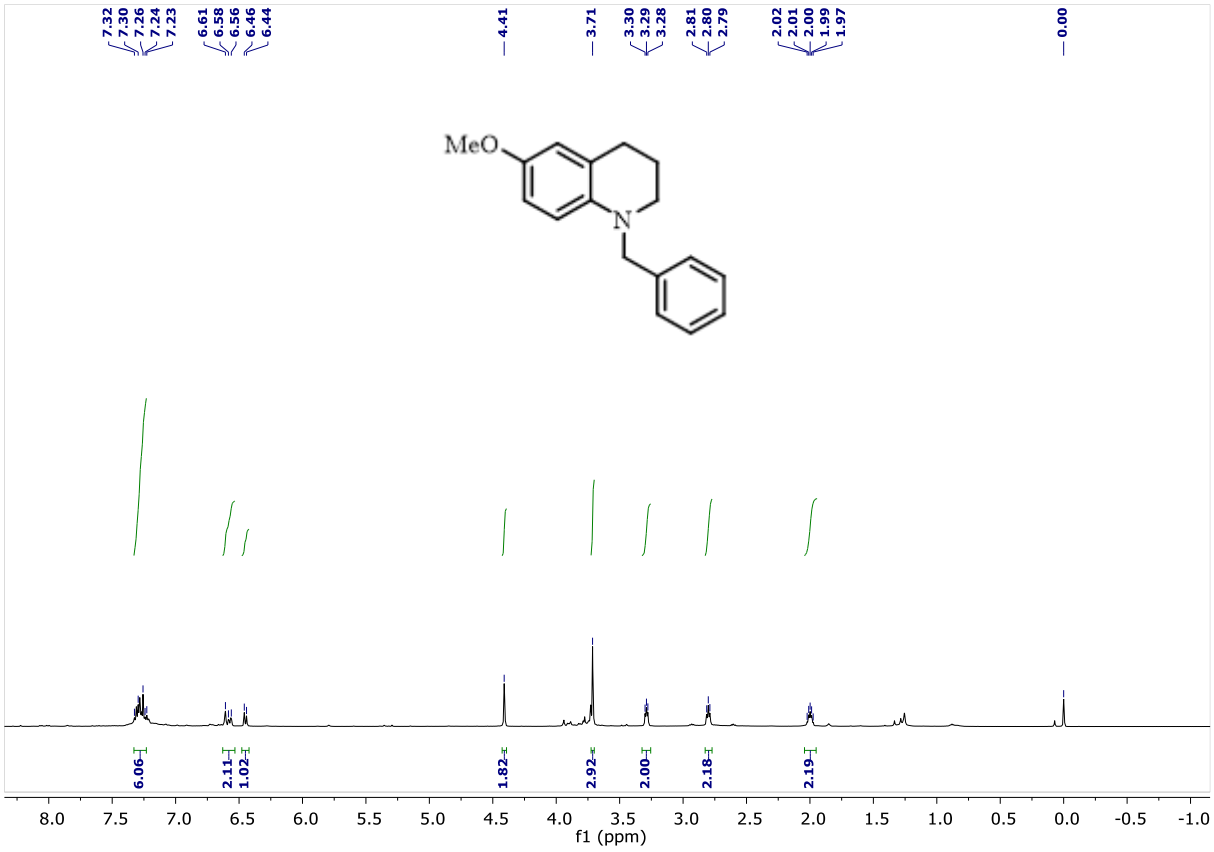


Figure S102: ^{1}H NMR Spectrum of **4f** ($CDCl_3$, 500 MHz, 298 K)

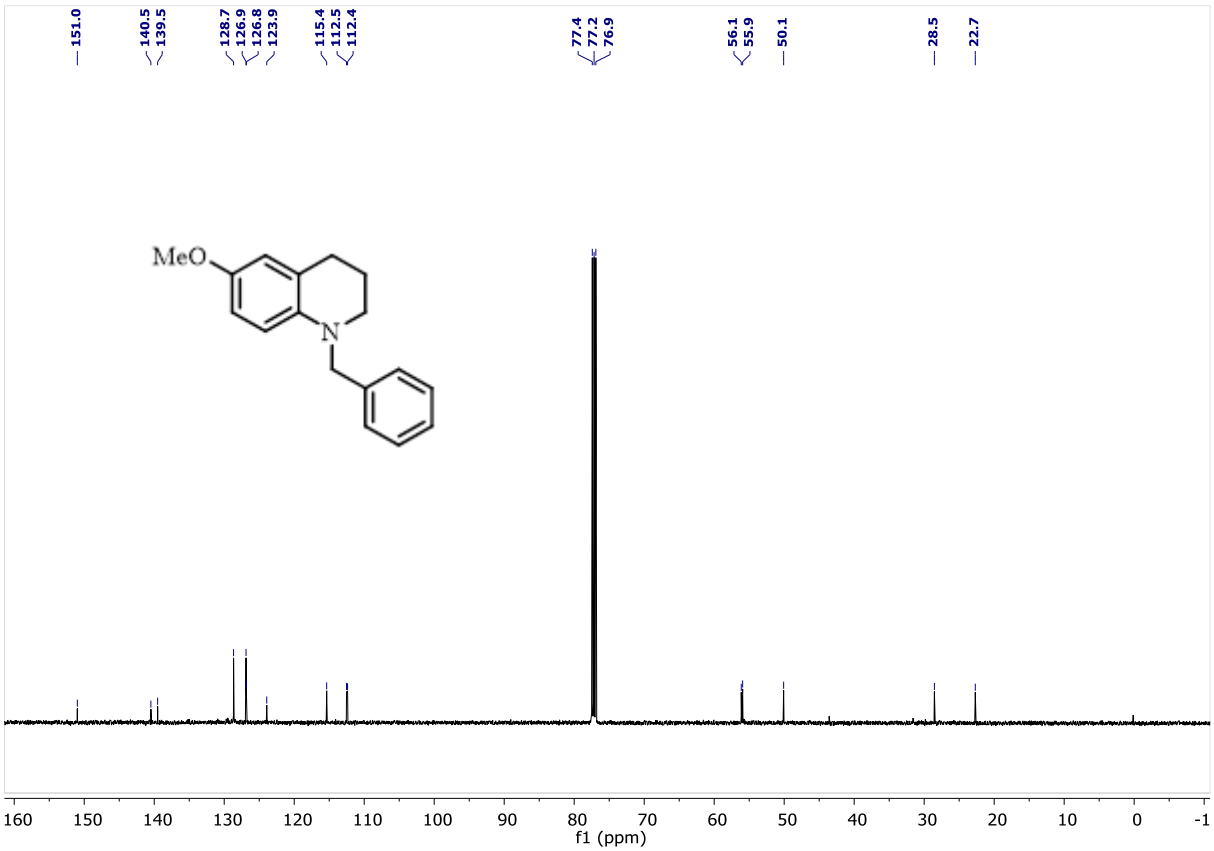


Figure S103: $^{13}C\{^{1}H\}$ NMR Spectrum of **4f** ($CDCl_3$, 126 MHz, 298 K)

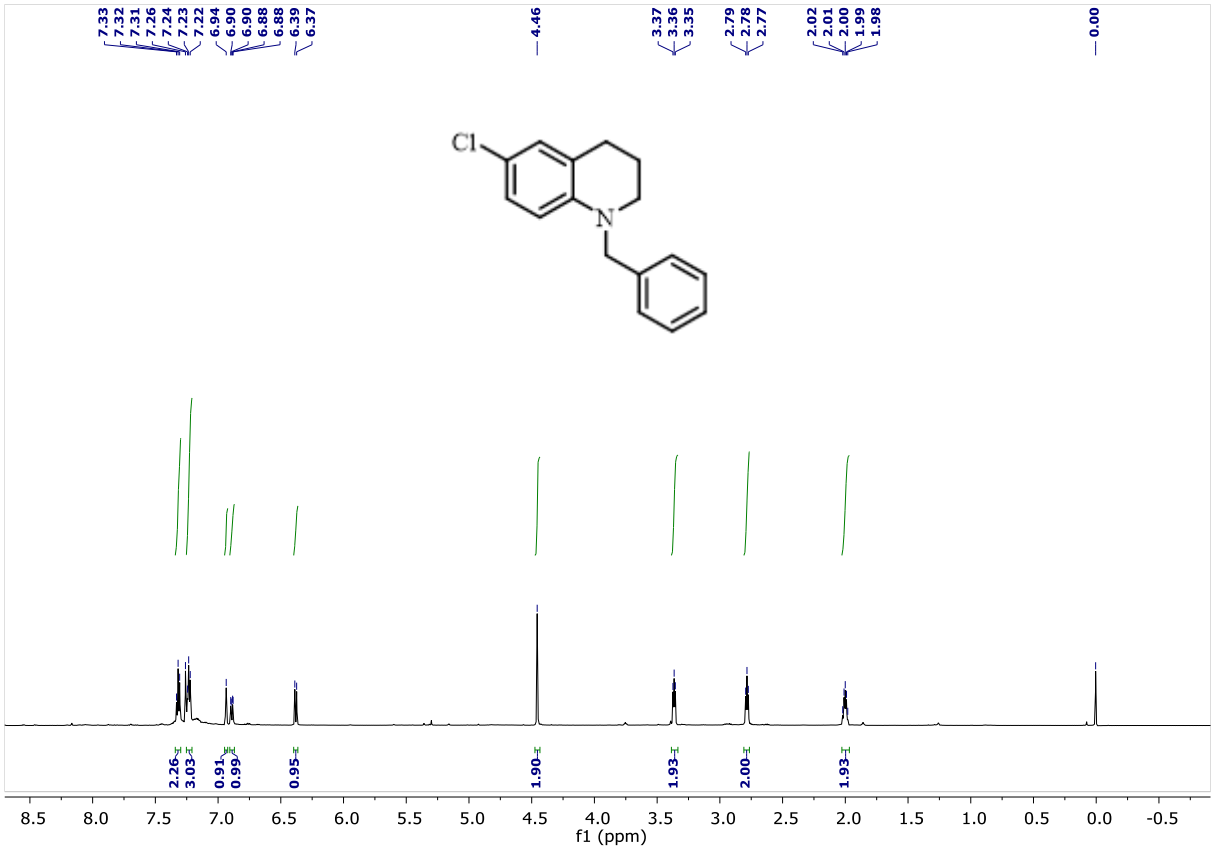


Figure S104: ^{1}H NMR Spectrum of **4g** ($CDCl_3$, 600 MHz, 298 K)

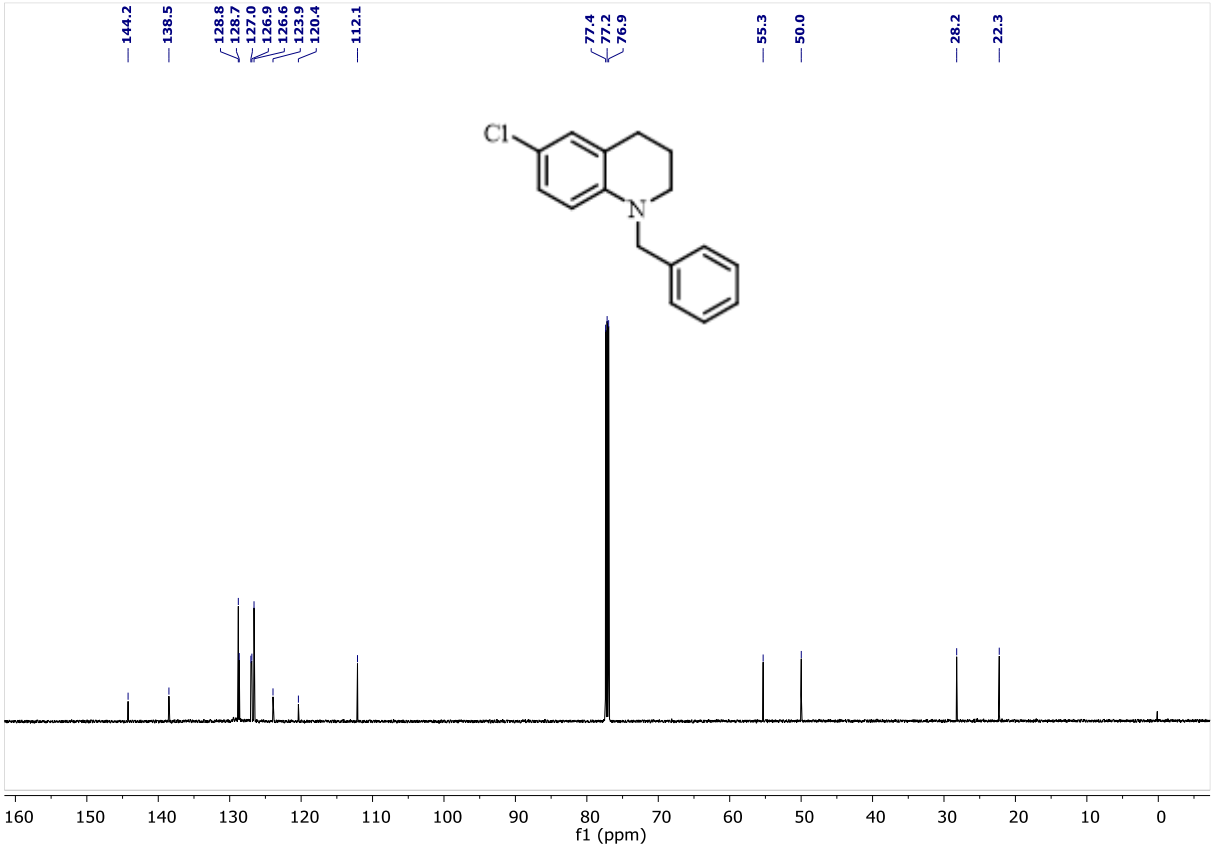


Figure S105: $^{13}C\{^{1}H\}$ NMR Spectrum of **4g** ($CDCl_3$, 151 MHz, 298 K)

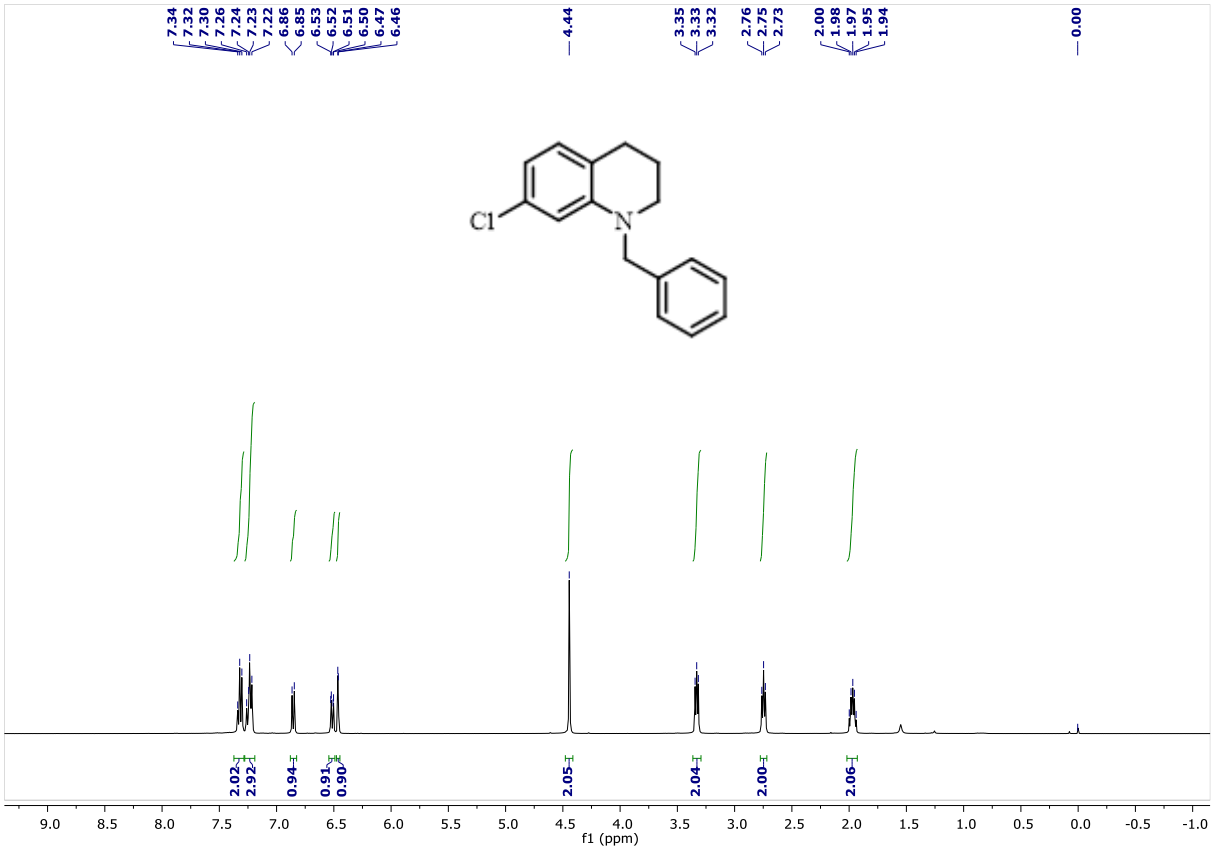


Figure S106: ^{1}H NMR Spectrum of **4h** ($CDCl_3$, 400 MHz, 298 K)

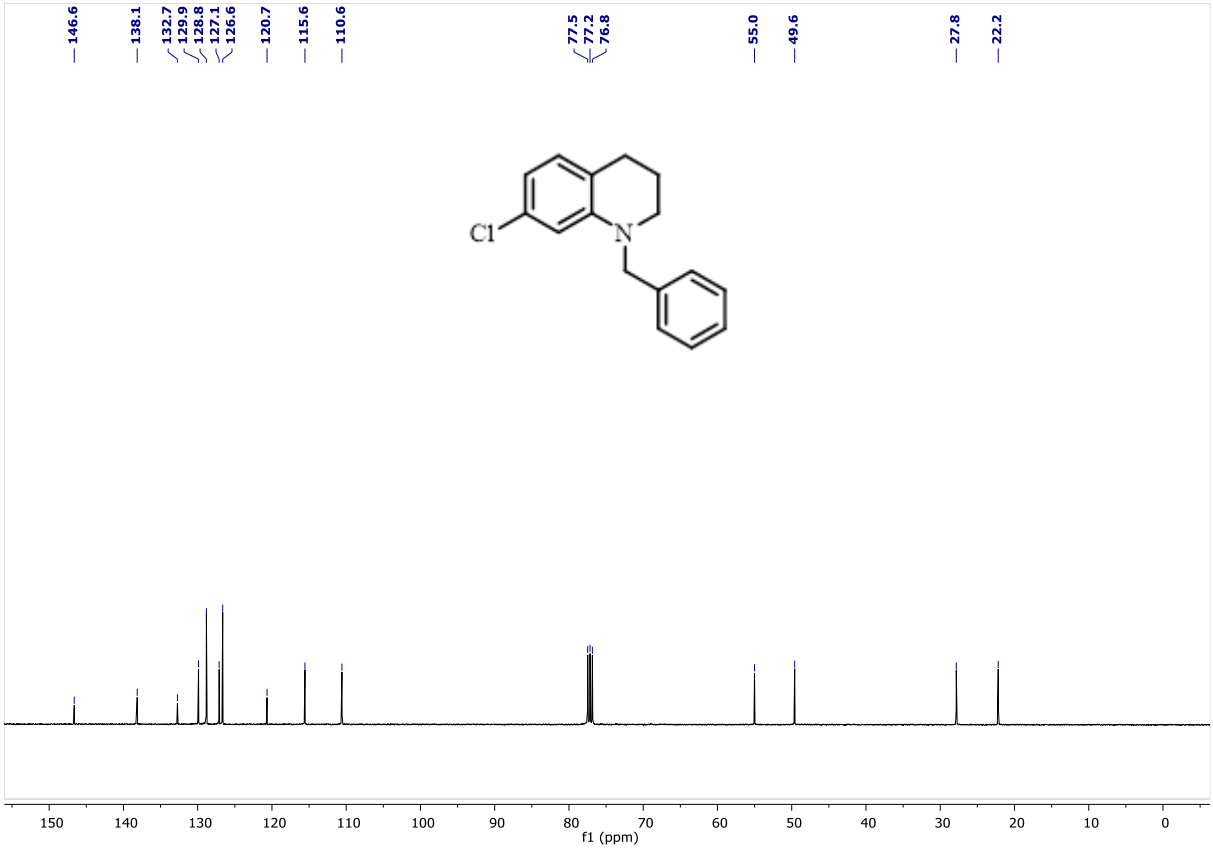


Figure S107: $^{13}C\{^{1}H\}$ NMR Spectrum of **4h** ($CDCl_3$, 101 MHz, 298 K)

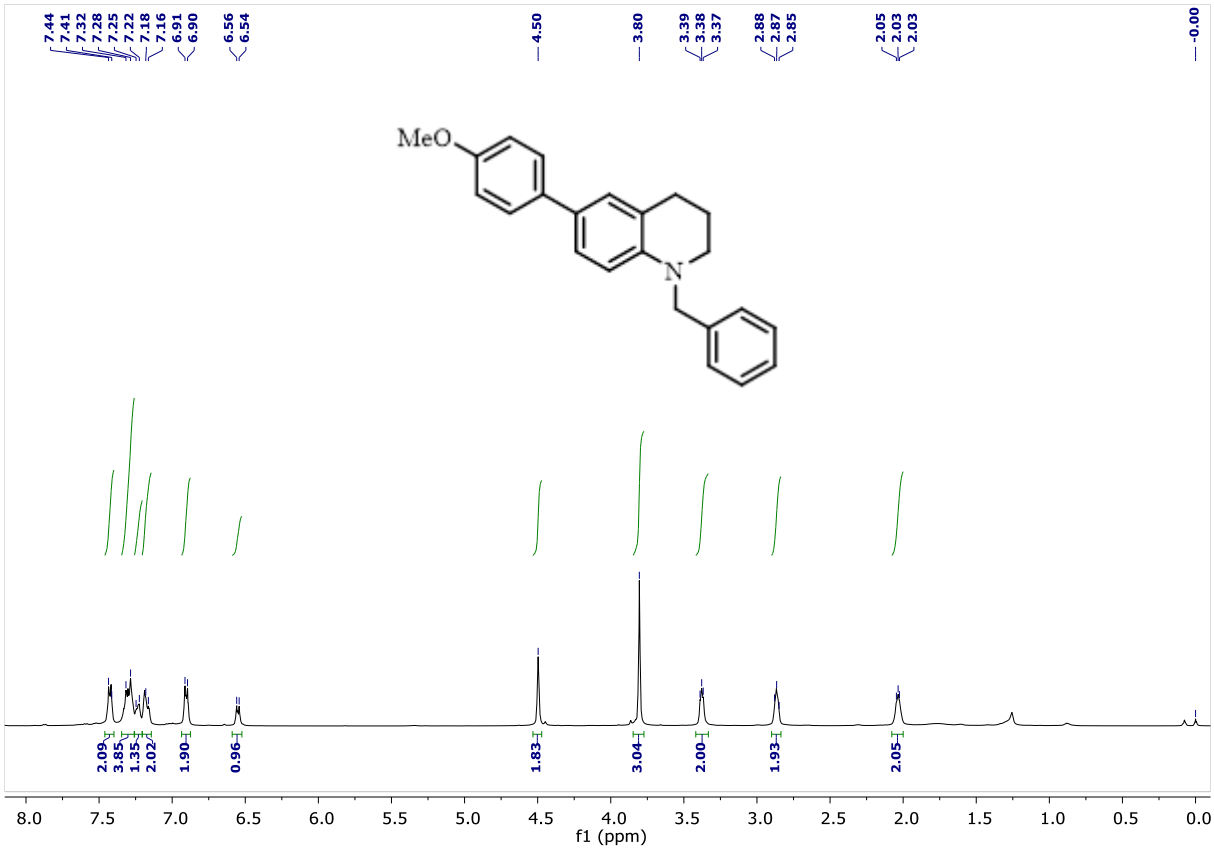


Figure S108: ^{1}H NMR Spectrum of **4i** ($CDCl_3$, 500 MHz, 298 K)

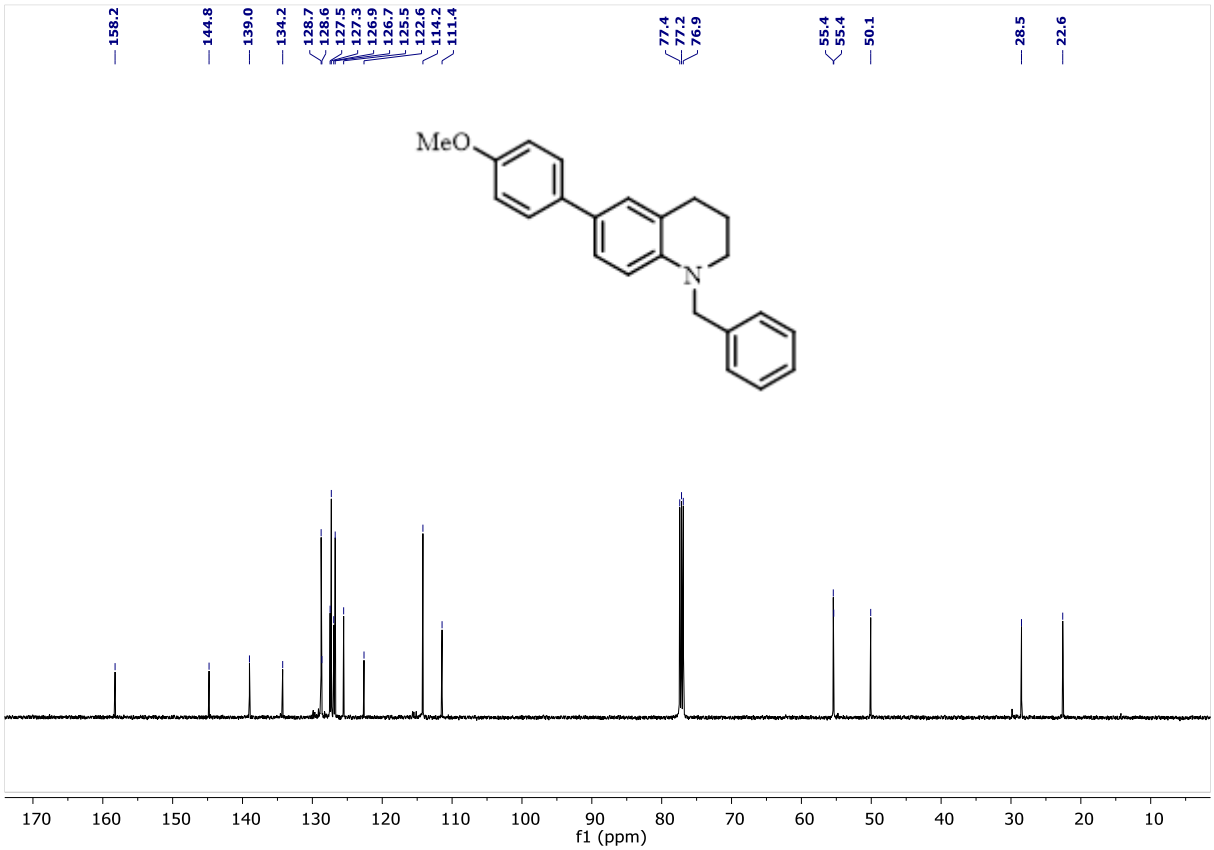


Figure S109: $^{13}C\{^{1}H\}$ NMR Spectrum of **4i** ($CDCl_3$, 126 MHz, 298 K)

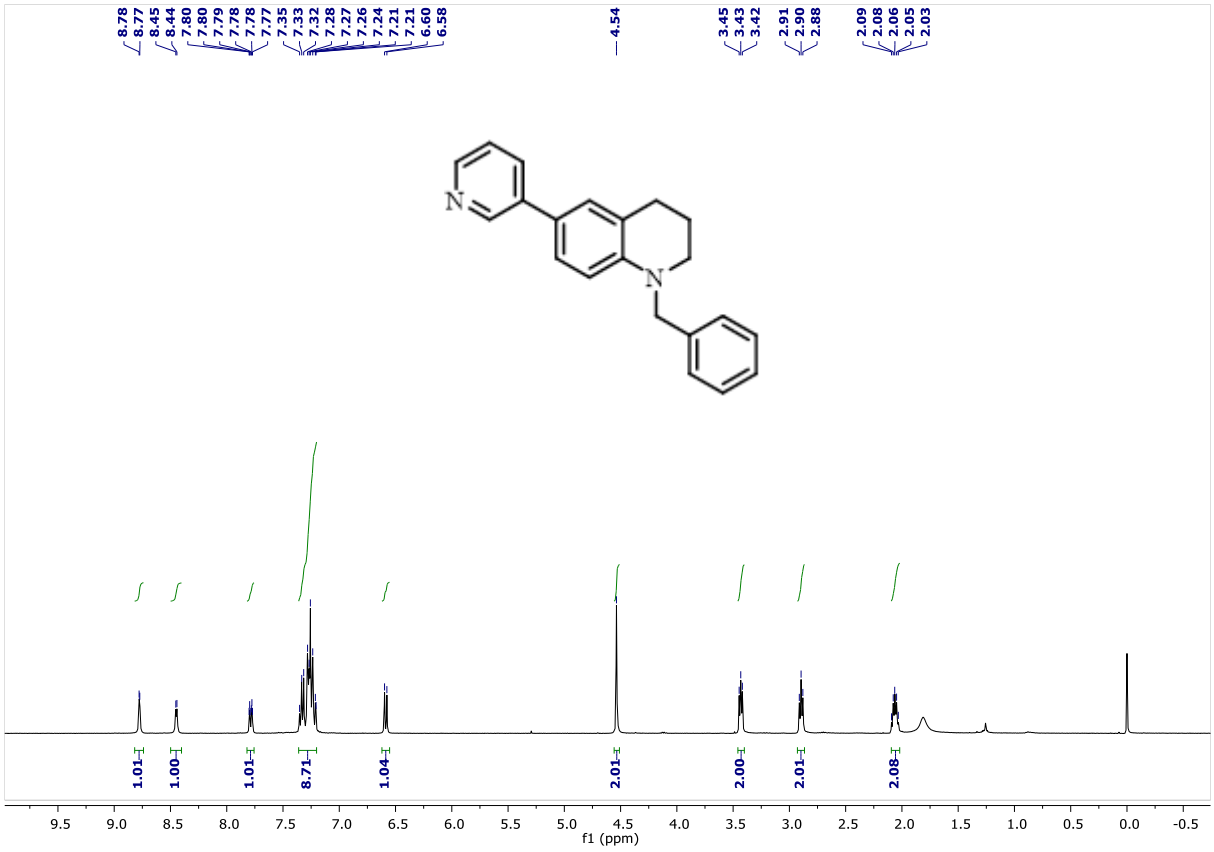


Figure S110: ^{1}H NMR Spectrum of **4j** ($CDCl_3$, 400 MHz, 298 K)

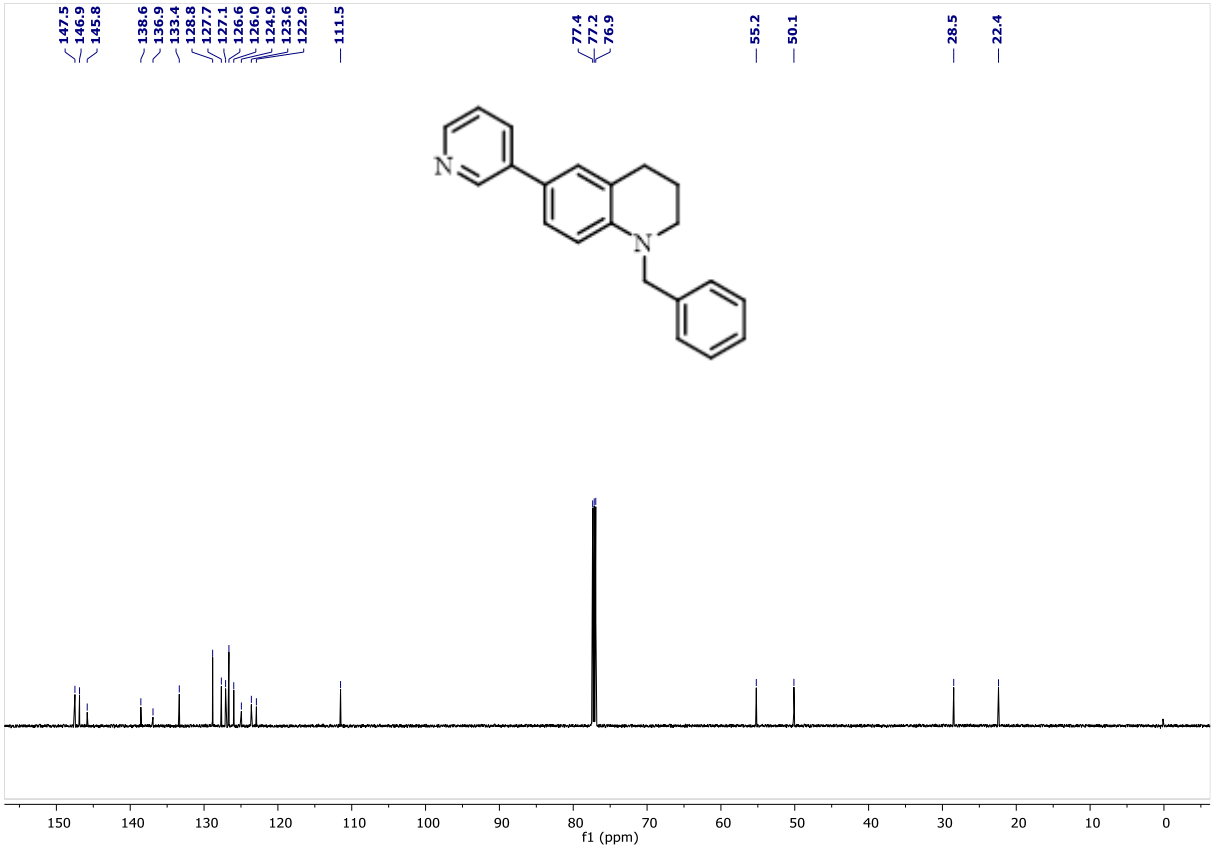


Figure S111: $^{13}C\{^{1}H\}$ NMR Spectrum of **4j** ($CDCl_3$, 151 MHz, 298 K)

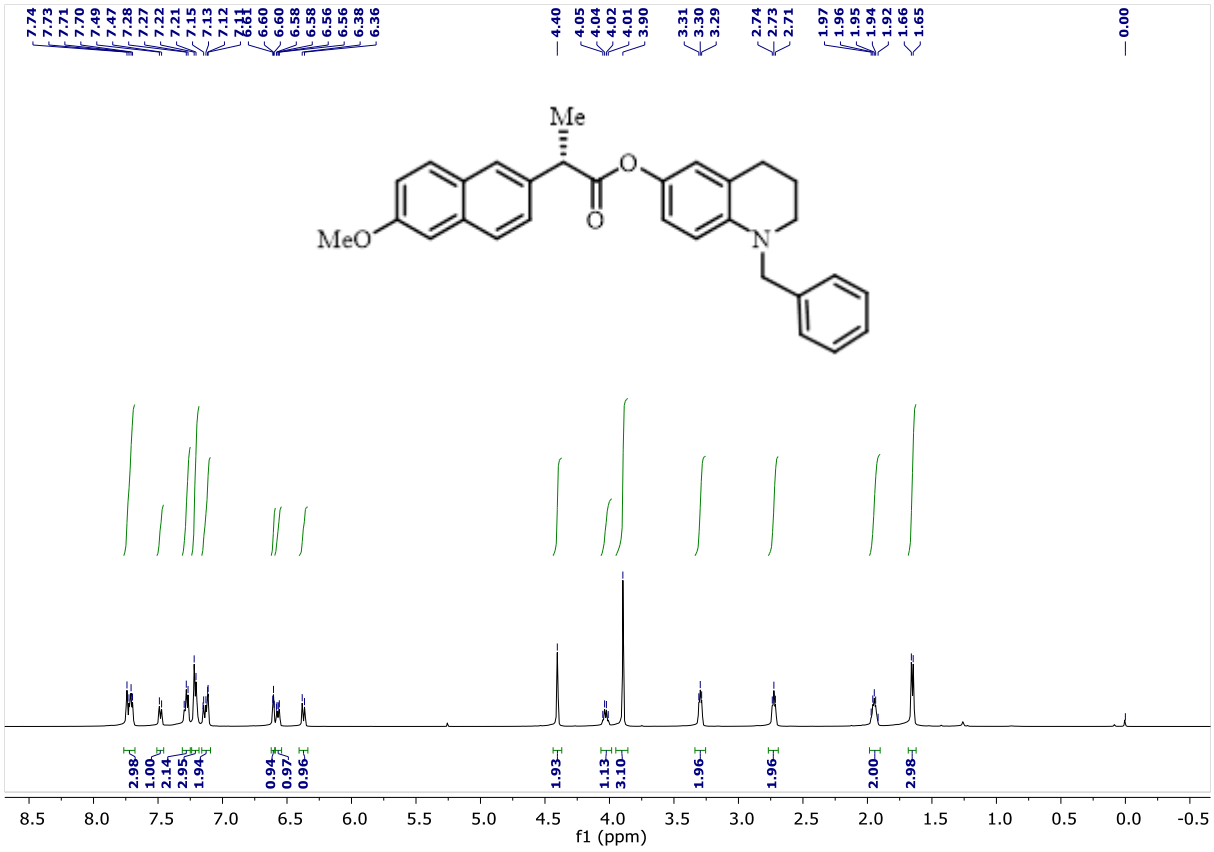


Figure S112: ^{1}H NMR Spectrum of **4k** ($CDCl_3$, 500 MHz, 298 K)

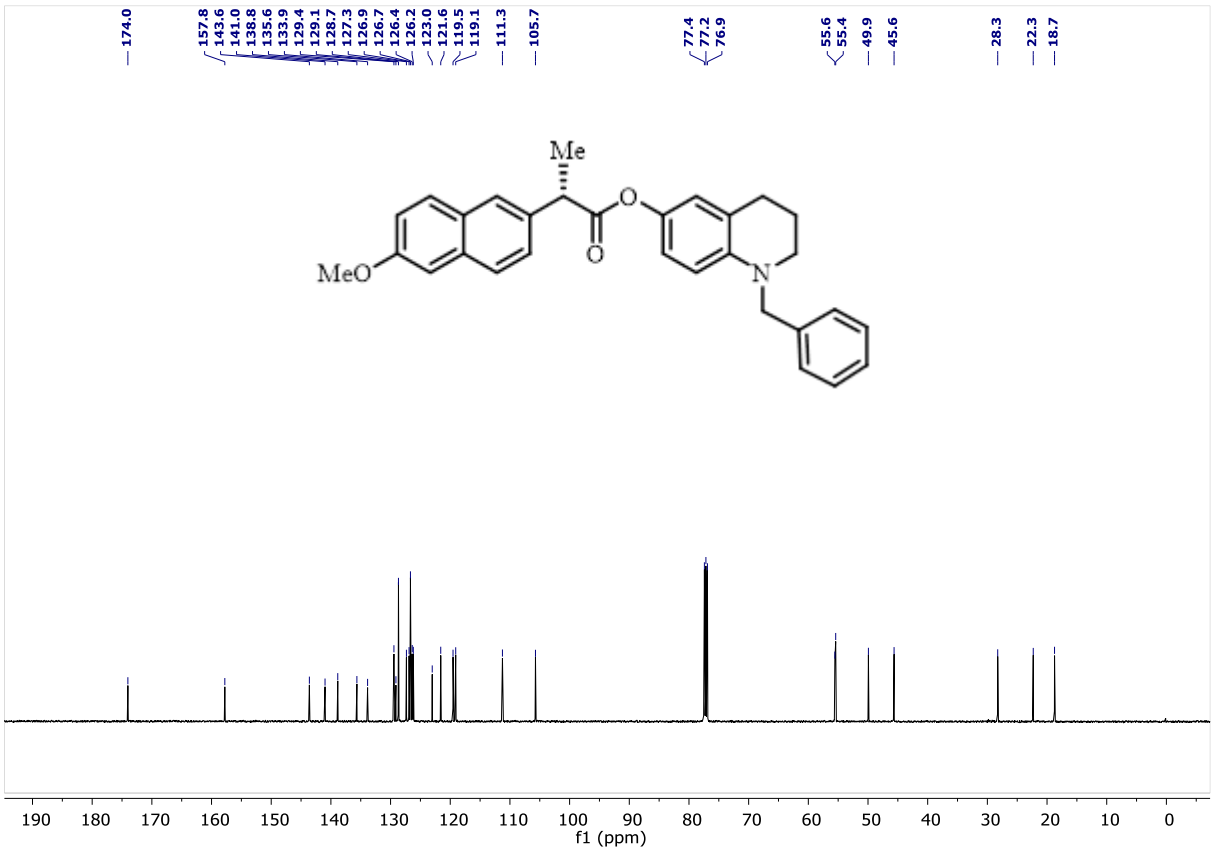


Figure S113: $^{13}C\{^{1}H\}$ NMR Spectrum of **4k** ($CDCl_3$, 126 MHz, 298 K)

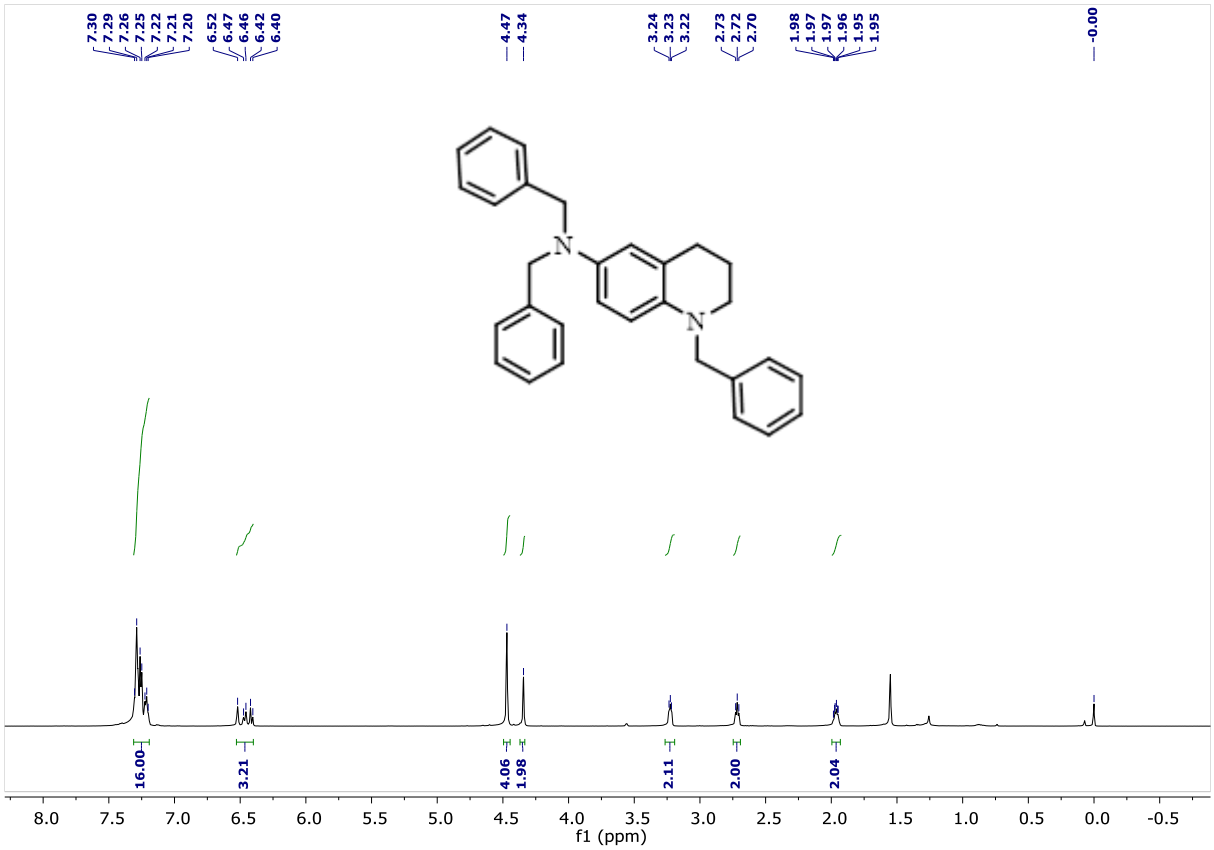


Figure S114: ^{1}H NMR Spectrum of **4l** ($CDCl_3$, 500 MHz, 298 K)

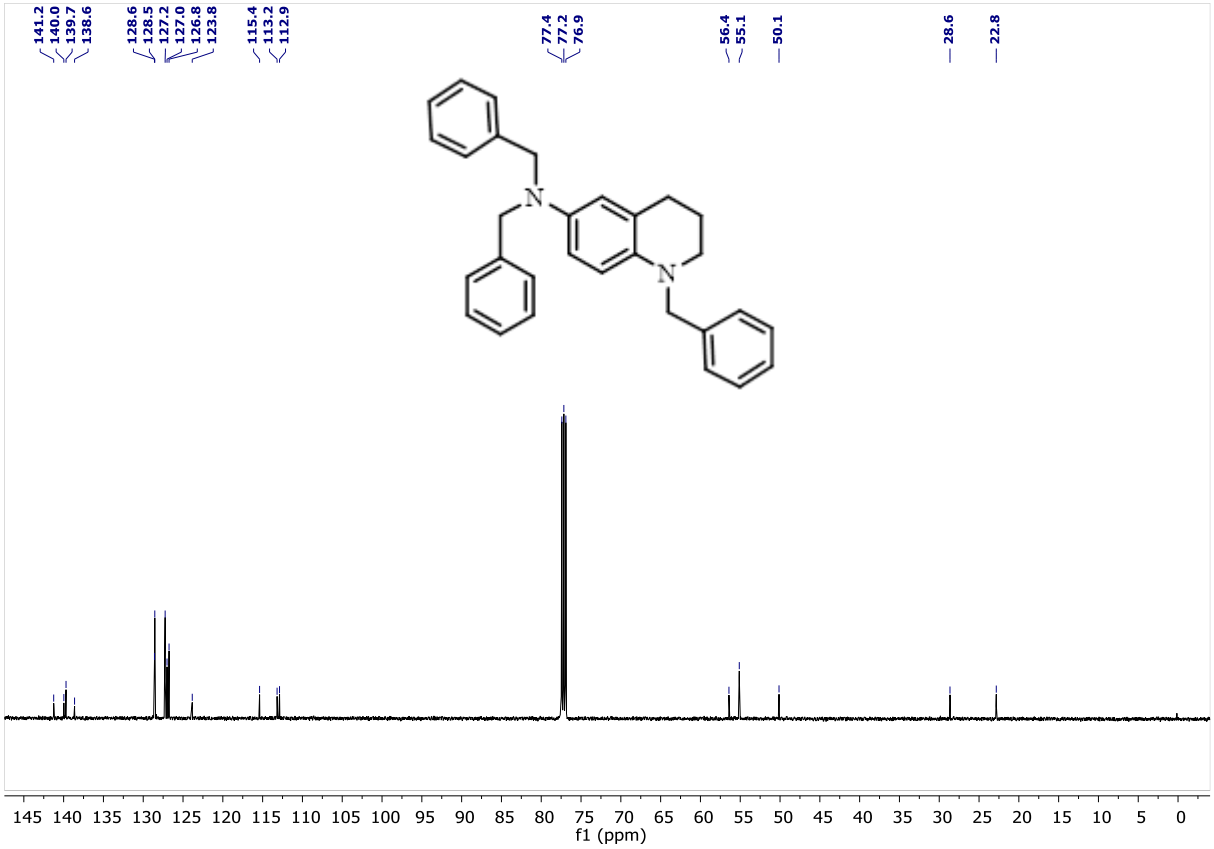


Figure S115: $^{13}C\{^{1}H\}$ NMR Spectrum of **4l** ($CDCl_3$, 126 MHz, 298 K)

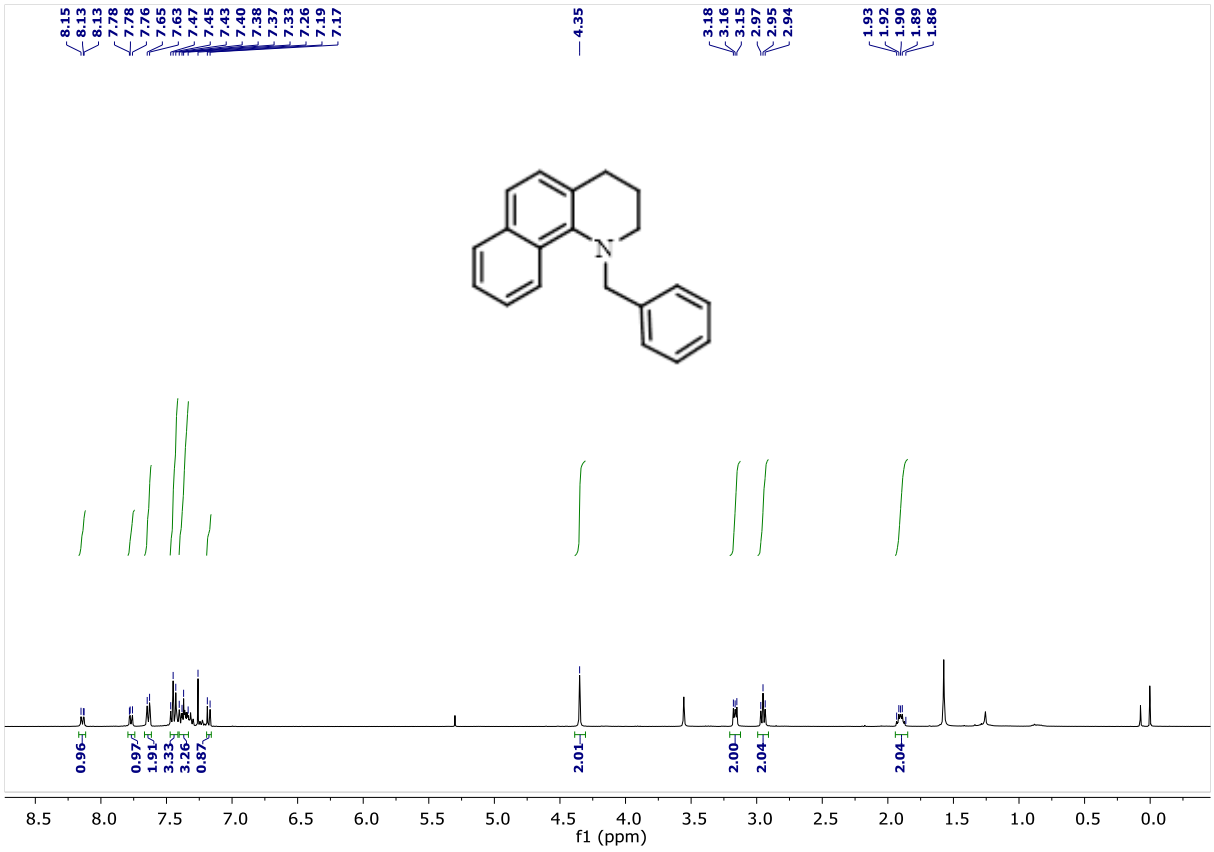


Figure S116: ^{1}H NMR Spectrum of **4m** ($CDCl_3$, 400 MHz, 298 K)

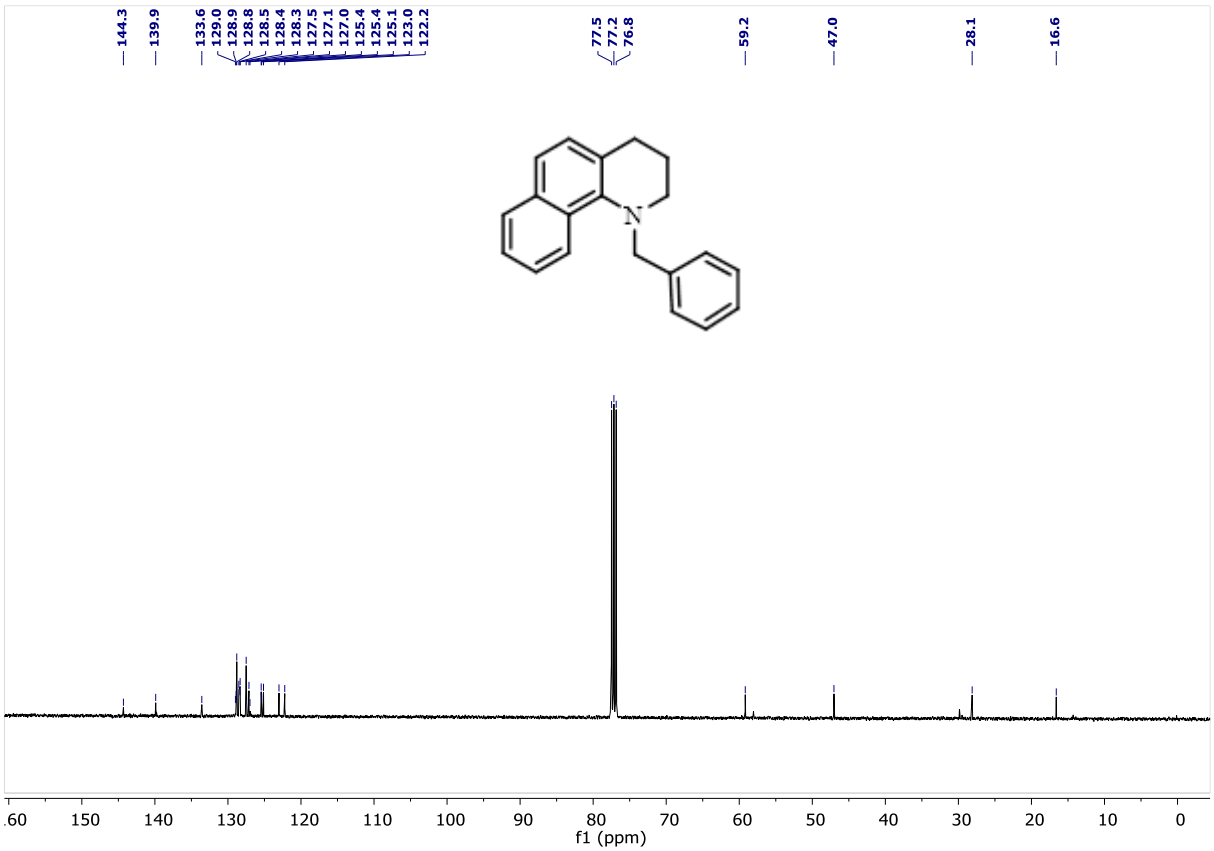


Figure S117: $^{13}C\{^{1}H\}$ NMR Spectrum of **4m** ($CDCl_3$, 101 MHz, 298 K)

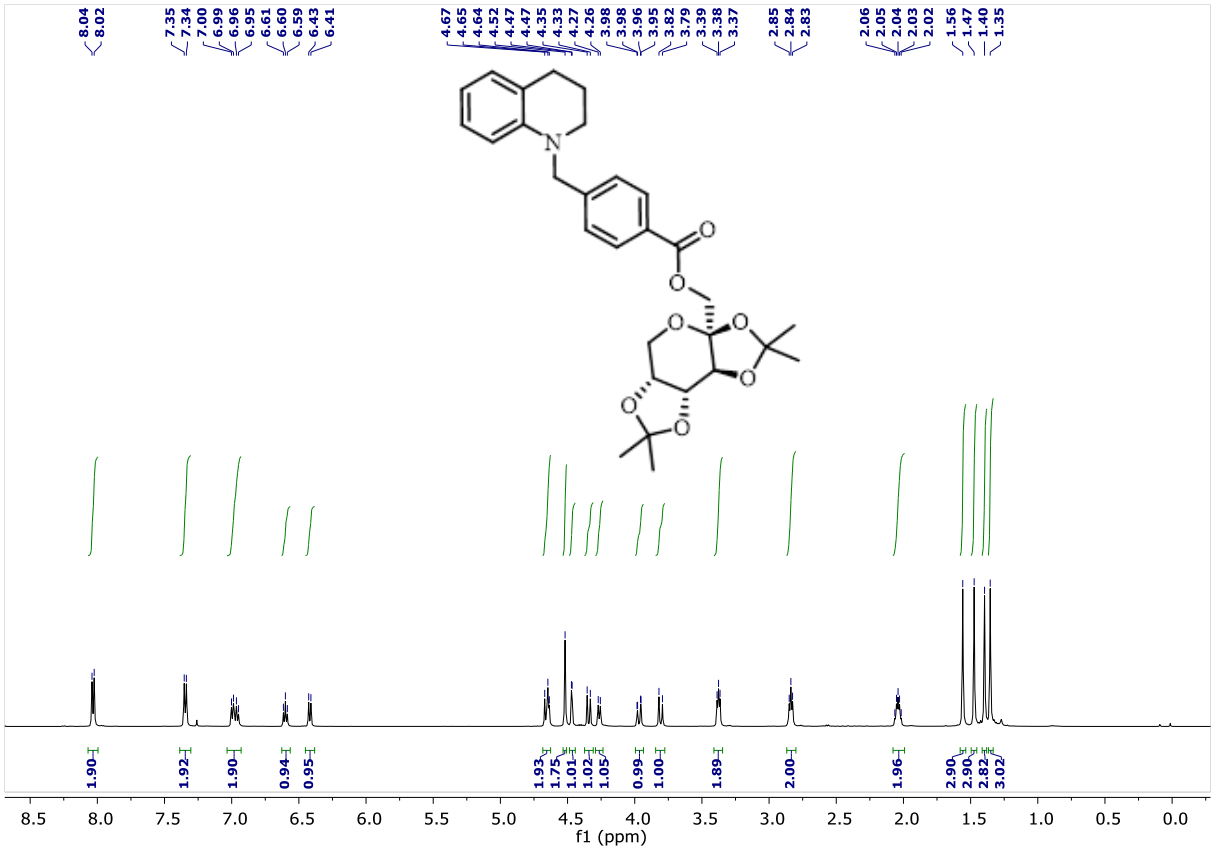


Figure S118: ^{1}H NMR Spectrum of **6a** ($CDCl_3$, 500 MHz, 298 K)

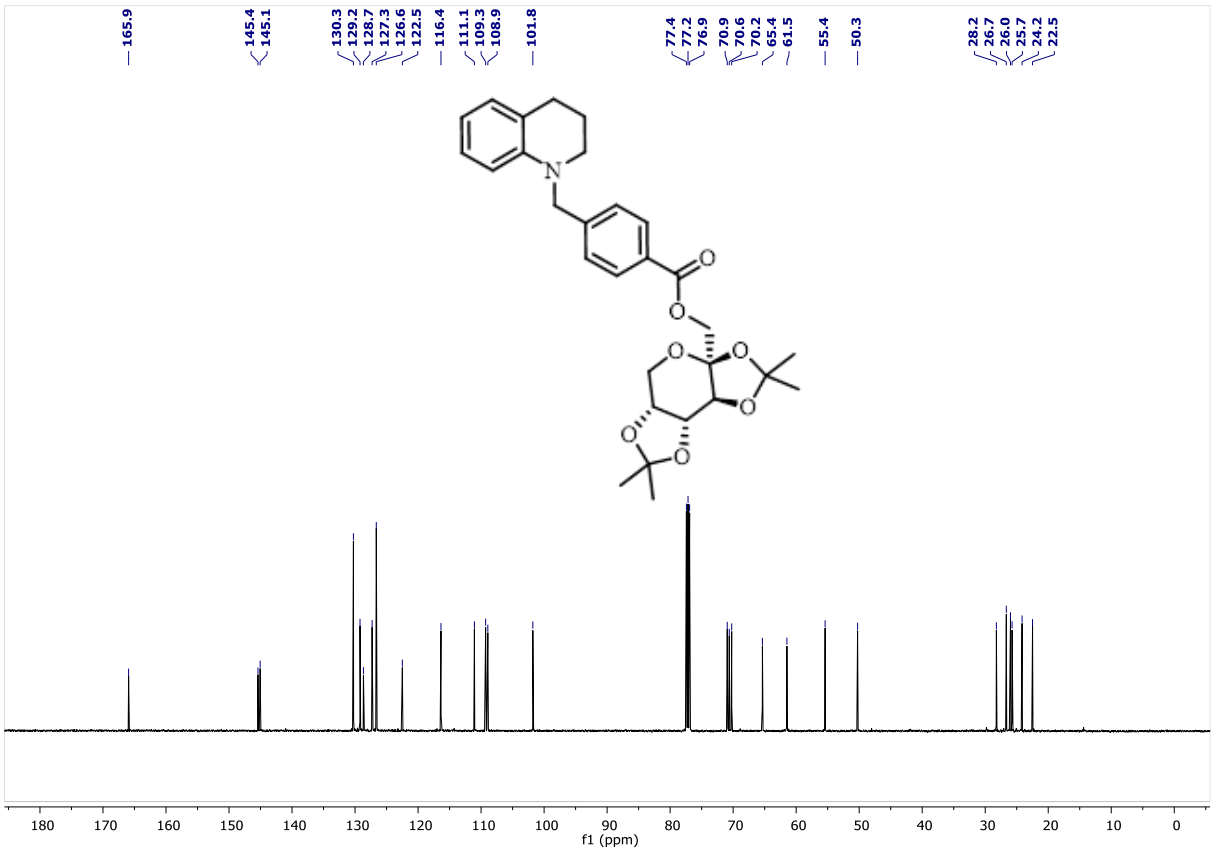


Figure S119: $^{13}C\{^{1}H\}$ NMR Spectrum of **6a** ($CDCl_3$, 126 MHz, 298 K)

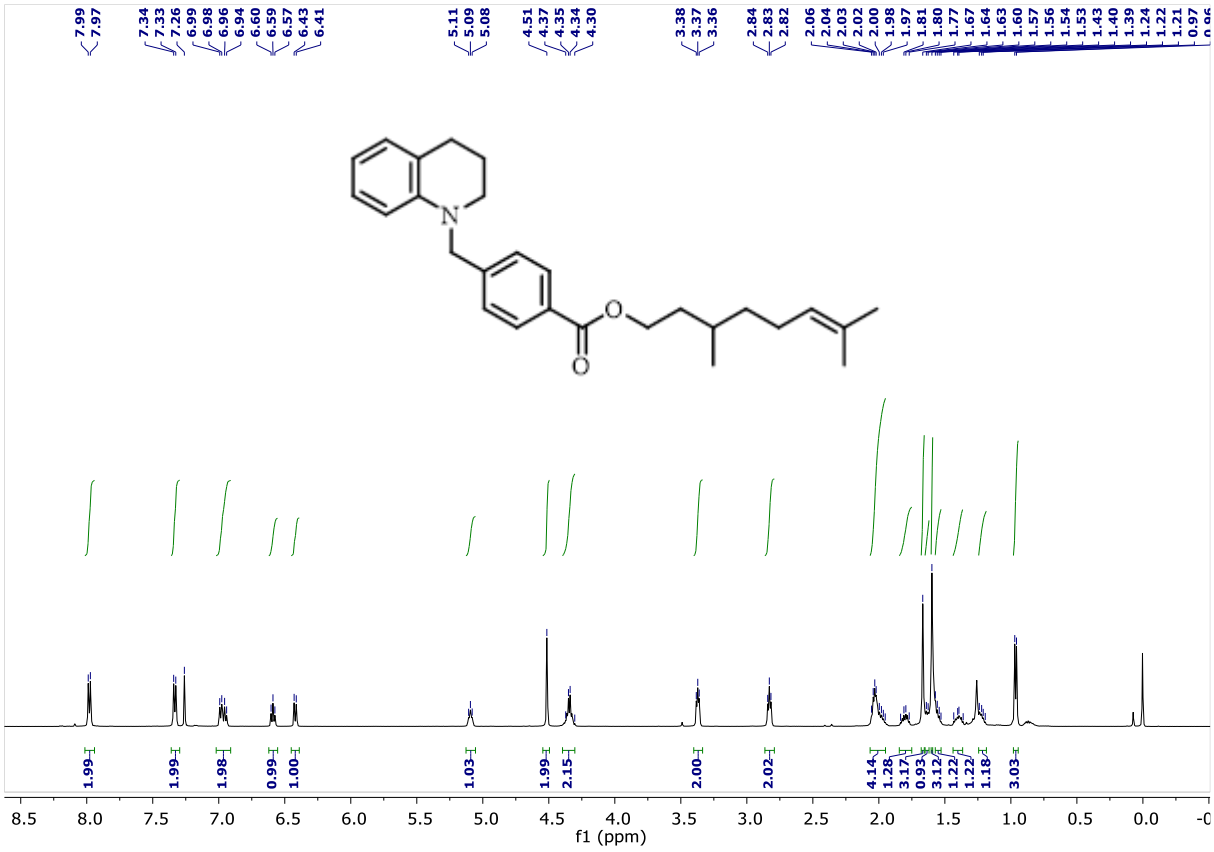


Figure S120: ^{1}H NMR Spectrum of **6b** ($CDCl_3$, 500 MHz, 298 K)

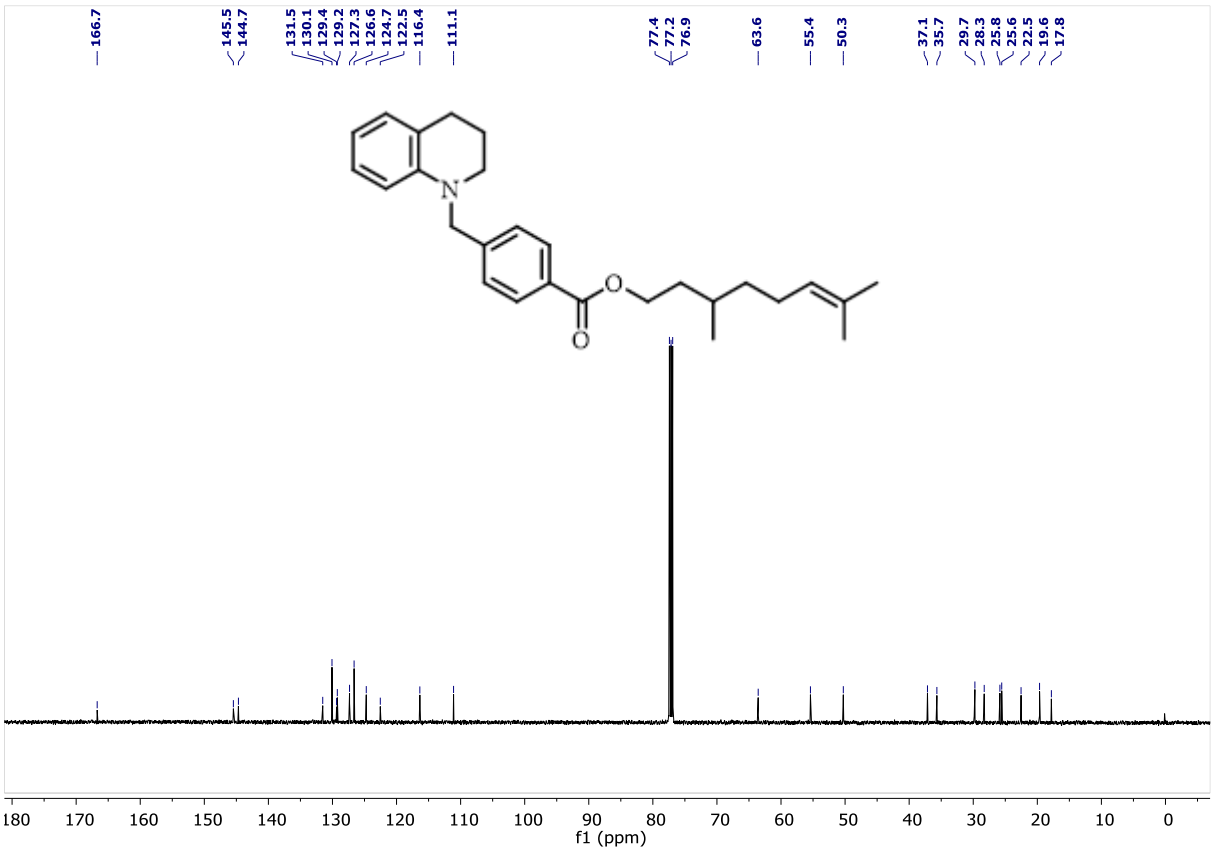


Figure S121: $^{13}C\{^{1}H\}$ NMR Spectrum of **6b** ($CDCl_3$, 126 MHz, 298 K)

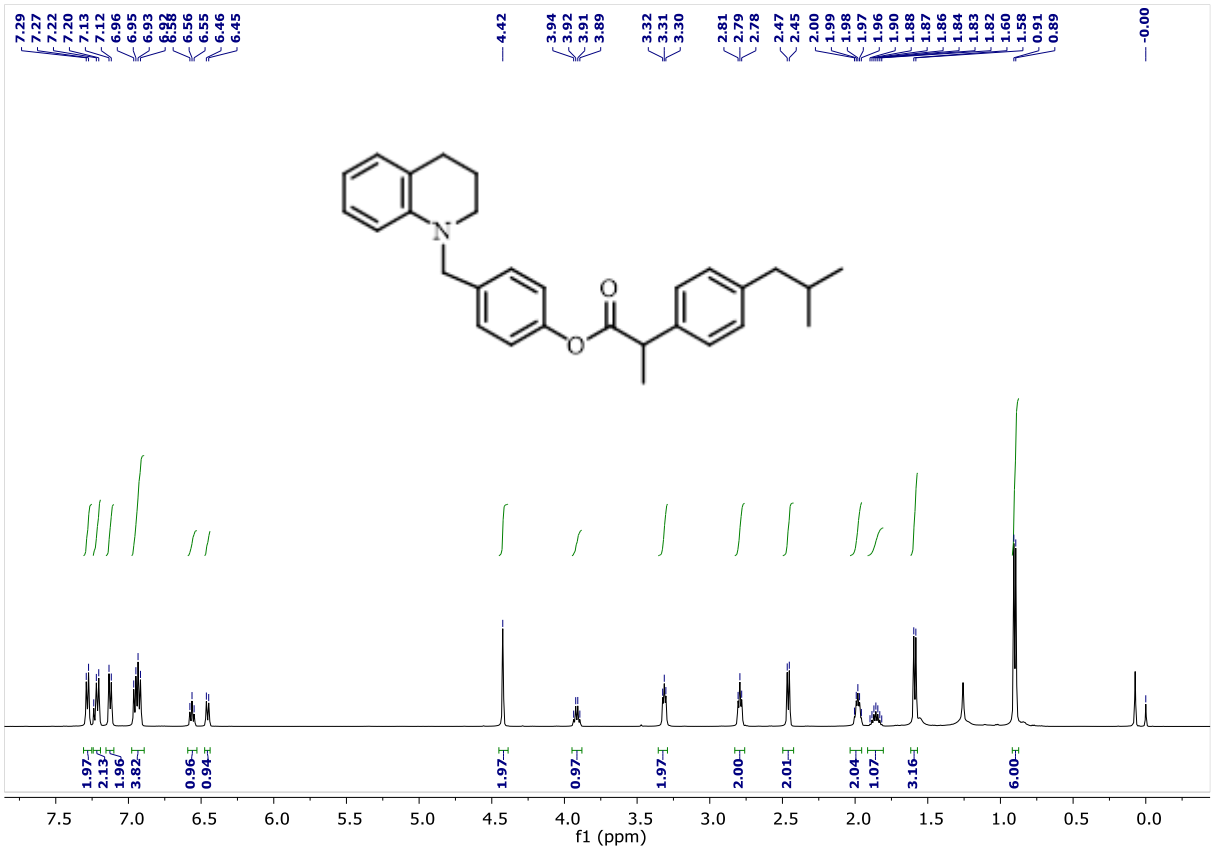


Figure S122: ^{1}H NMR Spectrum of **6c** ($CDCl_3$, 500 MHz, 298 K)

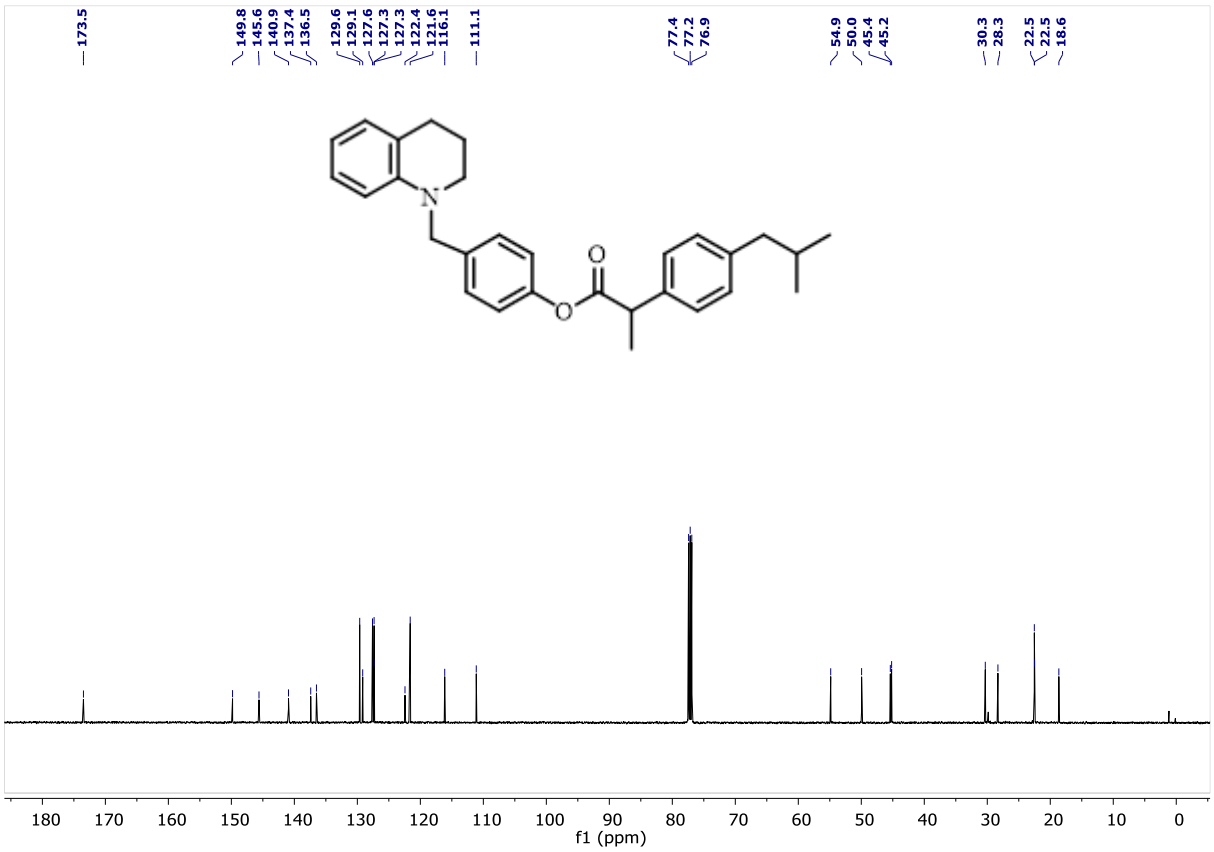


Figure S123: $^{13}C\{^{1}H\}$ NMR Spectrum of **6c** ($CDCl_3$, 126 MHz, 298 K)

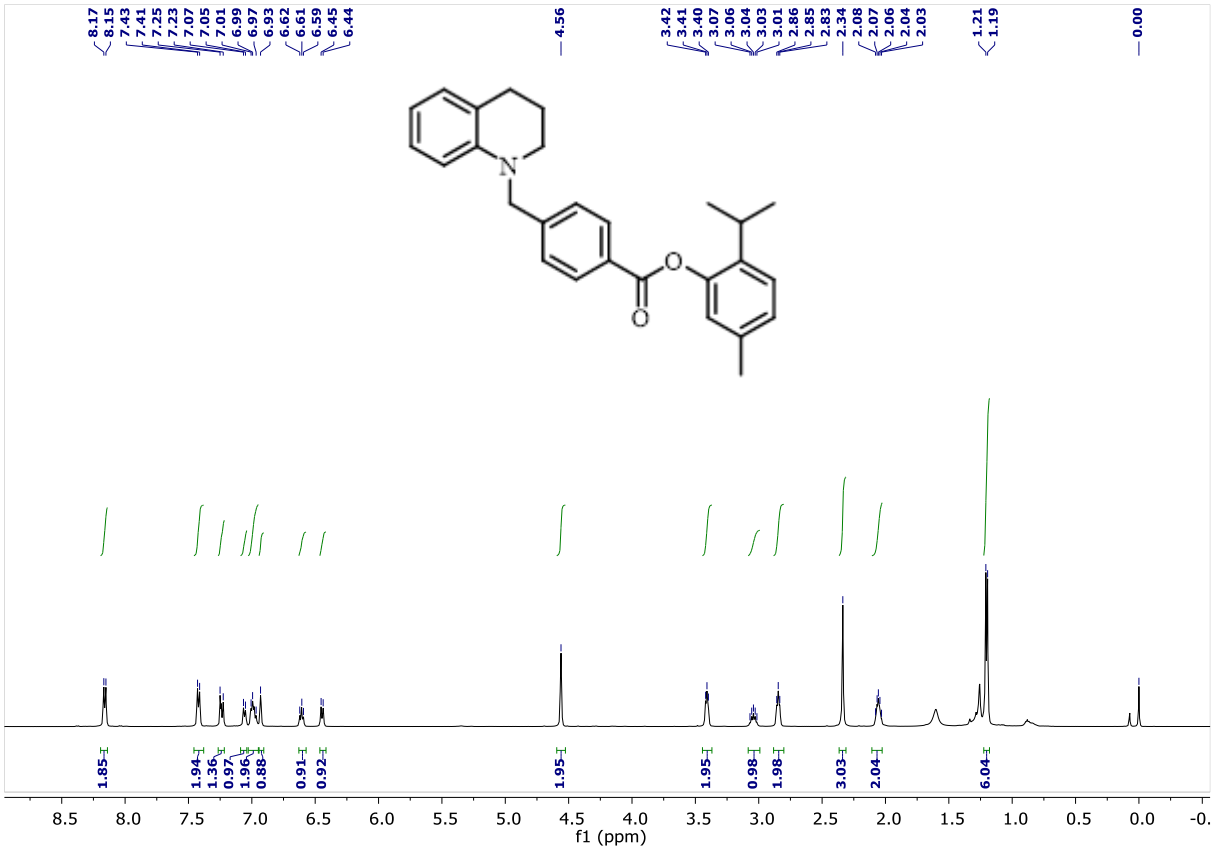


Figure S124: ^{1}H NMR Spectrum of **6d** ($CDCl_3$, 500 MHz, 298 K)

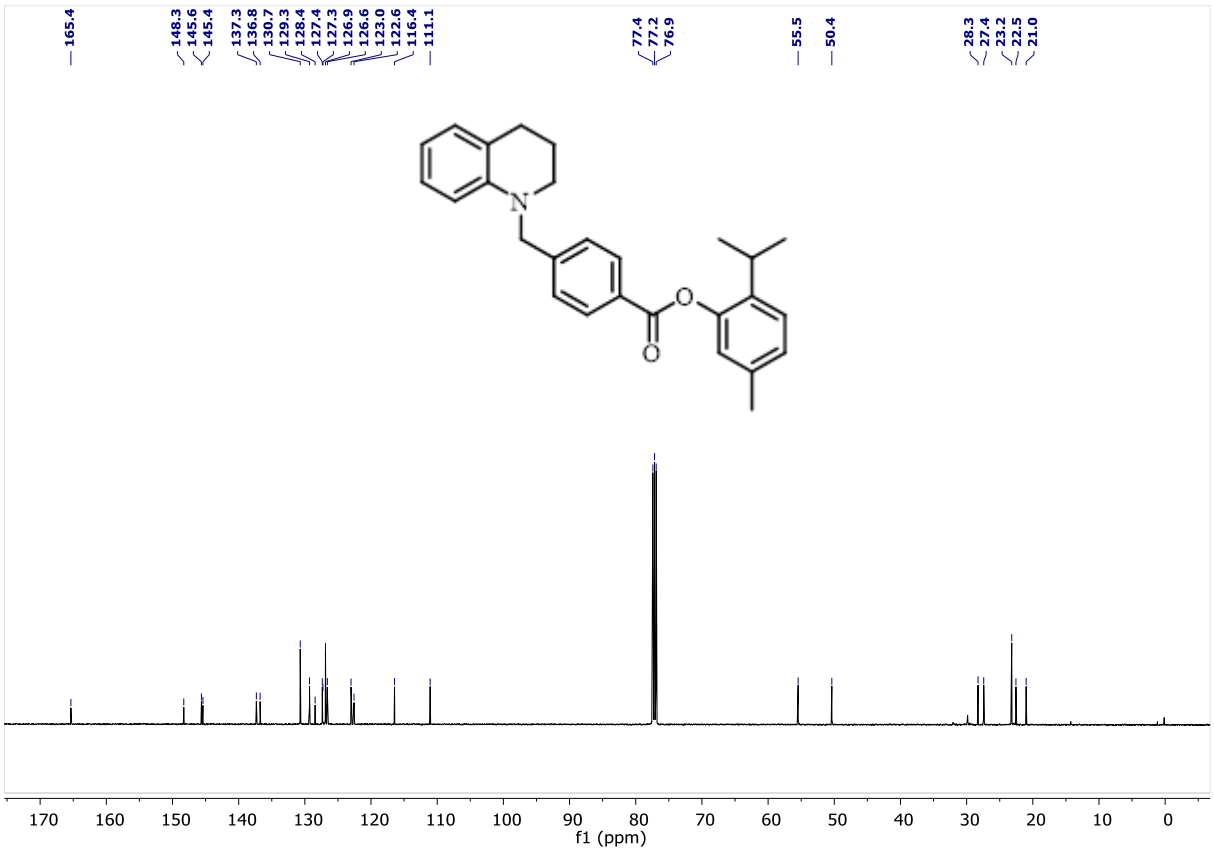


Figure S125: $^{13}C\{^{1}H\}$ NMR Spectrum of **6d** ($CDCl_3$, 126 MHz, 298 K)

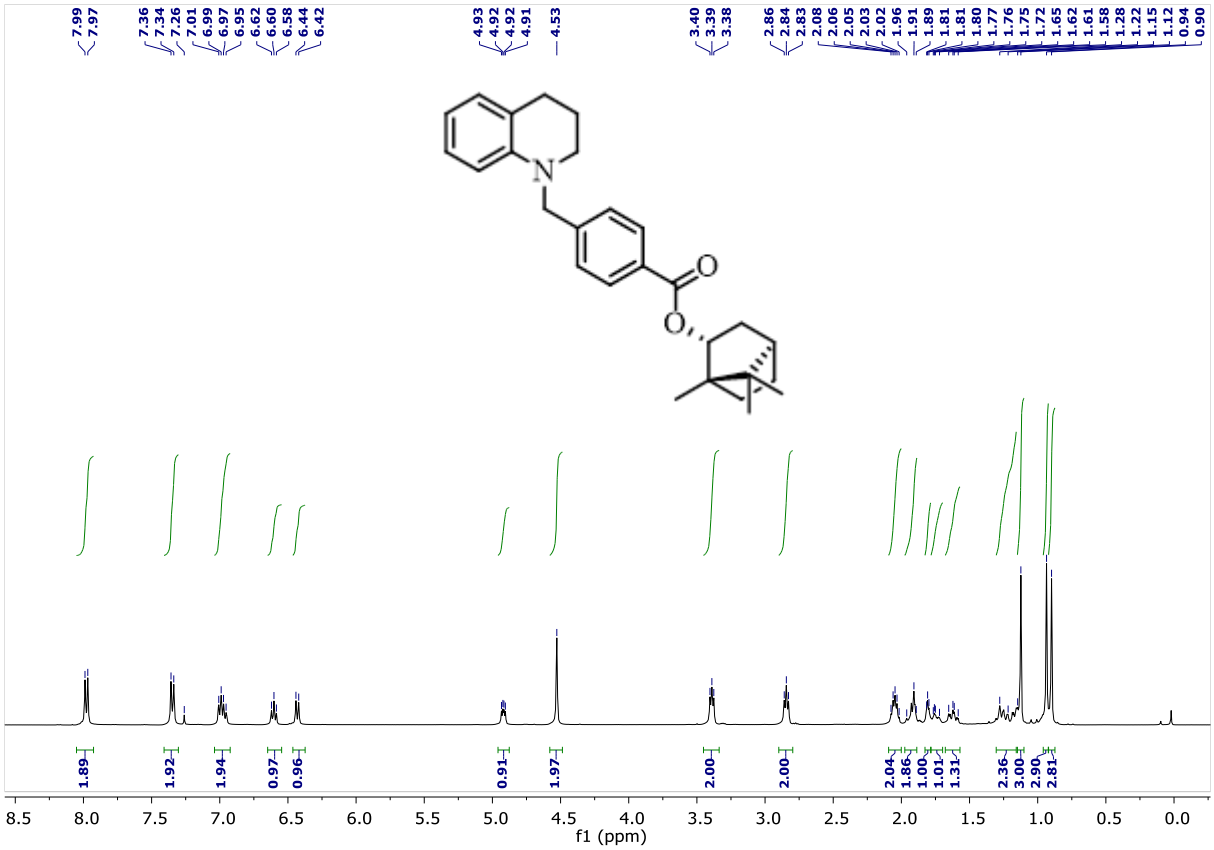


Figure S126: ^{1}H NMR Spectrum of **6e** ($CDCl_3$, 400 MHz, 298 K)

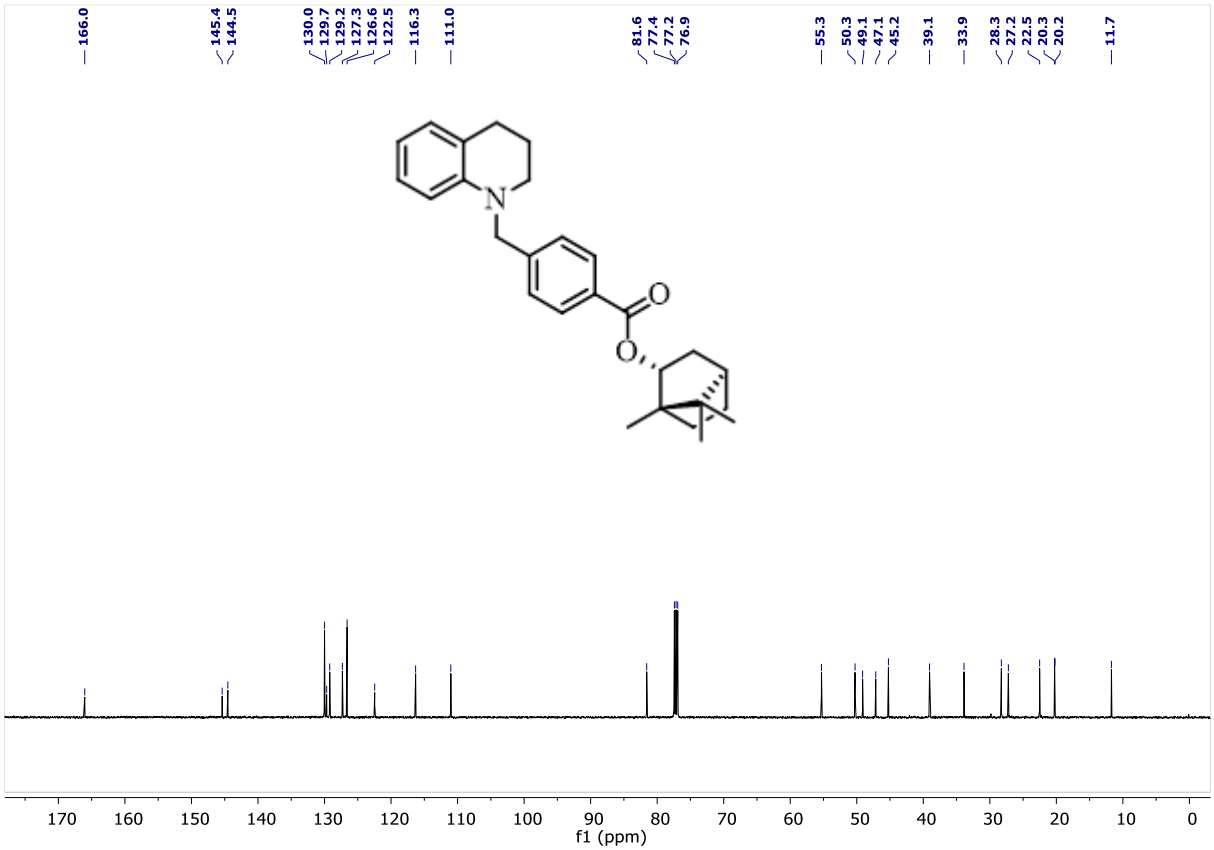


Figure S127: $^{13}C\{^{1}H\}$ NMR Spectrum of **6e** ($CDCl_3$, 126 MHz, 298 K)

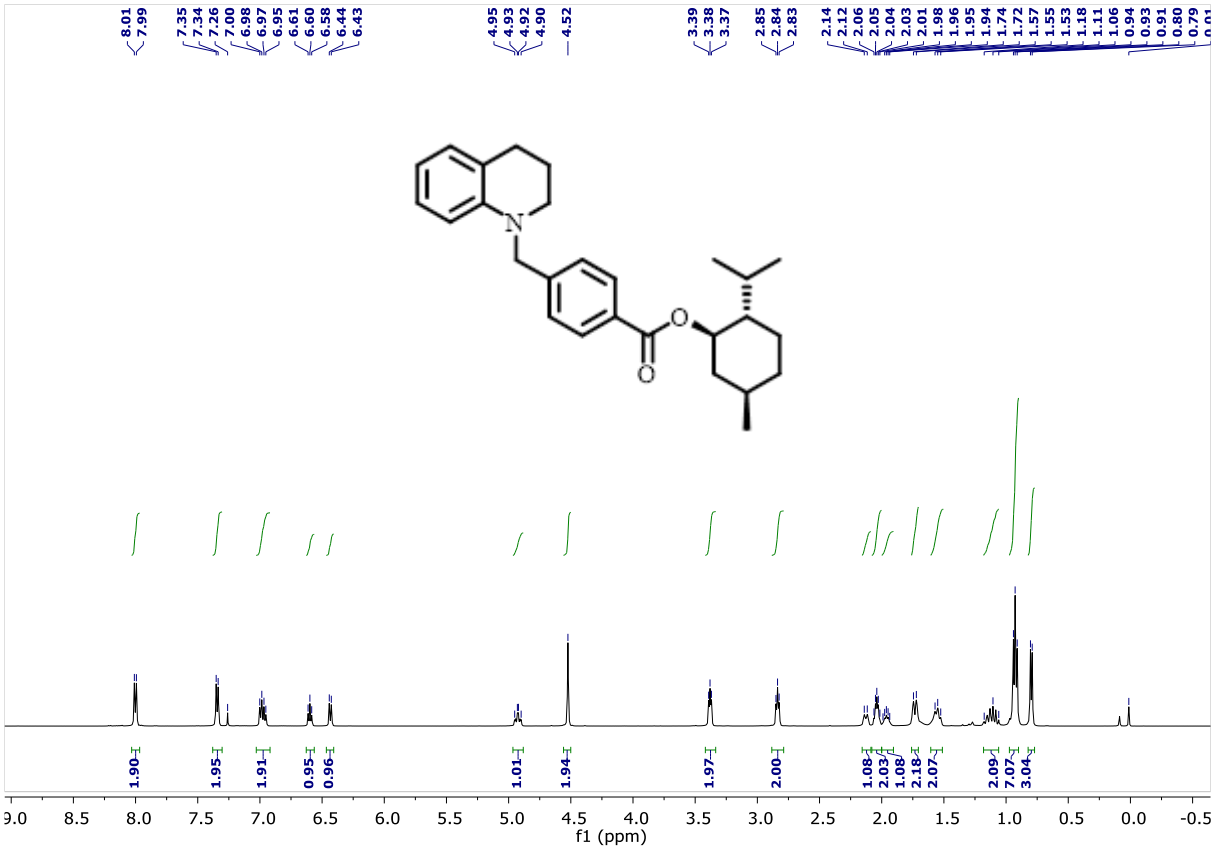


Figure S128: ^{1}H NMR Spectrum of **6f** ($CDCl_3$, 500 MHz, 298 K)

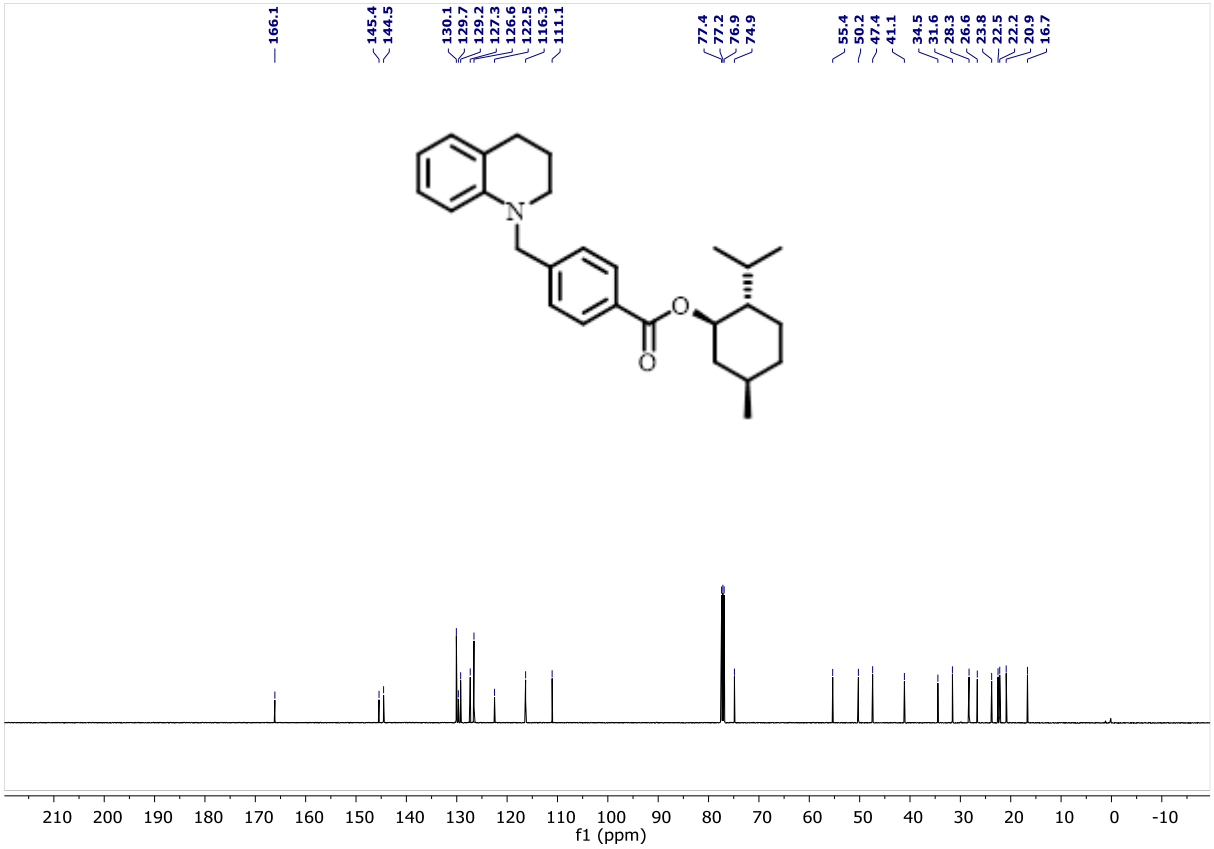


Figure S129: $^{13}C\{^{1}H\}$ NMR Spectrum of **6f** ($CDCl_3$, 126 MHz, 298 K)

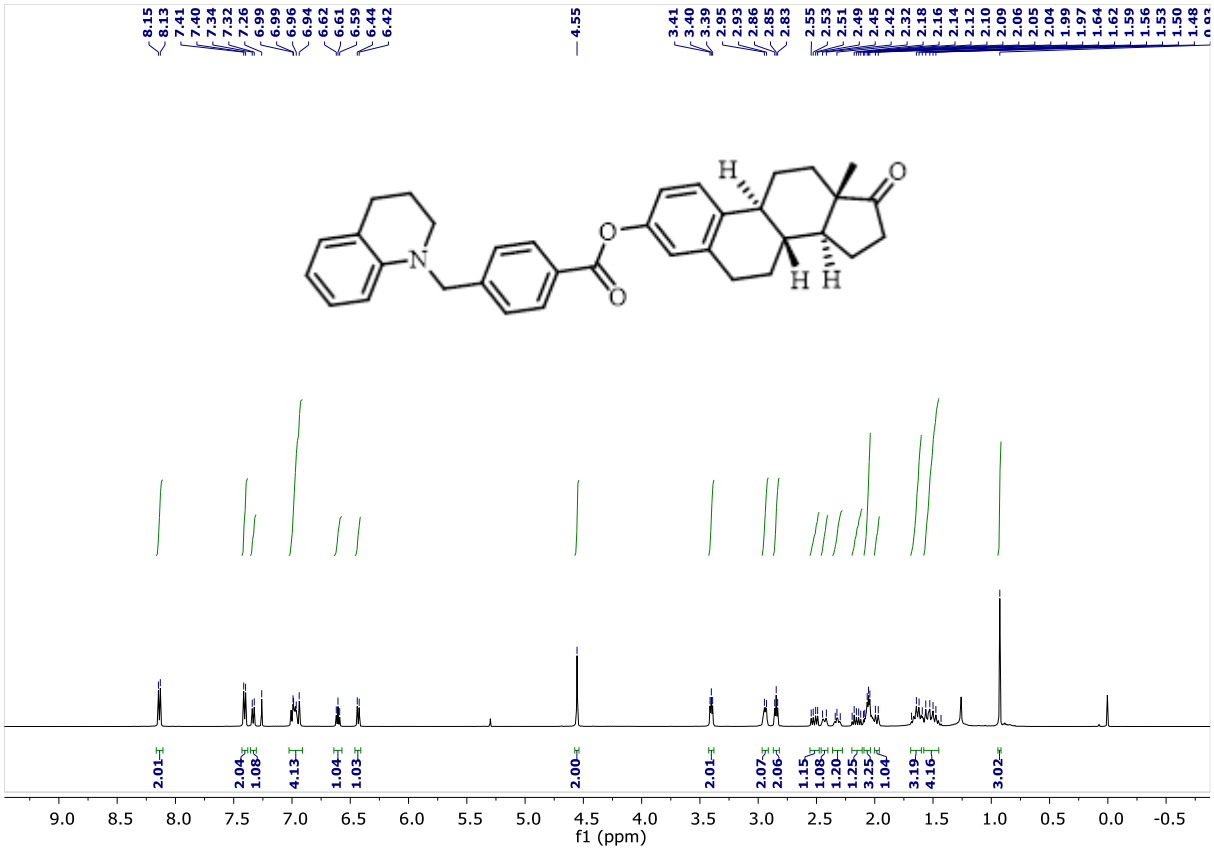


Figure S130: ^{1}H NMR Spectrum of **6g** ($CDCl_3$, 500 MHz, 298 K)

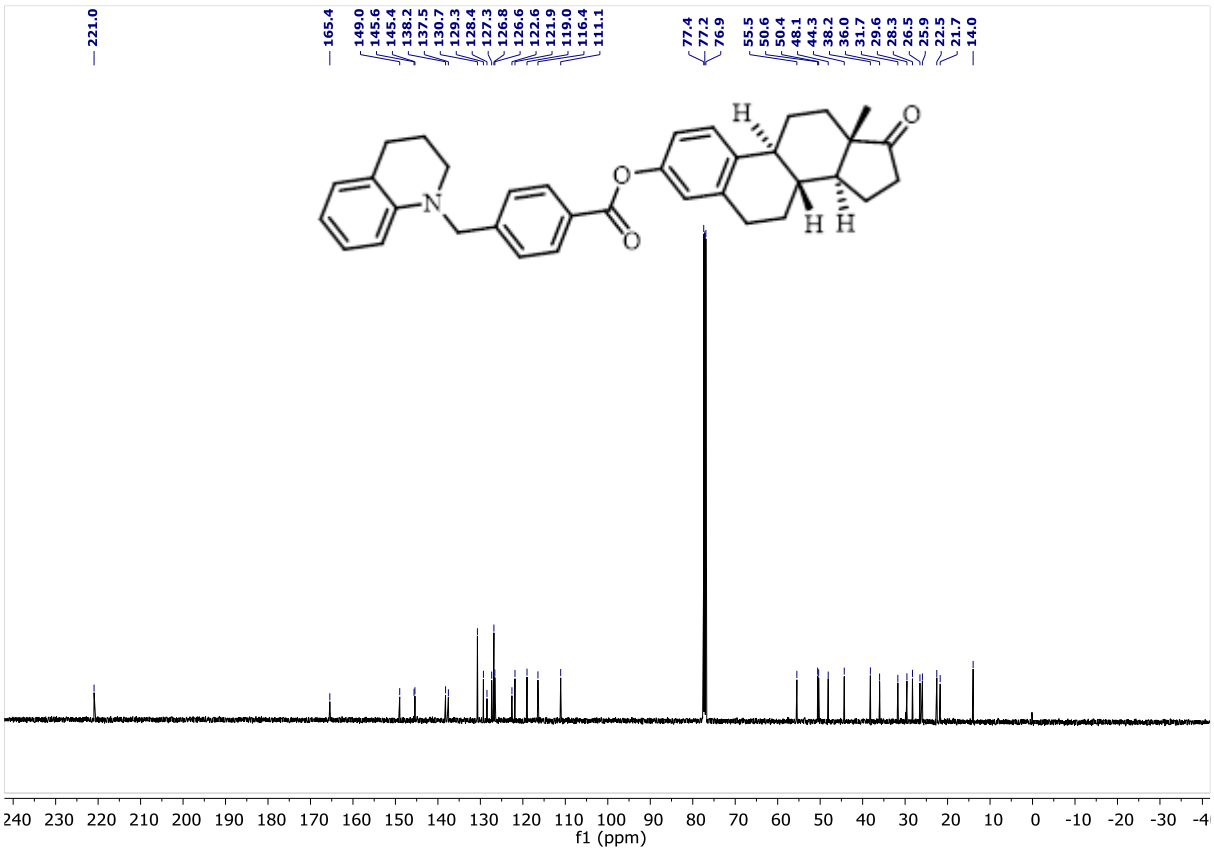


Figure S131: $^{13}C\{^{1}H\}$ NMR Spectrum of **6g** ($CDCl_3$, 126 MHz, 298 K)

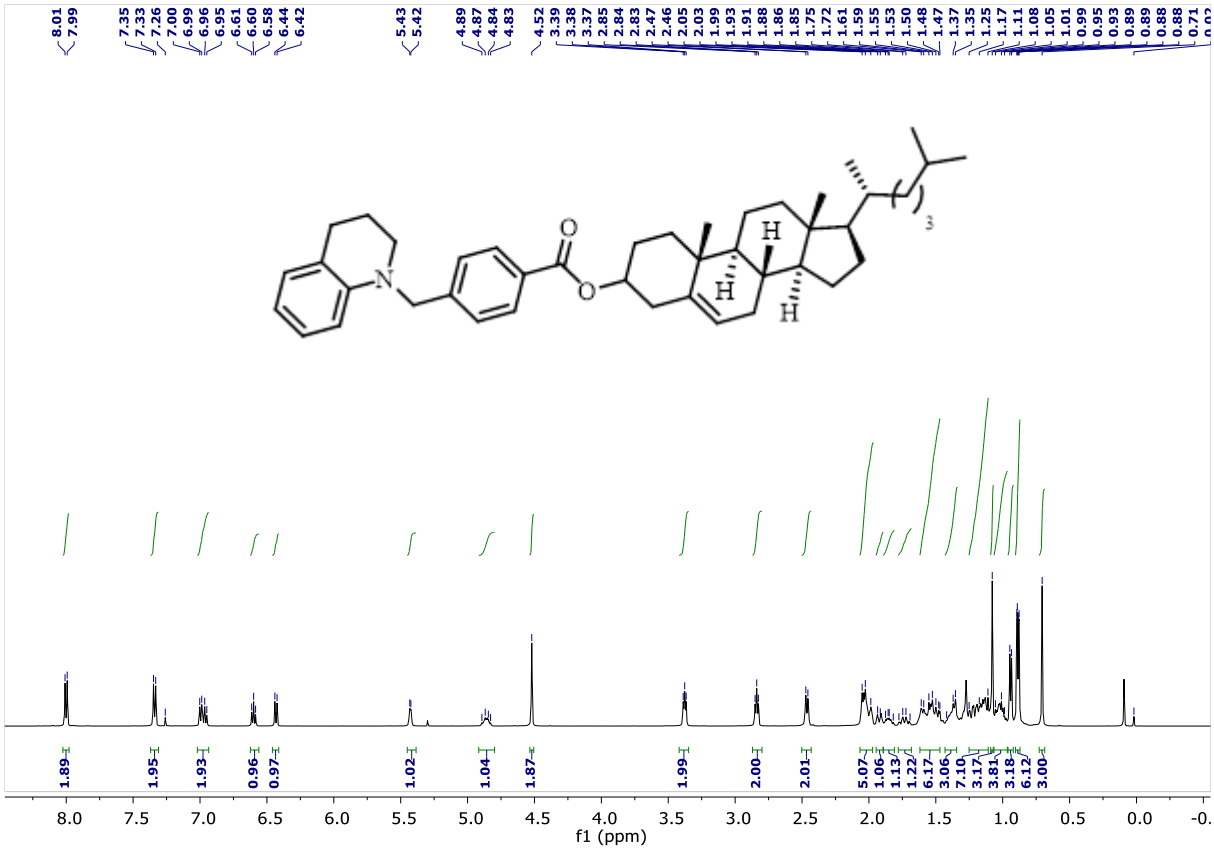


Figure S132: ^{1}H NMR Spectrum of **6h** ($CDCl_3$, 500 MHz, 298 K)

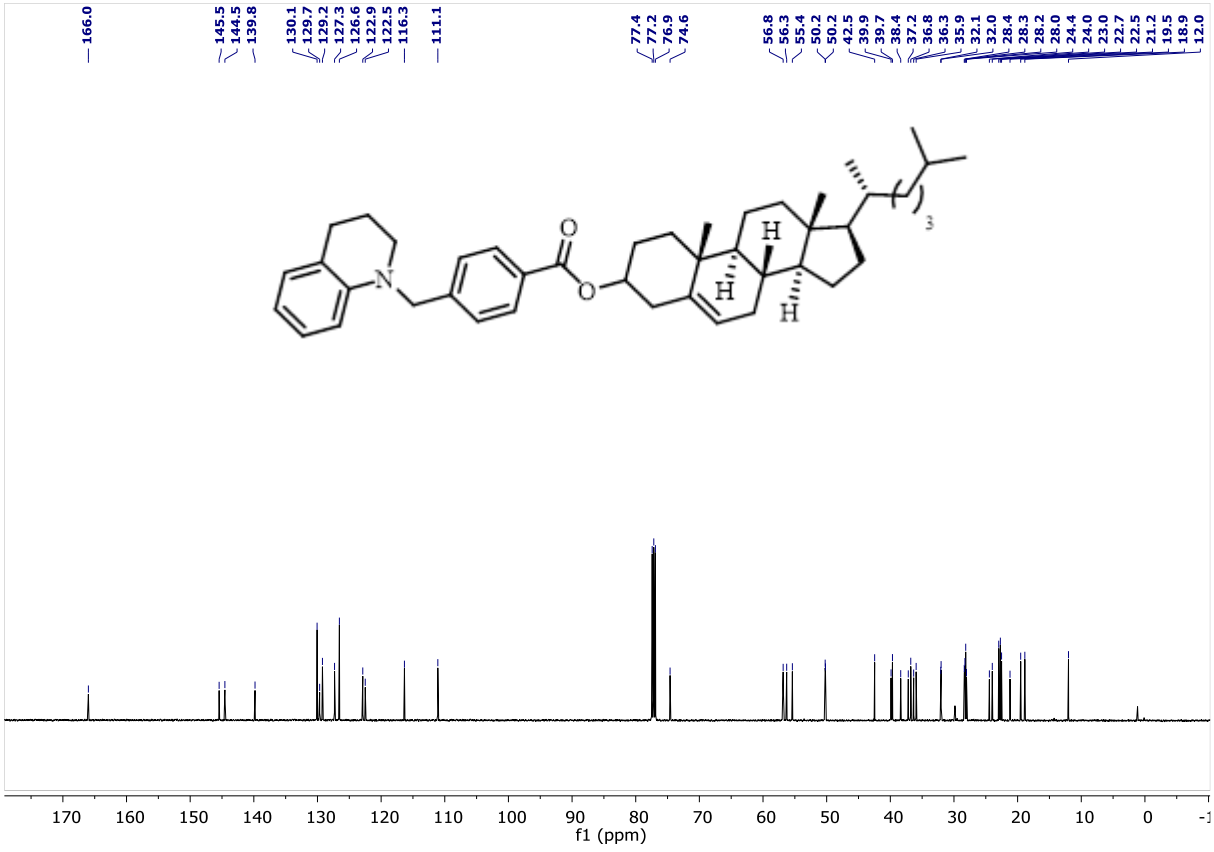


Figure S133: $^{13}C\{^{1}H\}$ NMR Spectrum of **6h** ($CDCl_3$, 126 MHz, 298 K)

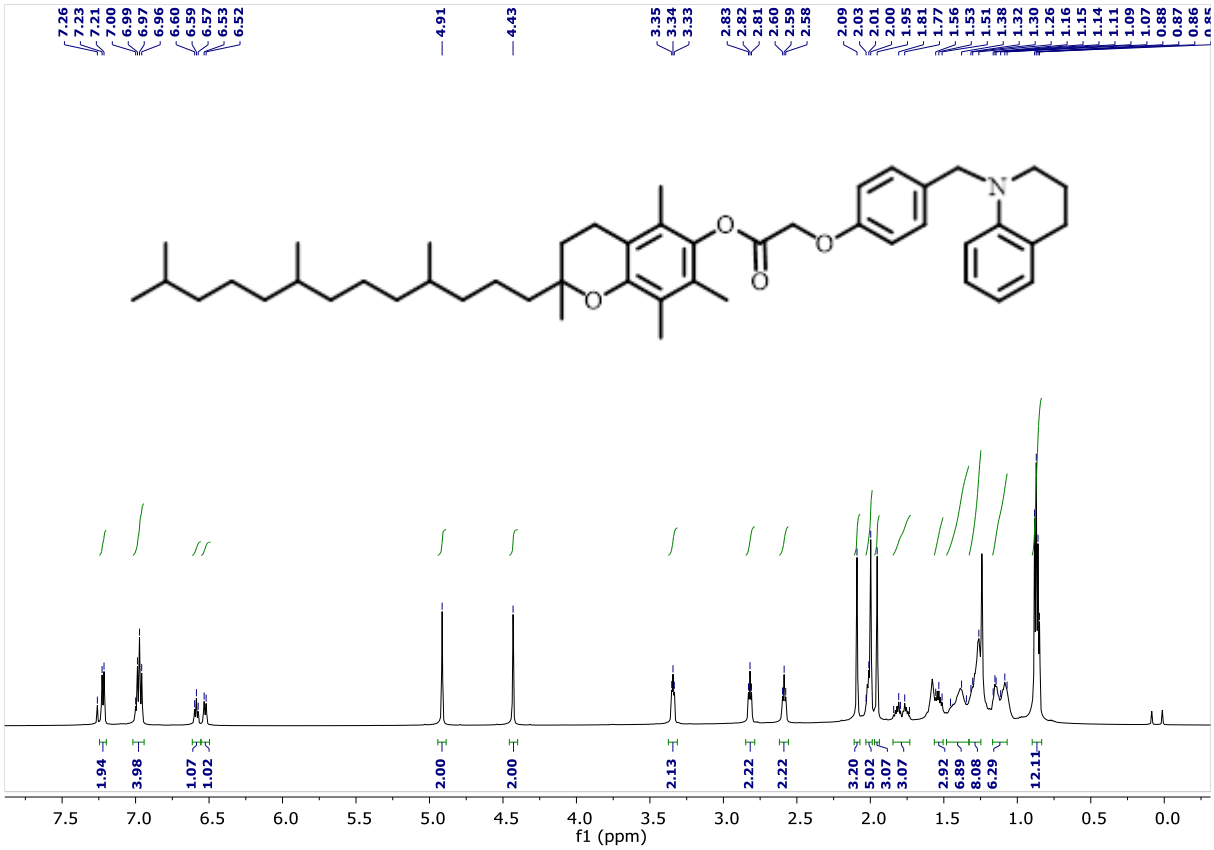


Figure S134: ^{1}H NMR Spectrum of **6i** ($CDCl_3$, 600 MHz, 298 K)

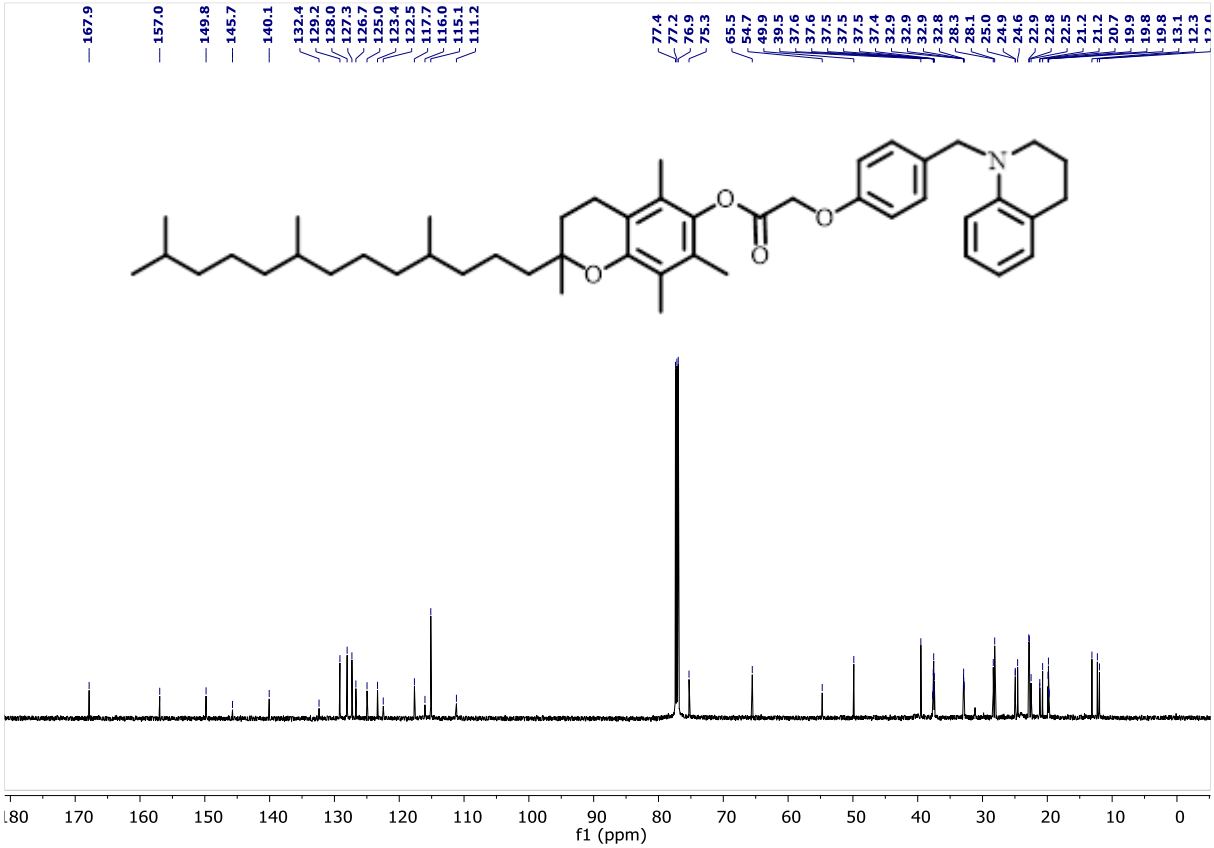


Figure S135: $^{13}C\{^{1}H\}$ NMR Spectrum of **6i** ($CDCl_3$, 151 MHz, 298 K)

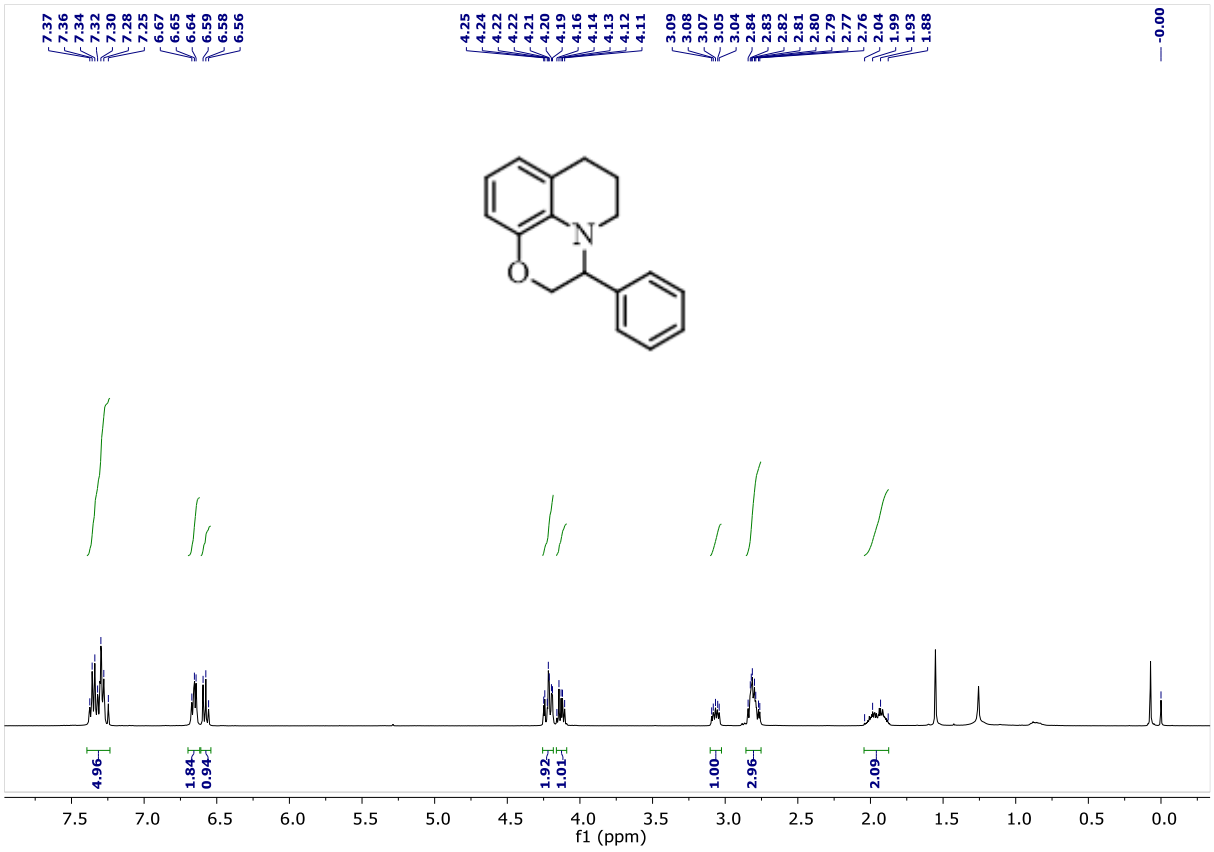


Figure S136: ^{1}H NMR Spectrum of **8a** ($CDCl_3$, 400 MHz, 298 K)

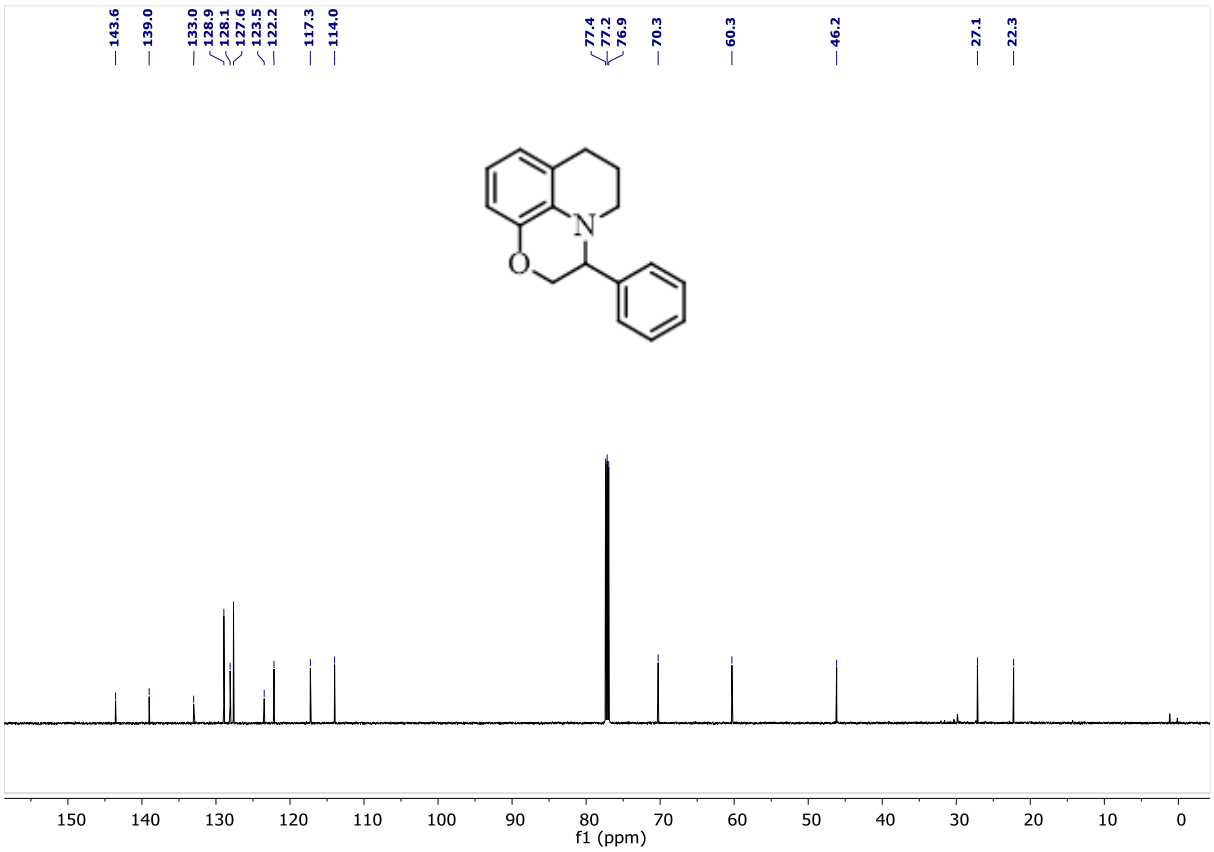


Figure S137: $^{13}C\{^{1}H\}$ NMR Spectrum of **8a** ($CDCl_3$, 151 MHz, 298 K)

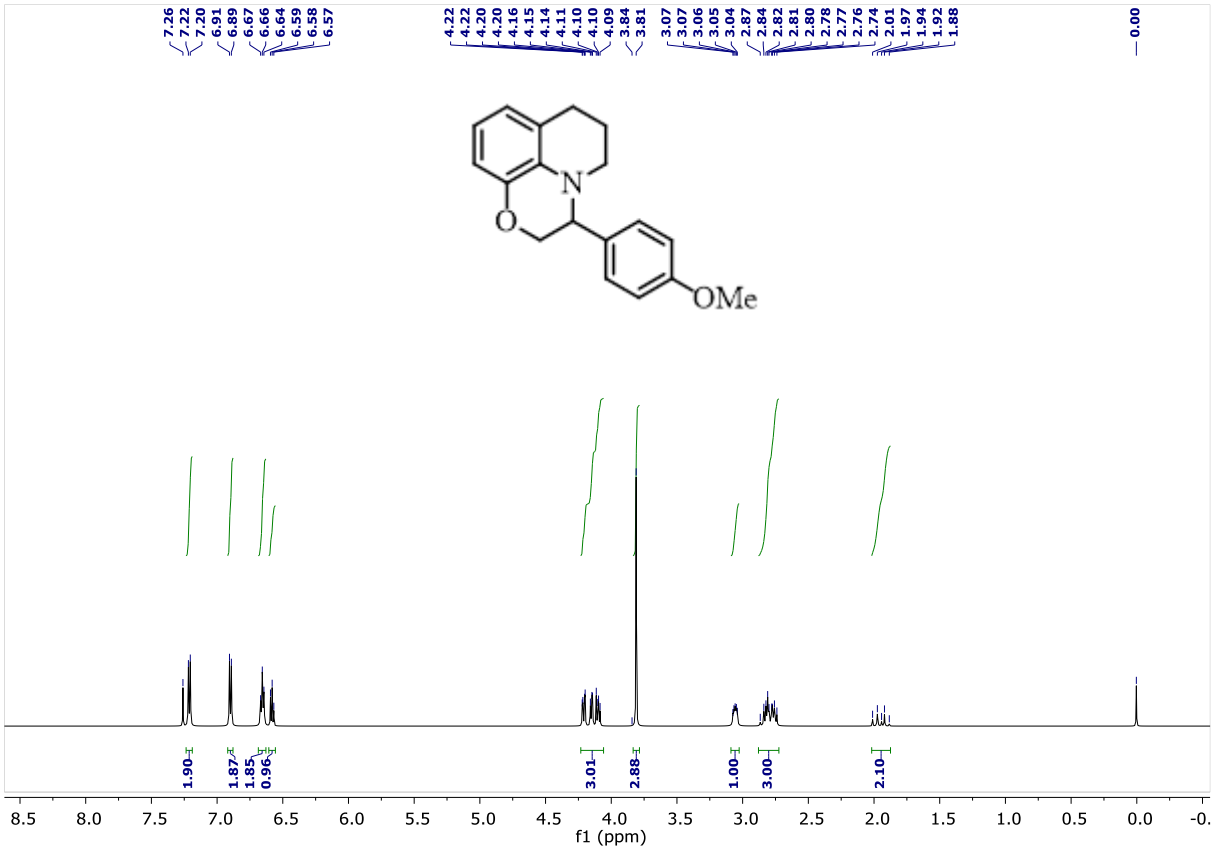


Figure S138: ^{1}H NMR Spectrum of **8b** ($CDCl_3$, 600 MHz, 298 K)

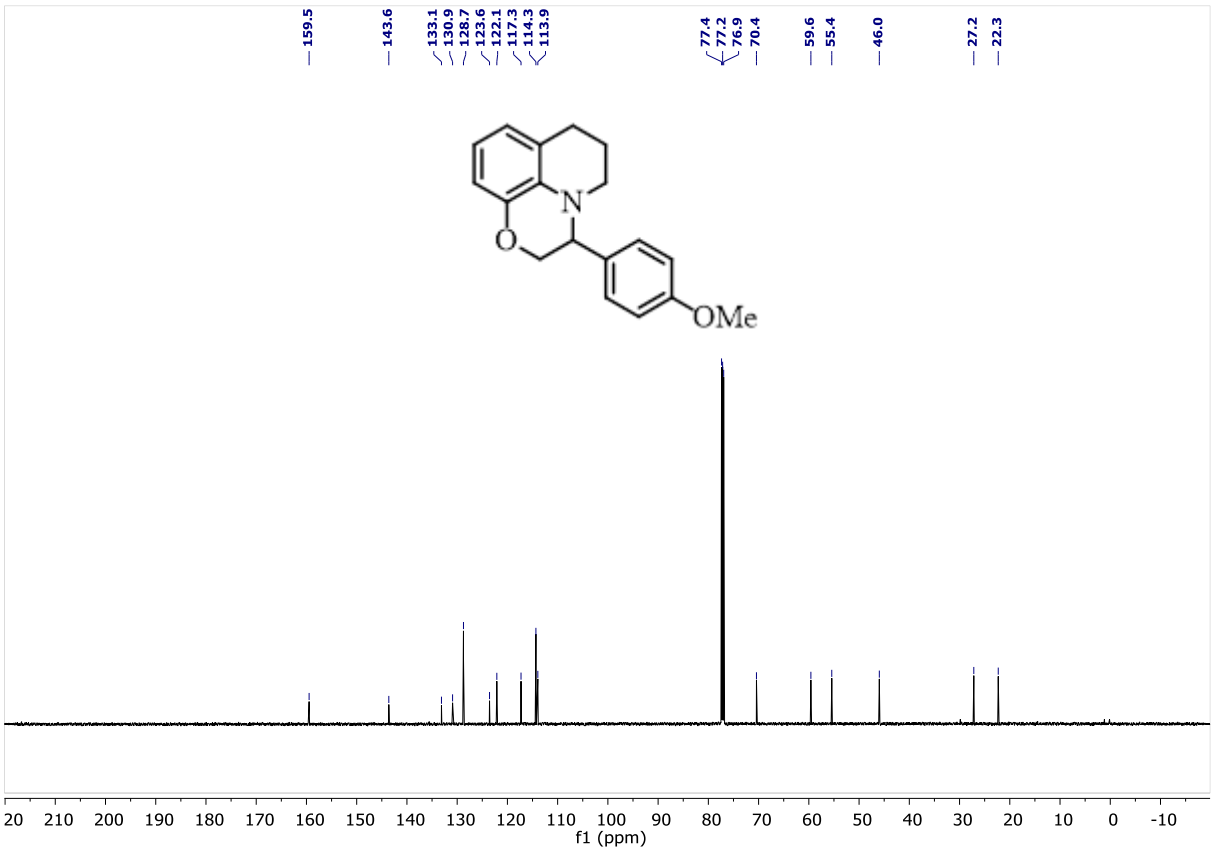


Figure S139: $^{13}C\{^{1}H\}$ NMR Spectrum of **8b** ($CDCl_3$, 151 MHz, 298 K)

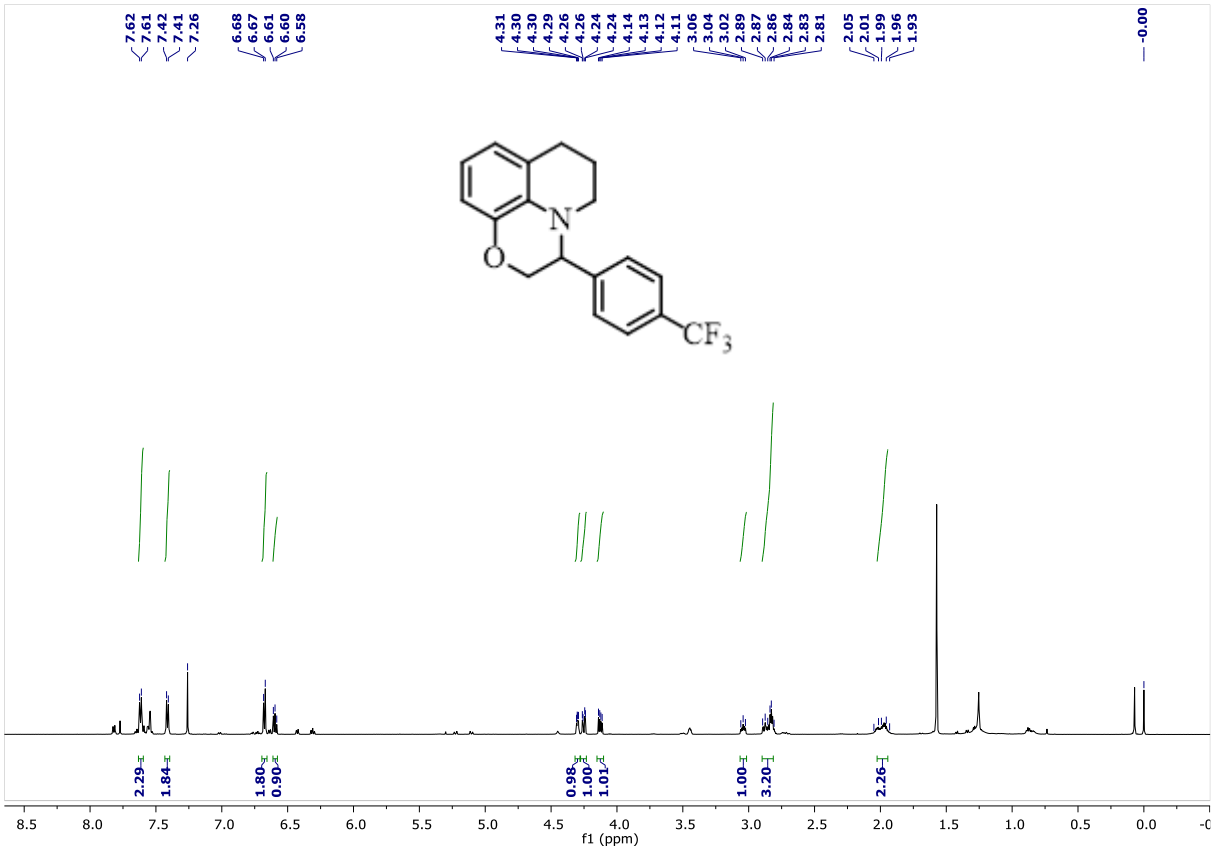


Figure S140: ^{1}H NMR Spectrum of **8c** ($CDCl_3$, 600 MHz, 298 K)

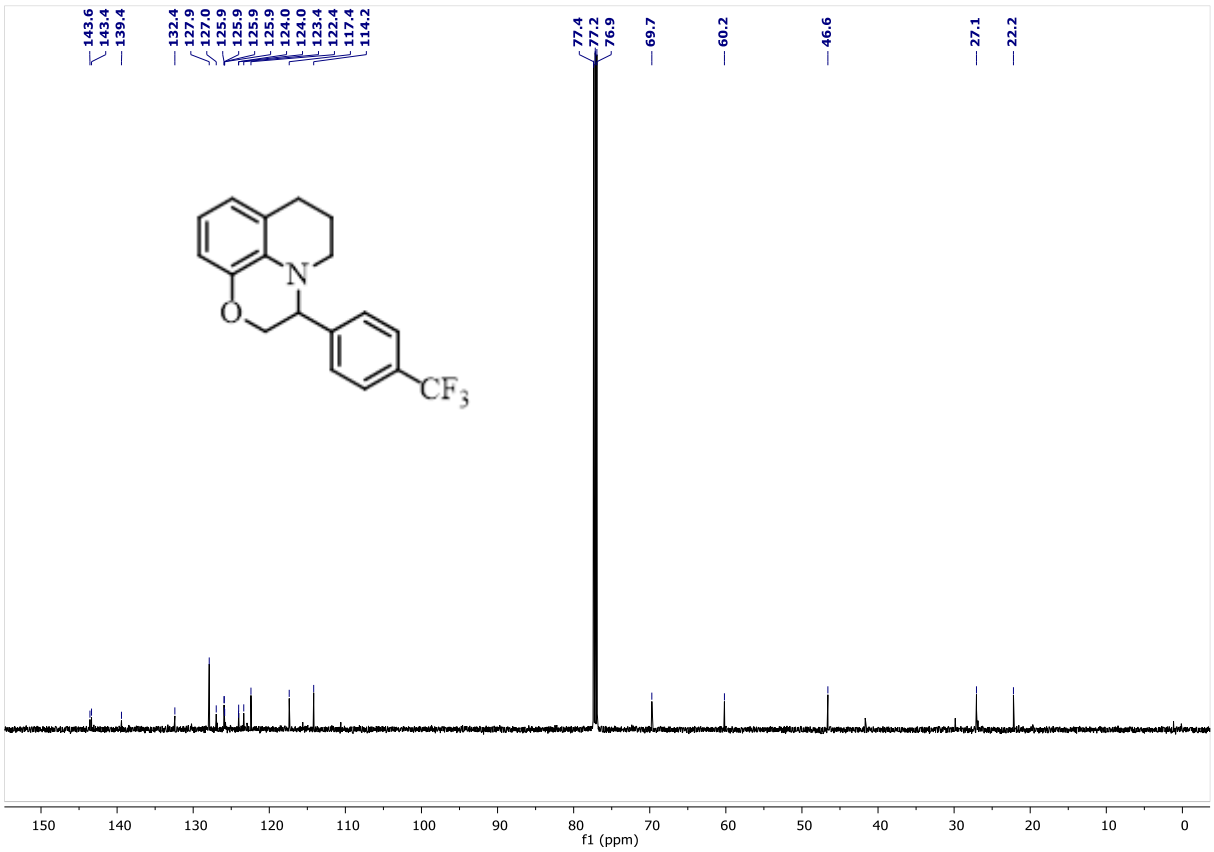


Figure S141: $^{13}C\{^{1}H\}$ NMR Spectrum of **8c** ($CDCl_3$, 151 MHz, 298 K)

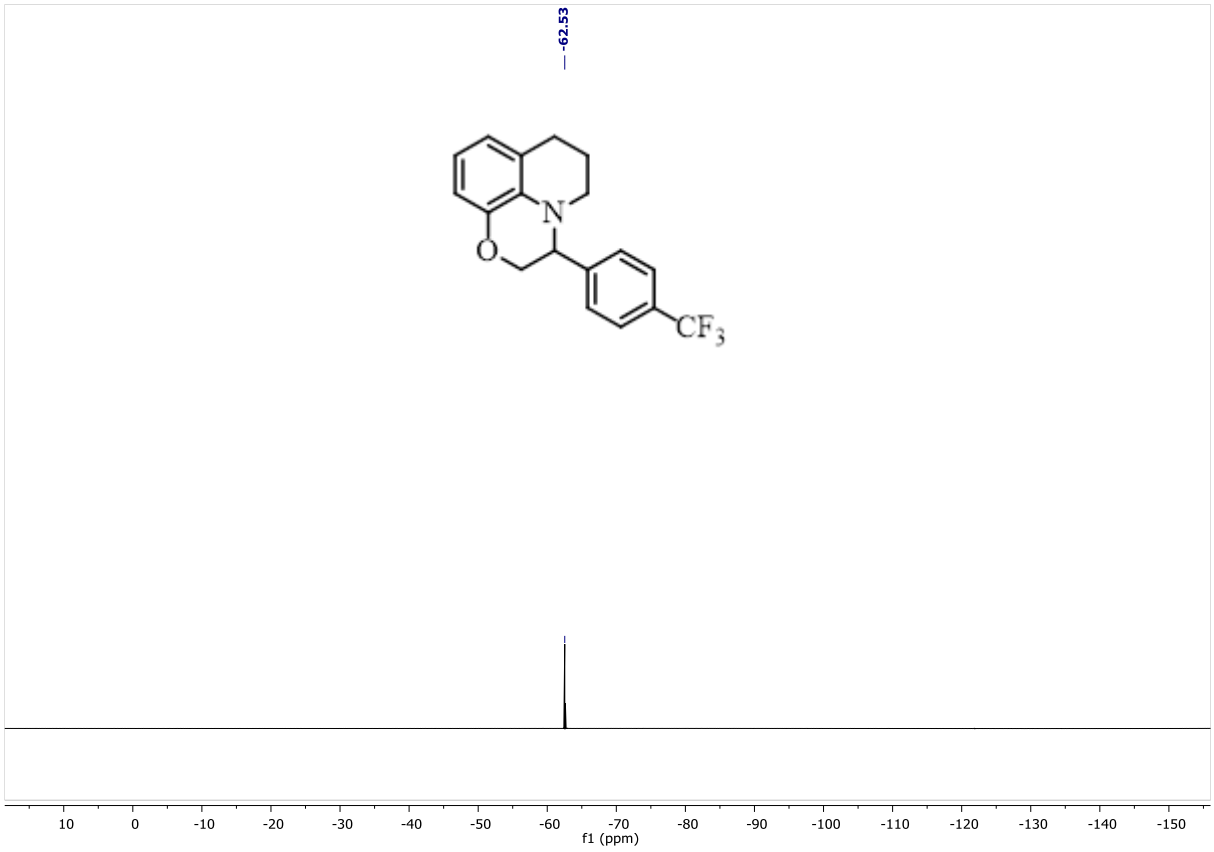


Figure S142: $^{19}F\{^{1}H\}$ NMR Spectrum of **8c** ($CDCl_3$, 565 MHz, 298 K)

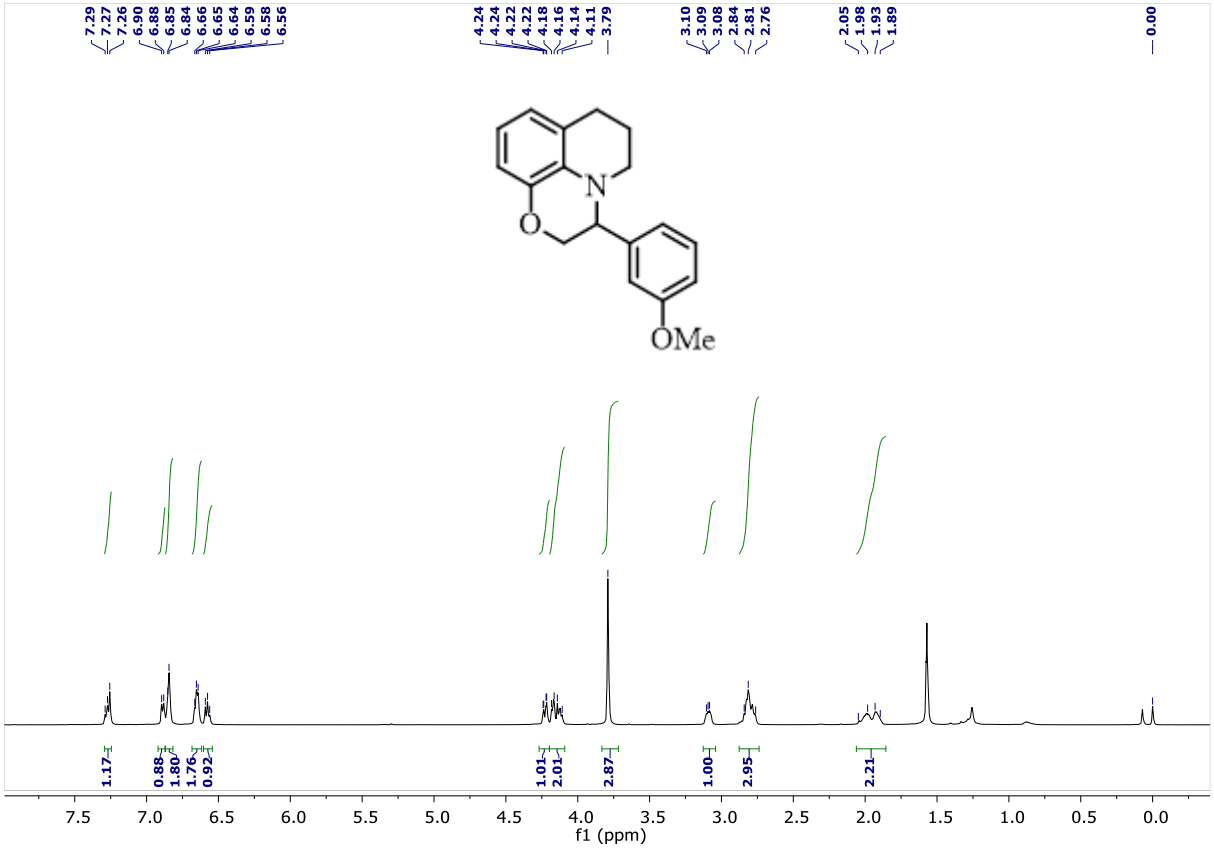


Figure S143: ^{1}H NMR Spectrum of **8d** ($CDCl_3$, 500 MHz, 298 K)

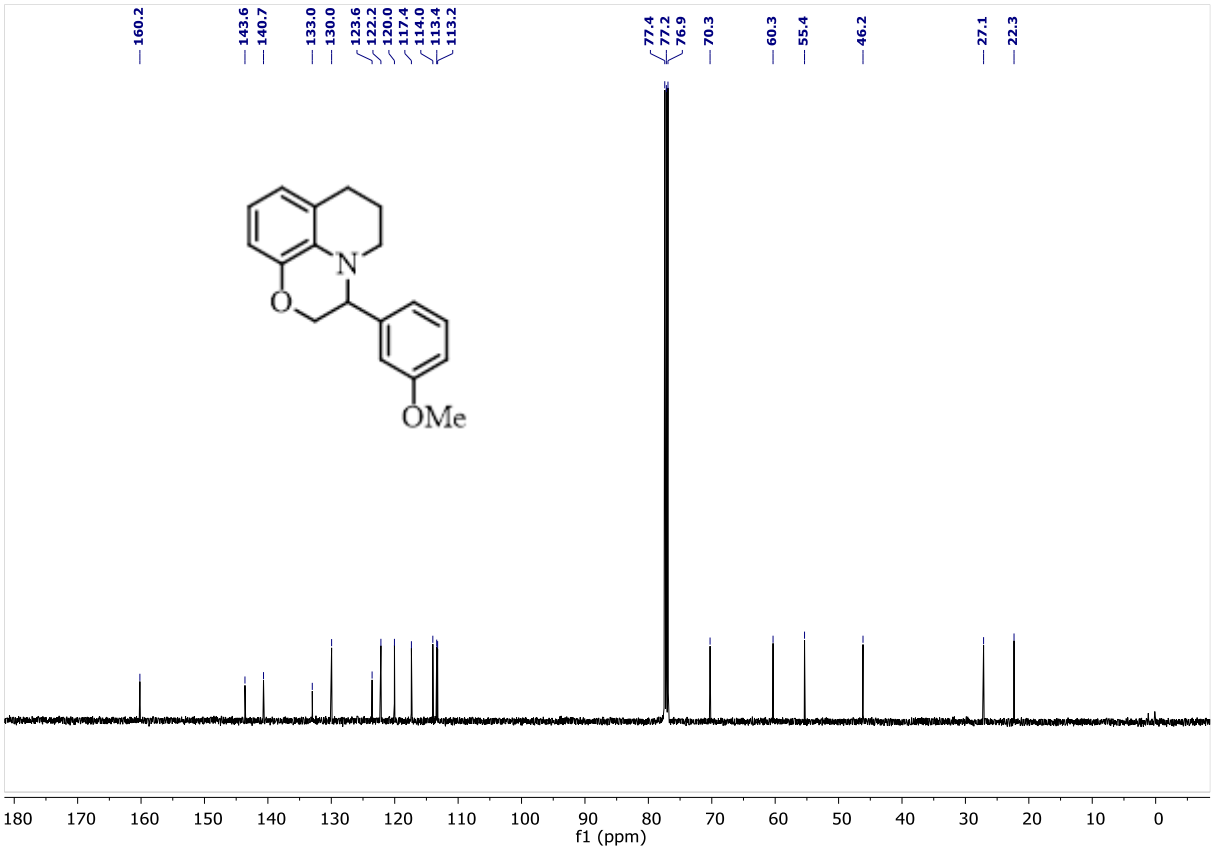


Figure S144: $^{13}C\{^{1}H\}$ NMR Spectrum of **8d** ($CDCl_3$, 126 MHz, 298 K)

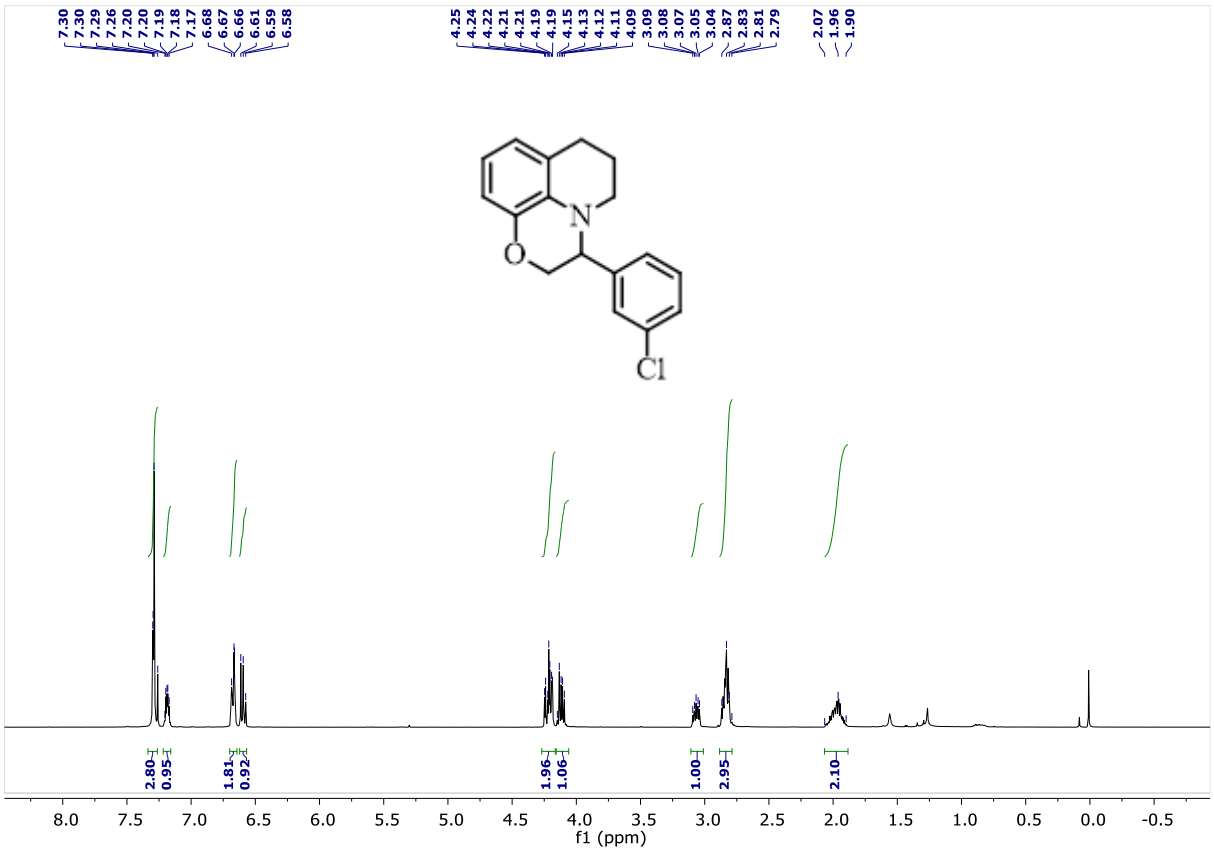


Figure S145: ^{1}H NMR Spectrum of **8e** ($CDCl_3$, 400 MHz, 298 K)

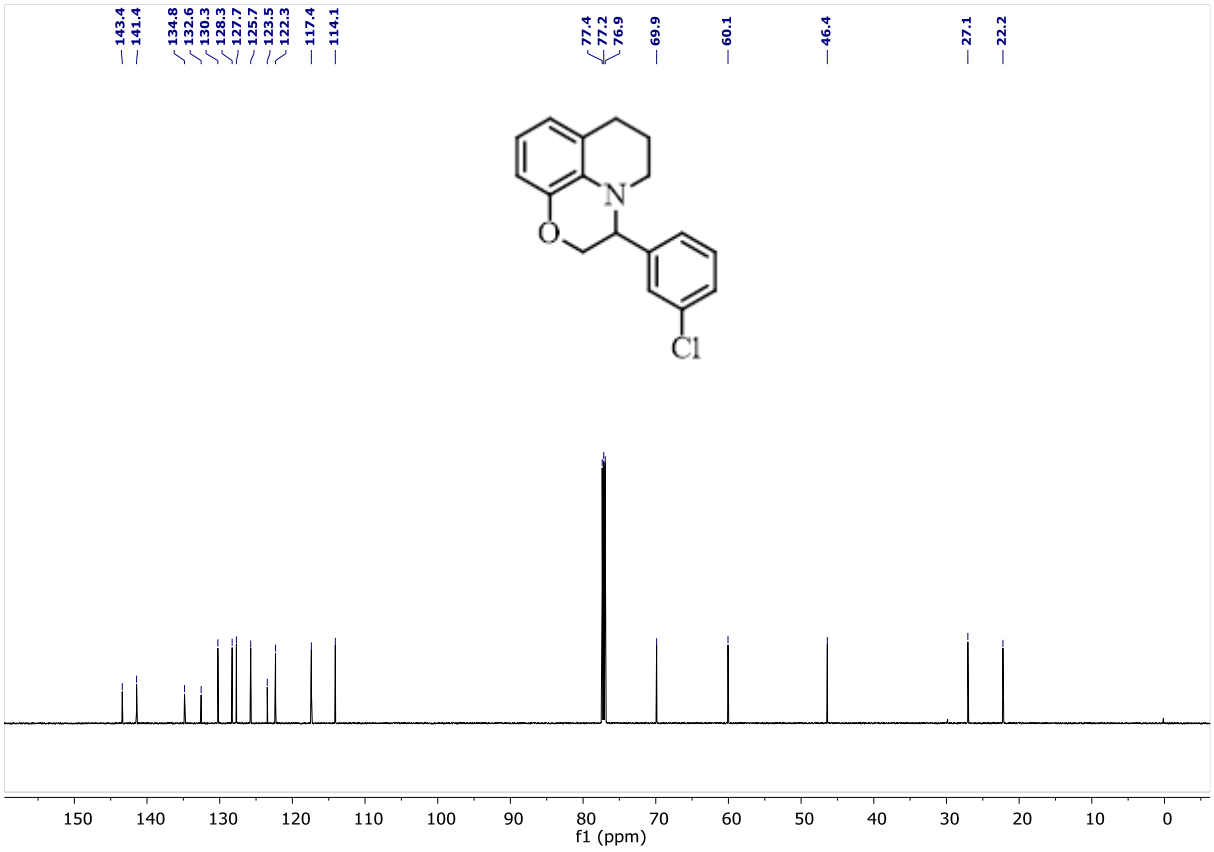


Figure S146: $^{13}C\{^{1}H\}$ NMR Spectrum of **8e** ($CDCl_3$, 151 MHz, 298 K)

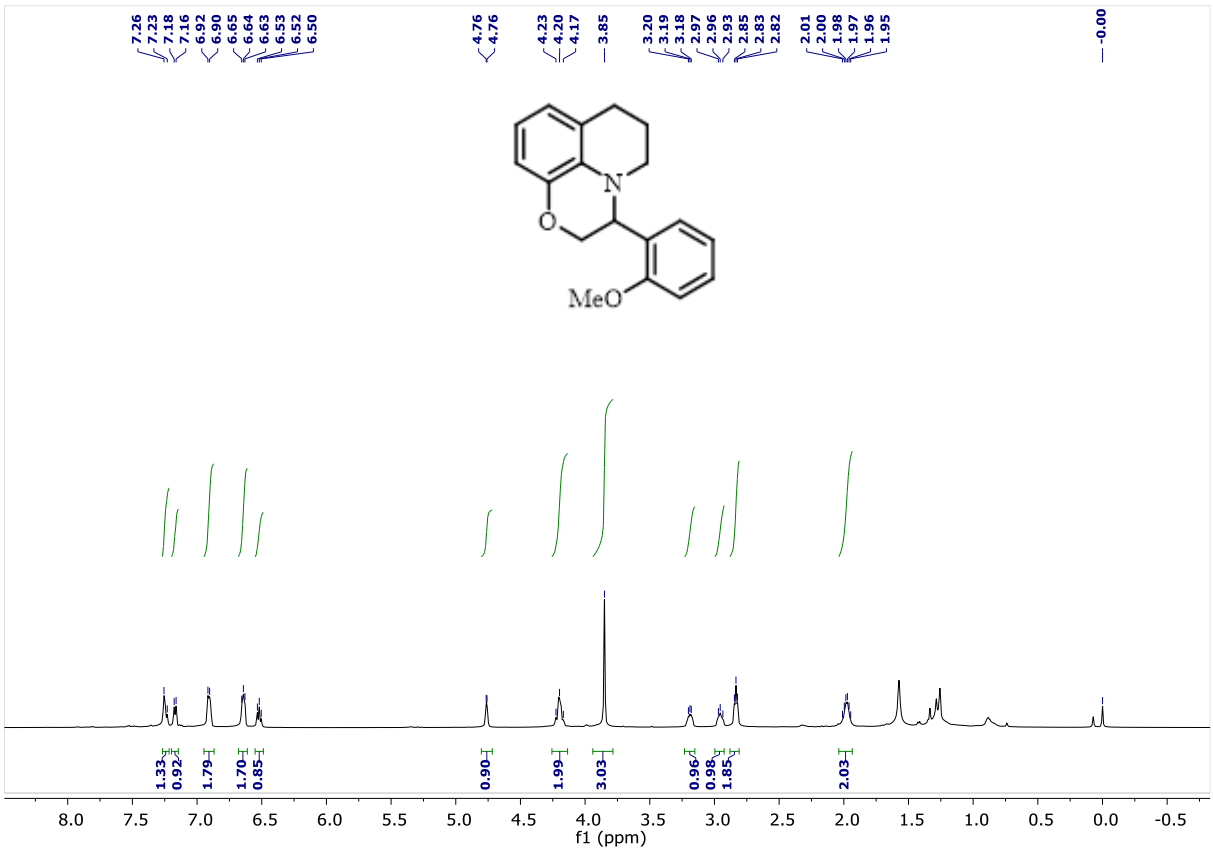


Figure S147: ^{1}H NMR Spectrum of **8f** ($CDCl_3$, 500 MHz, 298 K)

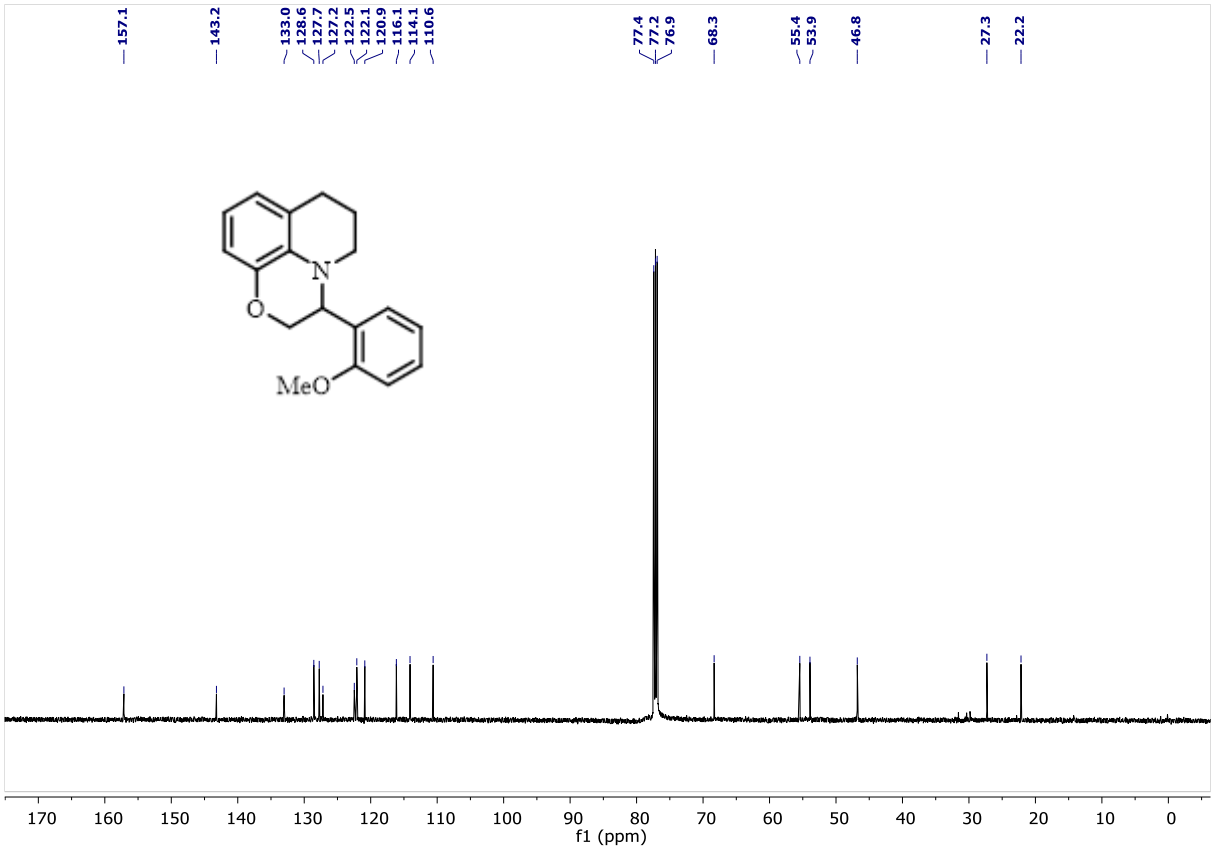


Figure S148: $^{13}C\{^{1}H\}$ NMR Spectrum of **8f** ($CDCl_3$, 126 MHz, 298 K)

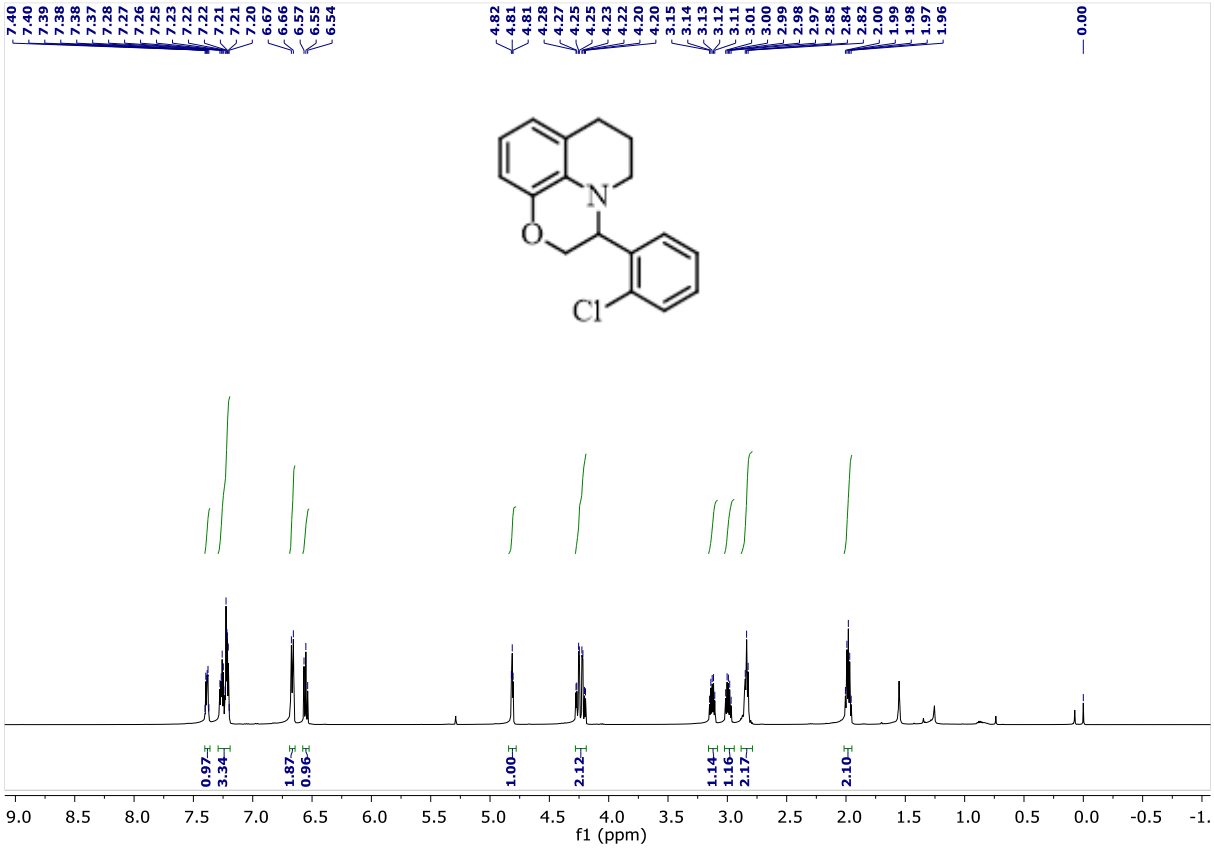


Figure S149: ^{1}H NMR Spectrum of **8g** ($CDCl_3$, 500 MHz, 298 K)

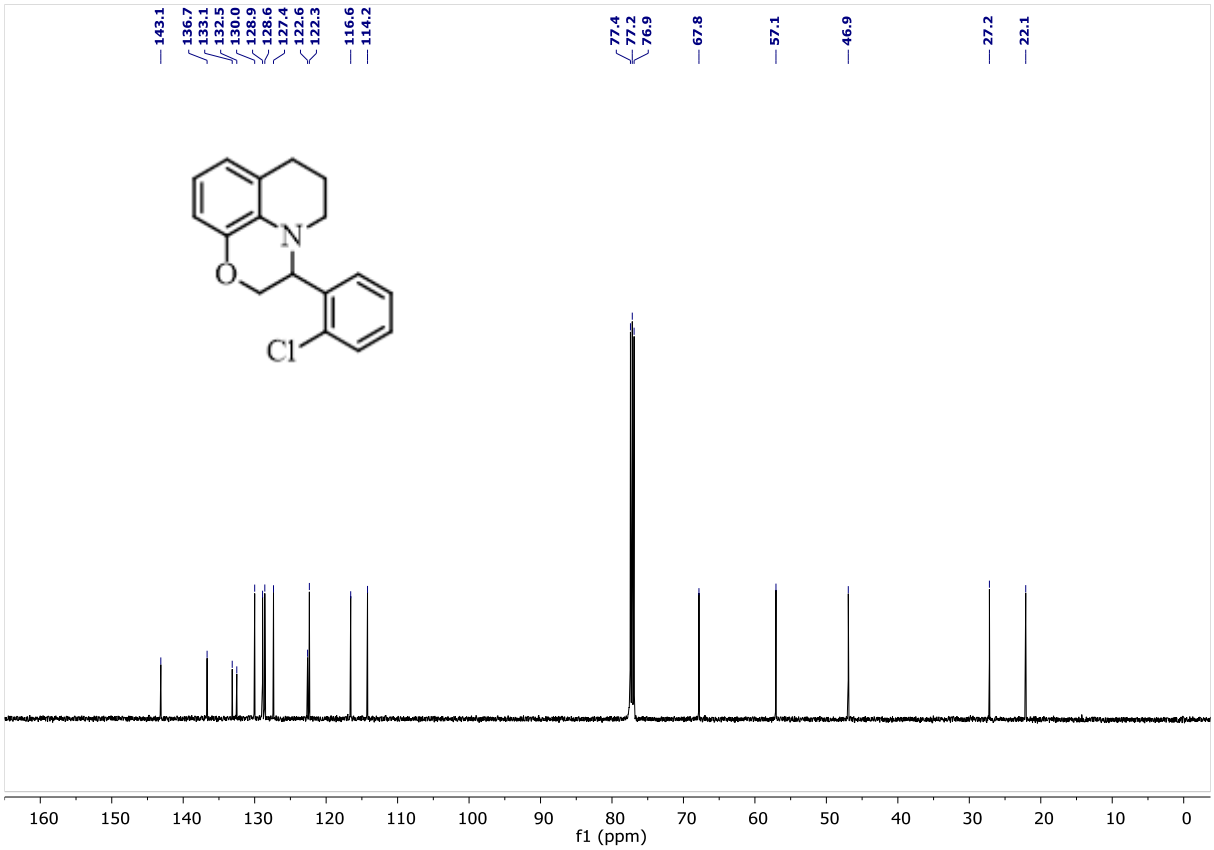


Figure S150: $^{13}C\{^{1}H\}$ NMR Spectrum of **8g** ($CDCl_3$, 126 MHz, 298 K)

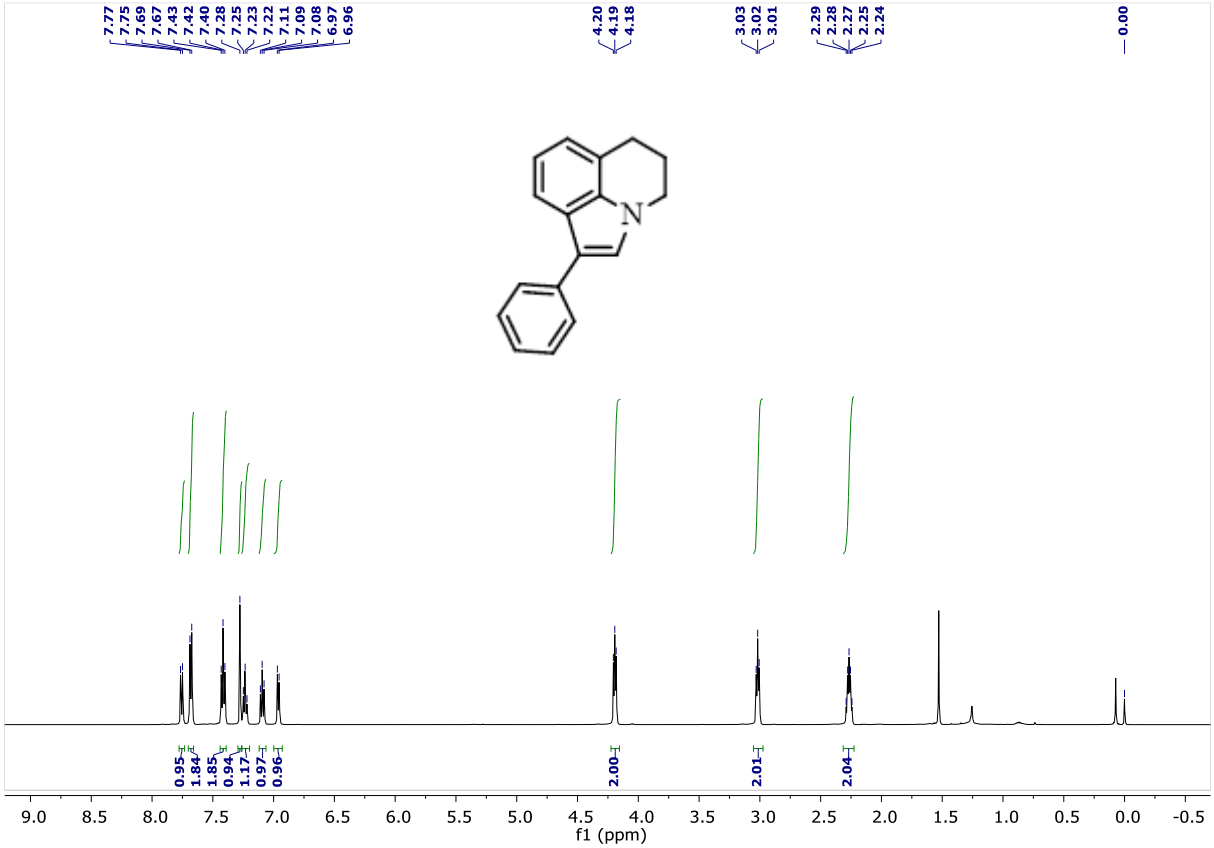


Figure S151: ^{1}H NMR Spectrum of **10a** ($CDCl_3$, 500 MHz, 298 K)

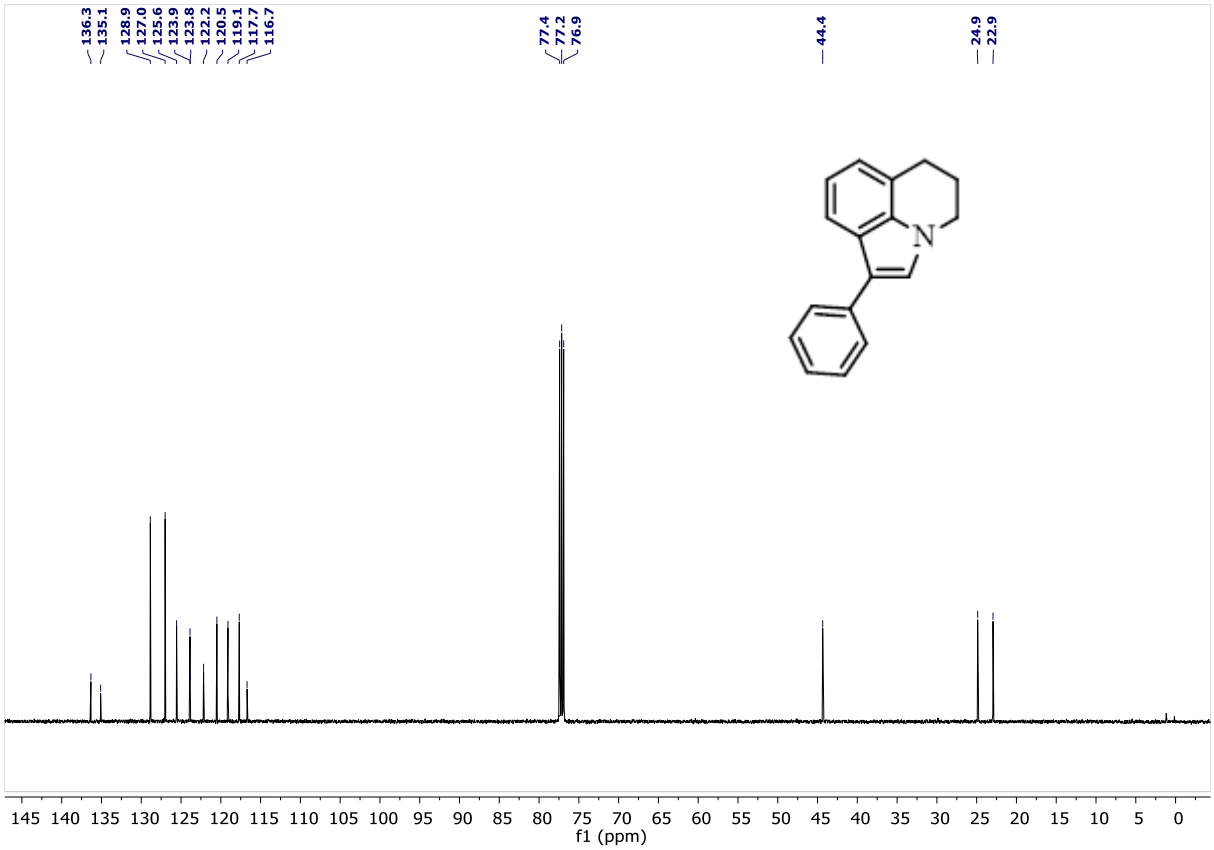


Figure S152: $^{13}C\{^{1}H\}$ NMR Spectrum of **10a** ($CDCl_3$, 126 MHz, 298 K)

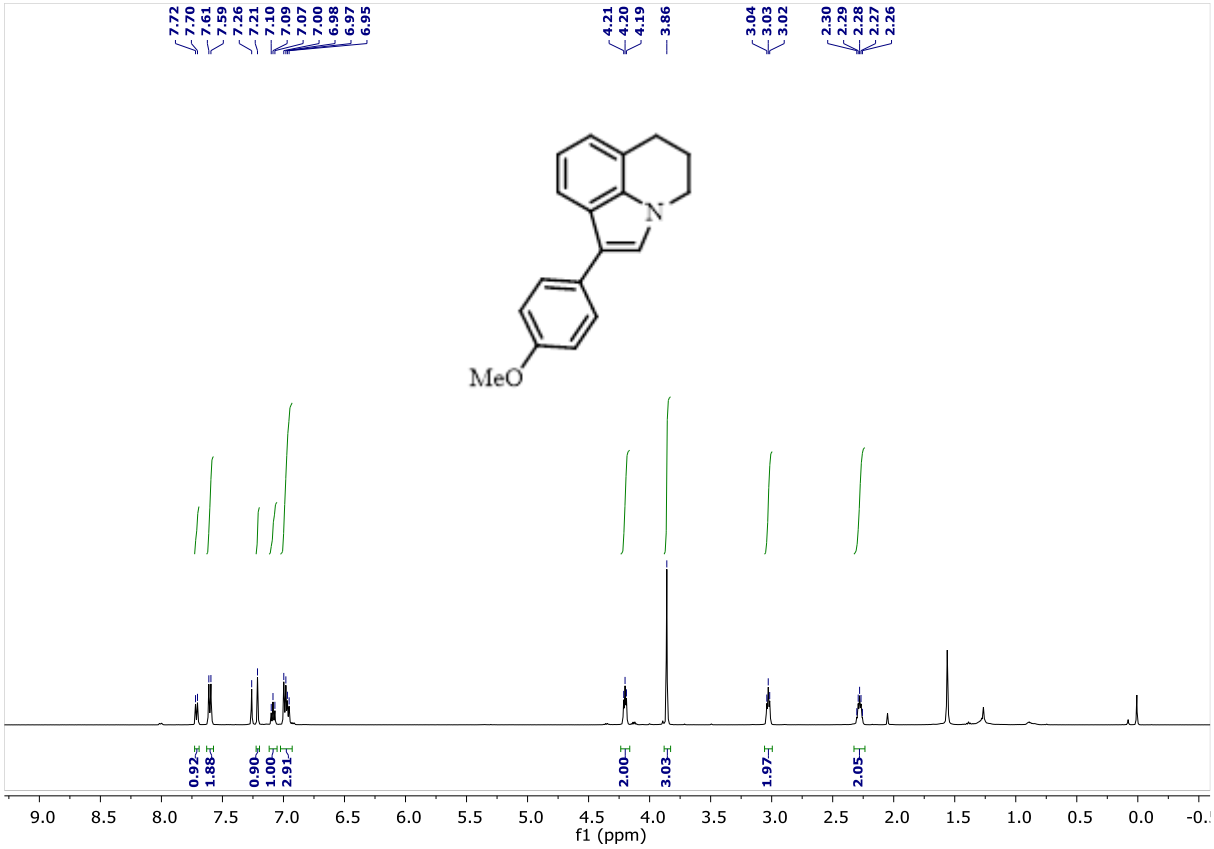


Figure S153: ^{1}H NMR Spectrum of **10b** ($CDCl_3$, 500 MHz, 298 K)

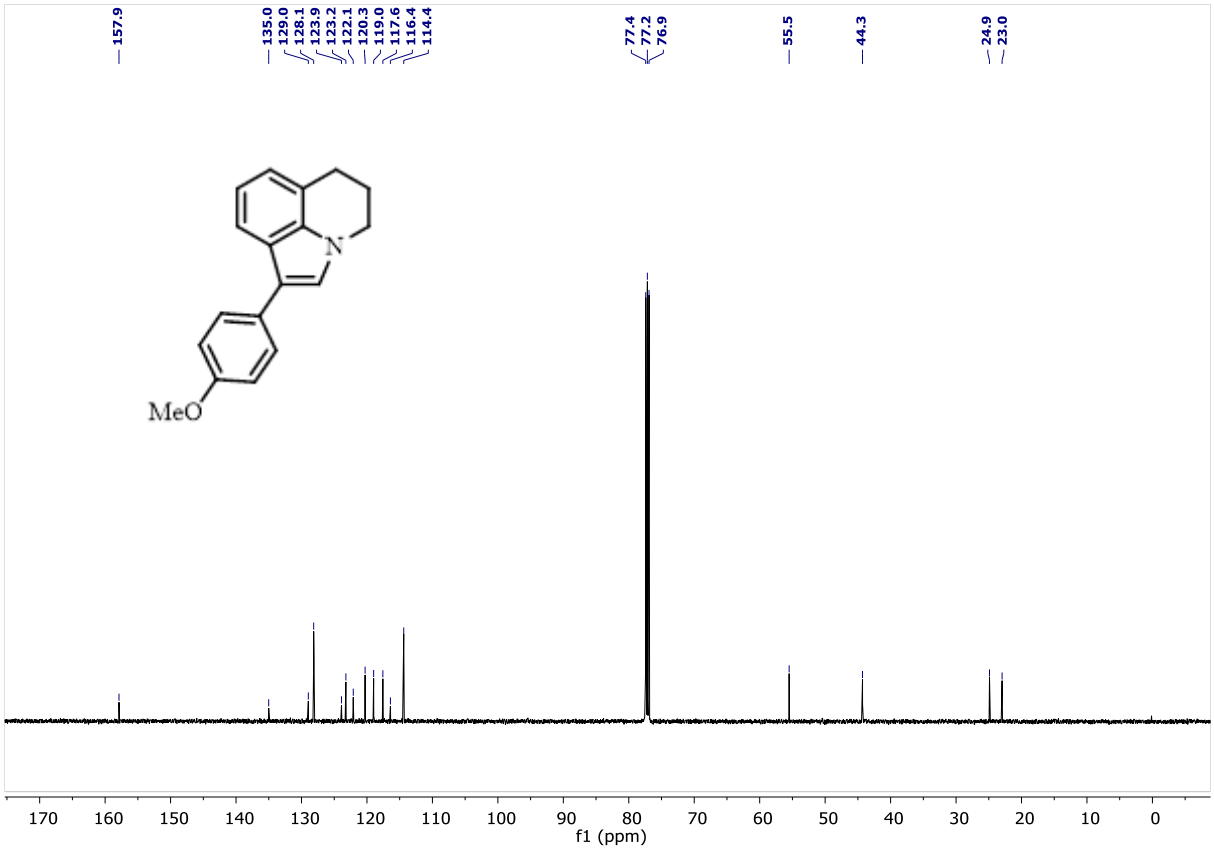


Figure S154: $^{13}C\{^{1}H\}$ NMR Spectrum of **10b** ($CDCl_3$, 126 MHz, 298 K)

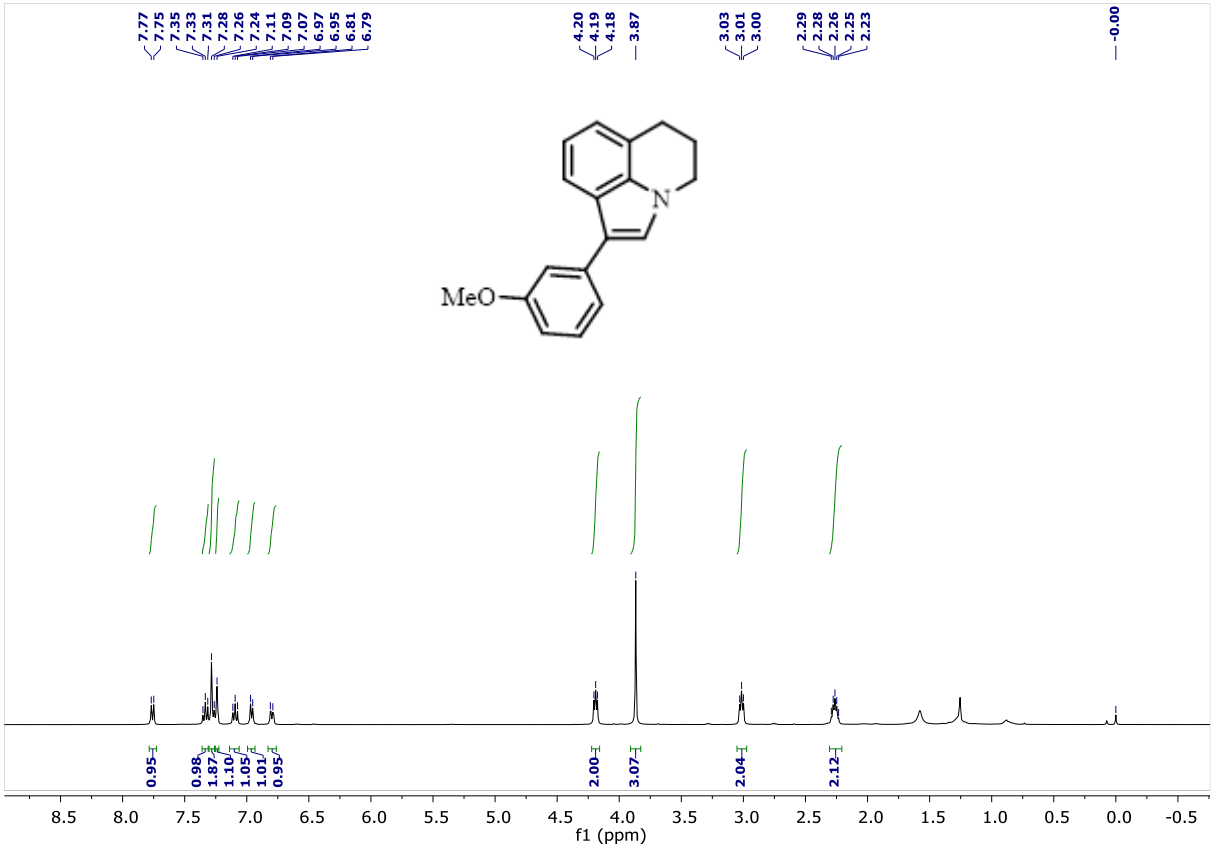


Figure S155: ^{1}H NMR Spectrum of **10c** ($CDCl_3$, 400 MHz, 298 K)

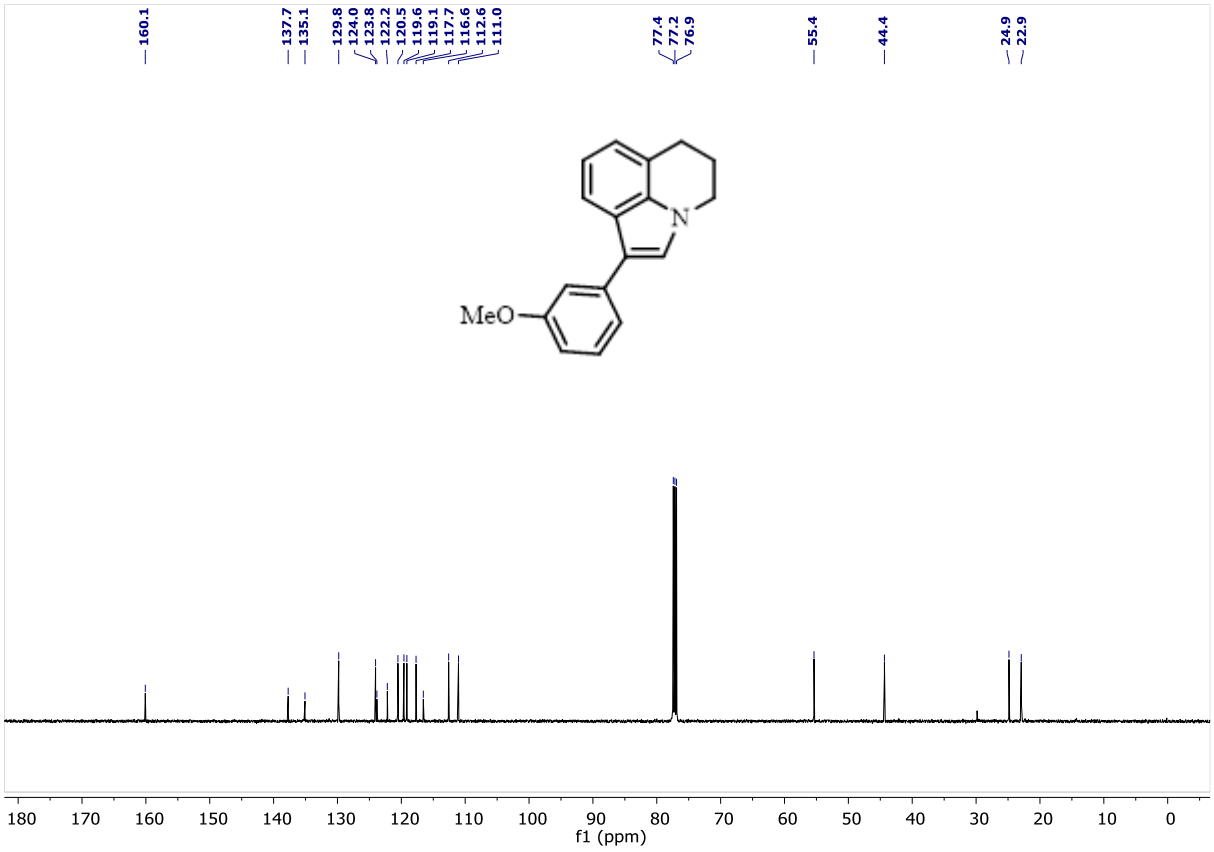


Figure S156: $^{13}C\{^{1}H\}$ NMR Spectrum of **10c** ($CDCl_3$, 126 MHz, 298 K)

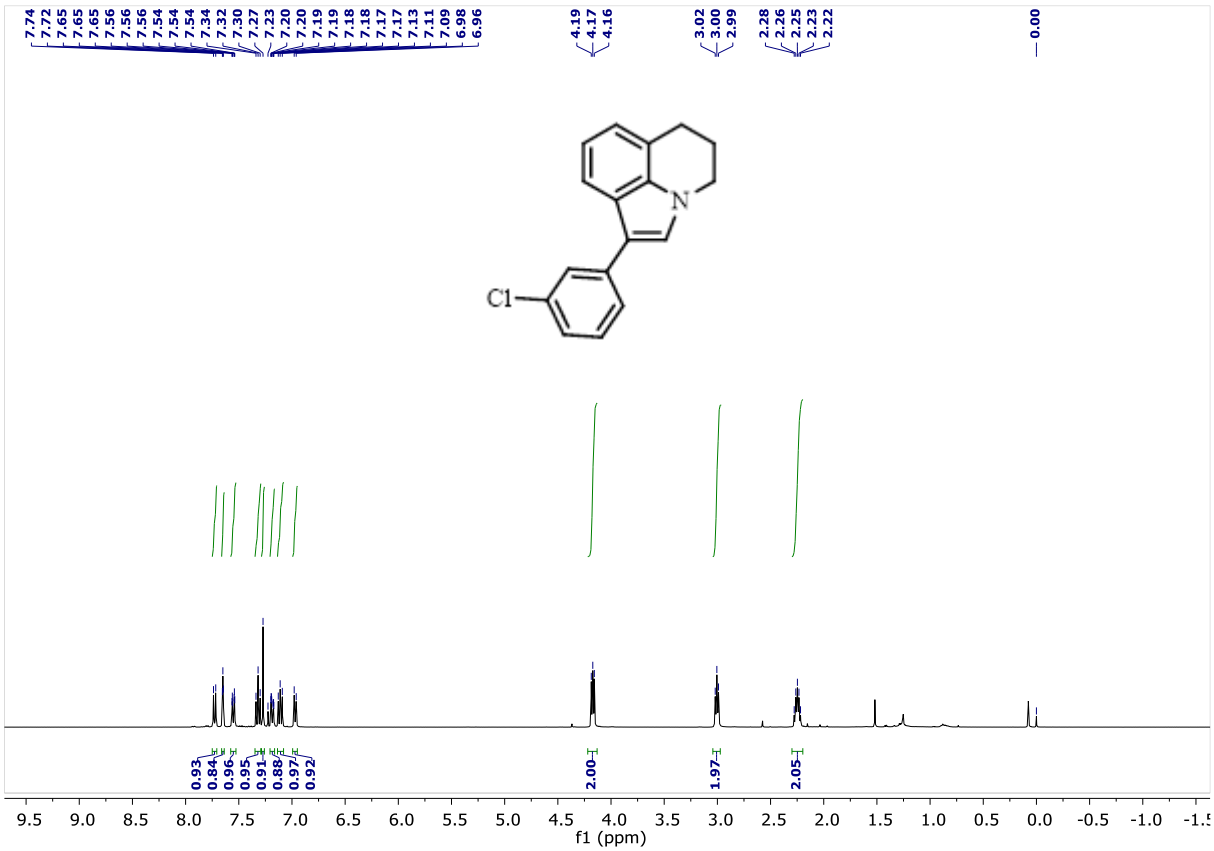


Figure S157: ^{1}H NMR Spectrum of **10d** ($CDCl_3$, 400 MHz, 298 K)

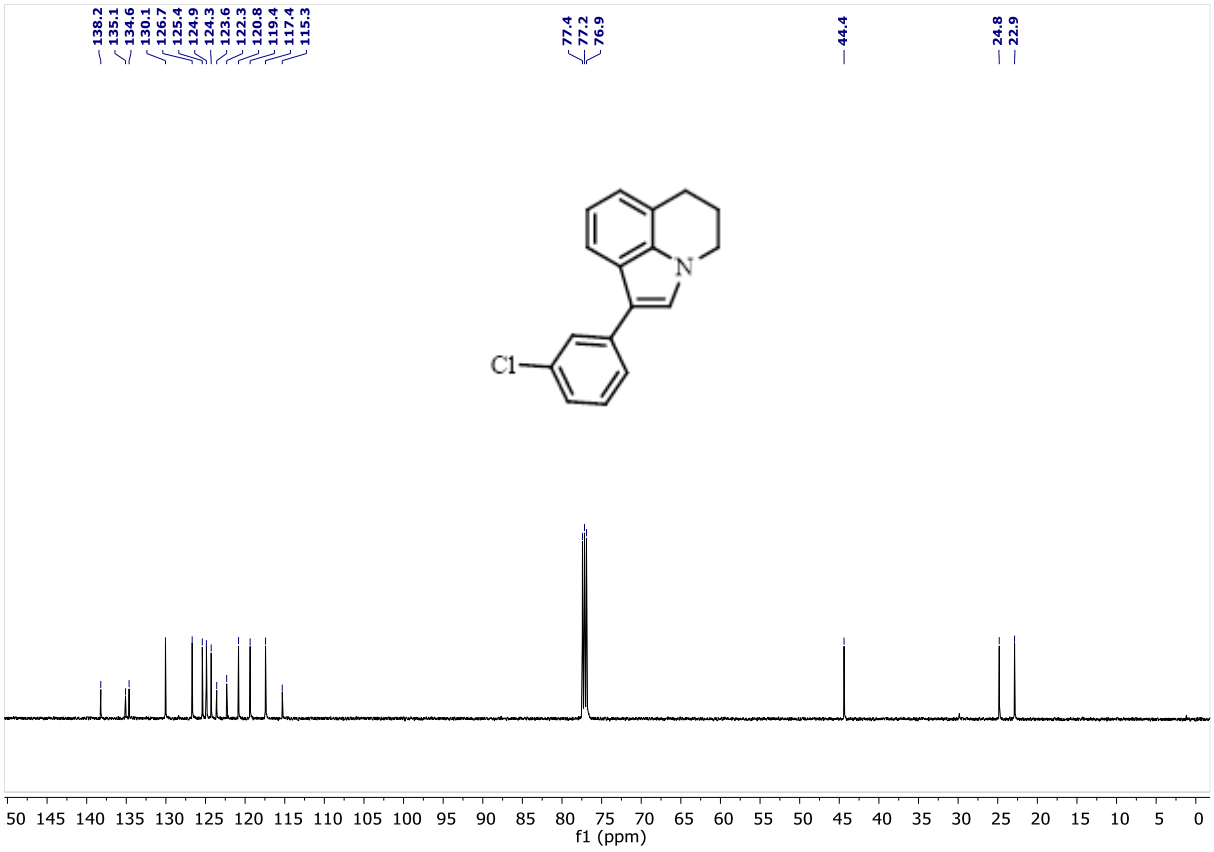


Figure S158: $^{13}C\{^{1}H\}$ NMR Spectrum of **10d** ($CDCl_3$, 126 MHz, 298 K)

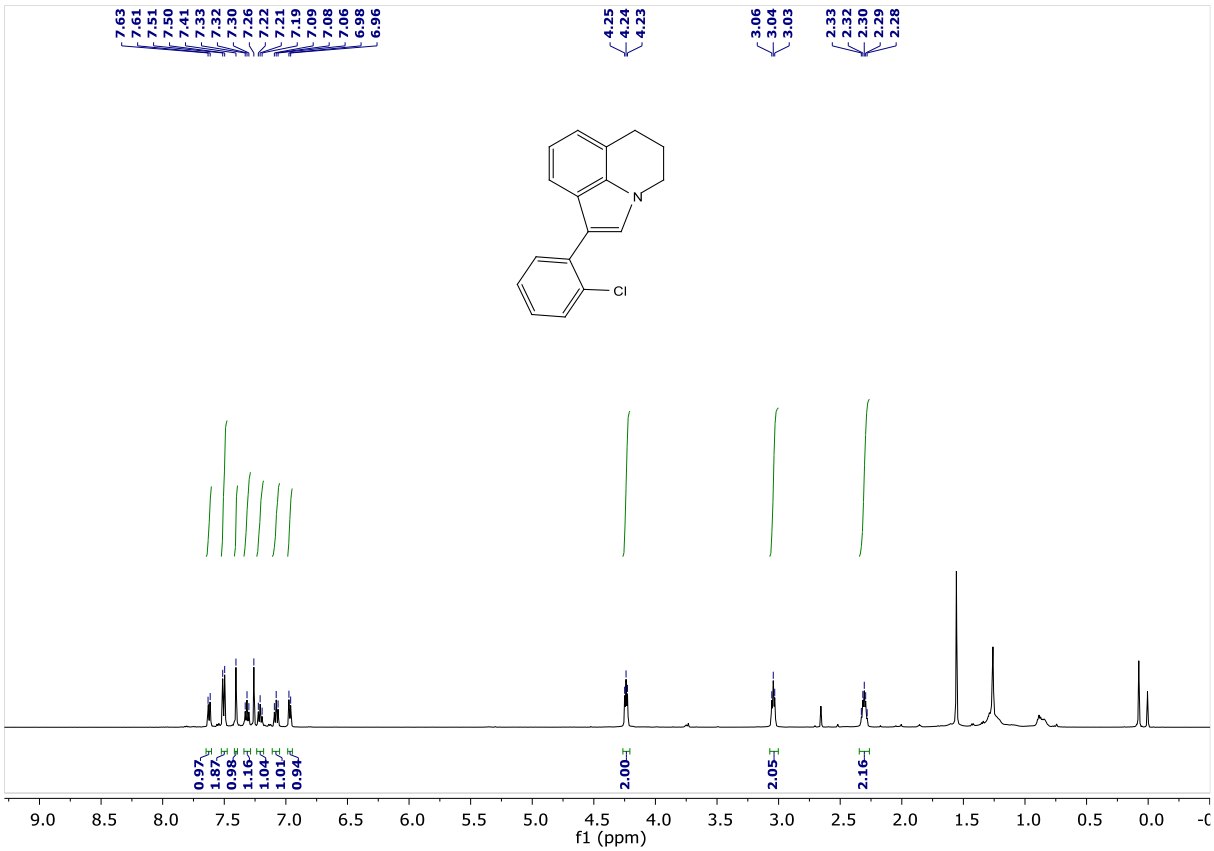


Figure S159: ^{1}H NMR Spectrum of **10e** ($CDCl_3$, 500 MHz, 298 K)

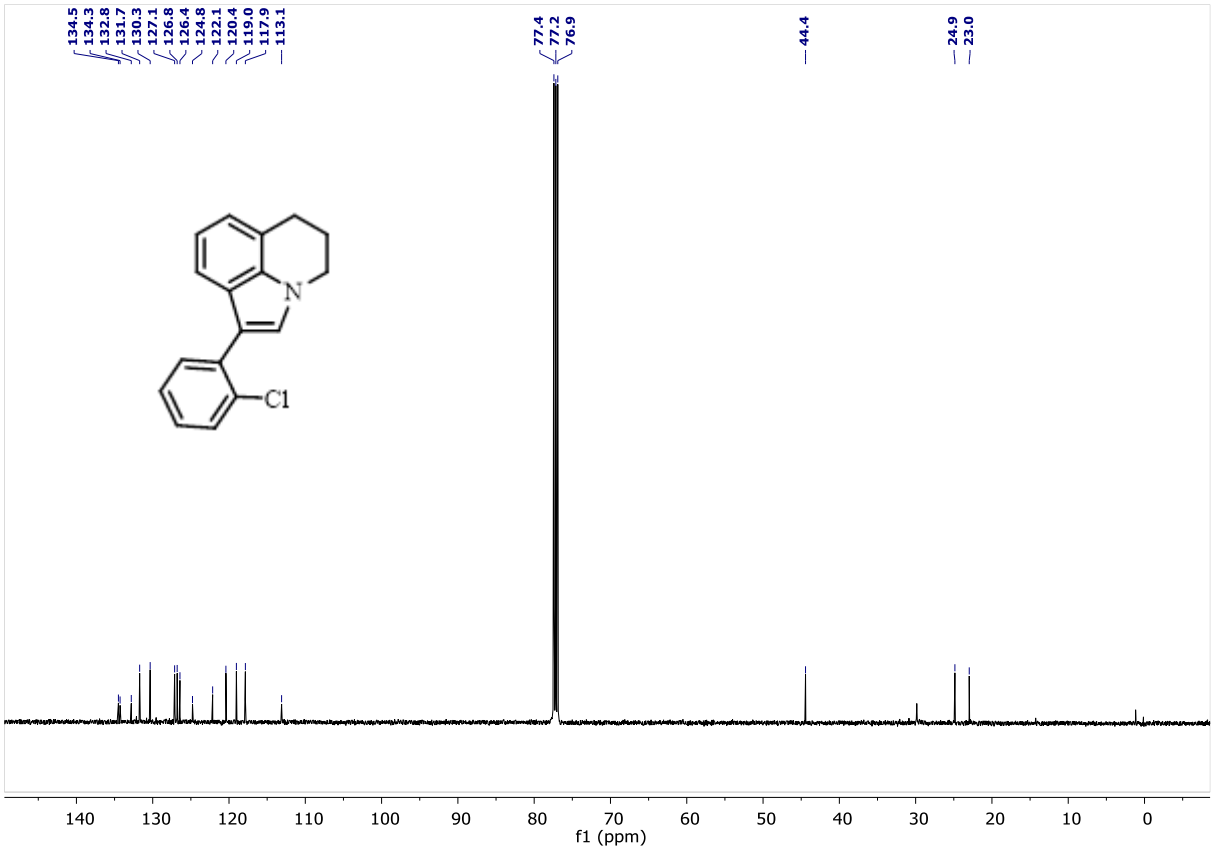


Figure S160: $^{13}C\{^{1}H\}$ NMR Spectrum of **10e** ($CDCl_3$, 126 MHz, 298 K)

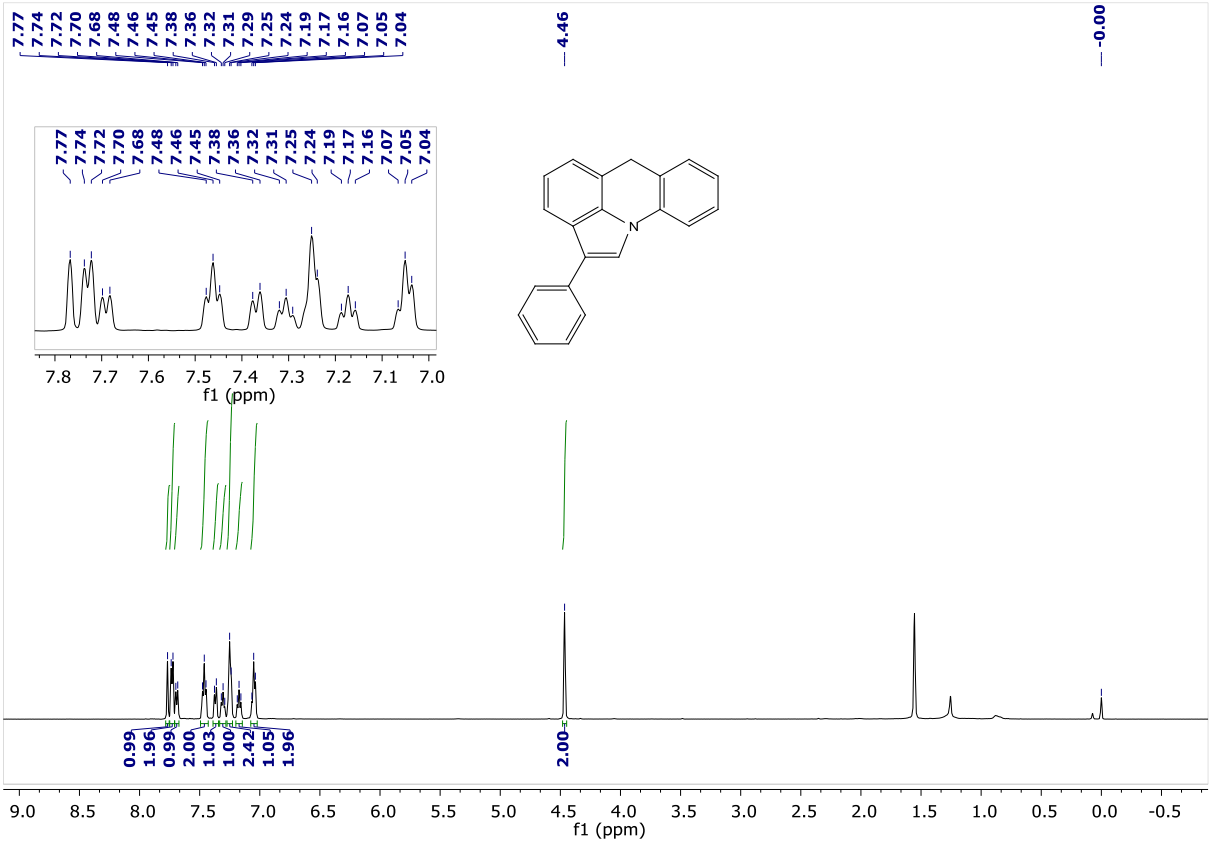


Figure S161: ^{1}H NMR Spectrum of **10f** ($CDCl_3$, 500 MHz, 298 K).

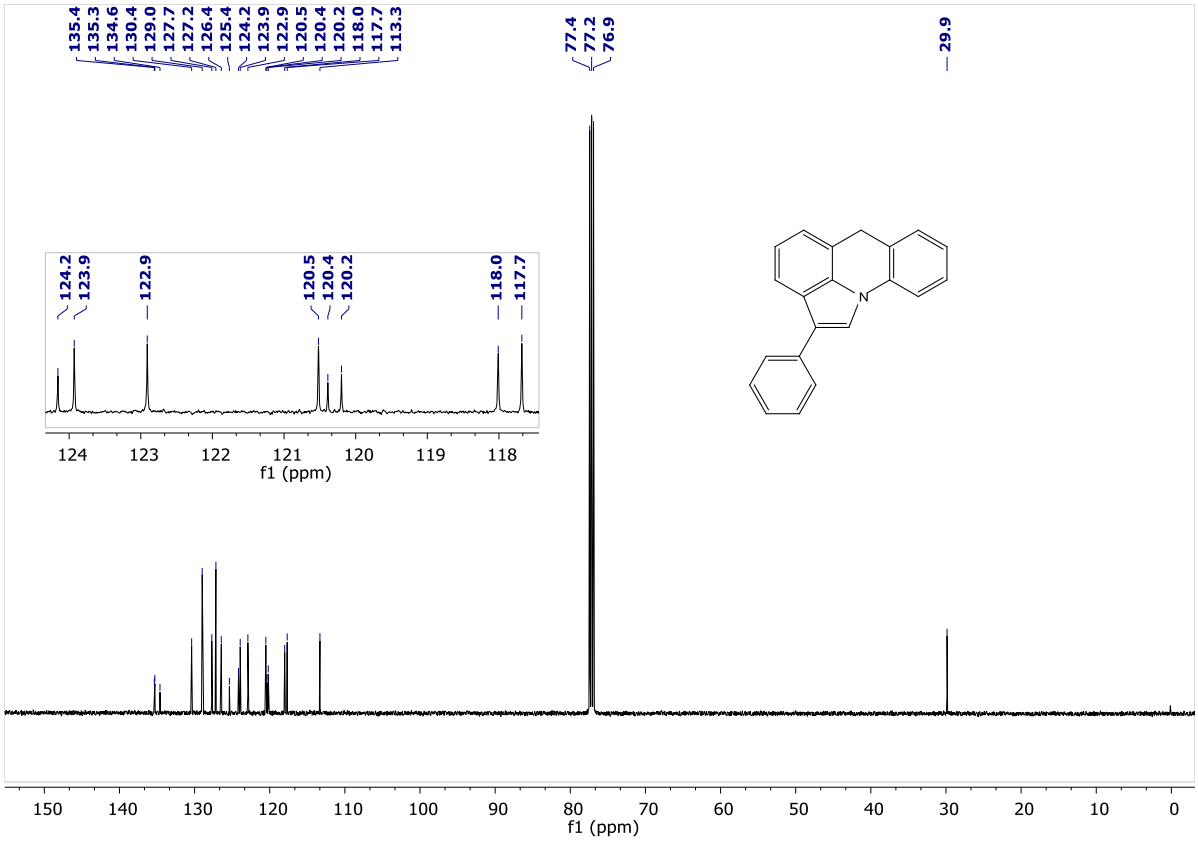


Figure S162: ^{13}C {^{1}H} NMR Spectrum of **10f** ($CDCl_3$, 126 MHz, 298 K).

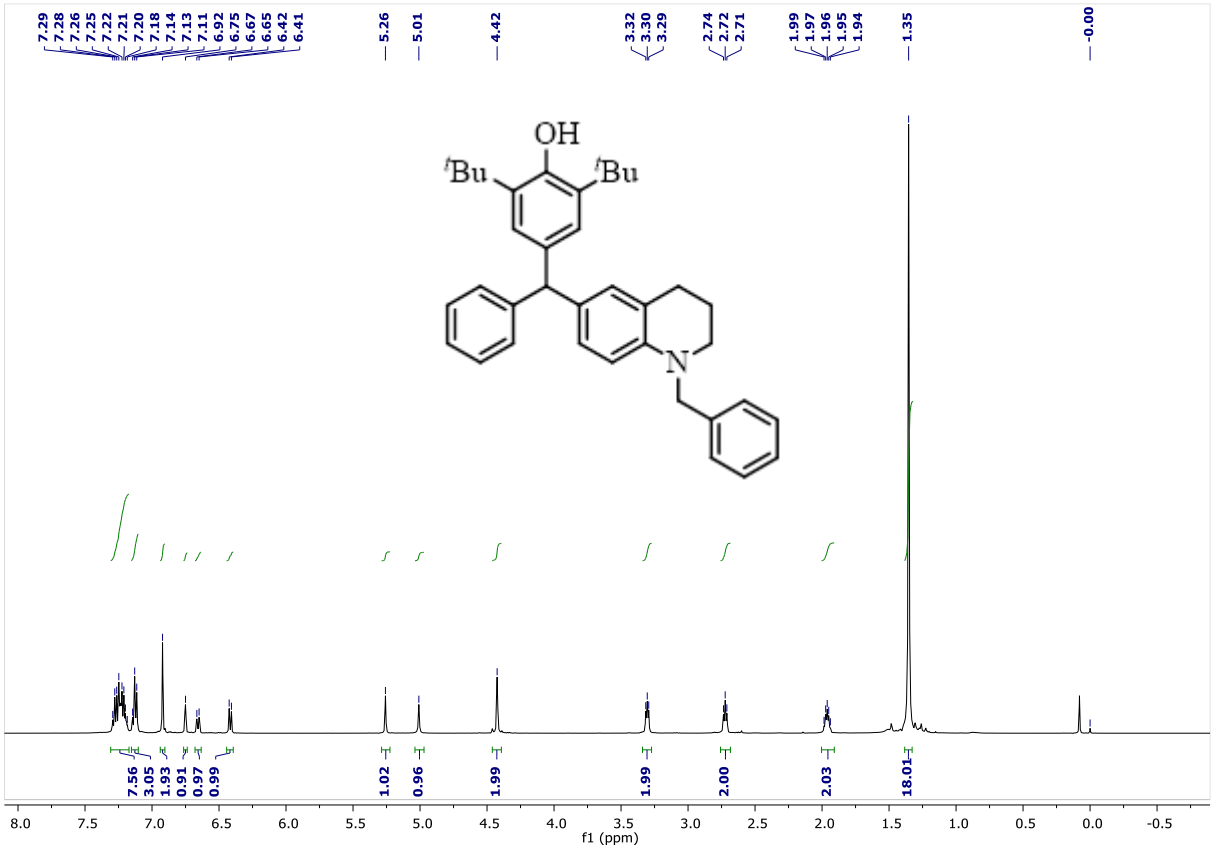


Figure S163: ^{1}H NMR Spectrum of **12a** ($CDCl_3$, 500 MHz, 298 K)

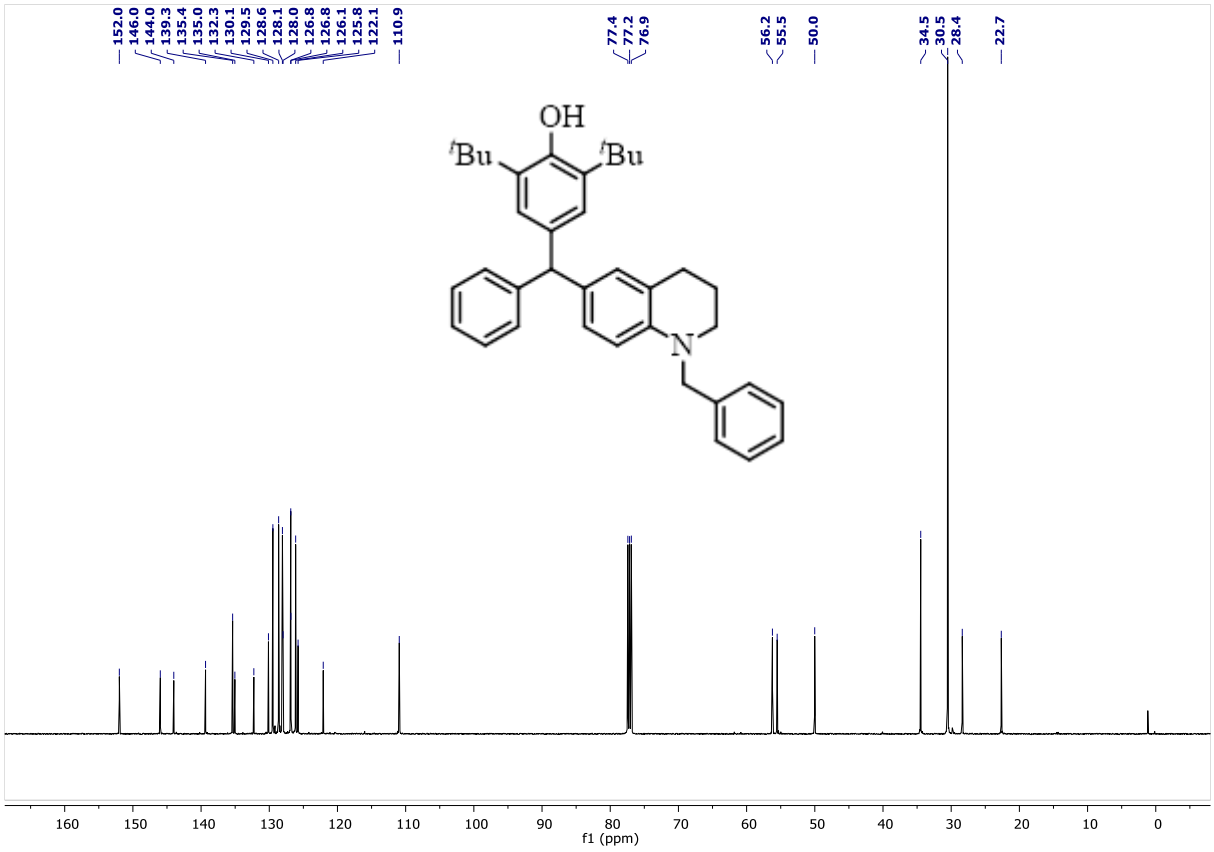


Figure S164: $^{13}C\{^{1}H\}$ NMR Spectrum of **12a** ($CDCl_3$, 126 MHz, 298 K)

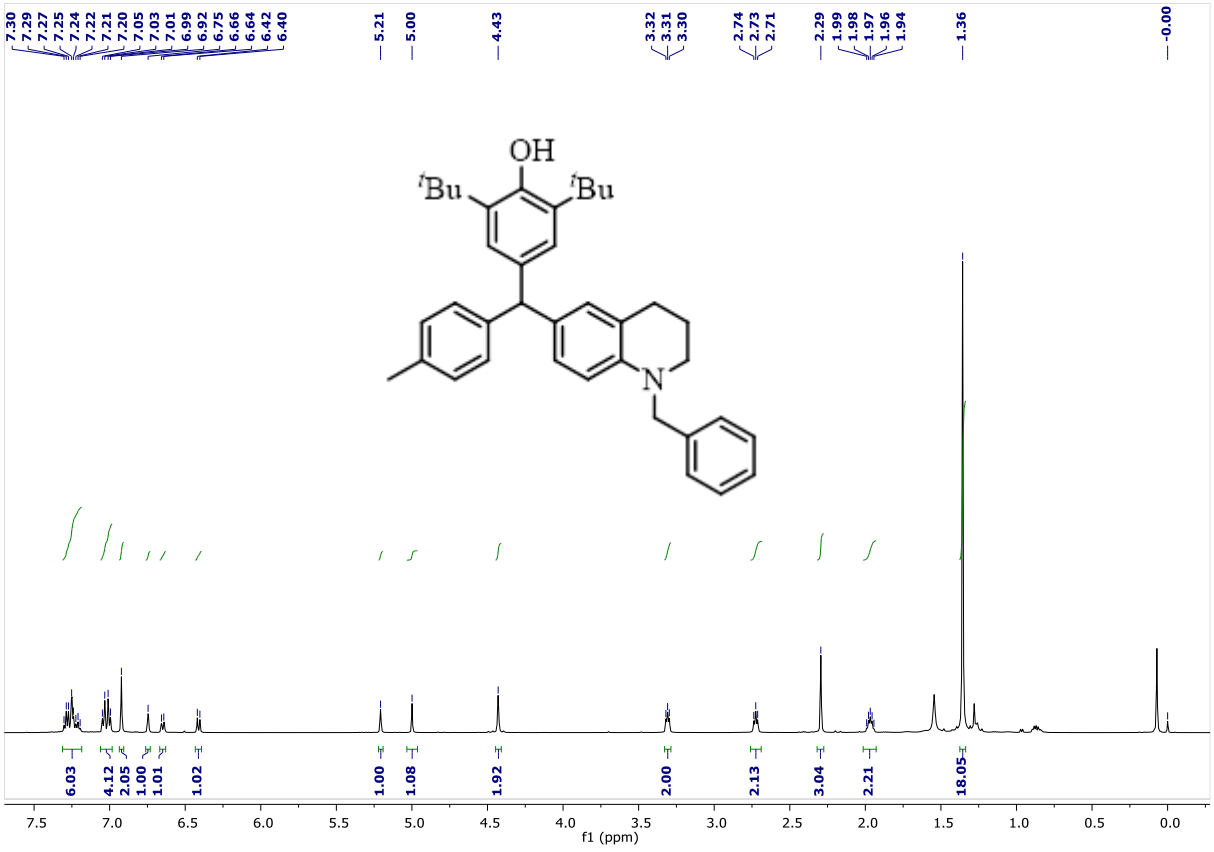


Figure S165: ^{1}H NMR Spectrum of **12b** ($CDCl_3$, 500 MHz, 298 K)

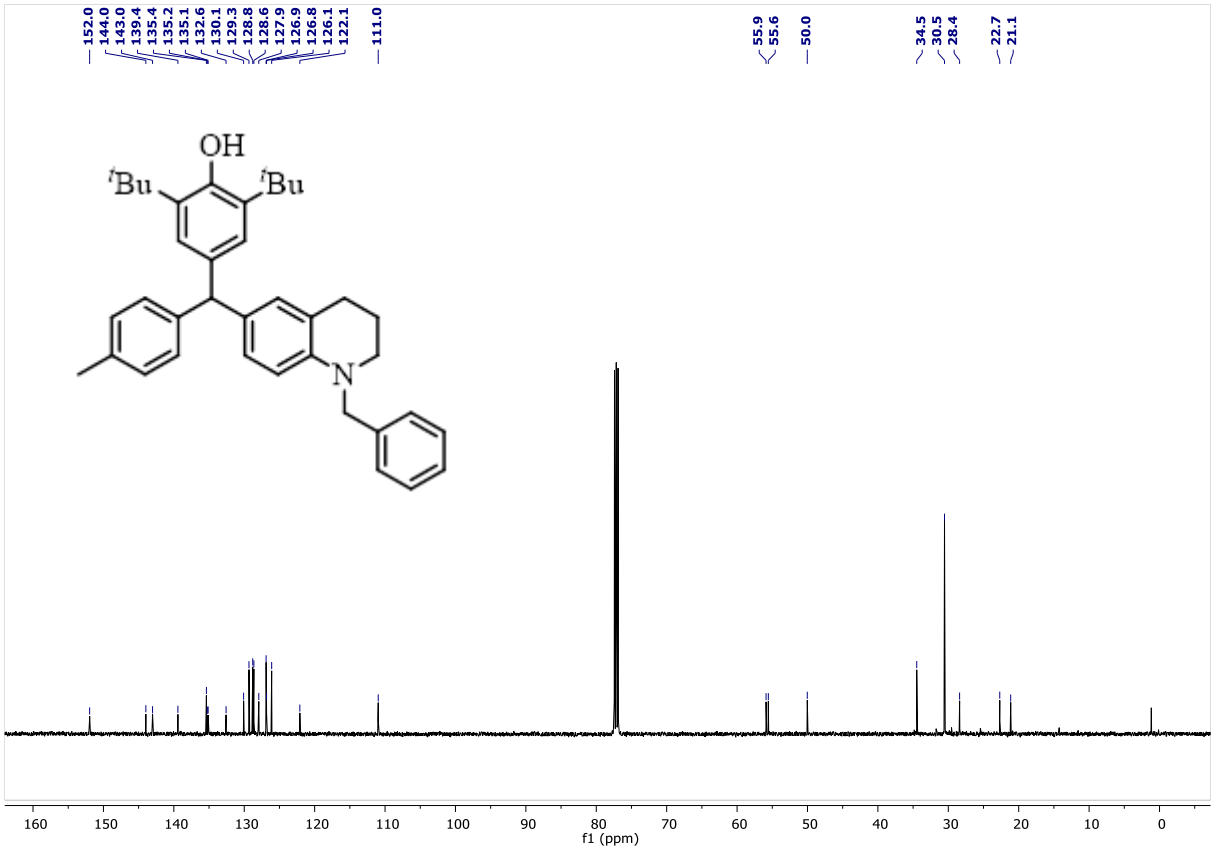


Figure S166: $^{13}C\{^{1}H\}$ NMR Spectrum of **12b** ($CDCl_3$, 126 MHz, 298 K)

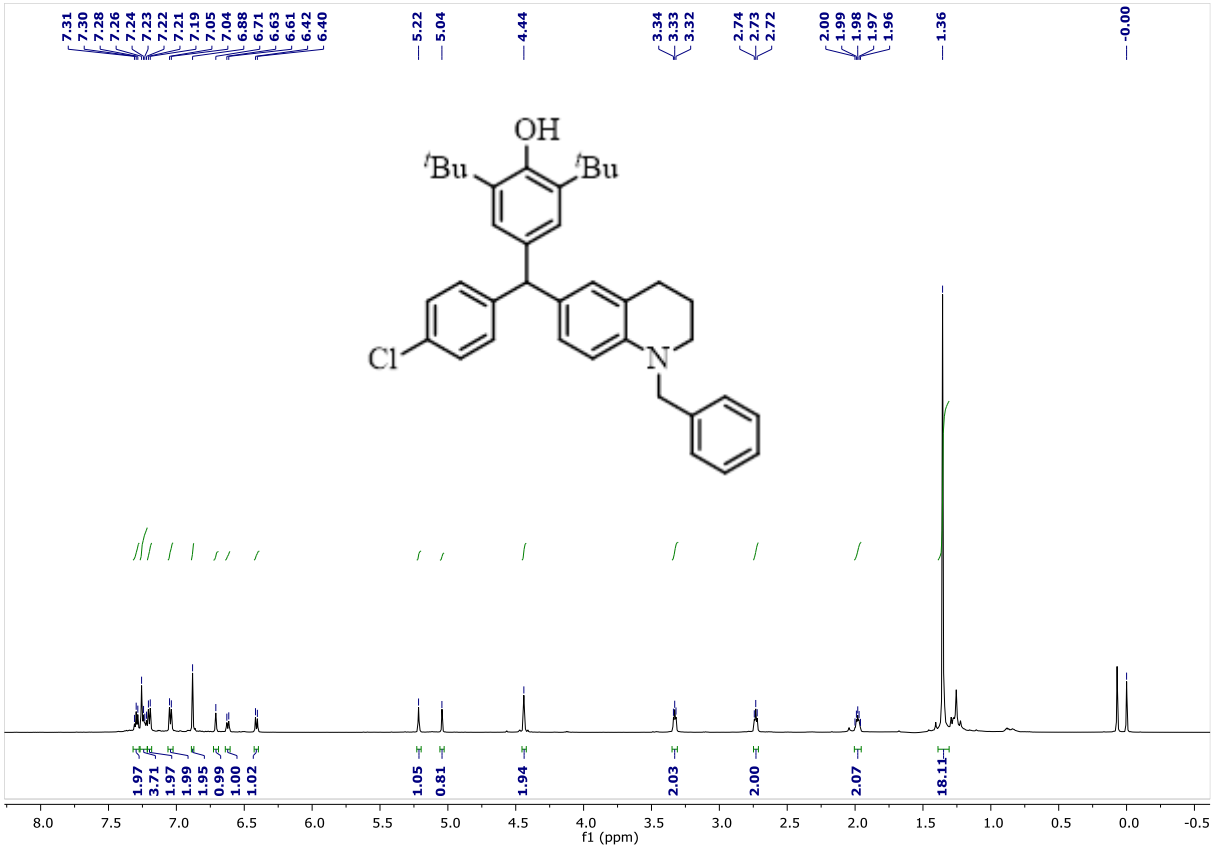


Figure S167: ^{1}H NMR Spectrum of **12c** ($CDCl_3$, 600 MHz, 298 K)

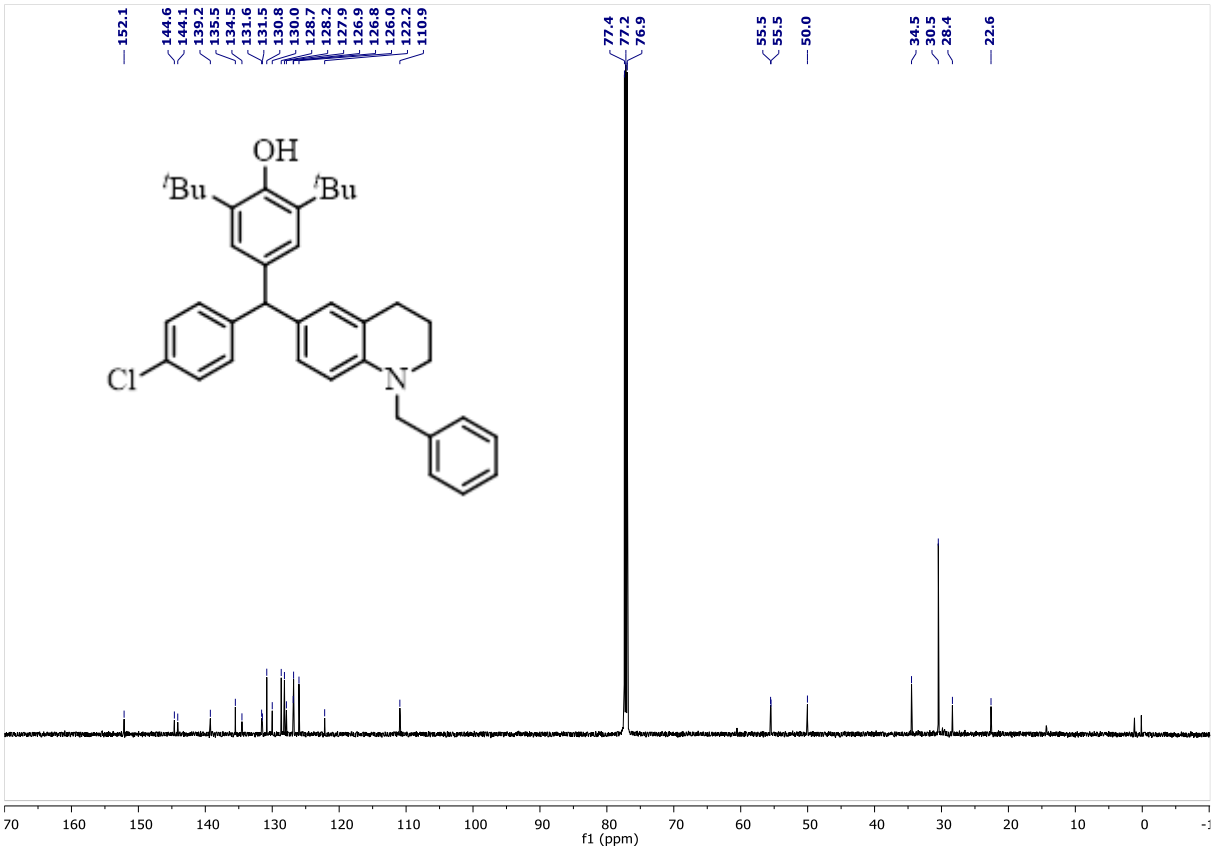


Figure S168: $^{13}C\{^{1}H\}$ NMR Spectrum of **12c** ($CDCl_3$, 151 MHz, 298 K)

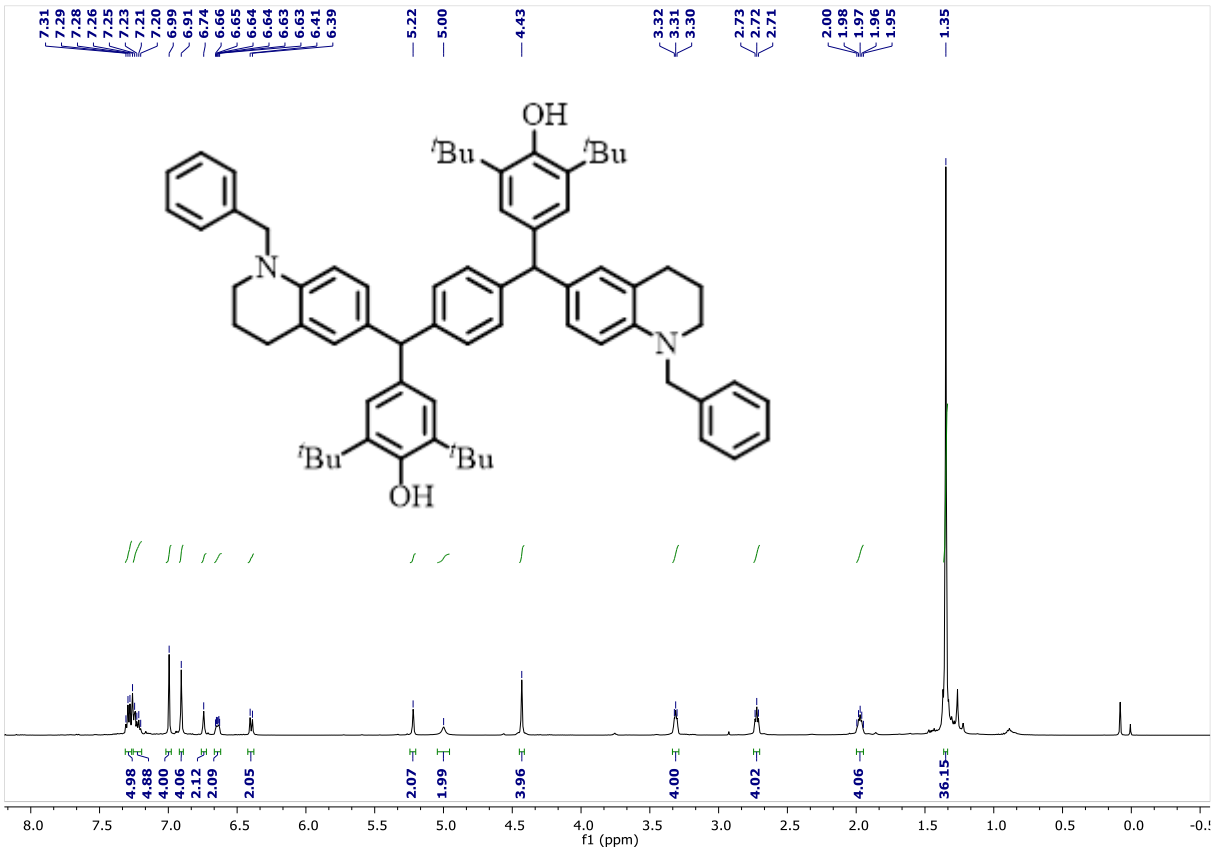


Figure S169: ^{1}H NMR Spectrum of **12d** ($CDCl_3$, 500 MHz, 298 K)

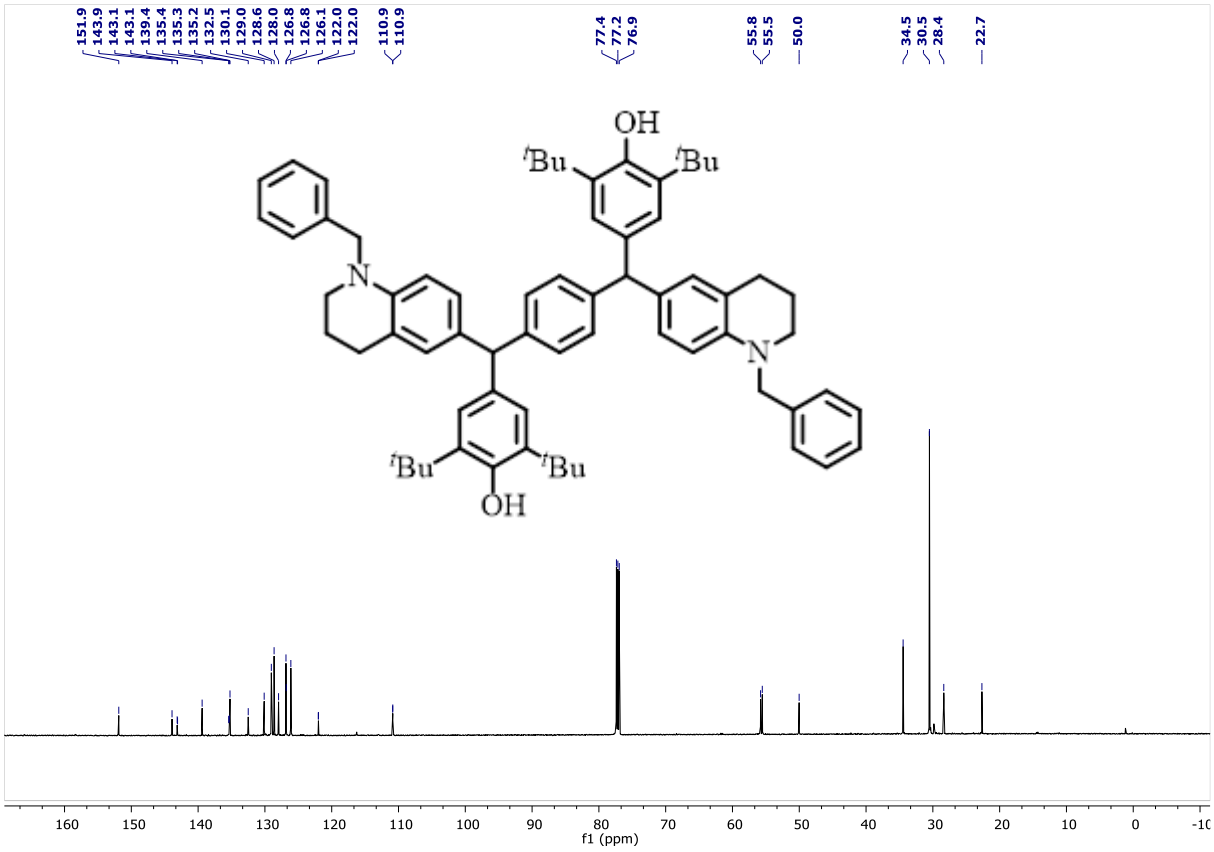


Figure S170: $^{13}C\{^{1}H\}$ NMR Spectrum of **12d** ($CDCl_3$, 151 MHz, 298 K)

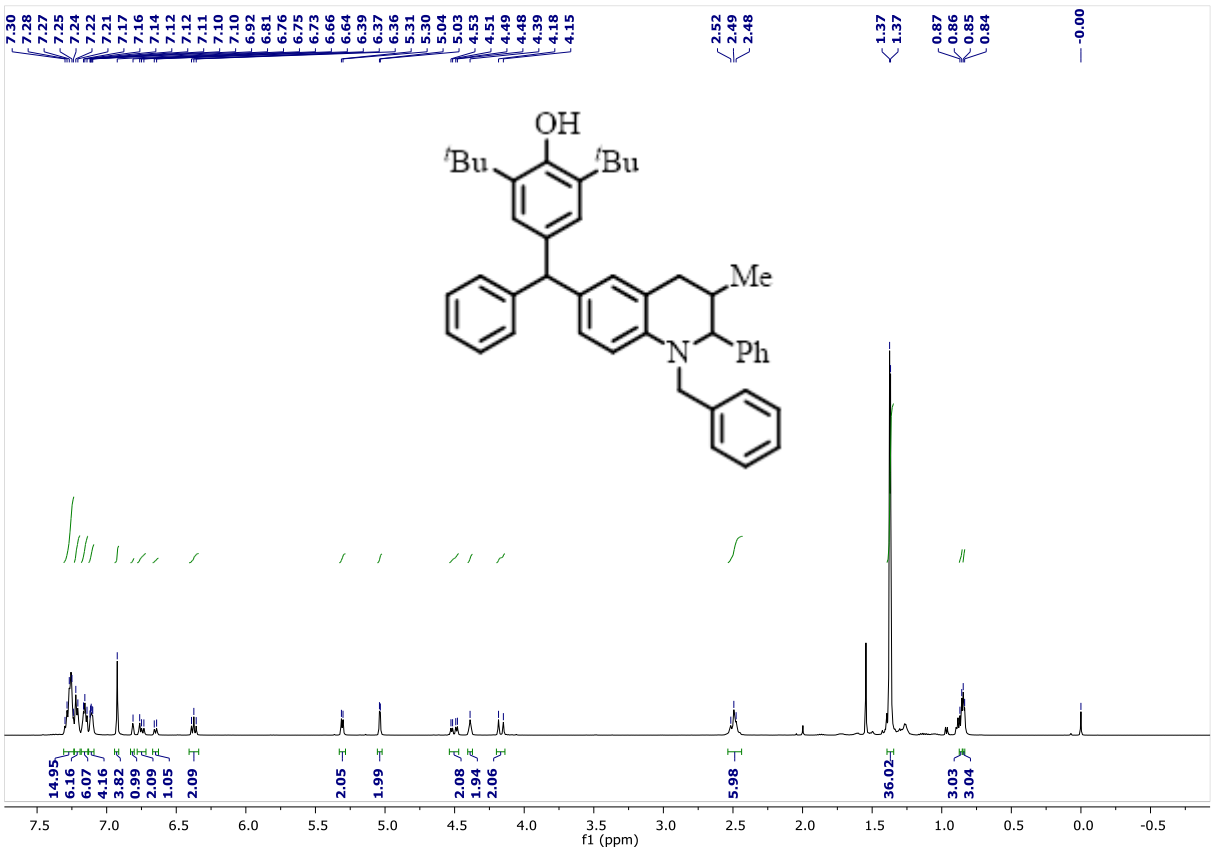


Figure S171: ^{1}H NMR Spectrum of **12e** ($CDCl_3$, 500 MHz, 298 K)

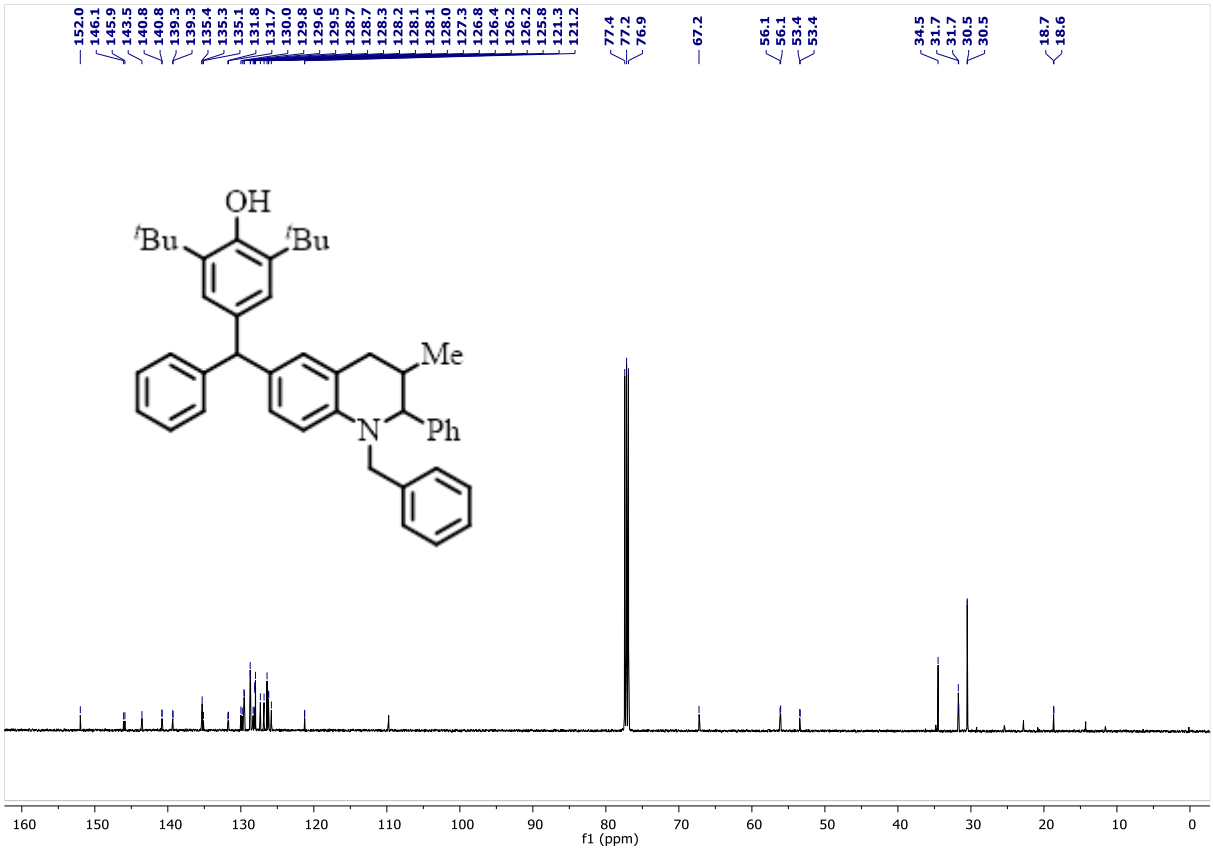


Figure S172: $^{13}C\{^{1}H\}$ NMR Spectrum of **12e** ($CDCl_3$, 126 MHz, 298 K)

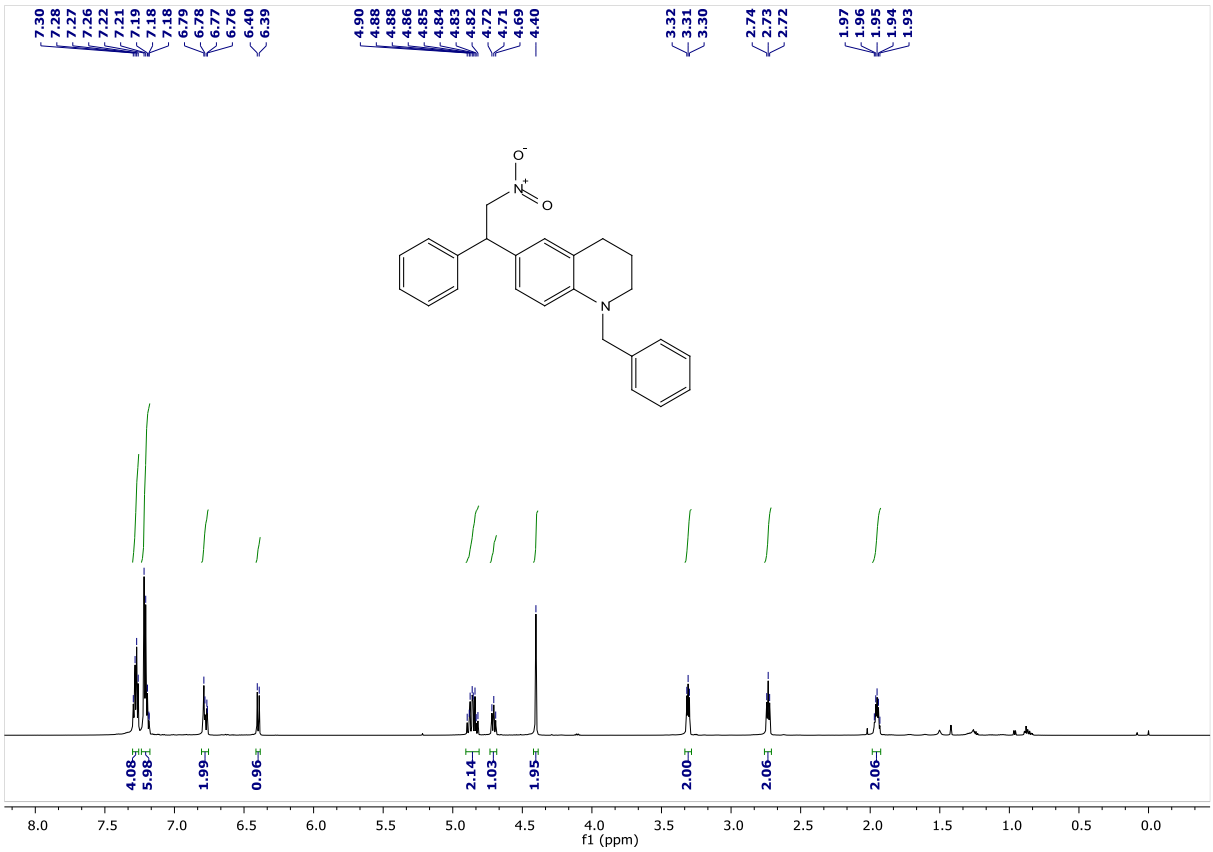


Figure S173: ^{1}H NMR Spectrum of **12f** ($CDCl_3$, 600 MHz, 298 K)

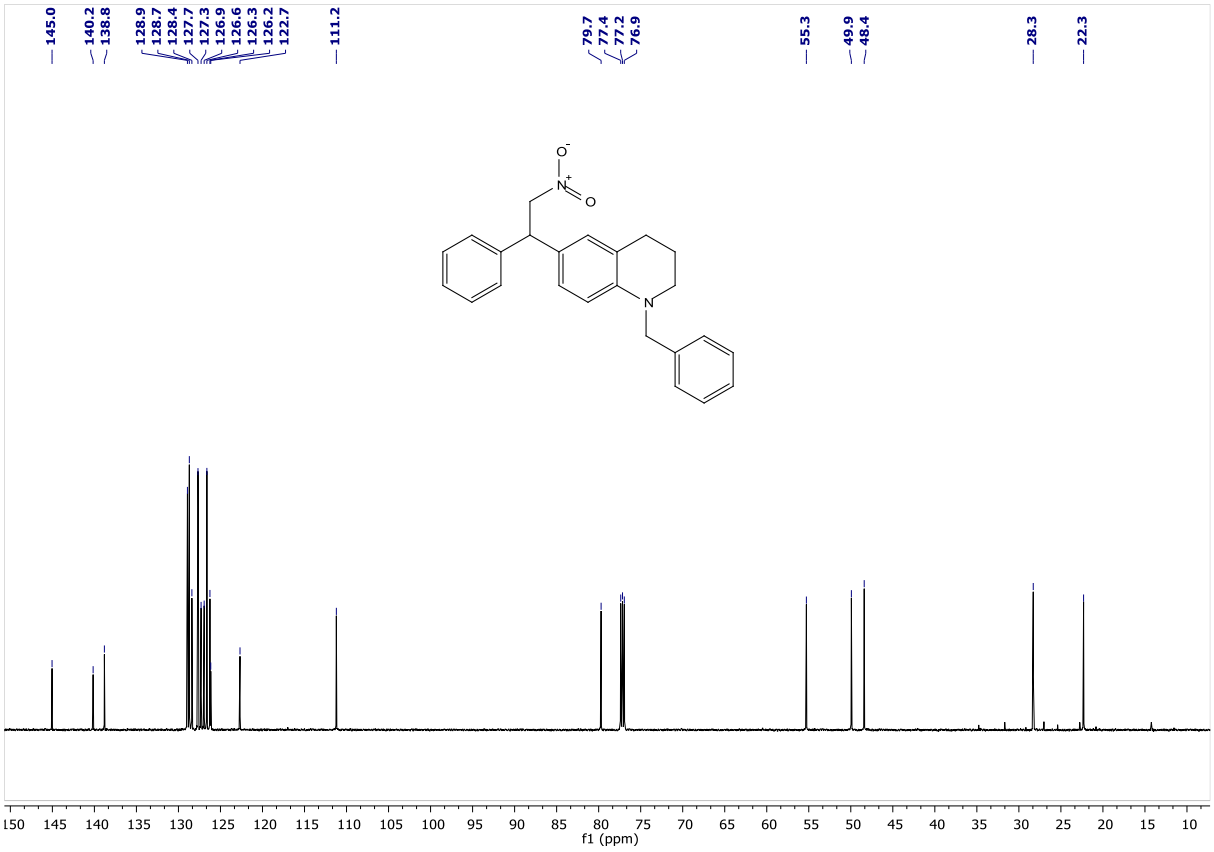


Figure S174: $^{13}C\{^{1}H\}$ NMR Spectrum of **12e** ($CDCl_3$, 151 MHz, 298 K)

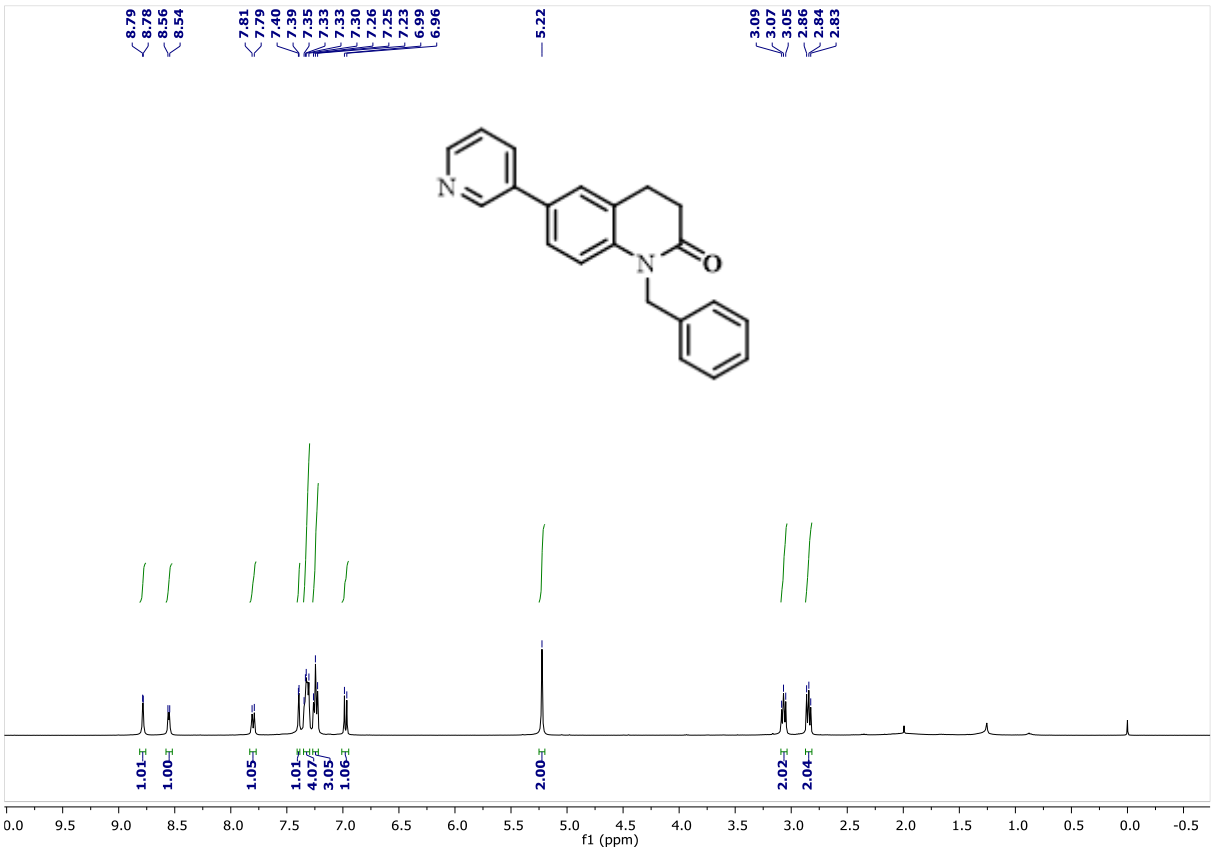


Figure S175: ^{1}H NMR Spectrum of **13** ($CDCl_3$, 400 MHz, 298 K)

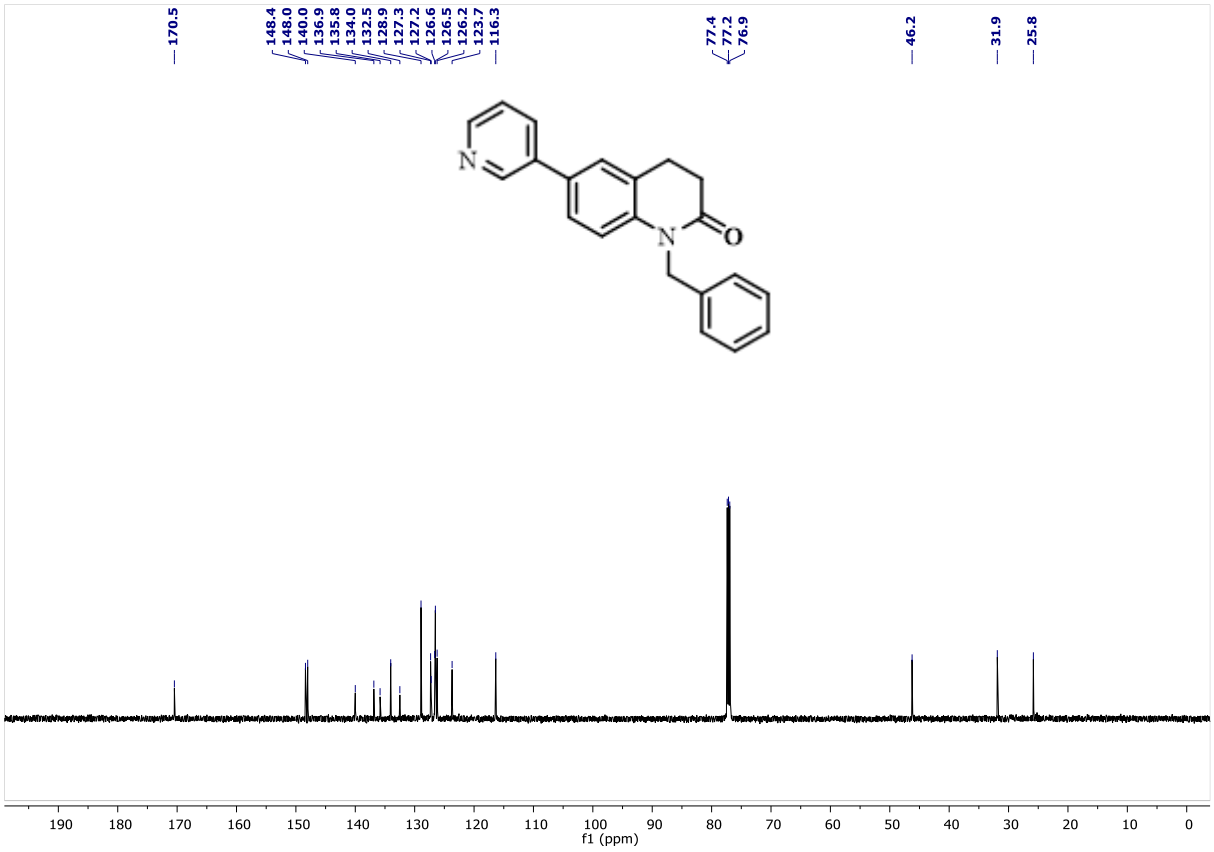


Figure S176: $^{13}C\{^{1}H\}$ NMR Spectrum of **13** ($CDCl_3$, 151 MHz, 298 K)

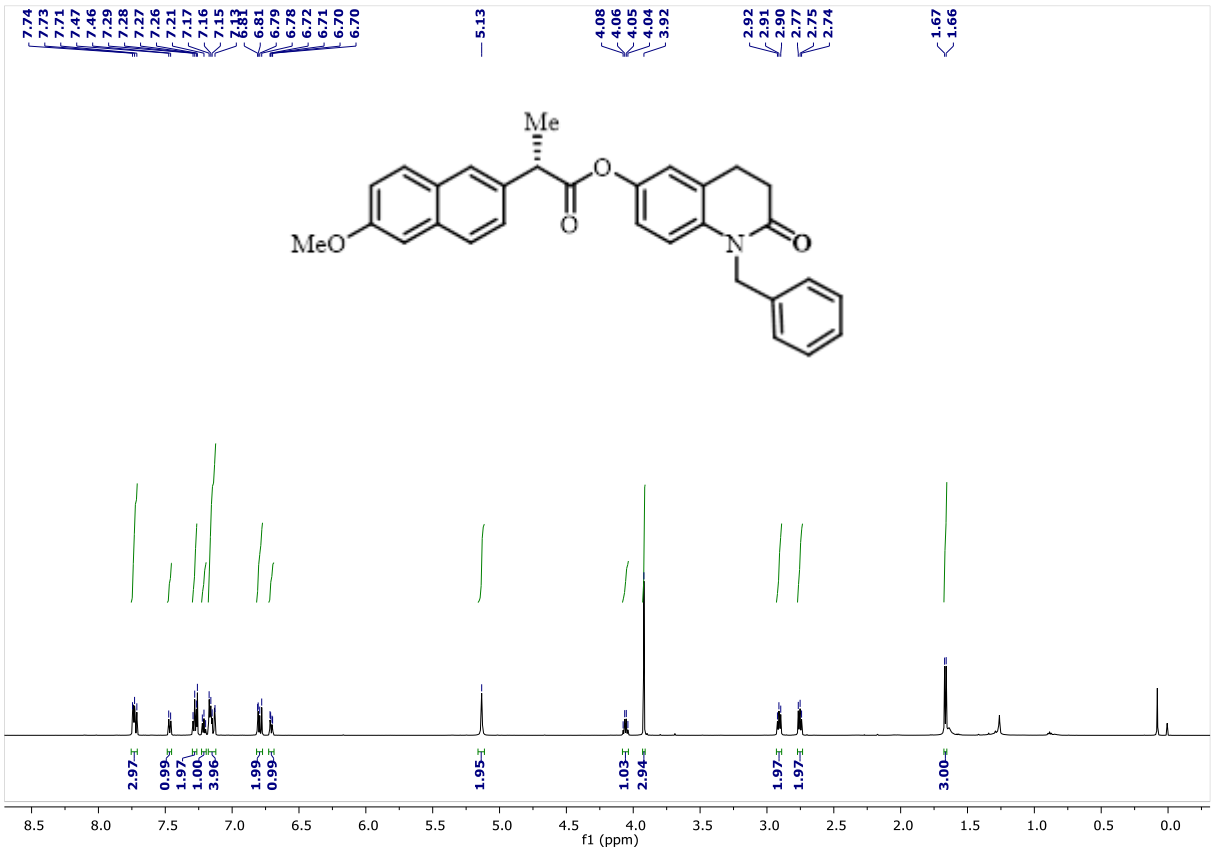


Figure S177: ^{1}H NMR Spectrum of **14** ($CDCl_3$, 600 MHz, 298 K)

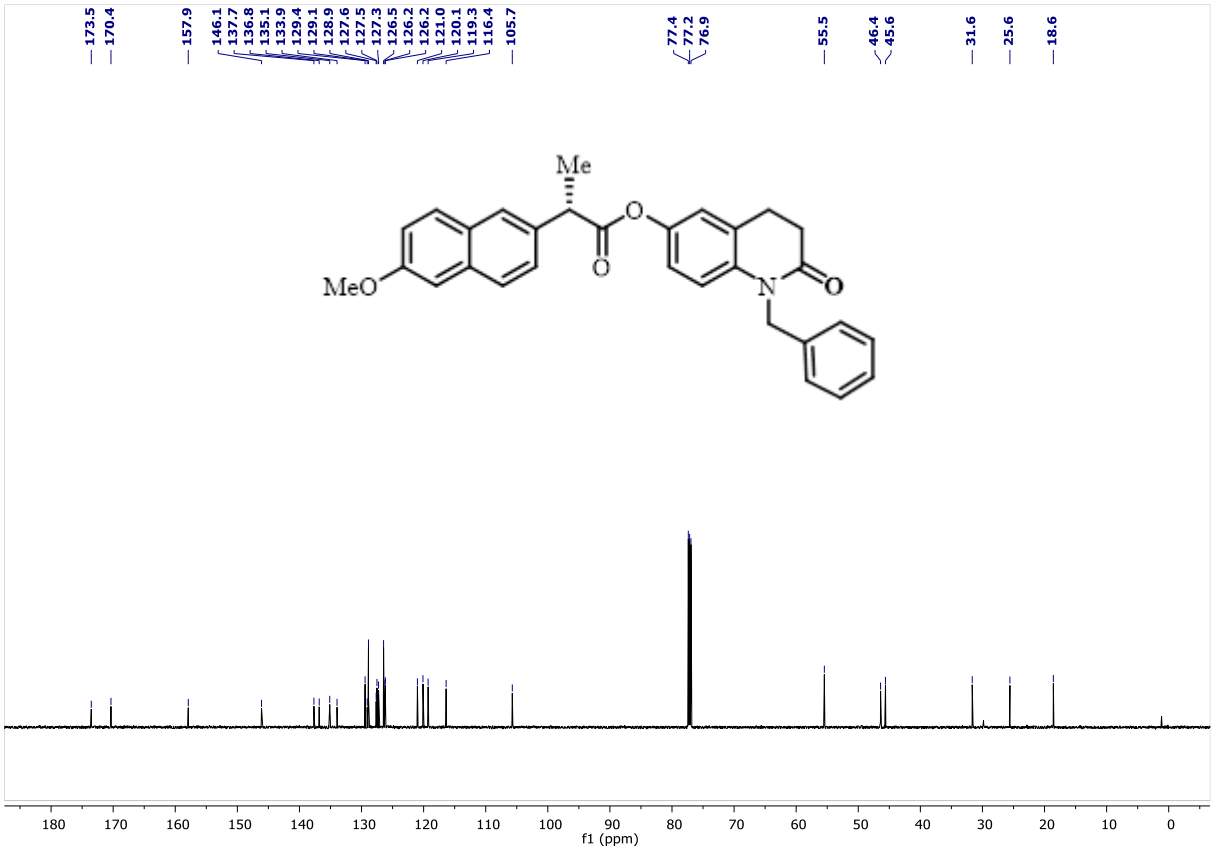


Figure S178: $^{13}C\{^{1}H\}$ NMR Spectrum of **14** ($CDCl_3$, 151 MHz, 298 K)

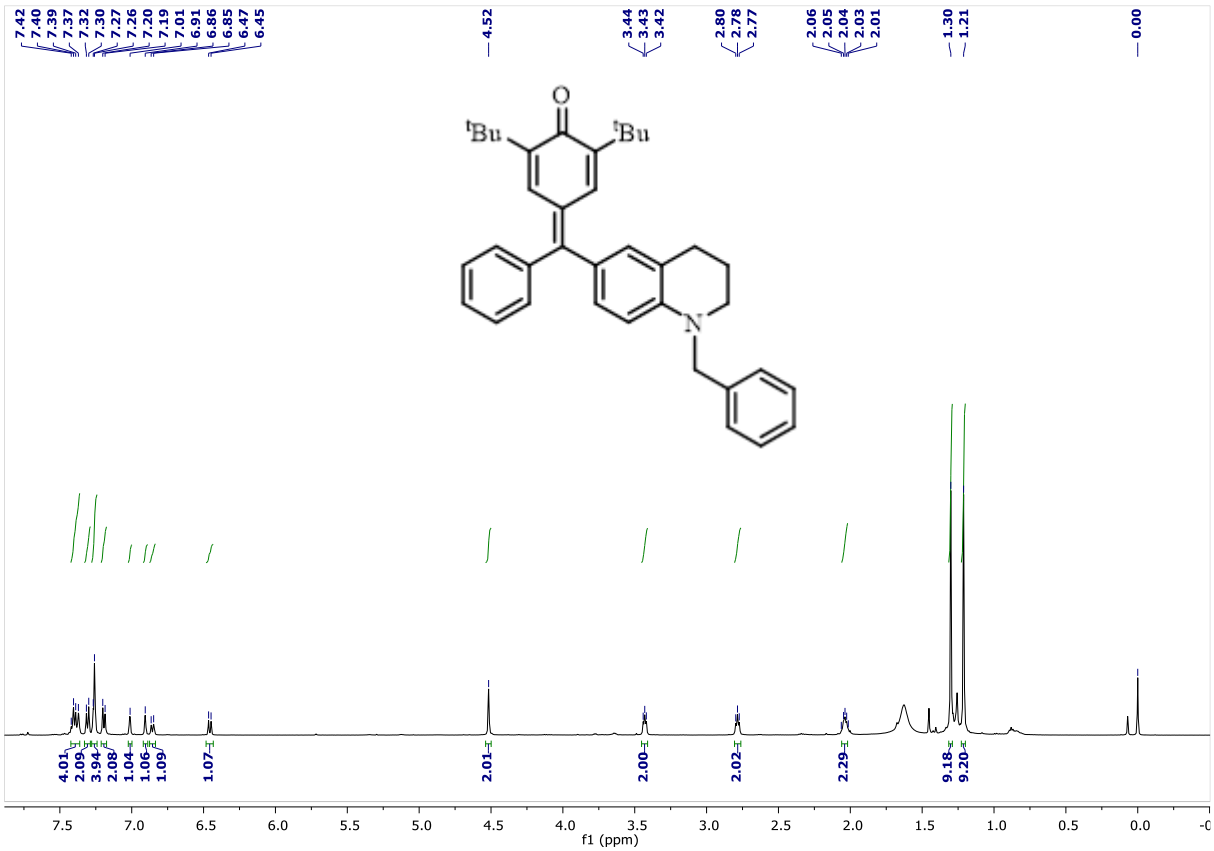


Figure S179: ^{1}H NMR Spectrum of **15** ($CDCl_3$, 500 MHz, 298 K)

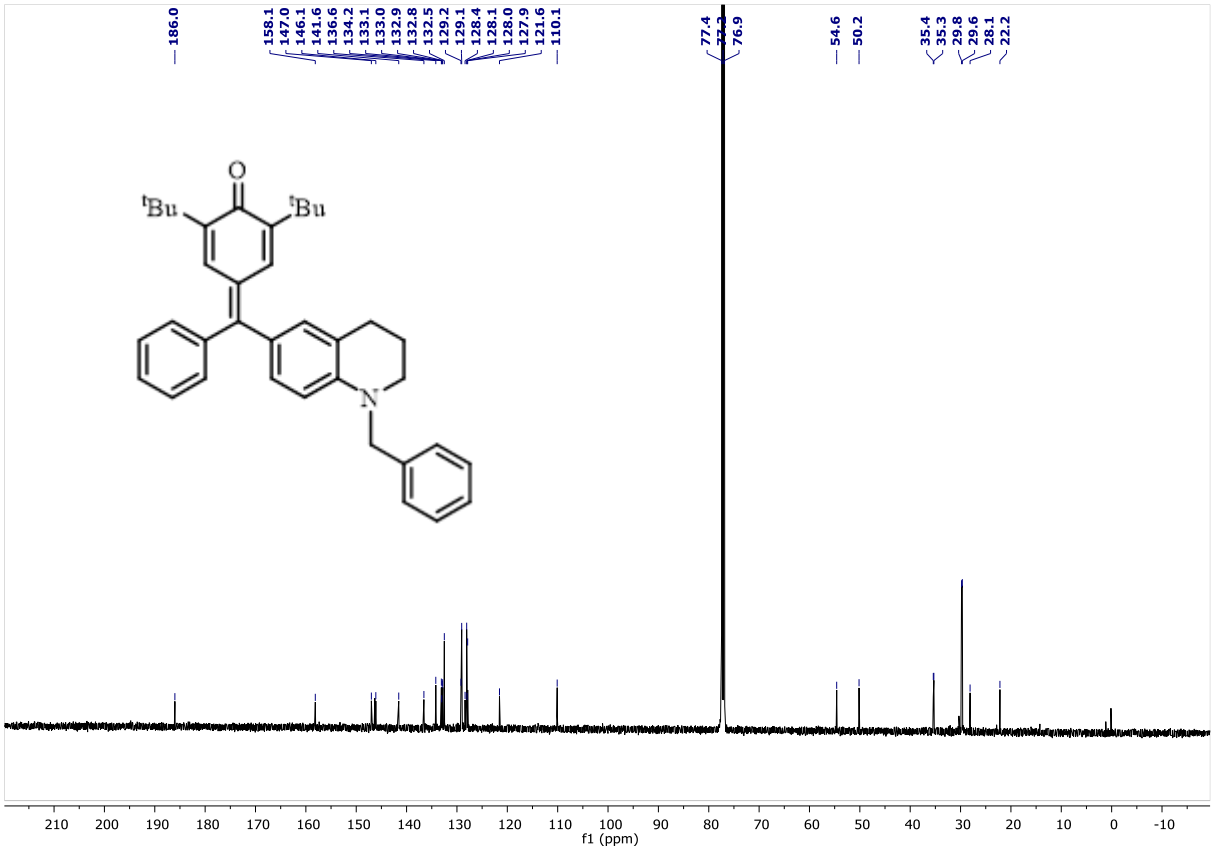


Figure S180: $^{13}C\{^{1}H\}$ NMR Spectrum of **15** ($CDCl_3$, 126 MHz, 298 K)

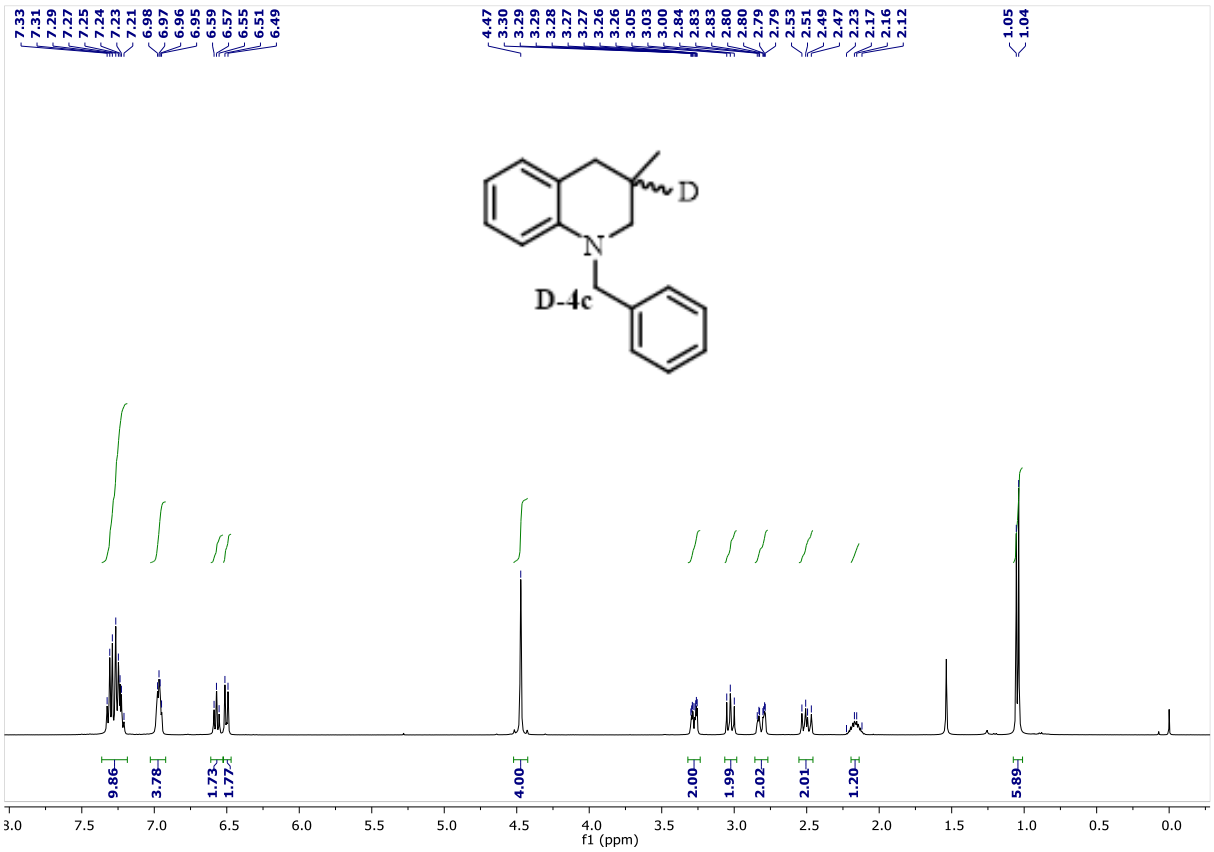


Figure S181: ^{1}H NMR Spectrum of **D-4c** ($CDCl_3$, 400 MHz, 298 K)

13. References

1. A. Hantzsch, *Justus Liebigs Ann. Chem.,* 1882, **215**, 1-82.
2. Y. Gong, J. He, X. Wen, H. Xi, Z. Wei and W. Liu, *Org. Chem. Front.*, 2021, **8**, 6901.
3. M. Konwar, T. Das and A. Das, *Org. Lett.*, 2024, **26**, 1184.
4. S.K. Senapati, A. Pal and A. Das, *Org. Biomol. Chem.*, 2024, **22**, 4041.
5. V. P. Patil, V. L. Markad, K. M. Kodam and S. B. Waghmode, *Bioorg. Med. Chem. Lett*., 2013, **23**, 6259.
6. S. Hu, Y. Jin, Y. Liu, M. Ljungman and N. Neamati, *Eur. J. Med. Chem.*, 2018, **158**, 884.
7. A. Y. Dubovtsev, D. V. Dar'in, M. Krasavin and V. Yu. Kukushkin, *Eur. J. Org. Chem.*, 2019, **8**, 1856.
8. G. V. Rao, B. N. Swamy, V. Chandregowda and G. C. Reddy, *Eur. J. Med. Chem.,* 2009, **44**, 2239.
9. S. Cao, D. Kim, W. Lee and S. Hong, *Angew. Chem., Int. Ed.,* 2023, **62**, e202312780.
10. M. Mandal, R. Pradhan, U. Lourderaj and R. Balamurugan, *J. Org. Chem*., 2023, **88**, 2260.
11. Y. Zhang, P. Ji, W. Hu, Y. Wei, H. Huang and W. Wang, *Chem. Eur. J.,* 2019, **25**, 8225.
12. Y. Zhai, X. Zhang and S. Ma, *Chem. Sci.,* 2021, **12**, 11330.
13. J. Li, Z. Liang, Y. Ren, J. Gao and D. Du, *Org. Chem. Front.,* 2023, **10**, 1669.
14. X. Jiang, G. Wang, Z. Zheng, X. Yu, Y. Hong, H. Xia and C. Yu, *Org. Lett.,* 2020, **22**, 9762.
15. P. Adhikari, D. Bhattacharyya, S. Nandi, P. K. Kancharla and A. Das, *Org. Lett*., 2021, **23**, 2437.
16. B. Debnath, T. Sarkar, P. Karjee, S. K. Purkayastha, A. K. Guha and T. Punniyamurthy, *J. Org. Chem.*, 2023, **88**, 9704.
17. V. Akyildiz, F. Lafzi, H. Kilic and N. Saracoglu, *Org. Biomol. Chem.*, 2022, **20**, 3570.
18. Q. A. Chen, M. W. Chen, C. B. Yu, L. Shi, D. S. Wang, Y. Yang and Y. G. Zhou, *J. Am. Chem. Soc.*, 2011, **133**, 16432.
19. D. Bhattacharyya, S. Nandi, P. Adhikari, B. K. Sarmah, M. Konwar and A. Das, *Org. Biomol. Chem.*, 2020, **18**, 1214.
20. C-H. Yang, X. Chen, H. Li, W. Wei, Z. Yang and J. Chang, *Chem. Commun.*, 2018, **54**, 8622-8625.
21. N. Yi, Y. Liu, Y. Xiong, H. Gong, J.-P. Tan, Z. Fang and B. Yi, *J. Org. Chem*., 2023, **88**, 11945.