Supporting Information

Triple role of boronic acid as a catalyst in the alkylation of quinoline to functionalized tetrahydroquinoline

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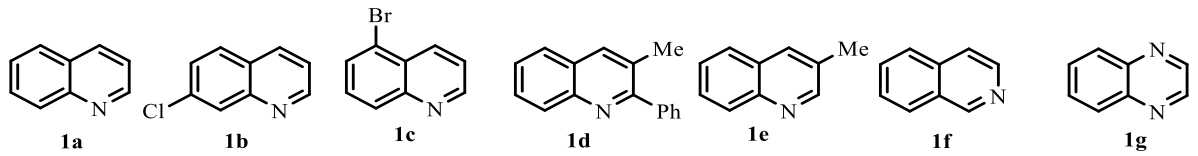
1. General Information

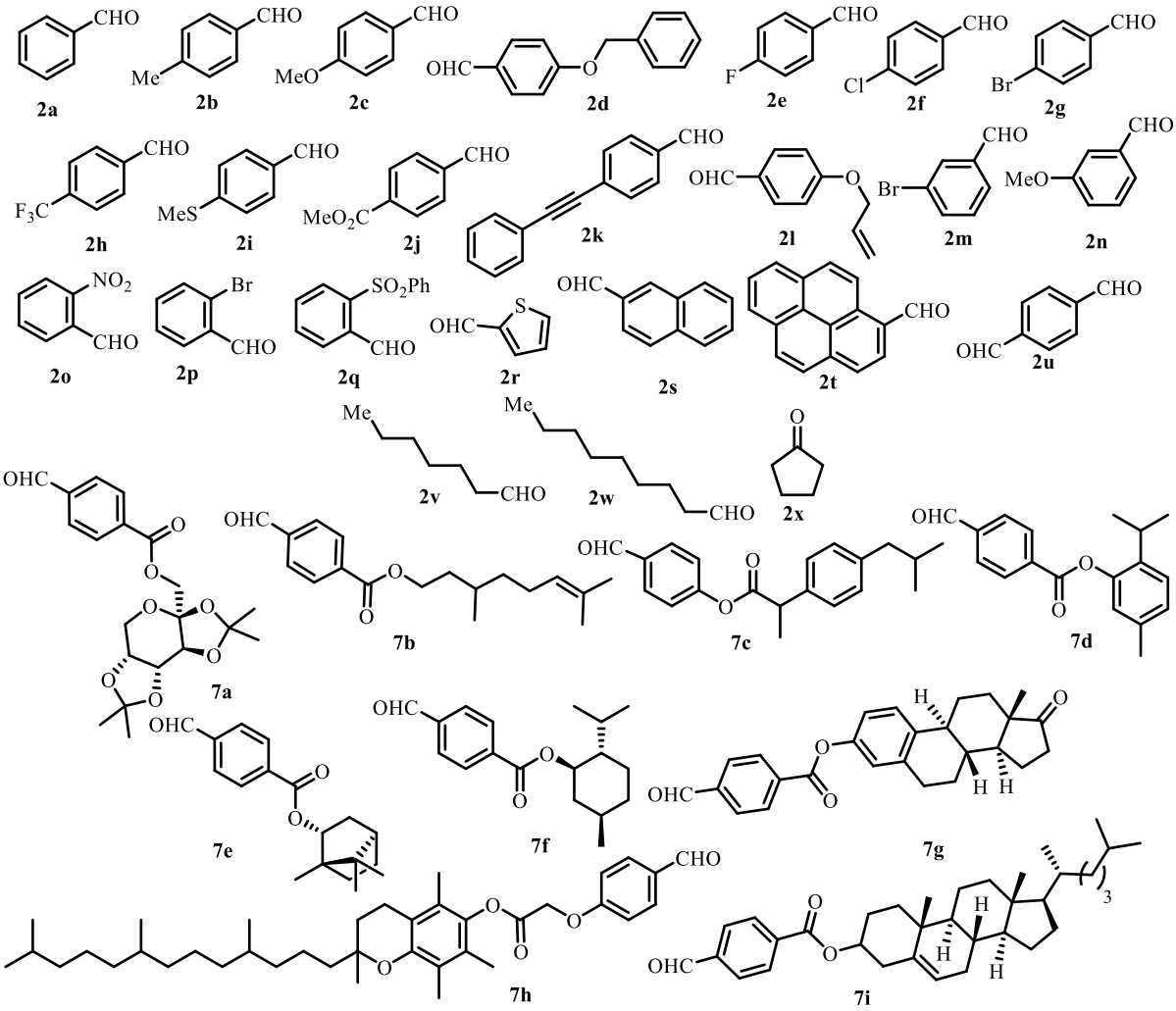
All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd., Finar Chemicals, and BLD Pharma directly used as received without any further purification unless otherwise mentioned. Hantzsch ester was synthesized according to the reported literature.[1] ^{1}H, ^{13}C, ^{11}B 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, pent = 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:

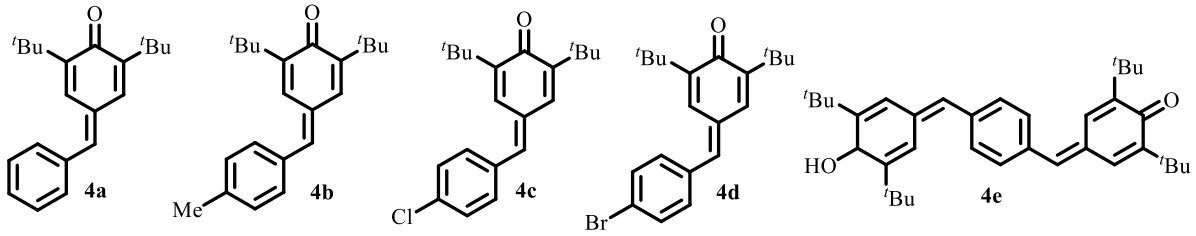


2.2 Aldehydes and ketone employed in the reaction:



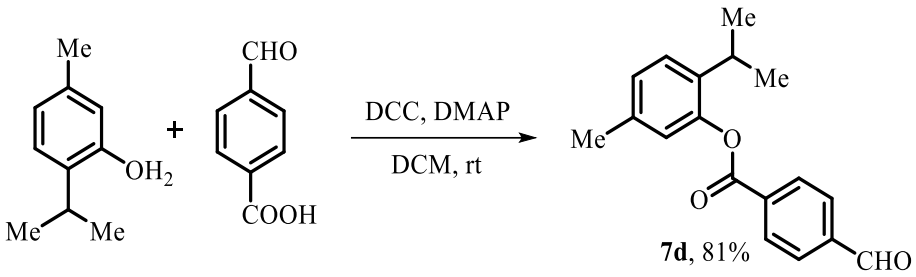
Compounds **2d**,[2] **2k**,[3] **2l**,[4] are synthesized by known procedure. The biologically relevant motifs containing aldehyde derivatives **7a**,[5] **7b,**[6] **7c,**[7] **7e**,[8] **7f**,[9] **7g**,[10] **7h**,[11], **7i** [9] were synthesized by the known procedure.

2.3 *para*-quinone methides (*p*-QMs) employed in the reaction:



Compounds **4b-4c**[12]**, 4d**[13] are synthesized by known procedures.

Synthesis of 2-isopropyl-5-methylphenyl 4-formylbenzoate (7d)



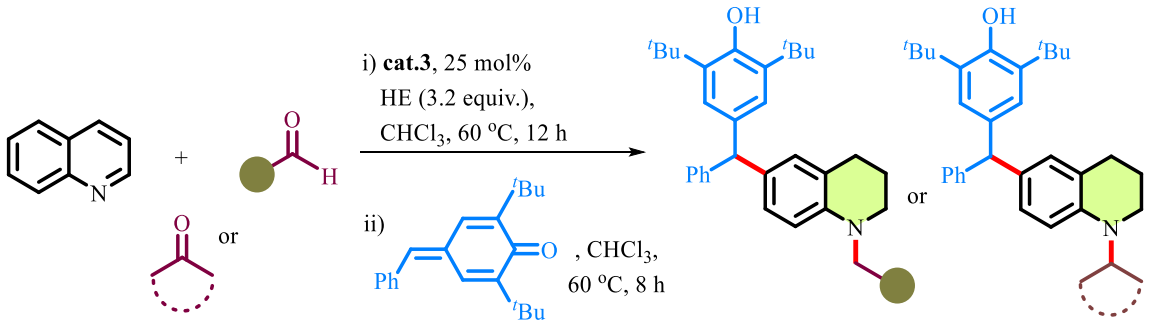
Scheme S1: Synthesis of 2-isopropyl-5-methylphenyl 4-formylbenzoate (**7d**)

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 **7d** as yellow oil (0.343 g, 81%). Compound **7d** was prepared for the first time following a known procedure. [9]

^{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 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 *C*-functionalized THQ derivatives

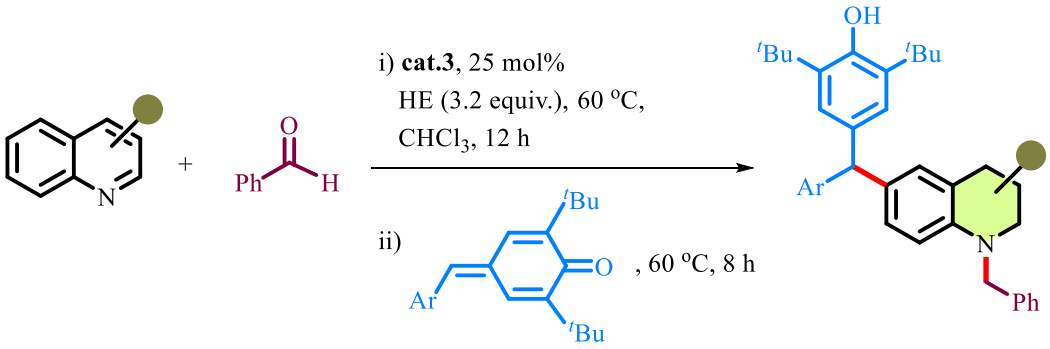
3.1 General procedure for synthesis of *C*-functionalized THQ derivatives with different carbonyls (GP-1)



Scheme S2. Synthesis of *C*-functionalized THQ derivatives

Reaction condition: A mixture of quinoline **1a** (1.0 mmol, 1.0 equiv.), substituted aldehyde or cyclic ketone **2** (1.0 mmol, 1.0 equiv.), HE (3.2 mmol, 3.2 equiv.) and cat.**3** (25 mol%) in $CHCl_3$ (2 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 12 h. Then *p*-QMs **4a** (1.0 mmol) was added in the same reaction tube at 60 °C with continuous stirring for 8 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 *C*-functionalized THQ derivatives with different quinolines and *p*-QMs (GP-2)

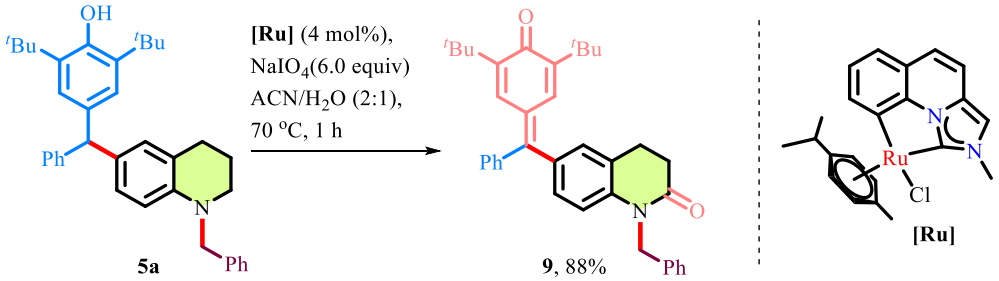


Scheme S2. Synthesis of *C*-functionalized THQ derivatives

Reaction condition: A mixture of substituted quinolines **1** (1.0 mmol, 1.0 equiv.), benzaldehyde (1.0 mmol, 1.0 equiv.), HE (3.2 mmol, 3.2 equiv.) and cat.**3** (25 mol%) in $CHCl_3$ (2 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 12 h. Then substituted *p*-QMs **4** (1.0 mmol, 1.0 equiv.) was added in the same reaction tube at 60 °C with continuous stirring for 8 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. Post synthetic modification

1-benzyl-6-((3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene) (phenyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (10)

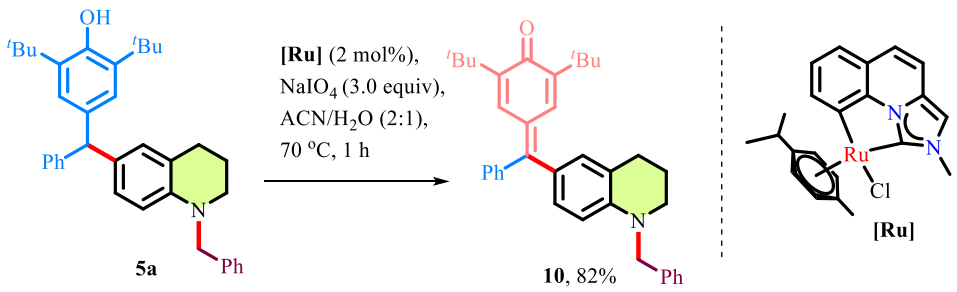


Scheme S3. Functionalization of (5a)

Experimental procedure: $NaIO_4$ (0.640 g, 3.0 mmol, 6 equiv.) was taken in a screw-capped reaction tube and dissolved it in water (1.0 mL). The **5a** (0.147 g, 0.5 mmol, 1 equiv.), **Ru-2** (4 mol%), and acetonitrile (2.0 mL) were added to the reaction tube and stirred the reaction mixture at 70 ºC 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 yield the desired compound **9** as orange solid (88%, 0.233 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 3H), 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 5H), 7.16 (d, J = 2.6 Hz, 1H), 7.09 (d, J = 2.6 Hz, 1H), 7.04 (s, 1H), 7.01 – 6.98 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.22 (s, 2H), 2.99 – 2.96 (m, 2H), 2.85 – 2.81 (m, 2H), 1.24 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 186.2, 170.5, 155.2, 147.54, 147.46, 140.9, 140.8, 136.8, 135.4, 132.13, 132.08, 131.9, 131.8, 131.7, 129.8, 129.4, 128.9, 128.2, 127.4, 126.6, 126.0, 115.2, 46.4, 35.45, 35.40, 31.9, 29.7, 29.6, 25.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{40}NO_2$: 530.3054; found 530.3058. Spectral data is in accordance to the reported literature. [14]

Synthesis of 4-((1-benzyl-1,2,3,4-tetrahydroquinolin-6-yl) (phenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (10)

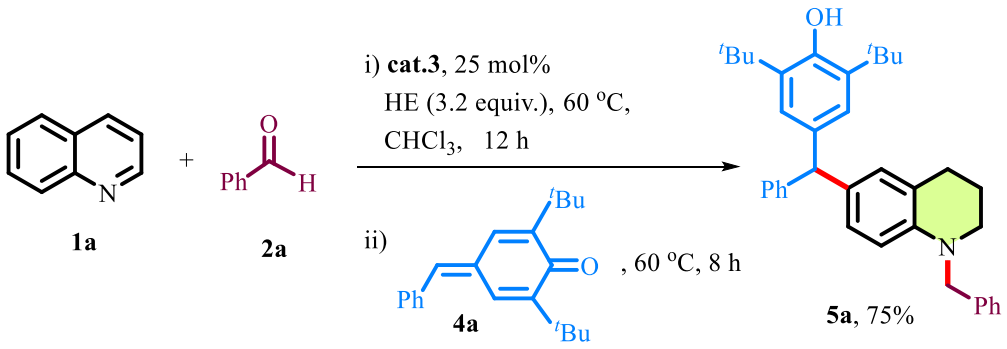


Scheme S4. Functionalization of (5a)

Experimental procedure [14]: $NaIO_4$ (0.320 g, 1.5 mmol, 3.0 equiv.) was taken in a screw-capped reaction tube and dissolved it in water (1.0 mL). The **5a** (0.147 g, 0.5 mmol, 1.0 equiv.), **Ru-2** (2 mol%), and acetonitrile (2.0 mL) were added to the reaction tube and stirred the reaction mixture at 70 ºC 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, 5.0 mL). The combined organic layer was washed with brine solution (8.0 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 yield the desired compound **10** as orange solid (82%, 0.211 g).

^{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 (m, 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. [14]

5. Gram scale reaction

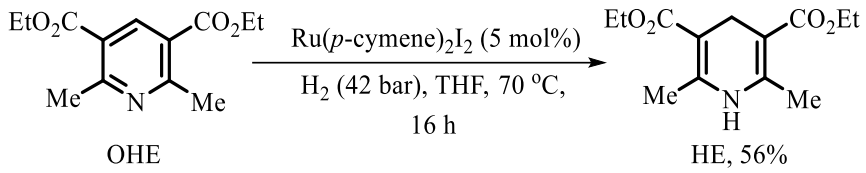


Scheme S5: Gram scale reaction

Reaction condition: A mixture of quinoline **1a** (1.0 g, 7.7 mmol, 1.0 equiv), benzaldehyde **2a** (0.817 g, 7.7 mmol, 1.0 equiv.), HE (6.257 g, 24.6 mmol, 3.2 equiv.) and cat.**3** (25 mol%) in $CHCl_3$ (10.0 ml) were added into a reaction tube (25 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 12 h. Then *p*-QMs **4a** (2.264 g, 7.7 mmol, 1.0 equiv.) was added in the same reaction tube at 60 °C with continuous stirring for 8 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 dark-red liquid of **5a** (3.0 g, 75%).

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

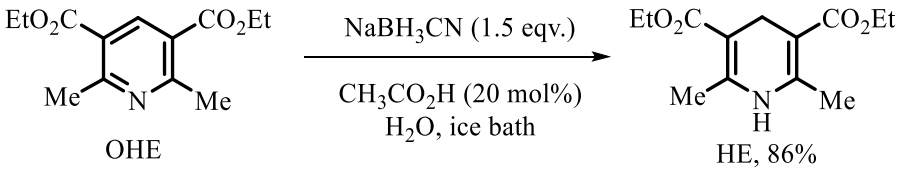
Route-A:



Scheme S6: Hydrogenation of oxidised Hantzsch ester

Experimental procedure: [15] A mixture of [Ru(*p*-cymene) I_2]$_2$ (10 mg, 0.01 mmol, 0.05 equiv.) and OHE (50.0 mg, 0.2 mmol, 1.0 equiv.) 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 ^oC under H_2 (42 bar) for 16 h. After carefully release of the hydrogen, the autoclave was opened. Isolated yield (yellow solid, 0.027 g, 56%).

Route-B



Scheme S7: Reduction of oxidised Hantzsch ester to Hantzsch-1,4-dihydropyridine ester

Experimental procedure: [16] In a 50 mL round bottom flask, OHE (1.0 gm, 3.9 mmol, 1.0 equiv.), water (10 mL) and acetic acid (45 µL, 20 mol%) were charged and placed in an ice bath. In the reaction mixture $NaBH_3CN$ (0.368 g, 5.85 mmol, 1.5 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: (0.83 g, 86%).

7. Control experiments and mechanistic studies

7.1 Interaction of Arylboronic acid with quinoline

To investigate the characteristics of the binding interaction with arylboronic acid and quinoline, the mixture of quinoline and 3-trifluoromethylphenylboronic acid (cat. **2**) (molar ratio 1:1, 2:1, and 3:1) in $CDCl_3$ at room temperature has been analyzed. The chemical shift for H2, H4, and H8 in quinoline is moved distinctly downfield, while the aromatic proton of boronic acid was shifted upfield. In addition, the hydroxyl peak of boronic acid was displaced downfield from δ

= 4.92 ppm to 5.86 ppm, indicating the hydrogen bonding interaction between the 'N'-atom of quinoline and the hydrogen atom of –OH in the boronic acid (Figure S1).

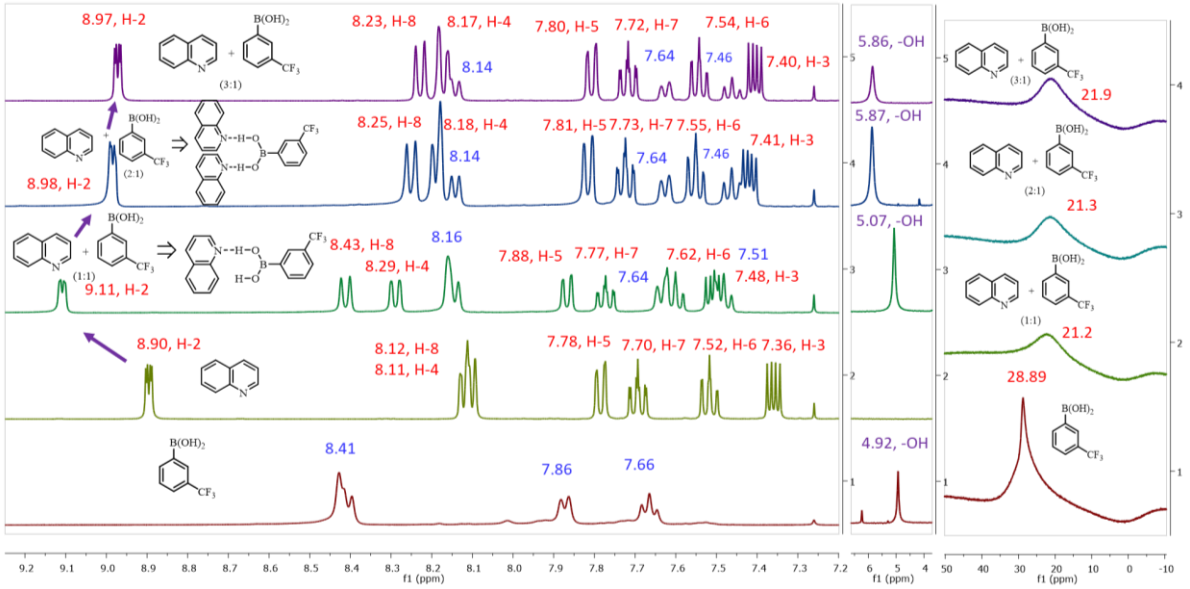


Figure S1: ^{1}H NMR spectra of quinoline (10 mg, 0.079 mmol), 3-trifluoromethylphenylboronic acid (cat.**2**) (16 mg, 0.079 mmol), and the mixture of quinoline and 3-trifluoromethylphenylboronic acid (cat.**2**) (molar ratio 1:1) in $CDCl_3$ at 298 K.

7.2 Interaction of Arylboronic acid with aldehyde

In order to illustrate the interaction of boronic acid and aldehyde, we performed the ^{1}H, ^{13}C, ^{11}B NMR, and IR spectroscopic experiments by using 3-trifluoromethylphenylboronic acid (cat.**2**), and 4-trifluoromethyl benzaldehyde, respectively. While one equivalent of 3-trifluoromethyl phenylboronic acid (cat.**2**) was added to 4-trifluoromethyl benzaldehyde in $CDCl_3$, a downfield shift of approximately 0.22 ppm for hydroxyl peak of boronic acid in ^{1}H NMR and 0.16 ppm for carbonyl signal of aldehyde in ^{13}C NMR were observed (Figure S2, S3). On the other hand, no shift was observed in ^{11}B NMR, which rules out the possibility of adduct formation with boron (Figure S4).

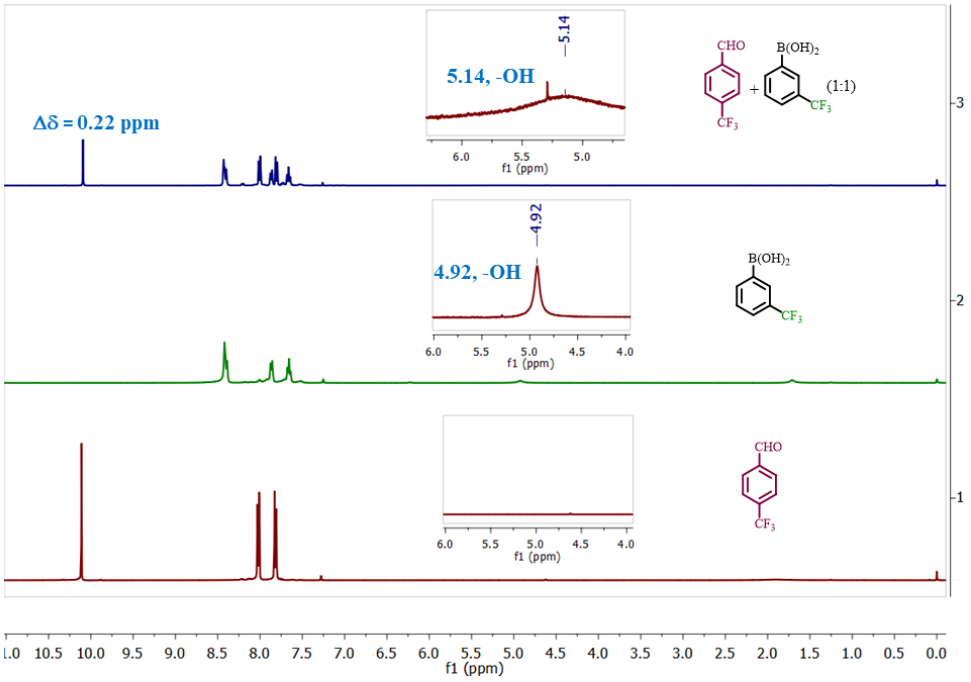


Figure S2: ^{1}H NMR spectra of 4-trifluoromethylbenzaldehyde (14 mg, 0.079 mmol), 3-trifluoromethylphenylboronic acid (cat.**2**) (16 mg, 0.079 mmol), and the mixture of 4-trifluoromethylbenzaldehyde and 3-trifluoromethylphenylboronic acid (cat.**2**) (molar ratio 1:1) in $CDCl_3$ at 298 K.

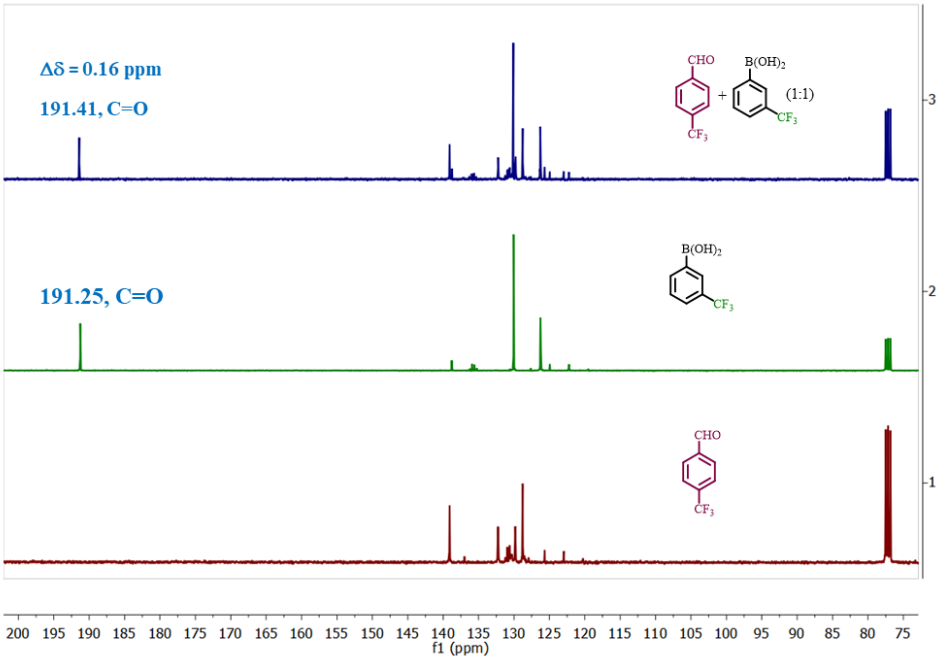


Figure S3: ^{13}C{^{1}H} NMR spectra of 4-trifluoromethylbenzaldehyde (14 mg, 0.079 mmol), 3-trifluoromethylphenylboronic acid (cat.**2**) (16mg, 0.079mmol), and the mixture of 4-trifluoromethylbenzaldehyde and 3-trifluoromethylphenylboronic acid (cat.**2**) (molar ratio 1:1) in $CDCl_3$ at 298 K.

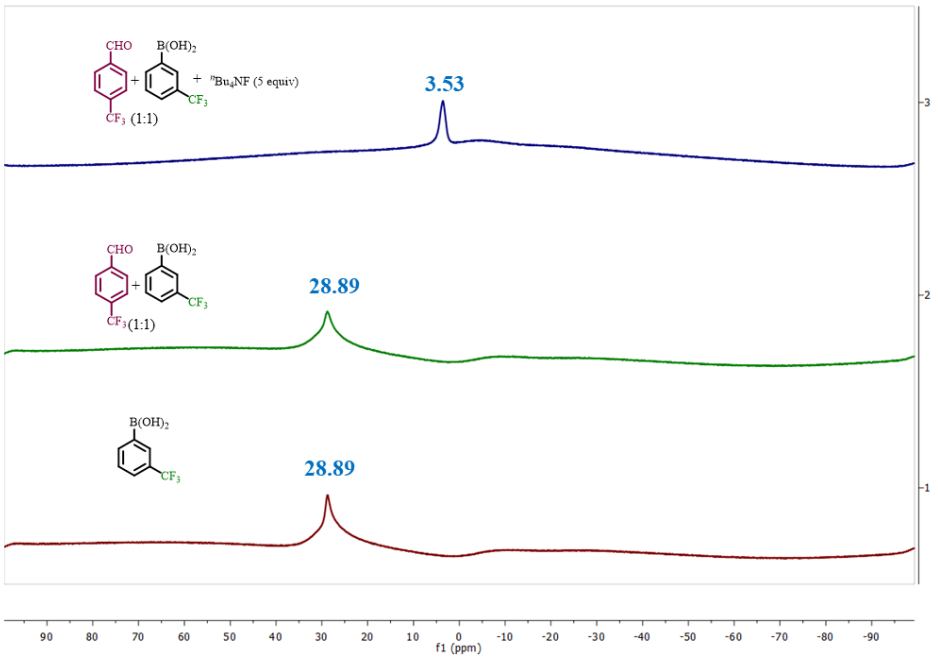


Figure S4: ^{11}B NMR spectra of 4-trifluoromethylbenzaldehyde (14 mg, 0.079 mmol), 3-trifluoromethylphenylboronic acid (cat.**2**) (16 mg, 0.079 mmol), and the mixture of 4-trifluoromethylbenzaldehyde and 3-trifluoromethylphenylboronic acid (cat.**2**) (molar ratio 1:1), 4-trifluoromethylbenzaldehyde, 3-trifluoromethylphenylboronic acid (cat.**2**) (molar ratio 1:1) and with TBAF (0.534 mmol) in $CDCl_3$ at 298 K.

For comparison, one equivalent of TBAF was added to the same reaction mixture, about 25 ppm upfield shift was observed, which indicates the same boron acts as a Lewis acid and take part in complexation with TBAF within. In IR, the carbonyl value shifted to a lower wave number from 1712.4 cm^{-1} to 1701.3 cm^{-1} after mixing with 3-trifluoromethylphenylboronic acid at room temperature (Figure S5). Approximately 10 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 boronic acid. A downfield shift for hydroxyl peak of boronic acid in ^{1}H NMR and ensuing downfield shift for carbonyl in aldehyde in ^{13}C NMR supports hydrogen bonding interaction with aldehyde and boronic acid. It has been further reinforced by using IR spectroscopic experiments in the solid-state.

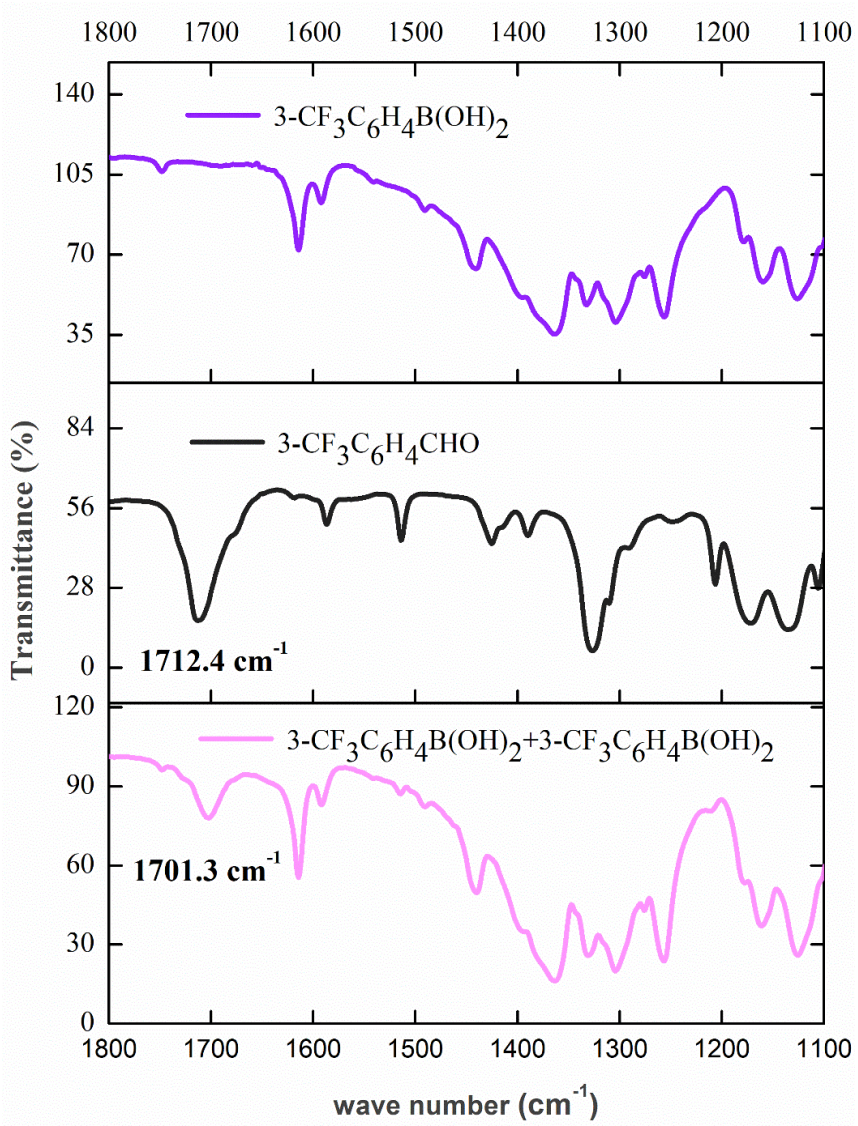


Figure S5: IR spectroscopy to support the interaction of 4-trifluoromethyl benzaldehyde and 3-trifluromethylphenylboronic acid (cat.**2**).

7.3 Interaction of Arylboronic acid with *p*-QMs

In order to illustrate the interaction of boronic acid and *p*-QMs, we performed the ^{1}H, ^{13}C, by using 3-trifluoromethylphenylboronic acid (cat.**2**), and 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **4a**, respectively. While one equivalent of 3- trifluoromethyl phenylboronic acid (cat.**2**) was added to 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **4a** in $CDCl_3$, a downfield shift of approximately 0.39 ppm for hydroxyl peak of boronic acid in ^{1}H NMR and 0.07 ppm for carbonyl signal of aldehyde in ^{13}C NMR were observed (Figure S6, S7).

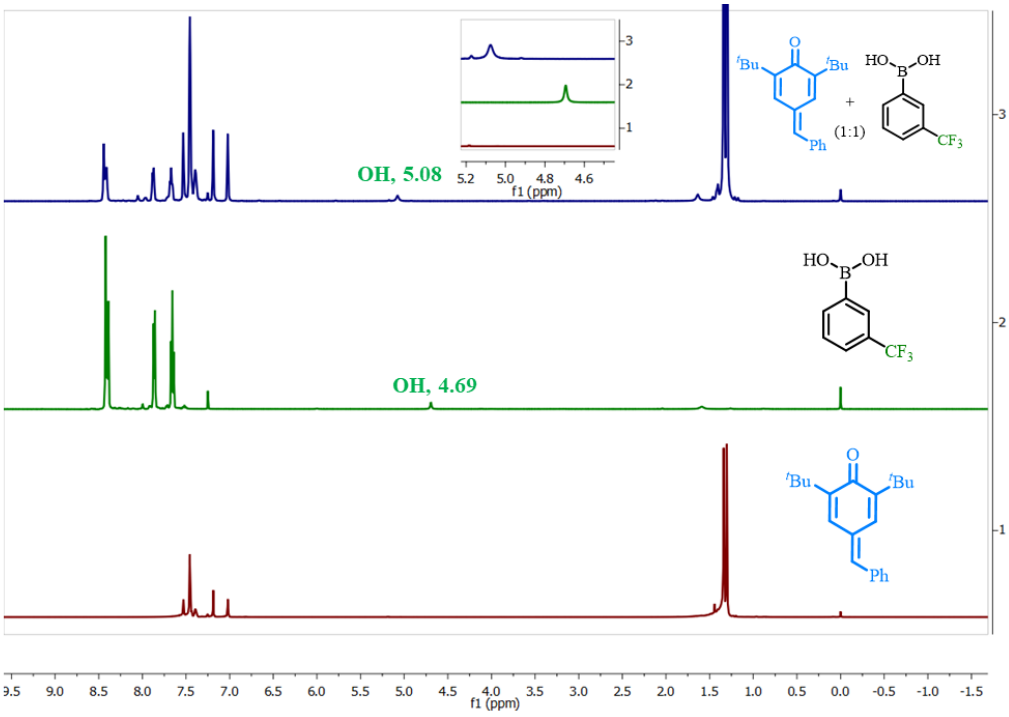


Figure S6: ^{1}H NMR spectra of 3-trifluoromethylphenylboronic acid (cat.**2**) (15 mg, 0.079 mmol), **4a** (0.023 g, 0.079 mmol), and the mixture of 3-trifluoromethylphenylboronic acid (cat.**2**) and **4a** (molar ratio 1:1) in $CDCl_3$ at 298 K.

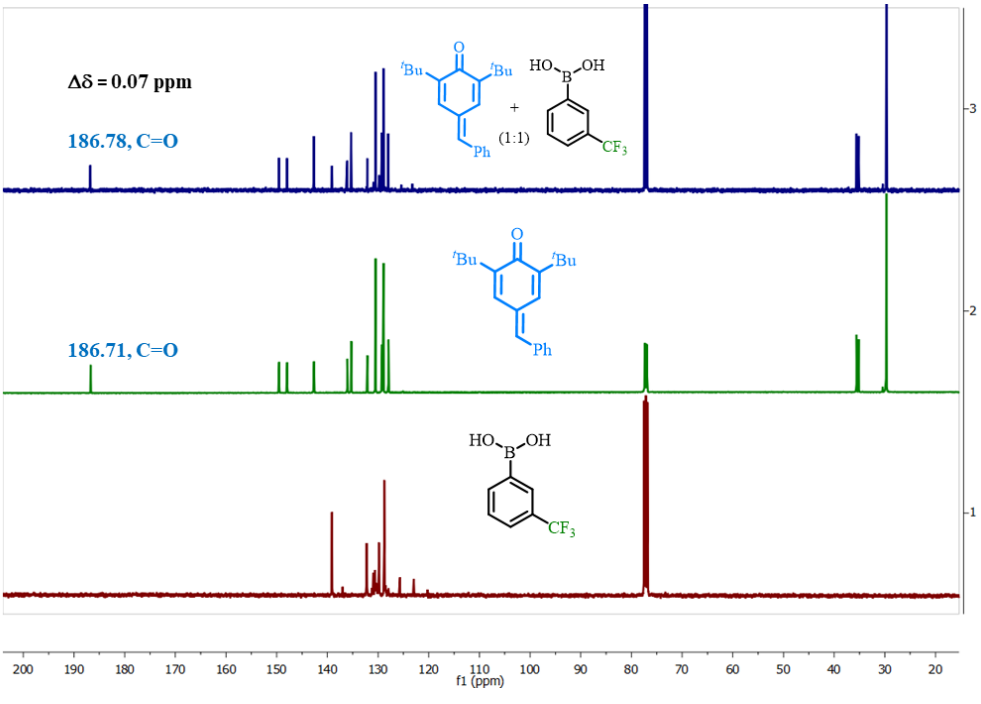


Figure S7: $^{13}C\{^{1}H\}$ NMR spectra of 3-trifluoromethylphenylboronic acid (cat.**2**) (15 mg, 0.079 mmol), **4a** (0.023 g, 0.079 mmol), and the mixture of 3-trifluoromethylphenylboronic acid (cat.**2**) and **4a** (molar ratio 1:1) in $CDCl_3$ at 298 K.

7.4 Interaction of Arylboronic acid with Hantzsch ester

To examine the interaction of boronic acid and Hantzsch ester, we have checked the ^{1}H NMR with the combination of (a) Hantzsch ester and phenylboronic acid (cat.**1**) (molar ratio 1:1) (b) Hantzsch ester and 3-trifluoromethyl boronic acid (cat.**2**) (molar ratio 1:2) in $CDCl_3$ at rt. In the case of phenylboronic acid (cat.**1**) approximately 0.41 ppm downfield was shifted for the hydroxyl peak, whereas no characteristic –OH proton signal was observed while mixing with 3- trifluoromethyl phenylboronic acid (cat.**2**) (Figure S8, S9).

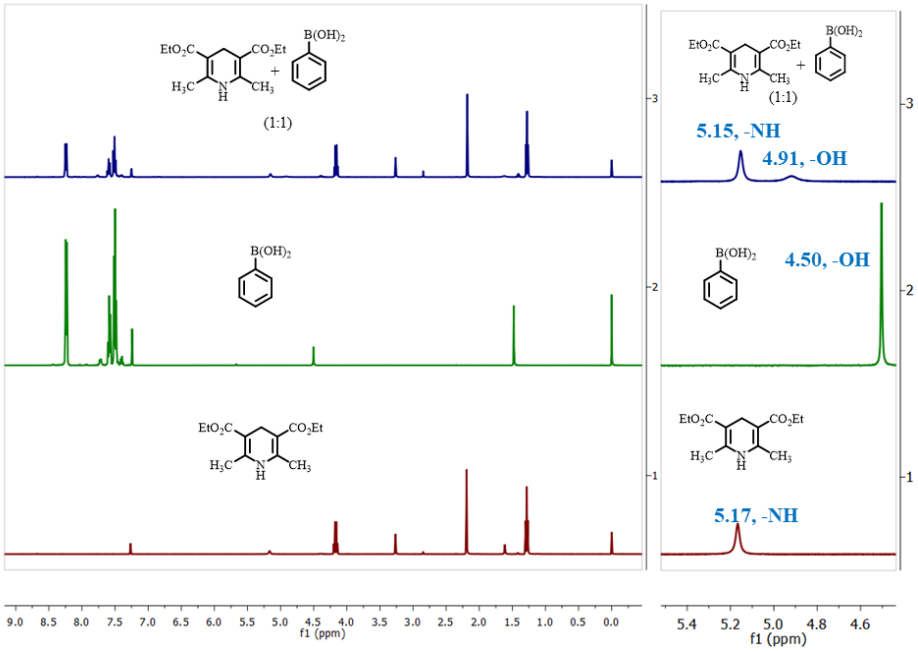


Figure S8: ^{1}H NMR spectra of Phenylboronic acid (cat.**1**) (10 mg, 0.079 mmol), Hantzsch ester (10 mg, 0.079 mmol), and the mixture of Phenylboronic acid (cat.**1**) and Hantzsch ester (molar ratio 1:1) in $CDCl_3$ at 298 K.

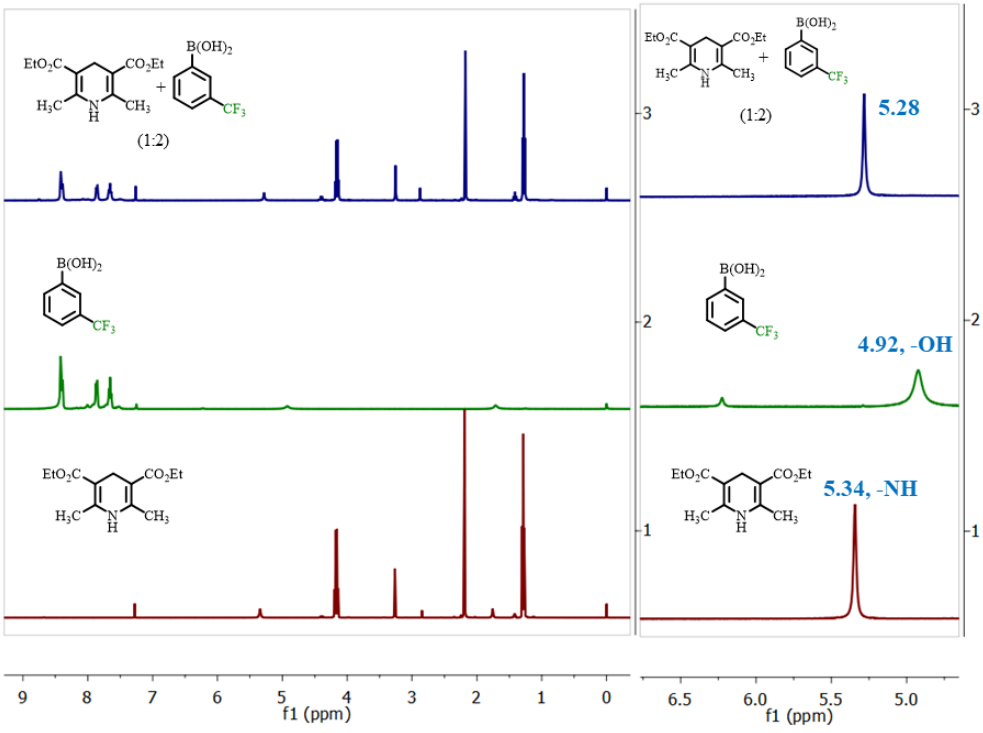


Figure S9: ^{1}H NMR spectra of 3-trifluoromethylphenylboronic acid (cat.**2**) (15 mg, 0.079 mmol), Hantzsch ester (5 mg, 0.039 mmol), and the mixture of 3-trifluoromethylphenylboronic acid (cat.**2**) and Hantzsch ester (molar ratio 2:1) in $CDCl_3$ at 298 K.

However, in ^{13}C NMR, the carbonyl value in Hantzsch ester was shifted downfield from 168.22 to 168.43 ppm ($\Delta\delta$ = 0.21 ppm). Using ^{11}B NMR spectroscopy, no noticeable shift was observed in boronic acid, which implies exclude Lewis acid-base adduct, and hydrogen bonding interaction may exist between Hantzsch ester and –OH of boronic acid (Figure S10).

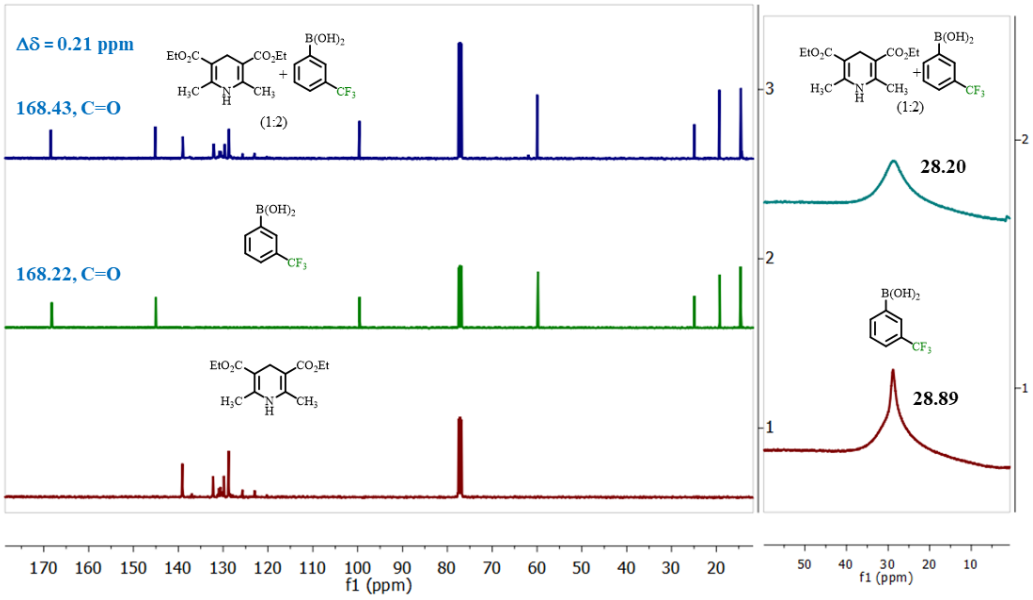
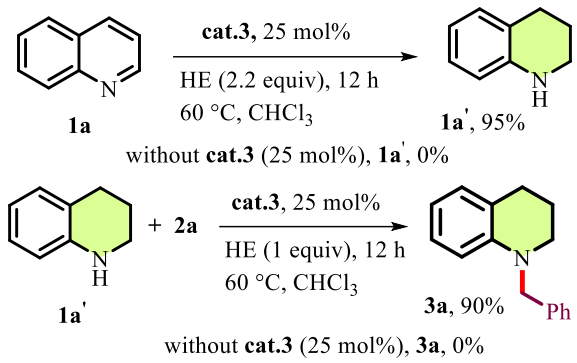


Figure S10. ^{13}C{^{1}H), and ^{11}B NMR spectra of 3-trifluoromethylphenylboronic acid (cat.**2**) (15 mg, 0.079 mmol), Hantzsch ester (5 mg, 0.039 mmol), and the mixture of 3-trifluoromethylphenylboronic acid (cat.**2**) and Hantzsch ester (molar ratio 2:1) (left, right) in $CDCl_3$ at 298 K.

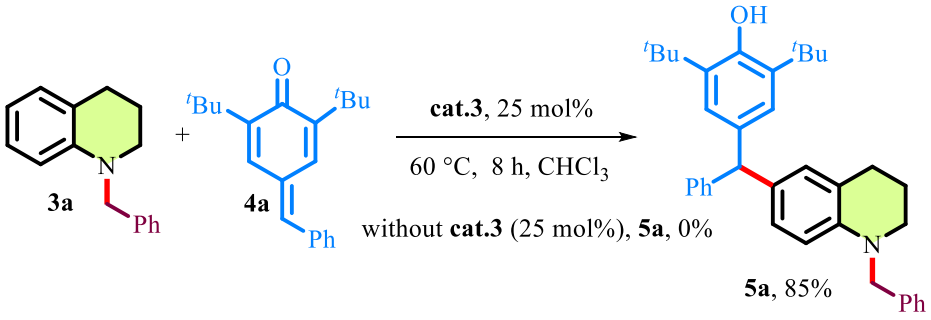
7.5 Proof of THQ, *N*-benzyl THQ as the intermediate

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 (0.279 g, 1.1 mmol, 2.2 equiv), and cat.**3** (20 mol%) were taken in a reaction tube. Then sealed with screw-cap, the resulting solution was heated at 60 °C for 12 h. As expected tetrahydroquinoline **1a'** obtained in 95% yield (0.063 g). For the subsequent step the reaction was conducted with the formed **1a'**, and benzaldehyde **2a** (0.050 g, 0.47 mmol, 1.0 equiv), HE (0.132 g, 0.52 mmol, 1.1 equiv), and cat.**3** (25 mol%) were taken in a reaction tube. Then sealed with screw-cap, the resulting solution was heated at 60 °C for 12 h), the desired product **3a** was obtained in 90% yield (0.094 g), from we can conclude, in both the reaction, 1,2,3,4-tetrahydroquinoline as the first intermediate (Scheme S7).



Scheme S7: Proof of 1,2,3,4-tetrahydroquinoline as the intermediate.

For the subsequent step the reaction was conducted with the formed **3a**, *p*-QM **4a** (0.132 g, 0.45 mmol, 1.0 equiv), and cat.**3** (25 mol%) at 60 °C for 8 h under standard conditions the desired product **5a** was obtained in 85% yield (0.198 g). From which we can conclude that *N*-benzyl THQ **3a** as the intermediate. The reaction possibly occurs in three steps (i) reduction of quinoline (ii) reductive *N*-alkylation of THQ and **(**iii) *C*-alkylation of *N*-alkylated THQ (Scheme S7 and S8).

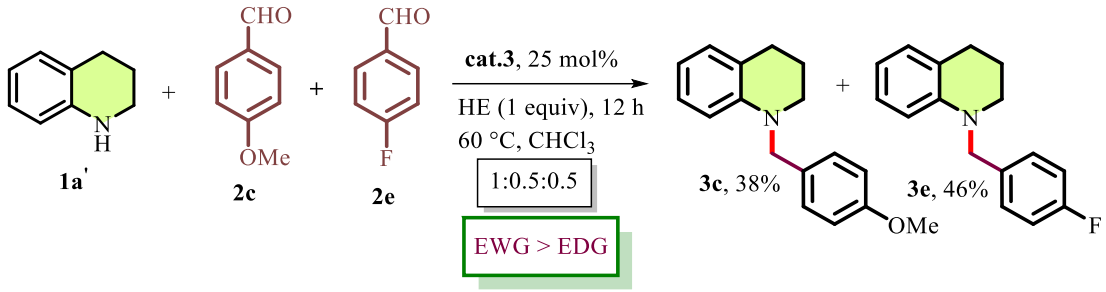


Scheme S8: Proof of *N*-benzyl THQ as the intermediate.

7.6 Electronic effect for the 2nd step

To know the electronic effect in the 2nd step, at first the reaction was examined with substituted aldehyde. A competitive reaction with aldehyde 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 S9).

Reaction conditions: 1,2,3,4 tetrahydroquinoline **1a'** (0.067 g, 0.5 mmol, 1.0 equiv), substituted aldehyde **2c** (0.034 g, 0.25 mmol, 0.5 equiv.), **2e** (0.031 g, 0.25 mmol, 0.5 equiv), HE (0.140 g, 0.55 mmol, 1.1 equiv), and cat.**3** (25 mol%) were taken in a reaction tube. Then sealed with screw-cap, the resulting solution was heated at 60 ℃ for 12 h under standard conditions, the product **3c** and **3e** was obtained in 38% yield and 46% yield respectively.

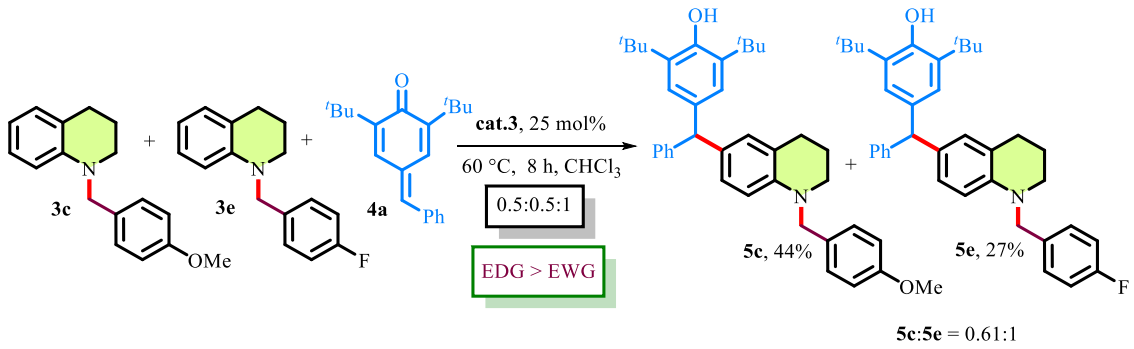


Scheme S9. Competitive reaction with substituted aldehyde

7.7 Electronic effect for the 3rd step

To know the electronic effect in the 3rd step, the reaction was examined with substituted *N*-benzyl THQ **3c** and **3e**. A competitive reaction suggested that the electron-donating group (-OMe) on the quinoline enhanced the rate of the reaction with respect to an electron-withdrawing group (*p*-F) (Scheme S10).

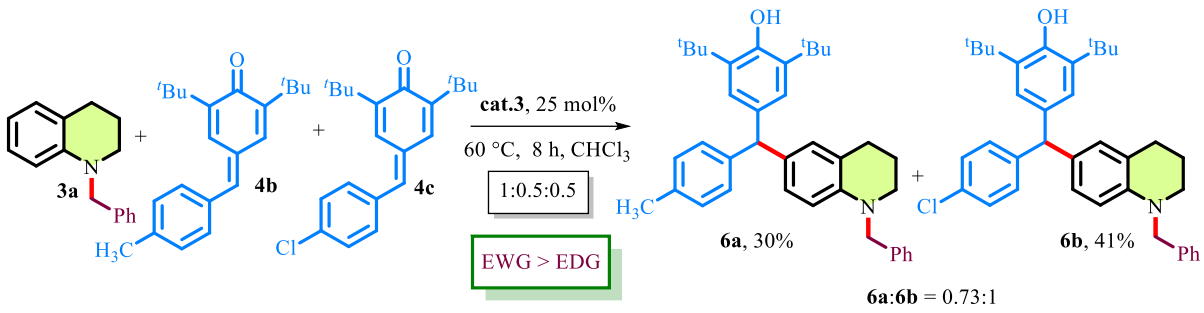
Reaction conditions: The substituted *N*-benzyl THQ **3c** (0.063 g, 0.25 mmol, 0.5 equiv), **3e** (0.060 g, 0.25 mmol, 0.5 equiv), *p*-QMs **4a** (0.147 g, 0.5 mmol, 1.0 equiv), and cat.**3** (25 mol%) were taken in a reaction tube. Then sealed with screw-cap, the resulting solution was heated at 60 °C for 8 h under standard conditions, the product **5c** and **5e** was obtained in 44% yield (0.120 g) and 27% yield (0.072 g) respectively.



Scheme S10. Competitive reaction with substituted *N*-benzyl THQ

Further, the reaction was examined with substituted *p*-QM **4b** and **4c**, respectively. A competitive reaction suggested that the electron-withdrawing group (*p*-Cl) in **4c** enhanced the rate of the reaction with respect to an electron-donating group (-Me) in **4b** (Scheme S11).

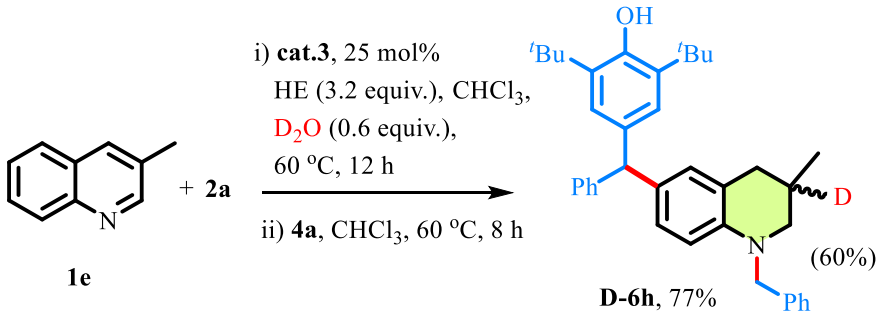
Reaction conditions: *N*-benzyl THQ **3a** (0.112 g, 0.5 mmol, 1.0 equiv), substituted *p*-QMs **4b** (0.077 g, 0.25 mmol, 1.0 equiv), **4c** (0.082 g, 0.25 mmol, 1.0 equiv), and cat.**3** (25 mol%) were taken in a reaction tube. Then sealed with screw-cap, the resulting solution was heated at 60 °C for 8 h under standard conditions, the product **6a** and **6b** was obtained in 30% yield (0.080 g) and 41% yield (0.113 g) respectively.



Scheme S11. Competitive reaction with substituted *p* -QMs

7.8 Deuterium-labelling experiment

In order to locate the hydridic proton and acidic proton in the *N*-benzyl-THQ product, we have performed the catalytic experiment with 3-methyl quinoline **1e** in the presence of D_2O. The outcome demonstrated that the deuterium atom was incorporated at the C-3 position of *N*-functionalized THQ **D-6h** (Scheme S12).



Scheme S12: Deuterium-labelled experiment with 3-methyl quinoline

Reaction conditions: In a reaction tube (15 mL), 3-methyl quinoline **1c** (0.072 g, 0.5 mmol, 1.0 equiv.), **2a** (0.053 g, 0.5 mmol, 1.0 equiv.), HE (0.406 g, 1.6 mmol, 3.2 equiv.), cat.**3** (25 mol%), and D_2O (0.3 mmol, 0.6 equiv.) were charged, then sealed with screw-cap, the resulting solution was heated at 60 °C for 12 h under standard conditions. Then *p*-QMs **4a** (0.147 g, 0.5 mmol, 1.0 equiv.) was added in the same reaction tube at 60 °C with continuous stirring for 8 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 dark-red liquid of **D-6h** (0.205 g, 77%).

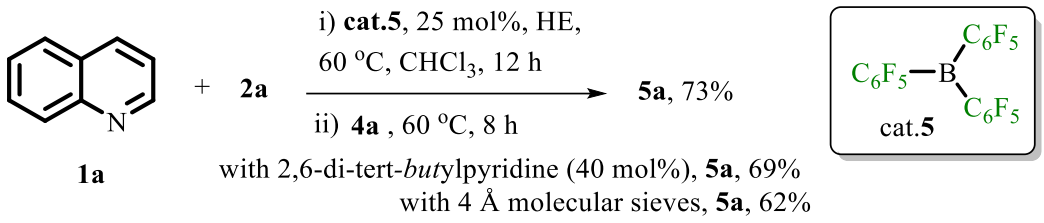
^{1}H NMR spectrum of deuterated 4-((1-benzyl-3-methyl-1,2,3,4-tetrahydroquinolin-6-yl) (phenyl)methyl)-2,6-di-*tert*-butylphenol (6h + D-6h):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 14H, **6h + D-6h**), 7.16 – 7.11 (m, 6H, **6h + D-6h**), 6.91 (s, 4H, **6h + D-6h**), 6.75 – 6.73 (m, 2H, **6h + D-6h**), 6.68 – 6.63 (m, 2H, **6h + D-6h**), 6.42 (d, J = 8.4 Hz, 2H, **6h + D-6h**), 5.26 (s, 2H, **6h + D-6h**), 5.03 (s, 2H, **6h + D-6h**), 4.44 (s, 4H, **6h + D-6h**), 3.25 – 3.22 (m, 2H, **6h + D-6h**), 3.01 – 2.96 (m, 2H, **6h + D-6h**), 2.73 – 2.69

(m, 2H, **6h + D-6h**), 2.47 – 2.40 (m, 2H, **6h + D-6h**), 2.19 – 2.10 (m, 1H, **6h**), 1.36 (s, 36H, **6h + D-6h**), 1.01 (s, 6H, **6h + D-6h**). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.0, 146.0, 143.5, 139.4, 135.3, 135.1, 132.25, 130.2, 130.2, 129.48, 129.47, 128.6, 128.1, 128.0, 127.9, 126.8, 126.1, 125.8, 121.7, 110.6, 57.0, 56.17, 56.17, 55.5, 55.4, 36.7, 34.5, 31.4, 30.5, 27.60, 27.57, 19.21, 19.18.

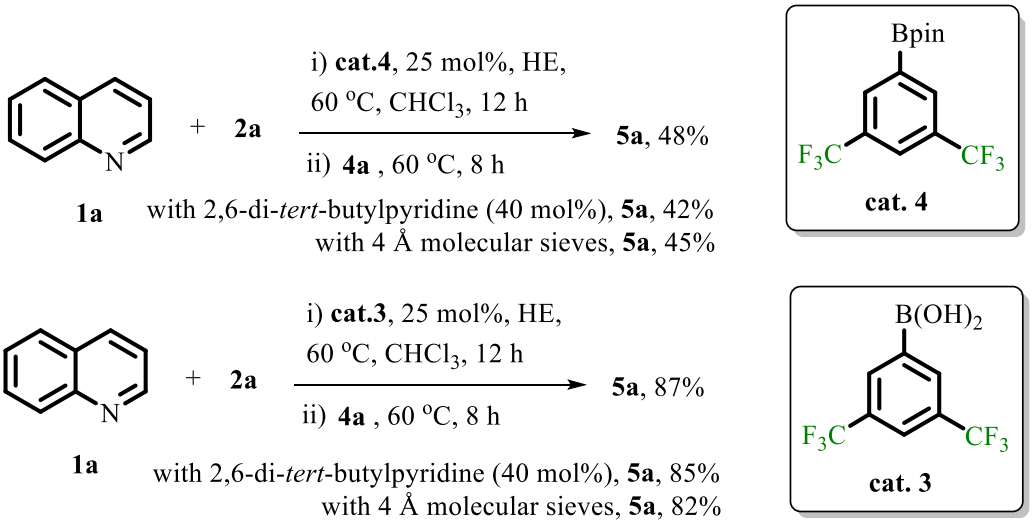
7.9 Mode of boronic acid catalysis in the alkylation of quinoline.

In general, the mode of boronic acid catalysis involves three possible pathways such as (a) Lewis acid catalysis, (b) Brønsted acid catalysis, and (c) H-bond donor catalysis. As the reaction produces H_2O as one of the by-products, the effect of water in this transformation was also studied. The bulky pyridine 2,6-di-*tert*-butylpyridine (DTBP) is commonly used to distinguish between boron or other Lewis acids and Brønsted acids because it does not form a complex with boron.



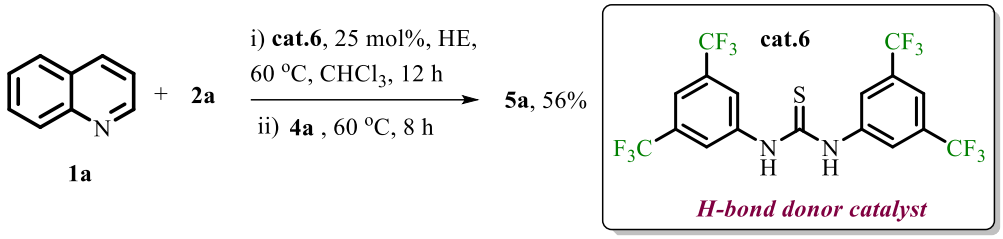
Scheme S13: Effect of water with **cat.5** in the *N*-alkylation reaction

Further, the role of an *in-situ* generated water-mediated Bronsted acid catalysis can be monitored in the presence of 4 Å molecular sieves. When pentafluorotriphenylboron **cat. 5** is used as a catalyst, product **5a** was obtained in 73% yield. Then the yield of **5a** was not decreased in the presence of DTBP (40 mol%) or with 4 Å molecular sieves, indicating the possible involvement of Lewis acid catalysis.



Scheme S14: Effect of water with **cat.3** and **cat.4** in the *N*-alkylation reaction

Likewise, the use of pinacol ester, **cat. 4**, product **5a** was obtained in 48% yield, and boronic acid **cat. 3** provided the product 87% yield. In both the case, hindered Brønsted base 2,6-di-*tert*-butylpyridine has failed to inhibit the reactivity of the pinacol ester and boronic acid in the reaction further, the yield of product is not suppressed in the presence of 4 Å molecular sieves, indicating the not involvement of *in-situ* generated water-mediated Bronsted acid catalysis. The higher yield of **5a** in **cat 3** (87%) with respect to **cat.4** (48%) suggests that the possible involvement of H-bonding catalysis in BA catalysis.

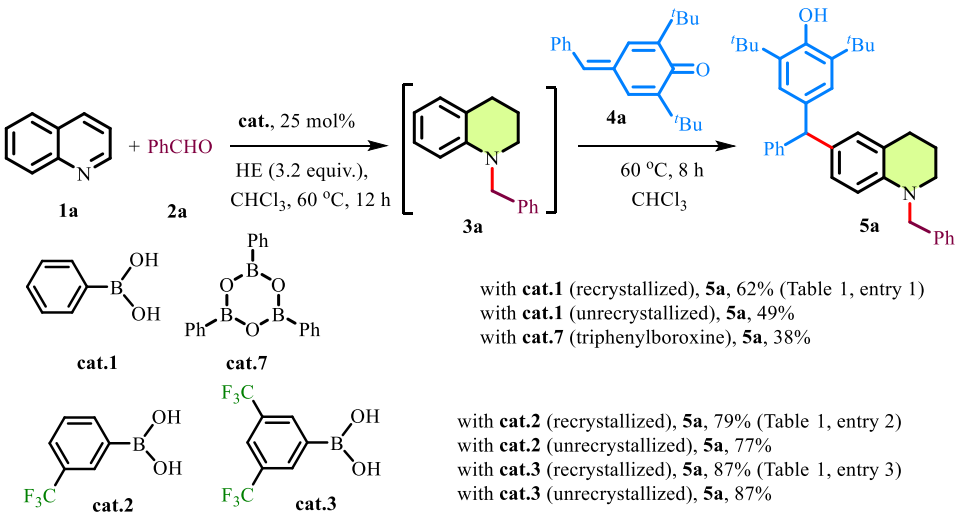


Scheme S15: cat.6 in the *N*-alkylation reaction

When the reaction was performed within an authentic hydrogen-bond donor catalyst, $-CF_3$ functionalized thiourea (**cat.6**), desired product **5a** was obtained in 56% yield. Based on above control studies, it can be concluded that the mode of boronic acid catalysis involves both H-bond donor catalysis and Lewis acid catalysis.

7.10. The effect of unrecrystallized borornic acid in the catalysis

The commercial boronic acids contain variable amounts of water and also triarylboroxine, which can affect the reaction. Hence, all the boronic acids used in the current manuscript were recrystallized from water prior to their use.



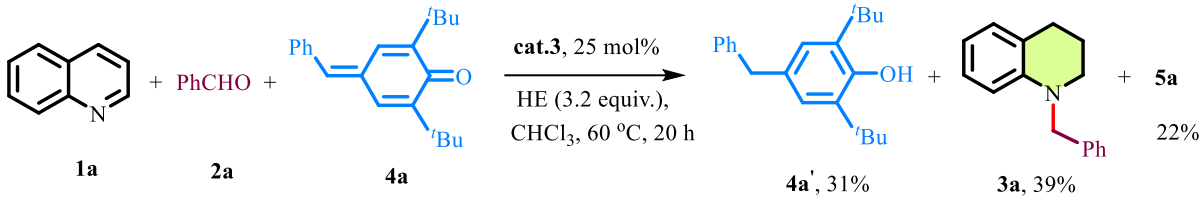
Scheme S16: effect of unrecrystallized borornic acid in the catalysis.

When the reaction was examined with unrecrystallized phenyl broronic acid, **cat.1**, the yield of product **5a** was obtained in 49% yield and with triphenylboroxine, **cat.7**,

product **5a** was obtained in 38% yield. It suggests that the reaction likely occur *via* the combinatorial effect of triphenylboroxine and residual boronic acid in the case of unrecrystallized phenylboronic acid **cat.1**. But, for electron-withdrawing $-CF_3$ substituent boronic acid **cat.2** or **cat.3** the reaction is most likely to proceed through boronic acid and not by the catalysis of triarylboroxine, since the yield of desired product **5a** is not altered under the reaction conditions.

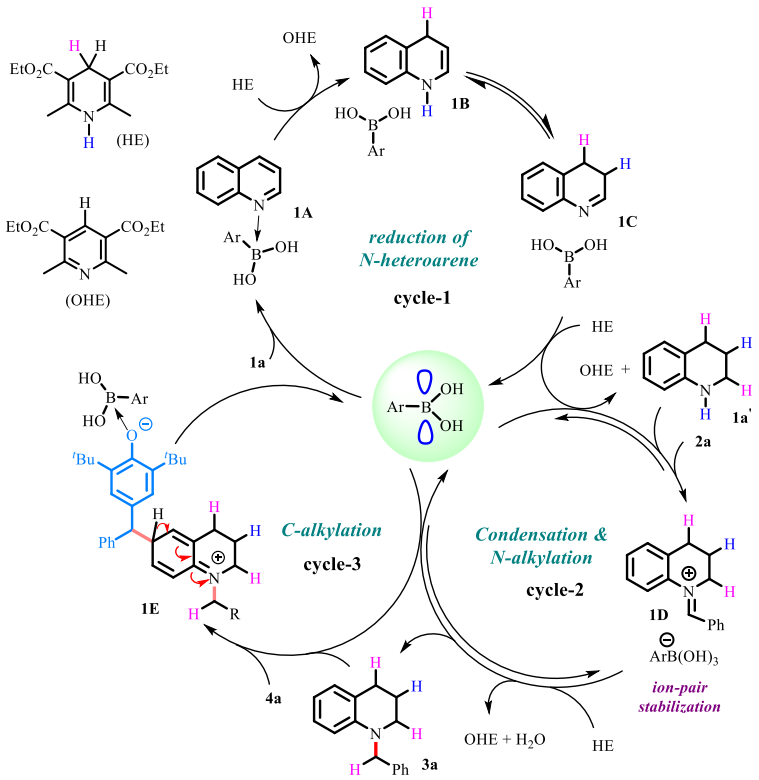
7.11. Synthesis of *C*-alkylated *N*-benzyl THQ in a one-pot fashion

We have attempted to synthesize *C*-alkylated product **5a** in a one-pot fashion, by adding *p*-QMs **4a** from the beginning, the desired *C*-alkylated product **5a** was obtained in only 22% yield, along with 39% *N*-benzyl THQ **3a** and 31% hydrogenated product **4a**'. This indicates that it is necessity to add *p*-QMs **4a** after the formation of *N*-alkylated THQ **3a**, otherwise, *p*-QMs readily react with Hantzsch ester to provide **4a**'.



Scheme S17: Synthesis of *C*-alkylated *N*-benzyl THQ in a one-pot fashion.

7.10. Mechanistic pathway by Lewis acid catalysis



Scheme 18: Mechanistic pathway by Lewis acid catalysis.

8. Crystallographic data

Crystallographic data of 5n

Single crystals of compound **5n** suitable for X-ray diffraction were obtained by slow evaporation of the saturated solution of the compound in petroleum ether at room temperature. X-ray crystallographic data were collected using Bruker D8 QUEST diffractometer. Data refinement and cell reduction were carried out by APEX4. Structures were solved by direct methods using Olex2 v1.5 and refined by a full-matrix least-squares method using Olex2 v1.5. All of the non-H atoms were refined anisotropically. The ORTEP diagram was obtained with ORTEP3 software with 30% thermal ellipsoid (see below, Figure S11). The crystallographic parameters and refinement data were listed in Table S1.

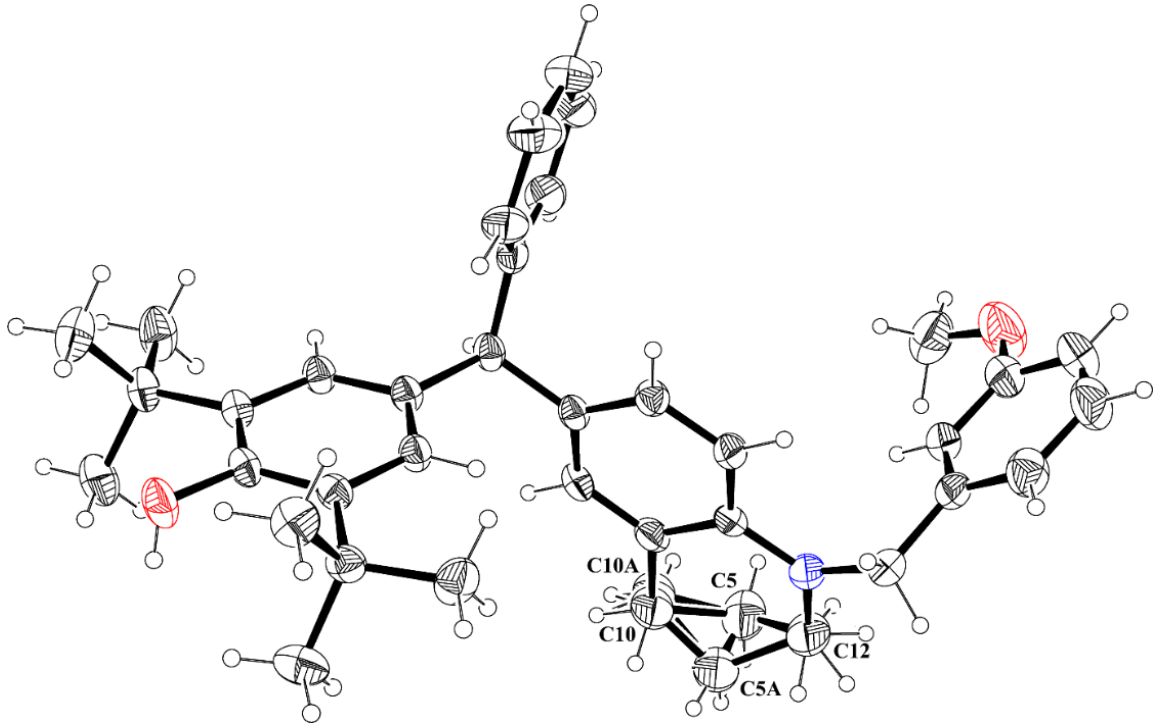


Figure S11: Molecular structure of compound **5n** (thermal ellipsoid 30% probability level).

Please note that the saturated carbon atoms of the tetrahydroquinoline moiety is unequally disordered over two sites. The disorder atoms C5, C10 and C12 are splitted over two positions with occupancy 0.68, and 0.32.

Table S1: Crystal data and structure refinement for 5n

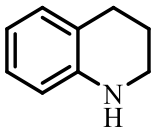
Identification code	SK_381_0m_a
Empirical formula	$C_{38}H_{45}NO_2$
Formula weight	547.75
Temperature/K	296.00
Crystal system	triclinic
Space group	P-1
a/Å	11.629(3)
b/Å	12.102(3)
c/Å	13.779(3)
α/°	68.406(6)
β/°	85.378(7)
γ/°	66.181(6)
Volume/Å^3	1644.1(7)
Z	2
ρ_{calc}g/cm^3	1.106
μ/mm^{-1}	0.067
F (000)	592.0
Crystal size/mm^3	0.38 × 0.34 × 0.31
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.258 to 52.748
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	48983
Independent reflections	6662 [R_{int} = 0.0367, R_{sigma} = 0.0214]
Data/restraints/parameters	6662/23/387
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0543, wR_2 = 0.1392
Final R indexes [all data]	R_1 = 0.0706, wR_2 = 0.1583
Largest diff. peak/hole / e Å^{-3}	0.27/-0.33

Table S2 Atomic Occupancy for SK_381_0m_a.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C10	0.681(8)	H10A	0.681(8)	H10B	0.681(8)
C5	0.681(8)	H5A	0.681(8)	H5B	0.681(8)
H12A	0.681(8)	H12B	0.681(8)	H12C	0.319(8)
H12D	0.319(8)	C5A	0.319(8)	H5AA	0.319(8)
H5AB	0.319(8)	C10A	0.319(8)	H10C	0.319(8)
H10D	0.319(8)				

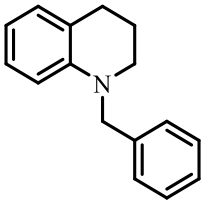
8. Analytical data of the products

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



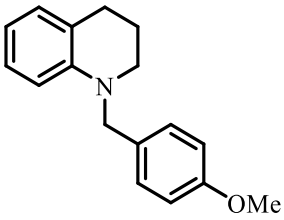
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 – 6.95 (m, 2H), 6.61 (t, J = 8.1 Hz, 1H), 6.48 (d, J = 7.9 Hz, 1H), 3.32 – 3.29 (m, 2H), 2.77 (t, J = 6.4 Hz, 2H), 1.98 – 1.92 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.9, 129.6, 126.8, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3. Spectral data is in accordance with the literature. [16]

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



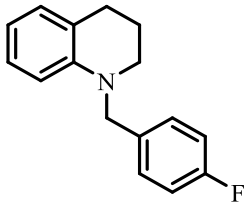
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.20 (m, 5H), 6.97 – 6.94 (m, 2H), 6.56 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 8.4 Hz, 1H), 4.46 (s, 2H), 3.37 – 3.34 (m, 2H), 2.80 (t, J = 6.2 Hz, 2H), 2.03 (pent, 6.2 Hz, 2H).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.7, 139.1, 129.1, 128.7, 127.3, 126.8, 126.7, 122.3, 115.9, 111.1, 55.3, 50.0, 28.3, 22.5. Spectral data is in accordance to the reported literature. [10]

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



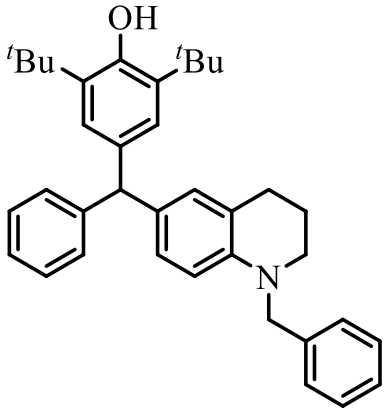
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 6.8 Hz, 2H), 7.03 – 7.00 (m, 2H), 6.86 (d, J = 7.6 Hz, 2H), 6.62 – 6.57 (m, 2H), 4.45 (s, 2H), 3.82 (s, 3H), 3.37 (t, J = 5.7 Hz, 2H), 2.85 (t, J = 6.3 Hz, 2H), 2.06 – 2.01 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.7, 145.8, 131.0, 129.1, 127.9, 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. [10]

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



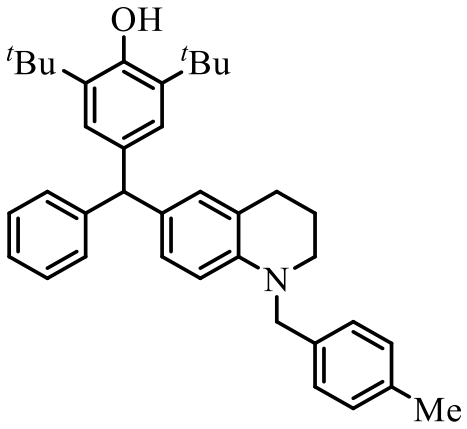
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 2H), 7.01 – 6.96 (m, 4H), 6.59 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.6 Hz, 1H), 4.44 (s, 2H), 3.34 (t, J = 5.6 Hz 2H), 2.81 (t, J = 6.3 Hz, 2H), 2.01 (pent, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.9 – 161.0 (C-F, $^{1}J_{C\text{-}F}$ = 244.3 Hz), 145.6, 134.6 (C-F, $^{4}J_{C\text{-}F}$ = 3 Hz), 129.2, 128.2 (C-F, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 127.3, 122.5, 116.2, 115.6 - 115.4 (C-F, $^{2}J_{C\text{-}F}$ = 21.4 Hz, 111.1, 54.8, 50.0, 28.3, 22.5. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$): δ -116.45. Spectral data is in accordance to the reported literature. [10]

4-((1-benzyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-*tert*-butylphenol (5a)



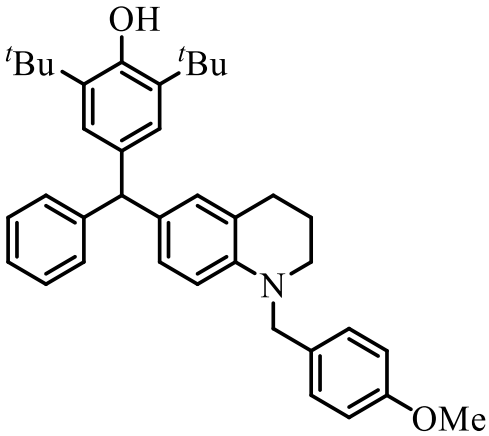
By following the **GP-1**, the title compound **5a** was isolated as dark-red liquid (0.450 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.25 – 7.18 (m, 5H), 7.13 (t, J = 7.6 Hz, 3H), 6.92 (s, 2H), 6.75 (s, 1H), 6.66 (d, J = 8.3 Hz, 1H), 6.42 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.01 (brs, 1H), 4.42 (s, 2H), 3.30 (t, J = 5.6 Hz, 2H), 2.72 (t, J = 6.2 Hz, 2H), 1.96 (pent, J = 6.0 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, 122.09, 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.

2, 6-di-*tert*-butyl-4-((1-(4-methylbenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl)methyl) phenol (5b)



By following the **GP-1**, the title compound **5b** was isolated as dark-red liquid (0.479 g, 90%) 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 7.23 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 8.5 Hz, 4H), 7.10 (t, J = 6.1 Hz, 3H), 6.92 (s, 2H), 6.74 (s, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 8.5 Hz, 1H), 5.25 (s, 1H), 5.01 (brs, 1H), 4.39 (s, 2H), 3.32 – 3.27 (m, 2H), 2.72 (t, J = 6.2 Hz, 2H), 2.31 (s, 3H), 1.96 (pent, J = 6.1 Hz, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0, 146.0, 144.1, 136.4, 135.7, 135.4, 132.2, 130.1, 129.5, 129.3, 128.1, 128.0, 126.9, 126.2, 125.8, 122.1, 110.9, 56.2, 55.2, 49.9, 34.5, 30.5, 28.4, 22.7, 21.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{46}NO$: 532.3574; found: 532.3577

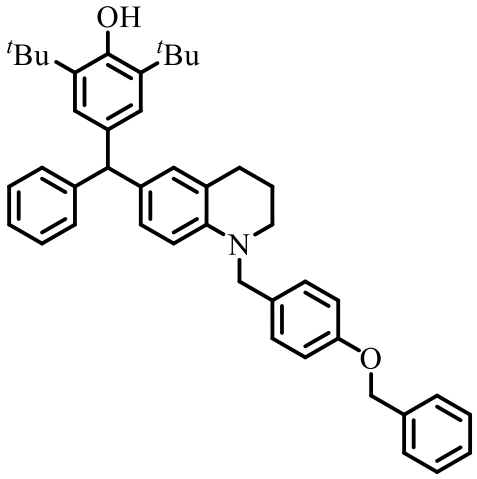
2, 6-di-*tert*-butyl-4-((1-(4-methoxybenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5c)



By following the **GP-1**, the title compound **5c** was isolated as dark-red liquid (0.509 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 7.22 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.5 Hz, 3H), 6.93 (s, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.75 (s, 1H), 6.67 (d, J = 9.4 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.35 (s, 2H), 3.73 (s, 3H), 3.26 (t, J = 5.7 Hz, 2H), 2.70 (t, J = 6.5 Hz, 2H), 1.93 (pent, J = 6.1 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 158.6, 152.0, 145.9, 144.0, 135.3, 135.0, 132.2, 131.2, 130.1, 129.4, 128.1,

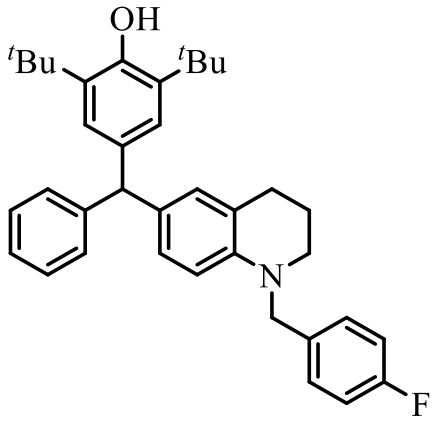
128.0, 127.9, 126.1, 125.8, 122.1, 114.0, 110.9, 56.2, 55.3, 54.8, 49.8, 34.4, 30.5, 28.3, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{46}NO_2$: 548.3524; found: 548.3528.

4-((1-(4-(benzyloxy) benzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-tert-butylphenol (5d)



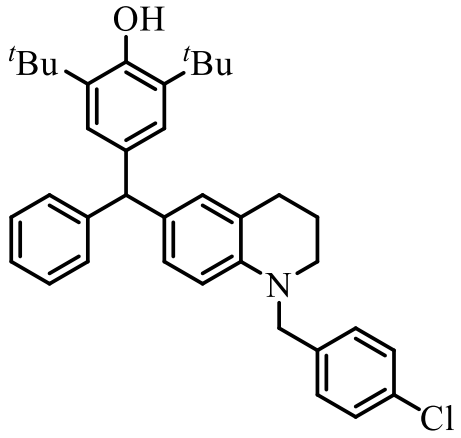
By following the **GP-1**, the title compound **5d** was isolated as dark-red liquid (0.568 g, 91%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.30 – 7.28 (m, 1H), 7.24 - 7.21 (m, 2H), 7.15 – 7.12 (m, 5H), 6.93 (s, 2H), 6.90 (d, J = 7.5 Hz, 2H), 6.75 (s, 1H), 6.67 (d, J = 8.2 Hz, 1H), 6.44 (d, J = 8.3 Hz, 1H), 5.26 (s, 1H), 5.01 (brs, 3H), 4.36 (s, 2H), 3.28 – 3.26 (m, 2H), 2.72 – 2.69 (m, 2H), 1.94 (pent, J = 5.8 Hz, 2H), 1.35 (s, 18H).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 157.8, 152.0, 146.0, 144.0, 137.2, 135.3, 135.0, 132.2, 131.5, 130.1, 129.5, 128.7, 128.1, 128.0, 127.9, 127.6, 126.1, 125.8, 122.1, 115.0, 110.9, 70.2, 56.2, 54.8, 49.8, 34.4, 30.5, 28.4, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{44}H_{50}NO_2$: 624.3837; found: 624.3836.

2, 6-di-*tert*-butyl-4-((1-(4-fluorobenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5e)



By following the **GP-1**, the title compound **5e** was isolated as dark-red liquid (0.429 g, 80%) 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 7.22 (q, J = 7.3 Hz, 3H), 7.19 (d, J = 5.6 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 7.12 (d, J = 7.4 Hz, 2H), 6.96 (t, J = 8.6 Hz, 2H), 6.92 (s, 2H), 6.75 (s, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.39 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.38 (s, 2H), 3.31 – 3.26 (m, 2H), 2.72 (t, J = 6.3 Hz, 2H), 1.96 (pent, J = 6.1 Hz, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.9 – 161.0 (C-F, $^1J_{C\text{-}F}$ = 244.8 Hz), 152.0, 145.9, 143.8, 135.4, 135.0, 134.9 (C-F, $^4J_{C\text{-}F}$ = 2.99 Hz), 132.5, 130.2, 129.5, 128.3 (C-F, $^3J_{C\text{-}F}$ = 7.9 Hz), 128.1, 128.0, 126.1, 125.8, 122.2, 115.5 – 115.4 (C-F, $^2J_{C\text{-}F}$ = 21.5 Hz), 110.9, 56.2, 54.9, 50.0, 34.5, 30.5, 28.3, 22.7. ^{19}F{^{1}H) NMR (471 MHz, $CDCl_3$): δ -116.45. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}FNO$: 536.3324; found: 536.3225.

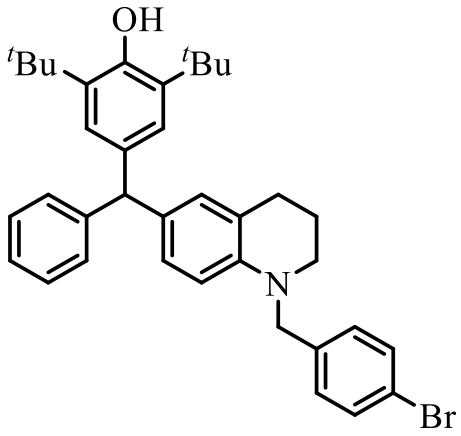
2, 6-di-*tert*-butyl-4-((1-(4-chlorobenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5f)



By following the **GP-1**, the title compound **5f** was isolated as dark-red liquid (0.464 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 7.26 – 7.24 (m, 2H), 7.24 – 7.22 (m, 2H), 7.19 – 7.17 (m, 2H), 7.16 - 7.14 (m, 1H), 7.12 (d, J = 7.6 Hz, 2H), 6.91 (s, 2H), 6.76 (s, 1H), 6.66 (d, J = 8.9 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 5.25 (s, 1H), 5.02 (brs, 1H), 4.39 (s, 2H), 3.29 (t, J = 5.5 Hz, 2H), 2.73 (t, J = 6.2 Hz, 2H), 1.99 – 1.95 (m, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0, 145.9, 143.7, 137.9, 135.4, 135.0, 132.7, 132.5, 130.2, 129.5, 128.8, 128.3, 128.1, 128.0, 126.1, 125.8, 122.3, 111.0, 56.2, 55.1, 50.1, 34.5, 30.5, 28.3, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}ClNO$: 552.3028; found: 552.3011.

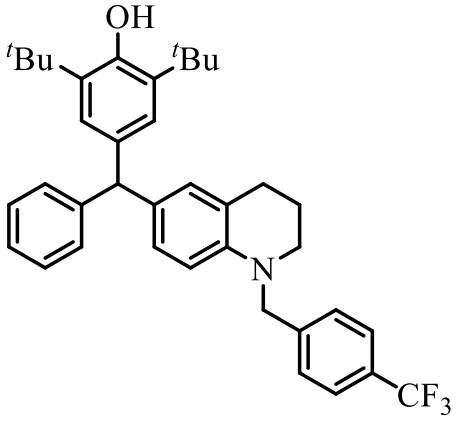
4-((1-(4-bromobenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)

-2, 6-di-*tert*-butylphenol (5g)



By following the **GP-1**, the title compound **5g** was isolated as dark-red liquid (0.513 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 7.40 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.15 (d, J = 7.0 Hz, 1H), 7.13 – 7.10 (m, 4H), 6.91 (s, 2H), 6.75 (s, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.35 (d, J = 8.5 Hz, 1H), 5.25 (s, 1H), 5.02 (s, 1H), 4.36 (s, 2H), 3.29 (t, J = 5.7 Hz, 2H), 2.72 (t, J = 6.4 Hz, 2H), 1.96 (pent, J = 6.0 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 145.9, 143.7, 138.4, 135.4, 134.9, 132.6, 131.7, 130.2, 129.5, 128.6, 128.1, 128.0, 126.1, 125.8, 122.2, 120.5, 110.9, 56.2, 55.1, 50.1, 34.5, 30.5, 28.3, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}BrNO$: 596.2523; found: 596.2524.

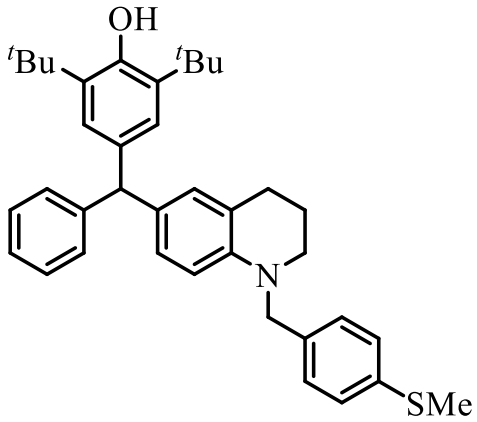
2,6-di-*tert*-butyl-4-(phenyl (1-(4-(trifluoromethyl) benzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) methyl) phenol (5h)



By following the **GP-1**, the title compound **5h** was isolated as dark-red liquid (0.463 g, 79%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.24 (t, J = 7.4 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.4 Hz, 2H), 6.91 (s, 2H), 6.77 (s, 1H), 6.65 (d, J = 8.3 Hz, 1H), 6.32 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.03 (s, 1H), 4.48 (s, 2H), 3.35 – 3.31 (m, 2H), 2.75 (t, J = 6.2 Hz, 2H), 2.00 (pent, J = 6.1 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 145.9, 143.7, 143.6, 135.4, 134.9, 132.8, 130.3, 129.5, 128.1, 128.0, 127.0, 126.1, 125.8, 125.6 (CF_3, q, $J_{C\text{-}F}$ = 3.7 Hz), 122.3, 110.9, 56.2, 55.4, 50.3, 34.5,

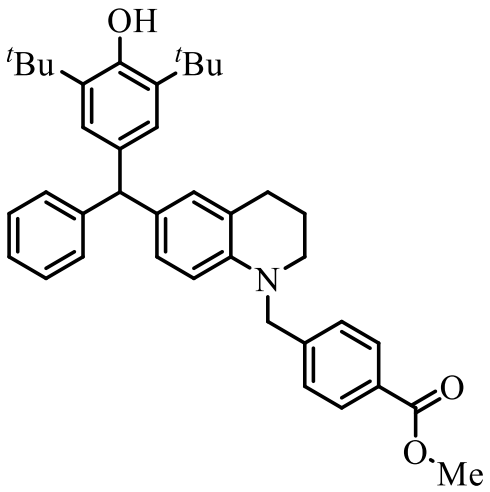
30.5, 28.3, 22.7. $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$): δ -62.34. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{43}F_3NO$: 586.3292; found: 586.3278.

2, 6-di-*tert*-butyl-4-((1-(4-(methylthio) benzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5i)



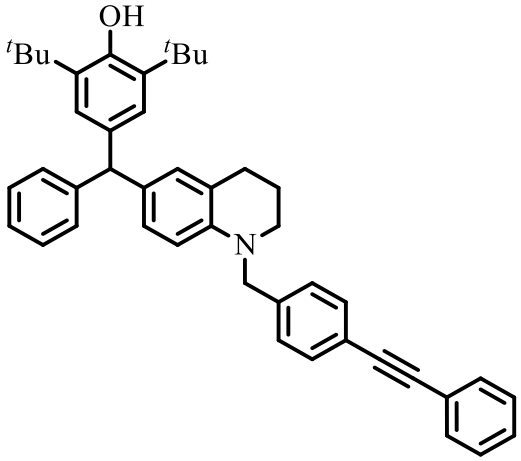
By following the **GP-1**, the title compound **5i** was isolated as dark-red liquid (0.490 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.92 (s, 2H), 6.75 (s, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.38 (s, 2H), 3.29 (t, *J* = 5.7 Hz, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 1.96 (pent, *J* = 6.1 Hz, 2H), 1.36 (s, 18H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.0, 145.9, 143.9, 136.5, 136.4, 135.3, 135.0, 132.3, 130.1, 129.5, 128.1, 127.9, 127.5, 127.2, 126.1, 125.8, 122.1, 110.9, 56.2, 55.1, 50.0, 34.5, 30.5, 28.3, 22.6, 16.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{46}NOS$: 564.3295; found: 564.3296.

Methyl 4-((6-((3,5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (5j)



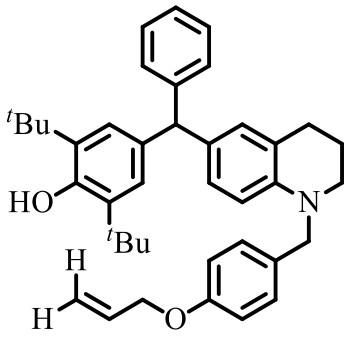
By following the **GP-1**, the title compound **5j** was isolated as dark-red liquid (0.461 g, 80%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.17 – 7.09 (m, 3H), 6.91 (s, 2H), 6.76 (s, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.47 (s, 2H), 3.89 (s, 3H), 3.35 – 3.31 (m, 2H), 2.74 (t, J = 6.1 Hz, 2H), 1.99 (pent, J = 5.6 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.2, 152.0, 145.9, 145.1, 143.7, 135.4, 134.9, 132.7, 130.2, 130.0, 129.5, 128.9, 128.1, 128.0, 126.7, 126.1, 125.8, 122.2, 110.9, 56.2, 55.6, 52.2, 50.3, 34.5, 30.5, 28.3, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{39}H_{46}NO_3$: 576.3473; found:576.3470.

2, 6-di-*tert*-butyl-4-(phenyl (1-(4-(phenyl ethynyl) benzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) methyl) phenol (5k)



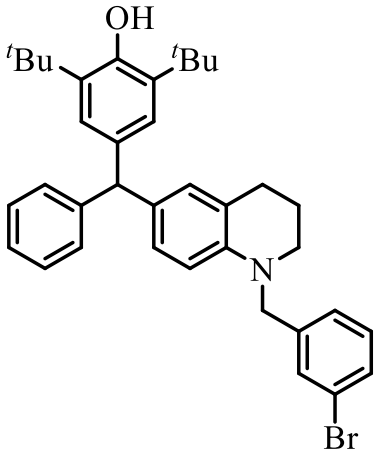
By following the **GP-1**, the title compound **5k** was isolated as dark-red liquid (0.500 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.50 (m, 2H), 7.45 (d, J = 8.1Hz, 2H), 7.32 – 7.29 (m, 3H), 7.24 - 7.21 (m, 4H), 7.15 – 7.12 (m, J = 8.2 Hz, 3H), 6.93 (s, 2H), 6.76 (s, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 5.02 (brs, 1H), 4.41 (s, 2H), 3.31 – 3.29 (m, 2H), 2.73 (t, J = 6.2 Hz, 2H), 1.97 (pent, J = 6.1 Hz, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 145.9, 143.8, 139.9, 134.0, 135.4, 135.0, 132.5, 131.9, 131.7, 130.2, 129.5, 128.4, 128.3, 128.1, 128.0, 126.9, 126.1, 125.8, 123.5, 122.2, 121.7, 111.0, 89.5, 89.2, 56.2, 55.5, 50.1, 34.5, 30.5, 28.3, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{45}H_{48}NO$: 618.3731; found:618.3727.

4-((1-(4-(allyloxy) benzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-*tert*-butylphenol (5l)



By following the **GP-1**, the title compound **5l** was isolated as dark-red liquid (0.482 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H), 7.16 – 7.14(m, 3H), 7.12 (d, J = 7.7 Hz, 2H), 6.92 (s, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.74 (s, 1H), 6.66 (d, J = 8.3 Hz, 1H), 6.44 (d, J = 8.5 Hz, 1H), 6.07 – 6.01 (m, 1H), 5.40 (d, J = 16.4 Hz, 1H), 5.28 – 5.26 (m, 2H), 5.02 (s, 1H), 4.50 (d, J = 5.2 Hz, 2H), 4.37 (s, 2H), 3.29– 3.27 (m, 2H), 2.72 (t, J = 6.2 Hz, 2H), 1.95 (pent, J = 5.9 Hz, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 157.7, 152.0, 146.0, 144.1, 135.3, 135.0, 133.6, 132.2, 131.4, 130.1, 129.5, 128.1, 128.02, 127.95, 126.1, 125.8, 122.1, 117.75, 114.9, 110.9, 69.0, 56.2, 54.9 49.8, 34.5, 30.5, 28.4, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{40}H_{48}NO_2$: 574.3680; found: 574.3677.

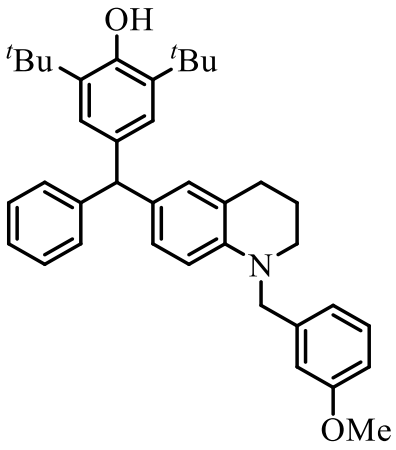
4-((1-(3-bromobenzyl)-1,2,3,4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-*tert*-butylphenol (5m)



By following the **GP-1**, the title compound **5m** was isolated as dark-red liquid (0.513 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 7.40 (s, 1H), 7.34 (d, J = 7.3 Hz, 1H), 7.23 (t, J = 7.1 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.10 (m, 3H), 6.92 (s, 2H), 6.76 (s, 1H), 6.66 (d, J = 8.2 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 5.26 (s, 1H), 5.01 (s, 1H), 4.38 (s, 2H), 3.30 (t, J = 5.6 Hz, 2H), 2.73 (t, J = 6.3 Hz, 2H), 1.98 (pent, J = 6.0 Hz, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0, 145.9, 143.7, 142.1, 135.4, 135.0, 132.7, 130.3, 130.2, 130.0, 129.8, 129.5,

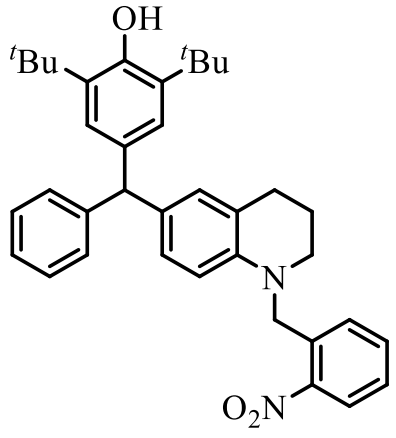
128.1, 128.0, 126.1, 125.8, 125.4, 122.9, 122.3, 111.0, 56.2, 55.3, 50.2, 34.5, 30.5, 28.3, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}BrNO$: 596.2523; found: 596.2523.

2, 6-di-*tert*-butyl-4-((1-(3-methoxybenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) Phenol (5n)



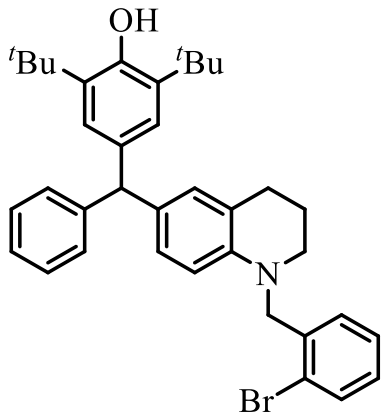
By following the **GP-1**, the title compound **5n** was isolated as dark-red liquid (0.498 g, 91%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (q, J = 9.2, 8.3 Hz, 3H), 7.12 (d, J = 6.0 Hz, 3H), 6.93 (d, J = 2.7 Hz, 2H), 6.88 – 6.78 (m, 2H), 6.75 (s, 2H), 6.66 (d, J = 8.2 Hz, 1H), 6.41 (dd, J = 8.4, 2.3 Hz, 1H), 5.26 (s, 1H), 5.01 (s, 1H), 4.39 (s, 2H), 3.74 (s, 3H), 3.34 – 3.28 (m, 2H), 2.72 (t, J = 5.5 Hz, 2H), 1.97 (pent, J = 6.5 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 160.1, 152.0, 146.0, 144.0, 141.2, 135.4, 135.1, 132.3, 130.1, 129.7, 129.5, 128.1, 128.0, 126.1, 125.8, 122.1, 119.2, 112.5, 112.1, 111.0, 56.2, 55.5, 55.2, 50.1, 34.5, 30.5, 28.4, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{46}NO_2$: 548.3524; found: 548.3522.

2, 6-di-*tert*-butyl-4-((1-(2-nitrobenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) Phenol (5o)



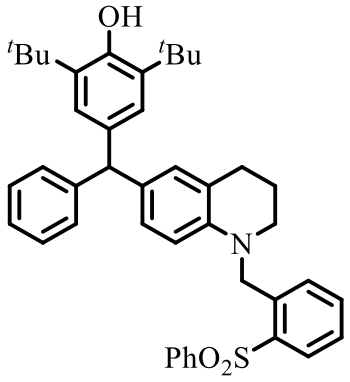
By following the **GP-1**, the title compound **5o** was isolated as dark-red liquid (0.422 g, 75%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.15 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 6.91 (s, 2H), 6.79 (s, 1H), 6.62 (d, J = 8.3 Hz, 1H), 6.15 (d, J = 8.4 Hz, 1H), 5.27 (s, 1H), 5.05 (brs, 1H), 4.80 (s, 2H), 3.38 – 3.35 (m, 2H), 2.78 (t, J = 6.1 Hz, 2H), 2.03 (m, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 148.2, 145.8, 135.3, 134.8, 134.0, 132.8, 130.2, 129.4, 128.7, 128.1, 128.0, 127.8, 126.1, 125.8, 125.6, 122.1, 110.6, 56.1, 54.2, 50.4, 34.4, 30.4, 28.2, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}N_2O_3$: 563.3269; found: 563.3254.

4-((1-(2-bromobenzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-*tert*-butylphenol (5p)



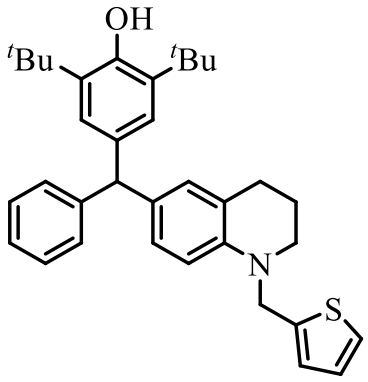
By following the **GP-1**, the title compound **5p** was isolated as dark-red liquid (0.489 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, J = 7.7 Hz, 1H), 7.25 – 7.21 (m, 4H), 7.16 – 7.09 (m, 4H), 6.91 (s, 2H), 6.77 (s, 1H), 6.63 (d, J = 8.4 Hz, 1H), 6.20 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.43 (s, 2H), 3.40 – 3.34 (m, 2H), 2.76 (t, J = 6.2 Hz, 2H), 2.02 (pent, J = 6.1 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 145.9, 143.5, 137.5, 135.4, 132.9, 132.5, 130.1, 129.5, 128.4, 128.09, 128.05, 128.0, 127.6, 126.1, 125.8, 123.0, 122.0, 110.7, 56.5, 56.2, 50.3, 34.5, 30.5, 28.3, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}BrNO$: 596.2523; found: 596.2524.

2, 6-di-*tert*-butyl-4-(phenyl (1-(2-(phenylsulfonyl) benzyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) methyl) phenol (5q)



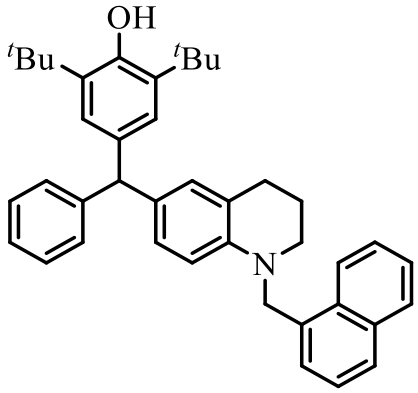
By following the **GP-1**, the title compound **5q** was isolated as dark-red liquid (0.559 g, 85%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.53 – 7.40 (m, 6H), 7.24 - 7.21 (m, 2H), 7.14 (t, J = 7.1 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 6.86 (s, 2H), 6.70 (s, 1H), 6.33 (d, J = 8.3 Hz, 1H), 5.45 (d, J = 8.4 Hz, 1H), 5.19 (s, 1H), 5.03 (brs, 1H), 4.58 (s, 2H), 3.26 – 3.24 (m, 2H), 2.70 (t, J = 6.1 Hz, 2H), 1.95 (p, J = 6.2 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 145.8, 143.1, 141.2, 139.1, 138.0, 135.4, 134.9, 134.2, 133.4, 132.5, 130.1, 130.0, 129.4, 129.3, 128.07, 128.05, 127.9, 127.8, 127.4, 126.1, 125.8, 121.9, 110.2, 56.1, 53.2, 50.5, 34.5, 30.5, 28.2, 22.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{43}H_{48}NO_3S$: 658.3350; found: 658.3349.

2, 6-di-*tert*-butyl-4-(phenyl (1-(thiophen-2-ylmethyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) methyl) phenol (5r)



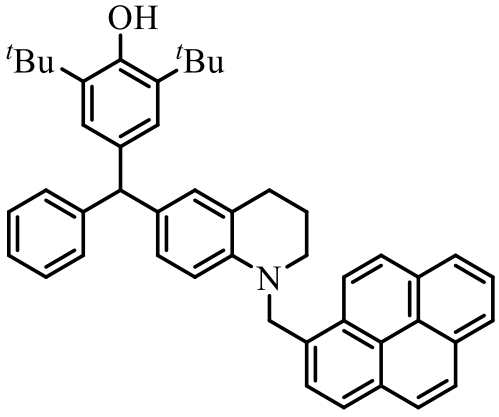
By following the **GP-1**, the title compound **5r** was isolated as dark-red liquid (0.425 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.20 (m, 2H), 7.17 – 7.09 (m, 4H), 6.91 (d, J = 8.8 Hz, 4H), 6.72 (d, J = 12.9 Hz, 2H), 6.61 (d, J = 8.3 Hz, 1H), 5.27 (s, 1H), 5.02 (s, 1H), 4.57 (s, 2H), 3.33 – 3.27 (m, 2H), 2.68 (t, J = 6.3 Hz, 2H), 1.94 (pent, J = 6.0 Hz, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0, 143.3, 145.9, 142.7, 135.4, 135.0, 132.9, 130.3, 129.5, 128.1, 127.9, 126.8, 126.2, 125.8, 124.9, 124.2, 122.8, 111.5, 56.2, 50.8, 49.6, 34.5, 30.5, 28.2, 22.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{35}H_{42}NOS$: 524.2982; found: 524.2975.

2, 6-di-*tert*-butyl-4-((1-(naphthalen-2-ylmethyl)-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5s)



By following the **GP-1**, the title compound **5s** was isolated as dark-red liquid (0.488 g, 86%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 7.3 Hz, 1H), 7.73 (d, J = 7.3 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.39 – 7.35 (m, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.14-7.13 (m, 3H), 6.94 (s, 2H), 6.80 (s, 1H), 6.64 (s, 1H), 6.36 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 5.01 (brs, 1H), 4.86 (s, 2H), 3.33 (t, J = 5.6 Hz, 2H), 2.77 (t, J = 6.4 Hz, 2H), 1.99 (pent, J = 6.2 Hz, 2H), 1.35 (s, 18H).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 146.0, 135.3, 135.0, 133.2, 130.0, 129.4, 128.9, 128.1, 128.0, 127.4, 126.1, 126.1, 125.8, 125.7, 123.9, 122.9, 122.2, 110.8, 56.2, 53.5, 49.7, 34.4, 30.5, 28.4, 22.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{41}H_{46}NO$: 568.3574; found: 568.3577.

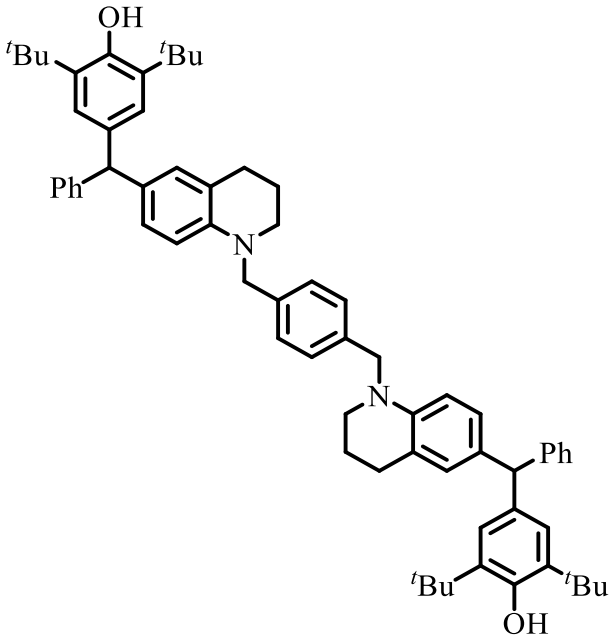
2,6-di-*tert*-butyl-4-((1-((4,6-dihydropyren-1-yl) methyl)-1,2,3,4-tetrahydroquinolin-6-yl) (phenyl)methyl) phenol (5t)



By following the **GP-1**, the title compound **5t** was isolated as dark-red liquid (0.533 g, 83%) 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 8.21 (d, J = 9.2 Hz, 1H), 8.14 (t, J = 7.0 Hz, 2H), 8.08 – 8.05 (m, 2H), 7.99 (s, 2H), 7.97 – 7.94 (m, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.23 (t, J = 7.5 Hz, 2H),

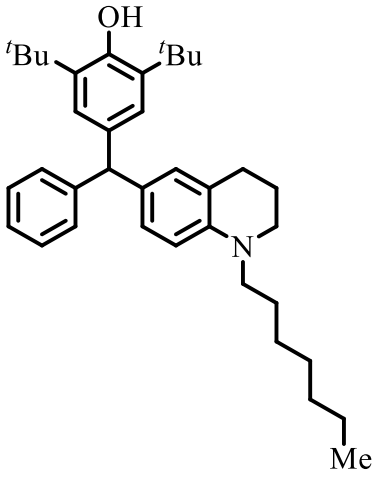
7.15 (d, J = 7.8 Hz, 3H), 6.95 (s, 2H), 6.84 (s, 1H), 6.66 (d, J = 8.3 Hz, 1H), 6.46 (d, J = 8.5 Hz, 1H), 5.29 (s, 1H), 5.10 (s, 2H), 5.00 (brs, 1H), 3.34 (t, J = 5.6 Hz, 2H), 2.79 (t, J = 6.4 Hz, 2H), 2.00 (pent, J = 6.2 Hz, 2H), 1.35 (s, 18H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.0, 146.0, 135.4, 135.0, 132.5, 131.9, 131.5, 130.9, 130.2, 129.5, 128.5, 128.1, 128.1, 127.6, 127.00, 126.1, 126.0, 125.8, 125.2, 125.2, 125.0, 124.9, 122.5, 122.5, 111.0, 56.3, 53.8, 49.7, 34.5, 30.5, 28.4, 22.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{47}H_{48}NO$: 642.3731; found: 642.3722.

4,4'-((1,1'-(1,4-phenylenebis(methylene)) bis(1,2,3,4-tetrahydroquinoline-6,1-diyl)) bis (phenyl methylene)) bis(2,6-di-*tert*-butylphenol) (5u)



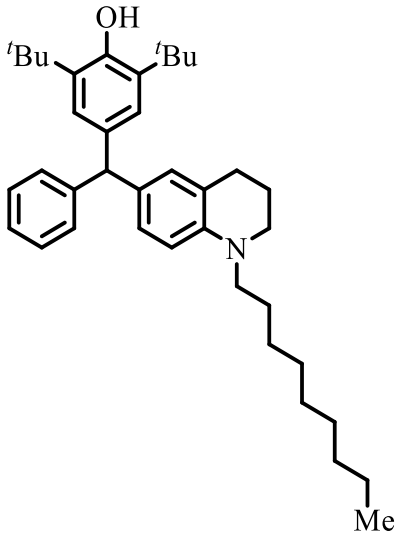
By following the **GP-1**, with 0.5 mmol of **2a**, and Hantzsch ester 6.5 mmol, the title compound **5u** was isolated as dark-red liquid (0.340 g, 71%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.23 (m, 2H), 7.21 (s, 1H), 7.17 (s, 4H), 7.15 (s, 1H), 7.15 – 7.11 (m, 5H), 6.91 (s, 4H), 6.85 – 6.78 (m, 1H), 6.74 (s, 2H), 6.65 (d, J = 8.3 Hz, 2H), 6.42 (d, J = 8.5 Hz, 2H), 5.25 (s, 2H), 5.01 (brs, 2H), 4.40 (s, 4H), 3.30 – 3.28 (m, 4H), 2.73 – 2.70 (m, 4H), 1.98 – 1.93 (m, 4H), 1.35 (s, 36H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.0, 146.0, 144.0, 137.8, 135.3, 135.0, 132.2, 130.1, 129.5, 128.1, 128.0, 127.0, 126.1, 125.8, 122.1, 110.9, 56.2, 55.2, 50.0, 34.5, 30.5, 28.4, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{68}H_{81}N_2O_2$: 957.6293; found: 957.6264.

2, 6-di-*tert*-butyl-4-((1-heptyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5v)



By following the **GP-1**, the title compound **5v** was isolated as dark-red liquid (0.415 g, 79%) 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 7.23 (d, J = 7.5 Hz, 2H), 7.16 - 7.13 (m, 3H), 6.93 (s, 2H), 6.72 - 6.70 (m, 2H), 6.45 (d, J = 8.1 Hz, 1H), 5.25 (s, 1H), 5.02 (s, 1H), 3.24 – 3.22 (m, 2H), 3.19 – 3.17 (m, 2H), 2.66 (t, J = 6.2 Hz, 2H), 1.91 (pent, J = 6.1 Hz, 2H), 1.36 (s, 18H), 1.31-1.25 (m, 9H), 0.88-0.86 (m, 4H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.0, 146.1, 143.7, 135.3, 135.1, 131.6, 130.2, 129.5, 128.1, 127.8, 126.2, 125.7, 122.0, 110.4, 56.2, 51.8, 49.5, 34.5, 32.0, 30.5, 29.4, 28.4, 27.4, 26.4, 22.8, 22.6, 14.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{52}NO$: 526.4044; found: 526.4032.

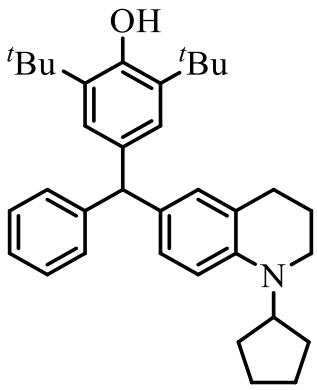
2, 6-di-*tert*-butyl-4-((1-nonyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5w)



By following the **GP-1**, the title compound **5w** was isolated as dark-red liquid (0.426 g, 77%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H), 7.16-7.13 (m, 3H), 6.94 (s, 2H), 6.72-6.70 (m, 2H), 6.45 (d, J = 8.1 Hz, 1H), 5.26 (s, 1H), 5.02 (brs, 1H), 3.25 – 3.21 (m, 2H), 3.21 – 3.15

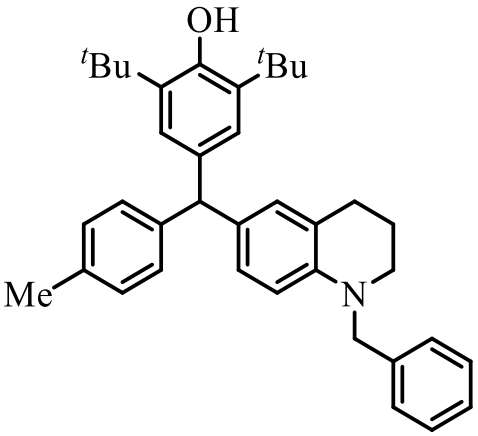
(m, 2H), 2.66 (t, J = 6.2 Hz, 2H), 1.91 – 1.89 (m, 2H), 1.56 – 1.54 (m, 2H), 1.36 (s, 18H), 1.30 (m, 12H), 0.88 - 0.86 (m, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.0, 146.1, 143.7, 135.3, 135.1, 131.6, 130.2, 129.5, 128.1, 127.8, 126.15, 125.7, 122.0, 110.4, 56.2, 51.8, 49.5, 34.5, 32.0, 30.5, 29.8, 29.7, 29.4, 28.4, 27.45, 26.4, 22.8, 22.6, 14.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{39}H_{56}NO$: 554.4357; found: 554.4364.

2, 6-di-*tert*-butyl-4-((1-cyclopentyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl) phenol (5x)



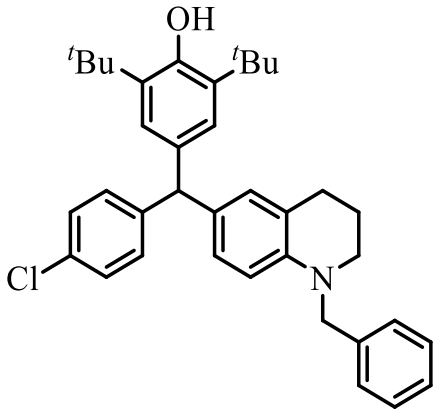
By following the **GP-1**, the title compound **5x** was isolated as dark-red liquid (0.322 g. 65%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 - 7.21 (m, 2H), 7.14-7.12 (m, 3H), 6.94 (s, 2H), 6.74 – 6.71 (m, 2H), 6.61 (d, J = 8.4 Hz, 1H), 5.26 (s, 1H), 5.01 (brs, 1H), 4.15 (pent, J = 7.8 Hz, 1H), 3.14 (t, J = 5.8 Hz, 2H), 2.64 (t, J = 6.4 Hz, 2H), 1.88 – 1.84 (m, 4H), 1.68 (br, 2H), 1.58 (br, 4H), 1.36 (s, 18H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 152.0, 146.1, 144.5 135.3, 135.1, 131.7, 130.1, 129.5, 128.0, 127.8, 126.1, 125.7, 123.1, 110.9, 58.8, 56.2, 42.1, 34.5, 30.5, 28.6, 28.1, 24.3, 22.9. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{35}H_{46}NO$: 496.3574; found: 496.3575.

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



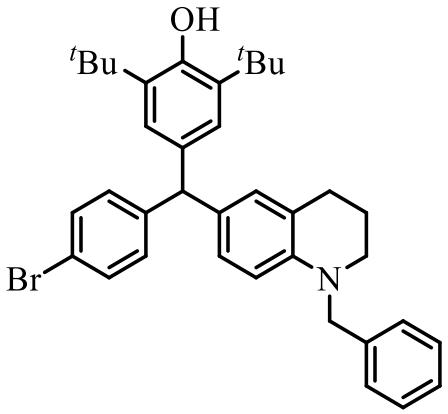
By following the **GP-2**, the title compound **6a** was isolated as dark-red liquid (0.431 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 2H), 7.25 (d, J = 6.0 Hz, 3H), 7.21 (t, J = 7.1 Hz, 1H), 7.04 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 7.9 Hz, 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), 3.31 (t, J = 5.7 Hz, 2H), 2.73 (t, J = 6.4 Hz, 2H), 2.29 (s, 3H), 1.97 (pent, 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 (6b)



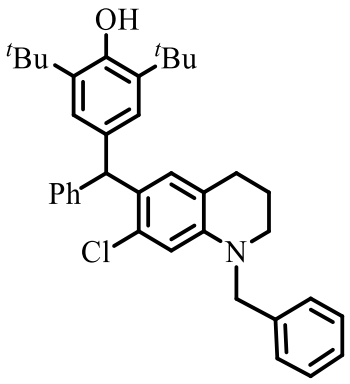
By following the **GP-2**, the title compound **6b** was isolated as dark-red liquid (0.480 g, 87%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (t, J = 7.4 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.20 (d, J = 8.2 Hz, 2H), 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 = 8.4 Hz, 1H), 5.22 (s, 1H), 5.04 (s, 1H), 4.44 (s, 2H), 3.33 (t, J = 5.6 Hz, 2H), 2.73 (t, J = 6.4 Hz, 2H), 1.98 (pent, J = 6.2 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 $C_{37}H_{42}ClNO$: 552.3028; found: 552.3025.

4-((1-benzyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (4-bromophenyl) methyl)-2, 6-di-*tert*-butylphenol (6c)



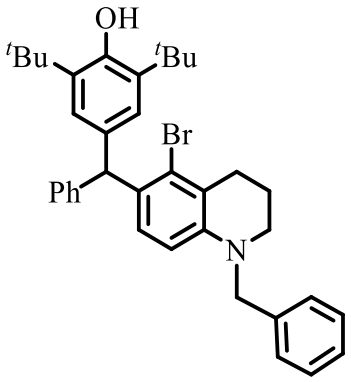
By following the **GP-2**, the title compound **6c** was isolated as dark-red liquid (0.531 g, 89%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H), 7.23 (d, J = 6.9 Hz, 2H), 7.22 – 7.17 (m, 1H), 6.99 (d, J = 8.2 Hz, 2H), 6.89 (s, 2H), 6.71 (s, 1H), 6.63 (d, J = 7.2 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 5.20 (s, 1H), 5.03 (s, 1H), 4.42 (s, 2H), 3.31 (t, J = 5.6 Hz, 2H), 2.72 (t, J = 6.3 Hz, 2H), 1.96 (pent, J = 6.0 Hz, 2H), 1.35 (s, 18H). ^{13}C{^{1}H) NMR (126 MHz, $CDCl_3$): δ 152.2, 145.2, 144.1, 139.2, 135.6, 134.48, 134.46, 131.5, 131.2, 131.1, 130.0, 128.6, 127.9, 126.9, 126.8, 126.0, 122.2, 119.6, 111.0, 55.6, 55.5, 50.0, 34.5, 30.5, 28.4, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}BrNO$: 596.2523; found: 596.2526.

4-((1-benzyl-7-chloro-1,2,3,4-tetrahydroquinolin-6-yl)(phenyl)methyl)-2,6-di-*tert*-butylphenol (6d)



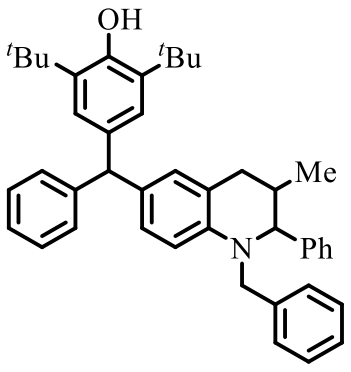
By following the **GP-2**, the title compound **6d** was isolated as dark-red liquid (0.453 g, 82%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.30 (m, 2H), 7.25 – 7.23 (m, 5H), 7.17 – 7.15 (m, 1H), 7.10 (d, J = 7.6 Hz, 2H), 6.89 (s, 2H), 6.55 (s, 1H), 6.52 (s, 1H), 5.69 (s, 1H), 5.04 (s, 1H), 4.42 (s, 2H), 3.29 – 3.27 (m, 2H), 2.65 – 2.63 (m, 2H), 1.95 – 1.91 (m, 2H), 1.36 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.1, 144.9, 144.7, 138.5, 135.4, 133.9, 132.7, 131.0, 129.5, 129.2, 128.8, 128.1, 127.1, 126.8, 126.3, 125.9, 120.9, 111.3, 55.2, 52.4, 49.5, 34.5, 30.5, 28.0, 22.4. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}ClNO$: 552.3028; found: 552.3026.

4-((1-benzyl-5-bromo-1,2,3,4-tetrahydroquinolin-6-yl)(phenyl)methyl)-2,6-di-tert-butylphenol (6e)



By following the **GP-2**, the title compound **6e** was isolated as dark-red liquid (0.447 g, 75%) 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 7.31 – 7.28 (m, 2H), 7.23 – 7.22 (m, 5H), 7.16 – 7.13 (m, 1H), 7.07 (d, J = 7.7 Hz, 2H), 6.84 (s, 2H), 6.53 (d, J = 8.6 Hz, 1H), 6.38 (d, J = 8.6 Hz, 1H), 5.79 (s, 1H), 5.01 (s, 1H), 4.49 – 4.40 (m, 2H), 3.33 – 3.31 (m, 2H), 2.89 – 2.87 (m, 2H), 2.05 – 2.00 (m, 2H), 1.33 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0, 145.6, 144.6, 138.85, 135.35, 134.3, 131.8, 129.6, 129.1, 128.7, 128.0, 127.0, 126.7, 126.5, 125.8, 122.0, 110.2, 56.0, 55.9, 49.7, 34.4, 30.5, 29.9, 22.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{37}H_{43}BrNO$: 596.2523; found: 596.2509.

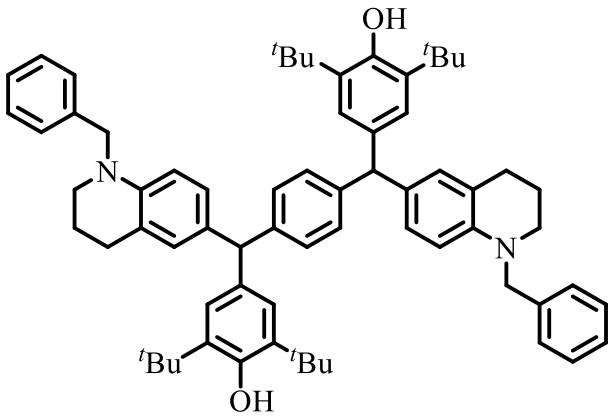
4-((1-benzyl-3-methyl-2-phenyl-1, 2, 3, 4-tetrahydroquinolin-6-yl) (phenyl) methyl)-2, 6-di-*tert*-butylphenol (6f)



By following the **GP-2**, the title compound **6f** was isolated as dark-red liquid (0.474 g, 78%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). cis: trans = 1:1. ^{1}H 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 {^{1}H} NMR (126 MHz, $CDCl_3$):

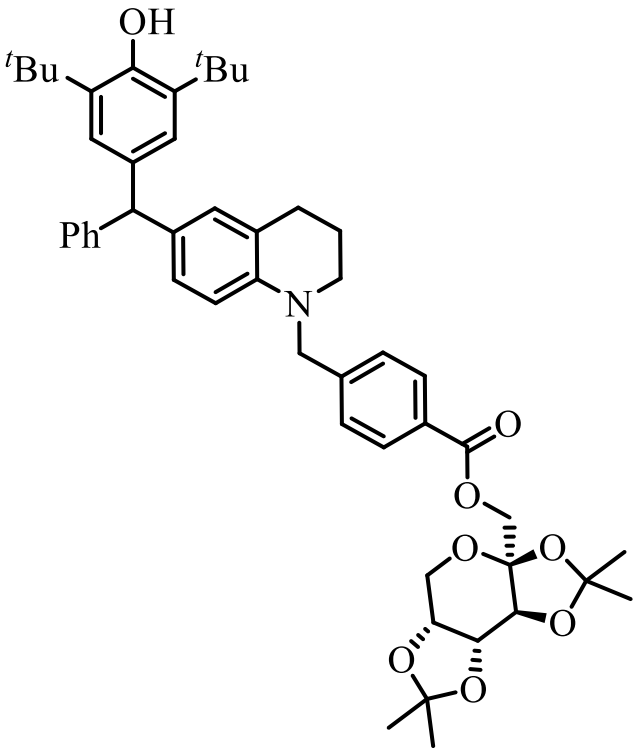
δ 152.0, 146.1, 145.9, 143.5, 140.81, 140.79, 139.32, 139.28, 135.3, 135.1, 131.8, 131.7, 130.0, 129.8, 129.6, 129.5, 128.72, 128.68, 128.3, 128.2, 128.11, 128.09, 128.0, 127.3, 126.8, 126.4, 126.22, 126.17, 125.8, 121.27, 121.25, 109.78, 109.75, 67.2, 56.14, 56.06, 53.4, 34.5, 31.72, 31.68, 30.51, 30.5, 18.7, 18.6. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{44}H_{50}NO$: 608.3887; found: 608.3895.

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



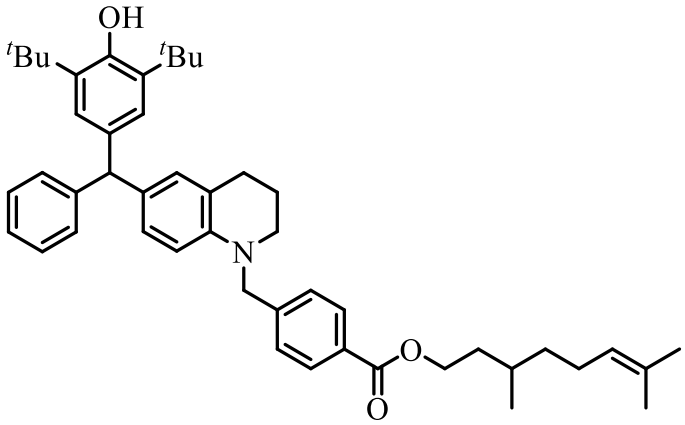
By following the **GP -2**, the title compound **6g** was isolated as dark-red liquid (0.613 g, 64%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 5H), 7.25 – 7.20 (m, 5H), 6.99 (s, 4H), 6.91 (s, 4H), 6.74 (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 (pent, J = 6.1 Hz, 4H), 1.35 (s, 36H). ^{13}C{^{1}H} 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.

((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-((6-((R)-(3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl)methyl)benzoate (8a)



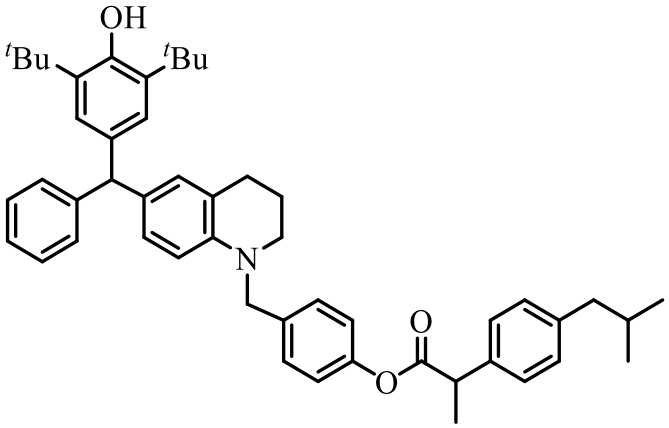
By following the **GP-1**, the title compound **8a** was isolated as dark-red liquid (0.571 g, 71%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 60/40, R_f = 0.38). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.17 – 7.09 (m, 3H), 6.92 (s, 2H), 6.77 (s, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.03 (s, 1H), 4.68 – 4.61 (m, 2H), 4.49 – 4.44 (m, 3H), 4.33 (d, J = 11.8 Hz, 1H), 4.25 (d, J = 8.5 Hz, 1H), 3.96 (dd, J = 13.0, 1.6 Hz, 1H), 3.80 (d, J = 13.0 Hz, 1H), 3.35 – 3.30 (m, 2H), 2.74 (t, J = 6.2 Hz, 2H), 1.99 (pent, J = 6.1 Hz, 2H), 1.54 (s, 3H), 1.46 (s, 3H), 1.39 – 1.33 (m, 24H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.0, 152.0, 145.8, 145.3, 143.6, 135.4, 134.9, 132.7, 130.2, 129.4, 128.6, 128.1, 127.95, 126.7, 126.1, 125.8, 122.2, 110.9, 109.3, 108.9, 101.8, 71.0, 70.6, 70.2, 65.4, 61.5, 56.2, 55.6, 50.3, 34.4, 30.5, 28.3, 26.7, 26.0, 25.8, 24.2, 22.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{50}H_{62}NO_8$:804.4470; found:804.4473.

3,7-dimethyloct-6-en-1-yl 4-((6-((3, 5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (8b)



By following the **GP-1**, the title compound **8b** was isolated as dark-red liquid (0.546 g, 78%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 7.4 Hz, 2H), 6.91 (s, 2H), 6.76 (s, 1H), 6.64 (d, J = 10.3 Hz, 1H), 6.33 (d, J = 8.5 Hz, 1H), 5.26 (s, 1H), 5.09 (t, J = 7.1 Hz, 1H), 5.02 (s, 1H), 4.47 (s, 2H), 4.34 (d, J = 7.1 Hz, 2H), 3.34 – 3.31 (m, 2H), 2.74 (t, J = 6.3 Hz, 2H), 2.05 – 1.95 (m, 4H), 1.78 (d, J = 12.6 Hz, 1H), 1.66 (s, 3H), 1.63 (d, J = 13.0 Hz, 1H), 1.59 (s, 3H), 1.57 (d, J = 14.0 Hz, 1H), 1.42 (s, 1H), 1.35 (s, 18H), 1.25 (d, J = 13.5 Hz, 1H), 0.96 (d, J = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 166.7, 152.0, 145.9, 144.9, 143.7, 135.4, 134.9, 132.7, 131.5, 130.2, 130.0, 129.46, 129.29, 128.08, 127.98, 126.72, 126.11, 125.80, 124.72, 122.22, 110.91, 63.51, 56.19, 55.6, 50.3, 37.1, 35.7, 34.5, 30.5, 29.7, 28.3, 25.8, 25.5, 22.7, 19.7, 17.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{48}H_{62}NO_3$:700.4725; found: 700.4721.

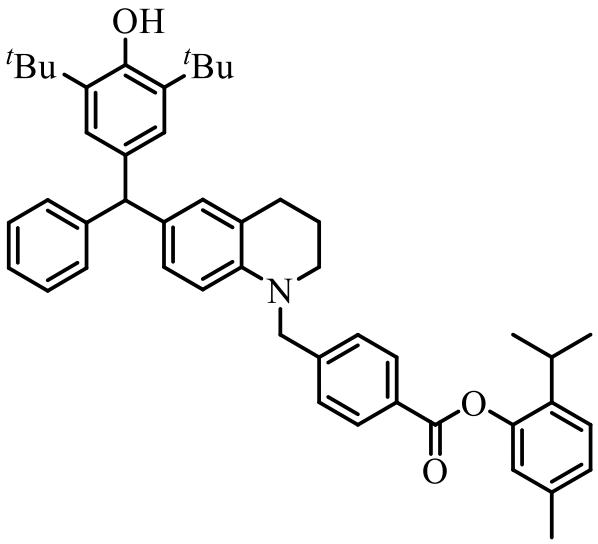
4-((6-((3, 5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl) methyl)-3, 4-dihydroquinolin-1(2H)-yl) methyl) phenyl 2-(4-isobutylphenyl) propanoate (8c)



By following the **GP-1**, the title compound **8c** was isolated as dark-red liquid (0.607 g, 84%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.68). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, J = 8.0 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.23 – 7.21 (m, 3H), 7.16 – 7.11 (m, 6H), 6.93 (s, 1H), 6.92 (s, 3H), 6.75 (br, 1H), 6.65 (d, J = 8.2 Hz, 1H),

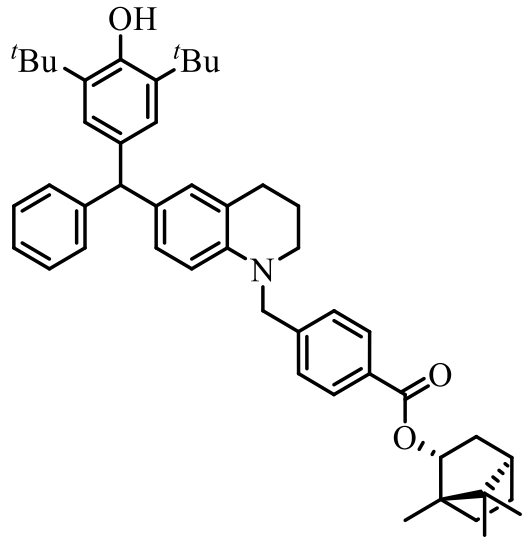
5.26 (s, 1H), 5.03 (s, 1H), 4.40 (s, 2H), 3.92 (q, J = 7.1 Hz, 1H), 3.29 – 3.27 (m, 2H), 2.72 (t, J = 6.2 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.98 – 1.94 (m, 2H), 1.89 – 1.85 (m, 2H), 1.60 (s, 2H), 1.36 (s, 18H), 0.91 (d, J = 6.6 Hz, 6H).$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 173.5, 152.0, 149.8, 145.9, 140.9, 137.4, 135.4, 135.0, 130.2, 129.6, 129.5, 128.1, 128.0, 127.4, 126.1, 125.8, 121.5, 56.2, 49.9, 45.4, 45.2, 34.5, 30.54, 30.51, 30.48, 30.3, 28.3, 22.5, 18.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{50}H_{60}NO_3$: 722.4568; found: 722.4566.

2-isopropyl-5-methylphenyl 4-((6-((3, 5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl) methyl)-3, 4-dihydroquinolin-1(2H)-yl) methyl) benzoate (8d)



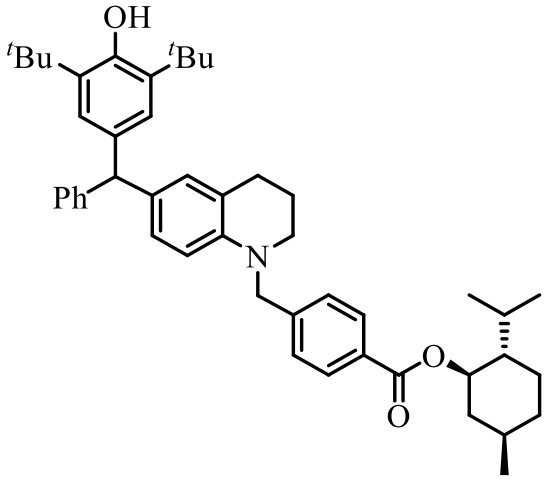
By following the **GP-1**, the title compound **8d** was isolated as dark-red liquid (0.638 g, 92%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/2, R_f = 0.62). ^1H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.16 – 7.12 (m, 3H), 7.05 (d, J = 7.8 Hz, 1H), 6.92 (s, 3H), 6.78 (s, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.35 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 5.03 (brs, 1H), 4.52 (s, 2H), 3.38 – 3.35 (m, 2H), 3.07 – 3.02 (m, 1H), 2.76 (t, J = 6.2 Hz, 2H), 2.33 (s, 3H), 2.04 – 1.99 (m, 2H), 1.36 (s, 18H), 1.20 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.4, 152.0, 148.3, 145.89, 145.85, 143.6, 137.3, 136.7, 135.4, 134.9, 132.7, 130.6, 130.3, 129.5, 128.4, 128.1, 128.0, 127.2, 127.0, 126.6, 126.1, 125.8, 123.0, 122.2, 110.9, 56.2, 55.6, 50.4, 34.5, 30.5, 28.3, 27.4, 23.2, 22.7, 21.0.(ESI) *m/z*: $[M+H]^+$ calculated for: $C_{48}H_{56}NO_3$:694.4255; found:694.4248.

(1S,2R,4R)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 4-((6-((3,5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (8e)



By following the **GP-1**, the title compound **8e** was isolated as dark-red liquid (0.579 g, 83%) 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 7.95 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.12 (d, J = 6.7 Hz, 3H), 6.92 (s, 2H), 6.78 (s, 1H), 6.65 (d, J = 8.3 Hz, 1H), 6.33 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 5.03 (brs, 1H), 4.92 – 4.90 (m, 1H), 4.45 (s, 2H), 3.32 – 3.30 (m, 2H), 2.73 (t, J = 6.2 Hz, 2H), 1.99 – 1.95 (m, 2H), 1.91 - 1.88 (m, 2H), 1.79 – 1.78 (m, 1H), 1.62 – 1.56 (m, 1H), 1.36 (s, 18H), 1.29 (d, J = 3.8 Hz, 2H), 1.11 (s, 3H), 0.92 (s, 3H), 0.88 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 166.0, 152.0, 145.8, 144.8, 143.5, 135.3, 134.9, 132.5, 130.2, 129.9, 129.5, 129.4, 128.0, 127.9, 126.7, 126.1, 125.7, 122.1, 110.8, 81.5, 56.1, 55.4, 50.2, 49.1, 47.1, 45.2, 39.0, 34.4, 33.8, 30.5, 28.2, 27.2, 22.6, 20.3, 20.2, 11.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{48}H_{60}NO_3$:698.4568; found: 698.4567.

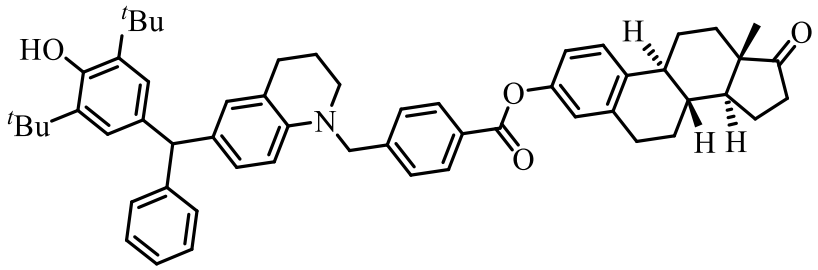
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl4-((6-((3,5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (8f)



By following the **GP-1**, the title compound **8f** was isolated as dark-red liquid (0.595 g, 85%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.68). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.29 – 7.26

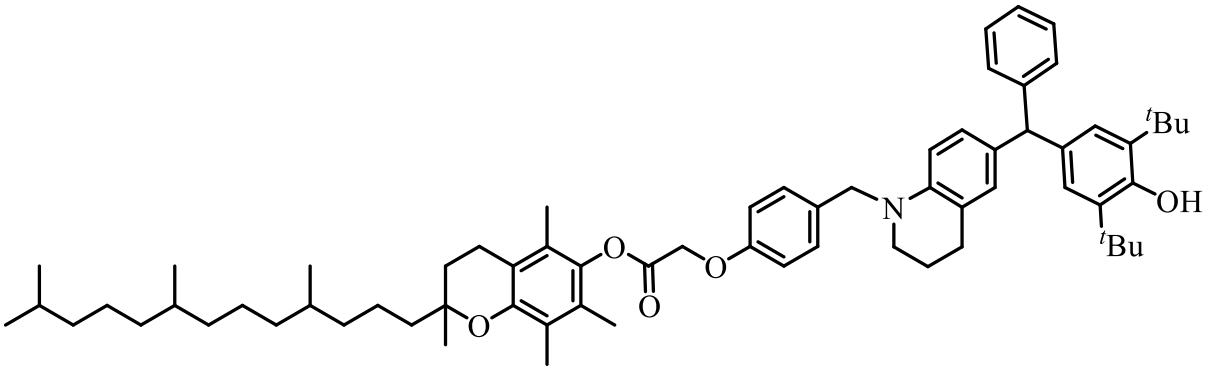
(m, 2H), 7.17 (dd, *J* = 21.4, 7.3 Hz, 3H), 6.95 (s, 2H), 6.80 (s, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 5.06 (s, 1H), 4.95 (td, *J* = 10.8, 4.4 Hz, 1H), 4.51 (s, 2H), 3.39 – 3.34 (m, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 2.15 (d, *J* = 11.9 Hz, 1H), 2.05 – 1.97 (m, 3H), 1.76 (d, *J* = 11.5 Hz, 2H), 1.58 (t, *J* = 12.5 Hz, 3H), 1.39 (s, 18H), 0.97 – 0.93 (m, 8H), 0.82 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): *δ* 166.3, 152.0, 145.9, 144.9, 143.7, 135.4, 135.0, 132.7, 130.2, 130.0, 129.6, 129.5, 128.1, 128.0, 126.7, 126.1, 125.8, 122.2, 110.9, 75.0, 56.2, 55.5, 50.3, 47.4, 41.1, 34.5, 31.6, 30.5, 28.3, 26.7, 23.8, 22.7, 22.2, 20.9, 16.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{48}H_{62}NO_3$:700.4725; found: 700.4714.

(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-((6-((3,5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (8g)



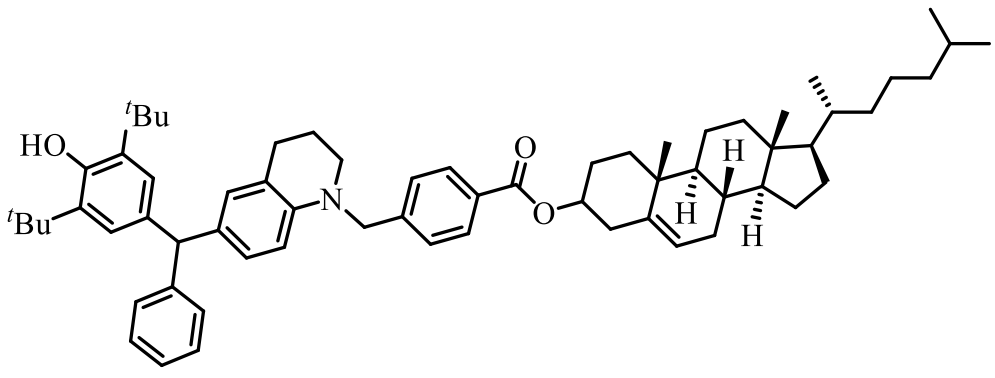
By following the **GP-1**, the title compound **8g** was isolated as dark-red liquid (0.529 g, 65%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 60/40, R_f = 0.38). ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.12 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.98 – 6.96 (m, 1H), 6.93 (s, 1H), 6.91 (s, 2H), 6.77 (s, 1H), 6.68 – 6.63 (m, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.26 (s, 1H), 5.03 (s, 1H), 4.51 (s, 2H), 3.37 – 3.35 (m, 2H), 2.95 – 2.93 (m, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.54 – 2.48 (m, 1H), 2.45 – 2.41 (m, 1H), 2.34 – 2.30 (m, 1H), 2.18 – 2.12 (m, 1H), 2.06 – 1.97 (m, 4H), 1.66 – 1.63 (m, 1H), 1.62 (d, *J* = 2.9 Hz, 1H), 1.59 – 1.56 (m, 3H), 1.55 – 1.52 (m, 2H), 1.36 (s, 18H), 0.92 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): *δ* 220.9, 165.5, 152.0, 149.0, 145.90, 145.88, 143.6, 138.2, 137.5, 135.4, 134.9, 132.8, 130.6, 130.3, 129.5, 128.4, 128.1, 128.0, 126.9, 126.6, 126.1, 125.8, 122.3, 121.9, 119.0, 110.9, 56.2, 55.7, 50.6, 50.4, 48.1, 44.4, 38.2, 36.0, 34.5, 31.7, 30.5, 29.6, 28.3, 26.5, 26.0, 22.7, 21.8, 14.0.HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{56}H_{64}NO_4$: 814.4830; found: 814.4824.

2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl) chroman-6-yl 2-(4-((6-((3,5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) phenoxy) acetate (8h)



By following the **GP-1**, the title compound **8h** was isolated as dark-red liquid (0.814 g, 81%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.68). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 3H), 7.15 – 7.10 (m, 4H), 6.94 – 6.93 (m, 4H), 6.76 (s, 1H), 6.68 (d, J = 8.5 Hz, 1H), 6.44 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 5.02 (s, 1H), 4.90 (s, 2H), 4.37 (s, 2H), 3.31 – 3.25 (m, 2H), 2.72 (t, J = 6.0 Hz, 2H), 2.57 (t, J = 6.4 Hz, 2H), 2.07 (s, 3H), 1.99 (s, 3H), 1.97 – 1.95 (m, 4H), 1.83 – 1.71 (m, 3H), 1.58 – 1.48 (m, 4H), 1.38 – 1.31 (m, 22H), 1.28 – 1.22 (m, 11H), 1.16 – 1.06 (m, 6H), 0.87 – 0.84 (m, 12H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 168.1, 156.9, 152.0, 149.8, 146.0, 144.0, 140.0, 135.4, 135.0, 132.7, 132.3, 130.2, 129.5, 128.2, 128.1, 128.0, 126.7, 126.1, 125.8, 124.9, 123.4, 122.2, 117.7, 115.0, 111.0, 75.3, 65.5, 56.2, 54.9, 49.8, 39.5, 37.69, 37.67, 37.6, 37.55, 37.53, 37.51, 37.48, 37.43, 34.5, 32.93, 32.91, 32.85, 32.82, 30.5, 28.4, 28.1, 24.9, 24.6, 22.9, 22.8, 22.6, 21.2, 20.7, 19.9, 19.83, 19.80, 19.77, 19.7, 13.1, 12.3, 11.9. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{68}H_{94}NO_5$:1004.7127; found:1004.7129.

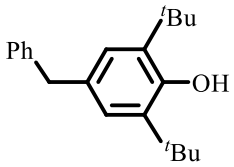
(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((6-((3,5-di-*tert*-butyl-4-hydroxyphenyl) (phenyl)methyl)-3,4-dihydroquinolin-1(2H)-yl) methyl) benzoate (8i)



By following the **GP-1**, the title compound **8i** was isolated as dark-red liquid (0.819 g, 88%) using silica gel column chromatography with pet-ether/ ethyl acetate (v/v = 50/4, R_f = 0.68). ^{1}H NMR (500 MHz, $CDcl_3$): δ 7.97 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.15 (d, J = 7.3 Hz, 1H), 7.11 (d, J = 7.4 Hz, 2H), 6.91 (s, 2H), 6.76 (s, 1H), 6.63 (d, J = 8.2 Hz, 1H), 6.33 (d, J = 8.5 Hz, 1H), 5.45 – 5.38 (m, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.84

(q, *J* = 12.1, 11.6 Hz, 1H), 4.47 (s, 2H), 3.37 – 3.29 (m, 2H), 2.74 (t, *J* = 6.1 Hz, 2H), 2.44 (d, *J* = 7.7 Hz, 2H), 2.03 – 1.94 (m, 5H), 1.91 (d, *J* = 13.5 Hz, 1H), 1.86 (s, 1H), 1.75 – 1.67 (m, 1H), 1.57 (d, *J* = 17.1 Hz, 3H), 1.54 – 1.50 (m, 2H), 1.47 (d, *J* = 13.5 Hz, 2H), 1.35 (s, 20H), 1.26 (t, *J* = 12.0 Hz, 2H), 1.22 – 1.18 (m, 1H), 1.17 – 0.95 (m, 11H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.1 Hz, 6H), 0.69 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 166.0, 152.0, 145.9, 144.8, 143.7, 139.8, 135.4, 134.9, 132.6, 130.2, 130.0, 129.6, 129.5, 128.1, 128.0, 126.7, 126.1, 125.8, 122.9, 122.2, 110.9, 74.6, 56.9, 56.3, 56.2, 55.6, 50.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.3, 36.0, 34.5, 32.1, 32.0, 30.5, 28.4, 28.3, 28.2, 28.0, 24.4, 24.0, 23.0, 22.72, 22.66, 21.2, 19.5, 18.9, 12.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{65}H_{88}NO_3$:930.6759; found: 930.6758.

4-benzyl-2,6-di-*tert*-butylphenol (4a'):



Light yellow solid (0.092 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.98 (s, 2H), 5.05 (s, 1H), 3.90 (s, 2H), 1.40 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.2, 141.9, 136.0, 131.7, 129.0, 128.5, 126.0, 125.6, 42.0, 34.4, 30.5. Spectral data is in accordance to the reported literature. [17]

9. ^{1}H, ^{13}C, and ^{19}F NMR spectra of the starting materials and products

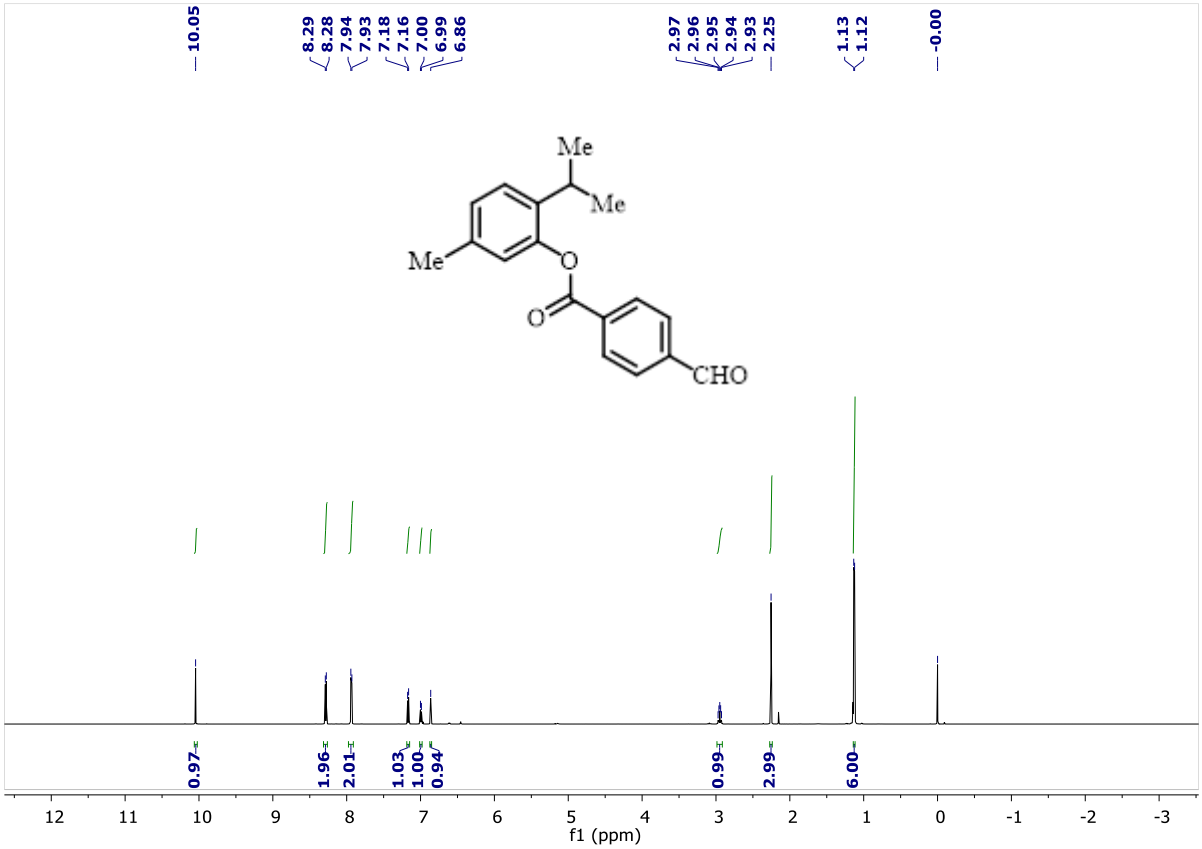


Figure S12: ^{1}H NMR Spectrum of **7d** ($CDCl_3$, 600 MHz, 298 K)

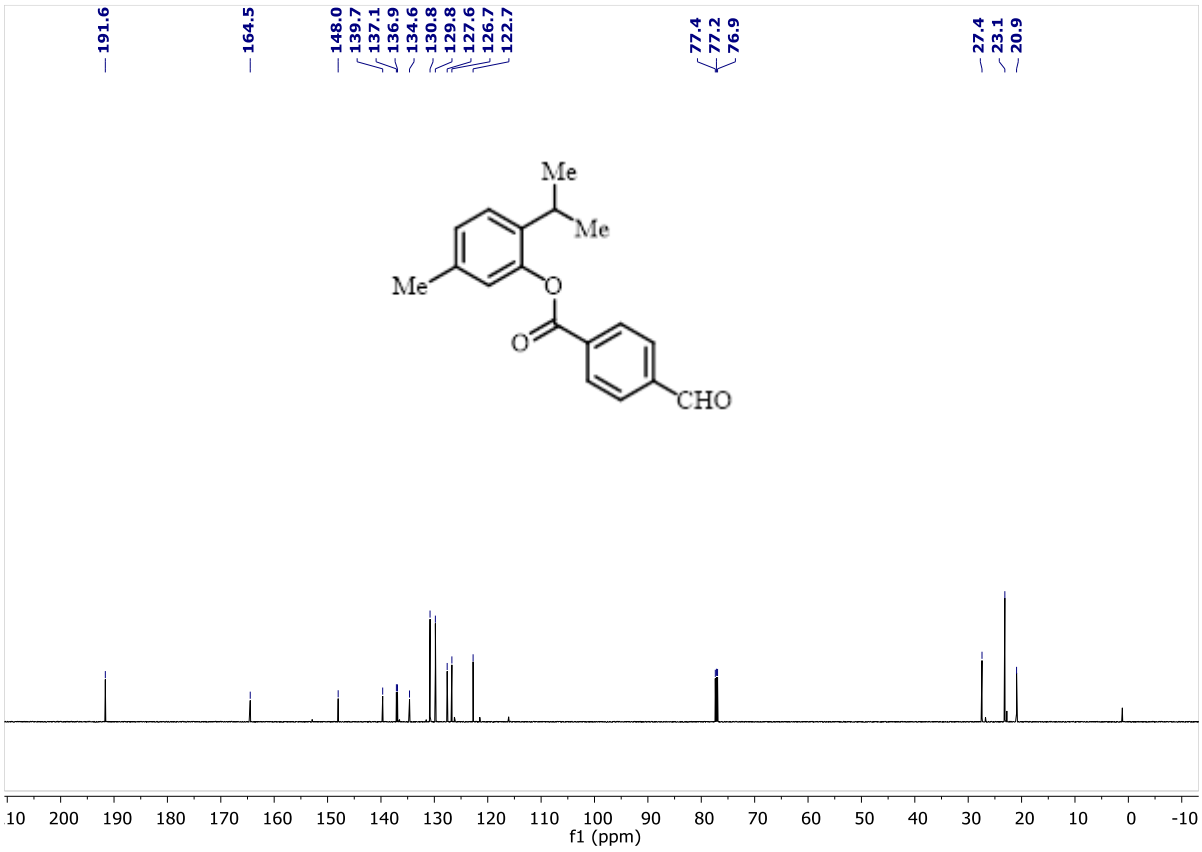


Figure S13: $^{13}C\{^{1}H\}$ NMR Spectrum of **7d** ($CDCl_3$, 151 MHz, 298 K)

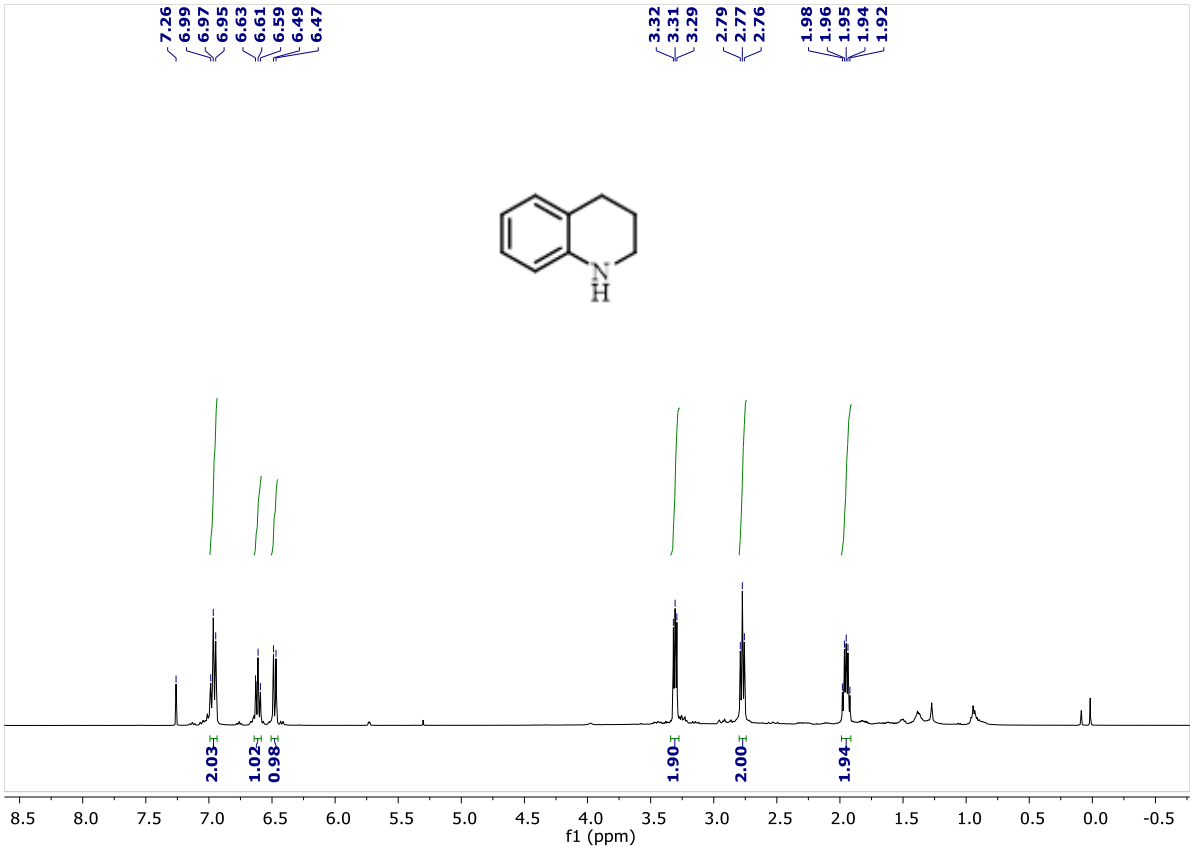


Figure S14: ^{1}H NMR Spectrum of **1a'** ($CDCl_3$, 400 MHz, 298 K)

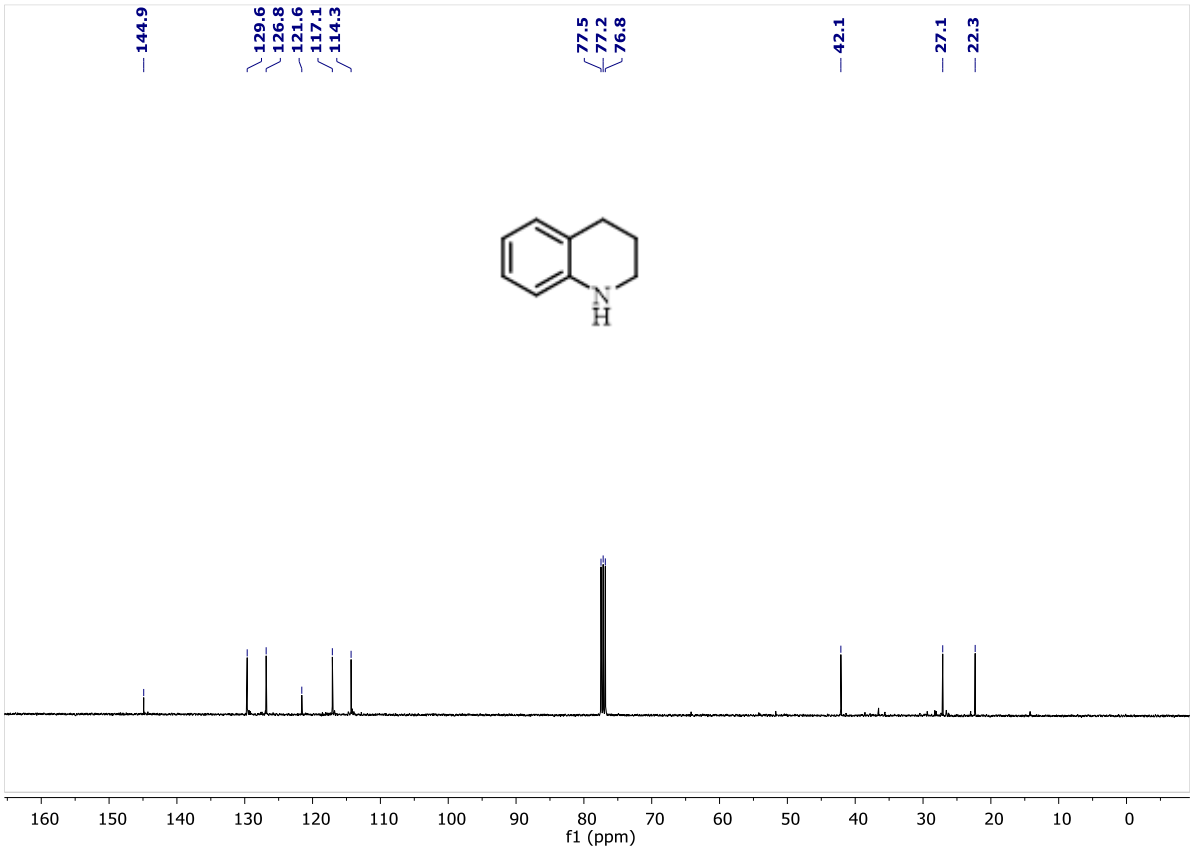


Figure S15: $^{13}C\{^{1}H\}$ NMR Spectrum of **1a'** ($CDCl_3$, 101 MHz, 298 K)

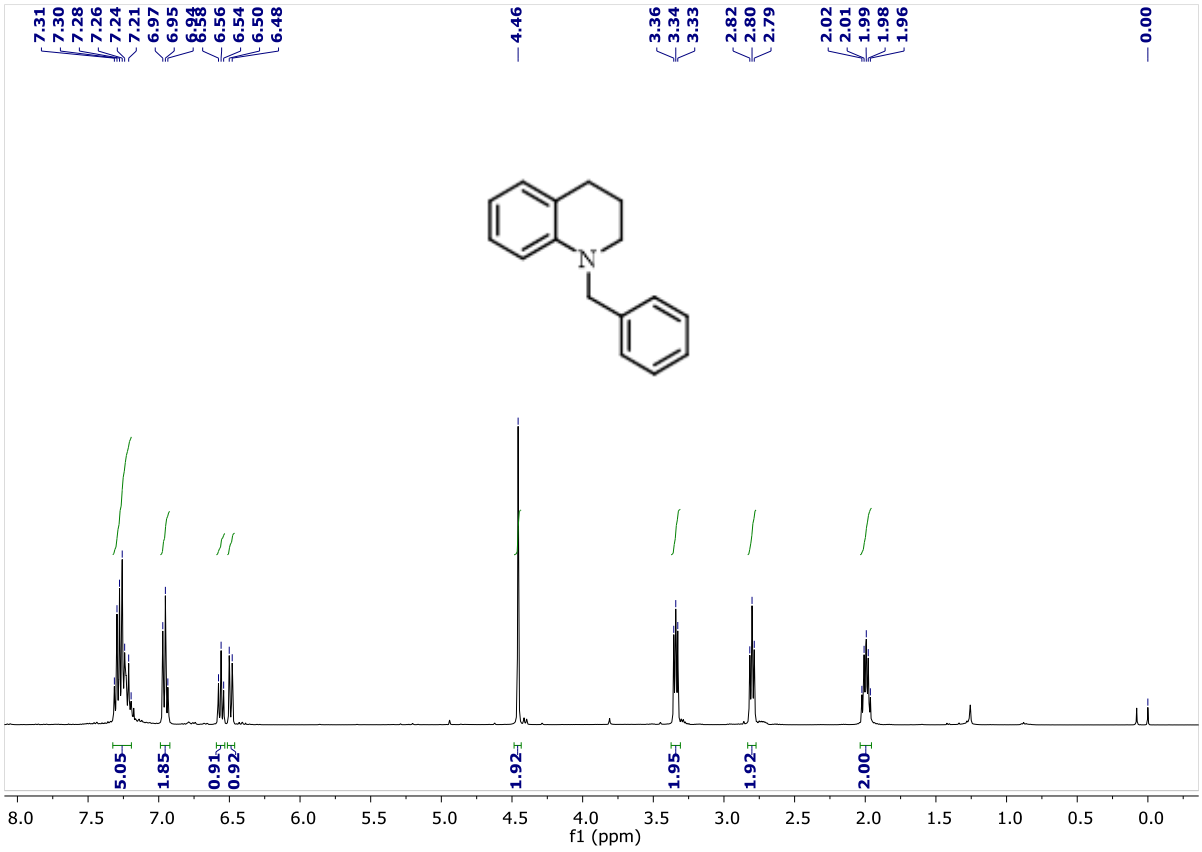


Figure S16: ^{1}H NMR Spectrum of **3a** ($CDCl_3$, 400 MHz, 298 K)

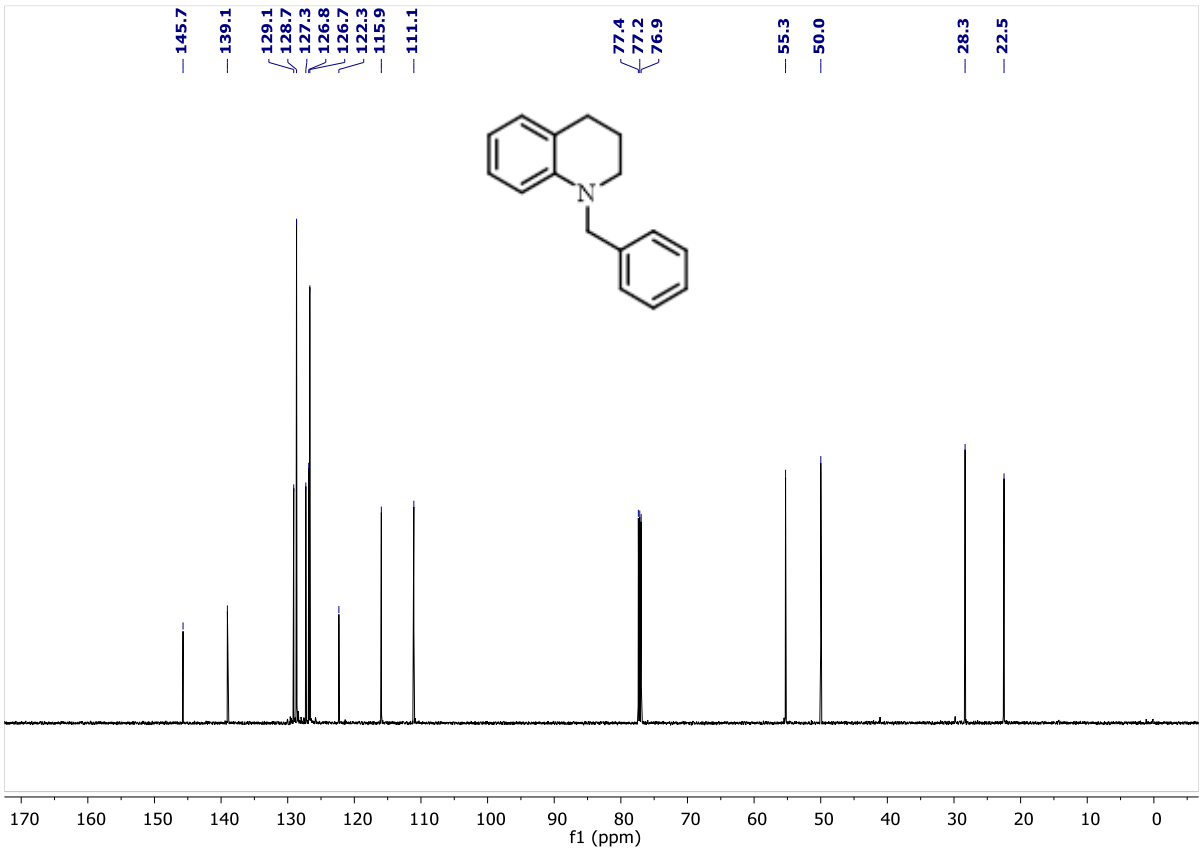


Figure S17: $^{13}C\{^{1}H\}$ NMR Spectrum of **3a** ($CDCl_3$, 151 MHz, 298 K)

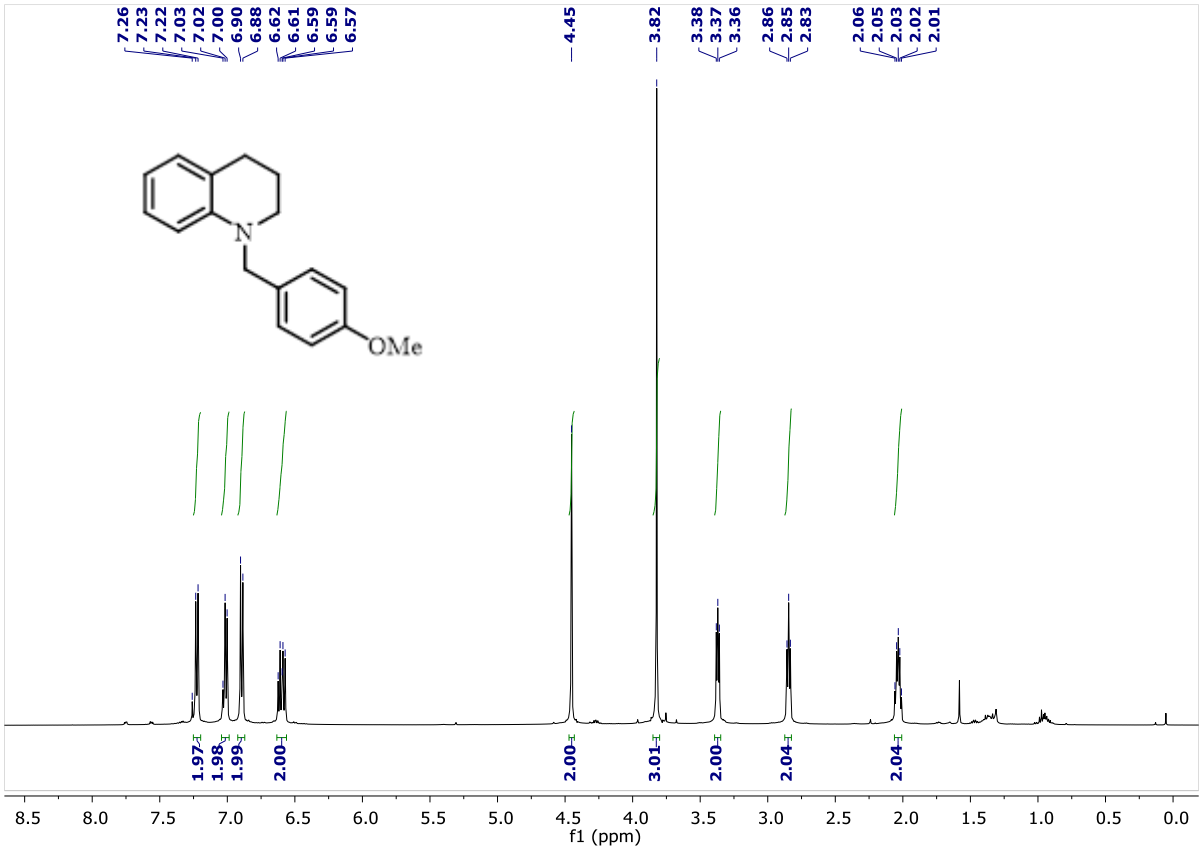


Figure S18: ^{1}H NMR Spectrum of **3c** ($CDCl_3$, 400 MHz, 298 K)

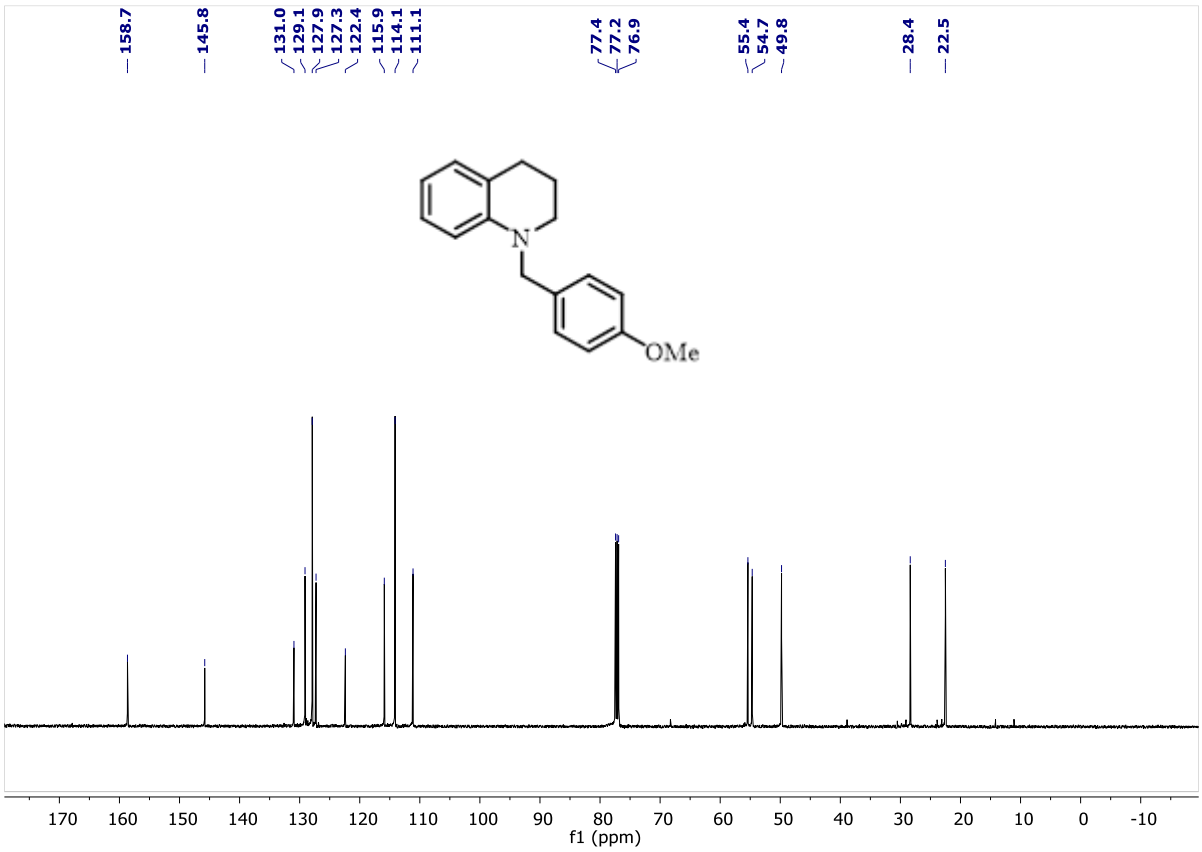


Figure S19: $^{13}C\{^{1}H\}$ NMR Spectrum of **3c** ($CDCl_3$, 101 MHz, 298 K)

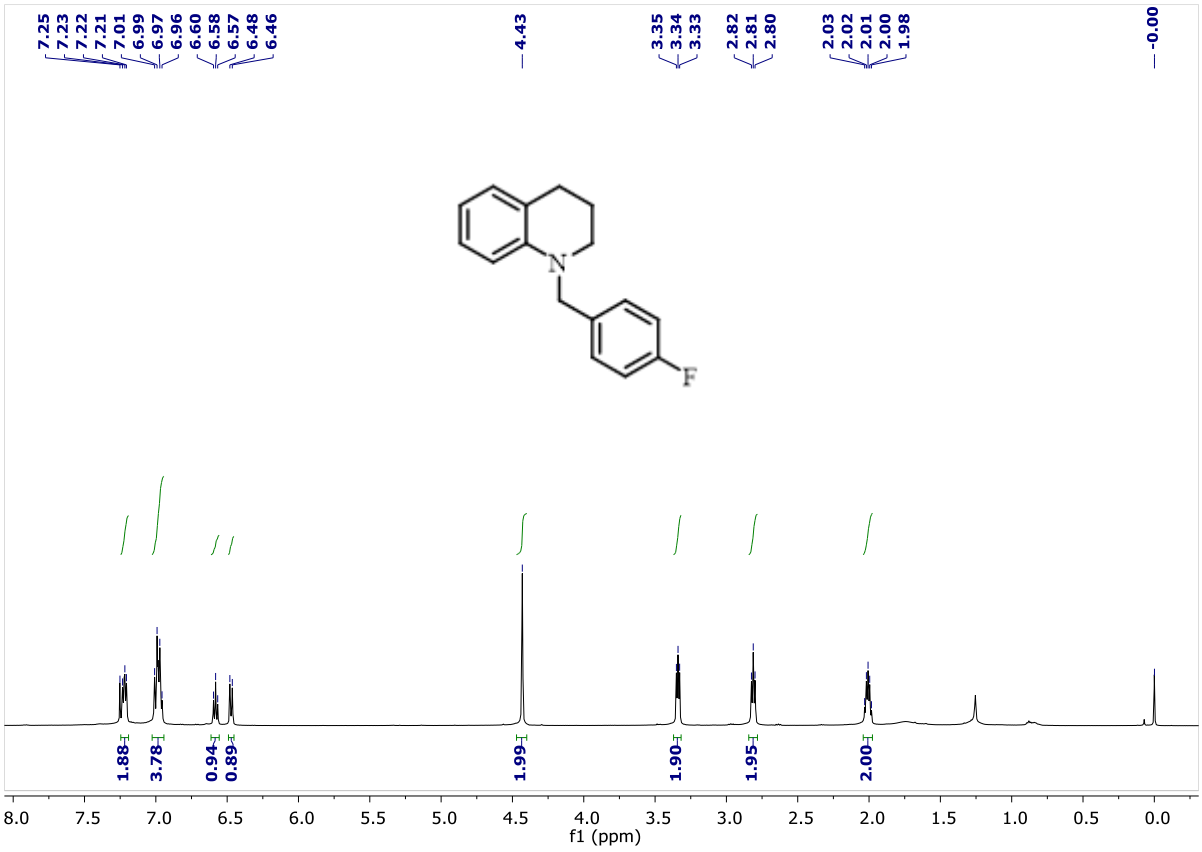


Figure S20: ^{1}H NMR Spectrum of **3e** ($CDCl_3$, 500 MHz, 298 K)

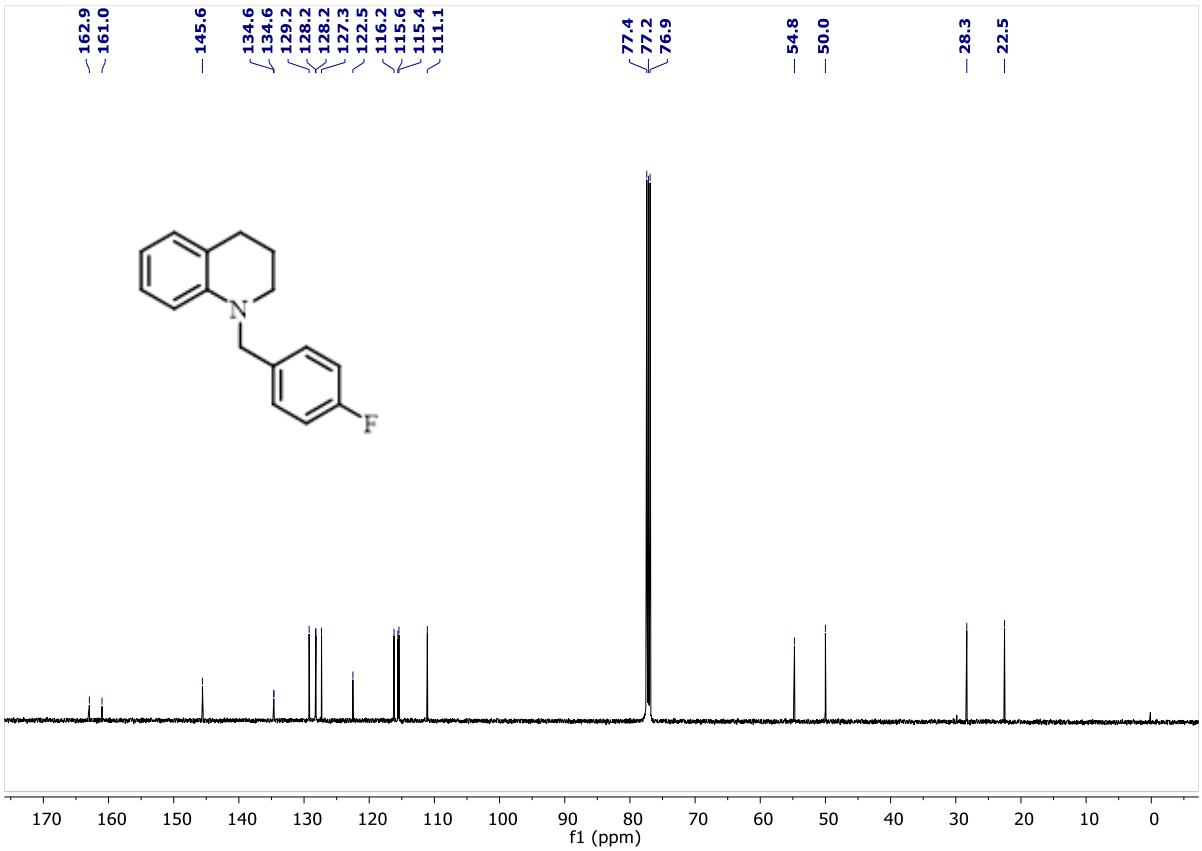


Figure S21: $^{13}C\{^{1}H\}$ NMR Spectrum of **3e** ($CDCl_3$, 126 MHz, 298 K)

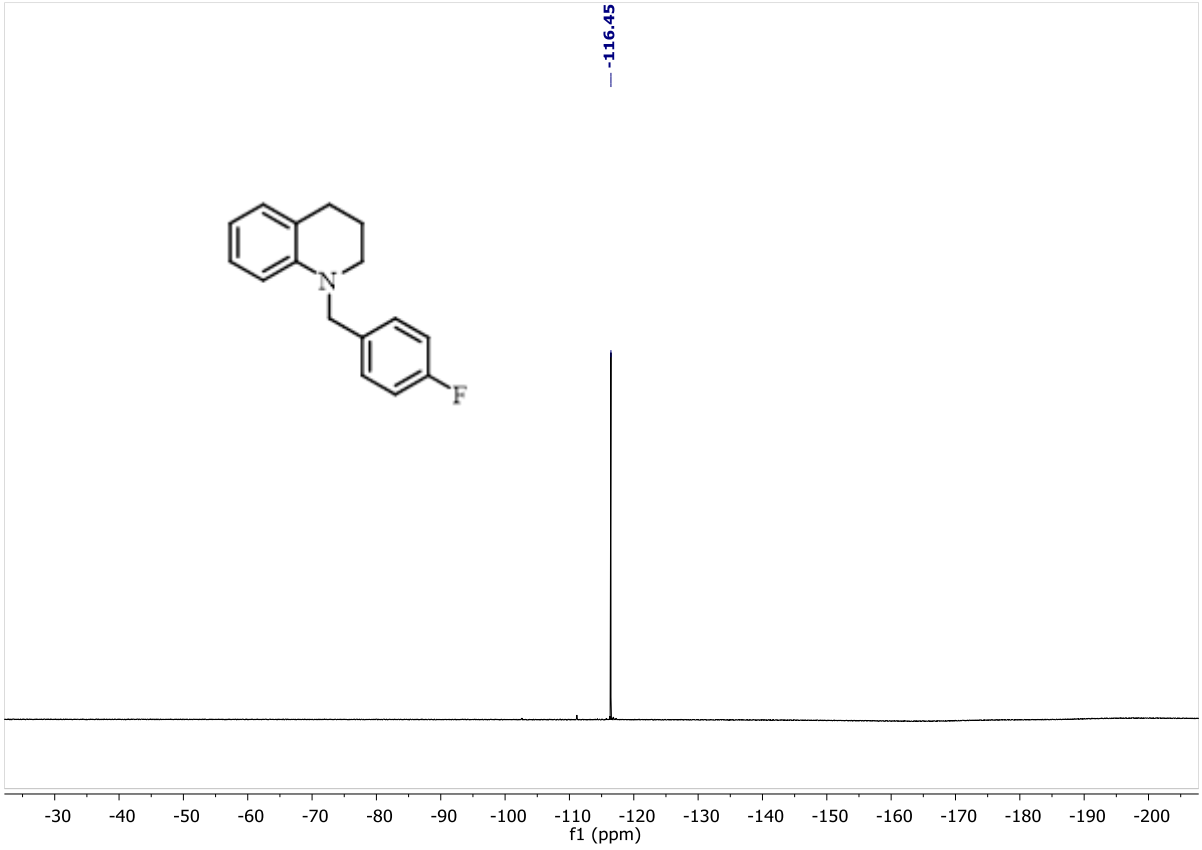


Figure S22: $^{19}F\{^{1}H\}$ NMR Spectrum of **3e** ($CDCl_3$, 471 MHz, 298 K)

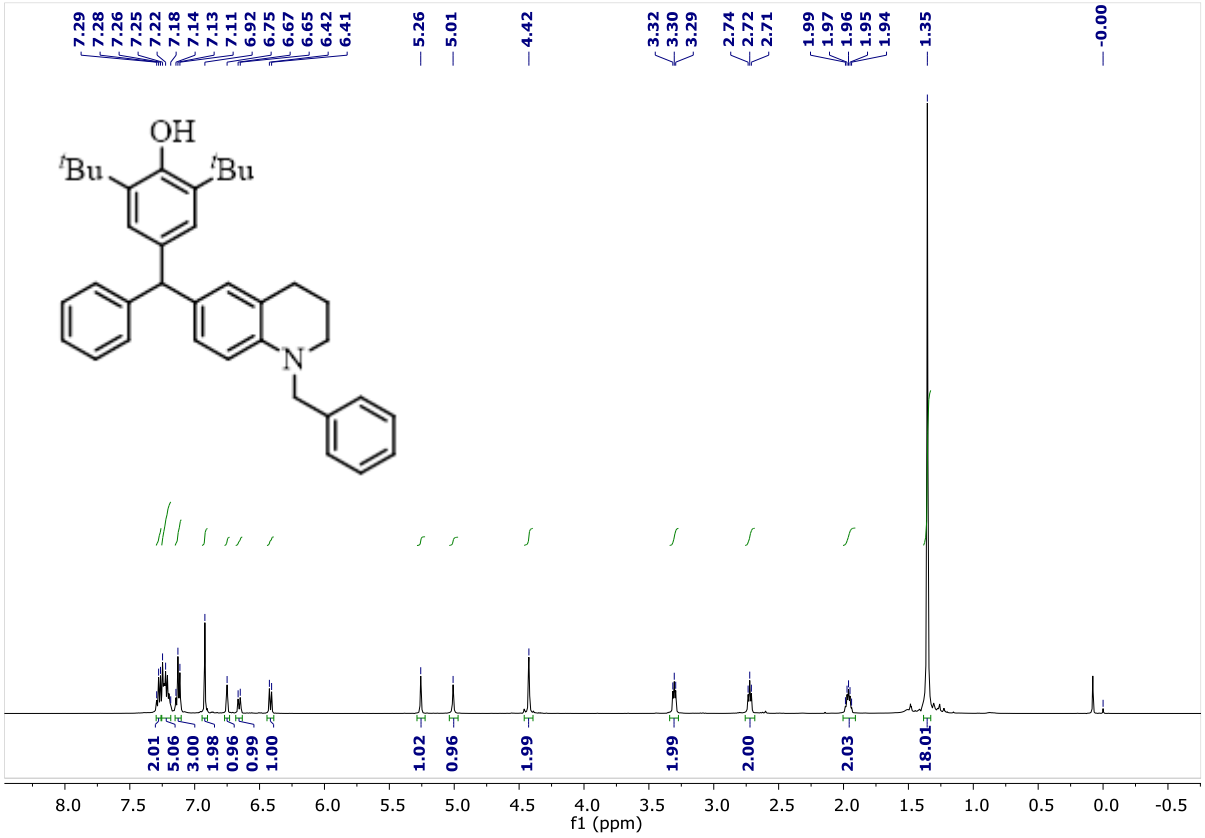


Figure S23: ^{1}H NMR Spectrum of **5a** ($CDCl_3$, 500 MHz, 298 K)

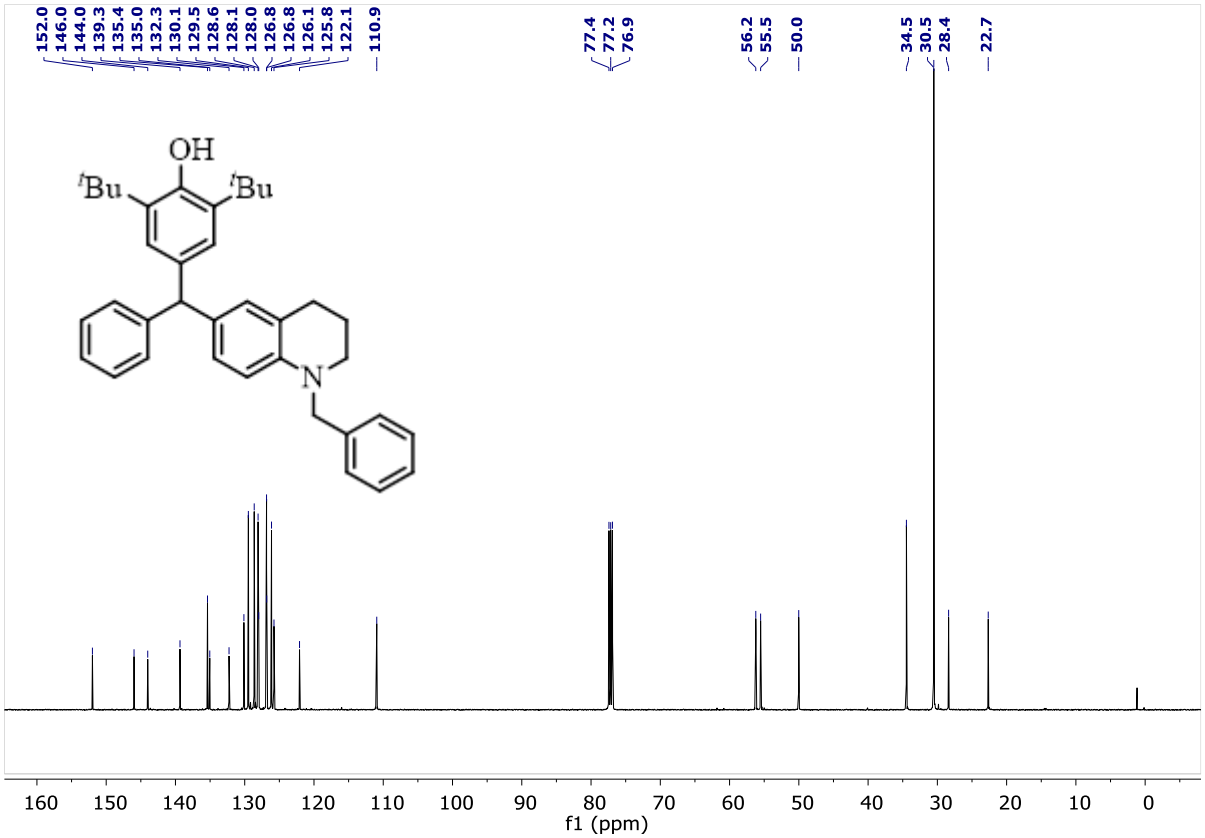


Figure S24: $^{13}C\{^{1}H\}$ NMR Spectrum of **5a** ($CDCl_3$, 126 MHz, 298 K)

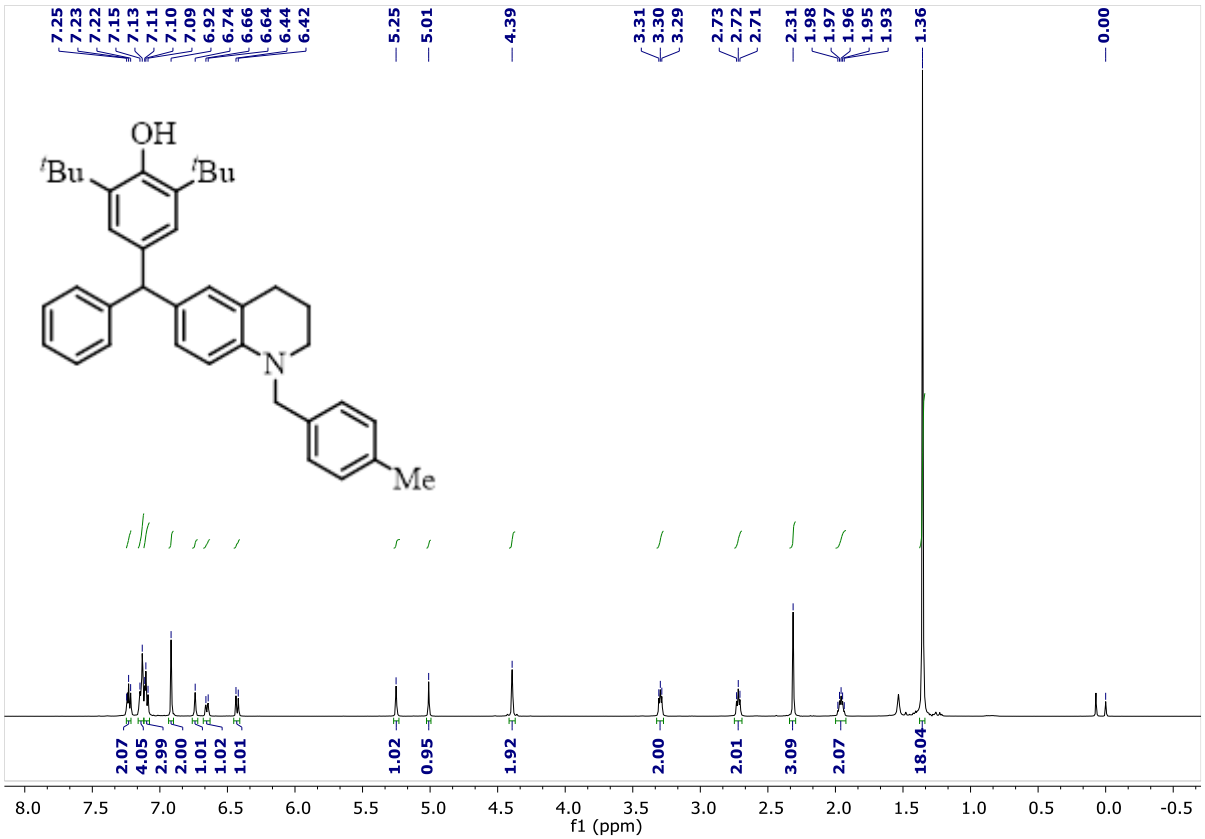


Figure S25: ^{1}H NMR Spectrum of **5b** ($CDCl_3$, 500 MHz, 298 K)

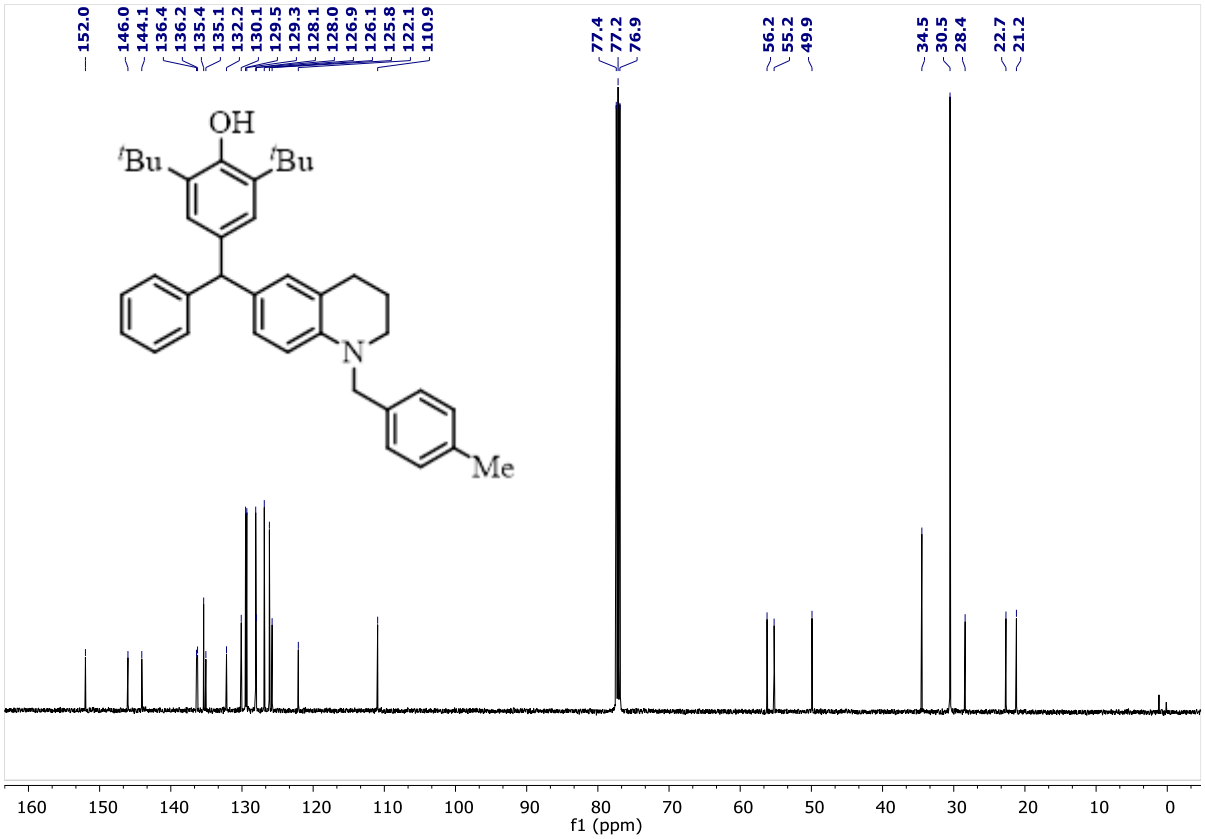


Figure S27: $^{13}C\{^{1}H\}$ NMR Spectrum of **5b** ($CDCl_3$, 126 MHz, 298 K)

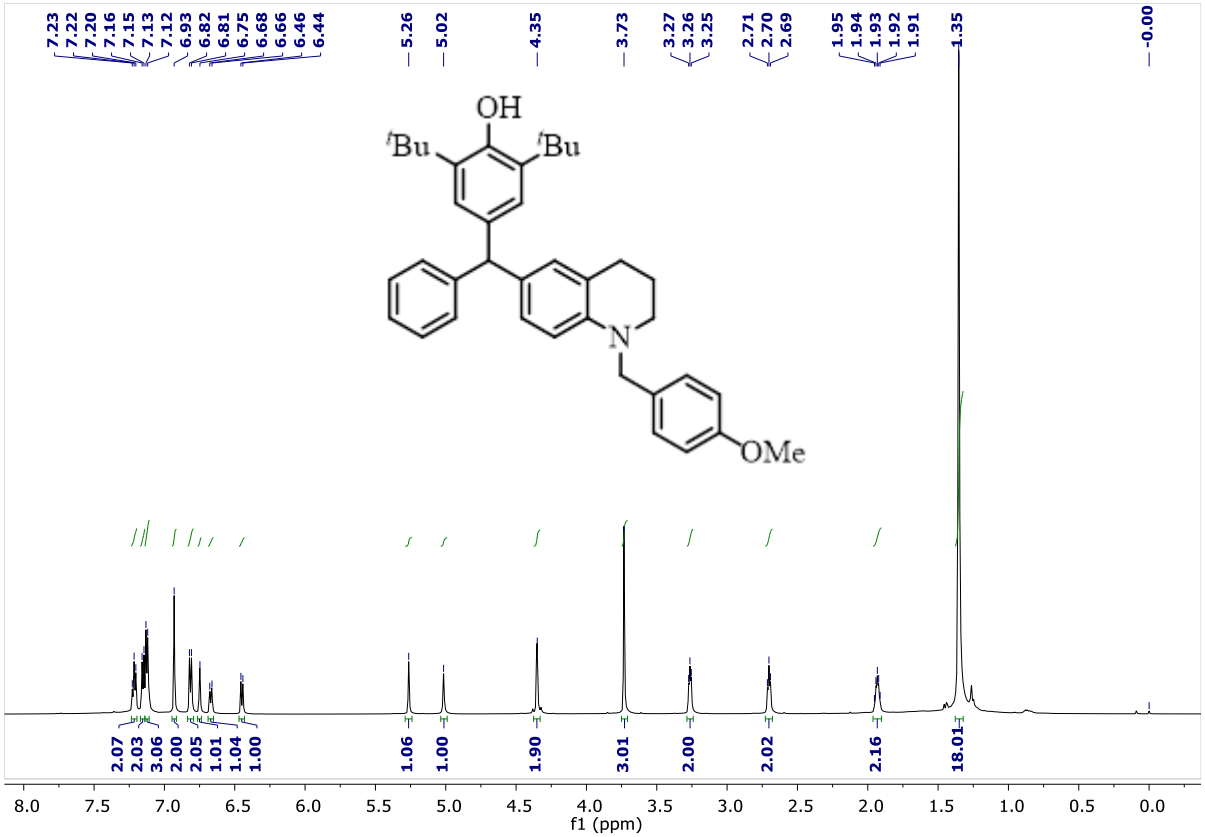


Figure S28: ^{1}H NMR Spectrum of **5c** ($CDCl_3$, 600 MHz, 298 K)

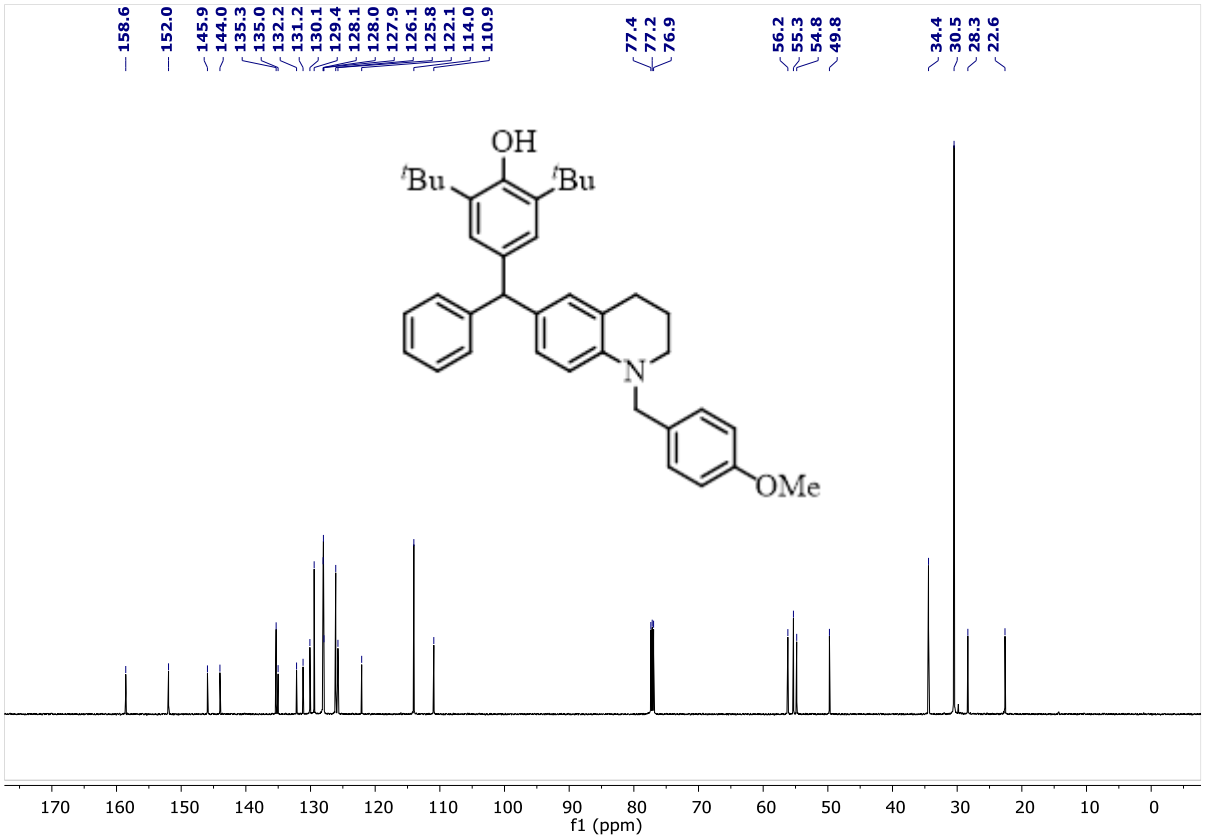


Figure S29: $^{13}C\{^{1}H\}$ NMR Spectrum of **5c** ($CDCl_3$, 151 MHz, 298 K)

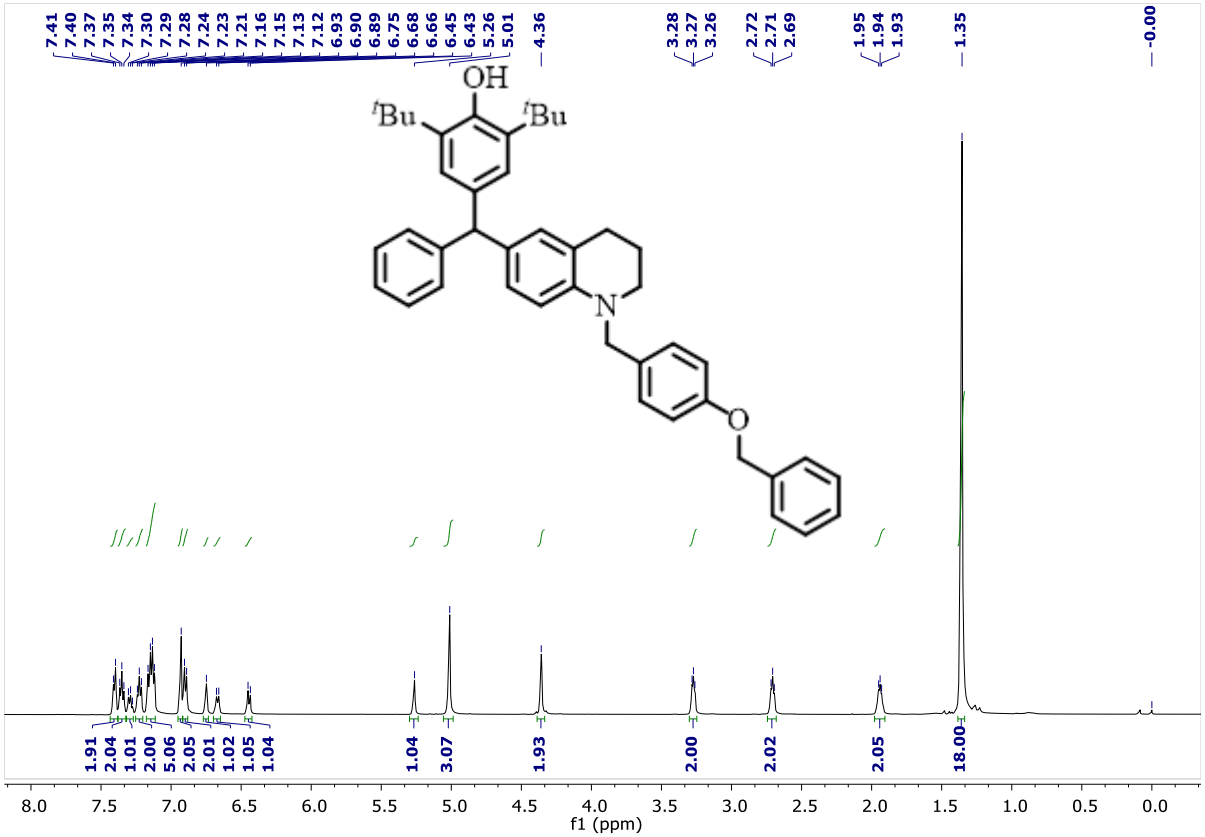


Figure S30: ^{1}H NMR Spectrum of **5d** ($CDCl_3$, 500 MHz, 298 K)

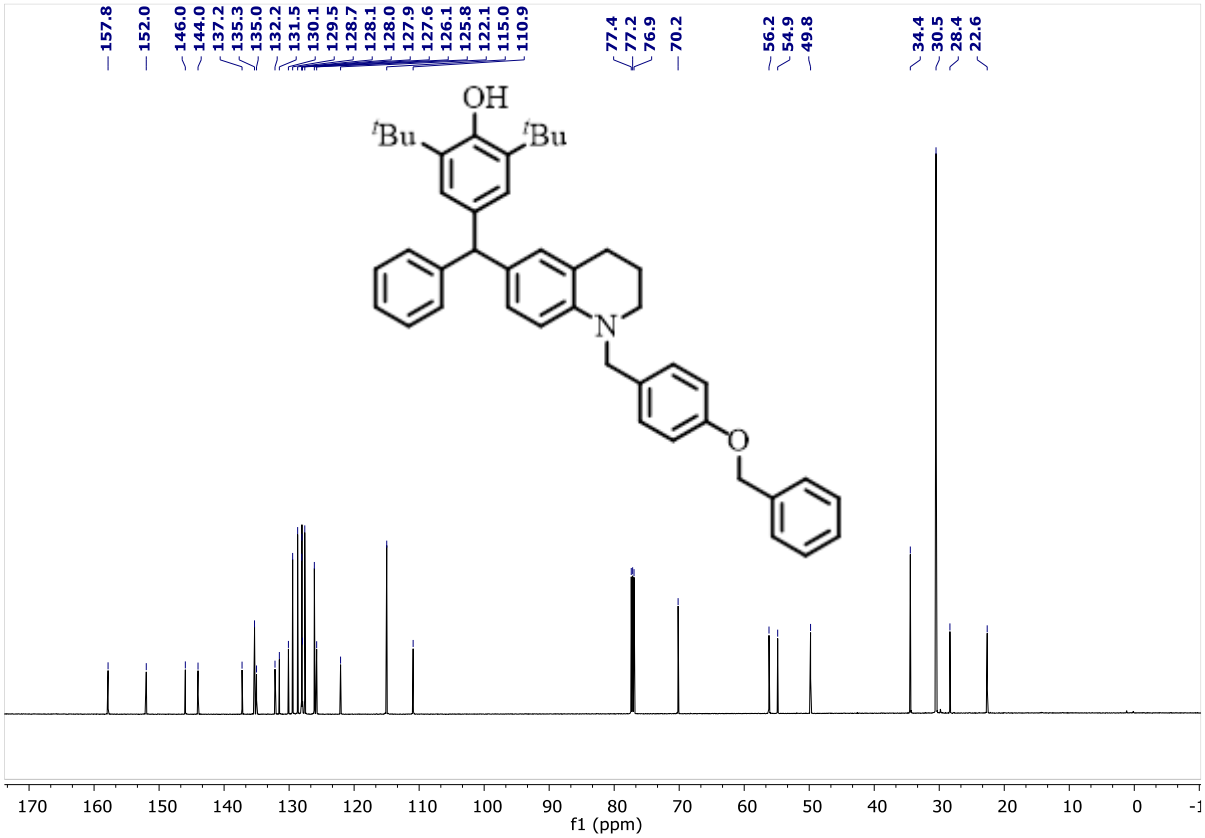


Figure S31: $^{13}C\{^{1}H\}$ NMR Spectrum of **5d** ($CDCl_3$, 151 MHz, 298 K)

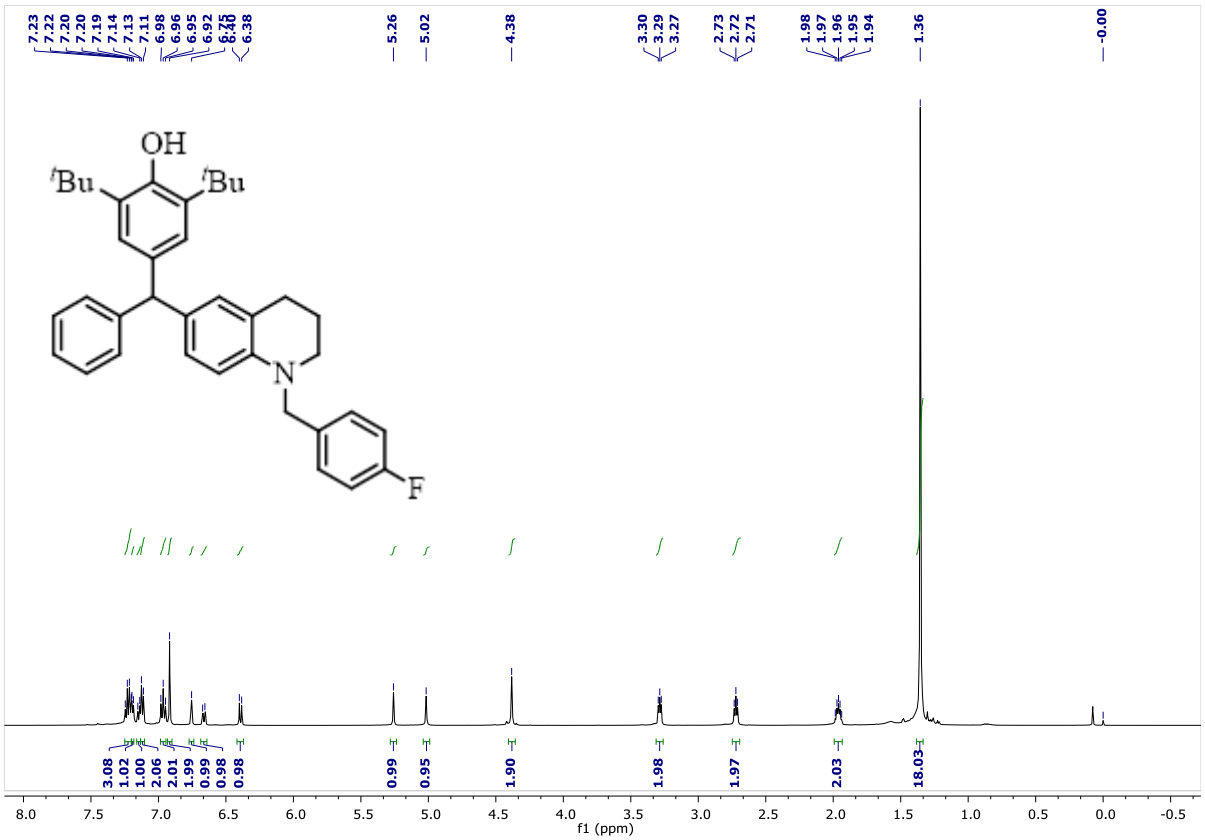


Figure S32: ^{1}H NMR Spectrum of **5e** ($CDCl_3$, 500 MHz, 298 K)

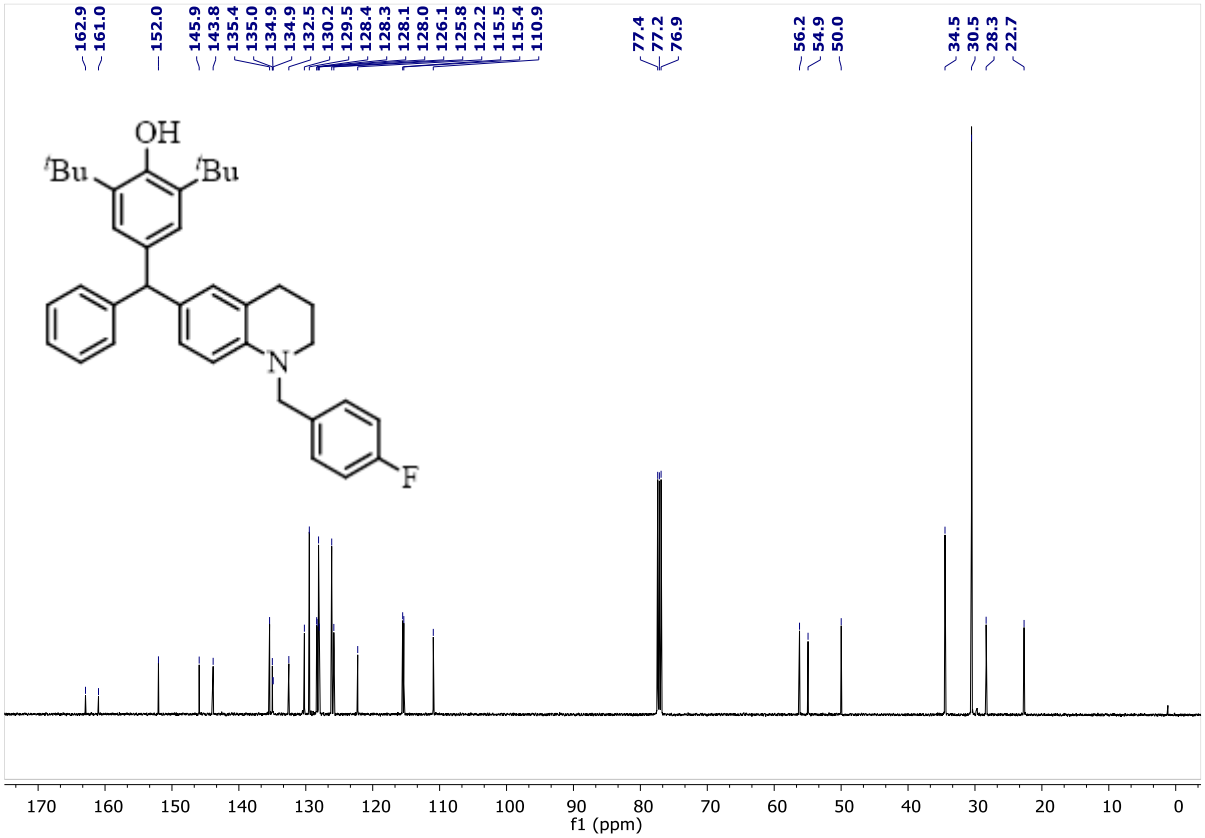


Figure S33: $^{13}C\{^{1}H\}$ NMR Spectrum of **5e** ($CDCl_3$, 126 MHz, 298 K)

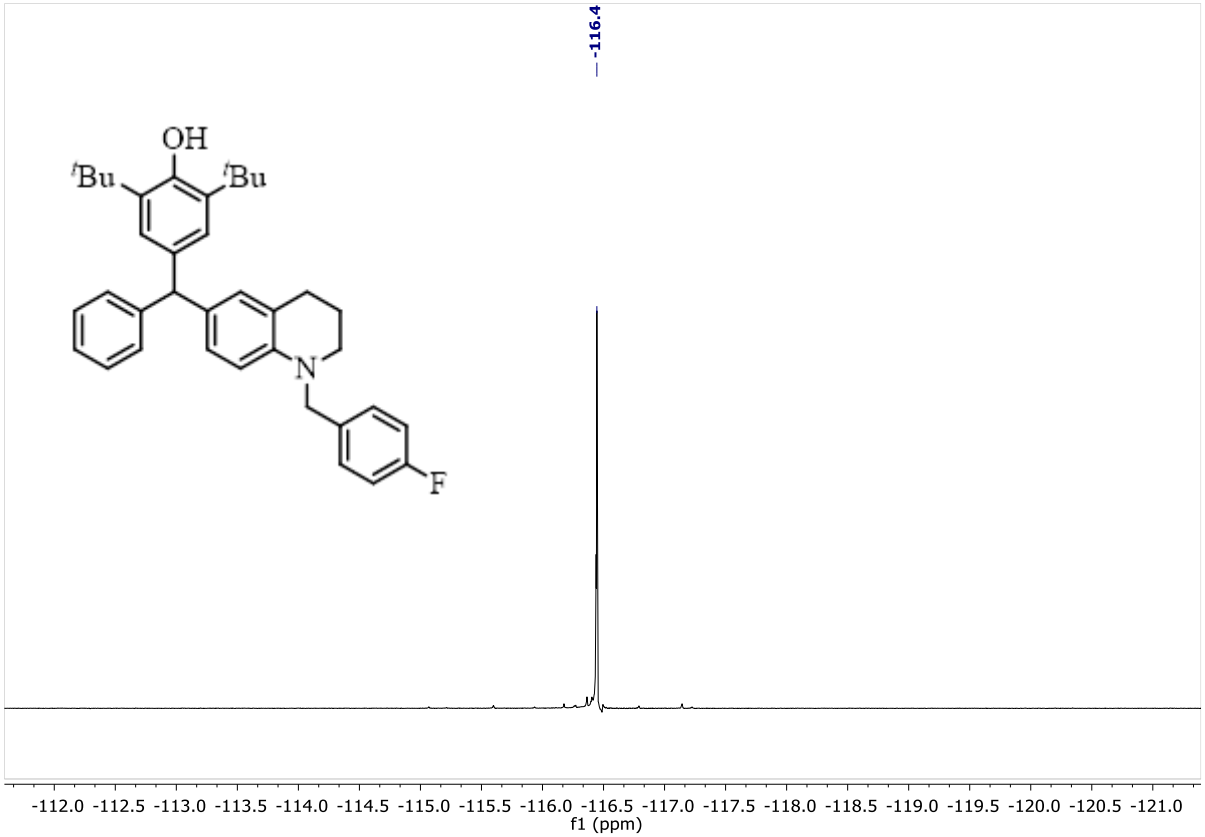


Figure S34: $^{19}F\{^{1}H\}$ NMR Spectrum of **5e** ($CDCl_3$, 471 MHz, 298 K)

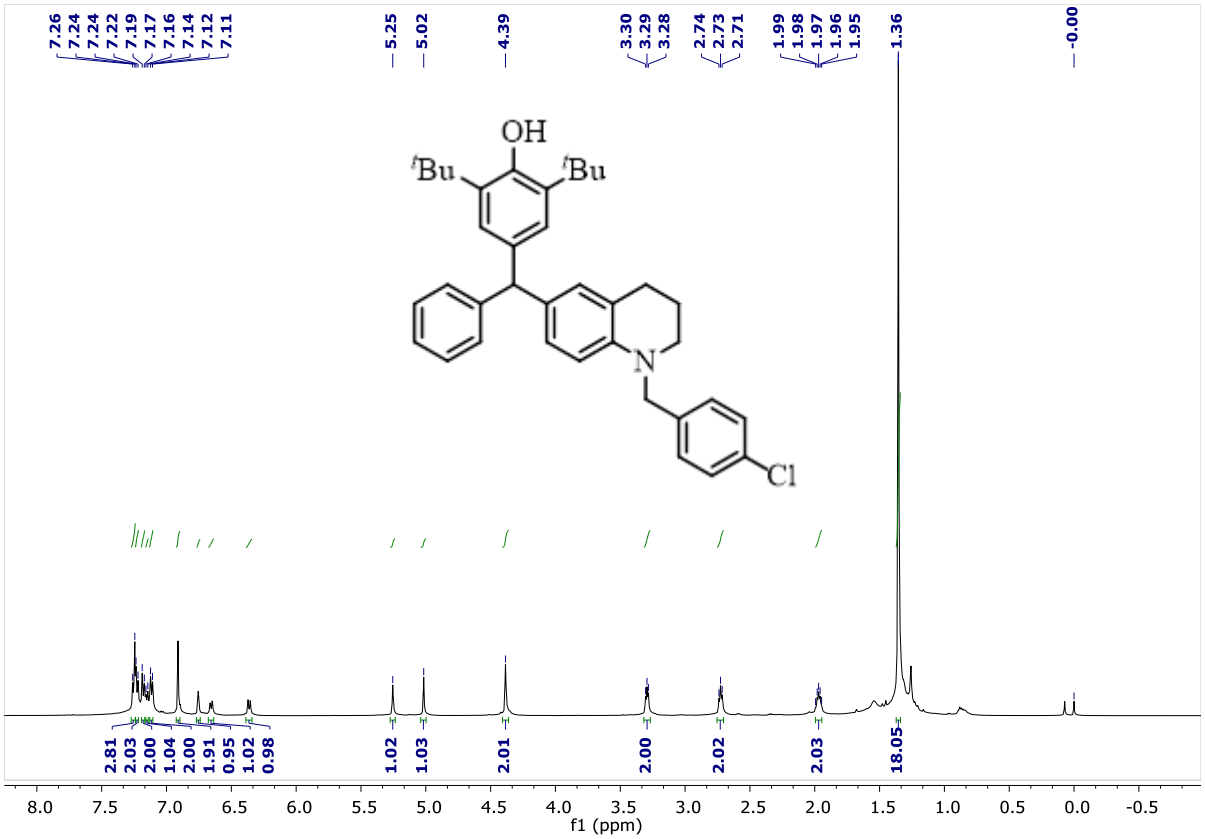


Figure S35: ^{1}H NMR Spectrum of **5f** ($CDCl_3$, 500 MHz, 298 K)

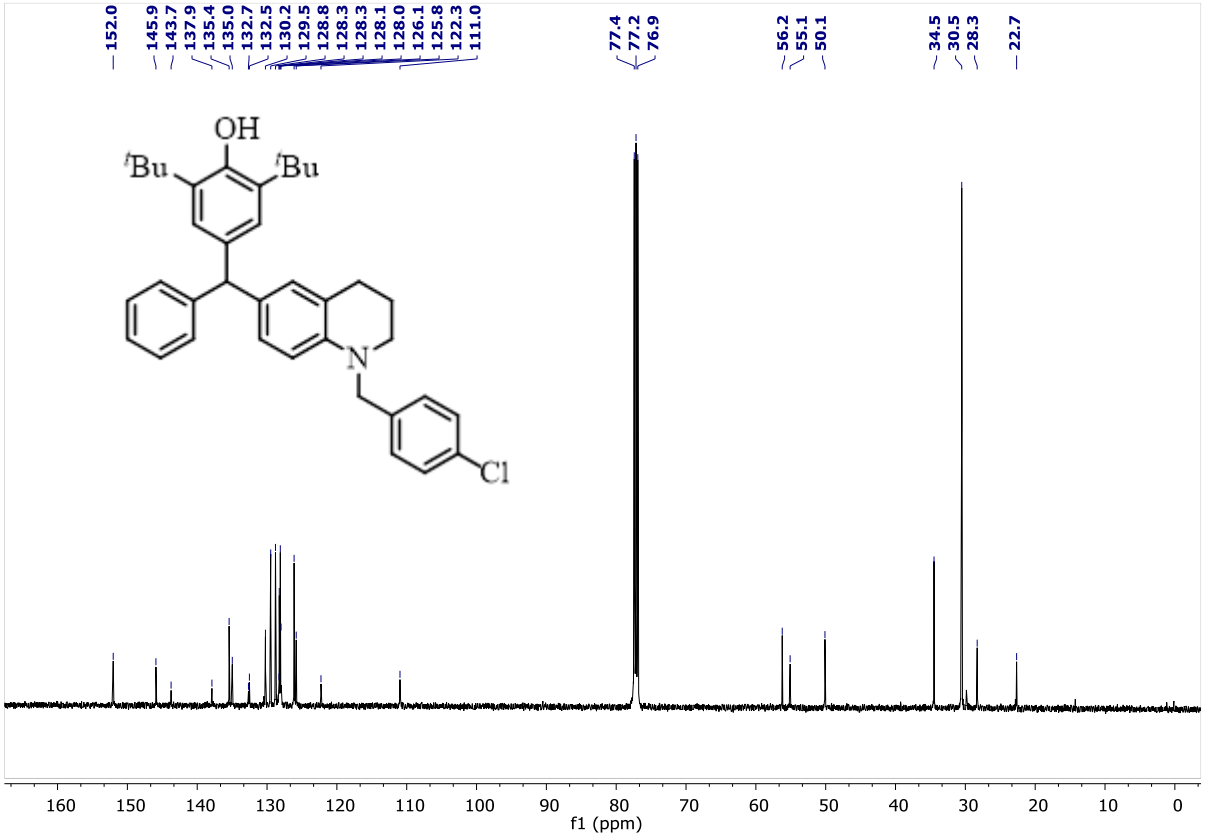


Figure S36: $^{13}C\{^{1}H\}$ NMR Spectrum of **5f** ($CDCl_3$, 126 MHz, 298 K)

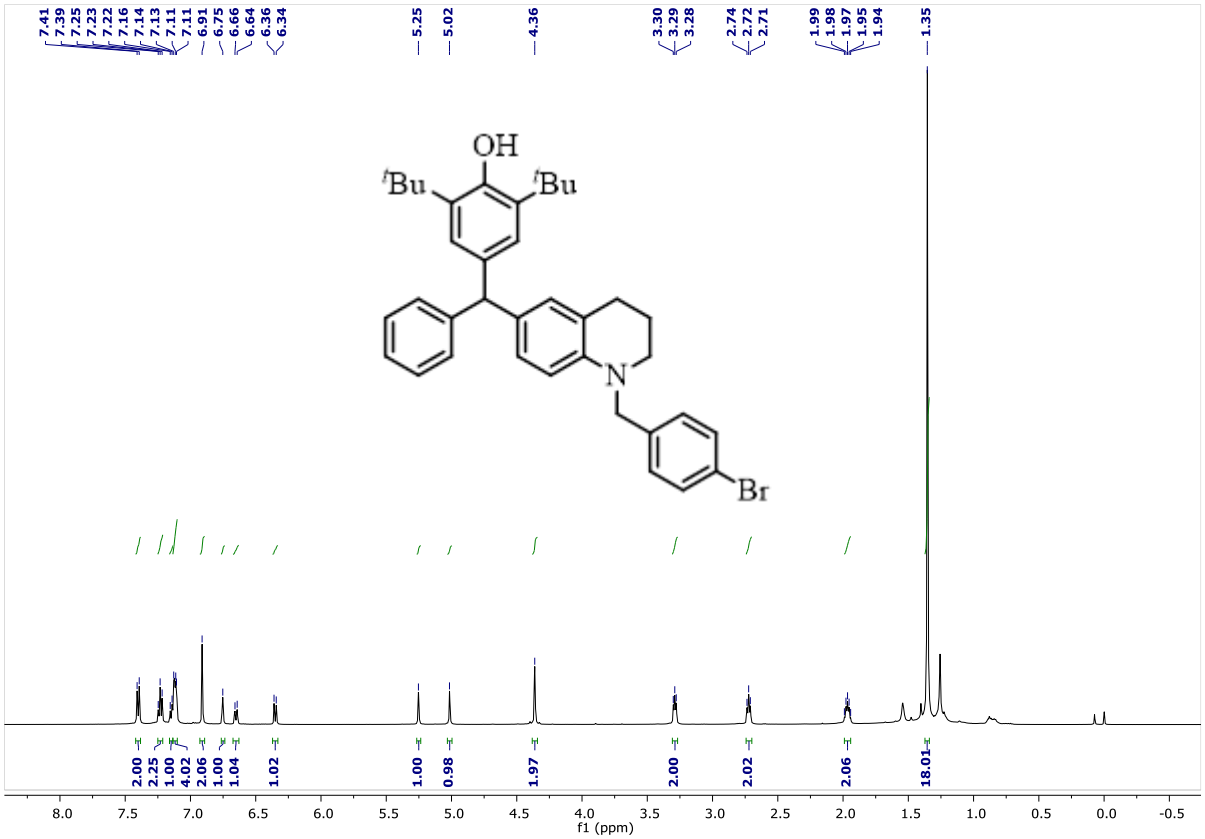


Figure S37: ^{1}H NMR Spectrum of **5f** ($CDCl_3$, 500 MHz, 298 K)

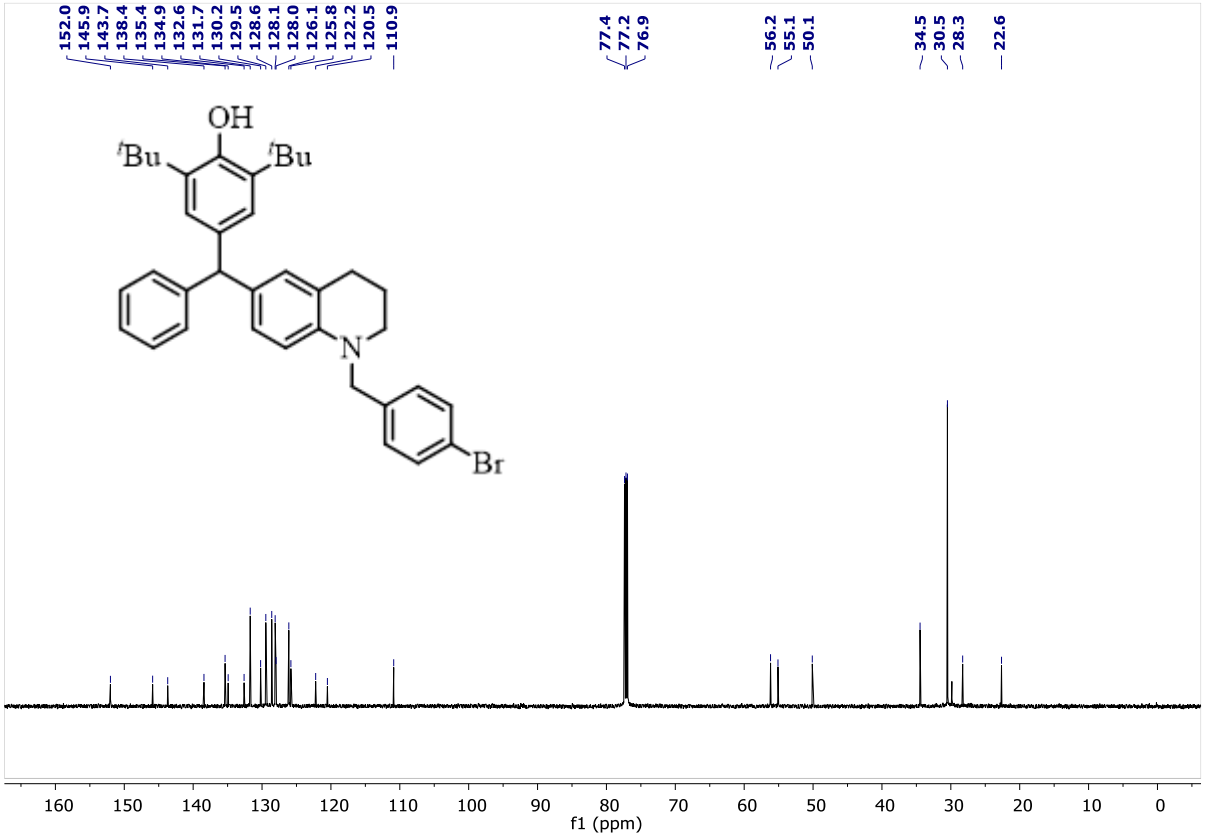


Figure S38: $^{13}C\{^{1}H\}$ NMR Spectrum of **5g** ($CDCl_3$, 151 MHz, 298 K)

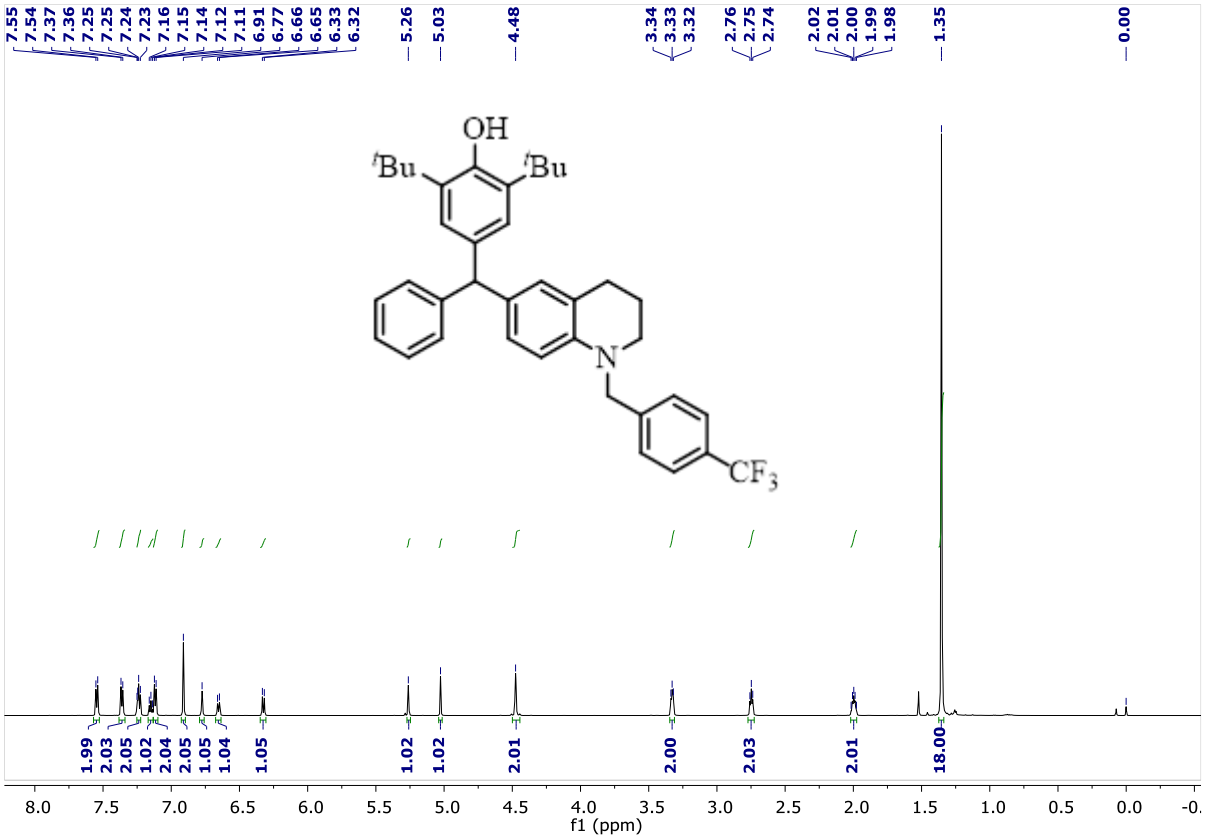


Figure S39: ^{1}H NMR Spectrum of **5g** ($CDCl_3$, 600 MHz, 298 K)

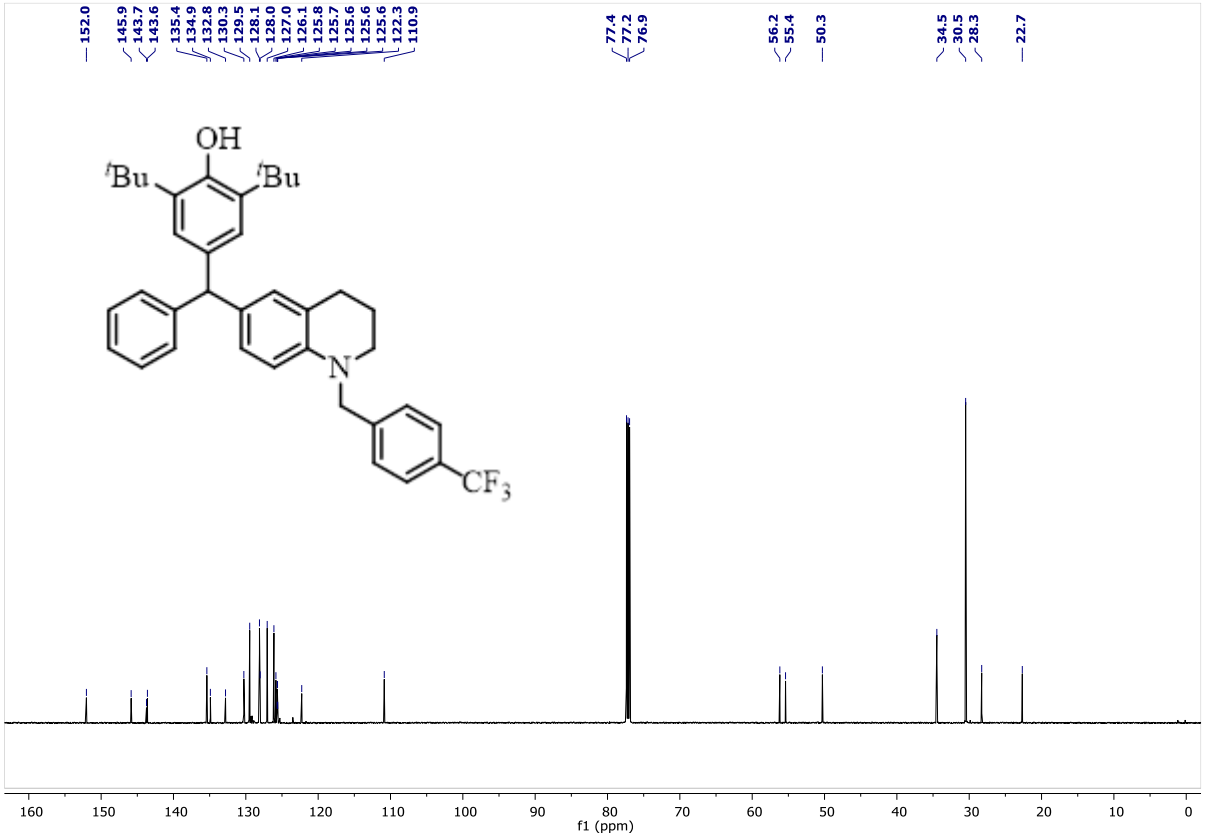


Figure S40: $^{13}C\{^{1}H\}$ NMR Spectrum of **5h** ($CDCl_3$, 151 MHz, 298 K)

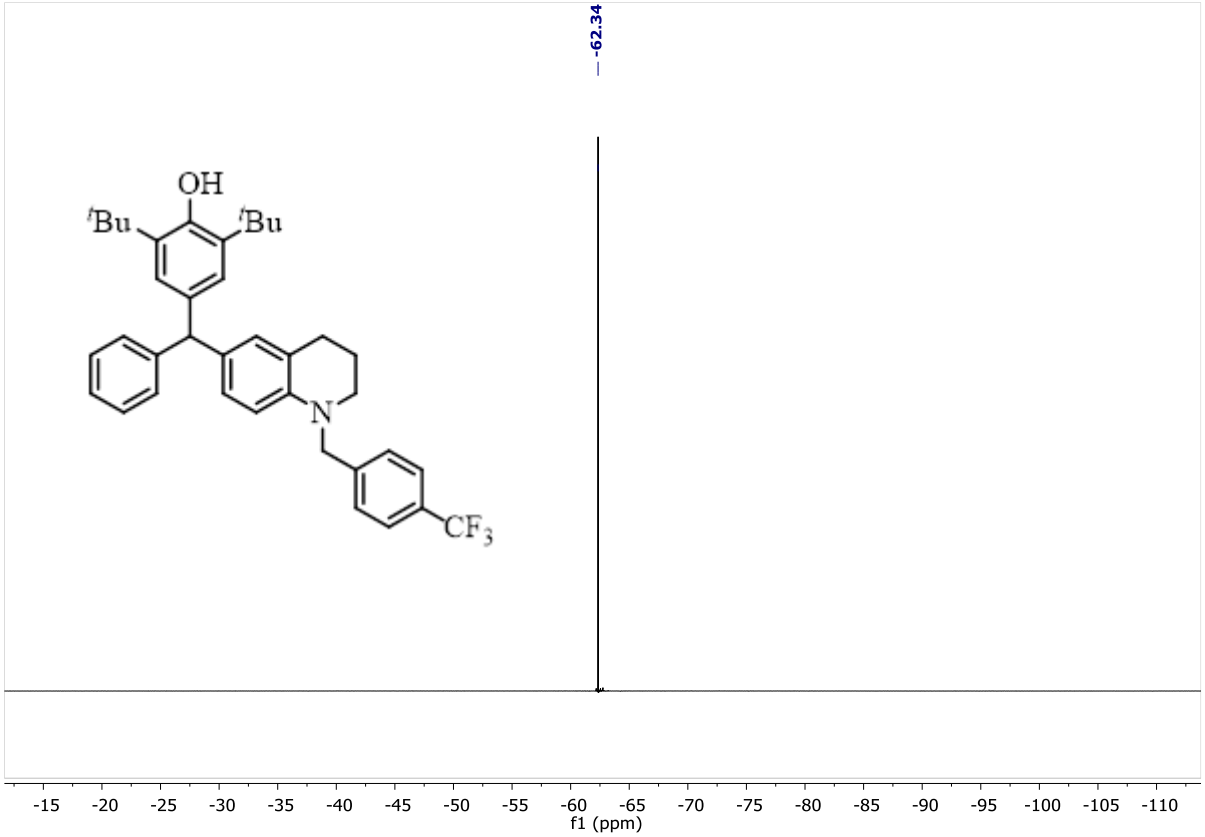


Figure S41: $^{19}F\{^{1}H\}$ NMR Spectrum of **5h** ($CDCl_3$, 471 MHz, 298 K)

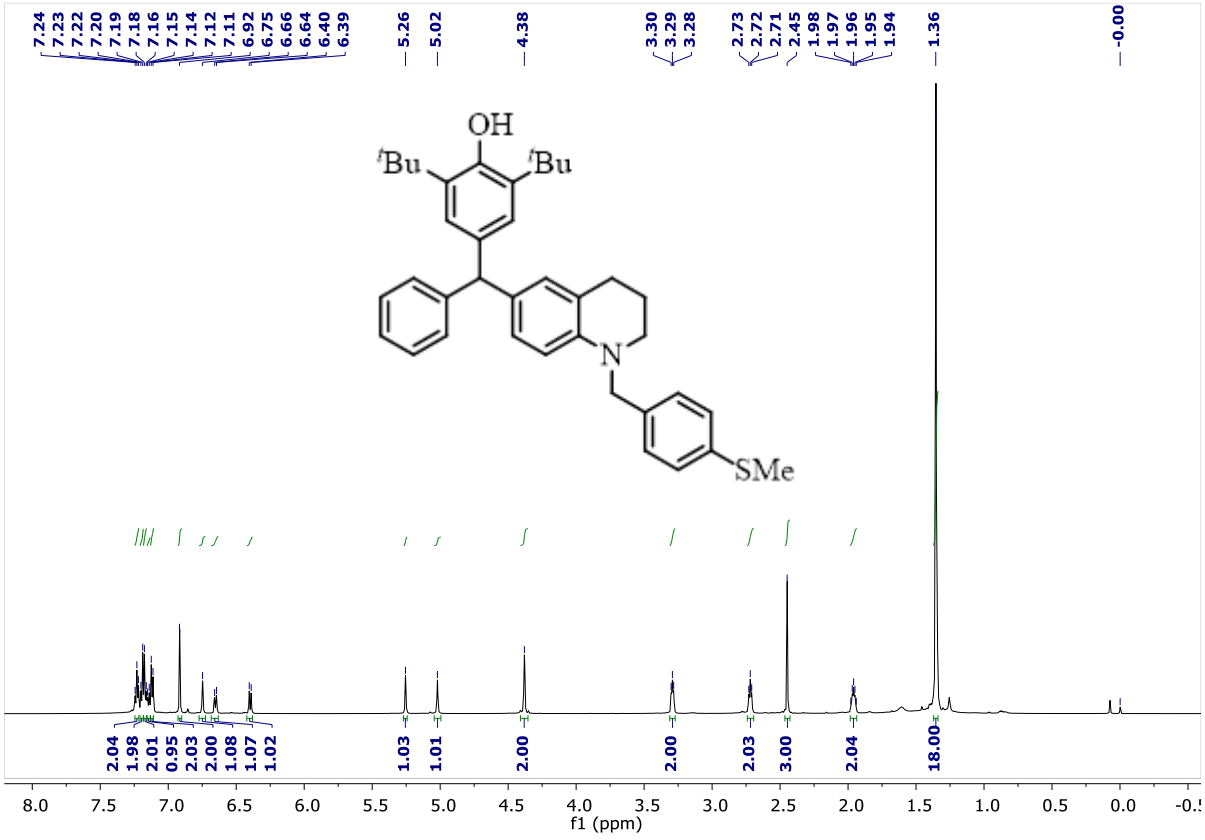


Figure S42: ^{1}H NMR Spectrum of **5i** ($CDCl_3$, 600 MHz, 298 K)

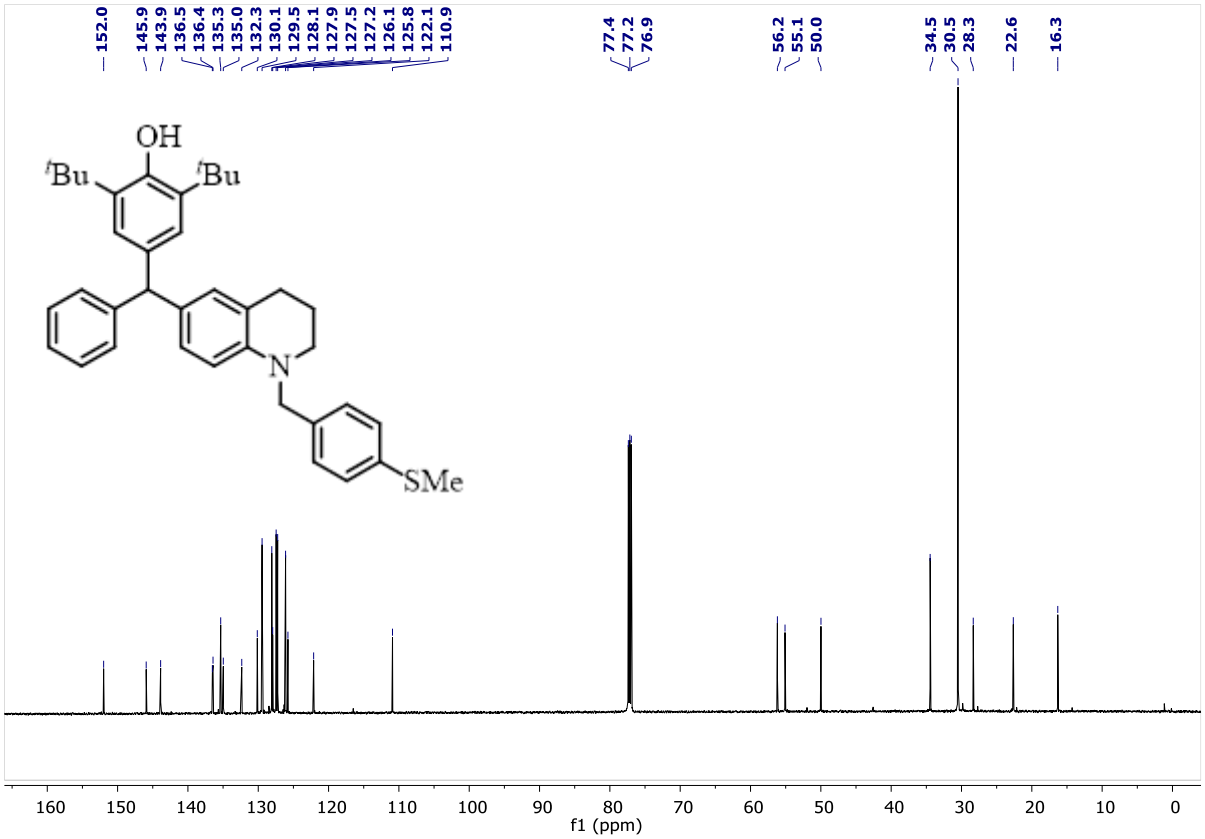


Figure S43: $^{13}C\{^{1}H\}$ NMR Spectrum of **5i** ($CDCl_3$, 151 MHz, 298 K)

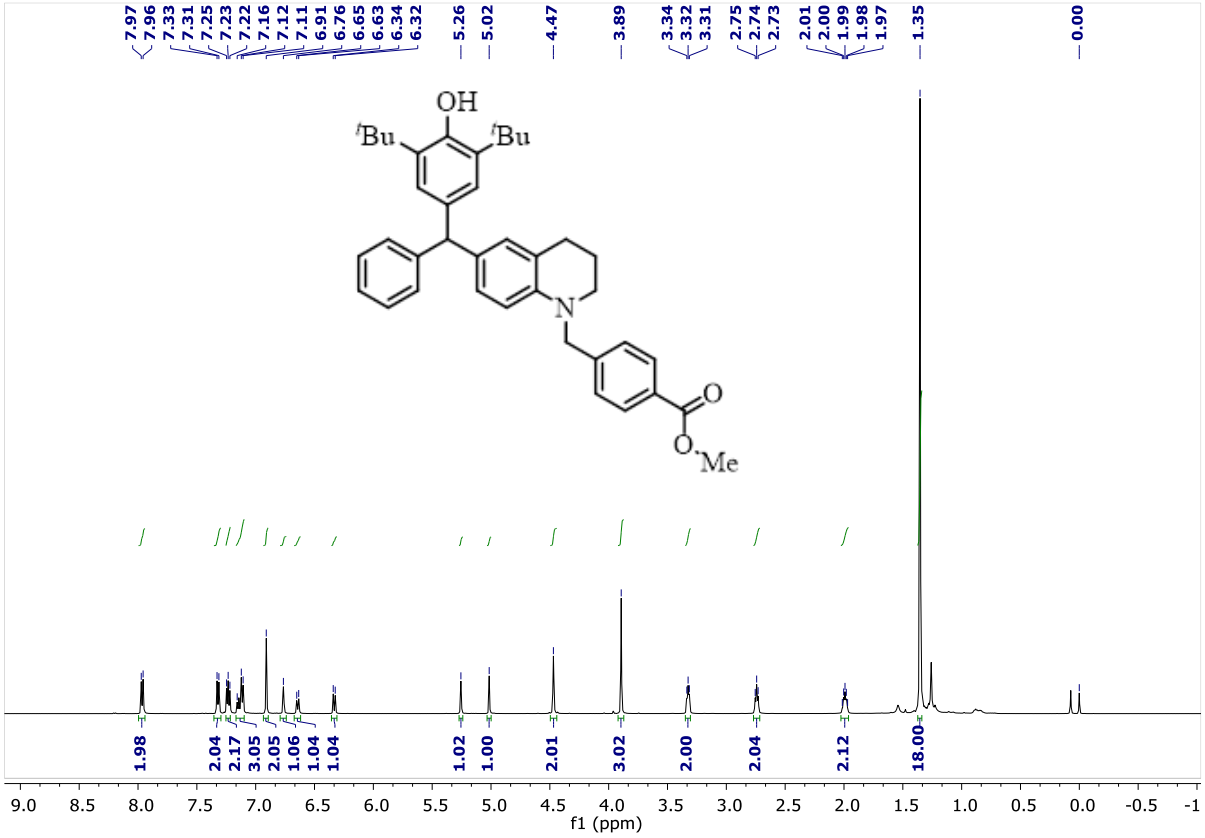


Figure S44: ^{1}H NMR Spectrum of **5j** ($CDCl_3$, 500 MHz, 298 K)

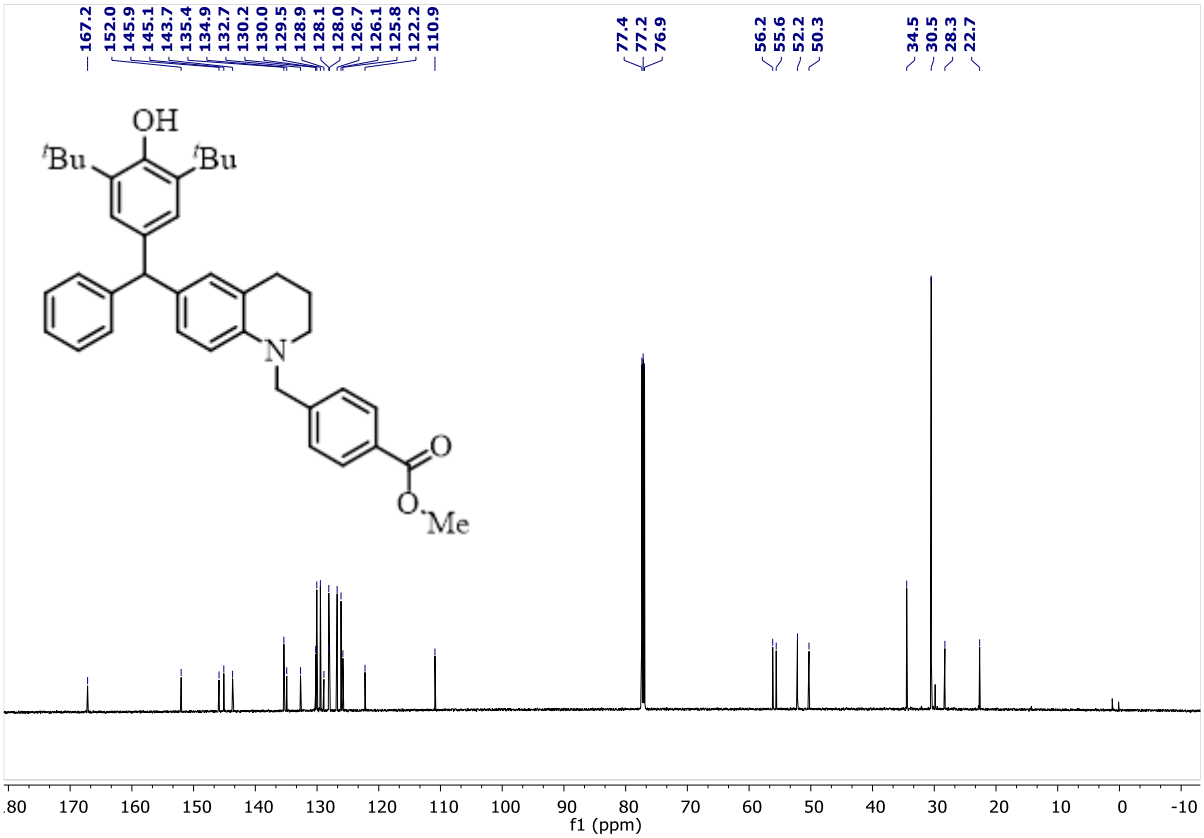


Figure S45: $^{13}C\{^{1}H\}$ NMR Spectrum of **5j** ($CDCl_3$, 151 MHz, 298 K)

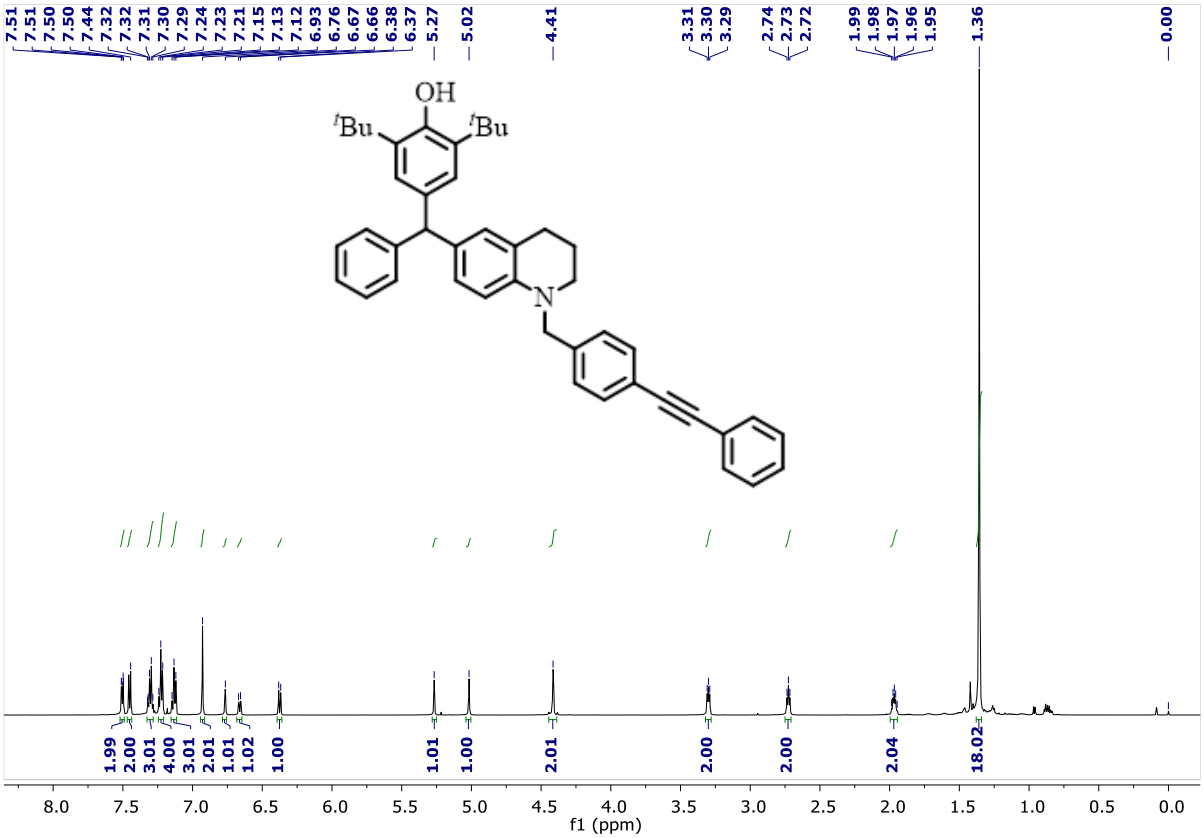


Figure S46: ^{1}H NMR Spectrum of **5k** ($CDCl_3$, 600 MHz, 298 K)

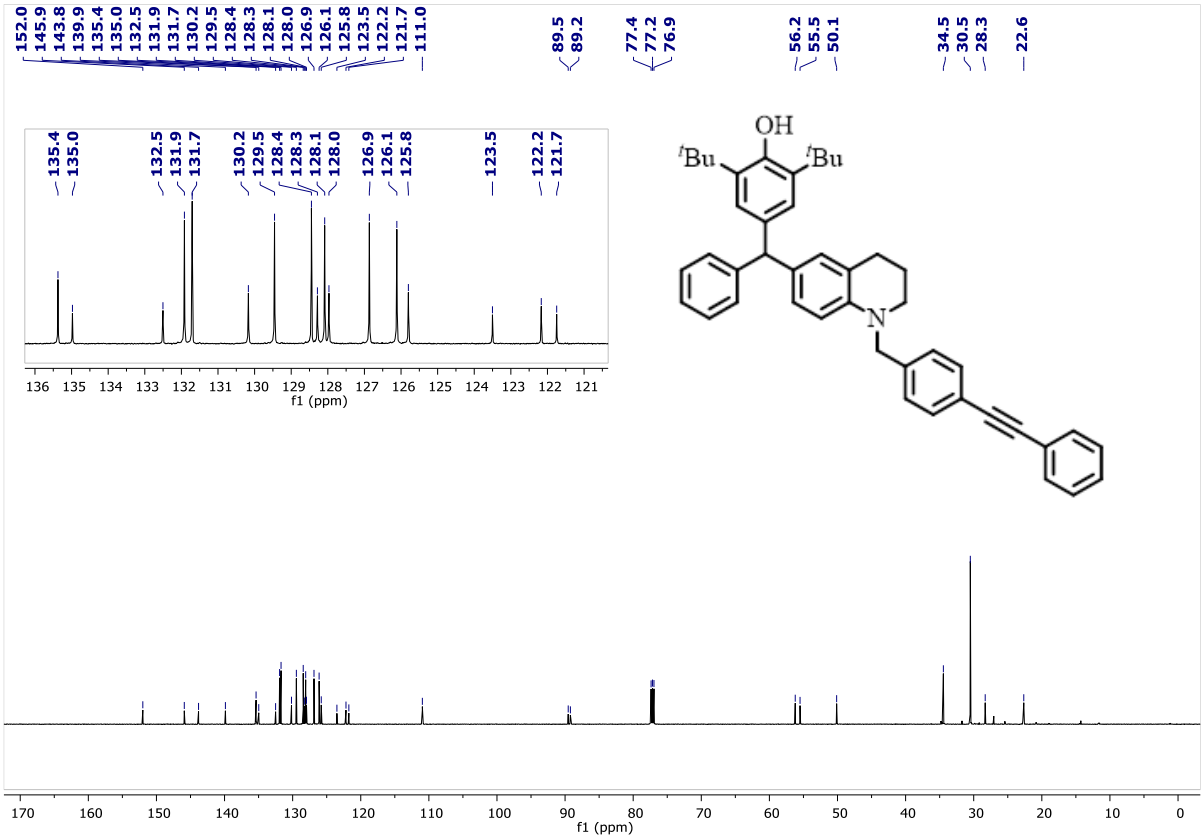


Figure S47: $^{13}C\{^{1}H\}$ NMR Spectrum of **5k** ($CDCl_3$, 151 MHz, 298 K)

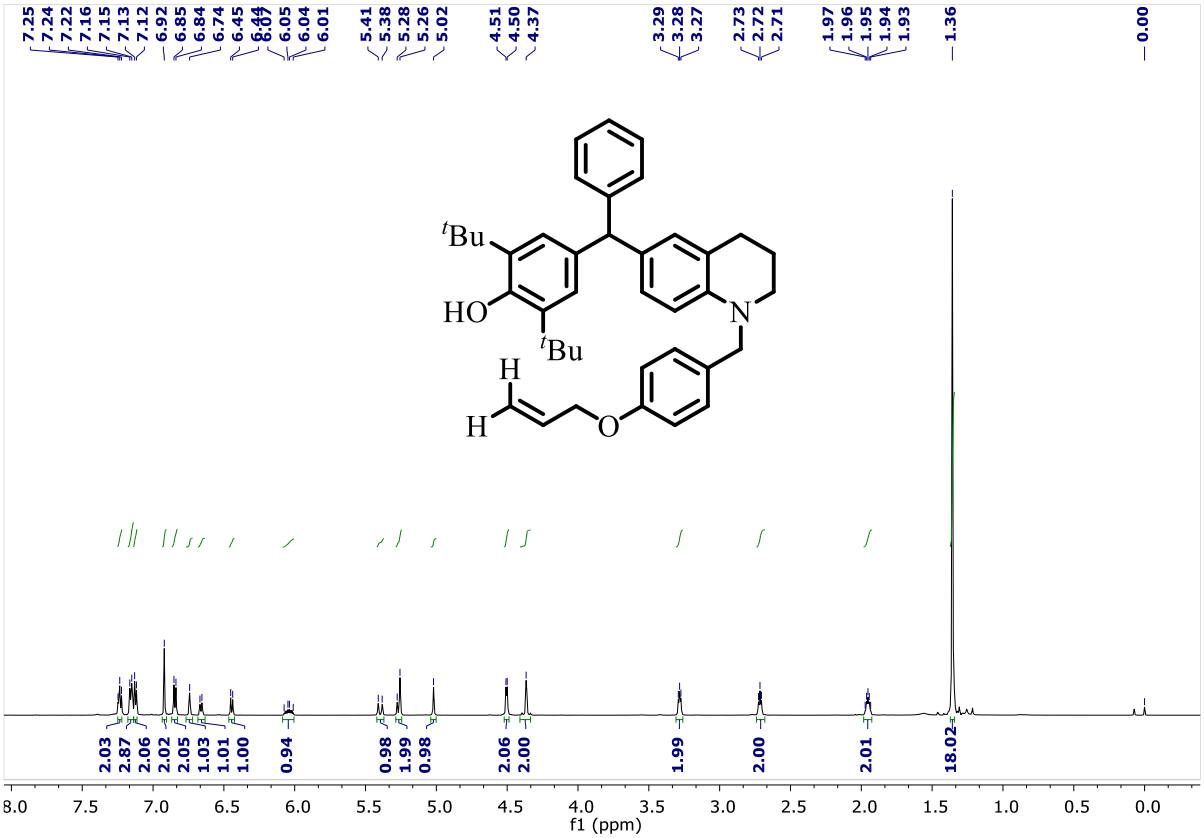


Figure S48: ^{1}H NMR Spectrum of **5l** ($CDCl_3$, 600 MHz, 298 K)

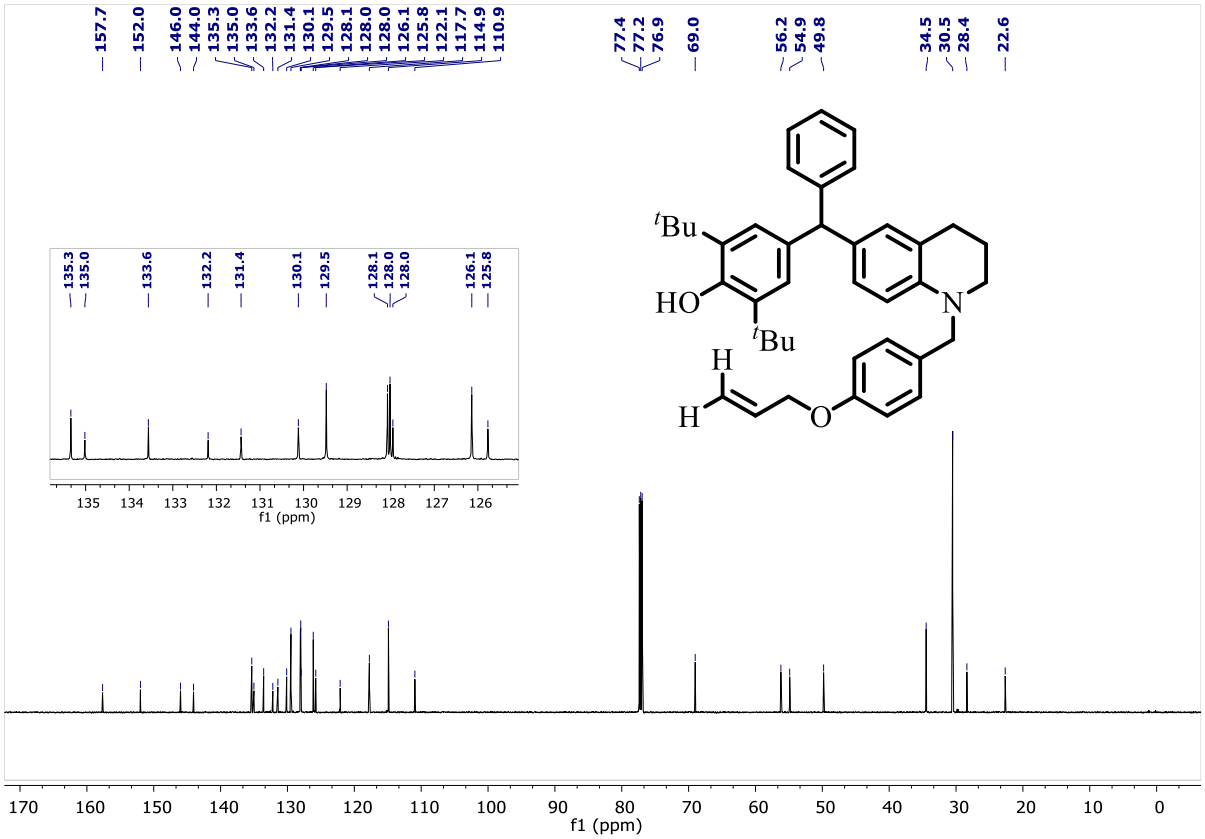


Figure S49: $^{13}C\{^{1}H\}$ NMR Spectrum of **5l** ($CDCl_3$, 151 MHz, 298 K)

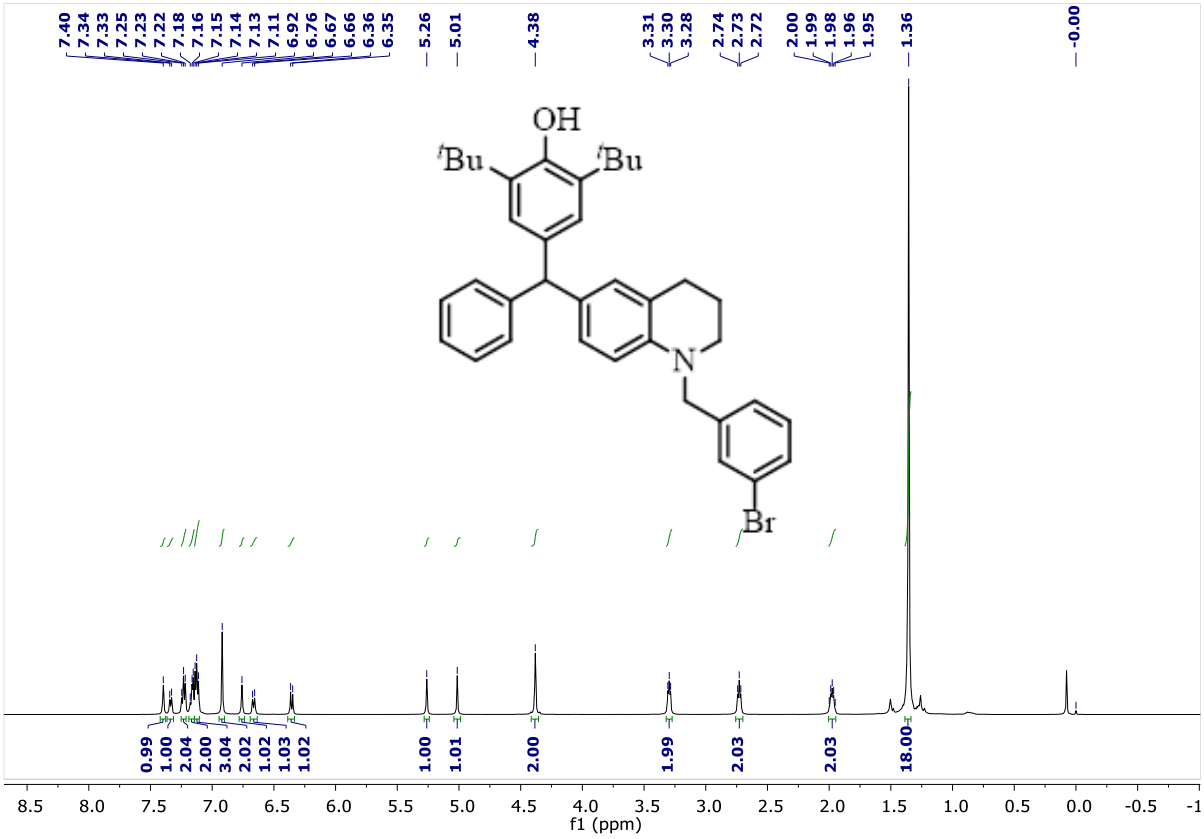


Figure S50: ^{1}H NMR Spectrum of **5m** ($CDCl_3$, 500 MHz, 298 K)

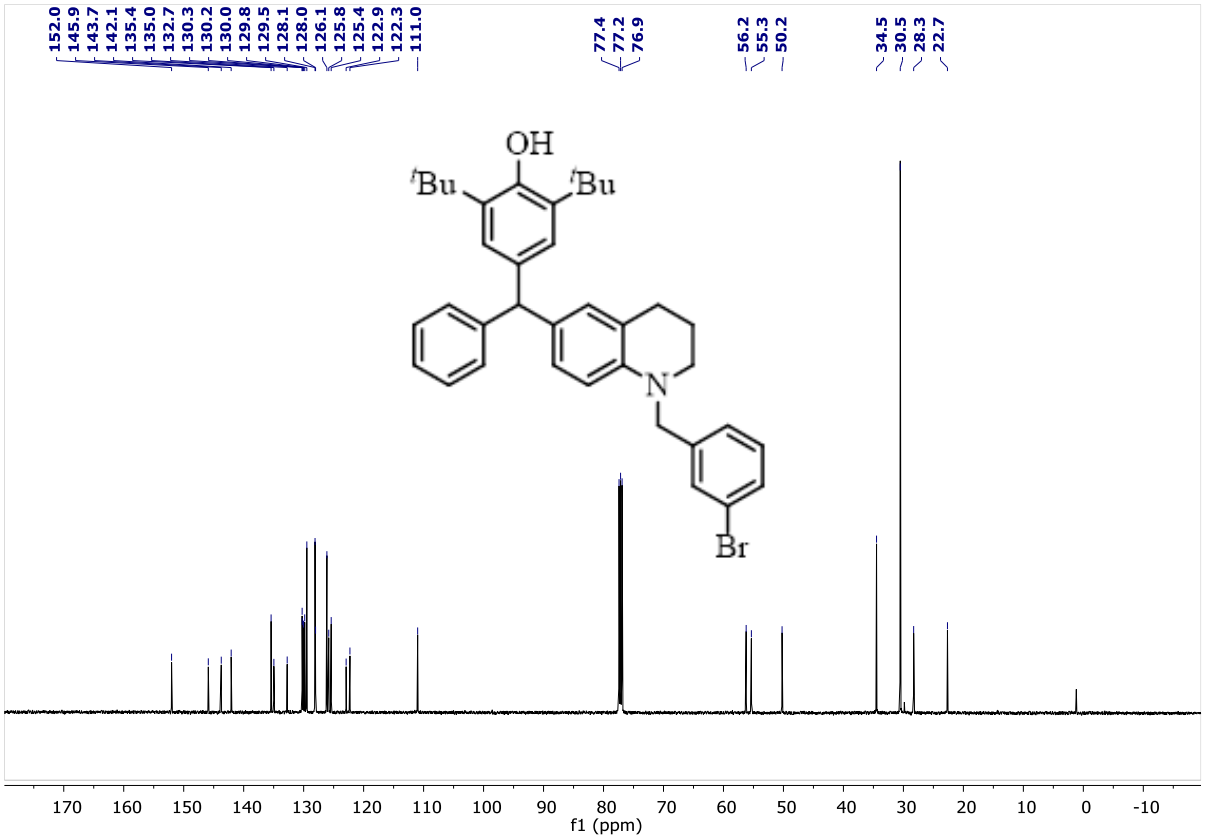


Figure S51: $^{13}C\{^{1}H\}$ NMR Spectrum of **5m** ($CDCl_3$, 126 MHz, 298 K)

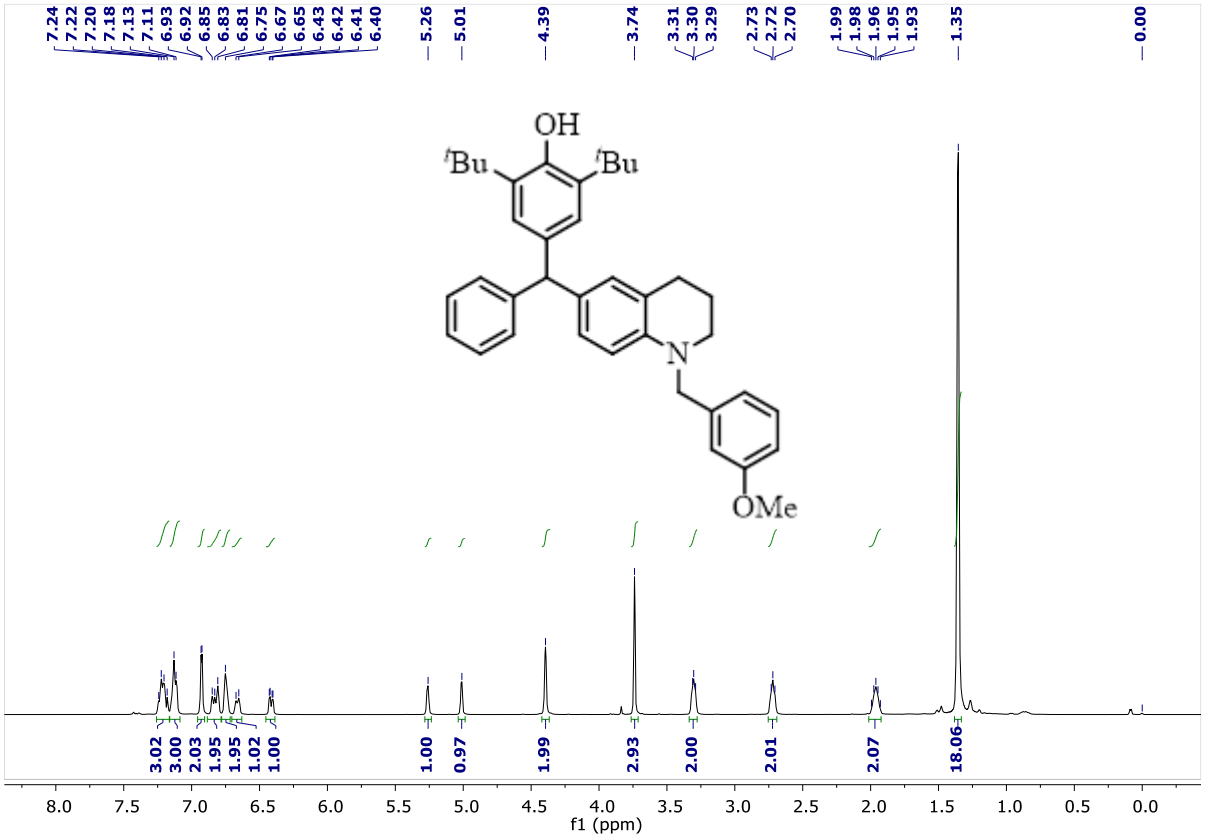


Figure S52: ^{1}H NMR Spectrum of **5n** ($CDCl_3$, 400 MHz, 298 K)

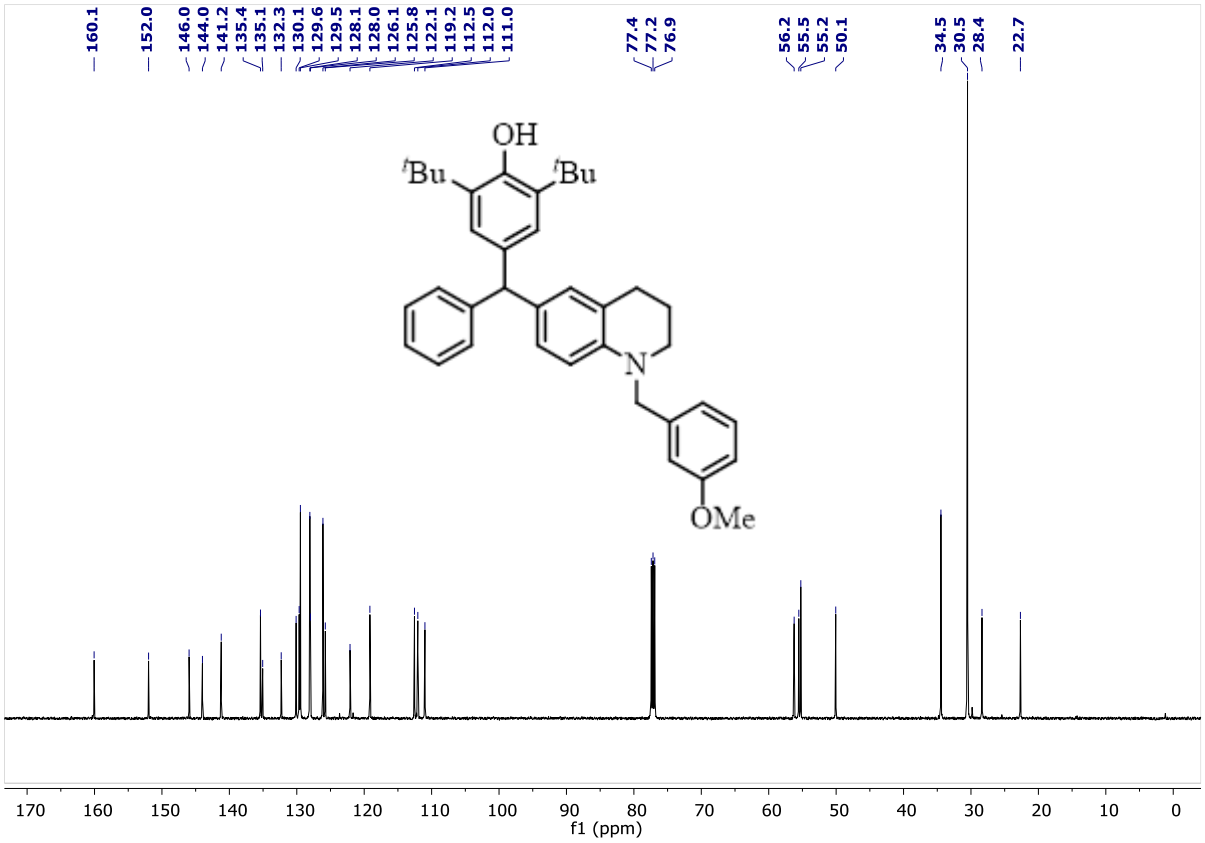


Figure S53: $^{13}C\{^{1}H\}$ NMR Spectrum of **5n** ($CDCl_3$, 126 MHz, 298 K)

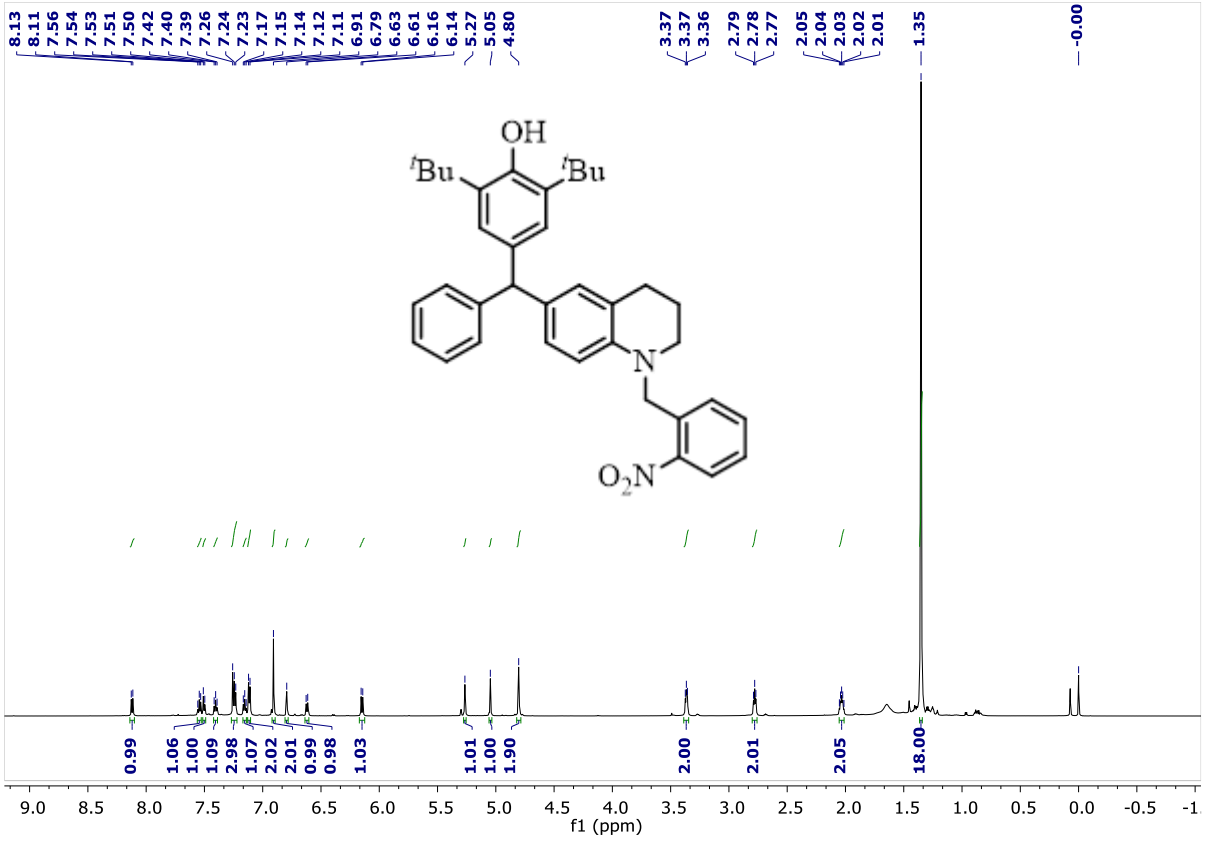


Figure S54: ^{1}H NMR Spectrum of **5o** ($CDCl_3$, 600 MHz, 298 K)

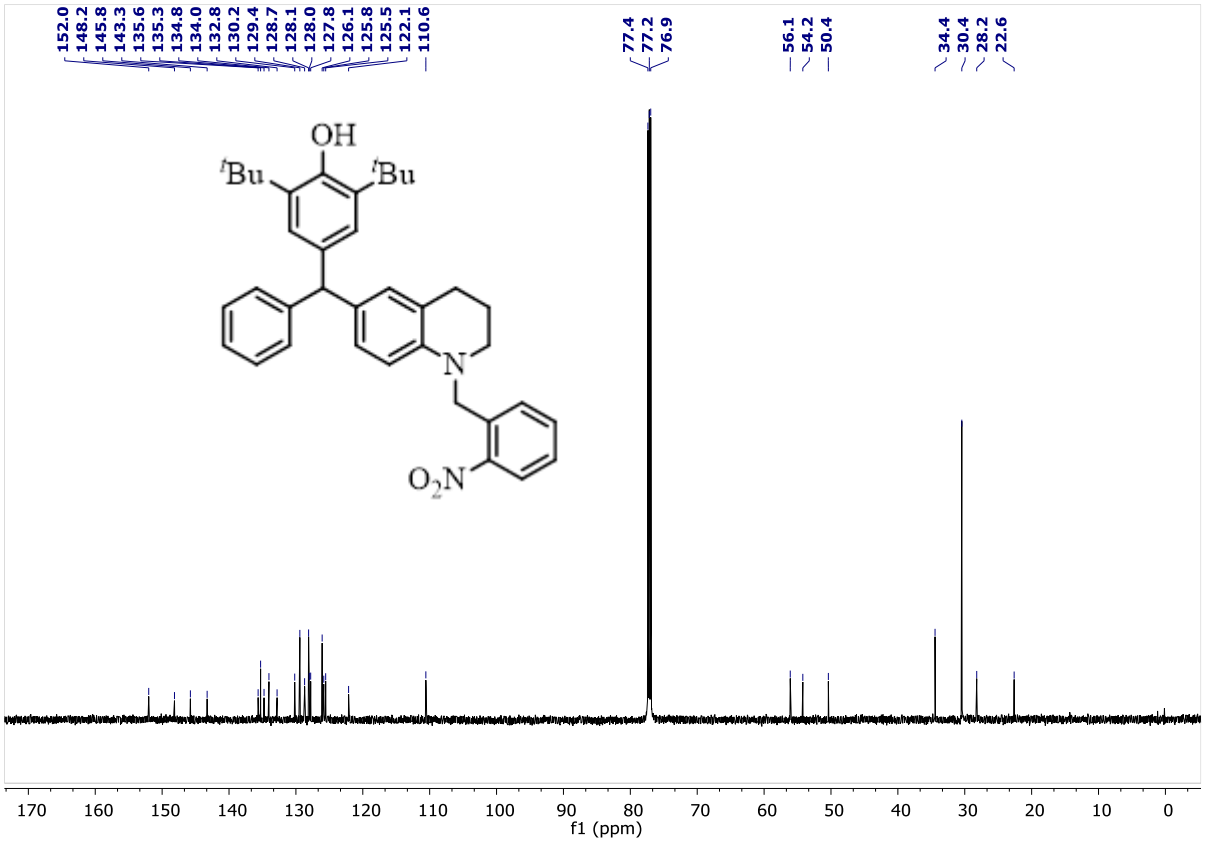


Figure S55: $^{13}C\{^{1}H\}$ NMR Spectrum of **5o** ($CDCl_3$, 151 MHz, 298 K)

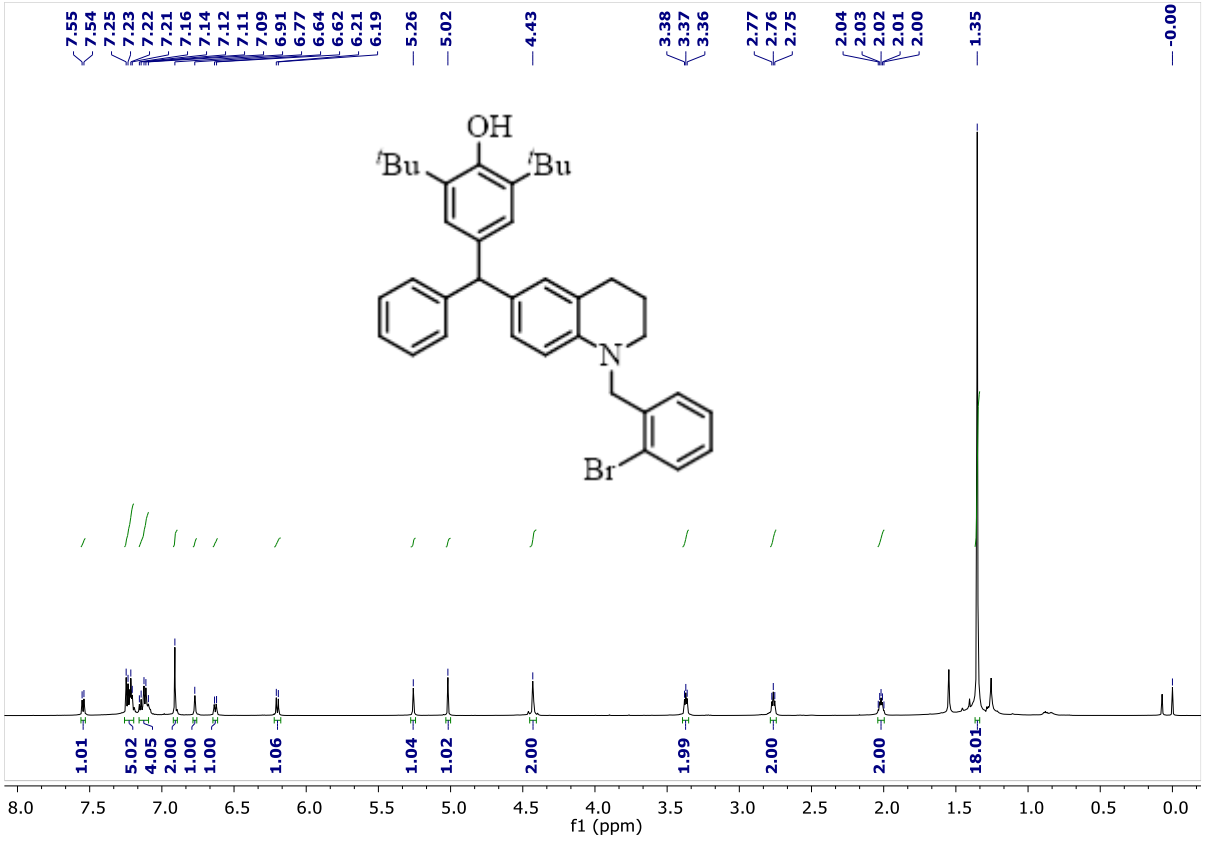


Figure S56: ^{1}H NMR Spectrum of **5p** ($CDCl_3$, 600 MHz, 298 K)

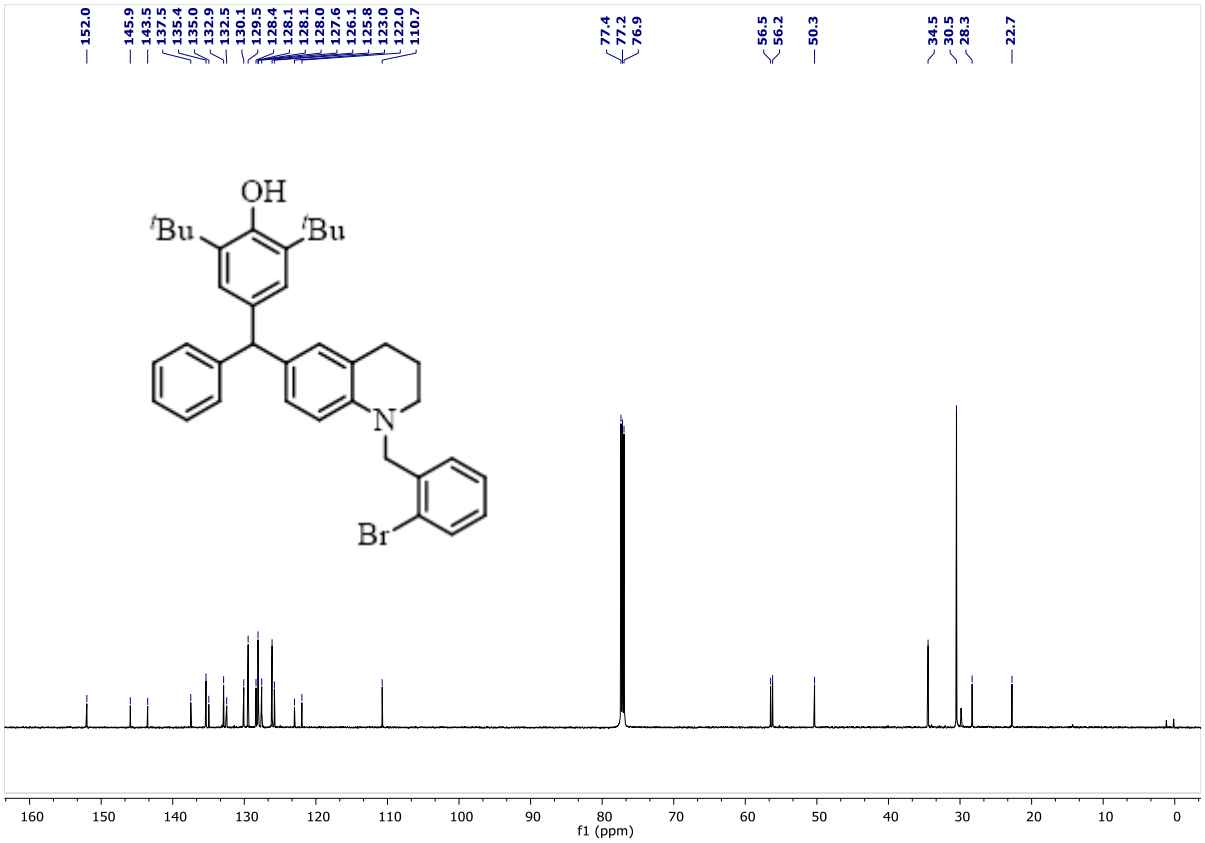


Figure S57: $^{13}C\{^{1}H\}$ NMR Spectrum of **5p** ($CDCl_3$, 151 MHz, 298 K)

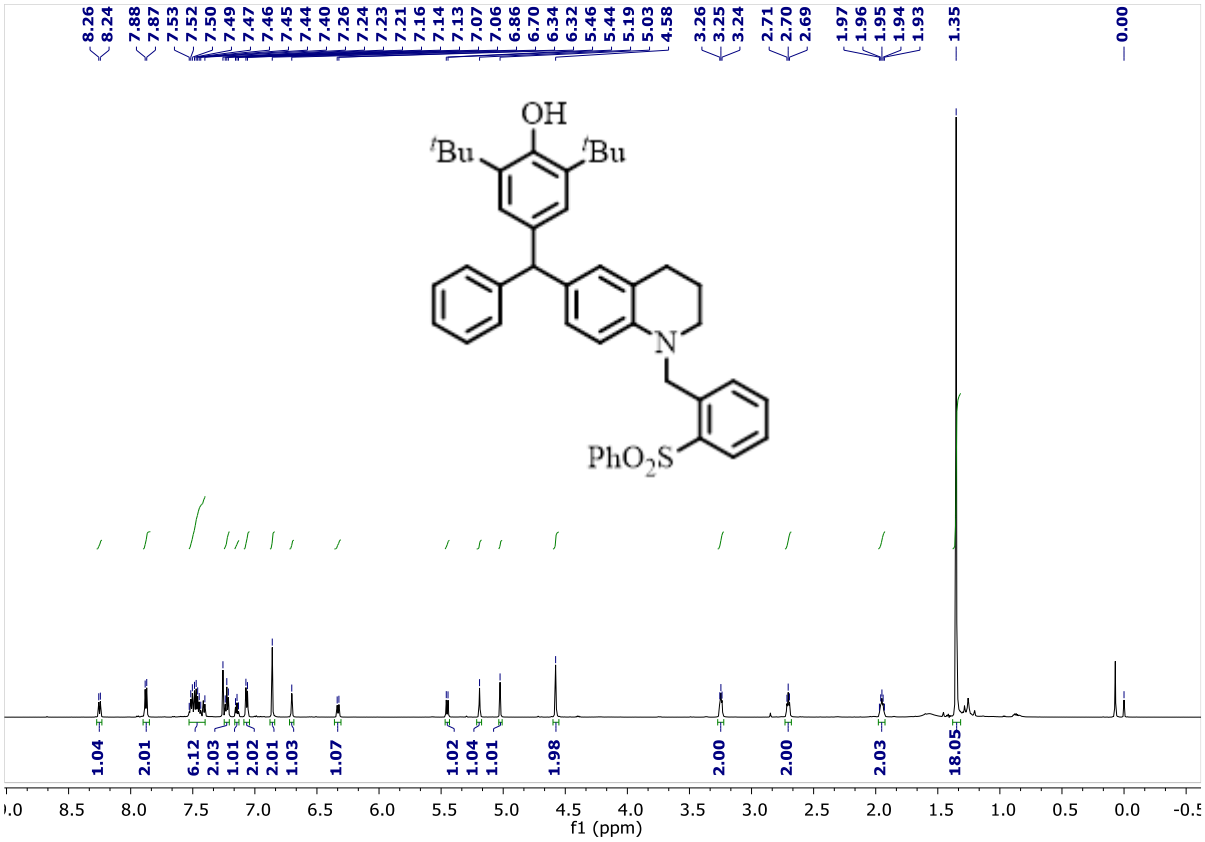


Figure S58: ^{1}H NMR Spectrum of **5q** ($CDCl_3$, 600 MHz, 298 K)

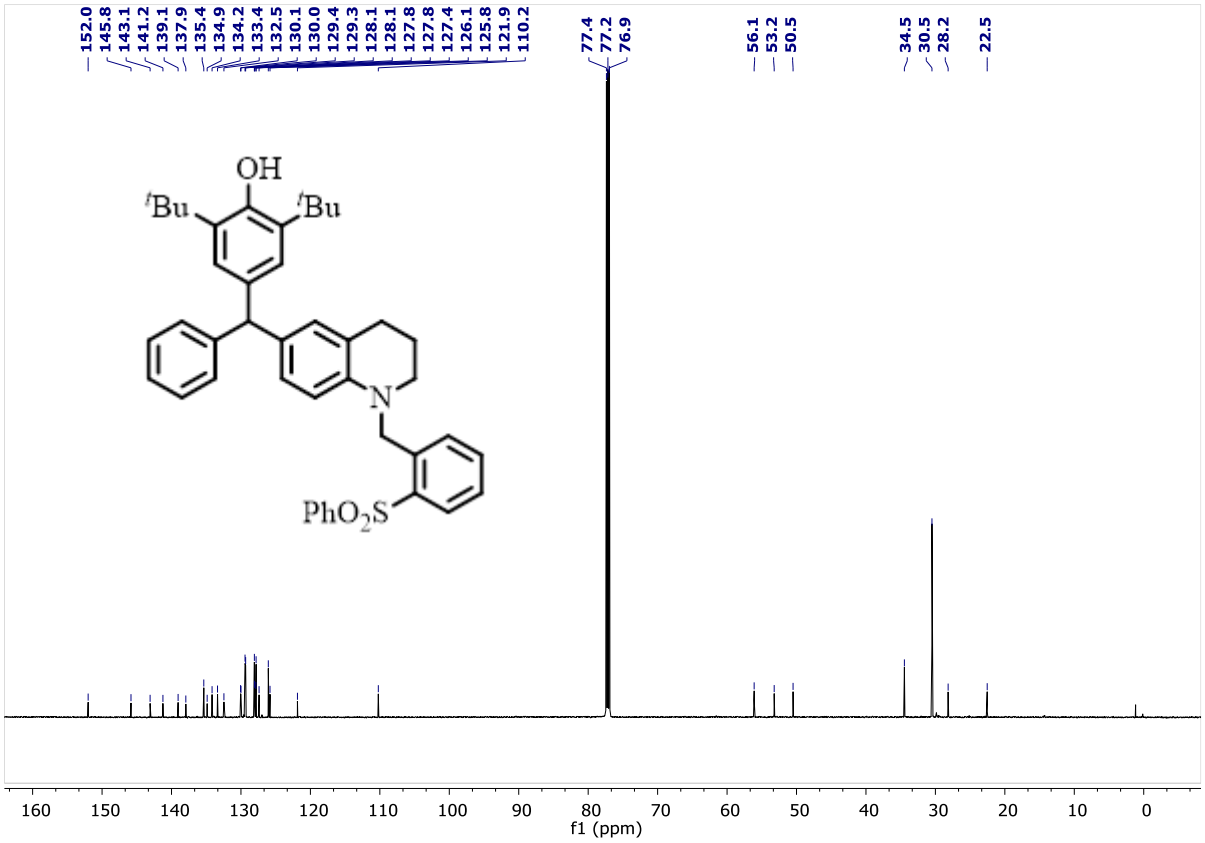


Figure S59: $^{13}C\{^{1}H\}$ NMR Spectrum of **5q** ($CDCl_3$, 151 MHz, 298 K)

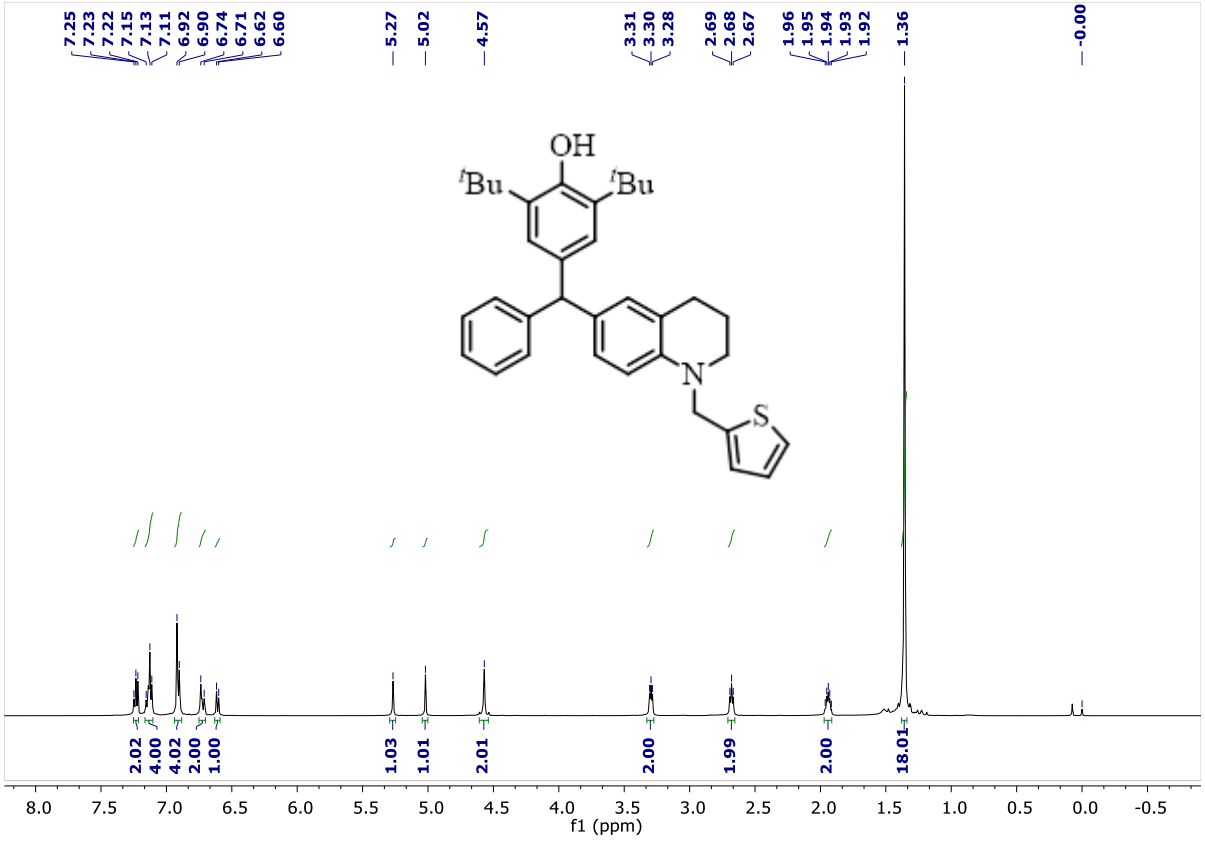


Figure S60: ^{1}H NMR Spectrum of **5r** ($CDCl_3$, 500 MHz, 298 K)

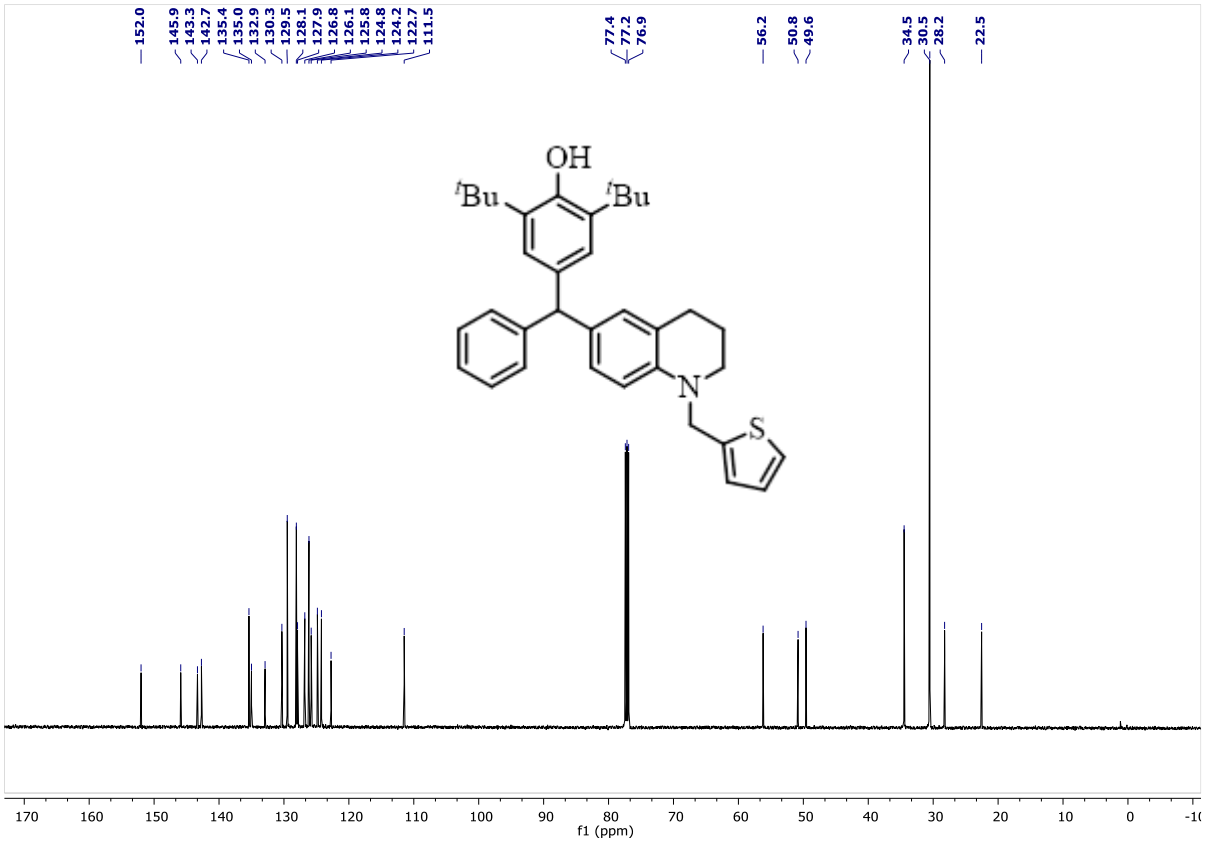


Figure S61: $^{13}C\{^{1}H\}$ NMR Spectrum of **5r** ($CDCl_3$, 126 MHz, 298 K)

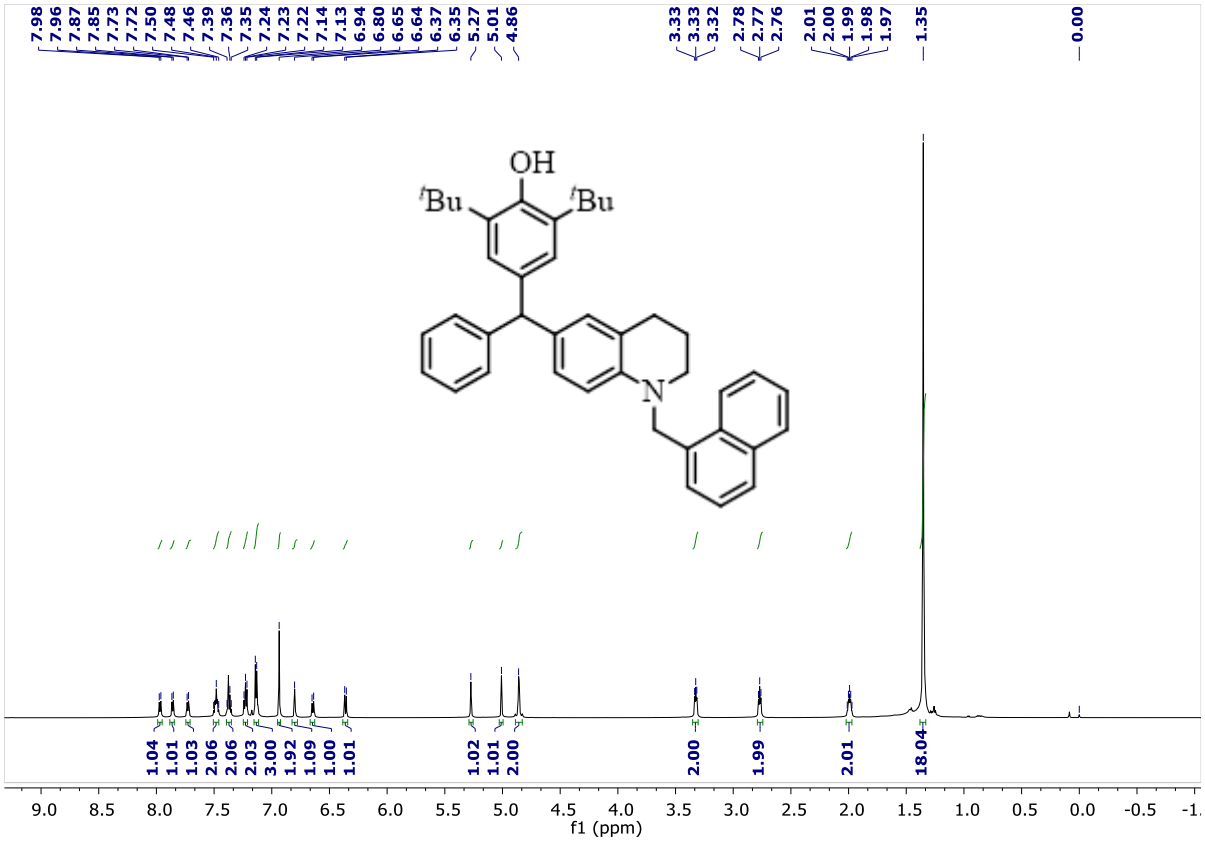


Figure S62: ^{1}H NMR Spectrum of **5s** ($CDCl_3$, 600 MHz, 298 K)

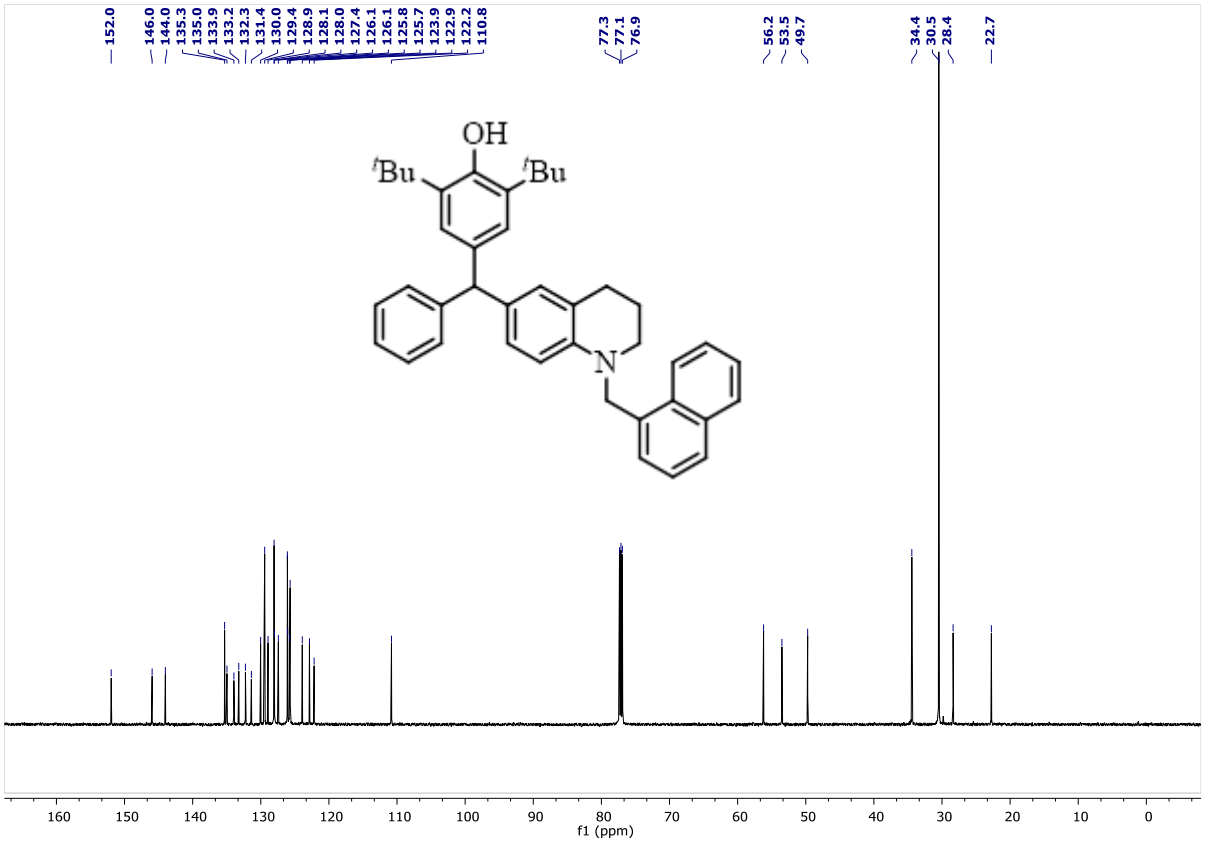


Figure S63: $^{13}C\{^{1}H\}$ NMR Spectrum of **5s** ($CDCl_3$, 151 MHz, 298 K)

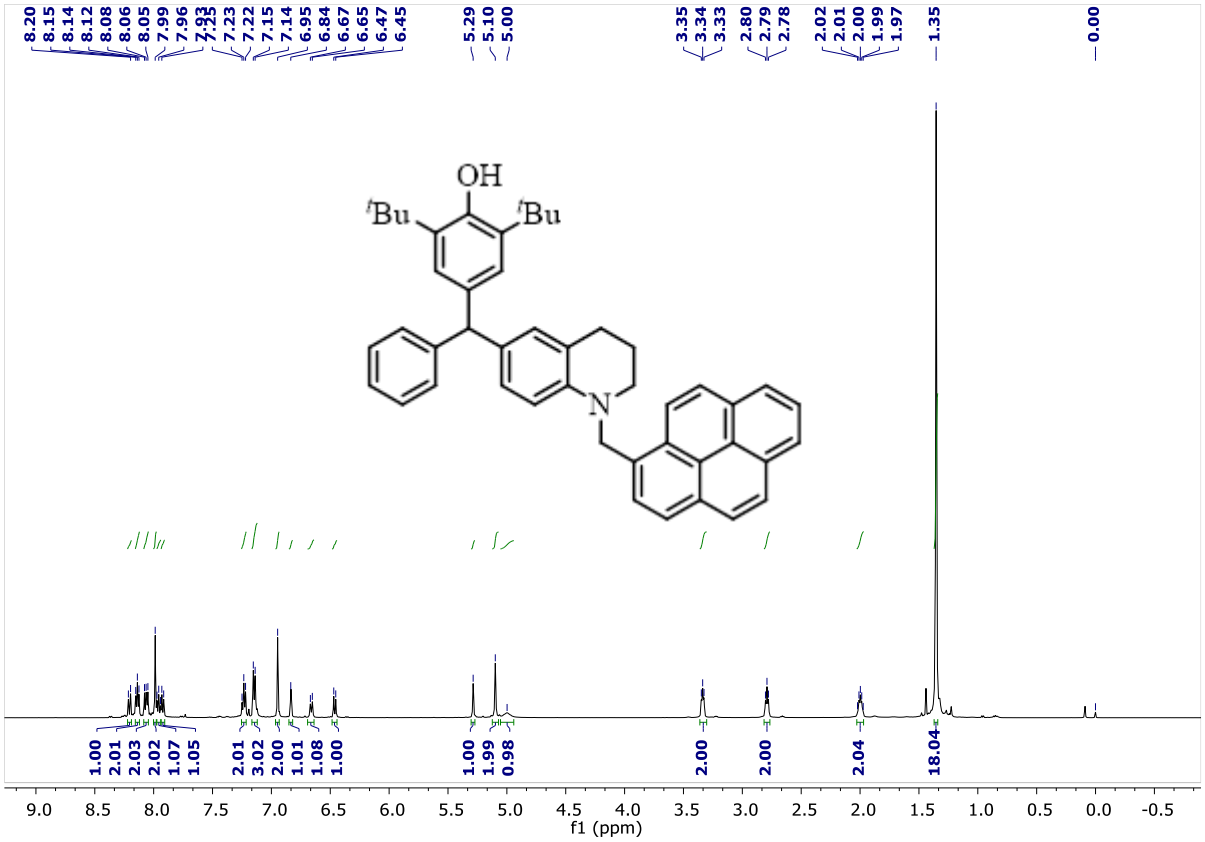


Figure S64: ^{1}H NMR Spectrum of **5t** ($CDCl_3$, 500 MHz, 298 K)

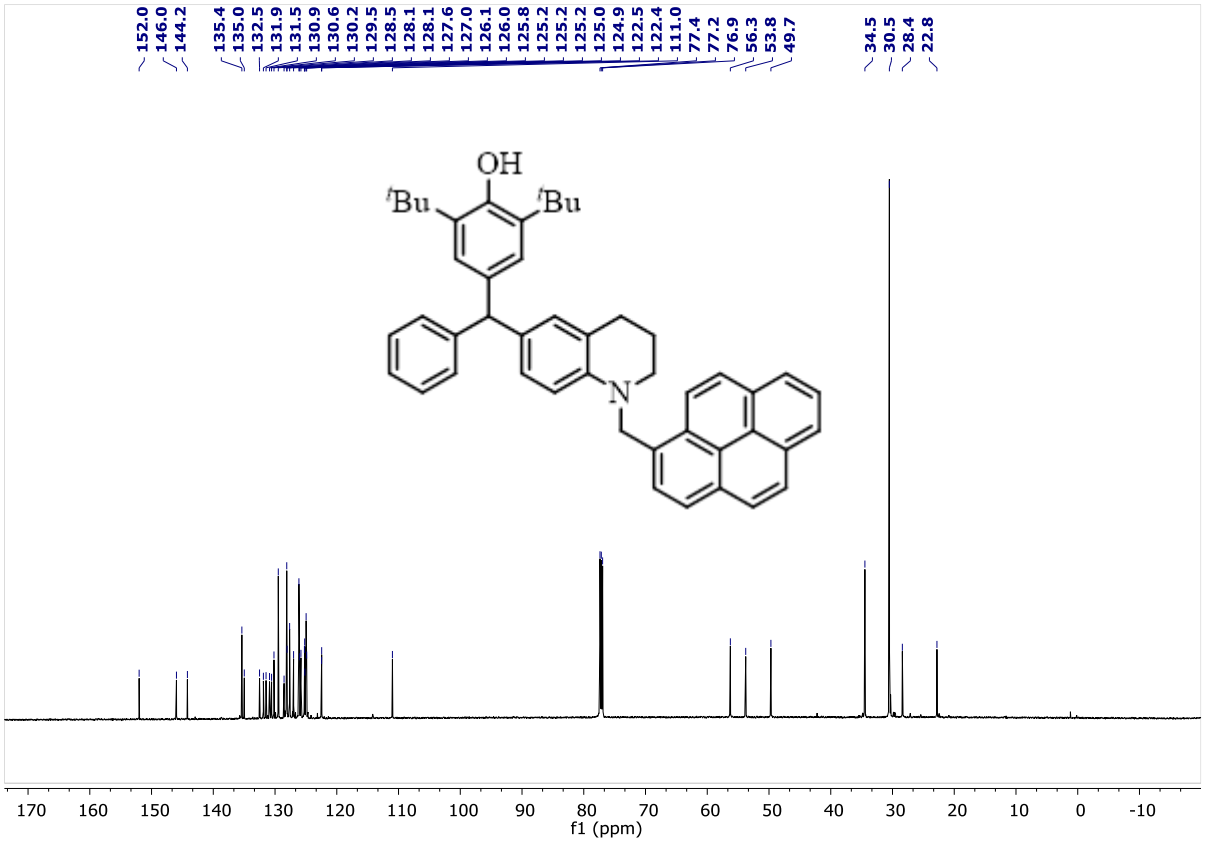


Figure S65: $^{13}C\{^{1}H\}$ NMR Spectrum of **5t** ($CDCl_3$, 151 MHz, 298 K)

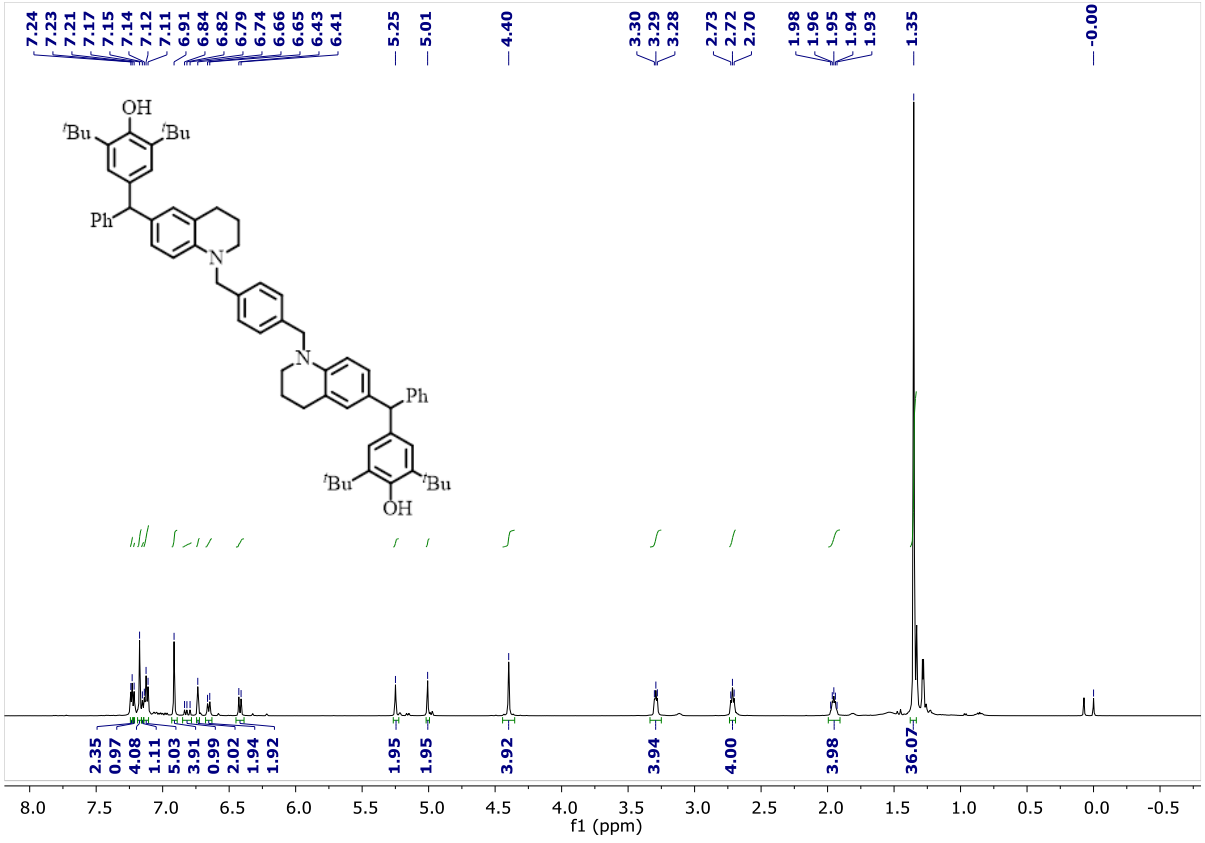


Figure S66: ^{1}H NMR Spectrum of **5u** ($CDCl_3$, 500 MHz, 298 K)

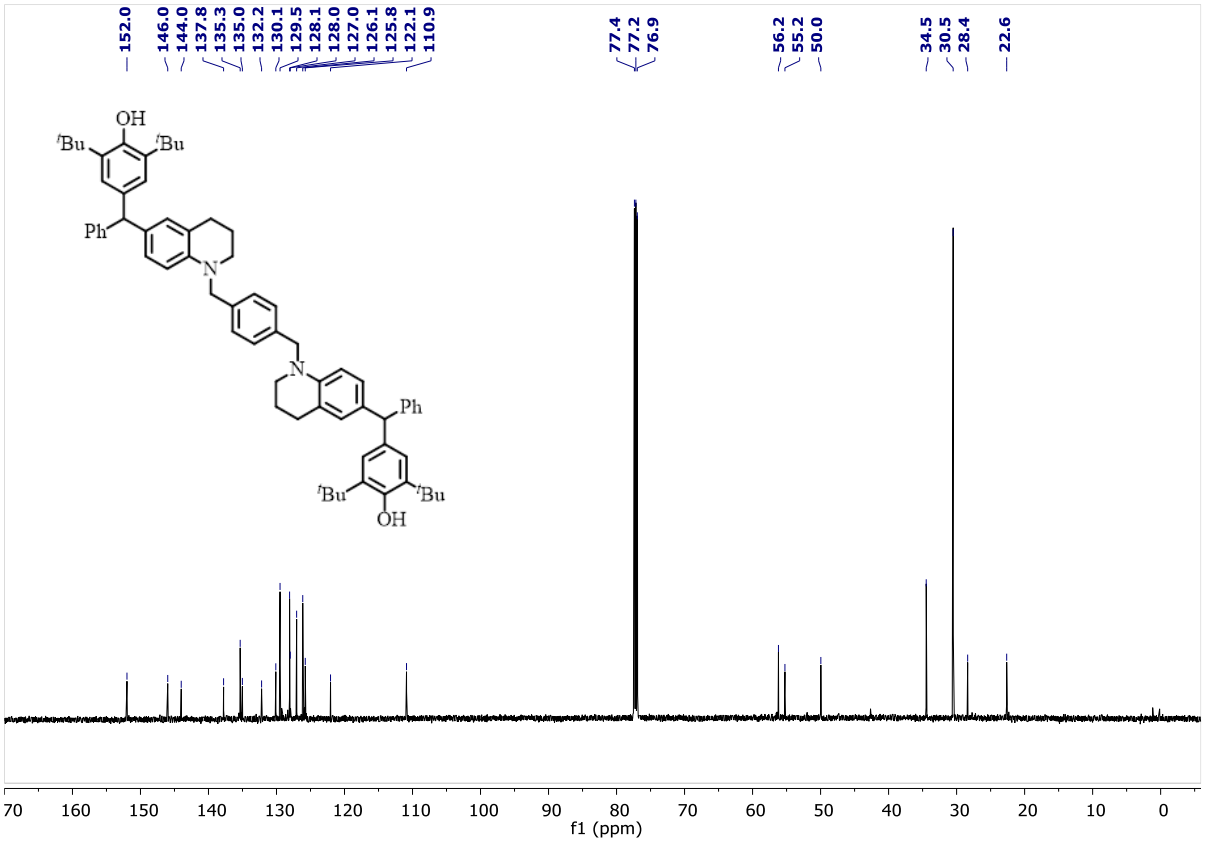


Figure S67: $^{13}C\{^{1}H\}$ NMR Spectrum of **5u** ($CDCl_3$, 151 MHz, 298 K)

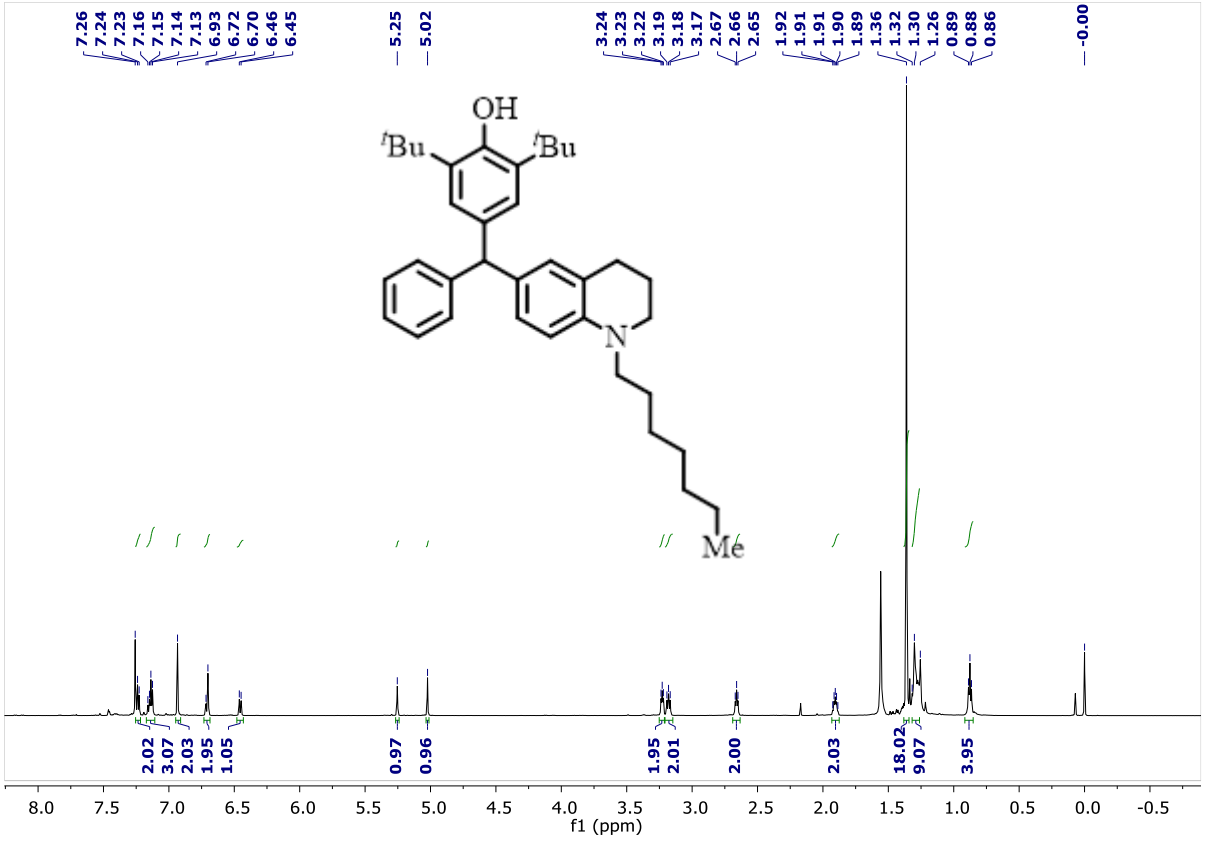


Figure S68: ^{1}H NMR Spectrum of **5v** ($CDCl_3$, 600 MHz, 298 K)

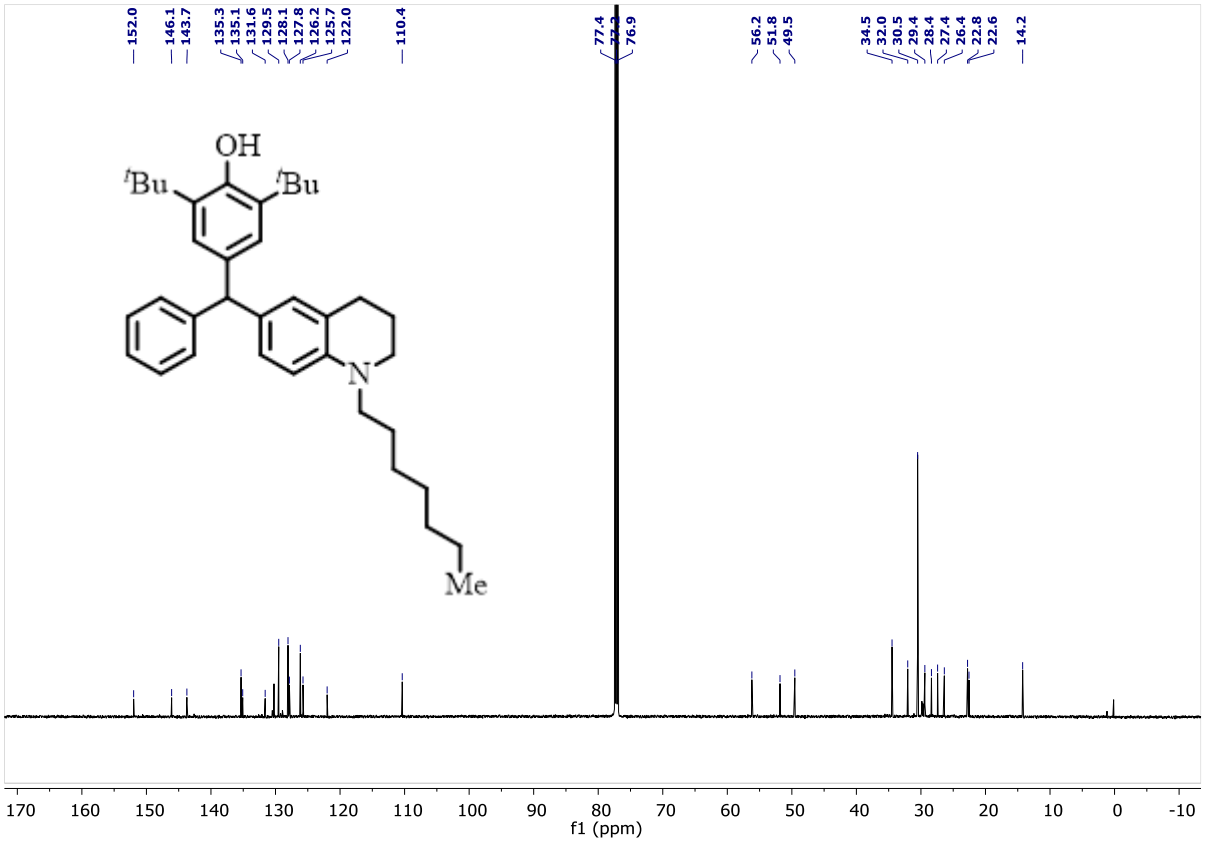


Figure S69: $^{13}C\{^{1}H\}$ NMR Spectrum of **5v** ($CDCl_3$, 151 MHz, 298 K)

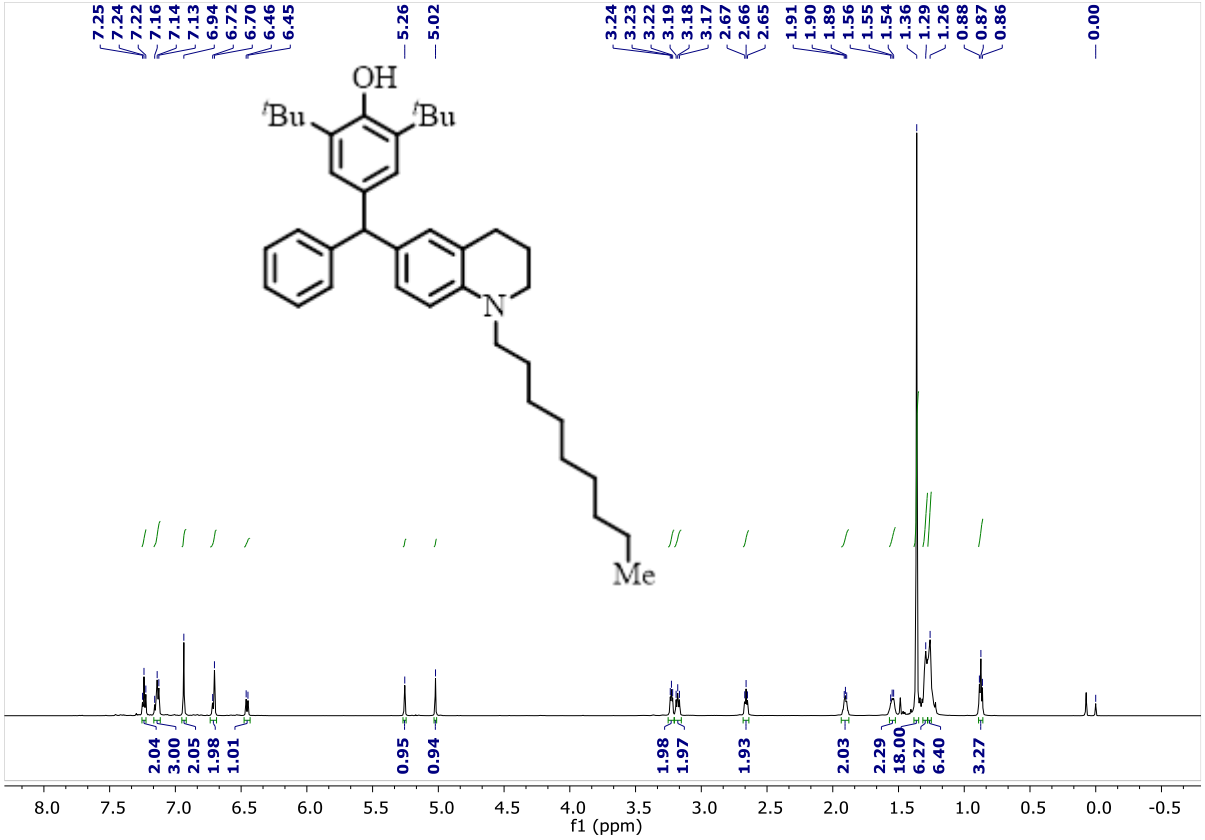


Figure S70: ^{1}H NMR Spectrum of **5w** ($CDCl_3$, 600 MHz, 298 K)

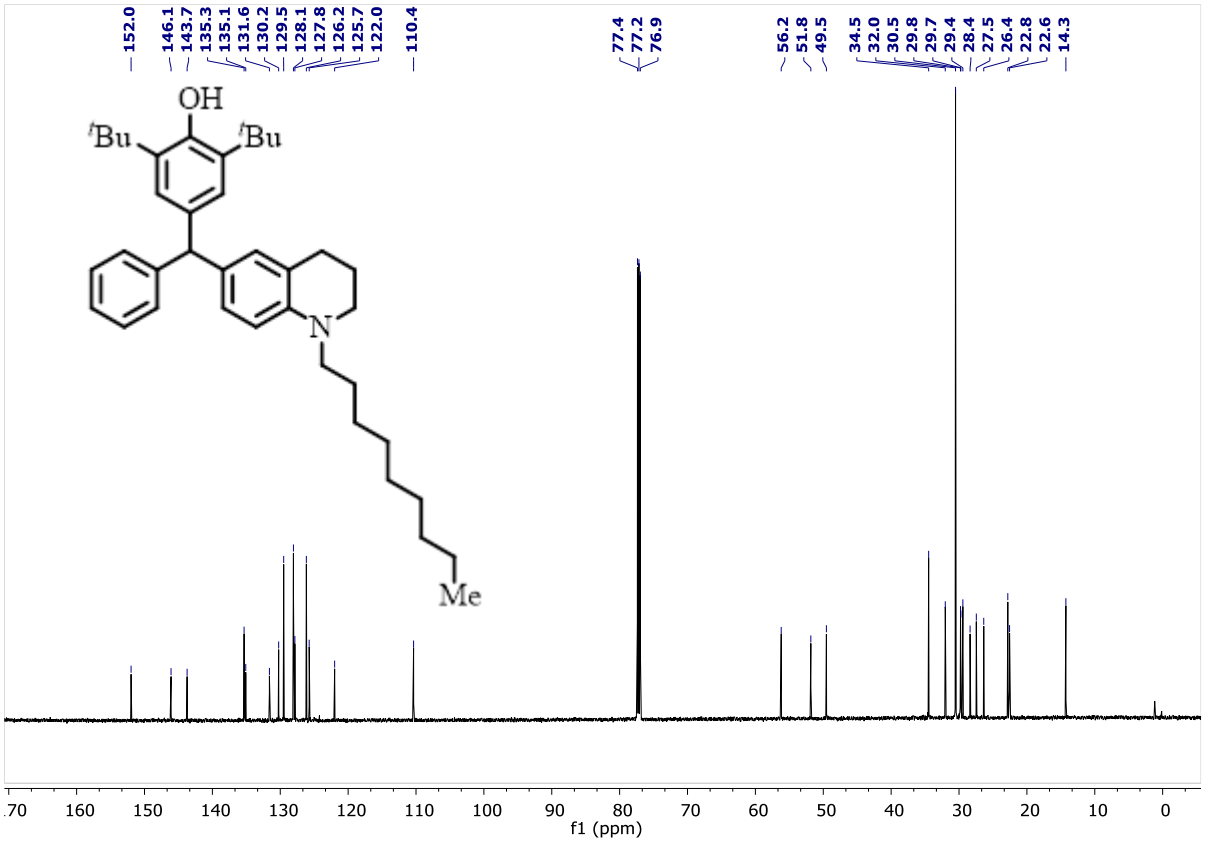


Figure S71: $^{13}C\{^{1}H\}$ NMR Spectrum of **5w** ($CDCl_3$, 151 MHz, 298 K)

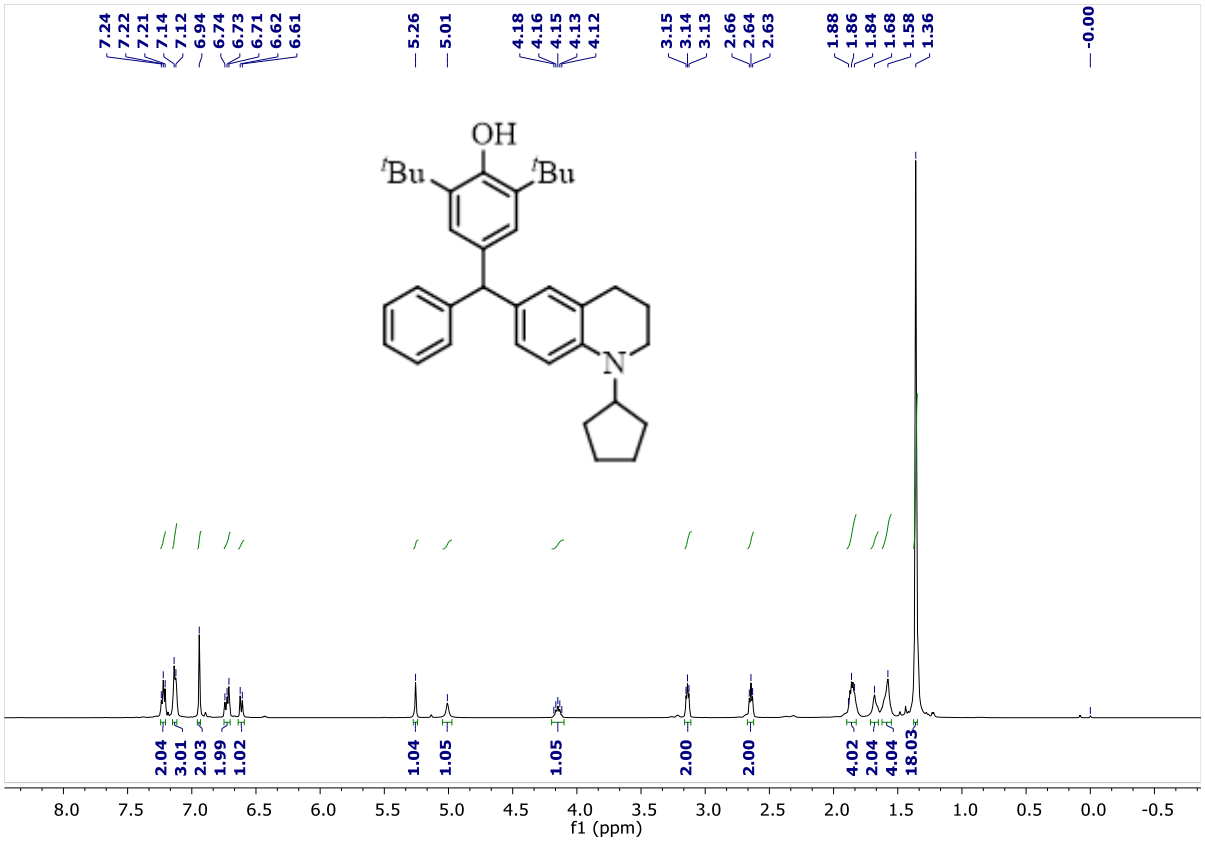


Figure S72: ^{1}H NMR Spectrum of **5x** ($CDCl_3$, 500 MHz, 298 K)

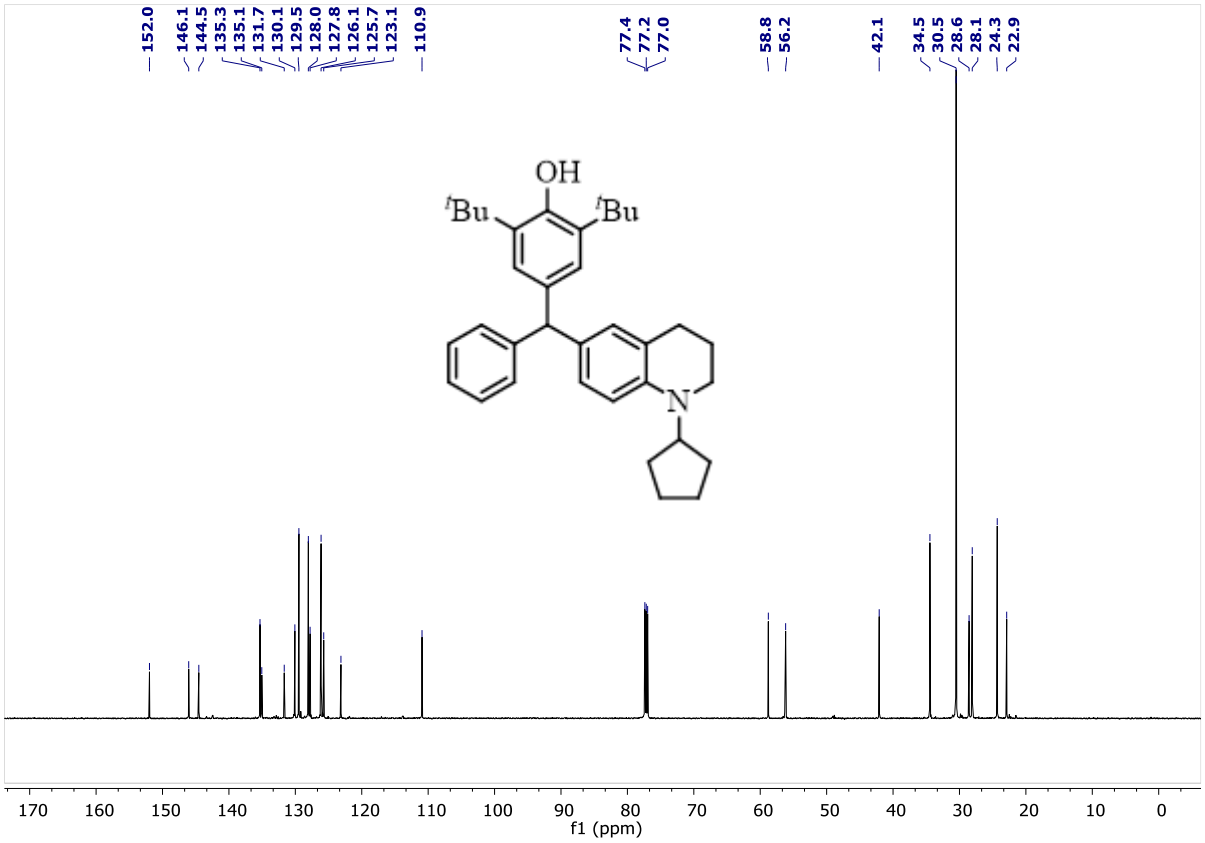


Figure S73: $^{13}C\{^{1}H\}$ NMR Spectrum of **5x** ($CDCl_3$, 151 MHz, 298 K)

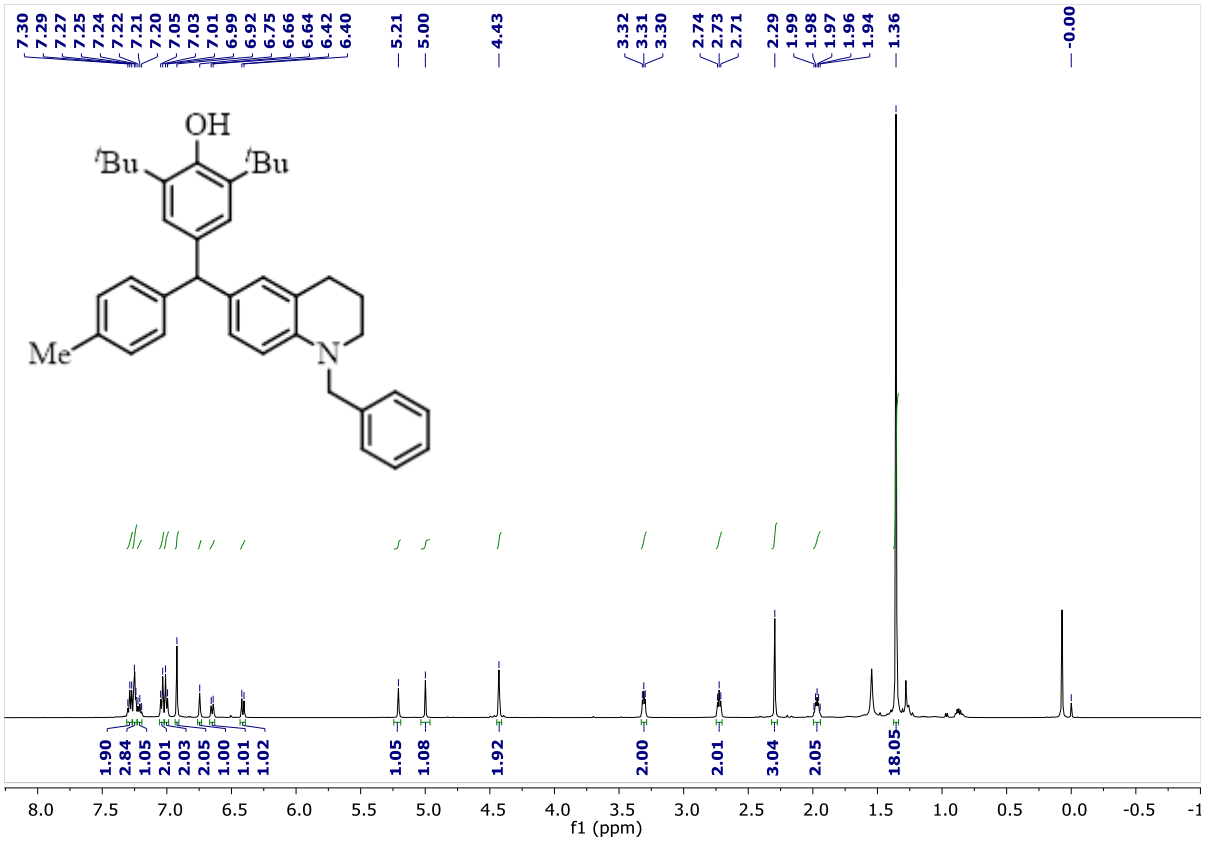


Figure S74: ^{1}H NMR Spectrum of **6a** ($CDCl_3$, 500 MHz, 298 K)

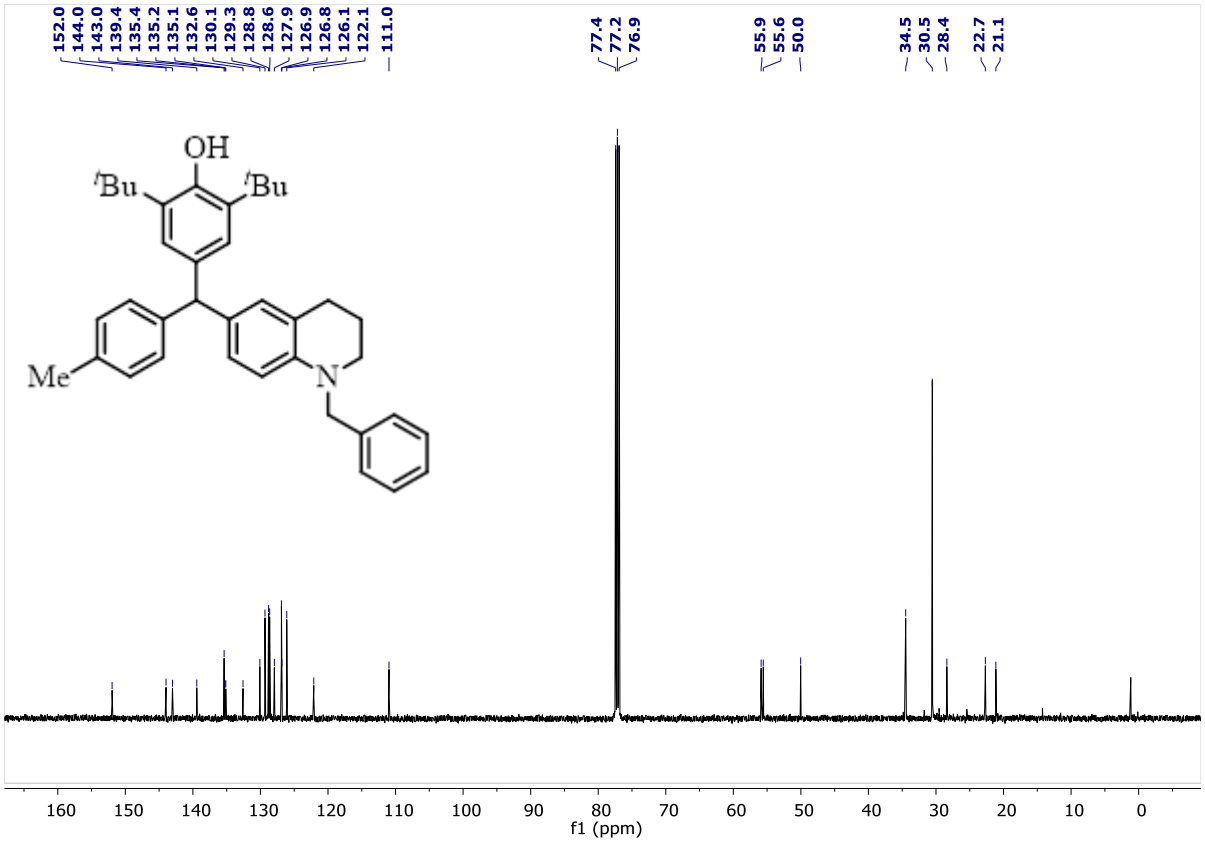


Figure S75: $^{13}C\{^{1}H\}$ NMR Spectrum of **6a** ($CDCl_3$, 126 MHz, 298 K)

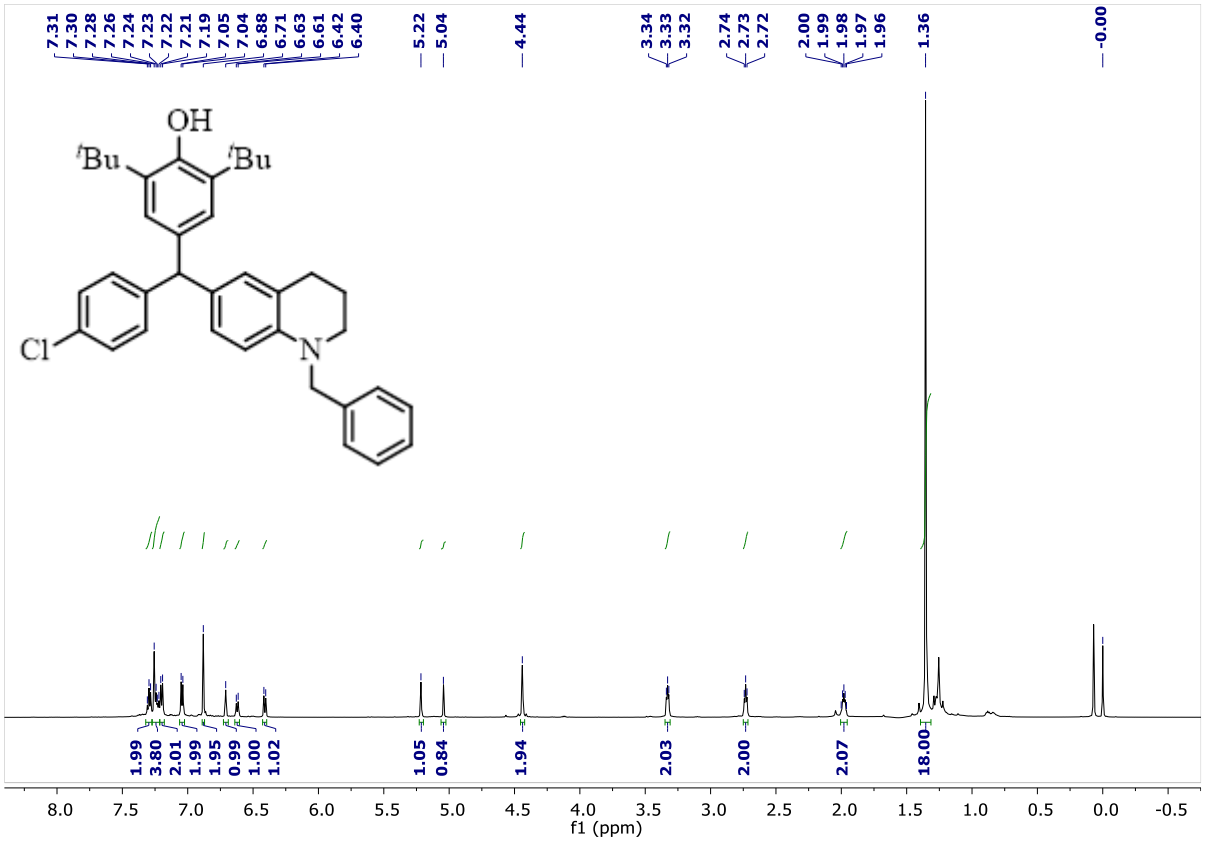


Figure S76: ^{1}H NMR Spectrum of **6b** ($CDCl_3$, 600 MHz, 298 K)

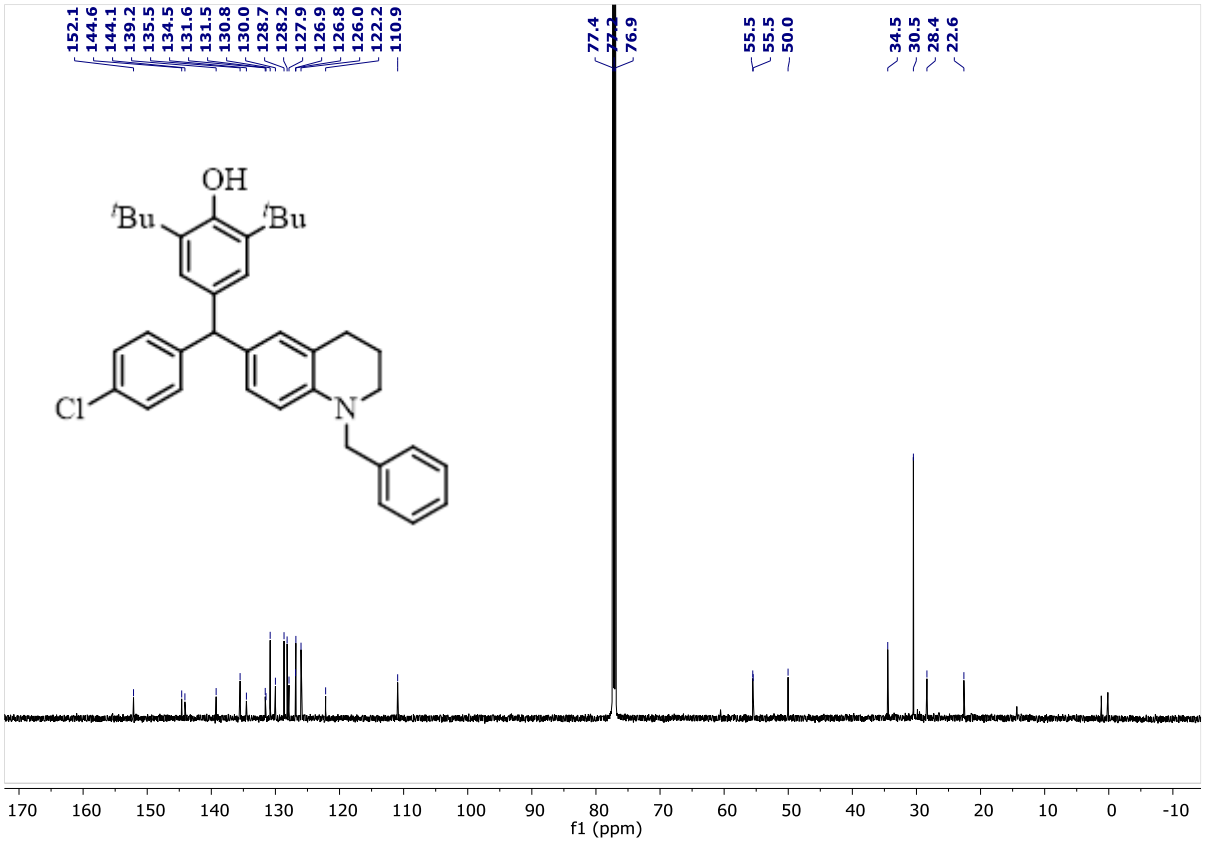


Figure S77: $^{13}C\{^{1}H\}$ NMR Spectrum of **6b** ($CDCl_3$, 151 MHz, 298 K)

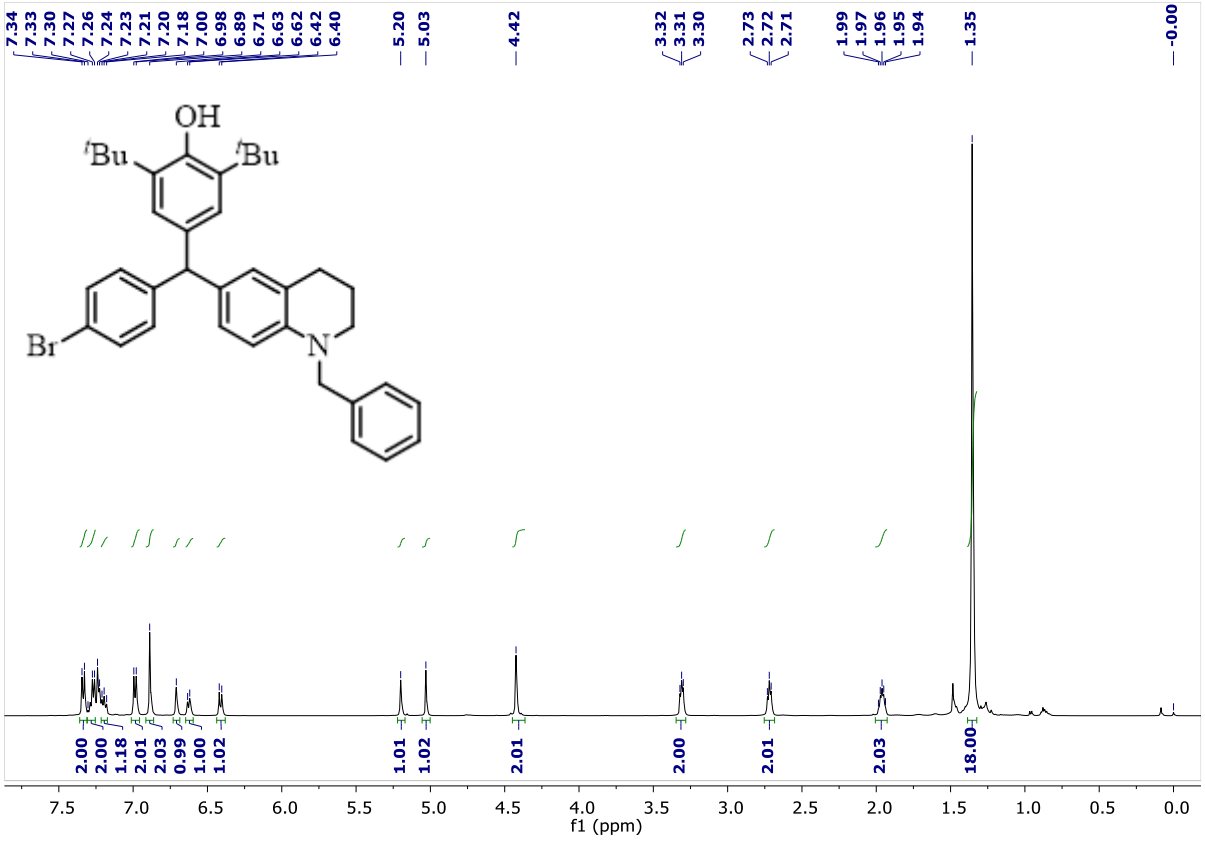


Figure S78: ^{1}H NMR Spectrum of **6c** ($CDCl_3$, 500 MHz, 298 K)

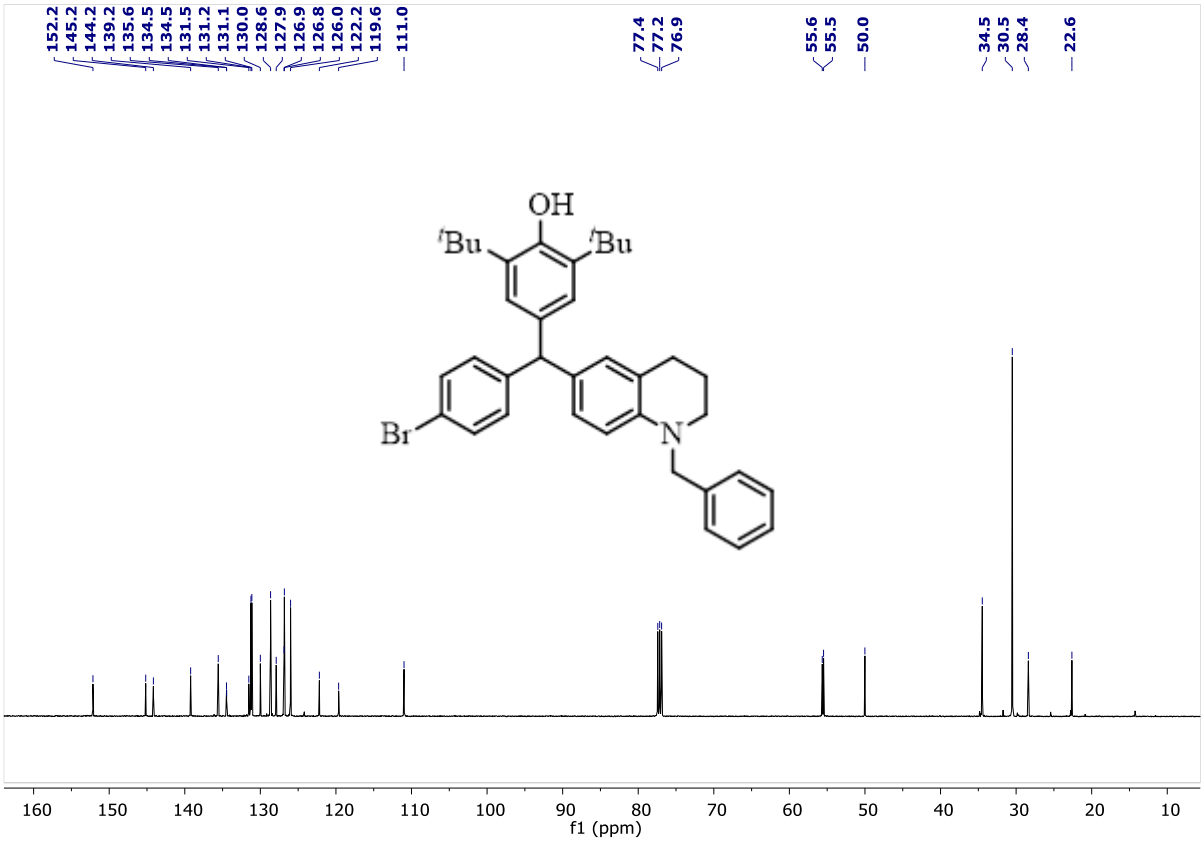


Figure S79: $^{13}C\{^{1}H\}$ NMR Spectrum of **6c** ($CDCl_3$, 126 MHz, 298 K)

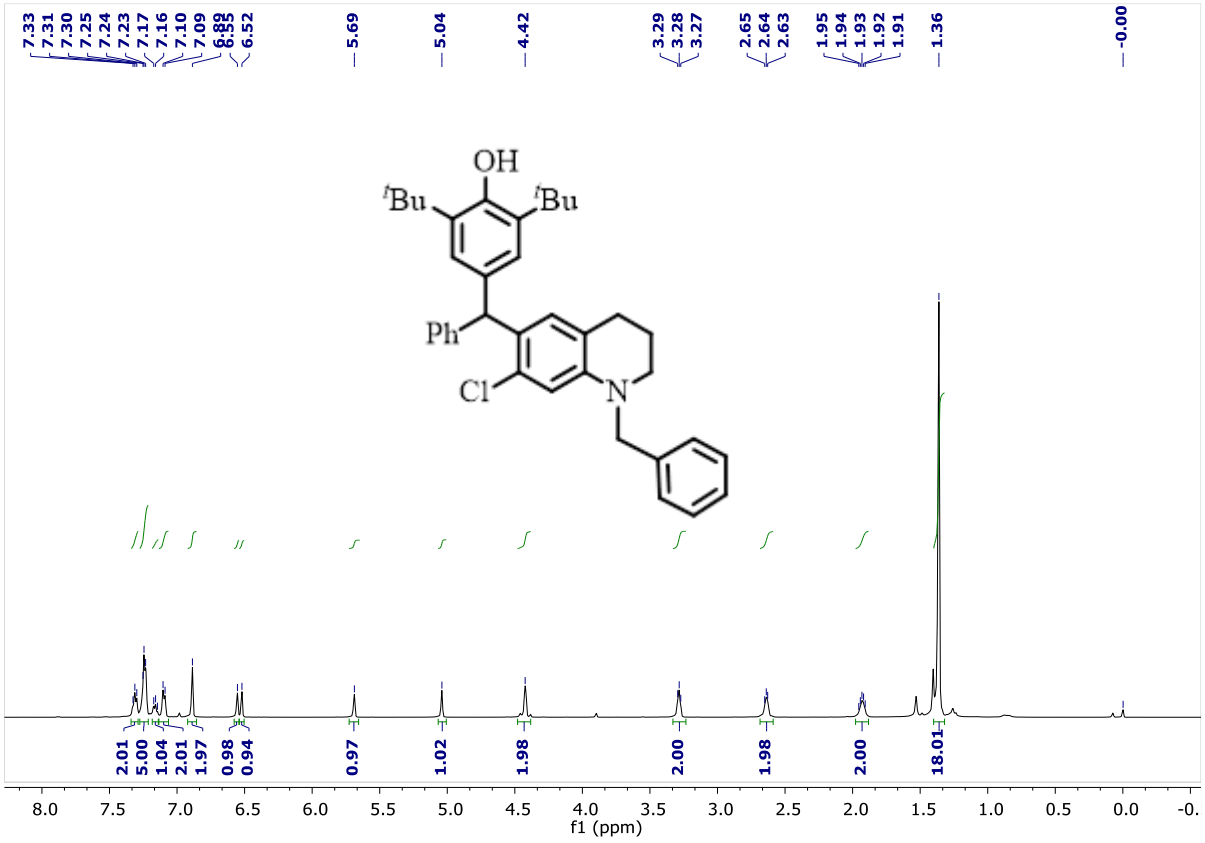


Figure S80: ^{1}H NMR Spectrum of **6d** ($CDCl_3$, 500 MHz, 298 K)

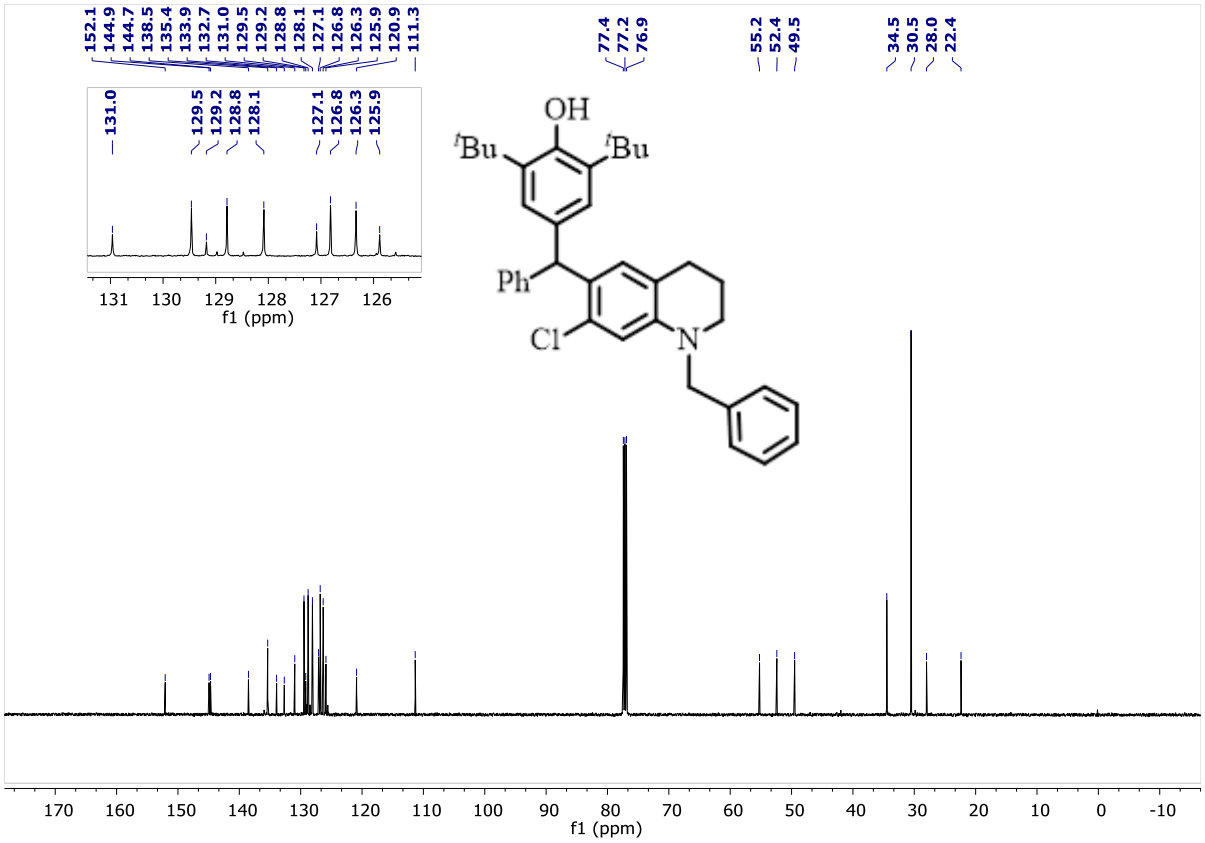


Figure S81: $^{13}C\{^{1}H\}$ NMR Spectrum of **6d** ($CDCl_3$, 126 MHz, 298 K)

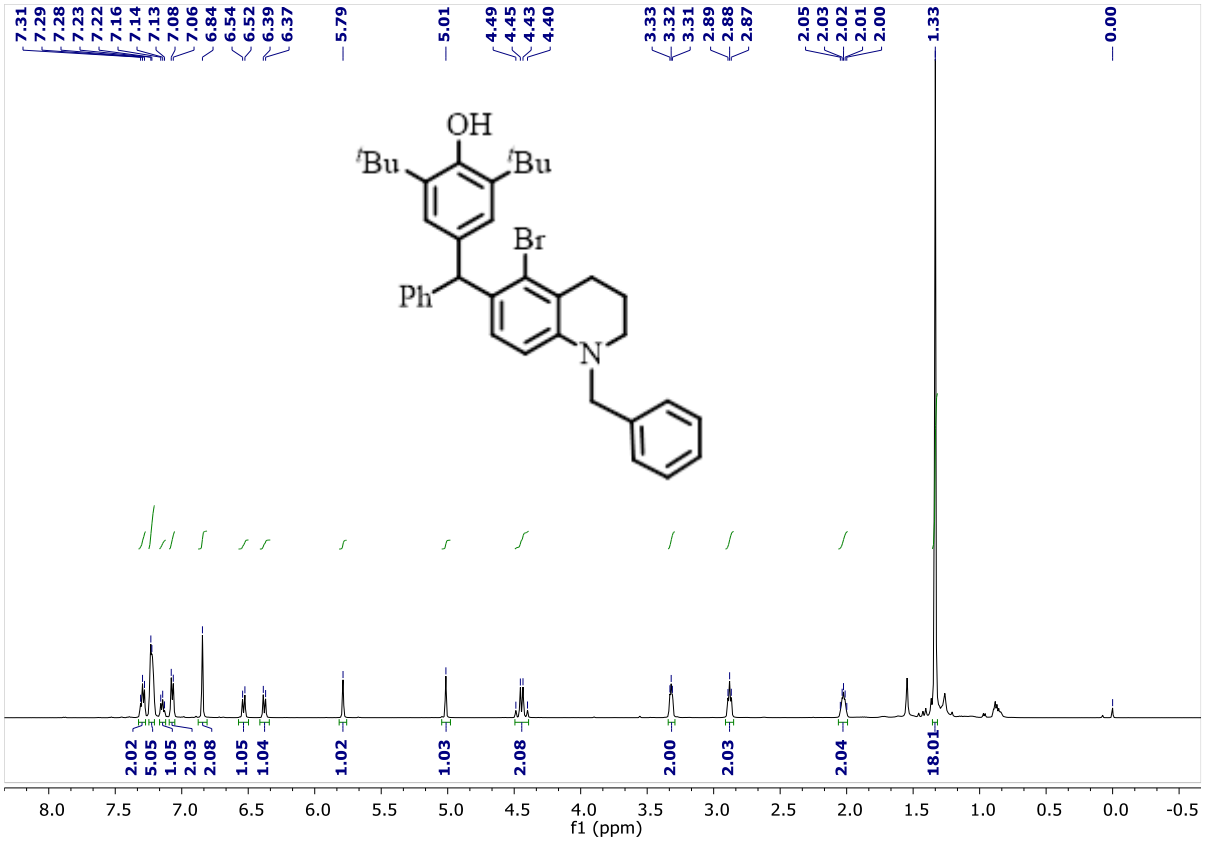


Figure S82: ^{1}H NMR Spectrum of **6e** ($CDCl_3$, 500 MHz, 298 K)

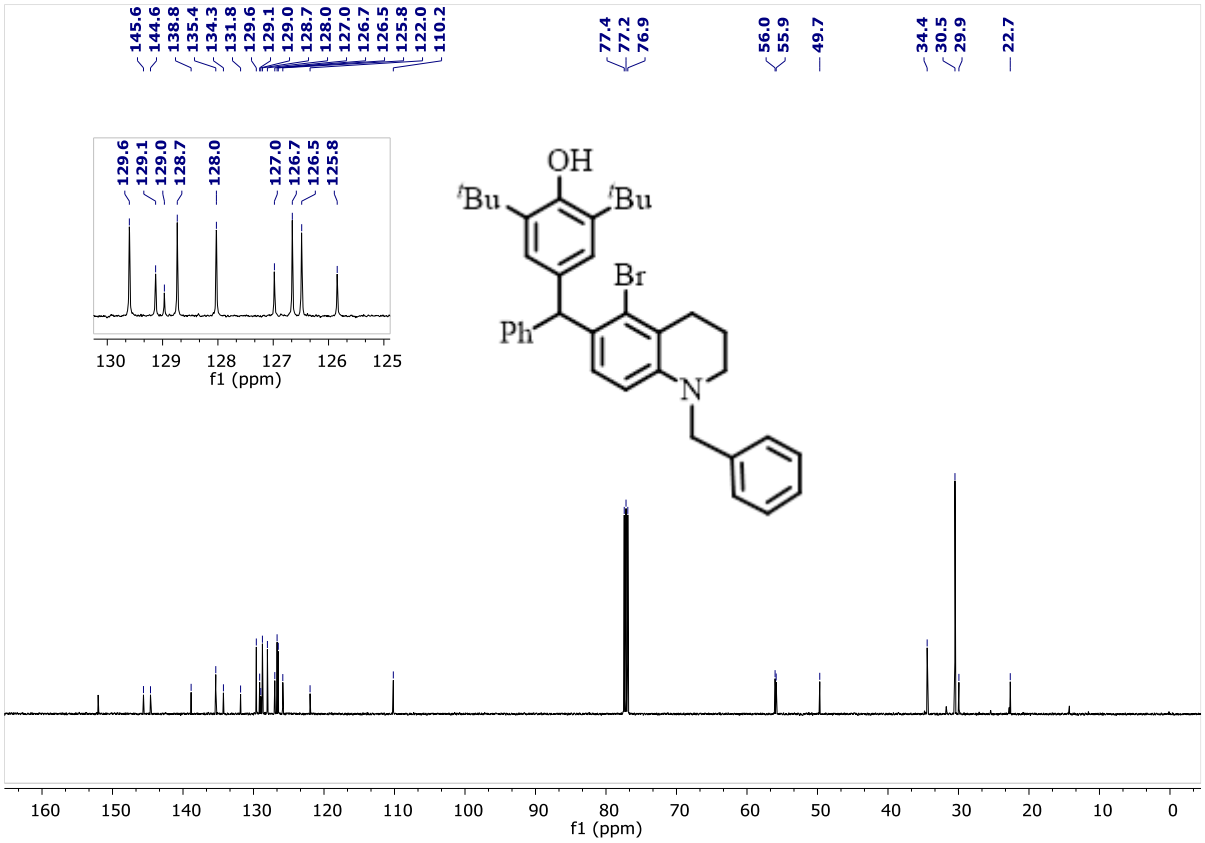


Figure S83: $^{13}C\{^{1}H\}$ NMR Spectrum of **6e** ($CDCl_3$, 126 MHz, 298 K)

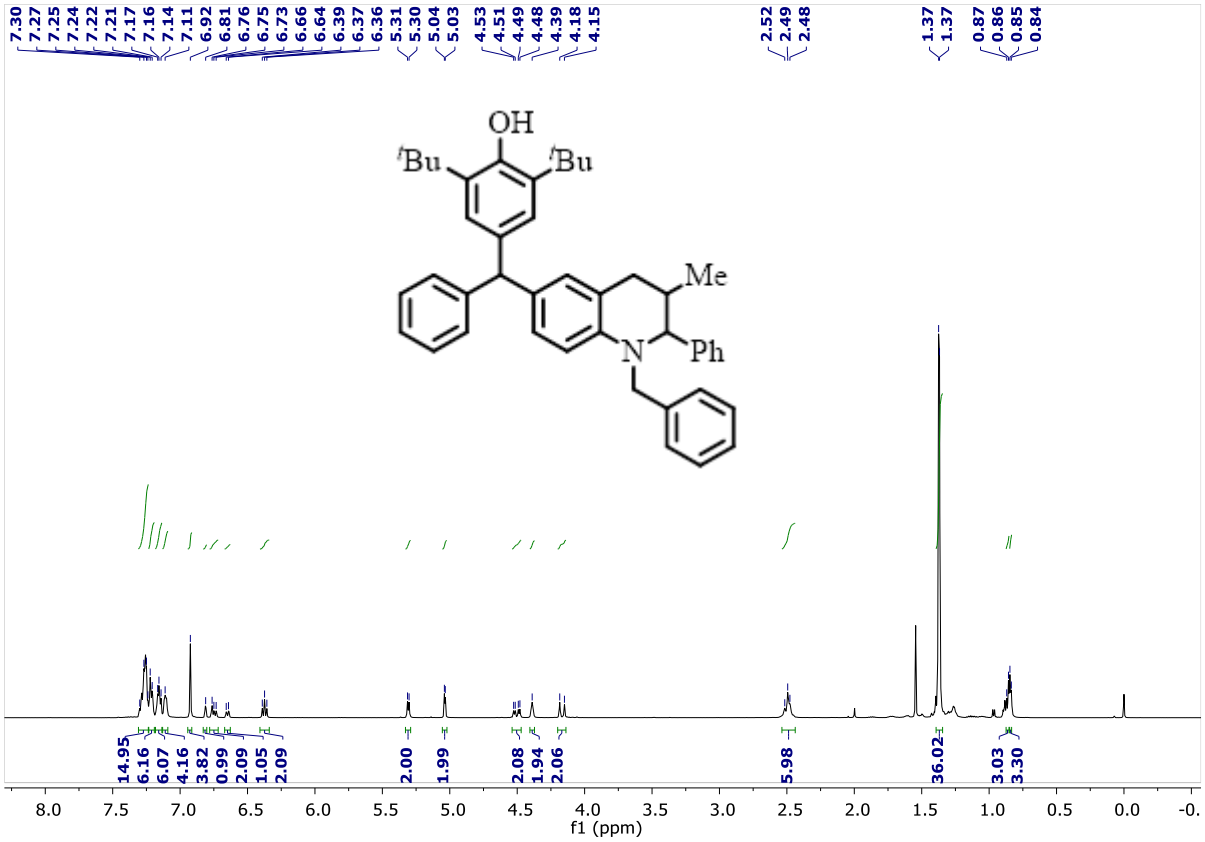


Figure S84: ^{1}H NMR Spectrum of **3d** ($CDCl_3$, 500 MHz, 298 K)

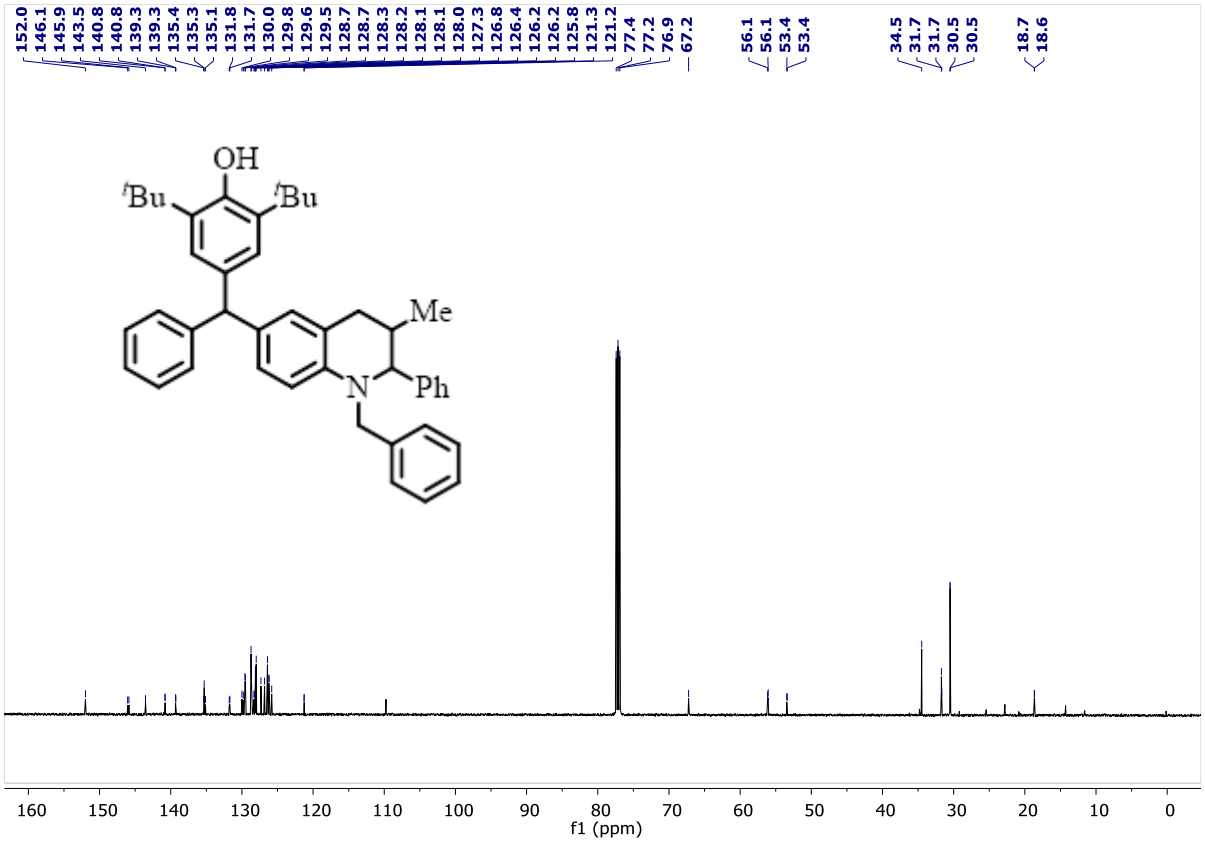


Figure S85: $^{13}C\{^{1}H\}$ NMR Spectrum of **3d** ($CDCl_3$, 126 MHz, 298 K)

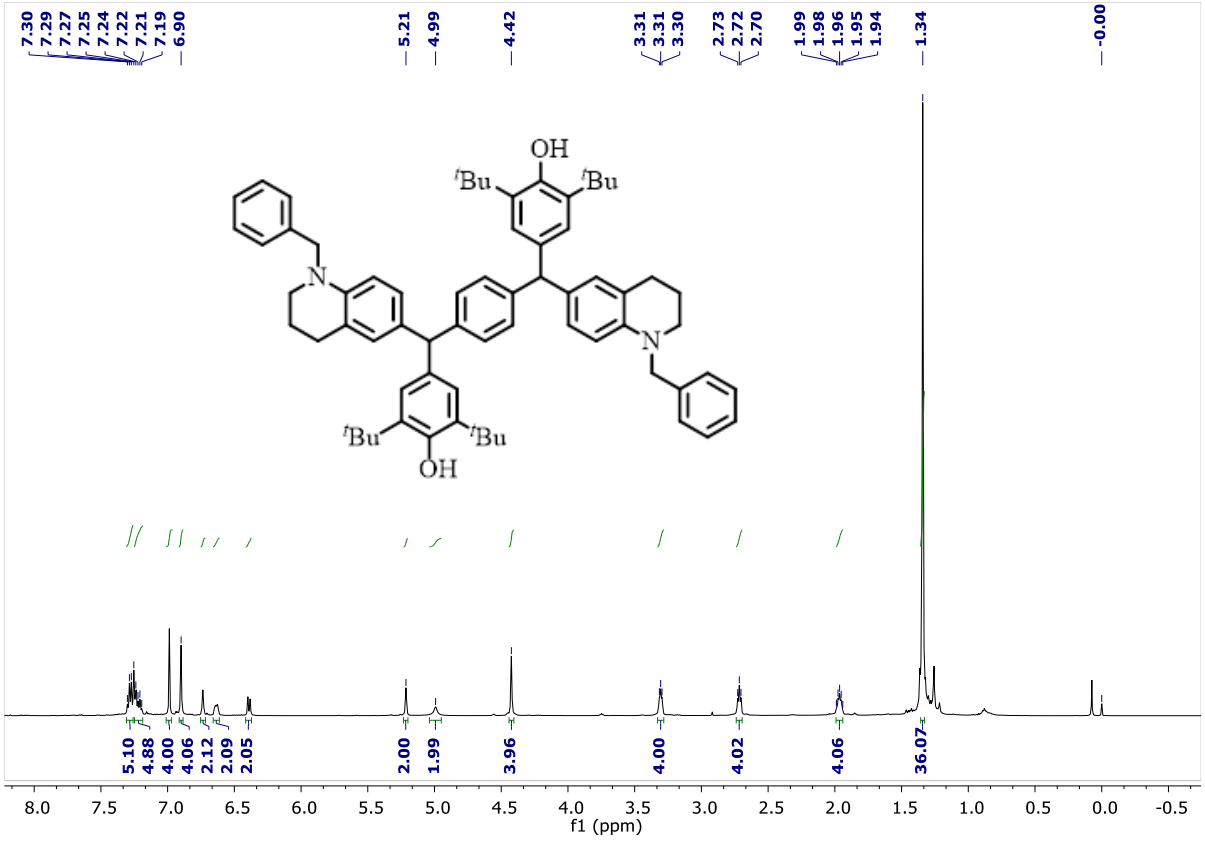


Figure S86: ^{1}H NMR Spectrum of **6f** ($CDCl_3$, 500 MHz, 298 K)

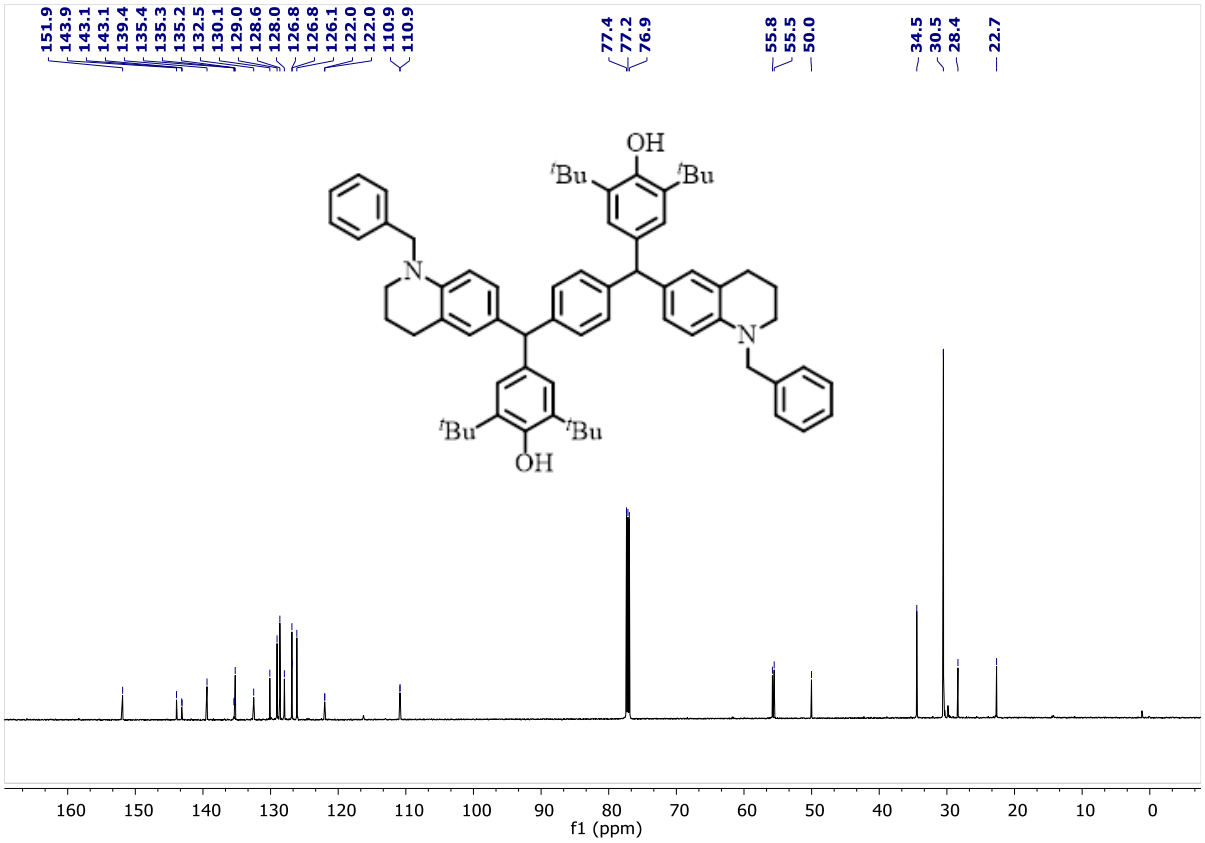


Figure S87: $^{13}C\{^{1}H\}$ NMR Spectrum of **6f** ($CDCl_3$, 151 MHz, 298 K)

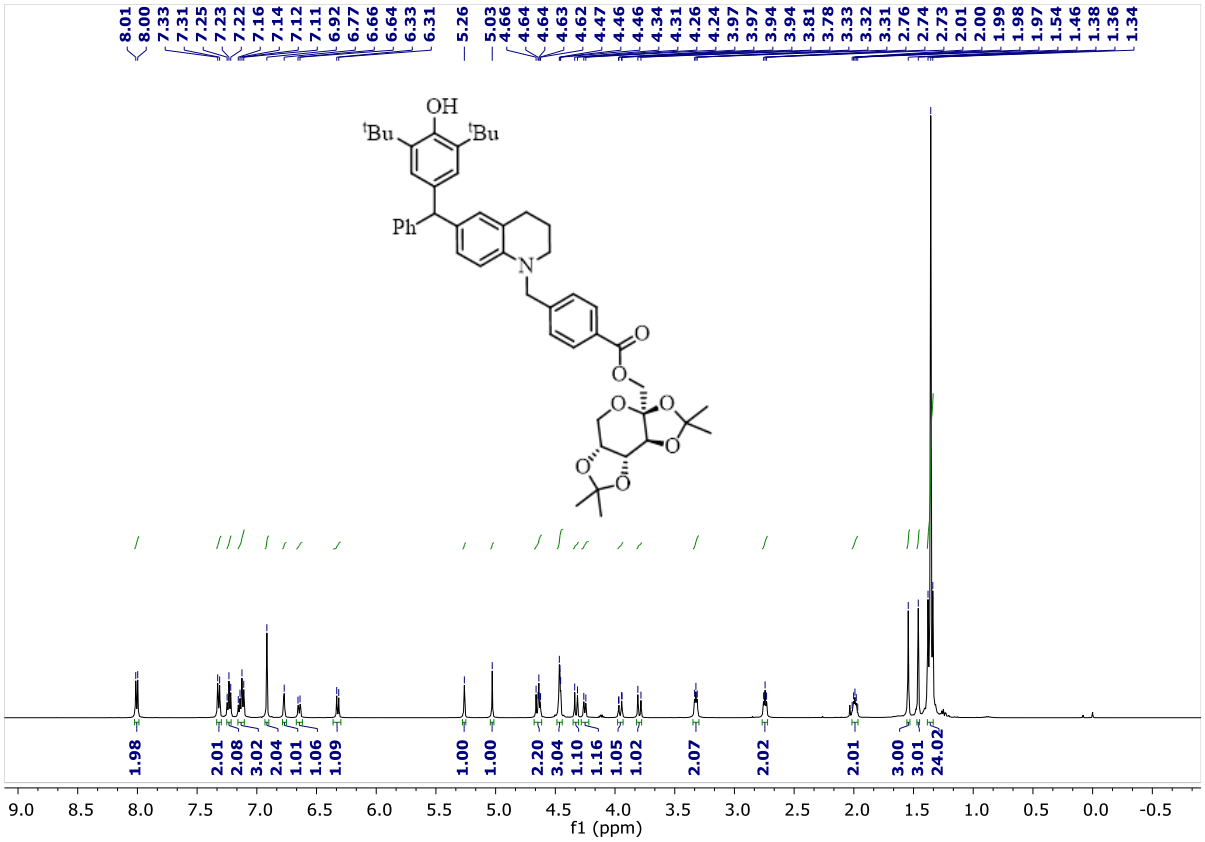


Figure S88: ^{1}H NMR Spectrum of **8a** ($CDCl_3$, 500 MHz, 298 K)

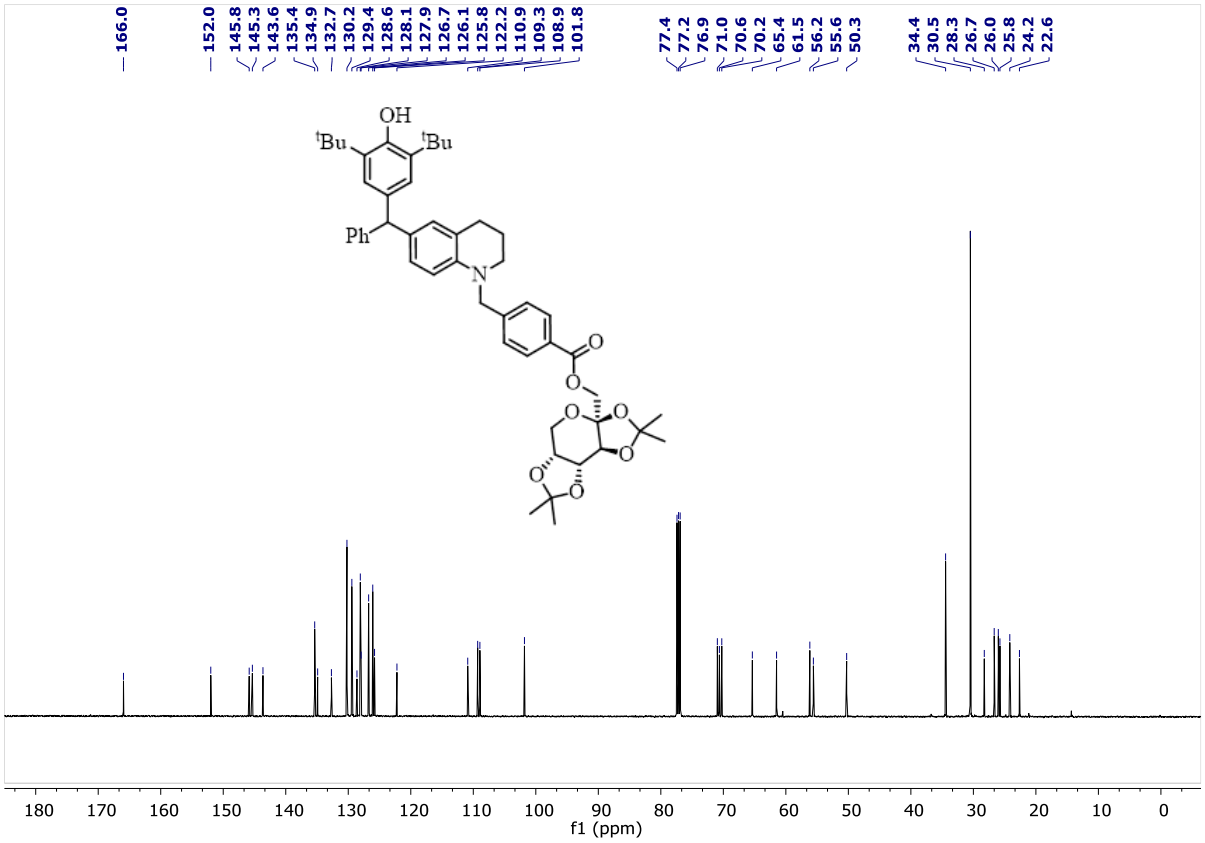


Figure S89: $^{13}C\{^{1}H\}$ NMR Spectrum of **8a** ($CDCl_3$, 126 MHz, 298 K)

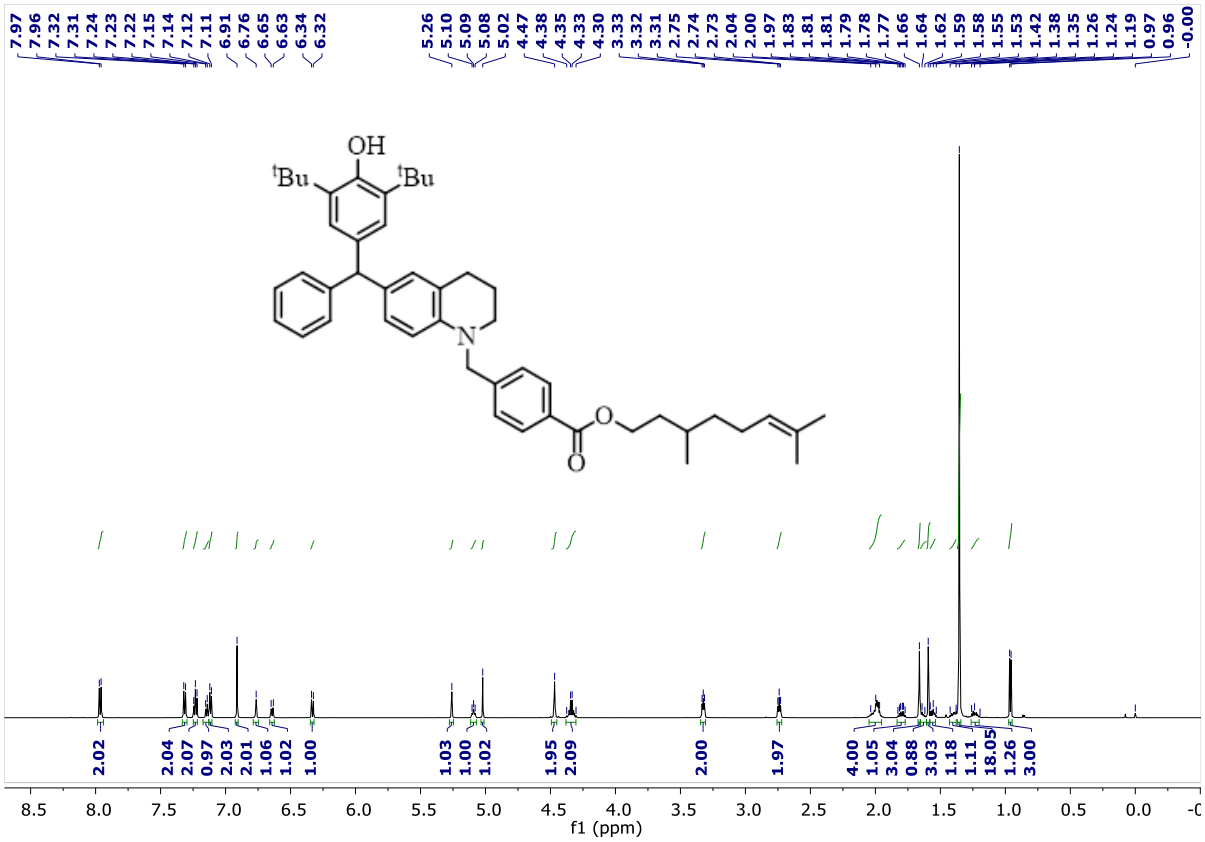


Figure S90: ^{1}H NMR Spectrum of **8b** ($CDCl_3$, 600 MHz, 298 K)

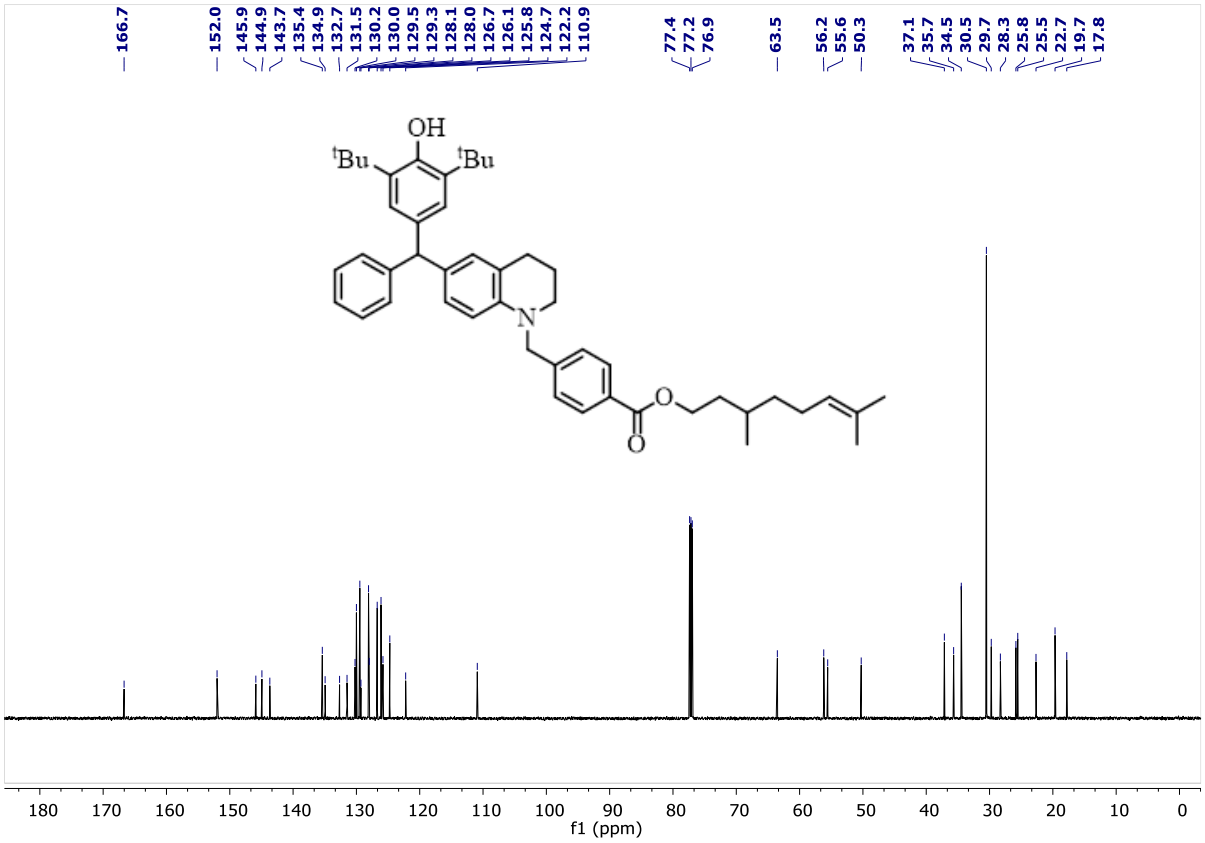


Figure S91: $^{13}C\{^{1}H\}$ NMR Spectrum of **8b** ($CDCl_3$, 151 MHz, 298 K)

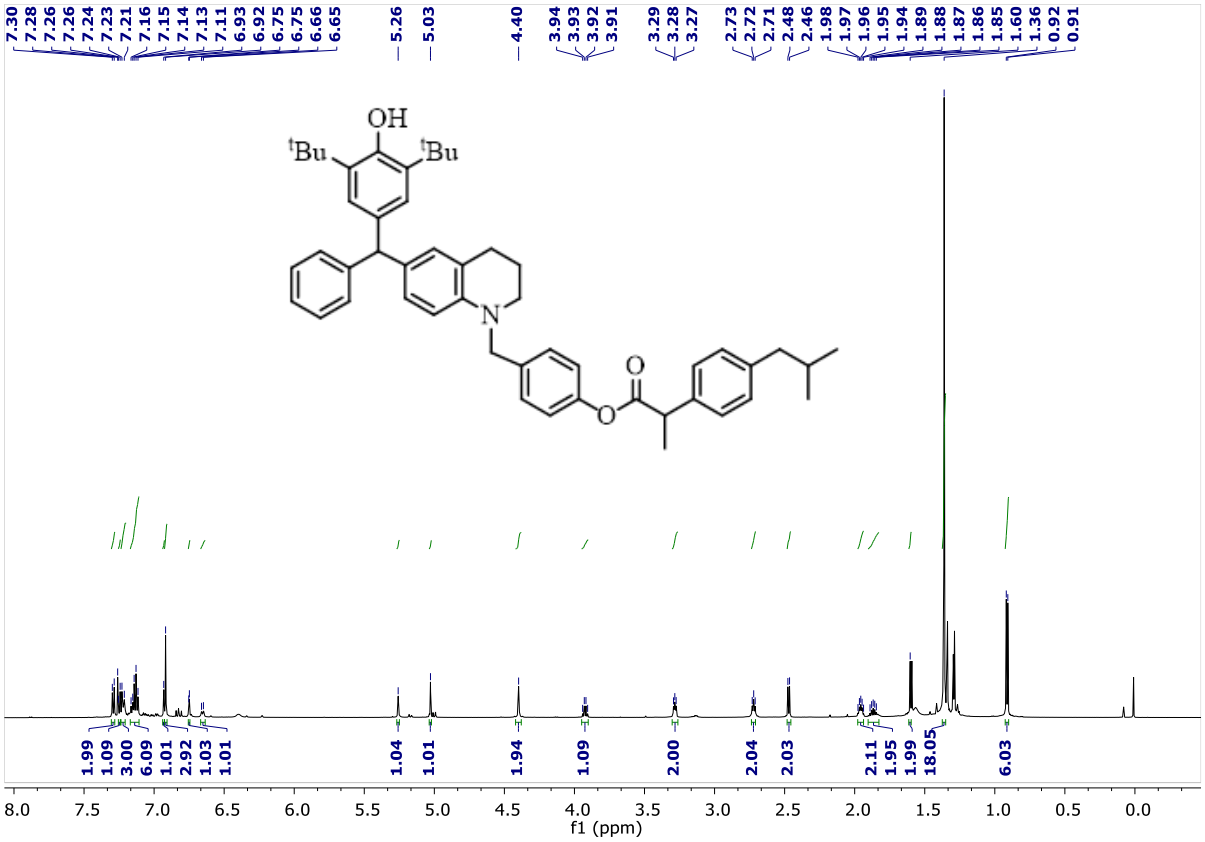


Figure S92: ^{1}H NMR Spectrum of **8c** ($CDCl_3$, 600 MHz, 298 K)

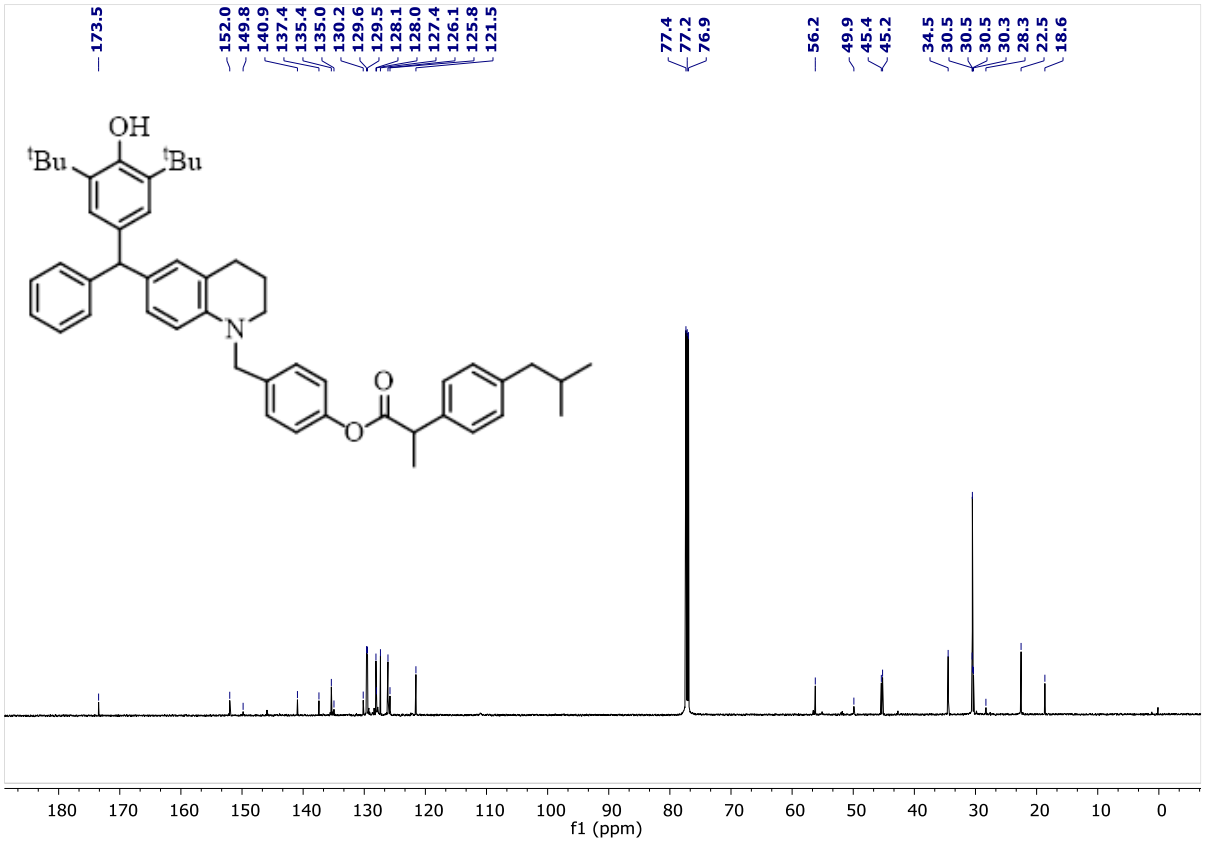


Figure S93: $^{13}C\{^{1}H\}$ NMR Spectrum of **8c** ($CDCl_3$, 151 MHz, 298 K)

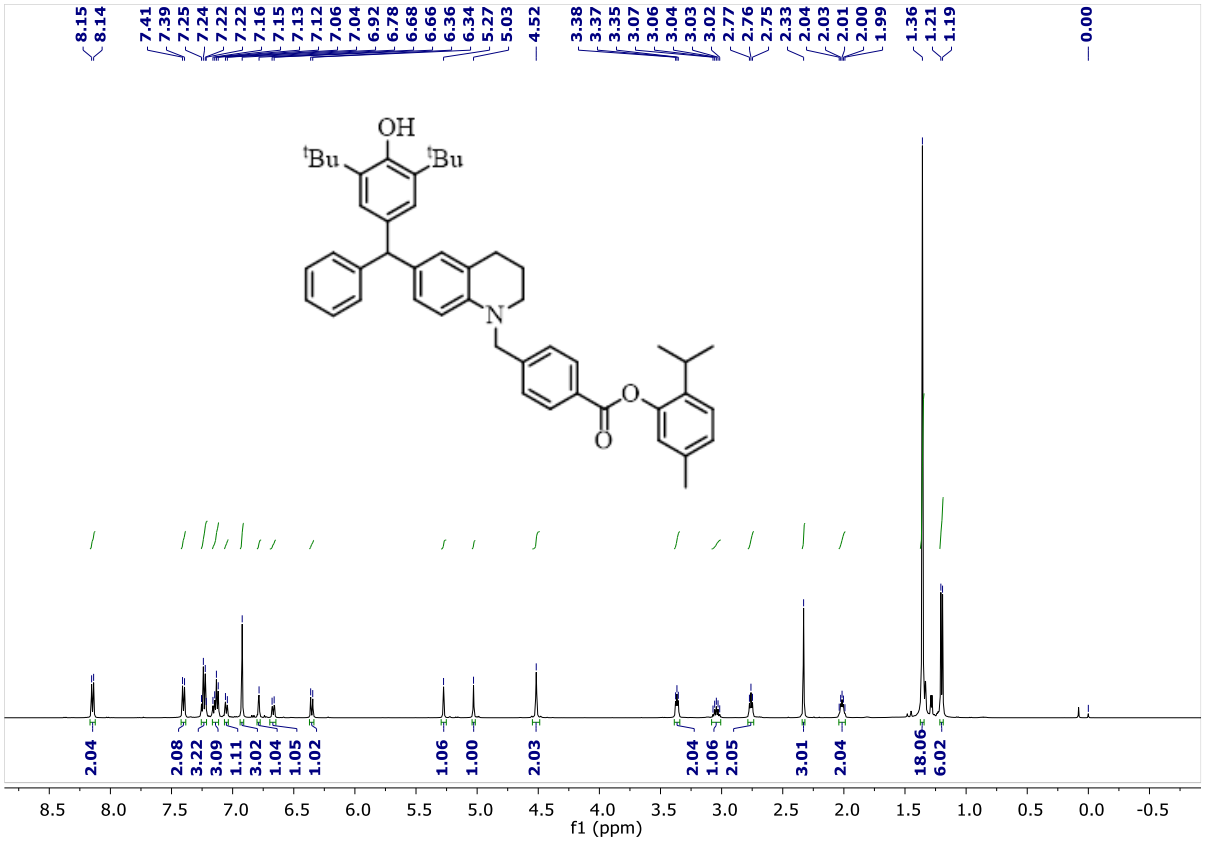


Figure S94: ^{1}H NMR Spectrum of **8d** ($CDCl_3$, 500 MHz, 298 K)

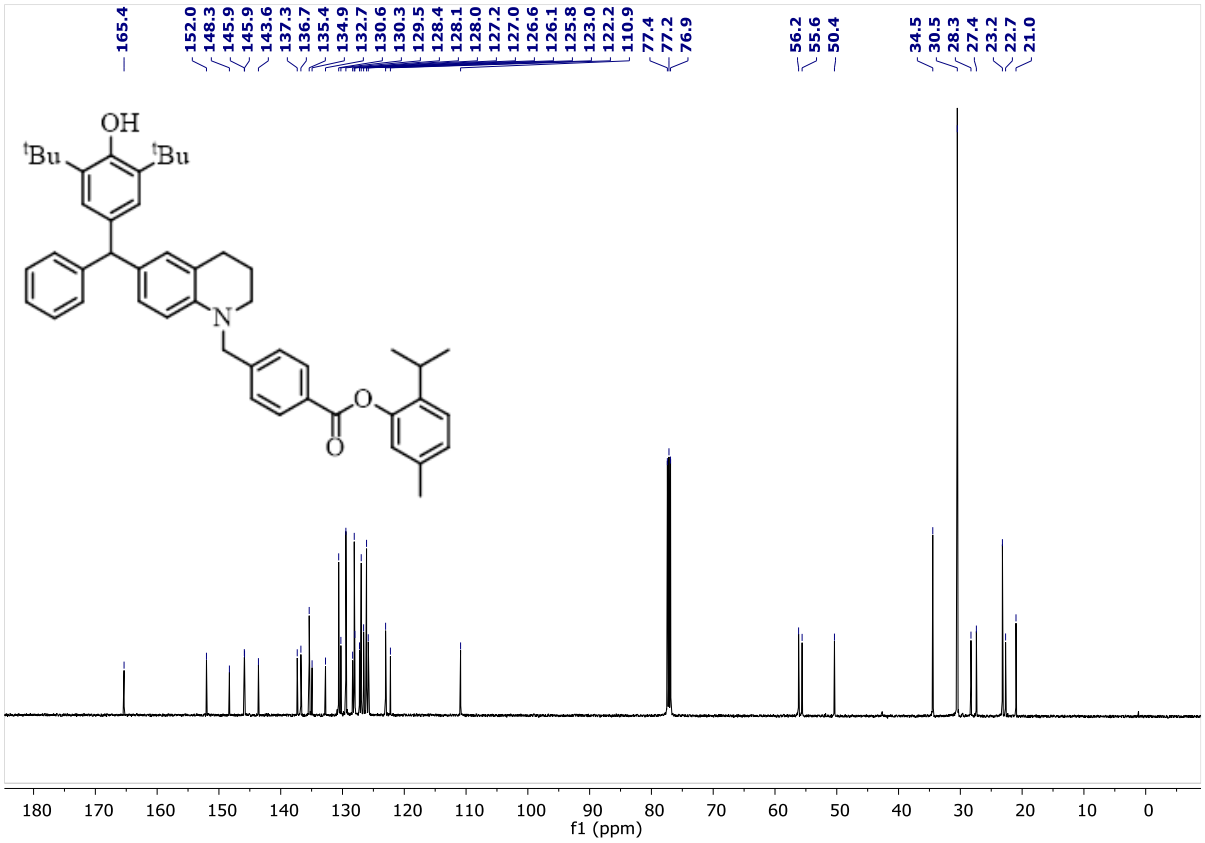


Figure S95: $^{13}C\{^{1}H\}$ NMR Spectrum of **8d** ($CDCl_3$, 126 MHz, 298 K)

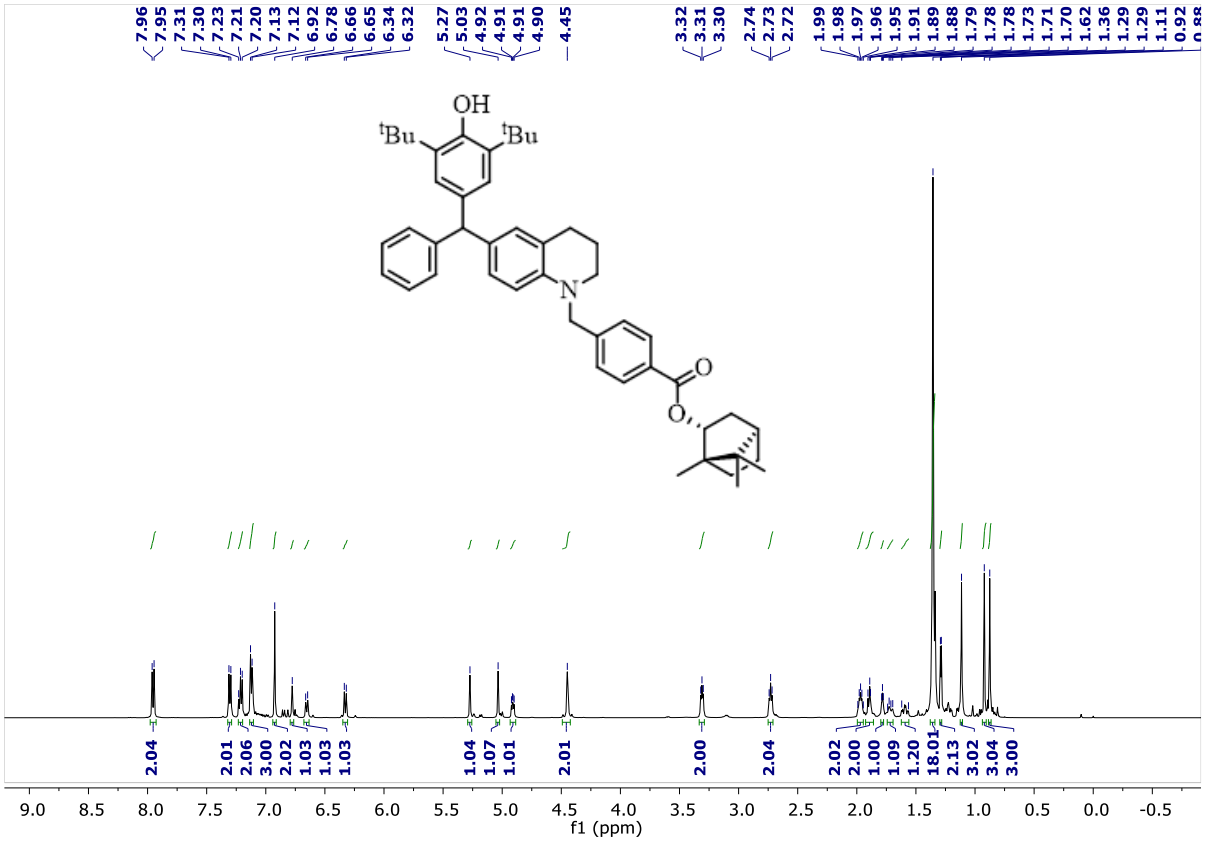


Figure S96: ^{1}H NMR Spectrum of **8e** ($CDCl_3$, 500 MHz, 298 K)

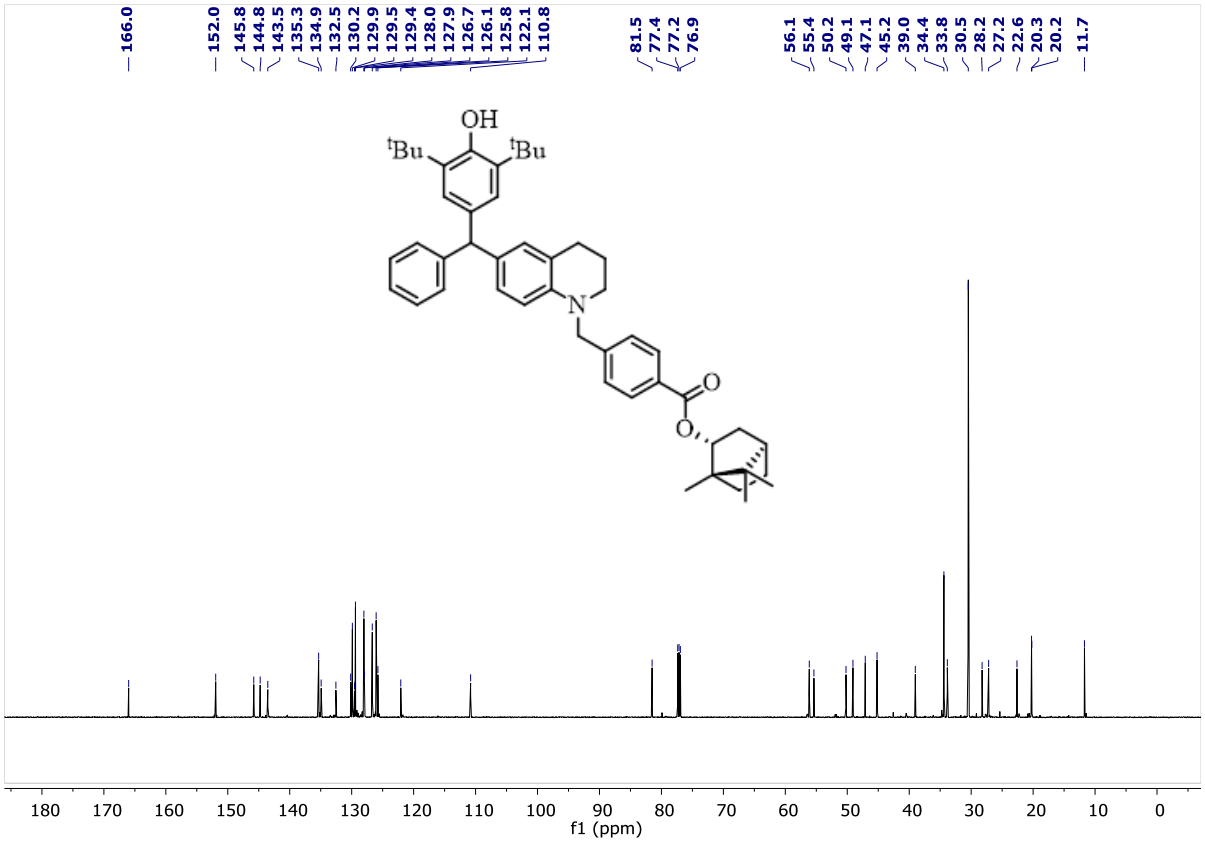


Figure S97: $^{13}C\{^{1}H\}$ NMR Spectrum of **8e** ($CDCl_3$, 151 MHz, 298 K)

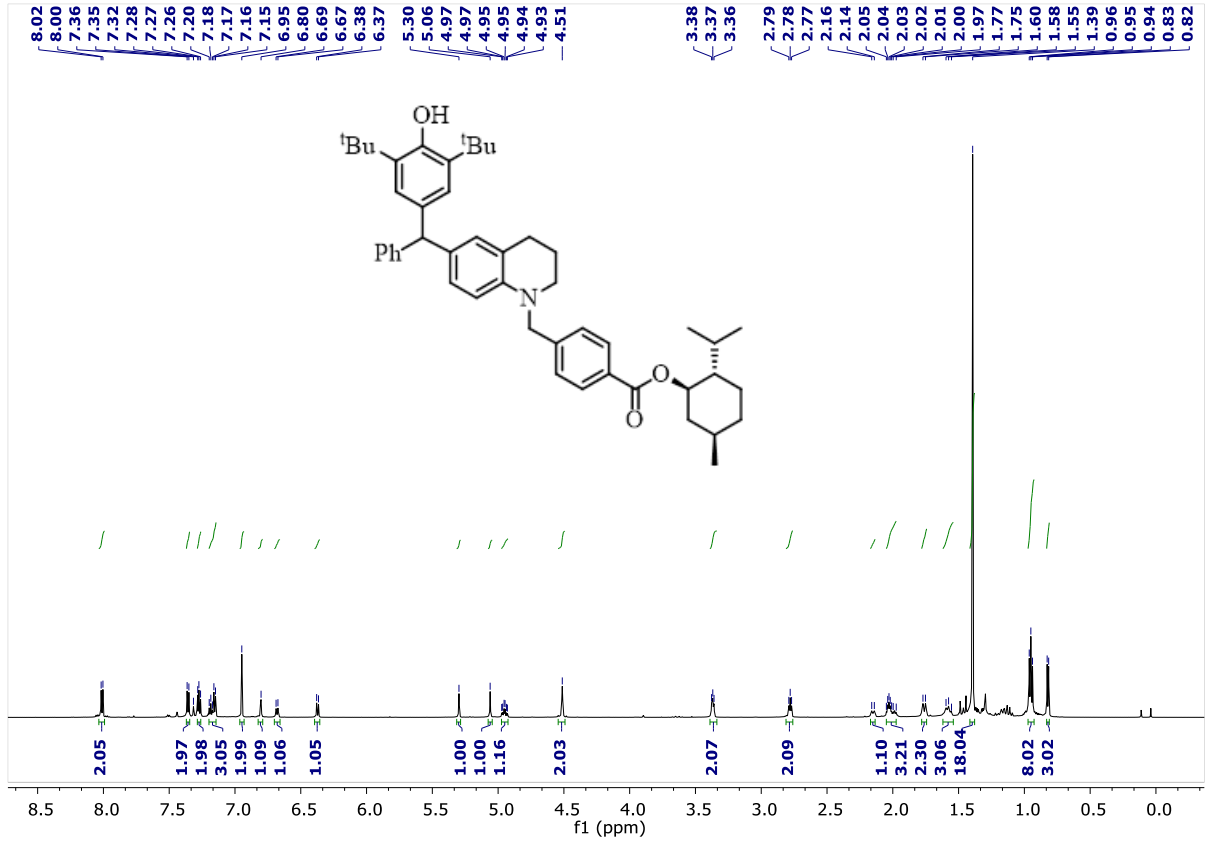


Figure S98: ^{1}H NMR Spectrum of **8f** ($CDCl_3$, 600 MHz, 298 K)

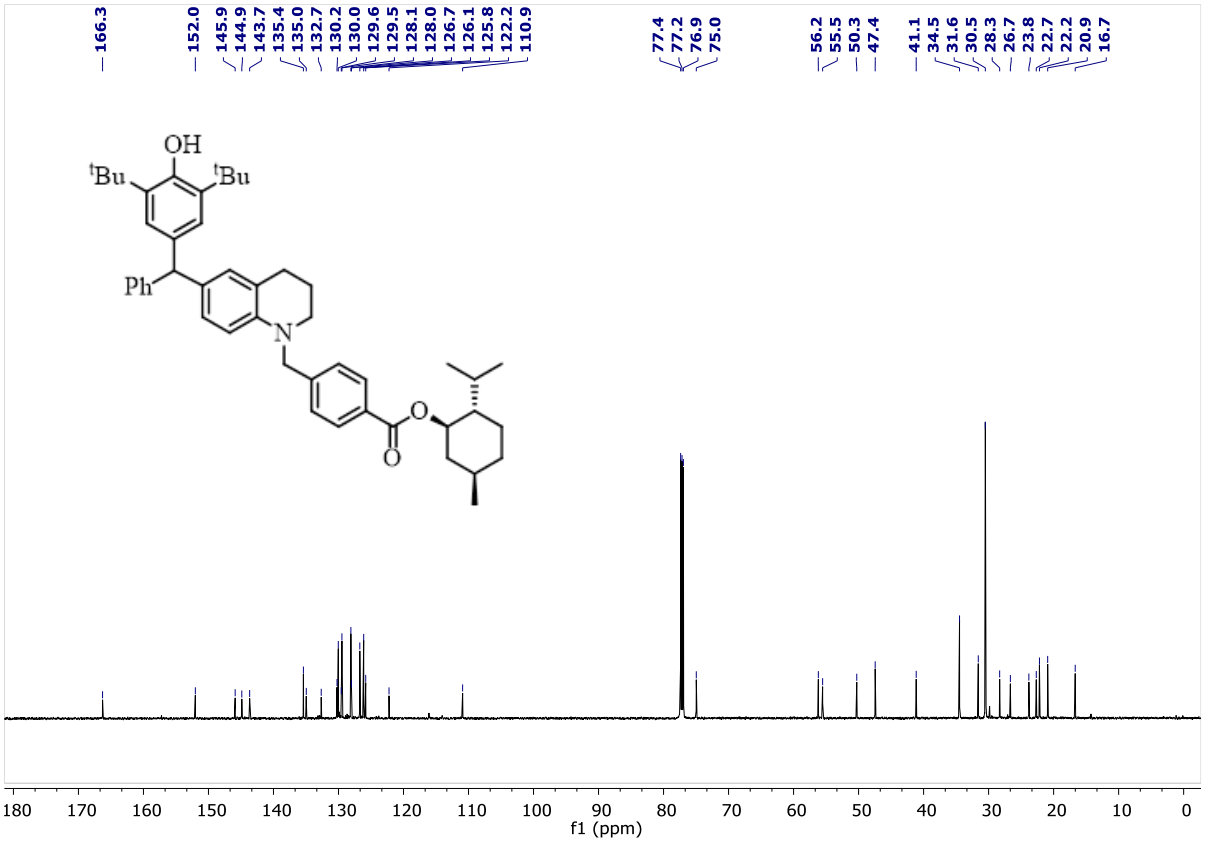


Figure S99: $^{13}C\{^{1}H\}$ NMR Spectrum of **8f** ($CDCl_3$, 151 MHz, 298 K)

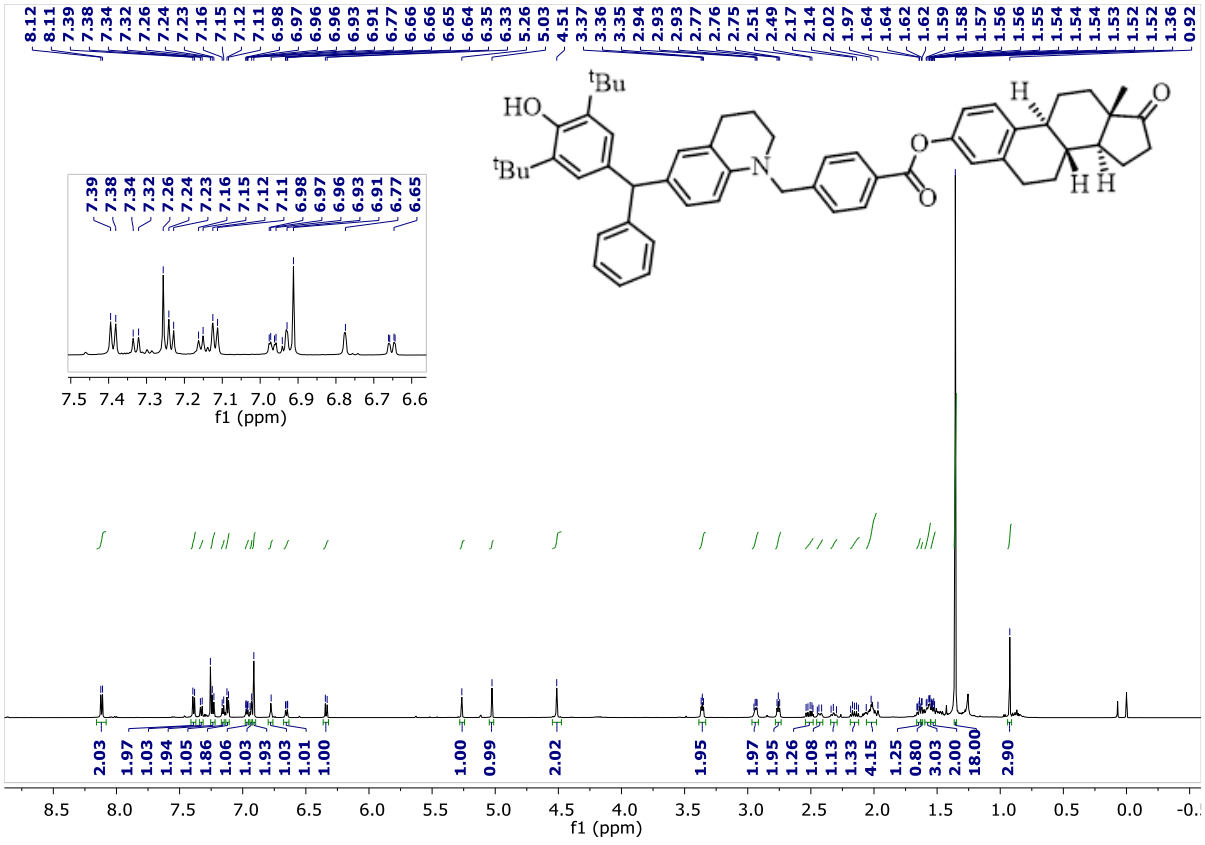


Figure S100: ^{1}H NMR Spectrum of **8g** ($CDCl_3$, 600 MHz, 298 K)

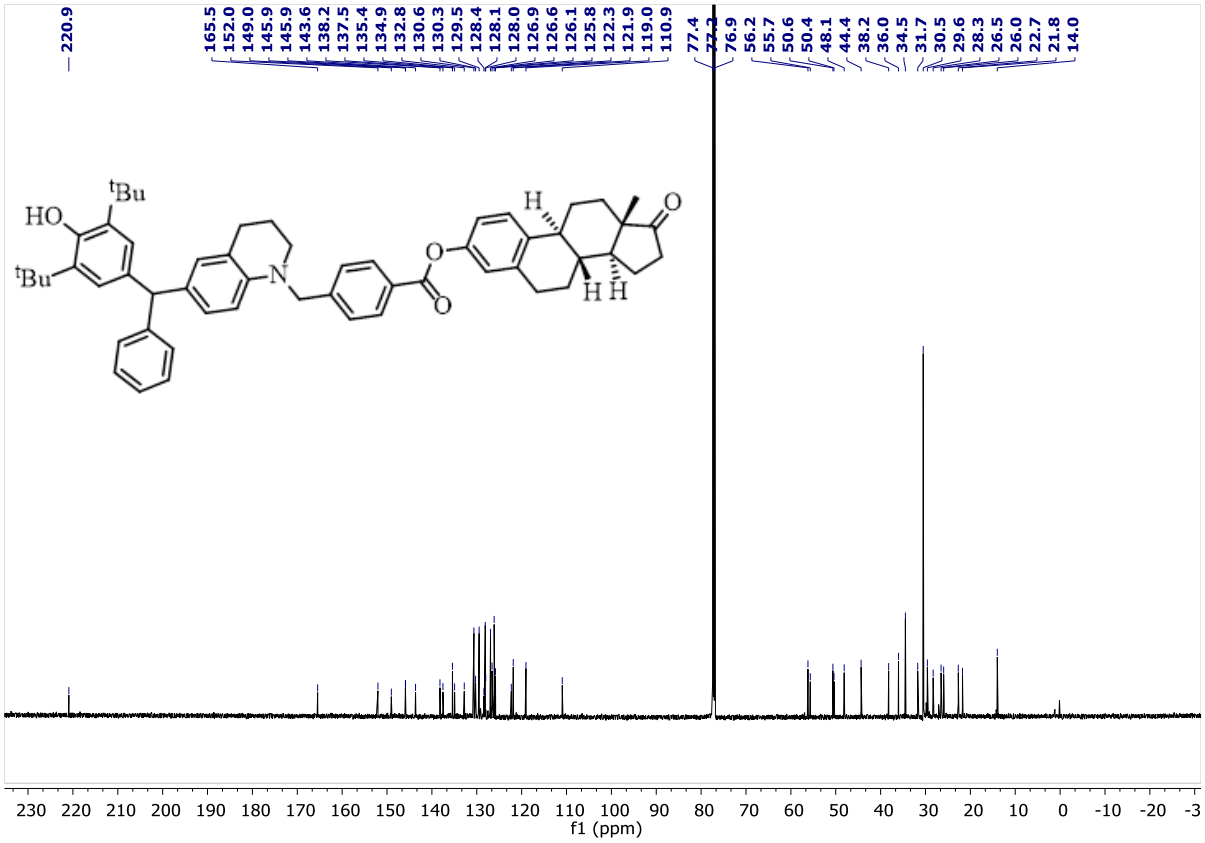


Figure S101: $^{13}C\{^{1}H\}$ NMR Spectrum of **8g** ($CDCl_3$, 151 MHz, 298 K)

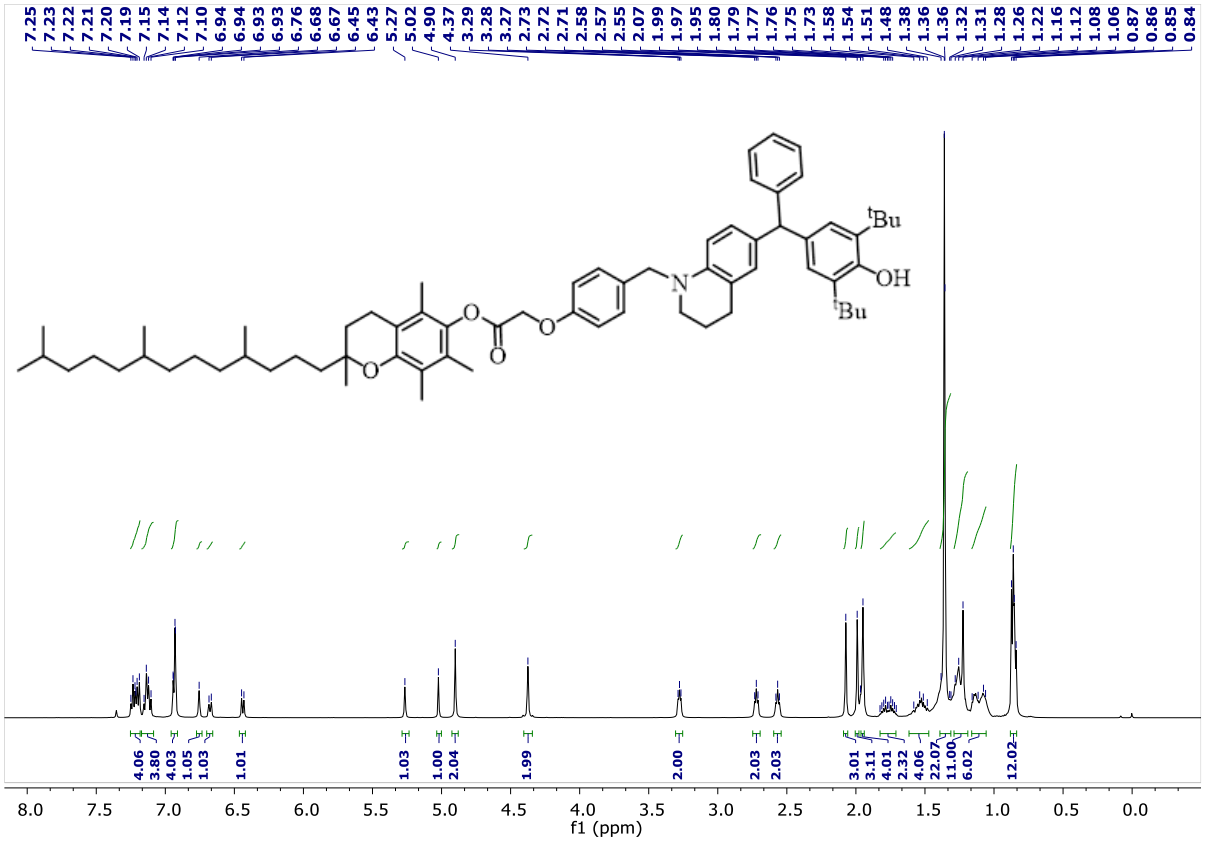


Figure S102: ^{1}H NMR Spectrum of **8h** ($CDCl_3$, 500 MHz, 298 K)

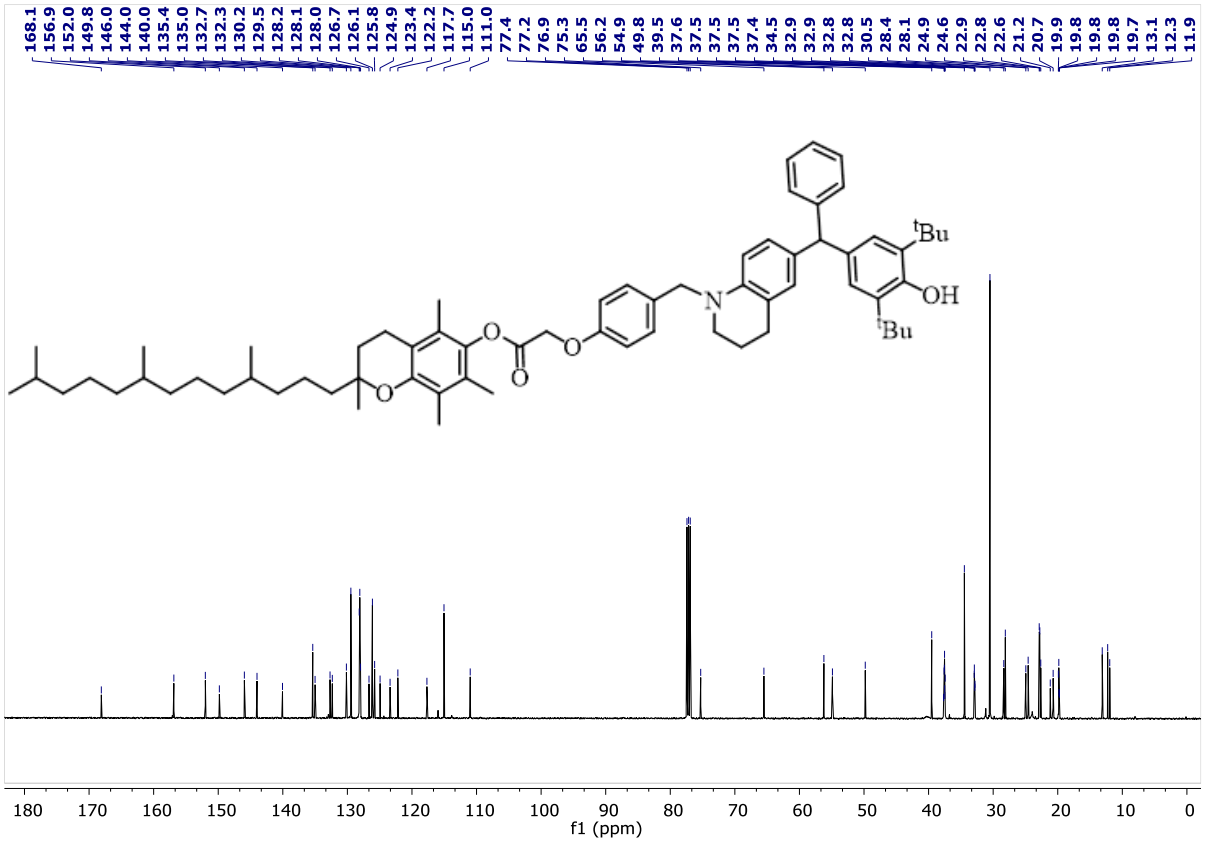


Figure S103: $^{13}C\{^{1}H\}$ NMR Spectrum of **8h** ($CDCl_3$, 126 MHz, 298 K)

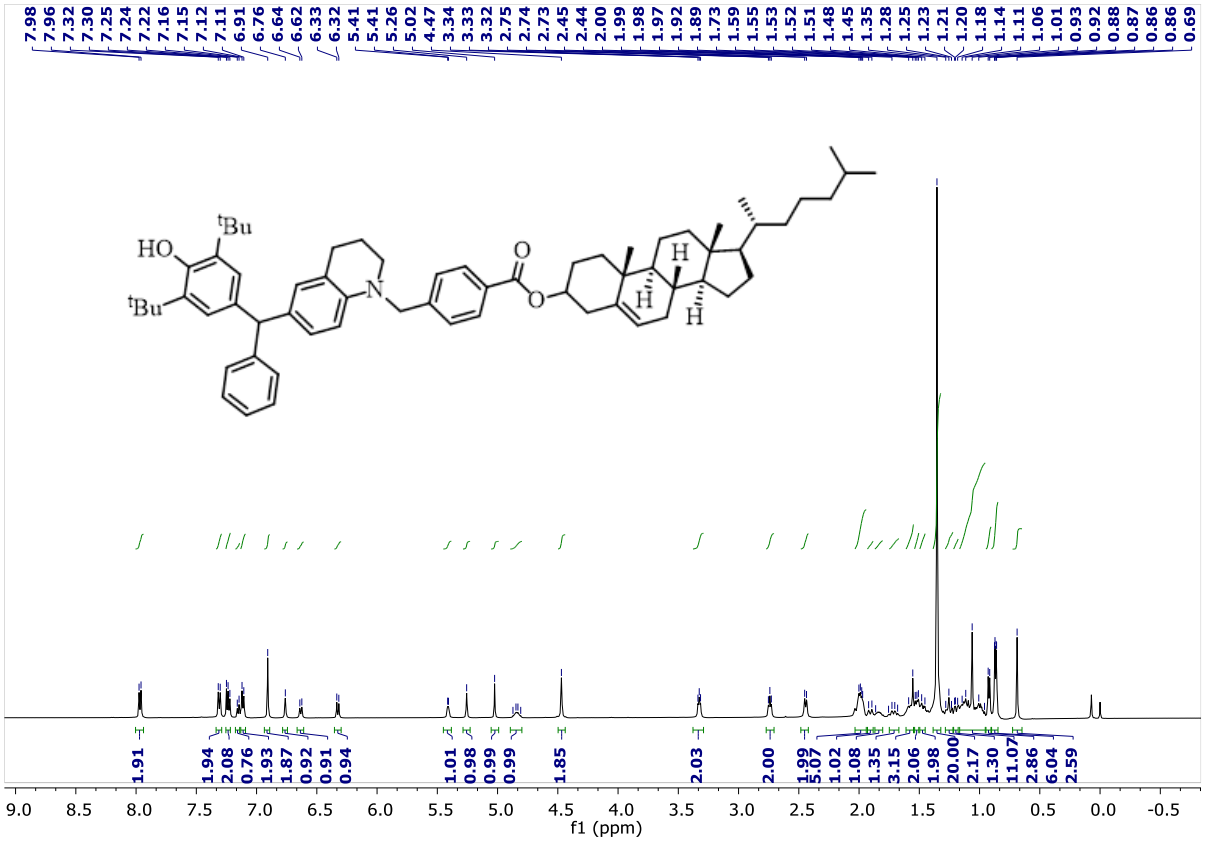


Figure S104: ^{1}H NMR Spectrum of **8i** ($CDCl_3$, 500 MHz, 298 K)

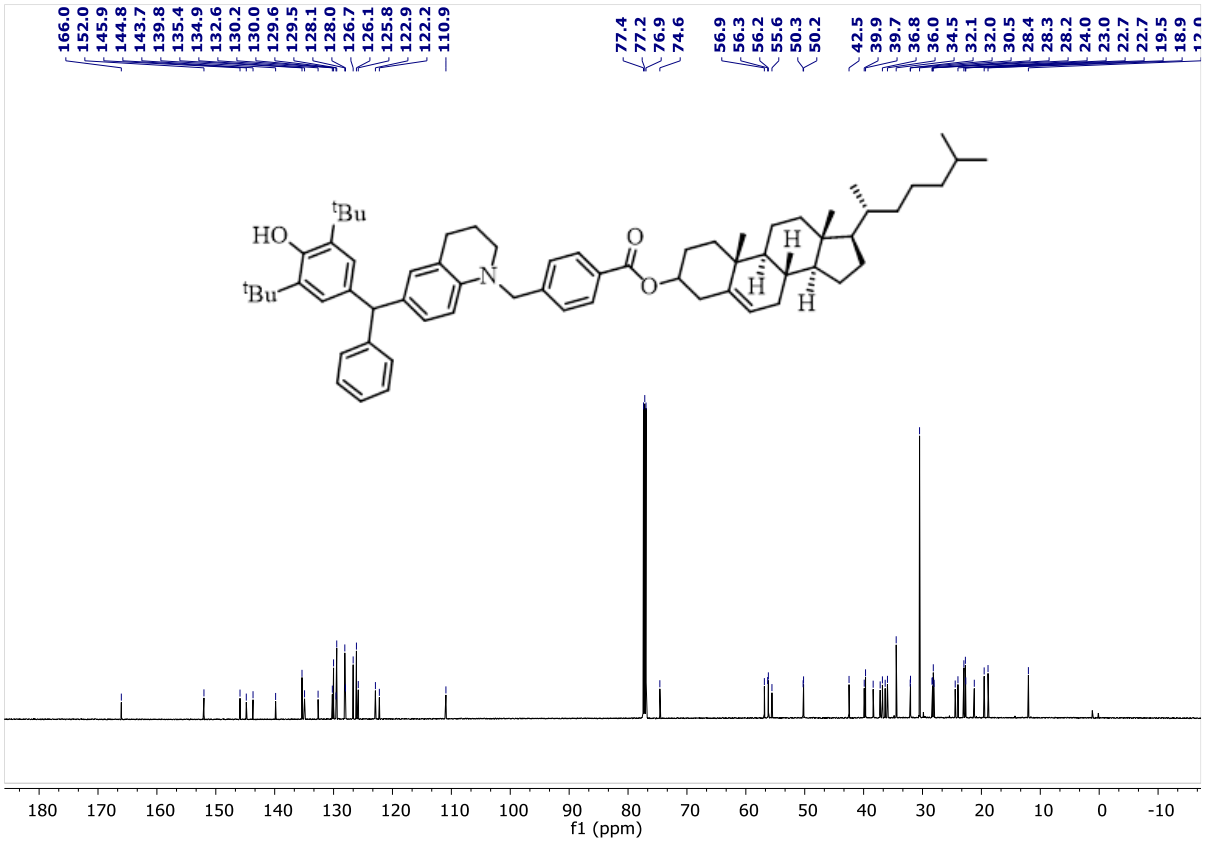


Figure S105: $^{13}C\{^{1}H\}$ NMR Spectrum of **8i** ($CDCl_3$, 151 MHz, 298 K)

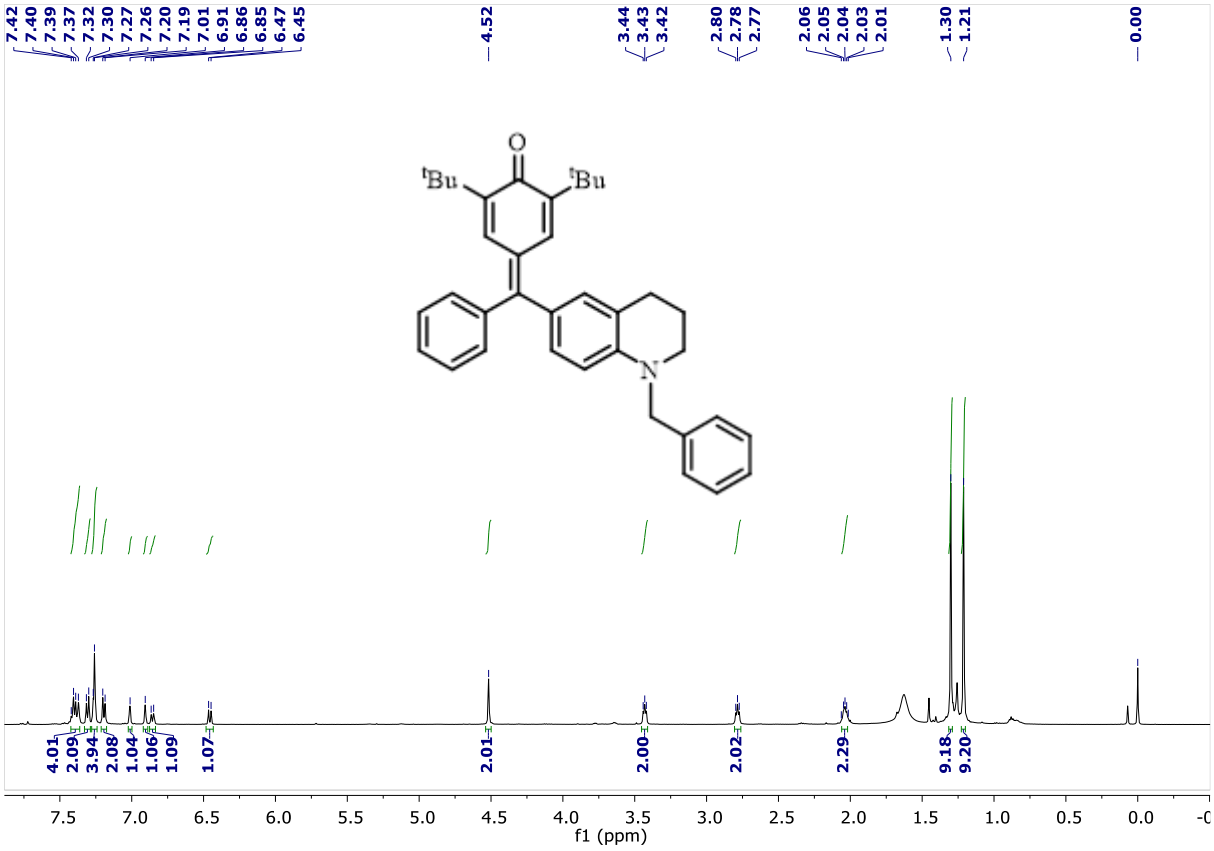


Figure S106: ^{1}H NMR Spectrum of **9** ($CDCl_3$, 500 MHz, 298 K)

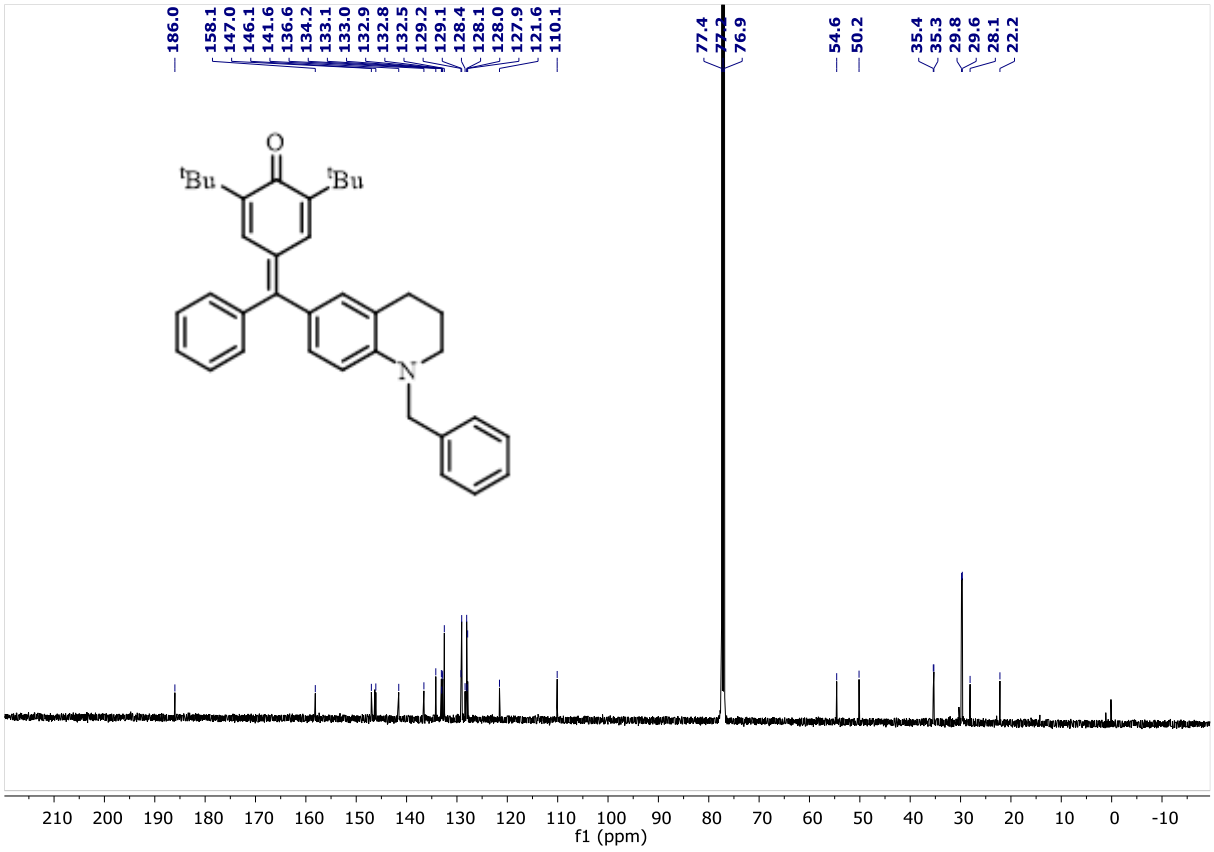


Figure S107: $^{13}C\{^{1}H\}$ NMR Spectrum of **9** ($CDCl_3$, 126 MHz, 298 K)

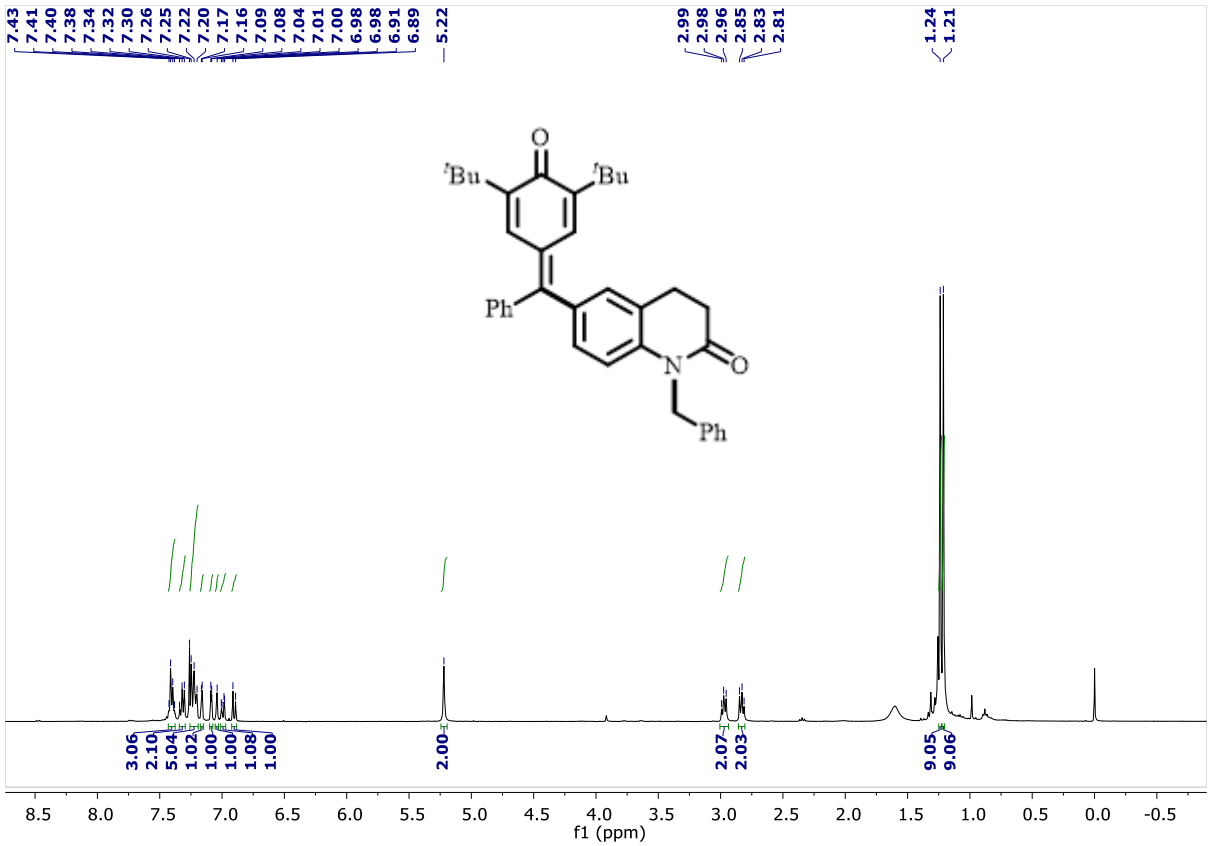


Figure S108: ^{1}H NMR Spectrum of **10** ($CDCl_3$, 400 MHz, 298 K)

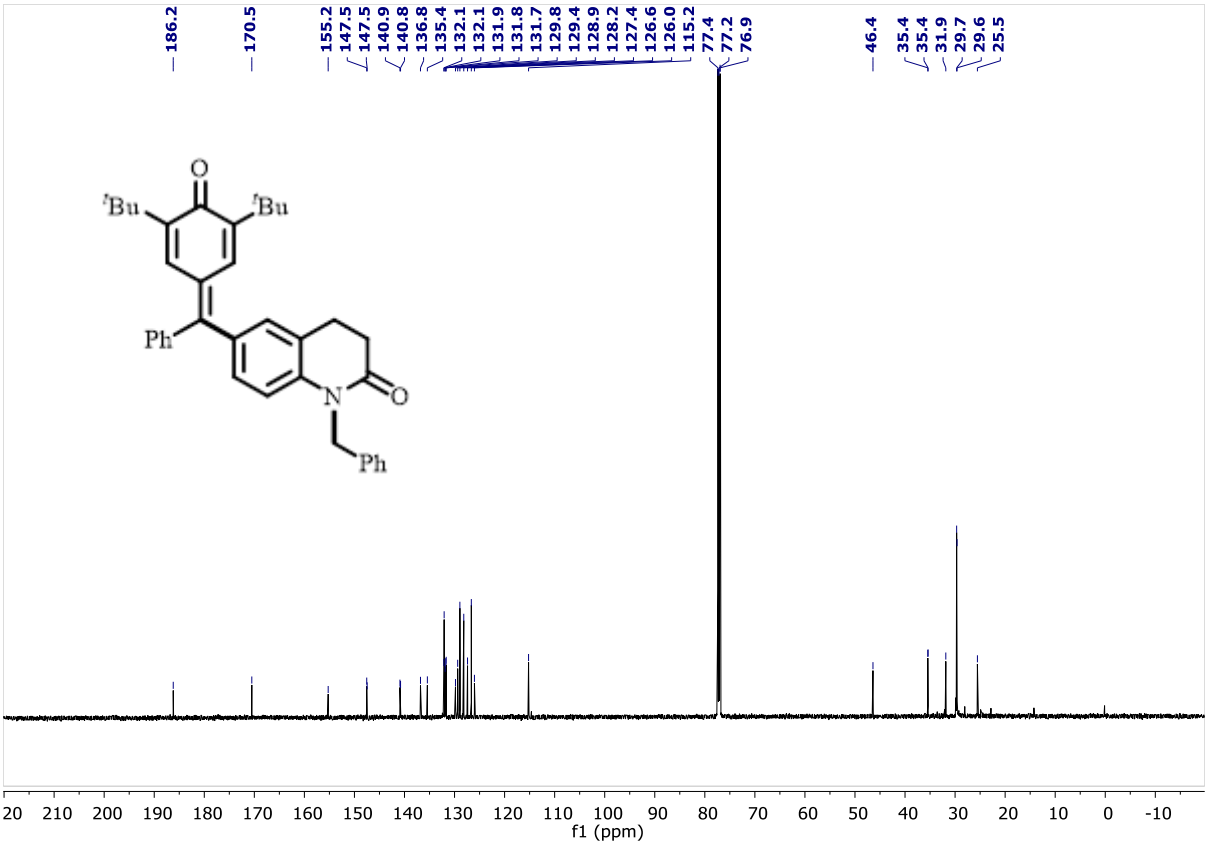


Figure S109: $^{13}C\{^{1}H\}$ NMR Spectrum of **10** ($CDCl_3$, 151 MHz, 298 K)

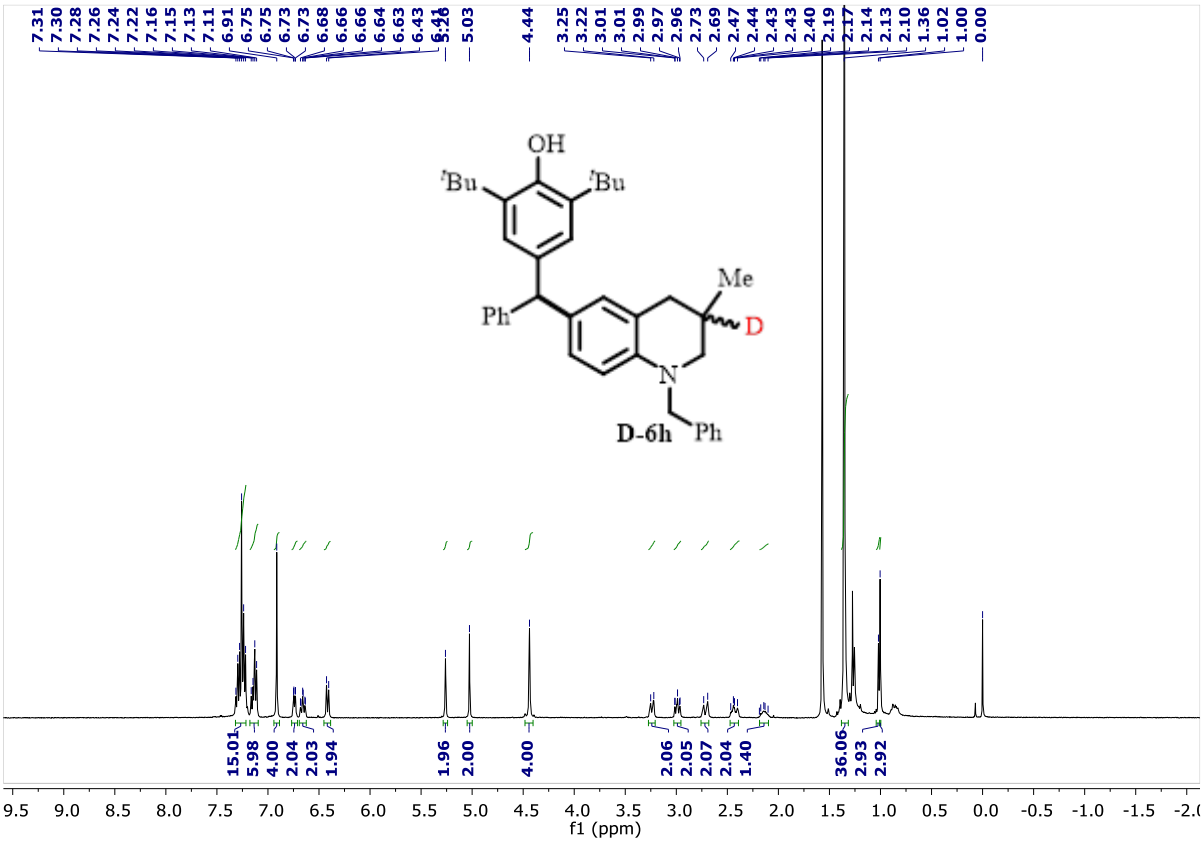


Figure S110: ^{1}H NMR Spectrum of **D-6h+ 6h** ($CDCl_3$, 400 MHz, 298 K)

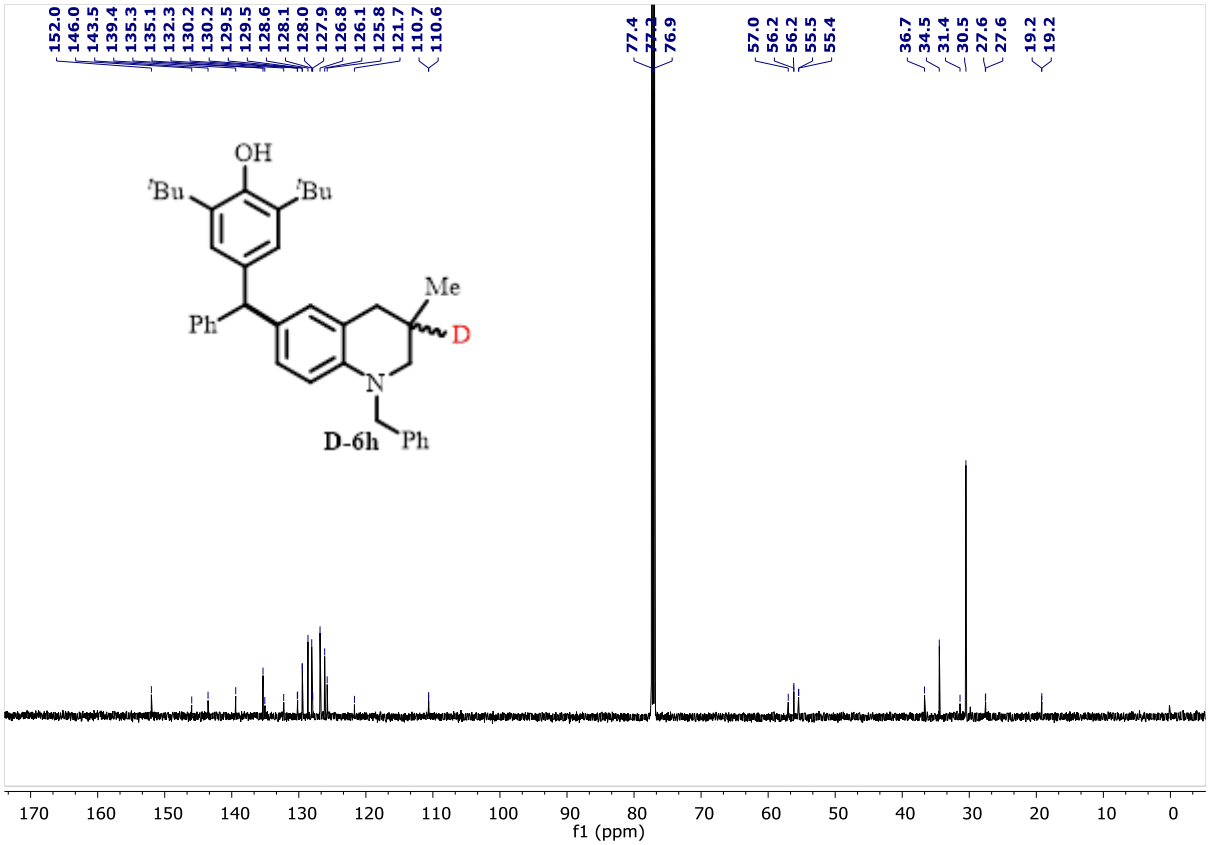


Figure S111: $^{13}C\{^{1}H\}$ NMR Spectrum of **D-6h + 6h** ($CDCl_3$, 151 MHz, 298 K)

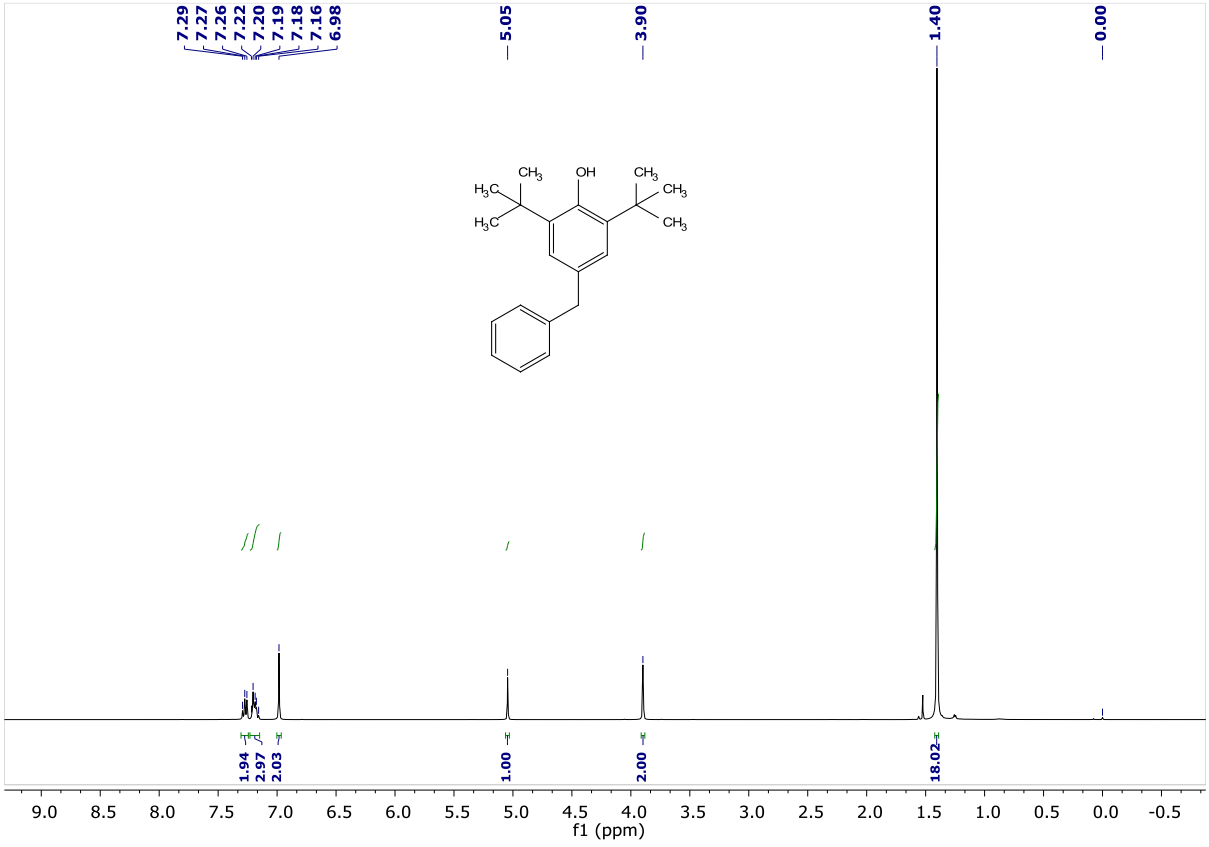


Figure S112: ^{1}H NMR Spectrum of **4a'** ($CDCl_3$, 400 MHz, 298 K).

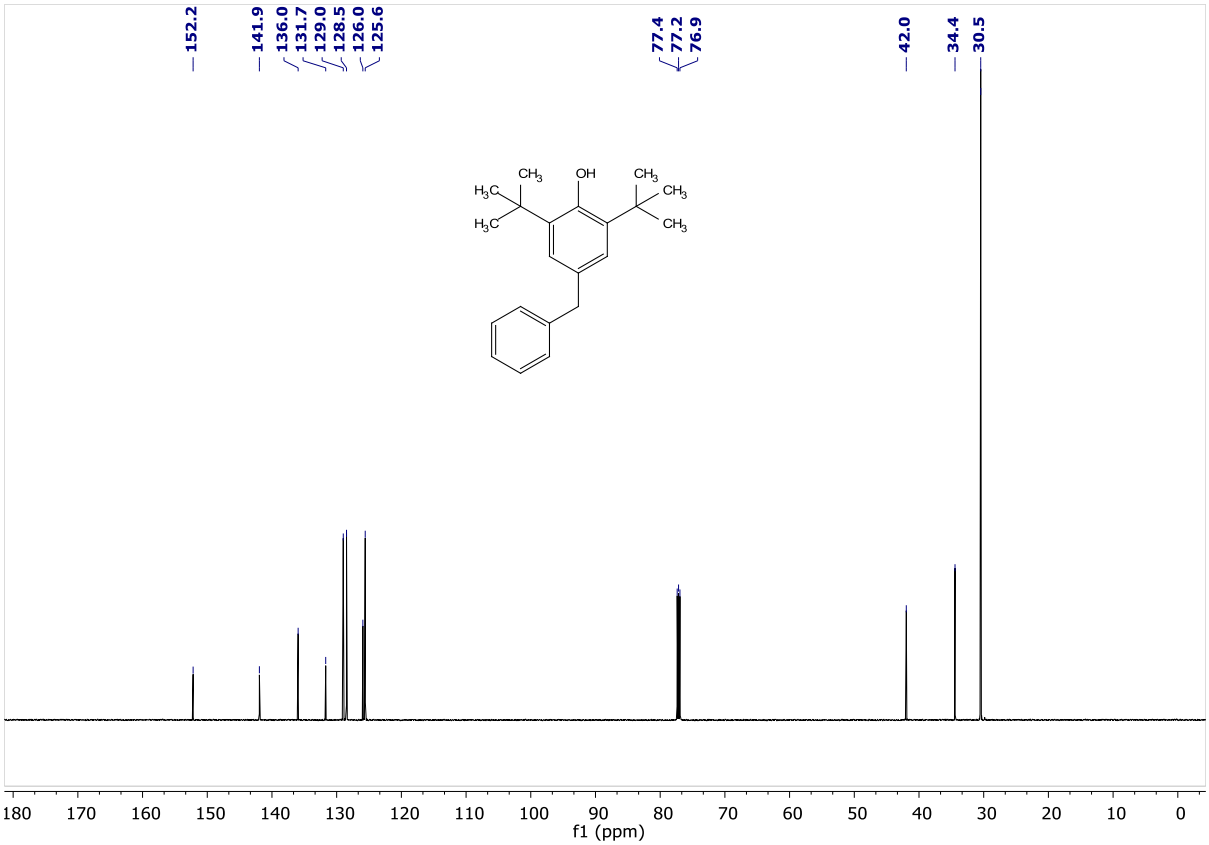


Figure S113: $^{13}C\{^{1}H\}$ NMR Spectrum of **4a'** ($CDCl_3$, 151 MHz, 298 K).

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