

## Supporting Information

# Chemoselective Transfer Hydrogenation and Deuteration of Substituted Quinolines using Hantzsch ester and D<sub>2</sub>O

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**1. General information:** All experiments were carried out in a 20 mL borosilicate glass vial purchased from India Mart. All reagents were obtained commercially from Aldrich, TCI, and BLD Pharma, and solvents were obtained from SRL Chemicals.

### Purification techniques Chromatography

Column chromatography was carried out using silica gel (60-120 and 100- 200 mesh). For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F254, 0.25 mm) were used and visualized with UV light and Ninhydrin strain solution (1.5 g ninhydrin 5 mL acetic acid 500 mL 95% ethanol) to detect NH<sub>2</sub> and NH group in the molecule during isolation.

### Analytical techniques

NMR spectra were recorded on a Bruker spectrometer at 400, 500, and 600 MHz (for <sup>1</sup>H-NMR), 100 MHz and 150 MHz (for <sup>13</sup>C-NMR), 376 MHz (for <sup>19</sup>F-NMR) using DMSO-d<sub>6</sub>, D<sub>2</sub>O, and CDCl<sub>3</sub> as solvents. For <sup>1</sup>H-NMR, data were reported: Chemical shifts ( $\delta$ ) are quoted in ppm downfield of tetramethyl silane (0.00 ppm). The residual solvent signals were used as references for <sup>1</sup>H and <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>:  $\delta$ H = 7.26 ppm,  $\delta$ C = 77.16 ppm; DMSO-d<sub>6</sub>:  $\delta$ H = 2.50 ppm,  $\delta$ C = 39.52 ppm; CD<sub>3</sub>OD:  $\delta$ H = 4.87 ppm,  $\delta$ C = 49.00 ppm; acetone-d<sub>6</sub>:  $\delta$ H = 2.05 ppm,  $\delta$ C = 206.26 ppm). <sup>19</sup>F NMR spectra were calibrated using absolute referencing to the <sup>1</sup>H NMR spectrum, as suggested by IUPAC Coupling constants (J) are quoted in Hz and rounded to the nearest 0.1 Hz. The multiplicity abbreviations used (or combinations thereof) are: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes.

### 2. General reaction procedure:



**Figure S1.** Borosilicate glass clear 20 ml Reaction vial

An oven-dried 20 mL glass vial equipped with a magnetic stir bar was charged with the substrate (0.5 mmol), Hantzsch ester (1.25 mmol, 2.5 equiv., 316.25 mg), dichloromethane (DCM, 1.5 mL), and water (1.5 mL). Acid (0.5 equiv., 0.022 mL) was then added slowly to the reaction mixture via micropipette. The vial was sealed and stirred at room temperature for 2 to 6 hours, depending on the substrate. Upon completion of the reaction, the mixture was diluted with ethyl acetate and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was then purified by column chromatography on silica gel (100-200 and 60-120 mesh) using a hexane/ethyl acetate gradient. The purified compound was subsequently submitted for further characterization.

### 3. General procedure for gram-scale synthesis experiment:

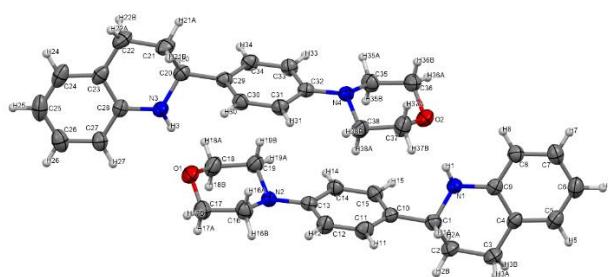
An oven-dried, 500 mL round-bottom flask with a star-shaped magnetic stir bar was charged with substrate (5g), (1 equiv.), Hantzsch ester (2.5 equiv.), dichloromethane (DCM, 35 mL), and water (35 mL). Acid (0.5 equiv.) was then added to the reaction mixture via micropipette. The round bottom flask was sealed and stirred at room temperature for 6 hours, depending on the substrate. Upon completion of the reaction, the mixture was diluted with ethyl acetate and extracted with ethyl acetate ( $6 \times 10$  mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was then purified by column chromatography on silica gel (100-200) using ethyl acetate/ hexane as a solvent gradient.



**Figure S2.** Gram scale experimental setup with a 500 ml round-bottom flask.

### 4. Crystallographic study of compound 1b:

The crystal was obtained by the crystallization of the compound in the presence of methanol and chloroform as solvents at room temperature using a slow evaporation technique. A suitable crystal was selected, and a nylon loop was used on a Bruker APEX-IV Photon II diffractometer. The crystal was kept at 298 K during data collection. Using Olex2<sup>[2]</sup>, the structure was solved with the XT<sup>[3]</sup> structure solution program using Intrinsic Phasing and refined with the XL<sup>[4]</sup> refinement package using Least Squares minimization. Data collection, structure refinement parameters, and crystallographic data for compound **(1b)** are given in **Table S1**. The CCDC number of compound **(1b)** is **CCDC 2428954**.



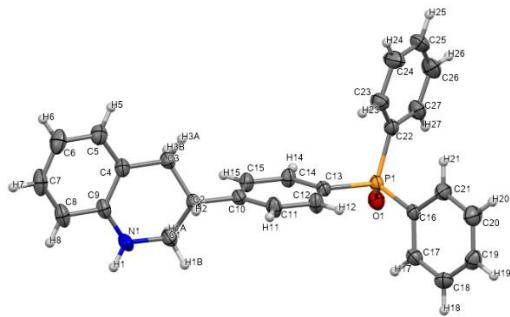
**Figure S3.** ORTEP view of complex compound (1b)

**Table S1.** Crystal data and structure refinement of a complex compound.

Compound	Substrate
Empirical formula	C <sub>38</sub> H <sub>44</sub> N <sub>4</sub> O <sub>2</sub>
Formula weight	588.77
Temperature/K	298
Crystal system	orthorhombic
Space group	Pna <sub>2</sub> <sub>1</sub>
a/Å	17.6633(15)
b/Å	8.3253(8)
c/Å	21.863(2)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	3215.0(5)
Z	4
Pcalc g/cm <sup>3</sup>	1.216
μ/mm-1	0.076
F(000)	1264.0
Crystal size/mm <sup>3</sup>	0.06 × 0.05 × 0.02
Radiation	MoKα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	4.612 to 54.362
Index ranges	-22 ≤ h ≤ 22, -10 ≤ k ≤ 10, -28 ≤ l ≤ 23
Reflections collected	34030
Independent reflections	6247 [R <sub>int</sub> = 0.0775, R <sub>sigma</sub> = 0.0590]
Data/restraints/parameters	6247/1/406
Goodness-of-fit on F <sup>2</sup>	1.027
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0475, wR <sub>2</sub> = 0.1054
Final R indexes [all data]	R <sub>1</sub> = 0.1097, wR <sub>2</sub> = 0.1381
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.16

### Crystallographic study of compound 40:

The crystal was obtained by the crystallization of the compound in the presence of methanol and chloroform as solvents at room temperature using a slow evaporation technique. A suitable crystal was selected, and a nylon loop was used on a Bruker APEX-IV Photon II diffractometer. The crystal was kept at 298 K during data collection. Using Olex2<sup>[2]</sup>, the structure was solved with the XT<sup>[3]</sup> structure solution program using Intrinsic Phasing and refined with the XL<sup>[4]</sup> refinement package using Least Squares minimization. Data collection, structure refinement parameters, and crystallographic data for compound (40) are given in **Table S2**. The CCDC number of the compound (40) is **CCDC 2428955**.



**Figure S4.** ORTEP view of complex compound 40.

**Table S2.** Crystal data and structure refinement of a complex compound.

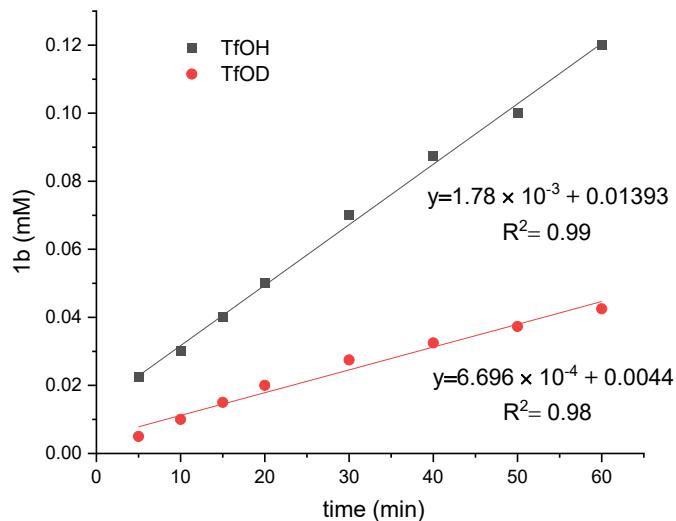
Compound	Substrate
Empirical formula	C <sub>27.5</sub> H <sub>27</sub> NO <sub>2</sub> P
Formula weight	434.47
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	8.5764(5)
b/Å	9.5269(7)
c/Å	15.3568(11)
α/°	100.161(2)
β/°	100.588(2)
γ/°	102.767(2)
Volume/Å <sup>3</sup>	1171.67(14)
Z	2
Pcalc g/cm <sup>3</sup>	1.232
μ/mm-1	0.141
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.06 × 0.05 × 0.04
Radiation	MoKα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	4.5 to 54.378
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19
Reflections collected	23914
Independent reflections	5206 [R <sub>int</sub> = 0.0552, R <sub>sigma</sub> = 0.0428]
Data/restraints/parameters	5206/0/272
Goodness-of-fit on F <sup>2</sup>	1.049
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0446, wR <sub>2</sub> = 0.1119
Final R indexes [all data]	R <sub>1</sub> = 0.0643, wR <sub>2</sub> = 0.1235
Largest diff. peak/hole / e Å <sup>-3</sup>	0.31/-0.26

## 5. Mechanistic studies:

### (1) Determination of kinetic isotopic effect (KIE)

#### KIE by using initial rates:

Deuterium kinetic isotope effects (DKIE) using the initial rate (~50% conversion of the substrate). Data points before ~50% conversion were subjected to linear regression analysis.



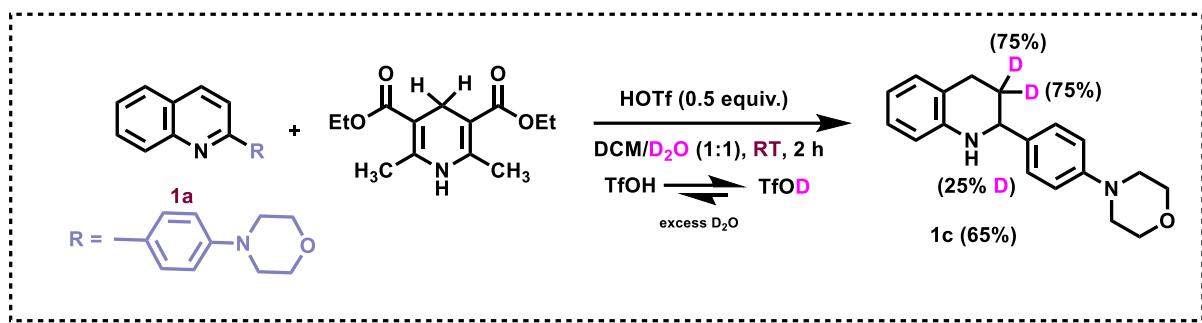
**Figure S5.** Kinetic isotopic experiment.

An oven-dried 5 mL glass vial equipped with a magnetic stir bar was charged with the substrate 1a (0.25 mmol), Hantzsch ester (0.625 mmol, 2.5 equiv., 158 mg), dichloromethane (DCM, 0.5 mL), and water (0.5 mL) (**Scheme S1, A**). TfOH (18.75 mg, 0.5 equiv., 0.011 mL) was then added slowly to the reaction mixture via micropipette. The crude reaction mixture at different time intervals was analyzed by NMR using 1,3,5-trimethoxybenzene as an internal reference.

In a separate reaction vial (**Scheme S1, B**), TfOD (18.75 mg, 0.5 equiv., 0.011 mL) was used in place of TfOH and D<sub>2</sub>O (0.5 mL) added instead of water. The Deuterium kinetic isotope effect (KIE) was calculated as  $k_{\text{TfOH}}/k_{\text{TfOD}} = 2.65$ .

#### (b) Deuterium labelling experiments

**Reaction procedure (A):** An oven-dried 20 mL glass vial equipped with a magnetic stir bar was charged with the substrate (0.5 mmol), Hantzsch ester (1.25 mmol, 2.5 equiv., 316.25 mg), dichloromethane (DCM, 1.5 mL), and D<sub>2</sub>O (1.5 mL) (**Scheme S1**). TfOH (37.5 mg, 0.5 equiv., 0.022 mL) was then added slowly to the reaction mixture via micropipette. The vial was closed and stirred at room temperature for 2 hours. Upon completion of the reaction, the mixture was diluted with ethyl acetate and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. After evaporating the solvent through a rotary evaporator, the crude mixture was purified using 100-200 mesh silica gel column chromatography to obtain the pure desired product **1c** (white crystalline solid). The isolated yield is **65% (95 mg)**.



**Scheme S1.** Deuterium labelling experiment with D<sub>2</sub>O as a solvent

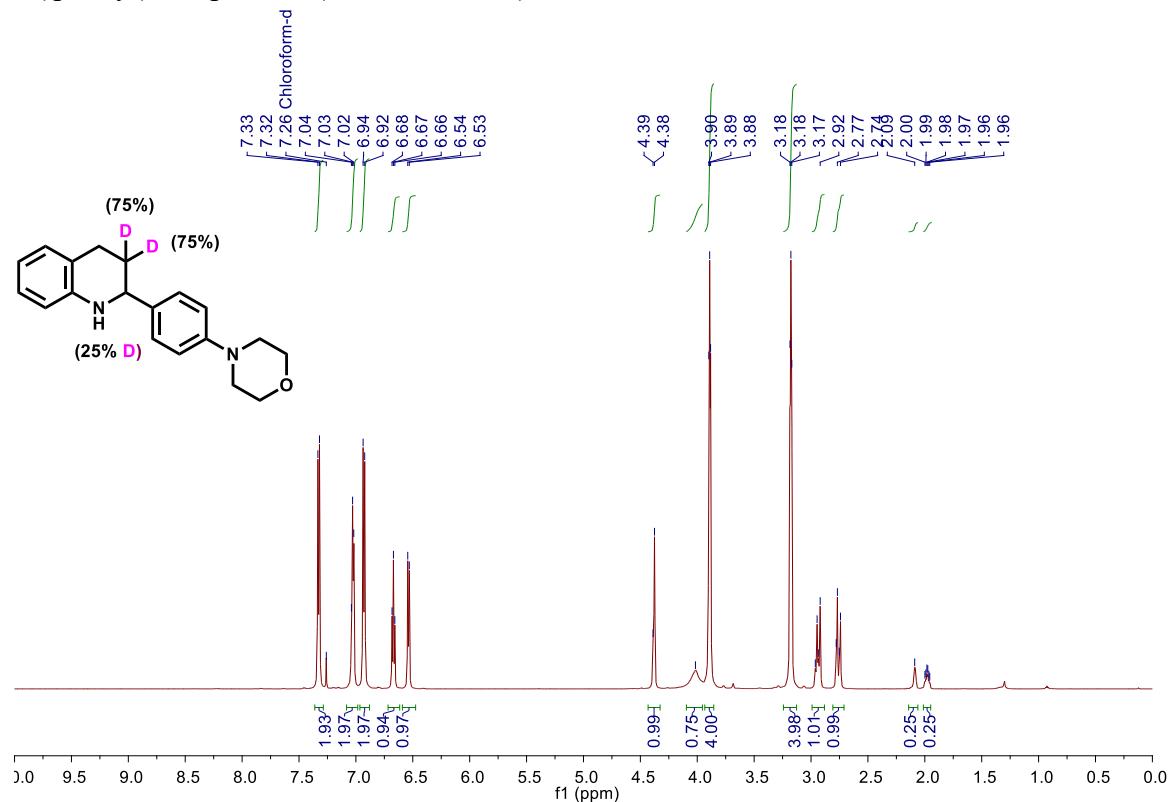
**$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.33 (d,  $J = 8.4$  Hz, 2H), 7.03 (t,  $J = 6.1$  Hz, 2H), 6.93 (d,  $J = 8.5$  Hz, 2H), 6.67 (t,  $J = 7.3$  Hz, 1H), 6.54 (d,  $J = 8.2$  Hz, 1H), 4.38 (d,  $J = 7.4$  Hz, 1H), 4.02 (s, 0.75H), 3.93 – 3.84 (m, 4H), 3.24 – 3.10 (m, 4H), 2.94 (dd,  $J = 16.0, 9.7$  Hz, 0.25H), 2.76 (dd,  $J = 16.3, 6.3$  Hz, 0.25H).

**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):**  $\delta$  150.71, 144.92, 136.23, 129.34, 127.44, 126.88, 120.90, 117.08, 115.76, 113.97, 66.96, 55.59, 49.46, 26.41.

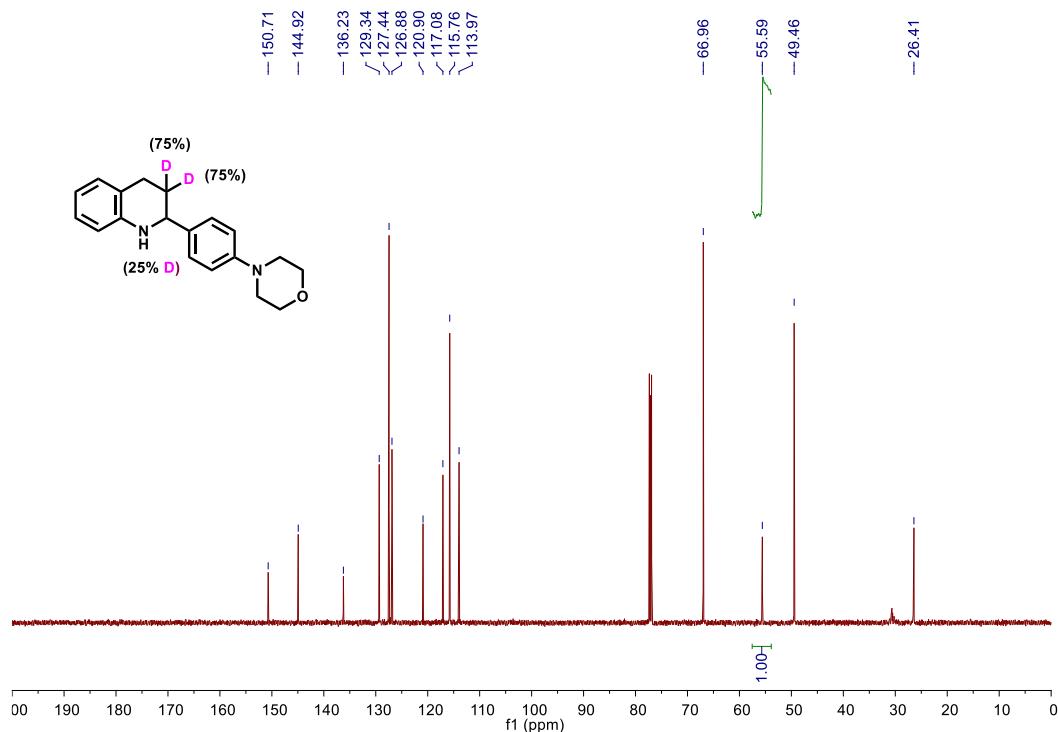
<sup>2</sup>H NMR (92 MHz, CDCl<sub>3</sub>): δ 2.09, 1.98.

**HRMS** (ESI) m/z:  $(M+H)^+$  Calcd for  $C_{19}H_{21}D_2N_2O$  297.1930; Found 297.1934

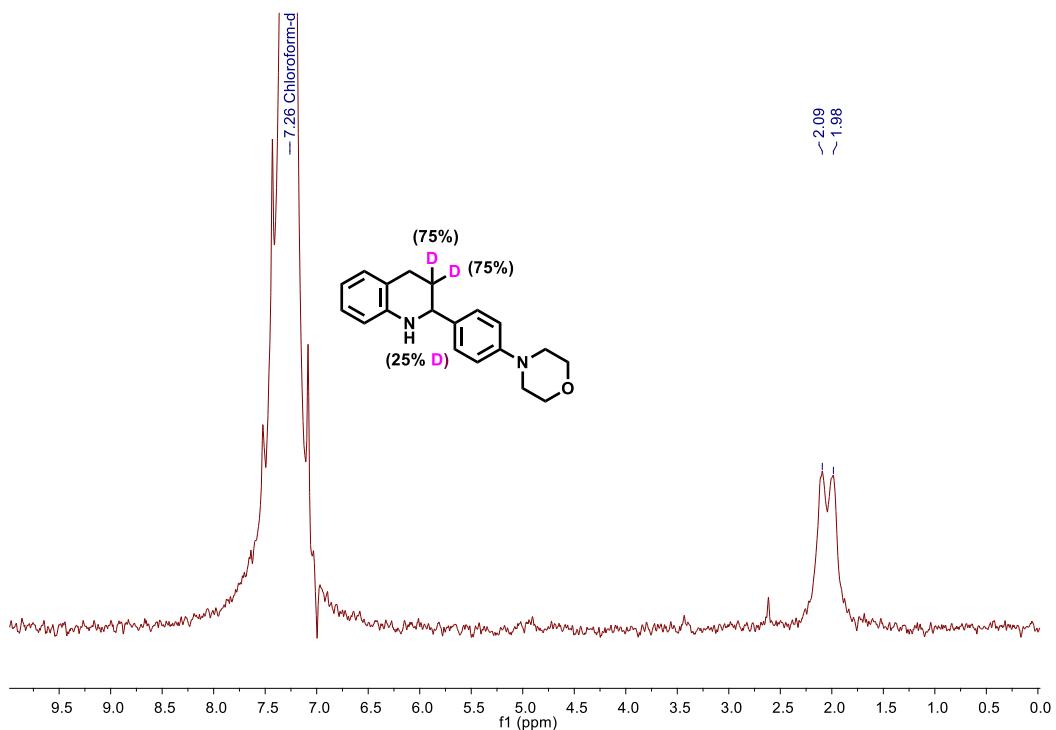
**Figure S6.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) (4-(4-(1,2,3,4-tetrahydroquinolin-2-yl-3,3-d2)phenyl) morpholine (**1c**, Scheme S1)



**Figure S6.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) (4-(4-(1,2,3,4-tetrahydroquinolin-2-yl-3,3-d2)phenyl) morpholine (**1c**, Scheme S1)

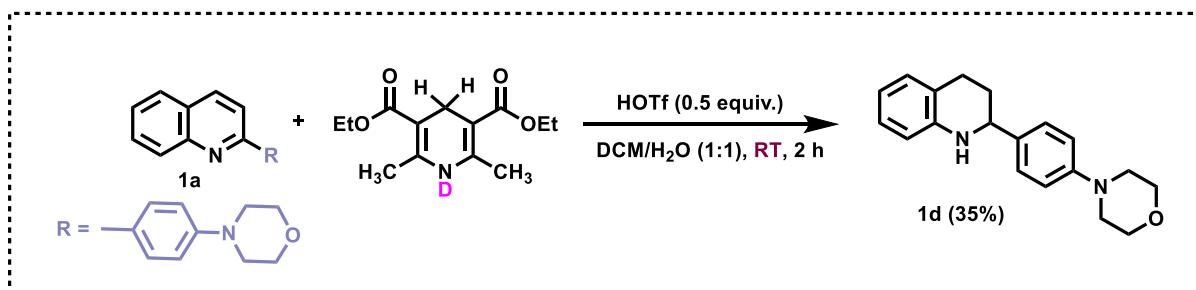


**Figure S7.**  $^2\text{H}$  NMR (92 MHz,  $\text{CDCl}_3$ ) (4-(4-(1,2,3,4-tetrahydroquinolin-2-yl-3,3-d2)phenyl) morpholine (**1c**, Scheme S1)



**Reaction procedure (B):** An oven-dried 20 mL glass vial equipped with a magnetic stir bar was charged with the substrate (0.5 mmol), Hantzsch ester-d (1.25 mmol, 2.5 equiv., 316.25

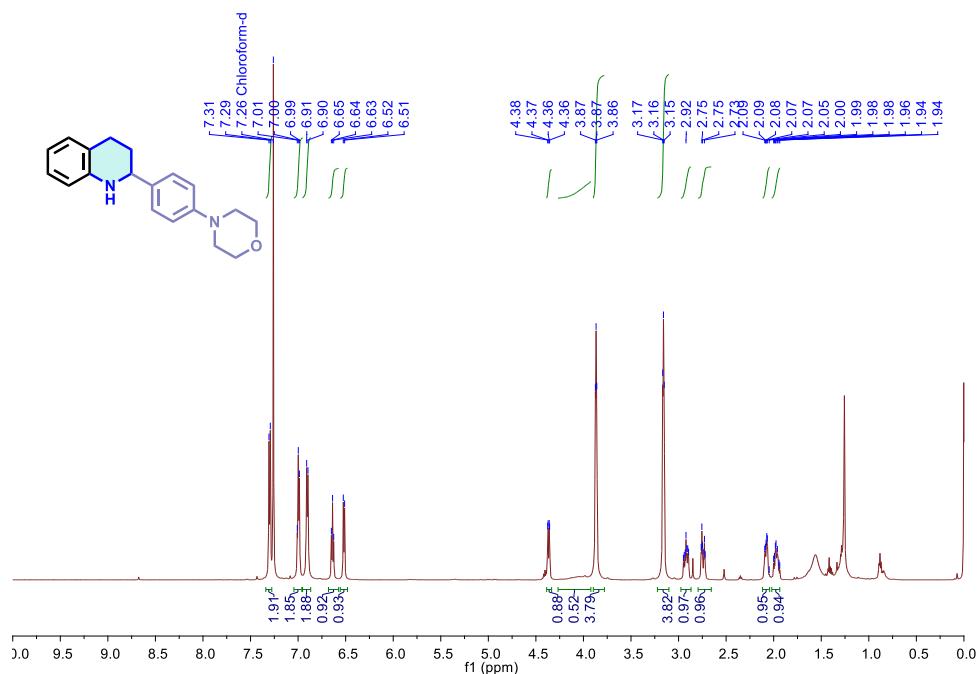
mg), dichloromethane (DCM, 1.5 mL), and H<sub>2</sub>O (1.5 mL) (**Scheme S2**). TfOH (37.5 mg, 0.5 equiv., 0.022 mL) was then added slowly to the reaction mixture via micropipette. The vial was closed and stirred at room temperature for 2 hours. Upon completion of the reaction, the mixture was diluted with ethyl acetate and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. After evaporating the solvent through a rotary evaporator, the crude mixture was purified using 100–200 mesh silica gel column chromatography to obtain the pure desired product **1d** (white crystalline solid). The isolated yield is **35%** (**51 mg**).



**Scheme S2.** Deuterium labelling experiment with Hantzsch ester-d

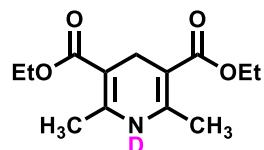
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 6.6 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 4.37 (dd, *J* = 9.5, 2.7 Hz, 1H), 3.90 – 3.82 (m, 4H), 3.20 – 3.10 (m, 4H), 2.92 (ddd, *J* = 16.2, 11.0, 5.3 Hz, 1H), 2.74 (dt, *J* = 16.2, 4.3 Hz, 1H), 2.07 (dt, *J* = 19.8, 8.0 Hz, 1H), 2.03 – 1.92 (m, 1H).

**Figure S8.** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) (4-(4-(1,2,3,4-tetrahydroquinolin-2-yl)-3-d<sub>2</sub>)phenyl) morpholine (**1d**, **Scheme S2**):



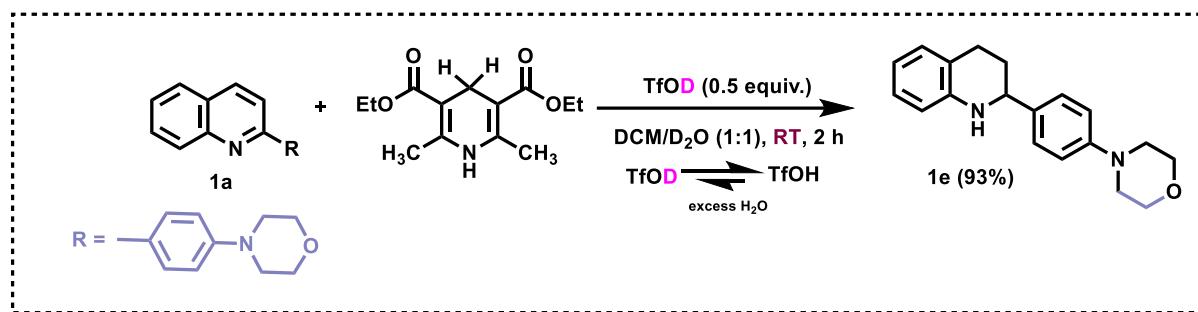
**Synthesis of deuterated Hantzsch esters:**

**1-deuterated diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate**



The compound was synthesized following a reported literature procedure.<sup>1</sup> In an oven-dried round-bottom flask, diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.25 g, 0.98 mmol) was mixed with CD<sub>3</sub>OD (3 mL) and stirred overnight under a nitrogen atmosphere. After solvent evaporation, the desired compound was obtained as a pale green solid (0.24 g, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.15 (q, *J* = 7.2 Hz, 4H), 3.26 (s, 2H), 2.19 (s, 6H), 1.28 (t, *J* = 6.8 Hz, 6H).

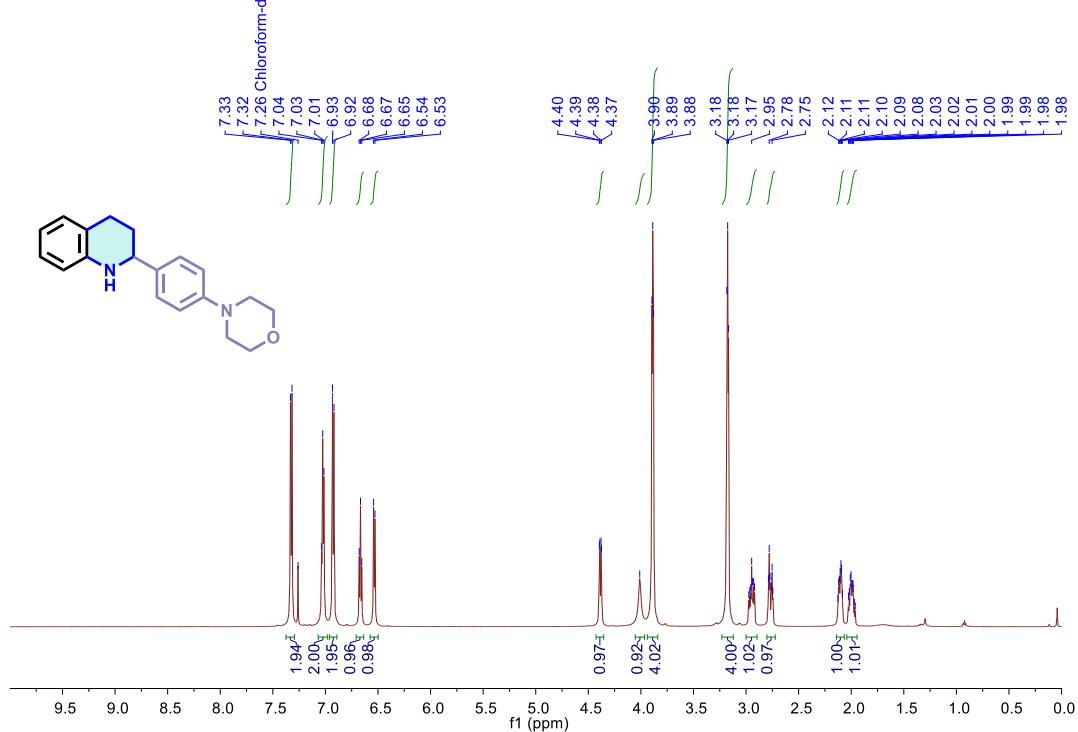
**Reaction procedure (C):** An oven-dried 20 mL glass vial equipped with a magnetic stir bar was charged with the substrate **1a** (0.5 mmol), Hantzsch ester (1.25 mmol, 2.5 equiv., 316.25 mg), dichloromethane (DCM, 1.5 mL), and H<sub>2</sub>O (1.5 mL) (**Scheme S3**). TfOD (37.5 mg, 0.5 equiv., 0.022 mL) was then added slowly to the reaction mixture via micropipette. The vial was closed and stirred at room temperature for 2 hours. Upon completion of the reaction, the mixture was diluted with ethyl acetate and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. After evaporating the solvent through a rotary evaporator, the crude mixture was purified using 100-200 mesh silica gel column chromatography to obtain the pure desired product **1e** (white crystalline solid). The isolated yield is **93% (166 mg)**.



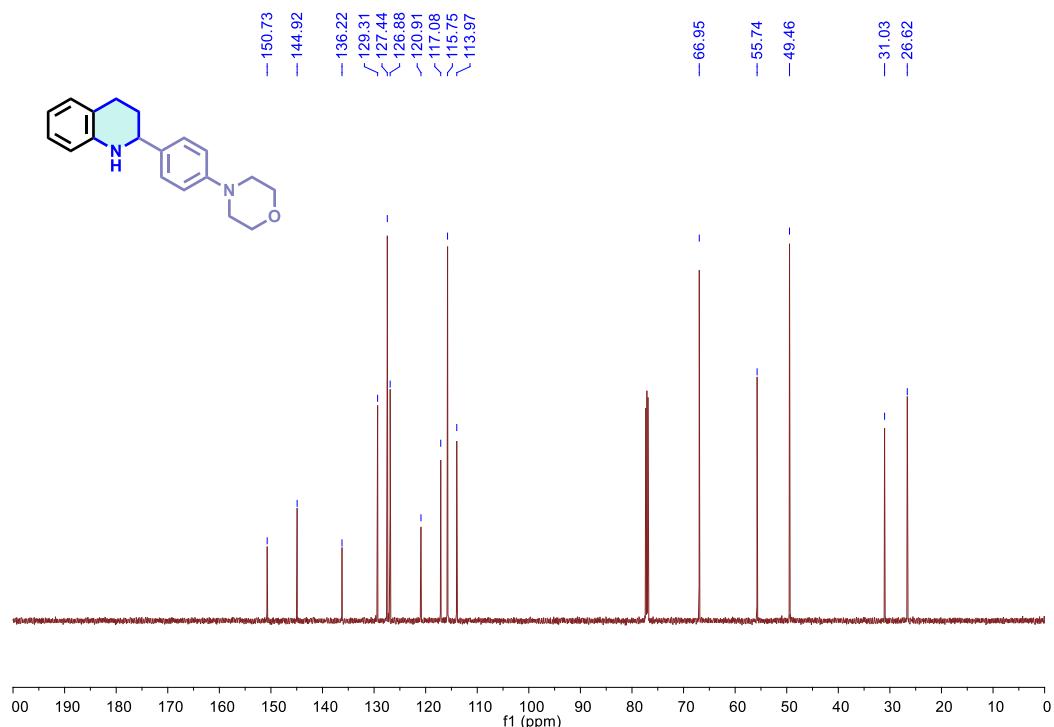
**Scheme S3.** Deuterium labelling experiment with Triflic acid-d

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.02 (t, *J* = 6.6 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 4.38 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.98 (d, *J* = 35.3 Hz, 1H), 3.92 – 3.83 (m, 4H), 3.22 – 3.12 (m, 4H), 2.95 (ddd, *J* = 16.2, 10.9, 5.4 Hz, 1H), 2.77 (dt, *J* = 16.2, 4.4 Hz, 1H), 2.11 (ddd, *J* = 12.6, 8.5, 4.5 Hz, 1H), 2.05 – 1.94 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 150.73, 144.92, 136.22, 129.31, 127.44, 126.88, 120.91, 117.08, 115.75, 113.97, 66.95, 55.74, 49.46, 31.03, 26.62.

**Figure S9.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl)phenyl)morpholine (**1e**, Scheme S3):

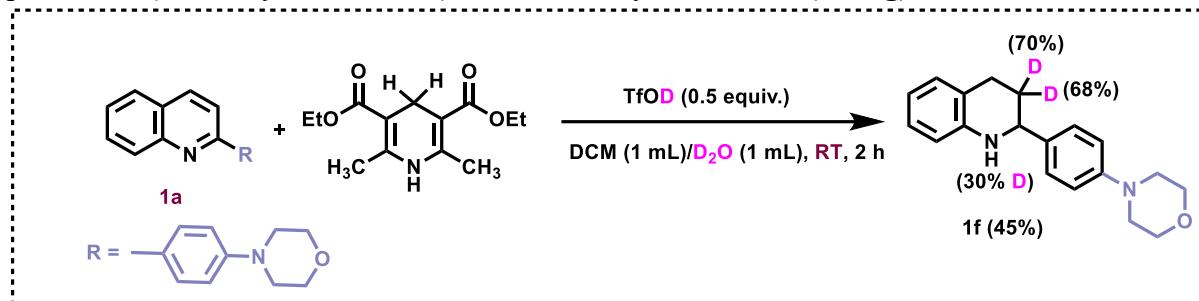


**Figure S10.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl)phenyl)morpholine (**1e**, Scheme S3):



**Reaction procedure (D):** An oven-dried 20 mL glass vial equipped with a magnetic stir bar was charged with the substrate (0.5 mmol), Hantzsch ester (1.25 mmol, 2.5 equiv., 316.25 mg), dichloromethane (DCM, 1.5 mL), and  $\text{D}_2\text{O}$  (1.5 mL) (Scheme S4). TfOD (37.5 mg, 0.5 equiv.,

0.022 mL) was then added slowly to the reaction mixture via micropipette. The vial was closed and stirred at room temperature for 2 hours. Upon completion of the reaction, the mixture was diluted with ethyl acetate and extracted with ethyl acetate ( $3 \times 10$  mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. After evaporating the solvent through a rotary evaporator, the crude mixture was purified using 100–200 mesh silica gel column chromatography to obtain the pure desired product **1f** (white crystalline solid). The isolated yield is **45%** (**66 mg**).



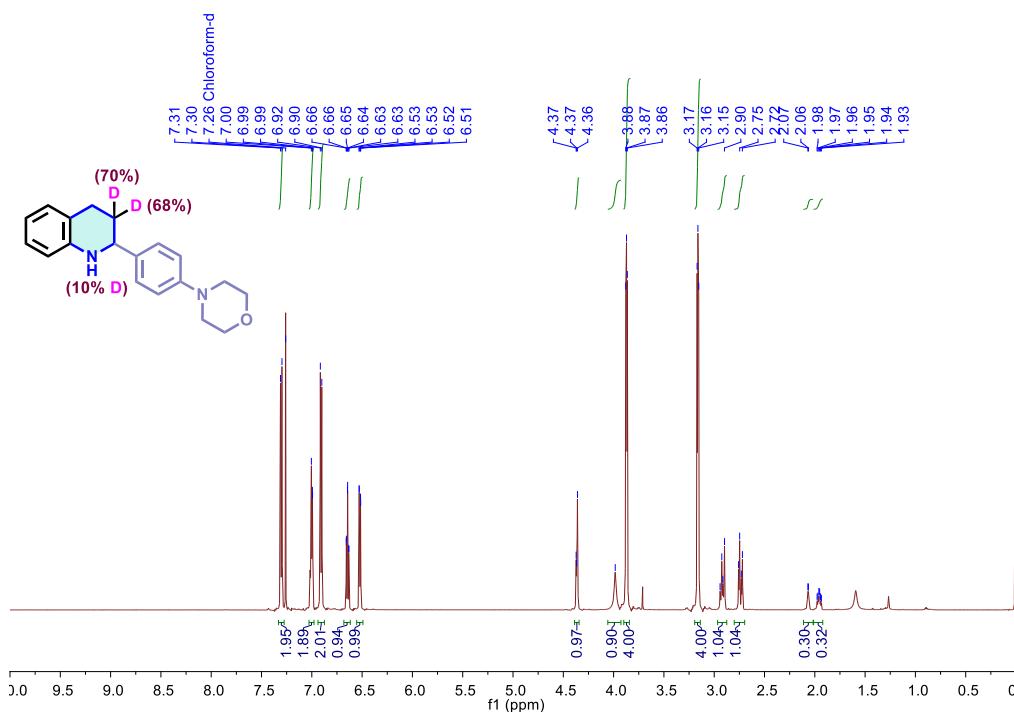
**Scheme S4.** Deuterium labeling experiment with Triflic acid-d and deuterated water ( $\text{D}_2\text{O}$ )

**$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.30 (d,  $J = 8.6$  Hz, 2H), 7.04 – 6.97 (m, 2H), 6.91 (d,  $J = 8.7$  Hz, 2H), 6.64 (td,  $J = 7.4, 1.0$  Hz, 1H), 6.52 (dd,  $J = 8.3, 0.7$  Hz, 1H), 4.41 – 4.31 (m, 1H), 3.98 (s, 1H), 3.91 – 3.78 (m, 4H), 3.22 – 3.12 (m, 4H), 2.92 (dd,  $J = 16.3, 10.3$  Hz, 1H), 2.74 (dd,  $J = 16.3, 6.5$  Hz, 1H), 2.07 (d,  $J = 3.0$  Hz, 1H), 1.96 (td,  $J = 10.4, 5.0$  Hz, 1H).

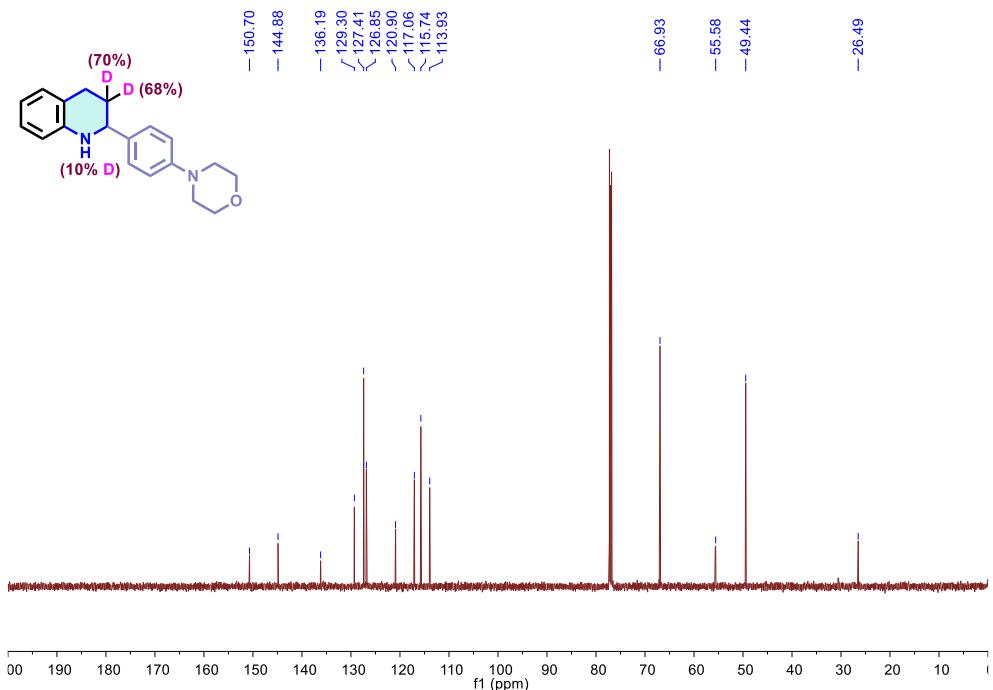
**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):**  $\delta$  150.70, 144.88, 136.19, 129.30, 127.41, 126.85, 120.90, 117.06, 115.74, 113.93, 66.93, 55.58, 49.44, 26.49.

**$^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ):**  $\delta$  2.07, 1.97.

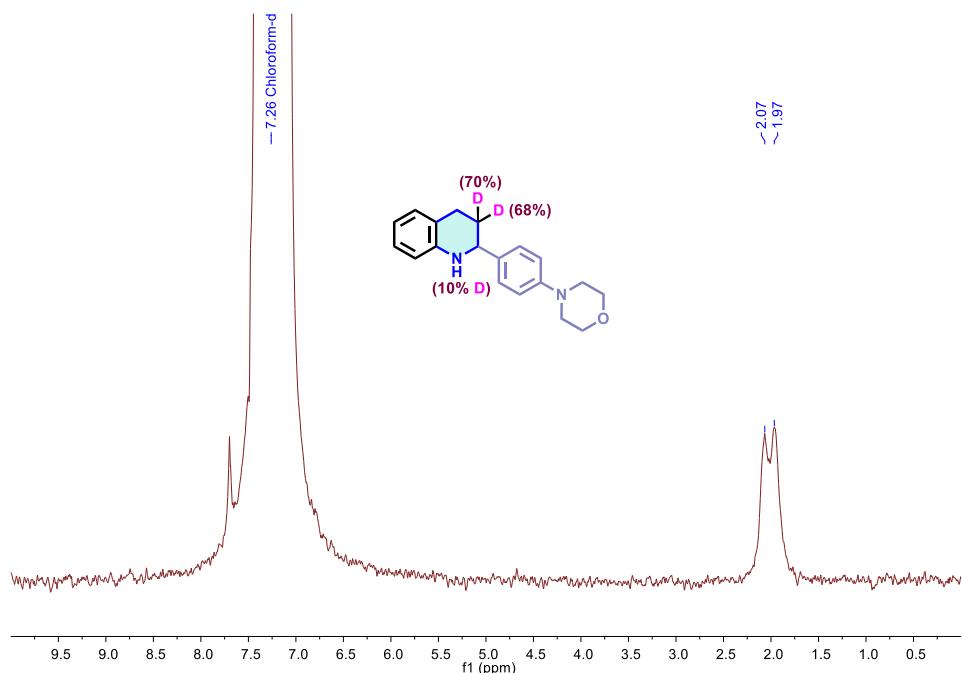
**Figure S11.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl-3,3-d2)phenyl)morpholine (**1f**, Scheme S4)



**Figure S12.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl-3,3-d2)phenyl)morpholine (**1f**, Scheme S4):

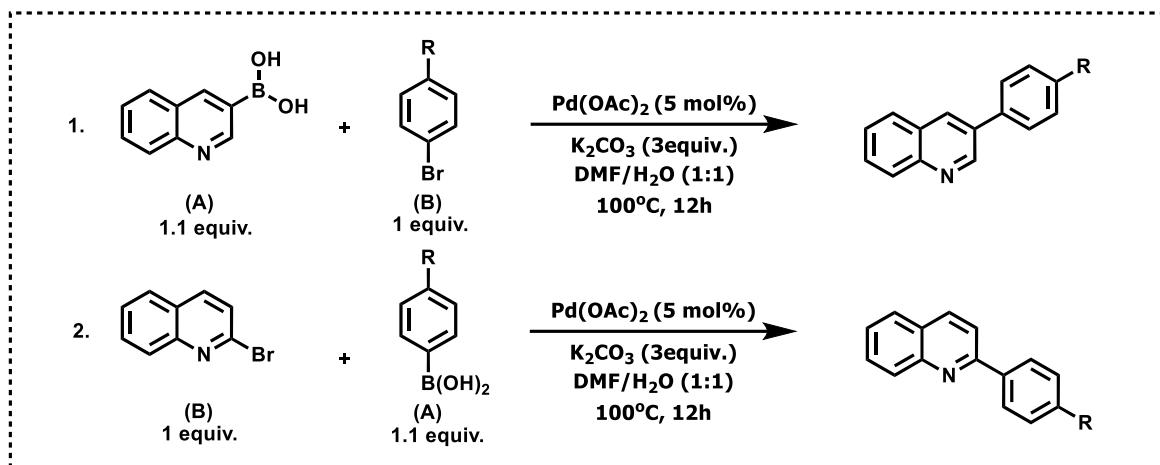


**Figure S13.**  $^2\text{H}$  NMR (92 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl-3,3-d2)phenyl)morpholine (**1f**, Scheme S4):



## 6. Synthesis of starting material:

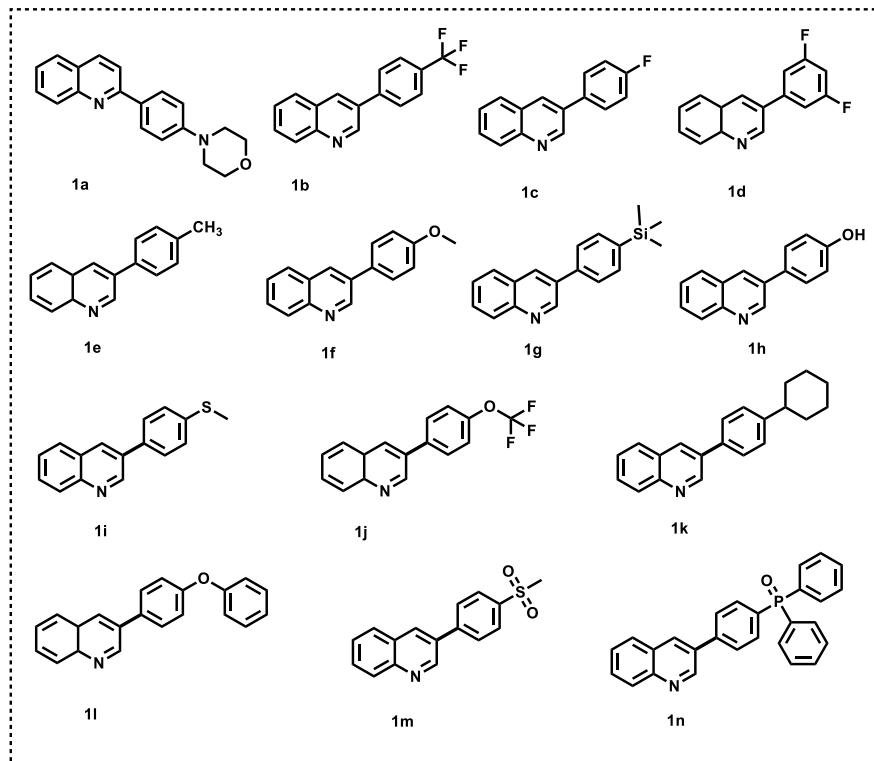
### Via Suzuki-Miyaura coupling: (Method 1)



**Scheme S5.** General reaction for Suzuki-Miyaura coupling

### General reaction procedure for Suzuki-Miyaura coupling (Scheme S5)

Charge a 50 mL round-bottomed flask equipped with a stirring bar with palladium acetate ( $\text{Pd(OAc)}_2$ , 22.4 mg, 0.1 mmol, 5 mol%), organohalide (**B**, 1 equiv.) and organoboronic acid (**A**, 1.1 equiv.),  $\text{K}_2\text{CO}_3$  (3 equiv.). Add DMF (5 mL) and water (5 mL) as a solvent in 1:1. Seal the round bottom flask and heat it in an oil bath at 100 °C for 10 hours. After cooling to room temperature, add ethyl acetate (10 mL). Extract the aqueous layer with ethyl acetate ( $3 \times 20$  mL). Remove the solvent under reduced pressure and purify the crude product by silica gel column chromatography using a gradient of n-hexane and ethyl acetate as the eluent.



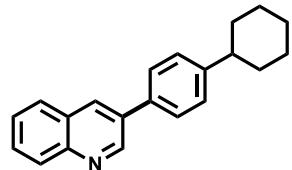
**Scheme S6.** Summary of all Suzuki-Miyaura coupling substrates

The 1a<sup>[11]</sup> and 1b<sup>[10]</sup>, 1c<sup>[6]</sup>, 1d, 1e<sup>[8]</sup>, 1f<sup>[5]</sup>, 1g<sup>[10]</sup>, 1h<sup>[9]</sup>, 1i<sup>[10]</sup>, and 1j<sup>[7]</sup> are known compounds that were prepared by the reported methods and used after the preparation.

**7. Characterization data of isolated starting materials:**

**(1k) prepared according to the following procedure:**

**3-(4-cyclohexylphenyl)quinoline**

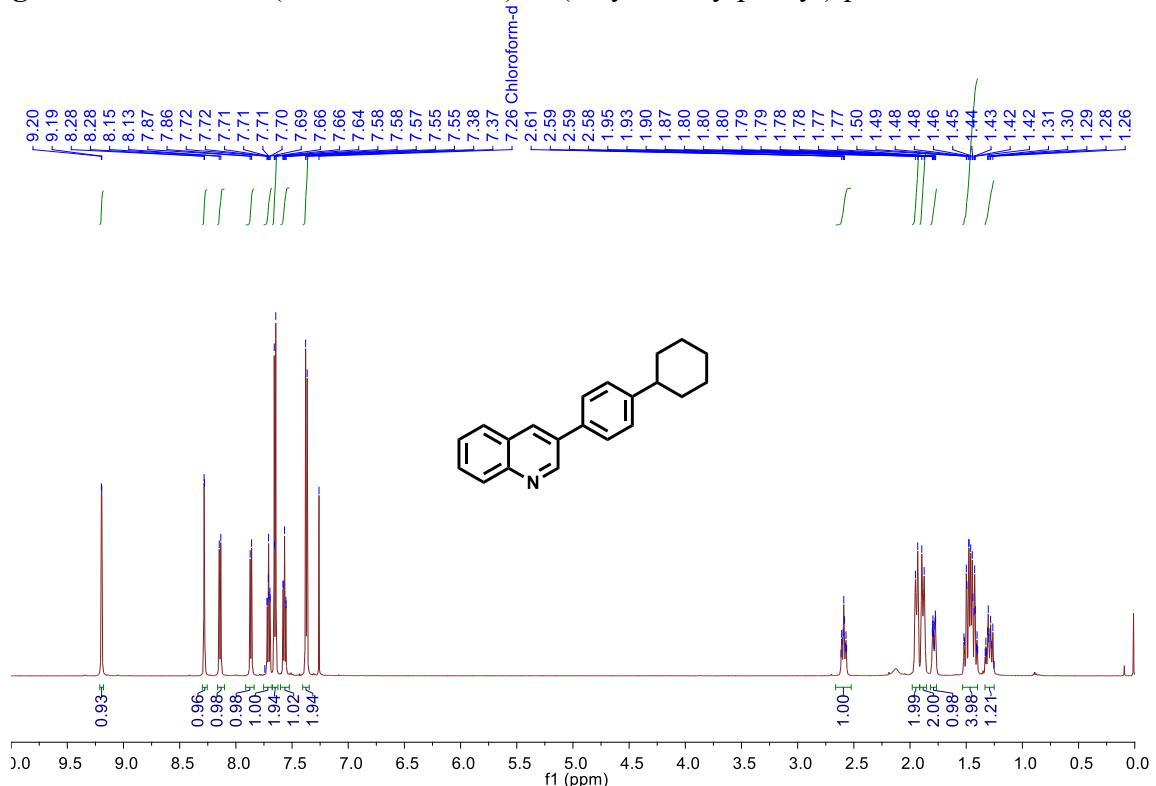


Charge a 50 mL round-bottomed flask equipped with a stirring bar with palladium acetate Pd(OAc)<sub>2</sub>, 22.4 mg, 0.1 mmol, 5 mol%), 1-bromo-4-cyclohexylbenzene (476 mg, 2.00 mmol, 1 equiv.) and quinolin-3-ylboronic acid (378 mg, 2.2 mmol, 1.1 equiv.), K<sub>2</sub>CO<sub>3</sub> (828 mg, 6 mmol, 3 equiv.). Add DMF (5 mL) and water (5 mL) as a solvent in 1:1. Seal the round bottom flask and heat it in an oil bath at 100 °C for 12 hours. After cooling to room temperature, add ethyl acetate (10 mL). Extract the aqueous layer with ethyl acetate (3 × 20 mL). Remove the solvent under reduced pressure and purify the crude product by silica gel column chromatography using a gradient 20% ethyl acetate/hexane as the eluent. The desired product (499 mg, 87%) as a white crystalline solid.

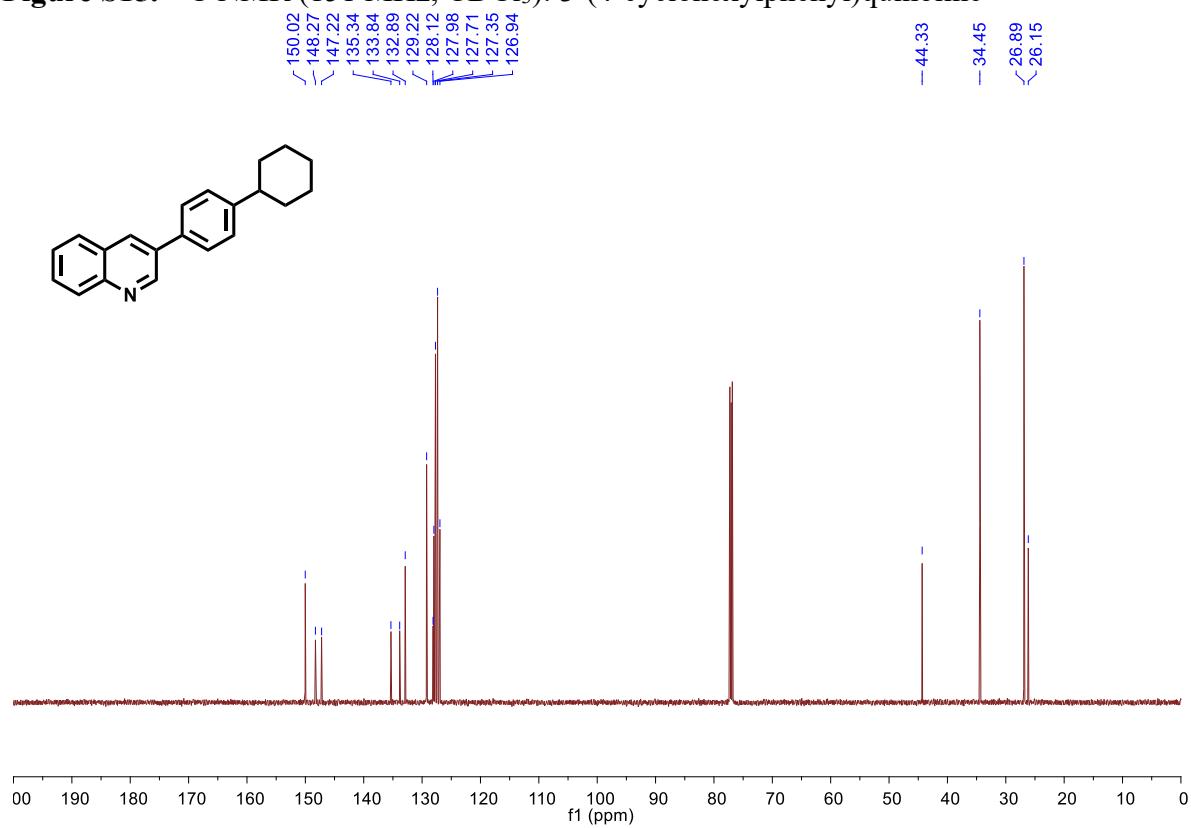
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 9.20 (d, *J* = 2.2 Hz, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.68 – 7.61 (m, 2H), 7.60 – 7.52 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.68 – 2.41 (m, 1H), 1.94 (d, *J* = 12.3 Hz, 2H), 1.88 (d, *J* = 12.7 Hz, 2H), 1.83 – 1.73 (m, 1H), 1.54 – 1.38 (m, 4H), 1.34 – 1.24 (m, 1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):** δ 150.02, 148.27, 147.22, 135.34, 133.84, 132.89, 129.22, 128.12, 127.98, 127.71, 127.35, 126.94, 44.33, 34.45, 26.89, 26.15. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>22</sub>N 288.1747; Found 288.1776

**Figure S14.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(4-cyclohexylphenyl)quinoline

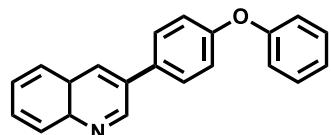


**Figure S15.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3-(4-cyclohexylphenyl)quinoline



(1l) prepared according to the following procedure:

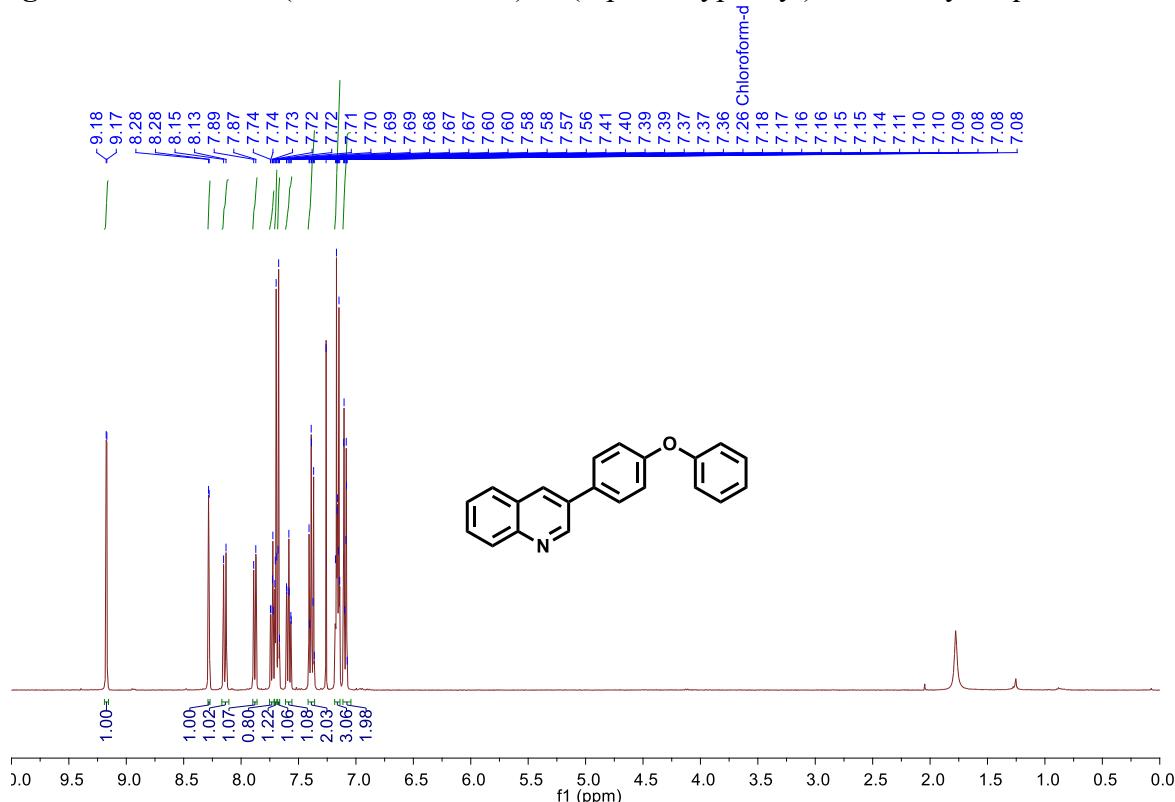
**3-(4-phenoxyphenyl)-4a,8a-dihydroquinoline<sup>1</sup>**



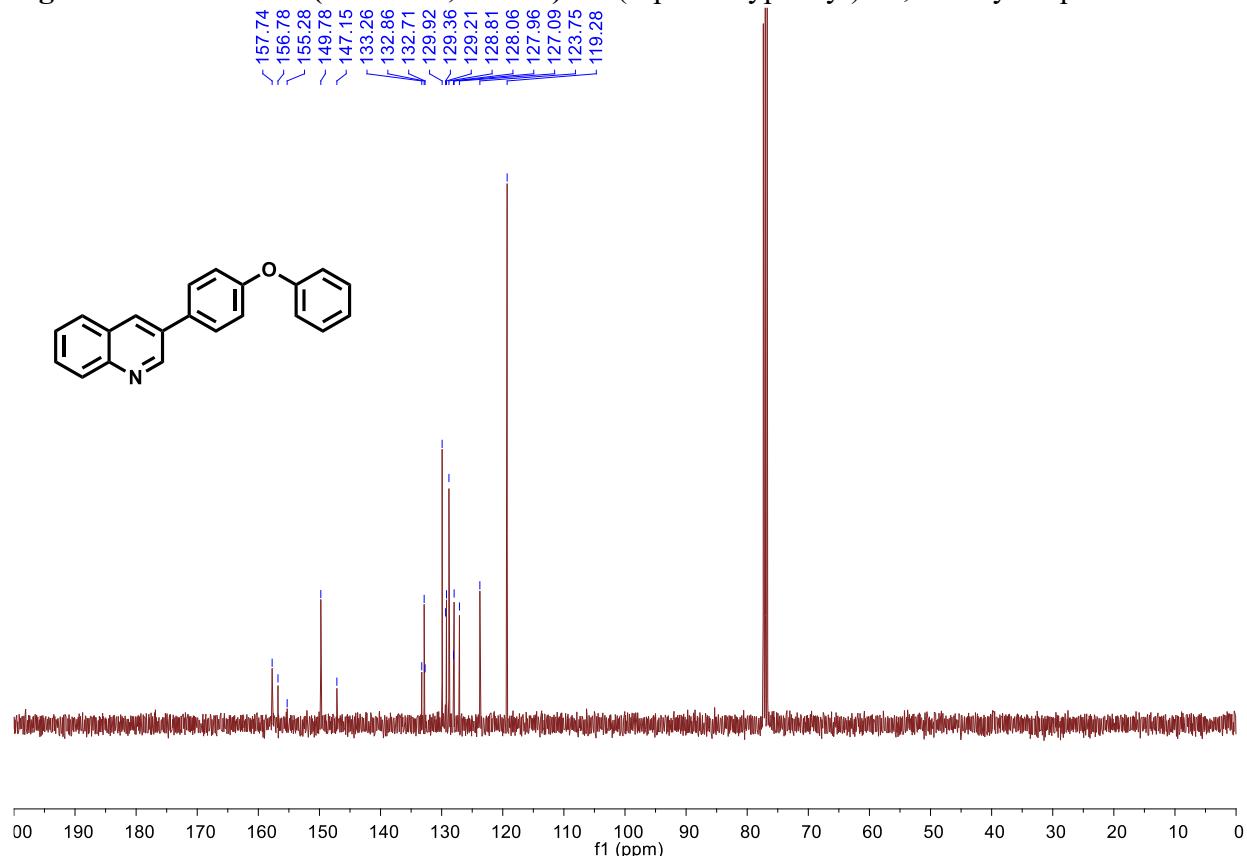
Charge a 50 mL round-bottomed flask equipped with a stirring bar with palladium acetate Pd(OAc)<sub>2</sub>, 22.4 mg, 0.1 mmol, 5 mol%), 1-bromo-4-phenoxybenzene (476 mg, 2.00 mmol, 1 equiv.) and quinolin-3-ylboronic acid (378 mg, 2.2 mmol, 1.1 equiv.), K<sub>2</sub>CO<sub>3</sub> (828 mg, 6 mmol, 3 equiv.). Add DMF (5 mL) and water (5 mL) as a solvent in 1:1. Seal the round bottom flask and heat it in an oil bath at 100 °C for 12 hours. After cooling to room temperature, add ethyl acetate (10 mL). Extract the aqueous layer with ethyl acetate (3 × 20 mL). Remove the solvent under reduced pressure and purify the crude product by silica gel column chromatography using a gradient of 25% ethyl acetate/hexane as the eluent. The desired product (508 mg, 85%) is an off-white solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.17 (d, *J* = 2.3 Hz, 1H), 8.28 (d, *J* = 2.1 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.70 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.61 – 7.55 (m, 1H), 7.43 – 7.35 (m, 2H), 7.19 – 7.13 (m, 3H), 7.12 – 7.07 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 157.74, 156.78, 155.28, 149.78, 147.15, 133.26, 132.86, 132.71, 129.92, 129.36, 129.21, 128.81, 128.06, 127.96, 127.09, 123.75, 119.28.

**Figure S16.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3-(4-phenoxyphenyl)-4a,8a-dihydroquinoline

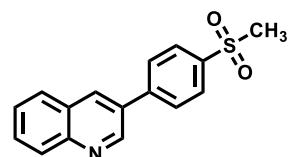


**Figure S17.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-phenoxyphenyl)-4a,8a-dihydroquinoline**



**(1m) prepared according to the following procedure:**

**3-(4-(methylsulfonyl)phenyl)quinoline**

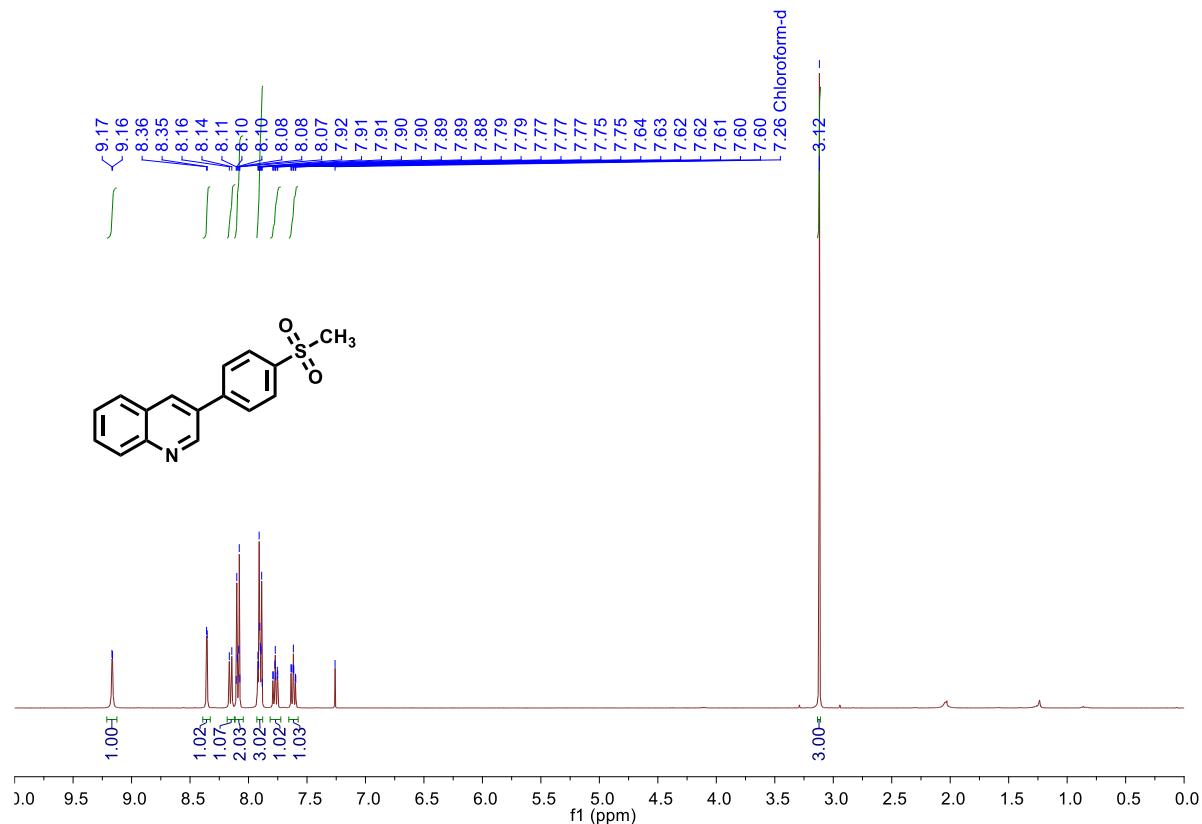


Charge a 50 mL round-bottomed flask equipped with a stirring bar with palladium acetate  $\text{Pd}(\text{OAc})_2$ , 22.4 mg, 0.1 mmol, 5 mol%), 1-bromo-4-(methylsulfonyl)benzene (470 mg, 2.00 mmol, 1 equiv.) and quinolin-3-ylboronic acid (380 mg, 2.2 mmol, 1.1 equiv.),  $\text{K}_2\text{CO}_3$  (828 mg, 6 mmol, 3 equiv.). Add DMF (5 mL) and water (5 mL) as a solvent in 1:1. Seal the round bottom flask and heat it in an oil bath at 100 °C for 10 hours. After cooling to room temperature, add ethyl acetate (10 mL). Extract the aqueous layer with ethyl acetate ( $3 \times 20$  mL). Remove the solvent under reduced pressure and purify the crude product by silica gel column chromatography using a gradient of 80% ethyl acetate/hexane as the eluent. The desired product (425 mg, 75%) is an white solid.

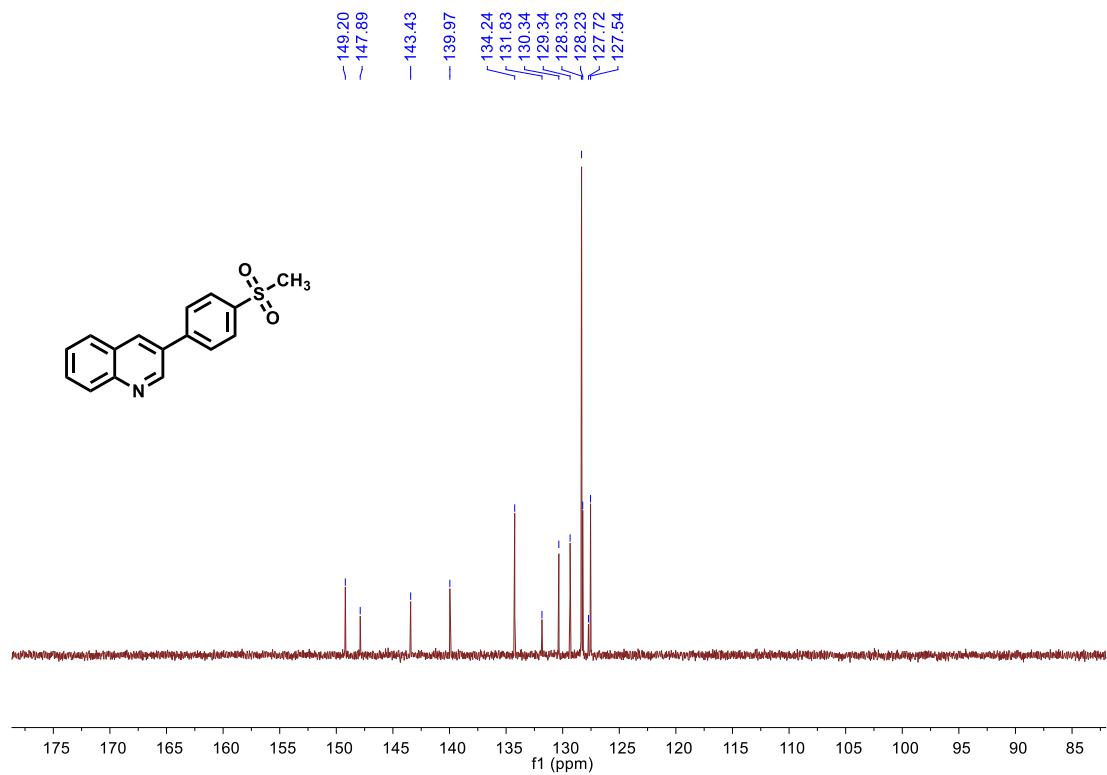
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.17 (d,  $J = 1.9$  Hz, 1H), 8.36 (d,  $J = 2.1$  Hz, 1H), 8.15 (d,  $J = 8.4$  Hz, 1H), 8.11 – 8.04 (m, 2H), 7.90 (dq,  $J = 8.4, 2.1$  Hz, 3H), 7.77 (ddd,  $J = 8.4, 6.9, 1.4$  Hz, 1H), 7.62 (ddd,  $J = 8.0, 7.0, 1.1$  Hz, 1H), 3.12 (s, 3H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):**  $\delta$

149.20, 147.89, 143.43, 139.97, 134.24, 131.83, 130.34, 129.34, 128.33, 128.23, 127.72, 127.54, 44.64. **HRMS** (ESI) m/z: ( $M+H$ )<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>NO<sub>2</sub>S 284.0740; Found 284.0758.

**Figure S18.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 3-(4-(methylsulfonyl)phenyl)quinoline

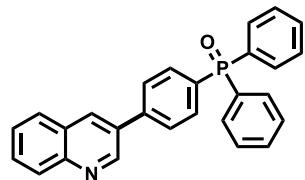


**Figure S19.** <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) 3-(4-(methylsulfonyl)phenyl)quinoline



**(1n) prepared according to the following procedure:**

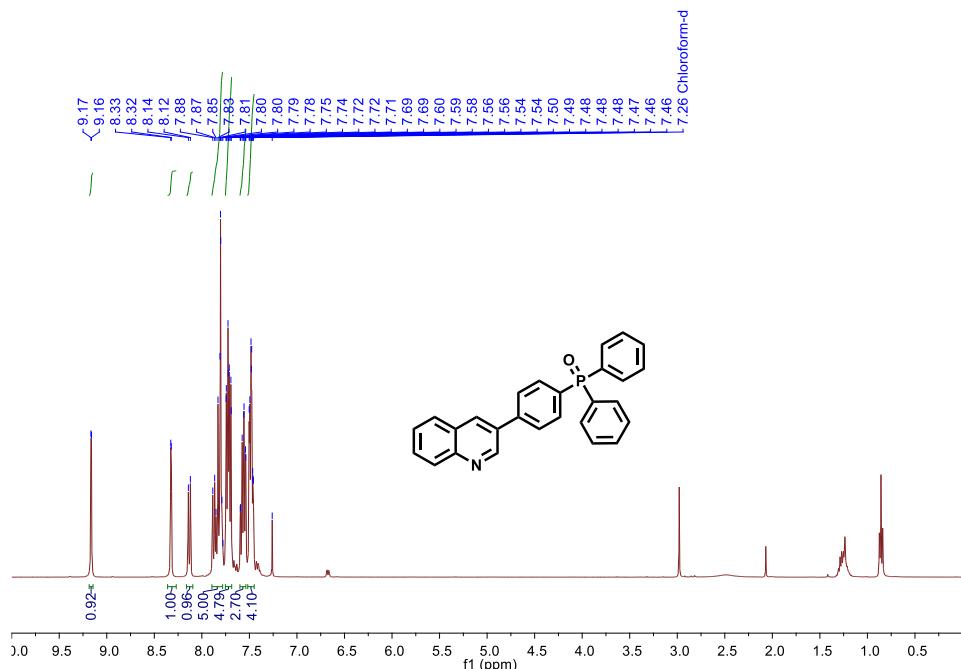
**diphenyl(4-(quinolin-3-yl)phenyl)phosphine oxide**



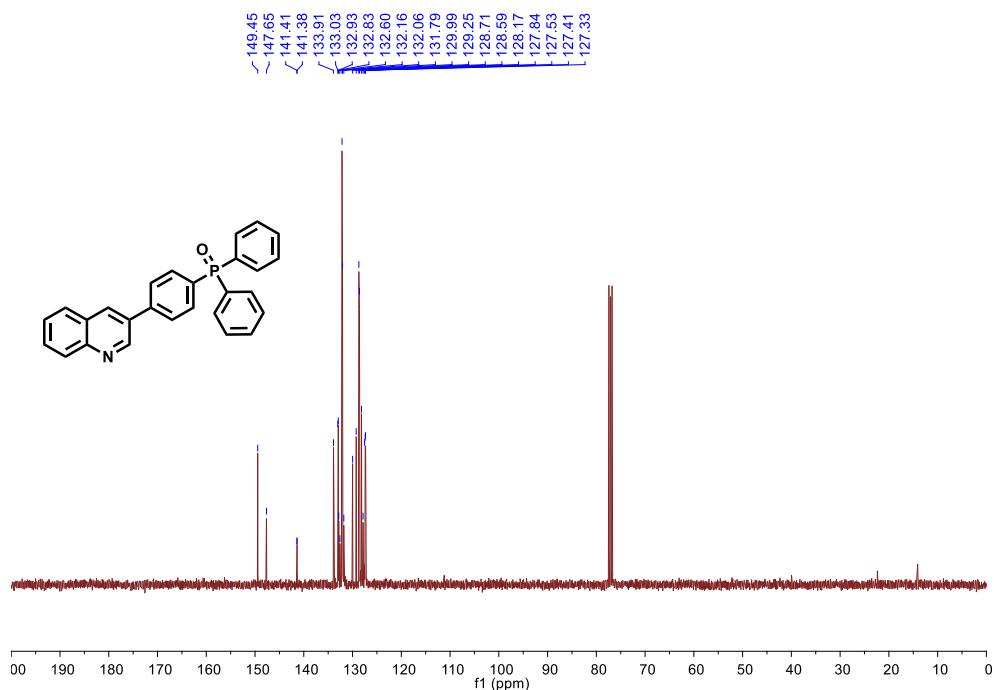
Charge a 50 mL round-bottomed flask equipped with a stirring bar with palladium acetate  $\text{Pd}(\text{OAc})_2$ , 22.4 mg, 0.1 mmol, 5 mol%), (4-bromophenyl)diphenylphosphine oxide (714 mg, 2.00 mmol, 1 equiv.) and quinolin-3-ylboronic acid (380 mg, 2.2 mmol, 1.1 equiv.),  $\text{K}_2\text{CO}_3$  (828 mg, 6 mmol, 3 equiv.). Add DMF (5 mL) and water (5 mL) as a solvent in 1:1. Seal the round bottom flask and heat it in an oil bath at 100 °C for 10 hours. After cooling to room temperature, add ethyl acetate (10 mL). Extract the aqueous layer with ethyl acetate ( $3 \times 20$  mL). Remove the solvent under reduced pressure and purify the crude product by silica gel column chromatography using a gradient of 80% ethyl acetate/hexane as the eluent. The desired product (648 mg, 80%) is an off-white solid.

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  9.16 (d,  $J = 2.2$  Hz, 1H), 8.32 (d,  $J = 2.0$  Hz, 1H), 8.13 (d,  $J = 8.4$  Hz, 1H), 7.91 – 7.78 (m, 5H), 7.76 – 7.67 (m, 5H), 7.57 (ddd,  $J = 8.5, 7.7, 1.2$  Hz, 3H), 7.48 (ddd,  $J = 8.4, 5.3, 2.2$  Hz, 4H).  **$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  149.45, 147.65, 141.41, 141.38, 133.91, 133.03, 132.93, 132.83, 132.60, 132.16, 132.06, 131.79, 129.99, 129.25, 128.71, 128.59, 128.17, 127.84, 127.53, 127.41, 127.33. **HRMS (ESI) m/z:** ( $\text{M}+\text{H})^+$  Calcd for  $\text{C}_{27}\text{H}_{21}\text{NOP}$  406.1355; Found 406.1354

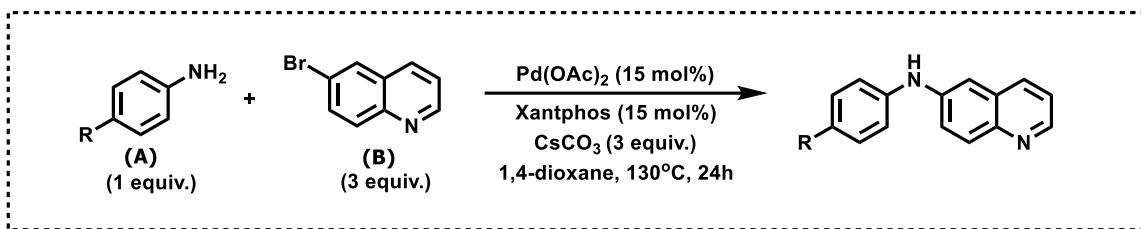
**Figure S20.**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): diphenyl(4-(quinolin-3-yl)phenyl)phosphine oxide



**Figure S21.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): diphenyl(4-(quinolin-3-yl)phenyl)phosphine oxide



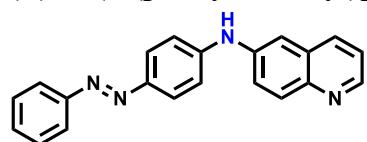
**Via Buchwald-Hartwig Cross-Coupling Reaction: (Method 2)**



**Scheme S7.** General reaction for Buchwald-Hartwig Cross-Coupling Reaction

**(2a) prepared according to the following procedure:**

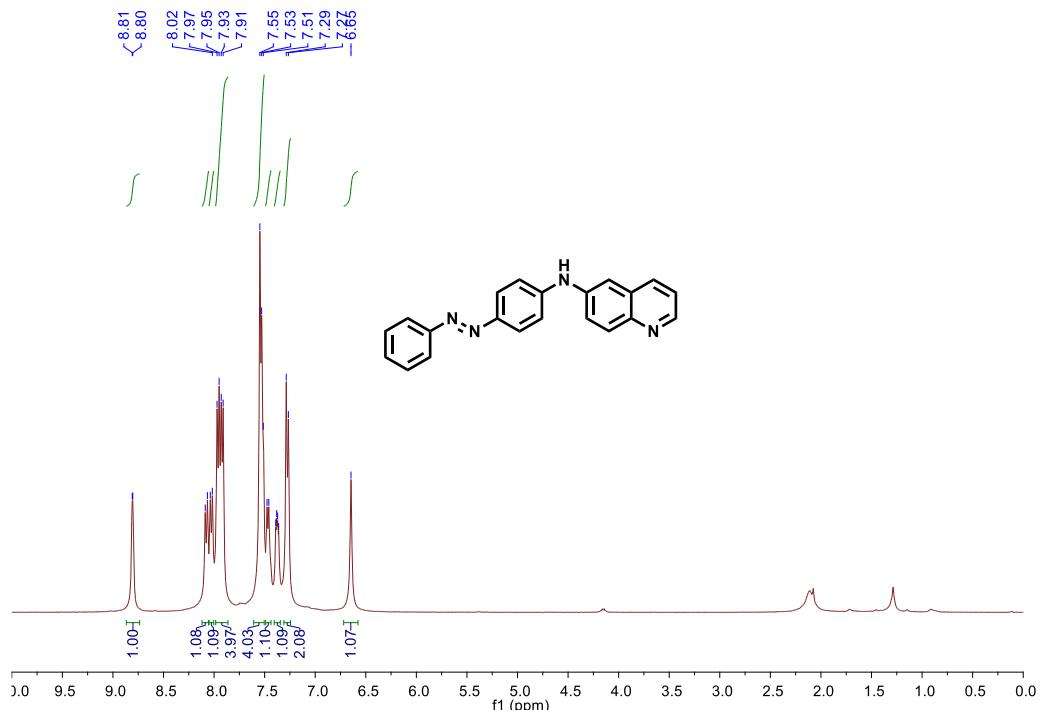
**(E)-N-(4-(phenyldiazenyl)phenyl)quinolin-6-amine**



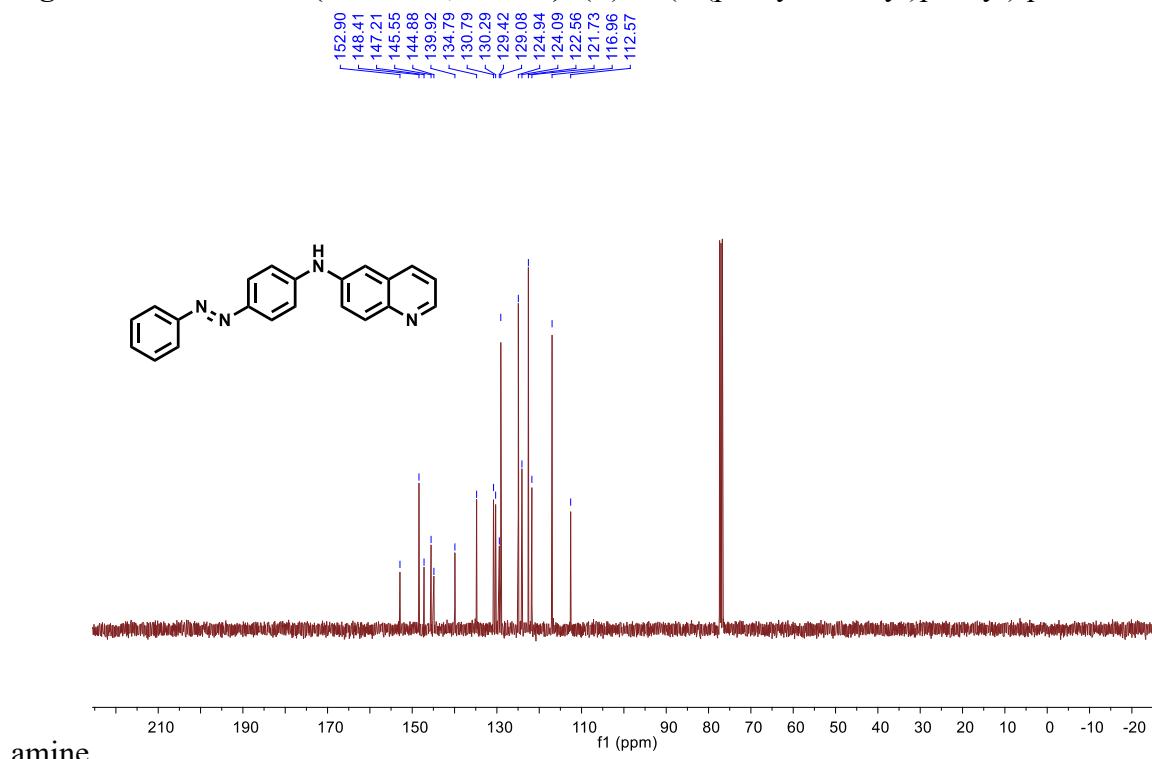
Under an inert atmosphere, a 25 mL Schlenk tube equipped with a stirring bar was charged with (E)-4-(phenyldiazenyl)aniline (**A**, 2 mmol, 394 mg, 1 equiv.), 6-bromoquinoline (**B**, 6 mmol, 1248 mg, 3 equiv.), palladium acetate (67 mg, 0.3 mmol, 15 mol%), Xantphos (173 mg, 0.3 mmol, 15 mol%), and cesium carbonate (1.953 g, 6 mmol, 3 equiv.). 1,4-Dioxane (10 mL) was added as a solvent, and the Schlenk tube was sealed and heated in an oil bath at 130 °C for 24 hours. Upon completion of the reaction, the mixture was cooled to room temperature, followed by the addition of ethyl acetate (10 mL). The aqueous layer was extracted with ethyl acetate ( $3 \times 20$  mL), and the combined organic layers were concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of 50% ethyl acetate/hexane as the eluent, affording the desired product as a reddish-brown solid (480 mg, 75% yield).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.81 (d, *J* = 2.2 Hz, 1H), 8.12 – 8.04 (m, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.94 (dd, *J* = 16.3, 7.9 Hz, 4H), 7.61 – 7.50 (m, 4H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.37 (dt, *J* = 18.9, 9.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.65 (s, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 152.90, 148.41, 147.21, 145.55, 144.88, 139.92, 134.79, 130.79, 130.29, 129.42, 129.08, 124.94, 124.09, 122.56, 121.73, 116.96, 112.57. **HRMS (ESI) m/z:** (M+NH<sub>4</sub>)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>5</sub> 342.1713; Found 342.1700

**Figure S22.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): (E)-N-(4-(phenyldiazenyl)phenyl)quinolin-6-amine

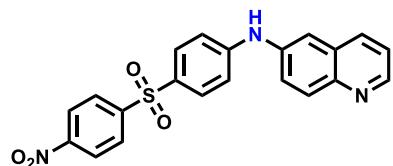


**Figure S23.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): (E)-N-(4-(phenyldiazenyl)phenyl)quinolin-6-



**(2b) prepared according to the following procedure:**

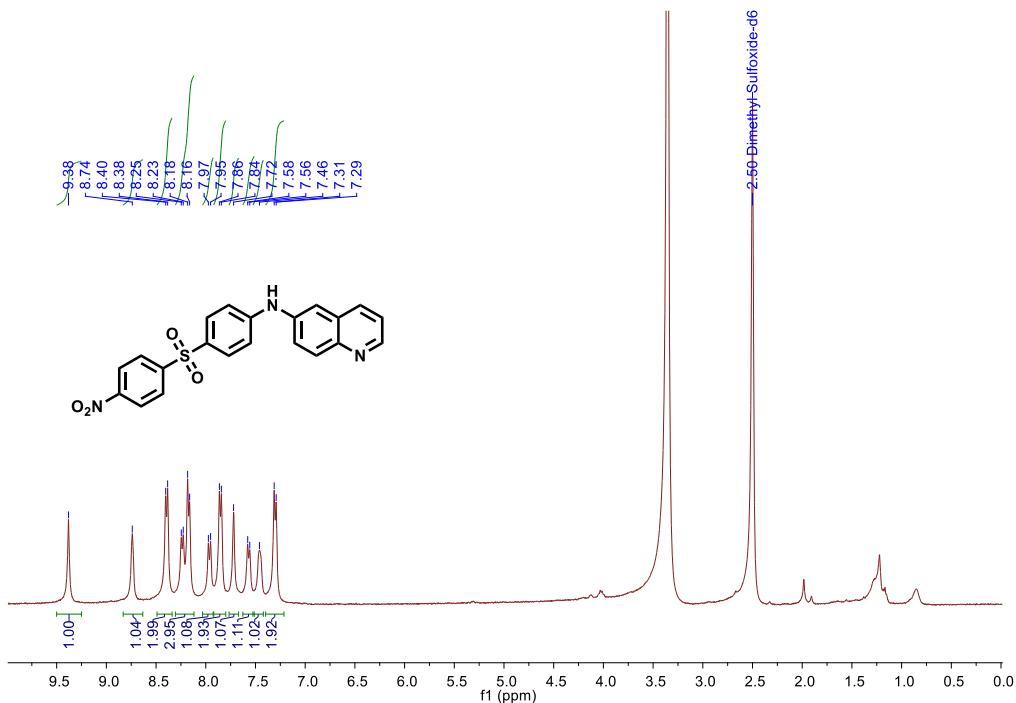
**N-(4-((4-nitrophenyl)sulfonyl)phenyl)quinolin-6-amine**



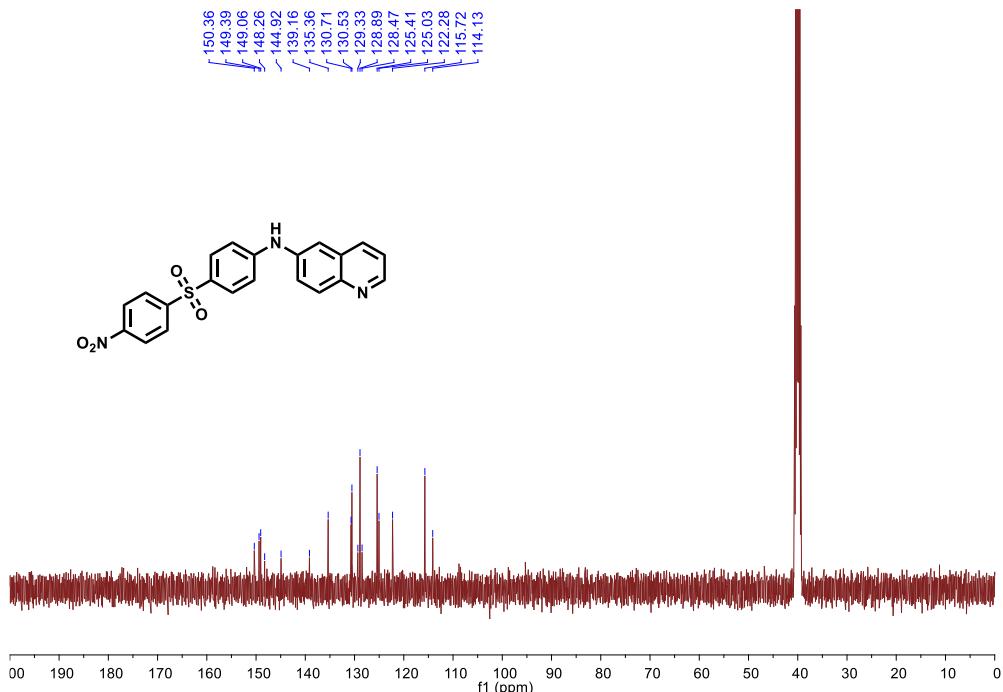
Under an inert atmosphere, a 25 mL Schlenk tube equipped with a stirring bar was charged with 4-((4-nitrophenyl)sulfonyl)aniline (2 mmol, 556 mg, 1 equiv.), 6-bromoquinoline (6 mmol, 1248 mg, 3 equiv.), palladium acetate (67 mg, 0.3 mmol, 15 mol%), Xantphos (173 mg, 0.3 mmol, 15 mol%), and cesium carbonate (1.953 g, 6 mmol, 3 equiv.). 1,4-Dioxane (10 mL) was added as a solvent, and the Schlenk tube was sealed and heated in an oil bath at 130 °C for 24 hours. Upon completion of the reaction, the mixture was cooled to room temperature, followed by the addition of ethyl acetate (10 mL). The aqueous layer was extracted with ethyl acetate ( $3 \times 20$  mL), and the combined organic layers were concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of 45% ethyl acetate/hexane as the eluent, affording the desired product as a dark yellow solid (648 mg, 80% yield).

**$^1\text{H}$  NMR (400 MHz, DMSO)** δ 9.39 (s, 1H), 8.75 (s, 1H), 8.41 (d,  $J = 7.7$  Hz, 2H), 8.22 (dd,  $J = 25.5, 7.9$  Hz, 3H), 7.97 (d,  $J = 8.7$  Hz, 1H), 7.87 (d,  $J = 7.8$  Hz, 2H), 7.73 (s, 1H), 7.58 (d,  $J = 8.3$  Hz, 1H), 7.47 (s, 1H), 7.31 (d,  $J = 8.0$  Hz, 2H).  **$^{13}\text{C}$  NMR (101 MHz, DMSO)**: δ 150.36, 149.39, 149.06, 148.26, 144.92, 139.16, 135.36, 130.71, 130.53, 129.33, 128.89, 128.47, 125.41, 125.03, 122.28, 115.72, 114.13. **HRMS (ESI)** m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>O<sub>4</sub>S 406.0856; Found 406.0853

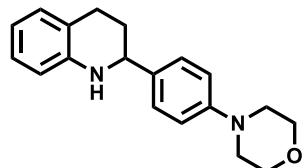
**Figure S24.**  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>): N-(4-((4-nitrophenyl)sulfonyl)phenyl)quinolin-6-amine



**Figure S25.**  $^{13}\text{C}$  NMR (101 MHz, DMSO): N-(4-((4-nitrophenyl)sulfonyl)phenyl)quinolin-6-amine

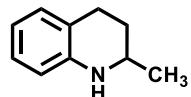


## 8. Characterization data of isolated products



### 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl)phenyl)morpholine (1)

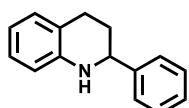
(silica gel: 100–200 mesh, solvent system: 30% ethyl acetate/n-hexane, 139 mg, 95%, white crystalline solid),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 (d,  $J = 7.8$  Hz, 2H), 7.06 (d,  $J = 5.8$  Hz, 2H), 6.96 (d,  $J = 7.9$  Hz, 2H), 6.71 (t,  $J = 6.7$  Hz, 1H), 6.56 (d,  $J = 7.7$  Hz, 1H), 4.41 (d,  $J = 7.4$  Hz, 1H), 4.06 (s, 1H), 3.92 (s, 4H), 3.20 (s, 4H), 3.07 – 2.90 (m, 1H), 2.80 (d,  $J = 16.0$  Hz, 1H), 2.13 (s, 1H), 2.04 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.78, 144.99, 136.27, 129.37, 127.49, 126.94, 120.93, 117.12, 115.79, 114.04, 66.99, 55.77, 49.49, 31.10, 26.68. HRMS (ESI) m/z: ( $M + H$ )<sup>+</sup> Calcd for  $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}$  295.1805; Found 295.1812



### 2-methyl-1,2,3,4-tetrahydroquinoline (2)<sup>19</sup>

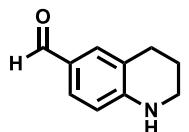
(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 68 mg, 93%, yellow oil),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.10 – 7.07 (m, 1H), 7.06 (s, 1H), 6.72 (td,  $J = 7.4, 1.1$  Hz, 1H), 6.60 – 6.53 (m, 1H), 3.70 (s, 1H), 3.49 (dqd,  $J = 12.6, 6.3, 2.9$  Hz, 1H), 2.94 (ddd,  $J = 17.0, 11.5, 5.6$  Hz, 1H), 2.83 (ddd,  $J = 16.4, 5.1, 3.7$  Hz, 1H), 2.02 (dtd,  $J = 6.2, 5.8, 3.4$  Hz,

1H), 1.69 (dddd,  $J = 12.8, 11.5, 9.9, 5.4$  Hz, 1H), 1.30 (d,  $J = 6.3$  Hz, 3H).  **$^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)**: δ 144.92, 129.40, 126.82, 121.20, 117.10, 114.18, 47.28, 30.27, 26.74, 22.73.



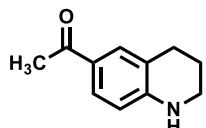
### 2-phenyl-1,2,3,4-tetrahydroquinoline (3)<sup>20</sup>

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 99 mg, 95%, colourless oil),  **$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.59 – 7.47 (m, 4H), 7.47 – 7.41 (m, 1H), 7.17 (t,  $J = 7.7$  Hz, 2H), 6.82 (td,  $J = 7.4, 1.0$  Hz, 1H), 6.66 (d,  $J = 7.8$  Hz, 1H), 4.66 – 4.45 (m, 1H), 4.13 (s, 1H), 3.06 (ddd,  $J = 16.1, 10.5, 5.5$  Hz, 1H), 2.88 (dt,  $J = 16.3, 4.8$  Hz, 1H), 2.33 – 2.19 (m, 1H), 2.22 – 2.05 (m, 1H).  **$^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)**: δ 145.08, 144.95, 129.52, 128.79, 127.64, 127.13, 126.79, 121.04, 117.37, 114.24, 56.41, 31.19, 26.57



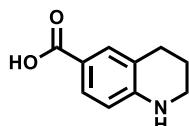
### 1,2,3,4-tetrahydroquinoline-6-carbaldehyde (4)<sup>12</sup>

(silica gel: 100–200 mesh, solvent system: 15% ethyl acetate/n-hexane, 71 mg, 89%, off white solid),  **$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)**: δ 9.66 (s, 1H), 7.47 (d,  $J = 7.9$  Hz, 2H), 6.45 (d,  $J = 8.2$  Hz, 1H), 4.57 (s, 1H), 3.46 – 3.34 (m, 2H), 2.79 (t,  $J = 6.2$  Hz, 2H), 1.95 (dt,  $J = 11.9, 6.1$  Hz, 2H).  **$^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)**: δ 190.33, 150.32, 131.76, 130.29, 125.93, 120.37, 112.94, 41.74, 26.85, 21.15.



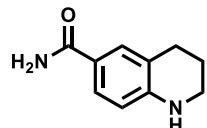
### 1-(1,2,3,4-tetrahydroquinolin-6-yl)ethan-1-one (5)<sup>13</sup>

(silica gel: 100–200 mesh, solvent system: 40% ethyl acetate/n-hexane, 80 mg, 92%, Pale white solid),  **$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.60 (d,  $J = 2.1$  Hz, 1H), 7.59 (dd,  $J = 1.9, 0.9$  Hz, 1H), 6.41 – 6.34 (m, 1H), 4.54 (s, 1H), 3.41 – 3.28 (m, 2H), 2.76 (t,  $J = 6.3$  Hz, 2H), 2.46 (s, 3H), 1.99 – 1.86 (m, 2H).  **$^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)**: δ 196.52, 149.22, 130.48, 128.61, 125.86, 119.79, 112.49, 41.71, 27.01, 25.97, 21.36.



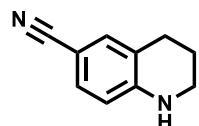
**1,2,3,4-tetrahydroquinoline-6-carboxylic acid (6)<sup>12</sup>**

(silica gel: 100–200 mesh, solvent system: 50% ethyl acetate/n-hexane, 76 mg, 86%, white crystalline solid, **<sup>1</sup>H NMR (400 MHz, DMSO)**: δ 11.85 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 6.48 (s, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 3.21 (s, 2H), 2.66 (s, 2H), 1.76 (s, 2H). **<sup>13</sup>C NMR (101 MHz, DMSO)**: δ 168.14, 149.82, 131.25, 129.28, 119.08, 116.37, 112.40, 40.98, 27.07, 21.28.



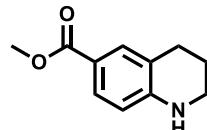
**1,2,3,4-tetrahydroquinoline-6-carboxamide (7)<sup>13</sup>**

(silica gel: 100–200 mesh, solvent system: 30% ethyl acetate/n-hexane, 81 mg, 92%, Pale yellow liquid, **<sup>1</sup>H NMR (400 MHz, DMSO)**: δ 7.52 – 7.37 (m, 3H), 6.77 (s, 1H), 6.42 – 6.33 (m, 1H), 6.21 (s, 1H), 3.19 (d, *J* = 3.5 Hz, 2H), 2.65 (t, *J* = 6.2 Hz, 2H), 1.83 – 1.71 (m, 2H). **<sup>13</sup>C NMR (101 MHz, DMSO)**: δ 168.14, 149.82, 131.25, 129.28, 119.02, 116.37, 112.40, 40.98, 27.07, 21.28.



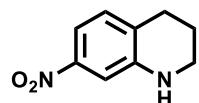
**1,2,3,4-tetrahydroquinoline-6-carbonitrile (8)<sup>14</sup>**

(silica gel: 100–200 mesh, solvent system: 20% ethyl acetate/n-hexane, 72 mg, 91%, white solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.22 – 7.15 (m, 2H), 6.38 (d, *J* = 8.2 Hz, 1H), 4.41 (s, 1H), 3.43 – 3.29 (m, 2H), 2.72 (t, *J* = 6.3 Hz, 2H), 2.10 – 1.78 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**: δ 148.25, 133.21, 131.27, 120.94, 120.87, 113.25, 97.64, 41.57, 26.72, 20.95.



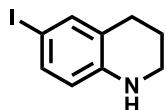
**methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (9)<sup>12</sup>**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 81 mg, 85%, off white solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.69 – 7.57 (m, 2H), 6.43 – 6.34 (m, 1H), 4.35 (s, 1H), 3.83 (s, 3H), 3.45 – 3.31 (m, 2H), 2.76 (t, *J* = 6.3 Hz, 2H), 2.14 – 1.81 (m, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**: δ 167.55, 148.72, 131.33, 129.13, 119.98, 117.53, 112.70, 51.46, 41.74, 26.90, 21.42.



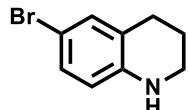
**7-nitro-1,2,3,4-tetrahydroquinoline (10)<sup>15</sup>**

(silica gel: 100–200 mesh, solvent system: 15% ethyl acetate/n-hexane, 70 mg, 79%, dark yellow solid. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.30 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.18 (t, *J* = 3.0 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 4.14 (s, 1H), 3.33 – 3.22 (m, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 1.86 (ddd, *J* = 11.6, 8.7, 6.3 Hz, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 147.20, 145.20, 129.69, 128.35, 111.19, 107.75, 41.52, 27.26, 21.05.



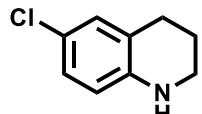
#### **6-iodo-1,2,3,4-tetrahydroquinoline (11)<sup>10</sup>**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 114 mg, 88%, dark green oil), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.14 – 7.06 (m, 1H), 6.15 (d, *J* = 8.3 Hz, 1H), 3.87 (s, 1H), 3.20 – 3.15 (m, 2H), 3.23 (s, 1H), 2.61 (t, *J* = 6.4 Hz, 2H), 1.84 – 1.75 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**: δ 144.19, 137.76, 135.26, 124.16, 116.22, 77.25, 41.75, 26.67, 21.58.



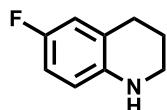
#### **6-bromo-1,2,3,4-tetrahydroquinoline (12)<sup>12</sup>**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 96 mg, 91%, yellow oil), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.06 – 7.04 (m, 1H), 7.04 – 7.01 (m, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 3.58 (s, 1H), 3.29 – 3.25 (m, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 1.93 – 1.88 (m, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 143.75, 131.88, 129.37, 123.40, 115.54, 108.18, 41.80, 26.84, 21.69.



#### **6-chloro-1,2,3,4-tetrahydroquinoline (13)<sup>12</sup>**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 76 mg, 91%, yellow oil), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**: δ 6.94 – 6.93 (m, 1H), 6.92 (t, *J* = 4.1 Hz, 1H), 6.41 – 6.36 (m, 1H), 3.78 (s, 1H), 3.32 – 3.24 (m, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 1.95 – 1.89 (m, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**: δ 143.38, 129.04, 126.53, 122.90, 121.09, 115.13, 41.89, 26.93, 21.78.



#### **6-fluoro-1,2,3,4-tetrahydroquinoline (14)<sup>13</sup>**

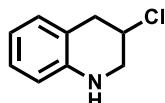
(silica gel: 200–300 mesh, solvent system: 10% ethyl acetate/n-hexane, 70 mg, 93%, yellow colourless oil), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**: δ 6.70 – 6.68 (m, 1H), 6.67 (d, *J* = 3.0 Hz, 1H),

6.41 (dd,  $J = 9.5, 4.9$  Hz, 1H), 3.29 – 3.25 (m, 2H), 2.74 (t,  $J = 6.5$  Hz, 2H), 1.92 (dt,  $J = 8.8, 6.4$  Hz, 2H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**:  $\delta$  156.26, 154.71, 140.89, 122.8 (d,  $J_{\text{C}-\text{F}} = 7.55$  Hz) 115.68 (d,  $J_{\text{C}-\text{F}} = 22.65$  Hz), 114.95 (d,  $J_{\text{C}-\text{F}} = 4.53$  Hz), 113.28, 113.13 (d,  $J_{\text{C}-\text{F}} = 22.65$  Hz), 42.09, 27.02, 21.99.



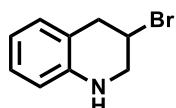
### 5-bromo-1,2,3,4-tetrahydroquinoline (15)<sup>14</sup>

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 97 mg, 92%, yellow oil),  **$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**:  $\delta$  6.89 (dd,  $J = 7.9, 1.2$  Hz, 1H), 6.83 (t,  $J = 7.9$  Hz, 1H), 6.42 (dd,  $J = 7.9, 1.1$  Hz, 1H), 3.93 (s, 1H), 3.31 – 3.14 (m, 2H), 2.79 (t,  $J = 6.6$  Hz, 2H), 1.97 (dtd,  $J = 8.8, 6.6, 4.2$  Hz, 2H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**:  $\delta$  146.58, 127.61, 126.00, 120.68, 113.22, 41.52, 27.70, 22.25.



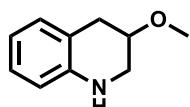
### 3-chloro-1,2,3,4-tetrahydroquinoline (16)<sup>14</sup>

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 80 mg, 95%, colourless oil),  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**:  $\delta$  7.10 (t,  $J = 7.5$  Hz, 1H), 7.02 (d,  $J = 7.4$  Hz, 1H), 6.76 (tt,  $J = 7.4, 3.6$  Hz, 1H), 6.59 (d,  $J = 7.9$  Hz, 1H), 4.51 – 4.35 (m, 1H), 3.81 (s, 1H), 3.62 (ddd,  $J = 11.8, 3.2, 1.8$  Hz, 1H), 3.41 (ddd,  $J = 11.8, 7.4, 0.8$  Hz, 1H), 3.33 (dd,  $J = 16.3, 4.6$  Hz, 1H), 3.10 (dd,  $J = 16.3, 7.5$  Hz, 1H).  **$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**:  $\delta$  142.91, 129.76, 127.60, 118.23, 118.06, 114.49, 52.70, 48.91, 37.18.



### 3-bromo-1,2,3,4-tetrahydroquinoline (17)<sup>14</sup>

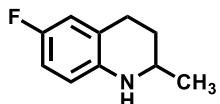
(silica gel: 100–200 mesh, solvent system: 30% ethyl acetate/n-hexane, 99 mg, 94%, reddish brown oil),  **$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**:  $\delta$  7.11 – 7.07 (m, 1H), 7.01 – 6.92 (m, 1H), 6.74 (td,  $J = 7.4, 1.1$  Hz, 1H), 6.57 (dd,  $J = 8.0, 0.9$  Hz, 1H), 3.90 (s, 1H), 3.67 (ddd,  $J = 12.1, 3.3, 1.8$  Hz, 1H), 3.54 – 3.48 (m, 1H), 3.43 (dd,  $J = 16.4, 4.7$  Hz, 1H), 3.23 (dd,  $J = 16.4, 7.5$  Hz, 1H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**:  $\delta$  142.70, 129.56, 127.63, 118.59, 118.09, 114.60, 49.41, 44.42, 37.87.



### 3-methoxy-1,2,3,4-tetrahydroquinoline (18)<sup>13</sup>

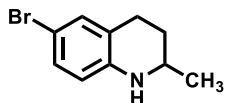
(silica gel: 100–200 mesh, solvent system: 20% ethyl acetate/n-hexane, 77 mg, 94%, yellow oil),  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**:  $\delta$  6.90 (d,  $J = 7.0$  Hz, 1H), 6.87 (s, 1H), 6.55 (t,  $J = 7.4$  Hz,

1H), 6.40 (d,  $J = 7.6$  Hz, 1H), 3.72 – 3.61 (m, 1H), 3.35 (d,  $J = 6.9$  Hz, 3H), 3.32 (dd,  $J = 3.1$ , 1.8 Hz, 1H), 3.16 – 3.06 (m, 1H), 2.94 (dd,  $J = 16.0$ , 4.1 Hz, 1H), 2.79 – 2.63 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.95, 130.04, 127.05, 118.95, 117.57, 114.04, 72.80, 56.28, 45.22, 32.72.



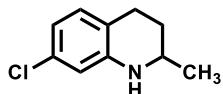
### 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (19)<sup>12</sup>

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 79 mg, 96%, colourless oil),  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.75 – 6.63 (m, 2H), 6.47 – 6.35 (m, 1H), 3.51 (s, 1H), 3.36 (dqd,  $J = 12.6$ , 6.3, 2.7 Hz, 1H), 2.92 – 2.78 (m, 1H), 2.77 – 2.65 (m, 1H), 1.93 (dtd,  $J = 8.8$ , 5.8, 2.9 Hz, 1H), 1.58 (dddd,  $J = 12.9$ , 11.6, 10.1, 5.5 Hz, 1H), 1.22 (d,  $J = 6.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.68, 154.35, 141.05 (d,  $J_{\text{C}-\text{F}} = 1.01$  Hz), 122.51 (d,  $J_{\text{C}-\text{F}} = 6.06$  Hz), 115.4 (d,  $J_{\text{C}-\text{F}} = 21.21$  Hz), 114.80 (d,  $J_{\text{C}-\text{F}} = 7.07$  Hz), 113.17 (d,  $J_{\text{C}-\text{F}} = 22.22$  Hz), 47.33, 29.91, 26.75, 22.50.



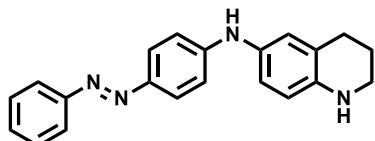
### 6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (20)<sup>18</sup>

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 104 mg, 92%, white crystalline solid),  $^1\text{H}$  NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.09 (dd,  $J = 5.4$ , 4.3 Hz, 1H), 7.06 (dd,  $J = 8.5$ , 2.3 Hz, 1H), 6.35 (d,  $J = 8.5$  Hz, 1H), 3.71 (s, 1H), 3.38 (dqd,  $J = 12.6$ , 6.3, 2.9 Hz, 1H), 2.88 – 2.75 (m, 1H), 2.76 – 2.64 (m, 1H), 1.93 (dddd,  $J = 12.8$ , 5.7, 3.5, 3.0 Hz, 1H), 1.56 (dddd,  $J = 12.9$ , 11.5, 9.9, 5.2 Hz, 1H), 1.23 (d,  $J = 6.3$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  143.89, 131.69, 129.36, 123.17, 115.51, 108.20, 47.15, 29.68, 26.50, 22.55.



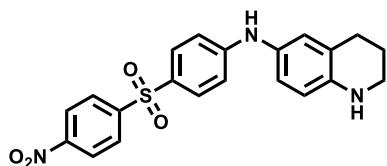
### 7-chloro-2-methyl-1,2,3,4-tetrahydroquinoline (21)<sup>5</sup>

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 81 mg, 90%, white solid),  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.86 (d,  $J = 8.0$  Hz, 1H), 6.55 (dd,  $J = 8.0$ , 2.1 Hz, 1H), 6.44 (d,  $J = 2.1$  Hz, 1H), 3.64 (s, 1H), 3.39 (dqd,  $J = 9.3$ , 6.3, 3.0 Hz, 1H), 2.89 – 2.60 (m, 2H), 2.00 – 1.86 (m, 1H), 1.55 (dddd,  $J = 12.9$ , 11.2, 9.8, 5.5 Hz, 1H), 1.21 (d,  $J = 6.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  145.74, 131.90, 130.20, 119.35, 116.57, 113.28, 47.01, 29.77, 26.09, 22.48.



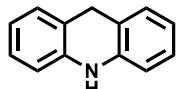
**(E)-N-(4-(phenyldiazenyl)phenyl)-1,2,3,4-tetrahydroquinolin-6-amine (22)**

(silica gel: 100–200 mesh, solvent system: 60% ethyl acetate/n-hexane, 131 mg, 80%, dark brown solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.00 – 7.68 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 1H), 6.86 (s, 4H), 6.51 (s, 1H), 5.82 (s, 1H), 3.32 (s, 2H), 3.13 (s, 1H), 2.76 (s, 2H), 2.07 – 1.89 (m, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 153.13, 149.45, 145.37, 141.94, 129.62, 129.10, 128.99, 125.15, 122.76, 122.58, 122.31, 117.10, 115.03, 113.75, 29.74, 27.01, 22.08. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>4</sub> 329.1761; Found 329.1755



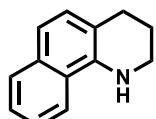
**N-(4-((4-nitrophenyl)sulfonyl)phenyl)-1,2,3,4-tetrahydroquinolin-6-amine (23)**

(silica gel: 100–200 mesh, solvent system: 40% ethyl acetate/n-hexane, 173 mg, 85%, dark red solid), **<sup>1</sup>H NMR (600 MHz, DMSO)** δ 8.49 (s, 1H), 8.35 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.74 – 6.61 (m, 2H), 6.43 (d, *J* = 8.2 Hz, 1H), 5.60 (s, 1H), 3.15 (s, 2H), 2.62 (t, *J* = 5.9 Hz, 2H), 1.85 – 1.67 (m, 2H). **<sup>13</sup>C NMR (151 MHz, DMSO)** δ 152.75, 150.06, 148.93, 143.35, 130.47, 128.55, 127.89, 125.29, 125.11, 124.74, 122.97, 121.15, 114.41, 112.99, 41.31, 27.13, 21.92. **HRMS (ESI) m/z:** (M+Na)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>S 432.0988; Found 432.0968



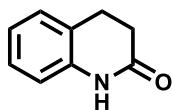
**9,10-dihydroacridine (24)<sup>20</sup>**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 83 mg, 92%, white crystalline solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.13 (dd, *J* = 11.9, 7.4 Hz, 4H), 6.90 (td, *J* = 7.4, 0.8 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 5.95 (s, 1H), 4.09 (s, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**: δ 140.17, 128.66, 127.05, 120.68, 120.08, 113.51, 31.43.



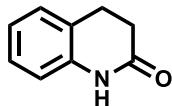
**1,2,3,4-tetrahydrobenzo[h]quinoline (25)<sup>18</sup>**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 82 mg, 90%, colourless oil), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.74 – 7.67 (m, 1H), 7.66 – 7.59 (m, 1H), 7.40 – 7.32 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 4.11 (s, 1H), 3.44 – 3.34 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 2H), 2.06 – 1.91 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**: δ 139.03, 133.12, 128.68, 128.60, 125.01, 124.81, 123.35, 119.56, 117.04, 115.93, 42.48, 27.53, 22.18.



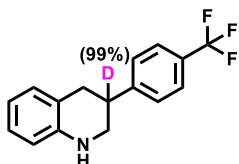
**3,4-dihydroquinolin-2(1H)-one (26)<sup>17</sup>**

(silica gel: 100–200 mesh, solvent system: 30% ethyl acetate/n-hexane, 66 mg, 90%, off white solid, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.06 (s, 1H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.1 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.18, 137.31, 127.94, 127.55, 123.64, 123.09, 115.54, 30.74, 25.34.



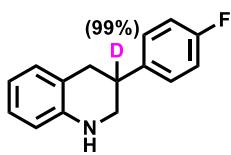
**3,4-dihydroquinolin-2(1H)-one (27)<sup>17</sup>**

(silica gel: 100–200 mesh, solvent system: 30% ethyl acetate/n-hexane, 64 mg, 87%, off white solid), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**: δ 8.77 (s, 1H), 7.17 (dd, *J* = 11.9, 7.4 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.71 – 2.60 (m, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**: δ 172.03, 137.26, 127.96, 127.55, 123.66, 123.11, 115.48, 30.73, 25.34.



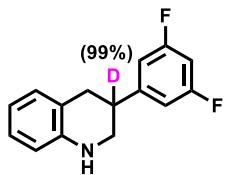
**3-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d (28)**

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 133 mg, 96%, white crystalline solid), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**: δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.06 (dd, *J* = 13.7, 7.3 Hz, 2H), 6.70 (td, *J* = 7.4, 0.8 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 4.01 (s, 1H), 3.49 (dd, *J* = 11.1, 1.2 Hz, 1H), 3.37 (d, *J* = 11.2 Hz, 1H), 3.15 – 2.90 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**: δ 147.95, 143.91, 129.59, 127.64, 127.21, 125.5 (q, *J*<sub>C-F</sub> = 4.0 Hz) 122.94, 120.74, 117.39, 114.21, 47.88, 34.23. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 3.25. **HRMS (ESI) m/z:** (M+Na)<sup>+</sup> Calcd for C<sub>16</sub>H<sub>13</sub>DF<sub>3</sub>NNa 301.1033; Found 301.1058



**3-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d (29)**

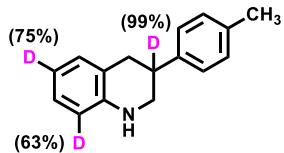
(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 108 mg, 95%, white solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.24 – 7.16 (m, 1H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 1H), 3.44 (d, *J* = 11.1 Hz, 1H), 3.30 (d, *J* = 11.1 Hz, 1H), 2.98 (s, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 162.90, 160.55, 143.94, 139.49, 129.56, 128.5 (d, *J*<sub>C-F</sub> = 7.07 Hz), 127.08, 126.97, 121.19, 117.26, 115.4 (d, *J*<sub>C-F</sub> = 21 Hz), 114.13, 48.32, 34.61. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 3.16. **HRMS (ESI) m/z:** (M+Na)<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>DFN 229.1246; Found 229.1248



### 3-(3,5-difluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d (30)

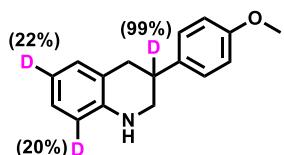
(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane), 114 mg, 93%, white crystalline solid, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.15 (dt, *J* = 10.2, 8.4 Hz, 1H), 7.07 (tdd, *J* = 7.5, 5.8, 1.9 Hz, 3H), 7.02 – 6.92 (m, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 1H), 3.46 (dd, *J* = 11.2, 1.5 Hz, 1H), 3.30 (d, *J* = 11.2 Hz, 1H), 3.06 – 2.89 (m, 2H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 151.30, 151.22, 150.01, 149.93, 149.67, 149.58, 148.38, 148.30, 143.90, 140.93, 129.59, 127.22, 123.14, 120.67, 117.38, 117.34, 117.23, 116.10, 115.99, 114.20, 48.06, 34.41. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 3.19. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>DF<sub>2</sub>N 247.1152; Found 247.1156



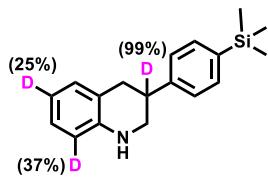
### 3-(p-tolyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (31)

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 102 mg, 91%, white solid), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**: δ 7.28 (q, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 3.6 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 3.96 (s, 1H), 3.53 (dd, *J* = 11.1, 1.9 Hz, 1H), 3.41 (d, *J* = 11.1 Hz, 1H), 3.10 (q, *J* = 16.0 Hz, 1H), 2.48 (s, 1H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 144.15, 140.96, 136.30, 129.67, 129.56, 129.43, 127.20, 126.96, 126.85, 121.53, 117.17, 114.16, 48.50, 34.71, 21.18. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.82, 6.69, 3.21. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>D<sub>3</sub>N 227.1622; Found 227.1628



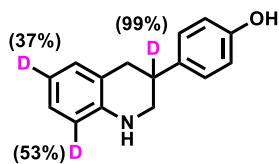
### 3-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (32)

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 114 mg, 95%, white solid), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 5.8 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 7.1 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 3.97 (s, 1H), 3.85 (s, 3H), 3.45 (d, *J* = 10.9 Hz, 1H), 3.32 (d, *J* = 11.0 Hz, 1H), 3.01 (q, *J* = 16.0 Hz, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.39, 144.14, 135.99, 129.61, 128.18, 127.02, 126.91, 121.47, 117.12, 114.09, 55.35, 48.55, 34.74. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.77, 6.66, 3.16. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>D<sub>3</sub>NO 243.1571; Found 243.1577



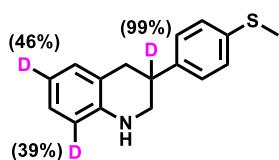
### 3-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (33)

(silica gel: 100–200 mesh, solvent system: 20% ethyl acetate/n-hexane, 132 mg, 93%, white solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.61 – 7.53 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.03 (m, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 3.50 (dd, *J* = 11.1, 1.9 Hz, 1H), 3.38 (d, *J* = 11.2 Hz, 1H), 3.09 (d, *J* = 16.1 Hz, 1H), 3.02 (d, *J* = 17.2 Hz, 1H), 0.33 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 145.45, 145.07, 145.01, 139.59, 134.73, 130.61, 130.50, 128.04, 127.93, 127.75, 122.40, 118.19, 115.14, 49.20, 35.46, -0.01. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.77, 6.66, 3.18. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>D<sub>3</sub>NO 243.1571; Found 243.1577



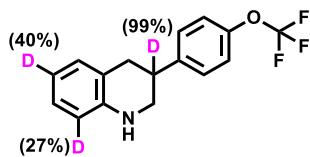
### 4-(1,2,3,4-tetrahydroquinolin-3-yl-3,6,8-d3)phenol (34)

(silica gel: 100–200 mesh, solvent system: 20% ethyl acetate/n-hexane, 101 mg, 89%, white solid), **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.11 (d, *J* = 8.3 Hz, 1H), 7.02 (s, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 3.94 (s, 1H), 3.42 (d, *J* = 11.0 Hz, 1H), 3.28 (d, *J* = 11.1 Hz, 1H), 3.07 – 2.83 (m, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 154.30, 143.90, 143.84, 135.97, 129.60, 129.49, 128.32, 127.00, 126.89, 126.78, 121.66, 117.38, 115.47, 114.28, 48.50, 34.64. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.74, 6.65, 3.10. **HRMS (ESI) m/z:** [(M+H)<sup>+</sup>[-H<sub>2</sub>O]] Calcd for C<sub>15</sub>H<sub>12</sub>D<sub>3</sub>NO 211.1309; Found 211.1311



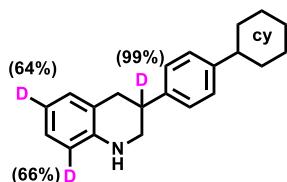
### 3-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (35)

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 118 mg, 92%, off white solid), **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.30 (d, *J* = 6.7 Hz, 2H), 7.22 (d, *J* = 6.7 Hz, 2H), 7.06 (s, 2H), 6.70 (s, 1H), 6.59 (d, *J* = 6.9 Hz, 1H), 3.91 (s, 1H), 3.41 (dd, *J* = 78.8, 10.4 Hz, 2H), 3.02 (s, 2H), 2.53 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 144.04, 143.99, 140.89, 136.46, 129.60, 127.80, 127.15, 127.07, 126.95, 126.84, 121.24, 117.19, 114.25, 34.48, 16.16. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.76, 6.64, 3.15. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>D<sub>3</sub>NS 259.1343; Found 259.1348.



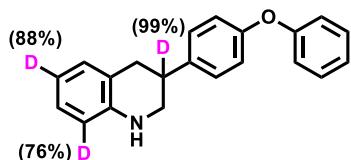
### 3-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (36)

(silica gel: 100–200 mesh, solvent system: 15% ethyl acetate/n-hexane, 133 mg, 90%, white solid, **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.32 – 7.27 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.03 (m, 2H), 6.71 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 1H), 3.48 (d, *J* = 11.1 Hz, 1H), 3.35 (d, *J* = 11.1 Hz, 1H), 3.02 (s, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**: δ 147.97, 143.98, 143.92, 142.63, 129.59, 129.49, 128.55, 127.18, 127.07, 126.95, 121.19, 120.93, 120.6 (q, *J*<sub>CD</sub> = 256.7), 117.32, 114.18, 48.14, 34.49. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.77, 6.66, 3.21. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>16</sub>H<sub>12</sub>D<sub>3</sub>F<sub>3</sub>NO 297.1289; Found 297.1286



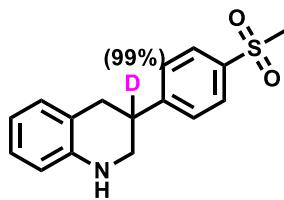
### 3-(4-cyclohexylphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (37)

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 136 mg, 93%, white crystalline solid, **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.26 (s, 4H), 7.09 (s, 2H), 6.79 – 6.70 (m, 1H), 6.63 (d, *J* = 7.4 Hz, 1H), 4.01 (s, 1H), 3.53 (d, *J* = 10.4 Hz, 1H), 3.40 (d, *J* = 10.7 Hz, 1H), 3.07 (dd, *J* = 30.0, 15.6 Hz, 1H), 2.59 (s, 1H), 1.96 (d, *J* = 17.3 Hz, 2H), 1.85 (d, *J* = 11.1 Hz, 1H), 1.51 (s, 4H), 1.36 (s, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 146.50, 144.06, 144.00, 141.12, 129.58, 129.47, 127.10, 127.05, 126.97, 126.86, 126.75, 121.55, 117.12, 114.08, 48.35, 44.20, 26.96, 26.20. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.73, 6.63, 3.14. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>23</sub>D<sub>3</sub>N 295.2248; Found 295.2249



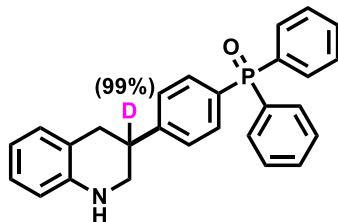
### 3-(4-phenoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3 (38)

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 136 mg, 90%, white solid, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.15 (dd, *J* = 12.7, 8.0 Hz, 5H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 4.01 (s, 1H), 3.56 (d, *J* = 11.1 Hz, 1H), 3.42 (d, *J* = 11.1 Hz, 1H), 3.22 – 3.02 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 157.49, 155.97, 144.09, 138.85, 129.88, 129.66, 129.56, 128.55, 127.03, 126.92, 123.30, 121.32, 119.18, 118.90, 117.21, 48.47, 34.77. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.81, 6.68, 3.21. **HRMS (ESI) m/z:** (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>17</sub>D<sub>3</sub>NO 305.1728; Found 305.1733



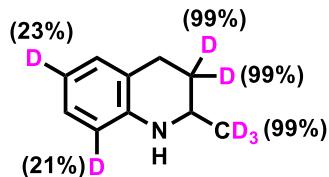
### 3-(4-(methylsulfonyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d (39)

(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 118 mg, 82%, light reddish brown solid),  **$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J$  = 7.1 Hz, 2H), 7.44 (d,  $J$  = 7.1 Hz, 2H), 7.10 – 6.97 (m, 2H), 6.68 (s, 1H), 6.57 (d,  $J$  = 7.2 Hz, 1H), 4.20 (s, 1H), 3.49 (d,  $J$  = 10.8 Hz, 1H), 3.36 (d,  $J$  = 10.7 Hz, 1H), 3.05 (s, 3H), 3.02 (s, 2H).  **$^{13}\text{C}$  NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta$  150.36, 143.68, 138.87, 129.54, 128.30, 127.73, 127.28, 120.44, 117.56, 114.31, 47.65, 44.56, 34.07.  **$^2\text{H}$  NMR** (92 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.27. **HRMS** (ESI) m/z: ( $\text{M}+\text{H}$ )<sup>+</sup> Calcd for  $\text{C}_{16}\text{H}_{17}\text{DNO}_2\text{S}$  289.1116; Found 289.1123



diphenyl(4-(1,2,3,4-tetrahydroquinolin-3-yl-3-d)phenyl)phosphine oxide (40)

(silica gel: 100–200 mesh, solvent system: 80% ethyl acetate/n-hexane, 174 mg, 85%, white solid),  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.60 (m, 6H), 7.55 (d,  $J$  = 6.5 Hz, 2H), 7.48 (s, 4H), 7.34 (d,  $J$  = 6.0 Hz, 2H), 7.02 (d,  $J$  = 6.9 Hz, 2H), 6.66 (t,  $J$  = 6.9 Hz, 1H), 6.57 (d,  $J$  = 7.6 Hz, 1H), 4.14 (s, 1H), 3.45 (d,  $J$  = 11.0 Hz, 1H), 3.32 (d,  $J$  = 11.0 Hz, 1H), 3.00 (s, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.25, 143.91, 133.10, 132.49, 132.39, 132.14, 132.05, 131.99, 131.97, 129.50, 128.60, 128.48, 127.59, 127.46, 127.13, 120.74, 117.21, 114.20, 47.78, 34.24.  **$^2\text{H}$  NMR** (92 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.17. **HRMS** (ESI) m/z: (M+K)<sup>+</sup> Calcd for  $\text{C}_{27}\text{H}_{23}\text{DNOPK}$  449.1290; Found 449.1296



### 2-(methyl-d<sub>3</sub>)-1,2,3,4-tetrahydroquinoline-3,3,6,8-d<sub>4</sub> (41)

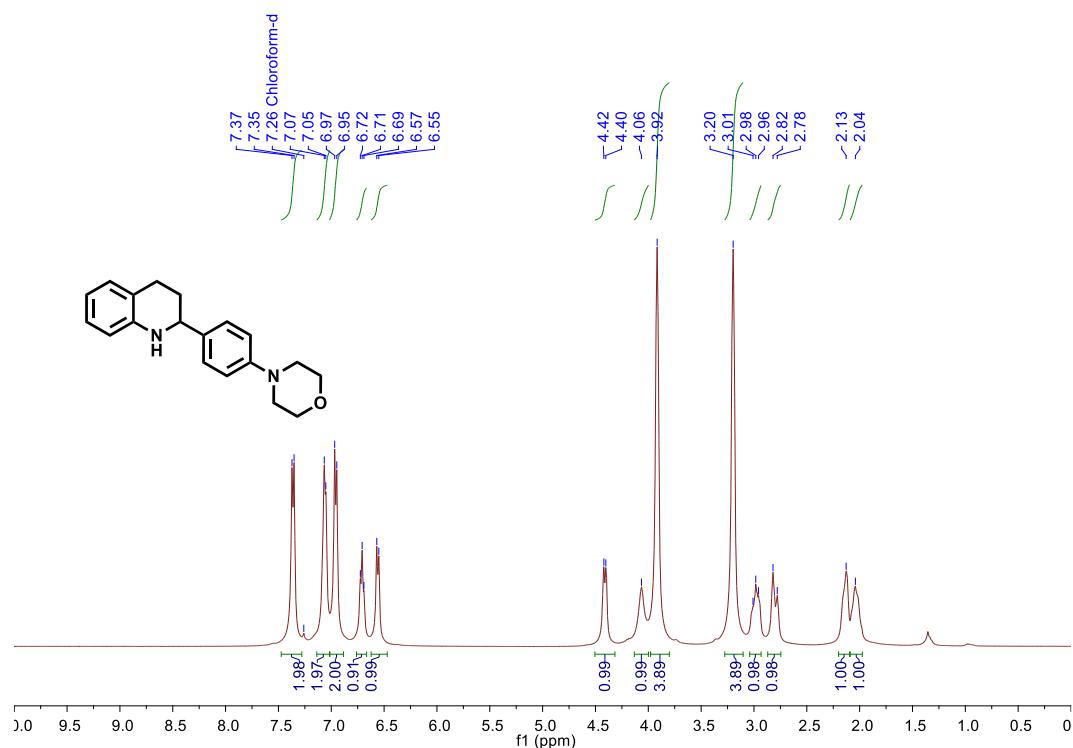
(silica gel: 100–200 mesh, solvent system: 10% ethyl acetate/n-hexane, 73 mg, 95%, yellow oil). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**: δ 7.04 – 6.96 (m, 2H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.53 – 6.46 (m, 1H), 3.64 (s, 1H), 3.45 – 3.35 (m, 1H), 2.90 – 2.81 (m, 1H), 2.79 – 2.69 (m, 1H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**: δ 144.84, 129.33, 126.72, 121.15, 117.01, 114.04, 46.87, 26.42. **<sup>2</sup>H NMR (92 MHz, CHCl<sub>3</sub>)**: δ 6.70, 6.56, 1.95, 1.61, 1.22.

## References:

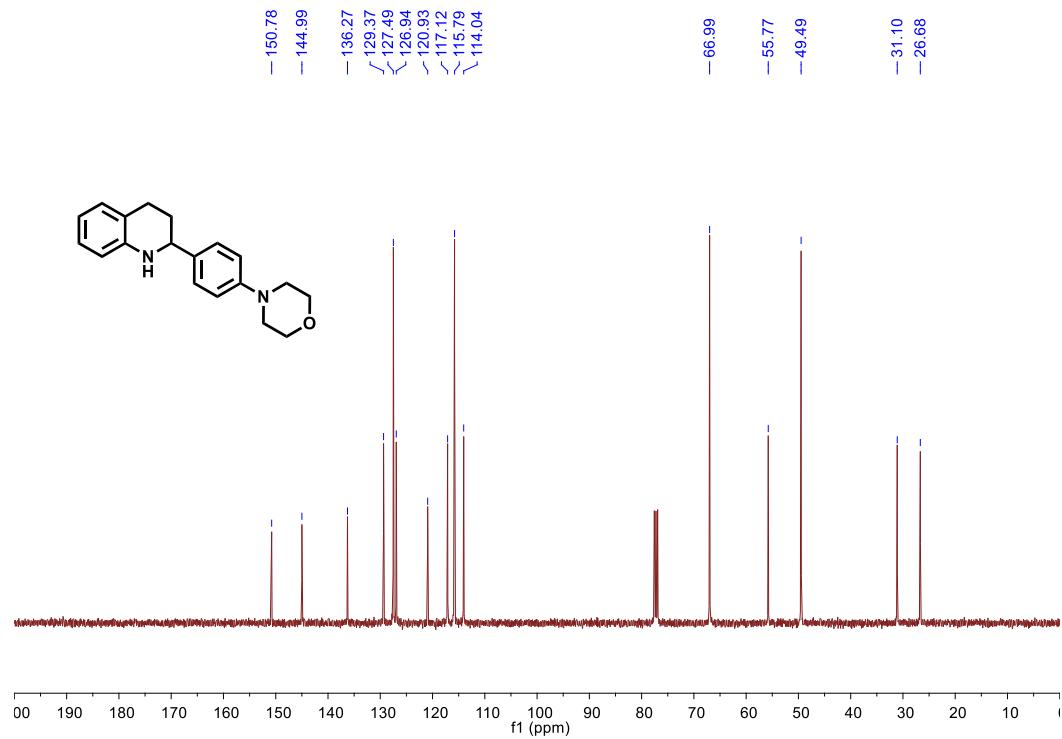
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## 10. NMR Spectra of Isolated Products:

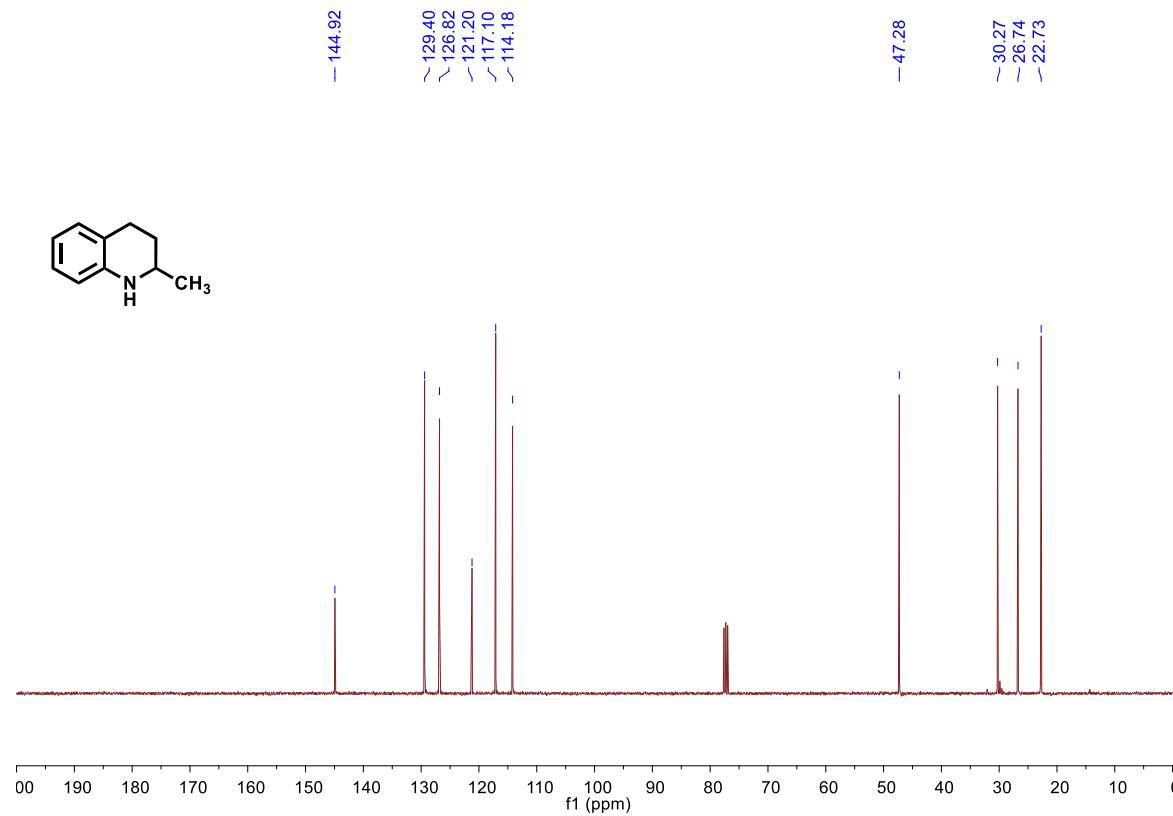
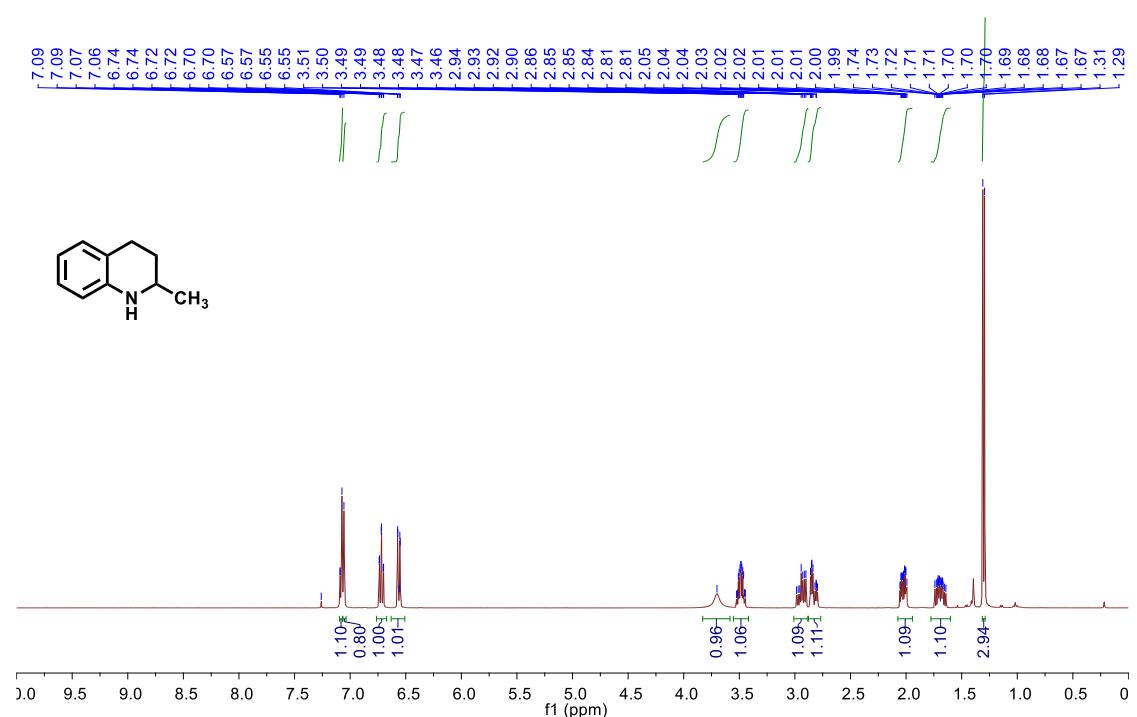
**Figure S26.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl)phenyl)morpholine (1)



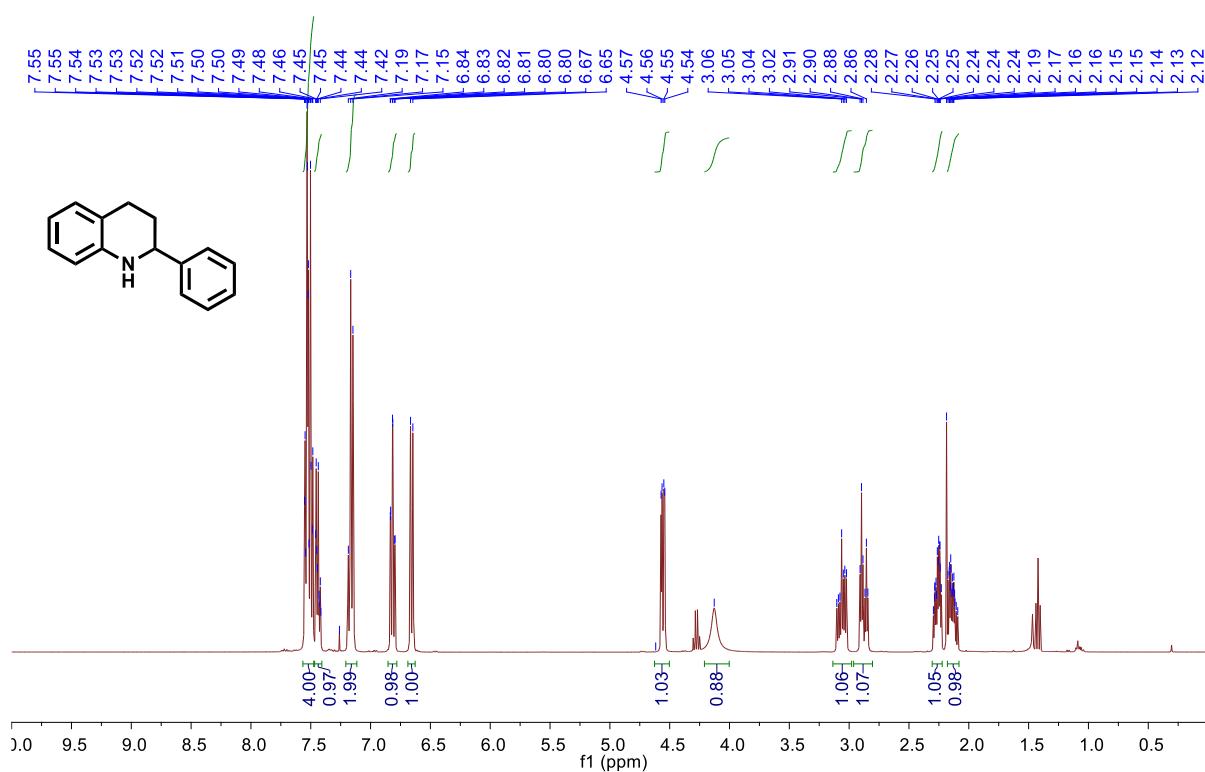
**Figure S27.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 4-(4-(1,2,3,4-tetrahydroquinolin-2-yl)phenyl)morpholine (1)



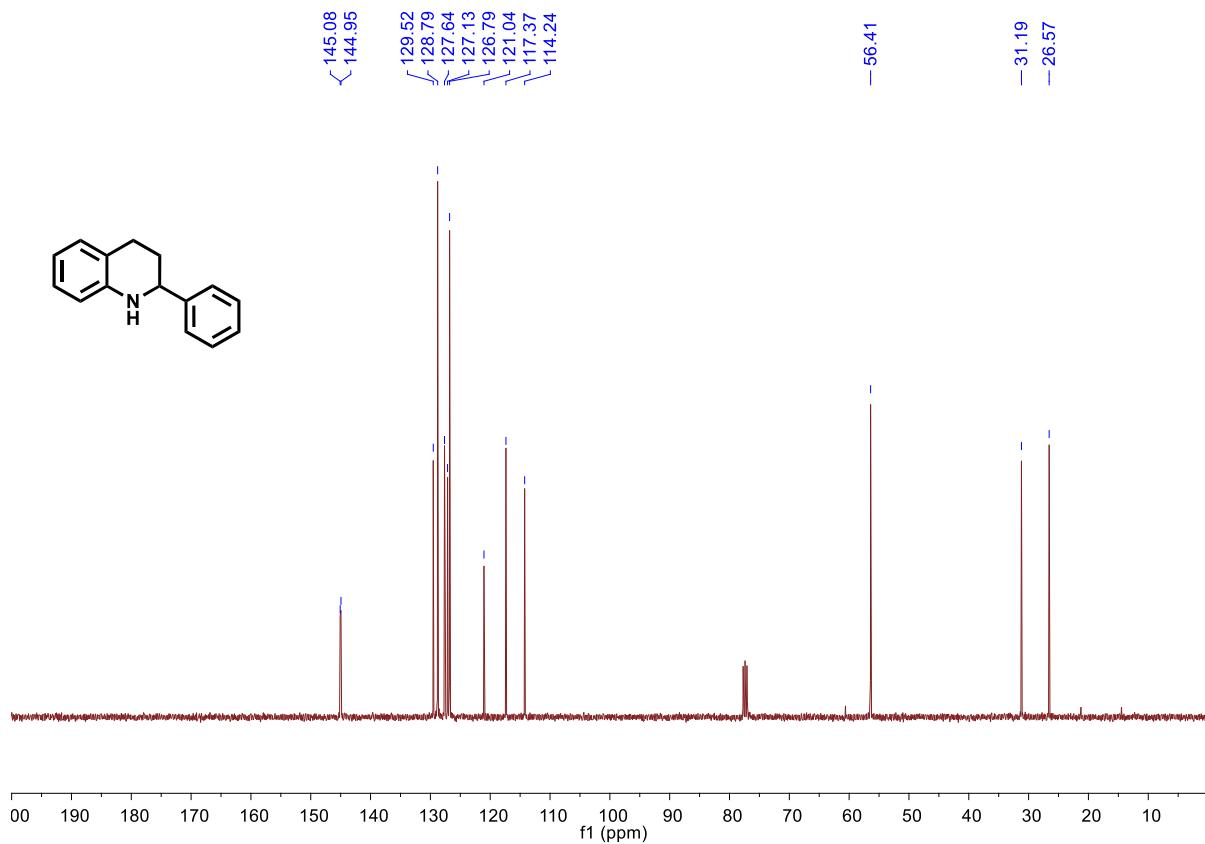
**Figure S28.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2-methyl-1,2,3,4-tetrahydroquinoline



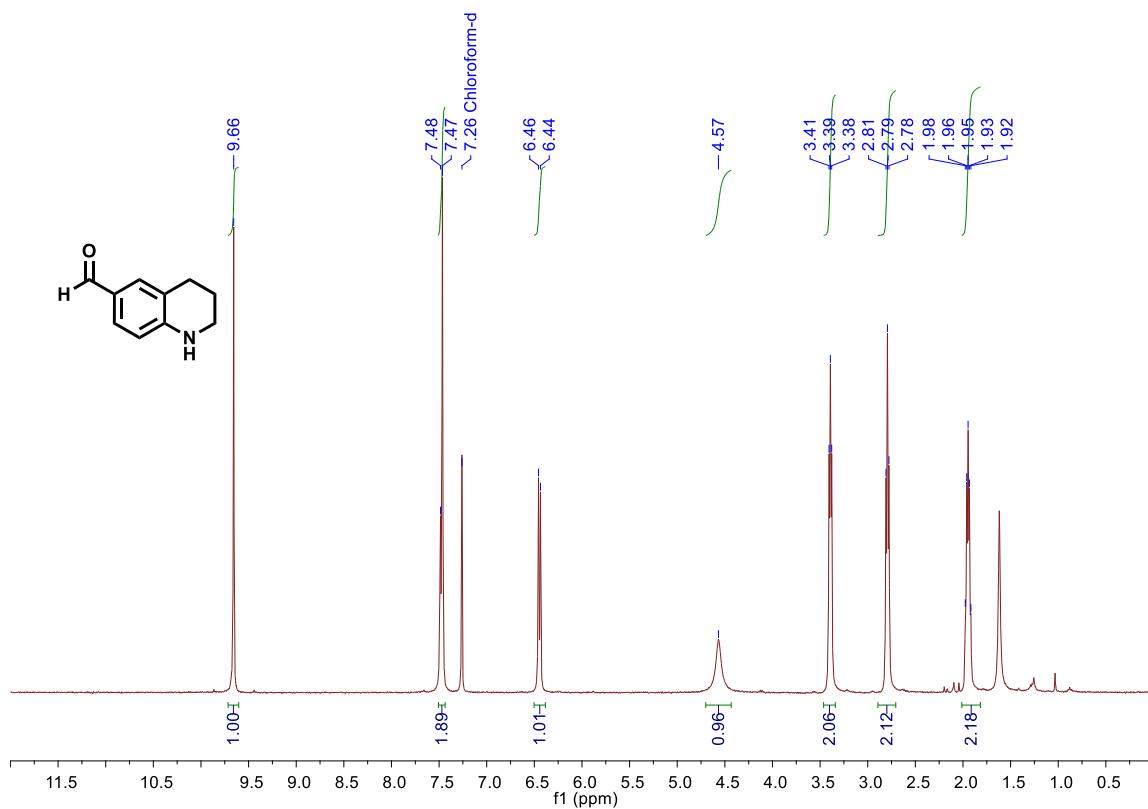
**Figure S30.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2-phenyl-1,2,3,4-tetrahydroquinoline



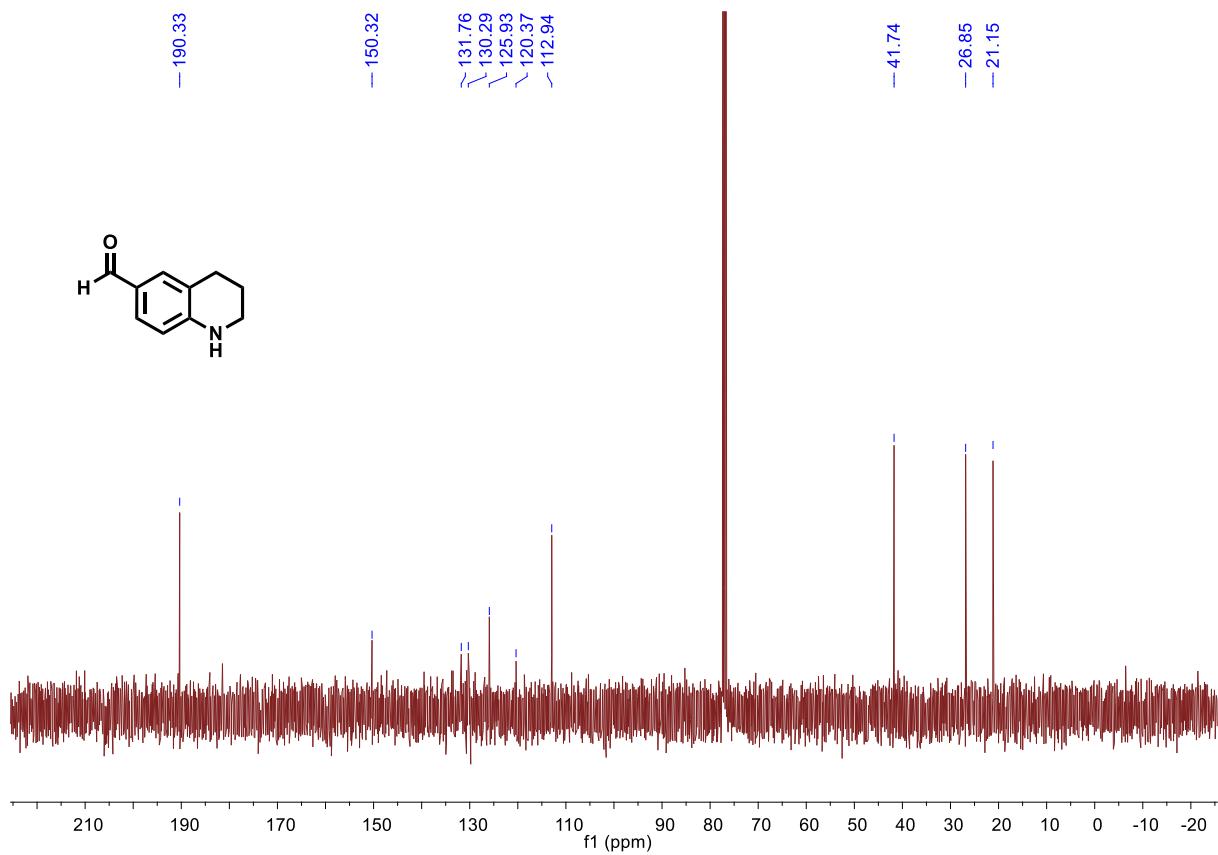
**Figure S31.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 2-phenyl-1,2,3,4-tetrahydroquinoline



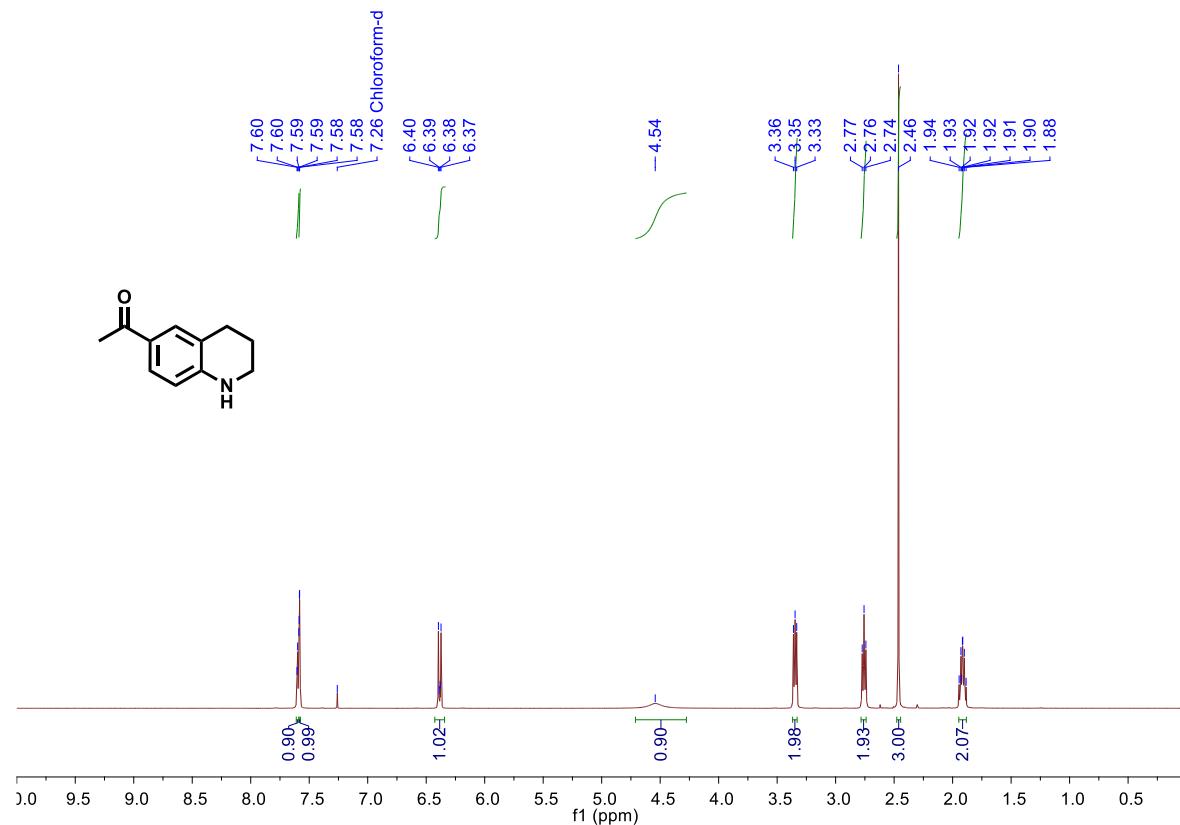
**Figure S32.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 1,2,3,4-tetrahydroquinoline-6-carbaldehyde (2)



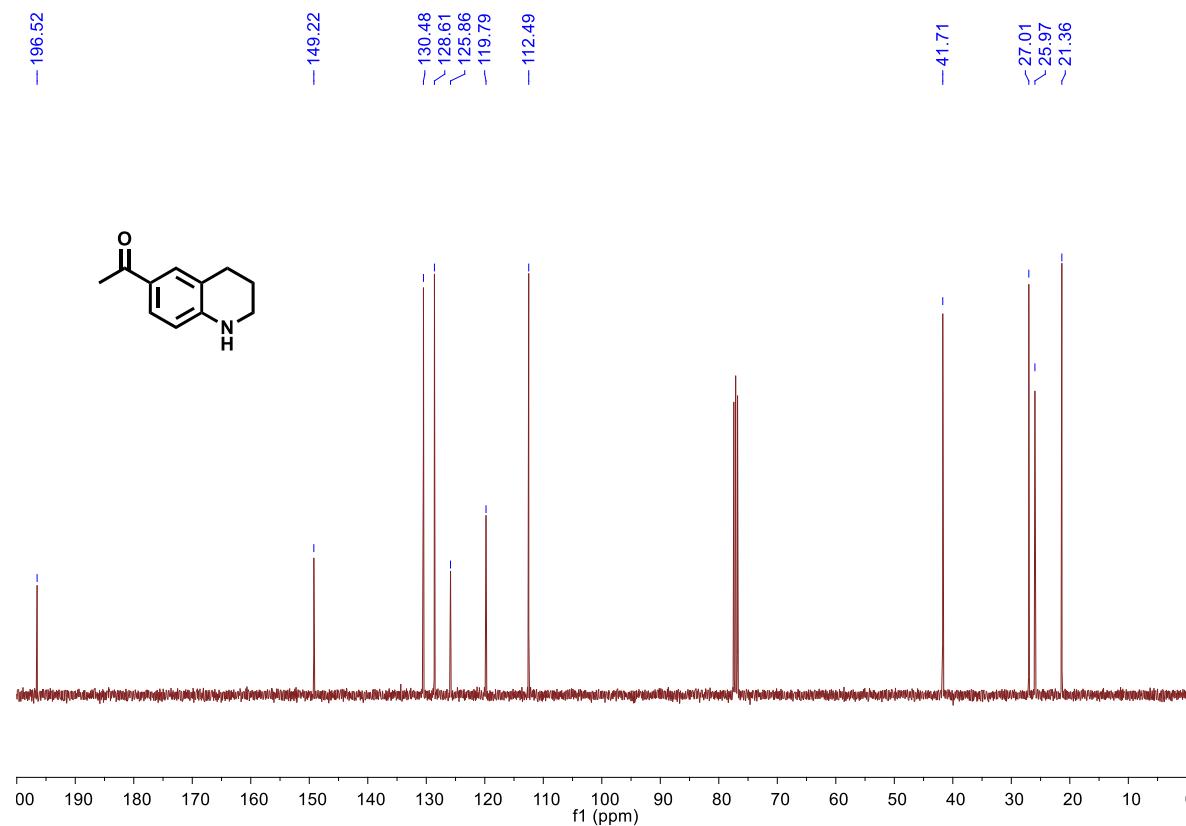
**Figure S33.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 1,2,3,4-tetrahydroquinoline-6-carbaldehyde



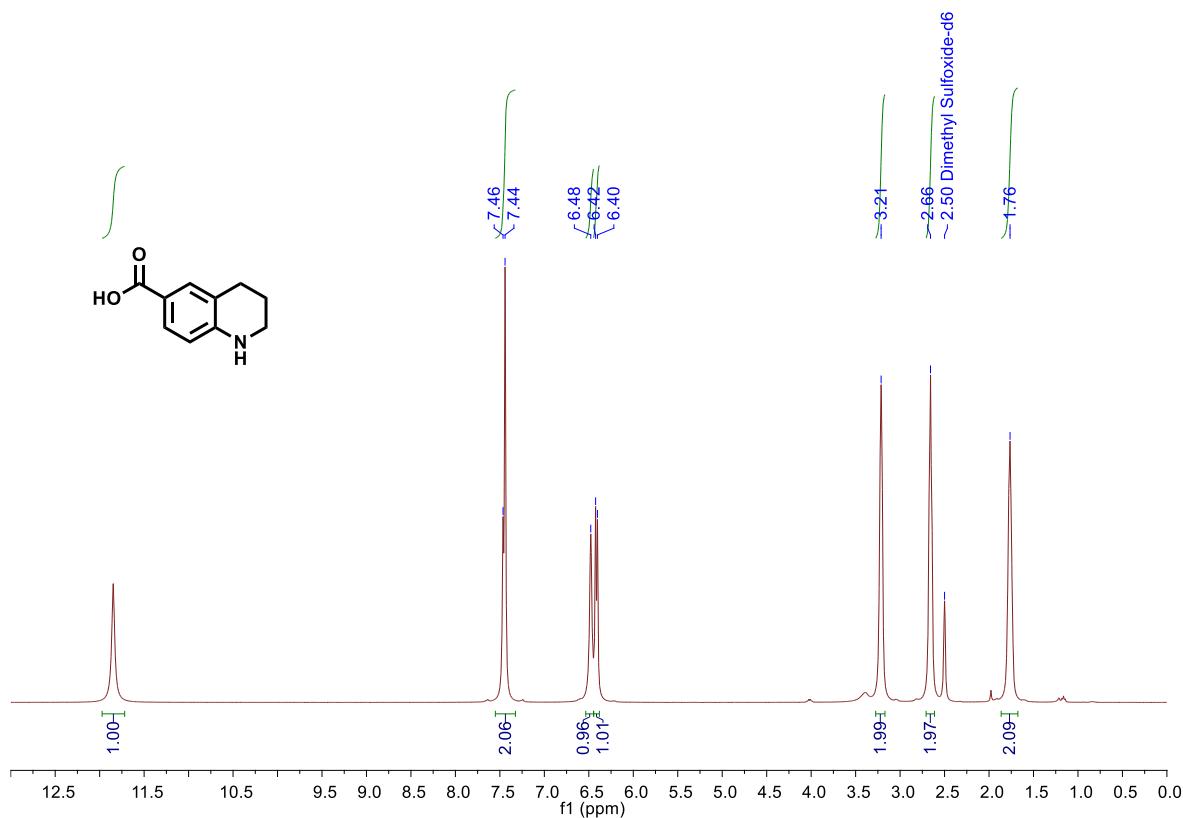
**Figure S34.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 1-(1,2,3,4-tetrahydroquinolin-6-yl)ethan-1-one



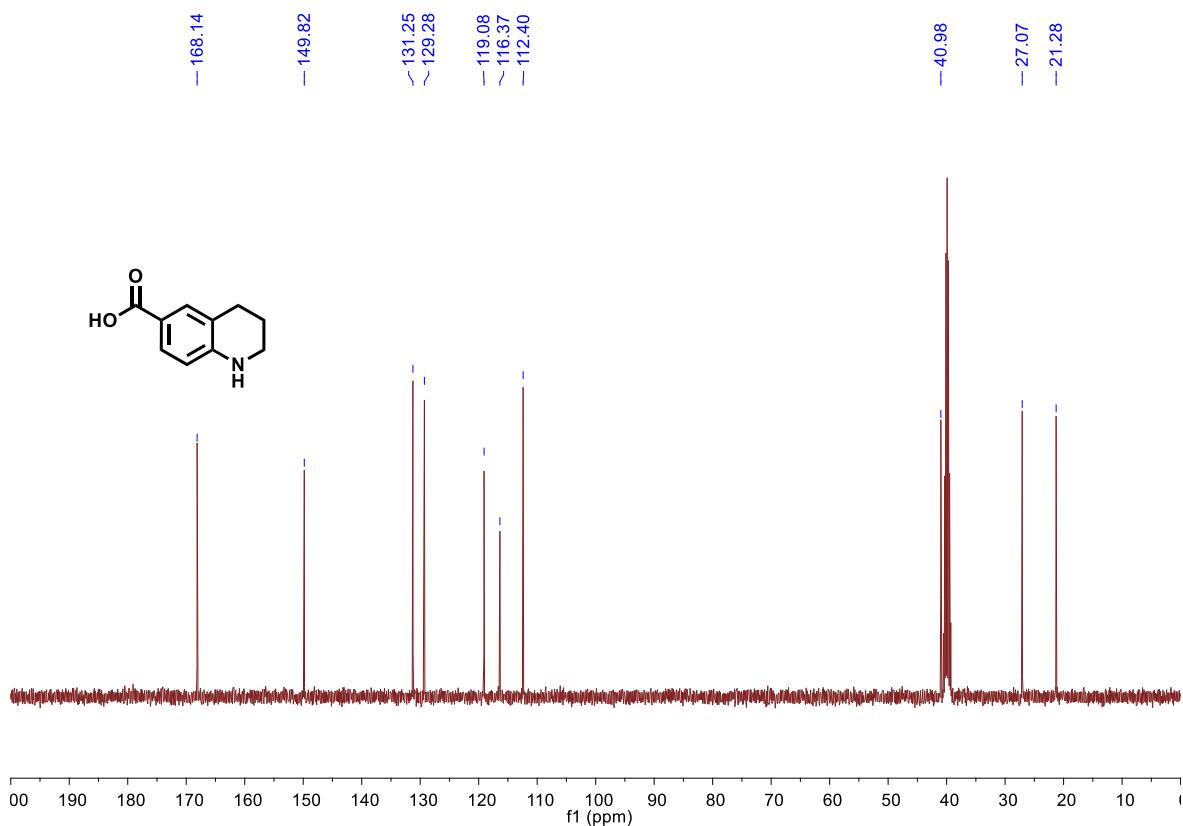
**Figure S35.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 1-(1,2,3,4-tetrahydroquinolin-6-yl)ethan-1-one



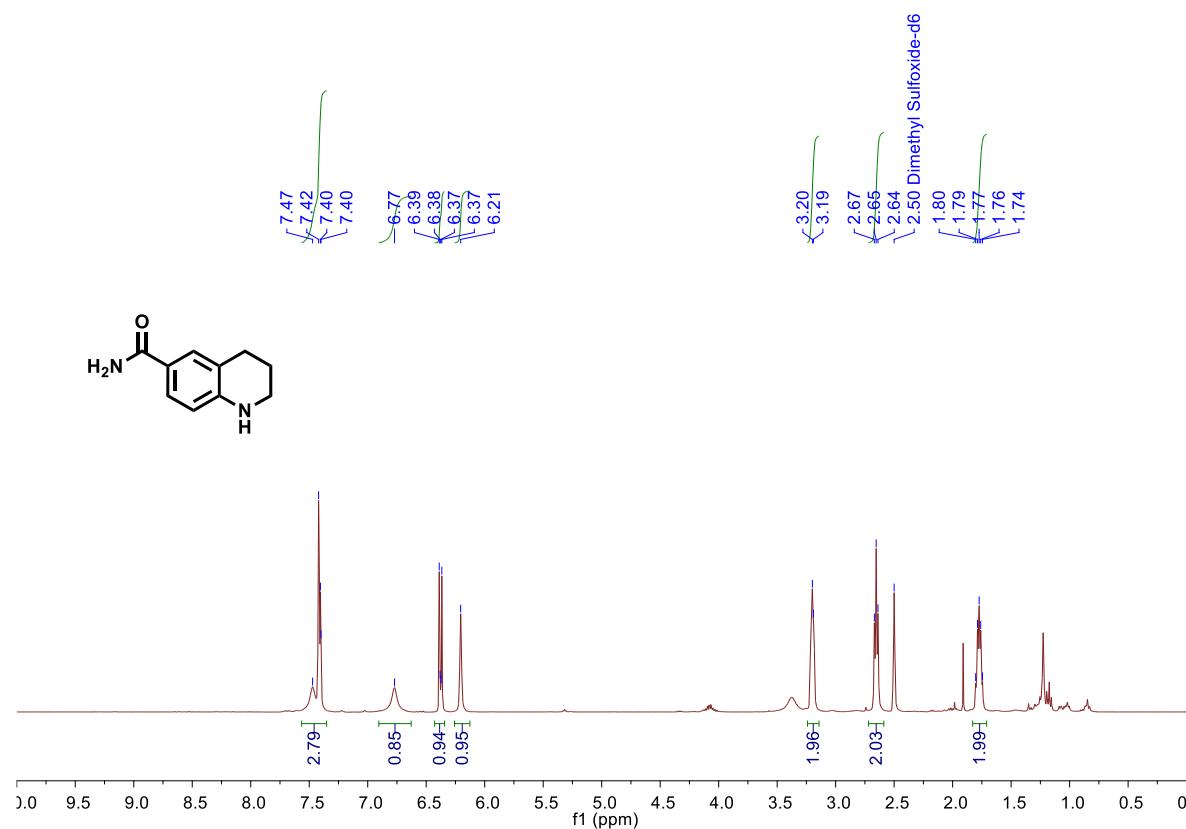
**Figure S36.**  $^1\text{H}$  NMR (400 MHz, DMSO) 1,2,3,4-tetrahydroquinoline-6-carboxylic acid



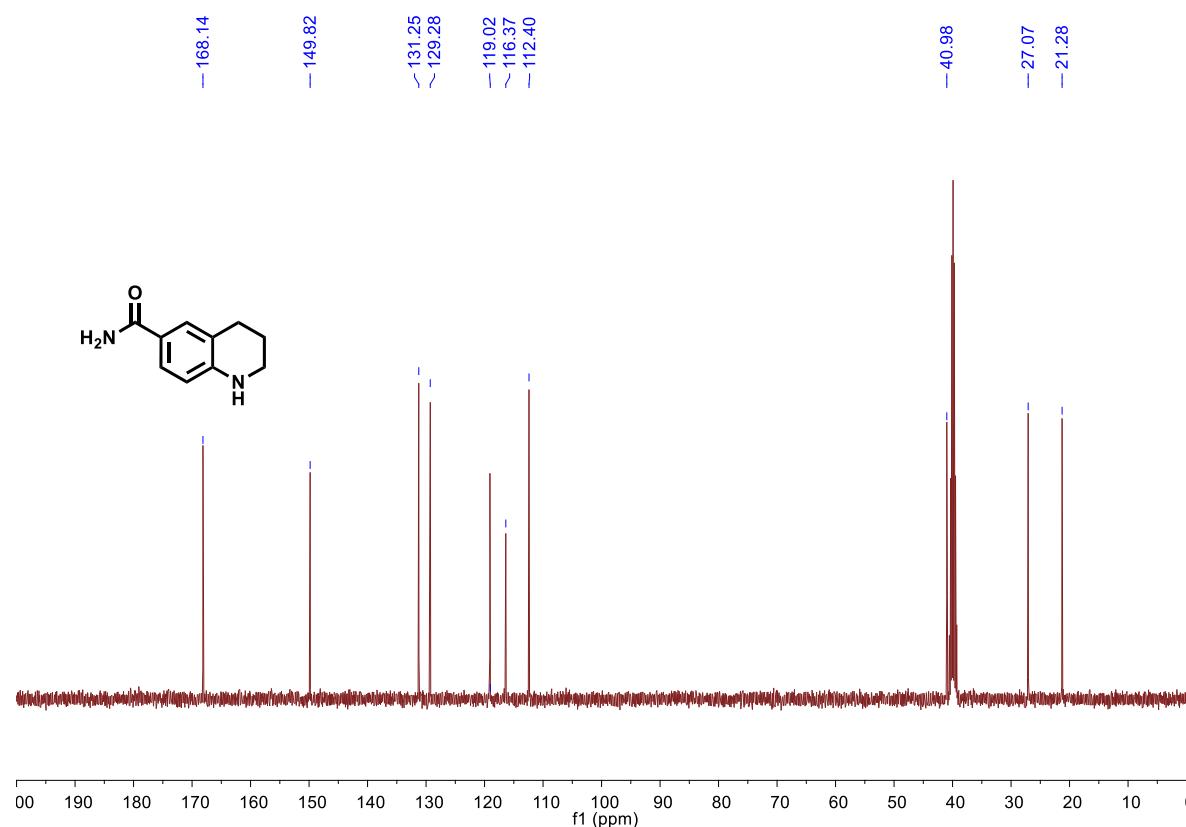
**Figure S37.**  $^{13}\text{C}$  NMR (101 MHz, DMSO) 1,2,3,4-tetrahydroquinoline-6-carboxylic acid



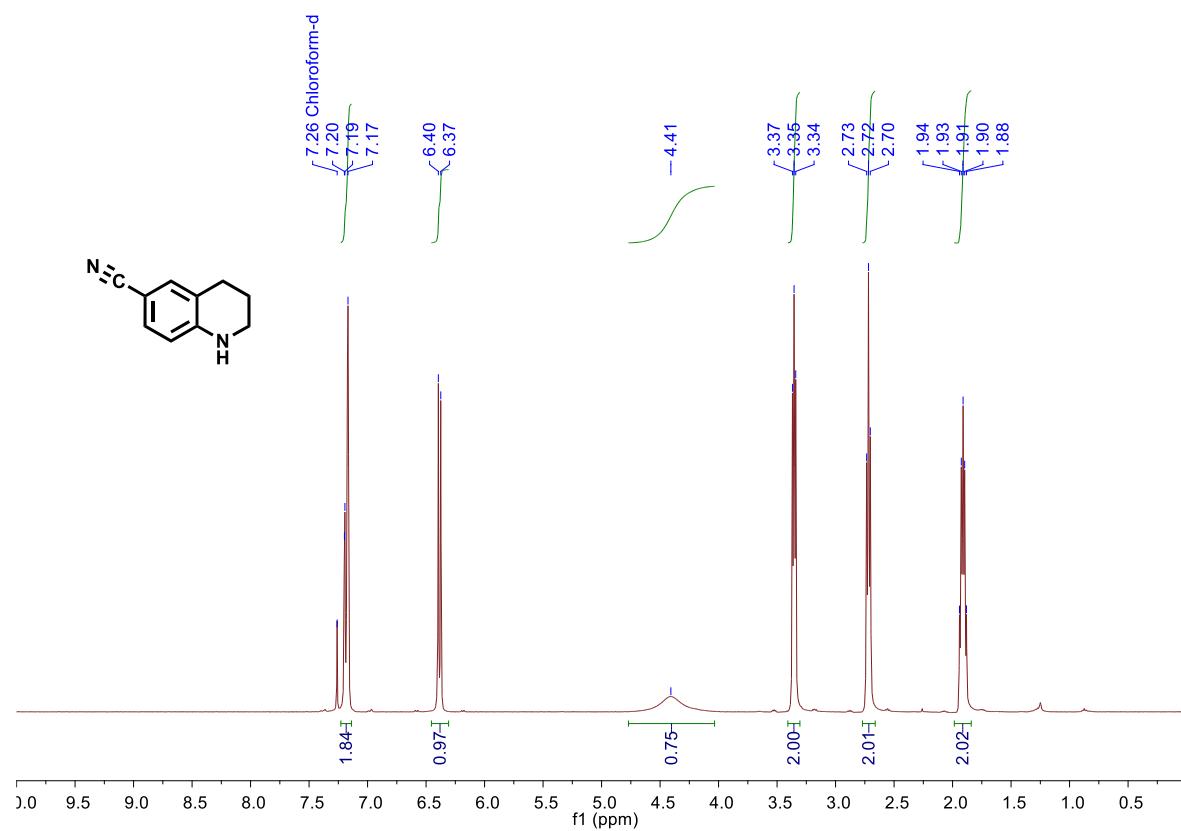
**Figure S38.**  $^1\text{H}$  NMR (400 MHz, DMSO) 1,2,3,4-tetrahydroquinoline-6-carboxamide:



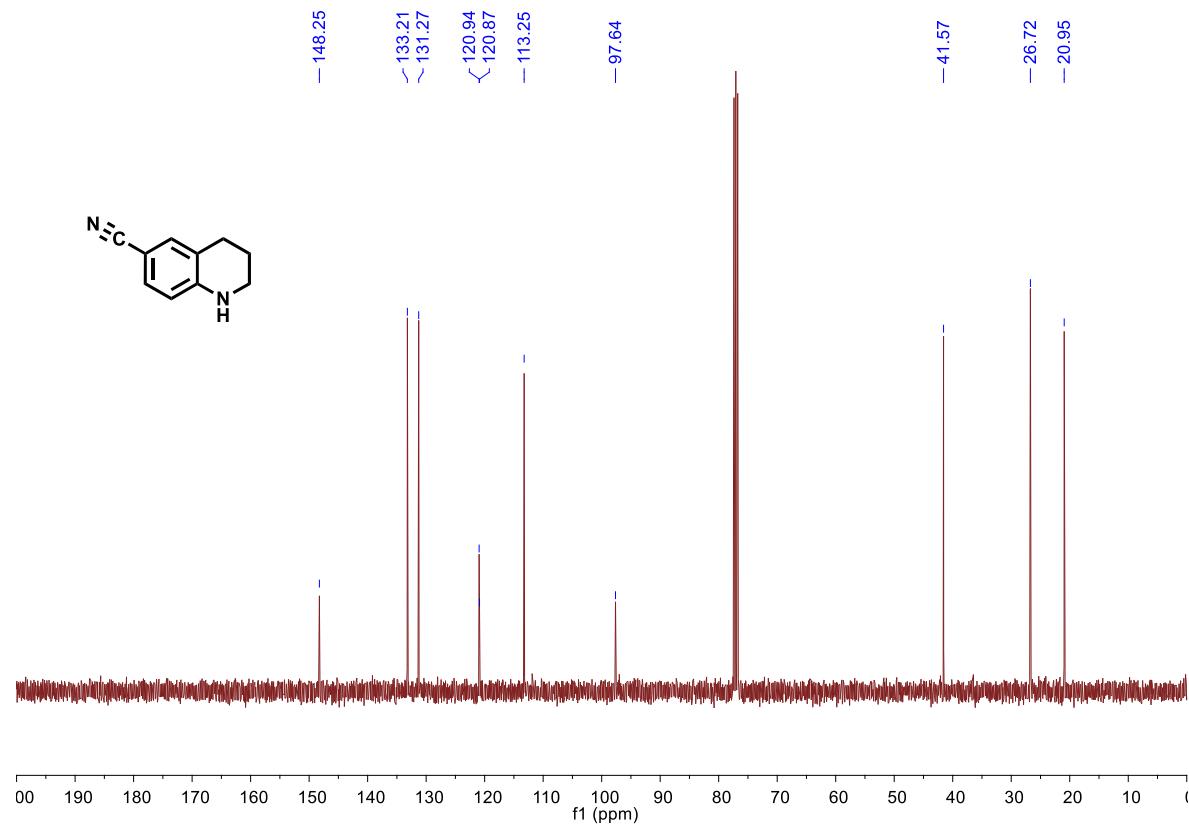
**Figure S39.**  $^{13}\text{C}$  NMR (101 MHz, DMSO) 1,2,3,4-tetrahydroquinoline-6-carboxamide:



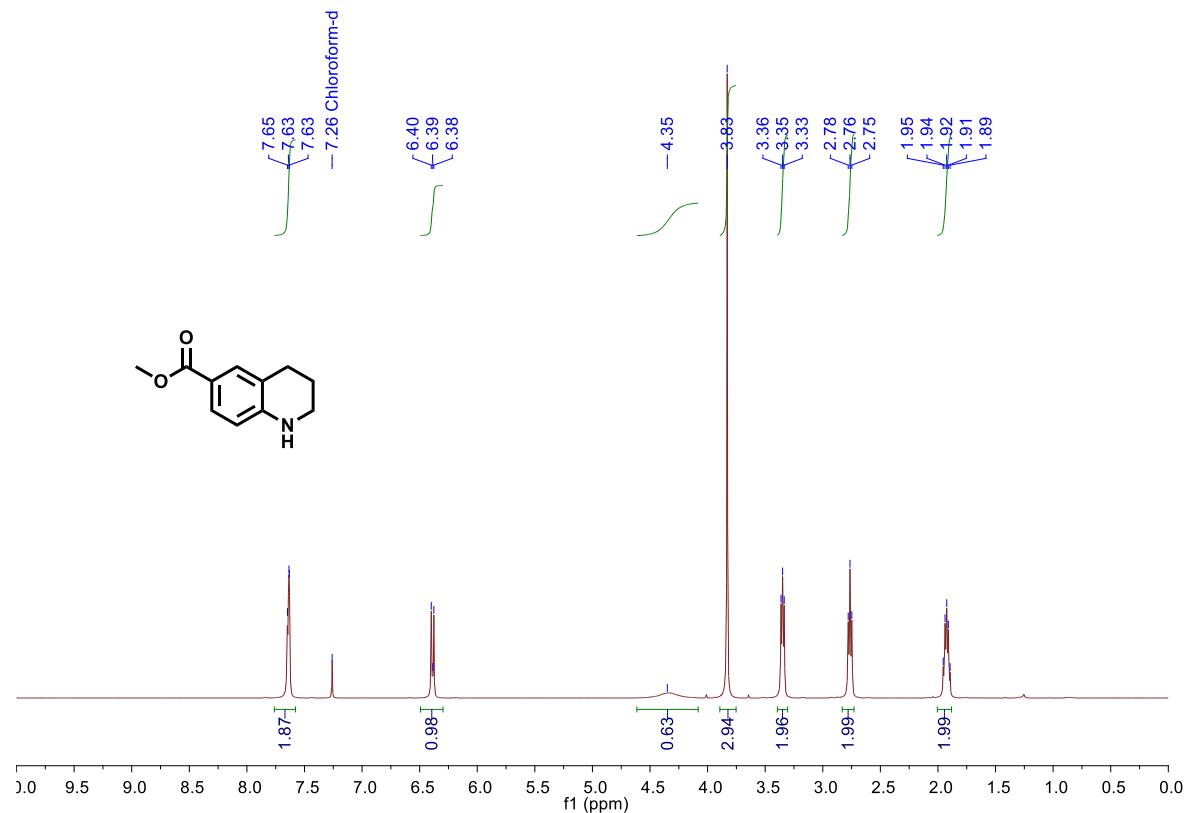
**Figure S40.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 1,2,3,4-tetrahydroquinoline-6-carbonitrile



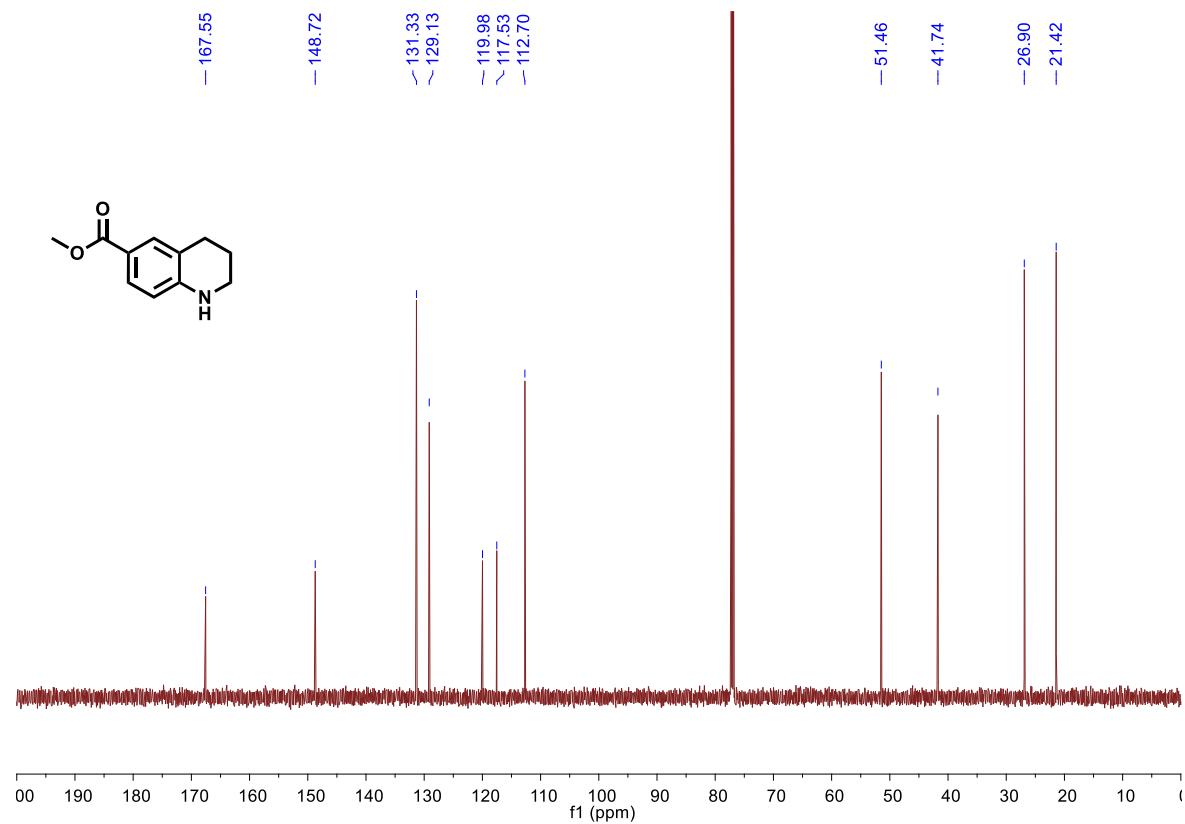
**Figure S41.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 1,2,3,4-tetrahydroquinoline-6-carbonitrile



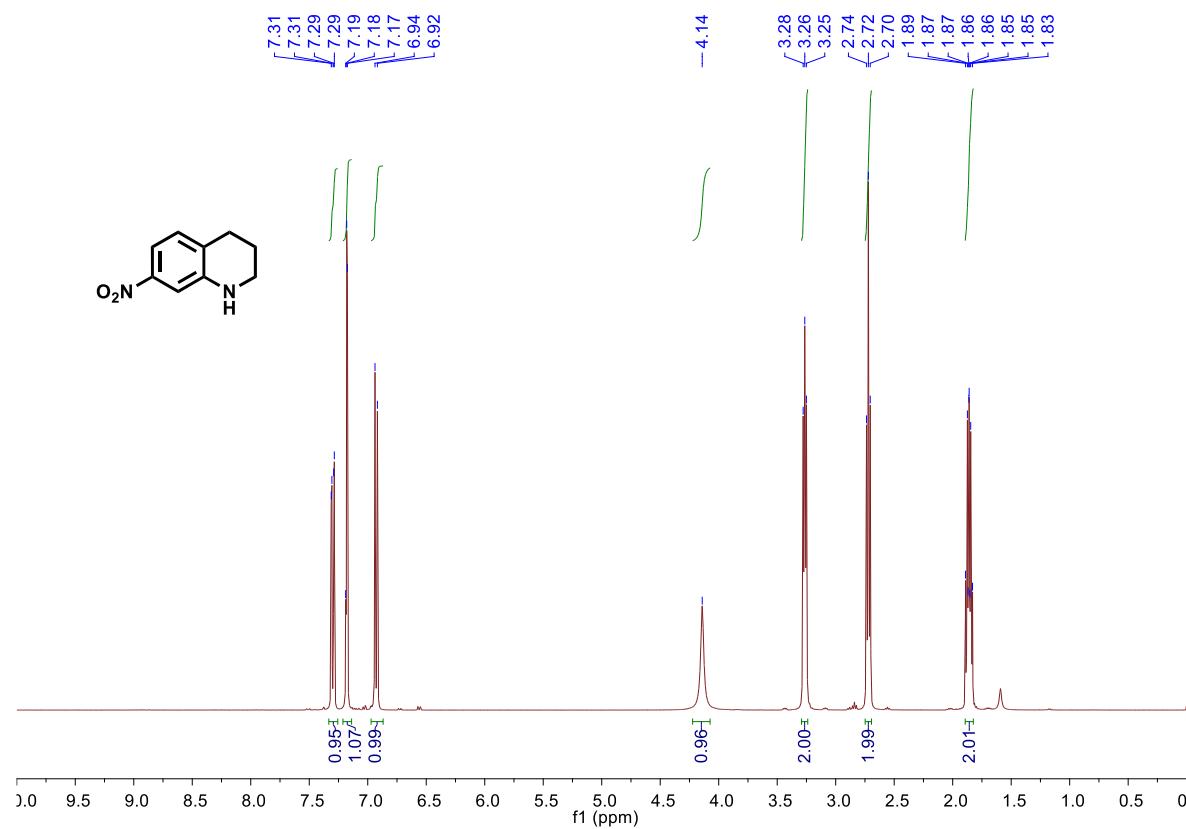
**Figure S42.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate



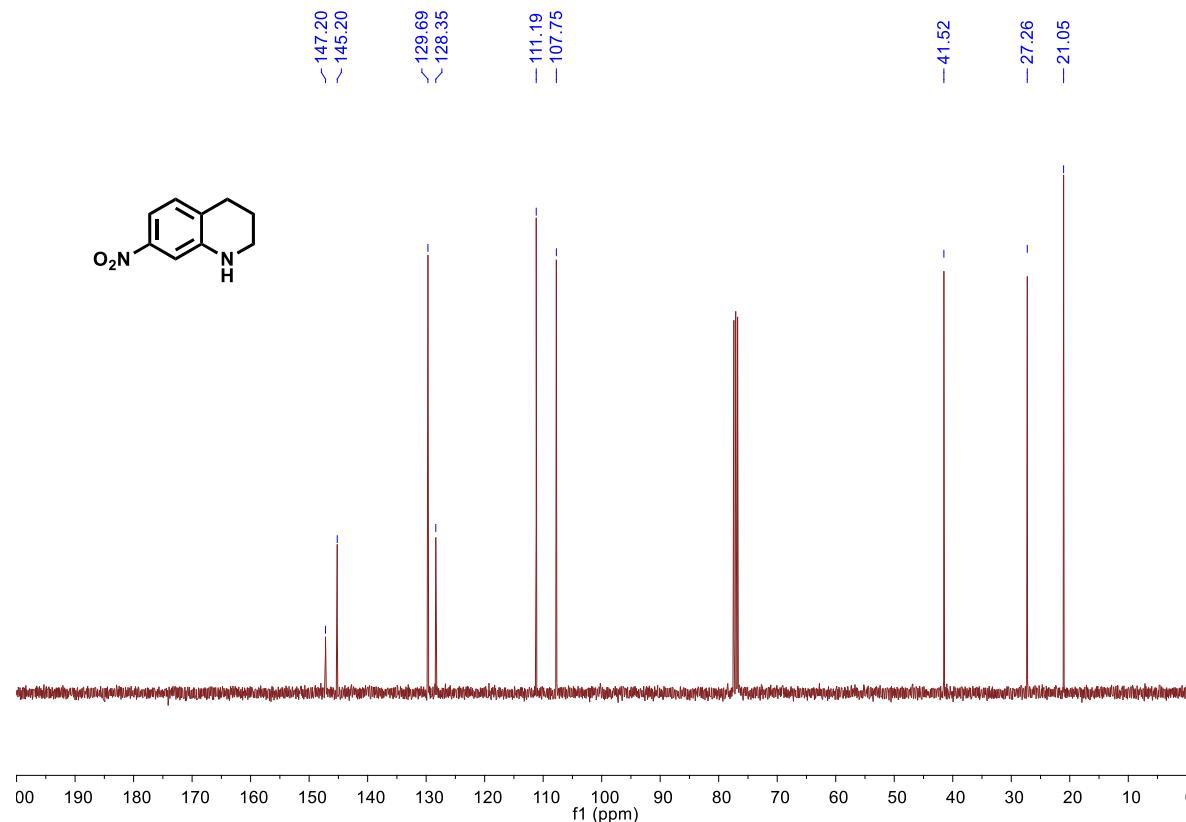
**Figure S43.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate



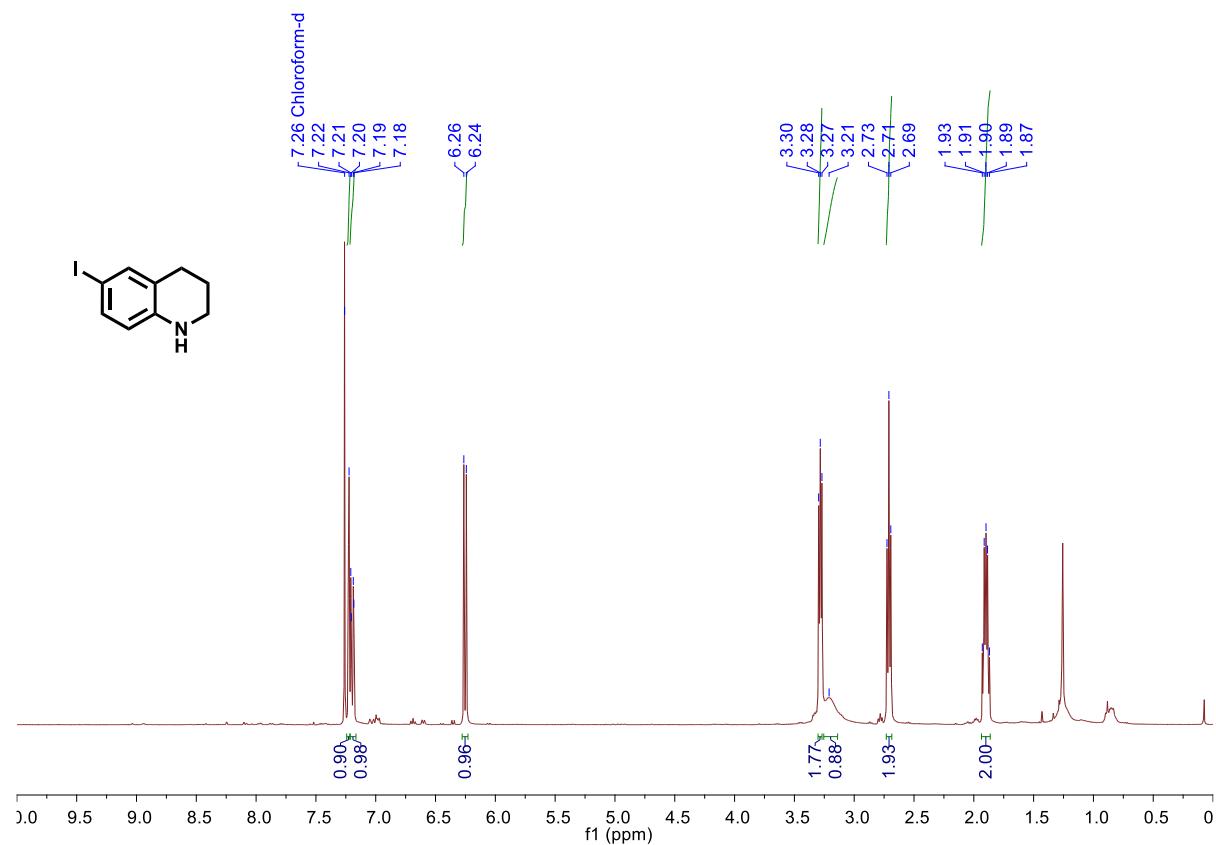
**Figure S44.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7-nitro-1,2,3,4-tetrahydroquinoline



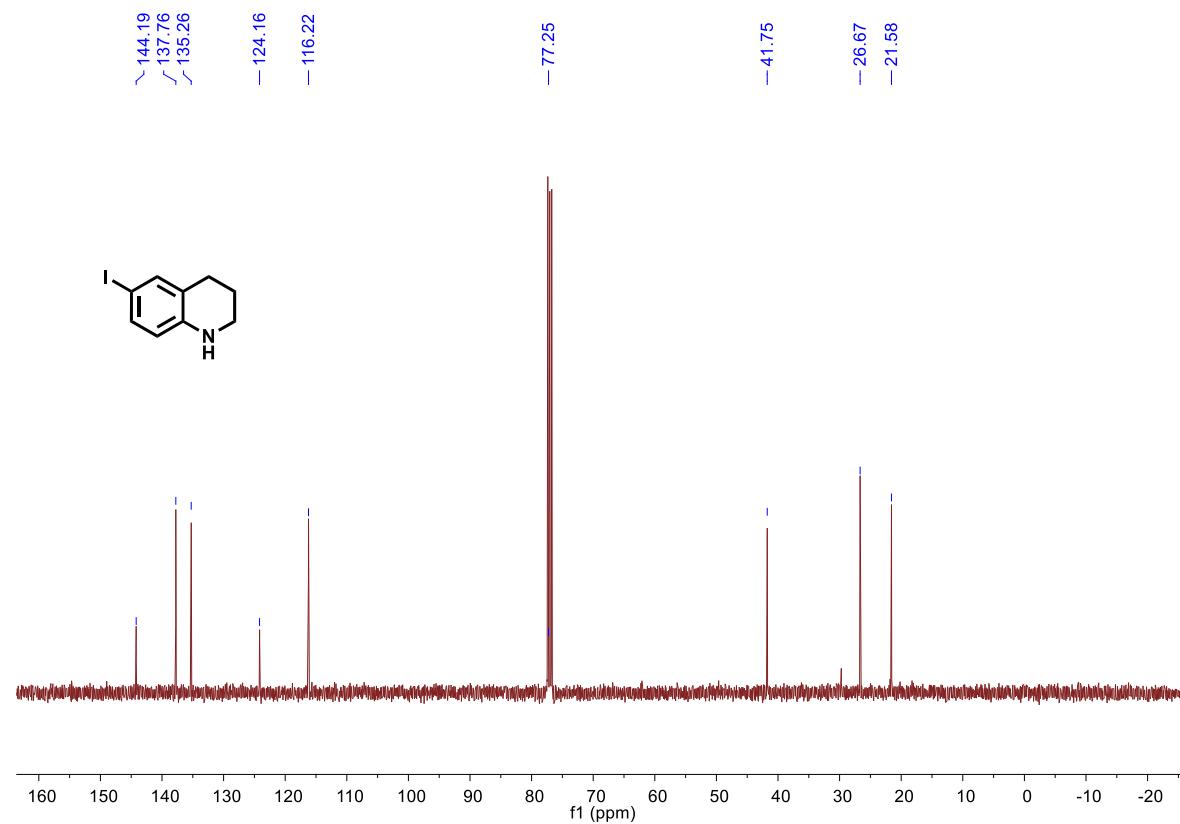
**Figure S45.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 7-nitro-1,2,3,4-tetrahydroquinoline



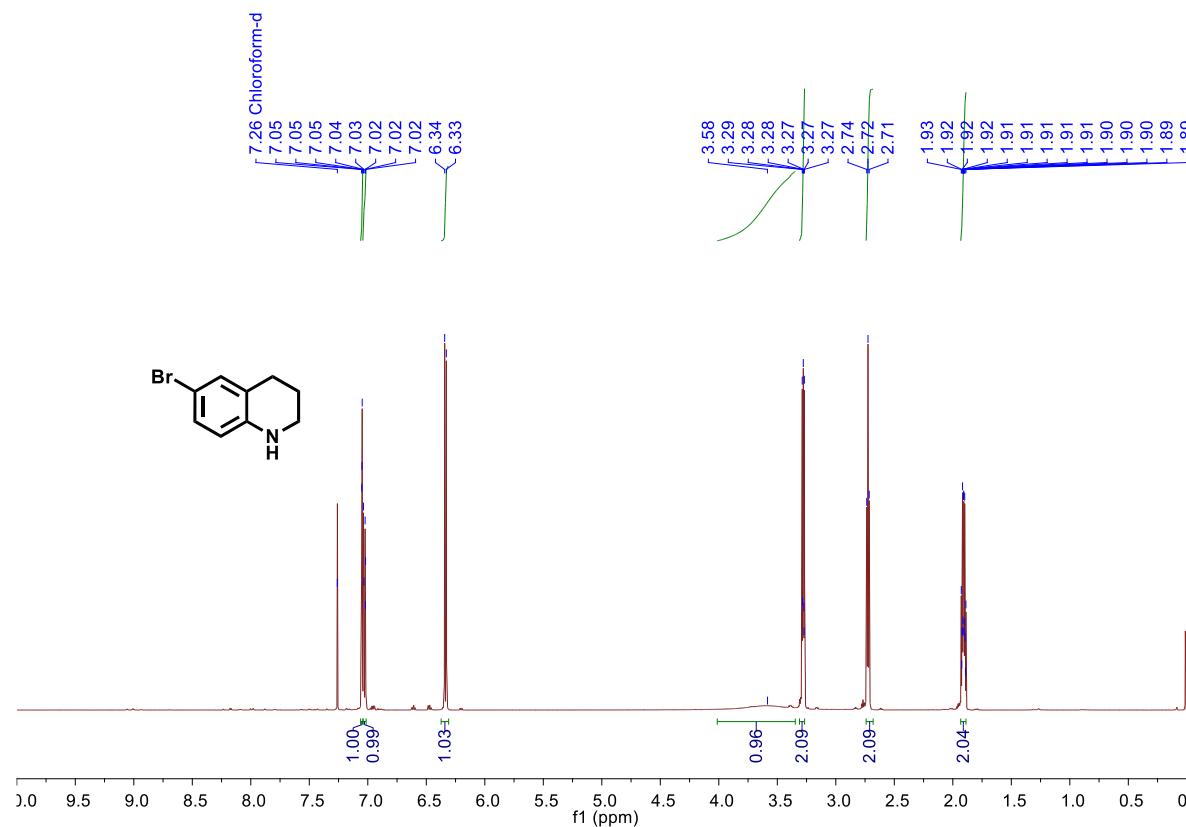
**Figure S46.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 6-iodo-1,2,3,4-tetrahydroquinoline



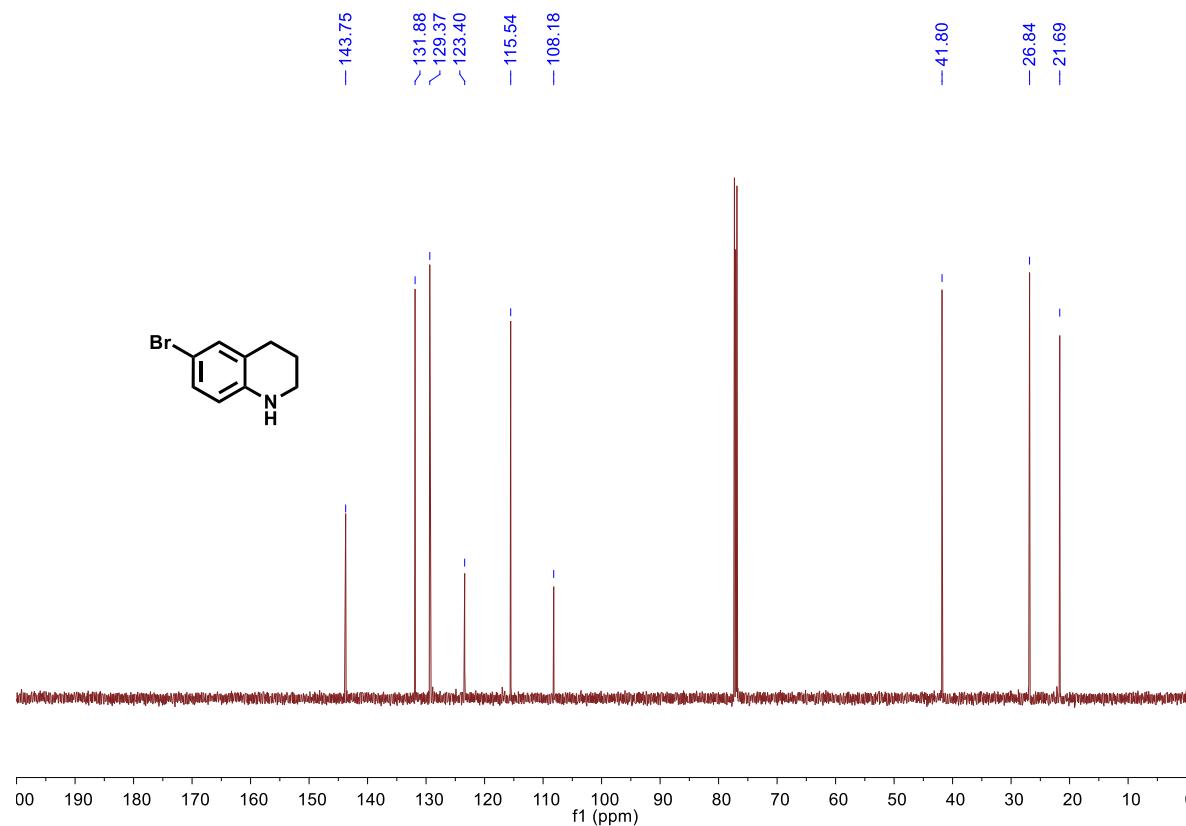
**Figure S47.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 6-iodo-1,2,3,4-tetrahydroquinoline



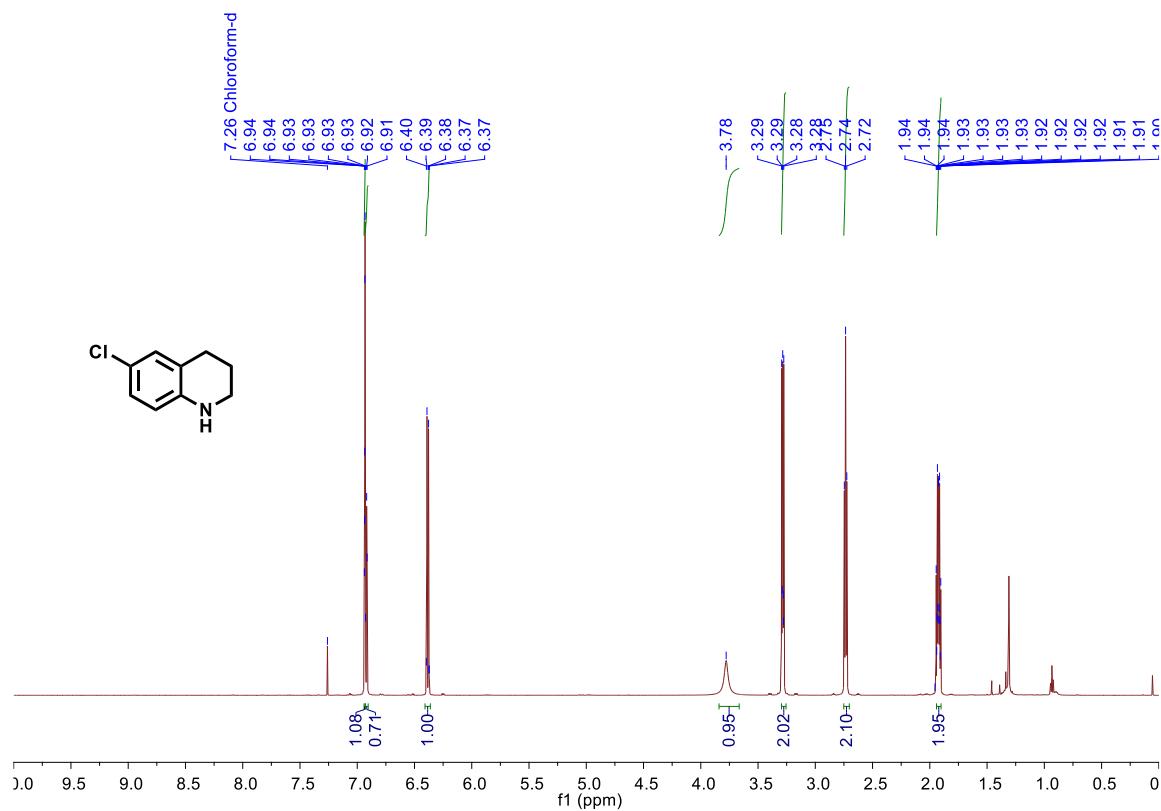
**Figure S48.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) 6-bromo-1,2,3,4-tetrahydroquinoline



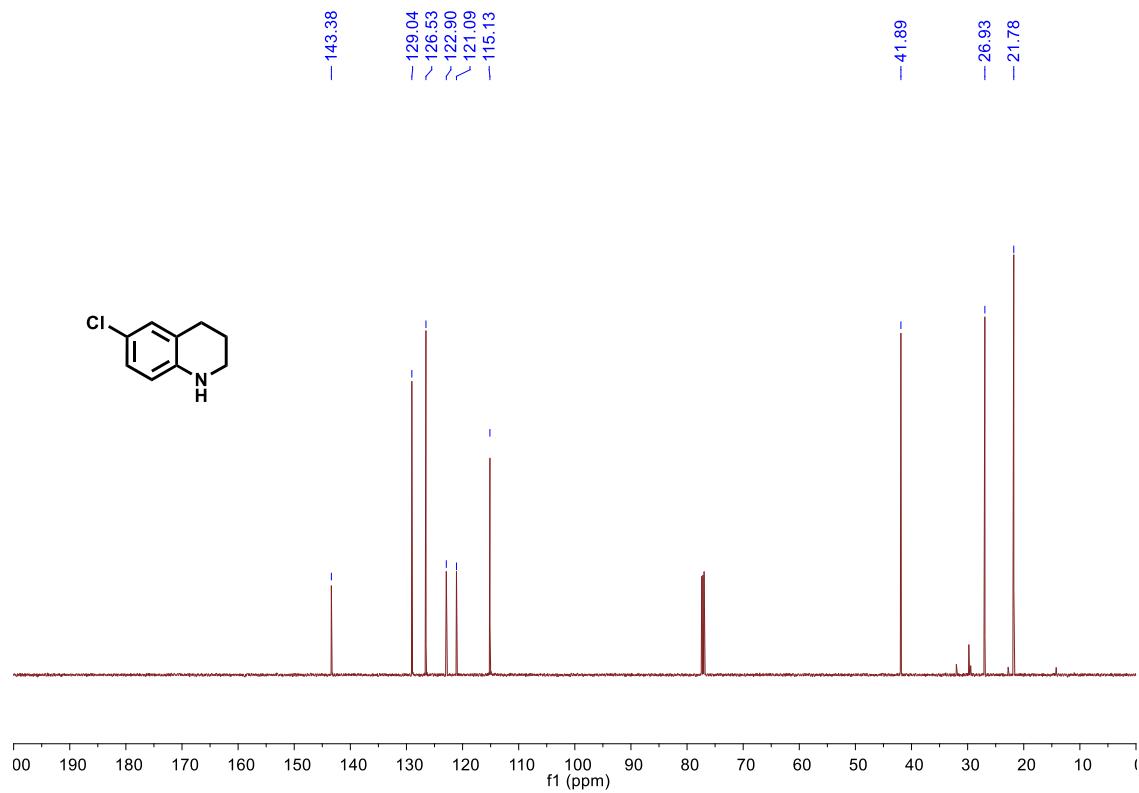
**Figure S49.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) 6-bromo-1,2,3,4-tetrahydroquinoline



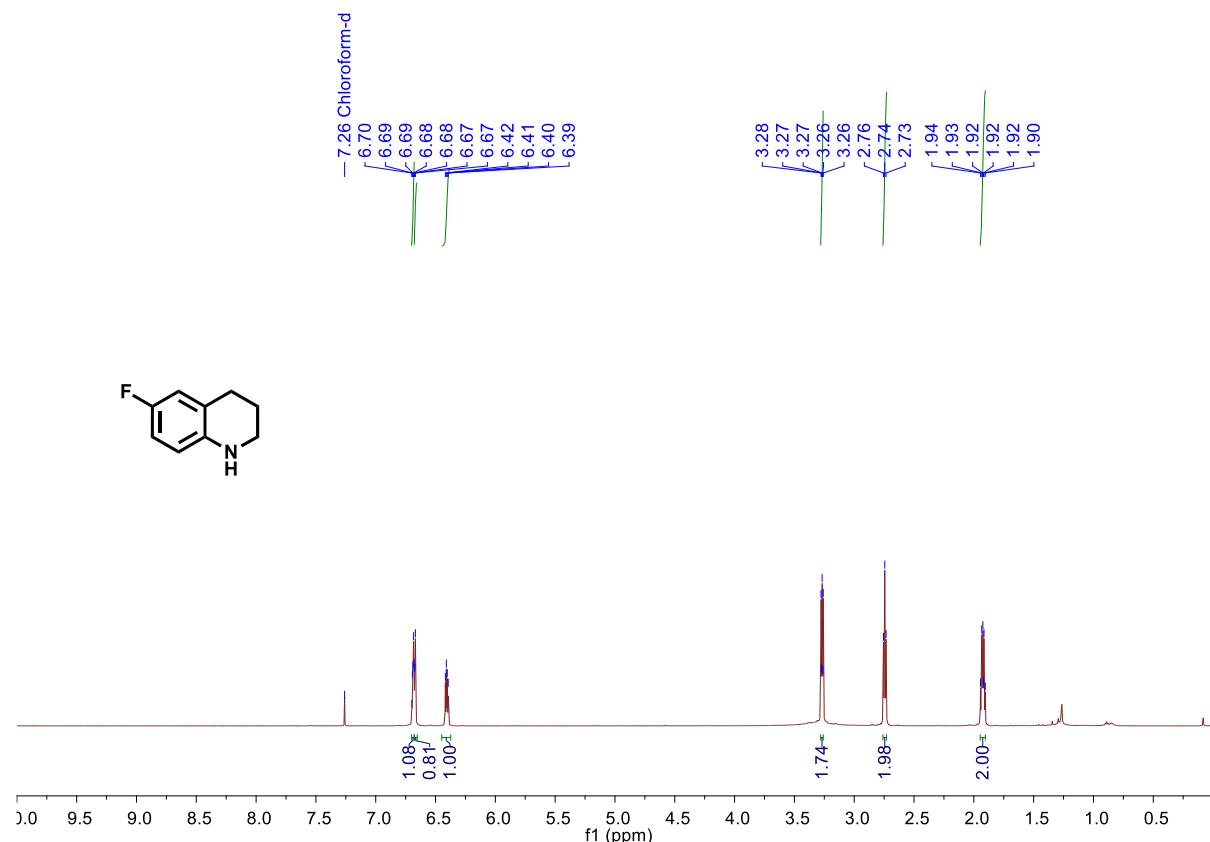
**Figure S50.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 6-chloro-1,2,3,4-tetrahydroquinoline



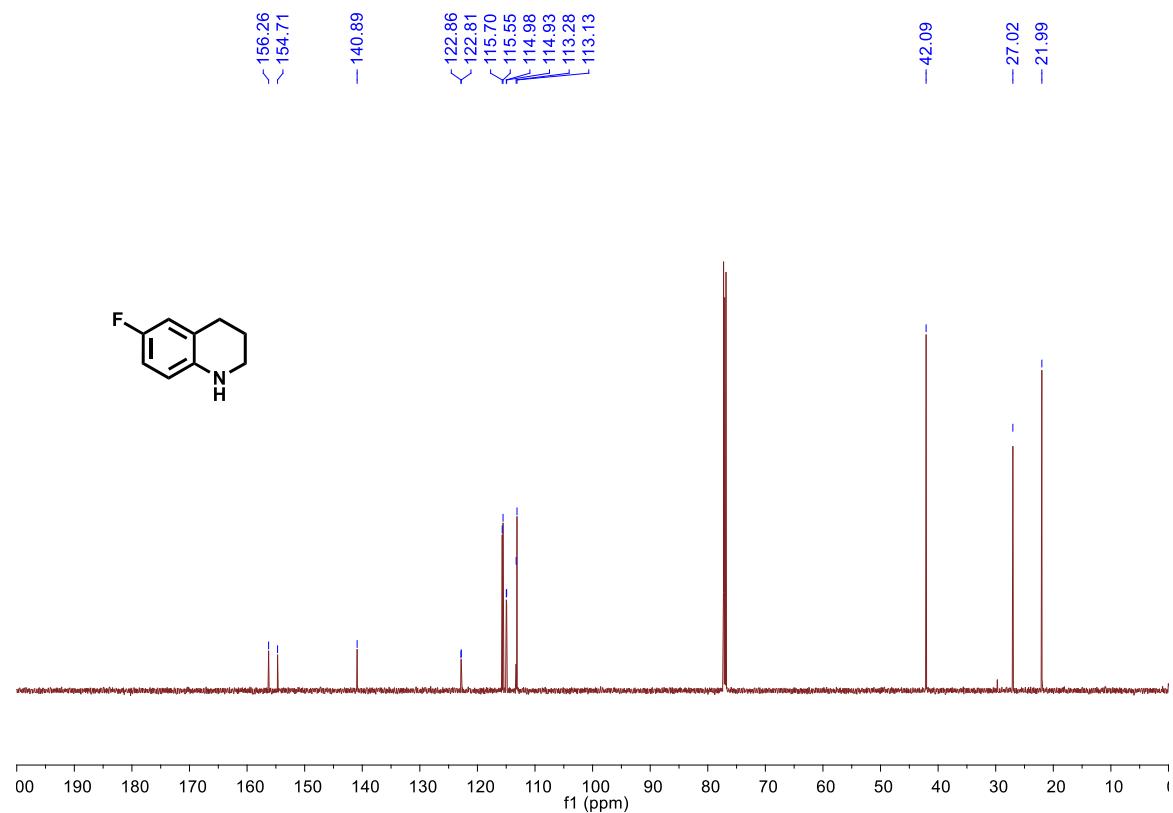
**Figure S51.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 6-chloro-1,2,3,4-tetrahydroquinoline



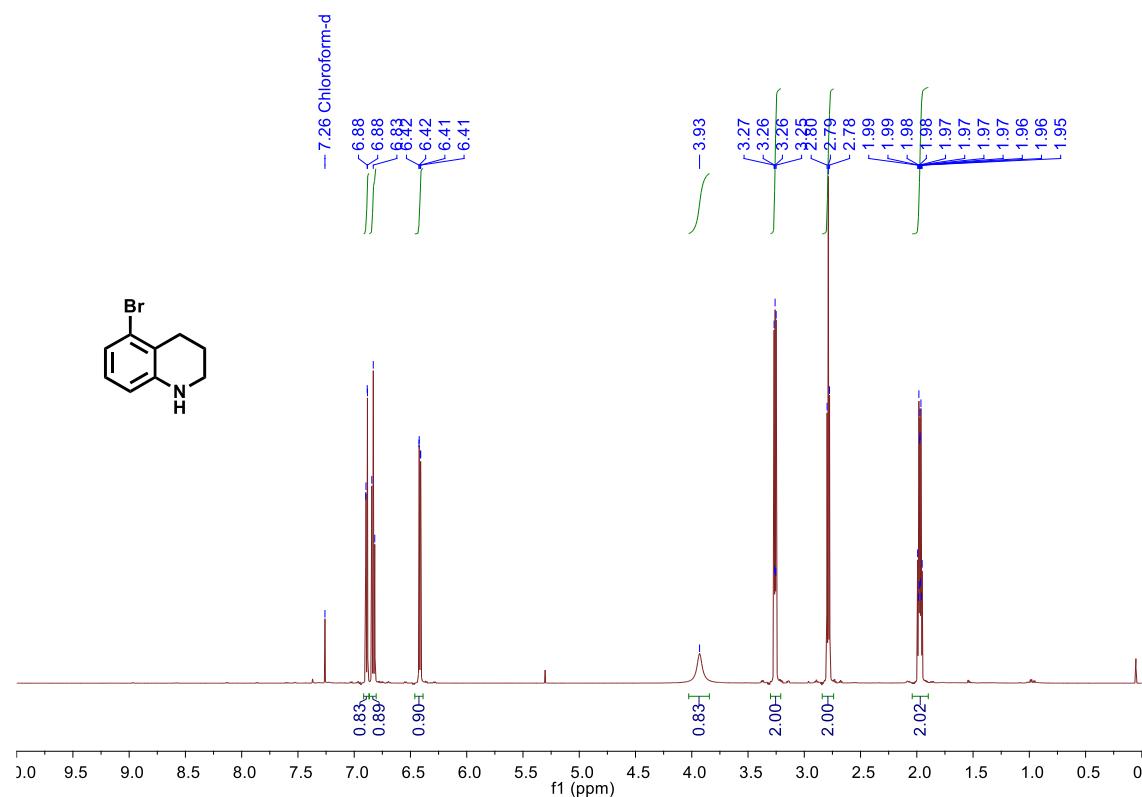
**Figure S52.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 6-fluoro-1,2,3,4-tetrahydroquinoline



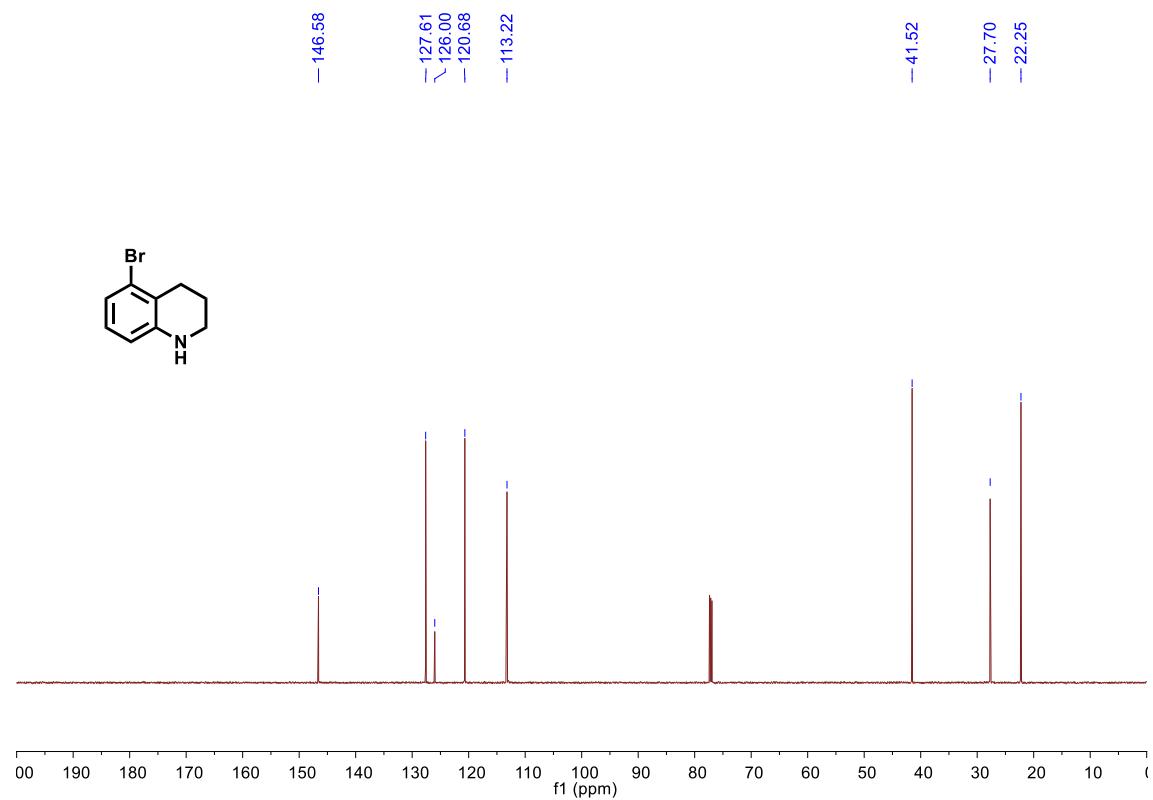
**Figure S53.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 6-fluoro-1,2,3,4-tetrahydroquinoline



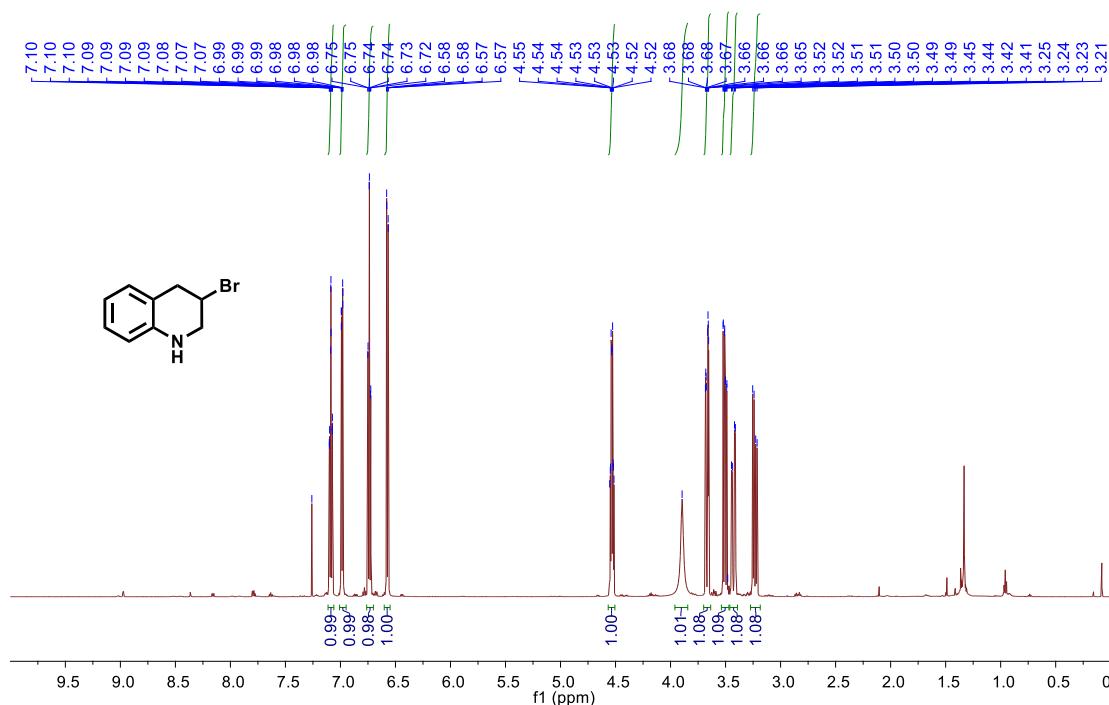
**Figure S54.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 5-bromo-1,2,3,4-tetrahydroquinoline



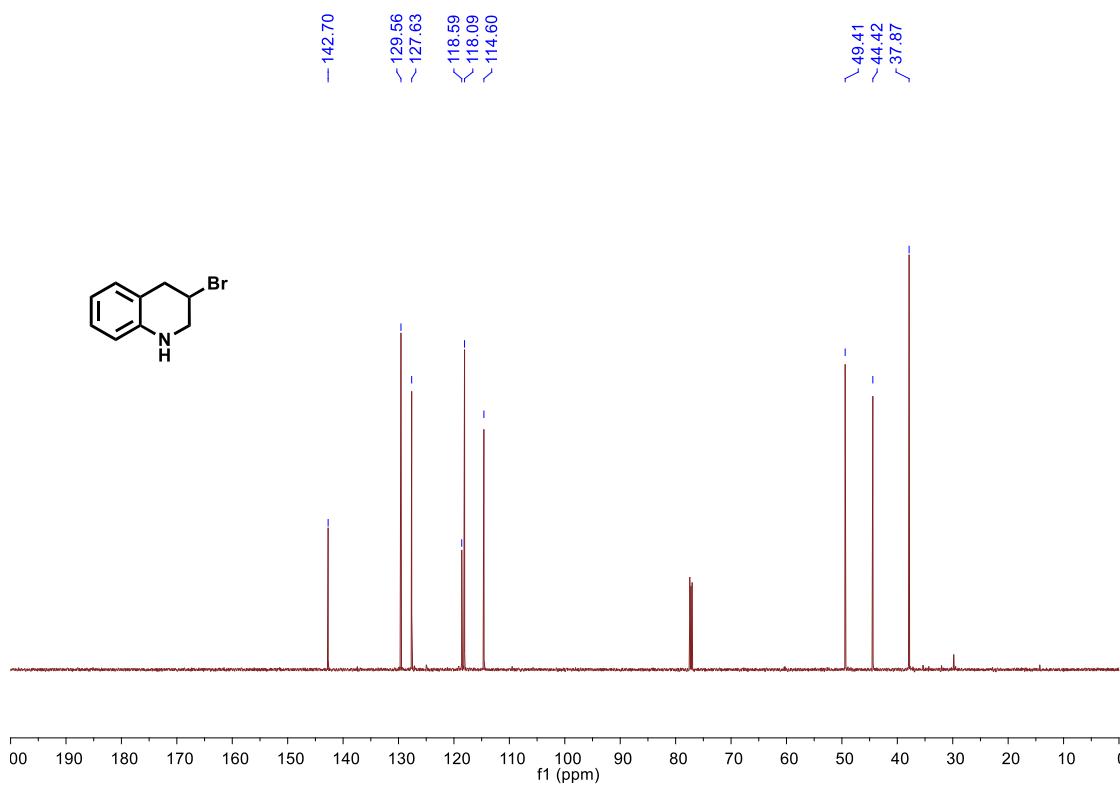
**Figure S55.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 5-bromo-1,2,3,4-tetrahydroquinoline



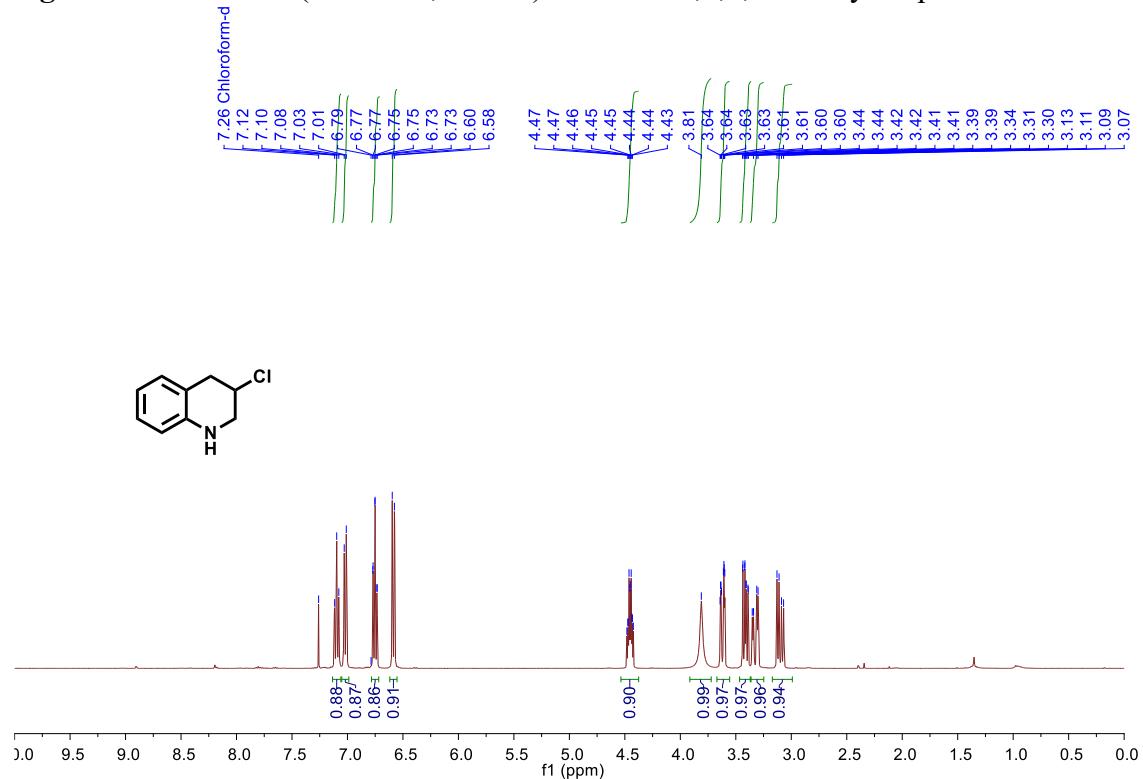
**Figure S56.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-bromo-1,2,3,4-tetrahydroquinoline



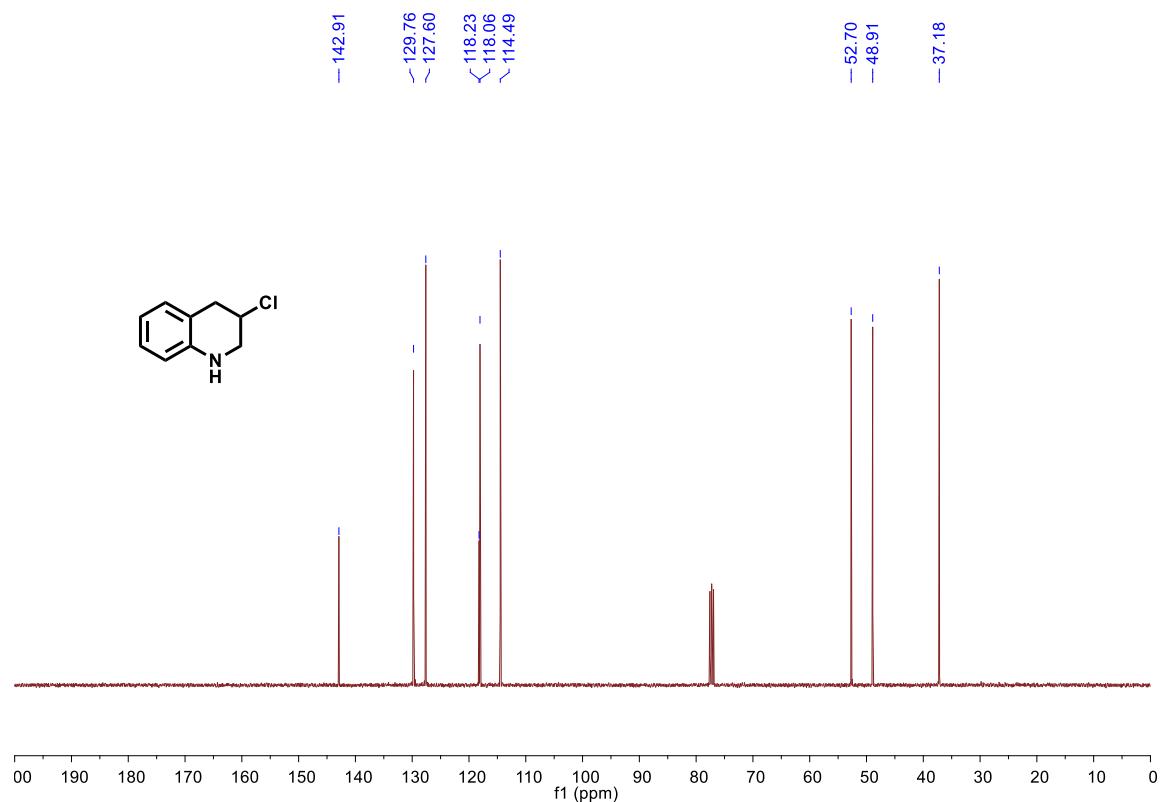
**Figure S57.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3-bromo-1,2,3,4-tetrahydroquinoline



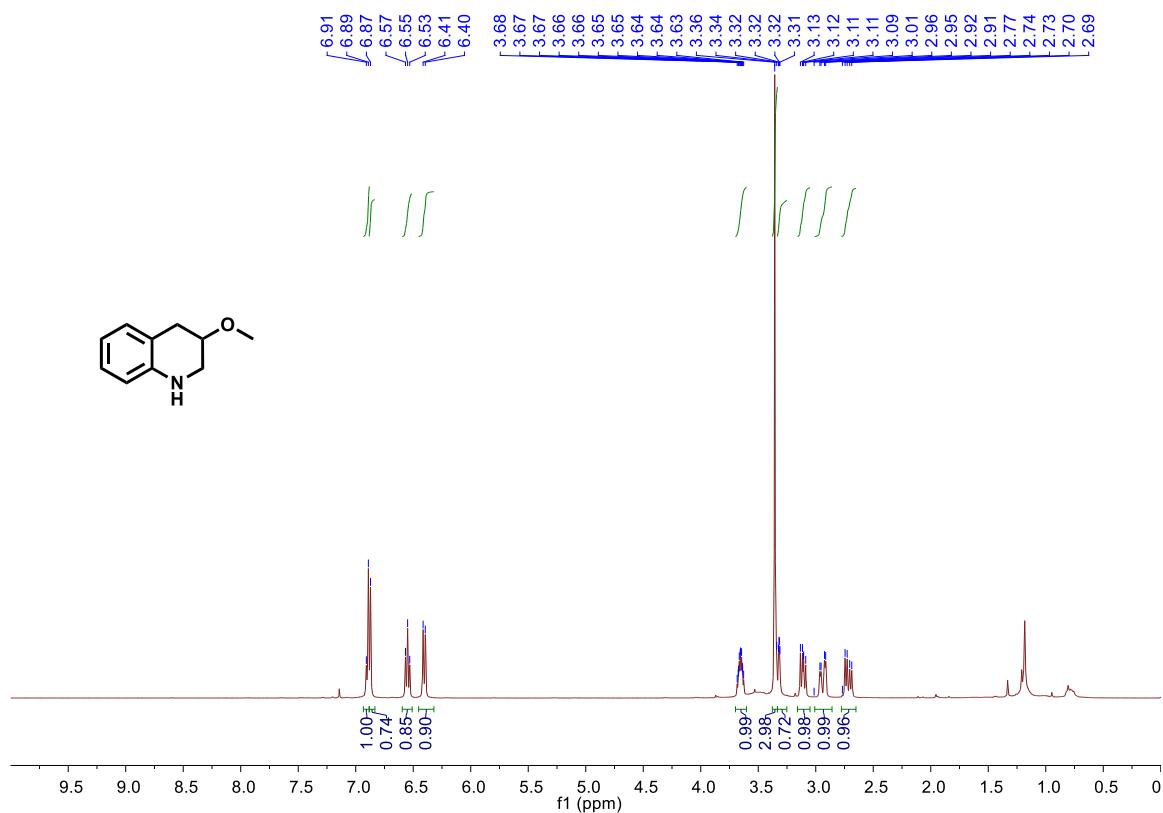
**Figure S58.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3-chloro-1,2,3,4-tetrahydroquinoline



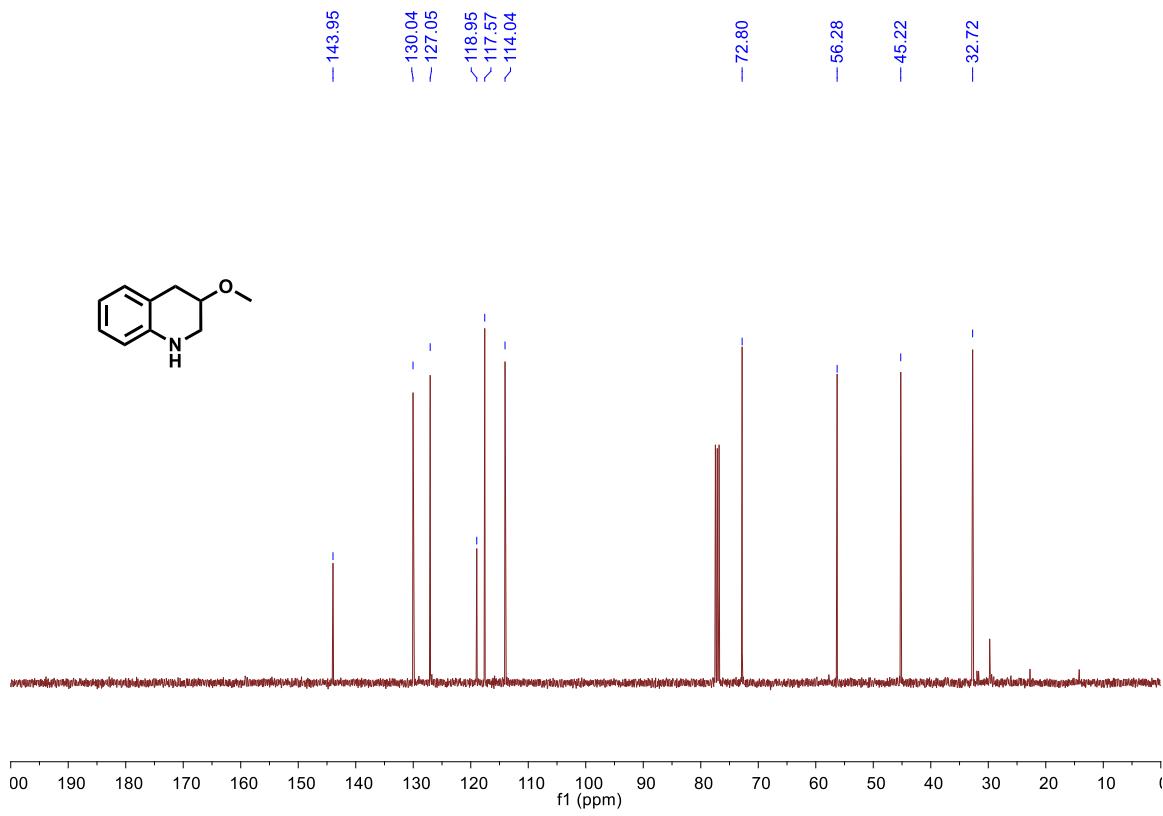
**Figure S59.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-chloro-1,2,3,4-tetrahydroquinoline



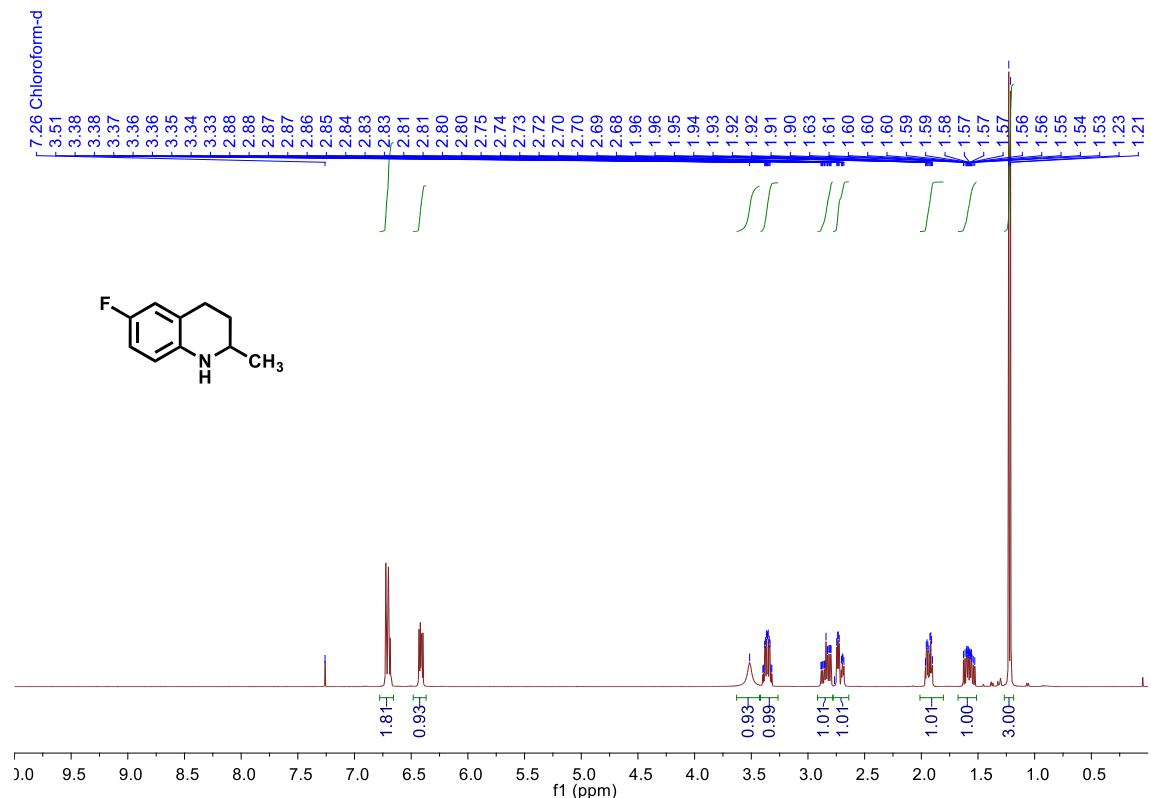
**Figure S60.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3-methoxy-1,2,3,4-tetrahydroquinoline



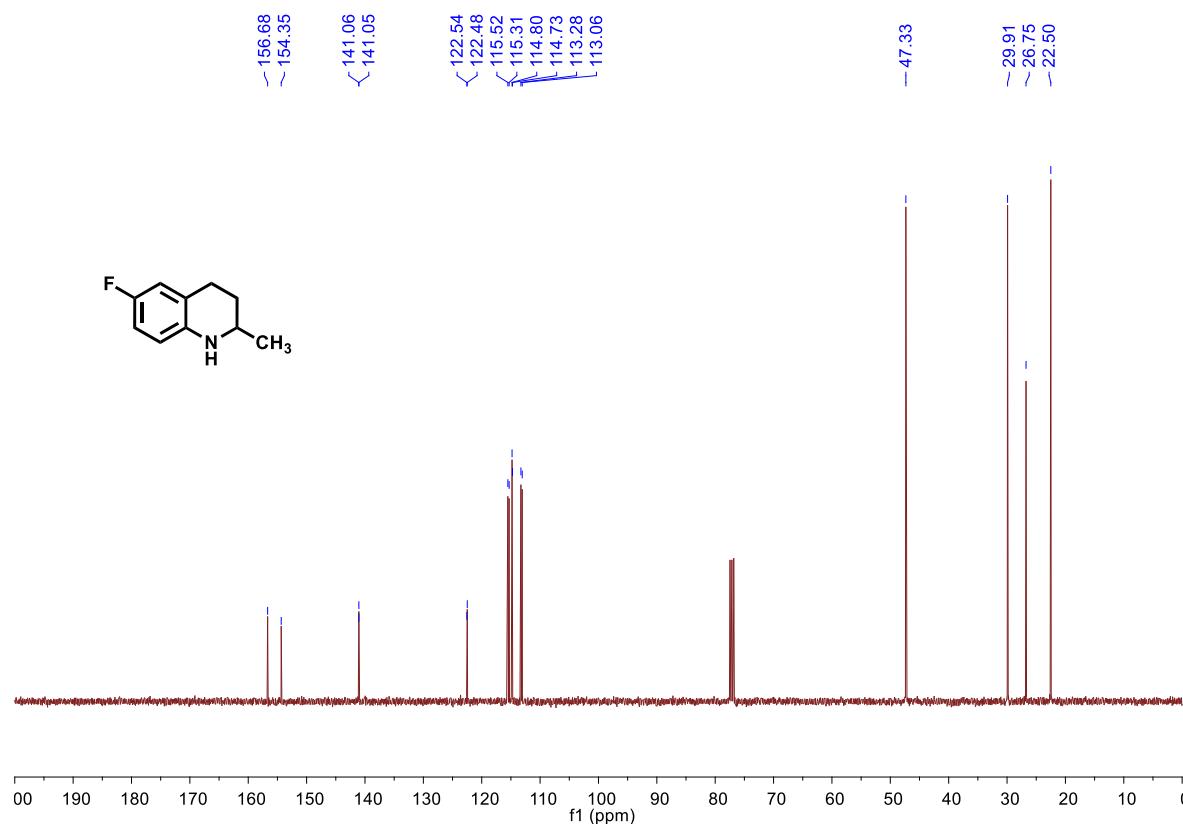
**Figure S61.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-methoxy-1,2,3,4-tetrahydroquinoline



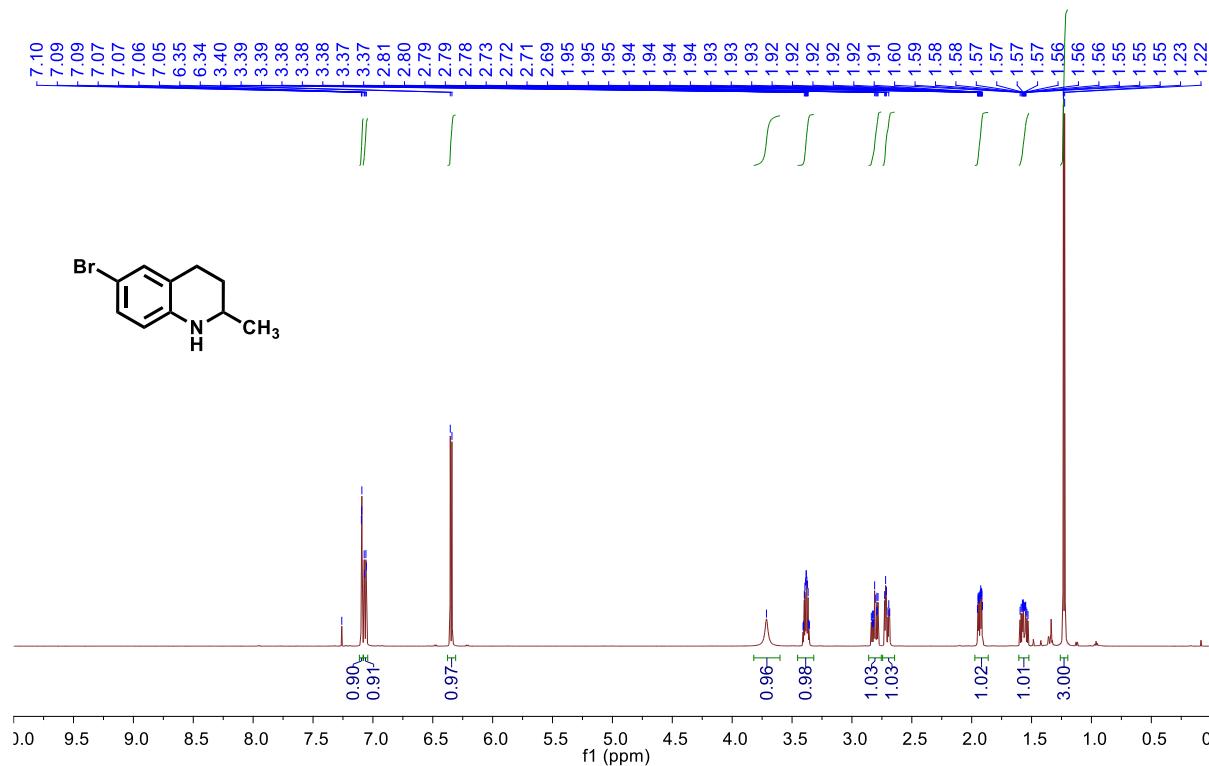
**Figure S62.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline



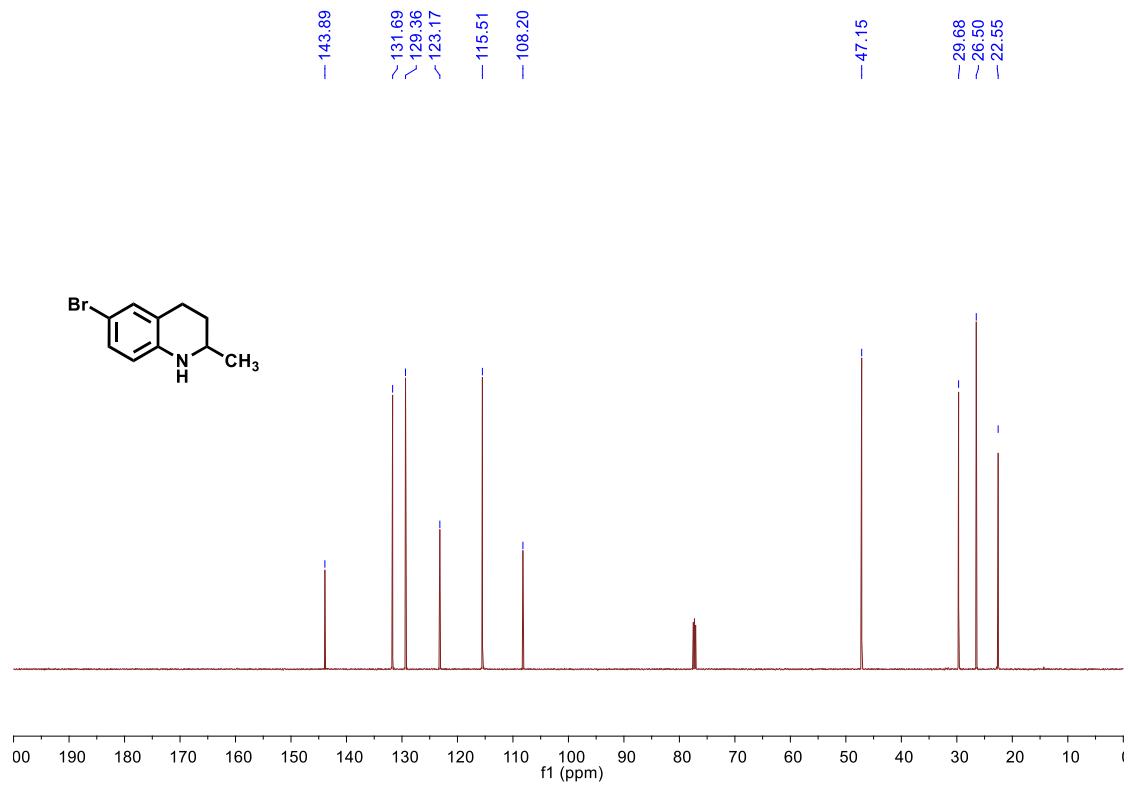
**Figure S63.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline



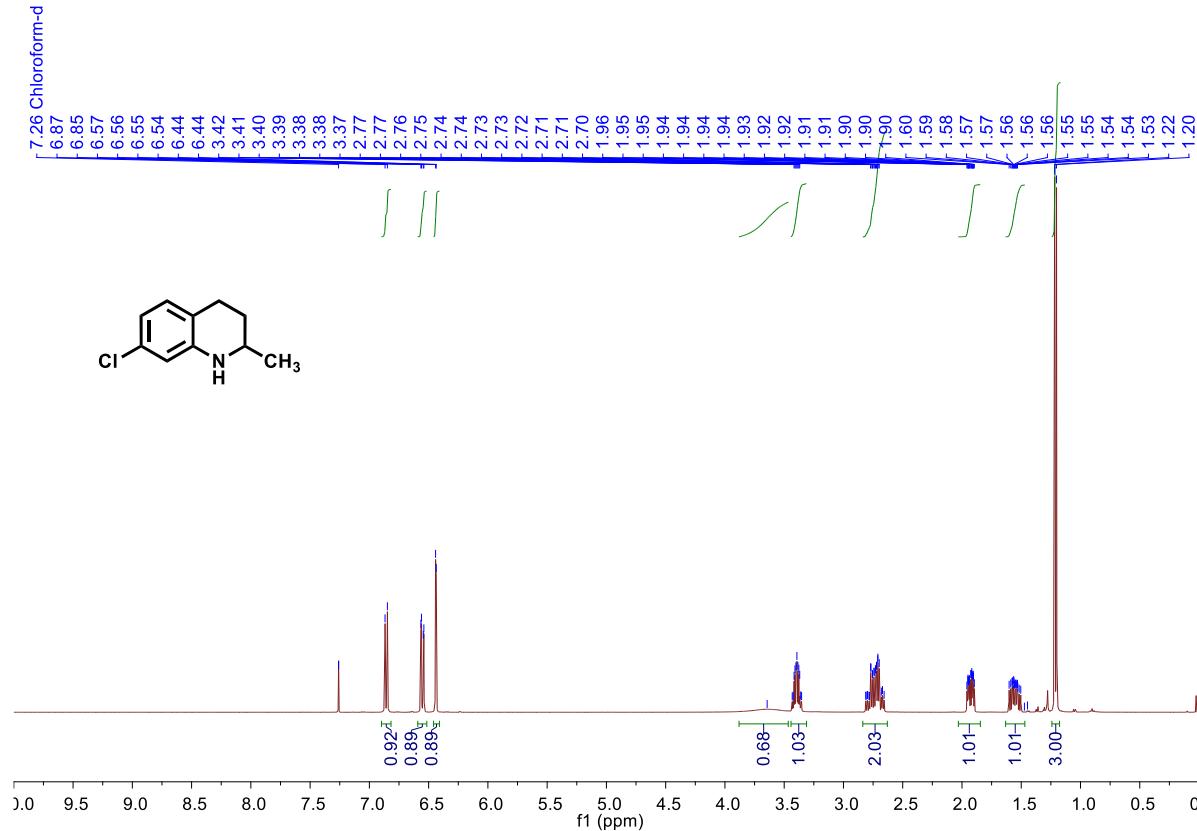
**Figure S64.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline



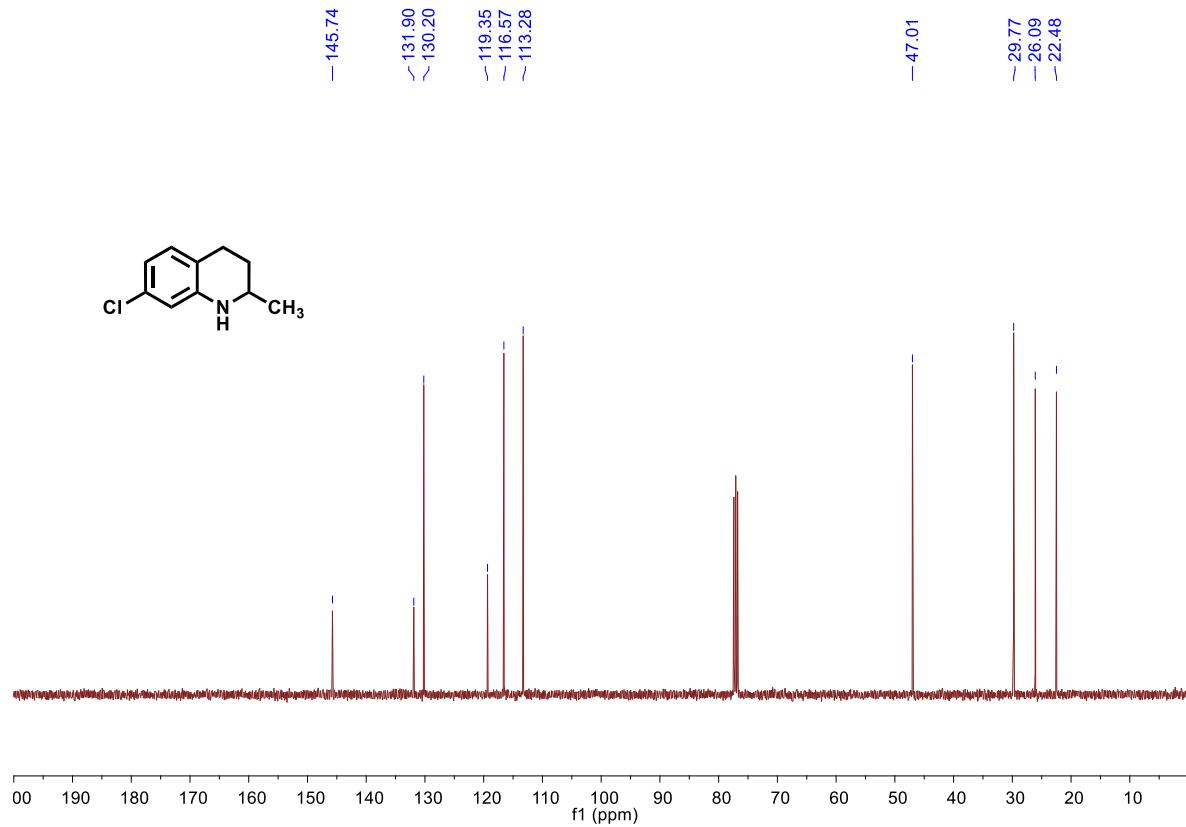
**Figure S65.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline



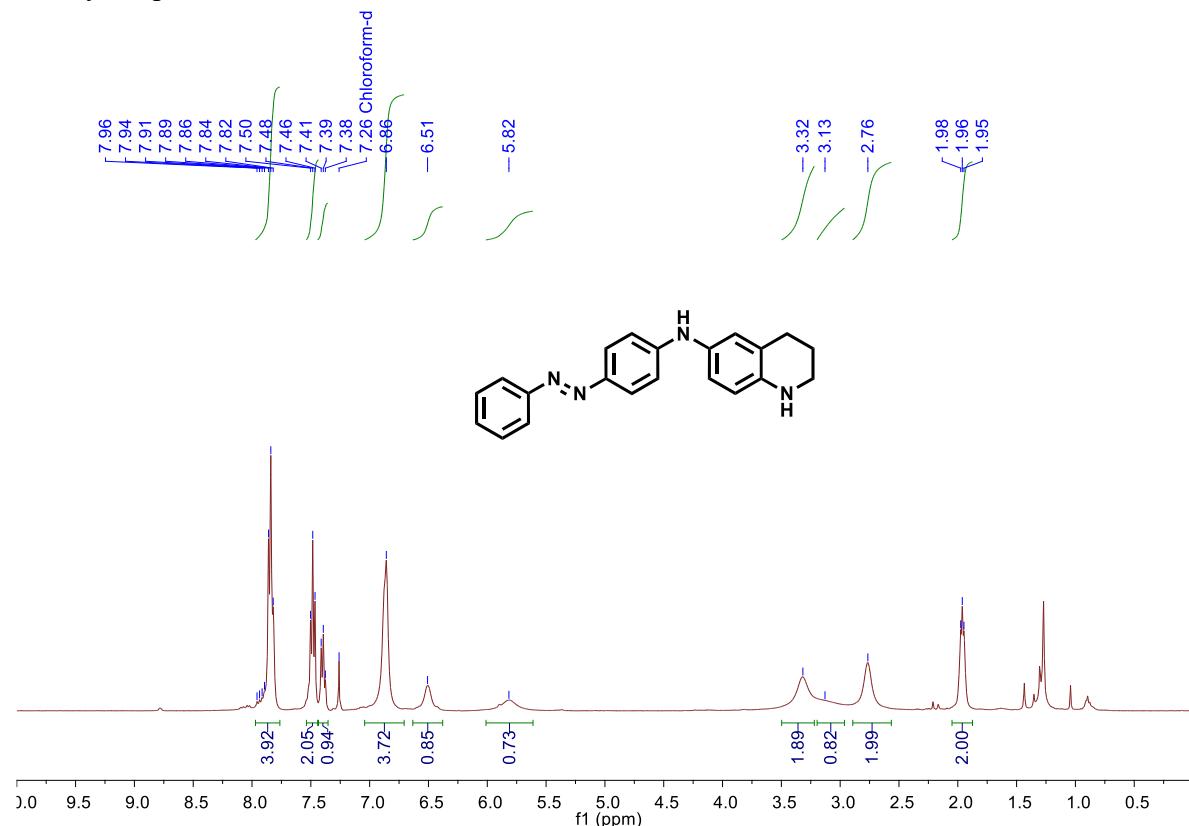
**Figure S66.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7-chloro-2-methyl-1,2,3,4-tetrahydroquinoline



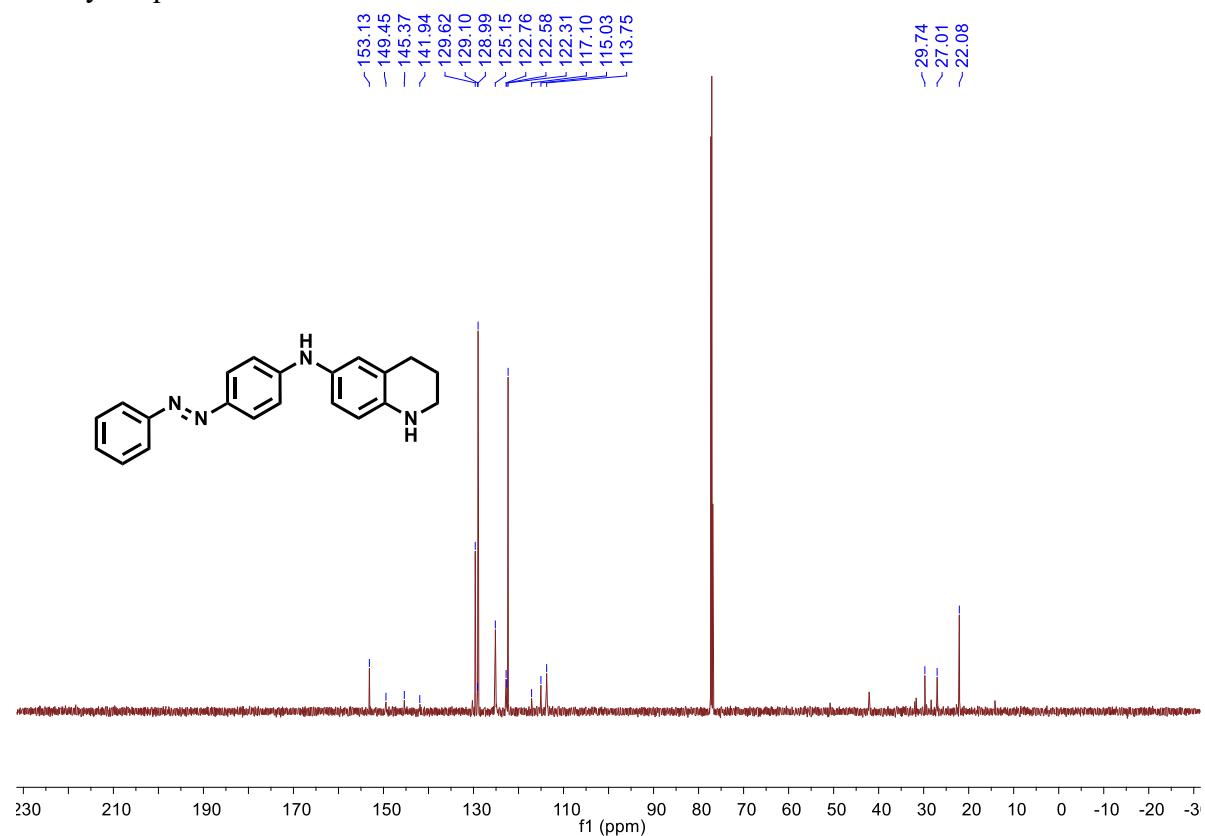
**Figure S67.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 7-chloro-2-methyl-1,2,3,4-tetrahydroquinoline



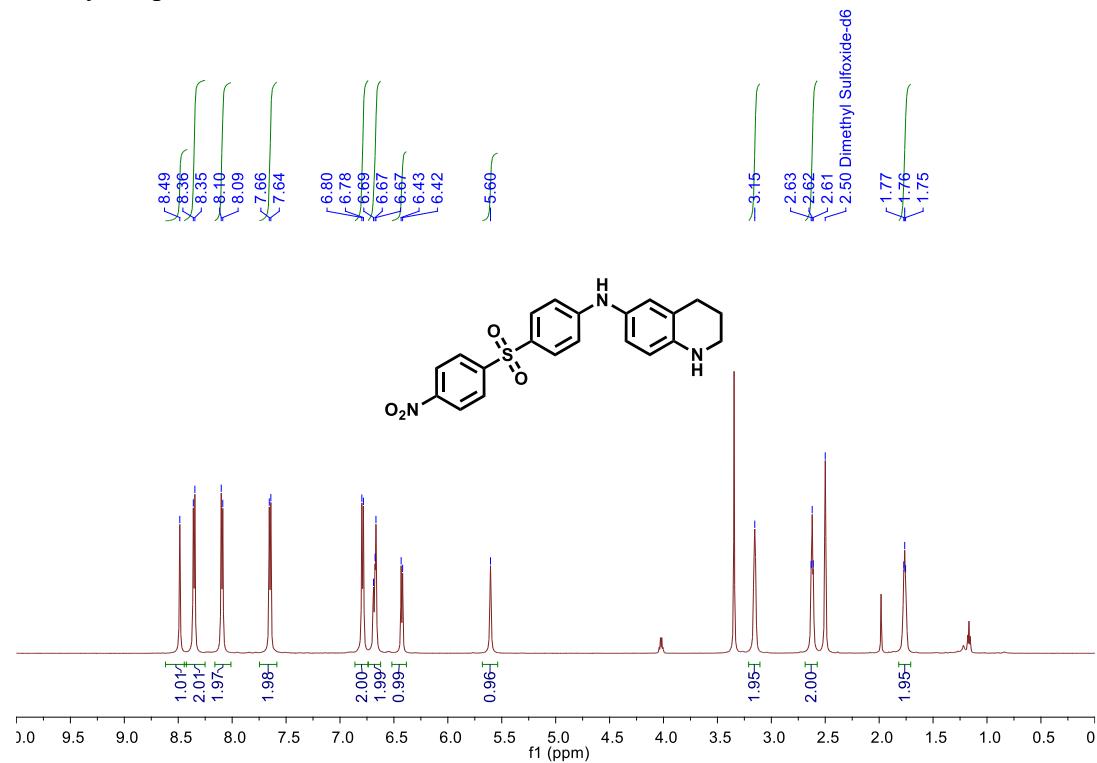
**Figure S68.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): (E)-N-(4-(phenyldiazenyl)phenyl)-1,2,3,4-tetrahydroquinolin-6-amine



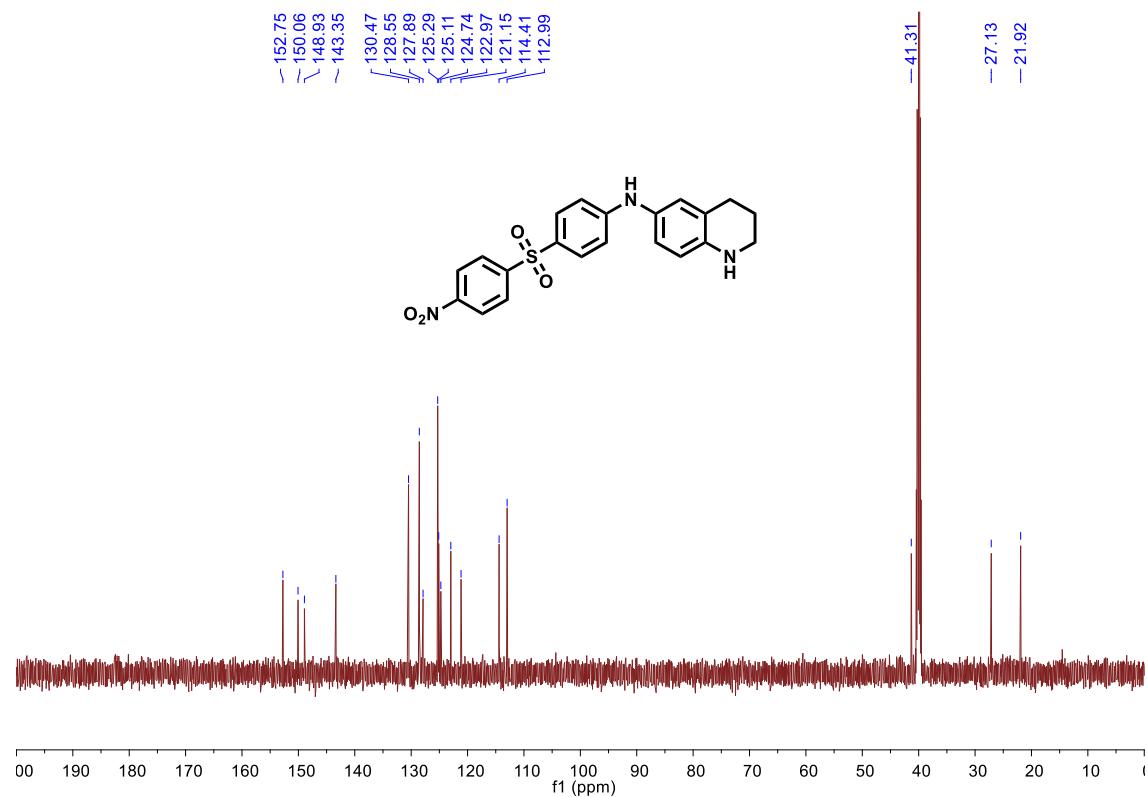
**Figure S69.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): (E)-N-(4-(phenyldiazenyl)phenyl)-1,2,3,4-tetrahydroquinolin-6-amine



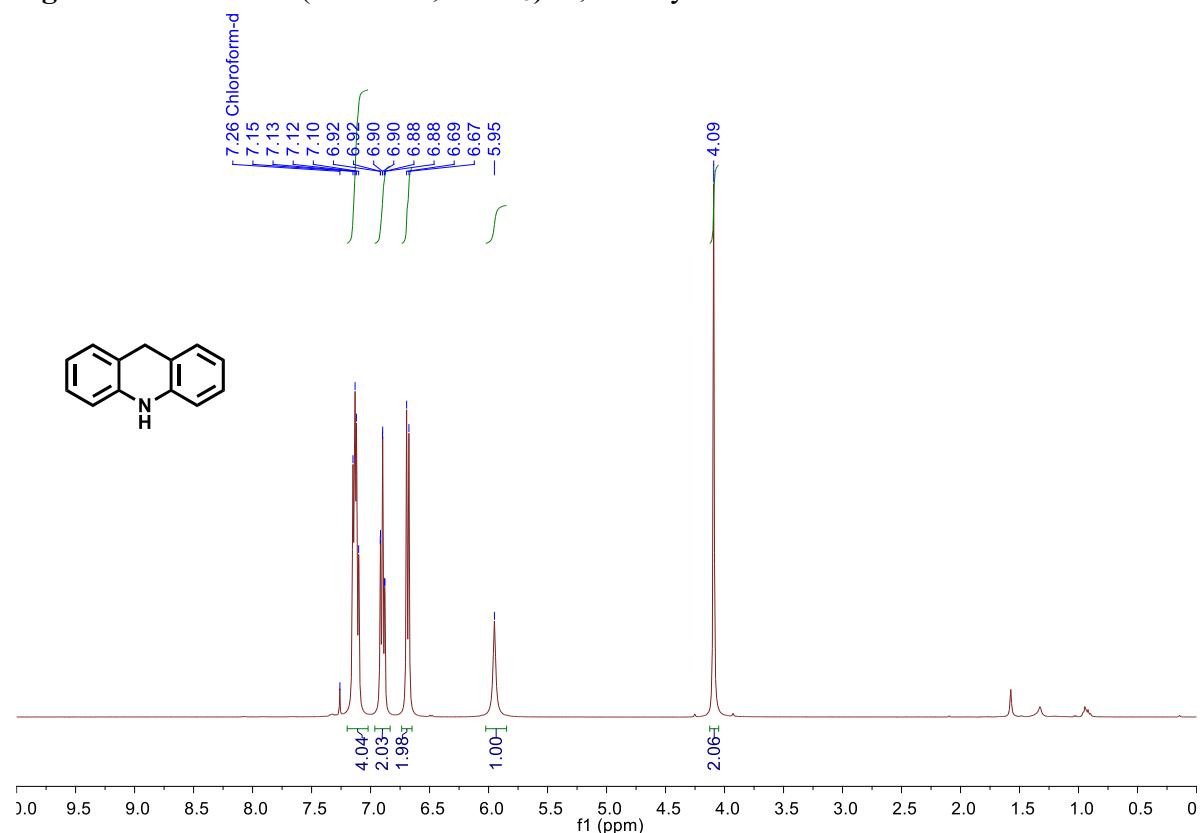
**Figure S70.**  $^1\text{H}$  NMR (600 MHz, DMSO): N-(4-((4-nitrophenyl)sulfonyl)phenyl)-1,2,3,4-tetrahydroquinolin-6-amine



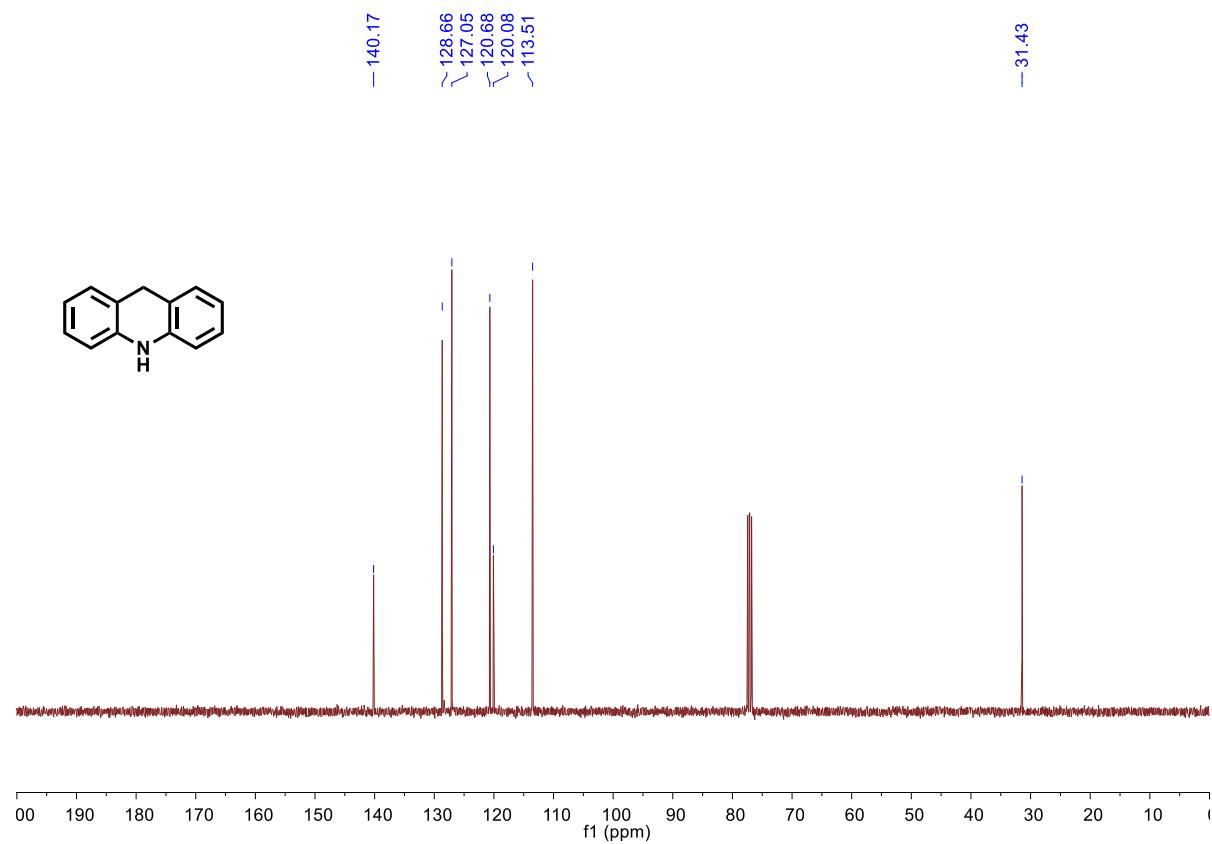
**Figure S71.**  $^{13}\text{C}$  NMR (151 MHz, DMSO): N-(4-((4-nitrophenyl)sulfonyl)phenyl)-1,2,3,4-tetrahydroquinolin-6-amine



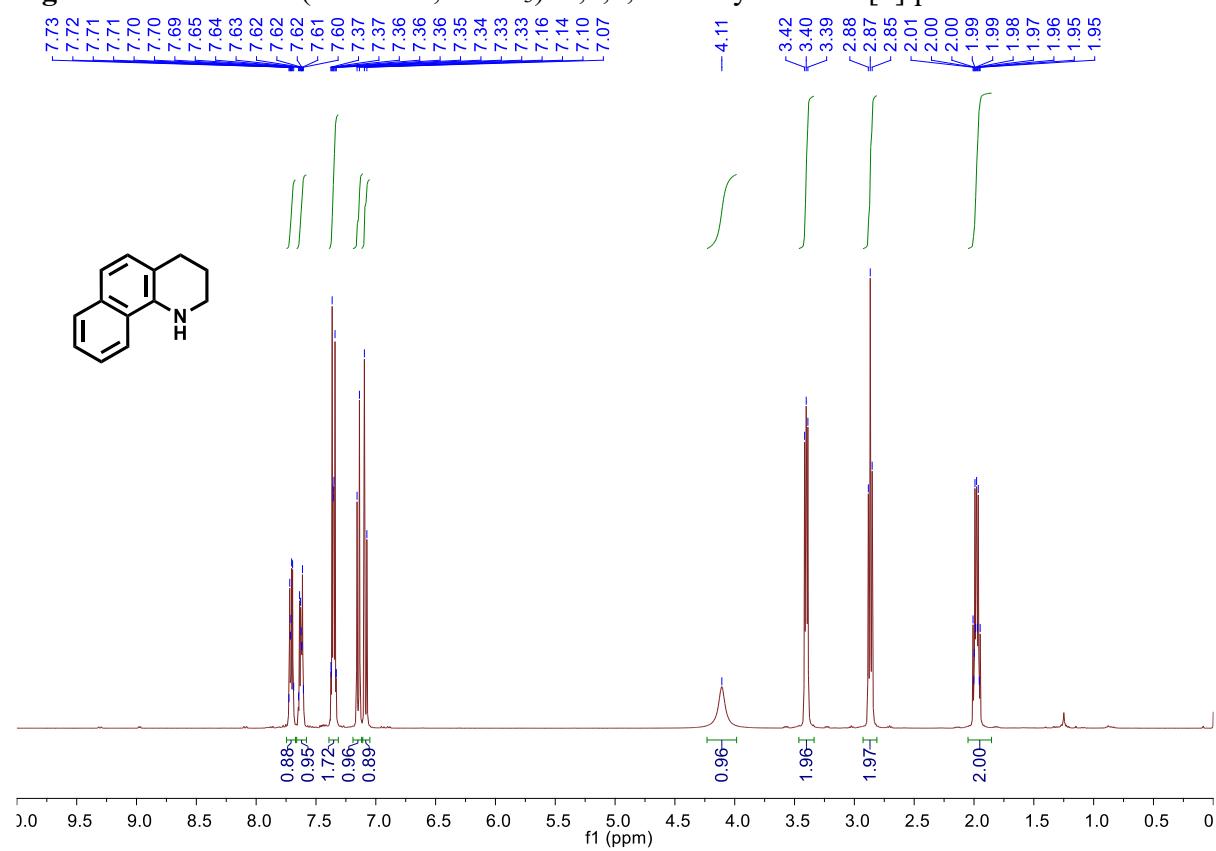
**Figure S72.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 9,10-dihydroacridine



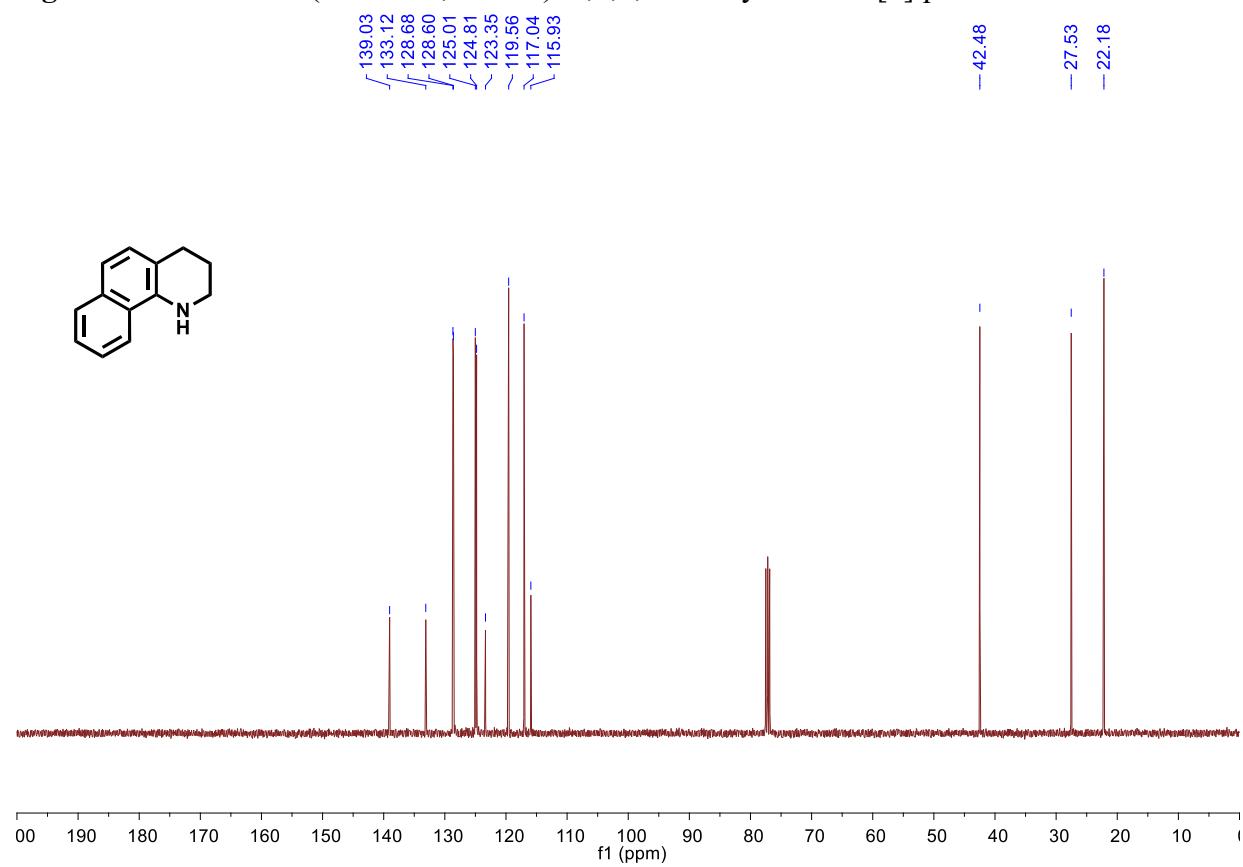
**Figure S73.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 9,10-dihydroacridine



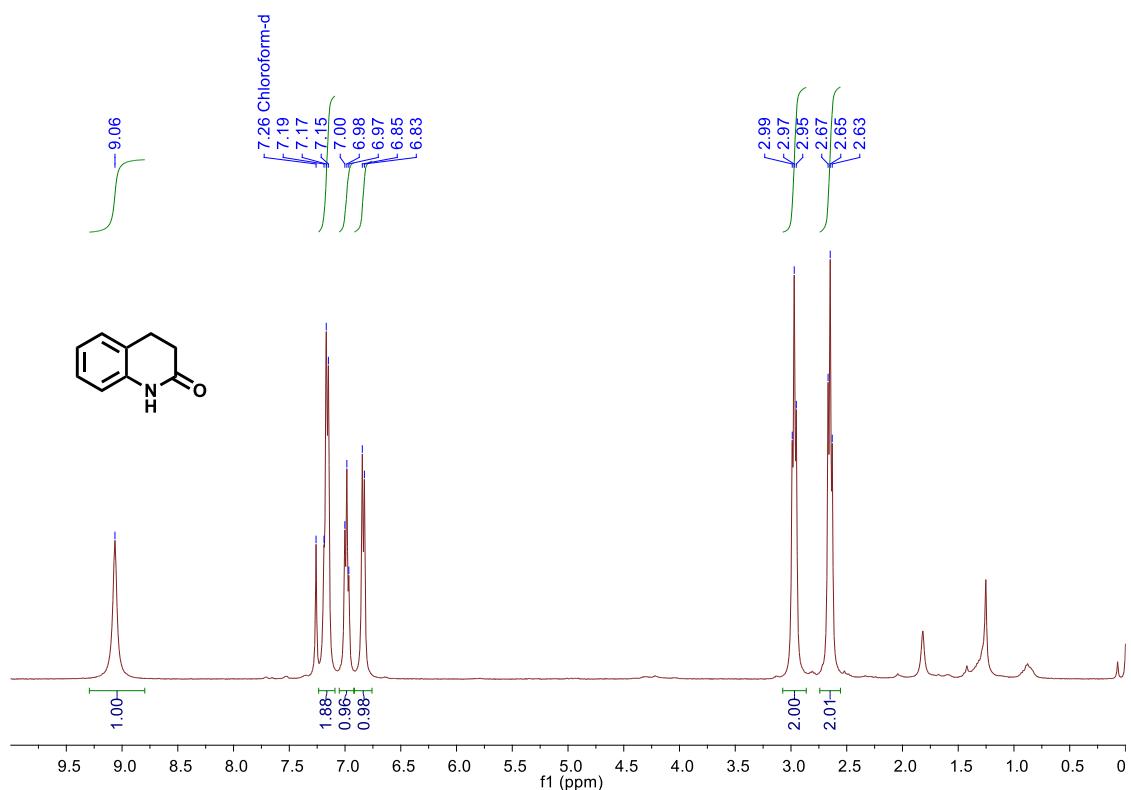
**Figure S74.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 1,2,3,4-tetrahydrobenzo[h]quinoline



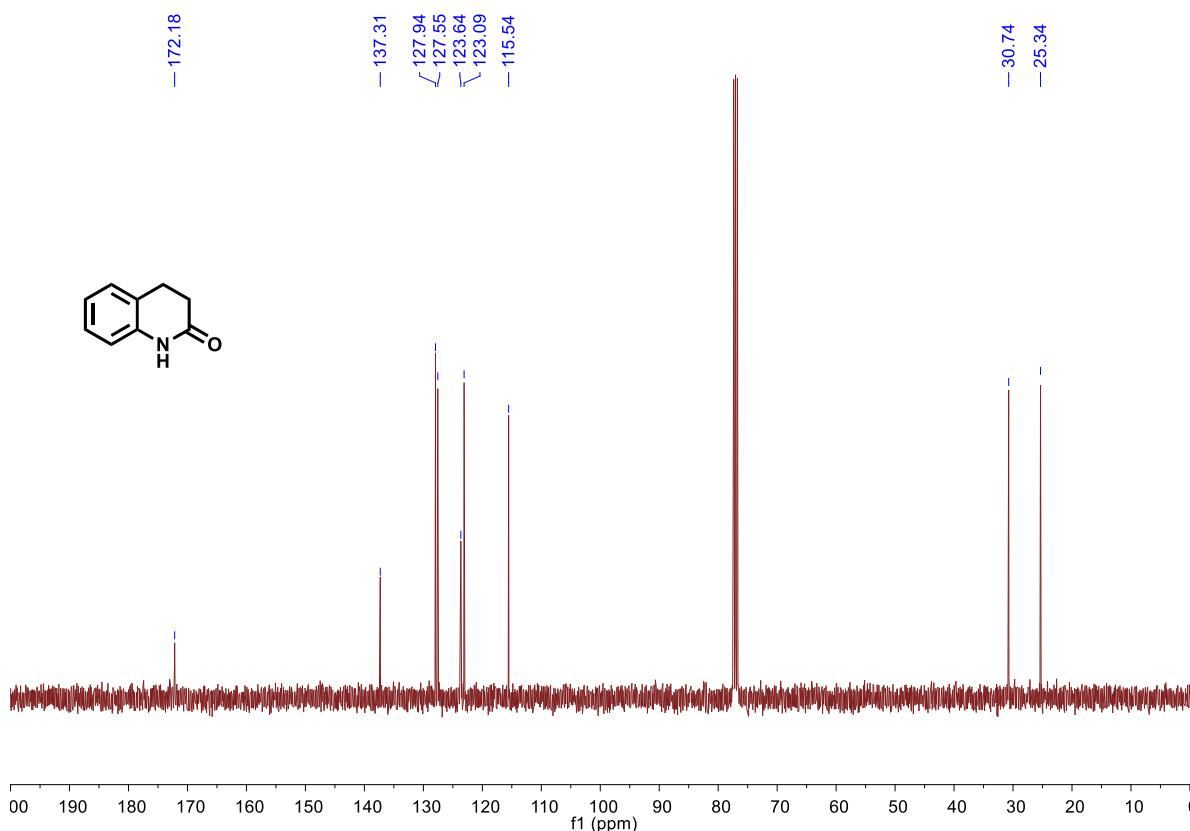
**Figure S75.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 1,2,3,4-tetrahydrobenzo[h]quinoline



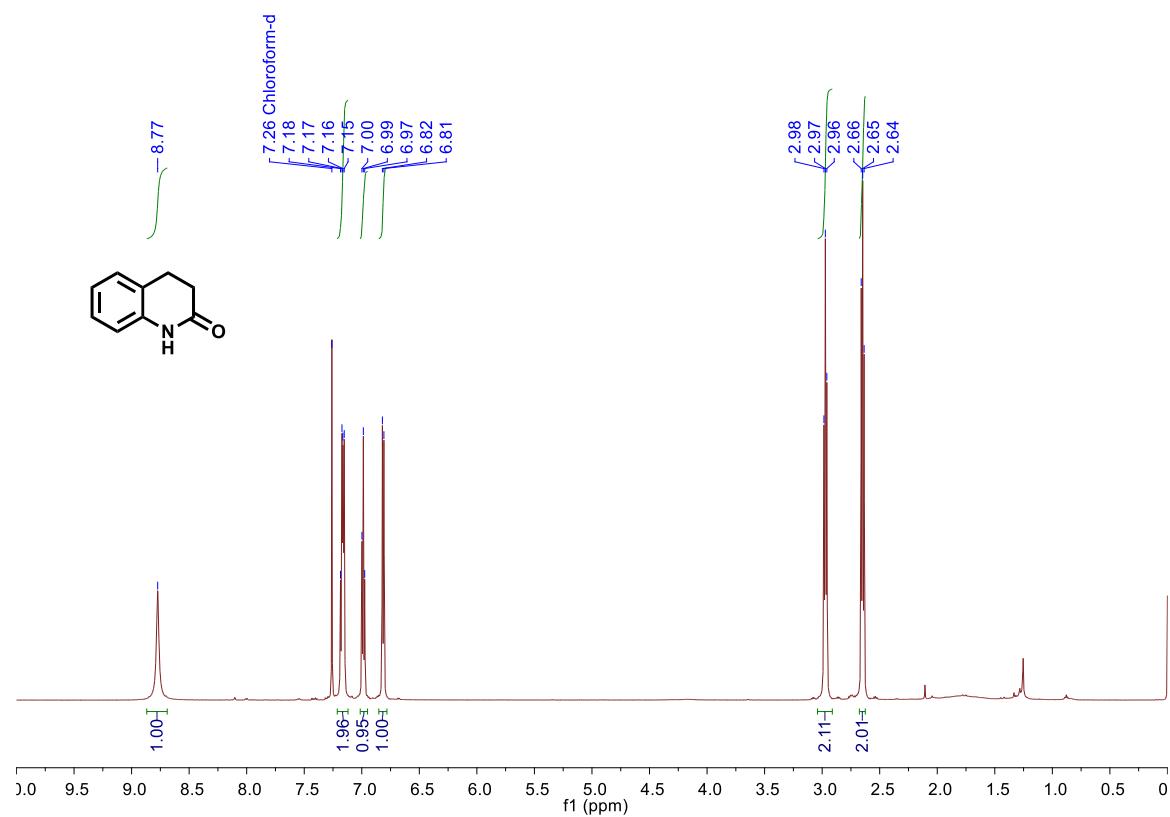
**Figure S76.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3,4-dihydroquinolin-2(1H)-one



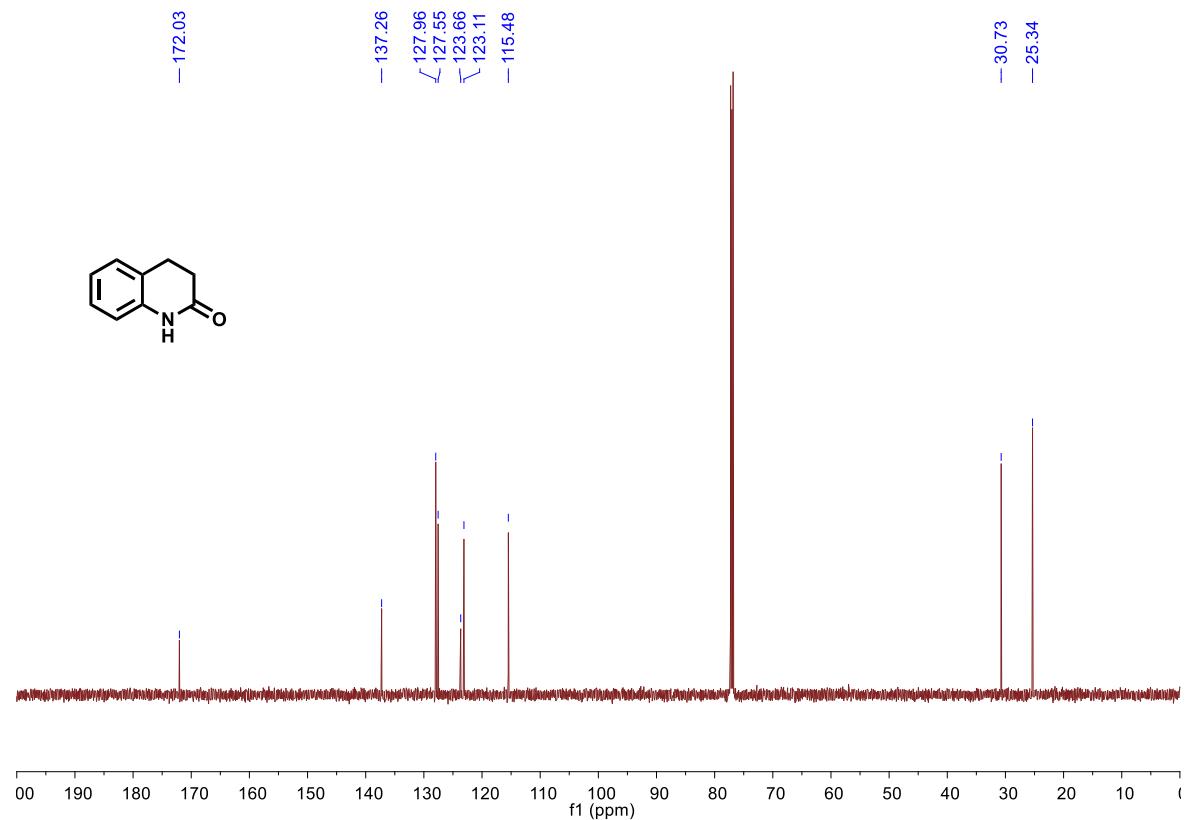
**Figure S77.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3,4-dihydroquinolin-2(1H)-one (20)



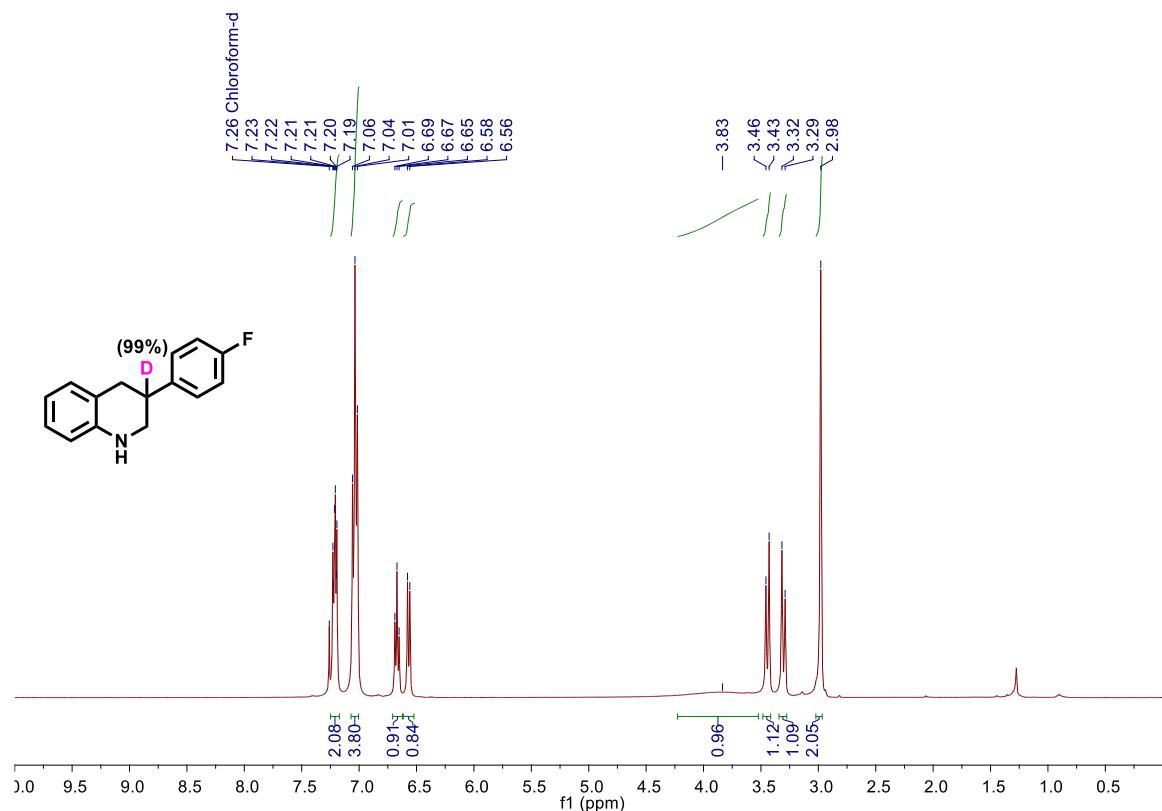
**Figure S78.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3,4-dihydroquinolin-2(1H)-one



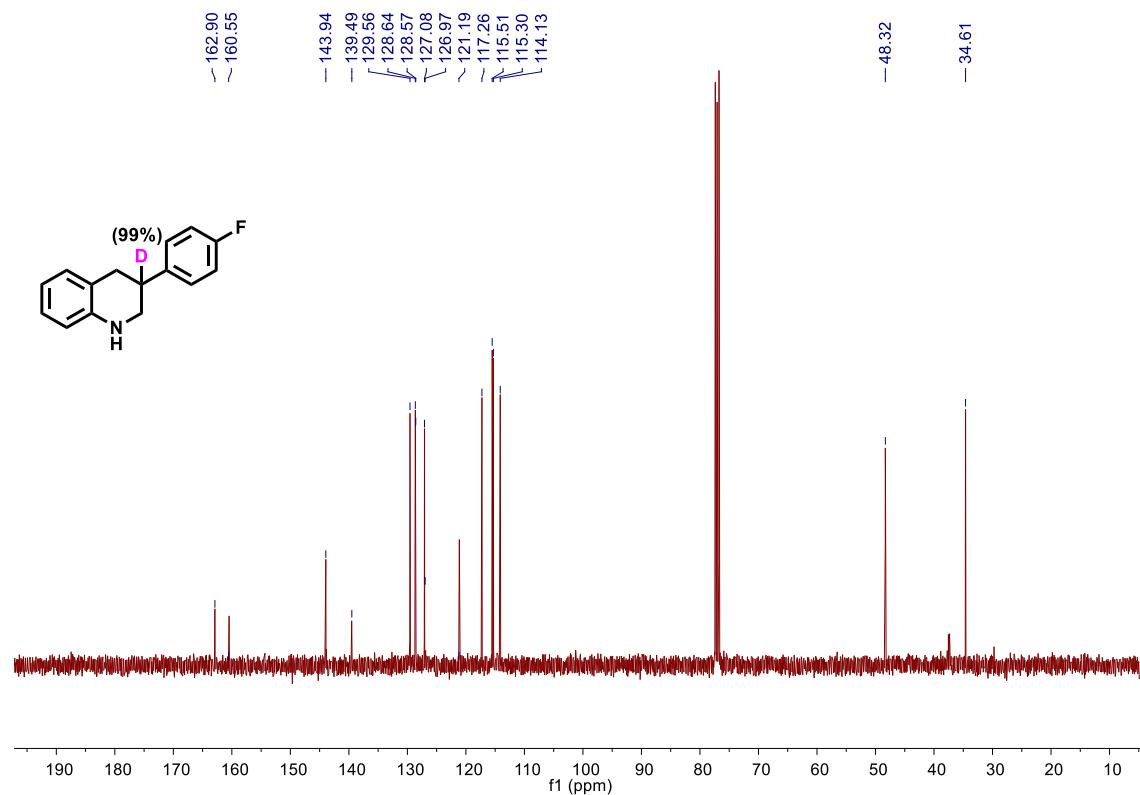
**Figure S79.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3,4-dihydroquinolin-2(1H)-one (21)



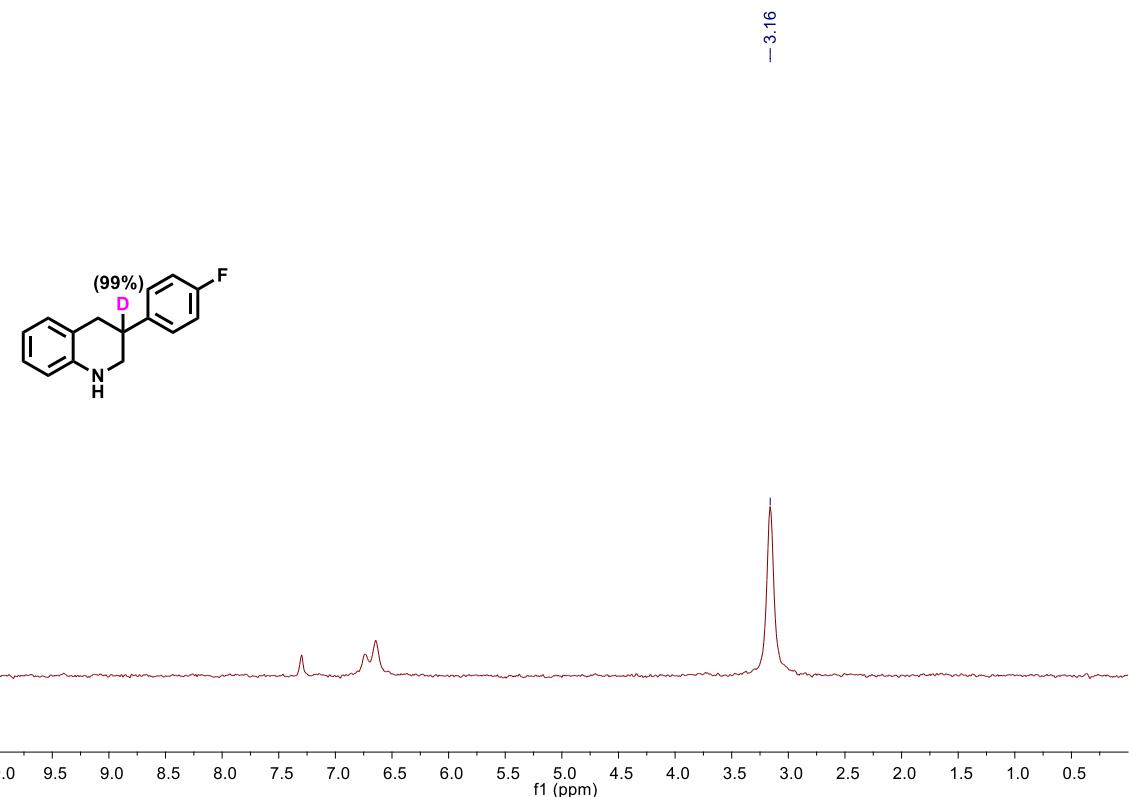
**Figure S80.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d



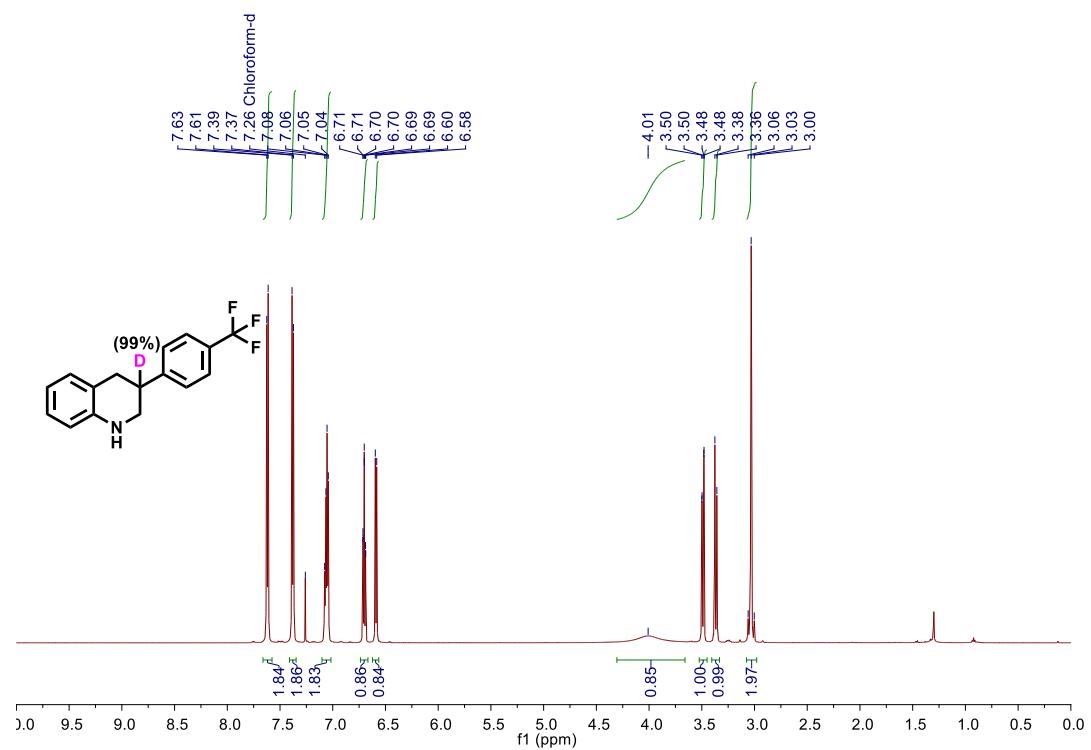
**Figure S81.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d



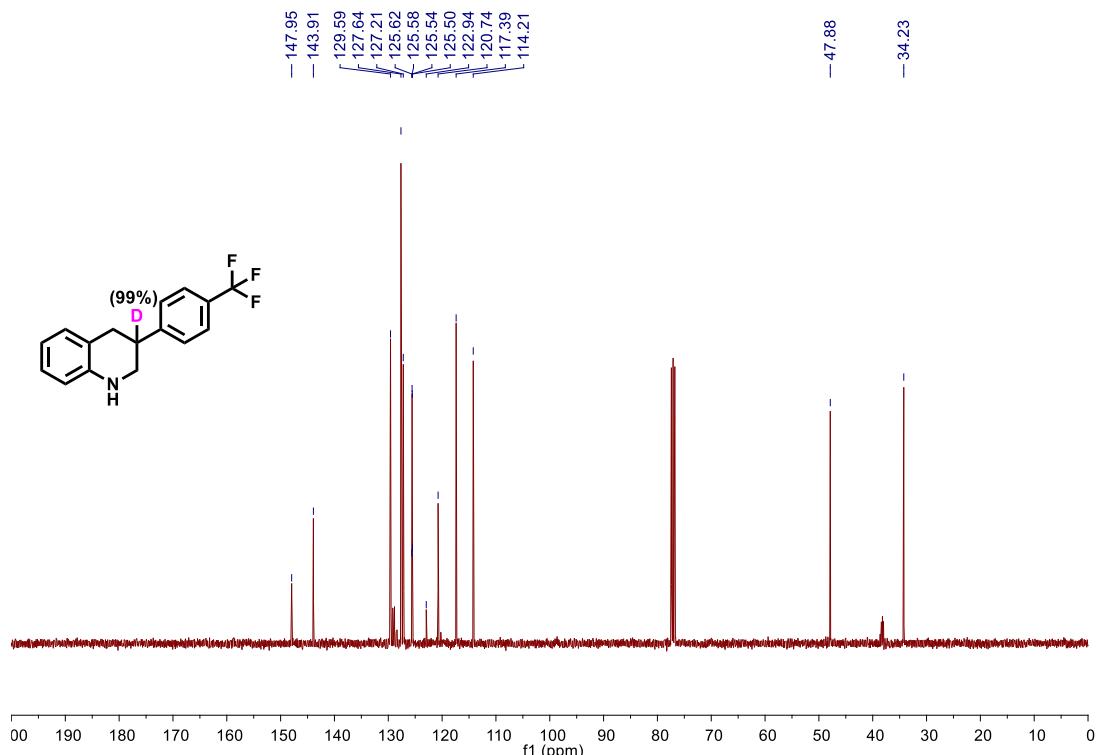
**Figure S82.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d



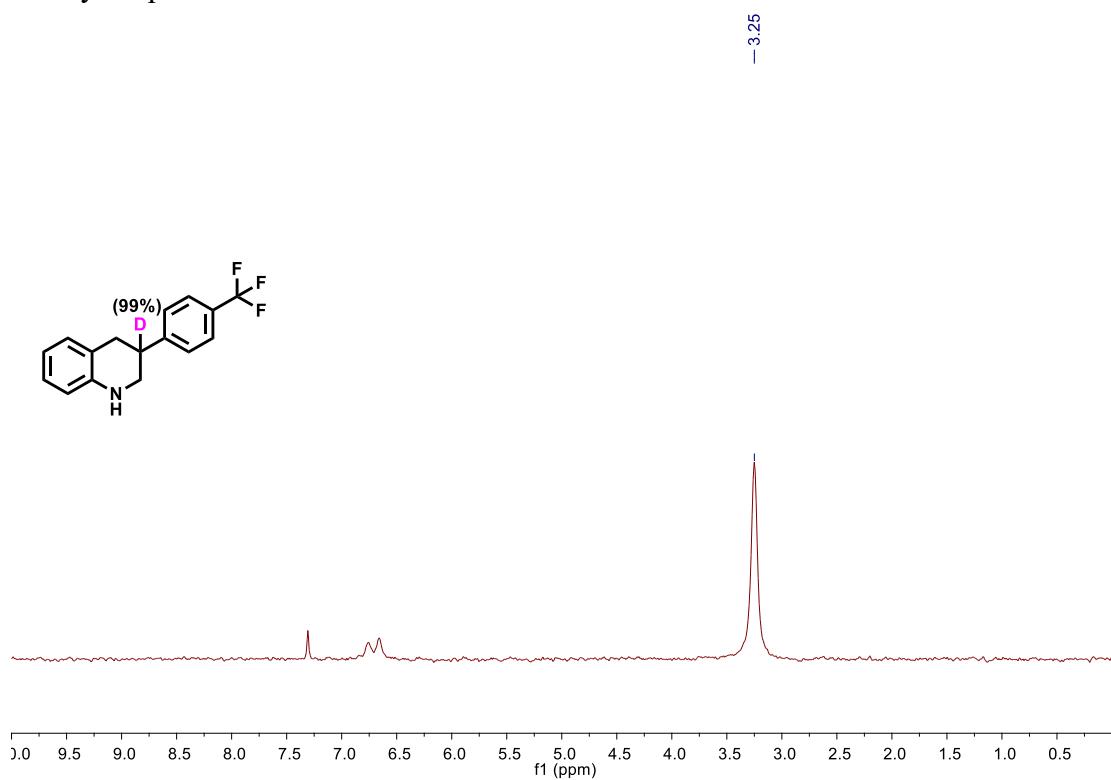
**Figure S83.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d



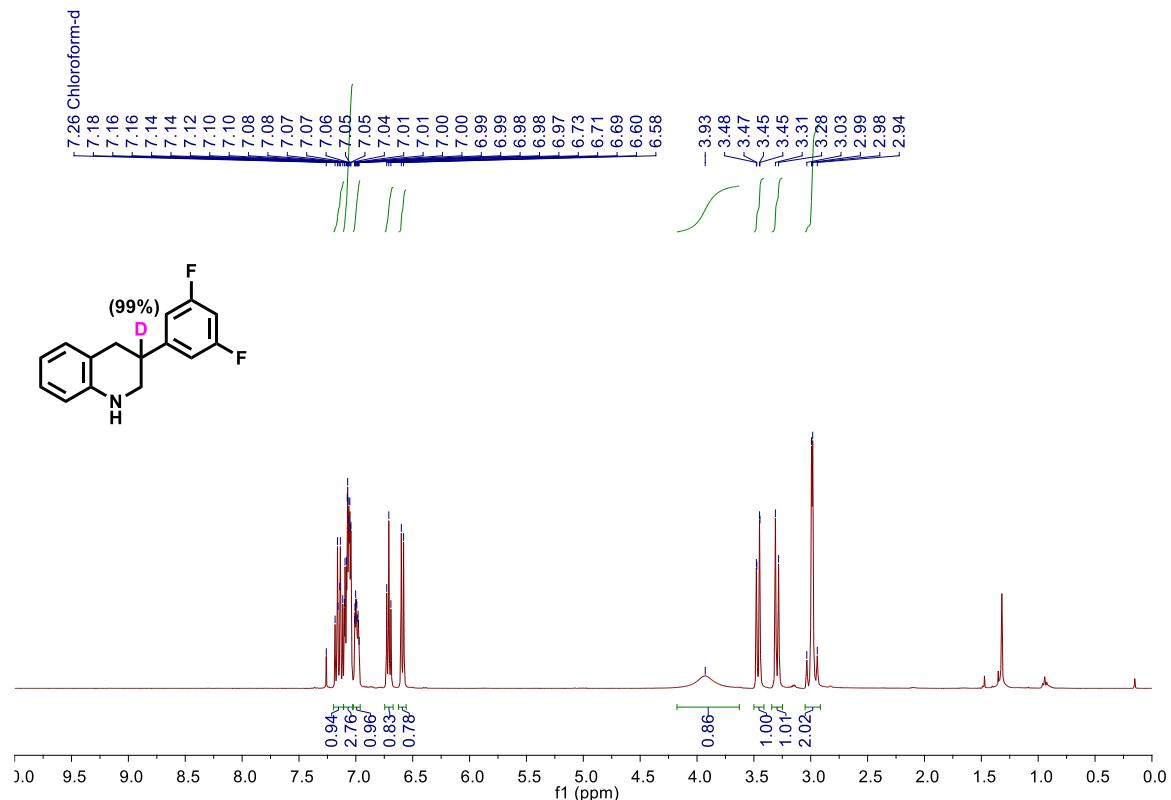
**Figure S84.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d



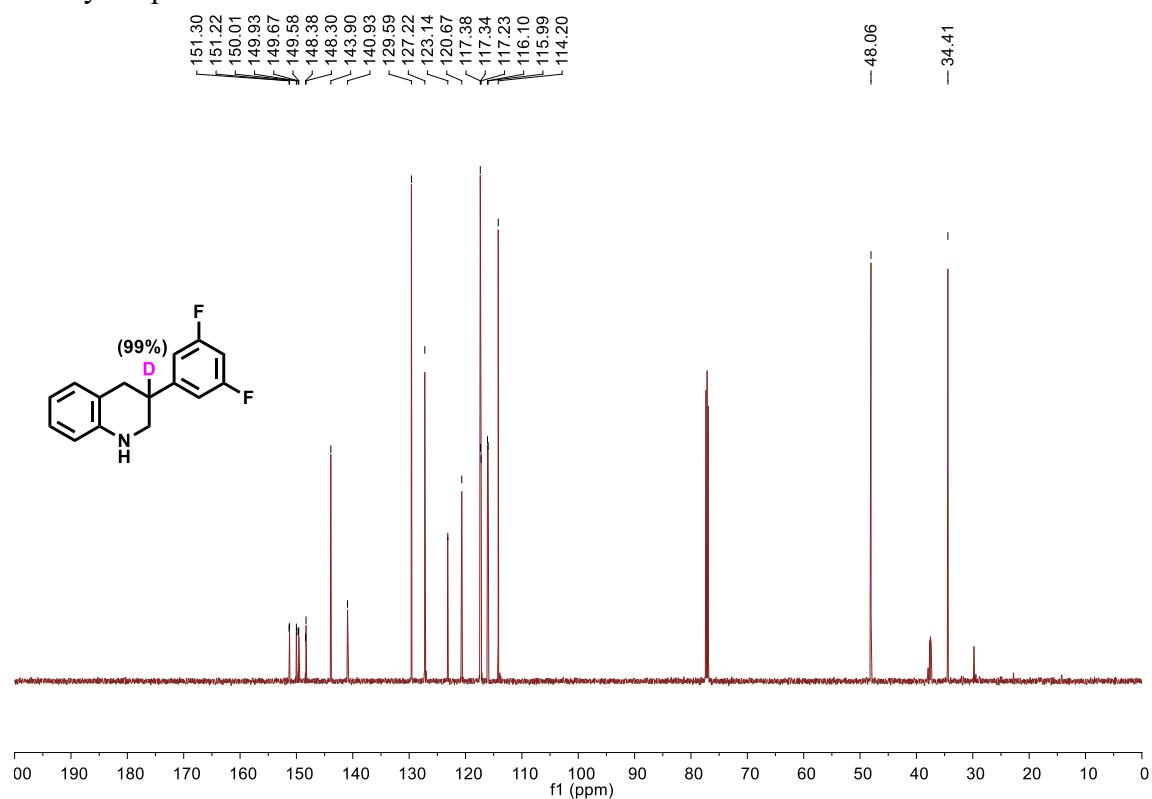
**Figure S85.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d



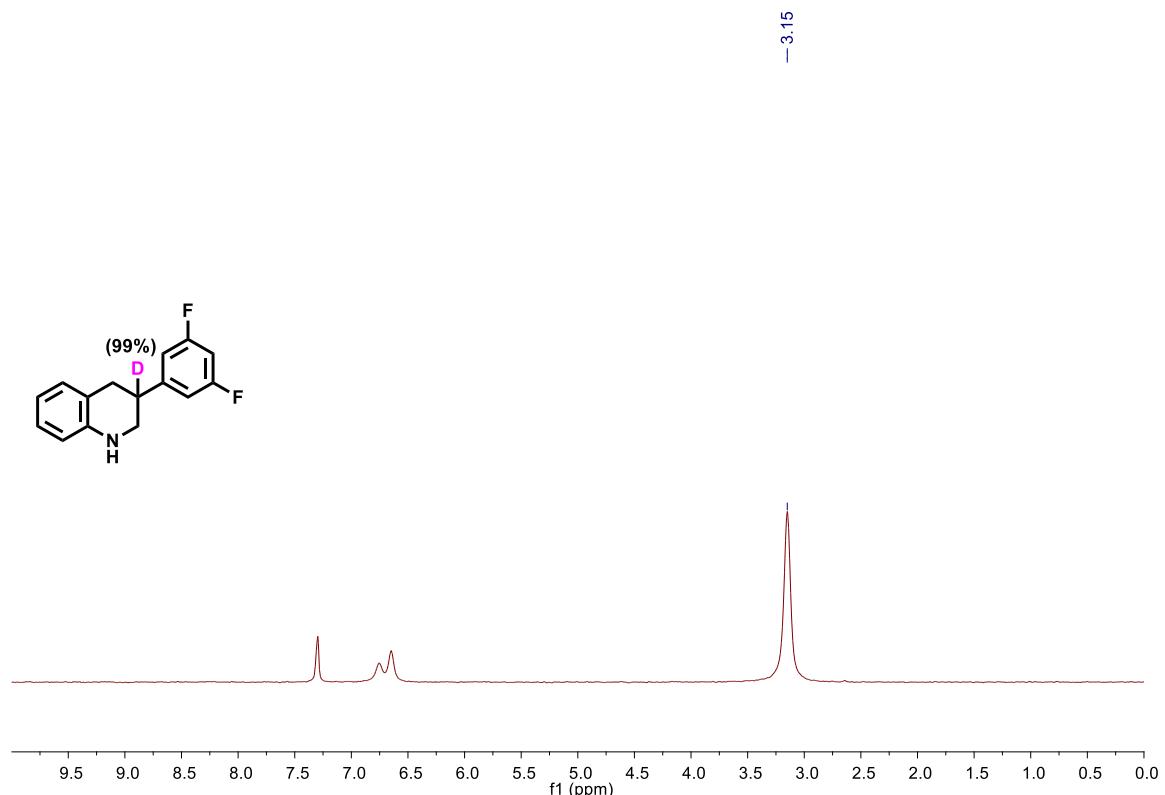
**Figure S86.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3-(3,5-difluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d



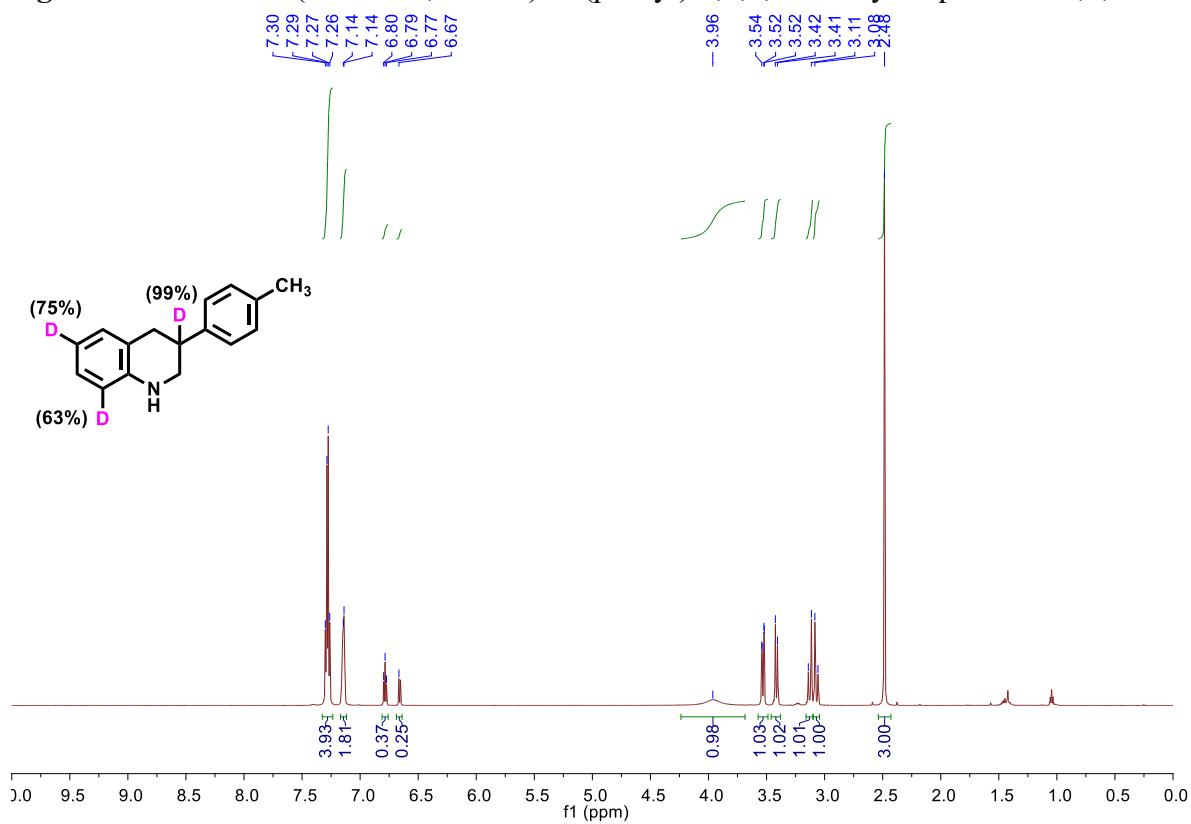
**Figure S87.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3-(3,5-difluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d



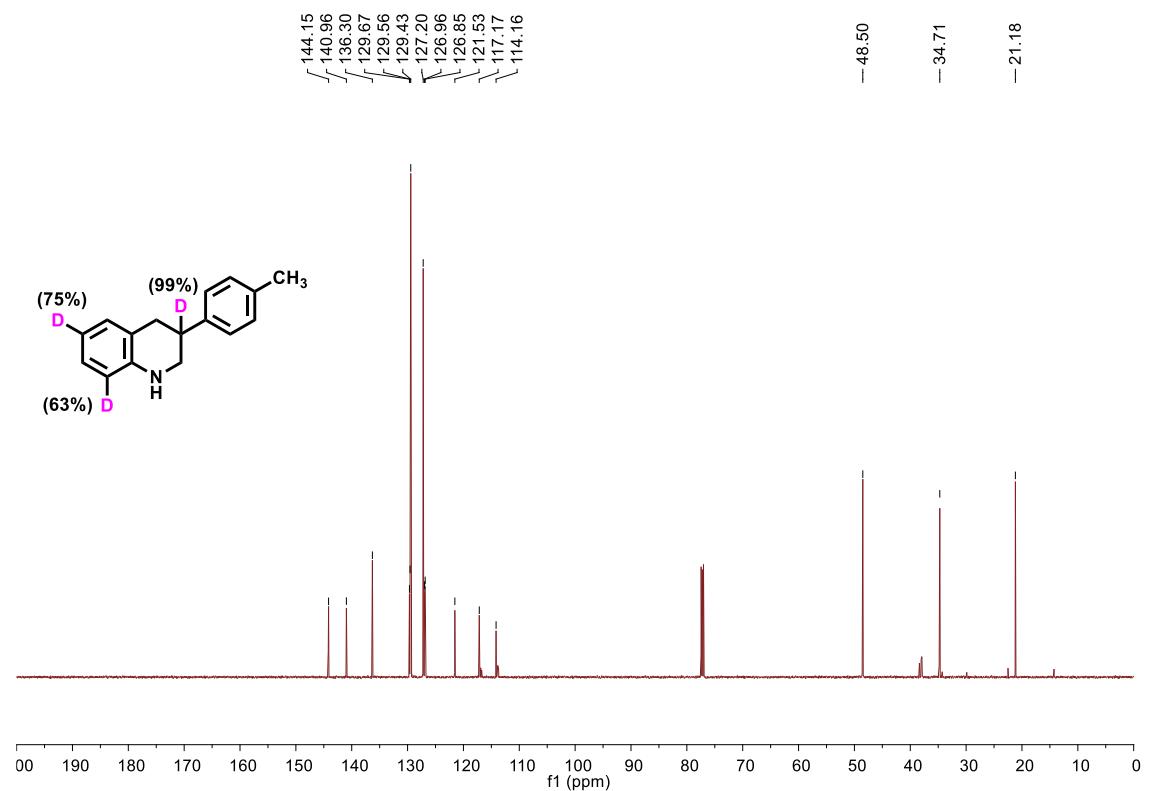
**Figure S88.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(3,5-difluorophenyl)-1,2,3,4-tetrahydroquinoline-3-d



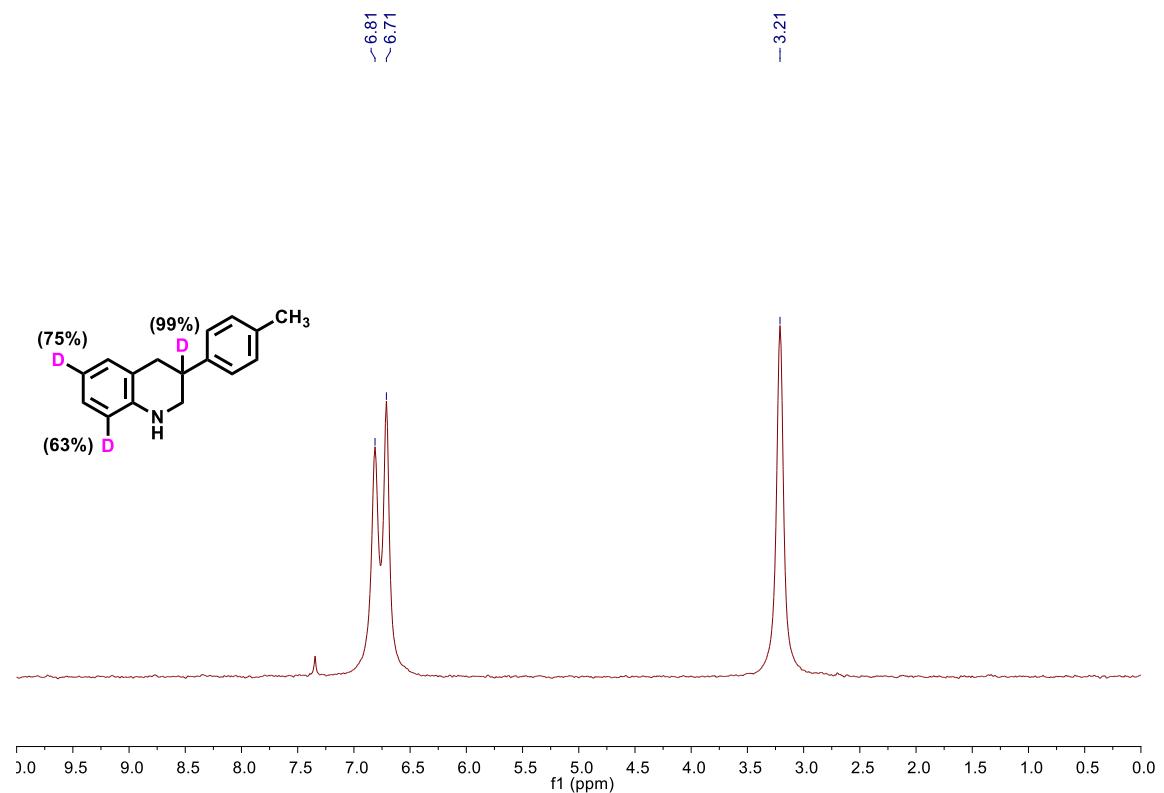
**Figure S89.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(p-tolyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



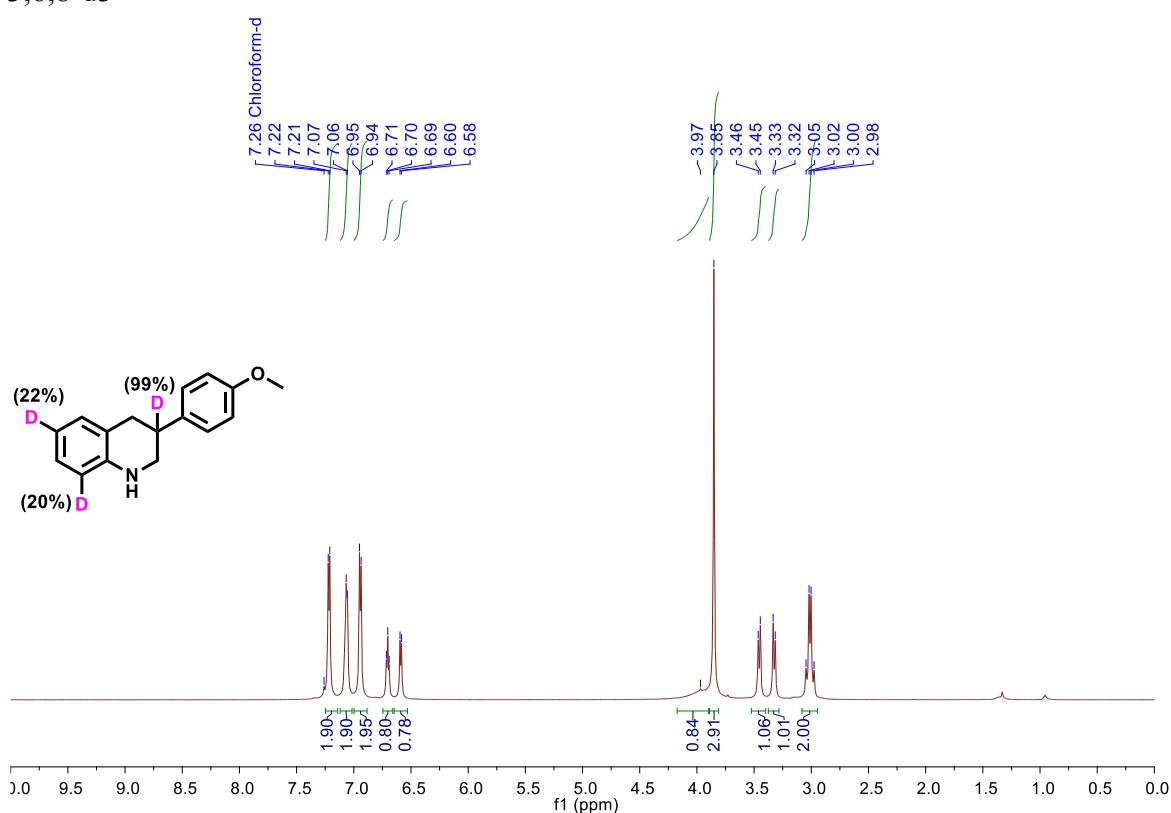
**Figure S90.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3-(p-tolyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



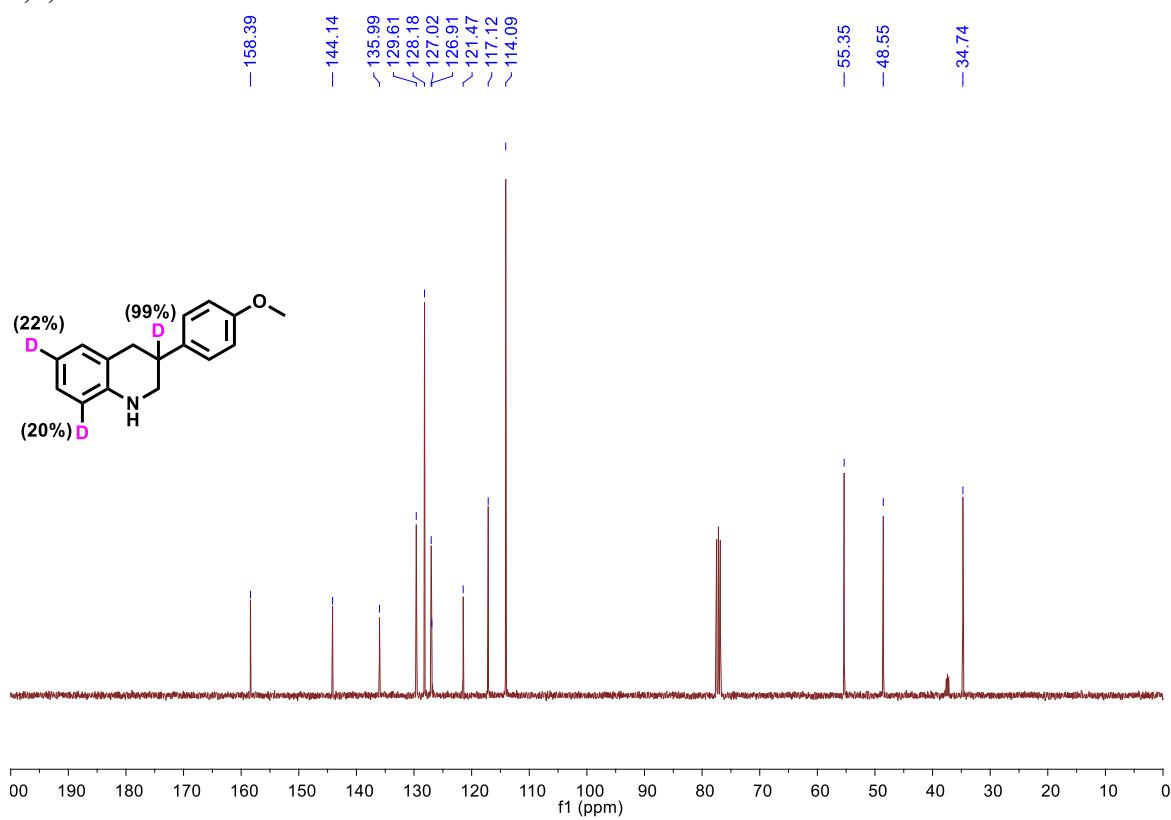
**Figure S91.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(p-tolyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



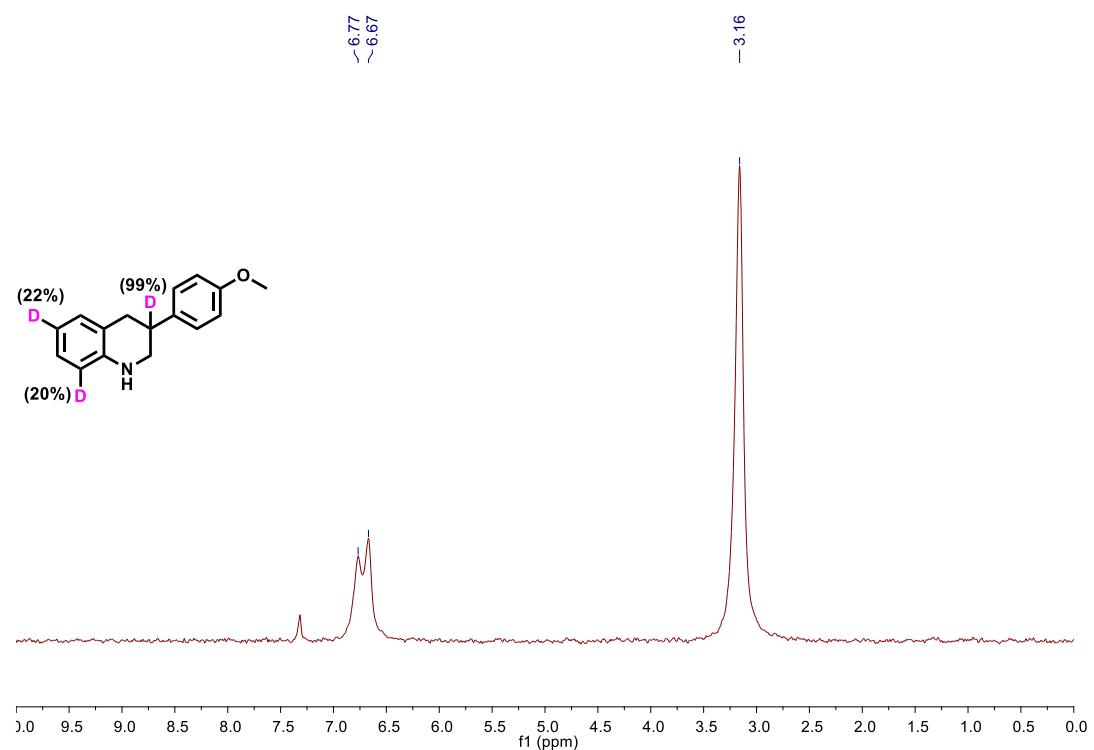
**Figure S92.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



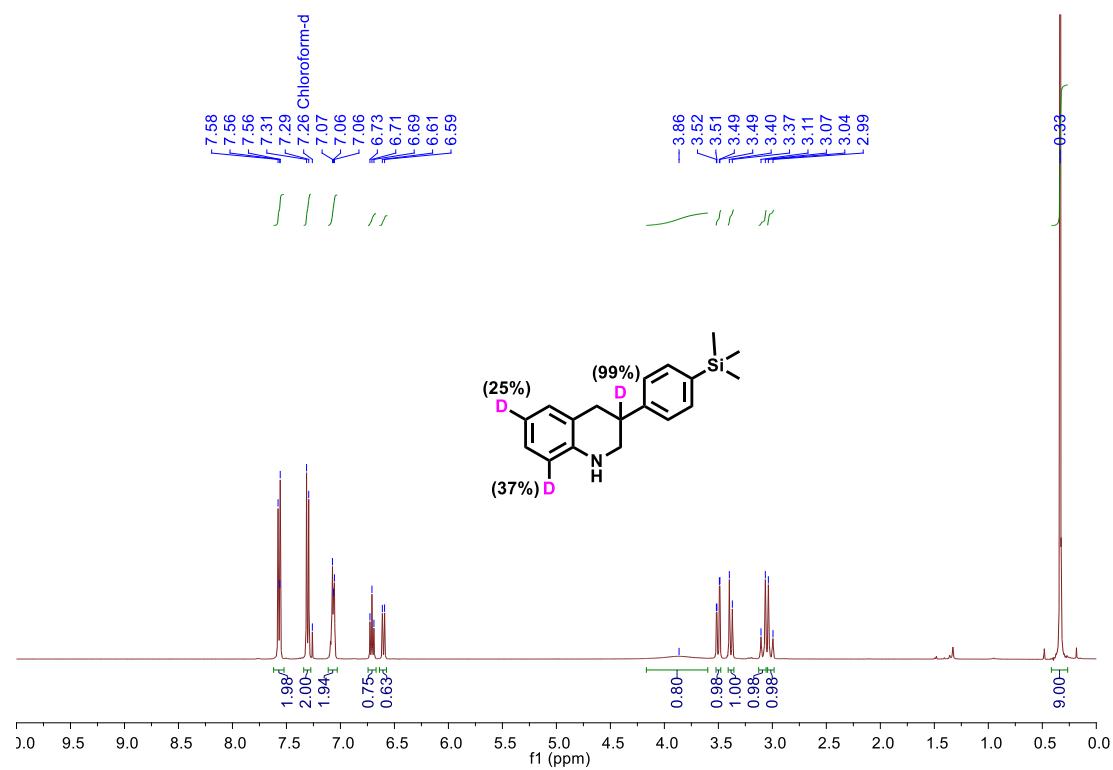
**Figure S93.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



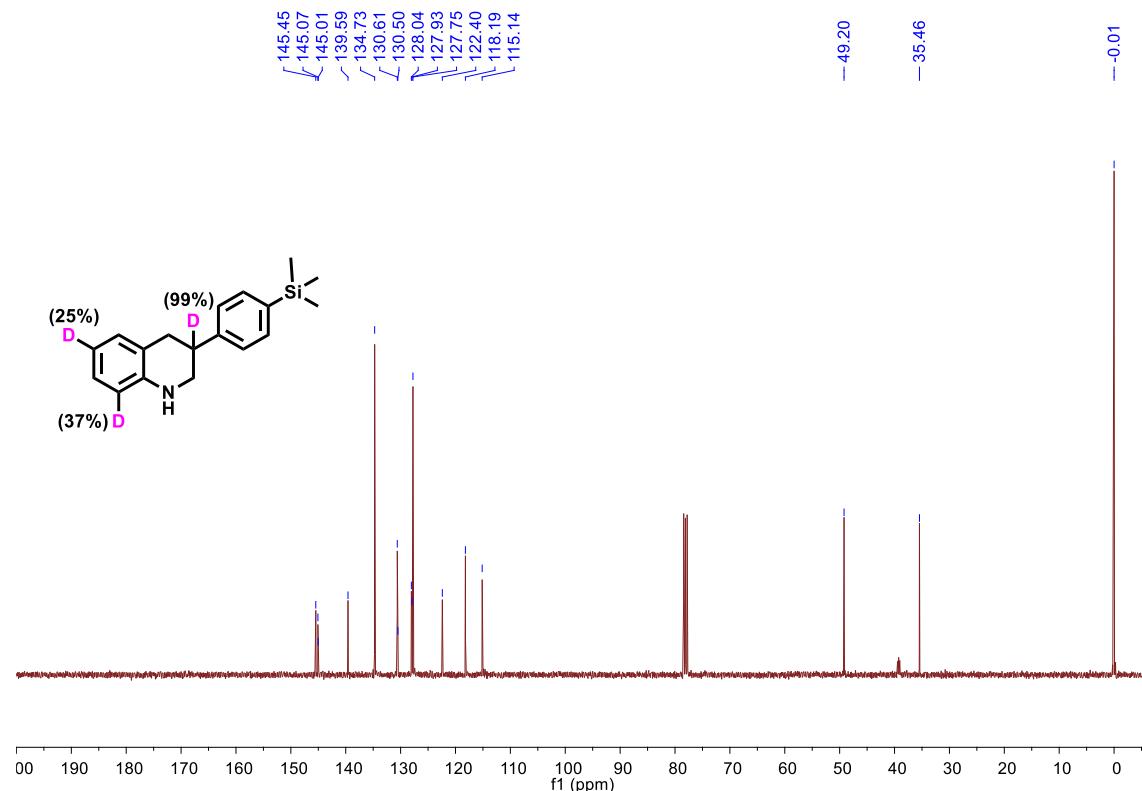
**Figure S94.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



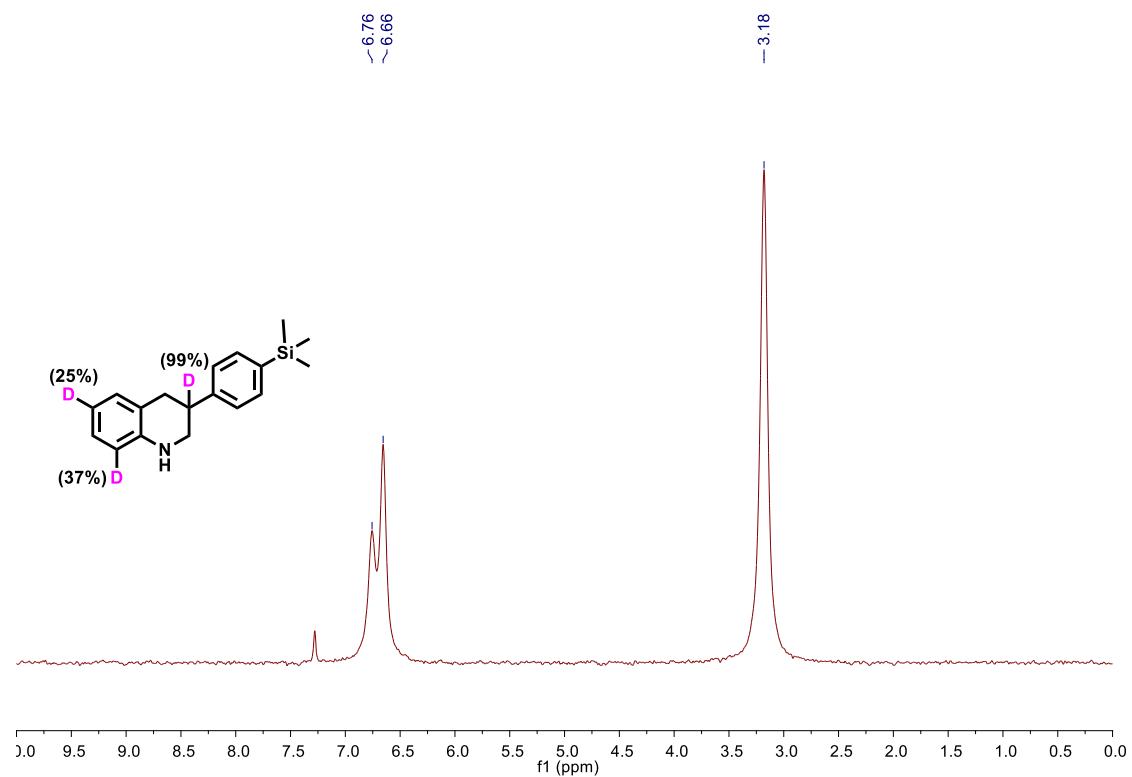
**Figure S95.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



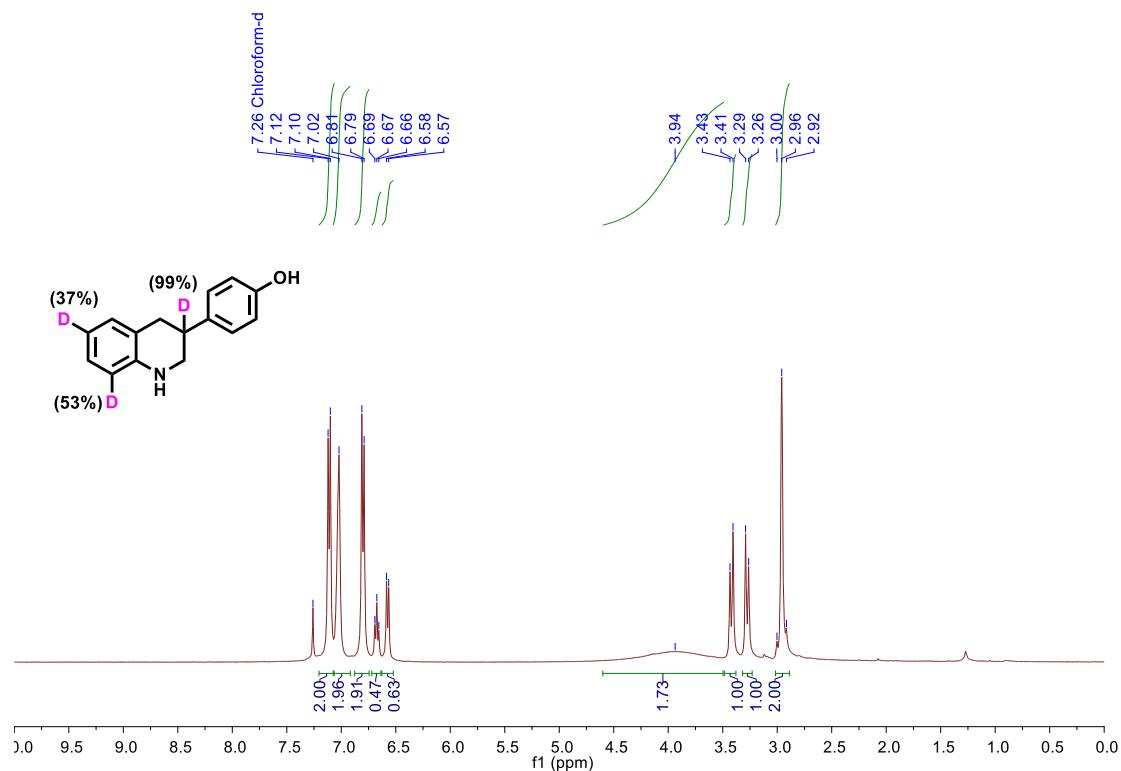
**Figure S96.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



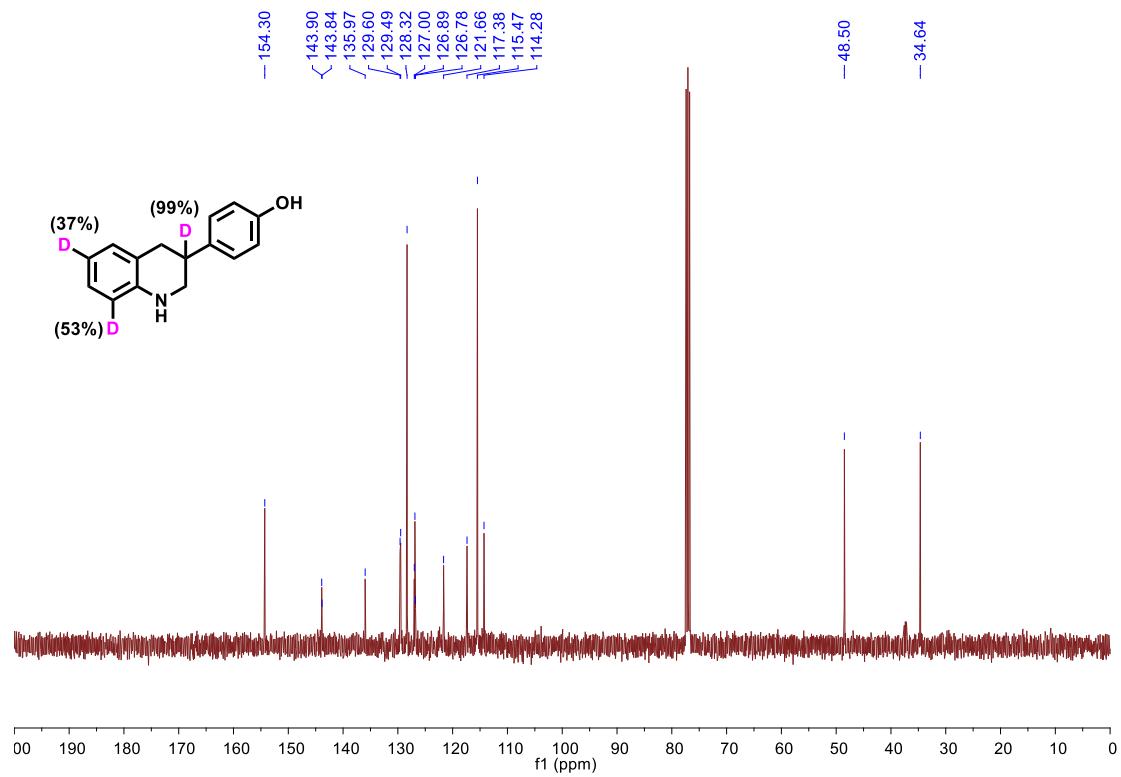
**Figure S97.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-(trimethylsilyl)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



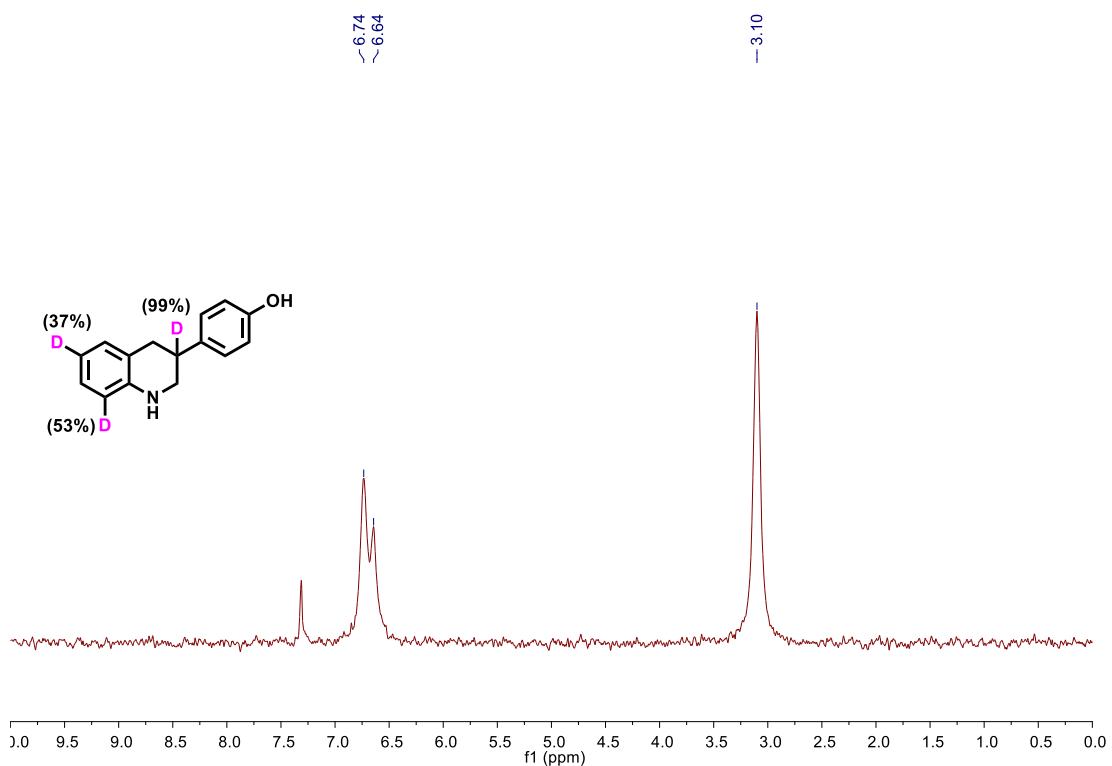
**Figure S98.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 4-(1,2,3,4-tetrahydroquinolin-3-yl-3,6,8-d<sub>3</sub>)phenol



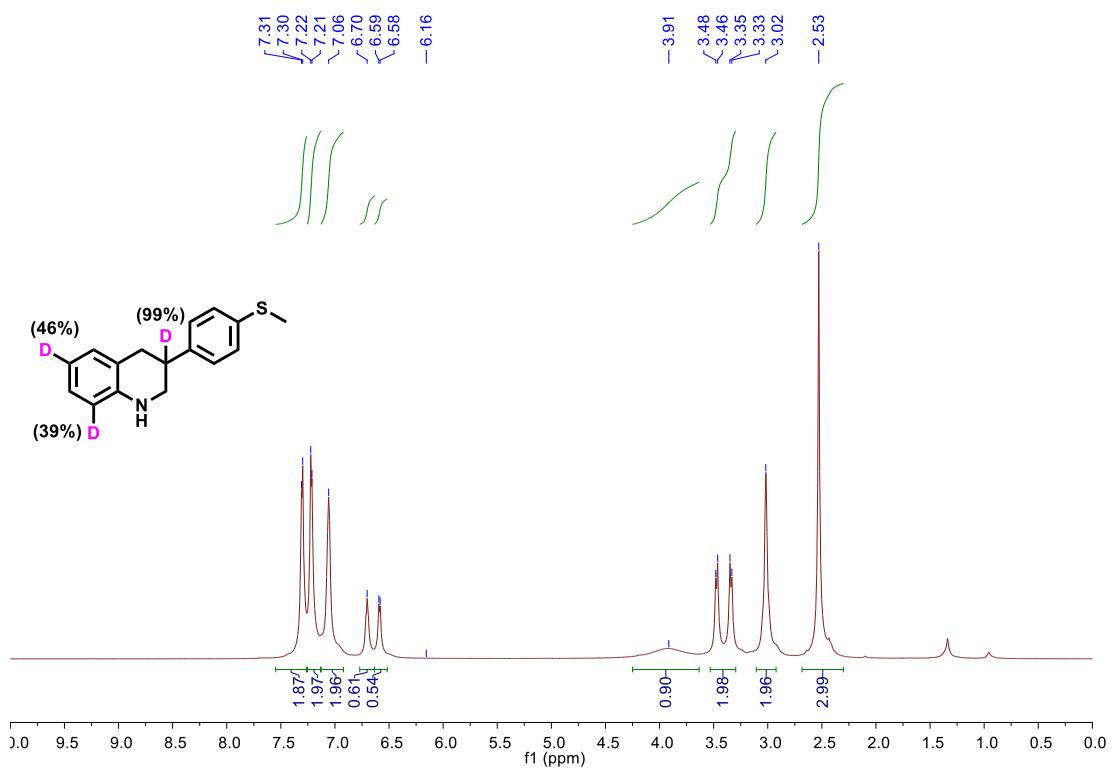
**Figure S99.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 4-(1,2,3,4-tetrahydroquinolin-3-yl-3,6,8-d<sub>3</sub>)phenol



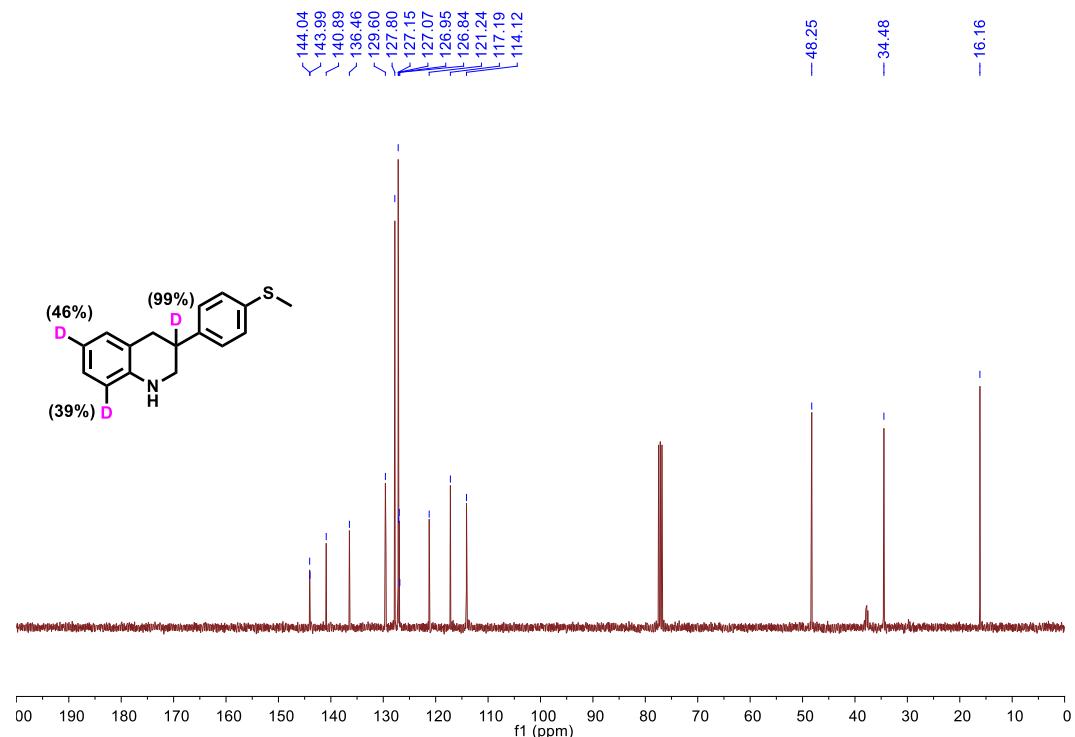
**Figure S100.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 4-(1,2,3,4-tetrahydroquinolin-3-yl)-3,6,8-d3phenol



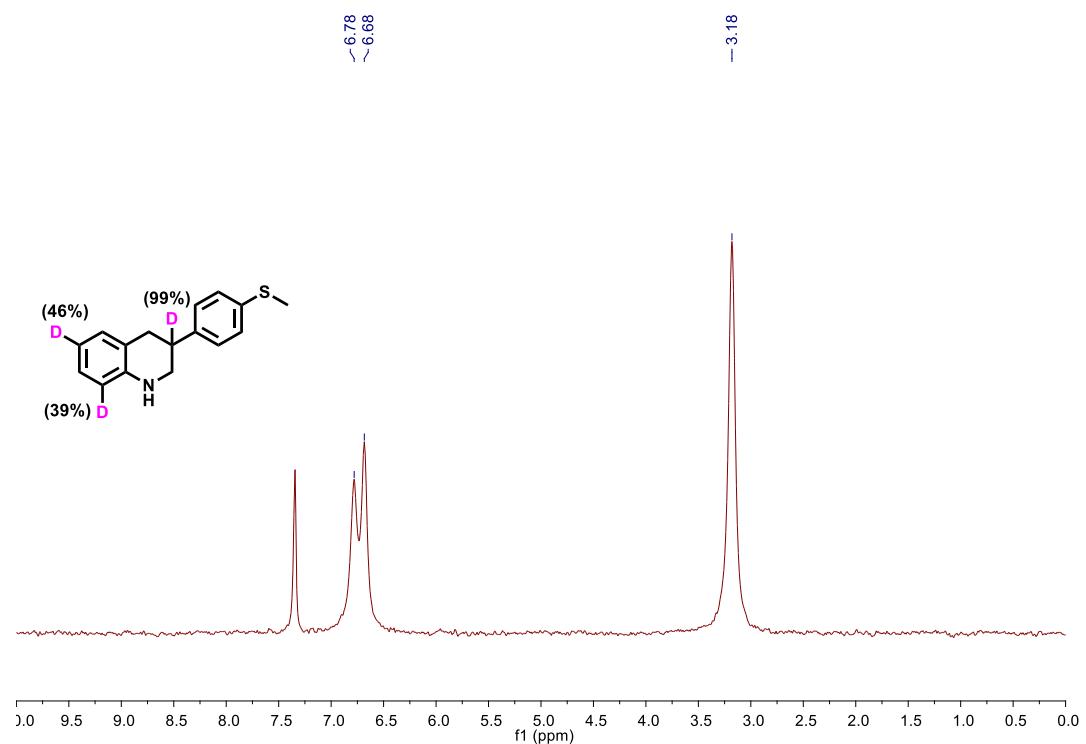
**Figure S101.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



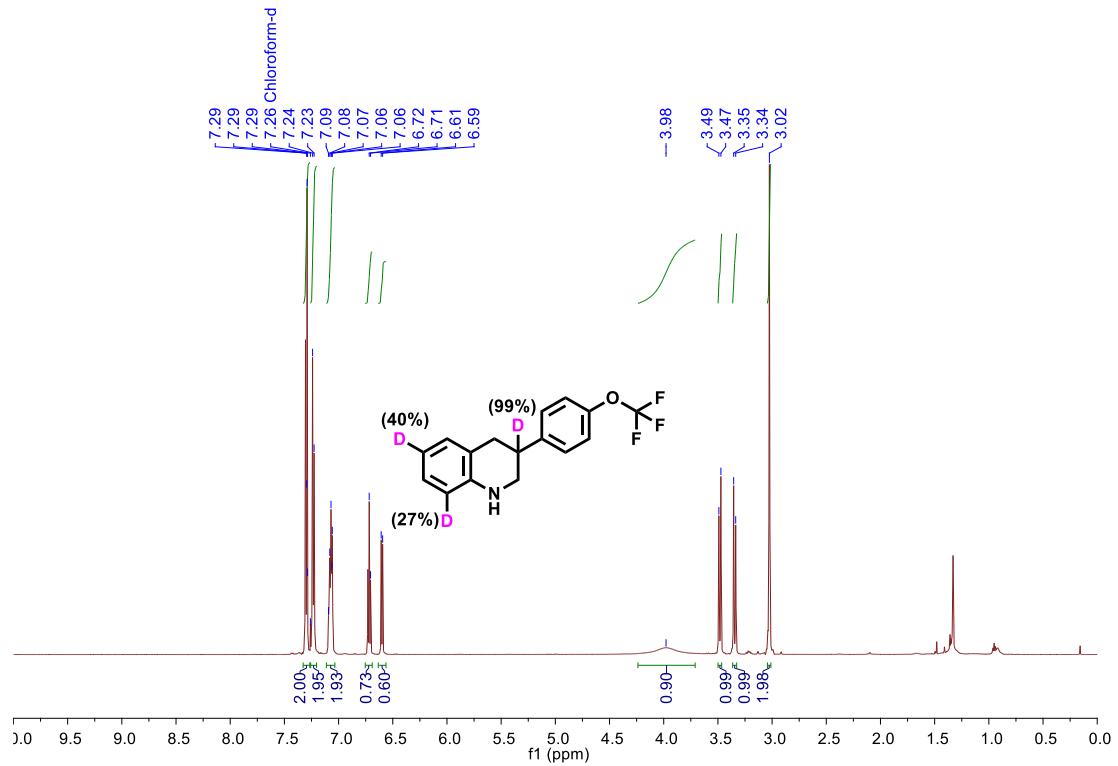
**Figure S102.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



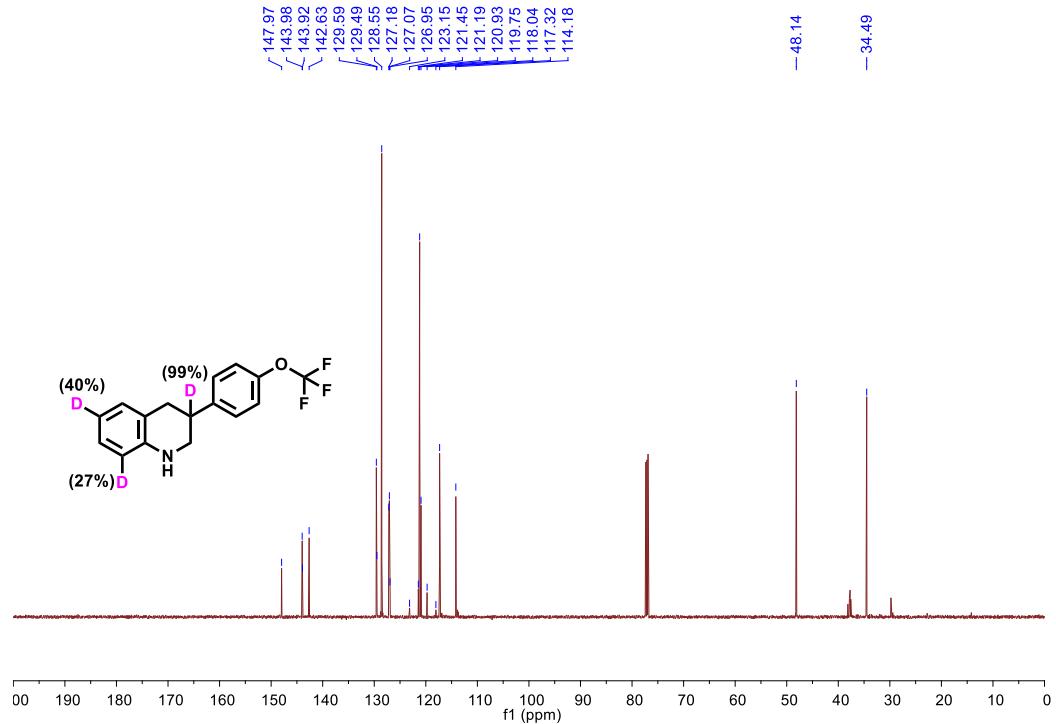
**Figure S103.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



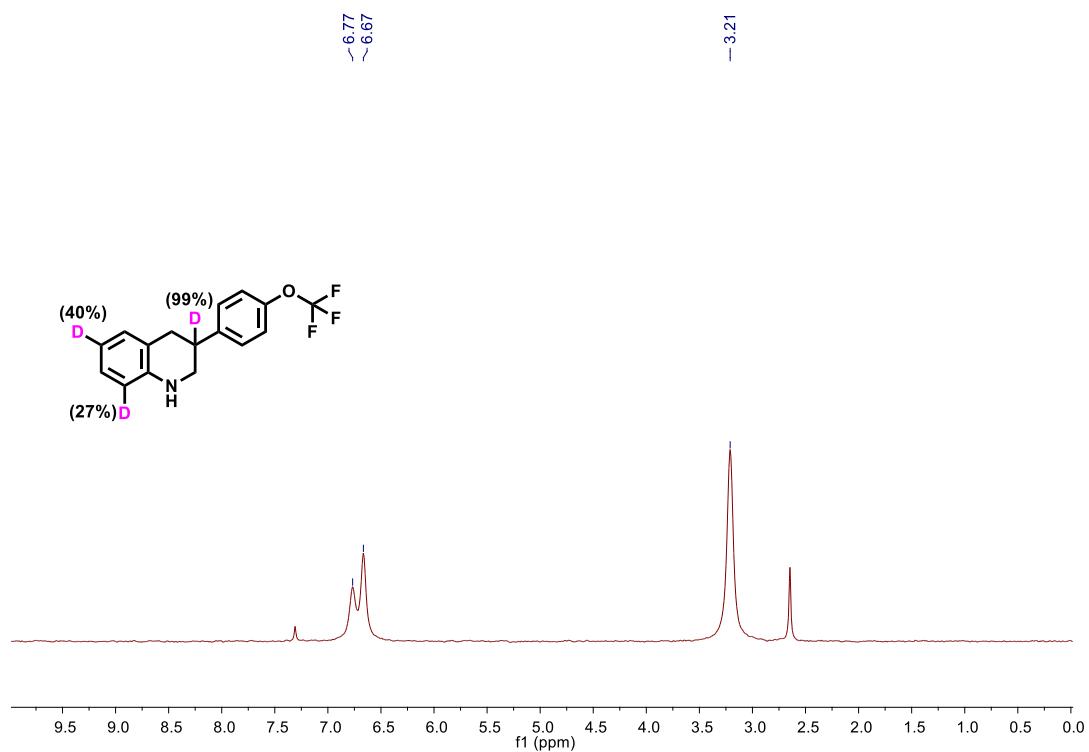
**Figure S104.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



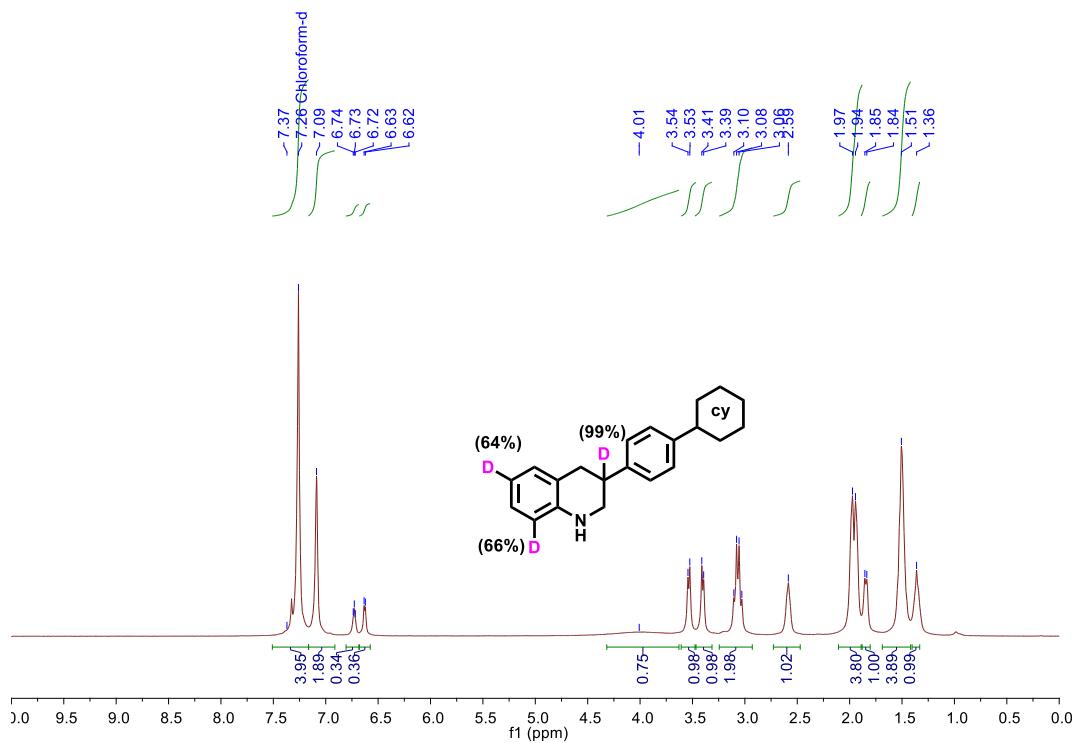
**Figure S105.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



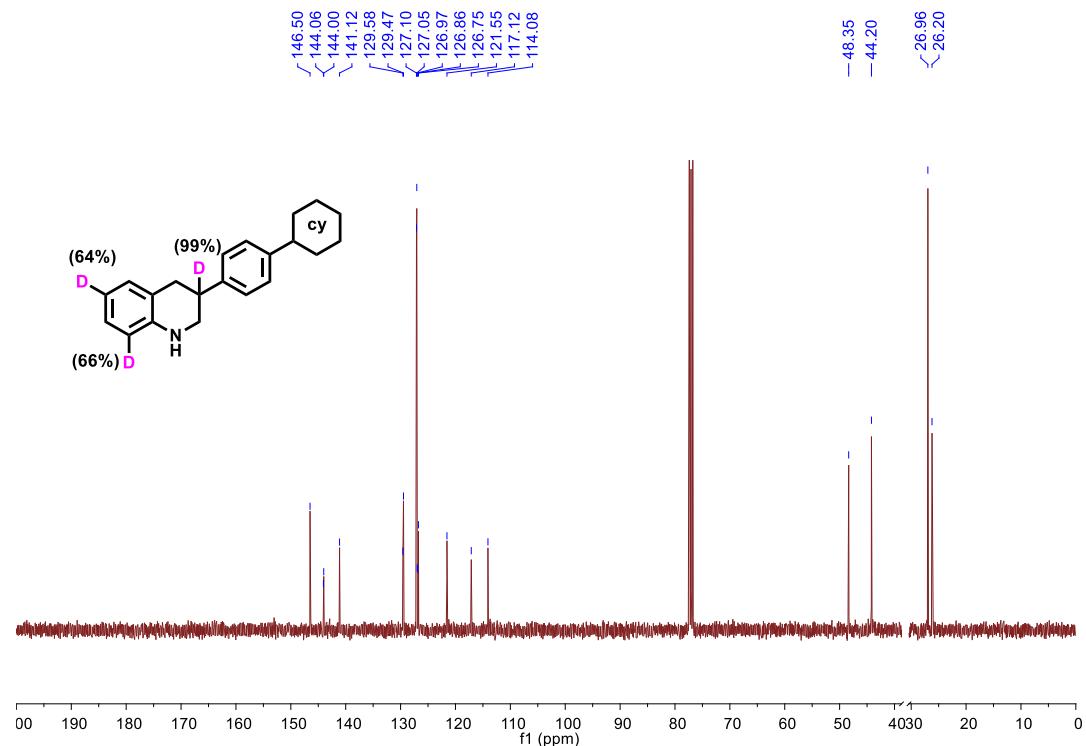
**Figure S106.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



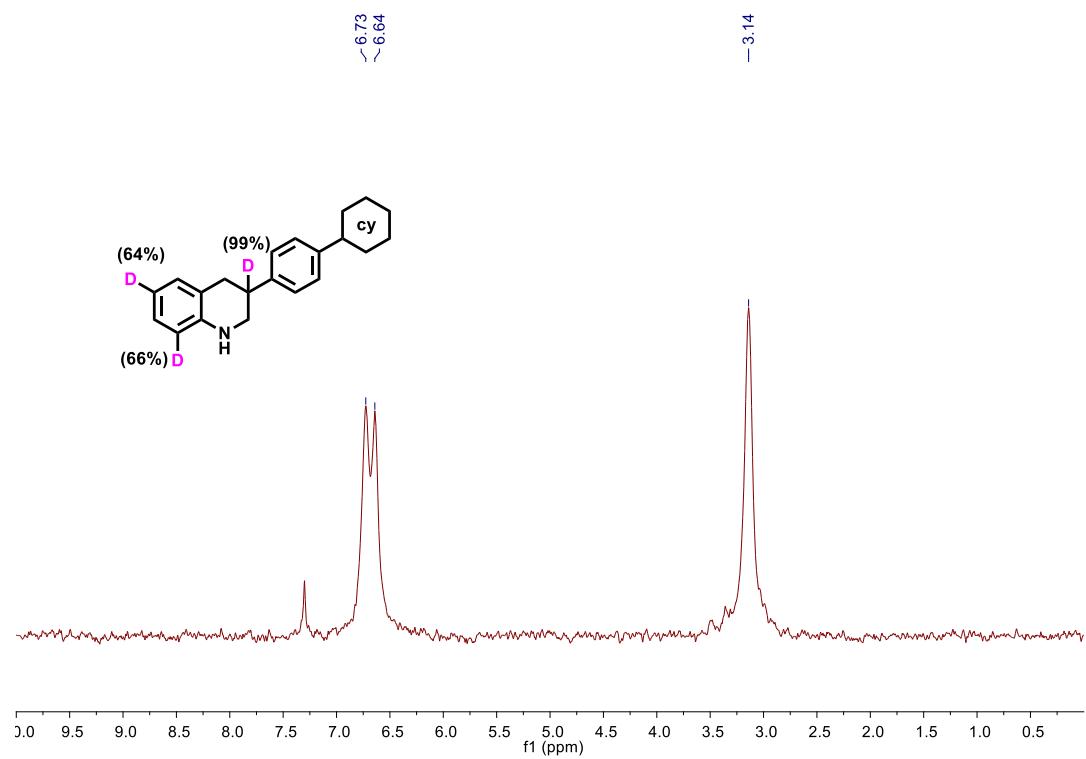
**Figure S107.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 3-(4-cyclohexylphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



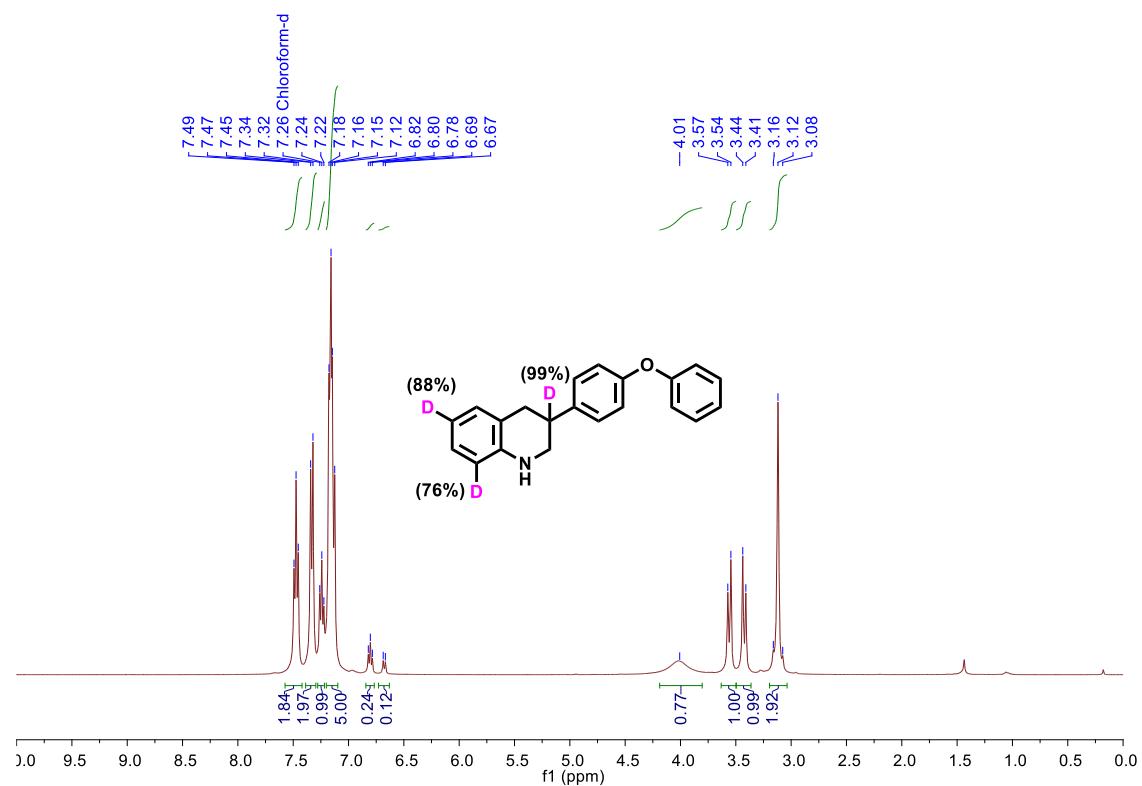
**Figure S108.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-cyclohexylphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



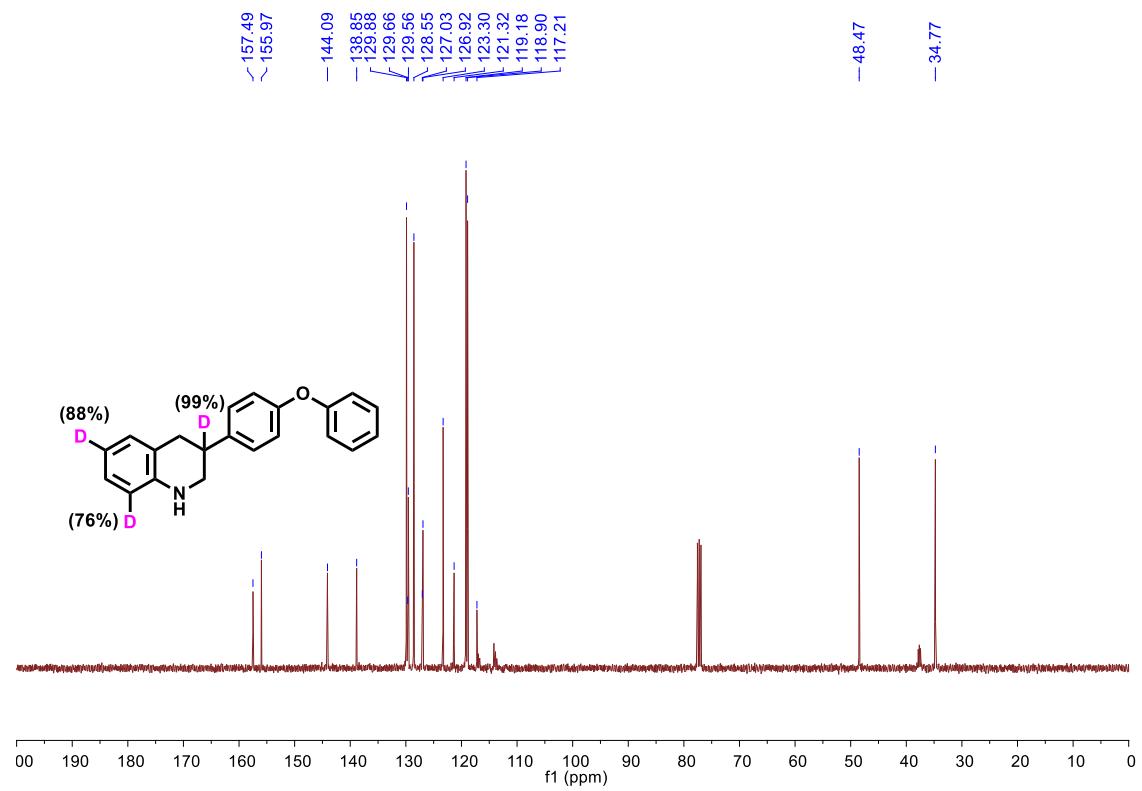
**Figure S109.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-cyclohexylphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



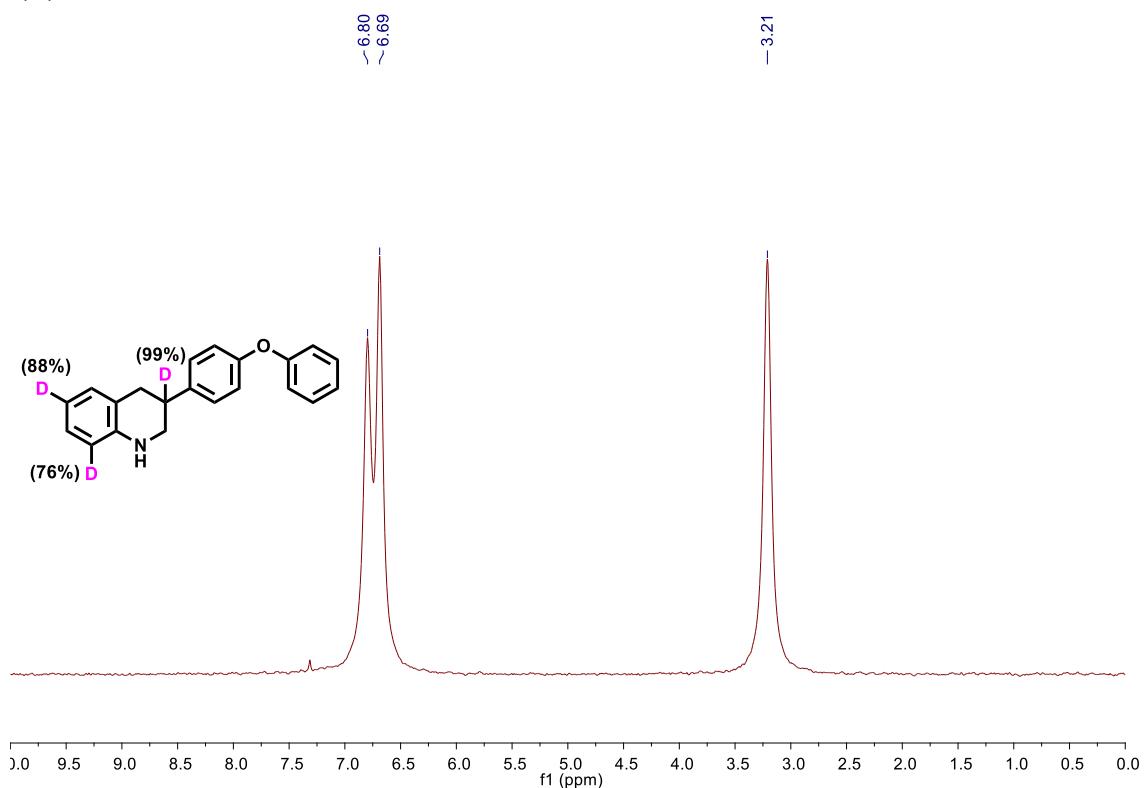
**Figure S110.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 3-(4-phenoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



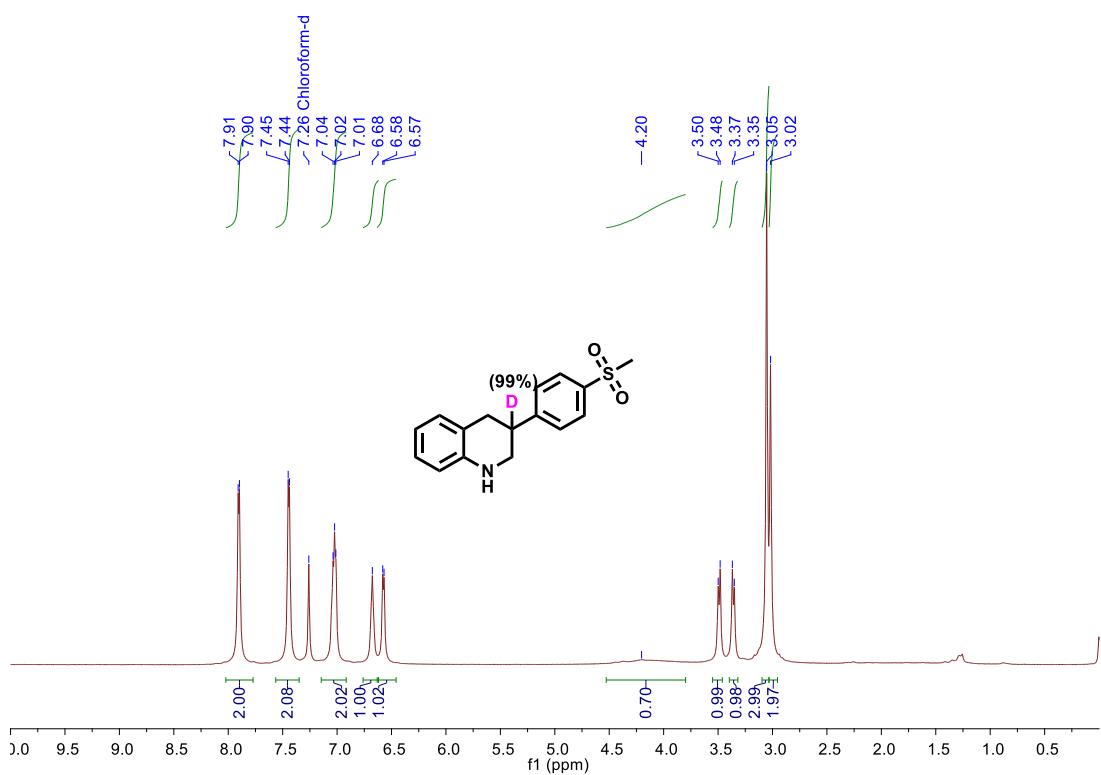
**Figure S111.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 3-(4-phenoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d3



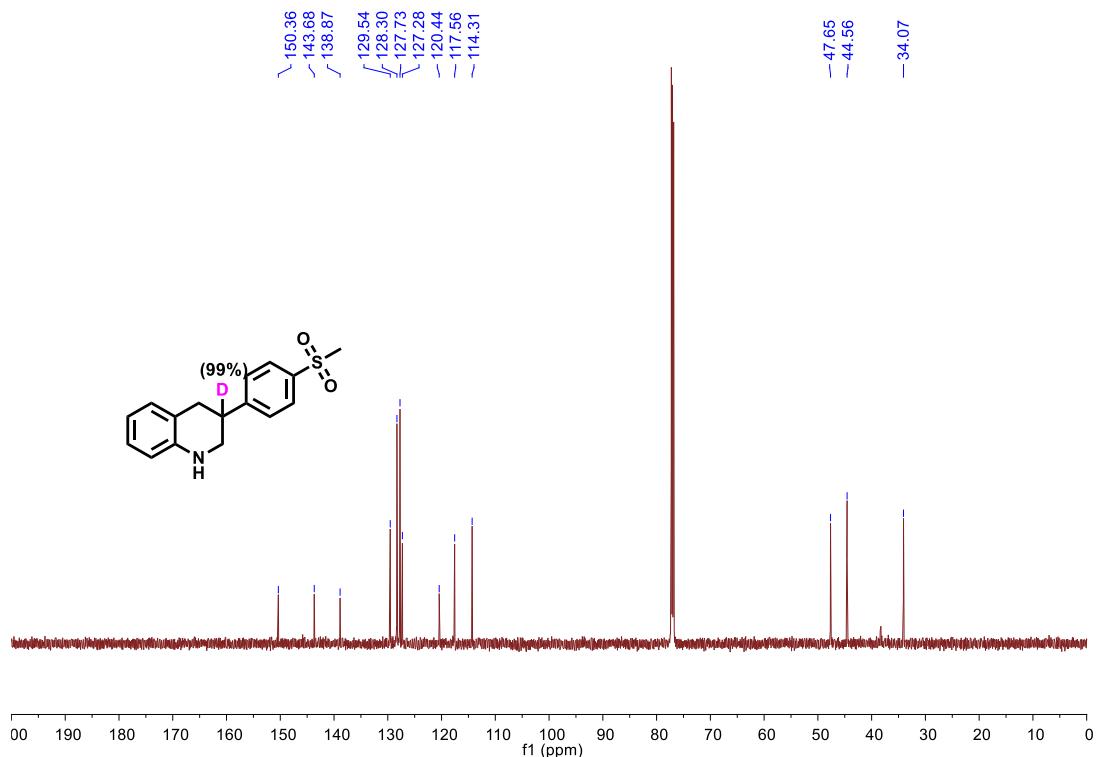
**Figure S112.**  $^2\text{H}$  NMR (92 MHz,  $\text{CHCl}_3$ ): 3-(4-phenoxyphenyl)-1,2,3,4-tetrahydroquinoline-3,6,8-d<sub>3</sub>



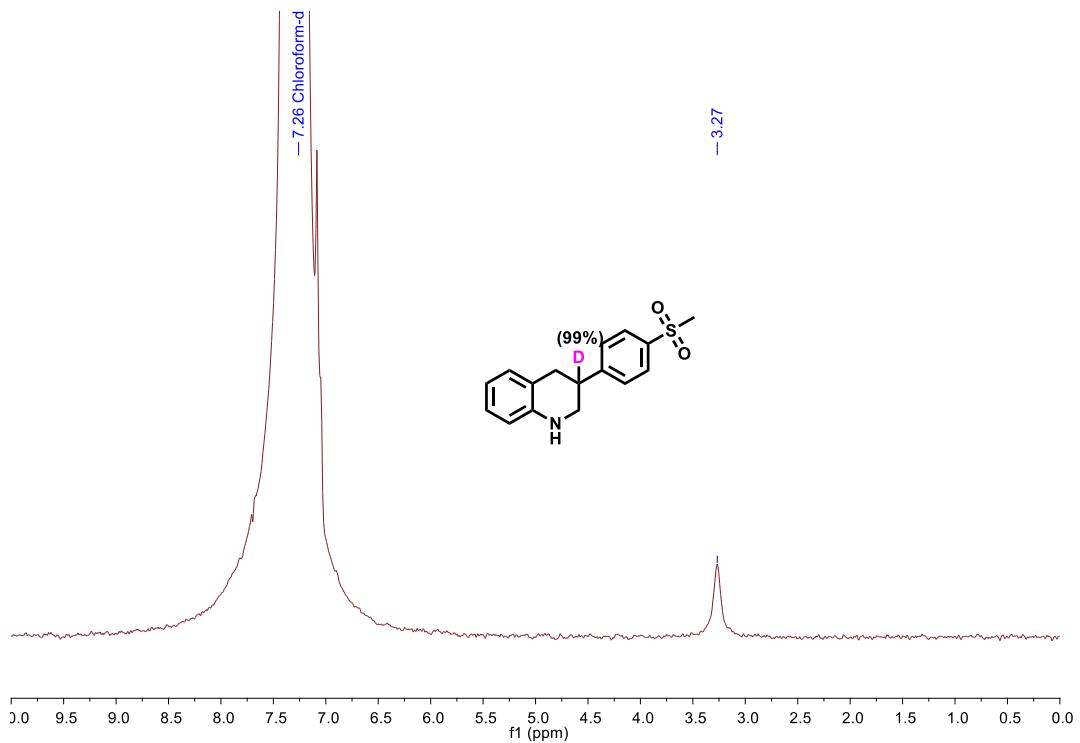
**Figure S113.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) 3-(4-(methylsulfonyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d



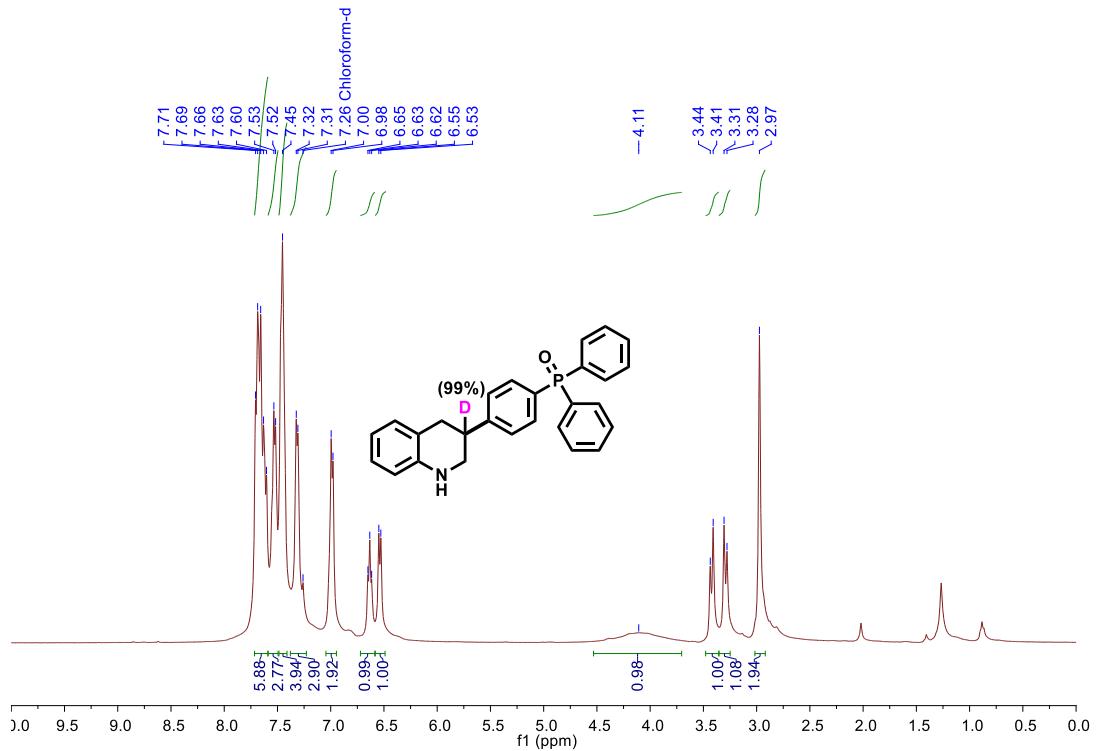
**Figure S114.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 3-(4-(methylsulfonyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d



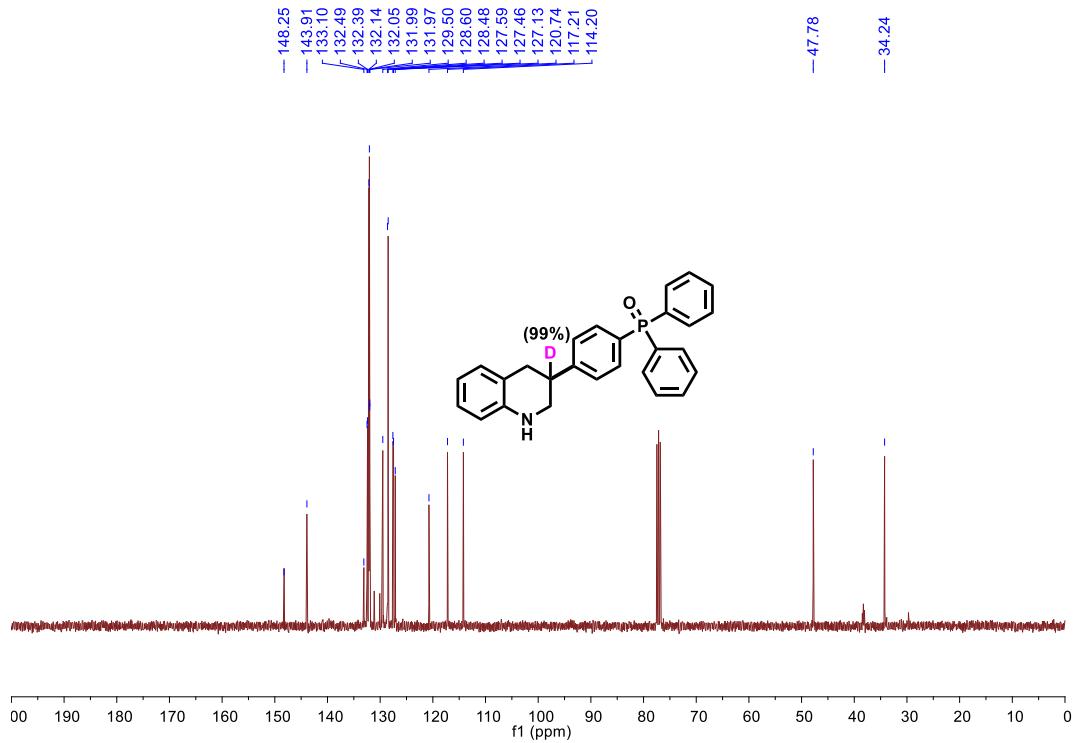
**Figure S115.**  $^2\text{H}$  NMR (92 MHz,  $\text{CDCl}_3$ ): 3-(4-(methylsulfonyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-d



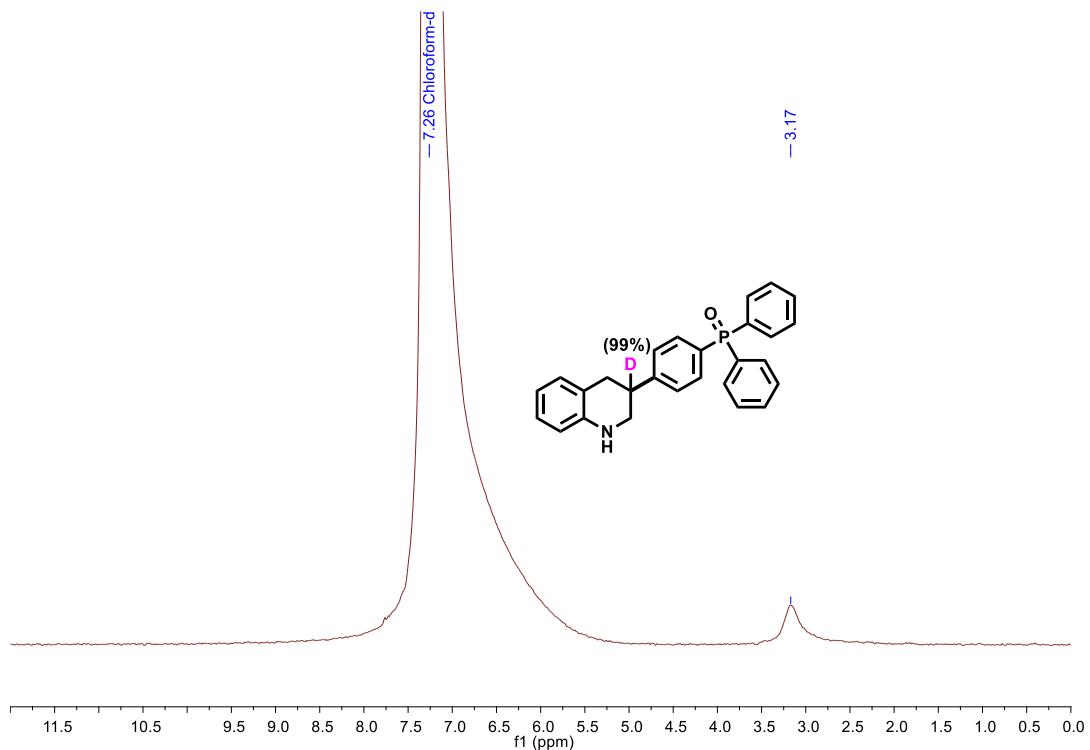
**Figure S116.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): diphenyl(4-(1,2,3,4-tetrahydroquinolin-3-yl-3-d)phenyl)phosphine oxide



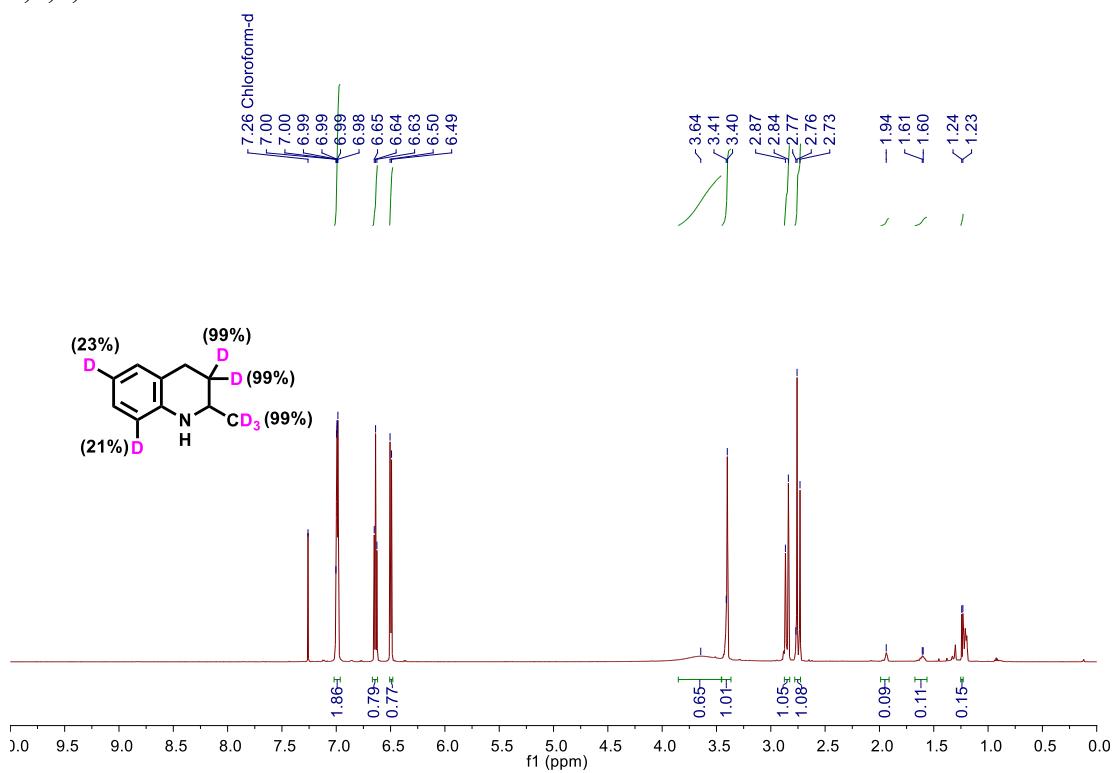
**Figure S117.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): diphenyl(4-(1,2,3,4-tetrahydroquinolin-3-yl-3-d)phenyl)phosphine oxide



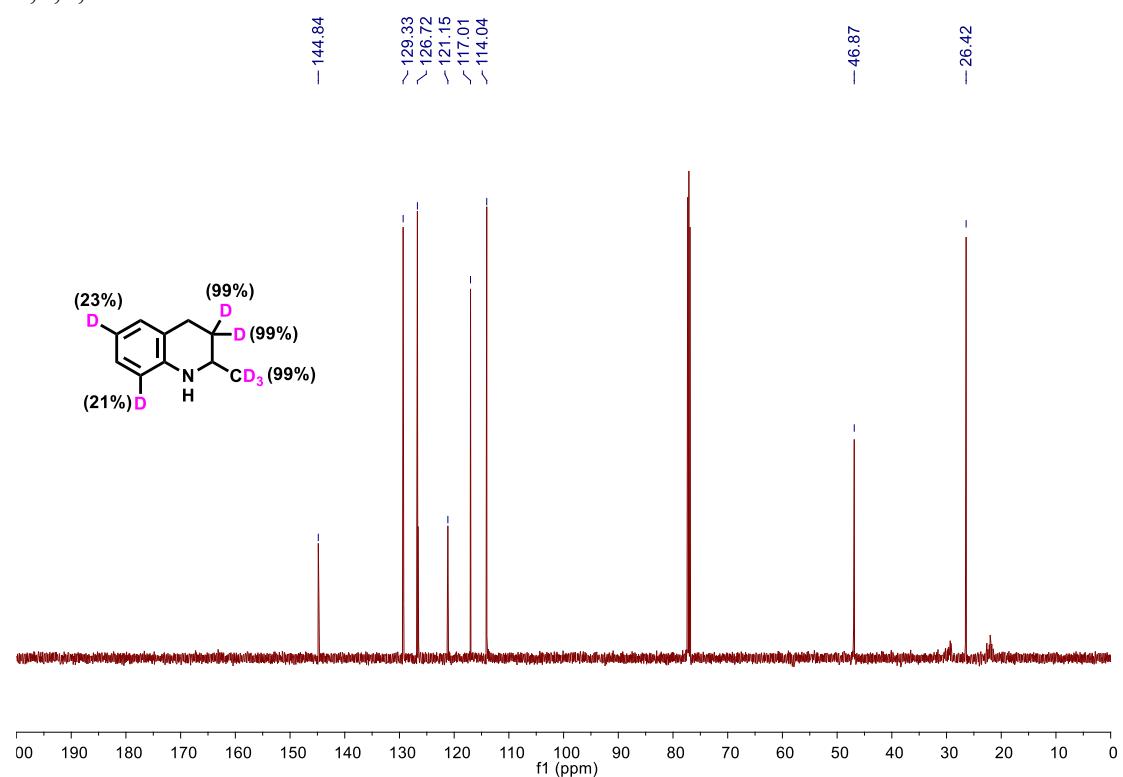
**Figure S118.**  $^2\text{H}$  NMR (92 MHz,  $\text{CDCl}_3$ ): diphenyl(4-(1,2,3,4-tetrahydroquinolin-3-yl-3-d)phenyl)phosphine oxide



**Figure S119.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 2-(methyl-d3)-1,2,3,4-tetrahydroquinoline-3,3,6,8-d4



**Figure S120.**  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 2-(methyl-d<sub>3</sub>)-1,2,3,4-tetrahydroquinoline-3,3,6,8-d<sub>4</sub>



**Figure S121.**  $^2\text{H}$  NMR (151 MHz,  $\text{CHCl}_3$ ): 2-(methyl-d<sub>3</sub>)-1,2,3,4-tetrahydroquinoline-3,3,6,8-d<sub>4</sub>

