BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

# Supporting Information

for

# Electrocatalytic hydrogenation of cyanoarenes, nitroarenes, quinolines, and pyridines under mild conditions with a proton-exchange membrane reactor

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*Beilstein J. Org. Chem.* **2024,** *20,* 1560–1571. doi:10.3762/bjoc.20.139

# Experimental part

**General**

Gas chromatography (GC) analyses were performed by using a SHIMADZU gas chromatograph (GC2014s with a capillary column thickness of film: 0.25 μm, length: 25.0 m, inner diameter: 0.22 mm (CBP1-M25-025, SHIMADZU GLC Ltd.), carrier gas: helium). Constant-current electrolysis was carried out with a DC power supply (KIKUSUI PMX350-0.2A). Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECZ600R ($^1$H 600 MHz, $^{13}$C 150 MHz, $^{19}$F 565 MHz), JEOL JNM-ECS400 ($^1$H 400 MHz, $^{13}$C 100 MHz, $^{19}$F 376 MHz), Varian 400-MR ASW ($^1$H 400 MHz, $^{13}$C 100 MHz) and Varian NMR System PS600 ($^1$H 600 MHz, $^{13}$C 150 MHz) spectrometers. Chemical shifts for $^1$H NMR are expressed in parts per million (ppm) relative to TMS (δ 0.00 ppm) or residual $CHCl_3$ in $CDCl_3$ (δ 7.26 ppm) or $H_2O$ in $D_2O$ (δ 4.79 ppm). Chemical shifts for $^{13}$C NMR are expressed in parts per million (ppm) relative to TMS (δ 0.00 ppm) or $CDCl_3$ (δ 77.16 ppm) with a complete proton decoupling. Chemical shifts for $^{19}$F NMR are expressed in ppm relative to α,α,α-trifluorotoluene (δ −63.9 ppm) or hexafluorobenzene (δ −162.9 ppm). IR spectra were recorded on a SHIMADZU IRAffinity-1 spectrophotometer. High-resolution mass spectrometry was performed on a Bruker micrOTOF II-SKA (ESI-MS). Analytic thin layer chromatography (TLC) was performed on Merck, pre-coated plate silica gel 60 $F_{254}$ (0.25 mm thickness). Column chromatography was performed on KANTO CHEMICAL silica gel 60N (40–50 μm).

**Materials**

All chemicals were purchased from commercial suppliers. All chemicals were used without further purification. Stainless steel end plates and carbon separators for a PEM reactor were purchased from CHEMIX Co., Ltd. As for manufacturing the membrane electrode assembly (MEA), Nafion® perfluorinated membrane (Nafion® NR212) was purchased from Furukawa agency Co., Ltd. Nafion® perfluorinated resin solution (5 wt % in mixture of lower aliphatic and water, Nafion® DE521) as ionomer solution was purchased from Sigma-Aldrich Co. or Wako Pure Chemical Industries. Fuel cell catalysts (TEC10E50E; Pt/C, TECRU(ONLY)E30; Ru/C, TEC66E50; Pt50Ru50/C and TEC62E58; Pt33Ru67/C) were purchased from Tanaka Kikinzoku Kogyo K.K. (TKK). Pd/C was purchased from ISHIFUKU Metal Industry Co., Ltd. PtPd/C, and Ir/C were supplied by ISHIFUKU Metal Industry Co., Ltd. DSE® electrode was supplied by De Nora Permelec Ltd. Gas diffusion layer (GDL39BB) was purchased from SGL CARBON GmbH. 2,3-Dimethylquinoline (**6i**)[1] and 6-(trifluoromethyl)quinoline (**6t**)[2] were synthesized according to the literature.

**Preparation of MEAs**

Fuel cell catalyst (244 mg), deionized water (1.2 g), Nafion® perfluorinated resin solution, and 1-propanol (1.4 g) were stirred in a glass vial. This mixture and zirconia balls (diameter: 3.0 mm, 10 pieces) were added to a Teflon® vessel. The vessel was placed in a planetary rotation pot mill (PULVERISETTE, Fritsch Japan Co. Ltd.) and rotated at 200 rpm for 20 min. After the rotation, catalyst dispersion was obtained. Gas diffusion electrodes (GDE, 5 cm × 5 cm) were homemade by spraying catalyst inks (Nafion®/catalysts weight ratio of 0.8:1, 1-propanol as dispersant) on commercialized GDL39BB to form a catalyst layer and then drying at 120 °C, 3 min. After spraying, the GDE sheet was cut into 1 cm × 4 cm pieces. Two sheets of this catalyst layer were used for the anode and the cathode. Nafion® perfluorinated membrane (3 cm × 10 cm) was put between the anode and the cathode, and their catalyst sides faced to the membrane. Finally, this was hot-pressed (0.4 MPa, 150 °C) for 10 min. Pt/C was used as an anode

catalyst material and Pt/C, Pd/C, Ir/C, Ru/C, PtPd/C, and PtRu/C were used as cathode catalyst materials. The loading amount of each catalyst was 0.5 mg/cm$^2$.

**Preparation of a PEM reactor**

As shown in Figure S1, stainless steel, carbon separators, Teflon® gaskets, and MEA were used to fabricate the PEM reactor, which was tightened to 2.0 Nm with M6 size screws using a torque wrench.

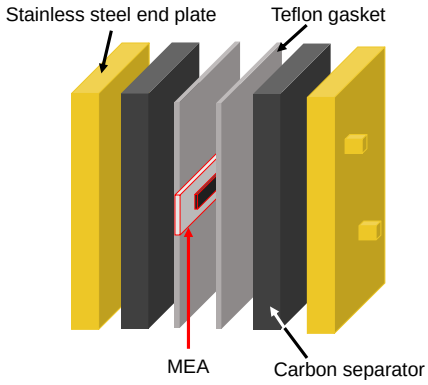



**Figure S1.** PEM reactor

**General procedure for hydrogenation of cyanoarenes and nitroarenes using a PEM reactor**

Electrocatalytic hydrogenations were carried out by using a PEM reactor (Figure S2). The MEA (3 cm × 10 cm, 1 cm × 4 cm: active area) was integrated into the PEM reactor. For the cathodic chamber, humidified nitrogen gas was supplied for 1 hour. After that, the solution of substrate solution was provided by a circular pump (YAMAZEN, MSP-001-0). For the anodic chamber, humidified hydrogen gas (flow rate: 100 mL/min) was supplied. A constant current was supplied at room temperature. The yields of products were determined by GC or NMR analyses.

**General procedure for hydrogenation of quinoline (6) using a PEM reactor**

Electrocatalytic hydrogenation was carried out by using a PEM reactor. The MEA (3 cm × 10 cm, 1 cm × 4 cm: active area) was integrated into the PEM reactor. For the cathodic chamber, humidified nitrogen gas was supplied for 1 hour. After that, the solution of the substrate (1.5 mmol) in $CH_2Cl_2$ (3 mL) was provided with 0.75 mL/min by a circular pump (YAMAZEN, MSP-001-0). For the anodic chamber, humidified hydrogen gas (flow rate: 100 mL/min) was supplied. A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. To the obtained cathodic reaction solution was added NaOH aq (1.0 M, 5 mL), and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phase was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc to afford 1,2,3,4-tetrahydroquinoline.

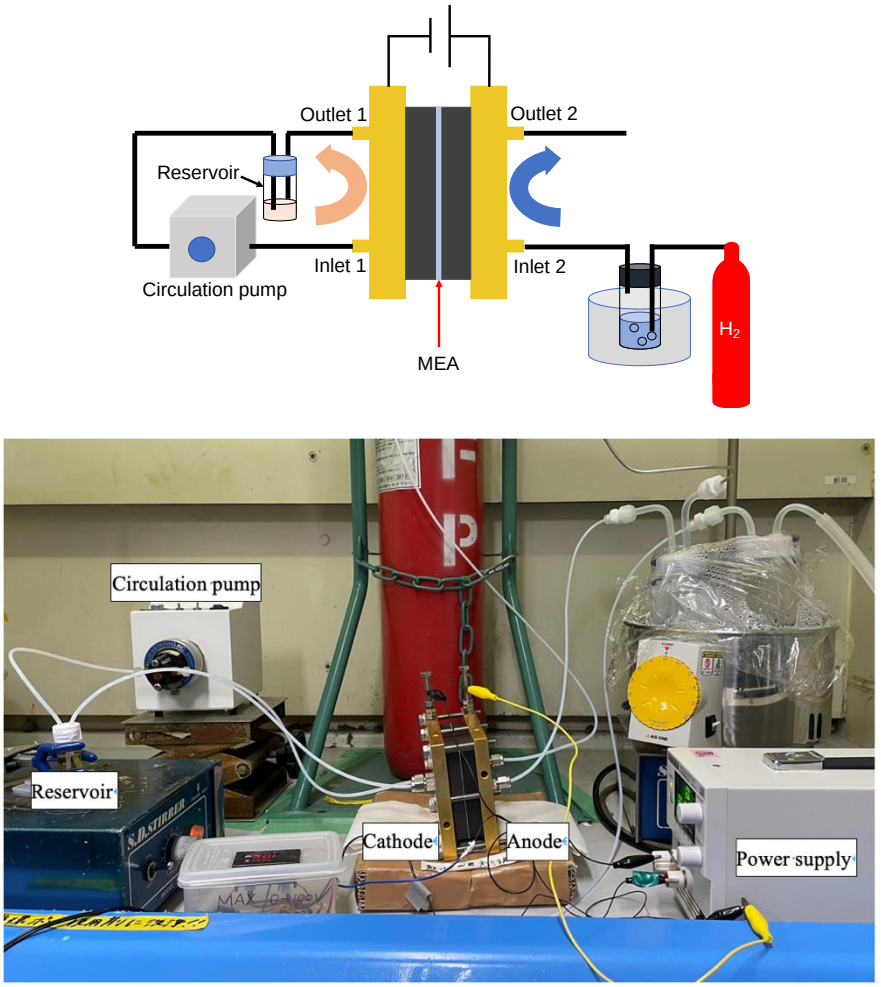
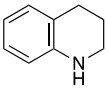


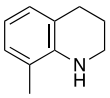

**Figure S2.** Hydrogenation system using a PEM reactor

**1,2,3,4-Tetrahydroquinoline (7a)**



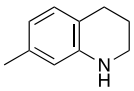
Prepared according to the general procedure from quinoline (**6a**, 194 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as yellow liquid (180 mg, 1.35 mmol, 90%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.95 (td, $J$ = 7.2, 1.0 Hz, 1H), 6.93 (d, $J$ = 7.2 Hz, 1H), 6.59 (td, $J$ = 7.2 Hz, 1H), 3.80 (brs, 1H), 3.29 (t, $J$ = 6.5 Hz, 2H), 2.75 (t, $J$ = 6.5 Hz, 2H), 1.93 (quint, $J$ = 6.5 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 144.9, 129.6, 126.8, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3; IR (neat) 3408, 2928, 2839, 2361, 1607, 1504, 1312, 1096, 1007, 746 cm$^{-1}$. The spectral data were in good agreement with literature.[3]

**8-Methyl-1,2,3,4-tetrahydroquinoline (7b)**



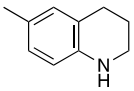
Prepared according to the general procedure from 8-methylquinoline (**6b**, 215 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (196 mg, 1.33 mmol, 89%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, $J$ = 7.6 Hz, 1H), 6.86 (d, $J$ = 7.6 Hz, 1H), 6.57 (td, $J$ = 7.6, 1.0 Hz, 1H), 3.65 (brs, 1H), 3.38 (t, $J$ = 6.2 Hz, 2H), 2.80 (t, $J$ = 6.2 Hz, 2H), 2.09 (s, 3H), 1.95 (quint, $J$ = 6.2 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 142.8, 127.9, 127.5, 121.3, 121.0, 116.5, 42.5, 27.4, 22.3, 17.3; IR (neat) 3426, 2928, 2841, 2359, 1599, 1495, 1308, 1267, 1109, 759 cm$^{-1}$. The spectral data were in good agreement with literature.[4]

**7-Methyl-1,2,3,4-tetrahydroquinoline (7c)**



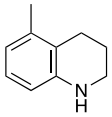
Prepared according to the general procedure from 7-methylquinoline (**6c**, 215 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (198 mg, 1.35 mmol, 90%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, $J$ = 7.6 Hz, 1H), 6.86 (d, $J$ = 7.6 Hz, 1H), 6.57 (td, $J$ = 7.6, 1.0 Hz, 1H), 3.65 (brs, 1H), 3.38 (t, $J$ = 6.2 Hz, 2H), 2.80 (t, $J$ = 6.2 Hz, 2H), 2.09 (s, 3H), 1.95 (quint, $J$ = 6.2 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 142.8, 127.9, 127.5, 121.3, 121.0, 116.5, 42.5, 27.4, 22.3, 17.3; IR (neat) 3426, 2928, 2841, 2359, 1599, 1495, 1308, 1267, 1109, 759 cm$^{-1}$. The spectral data were in good agreement with literature.[4]

**6-Methyl-1,2,3,4-tetrahydroquinoline (7d)**



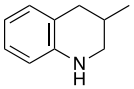
Prepared according to the general procedure from 6-methylquinoline (**6d**, 214 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless solid (187 mg, 1.27 mmol, 85%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.78–6.77 (m, 2H), 6.41–6.40 (m, 1H), 3.27 (t, $J$ = 5.5 Hz, 2H), 2.73 (t, $J$ = 6.5 Hz, 2H), 2.20 (s, 3H), 1.92 (tt, $J$ = 6.5, 5.5 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 142.5, 130.2, 127.4, 126.4, 121.7, 114.6, 42.3, 27.0, 22.5, 20.5; IR (KBr) 3364, 2911, 2837, 1616, 1512, 1350, 1306, 1260, 810, 635 cm$^{-1}$. The spectral data were in good agreement with literature.[3]

**5-Methyl-1,2,3,4-tetrahydroquinoline (7e)**



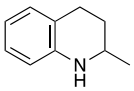
Prepared according to the general procedure from 5-methylquinoline (**6e**, 215 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (192 mg, 1.30 mmol, 87%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.89 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.3 Hz, 1H), 3.78 (brs, 1H), 3.26 (t, *J* = 5.5 Hz, 2H), 2.65 (t, *J* = 5.5 Hz, 2H), 2.18 (s, 3H), 1.99 (quint, *J* = 5.5 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 145.1, 137.4, 126.3, 120.4, 119.1, 112.6, 41.7, 24.2, 22.7, 19.5; IR (neat) 3401, 3046, 2941, 1589, 1348, 1306, 1269, 1113, 768, 714 cm$^{-1}$. The spectral data were in good agreement with literature.[4]

**3-Methyl-1,2,3,4-tetrahydroquinoline (7g)**



Prepared according to the general procedure from 3-methylquinoline (**6g**, 215 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (188 mg, 1.28 mmol, 85%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.96 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.60 (td, *J* = 7.4, 0.9 Hz, 1H), 6.48 (d, *J* = 7.4 Hz, 1H), 3.45 (brs, 1H), 3.27 (ddd, *J* = 10.6, 3.7, 1.8 Hz, 1H), 2.89 (t, *J* = 10.6 Hz, 1H), 2.77 (dd, *J* = 16.1, 5.0 Hz, 1H), 2.43 (dd, *J* = 16.1, 10.6 Hz, 1H), 2.10–2.02 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 3H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 144.3, 129.4, 126.6, 120.9, 116.7, 113.8, 48.7, 35.4, 27.1, 19.0; IR (neat) 3410, 2955, 2832, 1607, 1504, 1371, 1273, 1153, 835, 746 cm$^{-1}$. The spectral data were in good agreement with literature.[4]

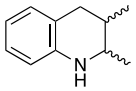
**2-Methyl-1,2,3,4-tetrahydroquinoline (7h)**



Prepared according to the general procedure from 2-methylquinoline (**6h**, 215 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (189 mg, 1.28 mmol, 85%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.98–6.96 (m, 2H), 6.61 (td, *J* = 7.4, 1.4 Hz, 1H), 6.48 (dd, *J* = 7.4, 1.4 Hz, 1H), 3.40 (dqd, *J* = 10.0, 6.2, 3.4 Hz, 1H), 2.85 (ddd, *J* = 16.2, 11.7, 5.2 Hz, 1H), 2.74 (ddd, *J* = 16.2, 5.2, 3.4 Hz, 1H), 1.94 (ddt, *J* = 12.5, 5.2, 3.4 Hz, 1H), 1.60 (dddd, *J* = 12.5, 11.7, 10.0, 5.2 Hz, 1H), 1.21 (d, *J* = 6.2 Hz, 3H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 144.7, 129.2, 126.6, 120.9, 116.8, 114.0, 46.9, 30.1, 26.5, 22.5; IR (neat) 3393, 2843,

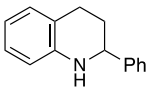
1609, 1487, 1377, 1310, 1258, 1153, 1124, 746 $cm^{-1}$. The spectral data were in good agreement with literature.[3]

**2,3-Dimethyl-1,2,3,4-tetrahydroquinoline (7i)**



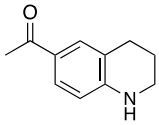
Prepared according to the general procedure from 2,3-dimethylquinoline (**6i**, 235 mg, 1.49 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 $mA/cm^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as yellow liquid (185 mg, 1.15 mmol, 77%). $^1H$ NMR (600 MHz, $CDCl_3$) δ 6.98 (t, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.8, 3.2 Hz, 1H), 6.63–6.60 (m, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 3.69 (brs, 1H), 3.47 (qd, *J* = 6.4, 3.2 Hz, 1H, *cis* isomer), 3.04–3.00 (m, 1H, *trans* isomer), 2.92 (dd, *J* = 16.1, 5.0 Hz, 1H, *cis* isomer), 2.74 (dd, *J* = 16.1, 5.0 Hz, 1H, *trans* isomer), 2.50 (dd, *J* = 16.5, 6.7 Hz, 1H), 2.08–2.02 (m, 1H, *cis* isomer), 1.68–1.60 (m, 1H, *trans* isomer), 1.21 (d, *J* = 6.4 Hz, 3H, *trans* isomer), 1.13 (d, *J* = 6.4 Hz, 3H, *cis* isomer), 1.04 (d *J* = 6.4 Hz, 3H, *trans* isomer), 0.95 (d, *J* = 6.4 Hz, 3H, *cis* isomer); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.6, 144.0, 129.9, 129.2, 126.8, 126.7, 121.5, 120.2, 117.0, 116.9, 114.0, 113.5, 53.4, 50.0, 35.6, 33.9, 33.6, 30.6, 20.9, 18.4, 18.2, 14.5; IR (neat) 3397, 2968, 2899, 2837, 1609, 1381, 1314, 1279, 1155, 748 $cm^{-1}$. The spectral data were in good agreement with literature.[5]

**2-Phenyl-1,2,3,4-tetrahydroquinoline (7j)**



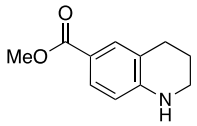
Prepared according to the general procedure from 2-phenylquinoline (**6j**, 308 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 $mA/cm^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless oil (256 mg, 1.22 mmol, 81%). $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.9 Hz, 2H), 7.35 (t, *J* = 6.9 Hz, 2H), 7.28 (t, *J* = 6.9 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 4.43 (dd, *J* = 10.7, 5.5 Hz, 1H), 4.03 (brs, 1H), 2.92 (ddd, *J* = 16.5, 10.7, 5.5 Hz, 1H), 2.73 (dt, *J* = 16.5, 5.5 Hz, 1H), 2.14–2.10 (m, 1H), 2.02–1.96 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.9, 144.8, 129.4, 128.6, 127.5, 127.0, 126.6, 120.9, 117.2, 114.1, 56.3, 31.0, 26.4; IR (neat) 3406, 3383, 3015, 2945, 2926, 2841, 1113, 926, 758, 700 $cm^{-1}$. The spectral data were in good agreement with literature.[3]

**6-Acetyl-1,2,3,4-tetrahydroquinoline (7k)**



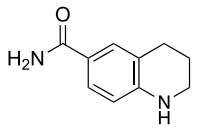
Prepared according to the general procedure from 6-acetylquinoline (**6k**, 256 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (12 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless solid (210 mg, 1.20 mmol, 80%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 6.40 (dd, *J* = 6.4, 2.8 Hz 1H), 4.40 (brs, 1H), 3.37 (td, *J* = 6.0, 2.8 Hz 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 3H), 1.94 (quint, *J* = 6.0 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 196.4, 149.1, 1330.5, 128.6, 126.1, 119.8, 112.5, 41.7, 27.0, 26.0, 21.4; IR (KBr) 3339, 1647, 1580, 1533, 1435, 1319, 1290, 1236, 1146, 827 cm$^{-1}$; HRMS (ESI) *m/z* calcd for $C_{11}H_{13}NNaO$ $[M + Na]^+$ 198.0889, found 198.0880; mp 101.5–102.9 °C.

**Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (7l)**



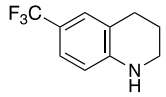

Prepared according to the general procedure from methyl quinoline-6-carboxylate (**6l**, 281 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (6 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless solid (141 mg, 0.74 mmol, 49%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.65–7.64 (m, 2H), 6.40–6.38 (m, 1H), 4.30 (brs, 1H), 3.83 (s, 3H), 3.36 (t, *J* = 6.2 Hz, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 1.93 (quint, *J* = 6.2 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 167.6, 148.1, 131.5, 129.2, 120.7, 118.3, 113.4, 51.7, 41.9, 26.9, 21.4; IR (KBr) 3381, 2943, 1682, 1605, 1531, 1441, 1325, 1288, 1234, 1144 cm$^{-1}$. The spectral data were in good agreement with literature.[4]

**1,2,3,4-Tetrahydroquinoline-6-carboxamide (7m)**



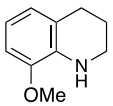

Prepared according to the general procedure from methyl quinoline-6-carboxamide (**6m**, 258 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in 1,4-dioxane/$H_2O$ 7:1 (6 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (EtOAc) to afford the title compound as colorless solid (230 mg, 1.31 mmol, 87%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.46–7.46 (m, 1H), 7.41 (dd, *J* = 8.3, 2.1 Hz 1H), 6.41 (d, *J* = 8.3 Hz 1H), 4.26 (brs, 1H), 3.35 (td, *J* = 6.2, 2.4 Hz 2H), 2.78 (t, *J* = 6.2 Hz, 2H), 1.93 (quint, *J* = 6.2 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 196.6, 148.2, 129.5, 126.8, 120.6, 120.4, 112.9, 41.9, 27.1, 21.6; IR (KBr) 3343, 2943, 2839, 1647, 1611, 1523, 1437, 1387, 1317, 772 cm$^{-1}$. The spectral data were in good agreement with literature.[6]

**6-(Trifluoromethyl)-1,2,3,4-tetrahydroquinoline (7n)**



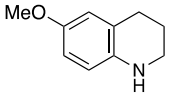
Prepared according to the general procedure from methyl 6-(trifluiromethyl)quinoline (**6n**, 296 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (30 mg, 0.16 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (244 mg, 1.21 mmol, 81%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 4.15 (brs, 1H), 3.34 (t, *J* = 6.5 Hz, 2H), 2.77 (t, *J* = 6.5 Hz, 2H), 1.96–1.92 (m, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 147.5, 126.5 (q, $^3J_{C–F}$ = 4.3 Hz), 125.3 (q, $^1J_{C–F}$ = 270.2 Hz), 124.1 (q, $^3J_{C–F}$ = 4.3 Hz), 120.1, 117.9 (q, $^2J_{C–F}$ = 31.8 Hz), 113.1, 41.7, 27.0, 21.5; $^{19}$F NMR (565 MHz, $CDCl_3$) δ −62.1; IR (neat) 3422, 2957, 2936, 2843, 1620, 1526, 1331, 1246, 1099, 816 cm$^{-1}$. The spectral data were in good agreement with literature.[7]

**8-Methoxy-1,2,3,4-tetrahydroquinoline (7o)**



Prepared according to the general procedure from 8-methoxyquinoline (**6o**, 238 mg, 1.49 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (214 mg, 1.31 mmol, 88%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.63–6.61 (m, 2H), 6.57 (td, *J* = 8.3, 0.9 Hz, 1H), 4.23 (brs, 1H), 3.83 (s, 3H), 3.34 (t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 1.96 (quint, *J* = 6.0 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 146.4, 134.6, 121.8, 121.5, 115.8, 107.5, 55.5, 41.6, 26.8, 22.2; IR (neat) 3418, 2947, 2833, 1612, 1587, 1331, 1248, 1267, 1192, 1105 cm$^{-1}$. The spectral data were in good agreement with literature.[4]

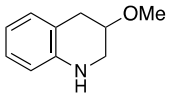
**6-Methoxy-1,2,3,4-tetrahydroquinoline (7p)**



Prepared according to the general procedure from 6-methoxyquinoline (**6p**, 239 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless solid (3 mg, 0.02 mmol, 1%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 8.6, 3.1 Hz, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 6.46 (d, *J* = 8.6 Hz, 1H), 3.73 (s, 3H), 3.25 (t, *J* = 5.5 Hz, 2H), 2.75 (t, *J* = 6.5 Hz, 2H), 1.93 (tt, *J* = 6.5, 5.5 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 152.0, 138.9, 123.1, 115.8, 115.0, 113.0, 55.9, 42.5, 27.3, 22.5; IR (KBr) 3367, 2361, 2332, 1506, 1298, 1254, 1233,

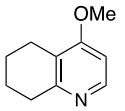
1152, 1040, 810 $cm^{-1}$. The spectral data were in good agreement with literature.[3]

**3-Methoxy-1,2,3,4-tetrahydroquinoline (7q)**



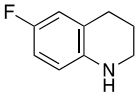

Prepared according to the general procedure from 3-methoxyquinoline (**6q**, 238 mg, 1.49 mmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/$cm^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as yellow liquid (37 mg, 0.23 mmol, 15%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.99–6.97 (m, 2H), 6.64 (td, *J* = 7.5, 1.2 Hz 1H), 6.51 (d, *J* = 7.5 Hz 1H), 3.76 (dddd, *J* = 10.6, 6.9, 4.1, 3.2 Hz 1H), 3.45 (s, 3H), 3.43 (dd, *J* = 3.2, 1.4 Hz 1H), 3.22 (ddd, *J* = 10.6, 6.9, 1.4 Hz 1H), 3.03 (dd, *J* = 15.8, 4.1 Hz 1H), 2.81 (dd, *J* = 15.8, 6.9 Hz 1H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 143.9, 130.2, 127.2, 119.1, 117.8, 114.2, 72.9, 56.4, 45.3, 32.8; IR (neat) 3383, 2826, 2359, 1607, 1585, 1285, 1200, 1096, 984, 748 $cm^{-1}$; HRMS (ESI) *m/z* calcd for $C_{11}H_{13}NNaO$ $[M + Na]^+$ 186.0889, found 186.0887.

**4-Methoxy-5,6,7,8-tetrahydroquinoline (7r′)**




Prepared according to the general procedure from 4-methoxyquinoline (**6r**, 239 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/$cm^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as yellow liquid (11 mg, 0.07 mmol, 5%). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.0 Hz, 1H), 6.58 (d, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 2.86 (t, *J* = 6.0 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 1.86–1.75 (m, 4H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 163.6, 157.9, 148.0, 121.3, 103.3, 55.3, 32.6, 22.9, 22.34, 22.30; IR (neat) 3383, 3308, 2938, 1576, 1337, 1290, 1111, 1090, 997, 810 $cm^{-1}$. The spectral data were in good agreement with literature.[8]

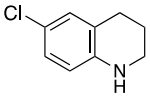
**6-Fluoro-1,2,3,4-tetrahydroquinoline (7s)**




Prepared according to the general procedure from 6-fluoroquinoline (**6s**, 221 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/$cm^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography

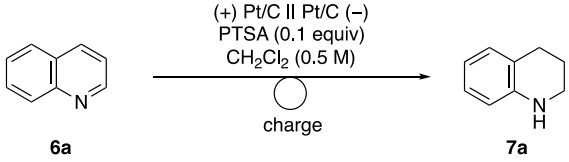
on silica gel (hexane/EtOAc 2:1) to afford the title compound as yellow liquid (203 mg, 1.34 mmol, 89%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.70–6.66 (m, 2H), 6.40 (dd, $J$ = 9.4, 5.0 Hz, 1H), 3.66 (brs, 1H), 3.27 (t, $J$ = 5.5 Hz, 2H), 2.74 (t, $J$ = 5.5 Hz, 2H), 1.92 (quint, $J$ = 5.5 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 155.6 (d, $^1J_{C–F}$ = 234.1 Hz), 141.0, 122.9 (d, $^4J_{C–F}$ = 5.8 Hz), 115.7 (d, $^2J_{C–F}$ = 21.7 Hz), 115.0 (d, $^3J_{C–F}$ = 7.2 Hz), 113.3 (d, $^2J_{C–F}$ = 21.7 Hz), 42.2, 27.1, 22.1; $^{19}$F NMR (565 MHz, $CDCl_3$) δ −129.6; IR (KBr) 3385, 2363, 1508, 1306, 1248, 1221, 1140, 926, 887, 772 cm$^{-1}$. The spectral data were in good agreement with literature.[9]

**6-Chloro-1,2,3,4-tetrahydroquinoline (7t)**




Prepared according to the general procedure from 6-chloroquinoline (**6t**, 246 mg, 1.50 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL). A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. After general work-up, the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to afford the title compound as colorless liquid (202 mg, 1.21 mmol, 80%). $^1$H NMR (600 MHz, $CDCl_3$) δ 6.91–6.89 (m, 2H), 6.38 (d, $J$ = 8.3 Hz, 1H), 3.81 (brs, 1H), 3.28 (t, $J$ = 6.4 Hz, 2H), 2.72 (t, $J$ = 6.4 Hz, 2H), 1.91 (quint, $J$ = 6.4 Hz, 2H); $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$) δ 143.4, 129.2, 126.6, 123.0, 121.3, 115.2, 42.0, 27.0, 21.9; IR (neat) 3418, 2841, 1603, 1497, 1470, 1352, 1300, 1269, 1184, 806 cm$^{-1}$. The spectral data were in good agreement with literature.[3]

**Table S1**. Effect of current density on the electrocatalytic reduction of **6a** using a PEM reactor



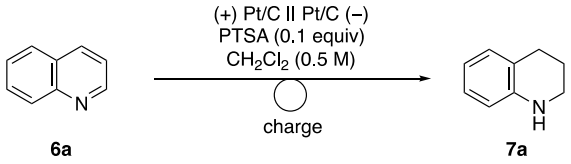

**6a** **7a**

Experimental conditions: cell temperature, rt; current density; flow rate of solution, 0.75 mL/min; flow rate of hydrogen, 100 mL/min.

| entry | current density (mA/cm$^2$) | charge (F/mol) | yield of 7**a** (%)[a] | recov. of 6**a** (%)[a] | current efficiency (%)[a] |
|---|---|---|---|---|---|
| 1 (10 runs) | 50 | 50 | 85–94 | N.D.[b] | 7–8 |
| 2 | 2.5 | 2.5 | 40 | 53 | 64 |
| 3 | 5 | 5 | 55 | 36 | 44 |
| 4 | 10 | 10 | 72 | 16 | 29 |
| 5 | 20 | 20 | 87 | 2 | 17 |
| 6 | 25 | 25 | 93 | N.D. | 15 |

[a] Determined by $^1$H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [b] Not Detected.

**Table S2**. Time course of the electrocatalytic reduction of **6a** using a PEM reactor



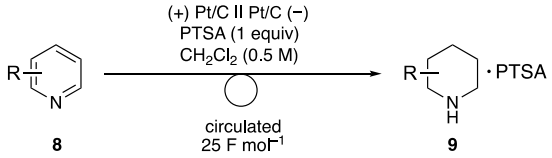

**6a** **7a**

Experimental conditions: cell temperature, rt; current density, 25 mA/cm$^2$; flow rate of solution, 0.75 mL/min; flow rate of hydrogen, 100 mL/min.

| charge (F/mol) | yield of **2a** (%)[a] | recov. of **1a** (%)[a] | current efficiency of **1a** (%)[a] |
|---|---|---|---|
| 5 | 55 | 42 | 44 |
| 10 | 82 | 14 | 33 |
| 15 | 87 | 6 | 23 |
| 20 | 91 | 2 | 18 |
| 25 | 93 | N.D.[b] | 15 |

[a] Determined by $^1$H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.
[b] Not Detected.

**General Procedure for hydrogenation of pyridines using a PEM reactor**

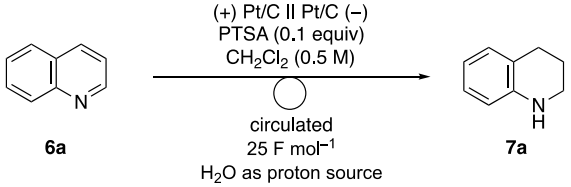



**8** **9**

Experimental conditions: cell temperature, rt; current density, 25 mA/cm$^2$; flow rate of solution, 0.75 mL/min; flow rate of hydrogen, 100 mL/min.

Electrocatalytic hydrogenations were carried out by using a PEM reactor (Figure S2). The MEA (3 cm × 10 cm, 1 cm × 4 cm: active area) was integrated into the PEM reactor. For the cathodic chamber, humidified nitrogen gas was supplied for 1 hour. After that, the solution of substrate **8** (1.5 mmol) and *p*-toluenesulfonic acid monohydrate (1.5 mmol, 1 equiv) in $CH_2Cl_2$ (3 mL) was provided with 0.75 mL/min by a circular pump (YAMAZEN, MSP-001-0). For the anodic chamber, humidified hydrogen gas (flow rate: 100 mL/min) was supplied. A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. The yield of **9**•PTSA was determined by $^1$H NMR analysis of the obtained cathodic reaction solution using 1,1,2,2-tetrachloroethane or ethylene carbonate as an internal standard. The spectra data were in good agreement with authentic samples.

**Procedure for Hydrogenation of Quinoline 6a in a PEM Reactor Using $H_2O$ as a $H^+$ Source**




**6a** **7a**

Experimental conditions: cell temperature, rt; current density, 25 mA/cm$^2$; flow rate of solution, 0.75 mL/min; flow rate of $H_2O$, 1.0 mL/min.

Electrocatalytic hydrogenations were carried out by using a PEM reactor (Figure S3). The MEA (3 cm × 10 cm, 1 cm × 4 cm: active area) including a DSE® electrode as an anolyte was integrated into the PEM reactor. For the

cathodic chamber, the solution of quinoline **6a** (193 mg, 1.5 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL) was provided with 0.75 mL/min by a circular pump (YAMAZEN, MSP-001-0). For the anodic chamber, $H_2O$ was provided with 1.0 mL/min by a circular pump. A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. To the obtained cathodic reaction solution was added NaOH aq (1.0 M, 5 mL), and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phase was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc 2:1 to afford 1,2,3,4-tetrahydroquinoline (**7a**, 110 mg, 0.82 mmol, 55%).

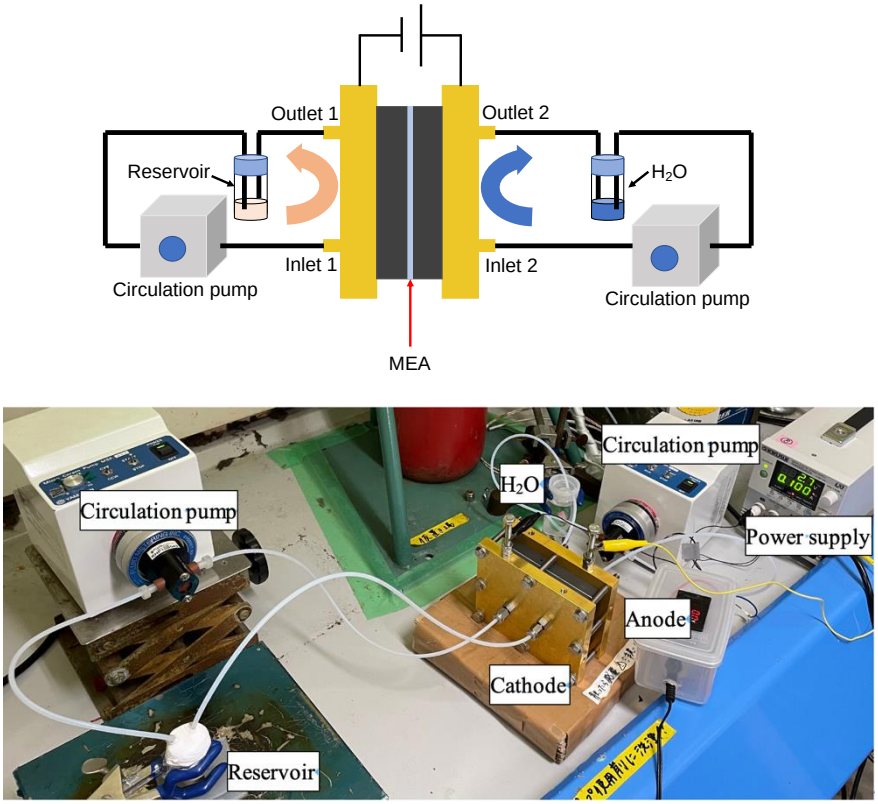
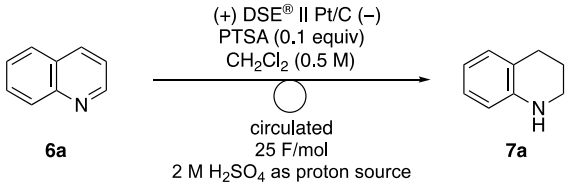



**Figure S3.** Hydrogenation system in a PEM reactor using $H_2O$ as a proton source.

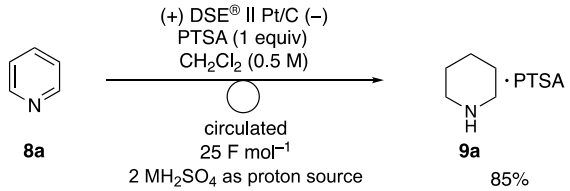
**Procedure for hydrogenation of quinoline (6a) in a PEM reactor using 2 M $H_2SO_4$ as a $H^+$ source**




Experimental conditions: cell temperature, rt; current density, 25 mA/cm$^2$; flow rate of solution, 0.75 mL/min; flow rate of 2 $MH_2SO_4$ aq,1.0 mL/min.

Electrocatalytic hydrogenations were carried out by using a PEM reactor. The MEA (3 cm × 10 cm, 1 cm × 4 cm: active area) including a DSE® electrode as an anolyte was integrated into the PEM reactor. For the cathodic chamber, the solution of quinoline **6a** (193 mg, 1.5 mmol) and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) in $CH_2Cl_2$ (3 mL) was provided with 0.75 mL/min by a circular pump (YAMAZEN, MSP-001-0). For the anodic chamber, 2 M $H_2SO_4$ was provided with 1.0 mL/min by a circular pump. A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. To the obtained cathodic reaction solution was added NaOH aq (1.0 M, 5 mL), and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic phase was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc 2:1 to afford 1,2,3,4-tetrahydroquinoline (**7a**, 156 mg, 1.2 mmol, 80%).

**Procedure for the hydrogenation of pyridine (8a) in a PEM reactor using 2 M $H_2SO_4$ as a proton source.**




Experimental conditions: cell temperature, rt; current density, 25 mA/cm$^2$; flow rate of solution, 0.75 mL/min; flow rate of 2 M $H_2SO_4$ aq, 1.0 mL/min.

Electrocatalytic hydrogenations were carried out by using a PEM reactor. The MEA (3 cm × 10 cm, 1 cm × 4 cm: active area) including a DSE® electrode as an anolyte was integrated into the PEM reactor. For the cathodic chamber, the solution of pyridine **8a** (119 mg, 1.5 mmol) and *p*-toluenesulfonic acid monohydrate (286 mg, 1.5 mmol) in $CH_2Cl_2$ (3 mL) was provided with 0.75 mL/min by a circular pump (YAMAZEN, MSP-001-0). For the anodic chamber, 2 M $H_2SO_4$ aq was provided with 1.0 mL/min by a circular pump. A constant current (25 mA/cm$^2$, 25 F/mol, 10 h) was supplied at room temperature. The yield of **9a**•PTSA was determined by the $^1$H NMR analysis of the obtained cathodic reaction solution using 1,1,2,2-tetrachloroethane as an internal standard (85% yield).

**References**

(1) Anand, N.; Koley, S.;Ramulu, J.; Singh, M. S. *Org. Biomol. Chem.* **2015**, *13*, 9570–9574.

(2) Ma, W.; Zhang, J.; Xu, C.; Chen, F.; He, Y.-M.; Fan, Q.-H. *Angew. Chem., Int. Ed.* **2016**, *55*, 12891–12894.

(3) Duan, Y.-N.; Du, Xi.; Cui, Z.; Zeng, Y.; Liu, Y.; Yang, T.; Wen, J.; Zhang, X. *J. Am. Chem. Soc.* **2019**, *141*, 20424–20433.

(4) Yang, C.-H.; Chen, X.; Li, H.; Wei, W.; Yang, Z.; Chang, J. *Chem. Commun*. **2018**, *54*, 8622–8625.

(5) Wu, J.; Wang, C.; Tang, W.; Pettman, A.; Xiao, J. *Chem. Eur. J*. **2012**, *18*, 9525–9529.

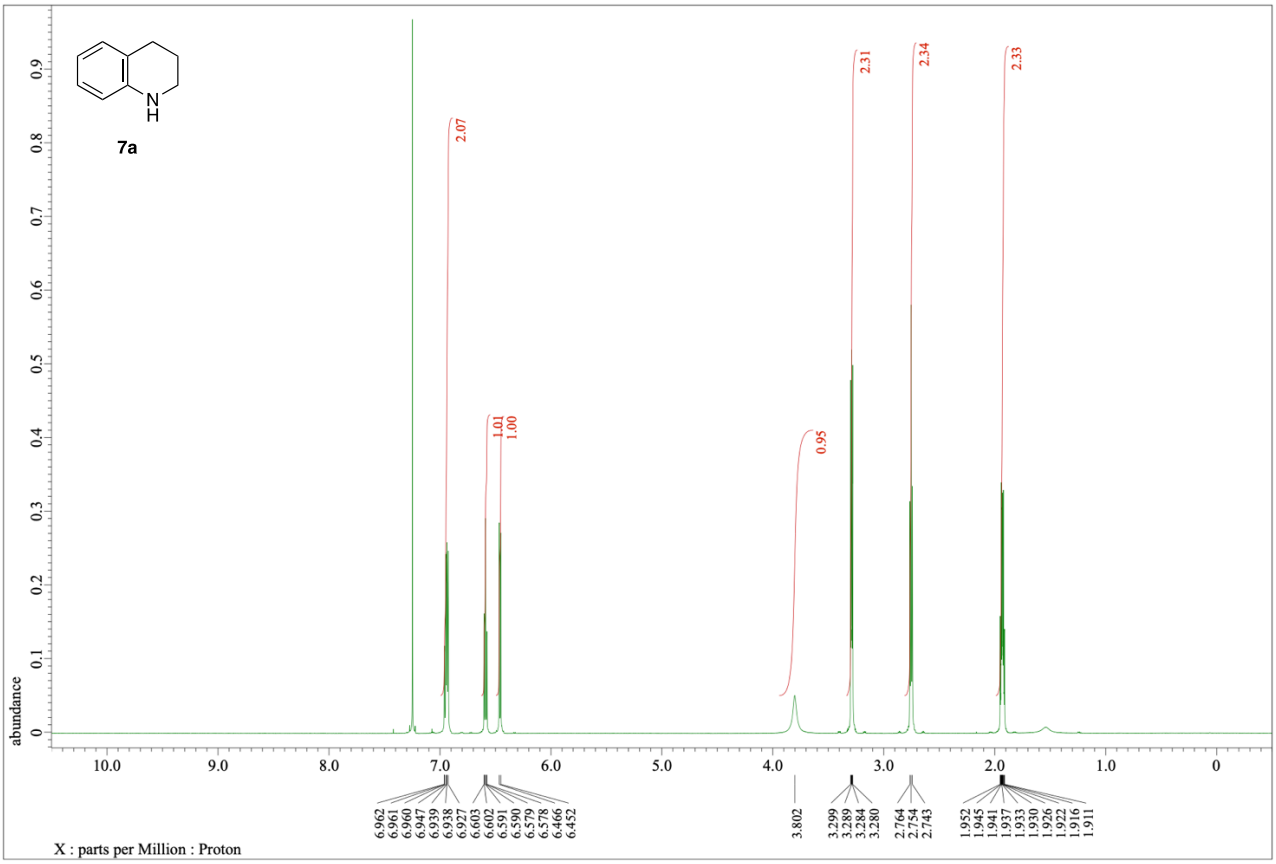
(6) Sorribes, I.; Liu, L.; Doménech-Carbó, A.; Corma, A. *ACS Catal*. **2018**, *8*, 4545–4557.

(7) Compain, G.; Bonneau, C.; Martin-Mingot, A.; Thibaudeau, S. *J. Org. Chem.* **2013**, *78*, 4463–4472.

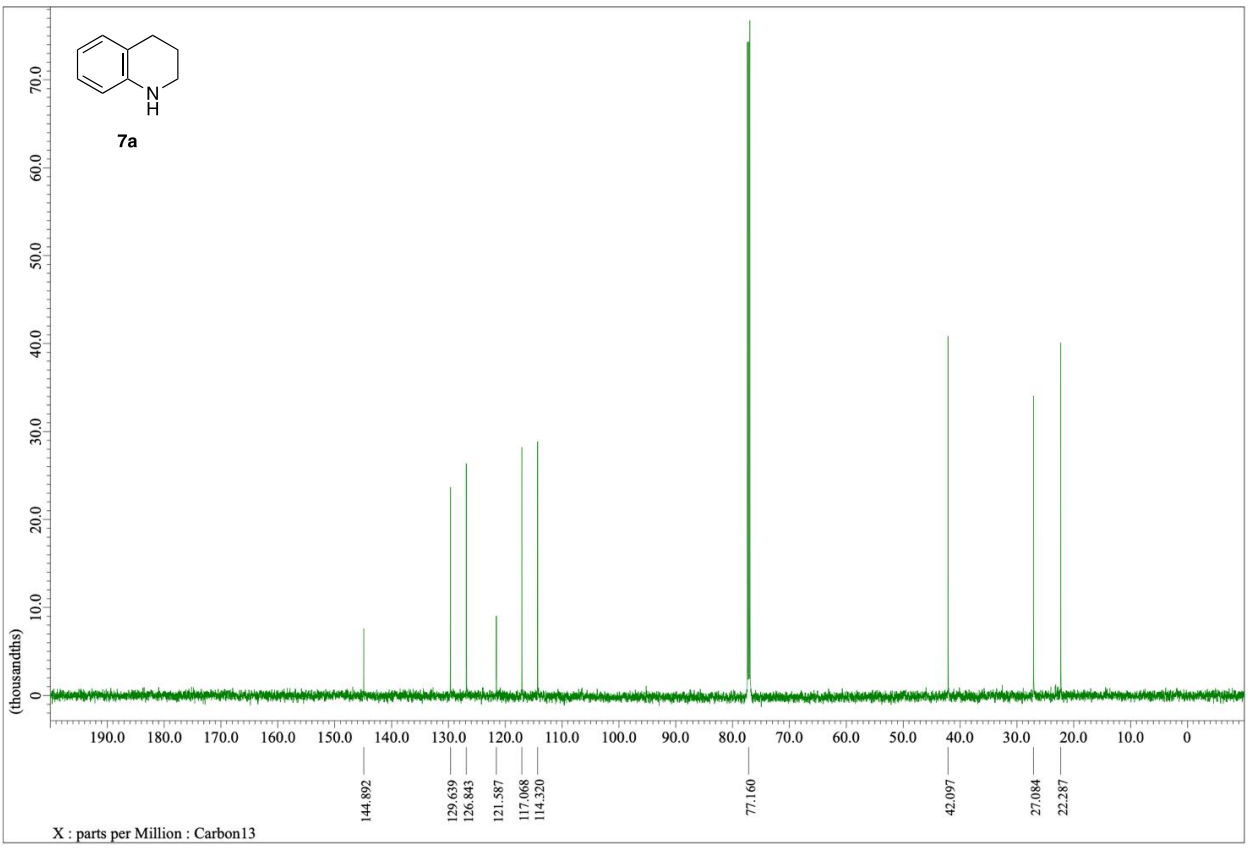
(8) Kuwano, R.; Ikeda, R.; Hirasada, K. *Chem*. *Commun*. **2015**, *51*, 7558–7561.

(9) Yadav, S.; Chaudhary, D.; Maurya, N. K., Kumar, D.; Ishu, K.; Kuram, M. R. *Chem*. *Commun*. **2022**, *58*, 4255–4258.

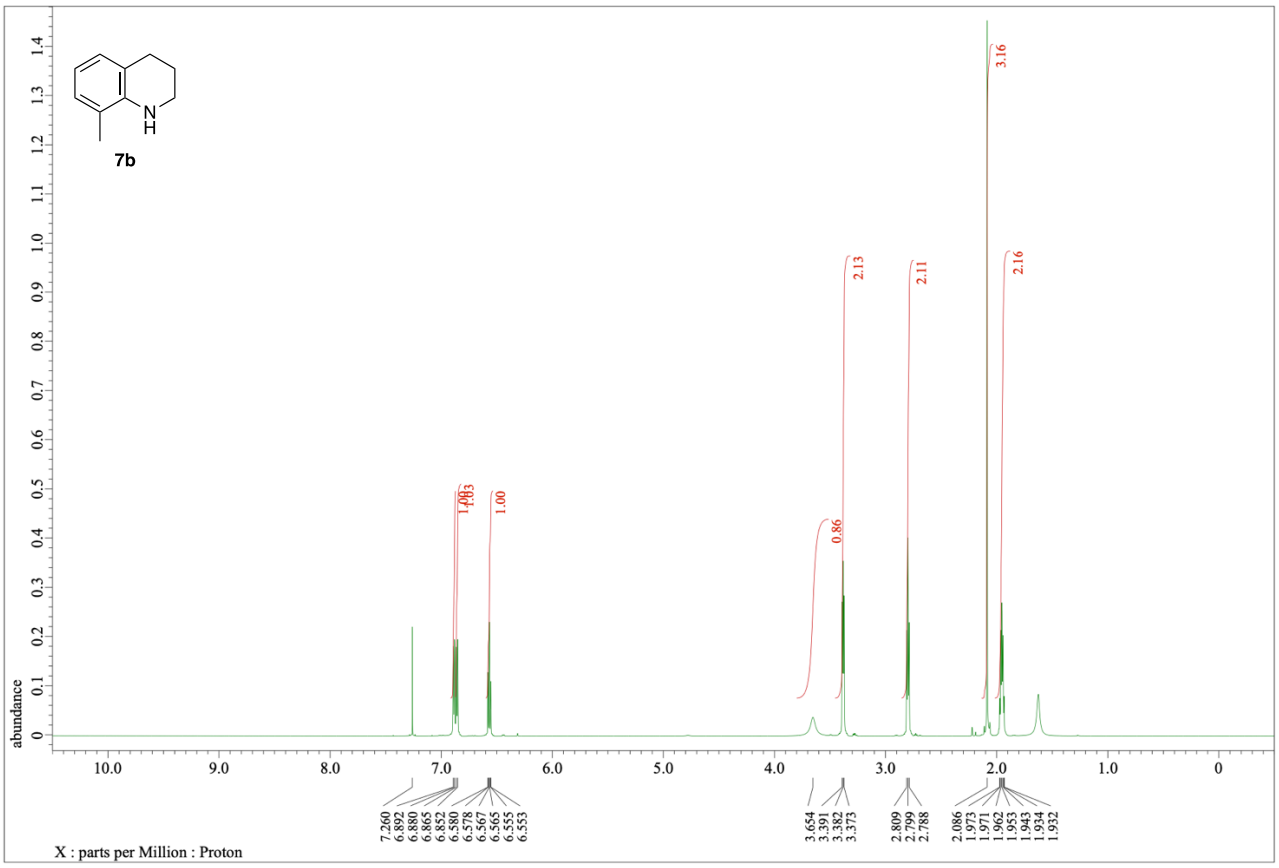
**1,2,3,4-Tetrahydroquinoline (7a) $^{1}H$ NMR (600 MHz, $CDCl_3$)**



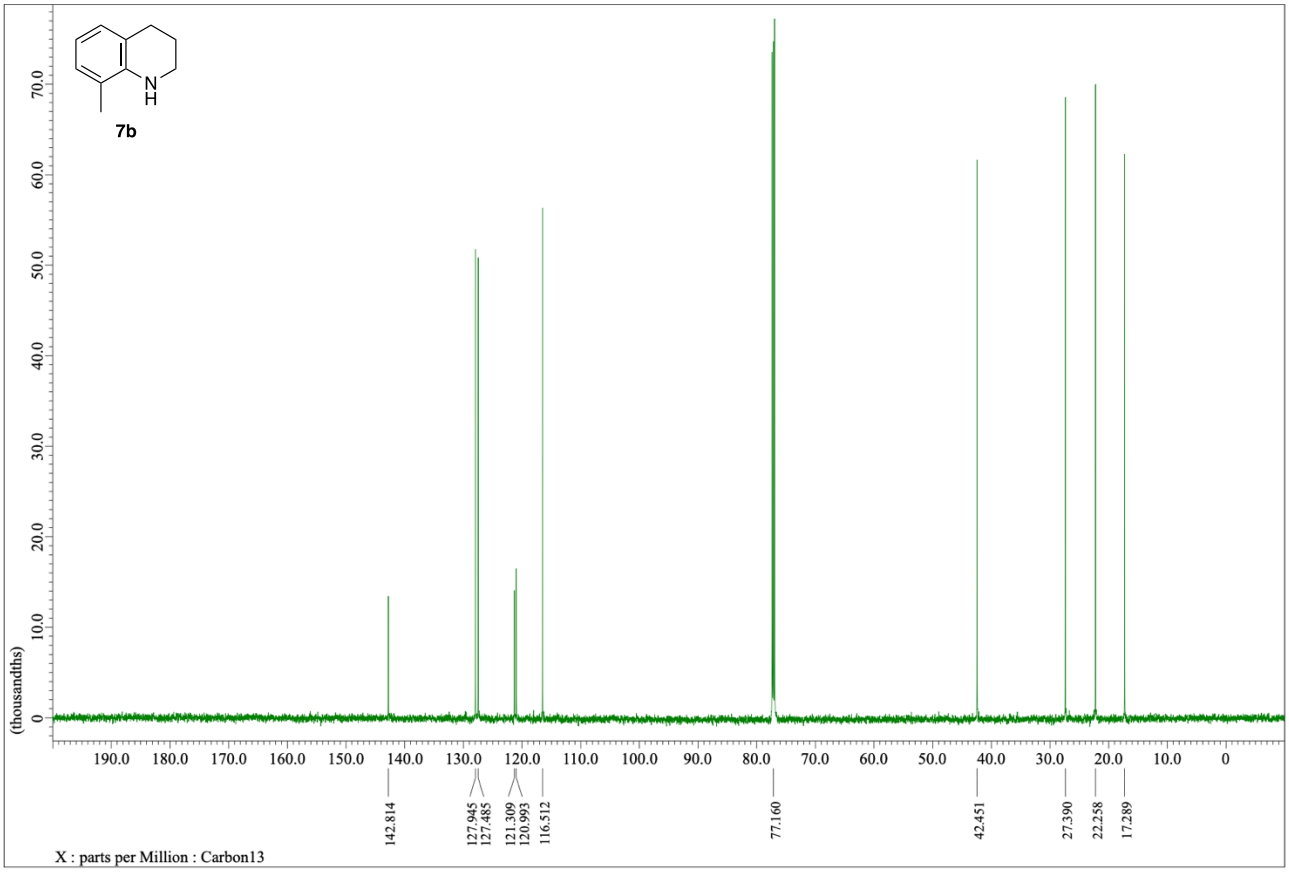

**1,2,3,4-Tetrahydroquinoline (7a) $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)**



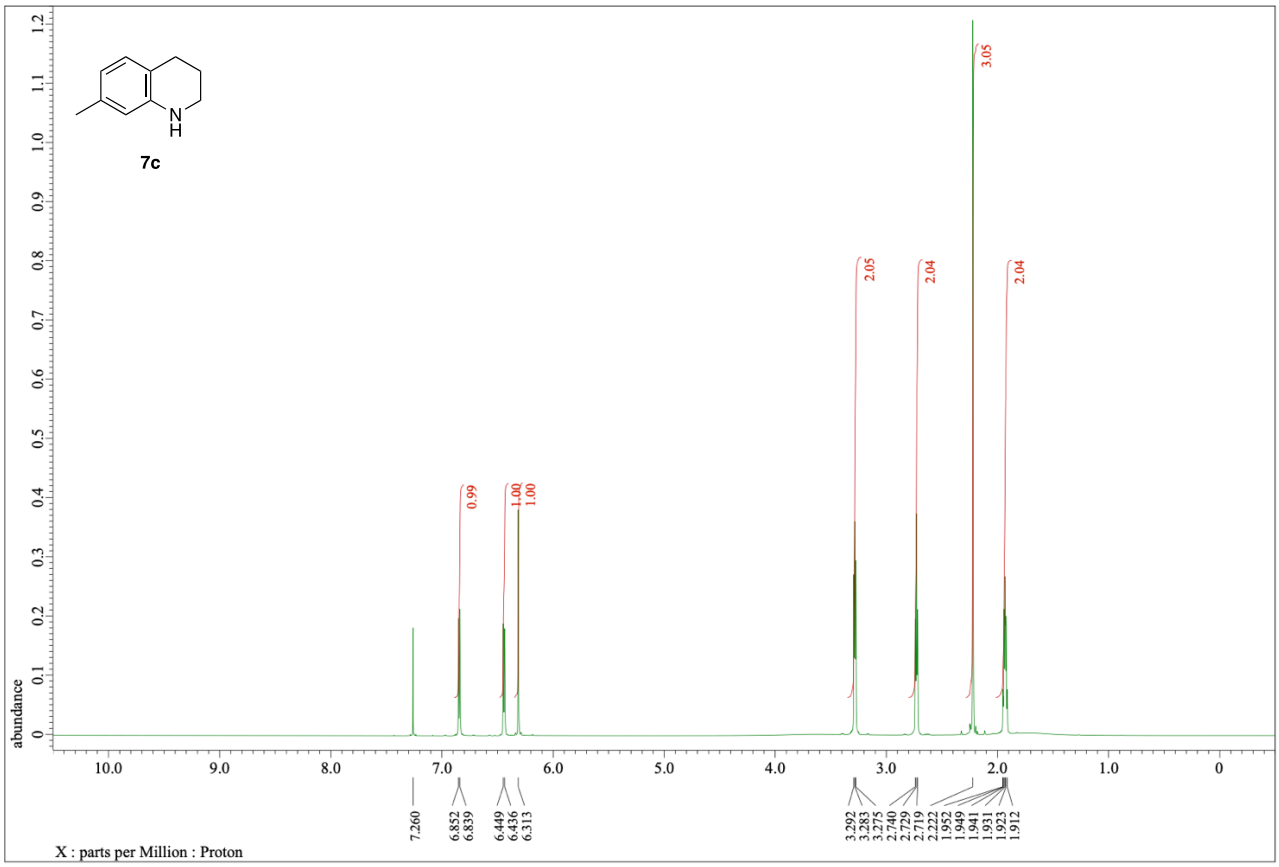
**8-Methyl-1,2,3,4-tetrahydroquinoline (7b) $^{1}H$ NMR (600 MHz, $CDCl_3$)**



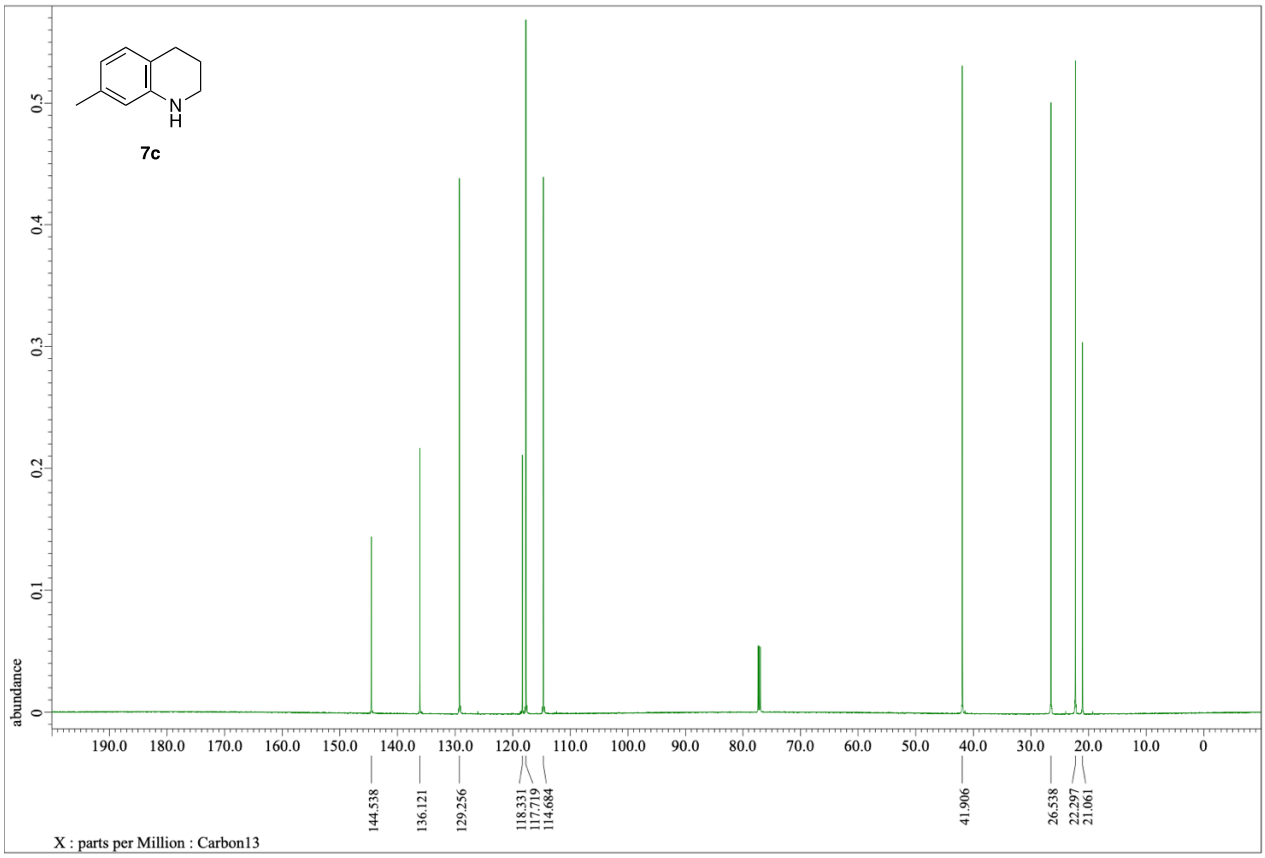

**8-Methyl-1,2,3,4-tetrahydroquinoline (7b) $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)**



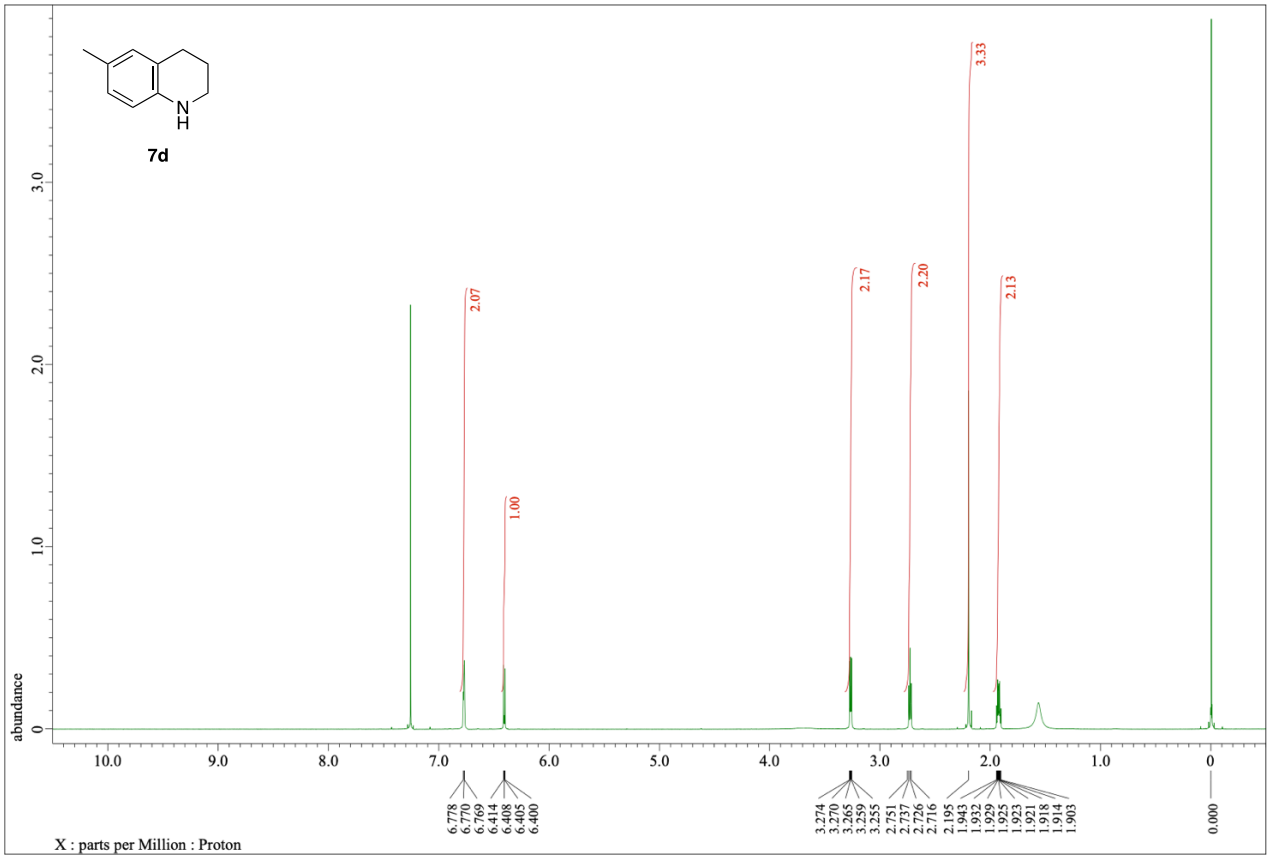
**7-Methyl-1,2,3,4-tetrahydroquinoline (7c) $^{1}$H NMR (600 MHz, $CDCl_3$)**



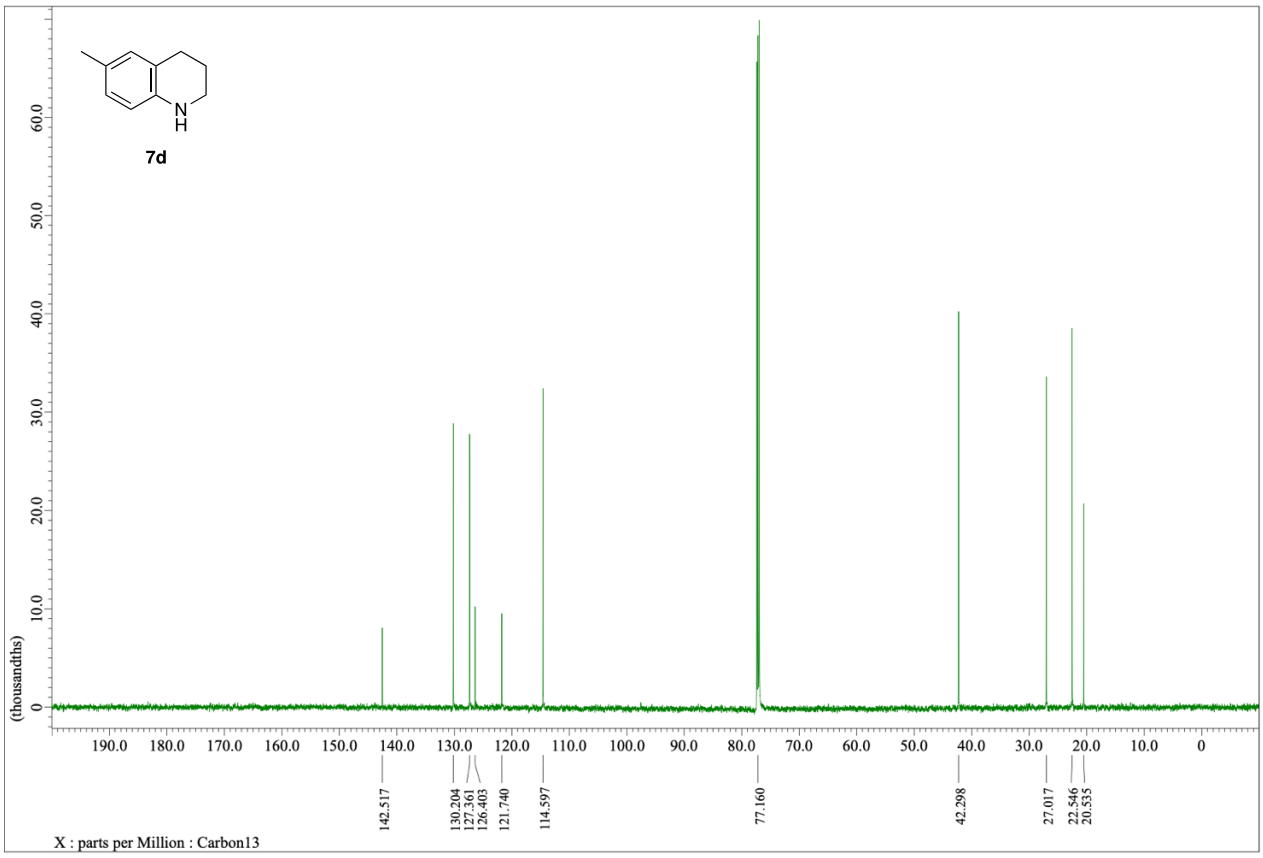

**7-Methyl-1,2,3,4-tetrahydroquinoline (7c) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



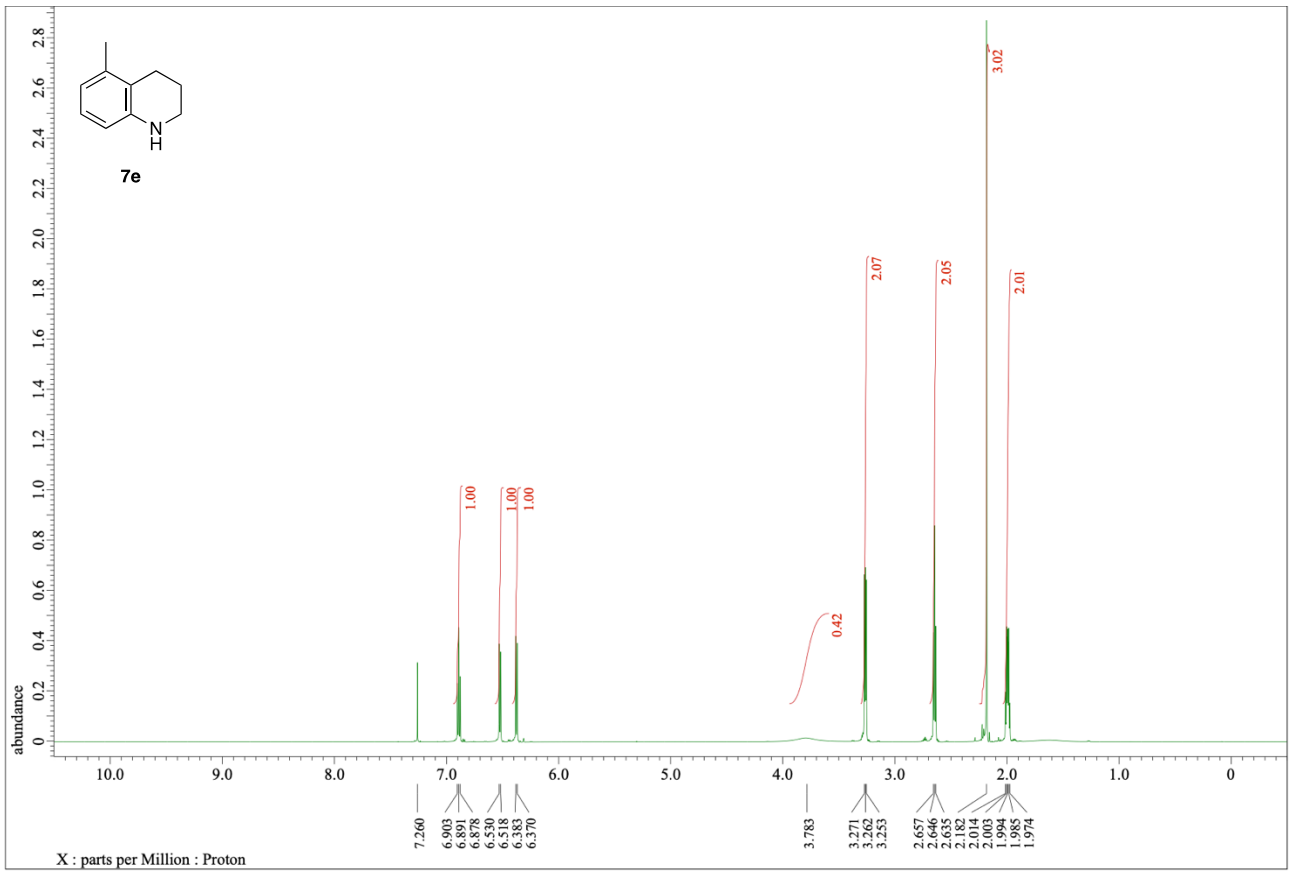
**6-Methyl-1,2,3,4-tetrahydroquinoline (7d) $^{1}H$ NMR (600 MHz, $CDCl_3$)**



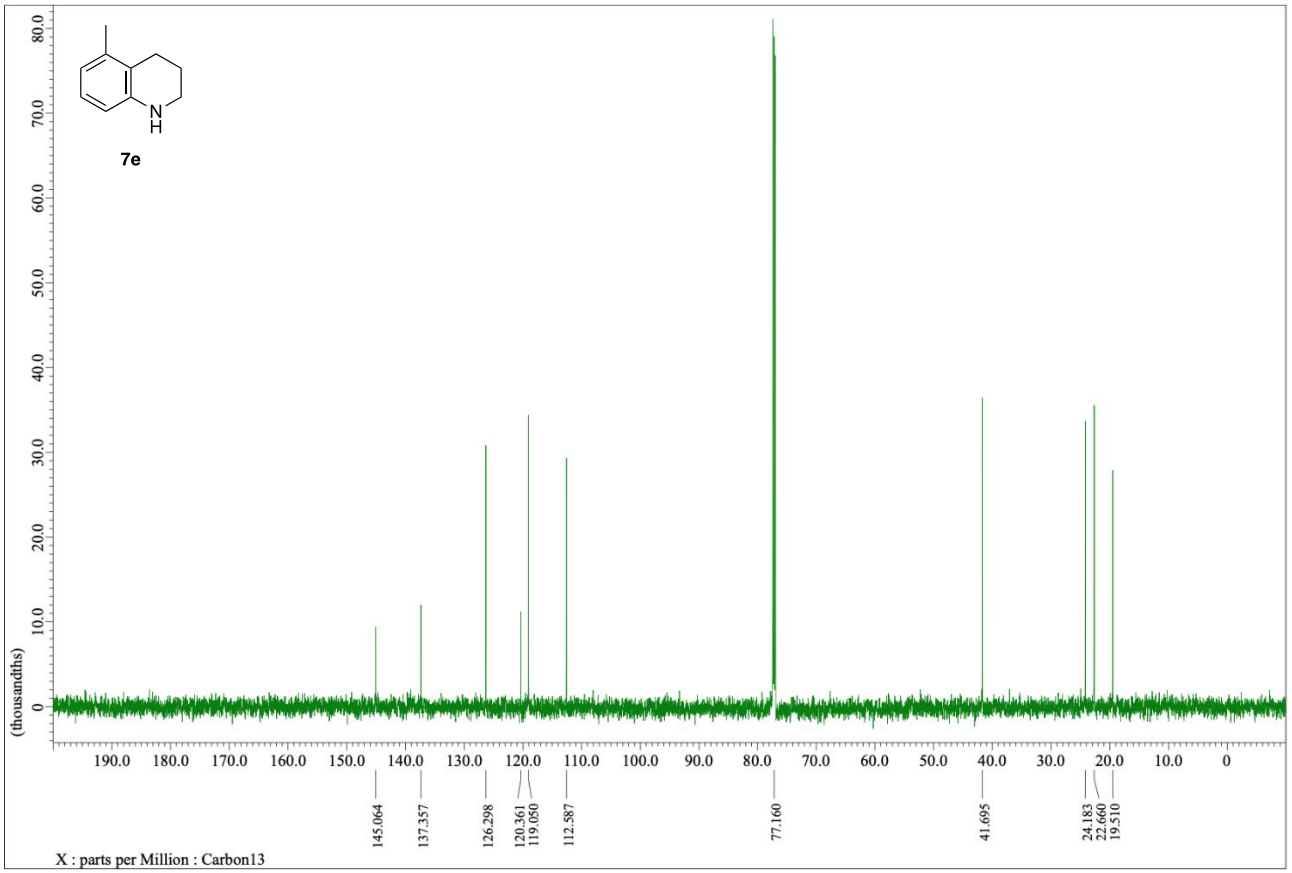

**6-Methyl-1,2,3,4-tetrahydroquinoline (7d) $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)**



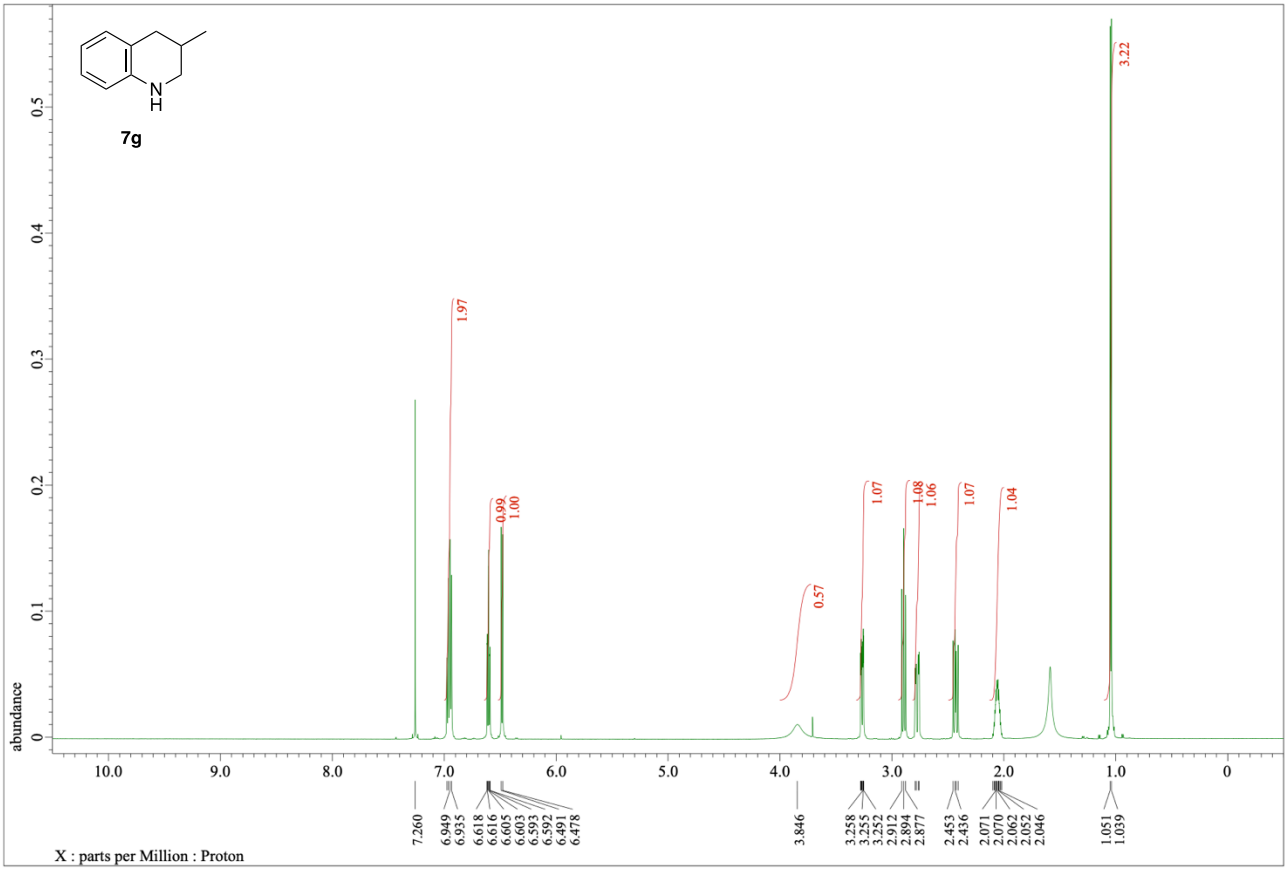
**5-Methyl-1,2,3,4-tetrahydroquinoline (7e) $^{1}$H NMR (600 MHz, $CDCl_3$)**



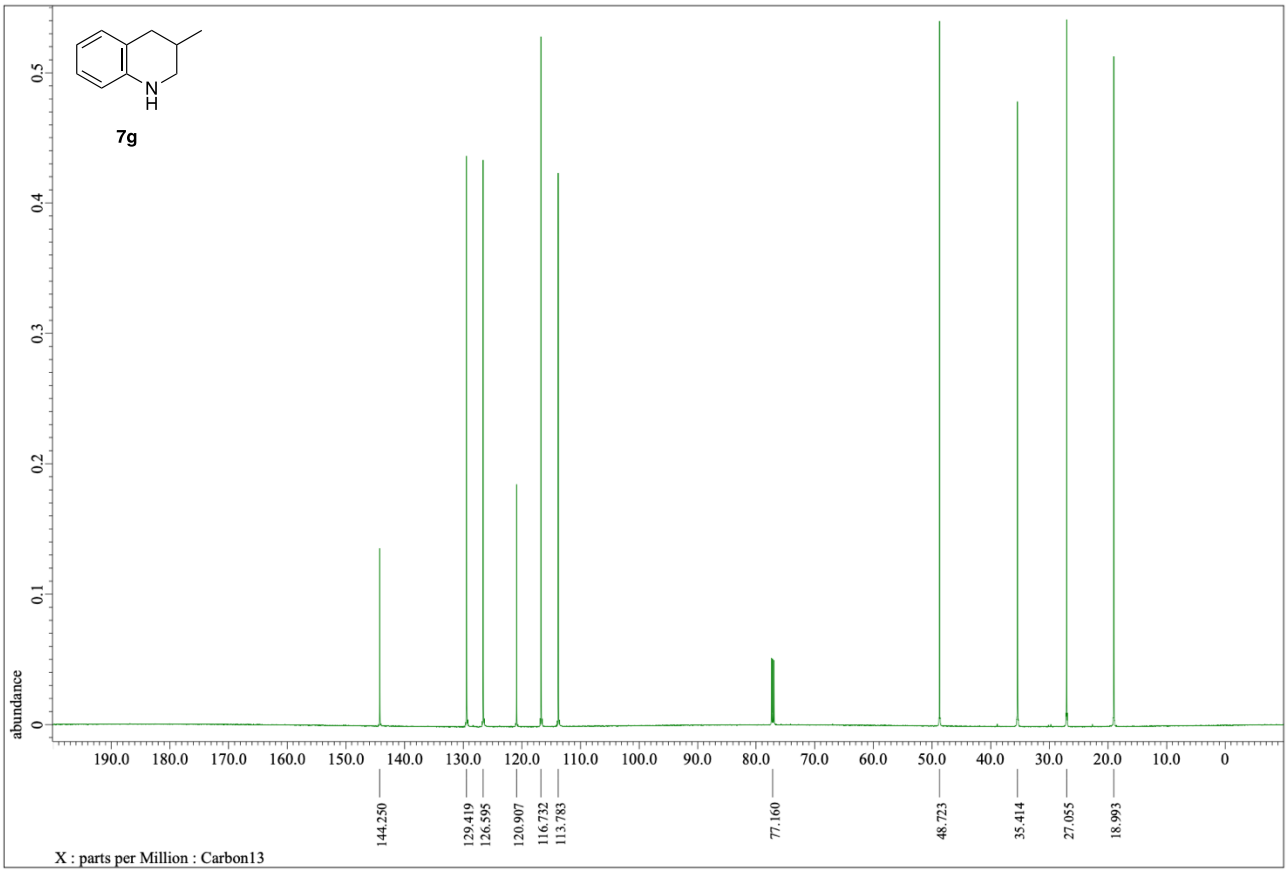

**5-Methyl-1,2,3,4-tetrahydroquinoline (7e) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



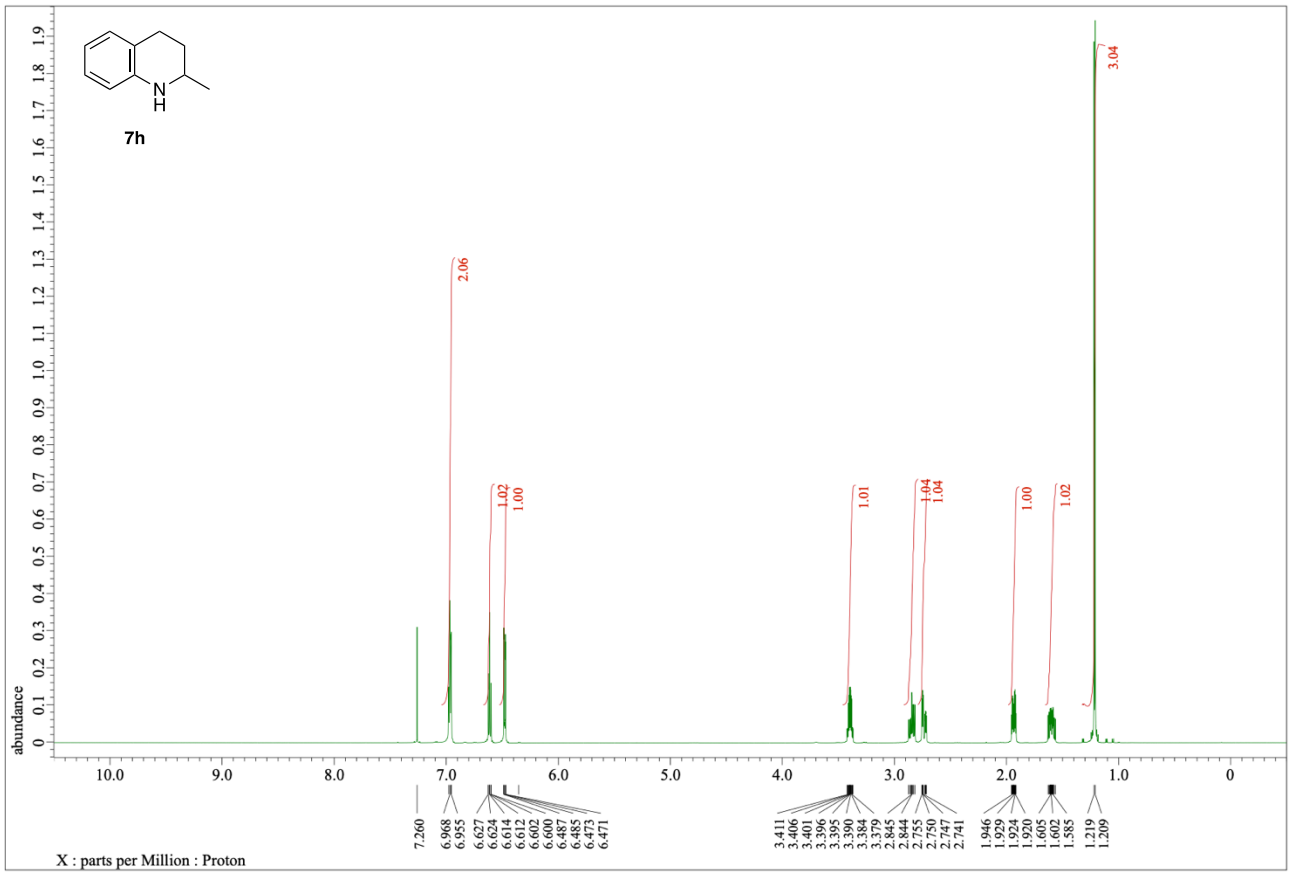
**3-Methyl-1,2,3,4-tetrahydroquinoline (7g) $^{1}$H NMR (600 MHz, $CDCl_3$)**



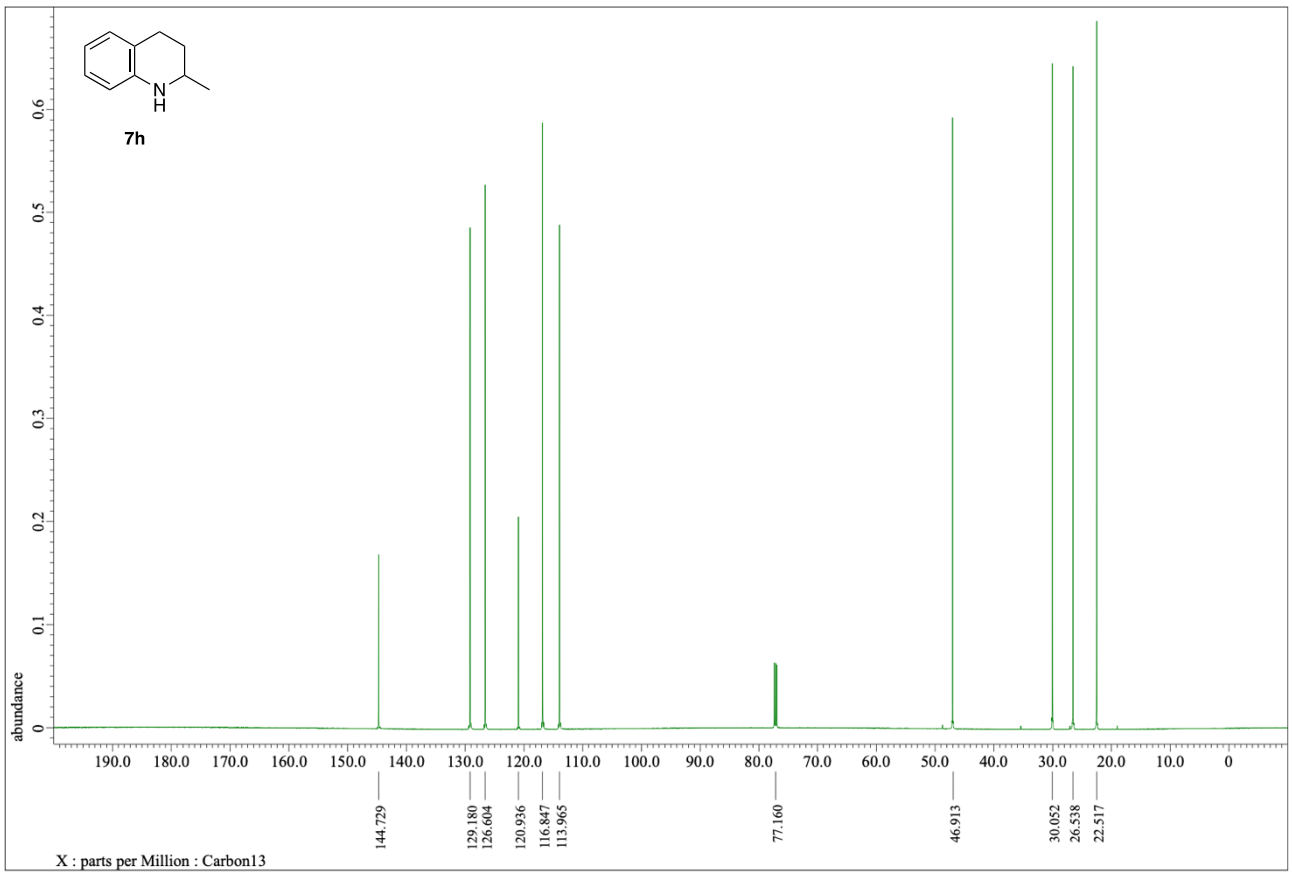

**3-Methyl-1,2,3,4-tetrahydroquinoline (7g) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



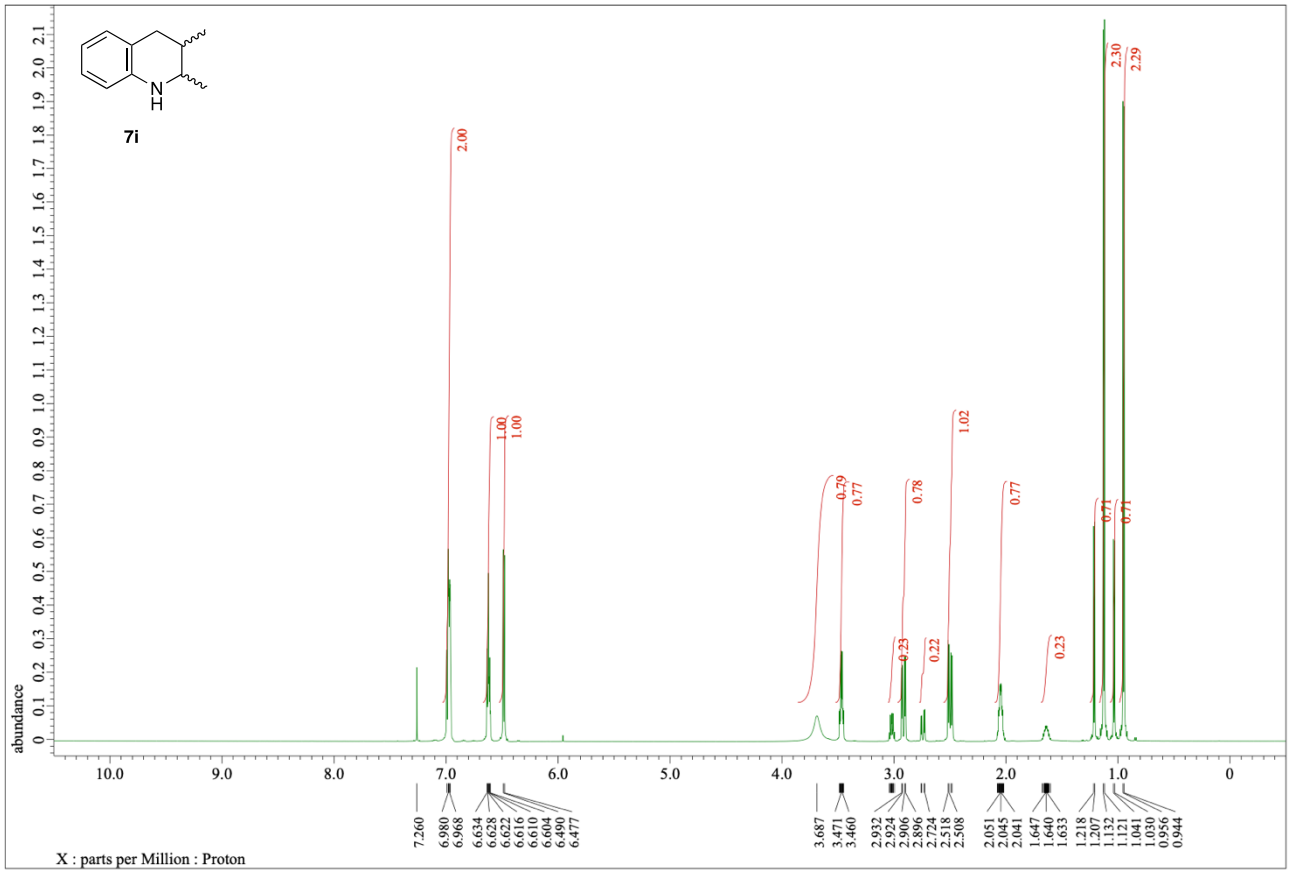
**2-Methyl-1,2,3,4-tetrahydroquinoline (7h) $^{1}$H NMR (600 MHz, $CDCl_3$)**



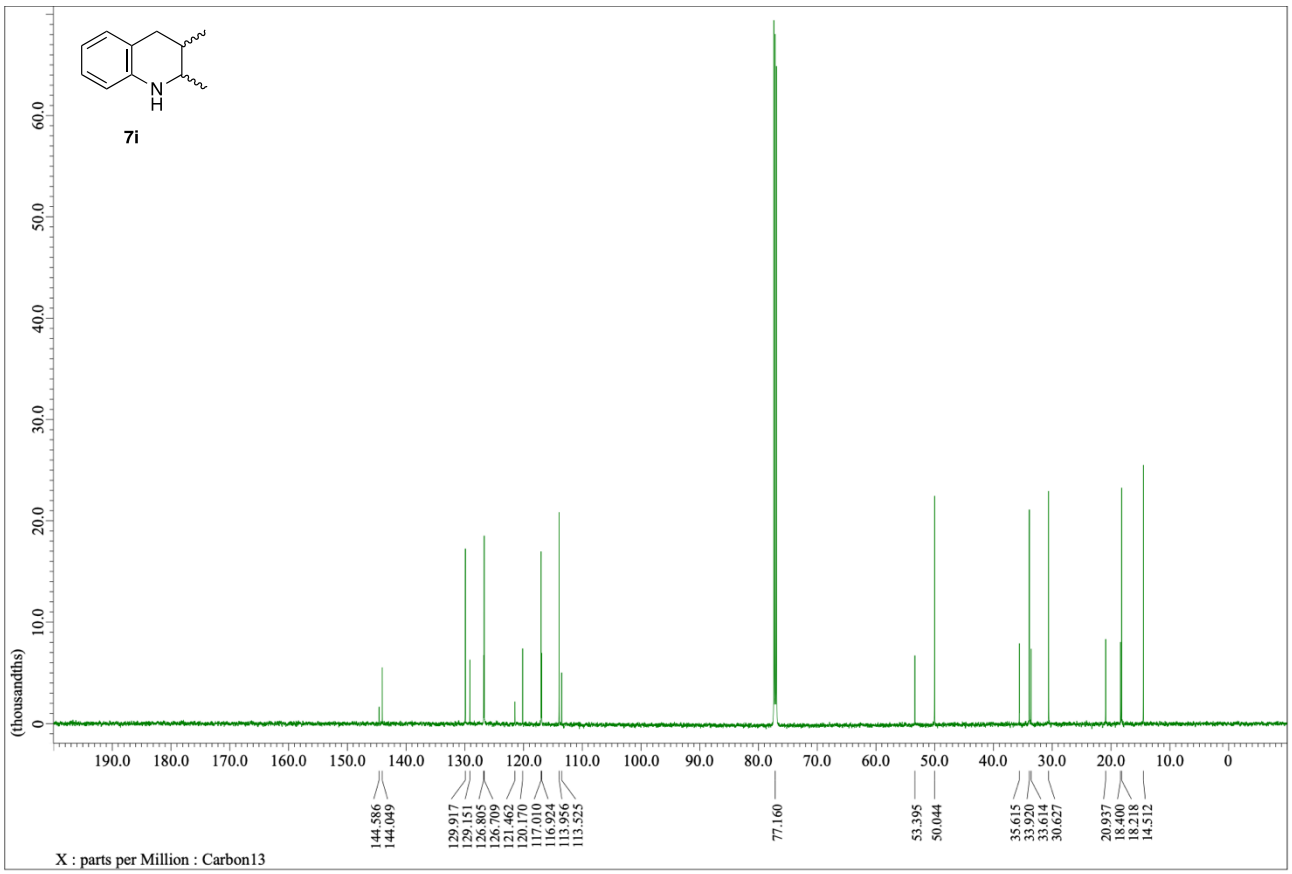

**2-Methyl-1,2,3,4-tetrahydroquinoline (7h) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



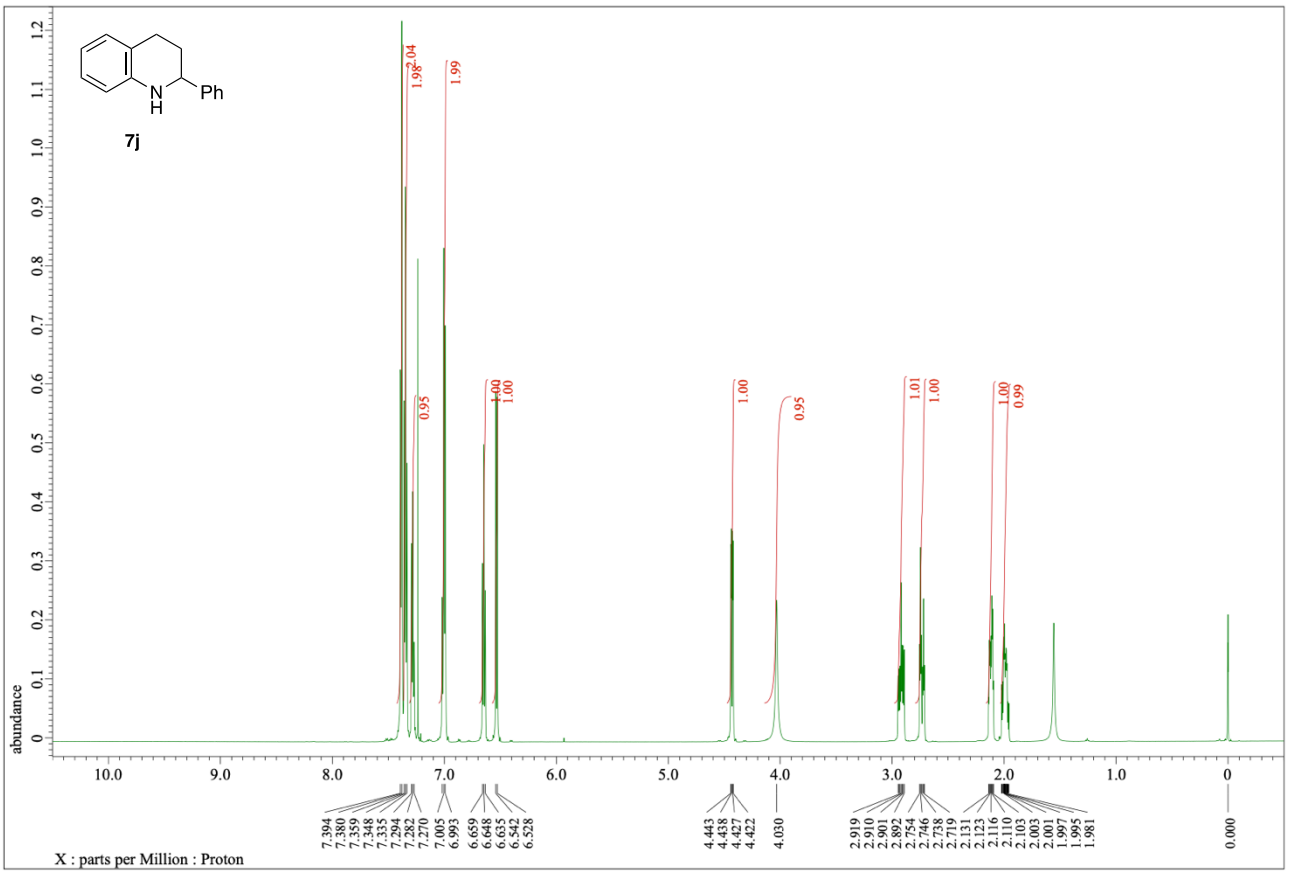
**2,3-Dimethyl-1,2,3,4-tetrahydroquinoline (7i) $^{1}$H NMR (600 MHz, $CDCl_3$)**



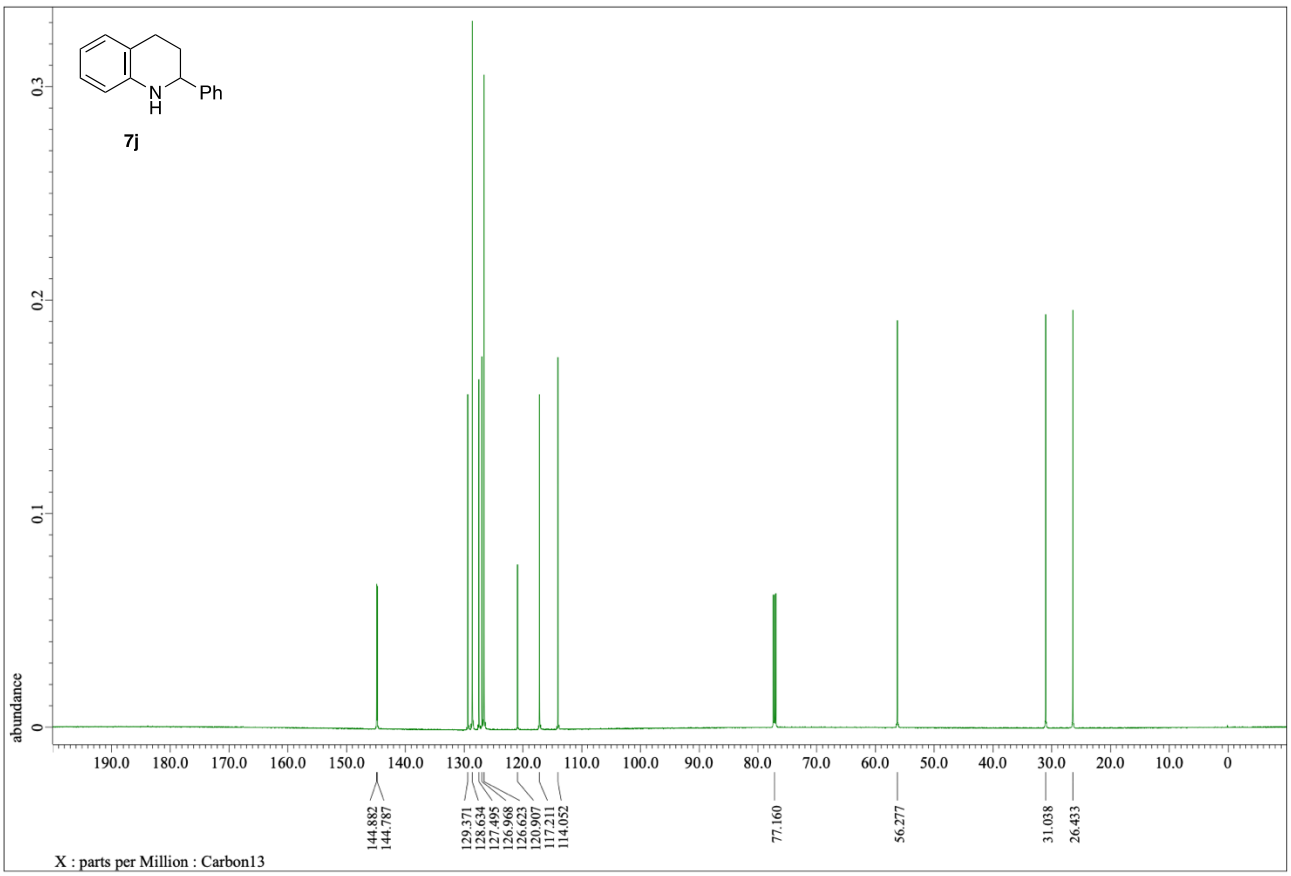

**2,3-Dimethyl-1,2,3,4-tetrahydroquinoline (7i) $^{13}$C {$^{1}$H} NMR (150 MHz, $CDCl_3$)**



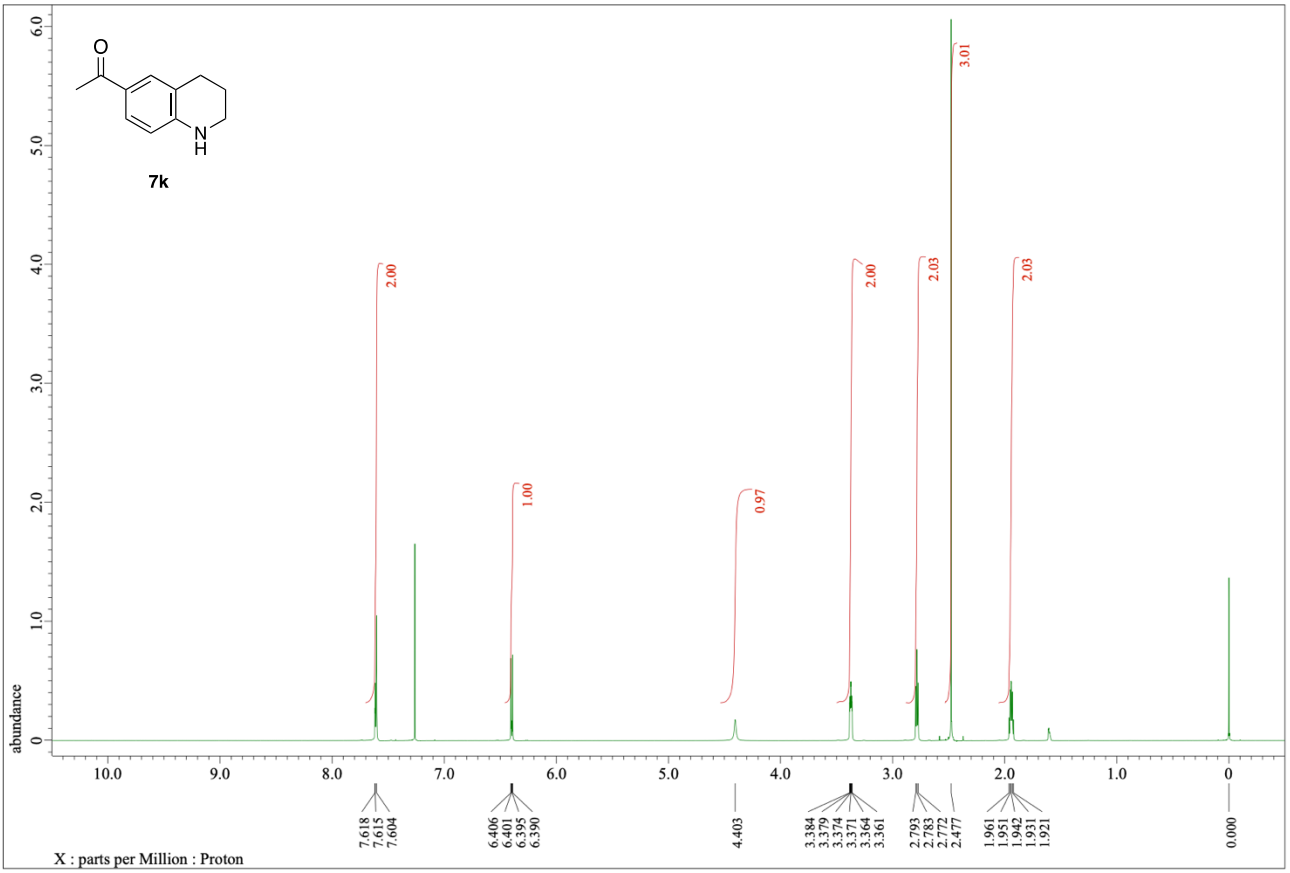
**2-Phenyl-1,2,3,4-tetrahydroquinoline (7j) $^{1}$H NMR (600 MHz, $CDCl_3$)**



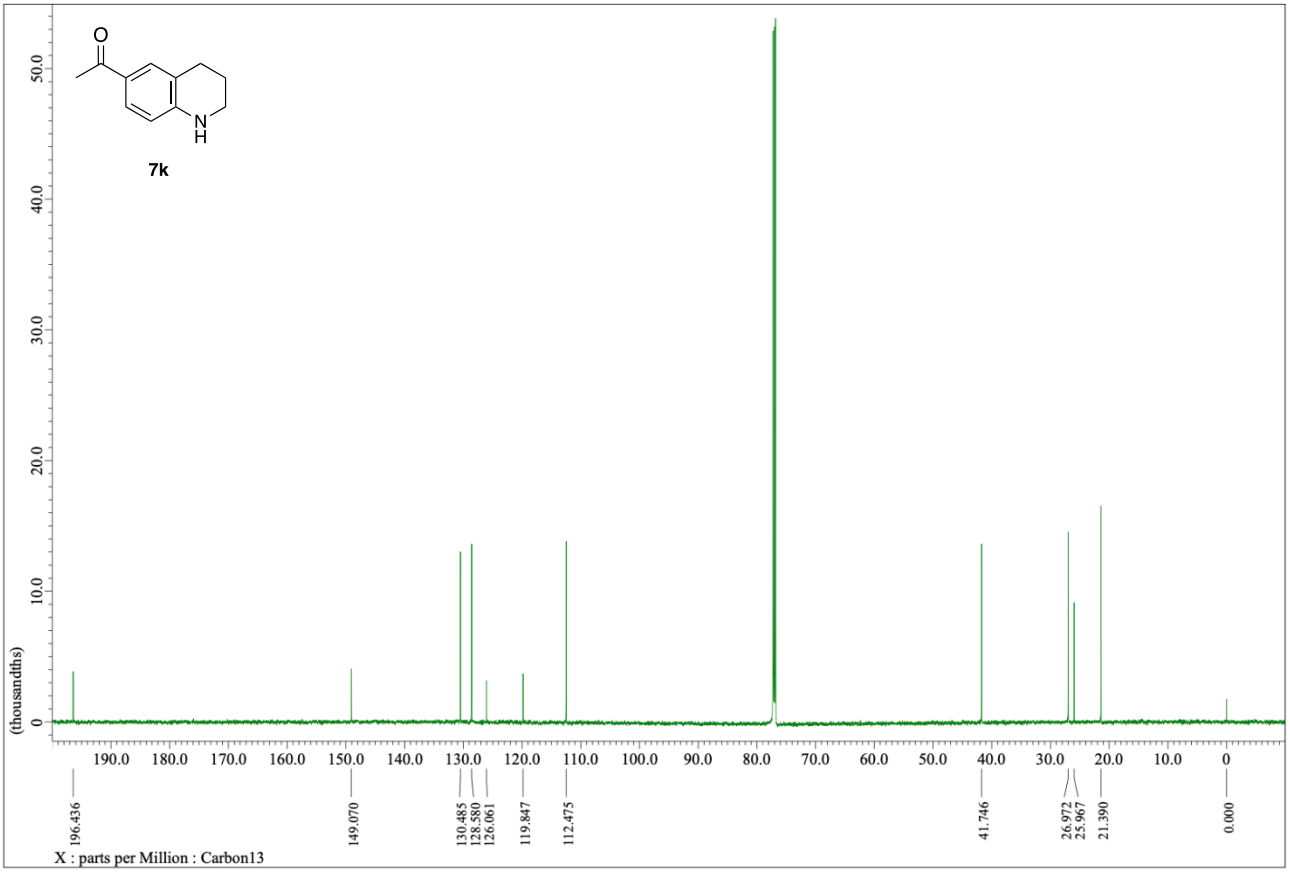

**2-Phenyl-1,2,3,4-tetrahydroquinoline (7j) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



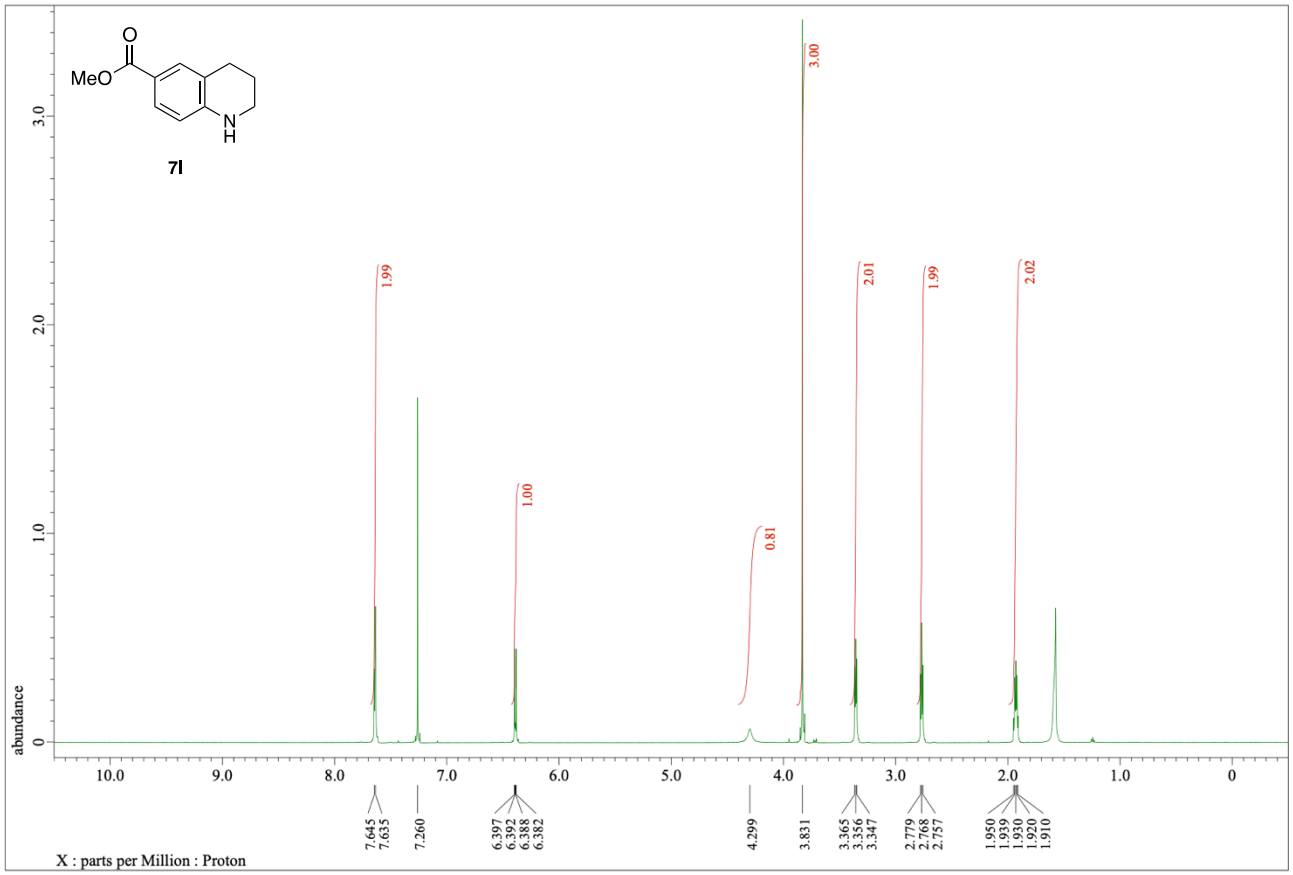
**6-Acetyl-1,2,3,4-tetrahydroquinoline (7k) $^{1}$H NMR (600 MHz, $CDCl_3$)**



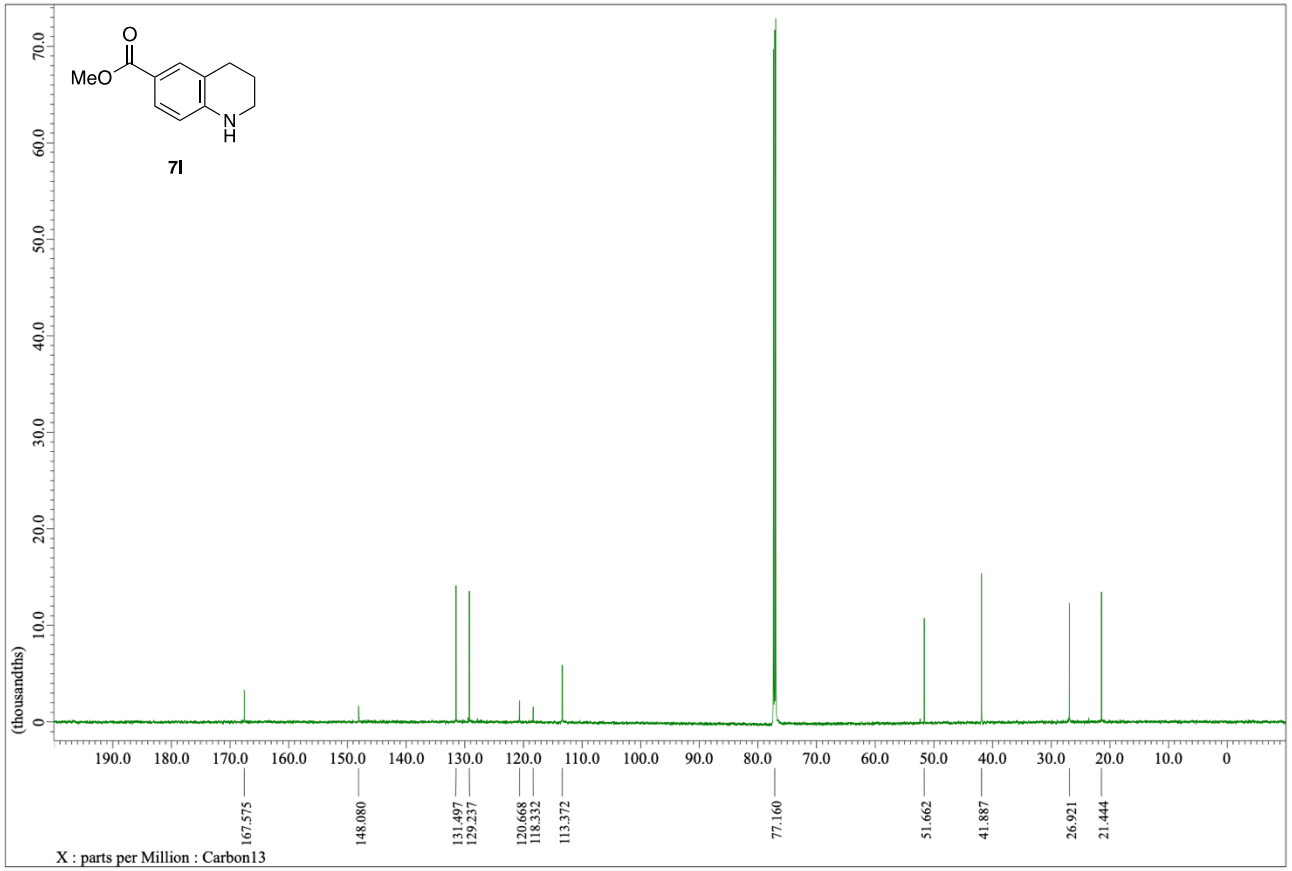

**6-Acetyl-1,2,3,4-tetrahydroquinoline (7k) $^{13}$C {$^{1}$H} NMR (150 MHz, $CDCl_3$)**



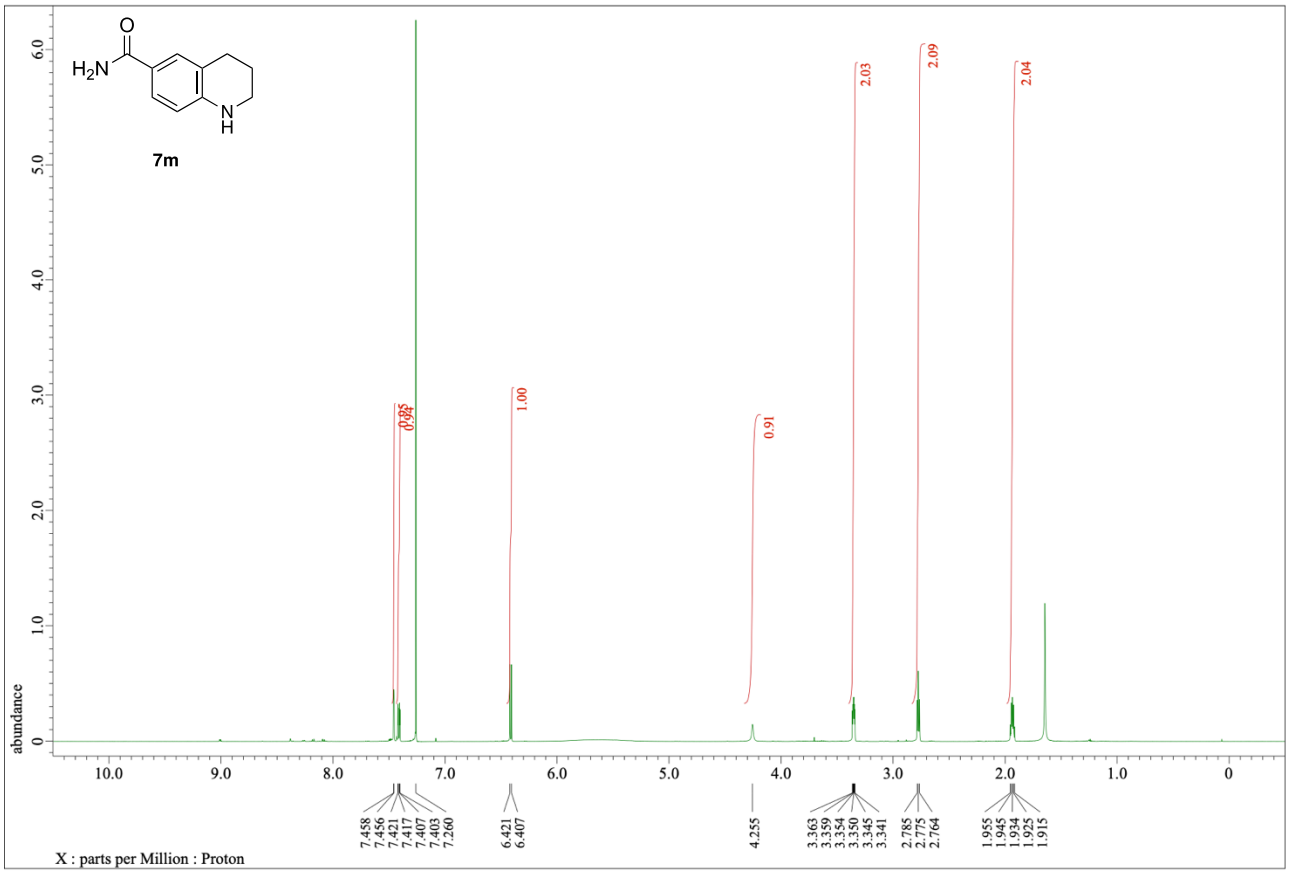
**Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (7l) $^{1}$H NMR (600 MHz, $CDCl_3$)**



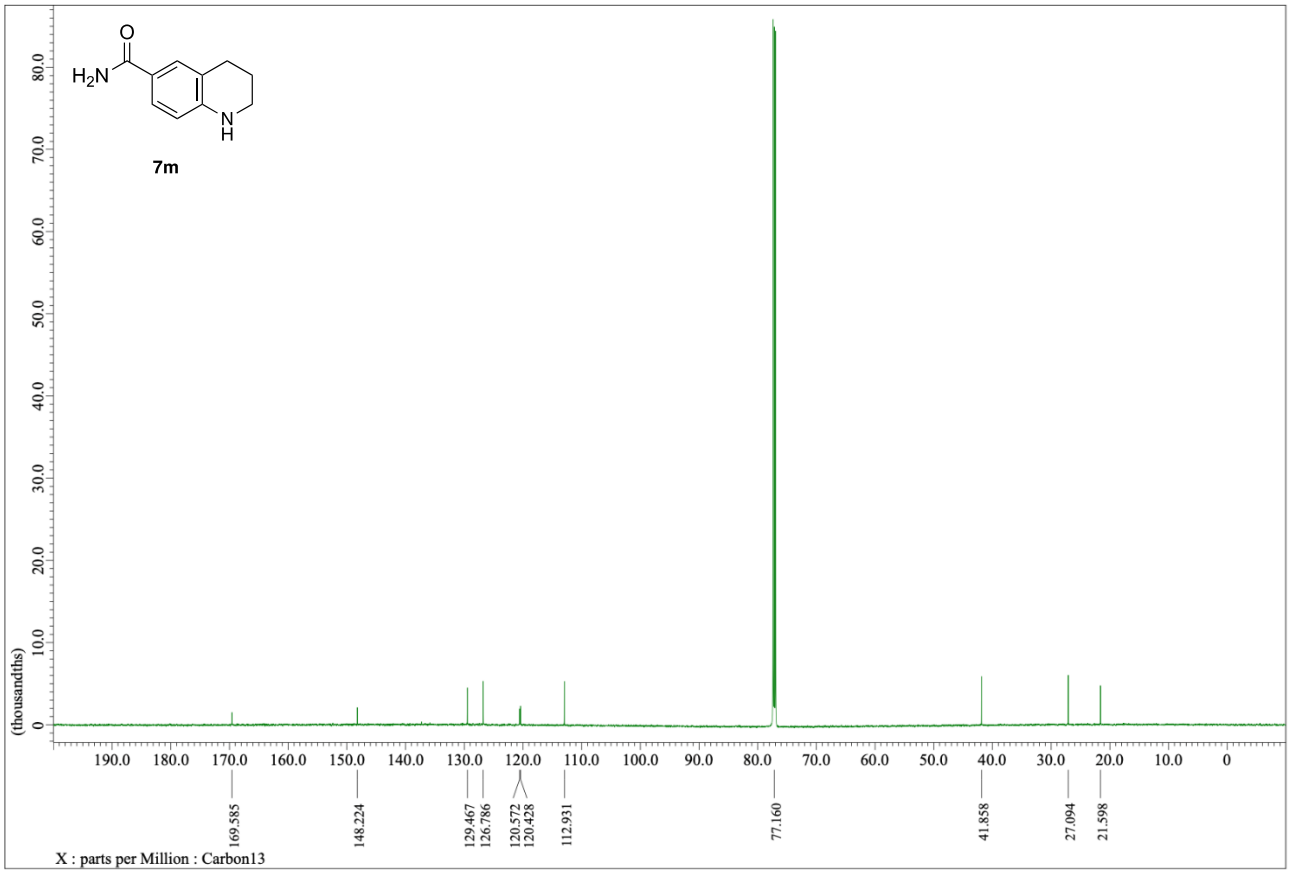

**Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (7l) $^{13}$C {$^{1}$H} NMR (150 MHz, $CDCl_3$)**



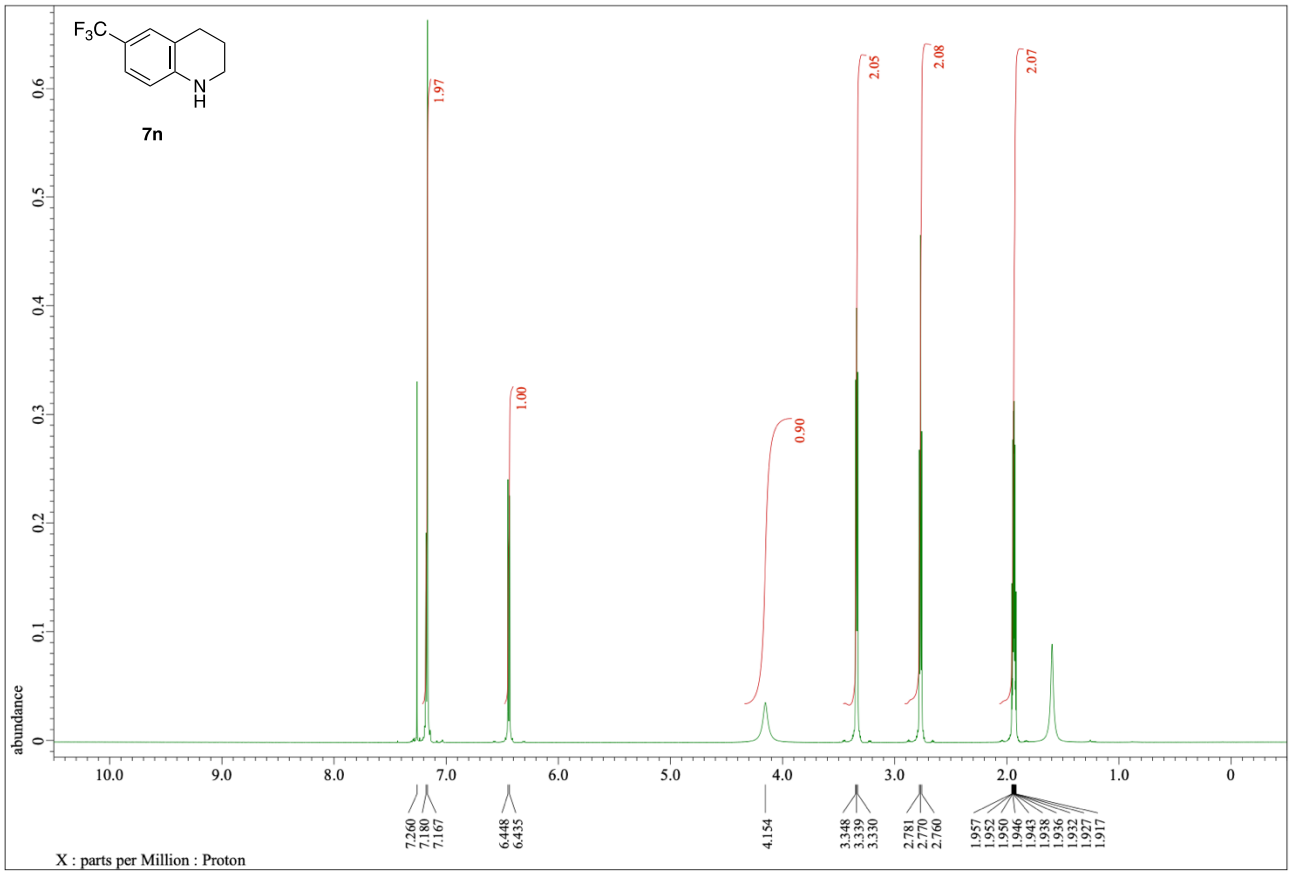
**1,2,3,4-Tetrahydroquinoline-6-carboxamide (7m) $^{1}$H NMR (600 MHz, $CDCl_3$)**



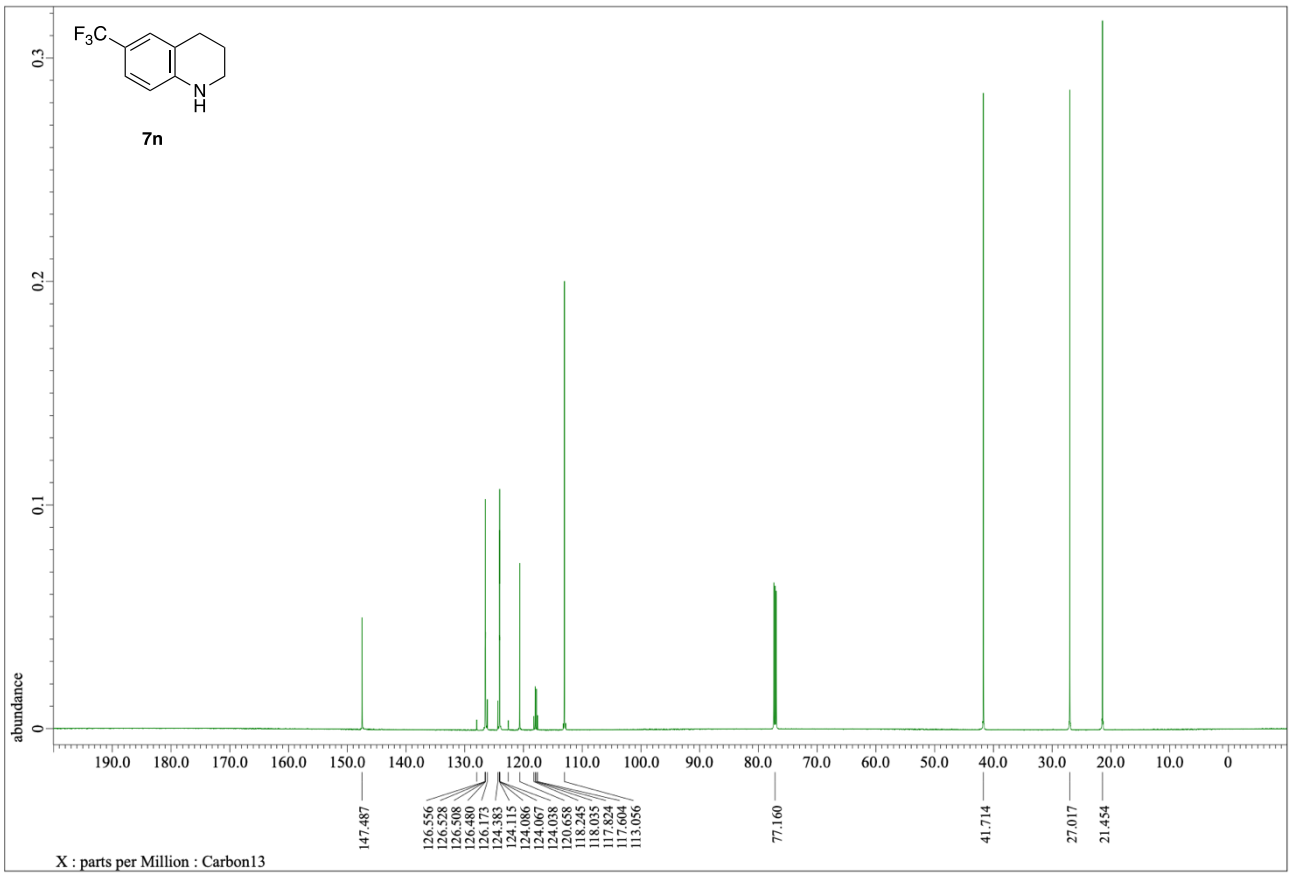

**1,2,3,4-Tetrahydroquinoline-6-carboxamide (7m) $^{13}$C {$^{1}$H} NMR (150 MHz, $CDCl_3$)**



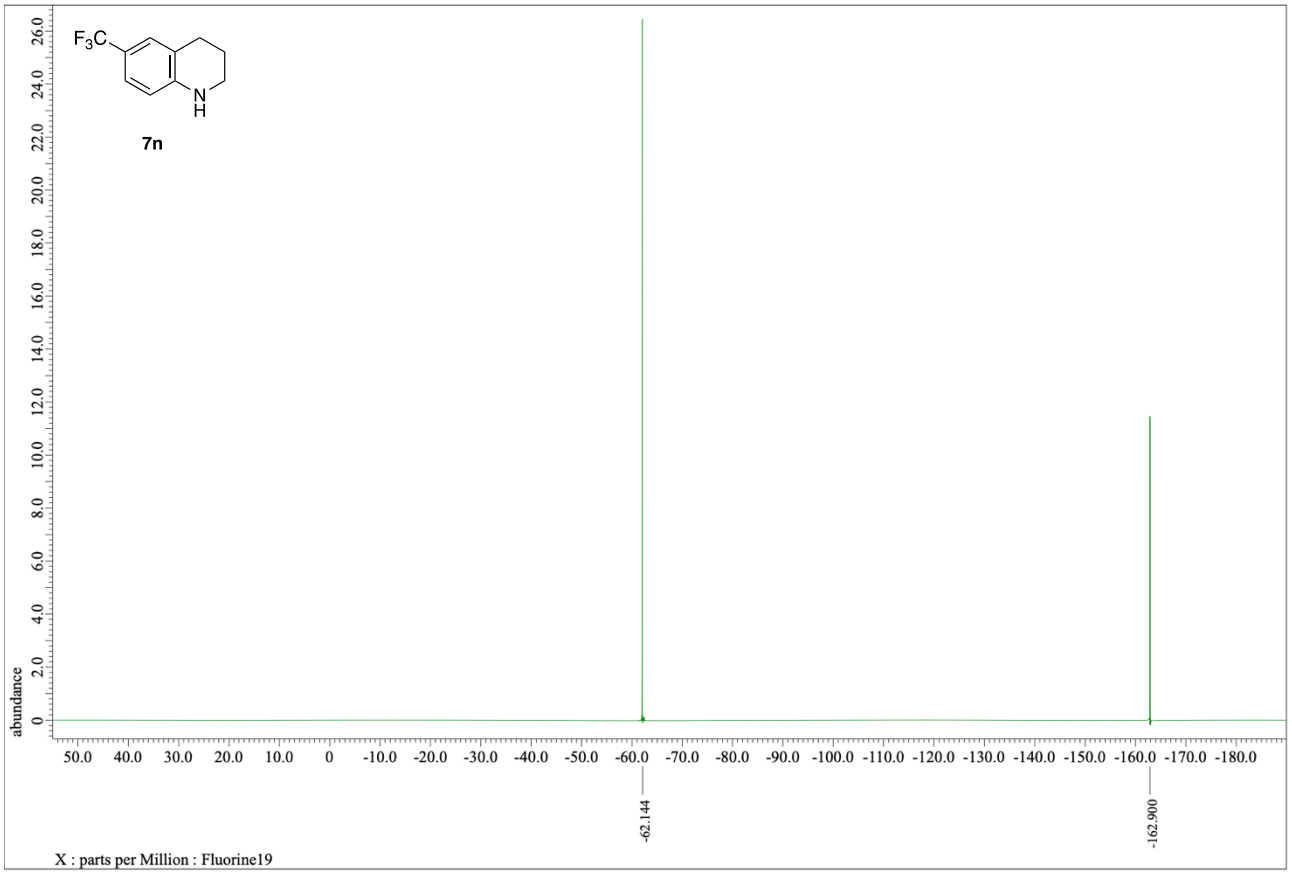
**6-(Trifluoromethyl)-1,2,3,4-tetrahydroquinoline (7n) $^{1}H$ NMR (600 MHz, $CDCl_3$)**



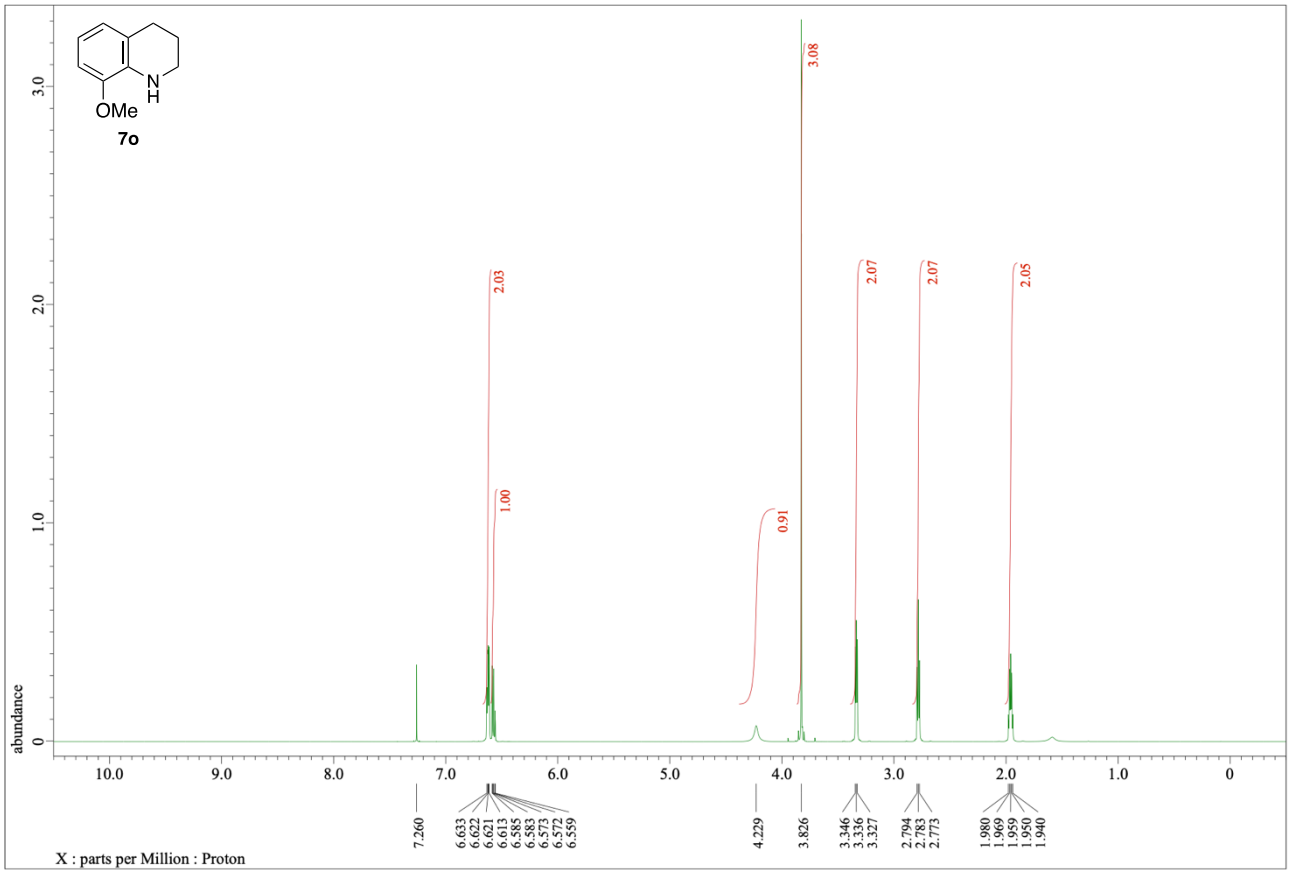

**6-(Trifluoromethyl)-1,2,3,4-tetrahydroquinoline (7n) $^{13}C$ {$^{1}H$} NMR (150 MHz, $CDCl_3$)**



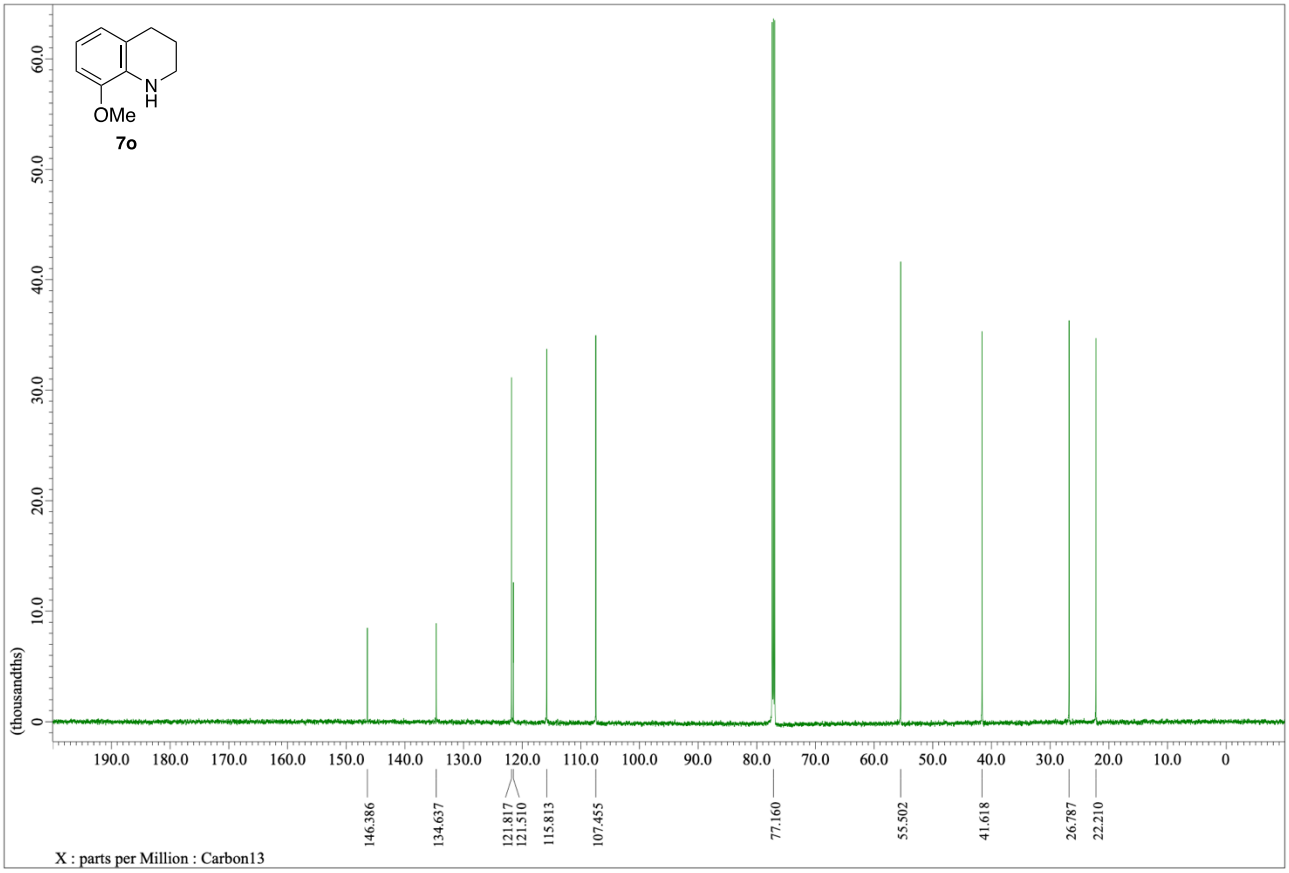
**6-(Trifluoromethyl)quinoline (7n) $^{19}F$ NMR (565 MHz, $CDCl_3$)**



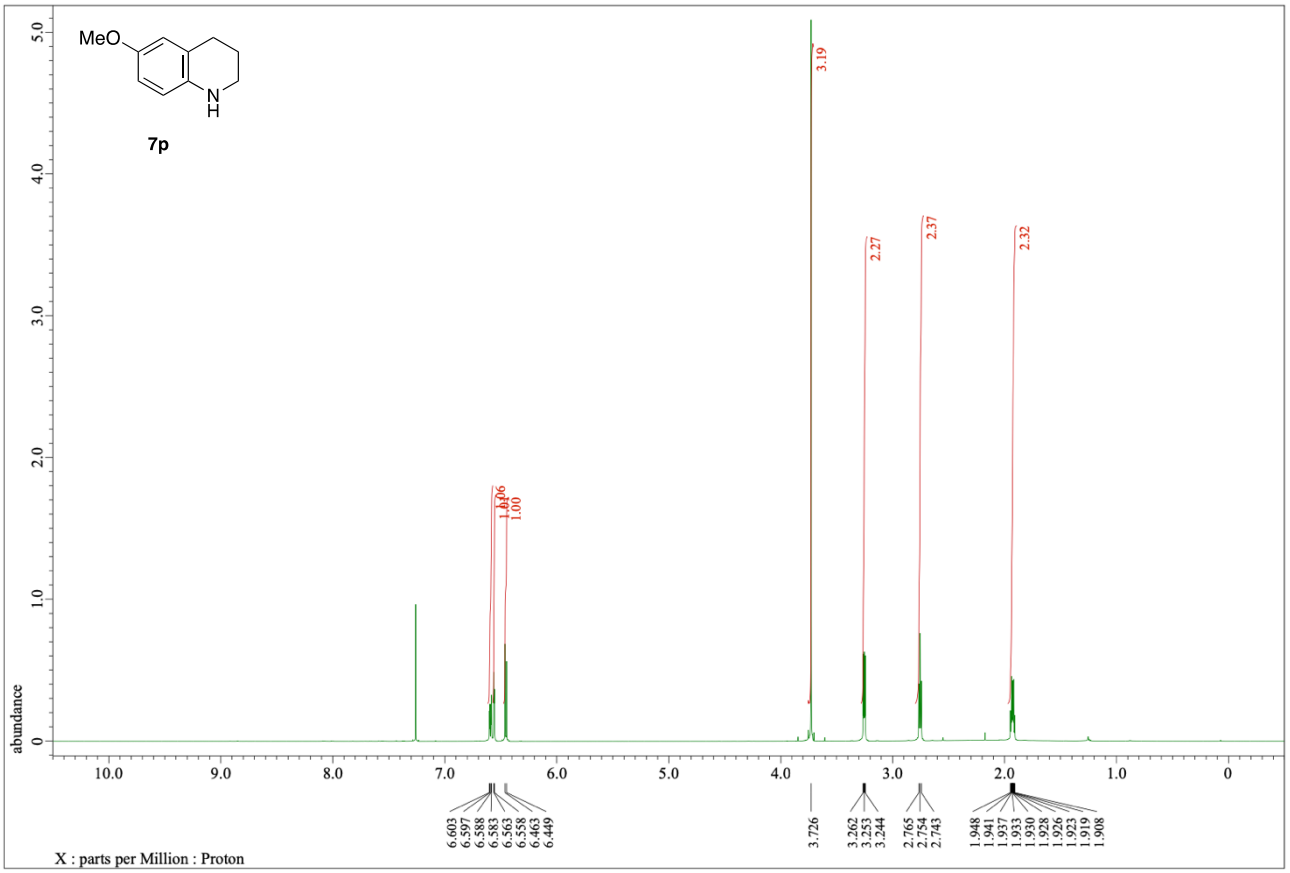
**8-Methoxy-1,2,3,4-tetrahydroquinoline (7o) $^{1}$H NMR (600 MHz, $CDCl_3$)**



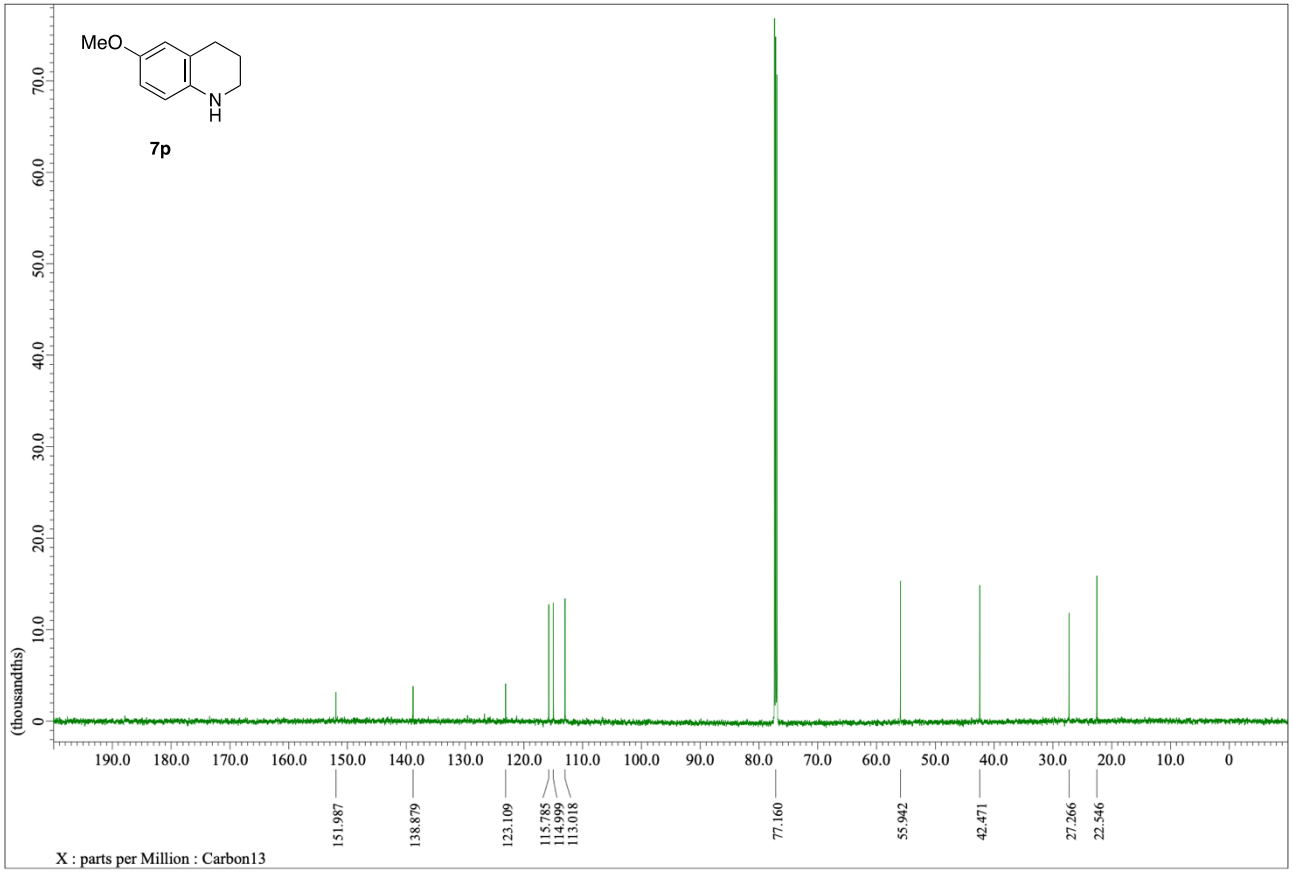

**8-Methoxy-1,2,3,4-tetrahydroquinoline (7o) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



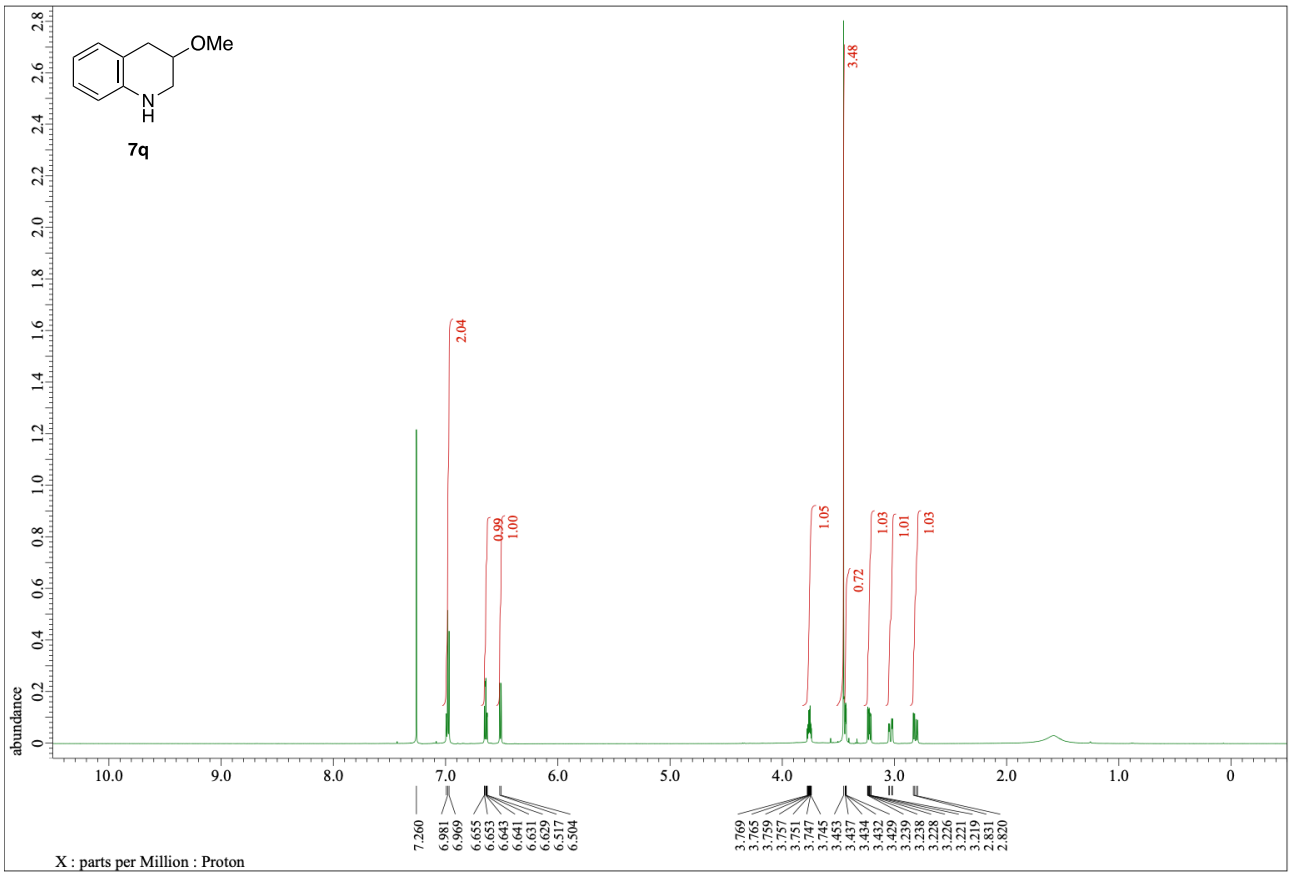
**6-Methoxy-1,2,3,4-tetrahydroquinoline (7p) $^{1}H$ NMR (600 MHz, $CDCl_3$)**



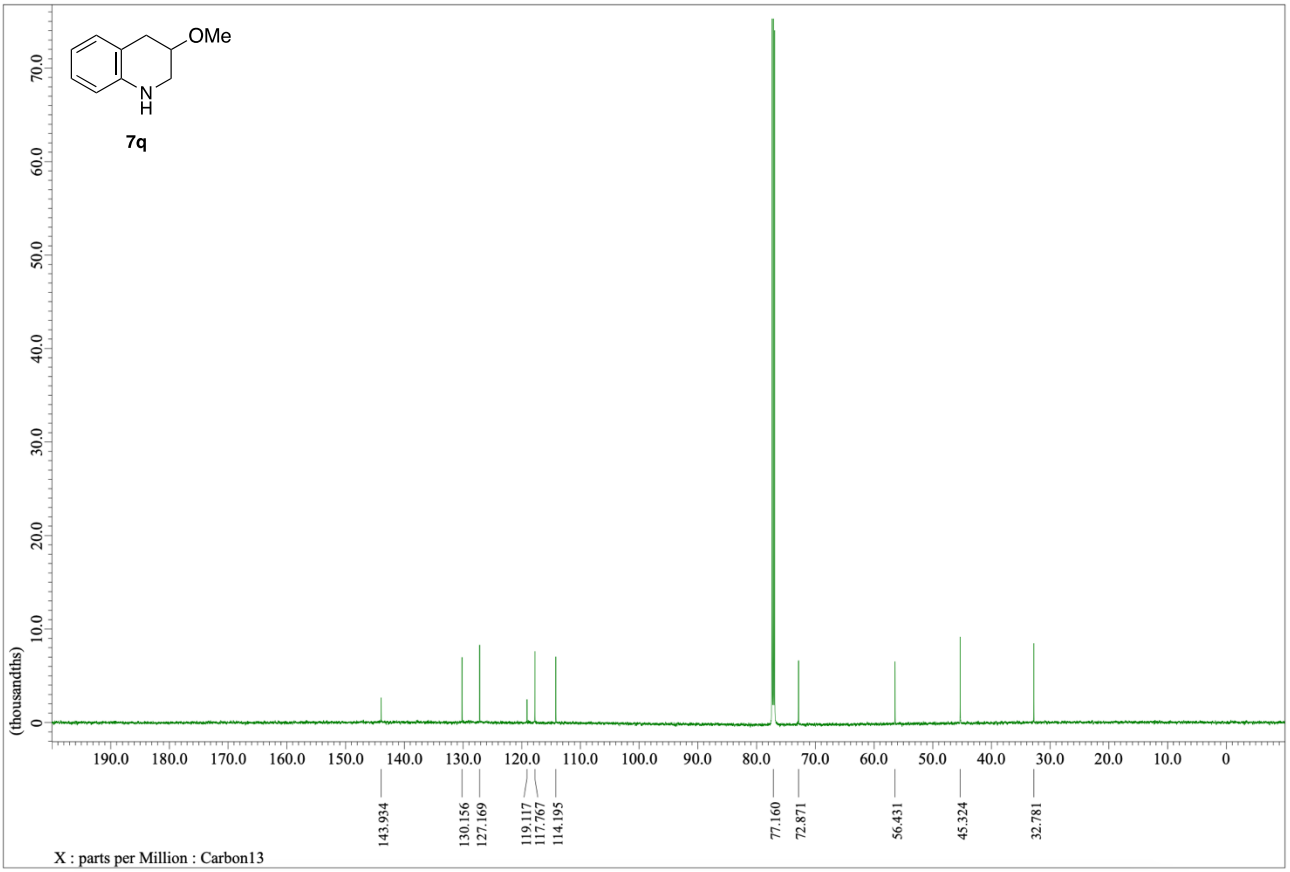

**6-Methoxy-1,2,3,4-tetrahydroquinoline (7p) $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)**



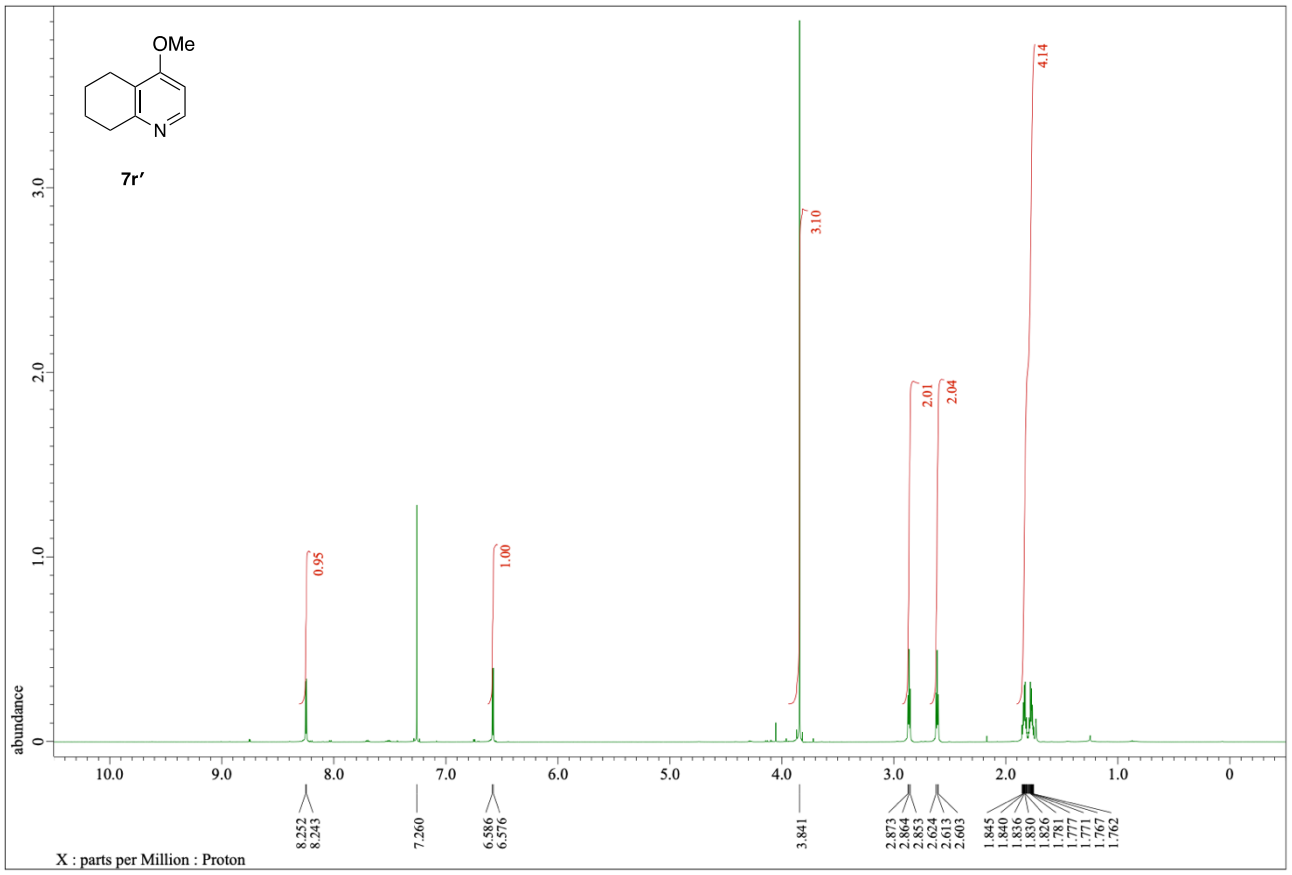
**3-Methoxy-1,2,3,4-tetrahydroquinoline (7q) $^{1}$H NMR (600 MHz, $CDCl_3$)**



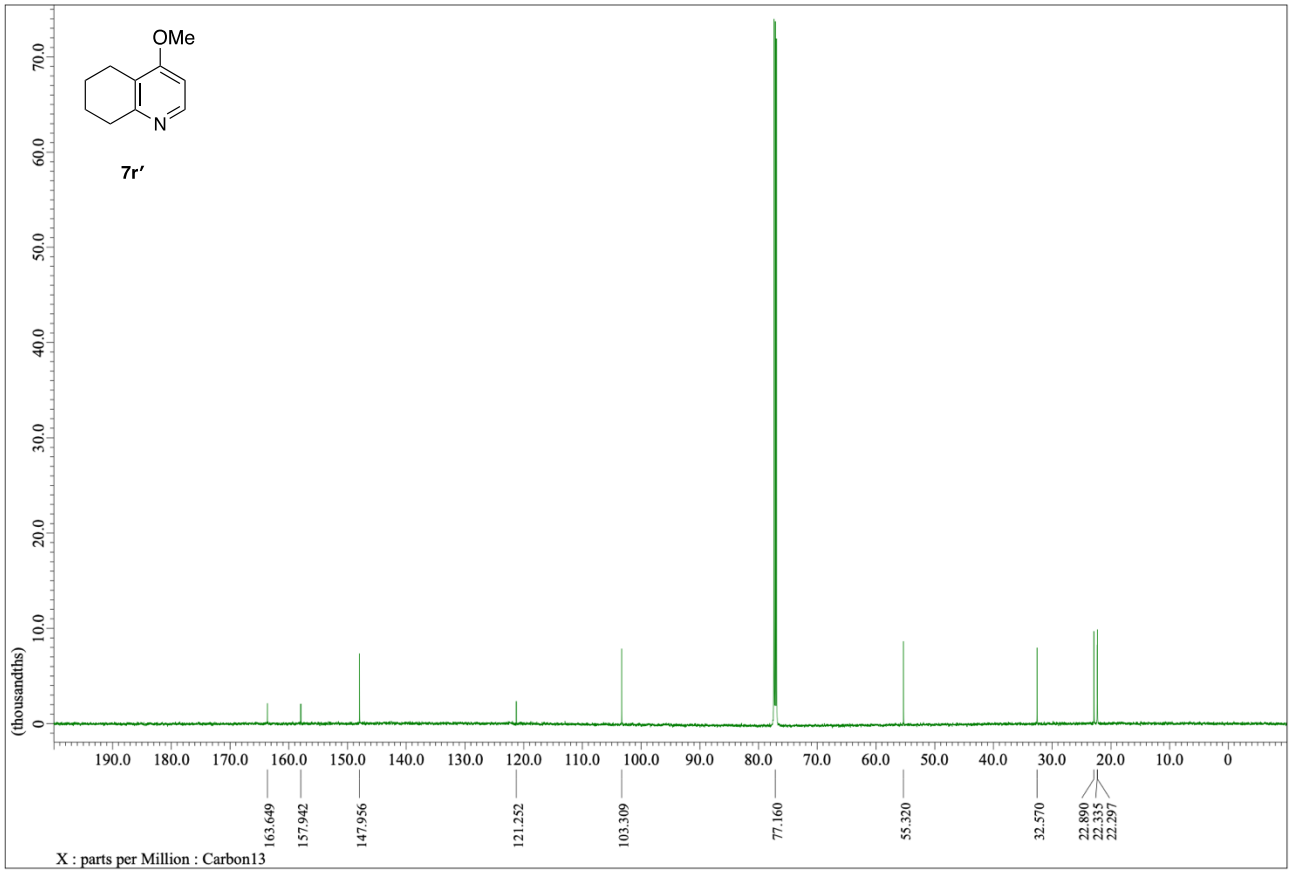

**3-Methoxy-1,2,3,4-tetrahydroquinoline (7q) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



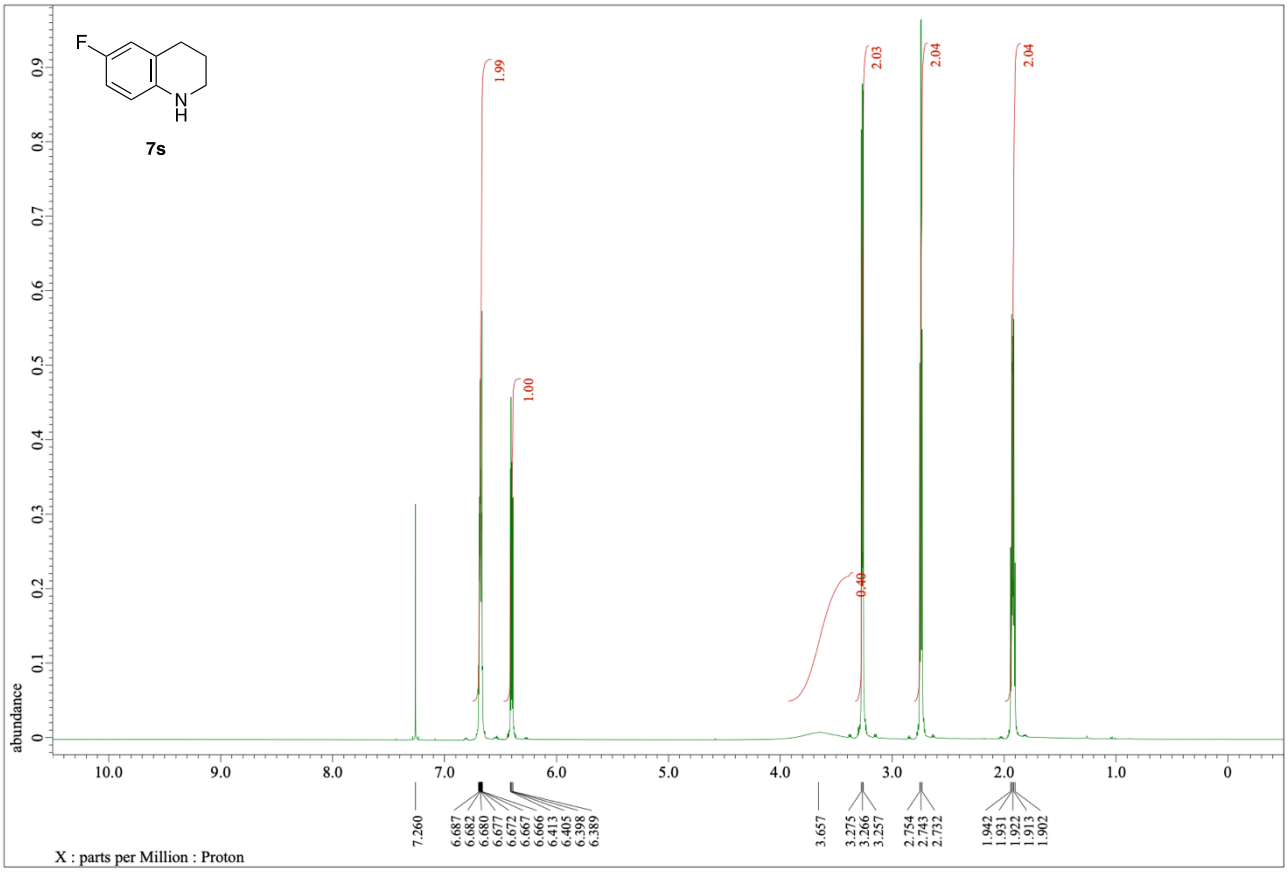
**4-Methoxy-5,6,7,8-tetrahydroquinoline (7r′) $^{1}$H NMR (600 MHz, $CDCl_3$)**



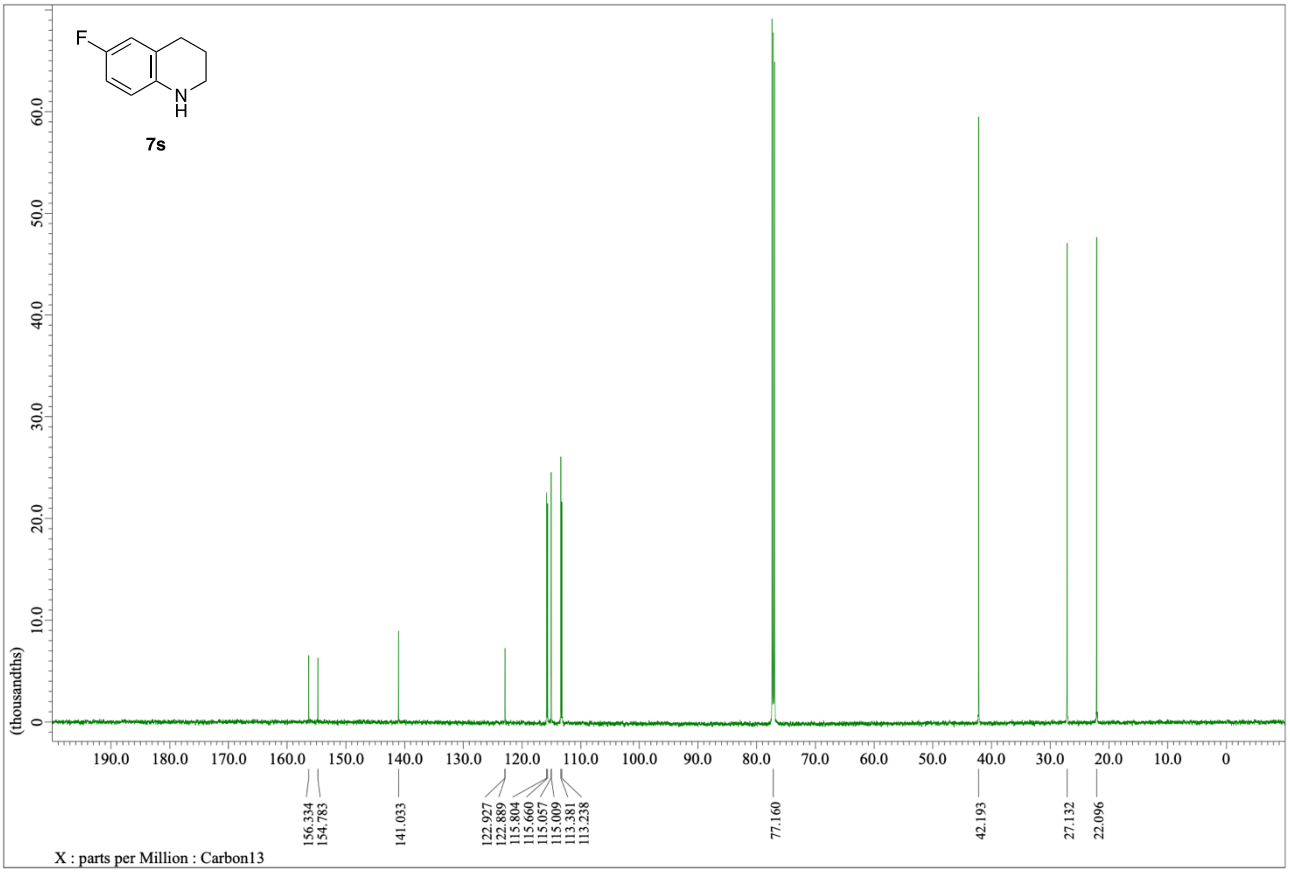

**4-Methoxy-5,6,7,8-tetrahydroquinoline (7r′) $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)**



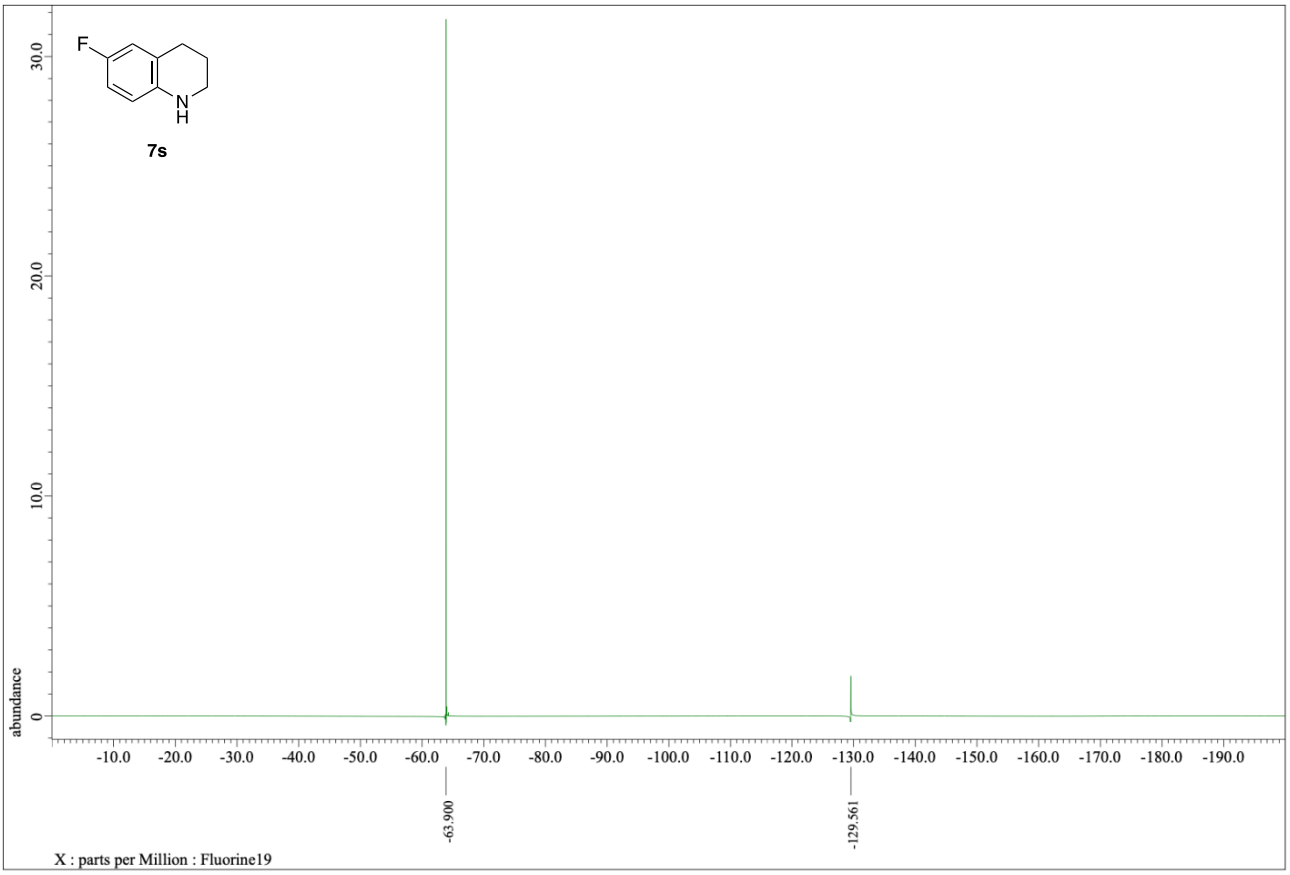
**6-Fluoro-1,2,3,4-tetrahydroquinoline (7s) $^{1}$H NMR (600 MHz, $CDCl_3$)**



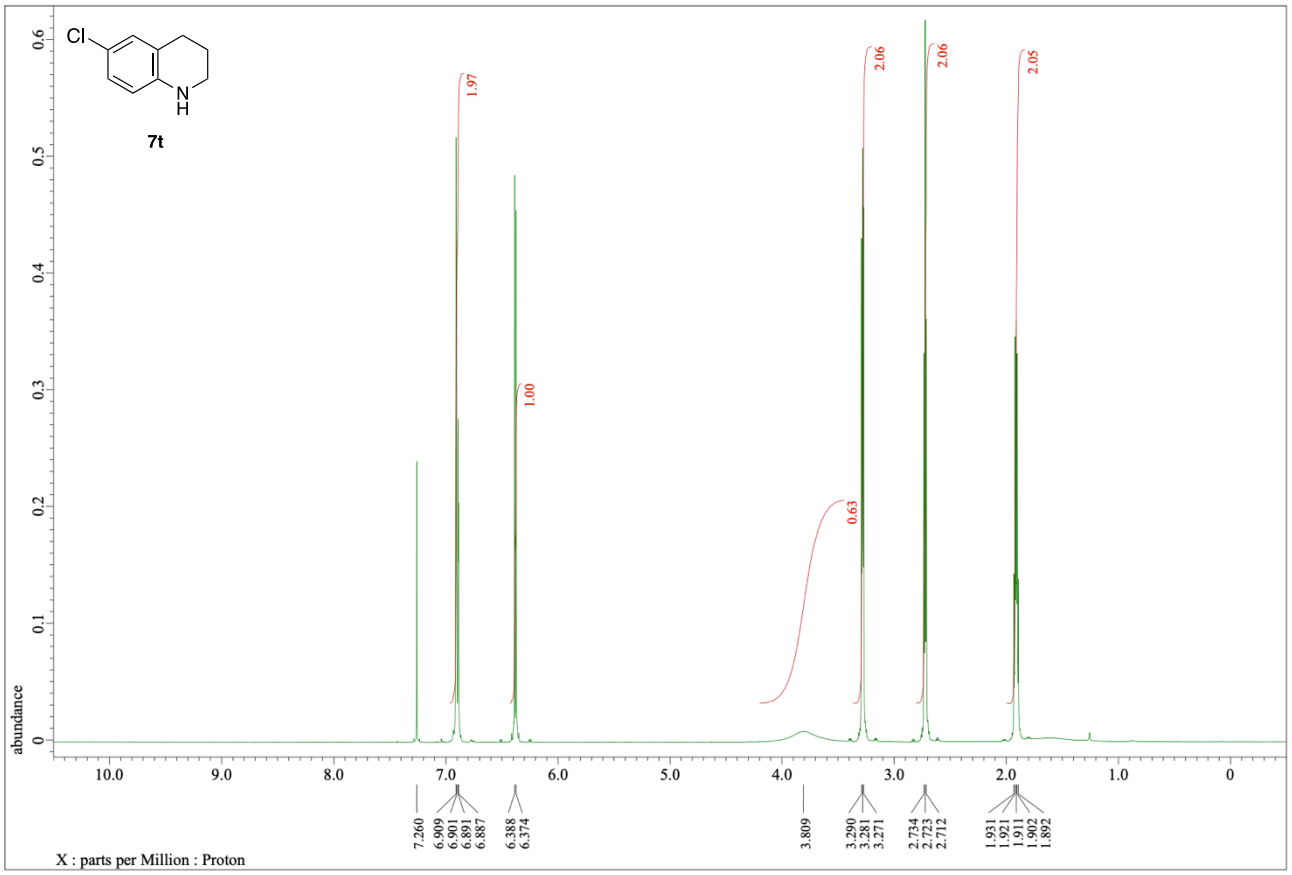

**6-Fluoro-1,2,3,4-tetrahydroquinoline (7s) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**



**6-Fluoro-1,2,3,4-tetrahydroquinoline (7s) $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)**



**6-Chloro-1,2,3,4-tetrahydroquinoline (7t) $^{1}$H NMR (600 MHz, $CDCl_3$)**




**6-Chloro-1,2,3,4-tetrahydroquinoline (7t) $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$)**