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SUPPORTING INFORMATION

Robust Cyclometallated Ir(III) Complexes for the Homogeneous Hydrogenation of *N*-Heterocycles under Mild Conditions

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Table of Contents

S1	Experimental procedures	S3
S1.1	General methods	S3
S1.2	Synthesis of the ligands	S3
S1.3	Synthesis of cyclometallated iridium complexes	S6
S1.4	Reactions of **6**	S11
S1.5	Hydrogenation of 2-methylquinoline in varying solvents at 20 bar H_2 pressure	S15
S1.6	Hydrogen bonding between 2,2,2-trifluoroethanol (TFE) and 2-methylquinoline	S16
S1.7	Typical procedure for the hydrogenation reactions	S17
S1.8	Inhibition of the **1f**-catalysed hydrogenation of 2-methylquinoline by chloride ions or triphenylphosphine	S18
S1.9	Comparison of **1f** with other catalysts	S19
S2	Analytical data for the hydrogenation products	S20
S3	NMR spectra	S29
S3.1	NMR spectra of ligands	S29
S3.2	NMR spectra of metal complexes	S33
S3.3	NMR spectra of the hydrogenation products	S44
S4	Crystallographic data of **1f** and **1g** minor isomer	S71
S5	References	S82

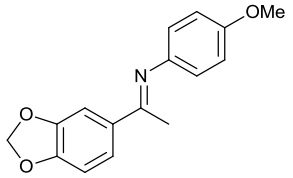
S1 Experimental procedures

S1.1 General methods

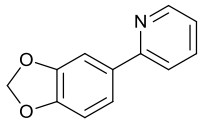
All reactions were performed in air unless otherwise specified. CH_2Cl_2 and hexane were dried over CaH and distilled under nitrogen. Tetrahydrofuran was dried over sodium in the presence of benzophenone and distilled under nitrogen. Toluene was dried over sodium and distilled under nitrogen. Methanol and ethanol were dried over magnesium turnings and distilled under nitrogen. Acetonitrile was dried over 4Å MS and distilled under nitrogen. All other solvents were used as received. $[Cp^*IrCl_2]_2$, was purchased from Strem Chemicals Inc. Complexes **1a**, **1b** and **1d** were prepared as following Wang *et al.*[S1] Complex **1c** was prepared as following Lei *et al.*[S2] Complex **1i** was prepared as following Barnard *et al.*[S3] Data was found to be consistent with that reported in all cases. Ketimine ligands were prepared by literature procedures.[S1],[S4] 2-Methylquinolinium tetrafluoroborate was prepared by a literature procedure. [S5] All other commercial compounds were purchased from Sigma-Aldrich Co. or Alfa Aesar and used without further purification. NMR spectra were recorded on a Bruker DPX-400 spectrometer with TMS as the internal standard and referenced to the residual solvent peak or TMS if the solvent peak was obscured by other resonances (ppm). The mass spectra were obtained by electrospray ionisation (ESI) or chemical ionisation (CI) at the Department of Chemistry, Liverpool University or by (FAB) at the EPSRC National Mass Spectrometry Service Centre, Swansea. Elemental analyses were performed by the Department of Chemistry, Liverpool University elemental analysis service.

S1.2 Synthesis of the ligands

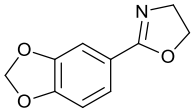
N-Aryl ketimine ligands **L1a-L1f**, **L1j**, **L1k** were prepared by the following procedure. A mixture of ketone and amine (0.95 eq.) in dry toluene was heated to reflux over 4Å molecular sieves for 18 h. The mixture was filtered through celite, eluting with ethyl acetate, and the solvent removed *in vacuo*. The crude mixture was recrystallised from hexanes to give the pure imine products. Analytical data was consistent with that reported in the literature.[S1], [S4]



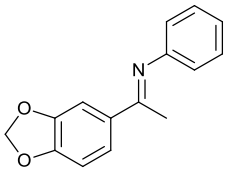
(*E*)-*N*-(1-(Benzo[d][1,3]dioxol-5-yl)ethylidene)-4-methoxyaniline (L1f). The compound was prepared on a 10 mmol scale using the standard method described above. White solid; yield 2.04 g, 76%; m.p. 85-90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 9.0 Hz, 2H), 6.01 (s, 2H) 3.81 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.99, 149.67, 148.12, 122.15, 121.00, 114.33, 107.81, 107.38, 101.56 (two resonances were not observed, possibly due to overlapping), 55.61, 17.42; *m/z* (ES$^+$) 270 (100%, MH$^+$); HRMS (ES$^+$) calcd. for $C_{16}H_{15}NO_3$ (MH$^+$) 270.1130; found 270.1127.



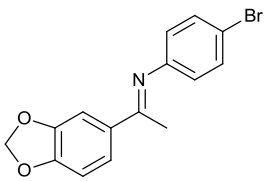
2-(Benzo[d][1,3]dioxol-5-yl)pyridine (L1g). To a thick-walled glass tube fitted with a J. Young type Teflon® cap was added benzo[d][1,3]dioxole-5-boronic acid (500 mg, 3.01 mmol), K_2CO_3 (831 mmol, 6.02 mmol) and $Pd(PPh_3)_4$ (34 mg, 0.03 mmol). The vessel was placed under a N_2 atmosphere and the cap replace by a septa. A 1:1 mixture of propan-2-ol and water (non-degassed) was added *via* syringe followed by 2-bromopyridine (476 mg, 3.0 mmol). The septa was replaced by the Teflon® cap, and then the vessel was sealed and heated at 70 ^{o}C for 18h. The reaction was diluted with EtOAc (20 mL) and sat. NaCl (aq.). The mixture was washed with water (3x20 mL), dried over $MgSO_4$, filtered and evaporated to give a crude product which was purified by silica gel chromatography (4:1 hexane/EtOAc) to give the product. The data was consistent with those reported by Monguchi *et al.*[S6] White solid; yield 477 mg, 80%; m.p. 50-52 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.9 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.19 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.02 (s,2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.98, 149.51, 148.61, 148.41, 136.97, 133.82, 121.82, 121.09, 120.17, 108.59, 107.49, 101.44; *m/z* (ES$^+$) 199.9 (100%, MH$^+$).



2-(Benzo[d][1,3]dioxol-5-yl)-4,5-dihydrooxazole (L1h). Using a modification of the method of Togo,[S7] ethanolamine (92 mg, 1.5 mmol) and piperonal (150 mg, 1.0 mmol) were added to thick-walled glass tube fitted with a stirrer bar, a Teflon® cap and a rubber septum along with *tert*-butanol (15 mL). The reaction was stirred vigorously at 30 ^{o}C for 0.5 h, after which time I_2 (317 mg, 1.25 mmol) and K_2CO_3 (414 mg, 3.0 mmol) were added and the mixture stirred vigorously at 70 ^{o}C for 3 h. The mixture was diluted with CH_2Cl_2 (100 mL), washed with sat. aqueous $Na_2S_2O_3$ (100 mL), brine (100 mL) and H_2O (5x100 mL). The organic layer was separated, dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give a crude solid, which was washed with hexane to give the pure product. White solid; yield 146 mg, 75%; m.p. 120-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.40 (d, *J* = 1.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 4.40 (t, *J* = 9.5 Hz, 2H), 4.02 (t, *J* = 9.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.37, 150.32, 147.73, 123.26, 121.77, 108.46, 108.18, 101.64, 67.79, 54.87; *m/z* (ES^+) 192 (100%, MH^+); HRMS (ES^+) calcd. for $C_{10}H_{10}NO_3$ (MH^+) 192.0655; found 192.0655.

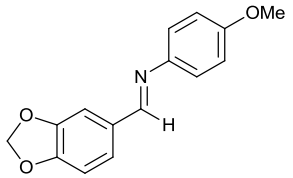


(*E*)-*N*-(1-(Benzo[d][1,3]dioxol-5-yl)ethylidene)aniline (L1j). The compound was prepared on a 10 mmol scale using the standard method described above. The product could not be obtained in its pure form (~90% purity by ^{1}H NMR). The crude product was used in the cyclometallation step with the mass adjusted to account for the impurity of the imine.



(*E*)-*N*-(1-(Benzo[d][1,3]dioxol-5-yl)ethylidene)-4-bromoaniline (L1k). The compound was prepared on a 10 mmol scale using the standard method described

above. The product could not be obtained in its pure form (~75% purity by ^{1}H NMR). The crude product was used in the cyclometallation step with the mass adjusted to account for the impurity of the imine.

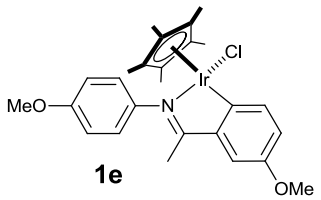


(*E*)-*N*-(Benzo[d][1,3]dioxol-5-ylmethylene)-4-methoxyaniline (L1l). Piperonal (175 mg, 1.67 mmol) and *p*-anisidine (143 mg, 1.67 mmol) were dissolved in absolute ethanol (5 mL) in a screw top vial. Formic acid (1 drop) was added and the mixture stirred at room temperature for 0.5 h. The mixture was filtered and the precipitate washed with cold MeOH (3x5 mL) and dried *in vacuo* to give the product. White solid; yield 222 mg, 75%; m.p. 115-120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.27-7.20 (m, 2H, overlapped with residual $CHCl_3$), 6.92 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.18, 157.69, 150.35, 148.53, 145.03, 131.56, 125.46, 122.24, 114.47, 108.33, 106.84, 101.69, 55.62; *m/z* (ES$^+$) 256 (100%, MH$^+$); HRMS (ES$^+$) calcd. for $C_{15}H_{14}NO_3$ (MH$^+$) 256.0975; found 256.0972.

S1.3 Synthesis of cyclometallated iridium complexes

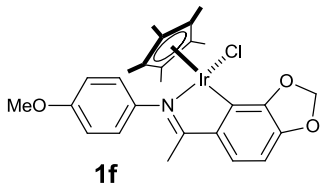
Complexes were synthesised using the method of Davies *et. al*.[S8] Unless specified, iridium complexes **1x** were synthesised from the corresponding ligands **L1x**. Ligand (2.05 eq.), $[Cp^*IrCl_2]_2$ (1.0 eq.) and NaOAc (20.0 eq.) were added to a thick-walled glass tube fitted with a stirrer bar, a Teflon® cap and a rubber septum. The vessel was degassed 3 times and placed under a dry N_2 atmosphere. Dry, degassed CH_2Cl_2 (10 mL) was added *via* syringe through the septum. The reaction was stirred vigorously at room temperature for 18 h. The reaction mixture was filtered through celite, eluting with CH_2Cl_2, dried over $MgSO_4$ and filtered. The solvent was evaporated to give a crude solid. Recrystallisation from 10:1 hexanes/DCM and drying *in vacuo* gave the pure products as fine powders often containing a molecule of DCM or H_2O of crystallisation. Please note that for *N*-arylketimine derived complexes such as **1e**, **1f**, **1j** and **1k** the resonances for the *N*-aryl protons are significantly broadened due to interaction with the Cp* ligand and the inability of the *N*-aryl ring to rotate due to

steric interactions with the Cp^* ligand and the ketimine methyl group (see crystal structures in Wang *et al.*[S1]). In contrast, in the aldimine derived complex **1l** the steric interactions are lessened due to the smaller size of H compared to CH_3 and such broadening effects are not observed.



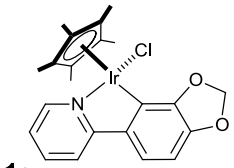
1e

Complex 1e: The complex formed as a single regioisomer as determined by ^{1}H NMR. Red solid; yield 23 mg, 90%; m.p. >250 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (s, br, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 3.0 Hz, 1H), 6.94 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.80 (s, br, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 2.41 (s, 3H), 1.43 (s, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.44, 158.19, 157.84, 155.29, 151.03 (br), 148.16, 144.44, 135.41, 124.34 (br), 119.63, 113.53, 89.00, 55.67, 55.60, 17.09, 8.73; *m/z* (FAB) 582 (100%, M^+-Cl); HRMS (FAB) for $C_{26}H_{31}ClIrNO_2$ (M^+-Cl), calcd. 582.1984; found 582.1980.



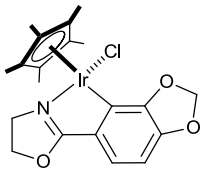
1f

Complex 1f: The compound was formed as a mixture of 2 stereoisomers in a 95:5 ratio (by ^{1}H NMR). Data is reported for the major isomer. Data was recorded at 298 K leading to broadening of the *p*-anisolyl resonances and lower than expected integrals. Yellow solid; yield 30 mg, 94% combined; m.p. >250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.0 Hz, 1H) 6.92 (s, br 2.2 H, corresponds to 4 protons), 6.56 (d, *J* = 8.0 Hz, 1H), 6.06 (d, *J* = 1.5 Hz, 1H), 5.99 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 2.35 (s, 3H), 1.48 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 181.44, 158.19, 157.84, 155.29, 151.03, 148.16, 144.44, 135.41, 124.34, 119.63, 113.53 (1 resonance was not observed), 89.00, 55.67, 55.60, 17.09, 8.73; *m/z* (ES^+) 596 (100%, M-Cl); HRMS (FAB) for $C_{26}H_{29}IrNO_3$ (M^+-Cl); calcd. 596.1772; found 596.1765.



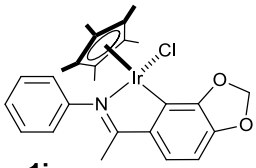
1g

Complex 1g: The reaction was performed at 80 ^{o}C in a sealed vessel. The compound was formed as a mixture of 2 stereoisomers in an 85:15 ratio (by ^{1}H NMR). Data is reported for the major isomer. Yellow solid; yield 24.5 mg, 87% combined; m.p. >250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 6.0, 1.0, 0.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 (td, *J* = 8.0, 1.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 6.99 (td, *J* = 6.0, 1.5 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.03 (d, *J* = 1.5 Hz, 1H), 5.98 (d, *J* = 1.5 Hz, 1H), 1.72 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.99, 151.39, 151.25, 147.83, 139.73, 138.87, 136.97, 121.59, 119.85, 118.88, 103.55, 99.42, 89.17, 9.41; *m/z* (FAB) 561 (100%, M^+); HRMS (FAB) for $C_{22}H_{23}IrClNO_2$ (M^+) calcd. 561.1033; found 561.1024.



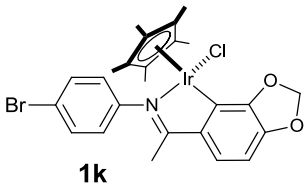
1h

Complex 1h: The compound was formed as a mixture of 2 stereoisomers in a 90:10 ratio (by ^{1}H NMR). Data is reported for the major isomer. Yellow solid; yield 19.7 mg, 71% combined; m.p. >250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.96 (d, *J* = 1.5 Hz, 1H), 4.78 (td, *J* = 8.5, 1.0 Hz, 2H), 4.06 (m, 1H), 3.94 (m, 1H), 1.82 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 179.59, 151.39, 149.00, 138.17, 125.88, 122.88, 103.45, 99.44, 88.17, 71.23, 50.19, 9.82; elemental analysis for $C_{20}H_{23}ClIrNO_3 \cdot 0.5H_2O$, calcd. C 42.74, H 4.30, N 2.49; found C 42.95, H 4.18, N 2.37.



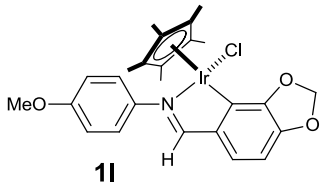
1j

Complex 1j: The compound was formed as a mixture of 2 stereoisomers in a 95:5 ratio (by ^{1}H NMR). Data is reported for the major isomer. Data was recorded at 298 K leading to broadening of the phenyl resonances and lower than expected integrals. Yellow solid; yield 25.6 mg, 85% combined; m.p. >250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, br, 1H), 7.42 (s, br, 3H), 7.20 (m, 1H overlapped with residual $CHCL_3$), 6.87 (s, br, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 6.00 (s, 1H), 2.37 (s, 3H), 1.47 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.91, 150.78, 149.99, 149.02, 143.02, 142.94, 125.82, 119.65, 103.17, 99.63 (two resonances were not observed), 89.75, 17.45, 9.02; elemental analysis for $C_{25}H_{27}ClIrNO_2$, calcd. C 49.95, H 4.53, N 2.33; found C 50.01, H 4.60, N 2.10.



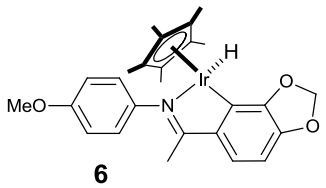
1k

Complex 1k: The compound was formed as a mixture of 2 stereoisomers in a 95:5 ratio (by ^{1}H NMR). Data is reported for the major isomer. Data was recorded at 298 K leading to broadening of the resonances corresponding to one set of 2 protons on the *p*-bromophenyl group. Yellow solid; yield 26 mg, 77% combined; m.p. >250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, br, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.76 (s, br, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 6.01 (s, 1H), 2.37 (s, 3H), 1.48 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.44, 151.02, 150.75, 148.79, 143.34, 142.69, 126.28, 125.46, 102.99, 99.56, (two resonances were not observed), 89.70, 17.45, 8.94; elemental analysis for $C_{25}H_{26}BrClIrNO_2 \cdot H_2O$, calcd. C 43.01, H 4.04, N 2.01; found C 42.53, H 4.15, N 2.05.



1l

Complex 1l: The compound was formed as a mixture of 2 stereoisomers in a 95:5 ratio (by ^{1}H NMR). Data is reported for the major isomer. Orange solid; yield 24 mg, 24% combined; m.p. >250 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 6.01 (d, *J* = 1.5 Hz, 1H), 3.84 (s, 3H), 1.53 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.84, 158.57, 151.08, 149.15, 145.50, 143.35, 142.82, 126.54, 123.66, 114.04, 103.65, 99.70, 89.55, 55.67, 9.20; elemental analysis for $C_{25}H_{27}ClIrNO_3{\cdot}CH_2Cl_2$, calcd. C 44.48, H 4.16, N 2.00; found C 44.27, H 4.16, N 1.87.



6

Complex 6: A solution of **1f** (6.6 mg, 1x10^{-2} mmol) in freshly distilled CH_2Cl_2 (2 mL) was added to a thick walled glass tube fitted with a J. Young type Teflon® cap. The solution was degassed by three freeze-pump-thaw cycles and placed under a dry N_2 atmosphere. A solution of NaOOCH (6.8 mg, 10 eq., 0.1 mmol) and a minimum quantity of TBA$^{\cdot}$OOCH (<0.5 mg) in deionised water (2 mL) was prepared and similarly degassed and placed under a dry N_2 atmosphere. The aqueous solution was added to the solution of **1** by cannulla and the vessel sealed under N_2 and stirred vigorously at room temperature. After 18 h the aqueous layer was removed by syringe and the organic layer washed with degassed water (5x3 mL) under N_2. The organic layer was evaporated *in vacuo* to give a moderately air sensitive bright yellow solid (6.0 mg, 99%). Complex **6** was formed as two regioisomers in a 95:5 ratio (by ^{1}H NMR), due to the starting compound **1f** existing as a mixture of regioisomers in the same ratio. Data is given for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 1H), 6.99 (s, br, 4H) 6.53 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 5.88 (s, 1H), 3.81 (s, 3H), 2.22 (s, 3H), 1.67 (s, 15H), -15.76 (s, 1H). Unfortunately satisfactory elemental analyses could not be obtained for compound **6** and its instability in air for

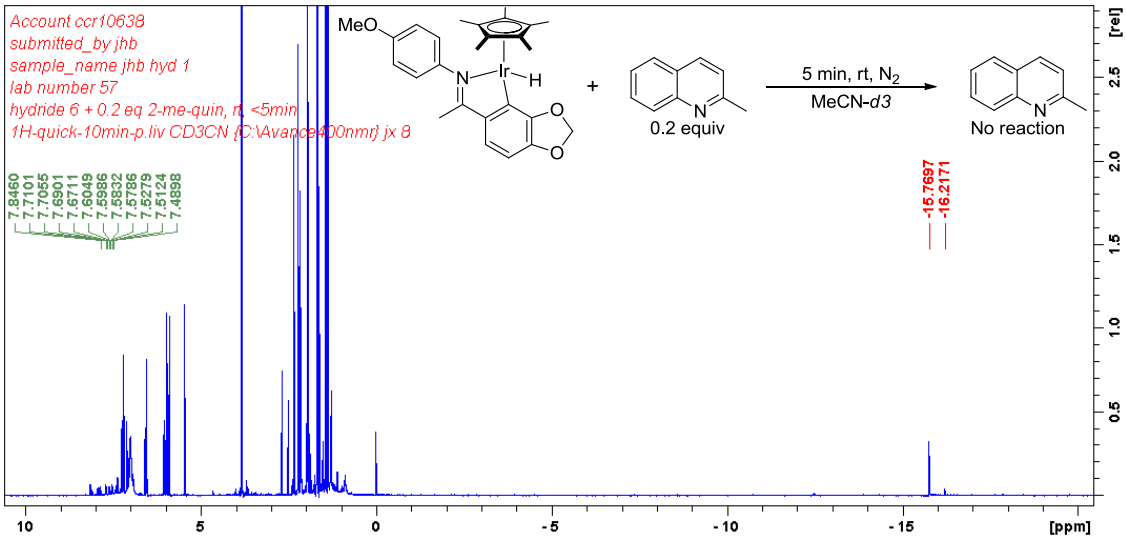
prolonged manipulation prevented further purification in addition to that described above. Thus **6** was used in its semi-crude form for subsequent reactions.

S1.4 Reactions of 6

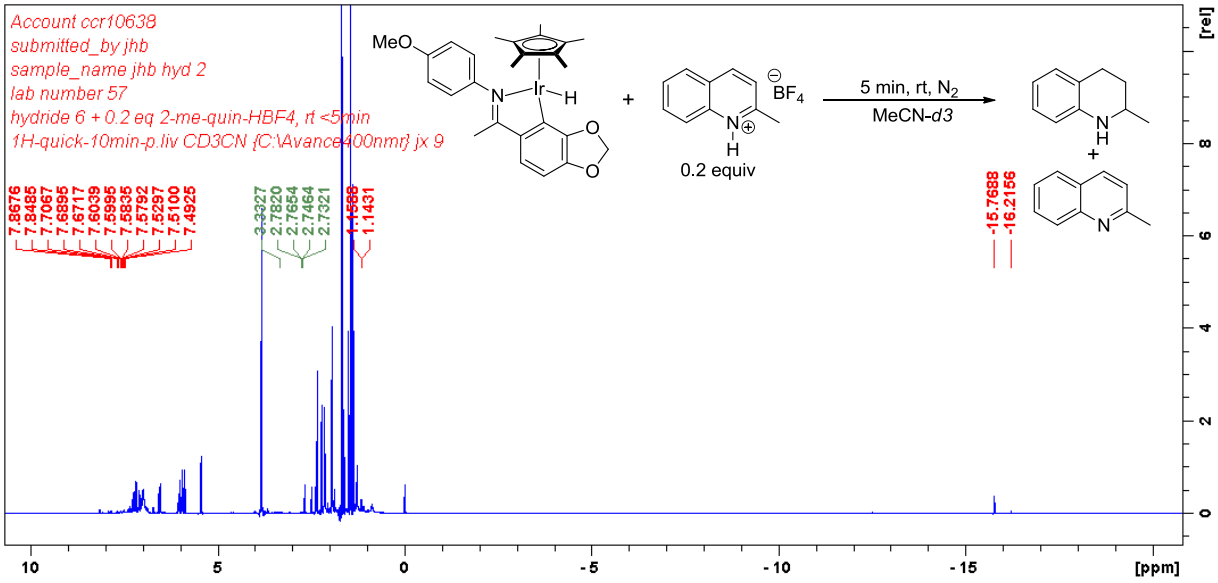
Reaction of iridium hydride 6 with 2-methylquinoline. In a dry, N_2 filled glovebox, a solution of **6** (8 mg, 13 µmol) in MeCN-*d3* (0.7 mL) was prepared and added to a vial containing 2-methylquinoline (0.2 eq.). The solution was transferred to an NMR tube fitted with a J. Young type Teflon® cap, the tube sealed, removed from the glovebox and analysed immediately by NMR spectroscopy.

Reaction of iridium hydride 6 with 2-methylquinolinium tetrafluoroborate. In a dry, N_2 filled glovebox, a solution of **6** (8 mg, 13 µmol) in MeCN-*d3* (0.7 mL) was prepared and added to a vial containing 2-methylquinolinium tetrafluoroborate (0.2 eq.). A slight color change from orange/yellow to yellow was observed. The solution was transferred to an NMR tube fitted with a J. Young type Teflon® cap, the tube sealed, removed from the glovebox and analysed immediately by NMR spectroscopy.

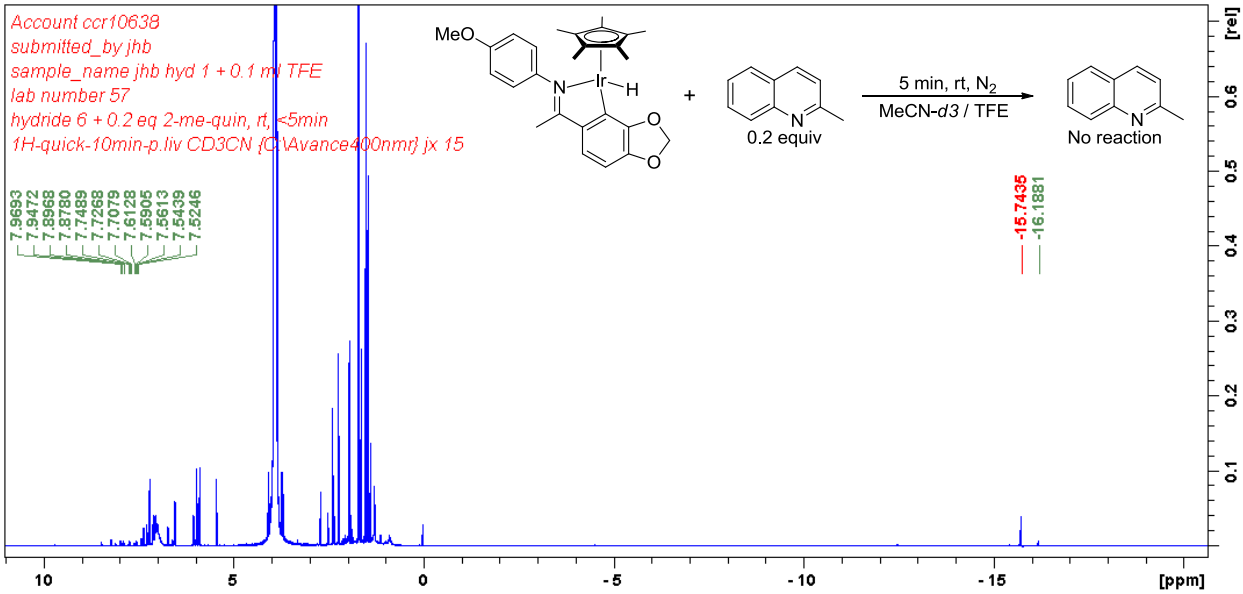
The above reactions were also repeated the presence of 0.1 mL of TFE.



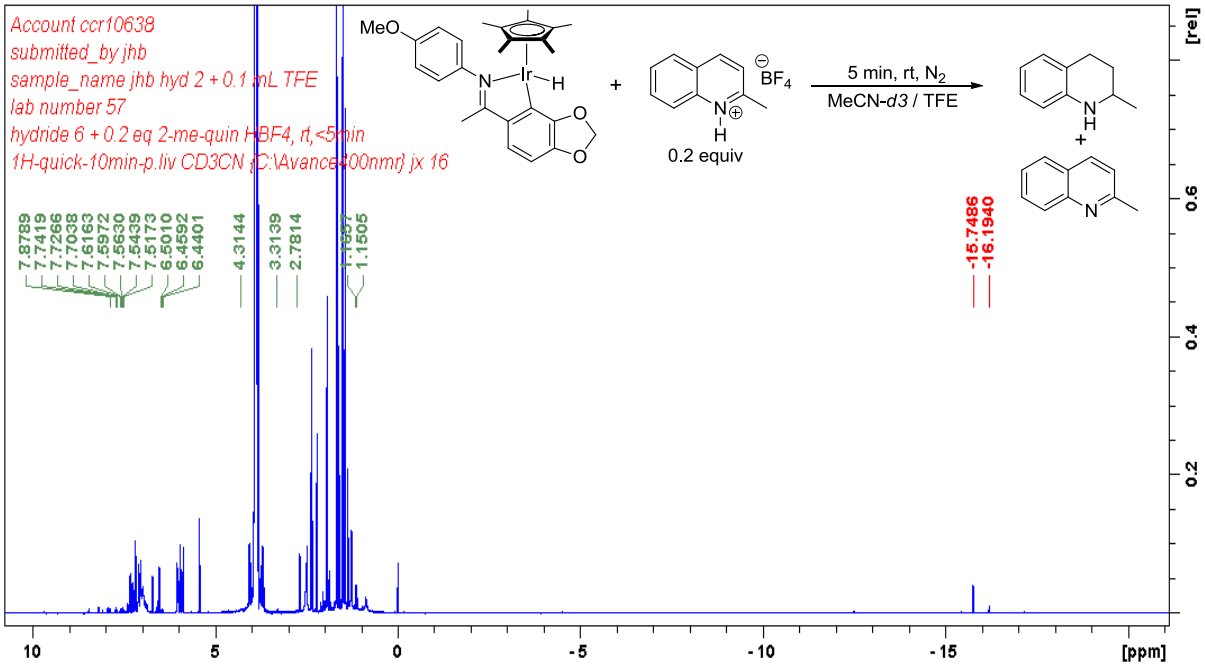
^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of the reaction of 2-methylquinoline with 5 equivalents of hydride **6** in MeCN-*d3* after *ca* 5 minutes at room temperature. No reaction has occurred.



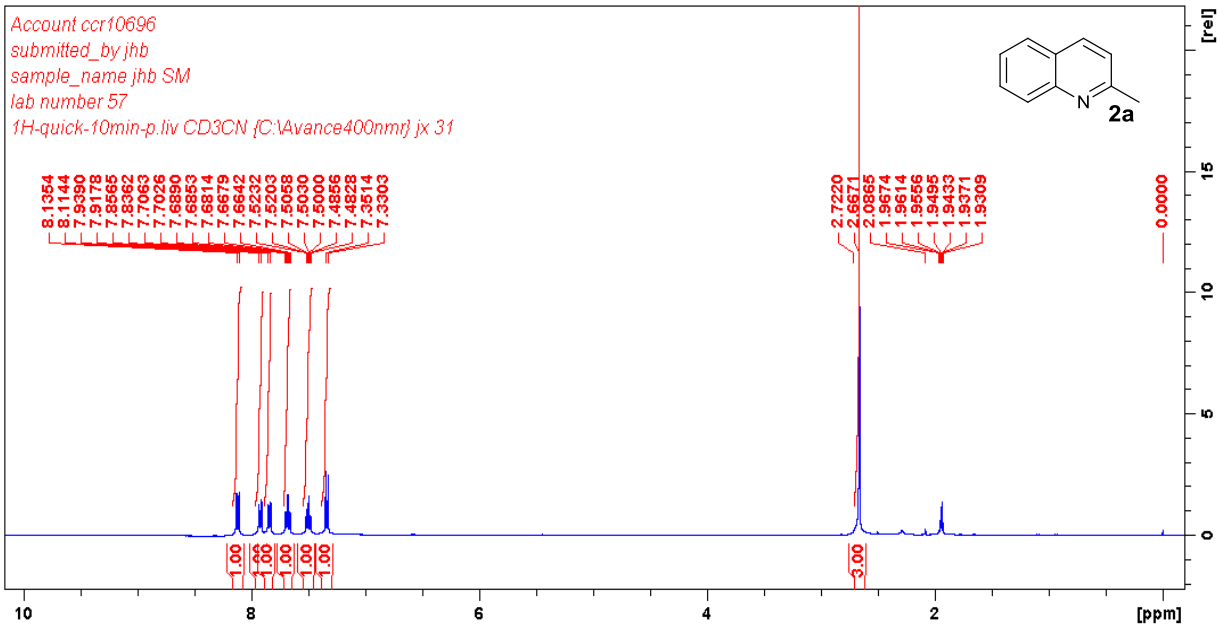
^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of the reaction of 2-methylquinolinium tetrafluoroborate with 5 equivalents of hydride **6** in MeCN-*d3* after *ca* 5 minutes at room temperature. Partial reaction (~50% conversion) has occurred giving a mixture of 2-methylquinoline and 1,2,3,4-tetrahydro-2-methylquinoline.



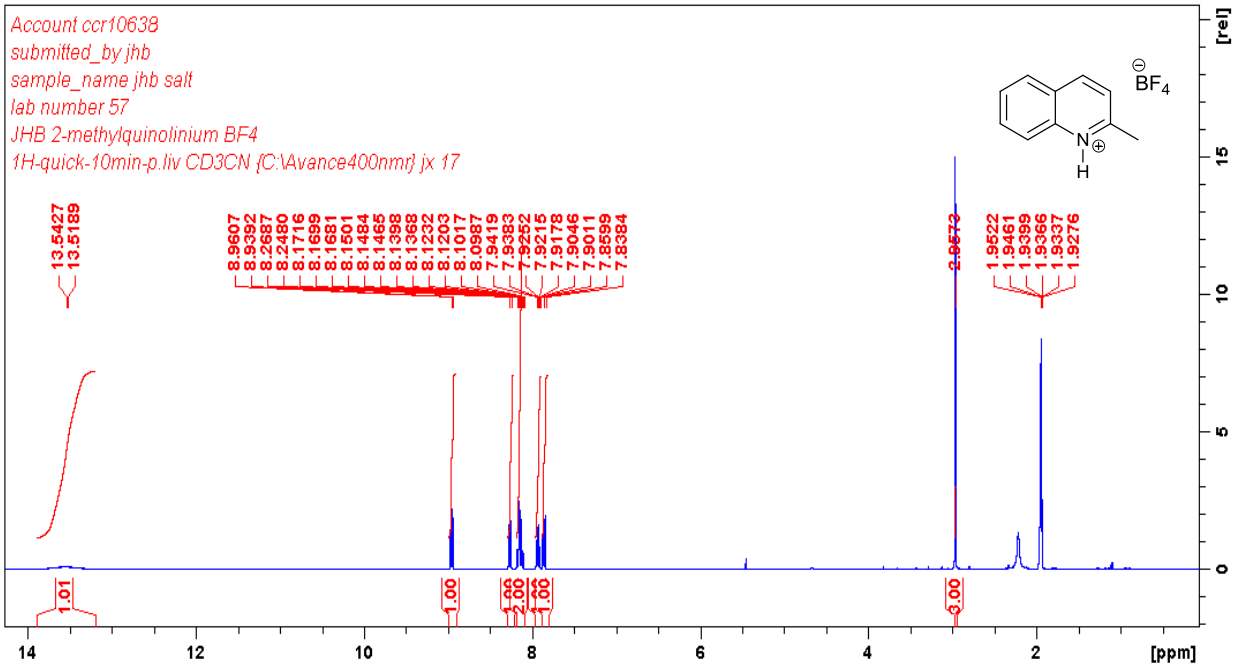
^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of the reaction of 2-methylquinoline with 5 equivalents of hydride **6** and 0.1 mL TFE in MeCN-*d3* after *ca* 5 minutes at room temperature. No reaction has occurred.



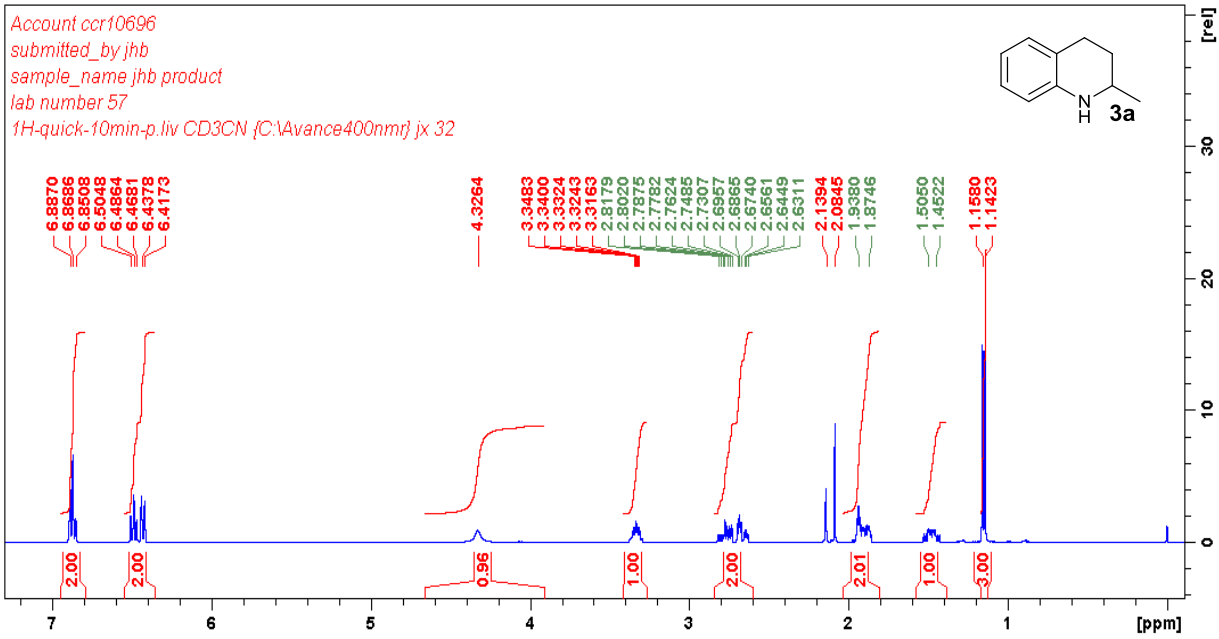
^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of the reaction of 2-methylquinolinium tetrafluoroborate with 5 equivalents of hydride **6** and 0.1 mL TFE in MeCN-*d3* after *ca* 5 minutes at room temperature. Partial reaction (~50% conversion) has occurred giving a mixture of 2-methylquinoline and 1,2,3,4-tetrahydro-2-methylquinoline.



^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of 2-methylquinoline **2a**



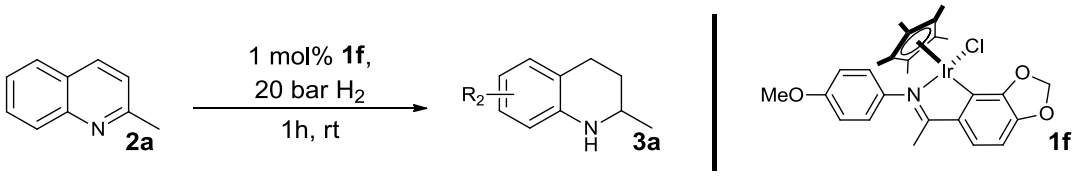
^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of 2-methylquinolinium tetrafluoroborate.



^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of 1,2,3,4-tetrahydro-2-methylquinoline **3a**.

S1.5 Hydrogenation of 2-methylquinoline in varying solvents at 20 bar H_2 pressure

Table S1

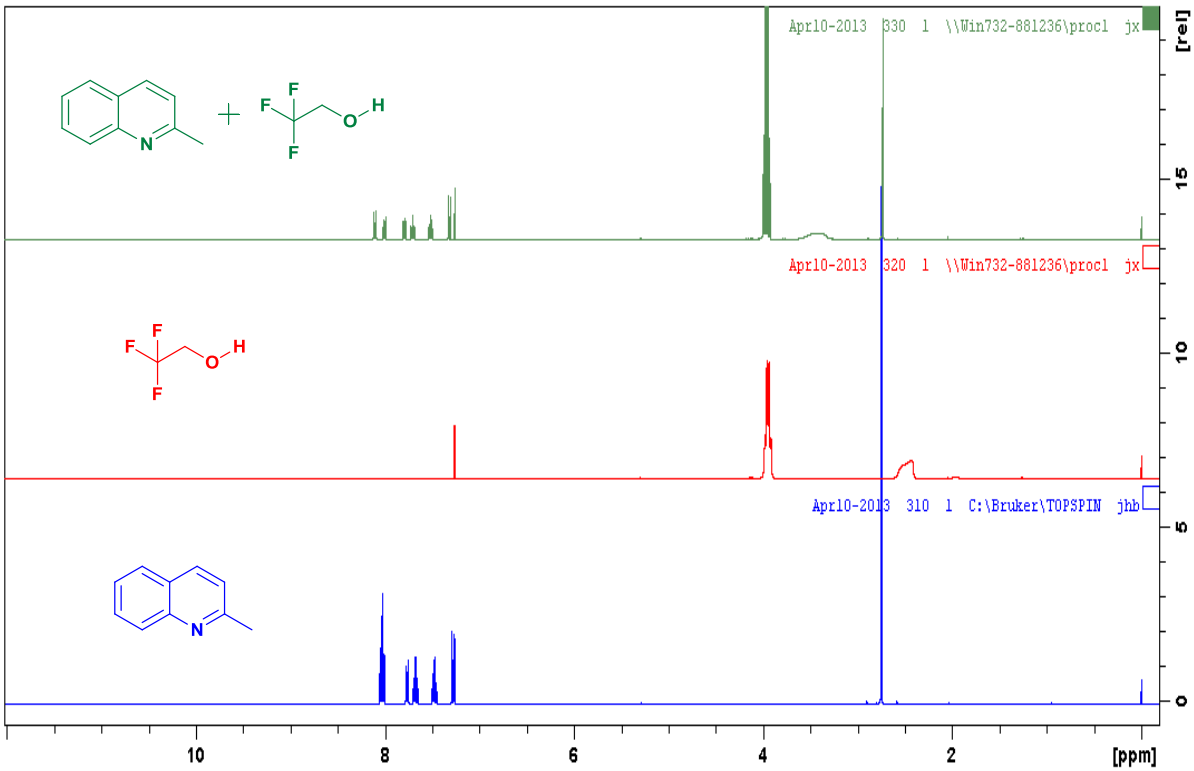


Entry[a]	Solvent	Solvent p*Ka*[b]	Conversion(%)[c]
1	TFE	12.5	83
2	MeOH	15.5	5
3	EtOH	15.8	1
4	^{i}PrOH	16.5	0
5	THF	-	0
6	DCM	-	0
7	EtOAc	-	0
8	H_2O	15.7	0
9	Toluene	41	0

[a]Conditions: 2-methylquinoline (0.5 mmol), complex **1f** (1 mol%), solvent (3 mL), 20 bar H_2, rt, 1h, stirred at 1300 rpm. [b]p*K*a data from http://evans.harvard.edu/pdf/evans_pka_table.pdf. [c]Conversion determined by ^{1}H NMR of the crude reaction mixture and normalising the sum of the product and starting material integrals to 100%.

Although complex **1f** is not soluble in toluene on its own, it was found that the mixture of **1f** (3.3 mg) and 2-methylquinoline (71 mg) dissolved completely in all the organic solvent examined to give bright yellow, clear solutions. In H_2O the catalyst dissolved in the substrate 2-methylquinoline which subsequently formed a suspension in water. Thus, the reaction with H_2O as solvent (Table S1, entry 8) is best described as 'on water.' To ensure accurate comparison the reactions were performed simultaneously in glass vials within a larger autoclave. This allowed slight differences in temperature, time and H_2 pressure to be eliminated. The vessel was pressurized with H_2 and then depressurized 3 times before being subsequent pressurized to 20 bar and stirred. After 1 hour the H_2 pressure was released and the reactions concentrated *in vacuo* before being analyzed by ^{1}H NMR spectroscopy to determine the percentage conversion.

S1.6 Hydrogen bonding between 2,2,2-trifluoroethanol (TFE) and 2-methylquinoline



Superimposed ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 2-methylquinoline (bottom, 1 drop, blue), TFE (middle, 1 drop, red), and 2-methylquinoline and TFE (top, 1 drop each, green). As shown above, the OH proton of TFE hydrogen bonds to 2-methylquinoline, resulting in a change of its ^{1}H NMR shift from 2.5 ppm to 3.5 ppm.

S1.7 Typical procedure for the hydrogenation reactions

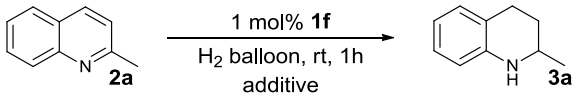
In a fume hood in air, a solution of the substrate was prepared by adding 3 mL of pre-prepared stock solution of **1f** in unpurified 2,2,2-trifluoroethanol (typically 1.66 M, 0.005 mmol in 3 mL) to a vial containing the substrate. Reactions were typically performed on a 0.5 mmol scale in 3 mL of solvent. The mixture was transferred into a N_2-filled carousel tube and the tube sealed. A H_2-filled party balloon attached to a length of rubber tubing and a hypodermic needle was connected to the reaction by inserting the needle through the septum of the carousel tube. The reaction was stirred at the described temperature for the appropriate period of time. The hydrogen was then released in the fume hood and the solution was concentrated *in vacuo* and analysed by ^{1}H NMR spectroscopy to give the percentage conversion. The reaction mixture was then purified by silica gel chromatography to give the analytically pure product.

Figure S1 The reduction of 0.5 mmol quinoxaline **4a** (see main text, Table 3, entry 1) by 1 mol% **1f** at ambient temperature.

S1.8 Inhibition of the 1f-catalysed hydrogenation of 2-methylquinoline by chloride ions or triphenylphosphine

Reductions of 2-methylquinoline (0.5 mmol scale) were performed as described above in S1.7 with 1 mol% of the catalyst, in the presence or absence (control experiment, entry 1) of 10 mol% tetra-*n*-butylammonium chloride (13.9 mg, 0.05 mmol, 10 equivalents w.r.t. catalyst **1f**), 100% NaCl (29.2 mg, 0.5 mmol, 100 equivalents w.r.t. catalyst **1f**) or 1% PPh_3 (1.3 mg, 0.005 mmol, 1 equivalent w.r.t. catalyst **1f**). The reactions were analyzed by ^{1}H NMR spectroscopy after 1 h.

Table S2



Entry[a]	Solvent	Additive	Conversion (%)[b]
1	TFE	none	91
2	TFE	10% TBACl	15
3	TFE	100% NaCl	48
4	TFE	1% PPh_3	0
5	MeOH[c]	1% $AgSbF_6$	0
6	MeOH[c,d]	2% $NaBAr^F{}_4$	0

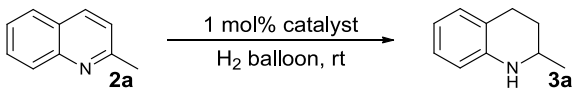
[a]Conditions: **2a** (0.5 mmol), catalyst (1 mol%), TFE (3 mL), rt, 1h, H_2 balloon. [b]Conversion determined by ^{1}H NMR of the crude reaction mixture and normalising the sum of the product and starting material integrals to 100%. [c]Dry, degassed solvent was used. [d]Reaction was prepared in an N_2 filled glovebox.

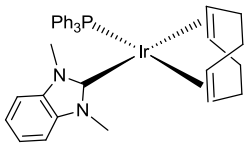
It is important to note that NaCl is poorly soluble in TFE so the amount of dissolved chloride ions is considerably less than the amount of NaCl used in entry 3. For entries 5 and 6, **1f** and the additive were stirred in 1 mL dry, degassed MeOH under N_2 for 30 minutes in the reaction vessel before the substrate in 2 mL of dry MeOH was added by syring *via* the septa. For entry 5, the formation of AgCl was observed as a white precipitate. The reactions were then stirred under H_2 as normally.

S1.9 Comparison of 1f with other catalysts[S9]

Reductions of 2-methylquinoline (0.5 mmol scale) were performed as described above in S1.7 (unless otherwise stated) with 1 mol% of the catalyst (1 mol% metal). The reactions were performed in the solvent that was previously suggested to be most effective in the literature. All solvents were dried and degassed apart from TFE which was used unpurified, without degassing. Super-stoichiometric amounts of Brønsted acids, often used as co-solvents for heterogeneous quinoline hydrogenations, were not employed. For entries 7-9, the additive required for activity (PPh_3 or I_2) was used in the reactions. For entries 5-9, the reactions were prepared in a dry, N_2 filled glovebox. For entry 7, the catalyst was prepared using a literature method.[S9a]

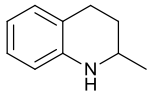
Table S3



Entry[a]	Catalyst	Solvent	Time (h)	Conversion (%)[b]
1	**1f**	TFE	1	91
2	Pd/C (10%)	MeOH[c]	3	5 (0 in TFE)
3	Rh/C (5%)	MeOH[c]	3	7 (4 in TFE)
4	PtO_2	MeOH[c]	3	4 (0 in TFE)
5	$Rh(PPh_3)_3Cl$	MeOH[c]	3	0 (0 in TFE)
6	$[Ir(Py)(PCy_3)(COD)][PF]_6$	DCM[c]	3	0 (0 in TFE)
7[d]	 + 1% PPh_3	Toluene[c]	1	7
8	$[Ru(p\text{-cymene})Cl_2]_2$ / 5% I_2	THF[c]	1	0
9	$[IrCl(COD)]_2$ /P-Phos / 5% I_2	THF[c]	1	15

[a]Conditions: **2a** (0.5 mmol), catalyst (1 mol%), solvent (3 mL), rt, H_2 balloon. [b]Conversion determined by ^{1}H NMR of the crude reaction mixture and normalising the sum of the product and starting material integrals to 100%. [c]Dry, degassed solvent was used. [d]Reaction was prepared in an N_2 filled glovebox.

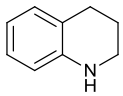
S2 Analytical data for the hydrogenation products[S10]



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

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

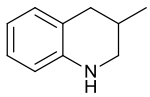
Clear oil; yield 70.5 mg, 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-6.96 (m, 2H), 6.62 (td, *J* = 7.5, 1.0 Hz, 1H), 6.49 (dd, *J* = 8.5, 1.0 Hz, 1H), 3.71 (s, br, 1H), 3.42 (m, 1H), 2.85 (m, 1H), 2.77 (m, 1H), 1.95 (m, 1H), 1.60 (m, 1H), 1.22 (d, *J* = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.87, 129.39, 126.81, 121.24, 117.11, 114.13, 47.28, 30.25, 26.72, 22.73; *m/z* (CI^+) 148 (100%, MH^+).



1,2,3,4-Tetrahydroquinoline (3b)

Known compound, see: G. Erős *et al.*, *Chem. Eur. J.* 2012, **18**, 574.

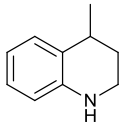
Clear oil; yield 63 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (m, 2H), 6.70 (m, 1H), 6.54 (d, *J* = 7.0 Hz, 1H), 3.78 (s, br, 1H), 3.35 (m, 2H), 2.84 (m, 2H), 2.02 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.78, 129.53, 126.74, 121.44, 116.94, 114.23, 41.99, 27.00, 22.18; *m/z* (CI^+) 134 (100%, MH^+).



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

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

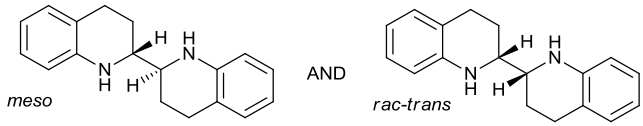
Clear oil; yield 71.3 mg, 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (m, 2H), 6.65 (td, *J* = 7.5, 1.0 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.81 (s, br, 1H), 3.30 (ddd, *J* = 11.0 4.0, 2.0 Hz, 1H), 2.92 (t, *J* = 10.0 Hz, 1H), 2.81 (ddd, *J* = 16.0, 5.0, 2.0 Hz, 1H), 2.47 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.10 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.34, 129.63, 126.79, 121.23, 117.04, 113.99, 48.93, 35.56, 27.27, 19.15; *m/z* (CI^+) 148 (100%, MH^+).



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

Known compound, see: D. Ren *et al.*, *J. Am. Chem. Soc.* 2012, **134**, 17592.

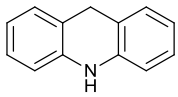
Clear oil; yield 72 mg, 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.5 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.64 (td, *J* = 7.5, 1.0 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.30 (m, 2H), 2.92 (m, 1H), 2.00 (m, 1H), 1.69 (m, 1H) 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.21, 128.58, 126.85, 126.82, 117.18, 114.37, one resonance was not observed, 39.13, 30.32, 29.95, 22.77; *m/z* (CI$^+$) 148 (100%, MH$^+$).



1,1',2,2',3,3',4,4'-Octahydro-2,2'-biquinoline (3e)

Known compound, see: K. Vehlow *et al.*, *Angew. Chem. Int. Ed.* 2007, **46**, 8082.

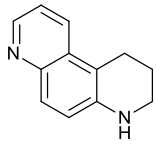
White solid; combined yield 128.3 mg, 97%; meso:racemic = 4.2:1, determined by NMR analysis. Data for the *meso* compound**;** m.p. 139-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-7.02 (m, 4H), 6.69 (td, *J* = 7.5, 1.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.00 (br, 2H), 3.48-3.44 (m, 2H), 2.92-2.80 (m, 4H), 2.02-1.90 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.79, 129.30, 126.99, 121.52, 117.42, 114.35, 55.37, 26.68, 23.12; *m/z* (CI$^+$) 265 (100%, MH$^+$).



9,10-Dihydroacridine (3f)

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

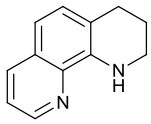
White solid; yield 89.6 mg, 99%; m.p. 169-70 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.07 (m, 4H), 6.87 (td, *J* = 7.5, 1.0 Hz, 2H), 6.67 (d, *J* = 7.5 Hz, 2H), 5.96 (s, br, 1H), 4.07 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.24, 128.73, 127.12, 120.76, 120.16, 113.56, 31.50; *m/z* (CI$^+$) 182 (100%, MH$^+$).



1,2,3,4-Tetrahydro-4,7-phenanthroline (3g)

Known compound, see: P. C. Keller *et al.*, *Polyhedron* 1983, **2**, 595.

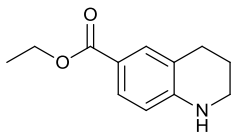
Pale oil; yield 84.2 mg, 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.0, 1.5 Hz, 1H) 8.03 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.28 (q, *J* = 8.5, 4.0 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 4.13 (s, br, 1H), 3.35 (t, *J* = 5.5 Hz, 2H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.10-2.04 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.45, 143.39, 142.40, 129.43, 128.70, 128.34, 121.77, 121.08, 110.62, 41.59, 22.27, 21.83; *m/z* (CI^+) 182 (100%, MH^+).



1,2,3,4-Tetrahydro-1,10-phenanthroline (3h)

Known compound, see: C. Metallinos *et al.*, *Org. Lett.* 2004, **6**, 3641.

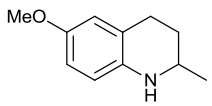
Pale oil; yield 72.4 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29 (q, *J* = 8.0, 4.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.95 (s, br, 1H), 3.53 (m, 2H), 2.93 (t, *J* = 6.5 Hz, 2H), 2.07 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.03, 140.77, 137.59, 135.93, 129.14, 127.44, 120.62, 116.62, 113.17, 41.35, 27.12, 21.90; *m/z* (CI^+) 182 (100%, MH^+).



Ethyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (3i)

Known compound, see: I. N. Gracheva *et al.*, *Chem. Heterocycl. Comp.*1988, **1**, 77.

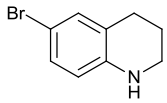
White solid; yield 99.4 mg, 97%; m.p. 80-82 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, 2H), 6.39 (d, *J* = 9.0 Hz, 1H), 4.29 (m, 3H overlapped), 3.35 (t, *J* = 5.5 Hz, 2H), 2.77 (t, *J* = 5.5 Hz, 2H), 1.92 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.20, 148.80, 131.36, 129.20, 119.99, 117.93, 112.72, 60.19, 41.84, 27.02, 21.56, 14.60; *m/z* (CI^+) 206 (100%, MH^+).



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

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

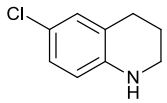
Clear oil; yield 81.4 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61-6.58 (m, overlapped, 2H), 6.46 (d, *J* = 8.5 Hz, 1H), 3.73 (s, 3H), 3.60-3.00, (s, br) overlapped with 3.50-3.30 (m, 1H), 2.90-2.81 (m, 1H), 2.74-2.69 (m, 1H), 1.94-1.89 (m, 1H), 1.64-1.55 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.05, 138.87, 122.73, 115.54, 114.75, 112.97, 55.92, 47.64, 30.40, 27.02, 22.64; *m/z* (CI^+) 178 (100%, MH^+).



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

Known compound, see: G. E. Dobereiner *et al.*, *J. Am. Chem. Soc.* 2011, **133**, 7547.

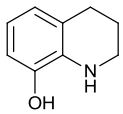
Clear oil; yield 102.3 mg, 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (m, 2H), 6.34 (d, *J* = 8.5 Hz, 1H), 3.84 (s, br, 1H), 3.29 (t, *J* = 5.5 Hz, 2H), 2.72 (t, *J* = 5.5 Hz, 2H), 1.91 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.83, 131.95, 129.44, 123.48, 115.61, 108.26, 41.88, 26.93, 21.77; *m/z* (CI^+) 212 (100%, MH^+) 214 (95%, MH^+).



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

Known compound, see: D. Ren *et al.*, *J. Am. Chem. Soc.* 2012, **134**, 17592.

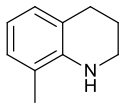
Clear oil; yield 80.2 mg, 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (m, 2H), 6.39 (d, *J* = 8.5 Hz, 1H), 3.79 (s, br, 1H), 3.28 (t, *J* = 5.5 Hz, 2H), 2.73 (t, *J* = 5.5 Hz, 2H), 1.92 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.34, 129.07, 126.54, 122.93, 121.15, 115.16, 41.90, 26.93, 21.78; *m/z* (CI^+) 168 (100%, MH^+), 170 (35%, MH^+).



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

Known compound, see: D. Ren *et al.*, *J. Am. Chem. Soc.* 2012, **134**, 17592.

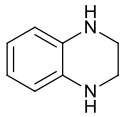
White solid; yield 73.0 mg, 98%; m.p. 117-120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60-6.53 (m, 3H), 4.78 (s, 2H), 3.31 (s, br 2H), 2.77 (s, br 2H), 1.95 (s, br 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.20, 133.54, 123.65, 122.02, 117.20, 112.53, 41.91, 26.68, 22.34; *m/z* (CI^{+}) 150 (100%, MH^{+}).



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

Known compound, see: G. Erős *et al.*, *Chem. Eur. J.* 2012, **18**, 574.

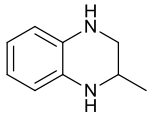
Clear oil; yield 71.3 mg, 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91-6.86 (m, 2H), 6.59 (t, *J* = 7.5 Hz, 1H), 3.76 (s, br, 1H), 3.40 (t, *J* = 5.5 Hz, 1H), 2.81 (t, *J* = 6.5 Hz, 1H), 2.10 (s, 3H), 1.96 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.70, 127.96, 127.49, 121.39, 121.06, 116.60, 42.46, 27.39, 22.24, 17.30; *m/z* (CI^{+}) 148 (100%, MH^{+}).



1,2,3,4-Tetrahydroquinoxaline (5a)

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

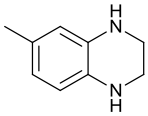
White solid; yield 64 mg, 95%; m.p. 95-97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (m, 2H), 6.50 (m, 2H), 3.52 (s, br, 2H), 3.42 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 133.67, 118.99, 114.94, 41.46; *m/z* (CI^{+}) 135 (100%, MH^{+}).



2-Methyl-1,2,3,4-tetrahydroquinoxaline (5b)

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

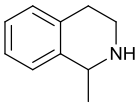
Yellow gum; yield 68 mg, 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (m, 2H), 6.53 (m, 2H), 3.63 (s, br, 2H), 3.52 (m, 1H), 3.30 (m, 1H), 3.02 (m, 1H), 1.20 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 133.58, 133.19, 118.92, 114.72, 114.67, one aromatic resonance is not observed, 48.29, 45.81, 19.92; *m/z* (CI^{+}) 149 (100%, MH^{+}).



6-Methyl-1,2,3,4-tetrahydroquinoxaline (5c)

Known compound, see: J. Wu *et al.*, *Chem. Eur. J.* 2012, **18**, 9525.

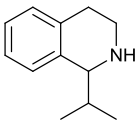
White solid; yield 70 mg, 95%; m.p. 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (m, 2H), 6.34 (s, 1H), 3.40 (s, 6H overlapped), 2.18 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 133.82, 131.07, 128.64, 119.28, 115.59, 115.19, 41.65, one resonance was not observed, 20.79; *m/z* (CI^+) 149 (100%, MH^+).



1-Methyl-1,2,3,4-tetrahydroisoquinoline (5d)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 13208.

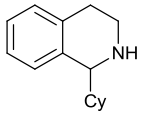
Clear oil; yield 65 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.08 (m, 4H), 4.16 (m, 1H), 3.32-3.27 (m ,1H) 3.08-3.02 (m, 1H), 2.97-2.87 (m, 1H), 2.78 (m, 2H), 1.49 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.53, 134.83, 129.36, 126.12, 126.04, one resonance was not observed, 51.68, 41.86, 30.09, 22.79; *m/z* (CI^+) 148 (100%, MH^+).



1-*iso*-Propyl-1,2,3,4-tetrahydroisoquinoline (5e)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 13208.

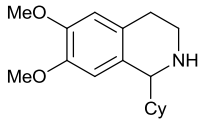
Clear oil; yield 82 mg, 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.07 (m, 4H), 3.96 (d, *J* = 3.0 Hz, 1H), 3.32-3.28 (m, 1H), 2.97-2.84 (m, 2H), 2.67 (m, 1H), 2.35 (m, 1H), 1.85 (s, br, 1H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 138.84, 136.34, 129.22, 126.02, 125.84, 125.71, 61.09, 42.61, 32.36, 30.50, 20.40, 15.83; *m/z* (CI^+) 176 (100%, MH^+).



1-Cyclohexyl-1,2,3,4-tetrahydroisoquinoline (5f)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 13208.

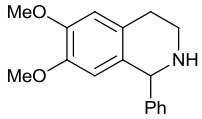
Clear oil; yield 95 mg, 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.06 (m, 4H), 3.92 (d, *J* = 3.5 Hz, 1H), 3.29 (m, 1H), 2.96-2.82 (m, 2H), 2.68 (m, 1H), 2.05-1.68 (m, 6H), 1.40-1.07 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.43, 136.28, 129.25, 126.20, 125.78, 125.74, 60.85, 43.07, 42.42, 31.03, 30.31, 27.17, 26.76, 26.68, 26.51; *m/z* (CI^+) 216 (100%, MH^+).



1-Cyclohexyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (5g)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 13208.

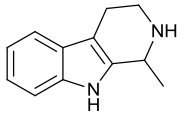
White solid; yield 125 mg, 91%; m.p. 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H), 6.55 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.25 (m, 1H), 2.92-2.85 (m, 1H), 2.78-2.71 (m, 1H), 2.60-2.55 (m, 1H), 1.84 (m, 2H), 1.70 (m, 4H), 1.39-1.12 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.16, 147.12, 130.43, 128.51, 111.79, 109.37, 60.47, 56.18, 55.89, 43.34, 42.58, 31.01, 29.95, 27.18, 26.80, 26.70, 26.46; *m/z* (CI^+) 276 (100%, MH^+).



1-Phenyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (5h)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 13208.

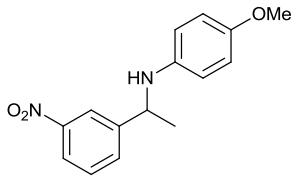
White solid; yield 121 mg, 90%; m.p. 109-111 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-26 (m, 5H), 6.64 (s, 1H), 6.24 (s, 1H), 5.07 (s, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 3.20 (m, 1H), 3.05 (m, 1H), 2.94 (m, 1H), 2.79 (m, 1H), 2.43 (s, br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.79, 147.20, 144.44, 129.48, 129.11, 128.56, 127.61, 127.59, 111.46, 110.99, 61.39, 55.96, 41.77, 29.16; *m/z* (CI^+) 270 (100%, MH^+).



1-Methyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5i)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 13208.

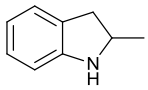
White solid; yield 79 mg, 85%; m.p. 165-170 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, br, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.16 (td, *J* = 8.0, 1.0 Hz, 1H), 7.10 (td, *J* = 8.0, 1.0 Hz, 1H), 4.19 (q, *J* = 6.5 Hz, 1H), 3.40-3.35 (m, 1H), 3.06 (m, 1H), 2.74 (m, 2H), 1.70 (s, br, 1H), 1.17 (d, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.62, 135.80, 127.50, 121.73, 119.54, 118.24, 110.92, 108.32, 48.26, 42.47, 22.44, 20.56; *m/z* (CI^+) 187 (100%, MH^+).



4-Methoxy-*N*-(1-(3-nitrophenyl)ethyl)aniline (5j)

Known compound, see: C. Li *et al.*, *J. Am. Chem. Soc.* 2008, **130**, 14450.

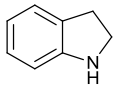
Yellow gum; yield 135 mg, 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.0 Hz, 1H), 8.08 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.43 (d, *J* = 9.0 Hz, 2H), 4.50 (m, 1H), 3.87 (s, br, 1H), 3.69 (s, 3H), 1.53 (d, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.36, 146.77, 146.21, 138.83, 130.30, 127.73, 120.15, 119.08, 112.92, 112.66, 53.78, 51.98, 23.20; *m/z* (CI^+) 273 (100%, MH^+).



2-Methylindoline (5k)

Known compound, see: A. Kulkarni *et al.*, *Org. Lett.* 2011, **13**, 5124.

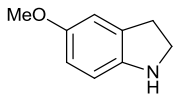
Clear oil; yield 55.2 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 4.00 (m, 1H), 3.59 (s, br, 1H), 3.15 (dd, *J* = 16.0, 8.5 Hz, 1H), 2.64 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.30 (d, *J* = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.92, 129.06, 127.34, 124.84, 118.73, 109.38, 55.35, 37.84, 22.35; *m/z* (CI^+) 134 (100%, MH^+).



Indoline (5l)

Known compound, see: A. Kulkarni *et al.*, *Org. Lett.* 2011, **13**, 5124.

Clear oil; yield 46.4 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.73 (td, *J* = 7.5, 1.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 3.73(s, br, 1H), 3.56 (t, *J* = 8.5 Hz, 2H), 3.05 (t, *J* = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.69, 129.40, 127.29, 124.72, 118.73, 109.53, 47.42, 29.93; *m/z* (CI^+) 120 (100%, MH^+).



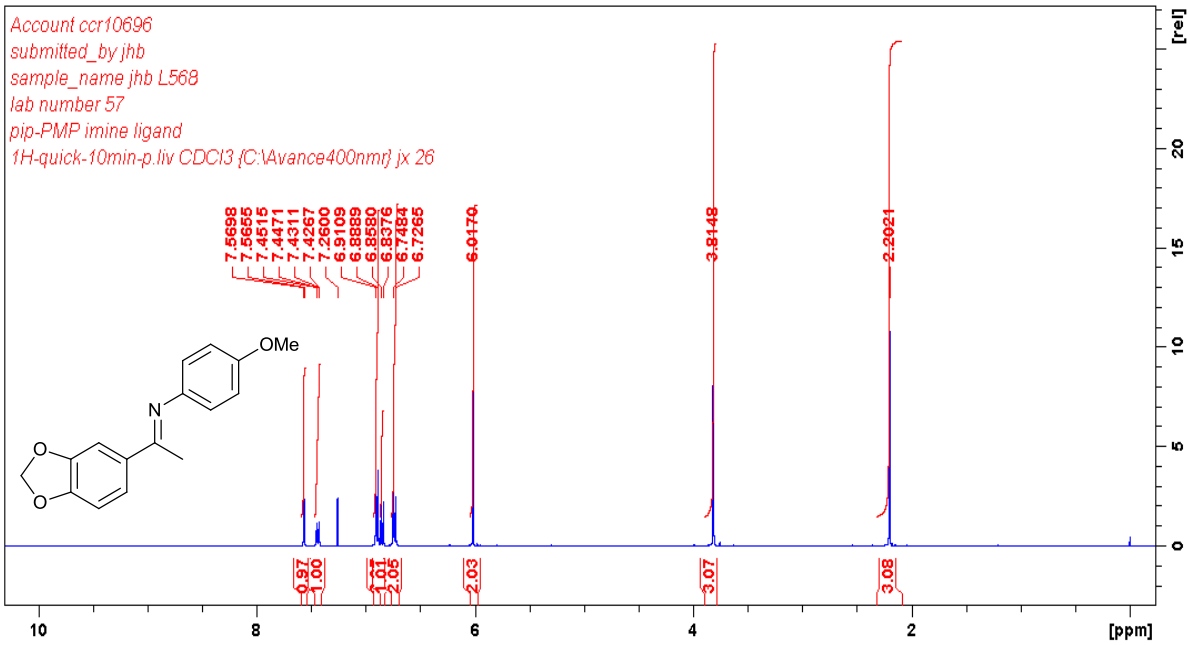
5-Methoxyindoline (5m)

Known compound, see: A. Kulkarni *et al.*, *Org. Lett.* 2011, **13**, 5124.

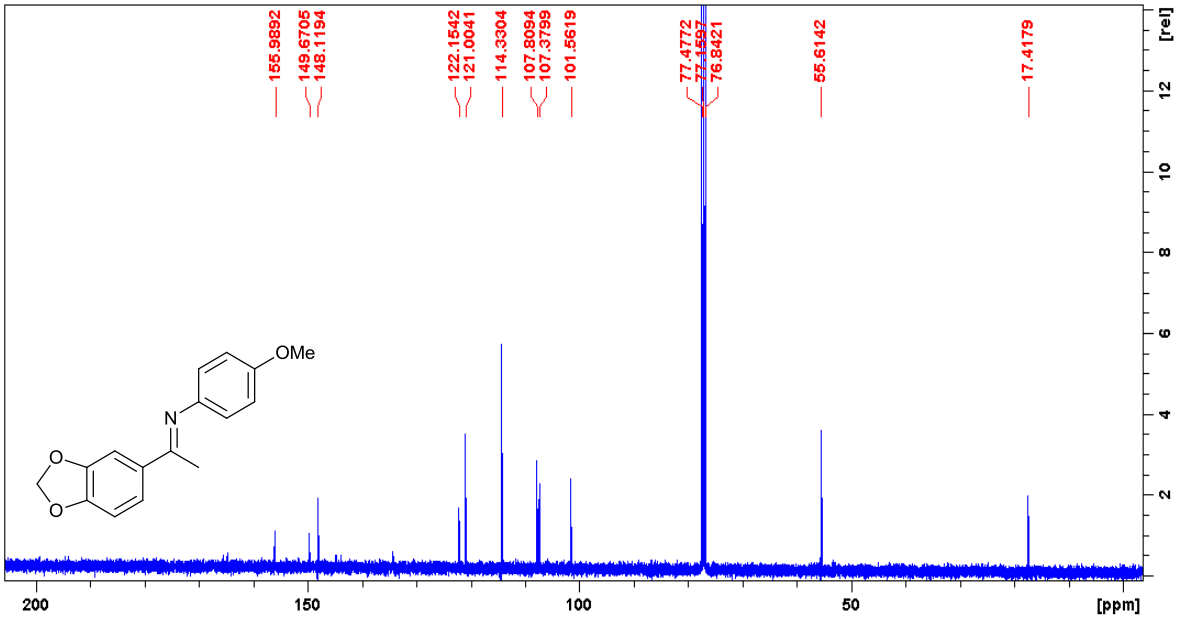
Clear oil; yield 70.8 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 1H), 6.60 (m, 2H), 3.75 (s, 3H), 3.53 (t, *J* = 8.5 Hz, 2H), 3.45 (s, br, 1H), 3.01 (t, *J* = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.62, 145.34, 131.26, 112.18, 111.61, 110.22, 56.03, 47.86, 30.53; *m/z* (CI^+) 150 (100%, MH^+).

3. NMR spectra

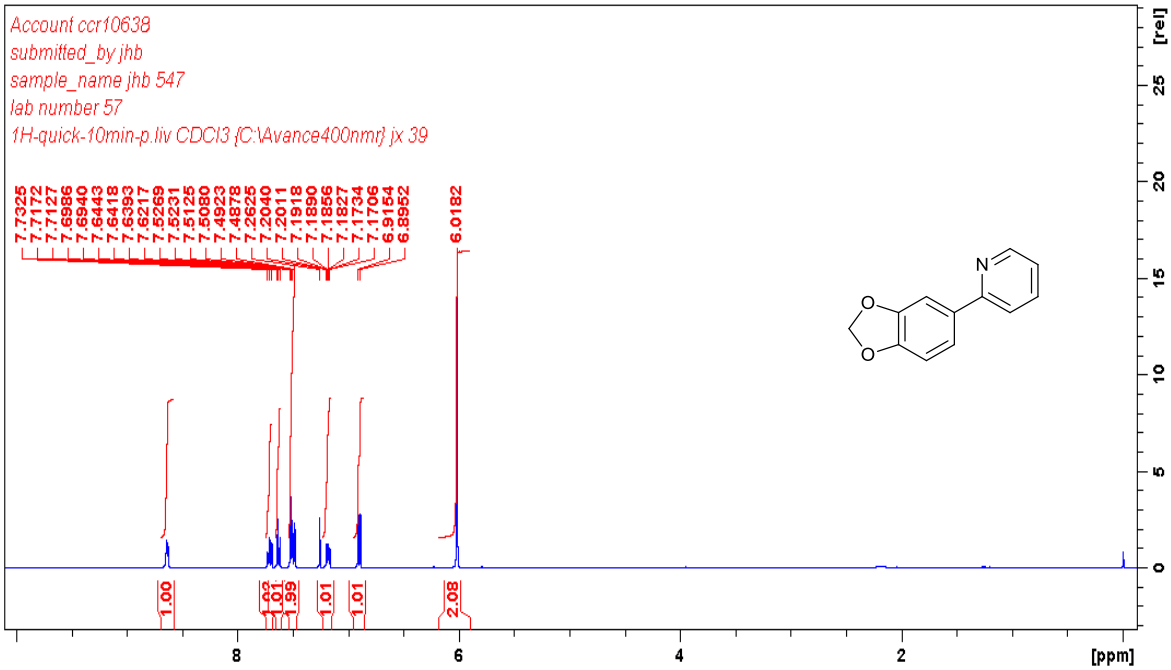
3.1 NMR spectra of ligands



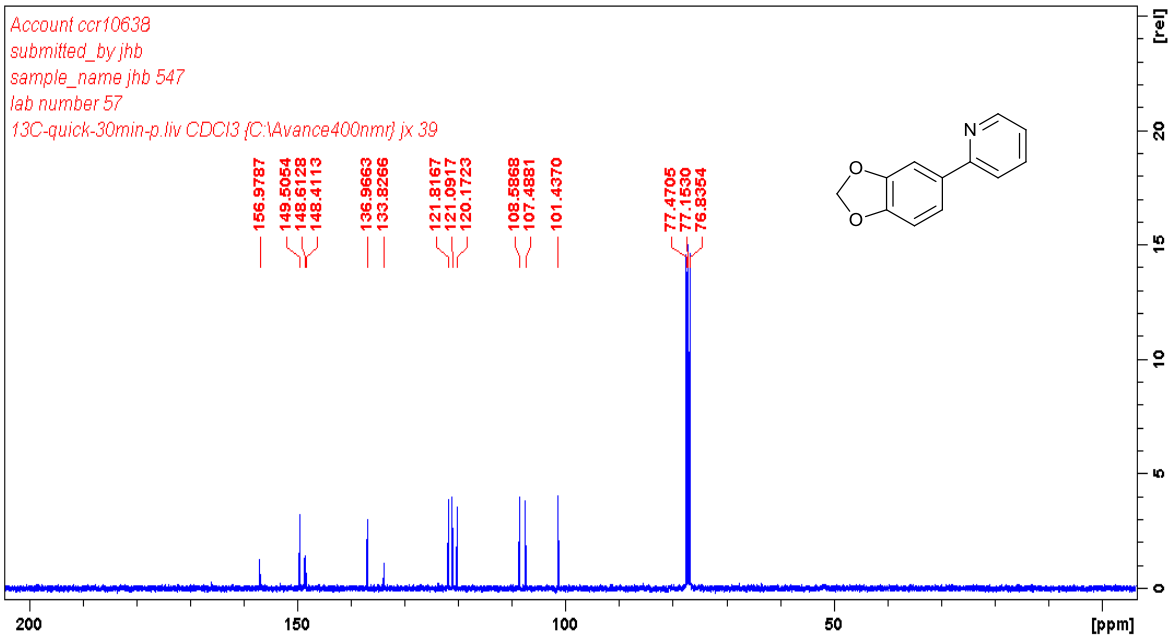
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*E*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl) ethylidene) -4-methoxyaniline (**L1f**).



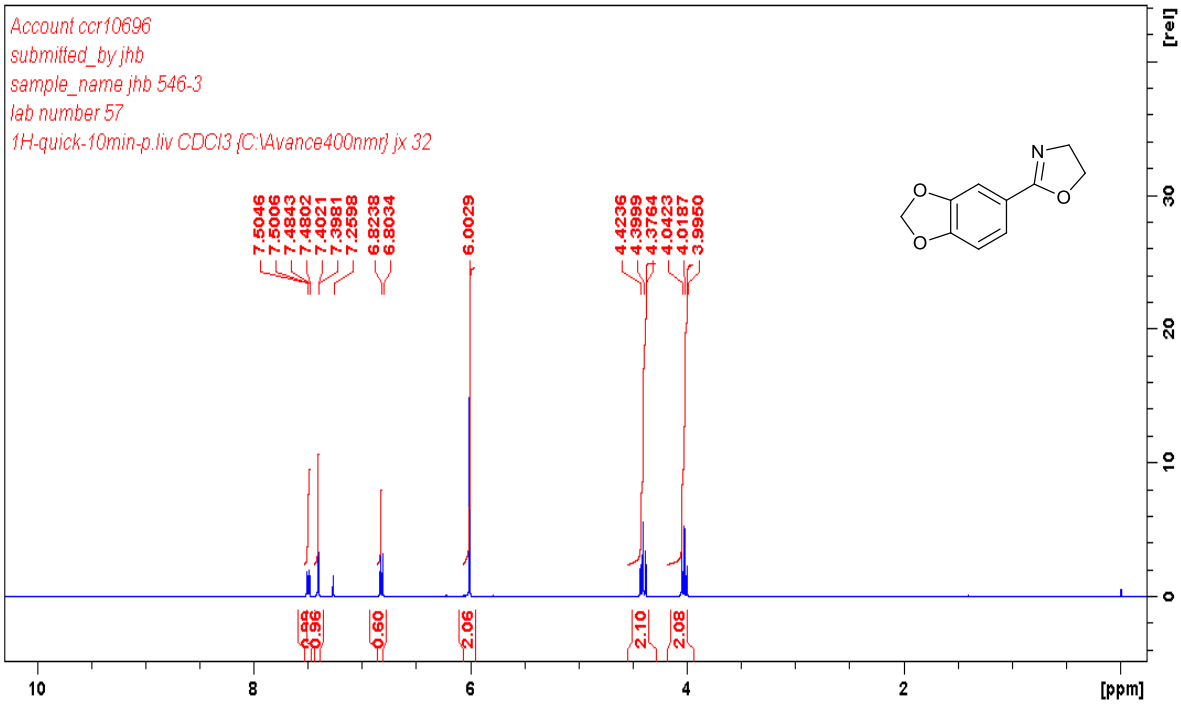
^{13}C {^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of (*E*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl) ethylidene)-4-methoxyaniline (**L1f**).



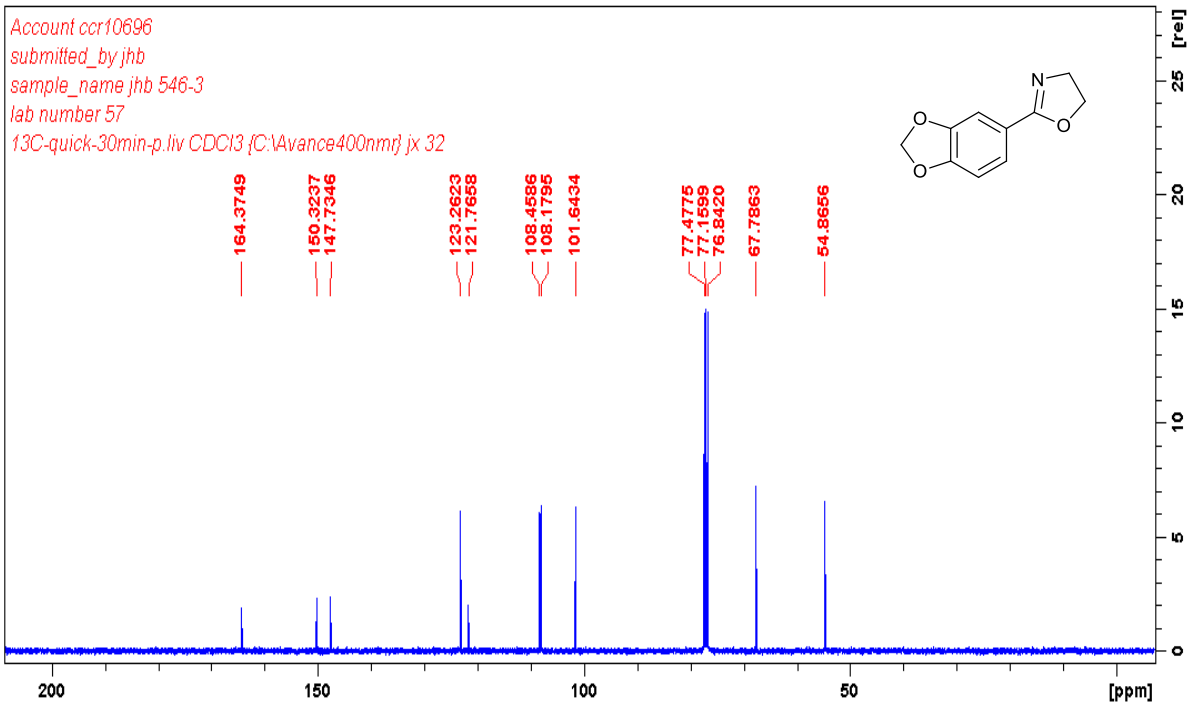
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-(benzo[d][1,3]dioxol-5-yl)pyridine (**L1g**).



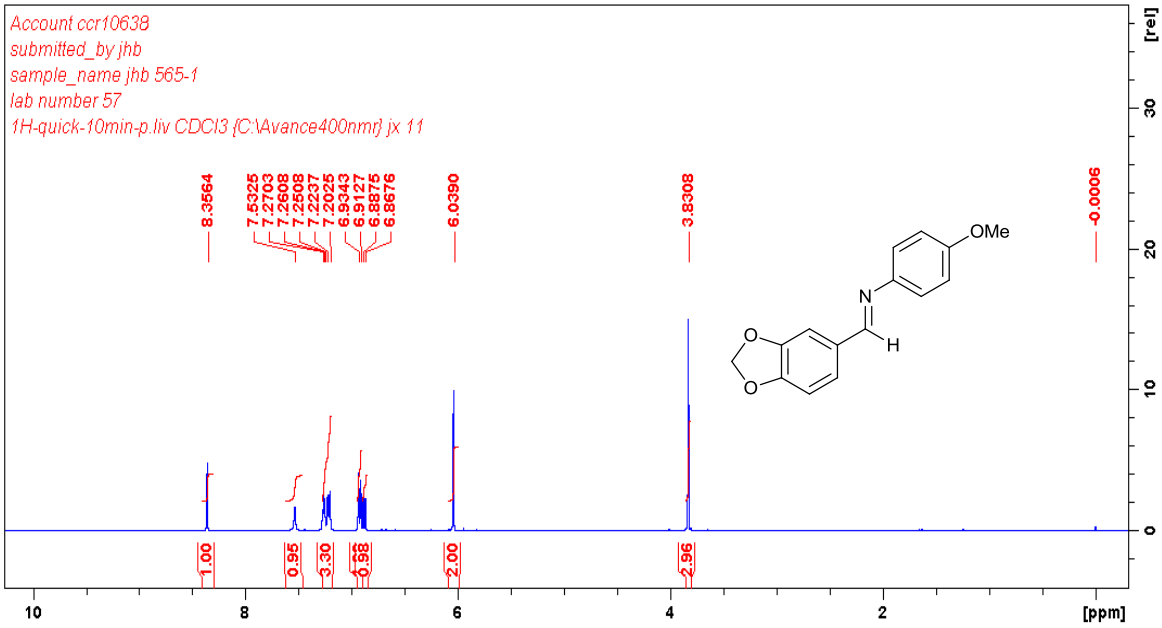
^{13}C{^{1}H}NMR spectrum (100 MHz, $CDCl_3$) of 2-(benzo[d][1,3]dioxol-5-yl)pyridine (**L1g**).



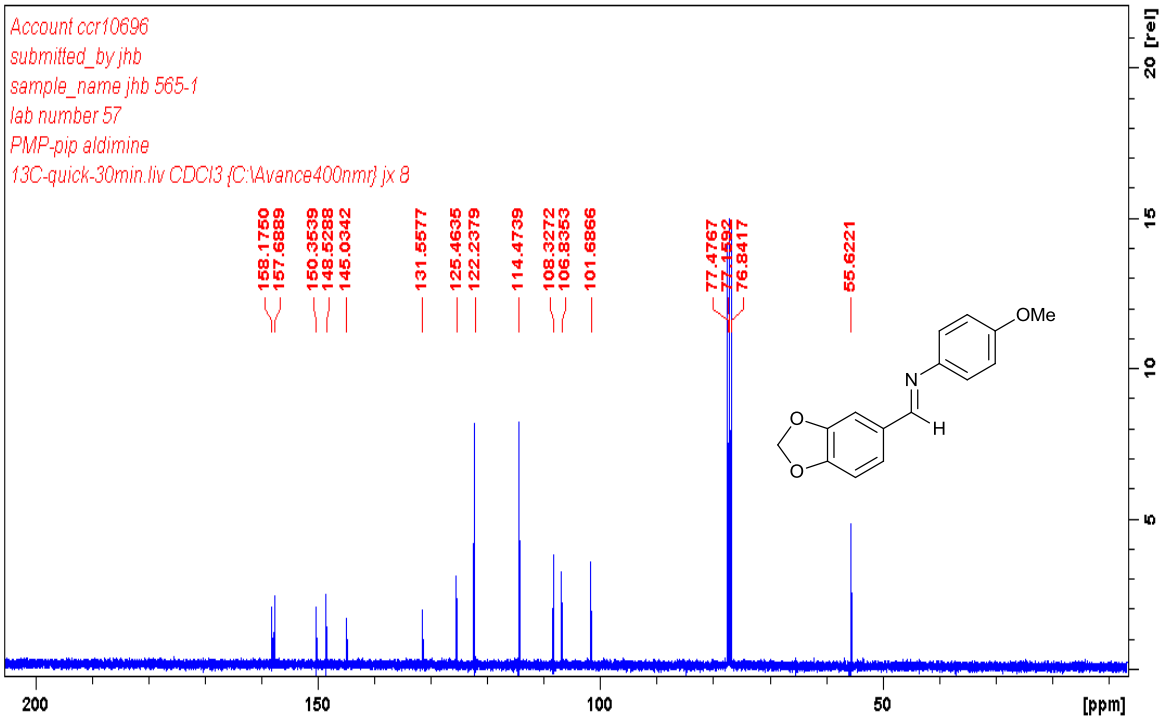
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-(benzo[d][1,3]dioxol-5-yl)-4,5-dihydro oxazole (**L1h**).



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of 2-(benzo[d][1,3]dioxol-5-yl)-4,5-dihydrooxazole (**L1h**).

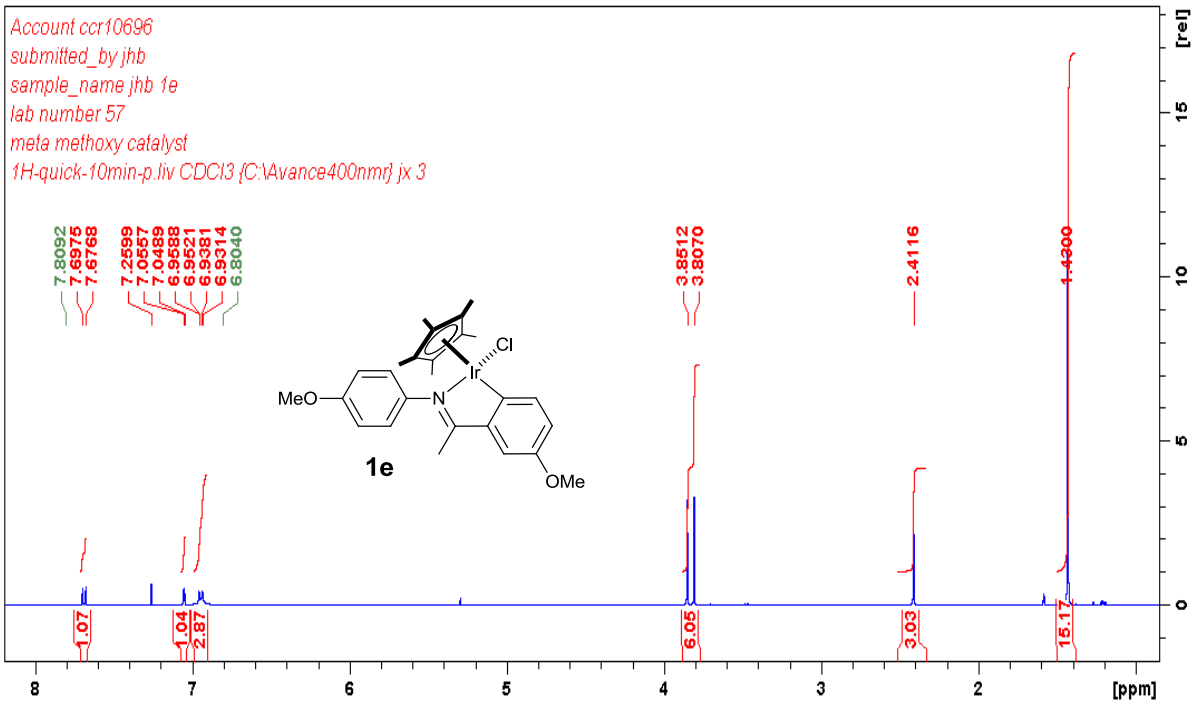


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*E*)-*N*-(benzo[d][1,3]dioxol-5-ylmethylene)-4-methoxyaniline (**L1l**).

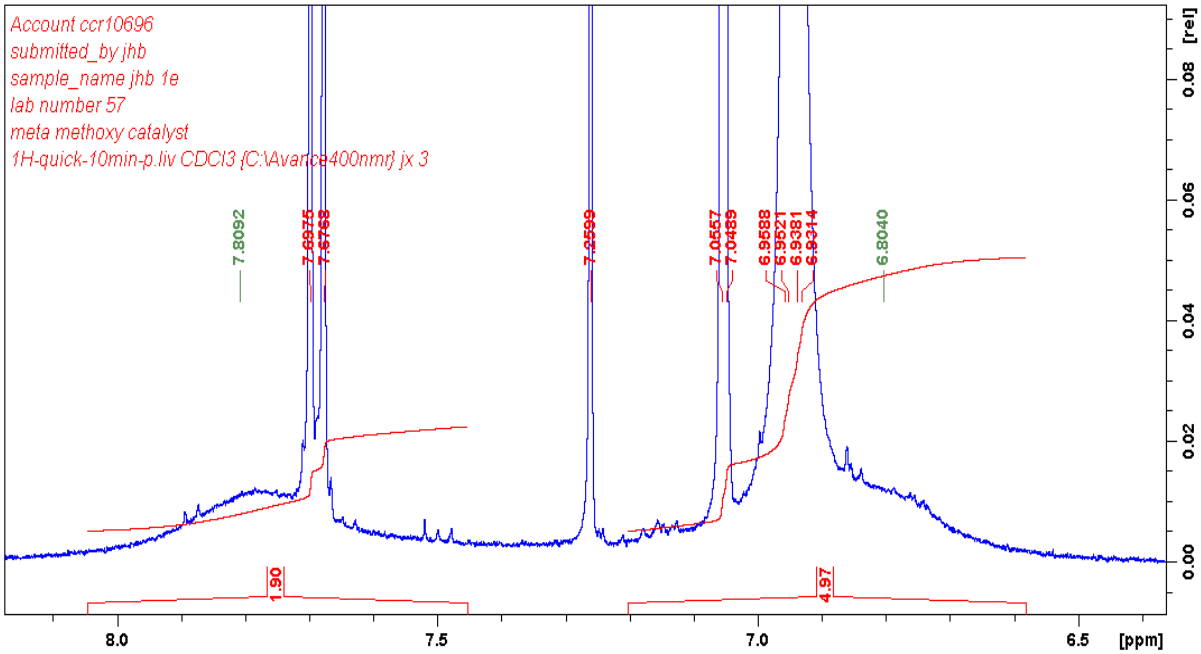


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of (*E*)-*N*-(benzo[d][1,3]dioxol-5-ylmethylene)-4-methoxyaniline (**L1l**).

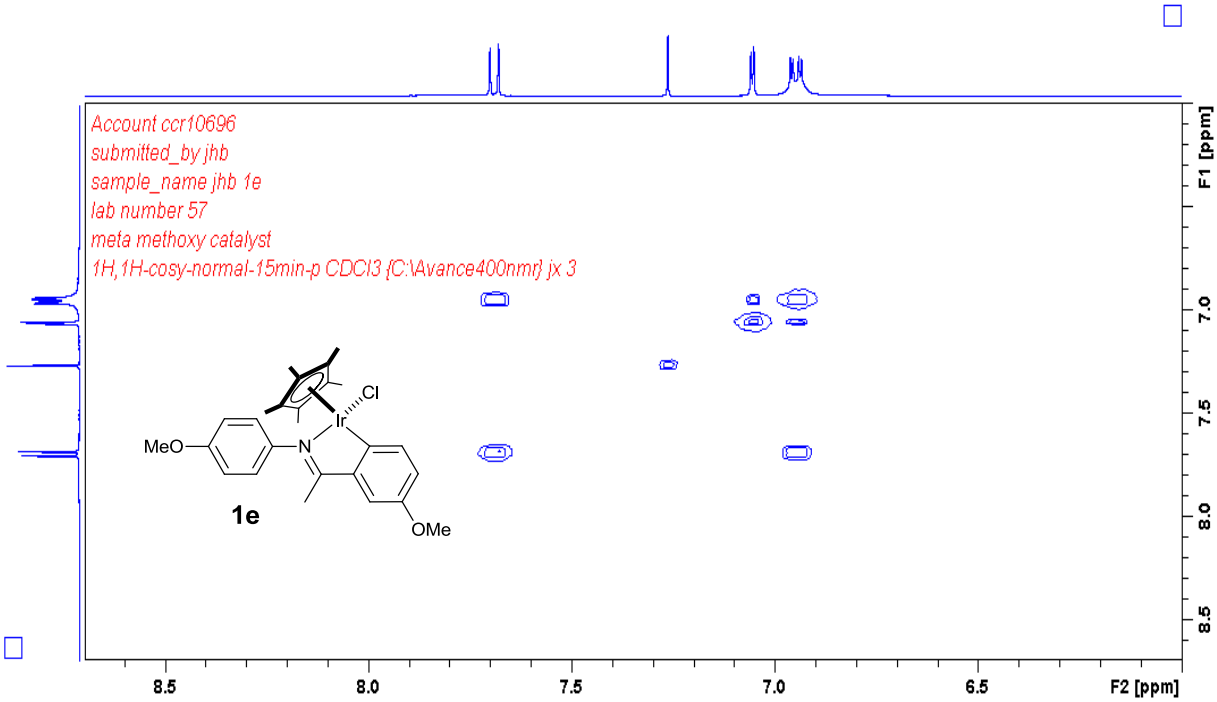
3.2 NMR spectra of metal complexes



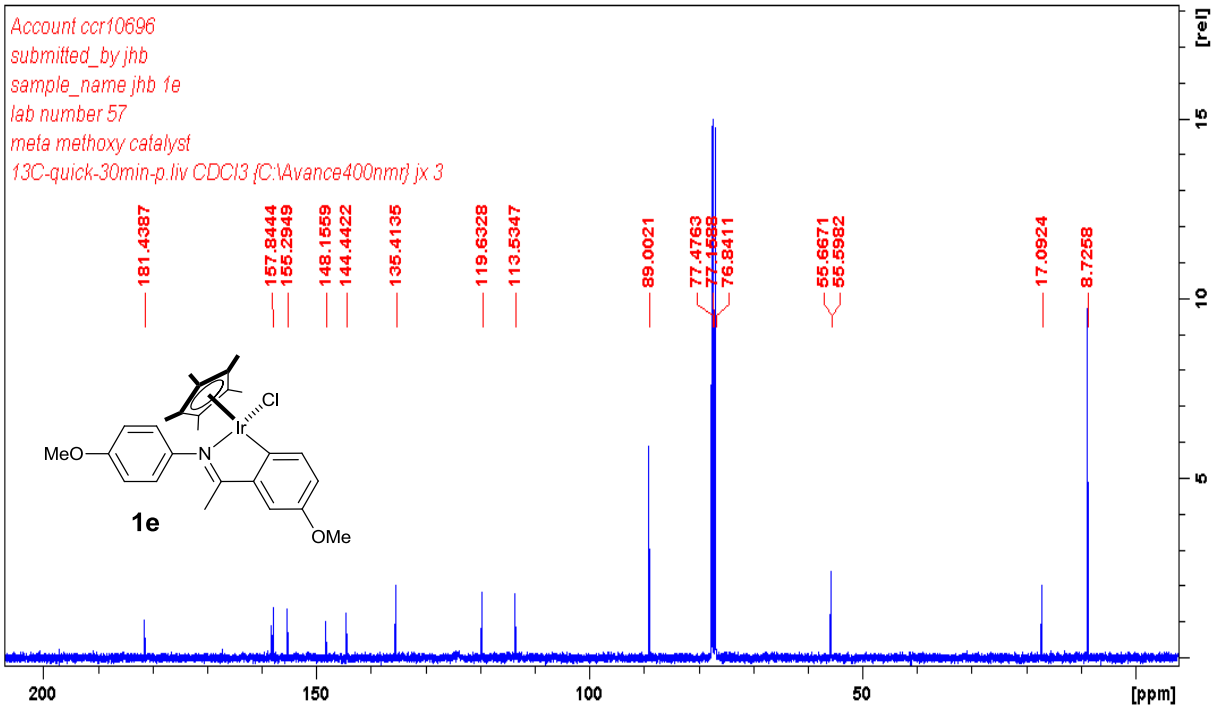
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1e**



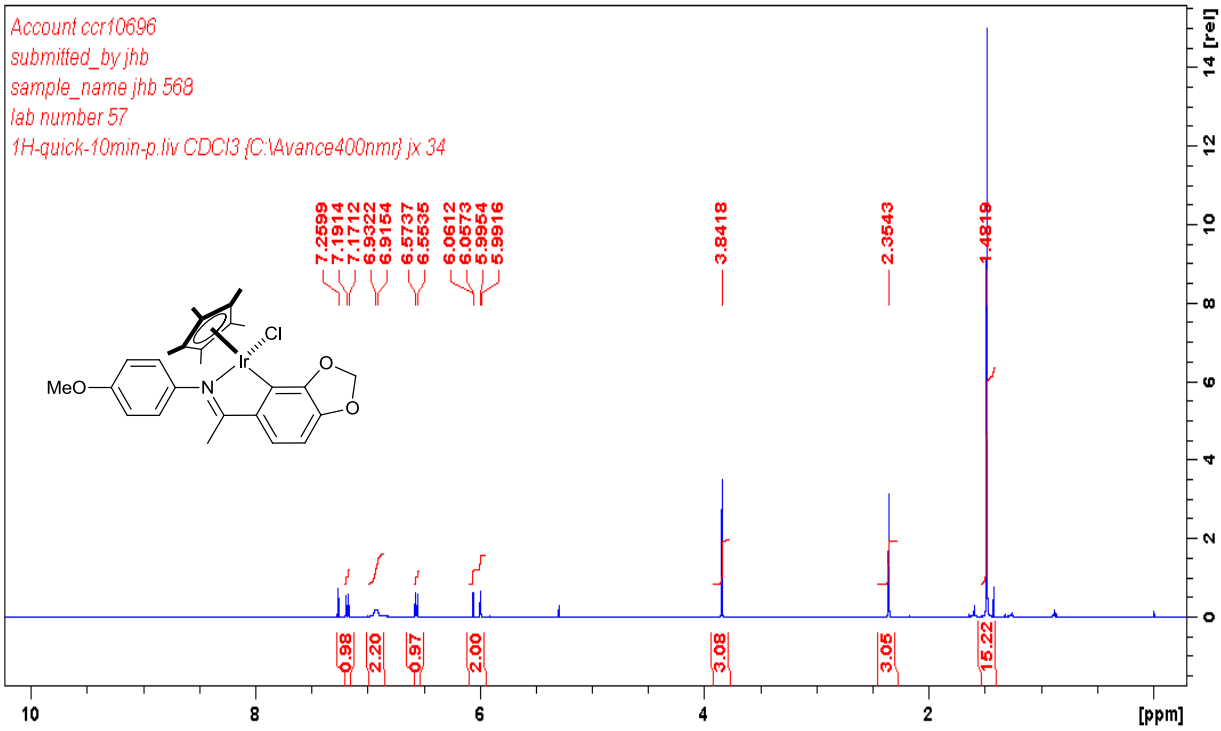
Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1e** showing the broadening of the *para*-methoxyphenyl proton resonances at 7.8 and 6.8 ppm



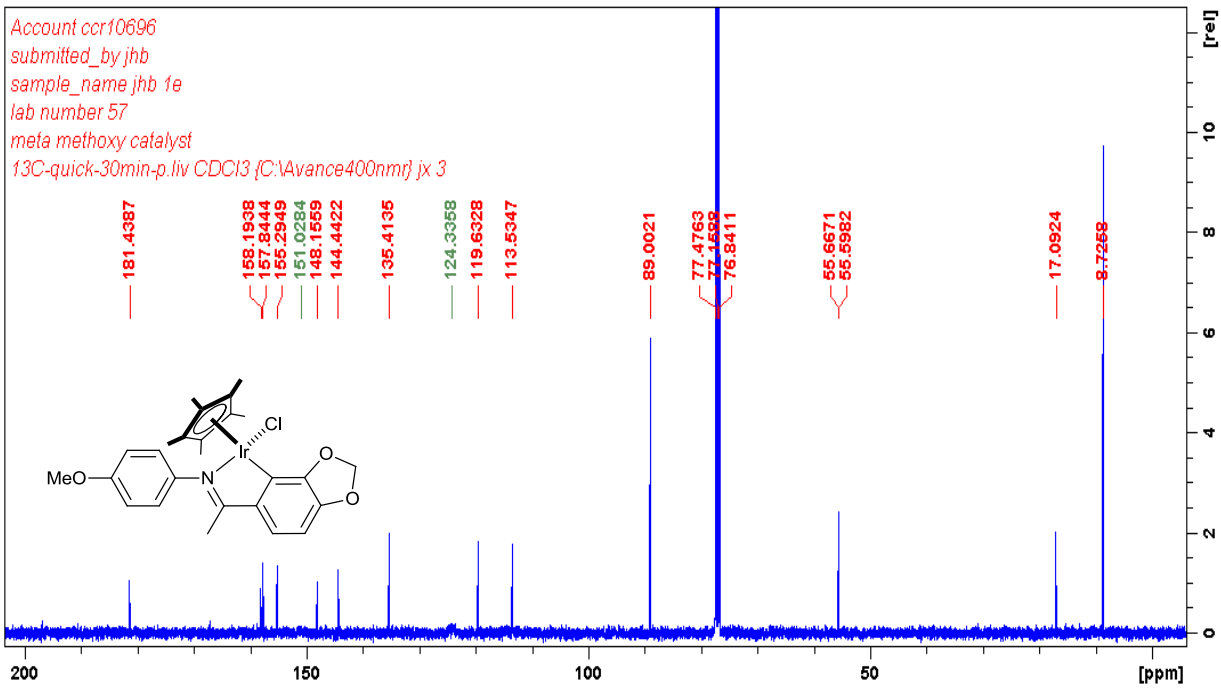
Partial ^{1}H ^{1}H COSY NMR spectrum (100 MHz, $CDCl_3$) of complex **1e** (aromatic region)



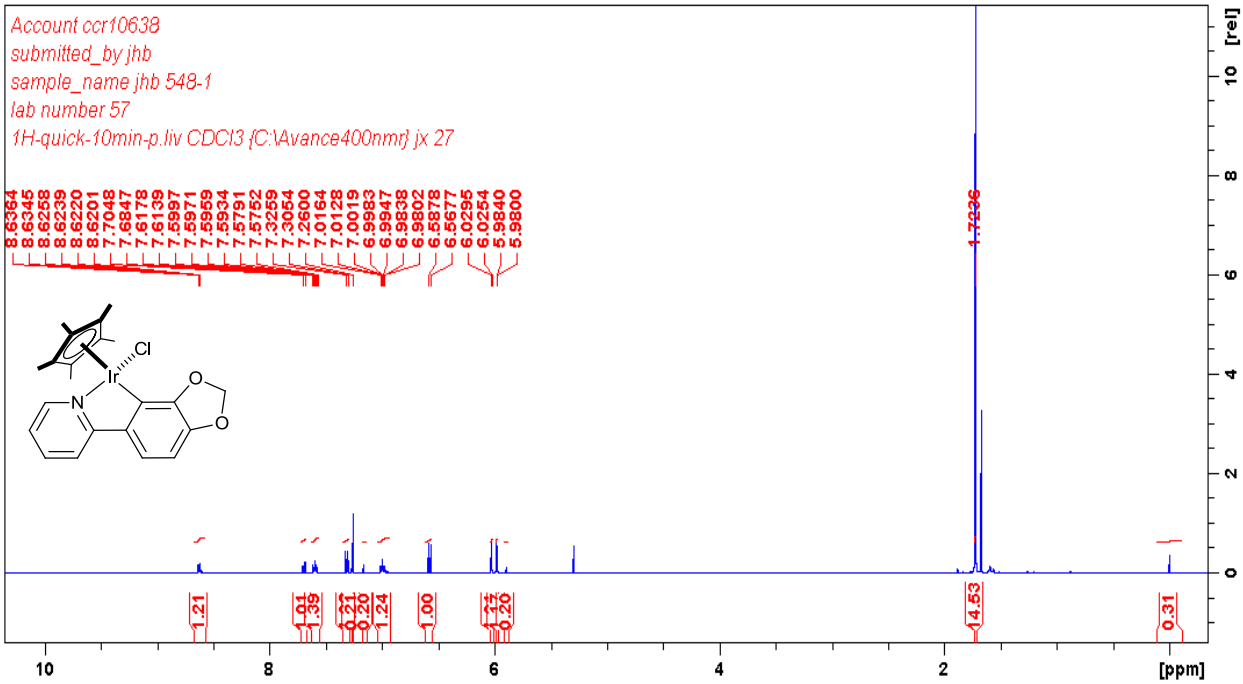
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of complex **1e**



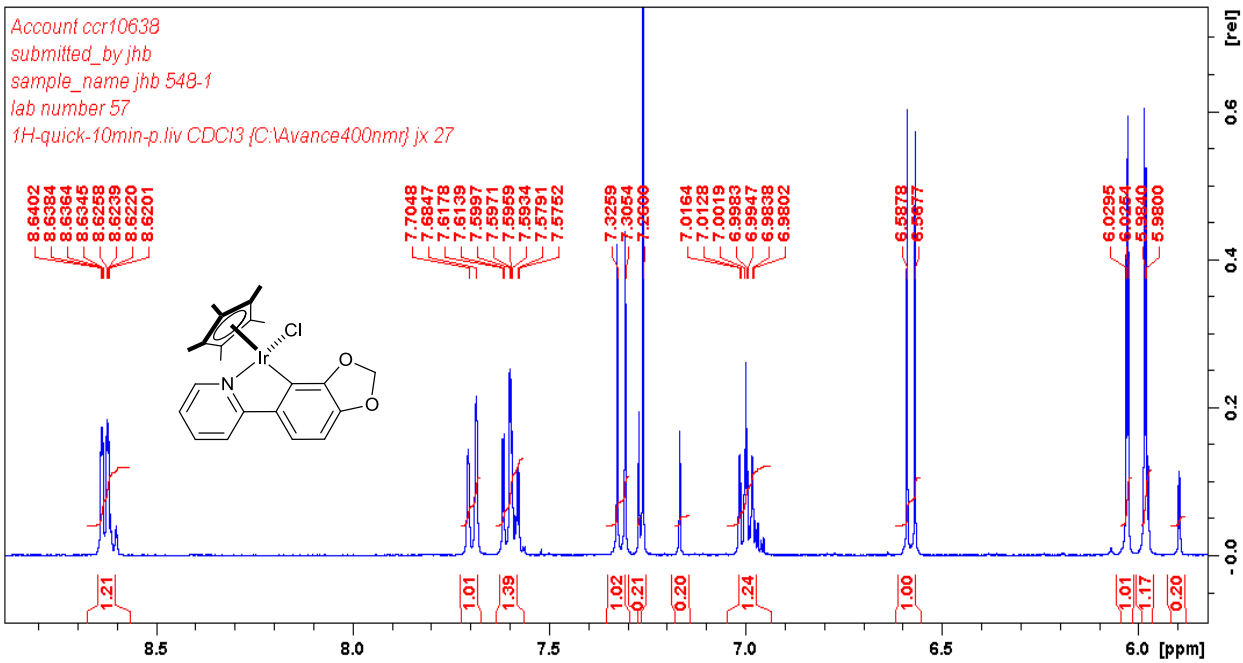
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1f**



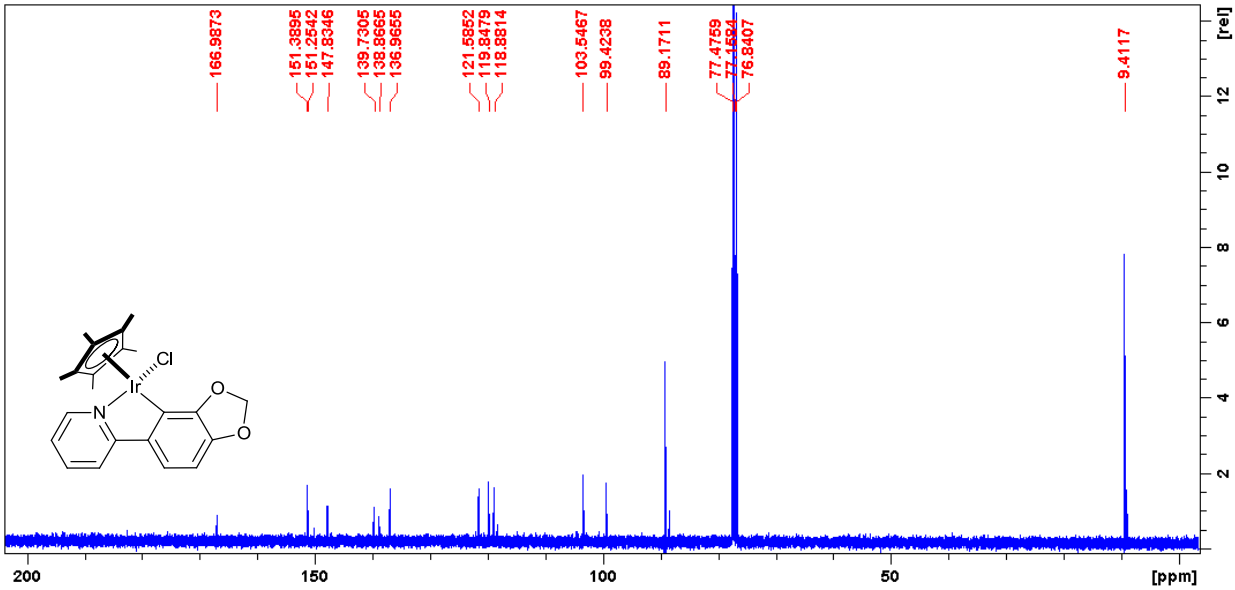
^{13}C{^{1}H}NMR spectrum (100 MHz, $CDCl_3$) of complex **1f**



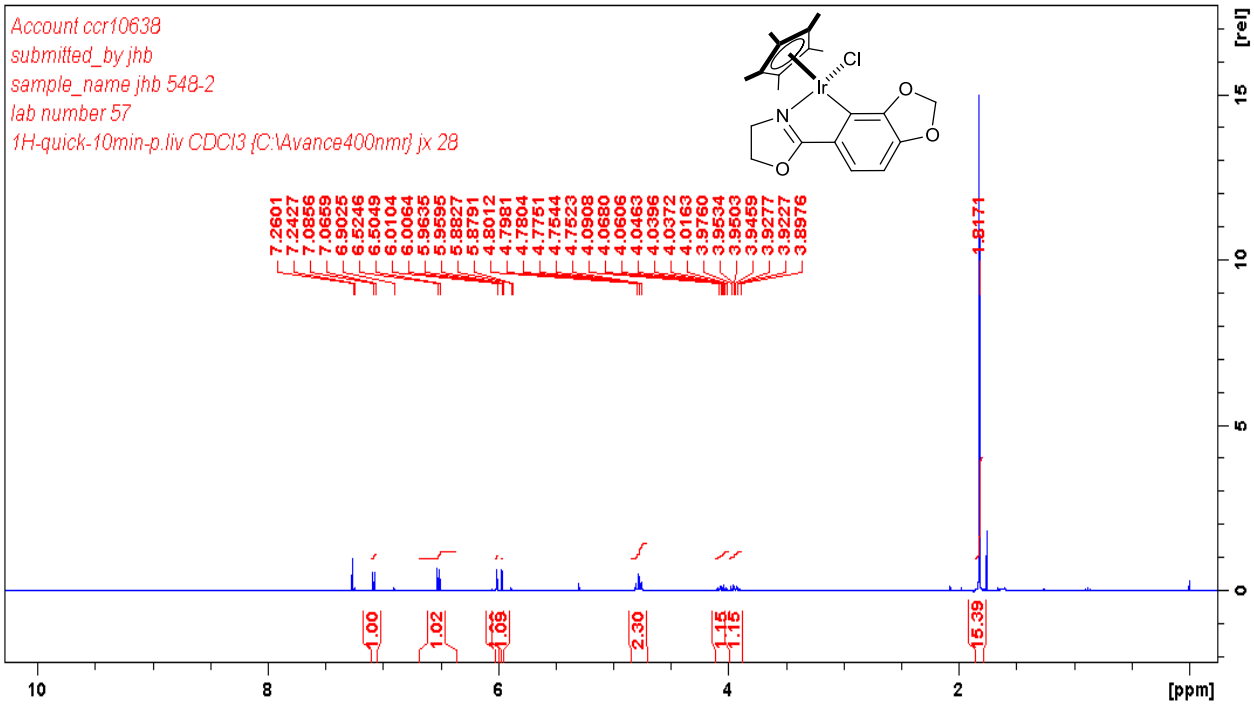
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1g**



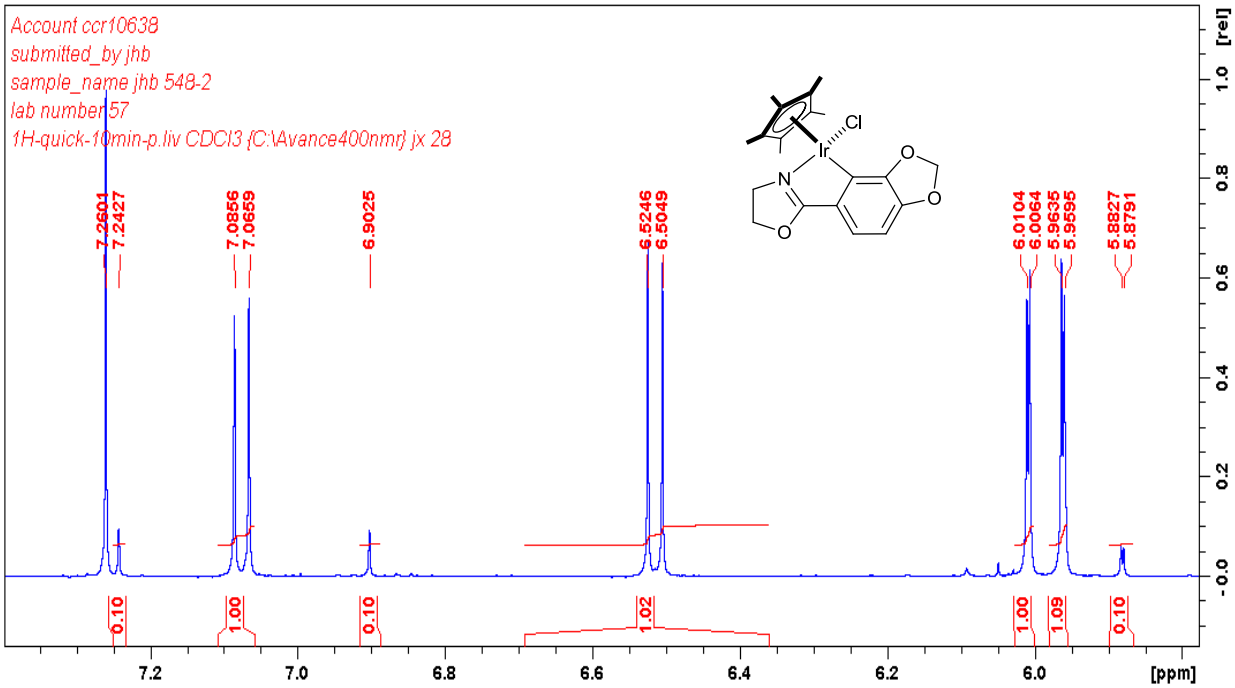
Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, aromatic region) of complex **1g** showing the major and minor isomers



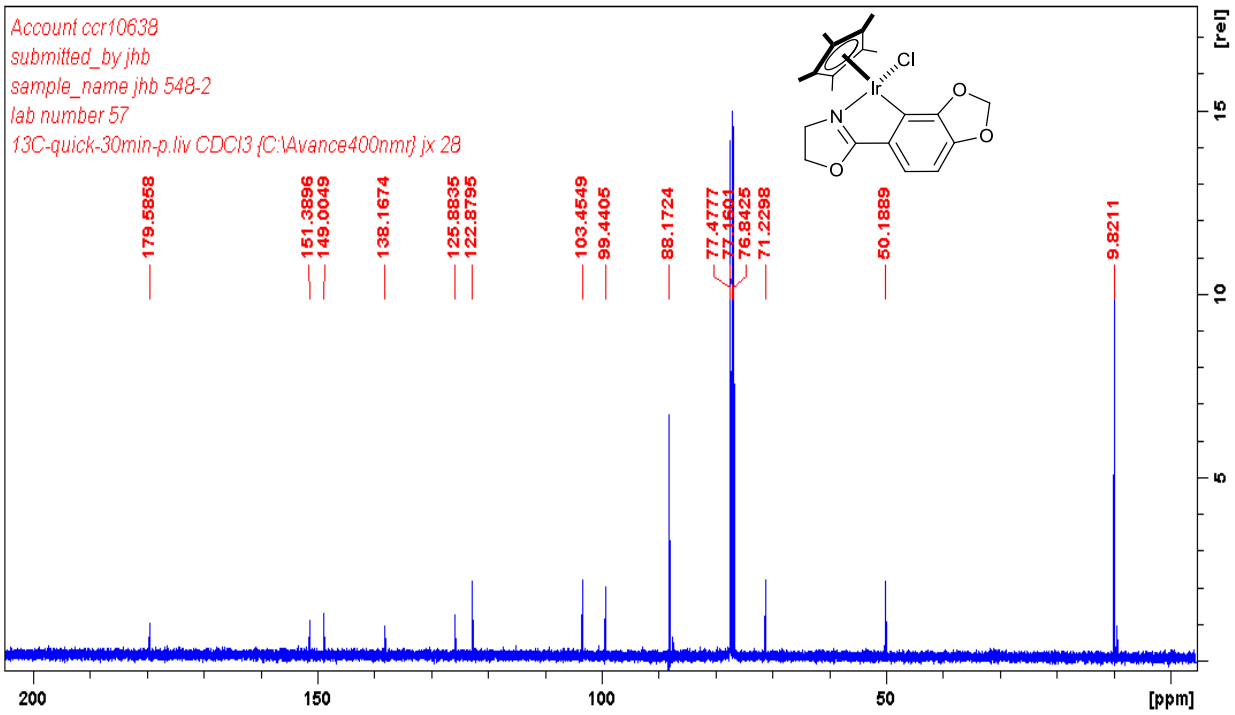
$^{13}C\{^{1}H\}$NMR spectrum (100 MHz, $CDCl_3$) of complex **1g**



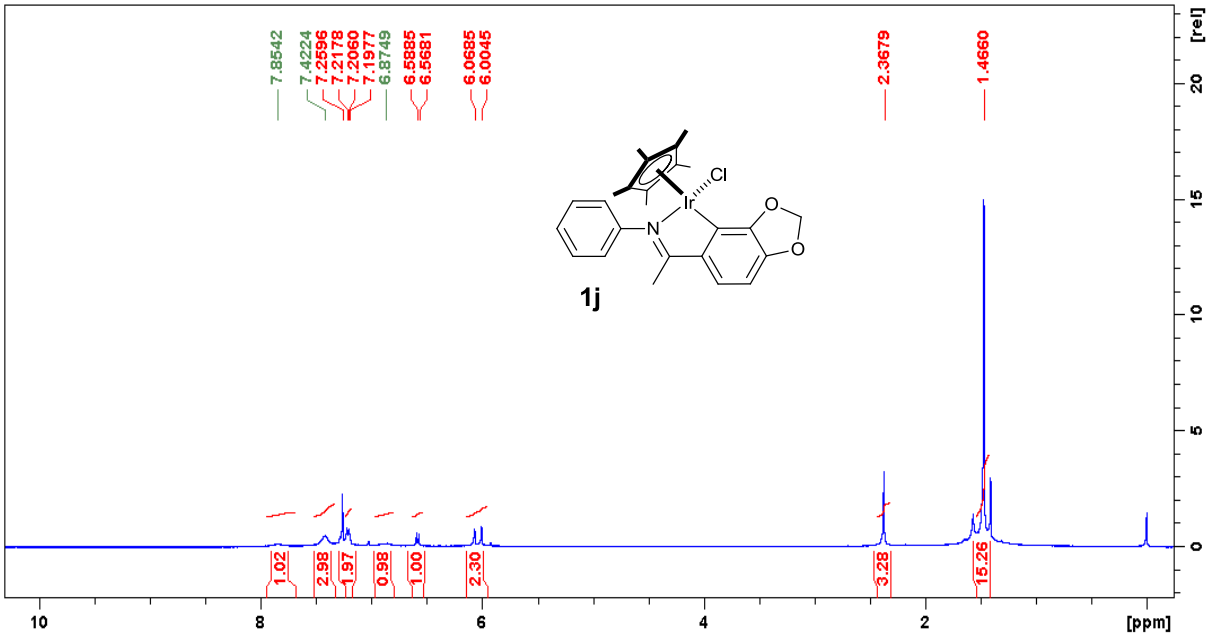
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1h**



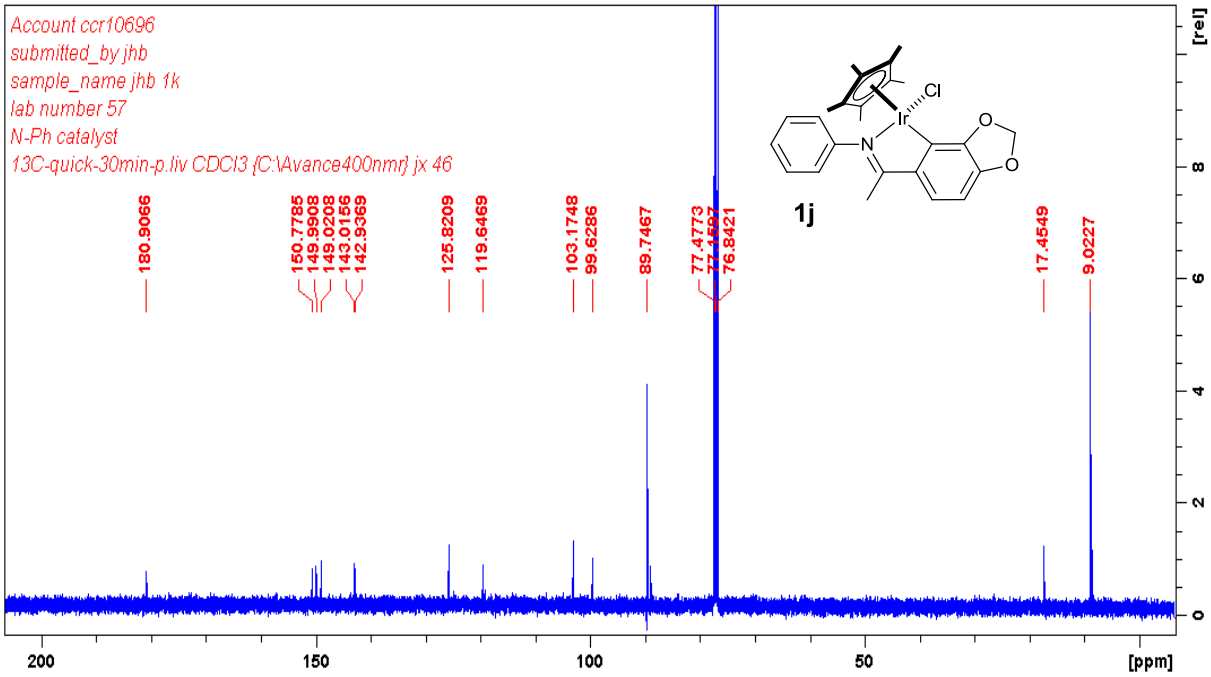
Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, aromatic region) of complex **1h**



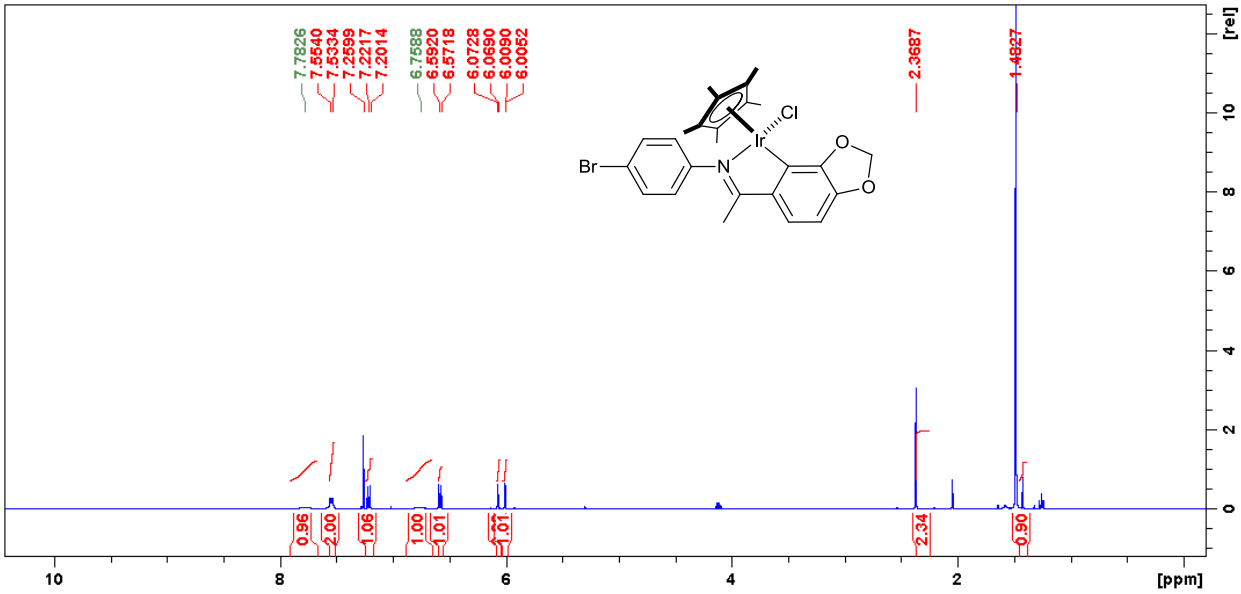
^{13}C{^{1}H}NMR spectrum (100 MHz, $CDCl_3$) of complex **1h**



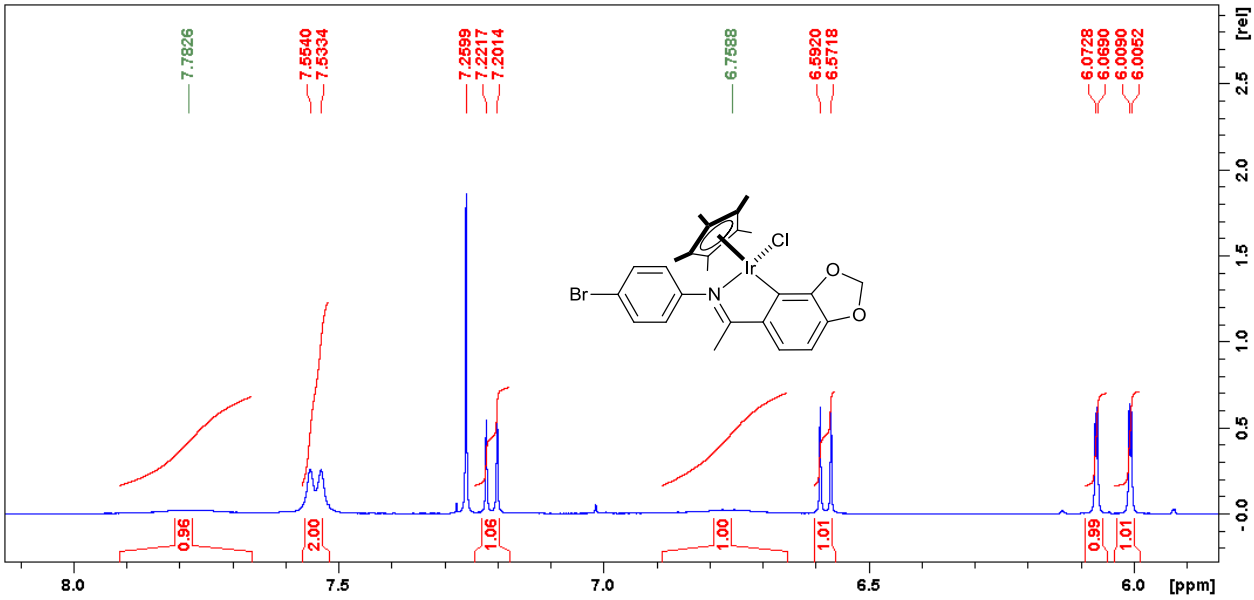
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1j**



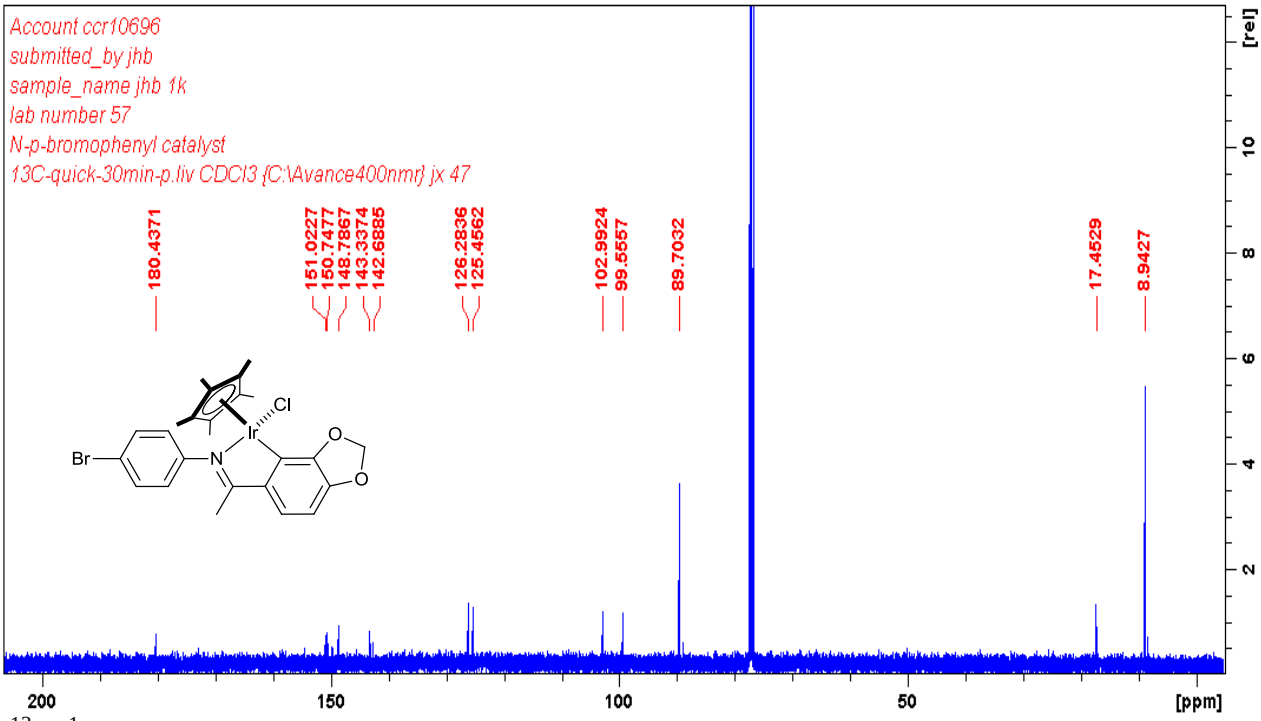
^{13}C{^{1}H}NMR spectrum (100 MHz, $CDCl_3$) of complex **1j**



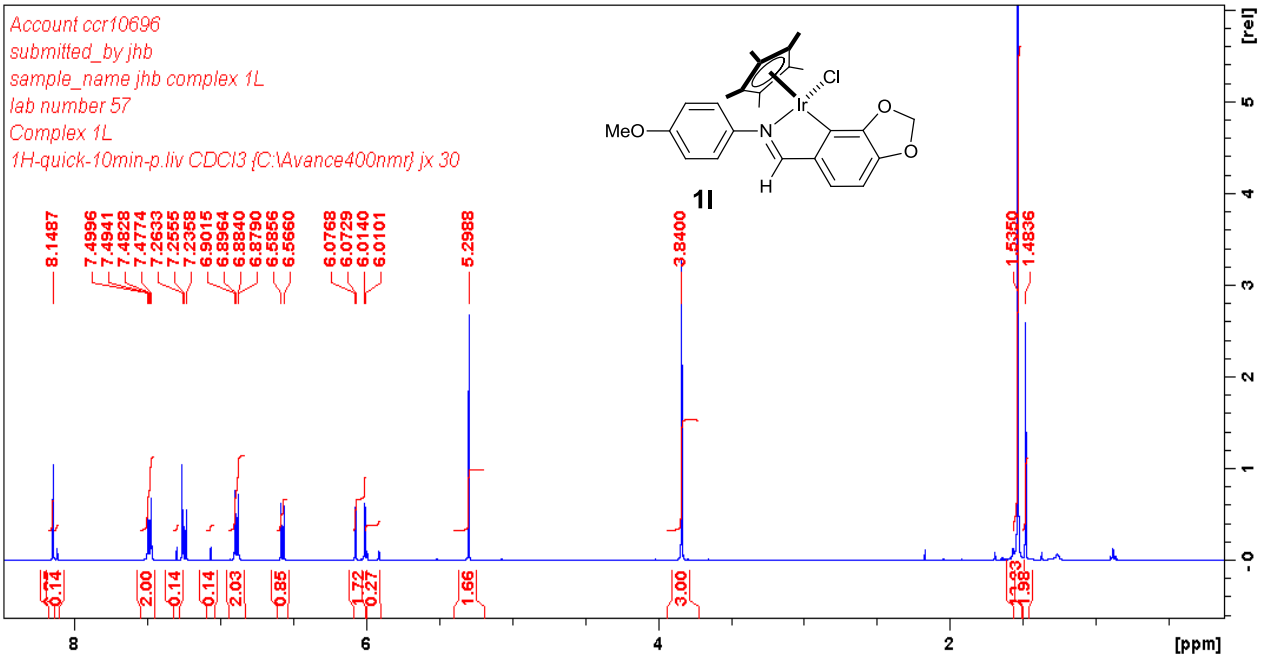
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1k**



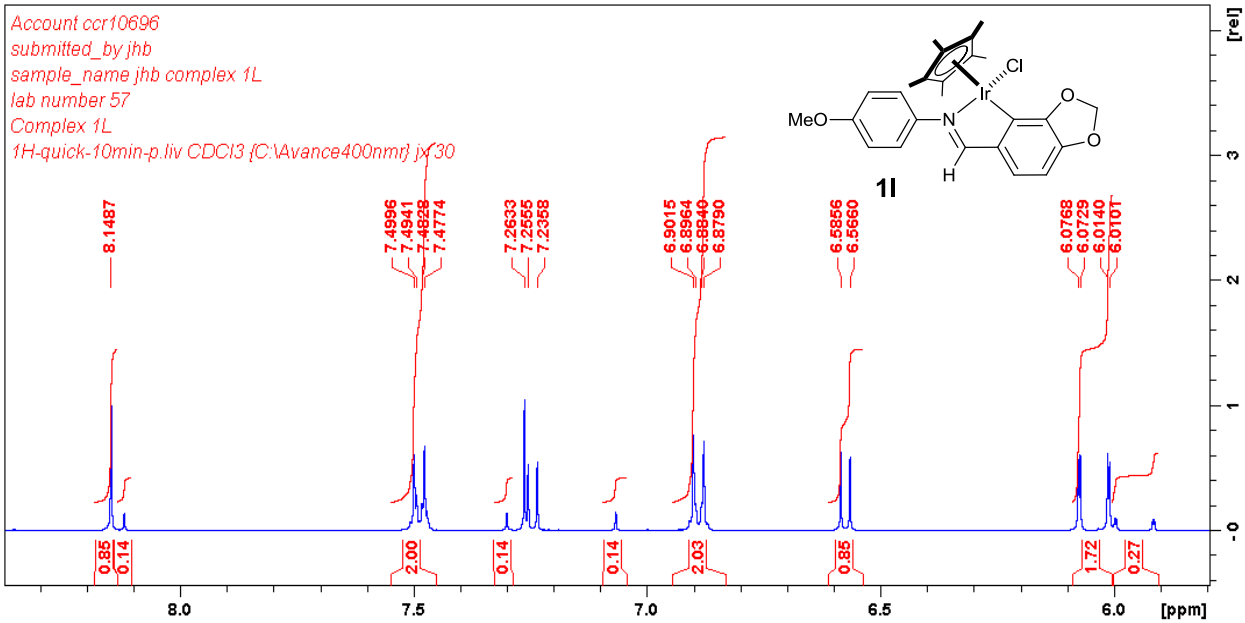
Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, aromatic region) of complex **1k**



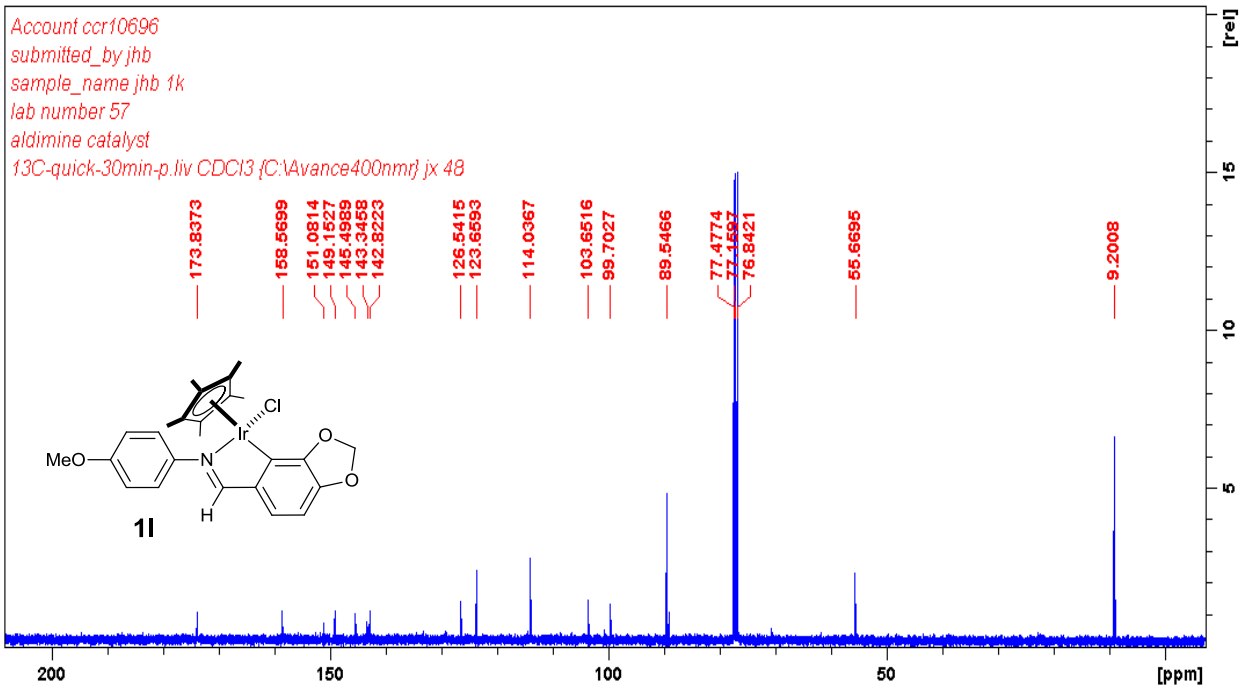
$^{13}C\{^{1}H\}$NMR spectrum (100 MHz, $CDCl_3$) of complex **1k**



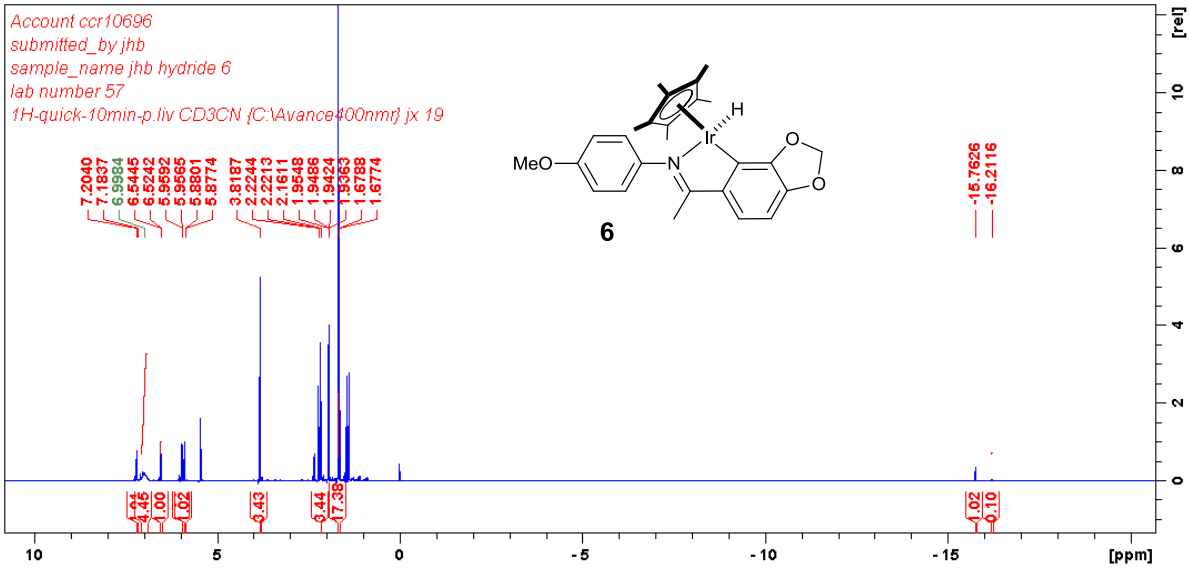
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **1l**



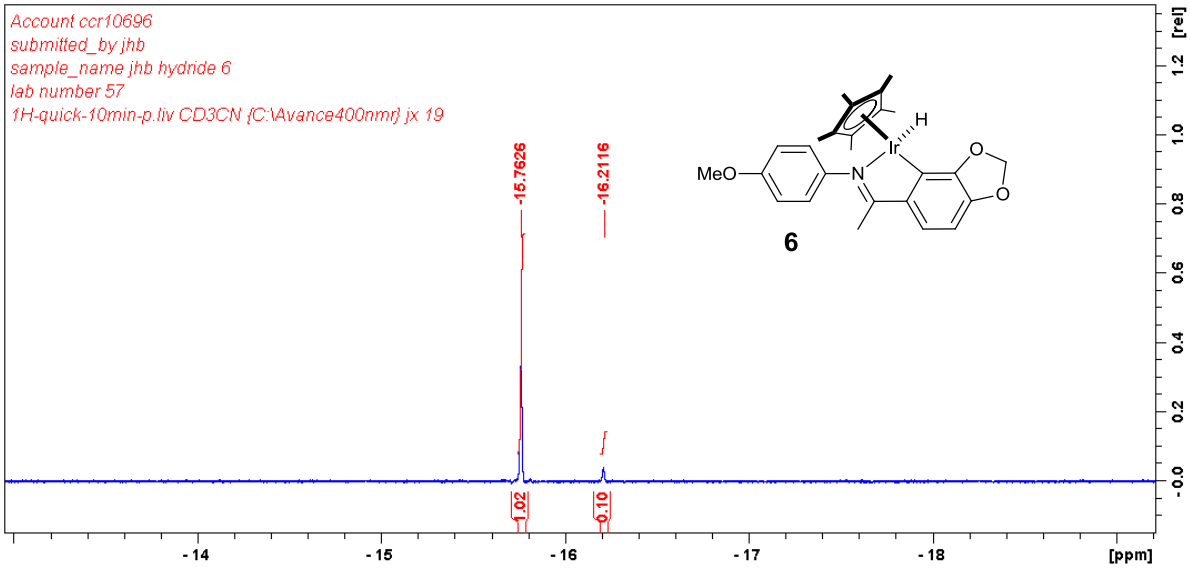
Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, aromatic region) of complex **1l**



^{13}C{^{1}H}NMR spectrum (100 MHz, $CDCl_3$) of complex **1l**

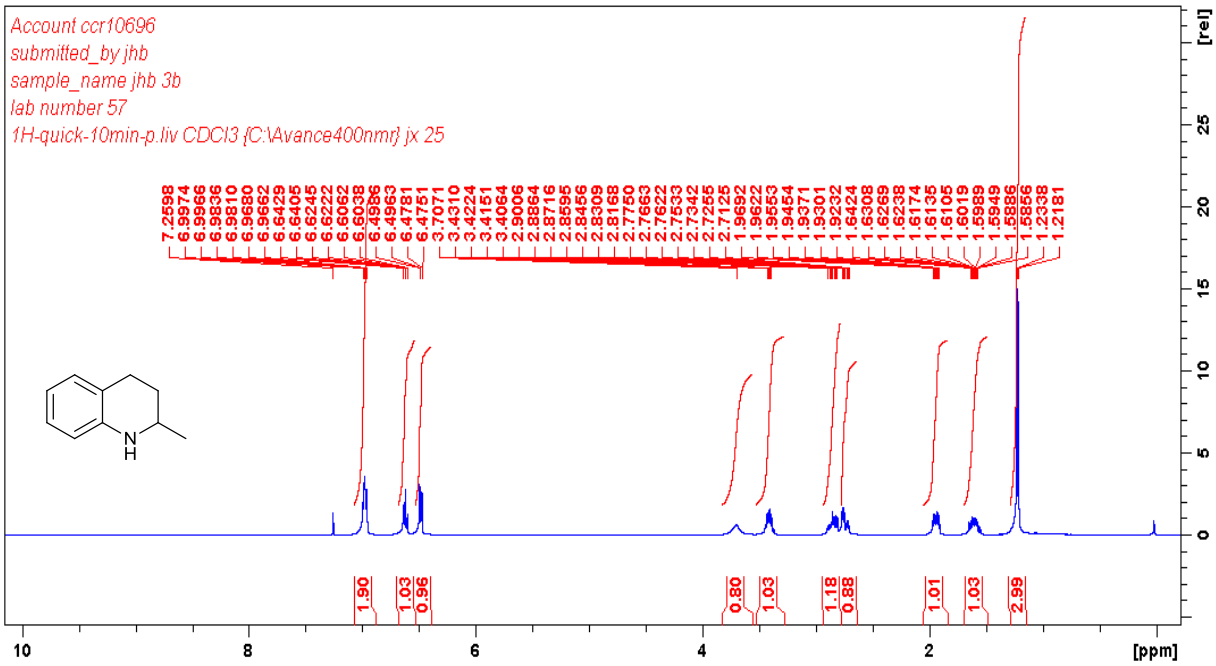


^{1}H NMR spectrum (400 MHz, MeCN-*d3*) of complex **6**.

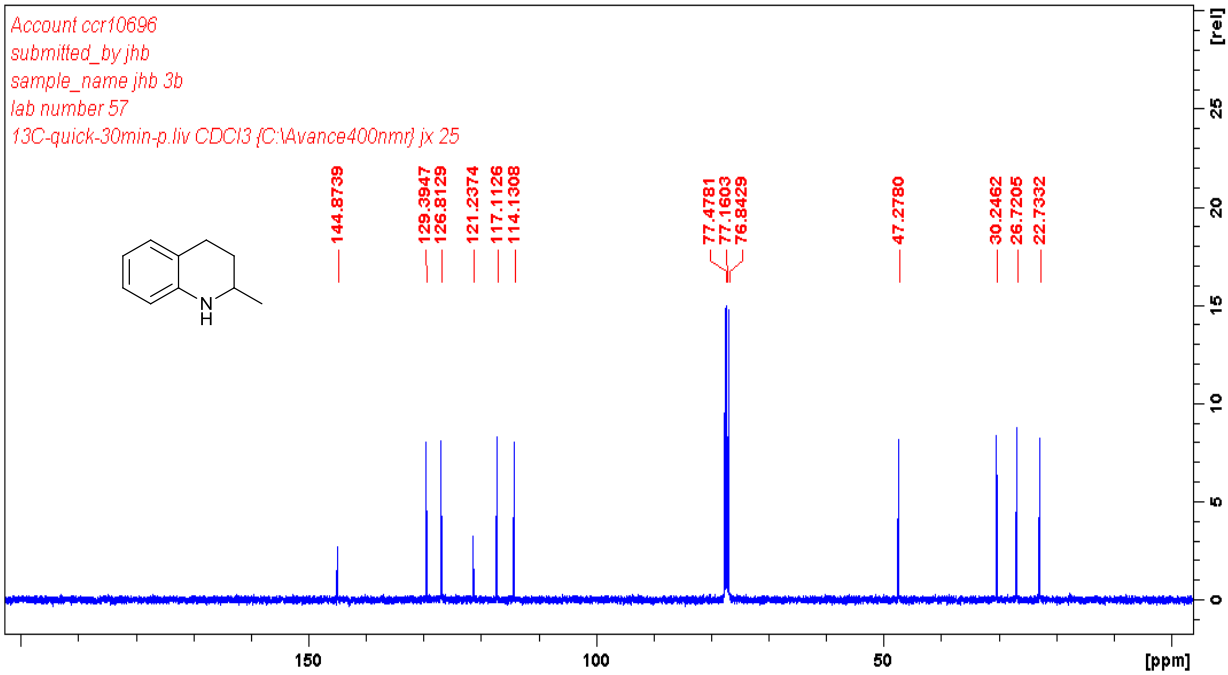


Partial ^{1}H NMR spectrum (400 MHz, MeCN-*d3*, hydride region) of complex **6**.

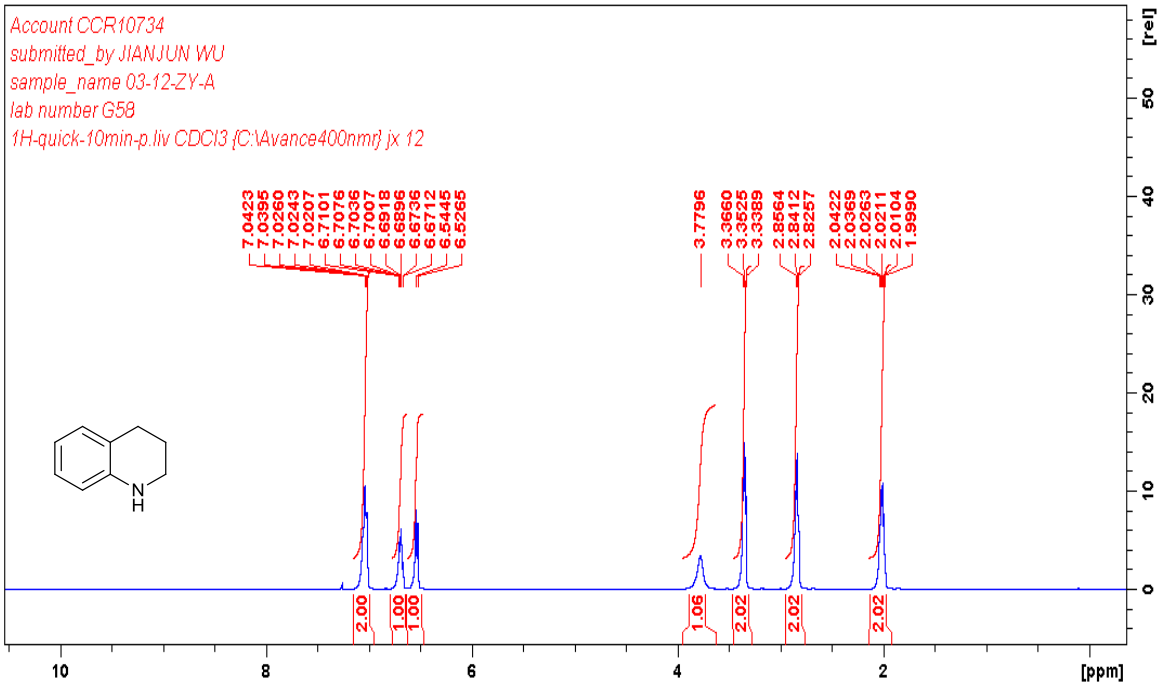
3.3 NMR spectra of hydrogenation products



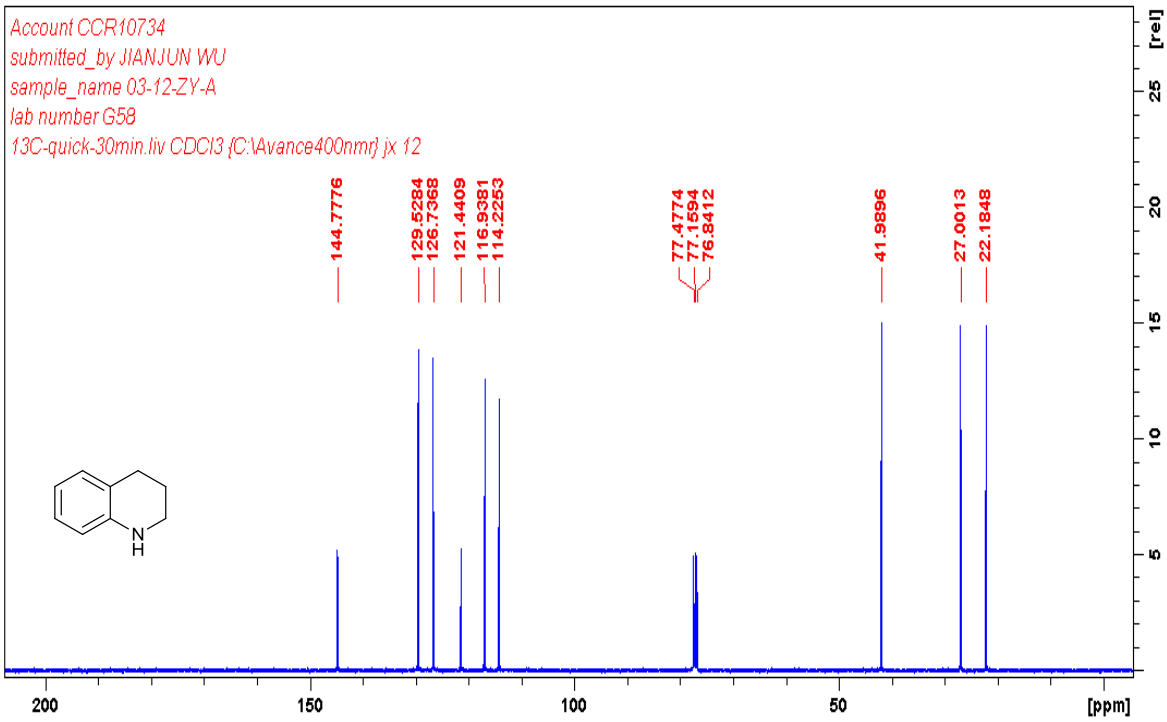
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline (**3a**)



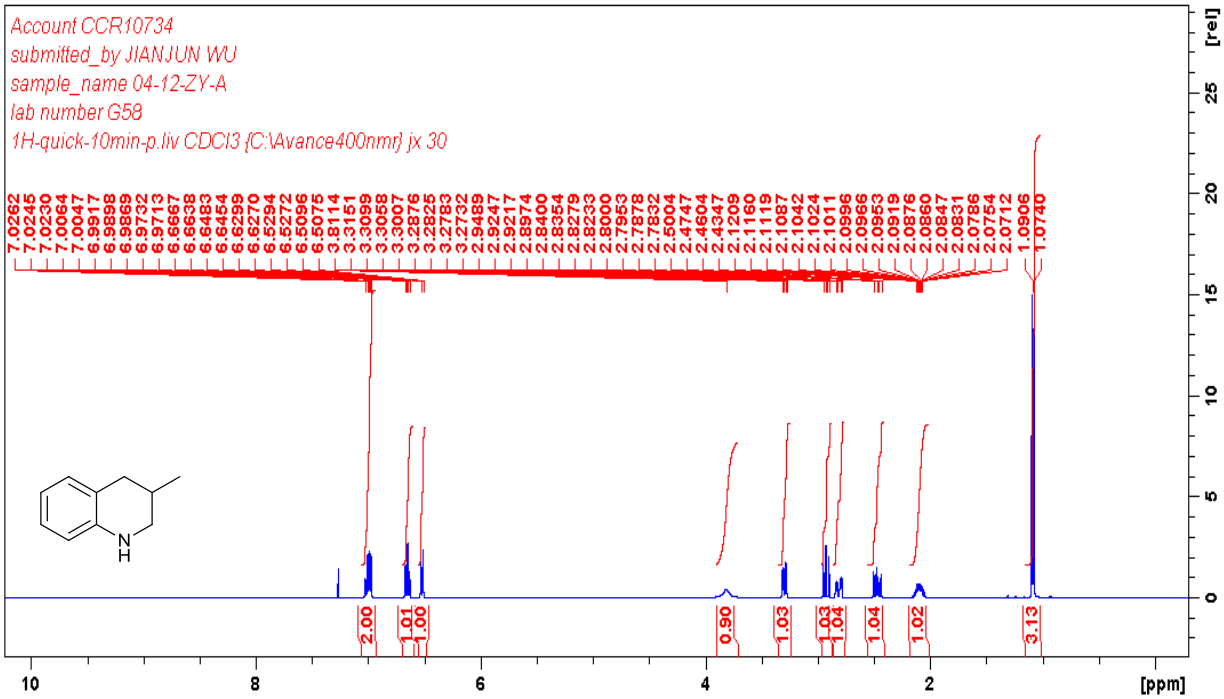
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline (**3a**)



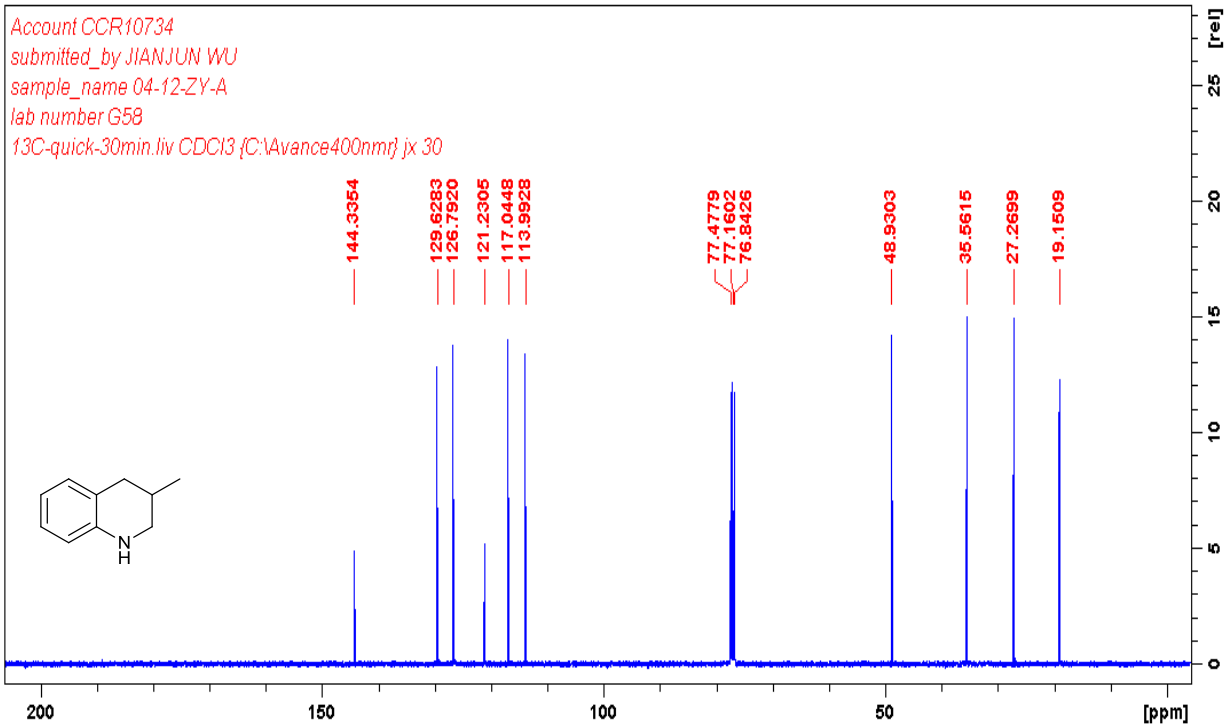
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydroquinoline (**3b**)



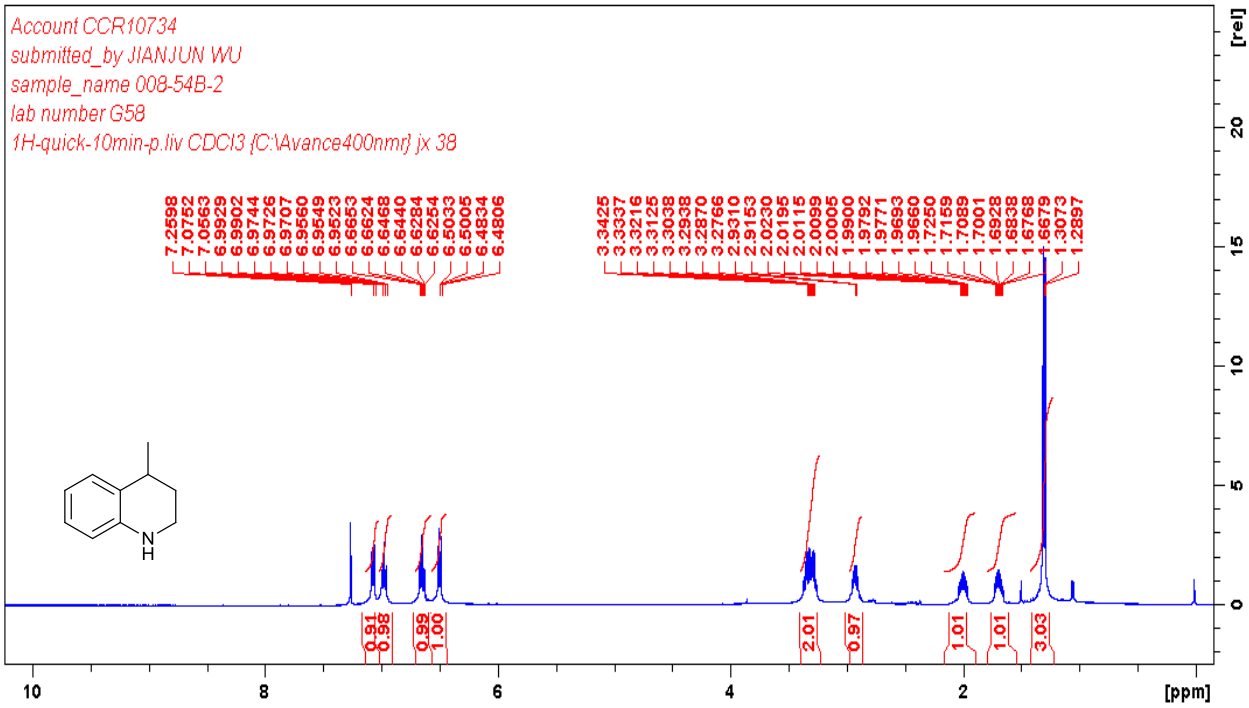
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of spectrum 1,2,3,4-tetrahydroquinoline (**3b**)



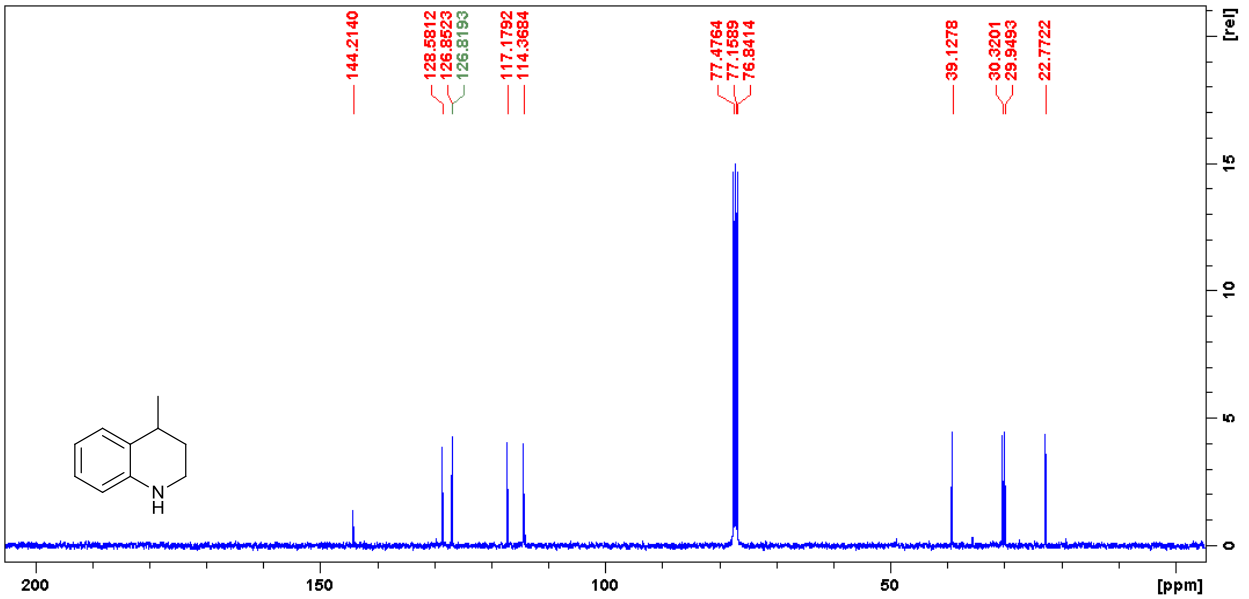
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-methyl-1,2,3,4-tetrahydroquinoline (**3c**)



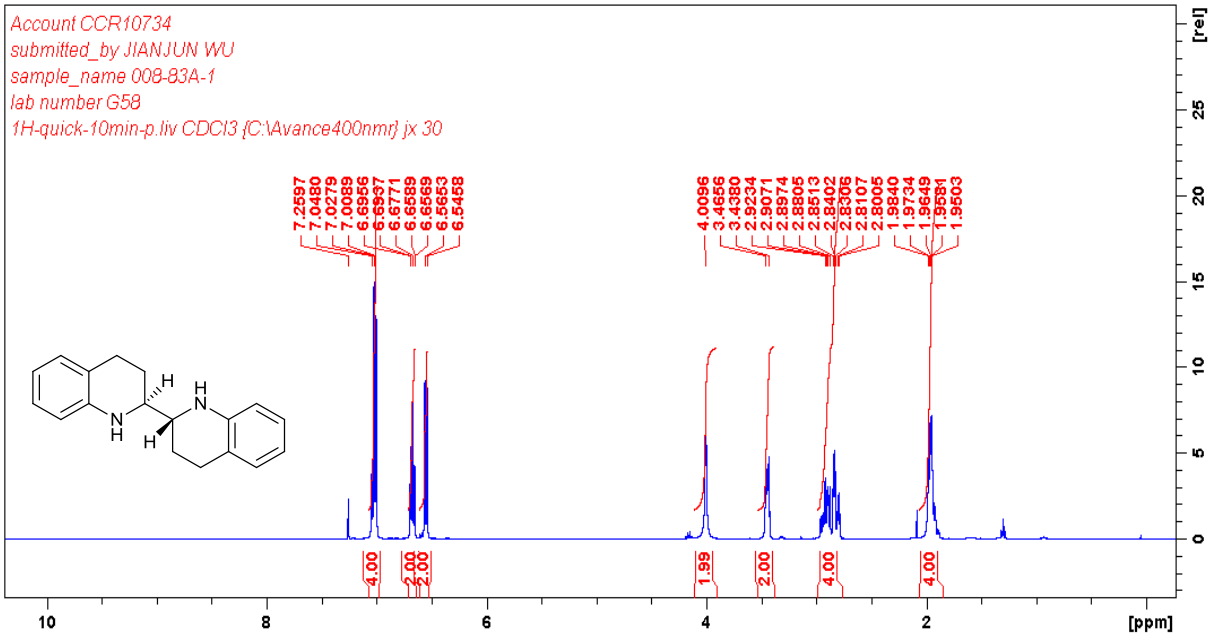
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 3-methyl-1,2,3,4-tetrahydroquinoline (**3c**)



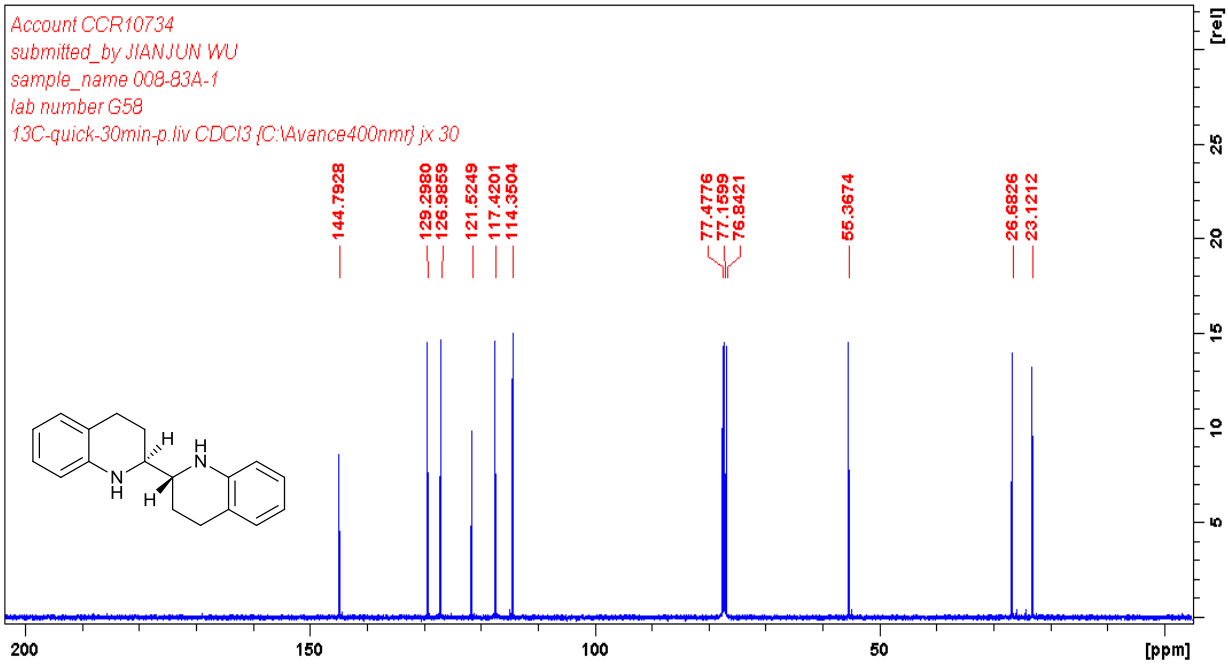
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-Methyl-1,2,3,4-tetrahydroquinoline (**3d**)



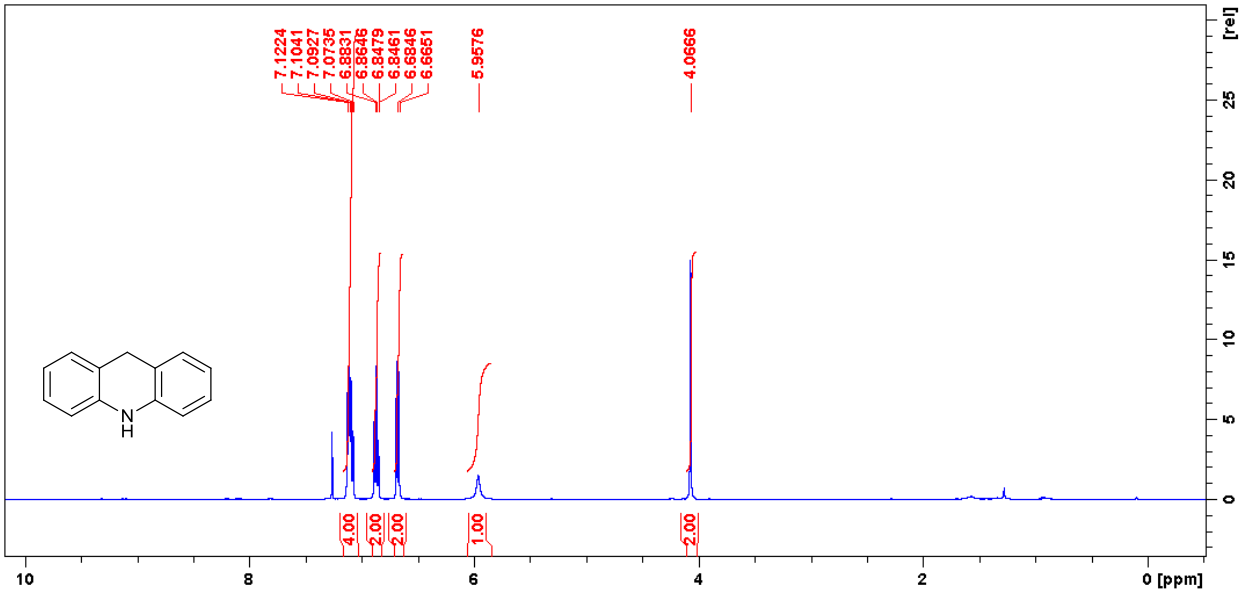
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 4-Methyl-1,2,3,4-tetrahydroquinoline (**3d**)



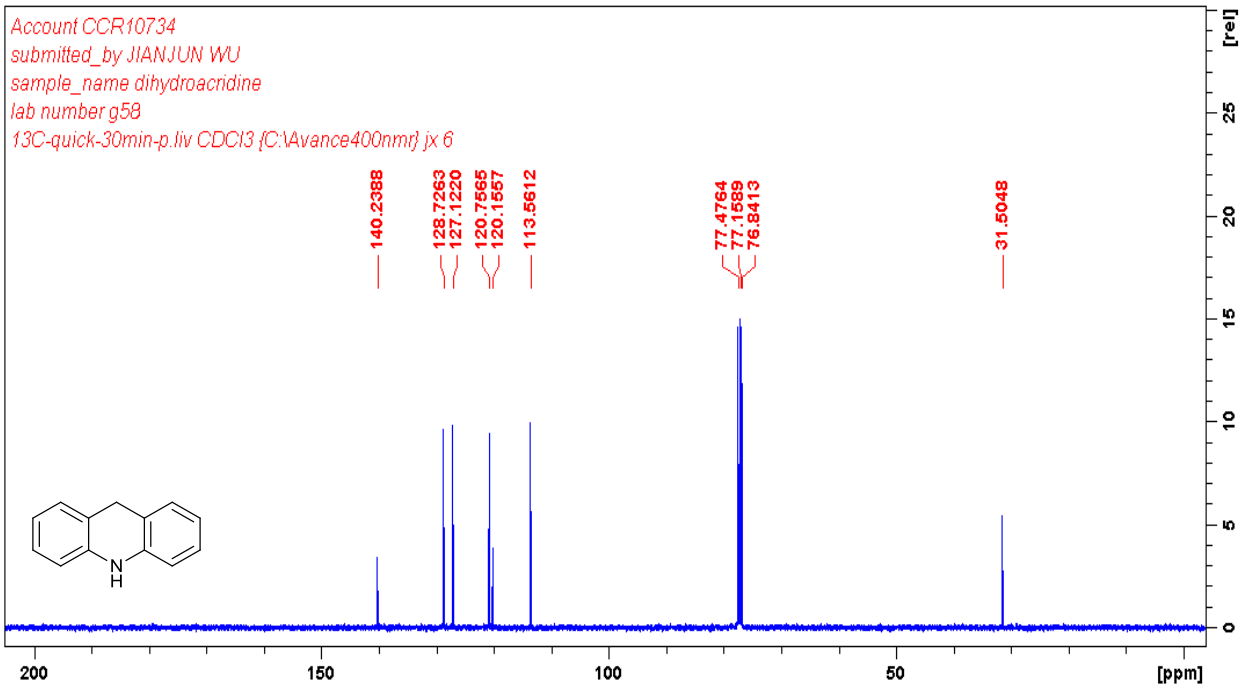
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *meso*-1,1',2,2',3,3',4,4'-octahydro-2,2'-biquinoline (**3e**)



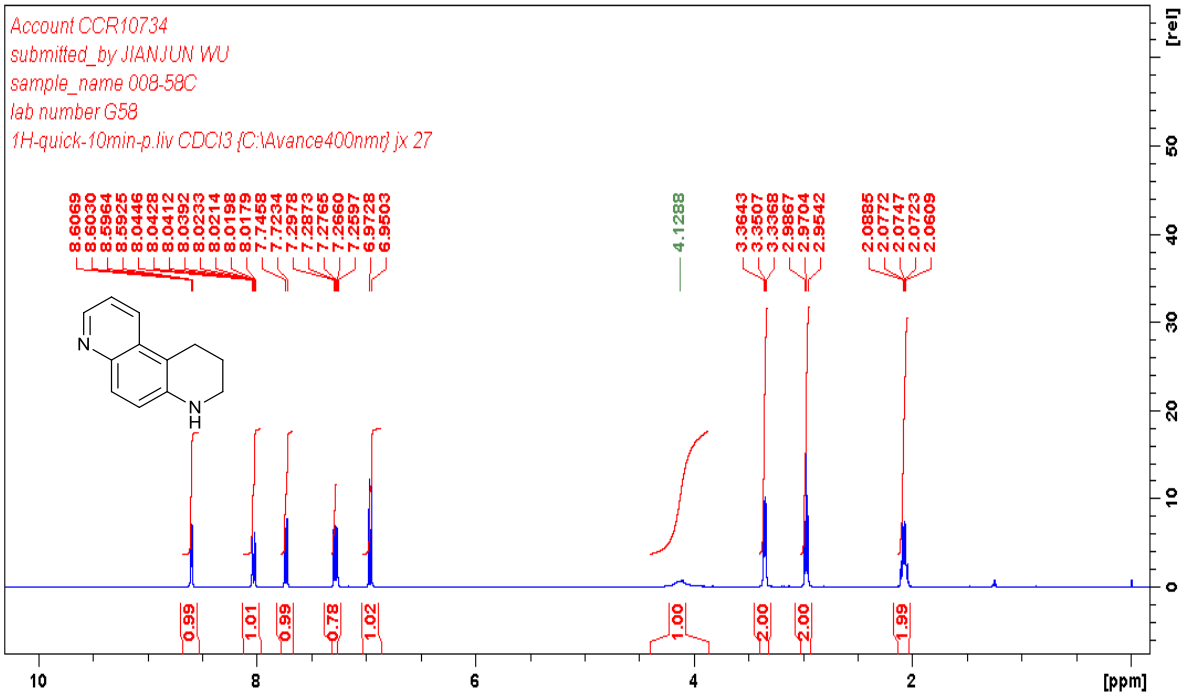
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of *meso*-1,1',2,2',3,3',4,4'-octahydro-2,2'-biquinoline (**3e**)



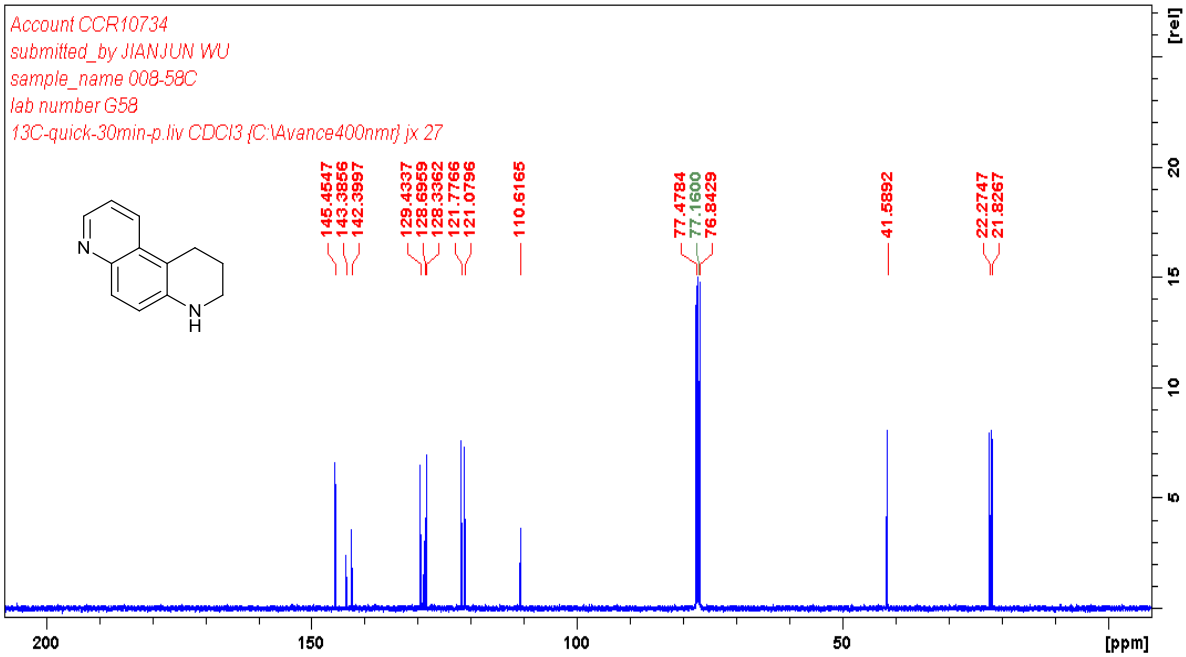
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9,10-dihydroacridine (**3f**)



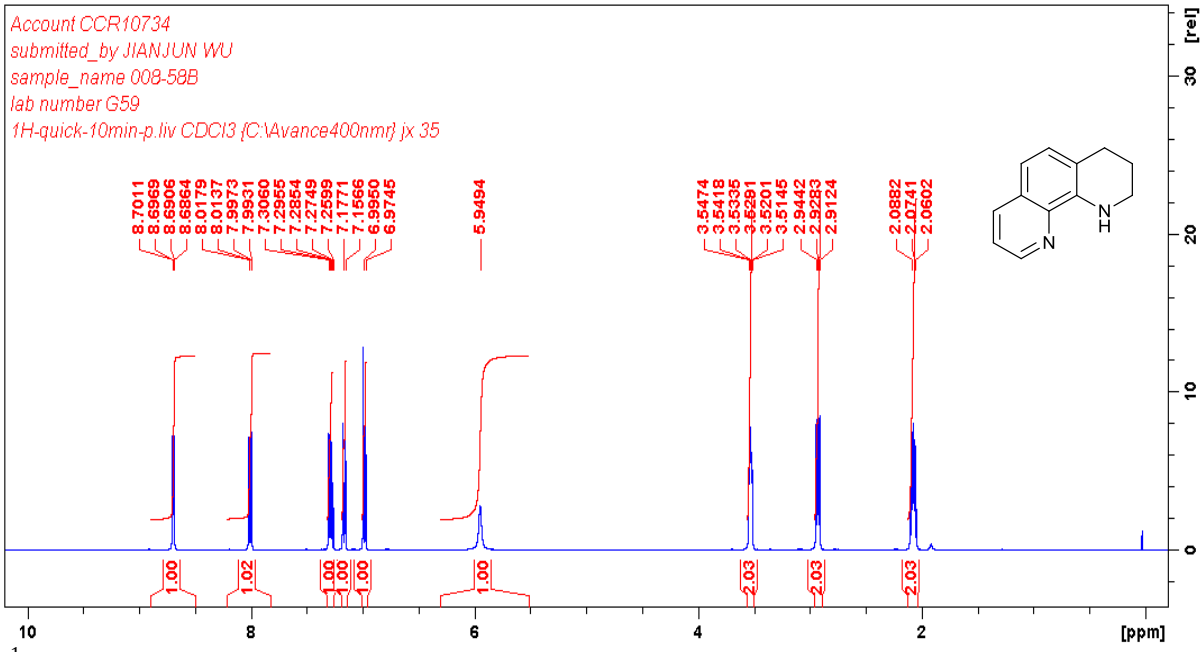
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 9,10-dihydroacridine (**3f**)



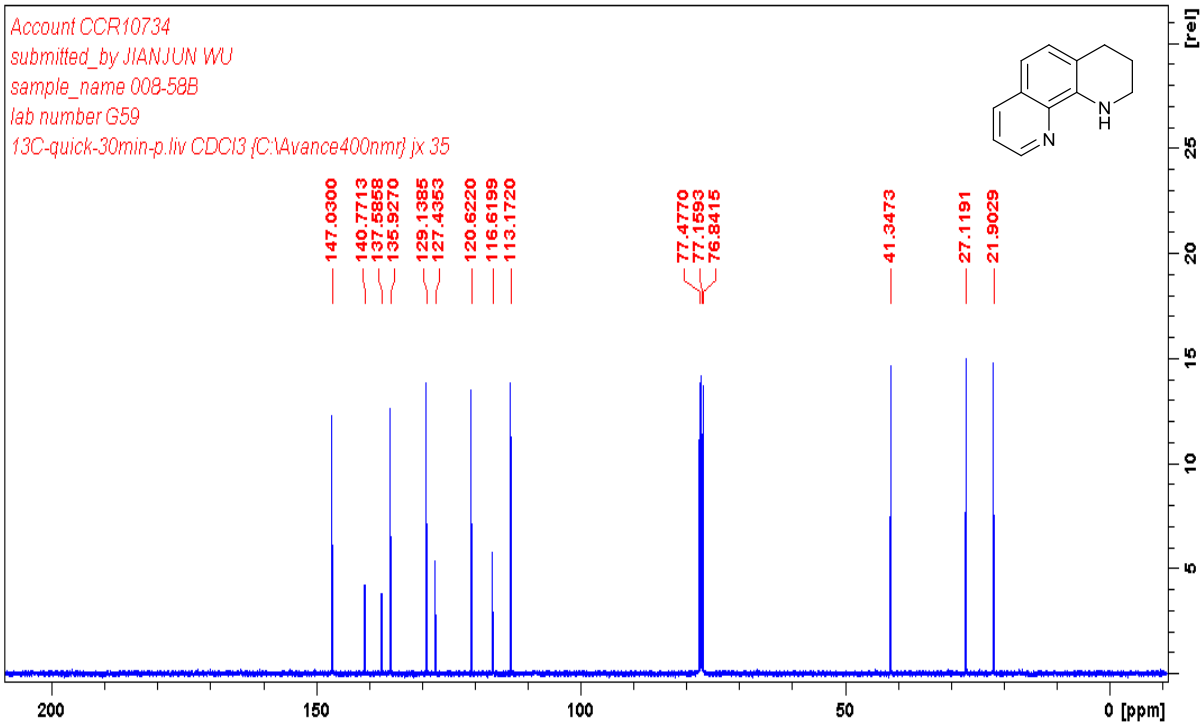
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydro-4,7-phenanthroline (**3g**)



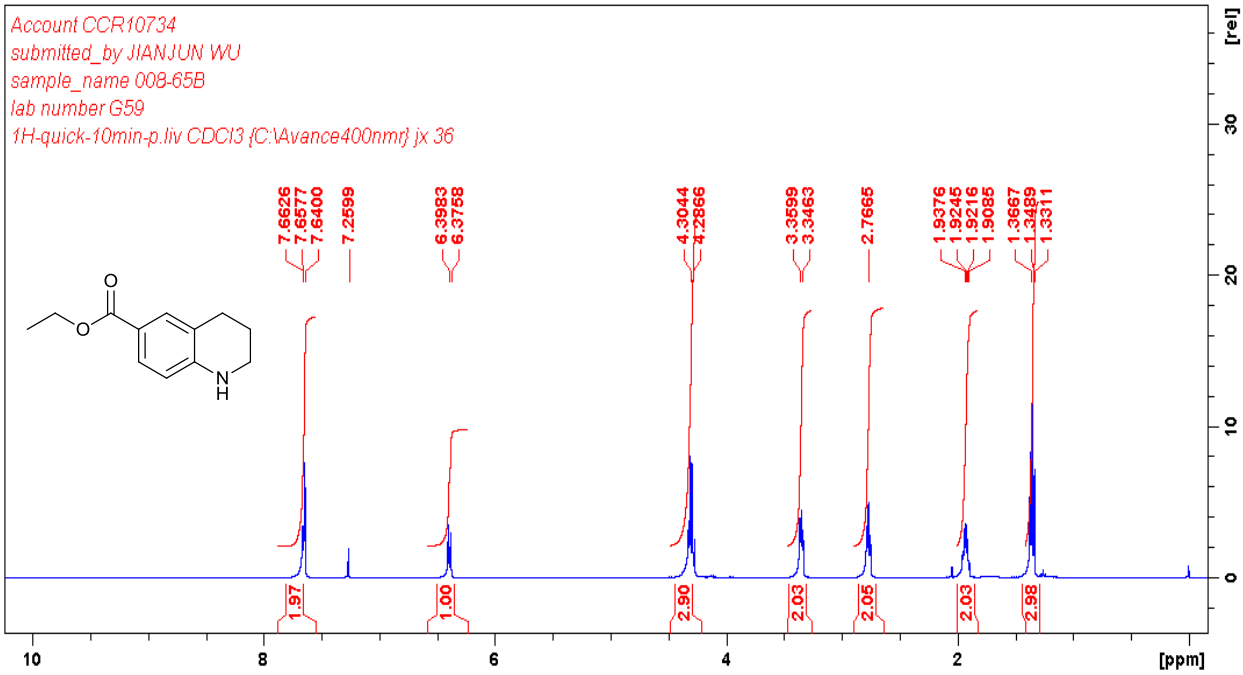
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydro-4,7,-phenanthroline (**3g**)



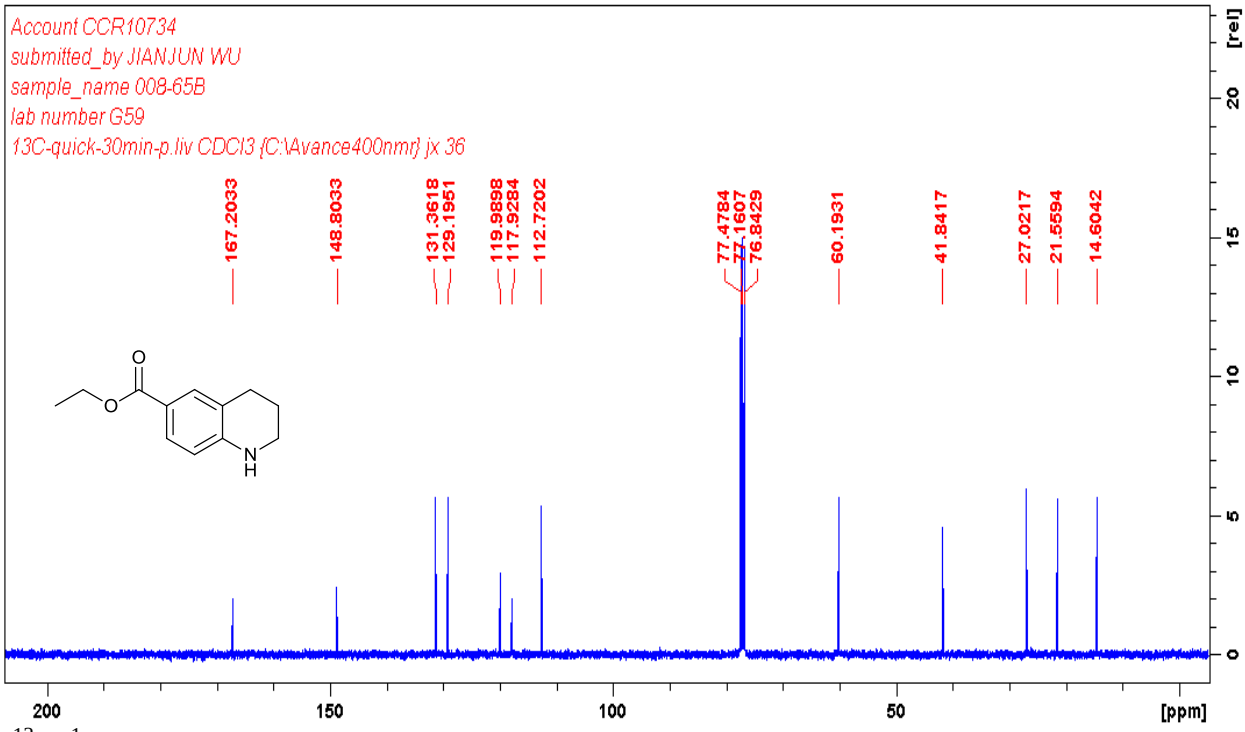
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydro-1,10-phenanthroline (**3h**)



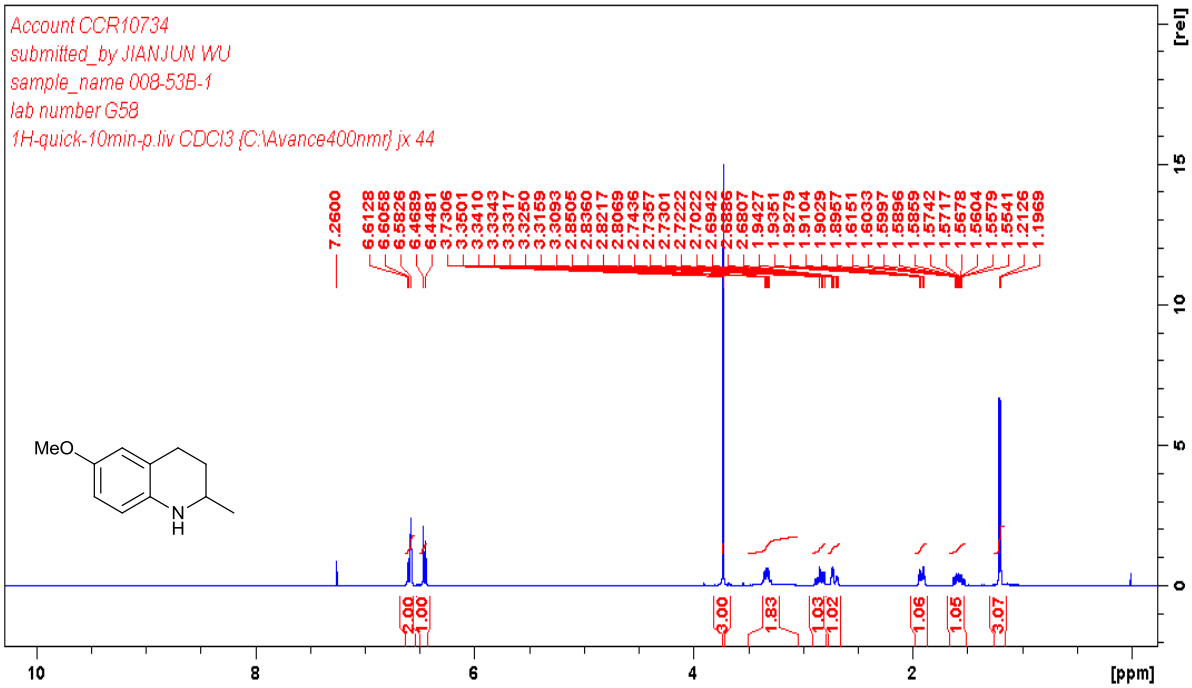
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydro-1,10 phenanthroline (**3h**)



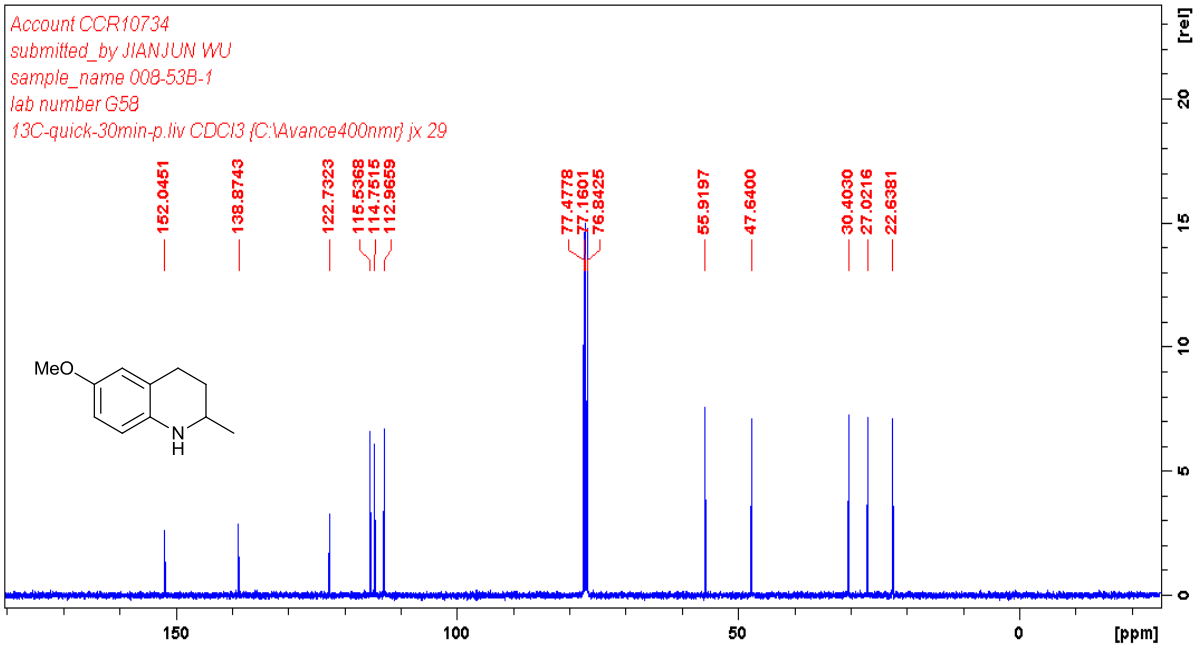
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (**3i**)



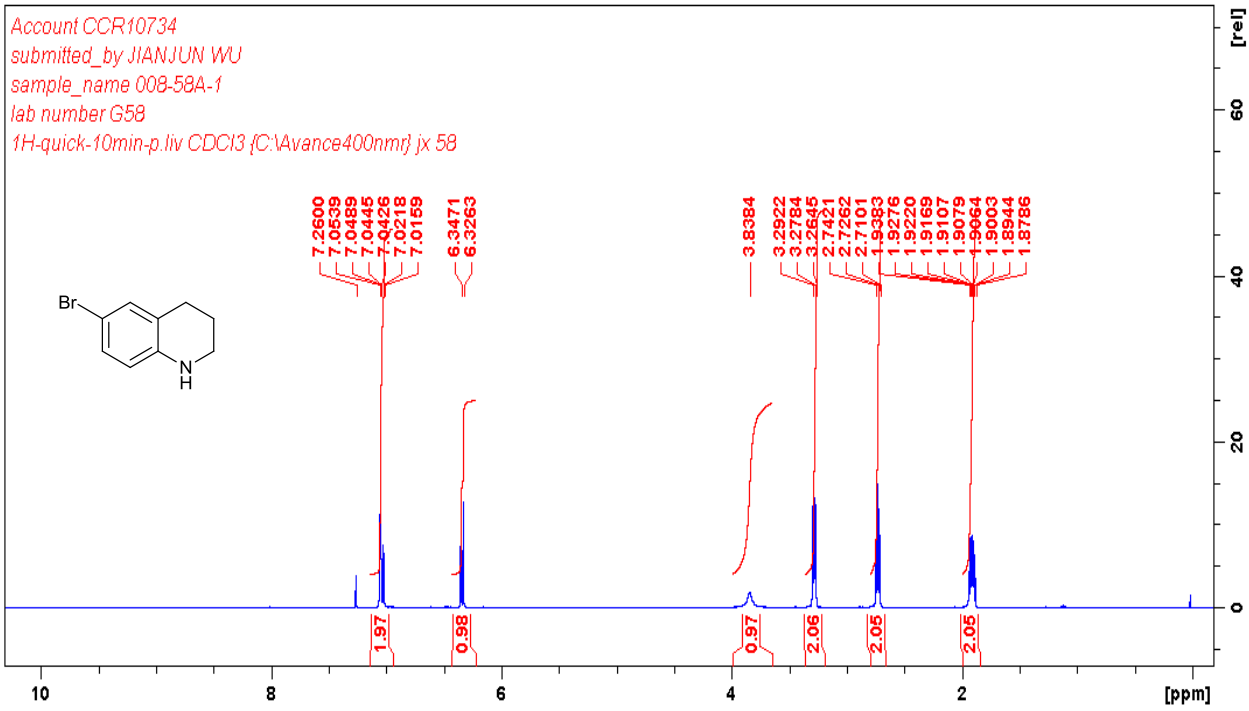
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of ethyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (**3i**)



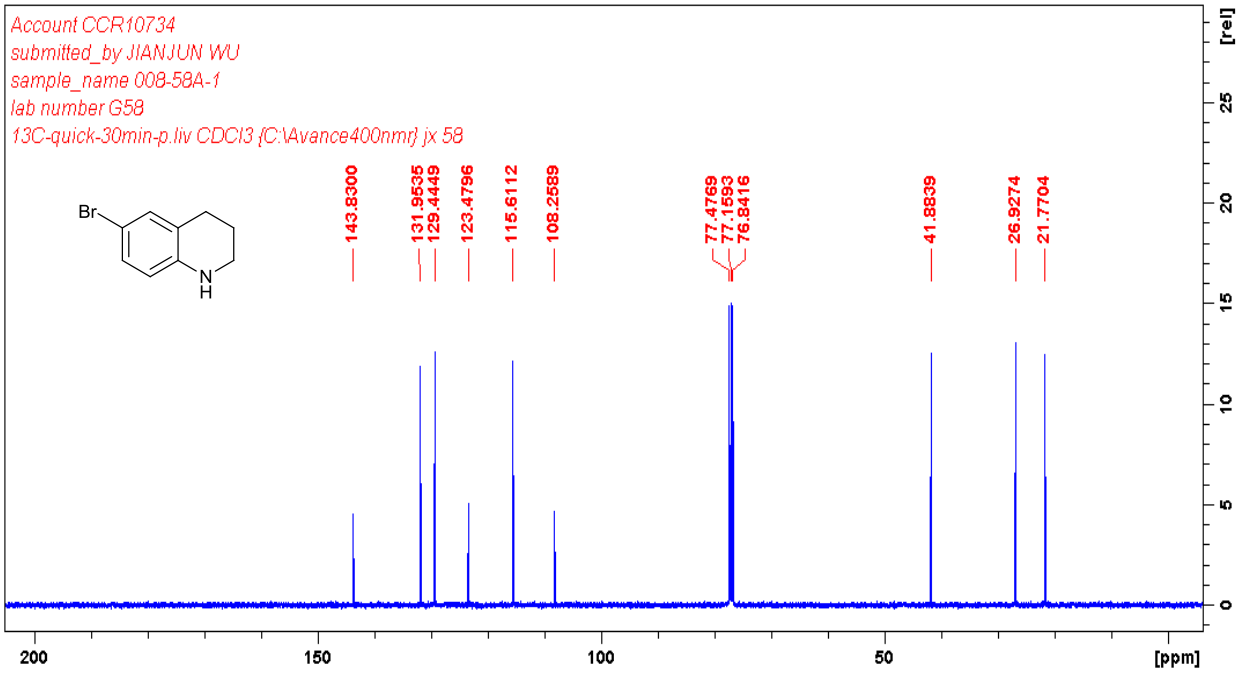
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-methoxy-2-methyl-1,2,3,4-tetrahydro quinoline (**3j**)



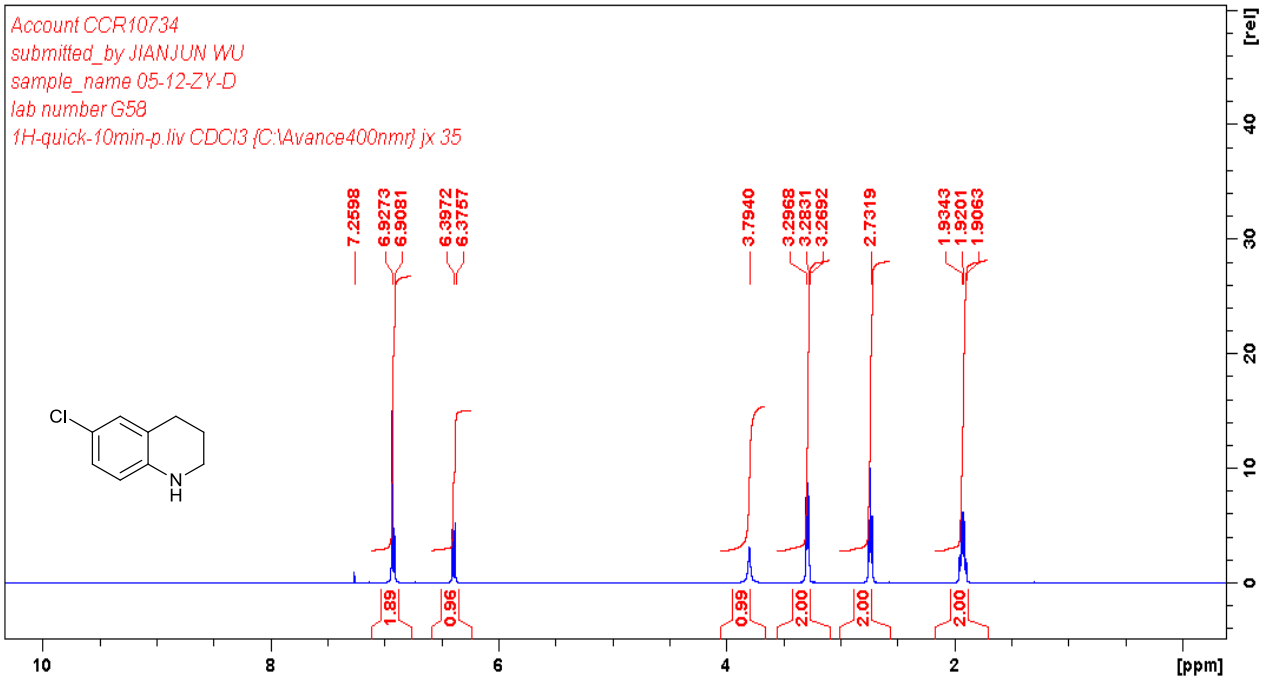
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 6-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (**3j**)



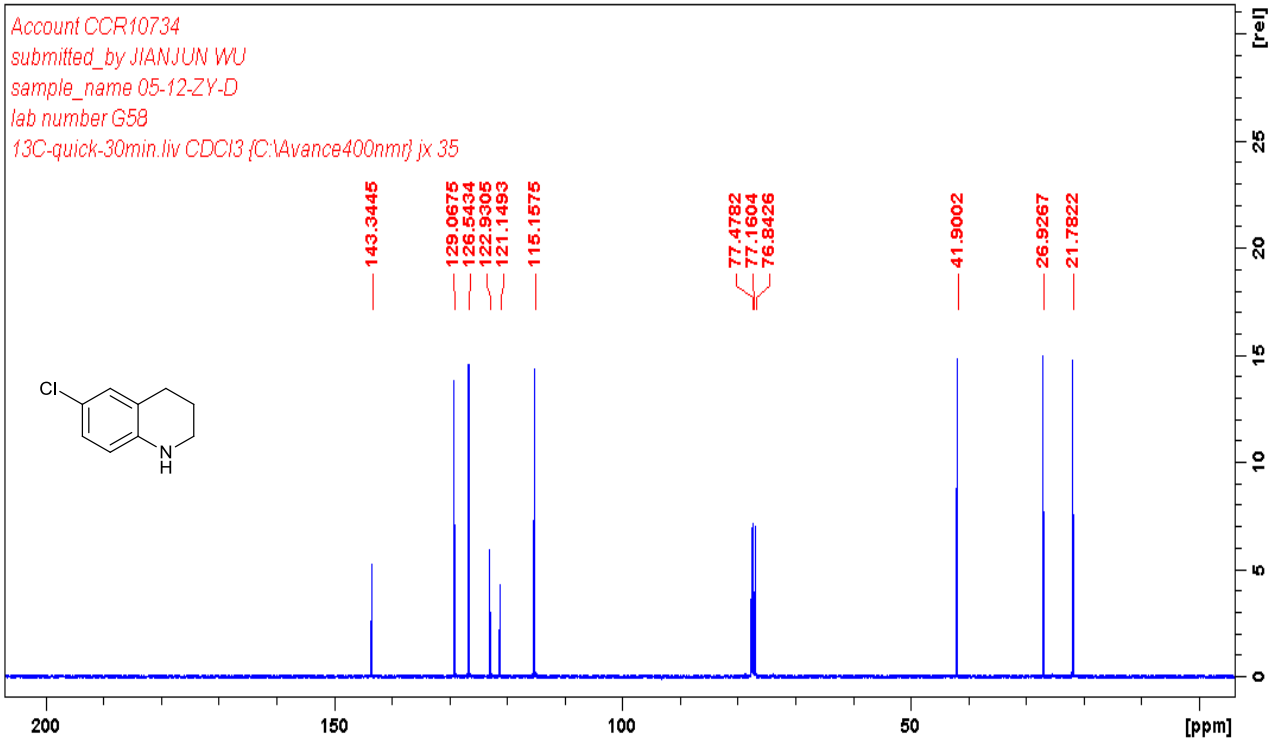
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-bromo-1,2,3,4-tetrahydroquinoline (**3k**)



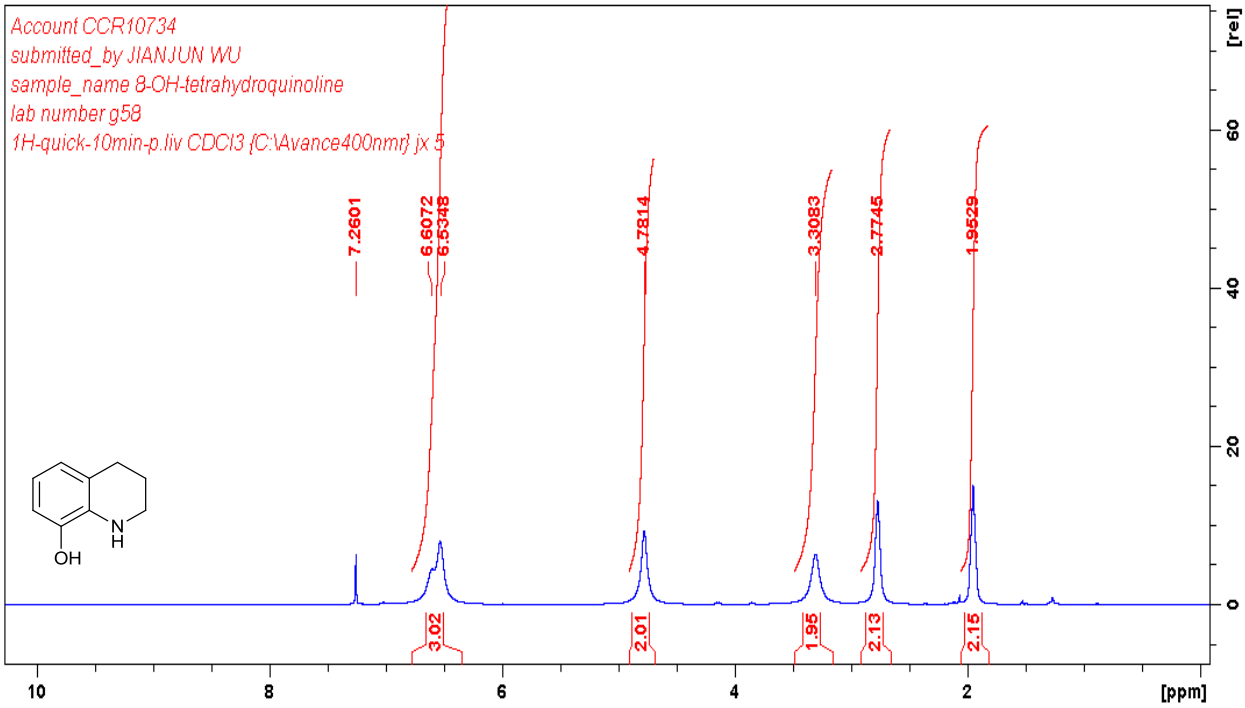
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 6-bromo-1,2,3,4-tetrahydroquinoline (**3k**)



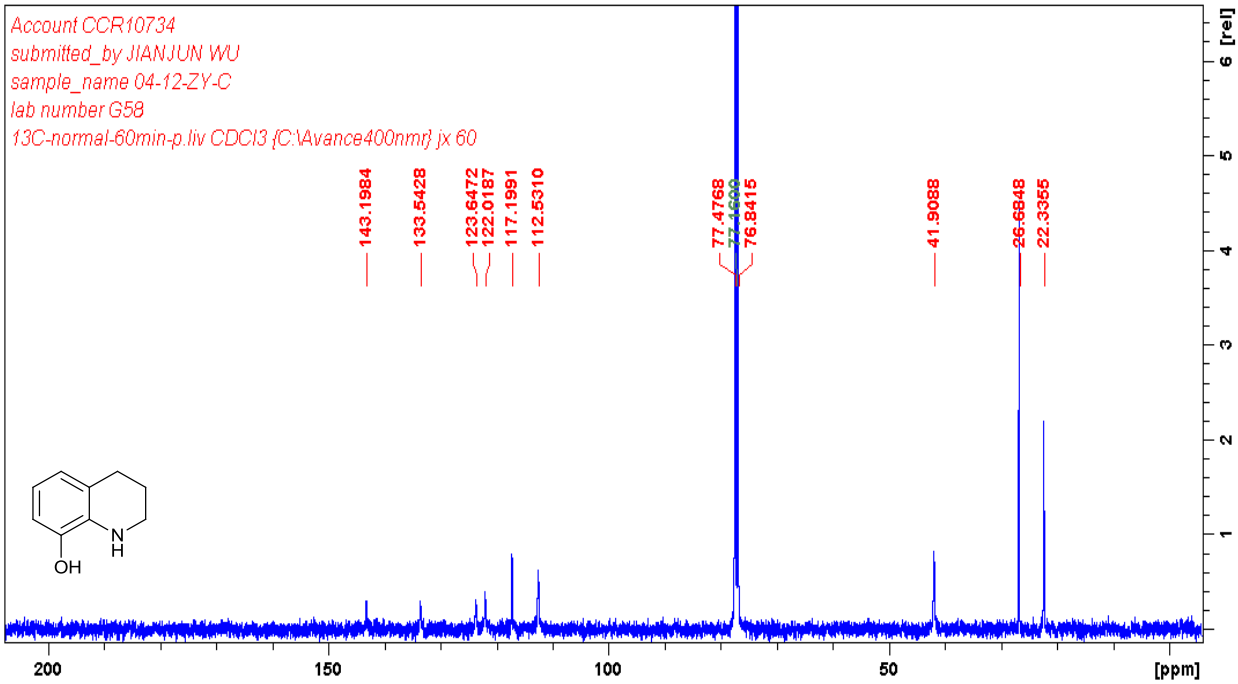
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-chloro-1,2,3,4-tetrahydroquinoline (**3l**)



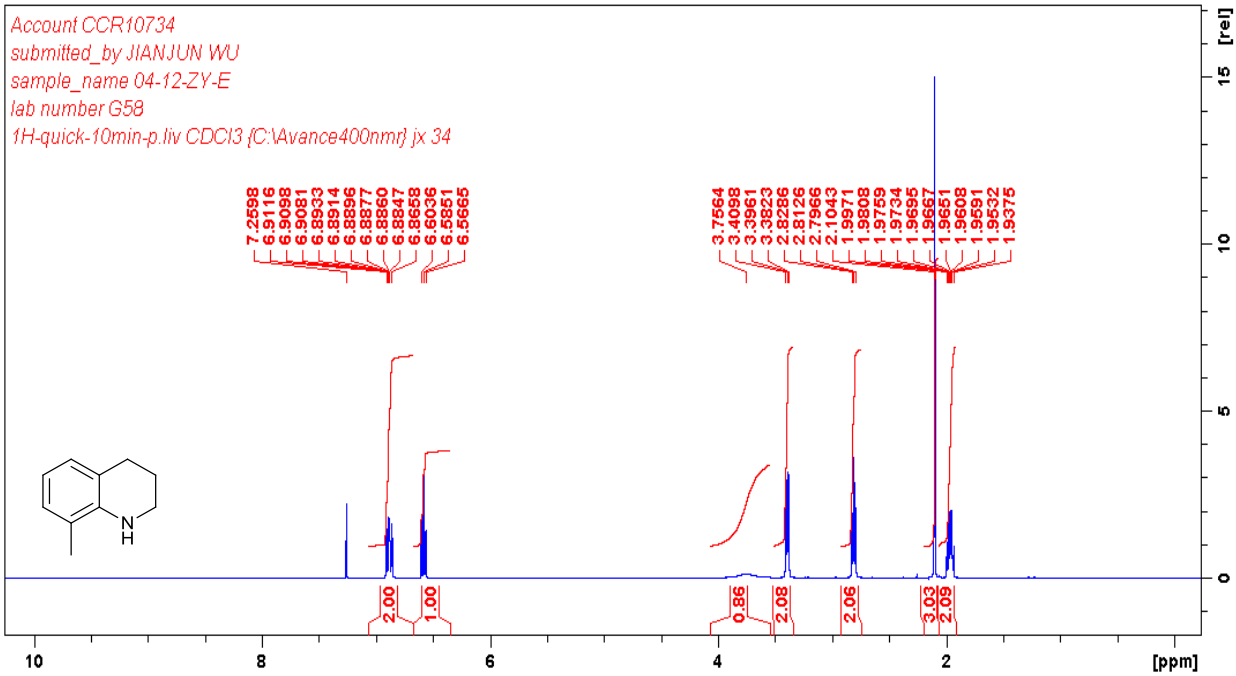
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 6-chloro-1,2,3,4-tetrahydroquinoline (**3l**)



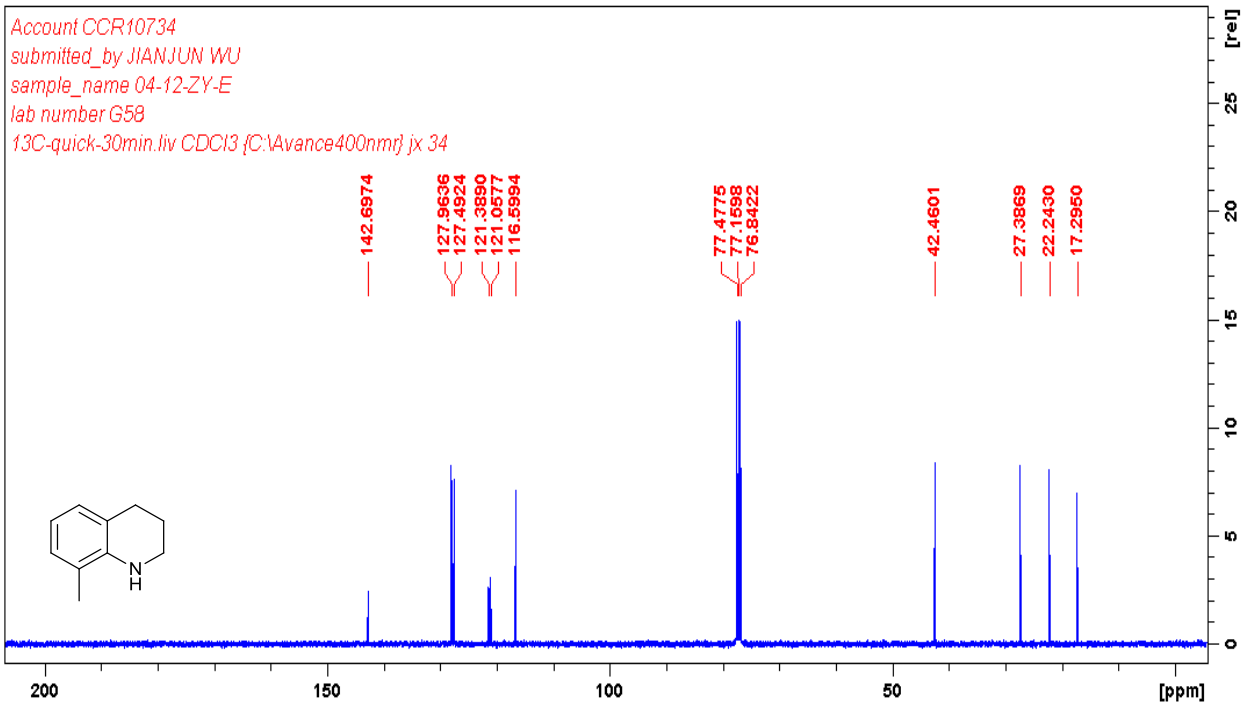
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8-hydroxy-1,2,3,4-tetrahydroquinoline (**3m**)



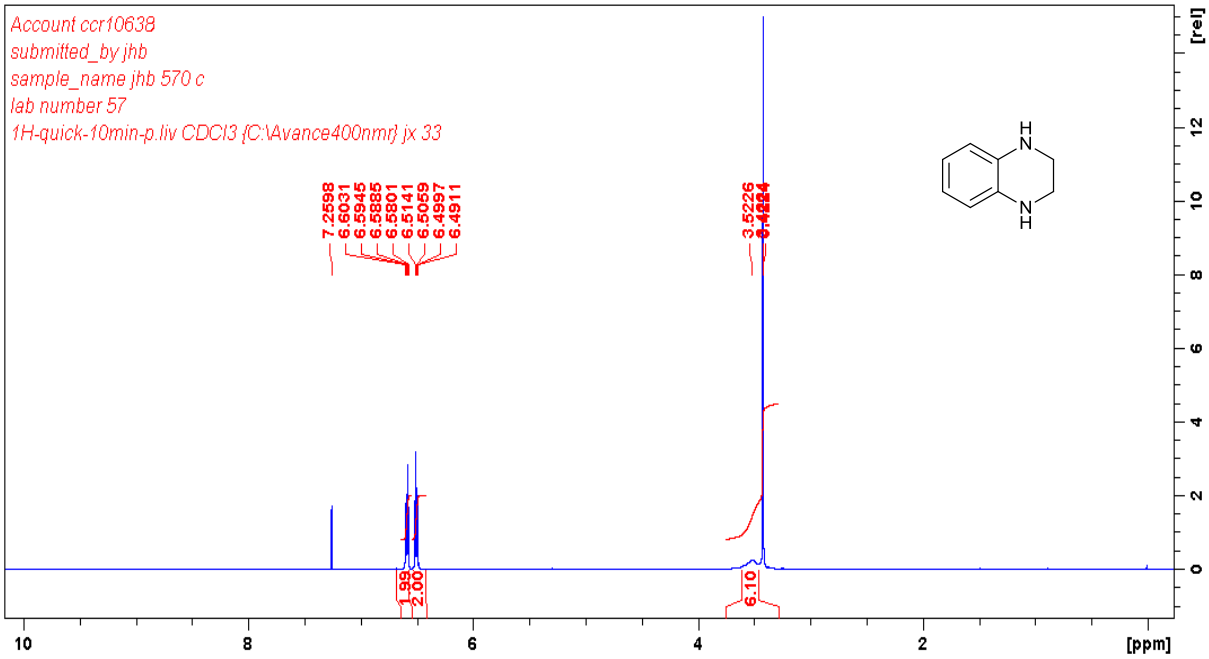
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 8-hydroxy-1,2,3,4-tetrahydroquinoline (**3m**)



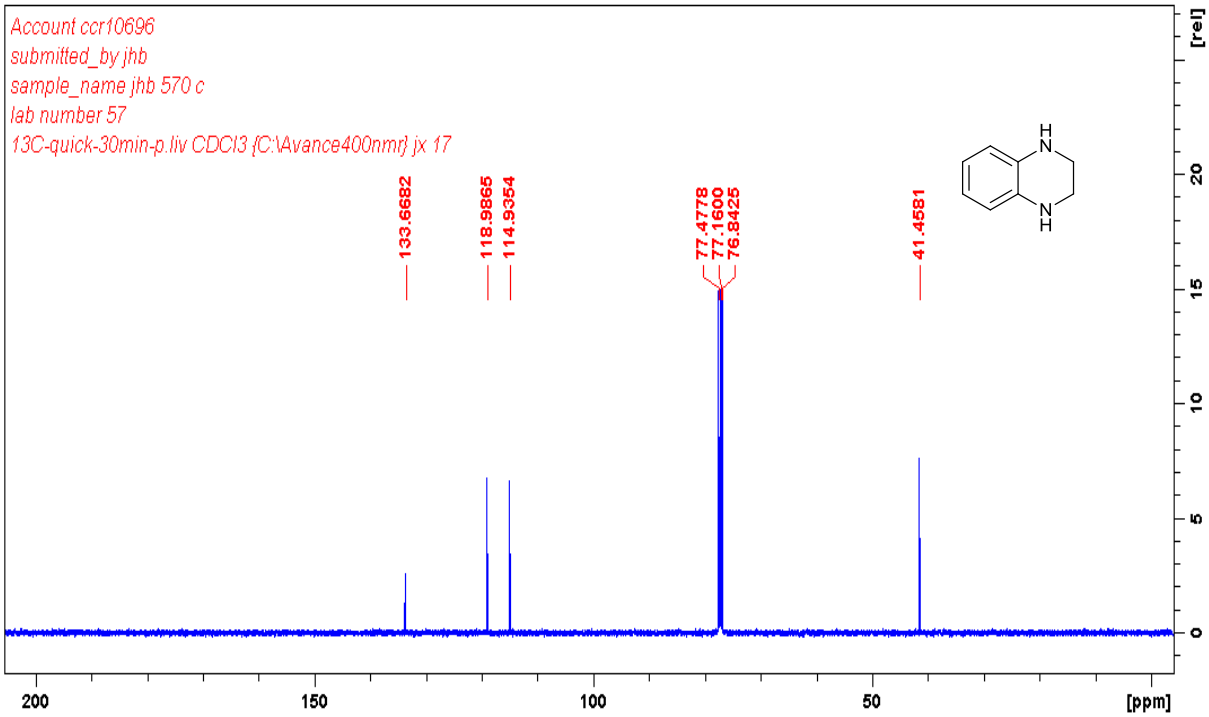
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8-methyl-1,2,3,4-tetrahydroquinoline (**3n**)



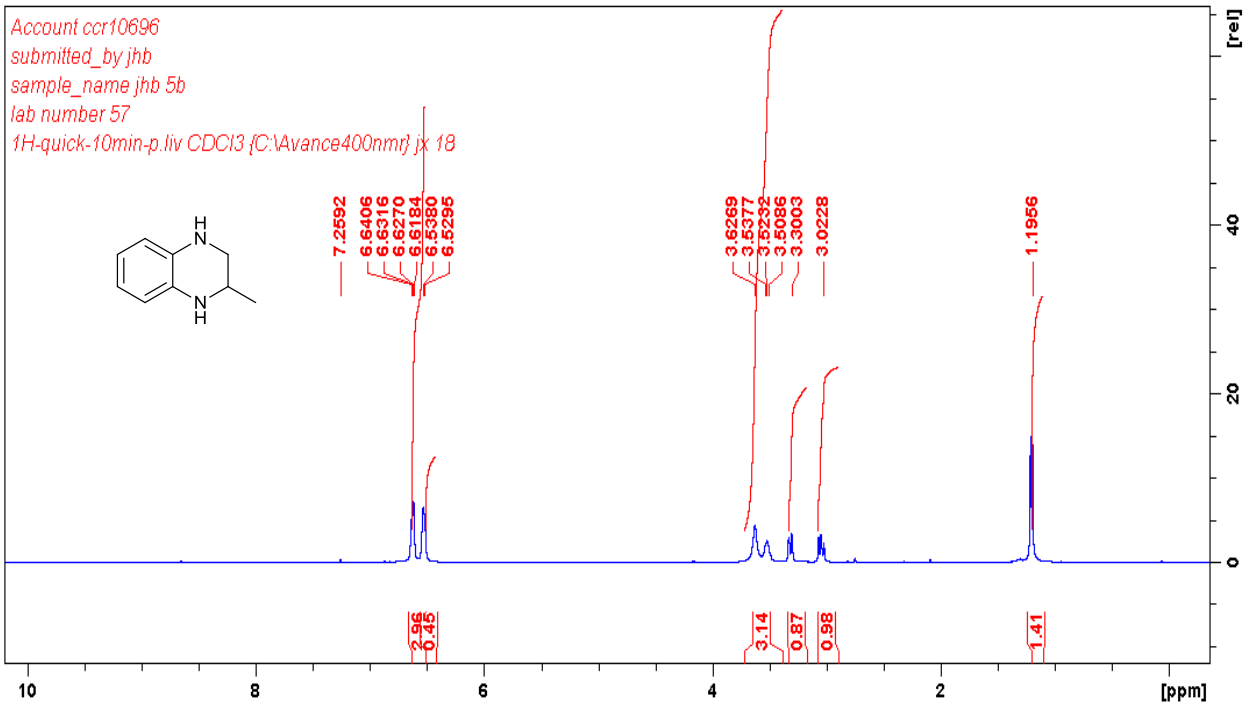
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 8-methyl-1,2,3,4-tetrahydroquinoline (**3n**)



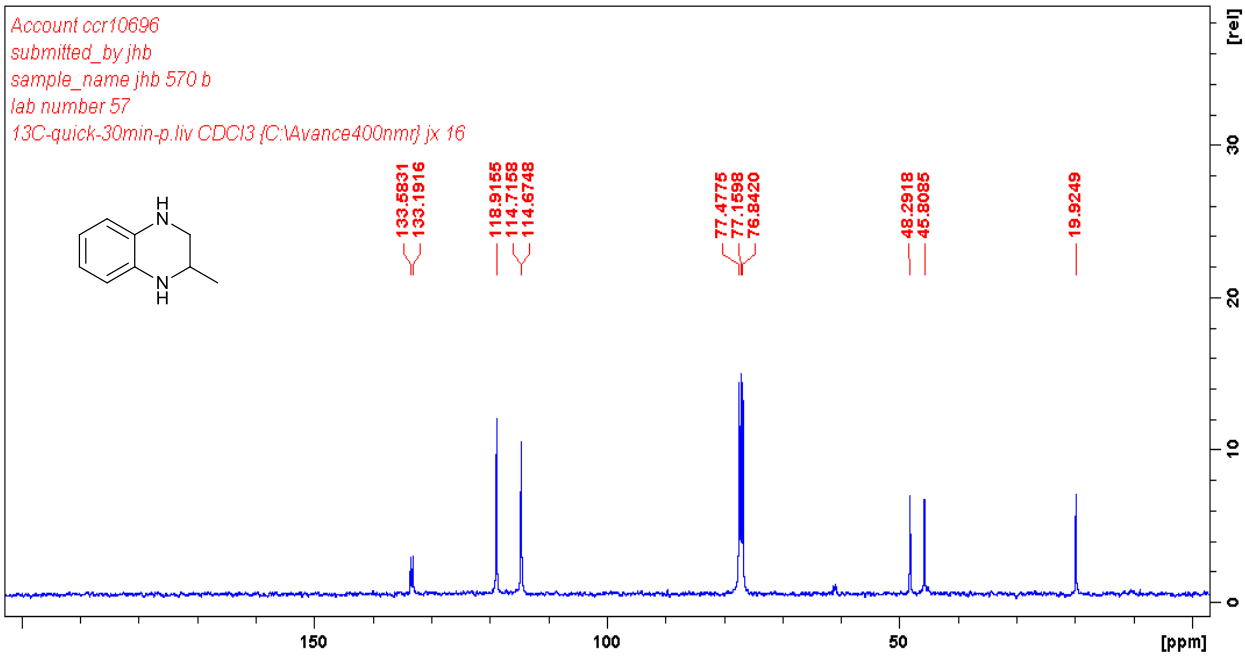
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydroquinoxaline (**5a**)



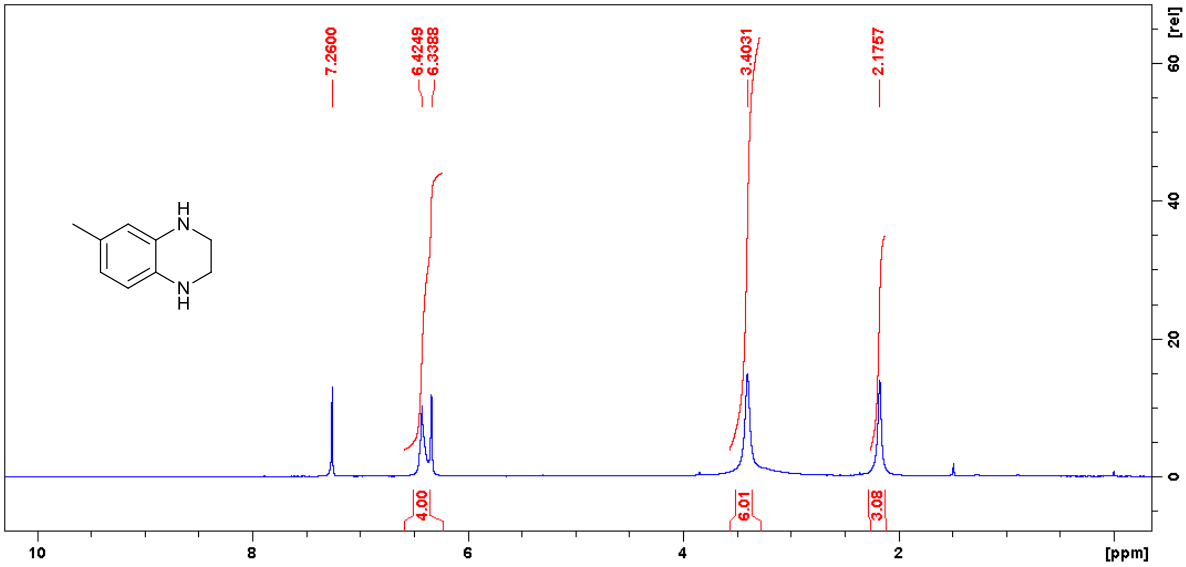
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1,2,3,4-tetrahydroquinoxaline (**5a**)



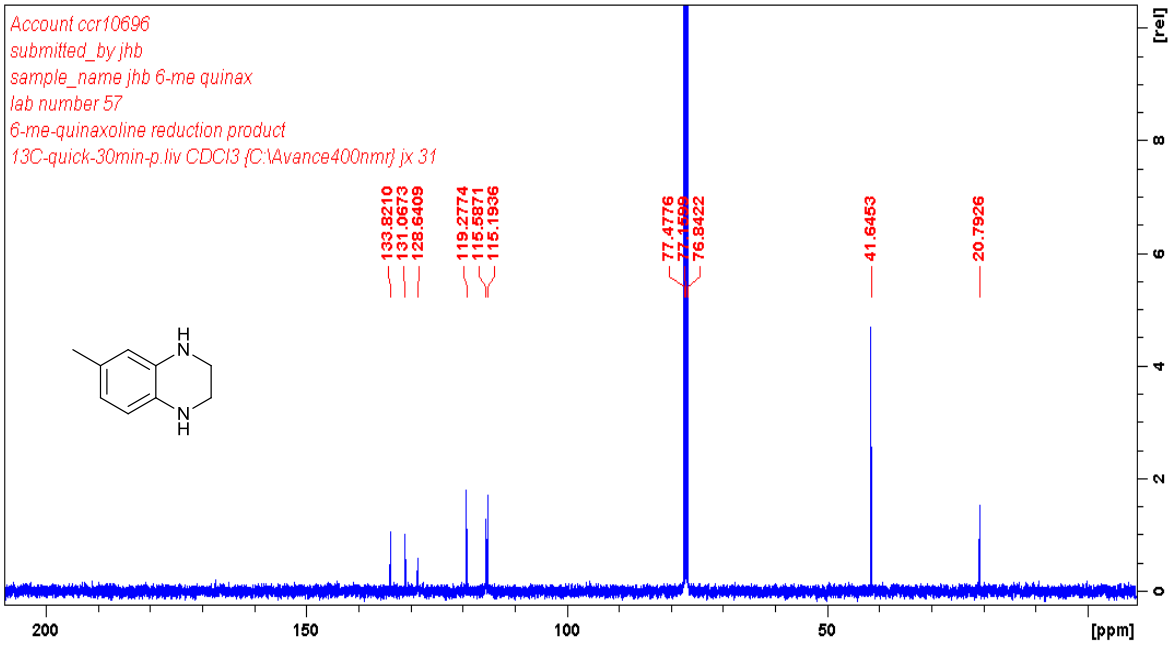
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-methyl-1,2,3,4-tetrahydroquinoxaline (**5b**)



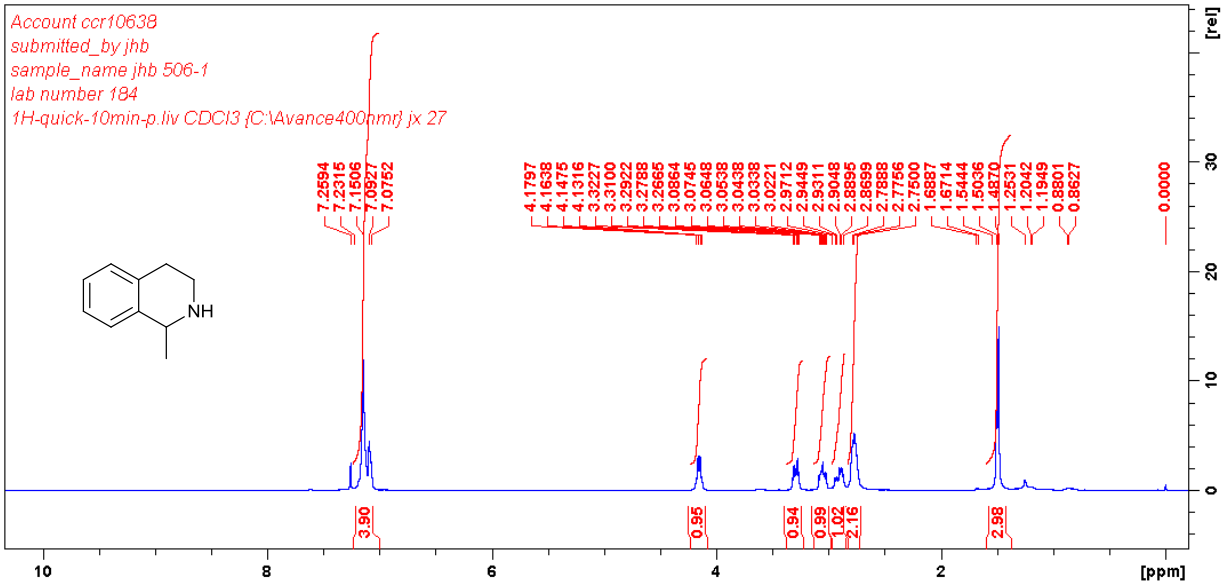
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 2-methyl-1,2,3,4-tetrahydro quinoxaline (**5b**)



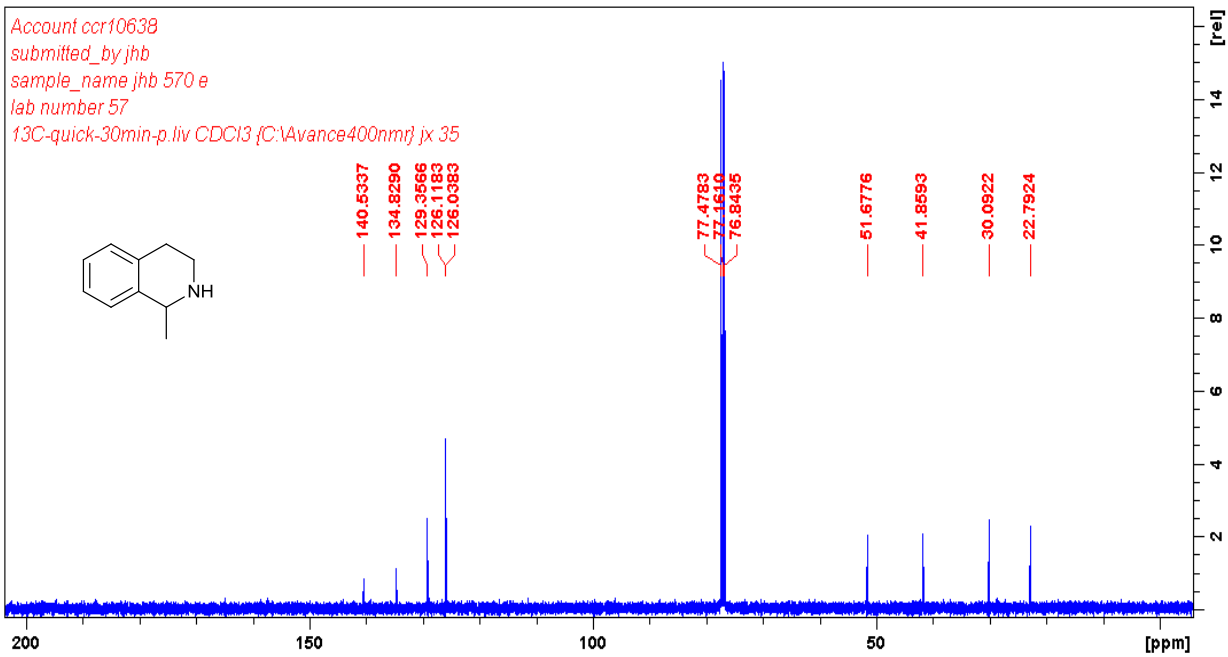
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-methyl-1,2,3,4-tetrahydroquinoxaline (**5c**)



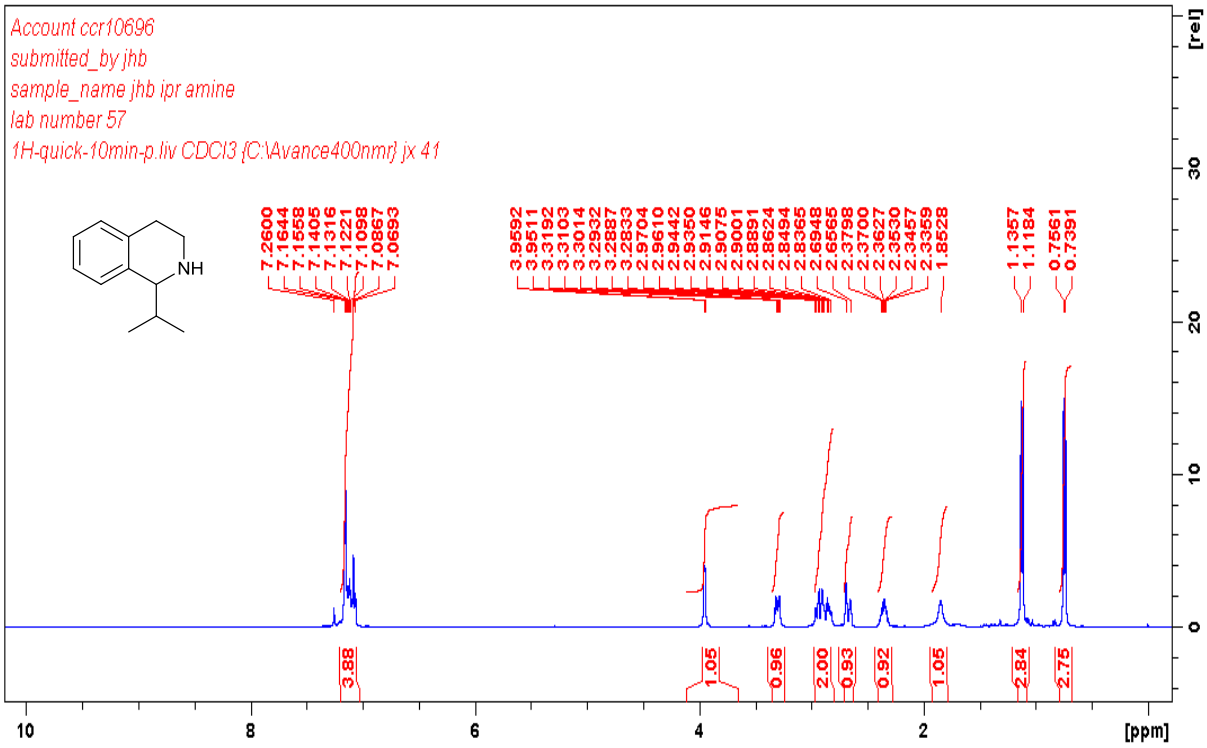
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 6-methyl-1,2,3,4-tetrahydro quinoxaline (**5c**)



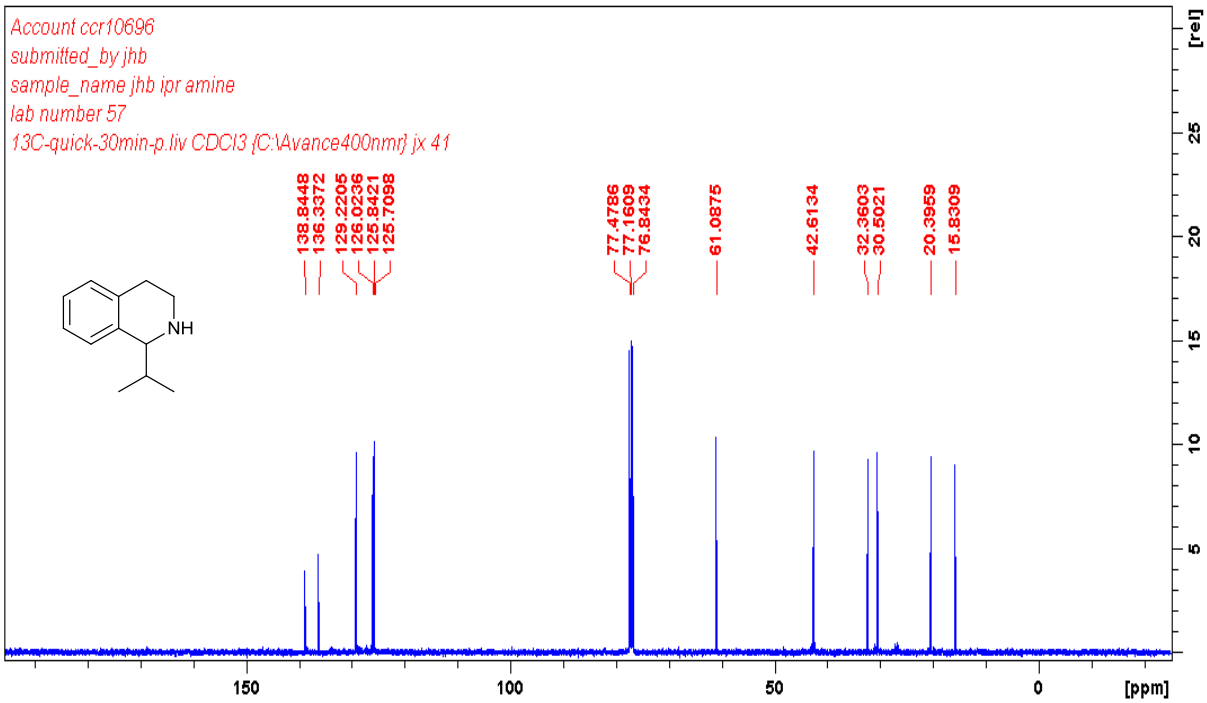
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-methyl-1,2,3,4-tetrahydroisoquinoline (**5d**)



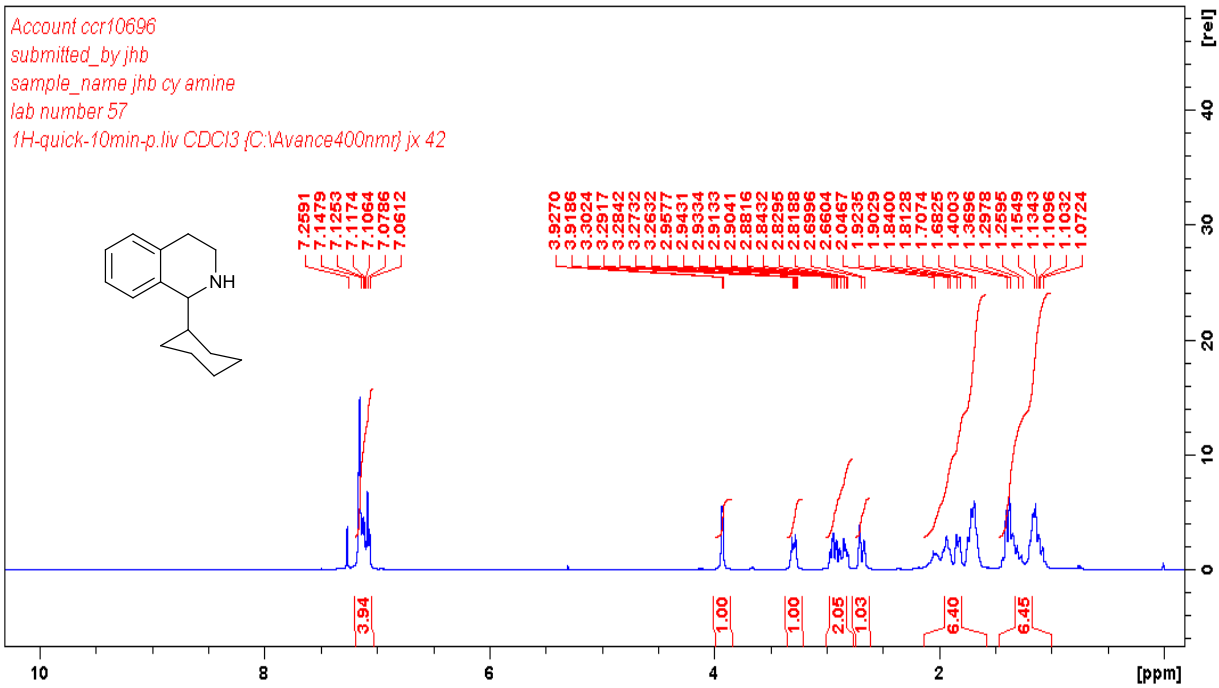
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1-methyl-1,2,3,4-tetrahydroisoquinoline (**5d**)



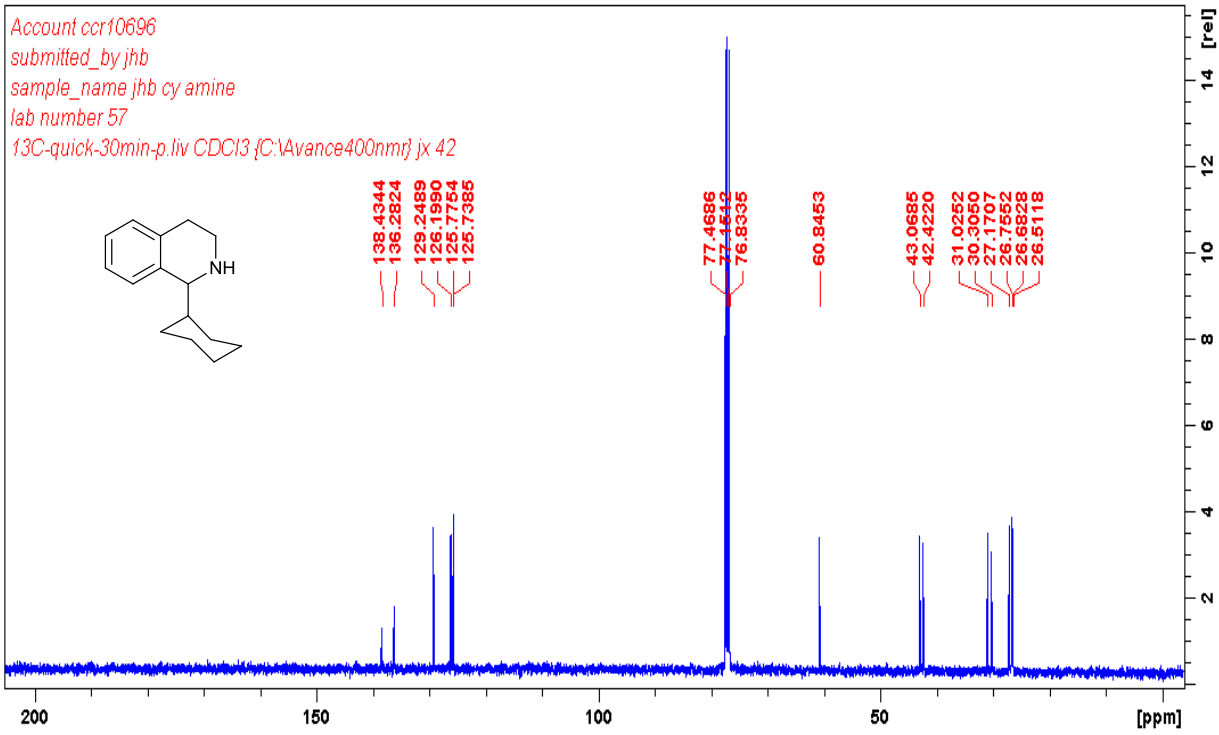
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-*iso*propyl-1,2,3,4-tetrahydroisoquinoline (**5e**)



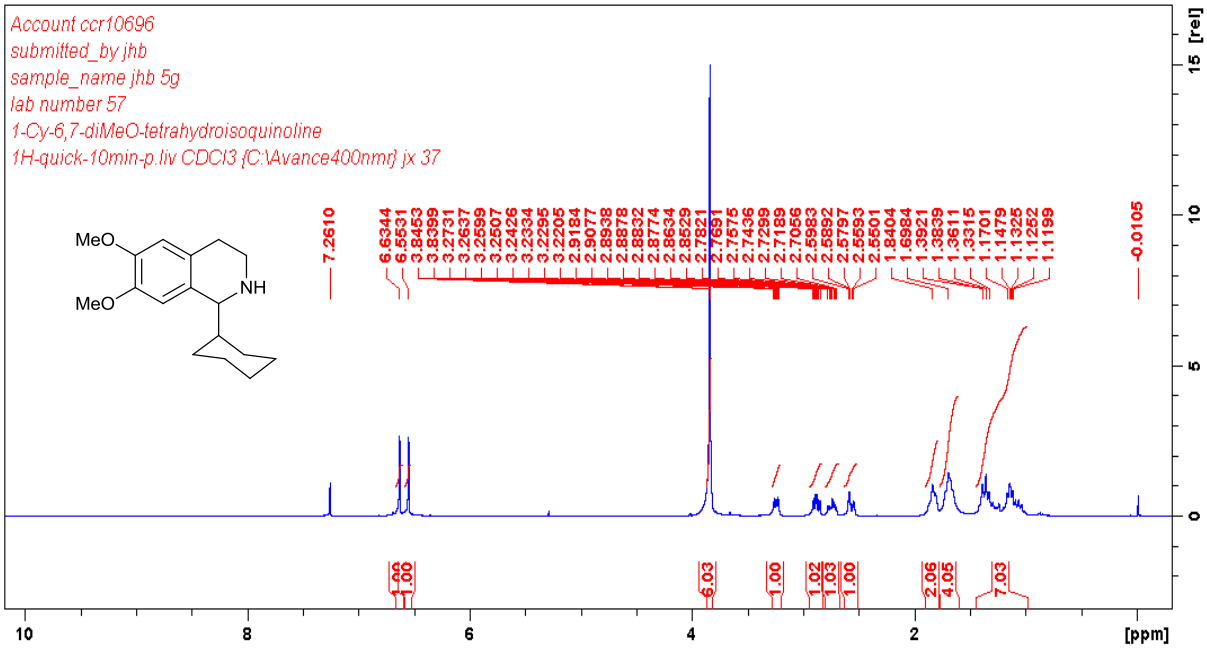
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1-*iso*propyl-1,2,3,4-tetrahydroisoquinoline (**5e**)



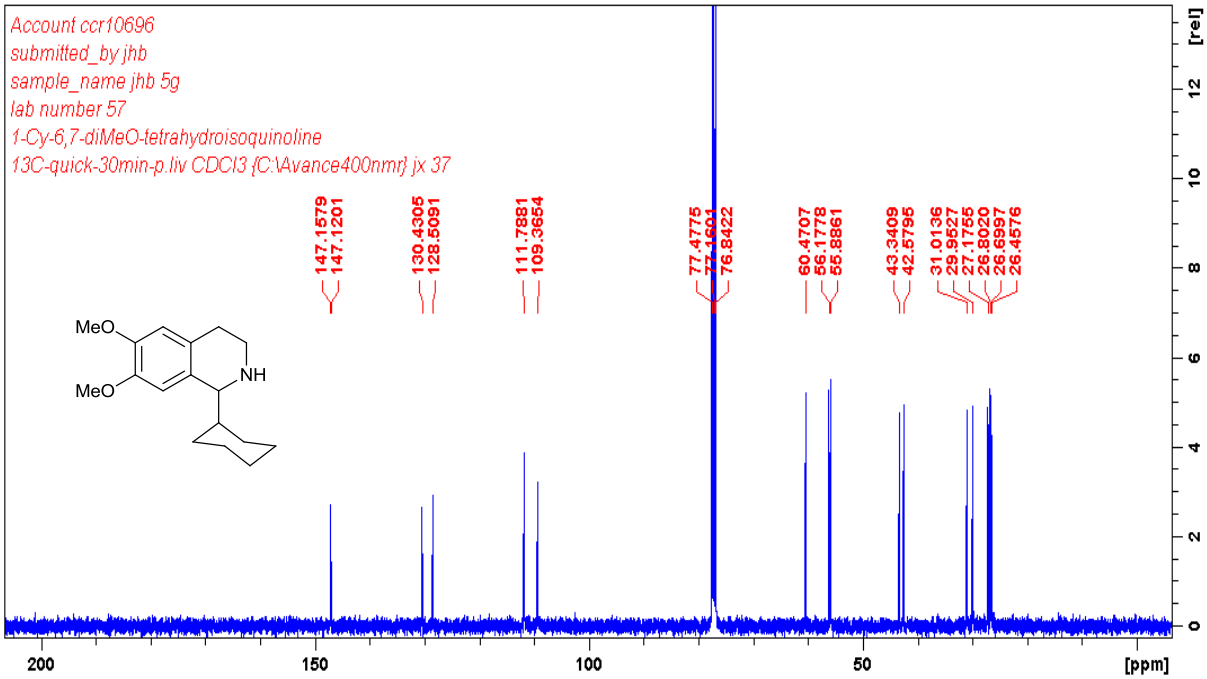
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-cyclohexyl-1,2,3,4-tetrahydroisoquinoline (**5f**)



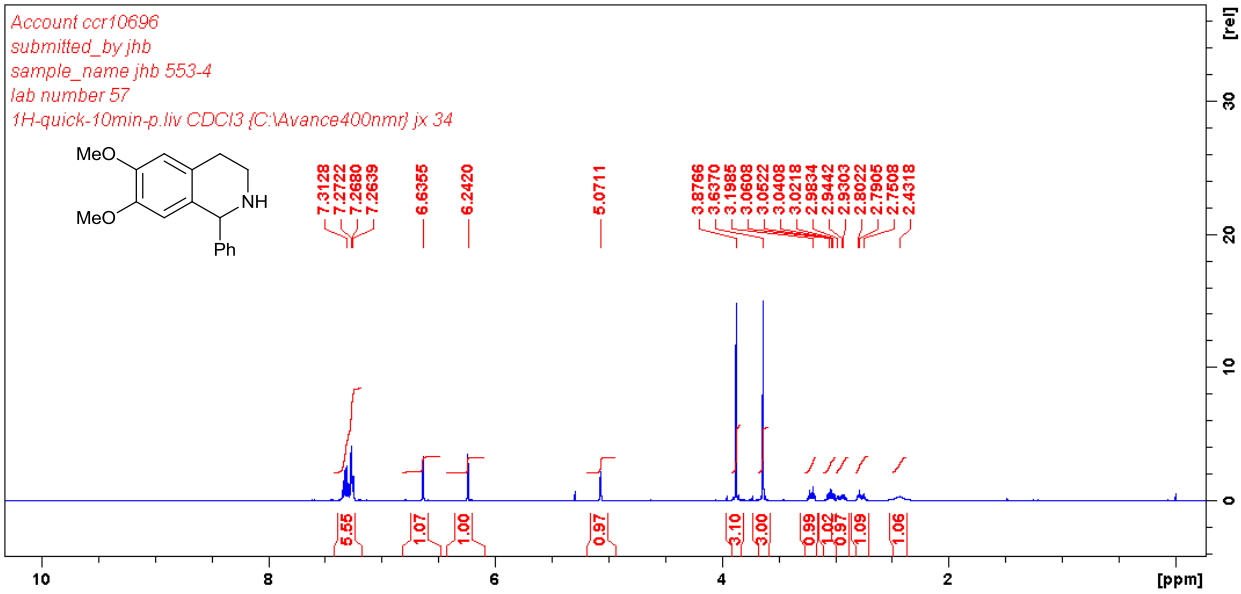
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1-cyclohexyl-1,2,3,4-tetrahydroisoquinoline (**5f**)



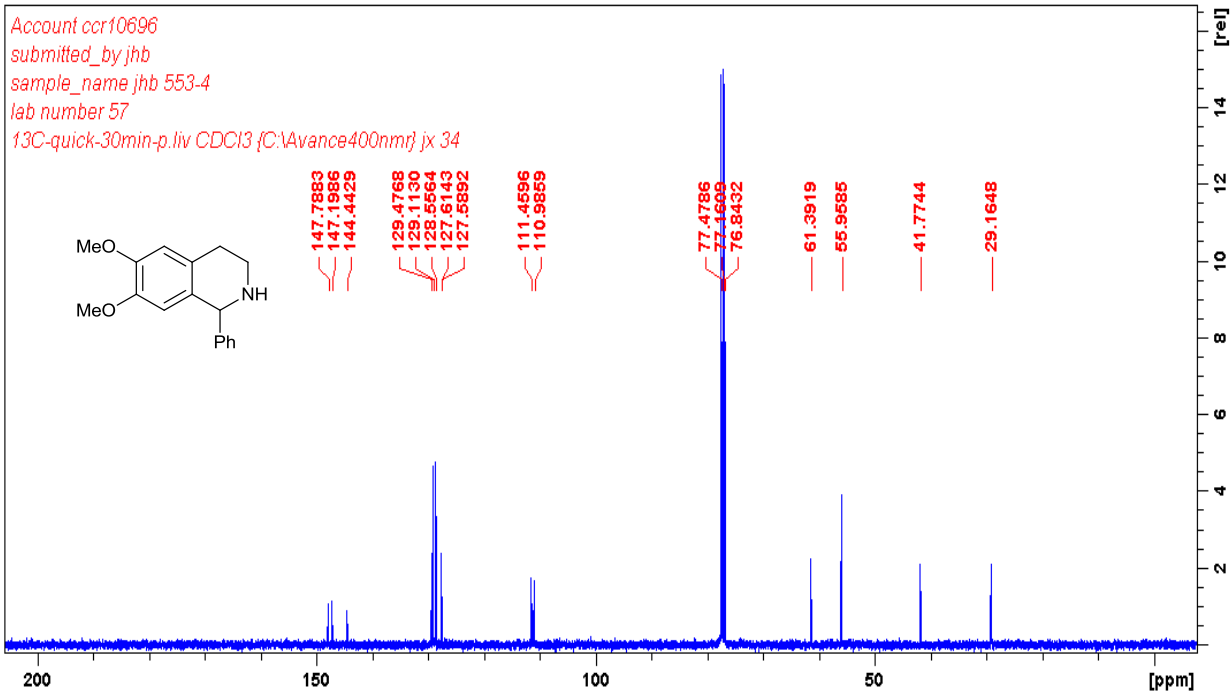
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-cyclohexyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (**5g**)



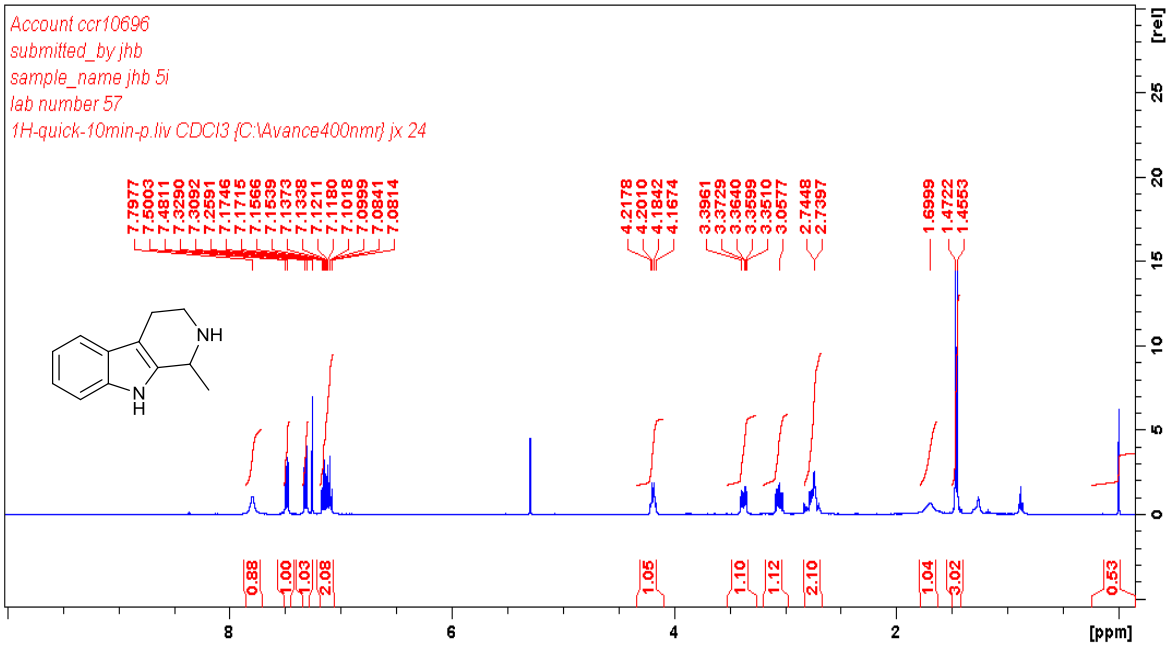
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-cyclohexyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (**5g**)



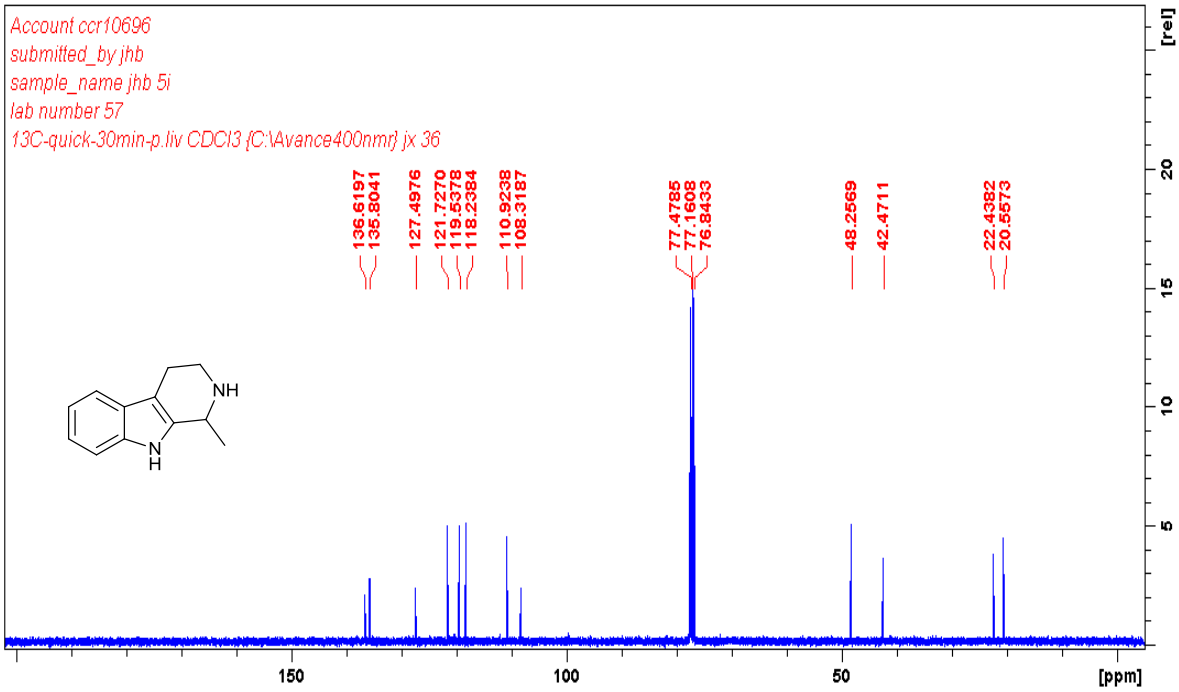
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-phenyl-6,7-dimethoxy-1,2,3,4-tetrahydro isoquinoline (**5h**)



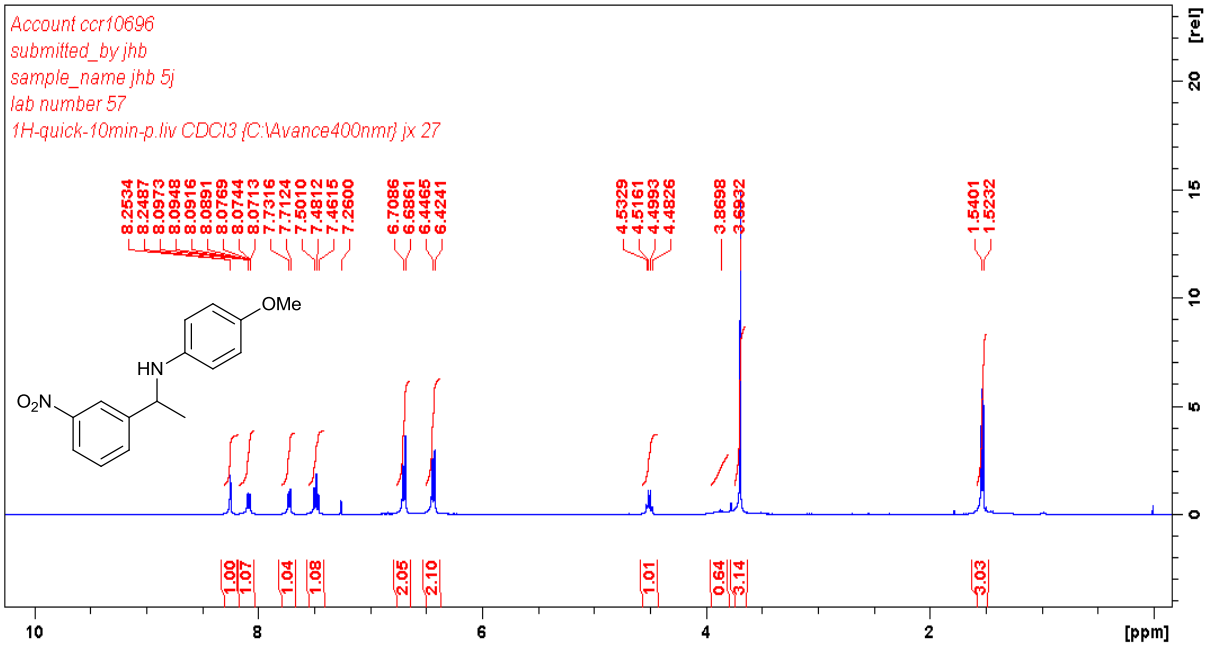
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1-phenyl-6,7-dimethoxy-1,2,3,4-tetrahydro isoquinoline (**5h**)



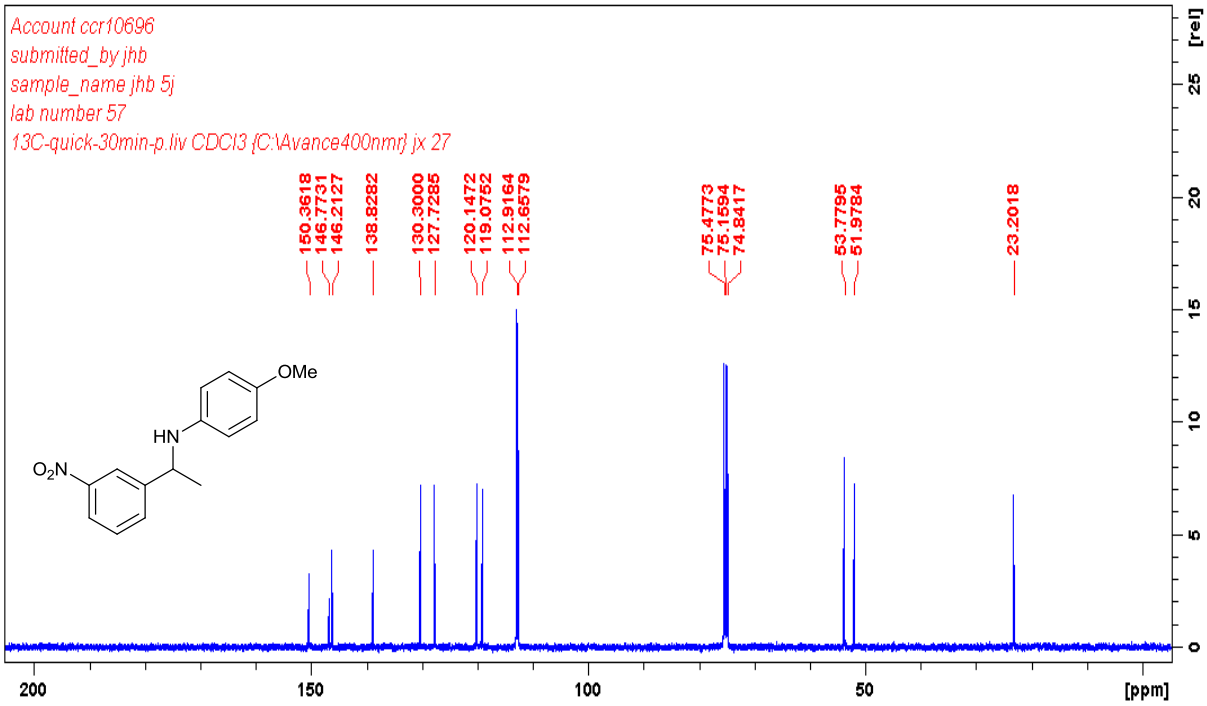
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-methyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (**5i**)



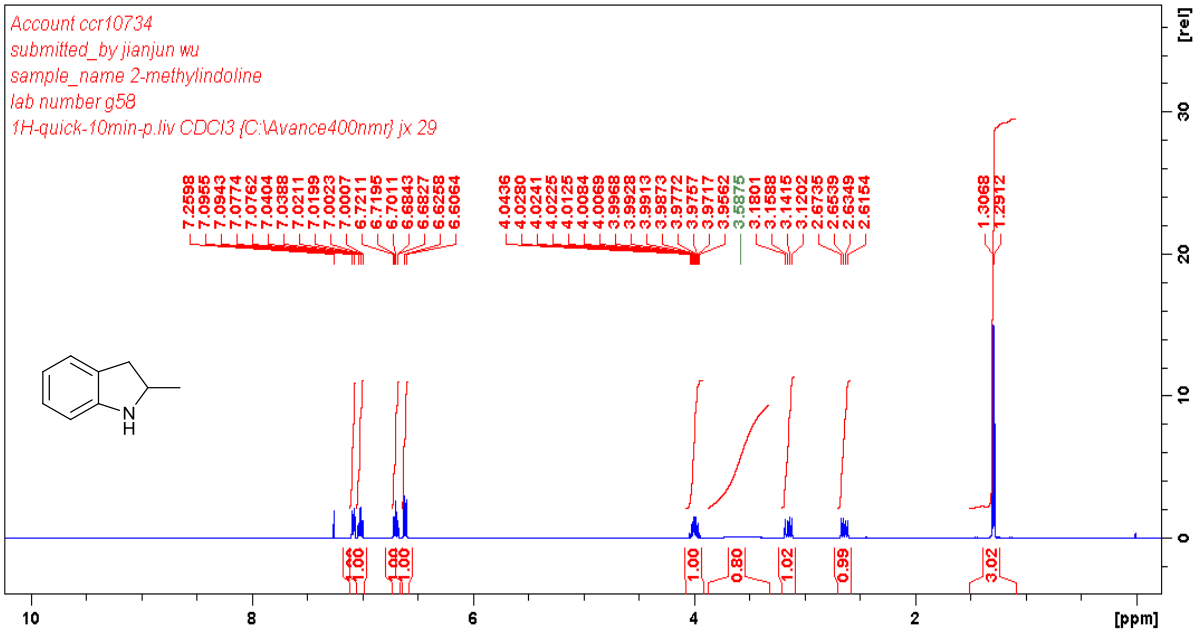
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 1-methyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (**5i**)



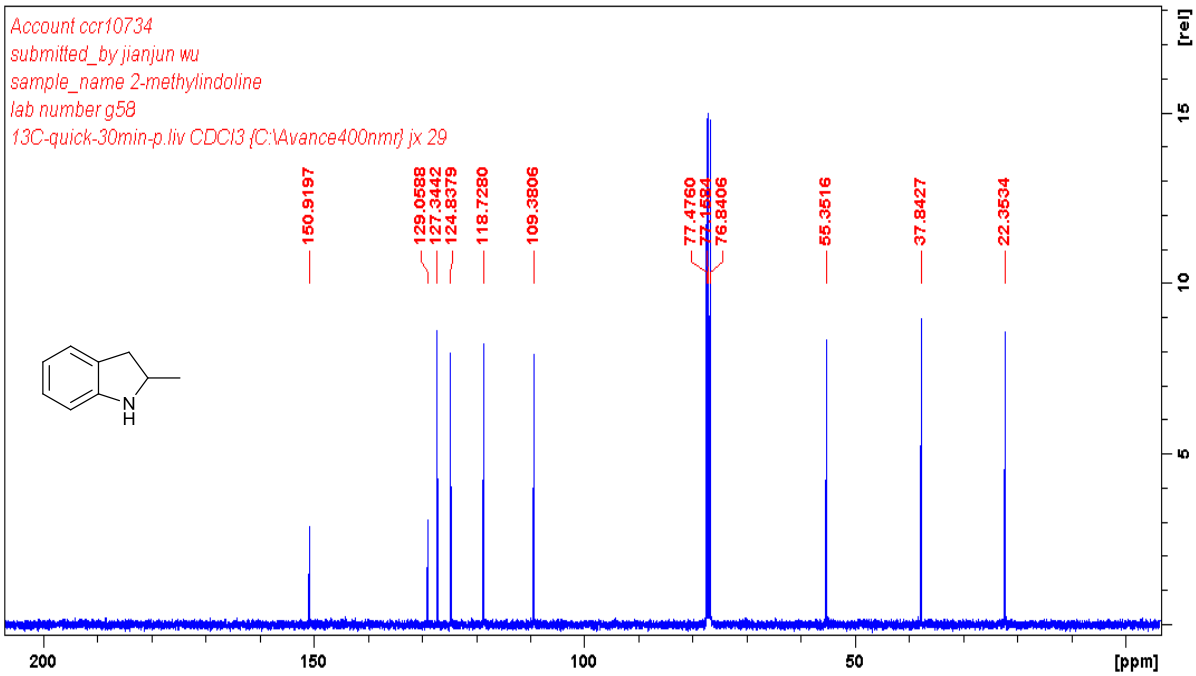
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(1-((4-methoxyphenyl)amino)ethyl) nitrobenzene (**5j**)



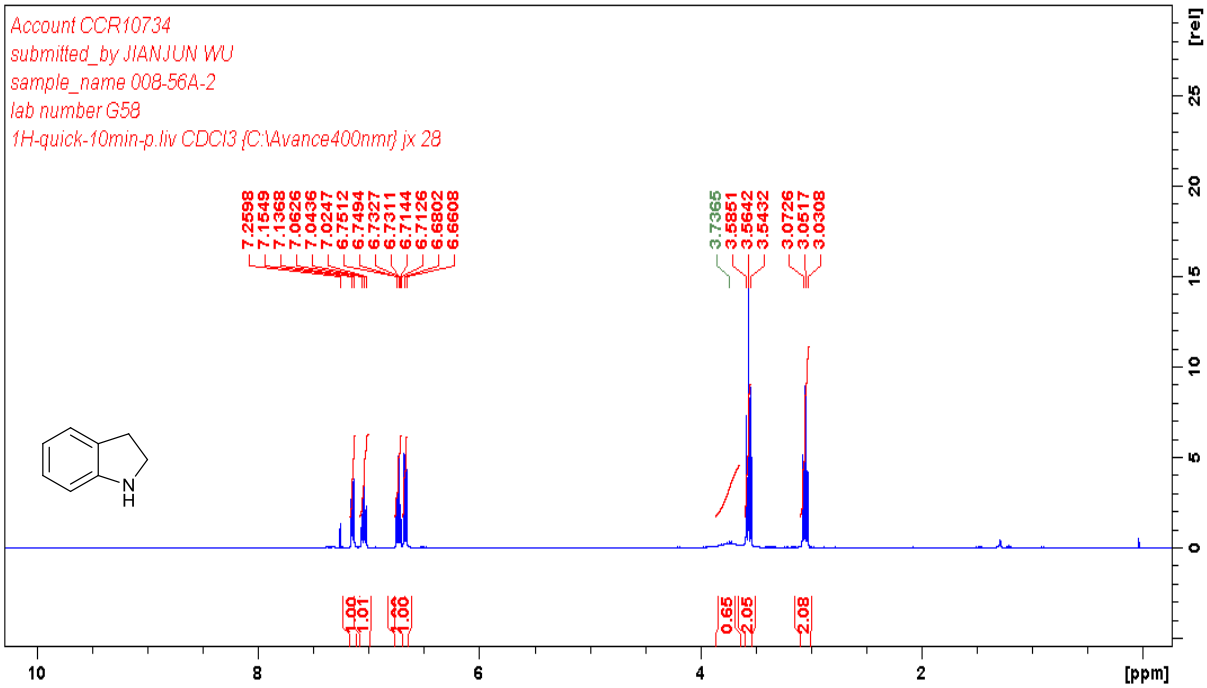
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 3-(1-((4-methoxyphenyl)amino)ethyl) nitrobenzene (**5j**)



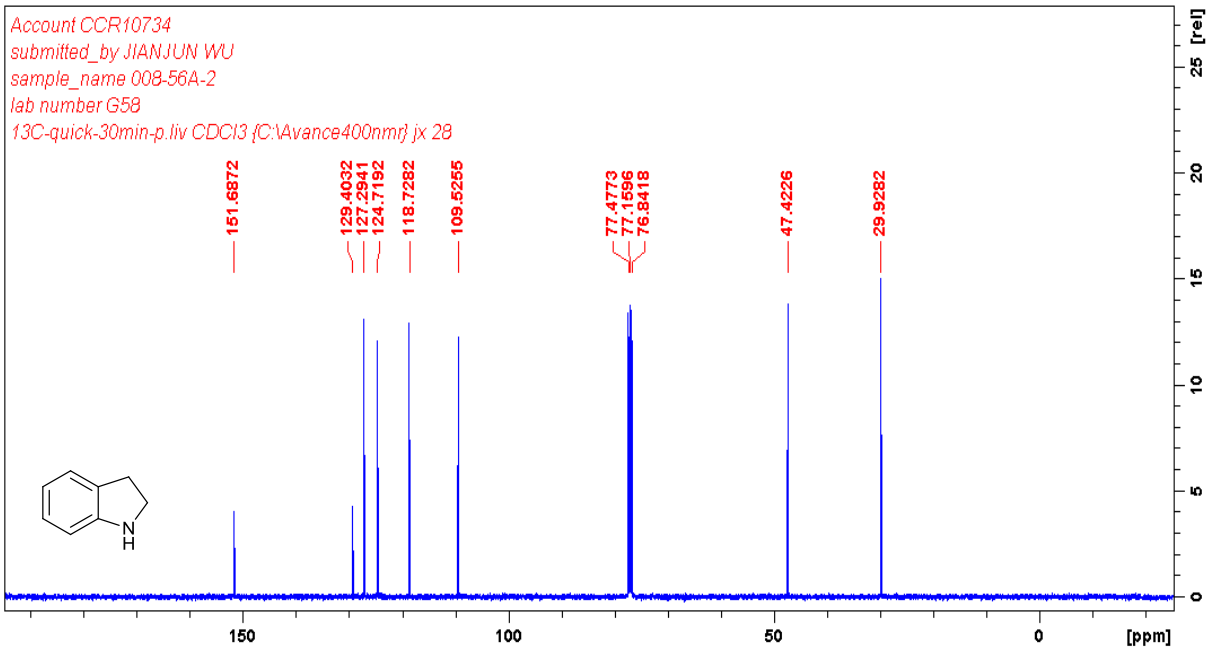
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-methylindoline (**5k**)



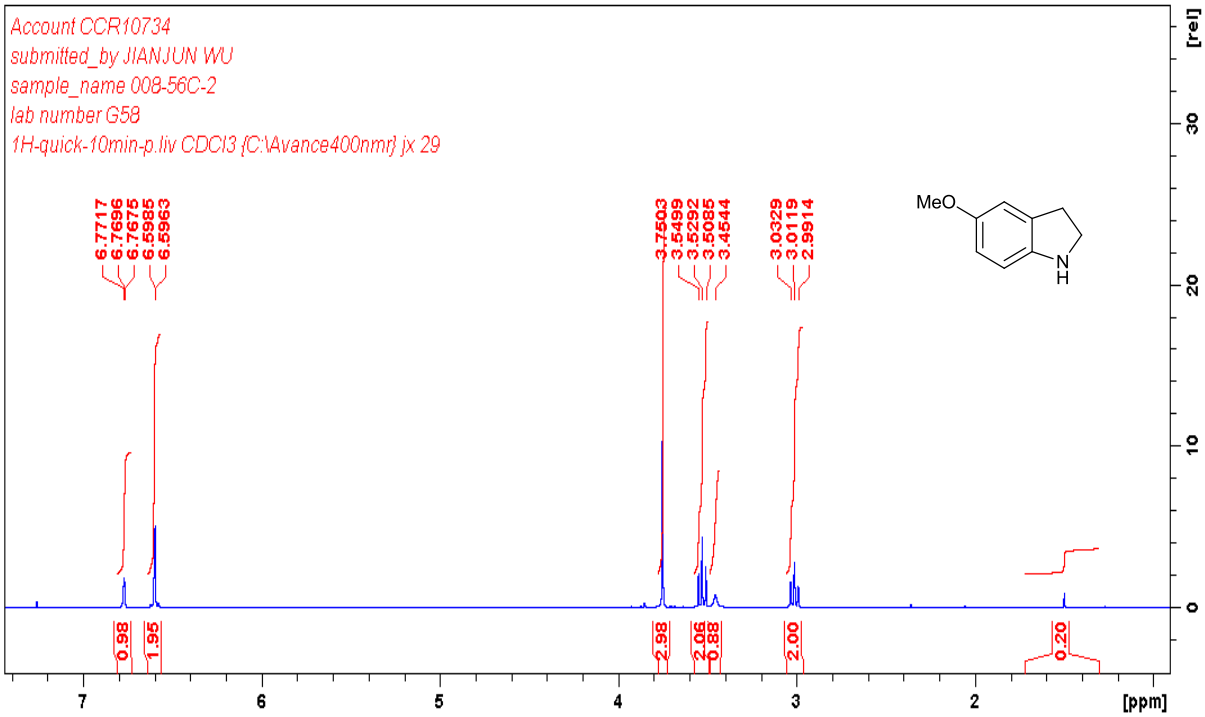
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 2-methylindoline (**5k**)



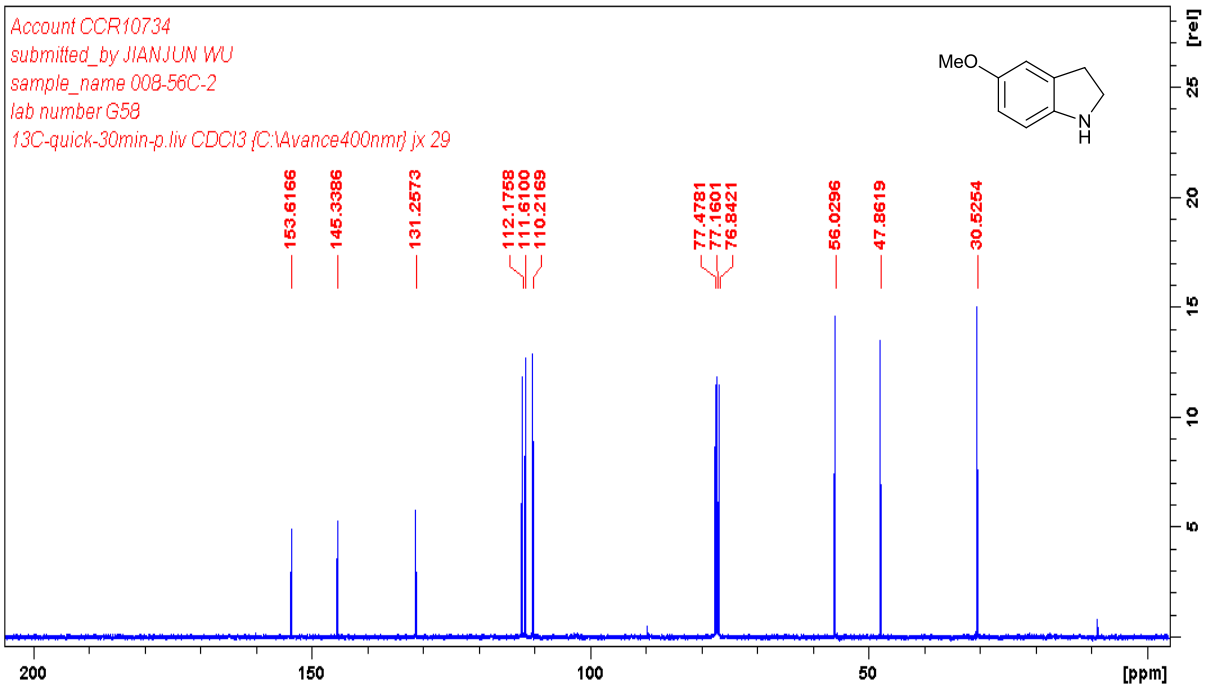
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of indoline (**5l**)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of indoline (**5l**)



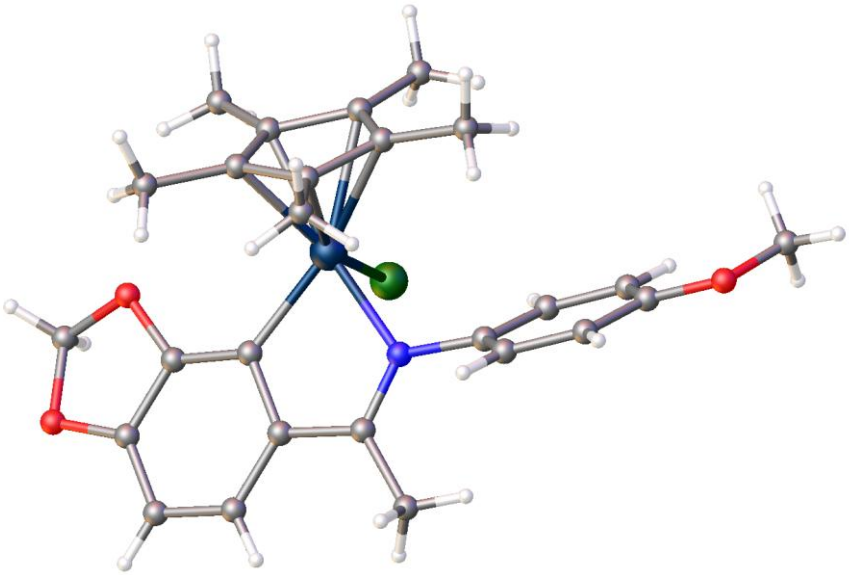
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-methoxyindoline (**5m**)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 5-methoxyindoline (**5m**)

4. Crystallographic data of 1f and 1g minor isomer

Complex 1f[S11]



CCDC 933834 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam.ac.uk/data_request/cif*.

Table 1 Crystal data and structure refinement for 1f

Identification code	frm_0m
Empirical formula	$C_{26}H_{29}ClIrNO_3$
Formula weight	631.15
Temperature/K	569.3
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4023(9)
b/Å	15.5707(19)
c/Å	20.203(3)
α/°	90.00
β/°	100.426(2)
γ/°	90.00
Volume/Å^3	2290.2(5)
Z	4
ρ_{calc}mg/mm^3	1.831
m/mm^{-1}	5.975
F(000)	1240.0
Crystal size/mm^3	.22 × .2 × .15

2Θ range for data collection	3.32 to 52.92°
Index ranges	$-9 \leq h \leq 9$, $-19 \leq k \leq 19$, $-25 \leq l \leq 24$
Reflections collected	19921
Independent reflections	4719[R(int) = 0.0254]
Data/restraints/parameters	4719/0/298
Goodness-of-fit on F^2	1.494
Final R indexes [I>=2σ (I)]	R_1 = 0.0565, wR_2 = 0.1378
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.1380
Largest diff. peak/hole / e $Å^{-3}$	3.47/-3.49

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for frm_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ir1	1779.5(5)	7583.3(2)	4129.40(19)	12.00(15)
Cl3	4938(3)	7410.8(16)	4696.5(12)	15.7(5)
O3	2762(11)	9848(5)	4342(4)	18.8(16)
C4	2685(14)	8559(7)	3606(5)	13.0(19)
C5	2977(14)	7424(7)	2820(5)	18(2)
O6	3822(12)	10805(5)	3630(4)	23.5(17)
C7	471(15)	8007(7)	4937(5)	15(2)
O8	1518(12)	3392(5)	3168(4)	21.7(17)
C9	616(15)	7066(7)	5012(6)	20(2)
N10	2468(12)	6954(6)	3296(4)	13.2(17)
C11	3335(14)	5520(7)	3737(5)	16(2)
C12	1212(16)	8630(8)	5483(5)	20(2)
C13	812(14)	4757(7)	2721(5)	17(2)
C14	3674(14)	10008(7)	3345(5)	16(2)
C15	1758(16)	6595(7)	5591(5)	20(2)
C16	-1140(14)	7382(7)	3969(5)	17(2)
C17	4065(15)	9773(8)	2720(6)	21(2)
C18	1020(15)	5640(7)	2733(5)	17(2)
C19	-726(15)	8171(7)	4308(6)	18(2)
C22	2468(17)	2867(7)	3687(6)	22(2)
C23	3145(14)	8320(7)	2974(5)	15(2)
C24	3807(14)	8917(7)	2551(5)	17(2)
C25	2284(14)	6030(7)	3247(5)	13.2(19)
C26	-743(15)	5754(7)	4284(6)	19(2)
C27	3122(15)	4639(7)	3731(5)	17(2)
C29	3689(17)	10652(7)	4327(6)	22(2)
C31	3026(15)	9413(7)	3766(6)	18(2)

C33	-358(14)	6694(7)	4423(5)	15(2)
C35	1837(14)	4251(7)	3220(5)	16(2)
C45	-1473(16)	9034(8)	4064(6)	22(2)
C1	3421(16)	7048(7)	2185(5)	21(2)
C2	-2389(14)	7262(9)	3308(6)	24(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for frm_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	13.4(2)	12.3(2)	10.6(2)	0.37(14)	2.92(13)	0.34(15)
Cl3	13.0(11)	20.8(12)	12.8(11)	-0.9(9)	0.8(8)	-0.4(9)
O3	26(4)	17(4)	15(4)	-3(3)	6(3)	-3(3)
C4	12(5)	22(5)	3(4)	1(4)	-2(4)	1(4)
C5	15(5)	16(5)	19(5)	-1(4)	-4(4)	4(4)
O6	30(5)	17(4)	25(4)	0(3)	10(4)	-4(3)
C7	21(5)	14(5)	10(5)	-1(4)	8(4)	1(4)
O8	30(4)	16(4)	20(4)	-3(3)	7(3)	1(3)
C9	17(5)	20(5)	25(6)	-9(4)	9(4)	-7(4)
N10	15(4)	20(4)	5(4)	-1(3)	3(3)	1(3)
C11	15(5)	21(5)	11(5)	-2(4)	2(4)	4(4)
C12	25(6)	27(6)	11(5)	-1(4)	9(4)	-3(5)
C13	14(5)	25(6)	11(5)	-4(4)	0(4)	0(4)
C14	15(5)	16(5)	17(5)	4(4)	0(4)	-2(4)
C15	22(6)	20(5)	16(5)	3(4)	0(4)	2(4)
C16	19(5)	21(5)	12(5)	4(4)	2(4)	-4(4)
C17	17(5)	25(6)	21(6)	6(5)	3(4)	0(4)
C18	19(5)	25(6)	8(5)	1(4)	2(4)	-1(4)
C19	13(5)	20(5)	22(6)	1(4)	7(4)	2(4)
C22	33(6)	13(5)	21(5)	5(4)	9(5)	1(4)
C23	14(5)	18(5)	12(5)	2(4)	0(4)	3(4)
C24	17(5)	18(5)	15(5)	4(4)	3(4)	4(4)
C25	16(5)	16(5)	9(4)	0(4)	5(4)	2(4)
C26	17(5)	22(5)	19(5)	2(4)	5(4)	-1(4)
C27	18(5)	22(5)	10(5)	1(4)	3(4)	7(4)
C29	28(6)	16(5)	23(6)	-1(4)	4(5)	-6(4)
C31	16(5)	21(5)	18(5)	0(4)	6(4)	2(4)
C33	13(5)	20(5)	13(5)	1(4)	7(4)	1(4)
C35	15(5)	21(5)	13(5)	-1(4)	6(4)	3(4)

C45	19(5)	26(6)	22(6)	2(5)	5(4)	5(5)
C1	30(6)	20(5)	16(5)	-1(4)	8(5)	-2(5)
C2	9(5)	41(7)	20(5)	-2(5)	-3(4)	4(5)

Table 4 Bond Lengths for 1f

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	Cl3	2.425(2)	O8	C22	1.412(13)
Ir1	C4	2.033(10)	O8	C35	1.360(13)
Ir1	C7	2.146(10)	C9	C15	1.503(16)
Ir1	C9	2.264(11)	C9	C33	1.401(15)
Ir1	N10	2.089(8)	N10	C25	1.447(13)
Ir1	C16	2.149(11)	C11	C25	1.393(14)
Ir1	C19	2.156(11)	C11	C27	1.381(15)
Ir1	C33	2.261(10)	C13	C18	1.384(16)
O3	C29	1.430(13)	C13	C35	1.391(15)
O3	C31	1.389(13)	C14	C17	1.394(16)
C4	C23	1.429(14)	C14	C31	1.400(15)
C4	C31	1.380(15)	C16	C19	1.413(15)
C5	N10	1.318(14)	C16	C33	1.460(15)
C5	C23	1.431(15)	C16	C2	1.492(14)
C5	C1	1.499(15)	C17	C24	1.381(16)
O6	C14	1.364(13)	C18	C25	1.404(14)
O6	C29	1.448(14)	C19	C45	1.502(15)
C7	C9	1.476(15)	C23	C24	1.408(15)
C7	C12	1.497(15)	C26	C33	1.508(15)
C7	C19	1.434(15)	C27	C35	1.407(15)

Table 5 Bond Angles for 1f

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	Ir1	Cl3	87.0(3)	C33	C9	Ir1	71.8(6)
C4	Ir1	C7	113.7(4)	C33	C9	C7	107.8(10)
C4	Ir1	C9	152.1(4)	C33	C9	C15	126.1(10)
C4	Ir1	N10	77.3(4)	C5	N10	Ir1	118.2(7)
C4	Ir1	C16	116.6(4)	C5	N10	C25	122.5(9)
C4	Ir1	C19	98.3(4)	C25	N10	Ir1	119.3(6)
C4	Ir1	C33	155.0(4)	C27	C11	C25	120.8(10)
C7	Ir1	Cl3	101.8(3)	C18	C13	C35	120.4(10)

C7	Ir1	C9	39.0(4)	O6	C14	C17	127.3(10)
C7	Ir1	C16	65.2(4)	O6	C14	C31	110.9(9)
C7	Ir1	C19	38.9(4)	C17	C14	C31	121.8(10)
C7	Ir1	C33	63.6(4)	C19	C16	Ir1	71.1(6)
C9	Ir1	Cl3	93.4(3)	C19	C16	C33	107.9(9)
N10	Ir1	Cl3	88.5(2)	C19	C16	C2	126.0(10)
N10	Ir1	C7	165.0(4)	C33	C16	Ir1	74.8(6)
N10	Ir1	C9	130.6(4)	C33	C16	C2	125.6(10)
N10	Ir1	C16	101.2(4)	C2	C16	Ir1	126.6(7)
N10	Ir1	C19	132.6(4)	C24	C17	C14	115.8(10)
N10	Ir1	C33	102.0(4)	C13	C18	C25	120.0(10)
C16	Ir1	Cl3	155.8(3)	C7	C19	Ir1	70.2(6)
C16	Ir1	C9	63.4(4)	C7	C19	C45	125.5(10)
C16	Ir1	C19	38.3(4)	C16	C19	Ir1	70.6(6)
C16	Ir1	C33	38.6(4)	C16	C19	C7	108.7(9)
C19	Ir1	Cl3	138.9(3)	C16	C19	C45	125.8(10)
C19	Ir1	C9	63.8(4)	C45	C19	Ir1	127.0(8)
C19	Ir1	C33	63.4(4)	C4	C23	C5	115.0(9)
C33	Ir1	Cl3	118.0(3)	C24	C23	C4	122.4(10)
C33	Ir1	C9	36.1(4)	C24	C23	C5	122.5(10)
C31	O3	C29	105.6(8)	C17	C24	C23	122.3(10)
C23	C4	Ir1	115.1(7)	C11	C25	N10	119.0(9)
C31	C4	Ir1	131.4(8)	C11	C25	C18	119.4(10)
C31	C4	C23	113.4(9)	C18	C25	N10	121.5(9)
N10	C5	C23	114.1(10)	C11	C27	C35	119.5(10)
N10	C5	C1	123.0(10)	O3	C29	O6	106.4(8)
C23	C5	C1	122.9(10)	O3	C31	C14	107.5(9)
C14	O6	C29	104.2(8)	C4	C31	O3	128.2(10)
C9	C7	Ir1	74.9(6)	C4	C31	C14	124.3(10)
C9	C7	C12	123.8(10)	C9	C33	Ir1	72.1(6)
C12	C7	Ir1	127.2(8)	C9	C33	C16	108.4(10)
C19	C7	Ir1	70.9(6)	C9	C33	C26	127.6(10)
C19	C7	C9	106.8(9)	C16	C33	Ir1	66.6(6)
C19	C7	C12	128.6(10)	C16	C33	C26	123.7(9)
C35	O8	C22	117.1(9)	C26	C33	Ir1	131.6(7)
C7	C9	Ir1	66.2(6)	O8	C35	C13	115.9(10)
C7	C9	C15	125.8(10)	O8	C35	C27	124.3(10)
C15	C9	Ir1	123.1(8)	C13	C35	C27	119.8(10)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1f

Atom	*x*	*y*	*Z*	U(eq)
H11	4191	5775	4073	19
H12A	2471	8493	5661	30
H12B	503	8594	5836	30
H12C	1138	9202	5303	30
H13	-17	4500	2377	20
H15A	1933	6012	5461	30
H15B	1140	6601	5970	30
H15C	2930	6872	5711	30
H17	4475	10168	2435	26
H18	322	5976	2400	21
H22A	2148	2277	3592	33
H22B	2135	3029	4108	33
H22C	3767	2940	3714	33
H24	4080	8727	2144	20
H26A	-922	5653	3808	28
H26B	-1831	5592	4449	28
H26C	278	5419	4506	28
H27	3823	4303	4063	20
H29A	4902	10626	4604	27
H29B	2999	11108	4493	27
H45A	-643	9475	4264	33
H45B	-2650	9118	4191	33
H45C	-1604	9060	3583	33
H1A	3562	6437	2235	32
H1B	4544	7294	2097	32
H1C	2443	7172	1817	32
H2A	-2417	7779	3048	36
H2B	-3604	7132	3382	36
H2C	-1948	6797	3068	36

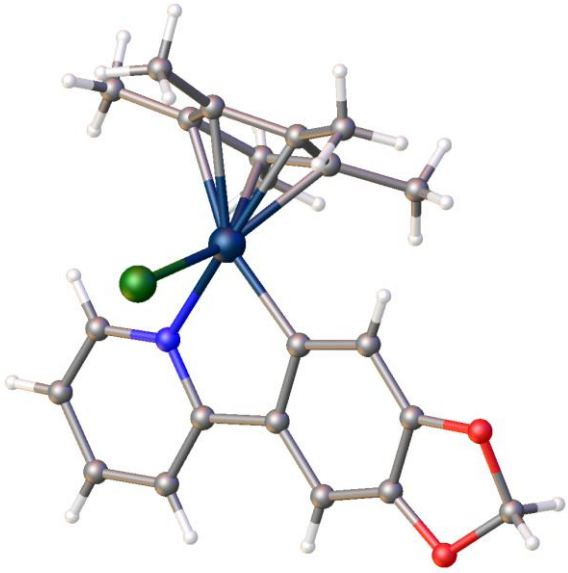
1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, **42**, 339-341.
2. SHELXS-97 (Sheldrick, 2008)
3. olex2.refine (L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, in preparation, 2011)

Crystal structure determination of 1f

Crystal Data. $C_{26}H_{29}ClIrNO_3$, *M* =631.15, monoclinic, *a* = 7.4023(9) Å, *b* = 15.5707(19) Å, *c* = 20.203(3) Å, *β* = 100.426(2)°, *V* = 2290.2(5) Å^3, *T* = 569.3, space

group $P2_1/c$ (no. 14), $Z = 4$, μ(MoKα) = 5.975, 19921 reflections measured, 4719 unique (R_{int} = 0.0254) which were used in all calculations. The final wR_2 was 0.1380 (all data) and R_1 was 0.0565 (>2 sigma(I)).

Complex 1g[S11] minor isomer



CCDC 933833 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam.ac.uk/data_request/cif*.

Table 1 Crystal data and structure refinement for 1g minor isomer

Identification code	**1g**
Empirical formula	$C_{22}H_{23}ClIrNO_2$
Formula weight	561.06
Temperature/K	569.3
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.4378(8)
b/Å	14.0123(16)
c/Å	18.702(2)
α/°	90.00
β/°	97.756(3)
γ/°	90.00
Volume/Å^3	1931.3(4)
Z	4

ρ_{calc}mg/mm^3	1.930
m/mm^{-1}	7.069
F(000)	1088.0
Crystal size/mm^3	0.30 × 0.150 × 0.10
2Θ range for data collection	3.64 to 53.02°
Index ranges	$-9 \leq h \leq 9$, $-17 \leq k \leq 17$, $-23 \leq l \leq 23$
Reflections collected	24448
Independent reflections	4009[R(int) = 0.0368]
Data/restraints/parameters	4009/0/249
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0167, wR_2 = 0.0379
Final R indexes [all data]	R_1 = 0.0198, wR_2 = 0.0394
Largest diff. peak/hole / e Å^{-3}	1.18/-0.56

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1g. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ir1	8748.03(12)	9080.12(6)	1842.68(5)	11.15(4)
Cl4	11532.8(8)	8432.8(4)	1541.2(4)	18.47(14)
N1	9605(3)	10374.9(15)	1440.4(12)	12.9(4)
O2	13219(3)	10920.8(13)	4527.4(11)	23.1(5)
O3	12060(3)	9411.1(15)	4669.4(10)	25.0(5)
C6	10637(3)	10956.4(17)	1922.9(15)	13.7(5)
C7	10974(3)	10568.8(18)	2650.4(15)	13.6(5)
C10	6341(3)	8800.1(18)	2335.2(15)	14.5(5)
C11	12226(4)	10620(2)	3878.9(15)	17.8(6)
C12	5828(3)	9214.2(18)	1638.0(15)	14.6(5)
C14	10225(3)	9658.2(18)	2729.9(14)	14.3(5)
C15	9792(4)	11510.3(19)	494.8(15)	19.8(6)
C16	5879(4)	9193.9(19)	3031.9(15)	18.8(6)
C17	12693(4)	10271(2)	5047.9(15)	24.5(6)
C20	4808(3)	10134.7(18)	1479.8(16)	17.7(6)
C21	11983(4)	11077.5(18)	3225.2(15)	16.5(6)
C27	10565(4)	9216.8(18)	3415.1(15)	16.6(6)
C30	9229(4)	10649.8(19)	745.9(15)	16.0(5)
C32	11546(4)	9716(2)	3968.2(15)	18.5(6)
C2	7261(3)	7909.0(18)	2228.4(15)	15.1(5)
C3	10822(4)	12114.5(18)	980.2(15)	18.8(6)
C4	7166(3)	7766.2(18)	1460.5(15)	16.0(5)

C5	11245(3)	11833.9(18)	1690.0(15)	17.0(6)
C8	6281(3)	8554.9(18)	1092.3(15)	15.4(5)
C9	8010(4)	7181.9(19)	2780.7(16)	19.6(6)
C13	5722(4)	8648(2)	298.1(16)	22.6(6)
C19	7875(4)	6899.6(19)	1125.0(16)	22.4(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1g. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ir1	11.55(6)	9.60(6)	12.28(6)	0.02(4)	1.57(4)	-0.32(4)
Cl4	14.4(3)	13.5(3)	28.2(4)	-0.1(3)	5.5(3)	1.9(2)
N1	12.9(10)	10.9(10)	15.4(12)	0.7(9)	3.4(9)	2.5(8)
O2	25.8(11)	27.4(11)	14.8(11)	-2.6(8)	-1.8(9)	-7.2(8)
O3	31.7(12)	28.1(11)	13.5(11)	3.5(9)	-3.3(9)	-4.9(9)
C6	10.4(12)	12.9(12)	18.4(14)	-1.2(10)	4.2(10)	2.0(9)
C7	11.0(12)	13.1(12)	17.4(14)	-0.8(10)	3.9(10)	2(1)
C10	10.9(12)	13.1(12)	20.4(15)	-1.0(11)	5.4(10)	-3.5(10)
C11	17.8(13)	20.8(13)	14.6(14)	-4.6(11)	1.4(11)	-1.7(11)
C12	10.2(12)	14.9(12)	19.0(15)	-0.3(10)	3.3(10)	-1.6(10)
C14	10.9(12)	15.5(13)	17.0(14)	-2.6(11)	3.5(10)	1.3(10)
C15	22.7(14)	22.1(14)	15.4(15)	6.5(11)	5.3(11)	3.9(11)
C16	21.8(14)	16.7(13)	19.2(15)	-2.7(11)	7.2(11)	-1.4(11)
C17	24.8(15)	34.3(17)	13.6(15)	-2.6(13)	-0.8(12)	-5.3(13)
C20	15.1(13)	14.7(13)	22.9(15)	-0.5(11)	1.5(11)	0.2(10)
C21	16.0(13)	14.4(13)	19.2(15)	-2.5(11)	2.3(11)	-1.9(10)
C27	16.6(13)	15.9(13)	17.4(15)	0.5(11)	2.8(11)	-4.1(10)
C30	16.5(13)	16.1(13)	15.9(14)	-1.2(11)	3.6(11)	0.7(10)
C32	17.3(13)	23.9(14)	14.2(14)	3.7(11)	1.9(11)	2.0(11)
C2	11.5(12)	13.7(13)	20.7(15)	0.4(11)	4(1)	-3(1)
C3	21.1(14)	13.8(13)	23.1(15)	6.4(11)	8.7(11)	2.6(11)
C4	12.4(12)	12.3(12)	23.1(15)	-2.7(11)	2.0(11)	-3.4(10)
C5	17.0(13)	12.0(12)	23.0(15)	-0.3(11)	6.2(11)	0.7(10)
C8	12.5(12)	14.8(12)	18.7(15)	-1.8(11)	1.4(11)	-2.8(10)
C9	17.0(13)	14.8(13)	27.0(16)	5.0(12)	3.1(11)	-2.8(11)
C13	20.2(14)	27.3(15)	19.3(16)	-3.6(12)	-0.7(12)	-0.7(12)
C19	24.8(15)	15.8(13)	27.0(17)	-5.6(12)	5.2(12)	-1.8(11)

Table 4 Bond Lengths for 1g minor isomer.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	Cl4	2.3971(7)	C10	C12	1.431(4)
Ir1	N1	2.096(2)	C10	C16	1.497(4)
Ir1	C10	2.157(2)	C10	C2	1.451(3)
Ir1	C12	2.162(3)	C11	C21	1.370(4)
Ir1	C14	2.031(3)	C11	C32	1.383(4)
Ir1	C2	2.157(2)	C12	C20	1.506(3)
Ir1	C4	2.249(2)	C12	C8	1.449(4)
Ir1	C8	2.277(3)	C14	C27	1.415(4)
N1	C6	1.371(3)	C15	C30	1.379(4)
N1	C30	1.347(3)	C15	C3	1.393(4)
O2	C11	1.397(3)	C27	C32	1.374(4)
O2	C17	1.426(3)	C2	C4	1.442(4)
O3	C17	1.444(3)	C2	C9	1.503(4)
O3	C32	1.383(3)	C3	C5	1.379(4)
C6	C7	1.455(4)	C4	C8	1.417(4)
C6	C5	1.400(3)	C4	C19	1.495(4)
C7	C14	1.408(3)	C8	C13	1.493(4)
C7	C21	1.418(4)			

Table 5 Bond Angles for 1g minor isomer.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ir1	Cl4	85.92(6)	C2	C10	Ir1	70.34(14)
N1	Ir1	C10	128.38(9)	C2	C10	C16	127.2(2)
N1	Ir1	C12	102.00(9)	C21	C11	O2	128.6(2)
N1	Ir1	C2	166.69(9)	C21	C11	C32	122.0(3)
N1	Ir1	C4	139.98(9)	C32	C11	O2	109.3(2)
N1	Ir1	C8	108.50(9)	C10	C12	Ir1	70.47(14)
C10	Ir1	Cl4	145.58(7)	C10	C12	C20	126.3(2)
C10	Ir1	C12	38.71(10)	C10	C12	C8	108.9(2)
C10	Ir1	C4	63.77(10)	C20	C12	Ir1	125.23(17)
C10	Ir1	C8	63.77(10)	C8	C12	Ir1	75.31(14)
C12	Ir1	Cl4	150.51(7)	C8	C12	C20	124.5(2)

C12	Ir1	C4	62.93(9)	C7	C14	Ir1	116.95(19)
C12	Ir1	C8	38.01(9)	C7	C14	C27	117.8(2)
C14	Ir1	Cl4	87.36(7)	C27	C14	Ir1	125.21(19)
C14	Ir1	N1	77.93(9)	C30	C15	C3	118.3(3)
C14	Ir1	C10	96.44(10)	O2	C17	O3	107.4(2)
C14	Ir1	C12	121.98(10)	C11	C21	C7	115.7(2)
C14	Ir1	C2	105.99(10)	C32	C27	C14	118.1(2)
C14	Ir1	C4	142.03(10)	N1	C30	C15	123.0(3)
C14	Ir1	C8	159.17(10)	O3	C32	C11	109.8(2)
C2	Ir1	Cl4	106.80(7)	C27	C32	O3	127.4(2)
C2	Ir1	C10	39.30(9)	C27	C32	C11	122.8(3)
C2	Ir1	C12	64.99(10)	C10	C2	Ir1	70.36(14)
C2	Ir1	C4	38.15(10)	C10	C2	C9	128.8(2)
C2	Ir1	C8	63.46(10)	C4	C2	Ir1	74.39(14)
C4	Ir1	Cl4	92.69(7)	C4	C2	C10	107.2(2)
C4	Ir1	C8	36.48(9)	C4	C2	C9	123.6(2)
C8	Ir1	Cl4	112.51(7)	C9	C2	Ir1	125.91(18)
C6	N1	Ir1	116.64(17)	C5	C3	C15	119.2(2)
C30	N1	Ir1	124.06(18)	C2	C4	Ir1	67.46(14)
C30	N1	C6	119.3(2)	C2	C4	C19	123.9(2)
C11	O2	C17	103.8(2)	C8	C4	Ir1	72.83(15)
C32	O3	C17	103.7(2)	C8	C4	C2	109.4(2)
N1	C6	C7	113.8(2)	C8	C4	C19	126.6(3)
N1	C6	C5	119.5(2)	C19	C4	Ir1	126.82(18)
C5	C6	C7	126.6(2)	C3	C5	C6	120.6(3)
C14	C7	C6	114.6(2)	C12	C8	Ir1	66.69(14)
C14	C7	C21	123.5(2)	C12	C8	C13	125.8(2)
C21	C7	C6	121.9(2)	C4	C8	Ir1	70.69(14)
C12	C10	Ir1	70.83(14)	C4	C8	C12	107.0(2)
C12	C10	C16	125.4(2)	C4	C8	C13	126.9(2)
C12	C10	C2	107.2(2)	C13	C8	Ir1	132.69(19)
C16	C10	Ir1	127.30(18)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1g minor isomer.

Atom	***x***	***y***	***z***	**U(eq)**
H15	9491	11683	13	24
H16A	6601	8882	3428	28
H16B	4617	9086	3062	28

H16C	6122	9867	3053	28
H17A	11734	10547	5286	29
H17B	13717	10130	5411	29
H20A	4688	10455	1925	27
H20B	3625	10001	1226	27
H20C	5460	10536	1188	27
H21	12451	11683	3163	20
H27	10136	8606	3489	20
H30	8560	10240	421	19
H3	11221	12700	828	23
H5	11939	12231	2017	20
H9A	9297	7126	2782	29
H9B	7445	6575	2664	29
H9C	7766	7380	3249	29
H13A	5887	9296	154	34
H13B	4468	8474	183	34
H13C	6452	8233	47	34
H19A	8083	7045	641	34
H19B	7003	6393	1115	34
H19C	8994	6704	1403	34

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Crystal structure determination of 1g minor isomer

Crystal Data. $C_{22}H_{23}ClIrNO_2$, M =561.06, monoclinic, a = 7.4378(8) Å, b = 14.0123(16) Å, c = 18.702(2) Å, β = 97.756(3)°, V = 1931.3(4) Å^3, T = 569.3, space group $P2_1/n$ (no. 14), Z = 4, μ(MoKα) = 7.069, 24448 reflections measured, 4009 unique (R_{int} = 0.0368) which were used in all calculations. The final wR_2 was 0.0394 (all data) and R_1 was 0.0167 (>2sigma(I)).

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