SUPPORTING INFORMATION

Long-Range Metal-Ligand Bifunctional Catalysis: Cyclometallated Iridium Catalysts for the Mild and Rapid Dehydrogenation of Formic Acid

Jonathan H. Barnard,[a] Chao Wang,[b] Neil G. Berry[a] and Jianliang Xiao*[a]

[a] Liverpool Centre for Materials and Catalysis, Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom

[b] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, P. R. China

Supporting information

Table of Contents

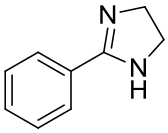
1. Experimental procedures

1.1 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. All other solvents were used as received. Formic acid and formic acid / amine mixtures were degassed by three freeze-pump-thaw cycles and stored under nitrogen. $[Cp^*IrCl_2]_2$, $[Cp^*RhCl_2]_2$, $IrCl_3{\cdot}nH_2O$ and $[Ru(p\text{-cymene})Cl_2]_2$ were purchased from Strem Chemicals Inc. [Cp*IrCl(2-phenylpyridine)] (**7**) was synthesised according to a literature procedure.[S1] (*E*)-4-Methoxy-*N*-(1-phenylethylidene)aniline (**L8**), (*E*)-4-methoxy-*N*-(1-(4-methoxyphenyl)ethylidene) aniline (**L9**) and *rac*-4-methoxy-*N*-(1-phenylethyl)aniline (**L10**) and complexes **8**, **9**, and **10** were prepared as described by Wang *et al.*[S2] (1*R*,2*R*)-1,2-Bis(2-hydroxyphenyl)ethylenediamine was purchased from Diaminopharm Inc. and used without further purification. Triphenylphosphonium tetrafluoroborate,[S3] and 2,6-lutidinium tetrafluoroborate,[S4] were prepared by literature procedures. 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 (ppm). The mass spectra were obtained by electrospray ionisation (ESI) or chemical ionisation (CI) at the Department of Chemistry, Liverpool University or by (EI) at the EPSRC National Mass Spectrometry Service Centre, Swansea. Elemental analyses were performed by the Department of Chemistry, Liverpool University elemental analysis service. FT-IR spectra of gases were recorded using a PerkinElmer Spectrum RX1 and a NaBr capped gas cell at the University of Liverpool. FT-IR spectra of solids were recorded using a JASCO FT/IR-4200 fitted with a Pike Technologies MIRacle ATR at the University of Liverpool.

1.2 Typical procedure for the synthesis of imidazoline ligands

Imidazolines were typically synthesised using a modification of the method of Togo.[S5] Diamine (1.0 eq.) and aldehyde (1.0-1.2 eq.) 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 (1.25 eq.) and K_2CO_3 (3.0 eq.) 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 (100 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 purified by silica gel chromatography (5:1 hexane / EtOAc) to give the pure product.

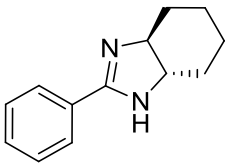


2-Phenyl-4,5-dihydro-1*H*-imidazole (L1)

Diamine = ethylenediamine (212 mg, 203 µL, 2.0 mmol)

Aldehyde = benzaldehyde (132 mg, 146 µL, 2.2 mmol)

White solid; yield 206 mg, 69%; m.p. 98-100 ^{o}C (lit. 101-2 ^{o}C[S6]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.55 (m, 2H), 7.43 – 7.30 (m, 3H), 4.94 (s, 1H), 3.72 (s, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.90, 130.67, 130.32, 128.44, 127.04, 50.22; *m/z* (CI^{+}) 147.1 (MH^{+}); elemental analysis for $C_9H_{10}N_2$ calcd: C 73.94, H 6.89, N 19.16; found: C 73.90, H 6.83, N 19.57.

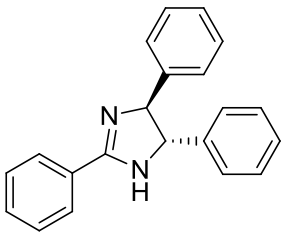


***Rac-trans*-2-phenyl-3,4,5,6,7,7-hexahydro-1*H*-benzo[*d*] imidazole (L3)**

Diamine = *rac-trans*-(1,2)-diaminocyclohexane (285 mg, 2.50 mmol)

Aldehyde = benzaldehyde (265 mg, 254 µL, 2.50 mmol)

White solid; yield 330 mg, 66%; m.p. 174-5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 2H), 7.50 – 7.34 (m, 3H), 5.08 (s br, 1H), 3.13 (d, *J* = 8.0 Hz, 2H), 2.31 (d, *J* = 8.0 Hz, 2H), 1.85(d, *J* = 8.0 Hz, 2H), 1.57 (m, 2H), 1.36 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.56, 130.96, 130.72, 128.55, 126.69, 69.72, 31.00, 25.13; *m/z* (CI^{+}) 201.1 (100%, MH^{+}), 202.1 (10%, MH^{+}); HRMS (ES^{+}) calcd. $C_{13}H_{16}N_2$, 201.1386; found, 201.1386.

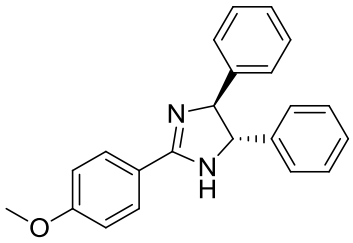


(4*S*,5*S*)-2,4,5-Triphenyl-4,5-dihydro-1*H*-imidazole (L4)

Diamine = *(*1*S*,2*S*) *trans*-(1,2)diphenylethylenediamine (233 mg, 1.1 mmol)

Aldehyde = benzaldehyde (106 mg, 117 µL, 1.0 mmol)

White solid; yield 581 mg, 78%; m.p. 199-204 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.85 (m, 2H), 7.55 – 7.41 (m, 3H), 7.40 – 7.27 (m, 10H), 5.52 (s, 1H), 4.89 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.18, 143.64, 131.09, 130.24, 128.81 two peaks overlapped, 128.68, 127.61, 127.50, 126.74; *m/z* (ES^+) 299 (100%, MH^+); HRMS (ES^+) calcd for $C_{21}H_{19}N_2$ (MH^+) 299.1548; found 299.1556; elemental analysis for $C_{18}H_{21}N_2$, calcd: C 84.53, H 6.08, N 9.39: found C 84.04, H 6.03, N 9.21.

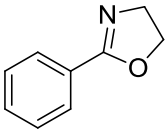


(4*S*,5*S*)-2-(4-Methoxyphenyl)-4,5-diphenyl-4,5-dihydro1*H*-imidazole (L5)

Diamine = *(*1*S*,2*S*) *trans*-(1,2)diphenylethylene diamine (583 mg, 2.75 mmol)

Aldehyde = *p*-anisaldehyde (340 mg, 266 µL, 2.50 mmol)

White solid; yield 590 mg, 72%; m.p. 197-201 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.33 (m, 10H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.30 (s, 1H), 4.89 (s, 2H), 3.87 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.83, 161.92, 143.77, 129.10, 128.83, 127.61, 126.77, 122.69, 114.01 one resonance was not observed, 55.55; *m/z* (ES^+) 329.2 (100%, MH^+); HRMS (ES^+) calcd. For $C_{22}H_{21}N_2O$ (MH^+) 329.1654; found, 329.1657.



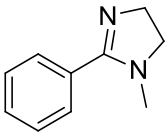
2-Phenyl-oxazoline (L6)

1-Ethanolamine (336 mg, 332 µL, 5.50 mmol)

Aldehyde = *p*-benzaldehyde (530 mg, 509 µL, 5.0 mmol)

The compound was prepared using the same method used for imidazoline synthesis and purified by silica gel chromatography (5:1 hexane/EtOAc) to give the pure product as a pale yellow oil. Yield 588 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.36 (m, 3H), 4.43 (t, *J* = 9.5 Hz, 2H), 4.06 (t, *J* = 9.5 Hz,

2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.75, 131.38, 128.44, 128.26, 127.86, 67.70, 55.04; *m/z* (EI^+) 148.2 (100%, MH^+), 149.2 (10%, MH^+); HRMS (CI^+) calcd. $C_9H_9N_2O$, 147.0679; found, 147.0681.

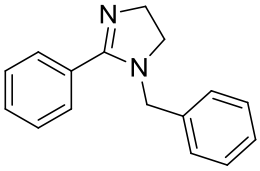


1-(4-Methylbenzyl)-2-phenyl-4,5-dihydro-1*H*-imidazole (L11)

Diamine = *N*-methylethylenediamine (148 mg, 2.0 mmol)

Aldehyde = benzaldehyde (233 mg, 2.2 mmol)

The compound was prepared using the same method used for imidazoline synthesis and purified by silica gel chromatography (5:1 hexane/EtOAc) to give the pure product as clear oil. The data are consistent with those previously reported by Salerno *et al.*[S7] Yield 224 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.39 (m, 3H), 3.85 (t, *J* = 10.0 Hz, 2H), 3.42 (t, *J* = 10.0 Hz, 2H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.30, 131.45, 129.79, 128.39, 128.25, 54.22, 53.34, 36.62; *m/z* (CI^+) 161.1 (MH^+).

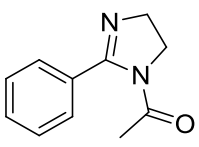


1-(Benzyl)-2-phenyl-4,5-dihydro-1*H*-imidazole (L12)

Diamine = *N*-(4-methylbenzyl)ethylenediamine (320 mg, 2.0 mmol)

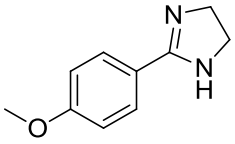
Aldehyde = benzaldehyde (212 mg, 235 µL, 2.0 mmol)

The compound was prepared using the same method used for imidazoline synthesis and purified by silica gel chromatography (5:1 hexane/EtOAc) to give the pure product as clear oil. Data are consistent with those reported by Kita and coworkers.[S8] Yield 372 mg, 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.31-7.16 (m, 8H), 4.20 (s, 2H), 3.82 (t, *J* = 10.0 Hz, 2H), 3.30 (t, *J* = 10.0 Hz, 2H; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.41, 137.06, 130.32, 128.92, 127.69, 127.51, 127.15, 126.33, 126.14, 52.40, 52.14, 50.09; *m/z* (CI^+) 237 (100%, MH^+).



1-(2-Phenyl-4,5-dihydro-1*H*-imidazol-1-yl)ethanone (L13). A solution of acetyl chloride (322 mg, 4.10 mmol) in dry CH_2Cl_2 was added dropwise to a cooled (0 ^{o}C) solution of **L1** (500 mg, 3.42 mmol) and NEt_3 (691 mg, 6.85 mmol) in dry CH_2Cl_2 (10 mL). After the addition the

mixture was allowed to warm to room temperature and stirred for 0.5 h, at which time it was diluted with CH_2Cl_2 (50 mL) and washed with brine (2x 15 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography eluting with neat EtOAc (rf = 0.2) to give the product as sticky clear oil. **L13** underwent slow hydrolysis to give **L1** and acetic acid under standard laboratory conditions and should be used promptly; yield 462 mg, 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.41 (m, 3H); 4.09 (t, *J* = 8.8 Hz, 2H), 3.96 (t, *J* = 8.8 Hz, 2H), 1.84 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.48, 159.47, 132.23, 130.53, 128.57, 128.31, 53.28, 48.37, 25.17; *m/z* (CI^+) 189.1 (100%, MH^+).

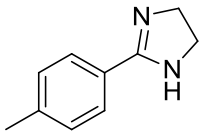


2-(4-Methoxyphenyl)-4,5-dihydro-1*H*-imidazole (L14)

Diamine = ethylenediamine (66 mg, 73 µL, 1.1 mmol)

Aldehyde = *p*-anisaldehyde (136 mg, 121 µL, 1.0 mmol)

White solid; yield 138 mg, 78%; m.p. 136-9 °C (lit. 137-9 °C[S9]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.38 (s, 1H), 3.81 (s, 3H), 3.73 (s, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.51, 161.55, 128.64, 122.96, 113.81, 55.42, 50.33; *m/z* (CI^+) 177.2 (MH^+); HRMS (ES^+) calcd. for $C_{10}H_{12}N_2O$, 177.1022; found, 177.1022.

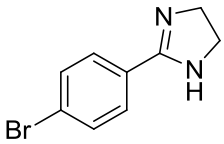


2-(*p*-Tolyl)-4,5-dihydro-1*H*-imidazole (L15)

Diamine = ethylenediamine (66 mg, 73 µL, 1.1 mmol)

Aldehyde = *p*-tolualdehyde (120 mg, 117 µL, 1.0 mmol)

White solid; yield 121 mg, 75%; m.p. 177-180 °C (lit. 177-180 °C[S10]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.43 (s, 1H), 3.72 (s, 4H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.85, 140.87, 129.16, 127.60, 126.96, 50.29, 21.49; *m/z* (CI^+) 162.1 (MH^+).

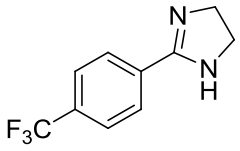


2-(4-(Bromophenyl)-4,5-dihydro-1*H*-imidazole (L16)

Diamine = ethylenediamine (132 mg, 146 µL, 2.2 mmol)

Aldehyde = *p*-bromobenzaldehyde (370 mg, 2.0 mmol)

White solid; yield 323 mg, 72%; m.p. 178-180 ^{o}C (lit. 177-177.5 ^{o}C[S11]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ163.96, 131.75, 129.50, 128.63, 125.12, 50.39; *m/z* (CI^+) 225.0 (90 %, MH^+), 227.0 (100%, MH^+); HRMS (ES^+) calcd. $C_9H_9BrN_2$, 225.0022; found, 225.0025.

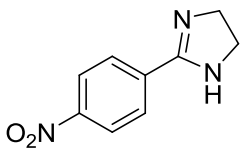


2-(4-(Trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazole (L17)

Diamine = ethylenediamine (73 mg, 81 µL, 1.2 mmol)

Aldehyde = *p*-CF_3-C_6H_4-CHO (191 mg, 1.1 mmol)

White solid; yield 144 mg, 61%; m.p. 187-9 ^{o}C (lit. 188-9 ^{o}C[S12]); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.87 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.66, 132.77 (q, $J_{C\text{-}F}$ 32.0 Hz), 127.48, 125.55 (q, $J_{C\text{-}F}$ 3.0 Hz), 125.97 (q, $J_{C\text{-}F}$ 270 Hz), 50.64; *m/z* (CI^+) 215 (100%, MH^+); HRMS (ES^+) calcd. $C_{10}H_9F_3N_2$, 215.0791; found, 215.0791.

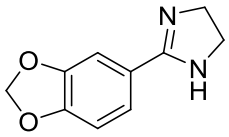


2-(4-(Nitrophenyl)-4,5-dihydro-1*H*-imidazole (L18)

Diamine = ethylenediamine (132 mg, 146 µL, 2.2 mmol)

Aldehyde = *p*-nitrobenzaldehyde (302 mg, 2.0 mmol)

Orange solid; yield 326 mg, 85%; m.p. 238-240 ^{o}C (lit. 235-7 ^{o}C[S13]); ^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.28 (s, 1H), 3.66 (s, 4H); ^{13}C NMR (101 MHz, DMSO-*d6*) δ 162.23, 148.42, 136.41, 128.40, 123.53, 49.85; *m/z* (CI^+) 192.1 (MH^+); elemental analysis for $C_9H_9N_3O_2$ calcd: C 56.54, H 4.74, N 21.98; found: C 56.15, H 4.60, N 21.90.



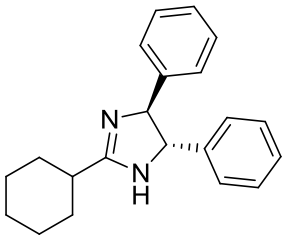
2-(Benzo[*d*][1,3]dioxol-5-yl)-4,5-dihydro-1*H*-imidazole (L19)

Diamine = ethylenediamine (145 mg, 162 µL, 2.42 mmol)

Aldehyde = piperonal (330 mg, 2.2 mmol)

White solid; yield 256 mg, 61%; m.p. 178-180 ^{o}C (lit. 178 ^{o}C[S14]); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.33 – 7.21 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 3.76 (s,

4H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.40, 149.69, 147.88, 124.72, 121.39, 108.11, 107.58, 101.5, 50.45; *m/z* (ES^+) 191.1 (100%, MH^+), 192.1 (10%, MH^+); HRMS (ES^+) calcd. $C_{10}H_{10}N_2O_2$, 191.0815; found, 191.0815.

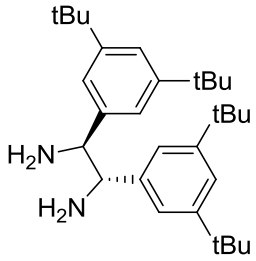


(4S,5S)-2-cyclohexyl-4,5-diphenyl-4,5-dihydro-1H-imidazole (L20)

Diamine = *(1S,2S) trans*-(1,2)diphenylethylenediamine 212 mg, 1.0 mmol)

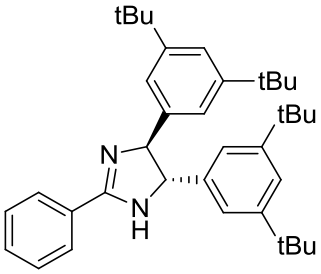
Aldehyde = cyclohexylcarbaldehyde (123 mg, 133 µL, 1.1 mmol)

The compound was prepared using the same method used for imidazoline synthesis and purified by silica gel chromatography (neat EtOAc) to give the pure product as white solid. White gum; 234 mg, 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 10H), 4.92 (s, br, 1H), 4.68 (s, 2H), 2.44 (m, 1H), 2.07 (m, 1H), 1.83 (m, 2H), 1.75 (m, 1H), 1.56 (m, 2H), 1.30 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.22, 144.19, 138.75, .127.45, 126.51, 38.99, 31.12, 31.08, 26.13, 26.09; *m/z* (ES^+) 305 (100%, M-H^+); HRMS (ES^+) calcd. $C_{21}H_{25}N_2$, 305.2018; found, 305.2024.



(1*S*,2*S*)-1,2-Bis (3,5-di-*tert*- butylphenyl) ethane-1,2-diamine. To a mixture of (1*R*,2*R*)-1,2-bis (2-hydroxyphenyl)ethylenediamine (508 mg, 2.09 mmol) in absolute ethanol (5 mL, partially dissolved) was added 3,5-di-*tert*-butylbenzaldehyde (1000 mg, 4.59 mmol, 2.2 eq). The solution became clear and was stirred for 1 h at room temperature. The precipitate was filtered, washed with cold ethanol and dried *in vacuo* to give a yellow solid. The solid was dissolved in a mixture of THF (20 mL) and conc. HCl (5 mL) and the solution stirred at room temperature overnight. The solution was diluted with H_2O (50 mL) and washed with diethyl ether (100 mL). The aqueous layer was basified with aqueous hydroxide and extracted with EtOAc (3x 100 mL). The organic layer was dried over K_2CO_3, filtered and the solvent evaporated to give a clear sticky oil; Yield 710 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 1.8 Hz, 2H), 6.95 (d, *J* = 1.8 Hz, 4H), 3.95 (s, 2H),

1.23 (s, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.39, 142.75, 121.29, 120.79, 64.01, 34.87, 31.64; *m/z* (ES^+) 437.4 (100%, MH^+); HRMS (ES^+) calcd. $C_{30}H_{48}N_2$, 437.3896; found, 437.3906.

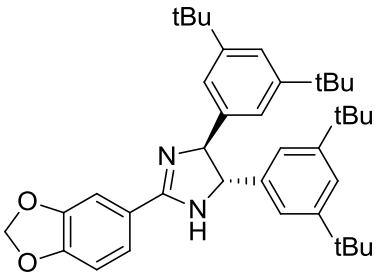


(4*S*,5*S*)-4,5-Bis(3,5-di-*tert*-butylphenyl)-2-phenyl-4,5-dihydro-1*H*-imidazole (L21).

Diamine = (1*S*,2*S*)-1,2-Bis(3,5-di-*tert*-butylphenyl) ethane-1,2-diamine (100 mg, 0.229 mmol)

Aldehyde = benzaldehyde (24 mg, 23 µL, 0.229 mmol)

The compound was prepared using the standard method for imidazoline synthesis and purified by silica gel chromatography (4:1 hexane/EtOAc, rf = 0.4) to give the pure product. White sticky gum / oil; yield 71 mg, 59%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.51 (m, *3*H), 7.38 (s, 2H), 7.22 (s, 4H), 5.36 (s, br, 1H), 5.00 (s, br, 2H); 1.34 (s, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.76, 151.13; 143.24, 130.90, 130.82, 128.70, 127.51, 121.69, 120.81, resonances corresponding to imidazoline CH carbons (which are typically broad peaks around 70 ppm) were not observed, 35.06, 31.67; *m/z* (ES^+) 523.4 (100%, MH^+), 524.4 (35%, MH^+); HRMS (ES^+) calcd. $C_{37}H_{50}N_2$, 523.4052; found, 523.4055.



(4*S*,5*S*)-2-(Benzo[*d*][1,3]dioxol-5-yl)-4,5bis(3,5-di-*tert*-butylphenyl)-4,5-dihydro-1*H*-imidazole (L22)

Diamine = (1*S*,2*S*)-1,2-Bis(3,5-di-*tert*-butyl phenyl) ethane-1,2-diamine (184 mg, 0.42 mmol)

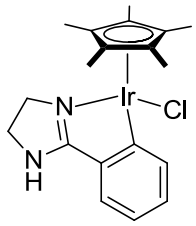
Aldehyde = piperonal (66.5 mg, 0.44 mmol)

The compound was prepared using the standard method for imidazoline synthesis and purified by silica gel chromatography (4:1 hexane/EtOAc, rf = 0.05) to give the pure product. White solid; yield 131 mg, 55%; m.p. 220-225 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.6 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.36 (s, 2H), 7.19 (s, 4H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H), 5.17 (s, br, 2H), 4.80 (s, br, 1H), 1.32 (s, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.35, 151.25, 149.92, 148.04, 143.46, 124.97, 121.78, 120.83, 108.29, 108.08, 101.64, resonances corresponding to

imidazoline CH carbons (which are typically broad peaks around 70 ppm) were not observed, 35.06, 31.67; *m/z* (ES^+) 567.4 (100%, MH^+), 568.4 (35%, MH^+); HRMS (ES^+) calcd. $C_{38}H_{51}N_2O_2$, 567.3951; found, 567.3934.

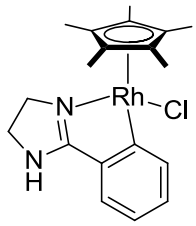
1.3 Typical procedure for the synthesis of cyclometallated iridium complexes

Complexes were synthesised using the method of Davies *et. al*.[S15] Unless specified, iridium complexes **X** were synthesised from the corresponding ligands **LX**. Ligand (2.05 eq.), $[Cp^*IrCl_2]_2$ (1.0 eq.) and NaOAc (20.0 eq.) were added to 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/Et_2O and drying *in vacuo* gave the pure products as fine powders often containing a molecule of DCM or H_2O of crystallisation.



1

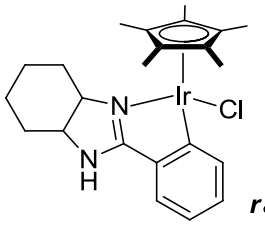
Yellow powder; 0.11 mmol scale, yield 65 mg, 99%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.13 (td, *J* = 7.4, 1.2 Hz, 1H), 6.94 (t, *J* = 7.1 Hz, 1H), 6.12 (s, 1H), 3.92 – 3.66 (m, 2H), 3.47 (dt, *J* = 18.9, 9.4 Hz, 1H), 2.67 (s, 1H), 1.72 (s, 15H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 176.52, 135.95, 135.31, 131.05, 125.11, 121.23, 87.18, 51.78, 44.96, 9.48; IR (solid) ν_{max} 3262 (N-H stretch), 3073, 1627 (C=N stretch), 1604, 1573, 1280, 1049, 1022, 725; *m/z* (EI^+) 506.1 (M^+), 508.1 (M^+); HRMS (EI^+) calcd. for $C_{19}H_{24}Cl^{191}IrN_2$, 506.1228; found, 506.1220.



Rh1

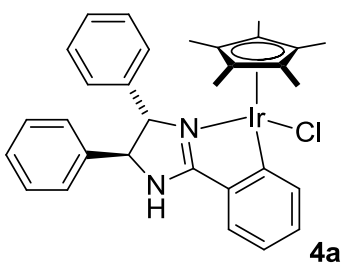
The compound was synthesised from ligand **L1** using the method of Davies *et. al*.[S15] described for the synthesis of cyclometallated iridium complexes (*vide supra*). $[Cp^*RhCl_2]_2$ was used as the rhodium precursor.

Dark red powder; 0.05 mmol scale, yield 18 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.21 (s, br, 1H), 3.90 (m, 1H0, 3.73 (m, 1H), 3.37 (m, 1H0, 2.50 (m, 1H), 1.70 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.51, 172.49, 170.53, 170.22, 134.36, 133.37, 130.29, 125.60, 123.11, 99.15, 99.10, 49.58, 43.84, 7.60; IR (solid) ν_{max} 3232 (N-H stretch), 2908, 1604 (C=N stretch), 1573, 1523, 1434, 1280, 1045, 1033, 732; *m/z* (EI^+) 418.1 (M^+); HRMS (EI^+) calcd. for $C_{19}H_{24}ClRhN_2$, 418.0678; found, 418.0676.



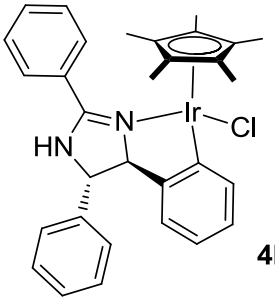
***rac-trans* 3**

Yellow powder; 0.05 mmol scale, yield 22 mg, 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.0 Hz, 1H), 6.93 (t, *J* = 7.0 Hz, 1H), 5.67 (s, 1H), 3.27 (t, *J* = 12.0 Hz, 1H), 2.89 (t, *J* = 12.0 Hz, 1H), 2.23 (m, 1H), 2.02 (m, 1H), 1.93 – 1.78 (m, 2H), 1.70 (s, 15H), 1.27 (m, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.21, 164.72, 136.03, 135.09, 131.51, 124.90, 121.41, 87.42, 70.00, 67.84, 30.63, 29.84, 24.99, 24.37, 9.80; IR (solid) ν_{max} 3234 (N-H stretch), 3012, 1608 (C=N stretch), 1581, 1523, 1473, 1361, 1284, 1168, 1049, 821, 682; elemental analysis for $C_{23}H_{30}ClIrN_2 \cdot 0.5CH_2Cl_2$ calcd: C 46.68, H 5.17, N 4.63; found: C 46.34, H 5.18, N 4.33.



4a

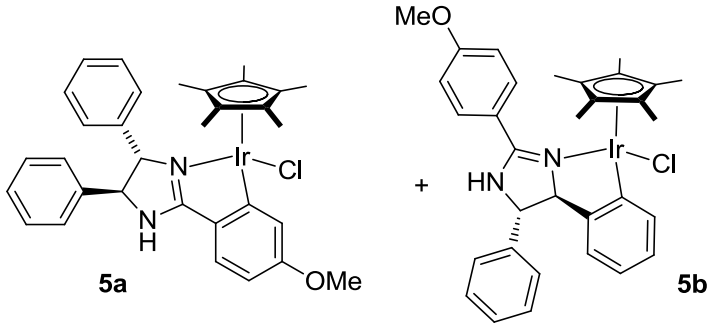
\+



4b

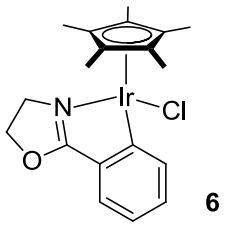
4 was formed as a mixture of regioisomers **4a** and **4b** with **4a** composed of 2 diastereoisomers; 1.5:1 ratio of **4a**:**4b**. Yellow powder; 0.05 mmol scale, yield 30 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (m, 0.3H), 7.77 - 7.32 (m, overlapped, 11H), 6.95 (m, 0.35 H), 6.80 (m, 0.5 H), 5.88 (s, br, 0.15 H), 5.70 (s, 0.5 H), 5.42 (s, 0.3 H), 5.07 (d, *J* = 8.0 Hz, 0.3 H), 4.92 (d, *J* = 12.0 Hz, 0.5 H), 4.87 (d, *J* = 12.0 Hz, 0.25 H), 4.75 (m, 0.5 H), 4.72 (m, 0.3 H), 1.38 (s, 15 H); ^{13}C {^{1}H} NMR (100 MHz $CDCl_3$) δ 177.58, 153.84, 142.52, 142.04, 141.58, 135.34, 134.74, 133.34, 130.08, 129.94, 129.48, 129.40, 129.28, 128.45, 128.10, 126.82, 125.56, 125.38, 95.73, 69.23,

40.84, 40.63, 40.42, 40.21, 9.36; IR (solid) ν_{max} 3212 (N-H stretch), 1600 (C=N stretch), 1565, 1511, 1454, 1346, 1280, 1025, 732, 698; elemental analysis for $C_{31}H_{32}ClIrN_2$ calcd: C 56.39, H 4.88, N 4.24; found: C 56.63, H 4.94, N 4.17.



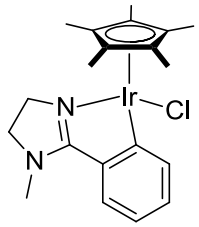
5a **5b**

5 was formed as a mixture of regioisomers **5a** and **5b** with **5a** composed of 2 diastereoisomers; 1.5:1 ratio of **5a**:**5b**. Yellow powder; 0.05 mmol scale, yield 32 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.15 (m, overlapped, 14H), 6.54 (dd, *J* = 8.0, 4.0 Hz, 0.4 H), 6.43 (dd, *J* = 8.0, 4.0 Hz, 0.6 H), 5.65 (s, 0.6 H), 5.31 (s, 0.4 H), 5.04 (d, *J* = 4.0 Hz, 0.4H), 4.89 (d, *J* = 12.0 Hz, 0.6 H), 4.72 (d, *J* = 12.0 Hz, 0.6 H), 4.60 (s, 0.4 H), 3.80 (s, 3H), 1.37 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.66, 176.00, 166.35, 162.12, 161.61, 143.77, 142.01, 140.09, 139.44, 128.89, 128.77, 128.68, 128.24, 128.04, 127.50, 127.33, 127.24, 126.02, 120.60, 129.17, 87.71, 87.12, 79.27, 72.29, 72.01, 54.97, 31.53, 22.60, 14.07, 9.34, 9.10; IR (solid) ν_{max} 3255 (N-H stretch), 2907, 1604 (C=N stretch), 1570, 1521, 1454, 1226, 1099, 755, 698; elemental analysis for $C_{32}H_{34}ClIrN_2O{\cdot}H_2O$ calcd: C 54.26, H 5.12, N 3.95; found: C 54.46, H 5.07, N 3.80.



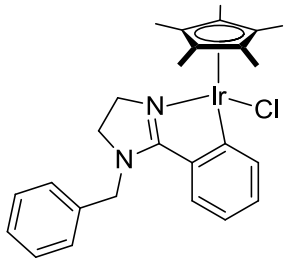
6

Yellow powder; 0.05 mmol scale, yield 24 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.21 (td, *J* = 7.5, 1.5 Hz, 1H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 4.95 – 4.66 (m, 2H), 4.02 (m, 2H), 1.77 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.33, 164.10, 135.67, 132.39, 130.72, 126.48, 121.82, 87.71, 71.40, 50.39, 9.49; IR (solid) ν_{max} 2914, 1632 (C=N stretch), 1450, 1396, 1241, 1029, 914, 752, 736; elemental analysis for $C_{19}H_{23}ClIrNO$ calcd: C 44.83, H 4.55, N 2.75; found: C 44.63, H 4.49, N 2.60.



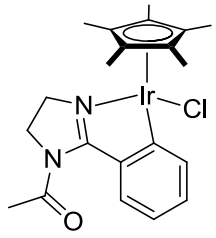
11

Yellow powder; 0.05 mmol scale, yield 25 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 3.82 (m, 4H), 3.36 (s, 3H), 1.74 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.25, 165.98, 136.46, 134.77, 130.61, 125.32, 120.96, 87.24, 55.77, 49.90, 35.24, 9.20; IR (solid) ν_{max} 3201, 2977, 2912, 1604 (C=N stretch), 1523, 1376, 1029, 817, 752, 632; elemental analysis for $C_{20}H_{26}ClIrN_2 \cdot H_2O$ calcd: C, 44.47, H, 5.23, N, 5.19; found: C 44.66, H 4.84, N 5.00.



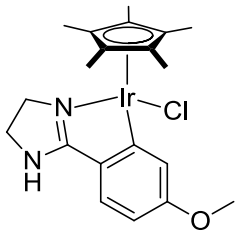
12

Yellow powder; 0.05 mmol scale, yield 27 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.35 (m, 5H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 8.0 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.71 (d, *J* = 16.0 Hz, 1H), 3.96 (m, 2H), 3.81 (m, 1H), 1.76 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.43, 166.17, 137.33, 136.71, 134.59, 130.92, 128.96, 127.69, 127.05, 125.28, 121.27, 87.56, 53.63, 52.50, 50.45, 9.43; IR (solid) ν_{max} 2977, 2907, 1652 (C=N stretch), 1531, 1450, 1380, 1290, 1153, 1076, 1030, 694, 609; elemental analysis for $C_{26}H_{30}ClIrN_2 \cdot 0.5CH_2Cl_2$ calcd: C 49.68, H 4.88 N 4.37; found: C 49.66, H 5.18, N 3.89.



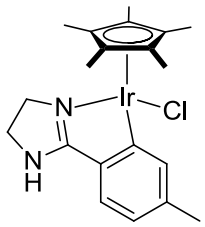
13

Yellow powder; 0.05 mmol scale, yield 24 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 4.27 (t, *J* = 8.5 Hz, 2H over lapped), 4.12 (dt, *J* = 13.5, 8.5 Hz, 1H), 4.01 (dt, *J* = 13.5, 8.5 Hz, 1H), 2.32 (s, 3H), 1.76 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.30, 168.37, 135.75, 134.77, 131.80, 129.83, 128.33, 121.60, 88.77, 51.57, 50.73, 25.16, 9.45; IR (solid) ν_{max} 2977, 2892, 1685 (amide C=O stretch), 1648 (C=N stretch), 1392 (amide C-N stretch), 1311, 1162, 1150, 1025, 728; elemental analysis for $C_{21}H_{26}ClIrN_2O$ calcd: C 45.85, H 4.76, N 5.09; found: C 46.27, H 4.87, N 4.89.



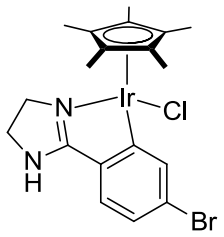
14

Yellow powder; 0.050 mmol scale, yield 24 mg, 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, H), overlapped with $CHCl_3$, 6.51 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.77 (s br, 1H), 3.86 (s, 3H) overlapped with 3.79 (m, 1H), 3.56 (m, 1H), 3.08 (m, 1H), 2.07 – 1.97 (m, 1H), 1.73 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.92, 166.04, 161.35, 128.54, 126.32, 120.24, 107.50, 87.10, 55.16, 51.59, 45.06, 9.48; IR (solid) ν_{max} 3212 (N-H stretch), 1610 (C=N stretch), 1581, 1528, 1454, 1326, 1226, 1155, 1029, 817; *m/z* (EI^+) 539.1 (MH^+), 541.1 (MH^+); HRMS (EI^+) calcd. for $C_{20}H_{27}Cl^{193}IrN_2O$ (MH^+), 541.1419; found, 541.1432.



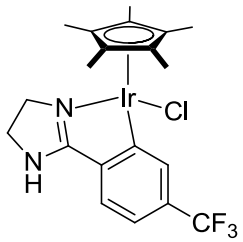
15

Yellow powder; 0.050 mmol scale, yield 25 mg, 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.20 (s, br, 1H), 3.80 (m, 1H), 3.67 (m, 1H), 3.38 (m, 1H), 2.55 (m, 1H), 2.37 (s, 3H), 1.71 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.30, 163.81, 140.86, 136.60, 132.79, 124.92, 122.16, 86.99, 51.67, 44.80, 22.00, 9.46; IR (solid) ν_{max} 3212 (N-H stretch), 2955, 2920, 1610 (C=N stretch), 1527, 1450, 1403, 1319, 1149, 1122, 1029, 825, 678; elemental analysis for $C_{20}H_{26}ClIrN_2 \cdot 0.5CH_2Cl_2$ calcd: C 43.61, H 4.82, N 4.96; found: C 43.37, H 4.78, N 4.95.

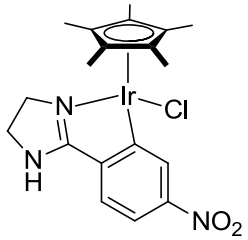


16

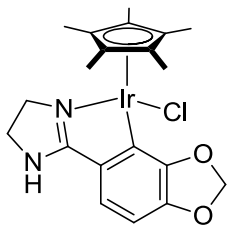
Yellow powder; 0.050 mmol scale, yield 18 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H overlapped with $CHCl_3$), 7.08 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.08 (s br, 1H), 3.86 (m, 1H), 3.71 (m, 1H), 3.52 (m, 1H), 2.81 (m, 1H), 1.72 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.68, 166.36, 138.17, 134.35, 126.74, 126.19, 124.12, 87.44, 51.81, 44.75, 9.40; IR (solid) ν_{max} 3210 (N-H stretch), 2910, 1604 (C=N stretch), 1569, 1034 (aryl C-Br stretch), 814, 732, 610; elemental analysis for $C_{19}H_{23}BrClIrN_2 \cdot CH_2Cl_2$ calcd: C 35.75, H 3.75, N 4.17; found: C 36.07, H 3.74, N 4.06.



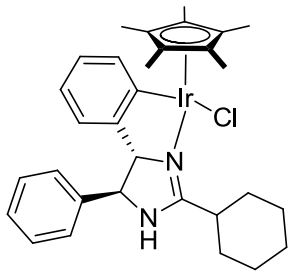
17 Yellow powder; 0.066 mmol scale, yield 30 mg, 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.56 (s, br, 1H), 3.83 (m, 1H), 3.64 (m, 1H), 3.39 (m, 1H), 2.39 (m, 1H), 1.71 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.55, 164.05, 138.85, 132.11, 131.67, 125.18, 123.25, 118.13, 118.10, 87.64, 51.81, 44.62, 9.39; ^{19}F{^{13}C} NMR (376 MHz, $CDCl_3$) δ -62.20; IR (solid) ν_{max} 3215 (N-H stretch), 2950, 2920, 1610 (C=N stretch), 1527, 1474, 1315, 1160, 1118, 1073, 682, 645; *m/z* (EI^+) 574.1 (M^+), 576.1 (M^+); HRMS (EI^+) calcd. for $C_{20}H_{23}ClF_3{}^{191}IrN_2$, 574.1102; found, 574.1100.



18 Dark red powder; 0.05 mmol scale, yield 23 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 6.18 (s br, 1H), 3.93 (td, *J* = 12.0, 8.5 Hz, 1H), 3.77 (td, *J* = 12.0, 8.5 Hz, 1H), 3.66 – 3.53 (m, 1H), 2.86 (m, 1H), 1.75 (s, 15H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.89, 165.26, 148.79, 141.50, 129.91, 125.54, 116.70, 88.06, 52.06, 44.96, 9.45; IR (solid) ν_{max} 3230 (N-H stretch), 2905, 1630 (C=N stretch), 1583, 1508 (NO_2), 1334 (NO_2), 1113, 1026, 725; elemental analysis for $C_{19}H_{23}ClIrN_3O_2{\cdot}CH_2Cl_2$ calcd: C 37.65, H 3.95, N 6.59; found: C 37.49, H 3.98, N 6.37.

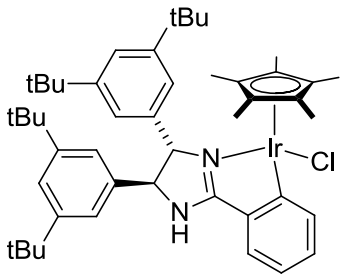


19 Yellow powder; 0.05 mmol scale, yield 20 mg, 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.99 (s, br, 1H), 5.93 (s, 1H), 5.89 (s, 1H), 3.85 (m, 1H, 3.75 (m, 1H), 3.52 (m, 1H), 2.85 (m, 1H), 1.78 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.87, 151.43, 147.73, 138.77, 130.76, 121.00, 102.40, 99.20, 87.70, 51.66, 44.82, 9.79; IR (solid) ν_{max} 3224 (N-H stretch), 2920, 1620 (C=N stretch), 1540, 1423, 1357, 1245, 1045, 892; elemental analysis for $C_{20}H_{24}ClIrN_2O_2$ calcd: C 43.51, H 4.38, N 5.07; found: C 43.65, H 4.49, N 4.83.



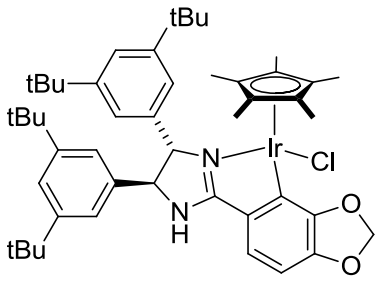
20

Single diastereoisomer. Yellow powder; 0.125 mmol scale, yield 51 mg, 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 3H overlapped), 7.44 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.98 (td, *J* =8.0, 2.0 Hz, 1H), 6.80 (m, 2H overlapped), 5.20 (s, br, 1H), 4.90 (m, 2H overlapped) 2.95 (tt, *J* = 12.0, 4.0 Hz, 1H), 2.38 (d, *J* = 16.0 Hz, 1H), 2.10-0.80 (m, overlapped cyclohexyl CH_2's, 9H), 1.71 (s, 15H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.72, 156.17, 147.04, 142.03, 136.77, 129.19, 128.41, 127.51, 127.44, 122.36, 118.43, 86.76, 82.95, 67.71, 40.44, 32.73, 31.33, 26.18, 25.96, 25.87, 9.50; IR (solid) ν_{max} 3217 (N-H stretch), 2916, 1615 (C=N stretch), 1573, 1450, 1380, 1149, 1133, 1029, 833, 701; elemental analysis for $C_{31}H_{38}ClIrN_2 \cdot CH_2Cl_2$ calcd: C 51.16, H 5.37, N 3.73; found: C 51.12 H 5.33, N 3.24.



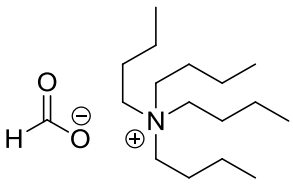
21

Formed as 1 regioisomer with 2 diastereoisomers. Yellow powder; 0.073 mmol scale, yield 56 mg, 84% ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 0.7 H), 7.81 (d, *J* = 8.0 Hz, 0.7 H), 7.43 (d, *J* = 8.0 Hz, 1.4 H), 7.34 (d, *J* = 8.0 Hz, 1.4 H), 7.31 (m, 0.7 H), 7.22 (m, 1.4), 7.17 (m, 1.4 H), 7.08 (m, 1.4 H), 7.03 (m, 1H), 5.62 (d, *J* = 0.7 H), 5.05 (m, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 8.0 Hz, 1 H), 1.48 (s, 7.5 H), 1.44 (s, 7.5 H), 9.37 (s, 9 H), 1.30 (m, 16 H), 1.26 (s, 11H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.85, 176.47, 151.52, 151.27, 150.68, 150.62, 136.23, 132.01, 131.19, 124.43, 124.31, 123.35, 122.76, 122.38, 122.24, 121.07, 87.65, 87.09, 80.29, 73.19, 72.52, 34.96, 34.90, 34.81, 31.64, 31.56, 31.47, 9.54, 9.16; IR (solid) ν_{max} 3218 (N-H stretch), 2958, 2911, 1727, 1654 (C=N stretch), 1600, 1558, 1457, 1261, 1230, 1025, 725, 1029, 671; *m/z* (EI^+) 882.4 (M^+), 883.4 ($M+H^+$), 884.4 (M^+); HRMS (EI^+) calcd. for $C_{48}H_{64}Cl^{191}IrN_2$ ($M+H^+$), 883.4302; found, 883.4298.

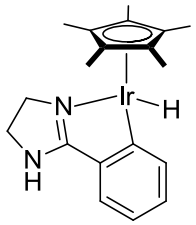


22

Formed as 1 regioisomer with 2 diastereoisomers. Yellow powder; 0.10 mmol scale, yield 69 mg, 75% ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1 H), 7.33 (d, *J* = 12.0 Hz, 1H), 7.22 (m, 0.5 H), 7.18 (m, 1 H), 7.14 (m, 1 H), 7.07 (m, 1 H), 7.06 (m, 0.5 H), 6.97 (d, *J* = 8.0 Hz, 0.5 H), 6.89 (d, *J* = 8.0 Hz, 0.5 H), 6.57 (m, 1 H), 6.05 (s, 1H), 5.98 (s, 1 H), 5.55 (s, 0.5 H), 5.03 9m, 1 H0, 4.79 (m, 0.5 H), 1.55 (s, 15 H), 1.33-1.26 (m, 36 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.33, 151.72, 151.62, 151.48, 151.27, 150.77, 148.73, 148.00, 143.43, 141.78, 140.47, 139.33, 139.27, 130.91, 129.56, 88.41, 82.03, 78.81, 72.71, 71.50, 35.12, 35.08, 32.05, 31.88, 31.57, 31.37, 31.18, 30.85, 10.73, 9.76, 9.64, 9.26, 9.14, 8.69; IR (solid) ν_{max} 3243 (N-H stretch), 2954, 2904, 1727, 1623 (C=N stretch), 1600, 1537, 1527, 1469, 1423, 1361, 1245, 1199, 1049, 944, 875, 682; *m/z* (EI^+) 926.4 (M^+); HRMS (EI^+) calcd. for $C_{48}H_{64}Cl^{191}IrN_2O_2$, 926.4257; found, 926.4254.



Tetra-*n*-butylammonium formate. The compound was prepared using a modification of the method of Thathagar *et al.*[S16] A column was charged with Dowex ion-exchange resin (40 g) suspended in a 1.5 M NaOH solution. The column was flushed further with 1.5 M NaOH solution (3 L) and colour change from yellow (chloride form) to orange (hydroxide form) was observed. The resin was flushed with distilled water (until the fractions became neutral pH) and then with 0.5 L of 0.2 M formic acid solution, followed by distilled water until the fractions returned to neutral pH. The eluent was changed to an organic solvent by flushing with 1 L MeOH and the beads were left to swell for 1 h and flushed with an 18 mM solution of tetra-*n*-butylammonium bromide (TBAB) in MeOH, until the elute tested positive for halides using the $AgNO_3/HNO_3$ test. Suitable fractions were combined and the solvent removed on a rotary evaporator to give a clear oil which was subsequently dried *in vacuo for* 24 h to give a white, sticky low melting point solid; ^{1}H NMR (400 MHz, CD_3CN) δ 8.67 (s, 1H), 3.20 – 3.03 (m, 8H), 1.67 – 1.53 (m, 8H), 1.35 (dd, *J* = 15, 7.5 Hz, 8H), 0.96 (t, *J* = 7.5 Hz, 12H); ^{13}C{^{1}H}NMR (101 MHz, CD_3CN) δ 166.53, 59.25, 24.28, 20.28, 13.75, *m/z* (ES^+) 242.3 (100%, $NBut_4^+$), 243.3 (15%, $NBut_4^+$).



23

[Cp*IrH(2-phenylimidazoline)] 23. A solution of **1** (10.2 mg, $2x10^{-2}$ 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 3 freeze-pump-thaw cycles and placed under a dry N_2 atmosphere. A solution of NaOOCH (6.8 mg, 5.0 equiv, 0.1 mmol) and a minimum quantity of TBA·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 one hour the aqueous layer was removed by syringe and the organic layer washed with degassed water (5 x 3 mL) under N_2. The organic layer was evaporated *in vacuo* to give an air sensitive bright yellow solid (9.4 mg, 99%.); ^{1}H NMR (400 MHz, CD_3CN) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 5.76 (s, br, 1H, NH), 3.93 (m, 1H), 3.72 (m, 2H), 3.66 (m, 1H), 1.94 (s, 15H), -15.68 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 137.24, 129.77, 125.61, 119.20, 118.32 (the imidazoline C_2 carbon is not observed and one aromatic resonance appears to be obscured by the solvent signal), 88.60, 56.00, 55.31, 46.29, 10.53; elemental analysis for $C_{19}H_{25}IrN_2$, calcd: C 48.18, H 5.32, N 5.91: found C 47.89, H 5.29, N 6.58 (nitrogen value is slightly high due the sample being prepared under a nitrogen atmosphere).

Reaction of 1 with TBA·OOCH to give 23. In a dry, N_2 filled glovebox, a solution of tetra-*n*-butylammonium formate (1.7 mg, 5.93 µmol) in anhydrous CD_3CN (0.7 mL) was added to a vial containing **1** (3.0 mg, 5.93 µmol). The vial was stirred rapidly until all the solids dissolved and the solution transferred to an NMR tube fitted with a J Young type Teflon® cap, sealed, removed from the glovebox and analyzed by ^{1}H NMR spectroscopy. Complete disappearance of the formate proton signal (δ 8.67 ppm) was observed and a single resonance in the hydride region (δ -15.68 ppm) appeared. In addition, the NH proton was observed as a broad singlet (δ 5.76 ppm). This compound remained unchanged by ^{1}H NMR spectroscopy after 5 days at room temperature under N_2.

2. Procedure for the hydrogen evolution experiments

Precatalyst (10 µmol, unless otherwise specified) was added to a thick walled glass vessel fitted with a side arm and a rubber septum which had been preheated to the appropriate temperature by means of an oil bath. The vessel was degassed three times and placed under an N_2 atmosphere. The vessel was connected to the gas collection apparatus (standard water displacement apparatus, using a graduated cylinder to determine volume) and the entire system was flushed with N_2 for 5 minutes and allowed to equilibrate for 5 minutes. The volume of gas present in the measuring vessel (if not zero) was noted. Formic acid/triethylamine (F/T, 5:2, 1.5 mL) was added by syringe through the septum and the reaction was stirred vigorously at a constant temperature. Any small volume of gas collected resulting from addition of the F/T was noted and subtracted from the values for gas collected. The catalytic activity was calculated from the volume of collected gas that passed through the water cylinder, supposing that all the gas consisted of hydrogen. This is consistent with the work of Tanaka *et al*. who used an identical method and assumptions for gas measurement for F/T dehydrogenation.[S17] The presence of hydrogen in the collected gas was confirmed by GC and ^{1}H NMR analysis.

2.1 TOF and TON calculations

The calculation of the volume of 1 mole H_2 at 25 ^{o}C was carried out using van der Waals eq. 1[S18]

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \qquad (1)$$

Where

R: 8.3145 m³ Pa mol^{-1} K^{-1} ***T***: 298.15 K ***p***: 101,325 Pa (1 atm)

a: 0.002476 m^6·Pa·mol^{-2} ***b***: 0.02661x10^{-3} m^3·mol^{-1}

Thus, $V_{(H_2, 25\,^oC, 1\ atm)}$ = 24.49 L·mol^{-1}

Hence, the turnover numbers of a dehydrogenation can be calculated as:

TON = ($V_{(H_2,25\ ^oC)}$ /24.49) / $n_{catalyst}$ where $n_{catalyst}$ is the number of moles of catalyst. The turnover frequency, TOF = TON / time in hours.

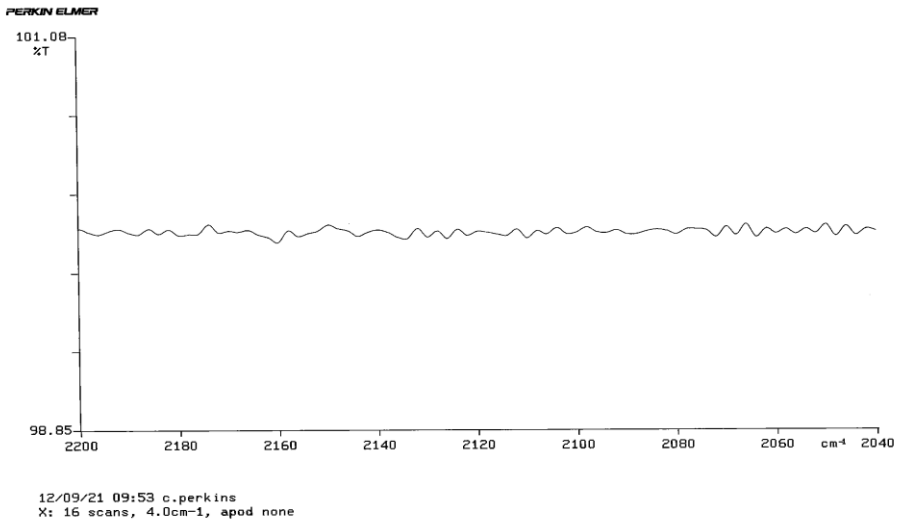
Initial TOF values were determined using the volume of gas collected within the first 3 minutes of the reaction and are an average TOF for that period.

Thus, for 13.33 mL (25 ^oC) of gas collected within 3 minutes using 10 µmol of **1** (Table 1, text), the average TOF = [(13.33 x 10^{-3} / 24.49) / 10^{-5}] / (180 / 3600) = 1090 h^{-1}.

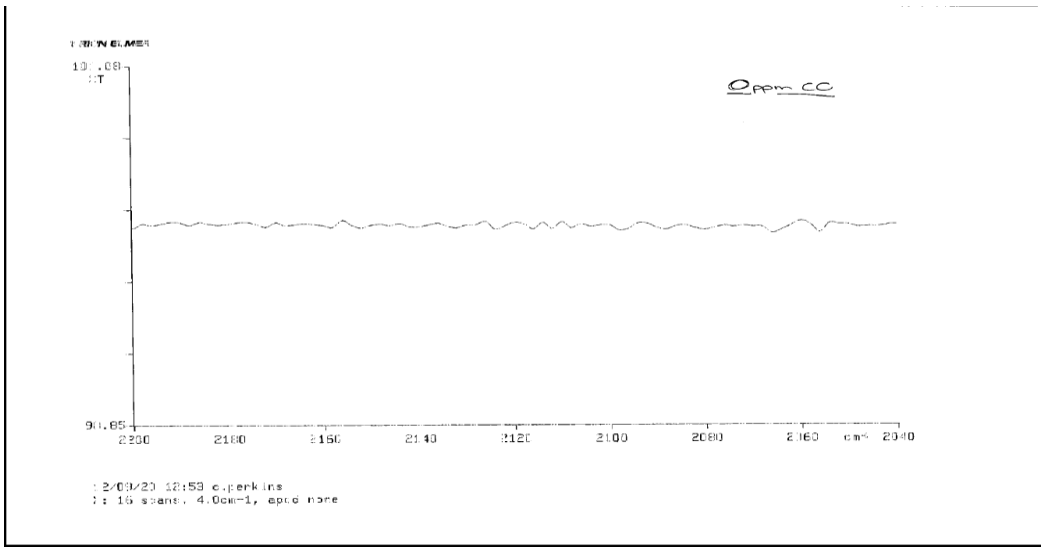
For 100 mL (25 ^oC) of gas collected within 10 s using 10 µmol of **22** (Text, Section 2.2), the average TOF = [(100 x 10^{-3} / 24.49) / 10^{-5}] / (10 / 3600) = 147,000 h^{-1}

2.2 CO detection in gas samples by FT-IR

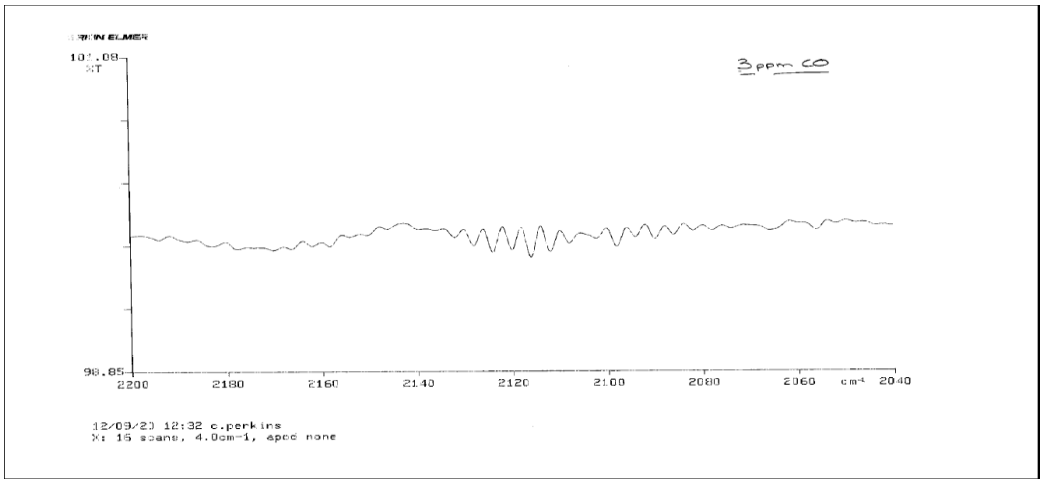
The amount of CO in the gases produced was analysed by a method described by Fellay *et al*[S19] using FT-IR and comparison of the produced gas to known concentrations of CO (0, 3, 5 and 10 ppm) in 1:1 H_2/CO_2 mixtures. The comparison below shows the CO content in the evolved gas to be undetectable (<3 ppm).



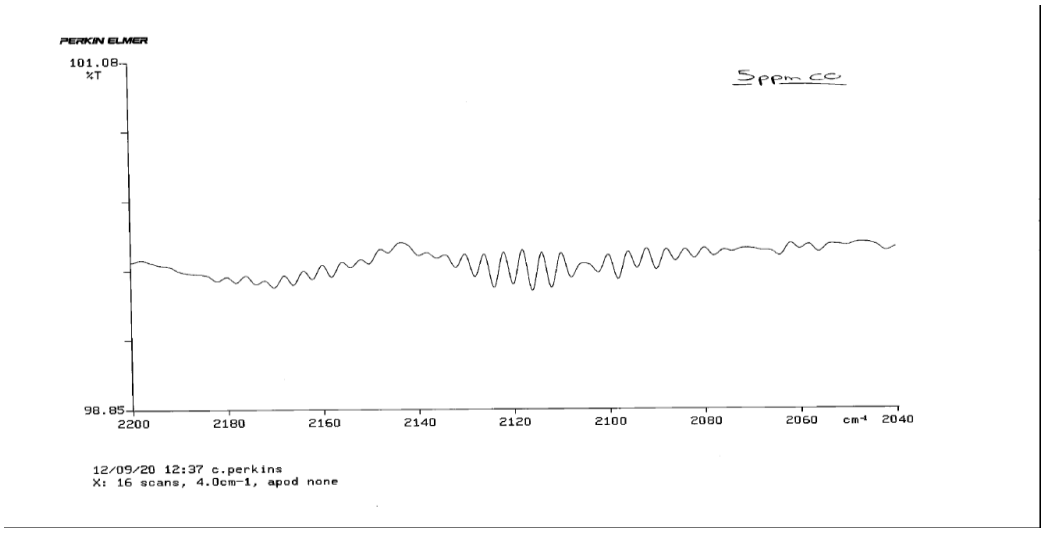
FT-IR of a sample of the gases produced (taken from the headspace of a dehydrogenation of 1.5 mL F/T catalysed by 10 µmol **1** in a sealed J. Young type tube sealed with a Teflon screw cap).



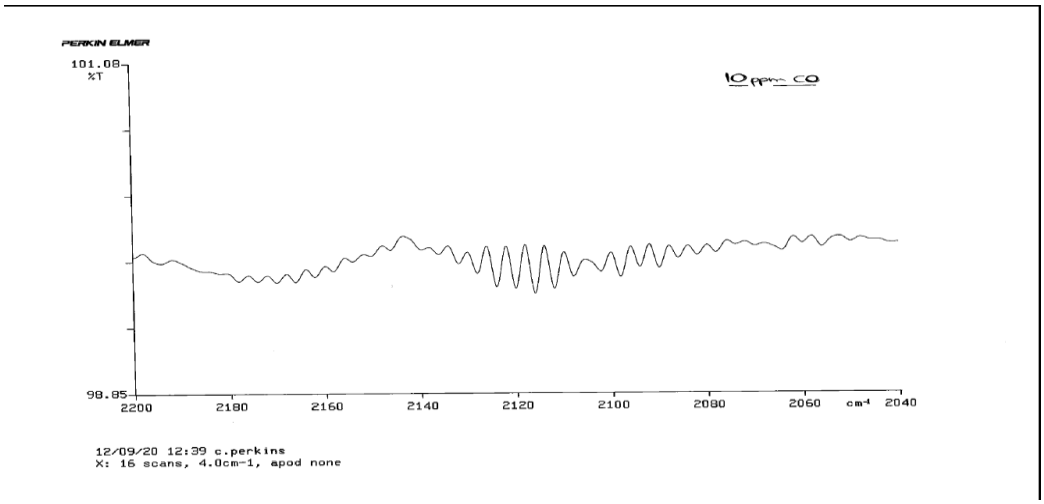
FT-IR of a sample of 0 ppm CO in 1:1 H_2 / CO_2.



FT-IR of a sample of 3 ppm CO in 1:1 H_2 / CO_2.



FT-IR of a sample of 5 ppm CO in 1:1 H_2 / CO_2.

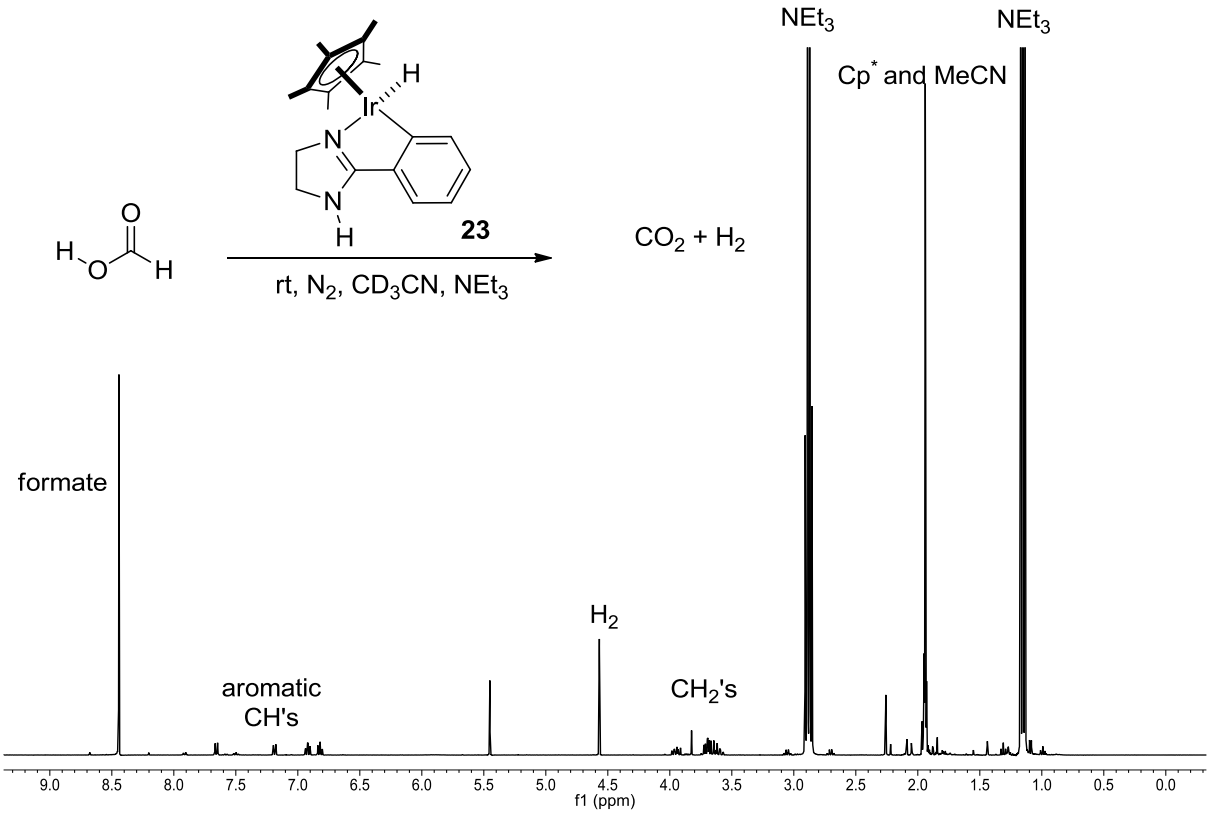


FT-IR of a sample of 10 ppm CO in 1:1 H_2 / CO_2.

3. NMR investigations

3.1 *In situ* ^{1}H NMR of hydrogen formation catalysed by 23.

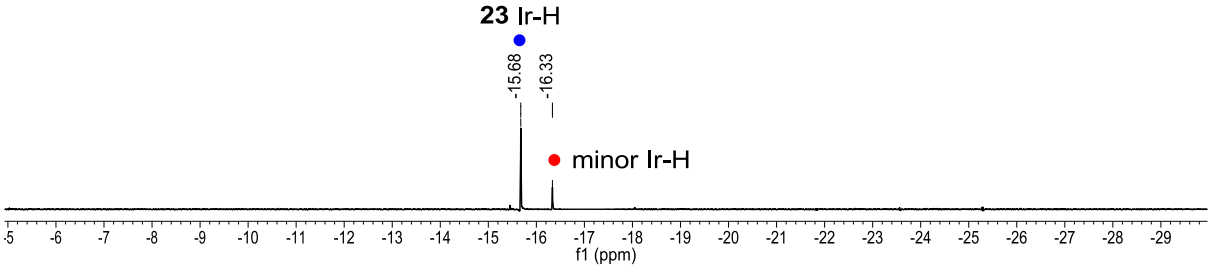
In a dry, N_2 filled glovebox, 5 equivalents of F/T (5:2) was added to a solution of **23** (3.0 mg, 5.93 µmol) in CD_3CN (0.7 mL). A slight colour change from bright yellow to darker yellow was observed along with constant gas evolution showing the catalytic reaction to be occurring. The solution was transferred to an NMR tube fitted with a J. Young type Teflon® screw cap, sealed, removed from the glovebox and analysed by ^{1}H NMR spectroscopy which showed the presence of H_2 (s, δ 4.59 ppm).



^{1}H NMR spectra (400 MHz, CD_3CN) of a hydrogen formation reaction from F/T catalysed by **23**. The NH resonance (typically ~ 5.8 ppm) is not observed.

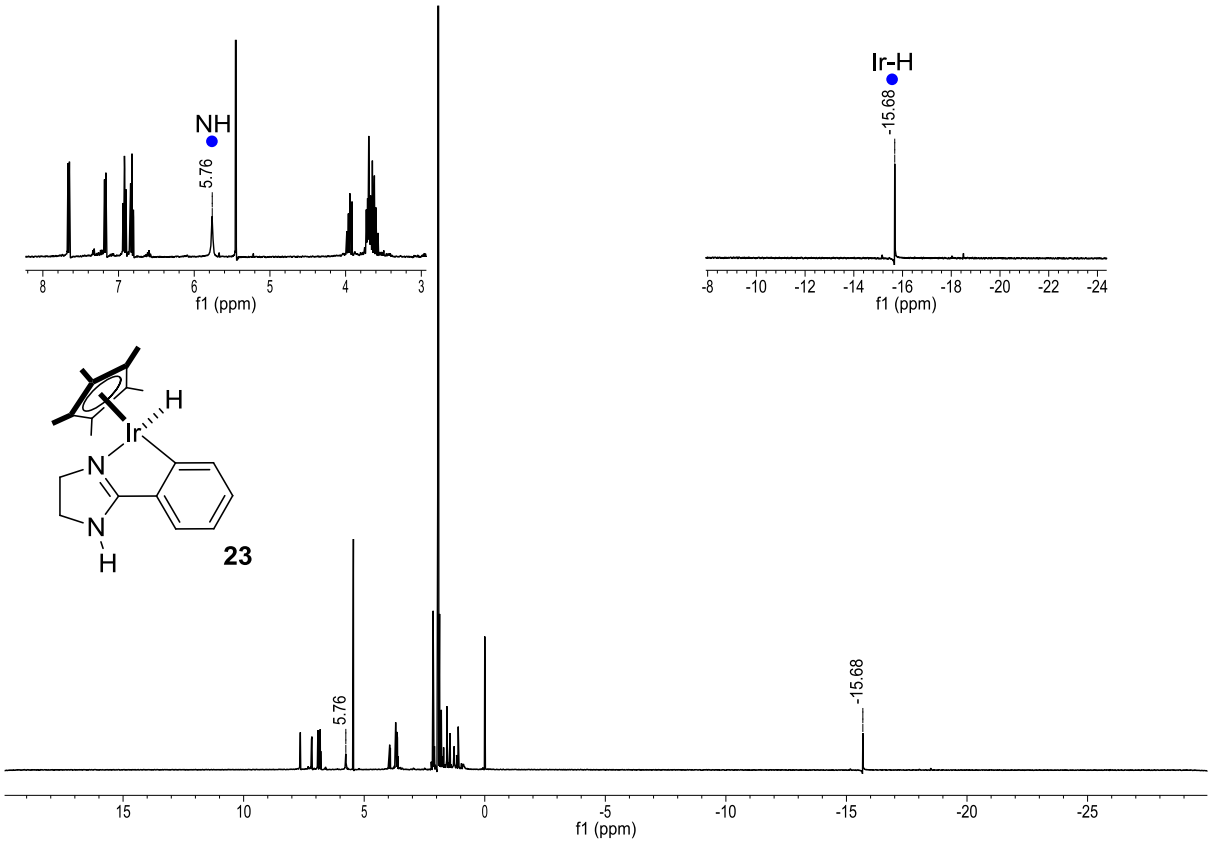
No resonances in the range 0 – 10 ppm were observed other than those corresponding to **23**, F/T azeotrope, H_2 or residual solvents. However, in the hydride region two resonances were observed, with the major resonance corresponding to the hydride of **23** (δ -15.68 ppm) and the minor resonance (δ -16.33 ppm). Analysis of the reactions

of $[Cp^*IrCl_2]_2$, $[Ir(Cl)COD]_2$ and $IrCl_3{\cdot}nH_2O$ with excess 5:2 F/T in CD_3CN under the same conditions by ^1H NMR spectroscopy did not show resonances which were consistent with that of the minor hydride species. In light of this, and the lack of any species that would be derived from catalyst breakdown (i.e. free ligand), the minor hydride species remains unassigned.



Partial ^1H NMR spectra (400 MHz, CD_3CN, hydride region) of a hydrogen formation reaction from F/T catalysed by **23**.

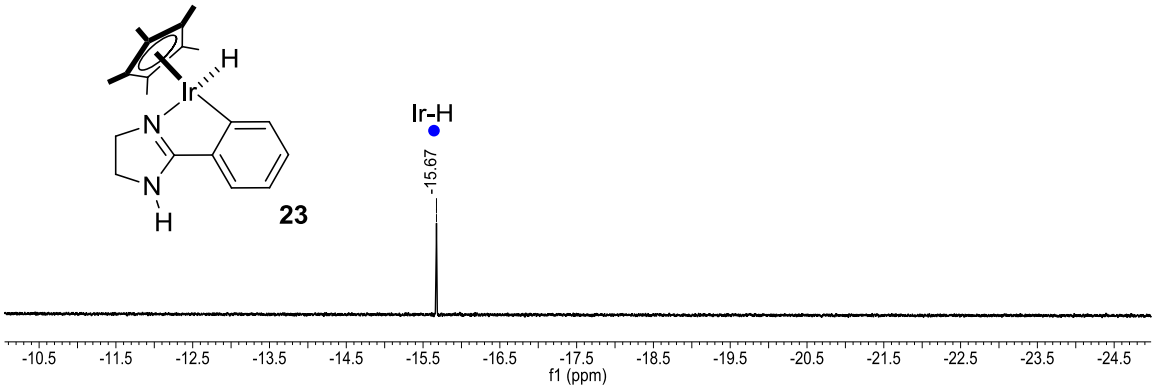
^{1}H NMR of isolated hydride 23



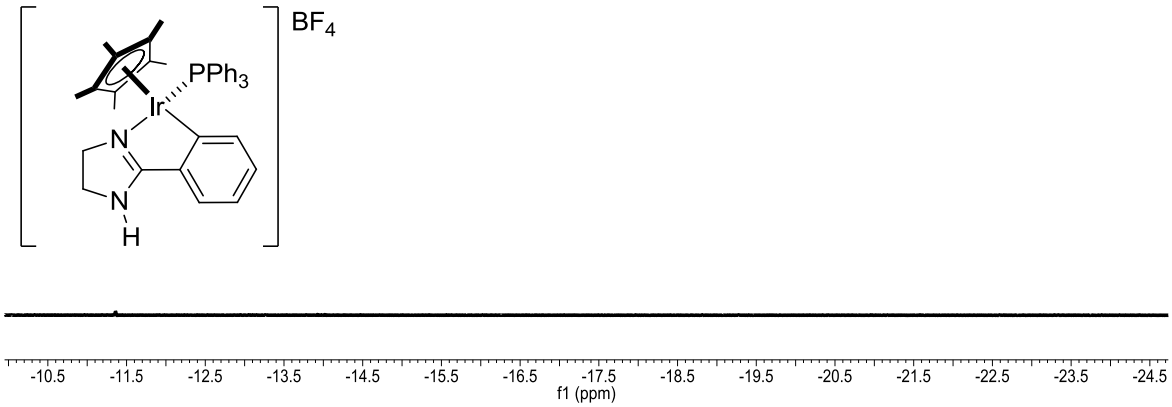
^{1}H NMR spectra (400 MHz, CD_3CN) of **23**.

3.2 Protonation of iridium hydrides

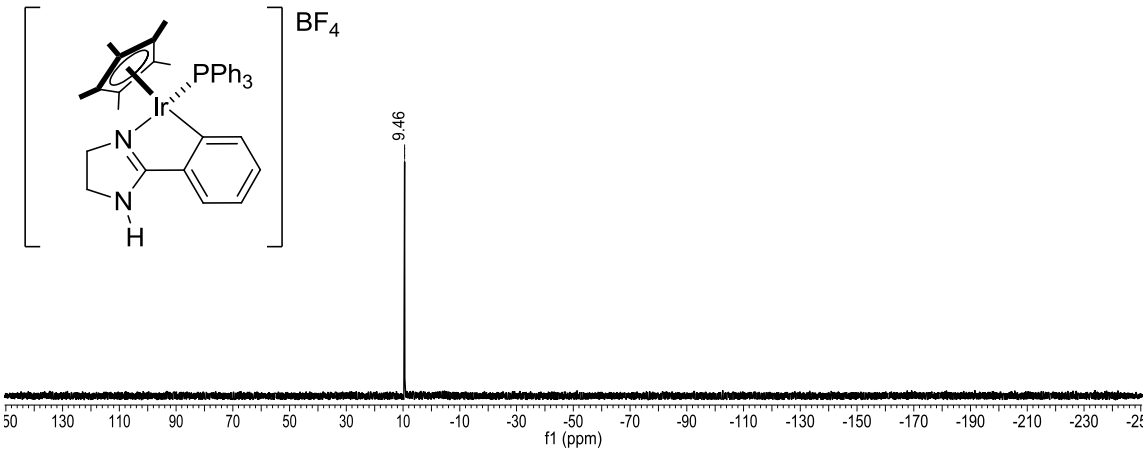
Reaction of iridium hydride 23 with $HPPh_3BF_4$. In a dry, N_2 filled glovebox, a solution of **23** (4.74 mg, 10 µmol) in CD_3CN (0.7 mL) was prepared and added to a vial containing triphenylphosphonium tetrafluoroborate (1.00 equiv.). An instant colour change from bright yellow to faint yellow was 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 by NMR spectroscopy.



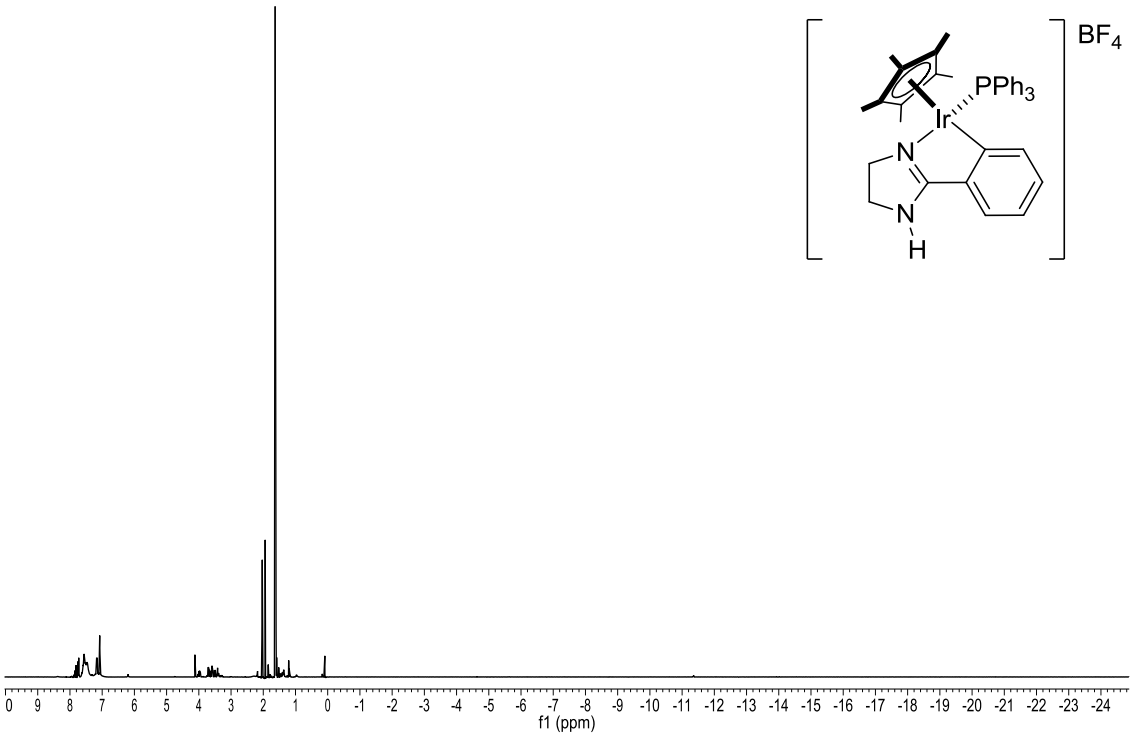
Partial ^1H NMR spectra (400 MHz, CD_3CN, hydride region) of **23** prior to reaction with 1.0 equivalent of $[HPPh_3][BF_4]$.



^1H NMR spectra (400 MHz, CD_3CN, hydride region) of the reaction of **23** with 1.0 equivalent of $[HPPh_3][BF_4]$, showing the disappearance of the hydride signal resulting from protonation and H_2 loss.



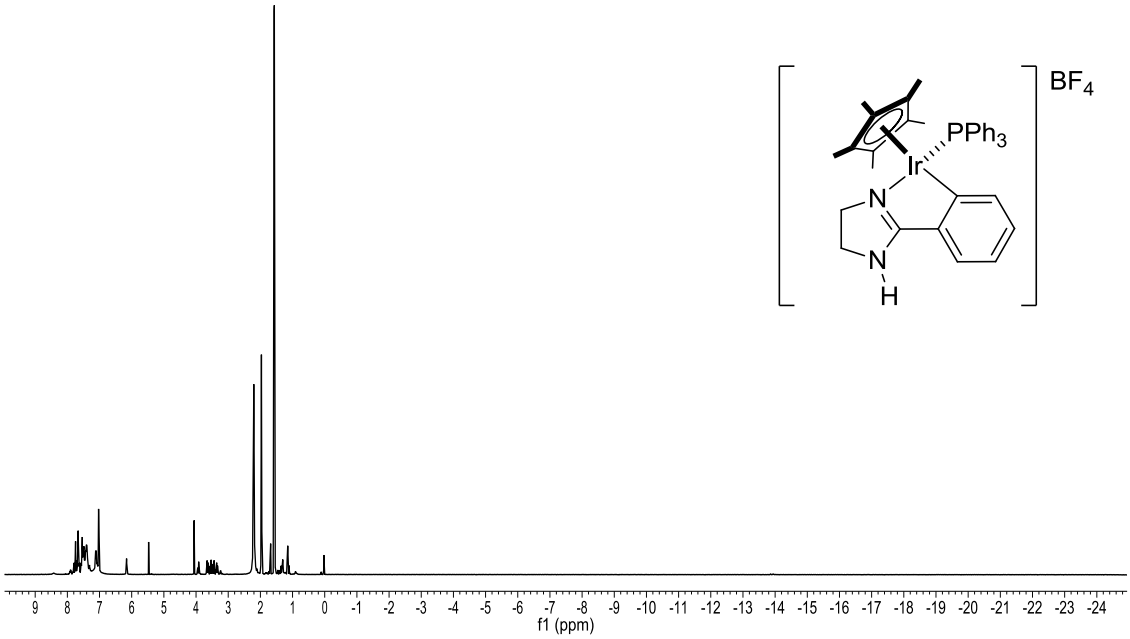
$^{31}P\{^{13}C\}$ NMR spectra (161 MHz, CD_3CN) of **23** after reaction with 1.0 equivalent of $[HPPh_3][BF_4]$ showing the coordination of PPh_3 to the iridium centre.



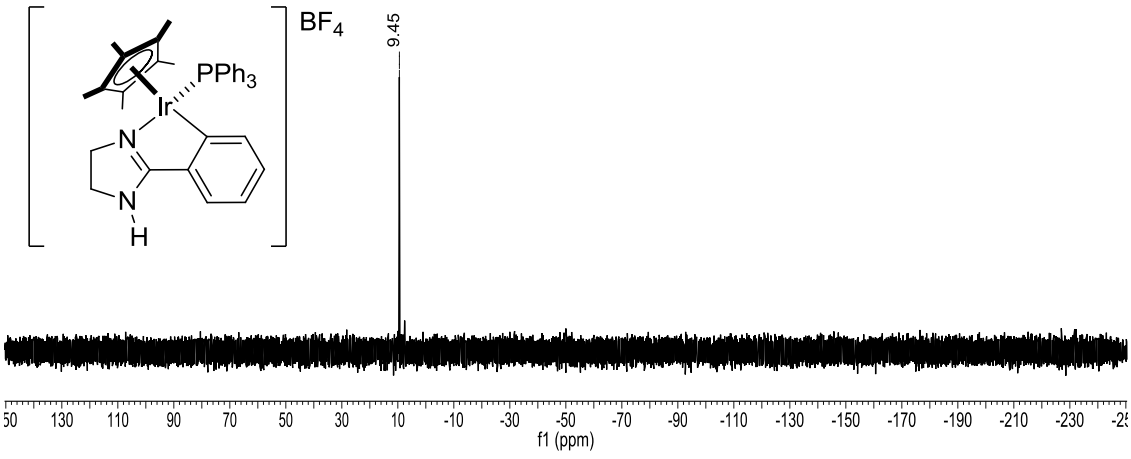
Full ^1H NMR spectra (400 MHz, CD_3CN) of **23** in CD_3CN after reaction with 1.0 equivalent of $[HPPh_3][BF_4]$ in CD_3CN.

Independent synthesis of [1-PPh$_3$][BF$_4$]. In a dry, N_2 filled glovebox, a solution of **1** (5.08 mg, 10 µmol) in THF (0.7 mL) was prepared and added to a vial containing silver tetrafluoroborate (2.0 mg, 1.05 equiv.). The solution was stirred at room temperature for 0.5 h and a colour change from bright yellow to brown was observed along with the formation of an insoluble white precipitate. The solution was filtered

through cotton wool to remove silver chloride and excess silver tetrafluoroborate and the brown clear solution was evaporated to give a brown solid which was dried *in vacuo*. The solid was dissolved in CD_3CN (1 mL) and added to a vial containing triphenylphosphine (2.62 mg, 10 µmol, 1.0 equiv.). An instant colour change from brown to pale yellow was observed. The solution was transferred to an NMR tube J. Young type Teflon® cap, the tube sealed, removed from the glovebox and analysed by NMR spectroscopy.

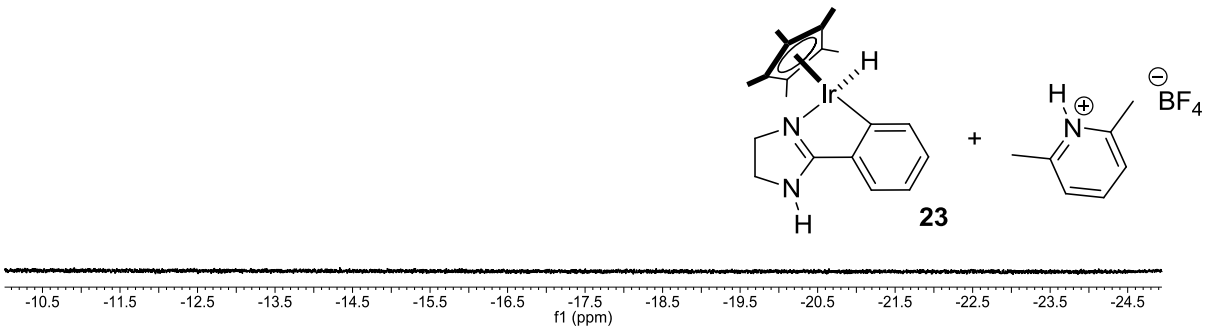


^{1}H NMR spectra (400 MHz, CD_3CN) of **[1-PPh$_3$][BF$_4$]** synthesised from **1** by chloride abstraction with $AgBF_4$ and subsequent reaction with PPh_3.

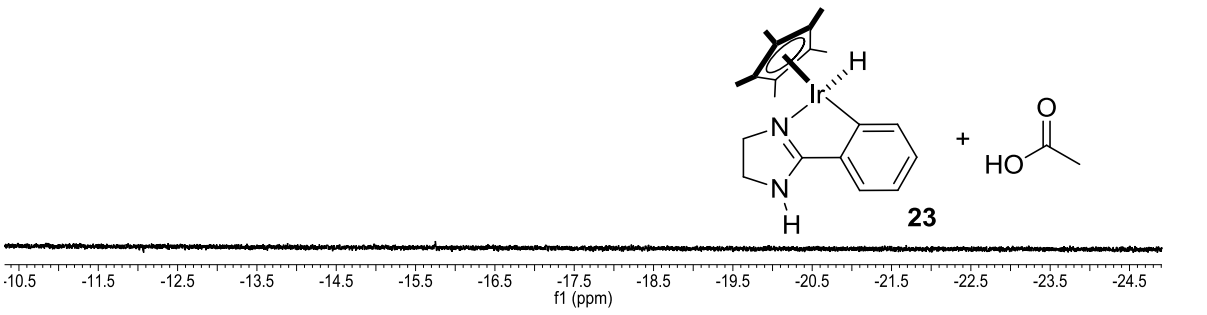


^{31}P{^{13}C} NMR spectra (161 MHz, CD_3CN) of **[1-PPh$_3$][BF$_4$]** synthesised from **1** by chloride abstraction with $AgBF_4$ and subsequent reaction with PPh_3.

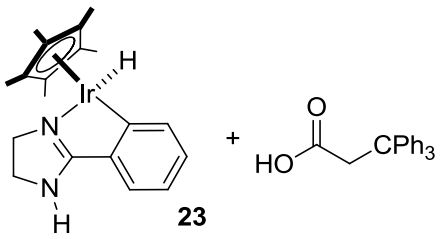
Reactions of hydride 23 with other proton sources in CD_3CN. In a dry, N_2 filled glovebox, a solution of **23** (4.7 mg, 10 µmol) in CD_3CN (0.7 mL) was prepared and transferred into a vial containing the appropriate reaction partner. (1.0 equivalent, 10 µmol unless otherwise stated). The vial was agitated for a few seconds to ensure full mixing and the entire solution was transferred into an NMR tube fitted with a J. Young type Teflon® cap and sealed. The sample was removed from the glovebox analysed by ^1H NMR spectroscopy immediately. In reactions in which the hydride was protonated, hydrogen was often observed as the byproduct by ^1H NMR. However, due to the small amounts used and the transfer of the reaction mixture from vial to NMR tube this was not always the case.

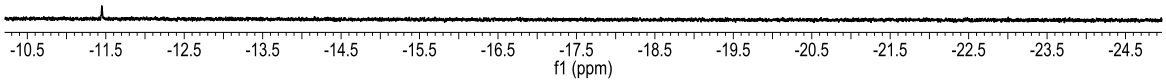


^1H NMR spectra (400 MHz, CD_3CN, hydride region) of the reaction of **23** with 1.0 equivalents of 2,6 lutidinium tetrafluoroborate showing the disappearance of the hydride signal resulting from protonation and H_2 loss.

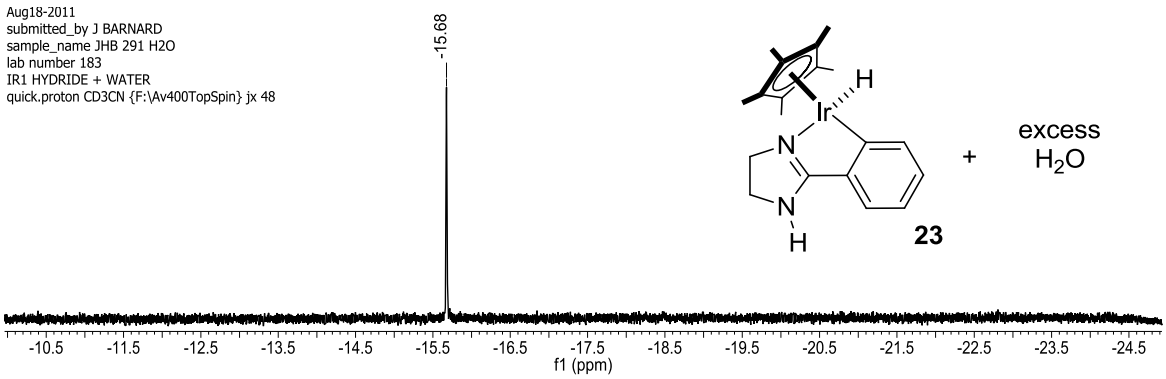


^1H NMR spectra (400 MHz, CD_3CN, hydride region) of the reaction of **23** with a slight excess of acetic acid showing the disappearance of the hydride signal resulting from protonation and H_2 loss.

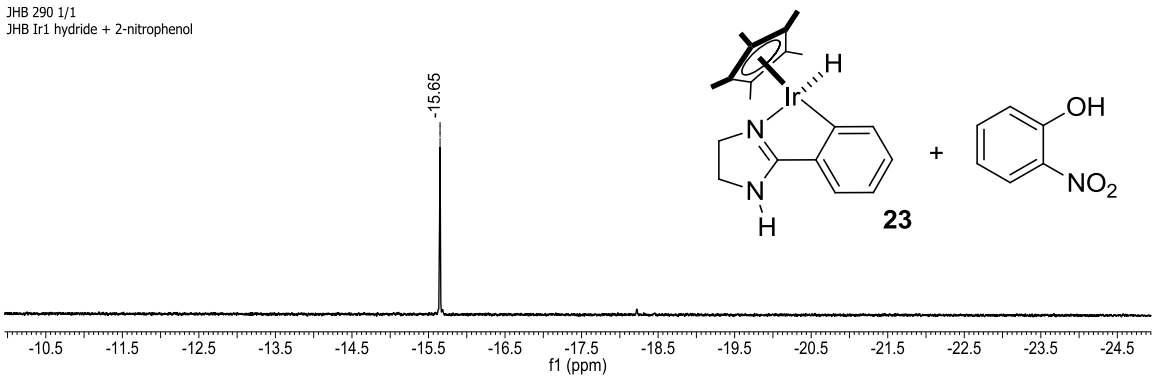




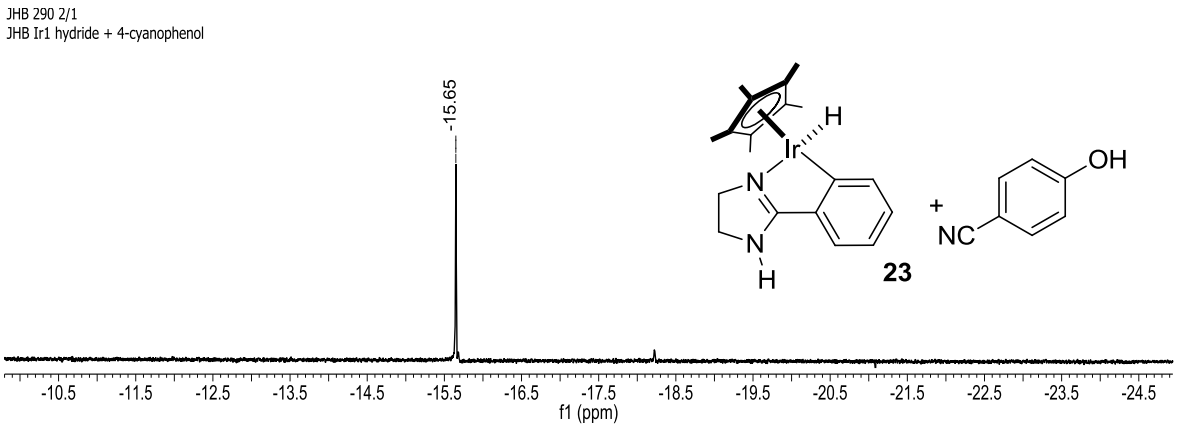
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of the reaction of **23** with one equivalent of 1-trityl acetic acid showing the disappearance of the hydride signal resulting from protonation and H_2 loss.



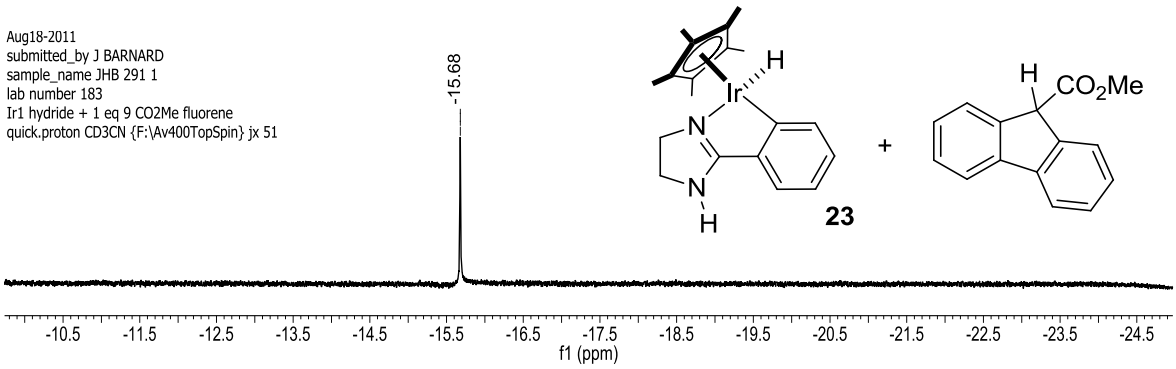
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **23** in the presence of excess H_2O. No reaction has occurred.



^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **23** in the presence of 1 equivalent of 2-nitrophenol. No reaction has occurred.

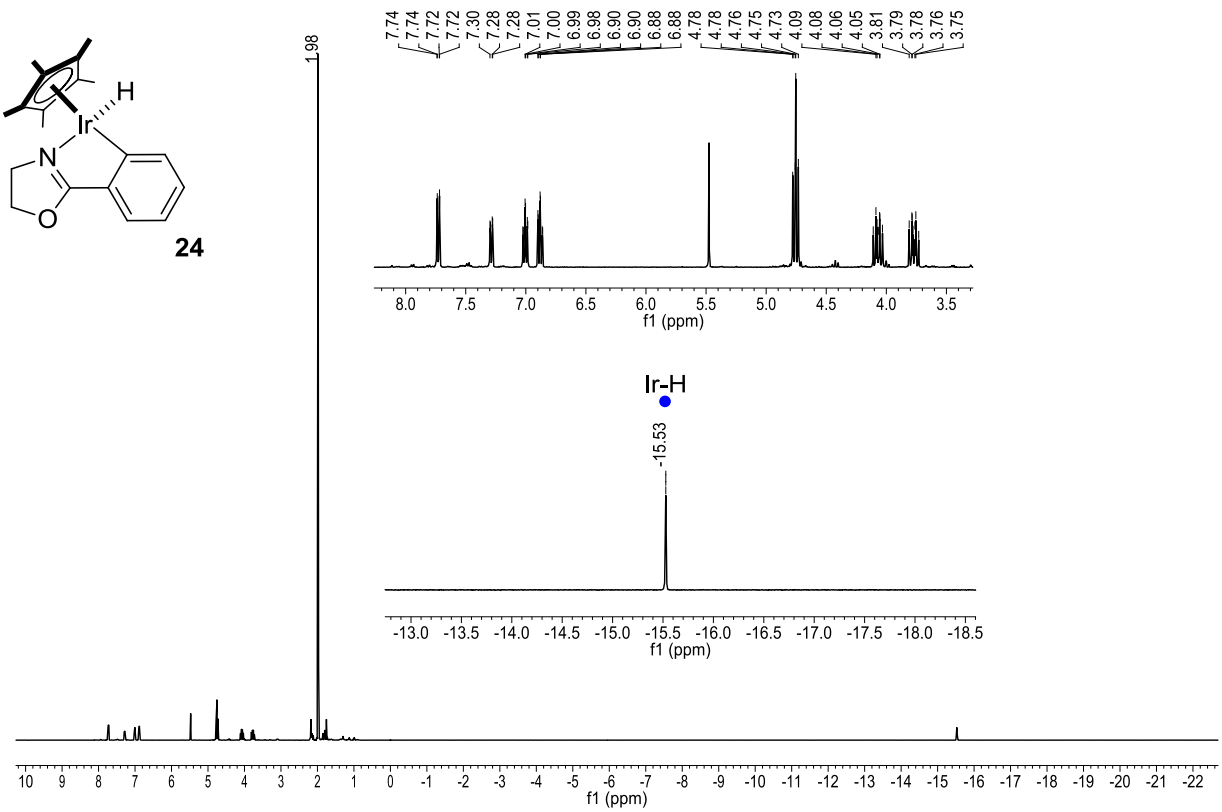


^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **23** in the presence of 1 equivalent of 4-cyanophenol. No reaction has occurred.



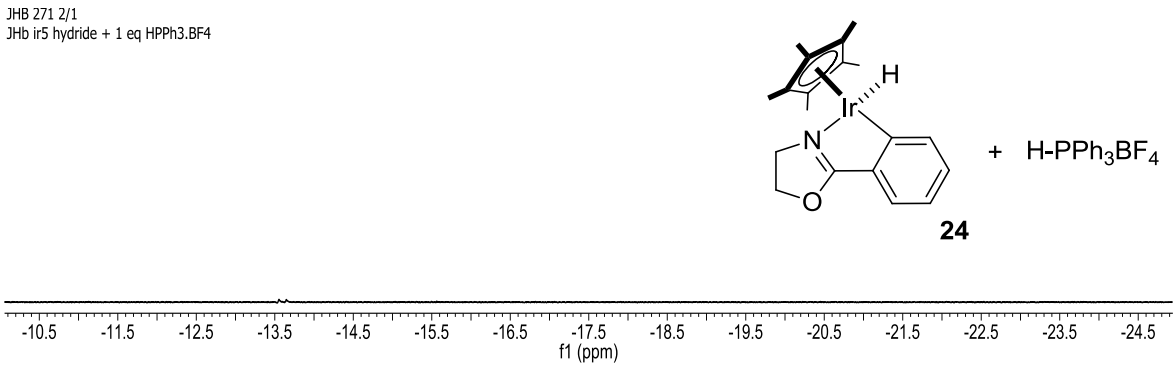
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **23** in the presence of 1 equivalent of 9-fluorene-9-carboxylic acid methyl ester. No reaction has occurred.

^{1}H NMR of isolated hydride 24

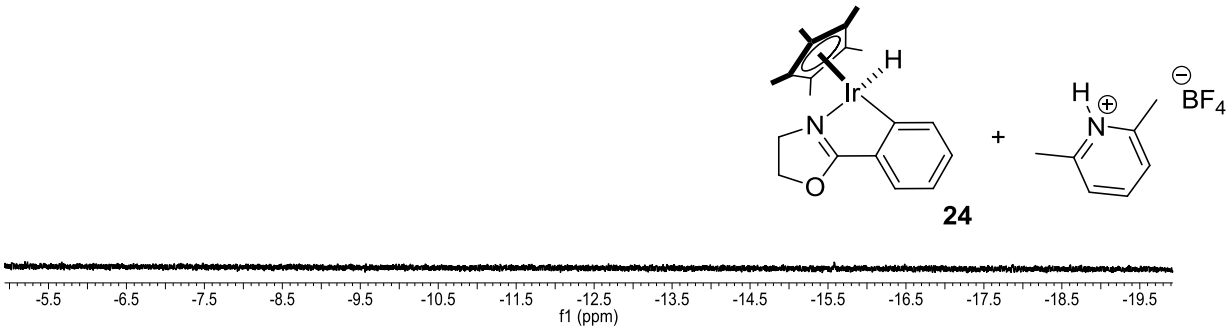


^{1}H NMR spectra (400 MHz, CD_3CN) of **24**

Reactions of hydride 24 with other proton sources in CD_3CN. In a dry, N_2 filled glovebox, a solution of **24** (4.7 mg, 10 µmol) in CD_3CN (0.7 mL) was prepared and transferred into a vial containing the appropriate reaction partner. (1.0 equivalent, 10 µmol unless otherwise stated). The vial was agitated for a few seconds to ensure full mixing and the entire solution was transferred into an NMR tube fitted with a J. Young type Teflon® cap and sealed. The sample was removed from the glovebox analysed by ^{1}H NMR spectroscopy immediately. In reactions in which the hydride was protonated, hydrogen was often observed as the byproduct by ^{1}H NMR. However, due to the small amounts used and the transfer of the reaction mixture from vial to NMR tube this was not always the case.

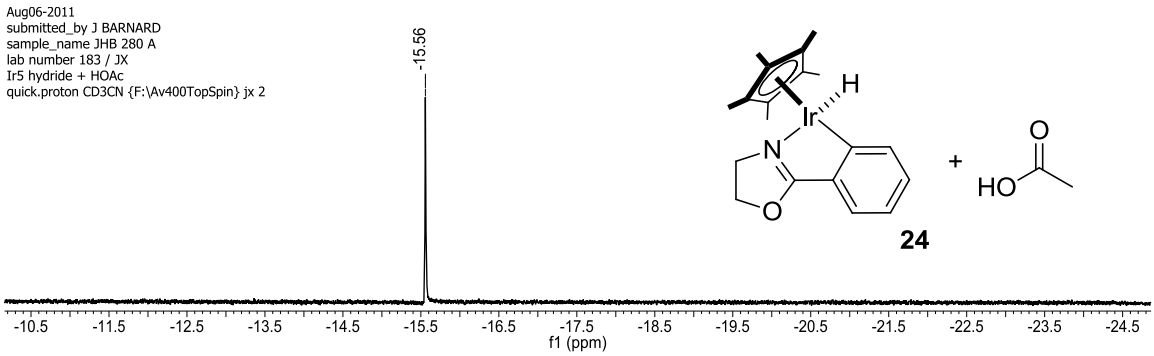


^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of the reaction of **24** with one equivalent of triphenylphosphonium tetrafluoroborate showing the disappearance of the hydride signal resulting from protonation and H_2 loss.

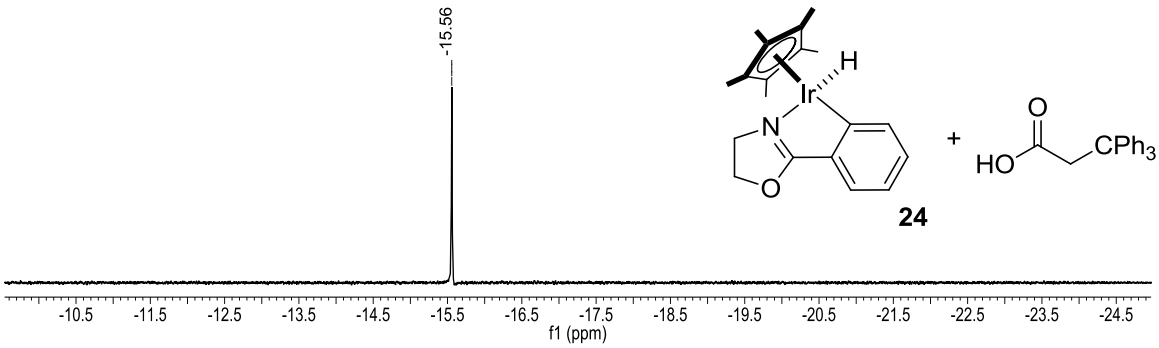


^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of the reaction of **24** with one equivalent of 2,6-lutidinium tetrafluoroborate showing the disappearance of the hydride signal resulting from protonation and H_2 loss

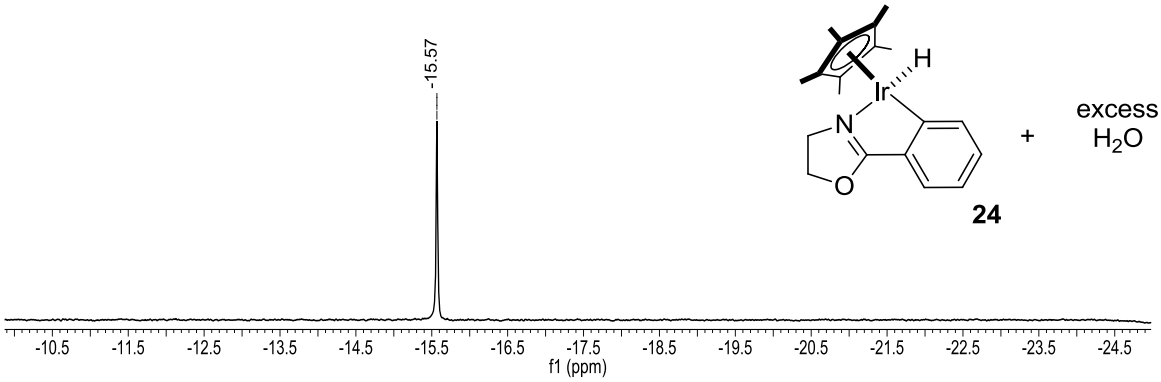
.



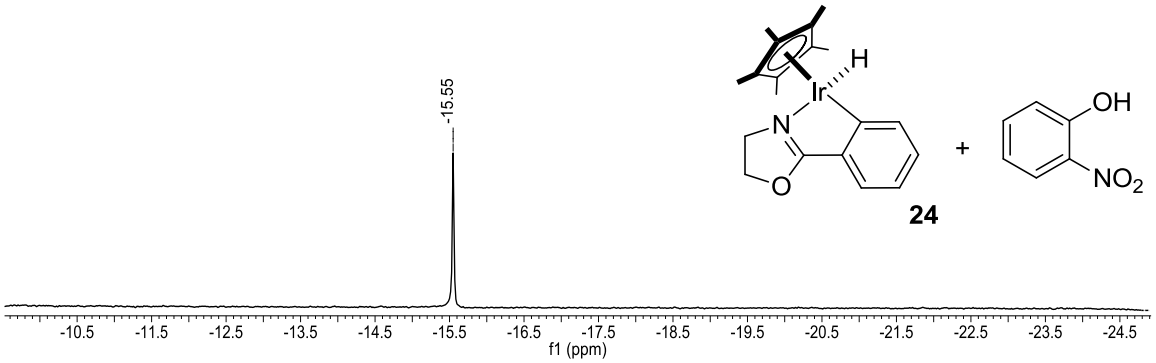
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **24** in the presence of a slight excess of acetic acid. No reaction has occurred.



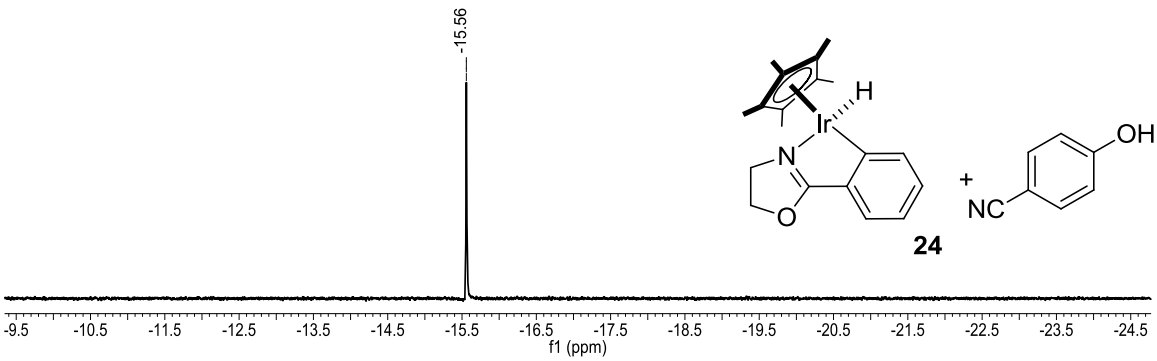
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **24** in the presence of 1 equivalent of 1-trityl acetic acid. No reaction has occurred.



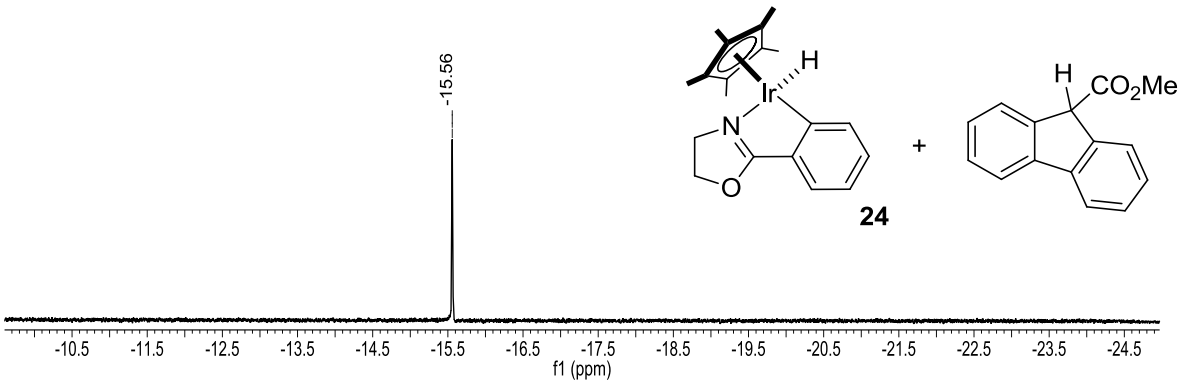
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **24** in the presence of excess H_2O. No reaction has occurred.



^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **24** in the presence of 1 equivalent of 2-nitrophenol. No reaction has occurred.



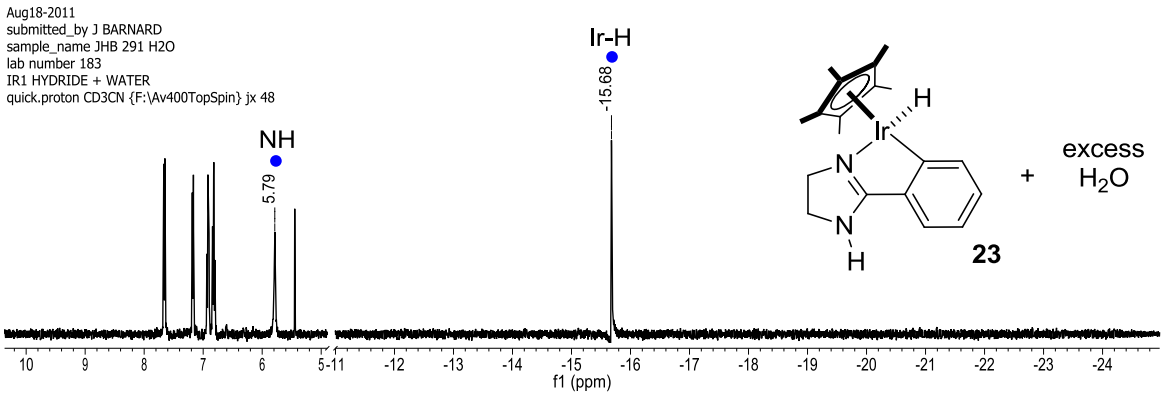
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **24** in the presence of 1 equivalent of 4-cyanophenol. No reaction has occurred.



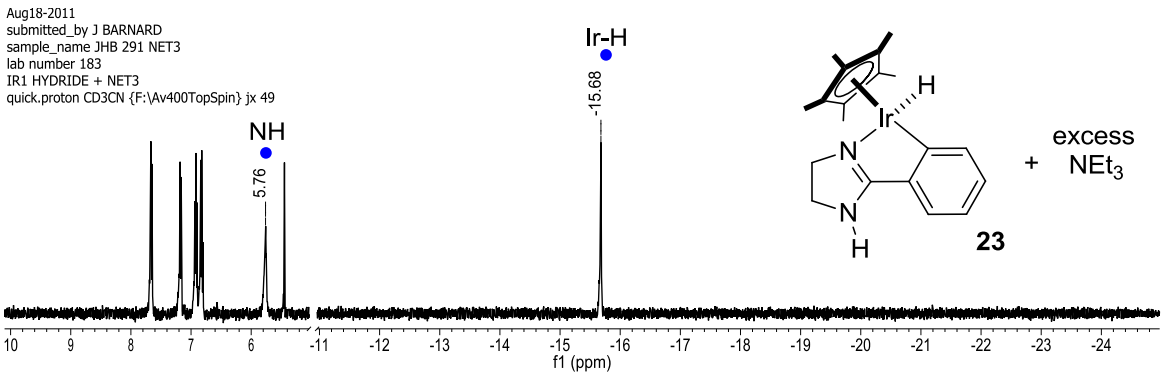
^{1}H NMR spectra (400 MHz, CD_3CN, hydride region) of **23** in the presence of 1 equivalent of 9-fluorene-9-carboxylic acid methyl ester. No reaction has occurred.

3.3 ^{1}H NMR study of the hydrogen bonding of 23

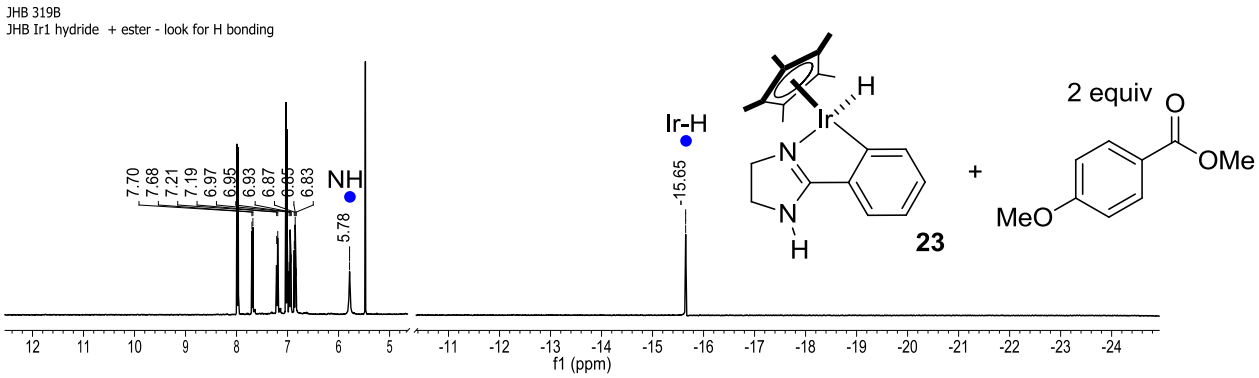
Reactions of 23 with hydrogen bond acceptors / donors. In a dry, N_2 filled glovebox, a solution of **23** (4.7 mg, 10 µmol) in CD_3CN (0.7 mL) was prepared and transferred into a vial containing the appropriate hydrogen bond acceptor / donor. The vial was agitated for a few seconds to ensure full mixing and the entire solution was transferred into an NMR tube fitted with a J. Young type Teflon® cap and sealed. The sample was removed from the glovebox and analysed by ^{1}H NMR spectroscopy immediately.[S20] In the cases in which both a hydrogen bond donor / acceptor and 4-cyanophenol (a potential proton source) were used, a solution of **23** and hydrogen bond donor / acceptor was prepared and transferred into an NMR tube fitted with a J. Young type Teflon® cap and sealed. After analysis by ^{1}H NMR the tube was returned to the glovebox, 4-cyanophenol was added and the tube sealed, removed from the glovebox and analysed by ^{1}H NMR.



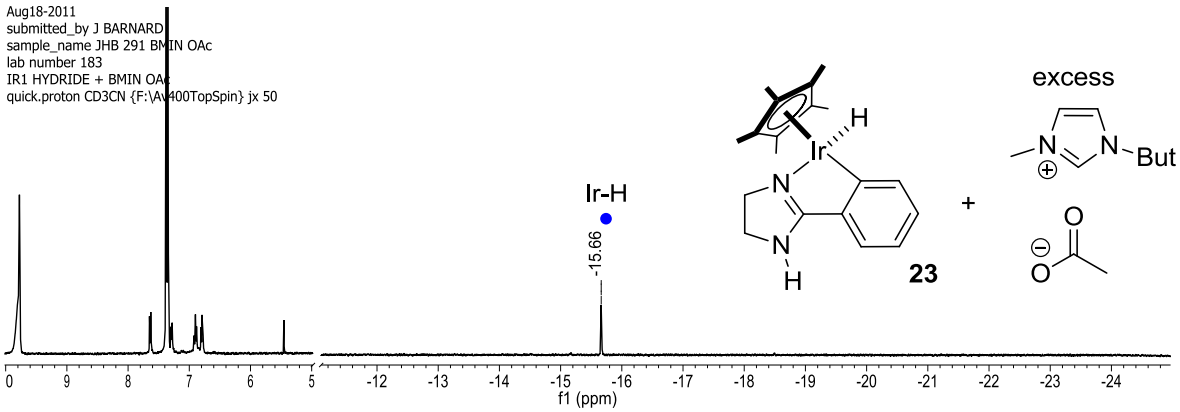
Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** in the presence of excess H_2O. Both the NH and Ir-H resonances remain unchanged, being observed at δ 5.79 and -15.68 ppm, respectively.



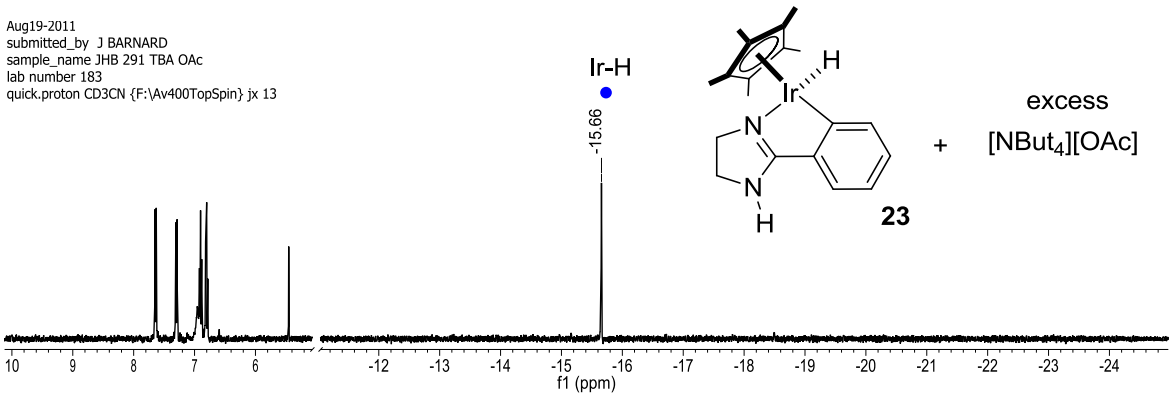
Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** in the presence of excess triethylamine. Both the NH and Ir-H resonances remain unchanged, being observed at δ 5.76 and -15.68 ppm, respectively.



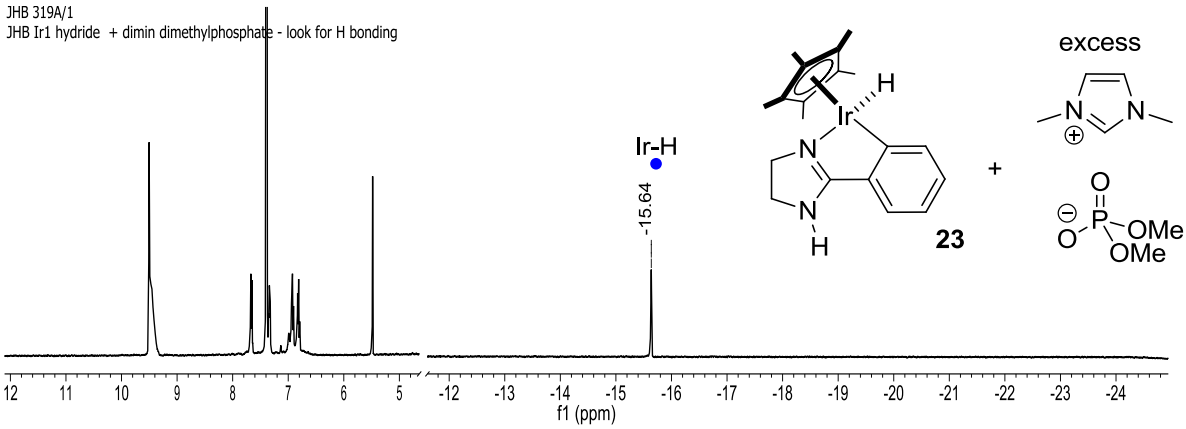
Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** in the presence of 2 equivalents of methyl 4-methoxybenzoate. Both the NH and Ir-H resonances remain unchanged, being observed at δ 5.78 and -15.65 ppm, respectively.



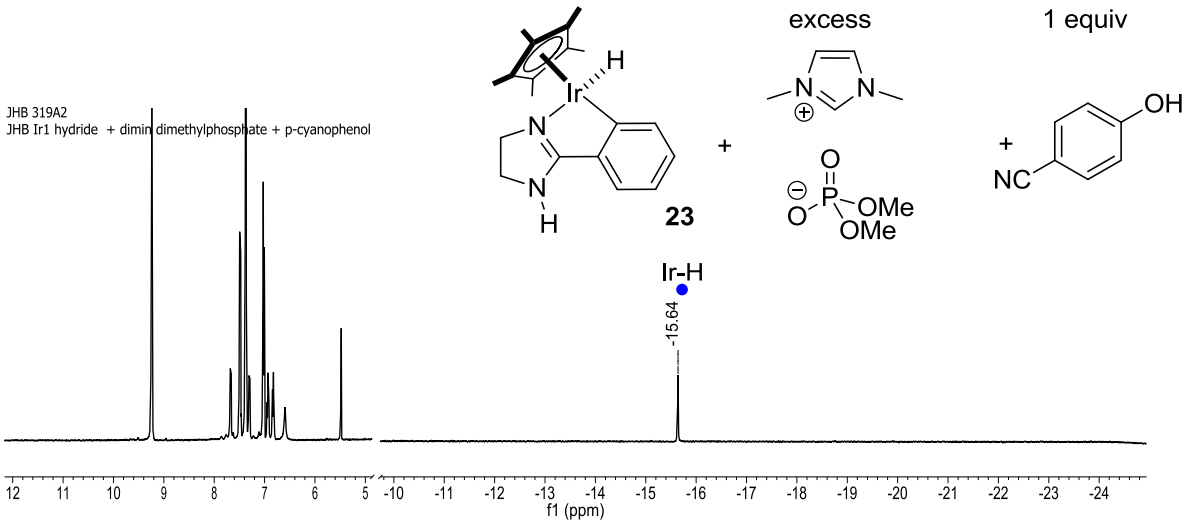
Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** in the presence of excess 1-butyl-3-methylimidazolium acetate. The NH (typically δ ~5.8 ppm) resonance is not observed due to hydrogen bonding but the Ir-H resonance remains unchanged at δ -15.66 ppm.



Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** in the presence of excess tetra-*n*-butylammonium acetate. The NH (typically δ ~5.8 ppm) resonance is not observed due to hydrogen bonding but the Ir-H resonance remains unchanged at δ -15.66 ppm.



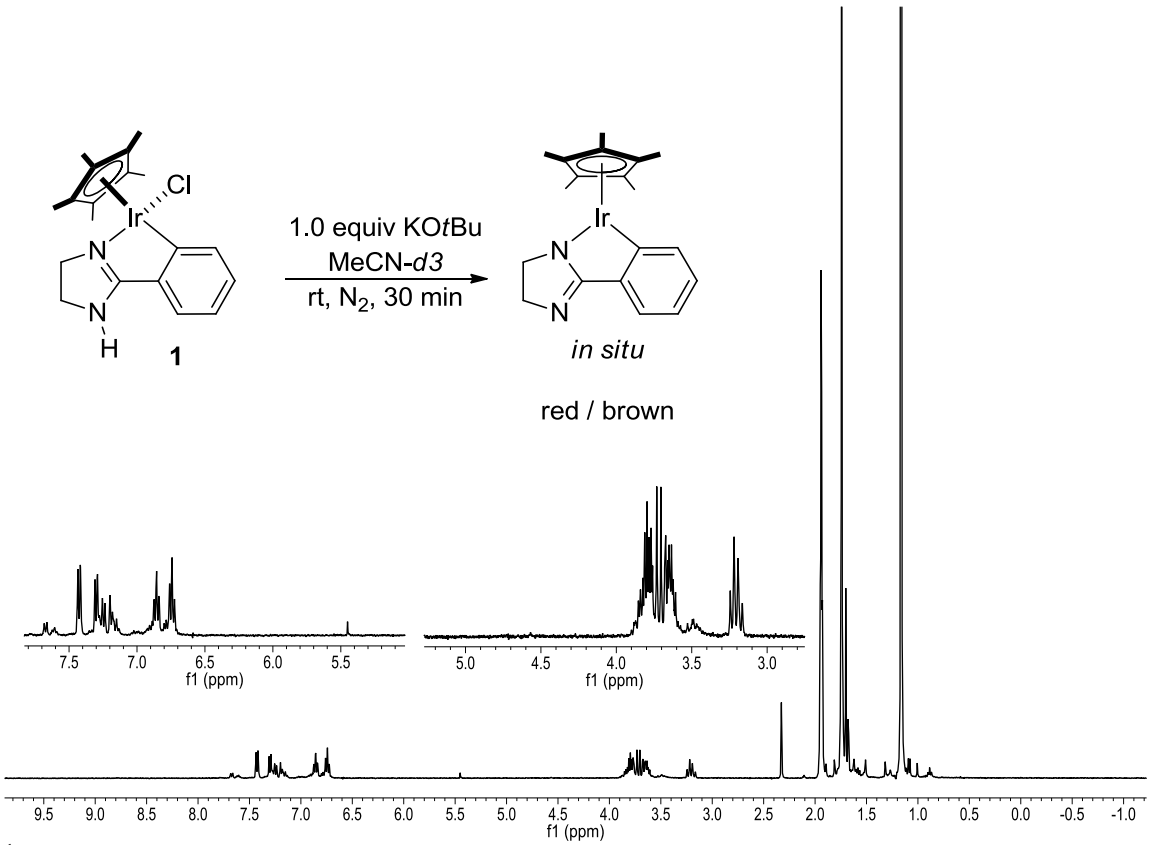
Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** in the presence of excess 1,3-dimethylimidazolium dimethylphosphate. The NH (typically δ ~5.8 ppm) resonance is not observed due to hydrogen bonding but the Ir-H resonance remains unchanged at δ -15.64 ppm.



Partial ^{1}H NMR spectra (400 MHz, CD_3CN, aromatic and hydride region) of **23** after reaction with 1 equivalent of 4-cyanophenol in the presence of excess 1,3-dimethylimidazolium dimethylphosphate. The NH (typically δ ~5.8 ppm) resonance is not observed due to hydrogen bonding with dimethylphosphate but the Ir-H resonance remains unchanged at δ -15.64 ppm.

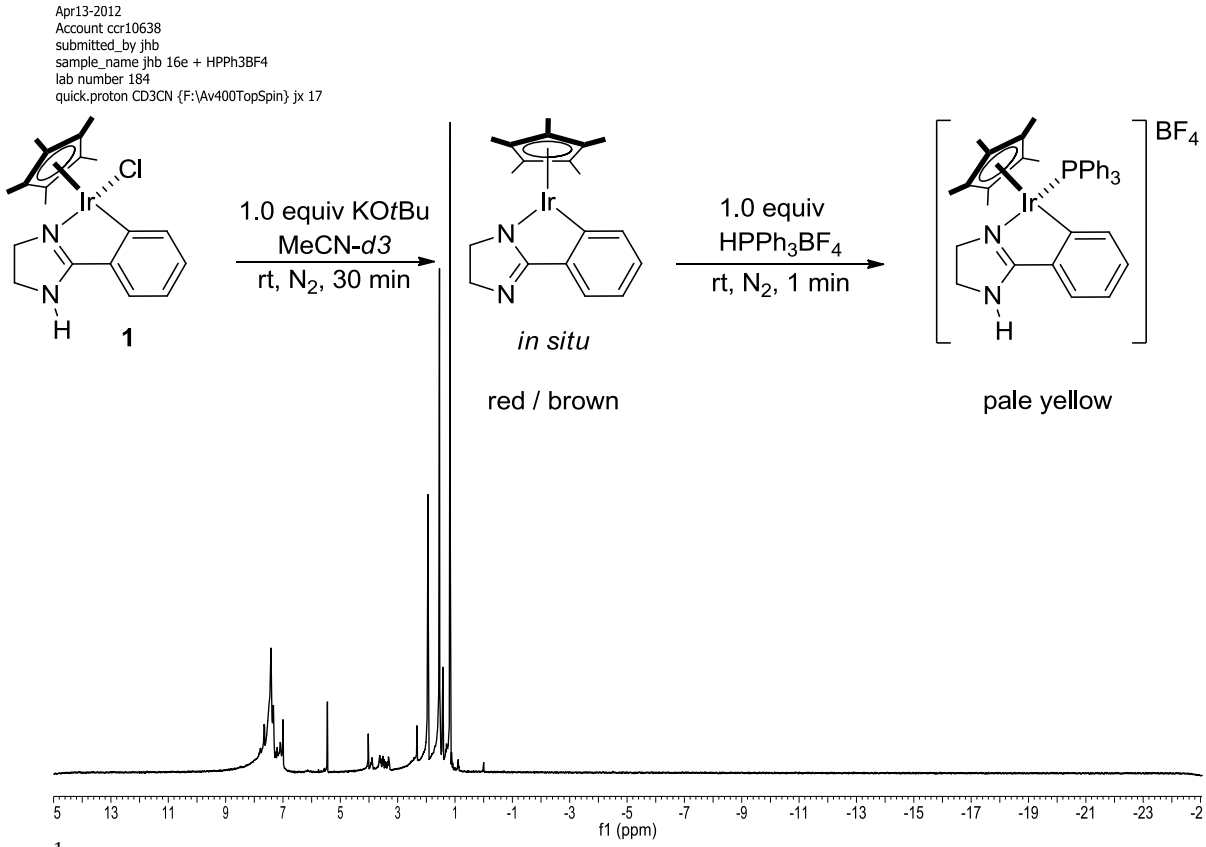
3.4 Deprotonation of chloride complex 1 and the subsequent reactions

Deprotonation of 1 with potassium *tert*-butoxide. In a dry, N_2 filled glovebox, a solution of **1** (5.08 mg, 10 µmol) in MeCN (0.7 mL) was prepared and added to a vial containing dried potassium *tert*-butoxide (1.05 equiv.). The solution was stirred at room temperature for 0.5 h and a colour change from bright yellow to red / brown was observed. The solution was filtered through cotton wool to remove potassium chloride and excess potassium *tert*-butoxide and the red / brown clear solution was evaporated to give a red / brown solid which was dried *in vacuo*. Addition of CD_3CN (0.7 mL) gave a red / brown solution that was transferred to an NMR tube fitted with a J. Young type Teflon® cap, the tube sealed, removed from the glovebox and analysed by NMR spectroscopy.

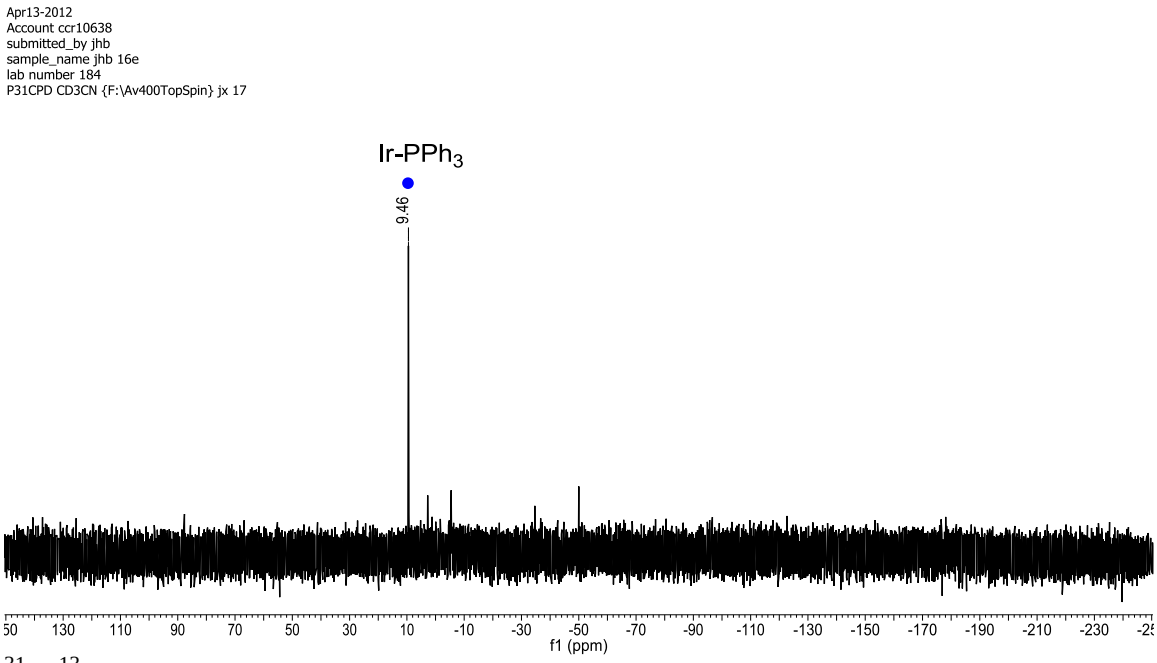


^{1}H NMR spectra (400 MHz, CD_3CN) of **1** after reaction with 1 equivalent of potassium *tert*-butoxide. No NH resonance (typically δ ~5.8 ppm) was observed.

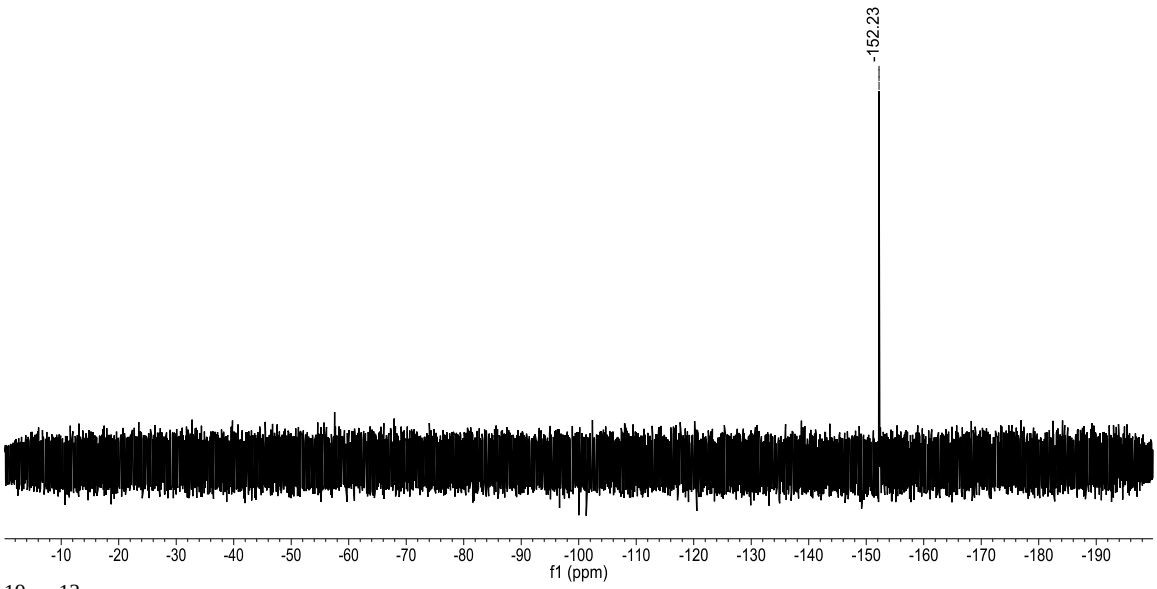
Subsequent reaction of the dehydrochlorination product with triphenylphosphonium tetrafluoroborate. After analysis by ^{1}H NMR, a solution of the dehydrochlorination product was transferred to a dry, N_2 filled glovebox. The tube was opened and the entire solution transferred to a vial containing 1.0 equivalent of $[HPPh_3][BF_4]$. An instant colour change from red / brown to pale yellow was observed. The solution was transferred back to the original NMR tube fitted with a J. Young type Teflon® cap, the tube sealed, removed from the glovebox and analysed by NMR spectroscopy. ^{1}H, ^{31}P{^{13}C} and ^{19}F{^{13}C} NMR spectra are consistent with those of **[1-PPh$_3$][BF$_4$]** prepared by the reaction of **23** with $HPPh_3BF_4$, or by the reaction of **1** with $AgBF_4$ and then PPh_3.



^{1}H NMR (400 MHz, CD_3CN) of the reaction of deprotonated **1** with 1.0 equivalent of $[HPPh_3][BF_4]$ to give **[1-PPh$_3$][BF$_4$]**.

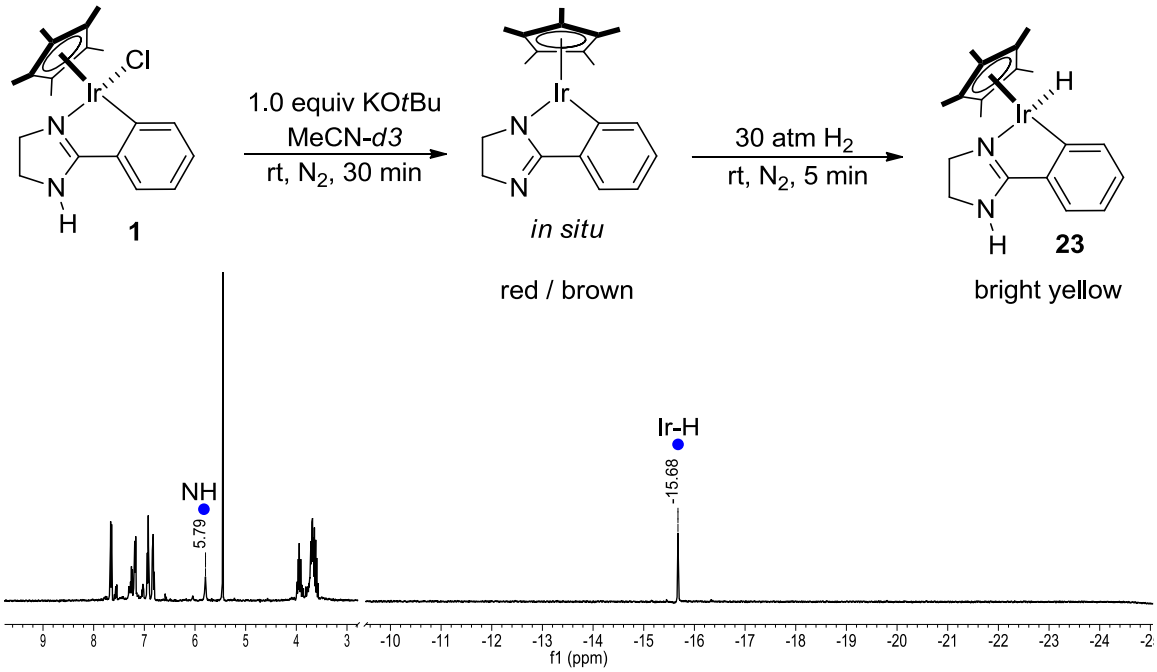


^{31}P{^{13}C} NMR (161 MHz, CD_3CN) of the reaction of deprotonated **1** with 1.0 equivalent of $[HPPh_3][BF_4]$ to give **[1-PPh$_3$][BF$_4$]**.



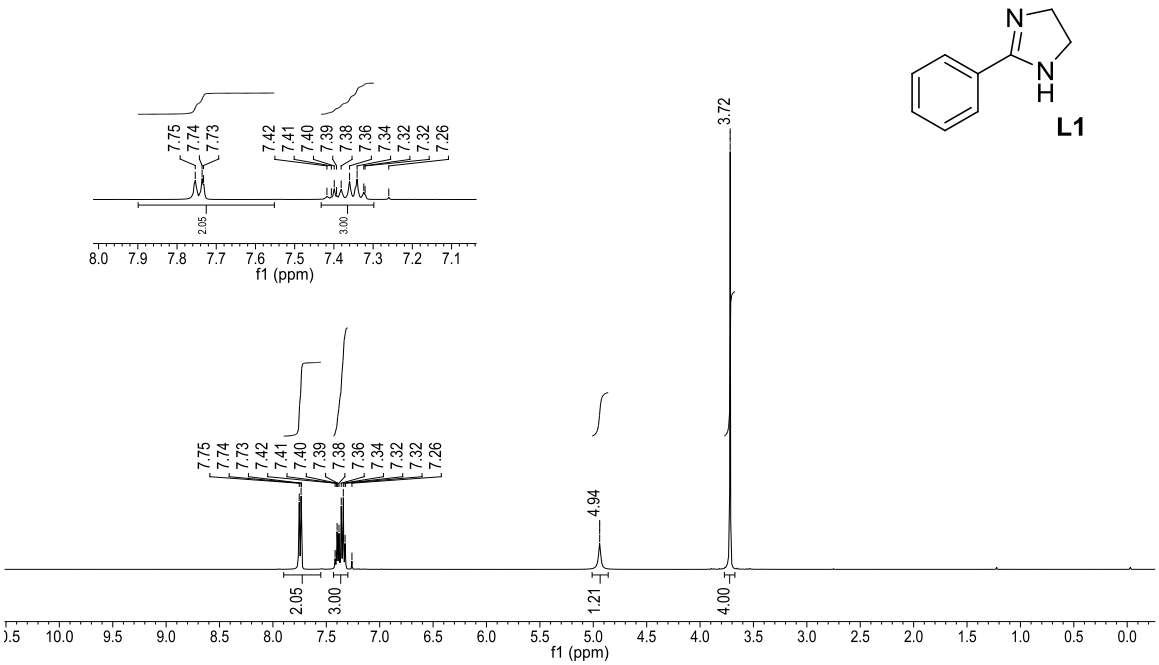
$^{19}F\{^{13}C\}$ NMR (376 MHz, CD_3CN) of the reaction of deprotonated **1** with 1.0 equivalent of $[HPPh_3][BF_4]$ to give **[1-PPh$_3$][BF$_4$]**.

Subsequent reaction of the dehydrochlorination product with dihydrogen. After analysis by ^1H NMR, a solution of the dehydrochlorination product was transferred to a dry, N_2 filled glovebox. The tube was opened and the entire solution transferred to a vial. The vial was sealed in a stainless steel autoclave and removed from the glovebox. The nitrogen filled autoclave was pressurised with H_2 to 30 bar. The autoclave was rapidly transferred to the glovebox and opened to reveal a bright yellow solution. The total time from initial pressurisation with H_2 to the release of H_2 was 5 minutes. 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 by NMR spectroscopy. The ^1H NMR spectrum is consistent with that of **23** and shows the presence of both NH (δ 5.79 ppm) and Ir-H (δ - 15.68 ppm) groups.

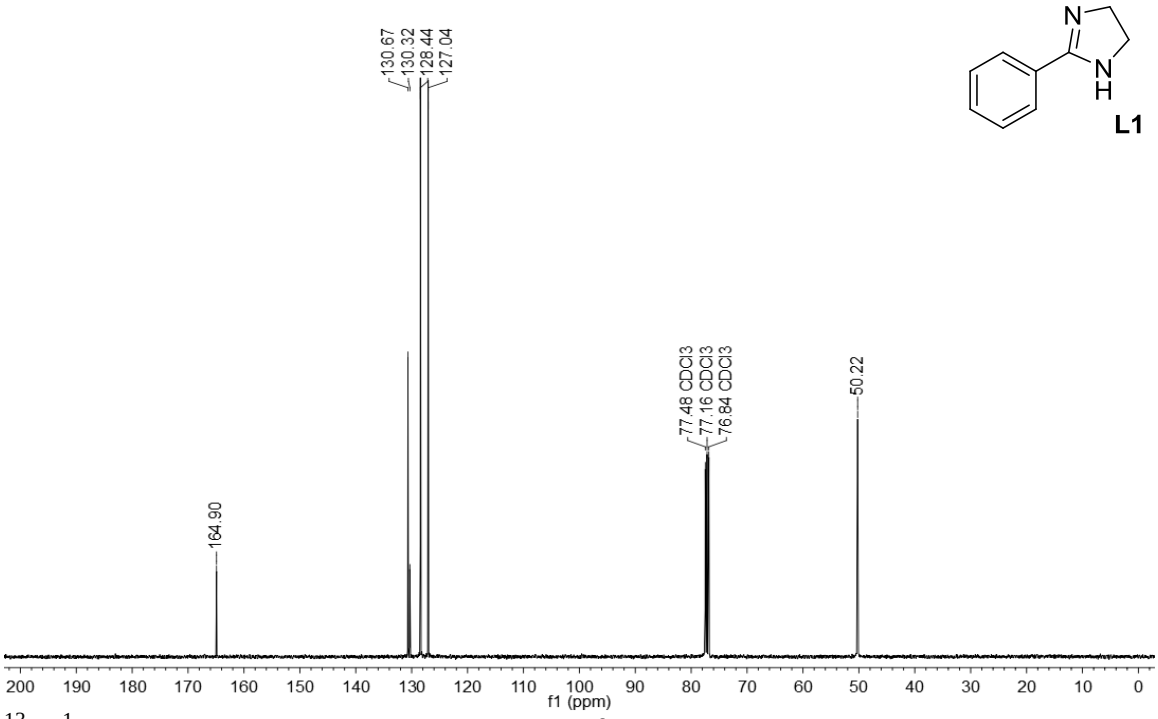


Partial ^{1}H NMR (400 MHz, CD_3CN, aromatic and hydride regions) of the reaction of deprotonated **1** with H_2 (30 atm, rt, 5 min, CD_3CN).

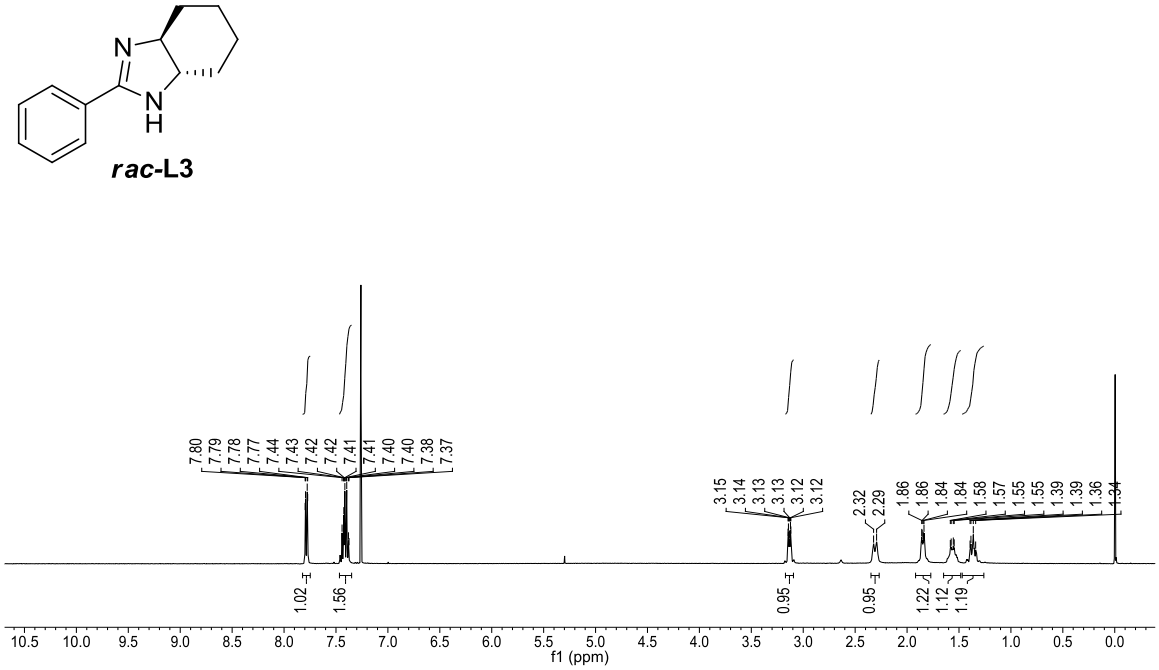
4. NMR spectra of ligands and metal complexes



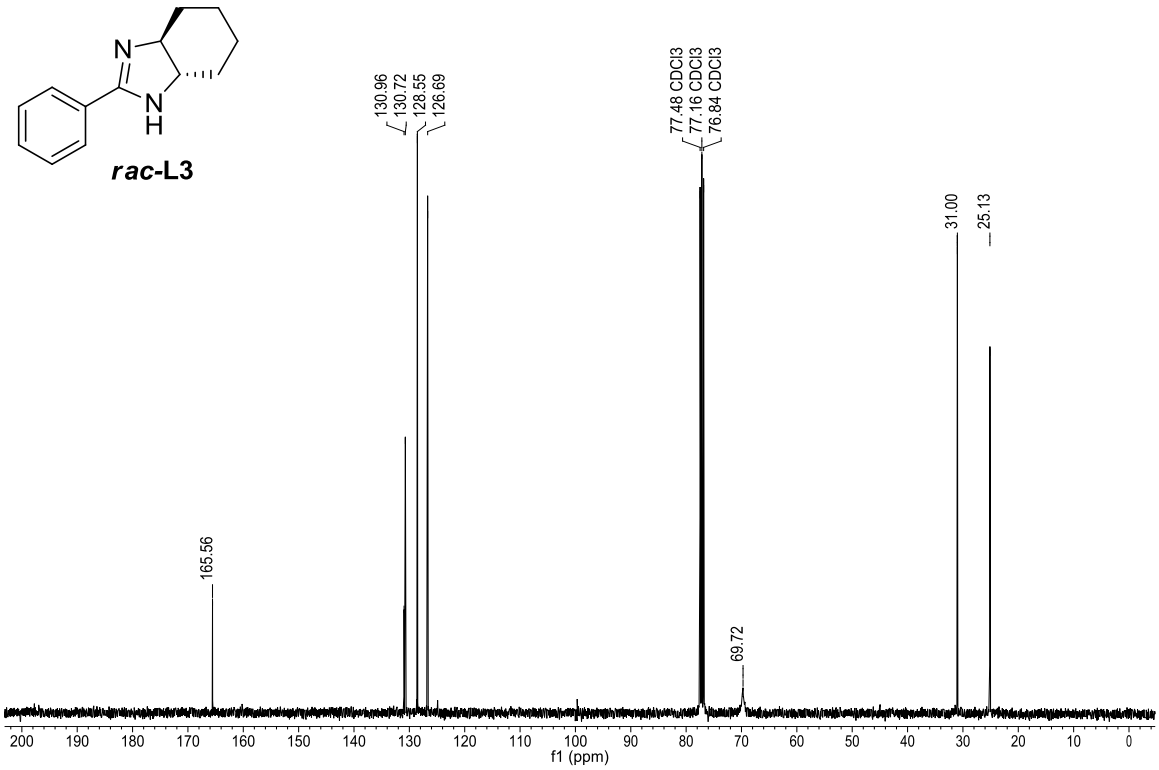
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L1**.



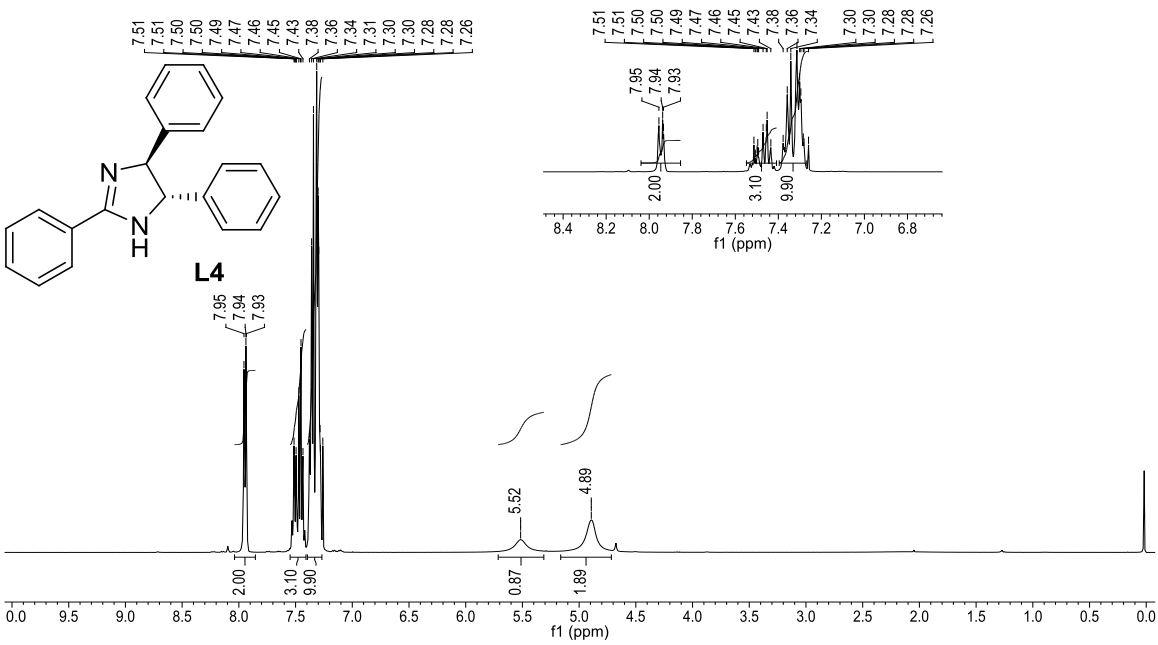
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L1**.



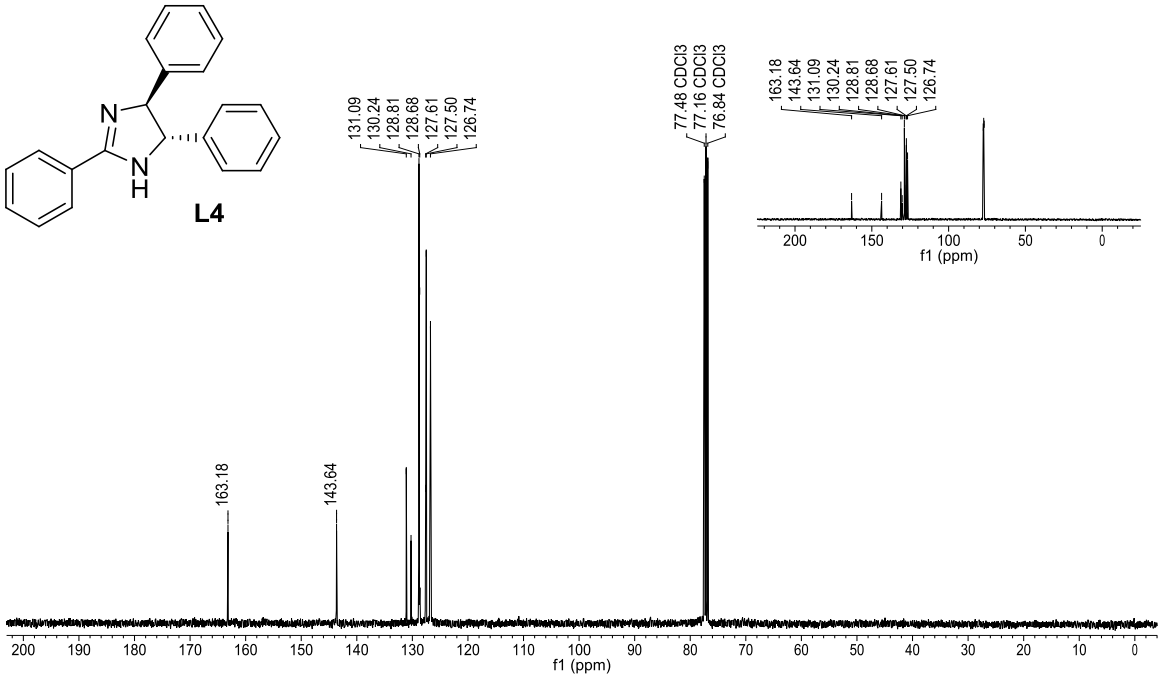
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***rac-trans* L3**.



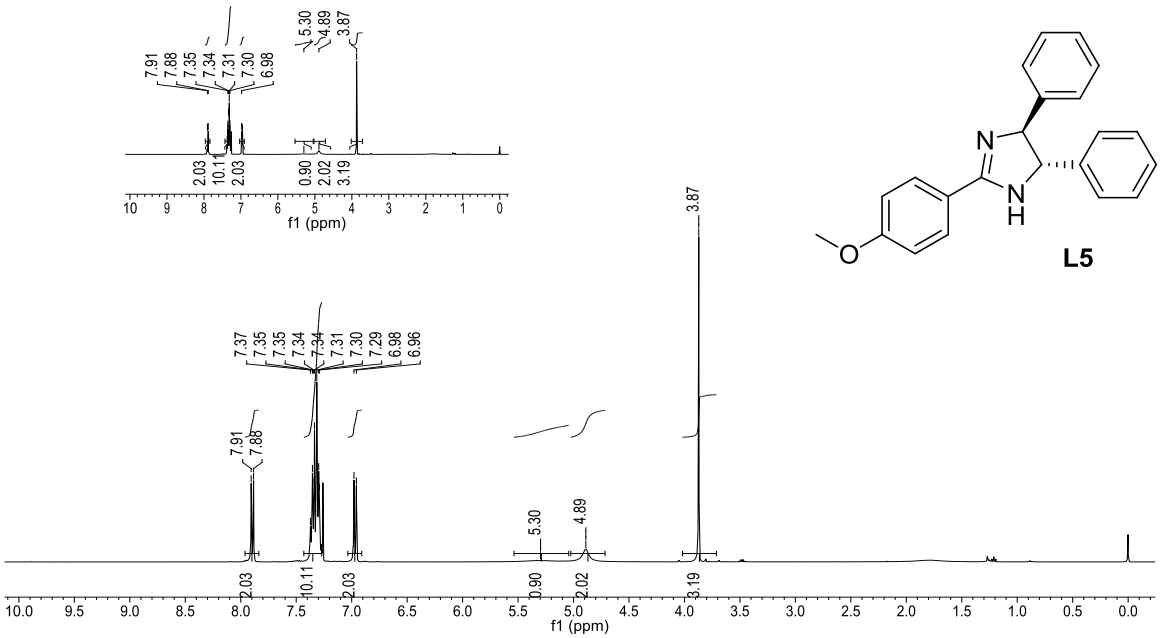
^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) spectrum of ***rac-trans* L3**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L4**.

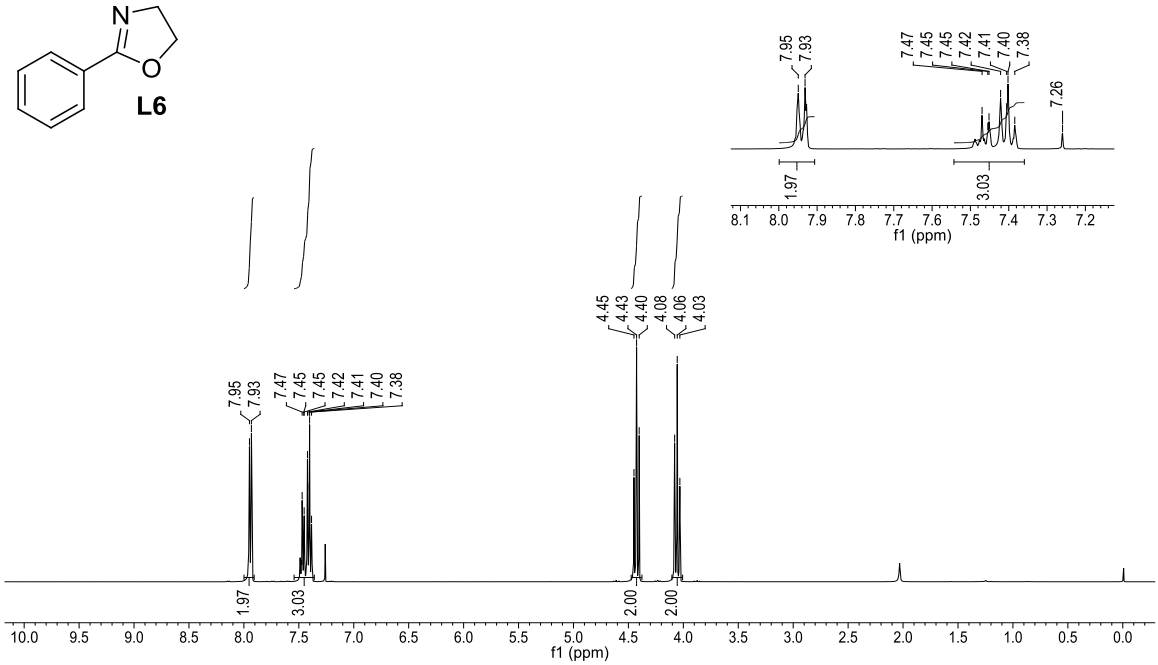


^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **L4**.

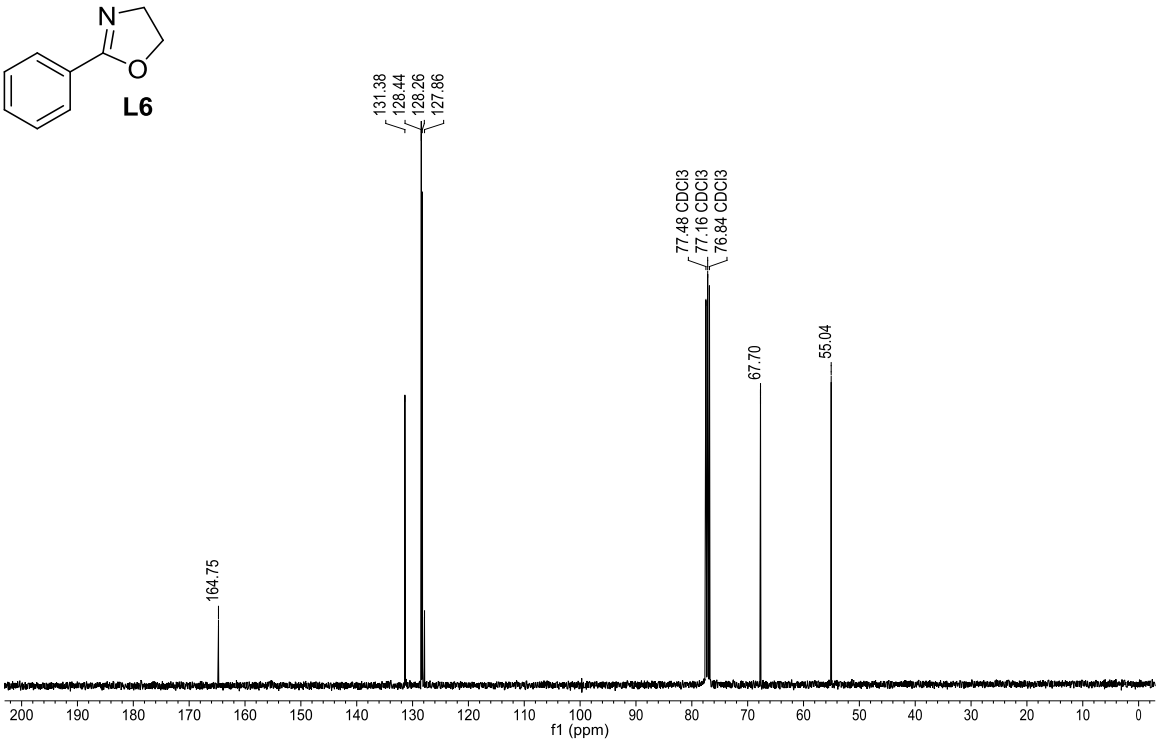


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L5**.

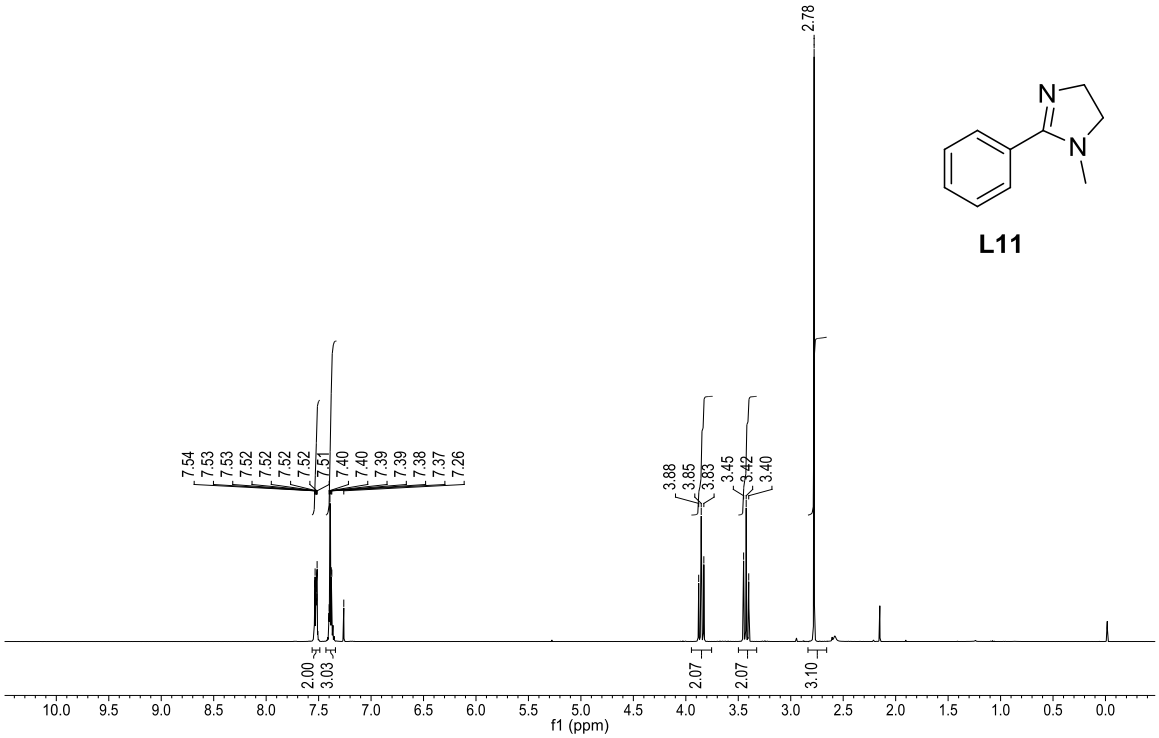
^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **L5**.



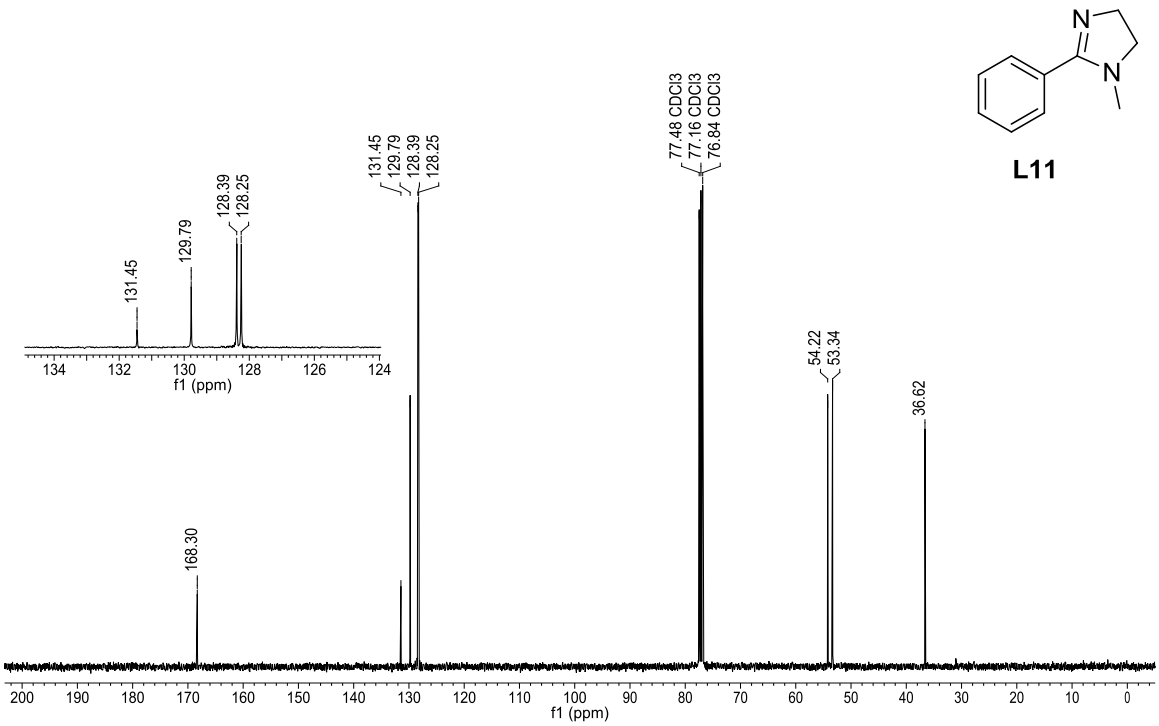
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L6**.



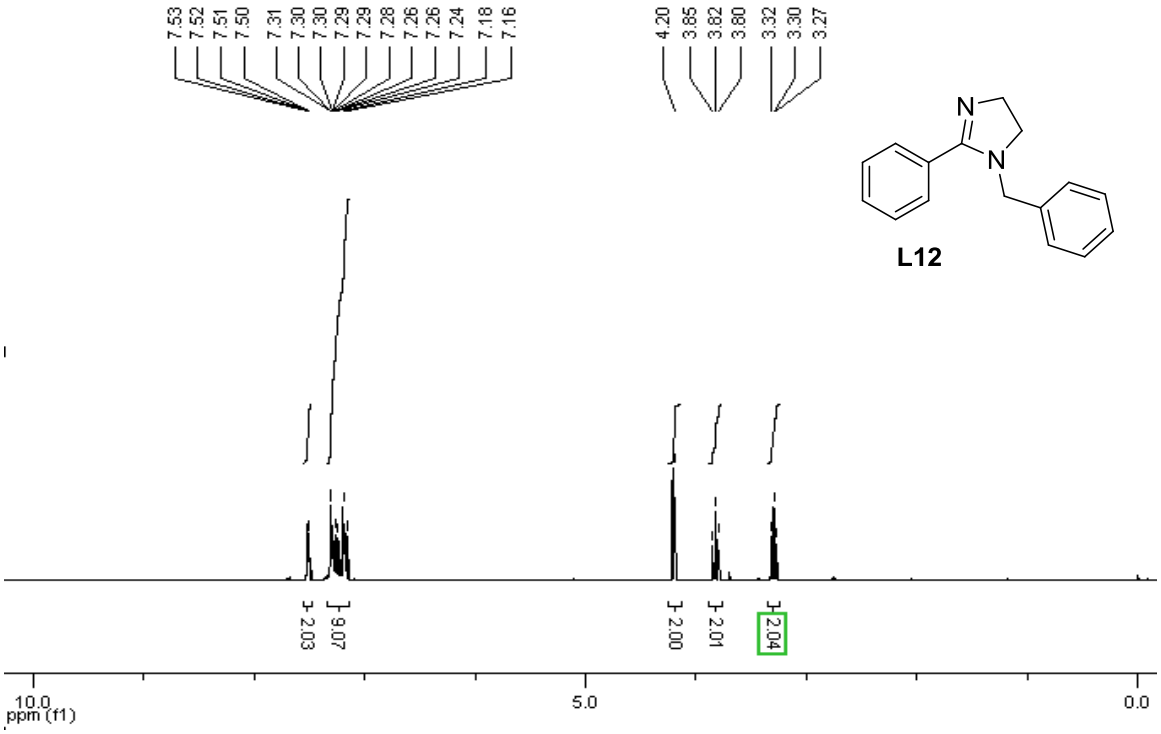
^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **L6**.



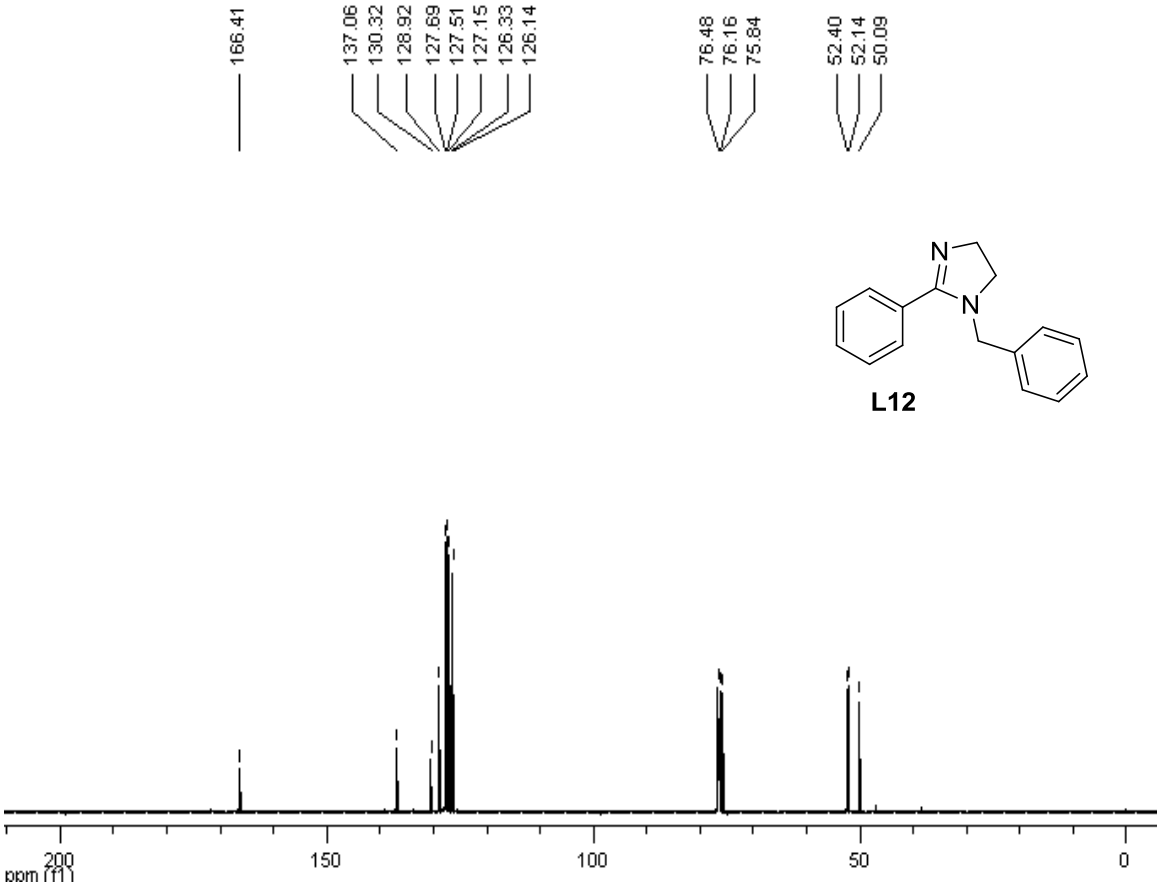
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L11**.



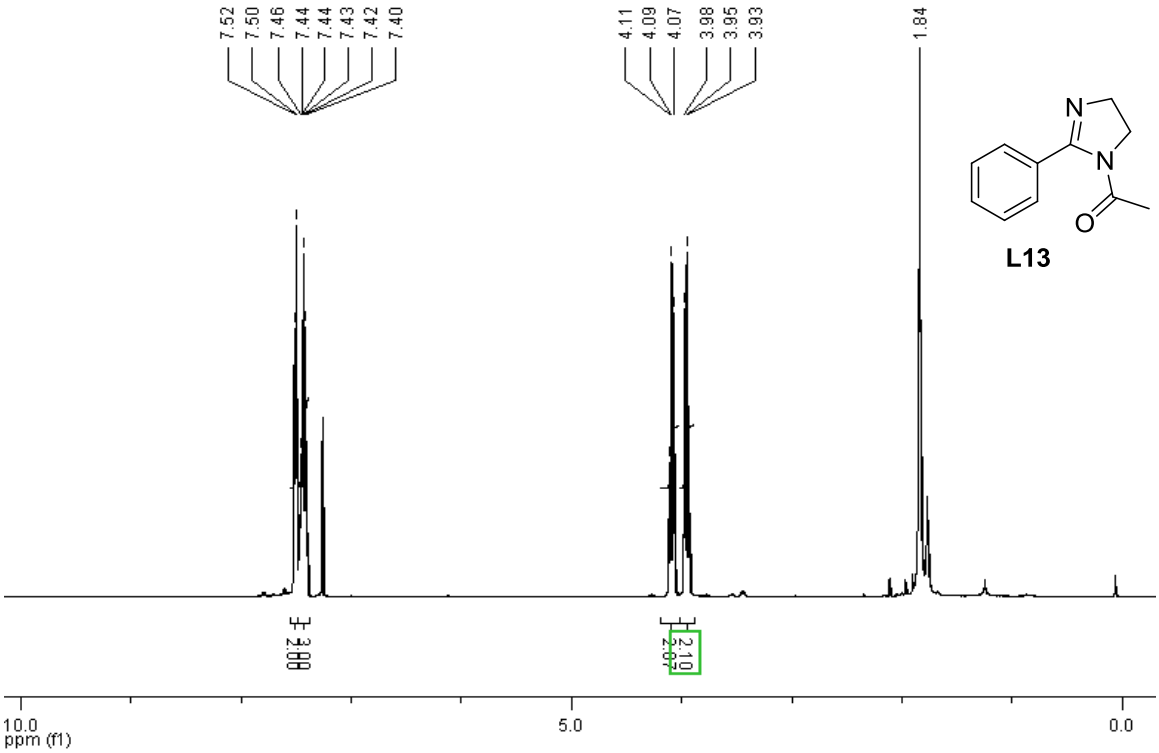
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L11**.



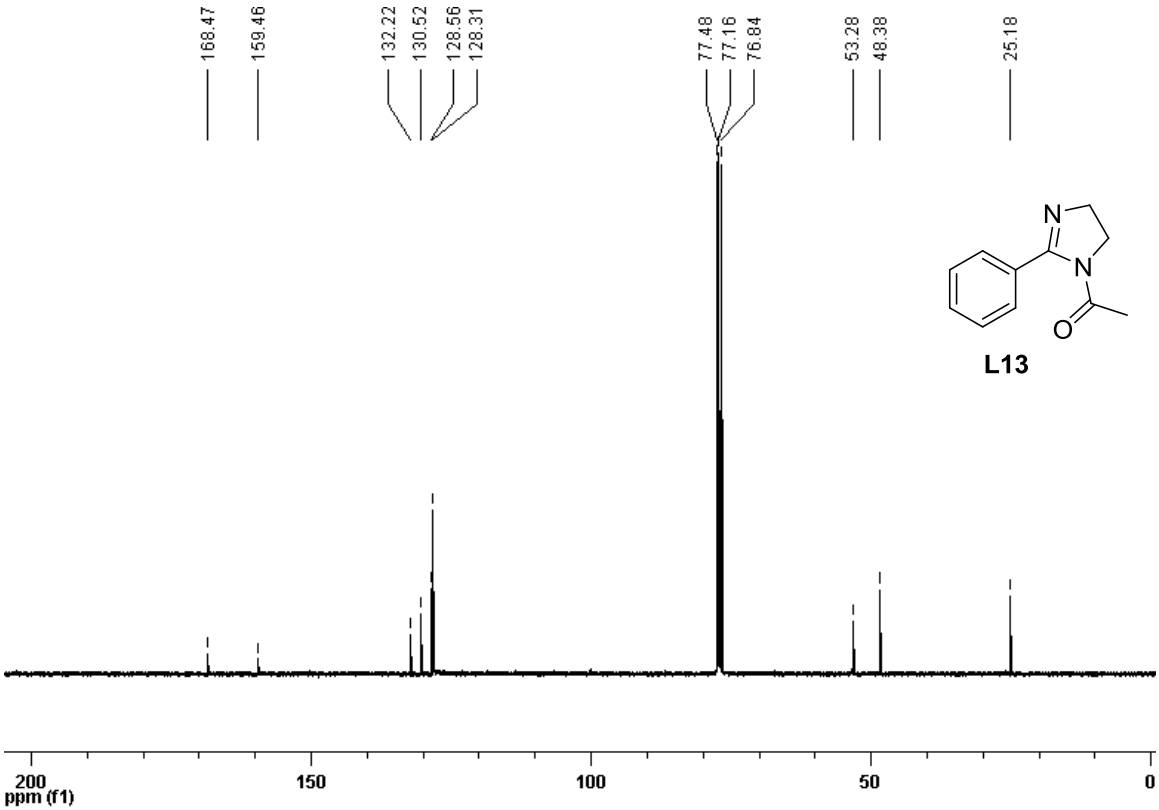
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L12**.



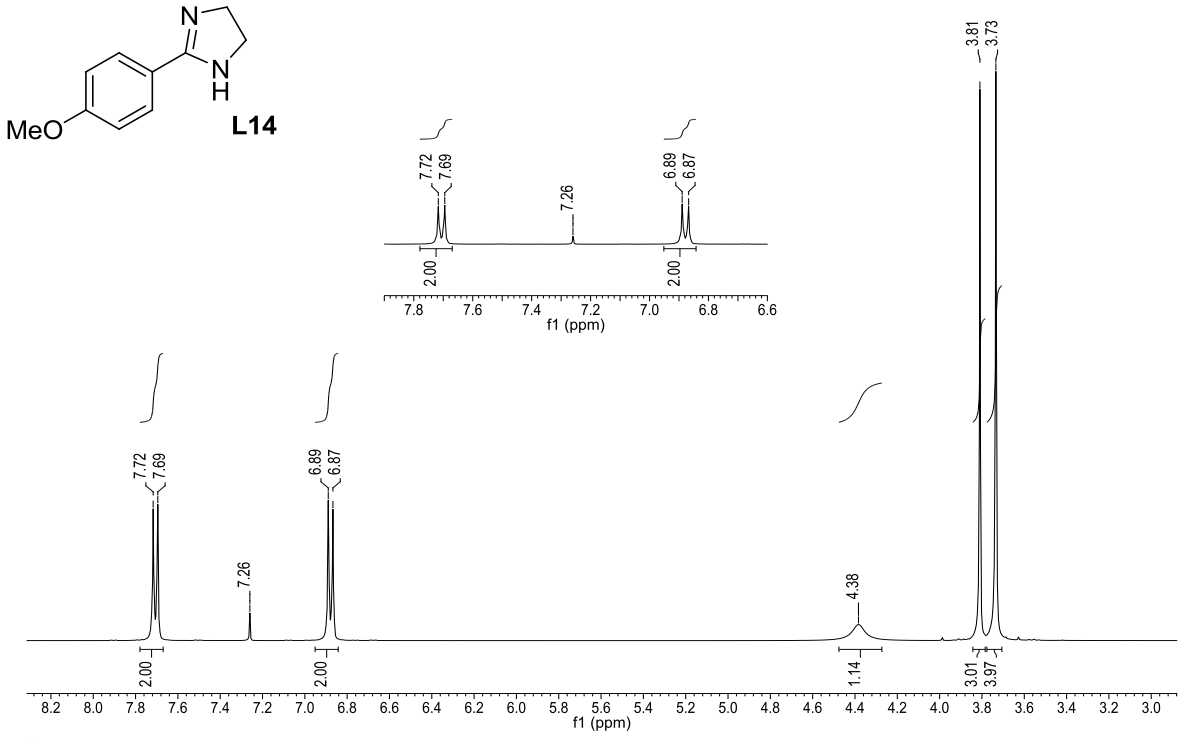
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L12**.



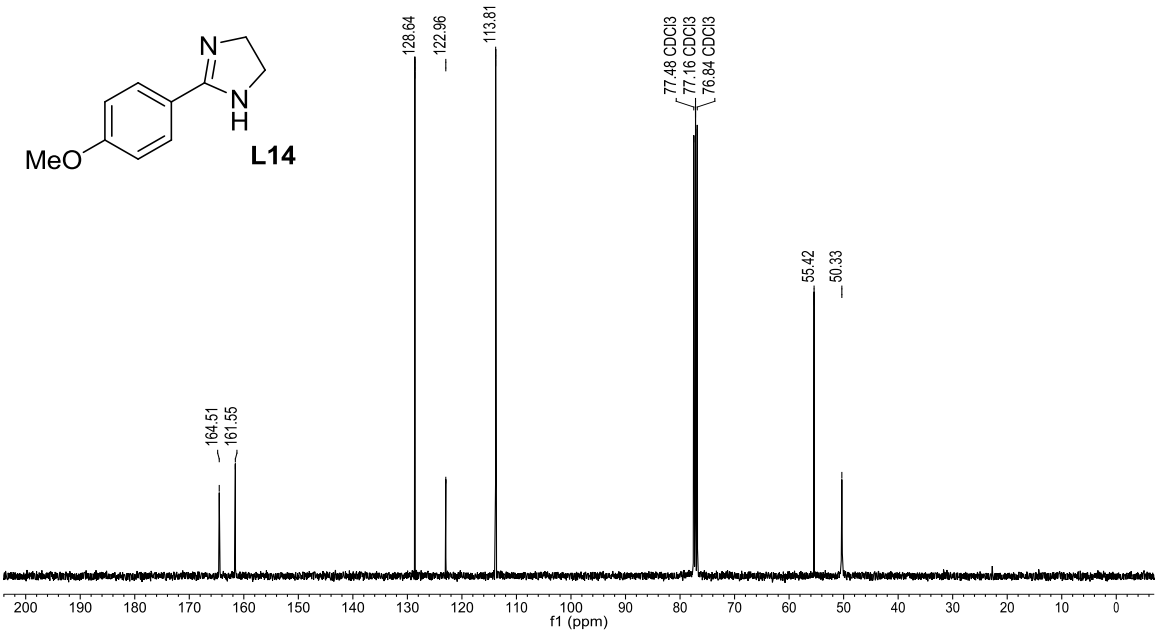
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L13**.



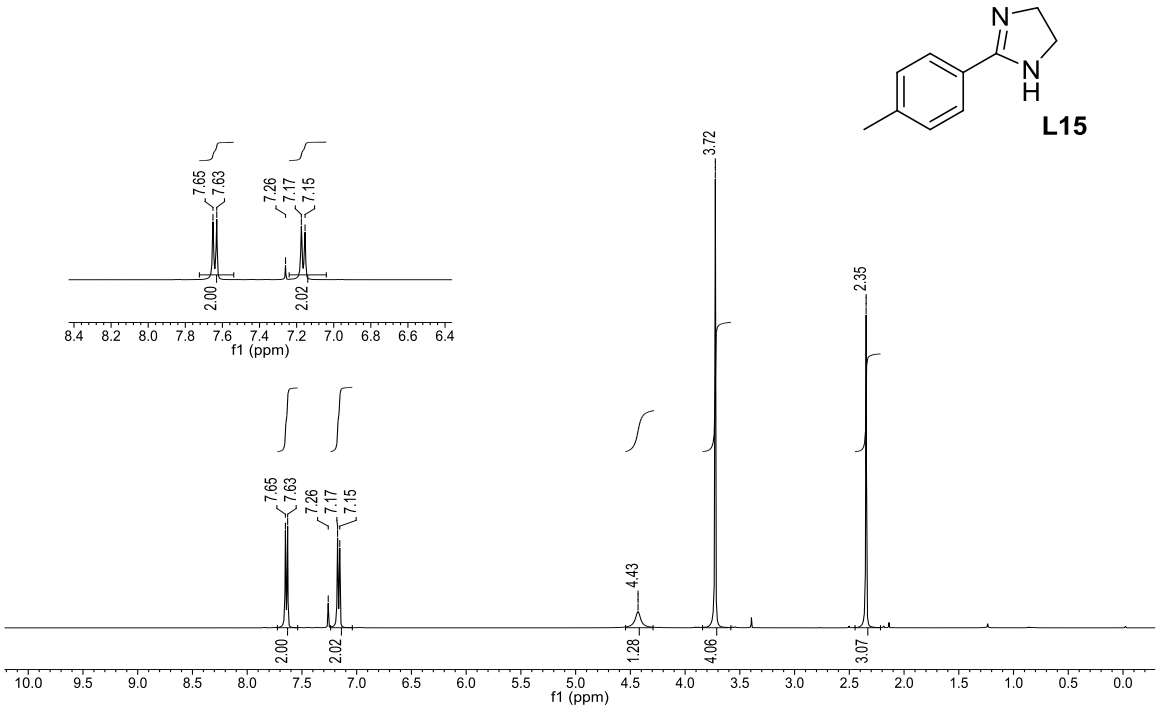
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **13**.



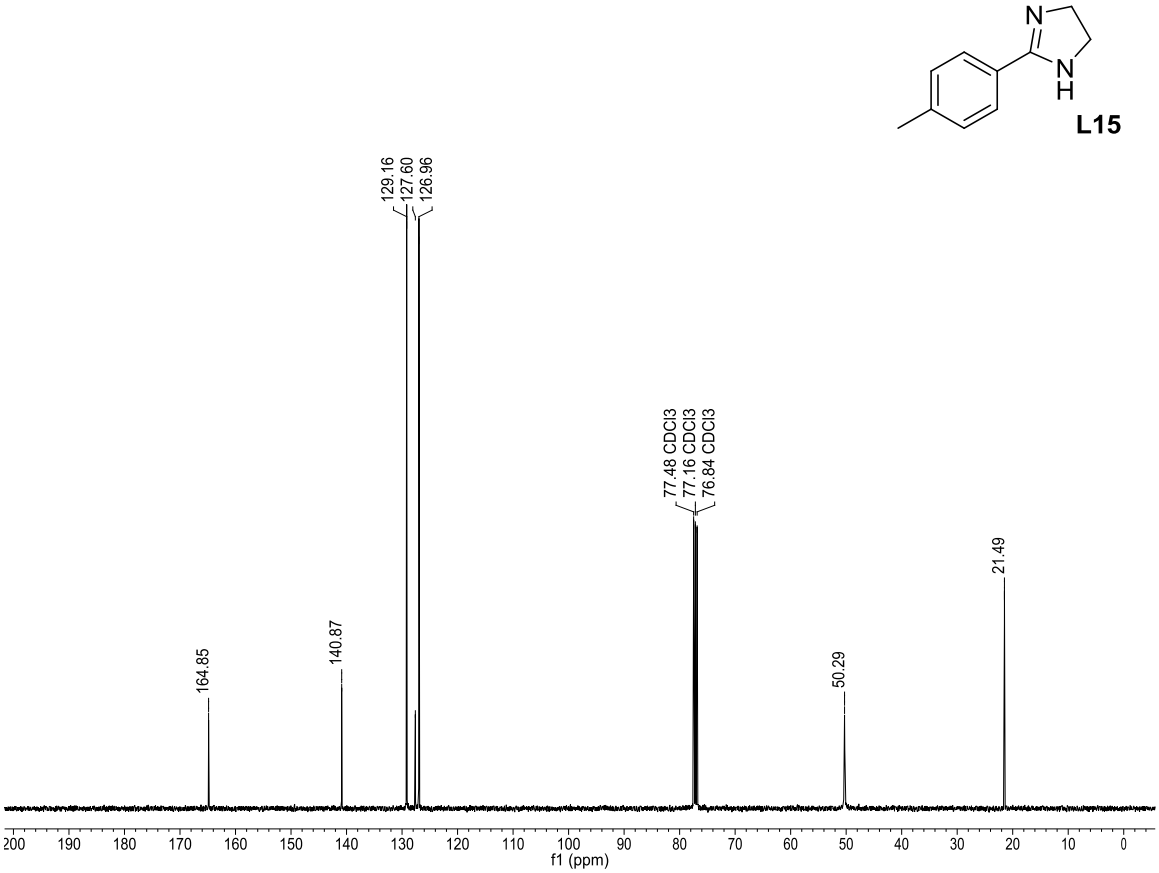
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L14**.



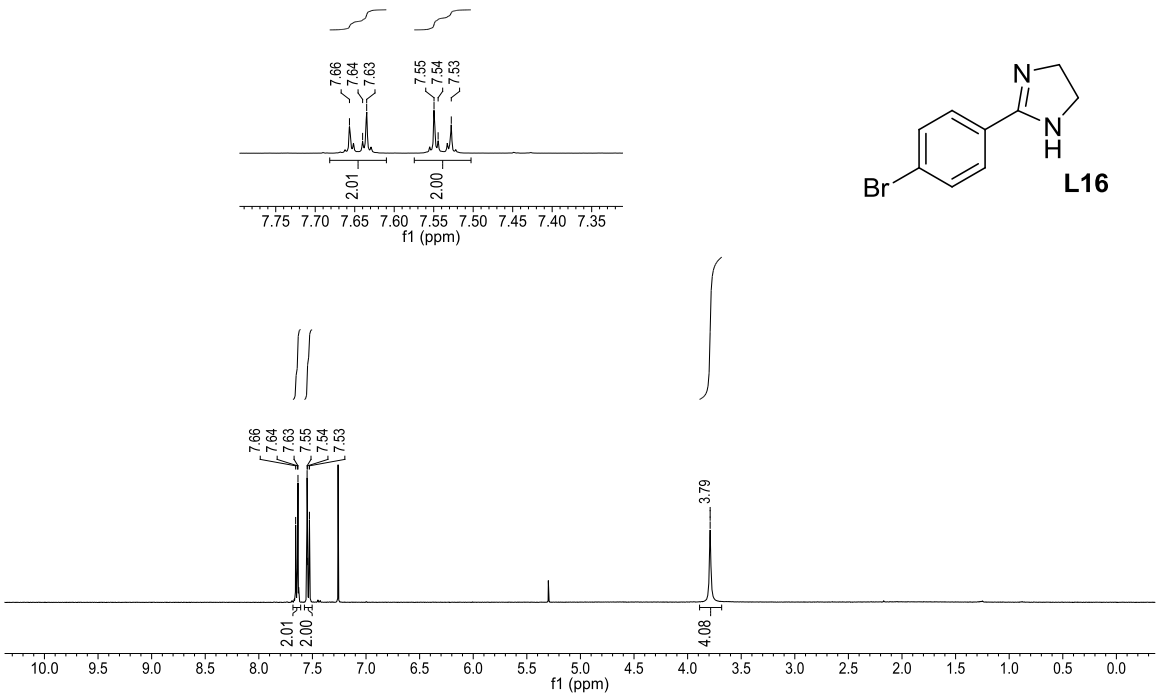
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L14**.



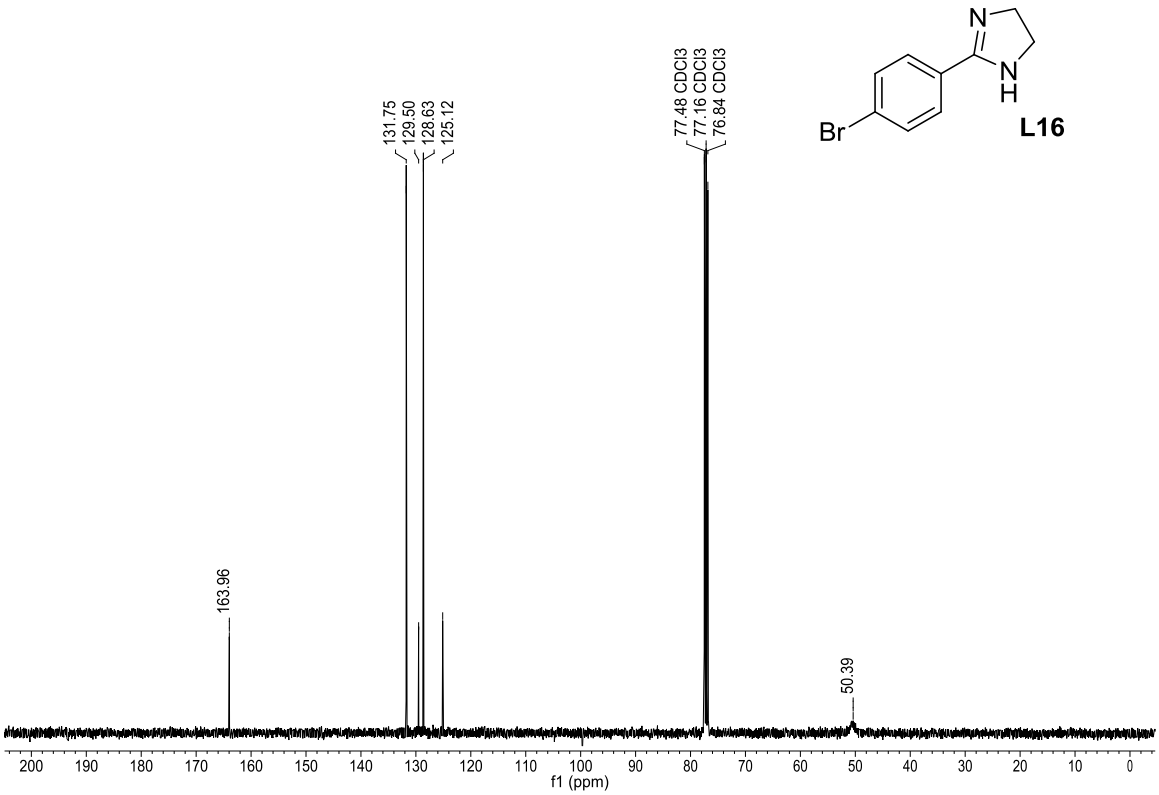
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L15**.



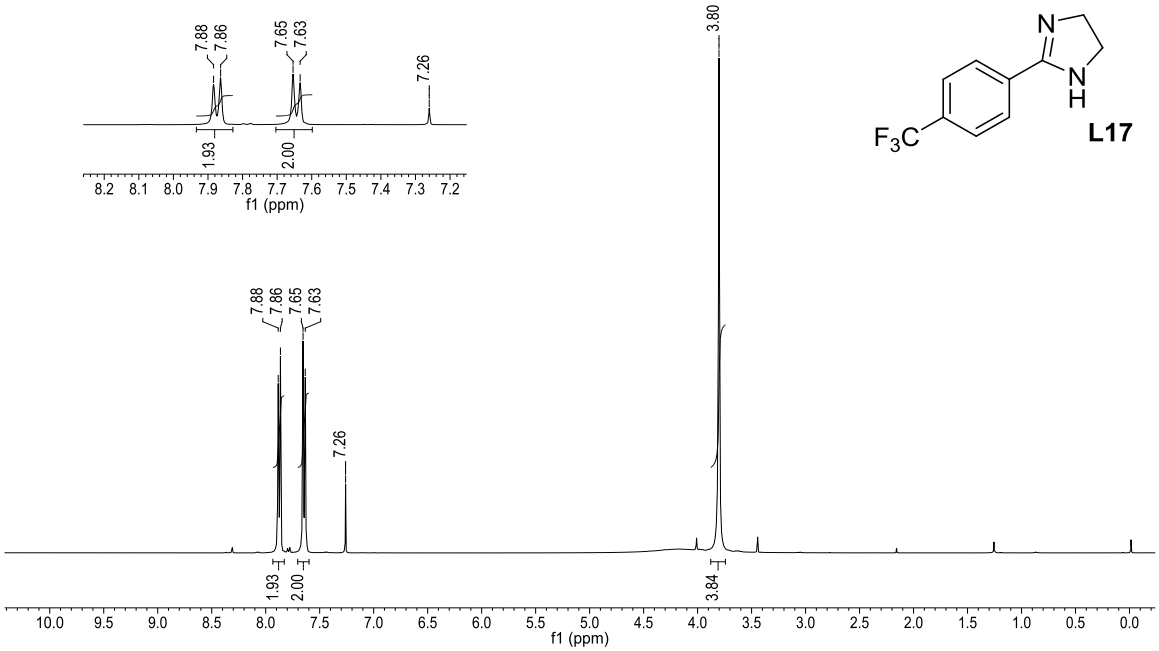
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L15**.



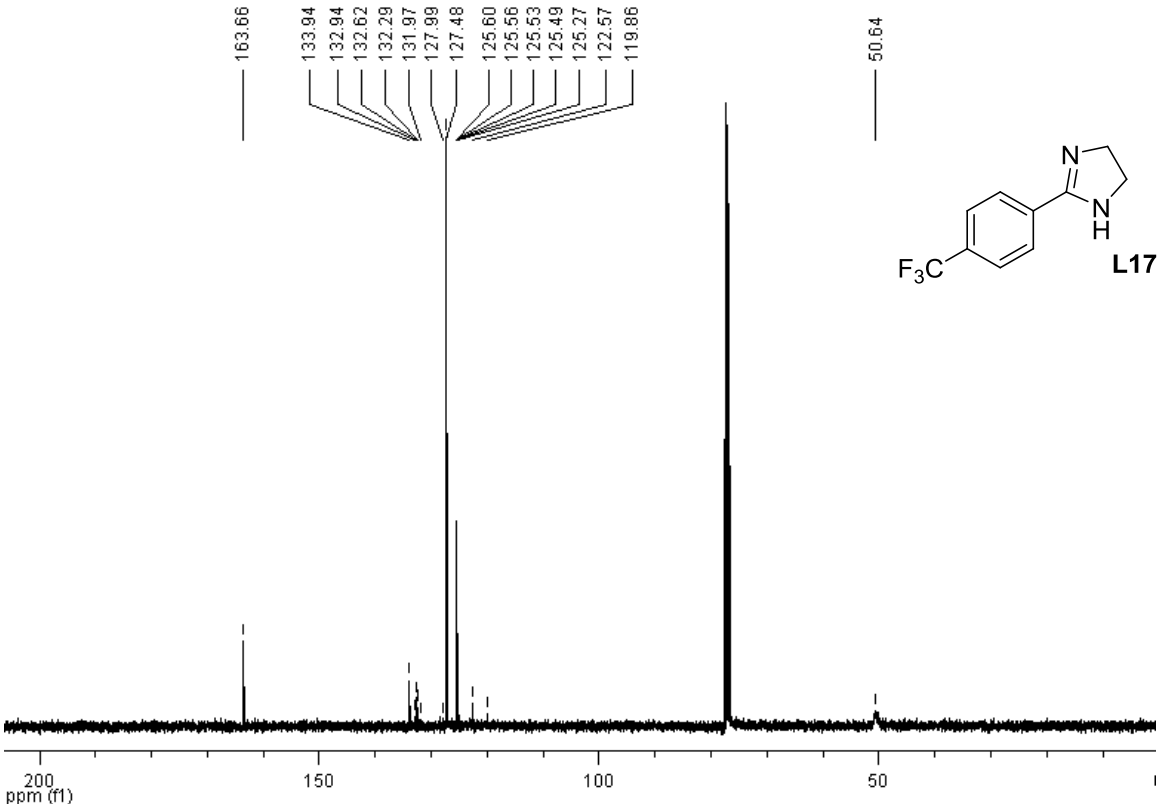
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L16**



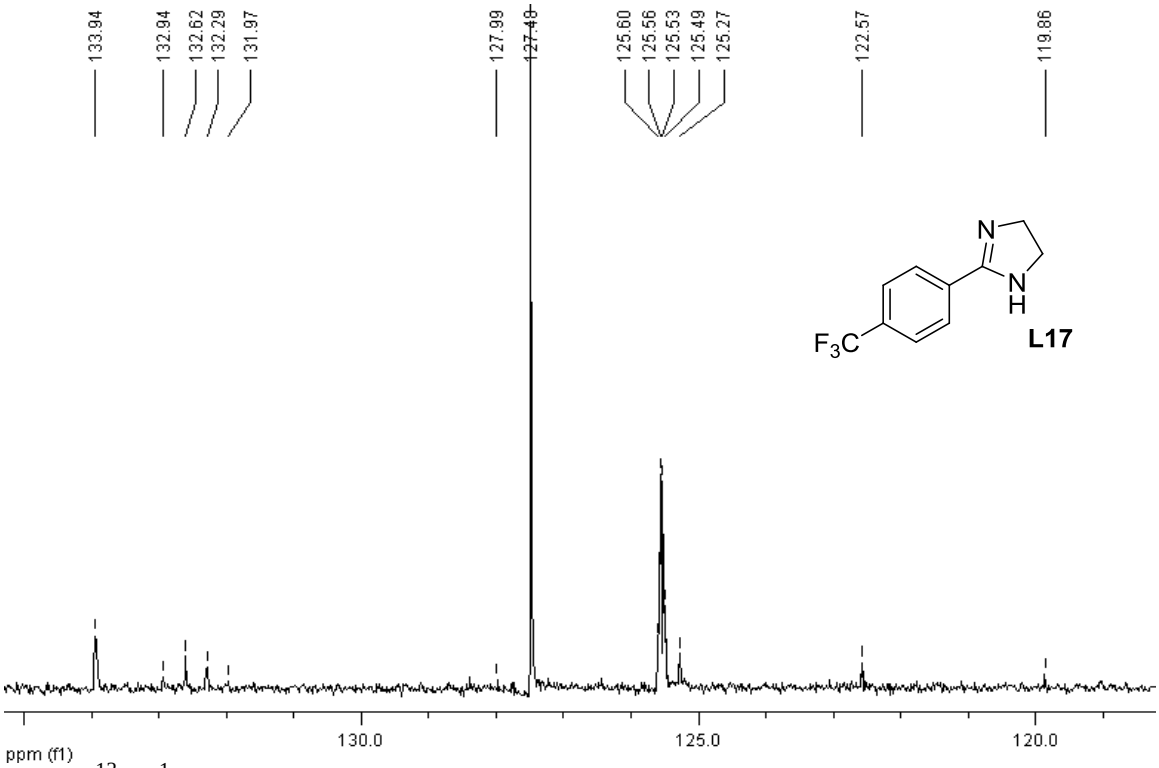
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **L16**.



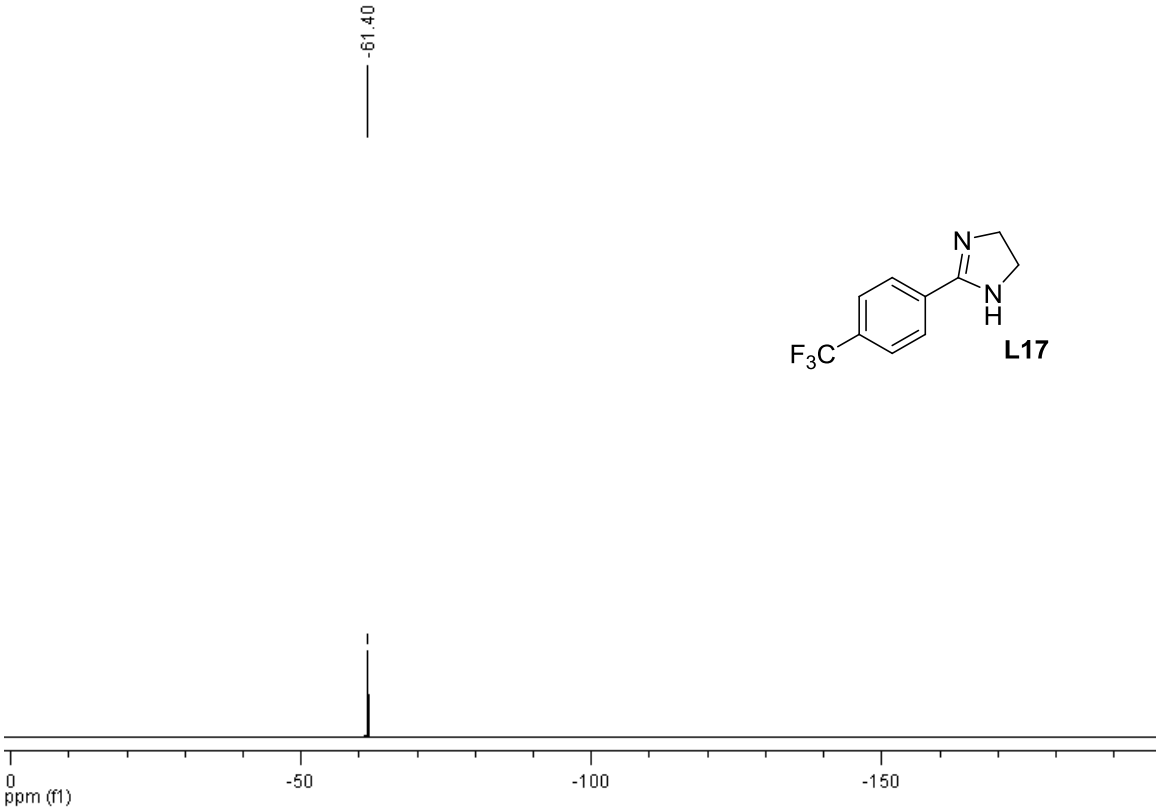
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L17**



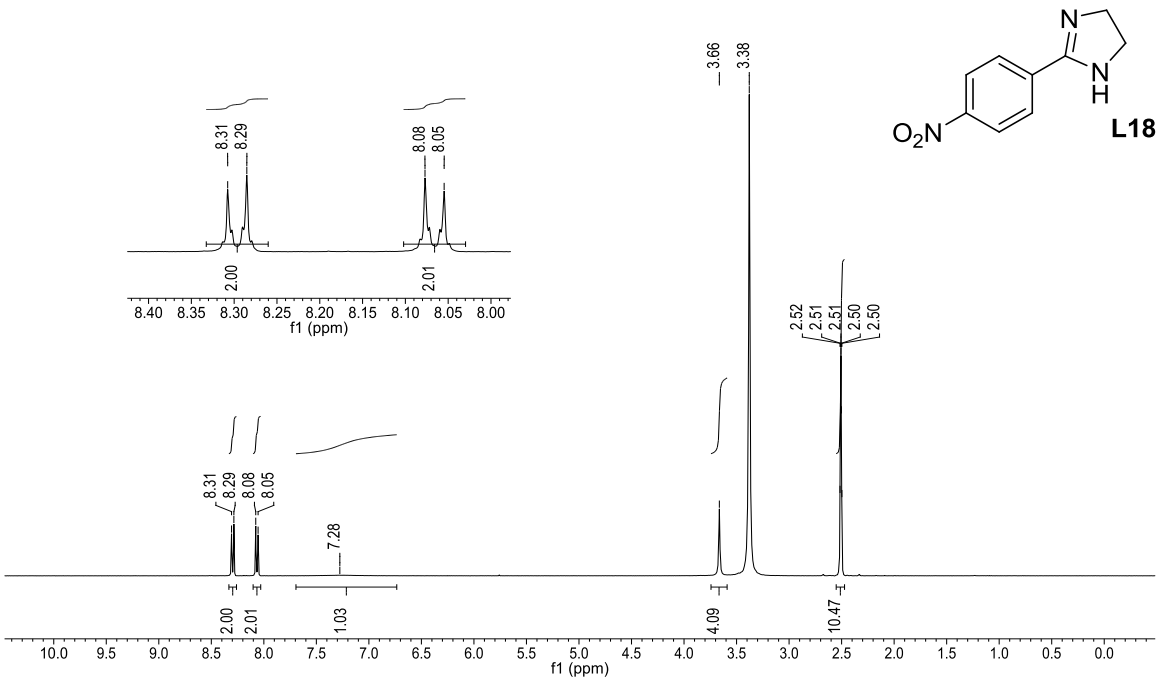
^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) spectrum of **L17**.



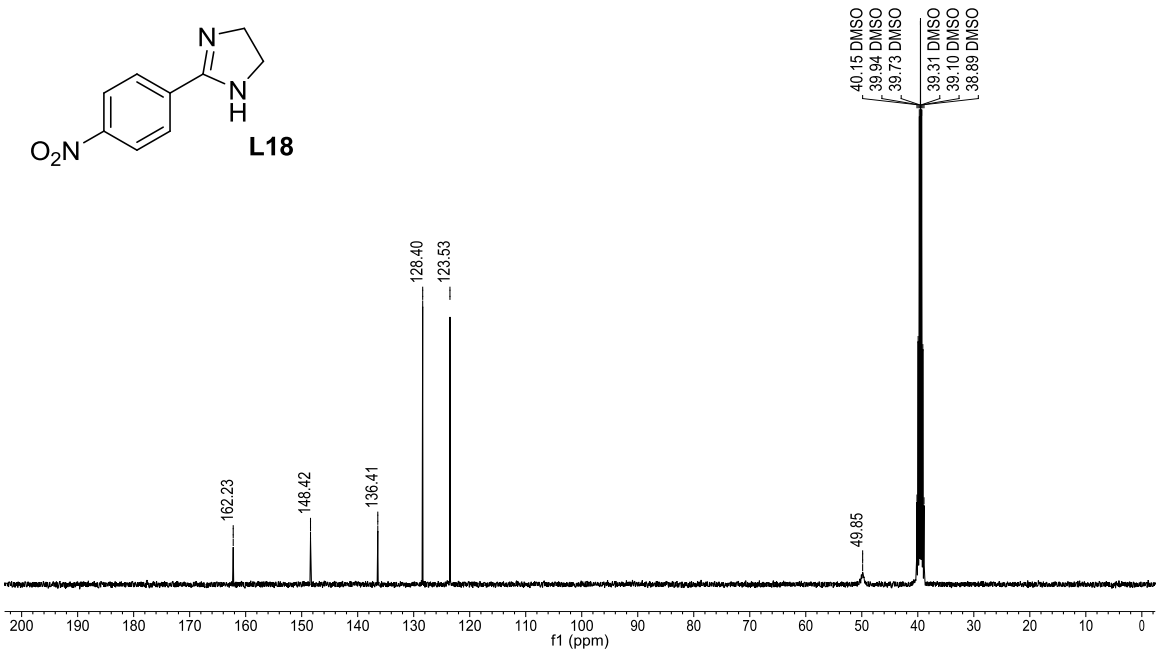
Partial $^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$) spectrum of **L17**.



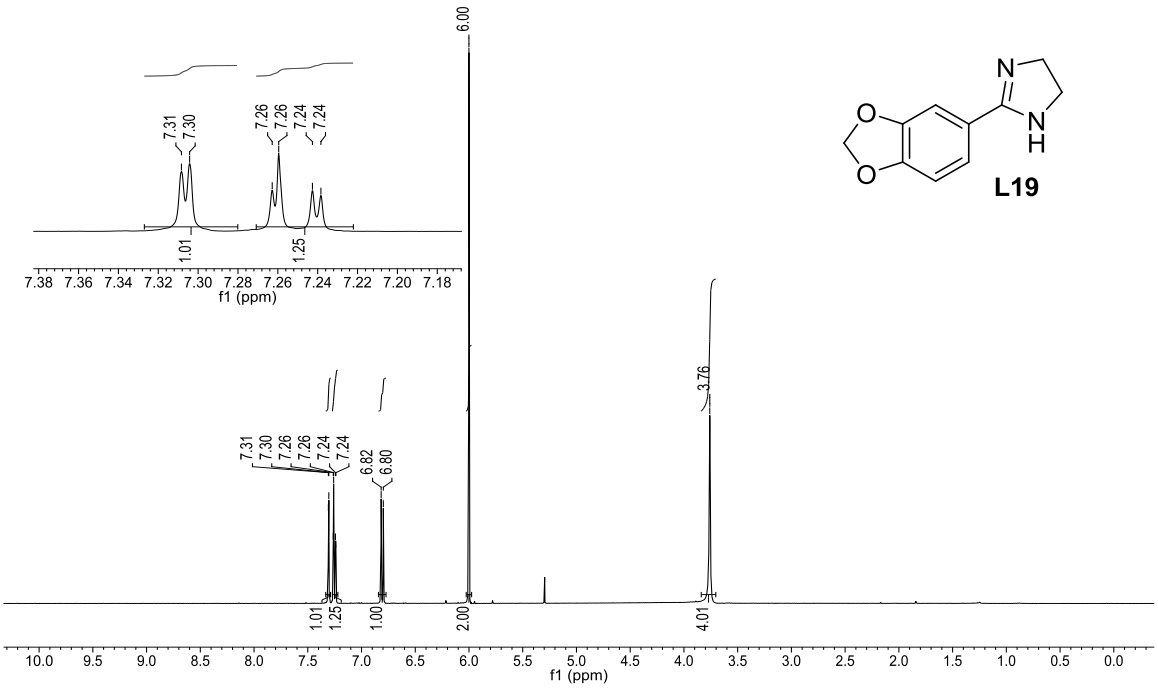
$^{19}F\{^{13}C\}$ NMR (376 MHz, $CDCl_3$) spectrum of **L17**.



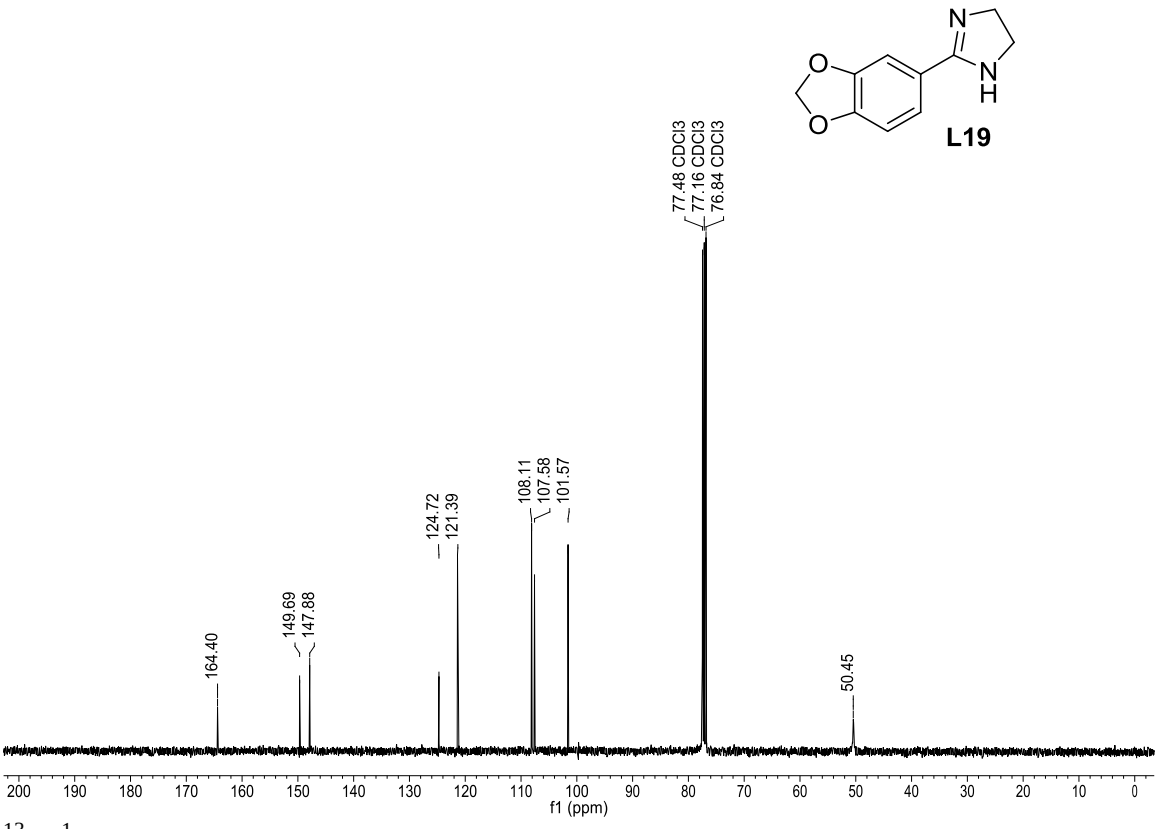
^{1}H NMR (400 MHz, DMSO-*d6*) spectrum of **L18**.



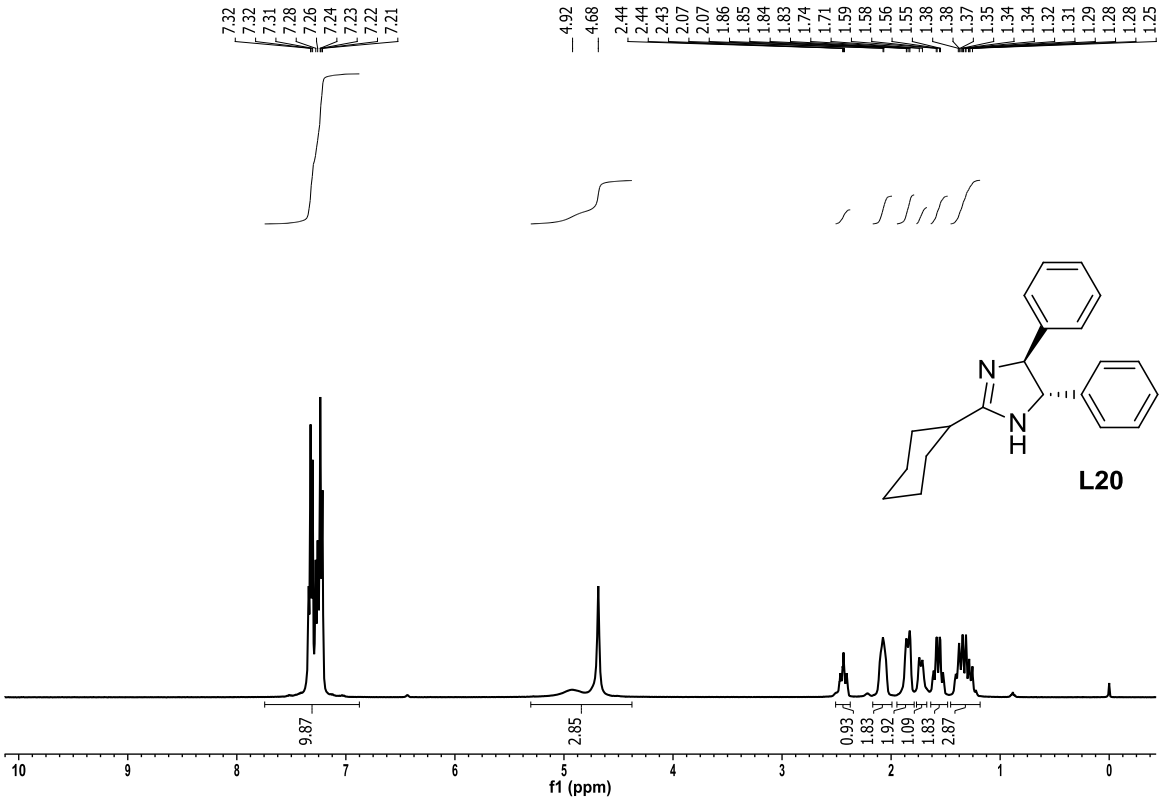
^{13}C{^{1}H}NMR (101 MHz, DMSO-*d6*) spectrum of **L18**.



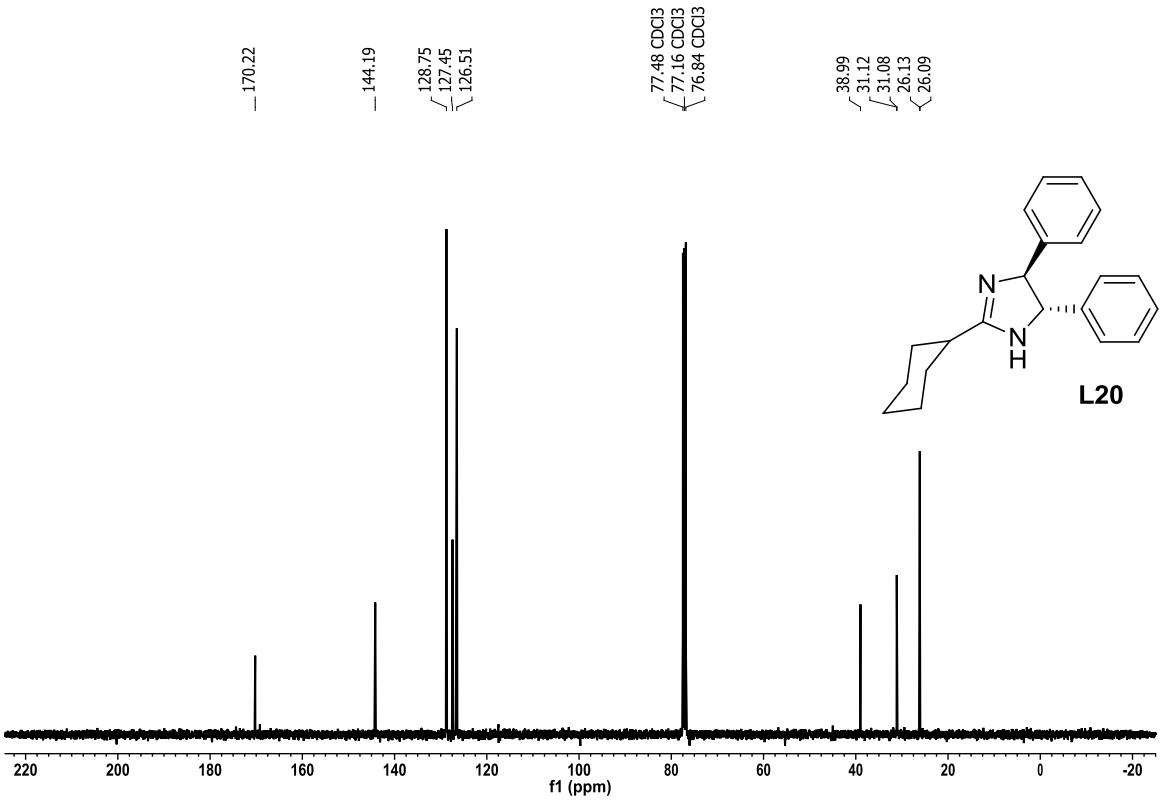
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L19**.



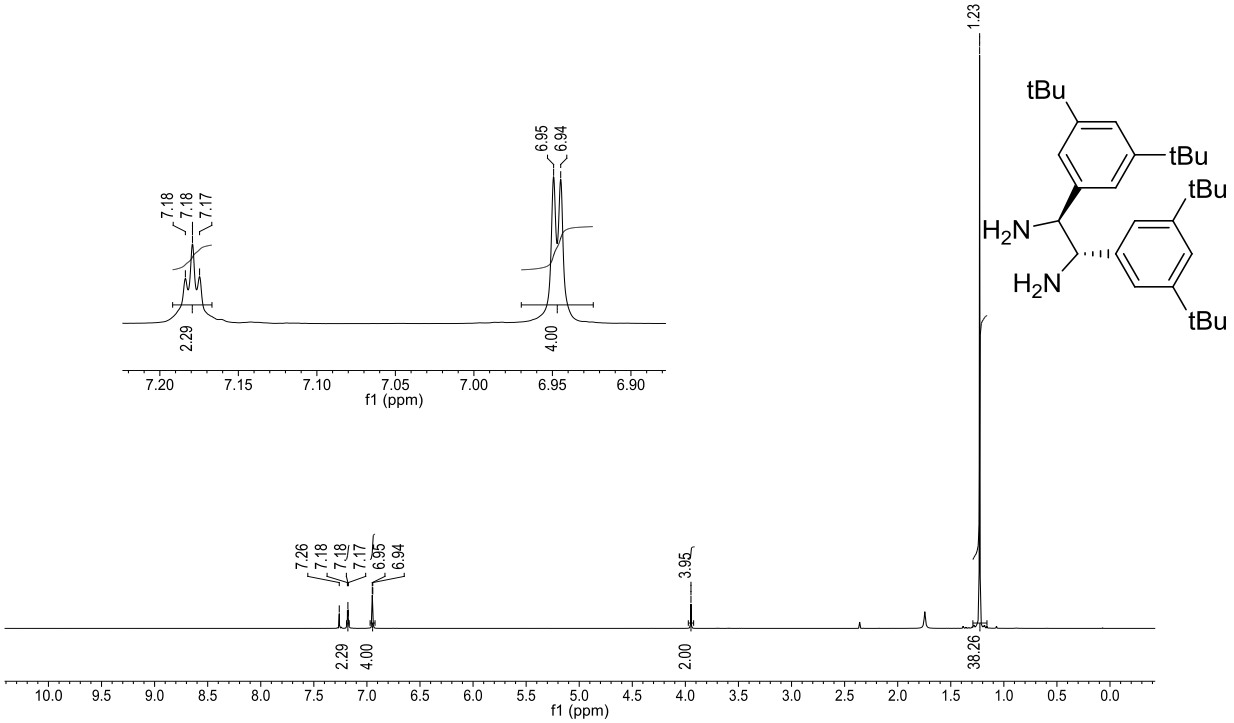
^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) spectrum of **L19**.



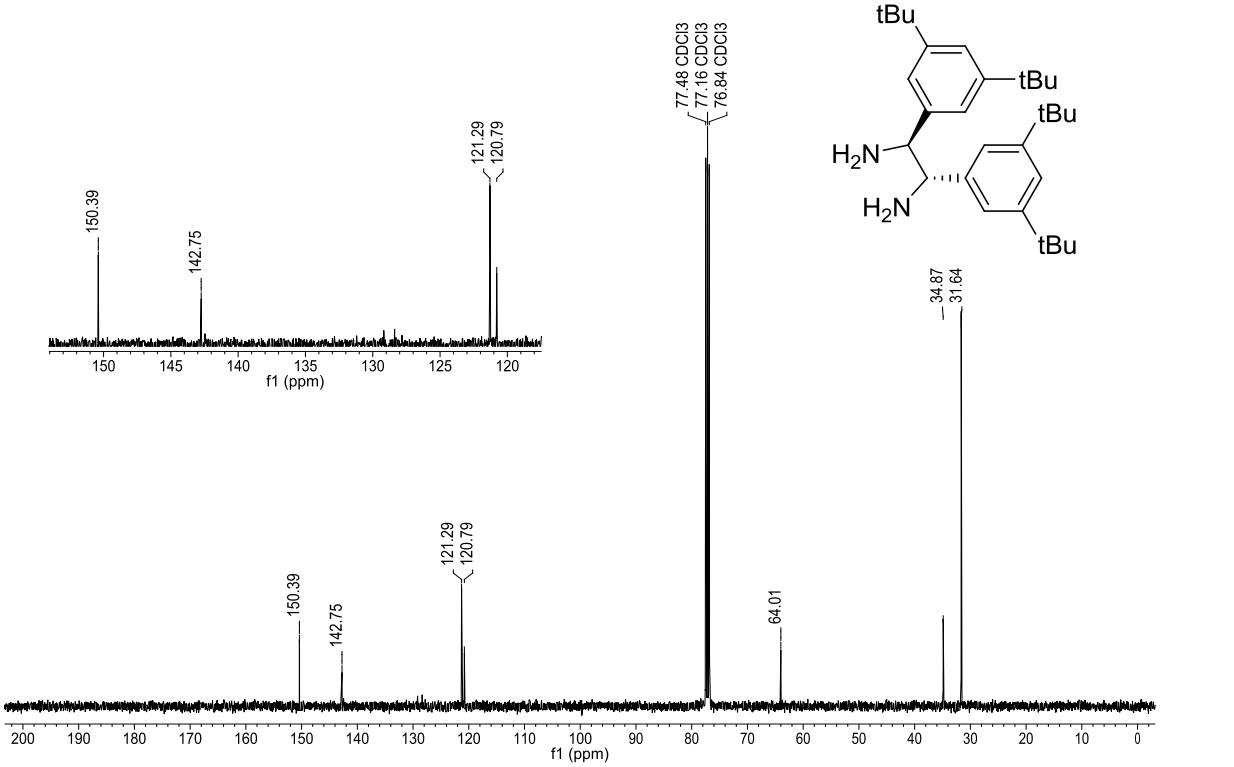
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L20**.



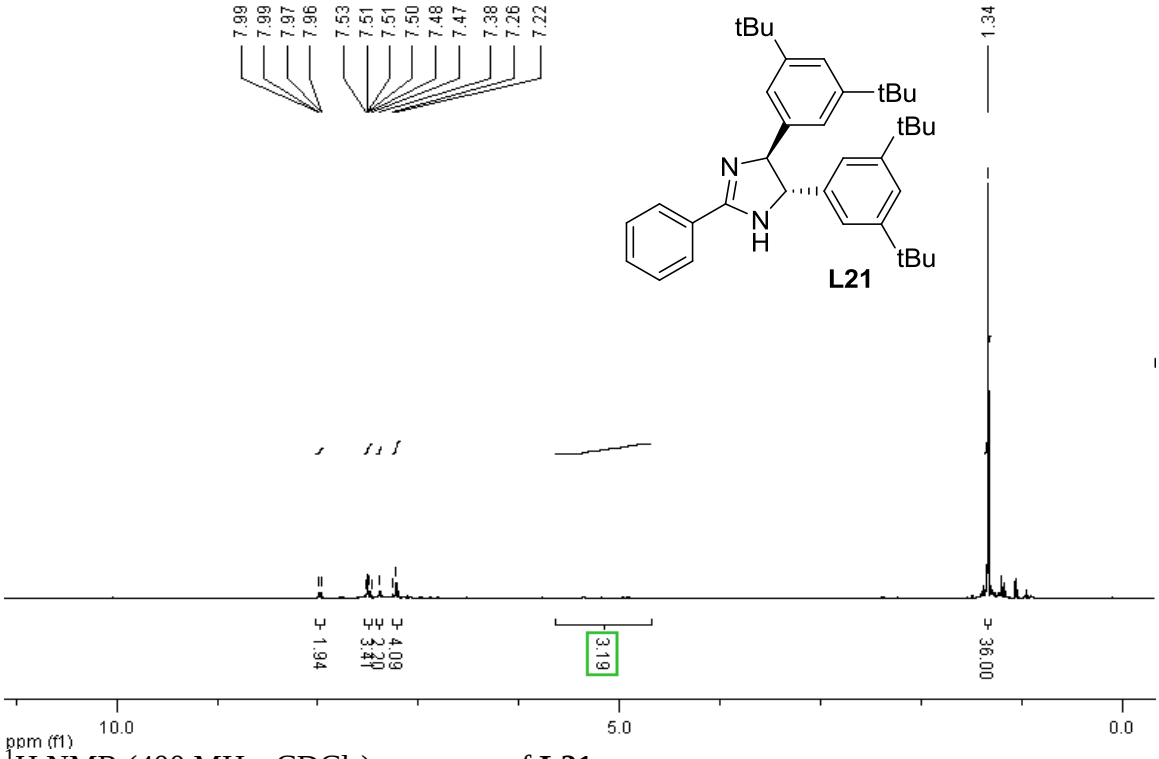
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L20**.



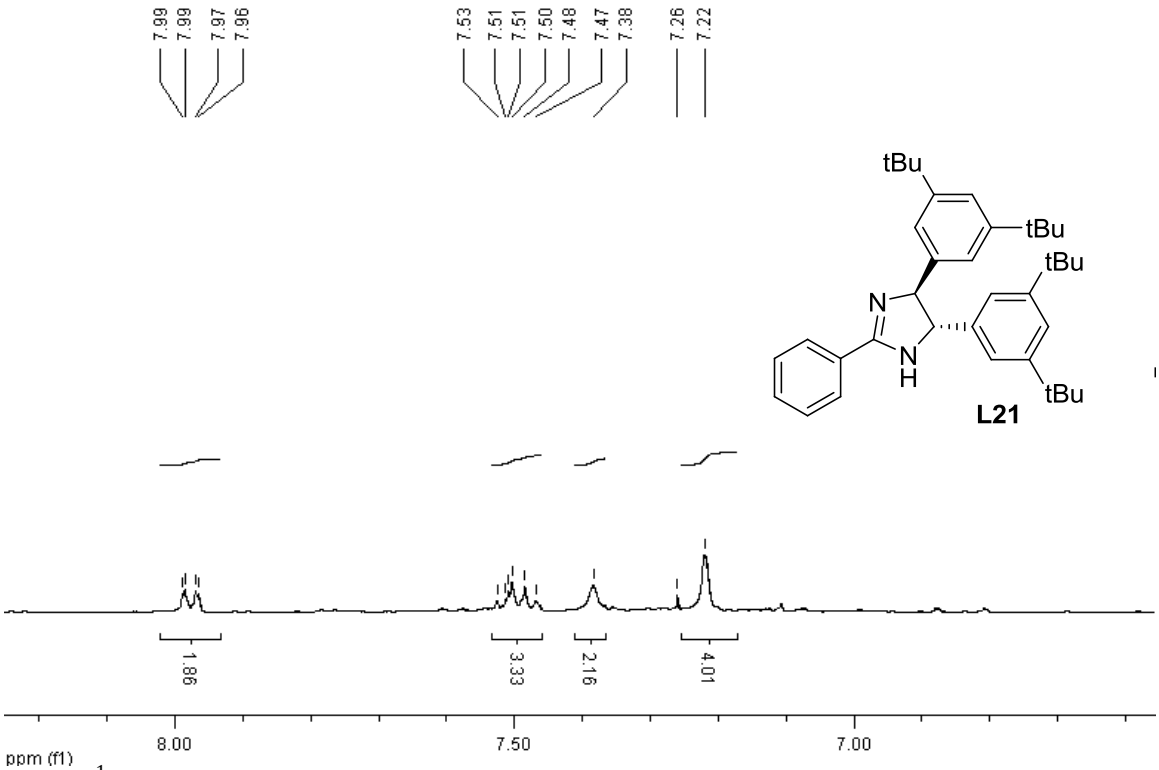
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **(1*S*,2*S*)-1,2-bis(3,5-di-*tert*-butyl phenyl)ethane-1,2-diamine**.



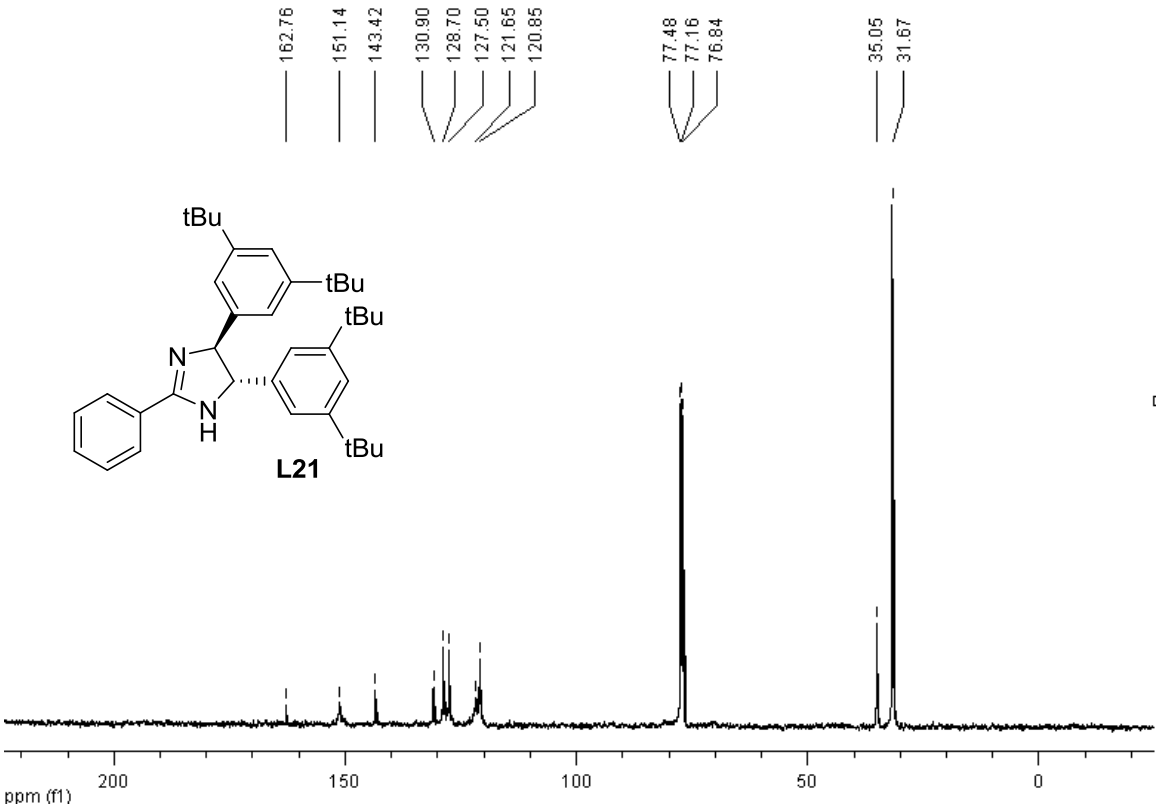
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **(1*S*,2*S*)-1,2-bis(3,5-di-*tert*-butyl phenyl)ethane-1,2-diamine**.



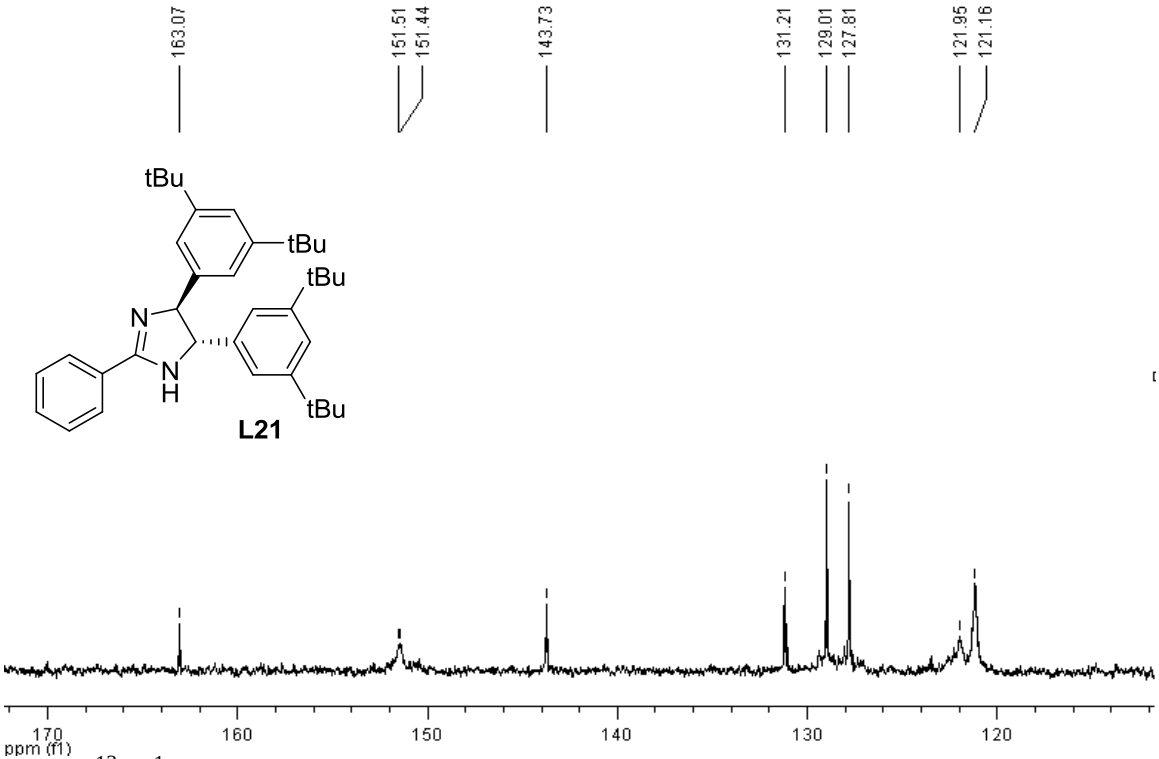
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L21**.



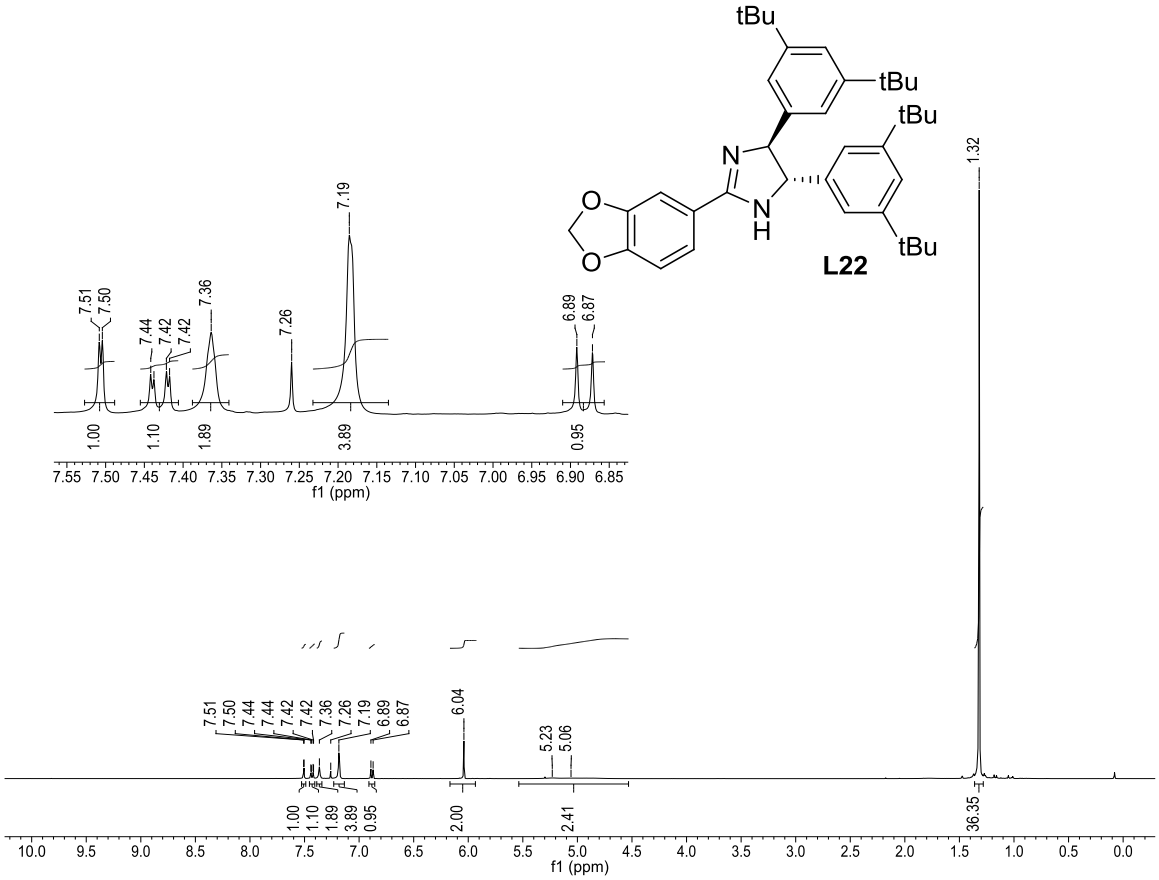
Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum (aromatic region) of **L21**.



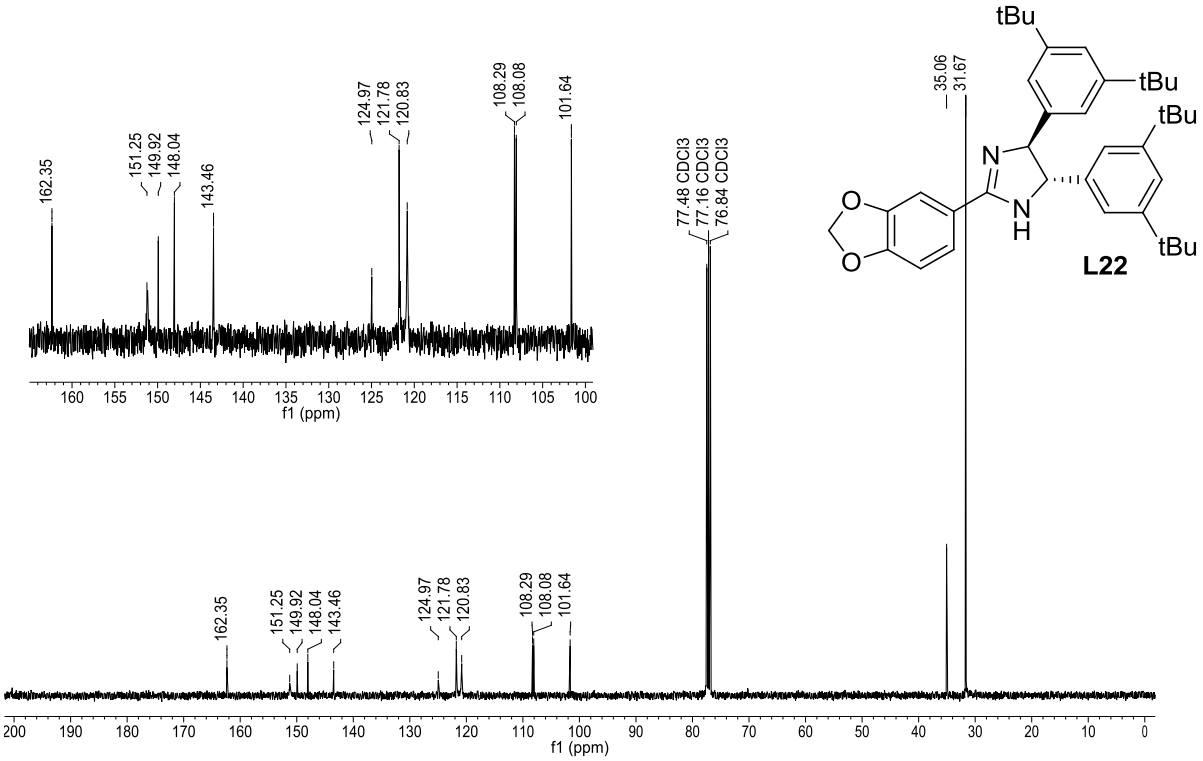
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **L21**.



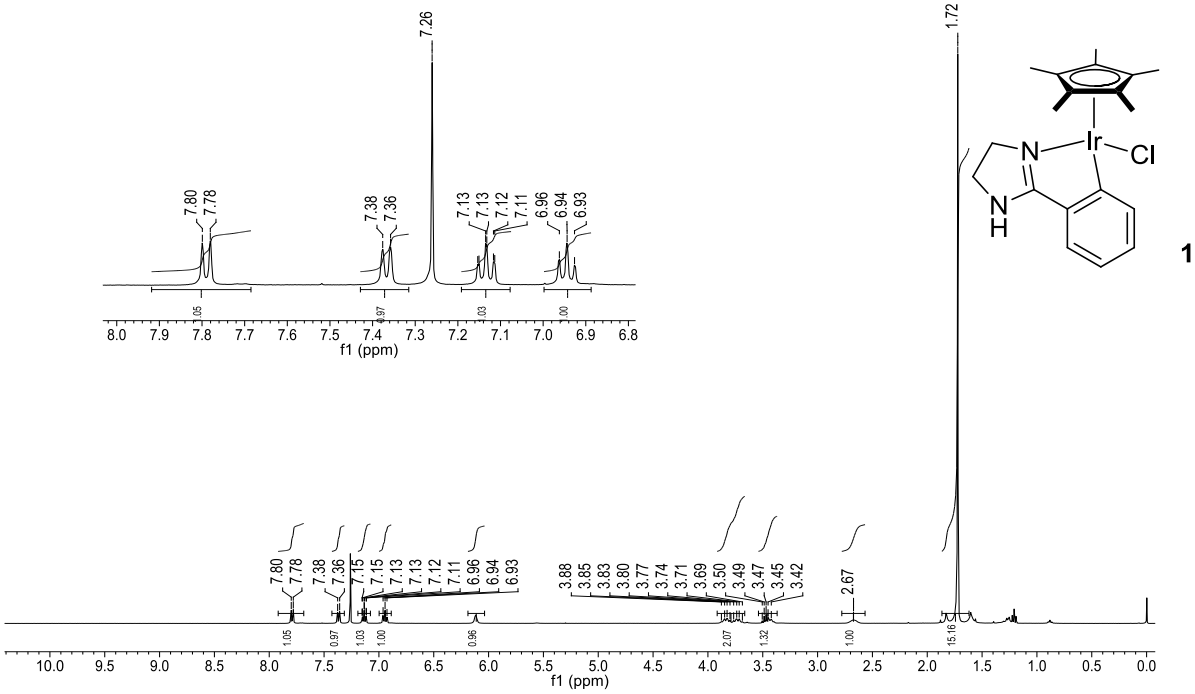
Partial $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **L21**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L22**.

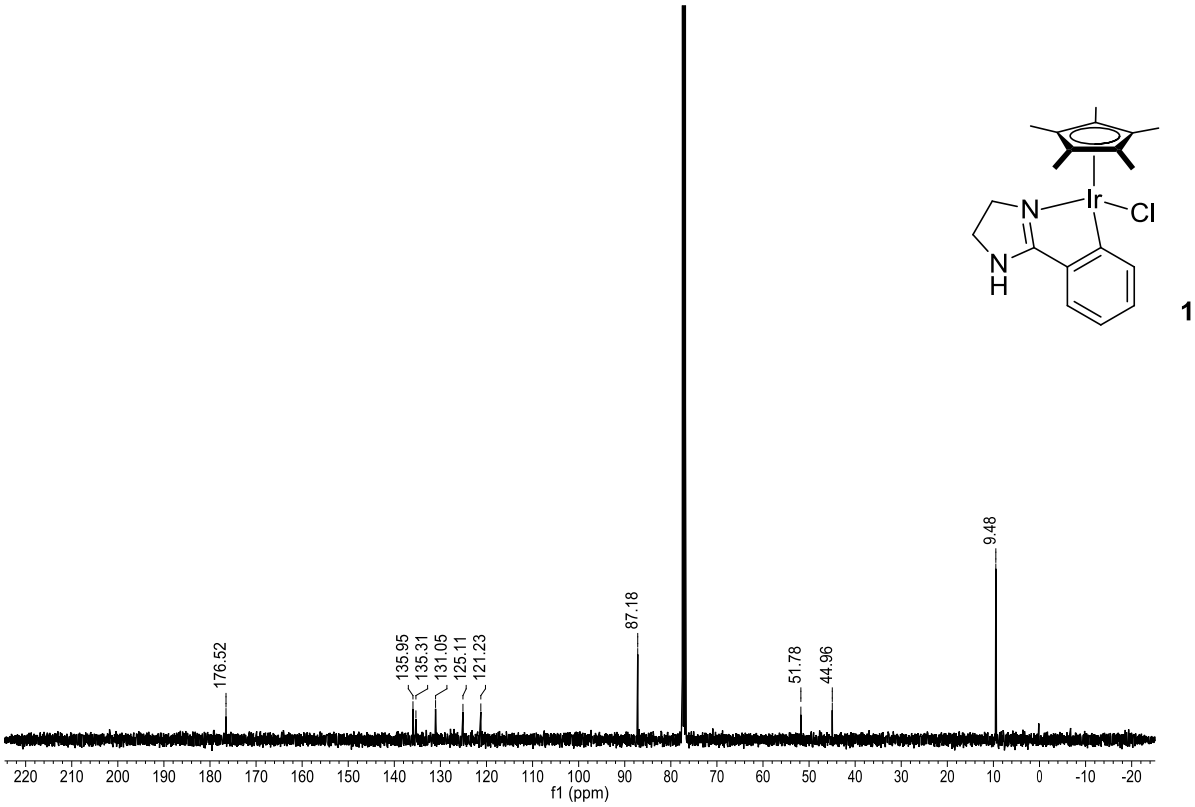


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **L22**.



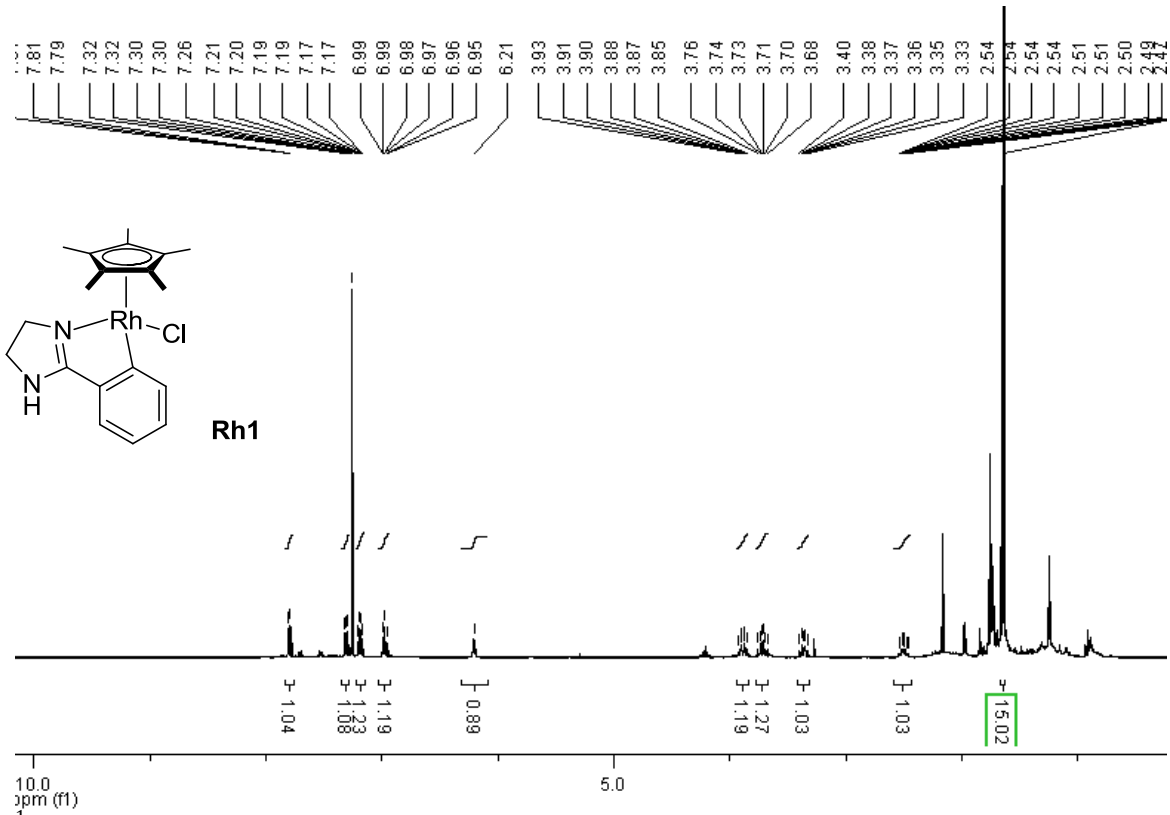
1

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

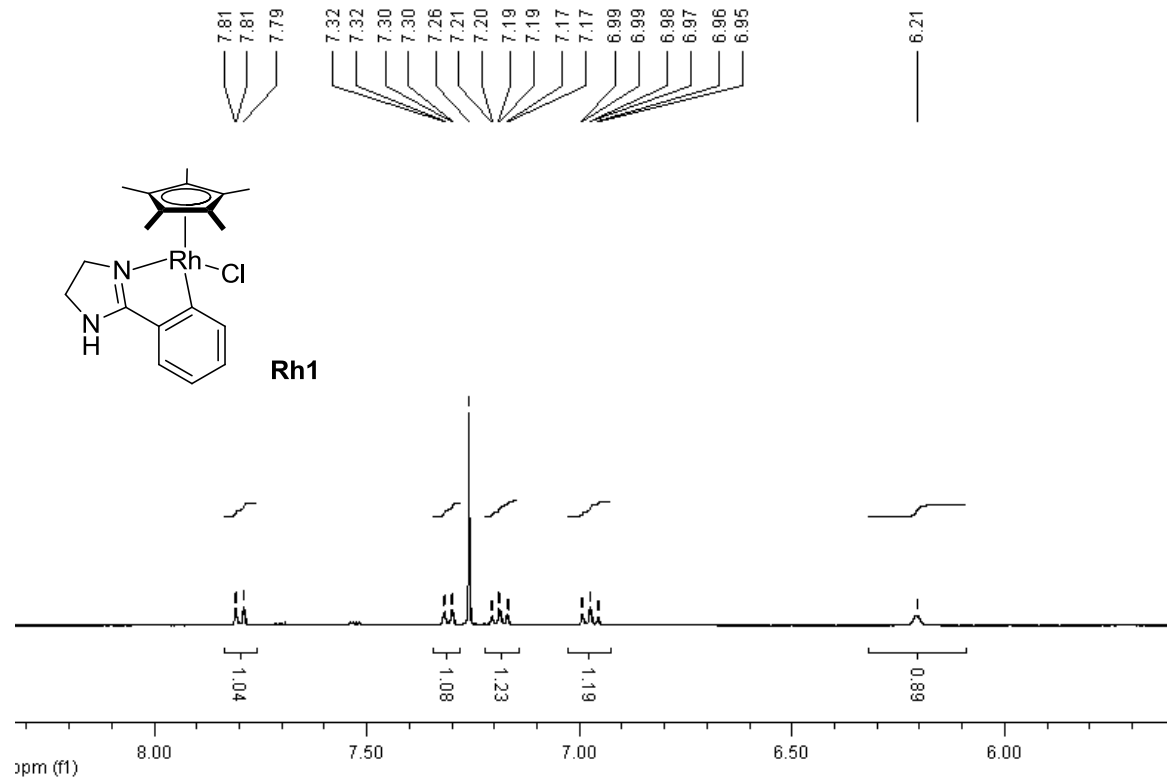


1

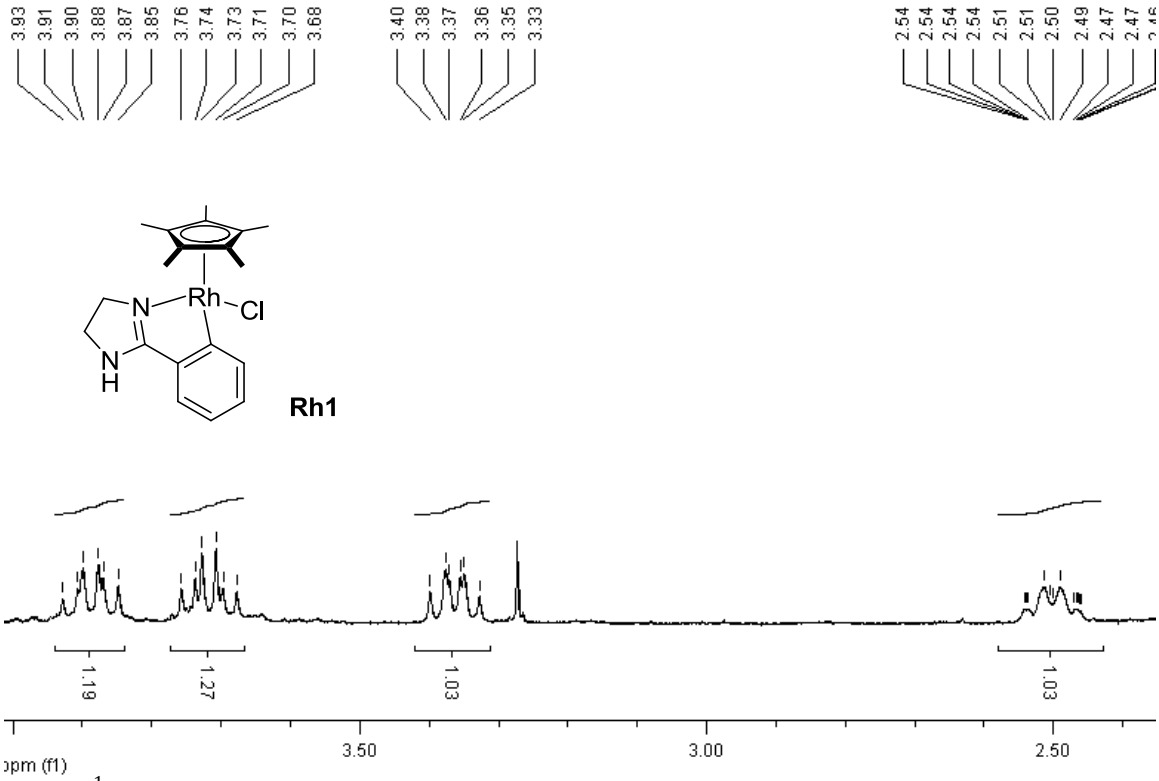
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **1**.



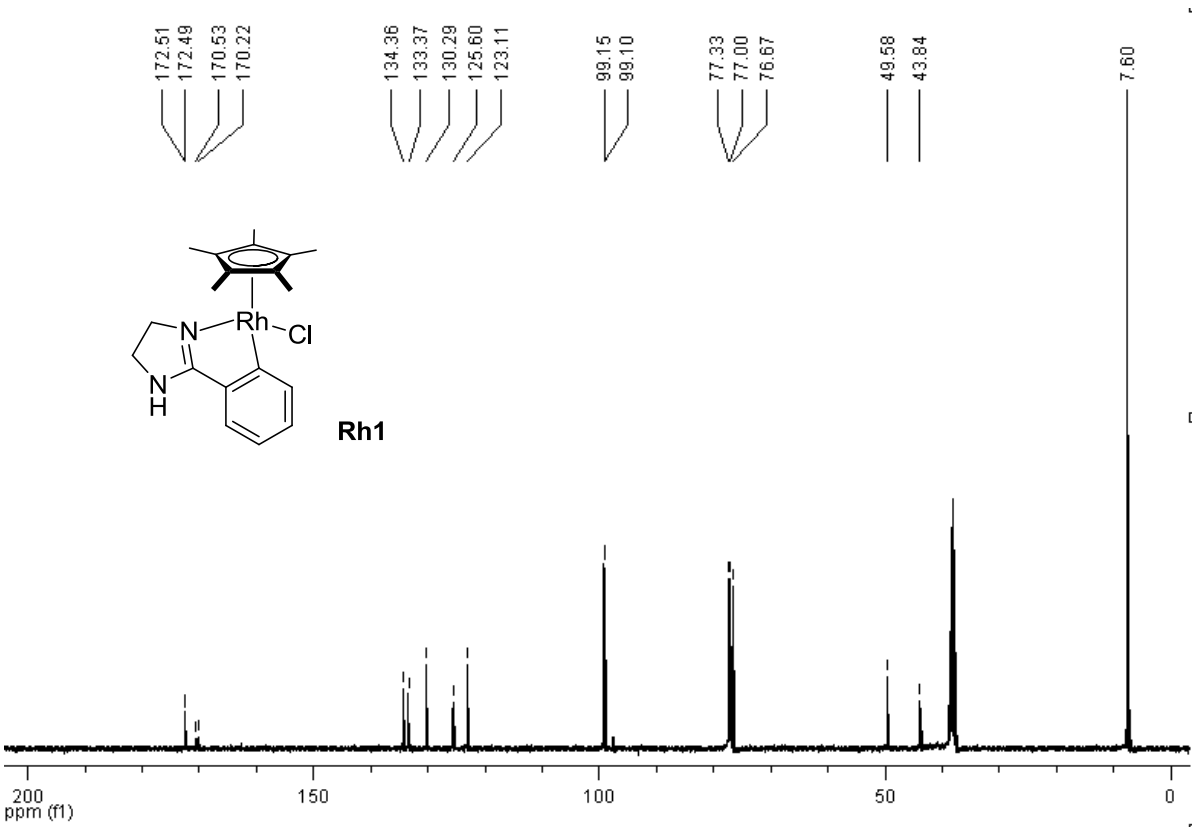
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Rh1**.



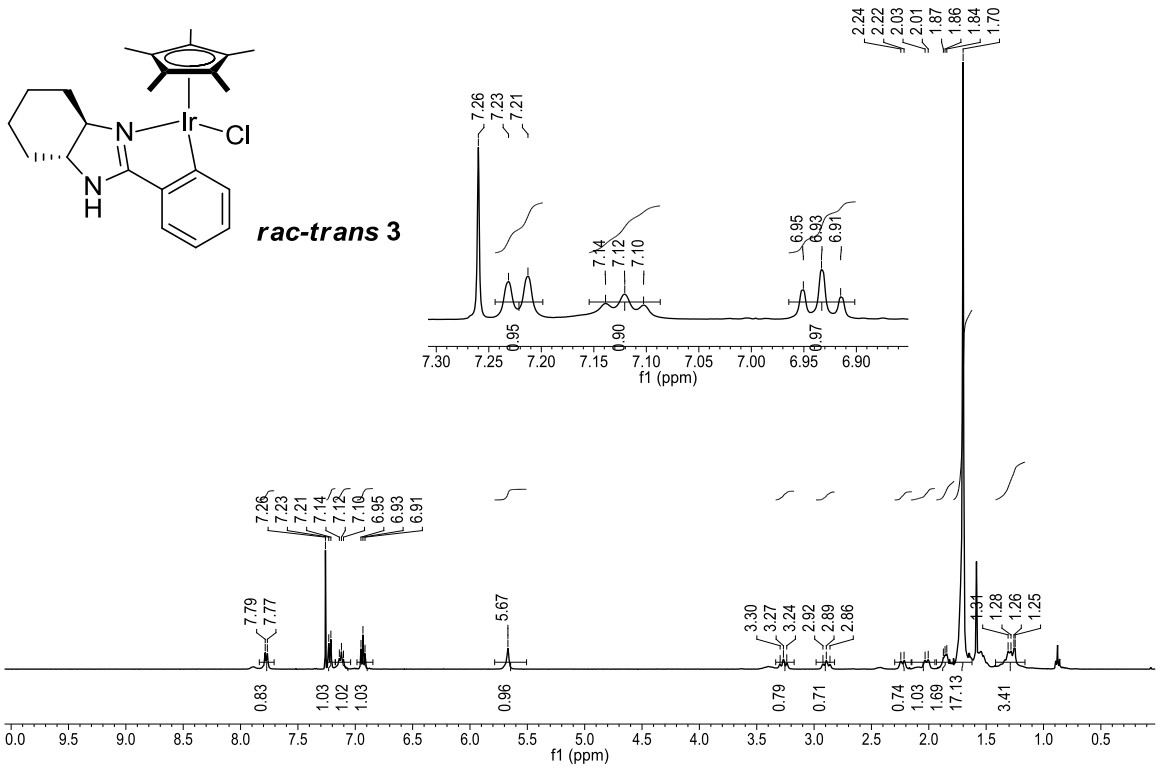
Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Rh1**.



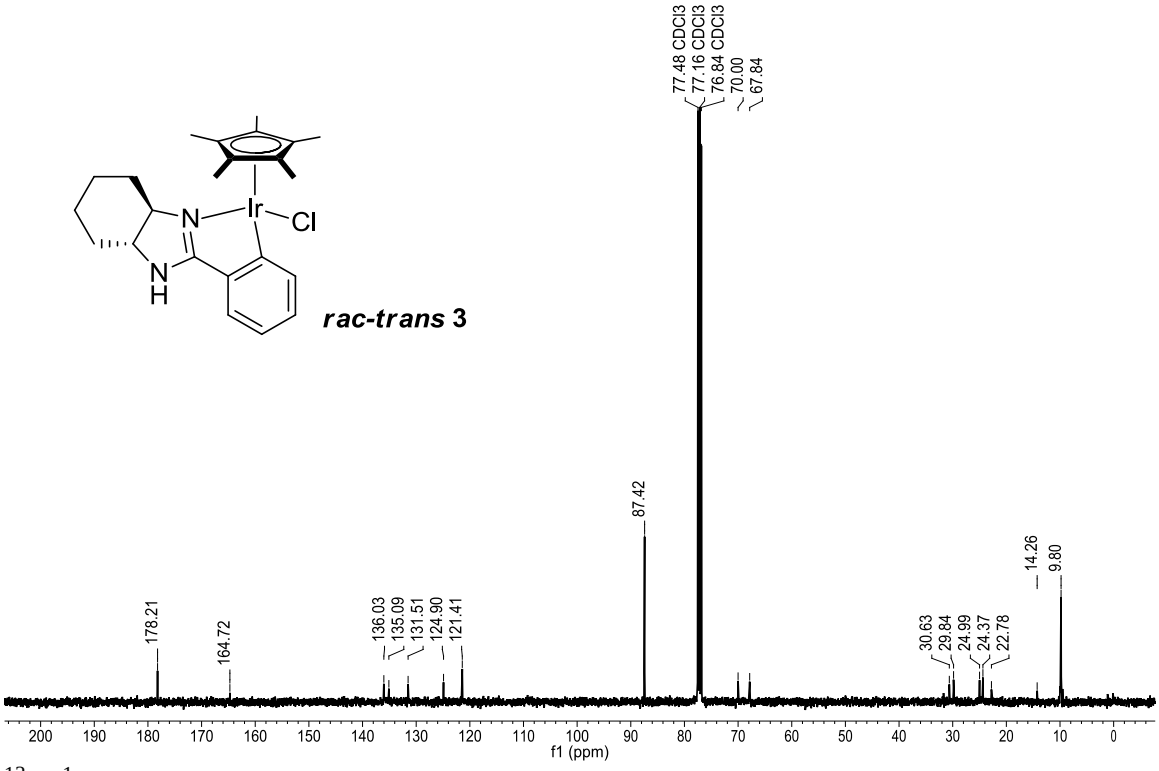
Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Rh1**.



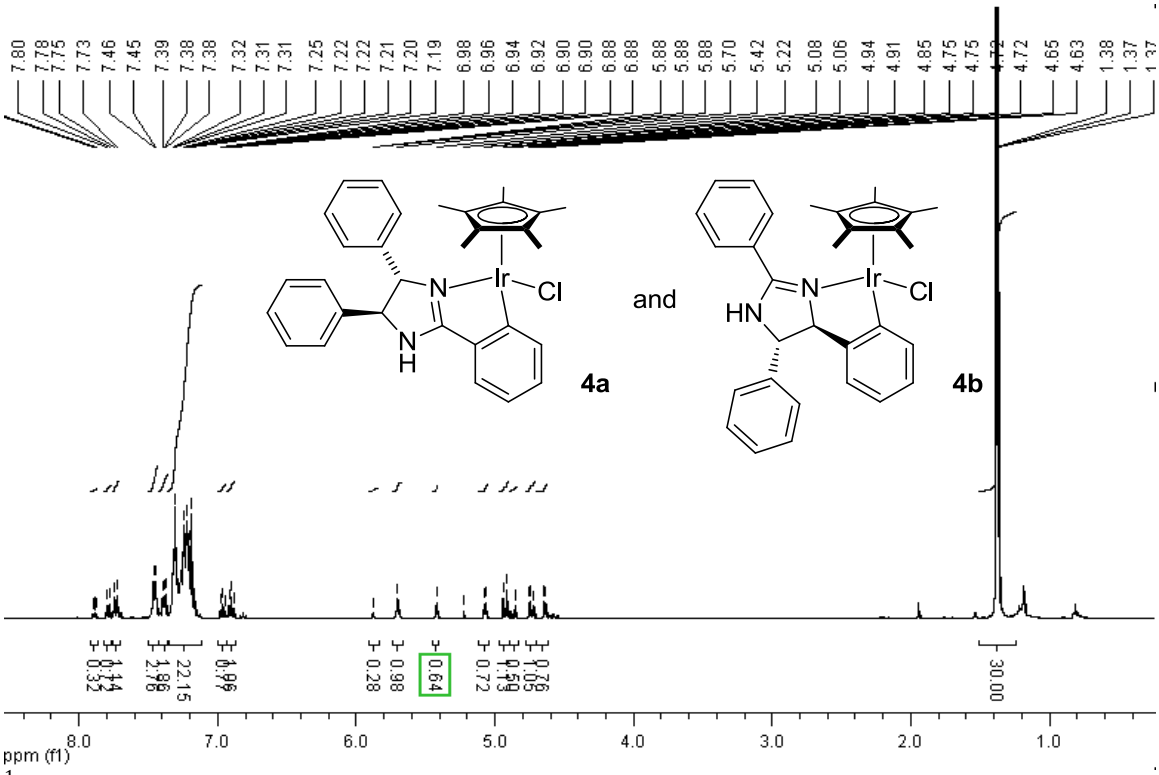
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **Rh1**.



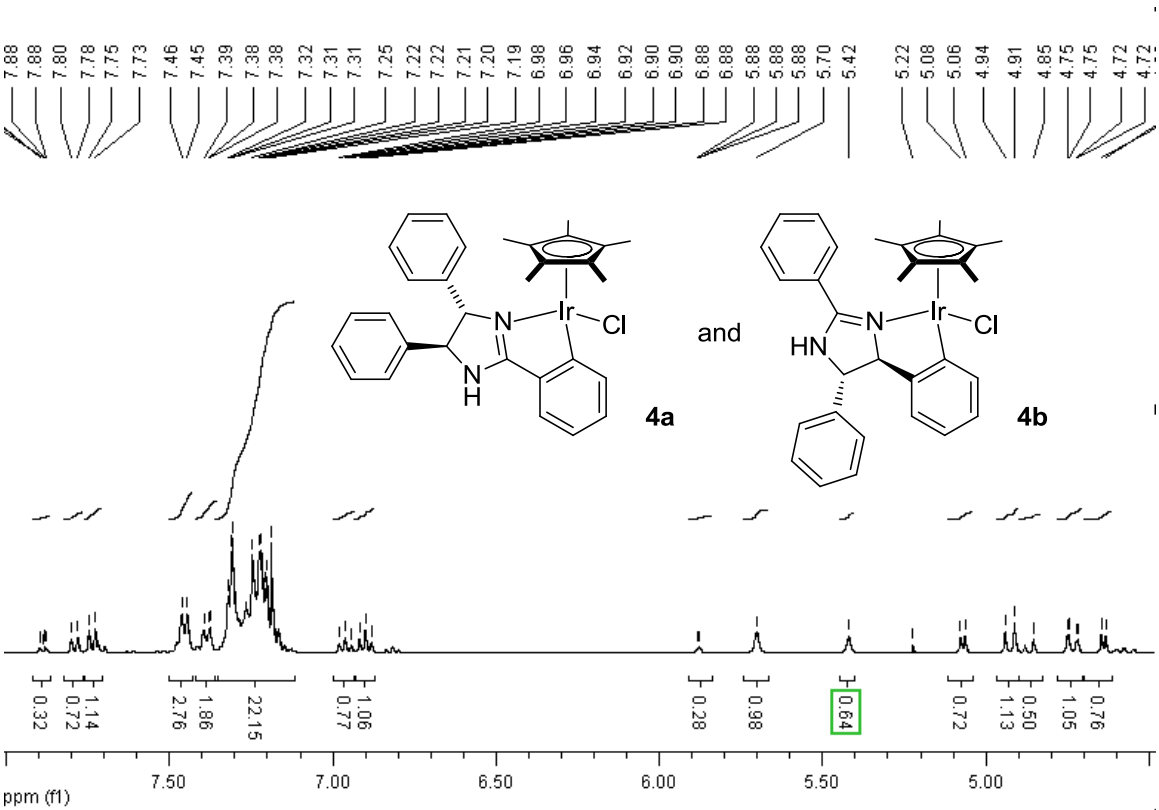
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.



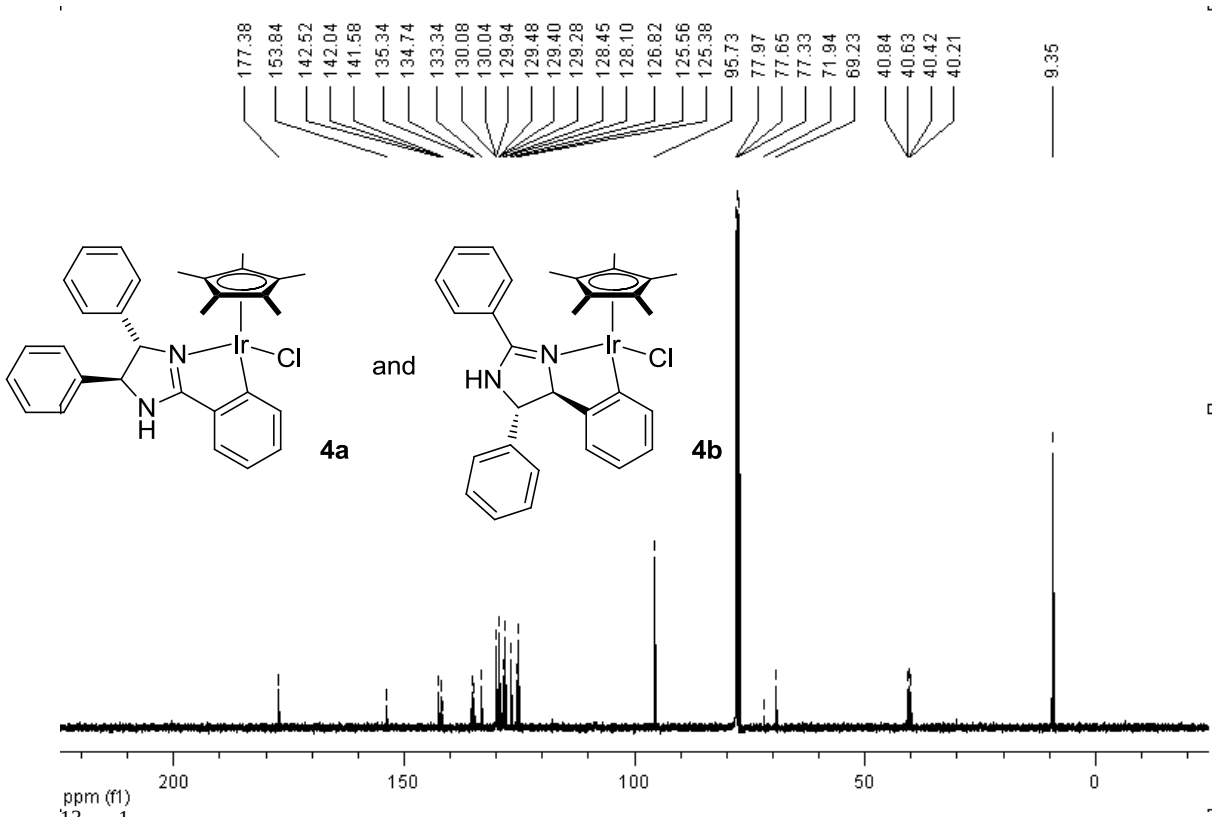
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3**.



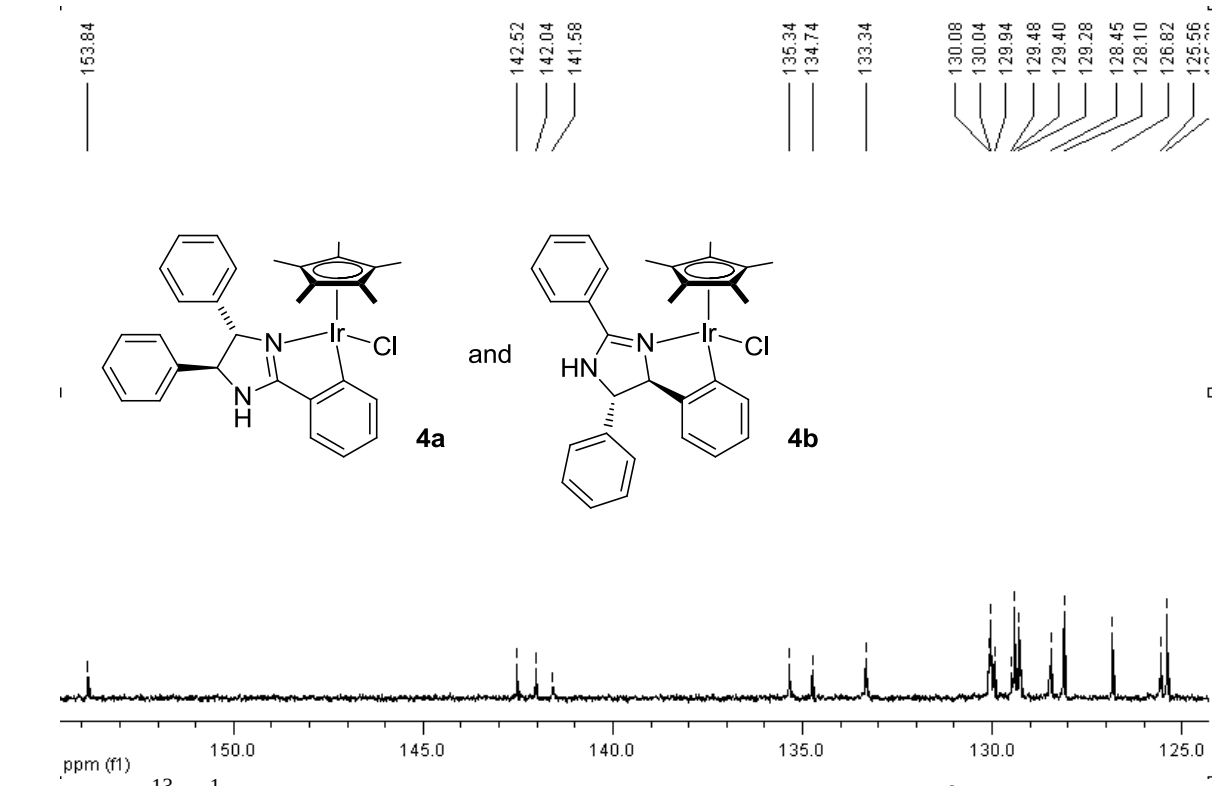
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a** and **4b**.



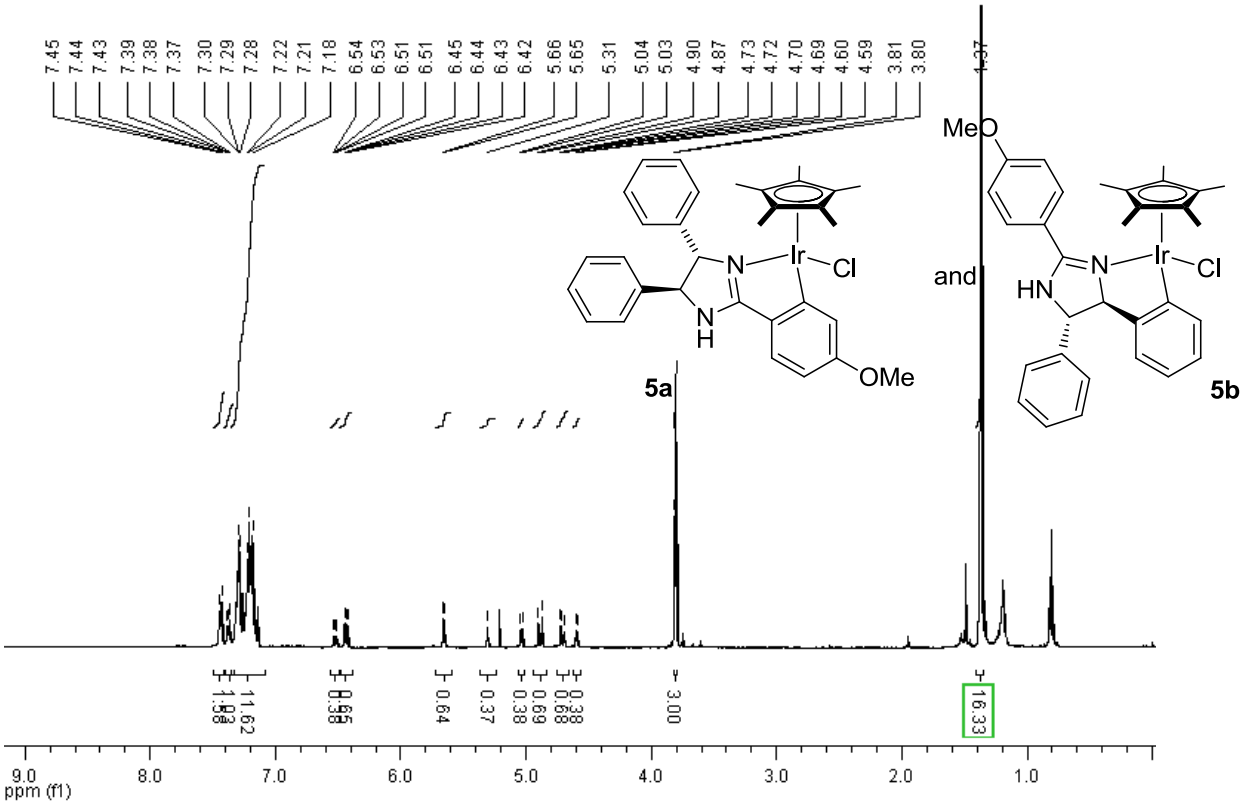
Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a** and **4b**.



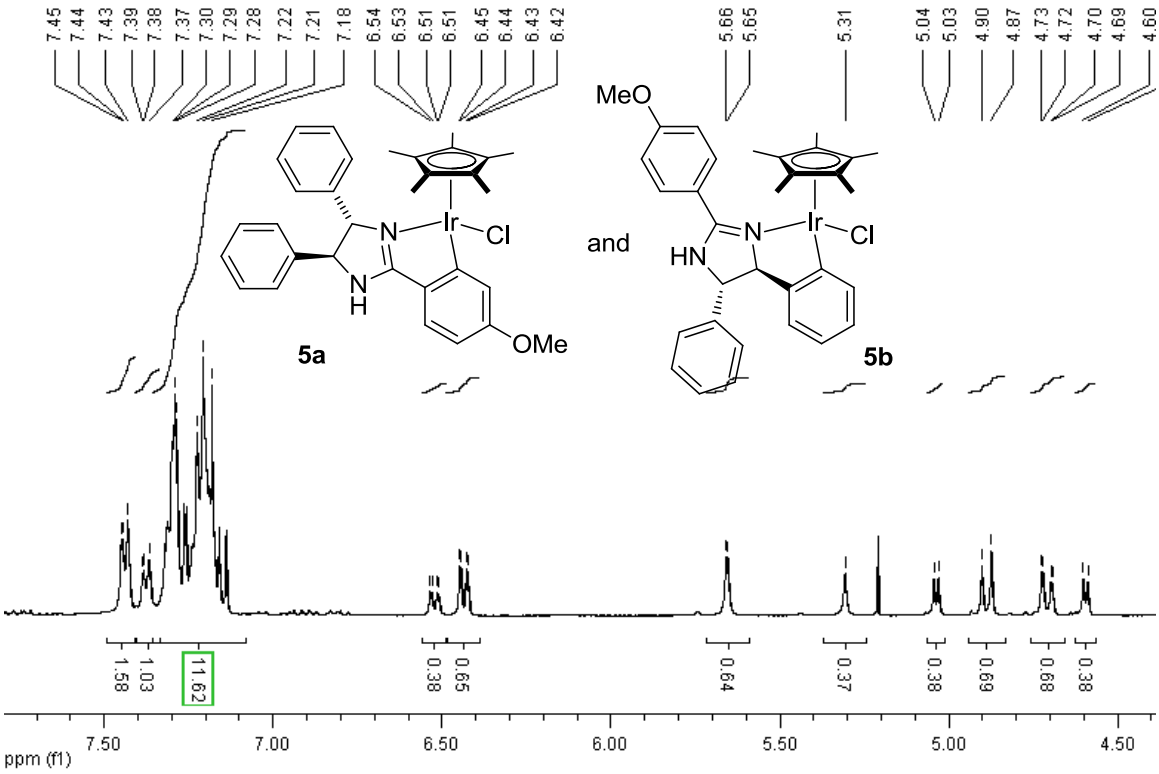
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-*d6* mix) spectrum of **4a** and **4b**.



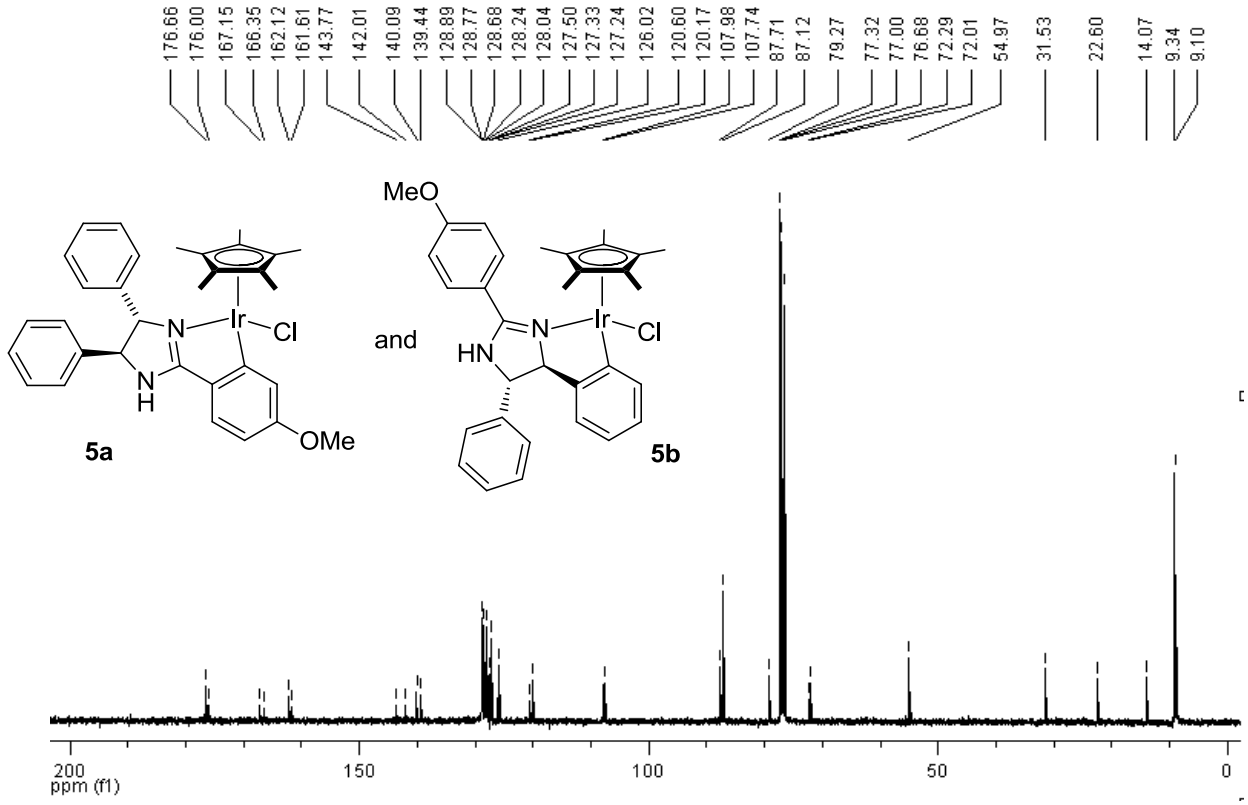
Partial $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/DMSO-*d6* mix) spectrum of **4a** and **4b** (aromatic region).



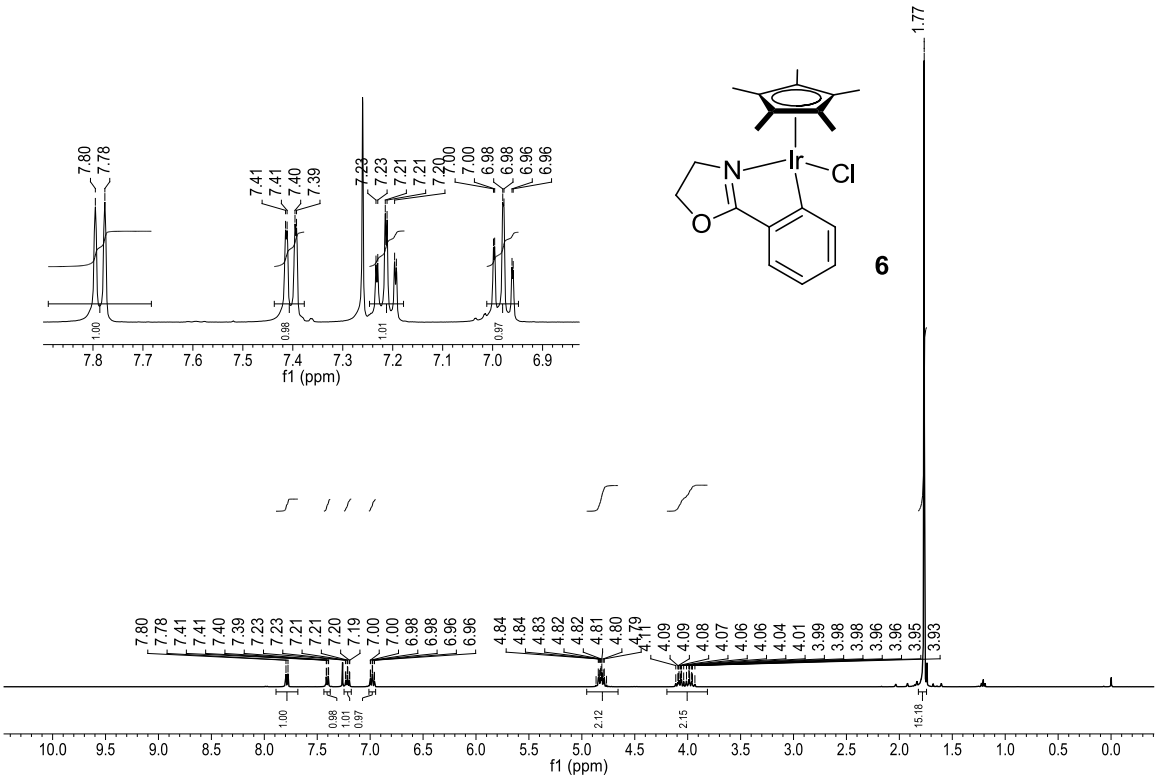
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a** and **5b**.



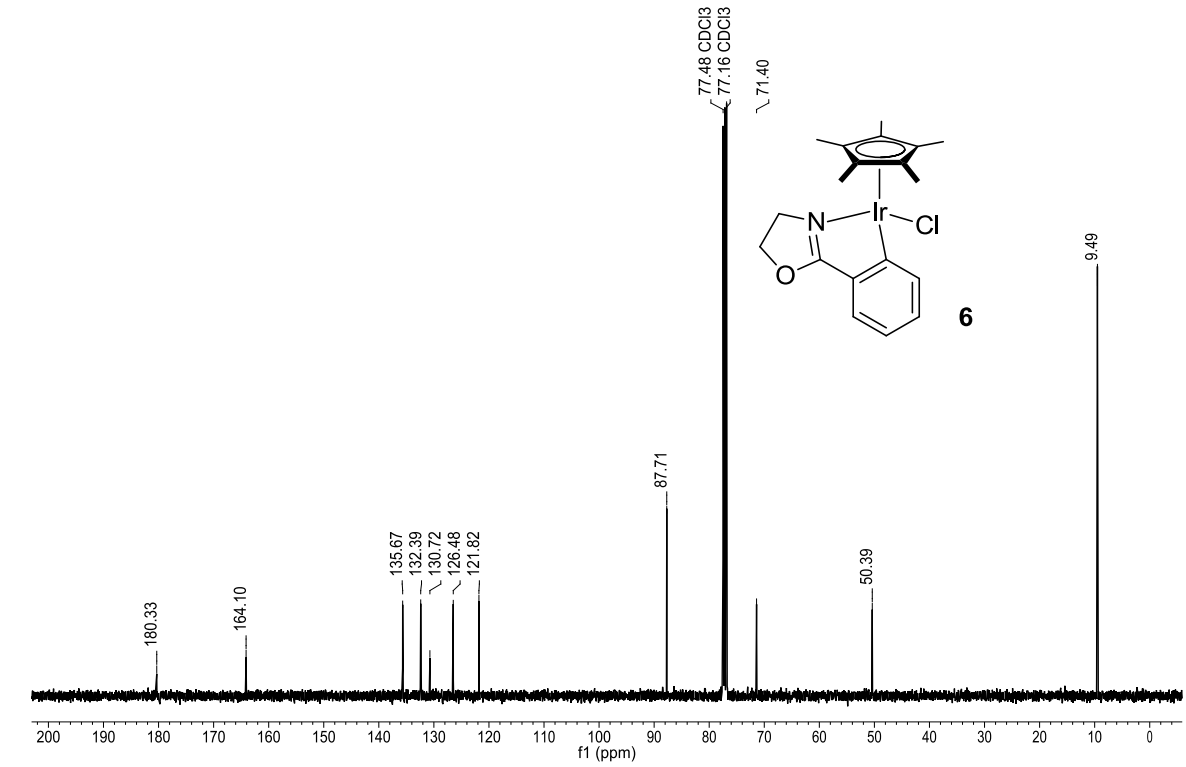
Partial ^{1}H NMR (7.60 - 4.50 ppm) (400 MHz, $CDCl_3$) spectrum of **5a** and **5b**.



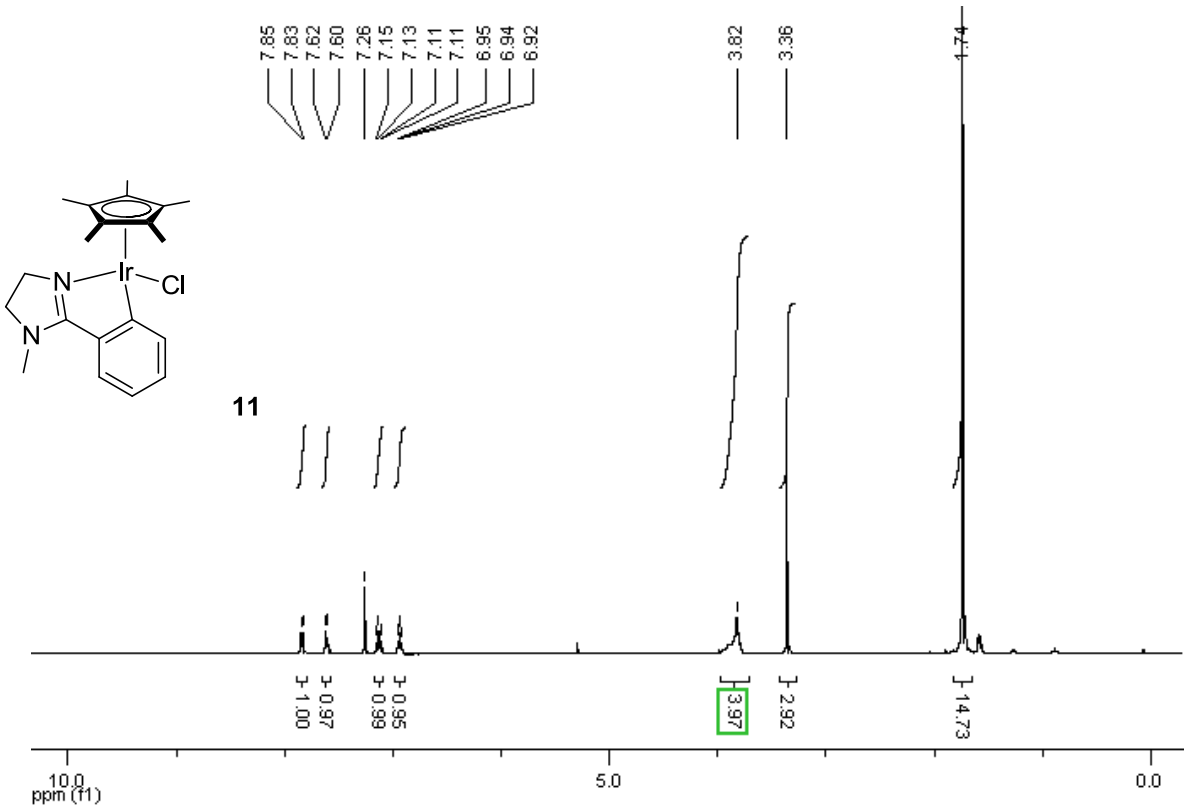
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5**.



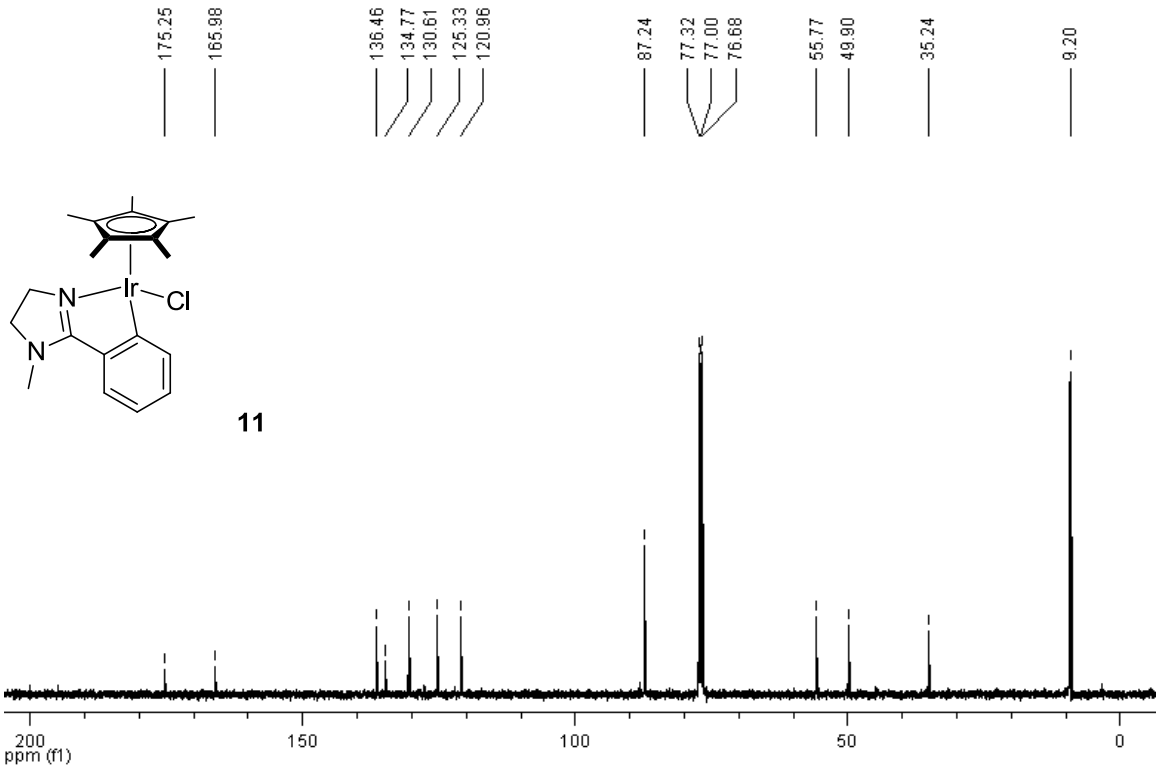
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**.



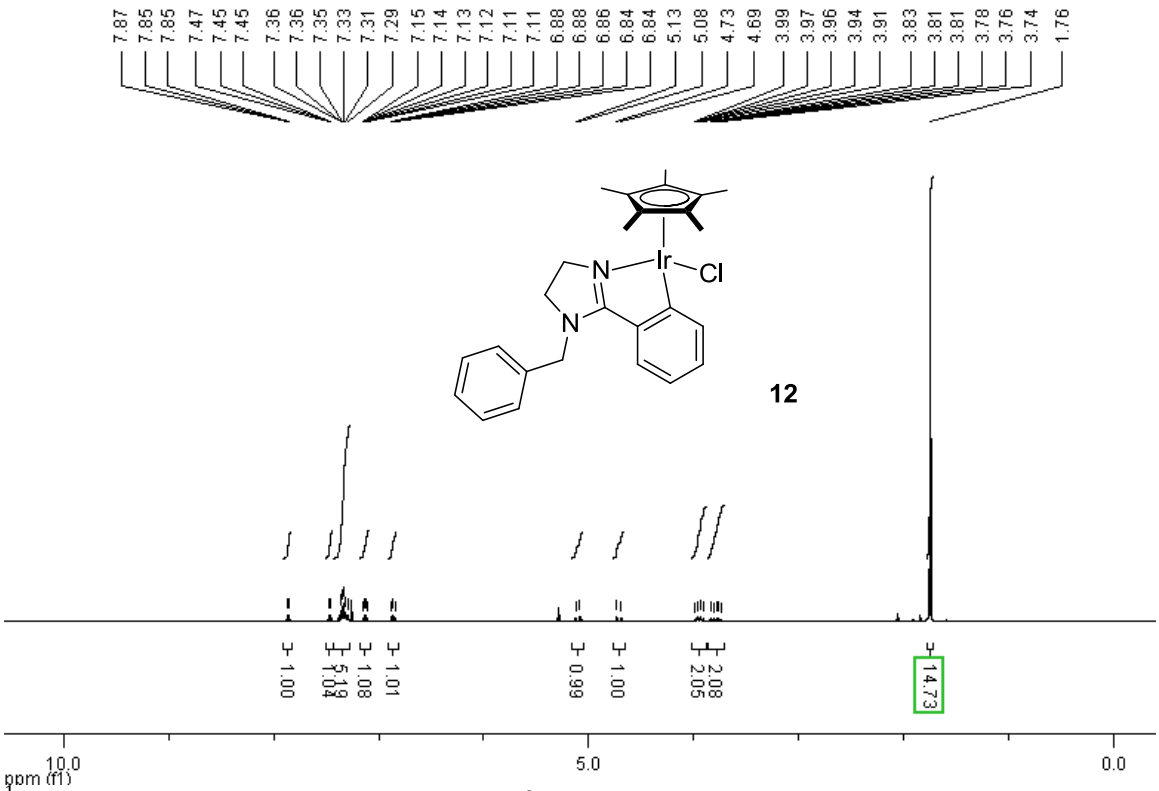
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **6**.



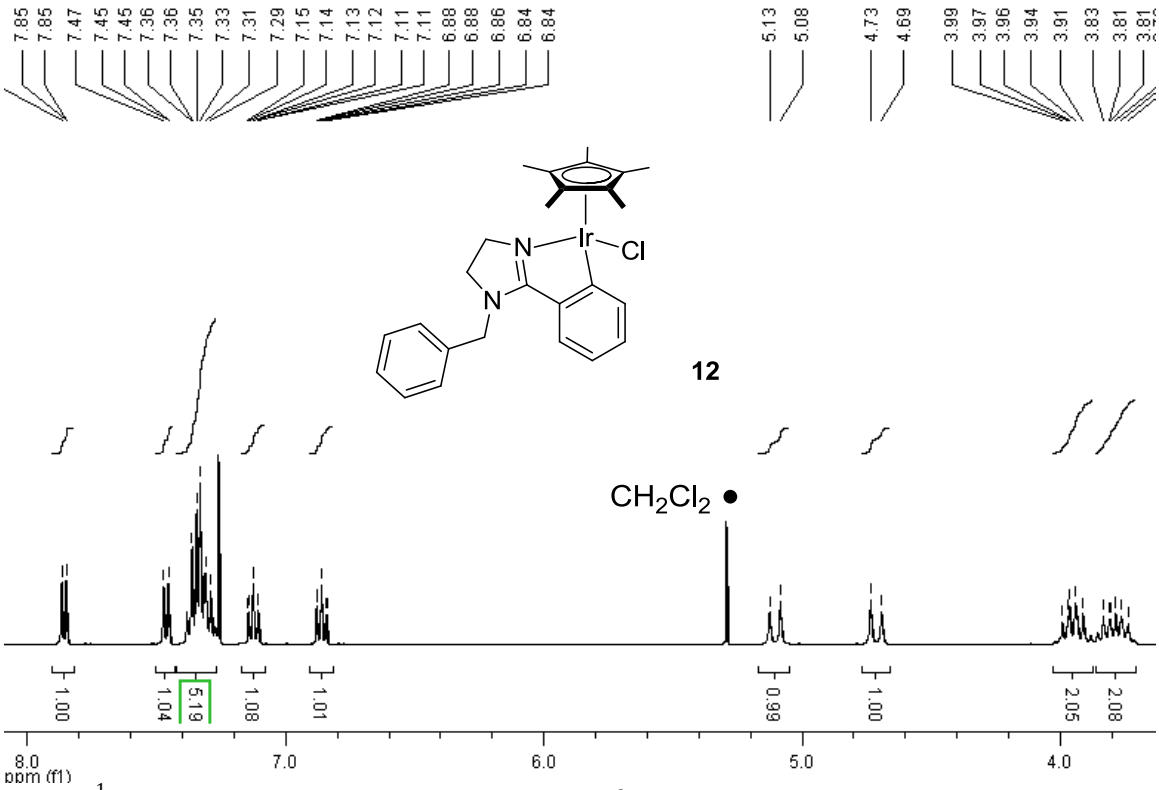
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**.



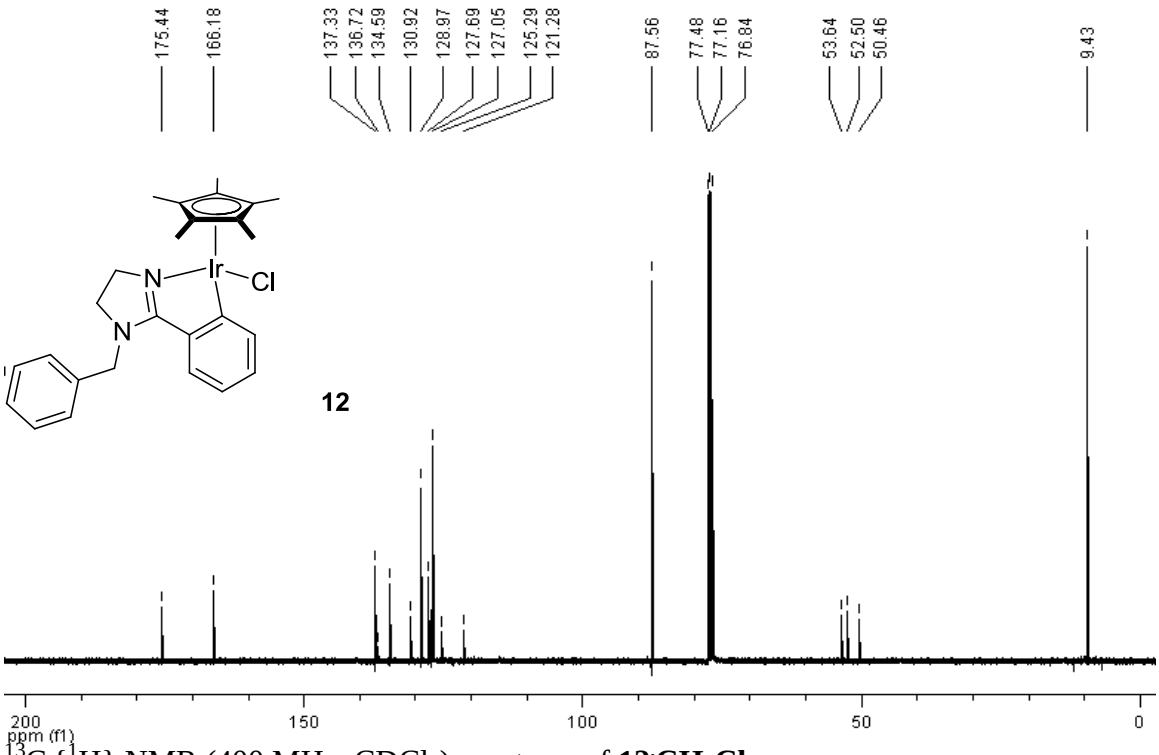
$^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$) spectrum of **11**.



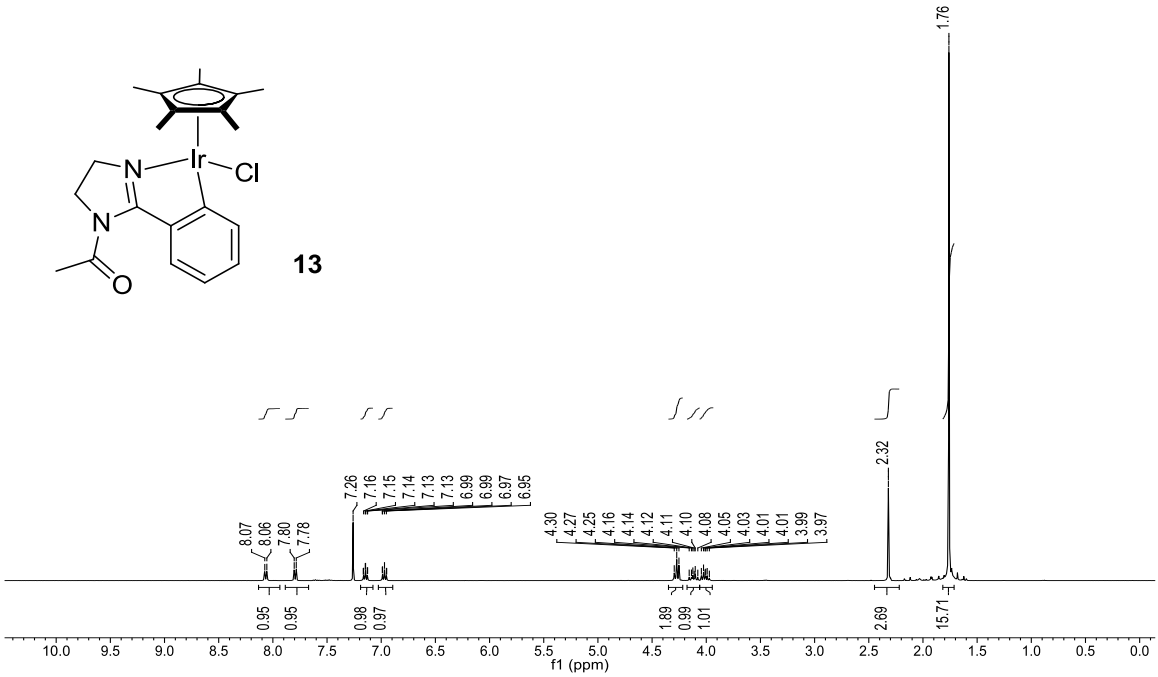
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**·$\mathbf{CH_2Cl_2}$.



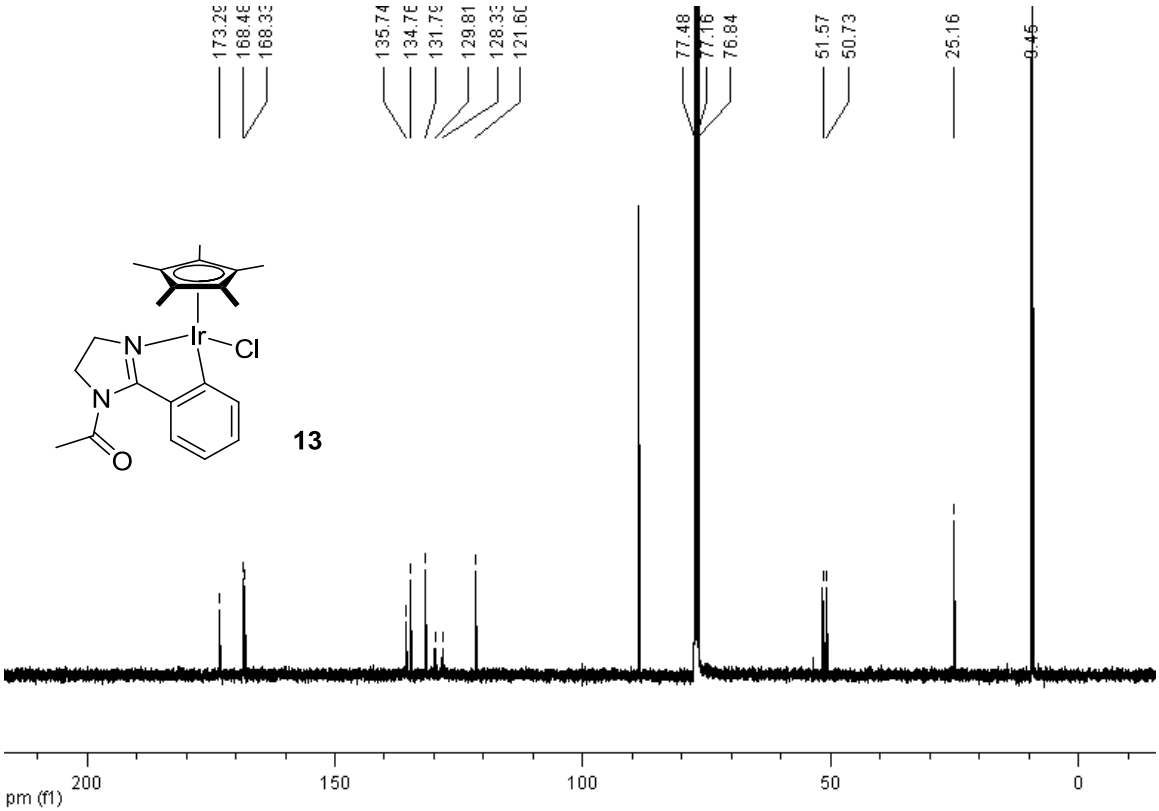
Partial ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**·$\mathbf{CH_2Cl_2}$.



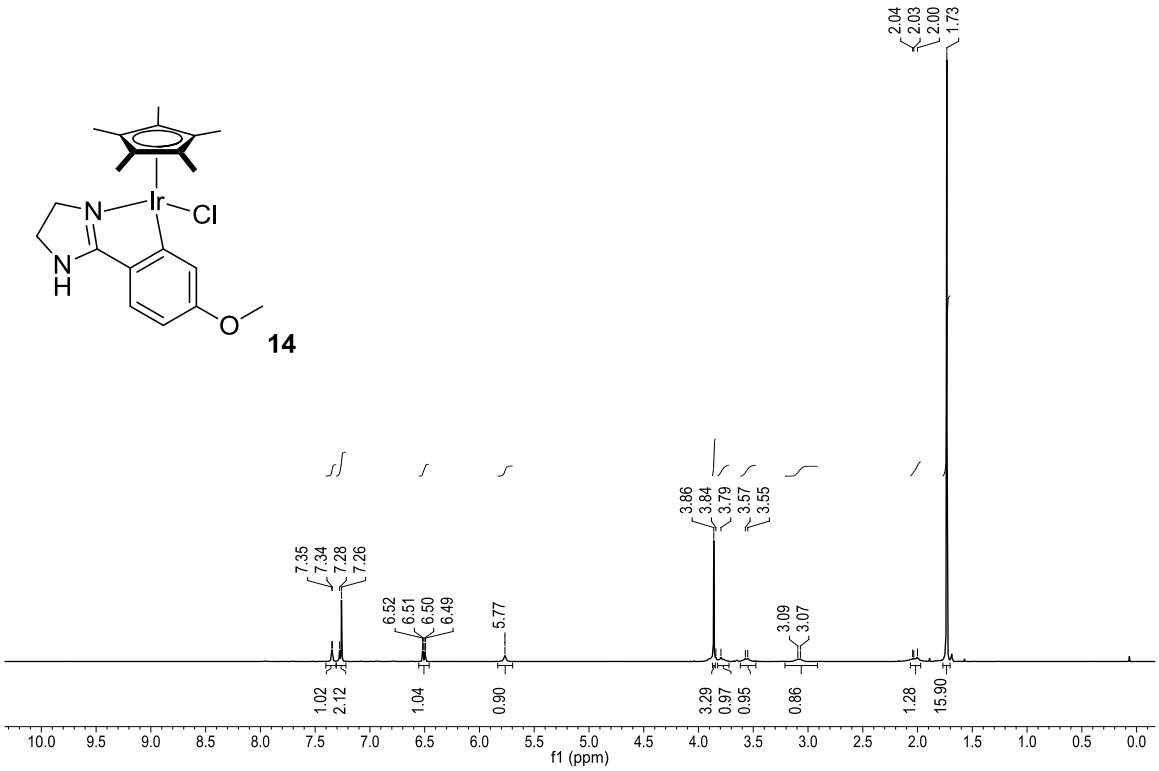
^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) spectrum of **12**·$\mathbf{CH_2Cl_2}$.



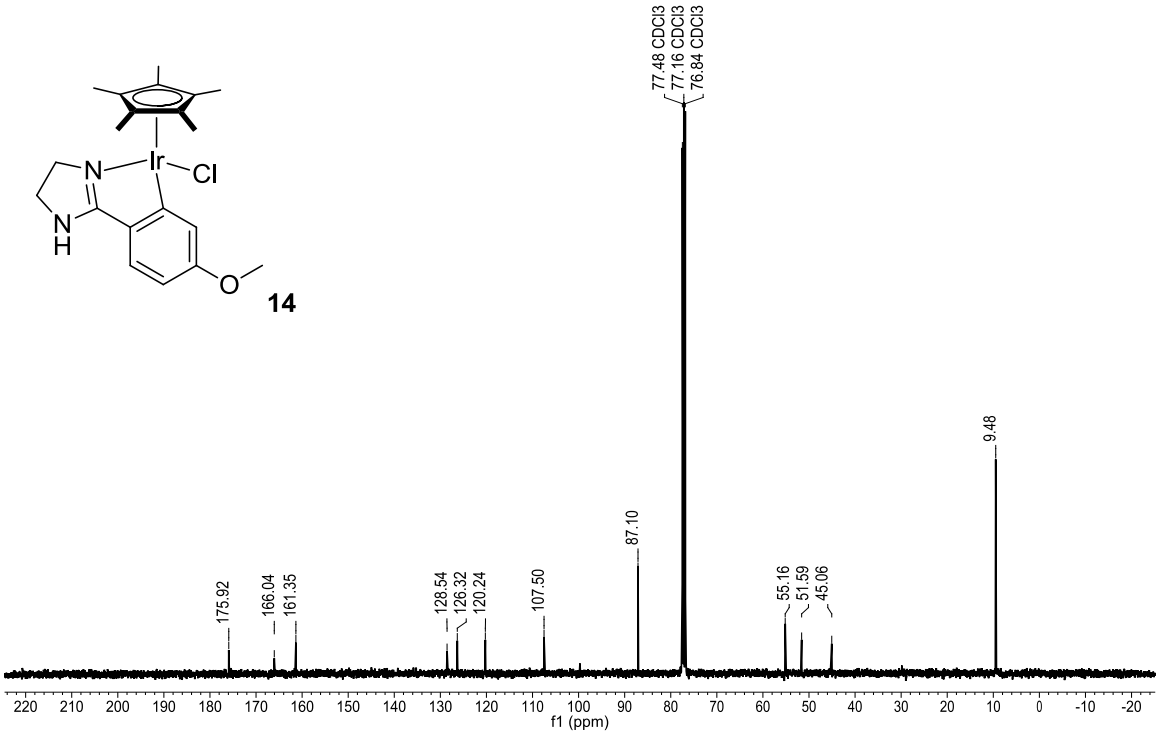
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**.



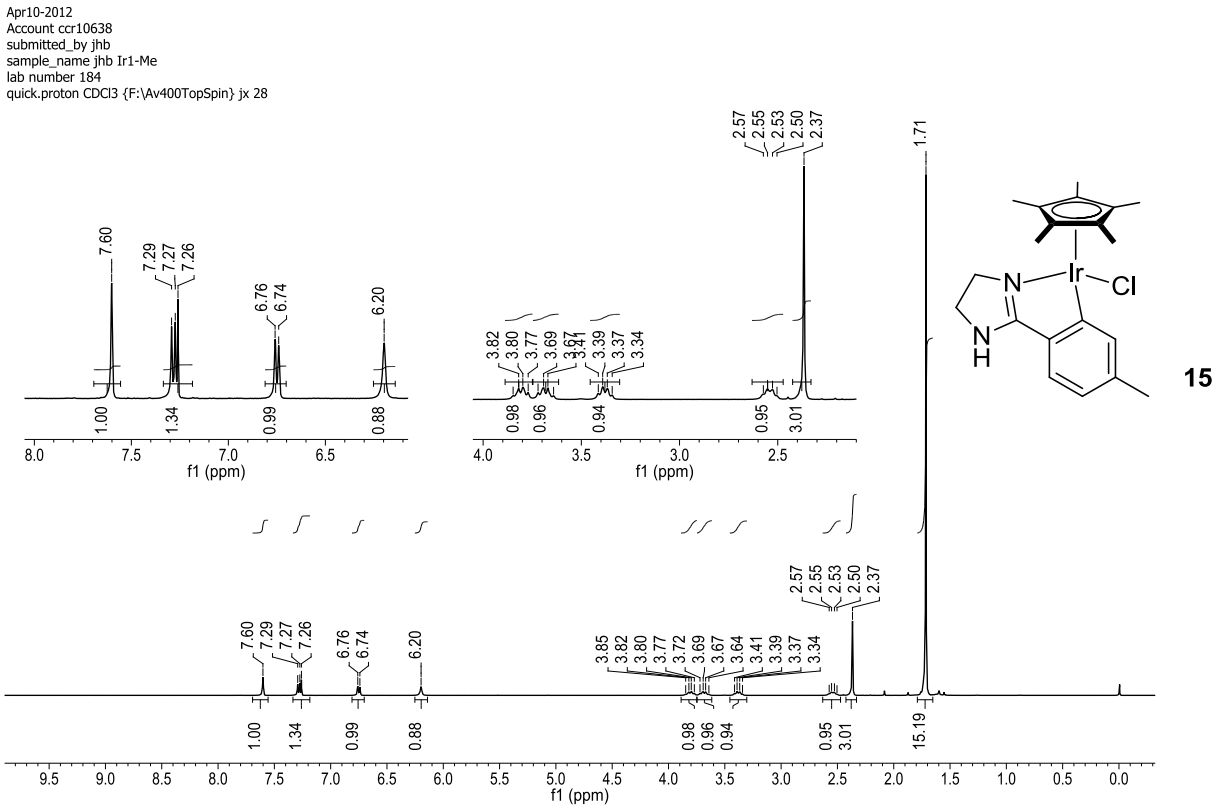
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **13**.



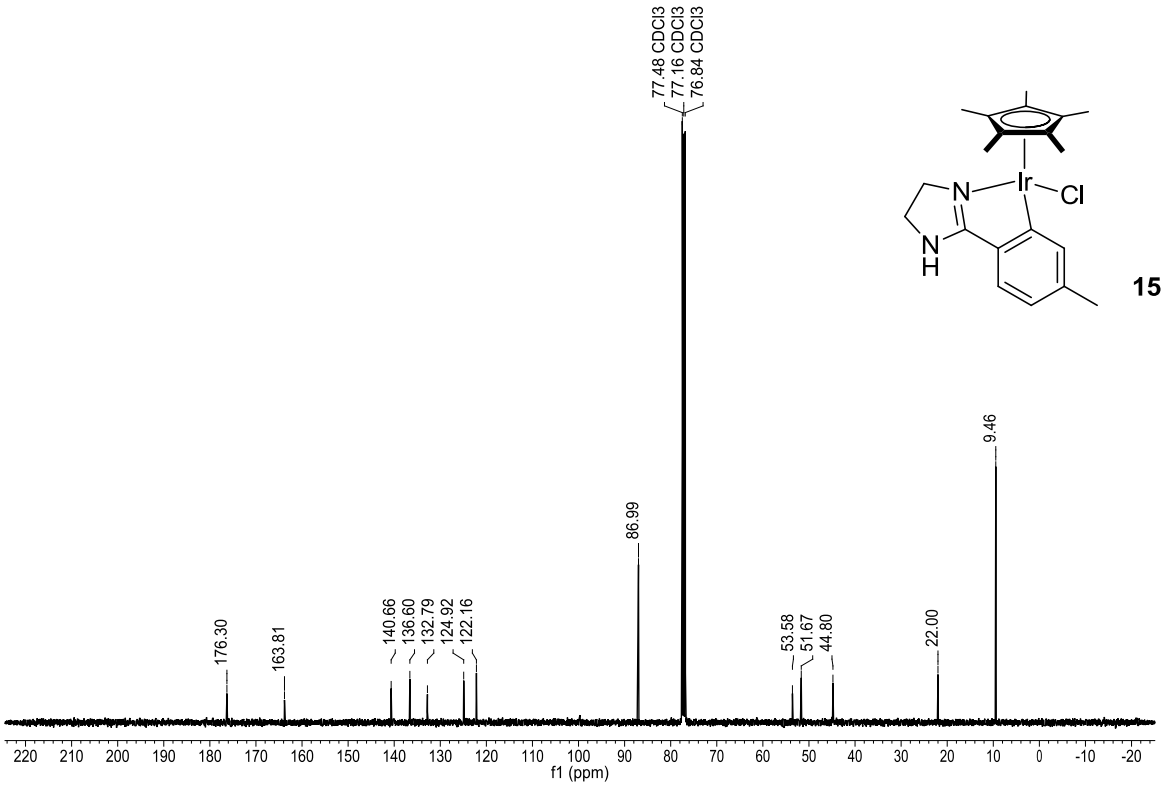
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14**.



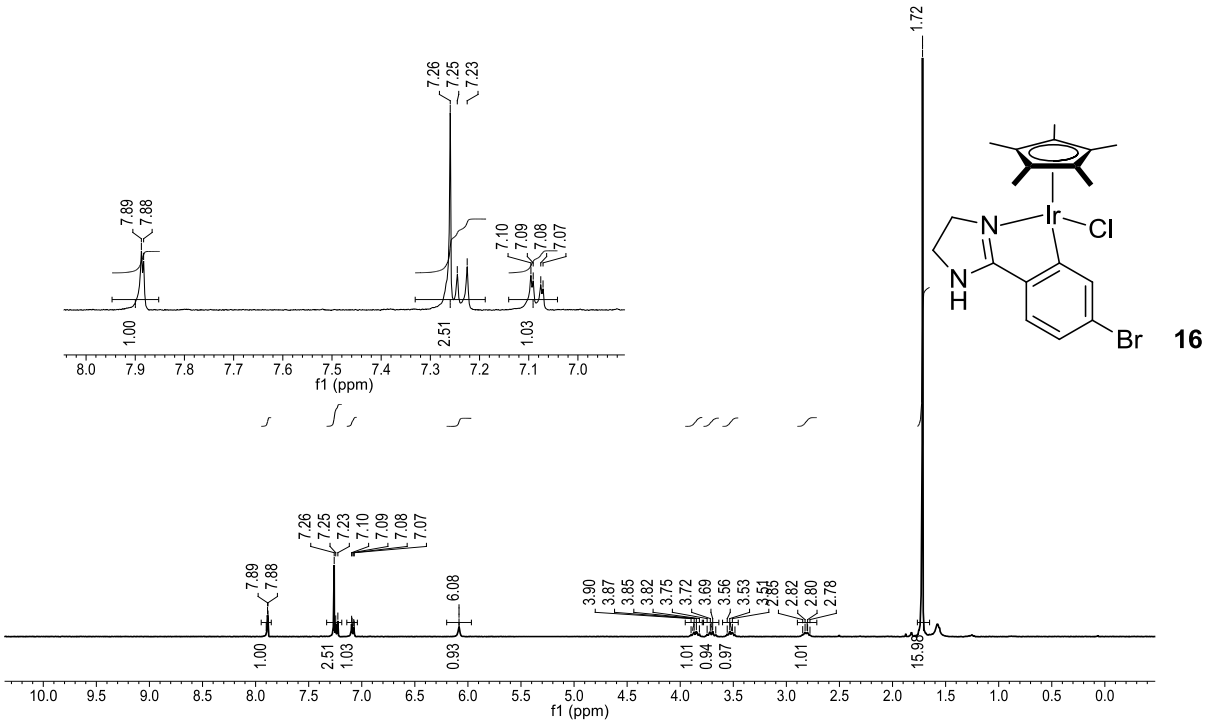
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **14**.



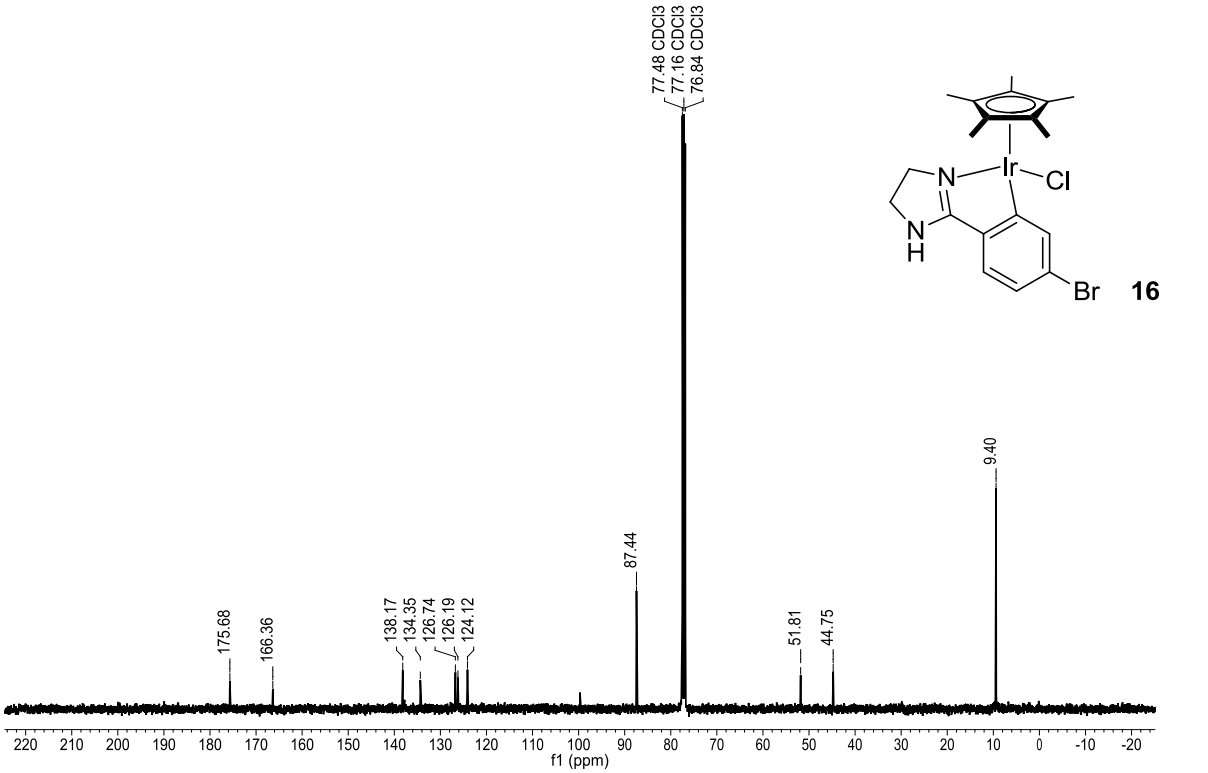
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15**.



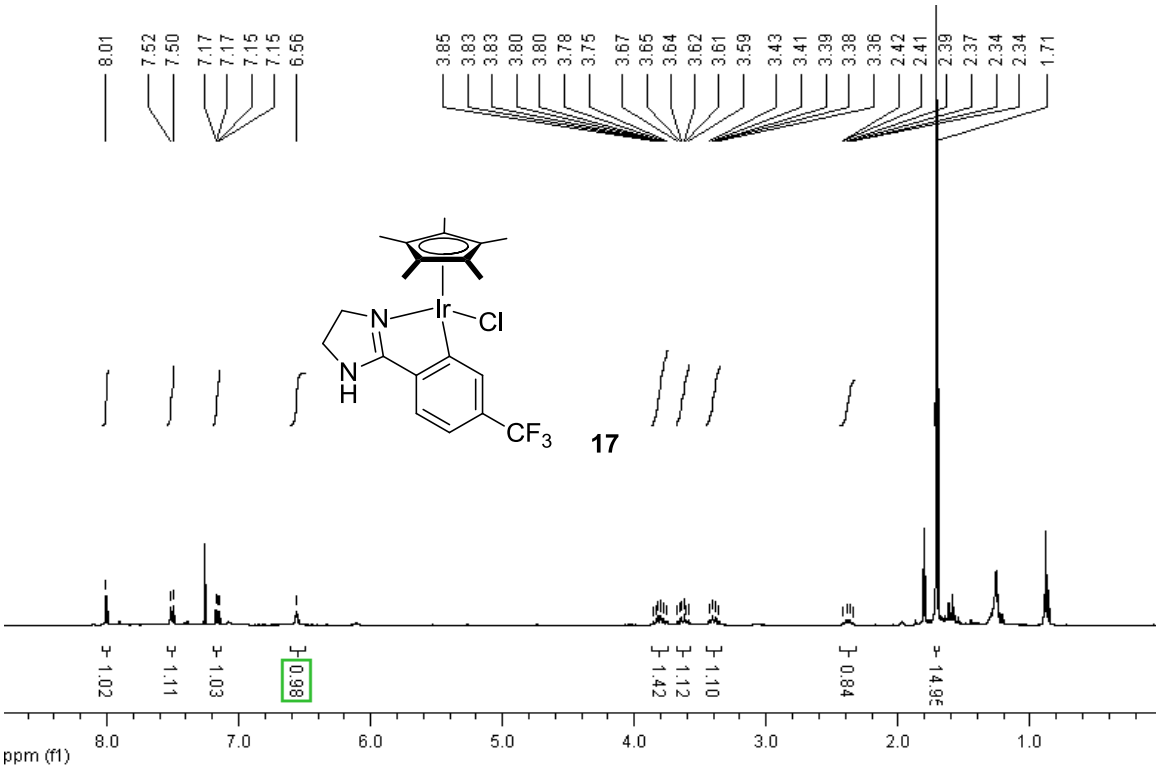
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **15**·$\mathbf{CH_2Cl_2}$.



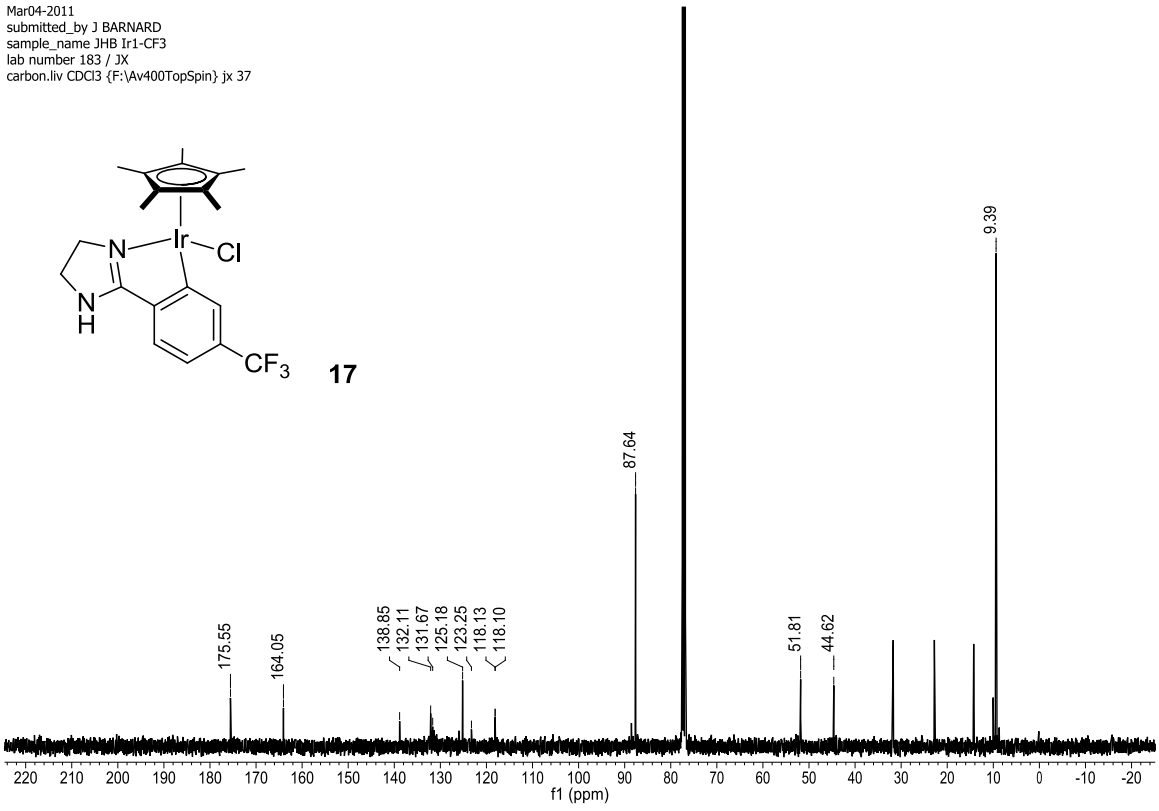
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16**.



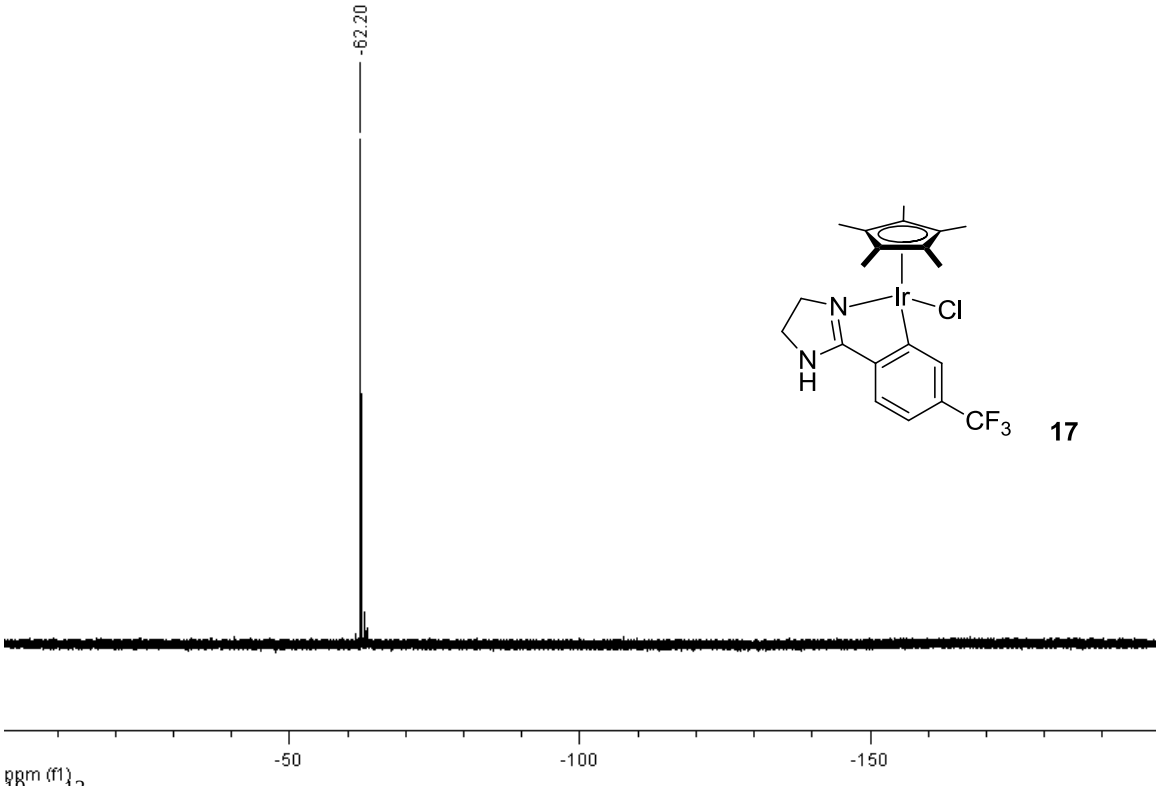
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **16**.



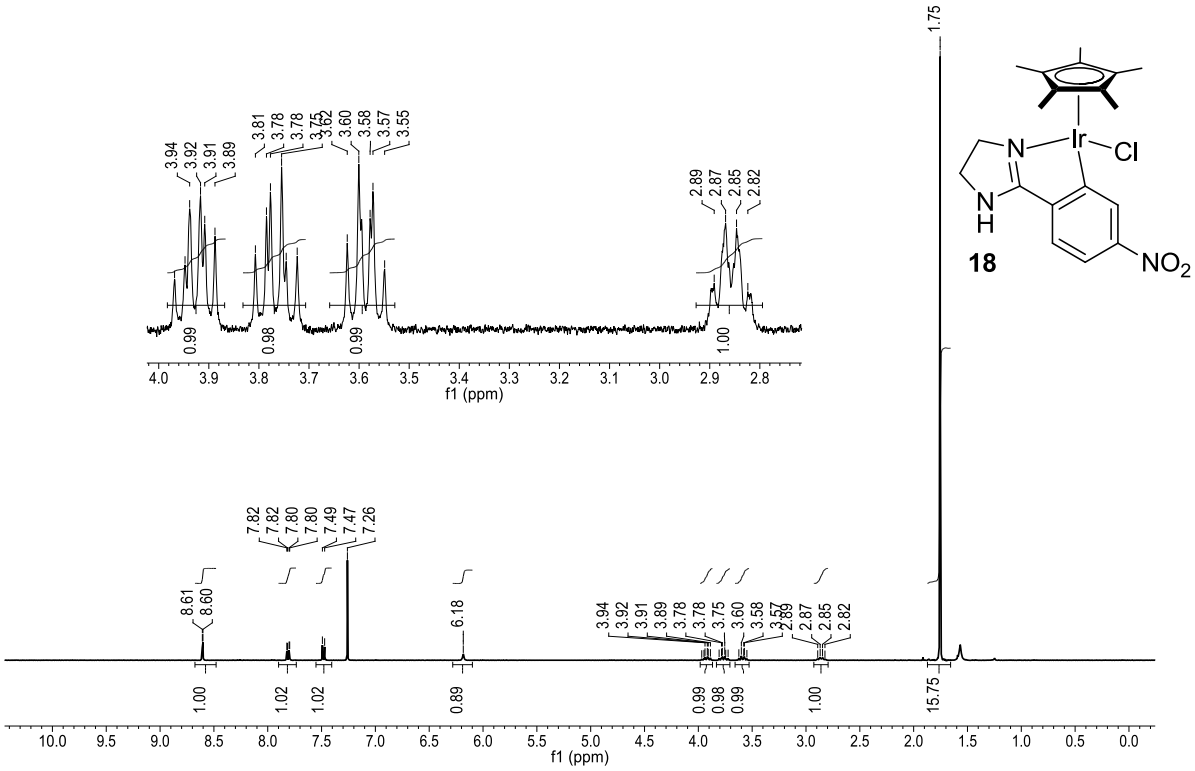
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **17**·***n*-hexane**.



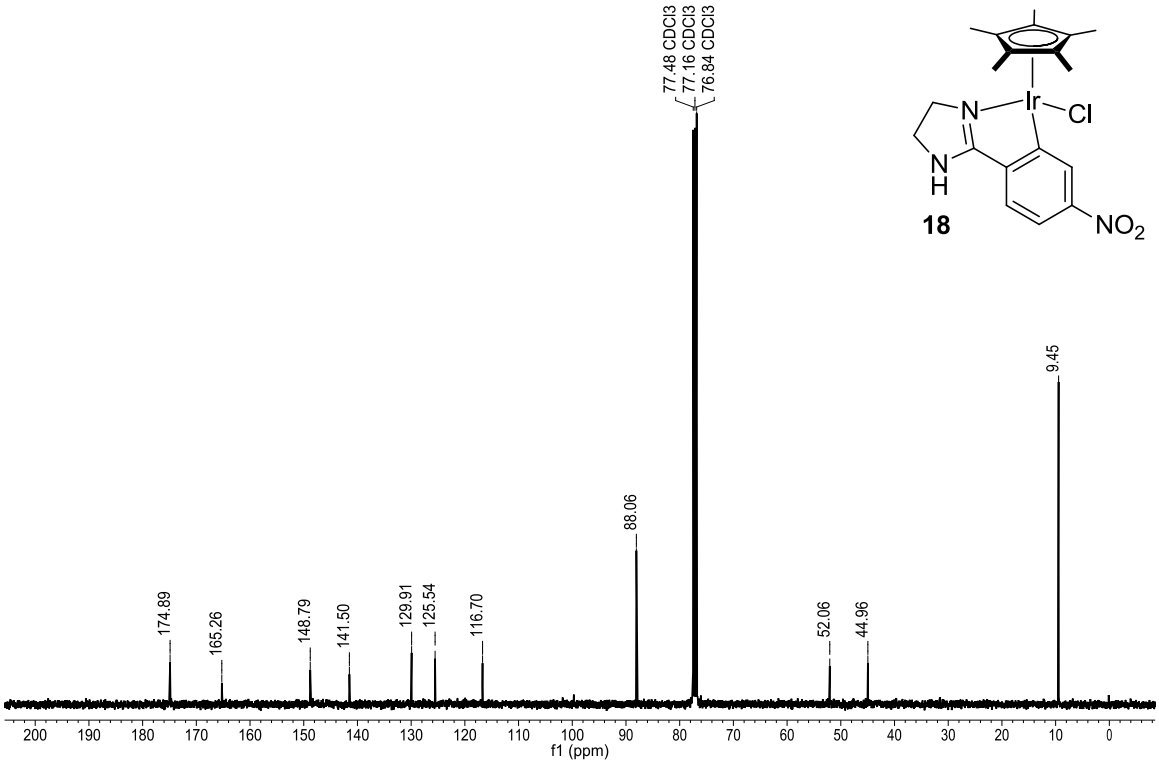
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **17**·***n*-hexane**.



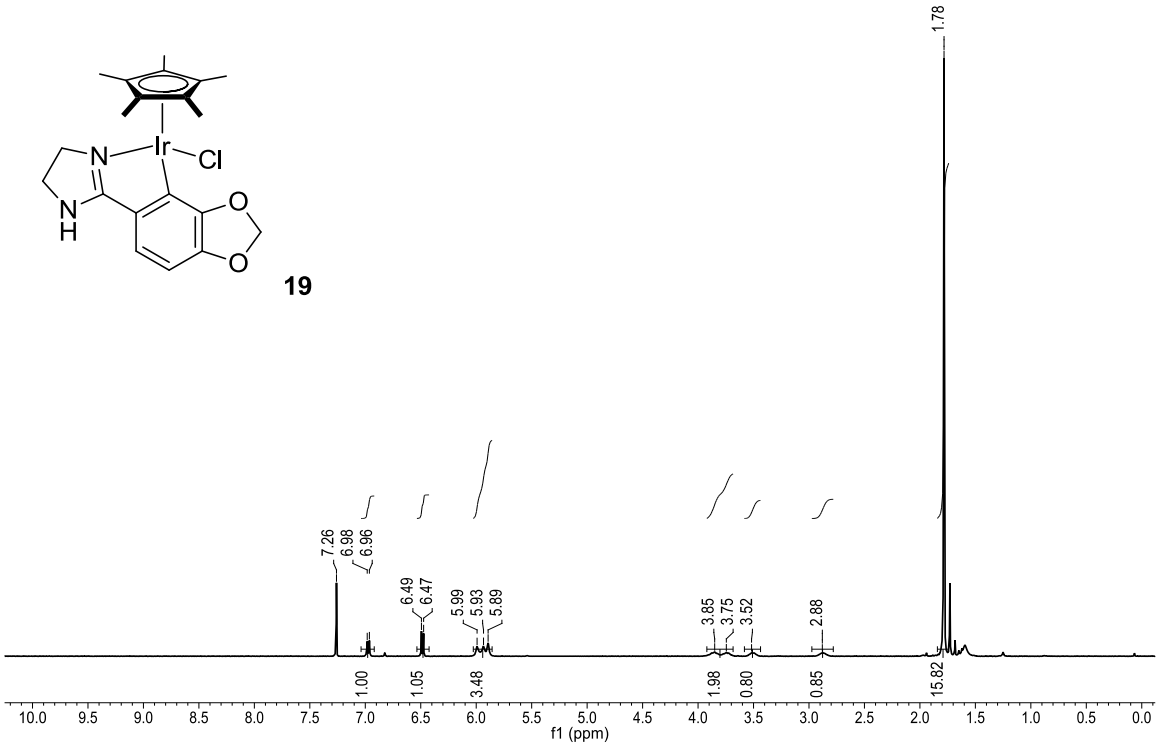
$^{19}F\{^{13}C\}$ NMR (376 MHz, $CDCl_3$) spectrum of **17**·***n*-hexane**.



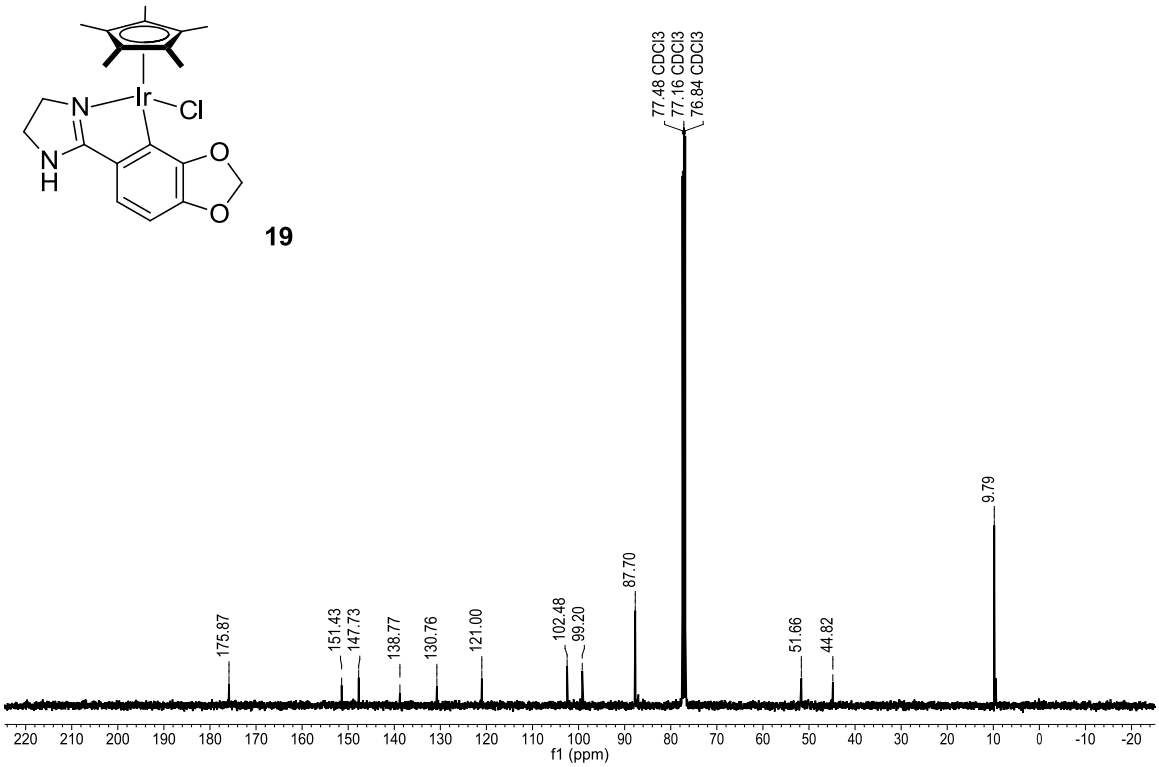
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Ir18**.



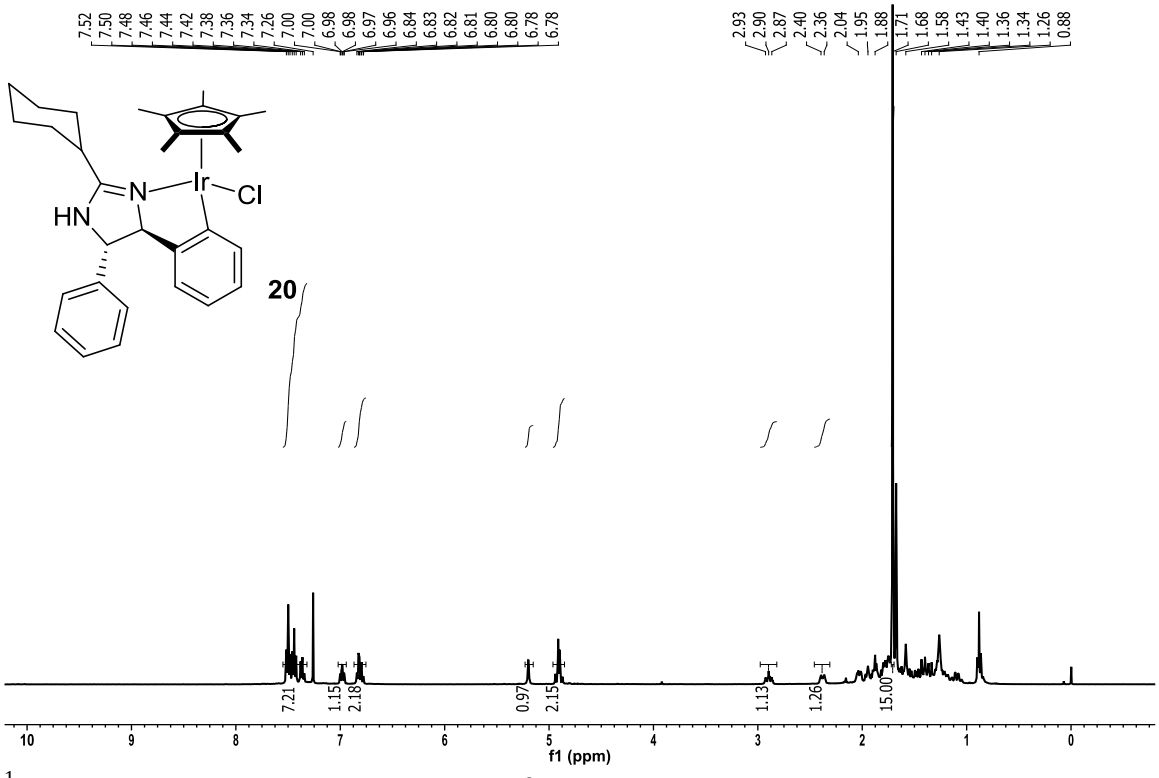
$^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$) spectrum of **18**.



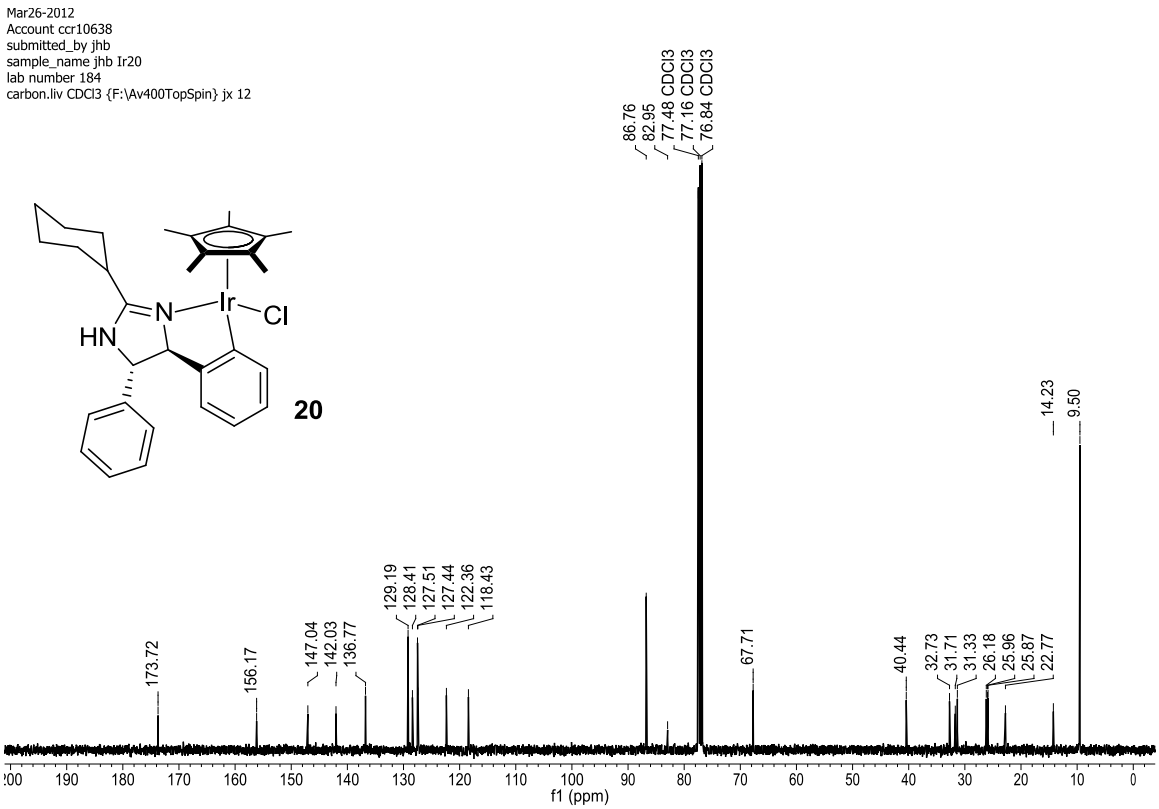
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**.



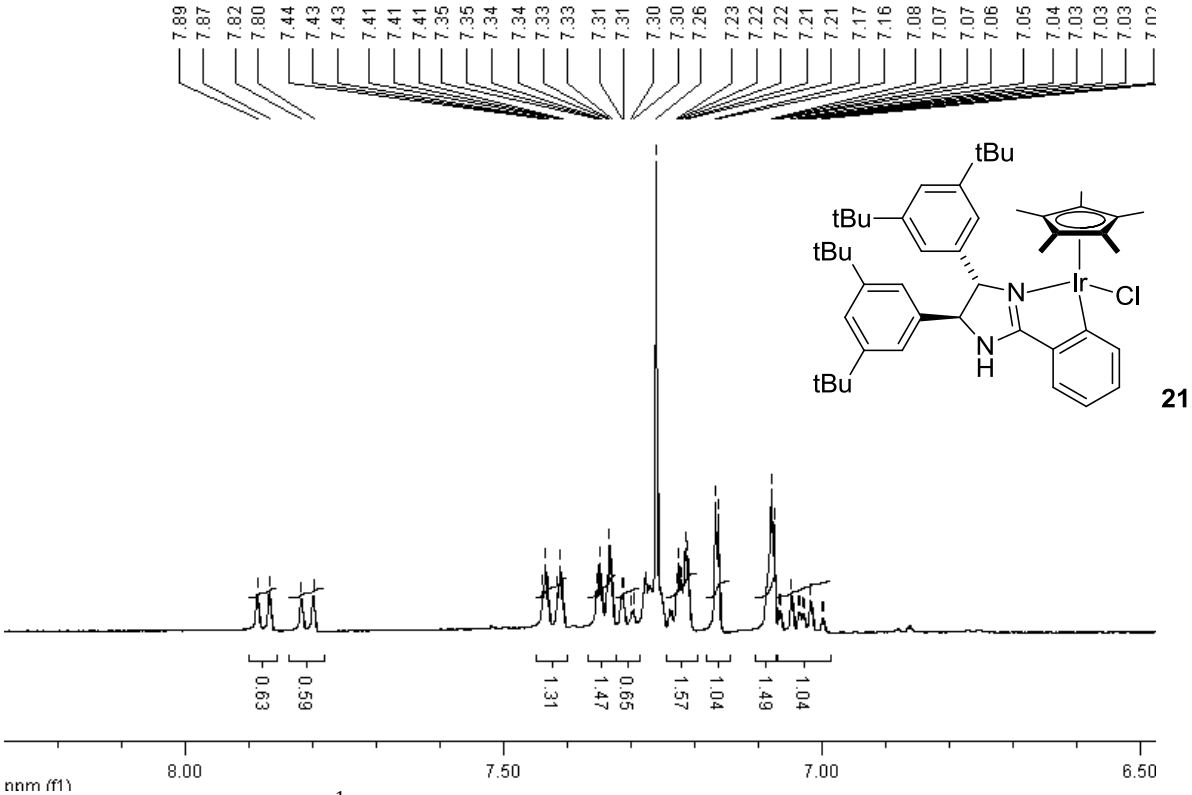
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **19**.



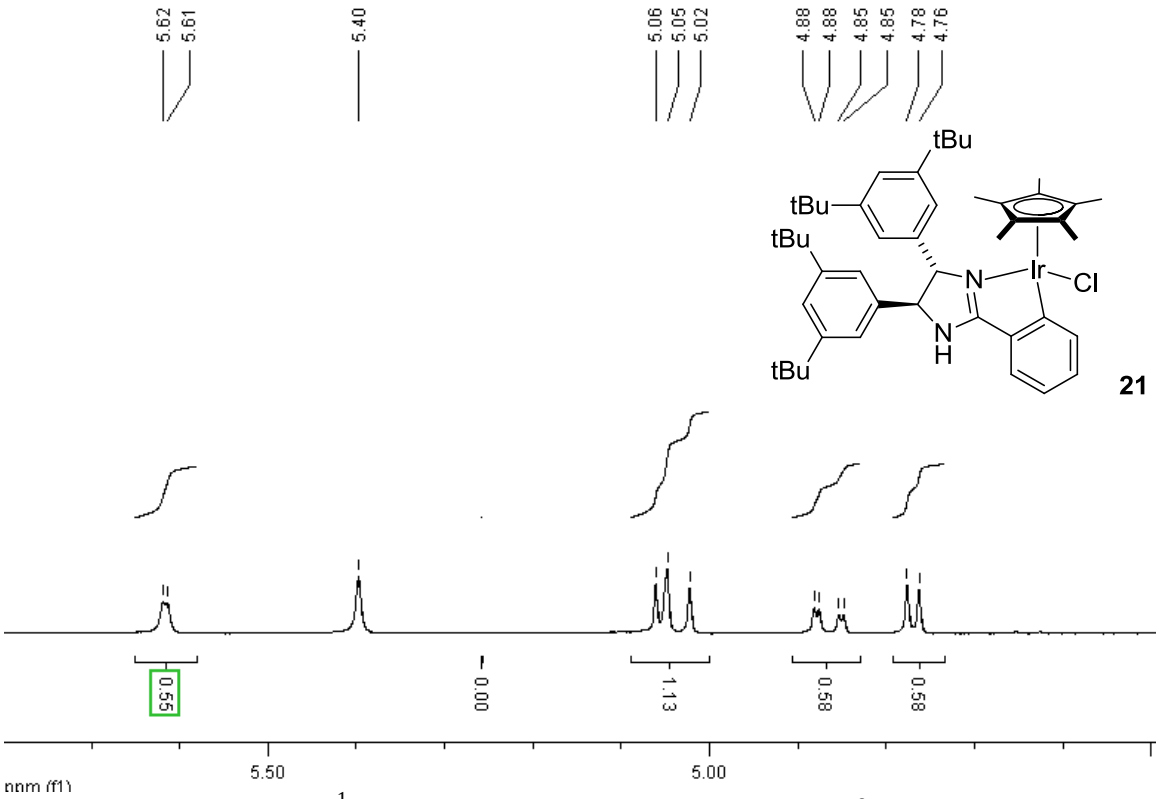
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **20**.



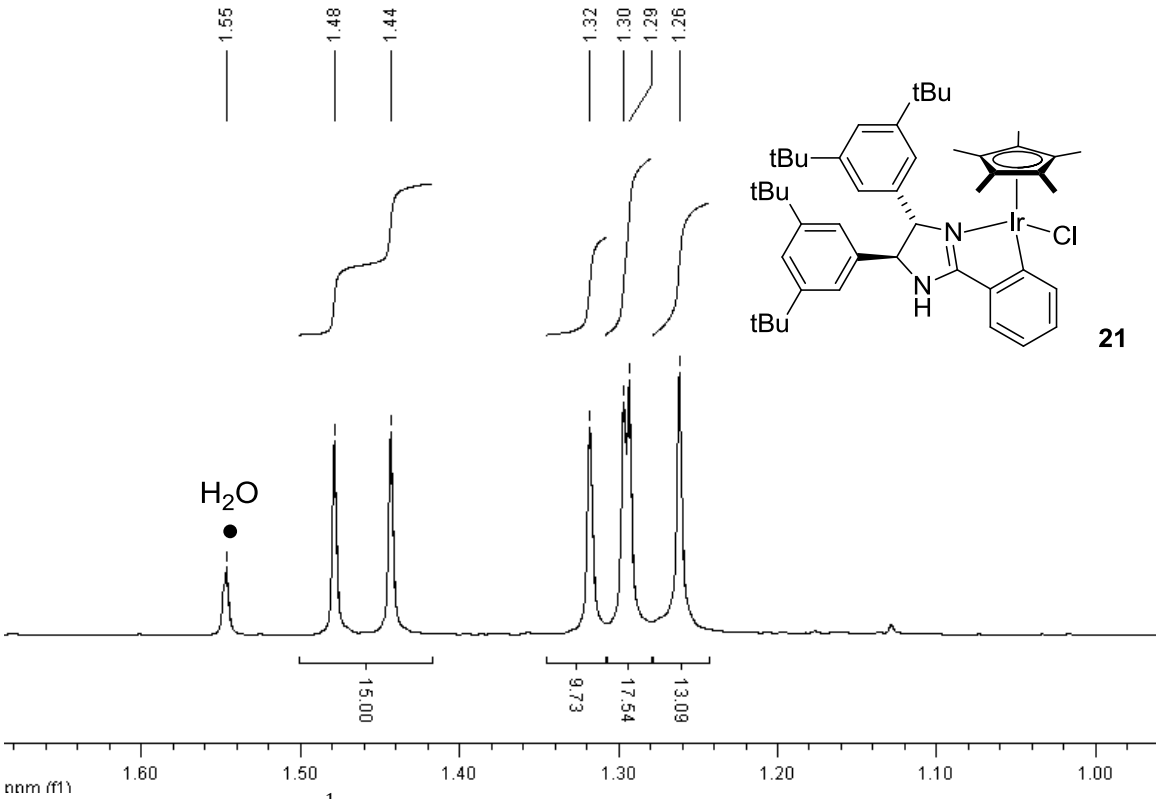
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **20**.



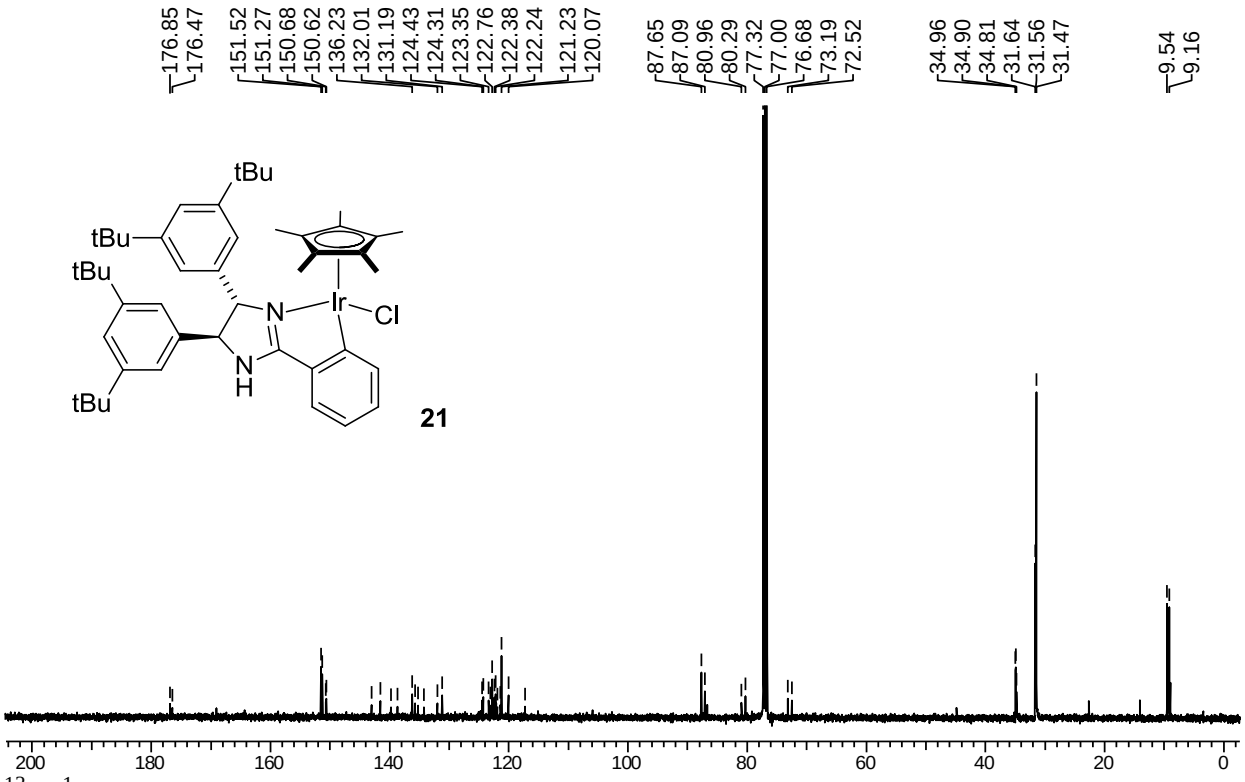
Partial (aromatic region) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **21**.



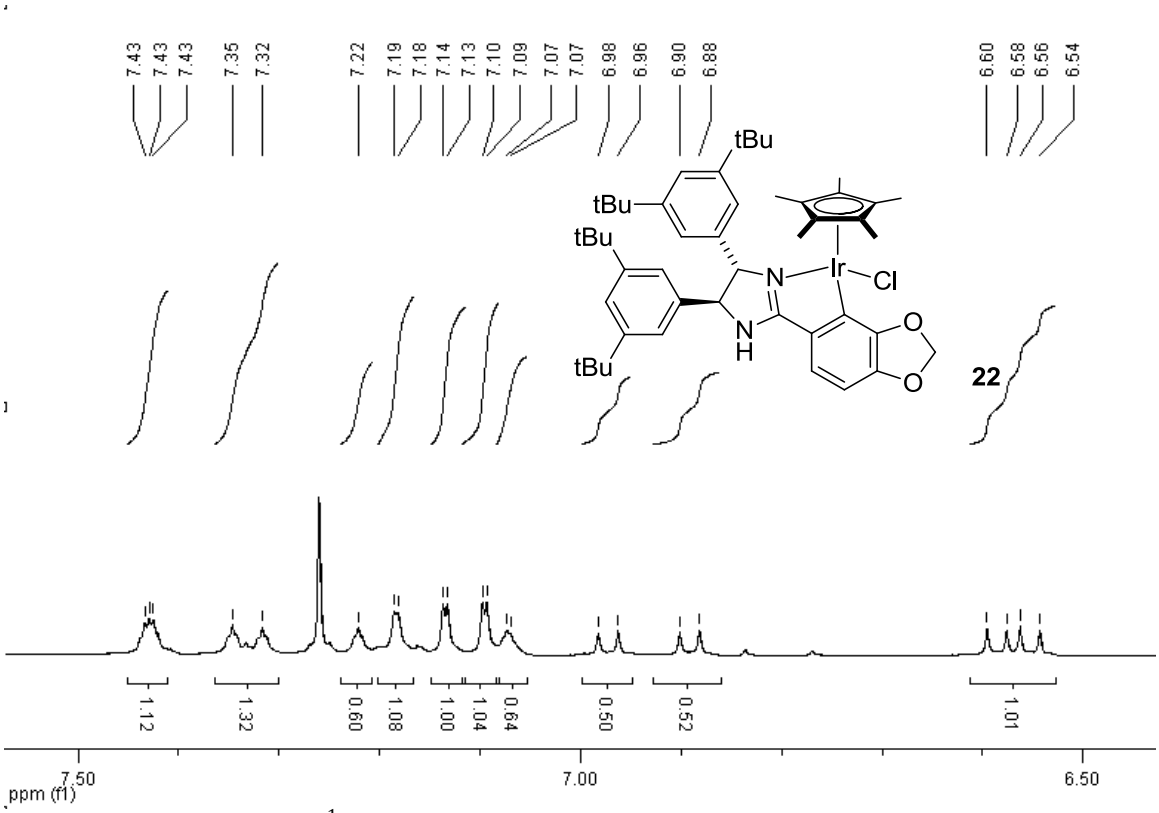
Partial (6.00 - 4.00 ppm) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Ir21**.



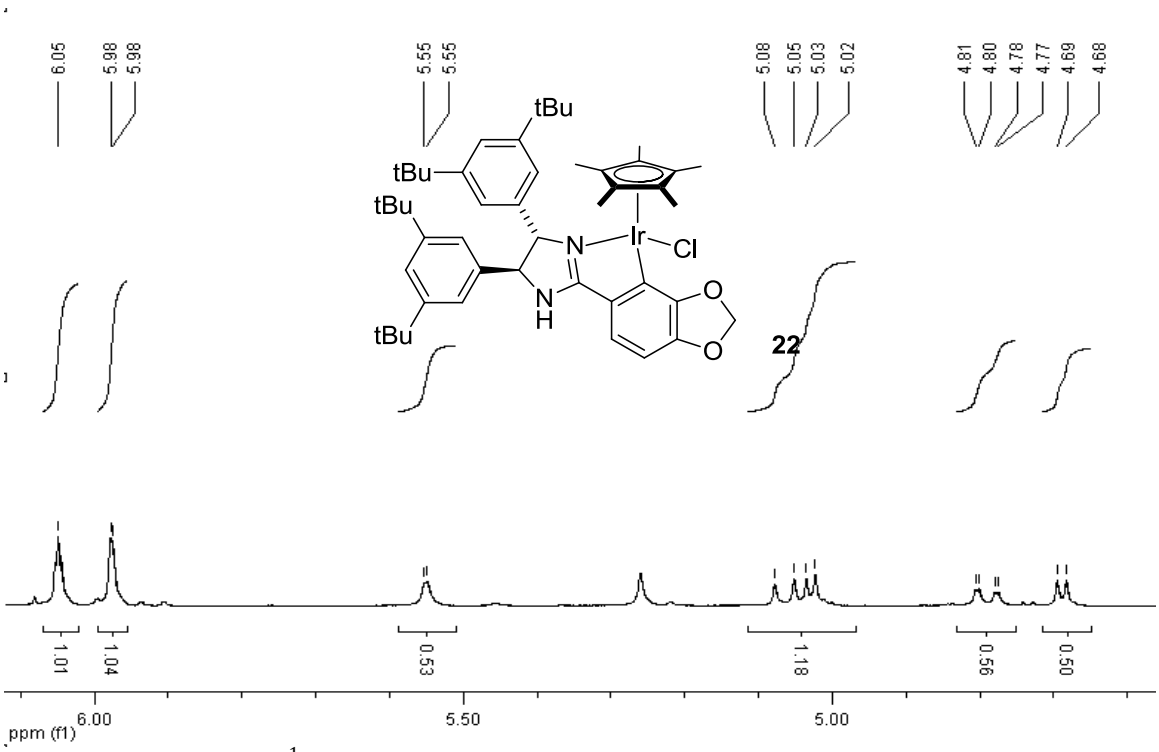
Partial (aliphatic region) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **21**.



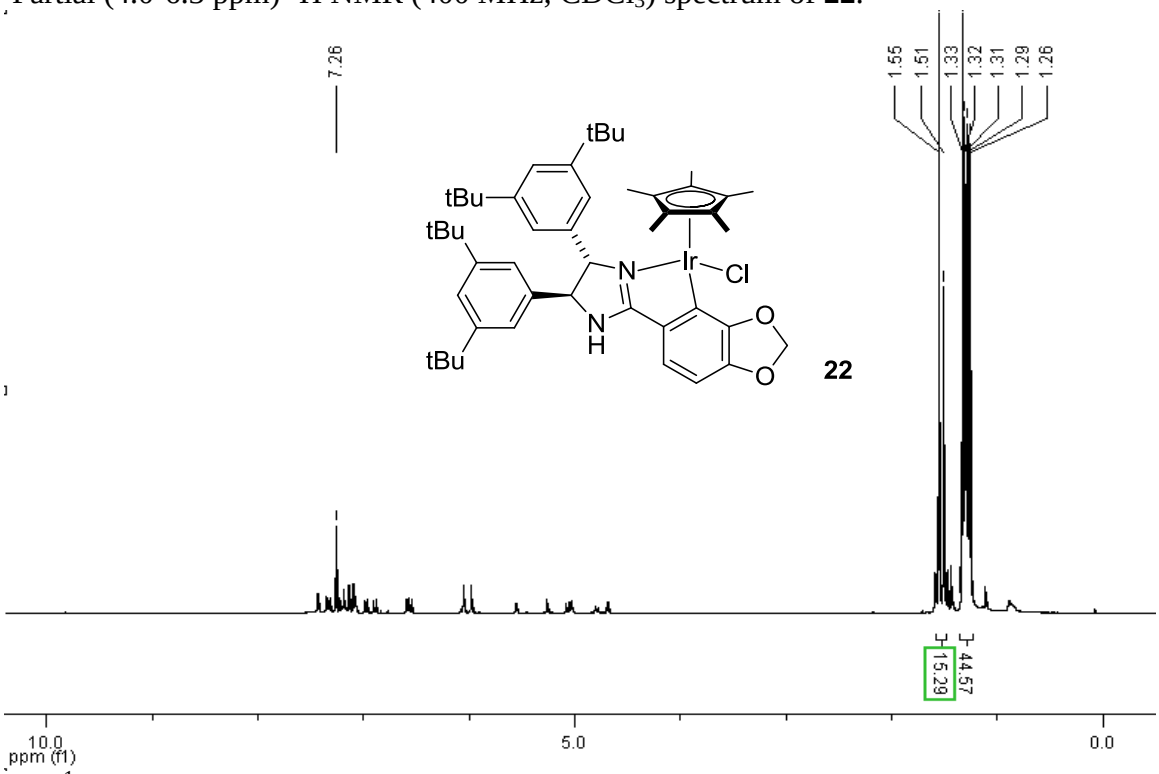
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **21**.



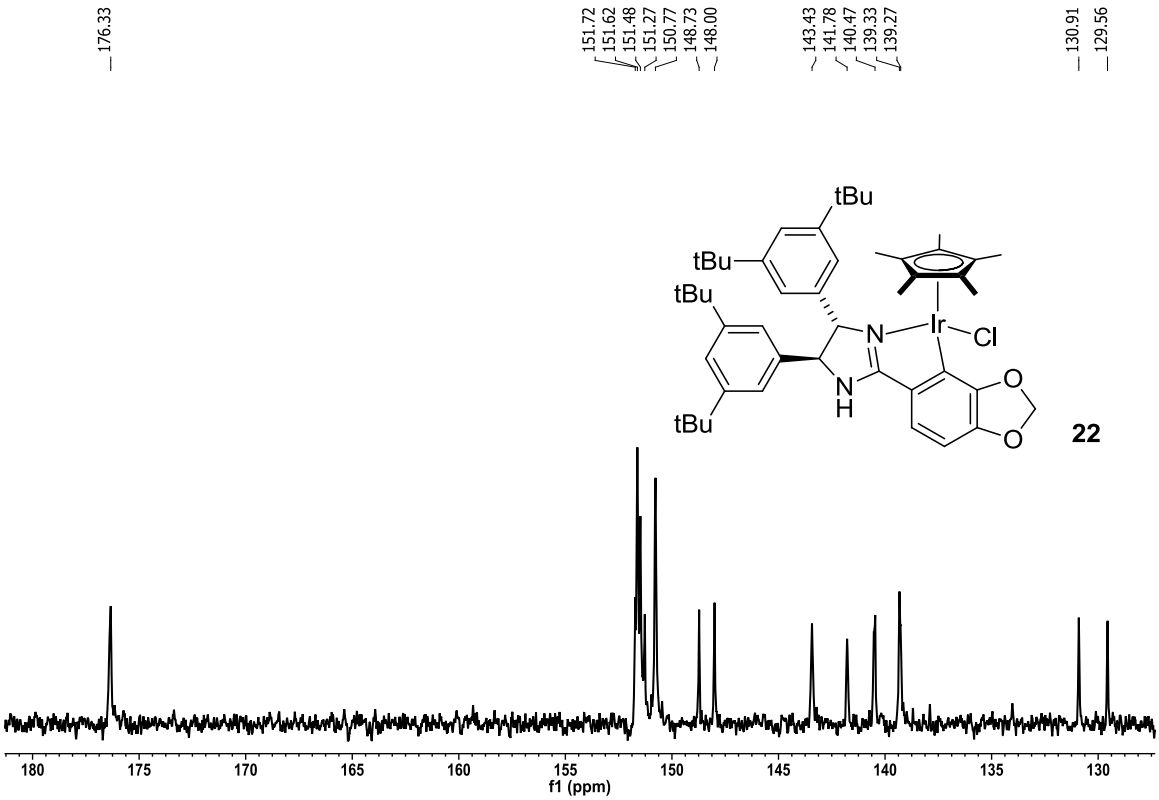
Partial (aromatic region) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **22**.



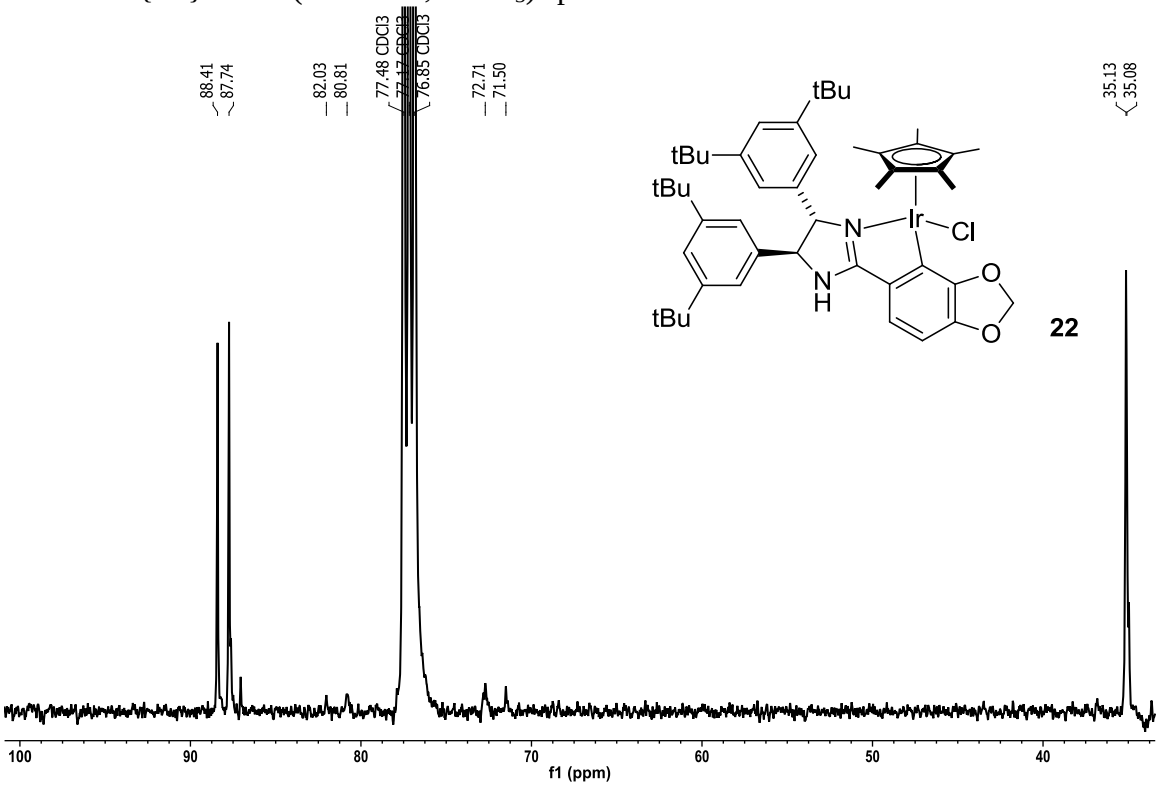
Partial (4.0-6.3 ppm) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **22**.



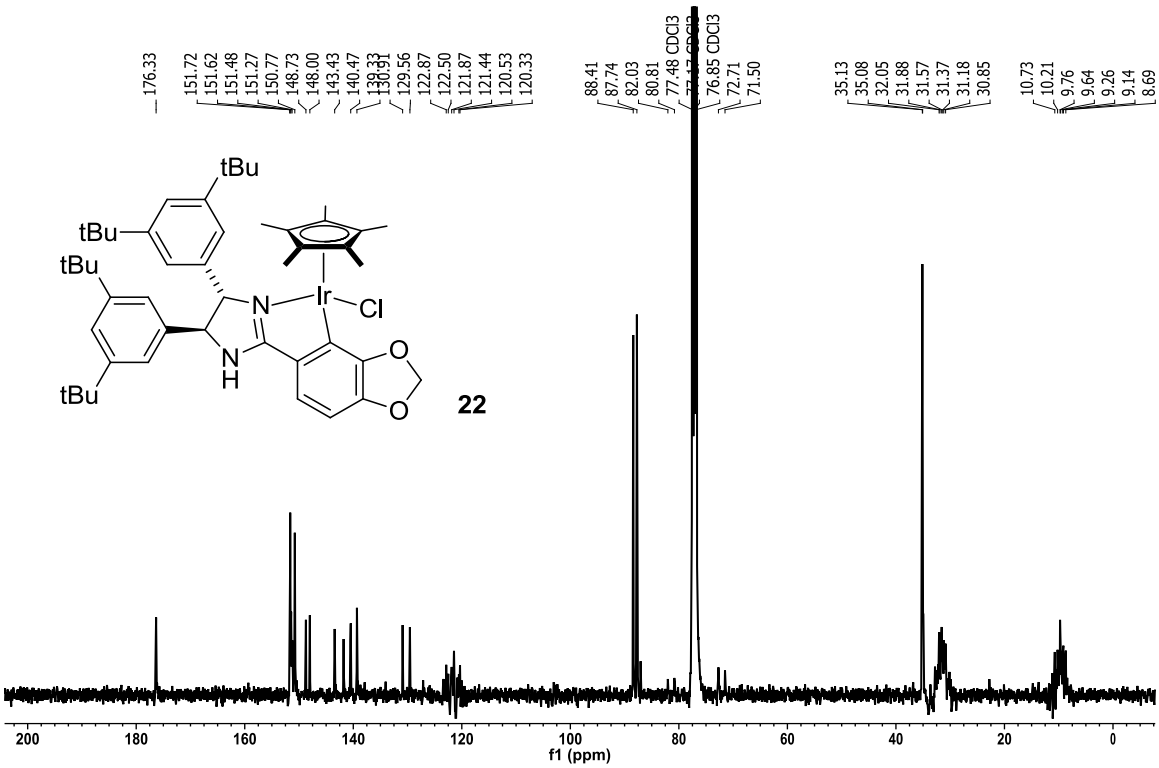
Full ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **22**.



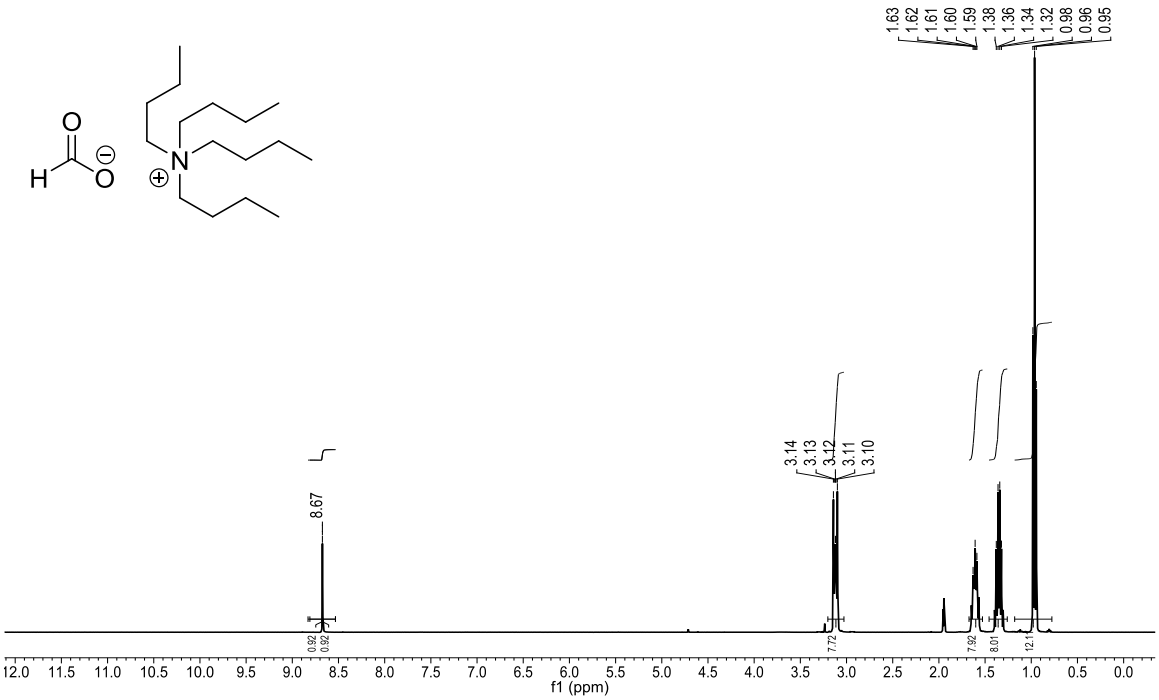
Partial $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **22**.



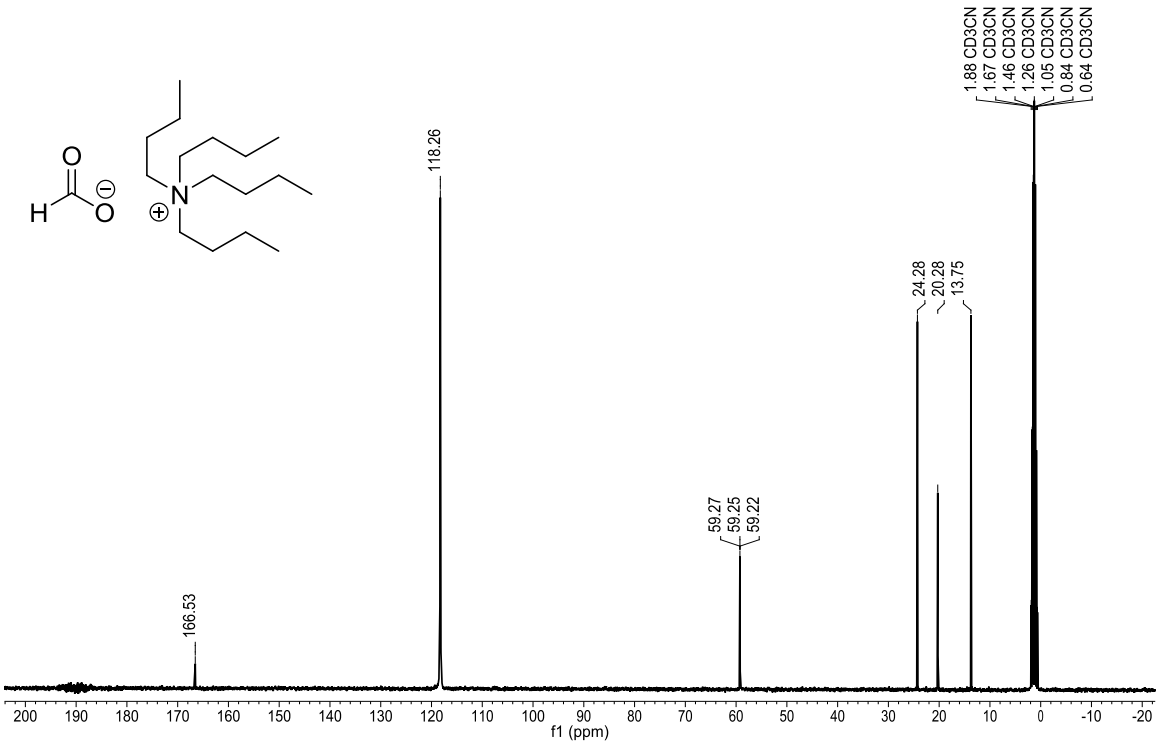
Partial $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **22**.



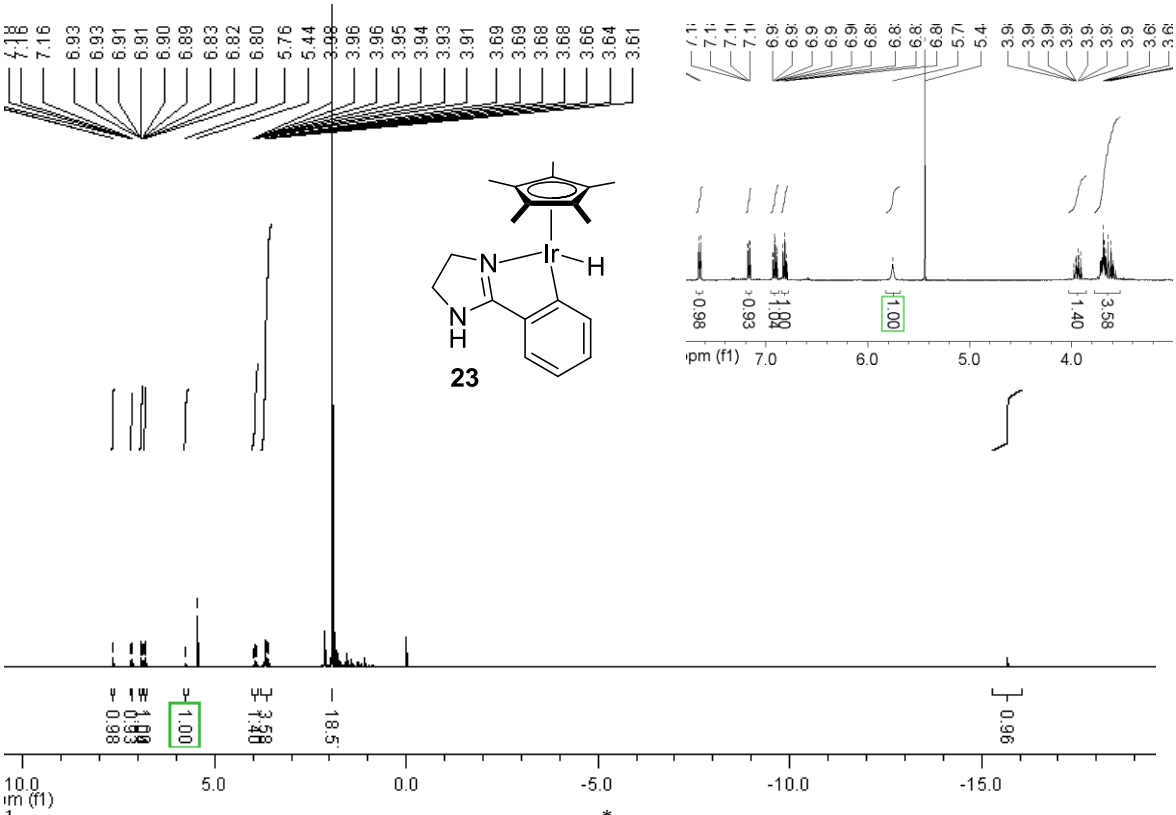
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **22**.



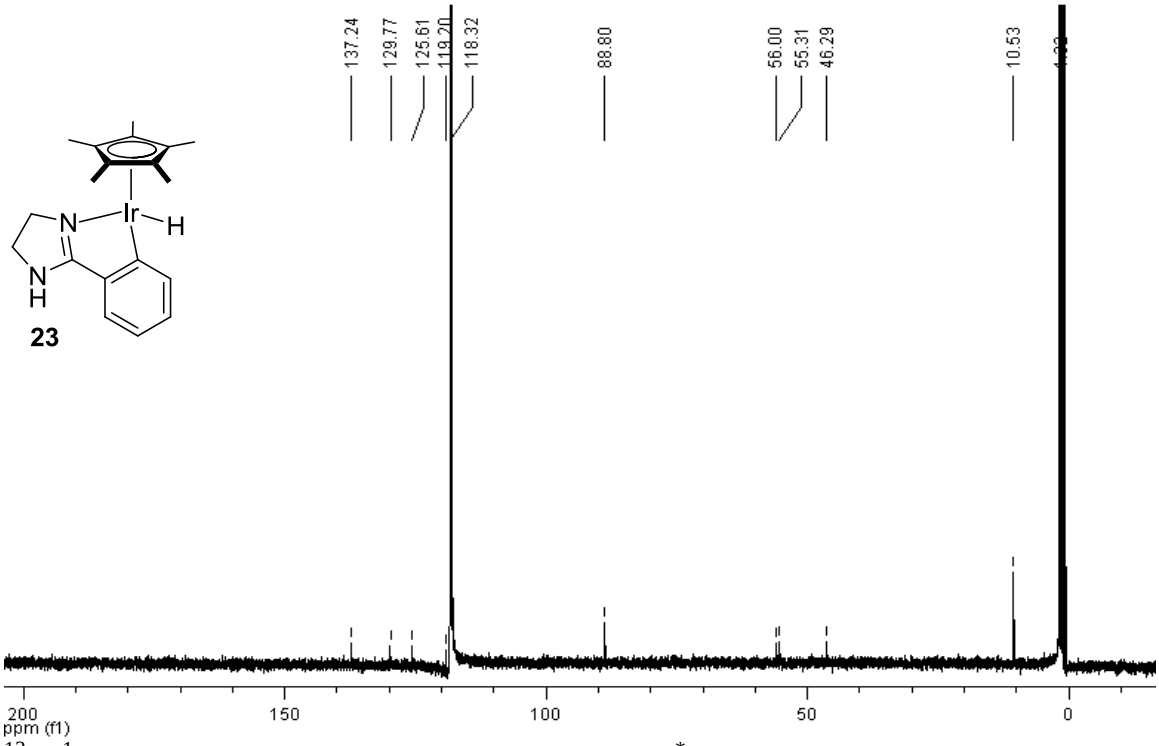
^{1}H NMR (400 MHz, CD_3CN) spectrum of tetra-*n*-butylammonium formate.



$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) spectrum of tetra-*n*-butylammonium formate.



^{1}H NMR (400 MHz, CD_3CN) spectrum of [Cp^*IrH(2-phenylimidazoline)] **23**.

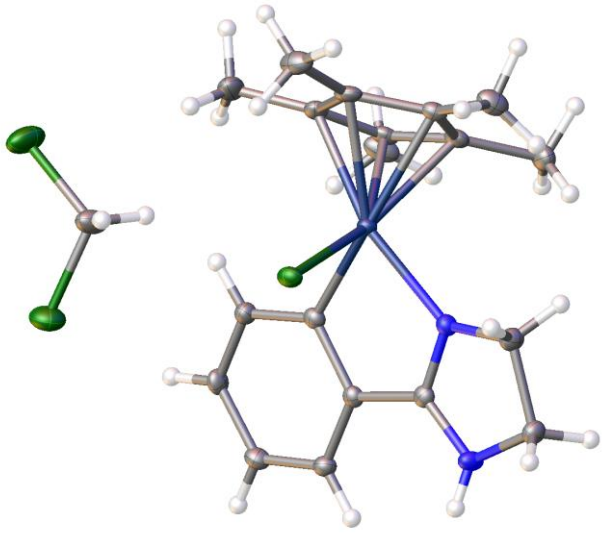


23

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) spectrum of [Cp^*IrH(2-phenylimidazoline)] **23**

5. Crystallographic data of Rh1 and 22

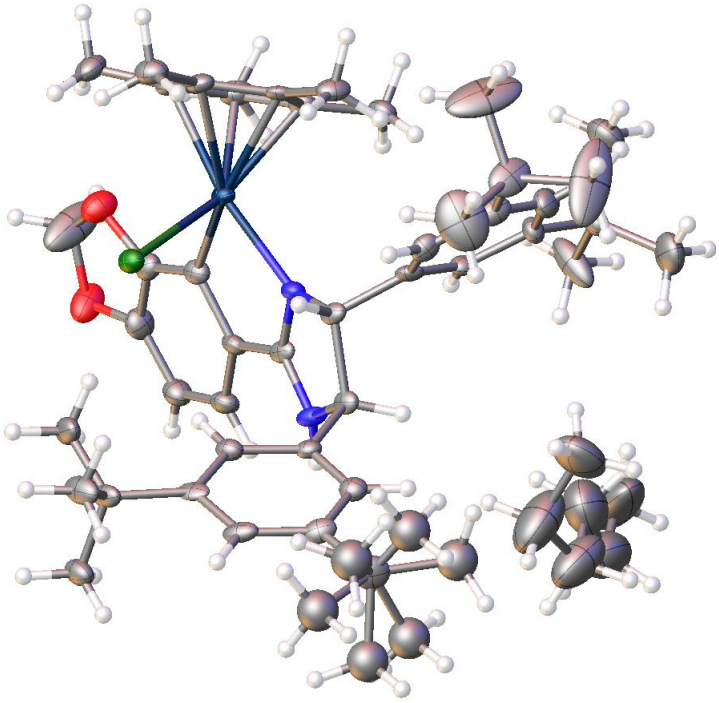
Complex Rh1[S21]



Formula	$C_{19}H_{24}ClN_2Rh{\cdot}CH_2Cl_2$
Space group	P-1
Cell Lengths	**a** 10.4990(5) **b** 10.5404(5) **c** 11.0455(6)
Cell angles	**α** 63.9860(10) **β** 85.7870(10) **γ** 69.8840(10)
Cell volume	1027.14
Z, Z’	Z: 2 Z': 0
R factor	2.41

CCDC 889583 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*.

Complex 22[S21]



Formula	$C_{54}H_{78}ClIrN_2O_2 \cdot$ *n*-hexane
Space group	$P2_12_12$
Cell Lengths	**a** 25.5236(14) **b** 13.7422(8) **c** 14.3634(8)
Cell angles	**α** 90.00 **β** 90.00 **γ** 90.00
Cell volume	5037.97
Z, Z’	Z: 4 Z': 0
R factor	3.95

CCDC 889584 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*.

6. References

[S1] C. Scheeren, F. Maasarani, A. Hijazi, J. Djukic, M. Pfeffer, *Organometallics* 2007, **26**, 3336.

[S2] C. Wang, A. Pettman, J. Basca, J. Xiao, *Angew. Chem. Int. Ed.* 2010, **49**, 7548.

[S3] P. J. C. Hausoul, A. N. Parvulescu, M. Lutz, A. L. Spek, P. C. A. Bruijnincx, B. M. Weckhuysen, R. J. M. K. Gebbink, *Angew. Chem., Int. Ed.* 2010, **49**, 7972.

[S4] F. Santoro, M. Althaus, C. Bonaccorsi, S. Gischig, A. Mezzetti, *Organometallics* 2008, **27**, 3866–3878.

[S5] M. Ishihara, H. Togo, *Synlett.* 2006, **2**, 227.

[S6] S. F. Hojati, I. Mohammadpoor-Baltork, B. Maleki, M. Gholizadeh, F. Shafiezadeh, M. Haghdoust, *Can. J. Chem* 2010, **88**, 135.

[S7] A. Salerno, I. A. Perillo, *Molecules* 2005, **10**, 435.

[S8] H. Fujioka, K. Murai, O. Kubo, Y. Ohba, Y. Kita, *Tetrahedron* 2007, **63**, 638.

[S9] B. George, E. P. Papadopoulos, *J. Org. Chem.* 1977, **42**, 441.

[S10] V. G. Nenajdenko, V. M. Muzalevskiy, A. V. Shastin, E. S. Balenkova, E. V. Kondrashov, I. A. Ushakov, A. Yu. Rulev, *J. Org. Chem.* 1977, **42**, 441.

[S11] M. Ishihara, H. Togo *Tetrahedron* 2006, **63**, 1474.

[S12] M. Sun, H.-T. Wei, D. Li, Y.-G. Zheng, J. Cai, M. Ji, *Synth. Commun.* 2008, **38**, 3151.

[S13] M. Ishihara, H. Togo, *Synthesis*, 2007, **13**, 1939.

[S14] W. J. Houlihan, L. Kelly, J. Pankuch, J. Koletar, L. Brand, A. Janowsky, T. A. Kopajtic, *J. Med. Chem.* 2002, **45**, 4097.

[S15] D. L. Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S. T. Hilton, D. R. Russell, *Dalton Trans.* 2003, 4132.

[S16] M. B. Thathagar, J. Beckers, G. Rothenberg, *J. Am. Chem. Soc.* 2002, **124**, 11858.

[S17] R. Tanaka, M. Yamashita, L. W. Chung, K. Morokuma, K. Nozaki, *Organometallics* 2011, **30**, 6742.

[S18] http://www.webqc.org/van_der_waals_gas_law.html

[S19] For the use of FT-IR in the detection of CO in 1:1 H_2/CO_2 mixtures, see the supporting information of C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem., Int. Ed.* 2008, **47**, 3966.

[S20] Hydrogen bonding to the imidazoline NH resulted in the disappearance of the resonance at ~5.8 ppm in the ^{1}H NMR spectra. For an example of the observation of hydrogen bonding between and *N*-heterocylic H-bond donor moiety (indolic NH) and basic anions (fluoride) by ^{1}H NMR spectroscopy see, Q. Li, Y. Guo, S. Shao, *Analyst* 2012, **137**, 4497.

[S21] Molecular structure images were created using OLEX2, O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K.; Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program *J. Appl. Cryst.* 2009, **42**, 339.