Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

for

Iridium(III) Homo- and Heterogeneous Catalysed Hydrogen Borrowing C-N Bond Formation

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SI-1 General Considerations

Unless otherwise stated, all manipulations were carried out under inert atmosphere using standard Schlenk or vacuum techniques[1] or in a nitrogen or argon-filled Braun glovebox. All reagents were purchased from Aldrich Chemical Company Inc. or Alfa Aesar Inc. and used as received unless otherwise noted. Glassy carbon electrodes (1 x 1 x 0.1 cm^3) were purchased from Goodfellow. Carbon black (XC-72R) was supplied by Cabot Corporation. $IrCl_3 \cdot xH_2O$ were purchased from Precious Metals Online PMO P/L. For the purposes of air sensitive manipulations and in the preparation of air sensitive metal complexes, dichloromethane, acetonitrile, diethyl ether and pentane were dispensed from a PuraSolv solvent purification system. Anhydrous methanol and hexane were used as received from Chem Supply. Bulk compressed gas argon (>99.999%) was obtained from Air Liquide and used as received. Nitrogen gas for Schlenk line operation was sourced from in-house liquid nitrogen boil-off. $[IrCp^*Cl]_2$,[2] 1-azidobenzene,[3] 1-azido-4-nitrobenzene,[3] 1-azido-4-trifluromethylbenzene,[3] 1-azido-3-triflouromethylbenzene,[3] 1-azido-4-methylbenzene,[3] 1-mesityl-1*H*-imidazole,[4] 1-mesityl-3-(prop-2-yn-1-yl)-1*H*-imidazol-3-ium bromide,[5, 6] 1-mesityl-3-((1-phenyl-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-imidazol-3-ium bromide (**1a**),[5] 1-mesityl-3-((1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-imidazol-3-ium bromide (**1b**),[7] 1-mesityl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide (**1c**), 1-mesityl-3-((1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-imidazol-3-ium bromide (**1d**), 1-mesityl-3-((1-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-imidazol-3-ium bromide (**1e**) and 3-((1-(4-aminophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1-mesityl-1*H*-imidazol-3-ium bromide (**1f**),[7] deuterated benzyl alcohol substrates[8, 9] were synthesised using literature procedures.

^1H, ^2H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance III series spectrometers operating at 300, 400, 500 or 600 MHz (^1H), 92 MHz (^2H), 75, 100, 125 or 150 MHz (^{13}C) respectively. ^1H and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. ^2H NMR chemical shifts were referenced externally to ^2H-toluene. Unless otherwise stated, spectra were recorded at 298 K and chemical shifts (δ), with uncertainties ± 0.01 Hz for ^1H and ^2H, ± 0.05 Hz for ^{13}C ^{15}N, are quoted in parts per million, ppm. Coupling constants (J) are quoted in Hz and have uncertainties of ± 0.05 Hz for ^1H-^1H, ^1H-^{15}N, ^1H-^{19}F and ^1H-^2H ± 0.5 Hz for ^{13}C-^{11}B and ^{13}C-^{19}F. Deuterated solvents were purchased from Cambridge Stable Isotopes or Sigma Aldrich and used as received. Air sensitive NMR samples were prepared in an inert gas glovebox or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Youngs' teflon valve. For air sensitive NMR samples, CD_2Cl_2 and $CDCl_3$ were distilled over calcium hydride.

Microanalyses were carried out at the Campbell Micro-analytical Laboratory, University of Otago, New Zealand or at the Research School of Chemistry, The Australian National University, Canberra, Australia or at the Chemical Analysis Facility, Department of Chemistry and Biomolecular Sciences, Macquarie University, Sydney, Australia.

Mass spectra were acquired using a Thermo Ion Trap LC-MS located in the School of Chemistry, UNSW or Thermo LTQ Orbitrap XL located in the Bioanalytical Mass Spectrometry Facility (BMSF), UNSW. M is defined as the molecular weight of the compound of interest or cationic fragment for cationic metal complexes.

Surface analyses of modified surfaces by X-ray photoelectron spectroscopy were performed by Dr Vinicius Gonçales. XPS using an EscaLab 250 Xi (Thermo Scientific) spectrometer with a monochromated Al Kα source. The measurements were recorded at a pressure of below 10^{-8} mbar in the analysis chamber and a take-off angle normal to the sample surface. The pass energy and the step size for the survey scan was 100 and 1.0 eV respectively, and 20 and 0.1 eV respectively, when monitoring narrow scans. Spectral analysis was performed using the Avantage 4.73 software, the background spectra were considered as Shirley type and curve fitting was carried out using a mixture of Gaussian–Lorentzian functions.

Thermogravimetric analysis was conducted using a Perkin Elmer Thermogravimetric Analyser Q5000 V3.15 instrument. The temperature scan was ramped from 20-100 °C with a scan rate of 20 °C min^{-1} and then kept at isothermal 100 °C for 10 minutes. The temperature was ramped again from 100-800 °C for carbon black samples with a scan rate of 10 °C min^{-1}. The TGA analysis for all samples were analysed in a nitrogen atmosphere with the gas flow rate of 40 mL per minute.

The Ir content in the immobilised catalyst was determined using Inductively Coupled Plasma (ICP-OES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with a PerkinElmer NexIon 300D instrument. The catalyst sample was digested in a mixture of refluxing H_2SO_4 and HNO_3 following a literature procedure.[10]

SI-2 Additional figures referenced in paper

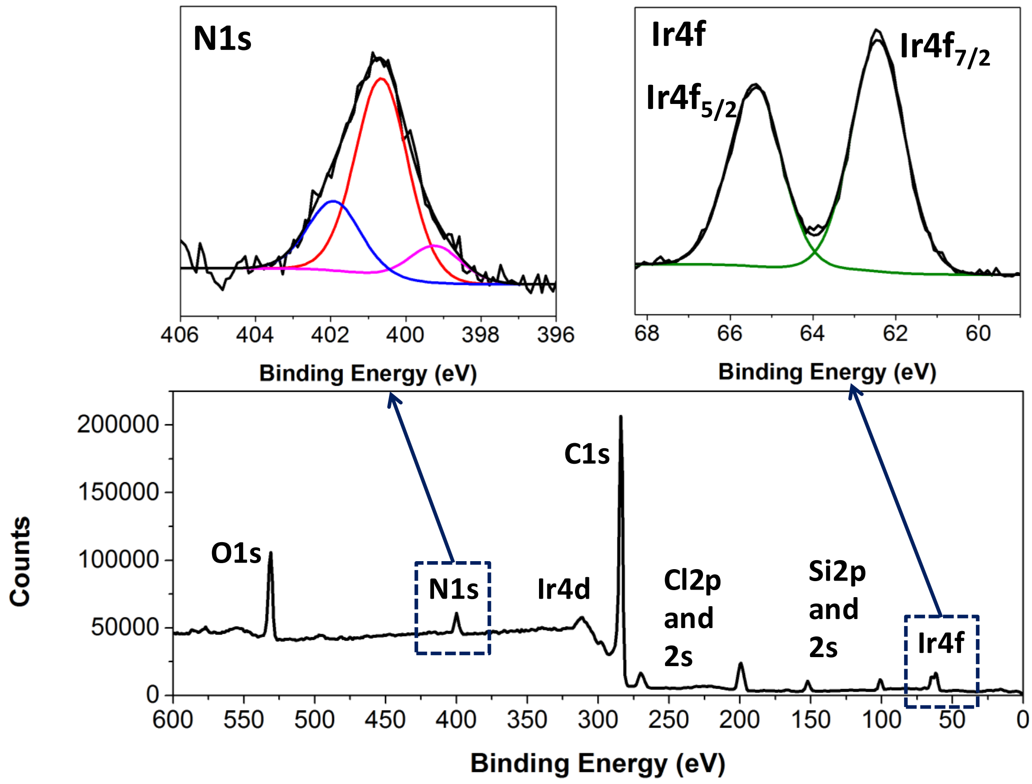


Figure S1 Survey scan and selected narrow scan of N1s and Ir4f for **2-GC**.

Table S1 Selected binding energies of N1s and Ir4f$_{7/2}$ as well as the atomic ratio of N:Ir for hybrid complexes **2-GC** and **2-CB**.

Hybrid Catalyst	Binding Energy (eV)				Atomic Ratio N:Ir
	N1s			Ir4f$_{7/2}$	
	N1s A	N1s B	N1s C		
2-GC	401.9	400.6	399.2	62.43	5.6:1
2-CB	402.9	401.7	400.6	63.04	5.0:1

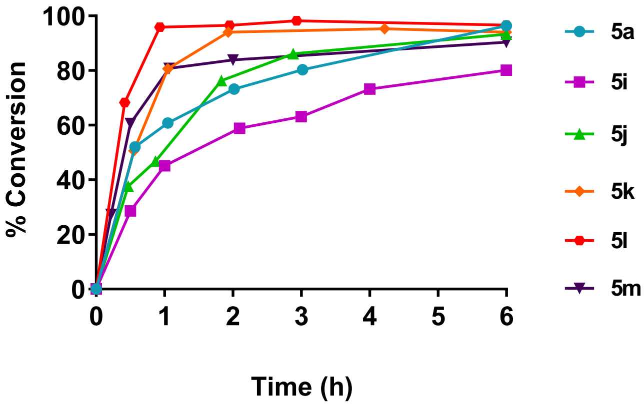
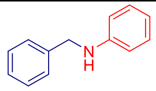
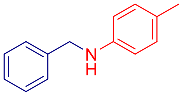
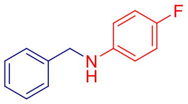
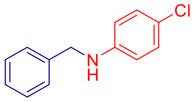
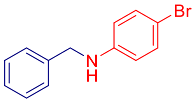
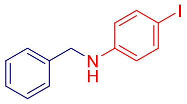


Figure S2 Reaction time courses when using catalyst **2d** to react benzyl alcohol (**3**) with a series of aniline substituted substrates (**4**, **4i-m**) to give products **5a** and **5i-m**.

Table S2 Summary of key results for the Ir(III) complex **2d** (0.5 mol%) catalysed reaction of benzyl alcohol (**3**) with various aniline substrates (**4**, **4i-m**) in the presence of KO^{t}Bu, toluene-d_8 at 100 °C to give products **5a** and **5i-m**.

Entry	**Product**	**% Conv.**[a]		**TOF (h^{-1})**[b]
		0.5 h	**1.0 h**	
1	 **5a**	52	61	176.5
2	 **5i**	29	45	58.8
3	 **5j**	38	47	115.4
4	 **5k**	51	81	181.8
5	 **5l**	68	96	327.9
6	 **5m**	61	81	242.4

[a] Determined using ^{1}H NMR spectroscopy; [b] TOF = turnover frequency at 50% conversion = (amount of substrate at 50% conversion (mol))/(amount of catalyst used (mol) x time at 50% conversion (h))

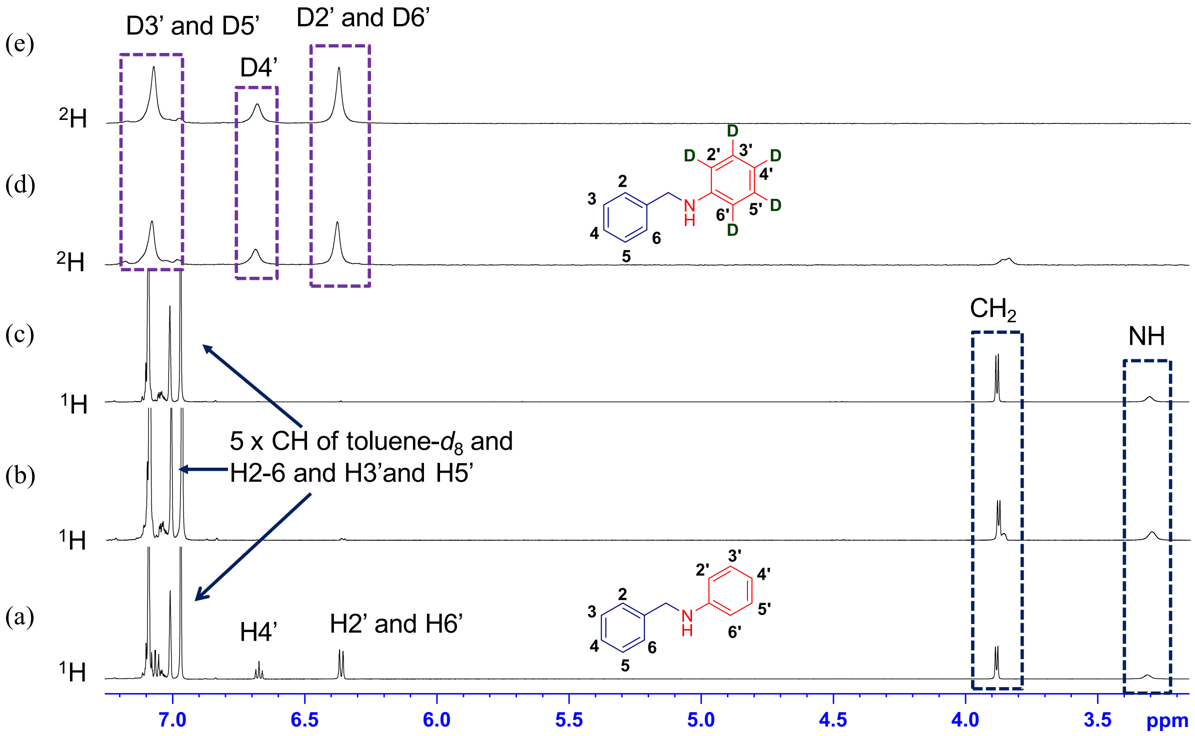


Figure S3 ^{1}H (600 MHz, toluene-d_8, 298K) and ^{2}H (92.1 MHz, toluene, 298K) NMR spectra. (a) ^{1}H NMR spectra of *N*-benzylaniline (**5a**); (b) ^{1}H NMR spectra of product from reaction of benzyl alcohol (**3**) with aniline-d_5 (**4-*d*$_5$**) (c) ^{1}H NMR spectra of product from reaction of benzyl alcohol (**3**) with aniline-d_7 (**4-*d*$_7$**); (d) ^{2}H NMR spectra of product from reaction of benzyl alcohol (**3**) with aniline-d_5 **4-*d*$_5$**; (e) ^{2}H NMR spectra of product from reaction of benzyl alcohol (**3**) with aniline-d_7 (**4-*d*$_7$**).

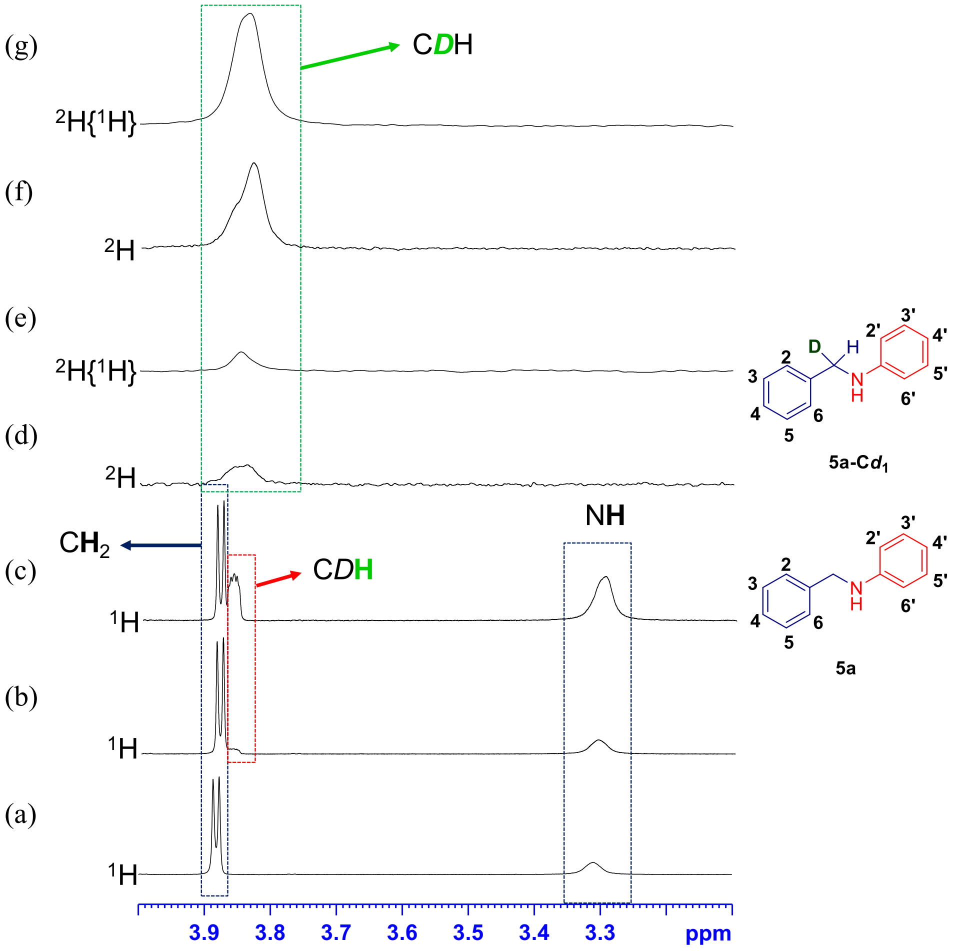


Figure S4 Selected benzylic CH$_2$ and OH region of ^{1}H (600 MHz, toluene-d_8, 298K), ^{2}H (92.1 MHz, toluene, 298K), ^{2}H{^{1}H} (92.1 MHz, toluene, 298K) NMR spectra. (a) ^{1}H NMR spectrum of *N*-benzylaniline (**5a**); (b) ^{1}H NMR spectrum of products from reaction of benzyl alcohol-OD (**3-O*d*$_1$**) with aniline (**4**); (c) ^{1}H NMR spectrum of products from reaction of benzyl alcohol-d_2 (**3-C*d*$_2$**) with aniline (**4**); (d) ^{2}H NMR spectrum of products from reaction of benzyl alcohol-OD (**3-O*d*$_1$**) with aniline (**4**); (e) ^{2}H NMR spectrum of products from reaction of benzyl alcohol-d_2 (**3-C*d*$_2$**) with aniline (**4**); (f) ^{2}H{^{1}H} NMR spectrum of products from reaction of benzyl alcohol-O*D* (**3-O*d*$_1$**) with aniline (**4**); (g) ^{2}H{^{1}H} NMR spectrum of products from reaction of benzyl alcohol-d_2 (**3-C*d*$_2$)** with aniline (**4**).

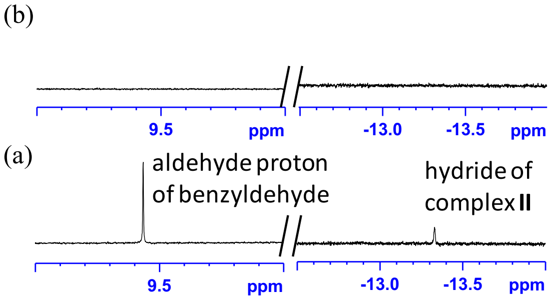
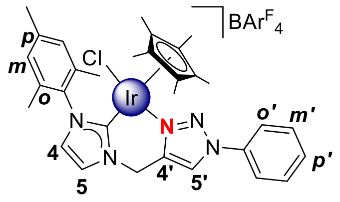


Figure S5 Selected region of ^{1}H (600 MHz, toluene-d_8, 298K) of (a) ^{1}H NMR spectrum of the reaction between Ir(III) complex **2d** and benzyl alcohol-OD (**3-O*d*$_1$**) and (b) ^{1}H NMR spectrum of the reaction between Ir(III) complex **2d** and benzyl alcohol-d_2 (**3-C*d*$_2$**).

SI-3 Synthesis of Ir(III) complexes

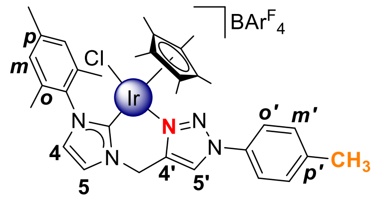
SI-3.1 Synthesis of Ir complex 2a



Ligand **1a** (74.7 mg, 0.176 mmol) was dissolved partially in acetone (20 mL). Ag_2O (44.3 mg, 0.191 mmol) was added to the suspension prior to heating the reaction mixture at reflux under argon for one hour. After cooling the reaction mixture, $[IrCp^*Cl_2]_2$ (70.1 mg, 88.0 µmol) was added. The mixture was heated at reflux for another one hour and then left to stir at room temperature overnight. The green mixture was filtered through celite, which was washed thoroughly with excess acetone to give a clear yellow solution. The solvent was removed *in vacuo* to give a yellow-orange solid. The crude product was dissolved in dichloromethane (15 mL) and $NaBAr^F_4$ (156 mg, 0.176 mmol) was added to the reaction mixture. After stirring for five minutes, the yellow solution turned slightly brown in colour and some white precipitate forms. The reaction mixture was stirred at room temperature under argon for 30 minutes. The mixture was filtered through celite®, which was washed thoroughly with excess dichloromethane to give a clear yellow solution. The solvent was concentrated *in vacuo* to *ca.* 2 mL and pentane (25 mL) was added. Yellow precipitate forms in solution with vigorous stirring. The precipitate was dried *in vacuo* to yield the product as a yellow solid. (173 mg, 0.110 mmol, 66%). **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 9.01 (s, 1H, Tz-**H**5'), 7.96 (m, 2H, *m'*-C**H** of Ph), 7.88 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**5), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (m, 7H, *o'*- and *p'*-C**H** of Ph overlapped with *p*-C**H** of BAr^F_4), 7.34 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**4), 7.05 (s, 1H, *m*-C**H** of Mes), 6.96 (s, 1H, *m*-C**H** of Mes), 5.97 (d, $^2J_{H\text{-}H}$ = 16.0 Hz, 1H, C**H**$_2$), 5.31 (d, $^2J_{H\text{-}H}$ = 16.0 Hz, 1H, C**H**$_2$), 2.33 (s, 3H, *p*-C**H**$_3$), 2.21 (s, 3H, *o*-C**H**$_3$), 2.06 (s, 3H, *o*-C**H**$_3$), 1.59 (s, 15H, C**H**$_3$ of Cp*) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $(CD_3)_2CO$): δ 162.6 (q, $^1J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C** to B of BAr^F_4), 153.7 (Im-**C**2), 142.7 (C$_q$, Tz-**C**4'), 139.9 (*o*-**C**CH$_3$ of Mes), 139.4 (*p*-**C**CH$_3$ of Mes), 137.3 (*ipso*-**C**$_q$ of Ph), 136.4 (*ipso*-**C**$_q$ of Mes), 136.0 (*o*-**C**CH3 of Mes),135.5 (br s, *o*-**C**H to B of BAr^F_4), 131.2 (*p'*-**C**H of Ph), 131.0 (*o'*-**C**H of Ph), 130.1 (*m*-CH of Mes overlapped with **C**CF$_3$ of BAr^F_4), 130.0 (q, $^2J_{F\text{-}C}$ = 32.8 Hz, **C**CF$_3$ of BAr^F_4 overlapped with *m*-**C**H of Mes), 128.7 (*m*-**C**H of Mes), 126.6 (Im-**C**4), 125.4 (q, $^1J_{F\text{-}C}$ = 272.5 Hz, **C**F$_3$ of BAr^F_4), 124.5 (Im-**C**5), 123.2 (Tz-**C**5'), 121.9 (*m'*-**C**H of Ph), 118.4 (br s, *p*-**C**H to B of BAr^F_4), 92.3 (**C**$_q$ of Cp*), 46.1 (**C**H$_2$), 21.0 (*p*-**C**H$_3$ of Mes), 20.5 (*o*-**C**H$_3$ of Mes), 19.4 (*o*-**C**H$_3$ of Mes), 9.51 (**C**H$_3$ of Cp*) ppm. **HRMS** (ESI$^+$, MeOH) : *m/z* (%): 706.2275 (100 %) $[M\text{-}BAr^F_4]^+$ (Calculated $[M\text{-}BAr^F_4]^+$ =

706.2288) amu. **Elemental Analysis**: Found C, 48.48; H, 3.02 and N, 4.52; Calculated for $C_{63}H_{48}BClF_{24}IrN_5$: C, 48.21; H, 3.08 and N, 4.46 %.

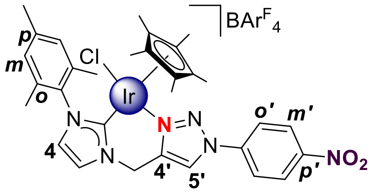
SI-3.2 Synthesis of Ir complex 2c



Ligand **1c** (76.1 mg, 0.174 mmol) was dissolved in dichloromethane (20 mL). Ag_2O (31.8 mg, 0.137 mmol) was added and the mixture was stirred at room temperature for one hour. $[IrCp^*Cl_2]_2$ (69.6 mg, 87.4 µmol) was then added and the mixture left to stir at room temperature overnight. The cloudy yellow mixture was filtered through celite, which was washed thoroughly with excess dichloromethane to give a clear yellow solution. The solvent was removed *in vacuo* to give a yellow solid. The crude product was dissolved in dichloromethane (15 mL) and NaBAr$^F{}_4$ (154 mg, 0.174 mmol) was added to the reaction mixture. After stirring for five minutes, the yellow solution turned slightly yellow-brown in colour and some white precipitate forms. The reaction mixture was stirred at room temperature under argon for one hour. The mixture was filtered through celite, which was washed thoroughly with excess dichloromethane to give a clear yellow solution. The solvent was concentrated *in vacuo* to *ca.* 2 mL and pentane (25 mL) was added. Yellow precipitate forms in solution with vigorous stirring. The precipitate was dried *in vacuo* to yield the product as a bright yellow solid. (154 mg, 0.097 mmol, 56%). **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 8.96 (s, Tz-**H**5'), 7.88 (d, $^3J_{H4\text{-}H5}$ = 1.4 Hz, 1H, Im-**H**5), 7.83 (d, $^3J_{Ho\text{-}Hm}$ = 8.4 Hz, 2H, *o'*-C**H** of Ar-CH_3), 7.80 (br s, 8H, *o*-C**H** of BAr$^F{}_4$), 7.68 (s, 4H, *p*-C**H** of BAr$^F{}_4$), 7.50 (d, $^3J_{Ho\text{-}Hm}$ = 8.2 Hz, 2H, *m'*-C**H** of Ar-CH_3), 7.34 (d, $^3J_{H4\text{-}H5}$ = 1.6 Hz, 1H, Im-**H**4), 7.05 (s, 1H, *m*-C**H** of Mes), 6.96 (s, 1H, *m*-C**H** of Mes), 5.96 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_2$), 5.30 (d, $^2J_{H\text{-}H}$ = 16.2 Hz, 1H, C**H**$_2$), 2.45 (s, 3H, *p*'-C**H**$_3$ of Ar-CH_3), 2.33 (s, 3H, *p*-C**H**$_3$ of Mes), 2.21(s, 3H, *o*-C**H**$_3$ of Mes), 2.07 (s, 3H, *o*-C**H**$_3$ of Mes), 1.59 (s, 15H, C**H**$_3$ of Cp*) ppm. **^{13}C{^{1}H} NMR** (150 MHz, $(CD_3)_2CO$): δ 162.6 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-**C** to B of BAr$^F{}_4$), 153.8 (Im-**C**2), 142.6 (C_q, Tz-**C**4'), 141.6 (*p'*-**C**CH$_3$ of Ar-CH_3), 139.9 (*p*-**C**CH$_3$ of Mes), 139.4 (*m*-**C**CH$_3$ of Mes), 136.4 (*ipso*-**C**$_q$ of Mes), 136.0 (*o*-**C**CH$_3$ of Mes), 135.6 (br s, *o*-**C**H to B of BAr$^F{}_4$), 135.1 (*ipso*-**C**$_q$ of Ar-CH_3), 131.4 (*m'*-**C**H of Ar-CH_3), 130.2 (*m*-**C**H of Mes), 130.0 (q, $^2J_{F\text{-}C}$ = 31.3 Hz, **C**CF$_3$ of BAr$^F{}_4$), 128.8 (*m*-**C**H of Mes), 126.6 (Im-**C**4), 125.4 (q, $^1J_{F\text{-}C}$ = 271.8 Hz, **C**F$_3$ of BAr$^F{}_4$), 124.5 (Im-**C**5), 123.1 (Tz-**C**5'), 121.7 (*o'*-**C**H of Ar-CH_3), 118.5 (br s, *p*-**C**H to B of BAr$^F{}_4$), 92.3 (**C**$_q$ of Cp*), 46.2 (**C**H$_2$), 21.1 (*p*'-**C**H$_3$ of Ar-CH_3), 21.0 (*p*-**C**H$_3$ of Mes), 20.5 (*o*-**C**H$_3$ of Mes), 19.4 (*o*-**C**H$_3$ of Mes), 9.51 (**C**H$_3$ of Cp*) ppm. **HRMS** (ESI$^+$, MeOH): *m/z* (%): (100 %) $[M\text{-}BAr^F{}_4]^+$ = $[C_{32}H_{38}ClIrN_5]^+$ = 720.2434

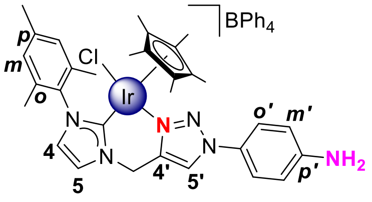
(Calculated $[M\text{-}BAr^F{}_4]^+$ = 720.2439) amu. **Elemental Analysis**: Found C, 48.07; H, 3.16 and N, 4.16 Calculated for $C_{64}H_{50}BClF_{24}IrN_5$: C, 48.54; H, 3.18 and N, 4.42%.

SI-3.3 Synthesis of Ir complex 2b



Complex **2b** was synthesised following the same procedure used to synthesise complex **2c** with ligand **1b** (80.5 mg, 0.172 mmol), Ag_2O (40.0 mg, 0.173 mmol) and $[IrCp^*Cl_2]_2$ (68.7 mg, 86.2 µmol) in dichloromethane (20 mL). Following work-up, a red solid crude product was dissolved in dichloromethane (15 mL) and $NaBAr^F{}_4$ (154 mg, 0.173 mmol) was added to the reaction mixture. After another work-up, the product **2b** was formed as a light red-brown solid. (171 mg, 0.106 mmol, 62%). **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 9.25 (Tz-**H**5'), 8.56 (d, $^3J_{Ho\text{-}Hm}$ = 9.0 Hz, *m'*-**CH** of Ar-NO_2), 8.31 (d, $^3J_{Ho\text{-}Hm}$ = 9.0 Hz, *o'*-**CH** of Ar-NO_2), 7.89 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, Im-**H**5), 7.79 (br s, 8H, *o*-**CH** of $BAr^F{}_4$), 7.67 (s, 4H, *p*-**CH** of $BAr^F{}_4$), 7.36 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, Im-**H**4), 7.05 (s, 1H, *m*-**CH** of Mes), 6.96 (s, 1H, *m*-**CH** of Mes), 6.02 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, $\mathbf{CH_2}$), 5.34 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, $\mathbf{CH_2}$), 2.34 (s, 3H, *p*-$\mathbf{CH_3}$ of Mes), 2.21 (s, 3H, *o*-$\mathbf{CH_3}$ of Mes), 2.06 (s, 3H, *o*-$\mathbf{CH_3}$ of Mes), 1.60 (s, 15H, $\mathbf{CH_3}$ of Cp*) ppm. **^{13}C{^{1}H} NMR** (150 MHz, $(CD_3)_2CO$): δ 162.6 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-**C** to B of $BAr^F{}_4$), 153.8 (Im-**C**2), 149.3 (*ipso*-$\mathbf{C_q}$ of Ar-NO_2), 143.3 (C_q, Tz-**C**4'), 141.3 (C_q, *p'*-**C**NO_2 of Ar-NO_2), 140.0 (*p*-**C**CH_3 of Mes), 139.4 (*o*-**C**CH_3 of Mes), 136.4 (*ipso*-$\mathbf{C_q}$ of Mes), 136.0 (*o*-**C**CH_3 of Mes), 135.5 (br s, *o*-**CH** to B of $BAr^F{}_4$), 130.1 (*m*-**C**H of Mes), 130.0 (q, $^2J_{F\text{-}C}$ = 31.4 Hz, **C**CF_3 of $BAr^F{}_4$), 128.8 (*m*-**C**H of Mes), 126.7 (Im-**C**4), 126.5 (*m'*-**C**H of Ar-NO_2), 125.4 (q, $^1J_{F\text{-}C}$ = 271.5 Hz, $\mathbf{C}F_3$ of $BAr^F{}_4$), 124.5 (Im-**C**5), 123.8 (Tz-**C**5'), 122.7 (*o'*-**C**H of Ar-NO_2), 118.4 (br s, *p*-**C**H to B of $BAr^F{}_4$), 92.5 ($\mathbf{C_q}$ of Cp*), 46.1 ($\mathbf{C}H_2$), 21.0 (*p*-**C**H_3 of Mes), 20.5 (*o*-**C**H_3 of Mes), 19.4 (*o*-**C**H_3 of Mes), 9.51 (**C**H_3 of Cp*) ppm. **HRMS** (ESI^+, MeOH) : *m/z* (%): (100 %) $[M\text{-}BAr^F{}_4]^+$ = $[C_{31}H_{35}ClIrN_6O_2]^+$ = 751.2133 (Calculated $[M\text{-}BAr^F{}_4]^+$ = 751.2134) amu. **Elemental Analysis**: Found C, 46.69; H, 2.80 and N, 4.85 %; Calculated for $C_{63}H_{47}BClF_{24}IrN_6O_2$: C, 46.87; H, 2.93 and N, 5.21%.

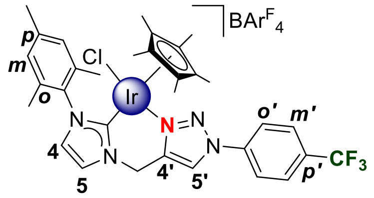
SI-3.4 Synthesis of Ir complex 2f



Complex **2f** was synthesised following the same procedure used to synthesise complex **2a** with ligand **1f** (92.9 mg, 0.211 mmol), Ag_2O (41.9 mg, 0.181 mmol) and $[IrCp^*Cl_2]_2$ (84.4

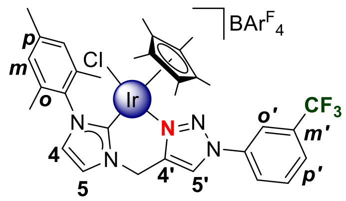
mg, 0.106 mmol) in acetone (20 mL). Following work-up, the orange-brown crude solid product was dissolved in dichloromethane (15 mL) and $NaBPh_4$ (73.5 mg, 0.215 mmol) was added to the reaction mixture. After another work-up, the product **2f** was formed as a light brown solid. (140 mg, 0.135 mmol, 63%). **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 8.64 (s, 1H, Tz-**H**5'), 7.81 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**5), 7.55 (d, $^3J_{Ho\text{-}Hm}$ = 8.7 Hz, 2H, *o'*-C**H** of Ar-NH_2), 7.34 (br s, 8H, *o*-C**H** of BPh_4), 7.30 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, 1H, Im-**H**4), 7.04 (s, 1H, *m*-C**H** of Mes), 6.95 (s, 1H, *m*-C**H** of Mes), 6.92 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.56 (d, $^3J_{Ho\text{-}Hm}$ = 8.7 Hz, 2H, *m'*-C**H** of Ar-NH_2), 6.77 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of BPh_4), 5.83 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_2$), 5.30 (s, 2H, *p*'-N**H**$_2$ of Ar-NH_2), 5.22 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_2$), 2.33 (s, 3H, *p*-C**H**$_3$ of Mes), 2.19 (s, 3H, *o*-C**H**$_3$ of Mes), 2.06 (s, 3H, *o*-C**H**$_3$ of Mes), 1.56 (s, 15H, C**H**$_3$ of Cp*) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $(CD_3)_2CO$): δ 165.0 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-**C** to B of BPh_4), 153.7 (Im-**C**2), 151.1 (*p'*-**C**NH_2 of Ar-NH_2), 142.0 (C_q, Tz-**C**4'), 139.8 (*p*-**C**CH_3 of Mes), 139.4 (*o*-**C**CH_3 of Mes), 137.0 (br s, *o*-**C**H to B of BPh_4), 136.5 (*ipso*-**C**$_q$ of Mes), 136.0 (*o*-**C**CH_3 of Mes), 130.1 (*m*-**C**H of Mes), 128.7 (*m*-**C**H of Mes), 126.9 (*ipso*-**C**$_q$ of Ar-NH_2), 126.5 (Im-**C**4), 126.0 (q, $^4J_{B\text{-}C}$ = 2.80 Hz, *m*-**C**H to B of BPh_4), 124.4 (Im-**C**5), 123.2 (*o'*-**C**H of Ar-NH_2), 122.5 (Tz-**C**5'), 122.2 (*p*-**C**H of BPh_4), 115.0 (*m'*-**C**H of Ar-NH_2), 92.2 (**C**$_q$ of Cp*), 46.1 (**C**H_2), 21.0 (*p*-**C**H_3 of Mes), 20.5 (*o*-**C**H_3 of Mes), 19.4 (*o*-**C**H_3 of Mes), 9.52 (**C**H_3 of Cp*) ppm. **HRMS** (ESI^+, MeOH) : *m/z* (%): (100 %) $[M\text{-}BAr^F{}_4]^+$ = $[C_{31}H_{37}ClIrN_6]^+$ = 721.2397 (Calculated $[M\text{-}BAr^F{}_4]^+$ = 721.2397) amu. **Elemental Analysis**: Found C, 61.36; H, 5.68 and N, 7.94 %; Calculated for $C_{55}H_{57}BClIrN_6.0.5CH_2Cl_2$: C, 61.55; H, 5.40and N, 7.76%.

SI-3.5 Synthesis of Ir complex 2d



Complex **2d** was synthesised following the same procedure used to synthesise complex **2b** with ligand **1d** (86.8 mg, 0.176 mmol), Ag_2O (30.7 mg, 0.132 mmol) and $[IrCp^*Cl_2]_2$ (70.5 mg, 88.5 µmol) in dichloromethane (20 mL). Following work-up, a crude yellow solid product was dissolved in dichloromethane (15 mL) and $NaBAr^F{}_4$ (157 mg, 0.177 mmol) was added to the reaction mixture. After another work-up, the product **2d** was formed as a yellow-brown solid. (191 mg, 0.117 mmol, 66%). **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 9.18 (Tz-**H**5'), 8.24 (d, $^3J_{Ho\text{-}Hm}$ = 8.6 Hz, *o'*-C**H** of Ar-CF_3), 8.07 (d, $^3J_{Ho\text{-}Hm}$ = 8.6 Hz, *m'*-C**H** of Ar-CF_3), 7.89 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, Im-**H**5), 7.79 (br s, 8H, *o*-C**H** of $BAr^F{}_4$), 7.67 (s, 4H, *p*-C**H** of $BAr^F{}_4$), 7.35 (d, $^3J_{H4\text{-}H5}$ = 2.0 Hz, Im-**H**4), 7.05 (s, 1H, *m*-C**H** of Mes), 6.96 (s, 1H, *m*-C**H** of Mes), 6.01 (d, $^2J_{H\text{-}H}$ = 15.5 Hz, 1H, C**H**$_2$), 5.33 (d, $^2J_{H\text{-}H}$ = 15.5 Hz, 1H, C**H**$_2$), 2.33 (s, 3H, *p*-C**H**$_3$ of Mes), 2.21 (s, 3H, *o*-C**H**$_3$ of Mes), 2.06 (s, 3H, *o*-C**H**$_3$ of Mes), 1.60 (s, 15H, C**H**$_3$ of Cp*) ppm. **^{13}C{^{1}H} NMR** (150 MHz, (CD$_3$)$_2$CO): δ 162.6 (q, $^1J_{\text{B-C}}$ = 49.9 Hz, *ipso*-**C** to B of BAr$^F{}_4$), 153.8 (Im-**C**2), 143.1 (C$_q$, Tz-**C**4'), 140.0 (*ipso*-**C**$_q$ of Ar-CF$_3$), 139.95 (*p*-**C**CH$_3$ of Mes), 139.4 (*o*-**C**CH$_3$ of Mes), 136.4 (*ipso*-**C**$_q$ of Mes), 136.0 (*o*-**C**CH$_3$ of Mes), 135.5 (br s, *o*-**CH** to B of BAr$^F{}_4$), 132.2 (q, $^2J_{\text{F-C}}$ = 32.4 Hz, *p*'-**C**CF$_3$ or Ar-CF$_3$), 130.1 (*m*-**C**H of Mes), 130.0 (q, $^2J_{\text{F-C}}$ = 31.7 Hz, **C**CF$_3$ of BAr$^F{}_4$), 128.8 (*m*-**C**H of Mes), 128.3 (q, $^4J_{\text{C-F}}$ = 3.65 Hz, *m'*-**C**H of Ar-CF$_3$), 126.7 (Im-**C**4), 125.4 (q, $^1J_{\text{F-C}}$ = 271.7 Hz, **C**F$_3$ of BAr$^F{}_4$), 124.7 (q, $^1J_{\text{F-C}}$ = 271.7 Hz, *p*'-**C**F$_3$ of Ar-CF$_3$) 124.5 (Im-**C**5), 123.6 (Tz-**C**5'), 122.5 (*o'*-**C**H of Ar-CF$_3$), 118.4 (br s, *p*-**C**H to B of BAr$^F{}_4$), 92.5 (**C**$_q$ of Cp*), 46.1 (**C**H$_2$), 21.0 (*p*-**C**H$_3$ of Mes), 20.5 (*o*-**C**H$_3$ of Mes), 19.4 (*o*-**C**H$_3$ of Mes), 9.51 (**C**H$_3$ of Cp*) ppm. **HRMS** (ESI$^+$, MeOH): *m/z* (%): (100 %) [M-BAr$^F{}_4$]$^+$ = [$C_{32}H_{35}ClF_3IrN_5$]$^+$ = 774.2156 (Calculated [M-BAr$^F{}_4$]$^+$ = 774.2157) amu. **Elemental Analysis**: Found C, 46.22; H, 2.82 and N, 4.03 Calculated for $C_{64}H_{47}BClF_{27}IrN_5.0.5CH_2Cl_2$: C, 46.11; H, 2.88 and N, 4.17%.

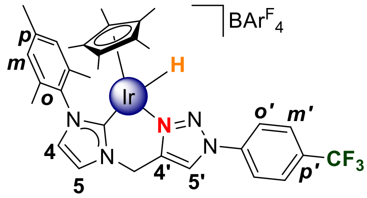
SI-3.6 Synthesis of Ir complex 2e



Complex **2e** was synthesised following the same procedure used to synthesise complex **2a** with ligand **1f** (77.3 mg, 0.157 mmol), Ag$_2$O (69.3 mg, 0.299mmol) and [IrCp*Cl$_2$]$_2$ (62.8 mg, 78.8 µmol) in acetone (20 mL). Following work-up, a yellow-orange crude solid product was dissolved in dichloromethane (15 mL) and NaBAr$^F{}_4$ (141 mg, 0.159 mmol) was added to the reaction mixture. After another work-up, the product **2e** was formed as a red-brown solid. (140 mg, 0.086 mmol, 54%). **^{1}H NMR** (600 MHz, CD$_2$Cl$_2$): *δ* 8.30 (Tz-**H**5'), 7.98 (s, 1H, *o'*-C**H** next to *m'*-CF$_3$ of Ar-*m*CF$_3$), 7.97 (d, $^3J_{\text{H-H}}$ = 8.4 Hz, 1H, *p'*-C**H** of Ar-*m*CF$_3$), 7.91 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 1H, *o'*-C**H** of Ar-*m*CF$_3$), 7.82 (t, $^3J_{\text{H-H}}$ = 7.9 Hz, 1H, *m'*-C**H** of Ar-*m*CF$_3$), 7.72 (br s, 8H, *o*-C**H** of BAr$^F{}_4$), 7.56 (s, 4H, *p*-C**H** of BAr$^F{}_4$), 7.36 (d, $^3J_{\text{H4-H5}}$ = 2.0 Hz, 1H, Im-**H**5), 6.99 (s, 2H, *m*-C**H** of Mes), 6.97 (d, $^3J_{\text{H4-H5}}$ = 2.0 Hz, 1H, Im-**H**4), 5.47 (d, $^2J_{\text{H-H}}$ = 15.7 Hz, 1H, C**H**$_2$), 4.95 (d, $^2J_{\text{H-H}}$ = 15.7 Hz, 1H, C**H**$_2$), 2.35 (s, 3H, *p*-C**H**$_3$ of Mes), 2.12 (s, 3H, *o*-C**H**$_3$ of Mes), 2.01 (s, 3H, *o*-C**H**$_3$ of Mes), 1.49 (s, 15H, C**H**$_3$ of Cp*) ppm. **^{13}C{^{1}H} NMR** (150 MHz, CD$_2$Cl$_2$): δ 162.2 (q, $^1J_{\text{B-C}}$ = 49.9 Hz, *ipso*-**C** to B of BAr$^F{}_4$), 153.5 (Im-**C**2), 142.1 (C$_q$, Tz-**C**4'), 140.5 (*p*-**C**CH$_3$ of Mes), 138.7 (*o*-**C**CH$_3$ of Mes), 136.4 (*ipso*-**C**$_q$ of Ar-*m*CF$_3$), 135.3 (*ipso*-**C**$_q$ of Mes), 135.2 (br s, *o*-**C**H to B of BAr$^F{}_4$), 134.9 (*o*-**C**CH$_3$ of Mes), 131.9 (*p'*-**C**H of Ar-*m*CF$_3$), 130.0 (*m*-**C**H of Mes), 129.3 (q, $^2J_{\text{F-C}}$ = 31.9 Hz, **C**CF$_3$ of BAr$^F{}_4$), 128.8 (q, $^2J_{\text{F-C}}$ = 31.2 Hz, *m*'-**C**CF$_3$ of Ar-*m*CF$_3$), 128.7 (*m*-**C**H of Mes), 128.2 (*o'*-**C**H furthest from *m'*-CF$_3$ of Ar-*m*CF$_3$), 126.5 (Im-**C**4), 125.0 (q, $^1J_{\text{F-C}}$ = 271.7 Hz,

CF$_3$ of BAr$^F{}_4$), 124.8 (*m'*-**C**H of Ar-*m*CF$_3$), 123.3 (q, $^1J_{\mathrm{F\text{-}C}}$ = 270.8 Hz, *m*'-**C**F$_3$ of Ar-*m*CF$_3$), 123.2 (Im-**C**5), 121.6 (Tz-**C**5'), 118.4 (br s, *o'*-**C**H closest to *m'*-CF$_3$ of Ar-*m*CF$_3$), 117.9 (br s, *p*-**C**H to B of BAr$^F{}_4$), 92.5 (**C**$_q$ of Cp*), 45.8 (**C**H$_2$), 21.2 (*p*-**C**H$_3$ of Mes), 20.0 (*o*-**C**H$_3$ of Mes), 19.3 (*o*-**C**H$_3$ of Mes), 9.64 (**C**H$_3$ of Cp*) ppm. **HRMS** (ESI$^+$, MeOH): *m/z* (%): (100 %) [M-BAr$^F{}_4$]$^+$ = [$C_{32}H_{35}ClF_3IrN_5$]$^+$ = 774.2156 (Calculated [M-BAr$^F{}_4$]$^+$ = 774.2157) amu.

SI-3.7 Synthesis of iridium hydride II



This reaction was performed on NMR scale in a Young's NMR tube. Complex **2d** (4.11 mg, 2.51 µmol) was dissolved in methanol (0.6 mL). NaBH$_4$ (0.95 mg, 0.0251 mmol) was added to the mixture. A lot of bubbling of the brown solution occurs. After overnight, the mixture was filtered through a small piece of cotton to give a bright yellow solution. The solvent was evaporated *in vacuo*. The yellow-brown solid was re-dissolved in toluene-*d*$_8$ (0.6 mL) and used for mechanistic investigations without further purification. **^{1}H NMR** (600 MHz, toluene-*d*$_8$): *δ* 8.28 (br s, 8H, *o*-C**H** of BAr$^F{}_4$), 7.63 (s, 4H, *p*-C**H** of BAr$^F{}_4$), 7.16 (d, $^3J_{\mathrm{H}o\text{-}\mathrm{H}m}$ = 8.3 Hz, 1H, *m'*-C**H** of Ar-CF$_3$), 6.89 (d, $^3J_{\mathrm{H}o\text{-}\mathrm{H}m}$ = 8.3 Hz, 1H, *o'*-C**H** of Ar-CF$_3$), 6.71 (s, 1H, Tz-**H**5'), 6.69 (s, 1H, *m*-C**H** of Mes), 6.65 (s, 1H, *m*-C**H** of Mes), 6.34 (d, $^3J_{\mathrm{H4\text{-}H5}}$ = 2.0 Hz, 1H, Im-**H**5), 5.92 (d, $^3J_{\mathrm{H4\text{-}H5}}$ = 2.0 Hz, 1H, Im-**H**4), 4.23 (s, 2H, C**H**$_2$), 2.10 (s, 3H, *p*-C**H**$_3$ of Mes), 1.78 (s, 3H, *o*-C**H**$_3$ of Mes), 1.75 (s, 3H, *o*-C**H**$_3$ of Mes), 1.37 (s, 15H, C**H**$_3$ of Cp*), -13.3 (s, 1H, hydride) ppm. **^{13}C{^{1}H} NMR** (150 MHz, toluene-*d*$_8$): δ 162.6 (q, $^1J_{\mathrm{B\text{-}C}}$ = 48.8 Hz, *ipso*-**C** to B of BAr$^F{}_4$), 155.1 (Im-**C**2), 142.6 (C$_q$, Tz-**C**4'), 139.7 (*p*-**C**CH$_3$ of Mes), 137.4 (*ipso*-**C**$_q$ of Ar-CF$_3$), 135.8 (*o*-**C**CH$_3$ of Mes), 135.5 (br s, *o*-**C**H to B of BAr$^F{}_4$ overlapped with *ipso*-**C**$_q$ of Mes), 135.0 (*o*-**C**CH$_3$ of Mes), 132.6 (q, $^2J_{\mathrm{F\text{-}C}}$ = 32.9 Hz, *p*'-**C**CF$_3$ of Ar-CF$_3$), 130.0 (q, $^2J_{\mathrm{F\text{-}C}}$ = 32.9 Hz, **C**CF$_3$ of BAr$^F{}_4$), 129.9 (*m*-**C**H of Mes), 129.2 (*m*-**C**H of Mes), 127.5 (q, $^4J_{\mathrm{C\text{-}F}}$ = 3.50 Hz, *m'*-**C**H of Ar-CF$_3$), 125.2 (q, $^1J_{\mathrm{F\text{-}C}}$ = 271.6 Hz, **C**F$_3$ of BAr$^F{}_4$), 123.7 (q, $^1J_{\mathrm{F\text{-}C}}$ = 271.5 Hz, *p*'-**C**F$_3$ of Ar-CF$_3$), 123.3 (Im-**C**4), 121.1 (Im-**C**5), 120.1 (*o'*-**C**H of Ar-CF$_3$), 119.6 (Tz-**C**5'), 118.1 (br s, *p*-**C**H to B of BAr$^F{}_4$), 91.9 (**C**$_q$ of Cp*), 45.3 (**C**H$_2$), 21.0 (*p*-**C**H$_3$ of Mes), 19.1 (*o*-**C**H$_3$ of Mes), 18.1 (*o*-**C**H$_3$ of Mes), 9.75 (**C**H$_3$ of Cp*) ppm. **HRMS** (ESI$^+$, MeOH): *m/z* (%): (100 %) [M-BAr$^F{}_4$]$^+$ = [$C_{32}H_{36}F_3IrN_5$]$^+$ = 740.2545 (Calculated [M-BAr$^F{}_4$]$^+$ = 740.2547) amu.

SI-3.8 NMR spectra of complexes

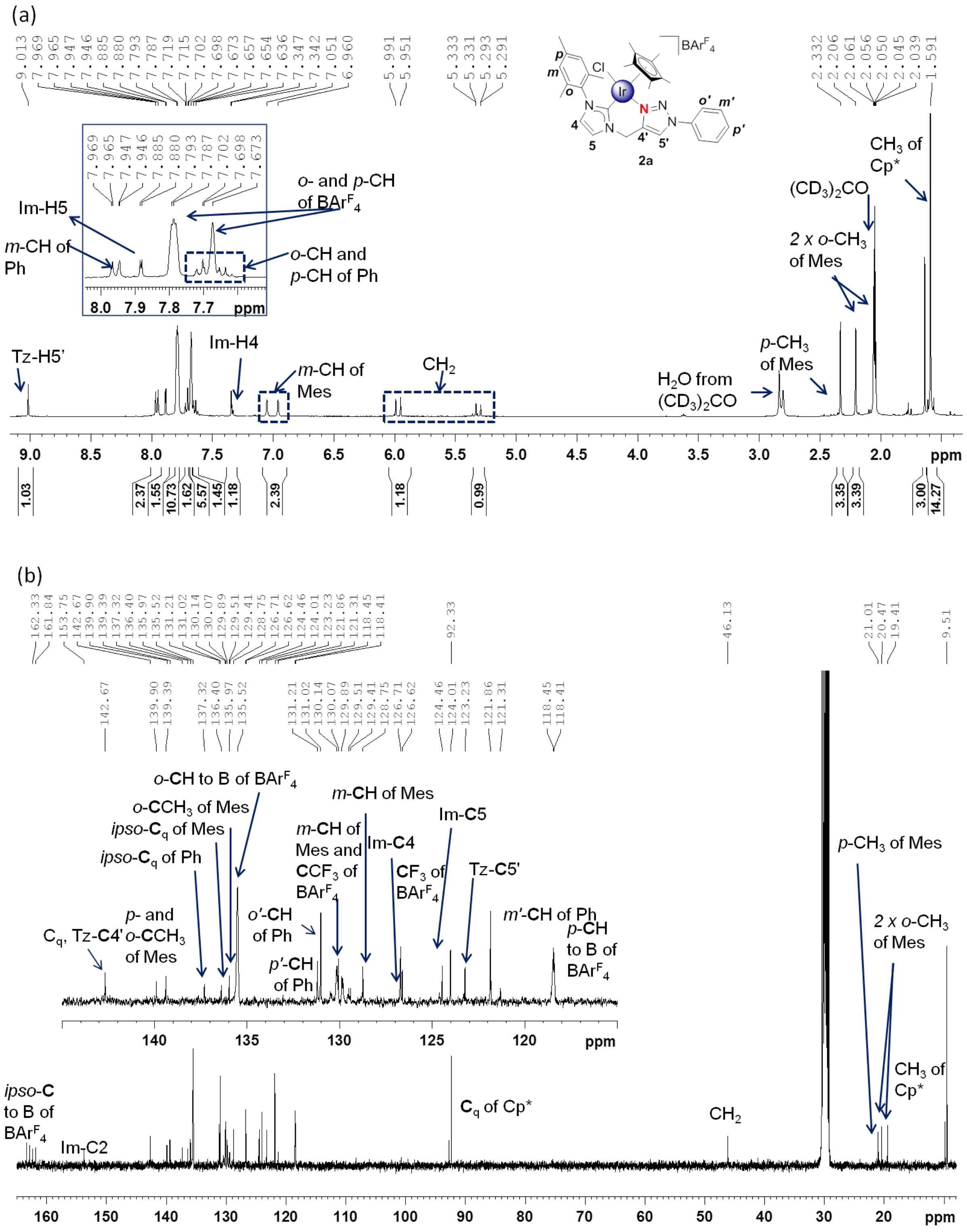


Figure S6 (a) ^{1}H NMR (400 MHz, $(CD_3)_2CO$) spectrum of complex **2a**, (b) $^{13}C\{^{1}H\}$ NMR (100 MHz, $(CD_3)_2CO$) spectrum of complex **2a**.

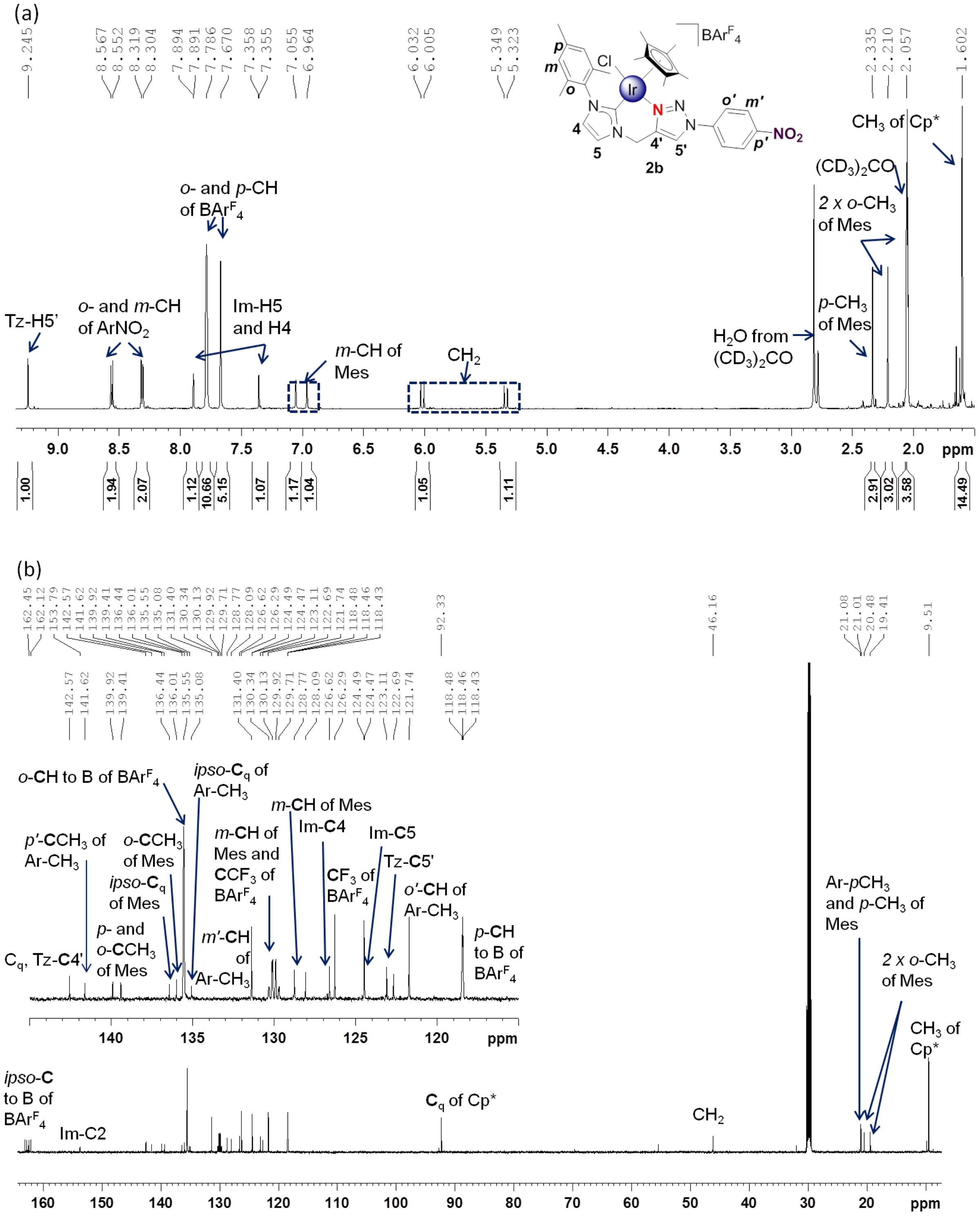


Figure S7 (a) ^{1}H NMR (600 MHz, $(CD_3)_2CO$) spectrum of complex **2b**, (b) ^{13}C{^{1}H} NMR (150 MHz, $(CD_3)_2CO$) spectrum of complex **2b**.

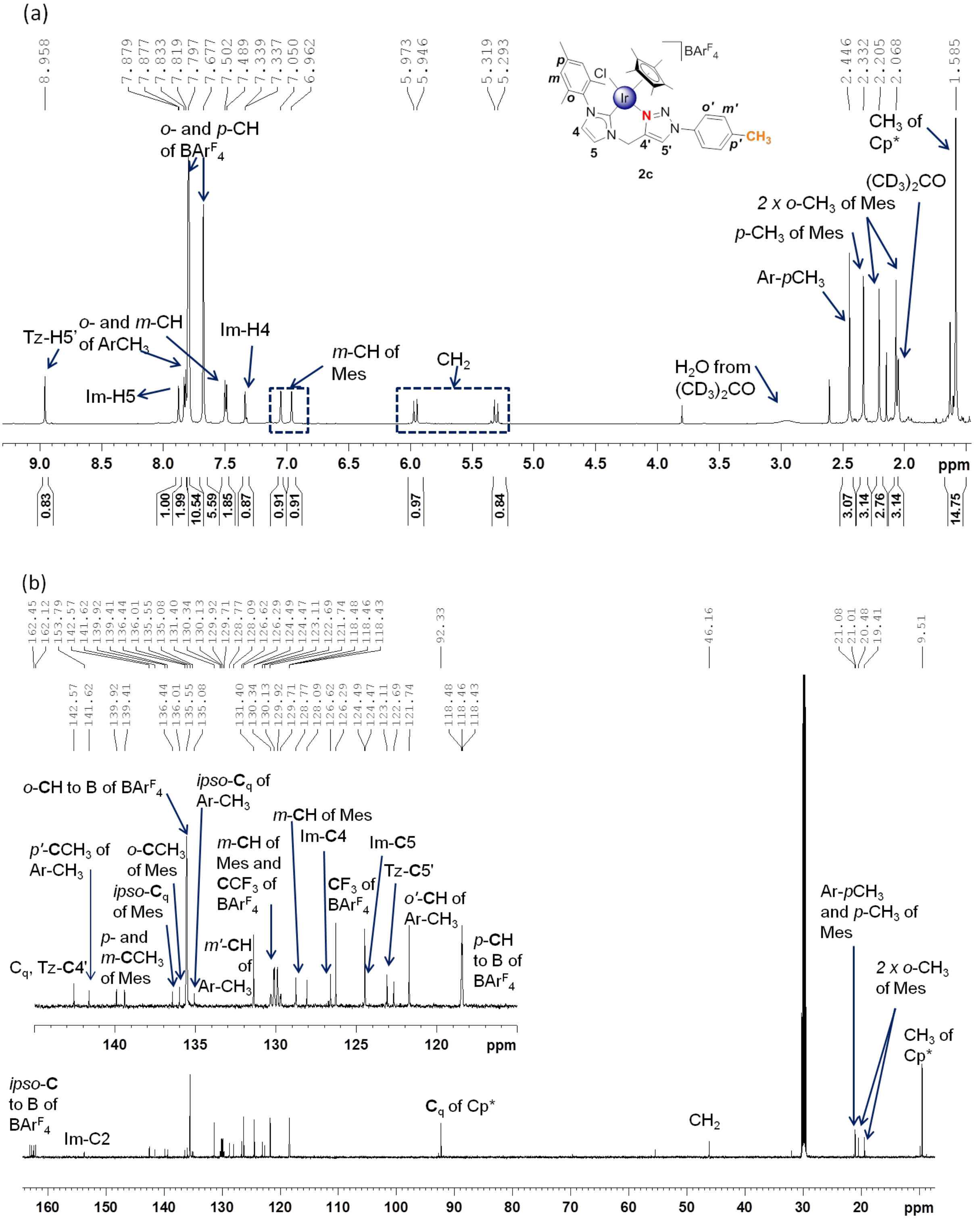


Figure S8 (a) ^{1}H NMR (600 MHz, (CD$_3$)$_2$CO) spectrum of complex **2c**, (b) ^{13}C{^{1}H} NMR (150 MHz, (CD$_3$)$_2$CO) spectrum of complex **2c**.

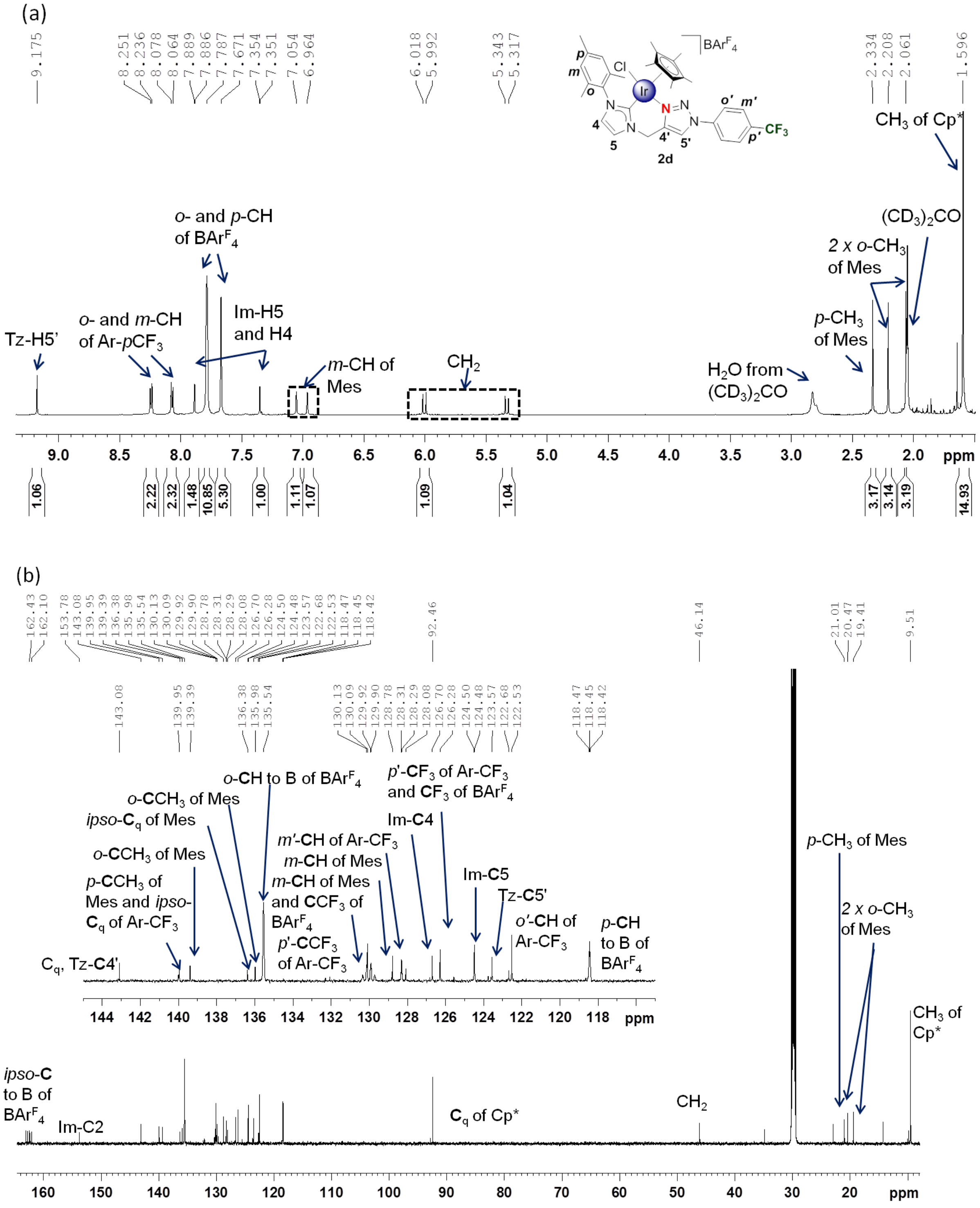


Figure S9 (a) ^{1}H NMR (600 MHz, $(CD_3)_2CO$) spectrum of complex **2d**, (b) $^{13}C\{^{1}H\}$ NMR (150 MHz, $(CD_3)_2CO$) spectrum of complex **2d**.

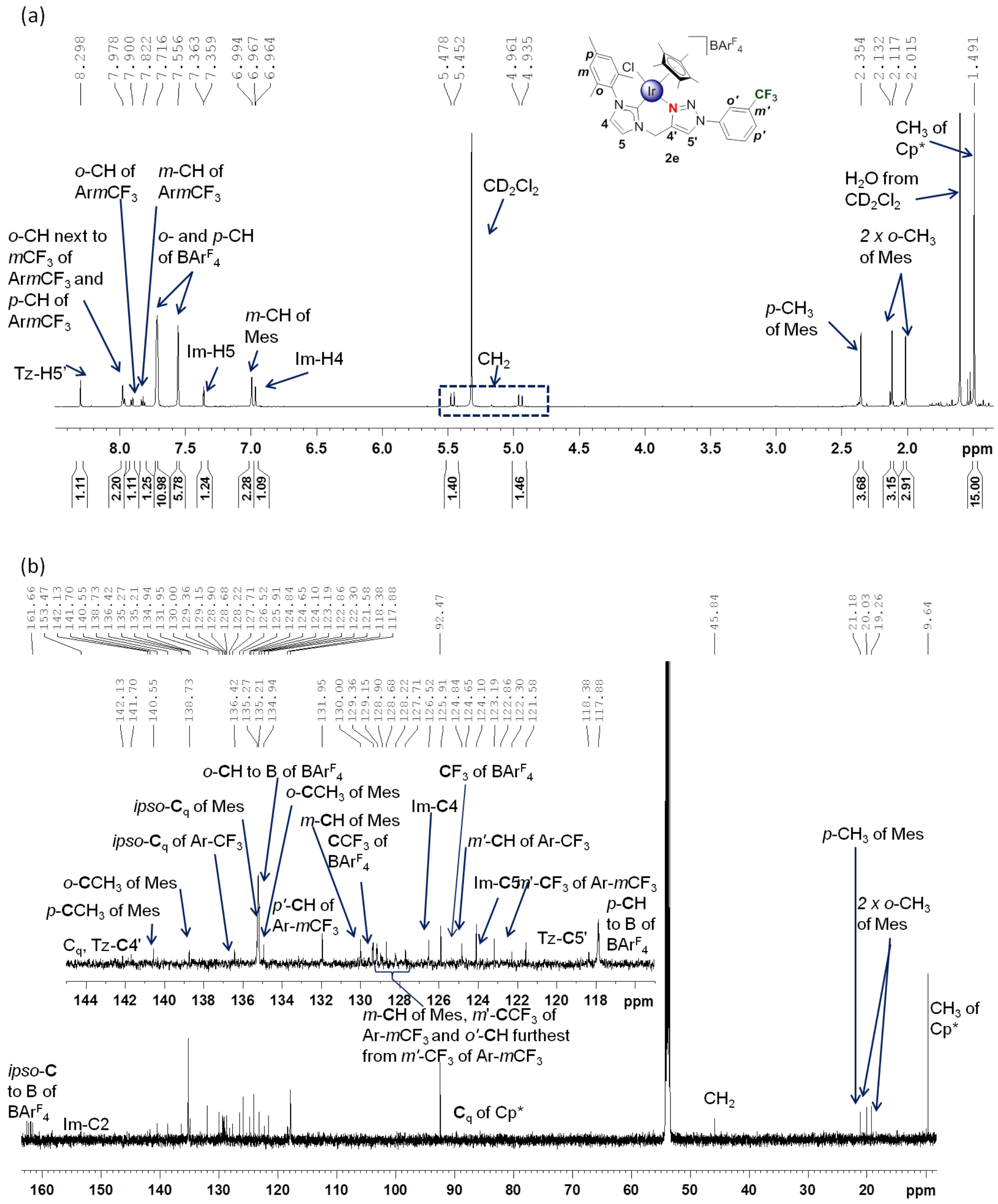


Figure S10 (a) ^{1}H NMR (600 MHz, CDCl$_2$) spectrum of complex **2e**, (b) ^{13}C{^{1}H} NMR (150 MHz, CDCl$_2$) spectrum of complex **2e**.

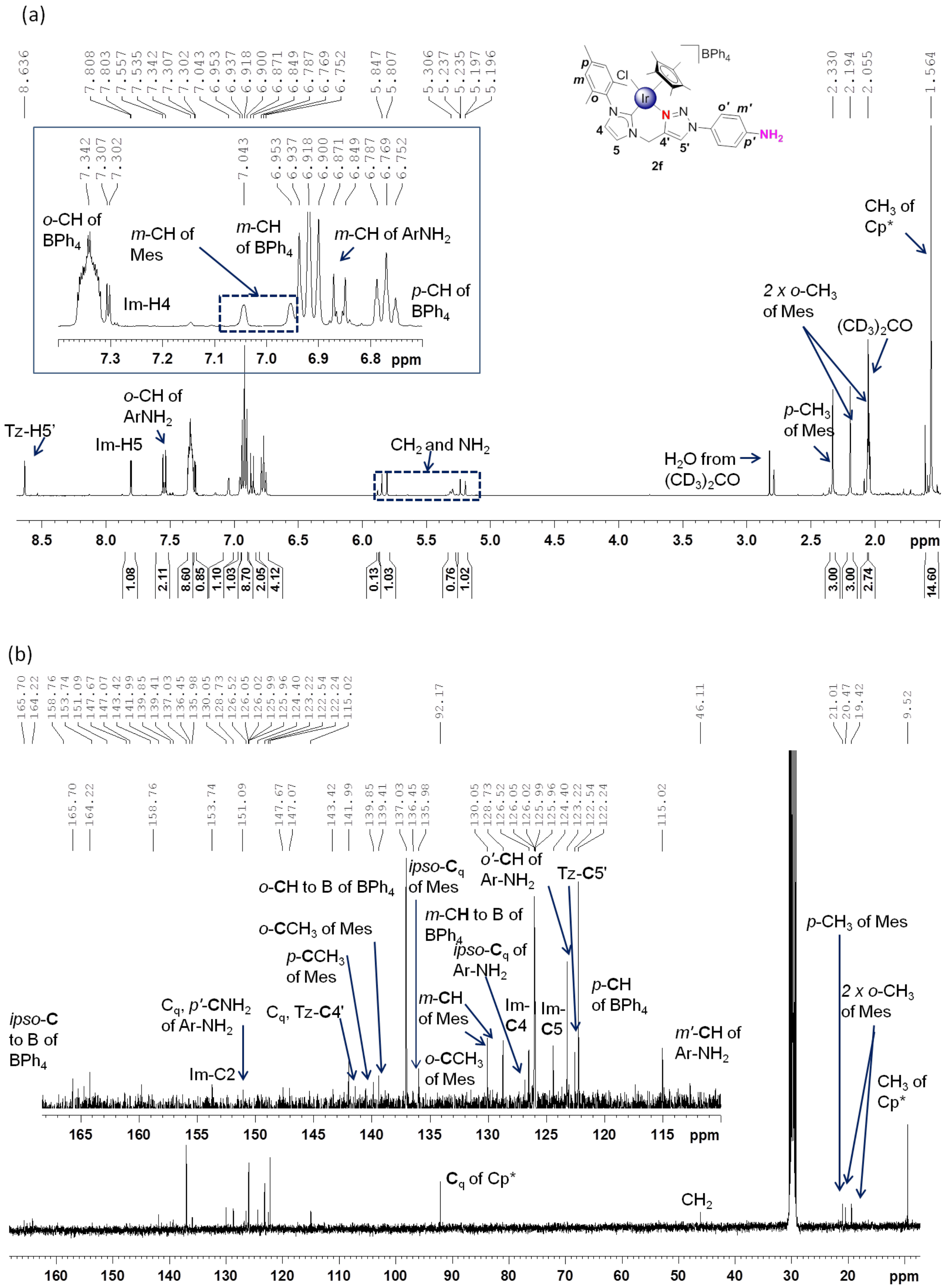


Figure S11 (a) ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) spectrum of complex **2f**, (b) ^{13}C{^{1}H} NMR (100 MHz, (CD$_3$)$_2$CO) spectrum of complex **2f**.

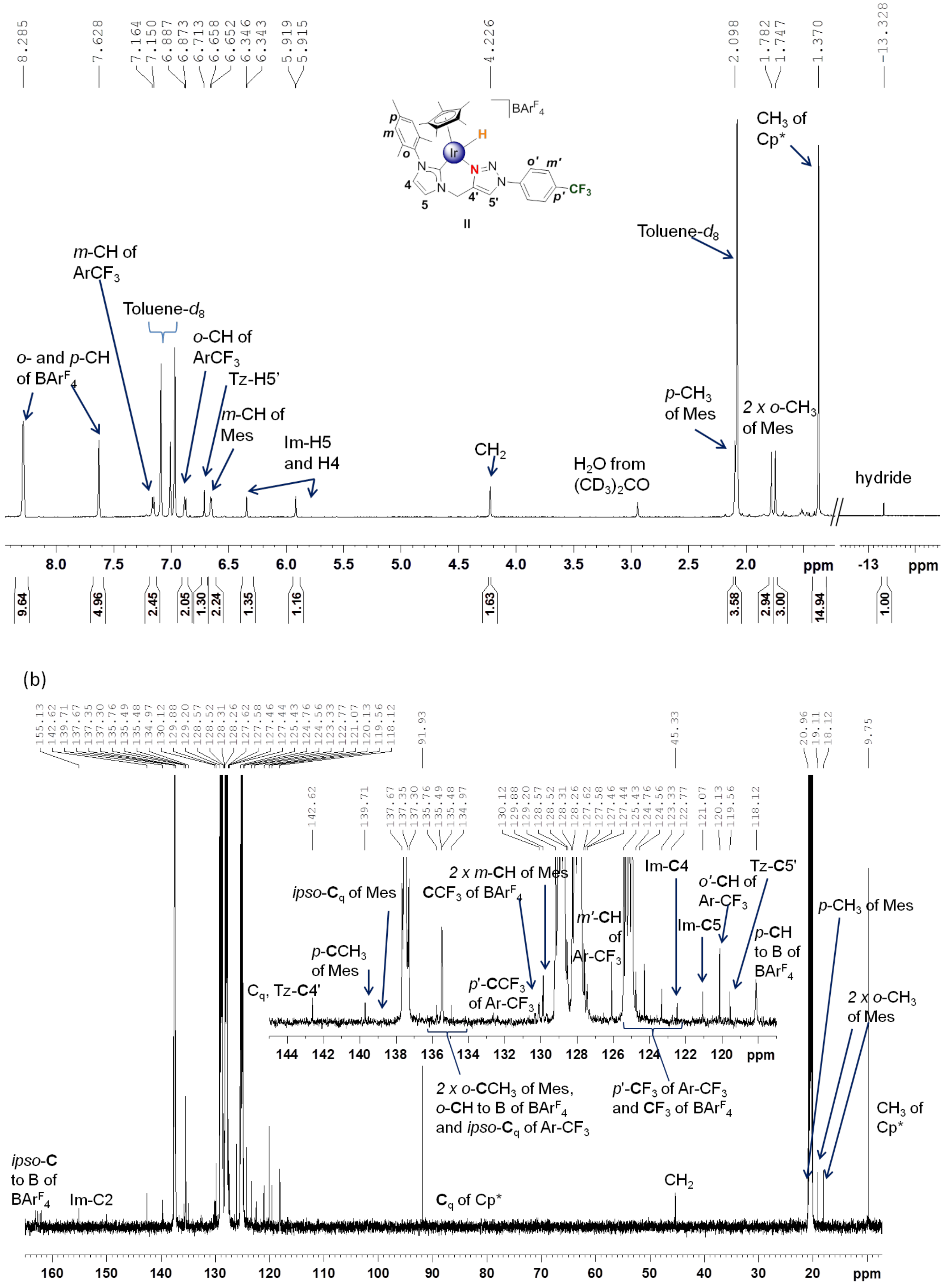


Figure S12 (a) ^{1}H NMR (600 MHz, toluene-d_8) spectrum of Ir(III) hydride complex **II**, (b) ^{13}C{^{1}H} NMR (150 MHz,toluene-d_8) spectrum of Ir(III) hydride complex **II**.

SI-4 Synthesis of Ir(III) hybrid complexes

SI-4.1 Synthesis of hybrid complex on glassy carbon 2-GC

The glassy carbon (GC) electrode was polished sequentially before immobilisation in alumina slurries (distilled water suspension) of 1.0, 0.3 and 0.05 µm on micropolishing cloth (Buehler, IL, USA) and rinsed with distilled water between each step. It was then washed thoroughly with ethanol and soaked for 30 mins in dichloromethane. The complex **2f** (30.2 mg, 27.9 µmol) was dissolved in a degassed solution of nitromethane (10 mL). The mixture was cooled in an ice bath for 5 minutes before hydrochloric acid (0.5 mL, 0.5 M) was added dropwise into the stirred yellow solution while keeping the mixture between 0-5 °C. Sodium nitrite (1.90 mg, 27.9 µmol) was then added followed by the GC electrode. The mixture was left to sit in the ice bath for another hour before allowing the mixture to gradually warm up to room temperature and remained at room temperature overnight. The modified GC electrodes was separated from the reaction media and washed consecutively with MilliQ water (5 mL), a mixture of methanol:MilliQ water (1:1, 20 mL) and methanol (5 x 10 mL). The washed modified **2-GC** electrode was dried under a gentle flow of nitrogen.

SI-4.2 Synthesis of hybrid complex on carbon black 2-CB

The complex **2f** (30.2 mg, 27.9 µmol) was dissolved in a degassed solution of nitromethane (10 mL). The mixture was cooled in an ice bath for 15 minutes before hydrochloric acid (0.5 mL, 0.5M) was added dropwise into the stirred yellow solution while keeping the mixture between 0-5 °C. Sodium nitrite (1.90 mg, 27.9 µmol) was then added and the mixture was stirred vigorously for another 5 minutes. After taking the mixture out of the ice bath, carbon black or graphene (50 mg) was added while the mixture was stirred vigorously to ensure that the carbon powders were diffused in solution properly. The mixture was allowed to gradually warm up to room temperature. The mixture was stirred under nitrogen at room temperature overnight. The modified carbon powder was separated from the reaction media *via* centrifugation (4000 rpm) for 5 minutes. It was consecutively washed and stirred vigorously with a methanol:MilliQ water (1:1, 20 mL) and methanol (5 x 10 mL) followed by centrifugation after each washing. The washed powder was dried under vacuum in a dessicator for 24 hours to give **2-CB** (42 mg, 84%) as a black powder.

SI-4.3 Evaluation of iridium content for 2-CB by ICP-MS

The **2-CB** samples for ICP-MS analysis was prepared were accurately weighed in a 25 ml conical flask. A mixture of concentrated sulfuric acid (98 %, 2 ml) and concentrated nitric acid (63 %, 4 ml) was cautiously added. A reflux condenser was attached and the resulting black suspension was refluxed until a clear yellow-orange solution was obtained. During refluxing, a bubbler filled with a saturated solution of $NaHCO_3$ was attached to the end of the condenser to neutralise the acid fumes. After the clear solution was obtained, the reaction mixture was allowed to cool to room temperature. A freshly prepared aqua regia solution (a mixture of concentrated $HCl:HNO_3$ in a 3:1 ratio) (4.0 ml) was then added to the solution slowly. Bubbling was observed. The resulting orange mixture was heated again at 120 °C for 1 hour or until the solution turns from pale yellow-orange to colourless and then allowed to cool to room temperature. The solutions were then transferred without loss into 25.0 mL volumetric flasks and Milli-Q water was added to reach the graduation mark. The solutions were analysed by ICP-MS and the concentrations of Ir obtained was used to calculate the Ir content in the hybrid catalysts.

For catalysis recycling reactions, after each catalysis cycle, the filtrate and washings were collected and the solvent evaporated at 120 °C for 30 minutes in a conical flask. A mixture of concentrated sulfuric acid (98 %, 2 ml) and concentrated nitric acid (63 %, 4 ml) was cautiously added. The reaction was heated at 120 °C for 30 minutes. A freshly prepared aqua regia solution (4.0 ml) was then added to the solution slowly. Bubbling was observed. The resulting orange mixture was heated again at 120 °C for 1 hour or until the solution turns from pale yellow-orange. The solutions were then transferred without loss into 10.0 or 25.0 mL volumetric flasks and Milli-Q water was added to reach the graduation mark. The solutions were analysed by ICP-MS and the concentrations of Ir obtained was used to calculate the Ir loss into solution during catalysis using the hybrid catalysts.

Table S3 Summary of ICP-MS of **2-CB**.

Hybrid catalyst	ICP-MS (µg L^{-1})	Ir wt%
Batch 1	1059	0.84
Batch 2	1000	1.81
After run 1	534	0.06
After run 2	1598	0.17
After run 3	356	0.10

Example Ir wt% calculation for batch 2: ICP-MS =1.000 mg L^{-1}

Ir wt% = (25/1000*1.000)/1.38*100 = 1.81 wt%

SI-4.4 XP survey spectra and peak tables for all hybrid complexes

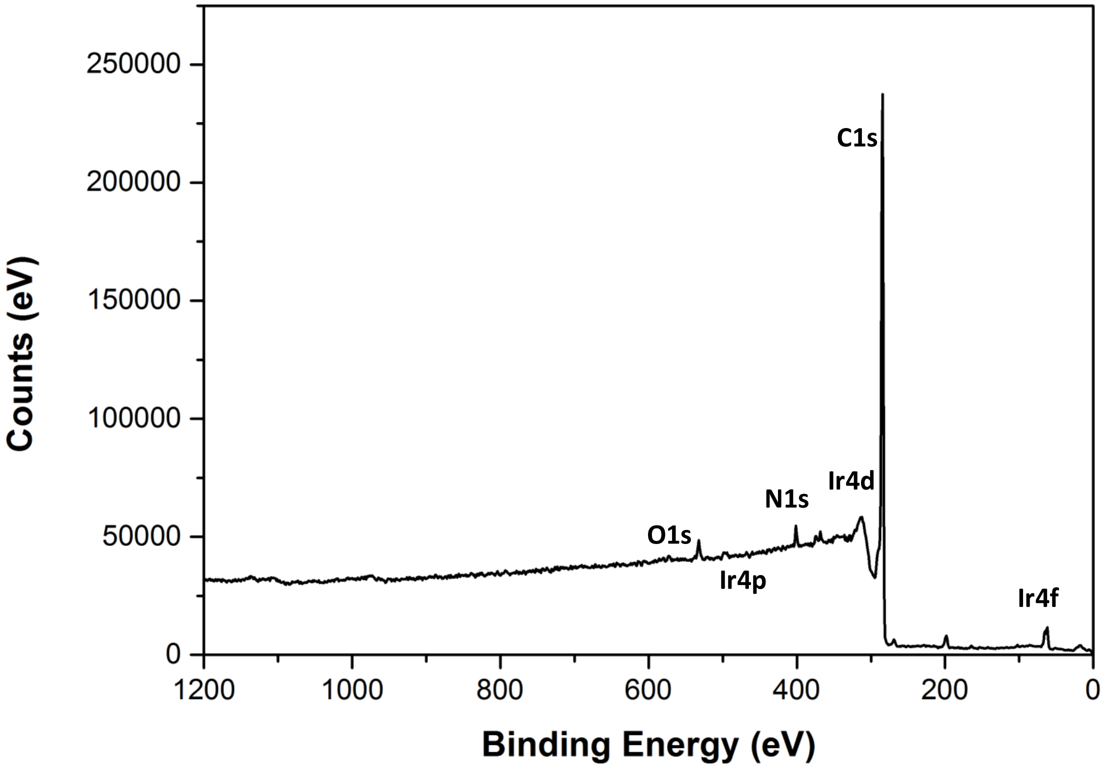


Figure S13 XP survey spectra for **2-CB**.

Table S4 Peak table for **2-CB**.

Name	Start BE (eV)	Peak BE (eV)	End BE (eV)	Atomic %
C1s	296.48	284.79	276.68	49.1
C1s A	296.48	285.56	276.68	45.3
C1s C	296.48	288.18	276.68	2.8
Ir4f$_{7/2}$	74.48	63.04	54.68	0.41
N1s	411.48	401.67	391.68	1.53
N1s A	411.48	402.92	391.68	0.51
N1s B	411.48	400.56	391.68	0.34

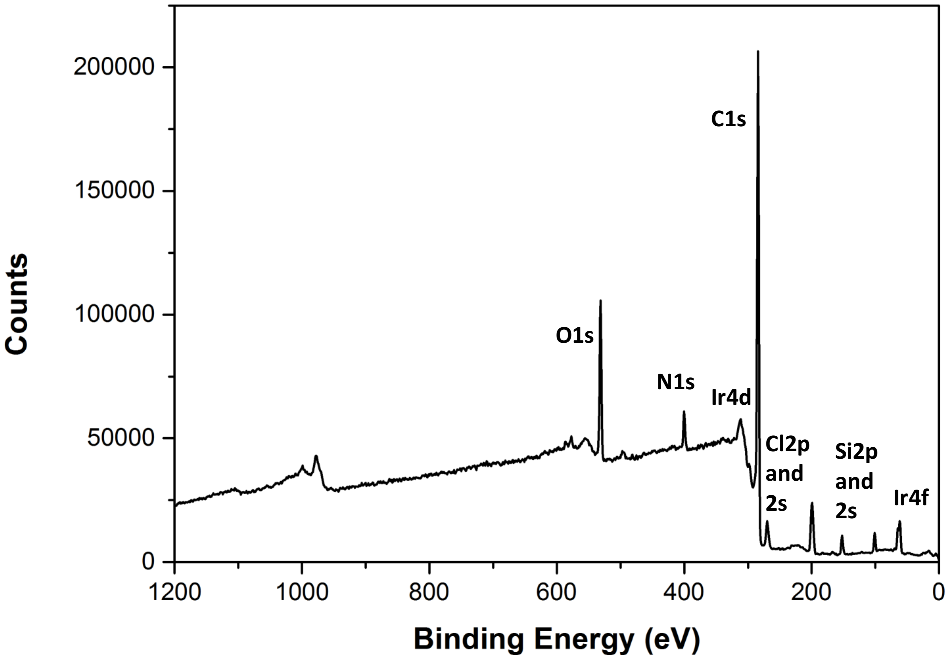


Figure S14 XP survey spectra for 2-GC.

Table S5 Peak table for **2-GC**.

Name	**Start BE (eV)**	**Peak BE (eV)**	**End BE (eV)**	**Atomic %**
C1s A	292.74	284.46	281.48	43.22
C1s B	292.74	284.95	281.48	20.46
C1s C	292.74	286.25	281.48	11.27
C1s D	292.74	287.95	281.48	1.92
C1s E	292.74	289.15	281.48	0.63
Cl2p$_{3/2}$ A	204.28	197.96	195.28	1.65
Cl2p$_{3/2}$ B	204.28	200.18	195.28	3.38
Ir4f$_{7/2}$	68.34	62.43	58.98	0.55
Si2p	105.58	101.75	98.98	3.3
N1s A	408.48	400.64	395.68	2.27
N1s B	408.48	399.23	395.68	0.42
N1s C	408.48	401.92	395.68	0.79
O1s A	537.88	531.94	527.58	7.85
O1s B	537.88	533.54	527.58	1.93
Cr2p$_{3/2}$ A	592.18	577.77	573.18	0.35

SI-4.5 TGA calculations

Total weight loss calculated from graph for **2-CB** from 100 °C to 542 °C

=% weight at 100 °C - % weight at 490 °C (assumption: there is hardly any change in the weight loss of the unmodified carbon black)

= 98.8-72.3 = 26.5%

From TGA weight loss, example calculation of amount of iridium (wt%) on carbon black is as follows:

For **2-CB**, from TGA, total weight loss is 26.5%.

Amount in mass loss from 3.777 mg weight of sample used for TGA

= 26.5/100 x 3.777 = 1.00 mg

Assuming all mass loss is due to the covalently attached Ir complex.

Amount of Ir complex on the carbon black surface

= mass loss/molecular weight of Ir complex

= 1.00 mg/706.331 g mol^{-1} = 0.00142 mmol

Mass of Ir metal on surface

= (amount of Ir complex=amount of Ir metal) x atomic weight of Ir

= 0.00142 mmol x 192.217 g mol^{-1}

= 0.273 mg

Hence, amount of Ir (wt%) on carbon black for **2-CB** = 0.273/3.777 x 100 = 7.23 wt%

SI-5 X-ray crystallographic data

Table S6 Summary of selected bond lengths and bond angles surrounding the Ir(III) metal centre in complexes **2a** - **2f**.

Ir(III) complex	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
CCDC #	1529837	1529855	1529838	1529842	1529843	1529841
Aryl substituent R	*p*-H	*p*-NO_2	*p*-CH_3	*p*-CF_3	*m*-CF_3	*p*-NH_2
Counter-ion X	BAr^F_4	BAr^F_4	BAr^F_4	BAr^F_4	BAr^F_4	BPh_4
Bond lengths (Å)						
Ir-C(carbene)	2.053(4)	1.985(18)	2.053(3)	2.058(7)	2.057(8)	2.064(6)
Ir-N(triazole)	2.093(3)	2.068(12)	2.088(2)	2.065(5)	2.089(7)	2.101(4)
Ir-C*[a]	1.814	1.810	1.814	1.824	1.811	1.817
Ir-Cl	2.392(1)	2.374(4)	2.3842(7)	2.404(2)	2.412(1)	2.414(1)
Bond angles (°)						
(carbene)C-Ir-N(triazole)	82.5(1)	82.3(5)	82.5(1)	82.9(2)	82.3(2)	84.8(2)
(triazole)N-Ir-Cl	88.80(8)	86.4(4)	88.52(7)	88.5(1)	87.7(2)	85.2(1)
(carbene)C-Ir-Cl	90.8(1)	93.0(4)	90.72(8)	93.1(2)	92.9(2)	92.8(2)
(triazole)N-Ir-C*[a]	123.01	126.48	124.38	123.84	125.03	126.57
(carbene)C-Ir-C*[a]	133.41	131.61	133.74	133.65	132.45	132.51
Cl-Ir-C*[a]	123.01	123.07	123.07	121.51	122.75	121.15

[a] C* = centroid of Cp* co-ligand.

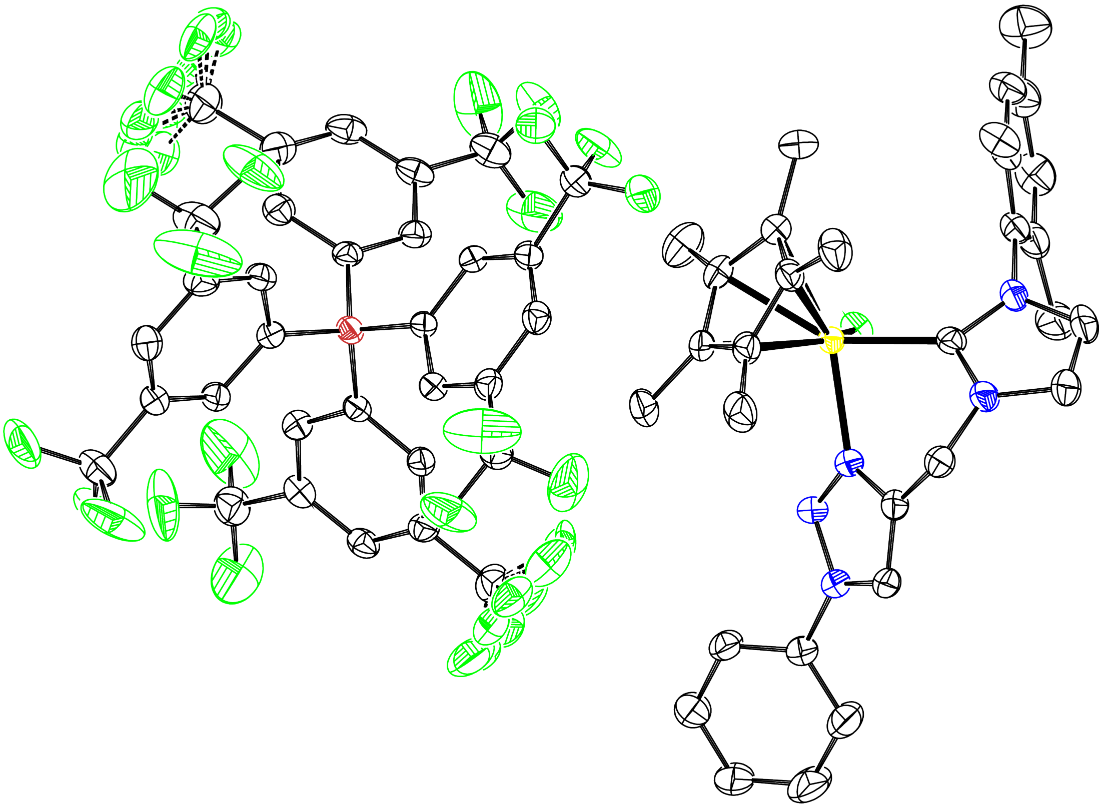


Figure S15 Ortep depiction of the crystal structure of **2a**, hydrogens omitted for clarity.

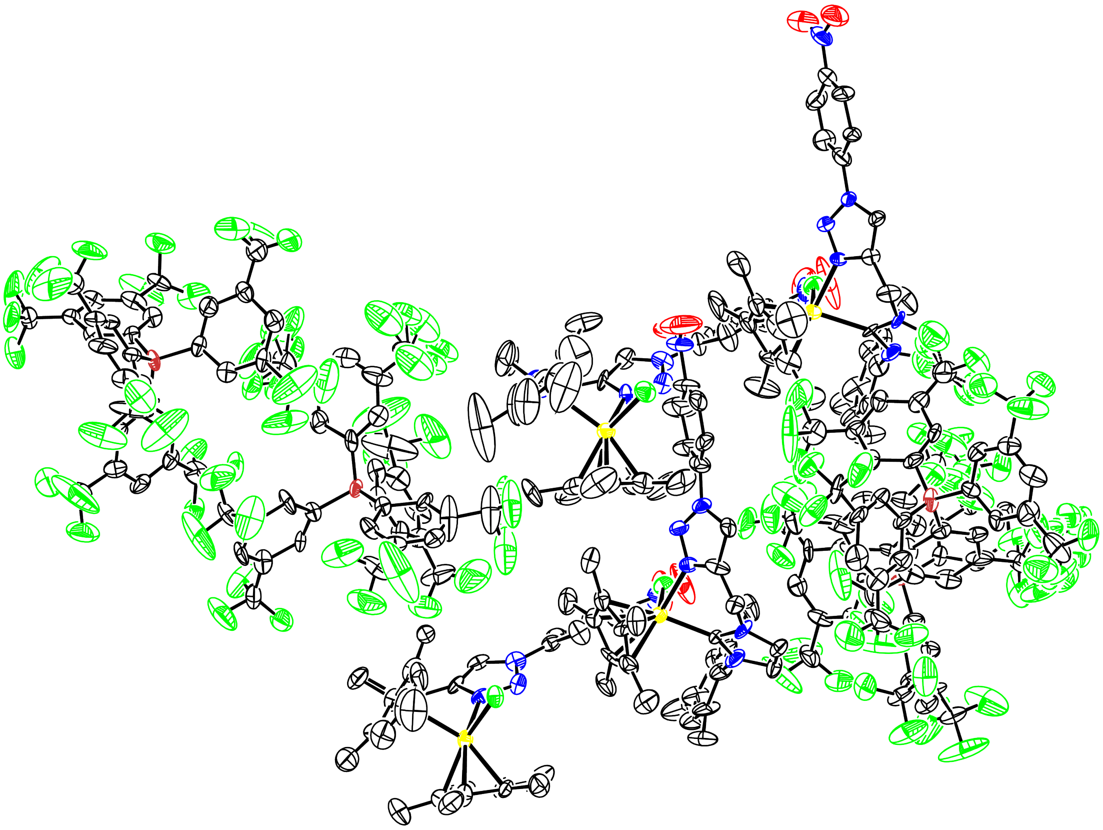


Figure S16 Ortep depiction of the crystal structure of **2b**, hydrogens omitted for clarity.

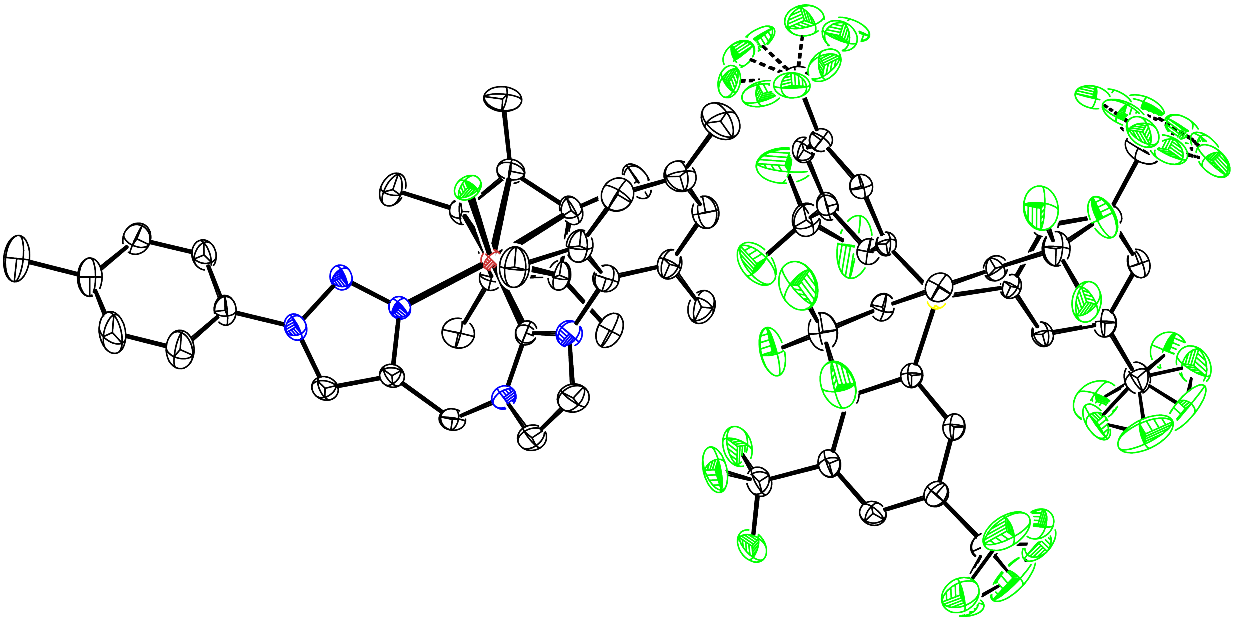


Figure S17 Ortep depiction of the crystal structure of **2c**, hydrogens omitted for clarity.

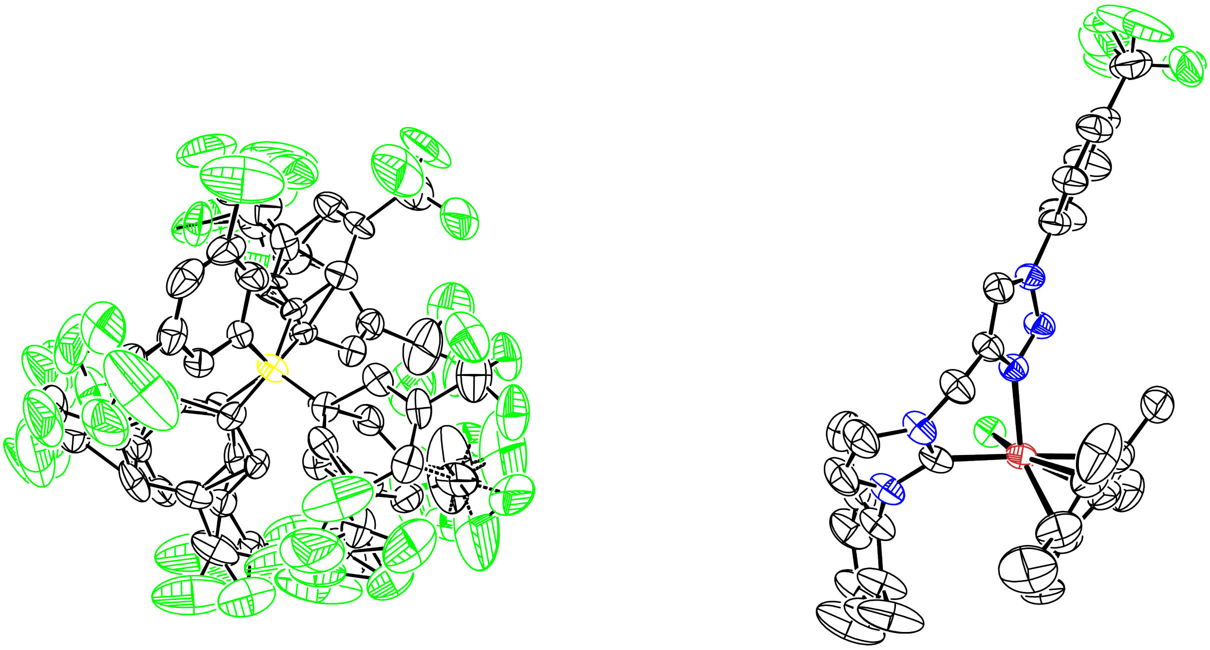


Figure S18 Ortep depiction of the crystal structure of **2d**, hydrogens omitted for clarity.

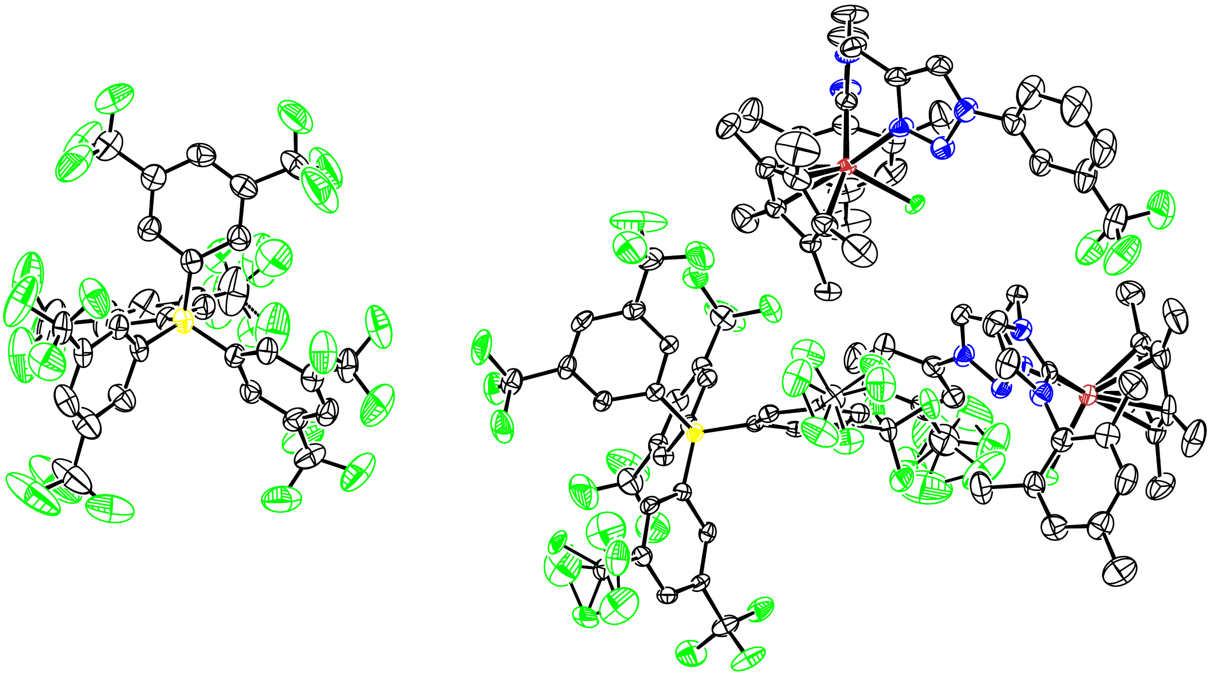


Figure S19 Ortep depiction of the crystal structure of **2e**, hydrogens omitted for clarity.

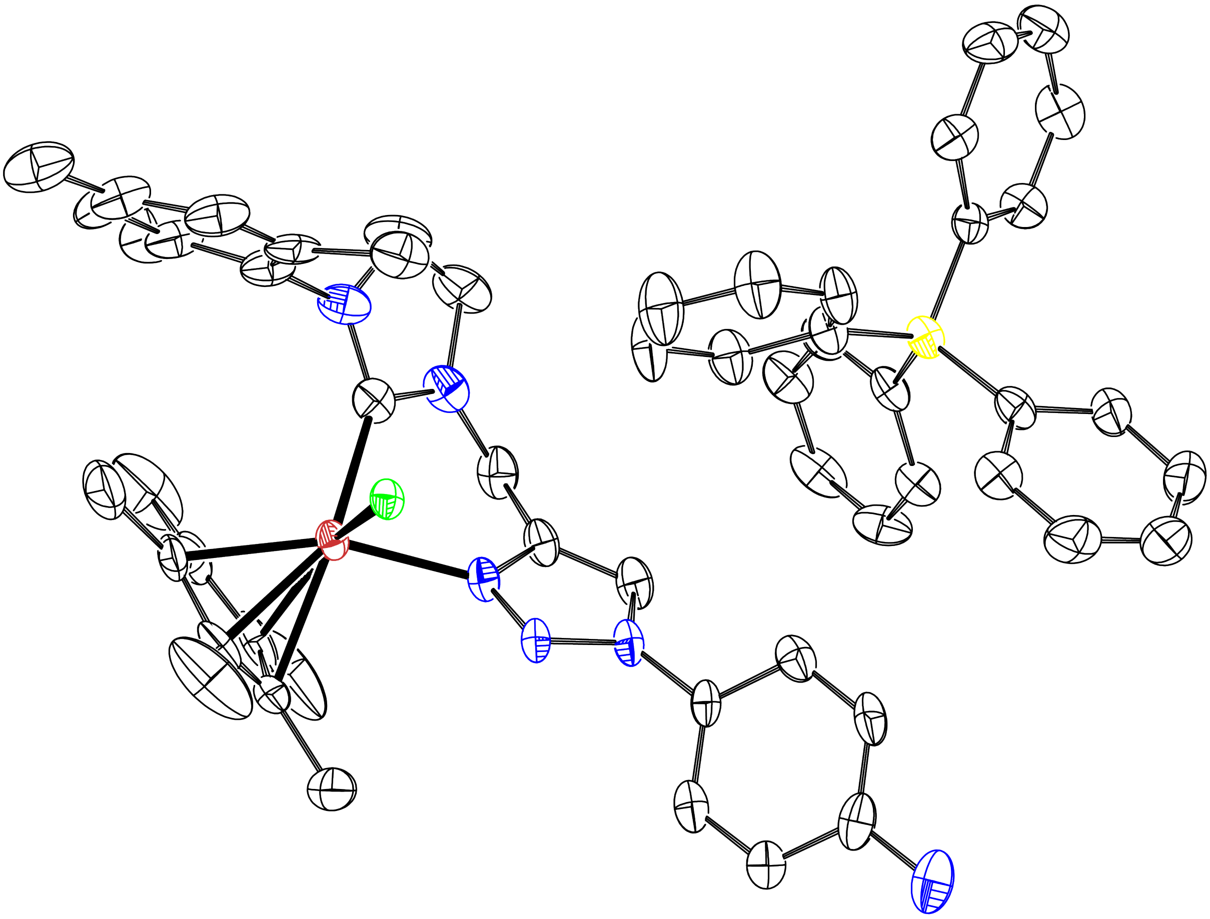


Figure S20 Ortep depiction of the crystal structure of **2f**, hydrogens omitted for clarity.

SI-6 General catalysis procedure

SI-6.1 Catalysis procedure using well-defined isolated Ir(III) complexes 2a-2f

All preparations of catalysis mixtures were performed in air. The chosen Ir(III) complex **2a-f** (0.0025 mmol, 0.5 mol%), aniline substrates (0.5 mmol), alcohol substrates (0.55 mmol), and KO^{t}Bu (0.55 mmol) were weighed into a 4 mL glass vial fitted with a close-top melamine cap with PTFE liner. Toluene-d_8 (300-600 mg) was then added to the mixture. The reaction mixture was stirred at room temperature for five minutes until a homogeneous mixture is observed. The reaction mixture was then placed in an oil bath at either 100 °C or 60 °C. After 6 or 24 hours respectively, the reaction mixture was taken out of the oil bath and immediately cooled in the fridge. Subsequently, an NMR sample was prepared by taking an aliquot of the mixture and dissolving it either in toluene-d_8 or chloroform-d_1. Percent conversions were obtained by integration of the ^{1}H NMR peaks of aniline functionalised substrate starting materials (limiting reagent) in comparison to the ^{1}H NMR peaks of the product at the chosen set time intervals. The products were identified and confirmed by comparing the ^{1}H NMR data with ^{1}H NMR data previously reported in the literature[11-17] or with ^{1}H NMR of starting materials or final products recorded in the same solvent and temperature. The turnover number (TON) was calculated as the number of moles of product obtained (at the time taken as the end of the reaction) divided by the number of moles of catalyst used to catalyse the reaction. The turnover frequency (TOF) was calculated as the number of moles of products produced per mole of catalyst used per hour and was calculated at the point of 50% conversion of substrates to product unless otherwise state.

SI-6.2 Catalysis procedure using Ir(III) hybrid complex 2-CB

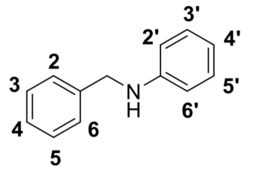
All preparations and analysis of the catalytic mixtures were performed using the same procedure used in Section SI-6.1 in a 3 mL glass v-vial fitted with a close-top teflon screw cap with PTFE liner and a stirrer bar with hybrid Ir(III) complex **2-CB** (5 mg), aniline (**4**) (0.5 mmol), benzyl alcohol (**3**) (0.55 mmol), and KO^{t}Bu (0.55 mmol) in toluene-d_8 (600 mg).

For recycling experiments, all preparations and analysis of the catalytic mixtures were performed using the same procedure used in Section SI-6.1 with hybrid Ir(III) complex **2-CB** (10 mg), aniline (**4**) (0.5 mmol), benzyl alcohol (**3**) (0.55 mmol), and KO^{t}Bu (0.55 mmol) in toluene-d_8 (600 mg). After each cycle, the mixture was centrifuged and the filtrate collected for NMR analysis. The mixture was then washed once with toluene-d_8 (600 mg), centrifuged and the collected washings were combined with the filtrate. The filtrate and washings were analysed by ICP-MS. The carbon solid was reused in subsequent cycles.

SI-6.3 Catalytic reaction quantities and yields for isolated products

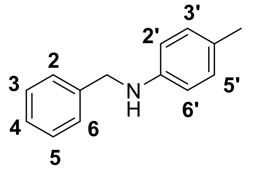
The catalysis reactions were conducted following the general procedures stated in Section SI-6.1 using catalyst **2d** at 100 °C and 6 hours reaction time. After completion of the reaction, the reaction mixture was filtered through a small plug of celite to remove the base, which was washed thoroughly using excess dichloromethane (5 x 2 mL). The solvent was evaporated to give the crude product. The crude product was purified by column chromatography (solvent: dichloromethane, R_f = *ca.* 0.4) to yield the products. The quantities of catalyst **2d**, alcohol substrate, amine substrate, KO^{t}Bu, toluene-d_8 and the product yields are listed below.

1. *N*-benzyl aniline (**5a**)[15]



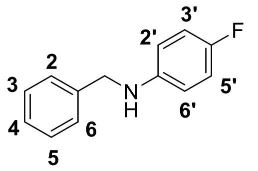
Catalyst **2d** (4.08 mg, 2.49 μmol), benzyl alcohol (**3**) (58.8 mg, 0.544 mmol), aniline (**4**) (63.1 mg, 0.494 mmol), KO^{t}Bu (60.9 mg, 0.543 mmol) and toluene-d_8 (305 mg). The product was isolated as a brown solid. Yield: 86.5 mg, 0.397 mmol, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.36 (overlapping t, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, **H**2,3,5,6), 7.28 (t, $^3J_{H\text{-}H}$ = 7.17 Hz, 1H, **H**4), 7.18 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 2H, **H**3' and **H**5'), 6.72 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, **H**4'), 6.65 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 2H, **H**2' and **H**6'), 4.34 (s, 2H, C**H**$_2$), 4.03 (br s, 1H, N**H**) ppm. **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$): δ 148.3 (**C**1'), 139.6 (**C**1), 129.4 (**C**3' and **C**5'), 128.8 (**C**3 and **C**5), 127.7 (**C**2 and **C**6), 127.4 (**C**4), 117.7 (**C**4'), 113.0 (**C**2' and **C**6'), 48.5 (C**H**$_2$) ppm.

2. *N*-benzyl-4-methylaniline (**5i**)[15]



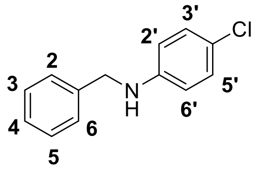
Catalyst **2d** (4.07 mg, 2.49 μmol), benzyl alcohol (**3**) (61.9 mg, 0.572 mmol), *p*-toluidine (53.8 mg, 0.501 mmol), KO^{t}Bu (63.0 mg, 0.562 mmol) and toluene-d_8 (356 mg) at 100 °C. The product was isolated as a brown oil. Yield: 58.7 mg, 0.298 mmol, 59%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (m, 4H, **H**2,3,5,6), 7.28 (m, 1H, **H**4), 6.99 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, **H**3' and **H**5' of Ar-CH_3), 6.57 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, **H**3' and **H**5' of Ar-CH_3), 4.32 (s, 2H, C**H**$_2$), 3.91 (br s, 1H, N**H**), 2.24 (s, 3H, C**H**$_3$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 146.1, 139.8, 129.9, 128.7, 127.6, 127.3, 126.9, 113.1, 48.8 (**C**H$_2$), 20.5 (**C**H$_3$) ppm.

3. *N*-benzyl-4-fluoroaniline (**5j**)[15]



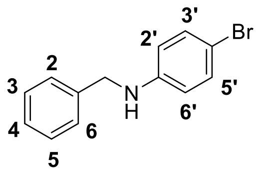
Catalyst **2d** (4.08 mg, 2.49 µmol), benzyl alcohol (**3**) (58.8 mg, 0.544 mmol), 4-chloroaniline (63.1 mg, 0.494 mmol), KO^{t}Bu (60.9 mg, 0.543 mmol) and toluene-d_8 (305 mg) at 100 °C. The product was isolated as a brown solid. Yield: 86.5 mg, 0.397 mmol, 80%. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H, **H**2,3,4,5,6), 6.88 (apparent t, $^3J_{\text{H-H}}$ = 8.8 Hz, 2H, **H**2' and **H**6'), 6.57 (m, 2H, **H**3' and **H**5') 4.29 (s, 2H, C**H**$_2$), 3.93 (br s, 1H, N**H**) ppm. **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz): δ 156.1 (d, $^1J_{\text{C-F}}$ = 235.7 Hz, **C**4'), 144.6, 139.4, 128.8, 127.6, 127.5, 115.8 (d, $^2J_{\text{C-F}}$ = 22.0 Hz, **C**3' and **C**5'), 113.8 (d, $^3J_{\text{C-F}}$ = 7.33 Hz, **C**2' and **C**6'), 49.1 (**C**H$_2$) ppm.

4. *N*-benzyl-4-chloroaniline (**5k**)[15]



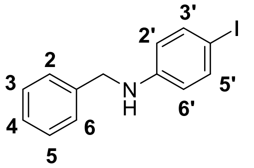
Catalyst **2d** (4.08 mg, 2.49 µmol), benzyl alcohol (**3**) (58.8 mg, 0.544 mmol), 4-chloroaniline (63.1 mg, 0.494 mmol), KO^{t}Bu (60.9 mg, 0.543 mmol) and toluene-d_8 (305 mg) at 100 °C. The product was isolated as a brown solid. Yield: 86.5 mg, 0.397 mmol, 80%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (apparent d, $^3J_{\text{H-H}}$ = 4.4 Hz, 3H, **H**2,4,6), 7.30 (m, 2H, **H**3,5), 7.11 (d, $^3J_{\text{H-H}}$ = 8.9 Hz, 2H, **H**3' and **H**5' of Ar-Cl), 7.57 (d, $^3J_{\text{H-H}}$ = 8.9 Hz, 2H, **H**2' and **H**6' of Ar-Cl), 4.31 (C**H**$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 146.48, 138.85, 129.23, 128.85, 127.63, 127.56, 122.56, 114.31, 48.66 (**C**H$_2$) ppm.

5. *N*-benzyl-4-bromoaniline (**5l**)[12]



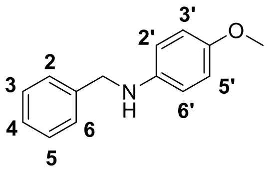
Catalyst **2d** (4.05 mg, 2.47 µmol), benzyl alcohol (**3**) (61.0 mg, 0.564 mmol), 4-bromoaniline (88.1 mg, 0.512 mmol), KO^{t}Bu (60.4 mg, 0.538 mmol) and toluene-d_8 (334 mg) at 100 °C. The product was isolated as a brown oil. Yield: 94.7 mg, 0.361 mmol, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (m, 5H, **H**2,3,4,5,6), 7.25 (d, $^3J_{\text{H-H}}$ = 8.9 Hz, 2H, **H**3' and **H**5' of Ar-Br), 6.53 (d, $^3J_{\text{H-H}}$ = 9.0 Hz, 2H, **H**2' and **H**6' of Ar-Br), 4.51 (br s, 1H, N**H**), 4.30 (s, 2H, C**H**$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 146.8, 138.7, 132.1, 128.9, 127.64, 127.59, 116.9, 114.9, 48.6 (**C**H$_2$) ppm.

6.*N*-benzyl-4-iodoaniline (**5m**)[12]



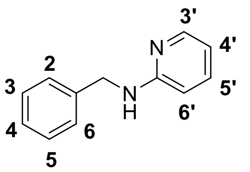
Catalyst **2d** (4.05 mg, 2.47 μmol), benzyl alcohol (**3**) (57.8 mg, 0.534 mmol), 4-iodoaniline (108 mg, 0.495 mmol), KO^{t}Bu (63.7 mg, 0.568 mmol) and toluene-d_8 (304 mg) at 100 °C. The product was isolated as a brown solid. Yield: 98.0 mg, 0.317 mmol, 64%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.42 (d, $^3J_{\text{H-H}}$ = 8.9 Hz, 2H, **H**3' and **H**5' of Ar-I), 7.32 (m, 5H, **H**2,3,4,5,6), 6.42 (d, $^3J_{\text{H-H}}$ = 8.9 Hz, 2H, **H**3' and **H**5' of Ar-I), 4.31 (s, 2H, C**H**$_2$),4.23 (br s, 1H, N**H**) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 147.7, 138.9, 137.9, 128.8, 127.8, 127.5, 115.3, 78.3, 48.2 (**C**H$_2$) ppm.

7. *N*-benzyl-4-methoxyaniline (**5n**)[15]



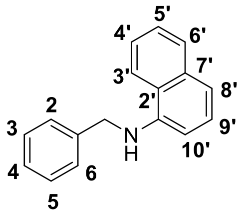
Catalyst **2d** (4.10 mg, 2.50 μmol), benzyl alcohol (**3**) (58.6 mg, 0.542 mmol), 4-methoxyaniline (62.5 mg, 0.507 mmol), KO^{t}Bu (61.7 mg, 0.550 mmol) and toluene-d_8 (414 mg) at 100 °C. The product was isolated as a brown oil. Yield: 67.2 mg, 0.315 mmol, 62%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.35 (m, 4H, **H**2,3,5,6), 7.28 (m, 1H, **H**4), 6.78 (d, $^3J_{\text{H-H}}$ = 9.0 Hz, 2H, **H**2' and **H**6' of Ar-OCH$_3$), 6.61 (d, $^3J_{\text{H-H}}$ = 9.1 Hz, 2H, **H**3' and **H**5' of Ar-OCH$_3$), 4.29 (s, 2H, C**H**$_2$), 3.74 (s, 3H, C**H**$_3$), 1.61 (br s, 1H, N**H**) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 152.3, 142.5, 139.8, 128.7, 127.7, 127.3, 115.0, 114.2, 59.9, 49.4 (**C**H$_2$) ppm.

8. *N*-benzylpyridin-2-amine (**5o**)[16]



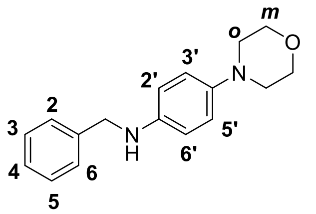
Catalyst **2d** (4.12 mg, 2.52 μmol), benzyl alcohol (**3**) (58.8 mg, 0.544 mmol), pyridin-2-amine (47.7 mg, 0.506 mmol), KO^{t}Bu (61.0 mg, 0.543 mmol) and toluene-d_8 (325 mg) at 100 °C. The product was isolated as a crystalline brown solid. Yield: 67.3 mg, 0.365 mmol, 72%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 8.14 (dd, $^3J_{\text{H-H}}$ = 4.9 Hz, $^4J_{\text{H-H}}$ = 1.0 Hz , 1H, **H**3'), 7.36 (m, 6H, **H**2,3,4,5,6 overlapped with **H**5'), 6.61 (ddd, $^3J_{\text{H-H}}$ = 7.10 Hz, $^3J_{\text{H-H}}$ = 7.17 Hz, $^4J_{\text{H-H}}$ = 0.65 Hz, **H**4'), 6.39 (d, $^3J_{\text{H-H}}$ = 8.34 Hz, 1H, **H**6'), 4.91 (br s, 1H, N**H**), 4.51 (d, $^3J_{\text{H-H}}$ = 5.81 Hz, 2H, C**H**$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 158.7, 148.2, 139.3, 137.7, 128.8, 127.5, 127.4, 113.3, 107.0, 46.5 (**C**H$_2$) ppm.

9. *N*-benzylnaphthalen-1-amine (**5p**)[16]



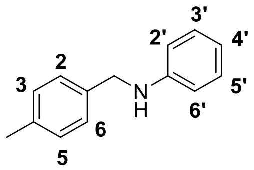
Catalyst **2d** (4.08 mg, 2.49 μmol), benzyl alcohol (**3**) (61.5 mg, 0.568 mmol), naphthalen-1-amine (74.9 mg, 0.523 mmol), KO^{t}Bu (60.6 mg, 0.540 mmol) and toluene-d_8 (325 mg) at 100 °C. The product was isolated as a thick dark brown oil. Yield: 89.4 mg, 0.383 mmol, 73%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.82 (m, 2H, **H**3' and **H**6'), 7.37 (m, 9H, **H**2,3,4,5,6 overlapped with **H**4',5',8',9'), 6.64 (dd, $^3J_{H\text{-}H}$ = 7.4 Hz, $^4J_{H\text{-}H}$ = 0.8 Hz, 1H, **H**10'), 4.71 (br s, 1H, N**H**), 4.51 (s, 2H, CH$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 143.3, 139.2, 134.4, 128.9, 128.8, 127.9, 127.5, 126.7, 125.9, 124.9, 123.5, 120.0, 117.8, 104.9, 48.8 (**C**H$_2$) ppm.

10. *N*-benzyl-4-morpholinoaniline (**5q**)



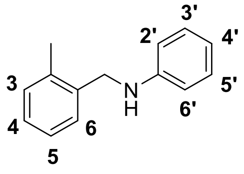
Catalyst **2d** (4.06 mg, 2.48 μmol), benzyl alcohol (**3**) (58.6 mg, 0.542 mmol), 4-morpholinoaniline (81.1 mg, 0.455 mmol), KO^{t}Bu (61.4 mg, 0.547 mmol) and toluene-d_8 (655 mg) at 100 °C. The product was isolated as a brown solid. Yield: 83.0 mg, 0.309 mmol, 68%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.34 (m, 5H, **H**2,3,4,5,6), 6.84 (d, $^3J_{H\text{-}H}$ = 8.80 Hz, 2H, **H**3' and **H**5'), 6.64 (d, $^3J_{H\text{-}H}$ = 8.90 Hz, 2H, **H**2' and **H**6'), 4.30 (s, 2H, C**H**$_2$), 3.86 (apparent t, $^3J_{H\text{-}H}$ = 4.71 Hz, 2H, *o*-C**H**$_2$ to N of morpholine), 3.03 (apparent t, , $^3J_{H\text{-}H}$ = 4.75 Hz, 2H, *m*-C**H**$_2$ to N of morpholine) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 143.0, 139.8, 131.1, 128.7, 127.7, 127.3, 118.4, 114.0, 67.3, 51.4, 49.2 ppm.

11. *N*-(4-methylbenzyl)aniline (**5b**)[15]



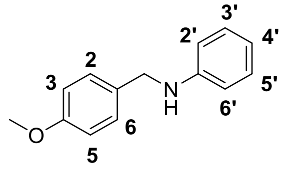
Catalyst **2d** (4.11 mg, 2.51 μmol), *p*-tolylmethanol (66.6 mg, 0.545 mmol), aniline (**4**) (46.0 mg, 0.494 mmol), KO^{t}Bu (69.5 mg, 0.619 mmol) and toluene-d_8 (314 mg) at 100 °C. The product was isolated as a brown oil. Yield: 60.7 mg, 0.308 mmol, 62%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.27 (d, $^3J_{H\text{-}H}$ = 7.69 Hz, 2H, **H**2 and **H**6 of Ar-CH$_3$), 7.17 (m, 4H, **H**3 and **H**5 of Ar-CH$_3$ overlapped with **H**3' and **H**5'), 6.72 (t, $^3J_{H\text{-}H}$ = 7.31 Hz, 1H, **H**4'), 6.65 (d, $^3J_{H\text{-}H}$ = 7.53 Hz, 2H, **H**2' and **H**6'), 4.29 (s, 2H, C**H**$_2$), 3.99 (br s, 1H, N**H**), 2.35 (s, 3H, C**H**$_3$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 148.3, 137.0, 136.5, 129.5, 129.4, 127.7, 117.6, 113.0, 48.2 (**C**H$_2$), 21.2 (**C**H$_3$) ppm.

12. *N*-(2-methylbenzyl)aniline (**5c**)[11]



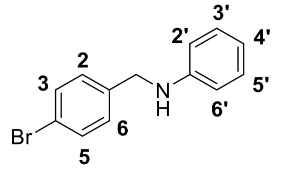
Catalyst **2d** (4.09 mg, 2.50 μmol), *o*-tolylmethanol (68.5 mg, 0.561 mmol), aniline (**4**) (46.5 mg, 0.500 mmol), KO^{t}Bu (63.9 mg, 0.569 mmol) and toluene-*d*$_8$ (334 mg) at 100 °C. The product was isolated as a brown oil. Yield: 73.4 mg, 0.372 mmol, 74%. **^{1}H NMR** (CDCl$_3$, 400 MHz): δ 7.34 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 1H, **H**6 of Ar-*o*CH$_3$), 7.19 (m, 5H, **H**3,4,5 of Ar-*o*CH$_3$ overlapped with **H**3' and **H**5'), 6.73 (t, $^3J_{\text{H-H}}$ = 7.3 Hz, 1H, **H**4'), 6.65 (d, $^3J_{\text{H-H}}$ = 7.4 Hz, 2H, **H**2' and **H**6'), 4.28 (s, 2H, C**H**$_2$), 3.88 (br s, 1H, N**H**), 2.38 (s, 3H, C**H**$_3$) ppm. **^{13}C{^{1}H} NMR** (CDCl$_3$, 100 MHz): δ 148.4, 137.1, 136.5, 130.5, 129.4, 128.4, 127.6, 126.3, 117.6, 112.9, 46.5 (**C**H$_2$), 19.1 (**C**H$_3$) ppm.

13. *N*-(4-methoxybenzyl)aniline (**5d**)[15]



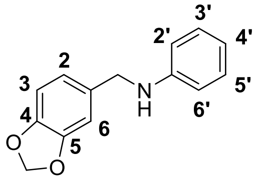
Catalyst **2d** (4.10 mg, 2.50 μmol), (4-methoxyphenyl)methanol (75.8 mg, 0.548 mmol), aniline (**4**) (47.9 mg, 0.514 mmol), KO^{t}Bu (65.0 mg, 0.579 mmol) and toluene-*d*$_8$ (327 mg) at 100 °C. The product was isolated as a pale brown solid. Yield: 72.9 mg, 0.342 mmol, 66%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.30 (d, $^3J_{\text{H-H}}$ = 8.79 Hz, 2H, **H**2 and **H**6 of Ar-OCH$_3$), 7.18 (m, 2H, Ar-**H**3' and **H**5'), 6.88 (d, $^3J_{\text{H-H}}$ = 8.71 Hz, 2H, **H**3 and **H**5 of Ar-OCH$_3$), 6.72 (t, $^3J_{\text{H-H}}$ = 7.26 Hz, 1H, Ar-**H**4'), 6.64 (d, $^3J_{\text{H-H}}$ = 7.52 Hz, 2H, **H**2' and **H**6'), 4.26 (s, 2H, C**H**$_2$), 3.93 (br s, 1H, N**H**), 3.81 (s, 3H, C**H**$_3$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 159.0, 148.3, 131.5, 129.4, 129.0, 117.6, 114.2, 113.0, 55.4, 47.9 ppm.

14. *N*-(4-bromobenzyl)aniline (**5e**)[15]



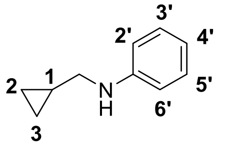
Catalyst **2d** (4.08 mg, 2.49 μmol), (4-bromophenyl)methanol (104 mg, 0.557 mmol), aniline (**4**) (46.7 mg, 0.501 mmol), KO^{t}Bu (60.3 mg, 0.537 mmol) and toluene-*d*$_8$ (320 mg) at 100 °C. The product was isolated as a brown oil. Yield: 95.9 mg, 0.366 mmol, 73%. **^{1}H NMR** (600 MHz, CDCl$_3$): δ 7.46 (d, $^3J_{\text{H-H}}$ = 8.42 Hz, 2H, **H**3 and **H**5 of Ar-Br),7.25 (d, $^3J_{\text{H-H}}$ = 8.53 Hz, 2H, Ar-**H**2 and **H**6 of Ar-Br), 7.17 (dd, $^3J_{\text{H-H}}$ = 8.47 Hz, $^3J_{\text{H-H}}$ = 7.37 Hz, 2H, **H**3' and **H**5'), 6.73 (tt, $^3J_{\text{H-H}}$ = 7.32 Hz, $^4J_{\text{H-H}}$ = 1.05 Hz, 1H, **H**4'), 6.61 (dd, $^3J_{\text{H-H}}$ = 8.57 Hz, $^4J_{\text{H-H}}$ = 1.04 Hz, 2H, **H**2' and **H**6'), 4.30 (s, 2H, C**H**$_2$), 4.05 (br s, 1H, N**H**) ppm. **^{13}C{^{1}H} NMR** (150 MHz, CDCl$_3$): δ 147.9, 138.7, 131.8, 129.4, 129.2, 127.7, 118.0, 113.0, 47.8 (**C**H$_2$) ppm.

15. *N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)aniline (**5s**)[15]



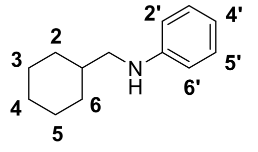
Catalyst **2d** (4.08 mg, 2.49 μmol), piperonyl alcohol (82.7 mg, 0.544 mmol), aniline (**4**) (48.4 mg, 0.520 mmol), KO^{t}Bu (60.4 mg, 0.538 mmol) and toluene-d_8 (313 mg) at 100 °C. The product was isolated as a brown solid. Yield: 54.2 mg, 0.238 mmol, 46%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.19 (dd, $^3J_{\text{H-H}}$ = 8.4 Hz, $^3J_{\text{H-H}}$ = 7.5 Hz, 2H, **H**3' and **H**5'), 6.89 (s, 1H, **H**6), 6.85 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 1H, **H**3), 6.79 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 1H, **H**2), 6.73 (t, $^3J_{\text{H-H}}$ = 7.4 Hz, 1H, **H**4'), 6.64 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 2H, **H**2' and **H**6'), 5.95 (s, 2H, -OC**H**$_2$O-),4.24 (s, 2H, C**H**$_2$NH), 3.98 (br s, 1H, N**H**) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 159.6, 148.2, 133.5, 129.4, 121.0, 120.7, 117.8, 113.0, 108.4, 108.2, 101.1, 48.3 (**C**H$_2$) ppm.

16. *N*-(cyclopropylmethyl)aniline (**5f**)[13]



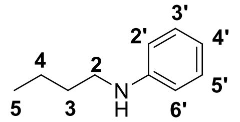
Catalyst **2d** (4.10 mg, 2.50 μmol), cyclopropylmethanol (42.7 mg, 0.593 mmol), aniline (**4**) (47.7 mg, 0.512 mmol), KO^{t}Bu (62.7 mg, 0.826 mmol) and toluene-d_8 (328 mg) at 100 °C. The product was isolated as a yellow oil. Yield: 45.5 mg, 0.309 mmol, 60%. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.18 (dd, $^3J_{\text{H-H}}$ = 8.19 Hz, $^3J_{\text{H-H}}$ = 7.41 Hz, 2H, **H**3' and **H**5'), 6.70 (tt, $^3J_{\text{H-H}}$ = 7.30 Hz, $^4J_{\text{H-H}}$ = 1.0 Hz, 1H, **H**4'), 6.62 (dd, $^3J_{\text{H-H}}$ = 8.6 Hz, $^4J_{\text{H-H}}$ = 1.0 Hz, 2H, **H**2' and **H**6'), 3.80 (br s, 1H, N**H**), 2.96 (d, $^3J_{\text{H-H}}$ = 7.0 Hz, 2H, C**H**$_2$),1.10 (m, 1H, C**H**), 0.55 (m, 2H, C**H**$_2$ at position 2), 0.24 (m, 2H, C**H**$_2$ at position 3) ppm. **^{13}C{^{1}H} NMR** (100 MHz, CDCl$_3$): δ 148.6, 129.4, 117.4, 112.9, 49.2, 11.0, 3.58 ppm.

17. *N*-(cyclohexylmethyl)aniline (**5g**)[14]



Catalyst **2d** (4.06 mg, 2.48 μmol), cyclohexylmethanol (61.5 mg, 0.539 mmol), aniline (**4**) (45.7 mg, 0.491 mmol), KO^{t}Bu (60.6 mg, 0.540 mmol) and toluene-d_8 (325 mg) at 100 °C. The product was isolated as a yellow oil. Yield: 71.5 mg, 0.378 mmol, 77%. **^{1}H NMR** (CDCl$_3$, 600 MHz): δ 7.16 (dd, $^3J_{\text{H-H}}$ = 8.4 Hz, $^3J_{\text{H-H}}$ = 7.3 Hz, 2H, **H**3' and **H**5'), 6.67 (tt, $^3J_{\text{H-H}}$ = 7.4 Hz, $^4J_{\text{H-H}}$ = 1.0 Hz, 1H, **H**4'), 6.60 (d, $^3J_{\text{H-H}}$ = 7.7 Hz, 2H, **H**2' and **H**6'), 3.76 (br s, 1H, N**H**), 2.95 (d, $^3J_{\text{H-H}}$ = 6.7 Hz, 2H, C**H**$_2$),1.82 (apparent d, $^3J_{\text{H-H}}$ = 13.5 Hz, 2H, Cy-C**H**$_2$ on position 2), 1.74 (apparent dt, $^3J_{\text{H-H}}$ = 12.8 Hz, $^3J_{\text{H-H}}$ = 3.5 Hz, 2H, Cy-C**H**$_2$ on position 6), 1.68 (apparent d, $^2J_{\text{H-H}}$ = 12.3 Hz, 1H, Cy-C**H** on position 1), 1.22 (m, 4H, Cy-C**H**$_2$ on position 3 and 5), 0.99 (qd, $^{3}J_{H\text{-}H}$ = 11.9, $^{3}J_{H\text{-}H}$ = 3.3, 2H, Cy-C**H**$_2$ at position 4) ppm. **^{13}C{^{1}H} NMR** (CDCl$_3$, 150 MHz): δ 148.7, 129.4, 117.1, 112.8, 50.8, 37.7, 31.5, 26.7, 26,1 ppm.

17. *N*-butylaniline (**5h**)[15]



Catalyst **2d** (4.10 mg, 2.50 μmol), 1-butanol (**3.5i**) (45.7 mg, 0.617 mmol), aniline (**4**) (46.2 mg, 0.496 mmol), KO^{t}Bu (62.0 mg, 0.550 mmol) and toluene-d_8 (362 mg) at 100 °C. The product was isolated as a yellow oil. Yield: 71.5 mg, 0.378 mmol, 77%. **^{1}H NMR** (CDCl$_3$, 600 MHz): δ 7.17 (dd, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, **H**3' and **H**5'), 6.68 (tt, $^{3}J_{H\text{-}H}$ = 7.2 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz, 1H, **H**4'), 6.60 (dd, $^{3}J_{H\text{-}H}$ = 8.7 Hz, $^{4}J_{H\text{-}H}$ = 1.0 Hz, 2H, **H**2' and **H**6'), 3.58 (br s, 1H, NH), 3.11 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2H, -NHC**H**$_2$-), 1.61 (qui, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, -C**H**$_2$CH$_2$CH$_3$), 1.43 (sxt, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, -C**H**$_2$CH$_3$) 0.96 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 3H, C**H**$_3$) ppm. **^{13}C{^{1}H} NMR** (CDCl$_3$, 150 MHz): δ 129.4, 117.2, 112.8, 43.8, 31.8, 20.5, 14.1 ppm.

SI-6. NMR analysis for catalysis products

(a) NMR analysis of product *N*-benzyl aniline (**5a**)

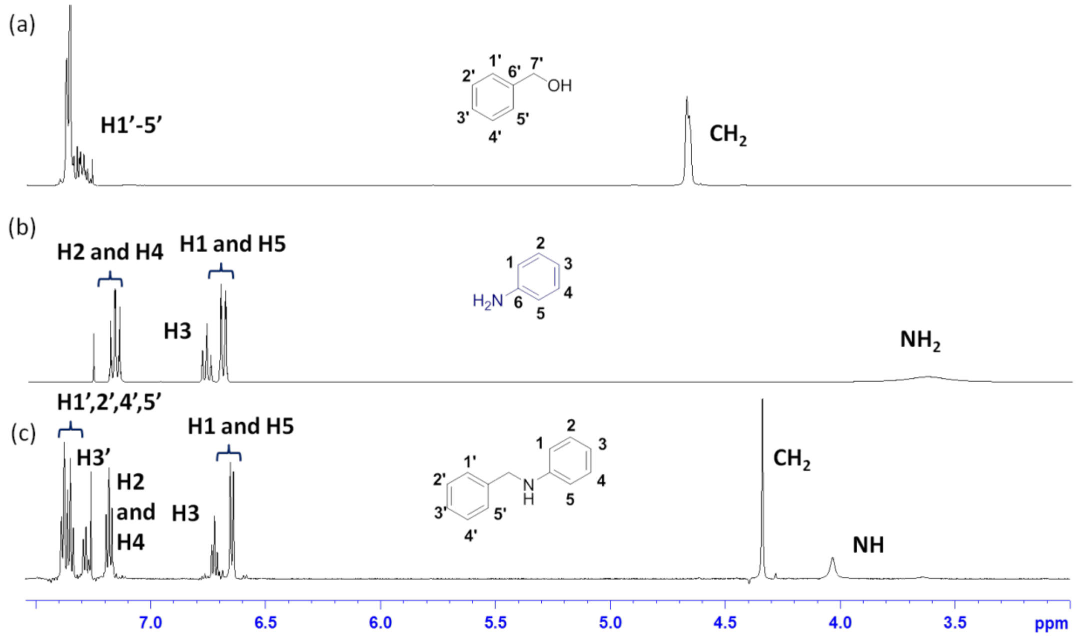


Figure S21 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material aniline (**4**), starting material benzyl alcohol (**3**), and (c) final product *N*-benzyl aniline (**5a**).

(b) NMR analysis of *N*-(4-methylbenzyl)aniline (**5b**)

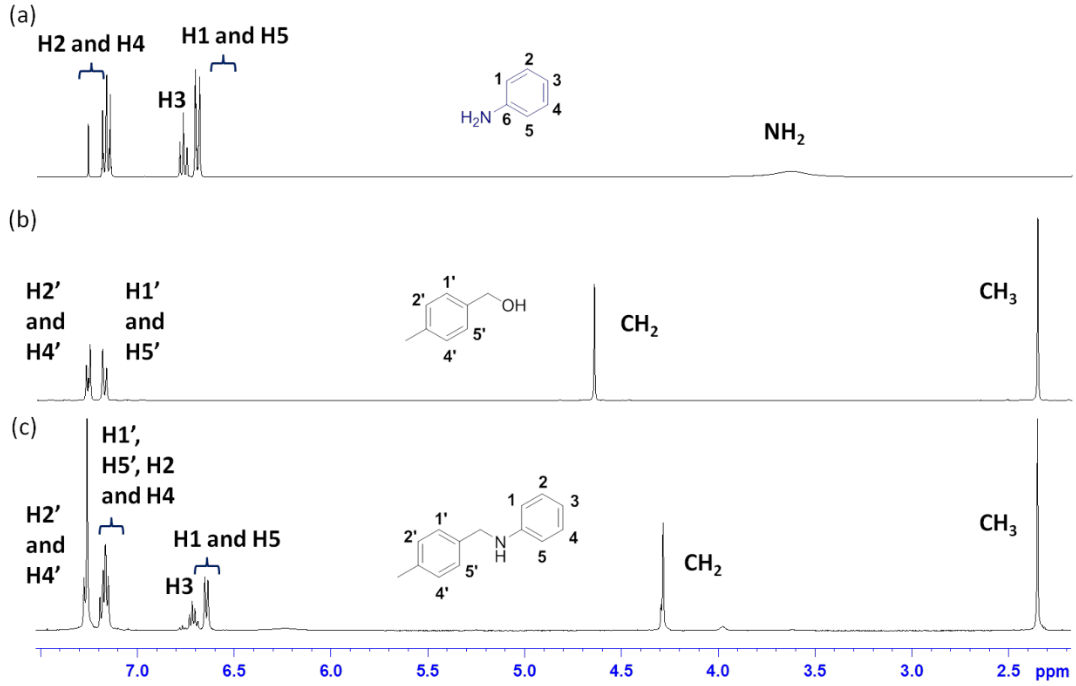


Figure S22 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material aniline (**4**), starting material 4-methylbenzyl alcohol, and (c) final product *N* (4-methylbenzyl)aniline (**5b**).

(c) NMR analysis of *N*-(2-methylbenzyl)aniline (**5c**)

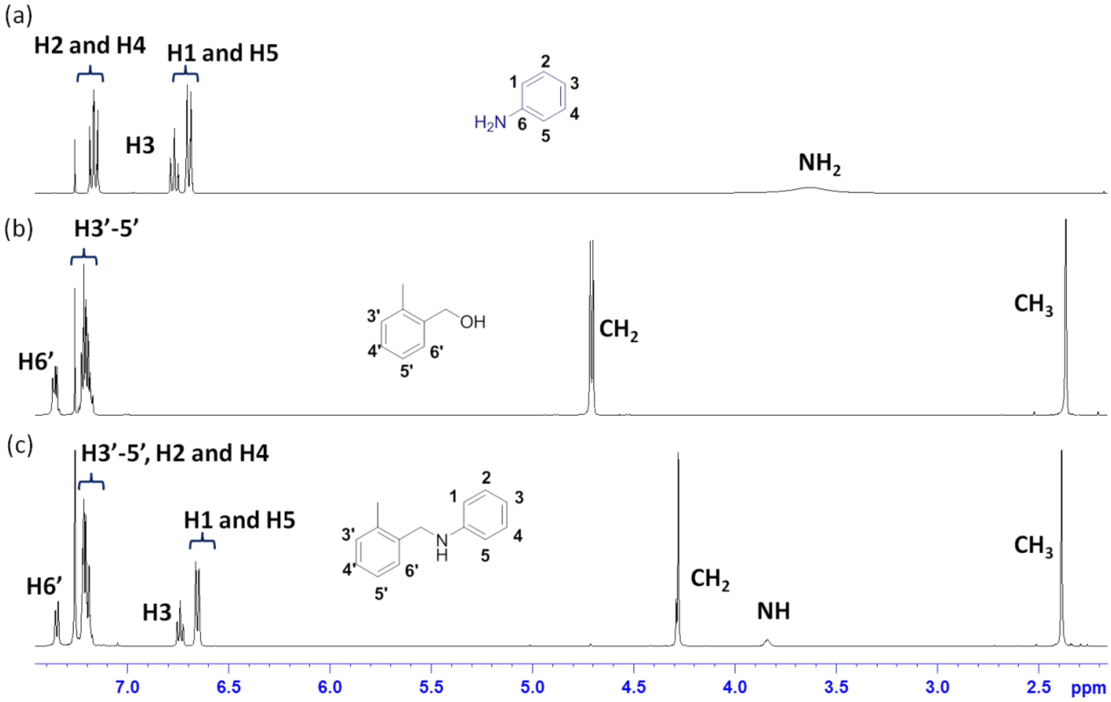


Figure S23 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material aniline (**4**), starting material 4-methylbenzyl alcohol, and (c) final product *N* (2-methylbenzyl)aniline (**5c**).

(d) NMR analysis of product *N*-(4-methoxybenzyl)aniline (**5d**)

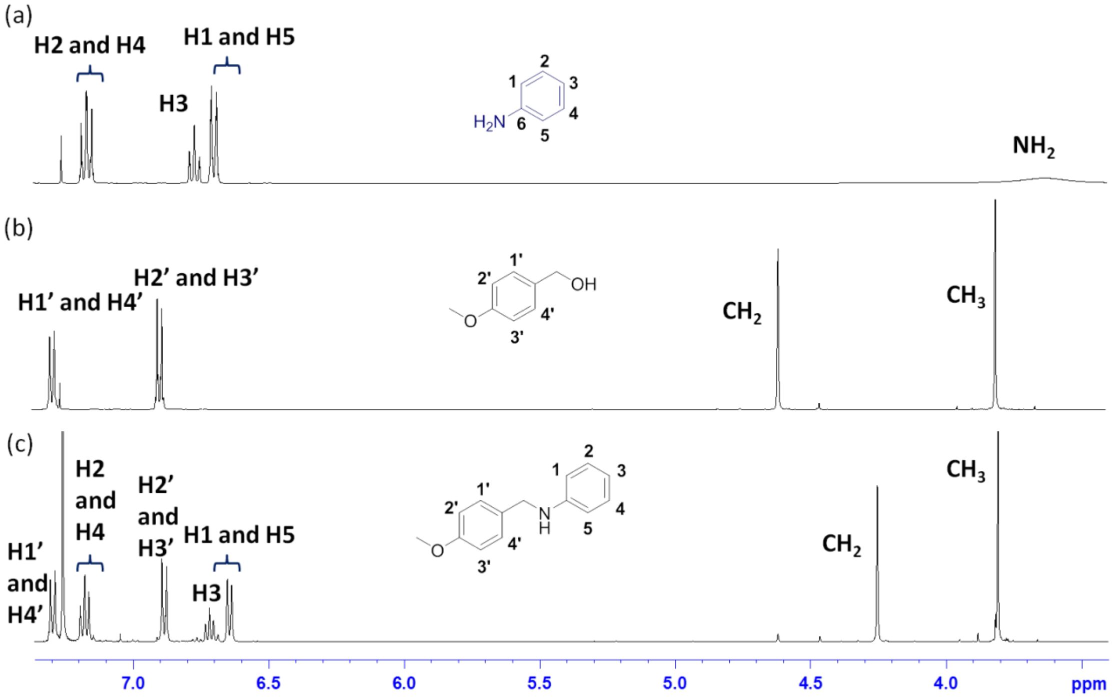


Figure S24 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material aniline (**4**), starting material 4-methoxybenzyl alcohol, and (c) final product *N*-(4-methoxybenzyl)aniline (**5d**).

(e) NMR analysis of product *N*-(4-bromobenzyl)aniline (**5e**)

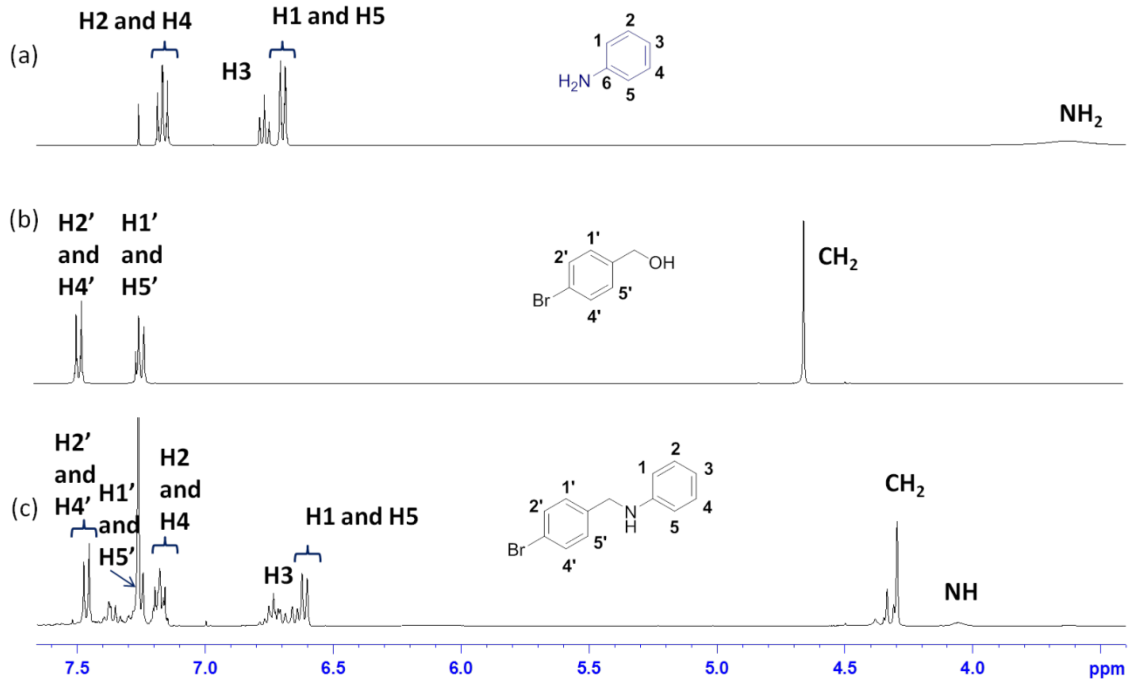


Figure S25 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material aniline (**4**), starting material 4-bromobenzyl alcohol, and (c) final product *N*-(4-bromobenzyl)aniline (**5e**).

(f) NMR analysis of product *N*-(cyclopropylmethyl)aniline (**5f**)

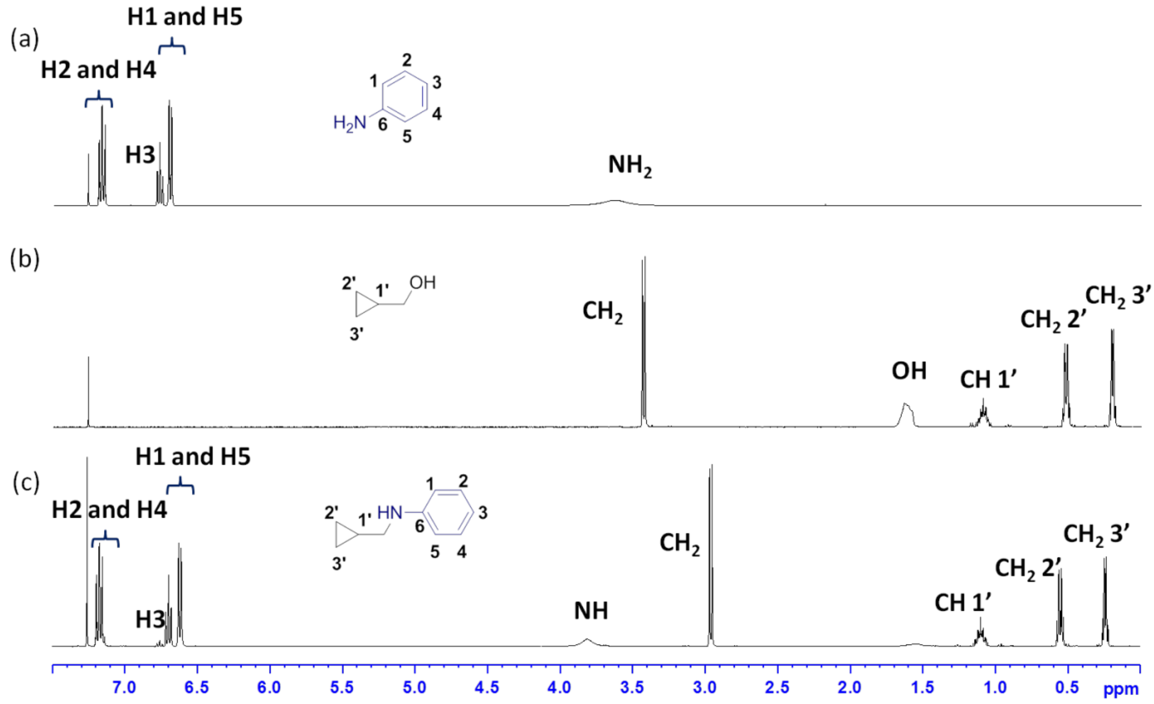


Figure S26 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material aniline (**4**), starting material cyclopropylmethanol, and (c) final product *N*-(cyclopropylmethyl)aniline (**5f**).

(g) NMR analysis of product *N*-(cyclohexylmethyl)aniline (**5g**)

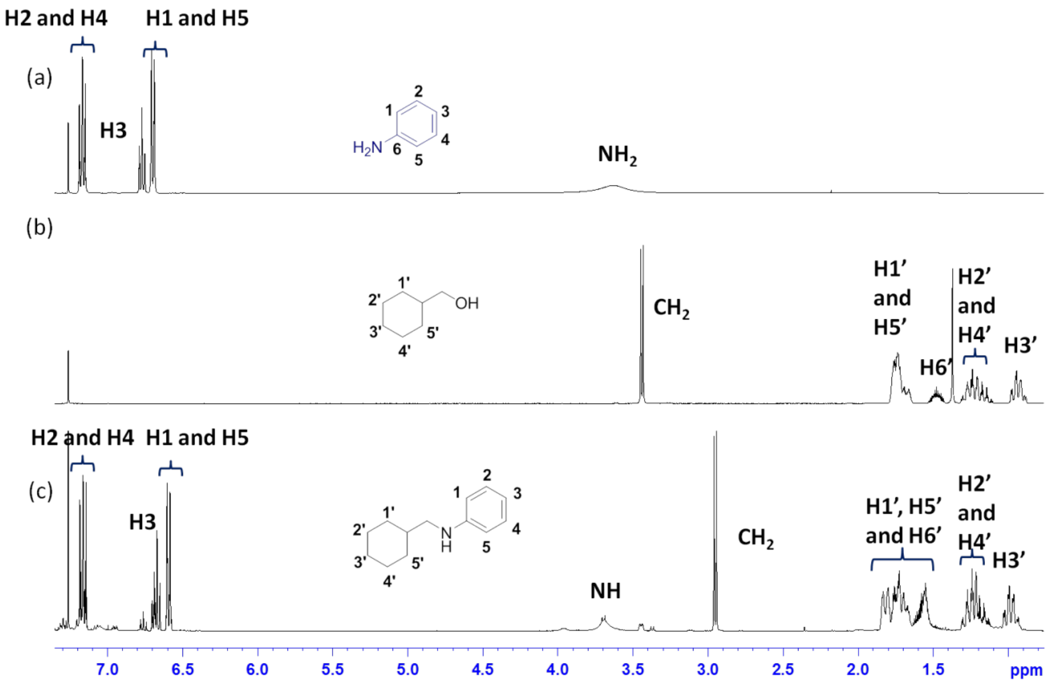


Figure S27 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material aniline (**4**), starting material cyclohexylmethanol, and (c) final product *N*-(cyclohexylmethyl)aniline (**5g**).

(h) NMR analysis of product *N*-butylaniline (**5h**)

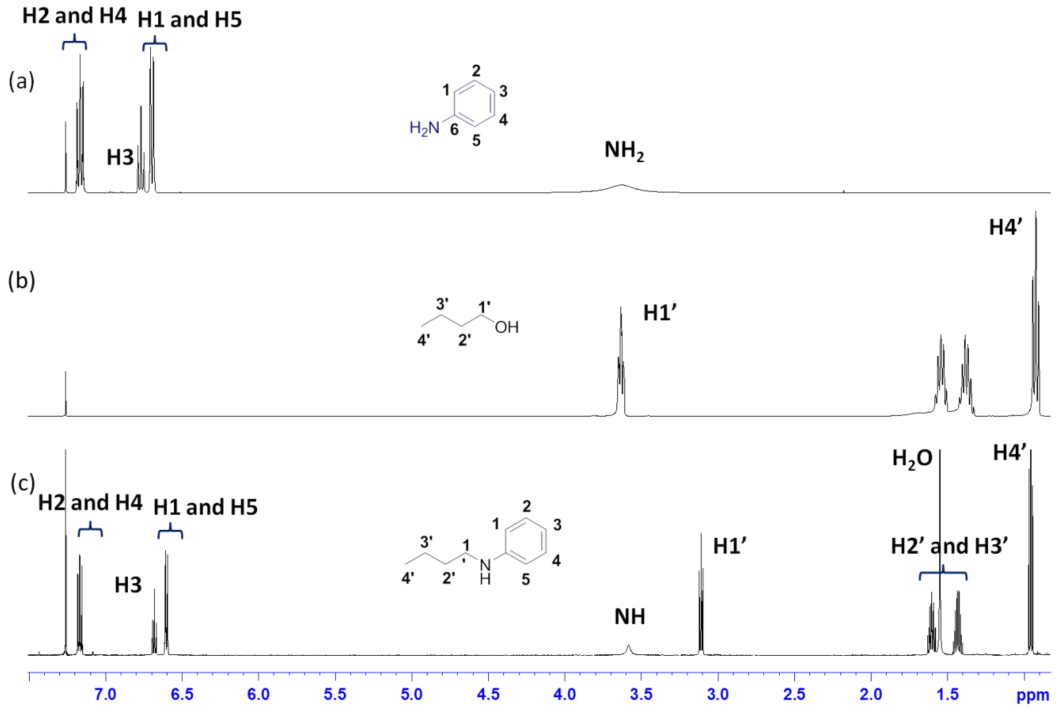


Figure S28 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material aniline (**4**), starting material 1-butanol, and (c) final product *N*-butylaniline (**5h**).

(i) NMR analysis of product *N*-benzyl-4-methylaniline (**5i**)

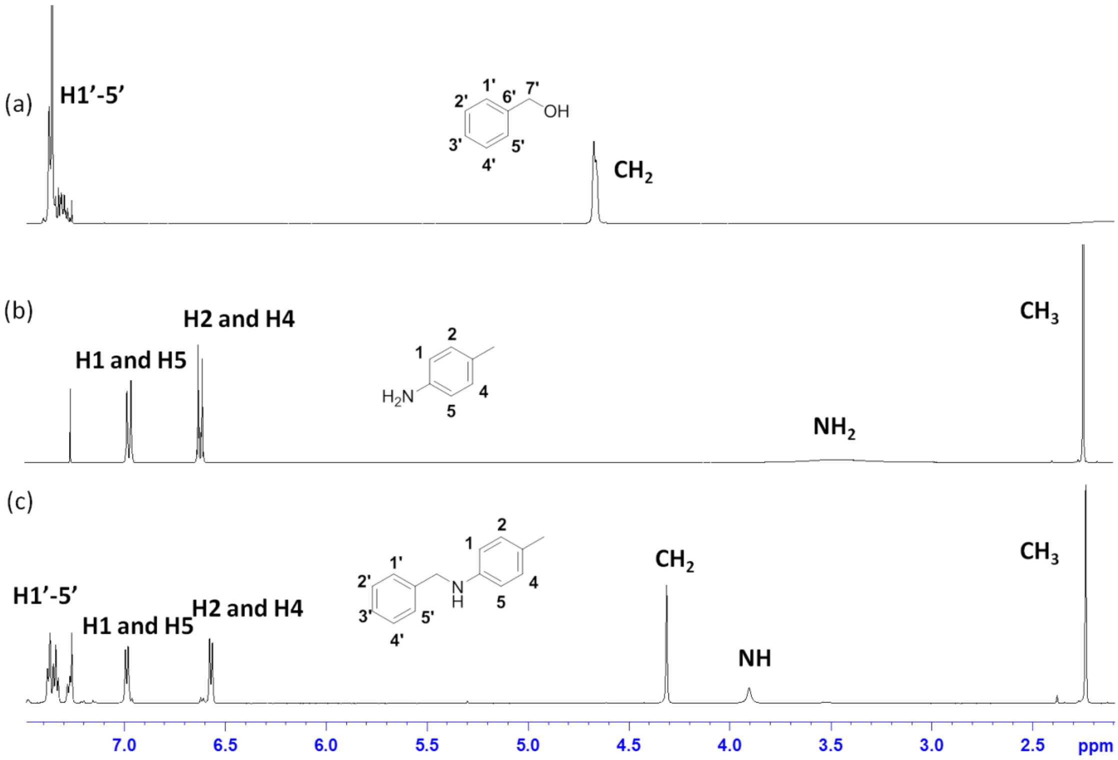


Figure S29 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-methylaniline, and (c) final product *N*-benzyl-4-methylaniline (**5i**).

(j) NMR analysis of product *N*-benzyl-4-fluoraniline (**5j**)

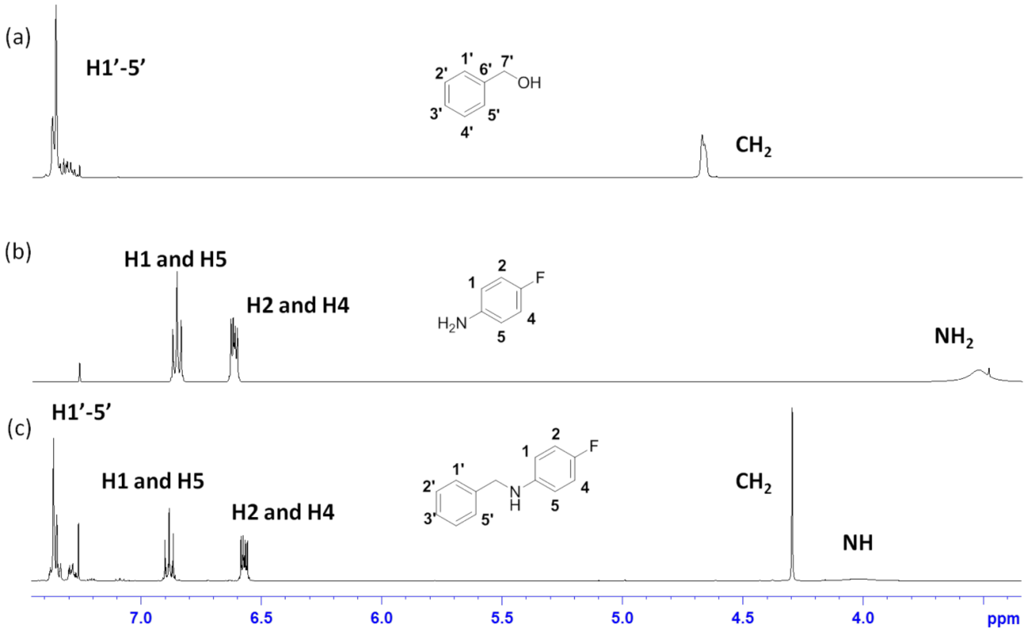


Figure S30 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-fluoroaniline, and (c) final product *N*-benzyl-4-fluoroaniline (**5j**).

(k) NMR analysis of product *N*-benzyl-4-chloroaniline (**5k**)

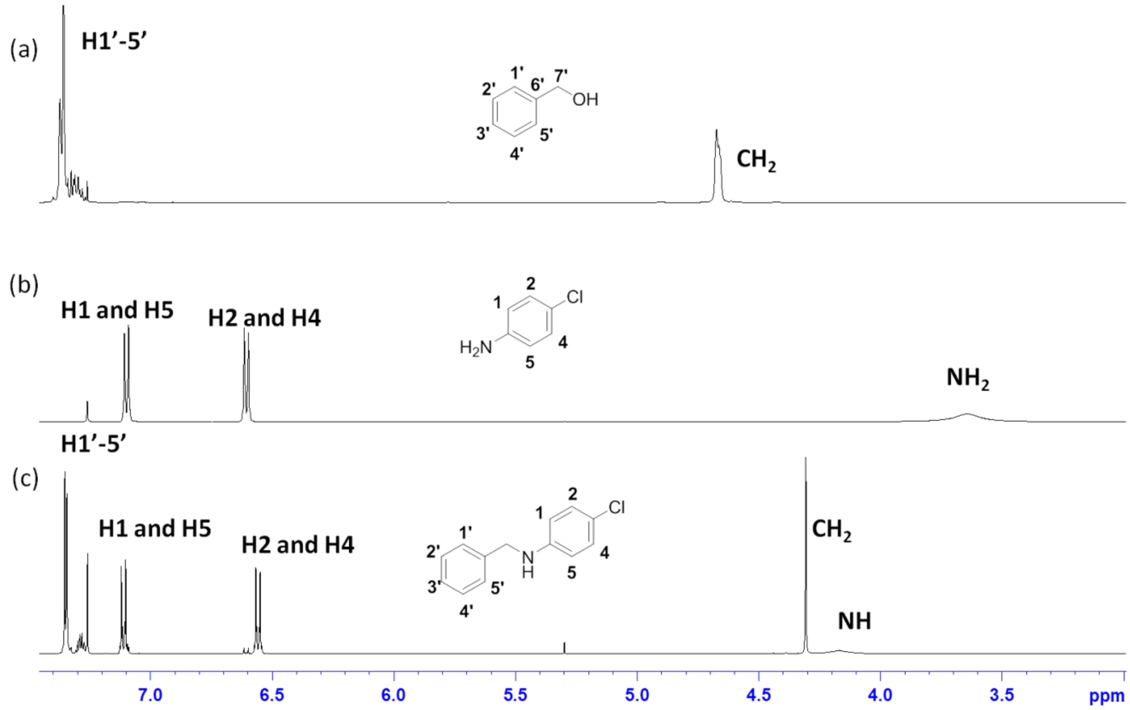


Figure S31 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-chloroaniline, and (c) final product *N*-benzyl-4-chloroaniline (**5k**).

(l) NMR analysis of product *N*-benzyl-4-bromoaniline (**5l**)

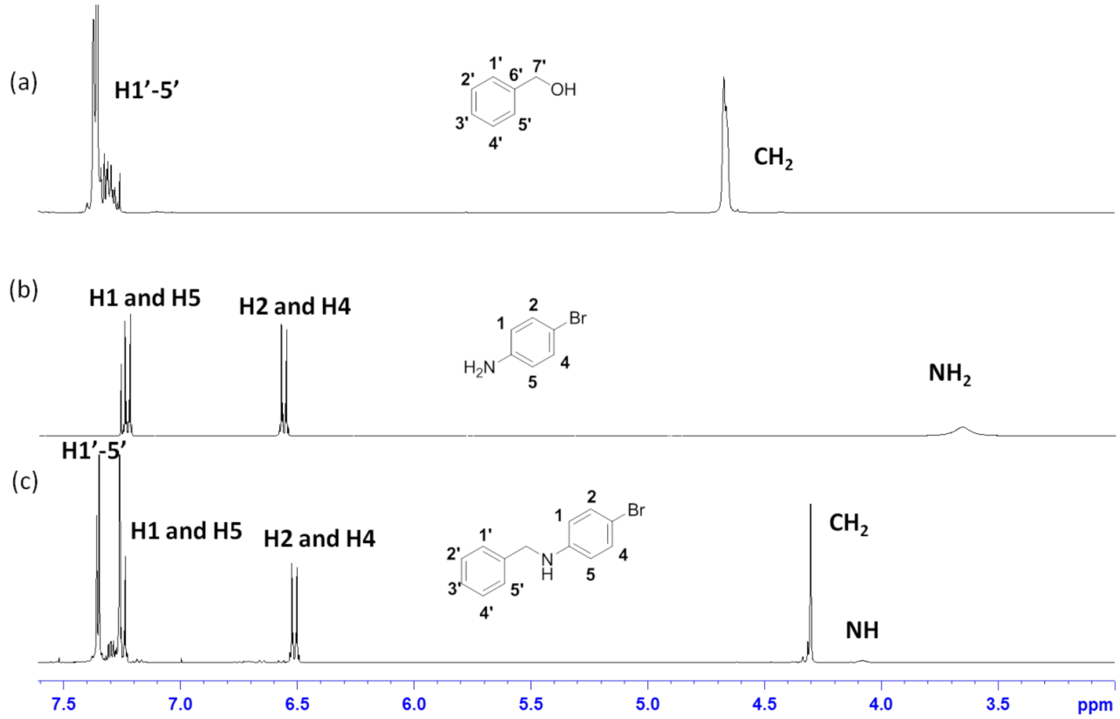


Figure S32 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-bromoaniline, and (c) final product *N*-benzyl-4-bromoaniline (**5l**).

(m) NMR analysis of product *N*-benzyl-4-iodoaniline (**5m**)

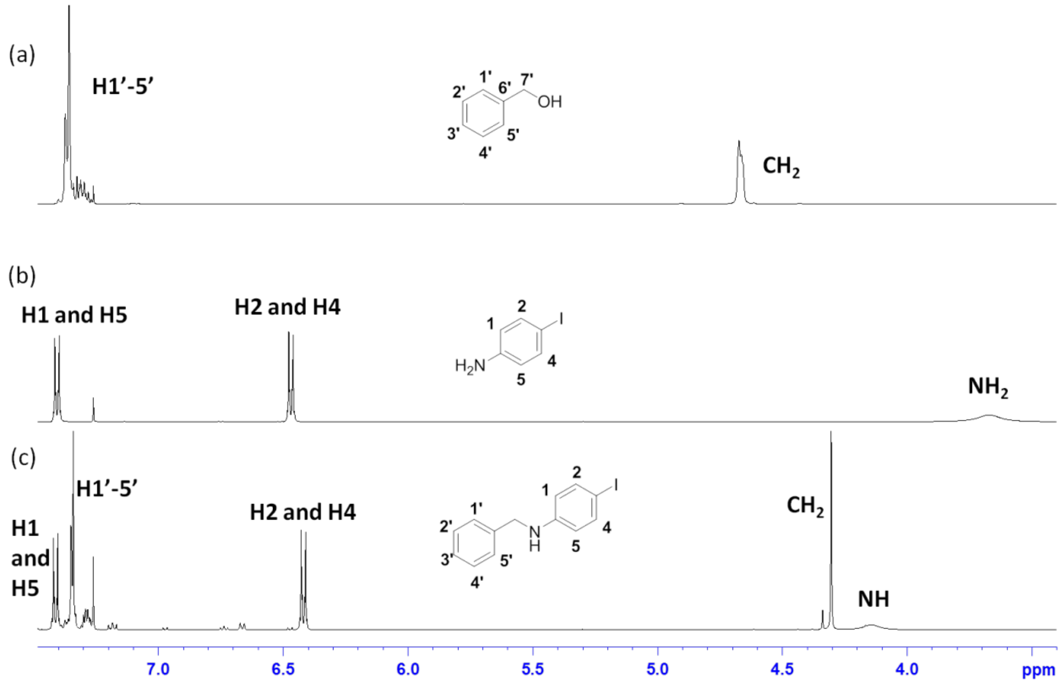


Figure S33 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-iodoaniline, and (c) final product *N*-benzyl-4-iodoaniline (**5m**).

(n) NMR analysis of product *N*-benzyl-4-methoxyaniline (**5n**)

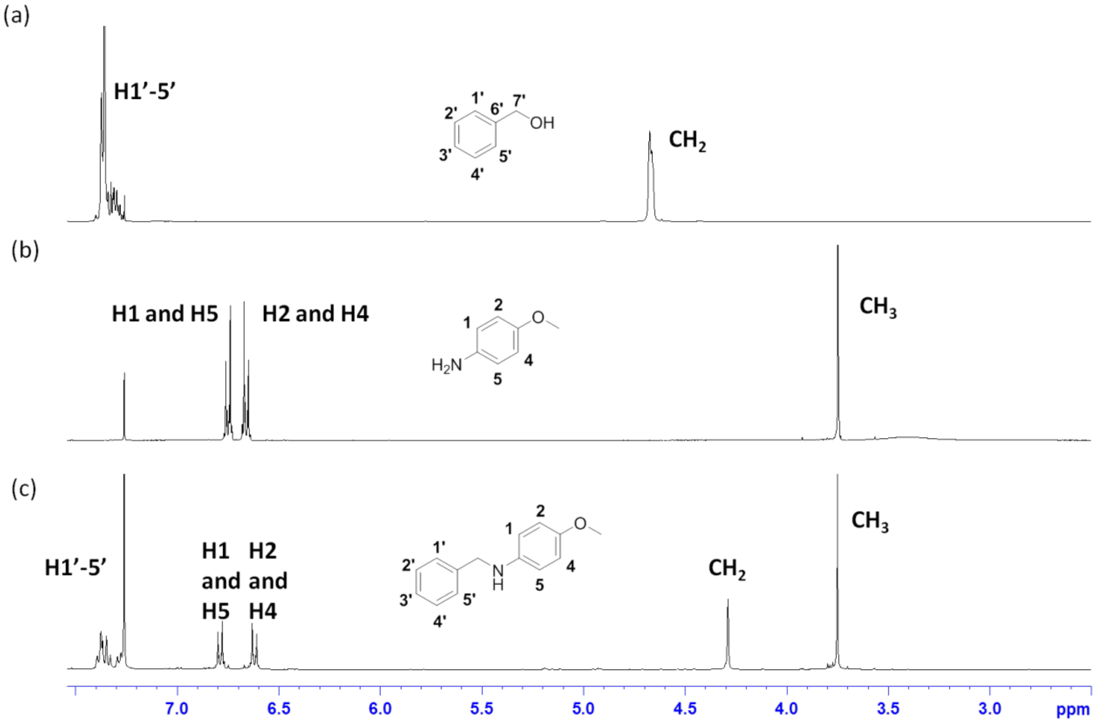


Figure S34 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-anisidine, and (c) final product *N*-benzyl-4-methoxyaniline (**5n**).

(o) NMR analysis of product *N*-benzylpyridin-2-amine (**5o**)

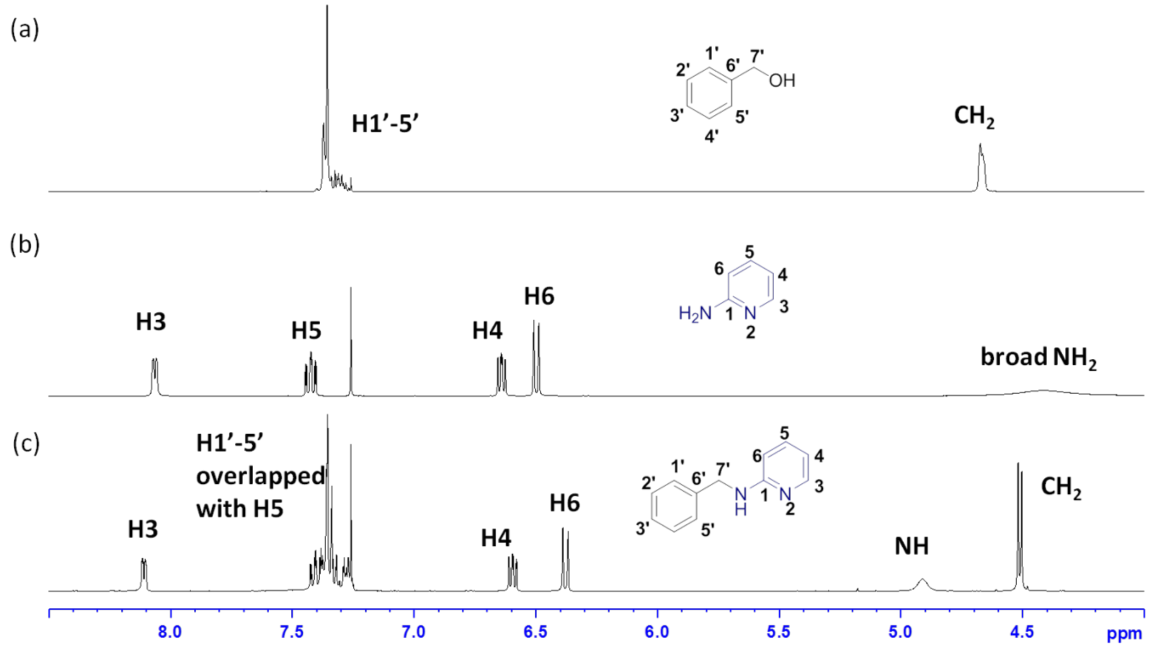


Figure S35 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material benzyl alcohol (**3**), starting material 2-aminopyridine, and (c) final product *N*-benzylpyridin-2-amine (**5o**).

(p) NMR analysis of product *N*-benzylnaphthalen-1-amine (**5p**)

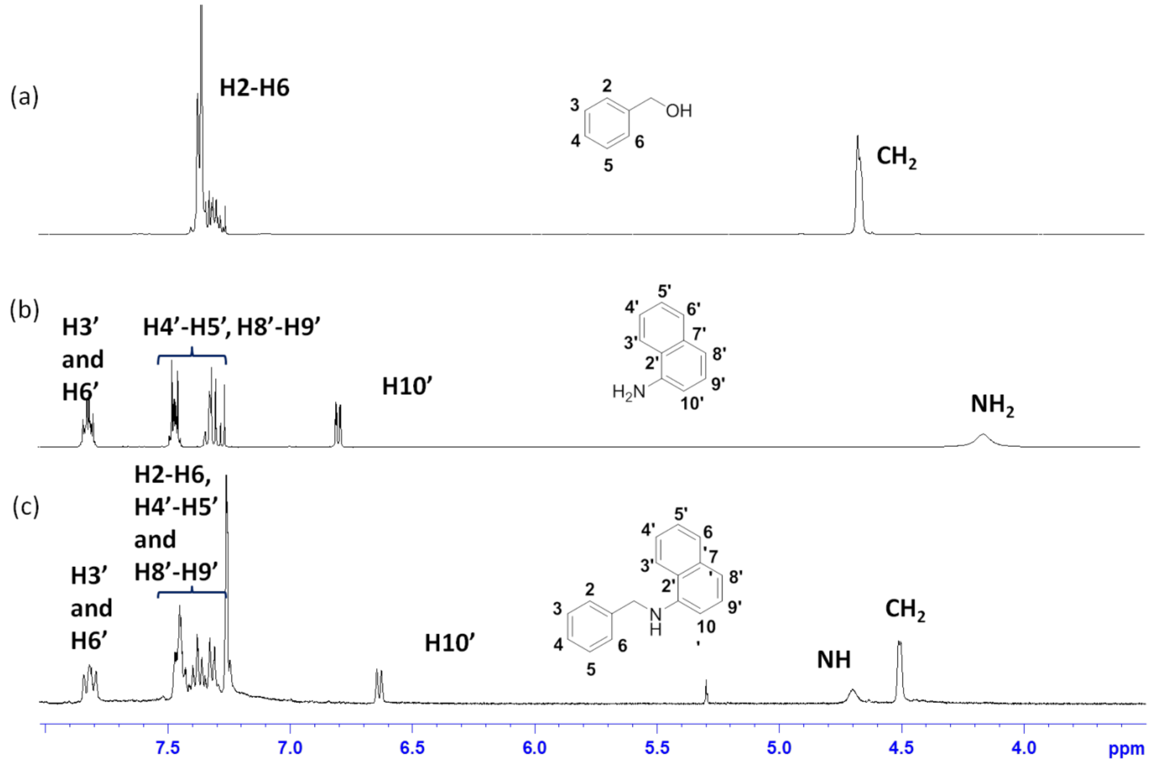


Figure S36 Stacked NMR plot (400MHz, $CDCl_3$) of (a) starting material benzyl alcohol (**3**), starting material naphthalen-1-amine, and (c) final product *N*-benzylnaphthalen-1-amine (**5p**).

(q) NMR analysis of product *N*-benzyl-4-morpholinoaniline (**5q**)

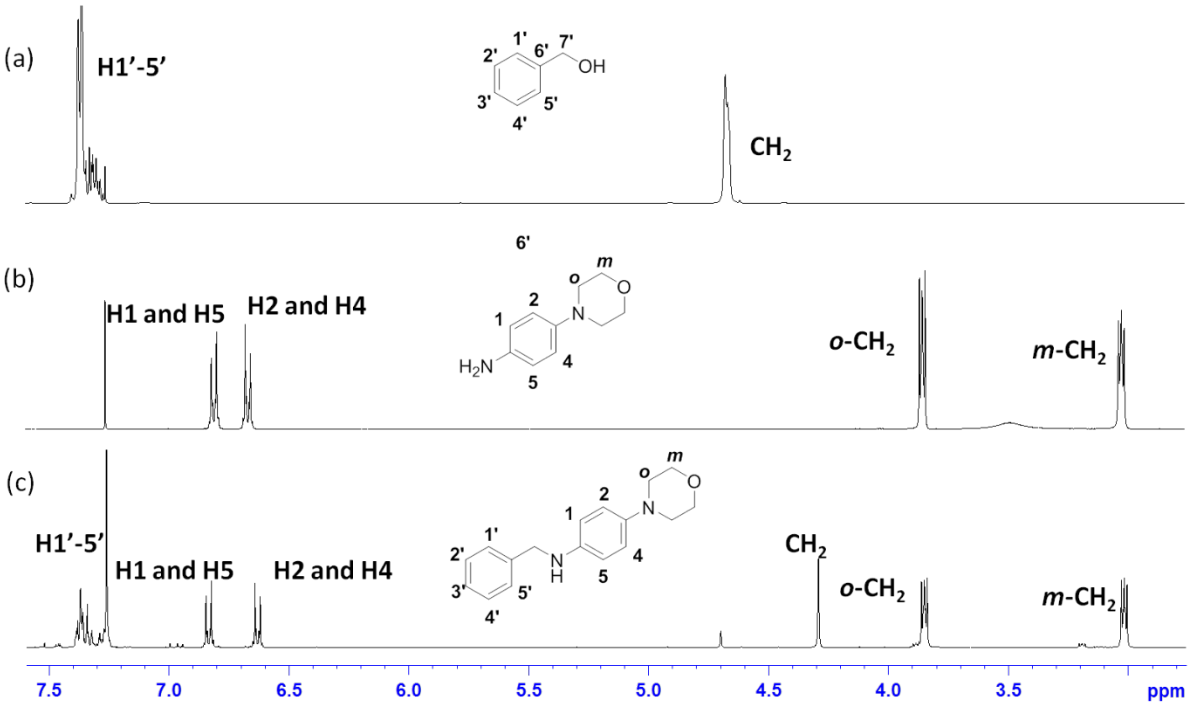


Figure S37 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material benzyl alcohol (**3**), starting material 4-morpholinoaniline, and (c) final product *N*-benzyl-4-morpholinoaniline (**5q**).

(r) NMR analysis of product dibenzylamine (**5r**) in catalysis mixture

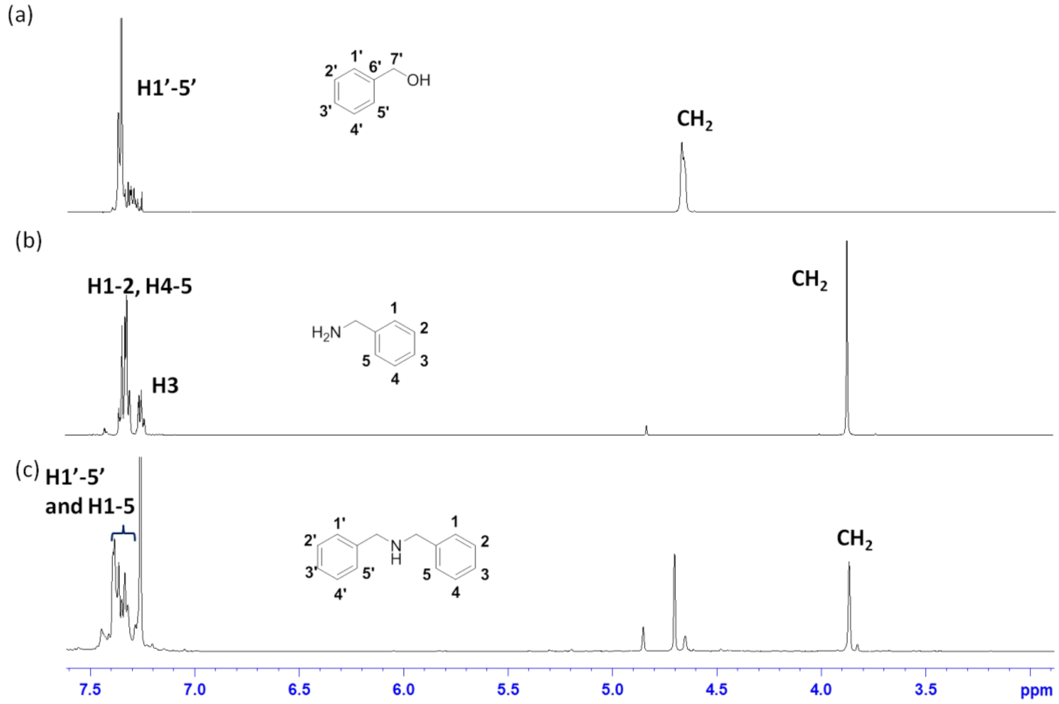


Figure S38 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material benzyl alcohol (**3**), starting material benzyl amine, and (c) dibenzylamine (**5r**) in catalysis mixture at end of reaction.

(s) NMR analysis of product *N*-(benzo[d][1,3]dioxol-5-ylmethyl)aniline (**5s**)

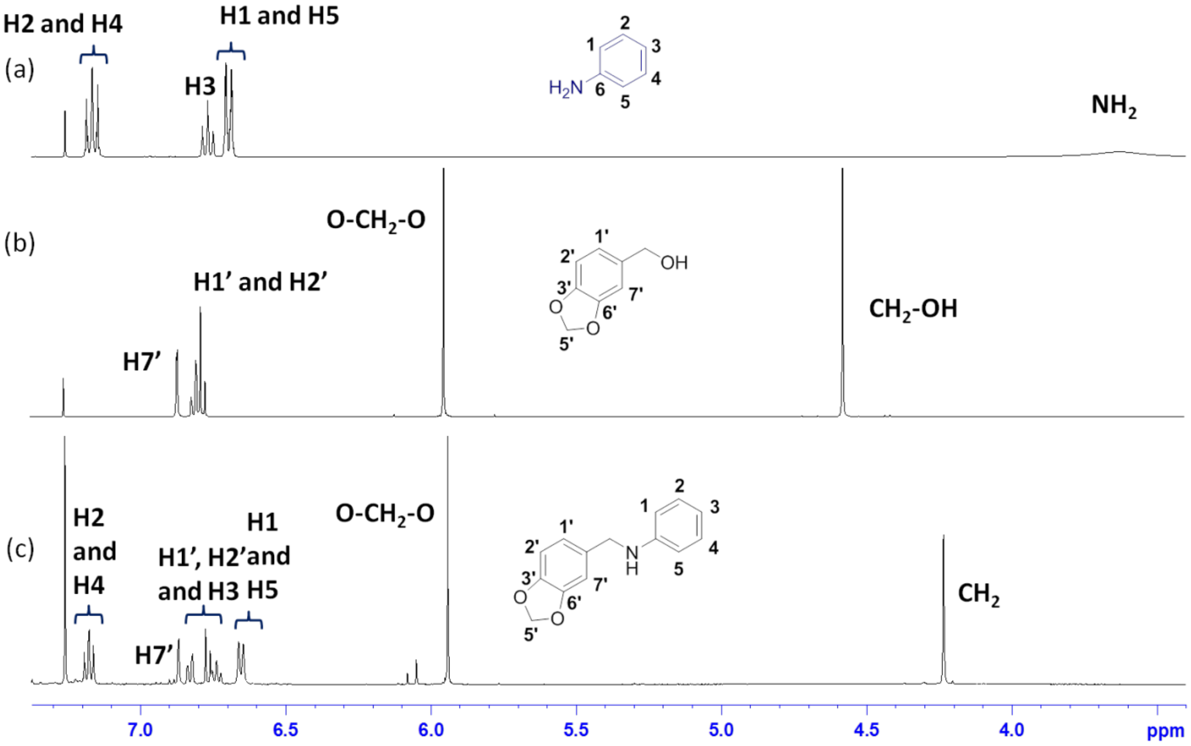


Figure S39 Stacked NMR plot (400MHz, CDCl$_3$) of (a) starting material benzyl alcohol (**3**), starting material benzo[d][1,3]dioxol-5-ylmethanol, and (c) final product *N*-(benzo[d][1,3]dioxol-5-ylmethyl)aniline (**5s**).

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