Supporting Information for

Catalysed Tandem C-N/C-C Bond Formation for the Synthesis of Tricyclic Indoles using Ir(III) Pyrazolyl-*1,2,3*-Triazolyl Complexes

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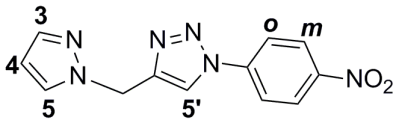
Part A: Synthesis of Ligands

Part B: Synthesis of Ir and Rh Complexes

Part C: X-ray Crystallography

Part A: Synthesis of Ligands

A.1 Synthesis of 4-((1*H*-pyrazol-1-yl)methyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazole (2c)

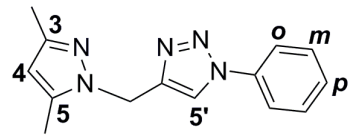


1-(Prop-2-yn-1-yl)-1*H*-pyrazole (96 mg, 0.90 mmol) and 1-azido-4-nitrobenzene (148 mg, 0.902 mmol) were added into a deoxygenated mixture of 2-propanol and water (2:1 (v/v), 8 mL). Sodium L-ascorbate (39 mg, 0.20 mmol, 20 mol%) was added and the reaction stirred for 5 mins prior to the addition of $CuSO_4.5H_2O$ (7.2 mg, 0.029 mmol, 3 mol%). The reaction mixture was stirred overnight at room temperature under nitrogen, during which time a dark brown precipitate formed. The 2-propanol was removed *in vacuo* and the residue was filtered and washed with a saturated aqueous solution of Na_2EDTA until the filtrate became colourless. The crude product was then dissolved in dichloromethane, dried with anhydrous magnesium sulphate and filtered through celite®. The solvent was removed *in vacuo* to yield ligand **2c** as a yellow solid (206 mg, 85 %). m.p. 129-132 °C (decomposed). HR-MS (ESI^+, MeOH): *m/z* (%): 293.0833 (100 %) $[M+Na]^+$ (Calculated $[M+Na]^+$ = 293.0757) amu.Elemental Analysis: Found: C, 52.80; H, 3.71 and N, 30.07; Calculated for $C_{12}H_{10}N_6O_2.0.25H_2O$: C, 52.46; H, 3.85 and N, 30.59 %.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H, *m*-C**H** of **Ph**NO_2), 8.07 (s, 1H, **H5'**), 7.94 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H, *o*-C**H** of **Ph**NO_2), 7.59 (d, $^3J_{H4\text{-}H5}$ = 2.1 Hz, 1H, **H5**), 7.57 (d, $^3J_{H3\text{-}H4}$ = 2.1 Hz, 1H, **H3**), 6.31 (t, $^3J_{H\text{-}H}$ = 2.1 Hz, 1H, **H4**), 5.56 (s, 2H, C**H**$_2$) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 147.5 (**C**$_q$ of **Ph**NO_2), 145.5 (**C**$_q$ of Triaz), 141.1 (*ipso*-**C** to NO_2 of **Ph**NO_2), 140.5 (**C**3), 129.9 (**C**5), 125.7 (*m*-**C**H of **Ph**NO_2), 120.9 (**C**5'), 120.7 (*o*-**C**H of **Ph**NO_2), 106.5 (**C**4), 47.4 (**C**H_2) ppm.

A.2 Synthesis of 4-((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-1-phenyl-1*H*-1,2,3-triazole (3a)



3,5-Dimethyl-1-(prop-2-yn-1-yl)-1*H*-pyrazole (566 mg, 4.22 mmol) and azidobenzene (517 mg, 4.34 mmol) were added into a deoxygenated mixture of 2-propanol and water (2:1 (v/v),12 mL). Sodium L-ascorbate (171 mg, 0.862 mmol, 20 mol %) was added and the reaction mixture was stirred for 5 mins prior to the addition of $CuSO_4.5H_2O$ (34 mg, 0.13 mmol, 3 mol%). The reaction mixture was then stirred for 3 days at room temperature under nitrogen, during which time a pale yellow precipitate formed. The 2-propanol was removed *in vacuo* and the residue was filtered and washed with a saturated aqueous solution of Na_2EDTA until the filtrate became colourless. The crude product was then dissolved in dichloromethane, dried with anhydrous magnesium sulphate and filtered through celite®. The solvent was removed *in vacuo* to yield ligand **3a** as a pale yellow solid (812 mg, 76 %). m.p. 101-113 °C.

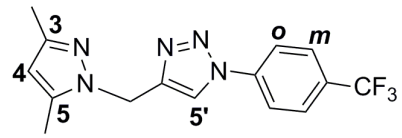
HR-MS (ESI^+, MeOH): *m/z* (%): 276.1667 (100 %) $[M + Na]^+$ (Calculated $[M + Na]^+$ = 276.1220) amu.

Elemental Analysis: Found: C, 65.37; H, 5.93 and N, 27.46; Calculated for $C_{14}H_{15}N_5.0.25H_2O$: C, 65.22; H, 6.06 and N, 27.17 %.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (s, 1H, **H5'**), 7.69 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, *o*-C**H** of **Ph**), 7.50 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, *m*-C**H** of **Ph**), 7.42 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, *p*-C**H** of **Ph**), 5.82 (s, 1H, **H4**), 5.38 (s, 2H, C$\mathbf{H}_2$), 2.34 (s, 3H, C5-C$\mathbf{H}_3$), 2.23 (s, 3H, C3-C$\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.3 (**C**3), 145.3 (**C$_q$** of Triaz), 137.1 (**C$_q$** of **Ph**), 139.6 (**C**5), 129.9 (*m*-**C**H of **Ph**), 129.0 (*p*-**C**H of **Ph**), 120.7 (**C**5'), 120.5 (*o*-**C**H of **Ph**), 105.8 (**C**4), 44.6 (**C**H_2), 13.7 (C3-**C**H_3), 11.3 (C5-**C**H_3) ppm.

A.3 Synthesis of 4-((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (3b)



3,5-Dimethyl-1-(prop-2-yn-1-yl)-1*H*-pyrazole (320 mg, 2.39 mmol) and 1-azido-4-(trifluoromethyl)benzene (394 mg, 2.11 mmol) were added into a deoxygenated mixture of 2-propanol and water (2:1 (v/v), 12 mL). Sodium L-ascorbate (104 mg, 5.27 mmol, 20 mol%) was added and the reaction stirred for 5 mins prior to the addition of $CuSO_4.5H_2O$ (22 mg, 0.14 mmol, 4 mol%). The reaction mixture was stirred overnight at room temperature under nitrogen, during which time a pale yellow precipitate formed. The 2-propanol was removed *in vacuo* and the residue was filtered and washed with a saturated aqueous solution of Na_2EDTA until the filtrate became colourless. The crude product was then dissolved in dichloromethane, dried with anhydrous magnesium sulphate and filtered through celite®. The solvent was removed *in vacuo* to yield ligand **6** as a yellow solid (615 mg, 91 %). m.p. 134-136 °C.

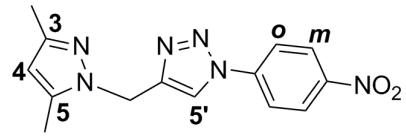
HR-MS (ESI^+, MeOH): *m/z* (%): 322.2500 (100 %) $[M+H]^+$ (Calculated $[M+H]^+$ = 322.1274) amu.

Elemental Analysis: Found: C, 55.85; H, 4.62 and N, 21.46; Calculated for $C_{15}H_{14}F_3N_5$: C, 56.07; H, 4.39 and N, 21.80 %.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1H, **H5'**), 8.39 (d, $^2J_{H\text{-}H}$ = 8.6 Hz, 2H, *m*-C**H** of **Ph**CF_3), 7.93 (d, $^2J_{H\text{-}H}$ = 8.6 Hz, 2H, *o*-C**H** of **Ph**CF_3), 5.83 (s, 1H, **H4**), 5.38 (s, 2H, C$\mathbf{H}_2$), 2.35 (s, 3H, C5-C$\mathbf{H}_3$), 2.23 (s, 3H, C3-C$\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.5 (**C**3), 145.8 ($\mathbf{C_q}$ of Triaz), 139.7 (**C**5), 139.4 ($\mathbf{C_q}$ of **Ph**CF_3), 130.9 (q, $^2J_{C\text{-}F}$ = 32.9, *ipso*-C to CF_3 of **Ph**CF_3), 127.2 (*m*-**C**H of **Ph**CF_3), 123.6 (q, $^1J_{C\text{-}F}$ = 269.0 Hz, **C**F_3), 120.7 (**C**5'), 120.6 (*o*-**C**H of **Ph**CF_3), 105.8 (**C**4), 44.4 (**C**H_2), 13.7 (C3-**C**H_3), 11.3 (C5-**C**H_3) ppm.

A.4 Synthesis of 4-((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazole (3c)



3,5-Dimethyl-1-(prop-2-yn-1-yl)-1*H*-pyrazole (230 mg, 1.71 mmol) and 1-azido-4-nitrobenzene (281 mg, 1.71 mmol) were added into a deoxygenated mixture of 2-propanol and water (2:1 (v/v), 12 mL). Sodium L-ascorbate (79 mg, 0.40 mmol, 20 mol %) was added and the reaction stirred for 5 mins prior to the addition of $CuSO_4.5H_2O$ (14 mg, 0.086 mmol, 3 mol%). The reaction mixture was stirred overnight at room temperature under nitrogen, during which time a pale yellow precipitate formed. The 2-propanol was removed *in vacuo* and the residue was filtered and washed with a saturated aqueous solution of Na_2EDTA until the filtrate became colourless. The crude product was then dissolved in dichloromethane, dried with anhydrous magnesium sulphate and filtered through celite®. The solvent was removed *in vacuo* to yield ligand **3c** as a pale yellow solid (357 mg, 70 %). m.p. 155-157 °C.

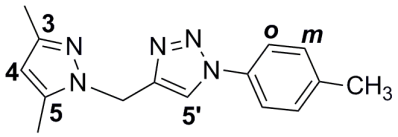
HR-MS (ESI^+, MeOH): *m/z* (%): 299.1667 (100 %) $[M+H]^+$ (Calculated $[M+H]^+$ = 299.1251) amu.

Elemental Analysis: Found: C, 55.46; H, 4.78 and N, 27.49; Calculated for $C_{14}H_{14}N_6O_2.0.25H_2O$: C, 55.53; H, 4.83 and N, 27.75 %.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.39 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, *m*-C**H** of **Ph**NO_2), 8.00 (s, 1H, **H5'**), 7.93 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, *o*-C**H** of **Ph**NO_2), 5.84 (s, 1H, **H4**), 5.39 (s, 2H, C$\mathbf{H}_2$), 2.35 (s, 3H, C5-C$\mathbf{H}_3$), 2.23 (s, 3H, C3-C$\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 148.6 (**C**3), 147.4 ($\mathbf{C_q}$ of **Ph**), 146.2 ($\mathbf{C_q}$ of Triaz), 141.2 (*ipso*-C to NO_2 of **Ph**NO_2), 139.7 (**C**5), 125.7 (*m*-**C**H of **Ph**NO_2), 120.7 (**C**5'), 120.6 (*o*-**C**H of **Ph**NO_2), 105.9 (**C**4), 44.3 (**C**H_2), 13.7 (C3-**C**H_3), 11.3 (C5-**C**H_3) ppm.

A.5 Synthesis of 4-((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-1-(p-tolyl)-1*H*-1,2,3-triazole (3d)



3,5-Dimethyl-1-(prop-2-yn-1-yl)-1*H*-pyrazole (249 mg, 1.86 mmol) and 1-azido-4-methylbenzene (249 mg, 1.87 mmol) were added into a deoxygenated mixture of 2-propanol and water (2:1 (v/v), 12 mL). Sodium L-ascorbate (75 mg, 0.38 mmol, 20 mol %) was added and the reaction stirred for 5 mins prior to the addition of $CuSO_4.5H_2O$ (15 mg, 0.060 mmol, 3 mol%). The reaction mixture was stirred for 4 days at room temperature under nitrogen, during which time a pale yellow precipitate formed. The 2-propanol was removed *in vacuo* and the residue was filtered and washed with a saturated aqueous solution of Na_2EDTA until the filtrate became colourless. The crude product was then dissolved in dichloromethane, dried with anhydrous magnesium sulphate and filtered through celite®. The solvent was removed *in vacuo* to yield ligand **3d** as a white solid (372 mg, 75 %). m.p. 142-143 °C.

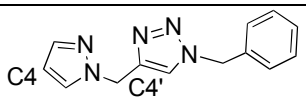
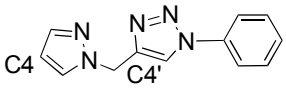
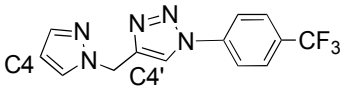
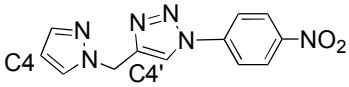
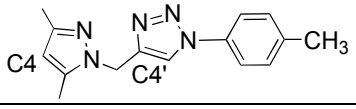
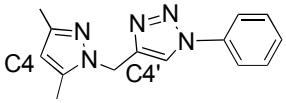
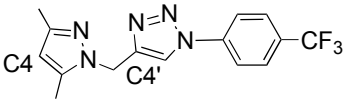
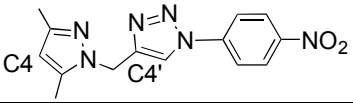
HR-MS (ESI^+, MeOH): *m/z* (%): 290.2500 (100 %) $[M]^+$ (Calculated $[M]^+$ = 290.1376) amu.

Elemental Analysis: Found: C, 67.55; H, 6.46 and N, 26.24; Calculated for $C_{13}H_{13}N_5$: C, 67.39; H, 6.41 and N, 26.20 %.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (s, 1H, **H5'**), 7.56 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *o*-C**H** of **Ph**CH_3), 7.28 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *m*-C**H** of **Ph**CH_3), 5.82 (s, 1H, **H4**), 5.37 (s, 2H, C**H**$_2$), 2.40 (s, 3H, C**H**$_3$ of **Ph**CH_3), 2.34 (s, 3H, C5-C**H**$_3$), 2.23 (s, 3H, C3-C**H**$_3$) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.2 (**C**3), 145.1 (**C$_q$** of Triaz), 139.6 (**C**5), 139.1 (**C$_q$** of **Ph**CH_3), 134.8 (*ipso*-C to CH_3 of **Ph**CH_3), 130.3 (*m*-**C**H of **Ph**CH_3), 120.7 (**C**5'), 120.6 (*o*-**C**H of **Ph**CH_3), 105.7 (**C**4), 44.6 (**C**H_2), 21.2 (**C**H_3 of **Ph**CH_3), 13.7 (C3-**C**H_3), 11.3 (C5-**C**H_3) ppm.

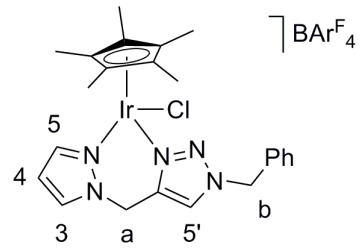
Table S1: Chemical shifts of pyrazolyl **C**4 (Pz-C4) and 1,2,3-triazolyl **C**4' (Tz-C4') ^{13}C resonances of Pyrazolyl-*1,2,*3-Triazolyl bidentate ligands in the ^{13}C NMR spectra.[a]

Ligands	δ ^{13}**C** **(Pz-*C*4)**	δ ^{13}**C** **(Tz-C4')**
1[b] 	106.2	144.4
2a[b] 	106.4	144.5
2b 	106.5	145.1
2c 	106.5	145.5
3d 	105.7	145.1
3a 	105.8	145.3
3b 	105.8	145.8
3c 	105.9	146.2

[a] The ^{1}H NMR spectra were acquired in $CDCl_3$. [b] From reference [1].

Part B: Synthesis of Ir and Rh Complexes

B.1 Synthesis of [Ir(1)Cp*Cl]BAr$^F_4$ (5)



[Ir(**1**)Cp*Cl]BAr$^F_4$ (**5**) was synthesised following the method used for the synthesis of rhodium complex **10a** from [IrCp*Cl$_2$]$_2$ (150 mg, 1.88 x 10^{-4} mol), ligand **1** (84.8 mg, 3.54 x 10^{-4} mol) and NaBAr$^F_4$ (367 mg, 4.14 x 10^{-4} mol) to yield complex **5** as a yellow solid (473 mg, 86%). m.p. 87-89 °C (decomposed).

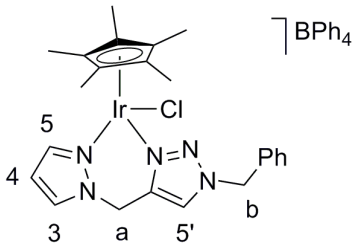
Elemental Analysis: Found: C, 44.52; H, 2.99 and N, 4.64; Calculated for $C_{55}H_{40}BF_{24}IrN_5$: C, 45.08; H, 2.75 and N, 4.78%.

ESI-MS (ESI$^+$, MeOH): 602.00 ([M]$^+$, 100%) amu.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.78 (d, $^3J_{H4\text{-}H5}$ = 2.1 Hz, 1H, **H5**), 7.75 (s, 1H, **H5'**), 7.72 (br s, 8H, *o*-C**H** of BAr$^F_4$), 7.68 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.56 (br s, 4H, *p*-C**H** of BAr$^F_4$), 7.44-7.43 (m, 3H, *p* & *m*-C**H** of **Ph**), 7.35-7.33 (m, 2H, *o*-C**H** of **Ph**), 6.53 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 5.70-5.61 (m, 2H, C**H**$_2^b$), 5.55 (d, $^2J_{H\text{-}H}$ = 18.0 Hz, 1H, C**H**$_A$ of CH$_A$H$_B^a$), 5.02 (d, $^2J_{H\text{-}H}$ = 18.0 Hz, 1H, C**H**$_B$ of CH$_A$H$_B^a$), 1.66 (s, 15 H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz): δ 162.0 (q, $^1J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C** to B, BAr$^F_4$), 145.3 (**C**5), 140.0 (**C$_q$** of Triaz), 134.2 (*o*-**C**H to B, BAr$^F_4$), 134.8 (**C**3), 132.7 (**C$_q$** of **Ph**), 130.2 (*p*-**C**H of **Ph**), 129.9 (*m*-**C**H of **Ph**), 129.4 (*o*-**C**H of **Ph**), 129.0 (app. q, $^2J_{F\text{-}C}$ = 35.0 Hz, **C**CF$_3$, BAr$^F_4$), 125.0 (q, $^1J_{F\text{-}C}$ = 271.0 Hz, **C**F$_3$, BAr$^F_4$), 124.2 (**C**5'), 117.9 (br s, *p*-**C**H to B, BAr$^F_4$), 109.1 (**C**4), 97.6 (d, $^2J_{Ir\text{-}C}$ = 8.0 Hz, **C**$_q$ of Cp*), 56.7 (**C**H$_2^b$), 45.4 (**C**H$_2^a$), 9.5 (s, **C**H$_3$ of Cp*) ppm.

B.2 Synthesis of [Ir(1)Cp*Cl]BPh$_4$ (5')



[Ir(**1**)Cp*Cl]BPh$_4$ (**5'**) was synthesised following the method used for the synthesis of the rhodium complex [Rh(**2a**)Cp*Cl]BPh$_4$ (**10a'**) from [IrCp*Cl$_2$]$_2$ (50.0 mg, 6.30 x 10^{-5} mol), ligand **1** (28.0 mg, 1.26 x 10^{-4} mol) and NaBPh$_4$ (47.4 mg, 1.40 x 10^{-4} mol) to yield **5'** as a pale yellow solid (93 mg, 84%). m.p. 247-249 °C.

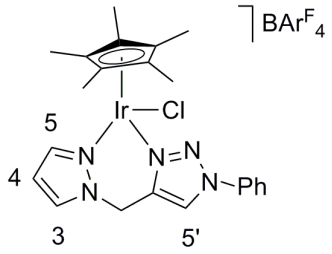
Elemental Analysis: Found: C, 61.49; H, 5.11 and N, 7.34; Calculated for $C_{47}H_{48}BIrN_5$: C, 61.27; H, 5.25 and N, 7.60%.

ESI-MS (ESI$^+$, MeOH): 602.06 ([M]$^+$, 100%) amu.

^{1}H NMR (Acetone-d_6, 400 MHz): δ 8.36 (s, 1H, **H5'**). 8.05 (d, $^3J_{H4\text{-}H5}$ = 2.8 Hz, 1H, **H5**), 7.86 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.45-7.41 (m, 5H, **Ph**), 7.36-7.32 (m, 8H, *o*-C**H** of B**Ph**$_4$), 6.92 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 8H, *m*-C**H** of B**Ph**$_4$), 6.77 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of B**Ph**$_4$), 6.60 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 5.99 (d, $^2J_{H\text{-}H}$ = 16.4 Hz, 1H, C**H**$_A$ of CH$_A$H$_B$[a]), 5.85 (s, 2H, C**H**$_2$[b]), 5.19 (d, $^2J_{H\text{-}H}$ = 16.4 Hz, 1H, C**H**$_B$ of CH$_A$H$_B$[a]), 1.69 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (Acetone-d_6, 150 MHz): δ 165.0 (q, $^1J_{B\text{-}C}$ = 50.0, *ipso*-**C** to B, B**Ph**$_4$), 145.8 (**C**3), 137.09 (*o*-**C**H of B**Ph**$_4$), 135.6 (**C**5), 135.4 (**C$_q$** of Triaz), 130.0 (**C**H of **Ph**), 129.9 (**C**H of **Ph**), 129.3 (**C**H of **Ph**), 126.1 (*m*-**C**H of B**Ph**$_4$), 126.1 (**C**5'), 125.9 (**C$_q$** of **Ph**), 122.29 (*p*-**C**H of B**Ph**$_4$), 109.1 (**C**4), 89.7 (**C**$_q$ of Cp*), 56.8 (**C**H$_2$[b]), 46.1 (**C**H$_2$[a]), 9.1 (**C**H$_3$ of Cp*) ppm.

B.3 Synthesis of [Ir(2a)Cp*Cl]BAr^F_4 (6a)



[Ir(**2a**)Cp*Cl]BAr^F_4 (**6a**) was synthesised following the method used for the synthesis of complex **10a** from $[IrCp^*Cl_2]_2$ (50 mg, 6.28 x 10^{-5} mol), ligand **9** (28.3 mg, 1.26 x 10^{-4} mol) and $NaBAr^F_4$ (122 mg, 1.38 x 10^{-4} mol) to yield **6a** as a light yellow solid (149 mg, 79%). m.p. 174-176 °C.

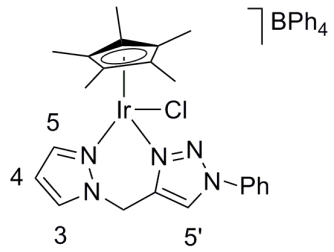
Elemental Analysis: Found: C, 44.41; H, 2.67 and N, 4.88; Calculated for $C_{54}H_{38}BClF_{24}IrN_5$: C, 44.69; H, 2.64 and N, 4.83 %.

HR-MS (ESI^+, MeOH): $[M]^+$ = 588.1499 (Calculated $[M]^+$ = 588.1506) amu.

^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.22 (s, 1H, **H5'**), 7.78 (d, $^3J_{H4\text{-}H5}$ = 2.4 Hz, 1H, **H5**), 7.74 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.72 (br s, 8H, *o*-C**H** of BAr^F_4), 7.70-7.69 (m, 2H, *o*-C**H** of **Ph**), 7.65-7.63 (m, 3H, *p* & *m*-C**H** of **Ph**), 7.56 (br s, 4H, *p*-C**H** of BAr^F_4), 6.60 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 5.66 (d, $^2J_{H\text{-}H}$ = 15.6 Hz, 1H, C$\mathbf{H}_A$ of CH_AH_B), 5.04 (d, $^2J_{H\text{-}H}$ = 15.6 Hz, 1H, C$\mathbf{H}_B$ of CH_AH_B), 1.68 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150 MHz): δ 162.2 (q, $^1J_{B\text{-}C}$ = 51.0 Hz, *ipso*-**C** to B, BAr^F_4), 145.6 (**C**5), 139.6 (**C$_q$** of Triaz), 135.9 (**C$_q$** of **Ph**), 135.2 (*o*-**C**H to B, BAr^F_4), 134.5 (**C**3), 131.7 (*p*-**C**H of **Ph**), 130.9 (*m*-**C**H of **Ph**), 129.3 (q, $^3J_{B\text{-}C}$ = 31.5 Hz, **C**CF_3, BAr^F_4), 125.0 (q, $^1J_{F\text{-}C}$ = 270.0 Hz, **C**F_3, BAr^F_4), 122.4 (**C**5'), 121.5 (*o*-**C**H of **Ph**), 117.9 (br s, *p*-**C**H to B, BAr^F_4), 109.6 (**C**4), 89.8 (**C$_q$** of Cp*), 45.8 (**C**H_2), 9.3 (**C**H_3 of Cp*) ppm.

B.4 Synthesis of [Ir(2a)Cp*Cl]BPh_4 (6a')



[Ir(**2a**)Cp*Cl]BPh_4 (**6a'**) was synthesised following the method used for the synthesis of complex **9'** from $[IrCp^*Cl_2]_2$ (50.0 mg, 6.30 x 10^{-5} mol), ligand **2a** (28.0 mg, 1.26 x 10^{-4} mol) and $NaBPh_4$ (47.4 mg, 1.40 x 10^{-4} mol) to yield **6a'** as a pale yellow solid (78.0 mg, 68%). m.p. 220-222 °C.

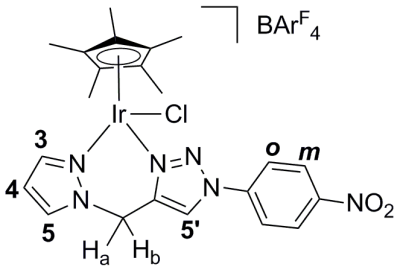
Elemental Analysis: Found: C, 60.79; H, 4.83 and N, 7.71; Calculated for $C_{46}H_{46}BClIrN_5$: C, 60.89; H, 5.11 and N, 7.72%.

HR-MS (ESI^+, MeOH): $[M]^+$ = 588.1502 (Calculated $[M]^+$ = 588.1506) amu.

^{1}H NMR (Acetone-d_6, 600 MHz): δ 8.78 (s, 1H, **H5'** (triazole)). 8.12 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.91 (d, $^3J_{H4\text{-}H5}$ = 2.4 Hz, 1H, **H5**), 7.91 (br s, 2H, *o*-C**H** of **Ph**), 7.70 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, *m*-C**H** of **Ph**), 7.64 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, *p*-C**H** of **Ph**), 7.36-7.34 (m, 8H, *o*-C**H** of B**Ph**$_4$), 6.92 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 8H, *m*-C**H** of B**Ph**$_4$), 6.77 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of B**Ph**$_4$), 6.64 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 6.08 (d, $^2J_{H\text{-}H}$ = 16.2 Hz, 1H, C$\mathbf{H}_A$ of CH_AH_B), 5.30 (d, $^2J_{H\text{-}H}$ = 16.2 Hz, 1H, C$\mathbf{H}_B$ of CH_AH_B), 1.77 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

$^{13}C\{^1H\}$ NMR (Acetone-d_6, 150 MHz): δ 165.0 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** to B, B**Ph**$_4$), 145.8 (**C**5), 141.1 (**C**5'), 137.0 (*o*-**C**H of B**Ph**$_4$ & $\mathbf{C_q}$ of Triaz), 135.7 (**C**3), 131.4 (*p*-**C**H of **Ph**), 131.0 (*m*-**C**H of **Ph**), 126.0 (*m*-**C**H of B**Ph**$_4$), 124.2 ($\mathbf{C_q}$ of **Ph**), 122.3 (*p*-**C**H of B**Ph**$_4$), 122.1 (*o*-**C**H of **Ph**), 109.1 (**C**4), 90.0 ($\mathbf{C}_q$ of Cp*), 46.1 (**C**H_2), 9.1 (**C**H_3 of Cp*) ppm.

B.5 Synthesis of [Ir(2c)Cp*Cl]BAr^F_4 (6c)



$[IrCp^*Cl_2]_2$ (52 mg, 0.0066 mmol) and ligand **2c** (35 mg, 0.13 mmol) were dissolved in dichloromethane (15 mL). After 5 minutes of stirring, $NaBAr^F_4$ (117 mg, 0.132 mmol) was added, resulting in the formation of a white precipitate in a yellow solution. The reaction mixture was stirred for 2 hours before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 3 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **6c** as an orange solid (108 mg, 56 %). m.p. 99-102 °C (decomposed).

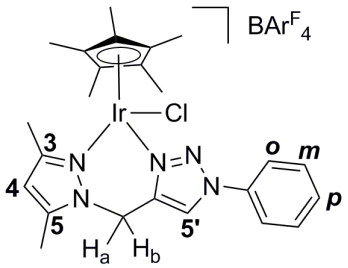
HR-MS (ESI^+, MeOH): *m/z* (%): 633.1667 (100 %) $[M]^+$ (Calculated $[M]^+$ = 633.1357)

Elemental Analysis: Found: C, 43.51; H, 2.68; N, 5.62. Calculated for $C_{54}H_{37}BClF_{24}IrN_6O_2$: C, 43.34; H, 2.49; N, 5.62 %.

^{1}H NMR (acetone-d_6, 400 MHz): δ 9.28 (s, 1H, **H5'**), 8.56 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H, *o*-C**H** of **Ph**NO_2), 8.32 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H, *m*-C**H** of **Ph**NO_2), 8.23 (d, $J_{H4\text{-}H5}$ = 2.4 Hz, 1H, **H5**), 7.93 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.67 (apparent t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 6.31 (d, $^2J_{H\text{-}H}$ = 16.1 Hz, 1H, C$\mathbf{H}_a$ of CH_aH_b), 5.42 (d, $^2J_{H\text{-}H}$ = 16.1 Hz, 1H, C$\mathbf{H}_b$ of CH_aH_b), 1.80 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 100 MHz): δ 162.6 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-**C** to B, BAr^F_4), 149.5 (**C**$_q$ of **Ph**NO_2), 145.9 (**C**3), 141.8 (**C**$_q$ of Triaz), 141.1 (*ipso*-**C** to NO_2 of **Ph**NO_2), 135.8 (**C**5), 135.2 (*o*-**C**H to B, BAr^F_4), 130.0 (q, $^2J_{F\text{-}C}$ = 30.6 Hz, *ipso*-**C** to CF_3, BAr^F_4), 126.7 (**C**$_q$ of CH_2), 126.5 (*m*-**C**H of **Ph**NO_2), 125.4 (q, $^1J_{F\text{-}C}$ = 270.7 Hz, **C**F_3, BAr^F_4), 124.8 (**C**5'), 123.1 (*o*-**C**H of **Ph** NO_2), 118.5 (br s, *p*-**C**H to B, BAr^F_4), 109.2 (**C**4), 90.2 (**C**$_q$ of Cp*), 46.2 (**C**H_2), 9.1 (**C**H_3 of Cp*) ppm.

B.6 Synthesis of [Ir(3a)Cp*Cl]BAr^F_4 (7a)



$[IrCp^*Cl_2]_2$ (52 mg, 0.065 mmol) and ligand **3a** (33 mg, 0.13 mmol) were dissolved in dichloromethane (10 mL). After 5 minutes of stirring, $NaBAr^F_4$ (121 mg, 0.136 mmol) was added, resulting in the formation of a white precipitate in a yellow solution. The reaction mixture was stirred for 2 hours before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 2 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **7a** as a pale yellow solid (134 mg, 70 %). m.p. 142-145 °C (decomposed).

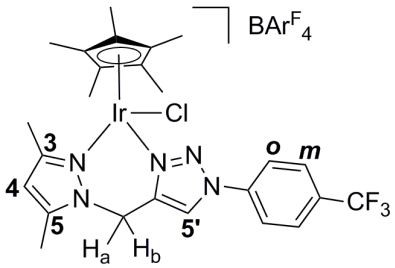
HR-MS (ESI^+, MeOH): *m/z* (%): 616.2500 (100 %) $[M]^+$ (Calculated $[M]^+$ = 616.1813) amu.

Elemental Analysis: Found: C, 45.29; H, 2.97; N, 4.40. Calculated for $C_{56}H_{42}BClF_{24}IrN_5$: C, 45.46; H, 2.86; N, 4.73 %.

^{1}H NMR (acetone-d_6, 400 MHz): δ 8.96 (s, 1H, **H5'**), 7.93 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *o*-C**H** of **Ph**), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.71 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *m*-C**H** of **Ph**), 7.67 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H, *p*-C**H** of **Ph**, overlapped with *p*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.31 (s, 1H, **H4**), 6.03 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C**H**$_a$ of CH_aH_b), 5.08 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C**H**$_b$ of CH_aH_b), 2.55 (s, 3H, C5-C**H**$_3$), 2.51 (s, 3H, C3-C**H**$_3$), 1.76 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 100 MHz): δ 162.6 (q, $^1J_{B\text{-}C}$ = 48.5 Hz, *ipso*-**C** to B, BAr^F_4), 154.3 (**C**3), 144.5 (**C**5), 141.5 (**C**$_q$ of Triaz), 137.1 (**C**$_q$ of **Ph**), 135.5 (br s, *o*-**C**H to B, BAr^F_4), 130.0 (q, $^2J_{F\text{-}C}$ = 31.4 Hz, $^3J_{B\text{-}C}$ = 2.9 Hz, *ipso*-**C** to CF_3, BAr^F_4), 131.1 (*m*-**C**H of **Ph**), 131.0 (*p*-**C**H of **Ph**), 125.4 (q, $^1J_{F\text{-}C}$ = 270.2 Hz, **C**F_3, BAr^F_4), 124.1 (**C**5'), 122.1 (*o*-**C**H of **Ph**), 118.4 (br s, *p*-**C**H to B, BAr^F_4), 109.1 (**C**4), 89.8 (**C**$_q$ of Cp*), 42.8 (**C**H_2), 15.6 (C3-**C**H_3), 11.7 (C5-**C**H_3), 9.3 (**C**H_3 of Cp*) ppm.

B.7 Synthesis of [Ir(3b)Cp*Cl]BAr^F_4 (7b)



$[IrCp^*Cl_2]_2$ (53 mg, 0.0066 mmol) and ligand **3b** (43 mg, 0.13 mmol) were dissolved in dichloromethane (15 mL). After 5 minutes of stirring, $NaBAr^F_4$ (119 mg, 0.134 mmol) was added, resulting in the formation of a white precipitate in a yellow solution. The reaction mixture was stirred overnight before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 2 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **7b** as a pale yellow solid (127 mg, 62 %). m.p. 188-191 °C (decomposed).

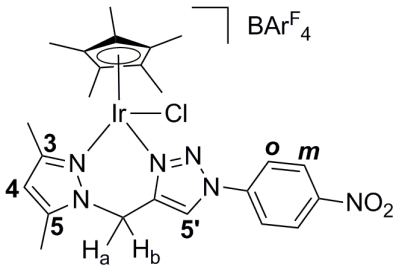
HR-MS (ESI^+, MeOH): *m/z* (%): 684.1667 (79 %) $[M]^+$ (Calculated $[M]^+$ = 684.1687) amu.

Elemental Analysis: Found: C, 44.65; H, 2.80; N, 4.35. Calculated for $C_{57}H_{41}BClF_{27}IrN_5$: C, 44.24; H, 2.67; N, 4.53 %.

^{1}H NMR (acetone-d_6, 600 MHz): δ 9.12 (s, 1H, **H5'**), 8.23 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, *m*-C**H** of **Ph**), 8.08 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, *o*-C**H** of **Ph**CF_3), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.32 (s, 1H, **H4**), 6.06 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C**H**$_a$ of CH_aH_b), 5.10 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C**H**$_b$ of CH_aH_b), 2.55 (s, 3H, C5-C**H**$_3$), 2.52 (s, 3H, C3-C**H**$_3$), 1.77 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 162.6 (q, $^1J_{B\text{-}C}$ = 49.6 Hz, *ipso*-**C** to B, BAr^F_4), 154.5 (**C**3), 144.6 (**C**5), 141.9 (**C**$_q$ of Triaz), 139.8 (**C**$_q$ of **Ph**CF_3), 135.5 (*o*-**C**H to B, BAr^F_4), 132.4 (q, $^2J_{C\text{-}F}$ = 33.2 Hz, *ipso*-**C** to CF_3 of **Ph**CF_3), 130.0 (q, $^2J_{F\text{-}C}$ = 31.6 Hz, $^3J_{B\text{-}C}$ = 2.8 Hz, *ipso*-**C**$_q$ to CF_3, BAr^F_4), 128.1 (*o*-**C**H of **Ph**CF_3), 125.4 (q, $^1J_{F\text{-}C}$ = 270.3 Hz, **C**F_3, BAr^F_4), 124.6 (q, $^1J_{C\text{-}F}$ = 270.7 Hz, Ph**C**F_3), 124.5 (**C**5'), 122.7 (*m*-**C**H of **Ph**CF_3), 118.4 (br s, *p*-**C**H to B, BAr^F_4), 109.2 (**C**4), 90.0 (**C**q of Cp*), 42.8 (**C**H_2), 15.6 (C3-**C**H_3), 11.7 (C5-**C**H_3), 9.3 (**C**H_3 of Cp*) ppm.

B.8 Synthesis of [Ir(3c)Cp*Cl]BAr^F_4 (7c)



$[IrCp^*Cl_2]_2$ (51 mg, 0.064 mmol) and ligand **3c** (39 mg, 0.13 mmol) were dissolved in dichloromethane (15 mL). After 5 minutes of stirring, $NaBAr^F_4$ (120 mg, 0.135 mmol) was added, resulting in the formation of a white precipitate in a brown solution. The reaction mixture was stirred for 2 hours before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 3 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **7c** as an orange solid (96 mg, 50 %). m.p. 107-110 °C (decomposed).

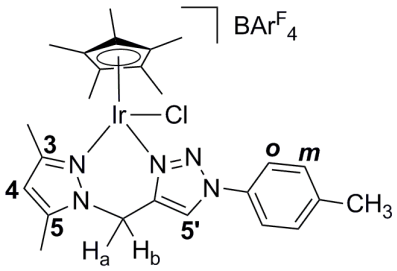
HR-MS (ESI^+, MeOH): *m/z* (%): 661.1667 (100 %) $[M]^+$ (Calculated $[M]^+$ = 661.1664) amu.

Elemental Analysis: Found: C, 44.26; H, 2.70; N, 5.53. Calculated for $C_{56}H_{41}BClF_{24}IrN_6O_2$: C, 44.12; H, 2.71; N, 5.51 %.

^{1}H NMR (acetone-d_6, 400 MHz): δ 9.19 (s, 1H, **H5'**), 8.56 (d, $^3J_{H\text{-}H}$ = 9.2 Hz, 2H, *m*-C**H** of **Ph**NO_2), 8.30 (d, $^3J_{H\text{-}H}$ = 9.2 Hz, 2H, *o*-C**H** of **Ph**NO_2), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.32 (s, 1H, **H4**), 6.08 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C$\mathbf{H}_a$ of CH_aH_b), 5.11 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C$\mathbf{H}_b$ of CH_aH_b), 2.55 (s, 3H, C5-C$\mathbf{H}_3$), 2.52 (s, 3H, C3-C$\mathbf{H}_3$), 1.77 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 100 MHz): δ 162.6 (q, $^1J_{B\text{-}C}$ = 48.9 Hz, *ipso*-**C** to B, BAr^F_4), 154.5 (**C**3), 149.5 ($\mathbf{C}_q$ of **Ph**NO_2), 142.1 ($\mathbf{C}_q$ of Triaz), 141.1 (*ipso*-**C** to NO_2 of **Ph**NO_2), 144.6 (**C**5), 135.5 (br s, *o*-**C**H to B, BAr^F_4), 130.0 (q, $^2J_{F\text{-}C}$ = 29.6 Hz, $^3J_{B\text{-}C}$ = 3.0 Hz, *ipso*-**C** of CF_3, BAr^F_4), 126.5 (*m*-**C**H of **Ph**NO_2), 125.4 (q, $^1J_{F\text{-}C}$ = 270.2 Hz, **C**F_3, BAr^F_4), 124.0 (**C**5'), 123.0 (*o*-**C**H of **Ph**NO_2), 118.5 (br s, *p*-**C**H to B, BAr^F_4), 109.2 (**C**4), 90.0 ($\mathbf{C}_q$ of Cp*), 42.9 ($\mathbf{C}H_2$), 15.6 (C3-**C**H_3), 11.7 (C5-**C**H_3), 9.3 (**C**H_3 of Cp*) ppm.

B.9 Synthesis of [Ir(3d)Cp*Cl]BAr^F_4 (7d)



$[IrCp^*Cl_2]_2$ (50 mg, 0.063 mmol) and ligand **3d** (31 mg, 0.13 mmol) were dissolved in dichloromethane (12 mL). After 5 minutes of stirring, $NaBAr^F_4$ (114 mg, 0.129 mmol) was added, resulting in the formation of a white precipitate in a yellow solution. The reaction mixture was stirred for 3 hours before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 2 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **7d** as a yellow solid (124 mg, 66 %). m.p. 196-198 °C.

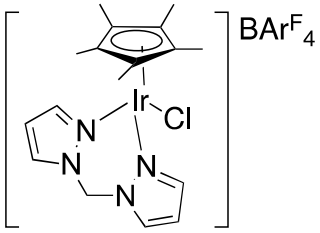
HR-MS (ESI^+, MeOH): *m/z* (%): 630.3333 (41 %) $[M]^+$ (Calculated $[M]^+$ = 630.1970) amu.

Elemental Analysis: Found: C, 46.09; H, 2.96; N, 4.73. Calculated for $C_{57}H_{44}BClF_{24}IrN_5$: C, 45.84; H, 2.97; N, 4.69 %.

^{1}H NMR (acetone-d_6, 600 MHz): δ 8.90 (s, 1H, **H5'**), 7.80 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *o*-C**H** of **Ph**CH_3, overlapped with *o*-C**H** of BAr^F_4), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4 overlapped with *o*-C**H** of **Ph**CH_3), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 7.50 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *m*-C**H** of **Ph**CH_3), 6.31 (s, 1H, **H4**), 6.00 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C**H**$_a$ of CH_aH_b), 5.07 (d, $^2J_{H\text{-}H}$ = 16.3 Hz, 1H, C**H**$_b$ of CH_aH_b), 2.55 (s, 3H, C5-C**H**$_3$), 2.51 (s, 3H, C3-C**H**$_3$), 2.45 (s, 3H, C**H**$_3$ of **Ph**CH_3), 1.76 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 162.6 (q, $^1J_{B\text{-}C}$ = 48.1 Hz, *ipso*-**C** to B, BAr^F_4), 154.4 (**C**3), 144.5 (**C**5), 141.9 (**C**$_q$ of Triaz), 141.4 (**C**$_q$ of **Ph**CH_3),135.5 (br s, *o*-**C**H to B, BAr^F_4), 134.9 (*ipso*-**C** to CH_3 of **Ph**CH_3), 131.5 (*m*-**C**H of **Ph**CH_3), 130.0 (q, $^2J_{F\text{-}C}$ = 31.4 Hz, *ipso*-**C** of CF_3, BAr^F_4), 125.4 (q, $^1J_{F\text{-}C}$ = 270.8 Hz, **C**F_3, BAr^F_4), 124.0 (**C**5'), 122.0 (*o*-**C**H of **Ph**NO_2), 118.5 (br s, *p*-**C**H to B, BAr^F_4), 109.1 (**C**4), 89.8 (**C**$_q$ of Cp*), 42.8 (**C**H_2), 21.1 (**C**H_3 of **Ph**CH_3), 15.6 (C3-**C**H_3), 11.7 (C5-**C**H_3), 9.32 (**C**H_3 of Cp*) ppm.

B.10 Synthesis of [Ir(4)Cp*Cl]BAr^F_4 (8)



$[IrCp^*Cl_2]_2$ (0.269 g, 0.335 mmol) was dissolved in CH_2Cl_2 (25 mL) prior to the addition of *bis*(1-pyrazolyl)methane (**4**, 0.101 g, 0.682 mmol) to the reaction mixture. The dark orange mixture turned bright orange. The reaction mixture was left to stir at room temperature for 30 minutes before $NaBAr^F_4$ (0.657 g, 0.741 mmol) was added to the mixture. The resulting murky pale yellow-orange mixture was stirred at room temperature for 1 hour and then filtered through celite® to yield a clear yellow solution. The solution was then reduced in volume to *ca.*15 mL and *n*-pentane was added with vigorous stirring to precipitate the product **8**, which was collected by filtration as a pale yellow crystalline solid (0.763 g, 83 %); m.p. 174-176°C.

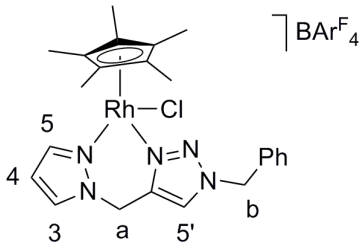
HR-MS (ESI^+, MeOH): *m/z* (%): 511.1236 (100 %) $[M]^+$ (Calculated $[M]^+$ = 511.12) amu.

Elemental Analysis: Found: C, 42.66; H, 2.53; N, 4.06. Calculated for $C_{49}H_{35}BClF_{24}IrN_4$: C, 42.82; H, 2.57; N, 4.08 %.

^{1}H NMR (600 MHz, acetone–d_6, 298 K): δ 8.25 (d, ^3J(H3-H4) = 2.4 Hz, 2H, **H**3), 7.94 (d, ^3J(H5-H4) = 1.8 Hz, 2H, **H**5), 7.79 (br s, 8H, *ortho*-C**H** of BAr^F_4), 7.67 (br s, 4H, *para*-C**H** of BAr^F_4), 7.28 (d, $^2J(H_B\text{-}H_A)$ = 14.5 Hz, 1H, C**H**H), 6.67 (apparent t, ^3J = 1.7 Hz, 2H, **H**4), 6.20 (d, $^2J(H_B\text{-}H_A)$ = 14.5 Hz, 1H, CH**H**), 1.78 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

^{31}C {^{1}H} NMR (150 MHz, acetone–d_6, 298 K): δ 162.63 (q, ^1J(B-C) = 49.7 Hz, quat **C** *ipso* to B of BAr^F_4), 146.65 (s, **C**5 of Pz), 135.75 (s, **C**3 of Pz), 135.58 (br s, *ortho*-**C**H of BAr^F_4), 130.07 (q, ^2J(F-C) = 30.3 Hz, **C** *ipso* to CF_3 of BAr^F_4), 125.42 (q, ^1J(F-C) = 270.15 Hz, **C**F_3 of BAr^F_4) 118.50 (s, ^3J(F-C) = 4.1 Hz, *para*-**C**H of BAr^F_4), 109.58 (s, **C**4 of Pz), 90.00 (s, quat **C** of Cp*), 64.24 (s, **C**H_2), 9.15 (s, **C**H_3 of Cp*) ppm.

B.11 Synthesis of [Rh(1)Cp*Cl]BAr^F_4 (9)



[Rh(PyT)Cp*Cl]BAr^F_4 (**9**) was synthesised following the method for the synthesis of complex **10a** from $[RhCp^*Cl_2]_2$ (150 mg, 2.43 x 10^{-5} mol), ligand **10** (109 mg, 4.56 x 10^{-4} mol) and $NaBAr^F_4$ (473 mg, 5.34 x 10^{-4} mol) to yield **9** as an orange solid (618 mg, 92%). m.p. 155-157 °C.

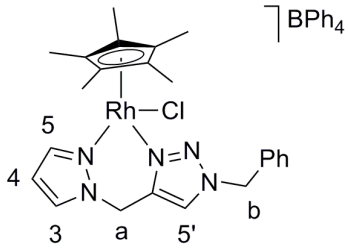
Elemental Analysis: Found: C, 48.07; H, 3.57 and N, 4.76; Calculated for $C_{55}H_{40}BClF_{24}N_5O_2Rh$: C, 48.01; H, 2.93 and N, 5.09 %.

ESI-MS (ESI^+, MeOH): 511.96 ($[M]^+$, 100%) amu.

^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.95 (s, 1H, **H5'**), 7.76 (d, $^3J_{H4\text{-}H5}$ = 1.8 Hz, 1H, **H5**), 7.72 (br s, 8H, *o*-C**H** of BAr^F_4), 7.70 (d, $^3J_{H4\text{-}H3}$ = 1.8 Hz, **H3**), 7.56 (br s, 4H, *p*-C**H** of BAr^F_4), 7.40 (m, 3H, *p* & *m*-C**H** of **Ph**), 7.34 (d, 2H, $^3J_{H\text{-}H}$ = 3.6 Hz, *o*-C**H** of **Ph**), 6.50 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 5.68-5.62 (m, 3H, C$\mathbf{H}_2^b$ & C$\mathbf{H}_A$ of $CH_AH_B{}^a$), 4.85 (d, $^2J_{H\text{-}H}$ = 15.6 Hz, 1H, C$\mathbf{H}_B$ of $CH_AH_B{}^a$), 1.60 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150 MHz): δ 162.2 (q, $^1J_{B\text{-}C}$ = 41.3 Hz, *ipso*-**C** to B, BAr^F_4), 145.3 (**C**5), 139.2 (**C$_q$** of Triaz), 135.2 (*o*-**C**H to B, BAr^F_4), 134.7 (**C**3), 132.9 (**C$_q$** of **Ph**), 130.2 (*p*-**C**H of **Ph**), 130.0 (*m*-**C**H of **Ph**), 129.3 (qq, $^2J_{F\text{-}C}$ = 22.5 Hz, $^3J_{B\text{-}C}$ = 2.5 Hz **C**CF_3, BAr^F_4), 129.0 (*o*-**C**H of **Ph**), 125.0 (q, $^1J_{F\text{-}C}$ = 226.3 Hz, **C**F_3, BAr^F_4), 124.6 (**C**5'), 117.9 (br s, *p*-**C**H to B, BAr^F_4), 109.3 (**C**4), 89.5 (**C**$_q$ of Cp*), 56.8 (**C**$H_2{}^b$), 45.9 (**C**$H_2{}^a$), 9.2 (s, **C**H_3 of Cp*) ppm.

B.12 Synthesis of [Rh(1)Cp*Cl]BPh_4 (9')



[Rh(**1**)Cp*Cl]BPh_4 (**9'**) was synthesised following the method for the synthesis of complex **10a'** from $[RhCp^*Cl_2]_2$ (50.0 mg, 8.10 x 10^{-5} mol), ligand **1** (36.0 mg, 1.62 x 10^{-4} mol) and $NaBPh_4$ (60.9 mg, 1.78 x 10^{-4} mol) to yield **9'** as a yellow solid (117 mg, 88%). m.p. 222-224 °C.

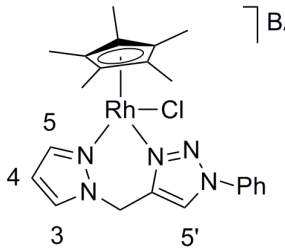
Elemental Analysis: Found: C, 67.76; H, 5.64 and N, 7.95; Calculated for $C_{47}H_{48}BN_5Rh$: C, 67.84; H, 5.81 and N, 8.42%.

ESI-MS (ESI^+, MeOH): 511.89 ($[M]^+$, 100%) amu.

^{1}H NMR (Acetone-d_6, 600 MHz): δ 8.40 (s, 1H, **H5'**). 8.07 (d, $^3J_{H4\text{-}H5}$ = 1.8 Hz, 1H, **H5**), 7.95 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.48-7.43 (m, 5H, **Ph**), 7.37-7.35 (m, 8H, *o*-C**H** of B**Ph**$_4$), 6.94 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 8H, *m*-C**H** of B**Ph**$_4$), 6.79 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of B**Ph**$_4$), 6.59 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 5.99 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_A$ of CH_AH_B[a]), 5.86 (s, 2H, C**H**$_2$[b]), 5.40 (d, $^2J_{H\text{-}H}$ = 15.9 Hz, 1H, C**H**$_B$ of CH_AH_B[a]), 1.73 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (Acetone-d_6, 150 MHz): δ 165.0 (q, $^1J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C** to B, B**Ph**$_4$), 146.0 (**C$_q$** of Triaz), 141.4 (**C**3), 137.1 (*o*-**C**H of B**Ph**$_4$), 135.9 (**C**5), 135.5 (**C$_q$** of **Ph**), 130.0 (**C**H of **Ph**), 129.9 (**C**H of **Ph**), 129.4 (**C**H of **Ph**), 126.1 (*m*-**C**H of B**Ph**$_4$), 125.9 (**C**5'), 122.3 (*p*-**C**H of B**Ph**$_4$), 108.8 (**C**4), 97.9 (d, $^2J_{Rh\text{-}C}$ = 7.5 Hz, **C**$_q$ of Cp*), 56.1 (**C**H_2[b]), 45.7 (**C**H_2[a]), 9.3 (**C**H_3 of Cp*) ppm.

B.13 Synthesis of [Rh(2a)Cp*Cl]BAr$^F_4$ (10a)



[RhCp*Cl$_2$]$_2$ (50.0 mg, 8.09 x 10^{-5} mol) and ligand **2a** (36.4 mg, 1.62 x 10^{-4} mol) were dissolved in CH_2Cl_2 (10 mL). NaBAr$^F_4$ (158 mg, 1.78 x 10^{-4} mol) was added, resulting in the formation of a white precipitate. The reaction mixture was stirred for 2 h before being filtered through celite. The volume of the filtrate was reduced to *ca.* 2 mL and *n*-pentane added (20 mL) yielding **10a** as an orange solid (154 mg, 71%). m.p. 125-130 °C.

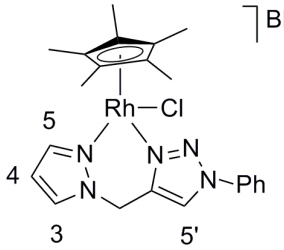
Elemental Analysis: Found: C, 47.82; H, 2.96 and N, 5.19; Calculated for $C_{54}H_{38}BClF_{24}N_5Rh$: C, 47.62; H, 2.81 and N, 5.14 %.

HR-MS (ESI$^+$, MeOH): $[M]^+$ = 498.0923 (Calculated $[M]^+$ = 498.0932) amu.

^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.20 (s, 1H, **H5'**), 7.82 (br s, 1H, **H5/H3**), 7.74 (d, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H5/H3**), 7.72 (br s, 10H, *o*-C**H** of BAr$^F_4$ & *o*-C**H** of **Ph**), 7.66-7.62 (m, 3H, *p* & *m*-C**H** of **Ph**), 7.55 (br s, 4H, *p*-C**H** of BAr$^F_4$), 6.59 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 5.68 (br s, 1H, C**H**$_A$ of CH_AH_B), 5.17 (br s, 1H, C**H**$_B$ of CH_AH_B), 1.70 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz): δ 162.2 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** to B, BAr$^F_4$), 145.4 (**C**5/3), 140.5 (**C$_q$** of Triaz), 136.0 (**C**$_q$ of **Ph**), 135.2 (*o*-**C**H to B, BAr$^F_4$), 134.9 (**C**5/3), 131.6 (*p*-**C**H of **Ph**), 130.9 (*m*-**C**H of **Ph**), 129.3 (q, $^3J_{B\text{-}C}$ = 30.0 Hz, **C**CF$_3$, BAr$^F_4$), 125.0 (q, $^1J_{F\text{-}C}$ = 270.0 Hz, **C**F$_3$, BAr$^F_4$), 122.6 (**C**5'), 121.5 (*o*-**C**H of **Ph**), 117.9 (br s, *p*-**C**H to B, BAr$^F_4$), 109.4 (**C**4), 97.9 (**C**$_q$ of Cp*), 45.5 (**C**H$_2$), 9.6 (**C**H$_3$ of Cp*) ppm.

B.14 Synthesis of [Rh(2a)Cp*Cl]BPh_4 (10a')



$[RhCp^*Cl_2]_2$ (50.0 mg, 8.10 x 10^{-5} mol) was suspended in MeOH (10 mL) and ligand **2a** (36.4 mg, 1.62 x 10^{-4} mol) added, resulting in a colour change from orange to bright yellow. $NaBPh_4$ (60.9 mg, 1.78 x 10^{-4} mol) was added after 5 minutes, resulting in the formation of a yellow precipitate. The reaction mixture was stirred for 1 h before the volume was reduced to *ca.* 1 mL and cooled in ice. The mixture was filtered, the solid washed with MeOH (3 x 10 mL) and dried to yield **21** as a yellow solid (100 mg, 75%). m.p. 209-211 °C (decomposed).

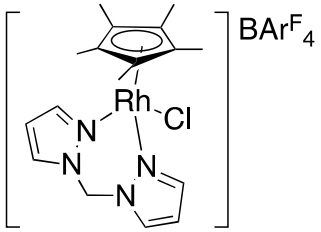
Elemental Analysis: Found: C, 67.44; H, 5.71 and N, 8.59; Calculated for $C_{46}H_{46}BClN_5Rh$: C, 67.54; H, 5.67 and N, 8.56%.

HR-MS (ESI^+, MeOH): $[M]^+$ = 498.0923 (Calculated $[M]^+$ = 498.0932) amu.

^{1}H NMR (Acetone-d_6, 600 MHz): δ 8.78 (s, 1H, **H5'**). 8.11 (d, $^3J_{H\text{-}H}$ = 3.0 Hz, 1H, **H5**/**H3**), 7.95 (d, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H3**/**H5**), 7.92 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H, *o*-C**H** of **Ph**), 7.69 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, *m*-C**H** of **Ph**), 7.64 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, *p*-C**H** of **Ph**), 7.36-7.34 (m, 8H, *o*-C**H** of B**Ph**$_4$), 6.92 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 8H, *m*-C**H** of B**Ph**$_4$), 6.77 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of B**Ph**$_4$), 6.60 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 6.05 (d, $^2J_{H\text{-}H}$ = 16.2 Hz, 1H, C$\mathbf{H}_A$ of CH_AH_B), 5.47 (d, $^2J_{H\text{-}H}$ = 16.2 Hz, 1H, C$\mathbf{H}_B$ of CH_AH_B), 1.80 (s, 15H, C$\mathbf{H}_3$ of Cp*) ppm.

$^{13}C\{^1H\}$ NMR (Acetone-d_6, 150 MHz): δ 165.0 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** to B, B**Ph**$_4$), 146.0 (**C5**/**C3**), 141.9 (**C$_q$** of Triaz), 137.2 (**C$_q$** of **Ph**), 137.0 (*o*-**C**H of B**Ph**$_4$), 135.9 (**C3**/**C5**), 131.3 (*p*-**C**H of **Ph**), 131.0 (*m*-**C**H of **Ph**), 126.0 (*m*-**C**H of B**Ph**$_4$), 124.3 (**C**5'), 122.3 (*p*-**C**H of B**Ph**$_4$), 122.0 (*o*-**C**H of **Ph**), 108.9 (**C**4), 98.1 (d, $^2J_{Rh\text{-}C}$ = 9.0 Hz, **C**$_q$ of Cp*), 45.7 (**C**H_2), 9.4 (s, **C**H_3 of Cp*) ppm.

B.15 Synthesis of [Rh(4)Cp*Cl]BAr^F_4 (11)



$[RhCp^*Cl_2]_2$ (0.209 g, 0.338 mmol) was dissolved in CH_2Cl_2 (25 mL) prior to the addition of *bis*(1-pyrazolyl)methane (0.102 g, 0.688 mmol) to the reaction mixture. The dark orange-red mixture turned slightly lighter in colour. The reaction mixture was left to stir at room temperature for 30 minutes before $NaBAr^F_4$ (0.658 g, 742 μmol) was added to the mixture. The resulting murky orange mixture was stirred at room temperature for 1 hour and then filtered through celite® to yield a clear bright orange solution. The solution was then reduced in volume to *ca.*15 mL and *n*-pentane was added with vigorous stirring to precipitate the product **8**, which was collected by filtration as a dark orange crystalline solid (0.687 g, 79 %). m.p. 189-192°C.

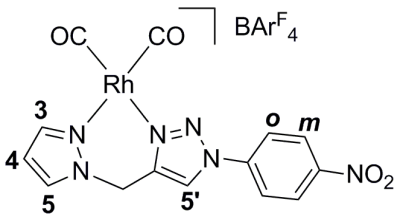
HR-MS (ESI^+, MeOH): *m/z* (%) 421.0661 (100 %) $[M]^+$ (Calculated $[M]^+$ = 421.07) amu.

Elemental Analysis: Found: C, 46.09; H, 2.78; N, 4.37. Calculated for $C_{49}H_{35}BClF_{24}N_4Rh$: C, 45.80; H, 2.75; N, 4.36 %.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.84 (d, ^3J(H3-H4) = 2.8 Hz, 2H, **H**3), 7.82 (d, ^3J(H5-H4) = 2.2 Hz, 2H, **H**5), 7.72 (br s, 8H, *ortho*-C**H** of BAr^F_4), 7.56 (br s, 4H, *para*-C**H** of BAr^F_4), 6.59 (apparent t, ^3J = 2.5 Hz, 2H, **H**4), 6.31 (d, $^2J(H_B\text{-}H_A)$ = 14.3 Hz, 1H, CH**H**), 6.01 (d, $^2J(H_A\text{-}H_B)$ = 14.3 Hz, 1H, C**H**H), 1.68 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{31}C {^{1}H} NMR (125 MHz, CD_2Cl_2, 298 K): δ 162.69 (q, ^1J(B-C) = 49.6 Hz,, q **C** *ipso* to B of BAr^F_4), 148.27 (s, **C**3 of Pz), 136.20 (br s, *ortho*-**C**H of BAr^F_4), 134.78 (s, **C**5 of Pz), 129.41 (q, ^2J(F-C) = 30.4 Hz, **C** *ipso* to CF_3 of BAr^F_4), 125.15 (q, ^1J(F-C) = 270.7 Hz, **C**F_3 of BAr^F_4) 118.04 (s, ^3J(F-C) = 4.1 Hz, 4C, *para*-**C**H of BAr^F_4), 110.33 (s, **C**4 of Pz), 97.84 (s, quat **C** of Cp*), 63.33 (s, **C**H_2), 9.77 (s, **C**H_3 of Cp*) ppm.

B.16 Synthesis of [Rh(2c)(CO)$_2$)]BAr$^F_4$ (14c)



$[Rh(CO)_2(Cl)]_2$ (38 mg, 0.096 mmol) was dissolved in dichloromethane (15 mL) prior to the addition of the ligand **2c** (52 mg, 0.19 mmol). After 5 minutes of stirring, $NaBAr^F_4$ (176 mg, 0.198 mmol) was added, resulting in the formation of a white precipitate and a colour change from yellow to dark brown. The reaction mixture was stirred for 2 hours before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 3 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **23** as a brown solid (157 mg, 63 %). m.p. 121-123 °C.

FTIR (CH_2Cl_2) ν: 2110 (s, νCO), 2054 (s, νCO) cm^{-1}.

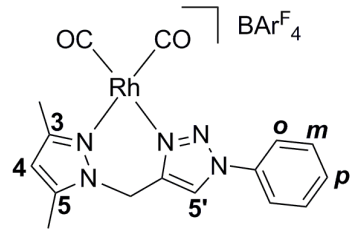
HR-MS (ESI^+, MeOH): *m/z* (%): 429.08334 (43 %) $[M]^+$ (Calculated $[M]^+$ = 428.9814) amu.

Elemental Analysis: Found: C, 43.20; H, 1.84; N, 6.21. Calculated for $C_{46}H_{22}BF_{24}N_6O_4Rh$: C, 42.75; H, 1.72; N, 6.50 %.

^{1}H NMR (acetone-d_6, 600 MHz): δ 9.37 (s, 1H, **H5'**), 8.58 (d, $^3J_{H\text{-}H}$ = 9.3 Hz, 2H, *m*-C**H** of **Ph**NO_2), 8.37 (d, $J_{H4\text{-}H5}$ = 2.4 Hz, 1H, **H5**, overlapped with *o*-C**H** of **Ph**NO_2), 8.36 (d, $^3J_{H\text{-}H}$ = 9.3 Hz, 2H, *o*-C**H** of **Ph**NO_2, overlapped with H5), 8.32 (d, $^3J_{H4\text{-}H3}$ = 2.4 Hz, 1H, **H3**), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.65 (apparent t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, **H4**), 6.14 (s, 2H, C**H**$_2$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 183.6 (d, $^1J_{Rh\text{-}C}$ = 68.7 Hz, 2 x **C**O (overlapped)), 162.9 (q, $^1J_{B\text{-}C}$ = 49.6 Hz, *ipso*-**C** to B, BAr^F_4), 149.3 (**C**$_q$ of **Ph**NO_2), 147.7 (**C**3), 143.0 (**C**$_q$ of Triaz), 140.8 (*ipso*-**C** to NO_2 of **Ph**NO_2), 136.9 (**C**5), 135.5 (*o*-**C**H to B, BAr^F_4), 130.0 (q, $^2J_{F\text{-}C}$ = 31.6 Hz, *ipso*-**C** to CF_3, BAr^F_4), 126.6 (*m*-**C**H of **Ph**), 125.4 (q, $^1J_{F\text{-}C}$ = 270.2 Hz, **C**F_3, BAr^F_4), 125.4 (**C**5'), 123.6 (*o*-**C**H of **Ph**NO_2), 118.4 (br s, *p*-**C**H to B, BAr^F_4), 109.0 (**C**4), 46.1 (**C**H_2) ppm.

B.17 Synthesis of [Rh(3a)(CO)$_2$]BAr$^F_4$ (15a)



[Rh(CO)$_2$Cl]$_2$ (31 mg, 0.080 mmol) was dissolved in dichloromethane (10 mL) prior to the addition of the ligand **3a** (41 mg, 0.16 mmol). After 5 minutes of stirring, NaBAr$^F_4$ (148 mg, 0.166 mmol) was added, resulting in the formation of a white precipitate and a colour change from yellow to brown. The reaction mixture was stirred overnight before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 2 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **15a** as a brown solid (83 mg, 41 %). m.p. 44-47 °C (decomposed).

FTIR (CH_2Cl_2) ν: 2106 (s, νCO), 2047 (s, νCO) cm^{-1}.

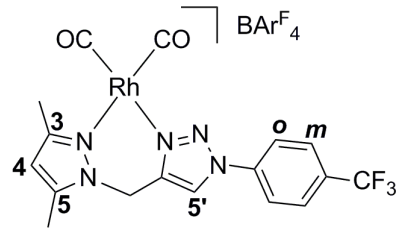
HR-MS (ESI$^+$, MeOH): *m/z* (%): 412.0833 (9 %) [M]$^+$ (Calculated [M]$^+$ = 412.0275) amu.

Elemental Analysis: Found: C, 45.07; H, 2.05; N, 4.97. Calculated for $C_{48}H_{27}BF_{24}N_5O_2Rh.0.25CH_2Cl_2$: C, 44.69; H, 2.14; N, 5.40 %.

^{1}H NMR (acetone-d_6, 400 MHz): δ 9.09 (s, 1H, **H5'**), 7.96 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, *o*-C**H** of **Ph**), 7.79 (br s, 8H, *o*-C**H** of BAr$^F_4$), 7.71 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, *m*-C**H** of **Ph**, overlapped with *p*-C**H** of **Ph**), 7.70 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, *p*-C**H** of **Ph**, overlapped with *m*-C**H** of **Ph**), 7.68 (br s, 4H, *p*-C**H** of BAr$^F_4$), 6.34 (s, 1H, **H4**), 5.89 (s, 2H, C**H**$_2$), 2.57 (s, 3H, C3-C**H**$_3$), 2.54 (s, 3H, C5-C**H**$_3$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 100 MHz): δ 183.4 (d, $^1J_{Rh\text{-}C}$ = 68.8 Hz, 2 x **C**O (overlapped)), 162.6 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** to B, BAr$^F_4$), 153.9 (**C**3), 146.2 (**C**5), 142.8 (**C**$_q$ of Triaz), 136.8 (**C**$_q$ of **Ph**), 135.5 (br s, *o*-**C**H to B, BAr$^F_4$), 130.0 (q, $^2J_{F\text{-}C}$ = 31.3 Hz, $^3J_{B\text{-}C}$ = 2.6 Hz, *ipso*-**C** to CF_3, BAr$^F_4$), 131.8 (*p*-**C**H of **Ph**), 131.2 (*m*-**C**H of **Ph**), 125.4 (q, $^1J_{F\text{-}C}$ = 270.1 Hz, **C**F$_3$, BAr$^F_4$), 124.8 (**C**5'), 122.4 (*o*-**C**H of **Ph**), 118.4 (br s, *p*-**C**H to B, BAr$^F_4$), 109.1 (**C**4), 42.6 (**C**H$_2$), 15.6 (C3-**C**H$_3$), 11.5 (C5-**C**H$_3$) ppm.

B.18 Synthesis of $[Rh(3b)(CO)_2]BAr^F_4$ (15b)



$[Rh(CO)_2(Cl)]_2$ (40 mg, 0.10 mmol) was dissolved in dichloromethane (15 mL) prior to the addition of ligand **3b** (66 mg, 0.21 mmol). After 5 minutes of stirring, $NaBAr^F_4$ (191 mg, 0.215 mmol) was added, resulting in the formation of a white precipitate and a colour change from yellow to brown. The reaction mixture was stirred overnight before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 3 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **15b** as a brown solid (177 mg, 64 %). m.p. 51-54 °C (decomposed).

FTIR (CH_2Cl_2) ν: 2107 (s, νCO), 2049 (s, νCO) cm^{-1}.

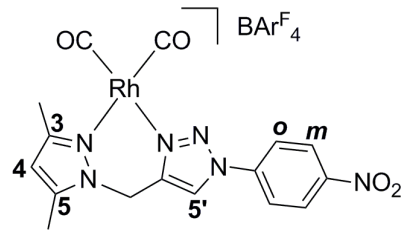
HR-MS (ESI^+, MeOH): *m/z* (%): 480.1667 (41 %) $[M]^+$ (Calculated $[M]^+$ = 480.0149) amu.

Elemental Analysis: Found: C, 44.27; H, 2.15; N, 4.77. Calculated for $C_{49}H_{26}BF_{27}N_5O_2Rh$: C, 43.81; H, 1.95; N, 5.21 %.

^{1}H NMR (acetone-d_6, 600 MHz): δ 9.24 (s, 1H, **H5'**), 8.25 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H, *m*-C**H** of **Ph**CF_3), 8.09 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H, *o*-C**H** of **Ph**CF_3), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.35 (s, 1H, **H4**), 5.92 (s, 2H, C$\mathbf{H}_2$), 2.57 (s, 3H, C3-C$\mathbf{H}_3$), 2.54 (s, 3H, C5-C$\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 183.7 (d, $^1J_{Rh\text{-}C}$ = 69.8 Hz, 2 x **C**O (overlapped)), 162.6 (q, $^1J_{B\text{-}C}$ = 49.6 Hz, *ipso*-**C** to B, BAr^F_4), 154.0 (**C**3), 146.3 (**C**5), 143.2 ($\mathbf{C}_q$ of Triaz), 139.8 ($\mathbf{C}_q$ of **Ph**CF_3), 135.5 (br s, *o*-**C**H to B, BAr^F_4), 132.7 (q, $^2J_{C\text{-}F}$ = 32.1, *ipso*-**C** to CF_3 of **Ph**CF_3), 130.0 (q, $^2J_{F\text{-}C}$ = 31.4 Hz, *ipso*-**C** of CF_3, BAr^F_4), 128.5 (*o*-**C**H of **Ph**CF_3), 125.4 (q, $^1J_{F\text{-}C}$ = 270.2 Hz, **C**F_3, BAr^F_4), 124.2 (q, $^1J_{C\text{-}F}$ = 274.9 Hz, **C**F_3 of **Ph**CF_3), 125.1 (**C**5'), 123.3 (*m*-**C**H of **Ph**CF_3), 118.5 (br s, *p*-**C**H to B, BAr^F_4), 108.9 (**C**4), 42.6 ($\mathbf{C}H_2$), 15.6 (C3-**C**H_3), 11.6 (C5-**C**H_3) ppm.

B.19 Synthesis of [Rh(3c)(CO)$_2$]BAr$^F_4$ (15c)



$[Rh(CO)_2(Cl)]_2$ (40 mg, 0.10 mmol) was dissolved in dichloromethane (15 mL) prior to the addition of ligand **3c** (61 mg, 0.20 mmol). After 5 minutes of stirring, $NaBAr^F_4$ (188 mg, 0.213 mmol) was added, resulting in the formation of a white precipitate and a colour change from yellow to brown. The reaction mixture was stirred for 2 hours before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 3 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **26** as a pale brown solid (151 mg, 56 %). m.p. 135-137 °C.

FTIR (CH_2Cl_2) *v*: 2108 (s, νCO), 2050 (s, νCO) cm^{-1}.

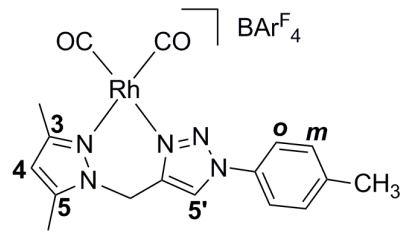
HR-MS (ESI$^+$, MeOH): *m/z* (%): 457.0152 (21 %) $[M]^+$ (Calculated $[M]^+$ = 457.0126) amu.

Elemental Analysis: Found: C, 43.62; H, 2.11; N, 6.08. Calculated for $C_{48}H_{26}BF_{24}N_6O_4Rh$: C, 43.66; H, 1.98; N, 6.36 %.

^{1}H NMR (acetone-d_6, 600 MHz): δ 9.31 (s, 1H, **H5'**), 8.57 (d, $^3J_{H\text{-}H}$ = 9.2 Hz, 2H, *m*-C**H** of **Ph**NO_2), 8.33 (d, $^3J_{H\text{-}H}$ = 9.3 Hz, 2H, *o*-C**H** of **Ph**NO_2), 7.79 (br s, 8H, *o*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 6.35 (s, 1H, **H4**), 5.90 (s, 2H, C**H**$_2$), 2.57 (s, 3H, C3-C**H**$_3$), 2.54 (s, 3H, C5-C**H**$_3$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 183.9 (d, $^1J_{Rh\text{-}C}$ = 68.7 Hz, 2 x **C**O (overlapped)), 162.6 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-**C** to B, BAr^F_4), 154.0 (**C**5), 149.8 (**C**$_q$ of **Ph**NO_2), 146.3 (**C**3), 143.3 (**C**$_q$ of Triaz), 140.9 (*ipso*-**C** to NO_2 of **Ph**NO_2), 135.5 (*o*-**C**H to B, BAr^F_4), 130.0 (q, $^2J_{F\text{-}C}$ = 31.2 Hz, *ipso*-**C** to CF_3, BAr^F_4), 126.3 (*m*-**C**H of **Ph**), 125.4 (q, $^1J_{F\text{-}C}$ = 270.0 Hz, **C**F_3, BAr^F_4), 125.3 (**C**5'), 123.5 (*o*-**C**H of **Ph**NO_2), 118.4 (br s, *p*-**C**H to B, BAr^F_4), 108.9 (**C**4), 42.6 (**C**H_2), 15.6 (C5-**C**H_3), 11.6 (C3-**C**H_3) ppm.

B.20 Synthesis of [Rh(3d)(CO)$_2$]BAr$^F_4$ (15d)



$[Rh(CO)_2(Cl)]_2$ (44 mg, 0.11 mmol) was dissolved in dichloromethane (15 mL) prior to the addition of ligand **3d** (54 mg, 0.22 mmol). After 5 minutes of stirring, $NaBAr^F_4$ (200 mg, 0.225 mmol) was added, resulting in the formation of a white precipitate and a colour change from yellow to dark brown. The reaction mixture was stirred overnight before being filtered through celite® and rinsed with dichloromethane. The volume of the filtrate was reduced to *ca.* 2 mL and *n*-pentane (20 mL) was added with vigorous stirring to yield **15d** as a brown solid (159 mg, 62 %). m.p. 49-52 °C (decomposed).

FTIR (CH_2Cl_2) ν: 2106 (s, νCO), 2047 (s, νCO) cm^{-1}.

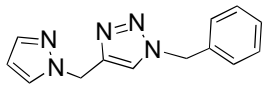
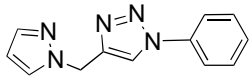
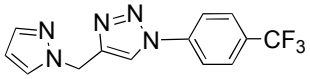
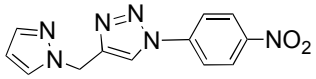
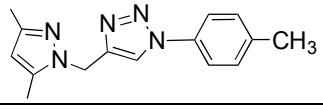
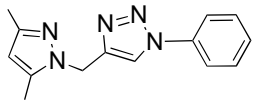
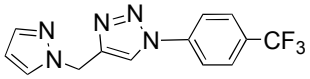
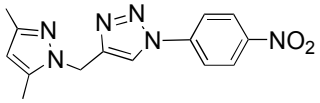
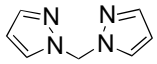
HR-MS (ESI^+, MeOH): *m/z* (%): 426.0567 (18 %) $[M]^+$ (Calculated $[M]^+$ = 426.0432) amu.

Elemental Analysis Found: C, 45.55; H, 2.29; N, 5.38. Calculated for $C_{49}H_{29}BF_{24}N_5O_2Rh$: C, 45.64; H, 2.27; N, 5.43 %.

^{1}H NMR (acetone-d_6, 600 MHz): δ 9.02 (s, 1H, **H5'**), 7.82 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H, *o*-C**H** of **Ph**CF_3), 7.79 (br s, 8H, *m*-C**H** of BAr^F_4), 7.67 (br s, 4H, *p*-C**H** of BAr^F_4), 7.51 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *o*-C**H** of **Ph**CF_3), 6.33 (s, 1H, **H4**), 5.87 (s, 2H, C**H**$_2$), 2.57 (s, 3H, C3-C**H**$_3$), 2.53 (s, 3H, C5-C**H**$_3$), 2.45 (s, 3H, C**H**$_3$ of **Ph**CH_3) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 183.8 (d, $^1J_{Rh\text{-}C}$ = 68.7 Hz, 2 x **C**O (overlapped)), 162.6 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-**C** to B, BAr^F_4), 154.0 (**C**3), 146.2 (**C**5), 142.7 (**C**$_q$ of Triaz), 142.4 (**C**$_q$ of **Ph**CH_3), 135.5 (br s, *o*-**C**H to B, BAr^F_4), 134.6 (*ipso*-**C** to CH_3 of **Ph**CH_3), 130.0 (q, $^2J_{F\text{-}C}$ = 31.7 Hz, *ipso*-**C** of CF_3, BAr^F_4), 131.6 (*m*-**C**H of **Ph**CH_3), 125.4 (q, $^1J_{F\text{-}C}$ = 270.6 Hz, **C**F_3, BAr^F_4), 124.5 (**C**5'), 122.2 (*o*-**C**H of **Ph**CH_3), 118.5 (br s, *p*-**C**H to B, BAr^F_4), 108.8 (**C**4), 42.6 (**C**H_2), 21.1 (**C**H_3 of **Ph**CH_3), 15.6 (C3-**C**H_3), 11.5 (C5-**C**H_3) ppm.

Table S2: *ν*CO vibrational frequencies and ^{13}**C** chemical shifts of ^{13}**C**O of [Rh(N-N')(CO)$_2$]BAr$^F_4$ (**13-16**).

Complexes [Rh(N-N')(CO)$_2$]BAr$^F_4$ (13-16); N-N' Ligand =	**IR[a] (cm^{-1})**	**δ (CO)[b] (ppm)**
13[c] 	2108, 2050	182.8, 182.0
14a[c] 	2108, 2051	182.6, 181.9
14b 	2110, 2053	183.7 [d]
14c 	2110, 2054	183.6 [d]
15d 	2106, 2047	183.8
15a 	2106, 2047	183.4
15b 	2107, 2049	183.7
15c 	2108, 2050	183.6
16 	2109, 2051	183.4[e]

[a] FTIR spectra were acquired as solution in dichloromethane. [b] NMR spectra were acquired in acetone-d_6 unless otherwise noted. [c] NMR spectra were acquired in CD_2Cl_2 (reference [1]). [d] The two resonances for ^{13}**C**O overlap with each other in acetone-d_6 and appear as slightly broad doublet with $^1J(^{103}\text{Rh}\text{-}^{13}\text{C}) \sim 70$ Hz). [e]Spectrum was acquired in THF-d_8 (reference 2).

Part C: X-ray Crystallography

General experimental for X-ray crystallography:

Suitable single crystals of **5**, **6a'**, **6b**, **7b**, **8**, **9**, **10a**, **10a**', **11** and **15c** selected under the polarizing microscope (Leica M165Z), were picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at *ca.*150 K by using graphite-monochromated Mo-Kα radiation (λ = 0.710723 Å). The single crystals, mounted on the goniometer using cryo loops for intensity measurements, were coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry related absorption corrections using the program SADABS[3] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software.[4] All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL.[5]

The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using Mercury.[6] In all the structures, the CF_3 groups of the anion exhibited extensive orientation disorder. Also, crystal lattice contained disordered solvent (mostly Dichloromethane), the treatment of these in the least-squares refinement have been outlined in the cifs.

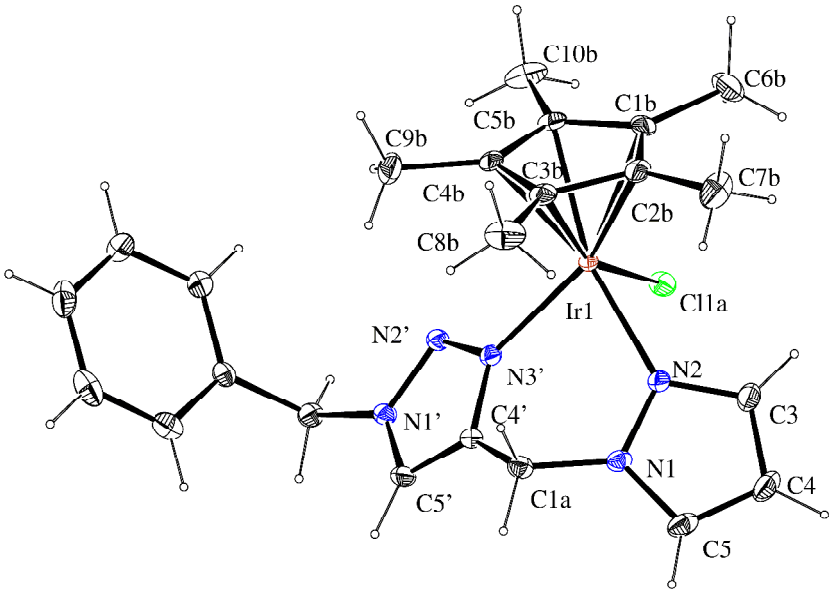


Figure S1: ORTEP depiction of [Ir(**1**)Cp*Cl]BAr^{F}_{4} (**5**) at 40% thermal ellipsoids for the non-hydrogen atoms.

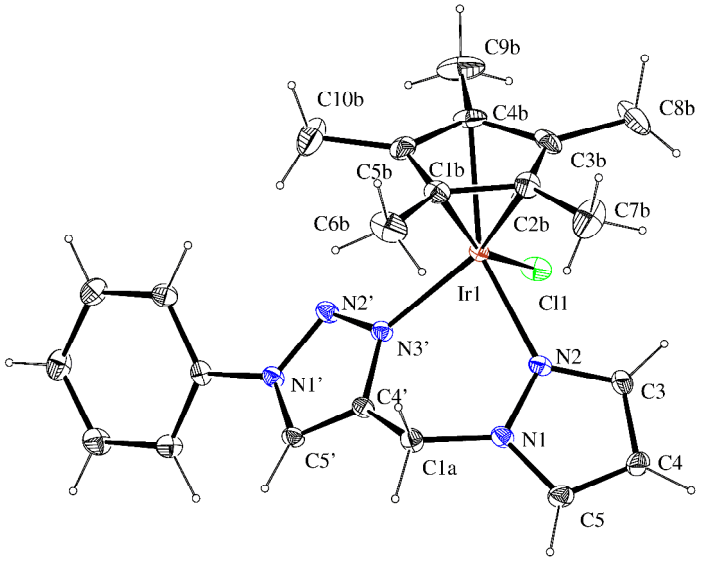


Figure S2: ORTEP depiction of [Ir(**2a**)Cp*Cl]BPh_4 (**6a'**) at 40% thermal ellipsoids for the non-hydrogen atoms.

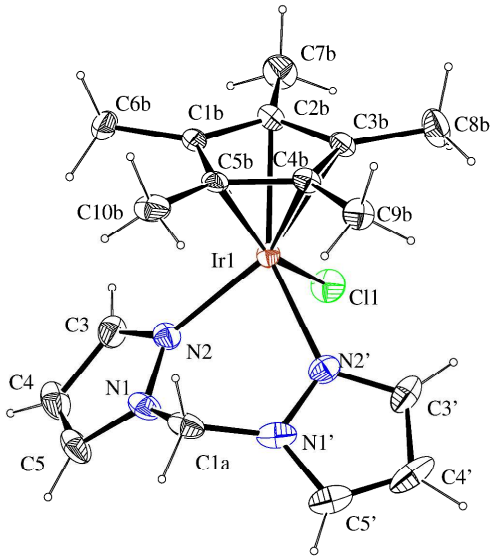


Figure S3: ORTEP depiction of [Ir(**4**)Cp*Cl]BPh_4 (**8**) at 40% thermal ellipsoids for the non-hydrogen atoms.

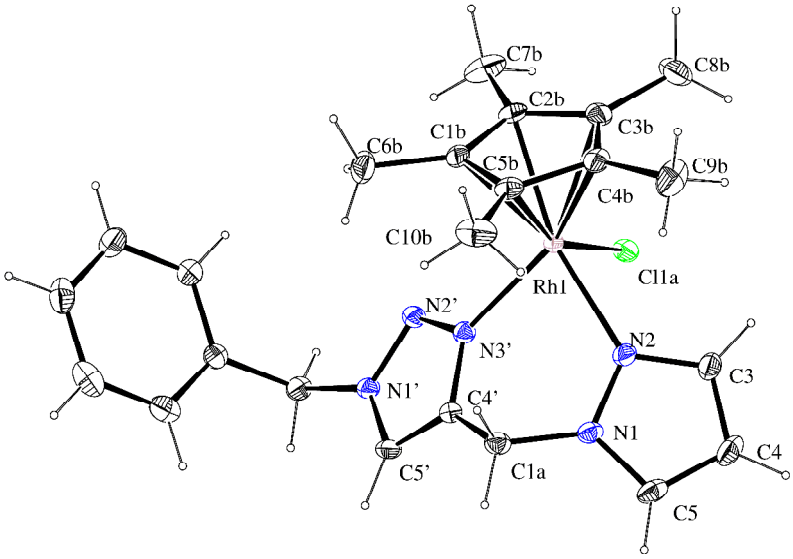


Figure S4: ORTEP depiction of [Rh(**1**)Cp*Cl]BAr^F_4 (**9**) at 40% thermal ellipsoids for the non-hydrogen atoms.

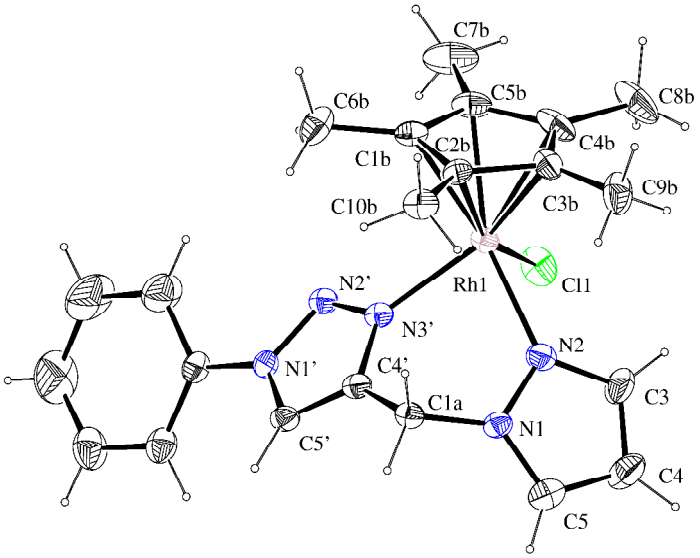


Figure S5: ORTEP depiction of [Rh(**1**)Cp*Cl]BPh_4 (**10a**) at 40% thermal ellipsoids for the non-hydrogen atoms.

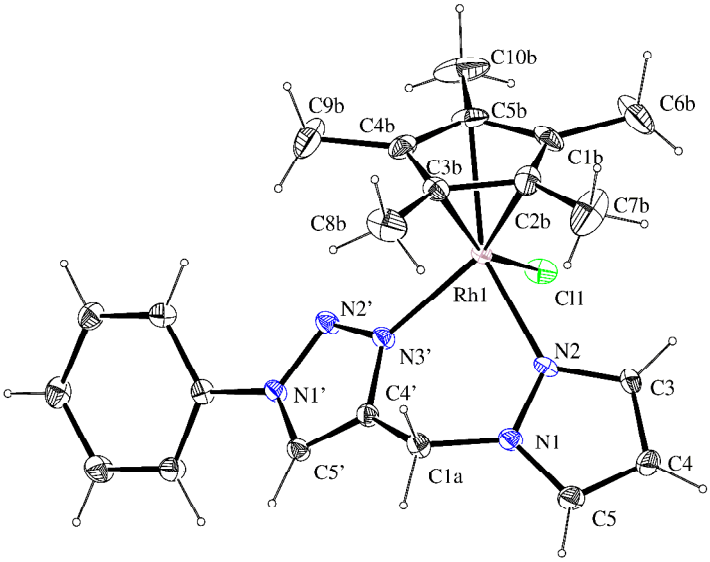


Figure S6: ORTEP depiction of [Rh(**1**)Cp*Cl]BPh_4 (**10a'**) at 40% thermal ellipsoids for the non-hydrogen atoms.

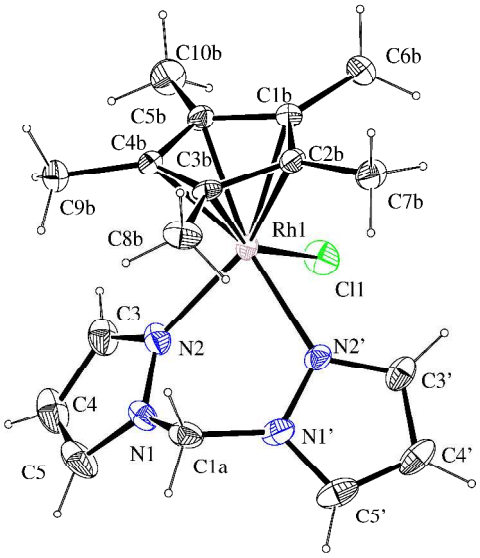


Figure S7: ORTEP depiction of [Rh(**4**)Cp*Cl]BPh_4 (**11**) at 40% thermal ellipsoids for the non-hydrogen atoms.

Table S3: Crystal structural data for the single crystal X-ray structures of Iridium complexes **8**, **6b**, **7b**, **6a'** and **5**.

	8	**6b**	**7b**	**6a'**	**5**
Chemical formula	$(C_{17}H_{23}ClIrN_4)$. $(C_{32}H_{12}BF_{23.97})$. $0.375(CCl_2)$	$(C_{23}H_{25}ClF_3IrN_5)$. $(C_{32}H_{12}BF_{24})$. $1(O)$	$(C_{25}H_{29}ClF_3IrN_5)$. $(C_{32}H_{12}BF_{24})$. $1(CH_2Cl_2)$	$(C_{22}H_{26}ClIrN_5)$. $(C_{24}H_{20}B)$.	$(C_{23}H_{28}ClIrN_5)$. $(C_{32}H_{12}BF_{24})$. $0.5(CH_2Cl_2)$
M (g mol-1)	1405.36	1535.36	1629.31	907.34	1507.84
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C2/c*	*C2/c*	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Crystal habit	yellow blocks	yellow plates	yellow blocks	yellow blocks	yellow blocks
Temperature (K)	155	170	170	156	151
a (Å)	28.8655(12)	29.5110(16)	19.4090 (8)	12.0829(5)	12.5013(14)
b (Å)	12.9022(5)	13.3179(7)	17.2163(8)	24.4058(10)	16.3750 (8)
c (Å)	29.8343(12)	32.1453(17)	21.637(1)	13.3522(5)	16.9370 (8)
α (°)	90	90	90	90	117.541(2)
β (°)	104.722 (1)	109.255(3)	112.133(2)	93.701(2)	96.775(2)
γ (°)	90	90	90	90	101.575(2)
V ($Å^3$)	10746.4(7)	11927.2(11)	6697.3(5)	3929.3(3)	2921.7(4)
Z	8	8	4	4	2
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
μ (mm-1)	2.70	2.41	2.23	3.51	2.50
Crystal size (mm)	0.36 × 0.26 × 0.18	0.32 × 0.10 × 0.04	0.28 × 0.26 × 0.14	0.35 × 0.25 × 0.21	0.41 × 0.38 × 0.16
Tmin, Tmax	0.440, 0.648	0.513, 0.901	0.570, 0.741	0.373, 0.522	0.426, 0.685
Refl. measured	38085	40150	45958	29202	37589
Unique reflections	9435	10497	11717	6884	10113
Obsd. Reflections [$I > 2\sigma(I)$]	8380	7764	9929	6549	9804
Rint	0.023	0.053	0.024	0.026	0.028
$R[F^2 > 2\sigma(F^2)]$	0.031	0.051	0.051	0.017	0.019
$wR(F^2)$	0.132	0.154	0.166	0.042	0.047
S	1.18	1.01	1.15	1.07	1.04
Reflections used	9435	10497	11717	6884	10113
Parameters	962	870	915	492	876
Restraints	341	34	57	492	204
Δρmax, Δρmin (e $Å^{-3}$)	1.41, -0.80	2.64, -1.39	1.39, -0.83	0.67, -0.62	0.61, -0.86

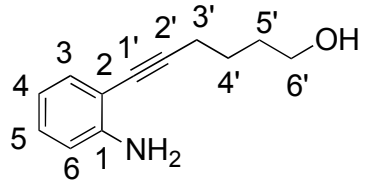
Table S4: Crystal structural data for the single crystal X-ray structures of Rhodium complexes **11**, **10a**, **10a'**, **9** and **15c**.

	11	**10a**	**10a'**	**9**	**15c**
Chemical formula	$(C_{17}H_{23}ClN_4Rh).$ $(C_{32}H_{12}BF_{24}).$ $0.125(CCl_2)$	$(C_{22}H_{26}ClN_5Rh).$ $(C_{32}H_{12}BF_{24}).$ $0.875(CH_2Cl_2)$	$(C_{22}H_{26}ClN_5Rh).$ $(C_{24}H_{20}B).$	$(C_{23}H_{28}ClN_5Rh).$ $(C_{32}H_{12}BF_{23.97}).$ $0.5(CH_2Cl_2)$	$(C_{16}H_{24}N_6O_4Rh).$ $(C_{32}H_{12}BF_{24}).$ $0.75(CCl_2)$
M (g mol-1)	1295.34	1436.37	818.05	1418.55	1382.65
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/n$	$P\bar{1}$	*C*2/*c*
Crystal habit	yellow blocks	Yellow blocks	Red orange blocks	Yellow blocks	Yellow blocks
Temperature (K)	152	151	155	152	160
a (Å)	28.8126(10)	29.9749(17)	12.0994(3)	12.4931(16)	39.396(4)
b (Å)	12.8881(4)	13.0963(8)	24.4422(7)	16.3598(8)	18.3734(16)
c (Å)	29.9049(11)	36.371(2)	13.3308(4)	16.8978 (10)	16.4800(16)
α (°)	90	90	90	117.365(2)	90
β (°)	104.623(2)	111.572(13)	93.565(1)	96.805(3)	106.912(5)
γ (°)	90	90	90	101.470(3)	90
V ($Å^3$)	10745.2(6)	13277.7(13)	3934.77(19)	2917.2(4)	11413.0(19)
Z	8	8	4	2	8
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
μ (mm-1)	0.50	0.47	0.54	0.50	0.50
Crystal size (mm)	0.18 × 0.15 × 0.05	0.34 × 0.23 × 0.15	0.29 × 0.17 × 0.16	0.33 × 0.12 × 0.06	0.21 × 0.21 × 0.09
Tmin, Tmax	0.913, 0.974	0.857, 0.931	0.860, 0.921	0.851, 0.972	0.903, 0.957
Refl. measured	39871	40705	25137	33968	123073
Unique reflections	9456	11579	6909	10077	10039
Obsd. Reflections [I > 2σ(I)]	7065	8562	5495	8671	8611
Rint	0.053	0.072	0.148	0.084	0.039
$R[F^2 > 2\sigma(F^2)]$	0.075	0.088	0.027	0.035	0.056
$wR(F^2)$	0.222	0.260	0.068	0.082	0.183
S	1.46	1.10	1.06	1.04	0.76
Reflections used	9456	11579	6909	10077	10039
Parameters	759	922	492	865	819
Restraints	124	336	0	174	36
Δρmax, Δρmin (e $Å^{-3}$)	1.47, -0.94	1.54, -1.49	1.06, -0.76	0.61, -0.82	1.25, -0.99

Part D: Synthesis of 2-(hydroxyalk-1-ynyl)aniline substrates

2-(Hydroxyalk-1-ynyl)aniline substrates: 2-(6-hydroxyhex-1-ynyl)aniline (**17S**), 2-(6-hydroxypent-1-ynyl)aniline (**18S**), 2-(6-hydroxyhept-1-ynyl)aniline (**19S**), 2-(6-hydroxy-6-methylhex-1-ynyl)aniline (**20S**) and were synthesised by the Sonogashira coupling reaction between 2-iodoaniline and the corresponding terminal alkynol. Several reagents used in the synthesis of **17S-20S**, namely 6-heptyn-2-ol,[7] 6-heptyn-1-ol[8] and $[Pd(PPh_3)_4]$[9] were prepared according to literature procedures. A typical synthesis procedure is included for compound **17S**. The syntheses of **18S-21S** were conducted in an analogous manner.

D.1 Synthesis of 2-(6-Hydroxy-1-hexyn-1-yl)aniline, 17S[10]



A solution of 2-iodoaniline (3.29 g, 15.0 mmol) and 5-hexyn-1-ol (1.65 mL, 15.0 mmol) in triethylamine (50 mL) was deoxygenated *via* three freeze-pump-thaw cycles, $[Pd(PPh_3)_4]$ (0.173 g, 0.150 mmol, 1.0 mol%) and CuI (0.057 g, 0.30 mmol, 2.0 mol%) were then added with minimal exposure to air. The reaction mixture was stirred under nitrogen overnight, during which time the solution turned brown and a small amount of solid formed. Saturated aqueous ammonium chloride solution (50 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane (5 x 40 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered over a pad of silica (~1 cm thick) and the solvent was removed in *vacuo* to give a brown oil. The crude product was purified by column chromatography, hexane: EtOAc = 4:6 (v/v), R_f = 0.43 to afford 8.1 as a yellow viscous oil. Yield: 2.23 g, 79 %.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (dd, ^3J(H4-H3) = 7.9 Hz, ^4J(H5-H3) = 1.5 Hz, 1H, **H**3), 7.07 (apparent td, ^3J(H6-H5) = ^3J(H4-H5) = 7.9 Hz, ^4J(H3-H5) = 1.5 Hz, 1H, **H**5), 6.67 (dd, ^4J(H5-H6) = 7.8 Hz, ^3J(H4-H6) = 1.5 Hz, 1H, **H**6), 6.65 (apparent td, ^3J(H5-H4) = 7.5 Hz, ^3J(H3-H4) = 7.8 Hz, ^4J(H6-H4) = 1.5 Hz, 1H, **H**4), 3.71 (t, ^3J(H5'-H6') = 6.3 Hz, 2H, **H**6'), 2.52 (t, ^3J = 6.7 Hz, 2H, **H**3'), 1.79-1.69 (m, 4H, H4' & H5') ppm.

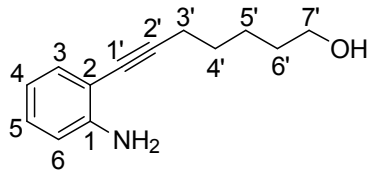
D.2 Synthesis of 2-(5- Hydroxy-1-pentyn-1-yl)aniline, 18S[11]

Starting with 2-iodoaniline (3.29 g, 15.0 mmol) and 4-pentyn-1-ol (1.39 mL, 15.0 mmol). Yield: 2.1 g, 80 %; yellow viscous oil; R_f = 0.43 (Hexane : EtOAc = 4:6 (v/v)).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (dd, ^3J(H4-H3) = 8.0 Hz, ^4J(H5-H3) = 1.5 Hz, 1H, **H**3), 7.07 (apparent td, ^3J(H6-H5) = ^3J(H4-H5) =7.5 Hz, ^4J(H3-H5) = 1.5 Hz, 1H, **H**5), 6.67 (dd, ^4J(H5-H6) = 7.5 Hz, ^3J(H4-H6) = 1.5 Hz, 1H, **H**6), 6.65 (apparent td, ^3J(H5-H4) = 7.5 Hz, ^3J(H3-H4) = 8.0 Hz, ^4J(H6-H4) = 1.5 Hz, 1H, **H**4), 3.76 (t, ^3J(H4'-H5') = 6.3 Hz, 2H, **H**5'), 3.66 (br s, 3H, N**H**$_2$ & O**H**), 2.56 (t, ^3J(H4'-H3') = 6.9 Hz, 2H, **H**3'), 1.84 (apparent p, ^3J(H3'-H4', H5'-H4') = 6.5 Hz, 2H, **H**4') ppm.

^{13}C{1H} NMR (75 MHz, $CDCl_3$): δ 147.7 (**C**2), 132.0 (**C**3), 129.0 (**C**5), 118.0 (**C**4), 114.4 (**C**6), 108.8 (**C**1), 94.9 (**C**2'), 77.5 (**C**1'), 61.5 (**C**5'), 31.6 (**C**4'), 16.2 (**C**3') ppm.

D.3 Synthesis of 2-(6-hydroxyhept-1-ynyl)aniline, 19S



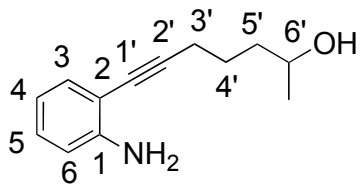
Starting with 2-iodoaniline (0.371 g, 1.69 mmol) and 6-heptyn-1-ol (0.190 g, 1.69 mmol). Yield: 0.201 g, 59 %; yellow viscous oil; R_f = 0.14 (Hexane : EtOAc = 7:3 (v/v)).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (dd, ^3J(H4-H3) = 7.6 Hz, ^4J(H5-H3) = 1.3 Hz, 1H, **H**3), 7.07 (apparent td, ^3J(H6-H5) = ^3J(H4-H5) =7.7 Hz, ^4J(H3-H5) = 1.5 Hz, 1H, **H**5), 6.68 (dd, ^4J(H5-H6) = 7.6 Hz, ^3J(H4-H6) = 1.5 Hz, 1H, **H**6), 6.66 (apparent td, ^3J(H5-H4) = 7.5 Hz, ^3J(H3-H4) = 8.0 Hz, ^4J(H6-H4) = 1.5 Hz, 1H, **H**4), 4.16 (br s, 3H, N**H**$_2$), 3.66 (t, ^3J(H6'-H7') = 6.3 Hz, 2H, **H**7'), 2.49 (t, ^3J(H4'-H3') = 7.0 Hz, 2H, **H**3'), 1.66 (apparent p, ^3J(H3'-H4', H5'-H4') = 7.3 Hz, 2H, **H**4'), 1.62 (apparent p, ^3J(H5'-H6', H6'-H7') = 6.4 Hz, 2H, **H**6'), 1.55 (m, 2H, **H**5') ppm.

^{13}C{1H} NMR (150 MHz, $CDCl_3$): δ 147.7 (**C**2), 132.2 (**C**3), 129.0 (**C**5), 118.0 (**C**4), 114.3 (**C**6), 109.0 (**C**1), 95.5 (**C**2'), 62.9 (**C**1'), 32.4 (**C**7'), 29.8 (**C**6'), 28.8 (**C**4'), 25.2 (**C**5'), 19.7 (**C**3') ppm.

D.4 Synthesis of 2-(6-Hydroxy-6-methylhex-1-ynyl)aniline, 20S

Starting with 2-iodoaniline (1.0 g, 5.0 mmol) and 6-heptyn-2-ol (0.60 g, 5.0 mmol). Yield: 0.80 g, 81 %; yellow viscous oil; R_f = 0.16 (Hexane : EtOAc = 1:3 (v/v)).



HRMS (ESI, MeOH): *m/z*: 226.1667. Calculated for $[C_{13}H_{17}NO + Na]^+$ = 226.1203 amu.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, ^3J(H4-H3) = 7.8 Hz, ^4J(H5-H3) = 1.5 Hz, 1H, **H**3), 7.07 (apparent td, ^3J(H6-H5) = ^3J(H4-H5) =7.6 Hz, ^4J(H3-H5) = 1.5 Hz, 1H, **H**5), 6.68 (dd, ^4J(H5-H6) = 7.6 Hz, ^3J(H4-H6) = 1.5 Hz, 1H, **H**6), 6.66 (apparent td, ^3J(H5-H4) = 7.6 Hz, ^3J(H3-H4) = 7.8 Hz, ^4J(H6-H4) = 1.5 Hz, 1H, **H**4), 3.85 (m, 1H, **H**6'), 3.28 (br s, 3H, N**H**$_2$ & O**H**), 2.49 (t, ^3J = 7.3 Hz, 2H, **H**3'), 1.76-1.58 (m, 2H, **H**4' and **H**5'), 1.20 (d, ^3J = 6.30 Hz, 3H, C**H**$_3$) ppm.

^{13}C{1H} NMR (75 MHz, $CDCl_3$): δ 147.7 (**C**2), 132.1 (**C**3), 129.0 (**C**5), 118.0 (**C**4), 114.3 (**C**6), 108.9 (**C**1), 94.5 (**C**2'), 77.4 (**C**1'), 67.7 (**C**6'), 38.5 (**C**5'), 25.2 (**C**4'), 23.7 (**C**H$_3$), 19.7 (**C**3') ppm.

Part E: General Catalytic Procedure, Time Course Profiles and NMR of Intermediates and Products

E.1 General Procedure for the Tandem Hydroamination/C-C Bond Formation Reactions

The metal catalysed tandem hydroamination/C-C bond formation reactions of the 2-(hydroxyalk-1-ynyl)aniline substrates (**17S-20S**) were performed on a small scale in J. Youngs NMR tubes. The metal complex (5.0 mol%) were weighed into the NMR tube prior to the addition of deuterated solvent (Toluene-d_8, 0.6 mL) to the tube in a nitrogen filled glovebox. The substrate (concentration 0.17-0.19 M) was then added into the NMR tube. The tube was then removed from the glovebox and immediately placed into an acetone/liquid nitrogen slush-bath. The solution was briefly thawed before the NMR tube was placed into the probe of the NMR spectrometer at 100 °C. The temperature in the NMR magnet was calibrated with neat ethylene glycol using an Omega Microprocessor Thermometer (Model HH23). ^{1}H NMR spectra were recorded periodically and the products were identified by comparison with reported spectroscopic ^{1}H NMR data. Upon complete conversion of the 2-(hydroxyalk-1-ynyl)aniline substrates (**17S-20S**) to the 2-(hydroxylalkyl)indole intermediates (**17I-20I**) as observed by ^{1}H NMR spectroscopy, the base (^{t}BuOK, KOH, DABCO or K[N(SiMe$_3$)$_2$], 1 equivalence), was added into the same NMR tube in the nitrogen filled glovebox. The tube was then removed from the glovebox, shaken and placed in a sonicator for 5 minutes. A ^{1}H NMR spectrum was obtained at 25 °C in the spectrometer before the NMR tube was placed in an oil bath at 110 °C. ^{1}H NMR spectra were obtained at regular time intervals at 25 °C in the spectrometer. The products were identified following reported ^{1}H NMR data.

The rate of conversion for all catalytic reactions was determined by the relative integration of ^{1}H resonances of the product to the starting material in the 1H NMR spectrum. Complete conversion (> 98%) was taken to be the time where no remaining substrate resonances were observed in the ^{1}H NMR spectrum. The turnover frequency (TOF) was calculated at the point of 50 % conversion as the number of moles of products produced per mole of catalyst used per hour.

The catalysed C-N bond formation (1st step) was performed in the same fashion as the catalysed tandem reaction without the addition of base. The efficiency of the catalysed intramolecular C3 alkylation was conducted mainly with isolated 2-(4-hydroxybutyl)indole (**21I**), which was isolated from the large scale (*ca.* 0.30 g) catalysed cyclisation of 2-(6-hydroxyhex-1ynyl)aniline (**21S**) using $[Rh(bpm)(CO)_2]BAr^F_4$ (**16**, bpm = *bis*(1-pyrazol-1-yl)methane) in toluene. The alkylation reaction was performed in the same way the 2nd step of the tandem C-N/C-C bond formation reaction.

E.2 Time Course Profiles for Selected Tandem Hydroamination/C-C Bond Formation Reactions

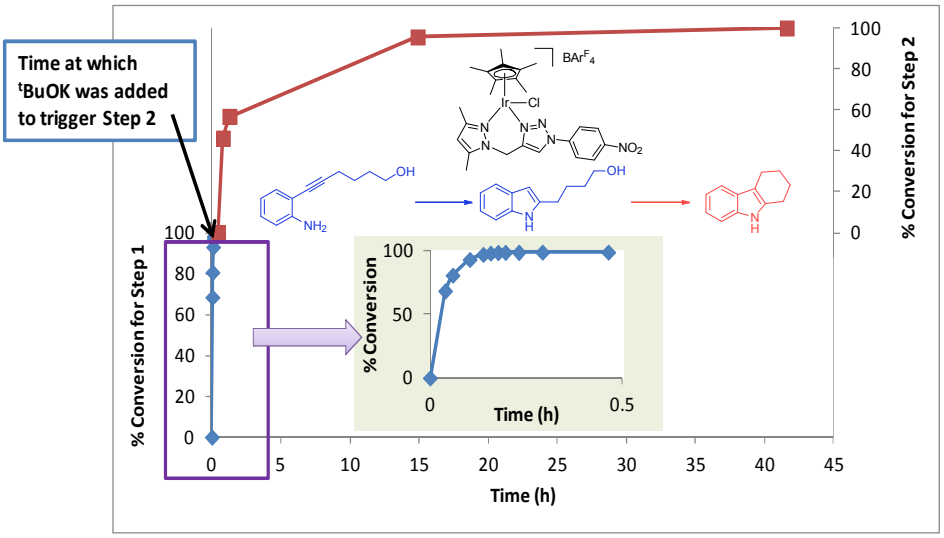


Figure S8: Time course profile for $[Ir(\mathbf{3c})(Cp^*)Cl]BAr^F_4$ (**7c**) catalysed one-pot tandem C-N and C-C bond formation in the synthesis of 1,2,3,4-tetrahydrocarbazole (**17P**) from 2-(6-hydroxyhex-1-ynyl)aniline (**17S**).

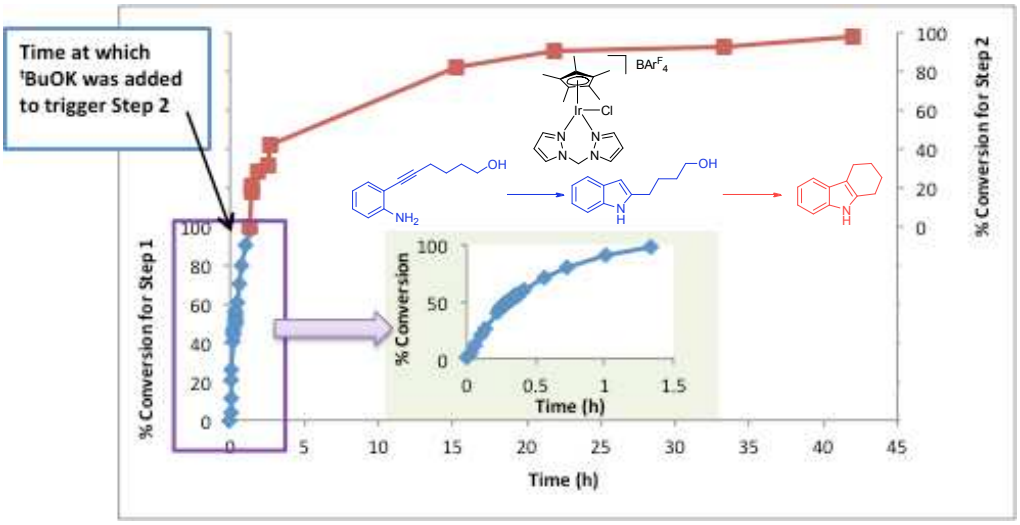
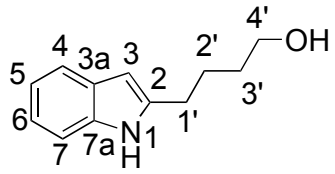


Figure S9: Time course profile for [Ir(**4**)(Cp*)Cl]BAr^F_4 (**8**) catalysed one-pot tandem C-N and C-C bond formation in the synthesis of 1,2,3,4-tetrahydrocarbazole (**17P**) from 2-(6-hydroxyhex-1-ynyl)aniline (**17S**).

E.3 Typical Isolation Procedure for 2-(Hydroxyalkyl)indole Intermediates, 17I-20I

When the cyclisation of **17S**, **18S** and **20S** to **17I**, **18I**, and **20I** have respectively completed as observed by ^{1}H NMR spectroscopy, the contents of the NMR tube were poured into a small vessel and the NMR tube rinsed out with dichloromethane (*ca.* 3 x 0.5 mL). The solution was passed through a pad of silica (ca. 0.7 cm thick) which was then rinsed with CH_2Cl_2 : Et_2O = 1:1 (v/v, 5 mL). The solvent was removed under reduced pressure and the remaining viscous oil or solid dried in a vacuum desiccator to afford the 2-(hydroxylalkyl)indole **17I**, **18I**, and **20I**. NMR data of 2-(5-hydroxypent-1-yl)indole, **19I** was obtained without isolation upon completion of the cyclisation form **19S** to **19I** as observed by ^{1}H NMR spectroscopy.

E.4 2-(4-Hydroxybut-1-yl)indole, 17I[10]

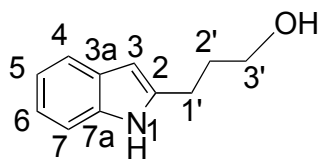


Yellow brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (br s, 1H, N**H**), 7.55 (d, ^3J(H5-H4) = 6.6 Hz, 1H, **H**4), 7.29 (d, ^3J(H6-H7) = 7.2 Hz, 1H, **H**7), 7.11 (m, 2H, **H**5 and **H**6), 6.25 (s, 1H, **H**3), 3.67 (t, ^3J = 6.1 Hz, 2H, **H**4'), 2.76 (t, ^3J = 7.4 Hz, 2H, **H**1'), 1.98 (br s, 1H, O**H**), 1.79 (apparent p, ^3J = 7.0 Hz, 2H, **H**2' or **H**3'), 1.63 (apparent p, ^3J = 7.4 Hz, 2H, **H**2') ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.7 (**C**2), 136.0 (**C**3a), 128.9 (**C**7a), 121.0 (**C**6), 119.8 (**C**4), 119.7 (**C**5), 110.5 (**C**7), 99.6 (**C**3), 62.6 (**C**4'), 32.1, 28.0, 25. 6 (last three **C**1', **C**2' and **C**3') ppm

E.5 2-(3-Hydroxyprop-1-yl)indole, 18I[12]



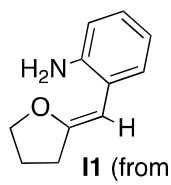
Yellow solid.

GC-MS (CI), *m/z* (%): 176 (76), $[M+ H]^+$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (br s, 1H, N**H**), 7.52 (d, ^3J(H5-H4) = 7.5 Hz, 1H, **H**4), 7.30 (d, ^3J(H6-H7) = 7.5 Hz, 1H, **H**7), 7.12 (apparent td, ^3J(H5-H6) = ^3J(H7-H6) = 7.5 Hz, ^4J(H4-H6) = 1.5 Hz, 1H, **H**6), 7.06 (apparent td, ^3J(H6-H5) = ^3J(H4-H5) = 7.5 Hz, ^4J(H7-H5) = 1.5 Hz, 1H, **H**5), 6.25 (s, 1H, **H**3), 3.75 (t, ^3J(H2'-H3') = 6.0 Hz, 2H, **H**3'), 2.90 (t, ^3J(H2'-H1') = 7.2 Hz, 2H, **H**1'), 1.98 (tt, ^3J(H3'-H2') = 6.0 Hz, ^3J(H1'-H2') = 7.2 Hz, 2H, **H**2'), 1.45 (br s, 1H, O**H**) ppm.

^{13}C{1H} NMR (75 MHz, $CDCl_3$): δ 138.9 (**C**2), 135.9 (**C**3a), 128.7 (**C**7a), 121.0 (**C**6), 119.7 (**C**4), 119.5 (**C**5), 110.3 (**C**7), 99.6 (**C**3), 62.0 (**C**3'), 31.7 (**C**2'), 24.6 (**C**1') ppm.

E.5' 2-[(*Z*)-(Dihydrofuran-2(*3H*)-yliden)methyl]benzenamine, I1 (from 18S)



I1 (from **18S**)

The intermediate **I1** (from **18S**) was observed following the catalysed cyclisation of 2-(5-hydroxypent-1-ynyl)aniline, **18S**, when the reaction was conducted at 60 °C. NMR assignments were determined using 2D NMR

techniques. The NMR spectral data was found to be similar to the data reported for an analogous compound, (Z)-2-benzylidenetetrahydrofuran.[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52 (dd, ^{3}J(H4'-H3') = 7.8 Hz, ^{4}J(H5'-H3') = 1.2 Hz, 1H, **H**3'), 7.01 (apparent td, ^{3}J(H6'-H5') = ^{3}J(H4'-H5') = 7.8 Hz, ^{4}J(H3'-H5') = 1.2 Hz, 1H, **H**5'), 6.80 (apparent td, ^{3}J(H5'-H4') = ^{3}J(H3'-H4') = 7.8 Hz, ^{4}J(H6'-H4') = 1.2 Hz, 1H, **H**4'), 6.70 (dd, ^{3}J(H5'-H6') = 7.8 Hz, ^{4}J(H4'-H6') = 1.2 Hz, 1H, **H**6'), 5.22 (s, 1H, **H**1''), 4.28 (t, ^{3}J(H5-H4) = 6.7 Hz, 2H, **H**4), 3.79 (very br, 2H, N**H**$_2$), 2.75 (td, ^{3}J(H4-H3) = 7.2 Hz), ^{4}J(H1''-H3) = 1.5 Hz, 2H, **H**$_3$), 2.05 (apparent p, ^{3}J(H4-H5) = ^{3}J(H3-H5) = 7.2Hz, 2H, H5) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 156.8 (**C**2), 142.7 (**C**1'), 129.2 (**C**3'), 126.3 (**C**2'), 122.6 (**C**5'), 118.8 (**C**4'), 116.1 (**C**6'), 91.7 (**C**1''), 71.9 (**C**5), 30.6 (**C**3), 24.5 (**C**4) ppm.

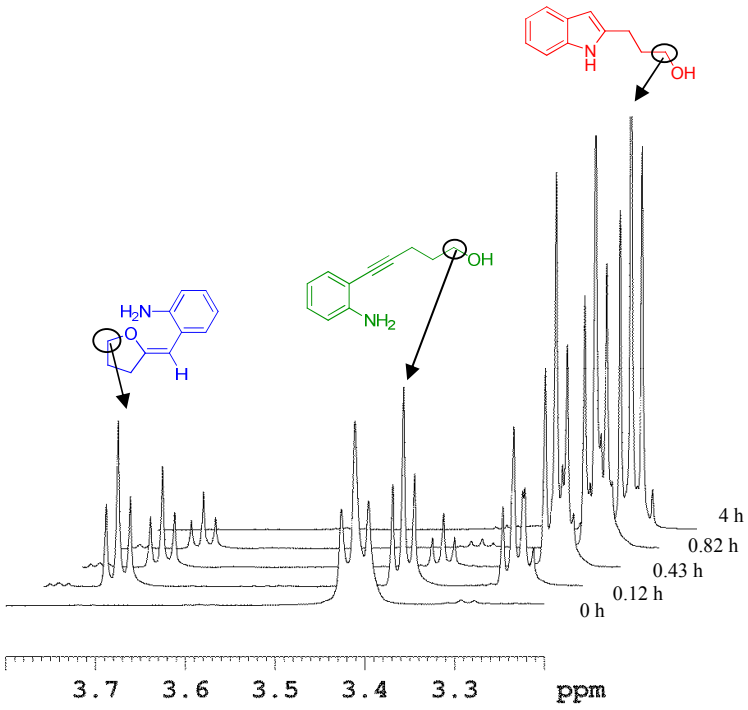
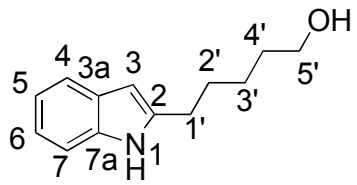


Figure S10: ^{1}H NMR stacked-plot showing the formation and disappearance of **I1** (from **18S**) in the catalysed cyclisation of 2-(5- hydroxy-1-pentyn-1-yl)aniline, **18S** using [Ir(**4**)Cp*Cl]BAr^{F}_{4} (**8**) in toluene-d_8 at 60 °C.

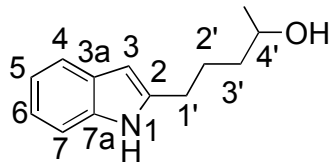
E.6 2-(5-Hydroxypent-1-yl)indole, 19I



^{1}H NMR (400 MHz, Toluene-d_8): δ 7.56 (^{3}J(H5-H4) = 6.7 Hz, 1H, **H**4), 7.22 (br s, 1H, N**H**), 7.14 (m, 3H, **H**5, **H**6 and **H**7), 6.16 (s, 1H, **H**3), 3.32 (t, ^{3}J = 6.3 Hz, 2H, **H**5'), 2.37 (t, ^{3}J = 7.5 Hz, 2H, **H**1'), 1.44 (apparent p, ^{3}J = 7.6 Hz, 2H, **H**2'), 1.34 (apparent p and br s overlap, ^{3}J = 6.2 Hz, 3H, **H**4' and O**H**), 1.23 (m, 2H, **H**3') ppm.

^{13}C{^{1}H} NMR (100 MHz, Toluene-d_8): δ 139.5 (**C**2), 136.6 (**C**3a), 129.6 (**C**7a), 121.1 (**C**4), 120.2 (**C**6), 119.9 (**C**1), 110.7 (**C**2'), 99.8 (**C**1'), 62.5 (**C**7'), 32.7 (**C**6'), 29.4 (**C**4'), 28.4 (**C**5'), 25.8 (**C**3') ppm.

E.7 2-(4-Hydroxy-4-methylbut-1-yl)indole, 20I



Yellow-brown oil.

HR-MS (ESI^{+}, MeOH): *m/z* (%): 226.1214 (18 %) $[M+Na]^{+}$ (Calculated $[M+Na]^{+}$ = 226.1202) amu.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (br s, 1H, N**H**), 7.55 (^{3}J(H5-H4) = 7.7 Hz, 1H, **H**4), 7.30 (d, ^{3}J(H6-H7) = 7.9 Hz, 1H, **H**7), 7.14 (apparent td, ^{3}J(H5-H6) = ^{3}J(H7-H6) = 7.2 Hz, ^{4}J(H4-H6) = 1.0 Hz, 1H, **H**6), 7.09 (apparent td, ^{3}J(H6-H5) = ^{3}J(H4-H5) = 7.2 Hz, ^{4}J(H7-H5) = 1.0 Hz, 1H, **H**5), 6.25 (s, 1H, **H**3), 3.85 (apparent sex, ^{3}J = 6.1 Hz, 1H, **H**4'), 2.76 (td, ^{3}J = 7.5 Hz, ^{4}J = 3.7 Hz, 2H, **H**1'), 1.98 (br s, 1H, O**H**), 1.86 (apparent sep, J = 7.6 Hz, 1H, **H**3'a or **H**3'b), 1.76 (apparent sep, J = 7.5 Hz, 1H, **H**3'a or **H**3'b), 1.53 (apparent q, ^{3}J = 7.3 Hz, 2H, **H**2'), 1.21 (d, ^{3}J = 6.2 Hz, 3H, C**H**$_3$) ppm.

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 139.7 (**C**2), 136.0 (**C**3a), 128.9 (**C**7a), 121.0 (**C**6), 119.8 (**C**4), 119.7 (**C**5), 110.5 (**C**7), 99.6 (**C**3), 68.0 (**C**4'), 38.6 (**C**2'), 28.2 (**C**1'), 25.5 (**C**3'), 23.8 (**C**H$_3$) ppm.

E.8 NMR Data for Final Products

The formation of products **17P**-**20P** were confirmed by comparing the ^{1}H NMR spectra obtained

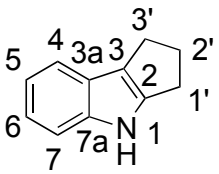
with that reported in the literature and also by comparing the NMR spectra during the catalytic reaction with the spectra of authentic samples purchased from Aldrich in case of product **17P**, **18P**.

E.9 1,2,3,4-Tetrahydrocarbazole, 17P [14 15]

^{1}H NMR (400 MHz, toluene-d_8): δ 7.47 (dd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, **H**4 or **H**7), 7.15 (apparent p of d, ^3J = 7.2 Hz, ^4J = 1.5 Hz, 2H, **H**5 and **H**6), 7.01 (dd, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, **H**7 or **H**4), 6.27 (br s, 1H, N**H**), 2.59 (m, 2H, **H**1' or **H**4'), 2.27 (m, 2H, **H**1' or **H**4'), 1.67 (m, 4H, **H**2' and **H**3') ppm.

^{13}C NMR (100 MHz, toluene-d_8): δ 136.3, 133.4, 128.6, 121.1, 119.3, 118.1, 110.6, 110.0, 23.8, 23.62 23.3, 21.26 ppm.

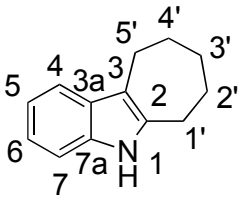
E.10 1,2,3,4-Tetrahydrocyclopent[*b*] indole, 18P [16]



^{1}H NMR (400 MHz, Toluene-d_8,): δ 7.47 (m, 1H, **H**4 or **H**7), 7.12 (apparent s, ^3J = 5.9 Hz, ^4J = 2.7 Hz, 2H, **H**5 and **H**6), 7.00 (m, 1H, **H**4 or **H**7), 6.38 (br s, 1H, N**H**), 2.71 (apparent t, ^3J = 6.9 Hz, 2H, **H**1' or **H**3'), 2.44 (apparent t, ^3J = 7.0 Hz, 2H, **H**1' or **H**3'), 2.27 (apparent p, ^3J = 7.0 Hz, 2H, **H**2') ppm.

^{13}C NMR (100 MHz, Toluene-d_8,): δ 143.1, 141.7, 125.4, 120.7, 119.7, 119.6, 118.9, 111.5, 28.9, 25.9, 24.7 ppm.

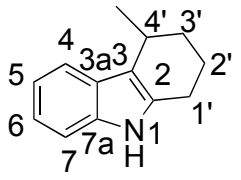
E.11 5,6,7,8,9,10-Hexahydrocyclohept[*b*]indole,19P [16, 14]



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (br s, 1H, N**H**), 7.49 (m, 1H, Ar-**H**), 7.27 (m, 1H, Ar-**H**), 7.11-7.08 (m, 2H, Ar-**H**s), 2.84 (m, 4H, C$\mathbf{H}_2$), 1.91 (m, 2H, C$\mathbf{H}_2$), 1.79 (m, 4H, C$\mathbf{H}_2$) ppm.

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 137.5, 134.3, 129.3, 120.5, 118.9, 117.6, 113.6, 110.2, 31.8, 29.6, 28.8, 27.6, 24.7 ppm.

E.12 4-Methyl-1,2,3,4-tetrahydrocarbazole, 20P[14]



^{1}H NMR (400 MHz, toluene-d_8): δ 7.57 (d, ^{3}J = 7.0 Hz, 1H, **H**4 or **H**7), 7.14 (apparent p of d, ^{3}J = 7.2 Hz, ^{4}J = 1.2 Hz, 2H, **H**5 and **H**6), 7.01 (dd, ^{3}J = 6.9 Hz, ^{4}J = 1.0 Hz, 1H, **H**7 or **H**4), [17]6.35 (br s, 1H, N**H**), 2.99 (m, 1H, **H**4'), 2.26 (m, 2H, **H**1' or **H**2'), 1.79 (m, 2H, **H**2' or **H**1'), 1.59 (m, 1H, **H**3'a or **H**3'b), 1.41 (m, 1H, **H**3'a or **H**3'b), 1.31 (d, ^{2}J = 6.9 Hz, 3H, C**H**$_3$) ppm.

^{13}C NMR (100 MHz, toluene-d_8): δ 136.5, 133.1, 128.1, 121.0, 119.3, 119.1, 114.9, 110.7, 32.6, 31.2, 27.6, 23.6, 20.9 ppm.

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