Supplementary Material

Unsymmetrical Indazolyl-pyridinyl-triazole Ligand Promoted Highly Active Iridium Complexes Supported on Hydrotalcite and Catalytic Application in Water †

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1. General experiments.

All the obtained products were characterized ¹H NMR spectra and ¹³C NMR spectra. NMR spectra were obtained on Varian 400 MHz spectrometers; Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 200-400 mesh silica gel plates; All the reagents were purchased from commercial sources (TCI, Energy Chemical, J&KChemic), and used without further purification. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000 – 400 cm⁻¹ region. TG analysis was carried out using a STA409 instrument in dry air at a heating rate of 25 °C/min from 25 to 900 °C. TEM was obtained using a JEOL JEM-2100 microscope operated at 200 kV. XRD patterns were collected on a Bruker D8 Advance powder diffractometer, using a Ni-filtered Cu/K α radiation source at 40 kV and 20 mA, from 3° to 80° with a scan rate of 4°/min. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method and the pore distribution was calculated by the BJH method from adsorption branches of isotherms. Hydrotalcite (HT) was bought from Mixcy Reagent (cas: 12304-65-3). Water used is deionized water.

2. Typical procedure for the synthesis of catalyst IPT-Ir-HT.

Synthesis of compound L1: A mixture of 2,6-dibromopyridine (1.185 g, 5.0 mmol), the 1,2,3-triazole (1.191 g, 10.0 mmol), CuI (0.190 g, 1.0 mmol, 10%), TMEDA (0.140 g, 1.2 mmol, 12%), and K_2CO_3 (2.070 g, 15.0 mmol) in DMSO (40 mL) was combined under nitrogen. The reaction mixture was stirred at 90 °C for 24 h. The reaction mixture was then added to deionized water (30 mL), and the resulting solution was extracted with ethyl acetate (3×30 mL). The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give the product L1. White solid, 55% yield.

Synthesis of compound **L2**: Product **L1** (275 mg, 1.0 mmol), 1H-indazole (118 mg, 1.0 mmol), CuI (38 mg, 0.2 mmol, 20%), DMEDA (36 mg, 0.4 mmol, 40%), and K₂CO₃ (207 mg, 1.5 mmol) in DMSO (10 mL) was combined under nitrogen. The reaction mixture was stirred 110 °C for 48 h. The reaction mixture was then added to deionized water (20 mL), and the resultingsolution was extracted with ethyl acetate (3×20 mL). The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give the ligand **L2**. White solid, 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, *J* = 8.6, 0.6 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 0.5 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.15 - 8.05 (m, 3H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.66 - 7.58 (m, 1H), 7.56 - 7.47 (m, 2H), 7.40 - 7.30 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 152.85, 149.38, 146.90, 141.21, 138.70, 137.68, 131.52, 128.88, 128.25, 126.29, 124.97, 122.92, 121.18, 120.17, 114.61, 113.93, 112.64, 111.24. HRMS (ESI) Calculated for C₁₈H₁₃N₆ [M+H]⁺ 313.1202, found 313.1204.

A solution of ligand L2 (312 mg, 1.0 mmol), $IrCl_3 \cdot 3H_2O$ (353 mg, 1.0 mmol) and the mixxtured solvents (2-ethoxyethanol/H₂O = 3:1, 16 mL) were stirred in a Schlenk tube under N₂ at 120 °C for 24 h. It was observed that the solution turned red. The product iridium complex (IPT-Ir) was filtered off and washed with ether. Next, iridium complex (30 mg, 0.056mmol), hydrotalcite (600 mg) and the DMSO (10 mL) were stirred in a Schlenk tube at 110 °C for 24 h. The product IPT-Ir-HT (2% loading w/w%) was filtered off by centrifuge and washed with EtOH, the solid was kept 2 h at -20 °C, and by vacuum refrigeration dryer machine dry for 24 h.

3. Characterization of catalyst IPT-Ir-HT.

3.1 TG and DTG analysis: It is found in the range of 25 - 150 °C is due to removal of water. Furthermore, the 33.0 % weight loss at 200 - 400 °C is due to decomposition of the Mg and Al in the HT, Then, the 24.6 % weight loss at 400 °C is due to decomposition of the Ir complex (46.9 % weight loss).



Fig. S1. TG and DTG pattern of IPT-Ir-HT.

3.2 XPS analysis: The surface electronic state and composition of HTTA-Ir was further investigated by X-ray photoelectron spectroscopy (XPS). The wide XPS spectra indicated the presence of Ir, Mg, Al, O, N, Cl and C elements. The C 1s spectrum in Figure S2 confirmed the formation of C-C/C=C (284.5 eV), C-N/C=N (286.5 eV), C-Cl (288.5 eV), C=O (289.5 eV) and Pi-Pi* (292.5 eV) in the HTTA-Ir. Furthermore, Mg^{2+} (1303.34 eV), Al^{3+} (74.25 eV) and Ir^{3+} (63.28 eV). Therefore, the XPS analysis proved that the TA-Ir was mostly within HT.



Fig. S2 (a), (b)XPS spectra of IPT-Ir-HT

3.3 XPS spectra of IPT-Ir



Fig. S3. XPS spectra of IPT-Ir

3.4 TEM for the recycled IPT-Ir-HT.



Fig. S4. TEM for the recycled IPT-Ir-HT.

3.5 XRD for the recycled IPT-Ir-HT.



Fig. S5. XRD for the recycled IPT-Ir-HT.

4. Typical procedure for the synthesis of 3.

A solution of benzylamine (1.1 mmol), amine (1.0 mmol), $AgNTf_2$ (3.9 mg, 1.0 mol%), IPT-Ir-HT (10 mg, 0.5 mol%) and H_2O (3.0 mL) was stirred in a Schlenk tube at 90 °C for 12 h.

After centrifugation and recovery the catalyst, the water mixture was diluted by water (5.0 mL) and extracted with EtOAc (3 x 10 mL). Next, the yield of product **3** was determined by GC.

5. Typical procedure for the synthesis of 4.

A solution of benzylamine (1.1 mmol), amine (1.0 mmol), IPT-Ir-HT (10 mg, 0.5 mol%), AgNTf₂ (3.9 mg, 1.0 mol%), *i*PrOH (300 mg, 5.0 mmol) and H₂O (3.0 mL) was stirred in a Schlenk tube at 90 °C for 24 h (checked by TLC). After centrifugation and recovery the catalyst, the water mixture was diluted by water (5.0 mL) and extracted with EtOAc (3 x 10 mL). After separating the water, the combined organic phase was concentrated to give the residue. Next, the resulting residue was directly purified by column chromatography with petroleum ether/ethyl acetate (40:1) as eluent to give the product **4**.

6. Hammett plot and mechanism studies.



Experimental procedure: A solution of substituted benzylamine (1.1 mmol), amine (1.0 mmol), AgNTf₂ (3.9 mg, 1.0 mol%), IPT-Ir-HT (10 mg, 0.5 mol%) and H₂O (3.0 mL) was stirred in a Schlenk tube at 90 °C for 0.5 h. After centrifugation and recovery the catalyst, the water mixture was diluted by water (5.0 mL) and extracted with EtOAc (3 x 10 mL). Next, the yield of product **3** was determined by GC.

R	Н	Me	OMe	F	CF ₃
Yield	16 %	7 %	6 %	19 %	24 %

Kinetic plot of benzylamine and benzylamine-d₂.



Experimental procedure: Conditions: $1a-d_2$ or 1a (1.0 mmol), 2a (1.1 mmol), IPT-Ir-HT (10 mg, 0.5 mol%), AgNTf₂ (3.9 mg, 1.0 mol%), H₂O (3.0 mL). The yield of product $1a-d_2$ or 1a was determined by GC.

Time	0 h	2 h	4 h	6 h	8 h
Concentration of 1a (mol/L)	0.50	0.44	0.29	0.15	0.08
Concentration of $1a-d_2$ (mol/L)	0.50	0.45	0.38	0.24	0.19

The IR for iridium complex IPT-Ir

IR of L2 (a, potassium bromide pellet): 3107 cm⁻¹ (γ -C-H of pyridine ring), 1620 cm⁻¹ (stretching vibration of C=N), 1475 - 1074 cm⁻¹ (skeleton stretching vibration of aromatic nucleus), 914 - 748 cm⁻¹ (γ -C-H of aromatic nucleus). Compared IR of (a) with (b), it was found that

infrared characteristic absorbing peaks of the groups have prominent change. Combined with the NMR and experimental data, the iridium metal was coordinated success.



Fig. S6. (a) IR of L2; (b) IR of iridium complex (IPT-Ir)

7. Typical procedure for the synthesis of L2, 4a - 4t.



1-(6-(1H-indazol-1-yl)pyridin-2-yl)-1H-benzo[d][1,2,3]triazole (L2) ¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, J = 8.6, 0.6 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 0.5 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 8.15 - 8.05 (m, 3H), 7.85 (d, J = 8.0 Hz, 1H), 7.66 - 7.58 (m, 1H), 7.56 - 7.47 (m, 2H), 7.40 - 7.30 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 152.85, 149.38, 146.90, 141.21, 138.70, 137.68, 131.52, 128.88, 128.25, 126.29, 124.97, 122.92, 121.18, 120.17, 114.61, 113.93, 112.64, 111.24. HRMS (ESI) Calculated for C₁₈H₁₃N₆ [M+H]⁺ 313.1202, found 313.1204.



N-benzylaniline (4a) ¹H NMR (400 MHz, CDCl₃) δ 7.33 - 7.22 (m, 4H), 7.22 - 7.14 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 2H), 4.21 (s, 2H), 4.07 - 3.81 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.18, 139.45, 129.27, 128.67, 127.53, 127.25, 117.62, 112.89, 48.38.



N-benzyl-3-chloroaniline (4b) ¹H NMR (400 MHz, CDCl₃) δ 7.26 - 7.21 (m, 4H), 7.20 - 7.16 (m, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.59 - 6.53 (m, 1H), 6.50 (t, *J* = 2.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.22 (s, 2H), 4.06 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 149.45, 138.96, 135.16, 130.41, 128.90, 127.63, 177.61, 117.53, 112.73, 111.32, 48.17.



N-benzyl-4-chloroaniline (4c) ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 7.4 Hz, 4H), 7.21 - 7.15 (m, 1H), 7.05 - 7.01 (m, 2H), 6.52 - 6.45 (m, 2H), 4.21 (s, 2H), 4.06 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 146.62, 138.93, 129.09, 128.72, 127.44, 127.41, 122.19, 113.98, 48.41.



N-benzyl-4-methoxyaniline (4d) ¹H NMR (400 MHz, CDCl₃) δ 7.26 (q, *J* = 7.6 Hz, 4H), 7.23 - 7.17 (m, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 3.79 - 3.59 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 152.22, 142.48, 139.71, 128.62, 127.58, 127.19, 114.94, 114.15, 55.83, 49.28.



N-benzyl-4-fluoroaniline (4e) ¹H NMR (400 MHz, CDCl₃) δ 7.29 - 7.21 (m, 4H), 7.19 - 7.13 (m, 1H), 6.82 - 6.71 (m, 2H), 6.45 (dt, *J* = 6.4, 4.0 Hz, 2H), 4.17 (s, 2H), 4.10 - 3.60 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.44 (d, *J* = 236.3 Hz), 144.56, 139.31, 128.73, 127.46 (d, *J* = 1.8 Hz), 115.71 (d, *J* = 21.8 Hz), 113.71, 48.98.



N-benzyl-2-chloroaniline (4f) ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, J = 8.0 Hz, 4H), 7.18 (t, J = 6.8 Hz, 2H), 6.97 (t, J = 7.6 Hz, 1H), 6.56 (t, J = 7.2 Hz, 2H), 4.64 (s, 1H), 4.31 (d, J = 5.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 143.93, 138.82, 129.17, 128.79, 127.86, 127.41, 127.32, 119.18, 117.47, 111.59, 47.91.



N-(4-chlorobenzyl)aniline (4g) ¹H NMR (400 MHz, CDCl₃) δ 7.21 (s, 4H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 2H), 4.01 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 146.82, 136.97, 131.88, 128.32, 127.73, 127.67, 116.78, 111.86, 46.61.



4-chloro-N-(4-chlorobenzyl)aniline (4h) ¹H NMR (400 MHz, CDCl₃) δ 7.35 - 7.26 (m, 4H), 7.19 - 7.01 (m, 2H), 6.53 (d, J = 8.8 Hz, 2H), 4.26 (s, 2H), 4.11 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 146.39, 137.54, 133.08, 129.13, 128.85, 128.63, 122.42, 114.02, 47.67.



3-chloro-N-(4-chlorobenzyl)aniline (4i) ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.49 (t, *J* = 2.0 Hz, 1H),

6.37 (dd, J = 8.4, 1.6 Hz, 1H), 4.17 (s, 2H), 4.02 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 149.04, 137.41, 135.11, 133.14, 130.36, 128.92, 128.73, 117.72, 112.65, 111.25, 47.43.



N-(4-methylbenzyl)aniline (4j) ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 2H), 7.33 (dd, J = 12.4, 7.6 Hz, 4H), 6.88 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 4.41 (s, 2H), 4.09 (s, 1H), 2.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.39, 136.98, 136.56, 129.48, 129.40, 127.67, 117.62, 113.00, 48.19, 21.28.



4-chloro-N-(4-methylbenzyl)aniline (4k) ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 8.0 Hz, 2H), 4.16 (s, 2H), 3.90 (s, 1H), 2.25 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.75, 137.07, 135.89, 129.41, 129.08, 127.46, 122.03, 113.93, 48.13, 21.14.



N-(4-methoxybenzyl)aniline (41) ¹H NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.88 (t, J = 7.2 Hz, 1H), 6.76 (d, J = 8.0 Hz, 2H), 4.35 (s, 2H), 4.16 - 3.98 (m, 1H), 3.90 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.06, 148.39, 131.61, 129.41, 128.94, 117.61, 114.21, 113.01, 55.39, 47.87.



MeO

4-chloro-N-(4-methoxybenzyl)aniline (4m) ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.11 (s, 2H), 3.85 (s, 1H), 3.71 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.98, 146.76, 130.94, 129.09, 128.77, 122.03, 114.06, 114.02, 55.34, 47.85.



N-(4-methoxybenzyl)pyridin-2-amine (4n) ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 4.8 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.47 (t, J = 6.0 Hz, 1H),

6.28 (d, J = 8.4 Hz, 1H), 4.88 (s, 1H), 4.32 (d, J = 5.6 Hz, 2H), 3.71 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.85, 158.71, 148.22, 137.45, 131.20, 128.73, 114.04, 113.06, 106.80, 55.30, 45.83.



MeO

N-(4-methoxybenzyl)naphthalen-1-amine (40) ¹H NMR (400 MHz, CDCl₃) δ 7.70 - 7.60 (m, 2H), 7.34 - 7.25 (m, 2H), 7.24 - 7.16 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 7.6 Hz, 1H), 4.50 (s, 1H), 4.25 (s, 2H), 3.67 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.10, 143.29, 134.39, 131.10, 129.17, 128.77, 126.73, 125.83, 124.82, 123.50, 120.05, 117.73, 114.20, 104.91, 55.39, 48.21.



N-(furan-2-ylmethyl)aniline (4p) ¹H NMR (400 MHz, CDCl₃) δ 7.28 (t, J = 5.6 Hz, 1H), 7.12 (t, J = 8.0 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 6.28 – 6.21 (m, 1H), 6.15 (t, J = 5.2 Hz, 1H), 4.25 (s, 2H), 4.01 - 3.86 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 151.73, 146.61, 140.89, 128.11, 117.01, 112.13, 109.30, 105.94, 40.43.



4-chloro-N-(furan-2-ylmethyl)aniline (4q) ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 1.2 Hz, 1H), 7.11 – 6.99 (m, 2H), 6.55 – 6.45 (m, 2H), 6.26 (dd, J = 3.2, 2.0 Hz, 1H), 6.16 (dd, J = 3.2, 0.4 Hz, 1H), 4.22 (s, 2H), 3.99 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 152.29, 146.17, 142.06, 129.07, 122.66, 114.25, 110.37, 107.16, 41.50.



3-chloro-N-(furan-2-ylmethyl)aniline (4r) ¹H NMR (400 MHz, CDCl₃) δ 7.26 (s, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.59 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.46 (t, *J* = 2.0 Hz, 1H), 6.36 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.22 (dd, *J* = 3.1, 1.7 Hz, 1H), 6.12 (d, *J* = 3.1 Hz, 1H), 4.15 (s, 2H), 4.02 (s, 1H).



N-butylaniline (4s) ¹H NMR (400 MHz, CDCl₃) δ 7.08 (t, J = 7.2 Hz, 2H), 6.61 (t, J = 7.2 Hz, 1H), 6.53 (d, J = 8.0 Hz, 2H), 3.71 - 3.42 (m, 1H), 3.01 (t, J = 7.2 Hz, 2H), 1.59 - 1.51 (m, 2H), 1.28 (d, J =

3.2 Hz, 2H), 0.85 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.58, 129.25, 117.09, 112.71, 44.01, 29.36, 22.56, 14.09.



N-(2-ethylhexyl)aniline (4t) ¹H NMR (400 MHz, CDCl₃) δ 7.09 (t, J = 7.6 Hz, 2H), 6.57 (t, J = 7.2 Hz, 1H), 6.50 (d, J = 7.6 Hz, 2H), 3.51 (s, 1H), 3.00 - 2.79 (m, 2H), 1.62 - 1.29 (m, 1H), 1.36 - 1.30 (m, 2H), 1.25 (d, J = 8.0 Hz, 6H), 0.82 (t, J = 7.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 148.82, 129.28, 116.95, 112.66, 47.09, 39.17, 31.40, 29.07, 24.57, 23.20, 14.19, 11.01.

8. Copies of NMR spectra.





¹³C NMR for L2



¹H NMR for 4a



¹³C NMR for 4a







¹³C NMR for 4b



¹H NMR for 4c



¹³C NMR for 4c





¹³C NMR for 4d











¹H NMR for 4f







¹H NMR for 4g



¹³C NMR for 4g



¹H NMR for 4h



¹³C NMR for 4h







¹³C NMR for 4i













¹³C NMR for 4k











¹³C NMR for 4m







¹³C NMR for 4n







¹³C NMR for 40







¹³C NMR for 4p







¹³C NMR for 4q



¹H NMR for 4r



¹H NMR for 4s







¹H NMR for 4t



¹³C NMR for 4t



¹H NMR for IPT-Ir