Supporting Information for

A Ratiometric Substrate for Rapid Evaluation of Transfer Hydrogenation Efficiency in Solution

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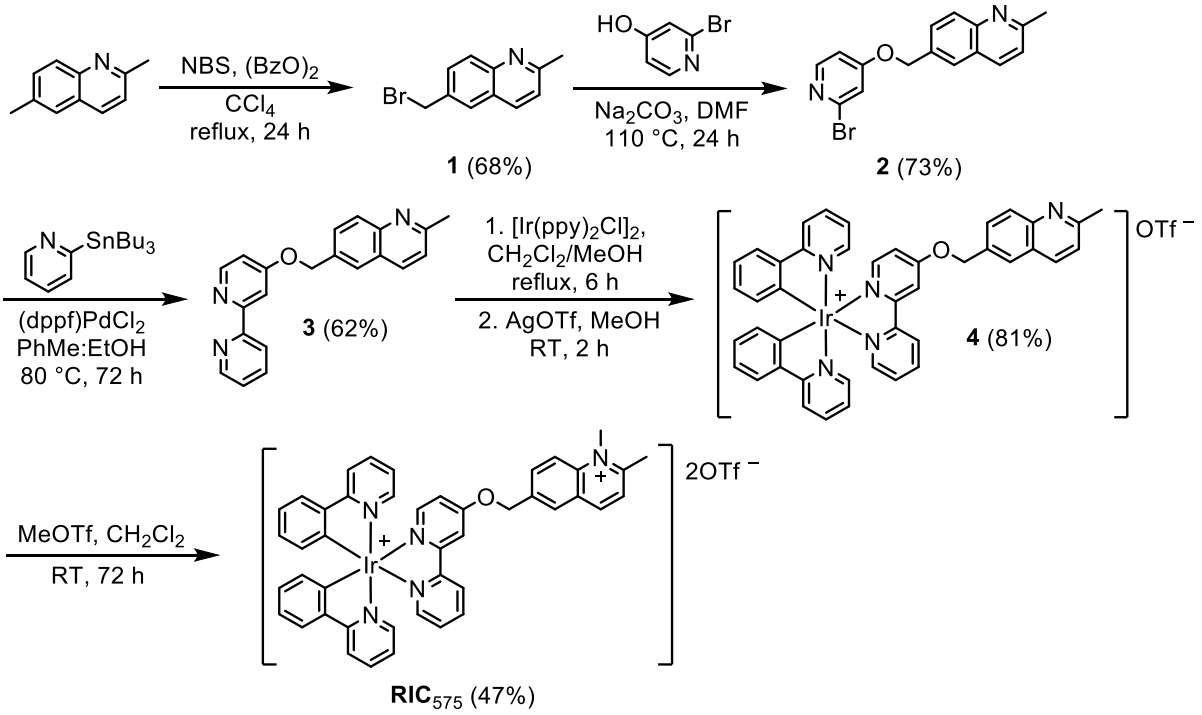
General Considerations

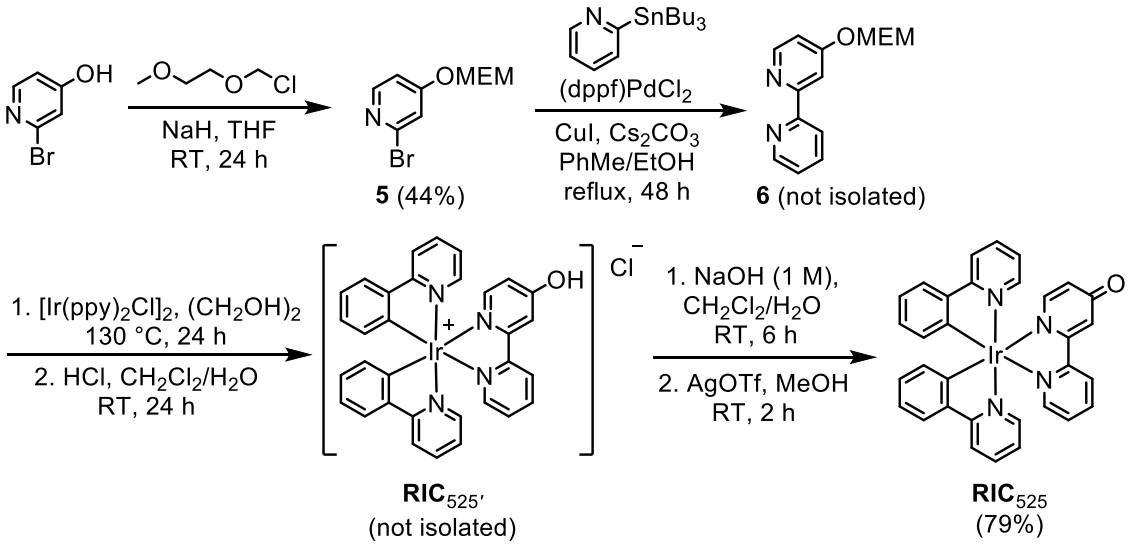
Commercial reagents were purchased from Sigma Aldrich, Alfa-Aesar, and Ambeed Inc., and used as received. All air- and water-sensitive manipulations were performed using standard Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and stored over activated molecular sieves prior to use. Anhydrous solvents were obtained from an Innovative Technology solvent drying system saturated with argon. Nitrogen and hydrogen (ultra-high purity grade) were purchased from Matheson TriGas. Organic solutions were concentrated under reduced pressure using a Heidolph rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel. All reactions were carried out in well-ventilated fume hoods. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Visualization of the developed chromatogram was performed by irradiation with UV light. Yields refer to purified compounds unless otherwise noted.

NMR spectra were acquired using JEOL spectrometers (ECA-400, -500, and -600) and internally referenced using residual solvent peaks. All ^{13}C NMR spectra were proton decoupled. All NMR data were processed using Delta software version 5.3.1 and presented with MestReNova software version 12.0.0-20080. Gas chromatography-mass spectrometry (GC-MS) was performed using an Agilent 7890 GC/5977A MSD instrument equipped with an HP-5MS capillary column. High-resolution mass spectra were obtained at the University of Texas at Austin Mass Spectrometry Facility using an Agilent 6546 Q-TOF LC/MS.

Synthesis and Characterization



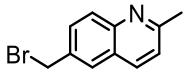
Scheme S1. Synthesis of ratiometric iridium complex **RIC**$_{575}$. Abbreviations: NBS = *N*-bromosuccinimide, $(BzO)_2$ = benzoyl peroxide, dppf = 1,1'-bis(diphenylphosphino)ferrocene, OTf^- = trifluoromethanesulfonate (triflate).



Scheme S2. Synthesis of iridium complex **RIC**$_{525}$. Abbreviations: MEM = 2-methoxyethoxymethyl, ppy = 2-phenylpyridine.

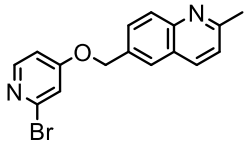
Experimental Details and Characterization for RIC$_{575}$ and RIC$_{525}$

Preparation of 1:



In a 100 mL round bottom flask equipped with a magnetic stir bar, solid 2,6-dimethylquinoline (3.05 g, 20 mmol, 1.0 equiv.), solid *N*-bromosuccinimide (3.63 g, 20.5 mmol, 1.02 equiv.), and solid benzoyl peroxide (78 mg, 0.032 mmol, 0.02 equiv.), and CCl_4 (35 mL) were combined. The reaction was refluxed for 24 h, giving a brown colored solution containing a black precipitate. After cooling to RT, the black precipitate was washed several times with ethyl acetate before discarding. The filtrate and the reaction solution were combined, washed with water (2 × 50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness to yield the crude product as a dark gray solid. Compound **1** was purified by silica gel column chromatography, using hexanes: ethyl acetate (6:1 to 1:1, *v/v*) as eluent, and was isolated as an off-white solid (2.4 g, 68%). Although the product darkens to a black solid after a few days at RT, no significant changes were observed by NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, J = 8.6 Hz, 1H, Ar*H*), 8.10 (d, J = 8.4 Hz, 1H, Ar*H*), 7.80 (d, J = 2.1 Hz, 1H, Ar*H*), 7.74 (dd, J = 8.7, 2.1 Hz, 1H, Ar*H*), 7.35 (d, J = 8.4 Hz, 1H, Ar*H*), 4.65 (s, 2H, C*H*$_2$), 2.81 (s, 3H, C*H*$_3$). GC-MS: calc. for $C_{11}H_{10}BrN$ $[M]^+$ = 235.0, found: 234.9. The characterization data for this material are consistent with those reported previously.[1]

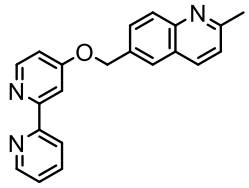
Preparation of 2:



In a 250 mL round bottom flask equipped with a magnetic stir bar, 100 mL of anhydrous DMF was purged with nitrogen gas for 30 min, followed by the addition of solid 2-bromo-4-hydroxypyridine (1.392 g, 6.82 mmol, 1.0 equiv.) and anhydrous sodium carbonate (1.696 g, 15 mmol, 2.2 equiv.). The mixture was then stirred under N_2 at RT for 30 min, then compound **1** (2.077 g, 7.5 mmol, 1.1 equiv.) was added. The reaction was stirred at 110 °C for 24 h. When the reaction was complete (monitored by TLC), 100 mL of CH_2Cl_2 was added to the mixture and washed with 200 mL of water. The organic layer was then washed with 50 mL of brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness to yield the crude product as a brown solid. The desired compound **2** was purified by silica gel column chromatography, using CH_2Cl_2:MeOH (gradient from 100:0 to 95:5, *v/v*) as the eluent, and was isolated as a white solid (1.65 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.19 (d, J = 5.8 Hz, 1H, Ar*H*), 8.06 (d, J = 2.3 Hz, 1H, Ar*H*), 8.04 (d, J = 2.1 Hz, 1H, Ar*H*), 7.80 – 7.78 (m, 1H, Ar*H*), 7.68 (dd, J = 8.6, 2.0 Hz, 1H, Ar*H*),

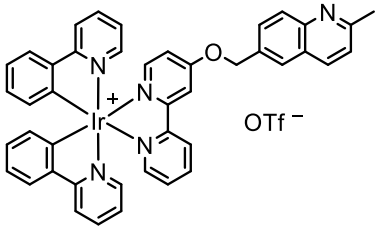
7.32 (d, J = 8.4 Hz, 1H, Ar*H*), 7.12 (d, J = 2.2 Hz, 1H, Ar*H*), 6.88 (dd, J = 5.8, 2.3 Hz, 1H, Ar*H*), 5.25 (s, 2H, OC*H*$_2$), 2.75 (s, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.96, 159.93, 150.97, 147.89, 143.22, 136.30, 132.45, 129.62, 128.62, 126.42, 126.35, 122.79, 114.24, 110.83, 70.17, 25.54. GC-MS: calc. for $C_{16}H_{13}BrN_2O$ $[M]^+$ = 329.2, found: 329.1. IR: ν (cm^{-1}) = 1574.8, 1473.9, 1380.0, 1295.2, 1221.6, 1110.9, 1021.7, 885.5, 824.4, 696.1, 433.3.

Preparation of 3:



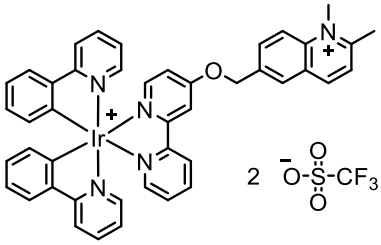
To a 100 mL three-neck round bottom flask equipped with a magnetic stir bar, compound **2** (330 mg, 1.0 mmol, 1.0 equiv.), cesium carbonate (65 mg, 0.2 mmol, 0.2 equiv.) and copper(I) iodide (19 mg, 0.1 mmol, 0.1 equiv.) were added. The flask was subsequently transferred into the glovebox before adding (dppf)$PdCl_2$ (33 mg, 0.05 mmol, 0.05 equiv.). It was then sealed with a rubber septum and Teflon tape and then taken out of the glovebox. In another 100 mL round bottom flask, 50 mL of toluene: EtOH (4:1, *v/v*) was purged with Ar or N_2 for 1 h. The solvent was then transferred to the reaction flask through a cannula and stirred under RT until the resulting mixture became golden yellow. 2-Tributylstannylpyridine (0.5 mL, 1.5 mmol, 1.5 equiv.) was then introduced to the reaction flask via syringe, and the mixture was performed under N_2 atmosphere at 80 °C for 72 h. After cooling the flask to RT, potassium fluoride (2.5 g) was added to the reaction flask and the suspension was stirred for 30 min. The insoluble residue was removed using a celite/silica gel-packed fritted funnel and washed with excess amount of toluene, giving a brown filtrate. The filtrate was collected, washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness to obtain a dark red crude product. Compound **3** was purified by silica gel column chromatography, using CH_2Cl_2:MeOH (100:0 to 98:2, *v/v*) as the eluent, and was isolated as an off-white (pink/orange tint) solid (202 mg, 62%) ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.68 (d, J = 4.7 Hz, 1H, Ar*H*), 8.51 (d, J = 5.7 Hz, 1H, Ar*H*), 8.40 (d, J = 8.0 Hz, 1H, Ar*H*), 8.12 (d, J = 2.5 Hz, 1H, Ar*H*), 8.06 (dd, J = 8.5, 2.5 Hz, 2H, Ar*H*), 7.86 (s, 1H, Ar*H*), 7.84 – 7.79 (m, 1H, Ar*H*), 7.75 (dd, J = 8.6, 2.0 Hz, 1H, Ar*H*), 7.32 (d, J = 8.2 Hz, 2H, Ar*H*), 6.94 (dd, J = 5.7, 2.6 Hz, 1H, Ar*H*), 5.39 (s, 2H, OC*H*$_2$), 2.76 (s, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.86, 159.66, 158.32, 156.00, 150.62, 149.24, 147.83, 137.12, 136.36, 133.35, 129.40, 128.86, 126.46, 126.26, 124.08, 122.65, 121.43, 111.52, 107.00, 69.71, 25.56. IR: ν (cm^{-1}) = 2925.0, 1557.7, 1454.0, 1300.6, 1197.7, 1090.4, 1010.2, 888.5, 794.4, 744.3, 630.8, 488.3.

Preparation of 4:



Precursor $[Ir(ppy)_2Cl]_2$ was prepared based on a literature procedure.[2] To a 200 mL round bottom flask equipped with a magnetic stir bar, compound **3** (426 mg, 1.3 mmol, 2.0 equiv.), $[Ir(ppy)_2Cl]_2$ (732 mg, 0.68 mmol, 1.0 equiv.), and a mixture of CH_2Cl_2/MeOH (4:1, *v/v*, 50 mL) was added. The reaction mixture was refluxed for 6 h. After cooling to RT, silver triflate (668 mg, 2.6 mmol, 4.0 equiv.) was added, and the resulting suspension was stirred continuously at RT for 1 h. The mixture was filtered to remove an insoluble material and washed with CH_2Cl_2. The solvent was removed under vacuum, giving a yellow crude product. Compound **4** was purified by silica gel chromatography, using CH_2Cl_2: MeOH (100:0 to 95:5, *v/v*) as the eluent, and was obtained as a yellow solid (456 mg, 81%). Trace amounts of impurities were obtained, which were removed after multiple washes with Et_2O. The ^{13}C NMR spectrum shows only 36 carbons out of 41 carbons due to the overlap of 5 carbon peaks on the pyridine ring of the ppy ligand. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.17 (d, J = 8.2 Hz, 1H), 8.57 (d, J = 2.6 Hz, 1H), 8.23 – 8.15 (m, 2H), 8.12 (d, J = 1.9 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.90 (t, J = 6.4 Hz, 3H), 7.81 – 7.71 (m, 3H), 7.67 (dd, J = 7.2, 5.4 Hz, 3H), 7.57 (d, J = 5.8 Hz, 1H), 7.48 (d, J = 5.5 Hz, 1H), 7.36 (ddd, J = 7.7, 5.5, 1.2 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.05 – 6.94 (m, 5H), 6.90 (tt, J = 7.4, 1.4 Hz, 2H), 6.32 – 6.26 (m, 2H), 5.76 – 5.62 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 168.02, 168.00, 167.20, 159.51, 158.16, 156.17, 150.78, 150.69, 150.52, 150.04, 148.75, 148.58, 143.68, 143.52, 140.16, 138.08, 138.05, 132.74, 131.91, 131.84, 130.90, 129.20, 128.70, 128.09, 127.45, 126.70, 126.55, 124.91, 124.88, 123.36, 123.30, 122.63, 122.62, 119.66, 116.77, 111.04, 71.46, 25.21. IR: ν (cm^{-1}) = 1602.8, 1474.2, 1427.4, 1251.8, 1150.0, 1021.7, 831.2, 746.0, 672.0, 566.5, 506.0.

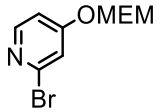
Preparation of RIC$_{575}$:



To a 100 mL round bottom flask equipped with a magnetic stir bar, compound **4** (200 mg, 0.2 mmol, 1.0 equiv.) and 50 mL of anhydrous CH_2Cl_2 were combined. The resulting mixture was purged and filled with Ar or N_2 for 30 min at RT. Methyl triflate (220 µL, 2.0 mmol, 10 equiv.)

was added to the reaction flask by syringe. The reaction was stirred under Ar at RT for 72 h. When the reaction was complete, the resulting solution was washed with 50 mL of water. The combined organic layer was collected, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness, giving a yellow crude solid. The desired product was purified by silica gel column chromatography, using THF: MeOH (95:5, *v/v*) to CH_2Cl_2: MeOH (90:10, *v/v*) as the eluent, and was obtained as a yellow solid (106 mg, 47%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 8.88 (d, J = 8.6 Hz, 1H), 8.57 (d, J = 8.2 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.37 (s, 1H), 8.24 (dd, J = 9.2, 2.0 Hz, 1H), 8.17 (d, J = 2.6 Hz, 1H), 8.14 (td, J = 7.9, 1.6 Hz, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.99 (dd, J = 5.4, 1.6 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.82 – 7.78 (m, 3H), 7.67 – 7.63 (m, 2H), 7.51 (ddd, J = 7.2, 5.4, 1.2 Hz, 1H), 7.16 (dd, J = 6.4, 2.6 Hz, 1H), 7.07 – 7.02 (m, 4H), 6.98 –6.89 (m, 2H), 6.28 (ddd, J = 7.1, 5.3, 1.2 Hz, 2H), 5.58 (s, 2H), 4.39 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 167.63, 167.51, 166.64, 161.48, 157.64, 155.79, 151.78, 150.78, 150.55, 150.50, 149.28, 149.13, 145.90, 144.23, 144.09, 139.62, 139.34, 138.59, 138.56, 136.97, 134.39, 131.64, 131.60, 130.44, 130.42, 128.69, 128.65, 128.34, 125.74, 124.98, 124.94, 124.76, 123.56, 123.50, 122.53, 122.47, 119.94, 119.89, 119.32, 114.58, 112.04, 69.47, 39.79, 22.92. ^{19}F NMR (470 MHz, CD_3CN): δ (ppm) = -79.25 (s). ESI-MS(+): calc for $C_{44}H_{36}IrN_5O$ $[M]^{2+}$ (m/z = 843.2549/2) = 421.6275, found: 421.6279. Fragment peaks were also observed as follows: 826/828 $[M–CH_3]^+$ and 671/673 $[Ir(ppy)_2(bpyO)]^+$ (ppy: phenylpyridine, bpyO: bipyridin-4-one). IR: ν (cm^{-1}) = 3068.3, 1606.7, 1476.4, 1429.8, 1246.3, 1153.0, 1023.2, 750.3, 628.0, 566.2, 506.5.

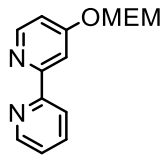
Preparation of 5:



To a 100 mL round bottom flask equipped with a magnetic stir bar, 2-bromo-4-hydroxypyridine (800 mg, 4.60 mmol, 1 equiv.), sodium hydride (60% in mineral oil, 600 mg) and 30 mL of anhydrous THF were combined. The mixture was stirred at RT for 1 h, followed by the addition of 2-methoxyethoxymethyl chloride (MEM-Cl, 600 µL, 5.25 mmol, 1.14 equiv.), and was stirred at 50 °C for 24 h. The reaction was quenched by the addition of 10 mL of water. The solvent was evaporated under vacuum to yield a brown viscous crude mixture. This product was dissolved in 50 mL of CH_2Cl_2 and washed with water (2 × 50 mL). The combined organic layer was collected, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness, giving a light brown oil. Compound **5** was purified by silica gel column chromatography, using hexanes: ethyl acetate (1:1, *v/v*), and was obtained as a colorless oil (525 mg, 44%).^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.12 (d, J = 5.7 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 6.86 (dd, J = 5.8, 2.2 Hz, 1H), 5.25 (s, 2H), 3.80 – 3.70 (m, 2H), 3.56 – 3.44 (m, 2H), 3.30 (d, J = 1.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 164.58, 150.87, 142.89, 115.36, 111.46, 93.07, 71.43, 68.49, 59.10. GC-MS: calc. for

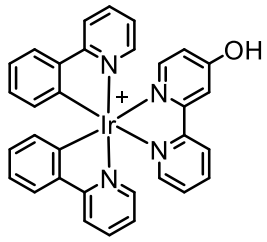
$C_9H_{12}BrNO_3$ $[M]^+$ = 261.0, found: 261.1. The characterization data for this material are consistent with those reported previously.[4]

Preparation of 6:



The synthesis of **6** was adapted from the procedure used for the preparation of compound **3** above. Amounts of starting materials used: compound **5** (420 mg, 1.60 mmol, 1.0 equiv.), Cs_2CO_3 (110 mg, 0.34 mmol, 0.21 equiv.) CuI (43 mg, 0.23 mmol, 0.14 equiv.), $(dppf)PdCl_2$ (73 mg, 0.12 mmol, 0.07 equiv.), 50 mL of toluene: EtOH (4:1, *v/v*), tributylstannylpyridine (800 µL, 2.4 mmol, 1.5 equiv.). The reaction was performed under N_2 at 80 °C for 72 h. After cooling to RT, potassium fluoride (2.5 g) was added to the reaction flask and the suspension was stirred for 30 min. The insoluble residue was removed by filtration through a celite/silica gel-packed fritted funnel and the filtrate was washed with excess toluene to a brown solution. The filtrate was collected, washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness to obtain a brown oil as a crude product. This compound was used for the next step without any further purification.

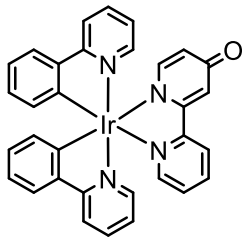
Preparation of RIC$_{525'}$:



In a 100 mL round bottom flask equipped with a magnetic stir bar, a mixture of compound **6** (290 mg), $[Ir(ppy)_2Cl]_2$ (160 mg, 0.15 mmol), and 30 mL of ethylene glycol were combined. The reaction flask was filled with N_2 and stirred at 130 °C for 24 h. After cooling to RT, 10 mL of HCl (3M in H_2O) was added to the solution and the resulting mixture was continuously stirred overnight. The solution was then diluted with 50 mL of CH_2Cl_2 and washed twice with 50 mL of brine. The combined organic layer was collected, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude product was re-dissolved in 20 mL of MeOH, treated with silver triflate (100 mg, 0.4 mmol), and stirred at RT for 1 h. When the reaction was complete, the insoluble materials were removed by vacuum filtration. The filtrate was evaporated to dryness, giving a yellow crude product. Purification of the product by silica gel column chromatography was attempted using CH_2Cl_2: MeOH (100:0 to 90:10, *v/v*) as the eluent; however, the impurities were unable to be

separated from the desired product. This material was used in the following step without any further purification.

Preparation of RIC$_{525}$:



In a 100 mL round bottom flask equipped with a magnetic stir bar, **RIC$_{525'}$** was dissolved in 20 mL of CH_2Cl_2, followed by the addition of NaOH (0.5 M in H_2O, 50 mL). The mixture was stirred at RT for 1 h. The combined organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness to afford a yellow solid. The desired product was purified by silica gel column chromatography using CH_2Cl_2: MeOH (97:3) as the eluent and was obtained as a yellow solid (160 mg, 79%, calculated yield was based on the amount of $[Ir(ppy)_2Cl]_2$) used in the previous step). ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) = 8.46 (d, J = 8.2 Hz, 1H), 8.24 – 8.19 (m, 2H), 8.05 (td, J = 7.9, 1.7 Hz, 1H), 7.93 – 7.83 (m, 4H), 7.77 (ddd, J = 5.5, 3.4, 1.5 Hz, 2H), 7.61 (dd, J = 5.9, 1.5 Hz, 1H), 7.47 (ddd, J = 7.2, 5.5, 1.2 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.17 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H), 6.94 (dtd, J = 16.6, 7.5, 1.3 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.81 (td, J = 7.4, 1.3 Hz, 1H), 6.24 (dd, J = 7.6, 1.2 Hz, 1H), 6.14 (dd, J = 7.6, 1.2 Hz, 1H), 6.06 (dd, J = 6.7, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 168.51, 168.10, 159.46, 154.76, 154.63, 153.51, 150.12, 149.36, 149.28, 148.70, 145.30, 144.65, 139.66, 139.19, 138.90, 132.47, 131.88, 130.99, 130.78, 127.67, 125.91, 125.69, 124.47, 124.09, 122.51, 122.29, 120.67, 120.60, 120.33, 118.02. *Note: Two C peaks were not observed, possibly due to overlapping signals*. ESI-MS(+): calc for $C_{32}H_{23}IrN_4O$ $[M+H]^+$ = 673.1579, found: 673.1581. IR: ν (cm^{-1}) = 3059.8, 1604.2, 1475.1, 1428.1, 1248.9, 1153.3, 1022.2, 748.6, 628.3, 566.1, 507.1.

Experimental Details and Characterization for Complexes Ir1 – Ir10

Precursor $[Cp^*IrCl_2]_2$,[5] 4-dimethylaminopicolinic acid,[6] and complexes **Ir1 – Ir7** were prepared as described in the literature.[7–9]

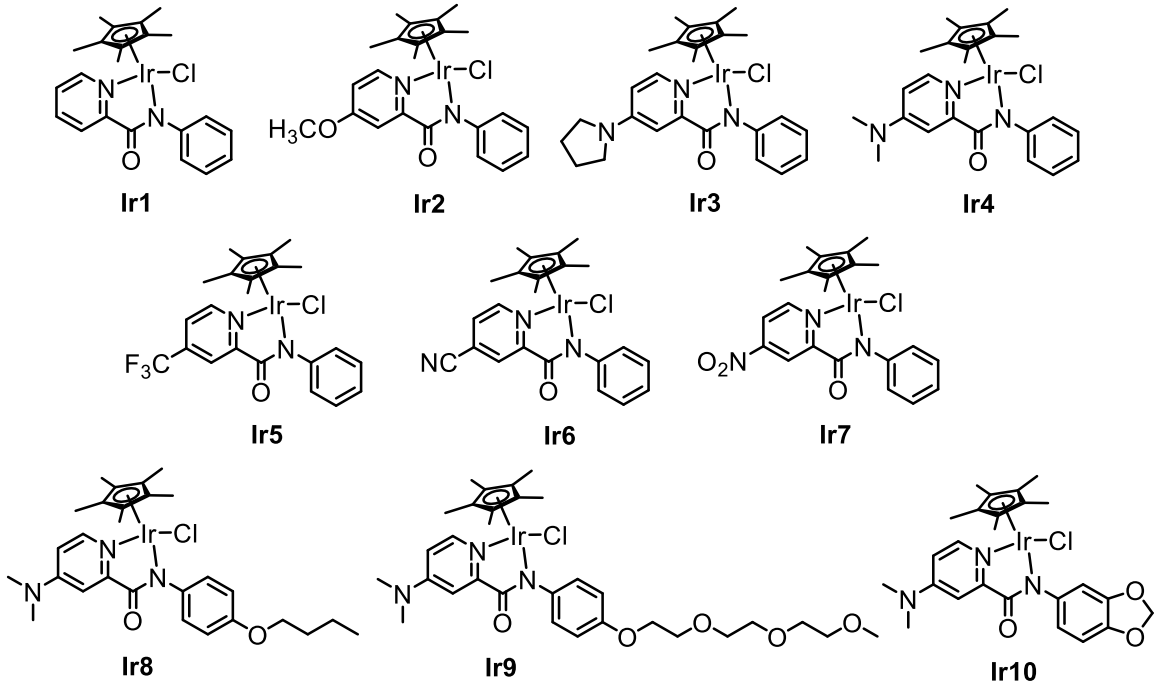
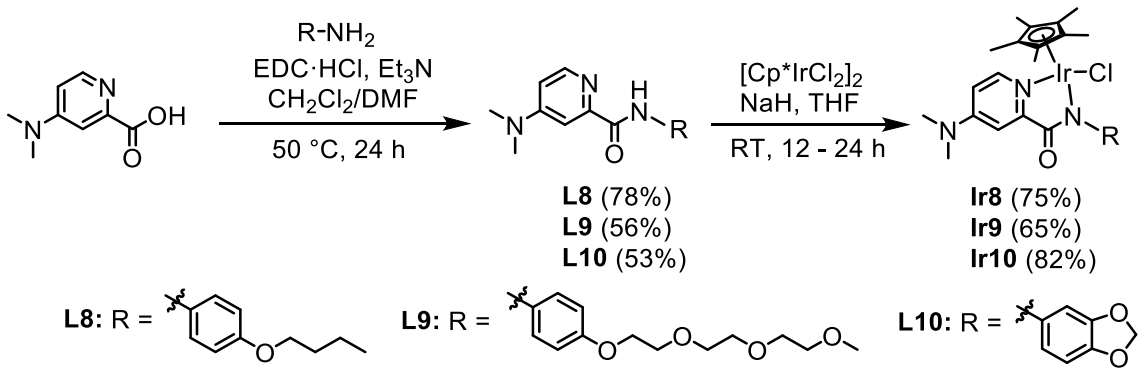
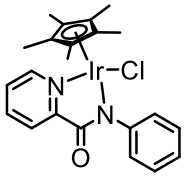


Chart S1. Structure of iridium catalysts **Ir1 – Ir10** used for transfer hydrogenation studies.



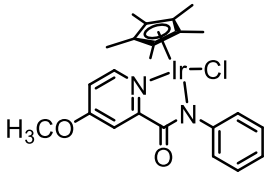
Scheme S3. Synthesis of complexes **Ir8**, **Ir9**, and **Ir10**.

Complex Ir1:



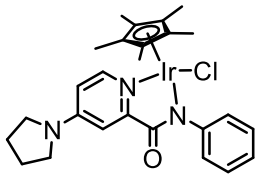
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.56 (ddd, J = 5.6, 1.6, 0.8 Hz, 1H, Ar*H*), 8.14 (ddd, J = 7.9, 1.6, 0.9 Hz, 1H, Ar*H*), 7.92 (td, J = 7.6, 1.4 Hz, 1H, Ar*H*), 7.65 – 7.61 (m, 2H, Ar*H*), 7.49 (ddd, J = 7.3, 5.6, 1.6 Hz, 1H, Ar*H*), 7.30 – 7.26 (m, 3H, Ar*H*), 1.41 (s, 15H, $C_5(CH_3)_5$). The characterization data for this material are consistent with those reported previously.[6]

Complex Ir2:



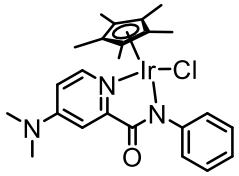
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.55 (dd, J = 5.6, 1.0 Hz, 1H, Ar*H*), 8.16 – 8.10 (m, 1H, Ar*H*), 7.90 (td, J = 7.8, 1.6 Hz, 1H, Ar*H*), 7.59 – 7.54 (m, 2H, Ar*H*), 7.47 (ddd, J = 7.4, 5.5, 1.6 Hz, 1H, Ar*H*), 6.88 – 6.82 (m, 2H, Ar*H*), 3.79 (s, 3H, OCH_3), 1.41 (s, 15H, $C_5(CH_3)_5$). The characterization data for this material are consistent with those reported previously.[8]

Complex Ir3:



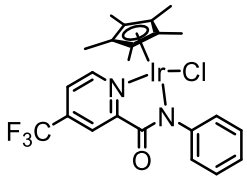
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, J = 6.6 Hz, 1H, Ar*H*), 7.64 (dd, J = 8.4, 1.4 Hz, 2H, Ar*H*), 7.30 – 7.26 (m, 2H, Ar*H*), 7.18 (d, J = 3.0 Hz, 1H, Ar*H*), 7.07 – 7.01 (m, 1H, Ar*H*), 6.44 (dd, J = 6.6, 3.0 Hz, 1H, Ar*H*), 3.47 – 3.43 (m, 4H, $2CH_2N$), 2.04 (q, J = 3.5 Hz, 4H, $2CH_2$), 1.38 (s, 15H, $C_5(CH_3)_5$). The characterization data for this material are consistent with those reported previously.[8]

Complex Ir4:



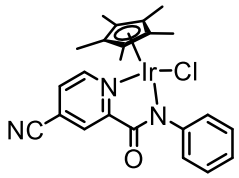
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06 (dd, J = 6.4, 2.1 Hz, 1H, Ar*H*), 7.63 (dd, J = 8.4, 1.4 Hz, 2H, Ar*H*), 7.32 (d, J = 3.2 Hz, 1H, Ar*H*), 7.28 (t, J = 7.9 Hz, 2H, Ar*H*), 7.09 – 7.02 (m, 1H, Ar*H*), 6.62 – 6.46 (m, 1H, Ar*H*), 3.12 (s, 6H, N(CH_3)$_2$), 1.38 (s, 15H, C_5(CH_3)$_5$). The characterization data for this material are consistent with those reported previously.[8]

Complex Ir5:



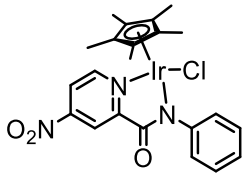
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.73 (d, J = 5.9 Hz, 1H, Ar*H*), 8.40 – 8.37 (m, 1H, Ar*H*), 7.69 (dd, J = 5.9, 2.1 Hz, 1H, Ar*H*), 7.62 – 7.58 (m, 2H, Ar*H*), 7.35 – 7.30 (m, 2H, Ar*H*), 7.11 (tt, J = 7.3, 1.3 Hz, 1H, Ar*H*), 1.41 (s, 15H, C_5(CH_3)$_5$). The characterization data for this material are consistent with those reported previously.[8]

Complex Ir6:



^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.70 (dd, J = 5.8, 0.8 Hz, 1H, Ar*H*), 8.36 (dd, J = 2.0, 0.7 Hz, 1H, Ar*H*), 7.67 (dd, J = 5.7, 2.0 Hz, 1H, Ar*H*), 7.60 – 7.56 (m, 2H, Ar*H*), 7.35 – 7.29 (m, 2H, Ar*H*), 7.12 (tt, J = 7.3, 1.3 Hz, 1H, Ar*H*), 1.40 (s, 15H, C_5(CH_3)$_5$). The characterization data for this material are consistent with those reported previously.[8]

Complex IrL7:

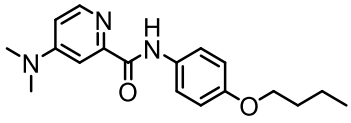


^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.60 (dd, J = 5.4, 1.1 Hz, 1H, Ar*H*), 8.21 – 8.14 (m, 3H, Ar*H*), 7.97 (td, J = 7.7, 1.5 Hz, 1H, Ar*H*), 7.93 – 7.90 (m, 2H, Ar*H*), 7.55 (ddd, J = 7.3, 5.6, 1.6 Hz, 1H, Ar*H*), 1.42 (s, 15H, $C_5(CH_3)_5$). The characterization data for this material are consistent with those reported previously.[8]

General Procedure for the Synthesis of Compounds L8 – L10

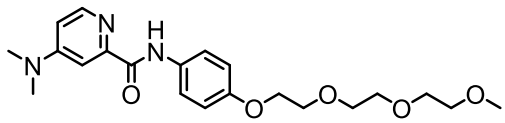
In a 50 mL round bottom flask, 4-dimethylaminopicolinic acid (3 mmol, 1.0 equiv.), EDC·HCl (1.5 equiv.), and Et_3N (5 equiv.) were combined in 5 mL of anhydrous DMF under N_2. The reaction flask was stirred at RT for 30 min, giving a dark solution. The corresponding aniline derivative (1.2 equiv.) in 5 mL of CH_2Cl_2 was added to the flask via a syringe, and the reaction mixture was stirred at 50 °C under N_2 for 24 h. When the reaction was complete, excess amounts of water were added to the mixture, followed by the addition of ethyl acetate. The combined organic layer was separated, dried over Na_2SO_4, filtered, and dried under vacuum. The crude mixture was purified by silica gel column chromatography using hexanes: ethyl acetate or hexanes: Et_2O: CH_2Cl_2 as the eluent.

Compound L8:



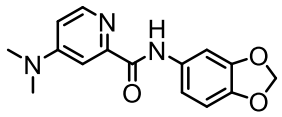
Compound **L8** was synthesized from 4-dimethylaminopicolinic acid and 4-butoxyaniline, and was purified by silica gel column chromatography using hexanes:ethyl acetate (3:1) to hexanes:ethyl acetate (1:1) as the eluent. The crude product was isolated as an off-white solid (730 mg, 78%). Further attempts to purify the product by recrystallization were made; however, traces of unknown impurities were unable to be separated from the crude mixture. This material was used in the metalation step without any further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.75 (br, 1H), 8.42 (d, J = 5.2 Hz, 1H), 8.20 (d, J = 2.1 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.40 – 7.38 (m, 1H), 6.93 – 6.84 (m, 2H), 4.09 – 4.05 (m, 2H), 3.82 – 3.78 (m, 2H), 3.70 – 3.67 (m, 2H), 3.65 – 3.58 (m, 6H), 3.32 (d, J = 3.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) =160.54, 155.82, 151.50, 148.95, 146.20, 130.92, 126.53, 122.94, 121.28, 115.10, 71.98, 70.61, 69.80, 67.76, 59.08.

Compound L9:



Compound **L9** was synthesized from 4-dimethylaminopicolinic acid and 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)aniline. In the work-up step, a mixture of $CHCl_3$/*i*PrOH (4:1) or CH_2Cl_2/*i*PrOH (5:1) was used instead of ethyl acetate to collect the crude product as a viscous light orange oil. The product was then purified by silica gel column chromatography using hexanes:Et_2O:CH_2Cl_2:Et_3N (1:0.5:0.5:0.01) as the eluent, and was isolated as a viscous colorless liquid (670 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.99 (br, 1H, CON*H*), 8.07 (d, *J* = 5.9 Hz, 1H, Ar*H*), 7.61 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.42 (d, *J* = 2.8 Hz, 1H, Ar*H*), 6.84 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.45 (dd, *J* = 5.9, 2.8 Hz, 1H, Ar*H*), 4.04 (t, *J* = 4.7 Hz, 2H, OCH_2), 3.76 (t, *J* = 4.8 Hz, 2H, OCH_2), 3.65 (dd, *J* = 6.0, 3.5 Hz, 2H, OCH_2), 3.63 – 3.55 (m, 4H, 2OCH_2), 3.47 (dd, *J* = 5.9, 3.4 Hz, 2H, OCH_2), 3.29 (s, 3H, OCH_3), 2.95 (s, 6H, N(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.59 (*C*ONH), 155.13 (2C), 149.82, 147.84, 131.40, 120.78 (2C), 114.77 (2C), 107.99, 104.82, 71.72 (O*C*H$_2$), 70.60 (O*C*H$_2$), 70.43 (O*C*H$_2$), 70.35 (O*C*H$_2$), 69.57 (O*C*H$_2$), 67.48 (O*C*H$_2$), 58.85 (O*C*H$_3$), 39.07 (N(*C*H$_3$)$_2$).

Compound L10:

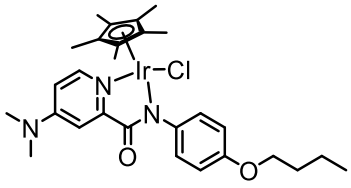


Compound **L10** was synthesized from 4-dimethylaminopicolinic acid and 3,4-(methylenedioxy)aniline, and was purified by silica gel column chromatography using hexanes:ethyl acetate (3:1) to hexanes:ethyl acetate (1:1) as the eluent. The product was isolated as an off-white solid (450 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.04 (br, 1H, CON*H*), 8.16 (d, *J* = 5.9 Hz, 1H, Ar*H*), 7.52 (dd, *J* = 7.6, 2.3 Hz, 2H, Ar*H*), 7.06 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar*H*), 6.78 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.56 (dd, *J* = 6.1, 2.7 Hz, 1H, Ar*H*), 5.95 (s, 2H, OCH_2O), 3.06 (s, 6H, N(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.86 (*C*ONH), 155.46, 150.02, 148.11, 147.88, 144.03, 132.63, 112.67, 108.29, 108.25, 105.19, 102.17, 101.28, 39.41 (N(*C*H$_3$)$_2$).

General Procedure for the Synthesis of Complexes Ir8 – Ir10:

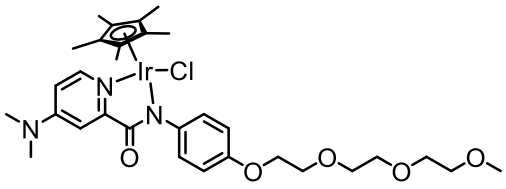
The procedure was adapted from the literature.[8] In a round bottom flask, the corresponding picolinamidate ligand (0.25 mmol, 1.0 equiv.) was added into 10 mL of anhydrous THF and stirred for 30 min at RT. The reaction mixture was treated with sodium hydride (0.5 mmol, 2.0 equiv.) and stirred for an additional 4 h (overnight for **Ir9**). Solid $[Cp^*IrCl_2]_2$ (0.1 mmol, 0.4 equiv.) was added, and the reaction solution immediately turned an orange/red brown color. After stirring for 12 h at RT, water was added to quench the reaction. The mixture was diluted with CH_2Cl_2, and the combined organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The product was purified by silica gel column chromatography using hexanes: ethyl acetate: MeOH as the eluent.

Complex Ir8:



This complex was purified by silica gel column chromatography using hexanes:ethyl acetate:MeOH (1:10:1) as the eluent and was isolated as a yellow solid, 51 mg, 75%. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, J = 6.7 Hz, 1H, Ar*H*), 7.51 (d, J = 8.3 Hz, 2H, Ar*H*), 7.26 (s, 1H, Ar*H*), 6.82 (d, J = 8.2 Hz, 2H, Ar*H*), 6.53 (dd, J = 6.8, 3.1 Hz, 1H, Ar*H*), 3.93 (t, J = 6.6 Hz, 2H, OCH_2), 3.08 (s, 6H, N(CH_3)$_2$), 1.77 – 1.71 (m, 2H, CH_2), 1.48 (t, J = 7.5 Hz, 2H, CH_2), 1.37 (s, 15H, C_5(CH_3)$_5$), 0.95 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) = 169.68 (*C*ONH), 155.72, 155.09, 154.31, 148.60, 141.80, 127.81, 113.96, 109.30, 108.44, 85.77, 68.01, 39.56, 31.52, 19.34, 14.02, 8.60. ESI-MS(+): calc for $C_{28}H_{37}IrN_3O_2$ $[M\text{-}Cl]^+$ = 640.2515, found: 640.2572. IR: ν (cm^{-1}) = 2925.8, 1590.8, 1502.3, 1371.7, 1230.5, 1033.0, 804.3, 596.3, 523.7.

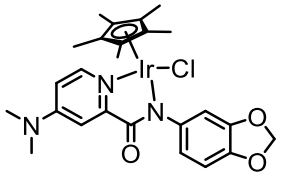
Complex Ir9:



This complex was purified by silica gel column chromatography using ethyl acetate: MeOH (95:5) as the eluent and was observed as a yellow colored amorphous solid, 50 mg, 65%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.05 (d, J = 6.7 Hz, 1H, Ar*H*), 7.58 – 7.53 (m, 2H, Ar*H*), 7.30 (d, J = 3.2 Hz, 1H, Ar*H*), 6.87 – 6.82 (m, 2H, Ar*H*), 6.55 (dd, J = 6.7, 3.1 Hz, 1H, Ar*H*), 4.12 (t, J = 4.9 Hz,

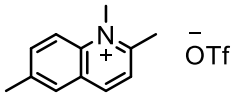
2H, OCH_2), 3.87 – 3.83 (m, 2H, OCH_2), 3.76 – 3.73 (m, 2H, OCH_2), 3.71 – 3.68 (m, 2H, OCH_2), 3.68 – 3.65 (m, 2H, OCH_2), 3.57 – 3.54 (m, 2H, OCH_2), 3.38 (s, 3H, OCH_3), 3.12 (s, 6H, N(CH_3)$_2$), 1.39 (s, 15H, C_5(CH_3)$_5$). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 169.59, 155.38, 155.20, 154.55, 148.57, 142.22, 127.91, 114.19, 109.26, 108.58, 85.77, 72.04, 70.89, 70.73, 70.65, 70.01, 67.79, 59.15, 39.56, 8.61. ESI-MS(+): calc for $C_{31}H_{43}IrN_3O_5$ $[M\text{-}Cl]^+$ = 730.2832, found: 730.2869. IR: ν (cm^{-1}) = 2880.3, 1590.4, 1499.8, 1441.2, 1367.3, 1231.2, 1110.7, 1035.6, 936.2, 807.7, 598.8, 524.5.

Complex Ir10:



This complex was purified using hexanes: ethyl acetate (1:1) to ethyl acetate: MeOH (95:5) as the eluent and was observed as a yellow colored solid, 53 mg, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.05 (d, J = 6.6 Hz, 1H, ArH), 7.30 (d, J = 3.0 Hz, 1H, ArH), 7.23 (d, J = 1.9 Hz, 1H, ArH), 7.15 (dd, J = 8.3, 2.0 Hz, 1H, ArH), 6.75 (d, J = 8.3 Hz, 1H, ArH), 6.55 (dd, J = 6.7, 3.2 Hz, 1H, ArH), 5.93 – 5.89 (m, 2H, OCH_2O), 3.12 (s, 6H, N(CH_3)$_2$), 1.42 (s, 15H, C_5(CH_3)$_5$). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 169.74, 155.21, 154.43, 148.59, 146.89, 143.90, 143.21, 119.89, 109.31, 108.84, 108.64, 107.48, 100.85, 85.79, 39.58, 8.64. ESI-MS(+): calc for $C_{25}H_{29}IrN_3O_3$ $[M\text{-}Cl]^+$ = 612.1838, found: 612.1887. IR: ν (cm^{-1}) = 1591.7, 1471.0, 1373.3, 1222.7, 1100.1, 1027.7, 922.3, 799.3, 567.4.

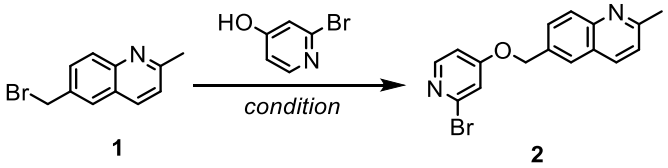
Preparation of 1,2,6-trimethylquinolinium triflate



To a 10 mL round bottom flask equipped with a magnetic stir bar, 2,6-dimethylquinoline (236 mg, 1.5 mmol, 1.0 equiv.) and 5 mL of anhydrous CH_2Cl_2 were combined. The resulting mixture was purged and filled with Ar for 5 min at RT. Methyl triflate (820 µL, 7.5 mmol, 5.0 equiv.) was added to the reaction flask by syringe. The reaction was stirred under Ar at RT for 15 h. When the reaction was complete, the solid was collected by filtration and washed with ~ 25 mL of hexanes and Et_2O, respectively. The desired product was obtained as a white solid and was used for the next step without any further purification. ^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 8.89 (t, J = 7.8 Hz, 1H, ArH), 8.48 – 8.32 (m, 1H, ArH), 8.10 (q, J = 11.7, 9.1 Hz, 2H, ArH), 8.02 – 7.84 (m, 1H, ArH), 4.50 (s, 3H, NCH_3), 3.09 (s, 3H, CH_3), 2.65 (s, 3H, CH_3). ^{19}F NMR (376 MHz, CD_3OD):

δ (ppm) = -80.02 (s). The characterization data for this material are consistent with those reported previously.[9]

Table S1. Screening Conditions for Nucleophilic Substitution

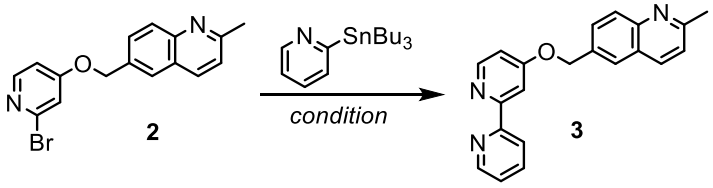


1 **2**

Entry	**Condition**[a]	**Yield** (%)
1	NaH, THF, 50 °C, 24 h	<5
2	KOH, DMF, reflux, 24 h	11
3	Na_2CO_3, DMF, 110 °C, 24 h	73

[a]Reaction conditions used: 2-bromo-4-hydroxypyridine (6.8 mmol, 1.0 equiv.), compound **1** (7.5 mmol, 1.1 equiv.), base (2.2 equiv.), solvent (100 mL). The amounts obtained are reported as isolated yields.

Table S2. Screening Conditions for Stille Coupling

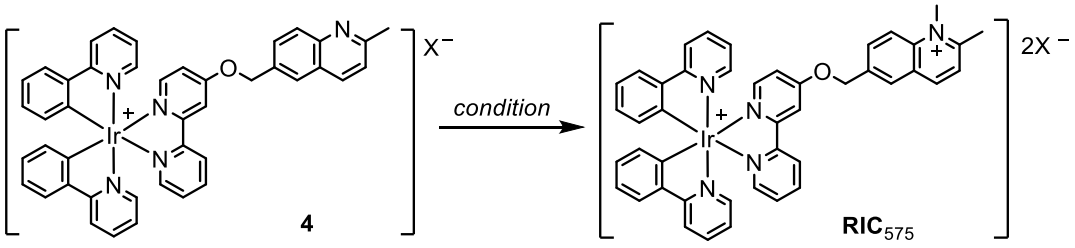


2 **3**

Entry	**Condition**[a]	**Yield** (%)
1	$Pd(PPh_3)_4$, CuI, Cs_2CO_3, PhMe/EtOH, reflux, 48 h	56
2	Same as entry **1**, performed in heavy wall pressure tube	30
3	$(dppf)PdCl_2$, CuI, Cs_2CO_3, PhMe/EtOH, reflux, 48 h	62

[a]Reaction conditions used: compound **2** (1.0 mmol), Pd catalyst (0.05 mmol), CuI (0.1 mmol), Cs_2CO_3 (0.2 mmol), toluene: EtOH (4:1, *v/v*, 50 mL), 2-tributylstannylpyridine (1.5 mmol). The amounts obtained are reported as isolated yields.

Table S3. Screening Conditions for Methylation



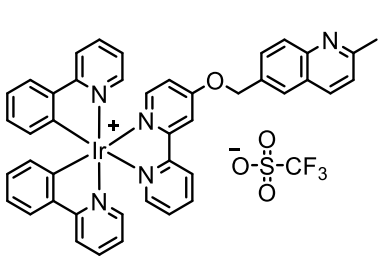
Entry	**Condition**[a]	**Yield** (%)
1	MeI, MeCN, 40 °C, 24 h	0
2	MeI, AgCl, MeCN, 40 °C, 24 h	0
3	MeOTf, CH_2Cl_2, RT, 48 h	not isolated, mixed anions (X^- = Cl^-, OTf^-)
4	Same as entry **3**, using THF as solvent	<5, precipitates of both **4** and **RIC**$_{575}$ were observed in THF)
5	Same as entry **3**, performed ion exchange first with AgOTf, RT, 72 h	48 (X^- = OTf^-)

[a]Reaction conditions used: **4** (0.2 mmol), methylating agent (2.0 mmol, 10 equiv.), solvent (50 mL). The reactions were set up using the standard procedure described in the experimental section. The amounts obtained are reported as isolated yields.

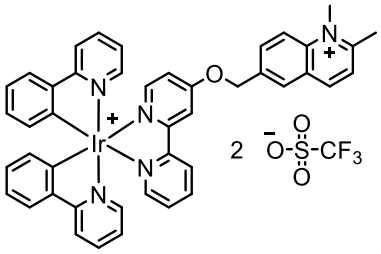
Photophysical Studies

UV-vis absorption spectra, emission spectra and lifetime were recorded in anhydrous methanol solutions in septum-sealed screw-capped quartz cuvettes. To exclude air, samples for emission and excitation measurements were prepared in a nitrogen-filled glovebox. UV-vis absorption spectra were recorded using an Agilent Cary 8454 UV-vis spectrophotometer. Emission and excitation spectra were recorded using a Horiba FluoroMax-4 spectrofluorometer. Luminescence lifetimes were measured with a Horiba DeltaFlex Lifetime System, using pulsed diode excitation and excited at 330 nm. Emission wavelengths were selected by using appropriate long-pass filters to exclude stray excitation light from detection. Emission quantum yields were determined relative to a standard of quinine sulfate in 0.5 M sulfuric acid solution, which has a reported phosphorescence quantum yield (Φ_F) of 0.546.[10] The quantum yields of the complexes (Φ_x) were calculated using equation: $\Phi_x = \Phi_{st}[m_x/m_{st}][\eta_x/\eta_{st}]^2$, where Φ_{st} = the quantum yield of the standard, m_x = the slope of emission intensity versus absorbance for the samples, m_{st} = the slope of emission intensity versus absorbance for the standard compound, and η_x and η_{st} are the refractive indexes of the solvents of the sample and standard, respectively. All photophysical data were processed using Origin 2017 from OriginLab.

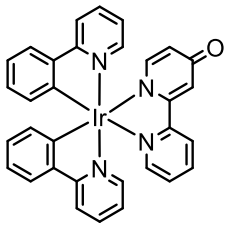
Table S4. Summary of Photoluminescence Data



4



RIC$_{575}$



RIC$_{525}$

Complex	λ_{ex} (nm)	λ_{em} (nm)	Φ_{PL}[a]	τ (μs)	(k_r, 10^{-5} s^{-1})/(k_{nr}, 10^{-5} s^{-1})[b]
4	310	597	0.349	0.74	4.72/8.80
RIC$_{575}$	350	575	0.006	1.03	0.06/9.65
RIC$_{525}$	350	525	0.438	1.26	3.48/4.46

[a]Relative quantum yield, measured using quinine sulfate in 0.5 M of H_2SO_4 (aqueous solution). [b]$k_r = \Phi_{PL}/\tau$, $k_{nr} = (1-\Phi_{PL})/\tau$, assuming 100% population of the emissive T_1 state. k_r: rate of radiative decay, k_{nr}: rate of non-radiative decay. The samples were prepared in methanol and the photoluminescence data were recorded at RT.

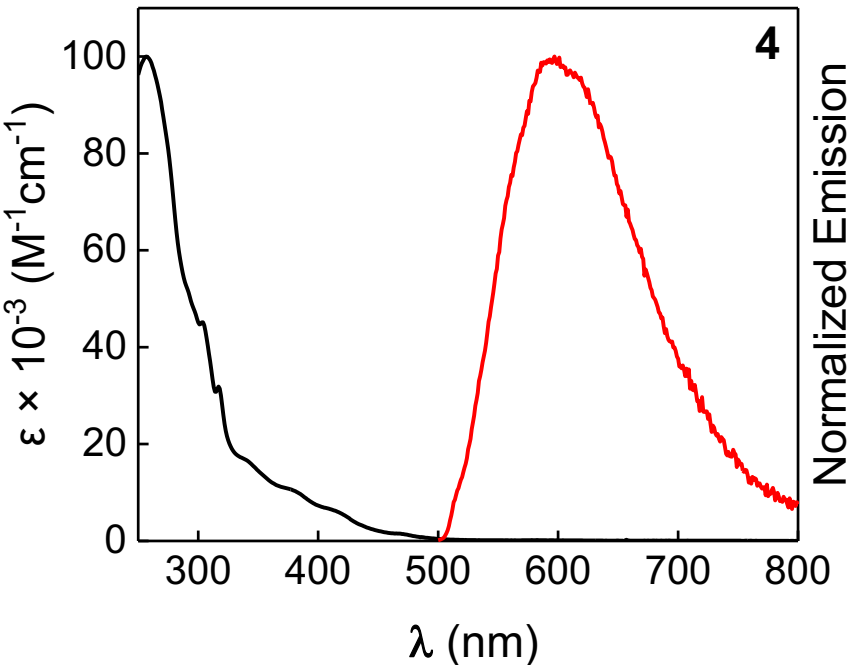


Figure S1. UV-vis absorption (black solid line) and emission (red solid line) spectra of complex **4** recorded at 20 °C in MeOH.

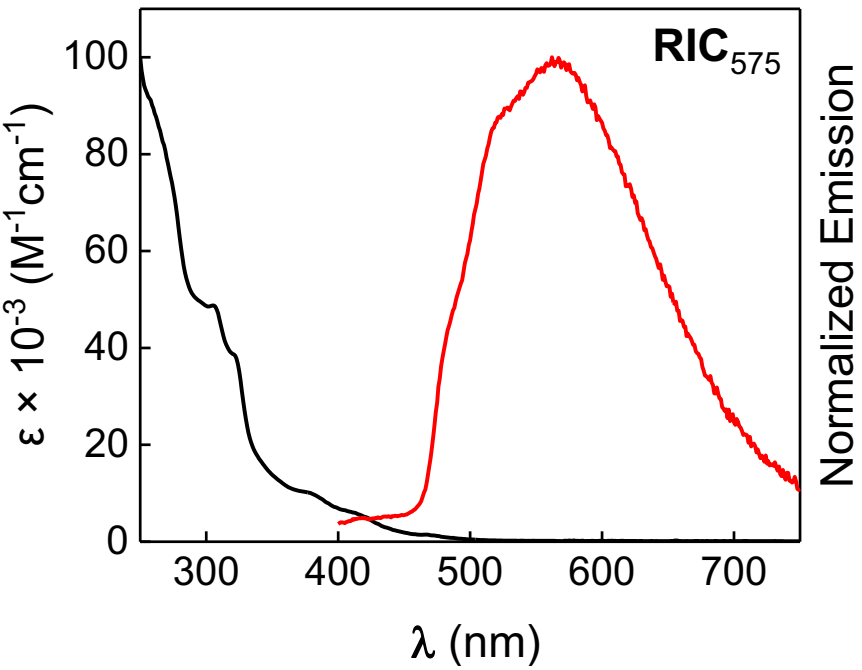


Figure S2. UV-vis absorption (black solid line) and emission (red solid line) spectra of complex **RIC**$_{575}$ recorded at 20 °C in MeOH.

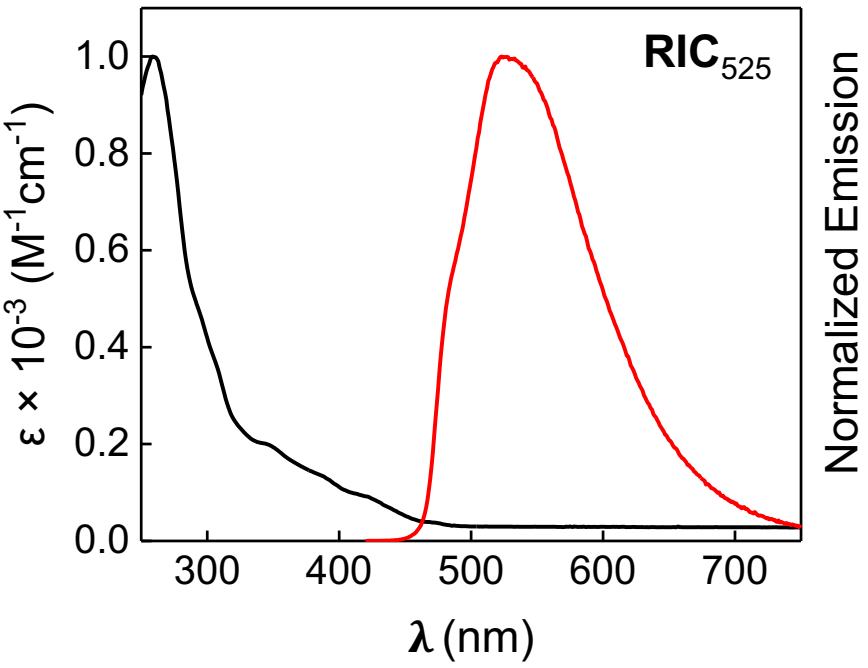


Figure S3 UV-vis absorption (black solid line) and emission (red solid line) spectra of complex **RIC**$_{525}$ recorded at 20 °C in MeOH.

Table S5. Summary of CIE$_x$ and CIE$_y$ Coordinates

Complex	Integral for *X*	Integral for *Y*	Integral for *Z*	CIE$_x$	CIE$_y$
4	7.53E+07	6.40E+07	5.04E+05	0.539	0.458
RIC$_{575}$	1.10E+07	1.32E+07	2.39E+06	0.413	0.497
RIC$_{525}$	1.71E+08	2.63E+08	4.72E+07	0.356	0.546

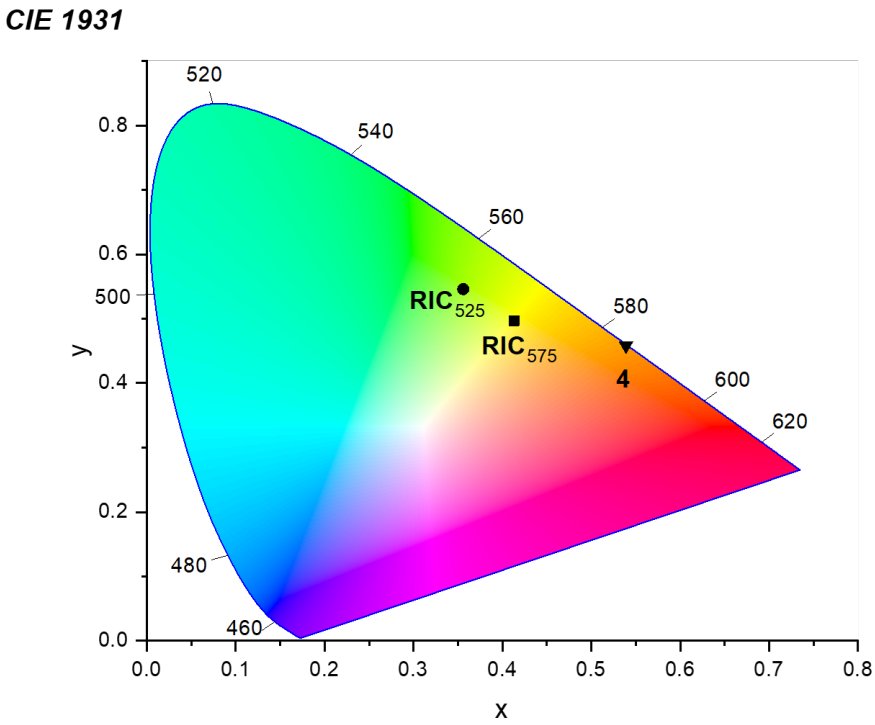


Figure S4. Chromaticity diagram (CIE 1931) for complexes **4** (▲), **RIC**$_{575}$ (■) and **RIC**$_{525}$, (●), determined from photoluminescence data recorded in MeOH at RT. Compound **4**, **RIC**$_{575}$, and **RIC**$_{525}$ fall in the orange, yellow, and green regions of the spectrum, respectively. The CIE 1931 diagram was exported from the free website-based app: sciapps.sci-sim.com/CIE1931.html, with the input presented in Table S5**.**

Figure S5. Photo of cuvettes containing solutions of compound **4** (*left*), **RIC**$_{575}$ (*middle*), and **RIC**$_{525}$ (*right*). Photos were taken using a Sony Xperia 1 III.

Transfer Hydrogenation Studies Using a Microplate Reader

The transfer hydrogenation reactions were performed in 24-well plates (Corning 3526) with spectral monitoring using a Tecan Infinite M200 Pro plate reader. Stock solutions of **RIC**$_{575}$ (0.4 mM), Ir catalyst (0.04 mM), sodium formate (4 mM), and sodium bicarbonate (10 mM) were prepared in MeOH. Stock solution of **RIC**$_{525}$ (0.4 mM) in MeOH was also prepared as a standard for comparison. It is important that the stock solutions of Ir catalyst are prepared fresh each time. Catalyst **Ir7** was not used for these studies due to its low solubility in MeOH. Inside an Eppendorf tube, the Ir catalyst (50 µL), sodium formate (150 µL), sodium bicarbonate (100 µL) stock solutions were diluted with 200 µL of methanol, and the tube was vortexed for 30 s. This mixture was then transferred to a 24-well plate and then 500 µL of the stock **RIC**$_{575}$ solution was added to each well. The phosphorescence changes were measured from the bottom of the well plate. The excitation wavelength was set at 350 nm (10 nm bandwidth), 30 flashes. The 550 nm and 600 nm emission signals (10 nm bandwidth) were collected at a fixed *z*-position of 30000 µm with 40 µs of integration time and 120 units of manual gain. All measurements were performed at ~ 28 °C, with 3 s of mechanical shaking between each acquisition, unless otherwise noted. The **RIC**$_{575}$ stock solution in methanol (500 µL) was added to the standard well. The formation of **RIC**$_{525}$ after transfer hydrogenation was determined based on the emission intensity ratio at 550/600 nm, using the following formula:

$$\text{Emission Intensity Ratio} = \frac{I_{550}}{I_{600}} = \frac{(100\text{-}X)I_{550\text{-}\mathbf{RIC}575} + (X)I_{550\text{-}\mathbf{RIC}525}}{(100\text{-}X)I_{600\text{-}\mathbf{RIC}575} + (X)I_{600\text{-}\mathbf{RIC}525}}$$

$$\%\ \text{Yield of } \mathbf{RIC}_{525} = X = \frac{100\left[\left(\frac{I_{550}}{I_{600}}\right)I_{600\text{-}\mathbf{RIC}575} - I_{550\text{-}\mathbf{RIC}575}\right]}{\left(\frac{I_{550}}{I_{600}}\right)\left[I_{600\text{-}\mathbf{RIC}575} - I_{600\text{-}\mathbf{RIC}525}\right] - I_{550\text{-}\mathbf{RIC}575} + I_{550\text{-}\mathbf{RIC}525}}$$

I_{550} = emission intensity at 550 nm obtained from the mixture
I_{600} = emission intensity at 600 nm obtained from the mixture
$I_{550\text{-}\mathbf{RIC}575}$ = emission intensity at 550 nm obtained from **RIC**$_{575}$ standard solution (0.2 mM)
$I_{600\text{-}\mathbf{RIC}575}$ = emission intensity at 600 nm obtained from **RIC**$_{575}$ standard solution (0.2 mM)
$I_{550\text{-}\mathbf{RIC}525}$ = emission intensity at 550 nm obtained from **RIC**$_{525}$ standard solution (0.2 mM)
$I_{600\text{-}\mathbf{RIC}525}$ = emission intensity at 600 nm obtained from **RIC**$_{525}$ standard solution (0.2 mM)
X = % yield of **RIC**$_{525}$

A calibration curve was constructed by plotting the emission intensity ratio I_{550}/I_{600} using standard solutions containing different amounts of **RIC**$_{525}$:**RIC**$_{575}$ (1:9, 2:8, 4:6, 6:4, 8:2, 9:1), along with 1 mM of sodium bicarbonate in methanol. The base was needed to favor the keto (**RIC**$_{525}$) rather than the enol (**RIC**$_{525'}$) form. The data fit well to a linear function, which indicates that our ratiometric quantification method is valid within the concentration range tested.

Table S6. Standard Solutions Used for the Calibration Curve[a]

Solution No.	**RIC$_{525}$:RIC$_{575}$ Ratio**	% of **RIC**$_{525}$	**I_{550}/I_{600}** (observed)
1	0:1	0 %	0.93
2	1:9	10 %	1.05
3	1:4	20 %	1.29
4	2:3	40 %	1.51
5	3:2	60 %	1.78
6	4:1	80 %	1.93
7	9:1	90 %	2.00
8	1:0	100 %	2.06

[a]Each standard solution contains 0.2 mM of the probe (**RIC**$_{575}$ and **RIC**$_{525}$ in various ratios) and 10 mM of $NaHCO_3$ in 500 µL of methanol.

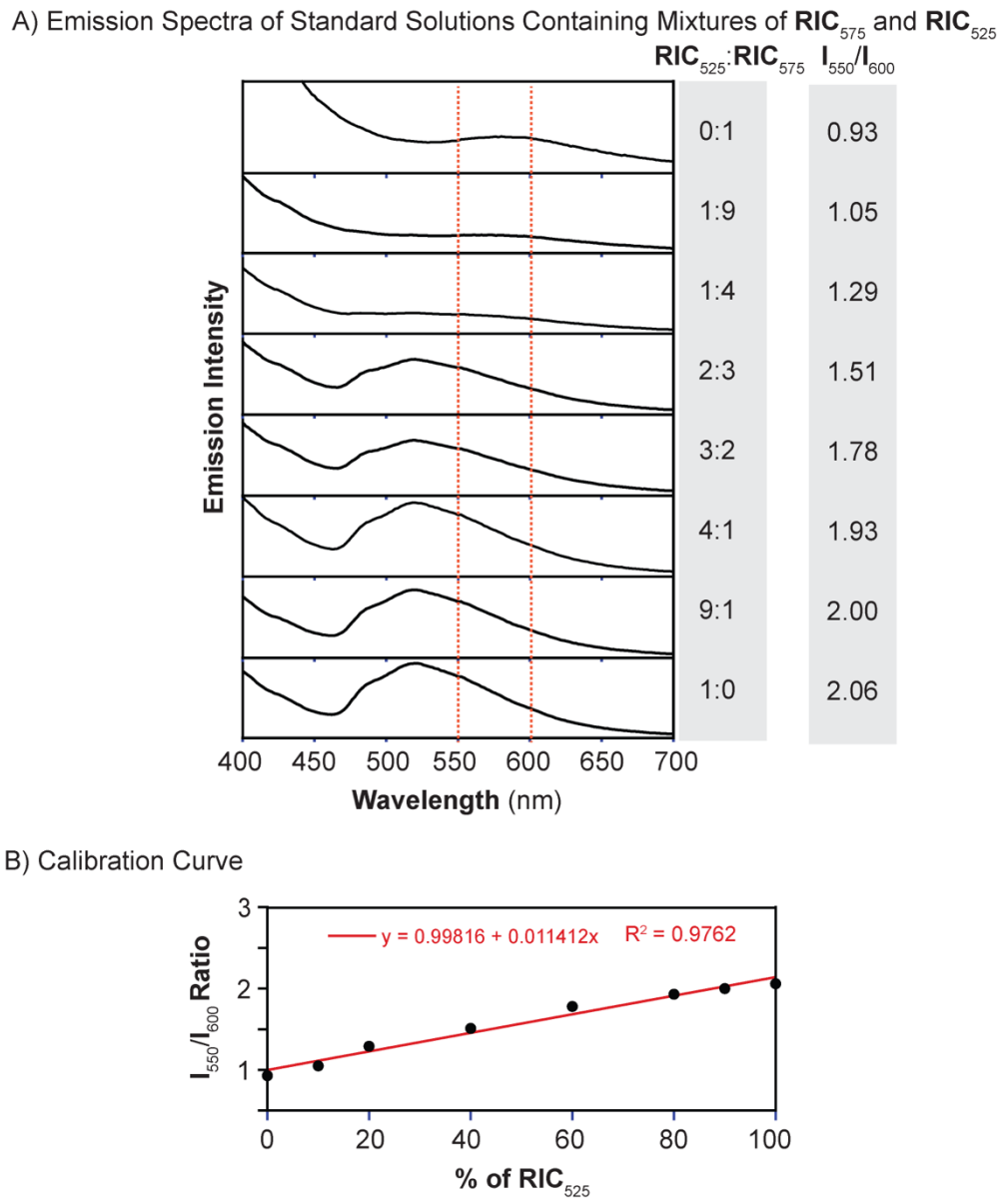


Figure S6. A) The emission spectra obtained from measurements of standard solutions containing varying amounts of **RIC**$_{525}$:**RIC**$_{575}$ ratios. The total concentration of **RIC**$_{525}$ and **RIC**$_{575}$ is 0.2 mM with 10 mM of $NaHCO_3$ in methanol. The data were acquired using a microplate reader with excitation at 350 nm (bandwidth = 10 nm) and spectral scanning from 400-800 nm. B) The calibration curve was constructed by plotting the % of **RIC**$_{525}$ present in the standard solutions vs. the I_{550}/I_{600} emission intensity ratio observed. The data were fit satisfactorily to a linear line (R^2 = 0.9762).

Table S7. Representative Data Obtained from TH Reactions Using **Ir1**[a]

Time (min)	$\mathbf{I}_{550}$[b]	$\mathbf{I}_{600}$[c]	$\mathbf{I}_{550}/\mathbf{I}_{600}$	**% Yield of RIC**$_{525}$[d]
1	2388	2700	0.884	0.3
5	2576	2769	0.930	0.7
10	3522	3140	1.122	2.6
15	4879	3664	1.332	5.1
20	6738	4262	1.581	9.0
25	8740	4882	1.790	13.4
30	10872	5614	1.937	17.3
35	13060	6332	2.062	21.5
40	15569	7067	2.203	27.6
45	18057	7846	2.301	33.1
50	20663	8759	2.359	36.9
55	22999	9490	2.423	41.9
60	25413	10246	2.480	47.1

[a]Reaction conditions used: **Ir1** (2.0 μM), **RIC**$_{575}$ (0.2 mM), HCOONa (0.75 mM), $NaHCO_3$ (1.25 mM) in 1.0 mL of MeOH at 28° C. The reaction was monitored at 550 and 600 nm over time using a microplate reader. Data were collected every 1 min for 1 h; however, only data at every 5 min interval are shown here for simplicity. [b]The emission intensity measured at 550 nm after correcting for background noise. [c]The emission intensity measured at 600 nm after correcting for background noise. [d]The % yield of **RIC**$_{525}$ was calculated using the equation shown on page S25. The following standard emission intensity values were used in the calculations: $I_{550\text{-}\mathbf{RIC}575} = 2149$, $I_{600\text{-}\mathbf{RIC}575} = 2531$, $I_{550\text{-}\mathbf{RIC}525} = 43536$, and $I_{600\text{-}\mathbf{RIC}525} = 15685$.

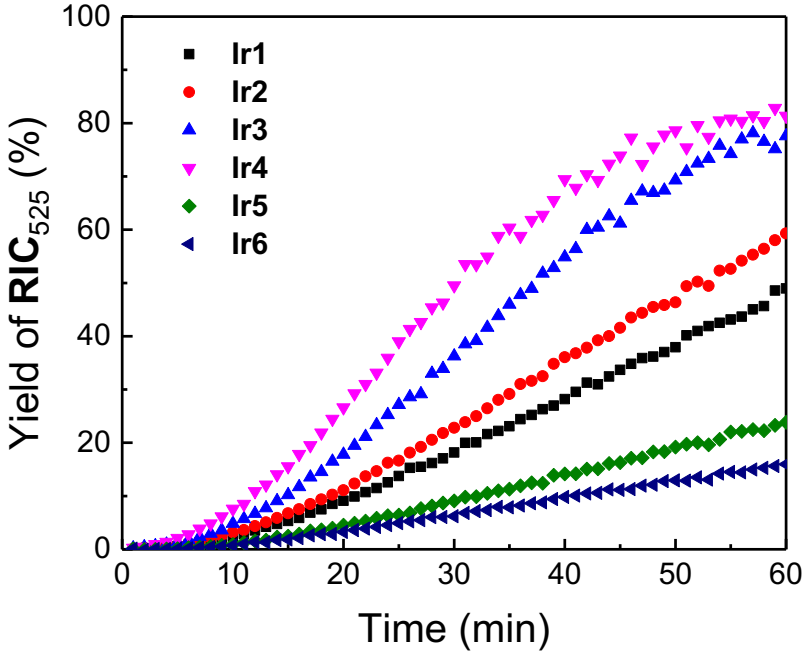


Figure S7. Kinetic plots for the formation of $\mathbf{RIC}_{525}$ catalyzed by **Ir1** – **Ir6** in the presence of HCOONa and $NaHCO_3$ after 60 min. The error bars are omitted for clarity.

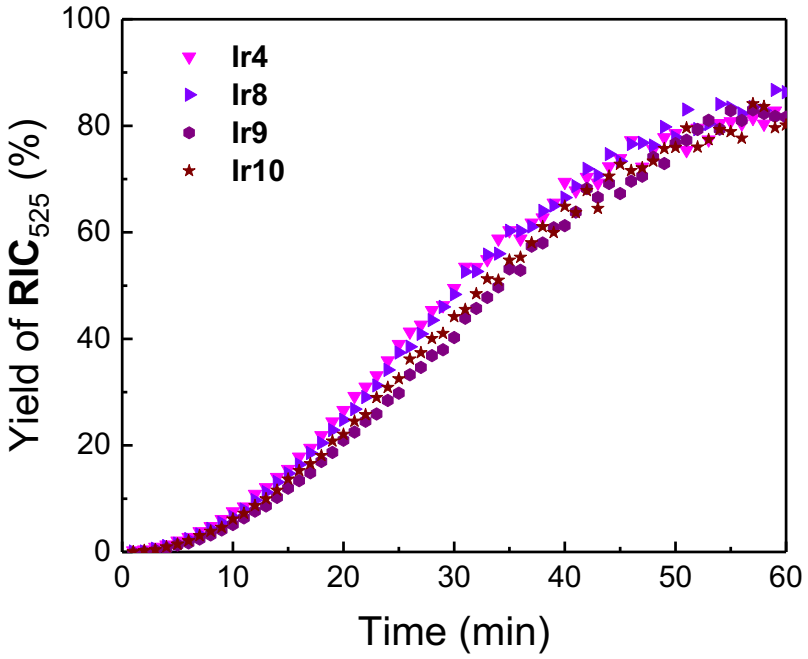


Figure S8. Kinetic plots for the formation of **RIC**$_{525}$ catalyzed by **Ir4, Ir8**, **Ir9**, and **Ir10** in the presence of HCOONa and $NaHCO_3$ after 60 min. The error bars are omitted for clarity.

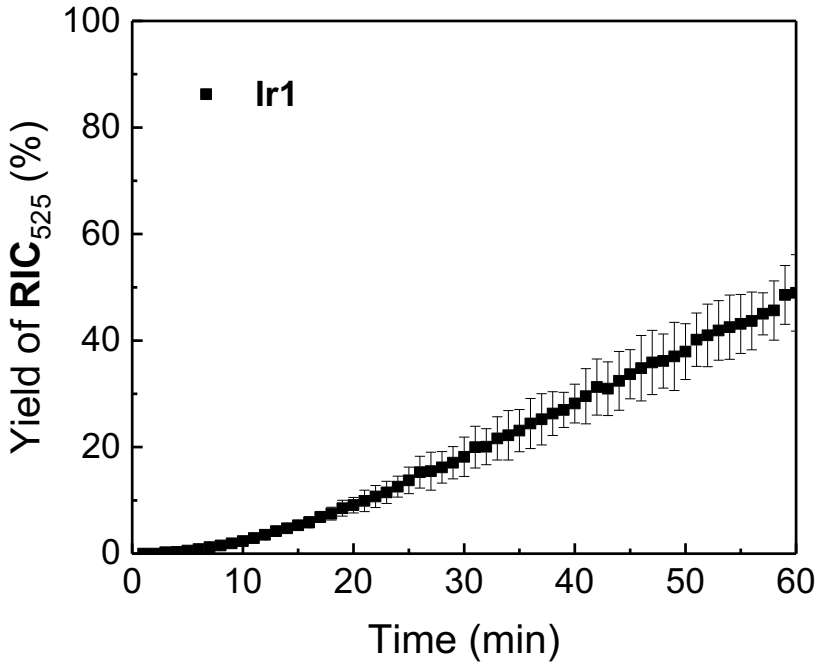


Figure S9. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir1** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

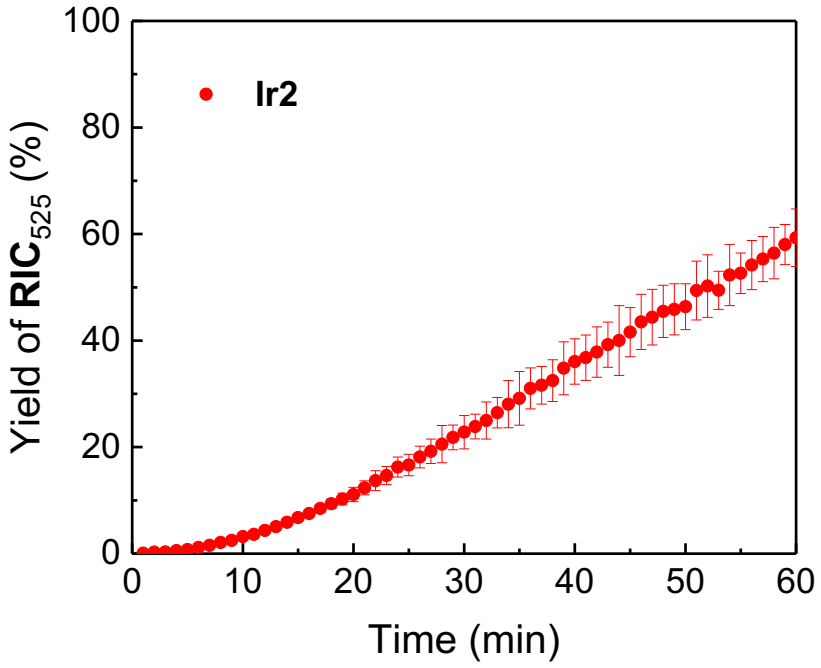


Figure S10. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir2** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

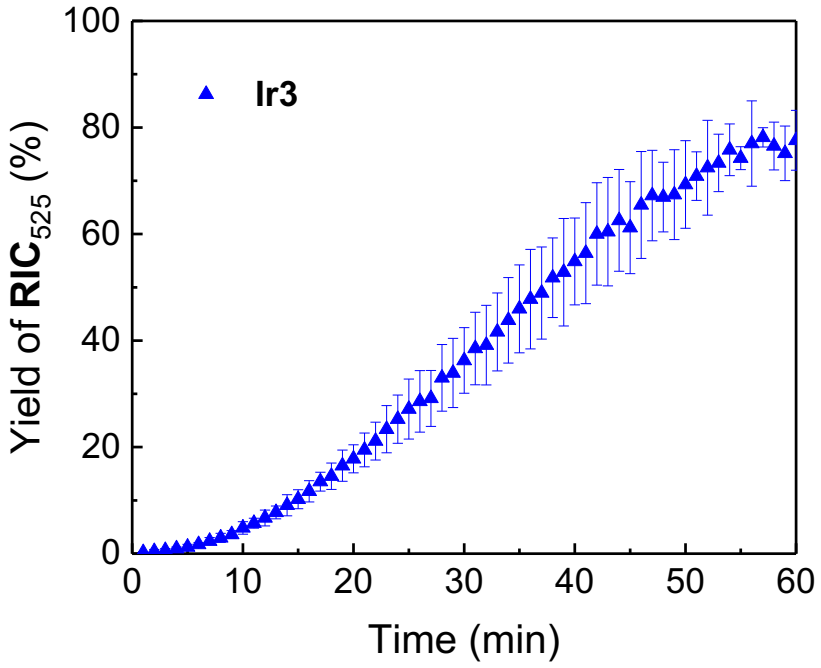


Figure S11. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir3** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

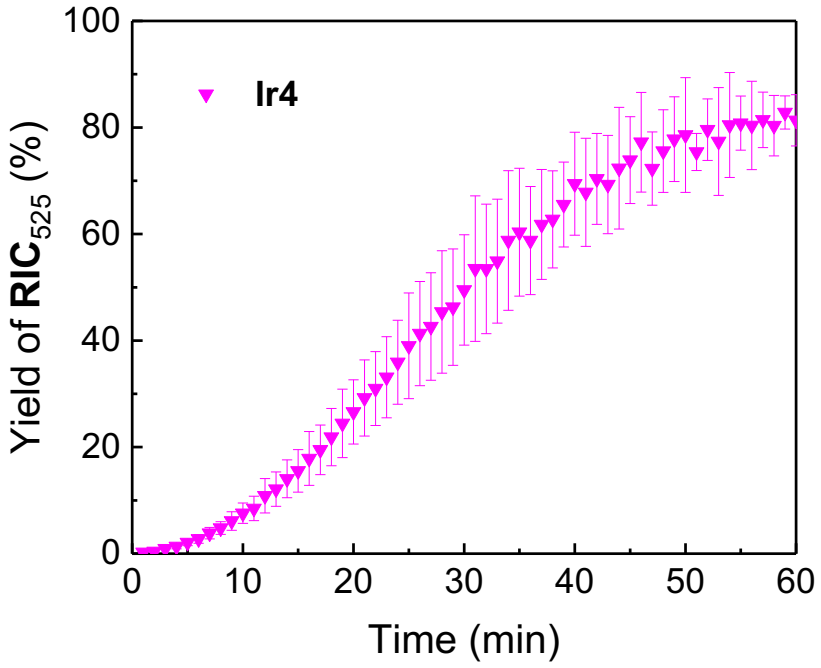


Figure S12. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir4** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

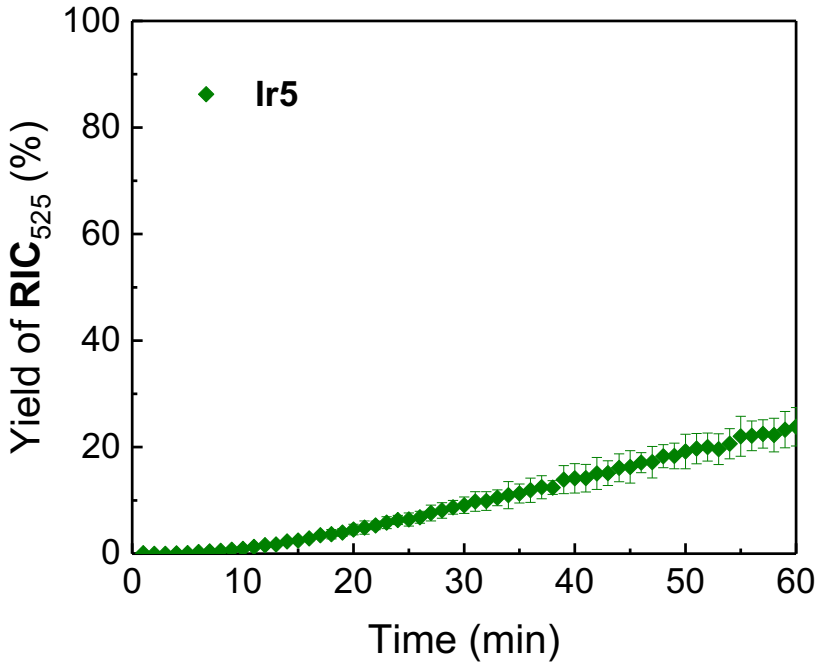


Figure S13. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir5** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

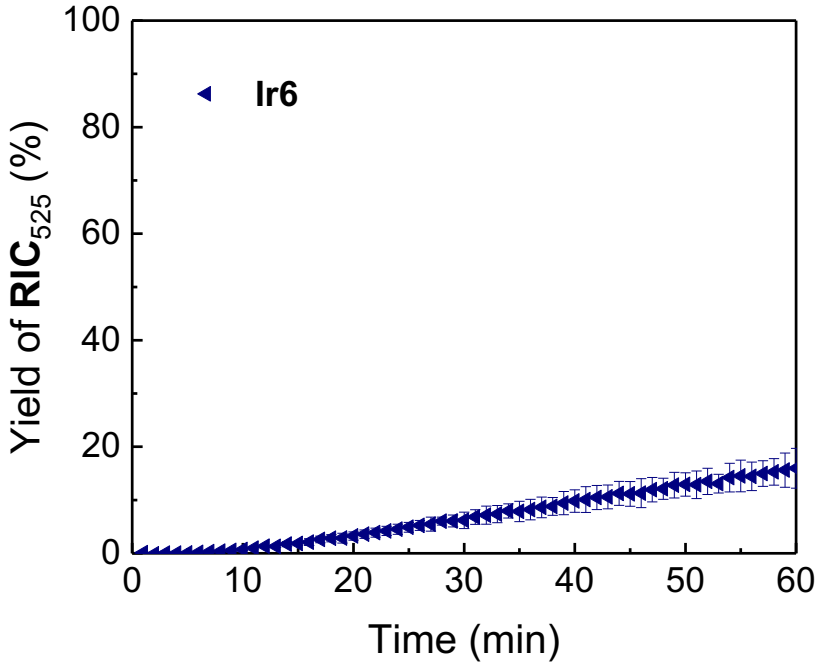


Figure S14. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir6** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

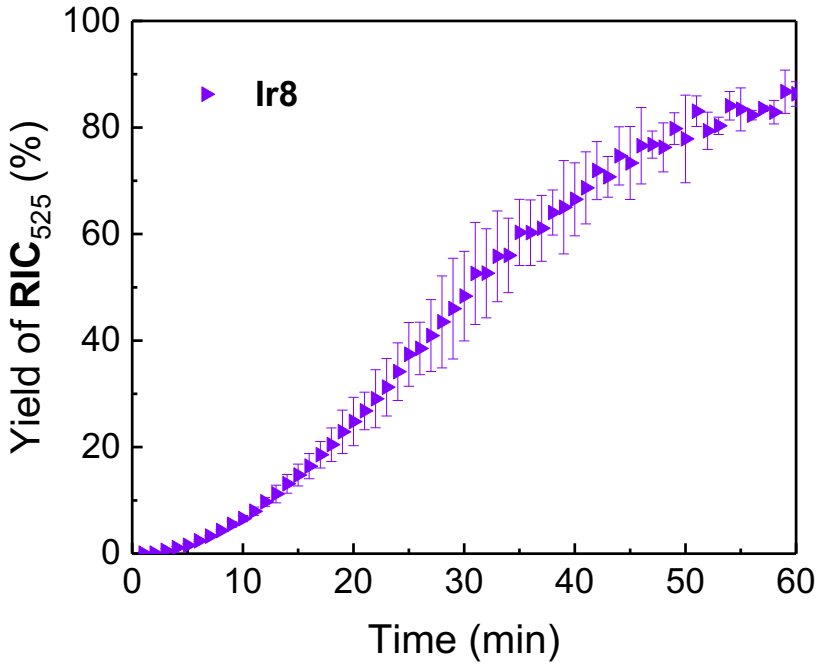


Figure S15. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir8** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

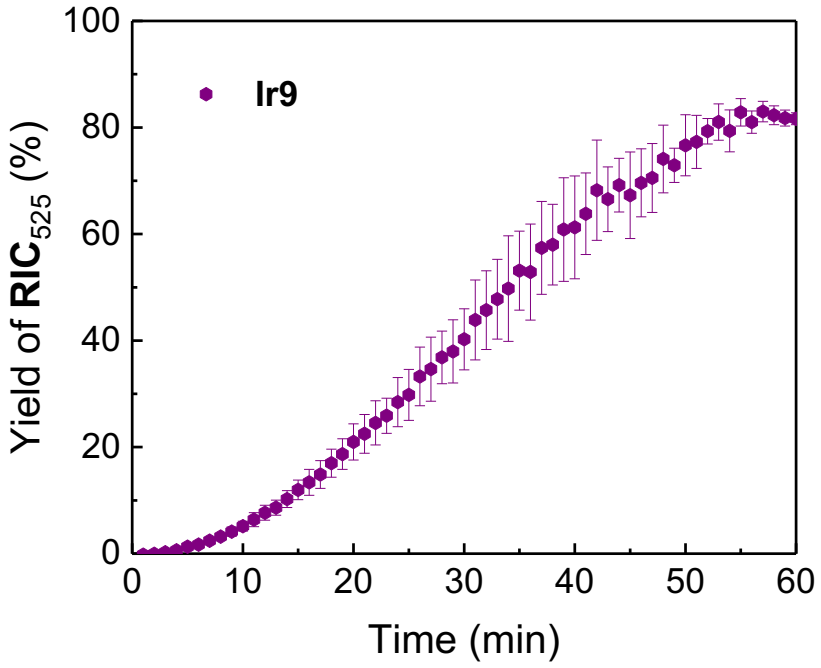


Figure S16. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir9** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

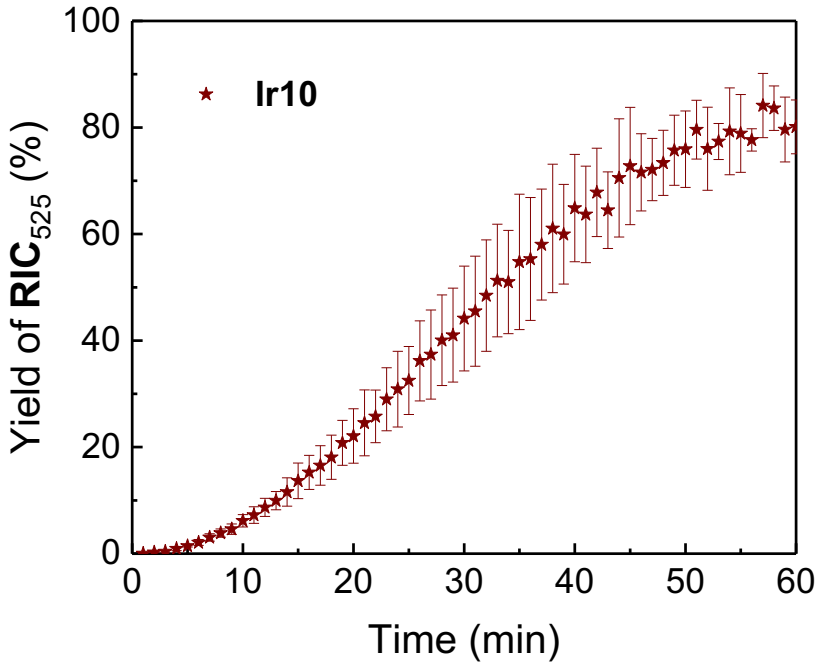


Figure S17. Kinetic plot for the formation of **RIC**$_{525}$ catalyzed by **Ir10** in the presence of HCOONa and $NaHCO_3$ after 60 min. The reaction conditions were described in the procedure section.

Mass Spectrometric Data

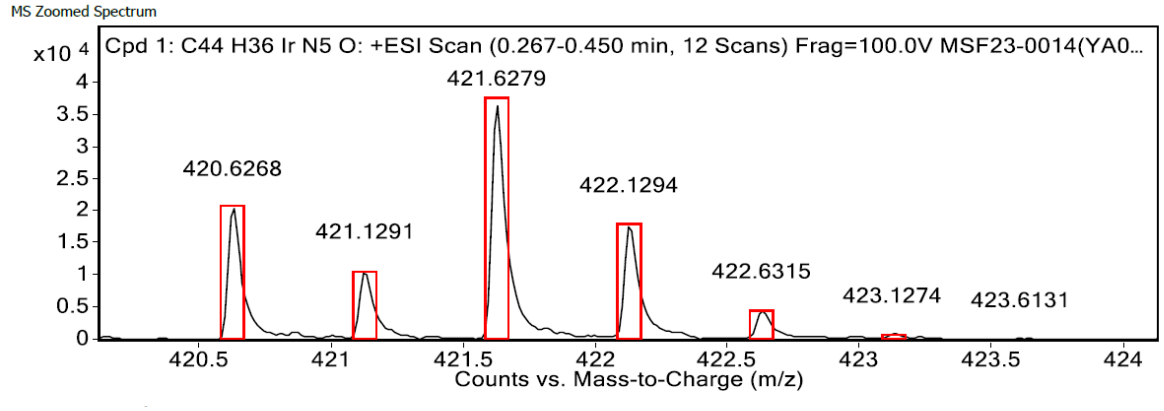


Figure S18. Mass spectrometry data (ESI-MS, positive mode) for **RIC**$_{575}$. The isotope pattern for the $[M]^{2+}$ ion is shown.

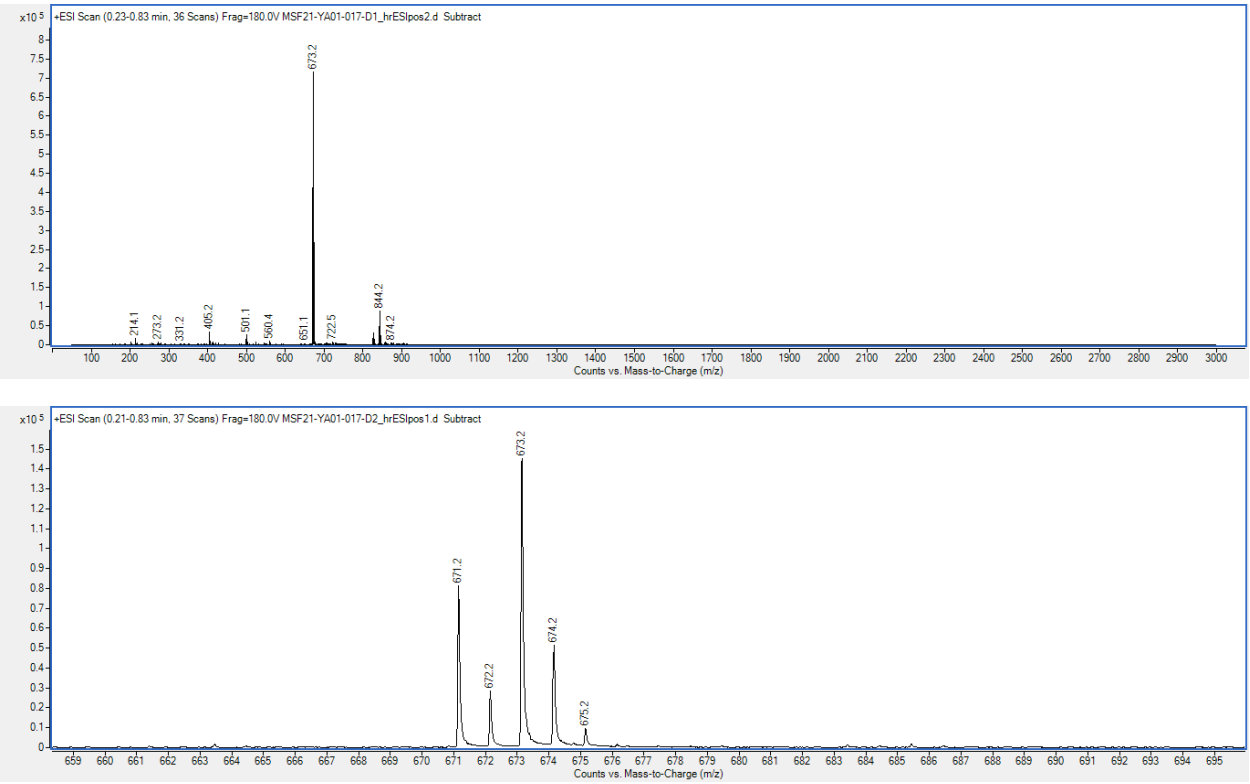


Figure S19. Mass spectrometry data (ESI-MS, positive mode) for the main fragment $[Ir(ppy)_2(bpyO)]^+$ (ppy: phenylpyridine, bpyO: bipyridin-4-one) of **RIC**$_{575}$ (*m/z* = 671/673). Full-scan *(top)* and expanded *(bottom)* spectrometric data are shown.

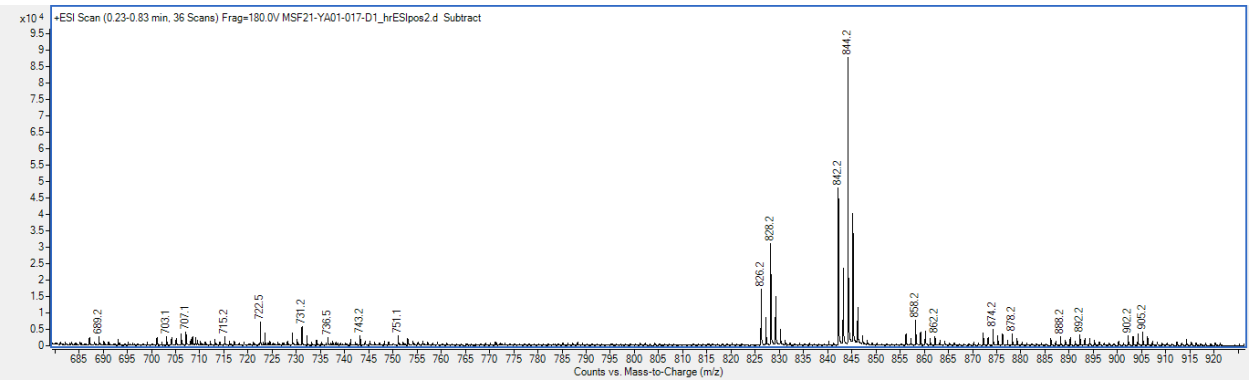


Figure S20. Mass spectrometry data (ESI-MS, positive mode) of the $[M–CH_3]^+$ fragment (*m/z* = 826/828) from **RIC**$_{575}$ observed.

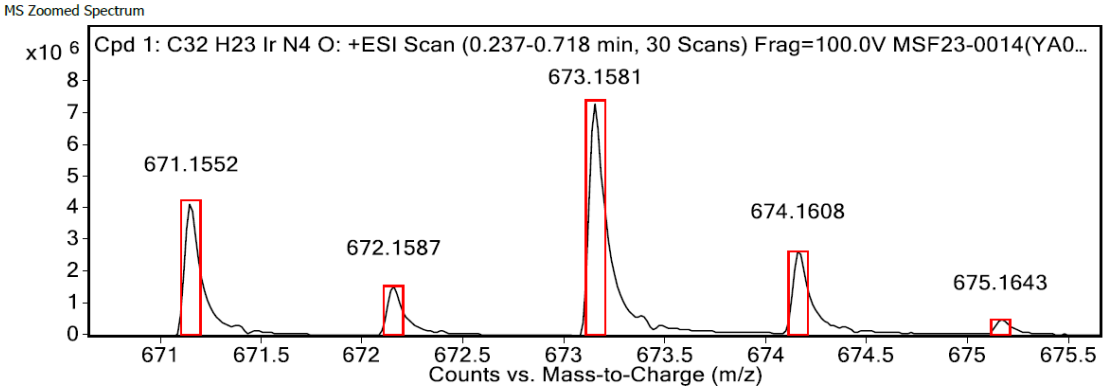


Figure S21. Mass spectrometry data (ESI-MS, positive mode) of complex **RIC**$_{525}$. The isotope pattern for the $[M+H]^+$ fragment is shown.

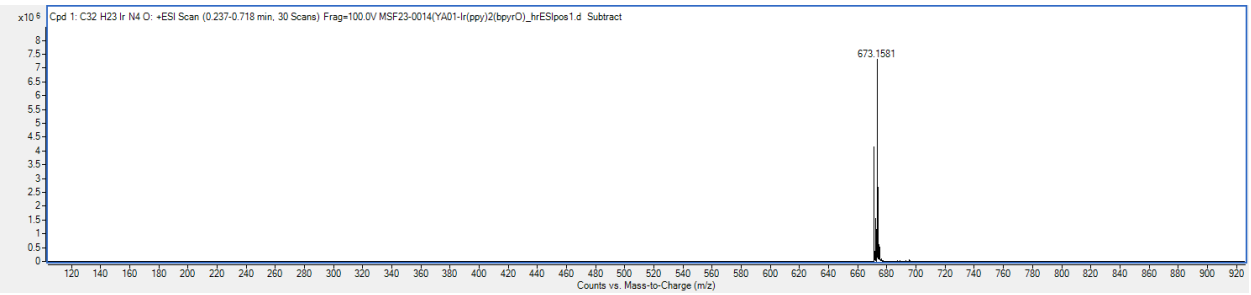


Figure S22. Mass spectrometry data (full scan) of complex **RIC**$_{525}$.

NMR Spectroscopic Data

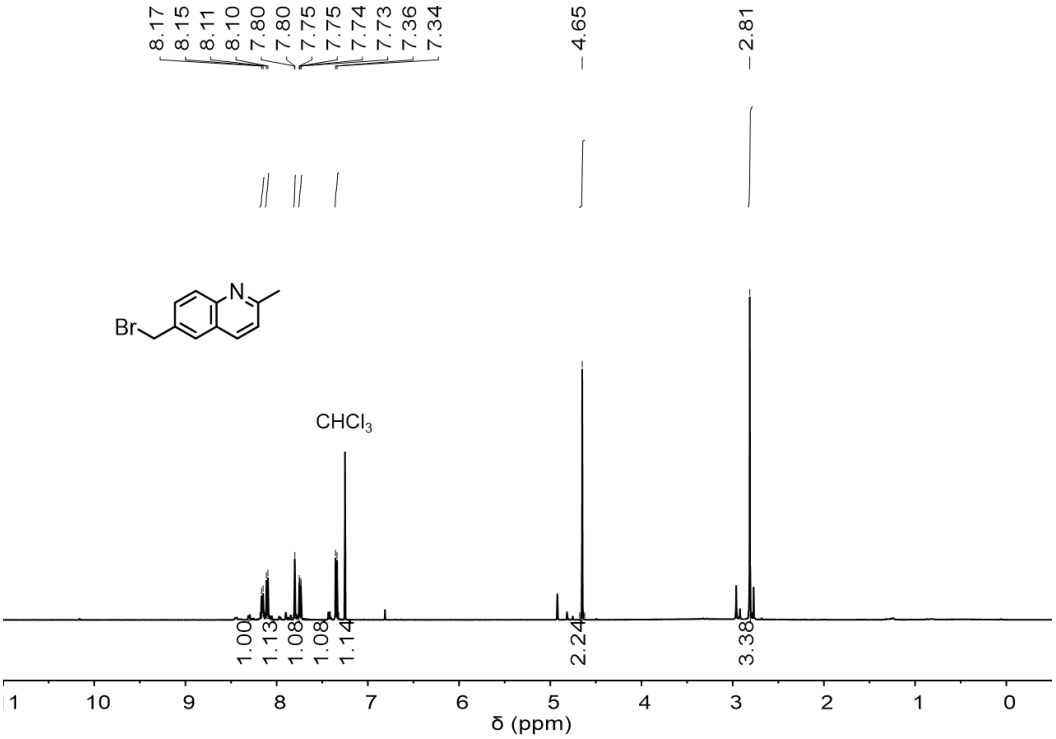


Figure S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **1**.

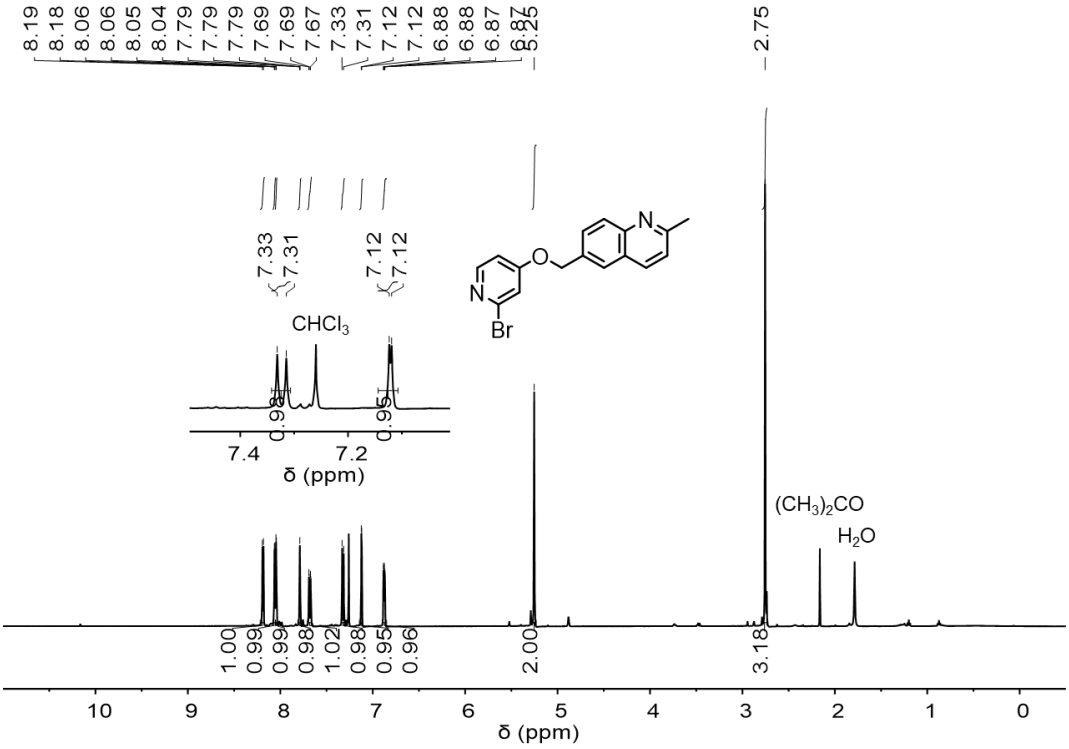


Figure S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2**.

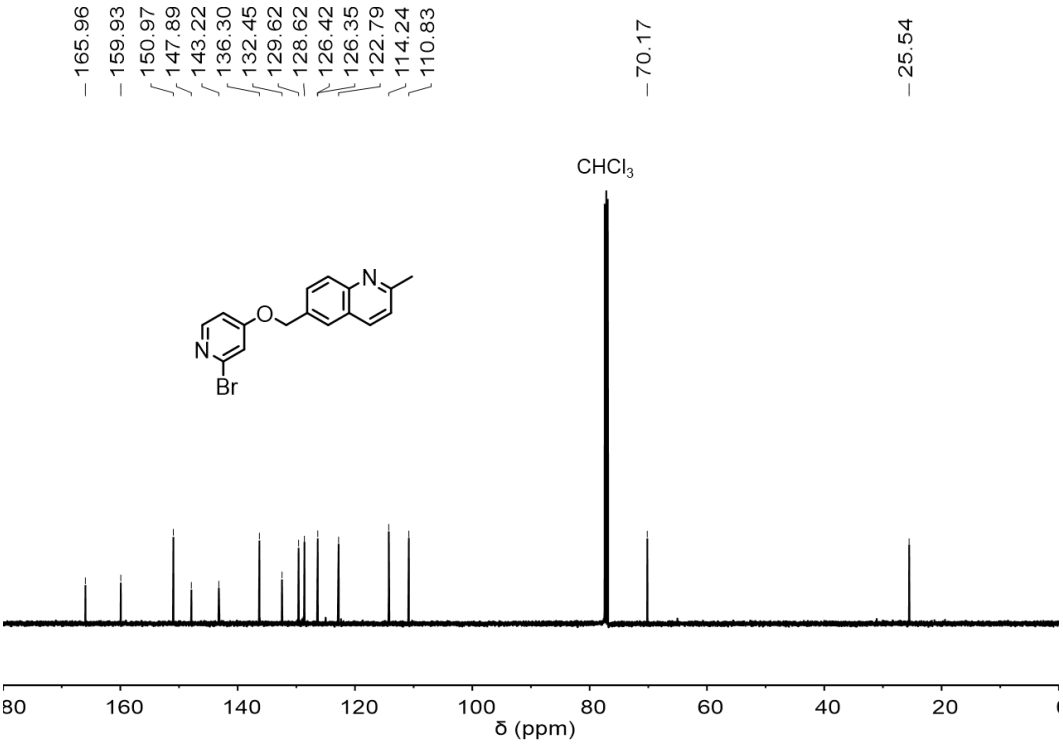


Figure S25. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2**.

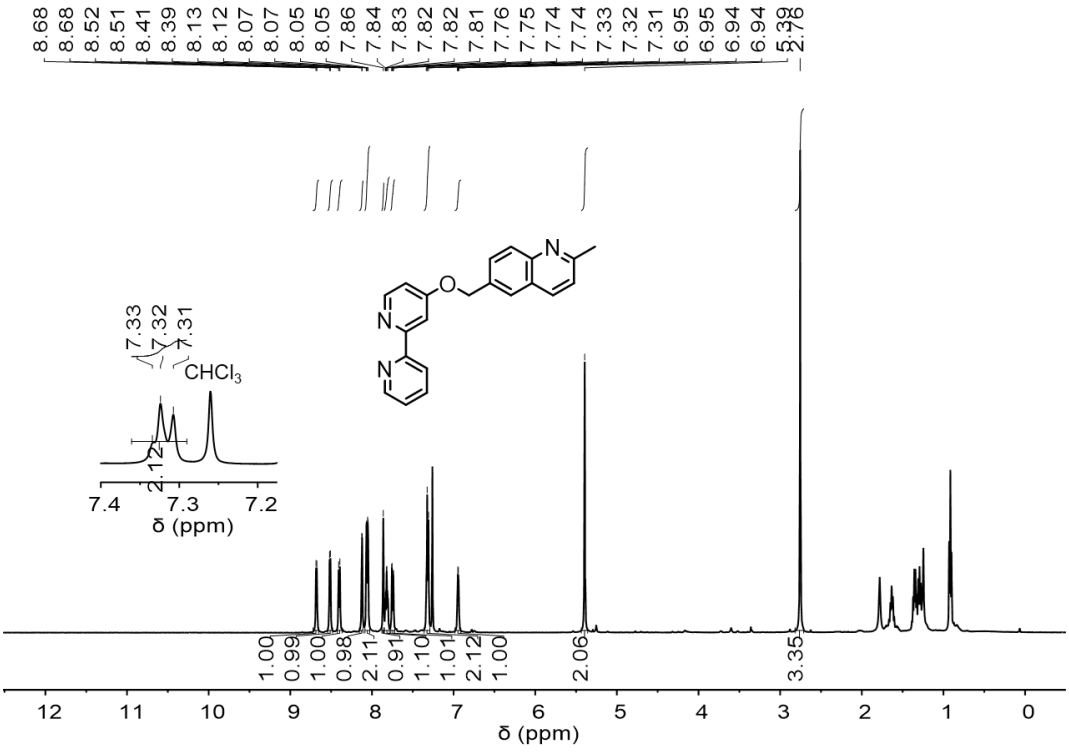


Figure S26. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3**. The peaks at ~ 0.90 – 1.78 ppm are unknown impurities that are unable to be separated by column chromatography.

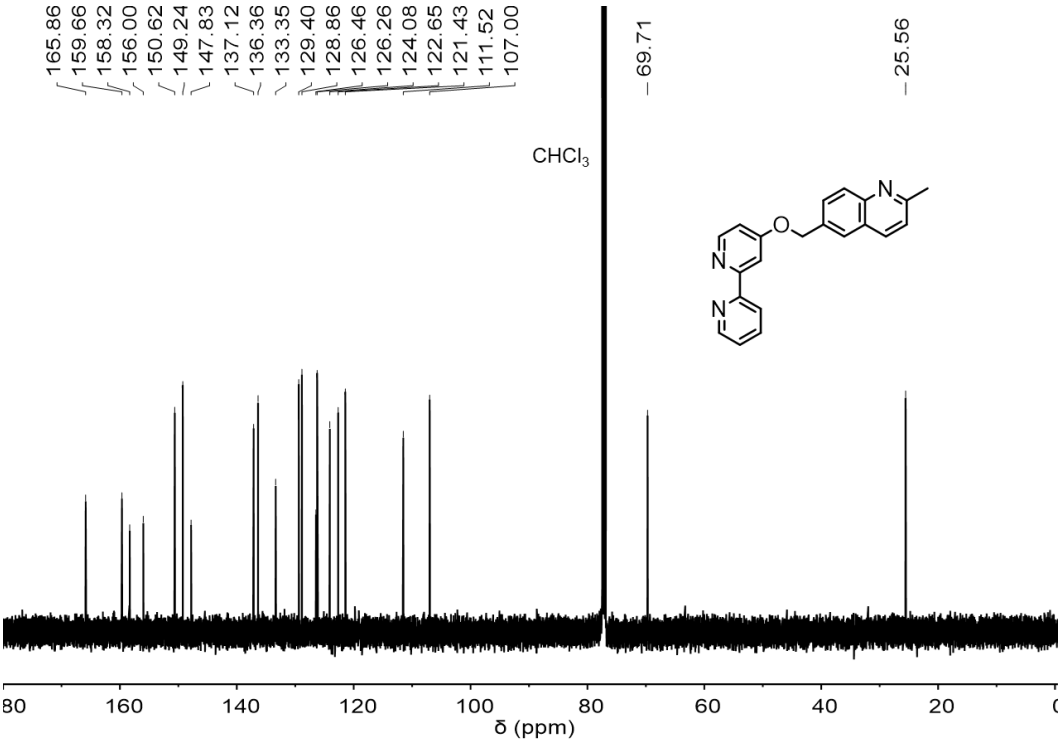


Figure S27. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **3**.

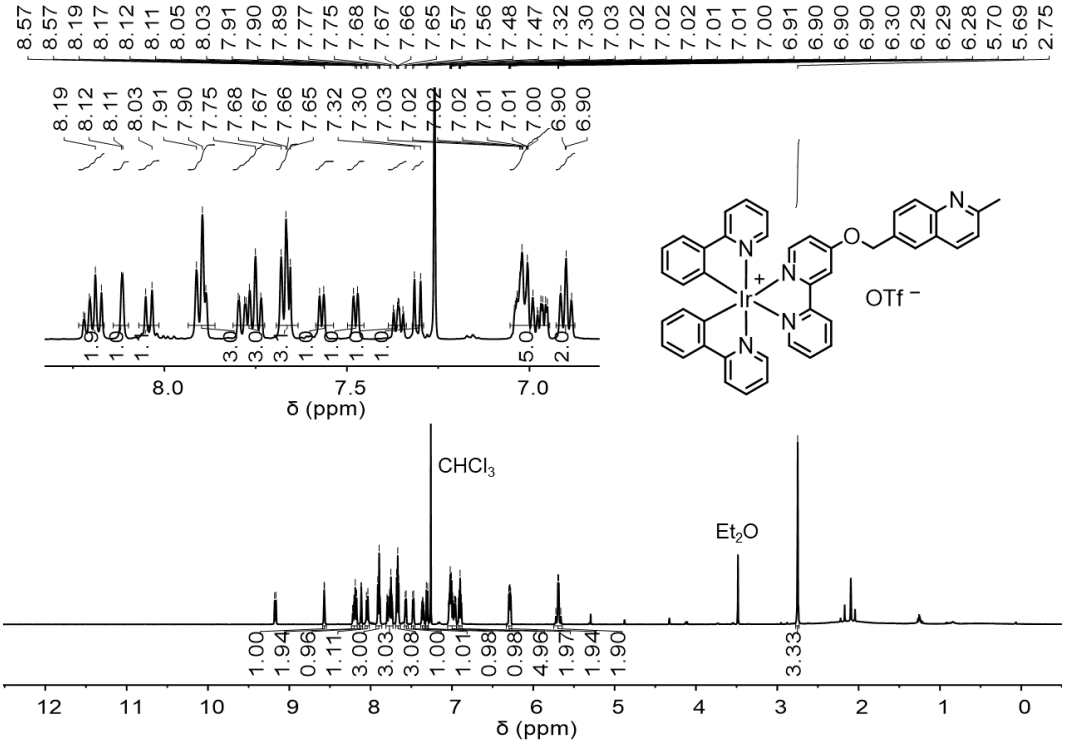


Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4**.

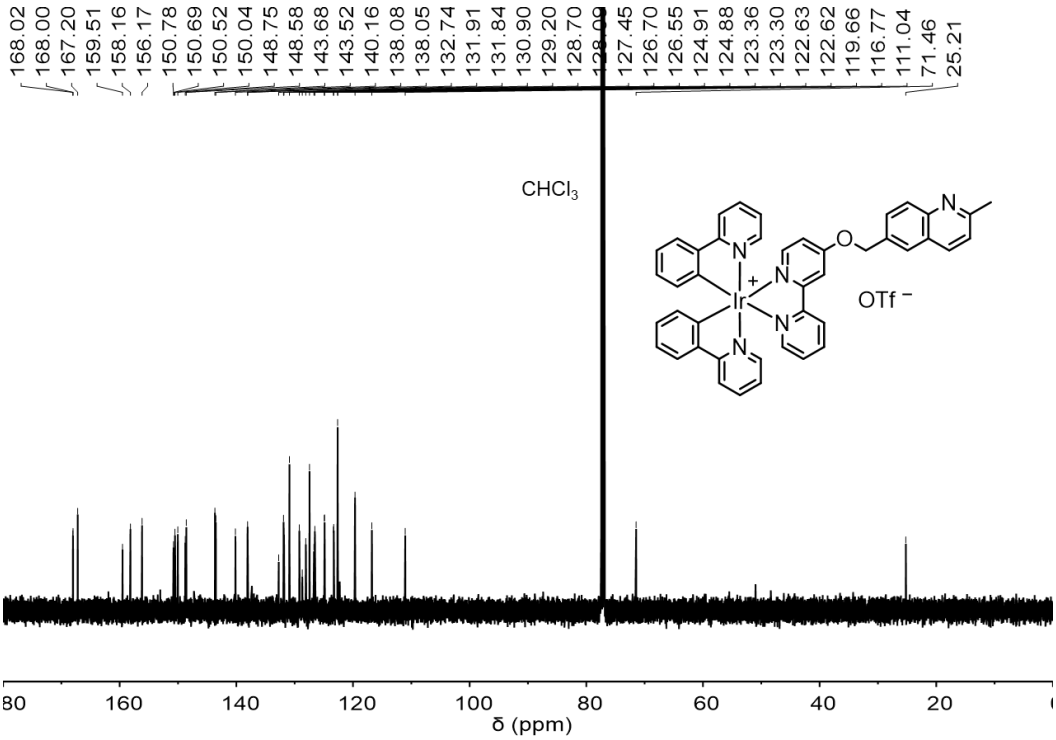


Figure S29. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4**.

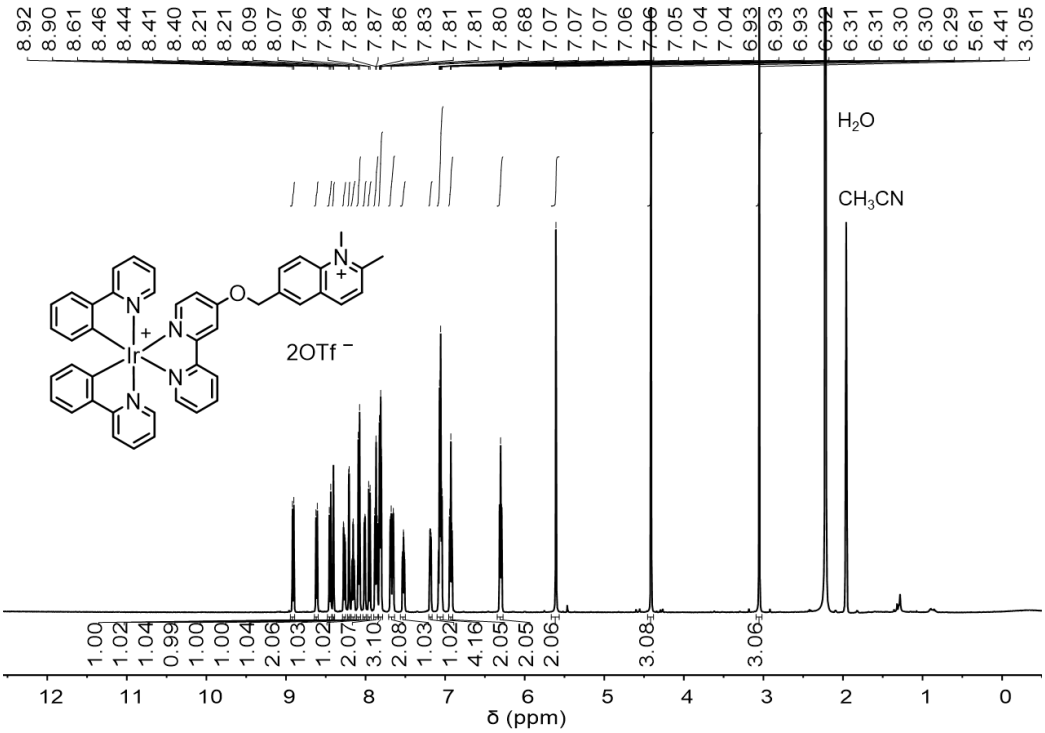


Figure S30. ^{1}H NMR spectrum (500 MHz, CD_3CN) of **RIC**$_{575}$.

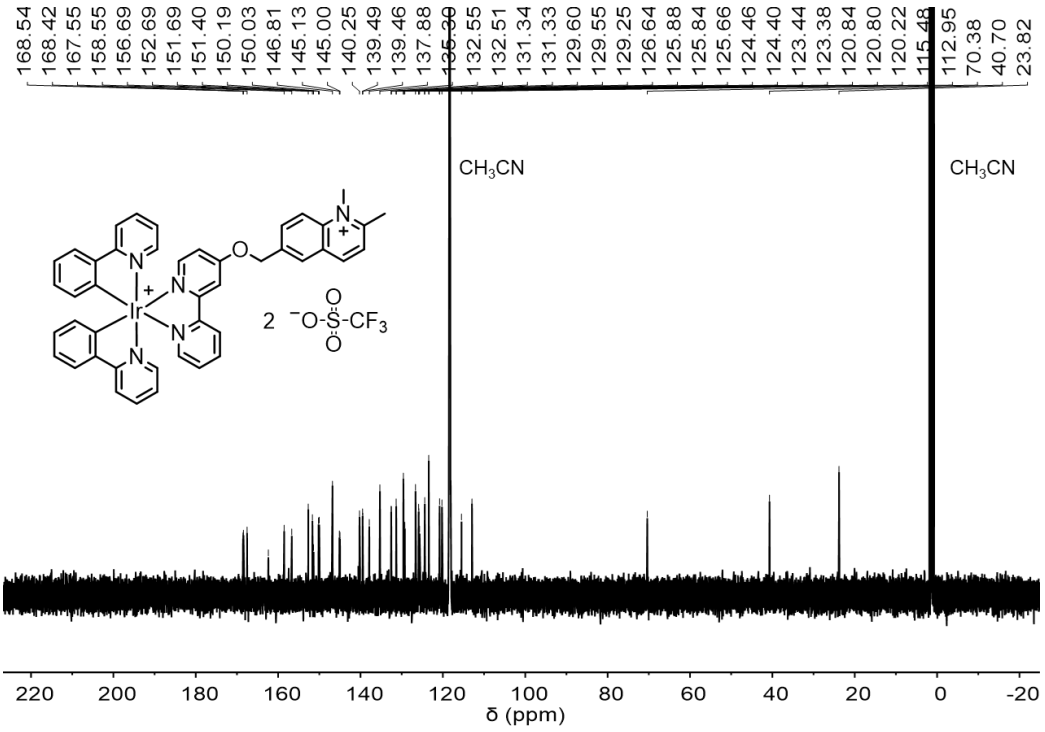


Figure S31. ^{13}C NMR spectrum (126 MHz, CD_3CN) of **RIC**$_{575}$.

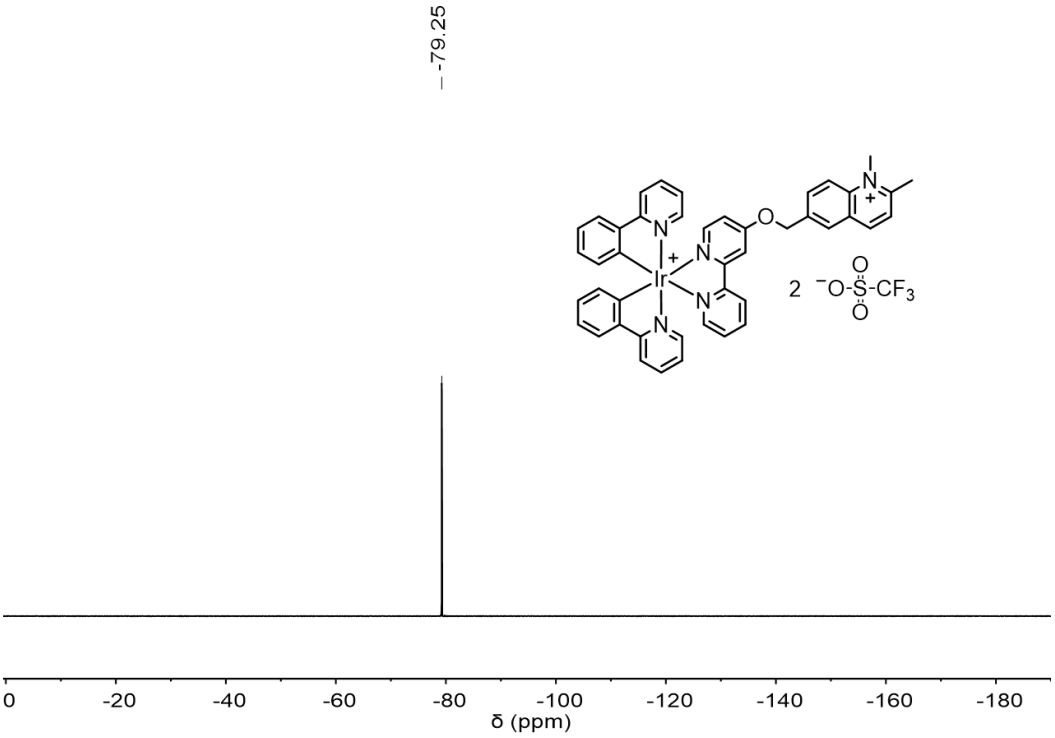


Figure S32. ^{19}F NMR spectrum (470 MHz, CD_3CN) of **RIC**$_{575}$.

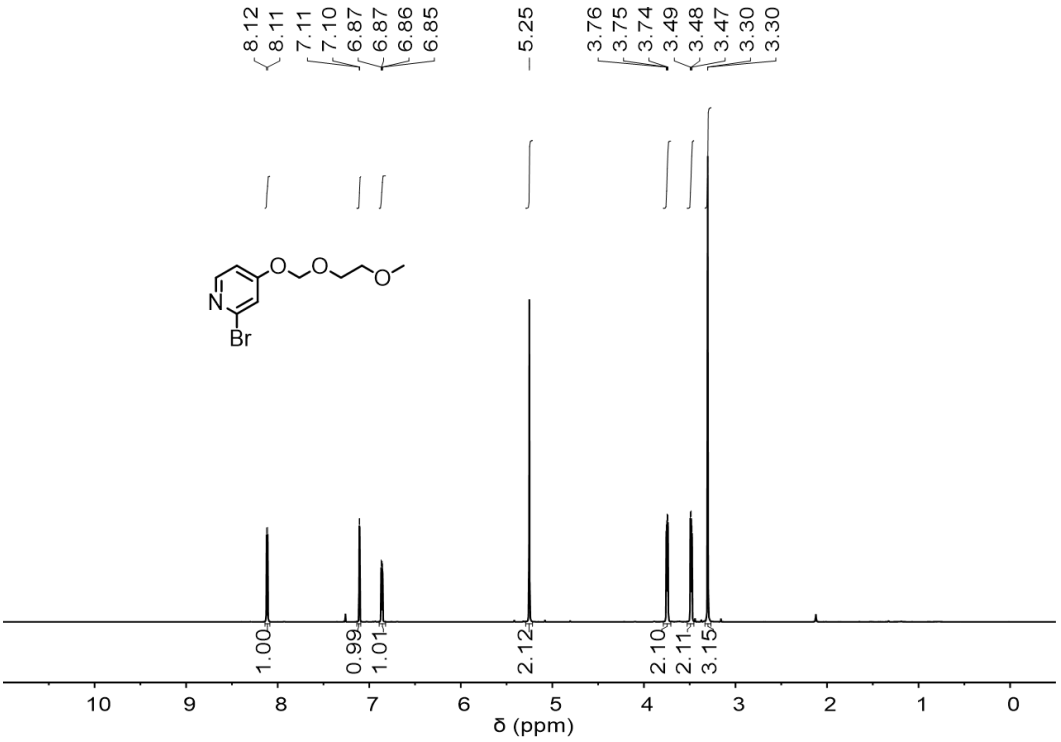


Figure S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5**.

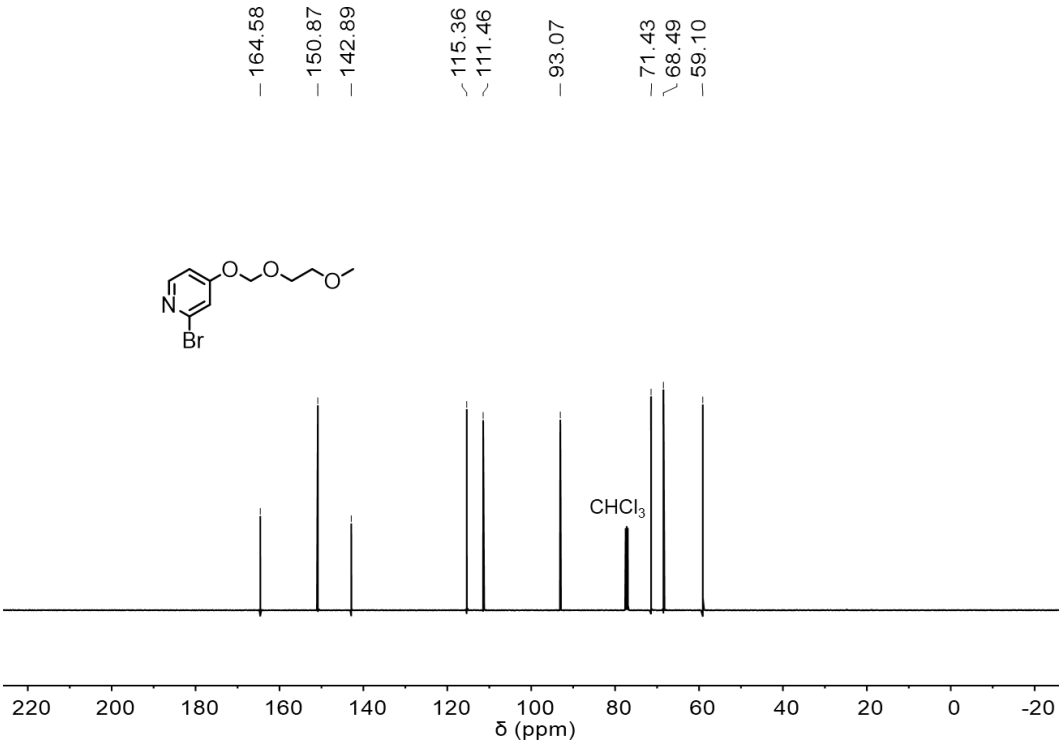


Figure S34. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **5**.

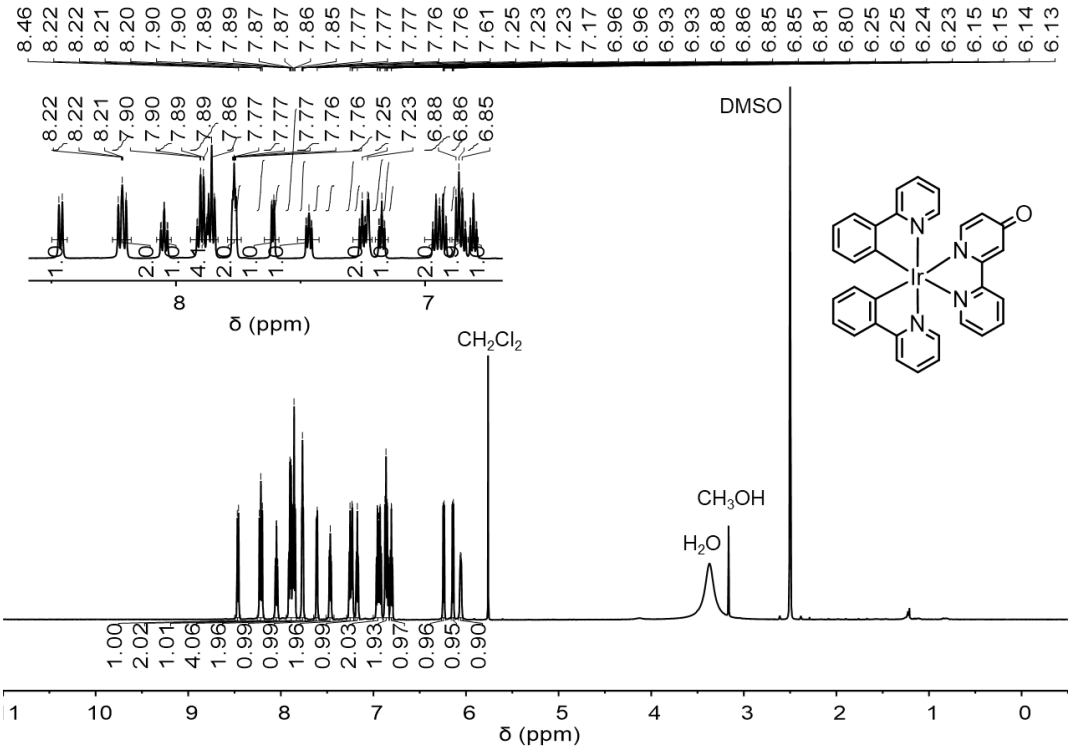


Figure S35. ^{1}H NMR spectrum (600 MHz, DMSO-*d*$_6$) of complex **RIC**$_{525}$.

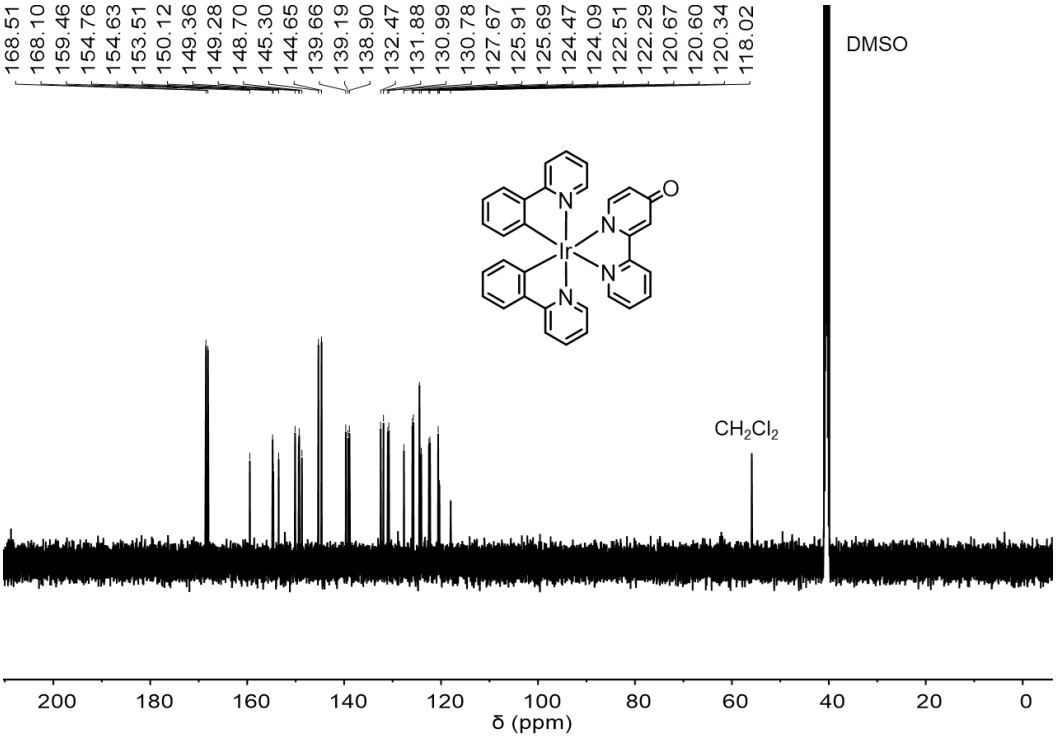


Figure S36. ^{13}C NMR spectrum (126 MHz, DMSO-*d*$_6$) of complex **RIC**$_{525}$.

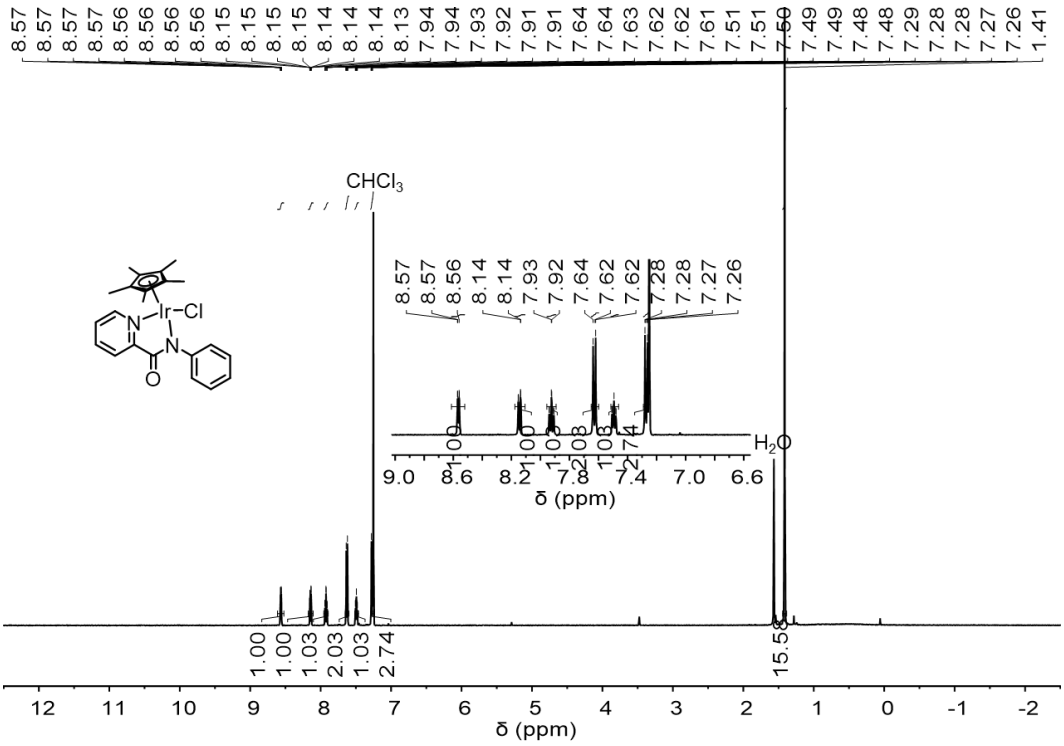


Figure S37. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir1**.

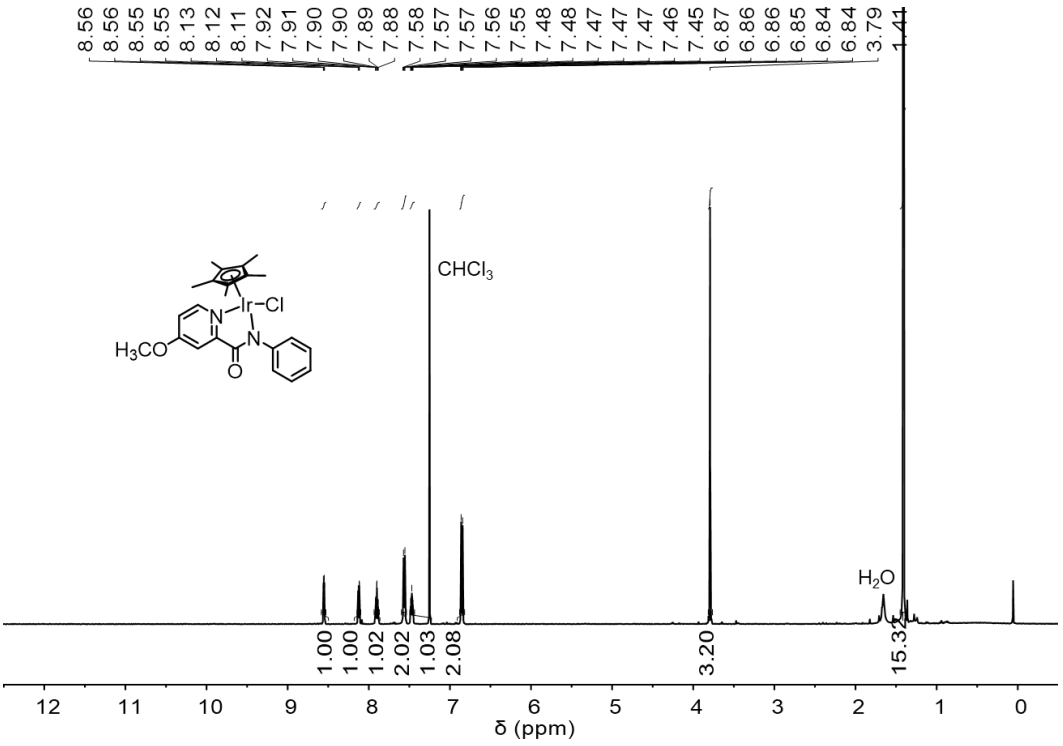


Figure S38. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir2**.

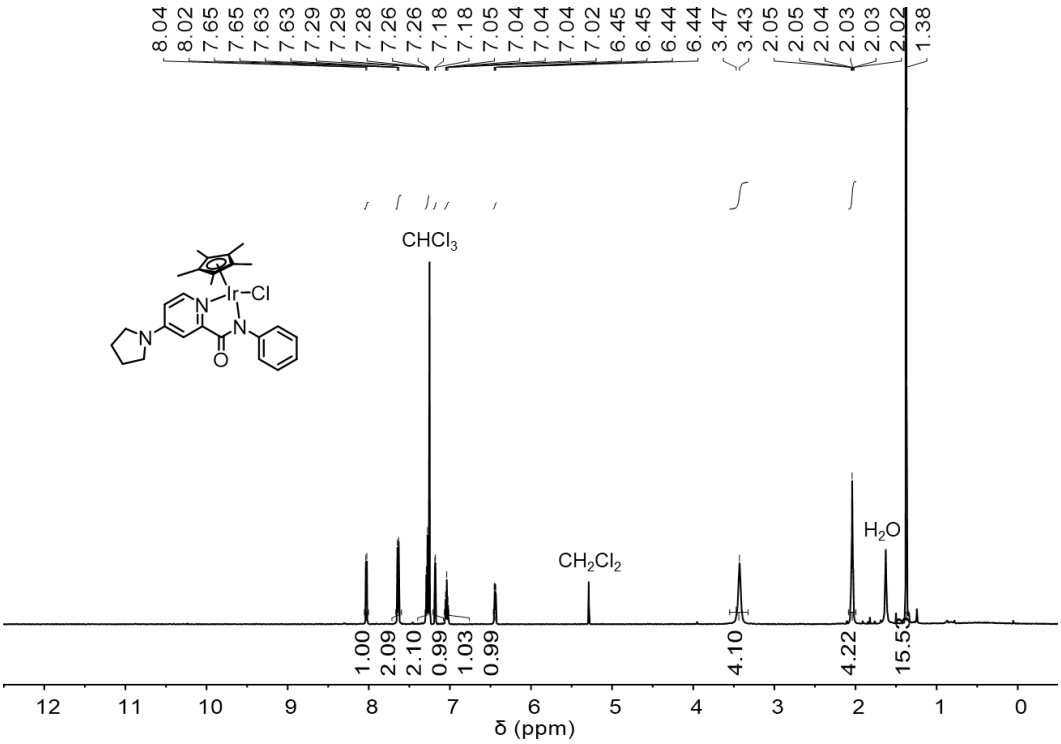


Figure S39. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir3**.

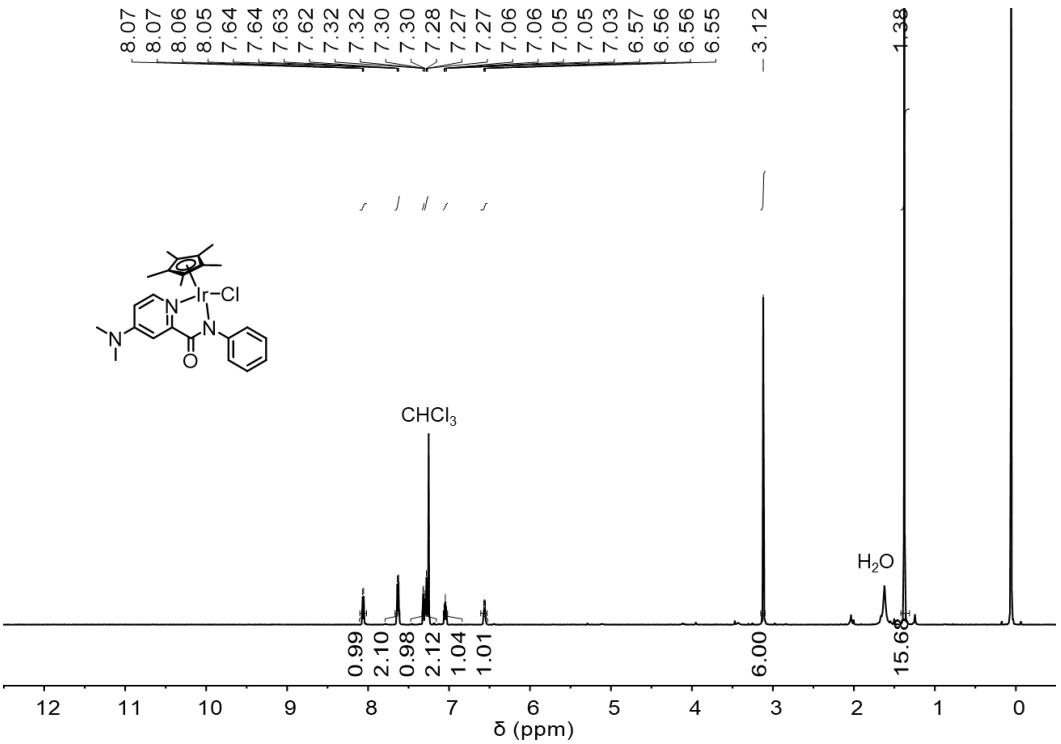


Figure S40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir4**.

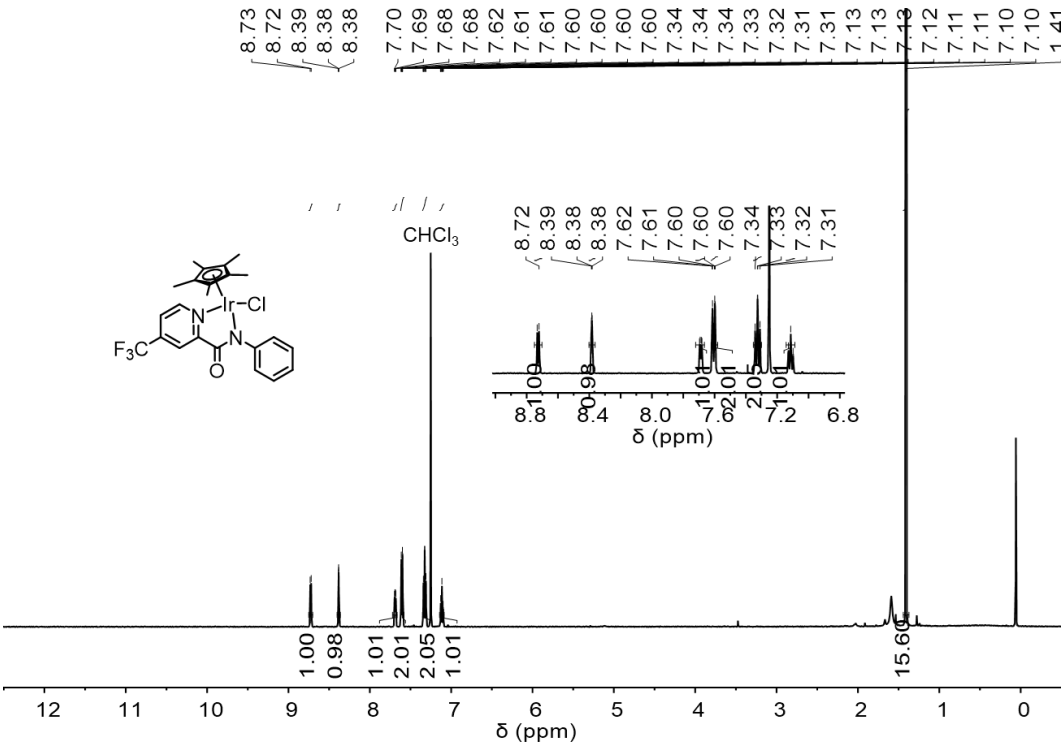


Figure S41. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir5**.

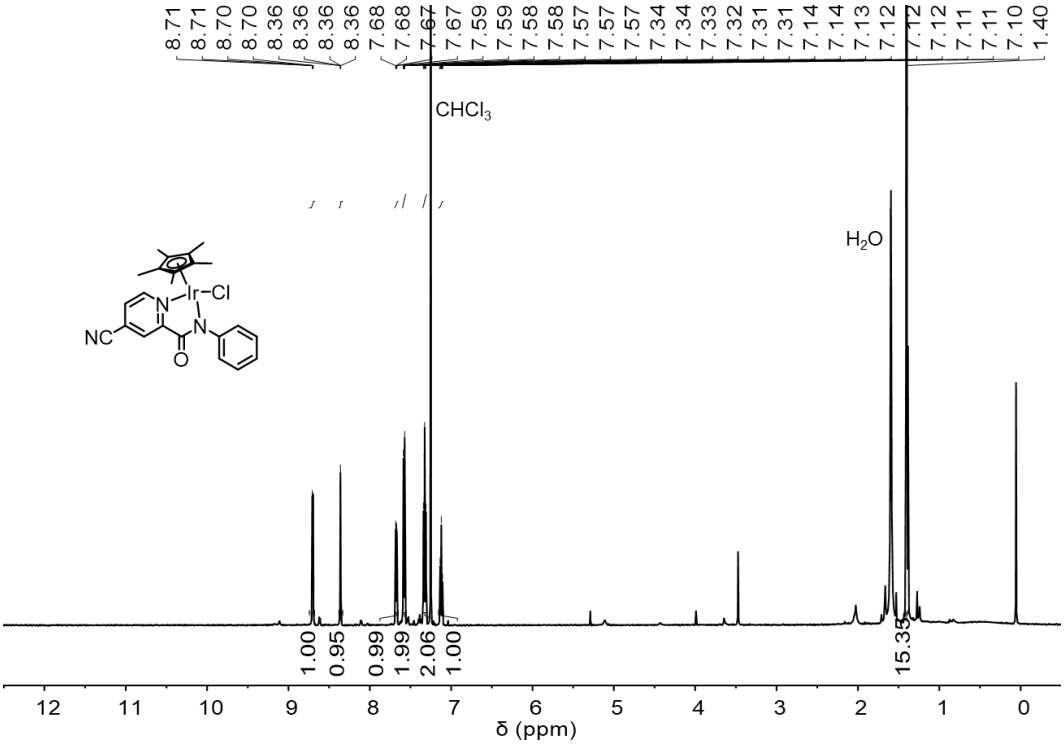


Figure S42. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir6**.

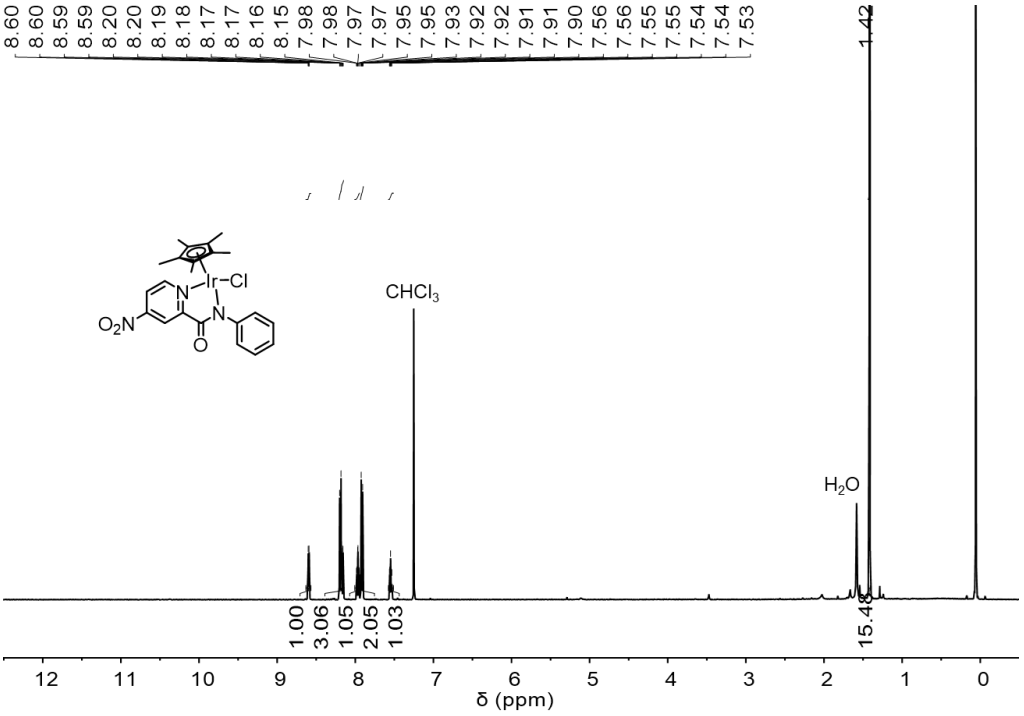


Figure S43. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **Ir7**.

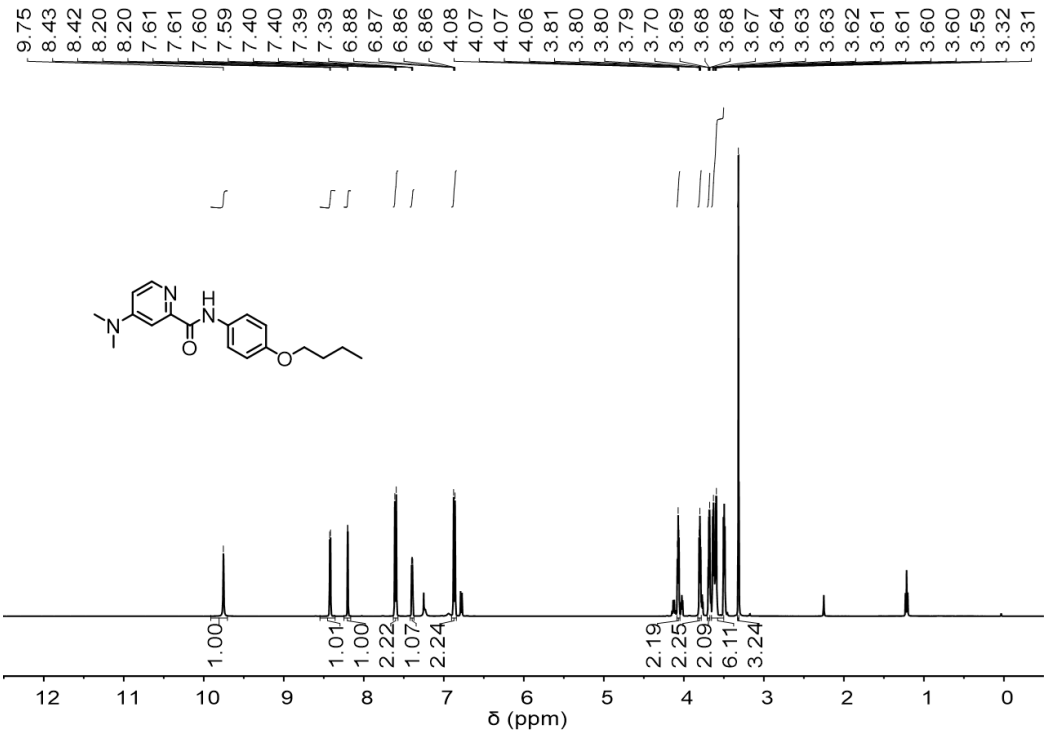


Figure S44. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **L8**. The peaks in the aliphatic region and at ~ 6.78 ppm were assigned to an impurity that could not be removed.

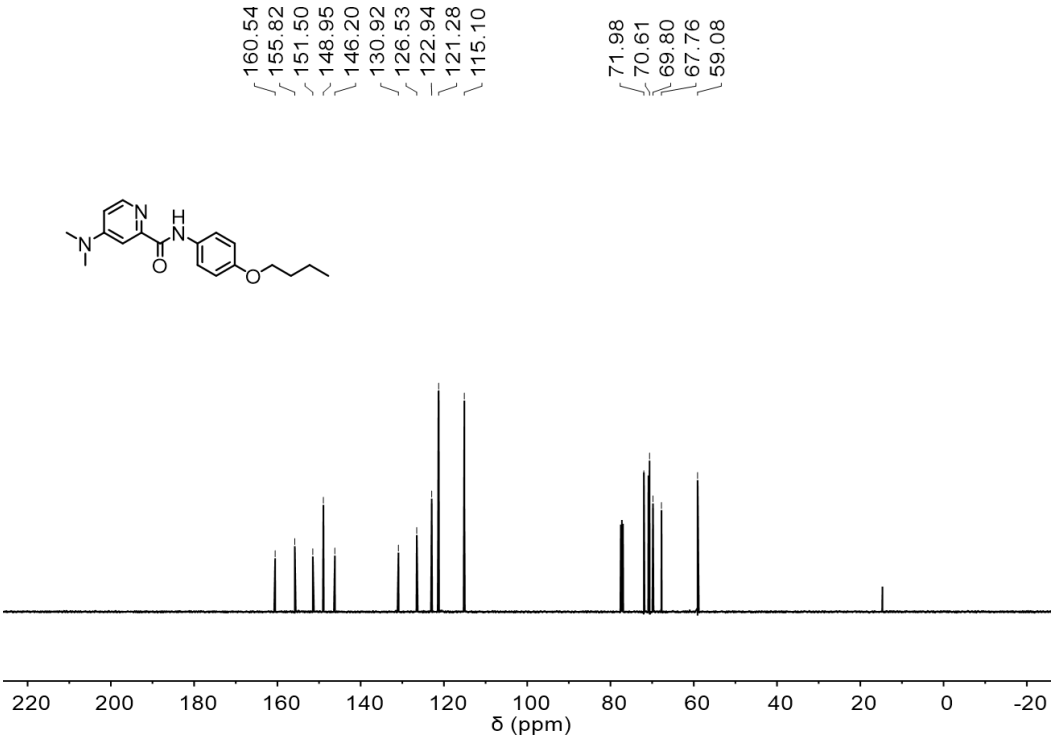


Figure S45. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **L8**.

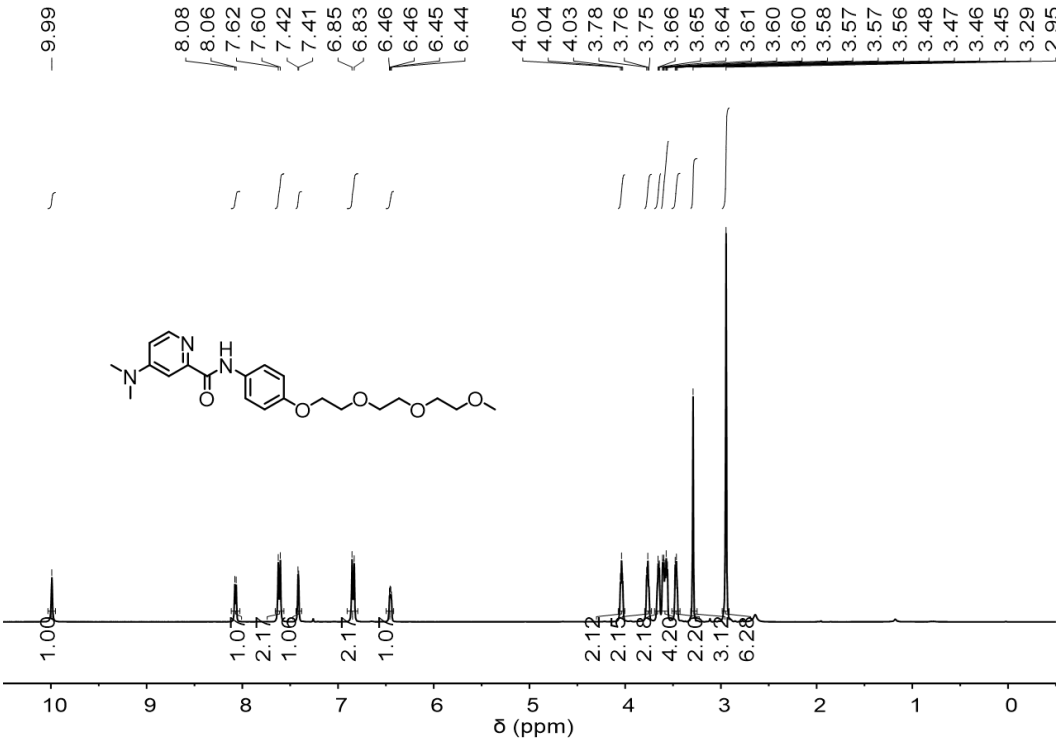


Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L9**.

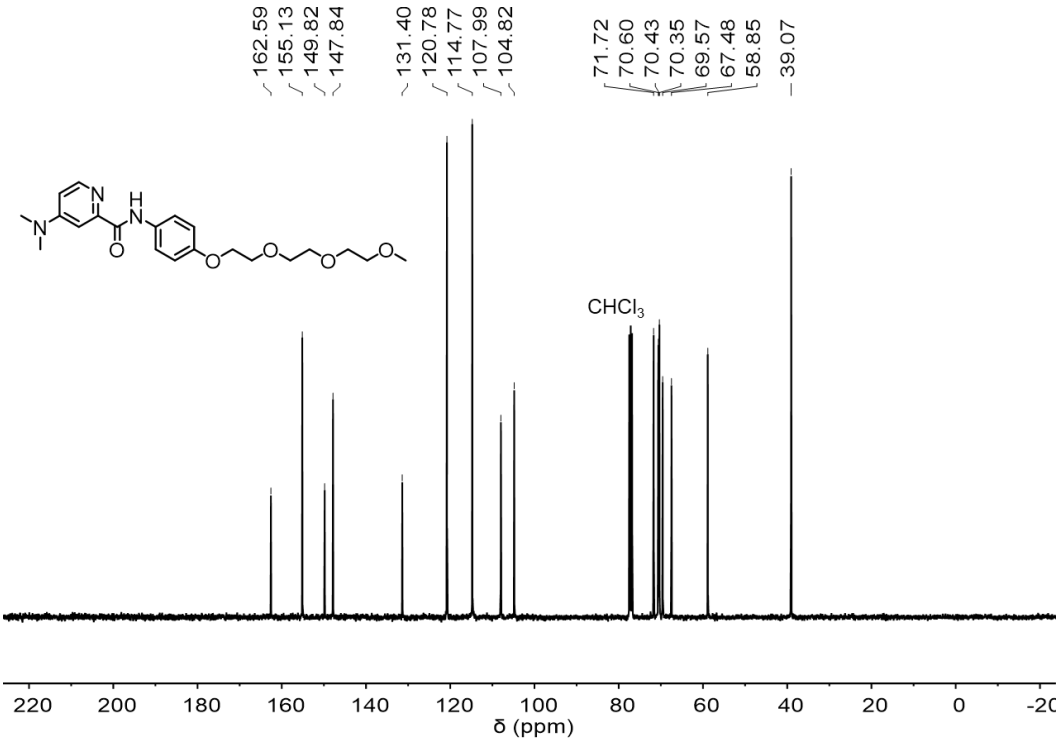


Figure S47. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **L9**.

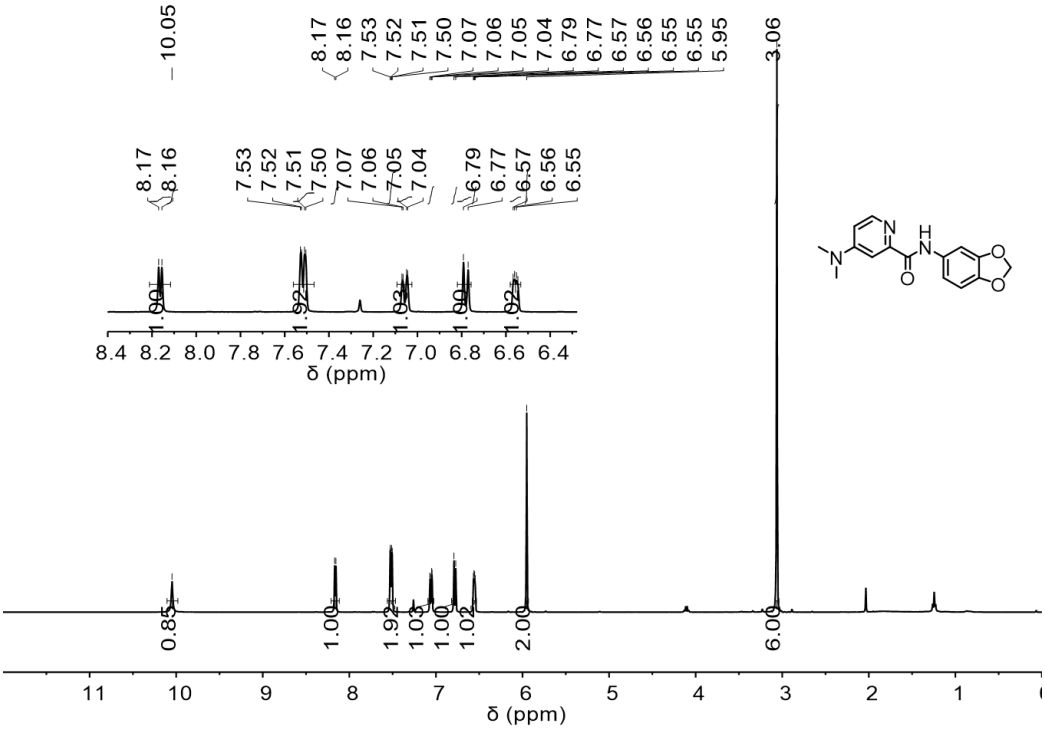


Figure S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L10**.

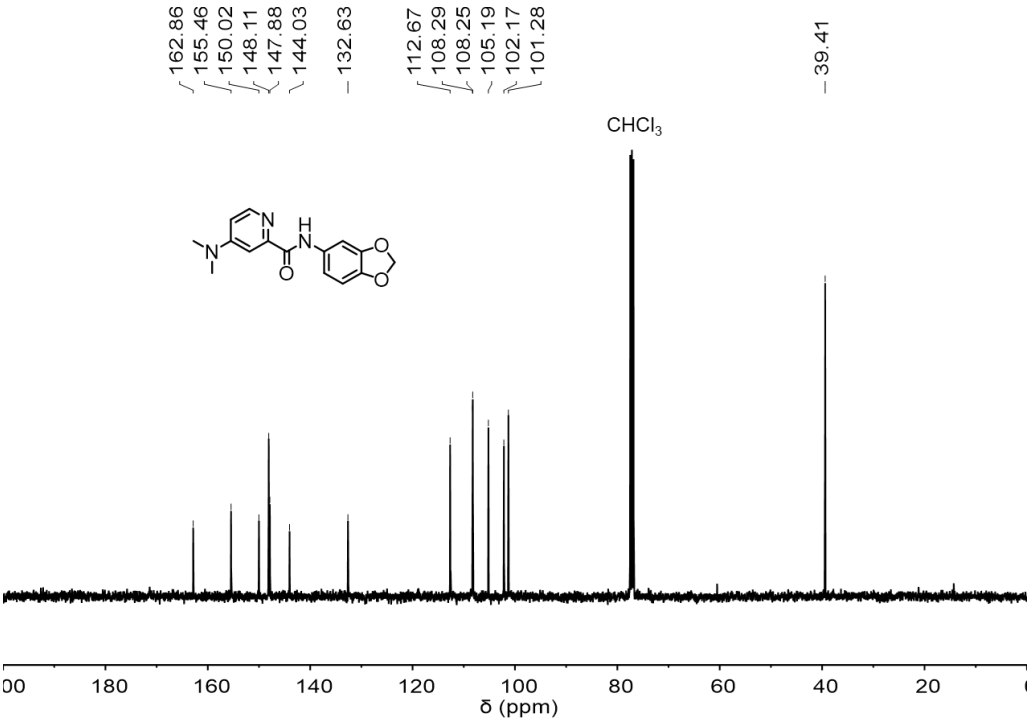


Figure S49. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **L10**.

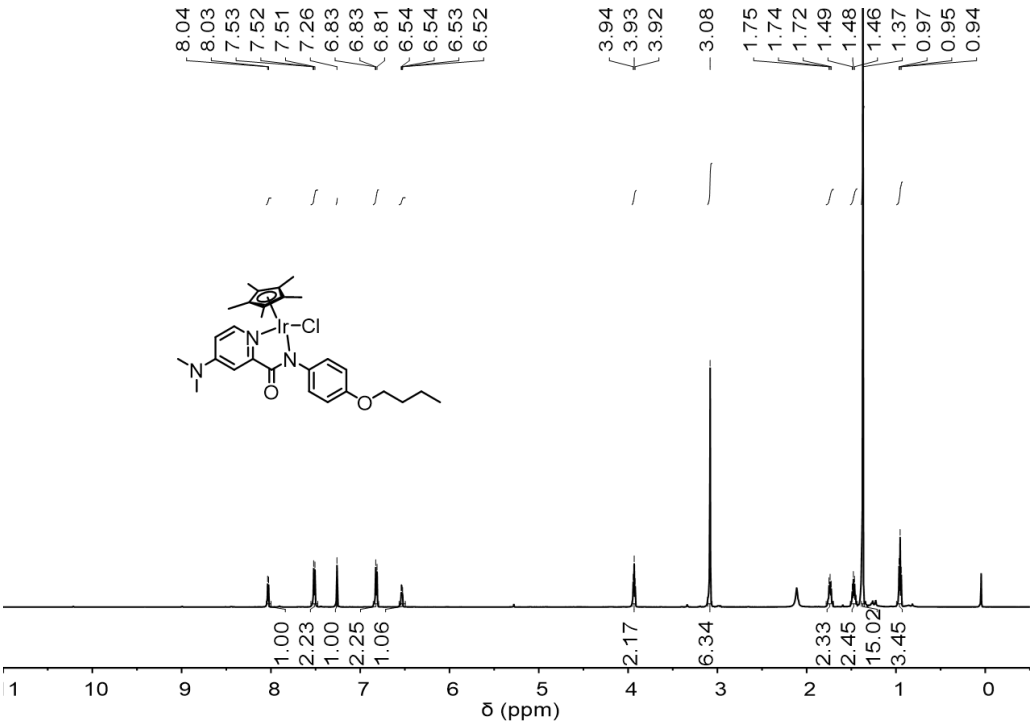


Figure S50. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **Ir8**.

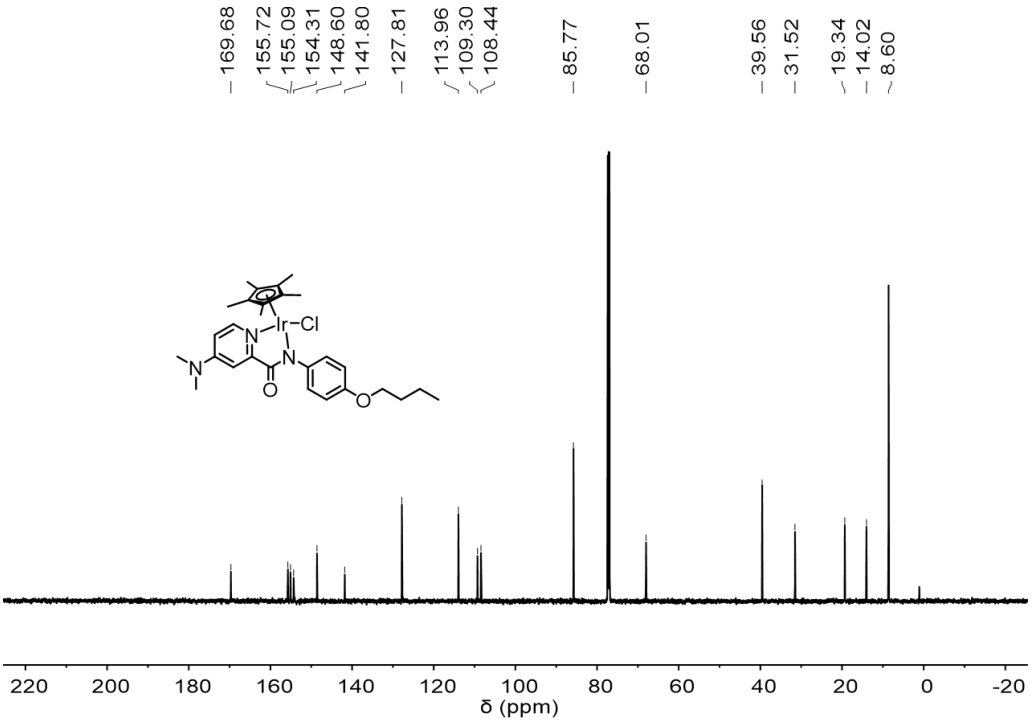


Figure S51. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **Ir8**.

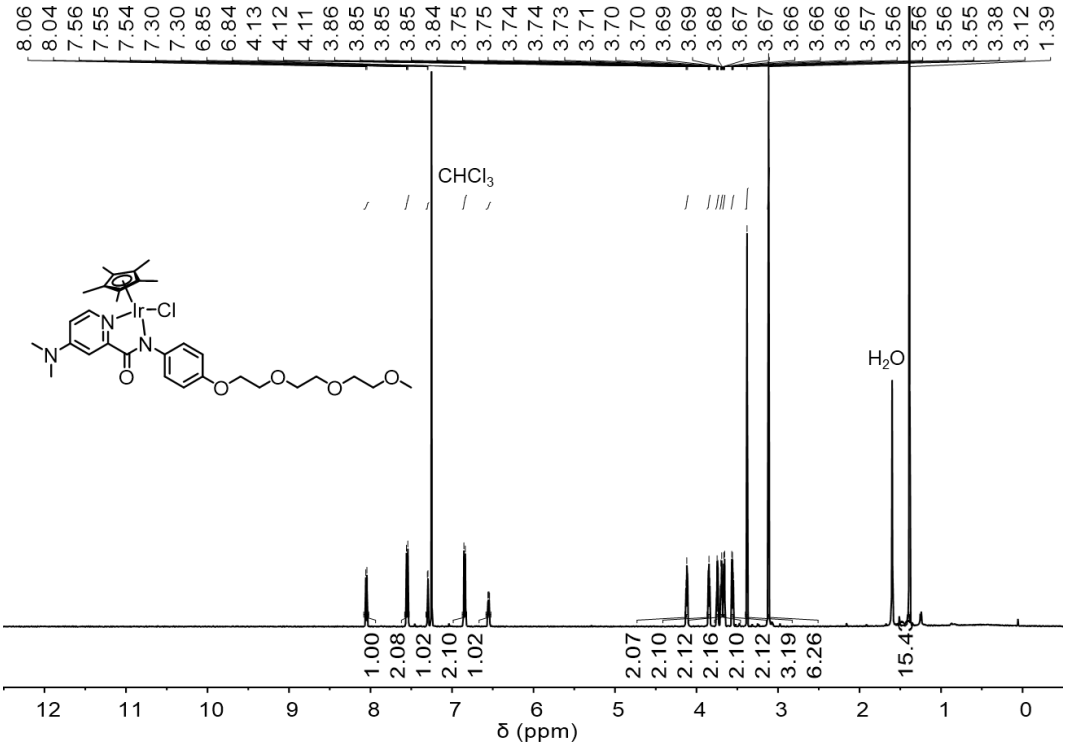


Figure S52. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **Ir9**.

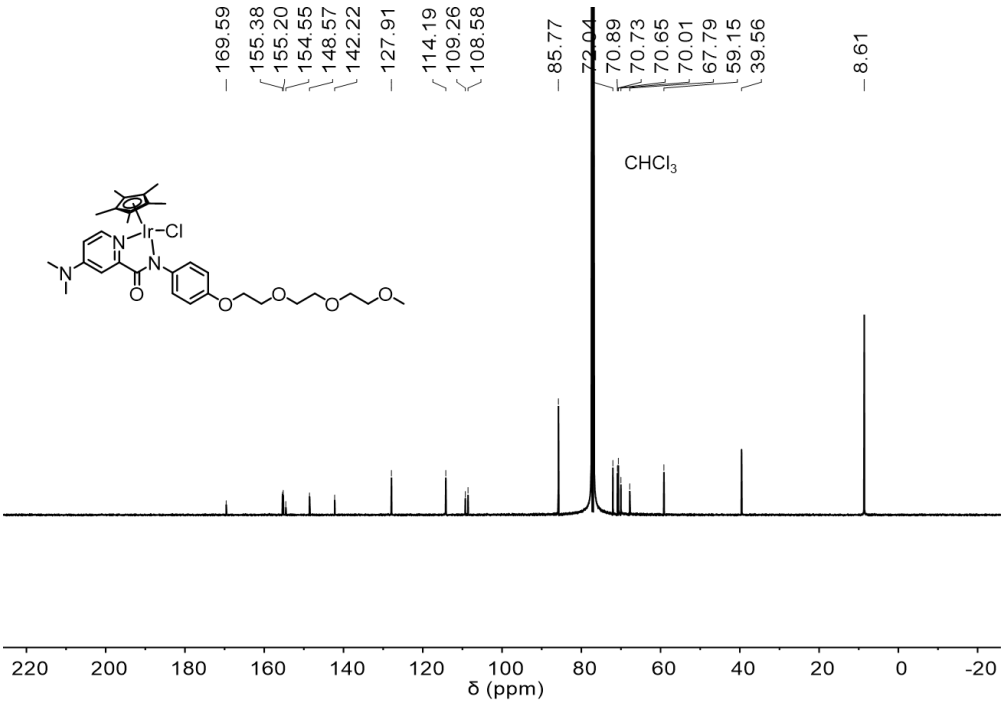


Figure S53. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **Ir9**.

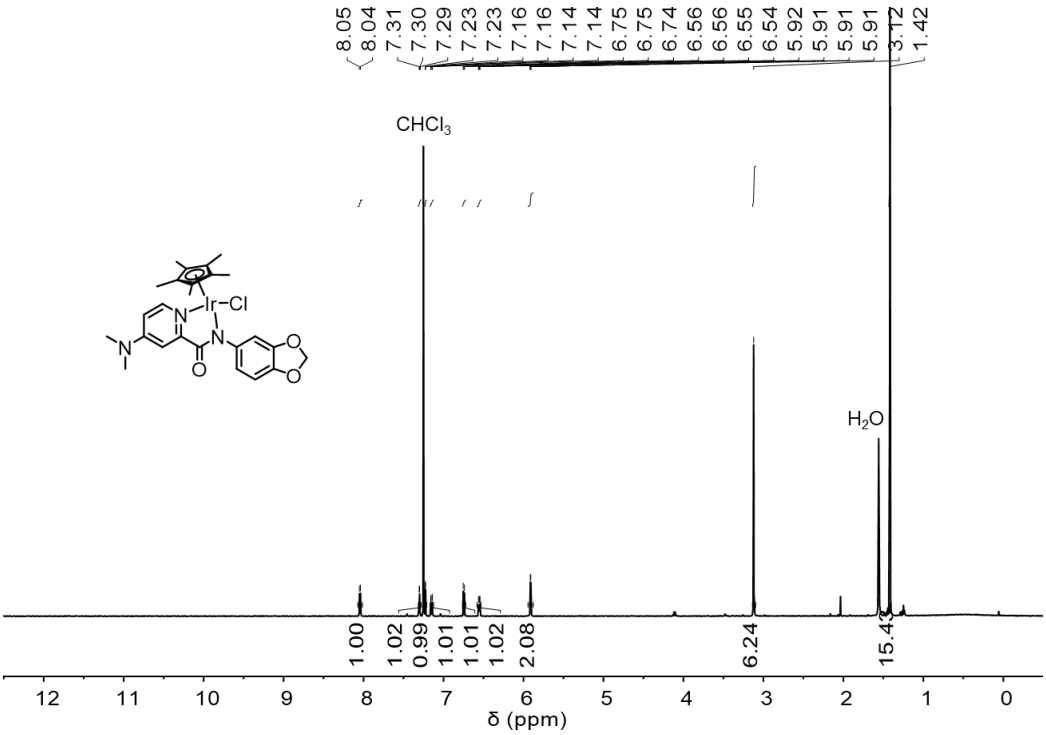


Figure S54. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **Ir10**.

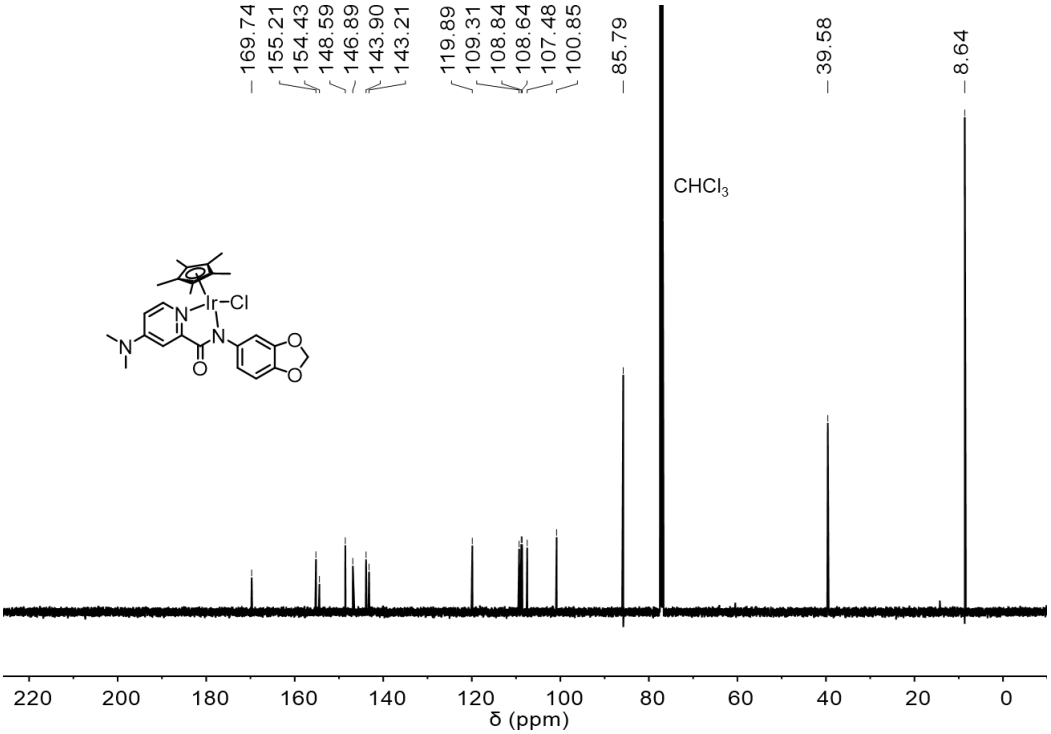


Figure S55. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **Ir10**.

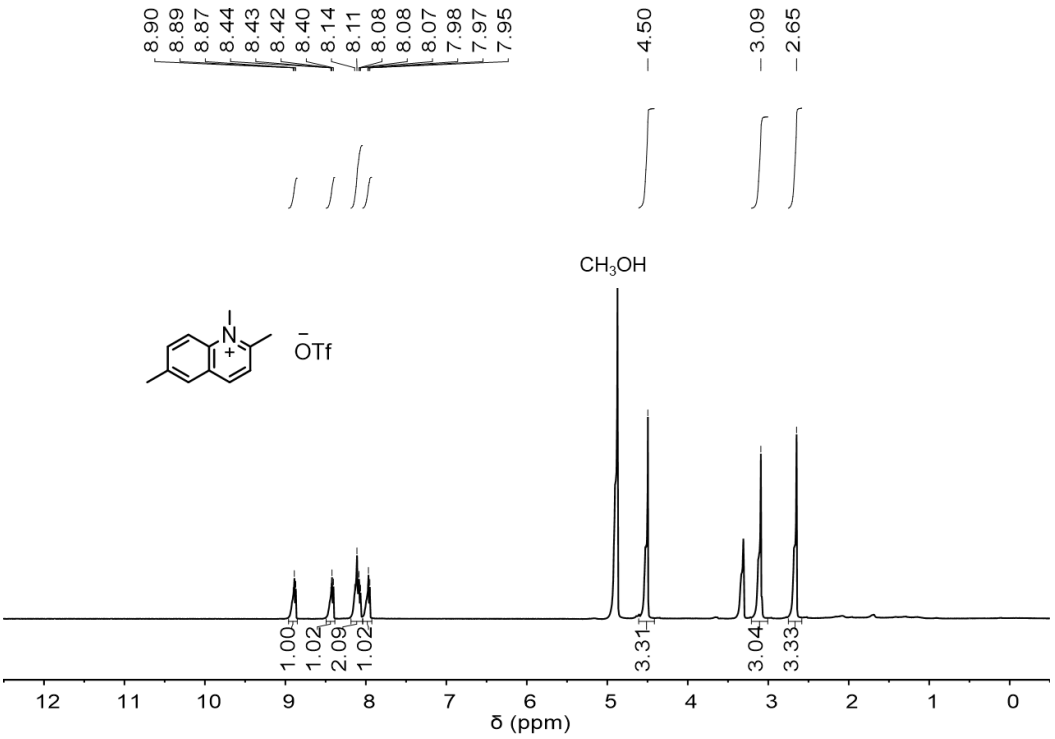


Figure S56. ^{1}H NMR spectrum (500 MHz, CD_3OD) of 1,2,6-trimethylquinolinium triflate.

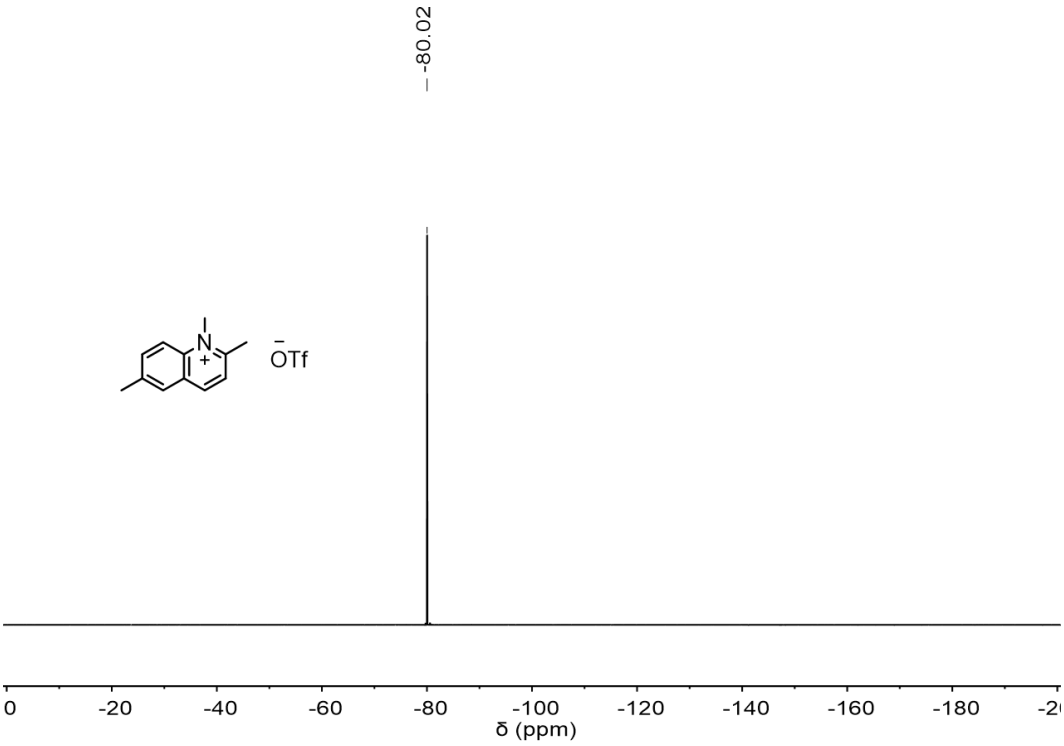


Figure S57. ^{19}F NMR spectrum (376 MHz, CD_3OD) of 1,2,6-trimethylquinolinium triflate.

Control Experiments

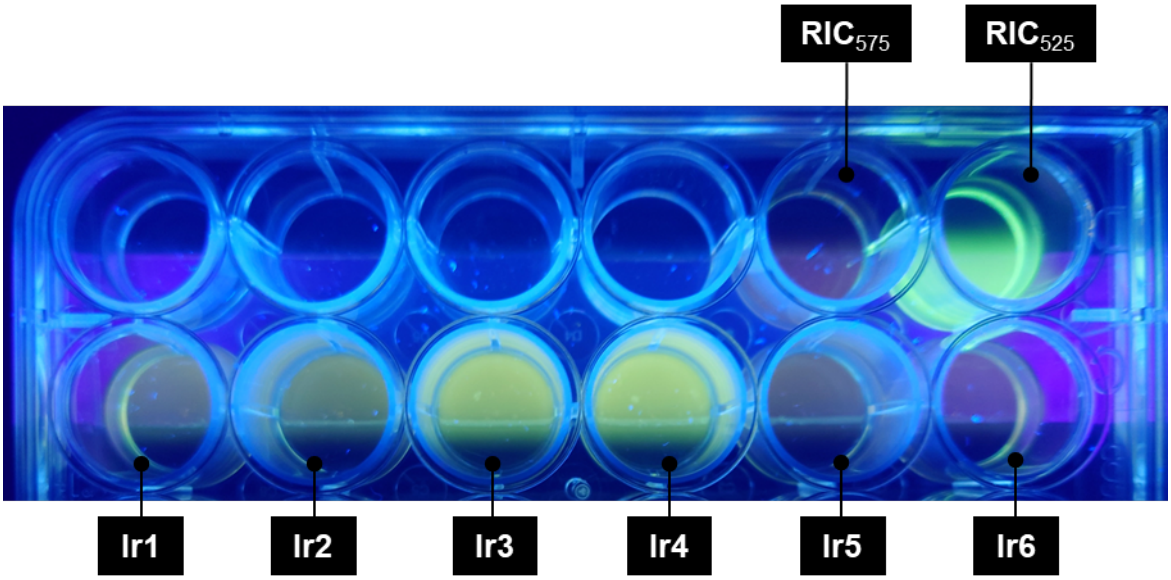
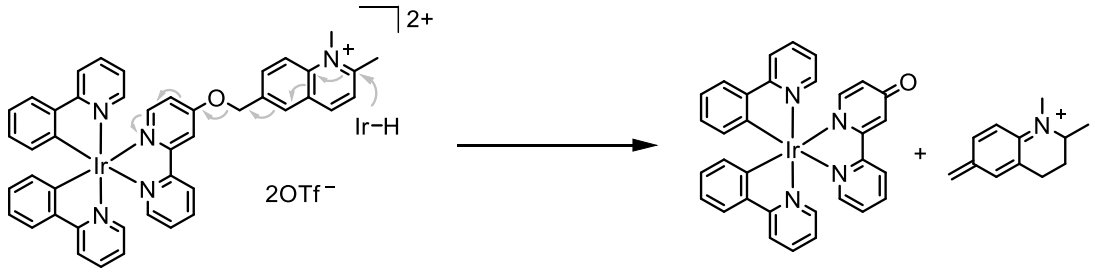


Figure S58. Photo of a well plate from a transfer hydrogenation study using **RIC**$_{575}$ with **Ir1** – **Ir6** catalysts in the presence of HCOONa and $NaHCO_3$ in MeOH after 30 min. The well plate was exposed to 325 nm light when the photo was taken. The first 3 wells on the left side of the top row are blank samples containing only methanol.



Scheme S4. Proposed mechanism for the reduction of **RIC**$_{575}$ via transfer hydrogenation. After the C=N of quinolinium is attacked by the iridium-hydride species (shown as gray-colored arrows), fragmentation occurs to generate **RIC**$_{525}$, which phosphoresces at a different wavelength than **RIC**$_{575}$. A second reduction of the quinolinium ring gives the product **QN** shown.

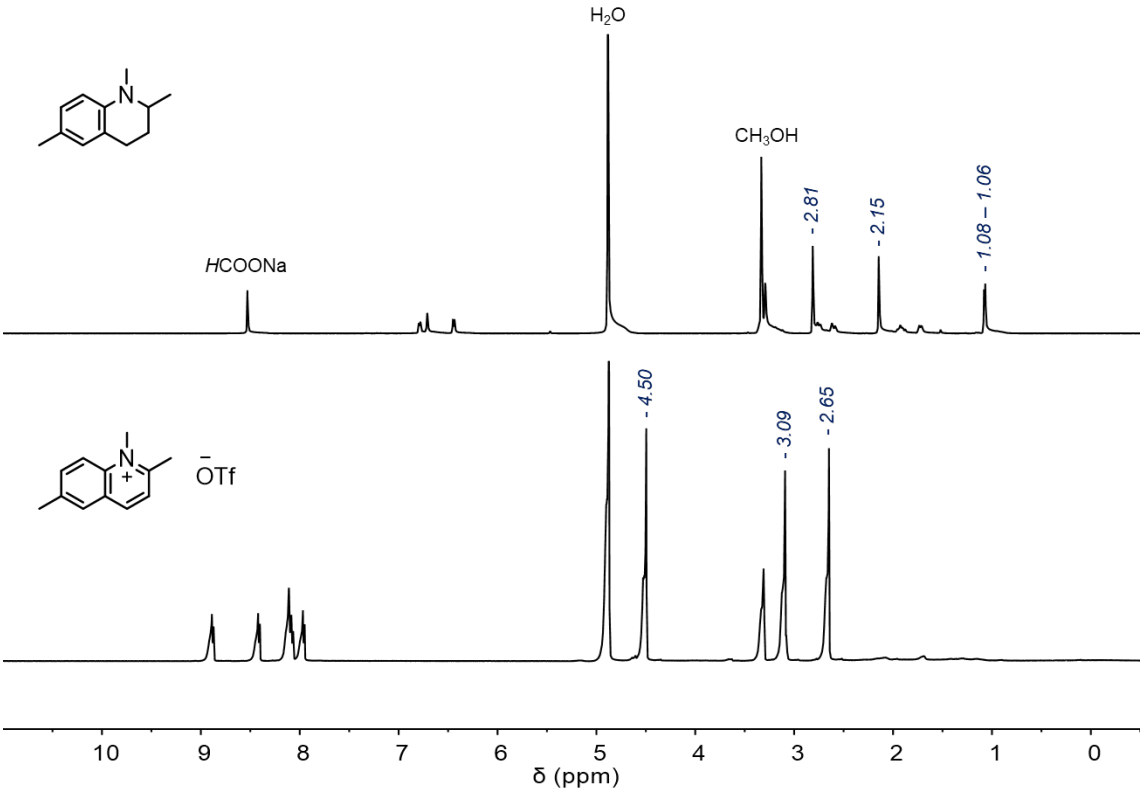


Figure S59. ^{1}H NMR spectra (500 MHz, 25 °C, CD_3OD) of the crude mixture after reaction of 1,2,6-trimethylquinolinium triflate with HCOONa and $NaHCO_3$ in the presence of **Ir4** (*top spectrum*). The bottom spectrum is the ^{1}H NMR spectra of 1,2,6-trimethylquinolinium triflate in CD_3OD alone. Reaction conditions: 1,2,6-trimethylquinolinium triflate (5 μmol, 5 mM, 1.0 equiv.), **Ir4** (1 mol%), HCOONa (3 equiv.), $NaHCO_3$ (5 equiv.), MeOH (10 mL), RT, 3 h. The reaction was performed in a 20 mL scintillation screw capped vial. Solvent was removed under vacuum when the reaction was complete. The mixture was redissolved in CD_3OD and the product formation was analyzed by ^{1}H NMR spectroscopy. After 3 h, 1,2,6-trimethyl-1,2,3,4-tetrahydroquinoline was observed as a major product.

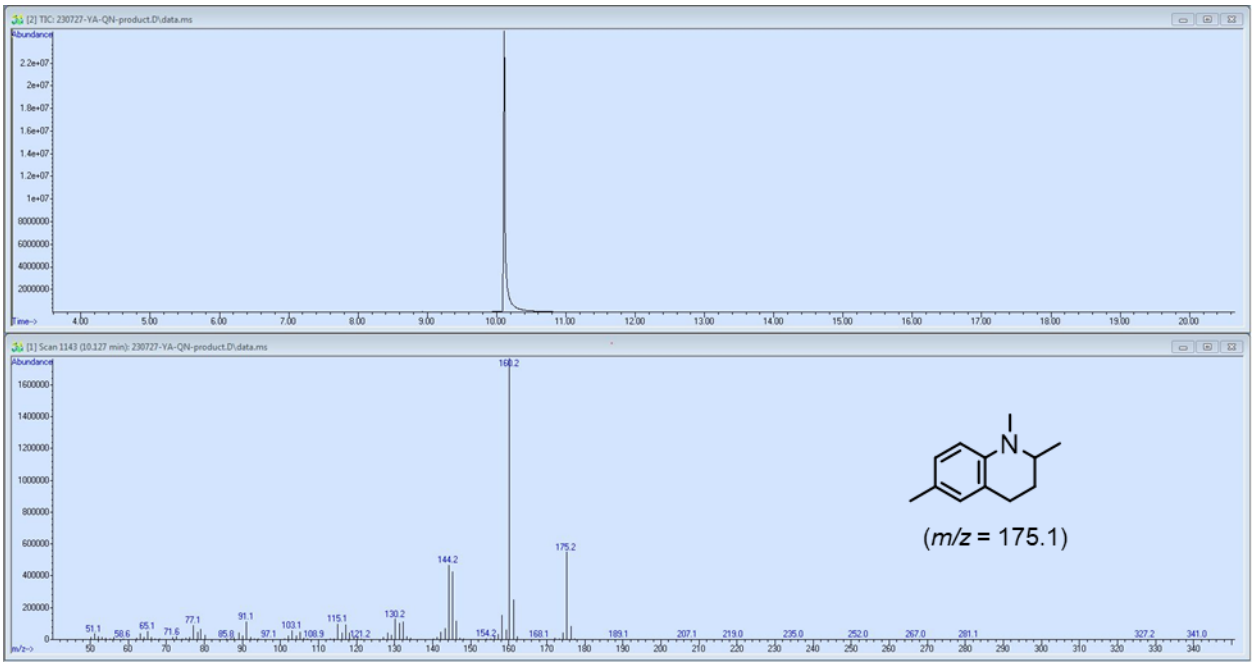
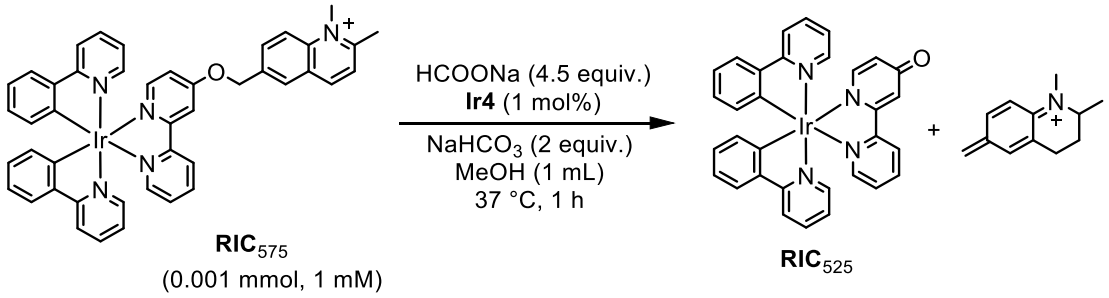


Figure S60. GC trace of product obtained reaction mixture after 3 h (*top*) and its mass spectrum (*bottom*). This result suggested that 1,2,6-trimethyl-1,2,3,4-tetrahydroquinoline was observed as a major product.

A) Reaction in 1-Dram Vial



B) Photo of the Reaction Vials

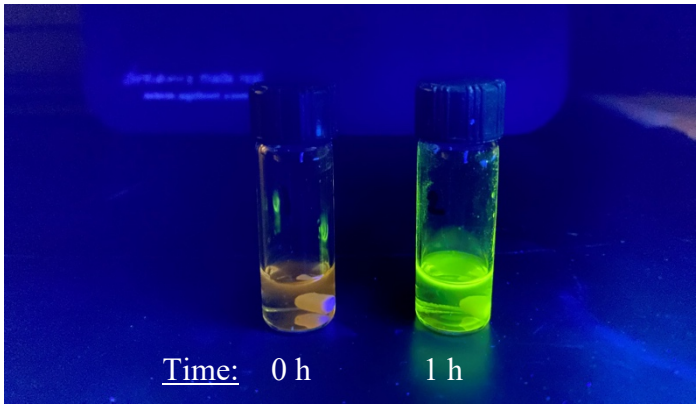


Figure S61. A) Scheme showing TH reactions performed in 1-dram vials. B) A photo of the reaction mixtures at the start of the reaction without **Ir4** (*left*) and after 1 h in the presence of **Ir4** (*right*). The vial samples were illuminated with a 365 nm handheld UV lamp and the photo was acquired using an iPhone 11 Pro.

X-ray Crystallographic Data

Single crystals of complexes **RIC**$_{575}$ and **RIC**$_{525}$ were grown by vapor diffusion. In a 1.5 mL crimp glass vial, the Ir complexes were dissolved in CH_2Cl_2. The vial was placed inside a 20 mL scintillation screw cap vial containing a mixture of CH_2Cl_2/Et_2O (1/4, *v/v*). The vial was capped, sealed with parafilm, and stored at ~4 °C for 72 h. The solvent in the reservoir was then replaced with Et_2O, and the crystallization was continued at ~4 °C. Single crystals were picked out of the crystallization vials and mounted onto Mitogen loops using Paratone oil. The crystals were collected at a 6.0 cm detector distance at –150°C on a Brucker Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXT and refined by SHELXLE. The structure of **RIC**$_{575}$ contains two slightly disordered triflate anions, which were refined using equal anisotropic displacement parameter constraints on the sulfur and fluorine atoms. A free water molecule was also located in the crystal lattice. The structure of **RIC**$_{525}$ contains diethyl ether, dichloromethane, and water molecules. The dichloromethane molecule was found to be severely disordered and required rigid bond restraints to achieve a stable refinement. It was modeled with a two-part disorder and a total occupancy of 50%. The hydrogen atoms of the water molecule could not be located from the electron density difference map.

Table S8. Crystal Data and Structure Refinement for **RIC**$_{575}$ and **RIC**$_{525}$.

	RIC$_{575}$	**RIC**$_{525}$
Empirical Formula	$IrC_{46}H_{38}F_6N_5O_8S_2$	$IrC_{36.5}H_{34}ClN_4O_3$
Temperature (°C)	-150	-150
Wavelength (Å)	0.71073	0.71073
Crystal System Space Group	Monoclinic, P2(1)/n	Monoclinic, P2(1)/c
Unit Cell Dimensions		
a (Å)	13.1936(4)	12.4845(4)
b (Å)	12.8662(3)	26.7158(7)
c (Å)	26.3864(7)	10.6048(3)
α (°)	90	90
β (°)	99.506(2)	92.362(2)
γ (°)	90	90
Volume (Å^3)	4417.6(2)	3534.05(18)
Z, Calculated Density (Mg/m^3)	4, 1.743	2, 1.512
Absorption Coefficient (mm^{-1})	3.204	3.893
F(000)	2304	1596
Theta Range for Data Collection (°)	1.565 to 25.057	1.524 to 25.093
Limiting Indices	-15≤ h ≤ 12	-14 ≤ h ≤ 14
	-15 ≤ k ≤ 15	-31 ≤ k ≤ 31
	-31 ≤ l ≤ 31	-12 ≤ l ≤ 12
Reflections Collected/ Unique	37025/7814	39214 / 6261
	[R(int) = 0.0546]	[R(int) = 0.0778]
Data/ Restraints/ Parameters	7814/0/594	6261/115/400
Goodness of Fit on F^2	1.018	1.069
Final R Indices	R1 = 0.0401	R1 = 0.0436
[I > 2σ(I)]	wR2 = 0.0893	wR2 = 0.1144
R Indices (All Data)*	R1 = 0.0574	R1 = 0.0644
	wR2 = 0.0967	wR2 = 0.1239

*$R_1 = \Sigma\ ||F_o|-|F_o||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)_2]]^{1/2}$; $GOF = [\Sigma[w(F_o^2 - F_c^2)_2]/(n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

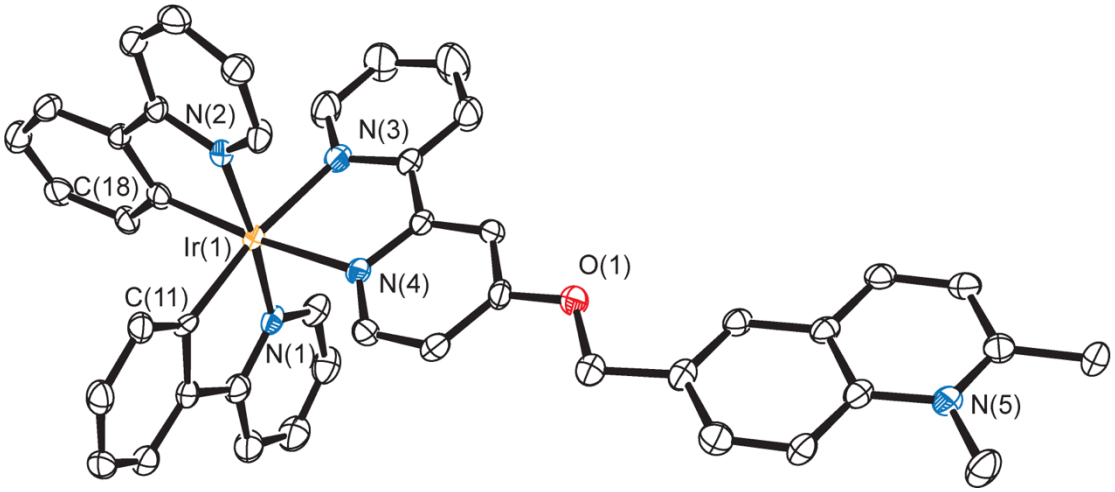


Figure S62. Crystallographic asymmetric unit showing **RIC**$_{575}$ with displacement ellipsoids drawn at 50% probability level. Hydrogen atoms, two triflate anions, and a water molecule have been omitted for clarity.

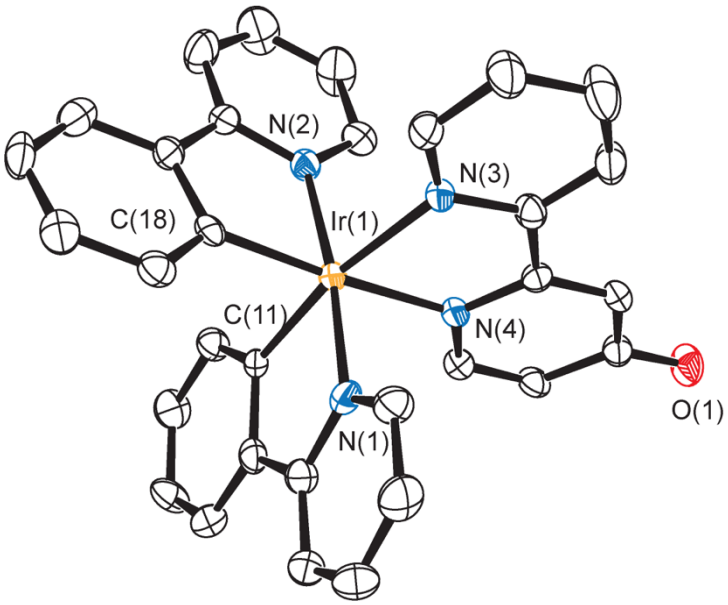


Figure S63. Crystallographic asymmetric unit showing **RIC**$_{525}$ with displacement ellipsoids drawn at 50% probability level. Hydrogen atoms and solvent molecules (dichloromethane, diethyl ether, and water) have been omitted for clarity.

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