

Electronic Supplementary Information

Iridium-catalyzed Highly Efficient Chemoselective Reduction of Aldehydes in Water using Formic Acid as the Hydrogen Source

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1. General information

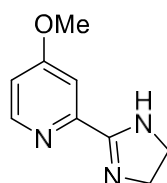
Unless mentioned otherwise, all experiments were carried out on water and in air. ^1H and ^{13}C NMR spectra were recorded on Varian UNITY INOVA 400 MHz or 500 MHz) NMR spectrometer, with CDCl_3 or d -DMSO as the solvent and tetramethylsilane as the internal standard. All the reagents were used directly as received without further purification.

2. Catalysts synthesis and characterization

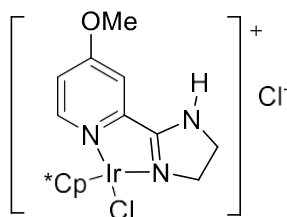
Synthesis of catalyst Ir-1 and Ir-2

These two catalysts were synthesized by following Xiao's procedure^{1,2} by mixing $[\text{IrCp}^*\text{Cl}_2]_2$ (1 equivalent) and the corresponding ligand (2 equivalents) in dry dichloromethane at room temperature. After stirring overnight, the yellow solution was evaporated to obtain a yellow solid, which was used directly in the TH reduction of aldehydes. The ^1H and ^{13}C NMR data are identical with those reported.^{1,2}

Synthesis of catalyst Ir-3



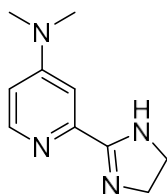
To the solution of 4-methoxypyridine-2-carbaldehyde (3.00 g, 21 mmol) in 50 mL of dichloromethane was dropwise added ethylenediamine (23 mmol, 1.6 mL) in an ice-water bath. The mixture was stirred for 1 h. Then *N*-bromosuccinimide (4.1 g, 23 mmol) was added at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. Washing the reaction mixture with 5% NaOH solution (50 mL) and then saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (50 mL), drying with Na_2SO_4 and removal of the dichloromethane under vacuum directly gave the desired crude product 2-(4,5-dihydro-1*H*-imidazol-2-yl)-4-methoxypyridine (3.55 g, yield 95%), which could be used directly in the next step.



To a suspension of $[\text{Cp}^*\text{IrCl}_2]_2$ (4.451 g, 5.6 mmol) in 50 ml of DCM was dropwise added the solution of 2-(4,5-dihydro-1*H*-imidazol-2-yl)-4-methoxypyridine (2.052 g, 12 mmol). After stirring overnight, DCM was

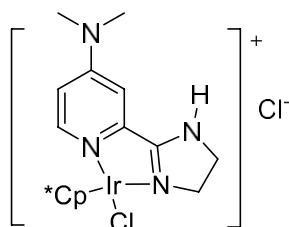
removed under reduced pressure, and the resultant yellow solid was dissolved in minimum amount of DCM. Then EtOAc was added to precipitate an orange solid as desired product, which was isolated by reduced-pressure filtration and further dried under vacuum at room temperature. Yield: 6.445 g, yield 98%. ^1H NMR (400 MHz, CDCl_3): δ 1.75 (s, 15 H), 3.92-3.97 (m, 1H), 4.14 (s, 6H), 7.12 (dd, $J = 2.8, 6.5$ Hz, 1H), 8.43 (d, $J = 6.5$ Hz, 1H), 9.06 (d, $J = 2.7$ Hz, 1H), 10.50 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 9.2, 46.1, 51.9, 58.2, 87.1, 112.9, 116.9, 148.8, 150.6, 168.4, 169.7; IR(powder): $\nu = 1597, 1479, 1254, 1043, 1025, 840$ cm^{-1} ; HRMS (ESI) for $\text{C}_{19}\text{H}_{26}\text{N}_3\text{ClOIr}$ (M^+), (Calc.) 540.1394, found 540.1386.

Synthesis of catalyst Ir-4



2-(Dimethylamino)ethanol (0.8 mL, 8 mmol) was cooled at -5 $^{\circ}\text{C}$, and BuLi (10 mL, 16 mmol, 1.6 M in hexane) was added dropwise under an argon atmosphere. After stirring for 30 min, the mixture was transferred to an ice-water bath at 0 $^{\circ}\text{C}$, then 4-dimethylaminopyridine (DMAP) (488 mg, 4 mmol) was added once as a solid. After stirring at 0 $^{\circ}\text{C}$ for 1 h, the mixture was cooled to -78 $^{\circ}\text{C}$, and a solution of DMF (10 mmol) in hexane (20 mL) was added dropwise. After addition, the temperature was stirred at 0 $^{\circ}\text{C}$ for 1.5 h. Quenching the reaction with water (20 mL), extraction with DCM (20 mL), drying with MgSO_4 , filtration, evaporation of solvents, and purification by column chromatography afforded desired product. Yield: 221 mg, 37%.

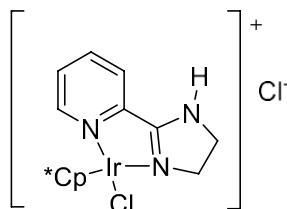
To the solution of 4-dimethylaminopyridine-2-carbaldehyde (221 mg, 1.47 mmol) in 20 mL of dichloromethane, ethylenediamine (0.133 mL, 2 mmol) was dropwise added. The mixture was stirred for 1 h. Then *N*-bromosuccinimide (356 mg, 2 mmol) was added when the mixture was cooled to 0 $^{\circ}\text{C}$ and the mixture was stirred overnight. Washing the reaction mixture with 5% NaOH solution (20 mL) and then saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL), drying with Na_2SO_4 and removal of the dichloromethane under vacuum directly gave the desired crude product 2-(4,5-dihydro-1*H*-imidazol-2-yl)-4-(*N,N*-dimethyl)pyridine, which was used directly in the next step. Yield: 274 mg, 98%.



To a solution of 2-(4,5-dihydro-1*H*-imidazol-2-yl)-4-(*N,N*-dimethyl)pyridine (274 mg, 1.44 mmol) in 5 mL of DCM was portionwise added $[\text{Cp}^*\text{IrCl}_2]_2$ (480 mg, 0.6 mmol), and a yellow solution was obtained. Similar workup as described for catalyst **Ir-3** afforded **Ir-4** as a yellow solid. Yield: 536 mg, 76%. ^1H NMR (400 MHz, D_2O) δ 8.27 (d, $J = 6.9$ Hz, 1H), 7.09 (s, 1H), 6.80 (d, $J = 6.9$ Hz, 1H), 4.14 (d, $J = 9.8$ Hz, 2H), 3.99 (t, $J = 9.8$ Hz,

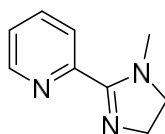
2H), 3.11 (s, 6H), 1.71 (s, 15H). ^{13}C NMR (101 MHz, D_2O) δ 155.01, 149.87, 145.34, 110.15, 107.63, 87.70, 52.21, 45.85, 38.95, 8.31. IR(powder): $\nu = 2920, 1637, 1567, 1518, 1317, 1034, 731, 699 \text{ cm}^{-1}$; HRMS (ESI) for $\text{C}_{20}\text{H}_{29}\text{N}_4\text{ClIr}$ (M^+), (Calc.) 553.1697, found 553.1688.

Synthesis of catalyst Ir-5

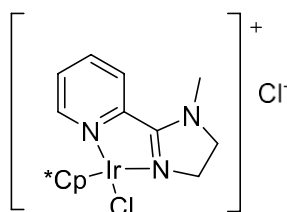


To a mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (80 mg, 0.1 mmol) in 10 mL of CH_2Cl_2 was slowly added the solution of ligand 2-(4,5-dihydro-1H-imidazol-2-yl)pyridine (28 mg, 0.2 mmol) in 5 mL of DCM. The mixture was stirred at room temperature overnight. Similar workup as described for catalyst **Ir-3** afforded **Ir-5** as a yellow solid. Yield: 105 mg, 98%. ^1H NMR (600 MHz, CDCl_3 , TMS): δ 1.76 (s, 15 H), 3.92-3.97 (m, 1H), 4.14-4.22 (m, 3H), 7.61 (t, $J = 6.6$ Hz, 1H), 8.13 (t, $J = 7.8$ Hz, 1H), 8.67 (d, $J = 5.4$ Hz, 1H), 9.38 (d, $J = 7.8$ Hz, 1H), 10.93 (brs, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 9.2, 46.3, 51.9, 87.6, 128.6, 128.7, 140.4, 147.5, 150.4, 169.5; IR(powder): $\nu = 1592, 1460, 1287, 1051, 1030, 758 \text{ cm}^{-1}$; HRMS (ESI) for $\text{C}_{18}\text{H}_{24}\text{N}_3\text{ClIr}$ (M^+), (Calc.) 510.1288, found 510.1274.

Synthesis of catalyst Ir-6

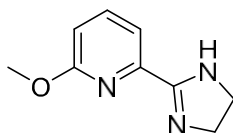


To the solution of pyridine-2-carboxaldehyde (107 mg, 1 mmol) in dichloromethane (10 mL) was dropwise added *N*-methylethylenediamine (78 mg, 1.05 mmol) in 5 mL of DCM. The mixture was stirred for 1 h, and was then cooled to 0 °C. *N*-Bromosuccinimide (196 mg, 1.1 mmol) was added and the mixture was stirred overnight. Washing the reaction mixture with 5% NaOH solution (10 mL) and then saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL), drying with Na_2SO_4 and removal of the dichloromethane under vacuum directly gave the desired crude product 2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine. Yield: 146 mg, 91%.

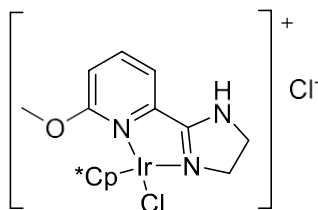


To a mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (80 mg, 0.1 mmol) in 10 mL of CH_2Cl_2 was slowly added the solution of ligand (39 mg, 0.24 mmol) in 5 mL of DCM. The mixture was stirred at room temperature overnight. Similar workup as described for catalyst **Ir-3** afforded **Ir-6** as a yellow solid. Yield: 92 mg, 82%. ^1H NMR (600 MHz, CDCl_3 , TMS): δ 1.79 (s, 15 H), 3.66 (s, 3H), 3.87-3.91 (m, 1H), 4.07-4.12 (m, 1H), 4.28-4.34 (m, 2H), 7.76 (t, $J = 6.6$ Hz, 1H), 8.29 (t, $J = 7.8$ Hz, 1H), 8.63 (d, $J = 7.8$ Hz, 1H), 8.86 (d, $J = 5.4$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 9.2, 36.2, 50.6, 55.8, 88.2, 127.5, 129.3, 140.6, 146.7, 152.2, 167.4; IR(powder): $\nu = 1583, 1453, 1288, 1030, 756$ cm^{-1} ; HRMS (ESI) for $\text{C}_{19}\text{H}_{26}\text{N}_3\text{ClIr}$ (M^+), (Calc.) 524.1444, found 524.1446.

Synthesis of catalyst Ir-7

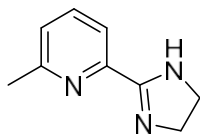


To the solution of 6-methoxypyridine-2-carboxaldehyde (300 mg, 2.1 mmol) in dichloromethane (20 mL) was dropwise added ethylenediamine (0.16 mL, 2.3 mmol). The mixture was stirred for 1 h, and then was cooled to 0 °C. *N*-Bromosuccinimide (410 mg, 2.3 mmol) was added and the mixture was stirred overnight. Washing the reaction mixture with 5% NaOH solution (20 mL) and then saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL), drying with Na_2SO_4 and removal of the dichloromethane under vacuum directly gave the desired crude product 2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine. Yield: 346 mg, 93%.

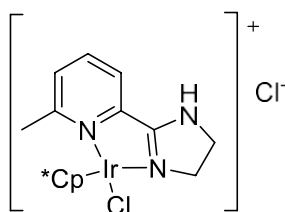


To a solution of ligand (200 mg, 1.13 mmol) in 10 mL of DCM was added the powder of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.5 mmol, 400 mg). The resulting orange solution was stirred overnight. Similar workup as described for catalyst **Ir-3** afforded **Ir-7** as a yellow solid. Yield: 465 mg, 80%. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.73 (s, 15 H), 3.86-3.95 (m, 1H), 4.15 (s, 6H), 7.17 (d, $J = 8.4$ Hz, 1H), 8.08 (t, $J = 8.1$ Hz, 1H), 8.87 (d, $J = 7.4$ Hz, 1H), 10.5 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 10.0, 46.2, 52.5, 58.0, 87.8, 110.7, 121.4, 143.8, 145.7, 163.9, 170.2; IR(powder): $\nu = 1593, 1479, 1307, 1065, 1052, 805$ cm^{-1} ; HRMS (ESI) for $\text{C}_{19}\text{H}_{26}\text{N}_3\text{ClOIr}$ (M^+), (Calc.) 540.1394, found 540.1383.

Synthesis of catalyst Ir-8

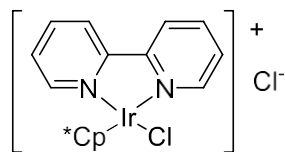


To the solution of 6-methylpyridine-2-carboxaldehyde (121 mg, 1 mmol) in dichloromethane (10 mL) was dropwise added ethylenediamine (0.8 mL, 1.2 mmol). The mixture was stirred for 1 h, and then was cooled to 0 °C. *N*-Bromosuccinimide (178 mg, 1.2 mmol) was added and the mixture was stirred overnight. Washing the reaction mixture with 5% NaOH solution (10 mL) and then saturated Na₂S₂O₃ solution (10 mL), drying with Na₂SO₄ and removal of the dichloromethane under vacuum directly gave the desired crude product 2-(4,5-dihydro-1H-imidazol-2-yl)-6-methylpyridine. Yield: 125 mg, 78%.



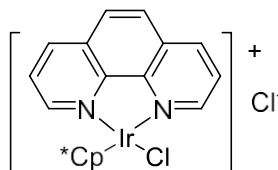
To a solution of ligand (161 mg, 0.78 mmol) in 5 mL of DCM was added the powder of [Cp*IrCl₂]₂ (239 mg, 0.3 mmol). The resulting orange solution was stirred overnight. Similar workup as described for catalyst **Ir-3** afforded **Ir-8** as a yellow solid. Yield: 307 mg, 91%. ¹H NMR (400 MHz, D₂O) δ 8.05 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 4.14 (dd, *J* = 76.7, 65.6 Hz, 4H), 3.01 (s, 3H), 1.67 (d, *J* = 1.1 Hz, 15H). ¹³C NMR (101 MHz, D₂O) δ 139.90, 129.84, 122.56, 88.90, 52.43, 45.57, 28.39, 8.80. IR(powder): ν = 2920, 2360, 2342, 1633, 1545, 1463, 1381, 1288, 1049, 1030, 815, 754 cm⁻¹; HRMS (ESI) for C₁₉H₂₆N₃ClIr (M⁺), (Calc.) 524.1431, found 524.1440.

Synthesis of catalyst Ir-9



To a solution of 2,2'-dipyridyl ligand (31.2 mg, 0.1 mmol) in 5 ml of DCM and was added the solid of [Cp*IrCl₂]₂ (80 mg, 0.05 mmol). The mixture was allowed to stir at room temperature overnight. After the addition of ether, yellow solid appeared. The solid was dried under vacuum at room temperature. Yield: 59 mg, 53%. ¹H NMR (400 MHz, D₂O) δ 8.95 (dd, *J* = 5.6, 0.7 Hz, 2H), 8.48 (d, *J* = 7.9 Hz, 2H), 8.23 (td, *J* = 8.1, 1.4 Hz, 2H), 7.81 (ddd, *J* = 7.1, 5.7, 1.3 Hz, 2H), 1.65 (s, 15H). ¹³C NMR (101 MHz, D₂O) δ 155.28, 151.54, 140.64, 129.02, 124.10, 90.05, 7.74. The analytical data are identical with those reported.³

Synthesis of catalyst Ir-10



The procedure is same to the synthesis of **Ir-9**. Phenanthroline (36 mg, 0.2 mmol) and $[\text{Cp}^*\text{IrCl}_2]_2$ (80 mg, 0.05 mmol) were used. Yield: 81mg, yield 70%. ^1H NMR (400 MHz, D_2O) δ 9.26 (dd, $J = 5.3, 1.2$ Hz, 1H), 8.70 (dd, $J = 8.3, 1.2$ Hz, 1H), 8.16 – 7.98 (m, 2H), 1.67 (s, 8H). ^{13}C NMR (101 MHz, D_2O) δ 151.39, 146.53, 139.45, 131.01, 127.86, 127.20, 89.95, 7.86. The analytical data are identical with those reported.³

3. General procedure for reduction of aldehydes:

To a mixture of formic acid (0.30 mL, 8 mmol) and aldehydes (2 mmol) in deionized water (2 mL) at 80 °C was added the aqueous solution of catalyst **Ir-4** (80 μL , 0.005 mol-1 L). For poorly soluble aldehydes as indicated in Table 3, 1.5 mL of water and 0.5 mL of ethanol was used. The resulting suspension was stirred for the time indicated in Table 2. Upon complete conversion of aldehydes was achieved as detected by TLC, water (10 mL) was added to dilute the mixture, followed by addition of ethyl acetate (10 mL) to extract the alcohol products. Drying the organic phase over Na_2SO_4 , filtration, and removal of the solvent under vacuum gave desired products in good yields with >95% purity by NMR.

4. Characterization data of products

All the products synthesized were known compounds, and their NMR data are identical with those reported.

4-Methoxybenzyl alcohol (2a)². Yellowish oil. Yield: 273 mg, 99%. ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 4.52 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.07, 133.23, 128.63, 113.89, 64.73, 55.30, 55.26.

4-(Pentyloxy)benzenemethanol (2b)⁴. Yellow solid, Yield: 368 mg, 95%. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 4.58 (s, 2H), 3.98 (t, $J = 6.6$ Hz, 2H), 2.52 (s, 1H), 1.97 – 1.68 (m, 2H), 1.64 – 1.26 (m, 4H), 0.98 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.70, 132.98, 128.63, 114.52, 68.08, 64.85, 29.00, 28.24, 22.52, 14.07.

4-(2-Propen-1-yloxy)benzenemethanol (2c)⁵. Yellowish oil. Yield: 301 mg, 92%. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, $J = 8.4$ Hz, 2H), 7.05 – 6.72 (m, 2H), 6.08 (ddt, $J = 17.2, 10.5, 5.3$ Hz, 1H), 5.38 (ddq, $J = 46.7, 10.5, 1.5$ Hz, 2H), 4.54 (dd, $J = 4.1, 2.8$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.09, 133.39, 133.32, 128.62, 117.70, 117.65, 114.74, , 68.85, 64.68, 64.66.

2,5-Dimethoxybenzenemethanol (2d).⁶ Yellow solid. Yield: 332 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 2H), 4.63 (d, *J* = 15.0 Hz, 2H), 3.85 – 3.66 (m, 6H), 3.09 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 153.60, 151.29, 130.33, 114.44, 112.82, 111.10, 61.28, 55.73, 55.68.

2,4,6-trimethoxy-Benzenemethanol (2e).⁷ Yellowish solid, Yield: 392 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 6.10 (s, 2H), 4.67 (s, 2H), 3.77 (d, *J* = 1.3 Hz, 9H), 2.50 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 161.01, 159.18, 109.90, 90.46, 55.61, 55.24, 54.09.

Benzyl alcohol (2f)². Yellow oil. Yield: 214 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.09 (m, 5H), 4.57 (s, 2H), 2.60 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 140.93, 128.55, 127.61, 127.04, 65.14.

4-Methylbenzyl alcohol (2g)². White solid, Yield: 241 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.22 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.64 (s, 2H), 2.35 (s, 3H), 1.61 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 137.92, 137.43, 129.26, 127.13, 65.32, 21.17.

4-(1,1-Dimethylethyl)benzenemethanol (2h).⁵ Yellowish oil. Yield: 324 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 2H), 1.40 (d, *J* = 0.7 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 150.63, 137.95, 126.98, 125.48, 65.00, 64.96, 64.93, 34.60, 31.44.

2,4,6-Trimethylbenzenemethanol (2i).⁸ Colorless oil. Yield: 291 mg, 97%. ¹H NMR (400 MHz, CDCl₃) δ 6.86 (s, 2H), 4.69 (s, 2H), 2.38 (s, 6H), 2.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.74, 137.31, 133.72, 129.16, 59.19, 21.00, 19.38.

4-Fluoro-3-phenoxybenzenemethanol (2j)². Yellow oil. Yield: 427 mg, 98%. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.31 (m, 2H), 7.21 – 7.11 (m, 2H), 7.10 – 6.98 (m, 4H), 4.56 (s, 2H), 3.95 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 157.23, 154.85, 152.38, 143.77, 143.65, 137.65, 137.61, 129.83, 123.35, 123.18, 123.11, 120.31, 117.44, 117.11, 116.93, 64.07.

4-Bromobenzenemethanol (2k)². White solid. Yield: 344 mg, 92%. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.61 (s, 2H), 2.17 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.75, 131.62, 128.60, 121.44, 64.51.

3-Bromobenzenemethanol(2l)². White solid. Yield: 344 mg, 92%. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 1H), 7.41 – 7.35 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.58 (d, *J* = 2.1 Hz, 2H), 3.76 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.95, 130.62, 130.13, 129.89, 125.40, 122.61, 64.23.

4-Chlorobenzenemethanol (2m)². White solid. Yield: 255 mg, 90%. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.18 (m, 4H), 4.65 (s, 2H), 2.08 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.24, 133.37, 128.69, 128.29, 64.55.

3-Cyanobenzenemethanol (2n)⁹. Yellowish oil. Yield: 255 mg, 96%. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (td, *J* = 1.7, 0.9 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 4.73 (s, 2H), 2.51 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.41, 131.12, 131.11, 130.17, 129.28, 118.86, 112.35, 63.85.

1,4-Benzenedimethanol (2o)⁸. White solid. Yield: 262 mg, 95%. ¹H NMR (400 MHz, DMSO) δ 7.25 (s, 4H), 5.12 (t, *J* = 5.7 Hz, 2H), 4.47 (d, *J* = 5.7 Hz, 4H). ¹³C NMR (101 MHz, DMSO) δ 141.31, 126.68, 63.23.

4-Acetylbenzyl alcohol (2p)⁵. Yellowish solid, Yield: 294 mg, 98%. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.52 – 7.34 (m, 2H), 4.76 (d, *J* = 3.0 Hz, 2H), 2.59 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.11, 146.38, 136.26, 128.61, 126.62, 64.53, 26.65.

4-(Carbomethoxy)benzyl alcohol (2q)⁵. Yellowish solid. Yield: 325 mg, 98%. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 8.0, 0.6 Hz, 2H), 4.73 (s, 2H), 3.90 (s, 3H), 2.54 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 167.06, 146.10, 129.81, 129.20, 126.45, 64.59, 52.13.

4-Nitrobenzenemethanol (2r)². Yellowish solid. Yield: 302 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.11 (m, 2H), 7.59 – 7.43 (m, 2H), 4.83 (s, 2H), 2.35 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 148.29, 127.01, 123.72, 63.97.

2-Chloro-6-nitrobenzenemethanol (2s)¹⁰. Yellowish solid. Yield: 336 mg, 90%. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.69 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 4.92 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 151.24, 136.91, 134.57, 132.59, 129.55, 123.18, 58.52.

4-(Trifluoromethyl)benzenemethanol (2t)¹¹. Yellowish oil. Yield: 344 mg, 98%. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.33 (m, 2H), 4.66 (s, 2H), 3.04 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.63, 129.88, 129.56, 129.24, 128.22, 126.80, 125.52, 125.41, 125.37, 122.81, 64.26, 64.22, 64.19.

1-Naphthylenemethanol (2u)². White solid. Yield: 300 mg, 95%. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, *J* = 6.6, 3.0 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.88 – 7.81 (m, 1H), 7.63 – 7.53 (m, 2H), 7.53 – 7.40 (m, 2H), 5.06 (s, 2H), 3.26 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 136.30, 133.81, 131.25, 128.71, 128.49, 126.34, 125.90, 125.48, 125.30, 123.71, 63.31, 63.26.

4-Methoxy-2-pyridinemethanol (2v)¹². Yellowish solid. Yield: 264 mg, 95%. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 5.8 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 5.8, 2.5 Hz, 1H), 4.68 (s, 2H), 3.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.44, 161.72, 149.66, 108.99, 106.05, 64.44, 64.39, 64.35, 55.22, 55.17.

2-Thienylmethanol (2w)². Yellowish oil. Yield: 225 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 7.27 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.97 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.81 (s, 2H), 2.05 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.99, 126.89, 125.64, 125.51, 59.99.

2-Furanmethanol (2x)². Yellow oil. Yield: 186 mg, 95%. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dt, *J* = 1.8, 0.9 Hz, 1H), 6.40 – 6.18 (m, 2H), 4.54 (s, 2H), 2.82 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 154.08, 142.50, 110.35, 107.72, 57.21.

3-Phenyl-2-propen-1-ol (2y)². Yellowish solid. Yield: 254 mg, 95%. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.15 (m, 5H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.31 (dd, *J* = 5.7, 1.5 Hz, 2H), 1.77 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 136.70, 131.13, 128.62, 128.54, 127.71, 126.49, 63.72.

2-Methyl-3-phenyl-2-propen-1-ol (2z)¹³. Yellowish solid. Yield: 269 mg, 91%. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.05 (m, 5H), 6.50 (s, 1H), 4.14 (d, *J* = 0.9 Hz, 2H), 1.86 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 154.67, 137.73, 137.68, 128.95, 128.21, 126.46, 124.98, 124.94, 68.81, 68.79, 15.35.

2-(Hydroxymethyl)phenol (2aa)¹⁴. White solid. Yield: 248 mg, 99%. ¹H NMR (500 MHz, DMSO) δ 9.34 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.86 – 6.82 (m, 2H), 5.00 (s, 1H), 4.55 (s, 2H). ¹³C NMR (125 MHz, DMSO) δ 163.54, 154.65, 129.01, 127.83, 119.16, 115.02, 58.78.

4-Fluoro-2-(hydroxymethyl)phenol (2ab)¹⁵. White solid. Yield: 284 mg, 99%. ¹H NMR (400 MHz, DMSO) δ 9.33 (s, 1H), 7.06 (dd, *J* = 9.6, 2.2 Hz, 1H), 6.84 (td, *J* = 8.6, 3.3 Hz, 1H), 6.73 (dd, *J* = 8.7, 4.7 Hz, 1H), 5.10 (t, *J* = 5.5 Hz, 1H), 4.45 (d, *J* = 5.1 Hz, 2H). ¹³C NMR (101 MHz, DMSO) δ 156.12 (d, *J* = 233.0 Hz), 150.43 (d, *J* = 1.8 Hz), 131.13 (d, *J* = 6.8 Hz), 115.55 (d, *J* = 8.0 Hz), 113.57 (d, *J* = 23.7 Hz), 113.41 (d, *J* = 22.5 Hz), 58.25.

2-Bromo-5-hydroxybenzenemethanol (2ac)¹⁶. Yellowish solid. Yield: 381 mg, 94%. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 6.94 (d, *J* = 3.0 Hz, 1H), 6.71 (dd, *J* = 8.6, 3.0 Hz, 1H), 5.24 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 157.46, 142.43, 132.92, 115.90, 115.56, 109.47, 63.01, 40.49, 40.29, 40.08, 39.87, 39.66, 39.45, 39.24.

4-Carboxybenzyl alcohol (2ad)¹⁷. White solid. Yield: 282 mg, 93%. ¹H NMR (400 MHz, DMSO) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 4.57 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 167.90, 148.08, 129.84, 129.63, 126.59, 62.91, 40.57, 40.36, 40.15, 39.94, 39.73, 39.53, 39.32.

3-Carboxybenzyl alcohol (2ae)¹⁸. White solid. Yield: 295 mg, 97%. ¹H NMR (500 MHz, DMSO) δ 12.95 (brs, 1H), 7.98 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 5.37 (brs, 1H), 4.61 (s, 2H). ¹³C NMR (125 MHz, DMSO) δ 167.92, 143.56, 131.29, 131.11, 128.81, 128.13, 127.70, 62.93

Isobenzofuran-1(3H)-one (3af)¹⁹. White solid. Yield: 243 mg, 91%. ¹H NMR (500 MHz, CDCl₃) δ 7.93 (dd, *J* = 7.8, 3.3 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.48 (m, 2H), 5.34 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 171.3, 146.6, 134.1, 129.1, 125.84, 125.79, 122.2, 69.8.

Benzenepropanol (2ag)²⁰. Colorless oil. Yield: 263 mg, 97%. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.08 (m, 5H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.82 – 2.57 (m, 2H), 2.00 – 1.76 (m, 2H), 1.63 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.86, 128.46, 128.43, 125.89, 62.27, 34.25, 32.11.

1-Pentanol (2ah)²¹. Colorless oil. Yield: 109 mg, 62%. ¹H NMR (400 MHz, CDCl₃) δ 3.62 (s, 2H), 2.26 (s, 1H), 1.70 – 1.46 (m, 2H), 1.42 – 1.22 (m, 4H), 0.91 (ddd, *J* = 7.1, 4.0, 2.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 62.81, 32.41, 27.91, 22.47, 14.00.

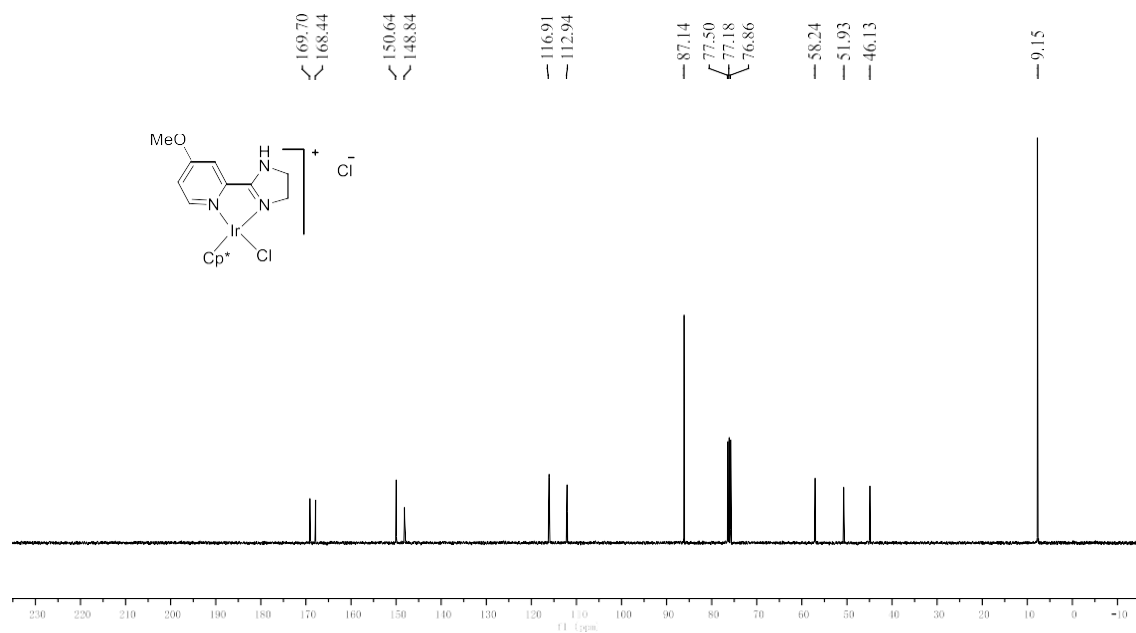
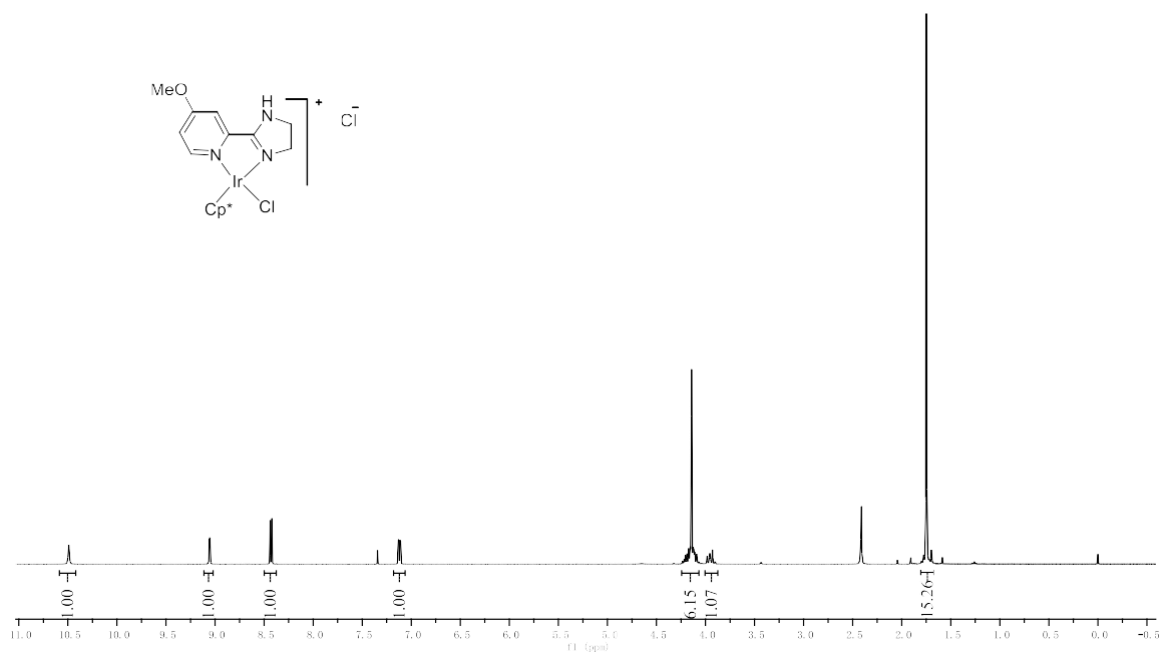
1-Octanol (2ai)⁵. Colorless oil, Yield: 257 mg, 99%. ¹H NMR (400 MHz, CDCl₃) δ 4.83 (t, *J* = 5.3 Hz, 1H), 1.78 – 1.57 (m, 2H), 1.49 – 1.12 (m, 11H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 101.72, 34.44, 31.79, 29.35, 29.18, 23.59, 22.66, 14.09.

5. Reference:

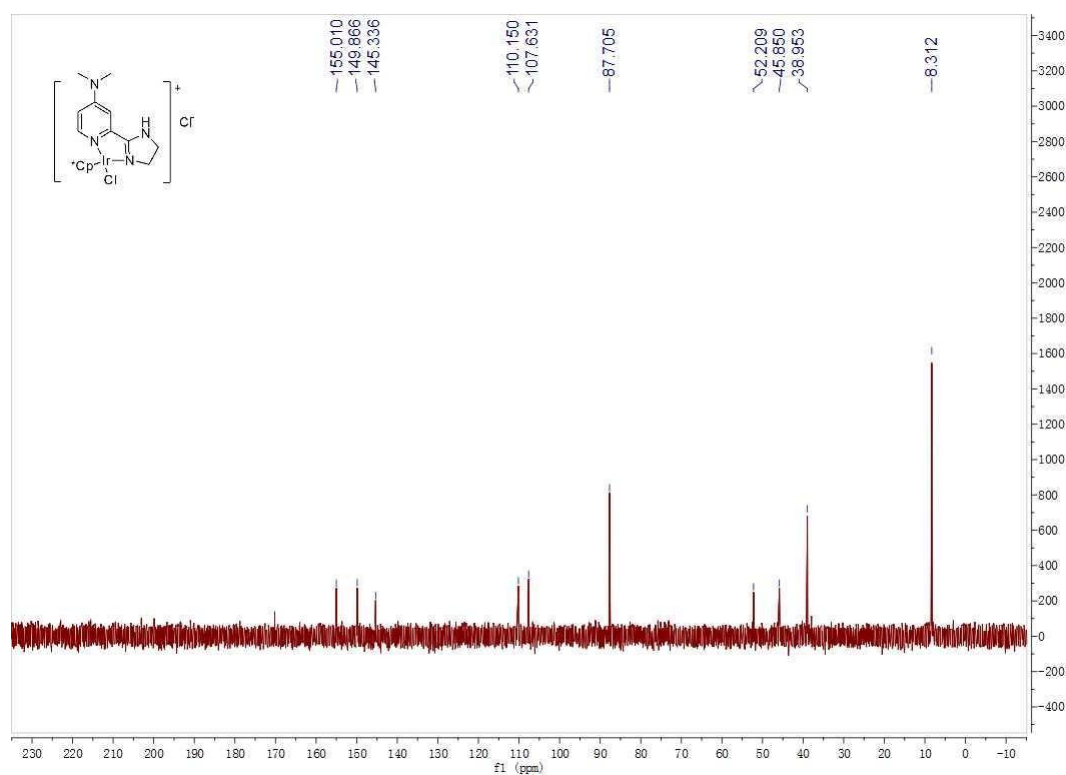
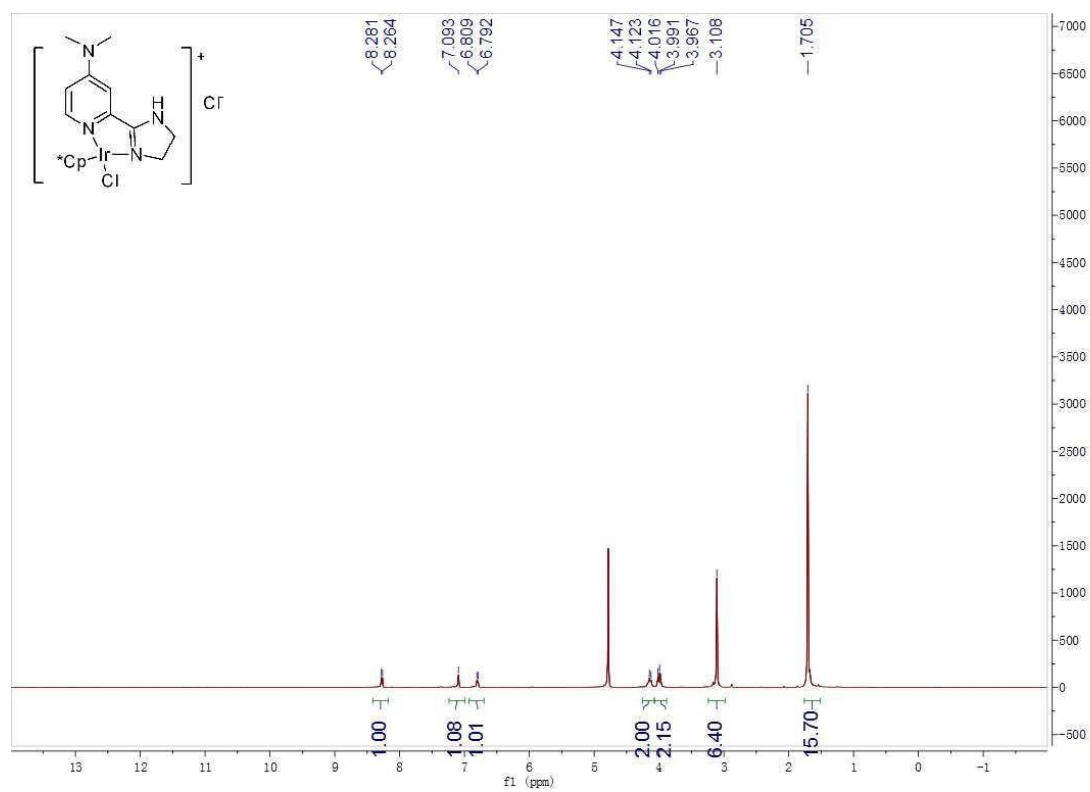
- (1) X. Wu, J. Liu, A. Zanotti-Gerosa, F. Hancock, D. Vinci, J. Ruan and J. Xiao. *Angew. Chem. Int. Ed.* 2006, **45**, 6718.
- (2) X. Wu, C. Corcoran, S. Yang, and J. Xiao. *ChemSusChem* 2008, **1**, 71.
- (3) T. P. Brewster, A. J. M. Miller, D. M. Heinekey, and K. I. Goldberg. *J. Am. Chem. Soc.*, 2013, **135**, 16022.
- (4) R. Wisastraa, P. A. M. Koka, N. Eleftheriadis, M. P. Baumgartner, C. J. Camacho, H. J. Haismaa, F. J. Dekker. *Bioorg. Med. Chem.* 2013, **21**, 7763.
- (5) G. Wienhçfer, F. A. Westerhaus, K. Junge, R. Ludwig, and M. Beller. *Chem. Eur. J.* 2013, **19**, 7701.
- (6) J. Forrester. *Tetrahedron* 2001, **57**, 2871.
- (7) D. V. Moiseev. *Inorg. Chem.* 2006, **45**, 10338.
- (8) N. Murai. *Org. Lett.* 2012, **14**, 1278.
- (9) C. Yang. *Org. Lett.* 2004, **6**, 2837.
- (10) S. Naik, V. Kavala, R. Gopinath and B. K. Patel. *ARKIVOC*, 2006, 21.
- (11) L. Zhang. *J. Org. Chem.* 2006, **71**, 3149.
- (12) C. X. Zhang. *Inorg. Chem.* 2003, **42**, 1807.
- (13) F. Luo. *Tetrahedron Lett.* 2010, **51**, 1693.
- (14) S. Gendler. *J. Am. Chem. Soc.* 2008, **130**, 2144.
- (15) Y. Cheng. *ACS Med. Chem. Lett.* 2010, **1**, 321.
- (16) A. N. Butkevich, A. Corbu, L. Meerpoel, I. Stansfield, P. Angibaud, P. Bonnet, and J. Cossy. *Org. Lett.*, 2012, **14**, 4998.
- (17) . S. Annen. *ChemCatChem* 2010, **2**, 1286.
- (18) G. A. Reed. *J. Org. Chem.* 1993, **58**, 6372.
- (19) D. W. Hughes, *Can. J. Chem.* 1976, **54**, 2252.
- (20) J.-J. Wu. *Tetrahedron* 2011, **67**, 285.
- (21) O. R. Ludek. *Synlett* 2005, 3145.

6. NMR spectra of catalysts and products

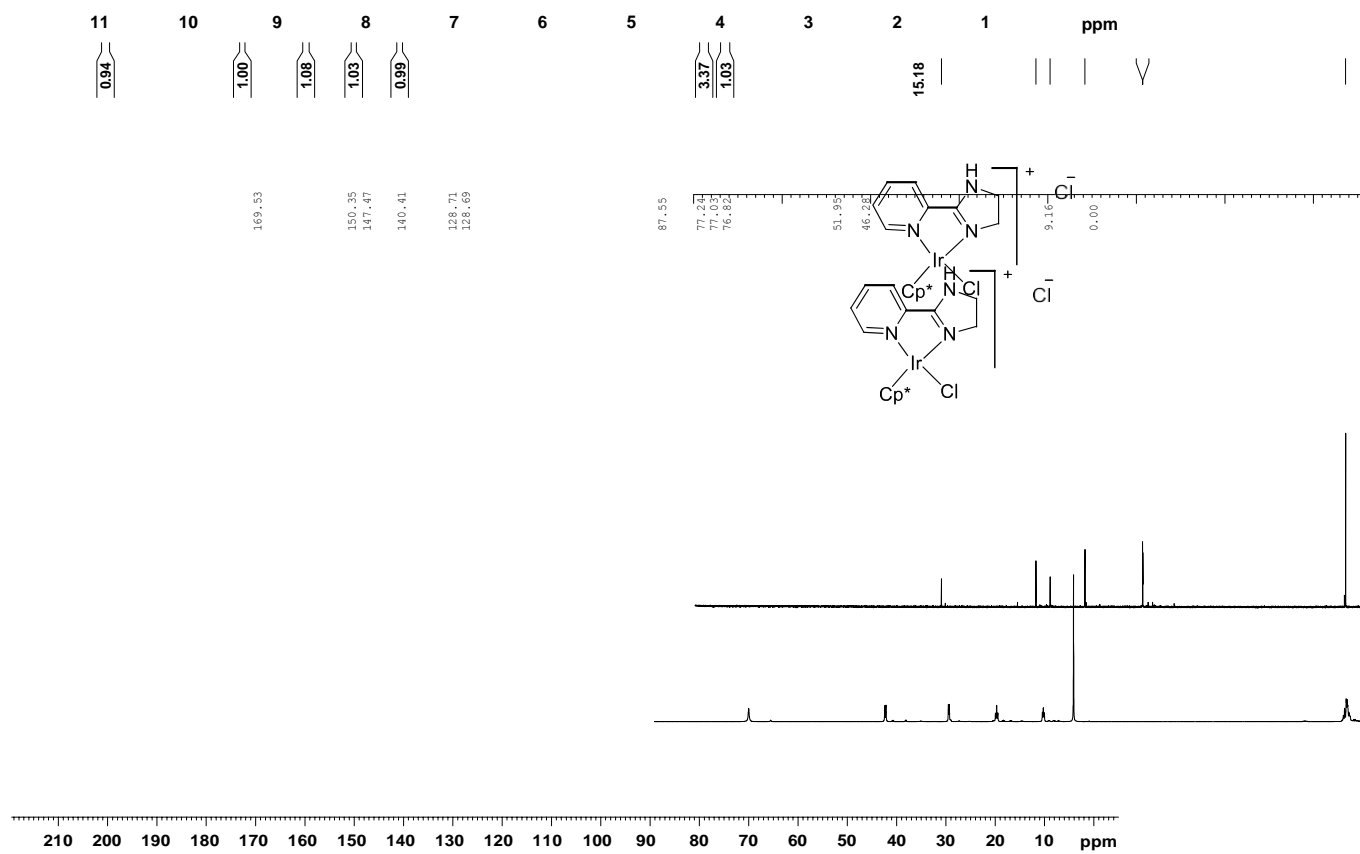
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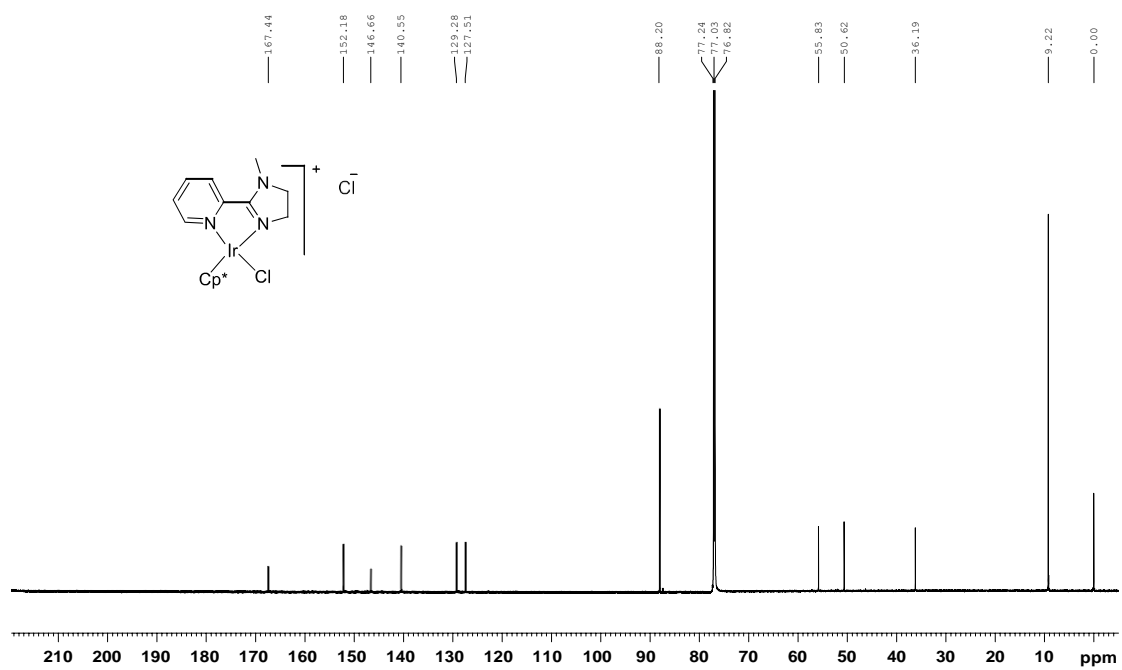
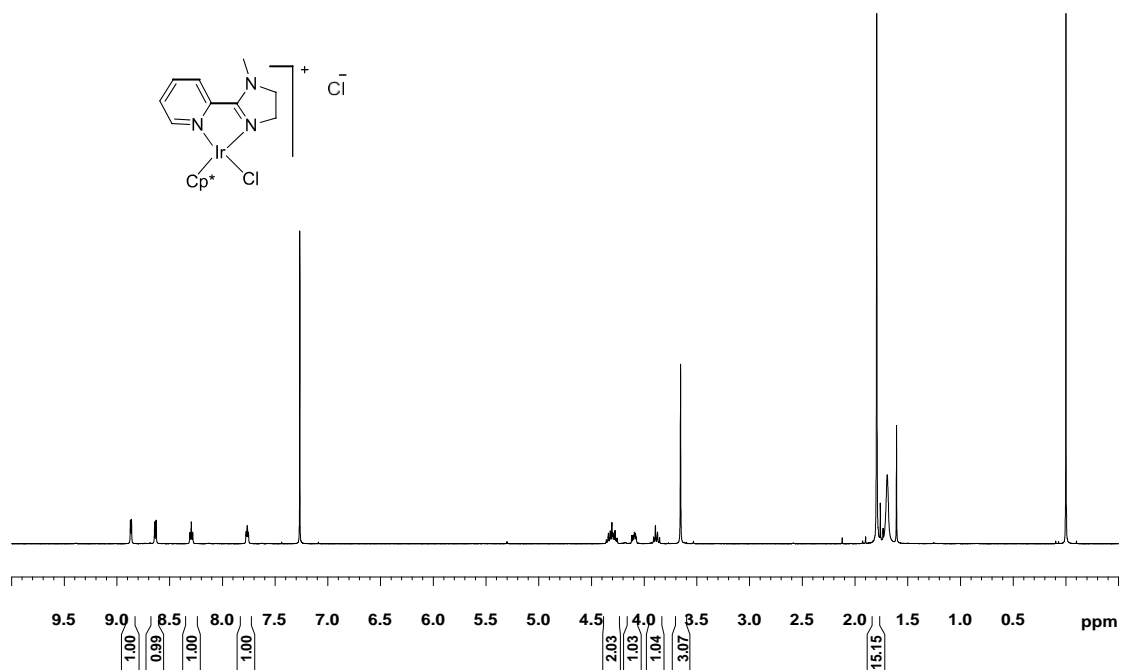
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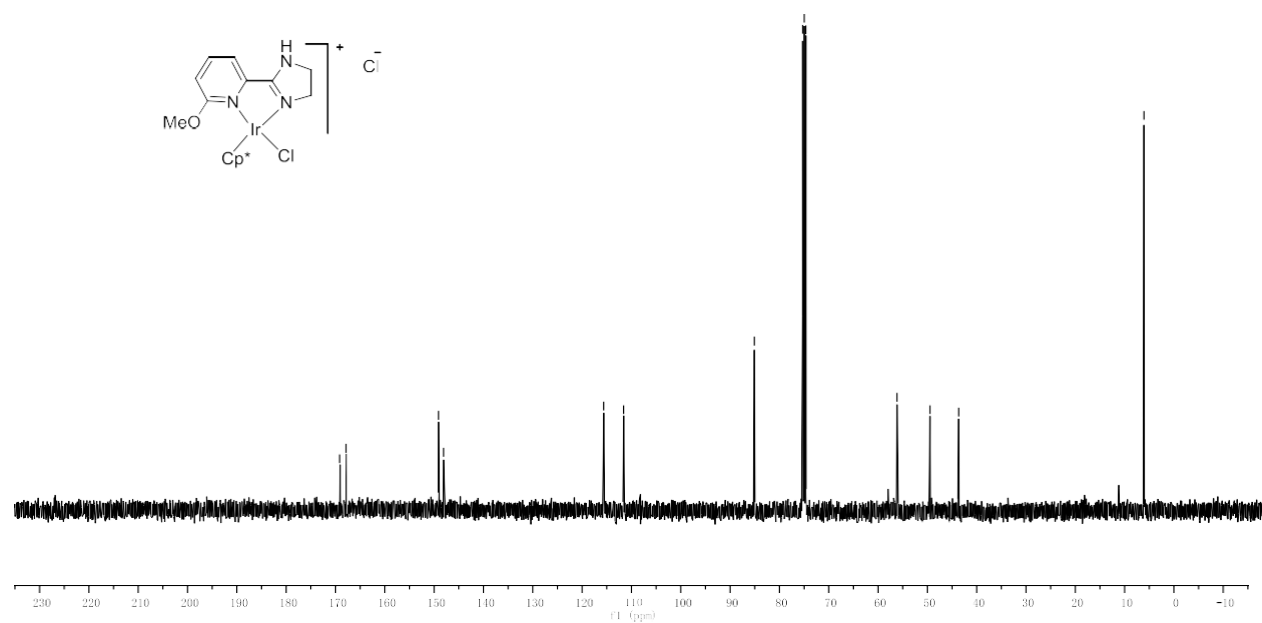
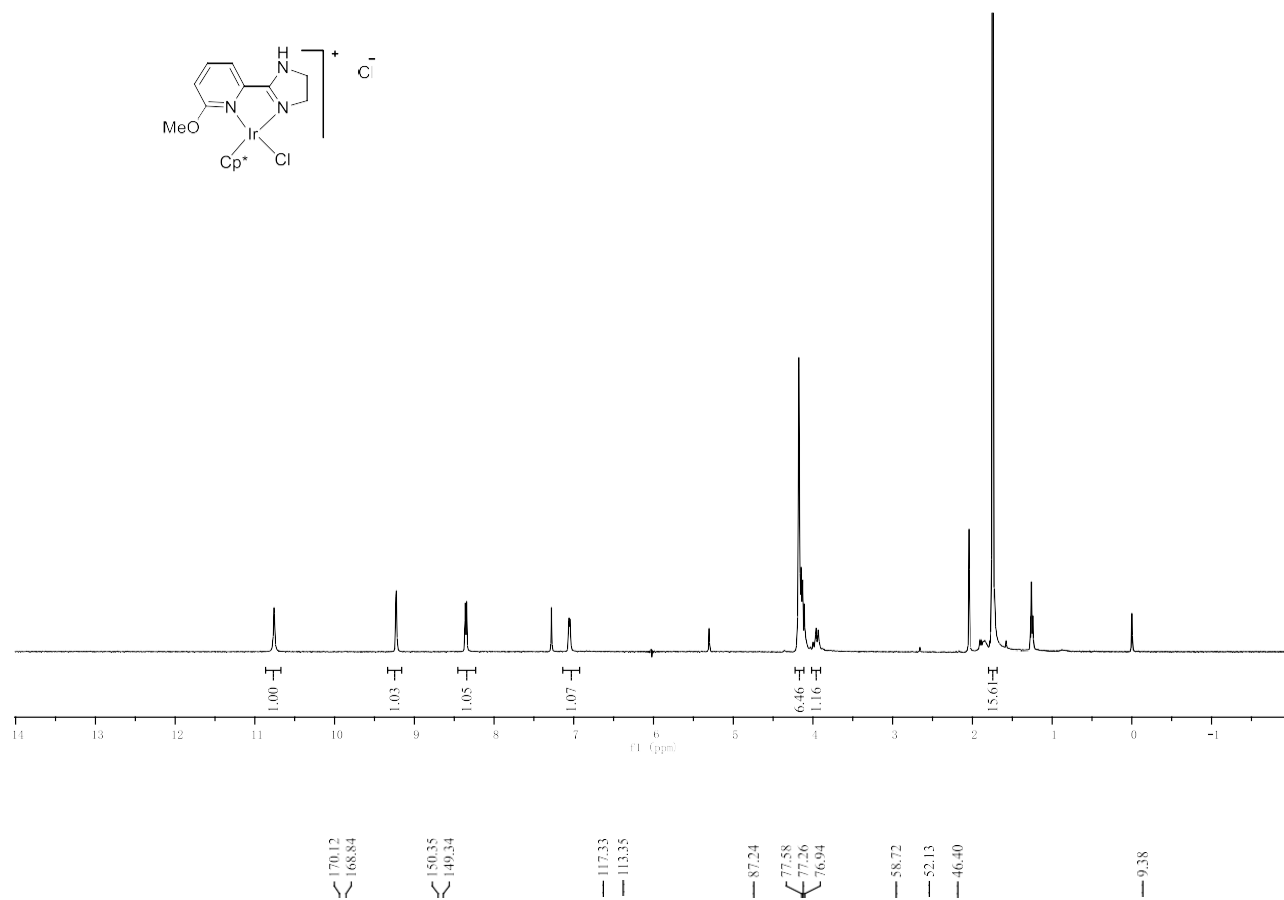
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Ir-6



Ir-7



Ir-8

