Supplementary: Optically Active Iridium Imidazol-2-ylidene-oxazoline Complexes: Preparation and Use in Asymmetric Hydrogenation

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- Chem3D diagrams from crystal structures of complexes **5ab**, **5ap**, **5dp**, and **6ap**
- comparison of enantioselectivities with some relevant literature values
- experimental procedures for the preparations of the ligands, complexes, and hydrogenation/deuteration procedures
- discussion of assignments of absolute configuration and tabulated details of these

Figure S1. Crystal structures of complexes **5ab**, **5ap**, **5dp**, and **6ap** ($BARF^-$ counter ion not shown).

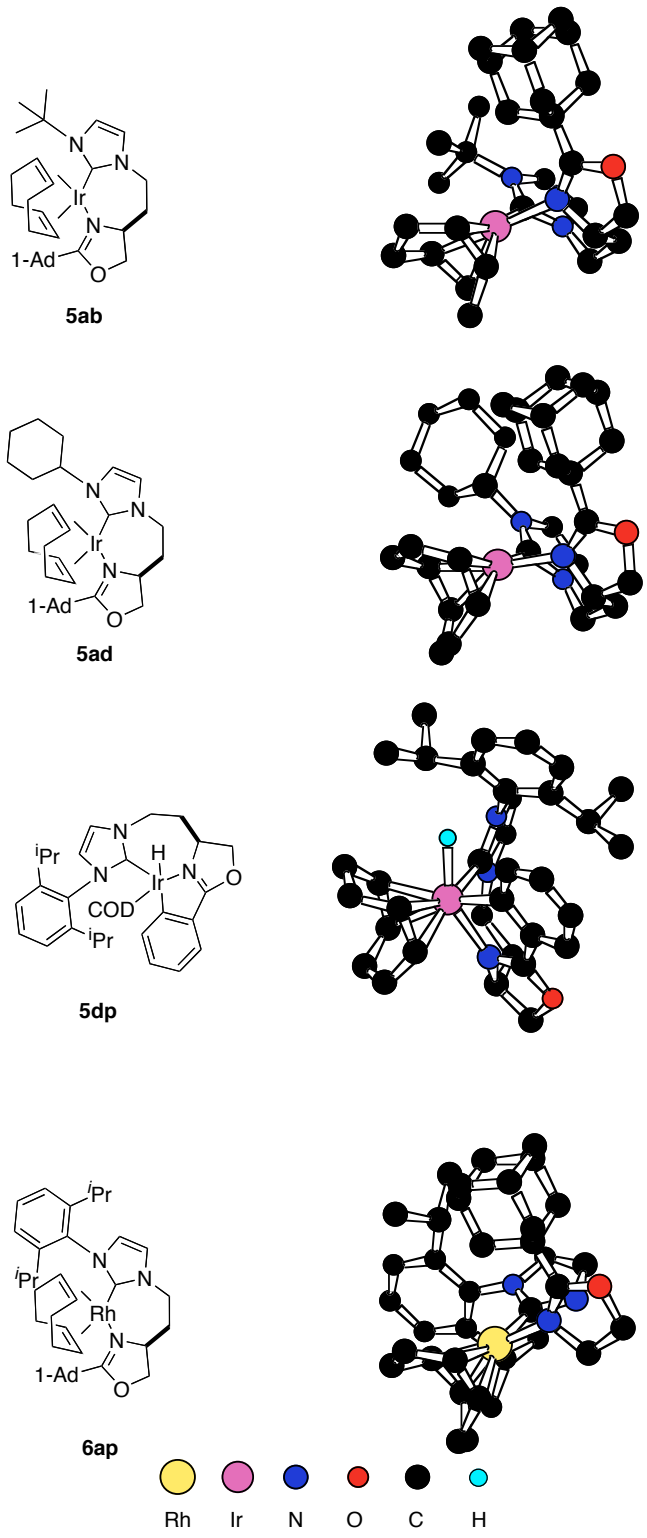
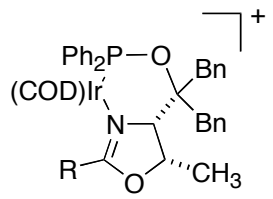
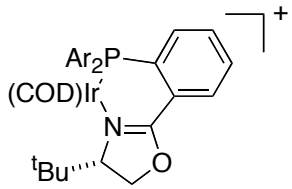


Chart S1. Some of the best ligands for asymmetric hydrogenations to emerge from Pfaltz' studies **10** - **11**, and the structure of our favored JM Phos ligand **12** for this reaction.

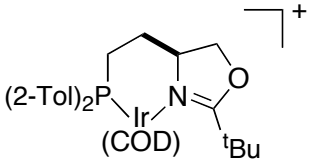


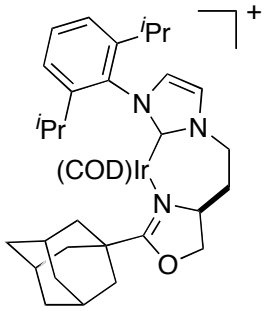


10a R = Ph
10b R = 3,5-$Me_2C_6H_3$

11 Ar = 2-MeC_6H_4

some of the most useful Pfaltz' catalysts

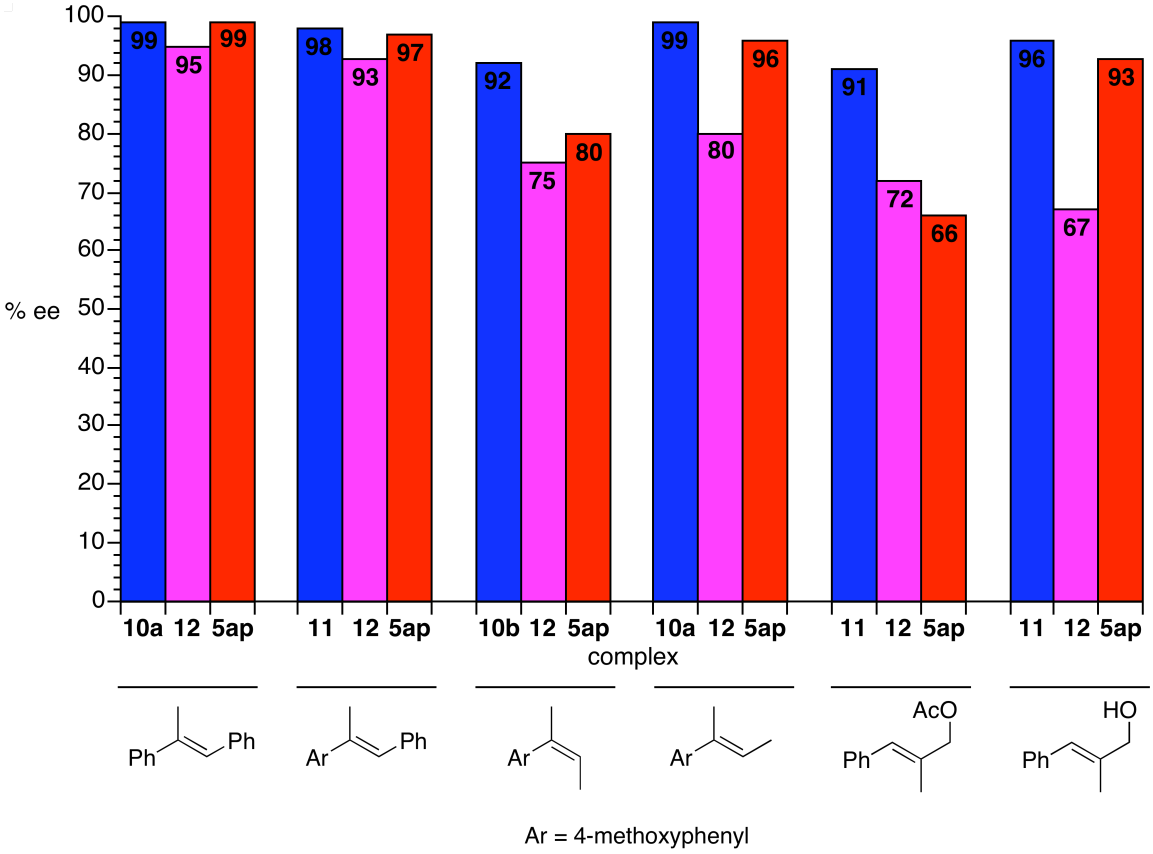




12 **5ap**

most useful complexes from these labs

Figure S2. Data for hydrogenations using complexes **10** and **11**, **12**, and **5ap**.



In most cases, the enantioselectivities observed for **5ap** are close to the best data reported for the phosphine- and phosphite-oxazolines. The critical difference is that complex **5ap** was used consistently to obtain the data shown in Figure S1 whereas the other data is from three different complexes.

General Procedures. High field NMR spectra were recorded on a Varian Unity Plus 300 spectrometer (^{1}H at 300 MHz, ^{2}H at 46 MHz, and ^{13}C at 75 MHz), or a Varian Inova 500 spectrometer (^{1}H at 500 MHz, ^{2}H at 61 MHz and ^{13}C at 126 MHz). Chemical shifts of ^{1}H, ^{2}H and ^{13}C spectra were referenced to the NMR solvents. IR spectra were recorded on a FTIR instrument. Melting points were uncorrected. Optical rotations were measured on Jasco DIP-360 digital polarimeter. Flash chromatography was performed using silica gel (230–600 mesh). Thin layer chromatography was performed using glass plates coated with silica gel 60 F254 (E. Merck, Darmstadt, Germany). Microanalyses were performed by Atlantic Microlab, Norcross, GA. CH_2Cl_2 and xylenes were distilled over CaH_2, Et_2O and THF over Na/benzophenone, and acetone over $CaSO_4$. Other solvents and reagents were used as received. 1,5-Cyclooctadiene iridium (I) chloride dimer was provided by Johnson Matthey. Deuterium gas under pressure was purchased from Praxair Inc. Danbury, CT.

Preparation of *N*-Substituted Imidazoles 4

Three known procedures were used to prepare the *N*-substituted imidazoles **4**.

Method A:[1] The amine (100 mmol) was mixed with 50 mL H_2O, H_3PO_4 (85%) was added until pH was around 2. Paraformaldehyde (100 mmol), glyoxal (100 mmol) and H_2O (100 mL) were added. If a solid was formed after the addition of H_3PO_4, then 1,4-dioxane (100 mL) was also added. The system was heated to 80 ˚C, then saturated NH_4Cl (100 mmol) was added dropwise over 30 min. The temperature was then increased to 100 ˚C, and maintained with stirring for 3 h. The reaction mixture was cooled to 0 ˚C, and solid NaOH was added until pH was above 12. In some cases a solid by-product precipitated at this stage, and was removed by filtration. The organic products were extracted with hexanes (500 mL × 3). Evaporation of the solvent gave crude products that were purified by recrystallization or distillation as indicated below.

Method B:[2] Phenyl bromide (5 mmol), imidazole (7.5 mmol), Cu(I)OTf (0.106 g, 0.5 mmol), 1,10-phenanthrolene (0.9011 g, 5.0 mmol), dibenzylidiene acetone (0.0586 g, 0.25 mmol), and Cs_2CO_3 (1.7920 g, 5.5 mmol) were placed in a Schlenk tube in a glove box. Xylene (1 mL) was added via a syringe, the system was heated at 125 ˚C for 36 h, then cooled to room temperature. Dichloromethane (90 mL) and saturated NH_4Cl (5 mL)

were added, the organic layer was separated, washed with brine, and dried over $MgSO_4$. The crude products were isolated by chromatography using ethyl acetate and hexanes.

Method C:[3] Thiophosgene (55.19 g, 0.48 mol, 37 mL) and H_2O (700 mL) were added to a 2 L, two-neck, round bottom flask with vigorous mechanical stirring. The aromatic amine (0.4 mol) was added slowly over 30 min, and the reaction mixture was stirred for an additional 30 min. The organic layer was separated, and the crude isothiocyanate was used for the next step without further purification.

Aminoacetylaldehyde diethyl acetal (53.28 g, 0.4 mol, 58 mL) was mixed with ethanol (800 mL), and the isothiocyanate (as prepared above) was added dropwise over 30 min. The reaction mixtures were refluxed until the isothiocyanate disappeared (approximately 1 h, monitored by TLC). The solvent was evaporated to obtain the crude aryl diethoxyethylthioureas. These were refluxed with 1N HCl (800 mL) for 30 min. The precipitated 1-aryl-2-mercaptoimidazole products were then collected by filtration.

CAUTION! The last step of the reaction sequence was generally performed on a smaller scale because of the release of large amount of gas. The 1-aryl-2-mercaptoimidazoles (15 g) were added to 20% HNO_3 (75 mL) in one liter round bottom flasks, then heated to 100 ˚C in an oil bath behind a shield. **CAUTION:** large amounts of gasses are evolved at this stage. When the evolution of brown gas had ceased (about 5 min), the solutions were treated with aqueous NH_3 (28%) until a pH around 10 was reached. A fraction of each imidazole product precipitated at this stage and was collected by filtration. The filtrates were extracted with chloroform (50 mL × 3), dried over $MgSO_4$ to obtain the rest of the material. The combined solid portions were purified by recrystallization from ethyl acetate and/or hexanes.

1-(1-Admantyl)-*1H*-imidazole (4a). (method A) The product was obtained as a white crystalline solid in 14 % yield after recrystallization from hexanes. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.64 (s, 1H), 7.07 (t, J = 1.0 Hz, 1H), 7.06 (t, J = 1.0 Hz, 1H), 2.23 (s, 3H), 2.09 (d, J = 2.5 Hz, 1H), 1.81 - 1.73 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 133.5, 128.7, 115.3, 55.0, 43.7, 35.9, 29.4. Mp 112.0 - 112.5 ˚C. MS (+ESI) *m/z* 203 $[M+H]^+$, 405 $[2M^+ + H]$. Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85; found: C, 77.18; H, 9.05; N, 13.81.

1-*tert*-Butyl-*1H*-imidazole (4b).[1] (method A) The product was obtained as colorless oil in 8 % yield after distillation at 110 °C/12 mmHg. The NMR data are in accordance with those reported. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48 (s, 1H), 6.89 (s, 2H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.7, 128.1, 115.9, 54.3, 30.0.

1-Diphenylmethyl-*1H*-imidazole (4c). (method A) The product was obtained as a colorless needle shape crystalline solid in 28 % yield after recrystallization from hexanes. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43 - 7.34 (m, 7H), 7.14 - 7.11 (m, 5H), 6.87 (t, J = 1.2 Hz, 1H), 6.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.0, 137.3, 129.3, 128.8, 128.3, 128.0, 119.3, 64.9. IR ($CHCl_3$): ν = 3058, 3027, 1496, 1450, 1224, 1076 cm^{-1}. Mp 85.0 - 86.0 ˚C. MS (+ESI) *m/z* 235 $[M+H]^+$. Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96; found: C, 82.32; H, 5.97; N, 11.99.

1-Cyclohexyl-*1H*-imidazole (4d).[1] (method A) The product was obtained as colorless crystalline solid in 36 % yield after recrystallization from hexanes. The NMR data are in accordance with those reported. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49 (s, 1H), 6.99 (s, 1H), 6.91 (s, 1H), 3.86 (tt, J = 3.9, 11.7 Hz, 1H), 2.09 - 2.04 (m, 1H), 1.86 (dt, J = 3.0, 12.9 Hz, 2H), 1.74 - 1.52 (m, 3H), 1.44 - 1.12 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.5, 129.1, 117.1, 56.9, 34.6, 25.6, 25.4. Mp 35.0 - 36.0 ˚C.

1-*iso*-Propyl-*1H*-imidazole (4e).[1] (method A) The product was obtained as colorless liquid in 22 % yield after distillation at 104 °C/7mmHg. The NMR data are in accordance with those reported. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38 (s, 1H), 6.89 (s, 2H), 4.19 (heptet, J = 1.2 Hz, 1H), 1.31 (d, J = 1.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.9, 128.8, 116.3, 48.8, 23.5.

1-Mesityl-*1H*-imidazole (4f). (method A). The product was obtained as colorless crystalline solid in 17 % yield after recrystallization from hexanes. The NMR data are in accordance with those reported.[4] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43 (t, J = 1.2 Hz, 1H),

7.23 (t, J = 1.2 Hz, 1H), 6.97 (s, 2H), 7.43 (t, J = 1.2 Hz, 1H), 2.34 (s, 3H), 1.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) □138.9, 137.5, 135.4, 133.5, 129.6, 129.0, 120.1, 21.1, 17.4.

1-(2-Admantyl)-*1H*-imidazole (4g). (method A) The product was obtained as colorless crystalline solid in 36 % yield after recrystallization from hexanes. ^{1}H NMR ($CDCl_3$, 300 MHz) □7.62 (s, 1H), 7.06 (t, J = 1.2 Hz, 1H), 7.01 (t, J = 1.2 Hz, 1H), 4.12 (s, 1H), 2.47 (s, 2H), 2.03 - 1.60 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) □135.2, 128.7, 116.8, 60.6, 37.1, 36,8, 31.6, 31.0, 27.0, 26.7. IR ($CHCl_3$): □= 2909, 2853, 1496, 1455, 1230, 1071 cm^{-1}. Mp 67.0 - 68.5 ˚C. MS (+ESI) *m/z* 203 $[M+H]^+$, 405 $[2M+H]^+$. Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85; found: C, 77.11; H, 9.07; N, 13.83.

1-(2,6-dichlorophenyl)–*1H*-imidazole (4h). (method A) The product was obtained as colorless crystalline in 21 % yield after recrystallization from hexanes. ^{1}H NMR ($CDCl_3$, 500 MHz) □7.56 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.0 Hz, 1H), 7.27 (t, J = 1.0 Hz, 1H), 7.01 (t, J = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) □137.4, 133.9, 133.3, 130.5, 130.0, 129.0, 120.0. IR ($CHCl_3$): □= 3113, 1564, 1505, 1440, 1200, 1076, 1069 cm^{-1}. Mp 97.0 - 98.0 ˚C. MS (+ESI) *m/z* 213 $[M+H]^+$. Anal. Calcd for $C_9H_6C_{l2}N_2$: C, 50.73; H, 2.84; Cl, 33.85; N, 13.15; found: C, 51.02; H, 2.91; Cl, 33.49; N, 13.24.

1-((1*R*, 2*R*, 3*R*, 5*S*)-(2,6,6-Trimethyl-bicyclo[3.1.1]-hept-3-yl))–*1H*-imidazole (4i). (method A) The product was obtained as colorless crystalline solid in 26 % yield after distillation at 140 °C/0.25 mmHg. ^{1}H NMR ($CDCl_3$, 300 MHz) □7.59 (s, 1H), 7.10 (s, 1H), 7.04 (t, J = 1.2 Hz, 1H), 4.44 - 4.36 (m, 1H), 2.67 - 2.52 (m, 2H), 2.23 (m, J = 1.5, 7.2 Hz, 1H), 2.12 - 2.01 (m, 2H), 1.94 (dt, J = 5.7, 1.5 Hz, 1H), 1.30 (s, 3H), 1.15 (d, J = 9.9 Hz, 1H), 1.10 - 1.08 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) □137.0, 130.0, 117.0, 57.1, 47.4, 45.7, 41.5, 38.8, 37.2, 35.0, 27.9, 23.5, 20.5. IR ($CHCl_3$): □= 2902, 1491, 1455, 1375, 1222, 1105, 1076 cm^{-1}. Mp 45.0 - 47.0 ˚C. MS (+ESI) *m/z* 205 $[M+H]^+$, 409 $[2M+H]^+$. Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71; found: C, 76.39; H, 10.04; N, 13.76.

1-(Cyclooctyl)-*1H*-imidazole (4j). (method A) The product was obtained as colorless oil in 29 % yield after chromatography using ethyl acetate as eluent. ^{1}H NMR ($CDCl_3$, 500 MHz) 7.38 (s, 1H), 6.88 (t, J = 1.0 Hz, 1H), 6.81 (t, J = 1.5 Hz, 1H), 4.05 (heptet, J = 4.5 Hz, 1H), 1.86 (m, 4H), 1.67 – 1.61 (m, 2H), 1.56 – 1.41 (m, 8H); ^{13}C NMR ($CDCl_3$, 126 MHz) 135.0, 128.5, 116.7, 57.6, 33.5, 26.4, 25.2, 23.7. IR ($CHCl_3$): = 2981, 2953, 1501, 1460, 1414, 1230, 1112, 1086, 1076 cm^{-1}. MS (+ESI) *m/z* 179 $[M+H]^+$, 357 $[2M+H]^+$. HR-MS: calcd for $C_{11}H_{18}N_2$: 179.1548; found: 179.1539.

1-(Cyclododecyl)-*1H*-imidazole (4k). (method A) The product was obtained as light yellow needle-shaped crystals in 30 % yield after recrystallization from ethyl acetate. ^{1}H NMR ($CDCl_3$, 500 MHz) 7.46 (s, 1H), 6.99 (t, J = 1.0 Hz, 1H), 6.88 (t, J = 1.0 Hz, 1H), 4.13 (quintet, J = 7.0 Hz, 1H), 1.95 - 1.88 (m, 2H), 1.63 - 1.56 (m, 2H), 1.36 - 1.29 (m, 18H); ^{13}C NMR ($CDCl_3$, 126 MHz) 135.9, 128.9, 116.9, 53.8, 31.2, 23.4, 23.3, 23.0, 21.6. IR ($CHCl_3$): = 2930, 2858, 1496, 1470, 1440, 1230, 1076 cm^{-1}. Mp 52.0 - 54.0 °C. MS (+ESI) *m/z* 235 $[M+H]^+$, 469 $[2M+H]^+$. Anal. Calcd for $C_{15}H_{26}N_2$: C, 76.87; H, 11.18; N, 11.95; found: C, 76.94; H, 11.23; N, 11.77.

1-(1-Naphthyl)-*1H*-imidazole (4l). (method B) The product was obtained as a colorless solid after chromatography using 30% hexanes/ethyl acetate as eluent in 85 % yield. ^{1}H NMR ($CDCl_3$, 300 MHz) 7.95 - 7.92 (m, 2H), 7.75 (t, J = 1.2 Hz, 1H), 7.61 - 7.41 (m, 5H), 7.30 (t, J = 1.2 Hz, 1H), 7.24 (t, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 138.2, 134.0, 133.8, 129.4, 129.3, 129.0, 128.1, 127.4, 126.8, 125.0, 123.4, 122.1, 121.5. IR ($CHCl_3$): = 3113, 3062, 1491, 1399, 1306, 1240, 1081, 1035 cm^{-1}. Mp 62.0 - 62.5 °C. MS (+ESI) *m/z* 195 $[M+H]^+$. Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39, H, 5.19, N, 14.42; found: C, 80.18; H, 5.12; N, 14.33.

1-(2-Naphthyl)-*1H*-imidazole (4m). (method B) The product was obtained as a colorless solid after chromatography using 20% hexanes/ethyl acetate as eluent in 54 % yield. ^{1}H NMR ($CDCl_3$, 300 MHz) 8.00 (m, 2H), 7.93 - 7.89 (m, 2H), 7.85 (d, J = 2.7 Hz, 1H), 7.63 - 7.53 (m, 3H), 7.43 (t, J = 1.2 Hz, 1H), 7.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 135.8, 133.5, 132.2, 130.6, 130.1, 127.9, 127.8, 126.5, 120.2, 119.1, 118.4. IR

($CHCl_3$): □ = 3127, 3098, 1600, 1491, 1309, 1062 cm^{-1}. Mp 121.0 - 122.0 °C. MS (+ESI) *m/z* 195 $[M+H]^+$. Anal. Calcd for $C_{15}H_{26}N_2$: C, 76.87; H, 11.18; N, 11.95; found: C, 80.14; H, 5.14; N, 14.24.

1-(3,5-Di-*tert*-butyl-4-methoxyl-phenyl)-*1H*-imidazole (4n). (method B) The product was obtained as a light yellow solid after chromatography using 40% hexanes/ethyl acetate as eluent in 93 % yield. ^1H NMR ($CDCl_3$, 500 MHz) □ 7.78 (t, J = 1.0 Hz, 1H), 7.23 (s, 2H), 7.23(t, J = 1.0 Hz, 1H), 7.20 (t, J = 1.0 Hz, 1H), 3.75 (s, 3H), 1.47 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 158.8, 145.4, 135.9, 132.3, 129.9, 120.3, 118.7, 64.4, 35.9, 31.8. IR ($CHCl_3$): □ = 2960, 2865, 1593, 1491, 1411, 1222, 1069, 1011 cm^{-1}. Mp 84.0 - 86.0 °C. MS (+ESI) *m/z* 287 $[M+H]^+$, 573 $[2M+H]^+$. Anal. Calcd for $C_{18}H_{26}N_2O$: C, 75.48; H, 9.15; N, 9.78; found: C, 75.65; H, 9.17; N, 9.71.

1-(2,6-Diethylphenyl)-*1H*-imidazole (4o).[3] (method C) The product was obtained as colorless needles after recrystallization from hexanes in 58% yield. ^1H NMR ($CDCl_3$, 500 MHz) □ 7.46 (t, J = 1.0 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 1.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H), 6.93 (t, J = 1.0 Hz, 1H), 2.29 (q, J = 7.5 Hz, 4H), 1.08 (t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 141.7, 137.9, 129.3, 129.2 126.56, 120.8, 24.0, 15.5. Mp 73.0 - 74.0 °C (Lit. 72 - 74 °C). MS (+ESI) *m/z* 201 $[M+H]^+$.

1-(2,6-Diisopropylphenyl)-*1H*-imidazole (4p).[3] (method C) The product was obtained as a white solid in 64% yield. ^1H NMR ($CDCl_3$, 300 MHz) □ 7.48 (t, J = 1.2 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.26 (s, 1H), 6.69 (t, J = 1.2 Hz, 1H), 2.42 (heptet, J = 6.9 Hz, 2H), 1.15 (d, J = 6.9 Hz, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 146.5, 138.4, 129.8, 129.3, 123.7, 121.5, 28.1, 24.3. MS (+ESI) *m/z* 229 $[M+H]^+$, 457 $[2M+H]^+$.

1-(2, 5-Di-*tert*-butylphenyl)-*1H*-imidazole (4q). (method C) The product was obtained as a yellow solid in 64% yield. ^1H NMR ($CDCl_3$, 500 MHz) □ 7.60 (s, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.43 (dd, J = 8.5, 7.5 Hz, 1H), 7.17 (s, 1H), 7.08 (s, 1H), 7.02 (d, J = 7.5 Hz, 1H), 1.30 (s, 9H), 1.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) □ 149.8, 143.7, 139.4,

135.4, 128.4, 127.7, 127.4, 126.4, 122.9, 35.3, 34.2, 31.6, 31.1. IR ($CHCl_3$): $\tilde{\nu}$ = 3115, 2962, 2869, 1505, 1405, 1365, 1312, 1252, 1059 cm^{-1}. Mp 120.0 - 121.5 °C. MS (+ESI) *m/z* 257 $[M+H]^+$, 513 $[2M+H]^+$. Anal. Calcd for $C_{17}H_{24}N_2$: C, 79.64; H, 9.44; N, 10.93; found: C, 79.41; H, 9.61; N, 10.90.

General procedure for preparation of ligands 2: The following procedure was used to prepare ligands **2** unless otherwise noted. The oxazolines **3** (1 eq) and imidazoles **4** (1 eq) were dissolved in DMF and heated to 80 °C for 12 h, and the solvent was then removed under vacuum. The white solids obtained were washed five times with diethyl ether and used for complex formation without further purification.

1-(((*S*)-4',5'-Dihydro-2'-(1-admantyl)-4'-oxazolyl)ethyl)-3-*tert*-butylimidazolium iodide (2ab). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4b** (12.5 mg, 0.1 mmol) and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.13(s, 1H), 7.58 (s, 1H), 7.46 (s, 1H), 4.69 (quintet, J = 7.0 Hz, 1H), 4.53 (quintet, J = 7.0 Hz, 1H), 4.11 - 4.05 (m, 1H), 3.94 (t, J = 8.0 Hz, 1H), 2.36 - 2.32 (m, 1H), 1.97 - 1.64 (m, 25H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 174.3, 135.3, 123.0, 119.0, 71.7, 62.7, 60.5, 47.3, 34.5, 36.4, 36.2, 35.1, 30.1, 27.7.

1-(((*S*)-4',5'-Dihydro-2'-(1-admantyl)-4'-oxazolyl)ethyl)-3-diphenylmethylimidazolium iodide (2ac). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4c** (23.4 mg, 0.1 mmol) and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.61 (s, 1H), 7.75 (t, J = 2.0 Hz, 1H), 7.40 - 7.26 (m, 1H), 7.16 (t, J = 2.0 Hz, 1H), 4.58 - 4.45 (m, 2H), 4.29 (t, J = 9.0 Hz, 1H), 4.04 - 3.98 (m, 1H), 3.87 (t, J = 9.0 Hz, 1H), 2.40 - 2.33 (m, 1H), 1.96 - 1.63 (m, 16H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 174.4, 136.6, 136.0, 135.9, 129.3 (three peaks), 128.3, 128.1, 123.1, 121.5, 71.7, 66.8, 62.4, 47.6, 39.4, 36.3, 35.7, 35.1, 27.7.

1-(((*S*)-4',5'-Dihydro-2'-(1-admantyl)-4'-oxazolyl)ethyl)-3-cyclohexylimidazolium iodide (2ad). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4c** (15.0 mg, 0.1 mmol), and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) δ

10.02 (s, 1H), 7.57 - 7.55 (m, 2H), 4.56 (quintet, J = 6.6 Hz, 1H), 4.43 (quintet, J = 6.6 Hz, 1H), 4.35 (dt, J = 3.9, 11.7 Hz, 1H), 4.24 (dd, J = 8.4, 9.3 Hz, 1H), 4.06 - 3.96 (m, 1H), 3.85 (t, J = 8.1 Hz, 1H), 2.31 - 2.16 (m, 3H), 1.94 - 1.57 (m, 21H), 1.41 (tq, J = 3.3, 12.9 Hz, 2H), 1.24 (tt, J = 3.3, 12.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 174.0, 135.0, 122.6, 120.1, 71.5, 62.6, 59.8, 47.1, 39.3, 36.2, 36.1, 33.3, 33.2, 27.5, 24.6, 24.2.

1-(((*S*)-4',5'-Dihydro-2'-(1-adamantyl)-4'-oxazolyl) ethyl)-3-(2,4,6-trimethylphenyl)imidazolium iodide (2af). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4f** (18.6 mg, 0.1 mmol), and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) 9.92 (t, J = 1.5 Hz, 1H), 8.11 (dd, J = 1.5, 2.1 Hz, 1H), 7.34 (dd, J = 1.5, 2.1 Hz, 1H), 7.02 (s, 2H), 4.88 (m, 1H), 4.77 (m, 1H), 4.34 (dd, J = 8.1, 9.0 Hz, 1H), 4.12 (m, 1H), 2.44 (m, 1H), 2.35 (s, 3H), 2.10 (s, 6H), 2.04 (m, 1H), 1.99 (s, 3H), 1.89 (m, 1H), 1.84 (m, 5H), 1.63 - 1.77 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 174.3, 144.2, 137.2, 134.1, 129.8, 128.9, 124.2, 123.3, 71.8, 62.7, 47.8, 39.5, 36.4, 36.3, 35.2, 27.8, 21.0, 17.8.

1-(((*S*)-4',5'-Dihydro-2'-(1-admantyl)-4'-oxazolyl)ethyl)-3-(3, 5-di-*tert*-butyl-4-methoxyl-phenyl)imidazolium iodide (2an). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4n** (28.6 mg, 0.1 mmol), and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) 11.80 (s, 1H), 7.83 (t, J = 1.8 Hz, 1H), 7.53 (t, J = 1.8 Hz, 1H), 7.43 (s, 2H), 4.83 (quintet, J = 6.6 Hz, 1H), 4.69 (quintet, J = 6.6 Hz, 1H), 4.29 (m, 1H), 4.20 - 4.10 (m, 1H), 3.93 (t, J = 7.8 Hz, 1H), 3.70 (s, 3H), 2.42 - 2.36 (m, 1H), 2.07 - 1.84 (m, 4H), 1.75 (d , J = 2.7 Hz, 6H), 1.69 - 1.57 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 171.2, 161.1, 146.8, 135.7, 129.4, 123.7, 120.6, 120.5, 71.8, 64.5, 63.1, 47.9, 39.4, 34.4, 36.3, 36.1, 35.1, 31.8, 27.8.

1-(((*S*)-4',5'-Dihydro-2'-(1-admantyl)-4'-oxazolyl)ethyl)-3-(2,6-diethylphenyl)imidazolium iodide (2ao). The above procedure was followed using iodide **3a** (71.8 mg, 0.2 mmol), imidazole **4o** (40.0 mg, 0.2 mmol) and DMF (0.2 mL). ^{1}H NMR ($CDCl_3$, 500 MHz) 9.95 (s, 1H), 8.12 (s, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.27 (d, J = 8.0 Hz, 2H), 4.98 - 4.76 (m, 2H), 4.33 (t, J = 8.5 H, 1H), 4.09 - 3.99 (m,

2H), 2.50 - 2.26 (m, 5H), 2.04 - 1.98 (m, 4H), 1.83 (s, 6H), 1.73 - 1.65 (m, 6H), 1.147 (q, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz) 174.9, 140.7, 137.7, 132.0, 131.9, 127.6 (two peaks), 124.5, 123.8, 72.1, 62.9, 48.1, 39.8, 36.7, 36.6, 35.5, 28.1, 24.5, 15.2 (two peaks).

1-(((*S*)-4',5'-Dihydro-2'-(1-admantyl)-4'-oxazolyl)ethyl)-3-(2,6-diisopropylphenyl)imidazolium iodide (2ap). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4c** (15.0 mg, 0.1 mmol), and DMF (0.1 mL). 1 ^{1}H NMR ($CDCl_3$, 300 MHz) 9.85 (t, J = 1.8 Hz, 1H), 8.20 (t, J = 1.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.26 (t, J = 1.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 4.80 (quintet, J = 6.6 Hz, 1H), 4.69 (quintet, J = 6.6 Hz, 1H), 4.21 (t, J = 8.4 Hz, 1H), 3.97 (m, 1H), 3.90 (t, J = 7.5 Hz, 1H), 2.33 (quintet, J = 5.1 Hz, 1H), 2.19 (heptet, J = 6.9 Hz, 2H), 1.98 (m, 1H), 1.86 (s, 3H), 1.72 (d, J = 2.7 Hz, 6H), 1.58 (m, 6H), 1.11 - 1.03 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) 173.8. 144.8, 136.7, 131.4, 129.5, 124.1 (two peaks), 124.0, 71.3, 62.1, 47.1, 39.0 36.1, 36.0 (two peaks), 34.7, 28.1 (two peaks), 27.3, 24.0 (four peaks).

1-(((*S*)-4',5'-Dihydro-2'-(1-adamantyl)-4'-oxazolyl) ethyl)-3-(2,5-di-*tert*-butylphenyl)imidazolium iodide (2aq). The above procedure was followed using iodide **3a** (35.9 mg, 0.1 mmol), imidazole **4q** (25.6 mg, 0.1 mmol), and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) 9.86 (bs, 1H), 7.54 (m, 3H), 7.34 (m, 1H), 7.26 (s, 1H), 4.92 (m, 1H), 4.78 (m, 1H), 4.35 (t, J = 9.0 Hz, 1H), 4.12 (m, 1H), 4.03 (m, 1H), 2.50 (m, 1H), 1.99 (bs, 4H), 1.90 (m, 1H), 1.85 (m, 5H), 1.76 (m, 1H), 1.70 (m, 4H), 1.65 (m, 1H), 1.32 (s, 9H), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) 174.5, 151.3, 142.8, 137.9, 132.2, 128.7, 126.7, 125.0, 123.1, 71.9, 62.6, 47.8, 39.7, 39.6, 36.5, 36.4, 35.5, 35.3, 34.5, 31.9, 31.0, 27.8.

1-(((*S*)-4',5'-Dihydro-2'-*tert*-butyl-4'-oxazolyl)ethyl)-3-(1-admantyl)imidazolium iodide (2ba). The above procedure was followed using iodide **3b** (28.3 mg, 0.1 mmol), imidazole **4a** (20.2 mg, 0.1 mmol), and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) 10.18 (t, J = 1.8 Hz, 1H), 7.55 (t, J = 1.8 Hz, 1H), 7.44 (t, J = 1.8 Hz, 1H), 4.73 (quintet, J = 6.9 Hz, 1H), 4.54 (quintet, J = 6.9 Hz, 1H), 4.34 (dd, J = 8.4, 9.3 Hz, 1H), 4.15 - 4.05

(m, 1H), 3.99 (t, J = 8.1 Hz, 1H), 2.40 - 1.19 (m, 1H), 1.76 (t, J = 3.0 Hz, 6H), 1.15 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) 175.0, 135.0, 122.7, 118.0, 72.2, 62.9, 60.7, 47.3, 42.8, 36.3, 35.2, 33.2, 29.3, 27.8.

1-(((*S*)-4',5'-Dihydro-2'-*tert*-butyl-4'-oxazolyl)ethyl)-3-*tert*-butylimidazolium iodide (2bb). The above procedure was followed using iodide 3**b** (28.3 mg, 0.1 mmol), imidazole **4b** (12.5 mg, 0.1 mmol), and DMF (0.1 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) 10.10 (t, J = 1.8 Hz, 1H), 7.59 (t, J = 1.8 Hz, 1H), 7.48 (t, J = 1.8 Hz, 1H), 4.67 (quintet, J = 6.9 Hz, 1H), 4.51 (quintet, J = 6.9 Hz, 1H), 4.32 (dd, J = 8.1, 9.3 Hz, 1H), 4.13 - 4.03 (m, 1H), 3.95 (dd, J = 7.2, 8.1 Hz, 1H), 2.37 - 2.26 (m, 1H), 2.01 - 1.89 (m, 1H), 1.70 (s, 9H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) 174.8, 135.2, 123.0, 119.1, 72.1, 63.0, 60.5, 47.2, 36.1, 33.0, 30.1, 27.7.

1-(((*S*)-4',5'-Dihydro-2'-(*tert*-butyl)-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide (2bp). The above procedure was followed using iodide **3b** (0.57 g, 2.0 mmol), imidazole **4p** (0.58 mg, 2.5 mmol), and DMF (2.0 mL). ^{1}H NMR ($CDCl_3$, 300 MHz) 8.75 (s, 1H), 7.47 - 7.30 (m, 4H), 7.20 (s, 1H), 4.66 - 4.45 (m, 1H), 4.38 - 4.20 (m, 2H), 3.86 - 3.60 (m, 2H), 2.20 - 2.00 (m, 3H), 1.82 - 1.65 (m, 1H), 1.10 (m, 21H); ^{13}C NMR ($CDCl_3$, 75 MHz) 176.7, 162.8, 162.2, 161.6, 160.9, 145.4, 137.1, 135.0, 132.9, 126.6, 125.5, 125.3, 125.2, 122.9, 117.7, 72.3, 62.0, 48.3, 35.2, 29.1, 29.0, 27.7, 24.3, 24.1, 23.7.

1-(((*S*)-4',5'-Dihydro-2'-(diphenylmethyl)-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide (2cp). The above procedure was followed using iodide **3c** (0.3g, 0.77 mmol), imidazole **4p** (0.26 g, 1.2 mmol), and DMF (1.0 mL). ^{1}H NMR (d^6-DMSO, 300 MHz) 9.60 (s, 1H), 8.20 (s, 1H), 8.19 (s, 1H), 7.70 - 7.50 (m, 3H), 7.45 - 7.20 (m, 10 H), 5.17 (s, 1H), 4.55 - 4.35 (m, 3H) 4.20 - 3.99 (m, 2H), 2.40 - 2.05 (m, 4H), 1.25 - 1.05 (m, 12H).

1-(((*S*)-4',5'-Dihydro-2'-phenyl-4'-oxazolyl) ethyl)-3-(2,6)-diisopropylphenyl)imidazolium iodide (2dp). The above procedure was followed using

iodide **3d** (2.5g, 8.3 mmol), imidazole **4p** (2.7 g, 8.3 mmol), and DMF (5.0 mL). ^{1}H NMR (d^6-DMSO, 300 MHz) 9.62 (s, 1H), 8.21 (s, 1H), 8.12 (s, 1H), 7.88 - 7.42 (m, 8H), 4.58 - 4.47 (m, 3H), 4.18 - 4.15 (m, 2H), 2.4 - 2.05 (m, 4H), 1.10 (t, J = 6.6 Hz, 12H); ^{13}C NMR (d^6-DMSO, 75 MHz) 162.7, 145.2, 137.6, 131.6, 131.4, 130.5, 128.5, 127.8, 127.1, 125.0, 124.3, 123.5, 72.0, 61.9, 47.1, 34.9, 28.0, 22.1.

General Procedure for Synthesis of 5. Imidazolium salt **2** was added to a Schlenk tube along with 1.5 equivalents lithium *tert*-butoxide and 0.5 equivalents of $[Ir(COD)Cl]_2$. The vessel was evacuated and flushed with N_2 three times. Enough THF was syringed in to make the solution 0.03 M in imidazolium salt. The mixture was heated to 70 ˚C in an oil bath and stirred for 16 h. After cooling to room temperature, the volatiles were removed *in vacuo* and 1.5 equivalents of NaBARF[5,6] dissolved in 5 mL CH_2Cl_2 was added. Water (5 mL) was added and the mixture was stirred vigorously for 15 min. The organic layer was removed and the aqueous layer was washed with an additional 5 mL CH_2Cl_2. The organic layers were combined, dried (Na_2SO_4) and the volatiles were removed *in vacuo*. The residue was chromatographed using a short silica column and 10 % hexanes/CH_2Cl_2 as the eluent.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(*tert*-butyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5ab). The above procedure was followed using **2ab** (58 mg, 0.12 mmol), LiO^{t}Bu (14 mg, 0.18 mmol), $[Ir(COD)Cl]_2$ (40 mg, 0.06 mmol) and NaBARF (160 mg, 0.18 mmol). The complex was isolated as a yellow solid (51 mg, 28 %); ^{1}H NMR ($CDCl_3$, 300 MHz) 7.72 (bs, 8H), 7.55 (bs, 4H), 7.01 (d, J = 2.4 Hz, 1H), 7.75 (d, J = 2.4 Hz, 1H), 5.03 (dd, J = 9.9, 14.7 Hz, 1H), 4.89 (m, 1H), 4.55 (m, 1H), 4.33 (t, J = 9.6 Hz, 1H), 4.12 (dd, J = 6.9, 14.7 Hz, 1H), 3.91 (dd, J = 4.8, 9.3 Hz, 1H), 3.71 (dt, J = 2.1, 7.2 Hz, 1H), 3.50 (m, 1H), 3.14 (dt, J = 4.2, 7.8 Hz, 1H), 2.13 - 2.49 (m, 3H), 1.87 - 2.12 (m, 6H), 1.86 - 1.96 (m, 3H), 1.84 (s, 9H), 1.72 - 1.83 (m, 7H), 1.58 - 1.70 (m, 4H), 1.39 - 1.56 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) 179.8, 171.4, 161.9 (q, J = 49.8 Hz), 135.0, 129.1 (qq, J = 2.7, 31.4 Hz), 124.7 (q, J = 273 Hz), 122.3, 120.8, 117.7 (heptet, J = 4.0 Hz), 82.9, 82.6, 72.5, 70.8, 65.2, 59.7, 53.6, 52.8, 50.9, 40.0, 38.2, 36.1,

35.8, 35.4, 32.9, 32.1, 29.9, 29.8, 27.4, 27.0; MS (+FAB) 657 $[C_{30}H_{46}IrN_3O]^+$; X-ray quality crystals were grown by slow diffusion of pentane into a $CDCl_3$ solution of the complex.

(η^4-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(diphenylmethyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5ac). The above procedure was followed using **2ac** (59 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as an orange solid (130 mg, 80%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (bs, 8H), 7.55 (bs, 4H), 7.33 - 7.41(m, 6H), 7.05 (s, 1H), 7.00 (m, 2H), 6.93 (m, 2H), 6.85 (d, J = 2.0 Hz, 1H), 6.84 (d, J = 2 Hz, 1H), 5.07 (dd, J = 10.0, 15.0 Hz, 1H), 4.71 (m, 1H), 4.36 (t, J = 9.5 Hz, 1H), 4.34 (m, 1H), 4.14 (dd, J = 10.0, 15.0 Hz, 1H), 3.95 (dd, J = 5.0, 9.0 Hz, 1H), 3.78 (m, 1H), 3.49 (dt, J = 1.5, 7.5 Hz, 1H), 3.20 (dt, J = 4.5, 7.5 Hz, 1H), 2.38 (m, 1H), 2.24 (m, 1H), 1.97 - 2.17 (m, 10H), 1.92 (m, 1H), 1.18 (m, 3H), 1.56 - 1.74 (m, 6H), 1.42 - 1.54 (m, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 179.5, 175.0, 161.9 (q, J = 49.8 Hz), 139.9, 138.6, 135.0,129.5, 129.3, 129.1 (qq, J = 2.7, 31.4 Hz), 128.3, 127.0, 124.7 (q, J = 273 Hz), 122.3, 121.5, 117.7 (heptet, J = 4.0 Hz), 84.8, 82.2, 73.0, 69.8, 67.4, 65.0, 55.0, 49.8, 39.5, 38.6, 35.9, 35.5, 34.9, 31.2, 30.6, 30.5, 29.9, 27.6; MS (+ESI) 767 $[C_{39}H_{48}IrN_3O]^+$.

(η^4-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(cyclohexyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5ad). The above procedure was followed using **2ad** (51 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as a yellow solid (106 mg, 68%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (bs, 8H), 7.55 (bs, 4H), 6.80 (d, J = 2.0 Hz,6.71 (d, J = 2.0 Hz, 1H), 4.95 (dd, J = 10.5, 14.4 Hz, 1H), 4.63 (m, 1H), 4.41 (tt, J = 3.5, 12.0 Hz, 1H), 4.29 (t, J = 9.0 Hz, 1H), 4.20 (m, 1H), 4.04 (dd, J = 7.0, 14.5 Hz), 3.79 (m, 1H), 3.66 (m, 1H), 3.47 (dt, J = 4.5, 7.5 Hz, 1H), 2.42 (m, 1H), 2.20 - 2.32 (m, 2H), 2.12 - 2.18 (m, 3H), 1.94 - 2.12 (m, 7H), 1.89 (m, 2H), 1.72 - 1.86 (m, 8H), 1.61 - 1.72 (m, 6H), 1.48 - 1.60 (m, 4H), 1.34 - 1.44 (m, 2H), 1.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 126

MHz) δ 179.0, 172.5, 161.9 (q, J = 49.8 Hz), 135.0, 129.1 (qq, J = 2.7, 31.4 Hz), 124.7 (q, J = 273 Hz), 122.5, 117.7 (heptet, J = 4.0 Hz), 117.6, 84.2, 81.4, 73.0, 69.4, 64.3, 60.3, 55.5, 49.3, 39.7, 38.2, 37.0, 36.1, 35.4, 35.1, 34.1, 31.3, 30.9, 30.5, 29.9, 27.8, 27.7, 26.0, 25.6, 25.0; MS (+ESI) 683 $[C_{32}H_{48}IrN_3O]^+$; X-ray quality crystals were grown by slow diffusion of pentane into a $CDCl_3$ solution of the complex.

(η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(2,4,6-trimethylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5af). The above procedure was followed using **2af** (100 mg, 0.18 mmol), LiO^{t}Bu (22 mg, 0.27 mmol), $[Ir(COD)Cl]_2$ (62 mg, 0.09 mmol) and NaBARF (239 mg, 0.27 mmol). The complex was isolated as an orange solid (213 mg, 75 %); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (bs, 8H), 7.55 (bs, 4H), 7.01 (s, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.39 (s, 1H), 6.71 (d, J = 2.0 Hz, 1H), 5.32 (dd, J = 9.5, 15.0 Hz, 1H), 4.57 (m, 1H), 4.44 (t, J = 9.5 Hz, 1H), 4.24 (dd, J = 8.0, 14.5 Hz, 1H), 4.00 (m, 1H), 3.94 (m, 1H), 3.86 (dd, J = 7.0, 9.0 Hz, 1H), 3.56 (dt, J = 2.0, 7.0 Hz, 1H), 3.42 (m, 1H), 2.36 (s, 3H), 2.17 - 2.28 (m, 4H), 2.02 - 2.16 (m, 3H), 1.98 (s, 6H), 1.85 - 1.94 (m, 4H), 1.77 - 1.84 (m, 6H), 1.56 - 1.73 (m, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 179.3, 174.1, 161.9 (q, J = 49.8 Hz), 140.5, 135.3, 135.0, 129.5, 129.1 (qq, J = 2.7, 31.4 Hz), 129.0, 128.0, 124.7 (q, J = 273 Hz), 123.7, 122.5, 117.7 (heptet, J = 4.0 Hz), 83.7, 76.3, 72.5, 70.3, 62.9, 61.9, 49.7, 38.8, 38.4, 36.1, 36.0, 33.2, 32.1, 30.5, 29.9, 28.4, 27.7, 21.2, 19.7, 17.8; MS (+ESI) 719 $[C_{35}H_{48}IrN_3O]^+$.

(η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(3,5-di-*tert*-butyl-4-methoxyphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5an). The above procedure was followed using **2an** (63 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as an orange solid (115 mg, 69%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (bs, 8H), 7.55 (bs, 4H), 7.13 (s, 2H), 6.96 (d, J = 2.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 5.07 (dd, J = 11.5, 14.5 Hz, 1H), 4.64(m, 1H), 4.25 (t, J = 9.0 Hz, 1H), 4.12 (dd, J = 7.0, 14.5 Hz, 1H), 4.01 (m, 1H), 3.98 (dd, J = 3.5, 9.0 Hz, 1H), 3.89 (bt, J = 6.0 Hz, 1H), 3.76 (m, 1H), 3.75 (s, 3H), 3.25 (m, 1H), 2.21 -

2.35 (m, 2H), 2.01 - 2.15 (m, 3H), 1.94 - 2.02 (m, 7H), 171 - 1.82 (m, 7H), 1.59 - 1.67 (m, 4H), 1.44 (s, 18H), 1.29 - 1.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) 179.3, 173.8, 161.9 (q, J = 49.8 Hz), 145.6, 135.0, 133.8, 129.1 (qq, J = 2.7, 31.4 Hz), 125.8, 125.0, 124.7 (q, J = 273 Hz), 124.4, 122.0, 117.7 (heptet, J = 4.0 Hz), 83.5, 79.9, 72.7, 69.6, 65.0, 63.8, 58.3, 49.9, 39.7, 37.4, 36.2, 35.8, 35.6, 34.5, 31.8, 31.5, 30.5, 30.2, 30.1, 29.9, 27.5, 27.4, 22.9, 21.4,; MS (+ESI) 819 $[C_{41}H_{60}IrN_3O_2]^+$.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-admantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diethylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5ao). The above procedure was followed using crude **2ao**, LiO^{t}Bu (16.0 mg, 0.2 mmol), $[Ir(COD)Cl]_2$ (67.2 mg, 0.1 mmol) and NaBARF (265.9 mg, 0.3 mmol). The complex was isolated as a yellow solid (210 mg, 66%)**;** ^{1}H NMR ($CDCl_3$, 500 MHz) 7.78 (s, 8H), 7.56 (s, 4H), 7.45 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.15 (d, J = 7.5 Hz,1H), 6.95 (d, J = 1.5 Hz, 1H), 6.83 (d, J = 1.5 Hz, 1H), 5.31 (dd, J = 9.5, 14.5 Hz, 1H), 4.56 (m, 1H), 4.43 (t, J = 10.0 Hz, 1H), 4.24 9dd, J = 8.0, 14.5 Hz, 1H), 3.94 (m, 1H), 3.85 (dt, J = 3.5, 7.5 Hz, 1H), 3.78 (dt, J = 2.5, 7.5 Hz, 1H), 3.59 (dt, J = 3.5, 7.5 Hz, 1H), 3.41 (dt, J = 3.5, 7.5 Hz, 1H), 2.49 (sextet, J = 7.5 Hz), 2.363 (sextet, J = 7.5 Hz, 1H), 2.22 - 1.57 (m, 27H), 1.12 (t, J = 7.5 Hz), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) 179.2, 174.1, 161.7 (q, J = 49.6 Hz), 141.7, 141.6, 135.5, 134.8, 130.8, 128.9 (qq, J = 2.7, 31.4 Hz), 127.0 (two peaks),124.5, 124.5 (q, J = 273.7 Hz), 121.7, 117.5 (heptet, J = 4 Hz), 83.6, 76.1, 72.3, 70.1, 62.6, 61.5, 50.0, 38.5, 38.3, 36.0 (two peaks), 33.0, 31.7, 30.3, 28.0, 27.4, 26.4, 24.4, 16.7, 15.4. MS (+ESI) 732 $[C_{36}H_{49}IrN_3O]^+$.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5ap). The above procedure was followed using **2ap** (135 mg, 0.23 mmol), LiO^{t}Bu (28 mg, 0.34 mmol), $[Ir(COD)Cl]_2$ (77 mg, 0.12 mmol) and NaBARF (301 mg, 0.34 mmol). The complex was isolated as an orange solid (240 mg, 64%); ^{1}H NMR ($CDCl_3$, 300 MHz) 7.72 (bs, 8H), 7.55 (bs, 4H), 7.49 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 7.8, 1.2 Hz, 1H), 7.22 (dd, J = 7.8, 1.5 Hz, 1H), 6.90 (d, J = 1.8 Hz,

1H), 6.78 (d, J = 1.8 Hz, 1H), 4.78 (m, 1H), 4.41 (t, J = 10.2 Hz, 1H), 4.01 (m, 3H), 3.89 (dd, J = 9.0, 7.1 Hz, 1H), 3.60 (m, 1H), 3.00 (m, 1H),1.61 - 2.19 (m, 21H), 1.56 (s, 3H), 1.43 (d, J = 6.9 Hz, 3H), 1.27 (m, 2H), 1.22 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 Hz) 179.5, 161.9 (q, J = 49.8 Hz), 146.8, 144.9, 135.0, 131.2, 129.1 (qq, J = 31.4, 2.7 Hz), 127.1, 124.7 (q, J = 271 Hz), 124.7, 124.5, 117.7 (heptet, J = 4.0 Hz), 84.0, 77.4, 71.3, 62.7, 39.5, 36.5, 36.0, 34.9, 31.8, 30.5, 29.4, 28.6, 27.7, 27.1, 25.5, 25.2, 23.1, 22.9, 22.5, 14.3; MS (+FAB) 761 $[C_{38}H_{53}IrN_3O]^+$; Anal. Calcd for ($C_{70}H_{65}BF_{24}IrN_3O$): C, 51.79; H, 4.03; N, 2.59; found: C, 51.88; H, 4.25; N, 2.59.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(2,5-di-*tert*-butylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5aq). The above procedure was followed using **2aq** (35 mg, 0.057 mmol), LiO^{t}Bu (7 mg, 0.085 mmol), $[Ir(COD)Cl]_2$ (19 mg, 0.028 mmol) and NaBARF (75 mg, 0.085 mmol). The complex was isolated as an orange solid as a mixture of two rotational isomers (56 mg, 60%); ^{1}H NMR ($CDCl_3$, 500 MHz) 7.72 (bs, 8H), 7.55 (bs, 4H), 7.48 - 7.54 (m, 2H), 7.01 (d, J = 2.0 Hz, 0.5H), 6.70 (s, 0.5H), 6.99 (s, 0.5 H), 6.89 (d, J = 2.0 Hz, 0.5H), 6.86 (d, J = 2.0 Hz, 0.5H), 5.30 (dd, J = 9.5, 14.5 Hz, 0.5H), 4.94 (bs, 0.5H), 4.54 (m, 0.5H), 4.45 (t, J = 10.5 Hz, 0.5H), 4.26 (bs, 2H), 4.14 (dd, J = 8.0, 14.5 Hz, 1H), 4.01 (m, 2H), 3.76 (m, 1H), 3.46 (bs, 0.5H), 3.41 (m, 0.5H), 2.11 - 2.28 (m, 6H), 1.85 - 2.10 (m, 5H), 1.77 - 1.84 (m, 5H), 1.62 - 1.76 (m, 7H), 1.45 (s, 3H), 1.41 (s, 4.5H), 1.32 (s, 4.5 H), 1.08 (s, 4.5 H), 1.02 (s, 4.5H); ^{13}C NMR ($CDCl_3$, 126 MHz) 179.5, 174.9, 161.9 (q, J = 49.8 Hz), 150.3, 149.8, 144.0, 143.4, 136.0, 135.2, 135.0, 130.2, 129.1 (qq, J = 2.7, 31.4 Hz), 128.7, 128.5, 127.9, 127.2, 126.6, 126.1, 125.7, 124.7 (q, J = 273 Hz), 122.1, 121.3, 117.7 (heptet, J = 4.0 Hz), 83.2, 82.2, 75.4, 72.5, 70.3, 63.5, 62.3, 56.9, 49.6, 39.6, 38.6, 36.3, 36.1, 36.0, 35.7, 34.7, 34.5, 32.9, 32.2, 31.9, 31.5, 31.3, 31.1, 30.5, 30.1, 29.9, 28.7, 27.6, 27.4; MS (+ESI) 789 $[C_{40}H_{58}IrN_3O]^+$.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-*tert*-butyl-4-5-dihydrooxazolyl)-ethyl]-3-(1-adamantyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5ba). The above procedure was followed using **2ba**

(28 mg, 0.057 mmol), LiO^{t}Bu (7 mg, 0.085 mmol), $[Ir(COD)Cl]_2$ (19 mg, 0.028 mmol) and NaBARF (75 mg, 0.085 mmol). The complex was isolated as a yellow solid (54 mg, 62%); ^{1}H NMR ($CDCl_3$, 500 MHz) 7.72 (bs, 8H), 7.55 (bs, 4H), 7.1 (d, J = 2.0 Hz, 1H), 6.76 (d, J = 2.0 Hz, 1H), 5.15 (dd, J = 10.0, 15.0 Hz, 1H), 4.86 (m, 1H), 4.32 (m, 1H), 4.31 (t, J = 9.5 Hz, 1H), 4.13, (dd, J = 7.5, 14.5 Hz, 1H), 3.93 (dd, J = 4.0, 9.0 Hz, 1H), 3.73 (bt, J = 6.0 Hz, 1H), 3.60 (m, 1H), 3.46 (dt, J = 4.5, 8.0 Hz, 1H), 2.66 (bd, J = 10.0 Hz, 2.24 - 2.42 (m, 6H), 2.12 - 2.23 (m, 4H), 1.98 - 2.10 (m, 3H), 1.87 (m, 1H), 1.84 (bd, J = 13.0 Hz, 3H), 1.74 (bd, J = 12.0 Hz, 3H), 1.44 - 1.59 (m, 3H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) 180.3, 170.7, 161.9 (q, J = 49.8 Hz), 135.0, 129.1 (qq, J = 2.7, 31.4 Hz), 125.7, 124.7 (q, J = 273 Hz), 121.9, 119.2, 117.7 (heptet, J = 4.0 Hz), 82.5, 73.0, 71.0, 65.4, 60.3, 54.1, 50.8, 45.1, 37.9, 35.8, 35.1, 34.1, 31.8, 30.5, 30.0, 28.9, 27.1; MS (+ESI) 657 $[C_{30}H_{46}IrN_3O]^+$.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-*tert*-butyl-4-5-dihydrooxazolyl)-ethyl]-3-(*tert*-butyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5bb). The above procedure was followed using **2bb** (41 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as a yellow solid (52 mg, 36%); ^{1}H NMR ($CDCl_3$, 500 MHz) 7.72 (bs, 8H), 7.55 (bs, 4H), 7.00 (d, J = 2.0 Hz, 1H), 6.76, (d, J = 2.0 Hz, 1H), 5.16 (dd, J = 10.5, 14.5 Hz, 1H), 4.83 (m, 1H), 4.34 (m, 1H), 4.30 (t, J = 9.5 Hz, 4.13 (dd, J = 7.0, 14.5 Hz, 1H), 3.94 (dd, J = 4.0, 9.0 Hz, 1H), 3.75 (m, 1H), 3.61 (m, 1H), 3.33 (dt, J = 4.5, 7.5 Hz1H), 2.38 (m, 1H), 2.28 (m, 1H), 2.18 (m, 1H), 1.99 - 2.10 (m, 3H), 1.90 (m, 1H), 1.81 (s, (H), 1.44 - 1.61 (m, 4H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) 180.3, 171.1, 161.9 (q, J = 49.8 Hz), 135.0, 129.1 (qq, J = 2.7, 31.4 Hz), 124.7 (q, J = 273 Hz), 122.3, 120.6, 117.7 (heptet, J = 4.0 Hz), 83.0, 82.9, 73.0, 70.9, 65.7, 59.6, 54.5, 50.7, 37.8, 35.3, 34.0, 33.0, 31.9, 29.8, 28.7, 27.1; MS (+ESI) 579 $[C_{24}H_{40}IrN_3O]^+$.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-*tert*-butyl-4-5-dihydrooxazolyl)-ethyl]-3-(diphenylmethyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5bc). The above procedure was followed using **2bc**

(52 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as a yellow solid (94 mg, 61%); ^{1}H NMR ($CDCl_3$, 500 MHz) 7.72 (bs, 8H), 7.55 (bs, 4H), 7.32 - 7.41 (m, 5H), 7.12 (bs, 2H), 7.11 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 6.85 (bs, 3H), 5.31 (s, 1H), 5.06 (dd, J = 10.5, 14.5 Hz, 1H), 4.71 (m, 1H), 4.30 (t, J = 9.0 Hz, 1H), 4.13 (m, 2H), 3.96 (dd, J = 4.5, 9.0 Hz, 1H), 3.79 (m, 1H), 3.70 (bt, J = 6.5 Hz, 1H), 3.40 (m, 1H), 2.38 (m, 1H), 2.30 (m, 1H), 2.15 (m, 1H), 1.99 - 2.12 (m, 4H), 1.41 - 1.65 (m, 6H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) 178.0, 174.1, 161.9 (q, J = 49.8 Hz), 140.0, 138.0, 135.0, 129.5, 129.4, 129.1 (qq, J = 2.7, 31.4 Hz), 128.5, 127.1, 125.8, 124.7 (q, J = 273 Hz), 122.4, 121.4, 117.7 (heptet, J = 4.0 Hz), 85.3, 84.2, 73.3, 70.1, 67.4, 65.3, 55.2, 53.6, 49.8, 37.9, 35.5, 34.4, 33.2, 31.4, 30.5, 30.3, 29.9, 28.3, 27.3; MS (+ESI) 689 $[C_{33}H_{42}IrN_3O]^+$.

(^{4}-1,5-Cyclooctadiene)(1-[(4*S*)-(2-*tert*-butyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5bp). The above procedure was followed using **2bp** (153 mg, 0.3 mmol), LiO^{t}Bu (36 mg, 0.45 mmol), $[Ir(COD)Cl]_2$ (101 mg, 0.15 mmol) and NaBARF (399 mg, 0.45 mmol). The complex was isolated as an orange solid (403 mg, 87%)**;** ^{1}H NMR ($CDCl_3$, 300 MHz) 7.73 (bs, 8H), 7.55 (bs, 4H), 7.49 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 7.8, 1.2 Hz, 1H), 7.21 (dd, J = 7.8, 1.5 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 4.96 (m, 1H), 4.70 (m, 1H), 4.36 (t, J = 9.6 Hz, 1H), 4.16 (m, 1H), 3.98 (dd, J = 9.6, 4.9 Hz, 1H), 3.61 - 3.83 (m, 3H), 3.15 (m, 1H), 2.94 (m,1H), 1.94 - 2.21 (m, 3H), 1.79 (m, 3H), 1.76 (h, J = 6.9 Hz, 1H), 1.43 - 1.69 (m, 2H), 1.38 (d, J = 6.9 Hz, 3H), 1.34 (s, 9H), 1.28 (m, 2H) 1.18 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 75 MHz) 180.1, 162.3 (q, J = 49.8 Hz), 147.5, 144.8, 135.0, 131.3, 129.2 (qq, J = 31.4, 2.7 Hz), 127.2, 124.8 (q, J = 271 Hz), 124.5, 124.2, 122.1, 117.7 (heptet, J = 4.0 Hz), 84.9, 81.3, 77.4, 72.5, 70.1, 62.6, 60.2, 49.9, 36.5, 34.0, 33.8, 31.7, 29.5, 29.0, 28.7, 28.6, 28.5, 27.2, 26.0, 23.0, 22.8, 22.3, 14.3; MS (+FAB) 683 $[C_{32}H_{47}IrN_3O]^+$; Anal. Calcd for ($C_{64}H_{59}BF_{24}IrN_3O$): C, 49.95; H, 3.85; N, 2.72; found: C, 49.89; H, 3.85; N, 2.72.

(η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-diphenylmethyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5cp). The above procedure was followed using **2cp** (40 mg, 0.065 mmol), LiO^{t}Bu (8 mg, 0.098 mmol), $[Ir(COD)Cl]_2$ (22 mg, 0.033 mmol) and NaBARF (82 mg, 0.098 mmol). The complex was isolated as an orange solid (49 mg, 46%)**;** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (bs, 8H), 7.55 (bs, 4H), 7.48 (t, J = 7.5 Hz, 1H), 7.45 (s, 5H), 7.24 (m, 5H), 7.08 (d, J = 1.8 Hz, 1H), 6.86 (d, J= 1.8 Hz, 1H), 6.49 (dd, J = 7.2, 0.9 Hz, 2H), 5.41 (s, 1H), 5.03 (m, 1H), 4.56 (m, 1H), 4.46 (t, J = 9.0 Hz, 1H), 4.20 (m, 2H), 3.99 (m,1H), 3.71 (m, 2H), 2.88 (m, 1H), 2.81 (heptet, J=7.2 Hz, 1H), 1.76 - 2.24 (m, 7H), 1.62 (m, 2H),1.24 - 1.32 (m, 1H), 1.21 (d, J = 6.9 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 1.05 (d, J = 6.6 Hz, 3H), 0.83 - 0.99 (m, 1H), 0.35 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.6, 173.3, 162.0 (q, J = 49.8 Hz), 147.4, 145.1, 137.1, 135.1, 134.5, 131.2, 129.8, 129.7, 129.5 (qq, J = 31.4, 2.7 Hz), 129.3, 129.2, 128.8, 128.4, 127.2, 126.9, 126.7,124.8 (q, J = 271 Hz), 124.5, 124.2, 121.9, 117.8 (heptet, J = 3.5 Hz), 84.4, 82.5, 77.3, 74.7, 69.3, 65.9, 63.6, 52.0, 50.2, 36.8, 34.3, 31.7, 30.6, 28.9, 28.4, 26.8, 25.2, 22.9, 22.4, 14.3; MS (+FAB) 793 $[C_{41}H_{49}IrN_3O]^+$.

(η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-phenyl-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (5dp). The above procedure was followed using **2dp** (53 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Ir(COD)Cl]_2$ (34 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as a yellow-orange solid (149 mg, 95%); This solid was composed of **5dp** (81%) and **5dp'** (19%). **5dp**; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.65 (dd, J = 8.4, 0.9 Hz, 2H), 7.73 (bs, 8H), 7.65 (m, 1H), 7.55 (bs, 4H), 7.37 (m, 3H), 7.11 (dd, J = 7.5, 1.5 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 6.87 (d, J = 2.1 Hz, 1H), 5.41 (dd, J = 14.7, 8.7 Hz, 1H)' 4.70 (m, 2H), 4.34 (dd, J = 14.4, 7.8 Hz, 1H), 4.07(m, 1H), 3.93 (m, 2H), 3.55 (m, 1H), 1.61-2.14 (m, 11H), 1.57 (s, 3H), 1.28 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.6 Hz, 3H), 0.70 (d, J = 6.6 Hz, 3H), 0.36 (d, J = 6.6 Hz, 3H); MS (+FAB) 702 $[C_{34}H_{43}IrN_3O]^+$. ^{13}C NMR was not obtained for **5dp**, because it is converted to **5dp'** when sitting in solution. Crystals suitable for X-ray analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **5dp'**.

(η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene)rhodium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (6ap). The above procedure was followed using **2ap** (59 mg, 0.1 mmol), LiO^{t}Bu (12 mg, 0.15 mmol), $[Rh(COD)Cl]_2$ (25 mg, 0.05 mmol) and NaBARF (133 mg, 0.15 mmol). The complex was isolated as a yellow solid (141 mg, 92%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (bs, 8H), 7.55 (bs, 4H), 7.49 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 6.91 (d, J = 1.5 Hz, 1H), 6.78 (d, J = 1.5 Hz, 1H), 4.85 (m, 1H), 4.45 (m, 1H), 4.40 (t, J = 10 Hz, 1H), 4.10 (m, 2H), 3.89 (t, J = 8.5 Hz, 1H), 3.13 (m, 1H), 3.04 (m, 1H), 2.37 (m, 2H), 2.10 (bs, 3H), 1.88 (m, 3H), 1.81 (m, 3H), 1.69 (m, 3H), 1.52 (m, 2H), 1.45 (s, 1H), 1.28 (s, 2H), 1.17 (d, J = 7.0 Hz, 3H), 1.04 (m, 3H), 0.98 (d, J = 6.5 Hz, 3H); Crystals were grown by slow diffusion of pentane into a solution of **6ap** in chloroform. This originally produced an oil to which neat hexanes was added. Crystals suitable for X-ray diffraction analysis formed over time.

Synthesis of Carbonyl Complexes (7) and (8). Complexes **5ap** and **5ad** (*ca* 2 mg) were each dissolved in $CDCl_3$ (0.5 mL). The solution stirred under 1 atm of CO for 3h. ^{1}HNMR showed complete loss of the 1,5-cyclooctadiene ligand and the IR showed two carbonyl bands for each complex at 2081 and 2016 cm^{-1} for **7** and at 2082 and 2015 cm^{-1} for **8**.

General Hydrogenation Procedure. Alkene substrate (0.2 mmol), iridium complex **5** (0.0012 mmol, 0.6 mol%), and CH_2Cl_2 (100 μL) were added to a test tube containing a small stir bar. The tube was placed in a bomb which was pressurized to 50 bar with hydrogen(deuterium). The mixture was stirred at 300 rpm's for 2 h. The bomb was then vented, and the reaction mixtures were passed through a short silica plug using 30% EtOAc/hexanes as the eluent. The product solutions were collected in vials containing a known amount of dodecane. The yield and *ee* of the reaction were then determined by GC analysis using a chiral column prepared by Vigh *et al.*;[7] (30.7 m x 0.25 mm, 30% β-*tert*-butyldimethylsilyl cyclodextrin derivative in OV-1701-vi of 0.25 μm film thickness).

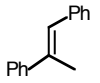
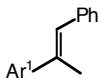
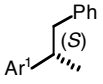
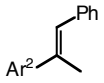
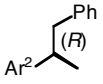
For the alkenes that gave marked variations of *ee* with pressure and temperature, the geometry of the reaction vessel can have effects on the data obtained. The data quoted in this paper is for tubes with approximately 1 cm diameter.

Procedure for Pressure Effects. Alkene substrate (0.2 mmol), iridium complex **5** (0.0012 mmol, 0.6 mol%) were added to a test tube containing a small stir bar. The test tube was sealed with a septum and was then evacuated and flushed with nitrogen three times. Then, dry/degassed CH_2Cl_2 (100 μL) was added. The septum was removed and the tube was quickly placed in a bomb. The bomb was flushed with nitrogen, then pressurized with the desired amount of hydrogen, and the mixture was stirred at 300 rpm's for 2 h. The bomb was vented, and the reaction mixture was passed through a short silica plug using 30% EtOAc/hexanes as the eluent. The product solution was collected in a vial containing a known amount of dodecane. The yield and *ee* of the reaction were then determined by GC analysis using a chiral column prepared by Vigh *et al.*;[7] (30.7 m x 0.25 mm, 30% β-*tert*-butyldimethylsilyl cyclodextrin derivative in OV-1701-vi of 0.25 μm film thickness).

Procedure for Temperature Effects. Alkene substrate (0.2 mmol), iridium complex **5** (0.0012 mmol, 0.6 mol%) were added to a test tube containing a small stir bar. The test tube was sealed with a septum and was then evacuated and flushed with nitrogen three times. Then, dry/degassed CH_2Cl_2 (100 μL) was added. The septum was removed and the tube was quickly placed in a bomb already at the desired temperature. The bomb was flushed with nitrogen and then pressurized to 50 bar with hydrogen. The bomb was placed in an isothermal bath at the desired temperature. The mixture was stirred at 300 rpm's for 2 h. The pressure was released, and the reaction mixture was passed through a short silica plug using 30% EtOAc/hexanes as the eluent. The product solution was collected in a vial containing a known amount of dodecane. The yield and *ee* of the reaction were then determined by GC analysis using a chiral column prepared by Vigh *et al.*;[7] (30.7 m x 0.25 mm, 30% β-*tert*-butyldimethylsilyl cyclodextrin derivative in OV-1701-vi of 0.25 μm film thickness).

Assignments of Absolute Configurations. The absolute configuration of 2-(2'-naphthyl)-1-phenylpropane was determined by comparison of the optical rotation with the one reported by Givens.[8] The absolute configuration of both 1,2-diphenylpropane and 2-(4'-methoxyphenyl)butane were determined by comparison of their optical rotations with those reported by Buchwald.[9] We were unable to find a literature optical rotation (or similar data) for 2-(4'-methoxyphenyl)-1-phenylpropane; the configuration shown in the text is tentatively assigned on the basis that the material probably has the same sign of rotation as 1,2-diphenylpropane (*vide supra*). The order of elution of the enantiomers in chiral GC analyses supports this assertion. Table S1 shows the assigned absolute configurations for the hydrogenation products.

Table S1. Absolute Configurations of the Alkanes.

substrate[a]	catalyst	H_2 pressure (bar)	temperature (°C)	product (configuration)
	**5ap**	50	25	
	5bp	50	25	
	5cp	50	25	
	5dp	50	25	
	**5ap**	50	25	
	5bp	50	25	
	**5ap**	50	25	
	5bp	50	25	
	**5ao**	1	23	
	5ap	1	23	
	5ap	50	23	
	**5ap**	50	23	
	**5ao**	1	23	
	5ao	85	-15	

[a] Ar^1 = 4-methoxyphenyl and Ar^2 = 2-naphthyl

General Procedure for Deuteration. Alkene substrate (0.2 mmol), and desired amount of iridium complex **5** were added to a test tube containing a small stir bar. The test tube was sealed with a septum and was then evacuated and flushed with nitrogen three times. Then, dry/degassed CH_2Cl_2 (100 μL) was added. The septum was removed and the tube was quickly placed in a bomb already at the desired temperature. The bomb was flushed with nitrogen, then pressurized with the desired amount of deuterium. The bomb was placed in an isothermal bath at the desired temperature. The mixture was stirred at 300 rpm's for 2 h. Upon completion, the bomb was vented, and the reaction mixture was placed in an NMR tube along with an additional 0.6 mL $CHCl_3$ and 1 drop of $CDCl_3$. ^2H NMR was then taken.

Solvent Effects in the Hydrogenation Studies. The narrow solvent tolerance of these types of reactions has been known since Crabtree's original studies.[10,11] In these initial studies, only the solvents that were shown by Pfaltz[12] to work well in an analogous phosphine-oxazoline system were investigated (*ie* CH_2Cl_2 and $CHCl_3$). These solvent tend to give very similar results. For example, hydrogenation of 2-(2-naphthyl)-1-phenylpropene using 0.6 mol% **5ap** under the standard reaction conditions gave 60% yield and 93% *ee* in both $CHCl_3$ and CH_2Cl_2.

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