Mild Iridium-Catalyzed Borylation of Arenes. High Turnover Numbers, Room Temperature Reactions, and Isolation of a Potential Intermediate

Tatsuo Ishiyama*, Jun Takagi, Kousaku Ishida, and Norio Miyaura*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Natia R. Anastasi and John F. Hartwig*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Supporting Information

General Methods. All the experiments were carried out under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using a JEOL EX-400 (400 or 100 MHz) or Bruker DPX 400 Spectrometer or a GE QE-Plus instrument and Me_4Si or residual protiated solvent as an internal standard. ^{11}B NMR spectra were measured in $CDCl_3$ solutions with a Bruker MSL-400 (128 MHz) or a GE omega-300 instrument using BF_3•OEt_2 as an external standard. High-resolution mass spectra were obtained on a JEOL JMS-DX303. GC analyses were performed on a Hitachi G-3500 or HP-5890 instrument equipped with a glass column (OV-101 on Uniport B, 2 m, or Alltech DB-1301, 10 m). Arenes were purified by distillation from appropriate drying reagents. Bis(pinacolato)diboron,[1] pinacolborane,[2] $[IrCl(COE)_2]_2$,[3] and $Pt(dba)_2$[4] were prepared according to the literature procedures. All of other compounds were used as received.

General Procedure for the Reaction of Arenes with Bis(pinacolato)diboron (Table 1). A 25 mL-flask assembled a magnetic stirring bar, a septum inlet, and a condenser was charged with $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), and bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and then flushed with nitrogen. An arene (60 mmol) was added, and the mixture was stirred at 80 °C for 16 h. The reaction mixture was analyzed by GC and GC mass spectroscopy. The product was extracted with benzene, washed with brine, and dried over $MgSO_4$. Kugelrohr distillation gave analytically pure samples.

The following pinacol arylboronates were prepared by the above general procedure.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (entry 1). ^{1}H NMR δ 1.35 (s, 12 H), 7.37 (t, 2 H, *J* = 7.4 Hz), 7.46 (t, 1 H, *J* = 7.3 Hz), 7.81 (d, 2 H, *J* = 7.3 Hz); ^{13}C NMR δ 24.87, 83.75, 127.69, 131.23, 134.72; ^{11}B NMR δ 31.16; HRMS calcd for $C_{12}H_{17}BO_2$: 204.1322; found: 204.1331.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (entry 2). ^{1}H NMR δ (ortho isomer) 1.35 (s, 12 H), 3.83 (s, 3 H), 6.86 (d, 1 H, *J* = 8.3 Hz), 6.94 (t, 1 H, *J* = 7.4 Hz), 7.35-7.45 (m, 1 H), 7.67 (d, 1 H, *J* = 7.1 Hz), (meta isomer) 1.35 (s, 12 H), 3.83 (s, 3 H), 7.01 (dd, 1 H, *J* = 2.7 and 8.3 Hz), 7.29 (t, 1 H, *J* = 7.7 Hz), 7.33 (d, 1 H, *J* = 2.4 Hz), 7.40 (d, 1 H, *J* = 6.8 Hz), (para isomer) 1.33 (s, 12 H), 3.83 (s, 3 H), 6.89 (d, 2 H, *J* = 8.1 Hz), 7.75 (d, 2 H, *J* = 8.3 Hz); ^{13}C NMR δ (ortho isomer) not observed, (meta isomer) 24.83, 55.22, 83.80, 117.89, 118.64, 127.15, 128.91, 159.01, (para isomer) 24.83, 55.06, 83.52, 113.28, 136.48, 162.14; ^{11}B NMR δ 29.41; HRMS calcd for $C_{13}H_{19}BO_3$: 234.1427; found: 234.1433.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (entry 3). ^{1}H NMR δ (meta isomer) 1.35 (s, 12 H), 2.36 (s, 3 H), 7.25-7.30 (m, 2 H), 7.61 (t, 1 H, *J* = 4.3 Hz), 7.64 (s, 1 H), (para isomer) 1.34 (s, 12 H), 2.37 (s, 3 H), 7.19 (d, 2 H, *J* = 7.6 Hz), 7.70 (d, 2 H, *J* = 7.8 Hz); ^{13}C NMR δ (meta isomer) 21.25, 24.84, 83.71, 127.68, 131.75, 132.02, 135.31, 137.12, (para isomer) 21.71, 24.84, 83.60, 128.50, 134.78, 141.39; ^{11}B NMR δ 31.27; HRMS calcd for $C_{13}H_{19}BO_2$: 218.1478; found: 218.1470.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trifluoromethyl)benzene (entry 4). ^{1}H NMR δ (meta isomer) 1.36 (s, 12 H), 7.48 (t, 1 H, *J* = 7.6 Hz), 7.70 (d, 1 H, *J* = 7.8 Hz), 7.97 (d, 1 H, *J* = 7.6 Hz), 8.06 (s, 1 H), (para isomer) 1.36 (s, 12 H), 7.61 (d, 2 H, *J* =

8.1 Hz), 7.91 (d, 2 H, J = 7.8 Hz); ^{13}C NMR δ (meta isomer) 24.82, 8426, 124.31 (q. J (CF) = 272.2 Hz) 127.75 (q. J (CF) = 4.1 Hz), 128.02, 130.04 (q. J (CF) = 3.3 Hz), 138, (para isomer) 24.82, 84.26, 124.15, (q, J (CF) = 272.4 Hz, 124. 29 (q, J (CF) = 3.3 Hz,), 132.82 (q, J (CF) = 32.0 Hz), 135.02; ^{11}B NMR δ 30.82; HRMS calcd for $C_{13}H_{16}BF_3O_2$: 272.1195; found: 272.1180.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*o*-xylene (entry 5). ^{1}H NMR δ 1.34 (s, 12 H), 2.27 (s, 3 H), 2.28 (s, 3 H), 7.15 (d, 1 H, J = 7.6 Hz), 7.55 (d, 1 H, J = 7.3 Hz), 7.58 (s, 1 H); ^{13}C NMR δ 19.46, 20.00, 24.83, 83.56, 129.15, 132.40, 135.87, 135.92, 140.13; ^{11}B NMR δ 30.83; HRMS calcd for $C_{14}H_{21}BO_2$ 232.1635, found: 232.1620.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)veratrole (entry 6). ^{1}H NMR δ 1.34 (s, 12 H), 3.91 (s, 3 H), 3.93 (s, 3 H), 6.89 (d, 1 H, J = 8.1 Hz), 7.29 (s, 1 H), 7.42 (d, 1 H, J = 8.1 Hz); ^{13}C NMR δ 24.82, 55.70, 55.81, 83.62, 110.45, 116.52, 128.52, 148.30, 151.60; ^{11}B NMR δ 31.01; HRMS calcd for $C_{14}H_{21}BO_4$: 264.1533; found: 264.1545.

1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (entry 7). ^{1}H NMR δ 1.34 (s, 12 H), 7.44 (d, 1 H, J = 7.8 Hz), 7.60 (dd, 1 H, J = 1.3 and 7.9 Hz), 7.87 (d, 1 H, J = 1.5 Hz); ^{13}C NMR δ 24.82, 84.32, 129.99, 132.24, 133.73, 135.48, 136.54; ^{11}B NMR δ 30.61; HRMS calcd for $C_{12}H_{15}BCl_2O_2$: 272.0542; found: 272.0515.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*p*-xylene (entry 8). ^{1}H NMR δ 1.34 (s, 12 H), 2.30 (s, 3 H), 2.49 (s, 3 H), 7.06 (d, 1 H, J = 7.1 Hz), 7.13 (d, 1 H, J = 7.8 Hz), 7.57 (s, 1 H); ^{13}C NMR δ 20.77, 21.68, 24.87, 83.34, 129.77, 131.53, 133. 88, 136.33, 141.69 ; ^{11}B NMR δ 31.27; HRMS calcd for $C_{14}H_{21}BO_2$: 232.1635; found: 232.1632.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene (entry 9). ^{1}H NMR δ 1.35 (s, 12 H), 2.32 (s, 6 H), 7.11 (s, 1 H), 7.44 (s, 2 H); ^{13}C NMR δ 21.12, 24.84, 83.66, 132.38, 132.97, 137.15; ^{11}B NMR δ 31.26; HRMS calcd for $C_{14}H_{21}BO_2$: 232.1635; found: 232.1623.

3-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (entry 10). ^{1}H NMR δ 1.34 (s, 12 H), 2.33 (s, 3 H), 3.82 (s, 3 H), 6.83 (s, 1 H), 7.13 (d, 1 H, J = 2.2 Hz),

7.24 (s, 1 H); ^{13}C NMR δ 21.29, 24.91, 55.33, 83.84, 115.60, 118.88, 128.09, 139.01, 159.22; ^{11}B NMR δ 30.88; HRMS calcd for $C_{14}H_{21}BO_3$: 248.1584: found: 248.1606.

3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (entry 11). ^{1}H NMR δ 1.34 (s, 12 H), 3.81 (s, 3 H), 7.15 (t, 1 H, *J* = 2.2 Hz), 7.24 (d, 1 H, J = 2.4 Hz), 7.52 (s, 1 H); ^{13}C NMR δ 24.81, 55.50, 84.16, 117.89, 120.56, 12.64, 129.71, 159.86. ^{11}B NMR δ 30.44; HRMS $C_{13}H_{18}BBrO_3$: 312.0532; found: 312.0533.

Crossover Experiments. A mixture of $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), bis(pinacolato)diboron (254.0 mg, 1.0 mmol), benzene (4.7 g, 60 mmol), and pinacol 2-, 3-, or 4-methoxyphenylboronate (234.1 mg, 1.0 mmol) was heated at 80 °C for 16 h. The resulting mixture was analyzed by GC and GC mass spectroscopy. Neither formation of anisole nor isomerization of pinacol methoxyphenylboronate was observed in any case.

Competition Experiments. A mixture of $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), bis(pinacolato)diboron (254.0 mg, 1.0 mmol), and a 1:1 mole ratio of arenes (30 mmol for each arene) was heated at 80 °C for 16 h. The resulting mixture was analyzed by GC and GC mass spectroscopy. The mole ratios of pinacol arylboronates produced were as follows: Trifluoromethylbenzene/toluene (90:10), trifluoromethylbenzene/anisole (85:15), toluene/anisole (40:60).

Time-Course Study. A mixture of $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), bis(pinacolato)diboron (254.0 mg, 1.0 mmol), and benzene (4.7 g, 60 mmol) was heated at 80 °C. At suitable time intervals, portions of solution were removed by syringe and analyzed by GC and GC mass spectroscopy. The conversions of the diboron compound and the yields of pinacol phenylboronate based on boron atoms in the diboron were as follows: 0 min (0%, 0%), 30 min (60%, 25%), 40 min (>99%, 48%), 60 min (100%, 61%), 120 min (100%, 86%), 240 min (100%, 88%).

Reaction of Benzene with pinacolborane (Eq 2). A mixture of $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), pinacolborane (128.0 mg, 1.0 mmol), and benzene (60 mmol) was heated at 80 °C for 16 h. GC and GC mass spectroscopic analyses revealed the formation of pinacol phenylboronate in 80% yield.

Room Temperature Reaction of Benzene with Bis(pinacolato)diboron (Eq 3). In an inert atmosphere glove box 4,4'-di-*t*-butyl-2,2'-bipyridine (3.4 mg, 0.012 mmol), bis(pinacolato)diboron (32 mg, 0.125 mmol) and hexamethylbenzene (4 mg, 0.024 mmol) were transferred to a screw capped vial equipped with a stir bar. C_6D_6 (60 mmol) was added to the mixture, and an initial ^{1}H NMR spectrum was collected to evaluate the ratio of starting material to standard. $[IrCl(COE)_2]_2$ (5.6 mg, 6.25×10^{-3} mmol) was added. The reaction was allowed to proceed at room temperature with vigorous stirring and checked periodically by ^{1}H NMR spectroscopy. After 40 min B_2pin_2 was fully consumed and the ^{1}H NMR revealed the formation of pinacolborane and ester product. From the product to standard ratio the yield of pinBPh-$_{d5}$ was found to be 83% to moles of boron atom.

Table S1. Maximum turnover numbers for the Borylation reactions with B_2pin_2

Precatalyst System	Catalyst Loading	yield (%)	Turnover Number	Reaction time (h)
$[Ir(COD)Cl]_2$/dtbpy	0.01 %	57	5700	15 h
$[Ir(COE)_2Cl]_2$/dtbpy	0.01 %	80	8000	16 h
$[Ir(COD)Cl]_2$ / bpy	0.01 %	36	3600	16 h
$[Ir(COE)_2Cl]_2$ / bpy	0.01 %	45	4500	17 h

Experiments to determine the maximum turnover numbers for the borylation of benzene with bis(pinacolato)diboron. Stock solutions of $[Ir(COE)_2Cl]_2$ (5.91 mM), $[Ir(COD)Cl]_2$ (7.29 mM), dtbpy (21.6 mM), and bpy (37.1 mM) in C_6D_6 were prepared in an inert atmosphere glove box. B_2pin_2 (150 mg, 0.590 mmol) and C_6Me_6 as an internal standard (14 mg, 0.086 mmol) were placed in an NMR tube. Aliquots of the appropriate stock solutions were added to the NMR tube by syringe. The NMR tube was then sealed under vacuum and heated at 100 ºC for 15 h. The yield was determined from the ratio of the product to starting material vs the internal standard. Quantities of iridium precatalyst and ligand: $[Ir(COD)Cl]_2$ (9.8 μL, 58 μmol), dtbpy (5.5 μL, 120 μmol), $[Ir(COD)Cl]_2$ (9.8 μL, 58 μmol), bpy (3.4 μL, 126 μmol), $[Ir(COE)_2Cl]_2$ (12.5 μL, 74 μmol) and dtbpy (5.5 μL, 120 μmol), $[Ir(COE)_2Cl]_2$ (9.9 μL, 58 μmol) and bpy (3.3 μL, 122 μmol).

Experiments to determine the maximum turnover numbers for the borylation of benzene with pinacolborane. HBpin (109 μL, 0.748 mmol) and C_6Me_6 as an internal standard (11 mg, 0.067 mmol) were placed in an NMR tube. Aliquots of the appropriate stock solutions or iridium precursor and dtbpy were added to the NMR tube by syringe. The NMR tube was subsequently sealed under vacuum and heated at 100 ºC for 15 h. The yield was determined from the ratio of the product to starting material vs the internal standard. Quantities of iridium precursor and ligand: $[Ir(COD)Cl]_2$ (19.6 μL, 116 μmol), (14 μL, 300 μmol); $[Ir(COD)Cl]_2$ (19.6 μL, 116 μmol), bpy (8.4 μL, 310 μmol); $[Ir(COE)_2Cl]_2$ (25 μL, 148 μmol) and dtbpy (14 μL, 310 μmol); $[Ir(COE)_2Cl]_2$ (25 μL, 148 μmol) and bpy (8.4 μL, 310 μmol).

Table S2. Borylation Reactions of benzene-d_6 with pinacolborane.

Precatalyst System	Catalyst Loading	yield (%)	Turnover Number	Reaction time (h)
$[Ir(COD)Cl]_2$/ dtbpy	0.02 %	45	2250	17 h
$[Ir(COE)_2Cl]_2$/ dtbpy	0.02 %	20	1000	17 h
$[Ir(COD)Cl]_2$ / bpy	0.02 %	50	2500	17 h
$[Ir(COE)_2Cl]_2$ / bpy	0.02 %	12	600	17 h

(dtbpy)Ir(COD)Cl. In the dry box $[IrCl(COD)_2]_2$ (305 mg, 0.454 mmol) and dtbipyridine (243 mg, 0.908 mmol) were dissolved in THF (10 ml). The reaction was allowed to stir at room temperature for 3 h. The solvent was evaporated, and the resulting dark blue solid was isolated in 88% yield. (482 mg, 0.80 mmol) ^{1}H NMR (CD_2Cl_2) δ 1.46 (s, 18 H), 1.73 (q, 4 H, *J* = 7.8 Hz), 2.34 (m, 4 H), 3.69 (m, 4 H) 7.54 (dd, 2 H, J = 6 Hz) 8.19 (d, 2H, J = 2.4 Hz) 8.21 (d, 2H, J = 6 Hz); ^{13}C NMR δ 30.78, 32.71, 34.91, 60.25, 120.5, 124.8, 147.5, 156.7, 162.0; Anal. calc'd for $C_{26}H_{36}IrN_2Cl$: C, 51.68; H, 6.01; found: C, 51.94; H 5.96.

(dtbpy)Ir(COD)OTf. In the dry box (dtbpy)Ir(COD)Cl (100 mg, 0.161 mmol) was transferred to a vial, and sodium trifluoromethanesulfonate (33 mg, 0.192 mmol) was

added. The mixture was dissolved in THF (10 mL) and was allowed to stir at room temperature for 3 h. Upon addition of solvent an immediate color change from dark blue to red was observed. The reaction mixture was placed in the freezer. The resulting red precipitate was isolated by filtration. Recrystallization by layering a concentrated solution with ether formed spectroscopically pure complex (102 mg, 88%). ^{1}H NMR (CD_2Cl_2) δ 1.47 (s, 18 H), 2.03 (q, 4 H, *J* = 8 Hz), 2.42 (m, 4 H), 4.37 (m, 4 H) 7.75 (dd, 2 H, *J* = 6 Hz) 8.07 (d, 2H, *J* = 6 Hz) 8.17 (d, 2H, *J* = 2.0 Hz); ^{13}C NMR δ 30.08, 31.28, 36.46, 70.85, 120.4, 125.8, 149.9, 157.9, 167.7; ^{19}F NMR (CD_2Cl_2) δ 150.64.

{(dtbpy)Ir(COD)(Bpin)$_2$}OTf. In the dry box a glass reaction vessel equipped with a Kontes vacuum valve was loaded with (dtbpy)Ir(COD)OTf (160 mg, 0.223 mmol), B_2pin_2 (85 mg, 0.335 mmol) and 8 mL of THF. The reaction was heated at 40 °C for 15 h at which time the color of the solution was pale yellow. The solvent was evaporated, and the residual oil was placed under high vacuum for 12 h. The resulting light brown solid was dissolved in THF and layered with toluene. Single crystals were obtained in 25 % yield (55 mg, 0.055 mmol). ^{1}H NMR (THF-d_8) δ 0.60 (s, 6 H), 0.81 (s, 6 H), 1.37 (s, 6 H), 1.42 (s, 6 H), 1.48 (s, 9 H), 1.49 (s, 9 H), 2.28 (m, 4 H), 2.78 (m, 1 H), 3.25 (m, 1 H), 3.62 (m, 1 H) , 3.82 (m, 1 H) 4.20 (m, 1 H), 4.34 (m, 1 H) 5.43 (m, 1 H), 7.63 (dd, 1 H J = 6 Hz and 1.6 Hz), 7.97 (dd, 1 H *J* = 6.4 Hz and 2 Hz), 8.60 (d, 1 H, *J* = 2 Hz), 8.71 (d, 1 H, *J* = 1.6 Hz), 9.28 (d, 1 H, *J* = 4.5 Hz) 9.88 (d, 1 H, *J* = 4.5 Hz); ^{13}C NMR (CD_2Cl_2) 23.95, 24.89, 25.33, 25.70, 25.90, 26.26, 26.88, 28.08, 30.33, 30.36, 35.86, 39.64, 68.08, 73.91, 82.28, 84.12, 106.11, 113.27, 120.91, 121.55, 124.79, 125.51, 151.49, 152.61, 156.44, 156.58, 163.85, 164.49 ; ^{19}F NMR (THF-d_8) δ 147.4; ^{11}B NMR δ 34; Anal. Calcd for $C_{41}H_{64}N_2B_2F_3IrO_{7.5}S$: C, 49.06; H, 6.02; Found: C, 49.33; H, 6.30.

Catalytic reaction using {(dtbpy)Ir(COD)(Bpin)$_2$}OTf as catalyst. In the dry box a screw capped NMR tube was loaded with {(dtbpy)Ir(COD)(Bpin)$_2$}OTf (3.1 mg, 3.09 μmol), B_2pin_2 (14 mg, 0.055 mmol) and hexamethylbenzene (2.0 mg, 0.01 mmol) as

an internal standard. C_6D_6 (0.6 ml) was then added. An initial ^{1}H NMR spectrum was obtained to assess the ratio of starting material to standard. The tube was then heated at 80 °C for 5 h. A second NMR spectrum showed that all of the B_2pin_2 starting material was consumed and that C_6D_5Bpin was produced. Integration of the product pinacol resonance to that of the standard showed the yield to be 80%.

Thermolysis of {(dtbpy)Ir(COD)(Bpin)$_2$}OTf in the absence of added B_2pin_2. In an inert atmosphere box, [(dtbpy)Ir(COD)(Bpin)$_2$]OTf (7.2 mg, 7.17 μmol) was placed in a screw-capped NMR tube, and C_6Me_6 (3.2 mg, 0.019 mmol) was added followed by C_6D_6 (0.6 ml). The reaction mixture was sonicated at room temperature for 15 min to ensure that [(dtbpy)Ir(COD)(Bpin)$_2$]OTf had completely dissolved. An initial ^{1}H NMR spectrum was obtained to determine the ratio of iridium complex to internal standard. The mixture was then heated at 80 °C for 15 min. A second ^{1}H NMR spectrum showed the formation of [(dtbpy)Ir(COD)]OTf and B_2pin_2. The ratio of B_2pin_2 to standard showed the yield of this material to be 75%. A small amount of μ-O (Bpin)$_2$ was also formed, as determined by ^{11}B NMR spectroscopy.

Evaluation of time course of the catalytic reaction using a combination of [Ir(COD)Cl]$_2$ and dtbpy as precatalyst. In an inert atmosphere dry box, a screw capped NMR tube was loaded with [Ir(COD)Cl]$_2$ (5.0 mg, mmol), dtbpy (4.1 mg, 0.015 mmol), B_2pin_2 (38.6 mg, 0.151 mmol) and hexamethyl benzene as an internal standard (3.5 mg, 0.022 mmol). C_6D_6 (0.6 mL) was added to the reaction. ^{1}H NMR spectra were recorded and processed with an automatic data collection program to generate tables of integration values. A representative reaction profile is shown in Fig S1. GC MS analysis during the first 35 min of the reaction showed the reduction of cyclooctadiene to cyclooctene-d_2. When the reaction was repeated with C_6H_6 as the substrate, protiated cyclooctene was obtained as the reduction product. The fate of the phenyl groups during this

hydrogenation us unknown and GC MS analysis at the end of the reaction showed no biphenyl.

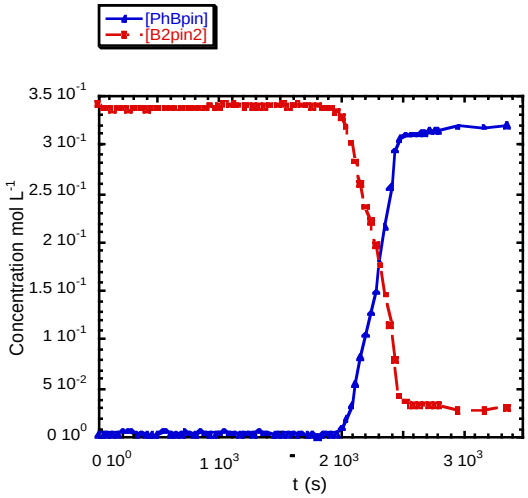

Figure S1. Reaction profile of the catalytic reaction with $[Ir(COD)Cl]_2$ and dtbpy as the precatalyst system at 60 °C.

Synthesis of (dtbpy)Ir(COE)(Bpin)$_3$. In the dry box a glass reaction vessel equipped with a Kontes vacuum valve was loaded with a mixture of $[Ir(COE)_2Cl]_2$ (350 mg, 0.390 mmol), dtbpy (209 mg, 0.778 mmol) and B_2pin_2 (494 mg, 1.95 mmol). Mesitylene (or p-xylene) 50 mL was added to the solids. The reaction was heated at 50 °C for 5 h with very slow stirring. The solvent was evaporated at room temperature, and the resulting solid was dissolved in diethyl ether. Recrystallization at room temperature by slow evaporation of the ether afforded red blocks in 28% yield (52 mg, 0.054 mmol). ^{1}H NMR (cyclohexane-d_{12}) δ 1.15 (s, 12 H) , 1.17 (s, 12 H) 1.18 (s, 12 H), 1.33 (m, 12 H), 1.41 (s, 18 H), 3.74 (d, 2 H, J = 10.8 Hz), 7.09 (dd, 2 H, J = 6.4 Hz and 2 Hz), 7.93 (s, 2H) 9.45 (d, 6.4 Hz); ^{11}B NMR δ 37.

Reaction of [4,4'di(*tert*-Butyl)bpy]Ir(COE)(Bpin)$_3$ with benzene. In an inert atmosphere glove box, a mixture of the isolated (dtbpy)Ir(COE)(Bpin)$_3$ (3.8 mg, 3.96 μmol) and C_6Me_6 (2.3 mg, 0.014 mmol) as an internal standard was transferred to a

screw-capped NMR tube. Cyclohexane-d_{12} (0.5 ml) was added to the reaction, and an initial spectrum was recorded to evaluate the ratio of starting material to standard. C_6D_6 (0.5 ml) was subsequently added to the solution, and the reaction immediately changed color from orange to brown. A ^{1}H NMR spectrum was collected. GC analysis showed the formation of pinBPh-d_5 in 80% yield based on the three boryl groups of the starting material.

Kinetic Isotope Effect of the Catalytic Reaction. In the glove box, $[Ir(COE)_2Cl]_2$ (7.1 mg, 7.92 μmol), dtbpy (5.0 mg, 0.018 mmol), and B_2pin_2 (39 mg, 0.150 mmol) were added to an NMR tube. A 0.6 ml aliquot of a mixture of C_6H_6 (2.0 ml, 0.023 mol) and C_6D_6 (2.0 ml, 0.023 mmol) was added to the solids by syringe. After 40 min when the diboron compound had been consumed and after 5 h when the HBpin had been consumed, the reaction was analyzed by GC/MS to determine the ratio of protiated and deuterated arylboronate esters by the abundance of their molecular ions. The ratio of protiated and deuterated arylboronate esters was the same at the two time points. The ratios determined for two experiments were 4.1 and 3.6. No detectable hydrogen-deuterium exchange had occurred between C_6H_6 and C_6D_6.

Kinetic Isotope Effect of the reaction of benzene with (dtbpy)Ir(COE)(Bpin)$_3$. In the glove box, (dtbpy)Ir(COE)(Bpin)$_3$ (4.0 mg, 4.2 μmol) was placed in an NMR tube. A 0.6 ml aliquot of a mixture of C_6H_6 (2.0 ml, 0.023 mol) and C_6D_6 (2.0 ml, 0.023 mmol) was added to the solution by syringe. The solution was analyzed by GC/MS to determine the ratio of protiated and deuterated arylboronate esters by the abundance of their molecular ions. The ratios determined for two experiments were 3.7 and 3.5. No detectable hydrogen-deuterium exchange had occurred between C_6H_6 and C_6D_6.

References

(1) Ishiyama, T.; Murata, M.; Ahiko, T.-a.; Miyaura, N. *Organic Syntheses* **2000**, *77*, 176.

(2) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.

(3) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorganic Syntheses* **1974**, *15*, 18.

(4) Cherwinski, W. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1405.

X-Ray structure report for {[4,4'di(*tert*-Butyl)bpy]Ir(COD)(Bpin)$_2$}OTf

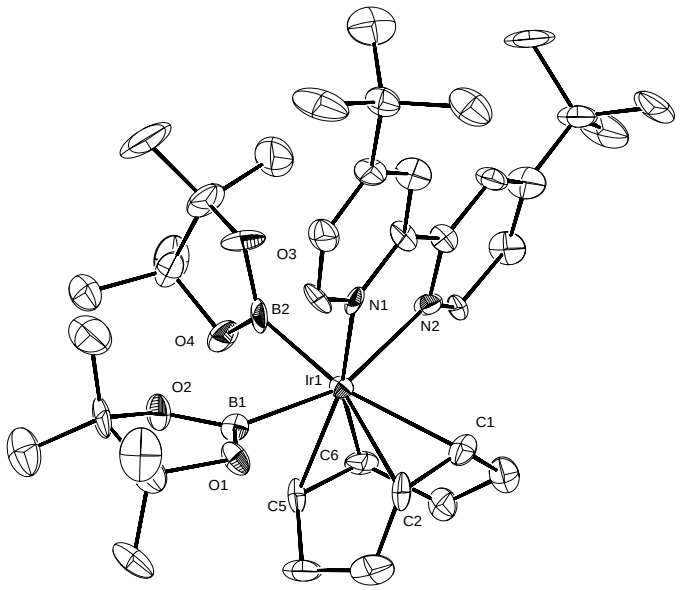

Figure S2. ORTEP diagram of {[4,4'di(*tert*-Butyl)bpy]Ir(COD)(Bpin)$_2$}OTf. The triflate counterion and hydrogens are omitted for clarity.

Data Collection

A colorless prism crystal of $C_{41}H_{60}B_2N_2O_{7.50}F_3SIr$ having approximate dimensions of 0.09 x 0.10 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in ω, 10 s exposure, de-zingered) data frames, corresponded to a primitive orthorhombic cell with dimensions: a = 22.403(1) Å, b = 18.8400(4) Å, c = 11.2769(2) Å, and V = 4759.8(2) Å^3. For Z = 4 and F.W. = 1003.83, the calculated density is 1.40 g/cm^3. Based on the systematic absences of: 0kl: k+l = 2n+1; h0l: h = 2n+1; packing considerations, a statistical analysis of intensity

distribution, and the successful solution and refinement of the structure, the space group was determined to be: $Pna2_1$ (#33).

The data were collected at a temperature of -90 $\pm$ 1 ^{o}C to a maximum 2θ value of 55.0^{o}. Two omega scans consisting of 65 and 52 data frames, respectively, were collected with a scan width of 1.6° and a detector-to-crystal distance, Dx, of 35 mm. Each frame was exposed twice (for the purpose of de-zingering) for 144 s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

Of the 26376 reflections which were collected, 6054 were unique (R_{int} = 0.071). No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 29.1 cm^{-1} and an absorption correction was applied [SORTAV: Blessing, R.H.; *Acta Cryst.*, A51, 33-37 (1995). Blessing, R.H.; *J. Appl. Cryst.*, 30, 421-426 (1997)]. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by heavy-atom Patterson methods[1] and expanded using Fourier techniques.[2] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. Hydrogens were omitted from the 50 per cent occupancy tetrahydrofuran solvent molecule. The final cycle of full-matrix

least-squares refinement[3] was based on 3490 observed reflections ($I > 5.00\sigma(I)$) and 540 variable parameters and converged (largest parameter shift was 0.07 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.038$$

$$R_W = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.047$$

The standard deviation of an observation of unit weight[4] was 1.24. The weighting scheme was based on counting statistics and included a factor ($p = 0.020$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.34 and -1.80 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References for X-Ray Analysis

(1) PATTY: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., Garcia-Granda, S., Gould, R.O., Smits, J.M.M. and Smykalla, C. (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $S w(|F_o|-|F_c|)^2$

where $w = 4F_o^2/^2(F_o^2)$

and $s^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[S w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr*., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{41}H_{60}B_2N_2O_{7.50}F_3SIr$
Formula Weight	1003.83
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.09 X 0.10 X 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 22.403(1)Å b = 18.8400(4) Å c = 11.2769(2) Å V = 4759.8(2) $Å^3$
Space Group	$Pna2_1$ (#33)

Z value	4
D_{calc}	1.401 g/cm^3
F_{000}	2040.00
μ(MoK_)	29.15 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8^o
Crystal to Detector Distance	35 mm
Temperature	-90.0 ^{o}C
Scan Rate	144 s/frame
Scan Width	1.6^o/frame
$2\theta_{max}$	55.0^o
No. of Reflections Measured	Total: 26376 Unique: 6054 (R_{int} = 0.071)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF92 PATTY)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\, w\, (\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/\sigma^2(Fo)$
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>5.00\sigma(I)$)	3490
No. Variables	540
Reflection/Parameter Ratio	6.46
Residuals: R; Rw	0.038 ; 0.047
Goodness of Fit Indicator	1.24
Max Shift/Error in Final Cycle	0.07
Maximum peak in Final Diff. Map	1.34 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.80 $e^-/Å^3$

Table S 3-1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ir(1)	0.07399(1)	0.22592(2)	1.0000	1.329(7)
S(1)	0.3006(1)	0.0049(2)	0.9407(3)	2.95(8)
F(1)	0.2190(5)	-0.0770(6)	0.850(1)	7.8(4)
F(2)	0.2353(6)	0.0150(6)	0.7474(10)	6.3(3)
F(3)	0.2985(7)	-0.0703(8)	0.745(1)	9.6(4)
O(1)	-0.0424(3)	0.2738(5)	1.1195(8)	2.2(2)
O(2)	-0.0538(3)	0.1665(4)	1.0307(7)	2.2(2)
O(3)	0.0228(4)	0.1699(5)	0.7692(8)	2.7(2)
O(4)	0.0468(4)	0.0794(4)	0.8968(8)	2.3(2)
O(5)	0.2542(4)	0.0445(5)	1.001(1)	5.0(3)
O(6)	0.3228(4)	-0.0558(5)	1.002(2)	4.5(2)
O(7)	0.3446(5)	0.0479(7)	0.885(1)	5.3(3)
O(8)	0.273(2)	0.038(1)	0.326(5)	12(1)
N(1)	0.0487(4)	0.3057(5)	0.8833(9)	1.4(2)
N(2)	0.1484(4)	0.2309(5)	0.8722(9)	1.6(2)
C(1)	0.1368(5)	0.3039(7)	1.106(1)	1.9(3)
C(2)	0.0850(6)	0.2999(9)	1.170(2)	1.9(3)
C(3)	0.0764(6)	0.2612(9)	1.282(1)	3.0(3)
C(4)	0.0555(6)	0.1826(8)	1.270(1)	2.5(3)
C(5)	0.0688(5)	0.1513(6)	1.151(1)	1.7(3)
C(6)	0.1260(5)	0.1496(7)	1.098(1)	1.9(3)
C(7)	0.1783(5)	0.1811(9)	1.165(1)	2.1(3)
C(8)	0.1926(7)	0.2605(7)	1.134(1)	2.6(3)
C(9)	-0.0016(5)	0.3441(6)	0.889(1)	1.6(2)
C(10)	-0.0186(5)	0.3937(7)	0.802(1)	2.3(3)
C(11)	0.0172(5)	0.4066(6)	0.708(1)	2.0(3)
C(12)	0.0716(5)	0.3697(7)	0.702(1)	2.2(3)
C(13)	0.0852(6)	0.3213(7)	0.787(1)	1.6(3)
C(14)	0.1407(5)	0.2782(6)	0.781(1)	1.6(2)
C(15)	0.1816(5)	0.2824(7)	0.690(1)	2.0(3)
C(16)	0.2325(5)	0.2384(7)	0.687(1)	2.6(3)
C(17)	0.2378(5)	0.1902(7)	0.777(1)	2.3(3)
C(18)	0.1952(6)	0.1864(8)	0.868(1)	1.6(3)
C(19)	0.0024(5)	0.4626(7)	0.612(1)	2.3(3)

Table S 3-1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
C(20)	-0.0627(7)	0.4870(10)	0.623(1)	4.2(4)
C(21)	0.0457(6)	0.5262(8)	0.630(1)	3.4(4)
C(22)	0.0108(6)	0.4313(6)	0.492(2)	3.7(3)
C(23)	0.2755(6)	0.2444(8)	0.586(1)	2.8(3)
C(24)	0.3048(6)	0.319(1)	0.584(1)	4.8(4)
C(25)	0.2428(7)	0.233(1)	0.468(1)	4.5(4)
C(26)	0.3254(6)	0.187(1)	0.594(1)	4.7(4)
C(27)	-0.1057(6)	0.2518(8)	1.142(1)	2.7(3)
C(28)	-0.1158(6)	0.1942(9)	1.046(1)	2.6(3)
C(29)	-0.1100(7)	0.2267(8)	1.268(1)	3.8(4)
C(30)	-0.1448(6)	0.3175(9)	1.125(2)	4.3(4)
C(31)	-0.1531(5)	0.1327(8)	1.088(2)	3.7(4)
C(32)	-0.1359(7)	0.220(1)	0.926(2)	4.4(5)
C(33)	0.0237(6)	0.1059(8)	0.697(1)	3.2(3)
C(34)	0.0193(5)	0.0470(7)	0.791(1)	2.5(3)
C(35)	-0.0269(8)	0.109(1)	0.608(2)	5.5(5)
C(36)	0.0827(8)	0.108(1)	0.629(2)	5.9(5)
C(37)	-0.0437(6)	0.0278(9)	0.825(1)	3.5(4)
C(38)	0.0551(6)	-0.0209(8)	0.762(2)	3.4(4)
C(39)	0.2629(8)	-0.0348(9)	0.812(2)	4.5(4)
C(40)	0.316(2)	-0.023(5)	0.379(5)	10(2)
C(41)	0.288(3)	-0.072(2)	0.396(3)	7(1)
C(42)	0.247(4)	-0.061(4)	0.326(5)	14(2)
C(43)	0.215(2)	0.005(2)	0.319(5)	7(1)
B(1)	-0.0152(6)	0.2193(7)	1.062(1)	1.4(3)
B(2)	0.0422(6)	0.1529(9)	0.879(2)	2.2(4)
H(1)	0.1381	0.3355	1.0405	2.3212
H(2)	0.0514	0.3246	1.1391	2.3178
H(3)	0.1134	0.2613	1.3232	3.5562
H(4)	0.0473	0.2859	1.3271	3.5562
H(5)	0.0752	0.1551	1.3283	3.0533
H(6)	0.0137	0.1808	1.2824	3.0533
H(7)	0.0366	0.1312	1.1076	2.0129
H(8)	0.1316	0.1290	1.0224	2.2364
H(9)	0.1699	0.1783	1.2476	2.5322

Table S 3-1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(10)	0.2127	0.1535	1.1478	2.5322
H(11)	0.2182	0.2615	1.0669	3.1049
H(12)	0.2124	0.2816	1.1998	3.1049
H(13)	-0.0273	0.3373	0.9546	1.9284
H(14)	-0.0553	0.4185	0.8104	2.7780
H(15)	0.0989	0.3788	0.6397	2.6556
H(16)	0.1754	0.3157	0.6284	2.4238
H(17)	0.2710	0.1588	0.7783	2.7980
H(18)	0.1995	0.1513	0.9274	1.8636
H(19)	-0.0689	0.5080	0.6983	5.0987
H(20)	-0.0712	0.5208	0.5625	5.0987
H(21)	-0.0885	0.4473	0.6139	5.0987
H(22)	0.0857	0.5100	0.6238	4.1340
H(23)	0.0384	0.5610	0.5705	4.1340
H(24)	0.0394	0.5464	0.7059	4.1340
H(25)	-0.0155	0.3921	0.4820	4.4122
H(26)	0.0022	0.4661	0.4330	4.4122
H(27)	0.0509	0.4157	0.4830	4.4122
H(28)	0.3257	0.3263	0.6566	5.6995
H(29)	0.3319	0.3217	0.5198	5.6995
H(30)	0.2747	0.3540	0.5757	5.6995
H(31)	0.2134	0.2691	0.4581	5.4474
H(32)	0.2707	0.2359	0.4045	5.4474
H(33)	0.2242	0.1880	0.4676	5.4474
H(34)	0.3077	0.1412	0.5939	5.6123
H(35)	0.3512	0.1914	0.5273	5.6123
H(36)	0.3476	0.1935	0.6646	5.6123
H(37)	-0.1498	0.2122	1.2836	4.5163
H(38)	-0.0838	0.1876	1.2790	4.5163
H(39)	-0.0993	0.2641	1.3197	4.5163
H(40)	-0.1333	0.3532	1.1796	5.1095
H(41)	-0.1401	0.3349	1.0462	5.1095
H(42)	-0.1855	0.3053	1.1375	5.1095
H(43)	-0.1933	0.1478	1.0986	4.4314
H(44)	-0.1518	0.0956	1.0314	4.4314

Table S 3-1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(45)	-0.1379	0.1160	1.1618	4.4314
H(46)	-0.1111	0.2586	0.9019	5.2889
H(47)	-0.1333	0.1829	0.8704	5.2889
H(48)	-0.1761	0.2363	0.9316	5.2889
H(49)	-0.0639	0.1120	0.6492	6.6400
H(50)	-0.0222	0.1495	0.5589	6.6400
H(51)	-0.0265	0.0673	0.5607	6.6400
H(52)	0.1149	0.1080	0.6837	7.0444
H(53)	0.0855	0.0671	0.5796	7.0444
H(54)	0.0842	0.1495	0.5817	7.0444
H(55)	-0.0650	0.0697	0.8453	4.1750
H(56)	-0.0628	0.0052	0.7597	4.1750
H(57)	-0.0430	-0.0035	0.8908	4.1750
H(58)	0.0532	-0.0525	0.8275	4.1357
H(59)	0.0384	-0.0432	0.6940	4.1357
H(60)	0.0955	-0.0088	0.7466	4.1357

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S 3-2. Anisotropic Displacement Parameters

atom	U11	U22	U33	U12	U13	U23
Ir(1)	0.0163(2)	0.0181(2)	0.0161(2)	0.0001(2)	0.0019(5)	0.0012(5)
S(1)	0.032(2)	0.043(2)	0.037(2)	0.000(2)	-0.005(2)	-0.002(2)
F(1)	0.113(9)	0.097(9)	0.088(9)	-0.058(8)	-0.063(7)	0.038(7)
F(2)	0.117(10)	0.063(8)	0.058(7)	-0.005(7)	-0.036(7)	0.031(6)
F(3)	0.15(1)	0.13(1)	0.08(1)	0.042(10)	-0.007(9)	-0.076(9)
O(1)	0.015(4)	0.033(5)	0.034(5)	0.003(4)	0.012(4)	0.002(5)
O(2)	0.012(3)	0.033(5)	0.040(8)	-0.001(3)	0.004(3)	-0.002(4)
O(3)	0.049(6)	0.042(6)	0.011(5)	0.011(5)	-0.002(4)	-0.007(5)
O(4)	0.031(4)	0.029(5)	0.027(5)	-0.002(4)	-0.005(4)	-0.012(4)
O(5)	0.070(6)	0.066(7)	0.054(6)	0.022(5)	-0.022(10)	-0.03(1)
O(6)	0.053(5)	0.051(5)	0.066(7)	0.010(5)	-0.027(9)	0.00(1)
O(7)	0.044(6)	0.092(9)	0.065(8)	-0.035(6)	0.005(6)	0.009(7)
O(8)	0.20(4)	0.04(2)	0.23(5)	-0.02(2)	-0.04(4)	0.01(3)
N(1)	0.015(5)	0.018(5)	0.021(5)	-0.005(4)	-0.003(4)	-0.010(5)
N(2)	0.015(5)	0.033(6)	0.013(5)	0.004(5)	-0.002(4)	-0.002(5)
C(1)	0.025(7)	0.018(7)	0.031(8)	0.000(5)	-0.012(6)	0.005(6)
C(2)	0.014(7)	0.015(9)	0.04(1)	-0.005(5)	0.001(7)	-0.007(7)
C(3)	0.031(7)	0.06(1)	0.025(7)	0.021(7)	0.007(6)	-0.011(7)
C(4)	0.035(7)	0.048(9)	0.014(7)	0.007(7)	0.001(6)	0.006(7)
C(5)	0.012(6)	0.014(6)	0.039(8)	-0.004(5)	-0.001(6)	0.004(6)
C(6)	0.034(7)	0.023(7)	0.014(6)	0.002(5)	0.003(5)	-0.007(6)
C(7)	0.014(6)	0.033(8)	0.032(10)	0.005(6)	0.004(6)	-0.003(8)
C(8)	0.030(7)	0.030(9)	0.039(9)	-0.005(6)	0.006(6)	-0.004(7)
C(9)	0.020(5)	0.016(6)	0.026(7)	0.002(5)	0.018(5)	0.001(5)
C(10)	0.021(6)	0.036(8)	0.031(8)	0.002(6)	0.006(6)	0.000(7)
C(11)	0.035(7)	0.018(7)	0.024(7)	0.000(6)	-0.004(6)	0.011(6)
C(12)	0.031(6)	0.022(7)	0.031(8)	0.010(6)	0.004(6)	-0.001(6)
C(13)	0.029(7)	0.003(7)	0.028(9)	-0.003(5)	0.006(6)	0.003(6)
C(14)	0.021(6)	0.016(6)	0.024(7)	0.002(5)	0.003(5)	0.002(6)
C(15)	0.025(6)	0.035(7)	0.017(6)	0.002(5)	0.003(5)	0.009(6)
C(16)	0.022(6)	0.046(9)	0.032(8)	0.018(6)	0.000(6)	0.006(7)
C(17)	0.019(6)	0.037(8)	0.032(8)	0.017(6)	0.007(5)	-0.003(7)
C(18)	0.012(6)	0.028(8)	0.019(8)	-0.004(6)	0.004(6)	0.002(7)
C(19)	0.028(7)	0.033(8)	0.026(7)	0.006(6)	0.009(6)	-0.002(6)

Table S 3-2. Anisotropic Displacement Parameters (continued)

atom	U11	U22	U33	U12	U13	U23
C(20)	0.061(10)	0.06(1)	0.039(10)	0.033(9)	0.013(8)	0.029(9)
C(21)	0.045(8)	0.038(9)	0.05(1)	0.009(7)	0.012(7)	0.015(8)
C(22)	0.070(8)	0.023(6)	0.047(8)	0.011(6)	0.00(1)	0.01(1)
C(23)	0.028(7)	0.064(10)	0.015(7)	0.010(7)	0.001(6)	0.006(7)
C(24)	0.036(8)	0.11(2)	0.033(9)	-0.012(10)	0.020(7)	0.02(1)
C(25)	0.051(9)	0.11(1)	0.009(9)	0.009(9)	-0.004(6)	0.007(8)
C(26)	0.033(8)	0.10(1)	0.04(1)	0.024(10)	0.027(7)	0.01(1)
C(27)	0.023(7)	0.037(8)	0.042(9)	0.009(6)	0.010(7)	-0.001(7)
C(28)	0.008(6)	0.039(10)	0.05(1)	-0.007(6)	0.006(6)	0.006(7)
C(29)	0.044(9)	0.06(1)	0.040(9)	-0.003(8)	0.025(7)	0.011(9)
C(30)	0.043(8)	0.034(9)	0.08(1)	0.011(8)	0.004(9)	-0.012(9)
C(31)	0.022(7)	0.043(9)	0.08(1)	0.005(7)	0.003(8)	0.014(9)
C(32)	0.036(10)	0.08(2)	0.05(1)	0.005(9)	0.001(9)	0.03(1)
C(33)	0.042(8)	0.050(10)	0.029(8)	-0.002(7)	-0.005(7)	-0.023(8)
C(34)	0.023(6)	0.035(8)	0.036(9)	-0.002(6)	-0.005(6)	-0.010(7)
C(35)	0.08(1)	0.10(2)	0.035(10)	-0.01(1)	-0.031(9)	-0.02(1)
C(36)	0.07(1)	0.11(2)	0.038(10)	-0.05(1)	0.026(9)	-0.03(1)
C(37)	0.034(8)	0.06(1)	0.039(10)	-0.012(7)	0.009(7)	-0.003(8)
C(38)	0.037(8)	0.029(8)	0.06(1)	0.001(6)	0.002(8)	-0.019(8)
C(39)	0.06(1)	0.05(1)	0.06(1)	-0.030(9)	-0.017(10)	0.009(10)
C(40)	0.06(3)	0.25(8)	0.09(5)	-0.03(4)	0.03(3)	0.03(5)
C(41)	0.25(7)	0.03(2)	0.01(2)	0.03(3)	-0.03(3)	0.01(1)
C(42)	0.4(1)	0.12(5)	0.07(4)	-0.12(7)	-0.01(6)	-0.01(4)
C(43)	0.06(3)	0.07(3)	0.13(5)	-0.04(2)	-0.01(3)	0.04(3)
B(1)	0.019(7)	0.012(7)	0.024(8)	0.006(6)	-0.006(6)	0.006(6)
B(2)	0.008(7)	0.04(1)	0.035(10)	-0.010(7)	0.007(6)	-0.006(8)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S 3-3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Ir(1)	N(1)	2.08(1)	Ir(1)	N(2)	2.206(10)
Ir(1)	C(1)	2.36(1)	Ir(1)	C(2)	2.38(2)
Ir(1)	C(5)	2.21(1)	Ir(1)	C(6)	2.16(1)
Ir(1)	B(1)	2.12(1)	Ir(1)	B(2)	2.06(2)
S(1)	O(5)	1.45(1)	S(1)	O(6)	1.42(1)
S(1)	O(7)	1.42(1)	S(1)	C(39)	1.84(2)
F(1)	C(39)	1.34(2)	F(2)	C(39)	1.34(2)
F(3)	C(39)	1.29(2)	O(1)	C(27)	1.50(2)
O(1)	B(1)	1.36(2)	O(2)	C(28)	1.49(1)
O(2)	B(1)	1.36(2)	O(3)	C(33)	1.46(2)
O(3)	B(2)	1.35(2)	O(4)	C(34)	1.48(2)
O(4)	B(2)	1.40(2)	O(8)	C(40)	1.60(7)
O(8)	C(43)	1.43(5)	N(1)	C(9)	1.34(1)
N(1)	C(13)	1.39(2)	N(2)	C(14)	1.37(1)
N(2)	C(18)	1.34(2)	C(1)	C(2)	1.37(2)
C(1)	C(8)	1.53(2)	C(2)	C(3)	1.47(2)
C(3)	C(4)	1.56(2)	C(4)	C(5)	1.49(2)
C(5)	C(6)	1.41(2)	C(6)	C(7)	1.51(2)
C(7)	C(8)	1.57(2)	C(9)	C(10)	1.40(2)
C(10)	C(11)	1.36(2)	C(11)	C(12)	1.40(2)
C(11)	C(19)	1.55(2)	C(12)	C(13)	1.36(2)
C(13)	C(14)	1.48(2)	C(14)	C(15)	1.38(2)
C(15)	C(16)	1.41(2)	C(16)	C(17)	1.37(2)
C(16)	C(23)	1.50(2)	C(17)	C(18)	1.40(2)
C(19)	C(20)	1.53(2)	C(19)	C(21)	1.55(2)
C(19)	C(22)	1.49(3)	C(23)	C(24)	1.55(2)
C(23)	C(25)	1.54(2)	C(23)	C(26)	1.56(2)
C(27)	C(28)	1.55(2)	C(27)	C(29)	1.50(2)
C(27)	C(30)	1.53(2)	C(28)	C(31)	1.51(2)
C(28)	C(32)	1.50(2)	C(33)	C(34)	1.54(2)
C(33)	C(35)	1.51(2)	C(33)	C(36)	1.53(2)

Table S 3-4. Bond Lengths(Å) for the Hydrogen Atoms

atom	atom	distance	atom	atom	distance
C(34)	C(37)	1.51(2)	C(34)	C(38)	1.55(2)
C(40)	C(41)	1.12(6)	C(40)	C(42)	1.80(9)
C(41)	C(42)	1.23(9)	C(42)	C(43)	1.44(9)
C(1)	H(1)	0.95	C(2)	H(2)	0.95
C(3)	H(3)	0.95	C(3)	H(4)	0.95
C(4)	H(5)	0.95	C(4)	H(6)	0.95
C(5)	H(7)	0.95	C(6)	H(8)	0.95
C(7)	H(9)	0.95	C(7)	H(10)	0.95
C(8)	H(11)	0.95	C(8)	H(12)	0.95
C(9)	H(13)	0.95	C(10)	H(14)	0.95
C(12)	H(15)	0.95	C(15)	H(16)	0.95
C(17)	H(17)	0.95	C(18)	H(18)	0.95
C(20)	H(19)	0.95	C(20)	H(20)	0.95
C(20)	H(21)	0.95	C(21)	H(22)	0.95
C(21)	H(23)	0.95	C(21)	H(24)	0.95
C(22)	H(25)	0.95	C(22)	H(26)	0.95
C(22)	H(27)	0.95	C(24)	H(28)	0.95
C(24)	H(29)	0.95	C(24)	H(30)	0.95
C(25)	H(31)	0.95	C(25)	H(32)	0.95
C(25)	H(33)	0.95	C(26)	H(34)	0.95
C(26)	H(35)	0.95	C(26)	H(36)	0.95
C(29)	H(37)	0.95	C(29)	H(38)	0.95
C(29)	H(39)	0.95	C(30)	H(40)	0.95
C(30)	H(41)	0.95	C(30)	H(42)	0.95
C(31)	H(43)	0.95	C(31)	H(44)	0.95
C(31)	H(45)	0.95	C(32)	H(46)	0.95
C(32)	H(47)	0.95	C(32)	H(48)	0.95
C(35)	H(49)	0.95	C(35)	H(50)	0.95
C(35)	H(51)	0.95	C(36)	H(52)	0.95
C(36)	H(53)	0.95	C(36)	H(54)	0.95
C(37)	H(55)	0.95	C(37)	H(56)	0.95
C(37)	H(57)	0.95	C(38)	H(58)	0.95
C(38)	H(59)	0.95	C(38)	H(60)	0.95

Table S 3-5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Ir(1)	N(2)	76.2(4)	N(1)	Ir(1)	C(1)	91.9(4)
N(1)	Ir(1)	C(2)	96.6(5)	N(1)	Ir(1)	C(5)	159.1(4)
N(1)	Ir(1)	C(6)	162.8(4)	N(1)	Ir(1)	B(1)	89.7(4)
N(1)	Ir(1)	B(2)	88.3(5)	N(2)	Ir(1)	C(1)	81.6(4)
N(2)	Ir(1)	C(2)	115.0(4)	N(2)	Ir(1)	C(5)	124.7(4)
N(2)	Ir(1)	C(6)	87.5(4)	N(2)	Ir(1)	B(1)	158.4(4)
N(2)	Ir(1)	B(2)	81.8(5)	C(1)	Ir(1)	C(2)	33.5(4)
C(1)	Ir(1)	C(5)	92.1(5)	C(1)	Ir(1)	C(6)	80.3(4)
C(1)	Ir(1)	B(1)	115.6(5)	C(1)	Ir(1)	B(2)	162.9(5)
C(2)	Ir(1)	C(5)	76.0(6)	C(2)	Ir(1)	C(6)	85.4(5)
C(2)	Ir(1)	B(1)	82.4(5)	C(2)	Ir(1)	B(2)	163.2(5)
C(5)	Ir(1)	C(6)	37.7(4)	C(5)	Ir(1)	B(1)	70.1(5)
C(5)	Ir(1)	B(2)	93.8(6)	C(6)	Ir(1)	B(1)	107.5(5)
C(6)	Ir(1)	B(2)	94.7(6)	B(1)	Ir(1)	B(2)	81.5(6)
O(5)	S(1)	O(6)	116.1(9)	O(5)	S(1)	O(7)	114.2(7)
O(5)	S(1)	C(39)	104.4(8)	O(6)	S(1)	O(7)	115.4(7)
O(6)	S(1)	C(39)	102.5(8)	O(7)	S(1)	C(39)	101.6(8)
C(27)	O(1)	B(1)	107.2(9)	C(28)	O(2)	B(1)	107.8(10)
C(33)	O(3)	B(2)	108(1)	C(34)	O(4)	B(2)	105(1)
C(40)	O(8)	C(43)	104(3)	Ir(1)	N(1)	C(9)	126.4(8)
Ir(1)	N(1)	C(13)	119.1(8)	C(9)	N(1)	C(13)	114(1)
Ir(1)	N(2)	C(14)	114.8(7)	Ir(1)	N(2)	C(18)	126.1(8)
C(14)	N(2)	C(18)	118(1)	Ir(1)	C(1)	C(2)	74.2(8)
Ir(1)	C(1)	C(8)	105.1(8)	C(2)	C(1)	C(8)	123(1)
Ir(1)	C(2)	C(1)	72.3(8)	Ir(1)	C(2)	C(3)	112.7(10)
C(1)	C(2)	C(3)	126(1)	C(2)	C(3)	C(4)	115(1)
C(3)	C(4)	C(5)	113(1)	Ir(1)	C(5)	C(4)	116.7(9)
Ir(1)	C(5)	C(6)	69.2(7)	C(4)	C(5)	C(6)	124(1)
Ir(1)	C(6)	C(5)	73.1(7)	Ir(1)	C(6)	C(7)	114.4(9)
C(5)	C(6)	C(7)	119(1)	C(6)	C(7)	C(8)	114(1)
C(1)	C(8)	C(7)	112(1)	N(1)	C(9)	C(10)	123(1)
C(9)	C(10)	C(11)	120(1)	C(10)	C(11)	C(12)	117(1)
C(10)	C(11)	C(19)	123(1)	C(12)	C(11)	C(19)	119(1)

Table S 3-5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(11)	C(12)	C(13)	119(1)	N(1)	C(13)	C(12)	123(1)
N(1)	C(13)	C(14)	114(1)	C(12)	C(13)	C(14)	121(1)
N(2)	C(14)	C(13)	115(1)	N(2)	C(14)	C(15)	120(1)
C(13)	C(14)	C(15)	123(1)	C(14)	C(15)	C(16)	121(1)
C(15)	C(16)	C(17)	116(1)	C(15)	C(16)	C(23)	119(1)
C(17)	C(16)	C(23)	123(1)	C(16)	C(17)	C(18)	121(1)
N(2)	C(18)	C(17)	121(1)	C(11)	C(19)	C(20)	110(1)
C(11)	C(19)	C(21)	107(1)	C(11)	C(19)	C(22)	109(1)
C(20)	C(19)	C(21)	110(1)	C(20)	C(19)	C(22)	108(1)
C(21)	C(19)	C(22)	110(1)	C(16)	C(23)	C(24)	110(1)
C(16)	C(23)	C(25)	110(1)	C(16)	C(23)	C(26)	111(1)
C(24)	C(23)	C(25)	108(1)	C(24)	C(23)	C(26)	108(1)
C(25)	C(23)	C(26)	107(1)	O(1)	C(27)	C(28)	102.3(9)
O(1)	C(27)	C(29)	108(1)	O(1)	C(27)	C(30)	107(1)
C(28)	C(27)	C(29)	115(1)	C(28)	C(27)	C(30)	113(1)
C(29)	C(27)	C(30)	109(1)	O(2)	C(28)	C(27)	100.9(10)
O(2)	C(28)	C(31)	106(1)	O(2)	C(28)	C(32)	107.0(10)
C(27)	C(28)	C(31)	113(1)	C(27)	C(28)	C(32)	116(1)
C(31)	C(28)	C(32)	111(1)	O(3)	C(33)	C(34)	102(1)
O(3)	C(33)	C(35)	109(1)	O(3)	C(33)	C(36)	105(1)
C(34)	C(33)	C(35)	115(1)	C(34)	C(33)	C(36)	114(1)
C(35)	C(33)	C(36)	108(1)	O(4)	C(34)	C(33)	103.5(10)
O(4)	C(34)	C(37)	106(1)	O(4)	C(34)	C(38)	107(1)
C(33)	C(34)	C(37)	114(1)	C(33)	C(34)	C(38)	114(1)
C(37)	C(34)	C(38)	109(1)	S(1)	C(39)	F(1)	108(1)
S(1)	C(39)	F(2)	110(1)	S(1)	C(39)	F(3)	112(1)
F(1)	C(39)	F(2)	104(1)	F(1)	C(39)	F(3)	109(1)
F(2)	C(39)	F(3)	109(1)	O(8)	C(40)	C(41)	108(5)
O(8)	C(40)	C(42)	69(3)	C(41)	C(40)	C(42)	42(3)
C(40)	C(41)	C(42)	99(4)	C(40)	C(42)	C(41)	37(3)
C(40)	C(42)	C(43)	95(4)	C(41)	C(42)	C(43)	122(4)
O(8)	C(43)	C(42)	85(4)	Ir(1)	B(1)	O(1)	122.4(9)
Ir(1)	B(1)	O(2)	123.8(9)	O(1)	B(1)	O(2)	112(1)
Ir(1)	B(2)	O(3)	124(1)	Ir(1)	B(2)	O(4)	122(1)
O(3)	B(2)	O(4)	112(1)				

Table S 3-6. Bond Angles(°) for the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
Ir(1)	C(1)	H(1)	90.8	C(2)	C(1)	H(1)	118.0
C(8)	C(1)	H(1)	118.1	Ir(1)	C(2)	H(2)	84.8
C(1)	C(2)	H(2)	117.0	C(3)	C(2)	H(2)	117.0
C(2)	C(3)	H(3)	107.9	C(2)	C(3)	H(4)	107.9
C(4)	C(3)	H(3)	107.9	C(4)	C(3)	H(4)	107.9
H(3)	C(3)	H(4)	109.5	C(3)	C(4)	H(5)	108.5
C(3)	C(4)	H(6)	108.5	C(5)	C(4)	H(5)	108.5
C(5)	C(4)	H(6)	108.5	H(5)	C(4)	H(6)	109.5
Ir(1)	C(5)	H(7)	84.2	C(4)	C(5)	H(7)	117.8
C(6)	C(5)	H(7)	117.8	Ir(1)	C(6)	H(8)	83.1
C(5)	C(6)	H(8)	120.4	C(7)	C(6)	H(8)	120.4
C(6)	C(7)	H(9)	108.1	C(6)	C(7)	H(10)	108.1
C(8)	C(7)	H(9)	108.1	C(8)	C(7)	H(10)	108.1
H(9)	C(7)	H(10)	109.5	C(1)	C(8)	H(11)	108.6
C(1)	C(8)	H(12)	108.6	C(7)	C(8)	H(11)	108.6
C(7)	C(8)	H(12)	108.6	H(11)	C(8)	H(12)	109.5
N(1)	C(9)	H(13)	118.0	C(10)	C(9)	H(13)	118.0
C(9)	C(10)	H(14)	119.8	C(11)	C(10)	H(14)	119.8
C(11)	C(12)	H(15)	120.0	C(13)	C(12)	H(15)	120.0
C(14)	C(15)	H(16)	119.2	C(16)	C(15)	H(16)	119.2
C(16)	C(17)	H(17)	119.5	C(18)	C(17)	H(17)	119.5
N(2)	C(18)	H(18)	119.0	C(17)	C(18)	H(18)	119.0
C(19)	C(20)	H(19)	109.5	C(19)	C(20)	H(20)	109.5
C(19)	C(20)	H(21)	109.5	H(19)	C(20)	H(20)	109.5
H(19)	C(20)	H(21)	109.5	H(20)	C(20)	H(21)	109.5
C(19)	C(21)	H(22)	109.5	C(19)	C(21)	H(23)	109.5
C(19)	C(21)	H(24)	109.5	H(22)	C(21)	H(23)	109.5
H(22)	C(21)	H(24)	109.5	H(23)	C(21)	H(24)	109.5
C(19)	C(22)	H(25)	109.5	C(19)	C(22)	H(26)	109.5
C(19)	C(22)	H(27)	109.5	H(25)	C(22)	H(26)	109.5
H(25)	C(22)	H(27)	109.5	H(26)	C(22)	H(27)	109.5
C(23)	C(24)	H(28)	109.5	C(23)	C(24)	H(29)	109.5
C(23)	C(24)	H(30)	109.5	H(28)	C(24)	H(29)	109.5

Table S 3-6. Bond Angles(°) for the Hydrogen Atoms (continued)

atom	atom	atom	angle	atom	atom	atom	angle
H(28)	C(24)	H(30)	109.5	H(29)	C(24)	H(30)	109.5
C(23)	C(25)	H(31)	109.5	C(23)	C(25)	H(32)	109.5
C(23)	C(25)	H(33)	109.5	H(31)	C(25)	H(32)	109.5
H(31)	C(25)	H(33)	109.5	H(32)	C(25)	H(33)	109.5
C(23)	C(26)	H(34)	109.5	C(23)	C(26)	H(35)	109.5
C(23)	C(26)	H(36)	109.5	H(34)	C(26)	H(35)	109.5
H(34)	C(26)	H(36)	109.5	H(35)	C(26)	H(36)	109.5
C(27)	C(29)	H(37)	109.5	C(27)	C(29)	H(38)	109.5
C(27)	C(29)	H(39)	109.5	H(37)	C(29)	H(38)	109.5
H(37)	C(29)	H(39)	109.5	H(38)	C(29)	H(39)	109.5
C(27)	C(30)	H(40)	109.5	C(27)	C(30)	H(41)	109.5
C(27)	C(30)	H(42)	109.5	H(40)	C(30)	H(41)	109.5
H(40)	C(30)	H(42)	109.5	H(41)	C(30)	H(42)	109.5
C(28)	C(31)	H(43)	109.5	C(28)	C(31)	H(44)	109.5
C(28)	C(31)	H(45)	109.5	H(43)	C(31)	H(44)	109.5
H(43)	C(31)	H(45)	109.5	H(44)	C(31)	H(45)	109.5
C(28)	C(32)	H(46)	109.5	C(28)	C(32)	H(47)	109.5
C(28)	C(32)	H(48)	109.5	H(46)	C(32)	H(47)	109.5
H(46)	C(32)	H(48)	109.5	H(47)	C(32)	H(48)	109.5
C(33)	C(35)	H(49)	109.5	C(33)	C(35)	H(50)	109.5
C(33)	C(35)	H(51)	109.5	H(49)	C(35)	H(50)	109.5
H(49)	C(35)	H(51)	109.5	H(50)	C(35)	H(51)	109.5
C(33)	C(36)	H(52)	109.5	C(33)	C(36)	H(53)	109.5
C(33)	C(36)	H(54)	109.5	H(52)	C(36)	H(53)	109.5
H(52)	C(36)	H(54)	109.5	H(53)	C(36)	H(54)	109.5
C(34)	C(37)	H(55)	109.5	C(34)	C(37)	H(56)	109.5
C(34)	C(37)	H(57)	109.5	H(55)	C(37)	H(56)	109.5
H(55)	C(37)	H(57)	109.5	H(56)	C(37)	H(57)	109.5
C(34)	C(38)	H(58)	109.5	C(34)	C(38)	H(59)	109.5
C(34)	C(38)	H(60)	109.5	H(58)	C(38)	H(59)	109.5
H(58)	C(38)	H(60)	109.5	H(59)	C(38)	H(60)	109.5

Table S 3-7. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Ir(1)	N(1)	C(9)	C(10)	-175.0(9)	Ir(1)	N(1)	C(13)	C(12)	176(1)
Ir(1)	N(1)	C(13)	C(14)	-1(1)	Ir(1)	N(2)	C(14)	C(13)	3(1)
Ir(1)	N(2)	C(14)	C(15)	-174.8(9)	Ir(1)	N(2)	C(18)	C(17)	174.7(10)
Ir(1)	C(1)	C(2)	C(3)	105(1)	Ir(1)	C(1)	C(8)	C(7)	-37(1)
Ir(1)	C(2)	C(1)	C(8)	-97(1)	Ir(1)	C(2)	C(3)	C(4)	-6(1)
Ir(1)	C(5)	C(4)	C(3)	-27(1)	Ir(1)	C(5)	C(6)	C(7)	108(1)
Ir(1)	C(6)	C(5)	C(4)	-108(1)	Ir(1)	C(6)	C(7)	C(8)	-10(1)
Ir(1)	B(1)	O(1)	C(27)	176.3(9)	Ir(1)	B(1)	O(2)	C(28)	-156.1(9)
Ir(1)	B(2)	O(3)	C(33)	160.5(10)	Ir(1)	B(2)	O(4)	C(34)	-179.7(9)
F(1)	C(39)	S(1)	O(5)	-60(1)	F(1)	C(39)	S(1)	O(6)	61(1)
F(1)	C(39)	S(1)	O(7)	-179(1)	F(2)	C(39)	S(1)	O(5)	54(1)
F(2)	C(39)	S(1)	O(6)	175(1)	F(2)	C(39)	S(1)	O(7)	-64(1)
F(3)	C(39)	S(1)	O(5)	177(1)	F(3)	C(39)	S(1)	O(6)	-61(1)
F(3)	C(39)	S(1)	O(7)	58(1)	O(1)	C(27)	C(28)	O(2)	28(1)
O(1)	C(27)	C(28)	C(31)	142(1)	O(1)	C(27)	C(28)	C(32)	-86(1)
O(1)	B(1)	Ir(1)	N(1)	-64(1)	O(1)	B(1)	Ir(1)	N(2)	-113(1)
O(1)	B(1)	Ir(1)	C(1)	27(1)	O(1)	B(1)	Ir(1)	C(2)	32(1)
O(1)	B(1)	Ir(1)	C(5)	109(1)	O(1)	B(1)	Ir(1)	C(6)	114.9(10)
O(1)	B(1)	Ir(1)	B(2)	-152(1)	O(1)	B(1)	O(2)	C(28)	12(1)
O(2)	C(28)	C(27)	C(29)	-88(1)	O(2)	C(28)	C(27)	C(30)	143(1)
O(2)	B(1)	Ir(1)	N(1)	103(1)	O(2)	B(1)	Ir(1)	N(2)	55(1)
O(2)	B(1)	Ir(1)	C(1)	-164.5(9)	O(2)	B(1)	Ir(1)	C(2)	-159(1)
O(2)	B(1)	Ir(1)	C(5)	-81(1)	O(2)	B(1)	Ir(1)	C(6)	-77(1)
O(2)	B(1)	Ir(1)	B(2)	15(1)	O(2)	B(1)	O(1)	C(27)	7(1)
O(3)	C(33)	C(34)	O(4)	-28(1)	O(3)	C(33)	C(34)	C(37)	87(1)
O(3)	C(33)	C(34)	C(38)	-144(1)	O(3)	B(2)	Ir(1)	N(1)	6(1)
O(3)	B(2)	Ir(1)	N(2)	-69(1)	O(3)	B(2)	Ir(1)	C(1)	-84(2)
O(3)	B(2)	Ir(1)	C(2)	113(2)	O(3)	B(2)	Ir(1)	C(5)	165(1)
O(3)	B(2)	Ir(1)	C(6)	-156(1)	O(3)	B(2)	Ir(1)	B(1)	96(1)
O(3)	B(2)	O(4)	C(34)	-8(1)	O(4)	C(34)	C(33)	C(35)	-146(1)
O(4)	C(34)	C(33)	C(36)	85(1)	O(4)	B(2)	Ir(1)	N(1)	177(1)
O(4)	B(2)	Ir(1)	N(2)	100(1)	O(4)	B(2)	Ir(1)	C(1)	86(2)
O(4)	B(2)	Ir(1)	C(2)	-75(2)	O(4)	B(2)	Ir(1)	C(5)	-23(1)

Table S 3-7. Torsion Angles(°) (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(4)	B(2)	Ir(1)	C(6)	14(1)	O(4)	B(2)	Ir(1)	B(1)	-92(1)
O(4)	B(2)	O(3)	C(33)	-10(1)	O(8)	C(40)	C(41)	C(42)	23(6)
O(8)	C(40)	C(42)	C(41)	-156(7)	O(8)	C(40)	C(42)	C(43)	-15(4)
O(8)	C(43)	C(42)	C(40)	16(4)	O(8)	C(43)	C(42)	C(41)	44(8)
N(1)	Ir(1)	N(2)	C(14)	-3.0(8)	N(1)	Ir(1)	N(2)	C(18)	-173(1)
N(1)	Ir(1)	C(1)	C(2)	99.0(9)	N(1)	Ir(1)	C(1)	C(8)	-139.4(9)
N(1)	Ir(1)	C(2)	C(1)	-83.6(9)	N(1)	Ir(1)	C(2)	C(3)	154.0(9)
N(1)	Ir(1)	C(5)	C(4)	-53(1)	N(1)	Ir(1)	C(5)	C(6)	-172.1(10)
N(1)	Ir(1)	C(6)	C(5)	170(1)	N(1)	Ir(1)	C(6)	C(7)	55(1)
N(1)	C(9)	C(10)	C(11)	-1(1)	N(1)	C(13)	C(12)	C(11)	-1(2)
N(1)	C(13)	C(14)	N(2)	-1(1)	N(1)	C(13)	C(14)	C(15)	176(1)
N(2)	Ir(1)	N(1)	C(9)	-179.7(10)	N(2)	Ir(1)	N(1)	C(13)	2.3(9)
N(2)	Ir(1)	C(1)	C(2)	174.7(9)	N(2)	Ir(1)	C(1)	C(8)	-63.7(9)
N(2)	Ir(1)	C(2)	C(1)	-5(1)	N(2)	Ir(1)	C(2)	C(3)	-128.2(9)
N(2)	Ir(1)	C(5)	C(4)	129.1(9)	N(2)	Ir(1)	C(5)	C(6)	10.2(9)
N(2)	Ir(1)	C(6)	C(5)	-171.7(7)	N(2)	Ir(1)	C(6)	C(7)	73.5(9)
N(2)	C(14)	C(13)	C(12)	-179(1)	N(2)	C(14)	C(15)	C(16)	0(1)
N(2)	C(18)	C(17)	C(16)	-2(2)	C(1)	Ir(1)	N(1)	C(9)	-98.8(10)
C(1)	Ir(1)	N(1)	C(13)	83.2(10)	C(1)	Ir(1)	N(2)	C(14)	-97.1(8)
C(1)	Ir(1)	N(2)	C(18)	92(1)	C(1)	Ir(1)	C(2)	C(3)	-122(1)
C(1)	Ir(1)	C(5)	C(4)	47.9(10)	C(1)	Ir(1)	C(5)	C(6)	-71.1(8)
C(1)	Ir(1)	C(6)	C(5)	106.4(8)	C(1)	Ir(1)	C(6)	C(7)	-8.5(9)
C(1)	C(2)	Ir(1)	C(5)	116.4(9)	C(1)	C(2)	Ir(1)	C(6)	79.3(9)
C(1)	C(2)	Ir(1)	B(1)	-172.3(9)	C(1)	C(2)	Ir(1)	B(2)	170(1)
C(1)	C(2)	C(3)	C(4)	-90(1)	C(1)	C(8)	C(7)	C(6)	34(1)
C(2)	Ir(1)	N(1)	C(9)	-65.5(10)	C(2)	Ir(1)	N(1)	C(13)	116.5(9)
C(2)	Ir(1)	N(2)	C(14)	-93.9(9)	C(2)	Ir(1)	N(2)	C(18)	95(1)
C(2)	Ir(1)	C(1)	C(8)	121(1)	C(2)	Ir(1)	C(5)	C(4)	18.2(9)
C(2)	Ir(1)	C(5)	C(6)	-100.8(8)	C(2)	Ir(1)	C(6)	C(5)	73.0(8)
C(2)	Ir(1)	C(6)	C(7)	-41.9(9)	C(2)	C(1)	Ir(1)	C(5	-60.5(9)
C(2)	C(1)	Ir(1)	C(6)	-96.4(9)	C(2)	C(1)	Ir(1)	B(1)	8(1)
C(2)	C(1)	Ir(1)	B(2)	-170(1)	C(2)	C(1)	C(8)	C(7)	43(1)
C(2)	C(3)	C(4)	C(5)	21(1)	C(3)	C(2)	Ir(1)	C(5)	-6.1(9)

Table S 3-7. Torsion Angles(°) (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(3)	C(2)	Ir(1)	C(6)	-43.1(9)	C(3)	C(2)	Ir(1)	B(1)	65.2(9)
C(3)	C(2)	Ir(1)	B(2)	48(2)	C(3)	C(2)	C(1)	C(8)	7(2)
C(3)	C(4)	C(5)	C(6)	54(1)	C(4)	C(5)	Ir(1)	C(6)	118(1)
C(4)	C(5)	Ir(1)	B(1)	-68.6(10)	C(4)	C(5)	Ir(1)	B(2)	-148.2(9)
C(4)	C(5)	C(6)	C(7)	0(1)	C(5)	Ir(1)	N(1)	C(9)	2(1)
C(5)	Ir(1)	N(1)	C(13)	-175(1)	C(5)	Ir(1)	N(2)	C(14)	176.1(8)
C(5)	Ir(1)	N(2)	C(18)	5(1)	C(5)	Ir(1)	C(1)	C(8)	61.1(9)
C(5)	Ir(1)	C(6)	C(7)	-114(1)	C(5)	C(6)	Ir(1)	B(1)	-7.5(9)
C(5)	C(6)	Ir(1)	B(2)	-90.1(9)	C(5)	C(6)	C(7)	C(8)	-93(1)
C(6)	Ir(1)	N(1)	C(9)	-161(1)	C(6)	Ir(1)	N(1)	C(13)	20(1)
C(6)	Ir(1)	N(2)	C(14)	-177.7(8)	C(6)	Ir(1)	N(2)	C(18)	11(1)
C(6)	Ir(1)	C(1)	C(8)	25.2(9)	C(6)	C(5)	Ir(1)	B(1)	172.4(9)
C(6)	C(5)	Ir(1)	B(2)	92.8(9)	C(7)	C(6)	Ir(1)	B(1)	-122.4(9)
C(7)	C(6)	Ir(1)	B(2)	155.0(9)	C(8)	C(1)	Ir(1)	B(1)	130.0(9)
C(8)	C(1)	Ir(1)	B(2)	-49(2)	C(9)	N(1)	Ir(1)	B(1)	16(1)
C(9)	N(1)	Ir(1)	B(2)	98(1)	C(9)	N(1)	C(13)	C(12)	-1(1)
C(9)	N(1)	C(13)	C(14)	-179(1)	C(9)	C(10)	C(11)	C(12)	-1(1)
C(9)	C(10)	C(11)	C(19)	-177(1)	C(10)	C(9)	N(1)	C(13)	3(1)
C(10)	C(11)	C(12)	C(13)	3(1)	C(10)	C(11)	C(19)	C(20)	-13(1)
C(10)	C(11)	C(19)	C(21)	107(1)	C(10)	C(11)	C(19)	C(22)	-132(1)
C(11)	C(12)	C(13)	C(14)	176(1)	C(12)	C(11)	C(19)	C(20)	170(1)
C(12)	C(11)	C(19)	C(21)	-68(1)	C(12)	C(11)	C(19)	C(22)	51(1)
C(12)	C(13)	C(14)	C(15)	-1(2)	C(13)	N(1)	Ir(1)	B(1)	-161.2(10)
C(13)	N(1)	Ir(1)	B(2)	-79.7(10)	C(13)	C(12)	C(11)	C(19)	178(1)
C(13)	C(14)	N(2)	C(18)	174(1)	C(13)	C(14)	C(15)	C(16)	-177(1)
C(14)	N(2)	Ir(1)	B(1)	47(1)	C(14)	N(2)	Ir(1)	B(2)	87.2(9)
C(14)	N(2)	C(18)	C(17)	4(1)	C(14)	C(15)	C(16)	C(17)	1(2)
C(14)	C(15)	C(16)	C(23)	179(1)	C(15)	C(14)	N(2)	C(18)	-3(1)
C(15)	C(16)	C(17)	C(18)	-1(2)	C(15)	C(16)	C(23)	C(24)	63(1)
C(15)	C(16)	C(23)	C(25)	-56(1)	C(15)	C(16)	C(23)	C(26)	-175(1)
C(17)	C(16)	C(23)	C(24)	-119(1)	C(17)	C(16)	C(23)	C(25)	121(1)
C(17)	C(16)	C(23)	C(26)	2(2)	C(18)	N(2)	Ir(1)	B(1)	-123(1)
C(18)	N(2)	Ir(1)	B(2)	-83(1)	C(18)	C(17)	C(16)	C(23)	-178(1)
C(27)	C(28)	O(2)	B(1)	-26(1)	C(28)	C(27)	O(1)	B(1)	-22(1)

Table S 3-7. Torsion Angles(°) (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(29)	C(27)	O(1)	B(1)	99(1)	C(29)	C(27)	C(28)	C(31)	24(1)
C(29)	C(27)	C(28)	C(32)	156(1)	C(30)	C(27)	O(1)	B(1)	-142(1)
C(30)	C(27)	C(28)	C(31)	-102(1)	C(30)	C(27)	C(28)	C(32)	28(1)
C(31)	C(28)	O(2)	B(1)	-144(1)	C(32)	C(28)	O(2)	B(1)	95(1)
C(33)	C(34)	O(4)	B(2)	22(1)	C(34)	C(33)	O(3)	B(2)	24(1)
C(35)	C(33)	O(3)	B(2)	147(1)	C(35)	C(33)	C(34)	C(37)	-31(1)
C(35)	C(33)	C(34)	C(38)	96(1)	C(36)	C(33)	O(3)	B(2)	-96(1)
C(36)	C(33)	C(34)	C(37)	-158(1)	C(36)	C(33)	C(34)	C(38)	-30(1)
C(37)	C(34)	O(4)	B(2)	-98(1)	C(38)	C(34)	O(4)	B(2)	144(1)
C(40)	O(8)	C(43)	C(42)	-19(5)	C(40)	C(41)	C(42)	C(43)	-48(9)
C(41)	C(40)	O(8)	C(43)	0(7)	C(41)	C(40)	C(42)	C(43)	140(7)
C(42)	C(40)	O(8)	C(43)	16(4)					

Table S 3-8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
F(1)	C(24)	3.33(2)	54503	F(1)	C(31)	3.46(2)	55402
F(2)	C(17)	3.32(2)	1	F(3)	C(1)	3.19(2)	54403
F(3)	C(8)	3.43(2)	54403	O(5)	C(18)	3.34(2)	1
O(5)	C(7)	3.60(2)	1	O(6)	C(12)	3.56(2)	54503
O(7)	C(10)	3.39(1)	4	C(14)	C(41)	3.49(4)	3

X-Ray structure report for [4,4'di(*tert*-Butyl)bpy]Ir(COE)(Bpin)$_3$

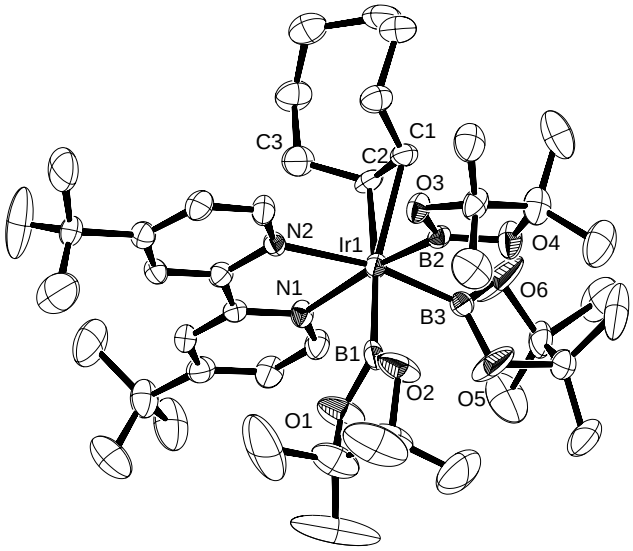

Figure S3. ORTEP diagram of (dtbpy)Ir(COD)(Bpin)$_3$. Hydrogens omitted for clarity.

<u>Data Collection</u>

An orange plate crystal of $C_{44}H_{74}N_2B_3O_6Ir$ having approximate dimensions of 0.05 x 0.08 x 0.12 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in ω, 10s exposure, de-zingered) data frames, corresponded to a primitive monoclinic cell with dimensions: a = 18.0720(4) Å, b = 11.7350(4) Å, θ = 92.574(2)^o, c = 22.2631(5) Å, and V = 4716.7(2) Å^3. For Z = 4 and F.W. = 951.73, the calculated density is 1.34 g/cm^3. The systematic absences of: h0l: l = 2n+1, 0k0: k = 2n+1; uniquely determine the space group to be: $P2_1/c$ (#14).

The data were collected at a temperature of -90 $\pm$ 1°C to a maximum 2θ value of 54.9^o. Two omega scans consisting of 89 and 73 data frames, respectively, were collected with a scan width of 1.3^o and a detector-to-crystal distance, Dx, of 35mm. Each frame was exposed twice (for the purpose of de-zingering) for 78 s. The data frames

were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

Of the 29047 reflections which were collected, 11248 were unique (R_{int} = 0.051); equivalent reflections were merged. No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 28.8 cm^{-1} and a SORTAV absorption correction was applied [SORTAV: Blessing, R.H.; *Acta Cryst.*, A51, 33-37 (1995). Blessing, R.H.; *J. Appl. Cryst.*, 30, 421-426 (1997)]. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Carbon atoms C39 and C40 were disordered between two positions (C39a, C39b and C40a, C40b) and were refined at 60% and 40% occupancy, respectively. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 6455 observed reflections ($I > 5.00\sigma(I)$) and 523 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.037$$

$$R_W = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.043$$

The standard deviation of an observation of unit weight[4] was 1.63. The weighting scheme was based on counting statistics and included a factor (p = 0.020) to downweight the intense reflections. Plots of $\Sigma\, w\, (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.61 (located 0.94 Å from the Ir atom) and -1.47 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{44}H_{74}N_2B_3O_6Ir$
Formula Weight	951.73
Crystal Color, Habit	orange, plate
Crystal Dimensions	0.05 X 0.08 X 0.12 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 18.0720(4)Å b = 11.7350(4) Å c = 22.2631(5) Å θ = 92.574(2)^o V = 4716.7(2) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
Dcalc	1.340 g/cm^3
F000	1968.00
μ(MoK_)	28.83 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoKα(λ = 0.71069 Å) graphite monochromated

Take-off Angle	2.8^{o}
Crystal to Detector Distance	35 mm
Temperature	-90.0 ^{o}C
Scan Rate	78 s/frame
Scan Width	1.3^{o}
2_max	54.9^{o}
No. of Reflections Measured	Total: 29047 Unique: 11248 (R_{int}=0.051)
Corrections	Lorentz-polarization SORTAV Absorption

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/\Sigma^2(Fo)$
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>5.00\sigma(I)$)	6455
No. Variables	523
Reflection/Parameter Ratio	12.34
Residuals: R; Rw	0.037 ; 0.043

Goodness of Fit Indicator	1.63
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	2.61 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.47 $e^-/Å^3$

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/\sigma^2(Fo)$
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>5.00\sigma(I)$)	6455
No. Variables	523
Reflection/Parameter Ratio	12.34
Residuals: R; Rw	0.037 ; 0.043
Goodness of Fit Indicator	1.63
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	2.61 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.47 $e^-/Å$

Table S 4-1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ir(1)	0.26421(1)	0.10412(2)	0.620918(9)	1.914(5)
O(1)	0.1625(2)	-0.0769(4)	0.6689(2)	4.5(1)
O(2)	0.0944(2)	0.0629(4)	0.6263(2)	4.3(1)
O(3)	0.1595(2)	0.2456(3)	0.5373(1)	2.36(9)
O(4)	0.1742(2)	0.3273(4)	0.6289(2)	3.32(10)
O(5)	0.2023(3)	0.1648(5)	0.7418(2)	6.9(2)
O(6)	0.3102(3)	0.2405(6)	0.7334(2)	7.8(2)
N(1)	0.3173(2)	-0.0555(4)	0.6479(2)	1.92(10)
N(2)	0.2610(2)	-0.0031(4)	0.5386(2)	1.86(10)
C(1)	0.3430(3)	0.2429(5)	0.5874(2)	2.2(1)
C(2)	0.3867(3)	0.1590(5)	0.6135(2)	2.4(1)
C(3)	0.4342(3)	0.0783(5)	0.5800(3)	3.2(1)
C(4)	0.5108(3)	0.1254(6)	0.5647(3)	3.5(2)
C(5)	0.5102(3)	0.2165(6)	0.5151(3)	4.0(2)
C(6)	0.4776(3)	0.3329(6)	0.5317(3)	3.9(2)
C(7)	0.3991(3)	0.3581(6)	0.5070(3)	3.6(2)
C(8)	0.3410(3)	0.2677(5)	0.5208(2)	3.0(1)
C(9)	0.3491(3)	-0.0762(5)	0.7017(2)	2.5(1)
C(10)	0.3845(3)	-0.1759(5)	0.7167(2)	2.7(1)
C(11)	0.3874(3)	-0.2634(5)	0.6747(2)	2.6(1)
C(12)	0.3539(3)	-0.2422(5)	0.6193(2)	2.3(1)
C(13)	0.3189(3)	-0.1400(5)	0.6056(2)	2.1(1)
C(14)	0.2845(3)	-0.1116(5)	0.5459(2)	2.0(1)
C(15)	0.2780(3)	-0.1911(5)	0.4999(2)	2.1(1)
C(16)	0.2478(3)	-0.1620(5)	0.4436(2)	2.1(1)
C(17)	0.2221(3)	-0.0509(5)	0.4377(2)	2.6(1)
C(18)	0.2295(3)	0.0255(5)	0.4849(2)	2.4(1)
C(19)	0.4267(4)	-0.3773(5)	0.6877(3)	3.3(2)
C(20)	0.4665(4)	-0.3793(6)	0.7487(3)	5.5(2)
C(21)	0.4828(4)	-0.4002(7)	0.6388(3)	5.6(2)

Table S 4-1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(22)	0.3687(4)	-0.4708(7)	0.6853(3)	5.6(2)
C(23)	0.2416(3)	-0.2501(5)	0.3929(2)	2.6(1)
C(24)	0.2353(5)	-0.1926(7)	0.3314(3)	7.1(2)
C(25)	0.1737(5)	-0.3187(8)	0.3998(4)	8.0(3)
C(26)	0.3092(5)	-0.3236(9)	0.3929(4)	8.2(3)
C(27)	0.0877(4)	-0.1195(7)	0.6640(4)	4.8(2)
C(28)	0.0417(4)	-0.0129(6)	0.6527(3)	4.6(2)
C(29)	0.0721(4)	-0.191(1)	0.7156(5)	11.4(4)
C(30)	0.0856(5)	-0.1971(9)	0.6085(6)	10.0(3)
C(31)	0.0207(6)	0.044(1)	0.7105(5)	11.8(4)
C(32)	-0.0253(4)	-0.0242(8)	0.6101(4)	7.8(3)
C(33)	0.1056(3)	0.3365(5)	0.5378(2)	2.7(1)
C(34)	0.1322(3)	0.4084(5)	0.5920(3)	3.1(1)
C(35)	0.1006(4)	0.3961(6)	0.4781(3)	3.9(2)
C(36)	0.0301(3)	0.2789(6)	0.5481(3)	4.5(2)
C(37)	0.0736(4)	0.4624(7)	0.6292(3)	5.4(2)
C(38)	0.1876(4)	0.5001(6)	0.5745(4)	5.4(2)
C(39b)	0.232(1)	0.197(2)	0.8033(8)	3.4(5)
C(39a)	0.2101(7)	0.254(1)	0.7891(5)	2.9(3)
C(40b)	0.2710(9)	0.308(1)	0.7825(6)	2.5(4)
C(40a)	0.2904(7)	0.234(1)	0.7999(5)	3.5(3)
C(41)	0.1615(4)	0.2135(7)	0.8378(3)	5.1(2)
C(42)	0.3021(5)	0.1235(7)	0.8363(3)	6.2(2)
C(43)	0.1973(5)	0.3833(7)	0.7688(3)	5.8(2)
C(44)	0.3331(4)	0.3442(7)	0.8254(3)	5.3(2)
B(1)	0.1660(4)	0.0275(6)	0.6408(3)	2.4(1)
B(2)	0.1937(3)	0.2339(5)	0.5943(3)	1.8(1)
B(3)	0.2587(3)	0.1765(6)	0.7032(3)	2.1(1)
H(1)	0.3127	0.2870	0.6123	2.6222
H(2)	0.3868	0.1516	0.6560	2.8843
H(3)	0.4418	0.0120	0.6040	3.8099
H(4)	0.4083	0.0585	0.5434	3.8099
H(5)	0.5330	0.1578	0.6002	4.2540
H(6)	0.5401	0.0633	0.5521	4.2540
H(7)	0.5599	0.2284	0.5043	4.7519

Table S 4-1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(8)	0.4819	0.1878	0.4814	4.7519
H(9)	0.4775	0.3371	0.5743	4.7034
H(10)	0.5093	0.3902	0.5171	4.7034
H(11)	0.3839	0.4284	0.5237	4.2857
H(12)	0.4005	0.3652	0.4646	4.2857
H(13)	0.3512	0.1998	0.4995	3.5408
H(14)	0.2932	0.2951	0.5084	3.5408
H(15)	0.3472	-0.0184	0.7315	3.0127
H(16)	0.4070	-0.1854	0.7558	3.2550
H(17)	0.3548	-0.2997	0.5893	2.8100
H(18)	0.2945	-0.2669	0.5071	2.4854
H(19)	0.1991	-0.0269	0.4006	3.1346
H(20)	0.2116	0.1010	0.4791	2.9137
H(21)	0.5052	-0.3245	0.7498	6.5903
H(22)	0.4867	-0.4530	0.7560	6.5903
H(23)	0.4325	-0.3617	0.7787	6.5903
H(24)	0.4951	-0.4789	0.6385	6.7553
H(25)	0.4615	-0.3791	0.6006	6.7553
H(26)	0.5264	-0.3566	0.6471	6.7553
H(27)	0.3346	-0.4577	0.6522	6.7022
H(28)	0.3430	-0.4709	0.7215	6.7022
H(29)	0.3922	-0.5425	0.6804	6.7022
H(30)	0.2778	-0.1468	0.3261	8.4995
H(31)	0.2319	-0.2491	0.3008	8.4995
H(32)	0.1922	-0.1461	0.3290	8.4995
H(33)	0.1799	-0.3661	0.4342	9.5988
H(34)	0.1327	-0.2693	0.4044	9.5988
H(35)	0.1649	-0.3647	0.3651	9.5988
H(36)	0.3245	-0.3418	0.4332	9.7870
H(37)	0.2983	-0.3918	0.3713	9.7870
H(38)	0.3479	-0.2838	0.3743	9.7870
H(39)	0.1077	-0.2504	0.7191	13.6684
H(40)	0.0746	-0.1460	0.7512	13.6684
H(41)	0.0240	-0.2227	0.7102	13.6684
H(42)	0.0373	-0.2281	0.6023	12.0168

Table S 4-1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(43)	0.0979	-0.1540	0.5742	12.0168
H(44)	0.1204	-0.2572	0.6146	12.0168
H(45)	0.0635	0.0515	0.7366	14.1449
H(46)	0.0006	0.1172	0.7018	14.1449
H(47)	-0.0151	-0.0013	0.7294	14.1449
H(48)	-0.0099	-0.0269	0.5699	9.3427
H(49)	-0.0570	0.0395	0.6147	9.3427
H(50)	-0.0512	-0.0922	0.6189	9.3427
H(51)	0.0728	0.4643	0.4816	4.6283
H(52)	0.1489	0.4139	0.4660	4.6283
H(53)	0.0767	0.3477	0.4490	4.6283
H(54)	0.0298	0.2509	0.5882	5.4454
H(55)	-0.0085	0.3331	0.5419	5.4454
H(56)	0.0228	0.2175	0.5207	5.4454
H(57)	0.0447	0.4044	0.6465	6.4403
H(58)	0.0968	0.5072	0.6602	6.4403
H(59)	0.0425	0.5095	0.6042	6.4403
H(60)	0.2253	0.4663	0.5519	6.4798
H(61)	0.2093	0.5340	0.6098	6.4798
H(62)	0.1627	0.5568	0.5508	6.4798
H(63)	0.1898	0.2087	0.8747	6.0712
H(64)	0.1220	0.2659	0.8419	6.0712
H(65)	0.1420	0.1405	0.8276	6.0712
H(66)	0.2927	0.1377	0.8773	7.3879
H(67)	0.2691	0.0664	0.8210	7.3879
H(68)	0.3517	0.0981	0.8333	7.3879
H(69)	0.2203	0.3963	0.7319	6.9088
H(70)	0.2182	0.4327	0.7988	6.9088
H(71)	0.1457	0.3977	0.7636	6.9088
H(72)	0.3747	0.3214	0.8501	6.3703
H(73)	0.3492	0.3887	0.7929	6.3703
H(74)	0.3006	0.3882	0.8485	6.3703

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S 4-2. Anisotropic Displacement Parameters

atom	U11	U22	U33	U12	U13	U23
Ir(1)	0.0279(1)	0.0234(1)	0.0216(1)	0.0039(1)	0.00246(9)	-0.0020(1)
O(1)	0.027(2)	0.051(3)	0.091(4)	-0.010(2)	-0.009(2)	0.027(3)
O(2)	0.029(2)	0.037(3)	0.096(4)	-0.004(2)	0.008(2)	0.023(3)
O(3)	0.031(2)	0.031(2)	0.028(2)	0.010(2)	0.002(2)	-0.004(2)
O(4)	0.062(3)	0.033(3)	0.030(2)	0.020(2)	-0.004(2)	-0.004(2)
O(5)	0.094(4)	0.124(5)	0.048(3)	-0.076(4)	0.047(3)	-0.056(3)
O(6)	0.068(3)	0.181(7)	0.049(3)	-0.072(4)	0.035(3)	-0.072(4)
N(1)	0.027(2)	0.022(3)	0.024(2)	0.010(2)	-0.002(2)	0.001(2)
N(2)	0.030(2)	0.019(3)	0.022(2)	0.002(2)	0.001(2)	0.000(2)
C(1)	0.025(3)	0.030(3)	0.029(3)	-0.001(3)	0.007(2)	0.003(3)
C(2)	0.029(3)	0.038(4)	0.025(3)	-0.001(3)	0.012(3)	0.001(3)
C(3)	0.035(3)	0.040(4)	0.046(4)	0.006(3)	0.005(3)	0.007(3)
C(4)	0.028(3)	0.054(5)	0.053(4)	0.000(3)	0.007(3)	0.005(3)
C(5)	0.038(4)	0.062(5)	0.051(4)	-0.005(4)	0.010(3)	0.003(3)
C(6)	0.048(4)	0.052(5)	0.050(4)	-0.020(4)	0.011(3)	0.008(3)
C(7)	0.045(4)	0.049(4)	0.042(4)	-0.008(3)	0.010(3)	0.009(3)
C(8)	0.031(3)	0.043(4)	0.039(3)	0.000(3)	0.006(3)	0.004(3)
C(9)	0.042(4)	0.031(4)	0.022(3)	0.007(3)	0.000(3)	-0.002(2)
C(10)	0.041(3)	0.037(4)	0.025(3)	0.015(3)	-0.004(3)	0.005(3)
C(11)	0.031(3)	0.033(4)	0.033(3)	0.006(3)	0.007(3)	0.006(3)
C(12)	0.035(3)	0.025(3)	0.030(3)	0.002(3)	0.007(3)	-0.006(3)
C(13)	0.030(3)	0.025(3)	0.028(3)	-0.005(3)	0.009(3)	-0.002(2)
C(14)	0.026(3)	0.026(3)	0.023(3)	0.002(3)	0.002(2)	0.000(2)
C(15)	0.029(3)	0.019(3)	0.030(3)	0.002(3)	0.002(2)	0.000(2)
C(16)	0.024(3)	0.028(3)	0.028(3)	-0.002(3)	0.000(2)	-0.004(3)
C(17)	0.036(3)	0.040(4)	0.023(3)	0.002(3)	-0.002(3)	-0.002(3)
C(18)	0.039(3)	0.027(3)	0.026(3)	0.007(3)	0.001(3)	-0.004(3)
C(19)	0.053(4)	0.037(4)	0.036(4)	0.018(3)	-0.009(3)	-0.002(3)

Table S 4-2. Anisotropic Displacement Parameters (continued)

atom	U11	U22	U33	U12	U13	U23
C(20)	0.089(6)	0.051(5)	0.066(5)	0.036(4)	-0.027(4)	-0.004(4)
C(21)	0.077(5)	0.073(6)	0.065(5)	0.047(4)	0.013(4)	0.001(4)
C(22)	0.088(6)	0.036(5)	0.087(6)	-0.001(4)	-0.017(5)	0.014(4)
C(23)	0.042(3)	0.033(4)	0.025(3)	-0.001(3)	0.004(3)	-0.010(3)
C(24)	0.180(9)	0.051(5)	0.039(4)	-0.002(6)	0.023(5)	-0.016(4)
C(25)	0.118(7)	0.109(8)	0.081(6)	-0.077(7)	0.042(5)	-0.056(6)
C(26)	0.092(6)	0.119(9)	0.096(7)	0.038(6)	-0.026(5)	-0.084(6)
C(27)	0.038(4)	0.055(5)	0.088(6)	-0.017(4)	-0.015(4)	0.020(4)
C(28)	0.038(4)	0.046(5)	0.089(5)	-0.011(4)	0.007(4)	0.021(4)
C(29)	0.065(6)	0.17(1)	0.19(1)	-0.052(7)	-0.031(6)	0.145(10)
C(30)	0.086(6)	0.063(7)	0.23(1)	-0.024(6)	-0.014(7)	-0.058(8)
C(31)	0.154(9)	0.13(1)	0.17(1)	-0.059(8)	0.130(9)	-0.065(9)
C(32)	0.038(4)	0.091(8)	0.165(9)	-0.016(5)	-0.026(5)	0.053(7)
C(33)	0.033(3)	0.036(4)	0.032(3)	0.016(3)	0.004(3)	0.001(3)
C(34)	0.043(4)	0.039(4)	0.033(3)	0.018(3)	-0.009(3)	-0.002(3)
C(35)	0.063(4)	0.044(4)	0.039(4)	0.018(4)	-0.004(3)	0.002(3)
C(36)	0.043(4)	0.056(5)	0.073(5)	0.010(4)	-0.009(3)	0.008(4)
C(37)	0.086(5)	0.067(6)	0.051(4)	0.046(5)	0.006(4)	0.002(4)
C(38)	0.079(5)	0.034(5)	0.091(6)	0.013(4)	-0.015(4)	-0.006(4)
C(39b)	0.07(2)	0.03(1)	0.03(1)	-0.01(1)	0.02(1)	0.005(9)
C(39a)	0.047(8)	0.034(8)	0.028(7)	-0.002(7)	0.003(6)	-0.006(6)
C(40b)	0.05(1)	0.034(10)	0.012(7)	-0.015(9)	0.010(7)	-0.009(7)
C(40a)	0.073(9)	0.034(7)	0.025(6)	0.011(7)	-0.001(6)	-0.009(5)
C(41)	0.078(5)	0.078(6)	0.038(4)	-0.007(4)	0.025(4)	-0.018(4)
C(42)	0.128(7)	0.050(6)	0.052(5)	0.008(5)	-0.040(5)	0.008(4)
C(43)	0.110(6)	0.067(6)	0.039(4)	0.055(5)	-0.016(4)	-0.023(4)
C(44)	0.061(5)	0.096(7)	0.045(4)	-0.023(4)	0.000(4)	-0.037(4)
B(1)	0.047(4)	0.017(3)	0.025(3)	0.006(3)	-0.001(3)	-0.004(3)
B(2)	0.018(3)	0.026(4)	0.025(3)	-0.001(3)	0.006(3)	-0.003(3)
B(3)	0.030(3)	0.021(4)	0.028(3)	0.006(3)	0.004(3)	0.004(3)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S 4 -3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Ir(1)	N(1)	2.177(4)	Ir(1)	N(2)	2.221(4)
Ir(1)	C(1)	2.308(5)	Ir(1)	C(2)	2.318(5)
Ir(1)	B(1)	2.055(7)	Ir(1)	B(2)	2.057(6)
Ir(1)	B(3)	2.027(6)	O(1)	C(27)	1.440(7)
O(1)	B(1)	1.379(7)	O(2)	C(28)	1.446(7)
O(2)	B(1)	1.384(7)	O(3)	C(33)	1.444(6)
O(3)	B(2)	1.392(7)	O(4)	C(34)	1.450(7)
O(4)	B(2)	1.395(7)	O(5)	C(39b)	1.50(2)
O(5)	C(39a)	1.48(1)	O(5)	B(3)	1.367(6)
O(6)	C(40b)	1.55(1)	O(6)	C(40a)	1.54(1)
O(6)	B(3)	1.352(7)	N(1)	C(9)	1.327(7)
N(1)	C(13)	1.368(7)	N(2)	C(14)	1.350(6)
N(2)	C(18)	1.345(6)	C(1)	C(2)	1.374(8)
C(1)	C(8)	1.510(7)	C(2)	C(3)	1.499(8)
C(3)	C(4)	1.543(8)	C(4)	C(5)	1.536(9)
C(5)	C(6)	1.538(9)	C(6)	C(7)	1.526(9)
C(7)	C(8)	1.533(8)	C(9)	C(10)	1.367(8)
C(10)	C(11)	1.392(8)	C(11)	C(12)	1.372(7)
C(11)	C(19)	1.534(8)	C(12)	C(13)	1.384(7)
C(13)	C(14)	1.480(8)	C(14)	C(15)	1.386(7)
C(15)	C(16)	1.388(7)	C(16)	C(17)	1.388(8)
C(16)	C(23)	1.532(7)	C(17)	C(18)	1.383(7)
C(19)	C(20)	1.508(9)	C(19)	C(21)	1.546(8)
C(19)	C(22)	1.517(10)	C(23)	C(24)	1.526(9)
C(23)	C(25)	1.482(9)	C(23)	C(26)	1.496(9)
C(27)	C(28)	1.517(10)	C(27)	C(29)	1.46(1)
C(27)	C(30)	1.54(1)	C(28)	C(31)	1.51(1)
C(28)	C(32)	1.51(1)	C(33)	C(34)	1.533(8)
C(33)	C(35)	1.500(8)	C(33)	C(36)	1.549(8)
C(34)	C(37)	1.512(8)	C(34)	C(38)	1.533(9)
C(39b)	C(39a)	0.82(2)	C(39b)	C(40b)	1.56(2)
C(39b)	C(40a)	1.15(2)	C(39b)	C(41)	1.52(2)

Table S 4-3. Bond Lengths(Å) (continued)

atom	atom	distance	atom	atom	distance
C(39b)	C(42)	1.68(3)	C(39a)	C(40b)	1.28(2)
C(39a)	C(40a)	1.48(2)	C(39a)	C(41)	1.50(1)
C(39a)	C(43)	1.60(1)	C(40b)	C(40a)	1.01(2)
C(40b)	C(43)	1.62(2)	C(40b)	C(44)	1.50(2)
C(40a)	C(42)	1.54(2)	C(40a)	C(44)	1.60(1)

Table S 4-4. Bond Lengths(Å) for the Hydrogen Atoms

atom	atom	distance	atom	atom	distance
C(1)	H(1)	0.95	C(2)	H(2)	0.95
C(3)	H(3)	0.95	C(3)	H(4)	0.95
C(4)	H(5)	0.95	C(4)	H(6)	0.95
C(5)	H(7)	0.95	C(5)	H(8)	0.95
C(6)	H(9)	0.95	C(6)	H(10)	0.95
C(7)	H(11)	0.95	C(7)	H(12)	0.95
C(8)	H(13)	0.95	C(8)	H(14)	0.95
C(9)	H(15)	0.95	C(10)	H(16)	0.95
C(12)	H(17)	0.95	C(15)	H(18)	0.95
C(17)	H(19)	0.95	C(18)	H(20)	0.95
C(20)	H(21)	0.95	C(20)	H(22)	0.95
C(20)	H(23)	0.95	C(21)	H(24)	0.95
C(21)	H(25)	0.95	C(21)	H(26)	0.95
C(22)	H(27)	0.95	C(22)	H(28)	0.95
C(22)	H(29)	0.95	C(24)	H(30)	0.95
C(24)	H(31)	0.95	C(24)	H(32)	0.95
C(25)	H(33)	0.95	C(25)	H(34)	0.95
C(25)	H(35)	0.95	C(26)	H(36)	0.95
C(26)	H(37)	0.95	C(26)	H(38)	0.95
C(29)	H(39)	0.95	C(29)	H(40)	0.95
C(29)	H(41)	0.95	C(30)	H(42)	0.95
C(30)	H(43)	0.95	C(30)	H(44)	0.95
C(31)	H(45)	0.95	C(31)	H(46)	0.95
C(31)	H(47)	0.95	C(32)	H(48)	0.95

C(32)	H(49)	0.95	C(32)	H(50)	0.95
C(35)	H(51)	0.95	C(35)	H(52)	0.95
C(35)	H(53)	0.95	C(36)	H(54)	0.95

Table S 4-4. Bond Lengths(Å) for the Hydrogen Atoms (continued)

atom	atom	distance	atom	atom	distance
C(36)	H(55)	0.95	C(36)	H(56)	0.95
C(37)	H(57)	0.95	C(37)	H(58)	0.95
C(37)	H(59)	0.95	C(38)	H(60)	0.95
C(38)	H(61)	0.95	C(38)	H(62)	0.95
C(41)	H(63)	0.95	C(41)	H(64)	0.95
C(41)	H(65)	0.95	C(42)	H(66)	0.95
C(42)	H(67)	0.95	C(42)	H(68)	0.95
C(43)	H(69)	0.95	C(43)	H(70)	0.95
C(43)	H(71)	0.95	C(44)	H(72)	0.95
C(44)	H(73)	0.95	C(44)	H(74)	0.95

Table S 4-5. Bond Angles(^{o})

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Ir(1)	N(2)	74.7(2)	N(1)	Ir(1)	C(1)	115.2(2)
N(1)	Ir(1)	C(2)	81.3(2)	N(1)	Ir(1)	B(1)	86.5(2)
N(1)	Ir(1)	B(2)	167.6(2)	N(1)	Ir(1)	B(3)	98.6(2)
N(2)	Ir(1)	C(1)	97.3(2)	N(2)	Ir(1)	C(2)	95.1(2)
N(2)	Ir(1)	B(1)	86.5(2)	N(2)	Ir(1)	B(2)	100.9(2)
N(2)	Ir(1)	B(3)	169.4(2)	C(1)	Ir(1)	C(2)	34.6(2)
C(1)	Ir(1)	B(1)	158.3(2)	C(1)	Ir(1)	B(2)	76.6(2)
C(1)	Ir(1)	B(3)	93.0(2)	C(2)	Ir(1)	B(1)	166.7(2)
C(2)	Ir(1)	B(2)	110.8(2)	C(2)	Ir(1)	B(3)	92.0(2)
B(1)	Ir(1)	B(2)	81.7(2)	B(1)	Ir(1)	B(3)	84.9(2)
B(2)	Ir(1)	B(3)	84.0(2)	C(27)	O(1)	B(1)	109.7(5)
C(28)	O(2)	B(1)	110.3(5)	C(33)	O(3)	B(2)	109.7(4)
C(34)	O(4)	B(2)	109.9(4)	C(39b)	O(5)	C(39a)	32.0(7)
C(39b)	O(5)	B(3)	107.8(9)	C(39a)	O(5)	B(3)	108.9(7)
C(40b)	O(6)	C(40a)	38.3(6)	C(40b)	O(6)	B(3)	107.9(7)
C(40a)	O(6)	B(3)	105.2(6)	Ir(1)	N(1)	C(9)	125.1(4)
Ir(1)	N(1)	C(13)	117.1(4)	C(9)	N(1)	C(13)	117.8(5)
Ir(1)	N(2)	C(14)	116.0(3)	Ir(1)	N(2)	C(18)	126.0(3)
C(14)	N(2)	C(18)	117.4(4)	Ir(1)	C(1)	C(2)	73.1(3)

Table S 4-5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
Ir(1)	C(1)	C(8)	117.8(4)	C(2)	C(1)	C(8)	122.8(5)
Ir(1)	C(2)	C(1)	72.3(3)	Ir(1)	C(2)	C(3)	115.5(4)
C(1)	C(2)	C(3)	125.0(5)	C(2)	C(3)	C(4)	115.1(5)
C(3)	C(4)	C(5)	115.5(5)	C(4)	C(5)	C(6)	115.9(5)
C(5)	C(6)	C(7)	116.4(6)	C(6)	C(7)	C(8)	115.3(5)
C(1)	C(8)	C(7)	110.1(5)	N(1)	C(9)	C(10)	123.8(5)
C(9)	C(10)	C(11)	119.9(5)	C(10)	C(11)	C(12)	116.2(5)
C(10)	C(11)	C(19)	123.2(5)	C(12)	C(11)	C(19)	120.6(5)
C(11)	C(12)	C(13)	122.3(5)	N(1)	C(13)	C(12)	120.0(5)
N(1)	C(13)	C(14)	115.7(5)	C(12)	C(13)	C(14)	124.2(5)
N(2)	C(14)	C(13)	115.9(5)	N(2)	C(14)	C(15)	122.0(5)
C(13)	C(14)	C(15)	122.1(5)	C(14)	C(15)	C(16)	121.3(5)
C(15)	C(16)	C(17)	115.7(5)	C(15)	C(16)	C(23)	120.9(5)
C(17)	C(16)	C(23)	123.4(5)	C(16)	C(17)	C(18)	121.1(5)
N(2)	C(18)	C(17)	122.5(5)	C(11)	C(19)	C(20)	112.4(5)
C(11)	C(19)	C(21)	109.3(5)	C(11)	C(19)	C(22)	108.1(5)
C(20)	C(19)	C(21)	109.3(6)	C(20)	C(19)	C(22)	108.8(6)
C(21)	C(19)	C(22)	108.8(6)	C(16)	C(23)	C(24)	111.3(5)
C(16)	C(23)	C(25)	108.9(5)	C(16)	C(23)	C(26)	110.8(5)
C(24)	C(23)	C(25)	107.7(6)	C(24)	C(23)	C(26)	106.5(6)
C(25)	C(23)	C(26)	111.6(8)	O(1)	C(27)	C(28)	103.4(5)
O(1)	C(27)	C(29)	110.7(6)	O(1)	C(27)	C(30)	104.7(6)
C(28)	C(27)	C(29)	118.8(8)	C(28)	C(27)	C(30)	111.2(7)
C(29)	C(27)	C(30)	107.1(9)	O(2)	C(28)	C(27)	102.1(5)
O(2)	C(28)	C(31)	105.6(6)	O(2)	C(28)	C(32)	108.9(6)
C(27)	C(28)	C(31)	112.2(8)	C(27)	C(28)	C(32)	116.8(7)
C(31)	C(28)	C(32)	110.4(7)	O(3)	C(33)	C(34)	103.0(4)
O(3)	C(33)	C(35)	110.6(4)	O(3)	C(33)	C(36)	106.1(5)
C(34)	C(33)	C(35)	116.4(5)	C(34)	C(33)	C(36)	111.7(5)
C(35)	C(33)	C(36)	108.4(5)	O(4)	C(34)	C(33)	102.9(5)
O(4)	C(34)	C(37)	109.0(5)	O(4)	C(34)	C(38)	105.9(5)
C(33)	C(34)	C(37)	117.4(5)	C(33)	C(34)	C(38)	111.8(5)
C(37)	C(34)	C(38)	109.1(6)	O(5)	C(39b)	C(39a)	73(2)
O(5)	C(39b)	C(40b)	95(1)	O(5)	C(39b)	C(40a)	108(1)

Table S 4-5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
O(5)	C(39b)	C(41)	103(1)	O(5)	C(39b)	C(42)	119(1)
C(39a)	C(39b)	C(40b)	55(1)	C(39a)	C(39b)	C(40a)	95(2)
C(39a)	C(39b)	C(41)	72(2)	C(39a)	C(39b)	C(42)	156(2)
C(40b)	C(39b)	C(40a)	40.4(9)	C(40b)	C(39b)	C(41)	116(1)
C(40b)	C(39b)	C(42)	102(1)	C(40a)	C(39b)	C(41)	141(1)
C(40a)	C(39b)	C(42)	62(1)	C(41)	C(39b)	C(42)	118(1)
O(5)	C(39a)	C(39b)	74(1)	O(5)	C(39a)	C(40b)	108(1)
O(5)	C(39a)	C(40a)	93.7(9)	O(5)	C(39a)	C(41)	104.6(9)
O(5)	C(39a)	C(43)	117.3(9)	C(39b)	C(39a)	C(40b)	92(2)
C(39b)	C(39a)	C(40a)	50(1)	C(39b)	C(39a)	C(41)	75(2)
C(39b)	C(39a)	C(43)	158(2)	C(40b)	C(39a)	C(40a)	42.2(8)
C(40b)	C(39a)	C(41)	140(1)	C(40b)	C(39a)	C(43)	67(1)
C(40a)	C(39a)	C(41)	115(1)	C(40a)	C(39a)	C(43)	109(1)
C(41)	C(39a)	C(43)	114.8(8)	O(6)	C(40b)	C(39b)	90(1)
O(6)	C(40b)	C(39a)	104(1)	O(6)	C(40b)	C(40a)	70(1)
O(6)	C(40b)	C(43)	123.1(10)	O(6)	C(40b)	C(44)	103(1)
C(39b)	C(40b)	C(39a)	31.8(9)	C(39b)	C(40b)	C(40a)	47(1)
C(39b)	C(40b)	C(43)	97(1)	C(39b)	C(40b)	C(44)	112(1)
C(39a)	C(40b)	C(40a)	79(1)	C(39a)	C(40b)	C(43)	65(1)
C(39a)	C(40b)	C(44)	133(1)	C(40a)	C(40b)	C(43)	144(1)
C(40a)	C(40b)	C(44)	76(1)	C(43)	C(40b)	C(44)	123(1)
O(6)	C(40a)	C(39b)	109(1)	O(6)	C(40a)	C(39a)	96.0(8)
O(6)	C(40a)	C(40b)	71(1)	O(6)	C(40a)	C(42)	121.3(8)
O(6)	C(40a)	C(44)	99.8(9)	C(39b)	C(40a)	C(39a)	33.6(10)
C(39b)	C(40a)	C(40b)	92(1)	C(39b)	C(40a)	C(42)	76(1)
C(39b)	C(40a)	C(44)	134(1)	C(39a)	C(40a)	C(40b)	58(1)
C(39a)	C(40a)	C(42)	109(1)	C(39a)	C(40a)	C(44)	112(1)
C(40b)	C(40a)	C(42)	164(1)	C(40b)	C(40a)	C(44)	65(1)
C(42)	C(40a)	C(44)	116.2(8)	C(39b)	C(41)	C(39a)	31.5(7)
C(39b)	C(42)	C(40a)	41.5(7)	C(39a)	C(43)	C(40b)	47.1(7)
C(40b)	C(44)	C(40a)	37.9(7)	Ir(1)	B(1)	O(1)	123.0(5)

Table S 4-6. Bond Angles(°) for the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
Ir(1)	C(1)	H(1)	79.4	C(2)	C(1)	H(1)	118.6
C(8)	C(1)	H(1)	118.6	Ir(1)	C(2)	H(2)	82.1
C(1)	C(2)	H(2)	117.5	C(3)	C(2)	H(2)	117.5
C(2)	C(3)	H(3)	108.1	C(2)	C(3)	H(4)	108.1
C(4)	C(3)	H(3)	108.1	C(4)	C(3)	H(4)	108.1
H(3)	C(3)	H(4)	109.5	C(3)	C(4)	H(5)	108.0
C(3)	C(4)	H(6)	108.0	C(5)	C(4)	H(5)	108.0
C(5)	C(4)	H(6)	108.0	H(5)	C(4)	H(6)	109.5
C(4)	C(5)	H(7)	107.8	C(4)	C(5)	H(8)	107.8
C(6)	C(5)	H(7)	107.8	C(6)	C(5)	H(8)	107.8
H(7)	C(5)	H(8)	109.5	C(5)	C(6)	H(9)	107.7
C(5)	C(6)	H(10)	107.7	C(7)	C(6)	H(9)	107.7
C(7)	C(6)	H(10)	107.7	H(9)	C(6)	H(10)	109.5
C(6)	C(7)	H(11)	108.0	C(6)	C(7)	H(12)	108.0
C(8)	C(7)	H(11)	108.0	C(8)	C(7)	H(12)	108.0
H(11)	C(7)	H(12)	109.5	C(1)	C(8)	H(13)	109.3
C(1)	C(8)	H(14)	109.3	C(7)	C(8)	H(13)	109.3
C(7)	C(8)	H(14)	109.3	H(13)	C(8)	H(14)	109.5
N(1)	C(9)	H(15)	118.1	C(10)	C(9)	H(15)	118.1
C(9)	C(10)	H(16)	120.0	C(11)	C(10)	H(16)	120.0
C(11)	C(12)	H(17)	118.9	C(13)	C(12)	H(17)	118.9
C(14)	C(15)	H(18)	119.4	C(16)	C(15)	H(18)	119.4
C(16)	C(17)	H(19)	119.5	C(18)	C(17)	H(19)	119.5
N(2)	C(18)	H(20)	118.8	C(17)	C(18)	H(20)	118.8
C(19)	C(20)	H(21)	109.5	C(19)	C(20)	H(22)	109.5
C(19)	C(20)	H(23)	109.5	H(21)	C(20)	H(22)	109.5
H(21)	C(20)	H(23)	109.5	H(22)	C(20)	H(23)	109.5
C(19)	C(21)	H(24)	109.5	C(19)	C(21)	H(25)	109.5
C(19)	C(21)	H(26)	109.5	H(24)	C(21)	H(25)	109.5
H(24)	C(21)	H(26)	109.5	H(25)	C(21)	H(26)	109.5
C(19)	C(22)	H(27)	109.5	C(19)	C(22)	H(28)	109.5
C(19)	C(22)	H(29)	109.5	H(27)	C(22)	H(28)	109.5
H(27)	C(22)	H(29)	109.5	H(28)	C(22)	H(29)	109.5

Table S 4-6. Bond Angles(°) for the Hydrogen Atoms (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(23)	C(24)	H(30)	109.5	C(23)	C(24)	H(31)	109.5
C(23)	C(24)	H(32)	109.5	H(30)	C(24)	H(31)	109.5
H(30)	C(24)	H(32)	109.5	H(31)	C(24)	H(32)	109.5
C(23)	C(25)	H(33)	109.5	C(23)	C(25)	H(34)	109.5
C(23)	C(25)	H(35)	109.5	H(33)	C(25)	H(34)	109.5
H(33)	C(25)	H(35)	109.5	H(34)	C(25)	H(35)	109.5
C(23)	C(26)	H(36)	109.5	C(23)	C(26)	H(37)	109.5
C(23)	C(26)	H(38)	109.5	H(36)	C(26)	H(37)	109.5
H(36)	C(26)	H(38)	109.5	H(37	C(26)	H(38)	109.5
C(27)	C(29)	H(39)	109.5	C(27)	C(29)	H(40)	109.5
C(27)	C(29)	H(41)	109.5	H(39)	C(29)	H(40)	109.5
H(39)	C(29)	H(41)	109.5	H(40)	C(29)	H(41)	109.5
C(27)	C(30)	H(42)	109.5	C(27)	C(30)	H(43)	109.5
C(27)	C(30)	H(44)	109.5	H(42)	C(30)	H(43)	109.5
H(42)	C(30)	H(44)	109.5	H(43)	C(30)	H(44)	109.5
C(28)	C(31)	H(45)	109.5	C(28)	C(31)	H(46)	109.5
C(28)	C(31)	H(47)	109.5	H(45)	C(31)	H(46)	109.5
H(45)	C(31)	H(47)	109.5	H(46)	C(31)	H(47)	109.5
C(28)	C(32)	H(48)	109.5	C(28)	C(32)	H(49)	109.5
C(28)	C(32)	H(50)	109.5	H(48)	C(32)	H(49)	109.5
H(48)	C(32)	H(50)	109.5	H(49)	C(32)	H(50)	109.5
C(33)	C(35)	H(51)	109.5	C(33)	C(35)	H(52)	109.5
C(33)	C(35)	H(53)	109.5	H(51)	C(35)	H(52)	109.5
H(51)	C(35)	H(53)	109.5	H(52)	C(35)	H(53)	109.5
C(33)	C(36)	H(54)	109.5	C(33)	C(36)	H(55)	109.5
C(33)	C(36)	H(56)	109.5	H(54)	C(36)	H(55)	109.5
H(54)	C(36)	H(56)	109.5	H(55)	C(36)	H(56)	109.5
C(34)	C(37)	H(57)	109.5	C(34)	C(37)	H(58)	109.5
C(34)	C(37)	H(59)	109.5	H(57)	C(37)	H(58)	109.5
H(57)	C(37)	H(59)	109.5	H(58)	C(37)	H(59)	109.5
C(34)	C(38)	H(60)	109.5	C(34)	C(38)	H(61)	109.5
C(34)	C(38)	H(62)	109.5	H(60)	C(38)	H(61)	109.5
H(60)	C(38)	H(62)	109.5	H(61)	C(38)	H(62)	109.5
C(39b)	C(41)	H(63)	90.1	C(39b)	C(41)	H(64)	140.8

Table S 4-6. Bond Angles(°) for the Hydrogen Atoms (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(39b)	C(41)	H(65)	94.4	C(39a)	C(41)	H(63)	109.5
C(39a)	C(41)	H(64)	109.5	C(39a)	C(41)	H(65)	109.5
H(63)	C(41)	H(64)	109.5	H(63)	C(41)	H(65)	109.5
H(64)	C(41)	H(65)	109.5	C(39b)	C(42)	H(66)	99.5
C(39b)	C(42)	H(67)	75.8	C(39b)	C(42)	H(68)	145.9
C(40a)	C(42)	H(66)	109.5	C(40a)	C(42)	H(67)	109.5
C(40a)	C(42)	H(68)	109.5	H(66)	C(42)	H(67)	109.5
H(66)	C(42)	H(68)	109.5	H(67)	C(42)	H(68)	109.5
C(39a)	C(43)	H(69)	109.5	C(39a)	C(43)	H(70)	109.5
C(39a)	C(43)	H(71)	109.5	C(40b)	C(43)	H(69)	82.0
C(40b)	C(43)	H(70)	84.4	C(40b)	C(43)	H(71)	156.5
H(69)	C(43)	H(70)	109.5	H(69)	C(43)	H(71)	109.5
H(70)	C(43)	H(71)	109.5	C(40b)	C(44)	H(72)	146.9
C(40b)	C(44)	H(73)	85.1	C(40b)	C(44)	H(74)	92.1
C(40a)	C(44)	H(72)	109.5	C(40a)	C(44)	H(73)	109.5
C(40a)	C(44)	H(74)	109.5	H(72)	C(44)	H(73)	109.5
H(72)	C(44)	H(74)	109.5	H(73)	C(44)	H(74)	109.5

Table S 4-7. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Ir(1)	N(1)	C(9)	C(10)	-177.5(4)	Ir(1)	N(1)	C(13)	C(12)	177.9(4)
Ir(1)	N(1)	C(13)	C(14)	0.5(6)	Ir(1)	N(2)	C(14)	C(13)	-8.2(6)
Ir(1)	N(2)	C(14)	C(15)	172.9(4)	Ir(1)	N(2)	C(18)	C(17)	-172.2(4)
Ir(1)	C(1)	C(2)	C(3)	109.2(6)	Ir(1)	C(1)	C(8)	C(7)	-177.6(4)
Ir(1)	C(2)	C(1)	C(8)	-112.6(5)	Ir(1)	C(2)	C(3)	C(4)	168.7(4)
Ir(1)	B(1)	O(1)	C(27)	-166.7(5)	Ir(1)	B(1)	O(2)	C(28)	-176.2(5)
Ir(1)	B(2)	O(3)	C(33)	171.4(4)	Ir(1)	B(2)	O(4)	C(34)	171.7(4)
Ir(1)	B(3)	O(5)	C(39b)	160.9(9)	Ir(1)	B(3)	O(5)	C(39a)	-165.4(7)
Ir(1)	B(3)	O(6)	C(40b)	161.0(8)	Ir(1)	B(3)	O(6)	C(40a)	-159.1(6)
O(1)	C(27)	C(28)	O(2)	24.8(7)	O(1)	C(27)	C(28)	C(31)	-87.8(7)
O(1)	C(27)	C(28)	C(32)	143.3(6)	O(1)	B(1)	Ir(1)	N(1)	8.6(5)
O(1)	B(1)	Ir(1)	N(2)	83.4(5)	O(1)	B(1)	Ir(1)	C(1)	-175.7(4)

Table S 4-7. Torsion Angles(°) (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	B(1)	Ir(1)	C(2)	-13(1)	O(1)	B(1)	Ir(1)	B(2)	-175.1(5)
O(1)	B(1)	Ir(1)	B(3)	-90.4(5)	O(1)	B(1)	O(2)	C(28)	7.8(7)
O(2)	C(28)	C(27)	C(29)	147.8(8)	O(2)	C(28)	C(27)	C(30)	-87.2(7)
O(2)	B(1)	Ir(1)	N(1)	-166.8(6)	O(2)	B(1)	Ir(1)	N(2)	-92.0(5)
O(2)	B(1)	Ir(1)	C(1)	8.9(10)	O(2)	B(1)	Ir(1)	C(2)	170.8(7)
O(2)	B(1)	Ir(1)	B(2)	9.5(5)	O(2)	B(1)	Ir(1)	B(3)	94.2(6)
O(2)	B(1)	O(1)	C(27)	9.5(7)	O(3)	C(33)	C(34)	O(4)	-24.1(5)
O(3)	C(33)	C(34)	C(37)	-143.8(5)	O(3)	C(33)	C(34)	C(38)	89.0(5)
O(3)	B(2)	Ir(1)	N(1)	-70.6(10)	O(3)	B(2)	Ir(1)	N(2)	-3.1(5)
O(3)	B(2)	Ir(1)	C(1)	91.9(4)	O(3)	B(2)	Ir(1)	C(2)	96.6(5)
O(3)	B(2)	Ir(1)	B(1)	-87.9(5)	O(3)	B(2)	Ir(1)	B(3)	-173.6(5)
O(3)	B(2)	O(4)	C(34)	-5.9(6)	O(4)	C(34)	C(33)	C(35)	-145.4(5)
O(4)	C(34)	C(33)	C(36)	89.3(5)	O(4)	B(2)	Ir(1)	N(1)	112.2(9)
O(4)	B(2)	Ir(1)	N(2)	179.7(4)	O(4)	B(2)	Ir(1)	C(1)	-85.3(5)
O(4)	B(2)	Ir(1)	C(2)	-80.6(5)	O(4)	B(2)	Ir(1)	B(1)	94.9(5)
O(4)	B(2)	Ir(1)	B(3)	9.3(5)	O(4)	B(2)	O(3)	C(33)	-11.0(6)
O(5)	C(39b)	C(39a)	C(40b)	-108.7(9)	O(5)	C(39b)	C(39a)	C(40a)	-108(1)
O(5)	C(39b)	C(39a)	C(41)	109.8(7)	O(5)	C(39b)	C(39a)	C(43)	-127(5)
O(5)	C(39b)	C(40b)	O(6)	-51(1)	O(5)	C(39b)	C(40b)	C(39a)	65(1)
O(5)	C(39b)	C(40b)	C(40a)	-113(1)	O(5)	C(39b)	C(40b)	C(43)	72(1)
O(5)	C(39b)	C(40b)	C(44)	-156(1)	O(5)	C(39b)	C(40a)	O(6)	4(2)
O(5)	C(39b)	C(40a)	C(39a)	74(2)	O(5)	C(39b)	C(40a)	C(40b)	75(1)
O(5)	C(39b)	C(40a)	C(42)	-114(1)	O(5)	C(39b)	C(40a)	C(44)	132(1)
O(5)	C(39b)	C(41)	C(39a)	-67(2)	O(5)	C(39b)	C(42)	C(40a)	96(1)
O(5)	C(39a)	C(39b)	C(40b)	108.7(9)	O(5)	C(39a)	C(39b)	C(40a)	108(1)
O(5)	C(39a)	C(39b)	C(41)	-109.8(7)	O(5)	C(39a)	C(39b)	C(42)	127(5)
O(5)	C(39a)	C(40b)	O(6)	-7(1)	O(5)	C(39a)	C(40b)	C(39b)	-74(1)
O(5)	C(39a)	C(40b)	C(40a)	-74(1)	O(5)	C(39a)	C(40b)	C(43)	112(1)
O(5)	C(39a)	C(40b)	C(44)	-133(1)	O(5)	C(39a)	C(40a)	O(6)	50(1)
O(5)	C(39a)	C(40a)	C(39b)	-66(2)	O(5)	C(39a)	C(40a)	C(40b)	114(1)
O(5)	C(39a)	C(40a)	C(42)	-75.8(9)	O(5)	C(39a)	C(40a)	C(44)	153.6(8)
O(5)	C(39a)	C(41)	C(39b)	69(2)	O(5)	C(39a)	C(43)	C(40b)	-100(1)
O(5)	B(3)	Ir(1)	N(1)	-88.7(6)	O(5)	B(3)	Ir(1)	N(2)	-38(1)
O(5)	B(3)	Ir(1)	C(1)	155.2(6)	O(5)	B(3)	Ir(1)	C(2)	170.2(6)

Table S 4-7. Torsion Angles(°) (conitnued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(5)	B(3)	Ir(1)	B(1)	-3.1(6)	O(5)	B(3)	Ir(1)	B(2)	79.1(6)
O(5)	B(3)	O(6)	C(40b)	-22.4(10)	O(5)	B(3)	O(6)	C(40a)	17.5(8)
O(6)	C(40b)	C(39b)	C(39a)	-116(2)	O(6)	C(40b)	C(39b)	C(40a)	62(1)
O(6)	C(40b)	C(39b)	C(41)	-158(1)	O(6)	C(40b)	C(39b)	C(42)	70(1)
O(6)	C(40b)	C(39a)	C(39b)	67(2)	O(6)	C(40b)	C(39a)	C(40a)	66(1)
O(6)	C(40b)	C(39a)	C(41)	137(1)	O(6)	C(40b)	C(39a)	C(43)	-120(1)
O(6)	C(40b)	C(40a)	C(39b)	-110(1)	O(6)	C(40b)	C(40a)	C(39a)	109.6(9)
O(6)	C(40b)	C(40a)	C(42)	-148(5)	O(6)	C(40b)	C(40a)	C(44)	110.5(6)
O(6)	C(40b)	C(43)	C(39a)	91(1)	O(6)	C(40b)	C(44)	C(40a)	-65(1)
O(6)	C(40a)	C(39b)	C(39a)	-70(2)	O(6)	C(40a)	C(39b)	C(40b)	-70(1)
O(6)	C(40a)	C(39b)	C(41)	-139(2)	O(6)	C(40a)	C(39b)	C(42)	118(1)
O(6)	C(40a)	C(39a)	C(39b)	117(2)	O(6)	C(40a)	C(39a)	C(40b)	-63(1)
O(6)	C(40a)	C(39a)	C(41)	158.5(8)	O(6)	C(40a)	C(39a)	C(43)	-70.2(9)
O(6)	C(40a)	C(40b)	C(39b)	110(1)	O(6)	C(40a)	C(40b)	C(39a)	109.6(9)
O(6)	C(40a)	C(40b)	C(43)	120(2)	O(6)	C(40a)	C(40b)	C(44)	-110.5(6)
O(6)	C(40a)	C(42)	C(39b)	-104(1)	O(6)	C(40a)	C(44)	C(40b)	64(1)
O(6)	B(3)	Ir(1)	N(1)	87.2(6)	O(6)	B(3)	Ir(1)	N(2)	137.3(9)
O(6)	B(3)	Ir(1)	C(1)	-28.9(6)	O(6)	B(3)	Ir(1)	C(2)	5.7(6)
O(6)	B(3)	Ir(1)	B(1)	172.8(7)	O(6)	B(3)	Ir(1)	B(2)	-105.0(6)
O(6)	B(3)	O(5)	C(39b)	-15(1)	O(6)	B(3)	O(5)	C(39a)	18.0(9)
N(1)	Ir(1)	N(2)	C(14)	6.3(3)	N(1)	Ir(1)	N(2)	C(18)	177.4(4)
N(1)	Ir(1)	C(1)	C(2)	-12.0(4)	N(1)	Ir(1)	C(1)	C(8)	106.7(4)
N(1)	Ir(1)	C(2)	C(1)	169.1(3)	N(1)	Ir(1)	C(2)	C(3)	48.1(4)
N(1)	C(9)	C(10)	C(11)	-1.0(9)	N(1)	C(13)	C(12)	C(11)	0.4(8)
N(1)	C(13)	C(14)	N(2)	5.2(7)	N(1)	C(13)	C(14)	C(15)	-175.9(5)
N(2)	Ir(1)	N(1)	C(9)	175.3(5)	N(2)	Ir(1)	N(1)	C(13)	-3.5(3)
N(2)	Ir(1)	C(1)	C(2)	-88.4(3)	N(2)	Ir(1)	C(1)	C(8)	30.3(4)
N(2)	Ir(1)	C(2)	C(1)	95.5(3)	N(2)	Ir(1)	C(2)	C(3)	-25.5(4)
N(2)	C(14)	C(13)	C(12)	-172.1(5)	N(2)	C(14)	C(15)	C(16)	1.0(8)
N(2)	C(18)	C(17)	C(16)	-0.5(9)	C(1)	Ir(1)	N(1)	C(9)	84.4(4)
C(1)	Ir(1)	N(1)	C(13)	-94.4(4)	C(1)	Ir(1)	N(2)	C(14)	120.6(4)
C(1)	Ir(1)	N(2)	C(18)	-68.4(4)	C(1)	Ir(1)	C(2)	C(3)	-121.0(6)
C(1)	C(2)	Ir(1)	B(1)	-168.3(8)	C(1)	C(2)	Ir(1)	B(2)	-8.2(4)
C(1)	C(2)	Ir(1)	B(3)	-92.5(3)	C(1)	C(2)	C(3)	C(4)	83.1(7)

Table S 4-7. Torsion Angles(°) (conitnued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(1)	C(8)	C(7)	C(6)	52.4(7)	C(2)	Ir(1)	N(1)	C(9)	77.5(4)
C(2)	Ir(1)	N(1)	C(13)	-101.2(4)	C(2)	Ir(1)	N(2)	C(14)	85.9(4)
C(2)	Ir(1)	N(2)	C(18)	-103.1(4)	C(2)	Ir(1)	C(1)	C(8)	118.6(5)
C(2)	C(1)	Ir(1)	B(1)	172.8(5)	C(2)	C(1)	Ir(1)	B(2)	172.1(4)
C(2)	C(1)	Ir(1)	B(3)	89.1(3)	C(2)	C(1)	C(8)	C(7)	-90.5(7)
C(2)	C(3)	C(4)	C(5)	-72.1(7)	C(3)	C(2)	Ir(1)	B(1)	70(1)
C(3)	C(2)	Ir(1)	B(2)	-129.2(4)	C(3)	C(2)	Ir(1)	B(3)	146.5(4)
C(3)	C(2)	C(1)	C(8)	-3.4(9)	C(3)	C(4)	C(5)	C(6)	69.8(7)
C(4)	C(5)	C(6)	C(7)	-102.6(6)	C(5)	C(6)	C(7)	C(8)	53.3(7)
C(8)	C(1)	Ir(1)	B(1)	-68.5(7)	C(8)	C(1)	Ir(1)	B(2)	-69.2(4)
C(8)	C(1)	Ir(1)	B(3)	-152.3(4)	C(9)	N(1)	Ir(1)	B(1)	-97.4(4)
C(9)	N(1)	Ir(1)	B(2)	-114.5(9)	C(9)	N(1)	Ir(1)	B(3)	-13.1(5)
C(9)	N(1)	C(13)	C(12)	-0.9(7)	C(9)	N(1)	C(13)	C(14)	-178.4(5)
C(9)	C(10)	C(11)	C(12)	0.4(8)	C(9)	C(10)	C(11)	C(19)	179.3(5)
C(10)	C(9)	N(1)	C(13)	1.3(8)	C(10)	C(11)	C(12)	C(13)	-0.1(8)
C(10)	C(11)	C(19)	C(20)	-4.7(8)	C(10)	C(11)	C(19)	C(21)	-126.3(6)
C(10)	C(11)	C(19)	C(22)	115.4(6)	C(11)	C(12)	C(13)	C(14)	177.6(5)
C(12)	C(11)	C(19)	C(20)	174.2(6)	C(12)	C(11)	C(19)	C(21)	52.6(8)
C(12)	C(11)	C(19)	C(22)	-65.8(7)	C(12)	C(13)	C(14)	C(15)	6.8(8)
C(13)	N(1)	Ir(1)	B(1)	83.9(4)	C(13)	N(1)	Ir(1)	B(2)	66.7(9)
C(13)	N(1)	Ir(1)	B(3)	168.1(4)	C(13)	C(12)	C(11)	C(19)	-179.1(5)
C(13)	C(14)	N(2)	C(18)	180.0(4)	C(13)	C(14)	C(15)	C(16)	-177.8(5)
C(14)	N(2)	Ir(1)	B(1)	-80.9(4)	C(14)	N(2)	Ir(1)	B(2)	-161.8(4)
C(14)	N(2)	Ir(1)	B(3)	-45(1)	C(14)	N(2)	C(18)	C(17)	-1.3(8)
C(14)	C(15)	C(16)	C(17)	-2.7(7)	C(14)	C(15)	C(16)	C(23)	179.4(5)
C(15)	C(14)	N(2)	C(18)	1.0(7)	C(15)	C(16)	C(17)	C(18)	2.4(8)
C(15)	C(16)	C(23)	C(24)	-158.4(6)	C(15)	C(16)	C(23)	C(25)	83.0(7)
C(15)	C(16)	C(23)	C(26)	-40.2(8)	C(17)	C(16)	C(23)	C(24)	23.7(8)
C(17)	C(16)	C(23)	C(25)	-94.8(7)	C(17)	C(16)	C(23)	C(26)	142.0(7)
C(18)	N(2)	Ir(1)	B(1)	90.1(5)	C(18)	N(2)	Ir(1)	B(2)	9.3(4)
C(18)	N(2)	Ir(1)	B(3)	125(1)	C(18)	C(17)	C(16)	C(23)	-179.7(5)
C(27)	C(28)	O(2)	B(1)	-20.5(7)	C(28)	C(27)	O(1)	B(1)	-21.8(7)
C(29)	C(27)	O(1)	B(1)	-150.0(8)	C(29)	C(27)	C(28)	C(31)	35(1)
C(29)	C(27)	C(28)	C(32)	-93.6(9)	C(30)	C(27)	O(1)	B(1)	94.8(7)

Table S 4-7. Torsion Angles(°) (conitnued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(30)	C(27)	C(28)	C(31)	160.2(7)	C(30)	C(27)	C(28)	C(32)	31.4(9)
C(31)	C(28)	O(2)	B(1)	96.9(8)	C(32)	C(28)	O(2)	B(1)	-144.6(6)
C(33)	C(34)	O(4)	B(2)	18.9(6)	C(34)	C(33)	O(3)	B(2)	22.1(6)
C(35)	C(33)	O(3)	B(2)	147.2(5)	C(35)	C(33)	C(34)	C(37)	94.9(7)
C(35)	C(33)	C(34)	C(38)	-32.2(7)	C(36)	C(33)	O(3)	B(2)	-95.4(5)
C(36)	C(33)	C(34)	C(37)	-30.3(8)	C(36)	C(33)	C(34)	C(38)	-157.5(5)
C(37)	C(34)	O(4)	B(2)	144.2(5)	C(38)	C(34)	O(4)	B(2)	-98.5(5)
C(39b)	O(5)	C(39a)	C(40b)	87(2)	C(39b)	O(5)	C(39a)	C(40a)	47(1)
C(39b)	O(5)	C(39a)	C(41)	-70(2)	C(39b)	O(5)	C(39a)	C(43)	161(2)
C(39b)	C(39a)	O(5)	B(3)	-93(2)	C(39b)	C(39a)	C(40b)	C(40a)	0(2)
C(39b)	C(39a)	C(40b)	C(43)	-172(2)	C(39b)	C(39a)	C(40b)	C(44)	-58(2)
C(39b)	C(39a)	C(40a)	C(40b)	-179(2)	C(39b)	C(39a)	C(40a)	C(42)	-9(2)
C(39b)	C(39a)	C(40a)	C(44)	-139(2)	C(39b)	C(39a)	C(43)	C(40b)	20(5)
C(39b)	C(40b)	O(6)	C(40a)	-43(1)	C(39b)	C(40b)	O(6)	B(3)	48(1)
C(39b)	C(40b)	C(39a)	C(40a)	0(2)	C(39b)	C(40b)	C(39a)	C(41)	70(2)
C(39b)	C(40b)	C(39a)	C(43)	172(2)	C(39b)	C(40b)	C(40a)	C(39a)	0(1)
C(39b)	C(40b)	C(40a)	C(42)	-38(5)	C(39b)	C(40b)	C(40a)	C(44)	-139(1)
C(39b)	C(40b)	C(43)	C(39a)	-3(1)	C(39b)	C(40b)	C(44)	C(40a)	31(1)
C(39b)	C(40a)	O(6)	C(40b)	85(1)	C(39b)	C(40a)	O(6)	B(3)	-14(1)
C(39b)	C(40a)	C(39a)	C(40b)	179(2)	C(39b)	C(40a)	C(39a)	C(41)	41(1)
C(39b)	C(40a)	C(39a)	C(43)	172(2)	C(39b)	C(40a)	C(40b)	C(39a)	0(1)
C(39b)	C(40a)	C(40b)	C(43)	9(2)	C(39b)	C(40a)	C(40b)	C(44)	139(1)
C(39b)	C(40a)	C(44)	C(40b)	-66(2)	C(39b)	C(41)	C(39a)	C(40b)	-76(2)
C(39b)	C(41)	C(39a)	C(40a)	-31(1)	C(39b)	C(41)	C(39a)	C(43)	-160(2)
C(39b)	C(42)	C(40a)	C(39a)	5(1)	C(39b)	C(42)	C(40a)	C(40b)	39(5)
C(39b)	C(42)	C(40a)	C(44)	133(1)	C(39a)	O(5)	C(39b)	C(40b)	-51(1)
C(39a)	O(5)	C(39b)	C(40a)	-90(2)	C(39a)	O(5)	C(39b)	C(41)	67(2)
C(39a)	O(5)	C(39b)	C(42)	-158(3)	C(39a)	C(39b)	O(5)	B(3)	97(2)
C(39a)	C(39b)	C(40b)	C(40a)	-179(2)	C(39a)	C(39b)	C(40b)	C(43)	6(1)
C(39a)	C(39b)	C(40b)	C(44)	137(2)	C(39a)	C(39b)	C(40a)	C(40b)	0(2)
C(39a)	C(39b)	C(40a)	C(42)	171(2)	C(39a)	C(39b)	C(40a)	C(44)	57(3)
C(39a)	C(39b)	C(42)	C(40a)	-22(5)	C(39a)	C(40b)	O(6)	C(40a)	-72(1)
C(39a)	C(40b)	O(6)	B(3)	19(1)	C(39a)	C(40b)	C(39b)	C(40a)	179(2)
C(39a)	C(40b)	C(39b)	C(41)	-41(1)	C(39a)	C(40b)	C(39b)	C(42)	-172(2)

Table S 2-7. Torsion Angles(°) (conitnued)

atom	atom	atom	atom	angle
C(39a)	C(40b)	C(40a)	C(42)	-38(6)
C(39a)	C(40b)	C(44)	C(40a)	60(1)
C(39a)	C(40a)	O(6)	B(3)	-45(1)
C(39a)	C(40a)	C(39b)	C(41)	-69(3)
C(39a)	C(40a)	C(40b)	C(43)	10(1)
C(39a)	C(40a)	C(44)	C(40b)	-36.5(10)
C(39a)	C(41)	C(39b)	C(40a)	77(3)
C(39a)	C(43)	C(40b)	C(40a)	-11(2)
C(40b)	O(6)	C(40a)	C(42)	170(2)
C(40b)	C(39b)	O(5)	B(3)	45(1)
C(40b)	C(39b)	C(39a)	C(41)	-141.5(10)
C(40b)	C(39b)	C(40a)	C(42)	170(1)
C(40b)	C(39b)	C(42)	C(40a)	-6.3(8)
C(40b)	C(39a)	C(39b)	C(40a)	0(1)
C(40b)	C(39a)	C(39b)	C(42)	19(6)
C(40b)	C(39a)	C(40a)	C(44)	39(1)
C(40b)	C(40a)	C(39b)	C(41)	-68(3)
C(40b)	C(40a)	C(39a)	C(41)	-137(1)
C(40b)	C(43)	C(39a)	C(40a)	4.7(8)
C(40b)	C(44)	C(40a)	C(42)	-163(1)
C(40a)	O(6)	C(40b)	C(44)	69(1)
C(40a)	C(39b)	C(39a)	C(41)	-142(1)
C(40a)	C(39b)	C(40b)	C(43)	-174(1)
C(40a)	C(39a)	O(5)	B(3)	-46(1)
C(40a)	C(39a)	C(39b)	C(42)	19(4)
C(40a)	C(39a)	C(40b)	C(44)	-59(1)
C(40a)	C(40b)	C(39b)	C(41)	139(2)
C(40a)	C(40b)	C(39a)	C(41)	71(2)
C(40a)	C(42)	C(39b)	C(41)	-135(2)
C(41)	C(39b)	O(5)	B(3)	164.8(8)
C(41)	C(39b)	C(40b)	C(43)	-34(1)
C(41)	C(39b)	C(40a)	C(42)	101(2)
C(41)	C(39a)	O(5)	B(3)	-163.8(7)
C(41)	C(39a)	C(40b)	C(43)	-101(2)

atom	atom	atom	atom	angle
C(39a)	C(40b)	C(40a)	C(44)	-139.9(9)
C(39a)	C(40a)	O(6)	C(40b)	53(1)
C(39a)	C(40a)	C(39b)	C(40b)	0(2)
C(39a)	C(40a)	C(39b)	C(42)	-171(2)
C(39a)	C(40a)	C(40b)	C(44)	139.9(9)
C(39a)	C(41)	C(39b)	C(40b)	34(1)
C(39a)	C(41)	C(39b)	C(42)	157(3)
C(39a)	C(43)	C(40b)	C(44)	-127(1)
C(40b)	O(6)	C(40a)	C(44)	-60(1)
C(40b)	C(39b)	C(39a)	C(40a)	0(1)
C(40b)	C(39b)	C(39a)	C(43)	-18(5)
C(40b)	C(39b)	C(40a)	C(44)	57(1)
C(40b)	C(39a)	O(5)	B(3)	-5(1)
C(40b)	C(39a)	C(39b)	C(41)	141.5(10)
C(40b)	C(39a)	C(40a)	C(42)	170(1)
C(40b)	C(40a)	O(6)	B(3)	-99(1)
C(40b)	C(40a)	C(39b)	C(42)	-170(1)
C(40b)	C(40a)	C(39a)	C(43)	-6(1)
C(40b)	C(43)	C(39a)	C(41)	136(1)
C(40a)	O(6)	C(40b)	C(43)	-143(1)
C(40a)	C(39b)	O(5)	B(3)	6(2)
C(40a)	C(39b)	C(39a)	C(43)	-19(6)
C(40a)	C(39b)	C(40b)	C(44)	-43(1)
C(40a)	C(39a)	C(39b)	C(41)	142(1)
C(40a)	C(39a)	C(40b)	C(43)	-173(1)
C(40a)	C(40b)	O(6)	B(3)	92(1)
C(40a)	C(40b)	C(39b)	C(42)	8(1)
C(40a)	C(40b)	C(39a)	C(43)	173(1)
C(40a)	C(44)	C(40b)	C(43)	147(1)
C(41)	C(39b)	C(39a)	C(43)	122(5)
C(41)	C(39b)	C(40b)	C(44)	96(2)
C(41)	C(39b)	C(40a)	C(44)	-11(4)
C(41)	C(39a)	C(39b)	C(42)	-122(5)
C(41)	C(39a)	C(40b)	C(44)	12(3)

Table S 3-7. Torsion Angles(°) (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(41)	C(39a)	C(40a)	C(42)	32(1)	C(41)	C(39a)	C(40a)	C(44)	-98(1)
C(42)	C(39b)	O(5)	B(3)	-61(1)	C(42)	C(39b)	C(39a)	C(43)	0(11)
C(42)	C(39b)	C(40b)	C(43)	-165.5(9)	C(42)	C(39b)	C(40b)	C(44)	-34(1)
C(42)	C(39b)	C(40a)	C(44)	-113(1)	C(42)	C(40a)	O(6)	B(3)	71(1)
C(42)	C(40a)	C(39a)	C(43)	163.6(7)	C(42)	C(40a)	C(40b)	C(43)	-28(7)
C(42)	C(40a)	C(40b)	C(44)	100(5)	C(43)	C(39a)	O(5)	B(3)	67(1)
C(43)	C(39a)	C(40b)	C(44)	114(2)	C(43)	C(39a)	C(40a)	C(44)	32(1)
C(43)	C(40b)	O(6)	B(3)	-50(1)	C(43)	C(40b)	C(40a)	C(44)	-129(2)
C(44)	C(40b)	O(6)	B(3)	161.8(8)	C(44)	C(40a)	O(6)	B(3)	-159.8(7)

Table S 4-8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
C(35)	C(41)	3.596(9)	55404				

Symmetry Operators:

(1)	X,	Y,	Z	(2)	-X,	1/2+Y,	1/2-Z
(3)	-X,	-Y,	-Z	(4)	X,	1/2-Y,	1/2+Z