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Methoxy-Substituted Bis-tridentate Iridium(III) Phosphors and Fabrication of Blue Organic Light Emitting Diodes

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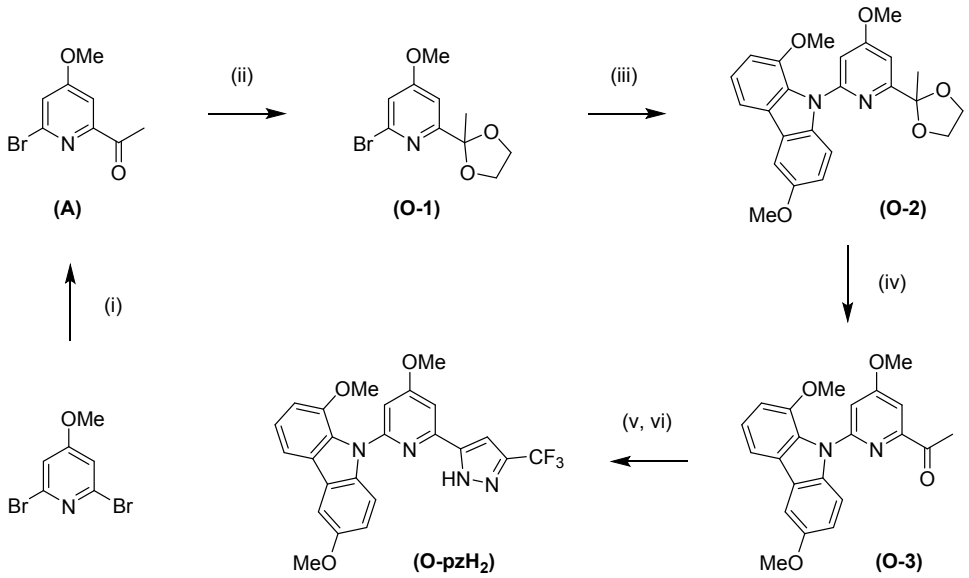
Experimental section:

General information and materials. All reactions were conducted under N_2 atmosphere and solvents were dried prior to use. Commercially available reagents were used without further purification. ^1H and ^{19}F NMR spectra were measured with Varian Mercury-400 instrument or Varian Mercury-500 instrument. Elemental analysis was carried out on a Heraeus CHN-O Rapid Elementary Analyzer. Mass spectra were recorded on a JEOL Model: JMS-T200GC AccuTOF GCx instrument operating in electron impact (EI) or field desorption (FD) mode.

Synthetic procedures for dianionic ligands used in this work.

The adopted synthetic procedures for 1,6-dimethoxy-9-(4-methoxy-6-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl)pyridin-2-yl)-9*H*-carbazole (**O-pzH$_2$**) were depicted in Scheme S1.



Scheme S1. Synthetic route to dianionic ligand **O-pzH$_2$**: (i) *n*-BuLi, ether, DMA, –78 °C to RT; (ii) ethylene glycol, *p*-toluenesulfonic acid, toluene, reflux; (iii) 1,6-dimethoxy-9*H*-carbazole, NaOBu^t, $Pd_2(dba)_3$, tri-*tert*-butylphosphonium tetrafluoroborate, toluene, reflux; (iv) 2 N HCl, reflux; (v) NaOEt, ethyl trifluoroacetate, dry THF, 0 °C to reflux; (vi) N_2H_4, *p*-toluenesulfonic acid, EtOH, reflux.

Synthesis of 1-(6-bromo-4-methoxypyridin-2-yl)ethanone (A)

To a suspension of 2,6-dibromo-4-methoxypyridine (4.98 g, 18.7 mmol) in dry diethyl ether (100 mL) was slowly added *n*-BuLi (2.5 M in hexane, 8.20 mL, 20.6 mmol) at -78 °C under N_2. The solution was stirred for 1 h at -78 °C. Dimethylacetamide (3.00 mL, 31.8 mmol) was then slowly added at -78 °C, and the solution was warmed to RT. This mixture was stirred for 12 hours at RT, followed by neutralization with 2N HCl. The mixture was extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was next purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:6) to afford a white solid (A); yield: 3.39 g, 79%.

Spectral data of A: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1 H), 7.15 (s, 1 H), 3.90 (s, 3 H), 2.68 (s, 3 H).

Synthesis of 2-bromo-4-methoxy-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (O-1)

A mixture of 1-(6-bromo-4-methoxypyridin-2-yl)ethanone (A) (5.22 g, 22.7 mmol), ethylene glycol (9.50 mL, 170 mmol) and *p*-toluenesulfonic acid monohydrate (432 mg, 2.27 mmol) in dry toluene (115 mL) was heated to reflux for 24 h. After cooled to RT, the mixture was neutralized with $NaHCO_{3(aq)}$, and then extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:4) to afford an orange oil (O-1); yield: 5.55 g, 89%.

Spectral data of O-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (s, 1 H), 6.91 (s, 1 H), 4.09 ~ 4.06 (m, 2 H), 3.89 ~ 3.87 (m, 2 H), 3.85 (s, 3 H), 1.69 (s, 3 H).

Synthesis of 1,6-dimethoxy-9-(4-methoxy-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)-9*H*-carbazole (O-2)

To a 100 mL of round-bottom flask was charged with 2-bromo-4-methoxy-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (O-1) (2.42 g, 8.83 mmol), 1,6-dimethoxy-9*H*-carbazole (1.54 g, 6.79 mmol), $NaOBu^t$ (1.96 g, 20.4 mmol), $Pd_2(dba)_3$ (622 mg, 0.68 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (788 mg, 2.72 mmol) in degassed toluene (35 mL). The mixture was heated to reflux for 12 h. After cooled to RT, the mixture was extracted into ethyl acetate, washed with deionized water three times and dried over anhydrous Na_2SO_4, and then concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:4) to afford a yellow solid (O-2); yield: 2.51 g, 88%.

Spectral data of O-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 9.0 Hz, 2 H), 7.51 (d, J = 2.4 Hz, 1 H), 7.22 (t, J = 7.8 Hz, 1 H), 7.11 (d, J = 2.0 Hz, 1 H), 7.02 (dd, J = 9.0 Hz, 2.4 Hz, 1 H), 6.94 (d, J = 7.8 Hz, 1 H), 6.67 (d, J = 2.0 Hz, 1 H), 4.16 ~ 4.12 (m, 2 H), 4.02 ~4.00 (m, 2 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 3.76 (s, 3 H), 1.84 (s, 3 H).

Synthesis of 1-(6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypyridin-2-yl)ethanone (O-3)

A mixture of 1,6-dimethoxy-9-(4-methoxy-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-2-yl)-9*H*-carbazole (O-2) (5.36 g, 12.7 mmol) in 2 N HCl (90 mL) was heated to reflux for 12 h. After cooled to RT, the mixture was neutralized with $NaHCO_{3(aq)}$, and then extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography, eluting

with a mixture of ethyl acetate and hexane (1:2) to afford a yellow solid (O-3); yield: 4.18 g, 87%.

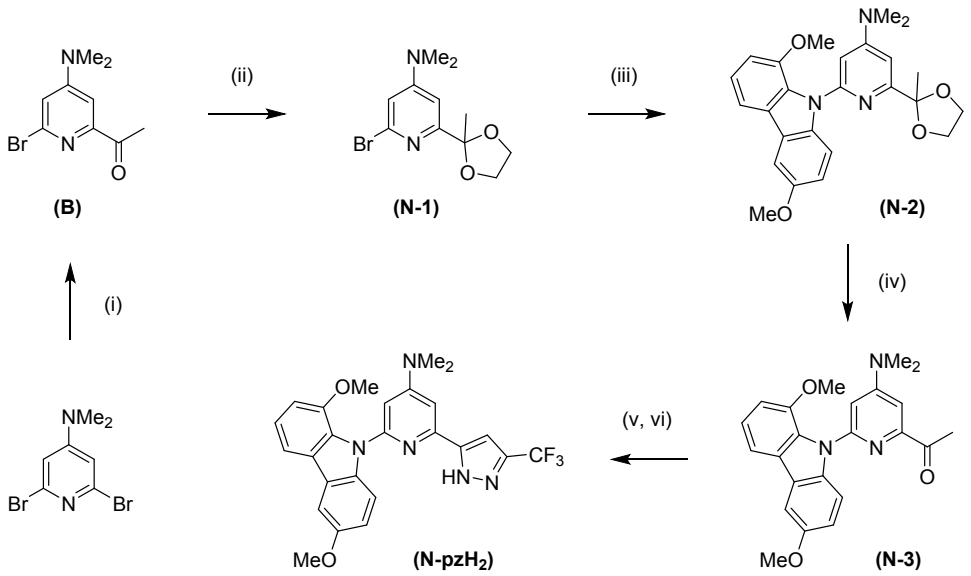
Spectral data of O-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (t, J = 7.9 Hz, 2 H), 7.59 (d, J = 2.3 Hz, 1 H), 7.54 (d, J = 2.6 Hz, 1 H), 7.27 (t, J = 7.9 Hz, 1 H), 7.05 (dd, J = 9.0 Hz, 2.6 Hz, 1 H), 6.97 (d, J = 7.9 Hz, 1 H), 6.88 (d, J = 2.3 Hz, 1 H), 3.94 (s, 3 H), 3.92 (s, 3 H), 3.79 (s, 3 H), 2.77 (s, 3 H).

Synthesis of 1,6-dimethoxy-9-(4-methoxy-6-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl) pyridin-2-yl)-9*H*-carbazole (**O-pzH$_2$**)

To a 100 mL of round-bottom flask was charged with 1-(6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypyridin-2-yl)ethanone (O-3) (1.55 g, 4.12 mmol) and NaOEt (336 mg, 4.94 mmol) in dry THF (40 mL). The mixture was stirred at 0 °C for 30 minutes. Ethyl trifluoroacetate (0.74 mL, 6.18 mmol) was then added at 0 °C and the mixture was heated to reflux for 12 hours. After cooled to RT, the solution was neutralized with 2N HCl. Excessive THF solvent was evaporated and the residue was extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. To this mixture was added hydrazine monohydrate (1.00 mL, 20.6 mmol) and catalytic amount of *p*-toluenesulfonic acid and ethanol (40 mL). The mixture was refluxed for 24 hours and then concentrated. The residue was extracted into ethyl acetate, washed with deionized water three times and dried over anhydrous Na_2SO_4, and then concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:3) to afford a white solid (**O-pzH$_2$**); yield: 1.21 g, 63%.

Spectral data of **O-pzH$_2$**: ^{1}H NMR (500 MHz, acetone-d_6): δ 13.55 (br, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.71 (d, J = 2.4 Hz, 1 H), 7.61 (d, J = 8.9 Hz, 1 H), 7.60 (d, J = 1.9 Hz, 1 H), 7.40 (s, 1 H), 7.26 (t, J = 8.0 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1 H), 7.03 (dd, J = 8.9 Hz, 2,4 Hz, 1 H), 6.94 (d, J = 1.9 Hz, 1 H), 4.04 (s, 3 H), 3.91 (s, 3 H), 3.80 (s, 3 H). ^{19}F NMR (470 MHz, acetone-d_6): δ -62.53 (s, 3 F). EI MS: m/z 468.2 M^+.

The adopted synthetic procedures for 2-(1,6-dimethoxy-9*H*-carbazol-9-yl)-*N*,*N*-dimethyl-6-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl)pyridin-4-amine (**N-pzH$_2$**) were depicted in Scheme S2.



Scheme S2. Synthetic route to dianionic ligand **N-pzH_2**: (i) *n*-BuLi, THF, DMA, –78 °C to RT; (ii) ethylene glycol, *p*-toluenesulfonic acid, toluene, reflux; (iii) 1,6-dimethoxy-9*H*-carbazole, $NaOBu^t$, $Pd_2(dba)_3$, tri-*tert*-butylphosphonium tetrafluoroborate, toluene, reflux; (iv) 2 N HCl, reflux; (v) NaOEt, ethyl trifluoroacetate, THF, 0 °C to reflux; (vi) N_2H_4, *p*-toluenesulfonic acid, EtOH, reflux.

Synthesis of 1-(6-bromo-4-(dimethylamino)pyridin-2-yl)ethanone (B)

To a suspension of 2,6-dibromo-*N*,*N*-dimethylpyridin-4-amine (6.50 g, 23.2 mmol) in dry THF (120 mL) was slowly added *n*-BuLi (1.6 M in hexane, 16.0 mL, 25.5 mmol) at -78 °C under N_2. The solution was stirred for 1 hour at -78 °C. Dimethylacetamide (3.70 mL, 39.4 mmol) was then slowly added at -78 °C, and the solution was warmed to RT. This mixture was stirred for 1 hour at RT, followed by neutralization with 2N HCl solution. The mixture was extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was next purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:5) to afford a white solid (B); yield: 3.32 g, 59%.

Spectral data of B: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 2.3 Hz, 1 H), 6.76 (d, J = 2.3 Hz, 1 H), 3.04 (s, 6 H), 2.65 (s, 3 H).

Synthesis of 2-bromo-*N*,*N*-dimethyl-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-4-amine (N-1)

A mixture of 1-(6-bromo-4-(dimethylamino)pyridin-2-yl)ethanone (B) (3.32 g, 13.7 mmol), ethylene glycol (5.70 mL, 102 mmol) and *p*-toluenesulfonic acid monohydrate (260

mg, 1.37 mmol) in dry toluene (75 mL) was heated to reflux for 24 h. After cooled to RT, the mixture was neutralized with $NaHCO_{3(aq)}$, and then extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:1) to afford a colorless oil (N-1); yield: 3.72 g, 95%.

Spectral data of N-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (d, *J* = 2.3 Hz, 1 H), 6.55 (d, *J* = 2.3 Hz, 1 H), 4.07 ~ 4.04 (m, 2 H), 3.89 ~ 3.85 (m, 2 H), 3.00 (s, 6 H), 1.68 (s, 3 H).

Synthesis of 2-(1,6-dimethoxy-9*H*-carbazol-9-yl)-*N*,*N*-dimethyl-6-(2-methyl-1,3-dioxolan-2-yl) pyridin-4-amine (N-2)

To a 100 mL of round-bottom flask was charged with 2-bromo-*N*,*N*-dimethyl-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-4-amine (N-1) (3.87 g, 13.5 mmol), 1,6-dimethoxy-9*H*-carbazole (2.36 g, 10.4 mmol), $NaOBu^t$ (2.99 g, 31.1 mmol), $Pd_2(dba)_3$ (949 mg, 1.04 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (1.20 mg, 4.15 mmol) in degassed toluene (55 mL). The mixture was heated to reflux for 12 h. After cooled to RT, the mixture was extracted into ethyl acetate, washed with deionized water three times and dried over anhydrous Na_2SO_4, and then concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:1) to afford a yellow solid (N-2); yield: 3.33 g, 74%.

Spectral data of N-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.8 Hz, 1 H), 7.57 (d, *J* = 9.0 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.00 (dd, *J* = 9.0 Hz, 2.4 Hz, 1 H), 6.91 (d, *J* = 7.8 Hz, 1 H), 6.87 (d, *J* = 2.4 Hz, 1 H), 6.39 (d, *J* = 2.4 Hz, 1 H), 4.14 ~ 4.11 (m,2 H), 4.01 ~ 3.98 (m, 2 H), 3.92 (s, 3 H), 3.73 (s, 3 H), 3.03 (s, 6 H), 1.83 (s, 3 H).

Synthesis of 1-(6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-(dimethylamino)pyridin-2-yl)ethanone (N-3)

A mixture of 2-(1,6-dimethoxy-9*H*-carbazol-9-yl)-*N*,*N*-dimethyl-6-(2-methyl-1,3-dioxolan-2-yl)pyridin-4-amine (N-2) (3.33 g, 7.68 mmol) in 2 N HCl (55 mL) was heated to reflux for 12 h. After cooled to RT, the mixture was neutralized with $NaHCO_{3(aq)}$, and then extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:2) to afford a yellow solid (N-3); yield: 2.79 g, 93%.

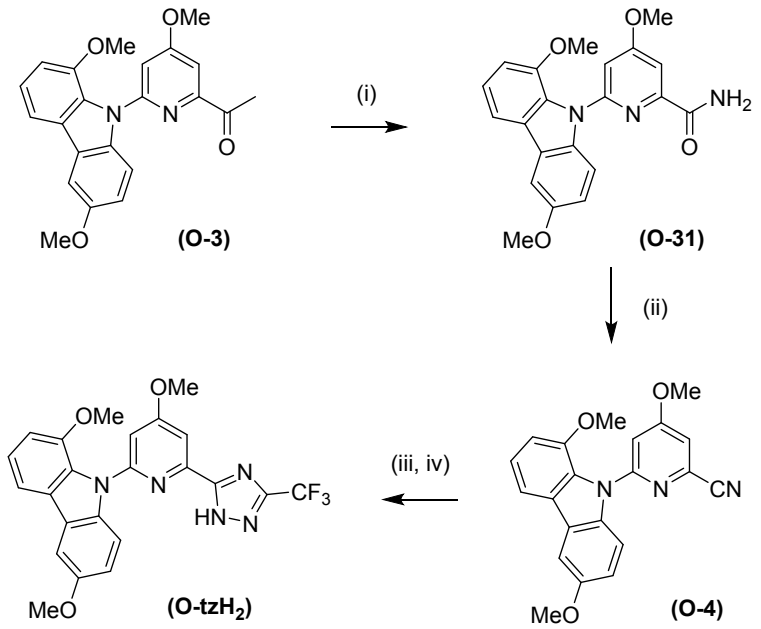
Spectral data of N-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.8 Hz, 1 H), 7.68 (d, J = 9.0 Hz, 1 H), 7.54 (d, J = 2.3 Hz, 1 H), 7.35 (d, J = 2.3 Hz, 1 H), 7.24 (t, J = 7.8 Hz, 1 H), 7.04 (dd, J = 9.0 Hz, 2.4 Hz, 1 H), 6.96 (d, J = 7.8 Hz, 1 H), 6.56 (d, J = 2.4 Hz, 1 H), 3.94 (s, 3 H), 3.77 (s, 3 H), 3.06 (s, 6 H), 2.74 (s, 3 H).

Synthesis of 2-(1,6-dimethoxy-9*H*-carbazol-9-yl)-*N*,*N*-dimethyl-6-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl)pyridin-4-amine (**N-pzH$_2$**)

To a 100 mL of round-bottom flask was charged with 1-(6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-(dimethylamino)pyridin-2-yl)ethanone (N-3) (2.79 g, 7.16 mmol) and NaOEt (585 mg, 8.59 mmol) in dry THF (70 mL). The mixture was stirred at 0 °C for 30 minutes. Ethyl trifluoroacetate (1.30 mL, 10.7 mmol) was then added at 0 °C and the mixture was heated to reflux for 12 hours. After cooled to RT, the solution was neutralized with 2N HCl. Excessive THF solvent was evaporated and the residue was extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. To this mixture was added hydrazine monohydrate (1.75 mL, 35.8 mmol) and catalytic amount of *p*-toluenesulfonic acid and ethanol (70 mL). The mixture was refluxed for 24 hours and then concentrated. The residue was extracted into ethyl acetate, washed with deionized water three times and dried over anhydrous Na_2SO_4, and then concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:1) to afford a white solid (**O-pzH$_2$**); yield: 1.98 g, 57%.

Spectral data of **N-pzH$_2$**: ^{1}H NMR (500 MHz, acetone-d_6): δ 13.39 (br, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.70 (d, J = 2.5 Hz, 1 H), 7.55 (d, J = 9.0 Hz, 1 H), 7.34 (s, 1 H), 7.32 (d, J = 2.5 Hz, 1 H), 7.23 (t, J = 8.0 Hz, 1 H), 7.04 (d, J = 8.0 Hz, 1 H), 7.01 (dd, J = 9.0 Hz, 2.5 Hz, 1 H), 6.61 (d, J = 2.5 Hz, 1 H), 3.91 (s, 3 H), 3.77 (s, 3 H), 3.17 (s, 6 H). ^{19}F NMR (470 MHz, acetone-d_6): δ -62.46 (s, 3 F). EI MS: m/z 481.2 M^+.

The adopted synthetic procedures for 1,6-dimethoxy-9-(4-methoxy-6-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridin-2-yl)-9*H*-carbazole (**O-tzH$_2$**) were depicted in Scheme S3.



Scheme S3. Synthetic route to dianionic ligand **O-tzH$_2$**: (i) $NH_{3(aq)}$, TBAI, *t*-BuOOH, 100 °C; (ii) Et_3N, trifluoroacetic anhydride, THF, 0 °C; (iii) LHMDS, HCl, THF, RT to reflux; (iv) 2,2,2-trifluoroacetohydrazide, NaOH, THF, reflux.

Synthesis of 6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypicolinamide (O-31)[1]

To a 50 mL of sealed tube was charged with 1-(6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypyridin-2-yl)ethanone (O-3) (2.45 g, 6.51 mmol), $NH_{3(aq)}$ (25% in H_2O, 6.65 mL, 97.6 mmol), tetrabutylammonium iodide (1.20 g, 3.25 mmol) and *t*-BuOOH (70% in H_2O, 7.13 mL, 52.1 mmol). The mixture was heated at 100 °C for 16 h. After cooled to RT, the mixture was extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:2) to afford an orange solid (O-31); yield: 1.10 g, 45%.

Spectral data of O-31: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (br, 1 H), 7.79 (d, J = 2.4 Hz, 1 H), 7.71 (d, J = 7.8 Hz, 1 H), 7.55 (s, 1 H), 7.53 (d, J = 5.5 Hz, 1 H), 7.27 (t, J = 9.0 Hz, 1 H), 7.04 (dd, J = 9.0 Hz, 2.4 Hz, 1 H), 6.96 (d, J = 7.8 Hz, 1 H), 6.92 (d, J = 2.4 Hz, 1 H), 5.62 (br, 1 H), 3.95 (s, 3 H), 3.94 (s, 3 H), 3.77 (s, 3 H).

Synthesis of 6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypicolinonitrile (O-4)[2]

To a 50 mL of round-bottom flask was charged with 6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypicolinamide (O-31) (1.09 g, 2.89 mmol) and Et_3N (0.97 mL, 6.96 mmol) in dry THF

(20 mL). Trifluoroacetic anhydride (0.48 mL, 3.43 mmol) was slowly added at 0 °C and stirred for 2 hours at 0 °C. After that, excessive THF solvent was evaporated and the residue was extracted into ethyl acetate, washed with deionized water three times, dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:2) to afford a yellow liquid (O-4); yield: 937 mg, 94%.

Spectral data of O-4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 9.0 Hz, 1 H), 7.70 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.51 (d, *J* = 2.3 Hz, 1 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 7.22 (d, *J* = 2.3 Hz, 1 H), 7.06 (dd, *J* = 9.0 Hz, 2.3 Hz, 1 H), 6.98 (dd, *J* = 7.8 Hz, 1.2 Hz, 1 H), 6.87 (d, *J* = 2.3 Hz, 1 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 3.82 (s, 3 H).

Synthesis of 1,6-dimethoxy-9-(4-methoxy-6-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl) pyridin-2-yl)-9*H*-carbazole (**O-tzH$_2$**)[3]

A solution of 6-(1,6-dimethoxy-9*H*-carbazol-9-yl)-4-methoxypicolinonitrile (O-31) (488 mg, 1.36 mmol) and lithium bis(trimethylsilyl)amide (1 M in THF, 4.80 mg, 4.75 mmol) in dry THF (20 mL) was stirred at RT for 6 h. The mixture was then added HCl (1 M in EtOH, 5.00 mL, 6.25 mmol) at 0 °C and the solution was warmed to RT. This mixture was stirred for 12 hours at RT. After that, the solvent was evaporated. To this mixture was added 2,2,2-trifluoroacetohydrazide (174 mg, 1.36 mmol), NaOH (60.0 mg, 1.50 mmol) and dry THF (20 mL). After refluxed for 12 hours, the mixture was concentrated and the residue was extracted into ethyl acetate, washed with deionized water three times and dried over anhydrous Na_2SO_4, and then concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:1) to afford a white solid (**O-tzH$_2$**); yield: 315 mg, 50%.

Spectral data of **O-tzH$_2$**: ^{1}H NMR (500 MHz, acetone-d_6): δ 14.66 (br, 1 H), 7.82 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 7.77 (d, *J* = 2.5 Hz, 1 H), 7.73 (d, *J* = 2.5 Hz, 1 H), 7.61 (d, *J* = 9.2 Hz, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 2.5 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 7.02 (dd, *J* = 9.2 Hz, 2.5 Hz, 1 H), 4.09 (s, 3 H), 3.92 (s, 3 H), 3.80 (s, 3 H). ^{19}F NMR (470 MHz, acetone-d_6): δ -65.74 (s, 3 F). EI MS: m/z 469.2 M^+.

X-Ray Structural Determination. Single crystal X-ray diffraction data were recorded on a Bruker D8 VENTURE diffractometer equipped with Oxford Cryostream 800+ controller. The data was collected using the SMART program, and cell refinement and data reduction were made with the SAINT program. The structure was determined using the SHELXTL/PC

program and refined using full-matrix least squares.[4] All non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms of hydrocarbyl fragments were placed at the calculated positions with fixed positional parameters, and hydride was independently located on the electron density map and included in the final stage of refinements. CCDC 1998097 contains the crystallographic data for I(III) metal complex **Cz6**. This data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

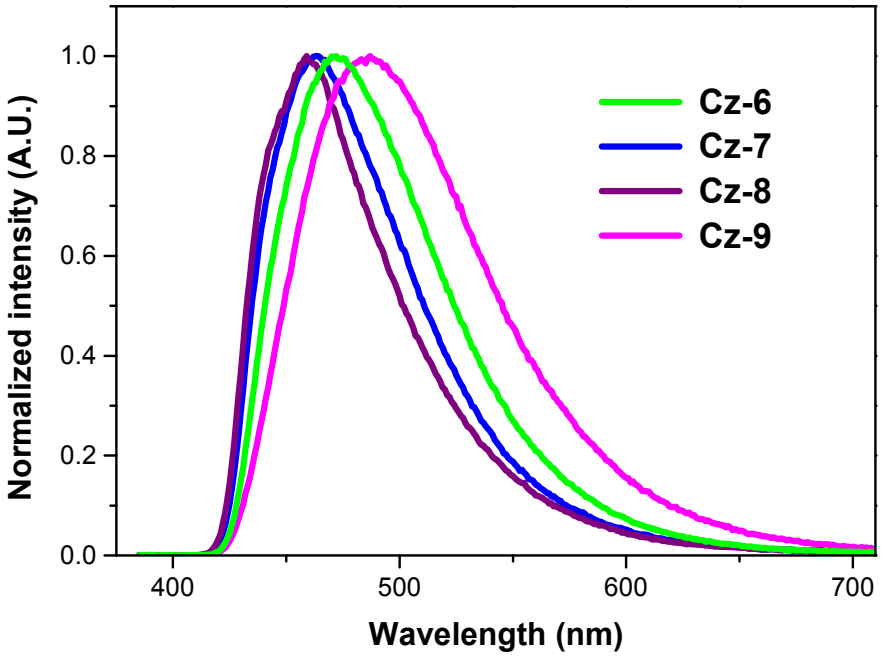


Figure S1. Emission of PMMA thin films doped with 2 wt.% of the studied bis-tridentate Ir(III) complexes at RT.

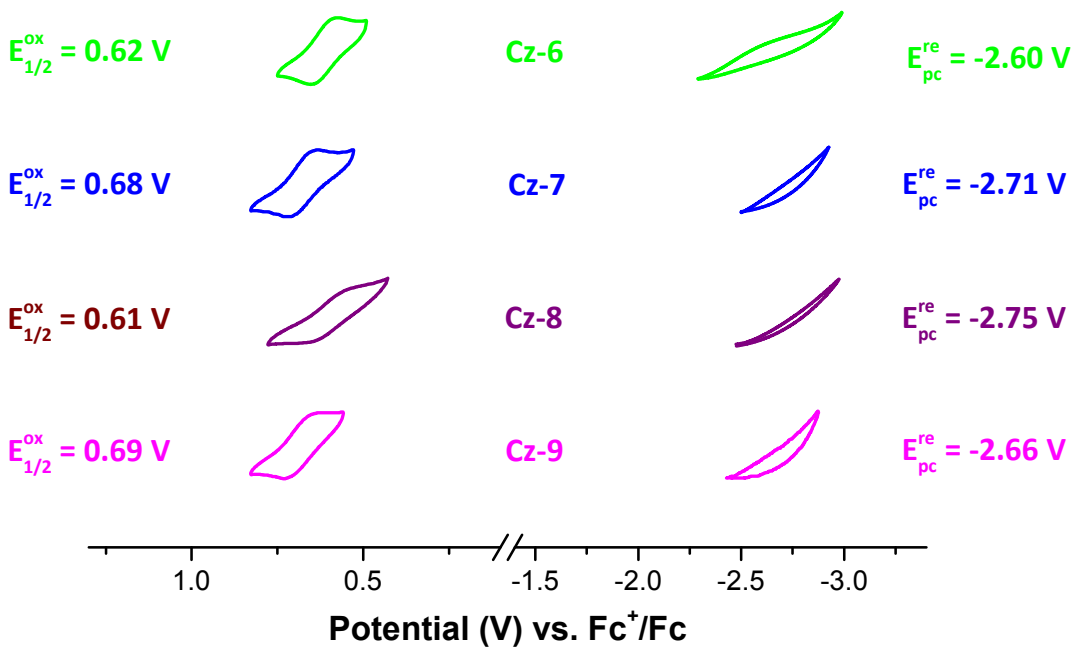


Figure S2. Cyclic voltammetry of the studied bis-tridentate Ir(III) complexes.

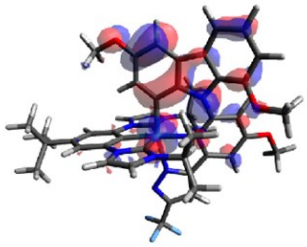
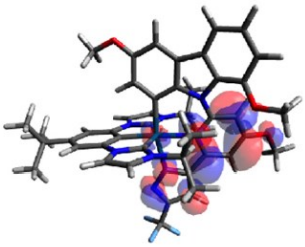
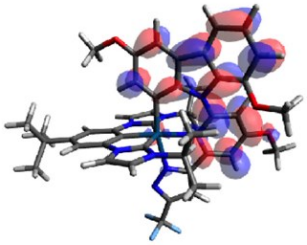
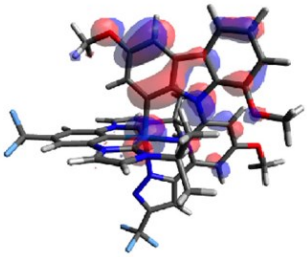
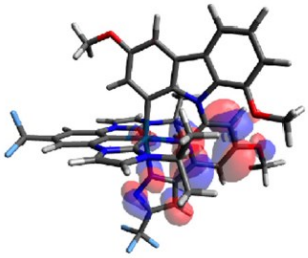
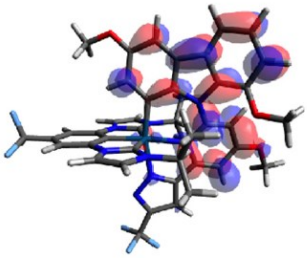
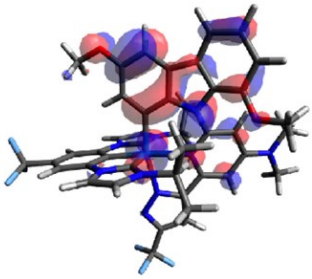
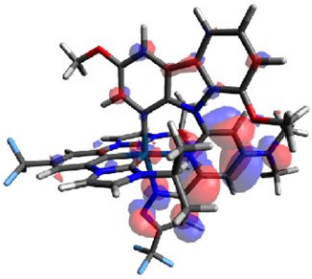
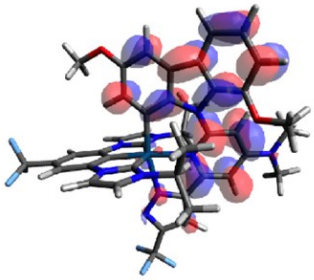
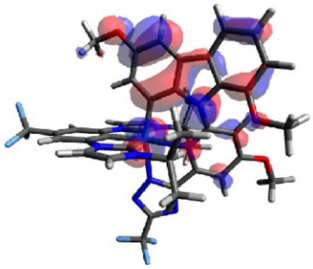
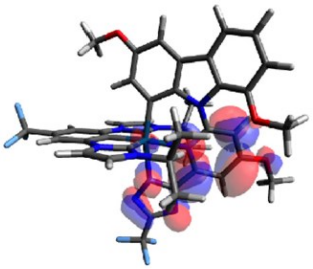
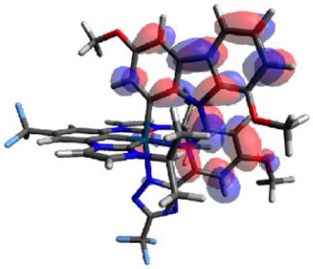
Cz6	 HOMO: -4.85 eV Ir: 16.1%	 LUMO: -1.02 eV Ir: 2.9%	 LUMO+1: -0.76 eV Ir: 1.2%
Cz7	 HOMO: -4.93 eV Ir: 13.3%	 LUMO: -1.08 eV Ir: 2.8%	 LUMO+1: -0.81 eV Ir: 1.3%
Cz8	 HOMO: -4.87 eV Ir: 13.5%	 LUMO: -0.84 eV Ir: 2.7%	 LUMO+1: -0.71 eV Ir: 1.1%
Cz9	 HOMO: -4.99 eV Ir: 12.5%	 LUMO: -1.27 eV Ir: 2.7%	 LUMO+1: -0.88 eV Ir: 1.5%

Figure S3. Molecular orbitals involved in the lowest singlet and triplet excitations calculated based on the optimized ground-state geometries of complexes **Cz6 – 9** at the B3LYP/6-31G** (LANL2DZ with ECP for Ir) level with PCM for modeling the CH_2Cl_2 solvent. The orbital energy level and the contribution from Ir atom are also provided.

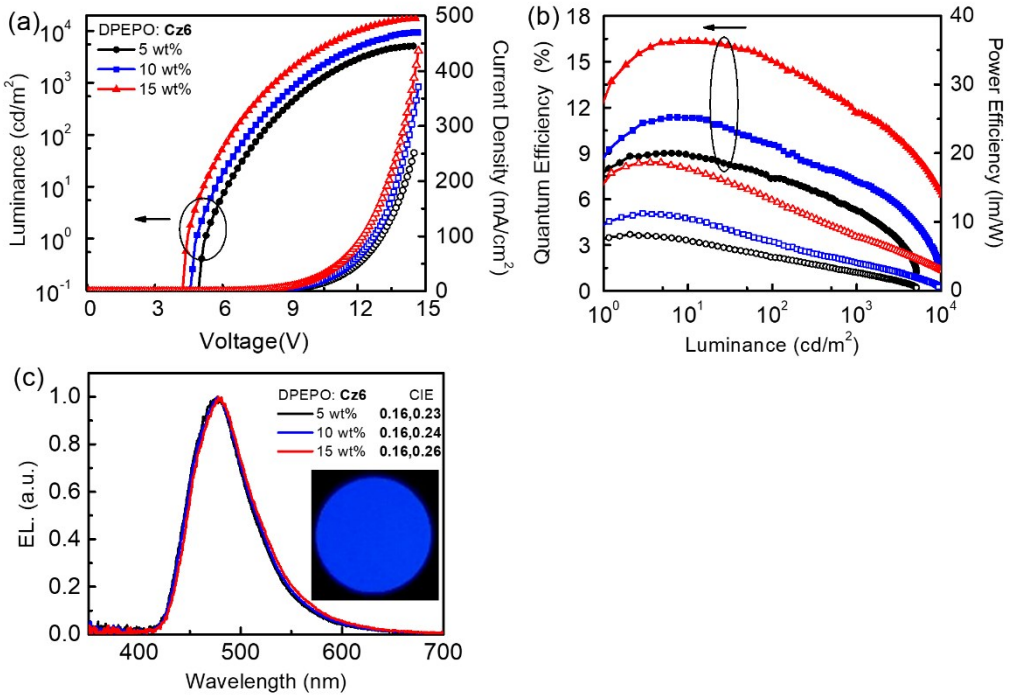


Figure S4. (a) J-V-L characteristics, (b) EQE–PE–L characteristics, and (c) normalized EL spectra of devices with DPEPO host doped with x wt.% of **Cz6**.

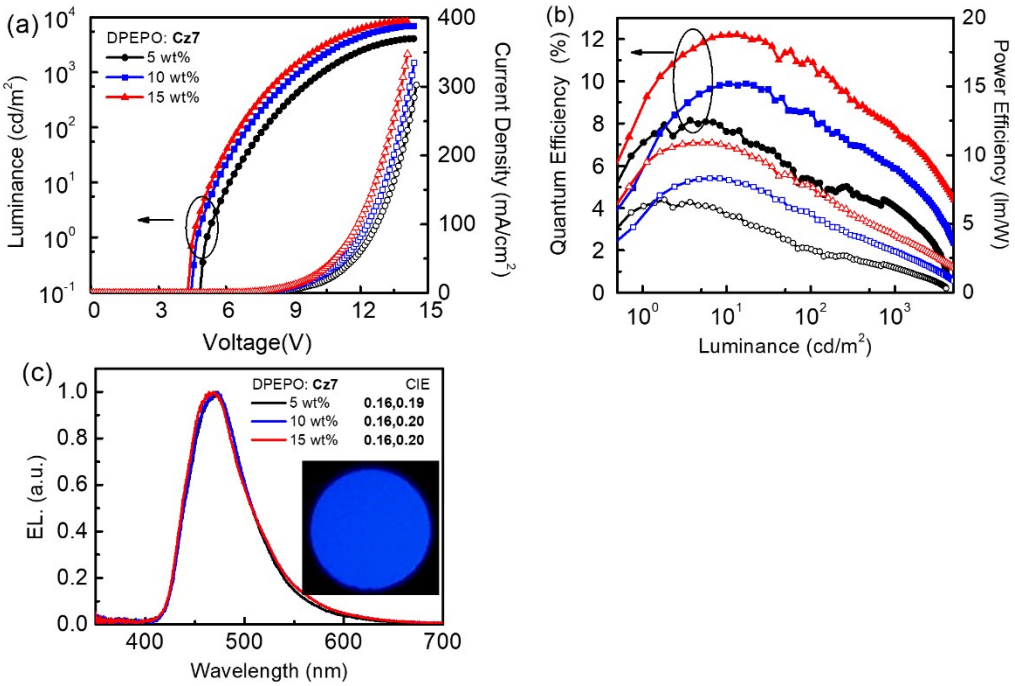


Figure S5. (a) J-V-L characteristics, (b) EQE–PE–L characteristics, and (c) normalized EL spectra of devices with DPEPO host doped with x wt.% of **Cz7**.

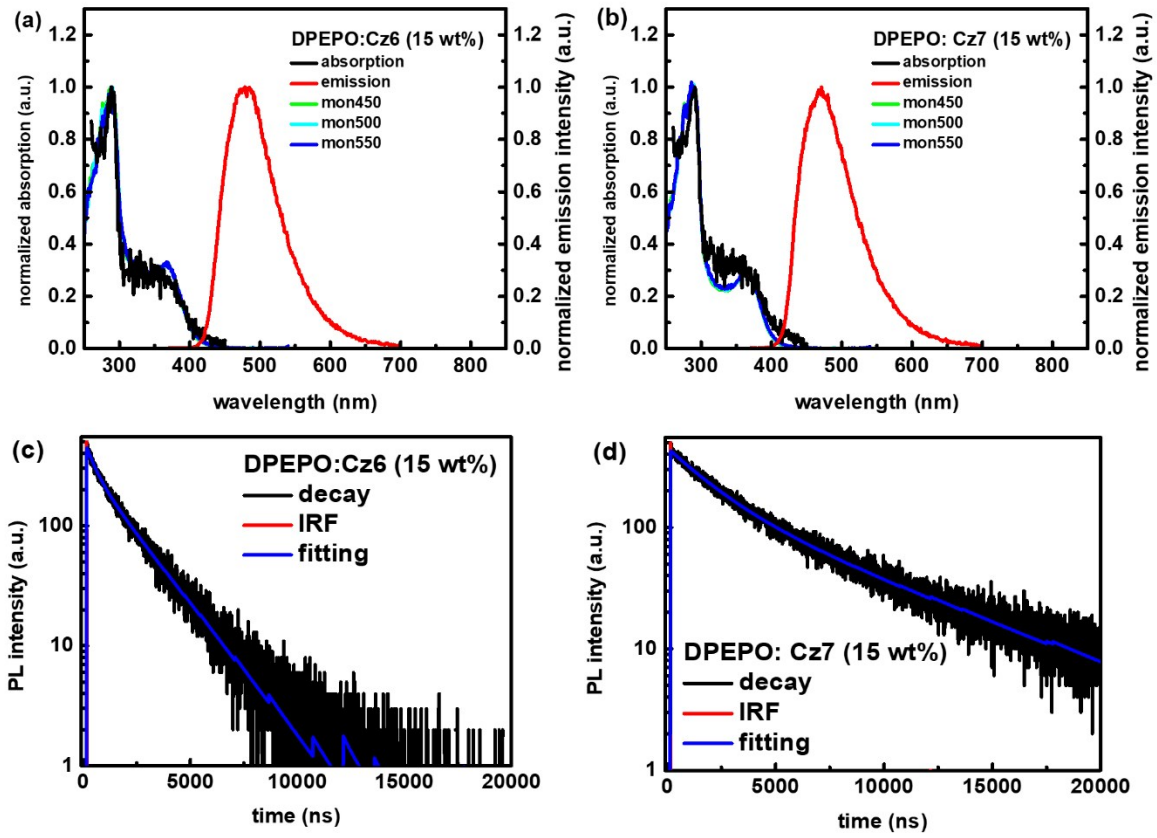


Figure S6. Absorption, photoluminescent spectra, and transient PL decays of DPEPO films doped with 15 wt.% of **Cz6** and **7** at RT.

Table S1. Cyclic Voltammetry data, HOMO/LUMO energy level and energy gap of the studied bis-tridentate Ir(III) complexes**.**

	$E^{ox}_{½}$ (V) [ΔE_p][a]	E^{re}_{pc} (V) [ΔE_p][a]	HOMO (eV)[b]	LUMO (eV)[c]	Energy gap (eV)[c]
Cz3	0.68 [0.09]	–2.72 [irr]	–5.48	–2.55	2.93
Cz6	0.62 [0.07]	–2.60 [irr]	–5.42	–2.47	2.95
Cz7	0.68 [0.09]	–2.71 [irr]	–5.48	–2.43	3.05
Cz8	0.61 [0.08]	–2.75 [irr]	–5.41	–2.43	2.98
Cz9	0.69 [0.09]	–2.66 [irr]	–5.49	–2.58	2.91

[a] $E^{ox}_{½}$ (V) refers to [(E_{pa} + E_{pc})/2], where E_{pa} and E_{pc} are the anodic and cathodic peak potential referenced to the ferrocene redox couple (Fc/Fc^+ = –4.8 eV), $\Delta E_p = E^{ox}_{½} - E^{ox}_{pa}$, "irr" denotes an irreversible process. The oxidation and reduction experiments were conducted in CH_2Cl_2 and THF solution, respectively. [b] HOMO = –4.8 – $E^{ox}_{½}$. [c] LUMO = HOMO + Energy gap. Energy gap (eV) = 1240/PL onset (nm).

Table S2. Cartesian coordinates of the optimized ground-state geometry of Ir(III) complexes **Cz6** – **9.**

Ir(III) complex **Cz6**

107

Ir	0.39118	0.06607	0.00506
N	-2.76477	-1.08608	-0.01008
N	-1.59196	0.94583	-0.11823
N	0.74376	2.12657	0.33260
N	1.82379	2.83967	0.59773
N	-0.17804	-0.48122	3.13042
N	1.77293	-0.94094	2.34889
N	2.37432	-0.08486	-2.11435
N	0.65137	0.65477	-3.16752
O	0.55329	-5.21639	-1.56818
O	-5.25250	-0.27224	1.32837
O	-5.02868	2.87697	-1.30839
C	-0.35694	-1.76483	-0.47316
C	0.39672	-2.87800	-0.88511
H	1.47208	-2.76254	-0.95676
C	-0.17167	-4.12970	-1.17155
C	-1.54183	-4.33816	-1.03492
H	-1.96501	-5.32120	-1.21515
C	-2.31982	-3.25360	-0.63987
C	-1.73500	-1.99568	-0.40168
C	-3.72524	-3.15456	-0.30899
C	-4.74331	-4.11024	-0.26488
H	-4.56351	-5.12696	-0.60026
C	-5.97673	-3.73101	0.24056
H	-6.79196	-4.44729	0.28263
C	-6.18410	-2.44333	0.75196
H	-7.14181	-2.20207	1.19830
C	-5.16559	-1.48906	0.74009
C	-3.95093	-1.83240	0.11677
C	-2.75186	0.28001	-0.29902
C	-3.89349	0.92897	-0.75487
H	-4.79110	0.37938	-0.99956
C	-3.88612	2.31953	-0.87741
C	-2.72899	3.02762	-0.55495
H	-2.67688	4.10726	-0.60021
C	-1.59389	2.30095	-0.20431
C	-0.32335	2.93143	0.09102
C	0.09108	4.25988	0.21009
H	-0.48489	5.16609	0.09602
C	1.44043	4.13132	0.53066
C	2.41640	5.21274	0.80631
C	1.94993	-5.06905	-1.69892
H	2.21167	-4.30914	-2.44620
H	2.32812	-6.03831	-2.02821
H	2.42455	-4.80404	-0.74553
C	-6.47955	0.08665	1.93534
H	-7.29936	0.09714	1.20783
H	-6.33494	1.09264	2.32975
H	-6.73331	-0.59252	2.75751
C	-5.06106	4.28516	-1.48195
H	-4.90066	4.80677	-0.53219
H	-6.05747	4.51706	-1.85710
H	-4.31192	4.61240	-2.21134
C	0.53757	-0.44867	1.98691
C	0.58050	-0.97525	4.18036
H	0.18968	-1.07955	5.18007
C	1.80939	-1.26445	3.68739
H	2.68536	-1.66358	4.17314
C	2.23972	-0.56864	0.12742
C	2.75465	-1.01941	1.33616
C	4.06352	-1.46910	1.44810
H	4.44863	-1.82251	2.40037
C	4.89738	-1.46543	0.31214
C	4.39081	-1.00457	-0.91338
H	5.02118	-0.99271	-1.79542
C	3.07074	-0.56372	-0.98040
C	1.05746	0.27695	-1.93694
C	2.76471	0.07339	-3.42547
H	3.75961	-0.15086	-3.77545
C	1.67973	0.54067	-4.08981
H	1.55866	0.79777	-5.13012
C	-1.57111	-0.04048	3.24343
H	-1.84255	0.24870	2.22671
C	-1.67487	1.17605	4.15489
H	-1.38960	0.93222	5.18368
H	-2.70704	1.53739	4.17069
H	-1.03063	1.98487	3.79907
C	-2.46751	-1.18998	3.68510
H	-2.34732	-2.05158	3.02288
H	-3.51260	-0.87142	3.64362
H	-2.24783	-1.50278	4.71145
C	6.33859	-1.96970	0.45280
C	6.32587	-3.43290	0.92594
H	5.80337	-4.07133	0.20553

H	5.82894	-3.54325	1.89459
H	7.35058	-3.80669	1.03239
C	7.08655	-1.10848	1.48403
H	8.11821	-1.46099	1.59610
H	6.61172	-1.14893	2.46902
H	7.11611	-0.06047	1.16840
C	7.10997	-1.90501	-0.86838
H	6.64600	-2.52606	-1.64214
H	8.12864	-2.27544	-0.71453
H	7.18476	-0.87996	-1.24653
C	-0.70244	1.11415	-3.49231
H	-1.25273	1.02381	-2.55427
C	-0.68297	2.57585	-3.92220
H	-0.22922	3.20167	-3.14865
H	-1.70577	2.92363	-4.09257
H	-0.12288	2.71081	-4.85342
C	-1.34536	0.19969	-4.52764
H	-0.82695	0.25211	-5.49057
H	-2.38289	0.50417	-4.69074
H	-1.34049	-0.83874	-4.18528
F	1.86510	6.42383	0.60170
F	2.86673	5.19660	2.07789
F	3.51014	5.13633	0.02332

Complex **Cz7**

98

Ir	-0.40348	0.05210	-0.01012
N	2.77134	-1.04879	0.00938
N	1.56460	0.96250	0.12487
N	-0.78619	2.10629	-0.32975
N	-1.87858	2.79995	-0.59482
N	0.19622	-0.46269	-3.13470
N	-1.75587	-0.94403	-2.37172
N	-2.38840	-0.12298	2.10155
N	-0.67366	0.62058	3.16337
O	-0.47974	-5.23846	1.54732
O	5.24813	-0.18814	-1.31814
O	4.96511	2.94359	1.33475
C	0.37467	-1.76987	0.46379
C	-0.36189	-2.89615	0.87019
H	-1.43931	-2.80098	0.94057
C	0.22667	-4.13906	1.15501
C	1.60063	-4.32337	1.02120
H	2.03971	-5.29962	1.20007
C	2.36127	-3.22528	0.63126
C	1.75609	-1.97658	0.39485
C	3.76595	-3.10168	0.30491
C	4.80014	-4.03977	0.26100
H	4.63692	-5.06043	0.59275
C	6.02831	-3.63772	-0.23972
H	6.85575	-4.33982	-0.28164
C	6.21526	-2.34517	-0.74653
H	7.17002	-2.08624	-1.18923
C	5.18070	-1.40834	-0.73468
C	3.97052	-1.77489	-0.11620
C	2.73498	0.31475	0.30568
C	3.86441	0.98033	0.76756
H	4.77022	0.44420	1.01177
C	3.83394	2.36988	0.89740
C	2.66606	3.06051	0.57471
H	2.59603	4.13890	0.62449
C	1.54442	2.31739	0.21729
C	0.26507	2.92854	-0.07986
C	-0.17338	4.24948	-0.19379
H	0.38529	5.16557	-0.07309
C	-1.51913	4.09779	-0.51992
C	-2.51405	5.16286	-0.79347
C	-1.87991	-5.11823	1.67007
H	-2.16047	-4.36529	2.41756
H	-2.24135	-6.09516	1.99516
H	-2.35324	-4.86100	0.71410
C	6.47096	0.19464	-1.91955
H	7.28801	0.21585	-1.18924
H	6.31020	1.19975	-2.30987
H	6.73878	-0.47637	-2.74389
C	4.97455	4.35158	1.51529
H	4.80977	4.87486	0.56729
H	5.96570	4.59706	1.89553
H	4.21749	4.66306	2.24329
C	-0.52612	-0.44627	-1.99660
C	-0.55225	-0.95217	-4.19444
H	-0.15385	-1.04394	-5.19233
C	-1.78208	-1.25535	-3.71421
H	-2.65159	-1.65640	-4.20978
C	-2.23955	-0.60139	-0.14586
C	-2.74024	-1.03974	-1.36850
C	-4.04853	-1.48499	-1.50016
H	-4.45345	-1.82535	-2.44736
C	-4.85867	-1.47336	-0.35715
C	-4.39228	-1.03397	0.88837
H	-5.05684	-1.03245	1.74571
C	-3.07533	-0.60036	0.96626
C	-1.07264	0.24833	1.93040
C	-2.78495	0.02426	3.41312

H	-3.77918	-0.20899	3.75906
C	-1.70473	0.49391	4.08187
H	-1.58829	0.74519	5.12410
C	1.58738	-0.01102	-3.23616
H	1.85090	0.27208	-2.21582
C	1.68687	1.21319	-4.13755
H	1.40993	0.97530	-5.16996
H	2.71645	1.58195	-4.14403
H	1.03468	2.01456	-3.77940
C	2.49377	-1.15112	-3.68129
H	2.37570	-2.01860	-3.02643
H	3.53616	-0.82531	-3.63078
H	2.28265	-1.45732	-4.71137
C	0.67652	1.08657	3.49728
H	1.22985	1.01184	2.55976
C	0.64362	2.54264	3.94459
H	0.18544	3.17407	3.17828
H	1.66334	2.89655	4.12021
H	0.08184	2.66178	4.87689
C	1.32292	0.16387	4.52290
H	0.80144	0.20039	5.48485
H	2.35752	0.47440	4.69269
H	1.32713	-0.87013	4.16742
F	-1.98346	6.38244	-0.58624
F	-2.96346	5.14068	-2.06493
F	-3.60584	5.06552	-0.01041
C	-6.24815	-2.01762	-0.45503
F	-7.07987	-1.45234	0.43823
F	-6.28847	-3.34742	-0.22329
F	-6.78292	-1.82993	-1.67477

Complex **Cz8**

102

Ir	-0.50175	0.03870	-0.02923
N	2.61762	-1.21706	-0.06854
N	1.51078	0.84795	0.03297
N	-0.78500	2.10379	-0.38419
N	-1.84780	2.84555	-0.64676
N	-0.01945	-0.56669	-3.15695
N	-1.97208	-0.92861	-2.33091
N	-2.42994	0.01009	2.14050
N	-0.64620	0.67736	3.13783
O	-0.79286	-5.20814	1.64676
O	5.10286	-0.50817	-1.47948
N	5.02307	2.78543	1.18786
C	0.20156	-1.80856	0.46503
C	-0.57756	-2.88818	0.91600
H	-1.64663	-2.73731	1.01291
C	-0.04375	-4.15343	1.21127
C	1.31437	-4.40931	1.04234
H	1.70920	-5.40303	1.22834
C	2.11732	-3.35821	0.60839
C	1.56976	-2.08462	0.36375
C	3.51543	-3.31219	0.23902
C	4.49638	-4.30548	0.17987
H	4.28906	-5.31027	0.53479
C	5.72675	-3.97947	-0.36723
H	6.51363	-4.72583	-0.42370
C	5.96474	-2.70682	-0.90294
H	6.91685	-2.50741	-1.38083
C	4.98365	-1.71466	-0.87413
C	3.77409	-2.00421	-0.21293
C	2.65246	0.15523	0.20951
C	3.82090	0.76129	0.65126
H	4.67512	0.14145	0.87565
C	3.88705	2.16357	0.77646
C	2.72068	2.88933	0.45434
H	2.69498	3.97002	0.49424
C	1.56549	2.20590	0.11713
C	0.31064	2.87655	-0.17296
C	-0.06348	4.21427	-0.31083
H	0.54338	5.10310	-0.22304
C	-1.42217	4.12395	-0.60914
C	-2.36843	5.23108	-0.88568
C	-2.18096	-5.01462	1.80567
H	-2.40210	-4.23328	2.54396
H	-2.58153	-5.96511	2.16193
H	-2.66843	-4.75320	0.85793
C	6.29355	-0.24014	-2.19585
H	7.17084	-0.24492	-1.53818
H	6.16865	0.75614	-2.62069
H	6.44535	-0.96436	-3.00463
C	-0.70694	-0.49008	-1.99974
C	-0.82257	-1.03585	-4.18549
H	-0.45824	-1.16876	-5.19176
C	-2.05270	-1.26338	-3.66570
H	-2.95542	-1.62717	-4.12979
C	-2.37200	-0.51841	-0.09983
C	-2.93127	-0.95154	-1.29911
C	-4.26543	-1.32563	-1.38524
H	-4.71628	-1.66000	-2.31353
C	-5.04062	-1.24751	-0.22069
C	-4.51499	-0.81168	1.00251
H	-5.15371	-0.75676	1.87756

C	-3.17468	-0.45050	1.03502
C	-1.10172	0.30771	1.92364
C	-2.77758	0.19891	3.46068
H	-3.77175	0.02528	3.84041
C	-1.65375	0.62001	4.08880
H	-1.49242	0.88141	5.12249
C	1.39058	-0.19291	-3.30410
H	1.69578	0.09916	-2.29776
C	1.53153	1.00306	-4.23740
H	1.21512	0.75756	-5.25666
H	2.57885	1.31540	-4.27857
H	0.93320	1.84665	-3.88214
C	2.22175	-1.39072	-3.74453
H	2.07806	-2.23342	-3.06292
H	3.28109	-1.12041	-3.73379
H	1.96321	-1.71143	-4.75931
C	0.73821	1.06866	3.42285
H	1.25208	0.96899	2.46543
C	0.80093	2.52205	3.87505
H	0.34904	3.18059	3.12814
H	1.84439	2.81953	4.01151
H	0.28301	2.66737	4.82887
C	1.37049	0.10740	4.42166
H	0.88679	0.16725	5.40213
H	2.42605	0.36042	4.55429
H	1.30547	-0.92344	4.06270
F	-1.77153	6.42741	-0.72697
F	-2.85544	5.19935	-2.14339
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C	-6.46032	-1.71415	-0.26755
F	-7.23629	-1.07256	0.62459
F	-6.57075	-3.03104	0.01195
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C	6.19289	2.00613	1.53573
C	5.03123	4.22035	1.38392
H	6.50701	1.36923	0.70099
H	6.01710	1.36560	2.40999
H	7.01556	2.68121	1.76931
H	4.28464	4.53385	2.12469
H	4.83363	4.75688	0.44808
H	6.01307	4.52605	1.74375

Complex **Cz9**

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Ir	-0.43150	0.05324	-0.02617
N	2.71698	-1.14040	0.03440
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N	-0.74467	2.12394	-0.36157
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N	0.17608	-0.52193	-3.14005
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N	-2.43434	-0.04060	2.07402
N	-0.70320	0.65587	3.14127
O	-0.68024	-5.20497	1.59570
O	5.23154	-0.38209	-1.28360
O	5.02287	2.81528	1.28719
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C	-0.48356	-2.87811	0.88678
H	-1.55803	-2.74865	0.94405
C	0.06329	-4.13387	1.19593
C	1.43256	-4.36108	1.08059
H	1.84004	-5.34717	1.27891
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H	6.69577	-4.56465	-0.16243
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H	7.09141	-2.33768	-1.10308
C	5.12033	-1.58927	-0.68059
C	3.89366	-1.90686	-0.06805
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C	3.87759	2.26591	0.86057
C	2.72689	2.98372	0.52645
H	2.66626	4.06360	0.55045
C	1.59570	2.25728	0.18569
C	0.32738	2.89626	-0.11800
N	0.04449	4.20020	-0.19959
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C	-2.07745	-5.04049	1.70230
H	-2.34200	-4.26860	2.43611
H	-2.47155	-6.00116	2.03753
H	-2.53303	-4.78308	0.73783
C	6.47191	-0.04698	-1.87828
H	7.28120	-0.03753	-1.13924
H	6.34565	0.95541	-2.28766
H	6.72748	-0.74041	-2.68775
C	5.07026	4.22687	1.44085
H	4.91620	4.73519	0.48325

H	6.06876	4.45229	1.81390
H	4.32357	4.57130	2.16432
C	-0.55430	-0.46661	-2.00872
C	-0.57842	-1.00569	-4.19804
H	-0.17499	-1.12608	-5.19085
C	-1.82054	-1.26428	-3.72344
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H	-4.52017	-1.72878	-2.47120
C	-4.92809	-1.33949	-0.38865
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C	-1.74347	0.56930	4.05392
H	-1.62562	0.82464	5.09500
C	1.58113	-0.11346	-3.23836
H	1.84572	0.18013	-2.22137
C	1.72371	1.09109	-4.16015
H	1.44853	0.84330	-5.19064
H	2.76364	1.42940	-4.16391
H	1.09273	1.91776	-3.82201
C	2.45608	-1.28800	-3.65589
H	2.30634	-2.14011	-2.98743
H	3.50741	-0.99295	-3.60204
H	2.24409	-1.60527	-4.68239
C	0.66104	1.07506	3.48148
H	1.21534	0.98121	2.54621
C	0.67790	2.53066	3.93090
H	0.24365	3.18119	3.16669
H	1.70914	2.84809	4.10853
H	0.11976	2.66773	4.86284
C	1.27020	0.12915	4.50875
H	0.74539	0.18296	5.46803
H	2.31394	0.40378	4.68405
H	1.24035	-0.90398	4.15197
F	-1.91112	6.27157	0.24881
F	-1.68999	6.00771	-1.87992
F	-3.37025	5.10986	-0.85472
C	-6.33427	-1.83973	-0.48957
F	-7.15583	-1.22341	0.37873
F	-6.42117	-3.16052	-0.22341
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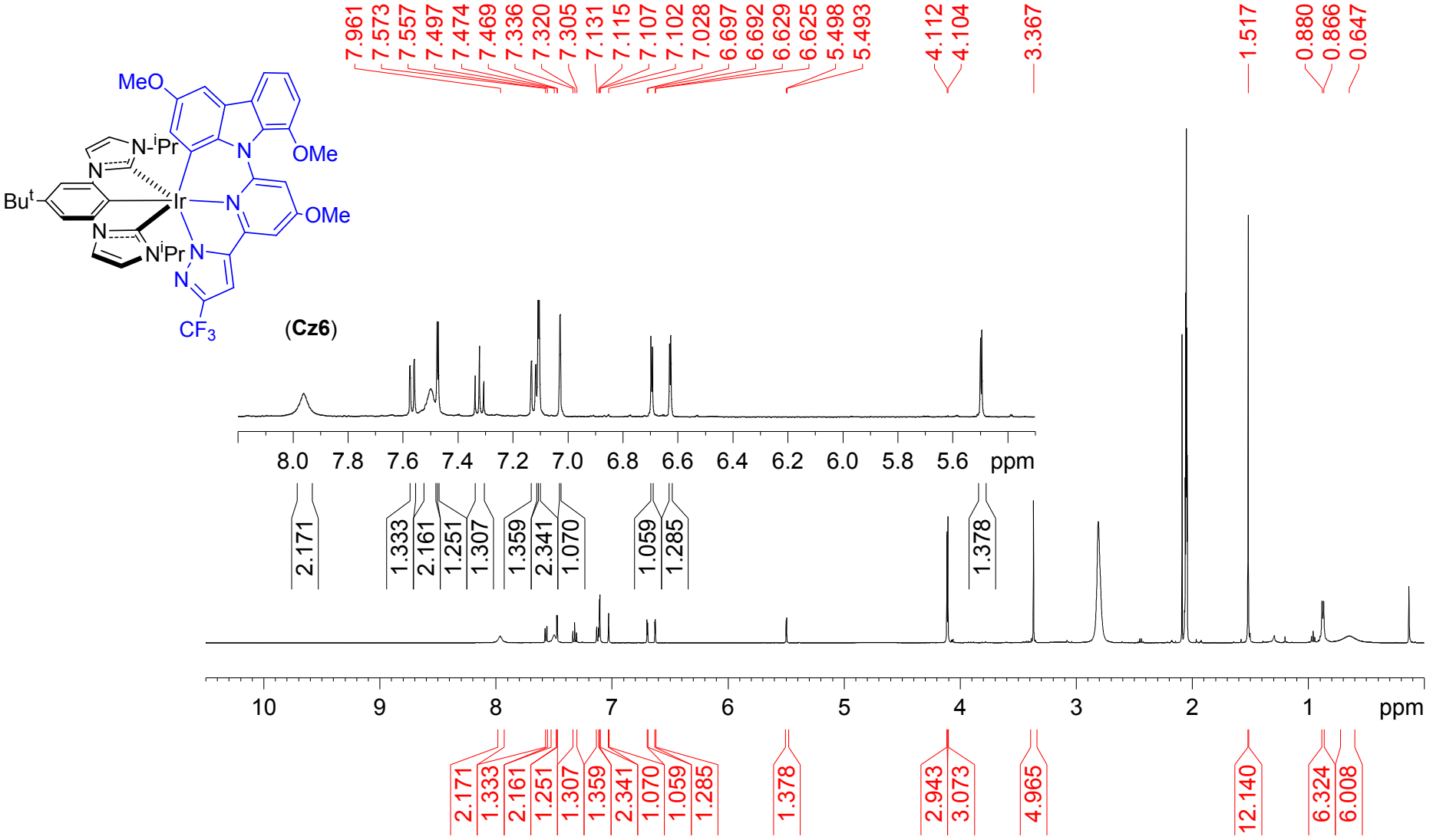

Figure S7. ^{1}H NMR spectra of Ir(III) complex **Cz6** in acetone-d_6 at RT.

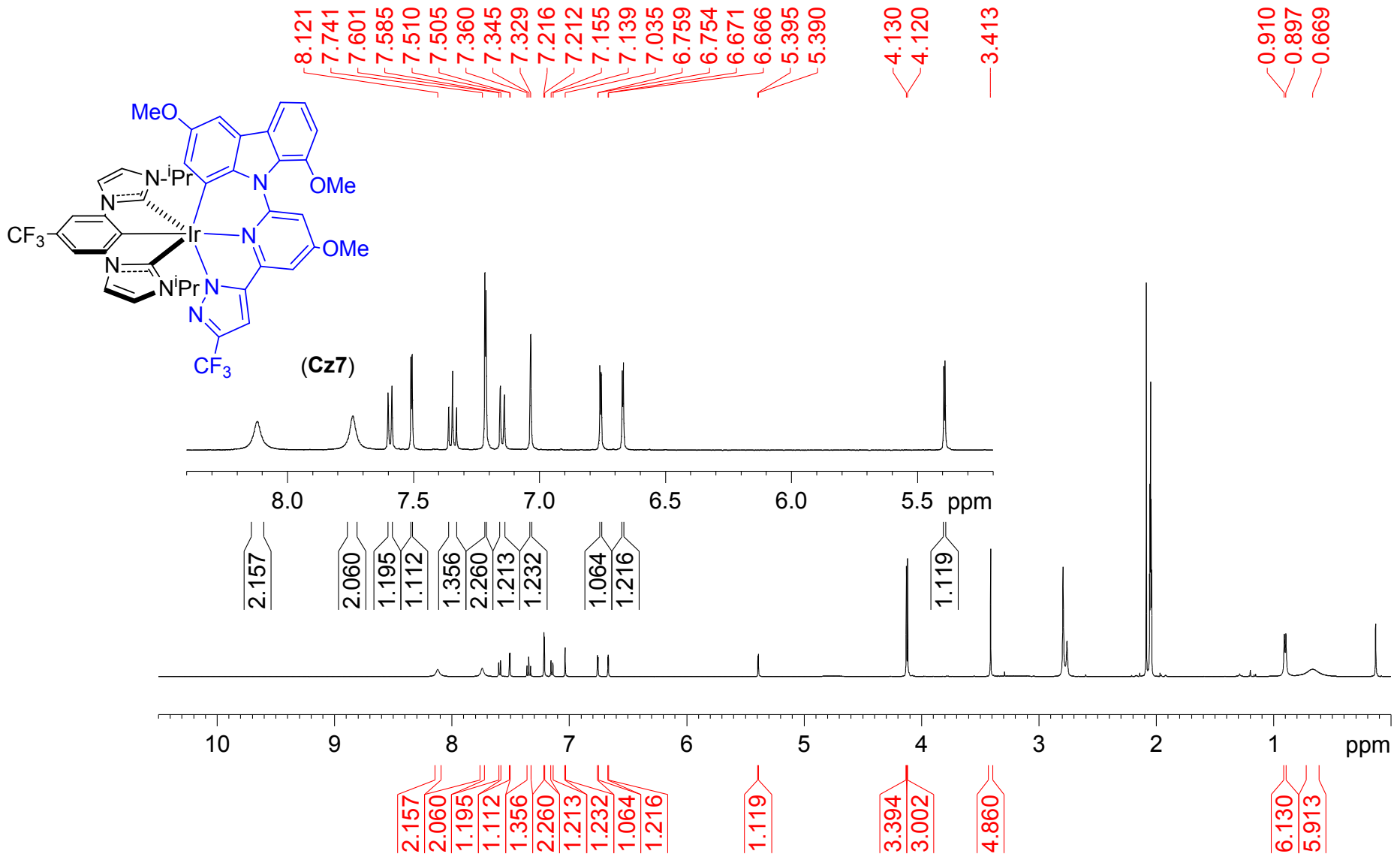

Figure S8. ^{1}H NMR spectra of Ir(III) complex **Cz7** in acetone-d_6 at RT.

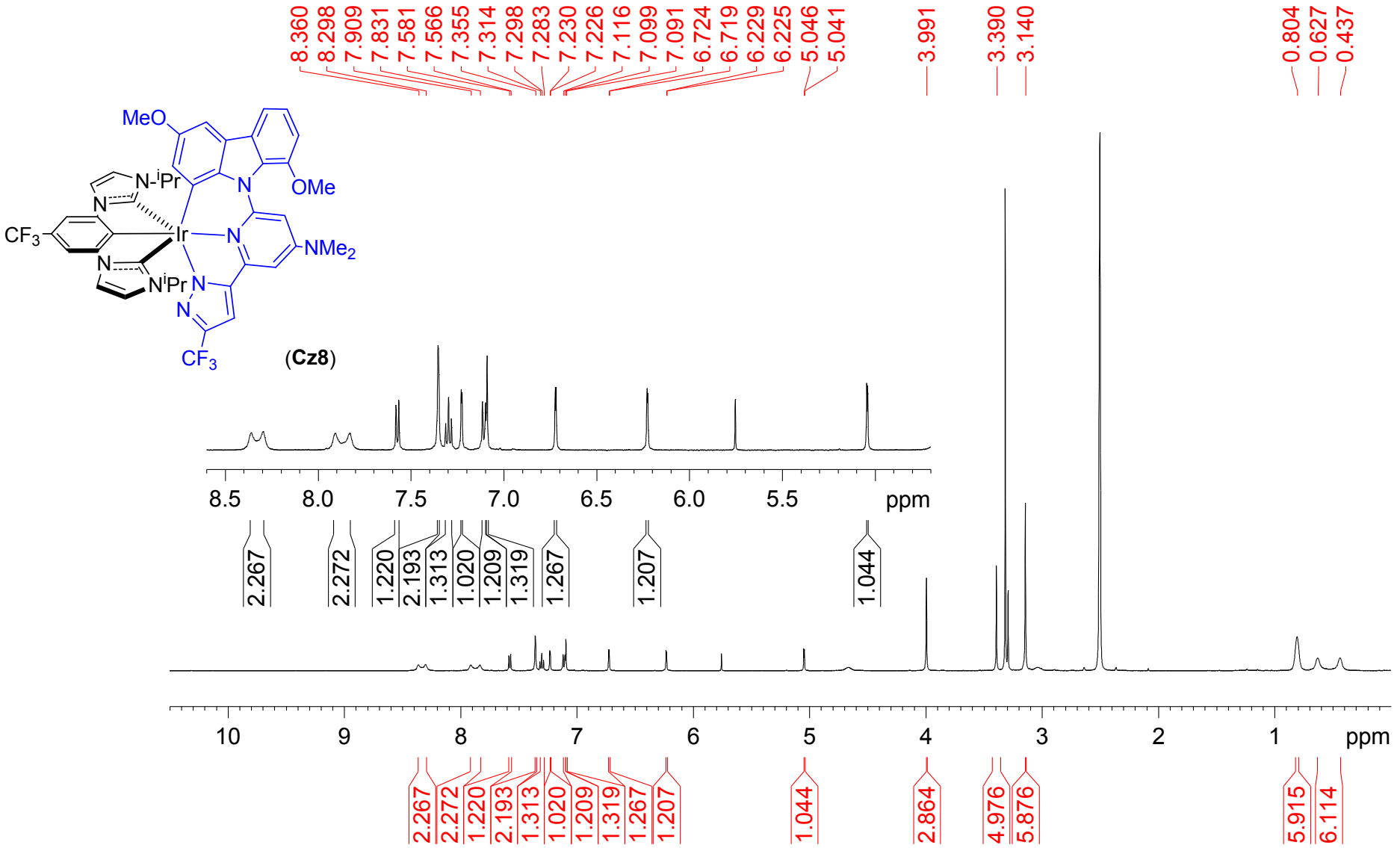

Figure S9. ^{1}H NMR spectra of Ir(III) complex **Cz8** in DMSO-d_6 at RT.

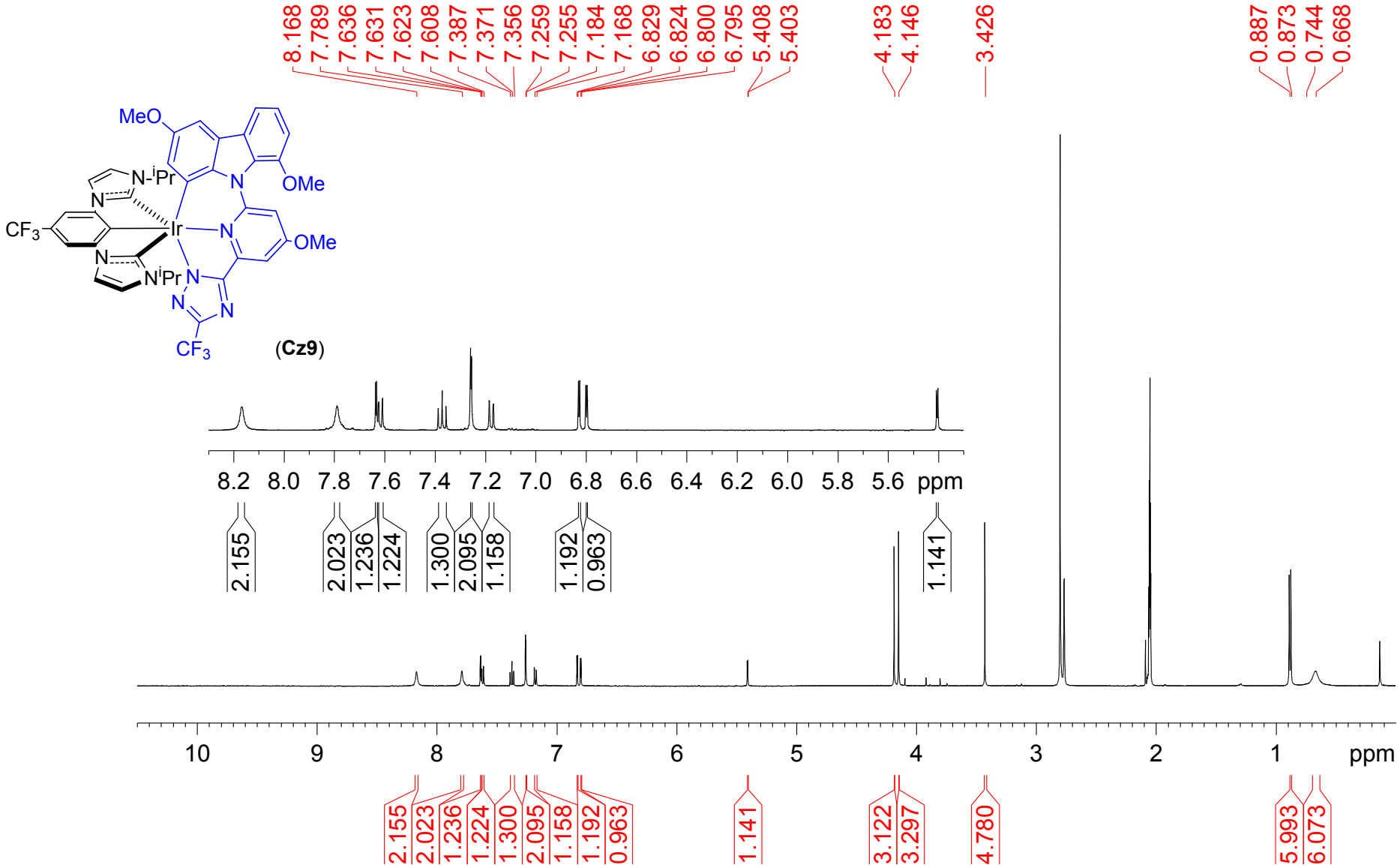

Figure S10. ^{1}H NMR spectra of Ir(III) complex **Cz9** in acetone-d_6 at RT.

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