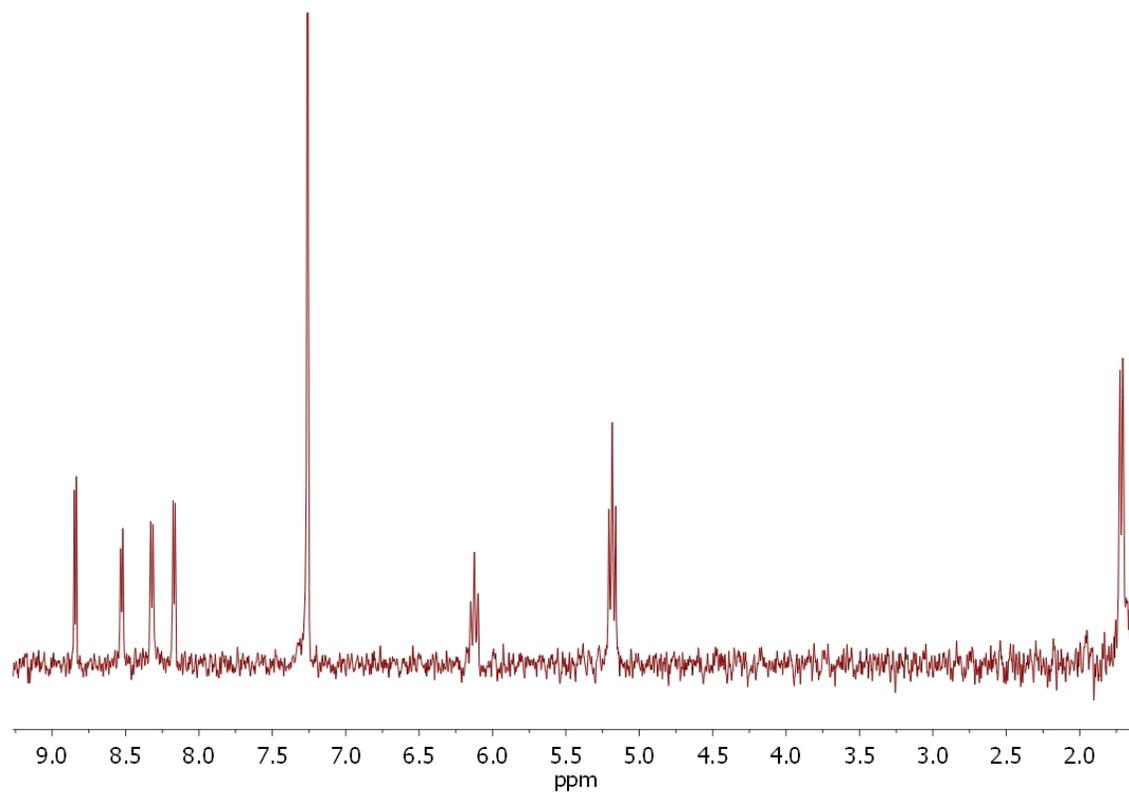


# Supplementary and Supporting Information for Group 9 Metallocorroles

## Characterization data:



**Figure 1:** 300 MHz  $^1\text{H}$  NMR of  $1\text{-Ir}(\text{py})_2$ .

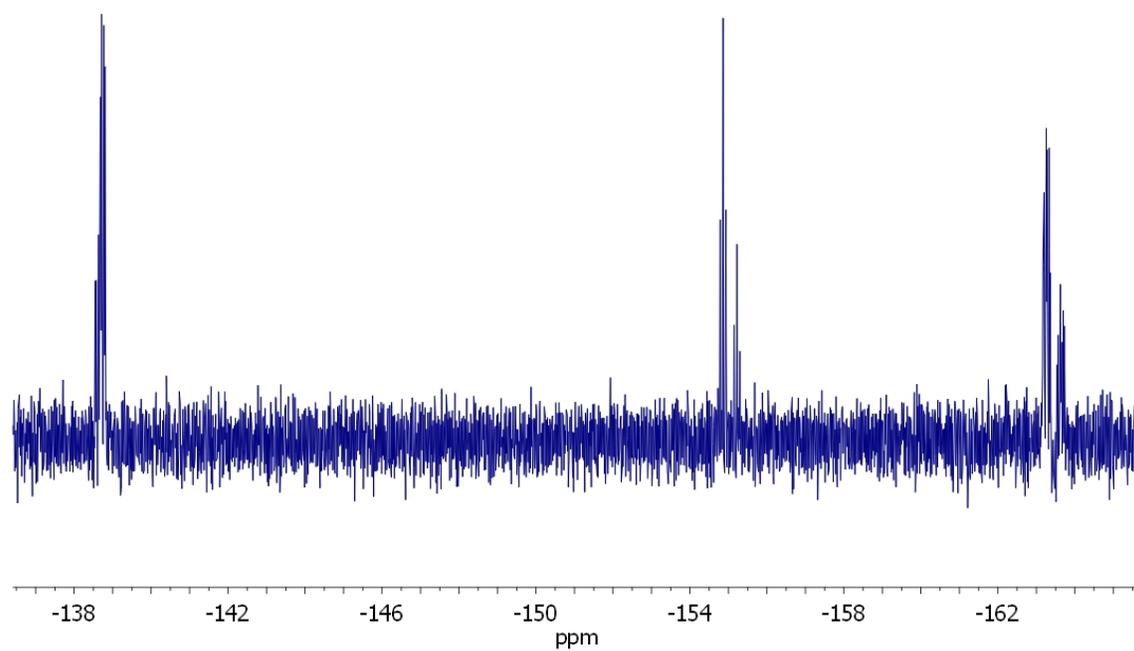


Figure 2: 300 MHz  $^{19}\text{F}$  NMR of 1-Ir(py) $_2$ .

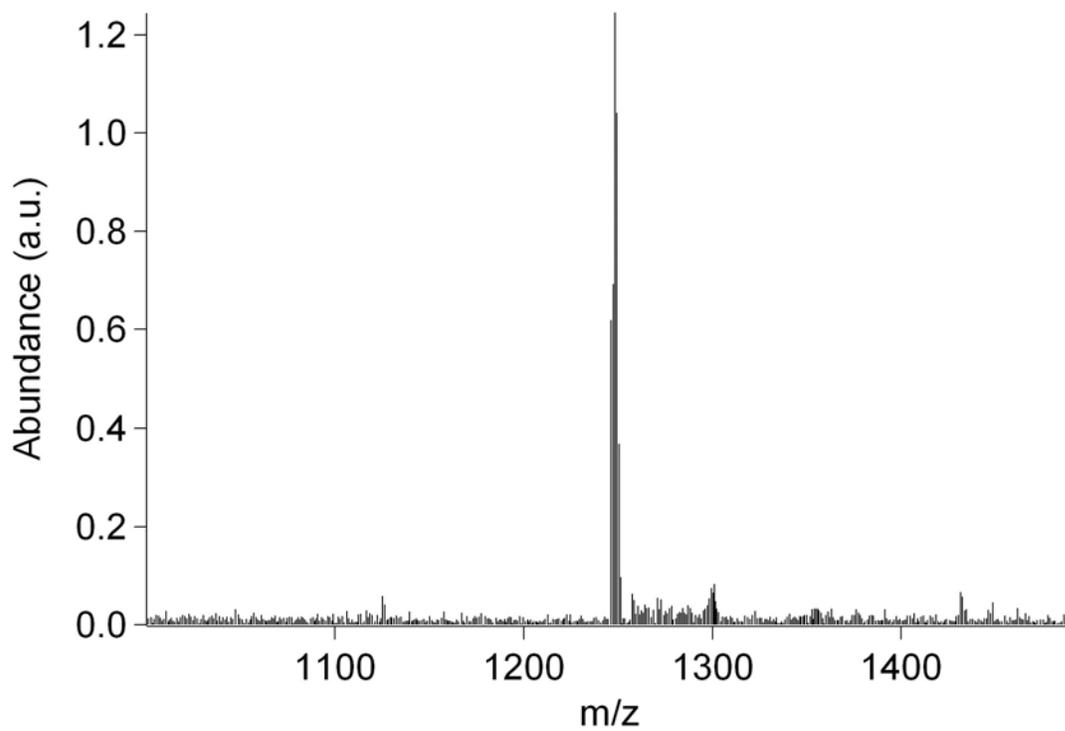


Figure 3: ESI-MS of 1-Ir(py) $_2$ .

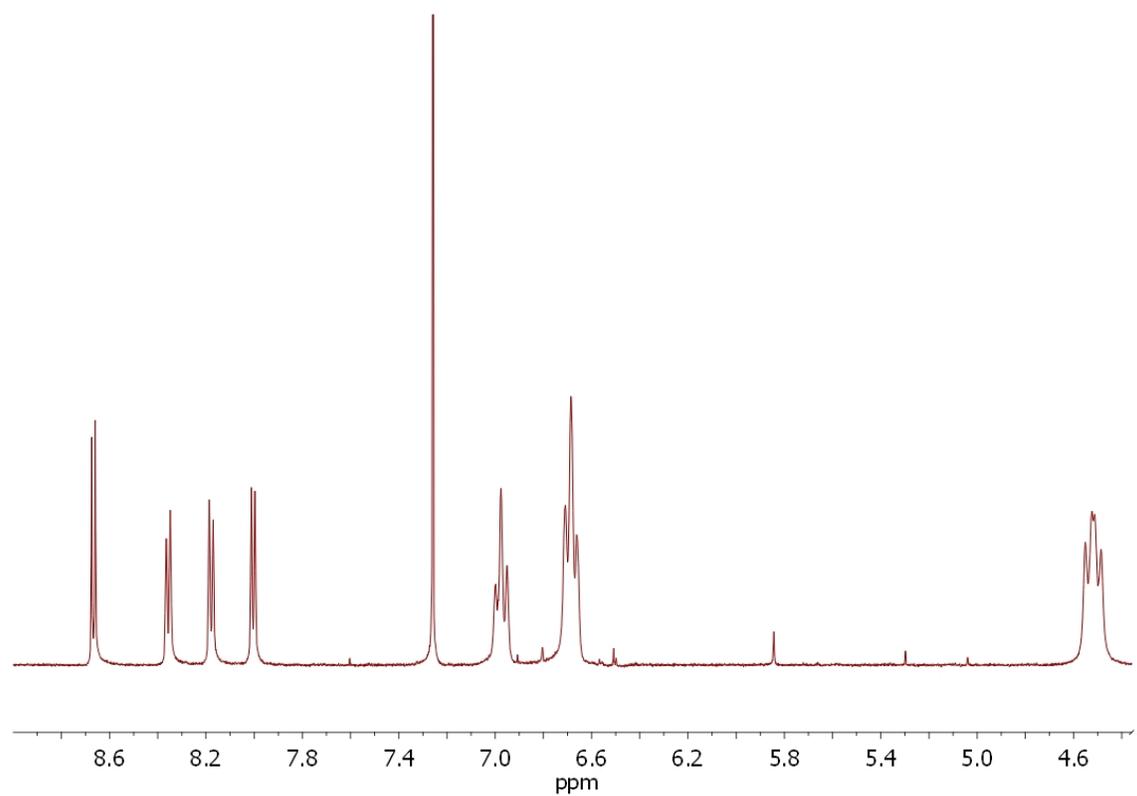


Figure 4: 300 MHz  $^1\text{H}$  NMR of 1-Ir(PPh<sub>3</sub>).

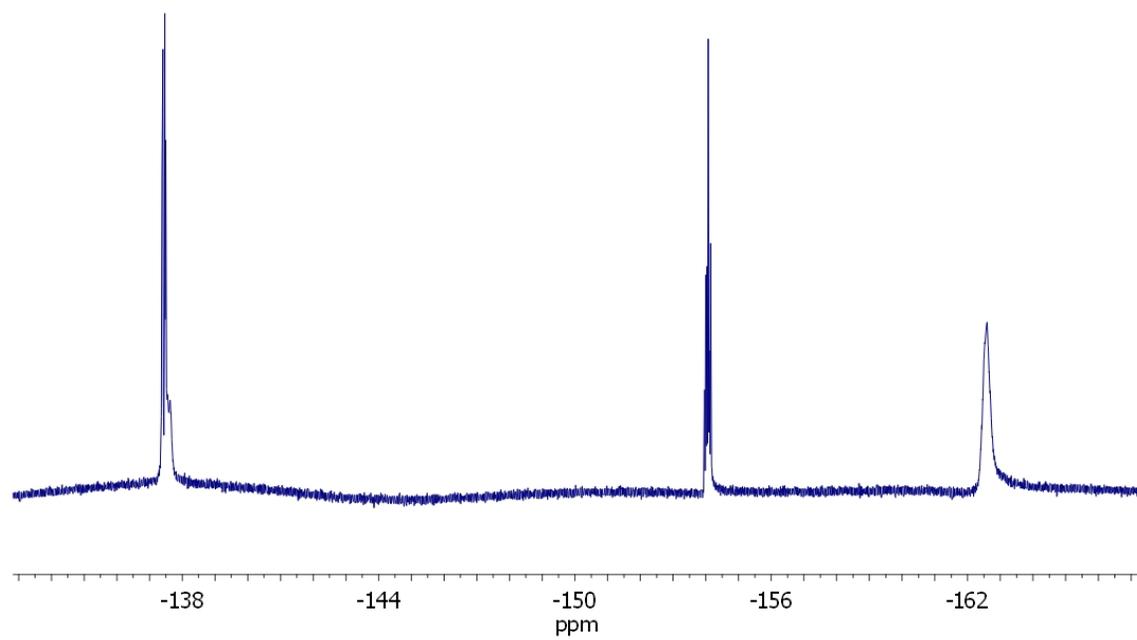
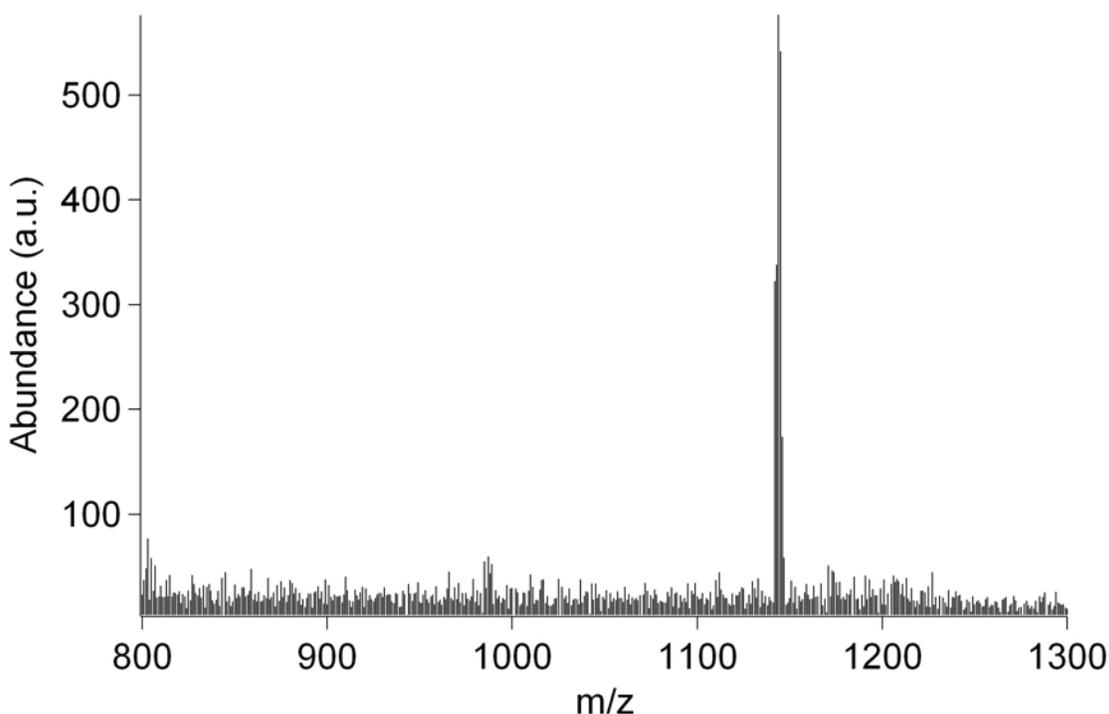


Figure 5: 300 MHz  $^{19}\text{F}$  NMR of 1-Ir(PPh<sub>3</sub>).



**Figure 6: ESI-MS of 1-Ir(PPh<sub>3</sub>).**

**Notes on synthesis:**

A number of corroles with different substituted pyridines could be synthesized using the same technique as was utilized for the creation of complex **1-Ir(py)<sub>2</sub>**. The ligands attached to iridium corroles in this manner include 4-cyanopyridine, 4-methoxypyridine, 3,5-dichloropyridine, and 3,5-*bis*(trifluoromethyl)pyridine. In all cases, the primary product was the six-coordinate *bis*-pyridine complex.

**Synthetic summary for substituted *bis*-pyridine iridium(III) corroles:**

**5,10,15-*tris*-pentafluorophenylcorrolato-iridium(III) *bis*-4-cyanopyridine.**

H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-Cyanopyridine (105 mg) was added, and the solution was allowed to slowly cool to room

temperature while open to the laboratory atmosphere. Column chromatography of the red-green mixture (silica, 4:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub> followed by 2:3 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) provided a bright red solution which upon evaporation provided (tpfc)Ir(III)(4-CNpy)<sub>2</sub> (36 mg, 66% yield) as a purple solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.91 (d, 2H, J = 4.5), 8.60 (d, 2H, J = 5.1), 8.39 (d, 2H, J = 4.8), 8.26 (d, 2H, J = 4.5), 5.43 (d/d, 4H, <sup>3</sup>J = 6.9, <sup>4</sup>J = -4.2), 1.75 (d/d, 4H, <sup>3</sup>J = 6.9, <sup>4</sup>J = -3.9). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -138.38 (d/d, 2F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.4), -138.95 (d/d, 4F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.4), -153.75 (t, 2F, J = 22.5), -154.11 (t, 1F, J = 22.2), -162.48 (m, 4F). -162.84 (m, 2F). MS (ESI): 1089.0 ([M<sup>+</sup>-4-CNpy]), 986.1 ([M<sup>+</sup>-2(4-CNpy)]) UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm, ε x 10<sup>-3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 388 (8.8), 406 (14), 580 (4.2), 608 (2.8).

**5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis-4-methoxypyridine.**

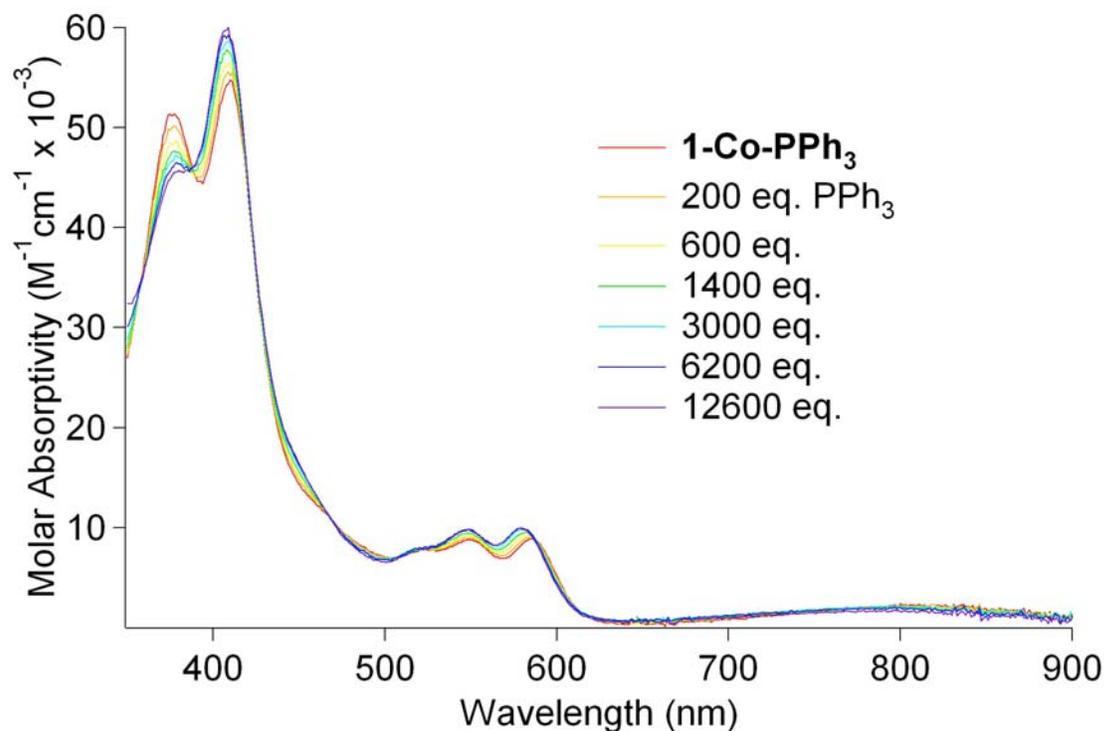
H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-Methoxypyridine (110 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the dark green mixture (silica, 4:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub> followed by 2:3 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) provided an olive solution which upon evaporation provided (tpfc)Ir(III)(4-MeOpy)<sub>2</sub> (28 mg, 50% yield) as a dark green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.81 (d, 2H, J = 4.2), 8.49 (d, 2H, J = 4.5), 8.31 (d, 2H, J = 4.5), 8.12 (d, 2H, J = 3.9), 4.69 (d/d, 4H, <sup>3</sup>J = 7.2, <sup>4</sup>J = -4.5), 2.93 (s, 6H), 1.56 (m, 4H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -138.40 (d/d, 2F, <sup>3</sup>J = 35.7, <sup>4</sup>J = 17.4), -138.64 (d/d, 4F, <sup>3</sup>J = 35.7, <sup>4</sup>J = 17.4), -154.98 (t, 2F, J = 22.5), -155.35 (t, 1F, J = 22.4), -163.33 (m, 4F). -163.69 (m, 2F). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm, ε x 10<sup>-3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 394 (42), 412 (57), 394 (42), 412 (57).

**5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis[3,5-bis(trifluoromethyl)pyridine].** H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 3,5-bis-trifluoromethylpyridine (215 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the deep green mixture (silica, 4:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub> followed by 100% CH<sub>2</sub>Cl<sub>2</sub>) provided a red-green solution, which upon evaporation yielded (tpfc)Ir[3,5-(CF<sub>3</sub>)<sub>2</sub>py]<sub>2</sub> (13 mg, 20% yield) as a filmy red-purple solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.00 (d, 2H, J = 4.2), 8.70 (d, 2H, J = 4.8), 8.44 (d, 2H, J = 4.8), 8.38 (d, 2H, J = 4.2), 6.65 (s, 2H), 1.97 (s, 4H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ = -64.29 (t, 12F, J = 7.5), -138.47 (m, 6F), -153.52 (t, 2F, J = 22.2), -153.82 (m, 1F), -162.35 (m, 6F). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm, ε x 10<sup>-3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 384 (9.7), 406 (15), 580 (4.5), 602 (2.8).

**5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis(3,5-dichloropyridine).** H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 3,5-dichloropyridine (150 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the bright green mixture (silica, 4:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub> followed by 100% CH<sub>2</sub>Cl<sub>2</sub>) provided a vivid green solution, from which dark green crystals of (tpfc)Ir(3,5-Cl<sub>2</sub>py)<sub>2</sub> (27 mg, 47% yield) could be grown by addition of toluene followed by slow evaporation. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.91 (d, 2H, J = 4.2), 8.64 (d, 2H, J = 4.5), 8.40 (d, 2H, J = 4.5), 8.30 (d, 2H, J = 4.2), 6.16 (t, 2H, J = 1.8), 1.52 (d, 4H, J = 1.8). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -137.49 (d/d, 2F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.7), -137.71 (d/d, 4F, <sup>3</sup>J = 34.8, <sup>4</sup>J =

17.1), -153.87 (t, 2F, J = 22.5), -154.28 (t, 1F, J = 22.2), -162.39 (m, 4F). -162.82 (m, 2F). UV-vis ( $\text{CH}_2\text{Cl}_2$ , nm,  $\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ): 390 (26), 406 (38), 580 (12), 608 (7.3).

**Titration not included in the main body of the article:**



**Figure 7: Changes to the electronic absorption spectrum of 1-Co(PPh<sub>3</sub>) in CH<sub>2</sub>Cl<sub>2</sub> upon addition of excess PPh<sub>3</sub>.**

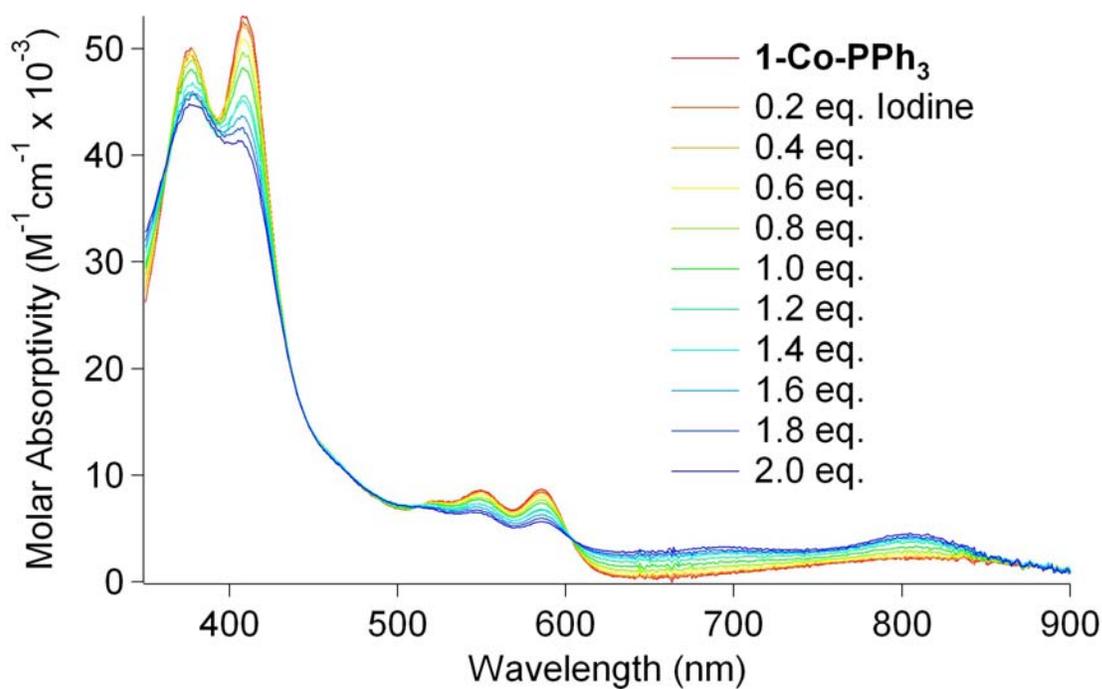


Figure 8: Reaction of  $1\text{-Co(PPh}_3\text{)}$  with iodine in  $\text{CH}_2\text{Cl}_2$ .

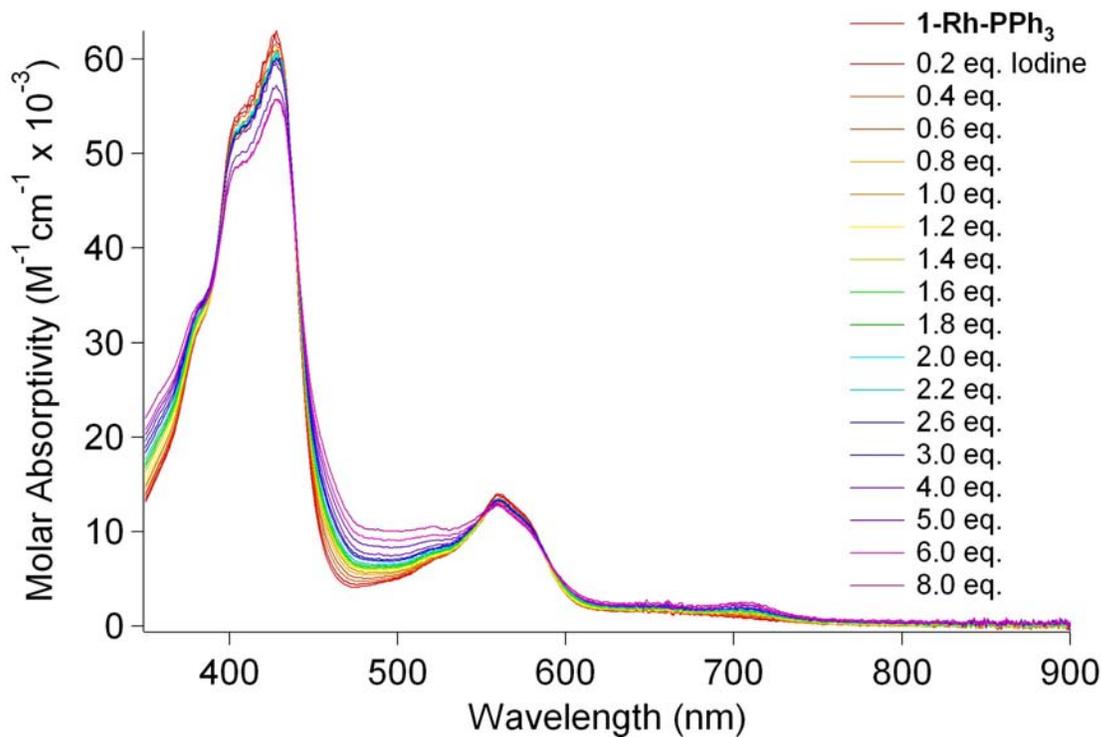


Figure 9: Reaction of  $1\text{-Rh(PPh}_3\text{)}$  with iodine in  $\text{CH}_2\text{Cl}_2$ .

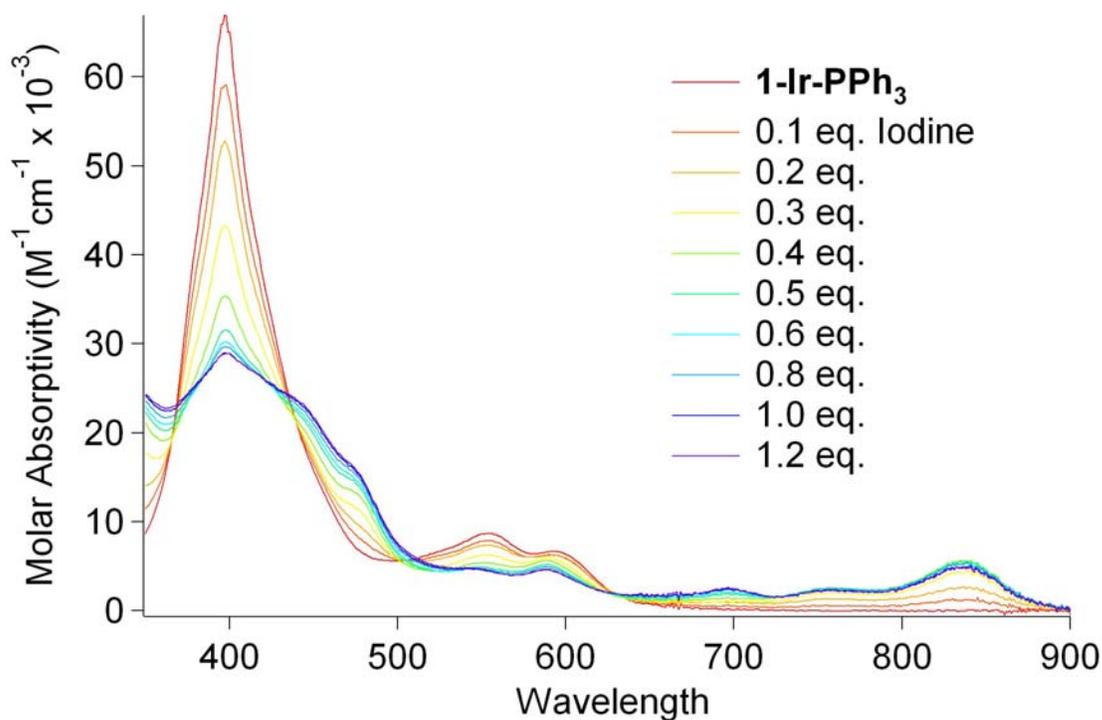


Figure 10: Reaction of 1-Ir(PPh<sub>3</sub>) with iodine in CH<sub>2</sub>Cl<sub>2</sub>.

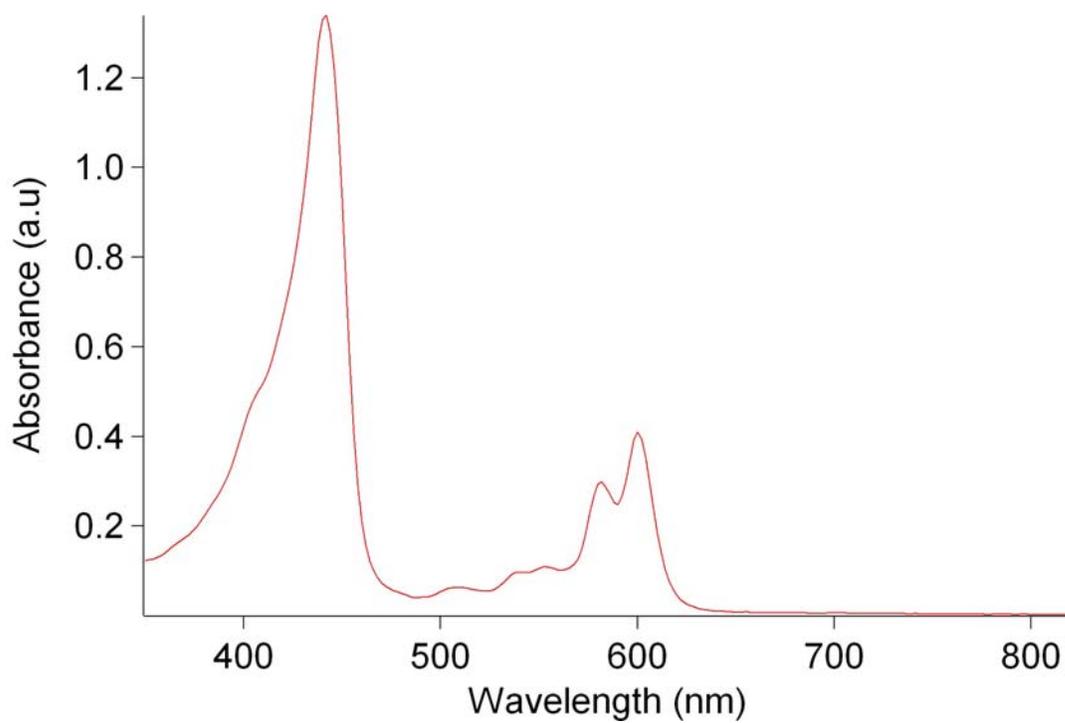
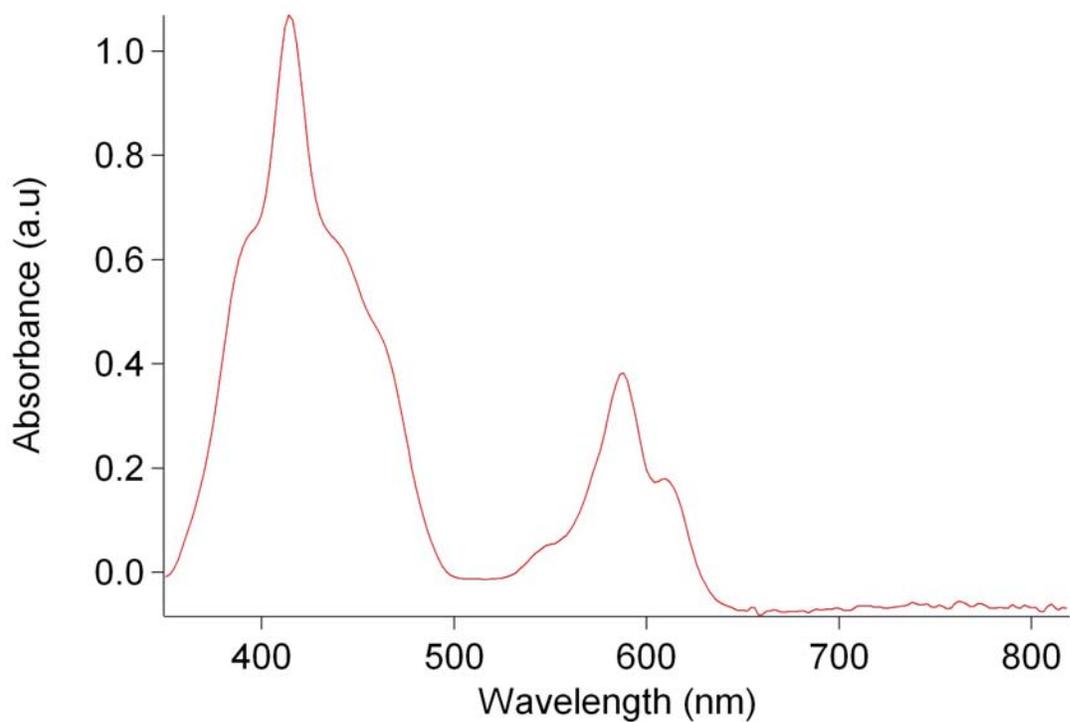
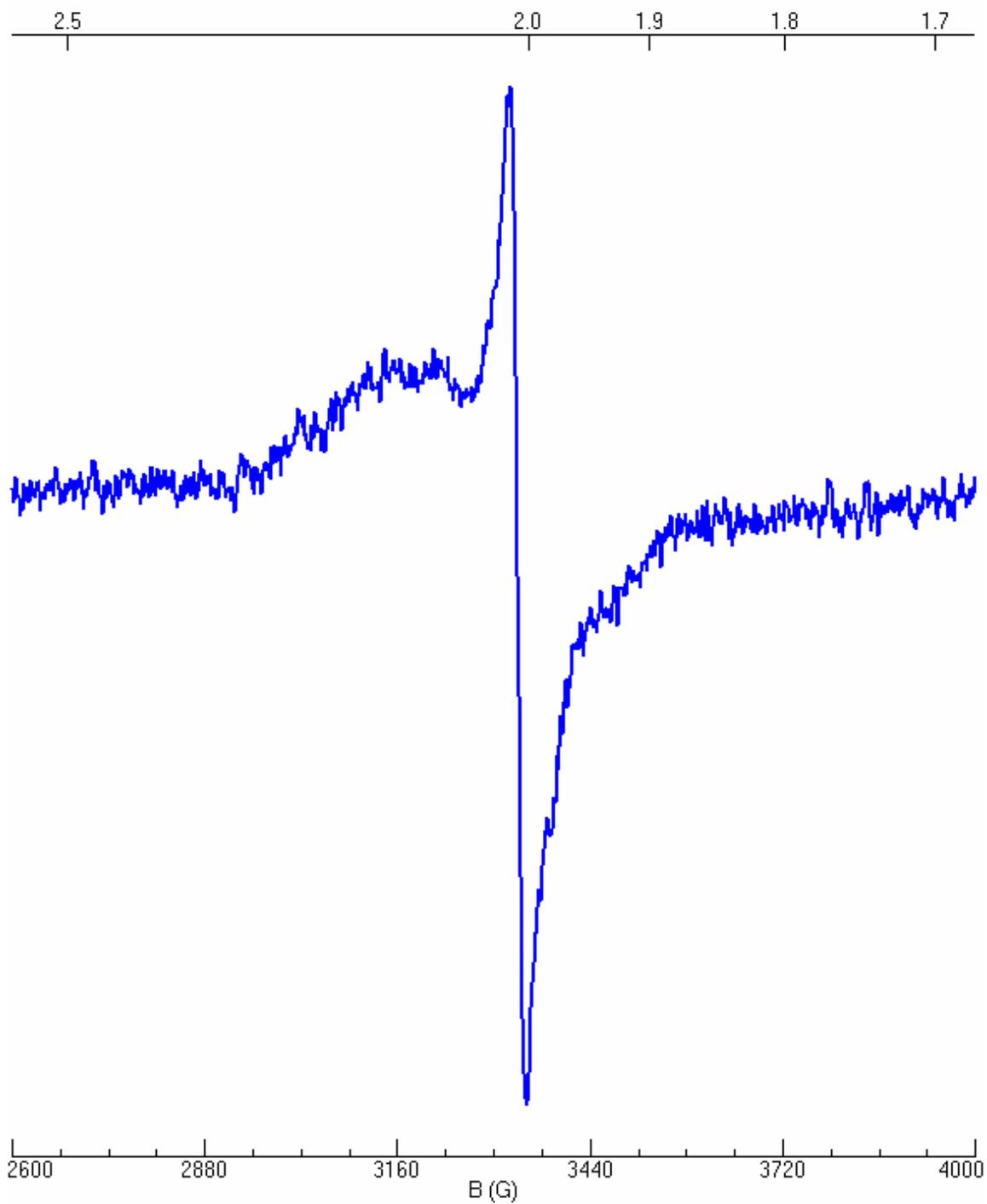


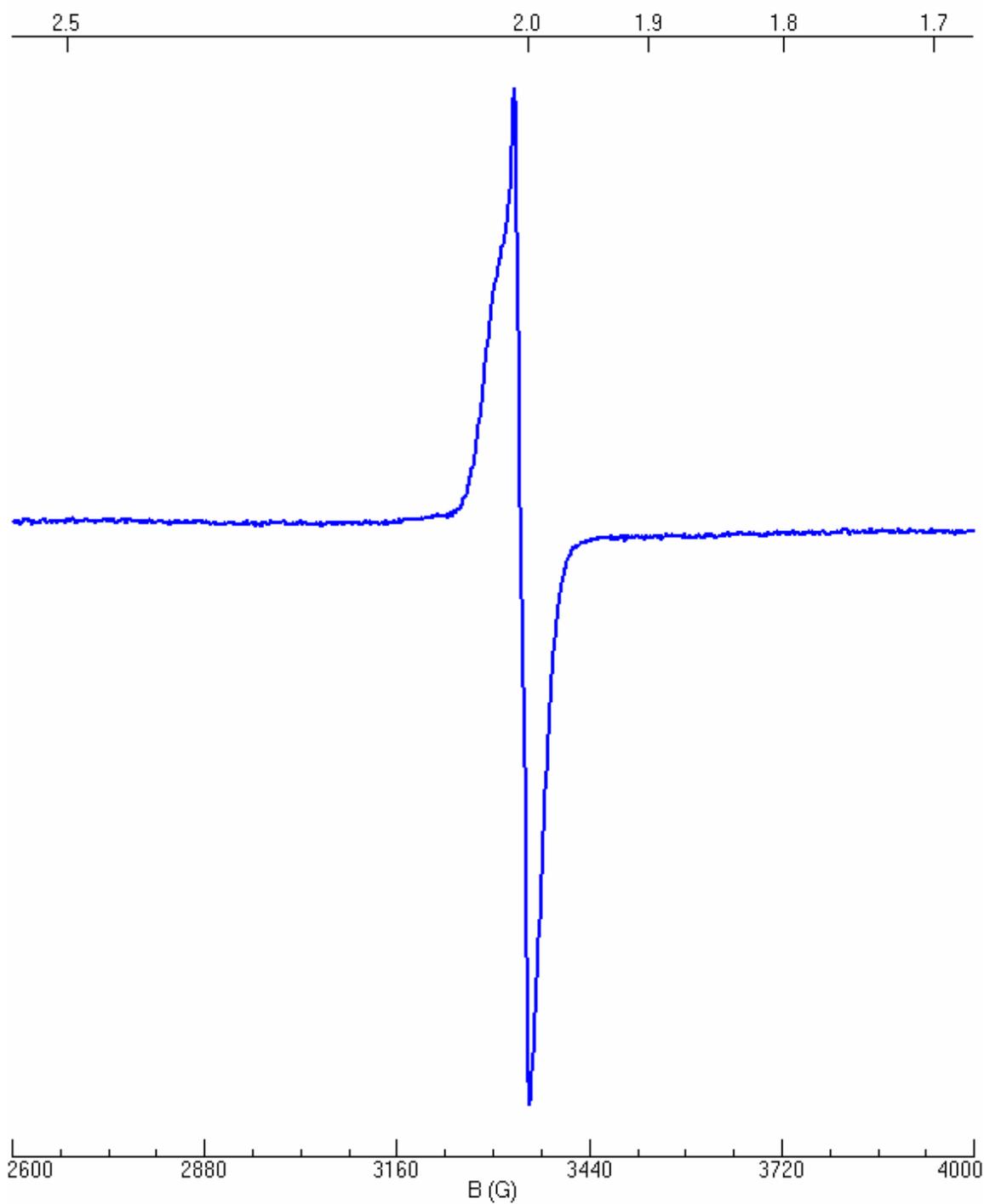
Figure 11: Electronic absorption spectrum of 1-Co(py)<sub>2</sub> in 5% pyridine/CH<sub>2</sub>Cl<sub>2</sub>.



**Figure 12: Electronic absorption spectrum of 1-Ir(PPh<sub>3</sub>) in 5% pyridine/CH<sub>2</sub>Cl<sub>2</sub>, showing that 1-Ir(PPh<sub>3</sub>) is not converted to 1-Ir(py)<sub>2</sub> under these conditions.**



**Figure 13: EPR spectrum, taken at 20K in frozen toluene, of singly oxidized corrole 1-Co(PPh<sub>3</sub>).**



**Figure 14: EPR spectrum, taken at 20K in frozen toluene, of singly oxidized corrole 1-Rh(PPh<sub>3</sub>).**