

**3,17-dibromo-5,10,15-(tris)pentafluorophenylmonoazaporphyrinatoiridium(III)**

(bis)ammine,

**2b<sub>2</sub>-Ir(NH<sub>3</sub>)<sub>2</sub>,**

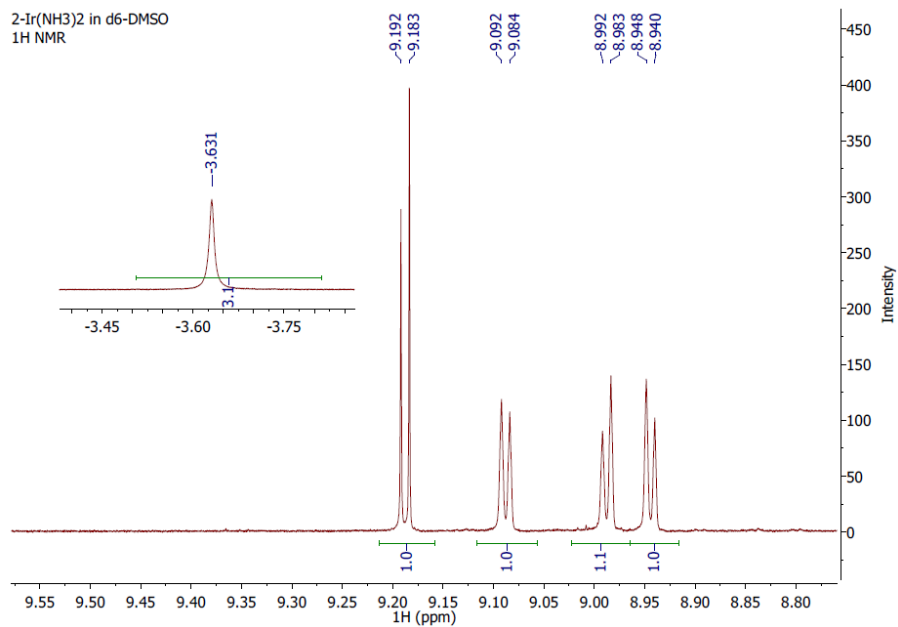
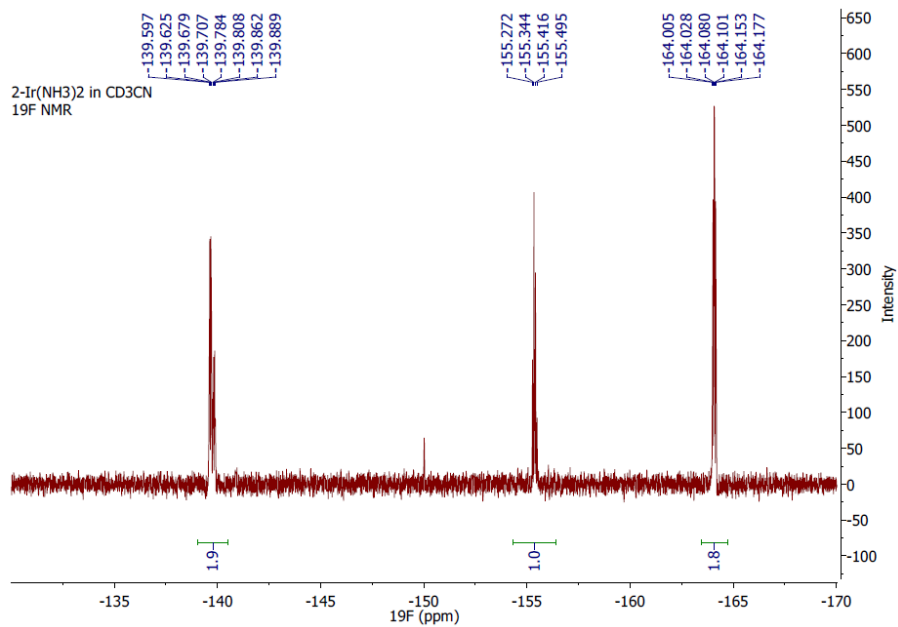
**3-bromo-5,10,15-**

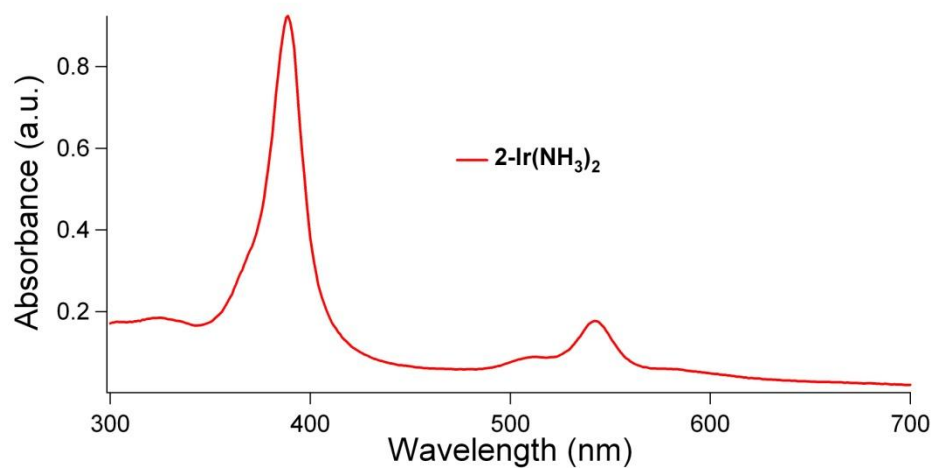
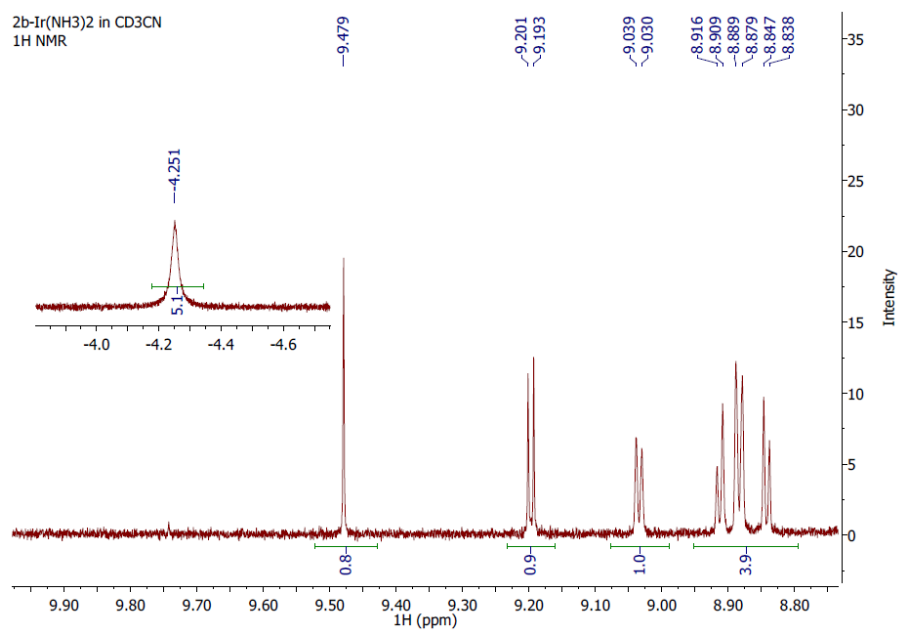
**(tris)pentafluorophenylmonoazaporphyrinatoiridium(III)**

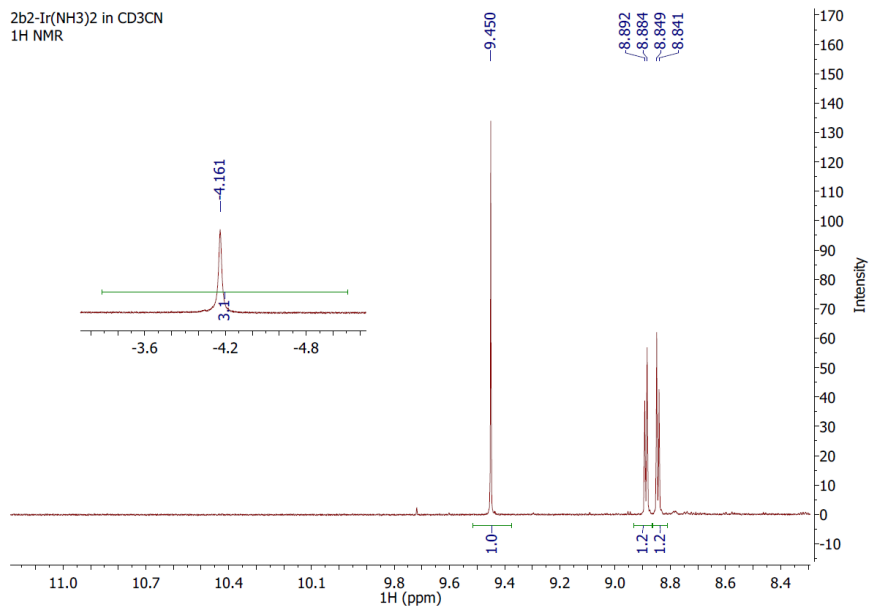
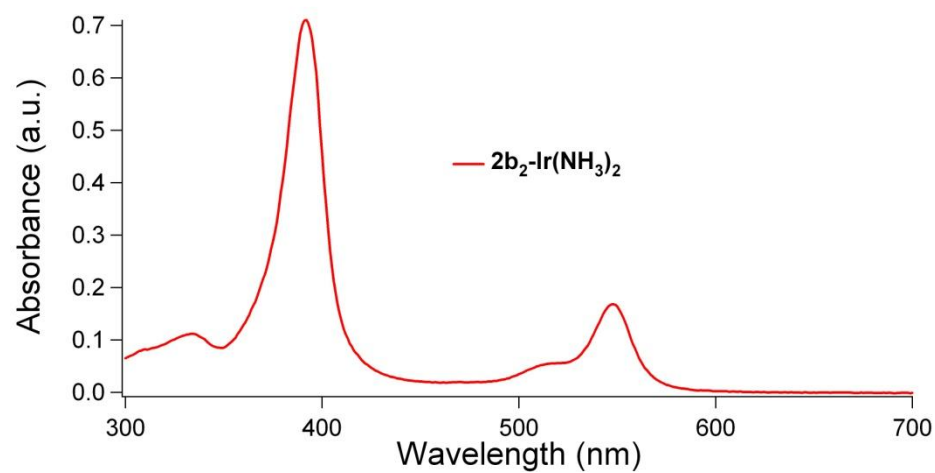
(bis)ammine, **2b-**

**Ir(NH<sub>3</sub>)<sub>2</sub>, and 5,10,15-(tris)pentafluorophenylmonoazaporphyrinatoiridium(III)**

(bis)ammine, **2-Ir(NH<sub>3</sub>)<sub>2</sub>**: To a rapidly stirring solution of **1-Ir(NH<sub>3</sub>)<sub>2</sub>** (22 mg) in methanol was added 250 μL of aqueous 6 N NH<sub>4</sub>OH. Shortly after, 104 mg N-bromosuccinimide was added and the reaction mixture immediately turned from green to purple and began to evolve gas. After five minutes, a new pink spot could be observed by TLC, and the reaction was allowed to stir for ten more minutes before being concentrated onto silica and subjected to column chromatography on silica. CH<sub>2</sub>Cl<sub>2</sub> was first used to elute any remaining corrole, followed by 2% MeOH in CH<sub>2</sub>Cl<sub>2</sub> to elute pink solutions of **2b<sub>2</sub>-Ir(NH<sub>3</sub>)<sub>2</sub>** (9 mg, 35% yield), 3% MeOH in CH<sub>2</sub>Cl<sub>2</sub> to elute **2b-Ir(NH<sub>3</sub>)<sub>2</sub>** (2 mg, 8% yield), and 4% MeOH in CH<sub>2</sub>Cl<sub>2</sub> to elute **2-Ir(NH<sub>3</sub>)<sub>2</sub>** (1 mg, 4% yield), all of which could be evaporated to yield red solid products. Characterization data: **2b<sub>2</sub>-Ir(NH<sub>3</sub>)<sub>2</sub>**. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 9.45 (s, 2H), 8.89 (d, 2H, J = 4.8), 8.85 (d, 2H, J = 4.8), -4.161 (s, 6H). UV-vis (CH<sub>3</sub>CN, nm): 392, 513 (sh), 548. Emission (CH<sub>3</sub>CN, nm): 695. **2b-Ir(NH<sub>3</sub>)<sub>2</sub>**. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 9.48 (s, 1H), 9.20 (d, 1H, J = 4.8), 9.03 (d, 1H, J = 5.4), 8.91 (d, 1H, J = 4.2), 8.88 (d, 2H, J = 6.0), 8.84 (d, 1H, J = 5.4), -4.251 (s, 6H). **2-Ir(NH<sub>3</sub>)<sub>2</sub>**. <sup>1</sup>H NMR (d<sup>6</sup>-DMSO): δ 9.19 (d, 2H, J = 5.4), 9.09 (d, 2H, J = 4.8), 8.99 (d, 2H, J = 5.4), 8.94 (d, 2H, J = 4.8), -3.361 (s, 6H). UV-vis (CH<sub>3</sub>CN, nm): 389, 506 (sh), 542. Emission (CH<sub>3</sub>CN, nm): 691

Figure B-34: <sup>1</sup>H NMR of **2-Ir(NH<sub>3</sub>)<sub>2</sub>** in d<sup>6</sup>-DMSOFigure B-35: <sup>19</sup>F NMR of **2-Ir(NH<sub>3</sub>)<sub>2</sub>** in CD<sub>3</sub>CN

Figure B-36: UV-vis of **2-Ir(NH<sub>3</sub>)<sub>2</sub>** in CD<sub>3</sub>CNFigure B-37: <sup>1</sup>H NMR of **2b-Ir(NH<sub>3</sub>)<sub>2</sub>** in CD<sub>3</sub>CN

Figure B-38: <sup>1</sup>H NMR of **2b<sub>2</sub>-Ir(NH<sub>3</sub>)<sub>2</sub>** in CD<sub>3</sub>CNFigure B-39: UV-vis of **2b<sub>2</sub>-Ir(NH<sub>3</sub>)<sub>2</sub>** in CD<sub>3</sub>CN