

Supplementary Material (ESI) for Chemical Communications  
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**Formazans as  $\beta$ -diketiminates analogues. First structural characterization of main group formazan complexes towards boraverdazyl radicals.**

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**SUPPORTING INFORMATION**

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**1,5-diphenyl-3-p-tolylformazan (3a).** Phenylhydrazine (9.82 mL, 100 mmol) was combined with p-tolualdehyde (11.8 mL, 100 mmol) and ethanol (100 mL) before the mixture was allowed to stir for 30 min at which time a yellow precipitate had formed. The reaction mixture was treated with sodium carbonate hydrate (40 g, 323 mmol), tetrabutylammonium bromide (3.0 g, 9 mmol), water (300 mL), and dichloromethane (300 mL) before being stirred at 0°C for 1 h. A solution of diazonium salt made from stirring aniline (9.2 mL, 100 mmol), sodium nitrite (7.5 g, 109 mmol), water (25 mL), and hydrochloric acid (25 mL) for 30 min at 0°C was then added dropwise. Upon addition, the organic phase in the biphasic reaction mixture turned blood red. After stirring for 2 h at RT the organic layer was collected, washed with water (4 x 250 mL) and taken to dryness *in vacuo*. Column chromatography (neutral alumina, dichloromethane) followed by trituration of the resulting solid with methanol afforded **3a** as a dark purple microcrystalline solid, yield 15.0 g (47.8 %). Mp. 154-156°C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 15.24 (s, 1H), 8.03 (d, 2H, <sup>3</sup>J = 8 Hz), 7.72 (d, 4H, <sup>3</sup>J = 8 Hz), 7.49 (t, 4H, <sup>3</sup>J = 8 Hz), 7.33-7.27 (m, 4H), 2.42 (s, 3H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 148.6, 141.9, 138.2, 135.1, 130.0, 129.7, 128.0, 126.3, 119.2, 21.5 ppm. FT-IR (KBr): 1597 (s), 1511 (s), 1497 (s), 1453 (s), 1353 (m), 1232 (s), 1035 (s), 1014 (s), 821 (s), 502 (m) cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 274 nm (ε = 20000), 301 nm (ε = 26250), 491 nm (ε = 15000). MS (LSIMS): *m/z* 315 {M+1<sup>+</sup>, 75 %}. Anal. Calcd for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>: C, 76.40; H, 5.77; N, 17.82. Found: C, 76.71; H, 5.64; N, 17.97.

**1,5-di-p-tolyl-3-phenylformazan (3b).** p-tolylhydrazine hydrochloride (12.50 g, 79 mmol) was combined with triethylamine (20.0 mL, 143 mmol) and ethanol (50 mL). After 30 min of stirring, benzaldehyde (8.1 mL, 79 mmol) was added and the mixture was allowed to stir for an additional 2 h at which time a yellow precipitate had formed. The reaction mixture was treated with sodium carbonate hydrate (33.2 g, 268 mmol), tetrabutylammonium bromide (2.5 g, 8 mmol), water (250 mL), and dichloromethane (250 mL) before being stirred at 0°C for 1 h. A solution of diazonium salt made from stirring p-toluidine (8.50 g, 79 mmol), sodium nitrite (6.3 g, 91 mmol), water (25 mL), and hydrochloric acid (21 mL) for 30 min at 0°C was then added dropwise. Upon addition, the organic phase in the biphasic reaction mixture turned blood red. After stirring for 2 h at RT the organic layer was collected, washed with water (5 x 100 mL) and taken to dryness *in vacuo*. Column chromatography (neutral alumina, dichloromethane) followed by trituration of the solid with methanol afforded **3b** as a dark purple microcrystalline solid, yield 10.1 g (30.8 %). Mp. 140-142°C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 15.46 (s, 1H), 8.14 (d, 2H, <sup>3</sup>J = 8 Hz), 7.62 (d, 4H, <sup>3</sup>J = 8 Hz), 7.45 (t, 2H, <sup>3</sup>J = 8 Hz), 7.36 (t, 1H, <sup>3</sup>J = 8 Hz), 7.29 (d, 4H, <sup>3</sup>J = 8 Hz), 2.41 (s, 6H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 146.4, 141.3, 138.4, 138.2, 130.9, 130.6, 130.0, 128.9, 128.0, 126.2, 119.2, 119.0, 108.2, 21.5 ppm. FT-IR (KBr): 1596 (s), 1515 (s), 1495 (s), 1240 (s), 1044 (s), 767 (s) cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 278 nm (ε = 17500), 308 nm (ε = 23500), 493 (ε = 16250). MS (LSIMS): *m/z* 329 {MH<sup>+</sup>, 100 %}. Anal. Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>4</sub>: C, 76.80; H, 6.14; N, 17.06. Found: C, 76.97; H, 6.12; N, 16.69.

**1,1-diacetate-2,6-diphenyl-3-p-tolylboratetrazine (4a).** Boric acid (0.8 g, 13 mmol) was combined with acetic acid (3.5 mL) and acetic anhydride (3.5 mL) and stirred at 80°C for 15 minutes until dissolution was observed. **3a** (1.0 g, 3.2 mmol) was then added as a solution in acetic acid (2.1 mL) and acetic anhydride (7.5 mL). The mixture was left to stir at 80°C for 16 h at which time the mixture was extracted with hexanes (5 x 100 mL). The hexanes was combined and washed with water (5 x 100 mL), dried with anhydrous magnesium sulfate and concentrated in vacuo. Compound **4a** was isolated as a dark purple solid, yield 0.420 g (29.7 %). X-Ray quality crystals were grown via slow evaporation of concentrated hexanes solutions of **4a**. Mp. 178-180°C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.01 (d, 2H, <sup>3</sup>J = 8 Hz), 7.95 (d of d, 4H, <sup>3</sup>J = 8 Hz), 7.48 (m, 6H), 7.32 (d, 2H, <sup>3</sup>J = 8 Hz), 2.43 (s, 3H), 1.82 (s, 6H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 171.7, 145.3, 139.4, 138.8, 132.3, 130.0, 129.9, 129.5, 125.6, 123.4, 22.7, 21.6 ppm. <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.32 ppm. FT-IR (KBr): 1724 (s), 1715 (s), 1305 (s), 1250 (s), 1054 (s), 966 (s), 764 (s), 688 (s), 506 (m) cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 256 nm (ε = 20000), 311 nm (ε = 11500), 558 (ε = 6500). MS (EI): *m/z* 442 {MH<sup>+</sup>, 65 %}. Anal. Calcd for C<sub>24</sub>H<sub>23</sub>N<sub>4</sub>O<sub>4</sub>B: C, 65.18; H, 5.24; N, 12.67. Found: C, 65.31; H, 5.56; N, 12.46.

**1,1-diacetate-2,6-di-p-tolyl-3-phenylboratetrazine (4b).** Boric acid (1.6 g, 26 mmol) was combined with acetic acid (7.0 mL) and acetic anhydride (7.0 mL) and stirred at 80°C for 15 minutes until dissolution was observed. **3b** (2.1 g, 6.4 mmol) was then added as a solution in acetic acid (4.2 mL) and acetic anhydride (15.1 mL). The mixture was left to stir at 80°C for 16 h at which time the mixture was extracted with hexanes (5 x 200 mL). The hexanes was combined and washed with water (5 x 200 mL), dried with anhydrous magnesium sulfate and concentrated in vacuo. Compound **4b** was isolated as a dark purple solid, yield 0.826 g (28.1 %). X-Ray quality crystals were grown via slow evaporation of concentrated hexanes solutions of **4b**. Mp. 170-172°C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.11 (d, 2H, <sup>3</sup>J = 8 Hz), 7.85 (d, 4H, <sup>3</sup>J = 8 Hz), 7.51-7.42 (m, 3H), 7.27 (d, 4H, <sup>3</sup>J = 8 Hz), 2.42 (s, 6H), 1.82 (s, 6H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 171.7, 143.1, 140.6, 135.3, 130.2, 129.2, 129.1, 125.6, 123.2, 22.7, 21.6 ppm. <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.31 ppm. FT-IR (KBr): 1717 (s), 1602 (m), 1371 (s), 1303 (s), 1251 (s), 1176 (m), 1042 (s), 971 (s), 817 (s), 504 (s) cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 260 nm (ε = 15750), 320 nm (ε = 14250), 560 (ε = 19750). MS (EI): *m/z* 456 {MH<sup>+</sup>, 100 %}. Anal. Calcd for C<sub>25</sub>H<sub>25</sub>N<sub>4</sub>O<sub>4</sub>B: C, 65.80; H, 5.52; N, 12.28. Found: C, 65.41; H, 5.66; N, 11.87.

**1,1-diacetate-2,6-diphenyl-3-p-tolylboratetrazinyl radical anion (5a).** Compound **4a** (0.085 g, 0.2 mmol) was dissolved in hexanes (50 mL) and stirred for 30 min at which time cobaltocene (0.039 mg, 0.2 mmol) in hexanes (50 mL) was added via cannula. Upon addition a green precipitate formed and after 10 min of stirring the mixture was filtered *in vacuo*, washed with hexanes (2 x 50 mL) and dried *in vacuo* for 1 hour. Compound **5a** was isolated as a dark green solid and was handled in the glovebox when possible, yield 0.040 g (31.6 %). Mp. 96-98°C (dec). FT-IR (KBr): 1707 (s), 1690 (s), 1587 (s), 1485 (s), 1267 (s), 1172 (m), 1104 (m), 1014 (m), 755 (m), 692 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>34</sub>H<sub>33</sub>N<sub>4</sub>O<sub>4</sub>BCo: C, 64.68; H, 5.27; N, 8.87. Found: C, 64.51; H, 5.23; N, 8.24.

**1,1-diacetate-2,6-di-p-tolyl-3-phenylboratetrazinyl radical anion (5b).** Compound **4b** (0.085 g, 0.2 mmol ) was dissolved in hexanes (75 mL) and stirred for 30 min at which time cobaltacene (0.039 g, 0.2 mmol ) in hexanes (50 mL) was added via cannula. Upon addition a green precipitate formed and after 1 h of stirring the mixture was filtered *in vacuo*, washed with hexanes (2 x 50 mL) and dried *in vacuo* for 1 hour. Compound **5b** was isolated as a dark green solid and was handled in the glovebox when possible, yield 0.050 g (38.8 %). Mp. 100-102°C (dec). FT-IR (KBr): 1707 (s), 1690 (s), 1606 (m), 1505 (s), 1414 (m), 1367 (m), 1279 (m), 1172 (m), 823 (s), 698 (m), 646 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>35</sub>H<sub>35</sub>N<sub>4</sub>O<sub>4</sub>BCo: C, 65.13; H, 5.47; N, 8.68. Found: C, 64.28; H, 5.67; N, 8.08.

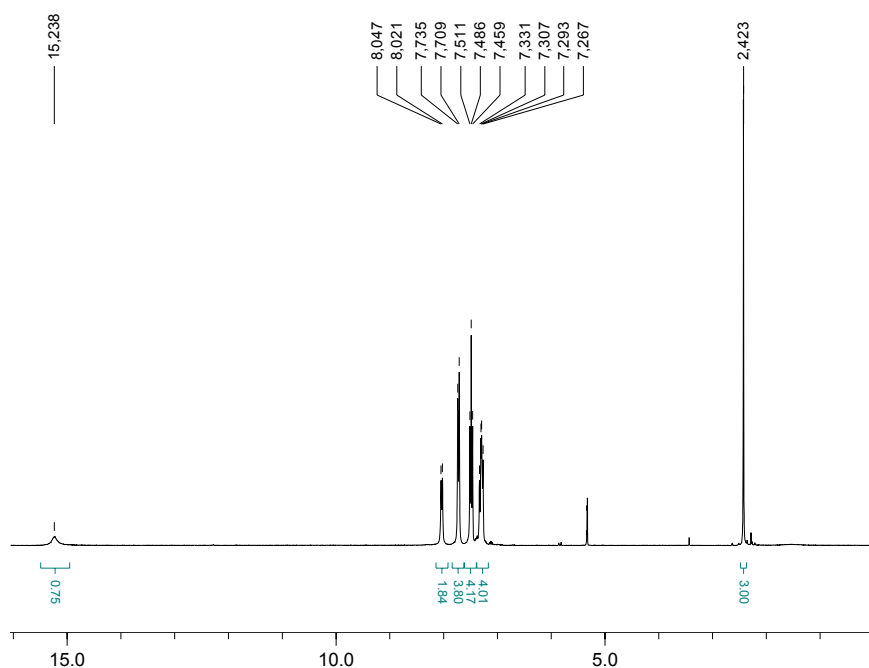


Figure S1.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **3a**

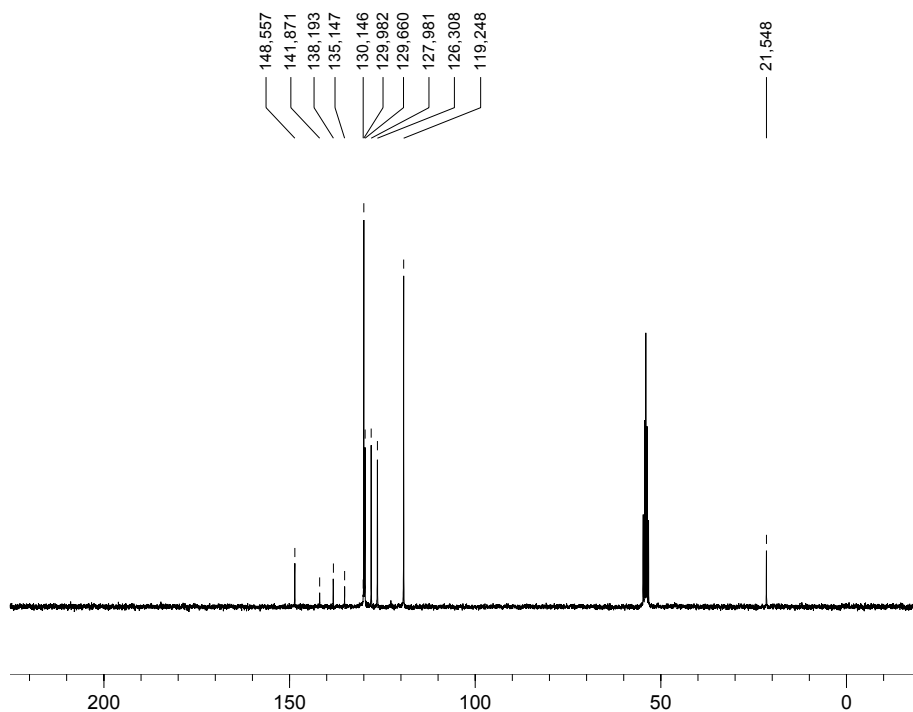


Figure S2.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **3a**

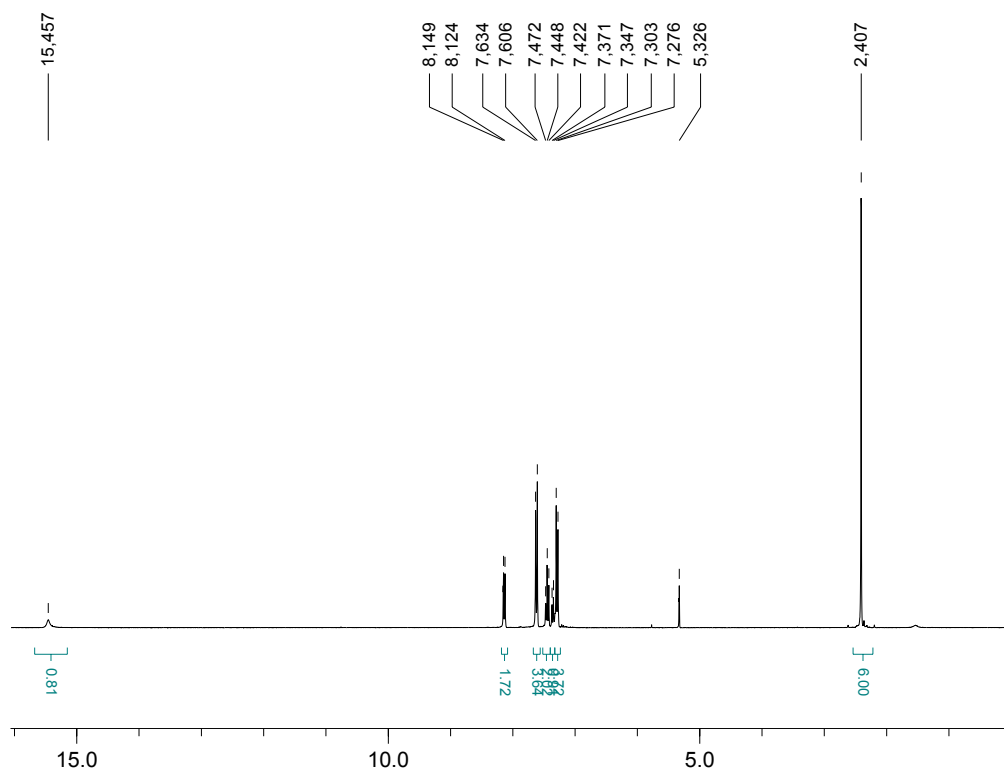


Figure S3.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **3b**

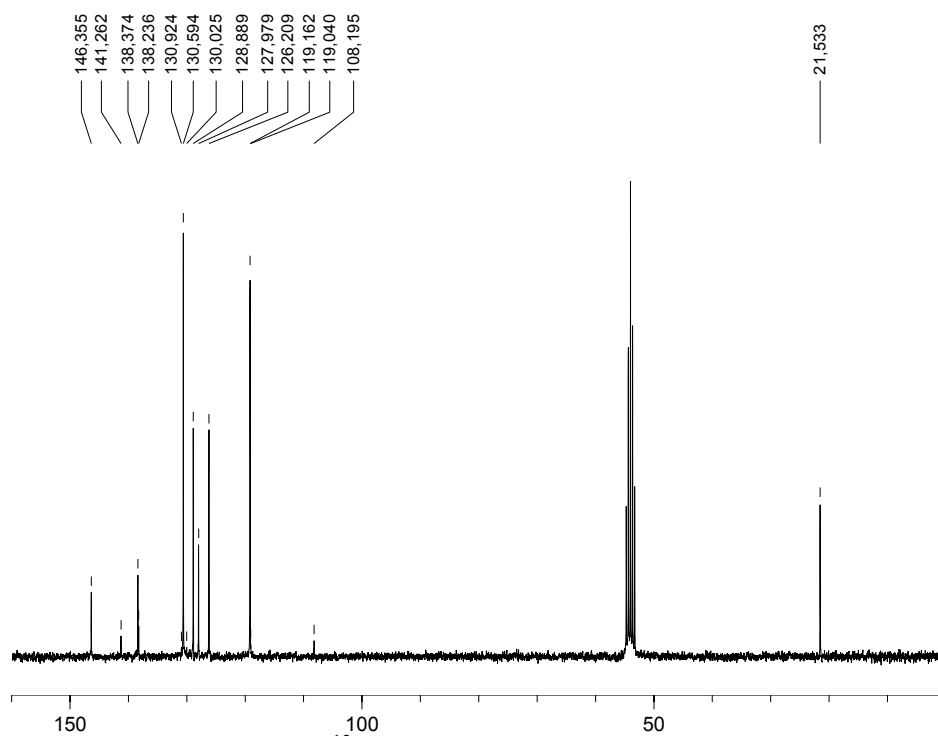


Figure S4.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **3b**

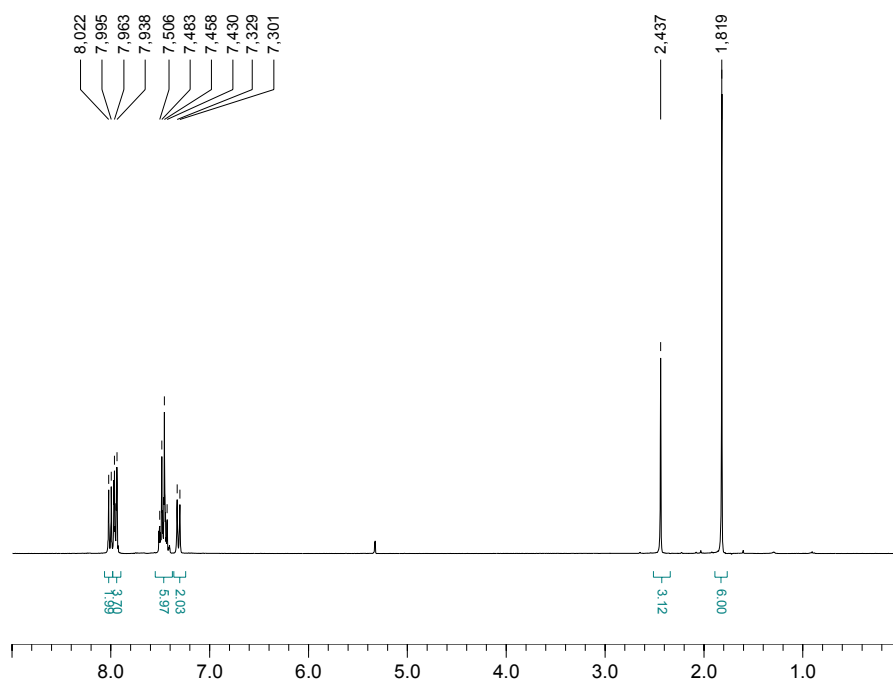


Figure S5.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **4a**

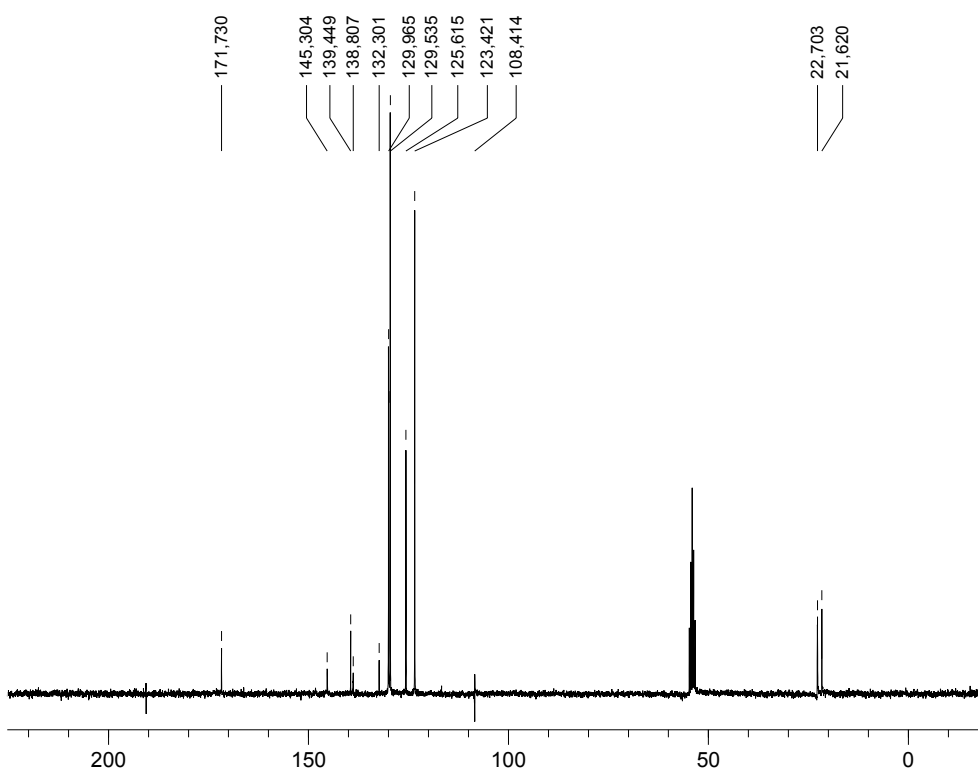


Figure S6.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **4a**

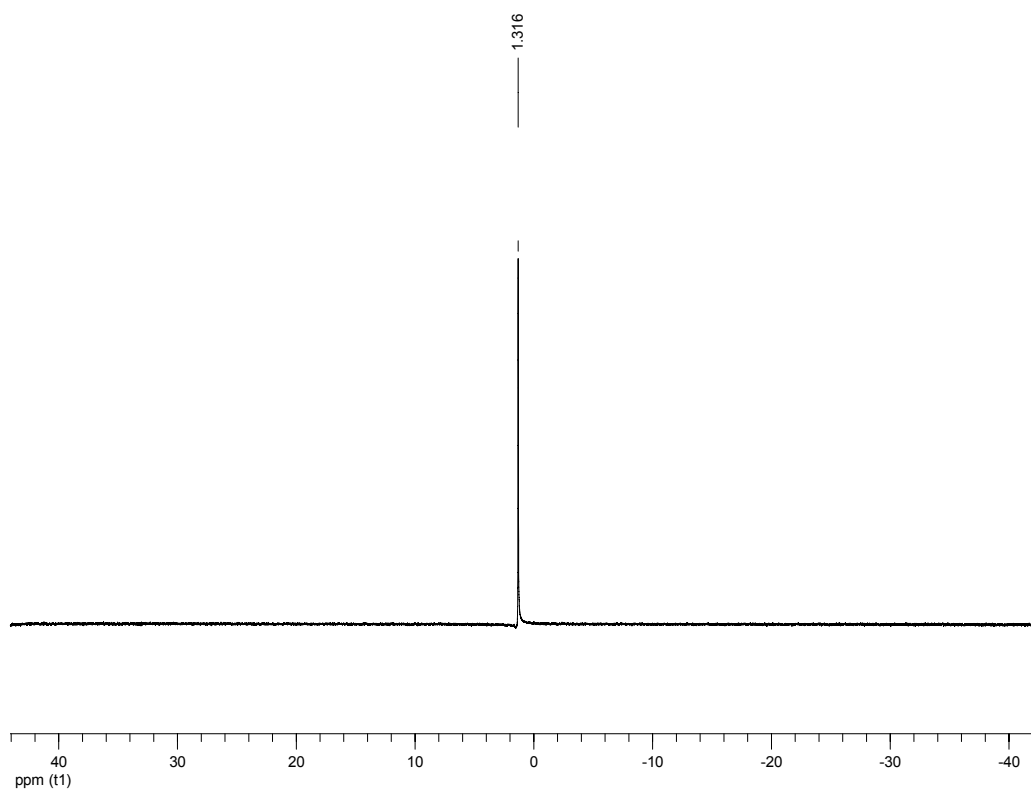


Figure S7.  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **4a**

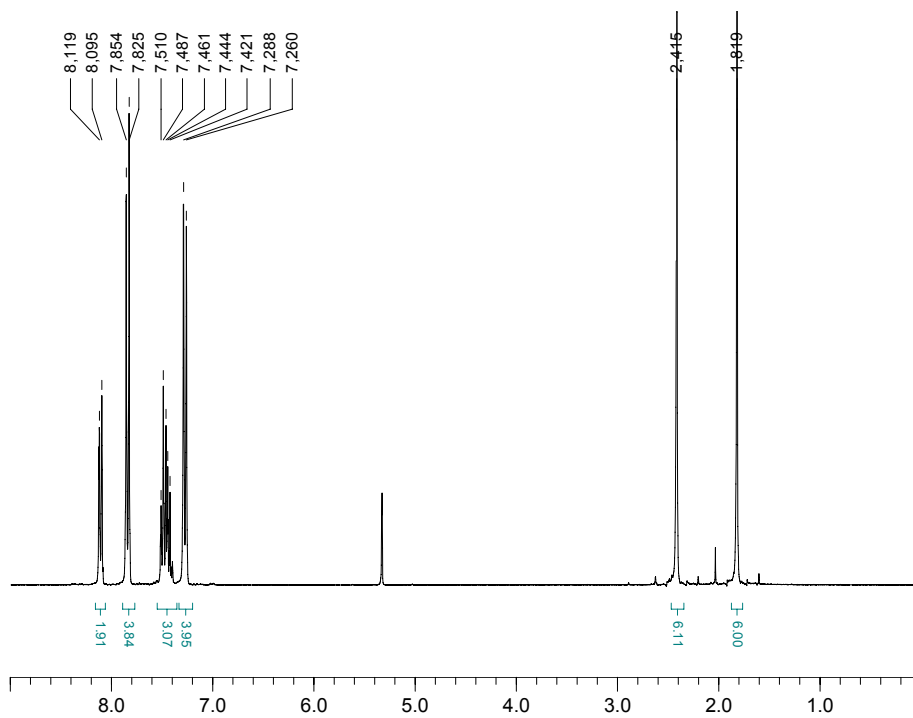
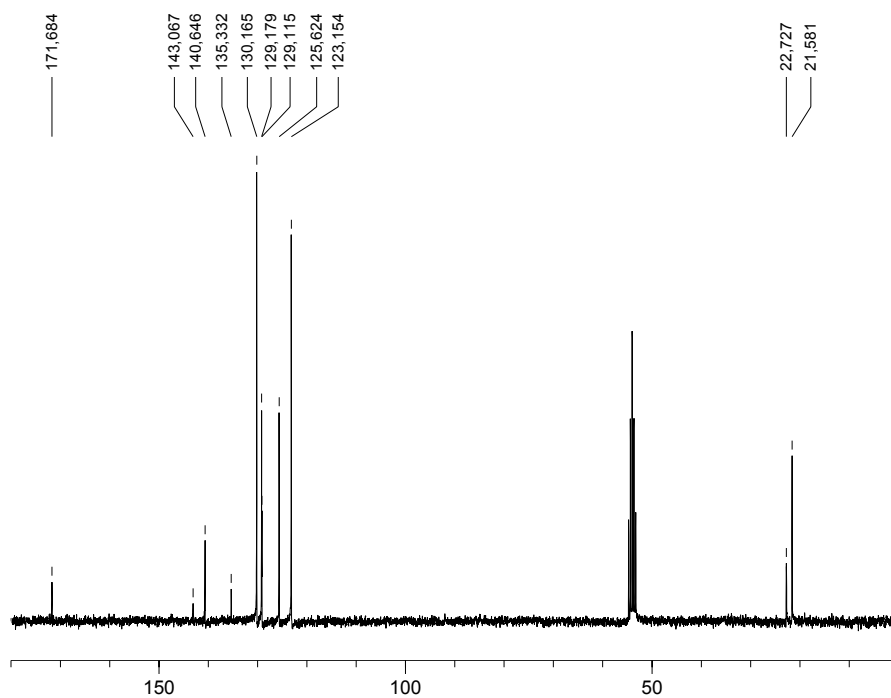
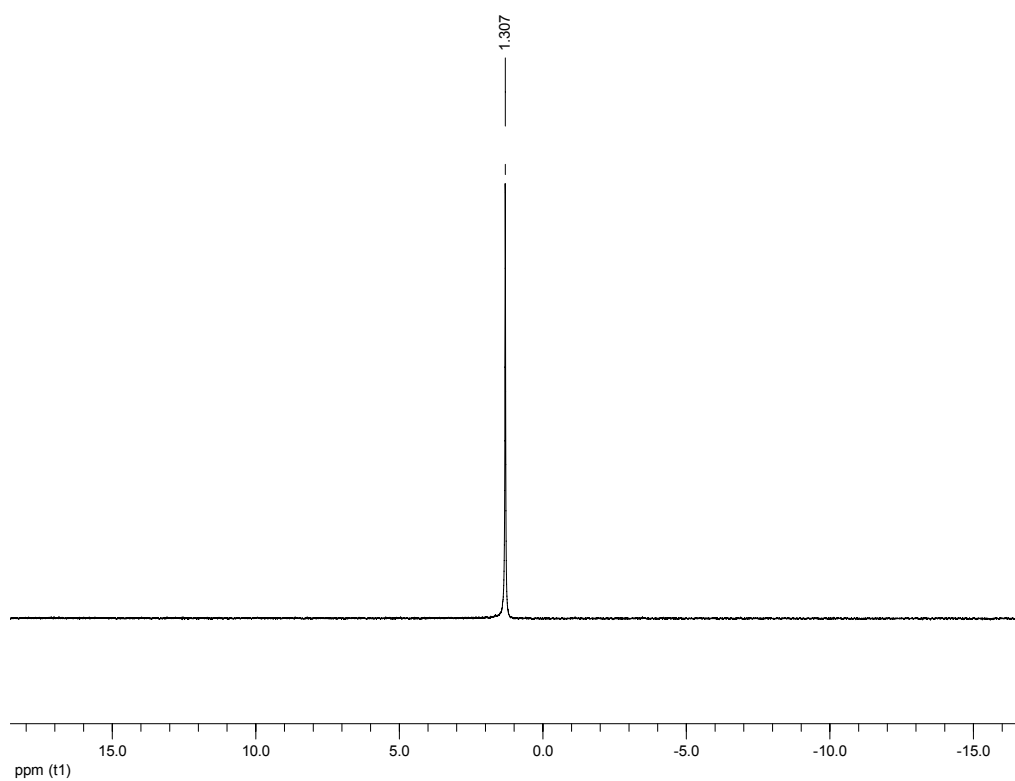


Figure S8.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **4b**

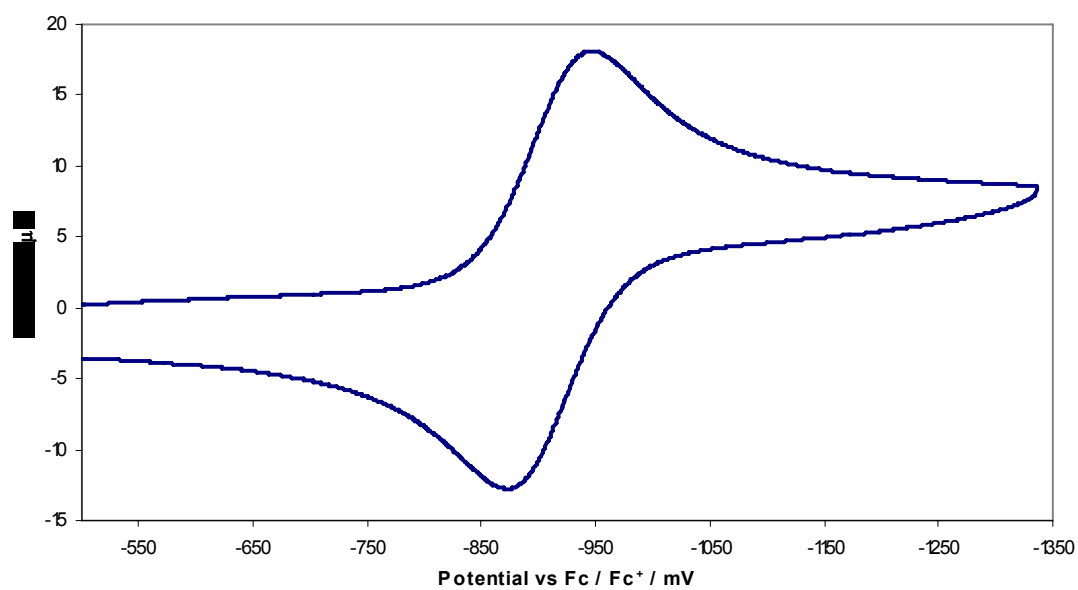




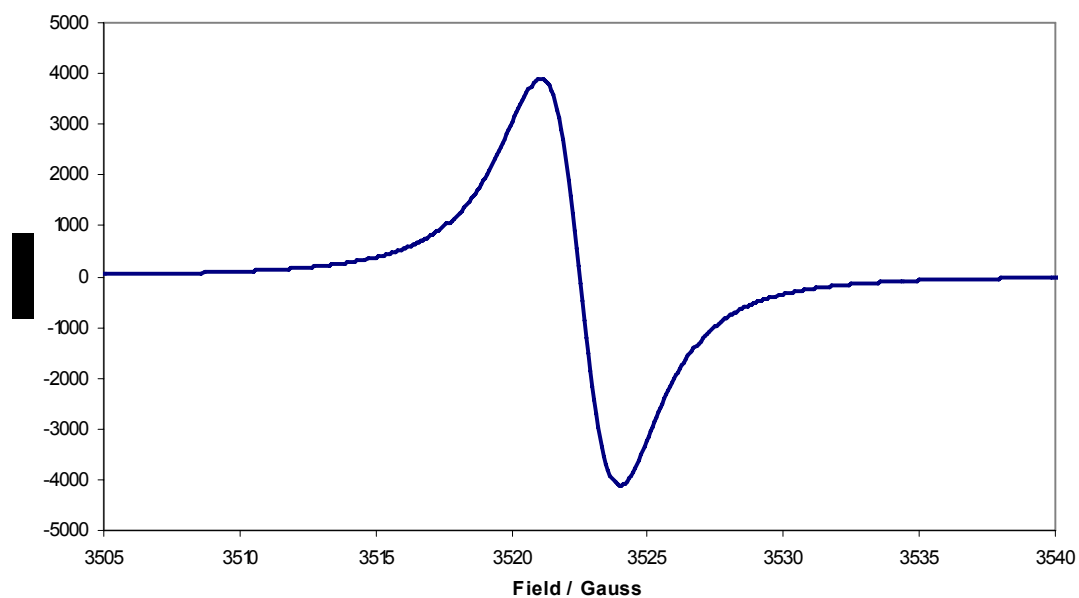
**Figure S9.**  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **4b**



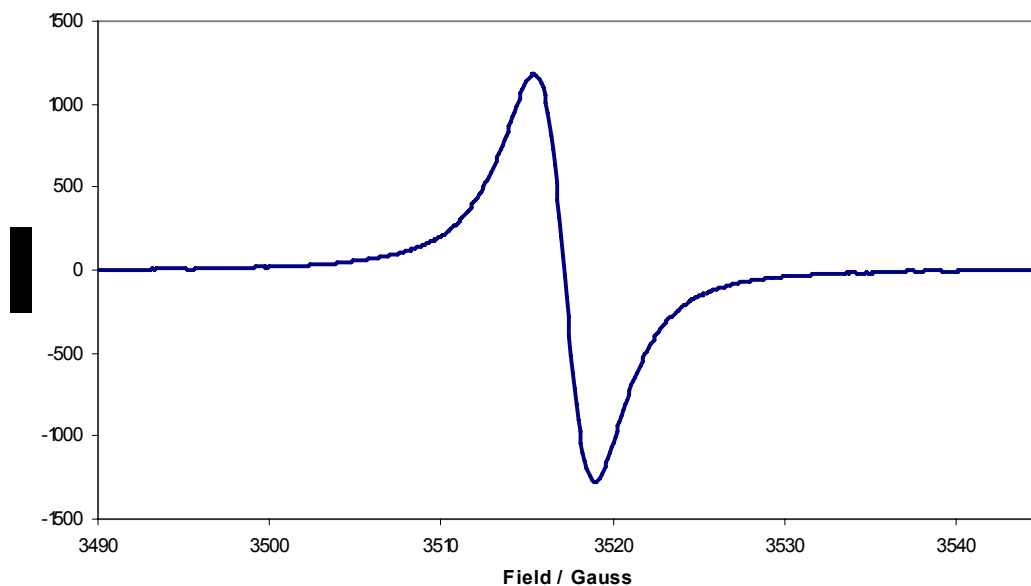
**Figure S10.**  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum of **4b**



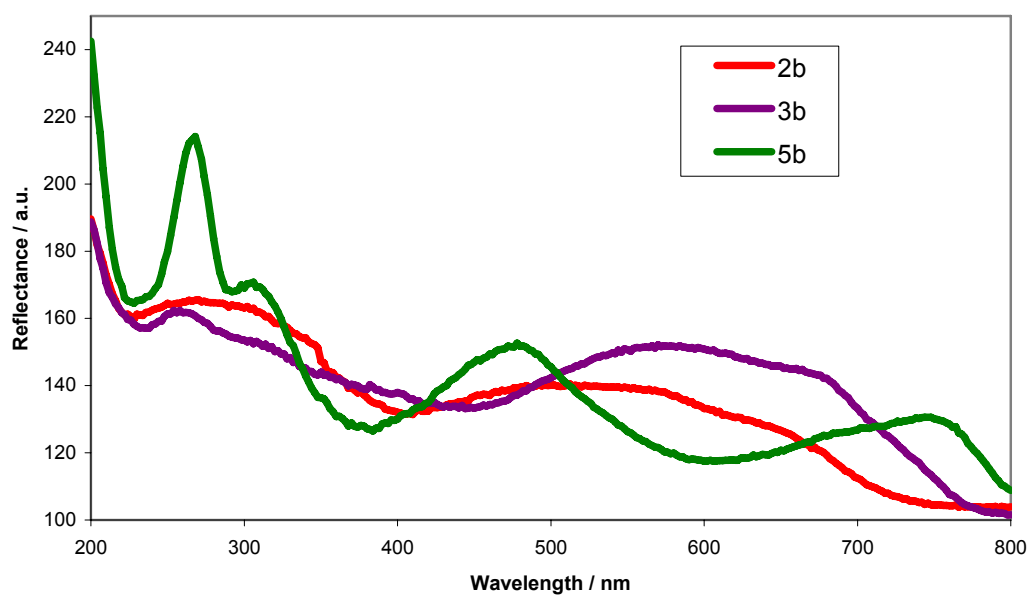
**Figure S11.** Cyclic voltammogram of **4b** in CH<sub>3</sub>CN. Scan rate 100 mv/S, Bu<sub>4</sub>NBF<sub>4</sub> electrolyte.



**Figure S14.** EPR Spectrum of **5a** (solid state),  $g = 2.0005$



**Figure S15.** EPR Spectrum of **5b** (solid state),  $g = 1.9999$



**Figure S16.** Diffuse Reflectance Spectra of **2b**, **3b**, and **5b** (1.1% in BaSO<sub>4</sub>)