

## Supporting Information

### *meso*-Aryl tribenzosubporphyrin – A totally substituted subporphyrin species

Elena A. Makarova,<sup>a</sup> Soji Shimizu,<sup>b</sup> Atsushi Matsuda,<sup>b</sup> Evgeny A. Lu'kyanets,<sup>\*a</sup> and Nagao Kobayashi<sup>\*b</sup>

*Organic Intermediates and Dyes Institute, B. Sadovaya 1/4, Moscow, 123995, Russia*

*and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

### 1. Experimental

#### General procedure

Electronic absorption spectra were recorded with Hitachi U-3410 and JASCO V-570 spectrophotometers. Magnetic circular dichroism (MCD) spectra were recorded with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet, which produces magnetic fields of up to 1.09 T (1T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla ( $[q]_M / \text{deg dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \text{ T}^{-1}$ ). Fluorescence spectrum was measured with a Hitachi F-4500 spectrofluorimeter with appropriate filters installed to eliminate scattered light.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and  $^1\text{H}$ - $^1\text{H}$  and  $^{13}\text{C}$ - $^1\text{H}$  two dimensional spectra were recorded on a JEOL ECA-600 spectrometer (operating as 594.17 MHz for  $^1\text{H}$  and 149.40 MHz for  $^{13}\text{C}$ ) using the residual solvent as the internal reference for  $^1\text{H}$  ( $\delta = 5.320$  ppm for  $\text{CD}_2\text{Cl}_2$ ), and  $^{13}\text{C}$  ( $\delta = 53.1$  ppm for  $\text{CD}_2\text{Cl}_2$ ). High resolution mass spectra of **2-OH** and **2-OEt** were recorded on a Bruker Daltonics Apex-III spectrometer. X-ray crystallographic studies were carried out on a Rigaku Saturn CCD spectrometer with graphite monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were derived using the SHELXS-97 program and refined on  $F^2$  using the SHELXL-97 program.<sup>[1]</sup> CV and DPV measurements were recorded on a Hokuto Denko HZ5000 potentiostat under argon in *o*-dichlorobenzene (DCB) solutions with tetrabutylammonium perchlorate (TBAP, 0.1 M) as the supporting electrolyte. Measurements were carried out with a glassy carbon electrode (area = 0.07 cm<sup>2</sup>), an Ag/AgCl reference electrode, and a Pt wire counter-electrode. The concentration of the solution was fixed at 0.5 mM and the sweep rates were 100 mV/s and 10mV/s for CV and DPV measurements, respectively. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple was used as internal standard. The Gaussian03 software package<sup>[2]</sup> was used to carry out DFT and TDDFT calculations using the B3LYP functional with 6-31G(d) basis sets.<sup>[3]</sup>

### Synthesis of *meso*-phenyl tribenzosubporphyrin 2

**method A:** A mixture of 3-benzalphthalimidine (1.00 g, 4.52 mmol) and boric acid (0.31 g, 5.03 mmol) was ground into a fine powder and heated to 360 °C under argon for 2 h. After cooling to room temperature the black residue was washed with hot water and then 10% aqueous NaOH solution. The crude residue was transferred to a Soxhlet apparatus and extracted with toluene. The toluene solution was concentrated to approximately 10 mL and purified by column chromatography on neutral alumina with toluene as eluent to remove impurities, which does not exhibit any green fluorescence and then with mixture toluene – diethyl ether (10:1 v/v) as eluent a fraction with  $R_f$  0.20 (toluene – diethyl ether, 10:1 v/v) and green fluorescence was collected. Further purification by a gel permeation column (Bio-beads SX-1, Bio-Rad) using toluene as eluent, followed by recrystallization from acetone/water gave *meso*-phenyl tribenzosubporphyrin hydroxyboron complex **2-OH** (0.075 g, 7.8%).

**method B:** A mixture of phthalimide (1.47 g, 0.01 mol), phenylacetic acid (2.04 g, 0.015 mol) and boric acid (0.62 g, 0.01 mol) was ground into a fine powder and heated to 260 °C under argon for 1 h. Then the temperature was increased up to 360 °C and the heating further was continued for 2 h more at this temperature. After cooling to room temperature the black residue was washed with hot water, 10% aqueous NaOH solution and then hot 50% EtOH. The crude residue was dissolved in chloroform and then passed through a short alumina column to remove impurities. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on neutral alumina with toluene collecting the first fraction with  $R_f$  0.39 (toluene) and green fluorescence. The hydroxyboron complex **2-OH** was further collected by using mixture toluene – diethyl ether (10:1 v/v) as eluent, followed by a gel permeation column (Bio-beads SX-1, Bio-Rad) using toluene as eluent. Recrystallization from acetone/water gave **2-OH** (0.077 g, 3.6%) as a reddish orange solid. The first fraction was further purified by repeated alumina column chromatography with mixture toluene – hexane (1:1 v/v), followed by a gel permeation column (Bio-beads SX-1, Bio-Rad) using toluene as eluent. Evaporation of the solvent followed by recrystallization from ethanol/water gave 0.058 g (2.6%) of *meso*-phenyl tribenzosubporphyrin ethoxyboron complex **2-OEt** as a reddish orange solid.

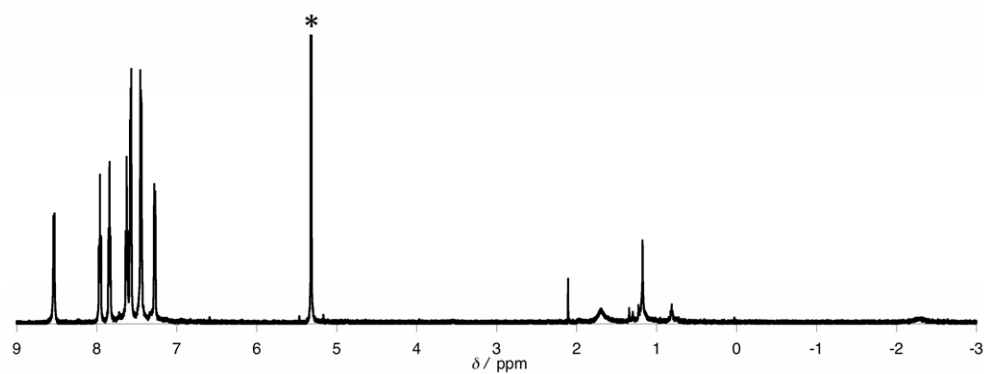
**2-OH:**  $^1\text{H}$  NMR (594.17 MHz,  $\text{CD}_2\text{Cl}_2$ , 213 K):  $\delta$  = 8.50 (d,  $J$  = 7.49 Hz, 3H; *ortho*), 7.92 (dd,  $J_1$  = 7.72 Hz,  $J_2$  = 7.49 Hz, 3H; *meta*), 7.79 (t,  $J$  = 7.66 Hz, 3H; *para*), 7.58 (dd,  $J_1$  = 7.31 Hz,  $J_2$  = 7.51 Hz, 3H; *meta*), 7.54 (m, 6H; *benzo*), 7.41 (m, 6H; *benzo*), 7.24 (d,  $J$  = 7.49 Hz, 3H; *ortho*), and -2.33 ppm (br s, 1H; OH);  $^{13}\text{C}$  NMR (149.40

MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  = 136.2 (*ipso*), 133.1 (pyrrole- $\alpha$ ), 132.0 (*ortho*), 131.8 (pyrrole- $\beta$ ), 130.9 (*ortho*), 128.8 (*meta*), 128.8 (*meta*), 128.7 (*para*), 126.1 (benzo- $\beta$ ), 122.8 (benzo- $\alpha$ ), and 116.4 ppm (*meso*); UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  [nm] ( $\epsilon$ ) = 353 (68000), 372 (194000), 485 (15000), and 517 (66000); HR-ESI-MS: *m/z* (% intensity): 660.2219 (57) [M<sup>++</sup>Na]; Calcd for C<sub>45</sub>H<sub>28</sub>N<sub>3</sub>O<sub>1</sub>B<sub>1</sub>Na<sub>1</sub>, 660.2218, and 620.2291 (100) [M<sup>+</sup>-OH]; Calcd for C<sub>45</sub>H<sub>27</sub>N<sub>3</sub>B<sub>1</sub>, 620.2293.

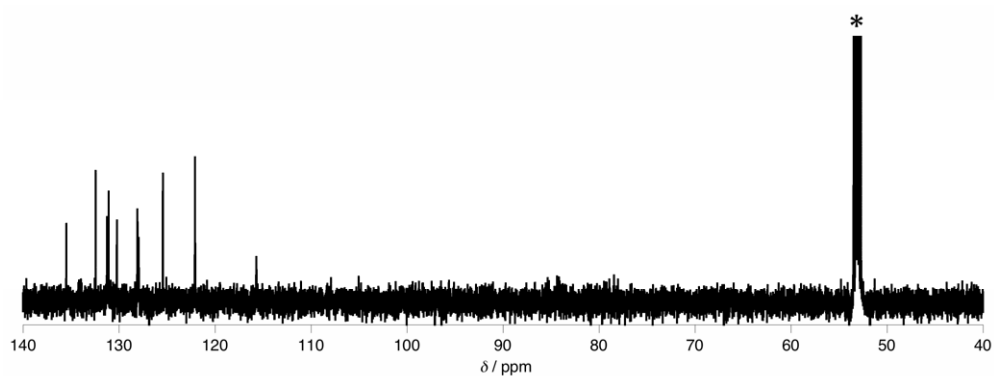
**2-OEt**: <sup>1</sup>H NMR (594.17 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  = 8.49 (d, *J* = 7.31 Hz, 3H; *ortho*), 7.92 (dd, *J*<sub>1</sub> = 7.19 Hz, *J*<sub>2</sub> = 6.98 Hz, 3H; *meta*), 7.80 (t, *J* = 7.01 Hz, 3H; *para*), 7.58 (dd, *J*<sub>1</sub> = 7.31 Hz, *J*<sub>2</sub> = 7.22 Hz, 3H; *meta*), 7.53 (br s, 6H; *benzo*), 7.41 (br s, 6H; *benzo*), 7.23 (d, *J* = 6.48 Hz, 3H; *ortho*), 0.77 (br s, 2H, CH<sub>3</sub>CH<sub>2</sub>O), and -0.23 ppm (t, *J* = 7.01 Hz, 3H; CH<sub>3</sub>CH<sub>2</sub>O); HR-ESI-MS: *m/z* (% intensity): 688.2527 (100) [M<sup>++</sup>Na]; Calcd for C<sub>47</sub>H<sub>32</sub>N<sub>3</sub>O<sub>1</sub>B<sub>1</sub>Na<sub>1</sub>, 688.2531.

**4**: <sup>1</sup>H NMR (500.16 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K):  $\delta$  = 8.03 (d, *J* = 6.60 Hz, 3H), 7.87 (dd, *J*<sub>1</sub> = 7.15 Hz, *J*<sub>2</sub> = 6.98 Hz, 3H), 7.80 (t, *J* = 7.70 Hz, 3H), 7.61 - 7.56 (m, 9H), 7.43 - 7.36 (m, 9H), 7.03 (t, *J* = 7.65 Hz, 3H), 6.84 (dd, *J*<sub>1</sub> = 7.65 Hz, *J*<sub>2</sub> = 7.68 Hz, 6H), and 6.44 ppm (d, *J* = 6.60 Hz, 6H)

## 2. NMR spectra of 2-OH



**Figure S1.** <sup>1</sup>H NMR spectrum of **2-OH** in CD<sub>2</sub>Cl<sub>2</sub> at -60 °C. \* indicates a solvent peak.



**Figure S2.** <sup>13</sup>C NMR spectrum of **2-OH** in CD<sub>2</sub>Cl<sub>2</sub> at -60 °C. \* indicates a solvent peak.

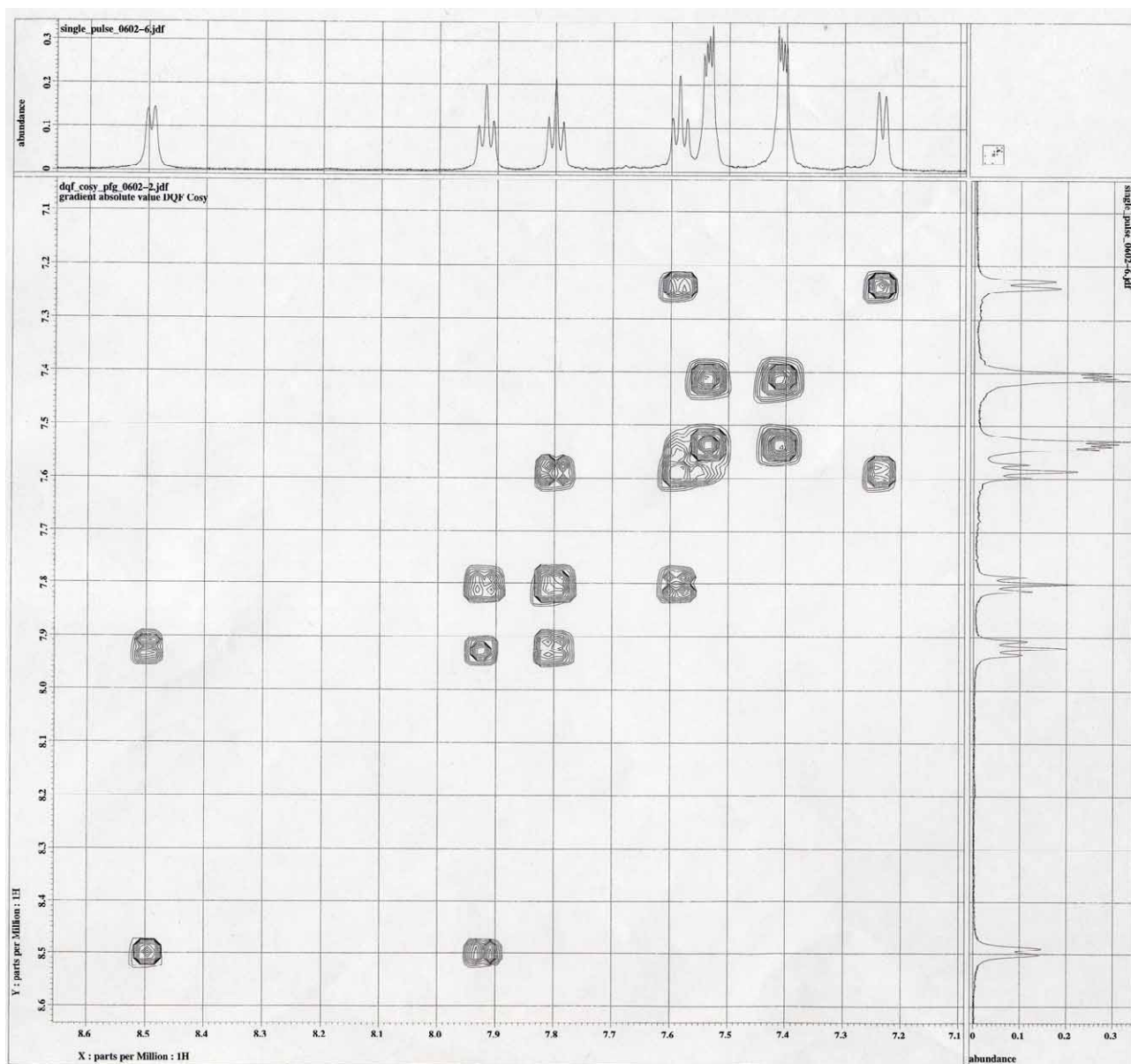


Figure S3.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **2-OH** measured in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .

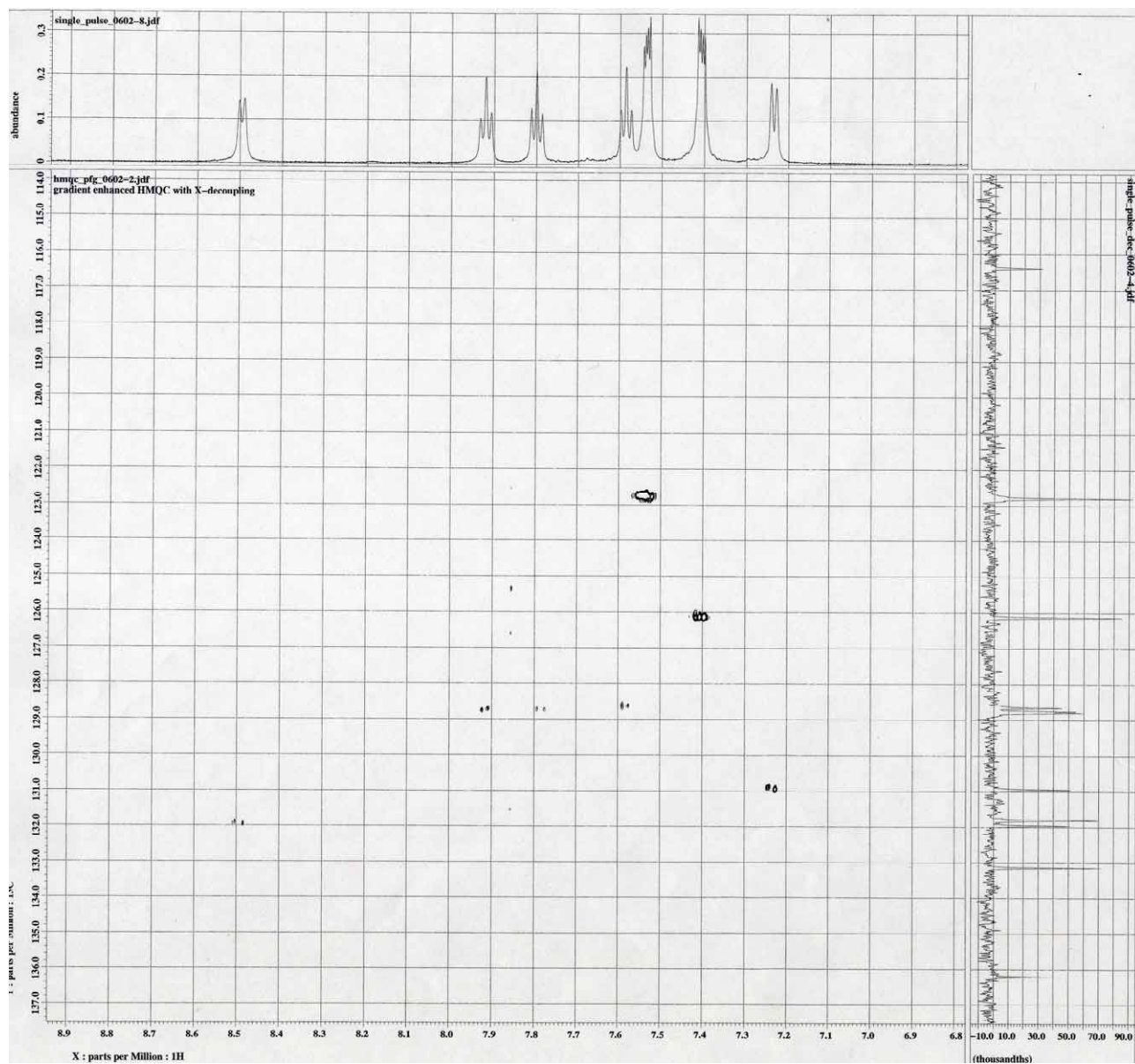


Figure S4. HMQC spectrum of 2-OH measured in CD<sub>2</sub>Cl<sub>2</sub> at -60 °C.

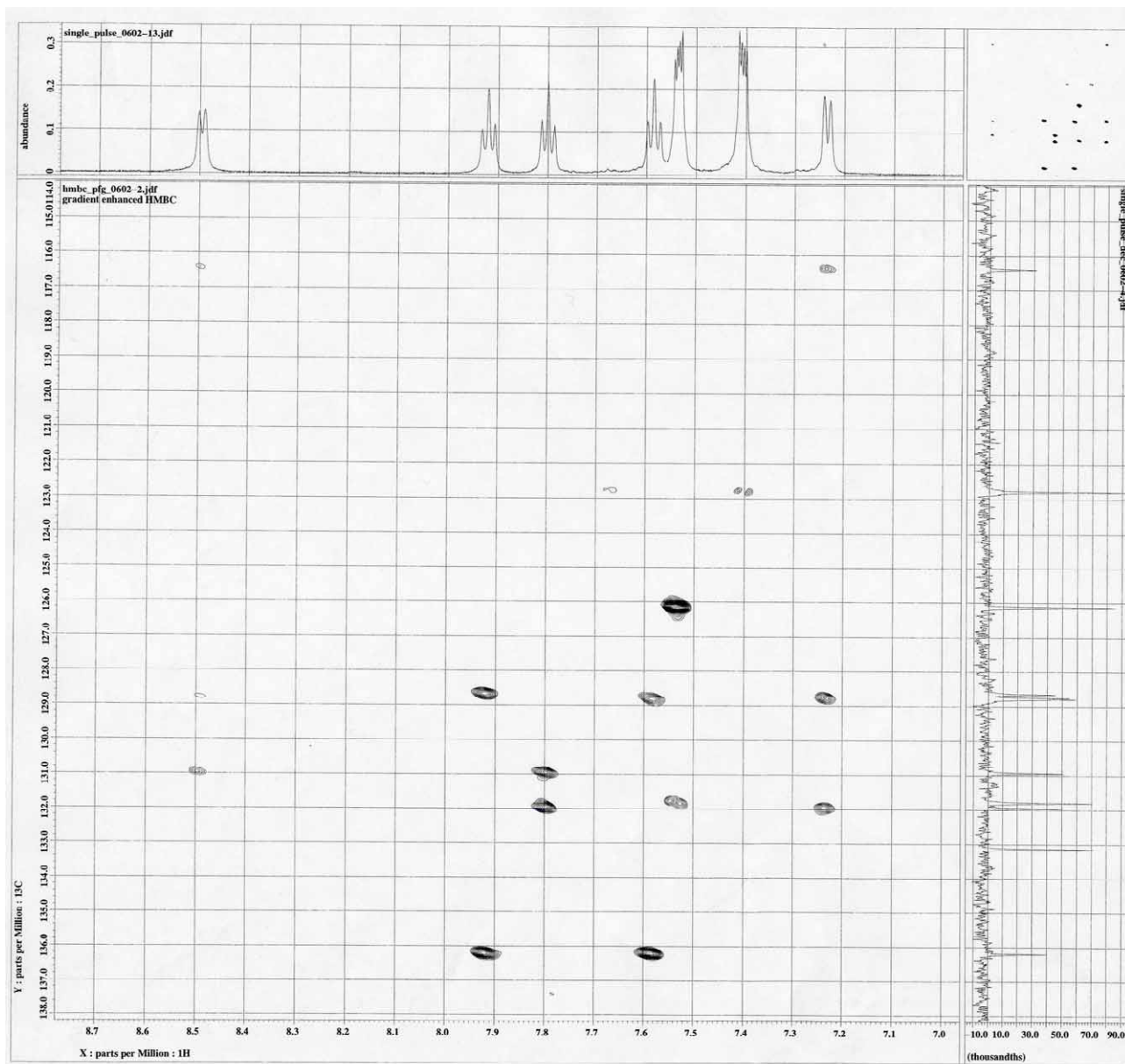
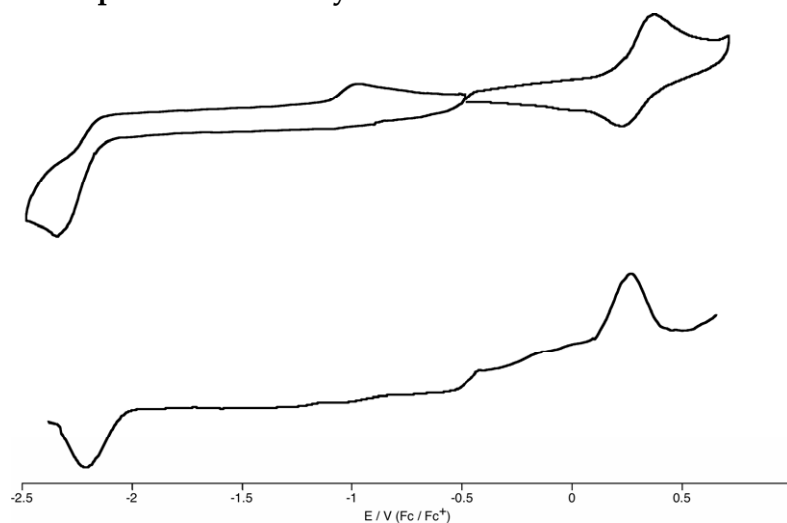


Figure S5. HMBC spectrum of 2-OH measured in CD<sub>2</sub>Cl<sub>2</sub> at -60 °C.

### 3. Cyclic and differential pulse voltammetry



**Figure S6.** Cyclic (top) and differential pulse (bottom) voltammetry of **2-OH** recorded under argon in *o*-dichlorobenzene (DCB) solutions with tetrabutylammonium perchlorate (TBAP, 0.1 M) as supporting electrolyte. Measurements were carried out with a glassy carbon electrode (area = 0.07 cm<sup>2</sup>), an Ag/AgCl reference electrode, and a Pt wire counter-electrode. The concentration of the solution was fixed at 0.5 mM and the sweep rates were 100 mV/s and 10mV/s for CV and DPV measurements, respectively. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple was used as internal standard.



## Reference

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