

# Electronic Supplementary Information

## Retro Baeyer–Villiger reaction: thermal conversion of the [60]fullerene-fused lactones to ketones

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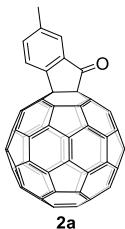
## 1. General Information

Compounds **1a–i** were synthesized according to the procedure developed by our group.<sup>1</sup> Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use. Other chemicals were obtained commercially and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker ASCEND III–400 or a Bruker ASCEND III–500 spectrometer at room temperature. <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts were determined relative to TMS. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. Compounds **2a–f**, **2h** and **2i** are known compounds, and their <sup>1</sup>H NMR data are consistent with those reported in the literature.<sup>2</sup> High resolution mass spectra were obtained on a Bruker UltraflexXtreme MALDI-TOF/TOF instrument. UV-vis spectra were obtained on a SHIMADZU UV-3600PLUS instrument. IR spectra were obtained on a Thermo Scientific Nicolet 6700 instrument. All electrochemical reactions, CV and DPV measurements were performed under an argon atmosphere using a Shanghai Chenhua CHI630D workstation.

## 2. Synthesis and Spectral Data of Compounds **2a–i**

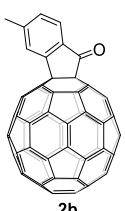
**General Procedure:** A dry 25 mL tube equipped with a magnetic stirrer was charged with **1** (0.015 mmol) and triflic anhydride ( $\text{Tf}_2\text{O}$ ) (0.045–0.150 mmol), which were dissolved in anhydrous 1,2-dichlorobenzene (1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>) (3 mL) under an air atmosphere. Then, the tube was sealed tightly and stirred in an oil bath at 120 °C for 10 h. The resulting mixture was filtered through a silica gel (200–300 mesh) plug with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) to remove insoluble materials. After the solvent had been evaporated in *vacuo*, the residue was separated on a silica gel column (300–400 mesh) with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (4:1 v/v) as the eluent to give product **2**.

### 2.1. Synthesis of **2a**



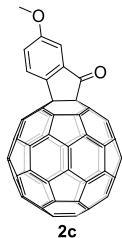
By following the general procedure, the reaction of **1a** (12.8 mg, 0.015 mmol) and Tf<sub>2</sub>O (7.5 μL, 0.045 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2a** (10.9 mg, 87%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.37 (d,  $J$  = 7.9 Hz, 1H), 8.21 (s, 1H), 7.87 (dd,  $J$  = 7.9, 1.1 Hz, 1H), 2.72 (s, 3H).

### 2.2. Synthesis of **2b**



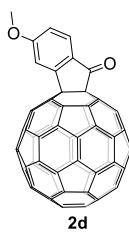
By following the general procedure, the reaction of **1b** (12.8 mg, 0.015 mmol) and Tf<sub>2</sub>O (7.5  $\mu$ L, 0.045 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2b** (11.2 mg, 89%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.32 (d, *J* = 8.1 Hz, 1H), 8.30 (s, 1H), 7.66 (dd, *J* = 7.9, 0.6 Hz, 1H), 2.72 (s, 3H).

### 2.3. Synthesis of **2c**



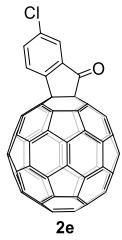
By following the general procedure, the reaction of **1c** (13.1 mg, 0.015 mmol) and Tf<sub>2</sub>O (12.5  $\mu$ L, 0.075 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2c** (11.3 mg, 88%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.34 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 2.6 Hz, 1H), 7.61 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.09 (s, 3H).

### 2.4. Synthesis of **2d**



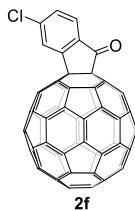
By following the general procedure, the reaction of **1d** (13.1 mg, 0.015 mmol) and Tf<sub>2</sub>O (12.5  $\mu$ L, 0.075 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2d** (11.1 mg, 86%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.31 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.2 Hz, 1H), 4.08 (s, 3H).

### 2.5. Synthesis of **2e**



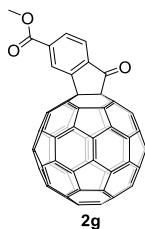
By following the general procedure, the reaction of **1e** (13.1 mg, 0.015 mmol) and Tf<sub>2</sub>O (25.0  $\mu$ L, 0.150 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2e** (10.5 mg, 81%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.43 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 2.0 Hz, 1H), 7.99 (dd, *J* = 8.2, 2.0 Hz, 1H).

### 2.6. Synthesis of **2f**



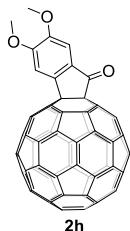
By following the general procedure, the reaction of **1f** (13.1 mg, 0.015 mmol) and Tf<sub>2</sub>O (25.0  $\mu$ L, 0.150 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2f** (10.6 mg, 82%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.47 (d, *J* = 1.7 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 7.81 (dd, *J* = 8.2, 1.7 Hz, 1H).

## 2.7. Synthesis of **2g**



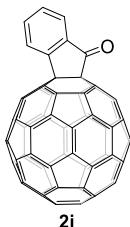
By following the general procedure, the reaction of **1g** (13.4 mg, 0.015 mmol) and Tf<sub>2</sub>O (12.5  $\mu$ L, 0.075 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2g** (10.5 mg, 80%): amorphous brown solid; <sup>1</sup>H NMR (500 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  9.11 (s, 1H), 8.50 (d, *J* = 7.9 Hz, 1H), 8.49 (d, *J* = 7.9 Hz, 1H), 4.04 (s, 3H); <sup>13</sup>C NMR (126 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) (all 2C unless indicated)  $\delta$  198.30 (*C=O*), 165.15 (*C=O*), 156.36, 153.39, 152.78, 147.38 (1C), 147.35, 147.14 (1C), 146.36 (4C), 146.10, 146.06, 145.71, 145.61, 145.54, 145.47, 145.37, 145.34, 144.55, 144.23, 143.08, 142.73, 142.67, 142.35, 142.08, 142.03, 142.00, 141.91, 141.57, 140.59, 140.56, 137.91 (1C, aryl C), 137.52 (1C, aryl C), 135.51 (1C, aryl C), 135.43, 131.11 (1C, aryl C), 128.00 (1C, aryl C), 127.17 (1C, aryl C), 78.74 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 70.62 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 52.75 (1C); FT-IR  $\nu$ /cm<sup>-1</sup> (KBr) 1727, 1608, 1588, 1513, 1433, 1414, 1285, 1214, 1137, 1100, 1079, 1013, 987, 850, 833, 800, 765, 728, 687, 553, 527; UV-vis (CHCl<sub>3</sub>)  $\lambda_{\max}$ /nm (log  $\epsilon$ ) 258 (5.06), 310 (4.55), 430 (3.54), 697 (2.52); MALDI-TOF MS *m/z* calcd for C<sub>69</sub>H<sub>6</sub>O<sub>3</sub> [M]<sup>+</sup> 882.0322, found 882.0316.

## 2.8. Synthesis of **2h**



By following the general procedure, the reaction of **1h** (13.5 mg, 0.015 mmol) and Tf<sub>2</sub>O (12.5  $\mu$ L, 0.075 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 3 h afforded **2h** (10.9 mg, 82%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  7.80 (s, 1H), 7.75 (s, 1H), 4.15 (s, 3H), 4.14 (s, 3H).

## 2.9. Synthesis of **2i**

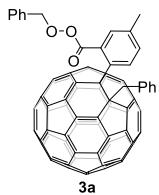


By following the general procedure, the reaction of **1i** (12.6 mg, 0.015 mmol) and Tf<sub>2</sub>O (7.5  $\mu$ L, 0.045 mmol) in 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (3 mL) at 120 °C for 10 h afforded **2i** (11.1 mg, 90%): amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 7.8 Hz, 1H), 8.42 (d, *J* = 7.7 Hz, 1H), 8.06 (td, *J* = 7.5, 1.2 Hz, 1H), 7.85 (td, *J* = 7.5, 0.8 Hz, 1H).

## 3. Synthesis and Spectral Data of Compounds **3a–5a**

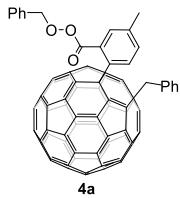
### 3.1. Synthesis of **3a** and **4a**

Compound **2a** (12.6 mg, 0.015 mmol) was electroreduced by controlled potential electrolysis (CPE) at -1.30 V vs. saturated calomel electrode (SCE) in 15 mL of 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> containing 0.1 M TBAP under an argon atmosphere at room temperature. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of **2a** to **2a**<sup>2-</sup> was reached. Then, the dianionic **2a**<sup>2-</sup> was allowed to react with benzyl bromide (PhCH<sub>2</sub>Br) (134.1  $\mu$ L, 1.125 mmol) and sodium hydride (NaH) (57–63% oil dispersion, 31.2 mg, 0.75 mmol). After being stirred at 50 °C for 6 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in *vacuo* to remove the solvent. Next, the residue was further separated on a silica gel column (300–400 mesh) with CS<sub>2</sub> as the eluent to afford product **3a** (5.0 mg, 29%) and product **4a** (4.4 mg, 25%) as amorphous brown solids.



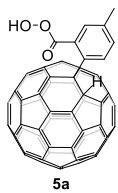
**Compound 3a:** <sup>1</sup>H NMR (500 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.60 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.40–7.24 (m, 7H), 7.15–7.06 (m, 3H), 5.47 (d, *J* = 12.3 Hz, 1H), 5.43 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.04 (d, *J* = 12.3 Hz, 1H), 2.55 (s, 3H); <sup>13</sup>C NMR (126 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) (all 1C unless indicated)  $\delta$  170.07 (*C=O*), 157.04, 156.68, 154.94, 153.16, 147.85, 147.64, 147.20, 146.73, 146.58 (2C), 146.56, 146.52, 146.39, 146.32, 146.25, 146.19, 146.03, 146.00, 145.88, 145.63, 145.62, 145.55 (2C), 145.47, 145.36, 145.31, 145.28, 145.03, 144.77 (2C), 144.58, 144.26, 143.38, 143.26, 142.74, 142.69, 142.67 (2C), 142.41, 142.30, 142.28 (2C), 142.08, 142.04, 141.57, 141.53, 141.44, 141.39, 141.23, 140.46, 139.77, 139.57, 138.96, 138.72, 138.50, 138.38 (aryl C), 137.84 (aryl C), 137.01 (aryl C), 136.67,

135.23 (aryl C), 135.06 (aryl C), 134.68, 134.11 (aryl C), 133.84, 132.05 (2C, aryl C), 131.36 (aryl C), 130.43 (aryl C), 128.87 (2C, aryl C), 128.69 (2C, aryl C), 128.61 (aryl C), 127.92 (2C, aryl C), 126.88 (aryl C), 71.52 ( $\text{sp}^3$ -C of C<sub>60</sub>), 67.98, 67.36 ( $\text{sp}^3$ -C of C<sub>60</sub>), 49.12, 21.18; FT-IR  $\nu/\text{cm}^{-1}$  (KBr) 1718, 1492, 1450, 1290, 1251, 1203, 1147, 1090, 1063, 817, 748, 733, 695, 576, 525; UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm}$  (log  $\varepsilon$ ) 258 (5.08), 314 (4.67), 436 (3.61), 705 (2.70); MALDI-TOF MS  $m/z$  calcd for C<sub>82</sub>H<sub>20</sub>O<sub>3</sub> [M]<sup>+</sup> 1152.1418, found 1152.1416.



**Compound 4a:** <sup>1</sup>H NMR (500 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.50 (d,  $J$  = 8.1 Hz, 1H), 7.52 (dd,  $J$  = 8.1, 1.3 Hz, 1H), 7.42 (d,  $J$  = 7.1 Hz, 2H), 7.37–7.27 (m, 7H), 7.23–7.16 (m, 2H), 5.26 (d,  $J$  = 12.4 Hz, 1H), 5.18 (d,  $J$  = 12.4 Hz, 1H), 4.17 (d,  $J$  = 13.0 Hz, 1H), 4.02 (d,  $J$  = 13.0 Hz, 1H), 2.53 (s, 3H); <sup>13</sup>C NMR (126 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) (all 1C unless indicated)  $\delta$  169.38 (C=O), 156.21, 155.93, 151.09, 149.91, 148.89, 148.60, 148.43, 148.02, 147.36, 147.02 (2C), 147.01, 146.95, 146.90, 146.81 (2C), 146.76, 146.73, 145.45, 145.39, 145.18, 145.07, 144.99, 144.85, 144.56, 144.40, 144.37, 144.29, 144.23 (3C), 144.20, 144.01 (2C), 143.82, 143.71, 143.64, 143.61, 143.39, 143.20, 143.13, 143.06, 143.01, 142.92, 142.76, 142.66, 142.63, 142.52, 142.37 (2C), 142.17, 141.97, 141.89, 141.57, 140.69, 139.19, 138.57, 138.30, 137.98 (aryl C), 137.73, 135.37 (aryl C), 135.05 (aryl C), 134.08 (aryl C), 133.39 (aryl C), 131.30 (aryl C), 130.55 (2C, aryl C), 129.63 (aryl C), 129.49 (aryl C), 128.58 (2C, aryl C), 128.32 (aryl C), 128.30 (2C, aryl C), 128.18 (2C, aryl C), 127.08 (aryl C), 67.45, 60.24 ( $\text{sp}^3$ -C of C<sub>60</sub>), 60.07 ( $\text{sp}^3$ -C of C<sub>60</sub>), 47.76, 20.99; FT-IR  $\nu/\text{cm}^{-1}$  (KBr) 1717, 1491, 1453, 1292, 1253, 1206, 1143, 1063, 819, 747, 729, 697, 578, 524; UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm}$  (log  $\varepsilon$ ) 258 (5.05), 330 (4.54), 445 (3.81), 690 (2.48); MALDI-TOF MS  $m/z$  calcd for C<sub>82</sub>H<sub>20</sub>O<sub>3</sub> [M]<sup>+</sup> 1152.1418, found 1152.1412.

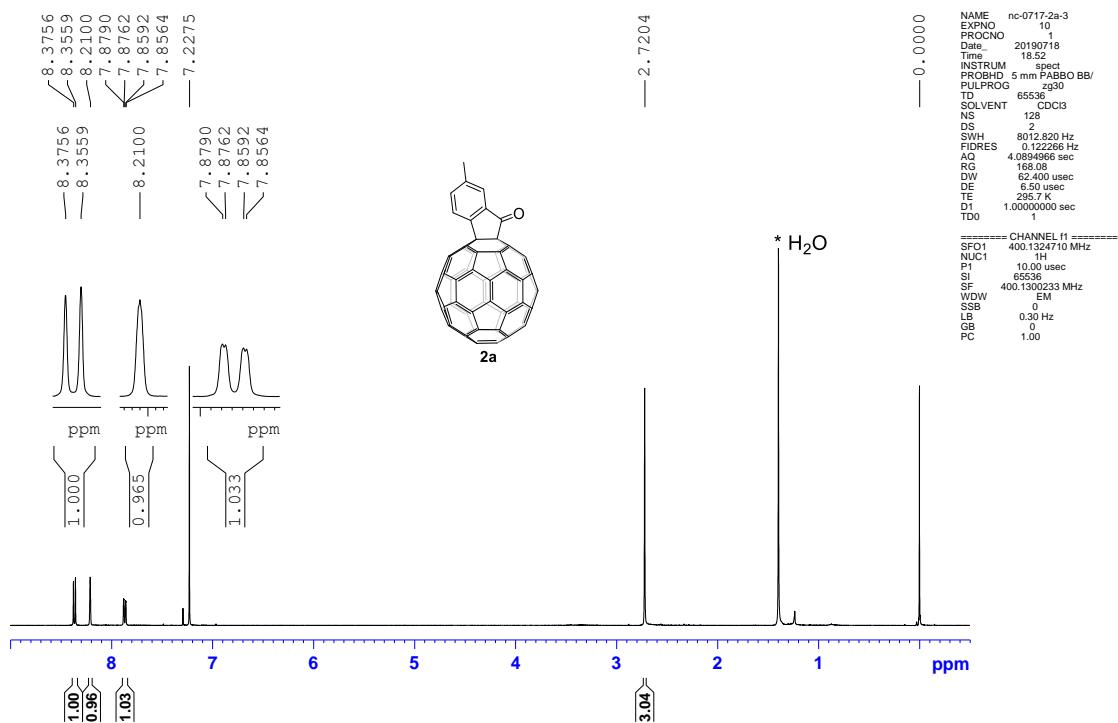
### 3.2. Synthesis of 5a



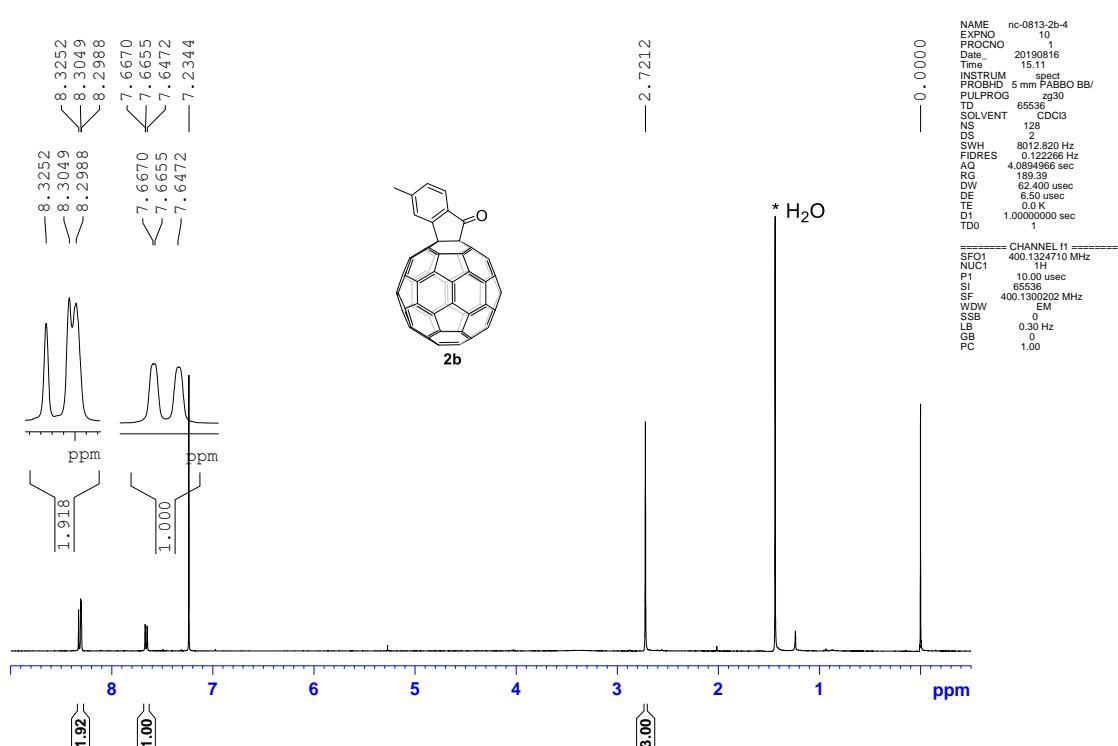
Compound **2a** (16.8 mg, 0.020 mmol) was electroreduced by CPE at -1.30 V vs. SCE in 15 mL of 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> containing 0.1 M TBAP under an argon atmosphere at room temperature. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of **2a** to **2a**<sup>2-</sup> was reached. Then, the dianionic **2a**<sup>2-</sup> was allowed to react with trifluoroacetic acid (TFA) (4.5  $\mu$ L, 0.060 mmol). After being stirred at 25 °C for 0.5 h, the resulting mixture was directly filtered through a neutral silica gel (200–300 mesh, pH: 6.5~7.5) plug with CS<sub>2</sub>/ethyl acetate (5:1 v/v) to

remove the supporting electrolyte and insoluble materials, and then evaporated in *vacuo* to remove the solvent. Next, the residue was further separated on a neutral silica gel column (200–300 mesh, pH: 6.5~7.5) with CS<sub>2</sub>/ethyl acetate (5:1 v/v) as the eluent to afford product **5a** (9.3 mg, 53%) as amorphous brown solid; <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.64 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.90 (s, 1H), 2.57 (s, 3H); <sup>13</sup>C NMR (126 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) (all 2C unless indicated)  $\delta$  174.30 (1C, C=O), 153.00 (4C), 147.44 (1C), 147.06 (1C), 146.85, 146.28, 146.21, 146.02 (6C), 145.67, 145.48, 145.31, 145.26, 145.20, 144.70, 144.34, 143.20, 142.46 (4C), 141.97, 141.95, 141.92, 141.83, 141.54, 141.41, 140.91, 140.07, 139.69, 138.10, 136.70 (1C, aryl C), 132.83 (1C, aryl C), 131.93 (1C, aryl C), 131.68 (1C, aryl C), 131.43 (1C, aryl C), 127.53 (1C, aryl C), 67.26 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 61.83 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 20.96 (1C); FT-IR  $\nu/\text{cm}^{-1}$  (KBr) 1698, 1512, 1461, 1425, 1258, 1215, 1038, 886, 834, 819, 769, 642, 585, 525; UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ) 255 (4.98), 330 (4.49), 430 (3.58), 704 (2.30); MALDI-TOF MS *m/z* calcd for C<sub>68</sub>H<sub>8</sub>O<sub>3</sub> [M]<sup>+</sup> 872.0479, found 872.0470.

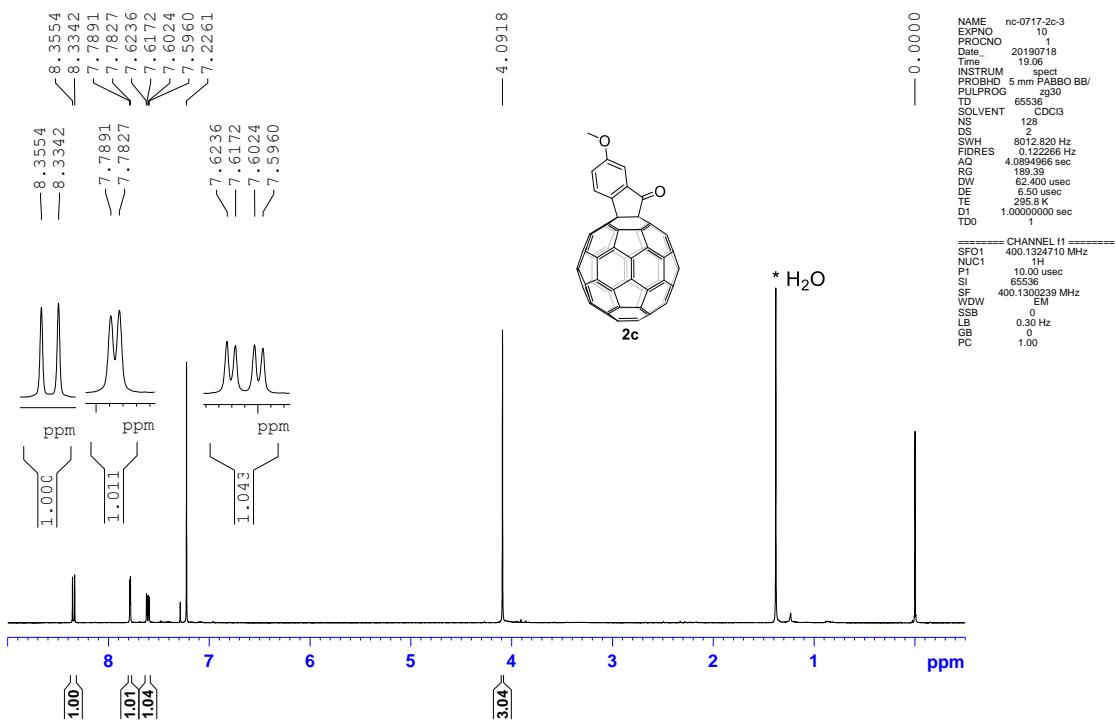
#### 4. NMR Spectra of Compounds 2a–i and 3a–5a



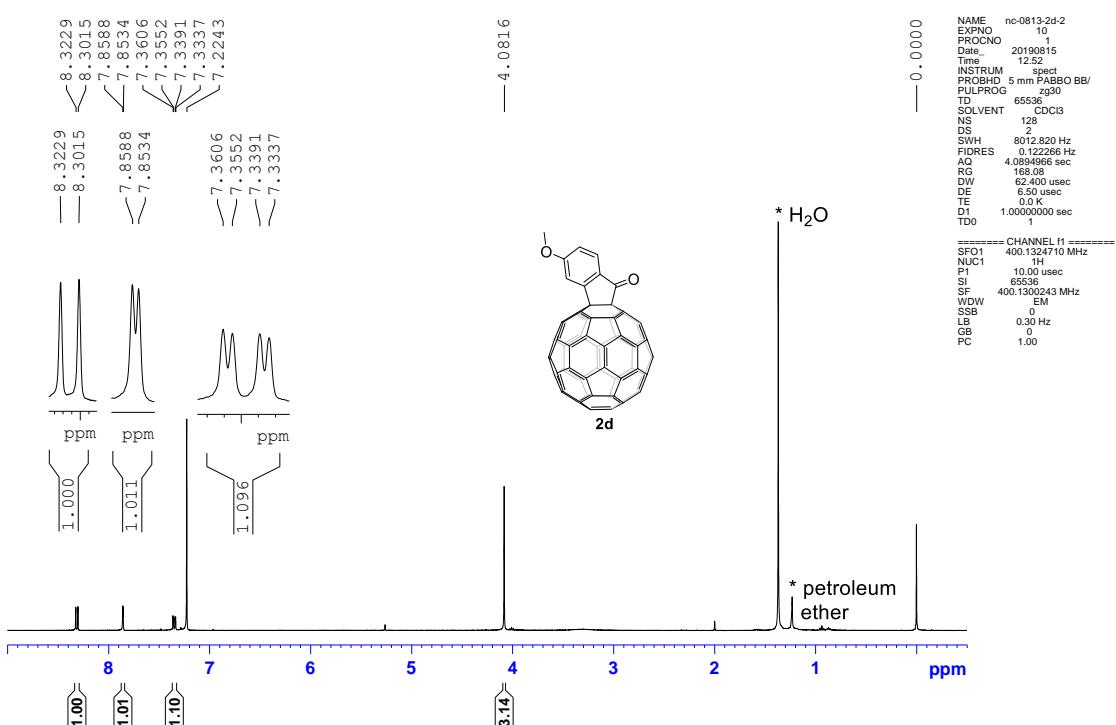
**Figure S1.**  $^1\text{H}$  NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2a**.



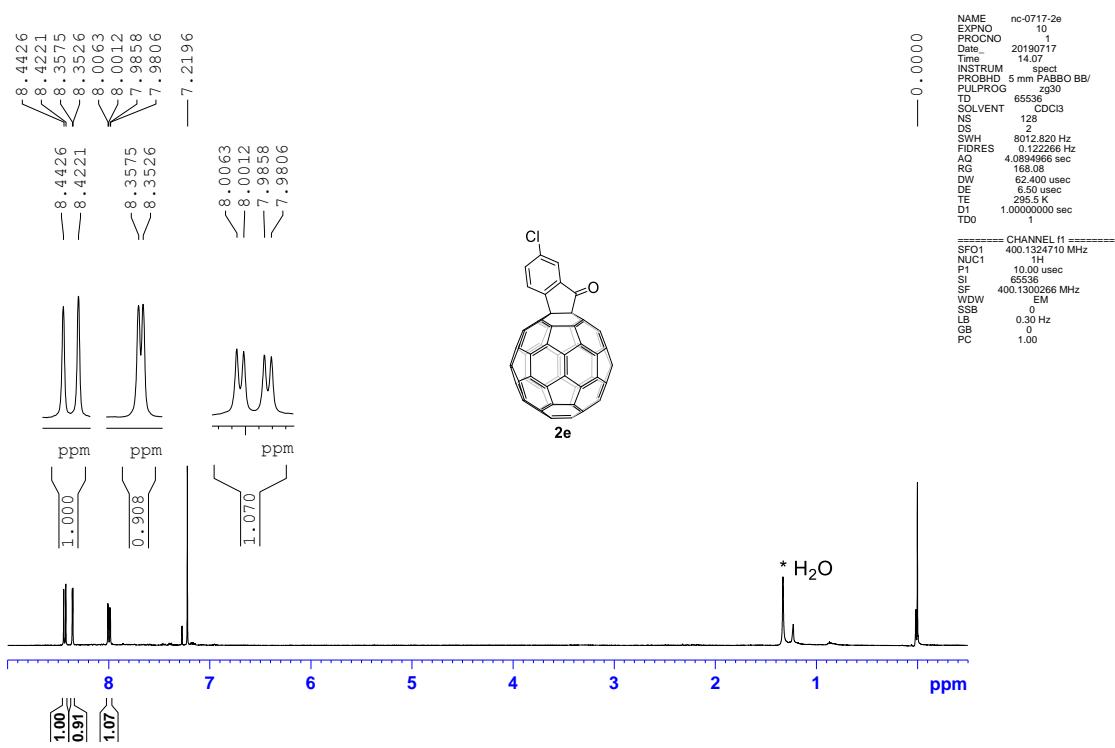
**Figure S2.**  $^1\text{H}$  NMR (400 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **2b**.



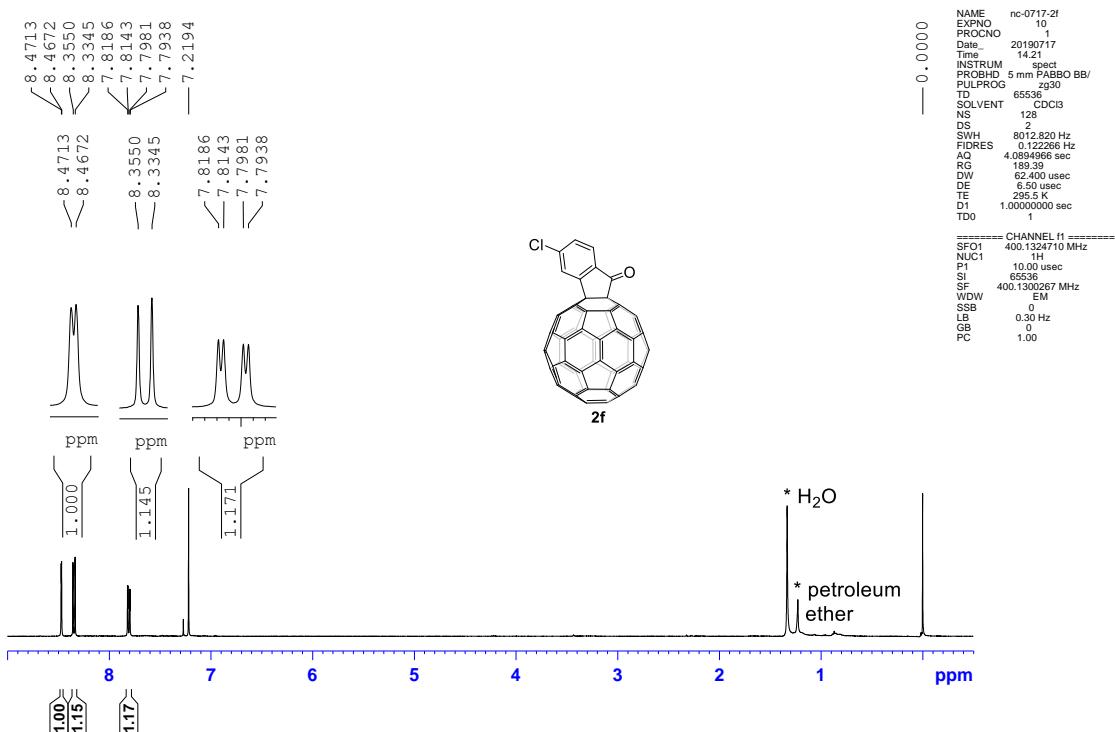
**Figure S3.** <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2c**.



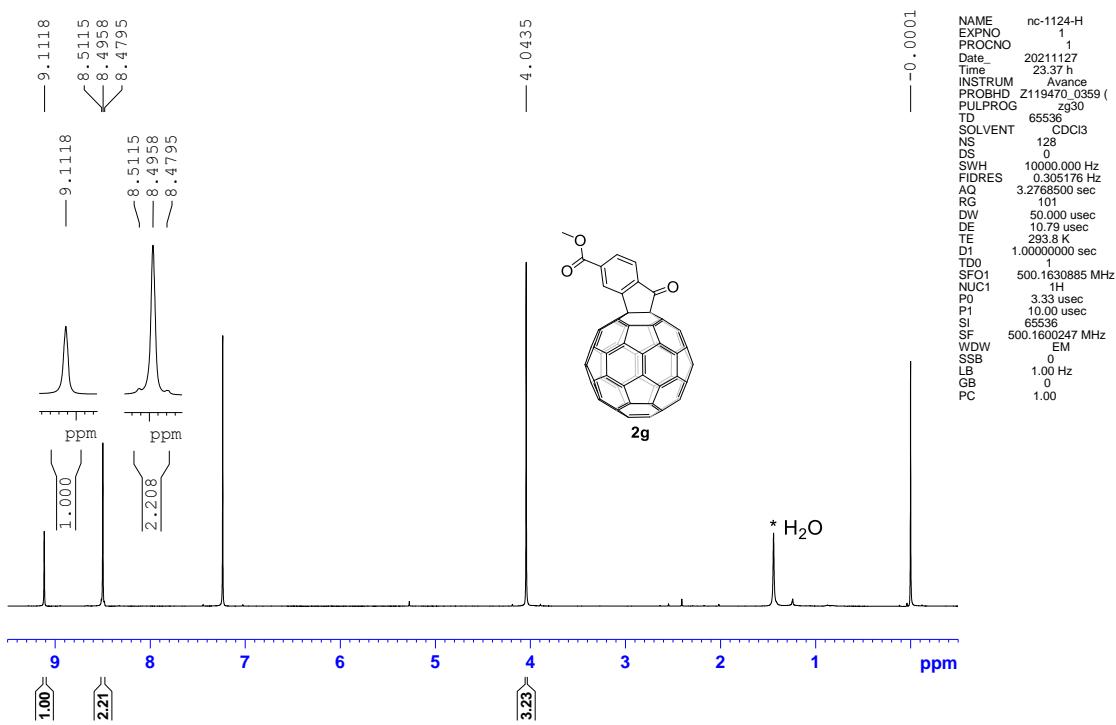
**Figure S4.** <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2d**.



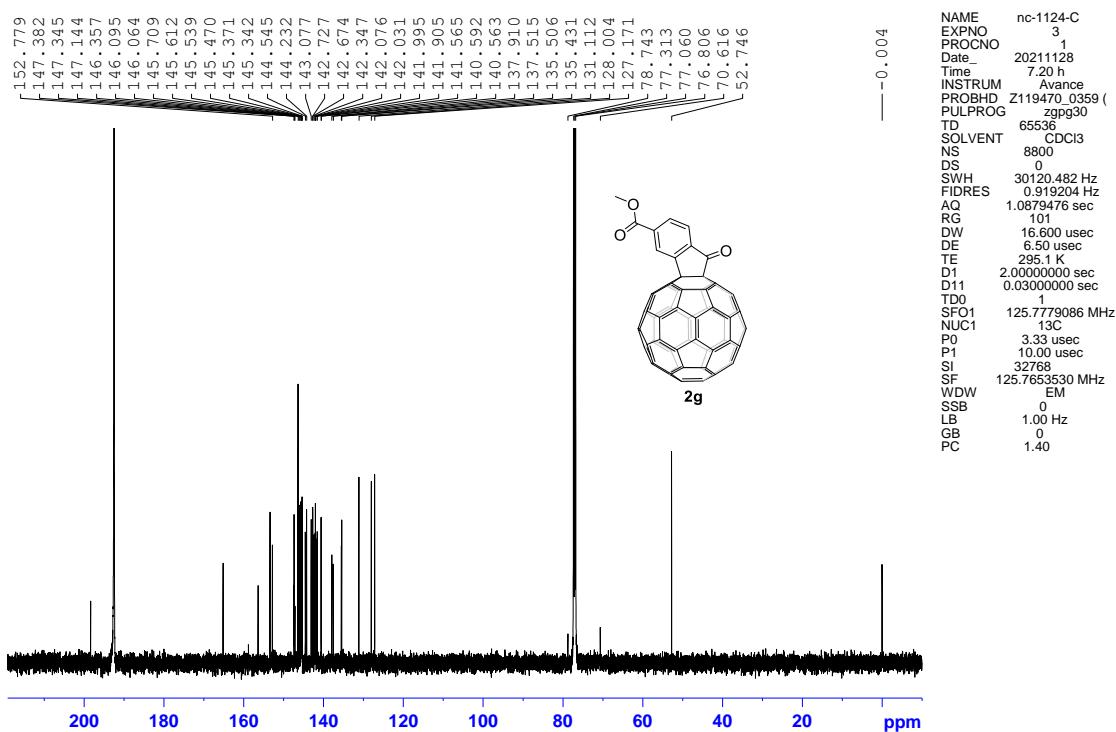
**Figure S5.** <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2e**.



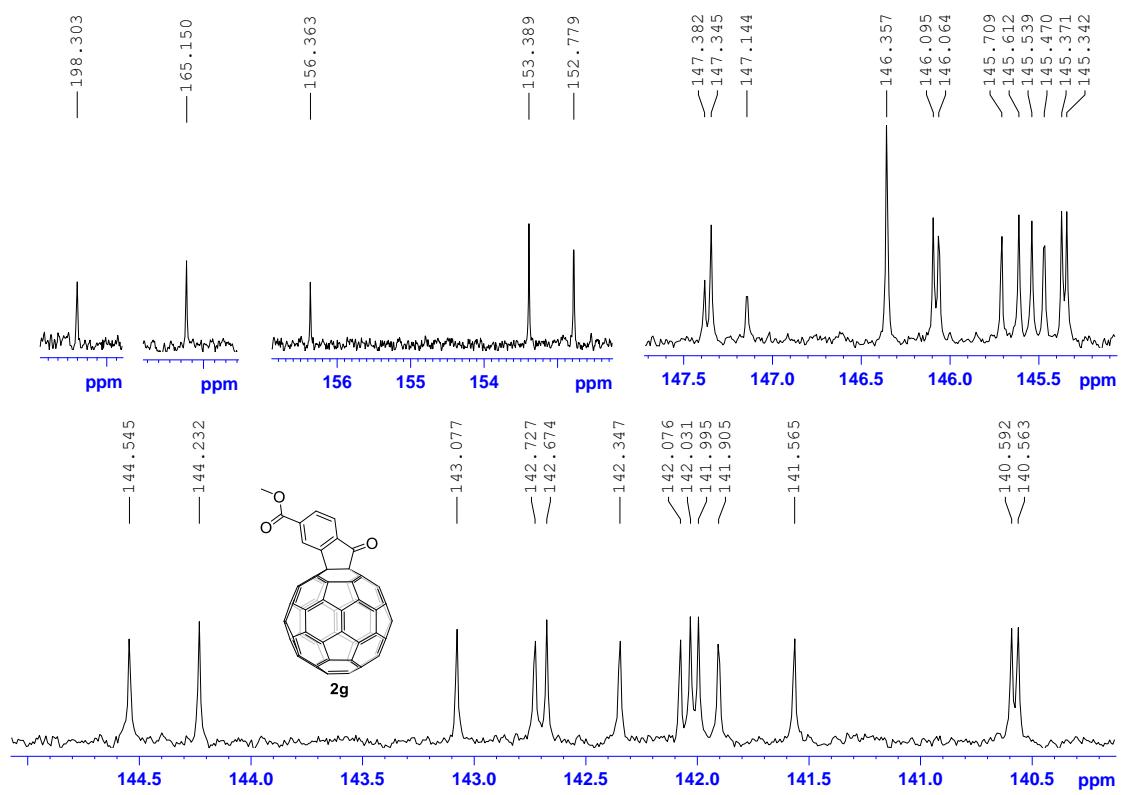
**Figure S6.** <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2f**.



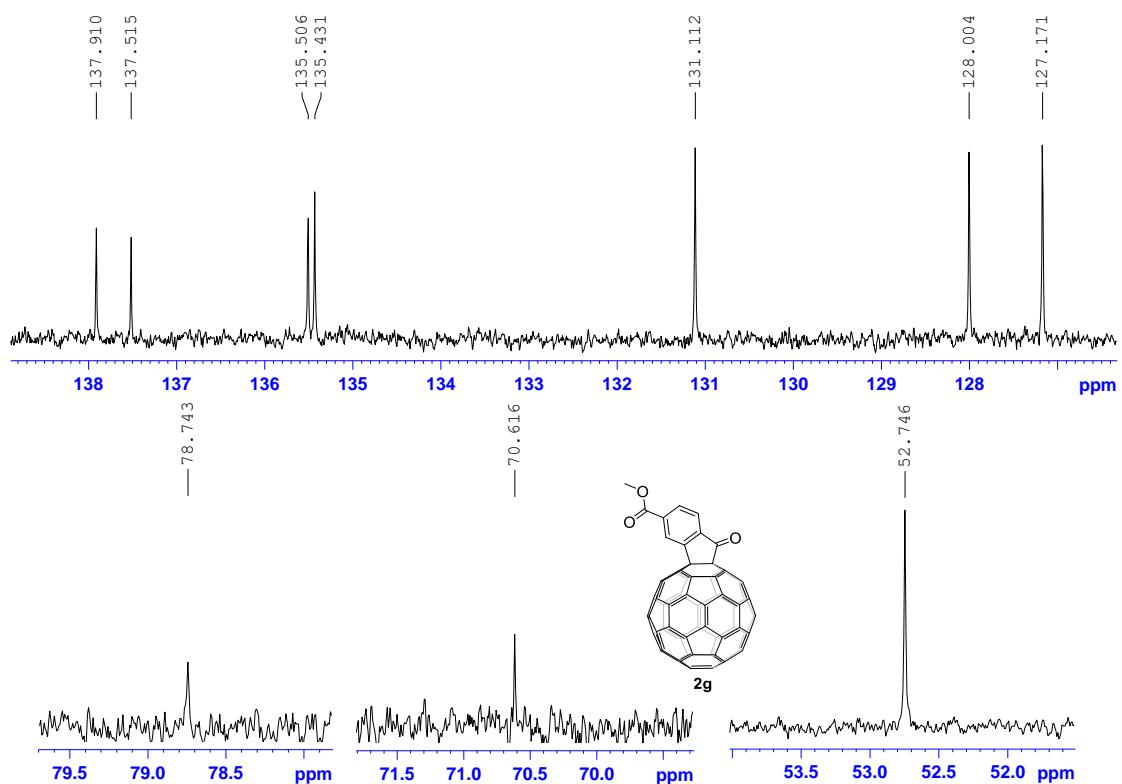
**Figure S7.** <sup>1</sup>H NMR (500 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2g**.



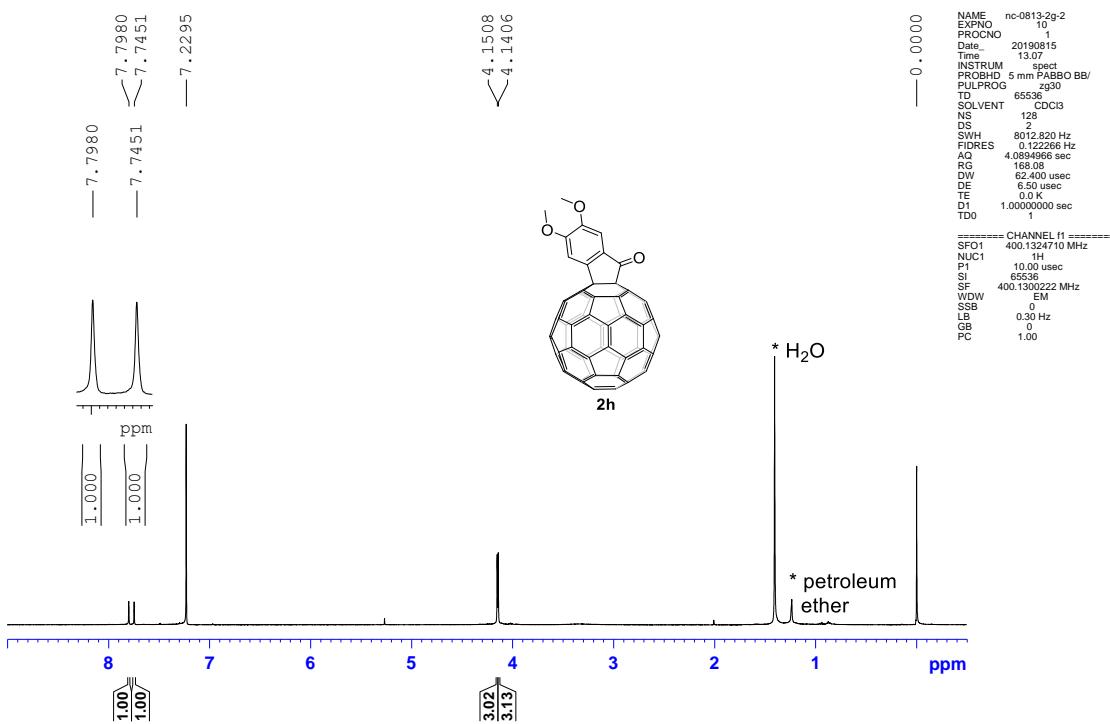
**Figure S8.** <sup>13</sup>C NMR (126 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2g**.



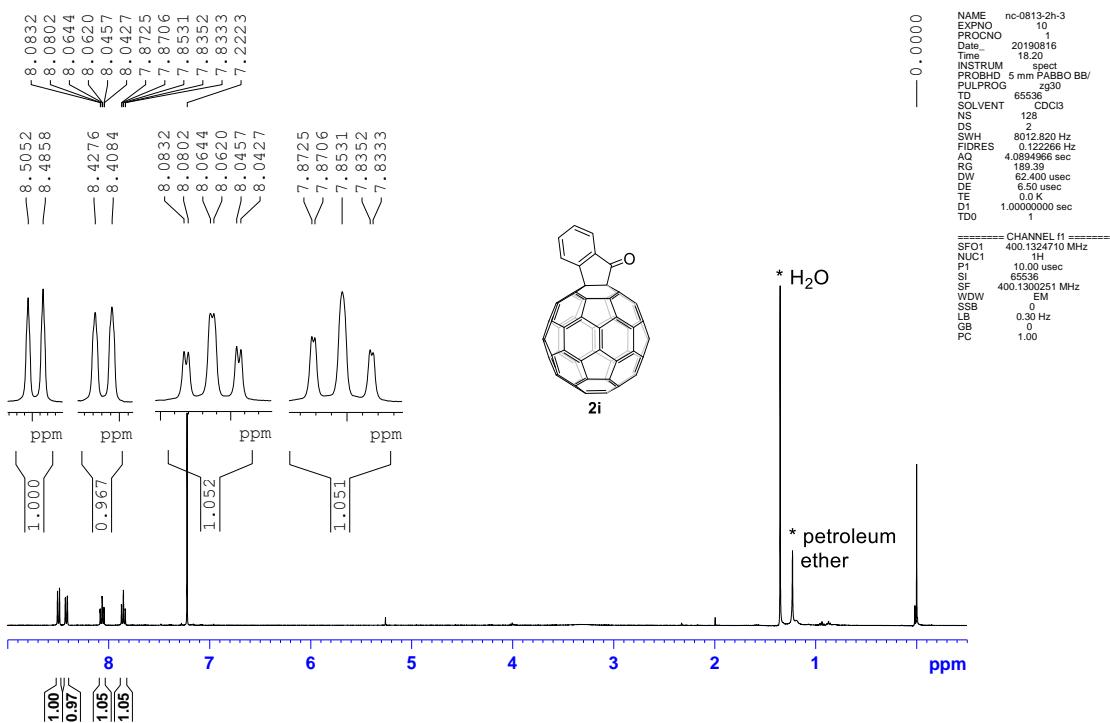
**Figure S9.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **2g**.



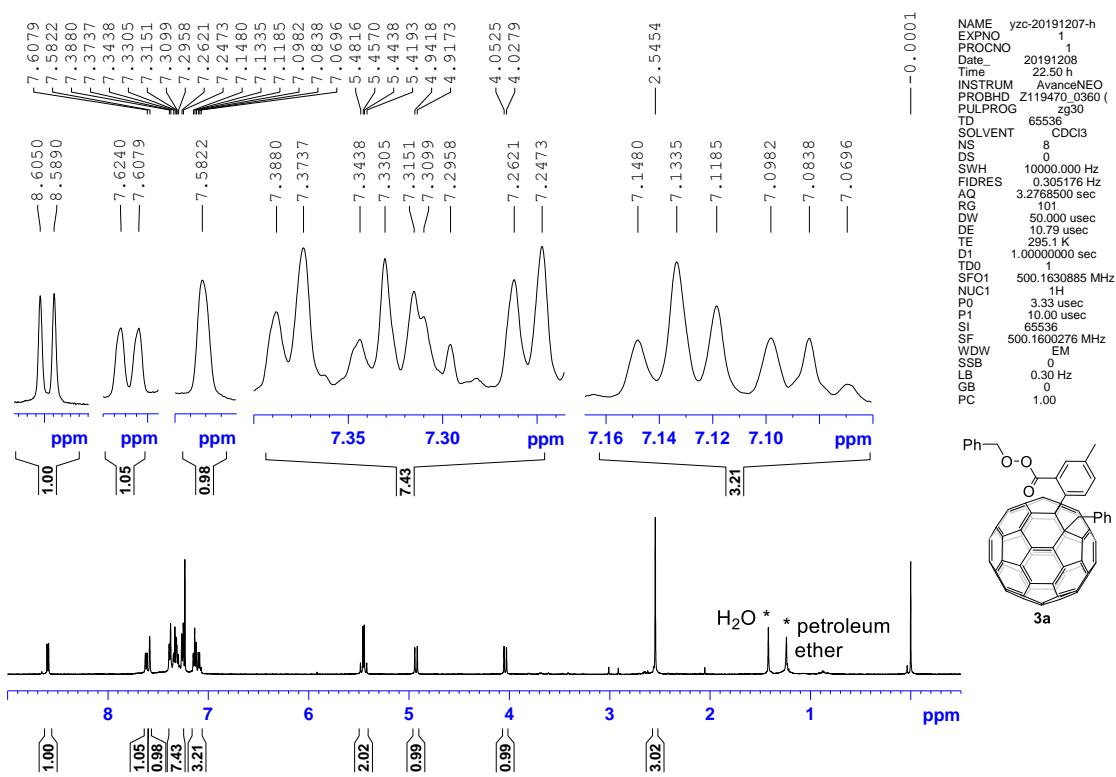
**Figure S10.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **2g**.



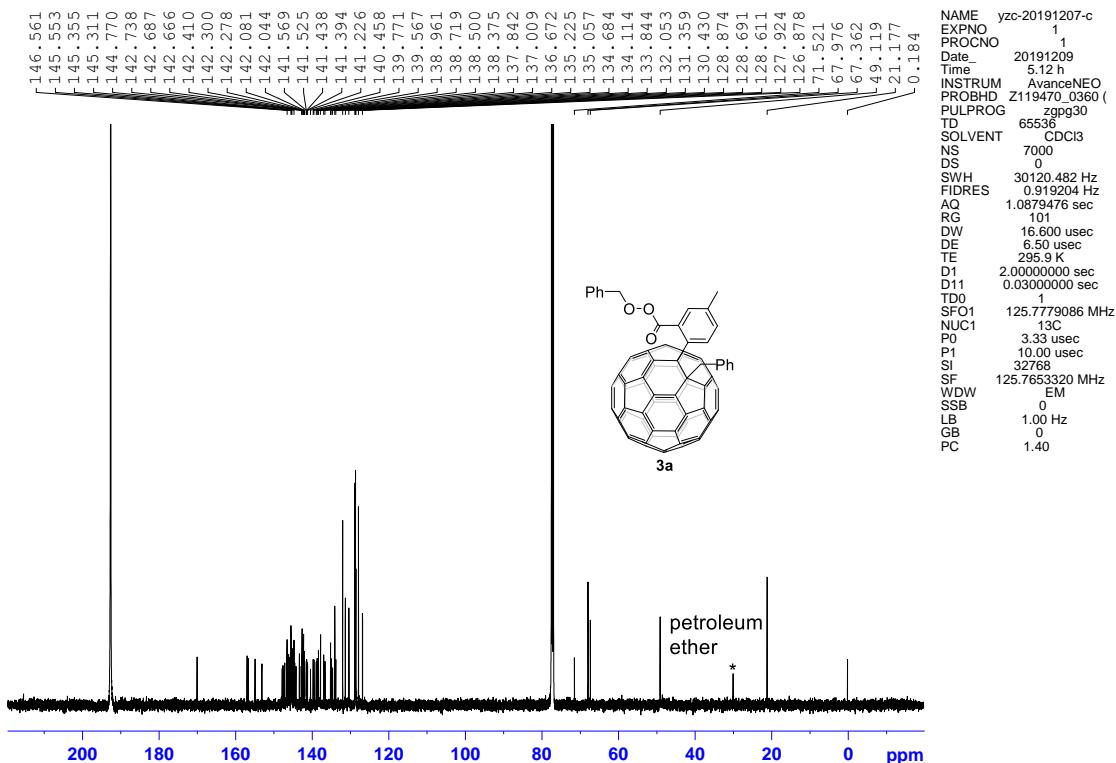
**Figure S11.** <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2h**.



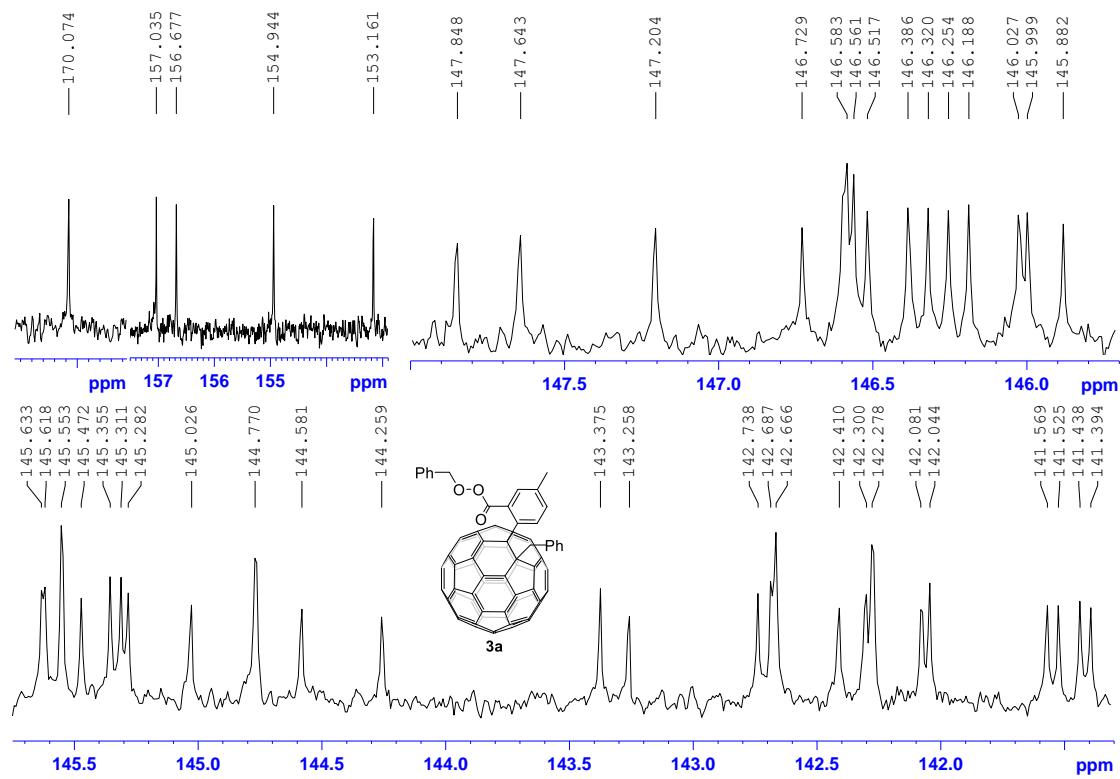
**Figure S12.** <sup>1</sup>H NMR (400 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **2i**.



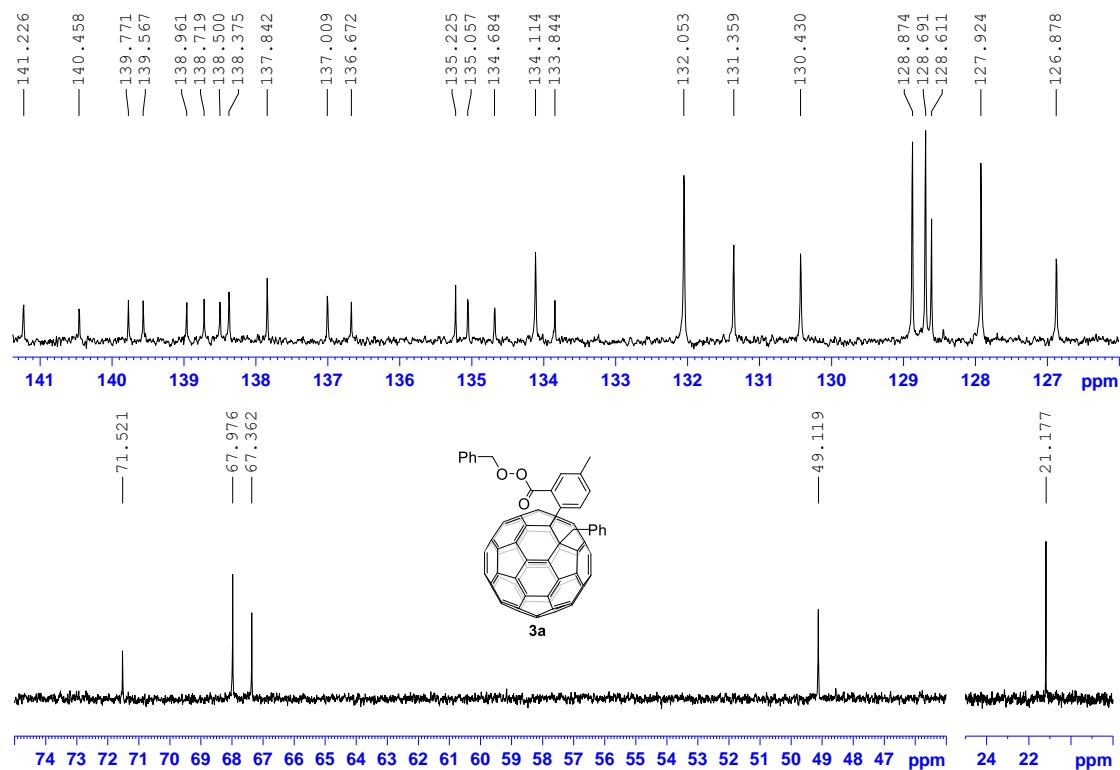
**Figure S13.** <sup>1</sup>H NMR (500 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **3a**.



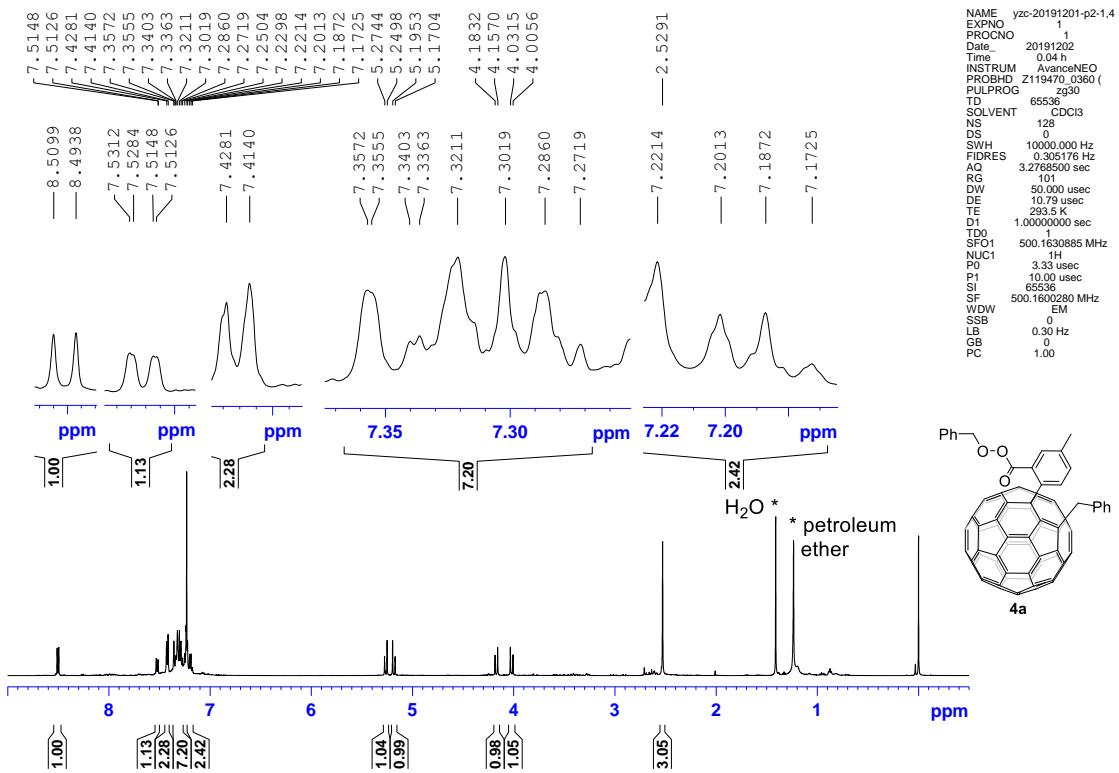
**Figure S14.** <sup>13</sup>C NMR (126 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **3a**.



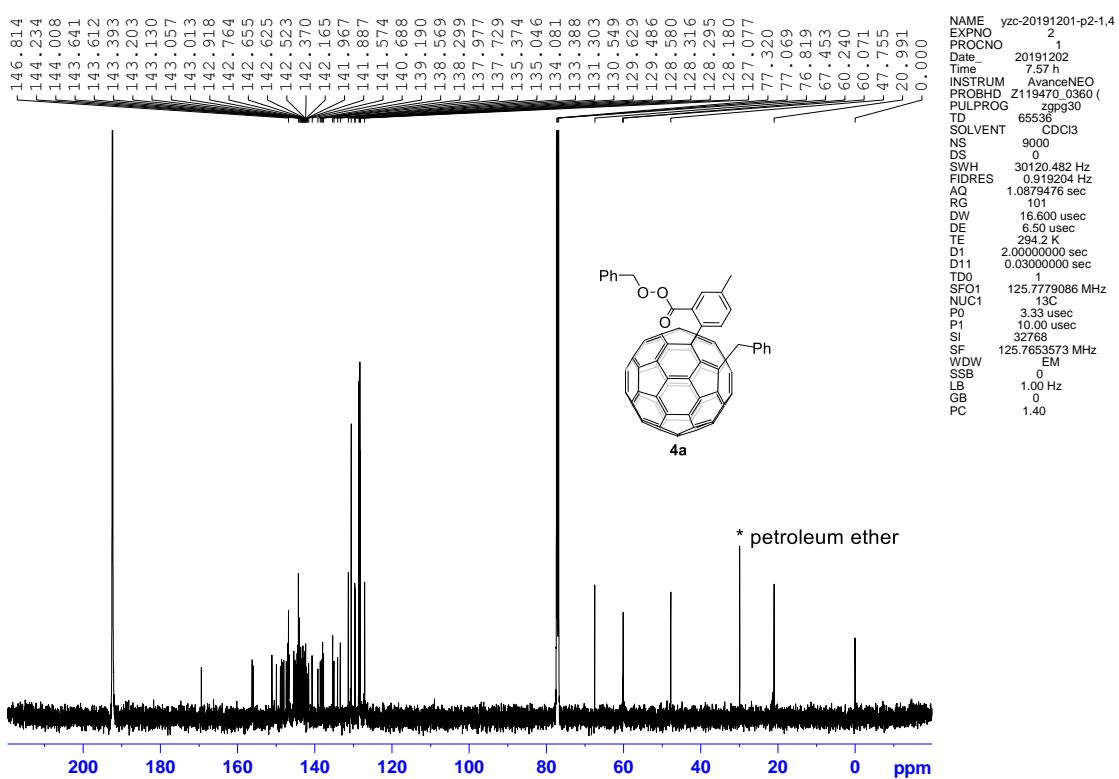
**Figure S15.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **3a**.



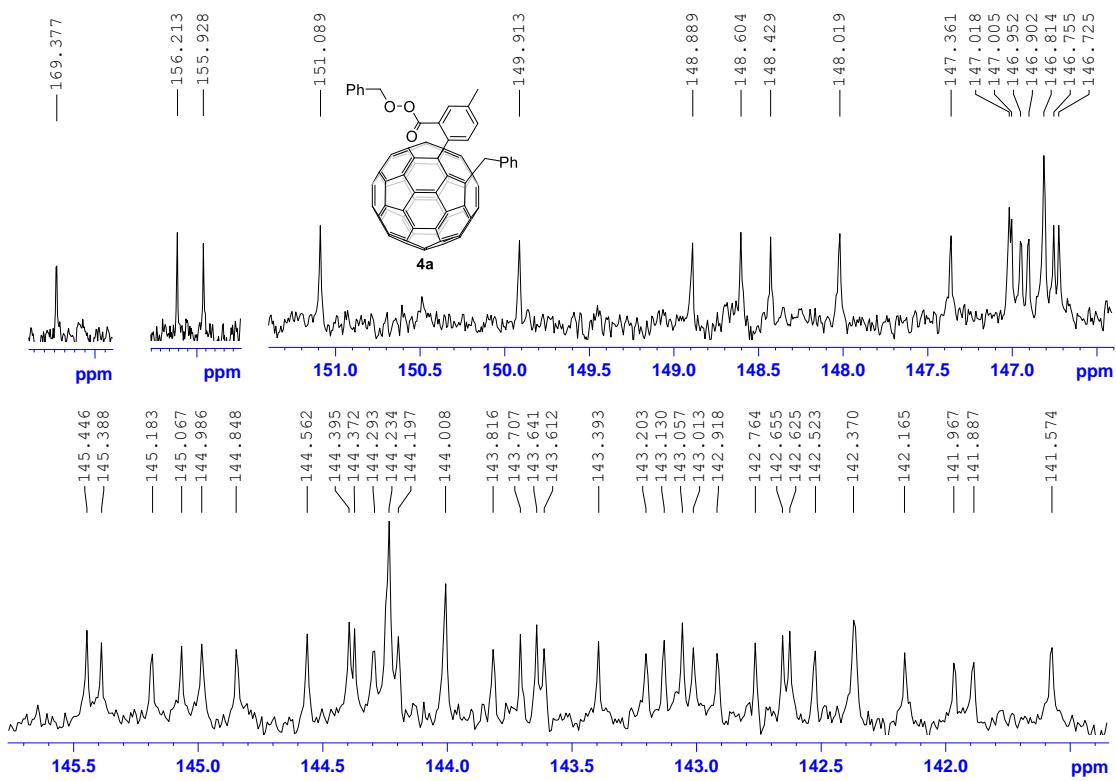
**Figure S16.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **3a**.



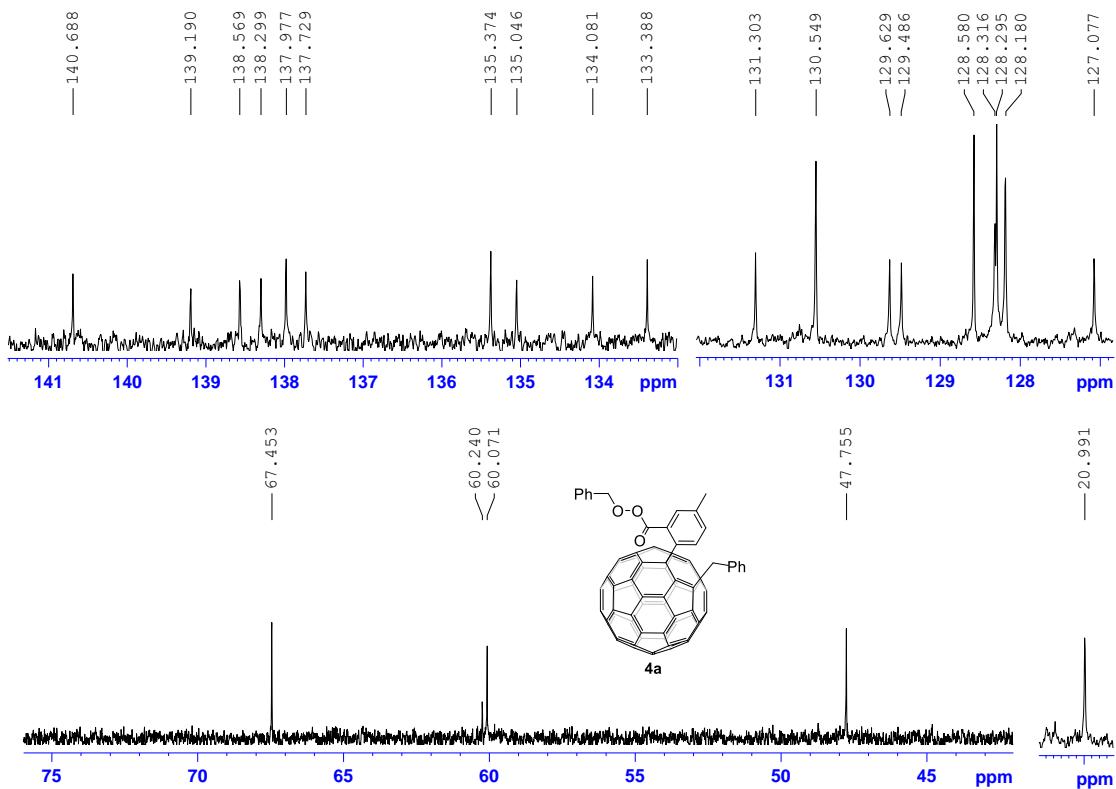
**Figure S17.**  $^1\text{H}$  NMR (500 MHz, 1:1 CS<sub>2</sub>/CDCl<sub>3</sub>) of compound **4a**.



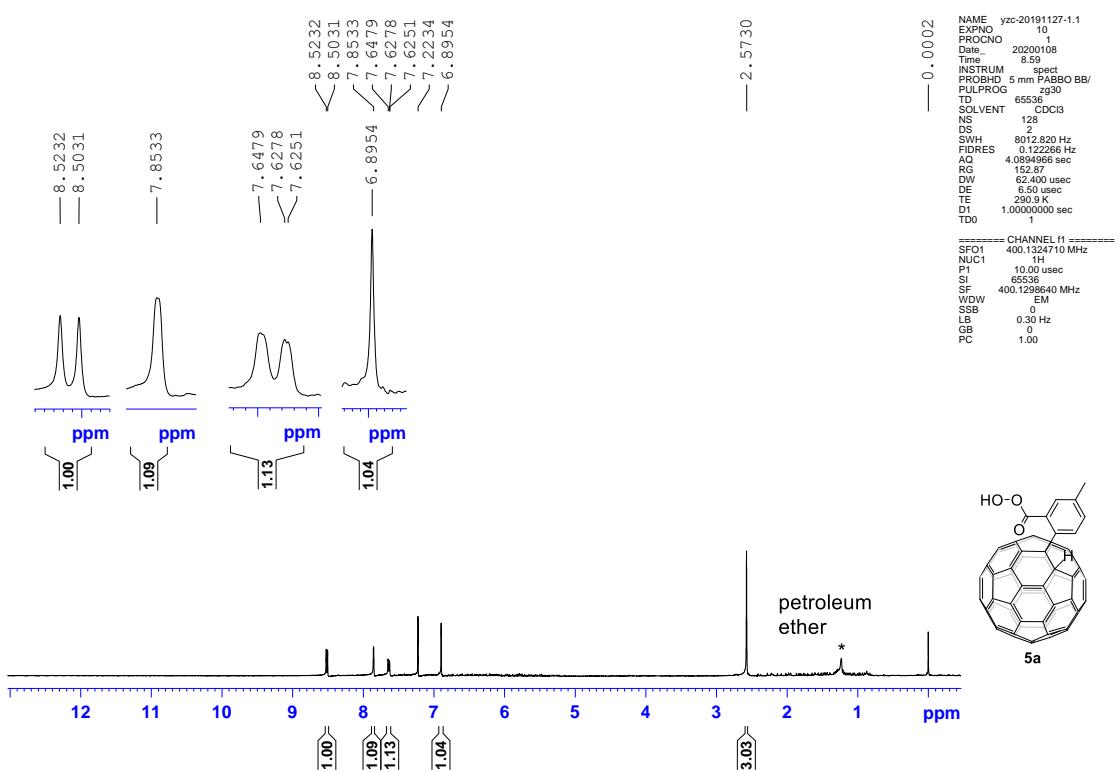
**Figure S18.**  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **4a**.



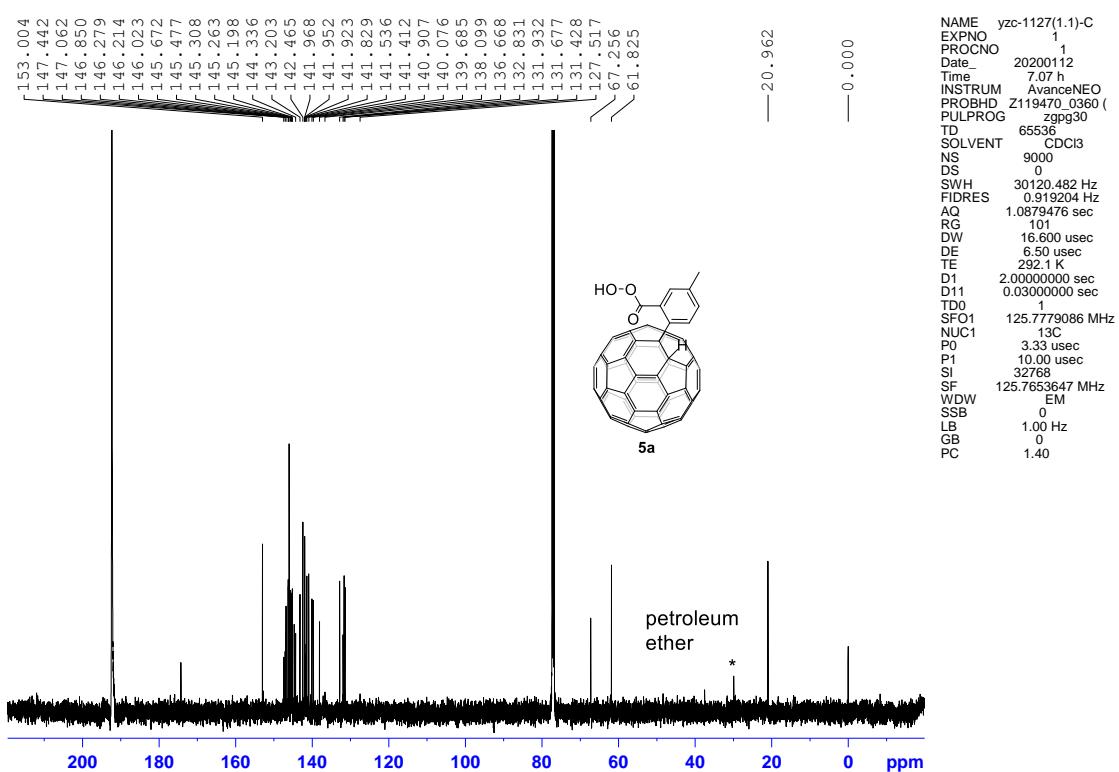
**Figure S19.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **4a**.



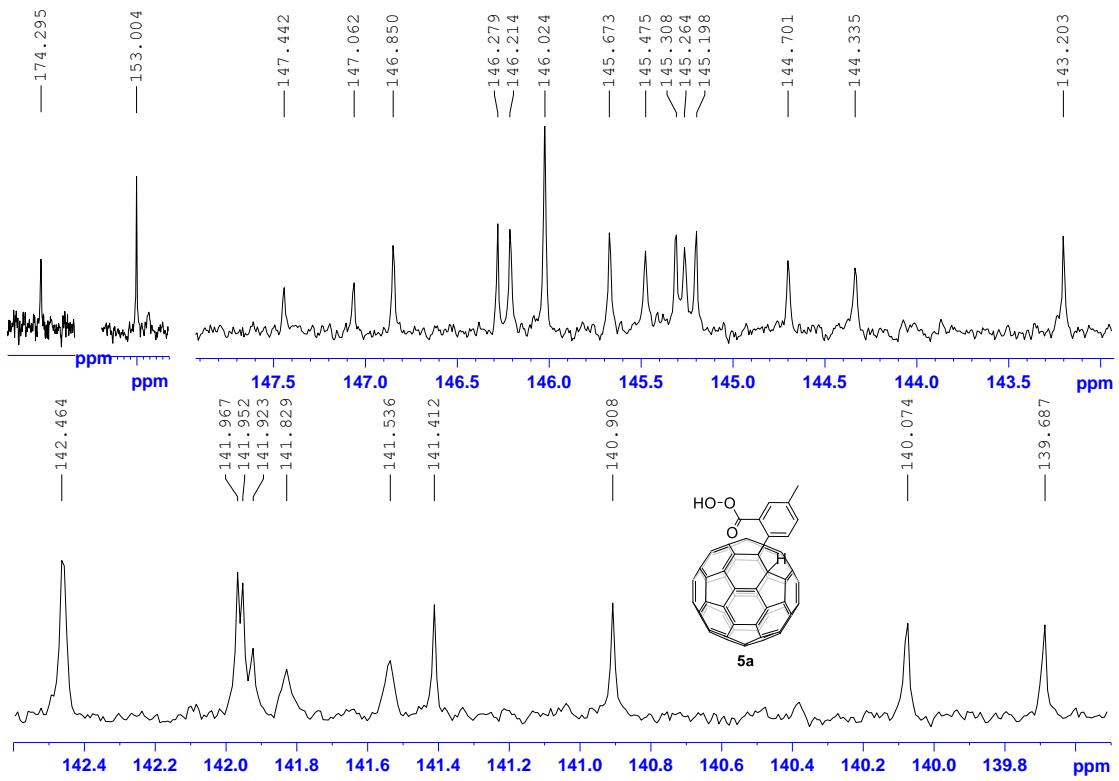
**Figure S20.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **4a**.



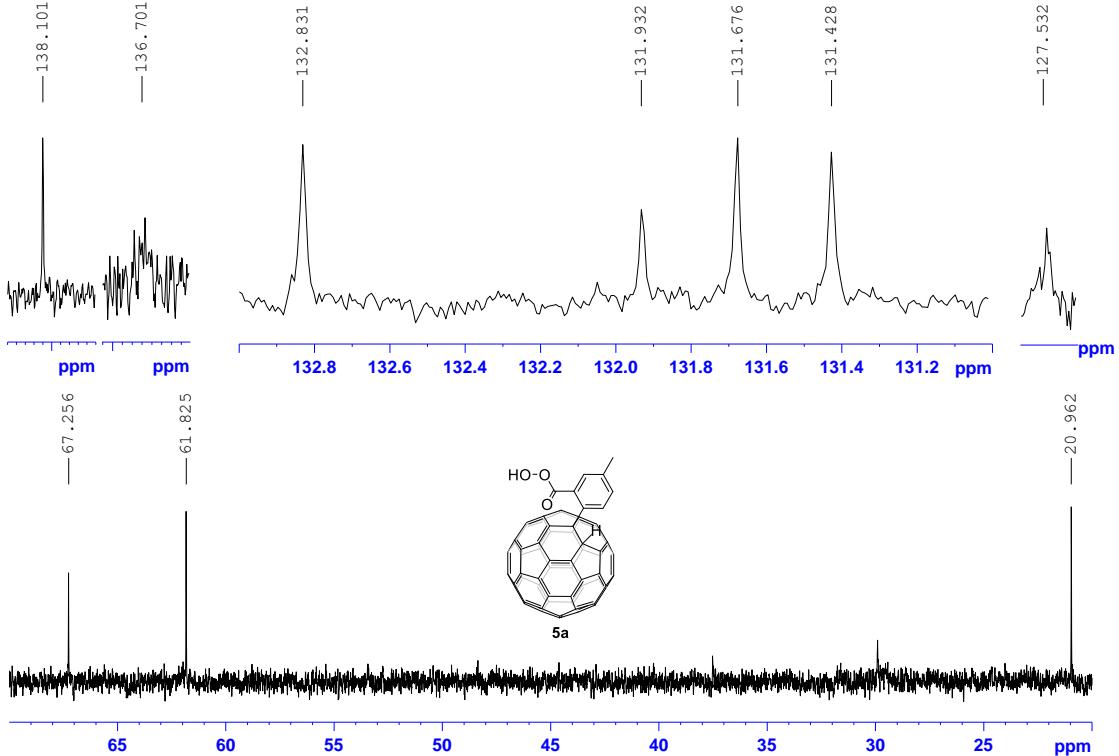
**Figure S21.**  $^1\text{H}$  NMR (400 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **5a**.



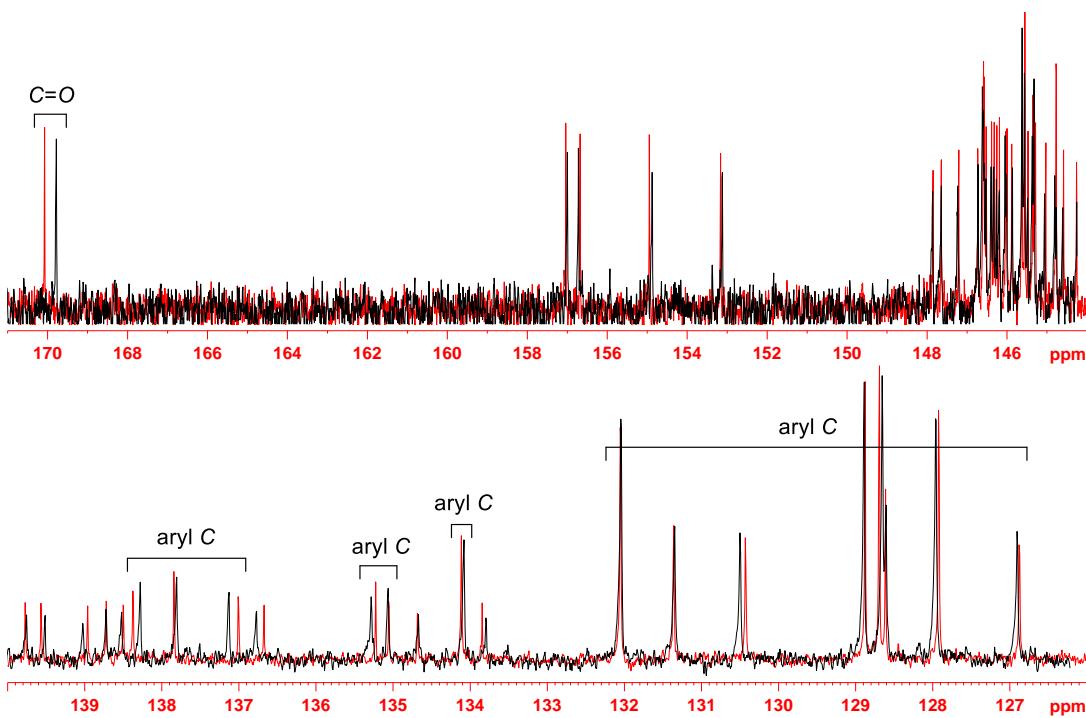
**Figure S22.**  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **5a**.



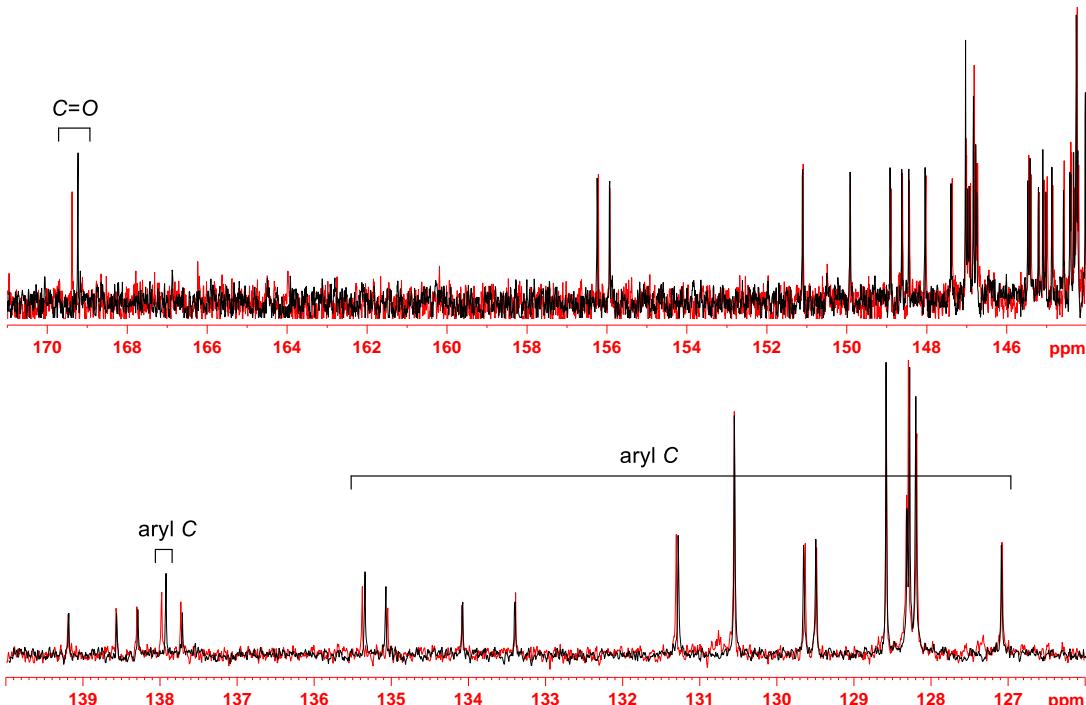
**Figure S23.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **5a**.



**Figure S24.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of compound **5a**.

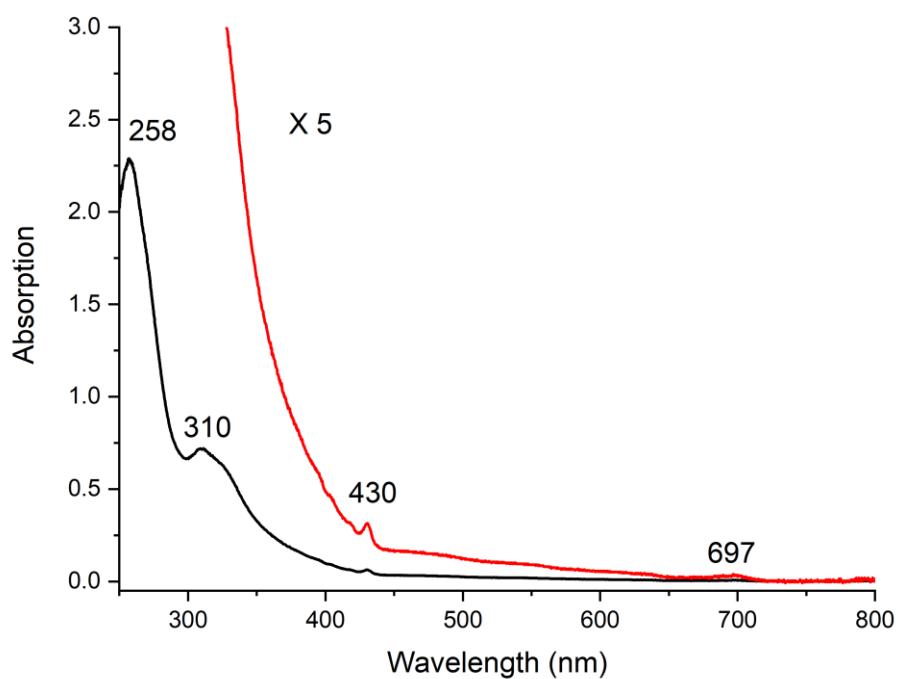


**Figure S25.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of  $3\mathbf{a}$  (red) and  $6^3$  (black) in the regions of 171–144 and 140–126 ppm.

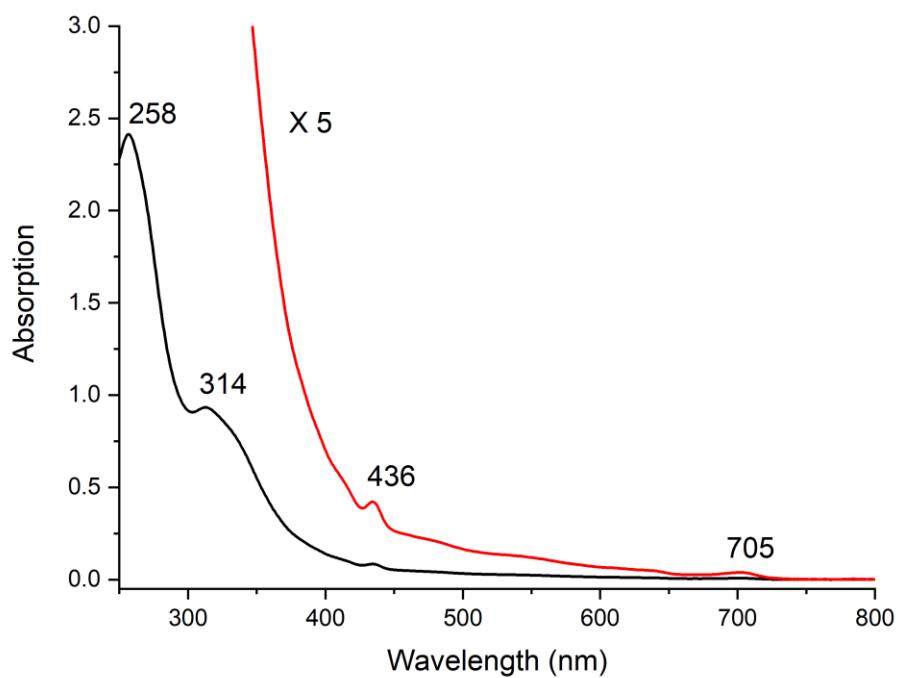


**Figure S26.** Expanded  $^{13}\text{C}$  NMR (126 MHz, 1:1  $\text{CS}_2/\text{CDCl}_3$ ) of  $4\mathbf{a}$  (red) and  $7^3$  (black) in the regions of 171–144 and 140–126 ppm.

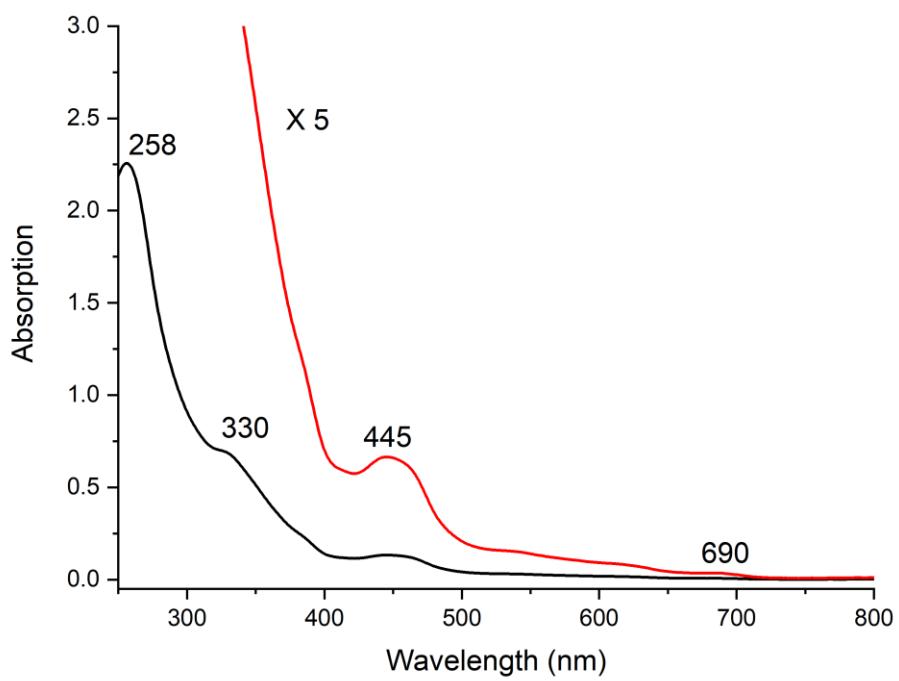
## 5. UV-vis Spectra of Compounds **2g** and **3a–5a**



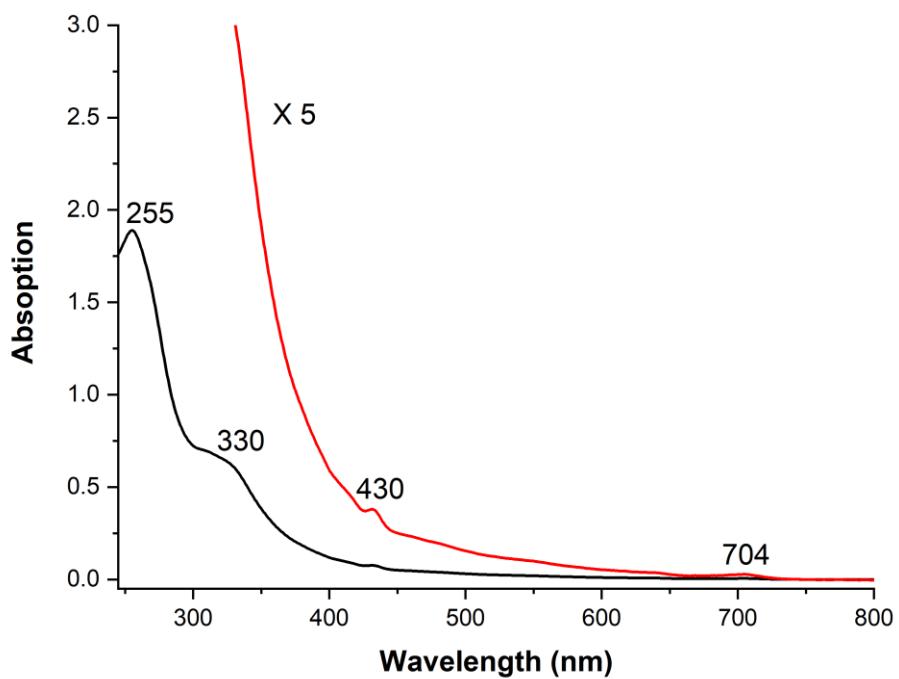
**Figure S27.** UV-vis absorption of **2g** in  $\text{CHCl}_3$ .



**Figure S28.** UV-vis absorption of **3a** in  $\text{CHCl}_3$ .

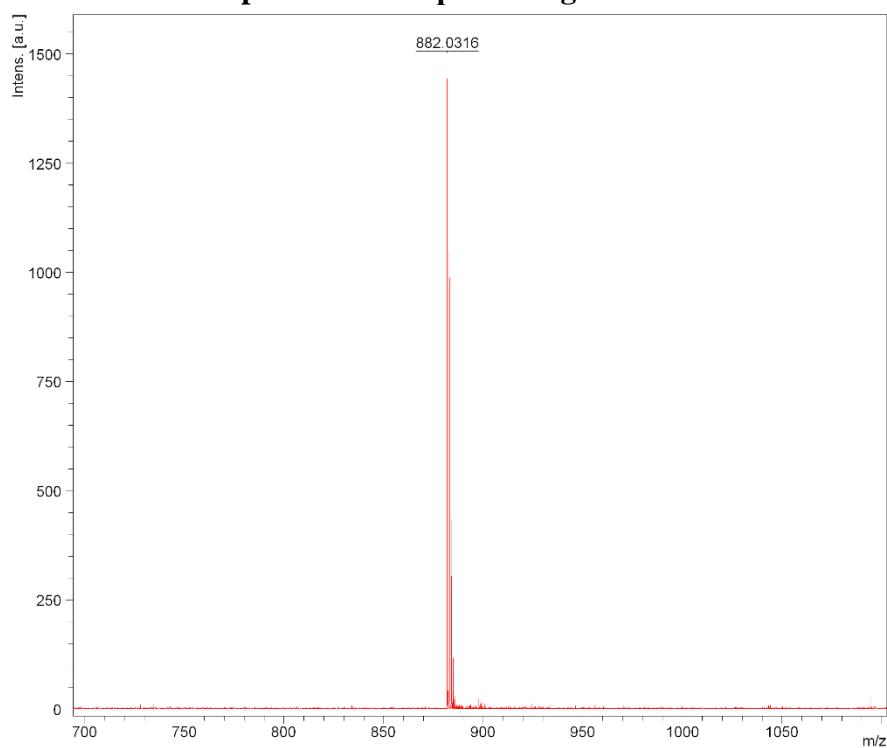


**Figure S29.** UV-vis absorption of **4a** in  $\text{CHCl}_3$ .

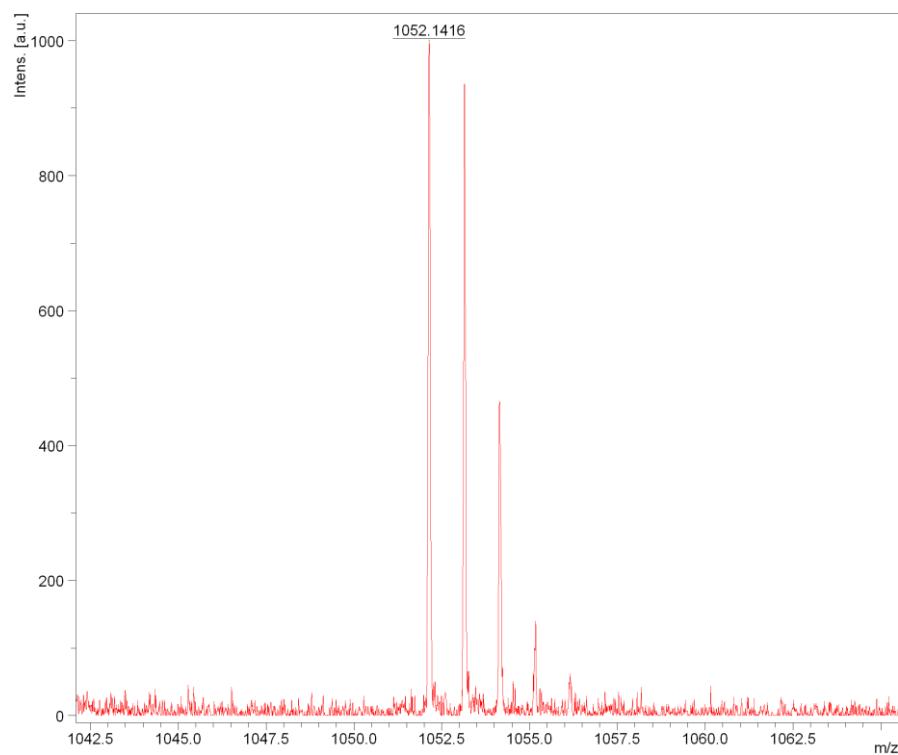


**Figure S30.** UV-vis absorption of **5a** in  $\text{CHCl}_3$ .

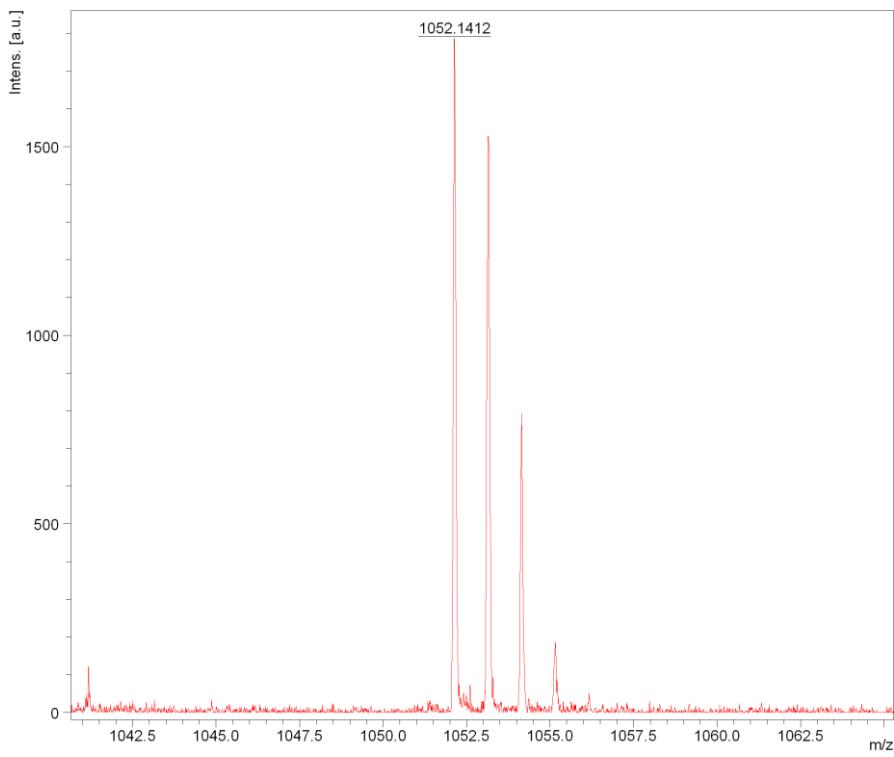
## 6. MALDI-TOF HRMS Spectra of Compounds 2g and 3a–5a



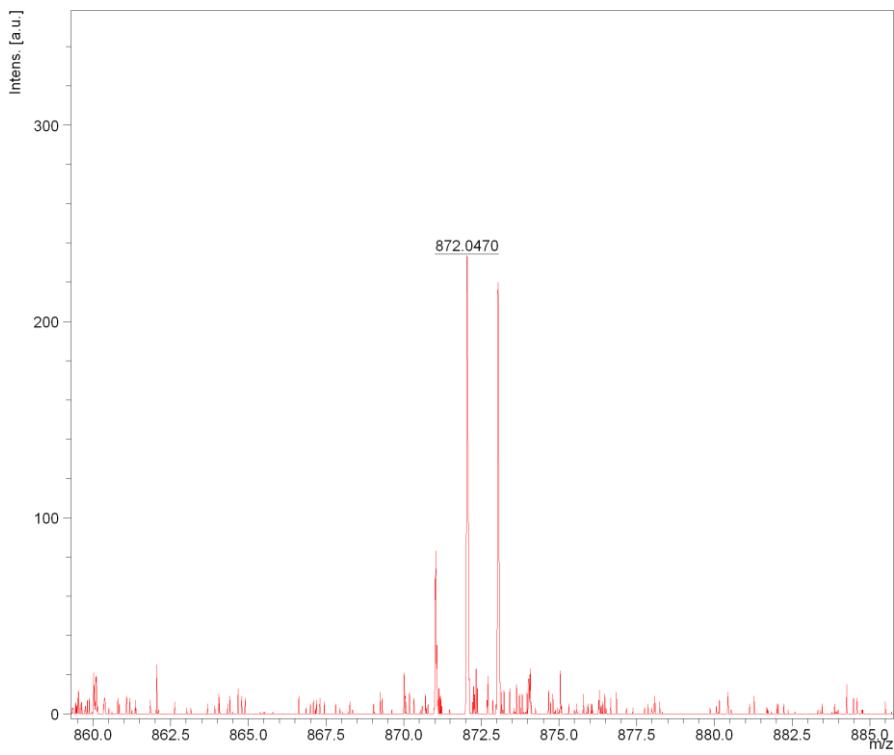
**Figure S31.** MALDI-TOF HRMS of **2g**.



**Figure S32.** MALDI-TOF HRMS of **3a**.

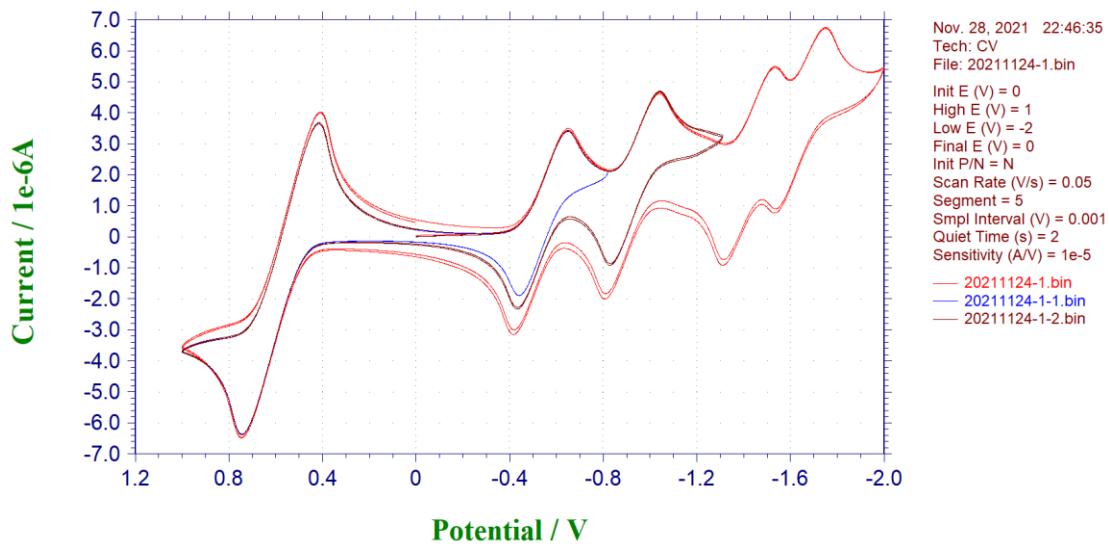


**Figure S33.** MALDI-TOF HRMS of **4a**.

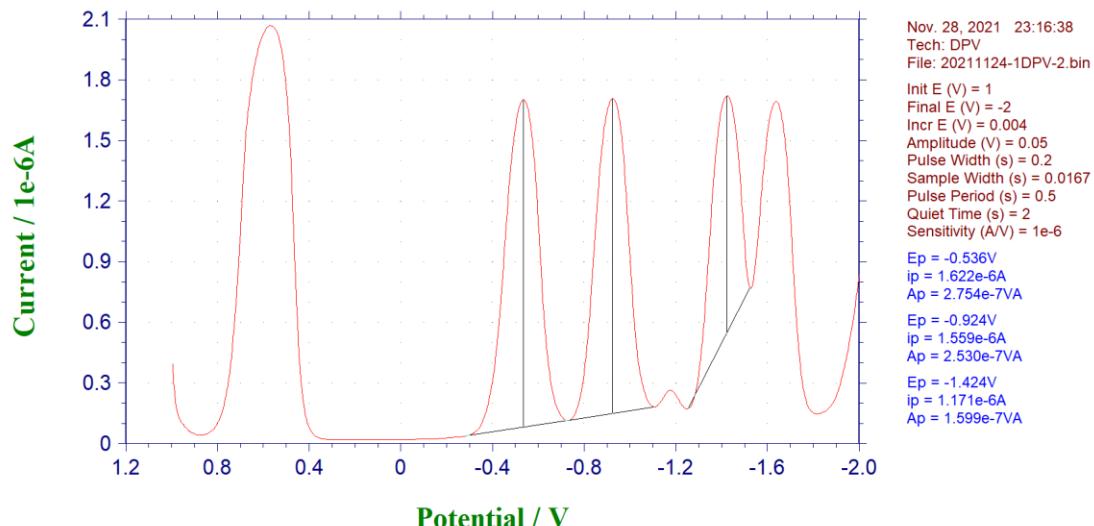


**Figure S34.** MALDI-TOF HRMS of **5a**.

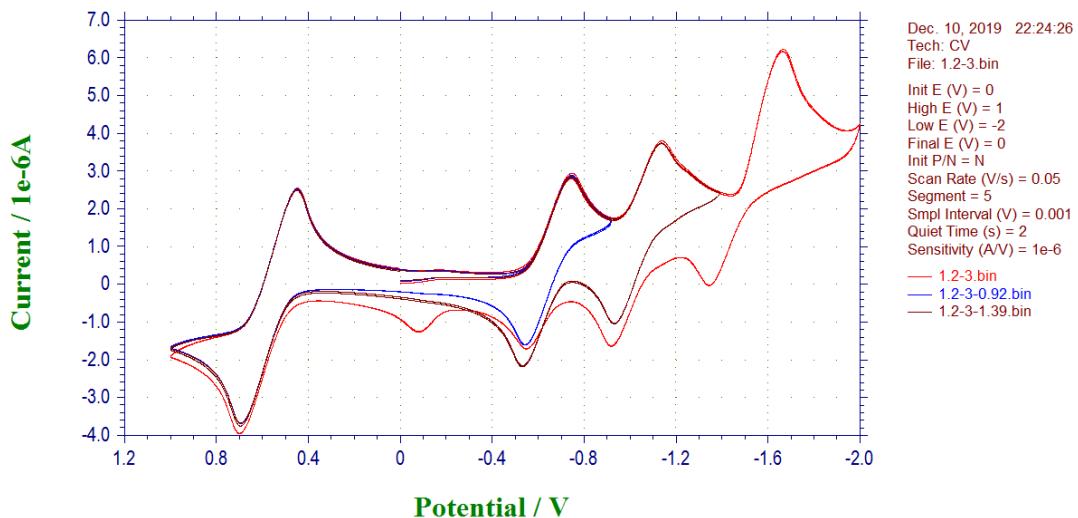
## 7. CVs and DPVs of 2g and 3a–5a



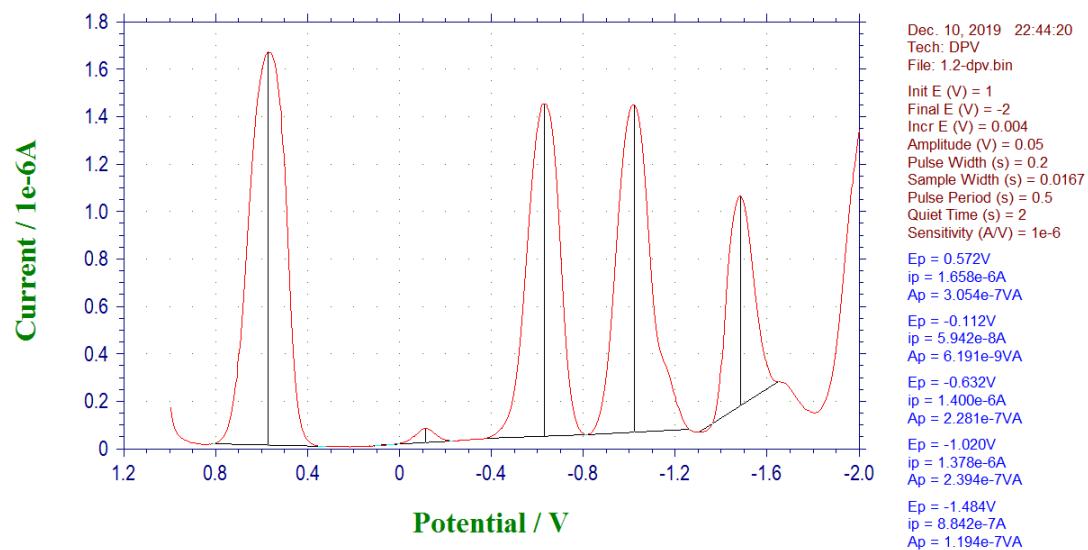
**Figure S35.** Cyclic voltammogram of **2g** (scanning rate: 50 mV s<sup>-1</sup>).



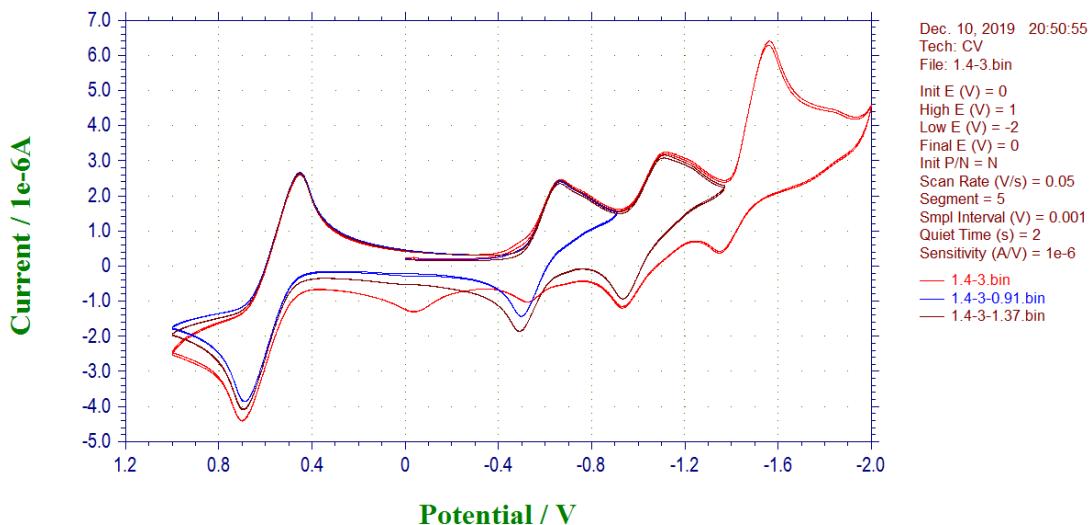
**Figure S36.** Differential pulse voltammogram of **2g**.



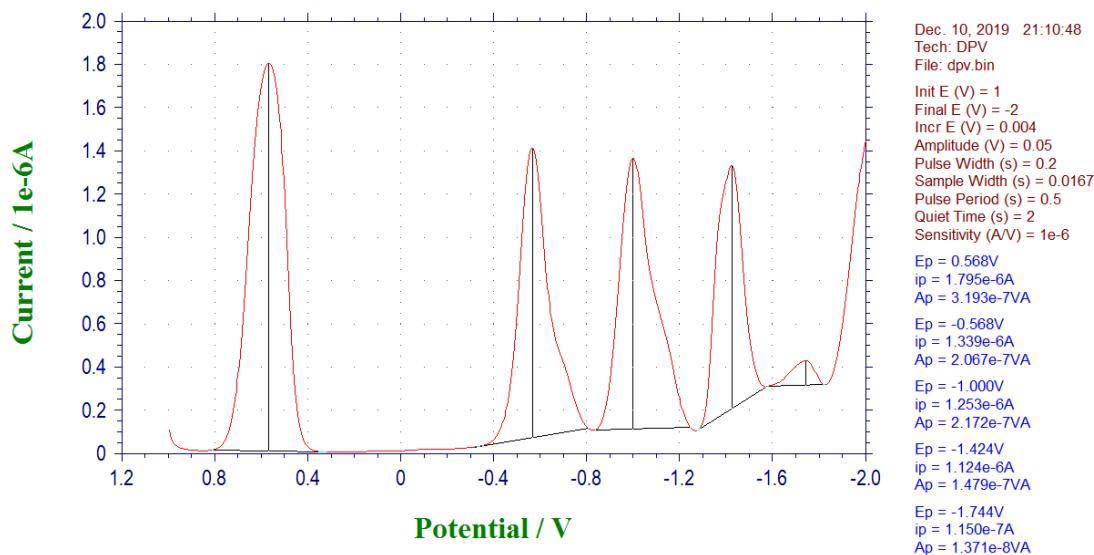
**Figure S37.** Cyclic voltammogram of **3a** (scanning rate: 50 mV s<sup>-1</sup>).



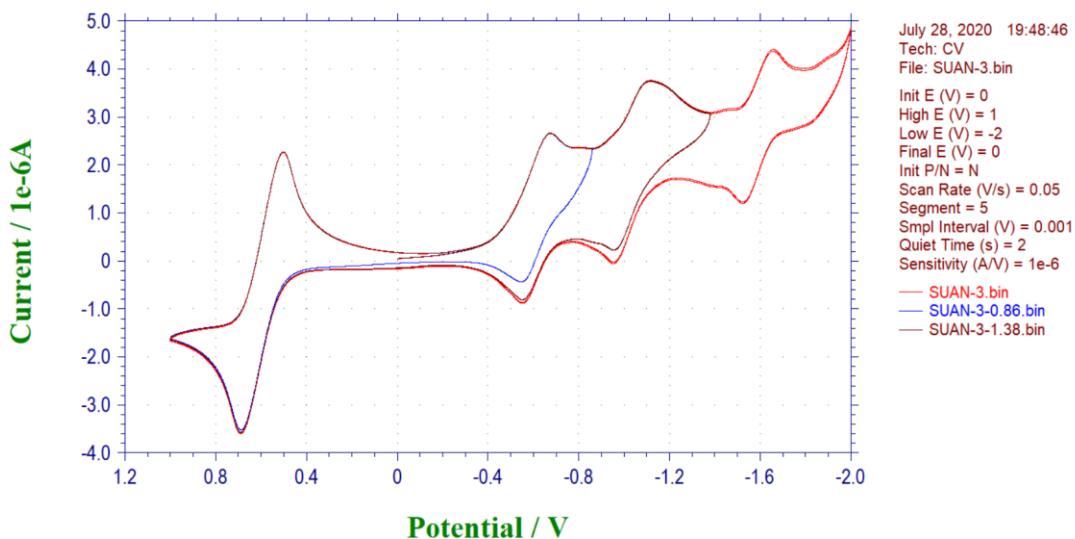
**Figure S38.** Differential pulse voltammogram of **3a**.



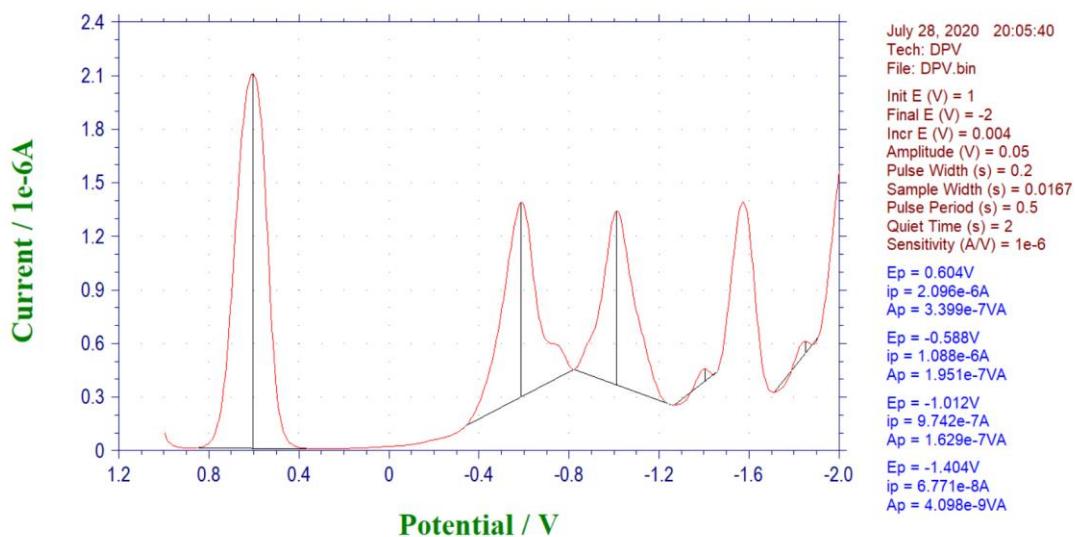
**Figure S39.** Cyclic voltammogram of **4a** (scanning rate: 50 mV s<sup>-1</sup>).



**Figure S40.** Differential pulse voltammogram of **4a**.



**Figure S41.** Cyclic voltammogram of **5a** (scanning rate: 50 mV s<sup>-1</sup>).



**Figure S42.** Differential pulse voltammogram of **5a**.

## 8. References

- 1 G.-W. Wang and B. Zhu, *Chem. Commun.*, 2009, 1769–1771.
- 2 C. Niu, D.-B. Zhou, Y. Yang, Z.-C. Yin and G.-W. Wang, *Chem. Sci.*, 2019, **10**, 3012–3017.
- 3 C. Niu, B. Li, Z.-C. Yin, S. Yang and G.-W. Wang, *Org. Lett.*, 2019, **21**, 7346–7350.