

# Supplementary Data for

## Synthesis of corrole-fullerene dyad *via* [4+2] cycloaddition reaction

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### Supporting Information

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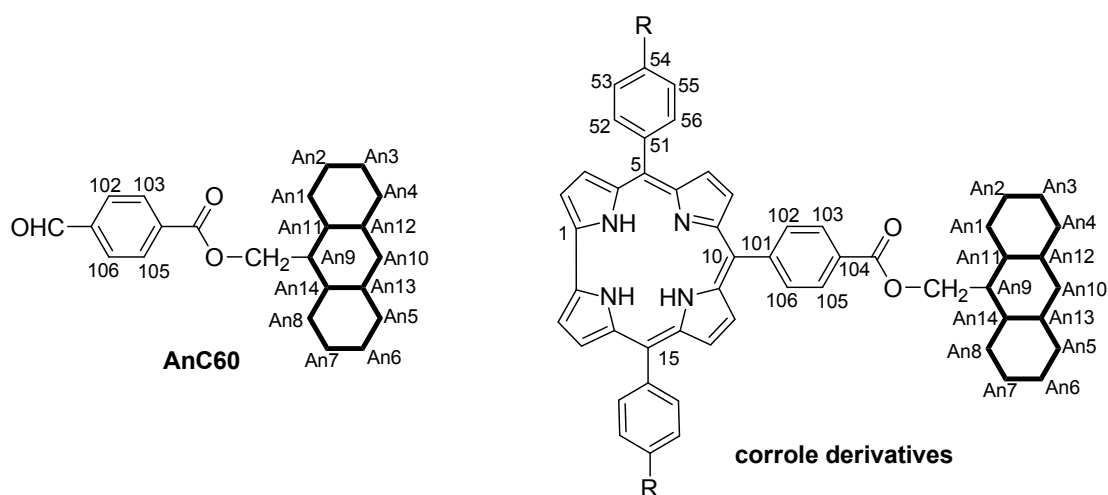
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## I. General experimental methods:

Pyrrole and TFA are distilled before use, the other starting materials are purchased and used as received; THF, *n*-C<sub>6</sub>H<sub>14</sub>, PhCH<sub>3</sub> and petroleum ether are used without further purification, but CH<sub>2</sub>Cl<sub>2</sub> is distilled and *o*-DCB is filtered through basic Al<sub>2</sub>O<sub>3</sub> before use.

Column chromatography (CC): silica gel (300-400 mesh). UV-Vis spectra: Shimadzu UV-1800 10 mm quartz cell; Fluorescence emission spectra: a Varian Cary Eclipse Spectrometer, emission wavelengths  $\lambda$  in nm; Fluorescence lifetime: HORIBA JY Fluorolog, single electron photoelectric counter (argon saturated CH<sub>2</sub>Cl<sub>2</sub>, excitation at 366 nm, detection at 667 nm); Nuclear magnetic resonance (<sup>1</sup>H-) spectra: Bruker AV400 and Varian Unityplus 500 chemical shifts ( $\delta$ ) in ppm, with  $\delta$  (CHCl<sub>3</sub>) = 7.26 ppm and  $\delta$  (CD<sub>2</sub>H<sub>2</sub>SOCD<sub>3</sub>) = 2.50 ppm for <sup>1</sup>H NMR and  $\delta$  (CDCl<sub>3</sub>) = 77.16 ppm for <sup>13</sup>C NMR; Mass spectra: HR-ESIMS Bruker microTof-QII with positive ion mode and Maldi-Tof Bruker Autoflex ToF/ToF III.

Number system in terms of <sup>1</sup>H- and <sup>13</sup>C-NMR assignment:



Scheme S1 Numbering of corrole derivatives in this study.

## II. Experimental Section:

### Synthesis of dipyrromethane (1a-c)

Compound **1a-c** was prepared according to the reported methods [ARKIVOC, 2007, (x): 307-324].

### Synthesis of Ald 1

To the solution of anthracene-9-carbaldehyde (100 mg, 0.485 mmol) in THF (25 mL) was added NaBH<sub>4</sub> (92.2 mg, 2.426 mmol, 5 eq.). The reaction mixture was refluxed until TLC revealed the total consuming of the starting materials. H<sub>2</sub>O (50 mL) was added to quench the reaction. The product was extracted by CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The organic layer was filter through hot cotton and concentrated to dryness under reduced pressure. The product anthracen-9-ylmethanol was obtained by re-crystallization in CH<sub>2</sub>Cl<sub>2</sub> / *n*-C<sub>6</sub>H<sub>14</sub>.

The anthracen-9-ylmethanol (100 mg, 0.481 mmol), 4-formylbenzoic acid (300 mg, 2 mmol, 4.2 eq) and DCC (618 mg, 3 mmol, 6.2 eq) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The reaction mixture was stirred at

room temperature for 48 h. The formed DCU was removed by filtration. The filtrate was washed with H<sub>2</sub>O (3 × 30 mL) and the organic phase was filtered through dried cotton and evaporated to dryness under reduced pressure. The residue was separated by silica gel column (CH<sub>2</sub>Cl<sub>2</sub> / petroleum ether = 2 / 1, v / v). The second fraction was collected. The product was obtained as yellow needle shape by 132.8 mg (82 %) after evaporation of the solvent. UV-Vis (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (nm) 257.0 (1.00), 333.5 (0.02), 349.5 (0.03), 368 (0.05), 388.5 (0.046); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 10.04 (s, 1H, CHO), 8.56 (s, 1H, An10H), 8.43 (d, *J* = 8.9 Hz, 2H, An1H & An8H), 8.15 (d, *J* = 8.2 Hz, 2H, *m*-PhH), 8.07 (d, *J* = 8.4 Hz, 2H, An4H & An5H), 7.87 (d, *J* = 8.2 Hz, 2H, *o*-PhH), 7.61 (t, *J* = 7.0 Hz, 2H, An2H & An7H), 7.52 (t, *J* = 7.1 Hz, 2H, An3H & An6H), 6.44 (s, 2H, OCH<sub>2</sub>); ESI-MS (C<sub>23</sub>H<sub>16</sub>O<sub>3</sub>: exact mass = 340.1099): calcd. for [M + H]<sup>+</sup>: 341.1172, found: 341.3.

#### Synthesis of reference compound AnC<sub>60</sub>

The solution of **Ald1** (5.1 mg, 15 μmol) and C<sub>60</sub> (21.6 mg, 30 μmol) in acid-free *o*-DCB (2.5 mL) was left under darkness in the presence of Ar for 3 days. Then the reaction mixture was filtered through size-exclusion column to remove the unreacted fullerene using toluene as the eluent. The collected green fraction was concentrated to dryness under reduced pressure and the green residue was separation by silica gel column with CH<sub>2</sub>Cl<sub>2</sub> as eluent. The brawn fraction was collected and the solvent was removed under reduced pressure and the residue precipitated by CH<sub>2</sub>Cl<sub>2</sub> / *n*-hexane. Finally, the product **AnC<sub>60</sub>** was obtained as dark brawn powder by 9.5 mg (60 %). UV/Vis spectra (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (nm, rel. intensity) 257.5 (1.00), 314.0 (0.25); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> + CS<sub>2</sub>, 0 °C) δ 10.10 (s, 1H, CHO), 8.21 (br. s, 2H, C103H & C105H), 7.94 (br. s, 2H, C102H & C106H), 7.83 (d, *J* = 7.1 Hz, 2H, An4H & An5H), 7.75 (br. s, 2H, An1H & An8H), 7.54 (t, *J* = 6.7 Hz, 2H, An3H & An6H), 7.49 (td, *J* = 6.7 Hz, 2H, An2H & An7H), 6.35 (br.s, 2H, OCH<sub>2</sub>), 5.89 (s, 1H, An10H). <sup>13</sup>C NMR (125MHz / 500MHz, CDCl<sub>3</sub> + CS<sub>2</sub>, 0 °C, based on HSQC and HMBC): 190.7 (CHO), 155.4 (saturated C of fullerene), 140.7 (An12C & An13C), 139.4 (An11C & An14C), 130.2 (C103 & C105), 129.3 (C102 & C106), 127.2 (An2C, An3C, An6C & An7C), 125.8 (An4C & An5C), 124.0 (An1C & An8C), 74.2 (unsaturated C of fullerene), 65.3 (OCH<sub>2</sub>), 58.5 (An10C). <sup>13</sup>C NMR (125 MHz / 500 MHz, CDCl<sub>3</sub> + CS<sub>2</sub>, 0 °C, based on <sup>13</sup>C NMR): 191.1, 155.6, 147.5, 147.4, 146.4, 146.3, 146.2, 146.1, 145.4, 145.3, 144.6, 144.4, 143.0, 142.9, 142.6, 142.1, 141.9, 141.8, 141.6, 140.1, 139.4, 134.2, 130.6, 129.7, 127.6, 127.5, 126.1, 77.4, 65.6, 58.8; Maldi-Tof (C<sub>83</sub>H<sub>16</sub>O<sub>3</sub>: exact mass = 1060.0133): calcd. for [M]<sup>+</sup> 1060.0133, found: 1061.3.

#### Synthesis of corrole (2a-c)

**Ald 1** (6.8 mg, 20.0 μmol) and the corresponding dipyrromethane (40.3 μmol) was dissolved in the solution of TFA (28 mM) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) and the reaction mixture was stirred under darkness in the presence of Ar for 10 h. Then the mixture was diluted to 10 mL with CH<sub>2</sub>Cl<sub>2</sub> and oxidized by addition of the solution of DDQ (11.8 mg, 52.7 μmol) in toluene (0.2 mL). After 2 h, the reaction mixture was diluted with 20 mL CH<sub>2</sub>Cl<sub>2</sub> and washed with NaHCO<sub>3</sub> aq. (3 × 30 mL) and H<sub>2</sub>O (2 × 20 mL). The organic phase was filtered through the dried cotton and evaporated to dryness under reduced pressure. The residue was

separated by silica gel column (CH<sub>2</sub>Cl<sub>2</sub> / petroleum ether = 2 / 1, v / v for **2a-b** and CH<sub>2</sub>Cl<sub>2</sub> for **2c**). The main green fraction was collected. The corrole was obtained after evaporation of the solvent and crystallization in CH<sub>2</sub>Cl<sub>2</sub> / *n*-C<sub>6</sub>H<sub>14</sub> = 1 / 3 (v / v).

Corrole **2a** (green): 1.3 mg (8 %); UV-Vis (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (nm) 250 (0.74), 258.0 (1.36), 350.0 (0.14), 368.5 (0.20), 388.5 (0.31), 420.5 (1.00), 519.0sh (0.06), 576.5 (0.15), 620.0 (0.12), 653.5 (0.10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.93 (d, *J* = 4.0 Hz, 2H, β-H), 8.84 (d, *J* = 4.0 Hz, 2H, β-H), 8.61 (d, *J* = 8.0 Hz, 3H, An1H, An8H & superimposed by An10H), 8.57 (d, *J* = 4.0 Hz, 2H, β-H), 8.42 (d, *J* = 4.0 Hz, 2H, β-H), 8.38 (d, *J* = 7.9 Hz, 2H, C103H & C105H), 8.22 (d, *J* = 7.6 Hz, 3H, C56H, C152H & C156H), 8.17 (d, *J* = 7.9 Hz, 2H, C102H & C106H), 8.10 (d, *J* = 8.3 Hz, 2H, An4H & An5H), 7.68 (t, *J* = 8.0 Hz, 2H, An2H & An7H), 7.61 (d, *J* = 7.6 Hz, 4H, C52H, C55H, C153H & C155H), 7.56 (t, *J* = 8.0 Hz, 3H, An3H, An6H & superimposed by C53H), 6.58 (s, 2H, OCH<sub>2</sub>), 2.66 (s, 6H, CH<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sup>6</sup>): δ 9.00 (br.s, 2H, β-H), 8.79 (s, 1H, An10H), 8.74 (br.s, 2H, β-H), 8.64 (m, 2H, An1H & An8H), 8.40 (d, *J* = 4.0 Hz, 2H, β-H), 8.35 (br.s, 4H, 2β-H, C102H & C103H), 8.28 (d, *J* = 7.1 Hz, 1H, C105H), 8.20 (dd, *J* = 2.3, 8.4 Hz, 3H, An4H, An5H & superimposed by C106H), 8.17 (d, *J* = 6.6 Hz, 3H, C56H, C152H & C156H), 7.96 (d, *J* = 6.4 Hz, 1H, C52H), 7.73 (t, *J* = 7.9 Hz, 2H, An2H & An7H), 7.65 (br.s, 3H, C55H, C153H & C155H), 7.62 (td, *J* = 2.0, 7.9 Hz, 2H, An3H & An6H), 7.57 (d, *J* = 6.5 Hz, 1H, C53H), 6.58 (s, 2H, OCH<sub>2</sub>), 2.61 (s, 6H, CH<sub>3</sub>), -2.65 (br.s, NH); HRMS (ESI) (C<sub>55</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>: exact mass = 788.3151): calcd. for [M+H]<sup>+</sup> 789.3224, found: 789.3224.

Corrole **2b** (green): 1.6 mg (10 %); UV/Vis (in CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm) 249.5 (0.64), 258.0 (1.25), 350.5 (0.11), 369 (0.17), 389 (0.28), 420.5 (1.00), 522sh (0.04), 577.5 (0.16), 619.0 (0.11), 651.5 (0.08); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.94 (br.s, 2H, β-H), 8.83 (br.s, 1H, β-H), 8.79 (br.s, 1H, β-H), 8.59 (m, 3H, An1H, An8H, & An10H), 8.53 (m, 3H, β-H), 8.44 (d, *J* = 7.0 Hz, 2H, C103H & superimposed by β-H), 8.38 (d, *J* = 6.7 Hz, 1H, C105H), 8.35 (d, *J* = 7.0 Hz, 1H, C102H), 8.25 (br.s, 3H, C56H, C152H & C156H), 8.15 (d, *J* = 6.7 Hz, 1H, C106H), 8.10 (m, 2H, An4H & An5H), 8.06 (d, *J* = 6.3 Hz, 1H, C52H), 7.79 (br.s, 3H, C55H, C153H & C155H), 7.72 (d, *J* = 6.3 Hz, 1H, C53H), 7.68 (t, *J* = 7.9 Hz, 2H, An2H & An7H), 7.56 (m, 2H, An3H & An6H), 6.57 (s, 2H, CH<sub>2</sub>), -2.30 (NH); HRMS (ESI) (C<sub>53</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: exact mass = 828.2059): calcd. for [M+H]<sup>+</sup> 829.2132, found: 829.2128.

Corrole **2c** (green): 1.3 mg (7.4 %); UV-Vis (in CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm) 250.0 (0.77), 257.5 (1.35), 350.0 (0.15), 368.5 (0.19), 388.5 (0.26), 426.5 (1.00), 522.5sh (0.05), 582.5 (0.18), 621.0 (0.12), 653.5 (0.08); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): 8.90 (s, 2H, β-H), 8.82 - 8.78 (m, 2H), 8.58 - 8.55 (m, 3H, An1H, An8H & An10H), 8.55 - 8.49 (m, 2H), 8.49 - 8.43 (m, 6H), 8.43 - 8.35 (m, 5H), 8.32 (d, *J* = 7.0 Hz, 1H), 8.21 (d, *J* = 7.0 Hz, 1H), 8.14 (d, *J* = 7.0 Hz, 1H), 8.07 (t, *J* = 8.0 Hz, 2H, An4H & An5H), 7.66 (m, 2H, An2H & An7H), 7.53 (m, 2H, An3H & an6H), 6.55 (br.s, 2H, CH<sub>2</sub>), 4.09 (br.s, 6H, COOCH<sub>3</sub>); HRMS (ESI) (C<sub>55</sub>H<sub>40</sub>N<sub>4</sub>O<sub>6</sub>: exact mass = 876.2948): calcd. for [M+H]<sup>+</sup> 877.3021, found: 877.3020.

#### Synthesis of corrole-fullerene dyad **3a-c**

The solution of **2a-c** (2 μmol) and C<sub>60</sub> (10.8 mg, 15 μmol) in acid-free *o*-DCB (1.5 mL) was left under

darkness in the presence of N<sub>2</sub> for 5 days. Then the reaction mixture was filtered through size-exclusion column to remove the unreacted fullerene using toluene as the eluent. The collected green fraction was concentrated to dryness under reduced pressure and the green residue was separation by silica gel column with toluene as eluent. The first fraction was collected and the solvent was removed under reduced pressure to obtain the corrole-fullerene dyad **3a** (1.4 mg, 46 %). UV/Vis spectra (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (nm) 258.5 (1.01), 314.0 (0.41), 421 (1.00), 522.5sh (0.06), 577.0 (0.15), 618.0 (0.12), 652.5 (0.10), 705; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> / CS<sub>2</sub>, 0 °C) δ 8.92 (br.s, 2H, β-H), 8.86 (br.s, 2H, β-H), 8.57 (br.s, 3H, 2β-H & C103H), 8.50 (br. s, 2H, β-H & C105H), 8.42 (br.s, 2H, β-H & C102H), 8.22 (br.s, 4H, C52H, C56H, C152H & C156H), 8.03 (d, *J* = 7.0 Hz, 1H, C106H), 7.95 (br.s, 2H, An1H & An8H), 7.85 (d, *J* = 4.7 Hz, 2H, An4H & An5H), 7.63 (br.s, 4H, C53H, C55H, C153H & C155H), 7.56 (m, 4H, An2H, An3H, An6H & An7H), 6.45 (br.s, 2H, CH<sub>2</sub>), 5.89 (s, 1H, An10H), 2.69 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 / 500 MHz, CDCl<sub>3</sub>, 0 °C, based on HSQC and HMBC): 141.3 (An12C&An13C), 139.6 (An11&An14), 137.1 (C54 & C154), 136.4 (C51 & C151), 134.9 (C52, C56, C152 & C156), 134.7 (C102 & C106), 128.7 (C53, C55, C153 & C155), 127.6 (An2C, An3C, An6C & An7C), 126.8 (β-C), 126.0 (An4C & An5C), 125.8 (β-C), 125.2 (β-C), 124.9 (An1C & An8C), 116.3 (β-C), 74.6 (unsaturated C of fullerene), 65.2 (OCH<sub>2</sub>), 58.8 (An10C), 21.5 (CH<sub>3</sub>); Maldi-Tof (C<sub>115</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>: exact mass = 1508.3151): calcd. for [M+H]<sup>+</sup> 1509.3224, found: 1509.3.

**3b** (1.3 mg, 42 %). UV/Vis spectra (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (nm) 258 (1.00), 314 (0.39), 420.5 (1.00), 521sh (0.06), 579.5 (0.14), 618.5 (0.10), 651.5 (0.07), 705; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> / CS<sub>2</sub>, 5 °C) δ 8.95 (s, 2H), 8.84 (s, 2H), 8.60 ~ 8.35 (overlap, 6H), 8.25 (br. s, 4H), 8.11 (m, 2H), 7.94 (br.s, 2H), 7.85 ~ 7.75 (m, 6H), 7.58 (m, 4H), 6.46 (br.s, 2H, OCH<sub>2</sub>), 5.89 (s, 1H, An10H), -3.43 (br. s); Maldi-Tof (C<sub>113</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: exact mass = 1548.2059): calcd. for [M]<sup>+</sup> 1548.2059, found: 1548.1.

**3c** (0.96 mg, 30 %). UV/Vis spectra (in CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (nm) 258 (1.01), 314.5 (0.44), 426 (1.00), 526sh (0.07), 582.5 (0.17), 622.0 (0.12), 655.5 (0.08), 707; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 5 °C) δ 9.03 (s, 2H), 8.89 (m, 2H), 8.61 (s, 2H), 8.56 (s, 2H), 8.49 ~ 8.45 (br. s, 10H), 8.26 (s, 2H), 7.98 (br.s, 2H), 7.87 (s, 2H), 7.58 (m, 4H), 6.49 (br.s, 2H, OCH<sub>2</sub>), 5.93 (s, 1H, An10H), 4.10 (s, 6H, COOCH<sub>3</sub>); Maldi-Tof (C<sub>117</sub>H<sub>40</sub>N<sub>4</sub>O<sub>6</sub>: exact mass = 1596.2948): calcd. for [M]<sup>+</sup> 1596.2948, found: 1596.1.

### III. NMR spectra of Ald1, 2a-c and 3a-c:

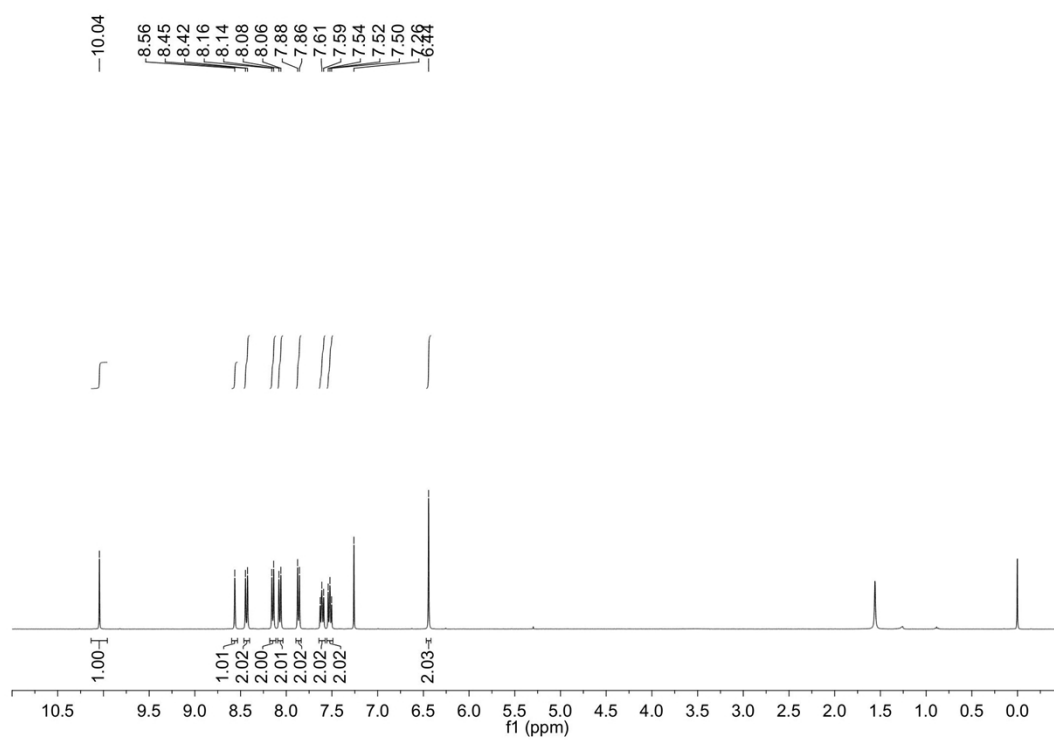


Fig. S1  $^1\text{H}$  NMR spectra of Ald1 (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

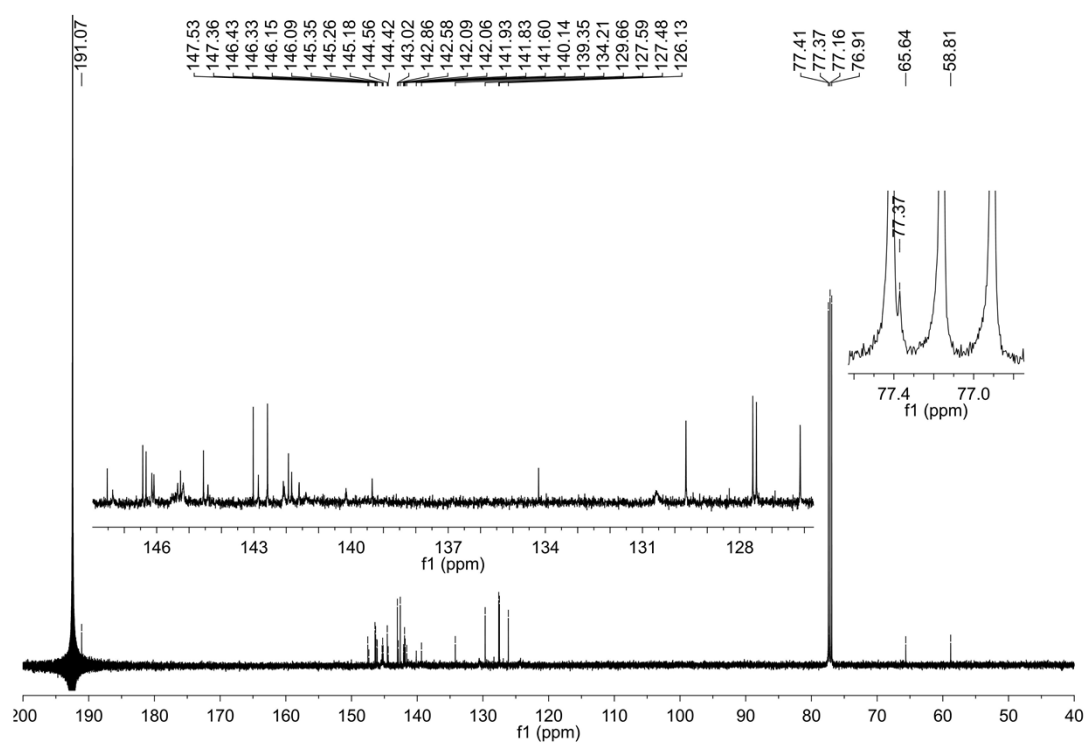
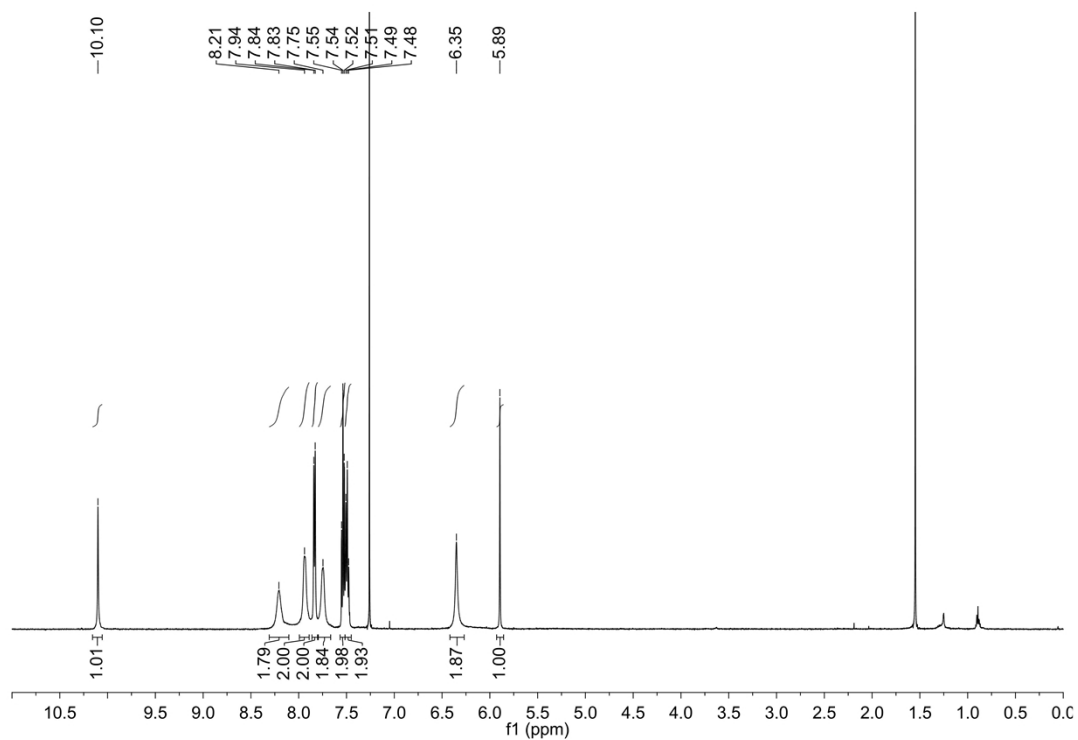


Fig. S2 <sup>1</sup>H (up) and <sup>13</sup>C (down) NMR spectra of AnC<sub>60</sub> (500 / 125 MHz, CDCl<sub>3</sub>, 0 °C)

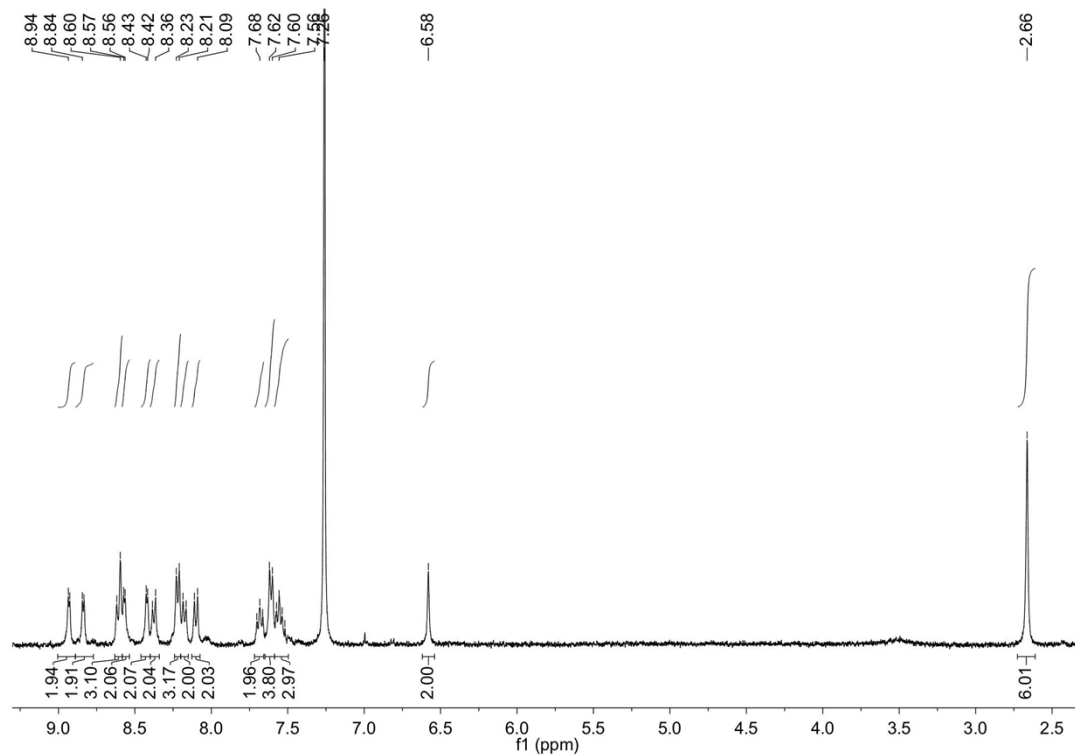


Fig. S3  $^1\text{H}$  NMR spectra of **2a** (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

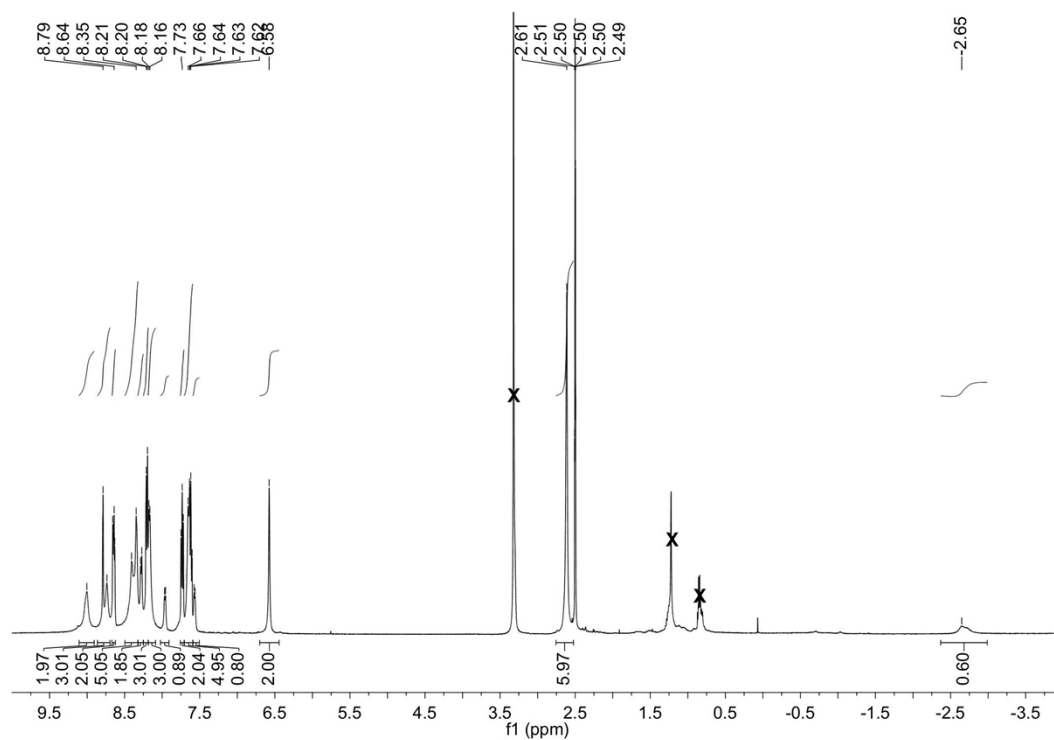


Fig. S4  $^1\text{H}$  NMR spectra of **2a** (500 MHz,  $\text{DMSO-d}_6$ , 25  $^\circ\text{C}$ )



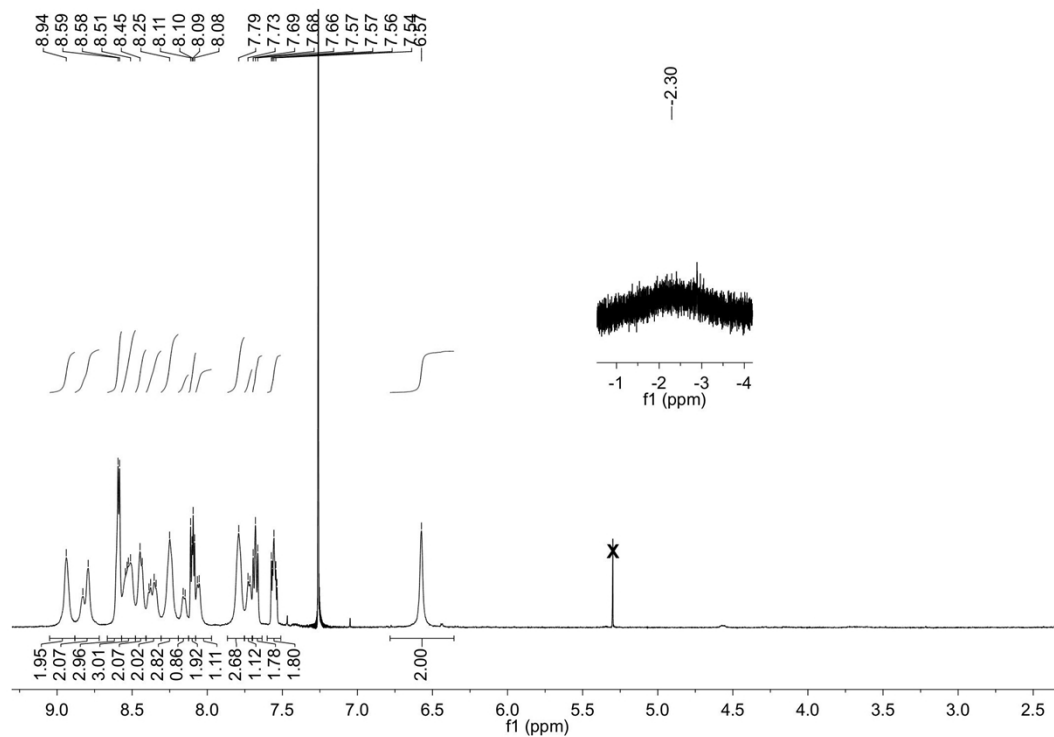


Fig. S5  $^1\text{H}$  NMR spectra of **2b** (500 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

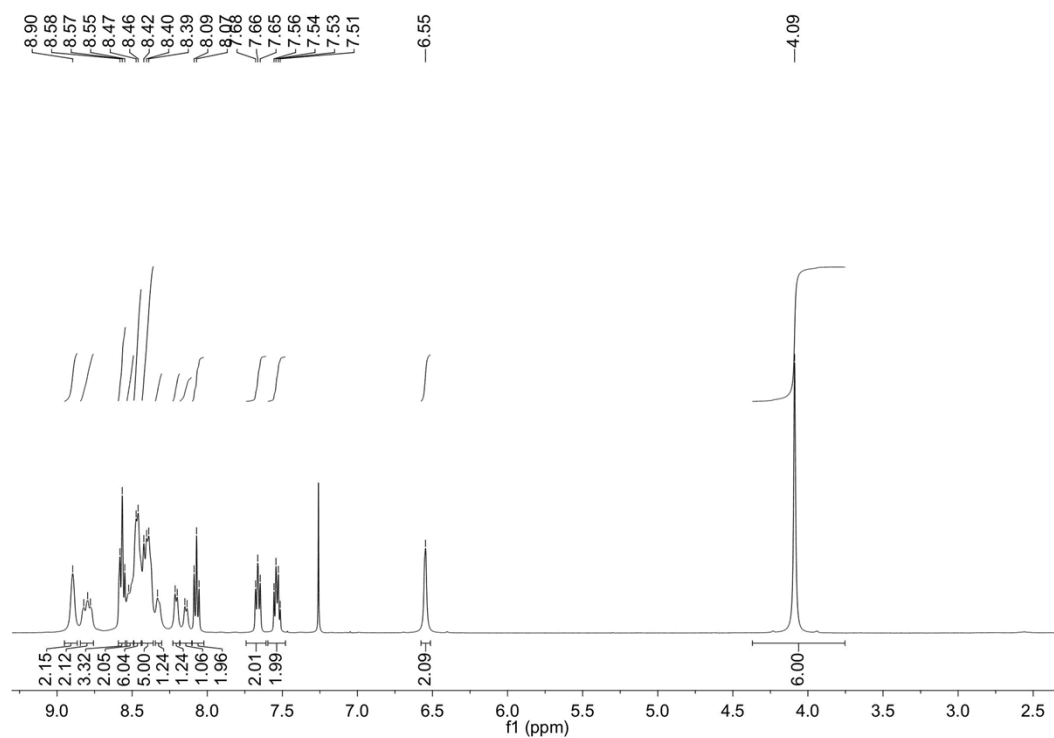


Fig. S6  $^1\text{H}$  NMR spectra of **2c** (500 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

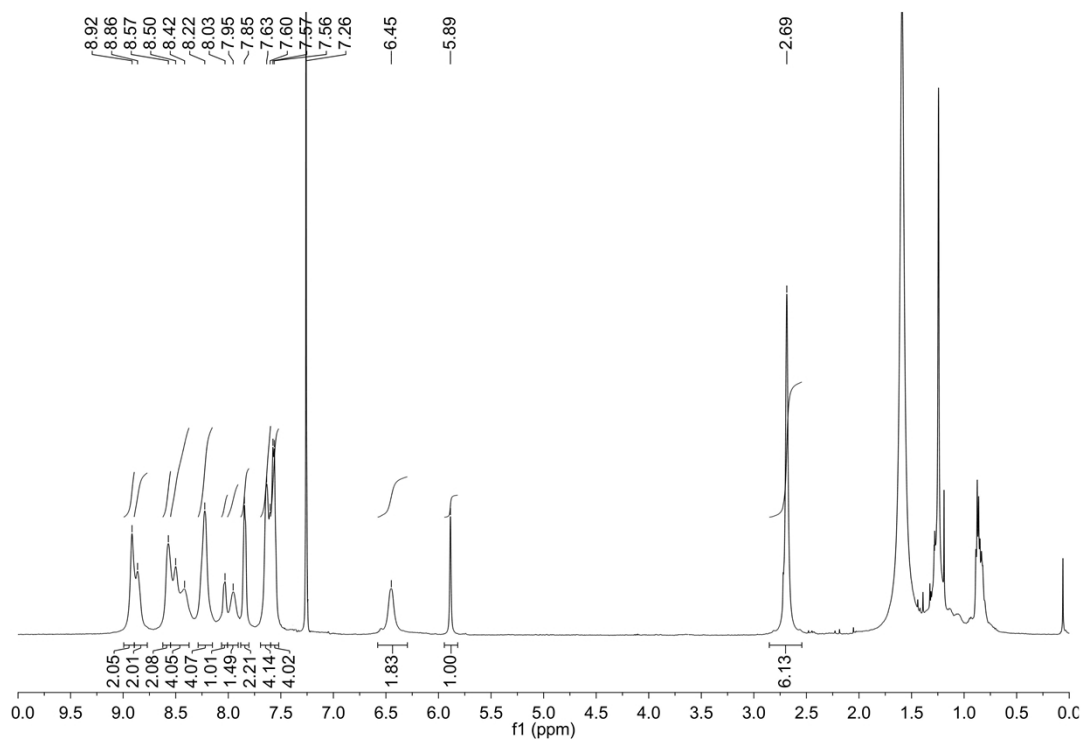


Fig. S7  $^1\text{H}$  NMR spectra of **3a** (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ ,  $0^\circ\text{C}$ )

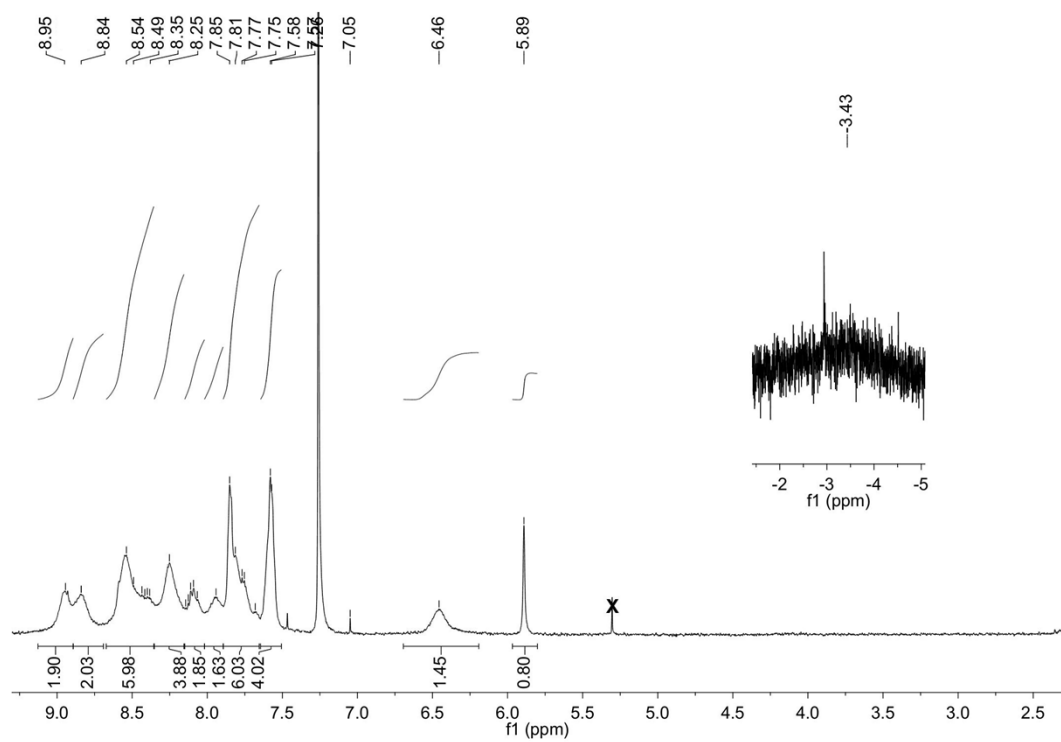


Fig. S8  $^1\text{H}$  NMR spectra of **3b** (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ ,  $5^\circ\text{C}$ )

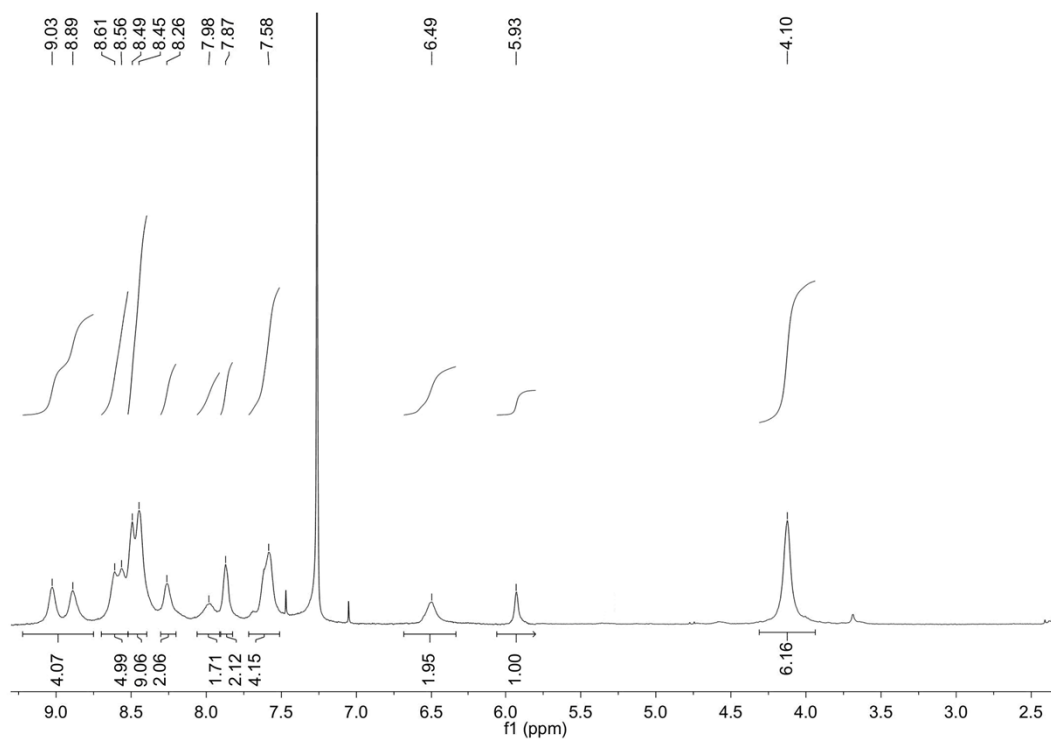


Fig. S9  $^1\text{H}$  NMR spectra of **3c** (500 MHz,  $\text{CDCl}_3$ , 5  $^\circ\text{C}$ )

#### IV. Maldi-Tof spectrum of **2b**

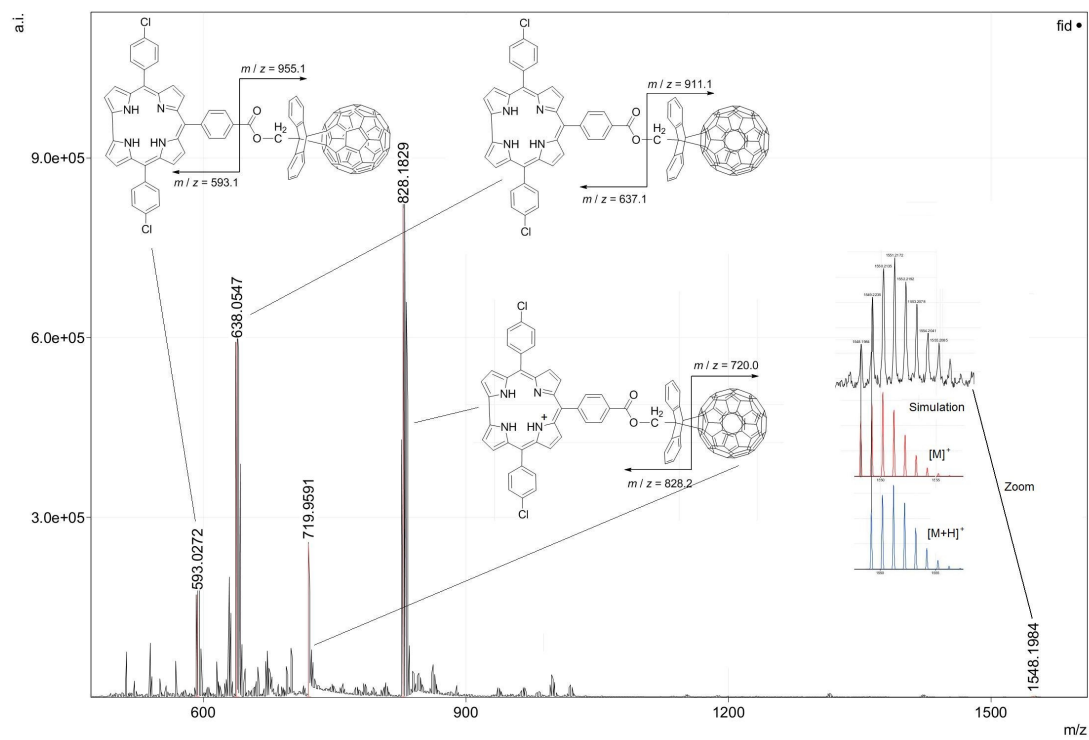
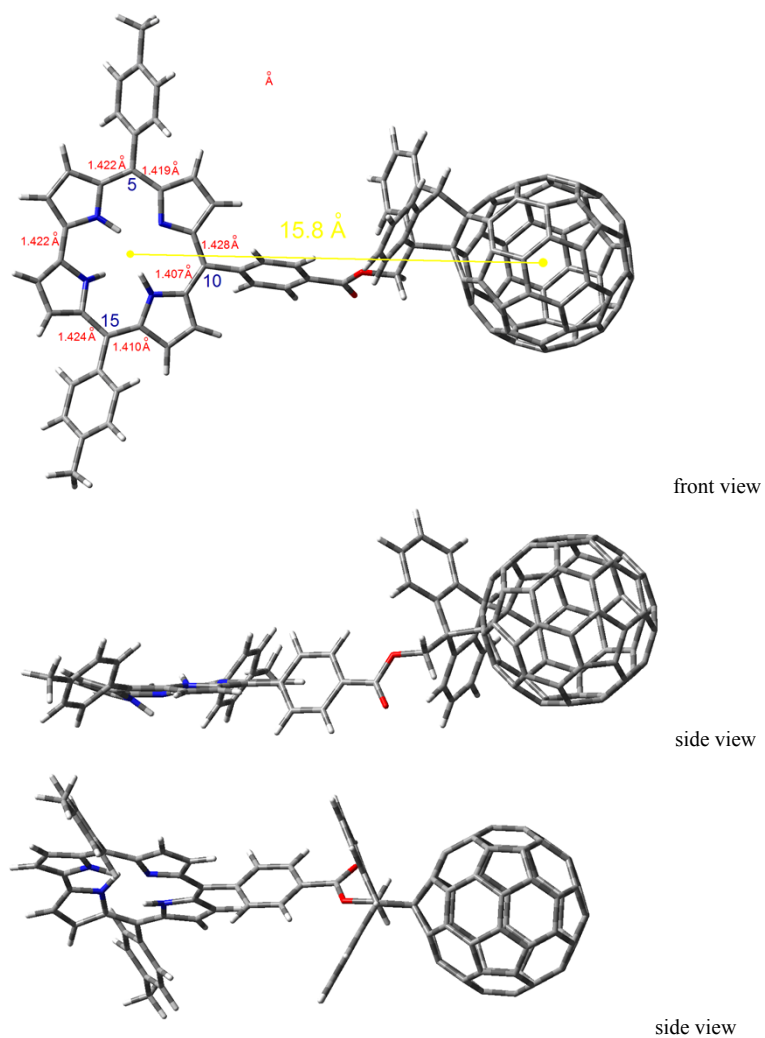


Fig. S10 Maldi-Tof spectrum of **2b**

V. Optimal structure of **3a**



**Fig. S11** The optimal structure of **3a** obtained from TD-DFT calculation (one front view and two side views)