

## Supplementary Information

for

### Reversible encapsulation and release of fullerenes using calix[n]phenoxazines

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## Table of Contents

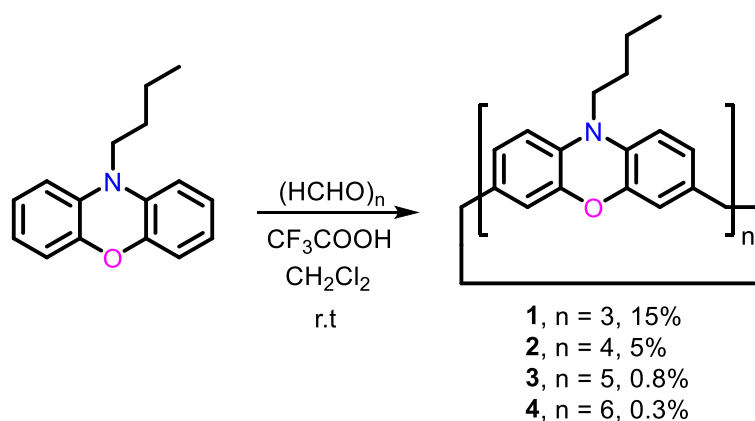
|                                              |     |
|----------------------------------------------|-----|
| 1. General information .....                 | S2  |
| 2. Synthesis of calix[n]phenothiazines ..... | S2  |
| 3. Host-guest complexation .....             | S4  |
| 3.1 Host-guest interaction .....             | S4  |
| 3.2 Job plot.....                            | S6  |
| 3.3 Competitive fluorescence titration.....  | S6  |
| 4. Theoretical calculation.....              | S7  |
| 5. Characterization data and spectra .....   | S21 |
| 6. Reference .....                           | S25 |

## 1. General information

All solvents were dried according to the standard procedures and all of them were degassed under N<sub>2</sub> for 30 minutes before use. All air-sensitive reactions were carried out under inert N<sub>2</sub> atmosphere. <sup>1</sup>H and <sup>13</sup>C were recorded at 400 MHz with a Mercury plus 400 spectrometer at 298 K and tetramethylsilane (TMS) as an internal reference. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to the residue solvent signals. Coupling constants (*J*) are denoted in Hz and chemical shifts ( $\delta$ ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were recorded with Thermo Scientific LCQ XL spectrometer with methanol or acetonitrile as solvents. UV-vis spectra were measured by SHIMADZU UV-2600 using a 10 mm quartz cuvette. Fluorescent spectra were recorded on a Edinburgh FS5 spectrofluorometer, using a 10 mm quartz cuvette.

CDCl<sub>3</sub> and toluene-*d*<sub>8</sub> were supplied by Cambridge Isotope Laboratories (CIL). Phenoxazine, bromobutane, KOH, triethylamine hydrochloride, C<sub>60</sub>, C<sub>70</sub>, paraformaldehyde, acetonitrile, CF<sub>3</sub>COOH, dichloromethane, and 1,2-dichloroethane were purchased from Energy Chemistry (Shanghai).

## 2. Synthesis of calix[n]phenothiazines



**Scheme S1.** Synthesis route to calix[n]phenothiazines 1–4.

To the solution of 10-butylphenoxazine (500 mg, 2.09 mmol) in dichloromethane (50 mL) was added paraformaldehyde (188 mg, 6.27 mmol). The suspension was stirred at room temperature for 30 min to crush the large paraformaldehyde particles. And then, CF<sub>3</sub>COOH (1.0 mL) was added to the solution. After continuing stirring at room temperature for 15 min, the reaction was quenched by addition of water. The organic phase was separated and washed with saturated aqueous NaHCO<sub>3</sub>, H<sub>2</sub>O and brine. The

crude product was purified by column chromatograph (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>) to yield **1** (white solid, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 3/1, v/v, *R<sub>f</sub>* = 0.3, 78.7 mg, 15%), **2** (white solid, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 2.5/1, v/v, *R<sub>f</sub>* = 0.3, 26.3 mg, 5%), **3** (white solid, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 2/1, v/v, *R<sub>f</sub>* = 0.3, 4.2 mg, 0.8%), and **4** (white solid, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1.5/1, v/v, *R<sub>f</sub>* = 0.3, 1.6 mg, 0.3%).

**1**: The <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HR-MS spectra of **1** were reported in " *Org. Lett.* **2023**, *25*, 5597–5601".<sup>[S1]</sup>

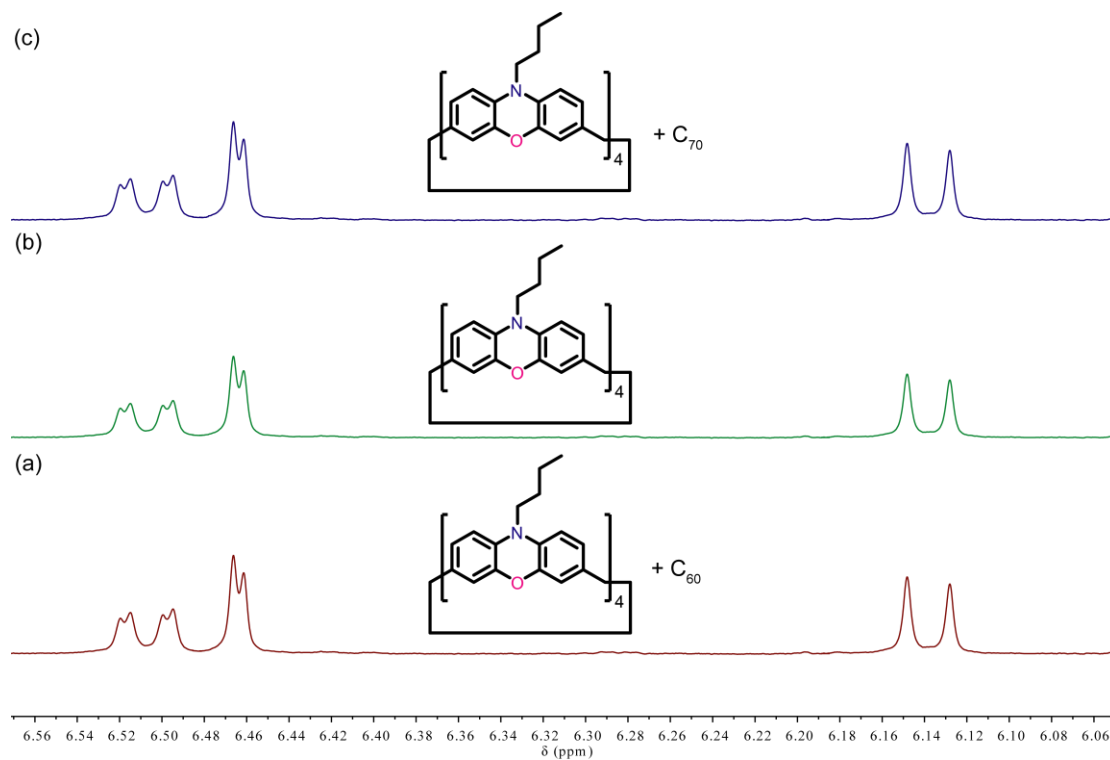
**2**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.62 (dd, *J* = 8.1, 1.7 Hz, 6H), 6.41 – 6.31 (m, 12H), 3.58 (s, 6H), 3.52 – 3.39 (m, 6H), 1.62 (m, 6H), 1.43 (m, 6H), 0.99 (t, *J* = 12.1 Hz, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.7, 133.2, 131.7, 122.9, 115.3, 110.3, 43.2, 39.5, 26.3, 20.0, 13.8. HR-MS (ESI) *m/z* calculated for C<sub>68</sub>H<sub>68</sub>N<sub>4</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 1027.5138, found: 1027.5139.

**3**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.59 (dd, *J* = 8.1, 1.7 Hz, 6H), 6.39 – 6.29 (m, 12H), 3.57 (s, 6H), 3.51 – 3.38 (m, 6H), 1.62 (m, 6H), 1.43 (m, 6H), 0.99 (t, *J* = 12.1 Hz, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.3, 132.8, 131.1, 122.4, 115.0, 110.0, 42.9, 39.2, 26.2, 19.9, 13.8. HR-MS (ESI) *m/z* calculated for C<sub>85</sub>H<sub>86</sub>N<sub>5</sub>O<sub>5</sub> [M+H]<sup>+</sup> 1256.6629, found: 1256.6620.

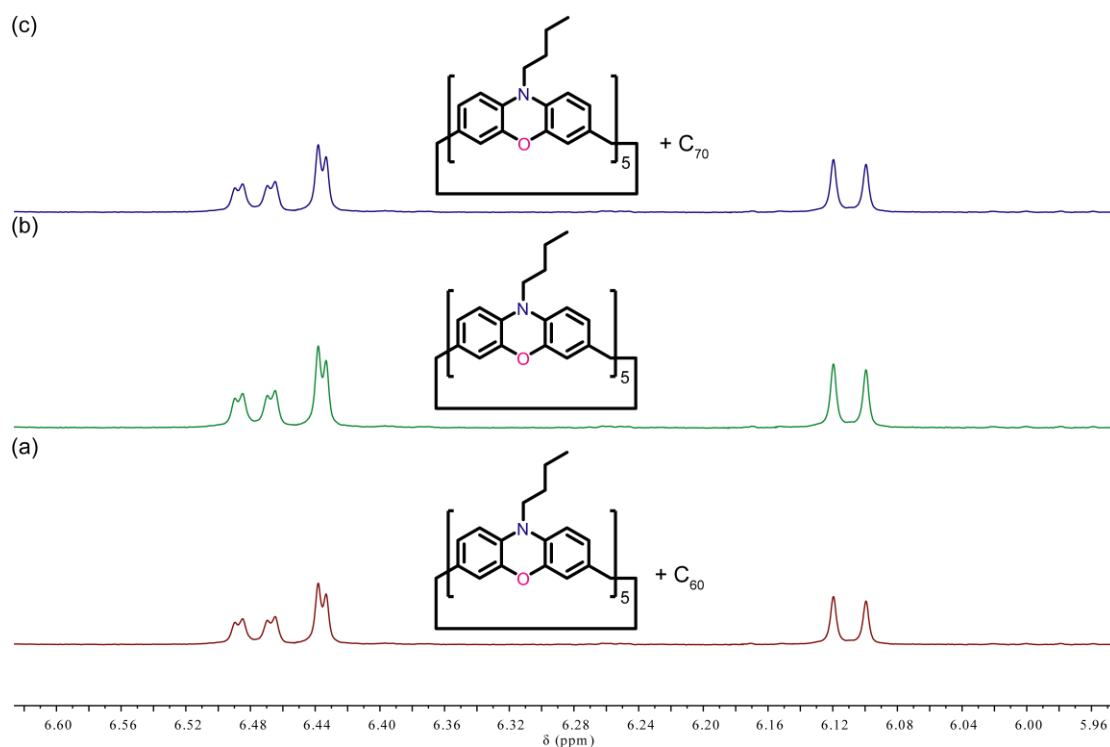
**4**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.57 (dd, *J* = 8.1, 1.7 Hz, 6H), 6.38 – 6.28 (m, 12H), 3.57 (s, 6H), 3.51 – 3.38 (m, 6H), 1.62 (m, 6H), 1.43 (m, 6H), 0.99 (t, *J* = 12.1 Hz, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.1, 132.5, 129.9, 122.2, 114.9, 109.8, 42.7, 39.0, 26.2, 19.9, 13.8. HR-MS (ESI) *m/z* calculated for C<sub>102</sub>H<sub>103</sub>N<sub>6</sub>O<sub>6</sub> [M+H]<sup>+</sup> 1507.7939, found: 1507.7928.

### 3. Host-guest complexation

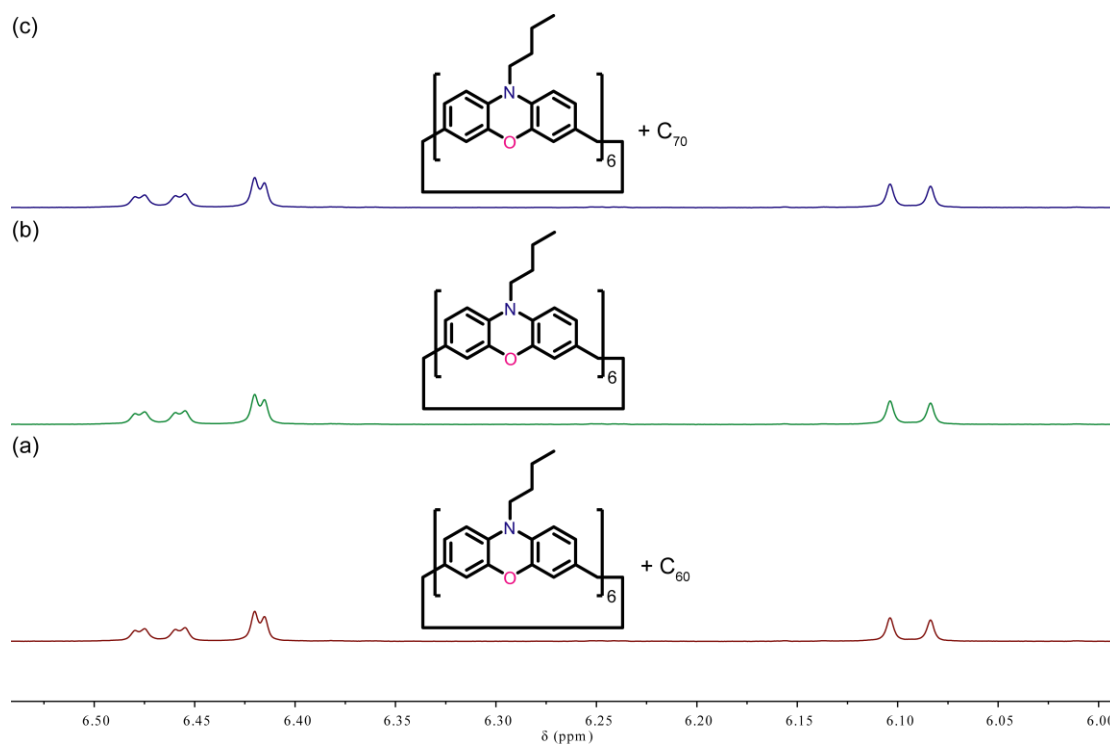
#### 3.1 Host-guest interaction



**Fig. S1** Partial <sup>1</sup>H NMR spectra (400 MHz, toluene-*d*<sub>8</sub>, 298 K) recorded for 2.0 mM **2** (b), 2.0 mM **2** + 2.0 mM C<sub>60</sub> (a), and 2.0 mM **2** + 2.0 mM C<sub>70</sub> (c).

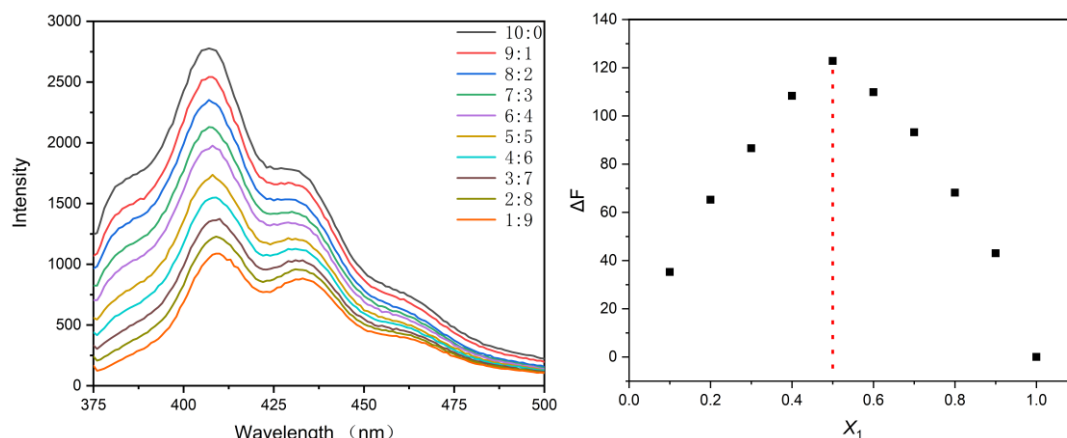


**Fig. S2** Partial  $^1\text{H}$  NMR spectra (400 MHz, toluene- $d_8$ , 298 K) recorded for 2.0 mM **3** (b), 2.0 mM **3** + 2.0 mM  $\text{C}_{60}$  (a), and 2.0 mM **3** + 2.0 mM  $\text{C}_{70}$  (c).

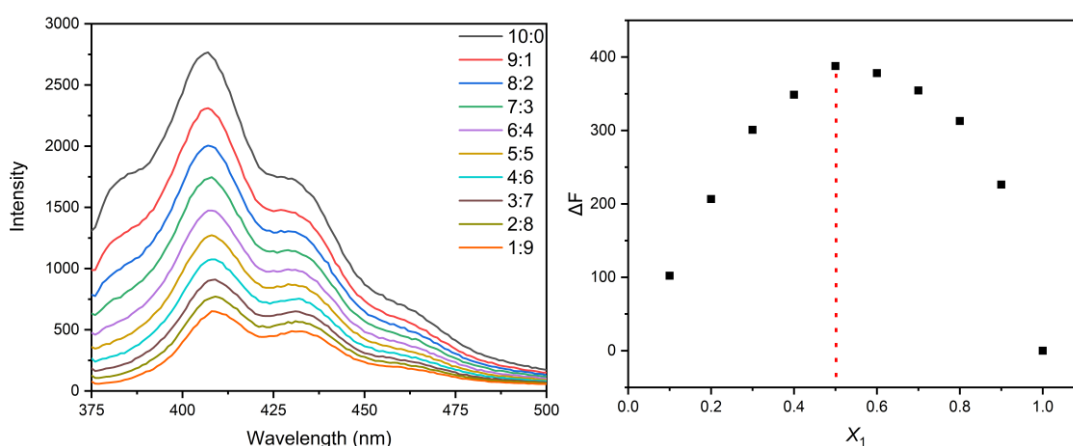


**Fig. S3** Partial  $^1\text{H}$  NMR spectra (400 MHz, toluene- $d_8$ , 298 K) recorded for 2.0 mM **4** (b), 2.0 mM **4** + 2.0 mM  $\text{C}_{60}$  (a), and 2.0 mM **4** + 2.0 mM  $\text{C}_{70}$  (c).

### 3.2 Job plot



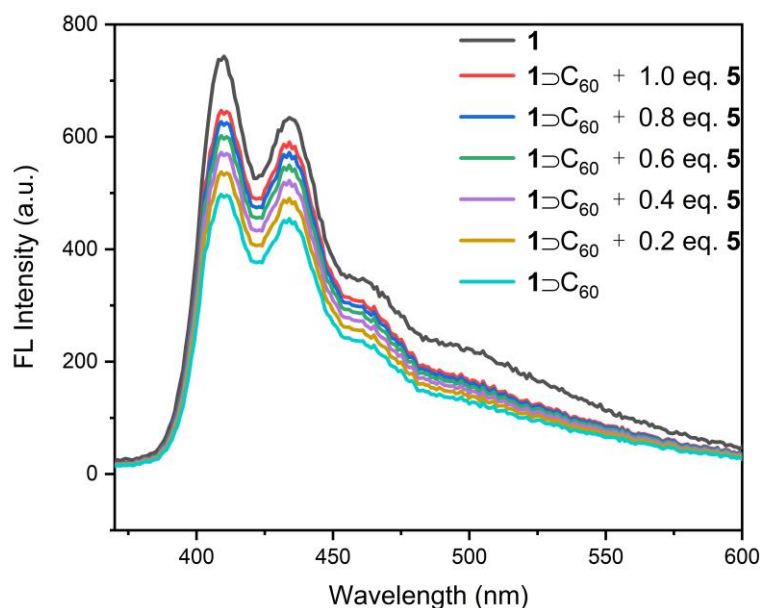
**Fig. S4** (a) Fluorescence spectra of **1** and C<sub>60</sub> with different molar ratio when the total concentration of **1** and C<sub>60</sub> were fixed at 100  $\mu$ M in toluene. (b) Job plot for the determination of stoichiometry in the complex formed by **1** and C<sub>60</sub> from absorbance measurement in toluene, [**1**] + [C<sub>60</sub>] = 100  $\mu$ M.



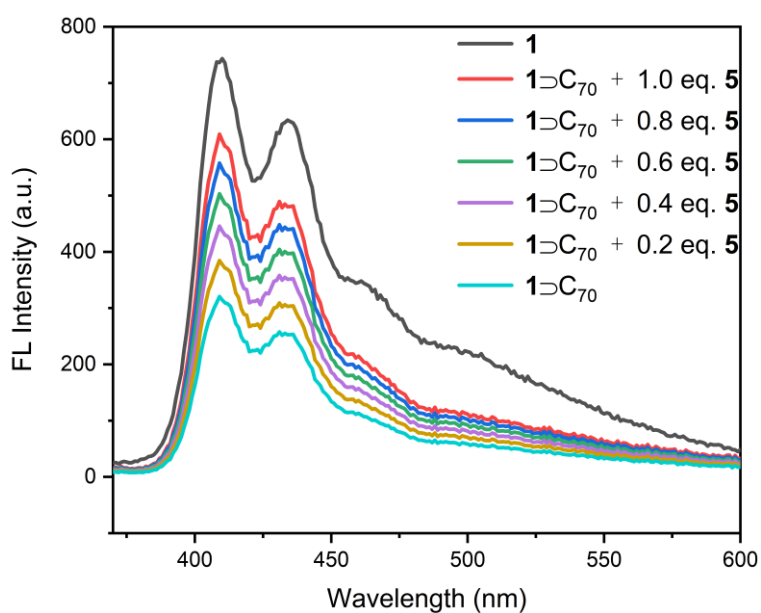
**Fig. S5** (a) Fluorescence spectra of **1** and C<sub>70</sub> with different molar ratio when the total concentration of **1** and C<sub>70</sub> were fixed at 100  $\mu$ M in toluene. (b) Job plot for the determination of stoichiometry in the complex formed by **1** and C<sub>70</sub> from absorbance measurement in toluene, [**1**] + [C<sub>70</sub>] = 100  $\mu$ M.

### 3.3 Competitive fluorescence titration

To further demonstrate that the decreased fluorescence intensity was due to the encapsulation of fullerenes within the cavity of calix[3]phenoxazine **1**, we conducted competitive fluorescence titration experiments.



**Fig. S6** Emission spectra ( $\lambda_{\text{ex}} = 350$  nm) of **1** (black line) and **1** $\text{C}_{60}$  ( $2.0 \times 10^{-5}$  M) in the presence of **5** in toluene/chloroform (2/1, v/v), [**5**] from bottom to top was 0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv.

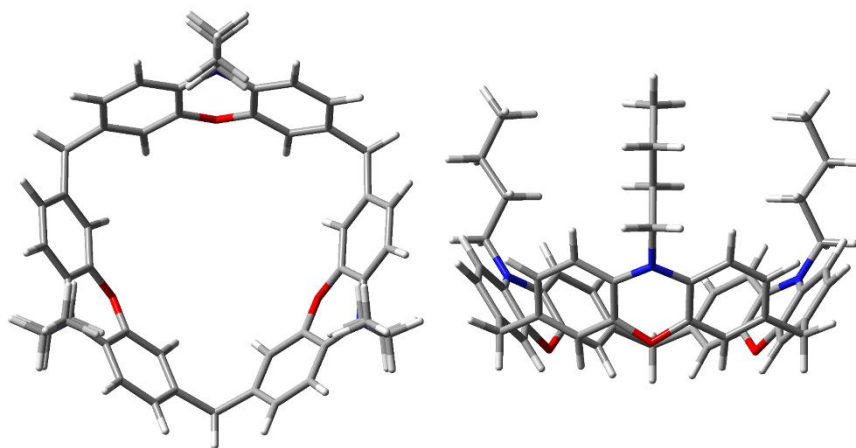


**Fig. S7** Emission spectra ( $\lambda_{\text{ex}} = 350$  nm) of **1** (black line) and **1** $\text{C}_{70}$  ( $2.0 \times 10^{-5}$  M) in the presence of **5** in toluene/chloroform (2/1, v/v), [**5**] from bottom to top was 0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv.

#### 4. Theoretical calculation

Geometries of molecules **1**,  $\text{C}_{60}$ ,  $\text{C}_{70}$ , **1** $\text{C}_{60}$ , and **1** $\text{C}_{70}$  were optimized at B3LYP/6-31G(d) level of theory with Grimme's dispersion correction followed by frequency

calculations to confirm the stationary points. The energy of molecules **1**, C<sub>60</sub>, C<sub>70</sub>, **1**⊃C<sub>60</sub>, and **1**⊃C<sub>70</sub> were optimized at M06-2X/def2-TZVP level of theory. The intermolecular interaction energy was corrected by basis set superposition error (BSSE).



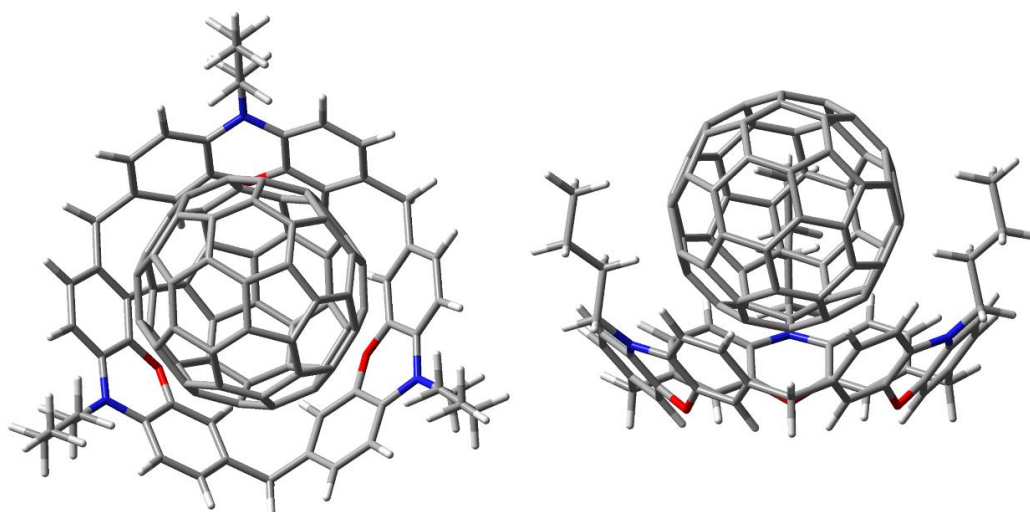
**Fig. S8** Top view (left) and side view (right) of optimized structure of **1** at the B3LYP/6-31G(d) level of theory.

**Table S1.** Atomic coordinates for the optimized structure of **1**.

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 7                | 0              | -5.118746               | -1.294693 | 0.024933  |
| 2                | 7                | 0              | 3.681238                | -3.783356 | 0.024594  |
| 3                | 7                | 0              | 1.437557                | 5.080145  | 0.028488  |
| 4                | 8                | 0              | -3.636087               | -0.919363 | -2.303554 |
| 5                | 8                | 0              | 2.613228                | -2.685469 | -2.302370 |
| 6                | 8                | 0              | 1.021971                | 3.610871  | -2.301731 |
| 7                | 6                | 0              | -4.859058               | 0.011272  | -0.427739 |
| 8                | 6                | 0              | -4.094234               | 0.176433  | -1.597989 |
| 9                | 6                | 0              | -3.798503               | 1.429078  | -2.102766 |
| 10               | 1                | 0              | -3.196163               | 1.483903  | -3.003996 |
| 11               | 6                | 0              | -4.263340               | 2.588501  | -1.465714 |
| 12               | 6                | 0              | -5.034043               | 2.435735  | -0.316407 |
| 13               | 1                | 0              | -5.405817               | 3.314548  | 0.203660  |
| 14               | 6                | 0              | -5.325403               | 1.169513  | 0.202170  |
| 15               | 1                | 0              | -5.915660               | 1.097943  | 1.107520  |
| 16               | 6                | 0              | -4.270167               | -2.320455 | -0.428658 |
| 17               | 6                | 0              | -3.518643               | -2.101774 | -1.598803 |
| 18               | 6                | 0              | -2.662568               | -3.062915 | -2.103659 |
| 19               | 1                | 0              | -2.105622               | -2.824200 | -3.004154 |
| 20               | 6                | 0              | -2.520385               | -4.304127 | -1.466958 |
| 21               | 6                | 0              | -3.271818               | -4.536788 | -0.318274 |
| 22               | 1                | 0              | -3.181137               | -5.486860 | 0.201459  |
| 23               | 6                | 0              | -4.130265               | -3.561614 | 0.200498  |
| 24               | 1                | 0              | -4.683718               | -3.779830 | 1.105611  |
| 25               | 6                | 0              | -1.503207               | -5.312337 | -1.967944 |
| 26               | 1                | 0              | -1.786906               | -6.316014 | -1.632680 |
| 27               | 1                | 0              | -1.507081               | -5.327778 | -3.064652 |
| 28               | 6                | 0              | -0.109290               | -4.985109 | -1.465758 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 29 | 6 | 0 | 0.661327  | -4.001401 | -2.101823 |
| 30 | 1 | 0 | 0.311694  | -3.506166 | -3.002131 |
| 31 | 6 | 0 | 1.894094  | -3.631133 | -1.597297 |
| 32 | 6 | 0 | 2.420437  | -4.211825 | -0.427905 |
| 33 | 6 | 0 | 1.651373  | -5.195945 | 0.201328  |
| 34 | 1 | 0 | 2.009390  | -5.671961 | 1.105985  |
| 35 | 6 | 0 | 0.409272  | -5.577223 | -0.317350 |
| 36 | 1 | 0 | -0.165218 | -6.339624 | 0.201979  |
| 37 | 6 | 0 | 4.144733  | -2.535132 | -0.428231 |
| 38 | 6 | 0 | 3.578923  | -1.993009 | -1.597736 |
| 39 | 6 | 0 | 3.983532  | -0.771215 | -2.102637 |
| 40 | 1 | 0 | 3.498270  | -0.408170 | -3.003065 |
| 41 | 6 | 0 | 4.988075  | -0.028047 | -1.466445 |
| 42 | 6 | 0 | 5.565479  | -0.562711 | -0.317978 |
| 43 | 1 | 0 | 6.343353  | -0.009447 | 0.201441  |
| 44 | 6 | 0 | 5.149962  | -1.793712 | 0.200773  |
| 45 | 1 | 0 | 5.615793  | -2.164369 | 1.105617  |
| 46 | 6 | 0 | 5.353470  | 1.356507  | -1.967997 |
| 47 | 1 | 0 | 5.368656  | 1.360776  | -3.064713 |
| 48 | 1 | 0 | 6.364717  | 1.612041  | -1.632849 |
| 49 | 6 | 0 | 4.373940  | 2.400625  | -1.465610 |
| 50 | 6 | 0 | 3.137422  | 2.578221  | -2.102435 |
| 51 | 1 | 0 | 2.883595  | 2.029567  | -3.003883 |
| 52 | 6 | 0 | 2.200316  | 3.459835  | -1.596601 |
| 53 | 6 | 0 | 2.439439  | 4.203578  | -0.425472 |
| 54 | 6 | 0 | 3.675922  | 4.027983  | 0.204006  |
| 55 | 1 | 0 | 3.908952  | 4.573711  | 1.110097  |
| 56 | 6 | 0 | 4.627069  | 3.143492  | -0.315671 |
| 57 | 1 | 0 | 5.573978  | 3.025401  | 0.204353  |
| 58 | 6 | 0 | 0.125053  | 4.857694  | -0.425236 |
| 59 | 6 | 0 | -0.060889 | 4.098852  | -1.596222 |
| 60 | 6 | 0 | -1.321078 | 3.838322  | -2.101652 |
| 61 | 1 | 0 | -1.392384 | 3.237962  | -3.003075 |
| 62 | 6 | 0 | -2.467323 | 4.335090  | -1.464913 |
| 63 | 6 | 0 | -2.293613 | 5.100913  | -0.315255 |
| 64 | 1 | 0 | -3.161940 | 5.496871  | 0.204592  |
| 65 | 6 | 0 | -1.019998 | 5.356082  | 0.204297  |
| 66 | 1 | 0 | -0.932207 | 5.943618  | 1.109971  |
| 67 | 6 | 0 | -3.848758 | 3.959129  | -1.967366 |
| 68 | 1 | 0 | -3.859208 | 3.970400  | -3.064069 |
| 69 | 1 | 0 | -4.576159 | 4.706857  | -1.632639 |
| 70 | 6 | 0 | -5.936816 | -1.501595 | 1.208955  |
| 71 | 1 | 0 | -6.360311 | -2.509611 | 1.150039  |
| 72 | 1 | 0 | -6.787723 | -0.814945 | 1.150847  |
| 73 | 6 | 0 | -5.191841 | -1.314310 | 2.538307  |
| 74 | 1 | 0 | -4.338303 | -2.002421 | 2.573818  |
| 75 | 1 | 0 | -4.768551 | -0.303015 | 2.575515  |
| 76 | 6 | 0 | -6.099632 | -1.545303 | 3.748924  |
| 77 | 1 | 0 | -6.954051 | -0.855206 | 3.700438  |
| 78 | 1 | 0 | -6.524310 | -2.558067 | 3.697889  |
| 79 | 6 | 0 | -5.368590 | -1.362776 | 5.080974  |
| 80 | 1 | 0 | -4.529554 | -2.063322 | 5.168129  |
| 81 | 1 | 0 | -6.037243 | -1.532714 | 5.931978  |
| 82 | 1 | 0 | -4.962328 | -0.348246 | 5.170594  |
| 83 | 6 | 0 | 4.270473  | -4.389391 | 1.207562  |
| 84 | 1 | 0 | 5.355083  | -4.251309 | 1.148473  |
| 85 | 1 | 0 | 4.101757  | -5.469631 | 1.148041  |
| 86 | 6 | 0 | 3.735620  | -3.839810 | 2.537641  |

|     |   |   |          |           |          |
|-----|---|---|----------|-----------|----------|
| 87  | 1 | 0 | 2.647990 | -3.977587 | 2.573492 |
| 88  | 1 | 0 | 3.906008 | -2.756857 | 2.575391 |
| 89  | 6 | 0 | 4.387567 | -4.513668 | 3.747609 |
| 90  | 1 | 0 | 4.217953 | -5.598646 | 3.695657 |
| 91  | 1 | 0 | 5.476977 | -4.374158 | 3.699200 |
| 92  | 6 | 0 | 3.860862 | -3.976098 | 5.080164 |
| 93  | 1 | 0 | 4.047280 | -2.899365 | 5.170961 |
| 94  | 1 | 0 | 4.340811 | -4.472494 | 5.930711 |
| 95  | 1 | 0 | 2.779023 | -4.132381 | 5.166995 |
| 96  | 6 | 0 | 1.666275 | 5.890236  | 1.213988 |
| 97  | 1 | 0 | 1.003476 | 6.759881  | 1.156628 |
| 98  | 1 | 0 | 2.685773 | 6.285548  | 1.156764 |
| 99  | 6 | 0 | 1.456925 | 5.148381  | 2.541812 |
| 100 | 1 | 0 | 0.434572 | 4.752465  | 2.576691 |
| 101 | 1 | 0 | 2.121484 | 4.276416  | 2.576720 |
| 102 | 6 | 0 | 1.710355 | 6.047233  | 3.754618 |
| 103 | 1 | 0 | 2.734842 | 6.443198  | 3.706958 |
| 104 | 1 | 0 | 1.044778 | 6.920889  | 3.705970 |
| 105 | 6 | 0 | 1.503813 | 5.319313  | 5.084860 |
| 106 | 1 | 0 | 0.477758 | 4.942428  | 5.171538 |
| 107 | 1 | 0 | 1.691188 | 5.981215  | 5.937478 |
| 108 | 1 | 0 | 2.179599 | 4.460197  | 5.171926 |



**Fig. S9** Top view (left) and side view (right) of optimized structure of  $1\supset C_{60}$  at the B3LYP/6-31G(d) level of theory.

**Table S2.** The intermolecular interaction energy of  $1\supset C_{60}$ .

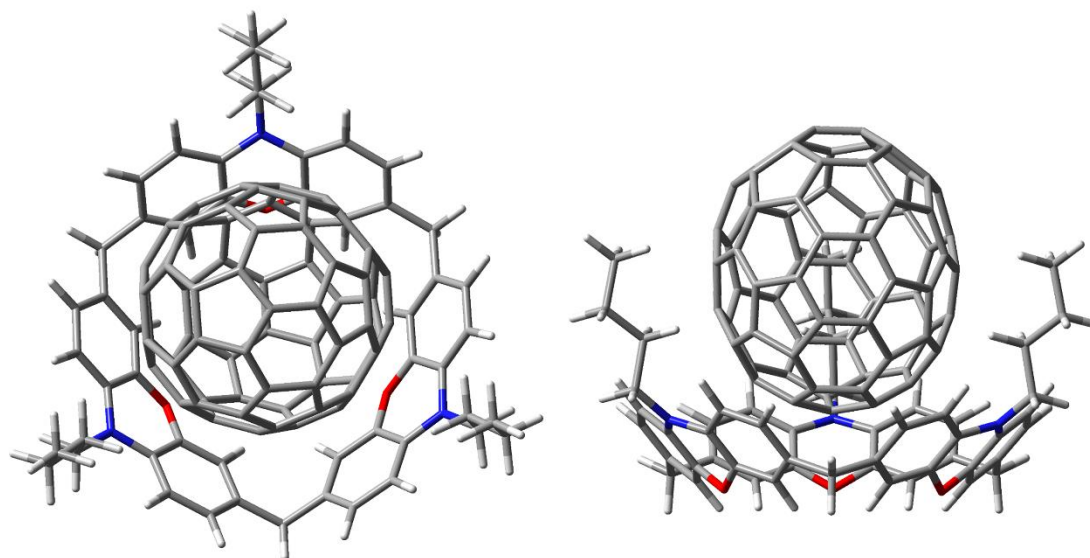
|                                   | Energy                                |
|-----------------------------------|---------------------------------------|
| <b>1</b>                          | -2363.990967 Hartree                  |
| <b>C<sub>60</sub></b>             | -2286.1813 Hartree                    |
| <b>1⊃C<sub>60</sub></b>           | -4650.233469 Hartree                  |
| <b>BSSE</b>                       | 0.004009056 Hartree                   |
| intermolecular interaction energy | -0.057192944 Hartree (-35.9 kcal/mol) |

**Table S3.** Atomic coordinates for the optimized structure of  $1\supset C_{60}$ .

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 7                | 0              | 2.377031                | 5.048936  | -1.820026 |
| 2                | 7                | 0              | -5.610327               | -0.433123 | -1.887276 |
| 3                | 7                | 0              | 3.177762                | -4.530479 | -1.900245 |
| 4                | 8                | 0              | 1.564953                | 3.408936  | -3.906030 |
| 5                | 8                | 0              | -3.680400               | -0.263542 | -3.876924 |
| 6                | 8                | 0              | 2.068292                | -2.974237 | -3.919275 |
| 7                | 6                | 0              | 3.188557                | 3.967227  | -2.198740 |
| 8                | 6                | 0              | 2.744977                | 3.132994  | -3.240877 |
| 9                | 6                | 0              | 3.476038                | 2.036454  | -3.657849 |
| 10               | 1                | 0              | 3.073127                | 1.443463  | -4.471597 |
| 11               | 6                | 0              | 4.698866                | 1.714480  | -3.050120 |
| 12               | 6                | 0              | 5.150118                | 2.541046  | -2.023093 |
| 13               | 1                | 0              | 6.092446                | 2.319251  | -1.529786 |
| 14               | 6                | 0              | 4.410321                | 3.650116  | -1.598429 |
| 15               | 1                | 0              | 4.786938                | 4.254710  | -0.782590 |
| 16               | 6                | 0              | 1.014026                | 4.980577  | -2.147400 |
| 17               | 6                | 0              | 0.622488                | 4.131054  | -3.199222 |
| 18               | 6                | 0              | -0.699674               | 4.007229  | -3.583168 |
| 19               | 1                | 0              | -0.921659               | 3.346940  | -4.414422 |
| 20               | 6                | 0              | -1.710097               | 4.716896  | -2.918574 |
| 21               | 6                | 0              | -1.331968               | 5.552131  | -1.867404 |
| 22               | 1                | 0              | -2.090721               | 6.111516  | -1.327210 |
| 23               | 6                | 0              | 0.006712                | 5.687595  | -1.484981 |
| 24               | 1                | 0              | 0.257505                | 6.334706  | -0.653214 |
| 25               | 6                | 0              | -3.162910               | 4.580643  | -3.340116 |
| 26               | 1                | 0              | -3.734932               | 5.410841  | -2.912458 |
| 27               | 1                | 0              | -3.225813               | 4.690255  | -4.431048 |
| 28               | 6                | 0              | -3.824765               | 3.273337  | -2.940195 |
| 29               | 6                | 0              | -3.473213               | 2.069617  | -3.569005 |
| 30               | 1                | 0              | -2.723949               | 2.035849  | -4.352052 |
| 31               | 6                | 0              | -4.072744               | 0.878730  | -3.206326 |
| 32               | 6                | 0              | -5.057660               | 0.817896  | -2.203866 |
| 33               | 6                | 0              | -5.406465               | 2.017218  | -1.576241 |
| 34               | 1                | 0              | -6.146143               | 2.020070  | -0.785020 |
| 35               | 6                | 0              | -4.797823               | 3.223040  | -1.944212 |
| 36               | 1                | 0              | -5.091400               | 4.135582  | -1.432796 |
| 37               | 6                | 0              | -4.860170               | -1.574146 | -2.216178 |
| 38               | 6                | 0              | -3.876374               | -1.460499 | -3.214400 |
| 39               | 6                | 0              | -3.085986               | -2.531906 | -3.585463 |
| 40               | 1                | 0              | -2.355649               | -2.365711 | -4.369267 |
| 41               | 6                | 0              | -3.237483               | -3.786967 | -2.975156 |
| 42               | 6                | 0              | -4.210742               | -3.908526 | -1.986083 |
| 43               | 1                | 0              | -4.354053               | -4.863090 | -1.487326 |
| 44               | 6                | 0              | -5.009528               | -2.822566 | -1.606128 |
| 45               | 1                | 0              | -5.741651               | -2.956876 | -0.819043 |
| 46               | 6                | 0              | -2.376825               | -4.967752 | -3.394739 |
| 47               | 1                | 0              | -2.432240               | -5.073346 | -4.486769 |
| 48               | 1                | 0              | -2.806506               | -5.883112 | -2.974280 |
| 49               | 6                | 0              | -0.916431               | -4.879002 | -2.985662 |
| 50               | 6                | 0              | -0.051215               | -3.967941 | -3.610332 |
| 51               | 1                | 0              | -0.390973               | -3.316343 | -4.407521 |
| 52               | 6                | 0              | 1.276186                | -3.877269 | -3.236824 |
| 53               | 6                | 0              | 1.820228                | -4.687543 | -2.223445 |
| 54               | 6                | 0              | 0.958876                | -5.597080 | -1.603395 |

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 55  | 1 | 0 | 1.326357  | -6.232011 | -0.806177 |
| 56  | 6 | 0 | -0.385723 | -5.689951 | -1.985318 |
| 57  | 1 | 0 | -1.026332 | -6.404176 | -1.475442 |
| 58  | 6 | 0 | 3.795275  | -3.320593 | -2.255711 |
| 59  | 6 | 0 | 3.208184  | -2.542048 | -3.270113 |
| 60  | 6 | 0 | 3.748495  | -1.334560 | -3.668973 |
| 61  | 1 | 0 | 3.243237  | -0.796065 | -4.463191 |
| 62  | 6 | 0 | 4.908994  | -0.831197 | -3.063496 |
| 63  | 6 | 0 | 5.495312  | -1.592635 | -2.053944 |
| 64  | 1 | 0 | 6.392090  | -1.229878 | -1.559279 |
| 65  | 6 | 0 | 4.951639  | -2.818534 | -1.652427 |
| 66  | 1 | 0 | 5.428011  | -3.370845 | -0.851542 |
| 67  | 6 | 0 | 5.493880  | 0.500981  | -3.499282 |
| 68  | 1 | 0 | 5.573205  | 0.512595  | -4.594467 |
| 69  | 1 | 0 | 6.515379  | 0.583447  | -3.113155 |
| 70  | 6 | 0 | 2.894474  | 6.091652  | -0.944105 |
| 71  | 1 | 0 | 2.348748  | 7.013879  | -1.173502 |
| 72  | 1 | 0 | 3.936746  | 6.268546  | -1.234051 |
| 73  | 6 | 0 | 2.814974  | 5.793218  | 0.558817  |
| 74  | 1 | 0 | 1.766594  | 5.704271  | 0.858996  |
| 75  | 1 | 0 | 3.265402  | 4.815446  | 0.760549  |
| 76  | 6 | 0 | 3.503304  | 6.858620  | 1.413666  |
| 77  | 1 | 0 | 4.561158  | 6.935293  | 1.124159  |
| 78  | 1 | 0 | 3.058693  | 7.842693  | 1.207676  |
| 79  | 6 | 0 | 3.398873  | 6.547309  | 2.909187  |
| 80  | 1 | 0 | 2.350877  | 6.500825  | 3.228030  |
| 81  | 1 | 0 | 3.902901  | 7.307958  | 3.515278  |
| 82  | 1 | 0 | 3.850746  | 5.575350  | 3.139637  |
| 83  | 6 | 0 | -6.793081 | -0.531795 | -1.043739 |
| 84  | 1 | 0 | -7.318659 | -1.452405 | -1.321981 |
| 85  | 1 | 0 | -7.457024 | 0.296995  | -1.314739 |
| 86  | 6 | 0 | -6.524268 | -0.516334 | 0.466174  |
| 87  | 1 | 0 | -5.958577 | 0.384609  | 0.726311  |
| 88  | 1 | 0 | -5.875169 | -1.358101 | 0.728390  |
| 89  | 6 | 0 | -7.803723 | -0.577525 | 1.301875  |
| 90  | 1 | 0 | -8.448483 | 0.276804  | 1.051045  |
| 91  | 1 | 0 | -8.374819 | -1.478852 | 1.037382  |
| 92  | 6 | 0 | -7.505982 | -0.577244 | 2.803787  |
| 93  | 1 | 0 | -6.891833 | -1.442023 | 3.081434  |
| 94  | 1 | 0 | -8.426112 | -0.611972 | 3.397108  |
| 95  | 1 | 0 | -6.949945 | 0.322303  | 3.093340  |
| 96  | 6 | 0 | 3.871824  | -5.507339 | -1.071802 |
| 97  | 1 | 0 | 4.927211  | -5.492489 | -1.367488 |
| 98  | 1 | 0 | 3.488601  | -6.497775 | -1.343260 |
| 99  | 6 | 0 | 3.751779  | -5.297318 | 0.443151  |
| 100 | 1 | 0 | 4.095510  | -4.289937 | 0.700825  |
| 101 | 1 | 0 | 2.697363  | -5.332161 | 0.735156  |
| 102 | 6 | 0 | 4.540486  | -6.328427 | 1.251812  |
| 103 | 1 | 0 | 4.190793  | -7.340359 | 1.002455  |
| 104 | 1 | 0 | 5.600607  | -6.291845 | 0.962974  |
| 105 | 6 | 0 | 4.407176  | -6.091685 | 2.758754  |
| 106 | 1 | 0 | 4.776201  | -5.096037 | 3.032447  |
| 107 | 1 | 0 | 4.972264  | -6.831959 | 3.335466  |
| 108 | 1 | 0 | 3.358147  | -6.146689 | 3.072872  |
| 109 | 6 | 0 | 3.069180  | -1.698372 | 1.394514  |
| 110 | 6 | 0 | 3.380855  | -0.348132 | 0.948101  |
| 111 | 6 | 0 | 3.483719  | 0.683629  | 1.881564  |
| 112 | 6 | 0 | 3.281359  | 0.409045  | 3.296920  |

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 113 | 6 | 0 | 2.988960  | -0.887303 | 3.723477  |
| 114 | 6 | 0 | 2.883427  | -1.965726 | 2.752102  |
| 115 | 6 | 0 | 2.187358  | -2.302798 | 0.409164  |
| 116 | 6 | 0 | 1.958391  | -1.334541 | -0.649035 |
| 117 | 6 | 0 | 2.694825  | -0.124974 | -0.317988 |
| 118 | 6 | 0 | 2.133898  | 1.119154  | -0.594504 |
| 119 | 6 | 0 | 2.901537  | 1.985880  | 1.590319  |
| 120 | 6 | 0 | 2.577536  | 1.542247  | 3.879256  |
| 121 | 6 | 0 | 1.610039  | 1.332714  | 4.862823  |
| 122 | 6 | 0 | 1.304877  | -0.018873 | 5.306172  |
| 123 | 6 | 0 | 1.979589  | -1.105508 | 4.748718  |
| 124 | 6 | 0 | 1.250658  | -2.319507 | 4.412374  |
| 125 | 6 | 0 | 1.808434  | -2.850816 | 3.177860  |
| 126 | 6 | 0 | 0.966106  | -3.432131 | 2.228781  |
| 127 | 6 | 0 | 1.159957  | -3.150167 | 0.815619  |
| 128 | 6 | 0 | 0.704922  | -1.251975 | -1.252218 |
| 129 | 6 | 0 | -0.368702 | -2.138139 | -0.827886 |
| 130 | 6 | 0 | -0.145344 | -3.071978 | 0.182659  |
| 131 | 6 | 0 | -1.152710 | -3.296015 | 1.208056  |
| 132 | 6 | 0 | -0.466152 | -3.516547 | 2.473855  |
| 133 | 6 | 0 | -0.999002 | -3.008831 | 3.659141  |
| 134 | 6 | 0 | -0.122928 | -2.395859 | 4.646521  |
| 135 | 6 | 0 | -0.825882 | -1.262495 | 5.228445  |
| 136 | 6 | 0 | -0.126999 | -0.099121 | 5.551414  |
| 137 | 6 | 0 | 2.342745  | 2.517179  | 2.824485  |
| 138 | 6 | 0 | -2.200016 | 2.263858  | 3.603336  |
| 139 | 6 | 0 | -1.170377 | 3.112150  | 3.194010  |
| 140 | 6 | 0 | -0.972732 | 3.387200  | 1.778932  |
| 141 | 6 | 0 | -1.809393 | 2.801901  | 0.827755  |
| 142 | 6 | 0 | -2.880815 | 1.914526  | 1.256036  |
| 143 | 6 | 0 | -3.378275 | 0.299835  | 3.058336  |
| 144 | 6 | 0 | -2.691626 | 0.075159  | 4.320979  |
| 145 | 6 | 0 | -1.962517 | 1.288693  | 4.657414  |
| 146 | 6 | 0 | -0.707172 | 1.202847  | 5.260169  |
| 147 | 6 | 0 | 0.366372  | 2.087939  | 4.834543  |
| 148 | 6 | 0 | 0.139752  | 3.021725  | 3.823209  |
| 149 | 6 | 0 | 0.459841  | 3.458992  | 1.535096  |
| 150 | 6 | 0 | 0.991679  | 2.941190  | 0.356302  |
| 151 | 6 | 0 | 0.120564  | 2.339825  | -0.639179 |
| 152 | 6 | 0 | -1.252709 | 2.271432  | -0.409556 |
| 153 | 6 | 0 | -1.977548 | 1.055377  | -0.743292 |
| 154 | 6 | 0 | -2.981746 | 0.835117  | 0.284966  |
| 155 | 6 | 0 | -3.266704 | -0.459766 | 0.712284  |
| 156 | 6 | 0 | -3.470496 | -0.733126 | 2.126372  |
| 157 | 6 | 0 | -2.135396 | -1.173950 | 4.600765  |
| 158 | 6 | 0 | -2.242168 | -2.253359 | 3.630731  |
| 159 | 6 | 0 | -2.897896 | -2.038186 | 2.417893  |
| 160 | 6 | 0 | -2.343706 | -2.570734 | 1.180761  |
| 161 | 6 | 0 | -2.575281 | -1.594862 | 0.126779  |
| 162 | 6 | 0 | -1.610414 | -1.383941 | -0.857913 |
| 163 | 6 | 0 | -1.305753 | -0.031473 | -1.301602 |
| 164 | 6 | 0 | 0.126103  | 0.048323  | -1.551098 |
| 165 | 6 | 0 | 0.825878  | 1.210069  | -1.225833 |
| 166 | 6 | 0 | 1.148033  | 3.240015  | 2.797159  |
| 167 | 6 | 0 | 2.236187  | 2.192155  | 0.382057  |
| 168 | 6 | 0 | -3.074238 | 1.653231  | 2.613493  |



**Fig. S10** Top view (left) and side view (right) of optimized structure of **1⊃C<sub>70</sub>** at the B3LYP/6-31G(d) level of theory.

**Table S4.** The intermolecular interaction energy of **1⊃C<sub>70</sub>**.

|                                   | Energy                                |
|-----------------------------------|---------------------------------------|
| <b>1</b>                          | -2363.990967 Hartree                  |
| <b>C<sub>70</sub></b>             | -2667.307754 Hartree                  |
| <b>1⊃C<sub>70</sub></b>           | -5031.362582 Hartree                  |
| BSSE                              | 0.003985775 Hartree                   |
| intermolecular interaction energy | -0.059875225 Hartree (-37.6 kcal/mol) |

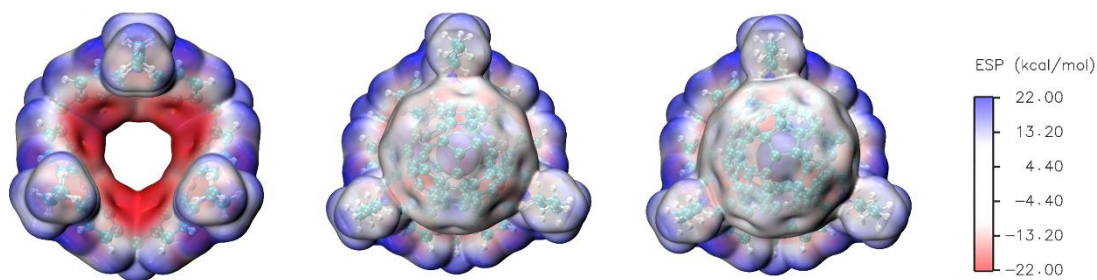
**Table S5.** Atomic coordinates for the optimized structure of **1⊃C<sub>70</sub>**.

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 7                | 0              | -5.432383               | -2.675924 | -1.035177 |
| 2                | 7                | 0              | 3.543709                | -1.506924 | -4.510014 |
| 3                | 7                | 0              | -1.013129               | 5.943515  | -0.523705 |
| 4                | 8                | 0              | -4.676341               | -1.077853 | -3.174378 |
| 5                | 8                | 0              | 1.235073                | -0.318237 | -5.493329 |
| 6                | 8                | 0              | -1.787731               | 4.636997  | -2.851479 |
| 7                | 6                | 0              | -5.609424               | -1.285010 | -0.949348 |
| 8                | 6                | 0              | -5.198716               | -0.492811 | -2.036259 |
| 9                | 6                | 0              | -5.313878               | 0.884758  | -2.020066 |
| 10               | 1                | 0              | -4.979796               | 1.425413  | -2.898656 |
| 11               | 6                | 0              | -5.856768               | 1.550604  | -0.909699 |
| 12               | 6                | 0              | -6.271030               | 0.772488  | 0.168833  |
| 13               | 1                | 0              | -6.692769               | 1.252891  | 1.047375  |
| 14               | 6                | 0              | -6.148837               | -0.622602 | 0.156441  |
| 15               | 1                | 0              | -6.465349               | -1.186829 | 1.025269  |
| 16               | 6                | 0              | -4.464727               | -3.148241 | -1.936486 |
| 17               | 6                | 0              | -4.088098               | -2.317394 | -3.006894 |
| 18               | 6                | 0              | -3.137022               | -2.704181 | -3.931461 |
| 19               | 1                | 0              | -2.903715               | -2.010115 | -4.731190 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 20 | 6 | 0 | -2.499118 | -3.949579 | -3.829929 |
| 21 | 6 | 0 | -2.864225 | -4.779169 | -2.771801 |
| 22 | 1 | 0 | -2.387192 | -5.748840 | -2.659568 |
| 23 | 6 | 0 | -3.829715 | -4.389598 | -1.836073 |
| 24 | 1 | 0 | -4.072329 | -5.058674 | -1.019625 |
| 25 | 6 | 0 | -1.448170 | -4.369420 | -4.842773 |
| 26 | 1 | 0 | -1.264573 | -5.443778 | -4.736309 |
| 27 | 1 | 0 | -1.851967 | -4.222741 | -5.853543 |
| 28 | 6 | 0 | -0.123784 | -3.632939 | -4.735278 |
| 29 | 6 | 0 | -0.010216 | -2.296510 | -5.145224 |
| 30 | 1 | 0 | -0.856966 | -1.751884 | -5.548159 |
| 31 | 6 | 0 | 1.196185  | -1.627946 | -5.055881 |
| 32 | 6 | 0 | 2.358348  | -2.255105 | -4.567933 |
| 33 | 6 | 0 | 2.244763  | -3.586631 | -4.158321 |
| 34 | 1 | 0 | 3.106949  | -4.103463 | -3.754427 |
| 35 | 6 | 0 | 1.020701  | -4.258933 | -4.241693 |
| 36 | 1 | 0 | 0.966595  | -5.292439 | -3.910926 |
| 37 | 6 | 0 | 3.428511  | -0.107881 | -4.488193 |
| 38 | 6 | 0 | 2.241539  | 0.472315  | -4.971093 |
| 39 | 6 | 0 | 2.046901  | 1.840700  | -4.970931 |
| 40 | 1 | 0 | 1.108675  | 2.214887  | -5.365508 |
| 41 | 6 | 0 | 3.035896  | 2.707389  | -4.482339 |
| 42 | 6 | 0 | 4.216766  | 2.141323  | -4.006136 |
| 43 | 1 | 0 | 5.002180  | 2.783933  | -3.617876 |
| 44 | 6 | 0 | 4.414987  | 0.756155  | -4.004762 |
| 45 | 1 | 0 | 5.339743  | 0.355234  | -3.608299 |
| 46 | 6 | 0 | 2.814537  | 4.209914  | -4.470579 |
| 47 | 1 | 0 | 2.461875  | 4.526149  | -5.461254 |
| 48 | 1 | 0 | 3.775982  | 4.708831  | -4.309150 |
| 49 | 6 | 0 | 1.827431  | 4.689152  | -3.420989 |
| 50 | 6 | 0 | 0.451571  | 4.470528  | -3.581808 |
| 51 | 1 | 0 | 0.054850  | 3.968860  | -4.457604 |
| 52 | 6 | 0 | -0.449024 | 4.889034  | -2.621379 |
| 53 | 6 | 0 | -0.035254 | 5.559147  | -1.455713 |
| 54 | 6 | 0 | 1.335925  | 5.778194  | -1.296533 |
| 55 | 1 | 0 | 1.706342  | 6.270740  | -0.405785 |
| 56 | 6 | 0 | 2.248201  | 5.346975  | -2.266602 |
| 57 | 1 | 0 | 3.307639  | 5.527243  | -2.106660 |
| 58 | 6 | 0 | -2.242428 | 5.265315  | -0.555917 |
| 59 | 6 | 0 | -2.604602 | 4.594143  | -1.738246 |
| 60 | 6 | 0 | -3.793035 | 3.896490  | -1.847218 |
| 61 | 1 | 0 | -4.004660 | 3.414010  | -2.795075 |
| 62 | 6 | 0 | -4.693936 | 3.833178  | -0.773296 |
| 63 | 6 | 0 | -4.347053 | 4.499964  | 0.399318  |
| 64 | 1 | 0 | -5.017290 | 4.469412  | 1.253915  |
| 65 | 6 | 0 | -3.140307 | 5.202155  | 0.513409  |
| 66 | 1 | 0 | -2.899530 | 5.688675  | 1.450995  |
| 67 | 6 | 0 | -5.997988 | 3.064109  | -0.898973 |
| 68 | 1 | 0 | -6.505168 | 3.377088  | -1.821613 |
| 69 | 1 | 0 | -6.657320 | 3.349653  | -0.072488 |
| 70 | 6 | 0 | -6.033719 | -3.568988 | -0.054226 |
| 71 | 1 | 0 | -6.188907 | -4.536102 | -0.545843 |
| 72 | 1 | 0 | -7.030457 | -3.177145 | 0.178299  |
| 73 | 6 | 0 | -5.228764 | -3.759249 | 1.237382  |
| 74 | 1 | 0 | -4.221892 | -4.111120 | 0.989525  |
| 75 | 1 | 0 | -5.090288 | -2.789301 | 1.725682  |
| 76 | 6 | 0 | -5.883996 | -4.734334 | 2.216516  |
| 77 | 1 | 0 | -6.896633 | -4.385342 | 2.463965  |

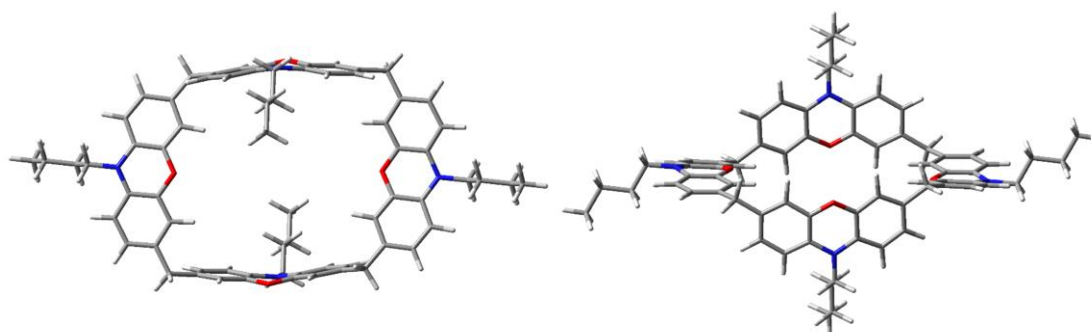
|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 78  | 1 | 0 | -6.008142 | -5.714058 | 1.733597  |
| 79  | 6 | 0 | -5.063558 | -4.890528 | 3.500071  |
| 80  | 1 | 0 | -4.053155 | -5.254043 | 3.278444  |
| 81  | 1 | 0 | -5.532144 | -5.596092 | 4.194647  |
| 82  | 1 | 0 | -4.956285 | -3.929006 | 4.015862  |
| 83  | 6 | 0 | 4.834512  | -2.148009 | -4.299068 |
| 84  | 1 | 0 | 5.589143  | -1.525774 | -4.794209 |
| 85  | 1 | 0 | 4.818924  | -3.102855 | -4.836861 |
| 86  | 6 | 0 | 5.224785  | -2.375368 | -2.833671 |
| 87  | 1 | 0 | 4.506751  | -3.054933 | -2.365531 |
| 88  | 1 | 0 | 5.141100  | -1.432047 | -2.283724 |
| 89  | 6 | 0 | 6.639219  | -2.936875 | -2.676656 |
| 90  | 1 | 0 | 6.722059  | -3.885884 | -3.225383 |
| 91  | 1 | 0 | 7.360354  | -2.251036 | -3.144012 |
| 92  | 6 | 0 | 7.014585  | -3.155445 | -1.208250 |
| 93  | 1 | 0 | 6.966136  | -2.215096 | -0.646993 |
| 94  | 1 | 0 | 8.028669  | -3.557706 | -1.108894 |
| 95  | 1 | 0 | 6.323644  | -3.856290 | -0.725413 |
| 96  | 6 | 0 | -0.688025 | 6.861252  | 0.560021  |
| 97  | 1 | 0 | -1.606224 | 7.400599  | 0.819455  |
| 98  | 1 | 0 | 0.005014  | 7.607927  | 0.155597  |
| 99  | 6 | 0 | -0.085877 | 6.216348  | 1.815194  |
| 100 | 1 | 0 | -0.794709 | 5.493253  | 2.230849  |
| 101 | 1 | 0 | 0.799783  | 5.635507  | 1.537172  |
| 102 | 6 | 0 | 0.291293  | 7.237170  | 2.889818  |
| 103 | 1 | 0 | 1.003008  | 7.964719  | 2.474173  |
| 104 | 1 | 0 | -0.598270 | 7.812964  | 3.182289  |
| 105 | 6 | 0 | 0.901542  | 6.565018  | 4.123098  |
| 106 | 1 | 0 | 0.199936  | 5.849419  | 4.567732  |
| 107 | 1 | 0 | 1.169158  | 7.298332  | 4.891552  |
| 108 | 1 | 0 | 1.807755  | 6.008011  | 3.856843  |
| 109 | 6 | 0 | 3.728176  | -2.308096 | 0.372451  |
| 110 | 6 | 0 | 3.880032  | -3.007466 | 1.633747  |
| 111 | 6 | 0 | 2.884664  | -3.875927 | 2.062399  |
| 112 | 6 | 0 | 1.703111  | -4.081390 | 1.244474  |
| 113 | 6 | 0 | 1.573187  | -3.481047 | -0.036534 |
| 114 | 6 | 0 | 2.623048  | -2.555423 | -0.483856 |
| 115 | 6 | 0 | 2.269507  | -1.505010 | -1.369593 |
| 116 | 6 | 0 | 2.807992  | -0.185120 | -1.216020 |
| 117 | 6 | 0 | 3.715096  | 0.122252  | -0.167687 |
| 118 | 6 | 0 | 4.268140  | -0.985771 | 0.528583  |
| 119 | 6 | 0 | 4.752029  | -0.859579 | 1.891121  |
| 120 | 6 | 0 | 4.526109  | -2.116750 | 2.579306  |
| 121 | 6 | 0 | 4.143755  | -2.123340 | 3.922465  |
| 122 | 6 | 0 | 3.101592  | -3.031917 | 4.371675  |
| 123 | 6 | 0 | 2.489200  | -3.892332 | 3.457652  |
| 124 | 6 | 0 | 1.051973  | -4.086213 | 3.487250  |
| 125 | 6 | 0 | 0.574162  | -4.211674 | 2.122410  |
| 126 | 6 | 0 | -0.710783 | -3.742360 | 1.739762  |
| 127 | 6 | 0 | -0.878694 | -3.410115 | 0.367861  |
| 128 | 6 | 0 | 0.248878  | -3.282718 | -0.512091 |
| 129 | 6 | 0 | -0.061942 | -2.258682 | -1.494944 |
| 130 | 6 | 0 | -1.394743 | -1.754293 | -1.228596 |
| 131 | 6 | 0 | -1.889797 | -2.462526 | -0.065084 |
| 132 | 6 | 0 | -2.652230 | -1.792658 | 0.879739  |
| 133 | 6 | 0 | -2.440914 | -2.047514 | 2.292291  |
| 134 | 6 | 0 | -1.525767 | -3.035482 | 2.740731  |
| 135 | 6 | 0 | -0.997004 | -2.853132 | 4.046538  |

|     |   |   |           |           |           |
|-----|---|---|-----------|-----------|-----------|
| 136 | 6 | 0 | 0.281142  | -3.421437 | 4.431573  |
| 137 | 6 | 0 | 0.911928  | -2.531754 | 5.388016  |
| 138 | 6 | 0 | 0.018738  | -1.403379 | 5.569220  |
| 139 | 6 | 0 | -1.159514 | -1.610307 | 4.748297  |
| 140 | 6 | 0 | -1.856890 | -0.519387 | 4.164034  |
| 141 | 6 | 0 | -2.612939 | -0.808719 | 2.996281  |
| 142 | 6 | 0 | -2.930966 | 0.217943  | 2.019202  |
| 143 | 6 | 0 | -2.971818 | -0.392513 | 0.704516  |
| 144 | 6 | 0 | -2.494054 | 0.297603  | -0.411439 |
| 145 | 6 | 0 | -1.685889 | -0.399859 | -1.399406 |
| 146 | 6 | 0 | -0.645181 | 0.510246  | -1.851903 |
| 147 | 6 | 0 | -0.807352 | 1.765549  | -1.137834 |
| 148 | 6 | 0 | -1.952095 | 1.635581  | -0.250130 |
| 149 | 6 | 0 | -1.916095 | 2.217626  | 1.017962  |
| 150 | 6 | 0 | -0.736581 | 2.937041  | 1.449535  |
| 151 | 6 | 0 | 0.353112  | 3.063909  | 0.603043  |
| 152 | 6 | 0 | 0.319703  | 2.473220  | -0.718369 |
| 153 | 6 | 0 | 1.650902  | 1.966465  | -0.988573 |
| 154 | 6 | 0 | 1.802352  | 0.762208  | -1.658235 |
| 155 | 6 | 0 | 0.638041  | 0.021960  | -2.104829 |
| 156 | 6 | 0 | 0.931211  | -1.385666 | -1.913980 |
| 157 | 6 | 0 | 2.498785  | 2.264715  | 0.153760  |
| 158 | 6 | 0 | 1.698160  | 2.945843  | 1.132499  |
| 159 | 6 | 0 | 1.934454  | 2.786133  | 2.524877  |
| 160 | 6 | 0 | 3.152975  | 2.151718  | 2.886730  |
| 161 | 6 | 0 | 3.950663  | 1.464097  | 1.910244  |
| 162 | 6 | 0 | 3.552436  | 1.396893  | 0.547593  |
| 163 | 6 | 0 | 4.594849  | 0.342391  | 2.568731  |
| 164 | 6 | 0 | 4.205133  | 0.341432  | 3.966011  |
| 165 | 6 | 0 | 3.299294  | 1.458599  | 4.153289  |
| 166 | 6 | 0 | 2.207559  | 1.333097  | 5.002051  |
| 167 | 6 | 0 | 1.971940  | 0.084709  | 5.702005  |
| 168 | 6 | 0 | 2.836812  | -0.996647 | 5.520676  |
| 169 | 6 | 0 | 3.979748  | -0.865292 | 4.632052  |
| 170 | 6 | 0 | 2.294215  | -2.335544 | 5.359790  |
| 171 | 6 | 0 | 0.536841  | -0.124361 | 5.723119  |
| 172 | 6 | 0 | -0.102917 | 0.996953  | 5.060803  |
| 173 | 6 | 0 | -1.308547 | 0.835321  | 4.326547  |
| 174 | 6 | 0 | -1.559477 | 1.794692  | 3.309069  |
| 175 | 6 | 0 | -0.527247 | 2.687559  | 2.862788  |
| 176 | 6 | 0 | 0.777409  | 2.651982  | 3.424118  |
| 177 | 6 | 0 | 0.926468  | 1.895139  | 4.616982  |
| 178 | 6 | 0 | -2.414972 | 1.496936  | 2.173012  |



**Fig. S11** The molecular surface electrostatic potential of **1** (left), **1⊃C<sub>60</sub>** (middle), and **1⊃C<sub>70</sub>** (right).

According to the structure of calix[4]phenothiazine,<sup>[S2]</sup> geometry of molecule **2** was optimized at B3LYP/6-31G(d) level of theory with Grimme's dispersion correction followed by frequency calculations to confirm the stationary points.



**Fig. S12** Top view (left) and side view (right) of optimized structure of **2** at the B3LYP/6-31G(d) level of theory.

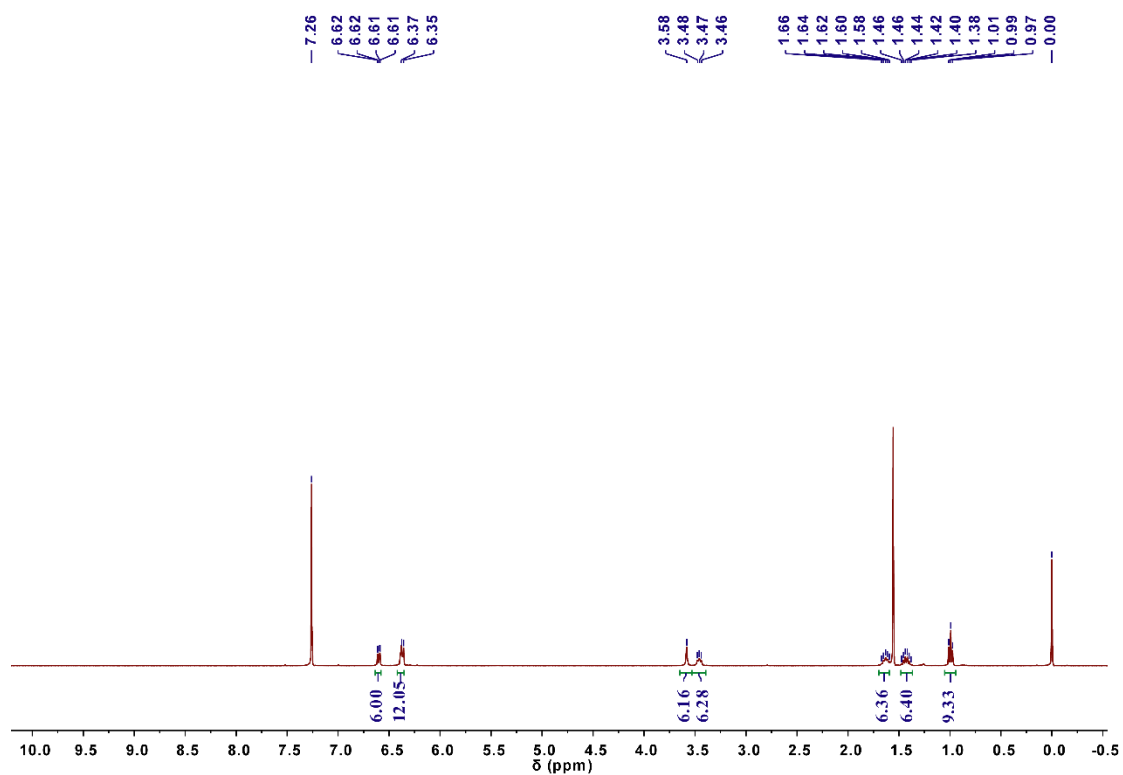
**Table S6.** Atomic coordinates for the optimized structure of **2**.

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | -2.943042               | 4.688557  | -1.339532 |
| 2                | 6                | 0              | -1.699694               | 4.678983  | -1.984617 |
| 3                | 6                | 0              | -0.541308               | 5.015360  | -1.304427 |
| 4                | 6                | 0              | -0.559862               | 5.355815  | 0.059664  |
| 5                | 6                | 0              | -1.802084               | 5.344176  | 0.705958  |
| 6                | 6                | 0              | -2.972449               | 5.026036  | 0.013130  |
| 7                | 7                | 0              | 0.649732                | 5.694696  | 0.689939  |
| 8                | 6                | 0              | 1.848981                | 5.338525  | 0.050555  |
| 9                | 6                | 0              | 1.815918                | 5.004729  | -1.314750 |
| 10               | 8                | 0              | 0.634702                | 5.027057  | -2.029626 |
| 11               | 6                | 0              | 2.967718                | 4.669813  | -2.008381 |
| 12               | 6                | 0              | 4.215276                | 4.665520  | -1.372810 |
| 13               | 6                | 0              | 4.257443                | 4.985951  | -0.016134 |
| 14               | 6                | 0              | 3.096326                | 5.310155  | 0.688118  |
| 15               | 6                | 0              | 0.657444                | 6.082957  | 2.090972  |
| 16               | 1                | 0              | -1.615310               | 4.417593  | -3.035264 |
| 17               | 1                | 0              | -1.868032               | 5.577972  | 1.761425  |
| 18               | 1                | 0              | -3.917647               | 5.020468  | 0.547232  |
| 19               | 1                | 0              | 2.874457                | 4.420855  | -3.061200 |
| 20               | 1                | 0              | 5.207292                | 4.966771  | 0.510927  |
| 21               | 1                | 0              | 3.171932                | 5.538458  | 1.744117  |
| 22               | 6                | 0              | -4.215243               | -4.665385 | 1.373075  |
| 23               | 6                | 0              | -2.967684               | -4.669634 | 2.008647  |
| 24               | 6                | 0              | -1.815902               | -5.004724 | 1.315068  |
| 25               | 6                | 0              | -1.848965               | -5.338625 | -0.050210 |
| 26               | 6                | 0              | -3.096317               | -5.310334 | -0.687766 |
| 27               | 6                | 0              | -4.257429               | -4.986042 | 0.016452  |
| 28               | 7                | 0              | -0.649705               | -5.694807 | -0.689572 |
| 29               | 6                | 0              | 0.559878                | -5.355774 | -0.059349 |
| 30               | 6                | 0              | 0.541323                | -5.015258 | 1.304727  |

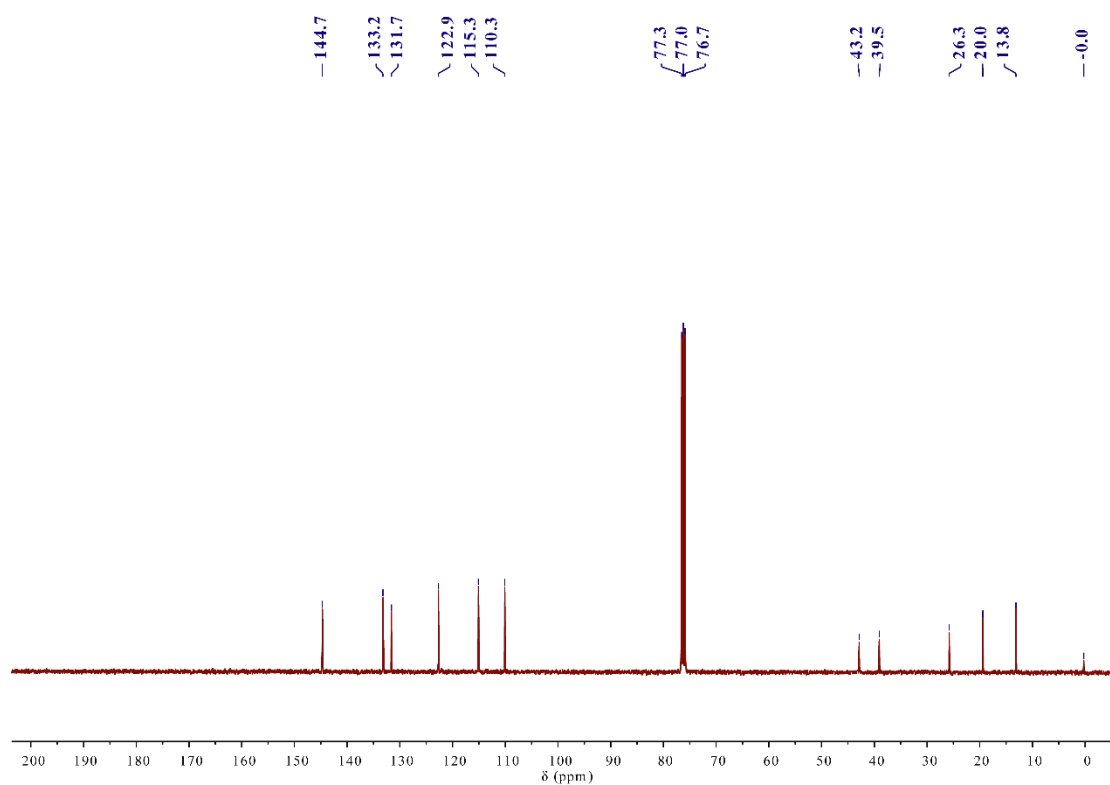
|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 31 | 8 | 0 | -0.634680 | -5.026962 | 2.029936  |
| 32 | 6 | 0 | 1.699695  | -4.678745 | 1.984878  |
| 33 | 6 | 0 | 2.943041  | -4.688318 | 1.339787  |
| 34 | 6 | 0 | 2.972456  | -5.025901 | -0.012849 |
| 35 | 6 | 0 | 1.802096  | -5.344111 | -0.705655 |
| 36 | 6 | 0 | -0.657414 | -6.083219 | -2.090563 |
| 37 | 1 | 0 | -2.874414 | -4.420542 | 3.061433  |
| 38 | 1 | 0 | -3.171934 | -5.538810 | -1.743727 |
| 39 | 1 | 0 | -5.207292 | -4.966976 | -0.510588 |
| 40 | 1 | 0 | 1.615314  | -4.417303 | 3.035511  |
| 41 | 1 | 0 | 3.917642  | -5.020263 | -0.546971 |
| 42 | 1 | 0 | 1.868046  | -5.577946 | -1.761114 |
| 43 | 1 | 0 | -1.535924 | -6.714417 | -2.258945 |
| 44 | 1 | 0 | 0.210459  | -6.727355 | -2.264699 |
| 45 | 6 | 0 | 6.099960  | 2.980722  | -1.673163 |
| 46 | 6 | 0 | 5.306376  | 1.897151  | -1.268721 |
| 47 | 6 | 0 | 5.883921  | 0.691737  | -0.912704 |
| 48 | 6 | 0 | 7.279174  | 0.503087  | -0.936412 |
| 49 | 6 | 0 | 8.067780  | 1.595948  | -1.309777 |
| 50 | 6 | 0 | 7.482130  | 2.811901  | -1.676979 |
| 51 | 7 | 0 | 7.797438  | -0.759261 | -0.603406 |
| 52 | 6 | 0 | 6.965074  | -1.660767 | 0.078388  |
| 53 | 6 | 0 | 5.576251  | -1.420082 | 0.098257  |
| 54 | 8 | 0 | 5.030952  | -0.334854 | -0.558269 |
| 55 | 6 | 0 | 4.700187  | -2.275252 | 0.740399  |
| 56 | 6 | 0 | 5.166508  | -3.434637 | 1.380547  |
| 57 | 6 | 0 | 6.534663  | -3.687084 | 1.355008  |
| 58 | 6 | 0 | 7.426261  | -2.809380 | 0.727897  |
| 59 | 6 | 0 | 9.225306  | -1.011184 | -0.698953 |
| 60 | 1 | 0 | 4.225708  | 1.981403  | -1.226384 |
| 61 | 1 | 0 | 9.147719  | 1.512772  | -1.312931 |
| 62 | 1 | 0 | 8.125536  | 3.637880  | -1.968942 |
| 63 | 1 | 0 | 3.641021  | -2.041261 | 0.712498  |
| 64 | 1 | 0 | 6.927509  | -4.576777 | 1.840035  |
| 65 | 1 | 0 | 8.485187  | -3.035900 | 0.748950  |
| 66 | 1 | 0 | 9.366588  | -2.082322 | -0.876873 |
| 67 | 6 | 0 | -6.099962 | -2.980580 | 1.673151  |
| 68 | 6 | 0 | -5.306390 | -1.896983 | 1.268740  |
| 69 | 6 | 0 | -5.883965 | -0.691639 | 0.912522  |
| 70 | 6 | 0 | -7.279231 | -0.503057 | 0.936099  |
| 71 | 6 | 0 | -8.067817 | -1.595935 | 1.309449  |
| 72 | 6 | 0 | -7.482142 | -2.811856 | 1.676736  |
| 73 | 7 | 0 | -7.797530 | 0.759263  | 0.603049  |
| 74 | 6 | 0 | -6.965144 | 1.660824  | -0.078644 |
| 75 | 6 | 0 | -5.576310 | 1.420200  | -0.098407 |
| 76 | 8 | 0 | -5.031014 | 0.335003  | 0.558179  |
| 77 | 6 | 0 | -4.700229 | 2.275418  | -0.740474 |
| 78 | 6 | 0 | -5.166531 | 3.434876  | -1.380505 |
| 79 | 6 | 0 | -6.534708 | 3.687219  | -1.355136 |
| 80 | 6 | 0 | -7.426327 | 2.809431  | -0.728172 |
| 81 | 6 | 0 | -9.225426 | 1.011086  | 0.698407  |
| 82 | 1 | 0 | -4.225710 | -1.981166 | 1.226577  |
| 83 | 1 | 0 | -9.147761 | -1.512820 | 1.312476  |
| 84 | 1 | 0 | -8.125536 | -3.637833 | 1.968731  |
| 85 | 1 | 0 | -3.641056 | 2.041470  | -0.712483 |
| 86 | 1 | 0 | -6.927548 | 4.576924  | -1.840147 |
| 87 | 1 | 0 | -8.485259 | 3.035915  | -0.749285 |
| 88 | 1 | 0 | -9.595315 | 0.506579  | 1.596899  |

|     |   |   |            |           |           |
|-----|---|---|------------|-----------|-----------|
| 89  | 6 | 0 | -4.208075  | 4.356778  | -2.105943 |
| 90  | 6 | 0 | 5.468538   | 4.284579  | -2.129025 |
| 91  | 6 | 0 | 4.208067   | -4.356416 | 2.106157  |
| 92  | 6 | 0 | -5.468498  | -4.284333 | 2.129252  |
| 93  | 1 | 0 | 9.595104   | -0.506760 | -1.597527 |
| 94  | 1 | 0 | -9.366803  | 2.082205  | 0.876372  |
| 95  | 1 | 0 | -4.741186  | 5.283160  | -2.360376 |
| 96  | 1 | 0 | -3.923275  | 3.906034  | -3.066657 |
| 97  | 1 | 0 | 5.226829   | 4.215474  | -3.198521 |
| 98  | 1 | 0 | 6.216150   | 5.083437  | -2.041558 |
| 99  | 1 | 0 | 3.923259   | -3.905508 | 3.066791  |
| 100 | 1 | 0 | 4.741185   | -5.282750 | 2.360746  |
| 101 | 1 | 0 | -6.216084  | -5.083233 | 2.041951  |
| 102 | 1 | 0 | -5.226765  | -4.215022 | 3.198729  |
| 103 | 6 | 0 | 0.651710   | 4.902980  | 3.072160  |
| 104 | 6 | 0 | -0.651682  | -4.903352 | -3.071885 |
| 105 | 6 | 0 | 10.028723  | -0.565852 | 0.530475  |
| 106 | 6 | 0 | -10.028641 | 0.565772  | -0.531159 |
| 107 | 6 | 0 | 0.652636   | 4.191040  | 5.519642  |
| 108 | 1 | 0 | -0.236172  | 3.564143  | 5.381167  |
| 109 | 1 | 0 | 1.532635   | 3.552613  | 5.377318  |
| 110 | 6 | 0 | -0.652694  | -4.191698 | -5.519452 |
| 111 | 1 | 0 | -1.532709  | -3.553287 | -5.377163 |
| 112 | 1 | 0 | 0.236098   | -3.564756 | -5.381085 |
| 113 | 6 | 0 | -12.336411 | 0.414073  | -1.604340 |
| 114 | 1 | 0 | -12.231206 | -0.663326 | -1.779025 |
| 115 | 1 | 0 | -11.996100 | 0.930443  | -2.509824 |
| 116 | 6 | 0 | 12.336662  | -0.414197 | 1.603302  |
| 117 | 1 | 0 | 12.231550  | 0.663224  | 1.777906  |
| 118 | 1 | 0 | 11.996450  | -0.930466 | 2.508880  |
| 119 | 6 | 0 | 0.658072   | 5.360736  | 4.532785  |
| 120 | 1 | 0 | 0.657189   | 4.542273  | 6.557328  |
| 121 | 1 | 0 | 1.540830   | 5.990764  | 4.713169  |
| 122 | 1 | 0 | -0.215674  | 6.002027  | 4.717081  |
| 123 | 1 | 0 | -0.229917  | 4.279118  | 2.879243  |
| 124 | 1 | 0 | 1.523884   | 4.267058  | 2.875330  |
| 125 | 1 | 0 | 1.535954   | 6.714139  | 2.259421  |
| 126 | 1 | 0 | -0.210434  | 6.727072  | 2.265178  |
| 127 | 6 | 0 | 11.524778  | -0.854174 | 0.382942  |
| 128 | 1 | 0 | 9.868459   | 0.507020  | 0.695521  |
| 129 | 1 | 0 | 9.635425   | -1.073341 | 1.420199  |
| 130 | 1 | 0 | 11.906243  | -0.347655 | -0.515116 |
| 131 | 1 | 0 | 11.672763  | -1.929827 | 0.210740  |
| 132 | 1 | 0 | 13.402854  | -0.630495 | 1.474591  |
| 133 | 6 | 0 | -0.658050  | -5.361279 | -4.532456 |
| 134 | 1 | 0 | -1.523856  | -4.267406 | -2.875129 |
| 135 | 1 | 0 | 0.229943   | -4.279463 | -2.879047 |
| 136 | 1 | 0 | 0.215727   | -6.002543 | -4.716694 |
| 137 | 1 | 0 | -1.540777  | -5.991376 | -4.712751 |
| 138 | 6 | 0 | -11.524733 | 0.853995  | -0.383824 |
| 139 | 1 | 0 | -13.402634 | 0.630292  | -1.475766 |
| 140 | 1 | 0 | -11.672805 | 1.929625  | -0.211555 |
| 141 | 1 | 0 | -11.906302 | 0.347381  | 0.514137  |
| 142 | 1 | 0 | -9.635248  | 1.073332  | -1.420800 |
| 143 | 1 | 0 | -9.868289  | -0.507081 | -0.696242 |
| 144 | 1 | 0 | -0.657278  | -4.543050 | -6.557097 |

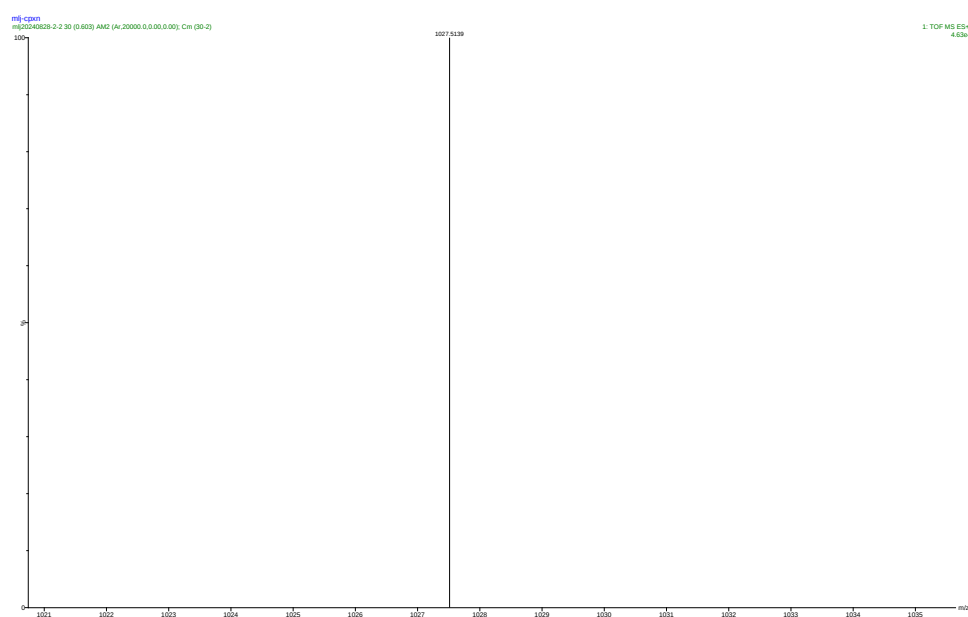
## 5. Characterization data and spectra



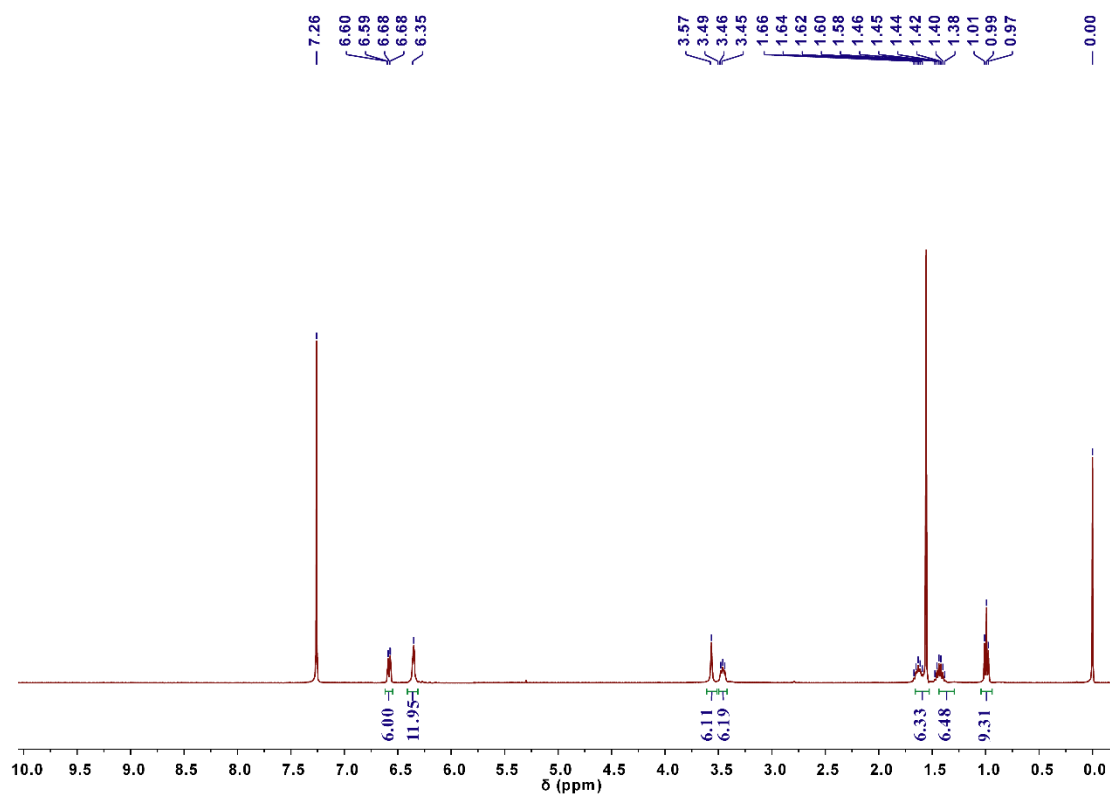
**Fig. S13** The <sup>1</sup>H NMR (400 MHz, 298 K) spectrum of compound **2** in CDCl<sub>3</sub>.



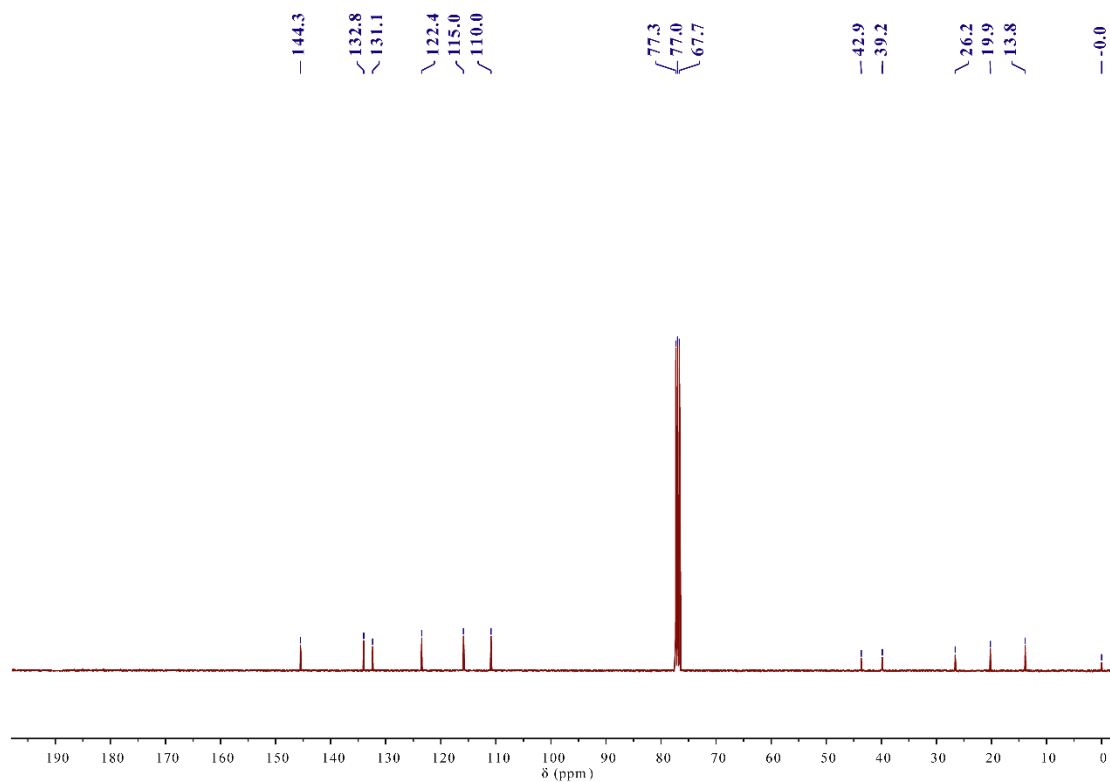
**Fig. S14** The <sup>13</sup>C NMR (100 MHz, 298 K) spectrum of compound **2** in CDCl<sub>3</sub>.



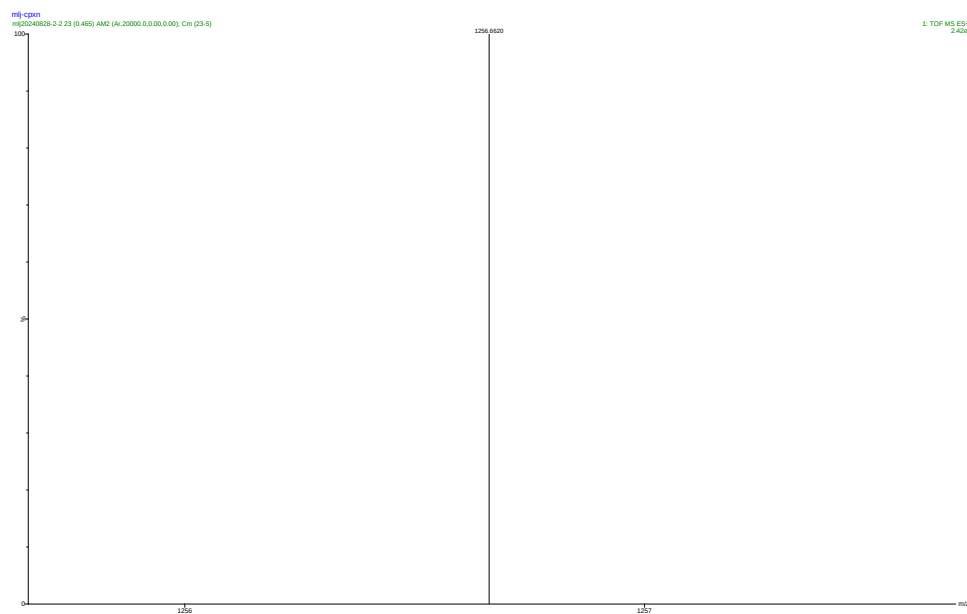
**Fig. S15** HRMS spectrum of **2**.



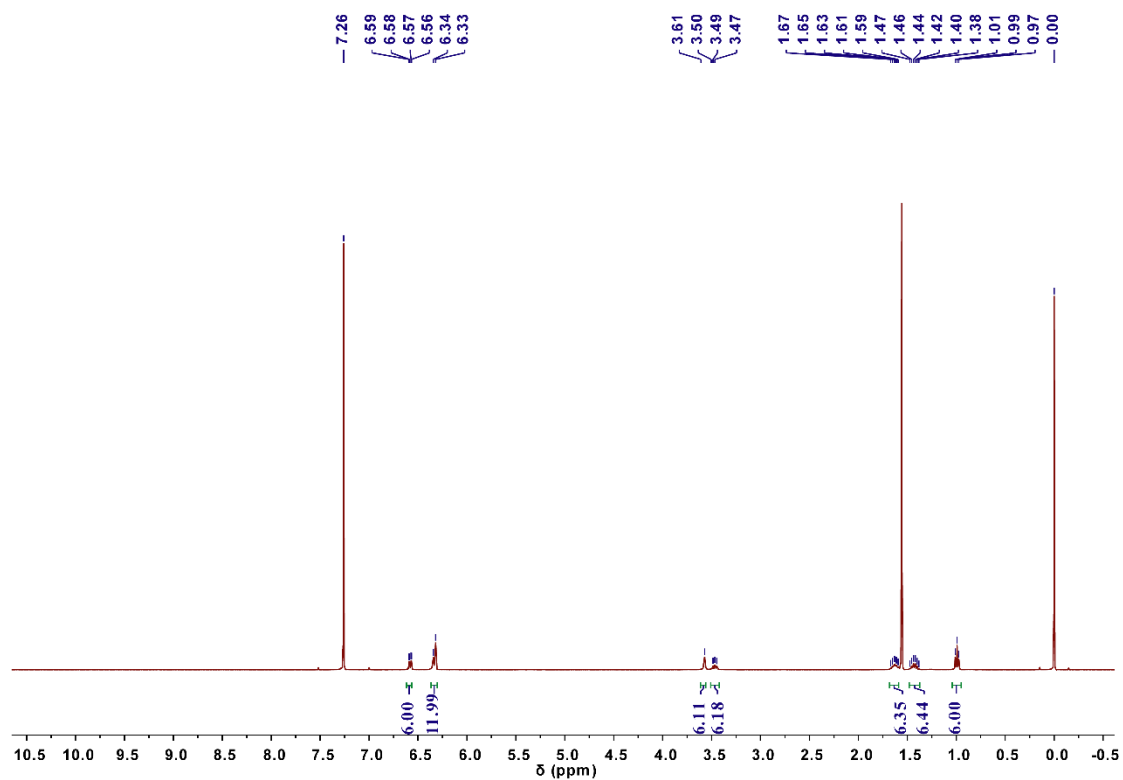
**Fig. S16** The <sup>1</sup>H NMR (400 MHz, 298 K) spectrum of compound **3** in CDCl<sub>3</sub>.



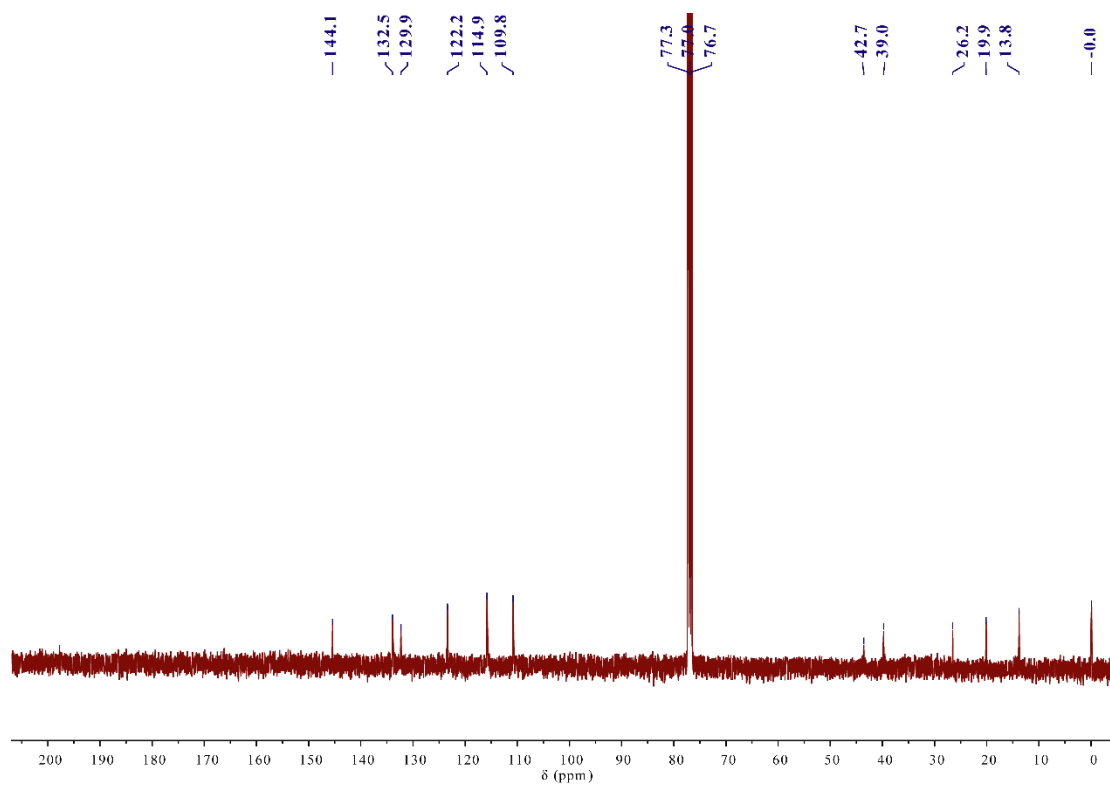
**Fig. S17** The  $^{13}\text{C}$  NMR (100 MHz, 298 K) spectrum of compound **3** in  $\text{CDCl}_3$ .



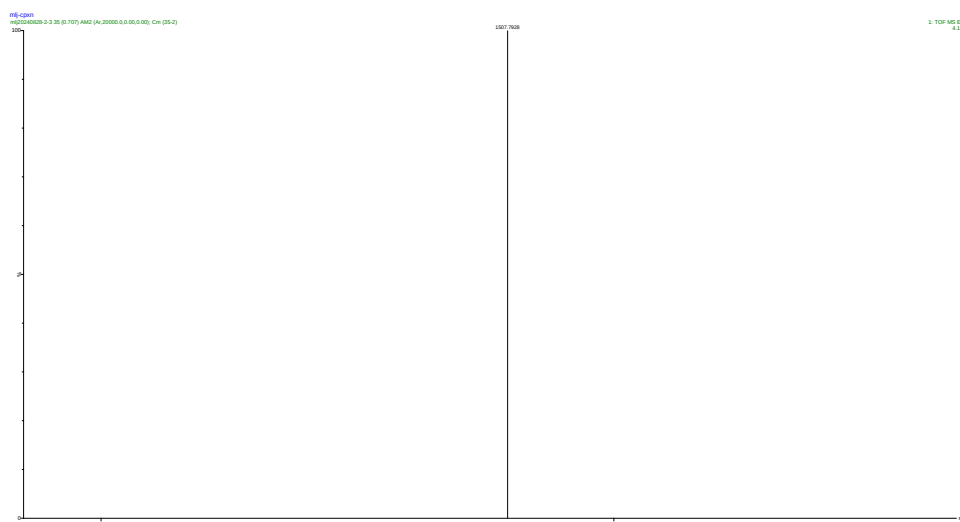
**Fig. S18** HRMS spectrum of **3**.



**Fig. S19** The  $^1\text{H}$  NMR (400 MHz, 298 K) spectrum of compound **4** in  $\text{CDCl}_3$ .



**Fig. S20** The  $^{13}\text{C}$  NMR (100 MHz, 298 K) spectrum of compound **4** in  $\text{CDCl}_3$ .



**Fig. S21** HRMS spectrum of **4**.

## 6. Reference

[S1] L. Mao, F. Li, L. Huang, X. Qu, K. Wang, Y. Zhang and D. Ma, *Org. Lett.*, 2023, **25**, 5597–5601.

[S2] L. Mao, M. Zhou, T. Wu, D. Ma, G. Dai and X. Shi, *Org. Lett.*, 2024, **26**, 7244–7248.