

## The Electronic Supplementary Information for

# Photochemical synthesis and photophysical properties of coumarins bearing extended polyaromatic rings studied by emission and transient absorption measurements

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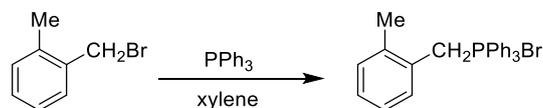
## Contents

- P. 2 1. Procedure for preparing the coumarin derivatives and the analytical data.**
- P. 17 2. Absorption and emission spectra of CM[*n*] and BCM[*n*].**
- P. 19 3. Decay profiles of fluorescence in CHCl<sub>3</sub>.**
- P. 22 4. Results of DFT and TD-DFT calculations (atom coordinates and sum of electronic and zero-point energies in vacuum).**
- P. 36 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra.**
- P. 49 6. References**

## 1. Procedure for preparing the coumarin derivatives and the analytical data.

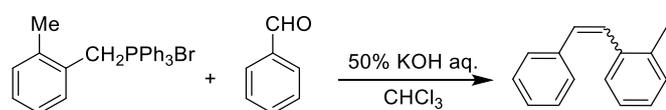
### 1-1. Preparation of 1-phenanthrene aldehyde.

#### 1-1-1. Synthesis of (*o*-methylbenzyl)triphenylphosphonium bromide.



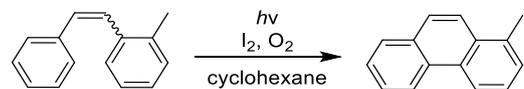
A xylene solution (120 ml) of *o*-bromo-*o*-xylene (3.12 ml, 23.3 mmol) and triphenylphosphine (7.5 g, 27.9 mmol) was refluxed under N<sub>2</sub> atmosphere for 12 h. After cooling to room temperature, the precipitate formed was collected, and washed with benzene, providing the desired phosphonium bromide (10.42 g, 99 %).

#### 1-1-2. Synthesis of 2-methylstilbene.



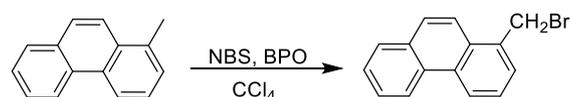
To a chloroform solution (130 ml) of (*o*-methylbenzyl)triphenylphosphonium bromide (4.5 g, 10.1 mmol) and benzaldehyde (1.0 ml, 9.8 mmol), aqueous KOH (50 %, 20 ml) was dropwise added. The mixture was stirred at 65 °C for 1 h. After cooling to room temperature, the organic layer was separated, washed with water and brine, and concentrated under reduced pressure. The product was purified by silica gel column chromatography with hexane as the eluent to obtain 2-methylstilbene (1.73 g, 91%).

#### 1-1-3. Synthesis of 1-methylphenanthrene.



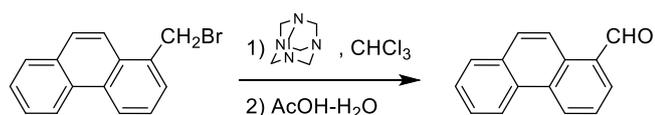
A cyclohexane solution (2000 ml) of 2-methylstilbene (1.78 g, 9.16 mmol) and 50 mg I<sub>2</sub> was photolyzed using with a home-made micro-flow photoreactor.<sup>1</sup> The photolyzed solution was washed with aqueous sodium thiosulfate and brine. After usual work-up, the product was purified by silica gel column chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 1-methylphenanthrene (1.69 g, 96 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.71 (d, 1H, *J* = 8.0 Hz), 8.60 (d, 1H, *J* = 8.2 Hz), 7.96 (d, 1H, *J* = 9.1 Hz), 7.90 (dd, 1H, *J* = 7.4, 1.4 Hz), 7.79 (d, 1H, *J* = 9.1 Hz), 7.51–7.69 (m, 3H), 7.45 (d, 1H, *J* = 7.4 Hz), 2.76 (s, 3H).

#### 1-1-4. Synthesis of 1-(bromomethyl)phenanthrene.



A CCl<sub>4</sub> solution (90 ml) of 1-methylphenanthrene (1.68 g, 8.7 mmol), *N*-bromosuccinimide (NBS, 2.18 g, 12.2 mmol) and benzoyl peroxide (BPO, 0.20 g, 0.60 mmol) was refluxed under N<sub>2</sub> atmosphere for 3 h. After cooling to room temperature, the filtrated solution was washed with water and brine. The product was purified by silica gel column chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 1-(bromomethyl)phenanthrene (1.65 g, 70 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.72 (d, 1H, *J* = 8.2 Hz), 8.70 (d, 1H, *J* = 8.4 Hz), 8.10 (d, 1H, *J* = 9.1 Hz), 7.88–7.96 (a doublet and a dd signals overlap, 2H), 7.56–7.96 (m, 4H), 5.02 (s, 2H).

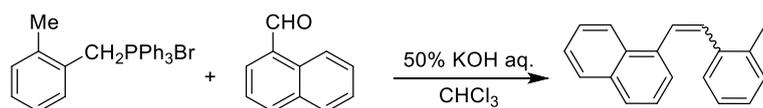
### 1-1-5. Synthesis of 1-phenanthrylcarbaldehyde.



A chloroform solution (60 ml) of 1-(bromomethyl)phenanthrene (1.65 g, 6.1 mmol) and hexamethylenetetramine (1.30 g, 9.3 mmol) was refluxed under  $\text{N}_2$  atmosphere for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. A mixture of acetic acid and water (1:1 v/v, 50 ml) was added to the residue. The solution was stirred under  $\text{N}_2$  atmosphere at 100 °C for 1 h. After cooling to room temperature, the solution was washed successively with aqueous  $\text{NaHCO}_3$ , water and brine. The product was purified by silica gel column chromatography with hexane/ethyl acetate (5:1, v/v) as the eluent to obtain 1-phenanthrenealdehyde (0.51 g, 41 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.53 (s, 1H), 9.15 (d, 1H,  $J = 9.1$  Hz), 9.01 (d, 1H,  $J = 8.4$  Hz), 8.70 (d, 1H,  $J = 8.4$  Hz), 8.10 (dd, 1H,  $J = 7.7$ , 1.2 Hz), 7.94–7.99 (a doublet and a dd signals overlap, 2H), 7.82 (dd, 1H,  $J = 7.2$ , 8.4 Hz), 7.72 (ddd, 1H,  $J = 8.4$ , 7.0, 1.4 Hz), 7.67 (ddd, 1H,  $J = 7.8$ , 7.0, 1.4 Hz).

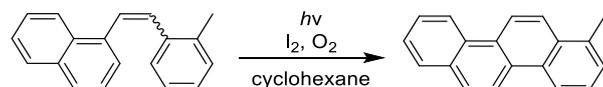
### 1-2. Preparation of 1-chrysenecarbaldehyde.

#### 1-2-1. Preparation of 1-(1-naphthyl)-2-(*o*-tolyl)ethene.



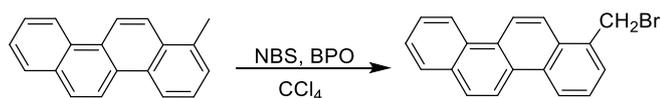
To a chloroform solution (150 ml) of *o*-methylbenzyltriphenylphosphonium 9.0 g (20.0 mmol) and 1-naphthaldehyde 2.7 ml (20.0 mmol), aqueous KOH (50 %, 50 ml) was dropwise added. The mixture was stirred at 65 °C for 1h. After cooling to room temperature, the organic layer was separated, washed with water and brine, and concentrated under reduced pressure. The product was purified by silica gel column chromatography with a hexane/chloroform mixture (1:1, v/v) to obtain 1-(1-naphthyl)-2-(*o*-tolyl)ethene (4.82 g, 98%). The compound obtained was used in the following photoreaction without further purification.

#### 1-2-2. Preparation of 1-methylchrysene.



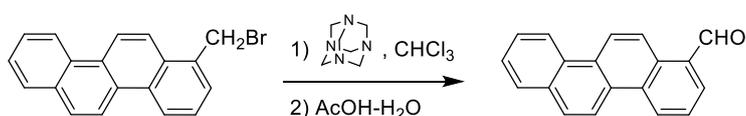
A cyclohexane solution (2000 ml) of 1-(1-naphthyl)-2-(*o*-tolyl)ethene (2.3 g, 9.4 mmol) and 50 mg  $\text{I}_2$  was photolyzed using with a home-made microflow photoreactor.<sup>1</sup> The photolyzed solution was washed with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and brine. After usual work-up, the product was purified by silica gel column chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 1-methylchrysene (1.69 g, 96 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.80 (d, 1H,  $J = 8.4$  Hz), 8.77 (d, 1H,  $J = 7.4$  Hz), 8.74 (d, 1H,  $J = 7.1$  Hz), 8.69 (d, 1H,  $J = 8.4$  Hz), 8.21 (brd, 1H,  $J = 9.3$  Hz), 7.98–8.05 (a doublet and a dd signals overlap, 2H), 7.72 (ddd, 1H,  $J = 8.4$ , 7.0, 1.4 Hz), 7.64 (ddd, 1H,  $J = 8.1$ , 7.0, 1.4 Hz), 7.60 (d, 1H,  $J = 7.0$  Hz), 7.48 (brd, 1H,  $J = 7.0$  Hz), 2.83 (s, 3H).

### 1-2-3. Preparation of 1-(bromomethyl)chrysene.



To a  $\text{CCl}_4$  solution (50 ml) of 1-methylchrysene (1.12 g, 4.6 mmol), *N*-bromosuccinimide (NBS) (1.00 g, 5.5 mmol) and benzoyl peroxide (BPO, 75 mg, 0.23 mmol) were added, the mixture was refluxed for 3 h under  $\text{N}_2$  atmosphere. After cooling to room temperature, the solution was washed with water (100 ml) and brine (100 ml). The product was purified by silica gel column chromatography with a hexane/chloroform mixture (10:1, v/v) as the eluent to obtain 1-(bromomethyl)chrysene (0.75 g 55 %).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.89 (d, 1H,  $J = 9.3$  Hz), 8.79–8.85 (two doublets overlap, 2H), 8.72 (d, 1H,  $J = 9.3$  Hz), 8.36 (d, 1H,  $J = 9.3$  Hz), 8.03 (d, 1H,  $J = 9.0$  Hz), 8.01 (d, 1H,  $J = 7.9$  Hz), 7.73 (t, 1H,  $J = 7.9$  Hz), 7.62–7.78 (m, 3H), 5.09 (s, 2H).

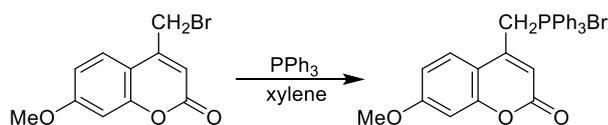
### 1-2-4. Synthesis of 1-chrysenecarbaldehyde.<sup>2</sup>



A chloroform solution (100 ml) of 1-(bromomethyl)chrysene (867 mg, 7.70 mmol) and hexamethylenetetramine (454 mg, 3.20 mmol) was refluxed for 16.5 hours. The solvent was evaporated under reduced pressure. The residue was suspended in a mixture of acetic acid (50 ml) and water (20 ml), and it was refluxed for 20 h. To the resulting mixture was added 50 ml of water, and the solid formed was collected and washed with water. The solid was triturated with a boiling toluene- $\text{CHCl}_3$  mixture for 0.5 h. The insoluble material was filtered off, and the filtrate was concentrated under reduced pressure to afford 1-chrysenecarbaldehyde (486 mg, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.52 (s, 1H), 9.39 (d, 1H,  $J = 9.5$  Hz), 9.06 (d, 1H,  $J = 8.4$  Hz), 8.90 (d, 1H,  $J = 9.5$  Hz), 8.80 (d, 1H,  $J = 8.2$  Hz), 8.67 (d, 1H,  $J = 9.1$  Hz), 8.01 (dd, 1H,  $J = 7.2, 1.1$  Hz), 8.02 (d, 1H,  $J = 9.1$  Hz), 8.01 (dd, 1H,  $J = 7.8, 1.4$  Hz), 7.84 (dd, 1H,  $J = 8.2, 7.1$  Hz), 7.74 (ddd, 1H,  $J = 8.2, 7.1, 1.1$  Hz), 7.68 (ddd, 1H,  $J = 7.9, 6.8, 1.0$  Hz).

### 1-3. Synthesis of MeOCM[*n*].

#### 1-3-1. Preparation of (7-methoxy coumarin-4-yl)methyltriphenylphosphonium bromide

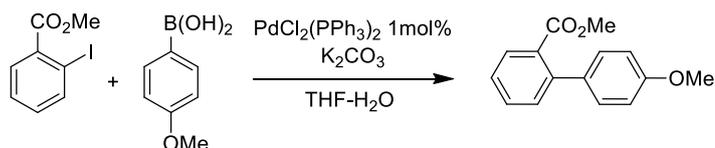


A xylene (75 ml) solution of 4-bromomethyl-7-methoxycoumarin (2.0 g, 7.4 mmol) and triphenylphosphine ( $\text{PPh}_3$ , 1.95 g, 7.4 mmol) was refluxed for 12 h under  $\text{N}_2$  atmosphere. The precipitate was collected and washed with benzene, providing the desired phosphonium salt (3.43 g, 88 %).

#### 1-3-2. Synthesis of MeOCM[1].

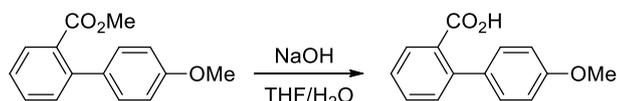
MeOCM[1] was prepared according to the literature.<sup>3</sup>

### 1-3-2-1. Preparation of methyl 2-(4-methoxyphenyl)benzoate.



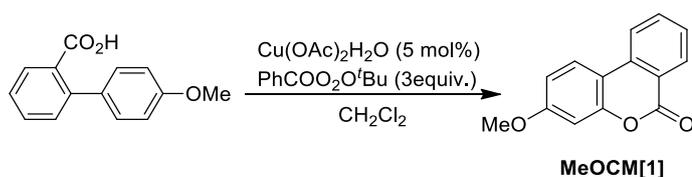
A solution of 4-methoxyphenylboronic acid (0.64 g, 4.2 mmol), dichlorobis(triphenylphosphine)palladium(II) (46 mg, 0.040 mmol), and potassium carbonate (1.1 g, 8.0 mmol) in a mixture of THF (10 ml) and water (10 ml) was stirred for 2 min, and methyl 2-iodobenzoate (1.05 g, 4.0 mmol) was added to the mixture. The solution was refluxed at 80°C for 12 h. After cooling to room temperature, the solution was washed with aqueous sodium thiosulfate, water and brine. The product was purified by silica gel column chromatography with a hexane/ethyl acetate mixture (10:1, v/v) as the eluent to obtain 2-(4-methoxyphenyl)benzoate (0.89 g, 91 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.66-7.90 (m, 1H), 7.46-7.50 (m, 1H), 7.33-7.37 (m, 2H), 7.22-7.26 (m, 2H), 6.90-6.94 (m, 2H), 3.82 (s, 1H), 3.66 (s, 1H).

### 1-3-2-2. Preparation of 2-(4-methoxyphenyl)benzoic acid.



To a THF solution (10 ml) of compound A (0.80 g, 3.3 mmol), aqueous NaOH (50 %, 10 ml) was dropwise added. The solution was heated at 100 °C for 12h. After cooling to room temperature, the solution was acidified with aqueous HCl. 2-(4-methoxyphenyl)benzoic acid was obtained after extraction with dichloromethane from the resulting mixture (0.34 g, 45 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.91 (dd, 1H, *J* = 0.92, 7.8 Hz), 7.50-7.55 (m, 1H), 7.34-7.40 (m, 2H), 7.25-7.29 (m, 3H), 6.90-6.94 (m, 2H), 3.83 (s, 3H).

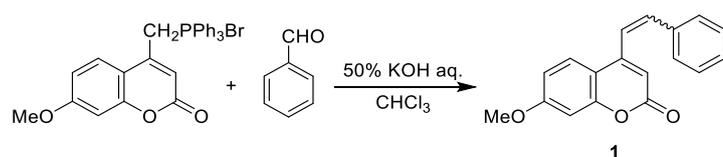
### 1-3-2-3. Synthesis of MeOCM[1].



A dichloromethane solution (20 ml) of 2-(4-methoxyphenyl)benzoic acid (0.34 g, 1.5 mmol) and copper(II) acetate monohydrate (13.5 mg, 0.075 mmol) was stirred for 5 min. To the mixture was added *tert*-butyl perbenzoate (0.83 ml, 4.5 mmol), the resulting mixture was refluxed for 12 h. After cooling to room temperature, the solution was washed with aqueous sodium thiosulfate, water and brine. The product was purified by silica gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent to obtain MeOCM[1] (0.13 g, 39 %). The NMR data agreed with those reported in the literature.<sup>3</sup>

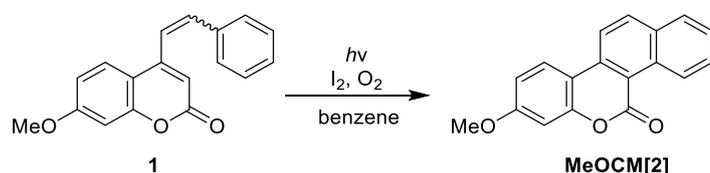
### 1-3-3. Synthesis of MeOCM[2].

#### 1-3-3-1. Preparation of compound 1.



To a chloroform solution (30 ml) of 4-bromomethyl-7-methoxycoumarin phosphonium salt (1.5 g, 2.8 mmol) and benzaldehyde (0.30 ml, 3.0 mmol), 15 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate (4:1, v/v) mixture as the eluent to obtain of compound **1** (0.44 g, 56 %).

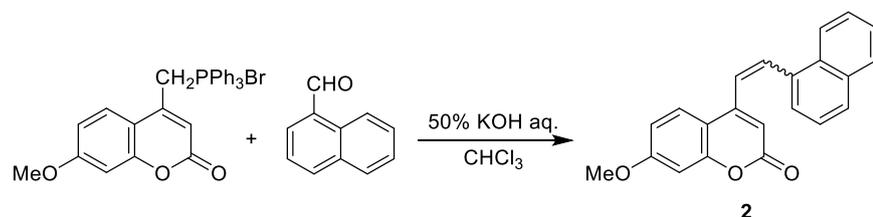
#### 1-3-3-2. Synthesis of MeOCM[2].



A benzene solution (500 ml) of compound **1** (0.44 g, 1.5 mmol) and 100 mg I<sub>2</sub> was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain MeOCM[2] (0.17 g, 38 %). Colorless needles, mp 163–164 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 9.74 (d, 2H, *J* = 8.7 Hz), 8.17 (d, 1H, *J* = 8.9 Hz), 8.06 (d, 1H, *J* = 8.9 Hz), 8.02 (d, 1H, *J* = 8.9 Hz), 7.88 (brd, 1H, *J* = 8.0 Hz), 7.76 (ddd, 1H, *J* = 8.3, 7.2, 1.1 Hz), 7.61 (ddd, 1H, *J* = 8.31, 7.2, 1.1 Hz), 6.94 (dd, 1H, *J* = 8.9, 2.7 Hz), 6.89 (d, 1H, *J* = 2.7 Hz), 3.89 (s, 3H). <sup>13</sup>C NMR δ<sub>c</sub> = 162.0, 160.8, 153.3, 137.3, 136.6, 132.8, 132.3, 129.7, 128.8, 127.1, 126.9, 124.6, 118.8, 113.4, 112.7, 111.5, 100.9, 55.9. HRMS (FAB) *m/z* calcd. for C<sub>18</sub>H<sub>12</sub>O<sub>3</sub> 276.0786 [M<sup>+</sup>], found 276.0810.

### 1-3-4. Synthesis of MeOCM[3].

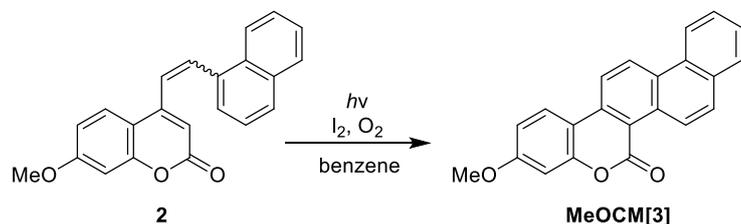
#### 1-3-4-1. Preparation of compound 2.



To a chloroform solution (20 ml) of [(7-methoxycoumarin-4-yl)methyl]triphenylphosphonium bromide (0.95 g, 1.79 mmol) and 1-naphthaldehyde (0.26 ml, 1.90 mmol), 10 ml aqueous 50 % KOH was added dropwise. The solution was refluxed for 3 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by

silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain compound **2** (0.60 g, 98 %).

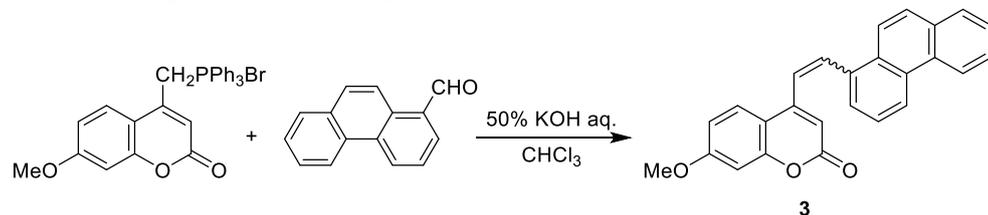
### 1-3-4-2. Synthesis of MeOCM[3].



A benzene solution (500 ml) of compound **2** (0.68 g, 2.07 mmol) and 100 mg I<sub>2</sub> was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography using a hexane/ethyl acetate mixture (4:1, v/v) as the eluent, providing MeOCM[3] (0.18 g, 30 %). Pale yellow needles, mp 221–223 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 9.71 (d, 1H, *J* = 9.4 Hz), 9.00 (d, 1H, *J* = 9.0 Hz), 8.62 (d, 1H, *J* = 8.2 Hz), 8.15 (d, 1H, *J* = 9.0 Hz), 7.95–8.00 (2H, two doublets overlapped), 7.91 (d, 1H, *J* = 7.8 Hz), 7.67 (ddd, 1H, *J* = 8.2, 7.1, 1.4 Hz), 7.62 (t, 1H, *J* = 7.1 Hz), 6.89 (dd, 1H, *J* = 8.2, 2.6 Hz), 3.86 (s, 3H). <sup>13</sup>C NMR δ<sub>C</sub> = 161.9, 161.0, 153.1, 136.6, 132.3, 131.7, 130.5, 130.1, 129.8, 129.7, 128.6, 127.23, 127.17, 124.6, 124.4, 122.6, 119.1, 114.2, 112.7, 111.3, 100.8, 55.8. HRMS (FAB) *m/z* calcd. for C<sub>22</sub>H<sub>14</sub>O<sub>3</sub> 326.0943 [M<sup>+</sup>], found 326.0981.

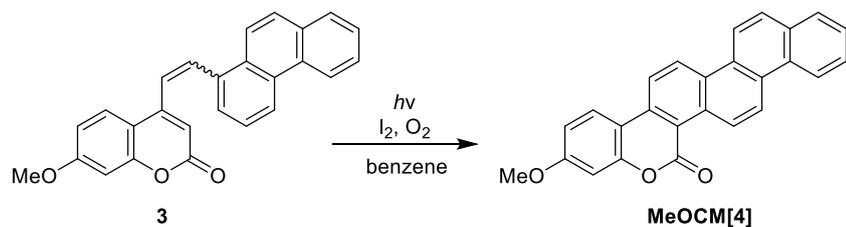
### 1-3-5. Synthesis of MeOCM[4].

#### 1-3-5-1. Preparation of compound 3.



To a chloroform solution (10 ml) of [(7-methoxycoumarin-4-yl)methyl]triphenylphosphonium bromide (0.95 g, 1.79 mmol) and 1-phenanthrenecarbaldehyde (0.20 g, 0.97 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The mixture was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent, providing compound **3** (70 mg, 21 %).

#### 1-3-5-2. Synthesis of MeOCM[4].

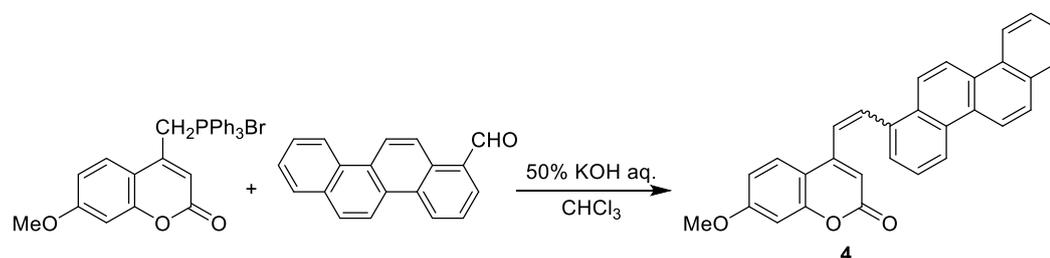


A benzene solution (200 ml) of compound **3** (70 mg, 0.20 mmol) and 50 mg I<sub>2</sub> was photolyzed with the

microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent, providing MeOCM[4] (15 mg, 21 %). Pale yellow needles, mp 284–285 °C. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 70 °C) δ<sub>H</sub> = 9.90 (d, 1H, *J* = 9.7 Hz), 9.48 (d, 1H, *J* = 9.2 Hz), 9.16 (d, 1H, *J* = 9.7 Hz), 8.96–9.01 (2H, two doublets overlapped), 8.64 (d, 1H, *J* = 9.2 Hz), 8.47 (m, 1H), 8.19 (d, 1H, *J* = 9.1 Hz), 8.13 (brd, *J* = 7.8 Hz), 7.81 (ddd, 1H, *J* = 8.0, 7.0, 1.4 Hz), 7.74 (ddd, 1H, *J* = 8.0, 7.8, 1.0 Hz), 7.10 (m, 2H), 3.94 (s, 3H). <sup>13</sup>C NMR was not observed due to low solubility. HRMS (FAB) *m/z* calcd. for C<sub>26</sub>H<sub>16</sub>O<sub>3</sub> 376.1099 [M<sup>+</sup>], found 376.1097.

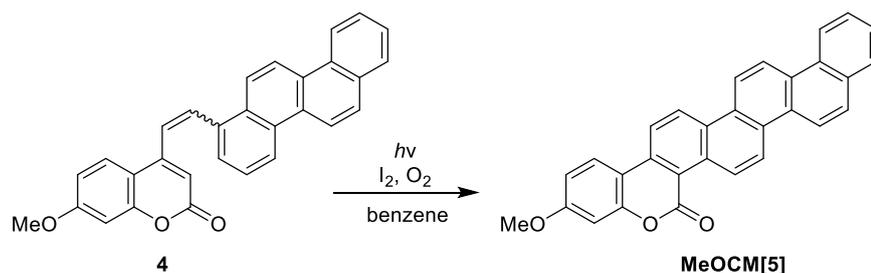
### 1-3-6. Synthesis of MeOCM[5].

#### 1-3-6-1. Preparation of compound 4.



To a chloroform solution (10 ml) of [(7-methoxycoumarin-4-yl)methyl]triphenylphosphonium bromide (0.37 g, 0.70 mmol) and 1-chrysenecarbaldehyde (0.08 g, 0.3 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (3:1, v/v) as the eluent, providing the compound 4 (50 mg, 38 %).

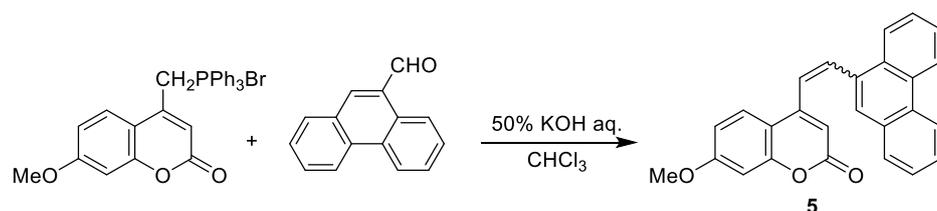
#### 1-3-6-2. Synthesis of MeOCM[5].



A benzene solution (200 ml) of compound 4 (50 mg, 0.12 mmol) and 50 mg I<sub>2</sub> was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by recrystallization from ethyl acetate to obtain MeOCM[5] (10 mg, 20 %). Pale yellow needles, mp 373–375 °C. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 70 °C) δ<sub>H</sub> = 9.93 (d, 1H, *J* = 9.3 Hz), 9.58 (d, 1H, *J* = 9.0 Hz), 9.20–9.23 (2H, two doublets overlapped), 9.18 (d, 1H, *J* = 9.4 Hz), 9.00–9.06 (2H, two doublets overlapped), 8.70 (d, 1H, *J* = 9.0 Hz), 8.50 (d, 1H, *J* = 9.8 Hz), 8.21 (d, 1H, *J* = 8.1 Hz), 8.15 (d, 1H, *J* = 7.2 Hz), 7.83 (t, 1H, *J* = 7.2 Hz), 7.76 (t, 1H, *J* = 7.2 Hz), 7.11 (m, 2H), 3.95 (s, 3H). <sup>13</sup>C NMR was not observed due to low solubility. Anal. Calcd for C<sub>30</sub>H<sub>18</sub>O<sub>3</sub>: C; 84.49 %, H; 4.25%. Found: C; 83.94 %, H; 4.09 %.

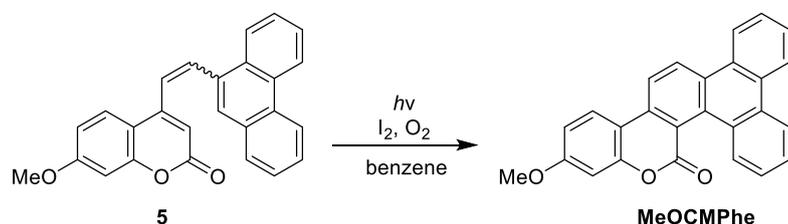
### 1-3-7. Synthesis of MeOCMPhe.

#### 1-3-7-1. Preparation of compound 5.



To a chloroform (30 ml) solution of 4-bromomethyl-7-methoxycoumarin phosphonium salt (1.6 g, 3.01 mmol) and 9-phenanthrenecarbaldehyde (0.62 g, 3.01 mmol), 10 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. The product was purified on silica-gel column chromatography with hexane/ethyl acetate (4:1, v/v) providing compound **5** (900 mg, 80 %).

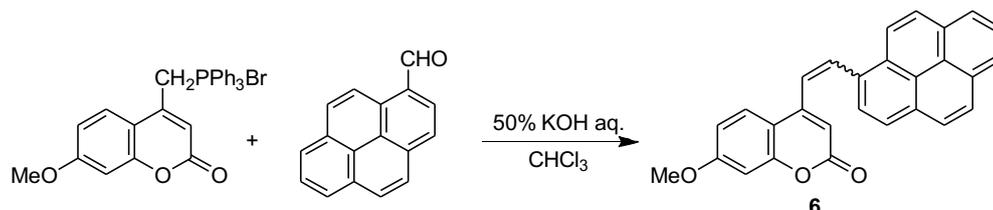
#### 1-3-7-2. Synthesis of MeOCMPhe.



A benzene solution (500 ml) of compound **5** (0.90 g, 2.37 mmol) and I<sub>2</sub> (100 mg). The solution was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by recrystallization from chloroform to obtain MeOCMPhe (53 mg, 6 %). Pale yellow needles, mp 285–290 °C. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> = 9.16 (d, 1H, *J* = 8.9 Hz), 8.80–8.85 (m, 2H), 8.73 (d, 1H, *J* = 8.0 Hz), 8.55 (d, 1H, *J* = 8.9 Hz), 8.46 (d, 1H, *J* = 8.3 Hz), 8.36 (d, 1H, *J* = 8.3 Hz), 7.77–7.79 (m, 2H), 7.71 (ddd, 1H, *J* = 8.0, 7.0, 1.1 Hz), 7.51 (ddd, 1H, *J* = 8.3, 7.0, 1.0 Hz), 7.11 (d, 1H, *J* = 2.3 Hz), 7.08 (dd, 1H, *J* = 8.3, 2.3 Hz), 3.93 (s, 3H). <sup>13</sup>C NMR (150 MHz) δ<sub>C</sub> = 161.5, 159.9, 152.6, 136.4, 131.4, 131.1, 130.1, 129.6, 129.3, 128.2, 128.0, 127.8, 127.8, 127.2, 125.3, 125.0, 123.5, 123.3, 122.9, 120.6, 114.4, 112.1, 110.6, 100.8, 55.7. HRMS (FAB) *m/z* calcd. for C<sub>26</sub>H<sub>16</sub>O<sub>3</sub> 376.1099 [M<sup>+</sup>], found 376.1101.

### 1-3-8. Synthesis of MeOCMPy.

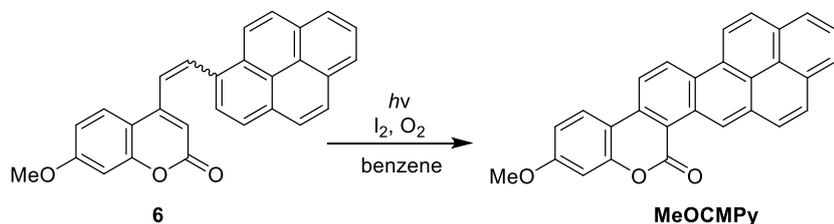
#### 1-3-8-1. Preparation of compound 6.



To a chloroform (30 ml) solution of [(7-methoxycoumarin-4-yl)methyl]triphenylphosphonium bromide (1.6 g, 3.0 mmol) and 1-pyrenecarboxaldehyde (0.76 g, 3.3 mmol), 10 ml aqueous KOH (50 %) was

added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified on silica-gel column chromatography with hexane/ethyl acetate (3:1, v/v), providing compound **6** (0.15 g, 12 %).

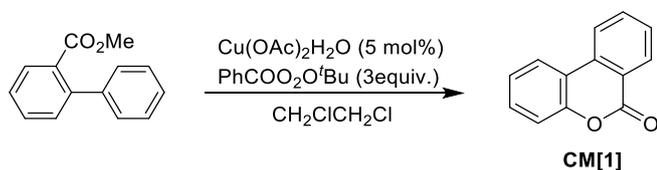
### 1-3-8-2. Synthesis of MeOCMPy.



A benzene solution (500 ml) of compound **6** (0.15 g, 0.37 mmol) and I<sub>2</sub> (100 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by recrystallization from chloroform to obtain MeOCMPy (19 mg, 13 %). Pale yellow needles, mp 285–288 °C. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> = 10.45 (s, 1H), 9.67 (d, 1H, *J* = 9.2 Hz), 9.29 (d, 1H, *J* = 9.1 Hz), 8.68 (d, 1H, *J* = 9.2 Hz), 8.46–8.52 (2H, two doublets overlapped), 8.41 (d, 1H, *J* = 7.7 Hz), 8.29 (d, 1H, *J* = 7.7 Hz), 8.23 (d, 1H, *J* = 9.0 Hz), 8.18 (d, 1H, *J* = 9.0 Hz), 8.11 (t, 1H, *J* = 7.7 Hz), 7.07–7.15 (m, 2H), 3.94 (s, 3H). <sup>13</sup>C NMR was not observed due to low solubility. HRMS (FAB) *m/z* calcd. for C<sub>28</sub>H<sub>16</sub>O<sub>3</sub> 400.1099 [*M*<sup>+</sup>], found 400.1130.

### 1-4. Synthesis of CM[*n*].

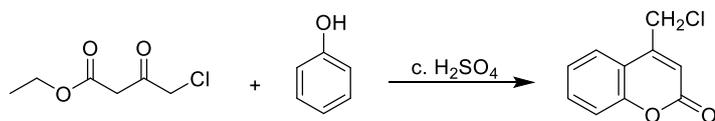
#### 1-4-1. Synthesis of CM[1].



CM[1] was prepared according to the literature.<sup>3</sup> Methyl 2-phenylbenzoate (0.40 g, 2.0 mmol) and copper(II) acetate monohydrate (18.1 mg, 0.10 mmol) were added to 1,2-dichloroethane (20 ml), and the solution was stirred for 5 min at room temperature. *tert*-Butyl perbenzoate (1.1 ml, 6.0 mmol) was added, and the solution was stirred at 85 °C under N<sub>2</sub> atmosphere for 12 h. After cooling to room temperature, the solution was washed with water and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent, providing CM[1] (59 mg, 15 %). The obtained NMR data agreed with those reported in the literature.<sup>3</sup>

#### 1-4-2. Preparation of 4-(chloromethyl)coumarin phosphonium salt.

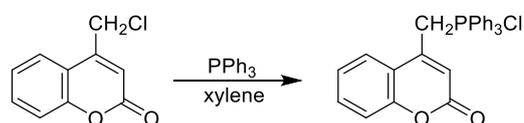
##### 1-4-2-1. Preparation of 4-(chloromethyl)coumarin.<sup>4</sup>



A mixture of ethyl-4-chloroacetoacetate (2.4 ml, 17.7 mmol), phenol (5.0 g, 53.1 mmol) and six drops of sulfuric acid was refluxed at 120 °C for 3 h under N<sub>2</sub> atmosphere. The product was extracted with ethyl

acetate (100 ml), and the solution was washed with aqueous  $\text{NaHCO}_3$  and brine. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent, providing 4-(chloromethyl)coumarin (330 mg, 10 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.63 (dd, 1H,  $J = 1.5, 7.9$  Hz), 7.49-7.55 (m, 1H), 7.27-7.33 (m, 2H), 6.54 (s, 1H), 4.65 (d, 2H,  $J = 1.1$  Hz).

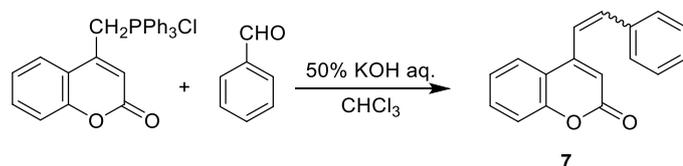
#### 1-4-2-2. Preparation of [(coumarin-4-yl)methyl]triphenylphosphonium chloride.



A xylene solution (20 ml) of 4-(chloromethyl)coumarin (330 mg, 1.7 mmol) and triphenylphosphine (500 mg, 1.9 mmol) was refluxed for 12 h under  $\text{N}_2$  atmosphere. The precipitate was collected and washed with benzene, providing the desired phosphonium salt (250 mg, 32 %).

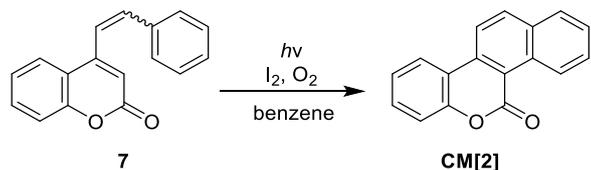
#### 1-4-3. Synthesis of CM[2].

##### 1-4-3-1. Preparation of compound 7.



To a chloroform solution (20 ml) of [(coumarin-4-yl)methyl]triphenylphosphonium chloride (0.29 g, 0.63 mmol) and benzaldehyde (0.20 ml, 2.0 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under  $\text{N}_2$  atmosphere, and washed with water and brine. The organic solution was separated, dried with  $\text{Na}_2\text{SO}_4$  and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain of compound 7 (0.11 g, 70 %).

##### 1-4-3-2. Synthesis of CM[2].

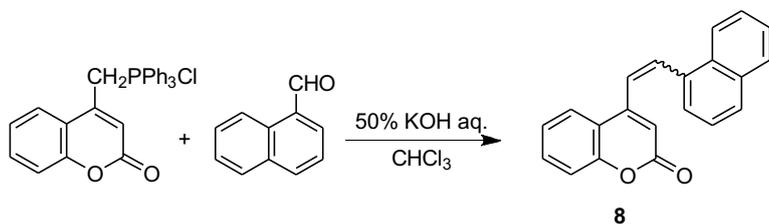


A benzene solution (200 ml) of compound 7 (0.11 g, 0.44 mmol) and  $\text{I}_2$  (50 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with  $\text{Na}_2\text{SO}_4$ . The product was purified by silica-gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent to obtain CM[2] (40 mg, 37 %). Pale yellow needles, mp 186–188 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  = 9.80 (brd, 1H,  $J = 8.4$  Hz), 8.22 (d, 1H,  $J = 8.9$  Hz), 8.18 (d, 1H,  $J = 8.9$  Hz), 8.16 (dd, 1H,  $J = 7.9, 1.4$  Hz), 7.92 (dd, 1H,  $J = 8.1, 1.3$  Hz), 7.77 (ddd, 1H,  $J = 8.4, 6.8, 1.3$  Hz), 7.63 (ddd, 1H,  $J = 8.1, 6.8, 1.1$  Hz), 7.53 (ddd, 1H,  $J = 8.3, 7.2, 1.4$  Hz), 7.42 (dd, 1H,  $J = 8.3, 1.1$  Hz), 7.37 (ddd, 1H,  $J = 8.2, 7.2, 1.1$  Hz).  $^{13}\text{C NMR}$   $\delta_{\text{C}}$  = 160.5, 151.8, 136.8, 136.6, 133.4, 132.2, 131.0, 129.8, 128.8, 127.45, 127.40, 124.5,

123.6, 118.9, 118.3, 117.4, 115.3. HRMS (FAB)  $m/z$  calcd. for  $C_{17}H_{10}O_2$  246.0681 [ $M^+$ ], found 246.0649.

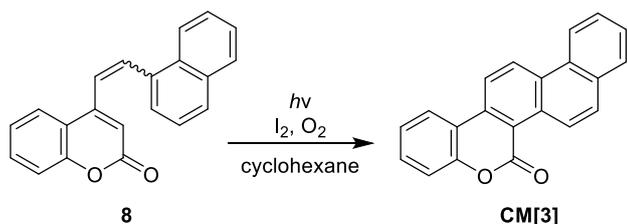
#### 1-4-4. Synthesis of CM[3].

##### 1-4-4-1. Preparation of compound 8.



To a chloroform solution (10 ml) of [(coumarin-4-yl)methyl]triphenylphosphonium chloride (0.25 g, 0.54 mmol) and 1-naphthaldehyde (0.06 ml, 0.59 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under  $N_2$  atmosphere, and washed with water and brine. The organic solution was separated, dried with  $Na_2SO_4$  and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain of compound **8** (0.15 g, 92 %).

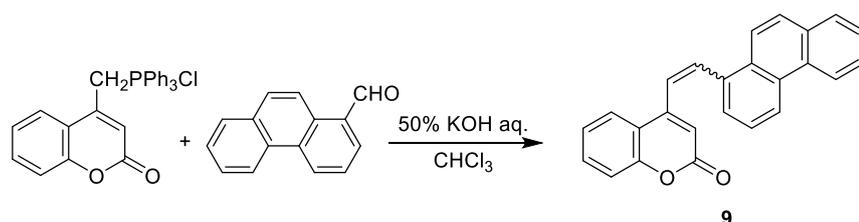
##### 1-4-4-2. Synthesis of CM[3].



A benzene solution (500 ml) of compound **8** 0.15 g (0.50 mmol) and  $I_2$  (100 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with  $Na_2SO_4$ . The product was purified by silica-gel column chromatography with hexane/chloroform (1:1, v/v) as the eluent to obtain CM[3] (0.05 g). Yield 34 %. Colorless needles, mp 240–243 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta_H$  = 9.80 (d, 1H,  $J$  = 9.5 Hz), 9.14 (d, 1H,  $J$  = 9.0 Hz), 7.81 (d, 1H,  $J$  = 8.3 Hz), 8.37 (d, 1H,  $J$  = 9.0 Hz), 8.21 (dd, 1H,  $J$  = 8.2, 1.4 Hz), 8.04 (d, 1H,  $J$  = 9.5 Hz), 7.97 (dd, 1H,  $J$  = 7.8, 1.2 Hz), 7.72 (ddd,  $J$  = 8.3, 6.8, 1.2 Hz), 7.67 (ddd, 1H,  $J$  = 7.8, 6.8, 1.2 Hz), 7.54 (ddd, 1H,  $J$  = 8.3, 7.1, 1.4 Hz), 7.42 (dd, 1H,  $J$  = 8.3, 1.2 Hz), 7.39 (ddd, 1H,  $J$  = 8.2, 7.1, 1.2 Hz).  $^{13}C$  NMR (150 MHz)  $\delta_C$  = 160.8, 151.7, 136.2, 132.4, 131.9, 130.9, 130.7 (two lines overlapped), 130.2, 129.8, 128.7, 127.6, 127.3, 124.8, 124.5, 123.5, 122.8, 119.5, 118.3, 117.3, 116.0. HRMS (FAB)  $m/z$  calcd. for  $C_{21}H_{12}O_2$  296.0837 [ $M^+$ ], found 296.0858.

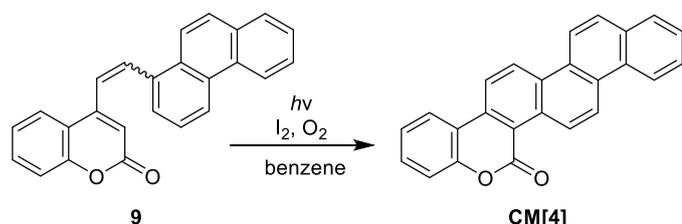
## 1-4-5. Synthesis of CM[4].

### 1-4-5-1. Preparation of compound 9.



To a chloroform solution (10 ml) of [(coumarin-4-yl)methyl]triphenylphosphonium chloride (0.46 g, 1.0 mmol) and 1-phenanthrenecarbaldehyde (0.20 g, 0.97 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain compound **9** (70 mg, 21 %).

### 1-4-5-2. Synthesis of CM[4].

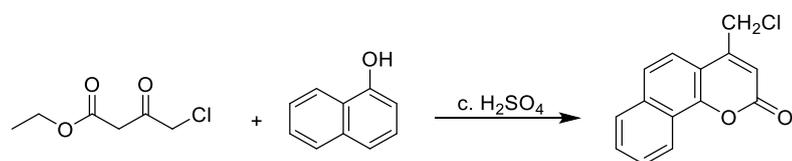


A benzene solution (500 ml) of compound **9** (70 mg, 0.20 mmol) and I<sub>2</sub> (100 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent to obtain CM[4] (15 mg, 21 %). Pale yellow needles, mp 340–345 °C. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 60 °C)  $\delta_{\text{H}}$  = 9.95 (d, 1H, *J* = 9.6 Hz), 9.57 (d, 1H, *J* = 9.1 Hz), 9.21 (d, 1H, *J* = 9.6 Hz), 9.00–9.04 (2H, two doublets overlapped), 8.78 (d, 1H, *J* = 9.2 Hz), 8.61 (dd, 1H, *J* = 8.0, 1.2 Hz), 8.22 (d, 1H, *J* = 7.2 Hz), 8.16 (brd, 1H, *J* = 7.8 Hz), 7.83 (ddd, 1H, *J* = 8.2, 7.0, 1.3 Hz), 7.76 (ddd, 1H, *J* = 7.8, 7.0, 1.2 Hz), 7.69 (ddd, 1H, *J* = 8.6, 7.1, 1.2 Hz), 7.50–7.54 (m, 2H). <sup>13</sup>C NMR was not observed due to low solubility. HRMS (FAB) *m/z* calcd. for C<sub>25</sub>H<sub>14</sub>O<sub>2</sub> 346.0994 [M<sup>+</sup>], found 346.0991.

## 1-5. Synthesis of BCM[*n*].

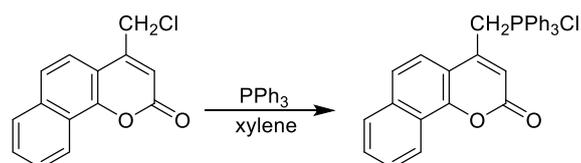
### 1-5-1. Preparation of [(4-chloromethyl-7,8-benzocoumarin-4-yl)methyl]triphenylphosphonium chloride.

#### 1-5-1-1. Preparation of 4-chloromethyl-7,8-benzocoumarin.



A mixture of ethyl-4-chloroacetoacetate (2.4 ml, 17.7 mmol), 1-naphthol (7.6 g, 53.1 mmol) and six drops of sulfuric acid was refluxed at 120 °C for 3 h under N<sub>2</sub> atmosphere. The product was extracted with ethyl acetate (100 ml), and the solution was washed with aqueous NaHCO<sub>3</sub> and brine. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent, providing 4-chloromethyl-7,8-benzocoumarin (1.62 g, 37 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.50-8.52 (m, 1H), 7.84-7.87 (m, 1H), 7.58-7.71 (m, 4H), 6.61 (s, 1H), 4.71 (s, 2H).

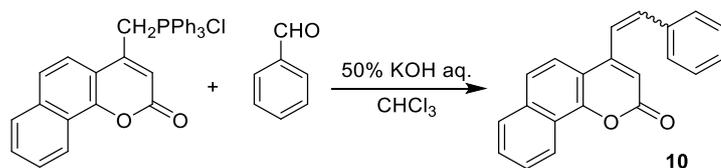
### 1-5-1-2. Preparation of [(4-chloromethyl-7,8-benzocoumarin-4-yl)methyl]triphenylphosphonium chloride.



A xylene solution (20 ml) of 4-chloromethyl-7,8-benzocoumarin (330 mg, 1.7 mmol) and triphenylphosphine (1.74 g, 6.6 mmol) was refluxed for 12 h under N<sub>2</sub> atmosphere. The precipitate was collected and washed with benzene, providing the desired phosphonium salt (1.76 g, 52 %).

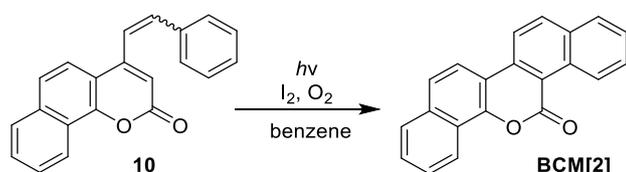
### 1-5-2. Synthesis of BCM[2].

#### 1-5-2-1. Preparation of Compound 10.



To a chloroform solution (20 ml) of [(4-chloromethyl-7,8-benzocoumarin-4-yl)methyl]triphenylphosphonium chloride (0.87 g, 1.7 mmol) and benzaldehyde (0.17 ml, 1.7 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain compound **10** (354 mg, 70 %).

#### 1-5-2-2. Synthesis of BCM[2].

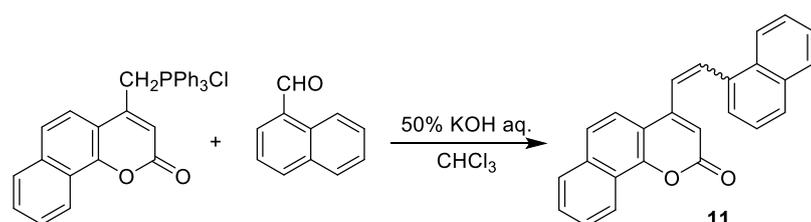


A benzene solution (400 ml) of compound **10** (300 mg, 1.7 mmol) and I<sub>2</sub> (100 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent

to obtain BCM[2] (97 mg, 32 %). Pale yellow needles, mp 226–229 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  = 9.74 (d, 2H,  $J$  = 8.7 Hz), 8.17 (d, 1H,  $J$  = 8.9 Hz), 8.06 (d, 1H,  $J$  = 8.9 Hz), 8.02 (d, 1H,  $J$  = 8.9 Hz), 7.88 (brd, 1H,  $J$  = 8.0 Hz), 7.76 (ddd, 1H,  $J$  = 8.3, 7.2, 1.1 Hz), 7.61 (ddd, 1H,  $J$  = 8.31, 7.2, 1.1 Hz), 6.94 (dd, 1H,  $J$  = 8.9, 2.7 Hz), 6.89 (d, 1H,  $J$  = 2.7 Hz), 3.89 (s, 3H).  $^{13}\text{C}$  NMR  $\delta_{\text{C}}$  = 162.0, 160.8, 153.3, 137.3, 136.6, 132.8, 132.3, 129.7, 128.8, 127.1, 126.9, 124.6, 118.8, 113.4, 112.7, 111.5, 100.9, 55.9. HRMS (FAB)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{12}\text{O}_2$  296.0837 [ $\text{M}^+$ ], found 296.0853.

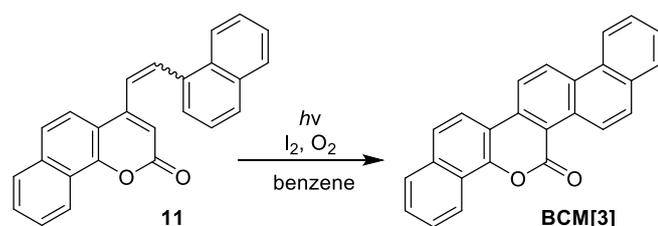
### 1-5-3. Synthesis of BCM[3].

#### 1-5-3-1. Preparation of Compound 11.



To a chloroform solution (20 ml) of [(4-chloromethyl-7,8-benzocoumarin-4-yl)methyl]triphenylphosphonium chloride (0.76 g, 1.5 mmol) and 1-naphthaldehyde (0.18 ml, 1.3 mmol), 5 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under  $\text{N}_2$  atmosphere, and washed with water and brine. The organic solution was separated, dried with  $\text{Na}_2\text{SO}_4$  and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (5:1, v/v) as the eluent to obtain compound **11** (160 mg, 35 %).

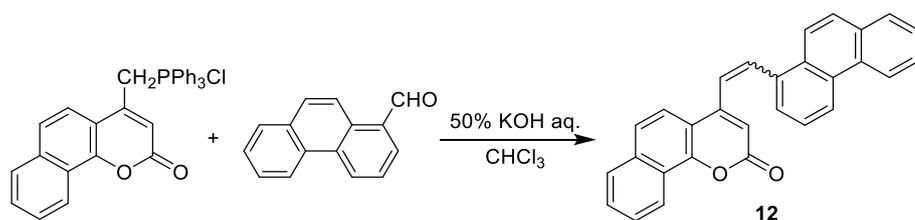
#### 1-5-3-2. Synthesis of BCM[3].



A benzene solution (500 ml) of compound **11** (160 mg, 0.46 mmol) and  $\text{I}_2$  (100 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with  $\text{Na}_2\text{SO}_4$ . The product was purified by silica-gel column chromatography with hexane/chloroform (1:4, v/v) as the eluent to obtain BCM[3] (67 mg, 42 %). Pale yellow needles, mp 312–314 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ , 70 °C)  $\delta_{\text{H}}$  = 9.76 (d, 1H,  $J$  = 9.5 Hz), 9.50 (d, 1H,  $J$  = 9.1 Hz), 9.04 (d, 1H,  $J$  = 8.2 Hz), 8.83 (d, 1H,  $J$  = 9.1 Hz), 8.60 (d, 1H,  $J$  = 8.8 Hz), 8.52 (d, 1H,  $J$  = 7.9 Hz), 8.22 (d, 1H,  $J$  = 9.5 Hz), 8.12 (brd, 1H,  $J$  = 7.8 Hz), 8.11 (d, 1H,  $J$  = 7.8 Hz), 8.10 (d, 1H,  $J$  = 7.8 Hz), 8.01 (d, 1H,  $J$  = 8.8 Hz), 7.83 (ddd, 1H,  $J$  = 8.2, 7.0, 1.4 Hz), 7.72–7.80 (m, 3H).  $^{13}\text{C}$  NMR was not observed due to low solubility. HRMS (FAB)  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{14}\text{O}_2$  346.0994 [ $\text{M}^+$ ], found 346.1032.

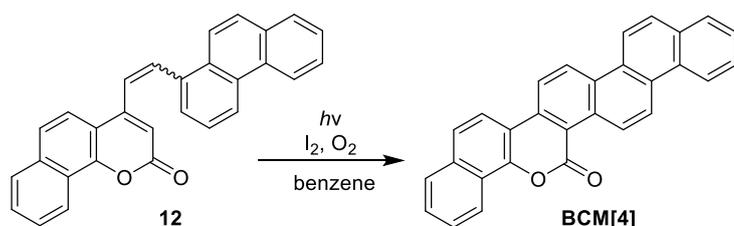
## 1-5-4. Synthesis of BCM[4]

### 1-5-4-1. Preparation of Compound 12



To a chloroform solution (30 ml) of [(4-chloromethyl-7,8-benzocoumarin-4-yl)methyl]triphenylphosphonium chloride (1.01 g, 2.0 mmol) and 1-phenanthrenecarbaldehyde (0.37 g, 1.8 mmol), 10 ml aqueous KOH (50 %) was added dropwise. The solution was refluxed for 1 h under N<sub>2</sub> atmosphere, and washed with water and brine. The organic solution was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by silica-gel column chromatography with a hexane/ethyl acetate mixture (4:1, v/v) as the eluent to obtain compound **12** (317 mg, 44 %).

### 1-5-4-2. Synthesis of BCM[4]



A benzene solution (200 ml) of compound **12** (300 mg, 0.75 mmol) and I<sub>2</sub> (50 mg) was photolyzed with the microflow photoreactor.<sup>1</sup> The photolyzed solution was successively washed with aqueous sodium thiosulfate, aqueous sodium hydrogen carbonate and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica-gel column chromatography with a hexane/chloroform mixture (1:5, v/v) as the eluent to obtain BCM[4] (97 mg, 32 %). Pale yellow needles, mp 385–389 °C. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 70 °C)  $\delta_{\text{H}}$  = 10.01 (d, 1H, *J* = 9.6 Hz), 9.61 (d, 1H, *J* = 9.1 Hz), 9.24 (d, 1H, *J* = 9.6 Hz), 9.01–9.06 (2H, two doublets overlapped), 8.87 (d, 1H, *J* = 9.1 Hz), 8.62 (d, 1H, *J* = 9.0 Hz), 8.56 (d, 1H, *J* = 8.1 Hz), 8.23 (d, 1H, *J* = 9.0 Hz), 8.16 (d, 1H, *J* = 7.9 Hz), 8.11 (d, 1H, *J* = 7.0 Hz), 8.02 (d, 1H, *J* = 9.0 Hz), 7.84 (ddd, 1H, *J* = 8.3, 7.0, 1.2 Hz), 7.73–7.82 (m, 3H). <sup>13</sup>C NMR was not observed due to low solubility. HRMS (FAB) *m/z* calcd. for C<sub>29</sub>H<sub>16</sub>O<sub>2</sub> 396.1150 [M<sup>+</sup>], found 396.1148.

## 2. Absorption and emission spectra of CM[n] and BCM[n].

Figures S1 and 2 show absorption and emission spectra of CM[n] and BCM[n] in chloroform, respectively.

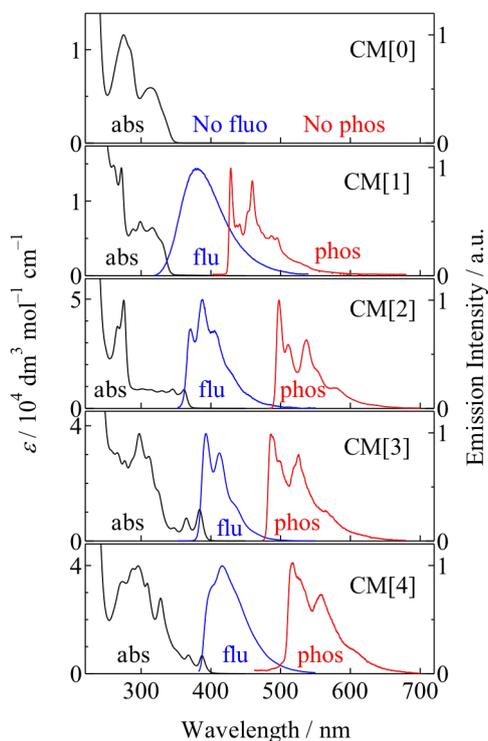
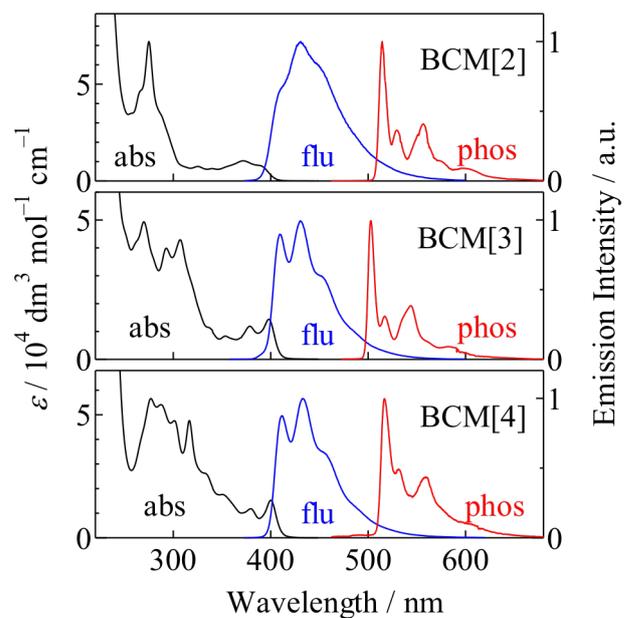


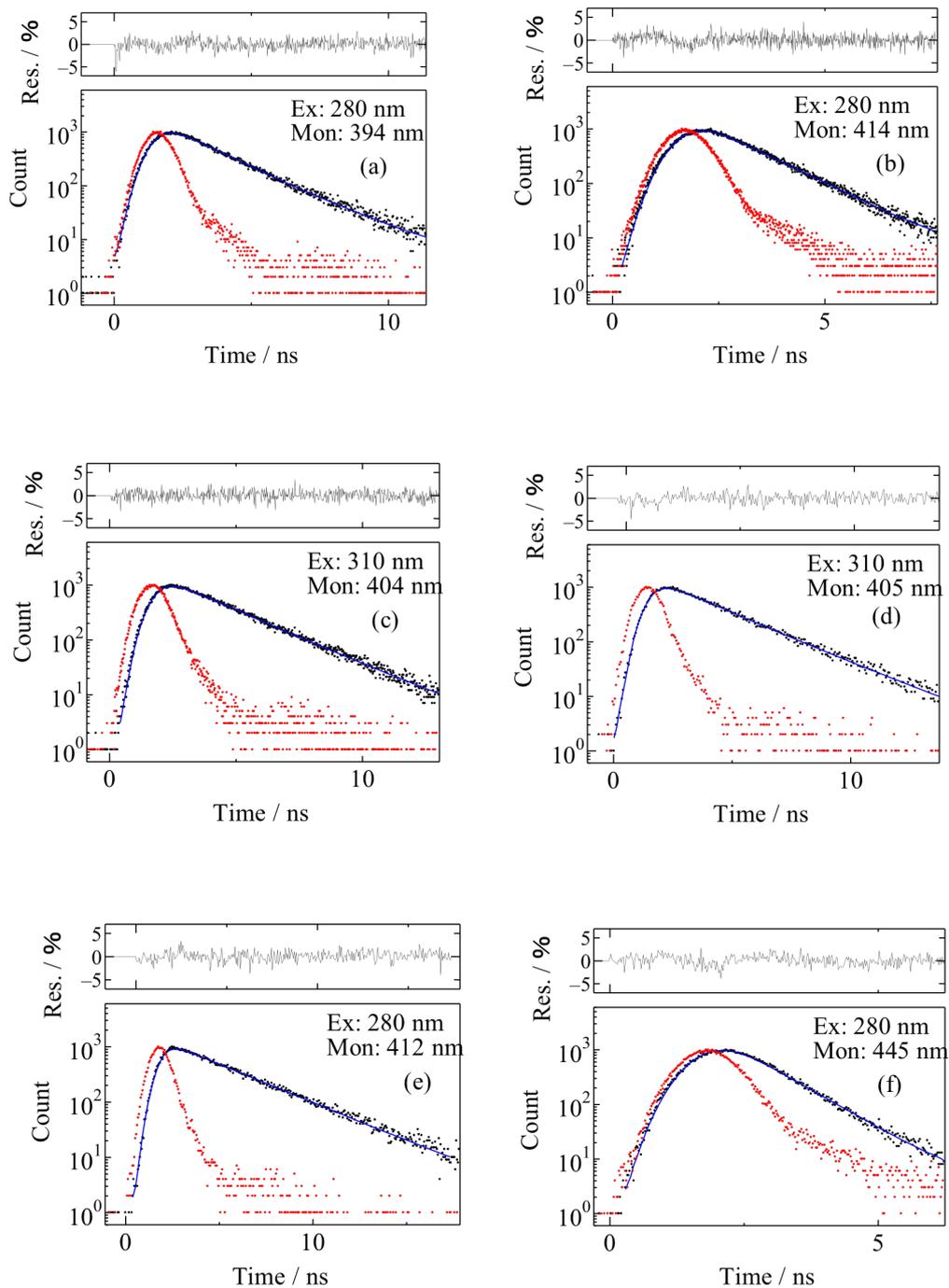
Figure S1. Absorption and fluorescence spectra in  $\text{CHCl}_3$  at 295 K and phosphorescence spectra in ethanol at 77 K for CM[n] ( $0 \leq n \leq 4$ ).

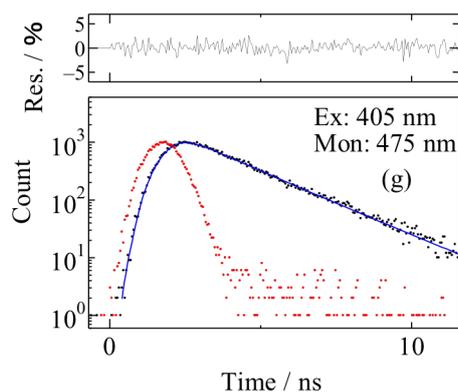


**Figure S2.** Absorption and fluorescence spectra in  $\text{CHCl}_3$  at 295 K and phosphorescence spectra in ethanol at 77 K for  $\text{BCM}[n]$  ( $2 \leq n \leq 4$ ).

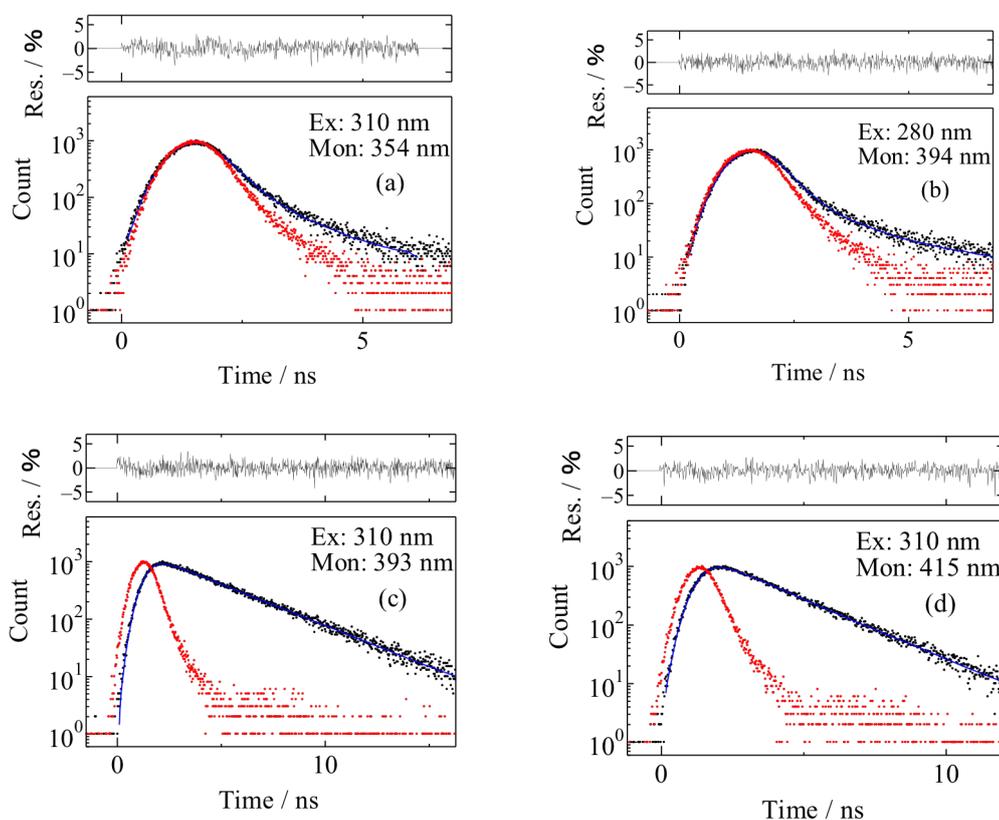
### 3. Decay profiles of fluorescence in $\text{CHCl}_3$ .

Figures S3-5 show decay profiles of fluorescence for the coumarin derivatives studied in this work.

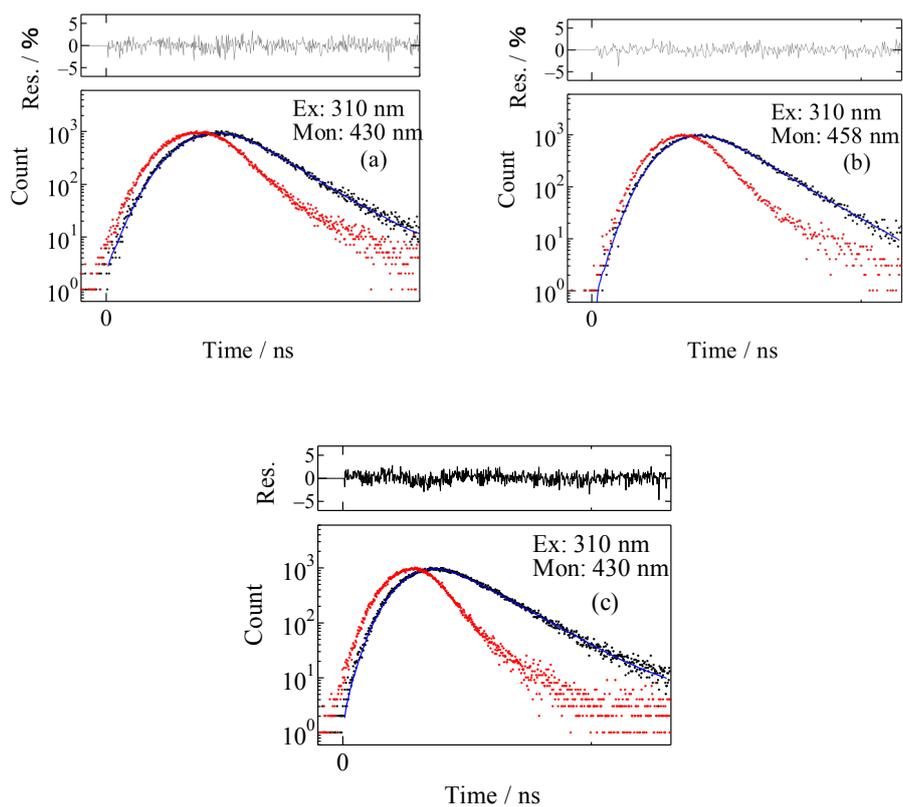




**Figure S3.** Decay profiles of fluorescence in  $\text{CHCl}_3$  for MeOCM[1] (a), MeOCM[2] (b), MeOCM[3] (c), MeOCM[4] (d), MeOCM[5] (e), MeOCMPhe (f) and MeOCMPy (g) at 295 K. Ex and Mon in the figure indicate the excitation and monitoring wavelengths, respectively.



**Figure S4.** Decay profiles of fluorescence in  $\text{CHCl}_3$  for CM[1] (a), CM[2] (b), CM[3] (c) and CM[4] (d) at 295 K. Ex and Mon in the figure indicate the excitation and monitoring wavelengths, respectively.



**Figure S5.** Decay profiles of fluorescence in  $\text{CHCl}_3$  for BCM[2] (a), BCM[3] (b) and BCM[4] (c) at 295 K. Ex and Mon in the figure indicate the excitation and monitoring wavelengths, respectively.

#### 4. Results of DFT and TD-DFT calculations (atom coordinates and sum of electronic and zero-point energies)

The calculation was carried out at the DFT level, using the Gaussian 09 software package.<sup>5</sup> The geometries of the coumarin derivatives were fully optimized by using the 6-31+G(d) base set at the B3LYP method. Atom coordinates for the optimized geometries of the coumarin derivatives in vacuum are as follows.

**Table S1.** Atom coordinates for the optimized geometry of MeOCM[0].

	X	Y	Z
C	-1.36185	0.69058	0.02208
C	-1.36185	-0.71676	0.02208
C	-0.16449	-1.44075	0.02208
C	1.03830	-0.72556	0.02247
C	1.05689	0.68307	0.02220
C	-0.16008	1.37524	0.02196
O	-2.48865	-1.50690	0.02229
C	-3.74091	-0.86535	0.01915
O	2.18884	-1.47830	0.02289
C	3.40049	-0.81476	0.02246
C	3.46834	0.65090	0.02215
C	2.33043	1.36732	0.02209
O	4.28980	-1.63778	0.02243
H	-2.30126	1.25505	0.02196
H	-0.16390	-2.53856	0.02202
H	-0.15366	2.47151	0.02158
H	-4.43277	-1.71213	0.02239
H	-3.89422	-0.25773	-0.88009
H	-3.89554	-0.24988	0.91286
H	4.46300	1.10830	0.02209
H	2.33371	2.46325	0.02191

Sum of electronic and zero-point energies = -611.410951114 Hartree

**Table S2.** Atom coordinates for the optimized geometry of MeOCM[1].

	X	Y	Z
C	-1.96063	-0.35425	0.02048
C	-1.96063	-1.77418	0.02166
C	-0.73089	-2.48417	0.02166
C	0.49886	-1.77418	0.02166
C	0.49886	-0.35420	0.02166
C	-0.73090	0.35577	0.02107
O	-3.13405	-2.45166	0.01106
C	-4.22045	-1.56555	-0.00002
O	1.61817	-2.53773	0.03340
C	2.89468	-1.86985	0.04678
C	2.95820	-0.35420	0.04745
C	1.72853	0.35580	0.03456
O	3.90905	-2.52582	0.04695

C	4.18770	0.35577	0.07292
C	4.18750	1.77569	0.08550
C	2.95845	2.48564	0.02285
C	1.72866	1.77573	0.02226
H	-2.91323	0.19572	0.02862
H	-0.73089	-3.58412	0.01214
H	-0.73092	1.45572	0.01154
H	-5.14039	-2.18840	-0.00825
H	-4.15956	-0.99770	-0.95298
H	-4.17770	-0.99610	0.95298
H	5.14039	-0.19410	0.07338
H	5.13886	2.32572	0.13420
H	2.95977	3.58412	-0.03468
H	0.77619	2.32564	0.00275

---

Sum of electronic and zero-point energies = -765.094450271 Hartree

**Table S3.** Atom coordinates for the optimized geometry of MeOCM[2].

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	X	Y	Z
C	-3.19027	-0.35505	0.01487
C	-3.19028	-1.76523	0.02017
C	-1.98640	-2.46729	0.02020
C	-0.77811	-1.75920	0.02122
C	-0.76749	-0.35363	0.02433
C	-1.98421	0.32576	0.01614
O	-4.35299	-2.51882	0.01569
C	-5.53631	-1.73587	0.00496
O	0.35401	-2.52273	0.03365
C	1.59193	-1.88284	0.05251
C	1.66028	-0.38333	0.05880
C	0.50084	0.34051	0.03757
O	2.56392	-2.60449	0.05272
C	2.91033	0.31299	0.07623
C	2.93489	1.72313	0.06588
C	1.71499	2.44947	0.03747
C	0.53585	1.76035	0.02435
C	4.13677	-0.40175	0.11073
C	5.33382	0.27747	0.14444
C	5.35652	1.68745	0.10042
C	4.17685	2.40401	0.06926
H	-4.13597	0.20247	0.01780
H	-1.99083	-3.56569	0.01142
H	-1.97466	1.42601	0.00718
H	-6.37436	-2.44579	0.00241
H	-5.54894	-1.15979	-0.93194
H	-5.56088	-1.15212	0.93691
H	1.73275	3.54669	0.02918
H	-0.40549	2.32853	-0.01373
H	4.12526	-1.50670	0.10637

H	6.27793	-0.27652	0.19833
H	6.31647	2.21658	0.06391
H	4.19786	3.50073	0.05107

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Sum of electronic and zero-point energies = -918.749108929 Hartree

**Table S4.** Atom coordinates for the optimized geometry of MeOCM[3].

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	X	Y	Z
C	-3.80493	-1.41903	0.01436
C	-3.80493	-2.83682	0.02007
C	-2.57630	-3.54040	0.02005
C	-1.35375	-2.82263	0.02017
C	-1.36315	-1.40182	0.02080
C	-2.57598	-0.71412	0.01711
O	-4.97902	-3.51982	0.01395
C	-6.07271	-2.63960	0.00214
O	-0.22792	-3.57741	0.03225
C	1.03773	-2.89857	0.05133
C	1.07971	-1.38412	0.05657
C	-0.13446	-0.68298	0.03602
O	2.05666	-3.54749	0.05222
C	2.29765	-0.65476	0.07160
C	2.27377	0.76404	0.06232
C	1.03078	1.44985	0.04999
C	-0.14100	0.73719	0.01755
C	3.53995	-1.34251	0.10674
C	4.74963	-0.61041	0.10997
C	4.71572	0.80865	0.10331
C	3.49454	1.49451	0.07723
C	5.92418	1.55026	0.13080
C	5.88199	2.96462	0.13680
C	4.63262	3.63463	0.06658
C	3.47561	2.91452	0.05546
H	-4.75717	-0.86865	0.01724
H	-2.57243	-4.64016	0.01055
H	-2.57293	0.38572	0.00763
H	-6.98762	-3.26825	-0.00224
H	-6.01817	-2.07401	-0.95169
H	-6.03255	-2.06632	0.95208
H	1.00907	2.54952	0.06178
H	-1.09498	1.28208	-0.03700
H	3.55939	-2.44249	0.12234
H	5.71315	-1.14048	0.10863
H	6.89090	1.02610	0.13838
H	6.81612	3.54264	0.18656
H	4.59966	4.73206	0.00466
H	2.51594	3.45127	0.02701

---

Sum of electronic and zero-point energies = -1072.39891794 Hartree

**Table S5.** Atom coordinates for the optimized geometry of MeOCM[4].

	X	Y	Z
C	-5.03474	-1.42004	0.01441
C	-5.03475	-2.83997	0.02009
C	-3.80501	-3.54996	0.02009
C	-2.57526	-2.83997	0.02009
C	-2.57526	-1.41999	0.02009
C	-3.80502	-0.71002	0.01725
O	-6.20819	-3.51747	0.01378
C	-7.29460	-2.63139	0.00188
O	-1.45595	-3.60352	0.03183
C	-0.17949	-2.93561	0.05118
C	-0.11607	-1.41997	0.05758
C	-1.34562	-0.71000	0.03523
O	0.83495	-3.59148	0.05174
C	1.11358	-0.70998	0.07271
C	1.11368	0.70999	0.06550
C	-0.11601	1.42000	0.05544
C	-1.34533	0.70985	0.01572
C	2.34290	-1.41986	0.10736
C	3.57297	-0.70997	0.09791
C	3.57288	0.71001	0.10299
C	2.34333	1.41998	0.08063
C	4.80253	1.42000	0.11812
C	4.80262	2.83996	0.11091
C	3.57308	3.54994	0.08855
C	2.34362	2.83983	0.06112
C	6.03184	0.71011	0.15277
C	7.26122	1.42019	0.18020
C	7.26207	2.83980	0.12380
C	6.03241	3.54986	0.11375
H	-5.98736	-0.87005	0.01734
H	-3.80501	-4.64991	0.01057
H	-3.80502	0.38993	0.00773
H	-8.21456	-3.25426	-0.00271
H	-7.23546	-2.06656	-0.95299
H	-7.25012	-2.05894	0.95299
H	-0.11628	2.51991	0.06889
H	-2.29657	1.25945	-0.03967
H	2.34259	-2.51958	0.13199
H	4.52537	-1.25995	0.07713
H	3.57315	4.64991	0.08296
H	1.39189	3.38946	0.01524
H	6.03203	-0.38987	0.14884
H	8.21275	0.87110	0.23556
H	8.21456	3.38816	0.07843
H	6.03257	4.64975	0.09863

Sum of electronic and zero-point energies = -1226.05409248 Hartree

**Table S6.** Atom coordinates for the optimized geometry of MeOCM[5].

	X	Y	Z
C	-5.64940	-2.48401	0.01426
C	-5.64940	-3.89974	0.02003
C	-4.42523	-4.60447	0.02002
C	-3.20145	-3.89303	0.02033
C	-3.19991	-2.47368	0.02169
C	-4.42553	-1.78317	0.01685
O	-6.82422	-4.59173	0.01424
C	-7.92968	-3.72141	0.00254
O	-2.07889	-4.65401	0.03284
C	-0.81376	-3.98602	0.05187
C	-0.76168	-2.47340	0.05613
C	-1.96089	-1.76396	0.03686
O	0.19731	-4.64730	0.05320
C	0.46419	-1.75367	0.07137
C	0.45196	-0.33652	0.06209
C	-0.78569	0.35748	0.04914
C	-1.95466	-0.34370	0.01967
C	1.70060	-2.45291	0.10897
C	2.91284	-1.73845	0.09861
C	2.89816	-0.31877	0.09837
C	1.68017	0.38417	0.07724
C	4.12030	0.41062	0.11286
C	4.09442	1.82587	0.09827
C	2.84758	2.50728	0.08082
C	1.67434	1.80615	0.05667
C	5.36190	-0.27976	0.15113
C	6.56884	0.44302	0.15438
C	6.54472	1.86247	0.14521
C	5.31597	2.55808	0.11246
C	7.75842	2.59478	0.17253
C	7.72771	4.00242	0.17662
C	6.48584	4.68122	0.10521
C	5.29757	3.97778	0.08512
H	-6.60098	-1.93297	0.01701
H	-4.42385	-5.70396	0.01059
H	-4.42212	-0.68344	0.00742
H	-8.83617	-4.35953	-0.00150
H	-7.88273	-3.15464	-0.94954
H	-7.89669	-3.14680	0.95050
H	-0.79968	1.45728	0.06083
H	-2.90389	0.20955	-0.03366
H	1.70952	-3.55330	0.13571
H	3.86997	-2.27971	0.08033
H	2.82171	3.60687	0.08837
H	0.72050	2.35114	0.00069
H	5.37954	-1.37919	0.16958
H	7.52948	-0.09122	0.15559

H	8.72071	2.06357	0.18204
H	8.66590	4.57272	0.22614
H	6.46202	5.77836	0.04205
H	4.33798	4.51446	0.05282

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Sum of electronic and zero-point energies = -1379.70497031 Hartree

**Table S7.** Atom coordinates for the optimized geometry of MeOCMPhe.

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	X	Y	Z
C	-3.80499	-1.41959	0.01551
C	-3.80500	-2.82498	0.02033
C	-2.59850	-3.53546	0.02037
C	-1.40847	-2.80119	0.02608
C	-1.37778	-1.40082	0.02559
C	-2.60487	-0.72947	0.01182
O	-4.92313	-3.62656	0.02259
C	-6.17847	-2.98817	0.01942
O	-0.24894	-3.51633	0.02297
C	0.98226	-2.88658	0.05465
C	1.15434	-1.40822	0.07742
C	-0.08244	-0.72305	0.04221
O	1.73885	-3.83905	0.00358
C	2.38699	-0.66037	0.15246
C	2.28020	0.75704	0.11240
C	1.02968	1.39005	0.00294
C	-0.13115	0.67583	0.01440
C	3.76645	-1.17561	0.29783
C	4.87539	-0.29515	0.35108
C	4.71144	1.14338	0.28016
C	3.42174	1.66444	0.17969
C	5.81607	2.01762	0.32615
C	5.64619	3.38378	0.26287
C	4.35778	3.91308	0.15453
C	3.26857	3.06759	0.13112
C	4.09767	-2.53608	0.42577
C	5.38638	-3.01329	0.58096
C	6.46164	-2.13031	0.58257
C	6.18859	-0.78594	0.47824
H	-4.74258	-0.85222	0.01640
H	-2.58982	-4.63303	0.01574
H	-2.61987	0.37071	0.00517
H	-6.89289	-3.81473	0.02215
H	-6.30805	-2.38056	-0.88282
H	-6.30937	-2.37351	0.91672
H	0.95109	2.48636	-0.03239
H	-1.09905	1.19684	-0.03531
H	6.83478	1.61361	0.41752
H	6.51435	4.05040	0.29281
H	4.21643	4.99692	0.08982

H	2.27144	3.52260	0.05542
H	3.34114	-3.32630	0.42247
H	5.55571	-4.08976	0.69444
H	7.48957	-2.49822	0.65858
H	7.03545	-0.08464	0.50150

---

Sum of electronic and zero-point energies = -1226.03865069 Hartree

**Table S8.** Atom coordinates for the optimized geometry of MeOCMPy.

---

	X	Y	Z
C	-5.03493	-1.41980	0.01576
C	-5.03494	-2.83973	0.02044
C	-3.80520	-3.54972	0.02044
C	-2.57545	-2.83973	0.02044
C	-2.57545	-1.41974	0.02044
C	-3.80521	-0.70978	0.01810
O	-6.20837	-3.51723	0.01317
C	-7.29479	-2.63114	0.00146
O	-1.45614	-3.60327	0.03217
C	-0.17966	-2.93537	0.05032
C	-0.11624	-1.41973	0.05682
C	-1.34580	-0.70975	0.03508
O	0.83478	-3.59123	0.04980
C	1.11341	-0.70973	0.07145
C	1.11351	0.71023	0.06435
C	-0.11619	1.42024	0.05491
C	-1.34552	0.71010	0.01568
C	2.34275	-1.41962	0.10549
C	3.57263	-0.70972	0.10783
C	3.57272	0.71025	0.10073
C	2.34316	1.42022	0.07899
C	4.80251	1.42015	0.10307
C	4.80273	2.84000	0.08367
C	3.57315	3.54995	0.06193
C	2.34344	2.84007	0.05959
C	4.80220	-1.41966	0.12957
C	6.03200	-0.70990	0.11974
C	6.03216	0.71006	0.11251
C	7.26186	1.41998	0.12702
C	7.26221	2.83957	0.08316
C	6.03259	3.54971	0.07372
H	-5.98755	-0.86981	0.01985
H	-3.80520	-4.64967	0.01091
H	-3.80521	0.39017	0.00857
H	-8.21474	-3.25400	-0.00394
H	-7.23525	-2.06563	-0.95299
H	-7.25068	-2.05935	0.95299
H	-0.11646	2.52015	0.06845
H	-2.29679	1.25969	-0.03923

H	2.34251	-2.51951	0.12051
H	3.57341	4.64967	0.03738
H	1.39109	3.38990	0.03323
H	4.80205	-2.51955	0.14450
H	6.98446	-1.26006	0.10820
H	8.21405	0.87039	0.16269
H	8.21474	3.38853	0.04699
H	6.03278	4.64943	0.04917

Sum of electronic and zero-point energies = -1302.30409383 Hartree

**Table S9.** Atom coordinates for the optimized geometry of CM[0].

	X	Y	Z
C	-2.86543	0.37133	0.00007
C	-2.60515	-1.00961	0.00005
C	-1.29752	-1.48824	-0.00001
C	-0.24225	-0.57323	-0.00006
C	-0.47602	0.81576	-0.00004
C	-1.80867	1.27310	0.00003
O	1.02804	-1.07943	-0.00015
C	2.16535	-0.27183	-0.00023
C	1.92966	1.16925	-0.00003
C	0.67687	1.68240	-0.00002
O	3.24612	-0.81717	0.00028
H	-3.88989	0.73179	0.00012
H	-3.43116	-1.71554	0.00009
H	-1.07645	-2.55087	-0.00002
H	-1.99684	2.34423	0.00006
H	2.81831	1.79031	0.00008
H	0.52158	2.75935	0.00006

Sum of electronic and zero-point energies = -496.891283430 Hartree

**Table S10.** Atom coordinates for the optimized geometry of CM[1].

	X	Y	Z
C	3.13145	-1.46098	0.00048
C	3.65234	-0.15875	0.00008
C	2.79223	0.93413	-0.00042
C	1.41208	0.71829	-0.00043
C	0.85806	-0.57345	0.00001
C	1.75569	-1.66003	0.00050
O	0.63139	1.85039	-0.00084
C	-0.74592	1.81610	0.00016
C	-1.37870	0.48232	-0.00002
C	-0.60199	-0.69845	-0.00006
O	-1.33728	2.87291	0.00090
C	-2.78191	0.42219	0.00002
C	-3.42795	-0.80692	0.00009
C	-2.66731	-1.98616	-0.00042

C	-1.27787	-1.93418	-0.00025
H	3.80056	-2.31670	0.00090
H	4.72698	0.00101	0.00009
H	3.16110	1.95500	-0.00076
H	1.37032	-2.67451	0.00100
H	-3.33783	1.35416	0.00021
H	-4.51316	-0.85505	0.00026
H	-3.16543	-2.95232	-0.00039
H	-0.71656	-2.86260	-0.00028

---

Sum of electronic and zero-point energies = -650.548714114 Hartree

**Table S11.** Atom coordinates for the optimized geometry of CM[2].

	X	Y	Z
C	-4.30387	-0.35505	-0.06463
C	-4.30387	-1.77498	-0.05929
C	-3.07413	-2.48498	-0.05929
C	-1.84439	-1.77498	-0.05929
C	-1.84439	-0.35500	-0.05929
C	-3.07414	0.35496	-0.06196
O	-0.72507	-2.53853	-0.04756
C	0.55140	-1.87063	-0.02896
C	0.61482	-0.35498	-0.02235
C	-0.61474	0.35499	-0.04433
O	1.56584	-2.52649	-0.02919
C	1.84447	0.35501	-0.00738
C	1.84456	1.77497	-0.01439
C	0.61501	2.48495	-0.03637
C	-0.61446	1.77484	-0.06363
C	3.07379	-0.35488	0.02689
C	4.30318	0.35520	0.05415
C	4.30401	1.77482	-0.00204
C	3.07435	2.48488	-0.01172
H	-5.25649	0.19493	-0.06131
H	-5.25648	-2.32498	-0.06468
H	-3.07413	-3.58493	-0.06882
H	-3.07415	1.45491	-0.07149
H	0.61507	3.58493	-0.04180
H	-1.56619	2.32448	-0.10922
H	3.07398	-1.45486	0.02279
H	5.25472	-0.19391	0.10922
H	5.25649	2.32318	-0.04755
H	3.07449	3.58477	-0.02668

---

Sum of electronic and zero-point energies = -804.213732080 Hartree

**Table S12.** Atom coordinates for the optimized geometry of CM[3].

	X	Y	Z
C	-4.91853	-1.41903	-0.05849

C	-4.91853	-2.83896	-0.05277
C	-3.68879	-3.54895	-0.05277
C	-2.45905	-2.83896	-0.05277
C	-2.45905	-1.41897	-0.05277
C	-3.68880	-0.70901	-0.05563
O	-1.33973	-3.60250	-0.04104
C	-0.06327	-2.93460	-0.02167
C	0.00015	-1.41895	-0.01526
C	-1.22940	-0.70898	-0.03762
O	0.95117	-3.59046	-0.02109
C	1.22980	-0.70896	-0.00010
C	1.22989	0.71100	-0.00731
C	0.00020	1.42101	-0.01738
C	-1.22912	0.71087	-0.05712
C	2.45911	-1.41885	0.03455
C	3.68899	-0.70894	0.03741
C	3.68909	0.71102	0.03020
C	2.45954	1.42099	0.00784
C	4.91851	1.42105	0.05765
C	4.91836	2.84102	0.06274
C	3.68965	3.55069	-0.00880
C	2.45983	2.84084	-0.01166
H	-5.87115	-0.86904	-0.05560
H	-5.87114	-3.38895	-0.05787
H	-3.68879	-4.64890	-0.06230
H	-3.68881	0.39094	-0.06516
H	-0.00007	2.52092	-0.00392
H	-2.18036	1.26046	-0.11252
H	2.45887	-2.51873	0.04966
H	4.64156	-1.25903	0.03569
H	5.87115	0.87114	0.06545
H	5.86954	3.39124	0.11252
H	3.69130	4.64890	-0.07146
H	1.50750	3.39069	-0.03851

---

Sum of electronic and zero-point energies = -957.872507334 Hartree

**Table S13.** Atom coordinates for the optimized geometry of CM[4].

---

	X	Y	Z
C	-6.14834	-1.42004	-0.08353
C	-6.14835	-2.83997	-0.07785
C	-4.91861	-3.54996	-0.07785
C	-3.68886	-2.83997	-0.07785
C	-3.68886	-1.41999	-0.07785
C	-4.91862	-0.71002	-0.08069
O	-2.56955	-3.60352	-0.06612
C	-1.29309	-2.93561	-0.04677
C	-1.22967	-1.41997	-0.04036
C	-2.45922	-0.71000	-0.06272

O	-0.27865	-3.59148	-0.04620
C	-0.00002	-0.70998	-0.02523
C	0.00008	0.70999	-0.03244
C	-1.22961	1.42000	-0.04250
C	-2.45893	0.70985	-0.08223
C	1.22930	-1.41986	0.00942
C	2.45937	-0.70997	-0.00004
C	2.45928	0.71001	0.00504
C	1.22973	1.41998	-0.01731
C	3.68893	1.42000	0.02018
C	3.68903	2.83996	0.01296
C	2.45948	3.54994	-0.00939
C	1.23002	2.83983	-0.03682
C	4.91824	0.71011	0.05483
C	6.14762	1.42019	0.08226
C	6.14847	2.83980	0.02586
C	4.91882	3.54986	0.01580
H	-7.10096	-0.87005	-0.08060
H	-7.10095	-3.38997	-0.08298
H	-4.91861	-4.64991	-0.08738
H	-4.91862	0.38993	-0.09022
H	-1.22988	2.51991	-0.02905
H	-3.41017	1.25945	-0.13762
H	1.22899	-2.51958	0.03405
H	3.41177	-1.25995	-0.02082
H	2.45955	4.64991	-0.01498
H	0.27829	3.38946	-0.08270
H	4.91843	-0.38987	0.05089
H	7.09915	0.87110	0.13762
H	7.10096	3.38816	-0.01952
H	4.91897	4.64975	0.00069

---

Sum of electronic and zero-point energies = -1111.52849153 Hartree

**Table S14.** Atom coordinates for the optimized geometry of BCM[2].

	X	Y	Z
C	-3.68895	0.70958	-0.06808
C	-3.68895	-0.71040	-0.06808
C	-2.45921	-1.42039	-0.06808
C	-1.22947	-0.71040	-0.06808
C	-1.22947	0.70958	-0.06808
C	-2.45920	1.41955	-0.07583
O	-0.11015	-1.47395	-0.05635
C	1.16621	-0.80604	-0.02996
C	1.22958	0.70960	-0.02202
C	0.00011	1.41957	-0.04804
O	2.18069	-1.46182	-0.02475
C	2.45916	1.41959	-0.00197
C	2.45927	2.83956	-0.00795

C	1.22979	3.54954	-0.03397
C	0.00044	2.83944	-0.06631
C	3.68836	0.70969	0.03634
C	4.91763	1.41976	0.06868
C	4.91865	2.83941	0.01352
C	3.68903	3.54947	-0.00020
C	-4.91865	-1.42037	-0.05578
C	-4.91863	-2.84034	-0.05039
C	-3.68895	-3.55029	-0.08578
C	-2.45921	-2.84032	-0.08038
H	-4.64144	1.25958	-0.05255
H	-2.45924	2.51933	-0.09736
H	1.22987	4.64952	-0.03861
H	-0.95112	3.38910	-0.11503
H	3.68857	-0.39029	0.03145
H	5.86897	0.87062	0.12688
H	5.87128	3.38782	-0.02805
H	3.68921	4.64937	-0.01436
H	-5.87128	-0.87042	-0.05997
H	-5.87086	-3.39057	-0.02833
H	-3.68915	-4.64952	-0.12688
H	-1.50663	-3.39019	-0.09525

---

Sum of electronic and zero-point energies = -957.880637490 Hartree

**Table S15.** Atom coordinates for the optimized geometry of BCM[3].

	X	Y	Z
C	-4.30362	-0.35440	-0.05725
C	-4.30362	-1.77438	-0.05725
C	-3.07388	-2.48437	-0.05725
C	-1.84414	-1.77438	-0.05725
C	-1.84414	-0.35440	-0.05725
C	-3.07389	0.35557	-0.06127
O	-0.72482	-2.53793	-0.04551
C	0.55162	-1.87002	-0.02475
C	0.61503	-0.35438	-0.01783
C	-0.61451	0.35560	-0.04093
O	1.56611	-2.52580	-0.02343
C	1.84466	0.35561	-0.00151
C	1.84476	1.77558	-0.00828
C	0.61508	2.48559	-0.01908
C	-0.61421	1.77545	-0.05999
C	3.07395	-0.35428	0.03388
C	4.30383	0.35563	0.03791
C	4.30393	1.77560	0.03114
C	3.07439	2.48557	0.00804
C	-5.53332	-2.48434	-0.04495
C	-5.53330	-3.90432	-0.03963
C	-4.30362	-4.61427	-0.07486

C	-3.07388	-3.90430	-0.06954
C	5.53332	2.48562	0.05975
C	5.53316	3.90559	0.06527
C	4.30450	4.61528	-0.00700
C	3.07469	3.90543	-0.01103
H	-5.25615	0.19560	-0.04460
H	-3.07396	1.45545	-0.07703
H	0.61479	3.58549	-0.00529
H	-1.56541	2.32506	-0.11596
H	3.07370	-1.45417	0.04865
H	5.25640	-0.19445	0.03675
H	-6.48595	-1.93439	-0.04907
H	-6.48553	-4.45455	-0.01777
H	-4.30381	-5.71350	-0.11578
H	-2.12130	-4.45417	-0.08448
H	6.48595	1.93572	0.06812
H	6.48430	4.45580	0.11596
H	4.30620	5.71350	-0.06932
H	2.12238	4.45528	-0.03844

---

Sum of electronic and zero-point energies = -1111.52847103 Hartree

**Table S16.** Atom coordinates for the optimized geometry of BCM[4].

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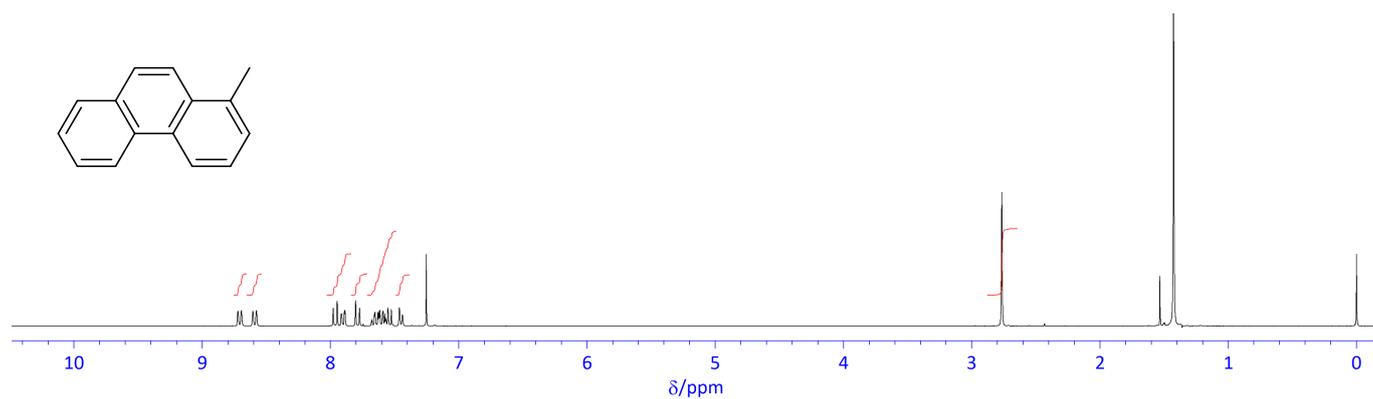
	X	Y	Z
C	-5.53340	-0.35537	-0.08936
C	-5.53340	-1.77535	-0.08936
C	-4.30366	-2.48535	-0.08936
C	-3.07392	-1.77535	-0.08936
C	-3.07392	-0.35537	-0.08936
C	-4.30367	0.35459	-0.09486
O	-1.95460	-2.53890	-0.07763
C	-0.67819	-1.87100	-0.05497
C	-0.61480	-0.35536	-0.04747
C	-1.84431	0.35462	-0.07157
O	0.33630	-2.52677	-0.05253
C	0.61482	0.35464	-0.02968
C	0.61492	1.77460	-0.03597
C	-0.61476	2.48461	-0.04777
C	-1.84400	1.77448	-0.09016
C	1.84408	-0.35526	0.00671
C	3.07415	0.35465	-0.00009
C	3.07404	1.77462	0.00591
C	1.84453	2.48460	-0.01818
C	-6.76310	-2.48532	-0.07707
C	-6.76309	-3.90529	-0.07239
C	-5.53340	-4.61525	-0.10634
C	-4.30366	-3.90528	-0.10166
C	4.30365	2.48461	0.02371
C	4.30375	3.90458	0.01741

C	3.07424	4.61456	-0.00668
C	1.84484	3.90446	-0.03677
C	5.53291	1.77471	0.06010
C	6.76224	2.48479	0.09018
C	6.76317	3.90443	0.03471
C	5.53353	4.61449	0.02291
H	-6.48592	0.19463	-0.07558
H	-4.30372	1.45444	-0.11291
H	-0.61507	3.58451	-0.03361
H	-2.79515	2.32410	-0.14689
H	1.84373	-1.45499	0.03062
H	4.02660	-0.19531	-0.01952
H	-7.71573	-1.93536	-0.08069
H	-7.71535	-4.45553	-0.05201
H	-5.53356	-5.71454	-0.14577
H	-3.35109	-4.45514	-0.11709
H	3.07431	5.71454	-0.01156
H	0.89319	4.45411	-0.08400
H	5.53312	0.67473	0.05545
H	7.71367	1.93566	0.14689
H	7.71573	4.45283	-0.00861
H	5.53370	5.71439	0.00851

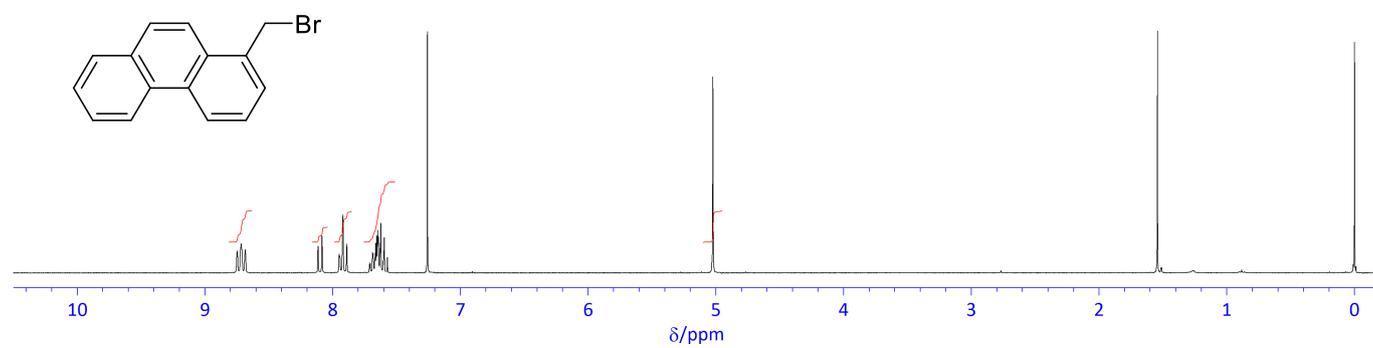
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Sum of electronic and zero-point energies = -1265.17797498 Hartree

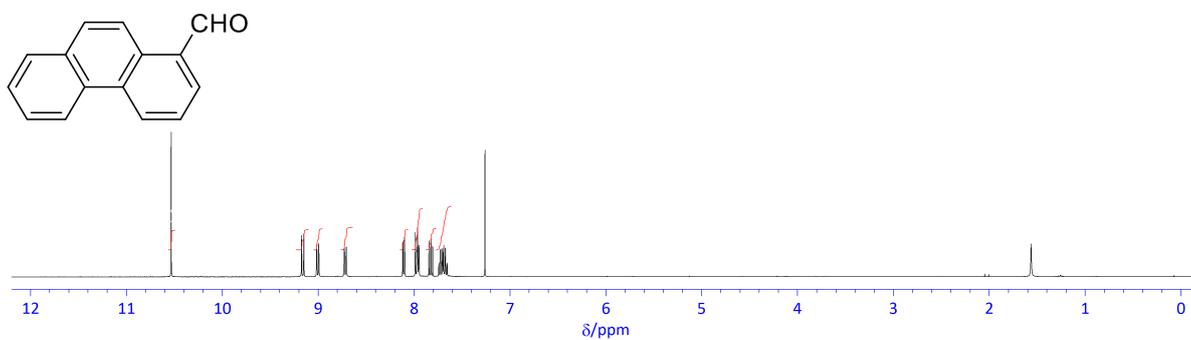
## 5. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra



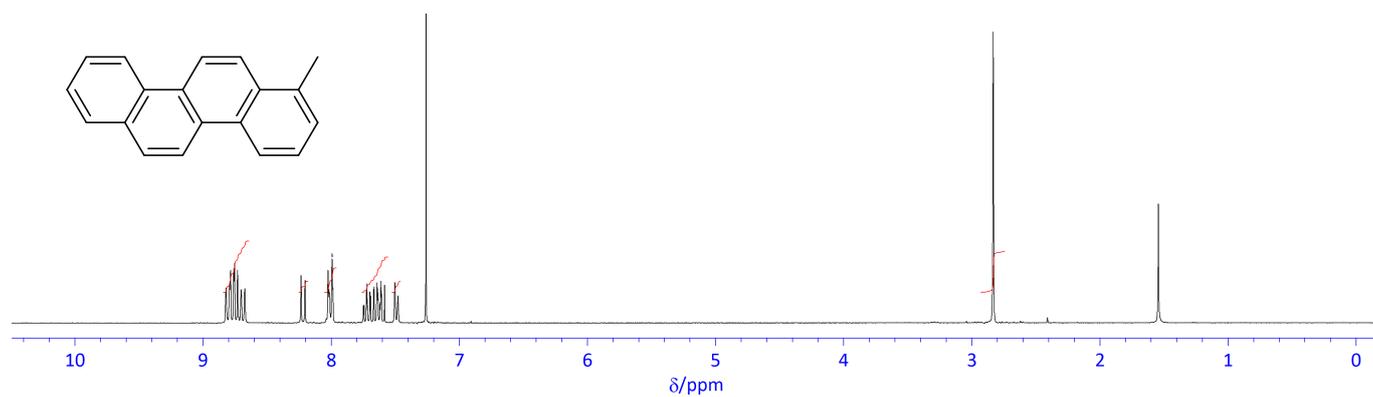
**Figure S6.**  $^1\text{H}$  (300 MHz) NMR spectrum of 1-methylphenanthrene in  $\text{CDCl}_3$ .



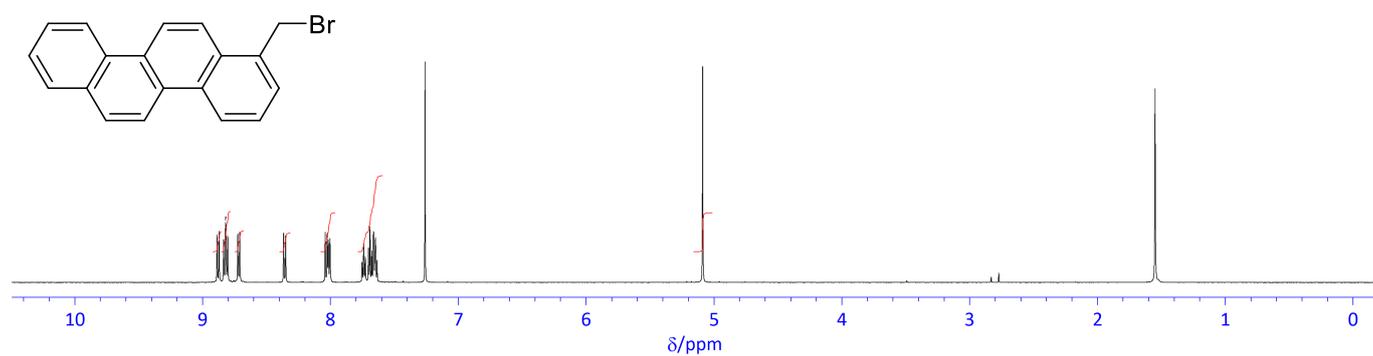
**Figure S7.**  $^1\text{H}$  (300 MHz) NMR spectrum of 1-(bromomethyl)phenanthrene in  $\text{CDCl}_3$ .



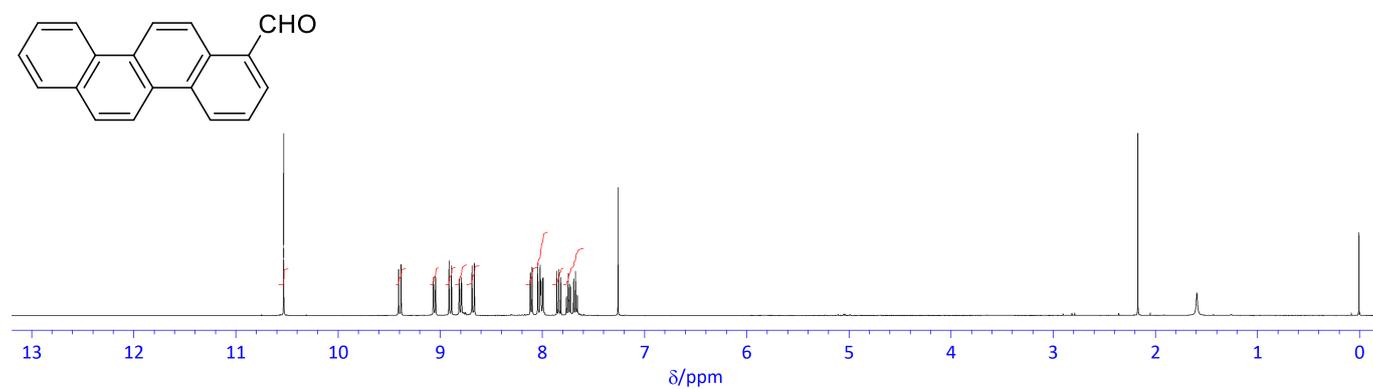
**Figure S8.**  $^1\text{H}$  (400 MHz) NMR spectrum of 1-phenanthrenecarbaldehyde in  $\text{CDCl}_3$ .



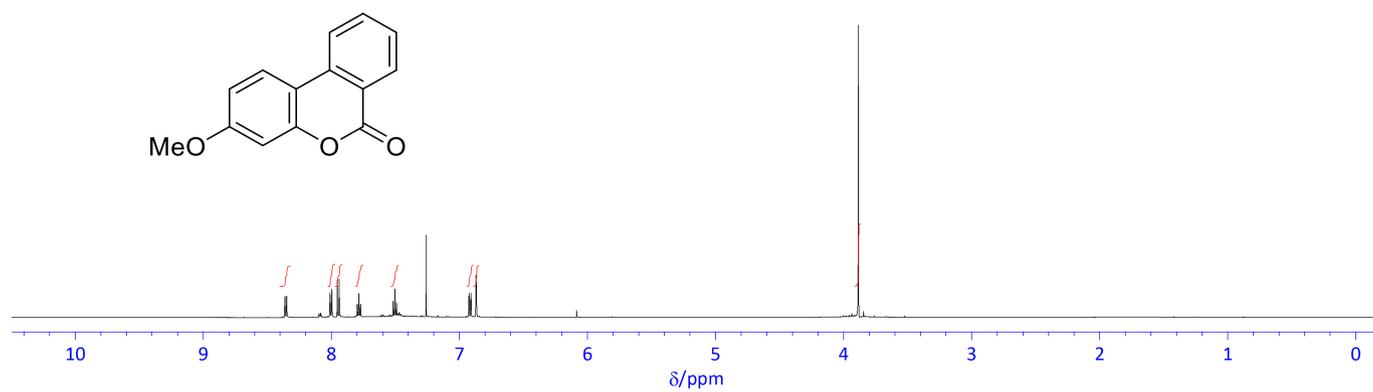
**Figure S9.**  $^1\text{H}$  (400 MHz) NMR spectrum of 1-methylchrysene in  $\text{CDCl}_3$ .



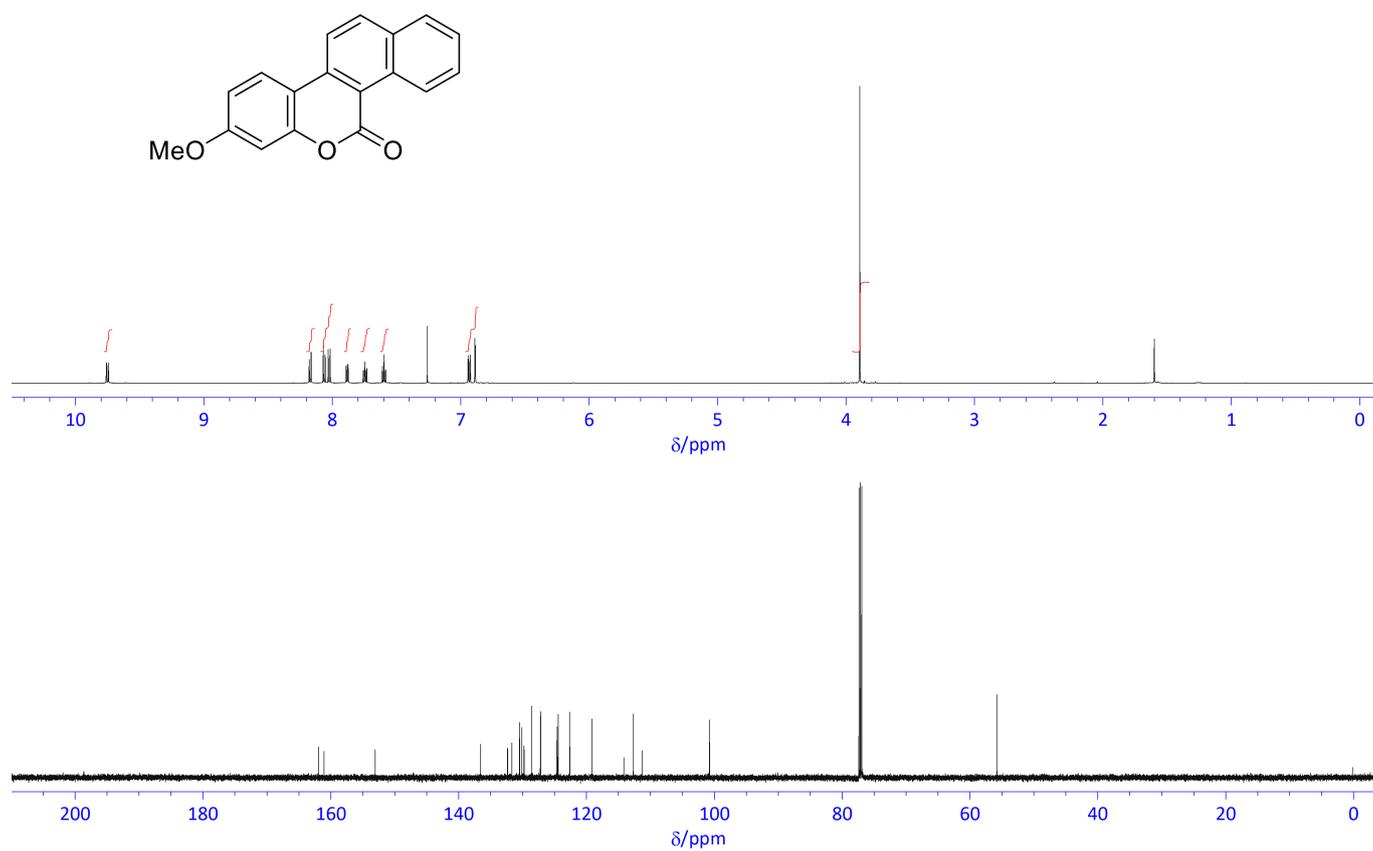
**Figure S10.**  $^1\text{H}$  (600 MHz) NMR spectrum of 1-(bromomethyl)chrysene in  $\text{CDCl}_3$ .



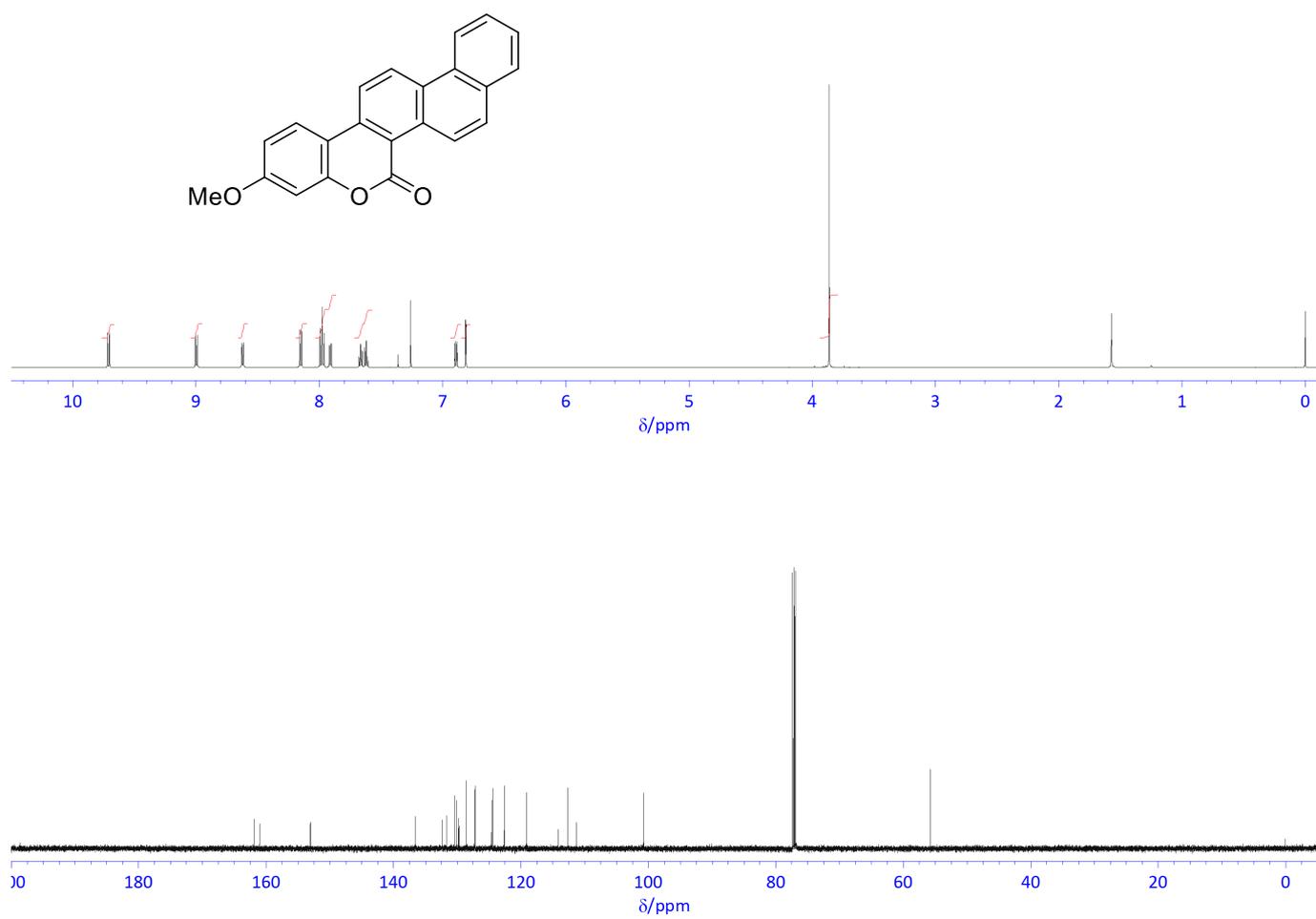
**Figure S11.**  $^1\text{H}$  (600 MHz) NMR spectrum of 1-crysenecarbaldehyde in  $\text{CDCl}_3$ .



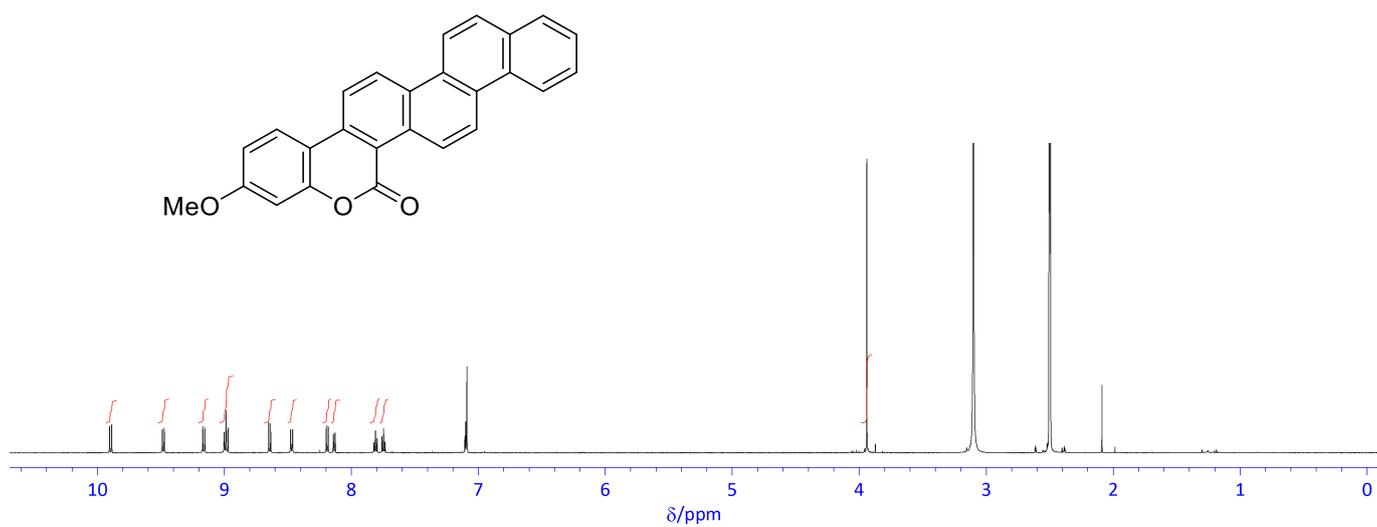
**Figure S12.**  $^1\text{H}$  (600 MHz) NMR spectrum of MeOCM[1] in  $\text{CDCl}_3$ .



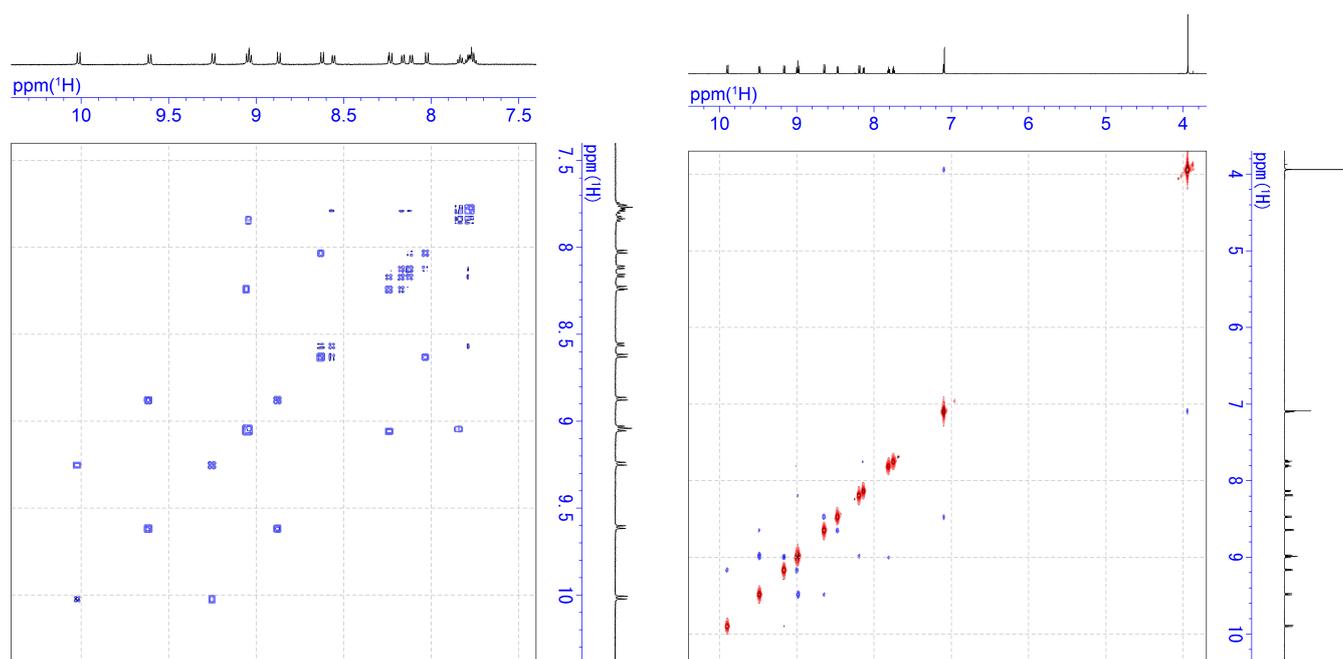
**Figure S13.**  $^1\text{H}$  (600 MHz, upper) and  $^{13}\text{C}$  (151 MHz, lower) NMR spectra of MeOCM[2] in  $\text{CDCl}_3$ .



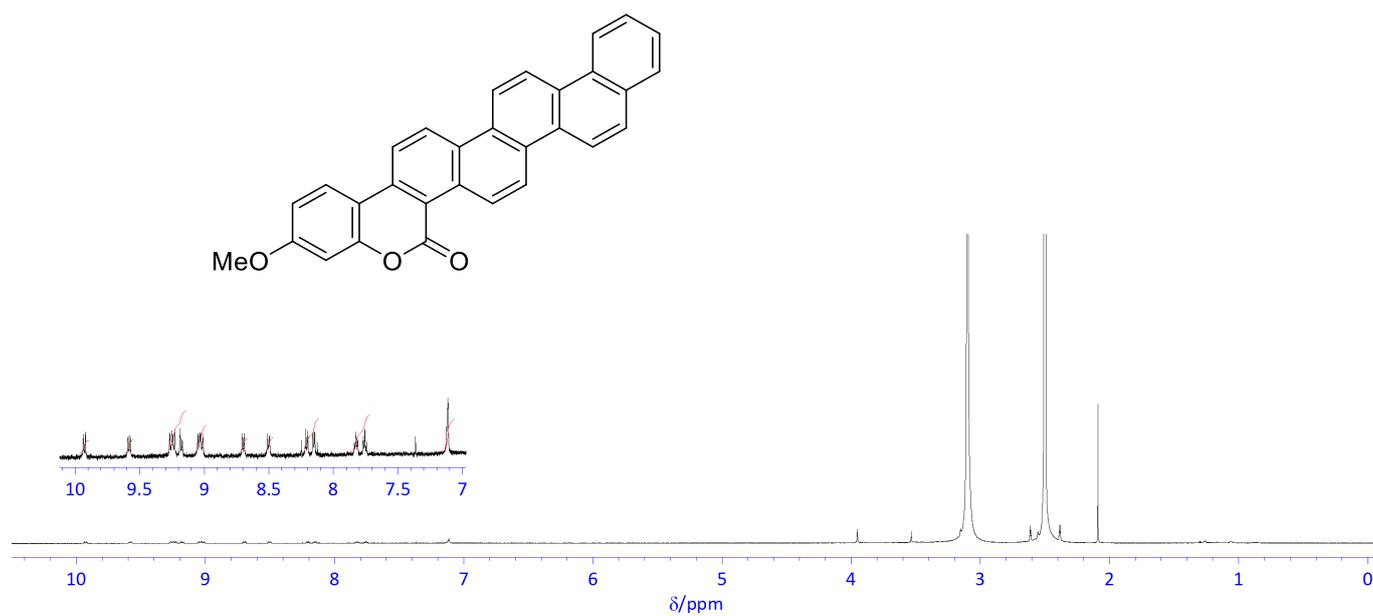
**Figure S14.** <sup>1</sup>H (600 MHz, upper) and <sup>13</sup>C (151 MHz, lower) NMR spectra of MeOCM[3] in CDCl<sub>3</sub>.



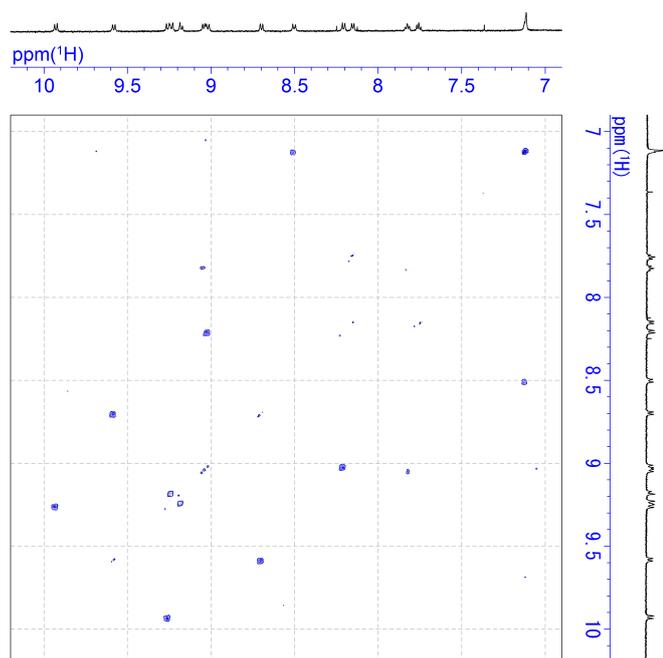
**Figure S15.** <sup>1</sup>H NMR spectrum of MeOCM[4] in DMSO-*d*<sub>6</sub> at 70 °C.



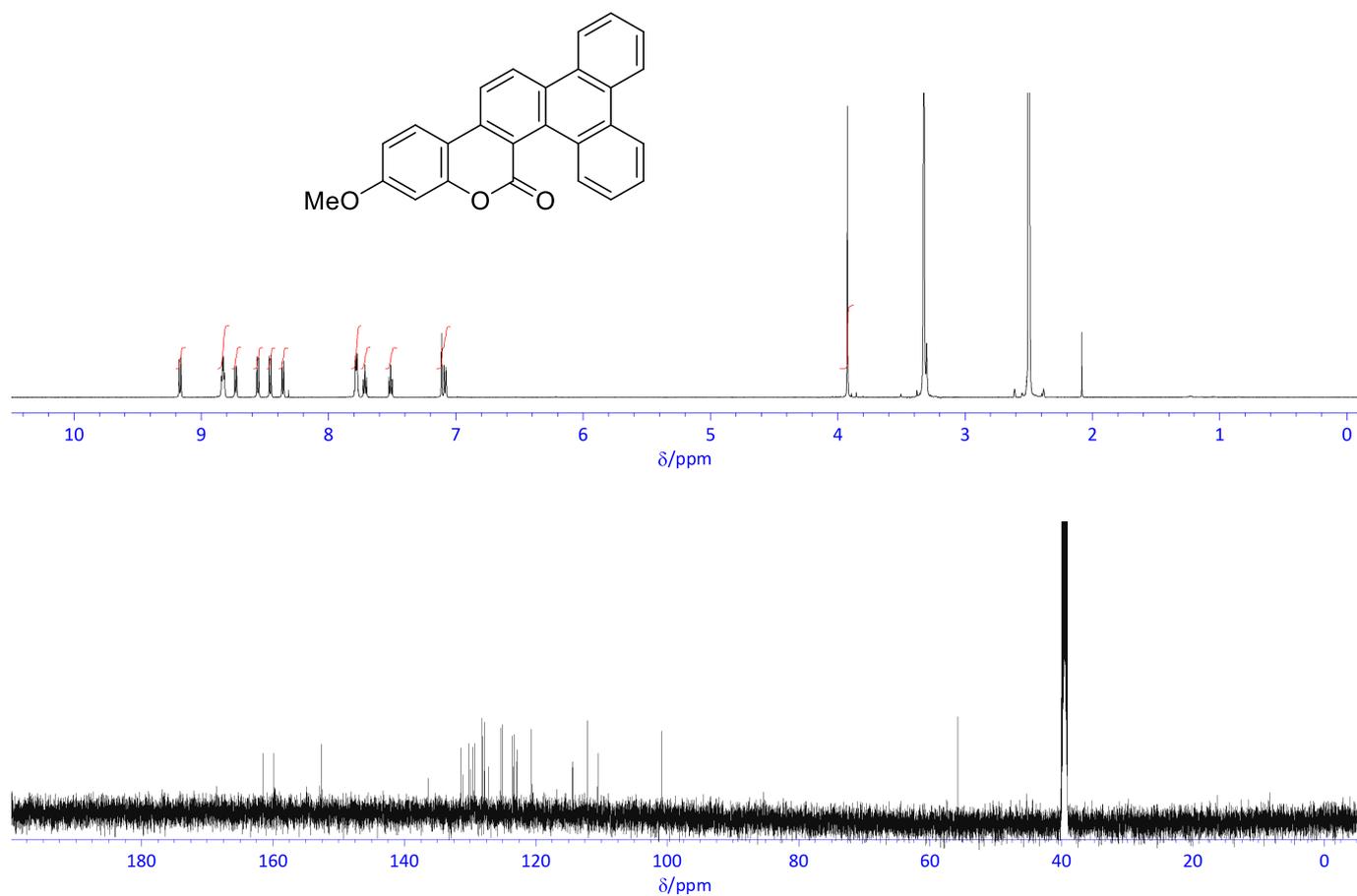
**Figure S16.** COSY (left) and NOESY (right) spectra of MeOCM[4] in DMSO-*d*<sub>6</sub> at 70 °C.



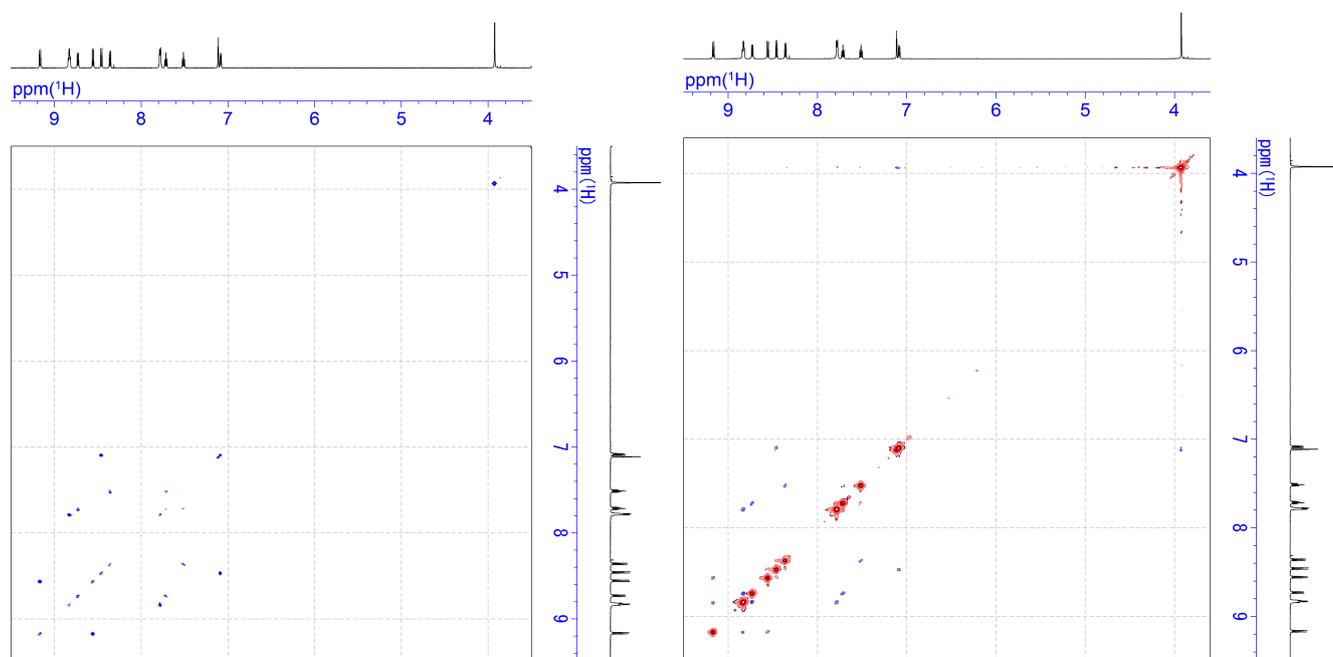
**Figure S17.**  $^1\text{H}$  NMR spectrum of MeOCM[5] in  $\text{DMSO-}d_6$  at  $70\text{ }^\circ\text{C}$ .



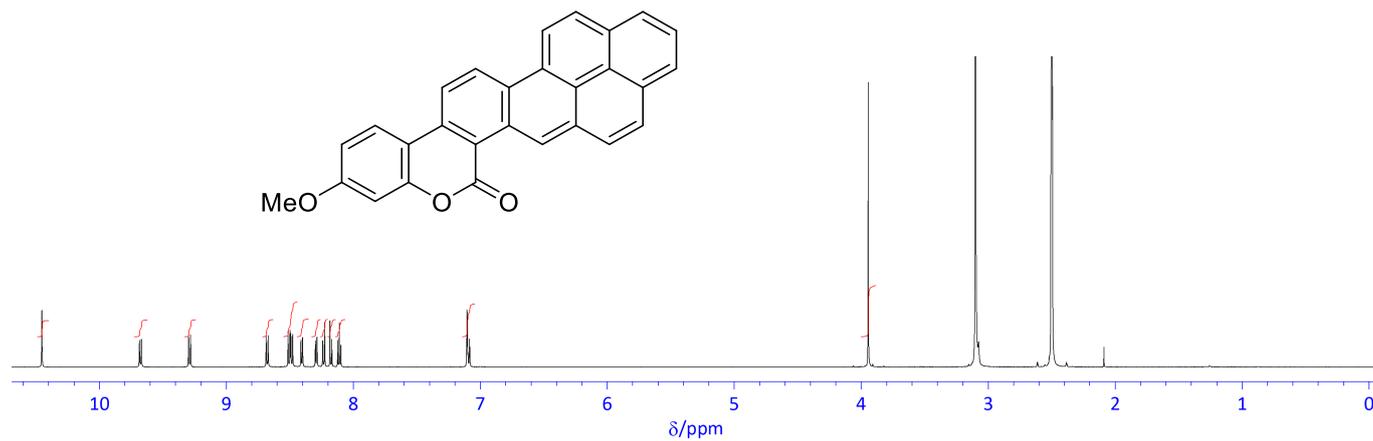
**Figure S18.** COSY spectrum of MeOCM[5] in  $\text{DMSO-}d_6$  at  $70\text{ }^\circ\text{C}$ .



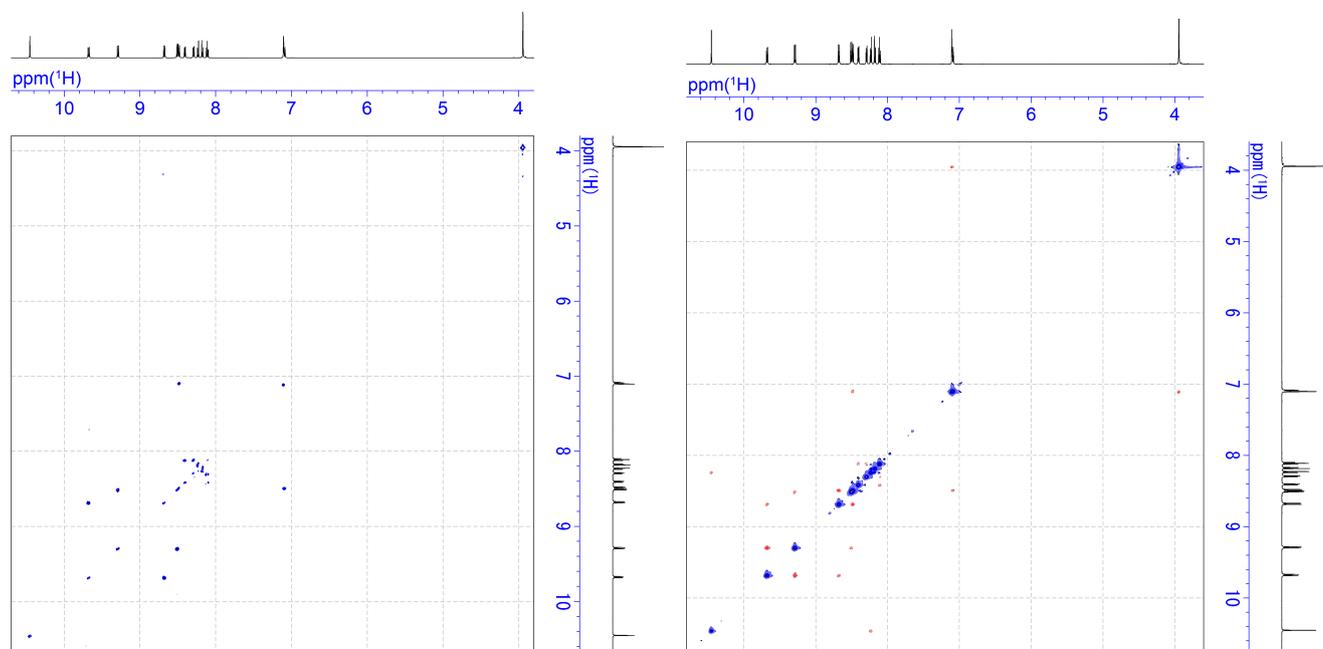
**Figure S19.**  $^1\text{H}$  (600 MHz, r.t., upper) and  $^{13}\text{C}$  (151 MHz, 50 °C, lower) NMR spectrum of MeOCMPhe in  $\text{DMSO-}d_6$ .



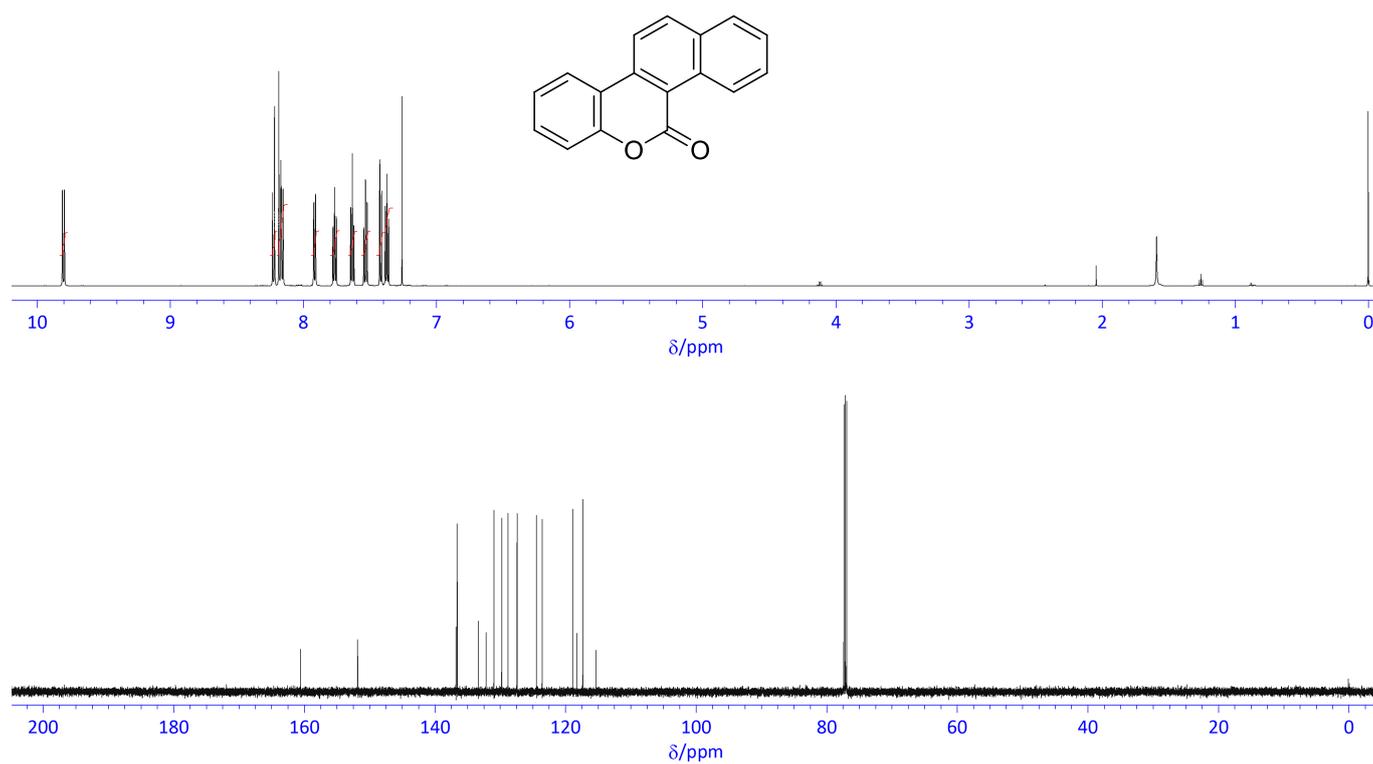
**Figure S20.** COSY (left) and NOESY (right) spectra of MeOCMPhe in  $\text{DMSO-}d_6$ , at 70 °C.



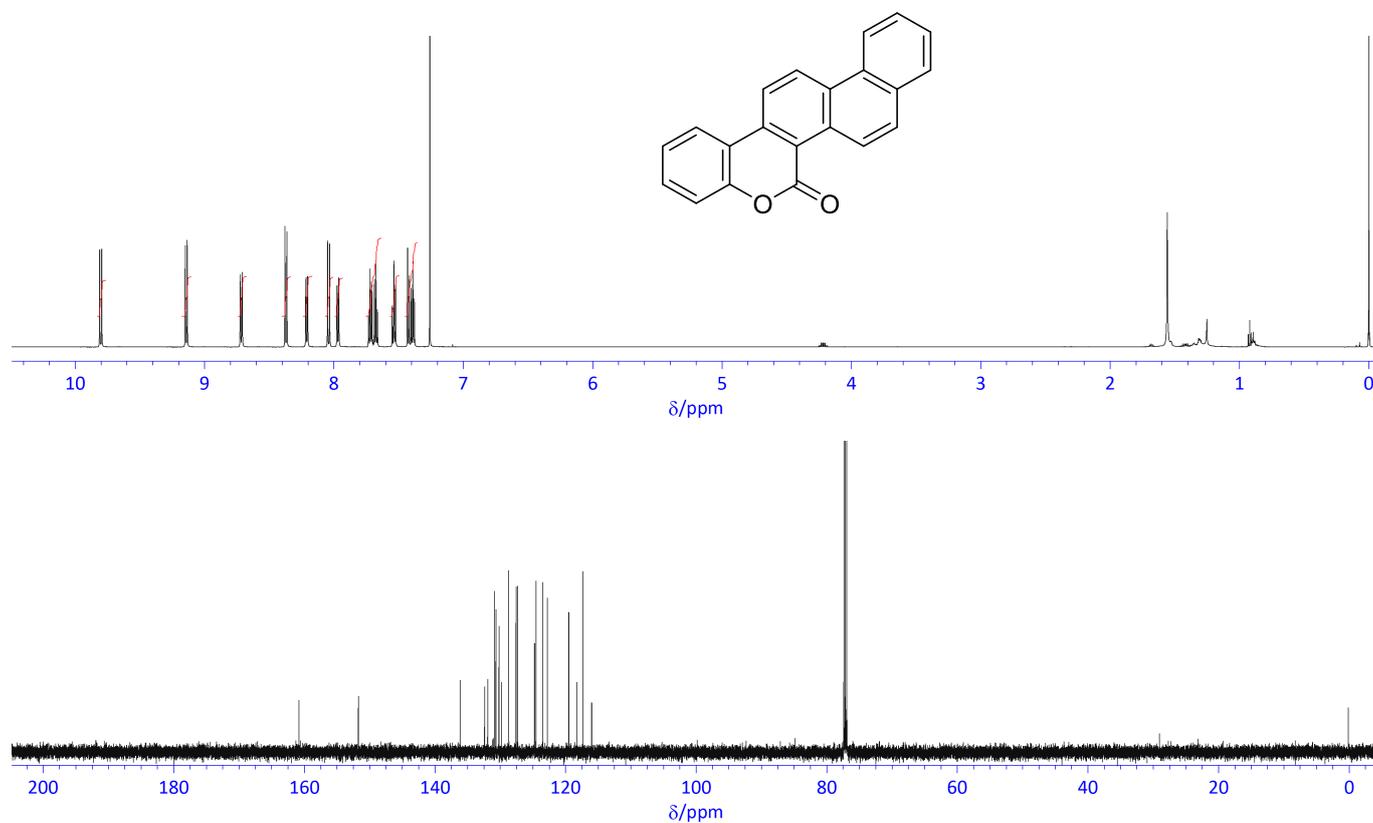
**Figure S21.**  $^1\text{H}$  NMR spectrum of MeOCMPy in  $\text{DMSO-}d_6$  at  $70\text{ }^\circ\text{C}$ .



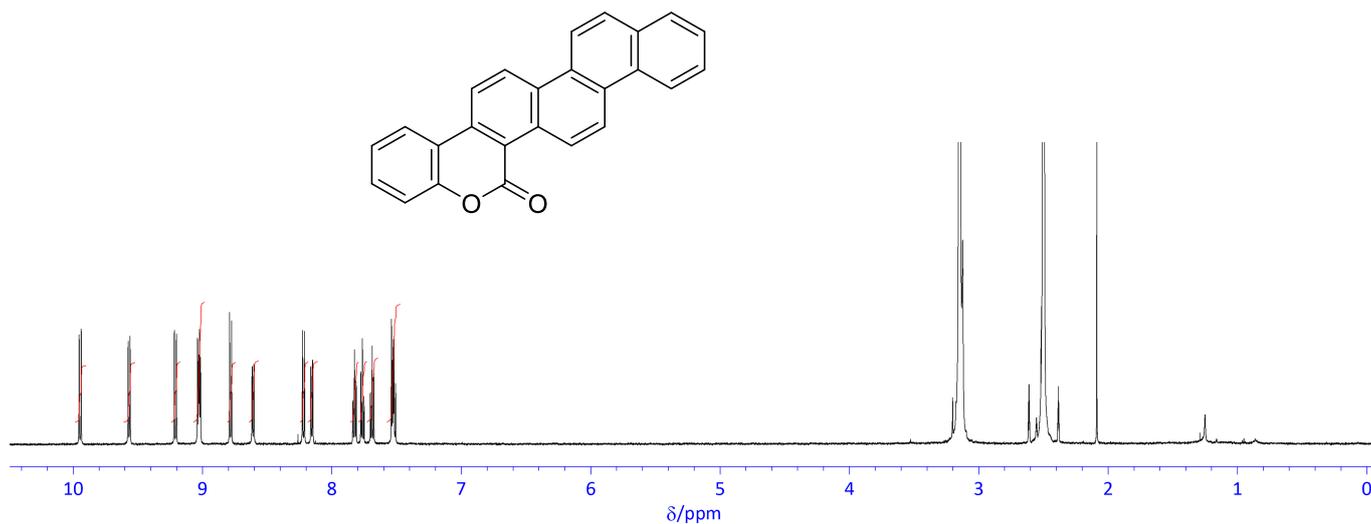
**Figure S22.** COSY (left) and NOESY (right) spectra of MeOCMPy in  $\text{DMSO-}d_6$  at  $70\text{ }^\circ\text{C}$ .



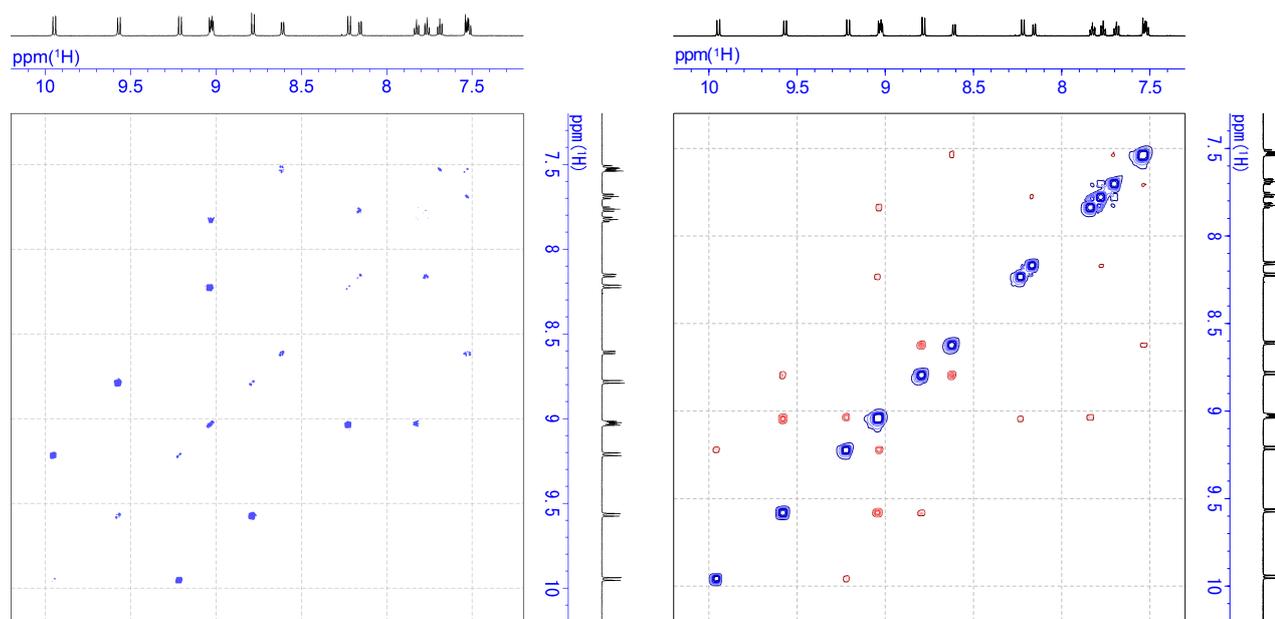
**Figure S23.** <sup>1</sup>H (600 MHz, upper) and <sup>13</sup>C (151 MHz, lower) NMR spectra of CM[2] in CDCl<sub>3</sub>.



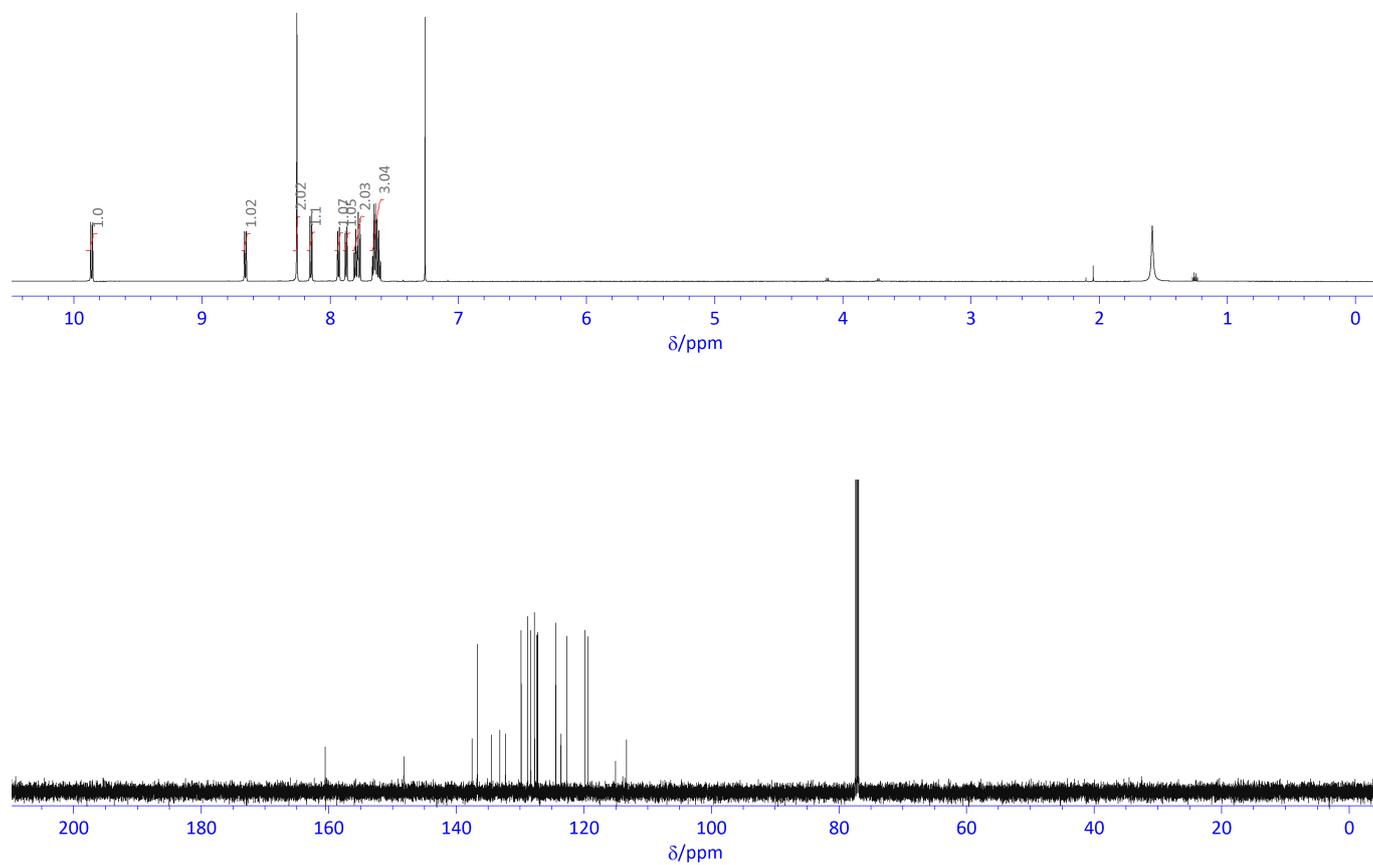
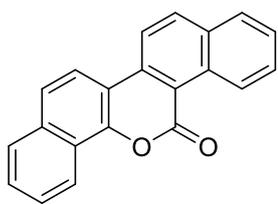
**Figure S24.** <sup>1</sup>H (600 MHz, upper) and <sup>13</sup>C (151 MHz, lower) NMR spectra of CM[3] in CDCl<sub>3</sub>.



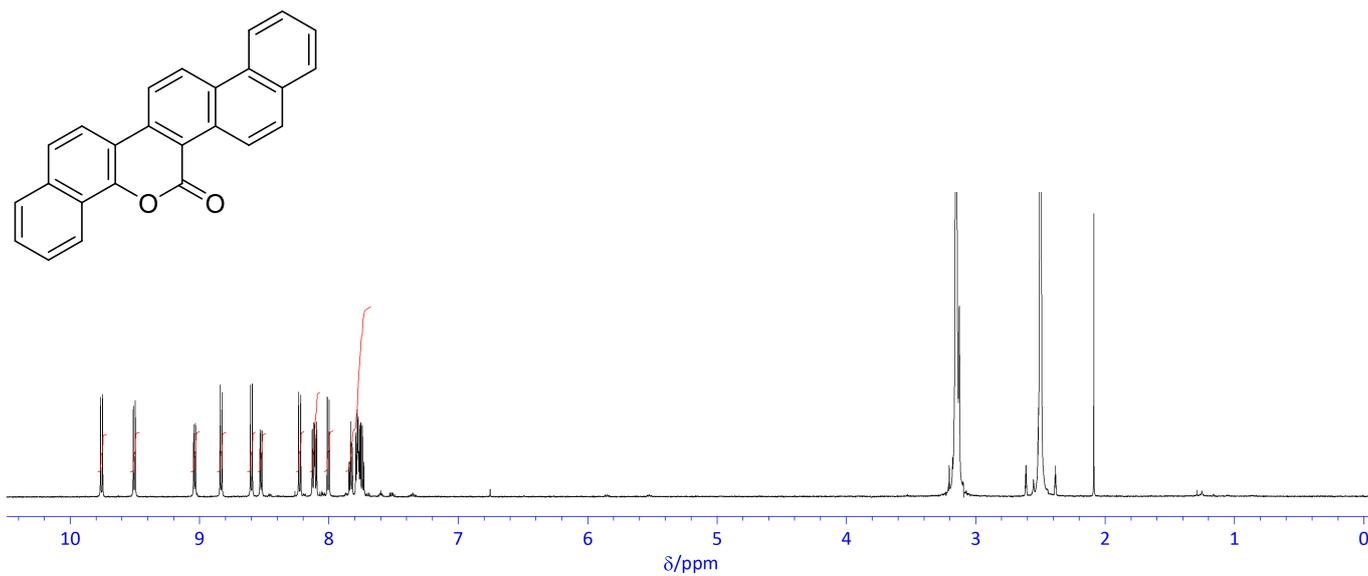
**Figure S25.** <sup>1</sup>H (600 MHz) spectrum of CM[4] in DMSO-*d*<sub>6</sub> at 60 °C.



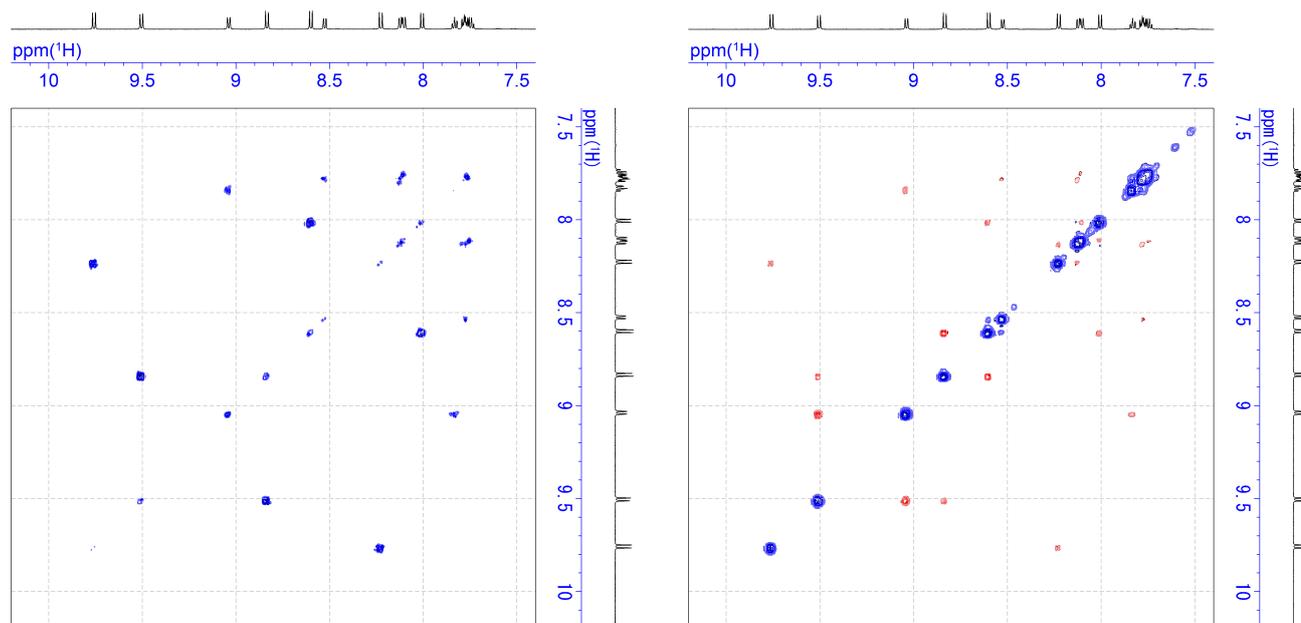
**Figure S26.** COSY (left) and NOESY (right) spectra of CM[4] in DMSO-*d*<sub>6</sub> at 60 °C.



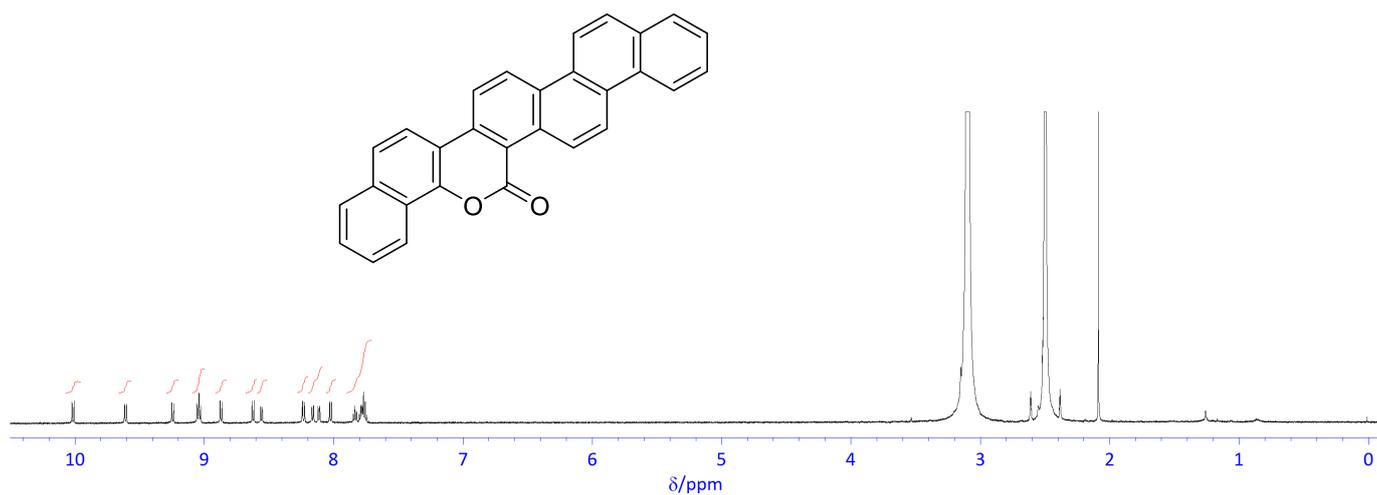
**Figure S27.** <sup>1</sup>H (600 MHz, upper) and <sup>13</sup>C (151 MHz, lower) NMR spectra of BCM[2] in CDCl<sub>3</sub>.



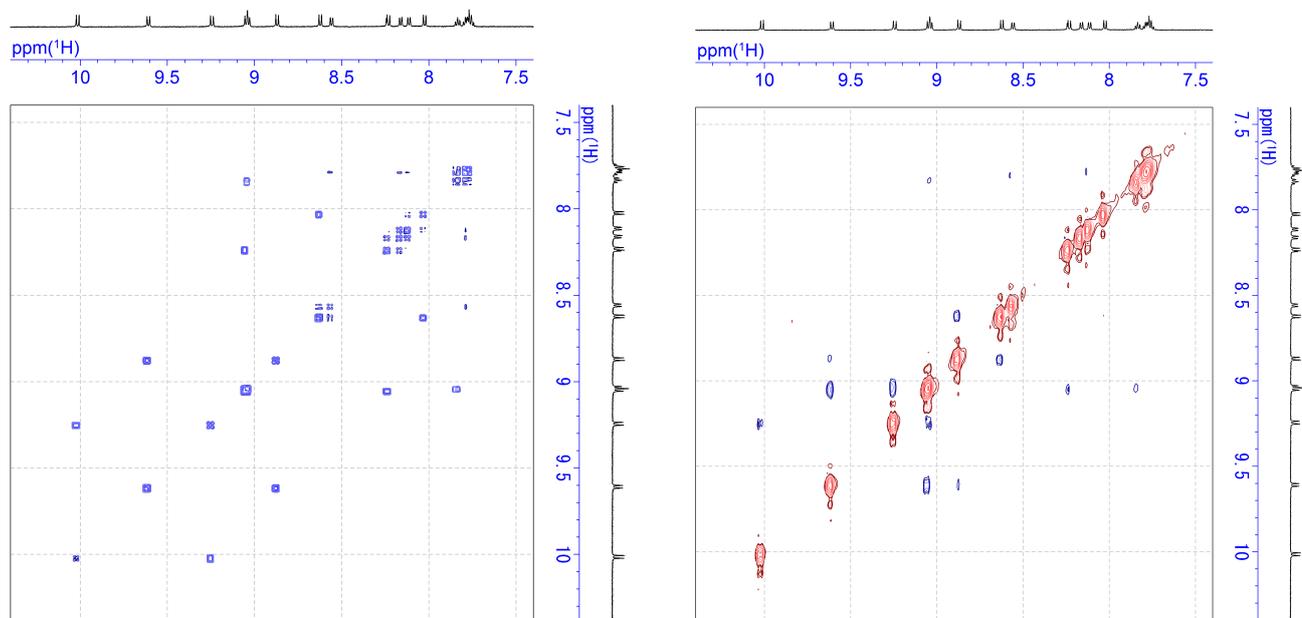
**Figure S28.** <sup>1</sup>H (600 MHz) spectrum of BCM[3] in DMSO-*d*<sub>6</sub> at 60 °C.



**Figure S29.** COSY (left) and NOESY (right) spectra of BCM[3] in DMSO-*d*<sub>6</sub> at 60 °C.



**Figure S30.**  $^1\text{H}$  (600 MHz) spectrum of BCM[4] in  $\text{DMSO-}d_6$  at  $70\text{ }^\circ\text{C}$ .



**Figure S31.** COSY (left) and NOESY (right) spectra of BCM[4] in  $\text{DMSO-}d_6$  at  $70\text{ }^\circ\text{C}$ .

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