

## SUPPORTING INFORMATION

### **Keto-enol equilibrium: stable tautomers of *ortho*-, *meta*-, and *para*-hydroquinones in large aromatics**

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## General methods:

Commercially available reagent grade materials such as 2-naphthaldehyde and 2,6-dimethoxy-4-bromobenzaldehyde were used as obtained from Sigma-Aldrich, Acros Organics, Fischer Scientific. The synthesis of 2-bromo-benzo[c]phenanthrene as well as its subsequent functionalization were carried out following methodology described in the literature<sup>[1]</sup> except for the photocyclization steps which were adapted and are described below. THF was distilled from sodium/benzophenone ketyl. Column chromatography was performed with silica gel from Merck (Kieselgel 60; 63-200  $\mu\text{m}$  or 40-63  $\mu\text{m}$ ).  $^1\text{H}$  NMR spectra were recorded on Bruker Avance 400 (400 MHz) or 500 (500 MHz) spectrometers. Chemical shifts are given in parts per million (ppm) by taking the solvent as a reference  $\delta_{\text{CHCl}_3} = 7.26$  ppm for  $^1\text{H}$  NMR and  $\delta_{\text{CHCl}_3} = 77.16$  ppm for  $^{13}\text{C}$  NMR. The coupling constants ( $J$ ) are given in Hertz (Hz) and the multiplicity of the signals are expressed as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectrometry (MS and HRMS) experiments were performed on a Bruker Daltonics microTOF spectrometer (Bruker Daltonik GmbH, Bremen, Germany) by the Service de Spectrométrie de Masse de la Fédération de Chimie "Le Bel" (FR 2010). Irradiation of stilbene derivatives was carried out with a Heraeus TQ 150 mercury vapor lamp in a 400 mL photoreactor. The protons of  $^1\text{H}$  spectra were assigned according to Martin's proposed nomenclature (see figure below).<sup>[2]</sup> Protons belonging to the [6]-helicene skeleton ( $\text{H}_5\text{-H}_{12}$ ) are typically observed as doublets with well-defined correlations observed by COSY analysis. However, the lack of correlation using ROESY and NOESY experiments, as well as the lack of resolution with  $^1\text{H}\text{-}^{13}\text{C}$  experiments such as HSQC and HMBC prevented the elucidation of their relative positions. These signals were then defined as groups of protons.

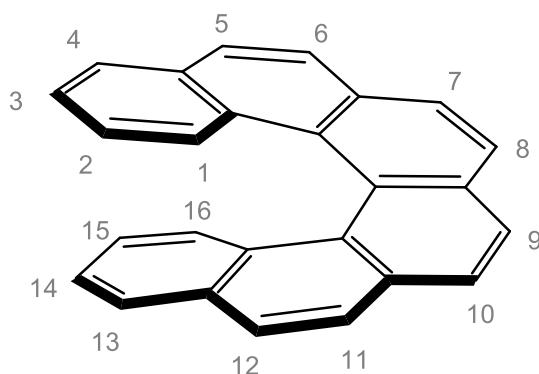
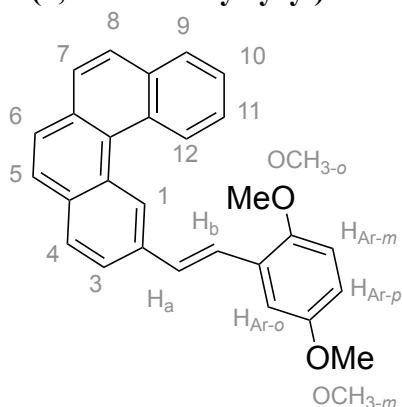


Figure S1: Helicene numbering defined by Martin<sup>[2]</sup>

## Experimental Data, $^1\text{H}$ , $^{13}\text{C}$ , DEPT135

### 2-(2,5-dimethoxystyryl)benzo[*c*]phenanthrene



Under argon, NaH (60% in mineral oil) (277 mg, 6.92 mmol, 1.32 eq.) was added to a solution of diethyl 2,5-dimethoxybenzylphosphonate (1.96 g, 6.81 mmol, 1.30 eq.) in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of benzo[*c*]phenanthrene-2-carbaldehyde (1.34 g, 5.24 mmol, 1 eq.) in freshly distilled THF (30 mL) was added dropwise. The resulting solution was heated at 50 °C for 16 h. After the solution was allowed to cool to room temperature, H<sub>2</sub>O (50 mL) was added. The THF was removed under reduced pressure. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the resulting solution was washed with a saturated aqueous solution of NH<sub>4</sub>Cl (3 x 20 mL), dried over MgSO<sub>4</sub>, and filtered. Subsequent purification of the crude product by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 30/70) afforded the desired product as a yellow solid (1.91 mg, 4.89 mmol, 93%).

**$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C):**  $\delta_{\text{H}}$  (ppm) = 9.18 (d,  $J$  = 8.5 Hz, 1H, H<sub>12</sub>), 9.15 (s, 1H, H<sub>1</sub>), 8.04 (dd,  $J$  = 8.0, 1.4 Hz, 1H, H<sub>9</sub>), 8.00 (d,  $J$  = 8.4 Hz, 1H, H<sub>4</sub>), 7.95 (dd,  $J$  = 8.4, 1.6 Hz, 1H, H<sub>3</sub>), 7.91 (d,  $J$  = 8.5 Hz, 1H, H<sub>5-8</sub>), 7.88 (d,  $J$  = 8.5 Hz, 1H, H<sub>5-8</sub>), 7.82 (m, 2H, 2\*H<sub>5-8</sub>), 7.74 (ddd,  $J$  = 8.4, 6.8, 1.5 Hz, 1H, H<sub>11</sub>), 7.68 (d,  $J$  = 16.4 Hz, 1H, H<sub>a</sub>), 7.66 (ddd,  $J$  = 8.0, 6.9, 1.1 Hz, 1H, H<sub>10</sub>), 7.39 (d,  $J$  = 16.4 Hz, 1H, H<sub>b</sub>), 7.27 (d,  $J$  = 2.9 Hz, 1H, H<sub>Ar-o</sub>), 6.88 (d,  $J$  = 8.9 Hz, 1H, H<sub>Ar-m</sub>), 6.84 (dd,  $J$  = 8.9, 2.9 Hz, 1H, H<sub>Ar-p</sub>), 3.90 (s, 3H, OCH<sub>3-m</sub>), 3.87 (s, 3H, OCH<sub>3-o</sub>).

**$^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta_{\text{C}}$  (ppm) = 153.9, 151.6, 135.8, 133.7, 133.1, 131.4, 130.8, 130.5, 130.0 (CH), 129.0 (CH), 128.7 (CH), 128.0 (CH), 127.7 (CH), 127.5, 127.4 (CH), 127.3 (CH), 127.3, 127.0 (CH), 126.9 (CH), 126.4, 126.0 (CH), 123.9 (CH), 123.5 (CH), 114.0 (CH), 112.5 (CH), 111.7 (CH), 56.5 (CH<sub>3</sub>), 56.0 (CH<sub>3</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ([M<sup>•+</sup>]) 390.1614; found 390.1633.

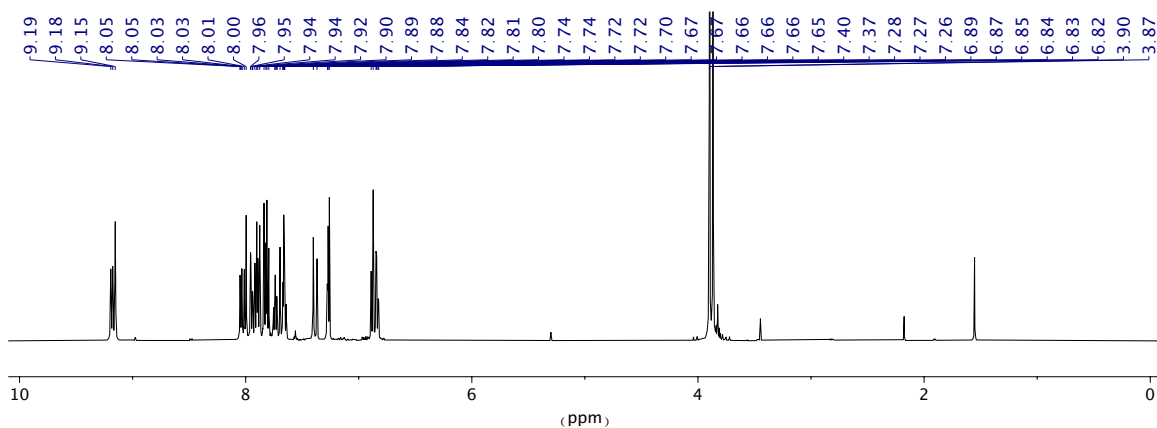


Figure S2:  $^1\text{H}$  NMR spectrum of 2-(2,5-dimethoxystyryl)benzo[*c*]phenanthrene

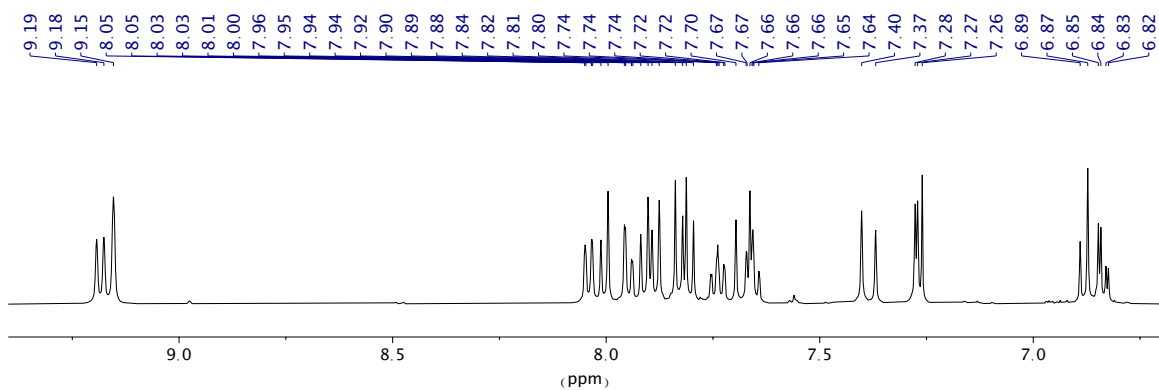


Figure S3:  $^1\text{H}$  NMR spectrum of 2-(2,5-dimethoxystyryl)benzo[c]phenanthrene (aromatic area)

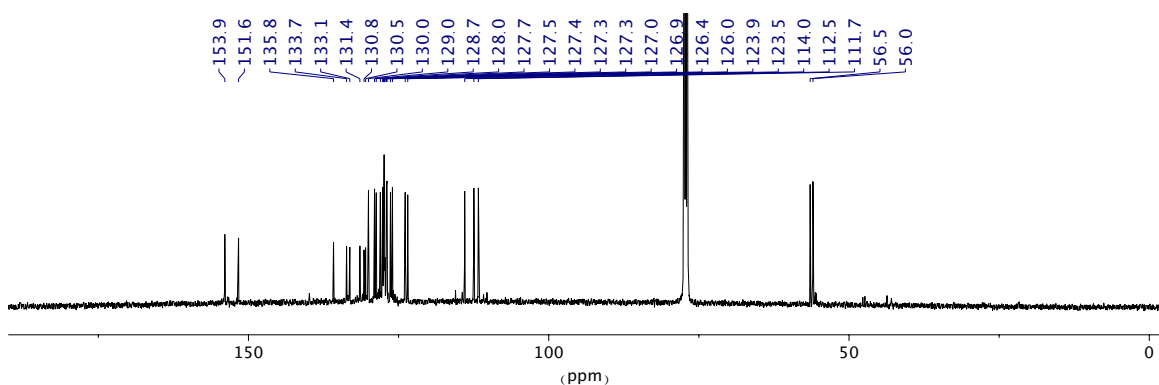


Figure S4:  $^{13}\text{C}$  NMR spectrum of 2-(2,5-dimethoxystyryl)benzo[c]phenanthrene

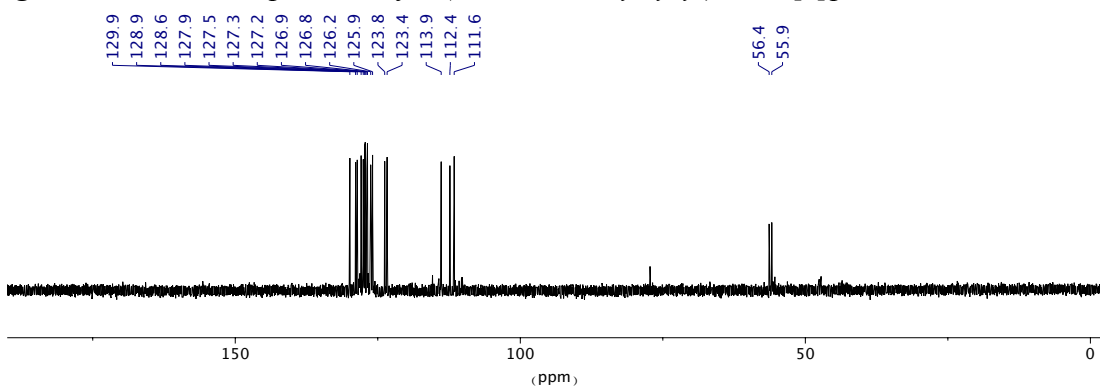


Figure S5: DEPT135 NMR spectrum of 2-(2,5-dimethoxystyryl)benzo[c]phenanthrene

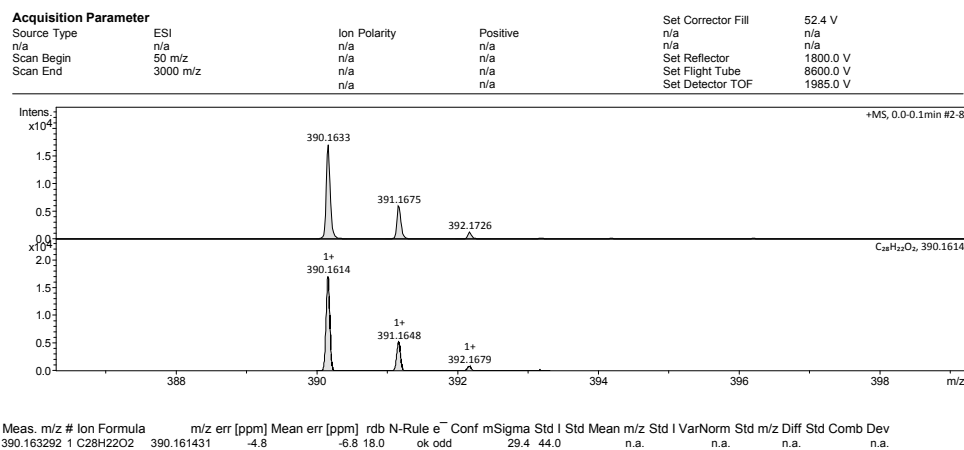
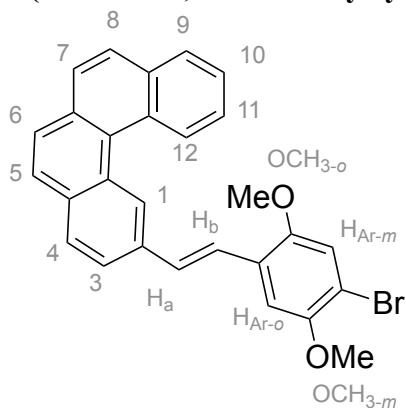


Figure S6: ESI-TOF-HRMS of 2-(2,5-dimethoxystyryl)benzo[c]phenanthrene

## 2-(4-bromo-2,5-dimethoxystyryl)benzo[*c*]phenanthrene



Under Argon, NaH (60% in mineral oil) (220 mg, 5.49 mmol, 1.1 eq.) was added to a solution of diethyl 4-bromo-2,5-dimethoxybenzylphosphonate (2.02 g, 5.49 mmol, 1.1 eq.) in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of benzo[*c*]phenanthrene-2-carbaldehyde (1.28 g, 4.99 mmol, 1.0 eq.) in freshly distilled THF (30 mL) was added dropwise. The resulting solution was heated at 50 °C for 16 h. After the solution was allowed to cool to room temperature, H<sub>2</sub>O (50 mL) was added. The THF was removed under reduced pressure. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the resulting solution was washed with a saturated aqueous solution of NH<sub>4</sub>Cl (3 x 20 mL), dried over MgSO<sub>4</sub>, and filtered. Subsequent purification of the crude product by column chromatography afforded the desired product as a yellow solid (2.23 mg, 4.74 mmol, 95%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C):** δ<sub>H</sub> (ppm) = 9.17 (d, *J* = 8.5 Hz, 1H, H<sub>12</sub>), 9.15 (s, 1H, H<sub>1</sub>), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H H<sub>9</sub>), 8.01 (d, *J* = 8.3 Hz, 1H, H<sub>4</sub>), 7.96 – 7.87 (m, 3H, H<sub>3</sub> + 2\*H<sub>5-8</sub>), 7.85 – 7.80 (2d, 2H, 2\*H<sub>5-8</sub>), 7.74 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H, H<sub>11</sub>), 7.65 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H, H<sub>10</sub>), 7.61 (d, *J* = 16.4 Hz, 1H, H<sub>b</sub>), 7.38 (d, *J* = 16.4 Hz, 1H, H<sub>a</sub>), 7.24 (s, 1H, H<sub>Ar-o</sub>), 7.14 (s, 1H, H<sub>Ar-m</sub>), 3.97 (s, 3H, OCH<sub>3-m</sub>), 3.89 (s, 3H, OCH<sub>3-o</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> (ppm) = 151.6, 150.4, 135.6, 133.7, 133.2, 131.5, 130.8, 130.5, 130.2 (CH), 129.1 (CH), 128.8 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.5, 127.3 (CH), 127.1 (CH), 127.0 (CH), 126.5, 126.3 (CH), 126.0 (CH), 123.4 (CH), 123.3 (CH), 116.8 (CH), 111.2, 109.9 (CH), 57.2 (CH<sub>3</sub>), 56.6 (CH<sub>3</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ([M+K<sup>+</sup>]) 507.0357; found 507.0329.

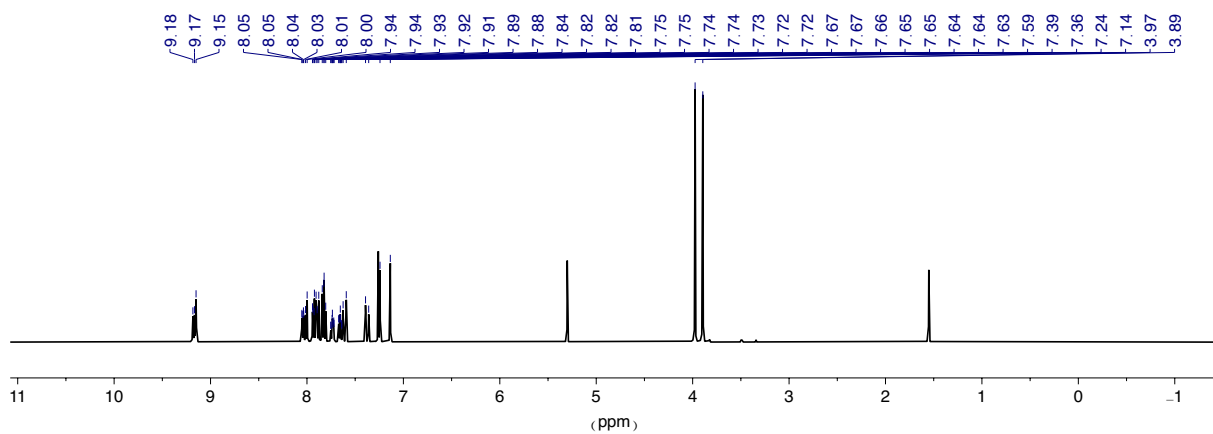


Figure S7:  $^1\text{H}$  NMR spectrum of 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene

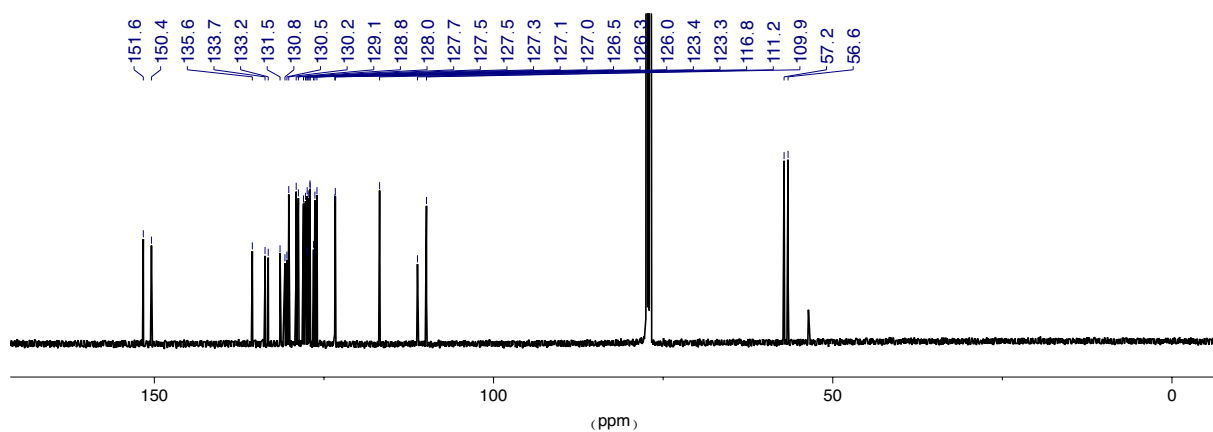


Figure S8:  $^{13}\text{C}$  NMR spectrum of 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene

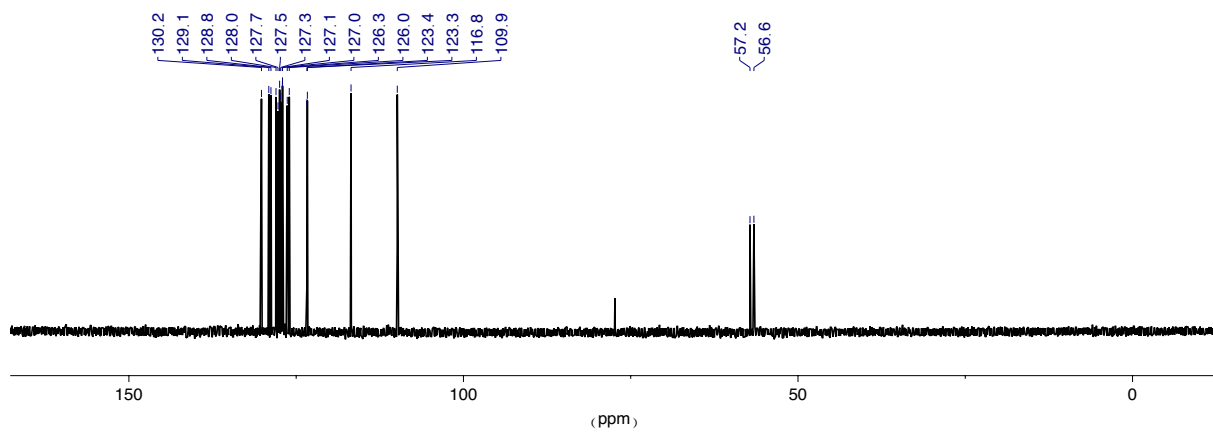
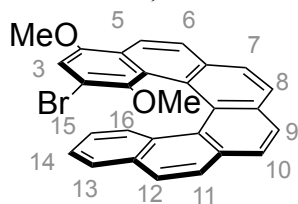


Figure S9: DEPT135 NMR spectrum of 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene

## 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**)



A solution of 2-(4-bromo-2,5-dimethoxystyryl)benzo[*c*]phenanthrene (1.12 g, 2.56 mmol, 1 eq.) and iodine (90 mg, 0.38 mmol, 15 mol%) in cyclohexane (400 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated and the crude product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 40/60) to afford (**1**) as a yellow solid (580 mg, 1.24 mmol, 52%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C):**  $\delta_{\text{H}}$  (ppm) = 8.39 (d,  $J$  = 8.7 Hz, 1H, H<sub>5</sub>), 8.10 – 7.87 (7d, 7H, H<sub>6</sub> + H<sub>7</sub> + H<sub>8</sub> + H<sub>9</sub> + H<sub>10</sub> + H<sub>11</sub> + H<sub>12</sub>) 7.81 (dd,  $J$  = 8.0, 1.4 Hz, 1H, H<sub>13</sub>), 7.28 – 7.20 (m, 1H, H<sub>14</sub>), 7.07 (dd,  $J$  = 8.5, 1.1 Hz, 1H, H<sub>16</sub>), 6.87 (s, 1H, H<sub>3</sub>), 6.60 (ddd,  $J$  = 8.5, 6.8, 1.4 Hz, 1H, H<sub>15</sub>), 4.02 (s, 3H, OCH<sub>3out</sub>), 2.08 (s, 3H, OCH<sub>3in</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta_{\text{C}}$  (ppm) = 151.9, 147.8, 132.6, 132.2, 132.2, 130.8, 129.1, 129.1, 128.1 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 125.6, 125.3 (CH), 125.3 (CH), 124.7, 124.1, 123.7, 123.3, 121.4 (CH), 114.4, 109.9 (CH), 58.4 (CH<sub>3</sub>), 56.4 (CH<sub>3</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ([M+Na<sup>+</sup>]) 489.0461; found 489.0465.

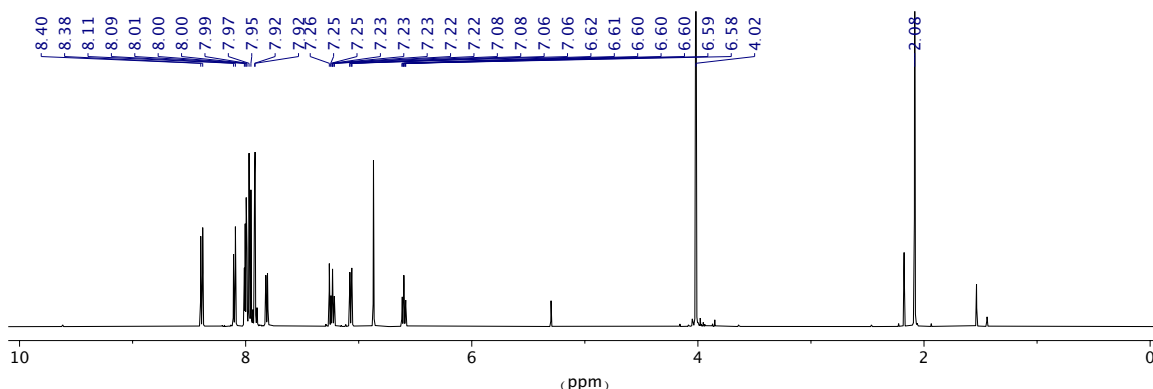


Figure S10: <sup>1</sup>H NMR spectrum of 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**)

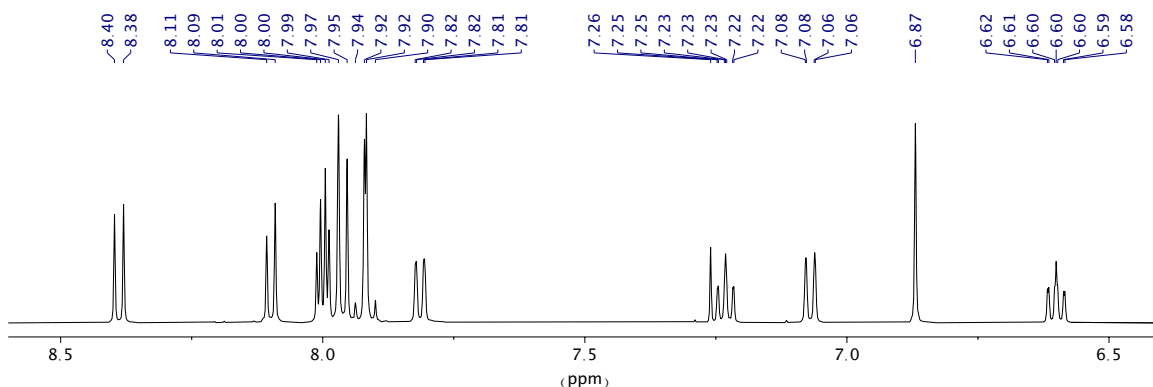


Figure S11: <sup>1</sup>H NMR spectrum of 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**)

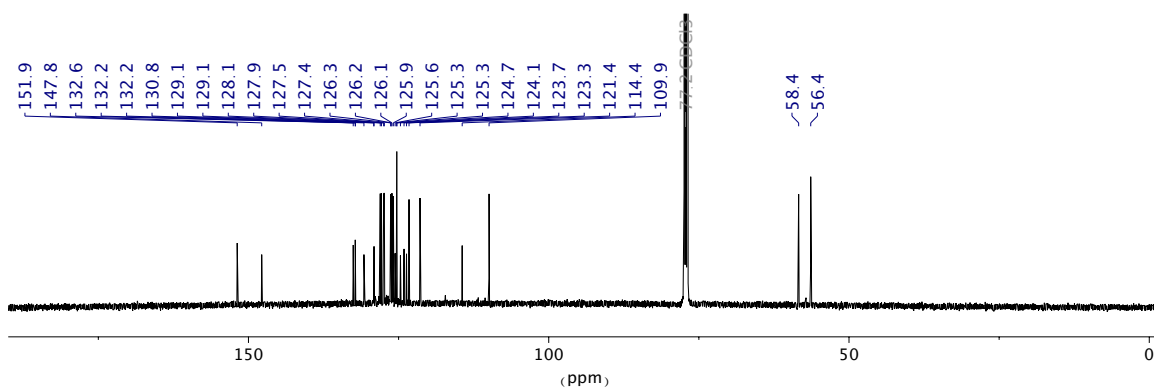


Figure S12:  $^{13}\text{C}$  NMR spectrum of 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**)

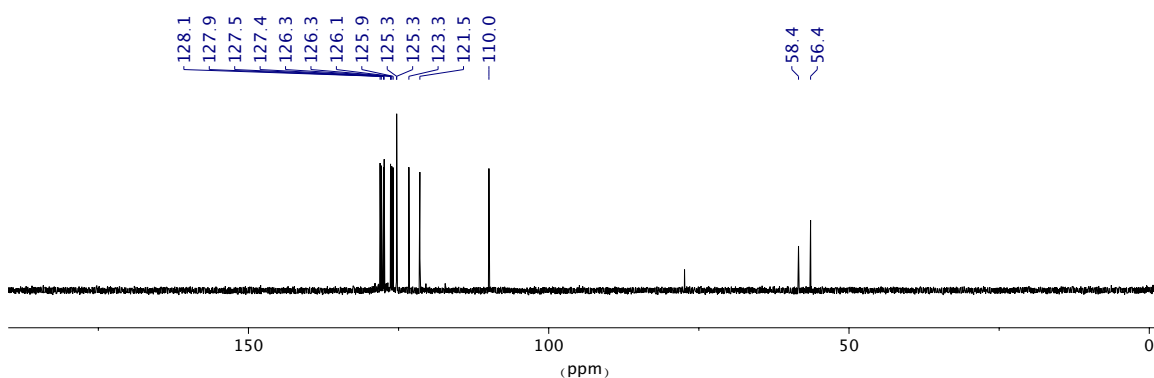


Figure S13: DEPT135 NMR spectrum of 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**)

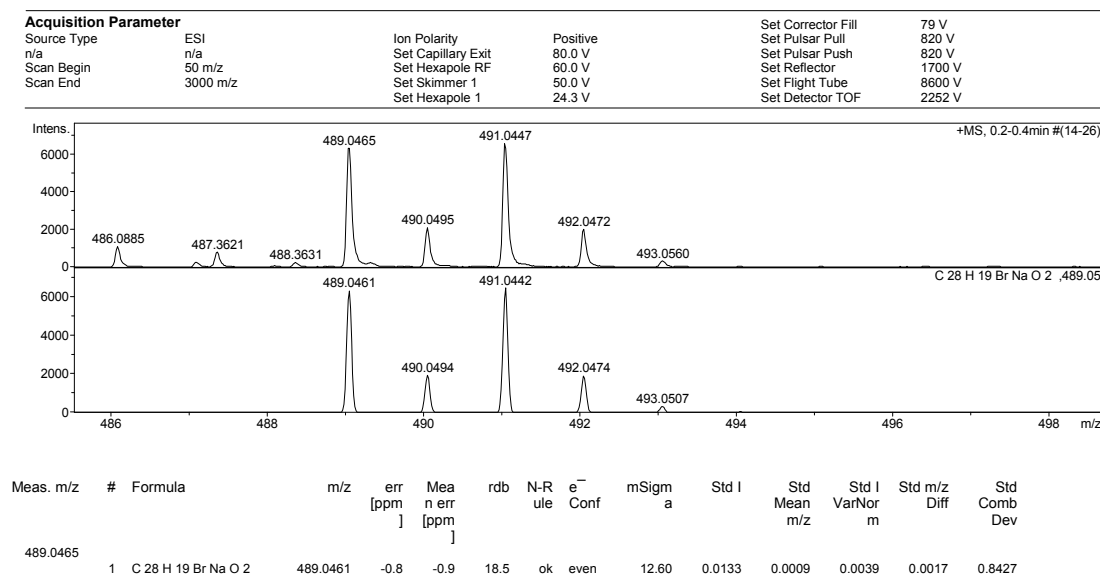
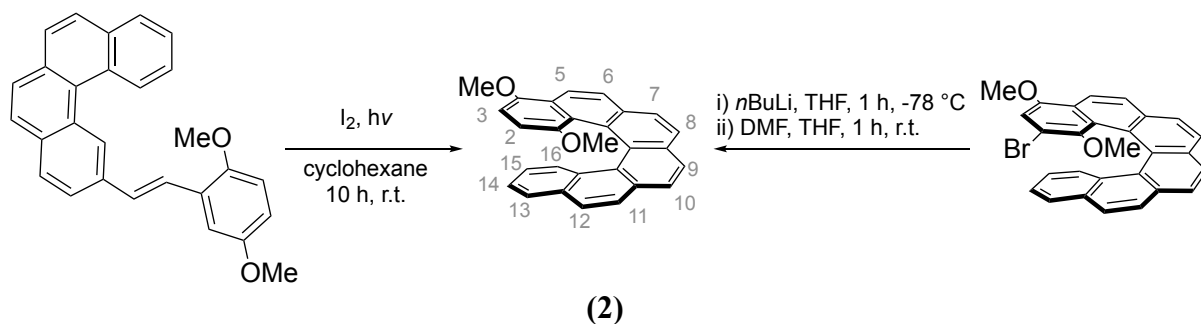


Figure S14: ESI-TOF-HRMS of 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**)



## 1,4-dimethoxyhexahelicene ( $\pm$ ) (**2**)



### Method 1:

A solution of 2-(2,5-dimethoxystyryl)benzo[*c*]phenanthrene (1.0 g, 2.56 mmol, 1 eq.) and iodine (49 mg, 0.38 mmol, 15 mol%) in cyclohexane (400 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated and the crude product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 40/60) to afford (**2**) as a yellow solid (337 mg, 0.87 mmol, 34%).

### Method 2:

Under argon, at -78 °C was added *n*BuLi (1.6 M in hexanes) (0.74 mL, 1.18 mmol, 1.1 eq.) to a solution of 2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (**1**) (500 mg, 1.07 mmol, 1.0 eq.) in 20 mL of distilled THF. After 1 h of stirring at this temperature, dry DMF (0.3 mL, 3.2 mmol, 3 eq.) was added and the solution was allowed to warm to room temperature. H<sub>2</sub>O (10 mL) was added. The solution was concentrated under reduced pressure to remove the THF, then 20 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. The organic layer was washed with a saturated aqueous solution of NH<sub>4</sub>Cl (5 x 30 mL), dried over MgSO<sub>4</sub>, filtered, and then vacuum dried. The desired compound was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 40/60) to give (**2**) as a yellow solid (76 mg, 0.2 mmol, 18%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C):**  $\delta_{\text{H}}$  (ppm) = 8.43 (d,  $J$  = 8.7 Hz, 1H, H<sub>5</sub>), 8.05 (d,  $J$  = 8.1 Hz, 1H, H<sub>7-12</sub>), 8.02 – 7.95 (m, 4H, H<sub>6</sub> + 3\*H<sub>7-12</sub>), 7.93 (d,  $J$  = 8.5 Hz, 1H, H<sub>7-12</sub>), 7.85 (d,  $J$  = 8.5 Hz, 1H, H<sub>7-12</sub>), 7.80 – 7.76 (m, 1H, H<sub>13</sub>), 7.15 (ddd,  $J$  = 7.9, 6.8, 1.2 Hz, 1H, H<sub>14</sub>), 7.11 (d,  $J$  = 8.5 Hz, 1H, H<sub>16</sub>), 6.68 (d,  $J$  = 8.5 Hz, 1H, H<sub>2-3</sub>), 6.58 (ddd,  $J$  = 8.4, 6.8, 1.4 Hz, 1H, H<sub>15</sub>), 6.02 (d,  $J$  = 8.5 Hz, 1H, H<sub>2-3</sub>), 4.02 (s, 3H, OCH<sub>3out</sub>), 2.53 (s, 3H, OCH<sub>3in</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta_{\text{C}}$  (ppm) = 149.6, 132.2, 132.0, 131.8, 130.9, 128.9, 128.6, 127.3 (CH), 127.0 (CH), 127.0 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 126.4 (CH), 126.1 (CH), 125.7, 125.1 (CH), 124.6, 124.2, 123.6 (CH), 122.9, 121.2 (CH), 105.8 (CH), 104.8 (CH), 56.4 (CH<sub>3</sub>), 53.8 (CH<sub>3</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ([M<sup>•+</sup>]) 388.1458; found 388.1448.

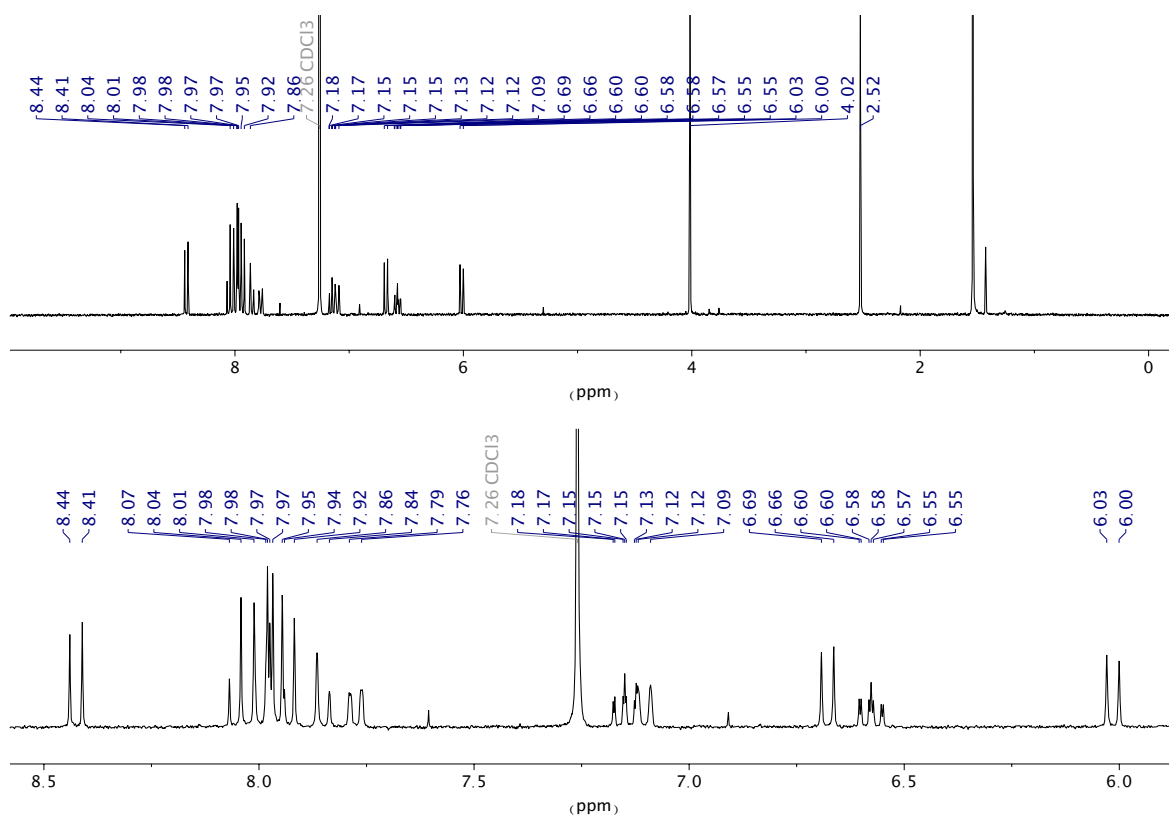


Figure S15:  $^1\text{H}$  NMR spectrum of 1,4-dimethoxyhexahelicene ( $\pm$ ) (**2**)

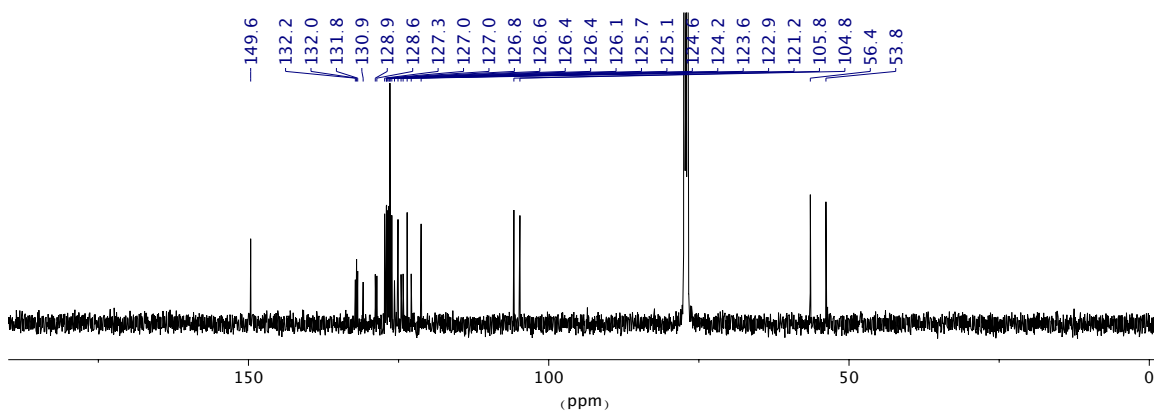


Figure S16:  $^{13}\text{C}$  NMR spectrum of 1,4-dimethoxyhexahelicene ( $\pm$ ) (**2**)

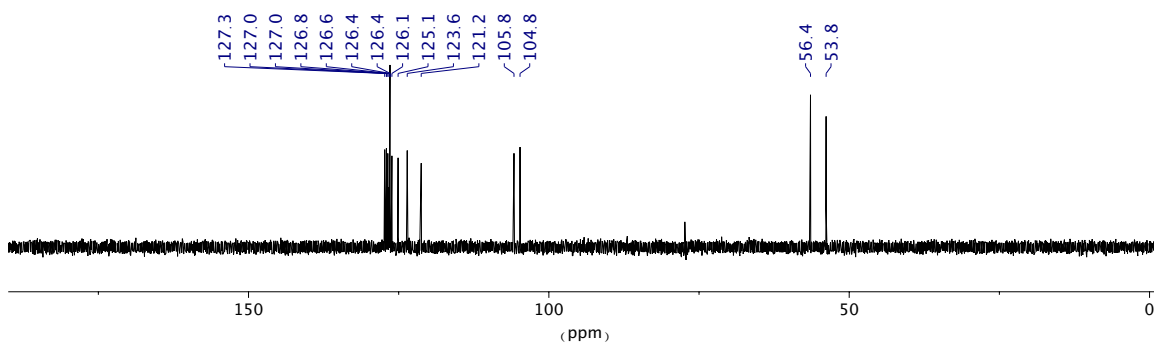
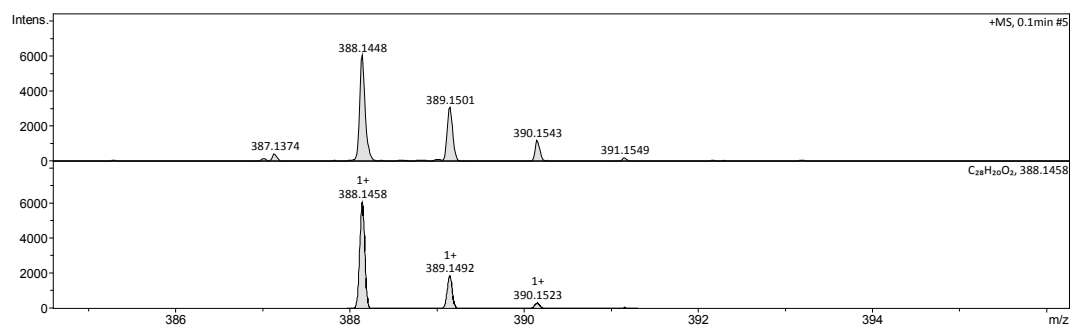


Figure S17: DEPT135 NMR spectrum of 1,4-dimethoxyhexahelicene ( $\pm$ ) (**2**)

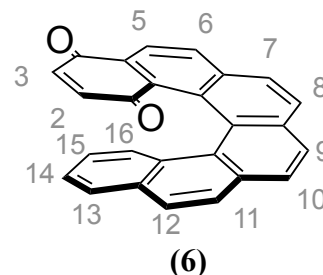
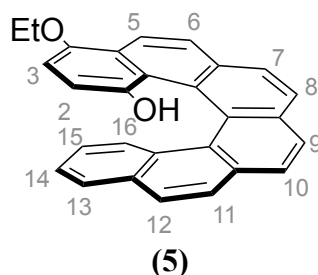
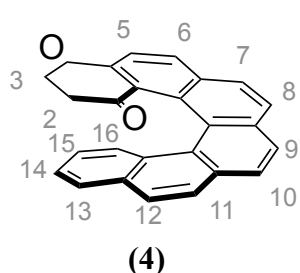
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n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	1985.0 V



Meas. m/z	#	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdB	N-Rule	e <sup>-</sup>	Conf	mSigma	Std	Std Mean	m/z	Std	VarNorm	Std m/z	Diff	Std Comb	Dev
388.144808	1	C <sub>28</sub> H <sub>20</sub> O <sub>2</sub>	388.145781	2.5	-0.4	19.0	ok	odd	143.1	184.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Figure S18: ESI-TOF-HRMS of 1,4-dimethoxyhexahelicene ( $\pm$ ) (2)

**2,3-dihydrohexahelicene-1,4-dione ( $\pm$ ) (4), 4-ethoxyhexahelicene-1-ol ( $\pm$ ) (5)  
and hexahelicene-1,4-dione ( $\pm$ ) (6)**



**Method 1:**

Under Argon, 4 mL of  $\text{BBr}_3$  (1M in  $\text{CH}_2\text{Cl}_2$ ) were added to the solid 1,4-dimethoxyhexahelicene (160 mg, 0.41 mmol, 1 eq.) and the resulting solution was stirred at room temperature for 1 h. The solution was poured in 50 mL of water. The organic layer was washed with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (2 x 20 mL), dried over  $\text{MgSO}_4$  and filtered. Column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2(\text{EtOH stabilized})/\text{cyclohexane}$  40/60) allowed to isolate (4) (m = 68 mg, 0.42 mmol, 43%), (5) (33 mg, 0.09 mmol, 22%) and (6) (51 mg, 0.14 mmol, 34%).

**Method 2:**

Under Argon, 4 mL of  $\text{BBr}_3$  (1M in  $\text{CH}_2\text{Cl}_2$ ) were added to the solid 1,4-dimethoxyhexahelicene (160 mg, 0.41 mmol, 1 eq.) and the resulting solution was stirred at room temperature for 1 h. The solution was poured in 50 mL of water. The organic layer was washed with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (2 x 20 mL), dried over  $\text{MgSO}_4$  and filtered. Column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2(\text{distilled})/\text{Cyclohexane}$  40/60) allowed to isolate (5) (77 mg, 0.21 mmol, 51%) and (6) (71 mg, 0.20 mmol, 48%).

## 2,3-dihydrohexahelicene-1,4-dione (4)

**$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 25°C):**  $\delta_{\text{H}}$  (ppm) = 8.14 (d,  $J = 8.3$  Hz, 1H, H<sub>5</sub>), 8.11 (d,  $J = 8.3$  Hz, 1H, H<sub>6</sub>), 8.08 (d,  $J = 8.4$  Hz, 1H, H<sub>13</sub>), 8.05 (d,  $J = 8.3$  Hz, 1H, H<sub>7-12</sub>), 7.99 – 7.93 (m, 2H, H<sub>7-12</sub> + H<sub>16</sub>), 7.91 (m, 2H, 2\*H<sub>7-12</sub>), 7.87 (bs, 2H, 2\*H<sub>7-12</sub>), 7.47 (ddd,  $J = 8.0, 7.0, 1.2$  Hz, 1H, H<sub>15</sub>), 7.29 – 7.19 (m, 1H, H<sub>14</sub>), 2.95 (ddd,  $J = 16.8, 8.0, 4.8$  Hz, 1H, H<sub>2-3</sub>), 2.69 (ddd,  $J = 16.6, 9.6, 6.7$  Hz, 1H, H<sub>2-3</sub>), 2.06 (ddd,  $J = 14.8, 6.7, 4.8$  Hz, 1H, H<sub>2-3</sub>), 1.78 (ddd,  $J = 14.8, 9.6, 8.0$  Hz, 1H, H<sub>2-3</sub>).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}}$  (ppm) = 196.7, 195.9, 139.2, 135.9, 133.5, 133.0, 133.0, 132.6 (CH), 131.1, 130.3 (CH), 130.1, 129.9, 129.1 (CH), 129.0 (CH), 127.9 (CH), 127.9 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 126.2 (CH), 125.4 (CH), 125.2, 123.5 (CH), 38.3 (CH<sub>2</sub>), 35.8 (CH<sub>2</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ( $[\text{M}+\text{K}^+]$ ) 399.0782; found 399.0793.

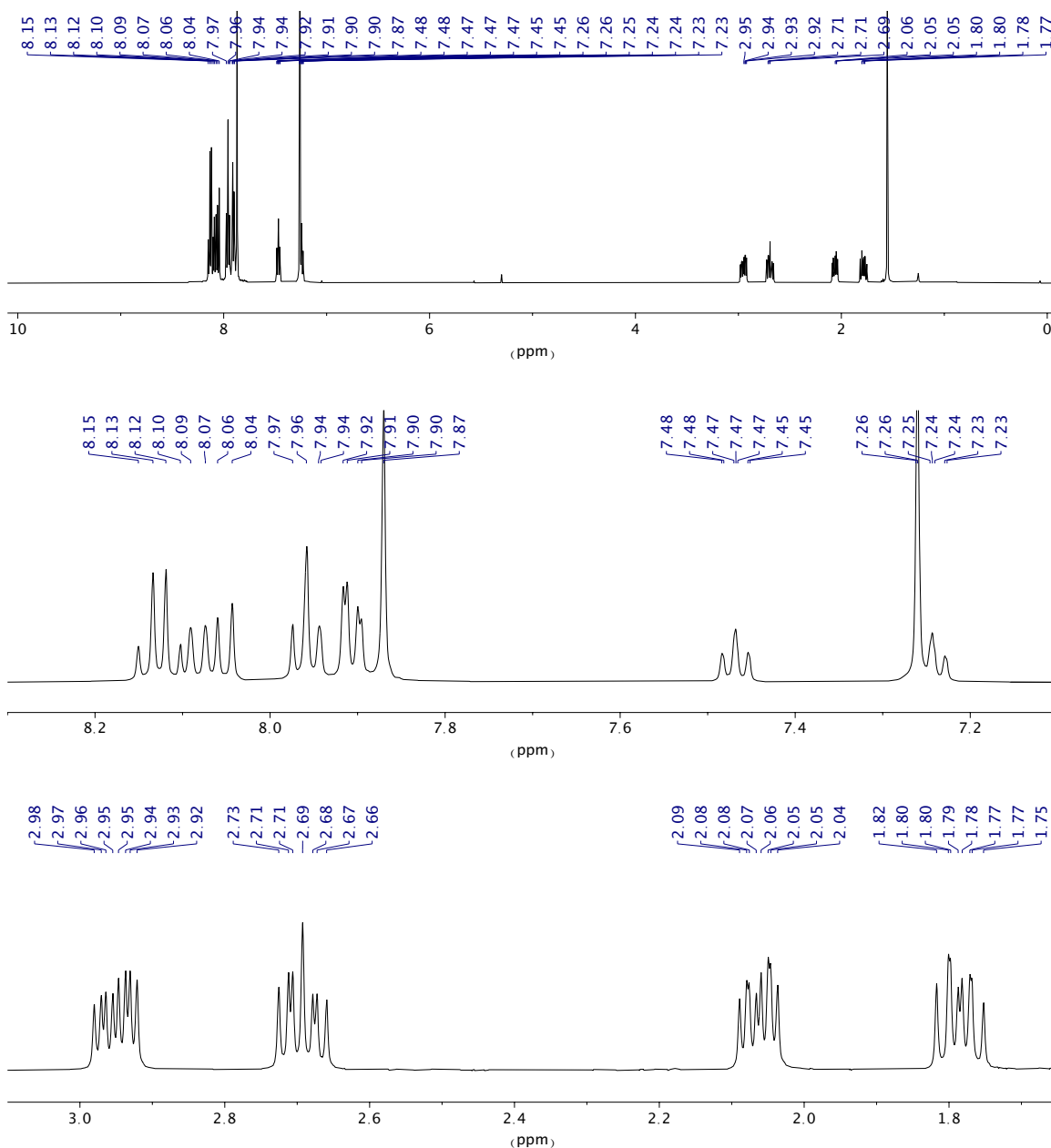


Figure S19:  $^1\text{H}$  NMR spectrum of 2,3-dihydrohexahelicene-1,4-dione (4)

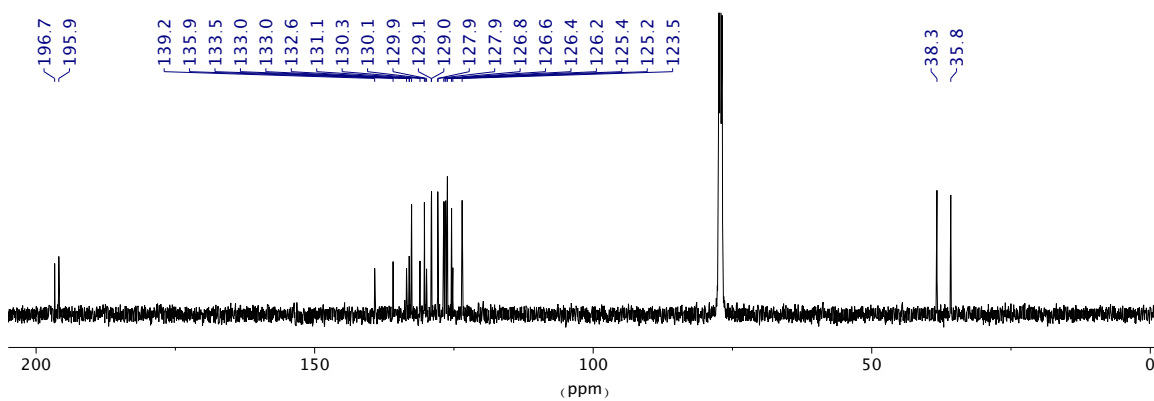


Figure S20:  $^{13}\text{C}$  NMR spectrum of 2,3-dihydrohexahelicene-1,4-dione (4)

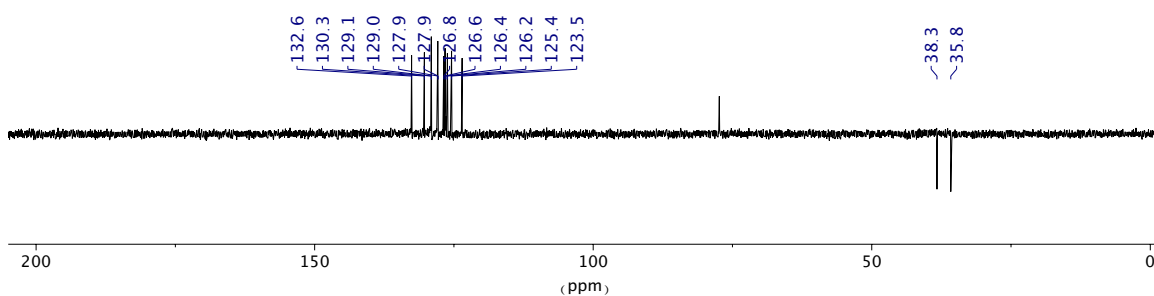


Figure S21: DEPT135 NMR spectrum of 2,3-dihydrohexahelicene-1,4-dione (4)

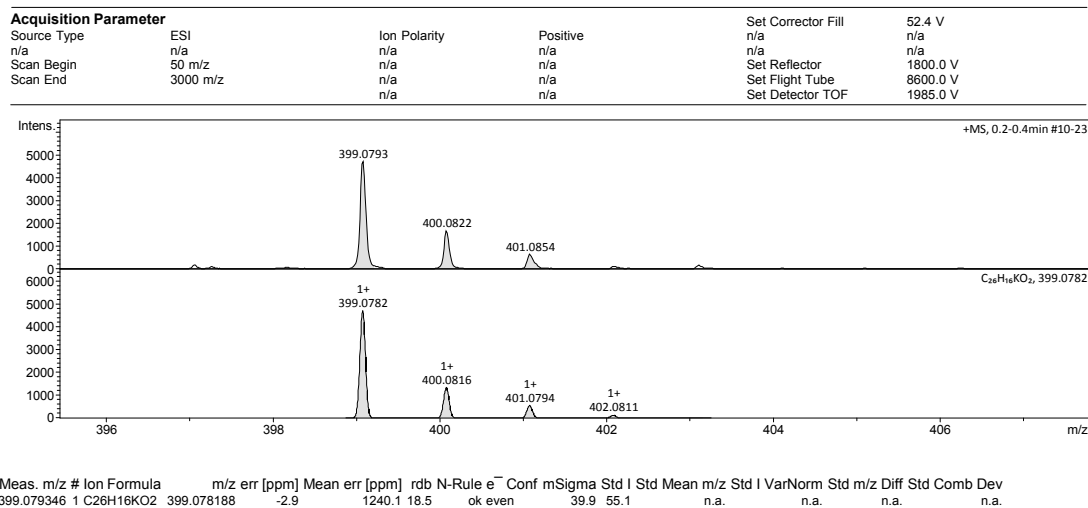


Figure S22: ESI-TOF HRMS of 2,3-dihydrohexahelicene-1,4-dione (4)

#### 4-ethoxyhexahelicen-1-ol ( $\pm$ ) (**5**)

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 25°C):  $\delta_{\text{H}}$  (ppm) = 8.51 (d,  $J = 8.6$  Hz, 1H,  $\text{H}_{5-12}$ ), 8.16 – 8.05 (m, 3H,  $3*\text{H}_{5-12}$ ), 8.03 (d,  $J = 8.1$  Hz, 1H,  $\text{H}_{5-12}$ ), 7.96 (bs, 2H,  $2*\text{H}_{5-12}$ ), 7.94 (d,  $J = 8.6$  Hz, 1H,  $\text{H}_{5-12}$ ), 7.83 (dd,  $J = 7.9, 1.5$  Hz, 1H,  $\text{H}_{13}$ ), 7.21 (ddd,  $J = 8.0, 7.0, 1.3$  Hz, 1H,  $\text{H}_{14}$ ), 7.03 (d,  $J = 8.6$  Hz, 1H,  $\text{H}_{2-3}$ ), 6.71 (d,  $J = 8.4$  Hz, 1H,  $\text{H}_{16}$ ), 6.63 (ddd,  $J = 8.5, 6.9, 1.5$  Hz, 1H,  $\text{H}_{15}$ ), 6.20 (d,  $J = 8.4$  Hz, 1H,  $\text{H}_{2-3}$ ), 4.28 (dq,  $J = 8.5, 6.9$  Hz, 1H,  $\text{CH}_2$ ), 4.13 (dq,  $J = 8.7, 6.9$  Hz, 1H,  $\text{CH}_2$ ), 3.86 (s, 1H, OH), 1.59 (t,  $J = 6.9$  Hz, 3H,  $\text{CH}_3$ ).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 148.9, 146.1, 132.5, 132.4, 132.0, 130.6, 128.7 (CH), 128.5, 127.5 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 127.2 (CH), 126.5 (CH), 126.2 (CH), 125.7 (CH), 125.6 (CH), 124.4, 123.9 (CH), 123.4, 123.0, 122.4 (CH), 121.6, 111.8 (CH), 108.7 (CH), 65.1 (CH<sub>2</sub>), 15.2 (CH<sub>3</sub>).

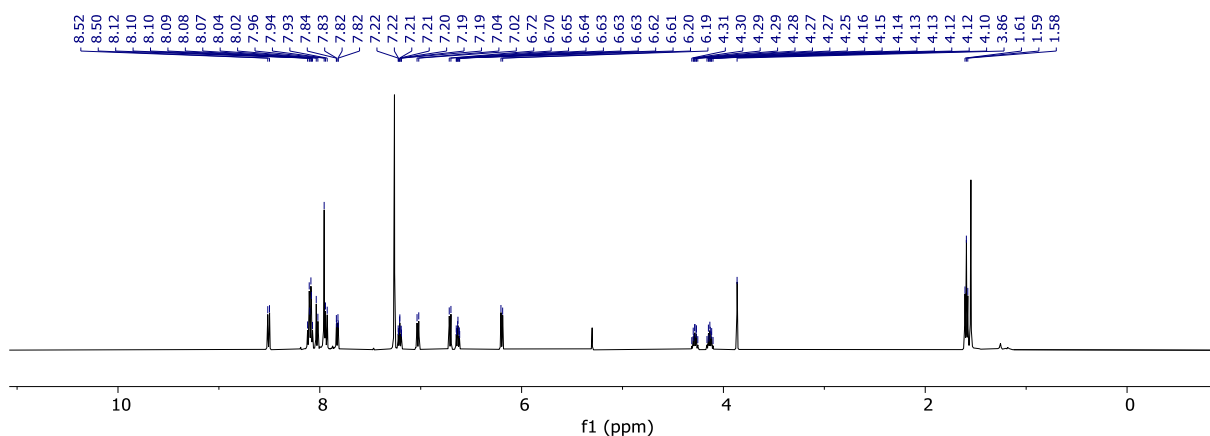


Figure S23:  $^1\text{H NMR}$  spectrum of 4-ethoxyhexahelicen-1-ol ( $\pm$ ) (**5**)

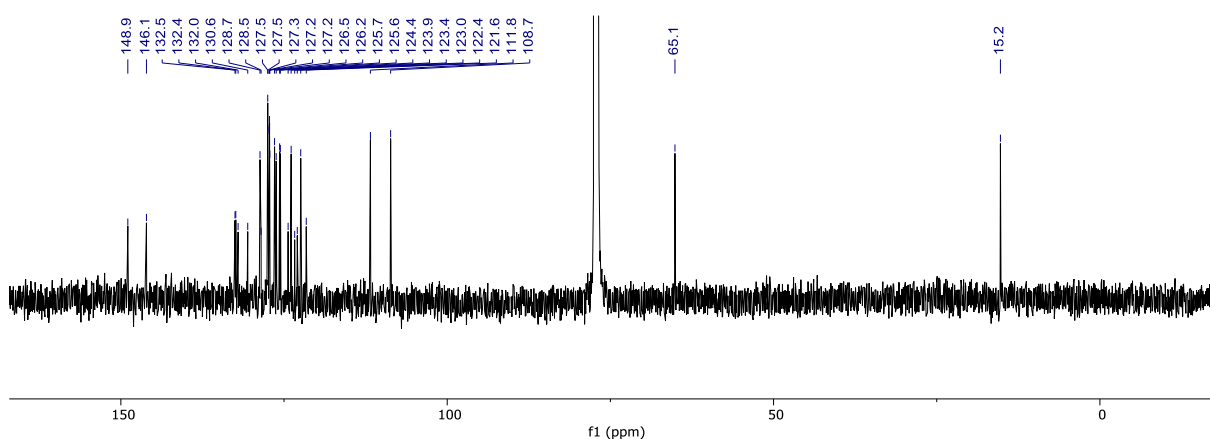


Figure S24:  $^{13}\text{C NMR}$  spectrum of 4-ethoxyhexahelicen-1-ol ( $\pm$ ) (**5**)

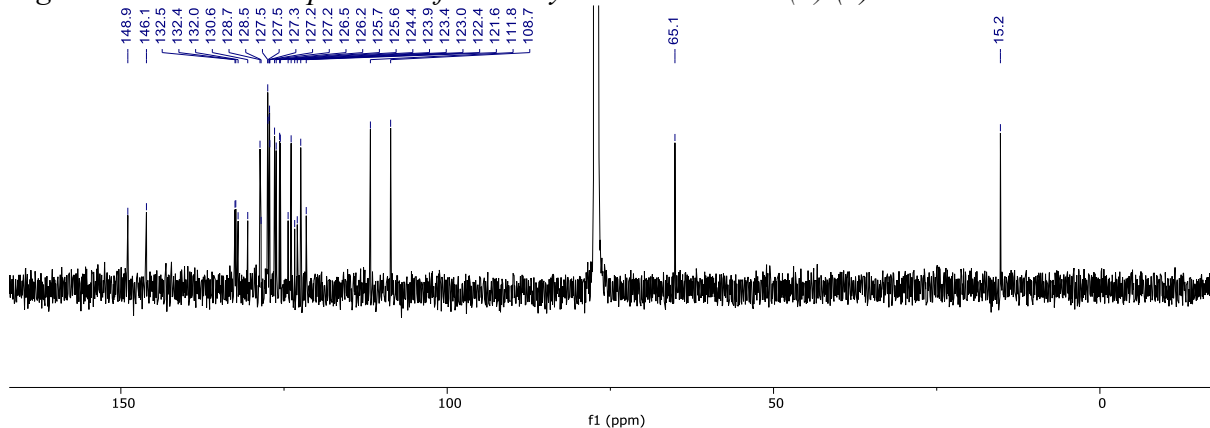


Figure S25: DEPT135 NMR spectrum of 4-ethoxyhexahelicen-1-ol ( $\pm$ ) (**5**)

### hexahelicene-1,4-dione (6)

**$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 25°C):**  $\delta_{\text{H}}$  (ppm) = 8.22 (d,  $J$  = 8.2 Hz, 1H,  $\text{H}_5$ ), 8.19 (d,  $J$  = 8.2 Hz, 1H,  $\text{H}_6$ ), 8.14 (d,  $J$  = 8.4 Hz, 1H,  $\text{H}_{13}$ ), 8.04 – 7.83 (6d + m, 7H, 6\* $\text{H}_{7-12}$  +  $\text{H}_{16}$ ), 7.40 (ddd,  $J$  = 7.9, 6.8, 1.2 Hz, 1H,  $\text{H}_{15}$ ), 7.14 (ddd,  $J$  = 8.4, 6.9, 1.4 Hz, 1H,  $\text{H}_{14}$ ), 6.54 (d,  $J$  = 10.1 Hz, 1H,  $\text{H}_2$ ), 6.00 (d,  $J$  = 10.1 Hz, 1H,  $\text{H}_3$ ).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}}$  (ppm) = 185.6, 185.2, 140.0 (CH), 135.9, 134.9 (CH), 134.4, 133.6, 133.0 (CH), 132.5, 131.3, 130.5 (CH), 130.0, 129.7, 129.4 (CH), 128.9 (CH), 127.9 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 126.1, 125.2, 123.0 (CH).

**ESI-TOF-HR-MS (m/z):** Calcd for ( $[\text{M}+\text{H}^+]$ ) 359.1067; found 359.1063.

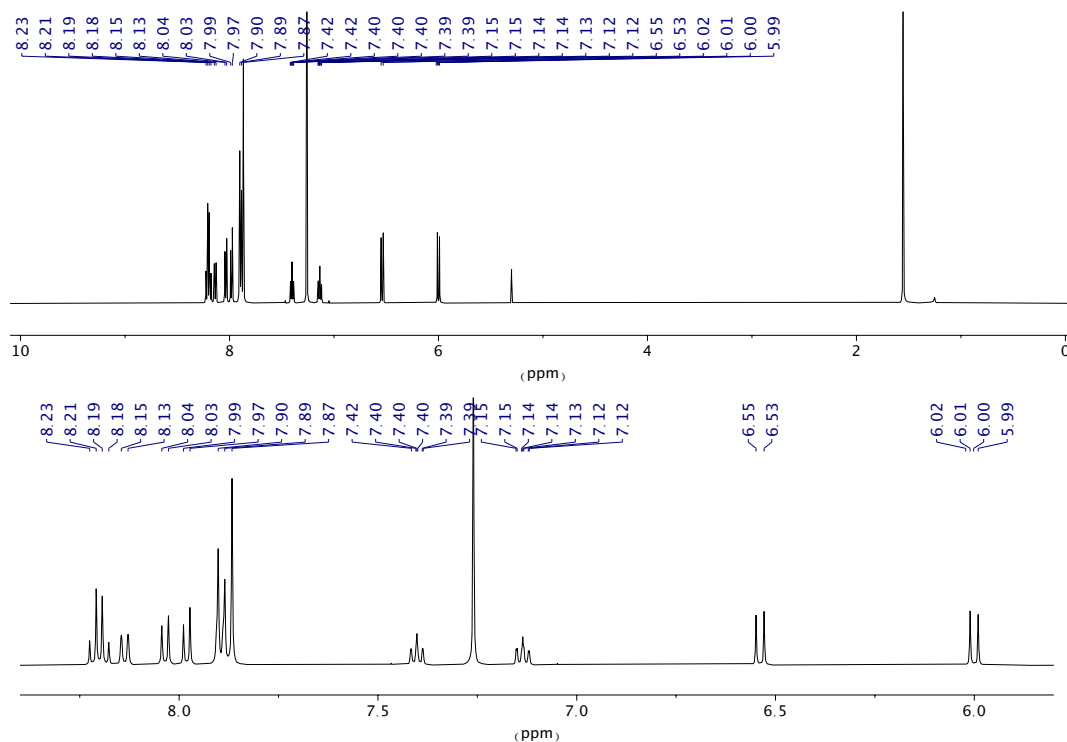


Figure S26:  $^1\text{H}$  NMR spectrum of hexahelicene-1,4-dione (6)

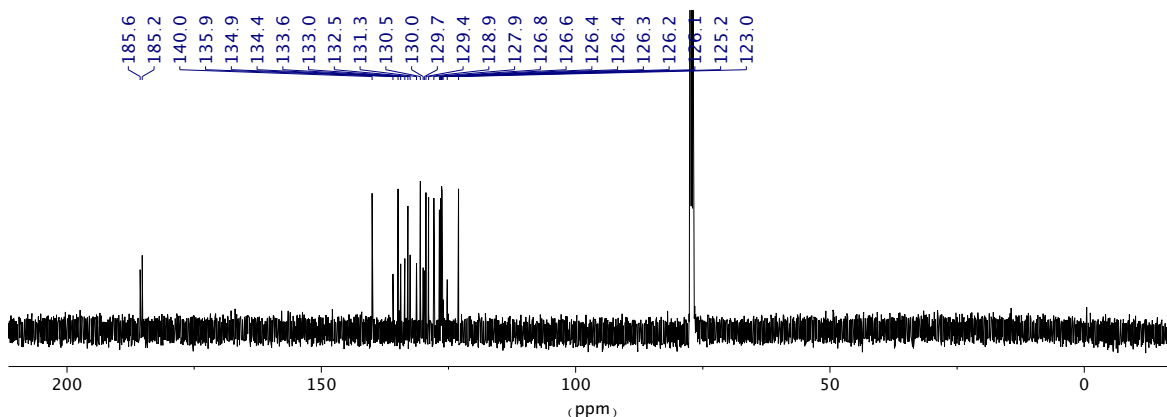


Figure S27:  $^{13}\text{C}$  NMR spectrum of hexahelicene-1,4-dione (6)



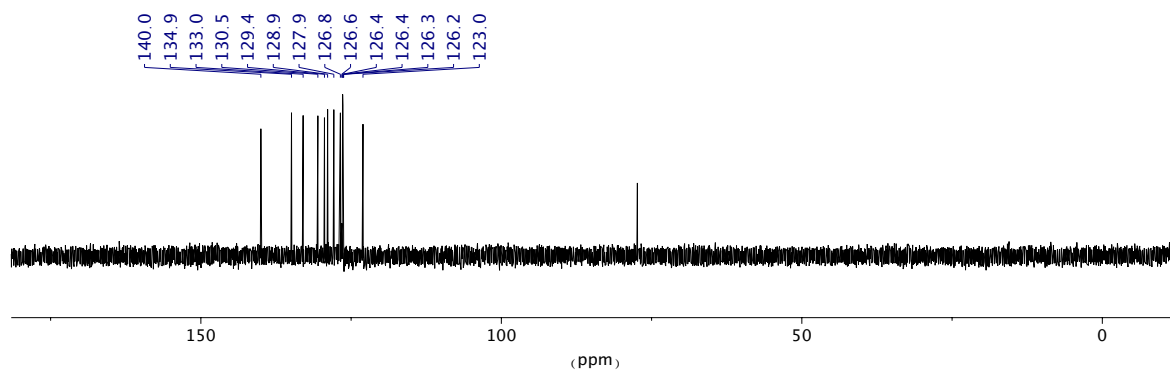


Figure S28: DEPT135 NMR spectrum of hexahelicene-1,4-dione (6)

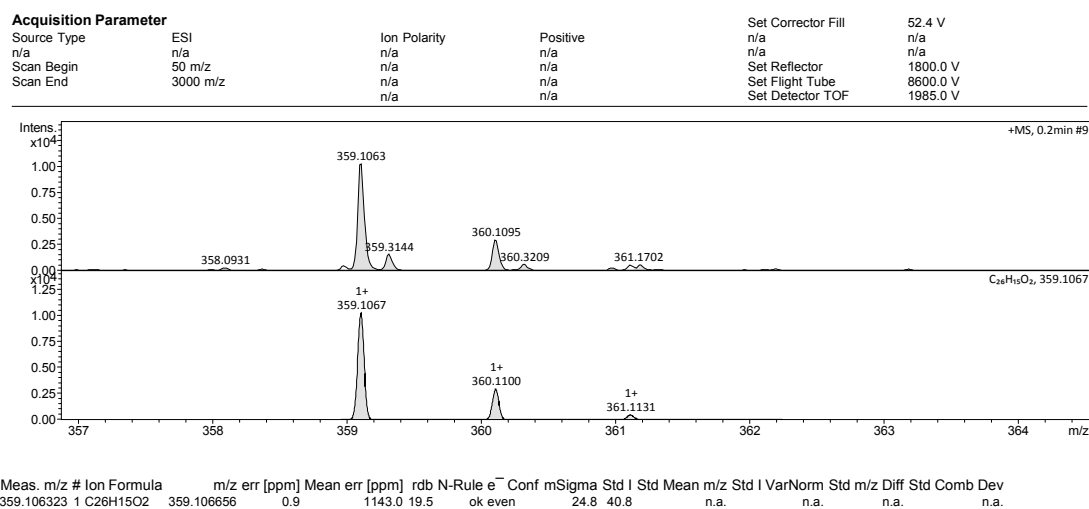
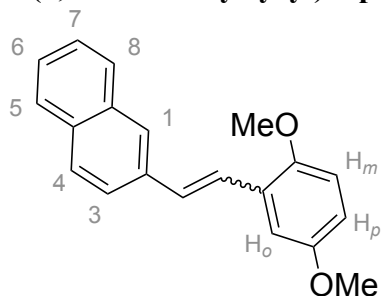


Figure S29: ESI-TOF HRMS of hexahelicene-1,4-dione (6)

## 2-(2,5-dimethoxystyryl)naphthalene



Under Argon, NaH (60% in mineral oil) (277 mg, 6.92 mmol, 1.32 eq.) was added to a solution of diethyl 2,5-dimethoxybenzylphosphonate (2.47 g, 9.0 mmol, 1.3 eq.) in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of 2-naphthaldehyde (1.34 g, 8.6 mmol, 1.0 eq.) in 30 mL of distilled THF (30 mL) was added dropwise and the resulting solution was heated at 50 °C for 16 h. After the solution was allowed to cool to room temperature, H<sub>2</sub>O (50 mL) was added. The THF was removed under reduced pressure. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the resulting solution was washed with NH<sub>4</sub>Cl<sub>(sat.)</sub> (3 x 20 mL), dried over MgSO<sub>4</sub>, and filtered. Subsequent purification of the crude solid by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 40/60) afforded the desired product as a yellow solid (2.08 g, 7.1 mmol, 83%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C):** δ<sub>H</sub> (ppm) = 7.91 – 7.80 (m, 5H, H<sub>1</sub> + H<sub>3</sub> + H<sub>4</sub> + H<sub>5</sub> + H<sub>8</sub>), 7.62 (d, *J* = 16.4 Hz, 1H, H<sub>alkene</sub>), 7.47 (m, 2H, H<sub>6</sub> + H<sub>7</sub>), 7.29 (d, *J* = 16.4 Hz, 1H, H<sub>alkene</sub>), 7.24 (d, *J* = 2.9 Hz, 1H, H<sub>o</sub>), 6.92 – 6.72 (m, 2H, H<sub>m</sub> + H<sub>p</sub>), 3.89 (s, 3H, OCH<sub>3</sub>), 3.86 (s, 3H, OCH<sub>3</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> (ppm) = 153.9, 151.6, 135.4, 133.8, 133.1, 129.5 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.3, 126.8 (CH), 126.4 (CH), 125.9, 123.8 (CH), 123.7 (CH), 113.9 (CH), 112.4 (CH), 111.6 (CH), 56.4 (CH<sub>3</sub>), 55.9 (CH<sub>3</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ([M<sup>•+</sup>]) 290.1301; found 290.1301

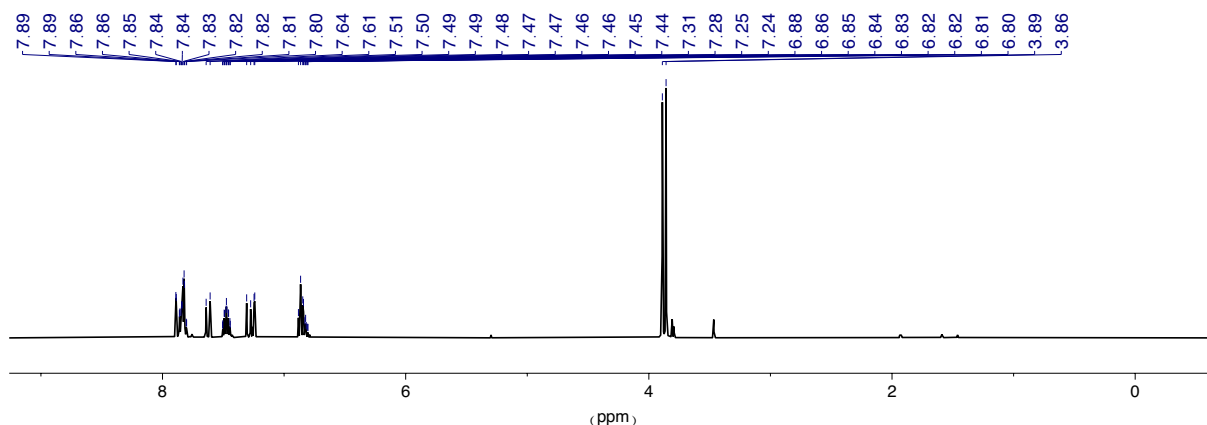


Figure S30: <sup>1</sup>H NMR spectrum of 2-(2,5-dimethoxystyryl)naphthalene

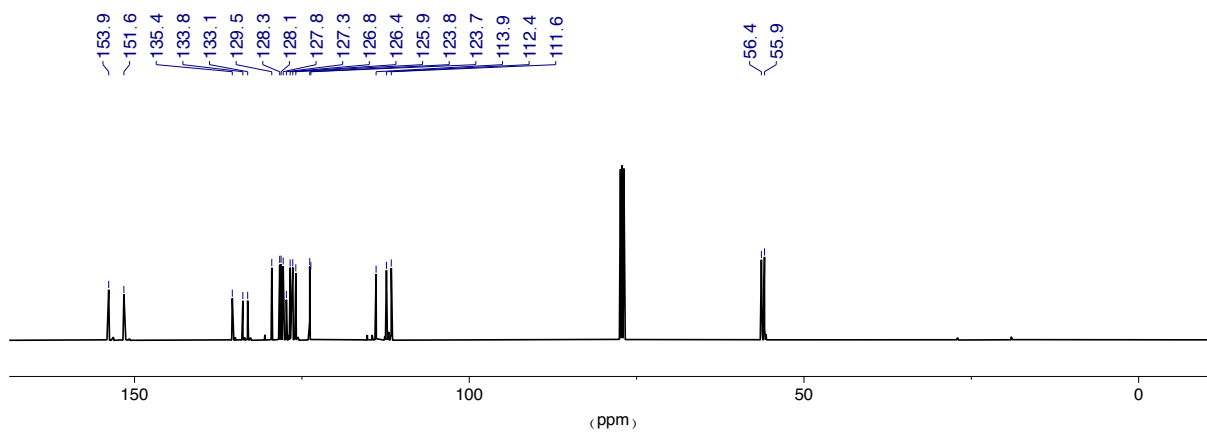


Figure S31:  $^{13}\text{C}$  NMR spectrum of 2-(2,5-dimethoxystyryl)naphthalene

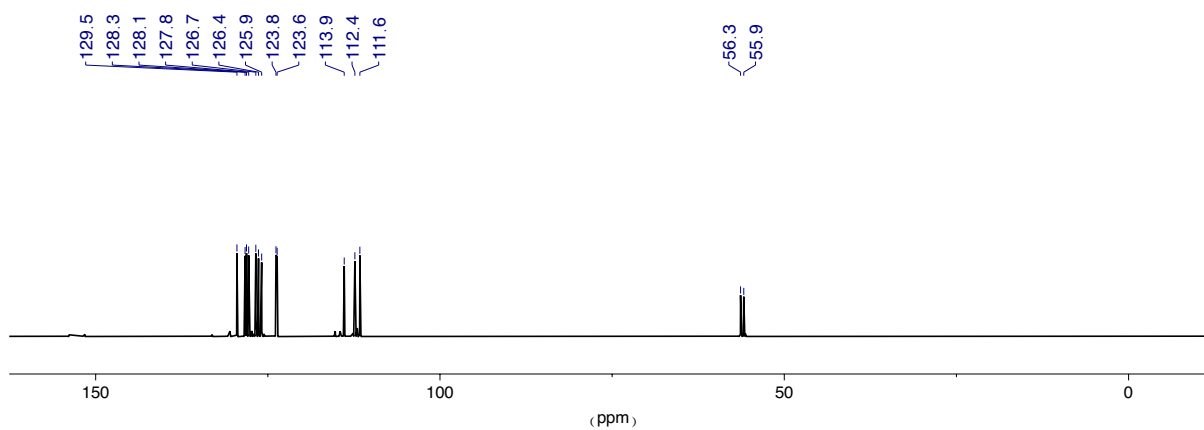
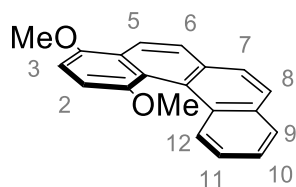


Figure S32: DEPT135 NMR spectrum of 2-(2,5-dimethoxystyryl)naphthalene

## 1,4-dimethoxybenzo[*c*]phenanthrene (11)



A solution of 2-(2,5-dimethoxystyryl)naphthalene (1.0 g, 3.44 mmol, 1 eq.) and iodine (49 mg, 0.38 mmol, 15 mol%) in cyclohexane (400 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated and the crude product was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 40/60) to afford (**2**) as a yellow solid (492 mg, 1.72 mmol, 49%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C):** δ<sub>H</sub> (ppm) = 8.35 (d, *J* = 8.7 Hz, 1H, H<sub>5</sub>), 8.14 (dd, *J* = 8.4, 1.3 Hz, 1H, H<sub>12</sub>), 7.98 – 7.89 (m, 2H, H<sub>8</sub> + H<sub>9</sub>), 7.82 (d, *J* = 8.5 Hz, 1H, H<sub>7</sub>), 7.81 (d, *J* = 8.7 Hz, 1H, H<sub>6</sub>), 7.55 (ddd, *J* = 8.0, 6.8, 1.4 Hz, 1H, H<sub>10</sub>), 7.51 (ddd, *J* = 8.3, 6.8, 1.6 Hz, 1H, H<sub>11</sub>), 7.07 (d, *J* = 8.6 Hz, 1H, H<sub>2</sub>), 7.02 (d, *J* = 8.5 Hz, 1H, H<sub>3</sub>), 4.06 (s, 3H, OCH<sub>3out</sub>), 3.76 (s, 3H, OCH<sub>3in</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> (ppm) = 150.8, 150.2, 132.5, 131.9, 131.3 (CH), 130.3, 127.9 (CH), 127.1 (CH), 126.6 (CH), 126.4, 125.9 (CH), 125.8, 125.5 (CH), 123.5 (CH), 121.2, 120.9 (CH), 107.6 (CH), 105.7 (CH), 56.3 (CH<sub>3</sub>), 55.1 (CH<sub>3</sub>).

**ESI-TOF-HR-MS (m/z):** Calcd for ([M+H<sup>+</sup>]) 288.1145; found 288.1151.

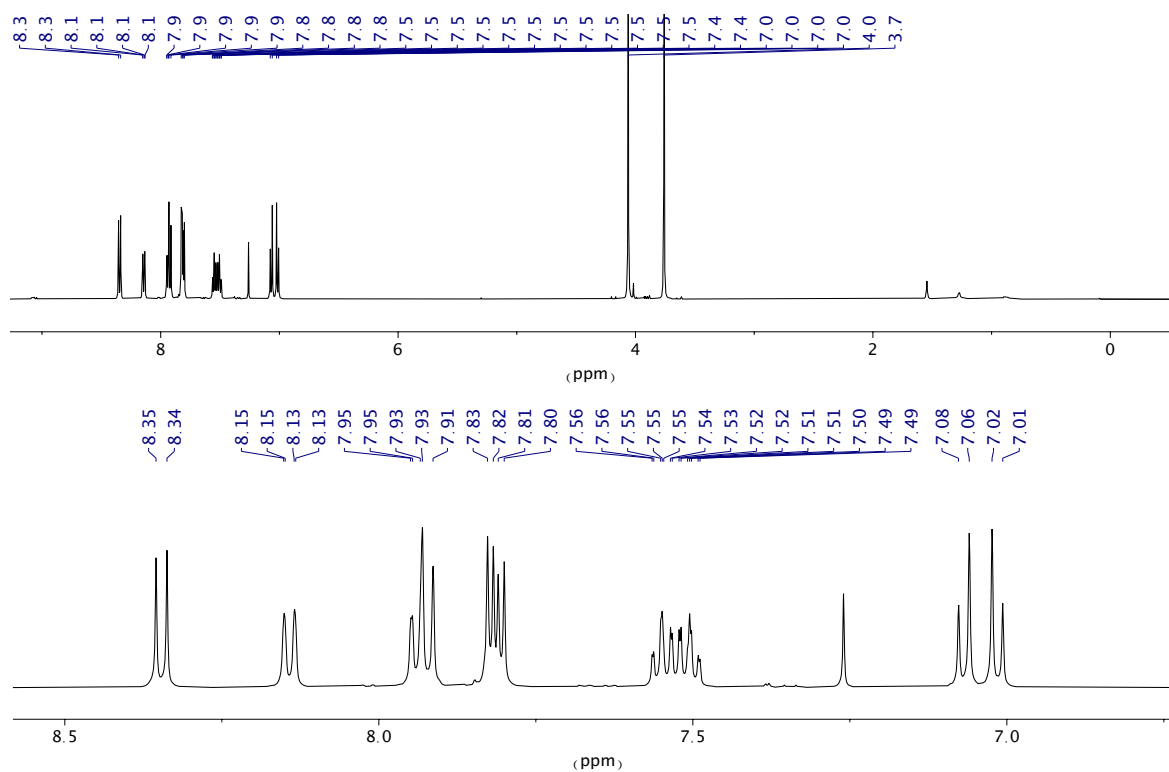


Figure S33: <sup>1</sup>H NMR spectrum of 1,4-dimethoxybenzo[*c*]phenanthrene (**11**)

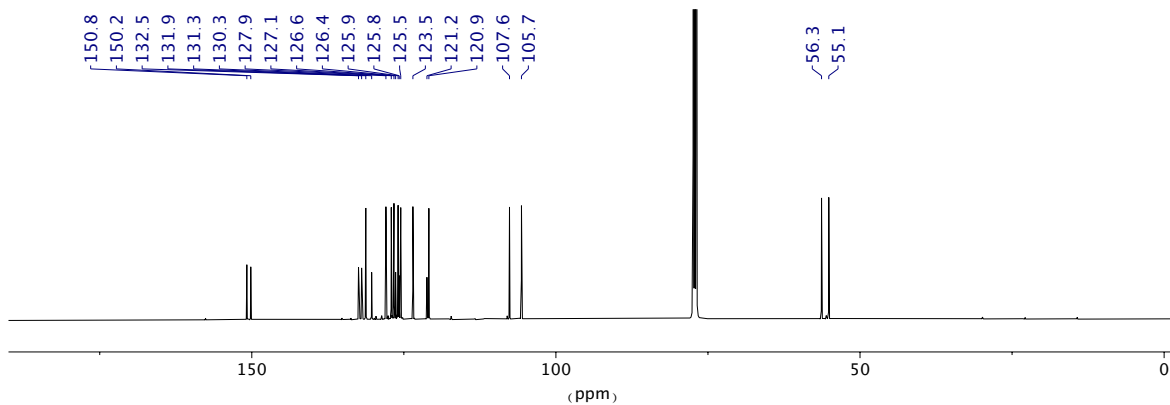


Figure S34:  $^{13}\text{C}$  NMR spectrum of 1,4-dimethoxybenzo[*c*]phenanthrene (**11**)

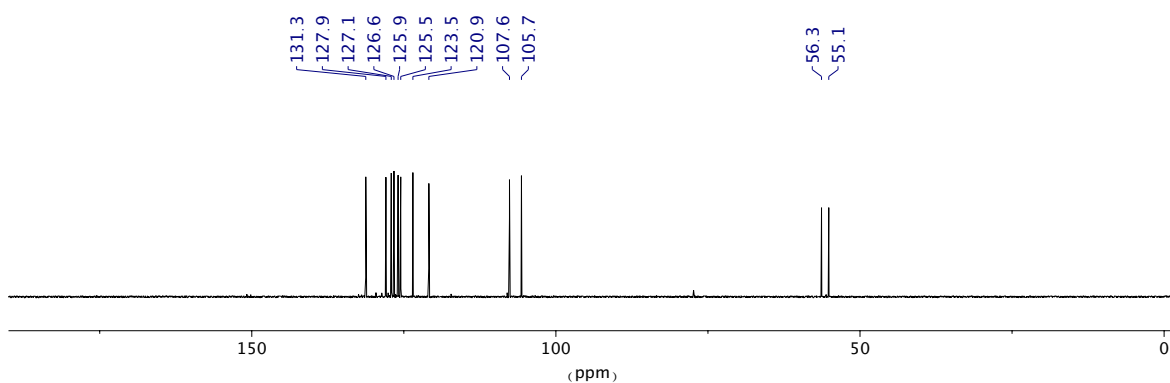
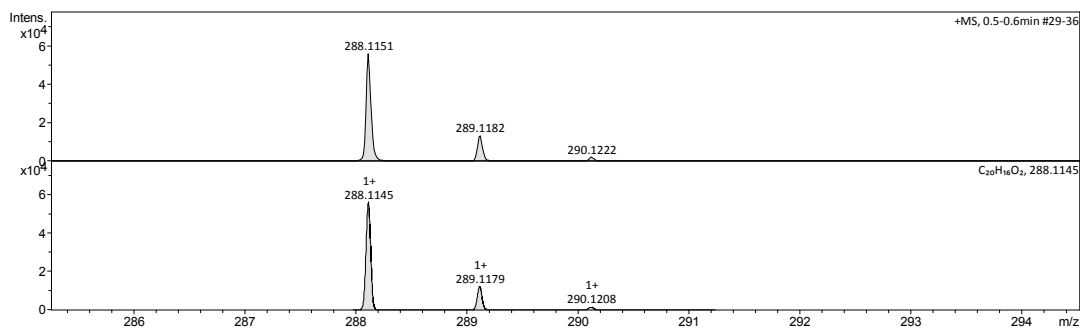


Figure S35: DEPT135 NMR spectrum of 1,4-dimethoxybenzo[*c*]phenanthrene (**11**)

**Acquisition Parameter**

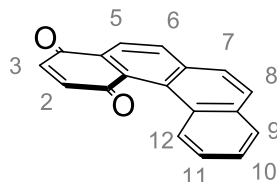
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	52.4 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	1985.0 V



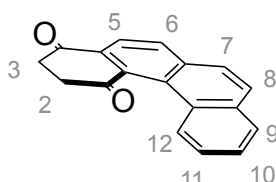
Meas. m/z	# Ion	Formula	m/z err [ppm]	Mean err [ppm]	rdB	N-Rule	e <sup>-</sup> Conf	mSigma	Std I	Std	Mean m/z	Std I	VarNorm	Std m/z	Diff	Std	Comb	Dev
288.115134	1	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub>	288.114481	-2.3	-2.4	13.0	ok	odd	8.2	15.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Figure S36: ESI-TOF HRMS of 1,4-dimethoxybenzo[*c*]phenanthrene (**11**)

**benzo[*c*]phenanthrene-1,4-dione (12) and 2,3-dihydrobenzo[*c*]phenanthrene-1,4-dione (13)**



**(14)**



**(12)**

Under Argon, 10 mL of BBr<sub>3</sub> (1M in CH<sub>2</sub>Cl<sub>2</sub>) were added to the solid 1,4-dimethoxybenzo[*c*]phenanthrene (**11**) (400 mg, 1.39 mmol, 1 eq.) and the resulting solution was stirred at room temperature for 1 h. The solution was poured in 50 mL of water. The organic layer was washed with a saturated aqueous solution of NH<sub>4</sub>Cl (2 x 30 mL), dried over MgSO<sub>4</sub> and the solvents were removed under reduced pressure. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>(distillated)/cyclohexane 40/60) allowed to isolate (**12**) (189 mg, 0.72 mmol, 52%) and (**14**) (170 mg, 0.66 mmol, 47%).

**benzo[*c*]phenanthrene-1,4-dione (14)**

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C)** : δ<sub>H</sub> (ppm) = 8.34 (d, *J* = 8.3 Hz, 1H, H<sub>12</sub>), 8.21 (d, *J* = 8.1 Hz, 1H, H<sub>5</sub>), 8.07 (d, *J* = 8.2 Hz, 1H, H<sub>6</sub>), 7.91 – 7.85 (m, 2H, H<sub>7/8</sub> + H<sub>9</sub>), 7.68 (d, *J* = 8.7 Hz, 1H, H<sub>7/8</sub>), 7.62 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H, H<sub>10</sub>), 7.48 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H<sub>11</sub>), 7.14 (d, *J* = 10.2 Hz, 1H, H<sub>2</sub>), 6.98 (d, *J* = 10.2 Hz, 1H, H<sub>3</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**: δ<sub>C</sub> (ppm) = 188.5, 185.3, 140.3 (CH), 136.9, 136.2 (CH), 134.0, 133.8 (CH), 132.9, 132.7, 131.2 (CH), 130.0 (CH), 129.4, 129.2, 128.3 (CH), 128.3 (CH), 125.9 (CH), 125.4 (CH), 123.3 (CH).

**ESI-TOF-HR-MS (m/z)**: Calcd for ([M+H<sup>+</sup>]) 259.0754; found 259.0751.

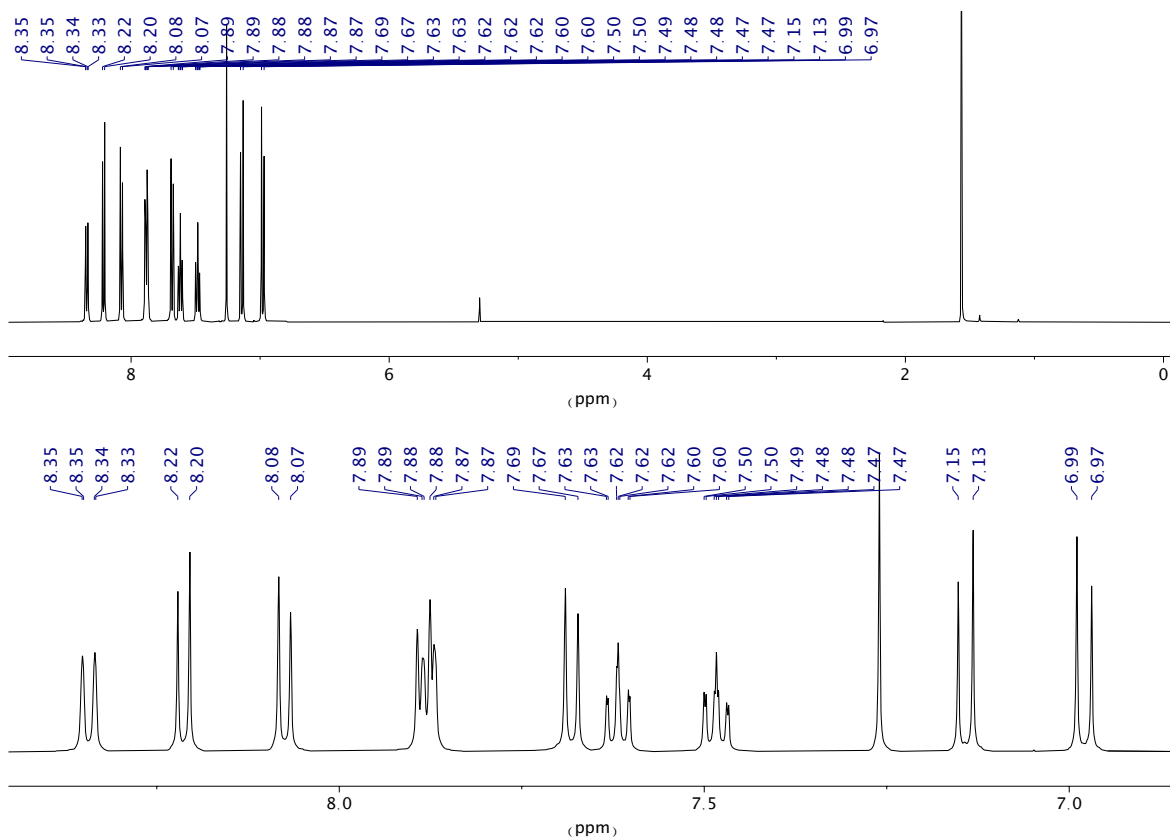


Figure S37: <sup>1</sup>H NMR spectrum of benzo[*c*]phenanthrene-1,4-dione (14)

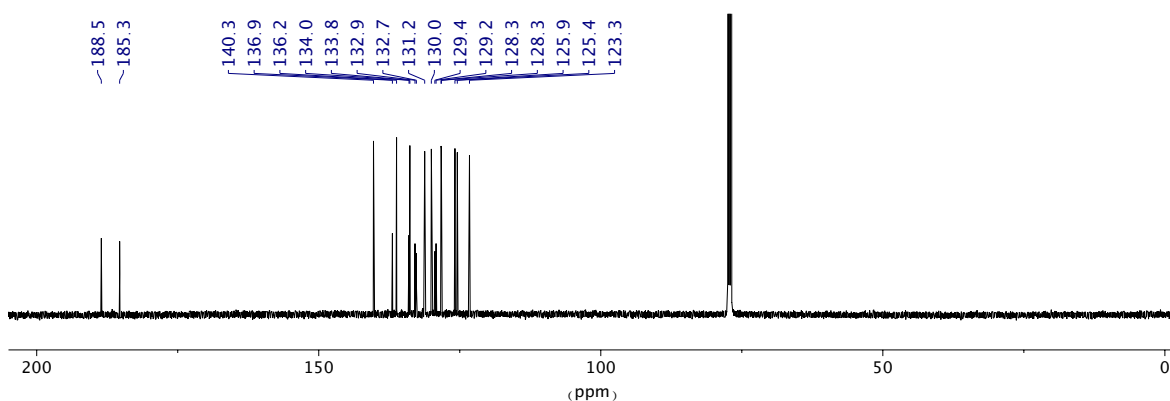


Figure S38: <sup>13</sup>C NMR spectrum of benzo[*c*]phenanthrene-1,4-dione (14)

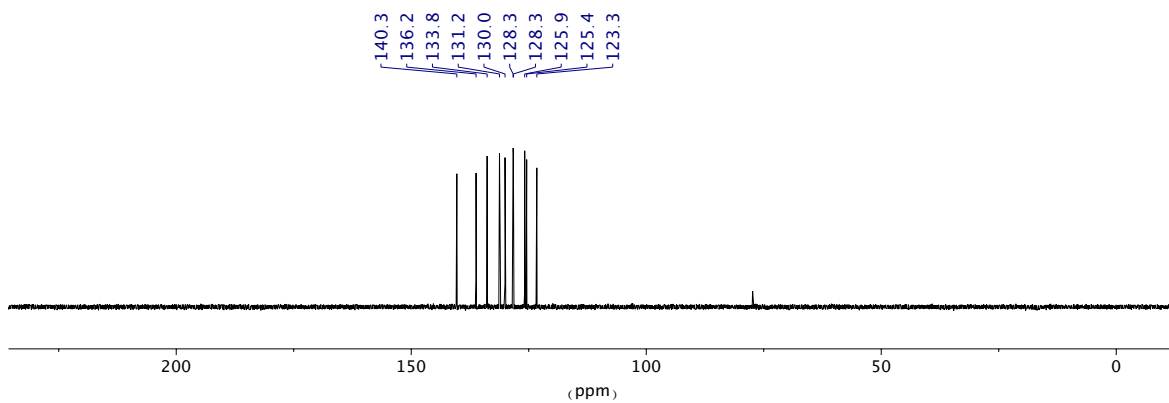
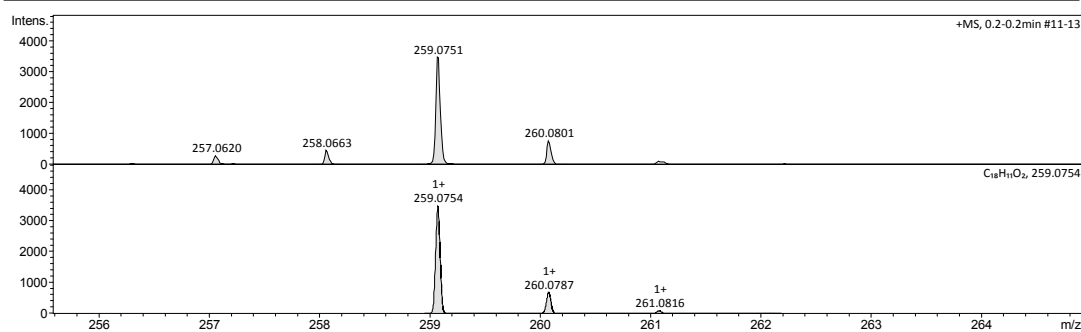


Figure S39: DEPT135 NMR spectrum of benzo[c]phenanthrene-1,4-dione (**14**)

Acquisition Parameter		Ion Polarity	Positive	Set Corrector Fill	52.4 V
Source Type	ESI	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	1985.0 V



Meas. m/z #	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdb	N-Rule	e <sup>-</sup>	Conf	mSigma	Std	Std Mean	m/z	Std	VarNorm	Std m/z	Diff	Std Comb	Dev
259.075099	1 C <sub>18</sub> H <sub>11</sub> O <sub>2</sub>	259.075356	1.0	1591.4	13.5	ok	even	18.8	26.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Figure S40: ESI-TOF HRMS of benzo[c]phenanthrene-1,4-dione (**14**)



### 2,3-dihydrobenzo[*c*]phenanthrene-1,4-dione (**12**)

Due to fast oxidation of the compound to the corresponding quinone, signals of the quinone were always found in the NMR data of the reduced form.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C)** : δ<sub>H</sub> (ppm) = 8.17 (m, 2H, H<sub>5</sub> + H<sub>12</sub>), 8.04 (d, *J* = 8.3 Hz, 1H, H<sub>6</sub>), 7.95 – 7.85 (m, 2H, H<sub>7/8</sub> + H<sub>9</sub>), 7.71 (d, *J* = 8.7 Hz, 1H, H<sub>7/8</sub>), 7.62 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H, H<sub>10</sub>), 7.52 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H, H<sub>11</sub>), 3.52 (t, *J* = 7.2 Hz, 2H, H<sub>2</sub>), 3.31 (t, *J* = 7.2 Hz, 2H, H<sub>3</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**: δ<sub>C</sub> (ppm) = 202.1, 195.1, 138.4, 137.1, 135.6, 133.8, 133.1 (CH), 131.4 (CH), 129.0 (CH), 129.0, 128.9 (CH), 128.0, 127.9 (CH), 126.1 (CH), 126.1 (CH), 123.8 (CH), 40.1 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>).

**ESI-TOF-HR-MS (m/z)**: Calcd for ([M+H<sup>+</sup>]) 261.0910; found 261.0921.

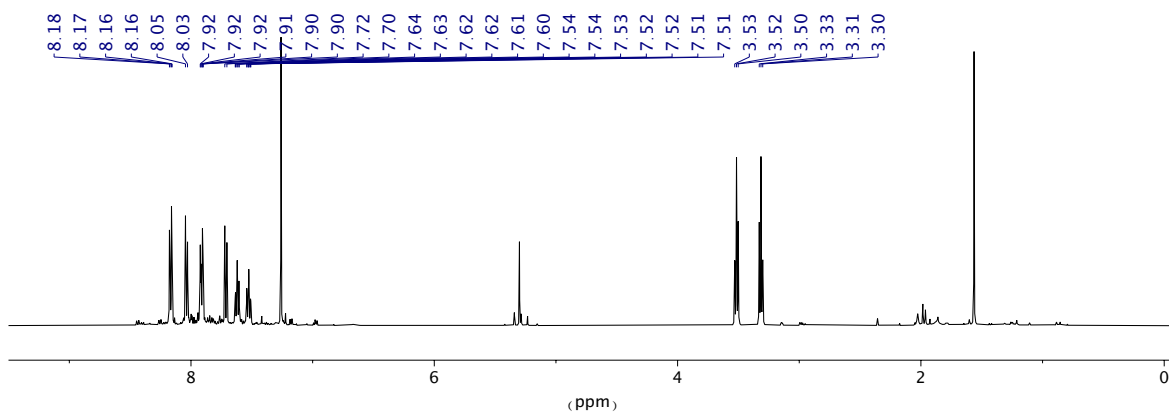


Figure S41: <sup>1</sup>H NMR spectrum of 2,3-dihydrobenzo[*c*]phenanthrene-1,4-dione (**12**)

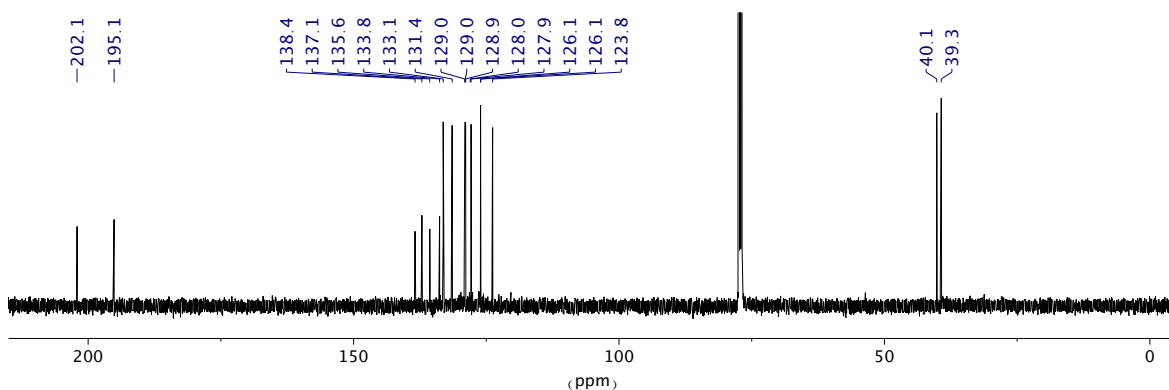


Figure S42: <sup>13</sup>C NMR spectrum of 2,3-dihydrobenzo[*c*]phenanthrene-1,4-dione (**12**)

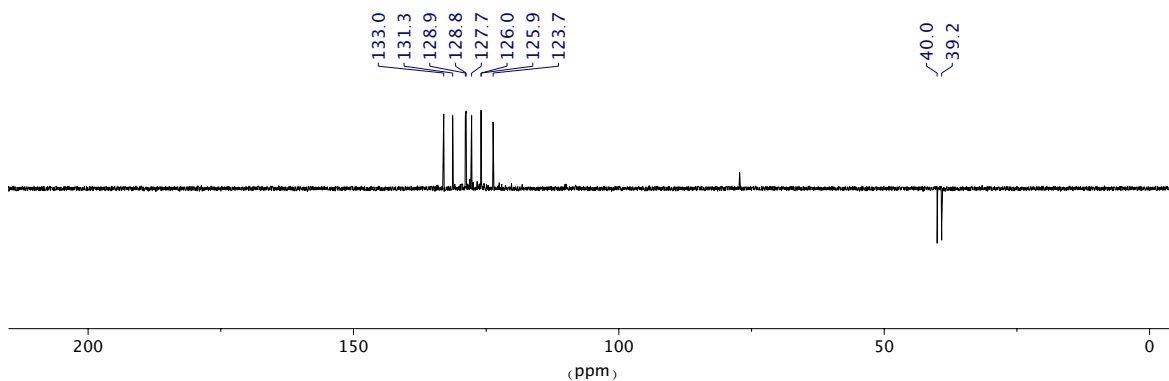
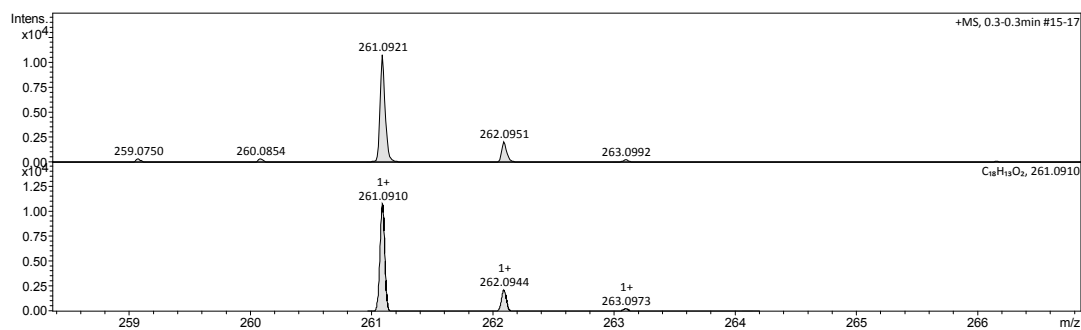


Figure S43: DEPT135 NMR spectrum of 2,3-dihydrobenzo[*c*]phenanthrene-1,4-dione (**12**)

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	52.4 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	1985.0 V



Meas. m/z #	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdB	N-Rule	e <sup>-</sup>	Conf	mSigma	Std I	Std	Mean m/z	Std I	VarNorm	Std m/z	Diff	Std	Comb	Dev
261.092064	1 C <sub>18</sub> H <sub>13</sub> O <sub>2</sub>	261.091006	-4.1	-4.4	12.5	ok	even	4.8	8.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Figure S43: ESI-TOF HRMS of 2,3-dihydrobenzo[*c*]phenanthrene-1,4-dione (**12**)

## Computational Study

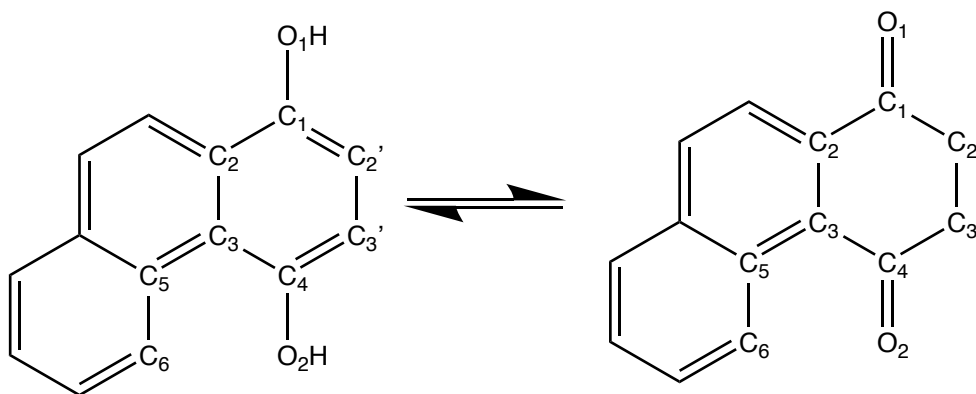


Figure S44: numbering of the atoms illustrated in the “[3]helicene” moiety (phenanthrene).

	N	1	2	3	4	5	6	7
OH	C <sub>1</sub> -C <sub>2</sub>	1.395	1.429	1.416	1.417	1.417	1.416	1.416
	C <sub>1</sub> -C <sub>2'</sub>	1.395	1.371	1.379	1.378	1.378	1.378	1.378
	C <sub>2</sub> -C <sub>3'</sub>	1.393	1.414	1.400	1.402	1.402	1.400	1.401
	C <sub>2</sub> -C <sub>3</sub>	1.393	1.426	1.423	1.427	1.424	1.424	1.422
	C <sub>3</sub> -C <sub>4</sub>	1.395	1.426	1.423	1.427	1.426	1.424	1.423
	O <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	180.0	179.9	178.3	176.8	176.6	176.9	176.4
	O <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub>	180.0	179.6	173.1	163.8	166.5	166.6	164.8
	C <sub>5</sub> -C <sub>3</sub> -C <sub>2</sub> -C <sub>4</sub>		179.4	178.9	174.6	173.7	176.6	176.5
C <sub>4</sub> -C <sub>3</sub> -C <sub>5</sub> -C <sub>6</sub>			14.1	29.5	28.1	25.2	28.6	
CO	O <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	172.2	172.2	179.0	167.9	168.4	164.1	166.1
	O <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub>	172.3	172.3	153.2	140.5	140.7	137.0	138.8
	C <sub>5</sub> -C <sub>3</sub> -C <sub>2</sub> -C <sub>4</sub>		178.1	179.9	165.5	164.8	167.7	166.6
	C <sub>4</sub> -C <sub>3</sub> -C <sub>5</sub> -C <sub>6</sub>			3.1	30.2	29.0	23.2	26.5

Table S1: Geometric parameter in the different helicene. Bond lengths are in Angströms and dihedral angle in degrees.

	Benzene	naphtalene	<b>8</b>	<b>9</b>
C1-C2		2.49	2.57	2.24
C2-C3		3.12	3.28	2.07
C3-C4		2.46	2.46	1.82
C4-C5		3.12	3.29	2.07
C5-C6		2.49	2.55	2.24
C6-C1	2.77	2.67	2.76	2.78
C6-C7	2.76	2.49	2.54	2.76
C7-C8	2.78	3.12	3.09	2.81
C8-C9	2.77	2.46	2.48	2.67
C9-C10	2.77	3.12	3.09	2.81
C10-C1	2.78	2.49	2.50	2.76
C2-O			1.43	2.34
C5-O			1.43	2.34

Table S2: electronic population of the ELF C-C and C-O basins (right: atom numbering).

## Computational Details

All calculations were done with GAUSSIAN 09 (version D01) at DFT level of theory ( $\omega$ B97XD functional). All atoms were described by 6-31+G\*\* basis set. Solvent corrections of dichloromethane were introduced through PCM model. Frequency calculations were done on the basis of optimized geometry within harmonic approximation. Gibbs Free Energies were extracted from this frequency analysis. The tautomerism equilibrium were computed from the reaction:  $\Delta G = G(\text{diketo}) - G(\text{diol})$ .

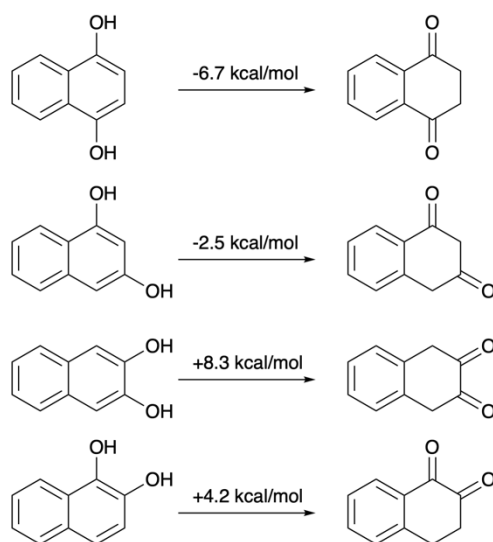


Figure S45: Calculated energy differences between the dihydroxy and the dione tautomers for the ortho, meta, and para isomers of naphthohydroquinones.

## Cystallographic data (CCDC Nr 2092869)

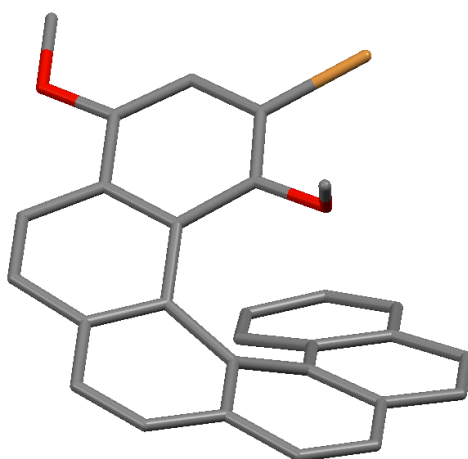


Figure S46: X-ray structure of the (*M*)-2-bromo-1,4-dimethoxyhexahelicene ( $\pm$ ) (1), protons were omitted for clarity, a single enantiomer was represented

A specimen of  $C_{28}H_{19}BrO_2$ , approximate dimensions 0.150 mm x 0.200 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ( $\lambda = 0.71073$  Å). The integration of the data using a monoclinic unit cell yielded a total of 91304 reflections to a maximum  $\theta$  angle of  $27.92^\circ$  (0.76 Å resolution), of which 9892 were independent (average redundancy 9.230, completeness = 99.9%,  $R_{int} = 4.68\%$ ,  $R_{sig} = 2.15\%$ ) and 8445 (85.37%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 14.6897(5)$  Å,  $b = 14.0457(6)$  Å,  $c = 20.6528(7)$  Å,  $\beta = 104.4410(10)^\circ$ , volume =  $4126.6(3)$  Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of reflections above  $20\sigma(I)$ . The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6577 and 0.7456. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P 1 21/c 1$ , with  $Z = 8$  for the formula unit,  $C_{28}H_{19}BrO_2$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 563 variables converged at  $R1 = 2.95\%$ , for the observed data and  $wR2 = 7.64\%$  for all data. The goodness-of-fit was 1.006. The largest peak in the final difference electron density synthesis was  $0.749 e^-/\text{Å}^3$  and the largest hole was  $-0.733 e^-/\text{Å}^3$  with an RMS deviation of  $0.061 e^-/\text{Å}^3$ . On the basis of the final model, the calculated density was  $1.504 \text{ g/cm}^3$  and  $F(000)$ , 1904  $e^-$ .

## References

- [1] M. Jakubec, T. Beránek, P. Jakubík, J. Sýkora, J. Žádný, V. Církva, and J. Storch, *Org. Chem.* **2018**, *83*, 3607–3616
- [2] R. H. Martin, *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660