# Synthesis and Characterization of 1,8-Naphthalimide with [6]helicene Skeleton

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# **Experimental section:**

**General.** Optical rotations  $[\alpha]_D$  were measured with a *Jasco DIP-316* polarimeter using a 0.5 dm cell. Circular dichroism spectra (CD) were measured with a *Jasco J-720W* spectropolarimeter using 1.0 mm path length cell. <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (125 or 100 MHz) spectra were obtained on a *Varian Unity* spectrometer in CDCl<sub>3</sub> with SiMe<sub>4</sub> as an internal standard. High-resolution mass spectra were recorded on a Bruker micrOTOF (ESI-TOF) spectrometer. All reactions were monitored by thin-layer chromatography carried out on E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto, 40-50 µm mesh). Gel permeation chromatography (GPC) was performed using a *JAI* model LC-908 recycling preparative HPLC (flow rate 3.8 mL/min) with chloroform as eluent.

#### Synthesis of compound 1 (oxidative photocyclization; batch condition).



Compound **3** (205.5 mg, 0.37 mmol) and iodine (103.3 mg, 0.41 mmol) were dissolved in toluene (370 mL, 1.0 mM) in a Pyrex glass flask. THF (1.3 mL) was added, and the mixture was placed in the middle of an array of UV lamps (photochemical reactor with a peak wavelength of 350 nm (20 W black light  $\times$  7 pieces, total 140 W, by Nomiyama Rika, Japan) (**Figure S2**). The solution was irradiated for 84 h. The reaction mixture was then washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water, and dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude brown oil was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> and GPC (CHCl<sub>3</sub>) to give the compound **3** (55.1 mg, 27% recovery), **16** (54.2 mg 27%), and **1** as a yellow solid (7.3 mg, 4%).

12-(4-Bromostyryl)-5-neopentyl-4*H*-benzo[*de*]naphtho[1,2-*g*]isoquinoline-4,6(5*H*)-dione (**16**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 9.40 (d, *J* = 8.1 Hz, 1H), 9.03 (s, 1H), 9.02 (s, 1H), 8.73 (d, *J* = 7.3 Hz, 1H), 8.04 (dd, *J* = 41.4 Hz, *J* = 8.6 Hz, 2H), 8.00 (s, 3H), 7.52 (dd, *J* = 21.8 Hz, *J* = 8.6 Hz, 4H), 7.35 (dd, *J* = 53.3 Hz, *J* = 16.5 Hz, 2H), 4.23 (s, 2H), 1.04 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 165.2, 164.7, 136.1, 135.95, 135.91, 134.5, 134.0, 133.8, 133.7, 133.3, 133.1, 132.0, 131.8, 131.1, 130.9, 131.0, 130.6, 130.5, 130.4, 130.0, 129.8, 129.6, 129.4, 129.2, 129.1, 129.0, 128.65, 128.6, 128.5, 128.1, 127.8, 127.7, 127.7, 127.5, 127.0, 124.9, 123.3, 123.0, 121.8, 121.4, 121.1, 49.7, 34.2, 28.8; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>26</sub>BrNO<sub>2</sub> 572.1021, found 572.1033.

15-Bromo-9-neopentyl-8*H*-benzo[*de*]benzo[5,6]phenanthro[4,3-*g*]isoquinoline-8,10(9*H*)-dione (**1**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ9.09 (s, 1H), 8.34 (dd, *J* = 1.1 Hz, *J* = 7.3 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* 

= 1.3 Hz, 1H), 7.28 (dd, J =1.9 Hz, J = 8.6 Hz, 1H), 6.91 (t, J = 8.4 Hz, 1H), 4.25 (s, 2H), 1.07 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 165.1, 164.8, 134.8, 133.5, 132.6, 132.2, 130.9, 130.5, 130.3, 130.1, 129.8, 129.3, 129.1, 129.0, 128.5, 128.4, 128.3, 128.0, 127.6, 126.7, 126.6, 126.4, 125.4, 123.5, 122.5, 121.5, 119.6, 117.8, 49.5, 34.3, 28.8; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>24</sub>BrNO<sub>2</sub> 570.0864, found 570.0866.

#### Synthesis of compound 1 from 13 (oxidative photocyclization).



**Batch Condition;** Compound **13** (257.0 mg, 0.49 mmol) and iodine (136.8 mg, 0.54 mmol) were dissolved in toluene (2000 mL, 0.25 mM) in a Pyrex glass flask. THF (4.0 mL) was added, and the mixture was placed in the middle of an array of UV lamps (photochemical reactor with a peak wavelength of 350 nm (20 W black light  $\times$  7 pieces, total 140 W, by Nomiyama Rika, Japan). The solution was irradiated for 72 h. The reaction mixture was then washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water, and dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude brown oil was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> and GPC (CHCl<sub>3</sub>) to give the compound **1** as a yellow solid (49.6 mg, 19%).

**Microflow system;** A mixture of compound **13** (2.35 mg, 4.5  $\mu$ mol), iodine (1.25 mg, 4.9 $\mu$ mol), toluene (18 mL, 0.25 mM) was loaded in a syringe. The syringe was connected to an inlet of the microreactor (1 mm width, 0.2 mm depth, and 560 mm length total hold-up volume: 112  $\mu$ L, by YMC Co., Ltd., Japan) (**Figure S3**). The substrate was introduced into microreactor by a syringe pump at the rate of 11.2  $\mu$ L/min (residence time: 10 min) and irradiated by UV-LEDs (250 mW × 6 pieces, total 1.5 W) with a peak wavelength of 365 nm. The mixture of the product was collected from the outlet. The reaction mixture was collected for 27 h. The reaction mixture was then washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water, and dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude brown oil was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> and GPC (CHCl<sub>3</sub>) to give the compound **1** as a yellow solid (1.32 mg, 55%).

#### Synthesis of compound 2



To a solution of compound **9** (105 mg, 0.26 mmol) in THF (9 mL) was added 60% NaH in mineral oil (52 mg, 1.3 mmol) in THF (15 mL) at 0  $^{\circ}$ C. The resulting solution was stirred at room temperature for 1 h. To a resulting solution was added compound **8** (76 mg, 0.26 mmol) in THF (15 mL) and the mixture was stirred at 0  $^{\circ}$ C for 30 min. The solution was then heated to ambient temperature and stirred at this temperature for overnight, and then quenched with saturated aqueous NH<sub>4</sub>Cl at 0  $^{\circ}$ C and extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic fractions were dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (2:3) to give the compound **2** as a yellow solid (140 mg, 98%).

5-(2-(6-Bromophenanthren-3-yl)vinyl)-2-neopentyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**2**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ8.96 (s, 1H), 8.89 (s, 1H), 8.74 (s, 1H), 8.56 (d, *J* = 7.3 Hz, 1H), 8.29 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 2H), 7.67-7.79 (m, 6H), 7.54 (d, *J* = 16.7 Hz, 1H), 4.20 (s, 2H), 1.05 (s, 9H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ164.9, 164.8, 136.3, 135.2, 133.5, 132.2, 132.2, 131.6, 131.2, 130.9, 130.8, 130.2, 130.0, 129.8, 129.5, 129.2, 128.9, 127.6, 127.5, 127.4, 127.1, 126.7, 125.5, 125.0, 123.3, 122.9, 121.9, 121.1, 49.7, 34.2, 28.8; HRMS (ESI):  $[M+Na]^+$  Calcd for C<sub>33</sub>H<sub>26</sub>BrNO<sub>2</sub> 570.1039, found 570.1033.

#### Synthesis of compound 3



To a solution of compound **12** (1.78 mL, 7.9 mmol) in THF (106 mL, 0.05 M) was added 60 % NaH in mineral oil (317 mg, 7.9 mmol). The resulting solution was stirred at room temperature for 30 min. To a resulting white solution was added compound **11** (2.1 g, 5.3 mmol) and the mixture was stirred at 0  $^{\circ}$ C for 30 min. The solution was then heated to 30  $^{\circ}$ C and stirred at this temperature for 1h, and then quenched with saturated aqueous NH<sub>4</sub>Cl

at 0  $^{\circ}$ C and extracted with CHCl<sub>3</sub> and the combined organic fractions were dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product as a yellow-brown solid. The crude product was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> to give the compound **3** as a yellow solid (2.2 g, 76%).

5-(4-(4-Bromostyryl)styryl)-2-neopentyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**3**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta 8.87$  (d, *J* = 1.5 Hz, 1H), 8.54 (d, *J* = 6.4 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 8.15 (s, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 7.57 (quartet, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 16.3 Hz, 1H), 7.30 (d, *J* = 16.5 Hz, 1H), 7.11 (d, *J* = 16.5 Hz, 1H), 7.06 (d, *J* = 16.3 Hz, 1H), 4.18 (s, 2H), 1.04 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta 164.9$ , 164.8, 137.1, 136.4, 136.2, 133.5, 132.1, 131.8, 131.1, 131.0, 130.7, 128.9, 128.8, 128.0, 127.8, 127.4, 127.2, 127.0, 126.8, 123.3, 122.9, 121.5, 49.6, 34.2, 28.8; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>28</sub>BrNO<sub>2</sub> 574.1177, found 574.1158.

#### Synthesis of compound 5



To a solution of 1,8-naphthalic anhydride **4** (20.0 g, 0.1 mol) in sulfuric acid (400 mL, 0.25 M) was added silver (I) sulfate (16 g, 51.3 mmol) and bromine (6.4 mL, 0.25 mol). The resulting brown solution was stirred at 65  $^{\circ}$ C for 10 h. The slurry was removed by filtration through a bed of Celite and the bed washed with sulfuric acid (100 mL). The filtrate was poured slowly into ice water to precipitate a white solid, which was collected by filtration using a Buchner funnel and washed with water until the washings reached pH 7; it was further washed with ethanol. The crude grayish-white solid was recrystallized from acetone to afford **5** (25.9 g, 93%) as white crystals.

5-Bromobenzo[*de*]isochromene-1,3-dione (**5**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 8.69 (d, *J* = 1.7 Hz, 1H), 8.64 (d, *J* = 7.1 Hz, 1H), 8.48 (d, *J* = 1.7 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 8.2 Hz, 1H); HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>5</sub>BrO<sub>3</sub> 298.9314, found 298.9298.

#### Synthesis of compound 6



Compound 5 (2 g, 7.2 mmol) was dissolved in 1,4-dioxane (72 mL, 0.1 M) followed by addition of neo pentylamine (1.3 mL, 11 mmol). The solution was left stirring at 100  $^{\circ}$ C for 4 h, and then cooled to room temperature. The solvent 1,4-dioxane was removed under reduced pressure to give 6 (2.52 g, quant.).

5-Bromo-2-neopentyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**6**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ8.66 (d, *J* =1.7 Hz, 1H), 8.59 (d, *J* = 7.1 Hz, 1H), 8.36 (d, *J* =1.5 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 7.9 Hz, 1H), 4.14 (s, 2H), 1.01 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ164.3, 163.7, 135.3, 134.1, 132.8, 132.5, 131.4, 128.0, 126.5, 124.4, 123.0, 121.1, 49.7, 34.2, 28.7; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>16</sub>BrNO<sub>2</sub> 368.0257, found 368.0231.

#### Synthesis of compound 7



A mixture of compound **6** (1.4 g, 4.2 mmol), CuCN (743 mg, 8.3 mmol), and L-proline (477 mg, 4.2 mmol) in DMF (83 mL) was stirring at 140  $^{\circ}$ C for 45 h. The slurry was removed by filtration through a bed of Celite and the bed washed with AcOEt. The filtrate was washed with water and the organic fraction was dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> to give the compound **7** as a yellow solid (1 g, 82%).

2-Neopentyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinoline-5-carbonitrile (**7**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta 8.72-8.75$  (m, 2H), 8.56 (s, 1H), 8.28 (d, J = 8.2 Hz 1H), 7.90 (t, J = 7.9 Hz, 1H), 4.15 (s, 2H), 1.01 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta 163.8$ , 163.2, 138.2, 134.0, 133.9, 131.6, 130.9, 129.1, 128.8, 124.4, 123.2, 117.5, 111.3, 49.9, 34.2, 28.7; HRMS (ESI): [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> 315.1104, found 315.1095.

#### Synthesis of compound 8



To a solution of compound 7 (12 g, 2.3 mmol) in 75% HCOOH (4 mL) was added Raney nickel (93 mg in H<sub>2</sub>O).<sup>1</sup> The resulting solution was refluxed at 105  $^{\circ}$ C for 12 h. The reaction mixture was adjusted to pH = 6 with NaHCO<sub>3</sub>

and extracted with AcOEt and the combined organic fractions were dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> to give the compound **8** as a yellow solid (22.4 mg, 29%).

2-Neopentyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinoline-5-carbaldehyde (**8**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta 10.29$  (s, 1H), 9.05 (s, 1H), 8.73-8.74 (m, 2H), 8.39 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 4.17 (s, 2H), 1.02 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta 190.6$ , 164.1, 163.9, 136.3, 135.1, 134.7, 133.8, 131.2, 130.5, 129.5, 128.2, 124.1, 123.3, 49.8, 34.2, 28.7; HRMS (ESI): [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>3</sub> 296.1281, found 296.1277.

#### Synthesis of compound 9



A stirred solution of **S3** (521 mg, 1.3 mmol), triethylphosphite (1 mL, 5.8 mmol) and toluene (4 mL) was heated at 140  $^{\circ}$ C for 8 h and cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by flash chromatography over silica gel with CHCl<sub>3</sub>-AcOEt (9:1) to give the compound **9** as colorless oil (547 mg, 98%).

Diethyl ((6-bromophenanthren-3-yl)methyl)phosphonate (**9**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta 8.79$  (d, J = 1.5 Hz,1H), 8.49 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.63-7.74 (m, 4H), 7.57-7.59 (m, 1H), 3.99-4.08 (m, 4H), 3.41 (d, J = 21.8 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta 131.4$ , 131.0 (d, J = 3.0 Hz), 130.6, 130.5, 130.4, 130.0, 129.8, 129.2 (d, J = 3.0 Hz), 129.0 (d, J = 5.3 Hz), 128.8 (d, J = 3.0 Hz), 127.0, 126.1, 125.5, 123.7 (d, J = 8.3 Hz), 120.8, 62.2 (d, J = 6.8 Hz), 35.0, 33.6, 16.4 (d, J = 6.0 Hz); HRMS (ESI): [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>BrO<sub>3</sub>P 407.0406, found 407.0398.

#### Synthesis of compound 10



A mixture of the compound **6** (9.65 g, 27.9 mmol), tributylvinylstannane (8.93 mL, 30.7 mmol),  $Pd_2(dba)_3$  (511 mg, 2 mol%) and  $P(tBu)_3$  (406 µl, 6 mol%) in 280 mL of toluene was refluxed under argon atmosphere for 24 h.

Thereafter, KF (16.2 g), H<sub>2</sub>O (280 mL) was added and the mixture was stirred at room temperature for 48 h. The resultant tin salt precipitate was removed by suction filtration and washed with  $Et_2O$ , then dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography over silica gel with CHCl<sub>3</sub>-hexanes (1:1 up to 7:3) to give the compound **10** as a yellow solid (7.38 g, 90%).

2-Neopentyl-5-vinyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**10**); <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>):  $\delta$ 8.74 (d, *J* =1.7 Hz, 1H), 8.17 (d, *J* =8.1 Hz, 1H), 8.54 (d, *J* = 7.3 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 8.10 (d, *J* = 1.1 Hz, 1H), 6.94 (dd, *J* = 11.2 Hz, *J* = 17.6 Hz, 1H), 6.07 (d, *J* =17.6 Hz, 1H), 5.51 (d, *J* = 11.0 Hz, 1H), 4.16 (s, 2H), 1.02 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 164.85, 164.76, 136.5, 135.4, 133.6, 131.9, 131.0, 130.9, 128.8, 127.6, 127.3, 123.1, 122.8, 116.9, 49.6, 34.1, 28.8; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub> 316.1308, found 316.1303.

## Synthesis of compound 11



The compound **10** (718.5 mg, 2.45 mmol), 4-bromobenzaldehyde (679.9 mg, 3.7 mmol), PPh<sub>3</sub> (128.5 mg, 20 mol%), AcONa (241.2 mg, 2.9 mmol) and Pd(OAc)<sub>2</sub> (55.0 mg, 10 mol%) were weighed into a dry flask that was then evacuated for 1 h at room temperature before back-filling with argon. To this was added 25 mL of DMF (0.1 M). The reaction mixture was heated to 120  $^{\circ}$ C with stirring for 12 h. The solvent DMF was removed under reduced pressure, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. After filtration, the filtrate was evaporated to give a crude product, which was subjected to flash chromatography over silica gel with CHCl<sub>3</sub> to give the compound **11** as a yellow solid (858.7 mg, 88%).

4-(2-(2-Neopentyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-5-yl)vinyl)benzaldehyde (**11**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 10.04 (s, 1H), 8.88 (d, *J* = 1.8 Hz, 1H), 8.57 (dd, *J* = 1.1 Hz, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.22 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.47 (s, 2H), 4.18 (s, 2H), 1.04 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 164.8, 164.6, 142.5, 135.9, 135.6, 133.6, 132.0, 131.9, 131.2, 130.3, 130.2, 130.1, 128.7, 127.7, 127.6, 127.2, 123.4, 122.9, 49.7, 34.2, 28.7; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>23</sub>NO<sub>3</sub> 420.1570, found 420.1560.

#### Synthesis of compound 12



A stirred solution of 4-bromobenzylbromide (15 g, 60 mmol), triethylphosphite (10.3 mL, 60 mmol) and toluene (30 mL, 2.0 M) was heated at 135  $^{\circ}$ C for 15 h and cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by flash chromatography over silica gel with acetone-hexanes (2:8 up to 3:7) to give the compound **12** as colorless oil (17 g, 93%).

Diethyl 4-bromobenzylphosphonate (**12**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$ 7.43 (dd, J = 0.8 Hz, J = 8.4 Hz, 2H), 7.18 (dd, J = 2.6 Hz, J = 8.6 Hz, 2H), 4.02 (double quintet, J = 1.7 Hz, J = 7.1 Hz, 2H), 3.09 (d, J = 21.7 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H); <sup>13</sup>C-NMR(100 MHz, CDCl<sub>3</sub>):  $\delta$ 131.6 (d,  $J_{PC} = 3.0$  Hz), 131.4 (d,  $J_{PC} = 6.0$  Hz),  $\delta$ 130.7 (d,  $J_{PC} = 9.8$  Hz), 120.9 (d,  $J_{PC} = 4.5$  Hz), 62.2 (d,  $J_{PC} = 6.8$  Hz), 33.2 (d,  $J_{PC} = 138.4$  Hz) , 16.3 (d,  $J_{PC} = 6.0$  Hz); HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>BrO<sub>3</sub>P 328.9913, found 328.9918.

#### Synthesis of compound 13



To a solution of AlCl<sub>3</sub> (624.0 mg, 4.7 mmol) in THF (60 mL, 0.03 M) was added LiAlH<sub>4</sub> (519.2 mg, 13.7 mmol) at 0  $^{\circ}$ C for 5 min. Thereafter, compound **3** (1.0 g, 1.8 mmol) was added and the mixture was stirred at this temperature for 20 min. The mixture was allowed to warm to room temperature and stirred for 1 h and then refluxed for 3.5 h. The reaction was quenched with H<sub>2</sub>O at 0  $^{\circ}$ C and extracted with CHCl<sub>3</sub> and the combined organic fractions were dried over anhydrous MgSO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified by flash column chromatography over silica gel with CHCl<sub>3</sub> to give the compound **13** as a yellow solid (902.3 mg, 95%).

5-(4-(4-Bromostyryl)styryl)-2-neopentyl-2,3-dihydro-1*H*-benzo[*de*]isoquinoline (**13**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.72 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.56-7.45 (m, 7H), 7.41-7.35 (m, 3H), 7.30-7.19 (m, 2H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 6.7 Hz, 2H), 4.10 (s, 2H), 4.07 (s, 2H), 2.32 (s, 2H), 0.96 (s, 9H); <sup>13</sup>C-NMR(100 MHz, CDCl<sub>3</sub>):  $\delta$ 137.1, 136.3, 134.6, 134.4, 134.2, 133.4, 131.8, 129.1, 129.0, 128.3, 127.9, 127.2, 126.9, 126.9, 126.1, 125.1, 122.1, 121.3, 119.2, 68.7, 59.3, 59.1, 33.3, 27.9; HRMS (ESI):[M+Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>32</sub>BrNO<sub>2</sub> 546.1592, found 546.1607.

#### Synthesis of compound 14



The compound **2** (14 mg, 0.026 mmol) and iodine (8.8 mg, 0.028 mmol) were dissolved in toluene (17 mL). THF (42  $\mu$ L, 0.52 mmol) was added, and the mixture was placed in the middle of an array of UV lamps (photochemical reactor with a peak wavelength of 300 nm (FL-20E 20W UV lamp (Kyokko Denki) × 7 pieces, total 140 W, by Nomiyama Rika, Japan)). The solution was irradiated for 39 h. The reaction mixture was then washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> water, and dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude brown oil was purified by flash column chromatography with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (2:1) to give the compound **14** as a yellow solid (13 mg, 91%).

9-Bromo-2-neopentyl-1*H*-benzo[*de*]tetrapheno[8,9-*g*]isoquinoline-1,3(2*H*)-dione (**14**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 9.47-9.51 (m, 2H), 9.18 (s, 1H), 9.00-9.03 (m, 2H), 8.74 (d, *J* = 7.3 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.97-8.01 (m, 3H), 7.26-7.80 (m, 3H), 4.23 (s, 2H), 1.07 (s, 9H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 165.2, 164.7, 133.4, 33.3, 133.1, 131.5, 131.1, 131.0, 130.8, 130.8, 130.6, 130.2, 130.0, 129.4, 129.1, 128.7, 128.6, 128.4, 127.8, 127.6, 127.2, 126.2, 123.4, 122.7, 121.3, 49.8, 34.3, 28.8; HRMS (ESI): [M+Na]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>24</sub>BrNO<sub>2</sub> 568.0883, found 568.0872.

#### Synthesis of compound 15



A mixture of the compound 14 (36 mg, 0.065 mmol), tributylvinylstannane (21 µL, 0.072 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (1 mg,

1.5 mol%), and P(*t*Bu)<sub>3</sub> (1.2 mg, 9 mol%) in 6 mL of toluene was refluxed under argon atmosphere for 2 days. Thereafter, 2 M KF aqueous solutions (3 mL) was added and the mixture was stirred at room temperature for 12 h. The resultant tin salt precipitate was removed by suction filtration and washed with toluene, then dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography over silica gel with hexanes and CH<sub>2</sub>Cl<sub>2</sub>-hexanes (2:1) and GPC (CHCl<sub>3</sub>) to give the compound **15** as a yellow solid (11 mg, 34%). 2-Neopentyl-9-vinyl-1*H*-benzo[*de*]tetrapheno[8,9-*g*]isoquinoline-1,3(2*H*)-dione (**15**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 9.46 (d, *J* = 8.1 Hz, 1H), 9.40 (s, 1H), 9.20 (s, 1H), 8.98 (s, 1H), 8.77 (s, 1H), 8.71 (d, *J* = 7.3 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.87-7.98 (m, 4H), 7.75-7.82 (m, 2H), 7.06 (dd, *J* = 10.9, 17.5 Hz, 1H), 6.04 (d, *J* = 17.4 Hz, 1H), 5.47 (d, *J* = 11.0 Hz, 1H), 4.29 (s, 2H), 1.07 (s, 9H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 165.1, 164.6, 137.0, 136.4, 133.3, 133.3, 132.8, 132.0, 131.2, 130.7, 130.3, 130.0, 129.9, 129.7, 129.3, 128.9, 128.4, 127.9, 127.7, 127.2, 127.1, 127.0, 125.5, 125.1, 123.2, 122.3, 121.6, 121.0, 114.9, 49.7, 34.2, 30.3; HRMS (ESI): [M+H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>27</sub>NO<sub>2</sub> 494.2115, found 494.2107.

#### Synthesis of compound S1



(*E*)-4-(4-bromostyryl)benzaldehyde (654 mg, 2.3 mmol) and iodine (772 mg, 3.5 mmol) were dissolved in toluene (1.5 L). THF (3.5 mL, 62.6 mmol) was added, and the mixture was placed in the middle of an array of UV lamps (photochemical reactor with a peak wavelength of 300 nm (FL-20E 20W UV lamp (Kyokko Denki) × 7 pieces, total 140 W, by Nomiyama Rika, Japan)). The solution was irradiated for 5 days. The reaction mixture was then washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water, and dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was recrystallized from dioxane to afford **S1** as white crystals (420 mg, 65%). 6-Bromophenanthrene-3-carbaldehyde (**S1**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 10.29 (s, 1H), 9.10 (s, 1H), 8.92 (s, 1H), 8.12 (dd, *J* = 1.5, 8.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.75-7.88 (m, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 192.0, 136.1, 134.4, 131.8, 130.7, 130.6, 130.3, 129.6, 129.5, 129.0, 127.0, 126.8, 125.7, 125.6, 121.9; HRMS (ESI):[M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>9</sub>BrO 306.9729, found 306.9716.

Synthesis of compound S2



Compound **S1** (200 mg, 0.7 mmol) was dissolved in THF (15 mL) followed by addition of EtOH (6 mL). To a resulting solution was added compound NaBH<sub>4</sub> (7.3 mg, 0.19 mmol) and the mixture was stirred at 0  $^{\circ}$ C for 1 h. The reaction mixture was adjusted to pH = 6 with 10 % HCl aqueous solution and extracted with AcOEt and the combined organic fractions were dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product. The crude product was purified by flash column chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1:1) to give the compound **S2** as a white solid (197 mg, 98%).

(6-Bromophenanthren-3-yl)methanol (**S2**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta 8.85$  (d, J = 1.6 Hz, 1H), 8.60 (s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.74-7.77 (m, 2H), 7.68-7.70 (m, 2H), 7.62-7.64 (m, 1H), 4.98 (d, J = 4.4 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta 139.5$ , 131.7, 130.7, 130.1, 129.8, 129.3, 128.9, 127.1, 126.3, 126.2, 125.6, 120.9, 120.6, 65.6; HRMS (ESI): [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>11</sub>BrO 308.9885, found 308.9871.

#### Synthesis of compound S3



Compound **S2** (424 mg, 1.48 mmol) was dissolved in CHCl<sub>3</sub> (49 mL) followed by addition of polymethylhydrosiloxane (PMHS, 3.75 mL) and iodine (375 mg, 1.48 mmol). The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was quenched with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and extracted with CHCl<sub>3</sub> and the combined organic fractions were dried over MsSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The obtained crude product was recrystallized from toluene to afford **S3** as white crystals (521 mg, 88%). 3-Bromo-6-(iodomethyl)phenanthrene (**S3**); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.79 (s, 1H), 8.58 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.68-7.76 (m, 4H), 7.64 (d, *J* = 8.2 Hz, 1H), 4.74 (s, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 137.9, 131.7, 131.3, 130.1, 130.0, 129.4, 129.3, 128.0, 126.8, 125.5, 122.4, 121.0; HRMS (ESI): [M+Na]+ Calcd for C<sub>15</sub>H<sub>10</sub>BrI 418.8903, found 418.8894.

## Key 2D-NMR correlations for 15:



Fig. S1 Key COSY, HBMC, and NOESY correlations for 15.2D spectra for 15 are shown on page S48, S49, S50 and S51.

# **Photochemical reactors:**



Fig. S2. Photochemical reactor (external configuration) with 20 W black lights.



Fig. S3 YMC photomicroreactor system with UV-LED.

# Chiral reolution of the enantiomers of (P)-(+)- and (M)-(-)-1:

The two enantiomers (*P* and *M*) of **1** could be separated by analytical HPLC on a chiral column (CHIRALPAK IA (5  $\mu$ m, 250 × 4.6 mm)) at room temperature using heptane and dichloromethane as the eluent (Figure S3).



**Fig S4.** Chiral HPLC chromatogram of racemic **1**. The mobile phase is heptane/ $CH_2Cl_2(80:20)$ . The retention times of (+)-(*P*)-**1** and (-)-(*M*)-**1** are 7.3 min and 8.3 min, respectively. Flow rate; 1.0 mL/min. Eluted peaks are detected by monitoring absorbance at 254 nm.

#### Plausible path of the aerobic photo-oxidation of benzylic carbon:



#### C-H Bond-Dissociation Enthalpy (BDE) at the benzylic positions in model compound A-E:

The BDE at the benzylic carbon with neighboring the nitrogen (**A**, **B**), carbon (**C**, **D**), and oxygen (**E**) were calculated by a combined density-functional-theory (DFT) method at 298.15 K, designated as B3LYP/6-311++G(2d,2p)//AM1/AM1, which takes advantage of accuracy and economy (**Table S1**).<sup>2-5</sup> C-H BDE related to eq. 1. The BDE at the benzylic carbon with neighboring the nitrogen atom were lower than that of other model compounds.

$$BDE = \Delta H^{0}_{Radical} + \Delta H^{0}_{H} - \Delta H^{0}_{Molecule} \quad (1)$$

**Table S1.**Calculated BDE of the model compound A-E.

	$\Delta H$ (kcal/mol)	$\Delta\Delta H$ (kcal/mol)
А	71.87	_
В	75.46	3.59
С	83.92	12.05
D	83.77	11.90
Е	79.50	7.64



**Table S2.**Coordinates and the energies (Hartree) of the model compounds shown in Table S1. *E* is the electronicenergy calculated at B3LYP/6-311++G(2d,2p)//AM1/AM1. *H* is the enthalpy at 298.15 K.

structure A (molecule)

E = -558.119644H = -557.883618



structure A (radical)

E = -557.492106

*H* = -557.269195



atom	Х	Y	Ζ
С	-0.14725	-0.349914	-2.427058
С	-0.271223	0.334207	-1.239788
С	-0.148689	-0.360385	0
С	0.100638	-1.754094	0
С	0.219989	-2.432276	-1.244059
С	0.097679	-1.743901	-2.426057
Н	-0.237281	0.17677	-3.388709
С	-0.271223	0.334207	1.239788
С	0.219989	-2.432276	1.244059
Н	0.411473	-3.515627	-1.238005
Н	0.189827	-2.266536	-3.389855
С	0.097679	-1.743901	2.426057
С	-0.14725	-0.349914	2.427058
Н	0.411473	-3.515627	1.238005
Н	0.189827	-2.266536	3.389855
Н	-0.237281	0.17677	3.388709
С	-0.565827	1.80633	1.206679
Н	-0.092994	2.306611	2.098203
Н	-1.685398	1.934869	1.293494
С	-0.565827	1.80633	-1.206679
Н	-1.685398	1.934869	-1.293494
Н	-0.092994	2.306611	-2.098203
Ν	-0.1599	2.514008	0
С	1.236049	2.896865	0
Н	1.43834	3.519319	-0.910786
Н	1.43834	3.519319	0.910786
Н	1.94297	2.023458	0

atom	Х	Y	Ζ
С	0.449731	2.456699	-0.010223
С	-0.280659	1.247206	-0.030301
С	0.431614	0.001302	-0.015971
С	1.856964	-0.006245	0.016932
С	2.551521	1.232042	0.034333
С	1.848534	2.436198	0.021633
Н	-0.088883	3.41408	-0.022145
С	-0.28309	-1.220027	-0.028965
С	2.532447	-1.252115	0.032933
Н	3.649933	1.229029	0.057964
Н	2.401116	3.387367	0.036064
С	1.814472	-2.442238	0.01936
С	0.408965	-2.432339	-0.010471
Н	3.631502	-1.264662	0.056256
Н	2.345537	-3.405137	0.031068
Н	-0.143561	-3.382554	-0.021144
С	-1.77985	-1.225689	-0.048356
Н	-2.137903	-1.724132	0.90374
Н	-2.128692	-1.864802	-0.913849
С	-1.691474	1.226156	-0.068719
Н	-2.260808	2.16919	-0.049632
Ν	-2.424153	0.067353	-0.200266
С	-3.81379	0.092865	0.175697
Н	-4.271859	1.068664	-0.132848
Н	-4.345012	-0.741895	-0.354371
Н	-3.954615	-0.039519	1.283475

#### structure B (molecule)



E = -518.805921H = -518.597741

atom	Х	Y	Ζ
С	0.0354	-0.081724	2.427979
С	0.062545	0.61384	1.241432
С	0.035546	-0.089249	0
С	-0.020155	-1.504158	0
С	-0.045049	-2.19331	1.243575
С	-0.016754	-1.496065	2.426314
Н	0.054444	0.452008	3.38985
С	0.062545	0.61384	-1.241432
С	-0.045049	-2.19331	-1.243575
Н	-0.08662	-3.292719	1.236485
Н	-0.035587	-2.027234	3.389663
С	-0.016754	-1.496065	-2.426314
С	0.0354	-0.081724	-2.427979
Н	-0.08662	-3.292719	-1.236485
Н	-0.035587	-2.027234	-3.389663
Н	0.054444	0.452008	-3.38985
С	0.146985	2.113298	-1.209137
Н	-0.411431	2.544941	-2.087254
Н	1.233821	2.401648	-1.3175
С	0.146985	2.113298	1.209137
Н	1.233821	2.401648	1.3175
Н	-0.411431	2.544941	2.087254
Ν	-0.34923	2.743561	0
Н	-1.354507	2.725768	0

# structure B (radical)



E = -518.805921*H* = -518.597741

atom	Х	Y	Ζ
С	-0.662427	-2.377626	0.004603
С	0.330298	-1.372803	0.006528
С	-0.069883	0.006315	-0.000211
С	-1.454584	0.346247	-0.00255
С	-2.419637	-0.69536	-0.004596
С	-2.018138	-2.030585	-0.001261
Н	-0.362226	-3.434395	0.005703
С	0.909565	1.028835	0.002594
С	-1.821774	1.715186	-0.001102
Н	-3.487111	-0.435242	-0.008865
Н	-2.778103	-2.826026	-0.003598
С	-0.846681	2.705648	0.004528
С	0.5182	2.36864	0.007084
Н	-2.888031	1.983095	-0.004428
Н	-1.139268	3.765714	0.005372
Н	1.276891	3.164124	0.00946
С	2.367614	0.684699	0.005654
Н	2.8273	1.122668	0.942777
Н	2.858447	1.194221	-0.877518
С	1.708908	-1.677845	0.019001
Н	2.051287	-2.72399	0.06012
Ν	2.688245	-0.722021	-0.094702
Н	3.574334	-0.964129	0.292261

#### structure C (molecule)



E = -542.100337H = -541.852235 E = -541.453079H = -541.218610

structure C (radical)



Z Y

atom	Х	Y	Ζ
С	-0.454272	2.429156	0.052691
С	0.250135	1.24556	0.103271
С	-0.446428	0	0.059279
С	-1.860977	0.000009	-0.035314
С	-2.555639	1.239635	-0.081827
С	-1.865185	2.425205	-0.038732
Н	0.075432	3.393042	0.082626
С	0.250121	-1.245569	0.103238
С	-2.555659	-1.239605	-0.081772
Н	-3.653319	1.22654	-0.153786
Н	-2.398474	3.386694	-0.075685
С	-1.865224	-2.425186	-0.038641
С	-0.454306	-2.429158	0.052673
Н	-3.653348	-1.226497	-0.153607
Н	-2.398526	-3.386666	-0.07567
Н	0.075388	-3.39305	0.082575
С	1.732936	1.249212	0.22484
Н	2.004844	1.313537	1.314312
Н	2.159277	2.157151	-0.279141
С	1.73294	-1.249263	0.224717
Н	2.159232	-2.157134	-0.279416
Н	2.004885	-1.31366	1.31417
С	2.35912	0.00001	-0.378046
С	3.856365	-0.000005	-0.16129
Н	4.314301	-0.906665	-0.625011
Н	4.31432	0.906654	-0.624994
Н	4.098388	-0.000016	0.928973
Н	2.154033	0.000065	-1.485857

atom	Х	Y	Ζ
С	-0.44737	2.458924	0.06062
С	0.291081	1.249226	-0.008908
С	-0.425886	-0.000091	0.004961
С	-1.852154	0.000848	-0.013512
С	-2.54726	1.239021	0.018675
С	-1.844819	2.442703	0.071681
Н	0.094131	3.414881	0.090755
С	0.277866	-1.230332	0.049173
С	-2.540617	-1.237478	-0.0499
Н	-3.646117	1.236057	0.007851
Н	-2.397031	3.39322	0.115903
С	-1.834377	-2.434209	-0.046089
С	-0.430368	-2.434274	0.012991
Н	-3.639586	-1.238202	-0.078639
Н	-2.373561	-3.391996	-0.081597
Н	0.112733	-3.390097	0.035953
С	1.755233	-1.233523	0.207696
Н	2.193032	-2.149917	-0.271051
Н	1.982729	-1.294293	1.308786
С	1.682543	1.246619	-0.128155
Н	2.246429	2.187376	-0.097987
С	2.437207	-0.00208	-0.377199
С	3.858605	0.099375	0.140647
Н	4.413651	-0.845119	-0.074621
Н	4.391395	0.94726	-0.352986
Н	3.864801	0.271331	1.24374
Н	2.479304	-0.128861	-1.502203

# structure D (molecule)



E = -502.773754H = -502.554455

atom	Х	Y	Ζ
С	0.094321	2.429474	-0.040952
С	-0.611261	1.246208	-0.077594
С	0.085297	0.000003	-0.047424
С	1.501547	0.000057	0.018901
С	2.197403	1.239486	0.051656
С	1.506757	2.425303	0.022433
Н	-0.435676	3.393473	-0.060481
С	-0.61117	-1.246241	-0.077582
С	2.19752	-1.239303	0.051608
Н	3.296305	1.225953	0.101699
Н	2.040943	3.386635	0.04873
С	1.506977	-2.42519	0.022355
С	0.094541	-2.42948	-0.040981
Н	3.296423	-1.225694	0.101687
Н	2.041273	-3.386464	0.04863
Н	-0.435387	-3.393517	-0.0605
С	-2.09677	1.250396	-0.168907
Н	-2.38706	1.327866	-1.252925
Н	-2.511323	2.154277	0.352026
С	-2.096728	-1.250603	-0.168686
Н	-2.511136	-2.154403	0.352536
Н	-2.387195	-1.328384	-1.252642
С	-2.708619	-0.000062	0.42842
Н	-3.814177	-0.000129	0.242797
Н	-2.551869	0.000087	1.538961

# structure D (radical)



E = -502.12663H = -501.921067

atom	Х	Y	Ζ
С	0.680506	-2.375422	0.070883
С	-0.329536	-1.379981	0.022035
С	0.063933	0.005781	0.020776
С	1.447941	0.348516	-0.02752
С	2.42205	-0.684952	-0.010255
С	2.03258	-2.022536	0.053805
Н	0.386445	-3.433767	0.10909
С	-0.914074	1.03105	0.074038
С	1.81747	1.715714	-0.080629
Н	3.487213	-0.416582	-0.042514
Н	2.798786	-2.81142	0.084347
С	0.844257	2.707462	-0.066847
С	-0.516896	2.369825	0.019132
Н	2.883281	1.98049	-0.130727
Н	1.136275	3.766542	-0.1157
Н	-1.273859	3.166866	0.048183
С	-1.682817	-1.713884	-0.064049
Н	-1.996529	-2.765335	-0.046856
С	-2.347179	0.684421	0.260091
Н	-2.995043	1.452792	-0.241187
Н	-2.567959	0.736859	1.36319
С	-2.724934	-0.690977	-0.256502
Н	-3.67682	-1.017392	0.243658
Н	-2.941598	-0.629149	-1.361241

#### structure E (molecule)



E = -538.675699H = -538.480638

atom	Х	Y	Ζ
С	0.031	-0.071282	2.426028
С	0.055505	0.621241	1.237174
С	0.031891	-0.086094	0
С	-0.016125	-1.500577	0
С	-0.036952	-2.186808	1.245105
С	-0.013225	-1.48605	2.426163
Н	0.043563	0.464413	3.386814
С	0.055505	0.621241	-1.237174
С	-0.036952	-2.186808	-1.245105
Н	-0.074092	-3.28639	1.241023
Н	-0.03028	-2.015185	3.390707
С	-0.013225	-1.48605	-2.426163
С	0.031	-0.071282	-2.426028
Н	-0.074092	-3.28639	-1.241023
Н	-0.03028	-2.015185	-3.390707
Н	0.043563	0.464413	-3.386814
С	0.126152	2.111118	1.19451
Н	1.197013	2.440208	1.302386
Н	-0.496791	2.575713	2.00697
С	0.126152	2.111118	-1.19451
Н	-0.496791	2.575713	-2.00697
Н	1.197013	2.440208	-1.302386

2.662987

# structure E (radical)



-0.003877

0.026972

-0.020488

-0.00096

-0.030632

-0.034695

0.002582

-0.028302

-0.054725

0.072523

-0.756496

1.066344

-0.073736

E = -538.035875H = -537.854046

Η

Η

С

С

Η Η

Η С

Η

С

Η

Η

0

atom	Х	Y	Ζ
С	0.819997	-2.32439	0.017319
С	-0.243017	-1.390044	0.002926
С	0.063903	0.012206	0.005269
С	1.419285	0.450767	-0.005311
С	2.454886	-0.520918	0.001914
С	2.146984	-1.881723	0.017269
Н	0.593507	-3.399402	0.02461
С	-0.991224	0.95311	0.015987
С	1.682349	1.843187	-0.019844

3.50182

2.961438

0.634199

-0.701723

2.72522

0.846262

-1.518199

-1.585895

-1.940886

-2.401375

-3.005094

-2.85371

-2.637572

-0.187378

-2.621529

2.756936

2.319303

2.191188

3.836108

3.055518

-1.7793

-2.818264

0.488933

0.954628

0.76753

-0.91835

<u>References:</u>		
1	0.	

-0.415398

0

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0

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 $^{13}\text{C}$  NMR (100 MHz, CDCl\_3) spectrum of compound  $\boldsymbol{1}$ 





 $^{13}C$  NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound  ${\bf 2}$ 





 $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound  ${\bf 3}$ 







 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound 6





 $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound  $\boldsymbol{7}$ 









 $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound  $\boldsymbol{9}$ 







 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound 10



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **12** 



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 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound 12





 $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 14





 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound 15





<sup>1</sup>H-<sup>1</sup>H COSY NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound **15** 

 $^1\mathrm{H}\text{-}^1\mathrm{H}$  NOESY NMR (500 MHz, CDCl\_3) spectrum of compound  $\mathbf{15}$ 





<sup>1</sup>H-<sup>13</sup>C HSQC NMR (500 MHz/125 MHz, CDCl<sub>3</sub>) spectrum of compound **15** 



 $^1\text{H-}{^{13}\text{C}}$  HMBC NMR(500 MHz/125 MHz, CDCl\_3) spectrum of compound 15















<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **S2** 





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