Synthesis of Symmetrical Polynitrohelicenes and Their Chiral Recognition in the Charge Transfer Complexation

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Received September 27, 2000

Derivatives of optically active 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid can be nitrated regioselectively, giving symmetrically polyfunctionalized helicenes. The dicarboxylic acid or its dimethyl ester is dinitrated with fuming nitric acid in acetic acid at the 4,9-positions. When the reaction is conducted in fuming nitric acid, a 2,4,9,11-tetranitrohelicene is obtained. Analogously, 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dinitrile gives 2,11-dinitro- or 4,9-dinitrohelicene depending on the conditions, and the former compound is converted to a 2,4,9,11-tetranitrohelicene. The tetranitrohelicenes form charge-transfer (CT) complexes with an electron-rich chiral diaminohelicene in solution. The studies on the chiral recognition reveal that the combinations of the same configuration of the helicenes form more stable complexes than that of the enantiomeric helicenes.

We previously developed a multigram synthesis of an optically pure helicene, 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid (**1**).[1] Its derivatives regarding the 5,8-substituents were synthesized,[1,2] and their properties were studied, which include the chiral recognition in the complexation with cyclodextrins,[3] chiral LB film formation,[4] and chiral catalysis.[1] It was therefore considered interesting to prepare functionalized derivatives of **1** at other positions of the polycyclic aromatic rings.[5] Described here is the regioselective nitration of **1** at the symmetrical positions (Figure 1). In general, selective functionalization of polycyclic aromatic compounds is not facile. It is especially problematic, if one tries to introduce functional groups simultaneously at two positions.[6] The present work therefore presents an interesting example of the selective aromatic polyfunctionalization. The chiral recognition in the charge-transfer (CT) complexation of the electron-deficient helicenes is also described.[5]

When the dimethyl ester (*P*)-**2** is treated with fuming nitric acid in acetic acid for 10 min at 0 °C, a 4,9-dinitrohelicene (*P*)-**9** is obtained as the major product in 74% yield, which is accompanied by a 2,9-dinitro compound (*P*)-**13** (18%) (Scheme 1). The structure of (*P*)-**9** is determined by the presence of NOE between 1-methyl protons and one of the aromatic doublet protons. The ester (*P*)-**9** is converted to the dicarboxylic acid (*P*)-**8**

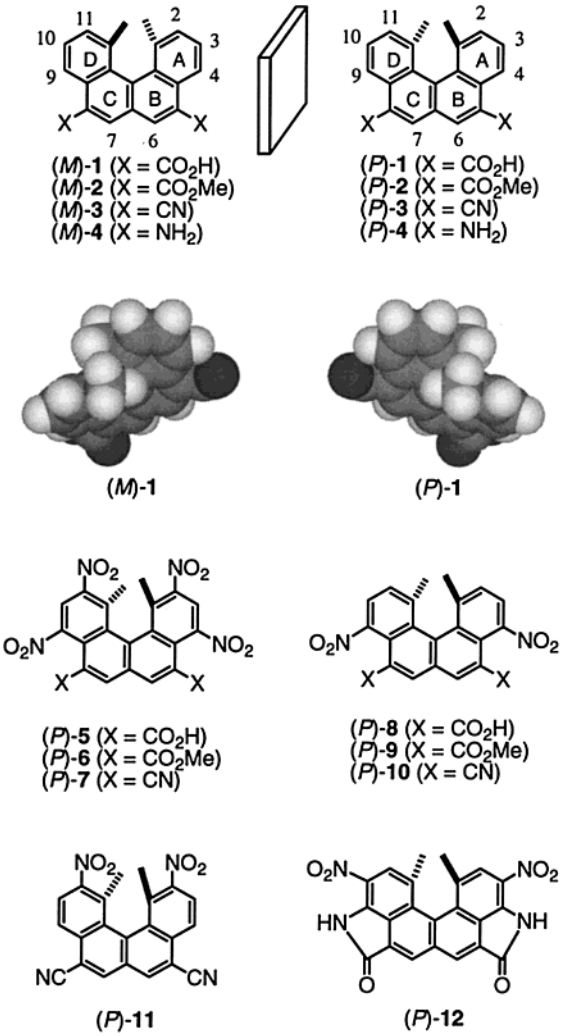

Figure 1. Symmetrically polynitrated helicenes.

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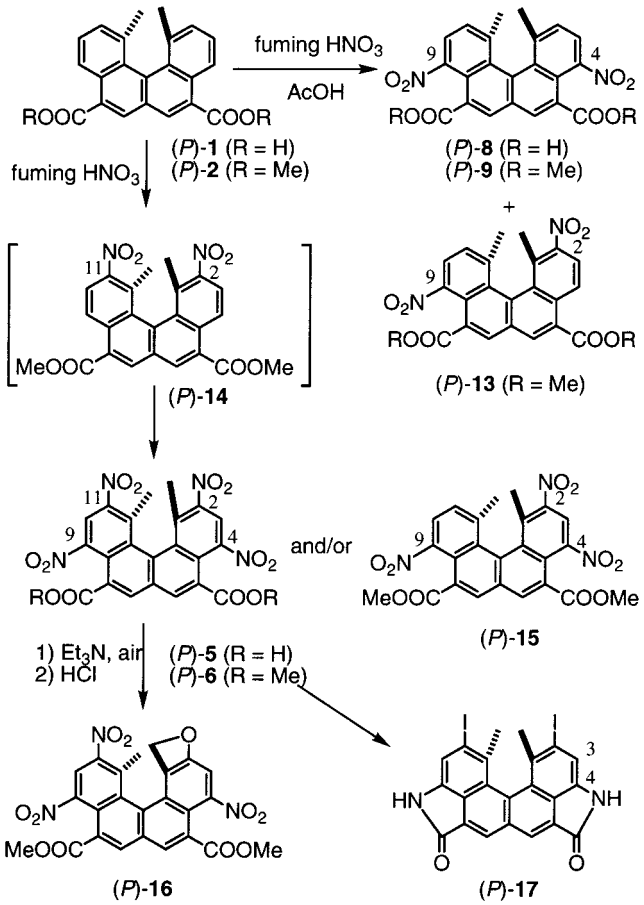
10.1021/jo001419a CCC: $20.00
Published on Web 12/21/2000

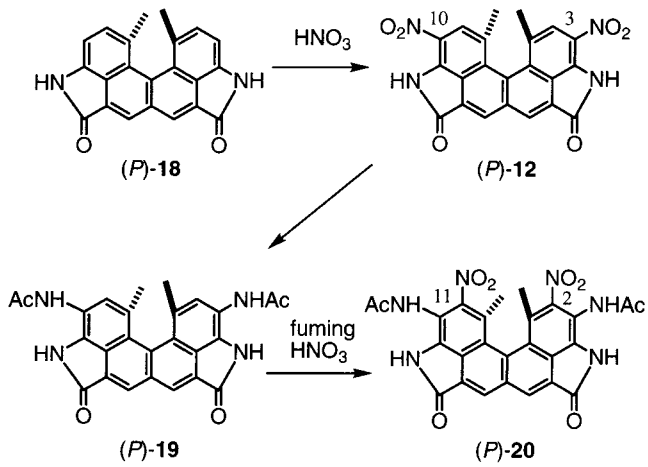
Scheme 1



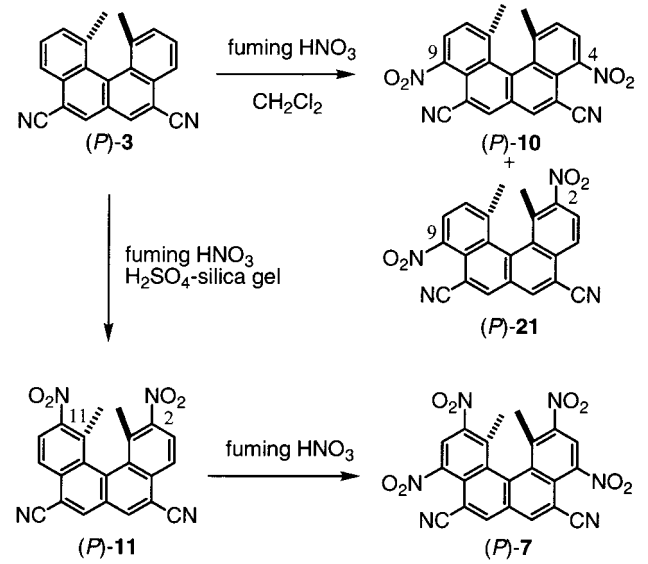
under nucleophilic conditions. Alternatively, (*P*)-**8** is obtained as the major product by the nitration of diacid (*P*)-**1**. When nitration of the diester (*P*)-**2** is conducted in fuming nitric acid at −45 °C for 30 min, a 2,4,9,11-tetranitrohelicene (*P*)-**6** (50%) and a trinitrohelicene (*P*)-**15** (25%), presumably a 2,4,9-isomer, are obtained. It is likely that (*P*)-**6** is formed via a 2,11-dinitrohelicene (*P*)-**14**, since attempted nitration of (*P*)-**9** results in the decomposition. Similarly the nitration of the diacid (*P*)-**1** gives the tetranitro acid (*P*)-**5** in 73% yield. The structure of (*P*)-**6** is confirmed by converting to lactam iodide (*P*)-**17** via reduction and iodination, which exhibits NOE between 3-H and NH. The facile lactamization under the mild acid conditions (2 M HCl, room temperature, 5 min) after the reduction may be due to the proximity effect. The different selectivity in the reaction of (*P*)-**1**/**2** giving either 2,4,9,11-tetranitrohelicene (*P*)-**5**/**6** or 4,9-dinitrohelicene (*P*)-**8**/**9** is ascribed to the solvent effect; reaction in fuming nitric acid gives the former, and in an organic solvent the latter, although the reason is not clear at present. The electron-deficient (*P*)-**6** turned out to be sensitive to bases in the presence of oxygen. When (*P*)-**6** is treated with triethylamine in chloroform at room temperature, a purple solution is formed. Addition of aqueous HCl then fades the color giving an optically active oxetene (*P*)-**16**. The ^{1}H NMR spectrum of (*P*)-**16** exhibits geminal diastereomeric protons, indicating that the methyl group is oxidized.

When the 4,9-dinitrohelicene (*P*)-**9** is reduced with ammonium formate in the presence of Pd/C[7] followed by an acid treatment, another bislactam (*P*)-**18** is obtained in 81% yield (Scheme 2). Next nitration of (*P*)-**18** in concentrated nitric acid at room temperature for 12 h gives a 3,10-dinitrohelicene (*P*)-**12** in 78% yield. After reduction and acetylation, the subsequent nitration of the acetamide (*P*)-**19** gives a 2,11-dinitrohelicene (*P*)-**20** (78%).

Scheme 2



Scheme 3



Dinitrile **3** obtained from **1** shows the similar regioselectivity with **2** in the nitration (Scheme 3). The 4,9-dinitration of (*P*)-**3** takes place by the reaction with fuming nitric acid in dichloromethane at room temperature for 5 min giving (*P*)-**10** in 42% yield, which is accompanied by a 2,9-dinitro derivative (*P*)-**21** (42%). In contrast, when (*P*)-**3** is nitrated in fuming nitric acid at −40 °C, a 2,11-dinitrated (*P*)-**11** is obtained. The yield of (*P*)-**11** can be increased to 50%, when sulfuric acid on silica gel[8] is used for the catalyst. Nitration of (*P*)-**11** with fuming nitric acid under forcing reaction conditions (room temperature, 6 h) gives a 2,4,9,11-tetranitrohelicene (*P*)-**7** in 80% yield, the structure of which is confirmed by X-ray analysis.[5] CT complexation analysis of (*P*)-**7** (vide infra) indicates that no racemization takes place during the nitration. It is noticed that (*P*)-**10** is not converted to (*P*)-**7**

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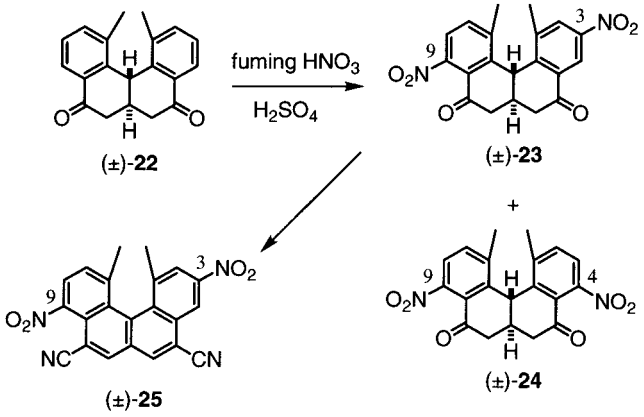
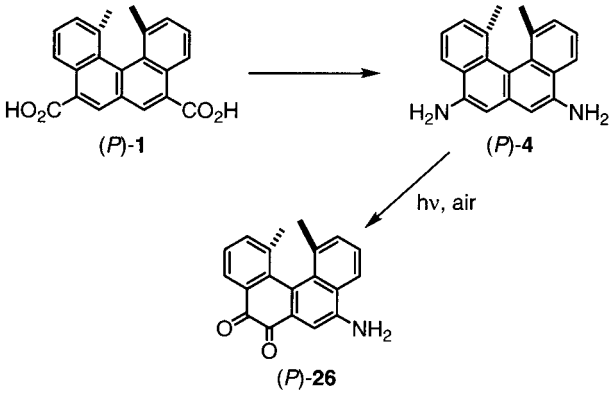
Scheme 4



Scheme 5



under forcing reaction conditions, and only the decomposition occurs. These experiments are consistent with the above discussions that (*P*)-**6** is formed via (*P*)-**14**. Nitration of (*P*)-**3** in fuming nitric acid gives (*P*)-**11**, while that of (*P*)-**2** gives (*P*)-**6**. It may be due to the reactivity of the aromatic ring system: Nitrile group is a stronger electron-withdrawing group than alkoxycarbonyl group.[9] These syntheses provide optically active helicenes with symmetrical substituents at A and D rings. Taking into advantage of the two carboxylate groups, helicene **1** can be functionalized selectively giving polyfunctionalized derivatives of C_2-symmetry.

A diketone (±)-**22**, which is an intermediate in the synthesis of **1**,[1] is also nitrated (Scheme 4). When (±)-**22** is treated with fuming nitric acid in the presence of sulfuric acid at 0 °C for 10 min, a 3,9-dinitro product (±)-**23** is obtained in 61% yield with a 4,9-derivative (±)-**24** as the minor product (38%). Reaction of (±)-**23** with trimethylsilyl cyanide in the presence of zinc iodide followed by dehydration with $POCl_3$[1] gives a 3,9-dinitrohelicene (±)-**25**. Analogously, (±)-**24** is converted to (±)-**10**.

Using the optically active polynitrohelicenes, we previously studied the CT complexation with pyrene.[5] Examined here is the chiral recognition in the CT complex formation. Chiral recognition between a helicene and a helicene has not been studied before, although that between a helicene and a compound with central chirality on the side chain has been studied in relation to the development of chiral HPLC.[10,11] The lack of the former study may be partially due to unavailability of the electron-deficient helicene. The tetranitrohelicenes **6** or **7** and an electron-rich 5,9-diaminohelicene **4** are employed here for the CT-acceptor and CT-donor, respectively.

The diaminohelicene (*P*)-**4** is prepared from (*P*)-**1** in two steps including the Curtius rearrangement. Diacid (*P*)-**1** is treated with diphenylphosphoryl azide[12] and ethyldiisopropylamine in refluxing toluene followed by benzyl alcohol giving bis(benzyloxycarbonyl) derivative in 85% yield (Scheme 5). Debenzylation by hydrogenolysis converts the carbamate to (*P*)-**4** in 88% yield. It turned out that (*P*)-**4** was readily photooxidized in the presence of oxygen. Irradiation of (*P*)-**4** with UV light at 300 nm in ethyl acetate under air at room temperature gives blue-colored quinone (*P*)-**26**, which decomposes on further irradiation. The diamine (*P*)-**4** therefore is stored under nitrogen in the dark.

The CT absorption band appears at 500−800 nm, when **4** is mixed either with **6** or **7** in THF (Figure 2a and 2b). The complexation of **4** and **7** is examined by ^{1}H NMR spectroscopy as well. ^{1}H NMR signals of (±)-**7** due to methyl and 6-proton shift high field and separates on addition of (*M*)-**4** in THF-d_8, which clearly shows the chiral recognition by the CT complexation (Figure 2c−f). In contrast, the shift of 3-proton is very small. The observations are consistent with the face-to-face structure of the complex. The binding constants are obtained as follows. The spectra of 2.9 mM solution of (±)-**7** in THF-d_8 are measured as a function of the concentration of (*M*)-**4** at 24 °C. The curve fitting of the data for 6-proton of NMR titration using nonlinear least-squares method[13] provides the binding constants (*K*) for the complexation (Figure 2g); complex of (*M*)-**4** and (*M*)-**7**, 12.2 ± 1.2 M^{-1}; complex of (*M*)-**4** and (*P*)-**7**, 10.2 ± 1.2 M^{-1}. The *K* values are in the range of those of known achiral CT complexes.[14] Notably, the same configuration of the helicenes form the more stable CT complexes than that of the enantiomeric helicenes. This is the first such observation in the chiral recognition of helicene, and to probe the generality of the stereochemical preference may be an interesting subject in future.

To summarize, helicene **1** and its derivatives are nitrated selectively at the symmetrical positions. The resulted tetranitrohelicene **7** form more stable CT-complex with **4**, when they have the same absolute configurations.

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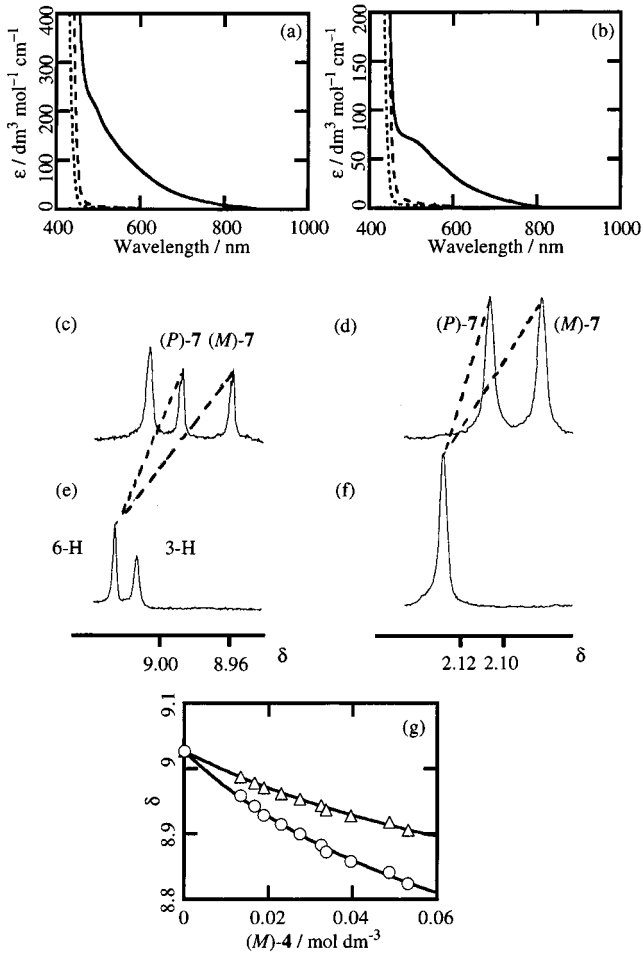

Figure 2. CT complexation of **4** with **6** or **7**. (a) UV−vis spectra of (*M*)-**4** (5.0 mM) (- - -), (*M*)-**7** (5.0 mM) (·····), and a mixture of (*M*)-**4** (5.0 mM) and (*M*)-**7** (5.0 mM) (—) in THF at 24 °C. (b) UV−vis spectra of (*P*)-**4** (0.1 M) (- - -), (*P*)-**6** (0.1 M) (·····), and a mixture of (*P*)-**4** (0.1 M) and (*P*)-**6** (0.1 M) (—) in THF at 25 °C. (c and d) ^{1}H NMR (THF-d_8, 24 °C) spectra of 2.9 mM (±)-**7** in the presence of 13 mM (*M*)-**4**. (e and f) ^{1}H NMR (THF-d_8, 24 °C) spectra of 2.9 mM (±)-**7**. (g) Shifts in the NMR signals due to 6-*H* of 3.0 mM (*P*)-**7** (△) and (*M*)-**7** (○) in THR-d_8 upon addition of (*M*)-**4** at 24 °C. The lines are the nonlinear fit of the data for the 1:1 binding model.

Experimental Section

Dimethyl (*P*)-1,12-Dimethyl-4,9-dinitrobenzo[*c*]phenanthrene-5,8-dicarboxylate (*P*)-9. To a suspension of (*P*)-**2** (6.9 g, 18 mmol) in acetic acid (70 mL) was added fuming nitric acid (70 mL) at 0 °C. After stirred at the temperature for 10 min, the reaction was quenched by adding ice−water. The resulted powder was collected by Buchner funnel and washed with water and aqueous sodium bicarbonate. The residue was dissolved in ethyl acetate, and the solution was washed with water and brine. After dried over sodium sulfate, the solution was filtered and concentrated. Silica gel column chromatography gave (*P*)-**9** (6.2 g, 13 mmol, 74%) and its 2,9-isomer (*P*)-**13** (1.5 g, 3.2 mmol, 18%). (*P*)-**9**: Mp 164−166 °C (AcOEt). $[\alpha]^{26}_D$ −94 (*c* 1.4, $CHCl_3$). MS (EI) *m*/*z* 462 (M^+, 13%), 416 ($M^+ - NO_2$ 100%). HRMS (EI, 70 eV) Calcd for $C_{24}H_{18}N_2O_4$: 462.1063. Found: 462.1076. IR (CH_2Cl_2) 1726, 1528, 1349 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (6H, br), 3.95 (6H, s), 7.61 (2H, dd, J = 8.0, 0.4 Hz), 8.27 (2H, d, J = 8.0 Hz), 8.16 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 52.6, 121.9, 124.6, 128.1, 128.3, 128.4, 130.2, 131.0, 132.3, 142.4, 145.8, 166.6. (*P*)-**13**: Mp 136−138 °C (AcOEt-hexane). $[\alpha]^{26}_D$ +272 (*c* 1.4, $CHCl_3$). MS (EI) *m*/*z* 462 (M^+, 23%), 416 ($M^+ - NO_2$ 100%). HRMS (EI, 70 eV) Calcd for $C_{24}H_{18}N_2O_4$: 462.1063. Found: 462.1058. IR (KBr) 1719, 1525, 1346 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (3H, s), 2.05 (3H, s), 3.96 (3H, s), 4.12 (3H, s), 7.63 (1H, d, J = 8 Hz), 8.18 (1H, d, J = 9 Hz), 8.27 (1H, d, J = 8 Hz), 8.54 (1H, s), 8.72 (1H, s), 9.12 (1H, J = 9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 24.2, 52.5, 53.0, 121.8, 123.0, 124.8, 125.2, 127.8, 128.0, 129.0, 129.4, 130.5, 130.8, 131.4, 132.0, 132.1, 132.2, 132.6, 142.4, 145.8, 150.2, 166.1, 166.6.

(*P*)-1,12-Dimethyl-4,9-dinitrobenzo[*c*]phenanthrene-5,8-dicarboxylic Acid (*P*)-8 by Hydrolysis of (*P*)-9. Under an argon atmosphere, a mixture of (*P*)-**9** (120 mg, 0.27 mmol), lithium iodide (710 mg, 5.3 mmol), and pyridine (8 mL) was heated at reflux for 18 h. After being cooled to room temperature, the reaction was quenched by addition of aqueous saturated potassium hydrogen sulfate, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water and brine and dried over sodium sulfate. After removing the solvent in vacuo, the resulting solid was recrystallized from AcOEt−toluene giving (*P*)-**8** (110 mg, 0.25 mmol, 94%). **Nitration of (*P*)-1.** To a suspension of (*P*)-**1** (250 mg, 0.74 mmol) in acetic acid (3 mL) was added fuming nitric acid (3 mL) at 0 °C. After stirred at the temperature for 10 min, the reaction was quenched by adding ice−water. The resulting powder was collected by Buchner funnel and washed with cold water giving the crude product (380 mg, quant), which contains (*P*)-**8** and its 2,9-dinitro isomer in a ratio of 7:3. Recrystallization from toluene-AcOEt (four times) gave pure (*P*)-**8** (100 mg, 0.23 mmol, 32%). Mp 270 °C dec (AcOEt−toluene). $[\alpha]^{26}_D$ −130 (*c* 0.9, acetone). LRMS (EI, 70 eV) *m*/*z* 434 (M^+, 7%), 388 ($M^+ - NO_2$, 100). HRMS (EI, 70 eV) Calcd for $C_{22}H_{14}N_2O_8$: 434.0750. Found: 434.0753. IR (KBr) 3600−2600, 1710, 1528, 1349 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6) δ 2.02 (6H, s), 7.75 (2H, d, J = 8 Hz), 8.33 (2H, d, J = 8 Hz), 8.77 (2H, s). ^{13}C NMR (100 MHz, acetone-d_6) δ 24.2, 122.7, 125.3, 125.6, 126.6, 131.5, 131.6, 131.8, 133.3, 143.5, 147.0, 167.6. The formation of the 2,9-dinitro isomer was confirmed by the treatment of the crude product with diazomethane, giving (*P*)-**9** and (*P*)-**12**.

Dimethyl (*P*)-1,12-Dimethyl-2,4,9,11-tetranitrobenzo-[*c*]phenanthrene-5,8-dicarboxylate (*P*)-6. Diester (*P*)-**2** (110 mg, 0.28 mmol) was added to fuming nitric acid (5 mL) at −45 °C. The mixture was stirred at the temperature for 30 min, during which the powder of (*P*)-**2** slowly dissolved. Then the reaction mixture was poured into ice−water, and the resulting powder was collected by Buchner funnel. The crude product was dissolved in ethyl acetate, and the solution was washed with saturated sodium bicarbonate, water, and brine. After being dried over magnesium sulfate, the solvent was removed in vacuo, and silica gel column chromatography gave (*P*)-**6** (83 mg, 0.14 mmol, 50%) and (*P*)-**15** (32 mg, 0.070 mmol, 25%). (*P*)-**6**: Mp 258−259 °C (AcOEt). $[\alpha]^{28}_D$ +296 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{16}N_4O_{12}$: C; 52.18, H; 2.92, N; 10.14%. Found: C; 52.40, H; 2.93, N; 10.05%. MS (EI, 70 eV) *m*/*z* 552 (M^+, 6%), 521 (M^+ − OMe, 5), 506 ($M^+ - NO_2$, 100). HRMS (EI, 70 eV) Calcd for $C_{24}H_{16}N_4O_{12}$: 552.0765. Found: 552.0771. IR ($CHCl_3$) 1733, 1541, 1352 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (6H, s), 4.00 (6H, s), 8.70 (2H, s), 8.82 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 53.0, 120.4, 123.3, 127.9, 129.3, 132.2, 133.4, 134.0, 136.2, 146.1, 148.6, 165.3. (*P*)-**15**: Mp 164−165 °C (ether). $[\alpha]^{28}_D$ −285 (*c* 1.4, $CHCl_3$). IR ($CHCl_3$) 1741, 1680, 1569, 1539, 1351 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (3H, s), 2.00 (3H, s), 3.87 (3H, s), 3.93 (3H, s), 7.17 (1H, s), 7.69 (1H, d, J = 8 Hz), 8.25 (1H, d, J = 8 Hz), 8.29 (1H, s), 8.63 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 22.3, 53.0, 54.7, 91.2, 120.7, 121.4, 125.1, 126.3, 129.9, 130.9, 131.6, 134.2, 134.5, 135.6, 136.1, 136.7, 142.7, 146.5, 148.5, 148.6, 161.5, 165.1.

(*P*)-1,12-Dimethyl-2,11-diiodo-5,4:8,9-benzo[*c*]phenanthrenebiscarbolactam (*P*)-17. Under a hydrogen atmosphere, a mixture of (*P*)-**6** (22 mg, 0.040 mmol) and palladium on carbon (20 mg) in tetrahydrofuran (2 mL) and methanol (2 mL) was vigorously stirred at room temperature for 1 h. The reaction mixture was filtered and concentrated. The residue was diluted with methanol, to which 2 M HCl was added, and the mixture was stirred for 5 min. Removal of the solvents gave crude bislactam (20 mg), which was dissolved in concd

HCl (3 mL). Then 10 M $NaNO_2$ (69 mg, 1.0 mmol) in water (0.1 mL) was added at 0 °C. After 5 min, this solution was transferred to saturated aqueous potassium iodide (5 mL) at 0 °C, and the mixture was stirred for another 5 min at the temperature. The reaction was quenched by adding water, and the organic materials were extracted with ethyl acetate twice. The combined organic layers were successively washed with 10% sodium sulfite, water, and brine and dried over magnesium sulfate. After the solvents were removed in vacuo, silica gel chromatography gave (*P*)-**17** (7.3 mg, 0.012 mmol, 31% for two steps). Mp 230 °C dec (toluene−methanol). $[\alpha]^{26}_D$ −450 (*c* 0.1, acetone). LRMS (EI, 70 eV) *m*/*z* 591 ($M^+ + 1$, 29%), 590 (M^+, 100), 464 ($M^+ - I+1$, 20), 321 ($M^+ - 2I$-Me, 81), 128 (HI, 74), 127 (I, 39). HRMS (EI, 70 eV) Calcd for $C_{22}H_{12}I_2N_2O_2$: 589.8988. Found: 589.8984. IR (KBr) 3500−3200, 1699 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 2.33 (6H, s), 7.59 (2H, s), 8.80 (2H, s), 10.93 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 23.5, 104.4, 118.4, 125.3, 127.2, 127.5, 128.0, 130.7, 131.9, 136.7, 136.9, 167.4.

(*P*)-1,12-Dimethyl-2,4,9,11-tetranitrobenzo[*c*]phenanthrene-5,8-dicarboxylic Acid (*P*)-5. Diacid (*P*)-**1** (100 mg, 0.29 mmol) was added to fuming nitric acid (3 mL) at −45 °C. After being stirred at the temperature for 1 h, the reaction was quenched by adding ice−water. The resulted powder was collected by Buchner funnel and washed with cold water. Recrystallization from ethyl acetate−hexane gave (*P*)-**5** (110 mg, 0.21 mmol, 73%). Mp 230 °C dec (AcOEt−hexane). Anal. Calcd for $C_{22}H_{12}N_4O_{12}$: C; 50.39, H; 2.31, N; 10.69%. Found: C; 50.45, H; 2.38, N; 10.49%. $[\alpha]_D^{26}$ +162 (*c* 0.45, H_2O). IR (KBr) 3600−2600, 1538, 1352 cm^{-1}. ^1H NMR (400 MHz, D_2O) δ 2.16 (6H, s), 8.54 (2H, s), 8.92 (2H, s). ^{13}C NMR (100 MHz, D_2O) δ 24.2, 122.6, 125.8, 128.3, 134.0, 135.9, 136.8, 137.5, 140.0, 148.4, 150.1, 175.6.

Dimethyl (*P*)-1,12-Dimethyl-2,4,9,11-tetranitrobenzo[*c*]phenanthrene-5,8-dicarboxylate oxetene (*P*)-16. To a solution of (*P*)-**6** (20 mg, 0.036 mmol) in chloroform (3 mL) was added triethylamine (0.010 mL, 0.070 mmol) at room temperature. After being stirred at the temperature for 10 min, the reaction was quenched by adding 2 M HCl, and the mixture was vigorously stirred for 1 h. The organic materials were extracted with ethyl acetate twice. The combined organic layers were washed with water and brine and dried over magnesium sulfate. After removing the solvent in vacuo, silica gel column chromatography gave (*P*)-**16** (8.0 mg, 0.15 mmol, 43%). Mp 200 °C dec (toluene). Anal. Calcd for $C_{24}H_{15}N_3O_{11}$: C; 55.29, H; 2.90, N; 8.06%. Found: C; 55.49, H; 2.95, N; 7.77%. $[\alpha]^{24}_D$ +150 (*c* 0.2, $CHCl_3$). MS (EI, 70 eV) *m*/*z* 522 ($M^+ + 1$, 11%), 521 (M^+, 33%), 491 ($M^+ - OMe$, 17%), 475 ($M^+ - NO_2$, 78%), 447 ($M^+ - NO_2 - CO$, 100%). HRMS (EI, 70 eV) Calcd for $C_{24}H_{16}N_4O_{12}$: 521.0707. Found: 521.0703. IR ($CHCl_3$) 1722, 1539, 1351 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (3H, s), 3.40 (1H, d, J = 18 Hz), 3.94 (3H, s), 3.97 (3H, s), 4.35 (1H, d, J = 18 Hz), 7.15 (1H, s), 8.61 (1H, s), 8.68 (1H, s), 8.81 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 47.7, 52.9, 53.0, 120.0, 120.8, 120.9, 121.5, 123.3, 127.0, 128.7, 129.6, 130.3, 130.5, 131.8, 133.2, 134.1, 135.5, 140.3, 146.5, 146.6, 157.7, 165.5, 165.6.

(*P*)-1,12-Dimethyl-5,4:8,9-benzo[*c*]phenanthrenebiscarbolactam (*P*)-18. To a mixture of (*P*)-**9** (4.3 g, 9.4 mmol) and palladium on carbon (8.3 g) in THF (320 mL) was added a solution of ammonium formate (8.4 g, 0.13 mol) in methanol (260 mL). After stirred at room temperature for 15 min, the reaction mixture was filtered, and concentrated. The residue was diluted with methanol (100 mL), to which 2 M HCl (30 mL) was added. After being stirred for 5 min, the solvents were evaporated in vacuo, and silica gel column chromatography gave (*P*)-**18** (2.6 g, 7.6 mmol, 81%). Mp 240 °C dec (AcOEt−hexane). $[\alpha]^{27}_D$ +385 (*c* 0.3, $CHCl_3$). MS (EI, 70 eV) *m*/*z* 338 (M^+, 100%), 323 ($M^+ - Me$, 29), 295 ($M^+ - CONH$, 47). HRMS (EI, 70 eV) Calcd for $C_{22}H_{14}N_2O_2$: 338.1055. Found: 338.1053. IR (KBr) 1698 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 2.35 (6H, brs), 7.12 (6H, dd, J = 1, 7 Hz), 7.43 (2H, d, J = 7 Hz), 8.79 (2H, s), 10.87 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.4, 108.4, 125.1, 127.1, 127.2, 128.6, 130.6, 131.8, 135.4, 135.8, 167.6.

(*P*)-1,12-Dimethyl-3,10-dinitro-5,4:8,9-benzo[*c*]phenanthrenebiscarbolactam (*P*)-12. Bislactam (*P*)-**18** (980 mg, 2.9 mmol) was added to nitric acid (50 mL) at 0 °C. After stirred at room temperature for 12 h, the reaction was quenched by adding ice−water. The resulted powder was collected by Buchner funnel and washed with water and ethyl acetate, giving (*P*)-**12** (970 mg, 2.3 mmol, 78%). Because of the low solubility of (*P*)-**12**, attempts for recrystallization failed. Mp 260 °C dec, $[\alpha]^{25}_D$ −680 (*c* 0.2, DMF). FABMS (NBA) *m*/*z* 428 (M^+). IR (KBr) 3500−3200, 1736, 1524, 1337 cm^{-1}. ^1H NMR (400 MHz, CD_3NO_2) δ 2.53 (6H, d, J = 1 Hz), 8.15 (2H, d, J = 1 Hz), 8.82 (2H, s), 9.56 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.1, 122.8, 126.8, 127.3, 127.7, 128.1, 129.8, 130.5, 130.9, 133.6, 138.4, 167.2.

(*P*)-3,10-Diamino-1,12-dimethyl-5,4:8,9-benzo[*c*]phenanthrenebiscarbolactam. Under a hydrogen atmosphere, a mixture of (*P*)-**12** (20 mg, 0.047 mmol) and palladium on carbon (80 mg) in tetrahydrofuran (4 mL) and methanol (2 mL) was vigorously stirred at room temperature for 1.5 h. Then, the mixture was filtered and concentrated. Silica gel (neutral) chromatography gave the (*P*)-diamine (10 mg, 27 mmol, 58%). Mp 275 °C dec (toluene−methanol). $[\alpha]^{28}_D$ +400 (*c* 0.5, MeOH). FABMS (NBA) *m*/*z* 368 (M^+). IR (KBr) 3500−3200, 1674 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 2.32 (6H, s), 5.70 (4H, s), 6.85 (2H, s), 8.58 (2H, s), 10.16 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.2, 115.1, 119.5, 120.9, 124.1, 126.1, 128.0, 130.0, 131.8, 132.4, 132.9, 166.6.

(*P*)-3,10-Bis(acetamido)-1,12-dimethyl-5,4:8,9-benzo[*c*]-phenanthrenebiscarbolactam (*P*)-19. Under an argon atmosphere, to a solution of the above (*P*)-diamine (27 mg, 0.074 mmol) in *N*-methylpyrrolidone (0.5 mL) and THF (4 mL) was added excess acetyl chloride (0.1 mL, 1.4 mmol) at −78 °C. After being stirred for 1 h at the temperature, the reaction was quenched by adding water. The resulted amorphous solid was collected on Buchner funnel and diluted with ethyl acetate. The solution was washed with water and brine and dried over magnesium sulfate. After removing the solvent in vacuo, silica gel column chromatography gave (*P*)-**19** (31 mg, 0.067 mmol, 91%). Mp 250 °C dec (toluene−methanol). $[\alpha]^{26}_D$ −520 (*c* 0.2, THF). FABMS (NBA) *m*/*z* 453 (M^+). IR ($CHCl_3$) 3600−3200, 1703 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 2.16 (6H, s), 2.37 (6H, brs), 7.56 (2H, brs), 8.80 (2H, s), 10.11 (2H, s), 10.14 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.4, 23.7, 120.2, 124.1, 124.4, 124.7, 126.1, 126.2, 127.9, 130.9, 131.7, 133.6, 166.3, 168.3.

(*P*)-3,10-Bis(acetamido)-1,12-dimethyl-2,11-dinitro-5,4:8,9-benzo[*c*]phenanthrenebiscarbolactam (*P*)-20. Diamide (*P*)-**19** (3.0 mg, 0.0064 mmol) was added to fuming nitric acid (0.5 mL) at −45 °C. After being stirred at the temperature for 3 min, the reaction was quenched by adding ice−water and saturated aqueous sodium bicarbonate. The organic materials were extracted with ethyl acetate three times. The combined organic layers were washed with water and brine and dried over magnesium sulfate. After removing the solvent in vacuo, silica gel column chromatography gave (*P*)-**20** (2.2 mg, 5.0 mmol, 78%). Mp 250 °C dec (toluene−methanol). $[\alpha]^{27}_D$ +53 (*c* 0.08, THF). FABMS (NBA) *m*/*z* 543 ($M^+ + 1$). IR (KBr) 1719, 1539, 1383 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 2.07 (6H, s), 2.30 (6H, s), 9.05 (2H, s), 9.98 (2H, s), 11.28 (2H, s). ^{13}C NMR (100 MHz, CD_3OD-$CDCl_3$) δ 16.7, 22.8, 112.2, 124.4, 125.8, 126.9, 127.6, 130.8, 132.9, 132.9, 137.1, 150.3, 168.1, 171.5.

(*P*)-1,12-Dimethylbenzo[*c*]phenanthrene-5,8-dicarbamide. Under an argon atmosphere, a mixture of (*P*)-**1** (570 mg, 1.7 mmol) and thionyl chloride (5.0 mL) was heated at reflux for 7 h. Then excess thionyl chloride was removed under reduced pressure, and the residue was azeotropically dried by evaporating with toluene (3 mL) twice. The crude acid chloride was dissolved in toluene (5 mL) and transferred to the mixture of toluene (5 mL) and liq NH_3 (ca 5 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. After solvents were evaporated, the resulting solid was washed with water. Silica gel chromatography gave the title compound (540 mg, 1.6 mmol, 95%). Mp 250 °C dec (toluene). $[\alpha]^{18}_D$ +158 (*c* 0.10, DMF). MS *m*/*z* 342 (M^+, 100%), 310 (M^+ −

N_2H_4, 26). HRMS (EI, 70 eV) Calcd for $C_{22}H_{18}N_2O_2$: 342.1368. Found: 342.1357. IR (KBr) 3328, 3177, 1654, 1603, 1417 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 1.85 (6H, s), 7.50 (2H, d, J = 7 Hz), 7.67 (2H, t, J = 7 Hz), 7.76 (2H, br), 8.06 (2H, s), 8.21 (2H, br), 8.29 (2H, d, J = 8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 23.1, 123.1, 123.9, 126.1, 126.7, 128.6, 129.4, 129.7, 130.5, 134.5, 135.8, 170.2.

(*P*)-1,12-Dimethylbenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*P*)-3. Under an argon atmosphere, a mixture of the above amide (340 mg, 1.0 mmol) and thionyl chloride (5.0 mL) was heated at reflux for 3 h. Then the solvents were removed under reduced pressure, to which were added ethyl acetate and 10% aqueous potassium hydrogen carbonate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over magnesium sulfate, and filtered. The solvents were removed under reduced pressure, and silica gel chromatography gave (*P*)-**3** (270 mg, 0.87 mmol, 87%). Mp 137−138 °C (toluene). $[\alpha]^{24}_D$ −17 (*c* 0.10, THF). Spectra data agreed with the reported data for (±)-**3**.[1]

(*P*)-1,12-Dimethyl-2,11-dinitrobenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*P*)-11. Sulfuric acid on silica gel was prepared by the method of Riego.[8] Silica gel (20 g) was soaked for several minutes in sulfuric acid (40 mL). The silica gel was filtered, dried at room temperature using an aspirator for 5 h, and oven-dried at 130 °C for 24 h. The catalyst (4.0 g) was added to fuming nitric acid (20 mL) at −40 °C with occasional shaking of the flask. Then (*P*)-**3** (100 mg, 0.3 mmol) was added. The mixture was allowed to stand at the temperature with occasional shaking for 30 min. The reaction was quenched by addition of ice, and the resulting solid was collected by filtration. The crude product was washed successively with cold water, aqueous saturated sodium bicarbonate solution, and cold water. Silica gel chromatography gave (*P*)-**11**, (60 mg, 0.15 mmol, 50%). Mp 250 °C dec (toluene). $[\alpha]^{20}_D$ +320 (*c* 0.14, DMF). MS (EI, 70 eV) *m*/*z* 396 (M^+, 98%), 364 (66), 333 (100). HRMS (EI, 70 eV) Calcd for $C_{22}H_{12}N_4O_4$: 396.0858. Found: 396.0849. IR (KBr) 2225, 1532, 1509, 1343 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 1.95 (6H, s), 8.45 (2H, d, J = 9 Hz), 8.50 (2H, d, J = 9 Hz), 9.03 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.2, 110.5, 116.5, 124.6, 124.9, 130.3, 130.7, 131.0, 131.2, 131.9, 136.0, 151.1.

(*P*)-1,12-Dimethyl-2,4,9,11-tetranitrobenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*P*)-7. Dinitrile (*P*)-**11** (340 mg, 1.0 mmol) was added to fuming nitric acid (20 mL) at −40 °C with occasional shaking of the flask. The mixture was allowed to stand for 6 h at room temperature. Then the reaction was quenched by addition of ice, and the resulting solid was collected by filtration. The crude product was washed successively with cold water, aqueous saturated sodium bicarbonate solution, and cold water. Silica gel chromatography gave (*P*)-**7**, (388 mg, 0.8 mmol, 80%). Optical purity (99%ee) was determined by ^1H NMR (THF-d_8, 25 °C) analysis of the CT complex with (*P*)-**4**. For example, 6-H of (±)-**7** was observed at δ 8.96 and 8.92 in a mixture of 2.0 mM (±)-**7** and 20 mM (*P*)-**4**. Mp 250 °C dec (toluene). $[\alpha]^{20}_D$ −15 (*c* 0.10, THF). MS (EI, 70 eV) *m*/*z* 487 (M^+ + 1, 28%), 486 (M^+, 100), 454 (38), 423 (39). HRMS (EI, 70 eV) Calcd for $C_{22}H_{10}N_6O_8$: 486.0560. Found: 486.0562. IR (KBr) 2229, 1541, 1344 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 2.23 (6H, s), 9.04 (2H, s), 9.24 (2H, s). ^{13}C NMR (100 MHz, acetone-d_6) δ 21.8, 108.9, 114.9, 121.7, 123.9, 130.7, 132.1, 134.2, 136.9, 140.6, 146.3, 150.4.

(*P*)-1,12-Dimethyl-4,9-dinitrobenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*P*)-10. To a solution of dinitrile (*P*)-**3** (65 mg, 0.21 mmol) in dichloromethane (5.0 mL) was slowly added fuming nitric acid (1.0 mL) at room temperature with continuous shaking of the flask. Then, the mixture was allowed to stand with occasional shaking at the temperature for 5 min. The reaction was quenched by addition of ice, and the organic materials were extracted with dichloromethane twice. The combined organic layers was washed with water, aqueous saturated sodium bicarbonate solution, and dried over magnesium sulfate. The solvents were removed in vacuo, and silica gel chromatography gave (*P*)-**10** (35 mg, 0.089 mmol, 42%) and 2,9-dinitro isomer (*P*)-**21** (35 mg, 0.089 mmol, 42%). (*P*)-**10**: Mp 290 °C dec (CH_2Cl_2). $[\alpha]^{26}_D$ −30 (*c* 0.10, $CHCl_3$). MS *m*/*z* 396 (M^+, 74%), 364 (50), 333 (100). HRMS (EI, 70 eV) Calcd for $C_{22}H_{12}N_4O_4$: 396.0859. Found: 396.0861. IR (KBr) 2220, 1524, 1344 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 2.35 (6H, s), 7.88 (2H, d, J = 8 Hz), 8.38 (2H, d, J = 8 Hz), 8.93 (2H, s). ^{13}C NMR (100 MHz, Acetone-d_6) δ 23.8, 107.8, 115.7, 122.3, 125.7, 130.1, 120.5, 130.8, 132.3, 137.9, 143.5, 146.0. (*P*)-**21**: Mp 245 °C dec (toluene). $[\alpha]^{30}_D$ −134 (*c* 0.10, $CHCl_3$). MS *m*/*z* 396 (M^+, 90%), 364 (9), 333 (100). HRMS (EI, 70 eV) Calcd for $C_{22}H_{12}N_4O_4$: 396.0859. Found: 396.0842. IR (KBr) 2223, 1533, 1348 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 1.88 (3H, s), 1.96 (3H, s), 7.89 (1H, d, J = 8 Hz), 8.44−8.51 (3H, m), 9.02 (1H, s), 9.04 (1H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.0, 23.4, 105.8, 110.5, 115.4, 116.4, 120.7, 124.6, 124.9, 125.2, 130.0, 130.1, 130.5, 131.2, 131.5, 132.1, 135.7, 138.0, 142.1, 144.6, 150.8.

(±)-5,6,6a,7,8,12b-Hexahydro-1,12-dimethyl-3,9-dinitrobenzo[*c*]phenanthrene-5,8-dione, (±)-23. To a mixture of fuming nitric acid (0.5 mL) and sulfuric acid (1.5 mL) was added diketone (±)-**22**[1] (300 mg, 1.0 mmol) at −20 °C with occasional shaking of the flask. The mixture was allowed to stand for 5 min at the temperature. Then the reaction was quenched by adding ice, and the resulting solid was collected by filtration. The crude product was washed successively with cold water, aqueous saturated sodium bicarbonate, and cold water. Silica gel chromatography gave (±)-**23** (230 mg, 0.61 mmol, 61%) and its 4,9-isomer (±)-**24** (140 mg, 0.38 mmol, 38%). (±)-**23**: Mp 230 °C dec (toluene). MS (EI, 70 eV) *m*/*z* 380 (M^+, 27%), 365 (M^+ − Me, 100). HRMS (EI, 70 eV) Calcd for $C_{20}H_{16}N_2O_6$: 380.1008. Found: 380.1016. IR (KBr) 1700, 1528, 1346 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.70 (3H, s), 2.17 (3H, s), 2.70−2.90 (4H, m), 3.00−3.10 (1H, m), 4.40 (1H, br), 7.47−7.56 (2H, m), 8.07 (1H, br), 8.55 (1H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.9, 37.3, 44.0, 46.1, 47.2, 121.2, 122.9, 125.5, 128.5, 129.3, 130.7, 134.9, 136.0, 137.3, 140.1, 143.2, 147.8, 194.1, 195.0. (±)-**24**: Mp 190 °C dec (toluene). MS (EI, 70 eV) *m*/*z* 380 (M^+, 100%), 365 (M^+ − Me, 25%). HRMS (EI, 70 eV) Calcd for $C_{20}H_{16}N_2O_6$: 380.1008. Found: 380.0993. IR (KBr) 1704, 1535, 1368 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.64 (3H, s), 2.18 (3H, s), 2.70−2.95 (4H, m), 3.20 (1H, dd, J = 6, 9 Hz), 4.15 (1H, d, J = 9 Hz), 7.28 (1H, d, J = 9 Hz), 7.47−7.52 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 21.5, 36.3, 43.5, 45.7, 46.4, 121.6, 122.5, 127.6, 129.2, 134.4, 135.7, 137.6, 139.7, 141.7, 142.9, 146.4, 147.2, 193.9, 194.6.

(±)-1,12-Dimethyl-3,9-dinitrobenzo[*c*]phenanthrene-5,8-dicarbonitrile, (±)-25. Under an argon atmosphere, trimethylsilyl cyanide (0.3 mL, 2.0 mmol) was added to a solution of (±)-**23** (380 mg, 1.0 mmol) and zinc iodide (3.0 mg) in dry toluene (5 mL). After stirred for 3 h at room temperature, hexane (5 mL) was added. The resulting powder was collected by filtration giving crude cyanohydrin (520 mg, 0.9 mmol, 90%) as a diastereomeric mixture. The crude product was diluted with pyridine (1 mL), to which phosphoryl chloride (0.3 mL, 3.0 mmol) was added. The mixture was heated at 90 °C for 3 h. After cooling, the solution was poured onto ice-cold 2 M hydrochloric acid, and the organic materials were extracted with ethyl acetate twice. The organic phases were combined, washed with water and brine, dried with magnesium sulfate, and filtered. The solvents were evaporated under reduced pressure, and silica gel chromatography gave (±)-**25** (270 mg, 0.67 mmol, 74%). Mp 160 °C dec (toluene). MS *m*/*z* 396 (M^+, 100%), 304 (M^+ − N_2O_4, 22). HRMS (EI, 70 eV) Calcd for $C_{22}H_{12}N_4O_4$: 396.0859. Found: 396.0855. IR (KBr) 2225, 1528, 1343 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (3H, s), 2.06 (3H, s), 7.69 (1H, d, J = 8 Hz), 8.24 (1H, d, J = 8 Hz), 8.43 (1H, br), 8.50 (1H, s), 8.51 (1H, s), 9.25 (1H, br). ^{13}C NMR (100 MHz, DMSO-d_6) δ 23.0, 23.3, 106.2, 111.5, 115.3, 116.3, 118.0, 120.8, 123.8, 125.2, 129.5, 130.1, 130.3, 130.7, 130.9, 132.8, 134.8, 137.8, 140.4, 142.6, 144.5, 146.6. The compound (±)-**24** was converted to (±)-**10** by the same procedures.

(*P*)-5,8-Bis(benzyloxycarbonylamino)-1,12-dimethylbenzo[*c*]phenanthrene. Under an argon atmosphere, a mixture of (*P*)-**1** (200 mg, 0.59 mmol), ethyldiisopropylamine (0.36 mL, 2.0 mmol), diphenylphosphoryl azide[12] (0.32 mL, 1.5 mmol), and toluene (25 mL) was heated at reflux for 3 h. After

being cooled to room temperature, benzyl alcohol (0.2 mL, 2 mmol) was added, and the mixture was stirred for another 1 h. After removing the solvent in vacuo, silica gel column chromatography gave the title compound (230 mg, 0.50 mmol, 85%). $[\alpha]^{26}_D$ +230 (*c* 0.95, $CHCl_3$). MS (EI, 70 eV) *m*/*z* 554 (M^+, 1%), 446 ($M^+ - OBn$, 21), 338 ($M^+ - 2OBn$, 100). HRMS (EI, 70 eV) Calcd for $C_{36}H_{30}N_2O_4$: 554.2206. Found: 554.2205. IR (neat) 3500−3200, 1703 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 1.86 (6H, s), 5.29 (4H, s), 7.30−7.45 (10H, m), 7.49 (4H, d, J = 8 Hz), 7.55 (2H, t, J = 8 Hz), 8.14 (2H, s), 8.26 (2H, d, J = 8 Hz), 8.88 (2H, s). ^{13}C NMR (100 MHz, acetone-d_6) δ 23.8, 67.3, 118.4, 120.1, 120.9, 126.1, 127.5, 128.7, 128.8, 129.1, 129.2, 132.4, 133.2, 133.6, 136.8, 137.7, 155.3.

(*P*)-5,8-Diamino-1,12-dimethylbenzo[*c*]phenanthrene (*P*)-4. Under a hydrogen atmosphere, a mixture of the above benzyloxycarbonyl derivative (510 mg, 1.1 mmol) and palladium on carbon (500 mg) in ethyl acetate (50 mL) was vigorously stirred at room temperature for 11 h. Then, the reaction mixture was filtered, and concentrated. Silica gel column chromatography gave (*P*)-**4** (280 mg, 0.99 mmol, 88%). Optical purity (>99% ee) was determined by ^1H NMR analysis of (*S*)-MTPA diamide. Mp 200 °C dec (toluene). Anal. Calcd for $C_{20}H_{18}N_2$: C; 83.88, H; 6.34, N; 9.78%. Found: C; 82.94, H; 6.52, N; 9.87%. $[\alpha]^{26}_D$ +220 (*c* 0.5, $CHCl_3$). MS (EI, 70 eV) *m*/*z* 286 (M^+, 100%), 270 ($M^+ - NH_2$, 13). HRMS (EI, 70 eV) Calcd for $C_{20}H_{18}N_2$: 286.1470. Found: 286.1469. IR (KBr) 3500−3100 cm^{-1}. ^1H NMR (400 MHz, THF-d_8) δ 1.89 (6H, s), 5.03 (4H, br), 6.70 (2H, s), 7.25 (2H, d, J = 8 Hz), 7.32 (2H, t, J = 8 Hz), 7.89 (2H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$−CD_3OD) δ 23.1, 106.1, 114.2, 117.6, 123.3, 123.4, 127.7, 132.3, 134.8, 135.4, 140.8.

(*P*)-5-Amino-1,12-dimethyl-7,8-dioxobenzo[*c*]phenanthrene (*P*)-26. A solution of (*P*)-**4** (10 mg, 0.035 mmol) in ethyl acetate (5 mL) was irradiated in a Pyrex tube for 5 min using Rayonet photochemical reactor equipped with RPR-3000 Å lamp. The solution was concentrated, and silica gel chromatography gave (*P*)-**26** (0.5 mg, 0.0017 mmol, 5%), and (*P*)-**4** (6.0 mg, 0.021 mmol, 60%) was recovered. Mp >300 °C (toluene-hexane). $[\alpha]^{26}_D$ −800 (*c* 0.1, $CHCl_3$). UV ($CHCl_3$) λ_{max} (ϵ) 317 nm (3.8×10^4), 547 (1.8×10^3). MS (EI, 70 eV) *m*/*z* 301 (M^+, 73%), 286 ($M^+ - Me$, 15), 273 ($M^+ - CO$, 100), 258 ($M^+ - CO$-Me, 19). HRMS (EI, 70 eV) Calcd for $C_{20}H_{15}NO_2$: 301.1103. Found: 301.1100. IR (KBr) 3500−3200, 1670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (3H, s), 2.11 (3H, s), 4.48 (2H, brs), 7.27 (1H, t, J = 7 Hz), 7.30 (1H, s), 7.38 (1H, d, J = 7 Hz), 7.43 (1H, d, J = 7 Hz), 7.54 (1H, dd, J = 8 Hz), 7.84 (1H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 29.8, 104.2, 119.4, 126.7, 127.3, 127.7, 127.7, 128.8, 130.2, 133.2, 136.6, 137.4, 137.8, 140.3, 143.8, 183.0, 184.4.

Acknowledgment. This work was supported by grants from the Japan Society of Promotion of Science.

Supporting Information Available: ^1H and ^{13}C NMR spectra of all the compounds from (*P*)-**4** to (*P*)-**26** except (*P*)-**14** and (±)-**22**; NOE data; titration experiment. These materials are available free of charge via the Internet at http://pubs.acs.org.

JO001419A