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Supporting Information

Spectral and Physical Data.

***N*-[(*S*)-1-Phenylethyl]-(*aS*)-1,1'-biphenanthryl-2,2'-diylthiophosphoramide (2a):** mp 170–171 °C, colorless crystals from acetonitrile; $[\alpha]_D^{25} +443.8$ (*c* 0.64, CHCl₃); IR (KBr) $\nu_{\max}$ 3385, 1455, 1233, 984, 876, 844, 817, 747 cm⁻¹; ¹H NMR (400 MHz; CDCl₃) δ 1.59 (3 H, d, *J* = 6.8 Hz, CH₃), 3.64–3.69 (1H, m, NH), 4.61–4.74 (1 H, m, CH), 7.16–7.92 (17 H, m, ArH), 8.66–9.00 (4 H, m, ArH).

(*aS*)-(-)-1,1'-Biphenanthryl-2,2'-diol (1): mp 244–245 °C, colorless crystals from EtOAc; $[\alpha]_D^{22} -34.0$ (*c* 0.95, CHCl₃); IR (KBr) $\nu_{\max}$ 3456, 1593, 1459, 1352, 1234, 1168, 1145, 815, 749 cm⁻¹; ¹H NMR (600 MHz; acetone-d₆) δ 7.08 (2 H, d, *J* = 9.1 Hz, ArH), 7.46 (2 H, d, *J* = 9.1 Hz, ArH), 7.49 (2 H, t, *J* = 8.3 Hz, ArH), 7.52 (2 H, d, *J* = 9.1 Hz, ArH), 7.62 (2 H, t, *J* = 8.3 Hz, ArH), 7.80 (2 H, d, *J* = 8.3 Hz, ArH), 8.06 (2 H, s, OH), 8.75 (2H, d, *J* = 8.3 Hz, ArH), 8.81 (2H, d, *J* = 9.1 Hz, ArH); ¹³C NMR (600 MHz; acetone-d₆) δ 118.3, 118.9, 123.5, 125.5, 125.8, 125.8, 126.8, 128.1, 128.6, 129.7, 132.1, 132.3, 134.7, 156.0.

(*aR,aR*)-(-)-Dinaphtho[2,1-*h*:1',2'-*j*]diphenanthro[2,1-*b*:1',2'-*d*][1,6]-dioxacyclododecin-16,29-dione (4): cyclic diester **4** was purified by chromatography on silica gel (hexane/CH₂Cl₂ 1:1); mp 258–259 °C, colorless crystals from hexane/EtOAc 10:1; $[\alpha]_D^{22} -397$ (*c* 0.51, CHCl₃); IR (KBr) $\nu_{\max}$ 1750, 1461, 1324, 1271, 1228, 1202, 1107, 1050, 820, 747 cm⁻¹; ¹H NMR (400 MHz; CDCl₃) δ 6.97 (2 H, d, *J* = 9.2 Hz, ArH), 7.14 (2 H, d, *J* = 7.7 Hz, ArH), 7.31 (2 H, t, *J* = 7.7 Hz, ArH), 7.43 (2 H, d, *J* = 9.2 Hz, ArH), 7.49 (2 H, d, *J* = 9.1 Hz, ArH), 7.53 (2 H, t, *J* = 7.7 Hz, ArH), 7.57 (2 H, t, *J* = 6.7 Hz, ArH), 7.66 (2 H, t, *J* = 6.7 Hz, ArH), 7.77 (2 H, d, *J* = 8.9 Hz, ArH), 7.79 (2 H, d, *J* = 6.7 Hz, ArH), 7.88 (2 H, d, *J* = 8.9 Hz, ArH), 7.90 (2 H, d, *J* = 7.7 Hz, ArH), 8.67 (2 H, d, *J* = 6.7 Hz, ArH), 8.69 (2 H, d, *J* = 9.1 Hz, ArH); ¹³C NMR (400 MHz; CDCl₃) δ 121.4, 122.7, 122.9, 123.6, 124.4, 124.9, 126.6, 126.9, 127.1, 127.5, 127.5, 127.6, 128.0, 128.1, 128.4, 128.5, 129.7, 130.0, 131.2, 132.8, 133.0, 134.3, 137.0, 147.7, 167.0; FD-MS *m/z* (rel intensity) 694 (8%), 693 (36%), 692 (100%, M⁺), 346 (2%, M₂⁺); Anal. Calcd for C₅₀H₂₈O₄: C, 86.69; H, 4.07. Found: C, 86.79; H, 4.32.

(*aR*)-(-)-6,6'-Dibromo-2,2'-dimethoxy-1,1'-binaphthyl (7): mp 238–239 °C, colorless crystals from benzene/cyclohexane 30:1; $[\alpha]_D^{24} -17.7$ (*c* 0.56, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 3.71 (6 H, s, OMe), 6.92 (2 H, d, *J* = 9.1 Hz, ArH), 7.23 (2 H, dd, *J* = 9.1, 2.2 Hz, ArH), 7.54 (2 H, d, *J* = 9.1 Hz, ArH), 7.93 (2 H, d, *J* = 9.1 Hz, ArH), 8.06 (2 H, d, *J* = 2.2 Hz, ArH).

(aR)-(-)-6,6'-Bis[(3-hydroxycarbonyl)propyl]-2,2'-dimethoxy-1,1'-binaphthyl (8): mp 120–121 °C, colorless crystals from CDCl₃; [α]_D²⁵ –8.83 (*c* 0.83, THF); IR (KBr) $\nu_{\max}$ 3435, 2935, 1705, 1595, 1501, 1267, 1252, 1097, 1069, 822, 806, 756 cm⁻¹; ¹H NMR (400 MHz; THF-d₈) δ 1.94 (4 H, tt, *J* = 7.6, 7.4 Hz, CH₂), 2.26 (4 H, t, *J* = 7.4 Hz, CH₂), 2.73 (4 H, t, *J* = 7.6 Hz, CH₂), 3.67 (6 H, s, OCH₃), 6.97 (2 H, d, *J* = 8.8 Hz, ArH), 7.01 (2 H, d, *J* = 8.8 Hz, ArH), 7.42 (2 H, d, *J* = 9.0 Hz, ArH), 7.62 (2 H, s, ArH), 7.86 (2 H, d, *J* = 9.0 Hz, ArH), 10.6 (2 H, br, CO₂H).

(aR)-(+)-5,5',6,6',7,7',8,8'-Octahydro-2,2'-dimethoxy-1,1'-biphenanthryl-5,5'-dione (9): [α]_D²⁶ +176.6 (*c* 1.10, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 2.17 (4 H, tt, *J* = 6.6, 6.1 Hz, CH₂), 2.79 (4 H, t, *J* = 6.6 Hz, CH₂), 3.02 (4 H, t, *J* = 6.1 Hz, CH₂), 3.75 (6 H, s, OCH₃), 7.04 (2 H, d, *J* = 8.7 Hz, ArH), 7.20 (2 H, d, *J* = 8.7 Hz, ArH), 7.54 (2 H, d, *J* = 9.6 Hz, ArH), 9.58 (2 H, d, *J* = 9.6 Hz, ArH); ¹³C NMR (400 MHz, CDCl₃) δ 23.1, 31.3, 41.2, 56.6, 115.9, 119.5, 126.7, 127.4, 127.7, 128.4, 131.3, 133.6, 144.5, 154.8, 200.8.

(aR)-(+)-5,5',6,6',7,7',8,8'-Octahydro-2,2'-dimethoxy-1,1'-biphenanthryl (10): [α]_D²⁵ +35.2 (*c* 1.67, CH₂Cl₂); ¹H NMR (400 MHz; CDCl₃) δ 1.82–1.89 (4 H, m, CH₂), 1.92–2.01 (4 H, m, CH₂), 2.81 (4 H, t, *J* = 6.0 Hz, CH₂), 3.18 (4 H, t, *J* = 6.3 Hz, CH₂), 3.73 (6 H, s, OCH₃), 6.87 (2 H, d, *J* = 8.8 Hz, ArH), 6.91 (2 H, d, *J* = 8.8 Hz, ArH), 7.42 (2 H, d, *J* = 9.3 Hz, ArH), 8.09 (2 H, d, *J* = 9.3 Hz, ArH).

(aR)-(-)-7,7',8,8'-Tetrahydro-2,2'-dimethoxy-1,1'-biphenanthryl (11): [α]_D²⁰ –29.2 (*c* 0.66, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 2.34–2.40 (4 H, m, CH₂), 2.85 (4 H, t, *J* = 8.6 Hz, CH₂), 3.74 (6 H, s, OCH₃), 6.24–6.30 (2 H, m, CH), 6.93 (2 H, d, *J* = 8.5 Hz, ArH), 7.00 (2 H, d, *J* = 8.5 Hz, ArH), 7.32 (2 H, d, *J* = 9.8 Hz, CH), 7.44 (2 H, d, *J* = 9.3 Hz, ArH), 8.23 (2 H, d, *J* = 9.3 Hz, ArH).

(aR)-(+)-2,2'-Dimethoxy-1,1'-biphenanthryl (5): mp 227–228 °C, colorless crystals from EtOAc; [α]_D²² +109.7 (*c* 1.29, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 3.78 (6 H, s, OCH₃), 7.07 (2 H, d, *J* = 9.2 Hz, ArH), 7.45 (2 H, d, *J* = 9.2 Hz, ArH), 7.50 (2 H, t, *J* = 8.4 Hz, ArH), 7.51 (2 H, d, *J* = 9.2 Hz, ArH), 7.63 (2 H, t, *J* = 8.4 Hz, ArH), 7.76 (2 H, d, *J* = 8.4 Hz, ArH), 8.69 (2 H, d, *J* = 8.4 Hz, ArH), 8.81 (2 H, d, *J* = 9.2 Hz, ArH); ¹³C NMR (400 MHz, CDCl₃) δ 56.6, 112.7, 121.4, 122.4, 124.0, 124.5, 125.0, 125.8, 126.7, 127.6, 128.5, 130.8, 131.0, 132.9, 156.1.

(aR)-(+)-1,1'-Biphenanthryl-2,2'-diol (1): [α]_D¹⁹ +37.0 (*c* 0.56, CHCl₃). The spectral data of this compound were identical with those of (S)-(-)-1.

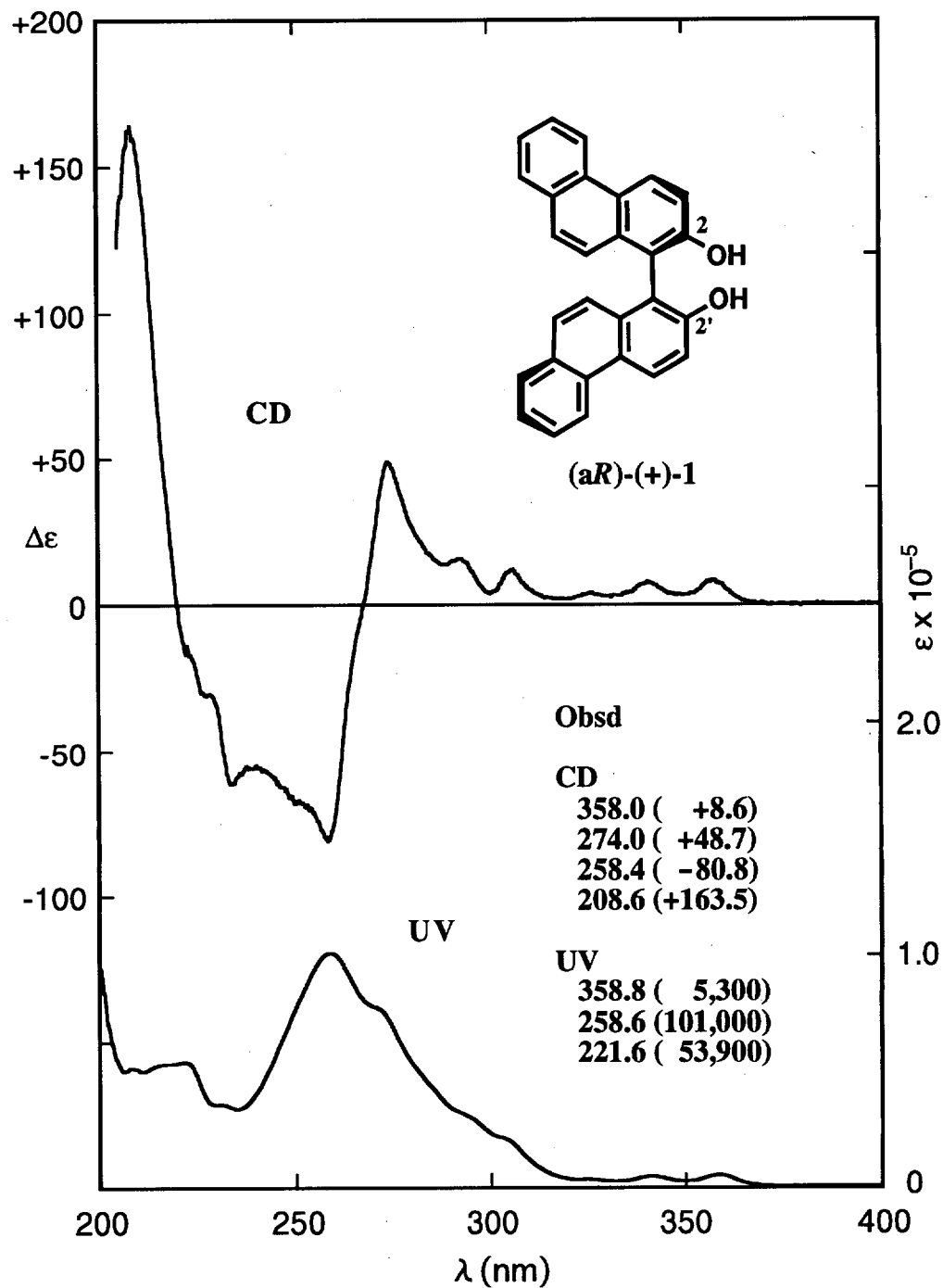


Figure 3. CD and UV spectra of (aR)-(+)-1,1'-biphenanthryl-2,2'-diol (**1**) in 10 (% v/v) 1,4-dioxane/EtOH.

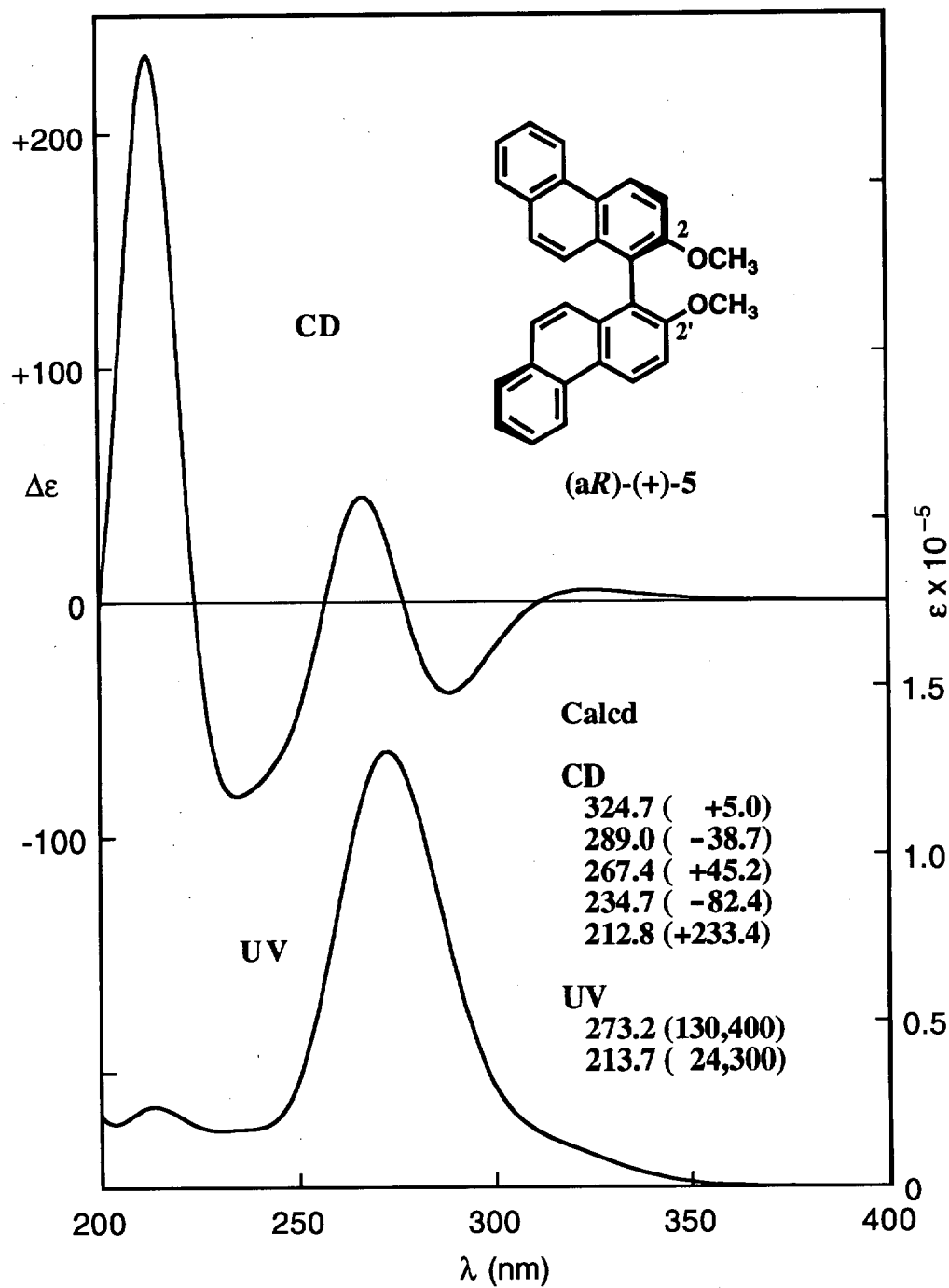


Figure 4. CD and UV spectral curves of (aR)-1,1'-biphenanthryl-2,2'-diol dimethyl ether (5) calculated by the π -electron SCF-CI-DV MO method.