Supporting Information

Isolation of a 1,4-diketone intermediate in oxidative dimerization of 2-hydroxyanthracene and its conversion to oxahelicene

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Instrumentation and Materials

¹H NMR (500 MHz) and ¹³C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl₃ (δ = 7.260 ppm) for ¹H NMR and CDCl₃ (δ = 77.0 ppm) for ¹³C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. Emission spectra were recorded on a JASCO FP-6500 spectrometer and absolute fluorescence quantum yields were measured by photon-counting method using an integration sphere. CD spectra of **6**-(*P*) and **6**-(*M*) were taken on a JASCO J-820 spectropolarimeter. Mass spectra were recorded on a Bruker microTOF using positive and negative mode ESI-TOF method for acetonitrile solutions. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All solvents used in the reactions were deoxygenated by N₂ bubbling.

Synthesis and Compound Data

2-Hydroxy-9,10-bis(triethylsilylethynyl)anthracene (1a)

To a solution of 2-boryl-9,10-bis(triethylsilylethynyl)anthracene (151 mg, 0.260 mmol) in a mixture of dry THF (5 mL), acetone (0.6 mL), and water (0.4 mL) was added Oxone (545 mg, 0.887 mmol). The reaction mixture was stirred at room temperature under N₂ for 1 h. The reaction was quenched with aqueous Na₂S₂O₃, and the resulting mixture was extracted with EtOAc. The organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) afforded **1a** (101 mg, 0.215 mmol) in 83% yield. ¹H NMR (CDCl₃): δ 8.56–8.50 (m, 3H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.60–7.52 (m, 2H), 7.26 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.25 (s, 1H, OH), 1.18 (t, *J* = 8.0 Hz, 9H), 1.18 (t, *J* = 8.0 Hz, 9H), 0.86 (q, *J* = 8.0, 6H), 0.85 (q, *J* = 8.0, 6H) ppm; ¹³C NMR (CDCl₃): δ 154.3, 133.7, 132.9, 131.0, 129.7, 128.6, 127.3, 127.0, 126.7, 126.0, 120.3, 118.9, 116.0, 107.5, 105.6,

105.3, 102.8, 102.5, 7.80, 7.75, 4.75, 4.63 ppm: HR-MS (ESI-MS): m/z = 469.2398, calcd for $(C_{30}H_{37}OSi_2)^- = 469.2388 [(M - H)^-].$

2-Hydroxy-9,10-bis(triisopropylsilylethynyl)anthracene (1b)

To a solution of 2-boryl-9,10-bis(triisopropylsilylethynyl)anthracene (126 mg, 0.189 mmol) in a mixture of dry THF (3 mL), acetone (0.4 mL), and water (0.2 mL) was added Oxone (475 mg, 0.771 mmol). The reaction mixture was stirred at room temperature under N₂ for 1 h. The reaction was quenched with aqueous Na₂S₂O₃, and the resulting mixture was extracted with EtOAc. The organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) afforded **1b** (95.4 mg, 0.172 mmol) in 91% yield. ¹H NMR (CDCl₃): δ 8.59–8.54 (m, 3H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.60–7.51 (m, 2H), 7.28–7.24 (m, 1H), 5.42 (s, 1H, OH), 1.33–1.20 (m, 42H, TIPS) ppm; ¹³C NMR (CDCl₃): δ 154.2, 133.8, 132.9, 131.1, 129.7, 128.7, 127.3, 126.8, 126.0, 120.3, 119.0, 116.2, 107.5 104.6, 104.2, 103.6, 103.3, 18.91, 18.87, 11.53, 11.49 ppm; λ_{max} (ϵ [M⁻¹ cm⁻¹]) = 275 (98000), 380 (14000), 428 (21000) and 455 (24000) nm: HR-MS (ESI-MS): *m*/*z* = 553.3277, calcd for (C₃₆H₄₉OSi₂)⁻ = 553.3327 [(*M* – *H*)⁻].

2-Hydroxy-9,10-bis(tert-butylethynyl)anthracene (1c)

To a solution of 2-boryl-9,10-bis(*tert*-butylethynyl)anthracene (90.8 mg, 0.196 mmol) in a mixture of dry THF (3 mL), acetone (0.4 mL), and water (0.2 mL) was added Oxone (470 mg, 0.765 mmol). The reaction mixture was stirred at room temperature under N₂ for 15 min. The reaction was quenched with aqueous Na₂S₂O₃, and the resulting mixture was extracted with EtOAc. The organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) afforded **1c** (52.1 mg, 0.147 mmol) in 75% yield. ¹H NMR (CDCl₃): δ 8.48–8.43 (m, 3H),

7.77 (d, J = 2.5 Hz, 1H), 7.56–7.47 (m, 2H), 7.21 (dd, J = 9.0, 2.5 Hz, 1H), 5.30 (s, 1H, OH), 1.54 (s, 9H, *t*-Bu), 1.53 (s, 9H, *t*-Bu) ppm; ¹³C NMR (CDCl₃): δ 153.8, 133.2, 132.5, 130.7, 129.8, 128.3, 127.3, 126.7, 126.5, 125.5, 119.7, 118.7, 115.9, 111.3, 111.1, 107.3, 102.8, 76.1, 75.9, 31.4, 31.3, 29.0, 28.9 ppm: HR-MS (ESI-MS): m/z = 353.1915, calcd for $(C_{26}H_{25}O)^{-} = 353.1911 [(<math>M - H$)^{-}].

9,9',10,10'-Tetrakis((triethylsilyl)ethynyl)-[1,1'-bianthracene]-2,2'(1H,1'H)-dione (2a)

To a solution of 2-hydroxyanthracene **1a** (203.4 mg, 432 µmol) in deoxygenated CH₂Cl₂ (20 mL) was added MnO₂ (1.84 g, 21.2 mmol), then stirred at room temperature under N₂ for 15 min. The resulting solution was filtered over a pad of Celite with CH₂Cl₂ as an eluent. Purification by silica-gel column chromatography (hexane/CH₂Cl₂ as an eluent) provided **2a** (126.9 mg, 135 µmol) in 63% yield as green liquid. ¹H NMR (CDCl₃): δ 8.39 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 10.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.58–7.51 (m, 2H), 7.44–7.41 (m, 2H), 6.35 (d, *J* = 10.0 Hz, 2H), 4.35 (s, 2H), 1.14 (t, *J* = 8.0 Hz, 18H), 0.83 (t, *J* = 8.0 Hz, 18H), 0.80 (q, *J* = 8.0 Hz, 12H), 0.57 (m, 12H) ppm; ¹³C NMR (CDCl₃): δ 200.9, 141.5, 134.5, 132.6, 132.6, 131.5, 128.3, 127.6, 127.3, 126.8, 126.5, 123.8, 121.3, 106.7, 103.5, 101.2, 99.88, 59.27, 7.60, 7.57, 4.41, 4.23, 11.5 ppm; HR-MS (ESI-MS): *m*/*z* = 961.4658, calcd for (C₆₀H₇₄O₂Si₄Na)⁺ = 961.4658 [(*M* + *Na*)⁺].

9,9',10,10'-Tetrakis((triisopropylsilyl)ethynyl)-[1,1'-bianthracene]-2,2'(1H,1'H)-dione (2b) and Compound 3b

To a solution of 2-hydroxyanthracene **1b** (27.4 mg, 49.3 µmol) in deoxygenated CH₂Cl₂ (100 mL) was added MnO₂ (213 mg, 2.47 mmol), then stirred at room temperature under N₂ for 42 h. The resulting solution was filtered over a pad of Celite with CH₂Cl₂ as an eluent. Purification by silica-gel column chromatography (hexane/CH₂Cl₂ as an eluent) provided **2b** (13.8 mg, 12.5 µmol) in 50% yield as green liquid and **3b** (8.20 mg, 14.4 µmol) in 29% yield as red liquid. ¹H NMR (CDCl₃):(**2b**) δ 8.34 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 10.2 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.58–

7.45 (m, 4H), 6.29 (d, J = 10.2 Hz, 2H), 4.51 (s, 2H), 1.29–1.14 (m, 42H, TIPS), 1.10–1.05 (m, 21H, TIPS), 0.99–0.95 (m, 21H, TIPS) ppm; ¹³C NMR (CDCl₃):(**2b**) δ 200.4, 141.5, 134.8, 132.7, 131.5, 128.4, 127.7, 127.5, 126.9, 126.6, 123.8, 121.3, 105.3, 103.9, 101.5, 101.3, 58.9, 18.6, 11.5 ppm; HR-MS (ESI-MS):(**2b**) m/z = 1107.6562, calcd for (C₇₂H₉₉O₂Si₄)⁺ = 1107.6717 [(M + H)⁺]; UV/vis (CH₂Cl₂):(**2b**) λ_{max} (ε [M⁻¹ cm⁻¹]) = 326 (45000), 344 (48000), and 360 nm; ¹H NMR (CDCl₃):(**3b**) δ 8.75 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.37 (d, J = 10.2 Hz, 2H), 7.78–7.69 (m, 2H), 6.61 (d, J = 10.2 Hz, 2H), 1.36–1.12 (m, 42H, TIPS) ppm; ¹³C NMR (CDCl₃):(**3b**) δ 180.9, 177.8, 144.2, 134.9, 134.0, 132.5, 130.9, 129.9, 128.3, 127.9, 126.5, 123.2, 111.4, 107.4, 102.4, 100.5, 18.7, 11.3 ppm; HR-MS (ESI-MS): (**3b**) m/z = 591.3364, calcd for (C₃₆H₄₈O₂Si₂Na)⁺ = 591.3085 [(M + Na)⁺].

9,9',10,10'-Tetrakis(*tert*-butylethynyl)-[1,1'-bianthracene]-2,2'(1H,1'H)-dione (2c)

To a solution of 2-hydroxyanthracene **1c** (50.4 mg, 142 µmol) in deoxygenated CH₂Cl₂ (10 mL) was added MnO₂ (689 mg, 7.93 mmol), then stirred at room temperature under N₂ for 15 min. The resulting solution was filtered over a pad of Celite with CH₂Cl₂ as an eluent. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) provided **2c** (42.3 mg, 59.8 µmol) in 84% yield as yellow liquid. ¹H NMR (CDCl₃): δ 8.30 (m, 2H), 8.16 (m, 2H), 7.57 (m, 6H), 7.58–7.51 (m, 2H), 5.93 (d, *J* = 10.0 Hz, 2H), 4.86 (s, 2H), 1.37 (s, 18H, *t*-Bu), 1.20 (s, 18H, *t*-Bu) ppm; ¹³C NMR (CDCl₃): δ 199.2, 141.9, 134.8, 130.0, 132.6, 130.7, 128.2, 127.4, 127.2, 127.1, 126.9, 122.2, 121.1, 111.2, 110.3, 74.3, 74.0, 58.66, 31.0, 30.8, 28.7, 28.5 ppm; HR-MS (ESI-MS): *m/z* = 707.3882, calcd for (C₅₂H₅₁O₂)⁺ = 707.3884 [(*M* + *H*)⁺].

9,9',10,10'-Tetrakis((triisopropylsilyl)ethynyl)-[1,1'-bianthracene]-2,2'-diol (4)

To a solution of **2b** (39.9 mg, 36.0 μ mol) in deoxygenated CH₂Cl₂ (20 mL) was added *t*-BuOK (24.6 mg, 0.219 mmol), then stirred for 20 h at room temperature. The reaction was quenched with

water and extracted with CH₂Cl₂. The organic layer was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) provided **4** (23.6 mg, 21.3 µmol) in 59% yield as yellow liquid. ¹H NMR (CDCl₃): δ 8.83 (d, *J* = 9.5 Hz, 2H), 8.65–8.60 (m, 4H), 7.58–7.50 (m, 4H) 7.40 (d, *J* = 9.5 Hz, 2H), 4.96 (s, 2H, OH), 1.36–1.24 (m, 42H, TIPS), 0.77 (d, *J* = 7.5 Hz, 18H), 0.54 (d, *J* = 7.5 Hz, 18H, TIPS), 0.38–0.30 (m, 6H, TIPS) ppm; ¹³C NMR (CDCl₃): δ 153.9, 153.5, 131.3, 131.2, 131.1, 129.7, 127.6, 127.0, 126.9, 126.2, 120.1, 117.0, 112.6, 109.1, 105.1, 103.6, 103.3, 18.9, 18.7, 11.9, 11.5 ppm; UV/vis (CH₂Cl₂): λ_{max} (ε [M⁻¹cm⁻¹]) = 385 (18000), 441 (27000), and 360 (29000) nm; HR-MS (ESI-MS): *m/z* = 1107.6743, calcd for (C₇₂H₉₉O₂Si₄)⁺ = 1107.6717 [(*M* + *H*)⁺].

5,11,16,17-Tetrakis((triethylsilylethynyl)-7a,8a-dimethoxy-7a,8a,17b,16c-tetrahydrodianthra[2,1b:1',2'-d]furan (5a)

To a solution of **2a** (57.2 mg, 60.9 µmol) in deoxygenated CH₂Cl₂/MeOH(1/1, 20 mL) was added trimethyl orthoformate (30 µL, 2.75 mmol) and *p*-toluenesulfonic acid monohydtrate (31.6 mg, 0.166 mmol), then stirred for 18 h at room temperature. The solution was washed with water and extracted with CH₂Cl₂. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) provided **5a** (34.4 mg, 34.9 µmol) in 57% yield as colorless solid. ¹H NMR (CDCl₃): δ 8.37 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.53–7.49 (m, 4H), 7.41–7.38 (m, 2H), 6.23 (d, *J* = 10.0 Hz, 2H), 4.40 (s, 2H), 3.38 (s, 6H), 1.16 (t, *J* = 8.0 Hz, 18H) 0.80 (q, *J* = 8.0 Hz, 12H) ppm, 0.74 (t, *J* = 8.0 Hz, 18H), 0.45 (m, 12H) ppm; ¹³C NMR (CDCl₃): δ 132.9, 1332.8, 132.7, 131.6, 129.4, 127.2, 127.0, 126.9, 126.7, 126.5, 122.4, 119.0, 104.8, 103.3, 102.1, 101.8, 100.9, 49.76, 48.83, 7.67, 7.49, 4.55, 4.30 ppm; HR-MS (ESI-MS): *m*/*z* = 1007.5251, calcd for (C₆₂H₈₀O₃Si₄Na)⁺ = 1007.5077 [(*M* + *Na*)⁺].

5,11,16,17-Tetrakis((triisopropylsilyl)ethynyl)-

7a,8a-dimethoxy-7a,8a,17b,16c-tetrahydrodianthra[2,1-b:1',2'-d]furan (5b)

To a solution of **2b** (99.0 mg, 89.4 µmol) in deoxygenated CH₂Cl₂/MeOH(1/1, 40 mL) was added trimethyl orthoformate (30 µL, 2.75 mmol) and *p*-toluenesulfonic acid monohydtrate (36.2 mg, 190 µmol), then stirred for 12 h at room temperature. The solution was washed with water and extracted with CH₂Cl₂. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) provided **5b** (66.3 mg, 57.5 µmol) in 64% yield as colorless solid. ¹H NMR (CDCl₃): δ 8.37 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.54–7.49 (m, 4H), 7.40 (t, *J* = 7.2 Hz, 2H), 6.27 (d, *J* = 10.2 Hz, 2H), 4.43 (s, 2H), 3.73 (s, 6H), 1.29–1.16 (m, 42H, TIPS) 0.95–0.75 (m, 42H, TIPS) ppm; ¹³C NMR (CDCl₃): δ 133.1, 133.0, 132.6, 131.5, 129.1, 127.2, 127.1, 127.0, 126.9, 126.7, 122.5, 119.4, 103.7, 103.3, 102.8, 102.2, 101.4, 49.60, 48.81, 18.91, 18.82, 18.64, 11.54, 11.47 ppm; HR-MS (ESI-MS): *m*/*z* = 1175.6903, calcd for (C₇₄H₁₀₄O₃Si₄Na)⁺ = 1175.6955 [(*M* + *Na*)⁺].

5,11,16,17-Tetrakis((triethylsilyl)ethynyl)dianthra[2,1-b:1',2'-d]furan (6a)

To a solution of **5a** (21.0 mg, 21.3 µmol) in THF (2 mL) was added trifluoromethanesulfonic acid (9.0 µL, 0.102 mmol), then stirred for 15 sec at room temperature. The reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane as an eluent) provided **6a** (3.0 mg, 3.3 µmol) in 16% yield as orange solid. ¹H NMR (CDCl₃): δ 8.74 (d, *J* = 9.0 Hz, 2H), 8.67 (d, *J* = 8.0 Hz, 2H), 8.63 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.67–7.61 (m, 4H), 1.22 (t, *J* = 8.0 Hz, 18H), 0.88 (q, *J* = 8.0 Hz, 12H), 0.44 (t, *J* = 8.0 Hz, 18H), -0.26 (m, 12H) ppm; ¹³C NMR (CDCl₃): δ 154.3, 132.0, 131.6, 130.8, 130.0, 127.4, 127.3, 127.0, 126.9, 126.6, 121.0, 119.2, 118.0, 114.1, 109.8, 105.5, 105.0, 103.4, 7.79, 7.17, 4.76, 3.49 ppm; UV/vis (CH₂Cl₂): λ_{max} (ε [M⁻¹ cm⁻¹]) = 277 (110000) and 504 (53000) nm; HR-MS (ESI-MS): *m*/*z* = 920.4487, calcd for (C₆₀H₇₂OSi₄)⁺ = 920.4655 [(*M*)⁺].

5,11,16,17-Tetrakis((triisopropylsilyl)ethynyl)dianthra[2,1-b:1',2'-d]furan (6b)

To a solution of **5b** (23.0 mg, 20.0 µmol) in THF (5 mL) was added trifluoromethanesulfonic acid (9.0 µL, 0.102 mmol), then stirred for 1 min at room temperature. The reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification by silica-gel column chromatography (hexane as an eluent) provided **6b** (10.2 mg, 9.37 µmol) in 47% yield as orange solid. ¹H NMR (CDCl₃): δ 8.74 (d, *J* = 9.5 Hz, 2H), 8.66 (d, *J* = 8.5 Hz, 4H), 7.87 (d, *J* = 9.5 Hz, 2H), 7.62 (m, 4H), 1.38–1.25 (m, 42H), 0.53 (d, *J* = 7.5 Hz, 18H) , 0.48 (d, *J* = 7.5 Hz 18H), 0.13–0.04 (m, 6H) ppm; ¹³C NMR (CDCl₃): δ 154.4, 132.4, 131.8, 131.0, 129.6, 127.8, 127.4, 126.9, 126.8, 126.5, 120.7, 119.1, 117.9, 113.9, 109.4, 106.0, 104.0, 103.9, 29.70, 18.92, 18.34, 18.24, 11.53, 11.43 ppm; UV/vis (CH₂Cl₂): λ_{max} (ε [M⁻¹ cm⁻¹]) = 278 (93000), 339 (21000), 383 (17000), 472 (31000), and 503 (47000) nm; HR-MS (ESI-MS): *m*/*z* = 1089.6577, calcd for (C₇₂H₉₇OSi₄)⁺ = 1089.6611 [(*M* + *H*)⁺].

1,1-Dimethoxy-2-oxo-9,10-bis(triisopropylsilylethynyl)anthracene

To a solution of 2-hydroxyanthracene **2b** (22.7 mg, 40.9 µmol) in deoxygenated CH₂Cl₂/MeOH(1/1, 10 mL) was added DDQ (46.0 mg, 0.205 mmol) and HCl (5.0 µL, 0.05%), then stirred for 17 h at room temperature. The resulting solution was filtered over a pad of Celite with CH₂Cl₂ as an eluent. Purification by silica-gel column chromatography (hexane/EtOAc as an eluent) provided the title compound (18.3 mg, 29.8 µmol) in 63% yield as colorless solid. ¹H NMR (CDCl₃): δ 8.68 (m, 1H), 8.44 (m, 1H), 8.27 (d, *J* = 10.2 Hz, 1H), 7.65 (m, 2H), 6.32 (d, *J* = 10.2 Hz, 1H), 3.32 (s, 6H), 1.30–1.14 (m, 42H, TIPS) ppm; ¹³C NMR (CDCl₃): δ 193.6, 142.9, 136.9, 134.3, 133.1, 131.3, 128.8, 128.6, 127.4, 126.1, 122.5, 51.7, 18.8, 11.4 ppm; HR-MS (ESI-MS): *m/z* = 637.3604, calcd for (C₃₈H₅₄O₂Si₂Na)⁺ = 673.3431 [(*M* + *Na*)⁺].



Fig. S2 ¹³C NMR spectrum of 1a in CDCl₃.



Fig. S4 ¹³C NMR spectrum of 1b in CDCl₃.





Fig. S8 ¹³C NMR spectrum of 2a in CDCl₃.



Fig. S10¹³C NMR spectrum of 2b in CDCl₃.



Fig. S12 13 C NMR spectrum of **2c** in CDCl₃.



Fig. S14¹³C NMR spectrum of 3b in CDCl₃.













Fig. S22 ¹³C NMR spectrum of 6a in CDCl₃.





Fig. S25. ¹H NMR spectrum of 1,1-dimethoxy-2-oxo-9,10-bis(triisopropylsilylethynyl)anthracene in CDCl₃.



Fig. S26. ¹³C NMR spectrum of 1,1-dimethoxy-2-oxo-9,10-bis(triisopropylsilylethynyl)anthracene in CDCl₃.

Optical Resolution of 6b

Optical resolution of compound **6b** was performed by HPLC equipped with a DAICEL CHIRALPAK IF column (10 mm × 250 mm) at 0 °C using hexane as eluent.



Fig. S27 Chromatographs of 6b on HPLC equipped with CHIRALPAK IF column.



1,1-dimethoxy-2-oxo-9,10-bis(triisopropylsilylethynyl)anthracene (dotted) in dichloromethane.



CPL Measurement

Fig. S29 Schematic diagram for circularly polarized luminescent (CPL) measurement.¹ A setup for CPL measurement was described below. The retardation of the emitted light was controlled by a photoelastic modulator (Hinds, PEM-100) with the frequency of 50 kHz. For detection of CPL signal, the circularly polarized light was converted to the linearly polarized light through the linearly polarized cubic prism (200,000:1), and then detected by a photomultiplier tube (PMT) (Hamamatsu, H7732-10). The AC component of the PMT output with frequency of 50 kHz was analyzed by a lock-in amplifier (EG&G, Model 7265), which can be modulated by the reference frequency signal from the PEM. The emission intensity was evaluated by the DC component. Finally, the CPL dissymmetry factor, $g_{lum} = 2(I_{left} - I_{right})/(I_{left} + I_{right})$ were calculated by the values AC and DC components. Other components in the measurement system were described below; achromatic depolarizer (THORLABS, DPU-26a), polarizing prism (EdmundOptics Japan Ltd., 47045-K), monochromators (SHIMADZU, SPG-120S (emission), SPG-120UV (excitation)), and preamplifier (Stanford Research Systems, SR570).

X-ray Diffraction Analysis

X-ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector for compounds **2b**, **4**, **5b**, and **6b** and on a Bruker D8 QUEST X-ray diffractometer with I μ S microfocus X-ray source and a large area (10 cm 10 cm) CMOS detector (PHOTON 100) for **6-**(*P*). Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 1041271 (**2a**), CCDC 1041274 (**4**), CCDC 1041272 (**5b**), CCDC 1041273 (**6b**), and CCDC 1041270 (**6-**(**P**)), contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).



Fig. S30. X-ray crystal structure of **6**-(**P**). Triisopropylsilylethynyl substituents are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level. The Flack parameter is -0.03(3).



Fig. S31. Crystal packing structure of (a) (b) racemic 6b and (c) (d) 6-(P).

Table 3	S1. (Crystallog	graphic	data	for	2b, 4	, 5 b,	6b ,	and	6-(1	P)
						,	, ,	,			

	2b	4	5b	6b	6-(<i>P</i>)
empirical formula	C72H98O2Si4	C ₇₂ H ₉₈ O ₂ Si ₄	C _{67.2} H _{91.2} N _{1.6} O _{2.4} Si _{3.2}	C ₇₂ H ₉₆ OSi ₄	C ₇₂ H ₉₆ OSi ₄
formula weight	1107.86	1107.86	1049.71	1089.85	1089.84
habit	prism	prism	prism	prism	prism
<i>Т</i> , К	123(2)	103(2)	103(2)	123(2)	93(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P2</i> ₁ /c (14)	<i>P</i> -1 (2)	<i>P2</i> ₁ /c (14)	<i>P2</i> ₁ /c (14)	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁ (19)
<i>a</i> , Å	13.426(2)	13.171(3)	13.3100(5)	19.768(3)	13.7114(7)
b, Å	18.425(3)	14.918(3)	29.8304(10)	21.986(4)	19.2562(11)
<i>c</i> , Å	28.086(5)	17.544(3)	19.4965(6)	16.670(3)	25.0769(13)
a, deg	90.00	85.743(6)	90	90	90
β , deg	94.327(3)	79.779(7)	93.590(2)	111.807(3)	90
γ, deg	90.00	84.496(7)	90	90	90
<i>V</i> , Å ³	6928(2)	3371.0(11)	7725.8(5)	6726(2)	6621.0(6)
Ζ	4	2	5	4	4
<i>Dc</i> , g/cm ³	1.062	1.091	1.128	1.076	1.093
<i>F</i> (000)	2408	1204	2848	2368	2368
crystal size, mm ³	0.20 x 0.10 x 0.10	0.16 x 0.16 x 0.01	0.50 x 0.20 x 0.20	0.40 x 0.40 x 0.10	0.29 x 0.089 x 0.078
$2 heta_{\max}$, °	52.0	55.0	55.0	50.0	50.17
$R_1 \ (I > 2\sigma(I))$	0.0833	0.0845	0.0712	0.0886	0.0388
wR2(all data)	0.2080	0.2661	0.1961	0.2738	0.0908
GOF	1.023	1.087	1.052	1.046	1.027
obs reflects	8593	9981	13754	6978	10672
total reflects	14114	14803	15087	11830	11700
parameters	727	703	875	717	718

Theoretical Calculations

All calculations were carried out using the Gaussian 09 program.^[2] Molecular orbitals of **2b** were estimated by DFT method at B3LYP/6-31G(d) level with the geometry of its crystal structure. The oscillator strength of compound **6-**(M) was calculated by time-dependent (TD) DFT method at B3LYP/6-31G(d) level based on its crystal structure.



Fig. S32. (a) HOMO and (b) LUMO of 2b.

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