

Supporting Information

Chirality Transfer from Atropisomeric Chiral Inducers to Nematic and Smectic Liquid Crystals - Synthesis and Characterization of *Di*- and *Tetra*-Substituted Axially Chiral Binaphthyl Derivatives

Munju Goh[†], Yehdong Han, Jinwoo Park, Sangbum Ahn, and Kazuo Akagi*

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

CORRESPONDING AUTHOR FOOTNOTE:

* Corresponding author E-mail: akagi@fps.polym.kyoto-u.ac.jp

[†] Present address: Institute of Advanced Composite Materials, Korea Institute of Science and Technology

1. Syntheses

3,3'-PCH5-2,2'-dimethoxy-1,1'-binaphthyl (3). 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (0.5 g, 1.06 mmol), **2**^{6c} (0.7 g, 2.54 mmol), NaHCO₃ (0.534 g, 6.4 mmol), and a catalytic amount of Pd(PPh₃)₄ were added to the reaction mixture. The mixture was refluxed in H₂O (20 mL) and THF (20 mL) for overnight at 70 °C, and then it was cooled down and washed several times with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The organic solvent removed by rotary evaporation. The organic layer was subjected to chromatography on silica gel using *n*-hexane / CHCl₃ = 1 as an eluent to give a white powder, **3** (0.65 g, 84.4%). ¹H-NMR (CDCl₃, 400 MHz, δ from TMS, ppm): 7.95 (s, 2H), 7.85 (d, *J* = 8 Hz, 2H), 7.67 (d, *J* = 8 Hz, 4H), 7.35 (m, 2H), 7.26 (m, 4H), 7.22 (m, 4H), 3.17 (s, 6H), 2.53 (t, *J* = 12 Hz, 2H), 1.94 (m, 8H), 1.53 (m, 4H), 1.30 (m, 18H), 1.11 (m, 4H), 0.93 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ from TMS, ppm): 154.01, 146.70, 136.11, 134.79, 133.31, 130.62, 130.14, 128.94, 127.77, 126.55, 125.86, 125.59, 124.59, 60.35, 44.30, 37.37, 37.30, 34.33, 33.61, 32.19, 26.64, 22.68, 14.1. HRMS (FAB, *m/z*): Calc. 770.5063. Found: 770.5067.

3,3'-PCH5-2,2'-dihydroxy-1,1'-binaphthyl (4). BBr₃ (0.14 mL, 1.43 mmol) was drop wise added to a cooled (−78 °C) mixture of **3** (0.5 g, 0.65 mmol) and dried CH₂Cl₂ (30 mL). The reaction mixture was stirred at room temperature for overnight. The reaction mixture was cooled down to 0 °C, and saturated NH₄Cl solution was added to reaction mixture. Then it was washed several times with H₂O and CHCl₃. The organic solvent removed by rotary evaporation. The organic layer was subjected to chromatography on silica gel using CHCl₃ as an eluent to give a white powder, **4** (0.45 g, 96%). ¹H-NMR (CDCl₃, 400 MHz, δ from TMS, ppm): 7.98 (s, 2H), 7.85 (d, *J* = 8 Hz, 2H), 7.62 (d, *J* = 8 Hz, 4H), 7.31 (m, 6H), 7.22 (m, 4H), 5.34 (s, 2H), 2.53 (t, *J* = 12 Hz, 2H), 1.93 (m, 8H), 1.47 (m, 4H), 1.30 (m, 18H), 1.04 (m, 4H), 0.9 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ from TMS, ppm): 149.97, 147.27, 134.62, 132.66, 130.90, 130.42, 129.27, 128.16, 126.92, 124.11, 123.99,

112.30, 44.35, 37.35, 37.27, 34.27, 33.57, 32.18, 26.63, 22.69, 14.11. HRMS (FAB, m/z): Calc. 724.4750. Found: 724.4754.

3,3'-PCH5-2,2'-diethoxy-1,1'-binaphthyl (D-3,3'). **4** (0.4 g, 0.55 mmol), bromoethane (0.25 mL, 3.3 mmol), K_2CO_3 (0.3 g, 2.2 mmol) and a catalytic amount of 18-crown-6-ether were dissolved in acetone (20 mL). The mixture was stirred for 24 h at 60 °C. The mixture was extracted with H_2O and $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4 . The organic solvent removed by rotary evaporation. The organic layer was subjected to chromatography on silica gel using n -hexane / $CHCl_3 = 1$ as an eluent to give a white powder, **D-3,3'** (0.405 g, 92%). 1H -NMR ($CDCl_3$, 400 MHz, δ from TMS, ppm): 7.93 (s, 2H), 7.86 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 4H), 7.36 (m, 4H), 7.28 (d, $J = 8.0$ Hz, 4H), 7.22 (d, $J = 3.6$ Hz, 2H), 3.53 (m, 2H), 3.25 (m, 2H), 2.54 (t, $J = 12.0$ Hz, 2H), 1.94 (d, $J = 16.0$ Hz, 8H), 1.55 (m, 4H), 1.32 (m, 18H), 1.09 (m, 10H), 0.91 (m, 6H). ^{13}C -NMR ($CDCl_3$, 100 MHz, δ from TMS, ppm): 153.65, 146.68, 136.46, 135.53, 133.48, 130.47, 129.8, 129.01, 127.71, 126.41, 126.13, 125.81, 125.72, 124.47, 68.65, 44.35, 37.39, 37.34, 34.39, 33.64, 32.21, 26.64, 22.70, 15.25, 14.10. HRMS (FAB, m/z): Calc. 798.5376. Found: 798.4280. Specific rotation: $[\alpha]_{589}^{25} = -25.29 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$.

6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl (6). **5** (2.0 g, 4 mmol), and CuCl (2.38 g, 24 mmol) was stirred in DMF at 110 °C for 3 days. The organic solvent was evaporated and the residue was extracted with H_2O and $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4 . Purification by silica gel column chromatography (n -hexane / $CHCl_3 = 1$) afforded **6** (1.59 g, 97%) of white powder. 1H -NMR ($CDCl_3$, 400 MHz, δ from TMS, ppm): 7.80 (d, $J = 2.0$ Hz, 2H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.3$ Hz, 2H), 7.02 (d, $J = 8.3$ Hz, 2H), 6.95 (d, $J = 10.0$ Hz, 2H), 4.03 (m, 4H), 1.04 (m, 6H). ^{13}C -NMR ($CDCl_3$, 100 MHz, δ from TMS, ppm): 154.26, 132.16, 129.54, 129.01, 128.28, 126.84, 126.82, 119.97, 116.40, 65.00, 14.88. HRMS (FAB, m/z): Calc. 410.0840. Found: 410.0834.

4,4'-dibromo-6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl (7). Bromine (4 mL, 77.6 mmol) was dropwised to a solution of **6** (1.59 g, 3.88 mmol) in CH₂Cl₂ at – 78 °C over 1 hour. The reaction mixture was warmed to room temperature. Excess bromine was quenched with saturated Na₂S₂O₃ aqua solution at 0 °C. The residue extracted with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. Purification by silica gel column chromatography (*n*-hexane / CHCl₃ = 1) afforded white powder of **7** (1 g, 100%). ¹H-NMR (CDCl₃, 400 MHz, δ from TMS, ppm): 8.22 (d, *J* = 2.2 Hz, 2H), 7.73 (s, 2H), 7.17 (d, *J* = 2.2 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 4.03 (m, 4H), 1.04 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ from TMS, ppm): 153.87, 132.64, 130.94, 128.30, 127.92, 127.1, 126.0, 122.32, 120.3, 65.29, 14.8. HRMS (FAB, *m/z*): Calc. 567.9030. Found: 567.9054.

4,4'-PCH5-6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl (8). **7** (1 g, 1.76 mmol), **2** (1.18 g, 4.3 mmol), NaHCO₃ (0.89 g, 10.6 mmol), and a catalytic amount of Pd(PPh₃)₄ were added to the reaction mixture. The mixture was refluxed in H₂O (30 mL) and THF (30 mL) for 4 hours, and then it was washed several times with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The organic solvent removed by rotary evaporation. Purification by silica gel column chromatography (*n*-hexane / CHCl₃ = 1) afforded white powder of **8** (3.43 g, 95%). ¹H-NMR (CDCl₃, 400 MHz, δ from TMS, ppm): 7.91(d, *J* = 2.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 3.0 Hz, 6H), 7.16 (m, 4H), 6.95 (d, *J* = 10.0 Hz, 2H), 4.03 (m, 4H), 2.6 (t, *J* = 10.0 Hz, 2H), 2.0 (d, *J* = 11.0 Hz, 8H), 1.60 (m, 4H), 1.33 (m, 18H), 1.1 (m, 10H), 0.92 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ from TMS, ppm): 153.73, 147.24, 140.93, 137.41, 132.72, 129.78, 129.28, 128.12, 127.29, 126.82, 126.72, 124.91, 117.45, 65.0, 44.42, 37.40, 37.37, 34.40, 33.65, 32.22, 26.67, 22.72, 14.98, 14.11. HRMS (FAB, *m/z*): Calc. 866.4596. Found: 866.4582.

4,4'-PCH5-2,2'-diethoxy-1,1'-binaphthyl (D-4,4'). **8** (1 g, 1.2 mmol), ammonium formate (2.27 g, 36 mmol) and Pd/C (10 wt% Pd, 5 mol%) were refluxed in 2-methoxyethanol (100 mL) at 80 °C for overnight. The mixture was cooled down and the Pd/C catalyst was filtered off. The

residue was washed several times with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The organic solvent removed by rotary evaporation. Purification by silica gel column chromatography (*n*-hexane / CHCl₃ = 1) afforded white powder of **D-4,4'** (0.83 g, 90%). ¹H-NMR (CDCl₃, 400 MHz, δ from TMS, ppm): 7.94 (d, *J* = 1.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 6H), 7.28 (m, 4H), 4.03 (m, 4H), 2.6 (t, *J* = 10.0 Hz, 2H), 2.0 (d, *J* = 11.0 Hz, 8H), 1.60 (m, 4H), 1.33 (m, 18H), 1.1 (m, 10H), 0.92 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ from TMS, ppm): 153.60, 146.82, 141.33, 138.28, 134.55, 129.96, 127.53, 126.04, 125.84, 125.72, 123.20, 116.88, 65.12, 44.43, 37.41, 37.39, 34.45, 33.69, 32.23, 26.67, 22.72, 15.07, 14.12. HRMS (FAB, *m/z*): Calc. 798.5376. Found: 798.5365. Specific rotation: $[\alpha]_{589}^{25} = +10.68 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$.

6,6'-PCH5-2,2'-diethoxy-1,1'-binaphthyl (D-6,6'). **5** (1 g, 2 mmol), **2** (1.37 g, 5 mmol), NaHCO₃ (0.67 g, 8 mmol), and a catalytic amount of Pd(PPh₃)₄ were refluxed in H₂O (50 mL) and THF (50 mL) for overnight. The reaction mixture was washed several times with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The organic solvent removed by rotary evaporation. Purification by silica gel column chromatography (*n*-hexane / CHCl₃ = 1) afforded white powder of **D-6,6'** (3.8 g, 95%). ¹H-NMR (CDCl₃, 400 MHz, δ from TMS, ppm): 8.04 (s, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 4H), 7.46 (m, *J* = 8.8 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.07 (m, 4H), 2.5 (t, *J* = 12.0 Hz, 2H), 1.94 (d, *J* = 16.0 Hz, 8H), 1.51 (m, 4H), 1.31 (m, 18H), 1.09 (m, 10H), 0.91 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ from TMS, ppm): 154.19, 146.56, 138.59, 135.95, 133.12, 129.38, 129.22, 127.10, 126.89, 125.85, 125.68, 125.27, 120.43, 116.09, 65.20, 44.27, 37.38, 37.32, 34.35, 33.62, 32.21, 26.63, 22.69, 15.02, 14.09. HRMS (FAB, *m/z*): Calc. 798.5376. Found: 798.5378. Specific rotation: $[\alpha]_{589}^{25} = -24.33 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$.

Ethyl 4-(decyloxy)benzoate (9). Ethyl 4-hydroxybenzoate (10 g, 60.178 mmol) and K₂CO₃ (20.79 g, 150.44 mmol) were dissolved in acetone (150 mL). Bromodecane (10.46 mL, 50.148 mmol) and 18-crown-6-ether added to solution, and the mixture was stirred for 12 h at 60 °C. After

12 h, the reaction mixture was extracted with H₂O and CHCl₃. After dealing with brine, the organic layer was dried over with Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using CHCl₃ / *n*-hexane = 1 as an eluting agent to give a colorless oil, **9** (15 g, 97%). ¹H-NMR (400 MHz, CDCl₃, δ from TMS, ppm) : 0.87-0.90 (t, 3H, CH₃), 1.27-1.46 (m, 17H, CH₂, CH₃), 1.76-1.83 (m, 2H, OCH₂-CH₂), 3.98-4.01 (t, 2H, OCH₂-CH₂-), 4.31-4.37 (q, 2H, OCH₂-CH₃-), 6.88, 7.97 (d, 4H, *J* = 8.792 Hz, Ar-*H*).

4-(Decyloxy)benzoic acid (10). **9** was dissolved in methanol / H₂O = 1 / 1, and KOH (3 eq) was added to solution. The reaction mixture is refluxed for 6 h at 75 °C. The reaction mixture was concentrated with a rotary evaporator, and diethyl ether was added to dissolve the residue. This solution was acidified with concentrated HCl, additional diethyl ether was added until all precipitate was dissolved. The organic layer was separated, the aqueous layer was extracted three times with H₂O and diethyl ether, and dried over with Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was purified by recrystallisation from ethanol to give a white powder, **10** (12.56 g, 90%). ¹H-NMR (400 MHz, CDCl₃, δ from TMS, ppm) : 0.87-0.90 (t, 3H, CH₃), 1.27-1.46 (m, 14H, CH₂), 1.79-1.82 (m, 2H, Ar-OCH₂-CH₂-), 4.01-4.04 (t, 2H, Ar-OCH₂-), 6.92, 8.04 (d, 4H, *J* = 8.792 Hz, Ar-*H*). HRMS (FAB, *m/z*) : Calc. for 278.1882. Found : 278.1893.

4-{(Tetrahydro-2H-pyran-2-yl)oxy}phenol (11). 3,4-Dihydro-pyran (4.2 g, 49.93 mmol) in 20ml of anhydrous THF was added dropwisely to a stirred solution of hydroquinone (5 g, 45.41 mmol) and pyridinium *p*-toluene sulfonate (PPTS) (1.14 g, 4.541 mmol) in 100 mL of anhydrous THF for 16 h at room temperature. The reaction mixture was extracted with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using ethyl acetate / *n*-hexane = 1 / 2 as an eluting agent to give a white powder, **11** (4.3755 g, 49.6%). ¹H-NMR (400 MHz, CDCl₃, δ from TMS, ppm) : 1.61-1.99 (m, 6H, CH₂), 3.58-3.94 (m, 2H, tetrahydro pyrane, OCH₂-),

5.31 (t, 1H, $J = 11.968$ Hz, Ar-OCH-), 6.68, 6.89 (d, 4H, $J = 8.548$ Hz, Ar-H). HRMS (FAB, m/z) :
Calc. for 194.0943. Found : 194.0939.

2-[4-{(4-Methylpentyl)oxy}phenoxy]tetrahydro-pyran (12). The solution of **11** (4.5 g, 23.17 mmol), 4-methylpentan-1-ol (3.46 mL, 27.8 mmol), and triphenylphosphine (TPP) (7.9 g, 30.12 mmol) in anhydrous THF (50 mL) was added dropwise to an diethyl azodicarboxylate (DEAD) (15.8 mL, 34.76 mmol) at 0 °C. It was allowed to reach room temperature overnight and extracted with H₂O and CHCl₃. The organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using CHCl₃ / *n*-hexane = 1 / 1 as an eluting agent to give a white powder, **12** (5 g, 78%). ¹H-NMR (400 MHz, CDCl₃, δ from TMS, ppm) : 0.87-0.93 (d, 6H, CH₃), 1.21-1.98 (m, 11H, CH, CH₂), 3.55-3.94 (m, 4H, tetrahydro pyrane, OCH₂-), 5.31 (s, 1H, Ar-OCH-), 6.73-6.79 (m, 4H, Ar-H). HRMS (FAB, m/z) : Calc. for 278.1882. Found : 278.1817.

4-{(4-Methylpentyl)oxy}phenol (13). **12** was dissolve in ethanol (100 mL) , and pyridinium *p*-toluene sulfonate (1 eq) was added to solution. The reaction mixture is refluxed for 18 h at 80 °C. The reaction mixture was extracted with H₂O and CHCl₃. The organic layer was dried over with Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using CHCl₃ only as an eluting agent to give a colorless oil, **13** (2.8 g, 80%). ¹H-NMR (400 MHz, CDCl₃, δ from TMS, ppm) : 0.90-0.91 (d, 6H, CH₃), 1.31-1.78 (m, 5H, CH, CH₂), 3.55-3.89 (t, 2H, Ar-OCH₂), 5.83 (s, 1H, Ar-OH), 6.73-6.78 (m, 4H, Ar-H). HRMS (FAB, m/z) : Calc. for 194.1307. Found : 194.1301.

4-{(4-Methylpentyl)oxy}phenyl 4-(decyloxy)benzoate (PhB1). **10** (4.81 g, 17.29 mmol), N,N'-dicyclohexyl carbodiimide (DCC) (3.57 g, 17.29 mmol), and 4-dimethylamino pyridine (DMAP) (2.11 g, 17.29 mmol) were dissolved in anhydrous CH₂Cl₂ (50 mL). **13** (2.8 g, 14.41 mmol) was added to solution mixture and stirred for 12 h at room temperature. The reaction mixture was extracted with H₂O and CHCl₃. The organic layer was dried over with Na₂SO₄. The solvent

and salt was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using CHCl_3 / *n*-hexane = 1 / 1 as an eluting agent to give a white solid, **PhB1** (5 g, 76.3%).
 ^1H -NMR (400 MHz, CDCl_3 , δ from TMS, ppm) : 0.87-0.93 (m, 9H, CH_3), 1.28-1.36 (m, 14H, CH_2), 1.43-1.49 (m, 2H, CH_2), 1.58-1.64 (m, 1H, CH), 1.75-1.83 (m, 4H, Ar- $\text{OCH}_2\text{-CH}_2\text{-}$), 3.93, 4.02 (t, 4H, J = 6.6 Hz, Ar- $\text{OCH}_2\text{-CH}_2\text{-}$), 6.90-6.97 (m, 4H, Ar- H), 7.08, 8.11 (d, 4H, J = 8.8 Hz, Ar- H).
HRMS (FAB, m/z) : Calc. for 454.3083. Found : 454.3070.

Reference

- 1 (a) W. Kuczynski and H. Stegemeyer, *Chem. Phys. Lett.*, 1980, **70**, 123-126; (b) H. Siemensmeyer and H. Stegemeyer, *Chem. Phys. Lett.*, 1988, **148**, 409-412; (c) S.T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.*, 1984, **114**, 151-187; (d) B. Otterholm, C. Alstermark, K. Flatischler, A. Dahlgren, S. T. Lagerwall and K. Skarp, *Mol. Cryst. Liq. Cryst.*, 1987, **146**, 189-216.
- 2 (a) S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 4554-4555; (b) H. Hashimoto, Y. Tanaka and K. Maruoka, *Tetrahedron: Asymmetry*, 2003, **14**, 1599-1602.