Supporting Information

Dramatic Enantioselectivity Reversal in the Propargylation of Aldehyde with Alkynyllithium Catalyzed by Dilithium Binaphtholate Derivatives

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General Methods.

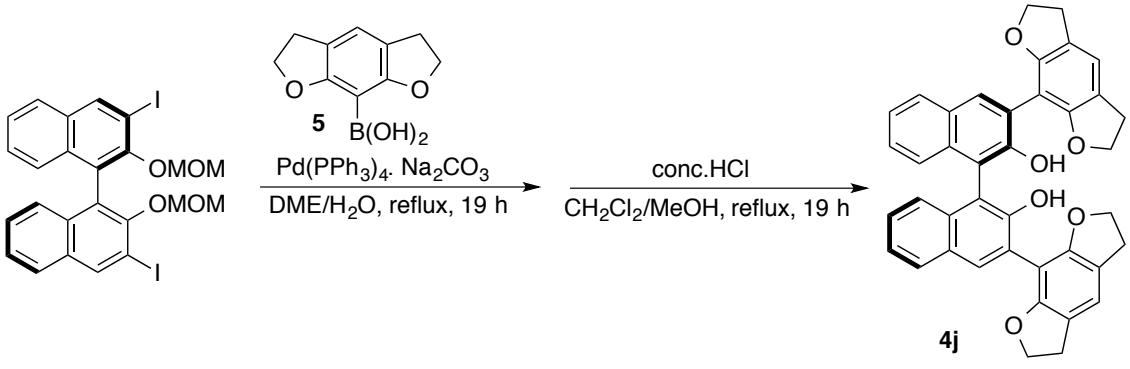
Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with JEOL JNM-ECX400 spectrometer. Tetramethylsilane (TMS) (δ = 0 ppm) and $CDCl_3$ (δ = 77.0 ppm) served as internal standards for ^{1}H and ^{13}C NMR, respectively. Infrared spectra were recorded on JEOL JIR 6500-W. Mass spectra were measured with JEOL JMS-DX303HF mass spectrometer. Optical rotations were recorded on JASCO P-1010 polarimeter. High-pressure liquid chromatography (HPLC) was performed on JASCO P-980 and UV-1575. Thin-layer chromatography (TLC) analysis was carried out using Merck silica gel plates. Visualization was accomplished with UV light, phosphomolybdic acid and/or anisaldehyde. Column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral, 63-210 μm). All the reactions under anhydrous conditions were performed under argon atmosphere using glassware equipped with a rubber septum and a magnetic stirring bar.

Solvents and Chemicals

Dry tetrahydrofuran (dehydrated) was purchased from Kanto Chemical. All the other solvents were purified based on standard procedures. *n*-Butyllithium in hexane was purchased from Kanto Chemical. BINOL derivatives **4a**, **4b**, and **4d**-**4f** were prepared by the literature methods.[1] All other chemicals were purchased and purified based on standard procedures.

Preparation and spectroscopic data for new BINOL derivatives (4c, 4f, 4h-j)

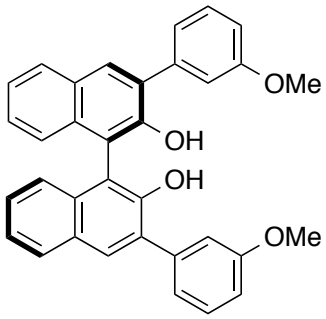
(*R*)-3,3'-Bis(2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b*']difuran-8-yl)-1,1'-binaphthalene-2,2'-diol (4j)



Benzodifuranylboric acid **5**[2] (1.29 g, 6.3 mmol, 2.3 eq.) and aq.Na_2CO_3 (2 M, 7 mL, 14 mmol, 5.0 eq.) were added to a solution of (*R*)-3,3'-diiode-2,2'-bis(methoxymethyl)-1,1'-binaphthalene[1c] (1.70 g, 2.7 mmol) and $Pd(Ph_3)_4$ (156 mg, 0.135 mmol, 5 mol %) in DME (35 mL) under an argon atmosphere. The resulting mixture was heated to reflux for 19 h. After cooling and filtration through a pad of Celite, the aqueous layer was extracted with AcOEt (3 × 50 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and evaporation, column chromatography (CH_2Cl_2, SiO_2, 60 g) furnished colorless needles (1.89 g), which was then dissolved in MeOH/CH_2Cl_2 (10 mL/20 mL). After adding conc. aq. HCl (5 mL), the solution was stirred at room temperature for 3 h. The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layer was washed with sat. aq. $NaHCO_3$ (30 mL) and brine (30 mL), and then dried over Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography (Hex/CH_2Cl_2 = 1/4, SiO_2 70 g) to furnish **4j** as light yellow needles (1.25 g, 76% yield in 2 steps).

mp: 220.0-222.0 °C.
TLC: R_f 0.17 (Hex/AcOEt = 2/1, stained blue with anisaldehyde).
$[\alpha]_D^{28}$ +84.5° (*c* 1.0, $CHCl_3$).
IR (ATR): 3527, 2894, 1599, 1421, 1256, 1045 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 3.20 (t, 8H, *J* = 8.0 Hz, OCH_2CH_2Ar), 4.61 (t, 8H, *J* = 8.0 Hz, OCH_2CH_2Ar), 6.17 (s, 2H, O*H*), 7.02 (s, 2H, Ar-*H*), 7.21-7.32 (m, 6H, Ar-*H*), 7.87 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 8.10 (s, 2H, Ar-*H*).
^{13}C NMR (100 MHz, $CDCl_3$): δ 29.6, 72.3, 104.7, 116.4, 118.7, 119.9, 122.2, 123.5, 125.1, 126.5, 128.3, 128.9, 131.8, 133.6, 150.2, 157.4.
MS (FAB): *m/z* 606 (M^+).
HRMS: Calcd for $C_{40}H_{30}O_6$ 606.2042, found 606.2045.

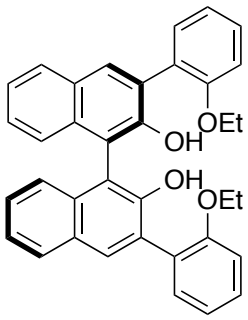
(*R*)-3,3'-Bis(3-methoxyphenyl)-1,1'-binaphthalene-2,2'-diol (4c)



mp: 99.0-101.0 °C.
TLC: R_f 0.41 (hex/AcOEt = 4:1, stained yellow with anisaldehyde).
$[\alpha]_D^{29}$ +51.7° (*c* 1.0, $CHCl_3$).
IR (ATR): 3495, 1597, 1579, 1245, 1123 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 6H, OCH_3), 5.43 (s, 2H, O*H*), 6.92-6.95 (m, 2H, Ar-*H*), 7.21-7.40 (m, 12H,

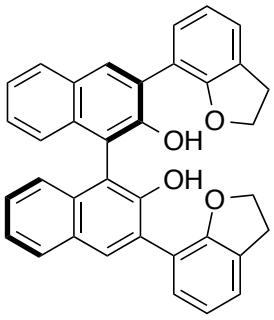
Ar-*H*), 7.89 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 8.00 (s, 2H, Ar-*H*).
^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 112.6, 113.5, 115.1, 121.9, 124.3, 127.3, 128.4, 129.3, 129.5, 130.4, 131.2, 133.0, 138.7, 150.0, 159.6 (one carbon overlapped).
MS (FAB): *m/z* 498 (M^+).
HRMS: Calcd for $C_{34}H_{26}O_4$ 498.1831, found 498.1831.

(*R*)-3,3'-Bis(2-ethoxyphenyl)-1,1'-binaphthalene-2,2'-diol (4g)



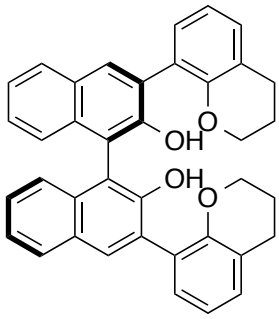
mp: 114.0-116.0 °C.
TLC: R_f 0.83 (Hex/AcOEt = 2/1, stained red with anisaldehyde).
$[\alpha]_D^{30}$ +193.1° (*c* 1.0, $CHCl_3$).
IR (ATR): 3517, 2979, 1595, 1492, 1118 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): 1.30 (t, 6H, *J* = 8.0 Hz, OCH_2CH_3), 4.07 (q, 4H, *J* = 8.0 Hz, OCH_2CH_3), 5.97 (s, 2H, O*H*), 7.02 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.13 (t, 2H, *J* = 6.0 Hz, Ar-*H*), 7.27-7.42 (m, 8H, Ar-*H*), 7.53 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.89 (d, 2H, *J* = 11.0 Hz, Ar-*H*), 7.93 (s, 2H, Ar-*H*).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 64.6, 112.5, 115.5, 121.6, 123.7, 124.8, 126.5, 127.7, 128.2, 129.0, 129.2, 129.4, 131.1, 132.3, 133.4, 150.5, 155.8.
MS (FAB): *m/z* 526 (M^+).
HRMS: Calcd for $C_{36}H_{30}O_4$ 526.2144, found 526.2148.

(*R*)-3,3'-Bis(2,3-dihydrobenzo[*b*]furan-7-yl)-1,1'-binaphthalene-2,2'-diol (4h)



mp: 242.0-244.0°C.
TLC: R_f 0.48 (Hex/AcOEt = 2/1, stained purplish red with anisaldehyde).
$[\alpha]_D^{24}$ +65.3° (*c* 1.0, $CHCl_3$).
IR (ATR): 3527, 2962, 1424, 1192 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (t, 4H, *J* = 8.0 Hz, OCH_2CH_2Ar), 4.62 (t, 4H, *J* = 8.0 Hz, OCH_2CH_2Ar), 6.31 (s, 2H, O*H*), 7.03 (t, 2H, *J* = 8.0 Hz, Ar-*H*), 7.27-7.36 (m, 6H, Ar-*H*), 7.45 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.90 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 8.06 (s, 2H, Ar-*H*).
^{13}C NMR (100 MHz, $CDCl_3$): δ 29.8, 71.4, 116.2, 120.4, 121.3, 123.8, 124.6, 124.9, 126.7, 127.0, 127.1, 128.2, 129.2, 130.2, 131.0, 133.5, 150.1, 156.5.
MS (FAB): *m/z* 522 (M^+).
HRMS: Calcd for $C_{36}H_{26}O_4$ 522.1831, found 522.1853.

(*R*)-3,3'-Bis (3,4-dihydro-2*H*-1-benzopyran-8-yl)-1,1'-binaphthalene-2,2'-diol (4i)



mp: 269.0-271.0 °C.

TLC: R_f 0.54 (Hex/AcOEt = 2/1, stained red with anisaldehyde).

$[\alpha]_D^{27}$ +72.6° (*c* 1.0, $CHCl_3$).

IR (ATR): 3509, 2932, 1424, 1223, 1188, 1077 cm^{-1}.

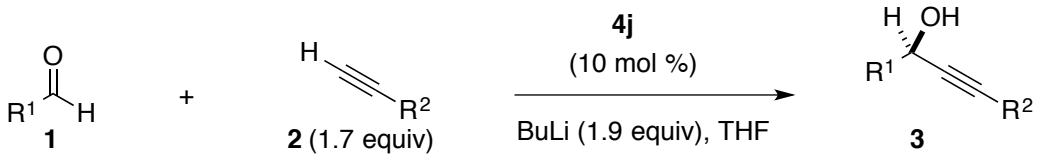
^1H NMR (400 MHz, $CDCl_3$): 2.00-2.03 (m, 4H, $OCH_2CH_2CH_2$), 2.85 (t, 4H, *J* = 6.4 Hz, OCH_2 CH_2CH_2), 4.45-4.50 (m, 4H, $OCH_2CH_2CH_2$), 6.92 (t, 2H, *J* = 7.6 Hz, O*H*), 7.06 (d, 2H, *J* = 6.9 Hz, Ar-*H*), 7.26-7.29 (m, 4H, Ar-*H*), 7.36-7.40 (m, 4H, Ar-*H*), 7.85 (d, 2H, *J* = 8.3 Hz, Ar-*H*), 7.88 (s, 2H, Ar-*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 25.0, 67.0, 115.5, 120.6, 122.5, 123.6, 124.9, 126.4, 126.5, 128.2, 128.7, 129.2, 129.9, 130.1, 131.1, 133.4, 150.4, 151.8.

MS (FAB): *m/z* 550 (M^+).

HRMS: Calcd for $C_{36}H_{30}O_4$ 550.2144, found 550.2145.

Typical Procedure for the Enantioselective Propargylation.



Under argon atmosphere, *n*-BuLi (1.6 M in hexane, 0.59 mL, 0.95 mmol) was added to a solution of **4j** (31 mg, 0.050 mmol) and phenylacetylene (**2a**) (0.10 mL, 0.85 mmol) in THF (1 mL) at -78 °C. To the mixture was added aldehyde **1h** (98 mg, 0.50 mmol) in THF (1 mL) over 10 min using syringe pump. The solution was stirred for an additional 20 min. The reaction was quenched with sat. aq. NH_4Cl and the mixture was extracted with AcOEt (3 × 10 mL). The organic layer was washed with brine. After drying over Na_2SO_4, the solvent was removed, and the residue was purified by silica gel column chromatography (Hex/CH_2Cl_2=1/1 SiO_2 5 g), affording **3ha** (144 mg, 97% yield) as a colorless oil. The ee was determined by chiral HPLC (Chiralcel OD-H [eluent: Hex/IPA = 2/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 6.9 min (major, *R*), 16.4 min (minor, *S*)]) to be 93% ee. $[\alpha]_D^{23}$ +5.8° (*c* 1.2, $CHCl_3$) [lit.[4]: $[\alpha]_D^{19}$ -6.1° (*c* 1.3, $CHCl_3$), 82% ee, *S*].

References

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2. G. Xu, M. Li, M. S. Wang, and W. Tang, *Org. Chem. Front.*, 2015, **2**, 1342. Benzodifuranylboric acid **5** was prepared from the correspoding benzodifuran.[3]
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4. S. Kotani, K. Kukita, K. Tanaka, T. Ichibakase, and M. Nakajima, *J. Org. Chem.*, 2014, **79**, 4817.