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Facile Preparation of Optically Pure 7,7′-Disubstituted BINOLs and Their Application in Asymmetric Catalysis

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Abstract: A family of optically pure 7,7′-disubsituted-2,2′-dihydroxy-1,1′-dinaphthyls have been conveniently prepared from easily accessible 7-alloxyl-2-naphthol by reaction sequences beginning with the asymmetric oxidative coupling and followed by key synthetic steps including deprotection, alkylation, and Suzuki coupling. Application of these binaphthols in catalytic phenylacetylene addition to aldehydes resulted in excellent enantioselectivities.

Optically pure 1,1′-binaphthol and its derivatives have been proven to be versatile chiral auxiliaries and ligands in a great number of asymmetric transformations with exciting stereoselectivities. Research on this area has provided many efficient and useful methods for the preparation of key chiral building blocks, some of which have been used for the construction of complex natural products.[1] In addition, some chiral organic materials have been prepared starting with them.[2] Subtle variation of dihedral angle or electrical densities of binaphthols and their analogues generally leads to the improvement of catalytic performance of the ligand.[3] Functionalization of BINOL at its 3,6-positions has furnished many efficient chiral ligands that have been used in numerous successful asymmetric transformations.[2a,4] Compared with the 3,6-substituted binaphthols, 7,7′-disubsituted binaphthols have much more easily tunable dihedral angles by changing the substituent size. Thus, a convenient method to easily approach 7,7′-disubsituted binaphthol is of great interest for asymmetric catalysis and organic material. However, reports on the syntheses of optically pure 7,7′-disubstituted binaphthols are scarce due to their synthetic challenges.[5] Here we will report a practical method for preparing optically pure 7,7′-disubstituted binaphthols based on our chiral oxovanadium complex **1** catalyzed asymmetric oxidative coupling of 2-naphthols.[6] The application of these 7,7′-disubstituted binaphthols in phenylacetylene additon to aldehydes will also be presented.

Preparation of 7,7′-disubstituted binaphthols: In the presence of 5 mol % of catalyst **1** that was developed in our laboratory,[6] the asymmetric oxidative coupling of 7-alloxyl-2-naphthol (**2**) in 5.0-g scale gave chiral 7,7′-dialloxyl-2,2′-dihydroxy-1,1′-dinaphthyl (**3**) in nearly quantitive yield with 95% ee, without loss of the enantioselectivity with respect to the small scale. After recrystallization, optically pure **3**, which is an important chiral starting material for the following synthesis, was obtained in 95% yield.[6] The treatment of optically pure **3** with methoxymethyl chloride (MOMCl) in the presence of excess sodium hydride (NaH) gave compound **4**. After removal of allyl groups from compound **4** by a palladium-catalyzed deprotection strategy,[7] the optically pure key synthetic intermediate **5** was provided in 90% yield (Scheme 1).

Alkylations of **5** with alkylbromides in the presence of a stoichiometric amount of CsOH in DMF at room temperature smoothly furnished compounds **6**. Without further purification, compounds **6** were directly subjected to hydrolysis with 6 N HCl in a solvent mixture of chloroform and ethanol at 65 °C, providing 7,7′-dialkoxyl-2,2′-dihydroxy-1,1′-dinaphthyl (**7**) in high yields ranging from 85% to 93% (2 steps) (Scheme 2).

Optically pure cyclo-disubsituted binaphthols (**8** and **9**) at 7,7′-positions linked by alkyl or crown ether were also furnished by reactions of **5** with alkyl dibromides or

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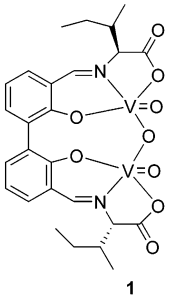

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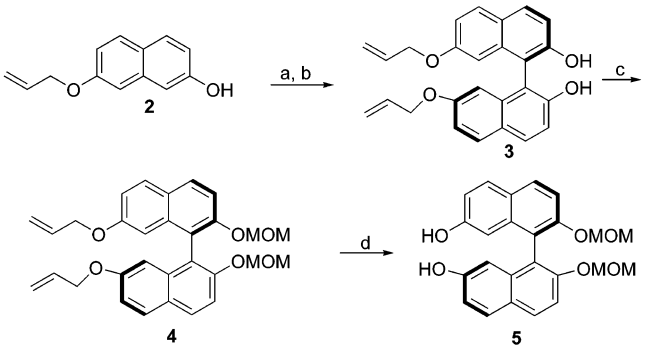
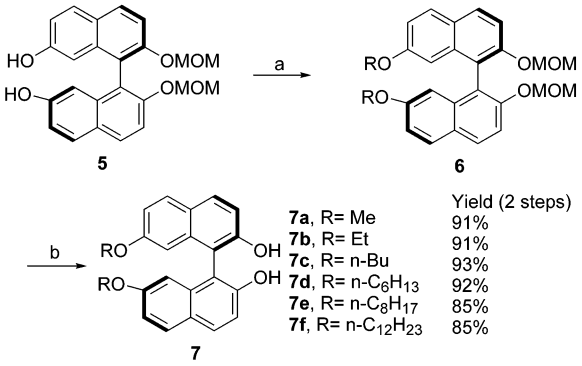
FIGURE 1. The catalyst used for this study.

SCHEME 1. Preparation of Compound 5[a]



[a] Reaction conditions: (a) 5 mol % of **1**, O_2, CCl_4, 0 °C, 99% yield, 95% ee; (b) recrystallization (solvent: EtOAc/PE = 1/20), 95% yield, >99% ee; (c) CH_3OCH_2Cl (MOMCl), NaH, THF, 0 °C to rt; (d) 1 mol % of $Pd(PPh_3)_4$, K_2CO_3, MeOH, reflux, 90%.

SCHEME 2. The Syntheses of 7,7′-Dialkoxyl-2,2′-dihydroxy-1,1′-dinaphthyls (7)[a]

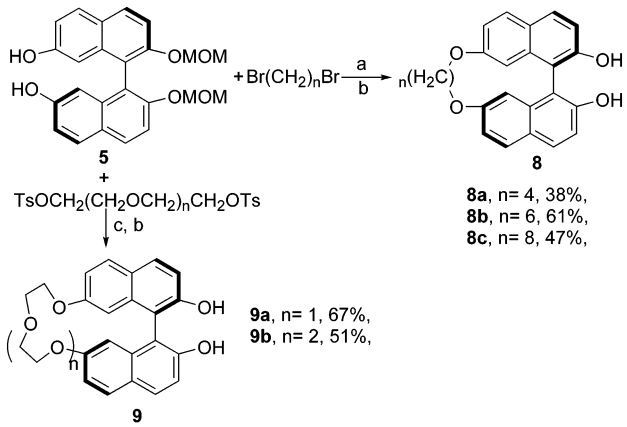


[a] Reaction conditions: (a) RBr, CsOH, DMF, rt, 2 h; (b) aqueous HCl, $CHCl_3$/EtOH, 65 °C, 2 h.

multiethylene glycol ditosylate and subsequent hydrolysis with 6 N HCl (Scheme 3). The yields of products were sharply dependent on the ring size. The yield is somewhat sacrificed when the ring size is too small or big. For example, moderate yields of 38% and 47% were observed with **8a** and **8c**, respectively.

A convenient reaction of **5** with trifluoromethanesulfonic anhydride in the presence of Et_3N at 0 °C led to **10** with 87% yield. Suzuki coupling of **10** with phenylboronic acid in the presence of 10 mol % of $Pd(PPh_3)_4$ and with K_3PO_4 as base at 80 °C for 24 h furnished the coupling products.[8] Without purification in this step, the crude product was subjected to a hydrolysis with 6 N HCl to give **11** with total 67% yield (Scheme 4).

SCHEME 3. The Preparation of Optically Pure Cyclo-Disubsituted Binaphthols 8 and 9[a]



[a] Reaction conditions: (a) CsOH, DMF, rt, 2 h; (b) aqueous HCl, $CHCl_3$/EtOH, 65 °C, 2 h. (c) CsOH, DMF, 80 °C, 5 h.

To determine the absolute configuration of the binaphthols, a dehydroxylation of **10** was performed in the presence of 1 mol % of $Pd(PPh_3)_4$ with HCO_2H as the hydrogen source and $^iPr_2NEt$ as the base to give (*R*)-BINOL (Scheme 5).[9] Therefore the 7,7′-disubstituted binaphthols (**3**, **7**−**9**, and **11**) were assigned to the (*R*)-configuration.

Enantioselective phenylacetylene addition to aldehydes catalyzed by Ti(IV) complexes of 7,7′-disubstituted binaphthols: These chiral 7,7-disubstituted BINOLs **7**−**9** and **11**, in combination with $Ti(O^iPr)_4$, were then surveyed to catalyze enantioselective phenylacetylene addition to aldehydes under the reported optimal conditions.[10] The results were summarized in Table 1.

Most of the 7,7′-disubstituted binaphthols exhibited high enantioselectivities of more than 90% ee (entries 2−11). Of them, **3** and **11** provided similar ee values as BINOL under the same reaction conditions (entries 1, 2, and 14). The substituent size on the ligand has no obvious influence on the enantioselectivity. Enantioselectivities ranging from 90% to 94% ee were provided by **7a**−**f**. Comparison of the results from **8a**−**c** implied that variation of dihedral angle by changing the ring size did not lead to any influence on the enantioselectivity (entries 9−11). However, reactions catalyzed by Ti(IV) complexes of **9a**,**b**, which were substituted by crown ether moiety at their 7,7′-positions, provided lower enantioselectivities (entries 12 and 13). The lower enantioselectivities might be due to the coordination of zinc with the crown ether of **9a**,**b.**

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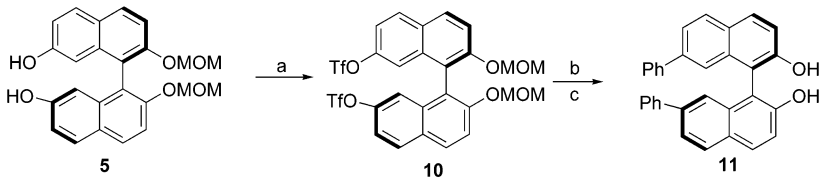
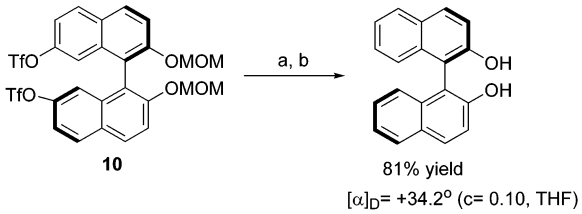
SCHEME 4. The Synthesis of 11 by Suzuki Coupling[a]



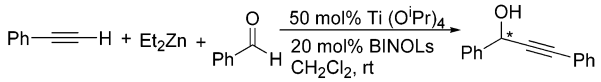
[a] Reaction conditions: (a) Tf_2O, Et_3N, 0 °C to rt, 87%; (b) 10 mol % of $Pd(PPh_3)_4$, $PhB(OH)_2$, K_3PO_4, DME, 80 °C; (c) aqueous HCl, $CHCl_3$/EtOH, 65 °C, 2 h, 67% (2 steps).

SCHEME 5. The Determination of Absolute Configuration of New BINOLs[a]



[a] Reaction conditions: (a) 1 mol % of $Pd(PPh_3)_4$, $^iPr_2NEt$, HCO_2H, DMF, 80 °C; (b) aqueous HCl, $CHCl_3$/EtOH, 65 °C, 2 h.

TABLE 1. Enantioselective Phenylacetylene Addition to Benzaldhyde by Ti(IV)-BINOLs



entry	BINOLs	yield (%)	ee (%)[a]	entry	BINOLs	yield (%)	ee (%)[a]
1	BINOL	79	95	8	**7f**	89	90
2	**3**	91	95	9	**8a**	82	92
3	**7a**	92	92	10	**8b**	88	92
4	**7b**	78	94	11	**8c**	75	92
5	**7c**	72	91	12	**9a**	89	87
6	**7d**	84	92	13	**9b**	91	88
7	**7e**	79	94	14	**11**	93	95

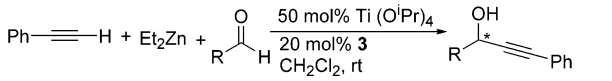
[a] The ee values were determined on HPLC.

The Ti(IV) complex of the optimal chiral ligand **3** was then extended to the catalytic enantioselective phenylacetylene additon to various types of aldehydes, including aromatic aldehydes, aliphatic aldehydes, and an α,β-unsaturated aldehyde. The results are given in Table 2.

All of examined aldehydes reacted smoothly with the combined reagent of diethylzinc and phenylacetylene to give high yields and excellent enantioselectivities. The enantioselectivity was not significantly dependent on the structure of the aldehyde. Enantioselectivities ranging from 91% to 95% ee were observed with Ti(IV)-**3** for all of the tested aldehydes.

In summary, a family of optically pure binaphthols has been prepared on the basis of our chiral oxovanadium complex **1** catalyzed asymmetric oxidative coupling of 7-alloxyl-2-naphthol. Most of their Ti(IV) complexes exhibited high enantioselectivity for the catalytic enantioselective phenylacetylene additon to benzaldehyde. 7,7′-Dialloxyl-2,2′-dihydroxy-1,1′-dinaphthyl (**3**), prepared directly from the asymmetric oxidative coupling, was applied in the catalytic phenylacetylene additon to aldehydes with excellent enantioselectvities of up to 95% ee. The results imply that these binaphthols have a high level of stereocontrol in some asymmetric catalytic transformations.

TABLE 2. Enantioselective Phenylacetylene Addition to Aldhydes Catalyzed by Ti(IV)-3



entry	aldehyde R =	yield (%)	ee (%)[a]	entry	aldehyde R =	yield (%)	ee (%)[a]
1	Ph	91	95	6	*trans*-PhCH=CH	69	93
2	4-MeC_6H_4	71	92	7	3-MeC_6H_4	80	92
3	α-Naph	83	94	8	4-$MeOC_6H_4$	93	91
4	piperonyl	87	92	9	^{i}Pr	64	92[b]
5	4-ClC_6H_4	79	93	10	^{n}Bu	73	93[b]

[a] The ee values were determined on HPLC. [b] Reactions were carried out in the presence of 100 mol % of $Ti(O^iPr)_4$ and 40 mol % of **3** in Et_2O.

Experimental Section

General. The Kromasil CHI-TBB column was purchased from Eka Chemicals AB. Chemicals were purchased from Acros and used directly. Dichloromethane (CH_2Cl_2) and carbon tetrachloride (CCl_4) were dried over CaH_2. Petroleum ether (PE) and ethyl acetate for column chromatography were distilled before use.

Preparation of Optically Pure 7,7′-Dialloxyl-2,2′-dihydroxy-1,1′-dinaphthyl (3). To a solution of chiral vanadium catalyst (892.5 mg, 1.45 mmol) in CCl_4 (100 mL) was added 7-alloxyl-2-naphthol (5.0 g, 25 mmol), and the resulting mixture was stirred at 0 °C under O_2 for about 4−6 days until the reaction was complete (monitored by TLC). After removal of solvent, the residue was purified by column chromatography on silica gel (R_f 0.35, ethyl acetate/PE = 1:5) to give crude **3** (5.0 g) in 95% ee. The crude **3** was dissolved in a solvent mixture of ethyl acetate (10 mL) and petroleum ether (200 mL). After the solution remained at room temperature for 5 h, some precipitate (**3** in lower than 10% ee) formed. Removal of the precipitate and concentration of the mother solution yielded 7,7′-dialloxyl-2,2′-dihydroxy-1,1′-dinaphthyl (**3**) (4.7 g, 95%) as a colorless sticky oil, $[\alpha]^{20}_D$ −234.8 (*c* 1.13, $CHCl_3$), >99% ee determined by HPLC (Chromasil CHI-TBB column, 10% IPA in hexane, flow rate 0.25 mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.25 (m, 4H), 5.05 (s, 2H), 5.12 (m, 4H), 5.88(m, 2H), 6.48 (d, J = 2.1 Hz, 2H), 7.05 (dd, J = 8.8, 2.1 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHZ, $CDCl_3$) δ (ppm) 68.6, 104.4, 109.9, 115.1, 116.3, 118.0, 124.7, 129.8, 130.9, 132.7, 134.6, 153.2, 157.9; MS (EI) *m*/*z* 398 (M^+); HRESI-MS (positive ion) $C_{26}H_{23}O_4$ ($[M + H]^+$) requires 399.1596, found 399.1591. IR (KBr) *v* 3502, 3078, 1620, 1512, 1452, 1270, 1214, 1022 cm^{-1}. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.45; H, 5.78.

Synthesis of 7,7′-Dihydroxyl-2,2′-bis(methoxymethoxy)-1,1′-dinaphthyl (5). To a suspension of NaH (1.92 g, 0.04 mol) in dry THF (100 mL) was slowly added a solution of **3** (4.0 g, 0.01 mol) in THF (20 mL). After the reaction mixture was stirred for 30 min, MOMCl (3.54 mL, 0.04 mmol) was added dropwise. After the reaction solution was stirred for 5 h, the reaction was

quenched with saturated aqueous Na_2CO_3 (50 mL). The organic layer was separated, and the aqueous solution was extracted with ethyl acetate (100 mL × 2). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was added to the solution of $Pd(Ph_3P)_4$ (115.5 mg) and K_2CO_3 (8.28 g) in MeOH (100 mL). After the mixture was refluxed for about 5 h, the yellow solution was concentrated and purified by column chromatography on silica gel (R_f 0.42, ethyl acetate/PE = 1:2) to yield **5** as pale yellow needle crystal (3.8 g, 90%), mp 185.9−188.3 °C; $[\alpha]^{20}_D$ +3.8 (*c* 0.912, $CHCl_3$). ^{1}HNMR (300 MHz, acetone-d_6) δ (ppm) 3.16 (s, 6H), 4.99 (d, J = 6.8 Hz, 2H), 5.08 (d, J = 6.8 Hz, 2H), 6.40 (d, J = 2.4 Hz, 2H), 6.99 (dd, J = 8.7, 2.4 Hz, 2H), 7.41 (d, J = 9.0 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 9.0 Hz, 2H), 8.34 (s, 2H); ^{13}CNMR (75 MHz, acetone-d_6) δ (ppm) 55.8, 95.5, 107.6, 114.8, 117.3, 120.5, 125.8, 129.6, 130.5, 136.6, 154.1, 156.6; MS (EI) m/z 406 (M^+); HRESI-MS (positive ion) $C_{24}H_{22}O_6Na$ ($[M + Na]^+$) requires 429.1314, found 429.1309. IR (KBr) υ 3365, 3286, 3060, 2923, 2850, 1624, 1511, 1237, 1078 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 71.00; H, 5.46.

8a: R_f 0.37 (ethyl acetate/PE = 1:3), yield 38%, white solid, mp 218.7−219.2 °C; $[\alpha]^{20}_D$ −647.8 (*c* 0.14, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.26−1.36 (m, 2H), 1.54−1.64 (m, 2H), 3.75−3.84 (m, 2H), 4.19−4.27 (m, 2H), 5.40 (br, 2H), 6.78 (d, J = 2.3 Hz, 2H), 7.09 (dd, J = 8.8, 2.3 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 22.2, 68.8, 110.2, 113.6, 116.1, 117.7, 125.7, 130.1, 131.2, 134.3, 152.7, 155.1; MS (EI) m/z 371 ($M^+ - H$); HRESI-MS (positive ion) $C_{24}H_{21}O_4$ ($[M + H]^+$) requires 373.1440, found 373.1434. IR (KBr) υ 3429, 3068, 2950, 2883, 1620, 1510, 1441, 1265, 1194 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.51; H, 5.40.

8b: R_f 0.47 (ethyl acetate/PE = 1:3), yield 61%; white solid, mp 253.7 °C dec; $[\alpha]^{20}_D$ −453.9 (*c* 0.128, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.19−1.27 (m, 4H), 1.33−1.36 (m, 2H), 1.42−1.46 (m, 2H), 3.81−3.88 (m, 2H), 3.99−4.04 (m, 2H), 5.32 (br, 2H), 6.51 (d, J = 2.3 Hz, 2H), 7.05 (dd, J = 8.9 Hz, 2.4 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 23.2, 27.4, 67.0, 109.0, 110.1, 115.4, 116.4, 124.9, 129.9, 131.1, 134.8, 152.8, 157.2; MS (EI) m/z 400 (M^+); HRESI-MS (positive ion) $C_{26}H_{25}O_4$ ($[M + H]^+$) requires 401.1753, found 401.1747. IR(KBr) υ 3504, 3066, 2932, 2903, 1620, 1510, 1451, 1265, 1203, 1062 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 78.09; H, 6.28.

8c: R_f 0.18 (ethyl acetate/PE = 1:5), yield 47%; white solid, mp 95.5−96.4 °C dec; $[\alpha]^{20}_D$ −360.9 (*c* 0.112, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ (ppm) 1.03−1.11 (m, 4H), 1.23−1.27 (m, 4H), 1.41−1.51 (m, 4H), 3.77−3.91 (m, 4H), 5.14 (s, 2H), 6.45 (d, J = 2.4 Hz, 2H), 7.03 (dd, J = 8.8 Hz, 2.4 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 24.3, 27.6, 27.4, 66.7, 105.9, 109.9, 115.0, 116.2, 124.7, 129.9, 131.1, 135.1, 153.0, 157.8; MS (EI) m/z 428 (M^+); HRESI-MS (positive ion) $C_{28}H_{29}O_4$ ($[M + H]^+$) requires 429.2066, found 429.2061. IR (KBr) υ 3448, 3061, 2932, 2858, 1621, 1512, 1452, 1214, 1066 cm^{-1}. Anal. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59. Found: C, 78.27; H, 6.53.

9a: R_f 0.40 (ethyl acetate/PE = 1:2), yield 67%, white solid, mp 89.5 °C dec; $[\alpha]^{20}_D$ −485.7 (*c* 0.112, $CHCl_3$). ^{1}H NMR (75 MHz, acetone-d_6) δ (ppm) 3.38−3.46 (m, 4H), 3.80−3.85 (m, 2H), 4.08−4.11 (m, 2H), 6.81 (d, J = 2.4 Hz, 2H), 6.88 (dd, J = 8.8, 2.4 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm) 67.6, 74.4, 109.7, 114.7, 117.9, 118.5, 126.2, 130.8, 131.1, 136.9, 155.5, 159.2; MS (EI) m/z 388 (M^+); HRESI-MS (positive ion) $C_{24}H_{21}O_5$ ($[M + H]^+$) requires 389.1389, found 389.1384. IR (KBr) υ 3439, 3061, 2945, 2860, 1660, 1620, 1510, 1447, 1210, 1161 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O_5$: C, 74.21; H, 5.19. Found: C, 73.98; H, 5.32.

9b: R_f 0.21(ethyl acetate/PE = 1:2), yield 51%, white solid, mp 104.5 °C dec; $[\alpha]^{20}_D$ −390 (*c* 0.278, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.39−3.55 (m, 8H), 3.96−3.99 (m, 4H), 5.30 (br s, 2H), 6.44 (d, J = 2.4 Hz, 2H), 7.06 (dd, J = 8.9, 2.4 Hz, 2H), 7.22 (d, J = 8.9 Hz, 2H), 7.77 (d, J = 8.9 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 67.6, 68.8, 70.9, 105.9, 110.1, 115.2, 116.6, 124.7, 130.0, 131.0, 134.8, 152.8, 157.4; MS (EI) m/z 432 (M^+); HRESI-MS (positive ion) $C_{26}H_{25}O_6$ ($[M + H]^+$) requires 433.1651, found 433.1646. IR (KBr) υ 3450, 3072, 2923, 2869, 1621, 1511, 1445, 1214, 1139 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.48; H, 5.46.

Preparation and characterization of compound 11: To a solution of **5** (203 mg, 0.5 mmol) in CH_2Cl_2 (15 mL) was added triethylamine (101 mg, 1.0 mmol) and triflic anhydride (282 mg, 1.0 mmol) dropwise at 0 °C. After the mixture was stirred at room temperature for 2 h, the reaction was quenched with water (10 mL). The organic layer was separated, washed with 1 N HCl and brine, and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by column chromatography on silica gel (PE:ethyl acetate = 5:1) to yield **10** (292 mg, 87%). The reaction solution of **10** (134 mg, 0.2 mmol), phenylboronic acid (49 mg, 0.4 mmol), K_3PO_4 (212 mg, 1 mmol), and $Pd(PPh_3)_4$ (23 mg, 10% mmol) in DME (30 mL) was stirred at 80 °C for about 24 h. The solution was diluted with water (10 mL) and ethyl acetate (30 mL). The organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was hydrolyzed with 6 N HCl. The reaction was worked up to give **11**. R_f 0.33 (ethyl acetate/PE = 1:3), yield 67%, white solid, mp 98.5−100.2 °C; $[\alpha]^{20}_D$ −547.5 (*c* 0.128, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.12 (s, 2H), 7.26−7.44 (m, 14H), 7.65−7.66 (m, 2H), 7.97−8.02 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 110.9, 117.8, 122.0, 124.0, 127.4, 127.5, 128.4, 128.7, 129.0, 131.3, 133.6, 140.4, 141.0, 153.2; MS (EI) m/z 438 (M^+); HRESI-MS (positive ion) $C_{32}H_{23}O_2$ ($[M + H]^+$) requires 439.1698, found 439.1693. IR (KBr) υ 3502, 3056, 1619, 1512, 1492, 1214, 1164, 1026 cm^{-1}. Anal. Calcd for $C_{32}H_{22}O_4$: C, 87.65; H, 5.06. Found: C, 87.45; H, 4.96.

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Supporting Information Available: Preparation and characterization of **7a**−**f**; general experimental procedure and HPLC analysis for the enantioselective phenylacetylene addition to aldehydes; ^{1}H NMR and ^{13}C NMR spectra for **5**, **7a**−**f**, **8a**−**c**, **9a**,**b** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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