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A facile synthesis of 3 or 3,3′-substituted binaphthols and their applications in the asymmetric addition of diethylzinc to aldehydes

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Abstract

By using a direct ortho-lithiation, the ligands (*S*)-3-methoxymethyl-1,1′-bi-2-naphthol [(*S*)-**1**], (*S*)-3,3′-bis(methoxymethyl)-1,1′-bi-2-naphthol [(*S*)-**2**], (*S*)-3-(quinolin-2-yl)-1,1′-bi-2-naphthol [(*S*)-**3**] and (*S*)-3,3′-bis(quinolin-2-yl)-1,1′-bi-2-naphthol [(*S*)-**4**] have been synthesized. (*S*)-**1** and (*S*)-**3** show moderate catalytic properties for the asymmetric diethylzinc addition to aromatic aldehydes.

Keywords: Lithiation; BINOL; Quinoline; Asymmetric catalysis

1. Introduction

Application of 1,1′-bi-2-naphthol (BINOL) and its derivatives in asymmetric catalysis has been extensively studied [1]. Substituents at the 3-position of BINOL are normally introduced via a two-step protocol that involves treatment of a suitably protected BINOL with an organolithium reagent, followed by reaction with an electrophile. Cram and co-workers synthesized two optical pure 3,3′-diaryl-substituted BINOLs by a Grignard cross-coupling reaction of 3,3′-dibromo-BINOL dimethyl ether and arylmagnesium bromides [2]. Snieckus and co-workers reported an expedient synthetic route to 3 or 3,3′-substituted-1,1′-bi-2-naphthols by directed ortho-metalation and Suzuki cross-coupling methods [3]. Qian's group synthesized (*S*)-3,3′-bis(methoxyethyl)-BINOL from (*S*)-BINOL in four steps [4].

Substituted BINOL ligands by introducing heteroaromatic groups at the 3 or 3,3′-positions were less reported. Jørgensen et al. [5] reported the synthesis of 3,3′-diaryl-BINOLs by the reaction of 3,3′-diboronic acid of bis-(methoxy)-BINOL with aromatic bromides by a Suzuki cross-coupling reaction. Heteroaromatic bromides, such as 2-bromopyridine and 2-bromothiophene, were also tried for the preparation of 3,3′-bis(heteroaryl)-BINOLs; however, only low yields were obtained. Ohta and co-workers preparied 3,3′-bis(2-oxazolyl)-1,1′-bi-2-naphthol (BINOL-Box) [6]. Gao and co-workers synthesized bis-binaphthyl units containing 2,2′-bipyridines via Suzuki cross-coupling reaction [7].

In this paper, we report the synthesis of four modified BINOL ligands (*S*)-**1**, (*S*)-**2**, (*S*)-**3** and (*S*)-**4** by directed ortho-lithiation (Fig. 1). (*S*)-**1** and (*S*)-**2** are known compounds [8] synthesized by the reaction of 3-hydroxymethyl-BINOL or 3,3′-bis (hydroxymethyl)-BINOL with iodomethane in the presence of base. But the new facile synthetic approach is first reported by us.

2. Results and discussion

The synthetic route to ligands (*S*)-**1**, (*S*)-**2**, (*S*)-**3** and (*S*)-**4** is outlined in Scheme 1. The hydroxyl groups of (*S*)-BINOL were protected with methoxymethyl (MOM) groups to afford (*S*)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*S*)-**5** [9].

The lithium salt of (*S*)-**5** reacted with chloromethyl methyl ether to afford (*S*)-3-(methoxymethyl)-2,2′-

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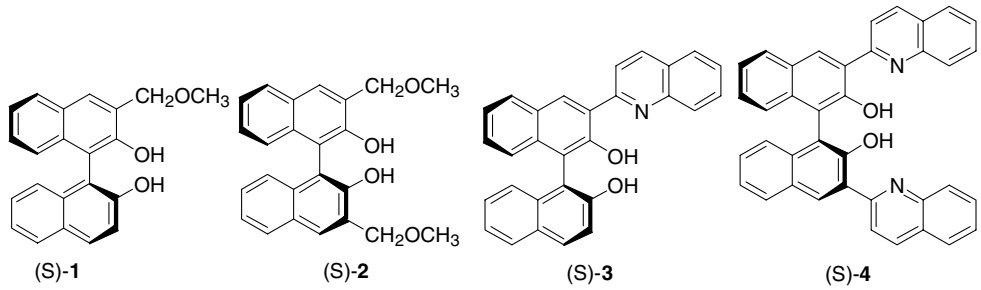
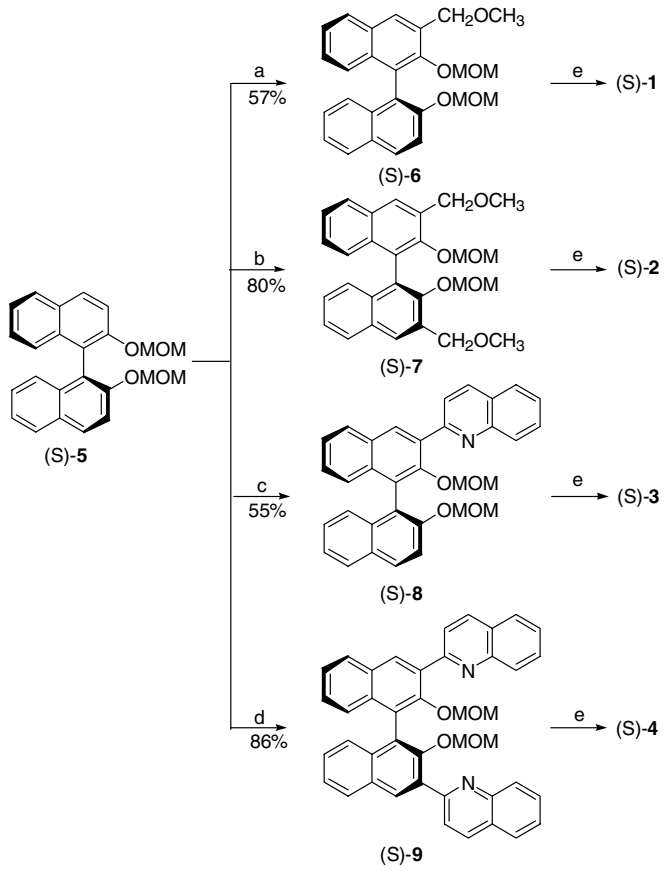


Fig. 1. The 3 or 3,3′-substituted binaphthols.



Scheme 1. Reagents and conditions: a: (i) 1.2 eq *n*-BuLi, −78 °C, (ii) 3.3 eq chloromethyl methyl ether, 0 °C ∼rt; b: (i) 1.9 eq *n*-BuLi, 0 °C, (ii) 3.4 eq chloromethyl methyl ether, 0 °C ∼rt; c: (i) 1.2 eq *n*-BuLi, −78 °C, (ii) 1.8 eq quinoline, 0 °C, (iii) $PhNO_2$, H_2O, reflux; d: (i) 3.0 eq *n*-BuLi, −78 °C, (ii) 4.0 eq quinoline, 0 °C, (iii) $PhNO_2$, H_2O, reflux; e: CH_2Cl_2, CH_3OH, 6 N HCl, rt.

bis(methoxymethoxy)-1,1′-binaphthalene (*S*)-**6** or (*S*)-3,3′-bis(methoxymethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*S*)-**7**. Such a direct C–C coupling reaction of chloromethyl methyl ether with aryl lithium has never been reported. After deprotection of (*S*)-**6** and (*S*)-**7**, ligands (*S*)-**1** and (*S*)-**2** were obtained.

The lithium salt of (*S*)-**5** reacted with quinoline, followed by hydrolysis and oxidation [10] to produce (*S*)-3-(quinolin-2-yl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*S*)-**8** or (*S*)-3,3′-bis(quinolin-2-yl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*S*)-**9**. Suzuki cross-coupling reaction was the general synthetic procedure to introduce aromatic or heteroaromatic groups at the 3 or 3,3′-positions of BINOL. In this paper, the direct coupling reaction was used to prepare (*S*)-**8** and (*S*)-**9**. After deprotection of (*S*)-**8** and (*S*)-**9**, ligands (*S*)-**3** and (*S*)-**4** were obtained. A pale yellow crystals of (*S*)-**3** was obtained from THF-ethanol solution. The crystal structure of (*S*)-**3** was determined by X-ray diffraction as shown in Fig. 2 [11]. The dihedral angle of C(11)–C(10)–C(9)–N(1) is 2.1°. The dihedral angle between the two naphthalene systems is 86.2°.

The effectiveness of the four ligands in the titanium complex-catalyzed enantioselective addition of diethylzinc to 1-naphthaldehyde was tested [12]. The active catalyst was formed in situ by mixing the ligand with titanium tetraisopropoxide in toluene [13]. In this reaction, the molar ratio of ligand/$Ti(O^iPr)_4$/Et_2Zn/1-naphthaldehyde was set up to be 0.2:1.4:3:1. (*S*)-**1** and (*S*)-**3** showed moderate catalytic properties in this reaction. Reducing the amount of (*S*)-**1** or (*S*)-**3** catalyst from 20% to 5% led to a large

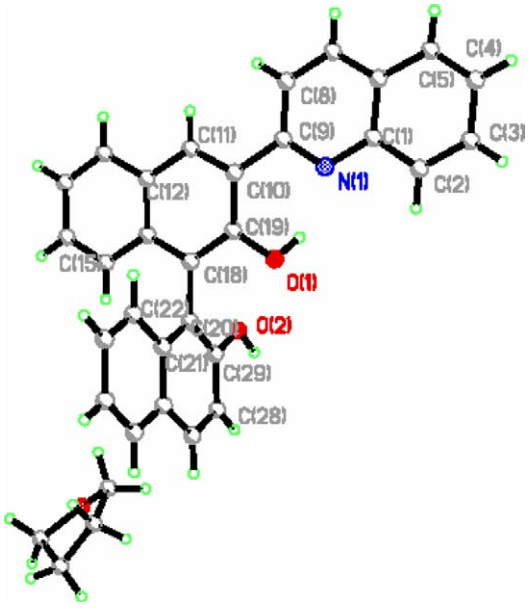
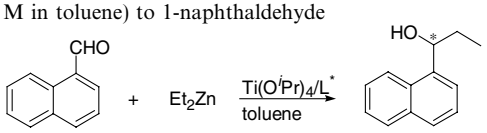


Fig. 2. The molecular structure of (*S*)-**3** including one THF molecule.

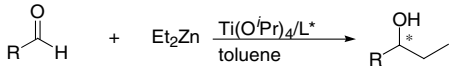
Table 1
Catalytic asymmetric addition of diethylzinc (1.0 M in toluene) to 1-naphthaldehyde



Entry	L*[a]	Yield (%)[b]	$[\alpha]_D$ (*c*, solvent)	ee (%)[c]
1	(*S*)-**1**	94	−48.0 (1.76, $CHCl_3$)	76 (80)
2	(*S*)-**2**	99	−28.7 (1.48, $CHCl_3$)	45 (51)
3	(*S*)-**3**	78	−43.2 (1.08, $CHCl_3$)	68 (71)
4	(*S*)-**4**	91	−14.52 (1.24, $CHCl_3$)	23
5	(*S*)-**1**[d]	83	−43.6 (0.93, $CHCl_3$)	71
6	(*S*)-**1**[e]	85	−41.6 (0.68, $CHCl_3$)	66
7	(*S*)-**3**[d]	79	−37.1 (0.76, $CHCl_3$)	59
8	(*S*)-**3**[e]	87	−31.0 (0.48, $CHCl_3$)	49

[a] L*/$Ti(O^iPr)_4$/Et_2Zn/1-naphthaldehyde = 0.2:1.4:3:1; Reaction temperature: 0 °C; Reaction time: 5 h.
[b] Isolated yield.
[c] Based on the reported value of $[\alpha]_D$ +45.5 (*c* = 0.8, $CHCl_3$) in 74% e.e. for (R)-1-(1′-naphthyl)-1-propanol [14]. Data in brackets were determined by GC analysis using a chiral column (Chrompack Chirasil-DEX-CB column) [15].
[d] 10 mol% of catalyst was used.
[e] 5 mol% of catalyst was used.

Table 2
Enantioselective addition of diethylzinc to aldehydes with (*S*)-**1** and (*S*)-**3**[a]



Entry	L*	R	Yield (%)[b]	$[\alpha]_D$ (*c*, solvent)	ee (%)[c]
1	(*S*)-**1**	Ph	99	−35.9 (0.96, $CHCl_3$)	74
2	(*S*)-**1**	*p*-ClC_6H_4	95	−16.5 (1.33, PhH)	66
3	(*S*)-**1**	*p*-BrC_6H_4	89	−14.24 (1.72, PhH)	81
4	(*S*)-**1**	*p*-$MeOC_6H_4$	99	−18.9 (1.0, PhH)	55 (59)
5	(*S*)-**1**	*o*-$MeOC_6H_4$	95	−40.6 (1.20, Ph-CH_3)	75
6	(*S*)-**1**	1-naphthyl	94	−48.0 (1.76, $CHCl_3$)	76 (80)
7	(*S*)-**3**	Ph	68	−33.3 (0.53, $CHCl_3$)	69
8	(*S*)-**3**	*p*-ClC_6H_4	83	−17.5 (1.04, PhH)	69
9	(*S*)-**3**	*p*-BrC_6H_4	76	−13.9 (1.07, PhH)	79
10	(*S*)-**3**	*p*-$MeOC_6H_4$	82	−22.1 (0.14, PhH)	64 (69)
11	(*S*)-**3**	*o*-$MeOC_6H_4$	84	−44.9 (1.15, Ph-CH_3)	83
12	(*S*)-**3**	1-naphthyl	78	−43.2 (1.08, $CHCl_3$)	68

[a] L*/$Ti(O^iPr)_4$/Et_2Zn/aldehyde = 0.2:1.4:3:1; Solvent: toluene; Reaction temperature: 0 °C; Reaction time: 5 h.
[b] Isolated yield.
[c] Based on the reported value of $[\alpha]_D$ −47.6 (*c* = 6.11, $CHCl_3$) in 98% ee for (*S*)-1-phenyl-1-propanol [16]; $[\alpha]_D$ −28.2 (*c* = 5.01, PhH) in 100% e.e. for (*S*)-1-(4′-chlorophenyl)-1-propanol [17]; $[\alpha]_D$ +13.33 (*c* = 1.0, PhH) in 76% e.e. for (R)-1-(4′-bromophenyl)-1-propanol [18]; $[\alpha]_D$ −34.6 (*c* = 5.0, PhH) in 90% ee for (*S*)-1-(4′- methoxyphenyl)-1-propanol [19]; $[\alpha]_D$ −44.9 (*c* = 1, toluene) in 83% e.e. for (*S*)-1-(2′-methoxyphenyl)-1-propanol [20]; $[\alpha]_D$ +45.5 (*c* = 0.8, $CHCl_3$) in 74% e.e. for (R)-1-(1′-naphthyl)-1-propanol [14]. Data in brackets were determined by GC analysis using a chiral column (Chrompack Chirasil-DEX-CB column) [15].

decrease in the enantioselectivity. The results were collected in Table 1.

With the ligands (*S*)-**1** and (*S*)-**3**, we also examined a number of aromatic aldehydes for the enantioselective ethylation with Et_2Zn (Table 2).

3. Conclusions

We have synthesized four modified-BINOL ligands (*S*)-**1**, (*S*)-**2**, (*S*)-**3** and (*S*)-**4** from (*S*)-BINOL through a very convenient route and used them in asymmetric addition of diethylzinc to aldehydes to give alcohols in high yields and good e.e. values.

4. Experimental section

4.1. General

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ solution with TMS as internal standard. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. IR spectra were recorded

as KBr plates on a Bruker Equinox 55 spectrometer. Elemental analysis was performed with a Yanaco CHN Corder MT-3 elemental analyzer. All experiments which are sensitive to moisture or air were carried out under an argon atmosphere using standard Schlenk techniques. All anhydrous solvents were purified and dried by standard techniques just before use.

4.2. Synthesis of (S)-3-(methoxymethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene [(S)-6]

To a solution of **5** (2.244 g, 6 mmol) in anhydrous THF (60 mL) was added *n*-BuLi (4.6 mL, 7.2 mmol, 1.57 M solution in hexane) at −78 °C under argon and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The resulting solution was cooled to 0 °C and chloromethyl methyl ether (1.5 mL, 20 mmol) in THF (10 mL) was added dropwise in 5 min. The mixture was then warmed to room temperature and stirred for another 5 h. Aqueous $NaHCO_3$ (40 ml) was added to the mixture to quench the reaction. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$. After removal of the solvent, the residue was submitted to column chromatographic separation on silica gel with petroleum ether/ethyl acetate (7/1) as eluent to give (*S*)-**6** (1.43 g, 57% yield) as a colorless oil. $[\alpha]_D^{25} = -86.9$ ($c = 1.14$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.88 (s, 3H), 3.14 (s, 3H), 3.56 (s, 3H), 4.57 (d, $J = 5.7$ Hz, 1H), 4.65 (d, $J = 6.34$ Hz, 1H), 4.81 (s, 2H), 5.01 (d, $J = 6.6$ Hz, 1H), 5.12 (d, $J = 6.9$ Hz, 1H), 7.16–7.41 (m, 6H), 7.58 (d, $J = 9.0$ Hz, 1H), 7.85–7.98 (m, 1H), 8.04 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.21, 56.87, 58.91, 70.86, 95.12, 99.59, 116.78, 121.00, 124.43, 125.28, 125.65, 125.81, 125.95, 126.32, 127.01, 128.14, 128.23, 128.59, 129.90, 130.11, 131.15, 132.00, 133.74, 134.28, 152.07, 153.11 ppm. IR (KBr): $\nu = 3056$, 1625, 1598, 1156, 1091, 796, 746 cm^{-1}. Anal. Calc. for $C_{26}H_{26}O_5$ (418.48): C, 74.62; H, 6.26. Found: C, 74.23; H, 6.43%.

4.3. Synthesis of (S)-3,3′-bis(methoxymethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene [(S)-7]

To a solution of **5** (1.0 g, 2.67 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (3.6 mL, 5.0 mmol, 1.4 M solution in hexane) at −78 °C under argon and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The resulting solution was cooled to 0 °C and chloromethyl methyl ether (0.7 mL, 9.2 mmol) in THF (5 mL) was added dropwise in 5 min. The mixture was then warmed to room temperature and stirred for another 5 h. Aqueous $NaHCO_3$ (30 mL) was added to the mixture to quench the reaction. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$. After removal of the solvent, the residue was submitted to column chromatographic separation on silica gel with petroleum ether/ethyl acetate (5/1) as eluent to give (*S*)-**7** (0.99 g, 80% yield) as a colorless oil. $[\alpha]_D^{25} = -125.1$ ($c = 0.53$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.82 (s, 6H), 3.54 (s, 6H), 4.49 (d, $J = 5.7$ Hz, 2H), 4.61 (d, $J = 6.0$ Hz, 2H), 4.81 (s, 4H), 7.21–7.39 (m, 6H), 7.88 (d, $J = 8.1$ Hz, 2H), 8.07 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.66, 70.52, 99.39, 125.16, 125.35, 126.11, 126.45, 128.03, 128.69, 130.81, 131.87, 133.73, 152.10 ppm. IR (KBr): $\nu = 3056$, 1446, 1360, 1162, 1100, 752 cm^{-1}. Anal. Calc. for $C_{28}H_{30}O_6$ (462.53): C, 72.71; H, 6.54. Found: C, 73.00; H, 6.61%.

4.4. Synthesis of (S)-3-(quinolin-2-yl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene [(S)-8]

To a solution of **5** (2.244 g, 6 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (5.2 mL, 7.28 mmol, 1.4 M solution in hexane) at −78 °C under argon and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The resulting solution was cooled to 0 °C and quinoline (1.3 mL, 11 mmol) in THF (5 mL) was added dropwise in 5 min. The mixture was then warmed to room temperature and stirred for another 12 h. Nitrobenzene (3 mL) and water (5 mL) were added and the mixture was refluxed for 20 min. After cooling to room temperature, water (30 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$. After removal of the solvent, the residue was submitted to column chromatographic separation on silica gel with petroleum ether/ethyl acetate (5/1) as eluent to give (*S*)-**8** (1.64 g, 55% yield) as a pale yellow oil. $[\alpha]_D^{25} = -22.8$ ($c = 0.82$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.22 (s, 3H), 4.41 (s, 2H), 5.07 (d, $J = 6.9$ Hz, 1H), 5.17 (d, $J = 6.9$ Hz, 1H), 7.23–8.05 (m, 15H), 8.20 (d, $J = 8.4$ Hz, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 8.46 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.04, 56.17, 95.09, 99.33, 116.66, 120.96, 123.60, 124.21, 125.34, 125.80, 125.90, 126.55, 126.64, 126.70, 126.87, 127.16, 127.59, 127.90, 128.81, 129.57, 129.76, 129.83, 131.22, 131.64, 134.21, 134.36, 134.74, 135.57, 148.51, 150.84, 153.06, 157.66 ppm. IR (KBr): $\nu = 3053$, 2949, 2889, 2828, 1596, 1500, 1522, 1016, 822, 754 cm^{-1}. Anal. Calc. for $C_{33}H_{27}NO_4$ (501.57): C, 79.02; H, 5.43; N, 2.79. Found: C, 78.91; H, 5.61; N, 2.78%.

4.5. Synthesis of (S)-3,3′-bis(quinolin-2-yl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene [(S)-9]

To a solution of **5** (1.87 g, 5 mmol) in anhydrous THF (60 mL) was added *n*-BuLi (14 mL, 15 mmol, 1.07 M solution in hexane) at 0 °C under argon and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The resulting solution was cooled to 0 °C and quinoline (2.58 g, 20 mmol) in THF (10 mL) was added dropwise in 5 min. The mixture was then warmed to room temperature

and stirred for another 12 h. Nitrobenzene (5 mL) and water (10 mL) were added and the mixture was refluxed for 30 min. After cooling to room temperature, water (30 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$. After removal of the solvent, the residue was submitted to column chromatographic separation on silica gel with petroleum ether/ethyl acetate (4/1) as eluent to give (*S*)-**9** (2.71 g, 86% yield) as a yellow oil. $[\alpha]_D^{25} = +72.86$ ($c = 0.56$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 6H), 4.49 (d, $J = 6.3$ Hz, 2H), 4.57 (d, $J = 5.1$ Hz, 2H), 7.31 (s, 2H), 7.32 (s, 2H), 7.42–7.47 (m, 2H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.77 (t, $J = 6.9$ Hz, 2H), 7.87 (d, $J = 8.4$ Hz, 2H), 8.01 (d, $J = 8.1$ Hz, 2H), 8.12 (d, $J = 8.4$ Hz, 2H), 8.23 (d, $J = 8.4$ Hz, 2H), 8.29 (d, $J = 8.1$ Hz, 2H), 8.50 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.28, 99.39, 123.48, 125.46, 126.34, 126.59, 127.12, 127.20, 127.58, 128.74, 129.61, 129.67, 129.73, 131.04, 132.07, 134.52, 135.71, 148.50, 151.21, 157.47 ppm. IR (KBr): $v = 3054$, 2945, 1598, 1498, 1154, 834, 756 cm^{-1}. Anal. Calc. for $C_{42}H_{32}N_2O_4$ (628.71): C, 80.24; H, 5.13; N, 4.46. Found: C, 80.08; H, 5.36; N, 4.66%.

*4.6. Synthesis of (S)-3-(methoxymethyl)-1,1′-bi-2-naphthol [(S)-**1**]: Deprotection of the MOM groups; typical procedure*

To a solution of (*S*)-**6** (1.43 g, 3.42 mmol) in CH_2Cl_2 (5 mL) and MeOH (20 mL) was added 6 N HCl (5 mL) and the mixture was stirred at room temperature for 12 h. The mixture was poured into water (40 mL), extracted with CH_2Cl_2, washed with water and saturated $NaHCO_3$, dried (Na_2SO_4), and concentrated in vacuo.

*4.6.1. (S)-3-(methoxymethyl)-1,1′-bi-2-naphthol [(S)-**1**]*

Colorless foam. $[\alpha]_D^{25} = -18.55$ ($c = 0.55$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 3.46 (s, 3H), 4.77 (s, 2H), 5.13 (b, 1H), 6.59 (s, 1H), 7.10–7.28 (m, 7H), 7.82–7.97 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.67, 72.26, 112.40, 112.68, 117.75, 123.72, 124.21, 124.44, 124.54, 125.87, 127.06, 127.29, 128.28, 128.37, 128.99, 129.16, 129.41, 130.76, 133.52, 133.62, 151.95, 152.19 ppm. IR (KBr): $v =$ 3392, 3058, 1621, 1597, 1146, 1111, 817, 750 cm^{-1}. Anal. Calc. for $C_{22}H_{18}O_3$ (330.38): C, 79.98; H, 5.49. Found: C, 79.36; H, 5.23%.

*4.6.2. (S)-3,3′-bis(methoxymethyl)-1,1′-bi-2-naphthol [(S)-**2**]*

White powder. M.p. 140–142 °C; $[\alpha]_D^{25} = -62.86$ ($c = 0.49$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 3.50 (s, 6H), 4.82 (d, $J = 4.5$ Hz, 4H), 6.64 (s, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 7.21–7.34 (m, 4H), 7.83 (s, 1H), 7.85 (b, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.58, 72.49, 114.04, 123.87, 124.60, 125.61, 126.89, 128.19, 128.58, 128.85, 133.58, 151.40 ppm. IR (KBr): $v = 3283$, 3063, 1445, 1388, 1205, 1093, 748 cm^{-1}. Anal. Calc. for $C_{24}H_{22}O_4$ (374.43): C, 76.99; H, 5.92. Found: C, 76.72; H, 6.08%.

*4.6.3. (S)-3-(quinolin-2-yl)-1,1′-bi-2-naphthol [(S)-**3**]*

Yellow powder. M.p. > 300 °C; $[\alpha]_D^{25} = +72.86$ ($c =$ 0.56, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 5.24 (s, 6H), 4.49 (s, 1H), 7.16–7.42 (m, 8H), 7.58 (t, $J = 8.4$ Hz, 1H), 7.72 (t, $J = 8.1$ Hz, 1H), 7.86–8.00 (m, 4H), 8.39 (d, 2H), 8.74 (s, 1H), 15.55 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.50, 115.27, 117.74, 117.81, 121.54, 123.26, 123.85, 124.57, 124.94, 126.49, 126.87, 127.29, 127.58, 127.70, 127.75, 128.26, 128.55, 129.07, 129.40, 129.94, 130.85, 133.71. 135.60, 138.13, 144.70, 151.50, 156.40, 157.44 ppm. IR (KBr): $v = 3510$, 3052, 1600, 1507, 1344, 1204, 819, 746 cm^{-1}. Anal. Calc. for $C_{29}H_{19}NO_2$ (413.47): C, 84.24; H, 4.63; N, 3.39. Found: C, 83.57; H, 4.61; N, 3.54%.

*4.6.4. (S)-3,3′-bis(quinolin-2-yl)-1,1′-bi-2-naphthol [(S)-**4**]*

Yellow powder. M.p. > 300 °C; $[\alpha]_D^{25} = +380.24$ ($c =$ 0.41, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.26–7.35 (m, 6H), 7.55 (t, $J = 7.5$ Hz, 2H), 7.68 (t, $J = 6.9$ Hz, 2H), 7.87 (d, $J = 7.8$ Hz, 2H), 7.98 (m, 4H), 8.40 (s, 4H), 8.74 (s, 2H), 15.23 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.11, 118.45, 121.50, 123.28, 124.71, 126.73, 126.92, 127.53, 127.71, 127.80, 127.94, 128.34, 129.07, 130.50, 135.62, 137.79, 144.81, 155.32, 158.09 ppm. IR (KBr): $v = 3423$, 3054, 2969, 1602, 1506, 1146, 832, 749 cm^{-1}. Anal. Calc. for $C_{38}H_{24}N_2O_2$ (540.61): C, 84.42; H, 4.47; N, 5.18. Found: C, 83.53; H, 4.80; N, 5.64%.

4.7. A typical procedure for the asymmetric addition of diethylzinc to benzaldehyde

Titanium tetraisopropoxide (0.43 mL, 1.25 mmol) was added to a solution of (*S*)-**1** (0.059 g, 0.179 mmol) in 3 mL of toluene at room temperature and was stirred for 15 min followed by the addition of diethylzinc (2.7 mL, 1.0 M solution in toluene) with continued stirring for 15 min. The solution was cooled to 0 °C and benzaldehyde (0.09 mL, 0.90 mmol) was introduced with a syringe. The reaction mixture was stirred at 0 °C for 5 h. The reaction was quenched with 20 mL of saturated NH_4Cl solution, the mixture was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated to solvent free. The residue was purified by column chromatography on silica gel affording 1-phenyl-1-propanol as a colorless liquid. The optical rotation was measured.

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