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Synthesis of novel chiral tridentate aminophenol ligands for enantioselective addition of diethylzinc to aldehydes

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ABSTRACT

Novel chiral tridentate aminophenol ligand (*S*)-**3a** was obtained by a Mannich-type reaction of cresol, paraformaldehyde, and (*S*)-1-(2-methoxyphenyl)-2-methylpropan-1-amine followed by a deprotection step. This tridentate aminophenol ligand shows high yield and enantioselectivity in the diethylzinc additions to a broad range of substrates, including alkyl, aryl, and α,β-unsaturated aldehydes.

1. Introduction

Over the last two decades, there has been a great deal of interest in the synthesis of chiral ligands which work for the catalytic asymmetric addition of diethylzinc to aldehydes since the first report of Oguni.[1] Most of the chiral ligands are based upon chiral bidentate aminoalcohols,[2] diols,[3] and diamine derivatives.[4] However, chiral tridentate ligands that effectively catalyze the diethylzinc addition with high levels of enantioselectivity have scarcely been reported.[5] On the other hand, approximately 600 chiral ligands for the asymmetric addition reactions have been shown in recent reviews[6a–c] and reports,[6d–q] although only a small number of effective ligands were obtained by simple synthetic methods. Furthermore, ligands suitable for the addition reactions to both aromatic and aliphatic or α,β-unsaturated aldehydes are rare. Therefore, easily accessible, stable, operationally simple, and effective ligands are still desirable. Herein, we report novel chiral tridentate aminophenol ligands obtained by introducing another phenolic hydroxyl group from cresol into a chiral aminophenol[7] using a Mannich-type reaction for the asymmetric addition of diethylzinc to aldehydes. The key features of these ligands include (a) ease of preparation and high stability; (b) the ability to operate at room temperature; and (c) versatility for a variety of aldehydes to afford the high ee products with high chemical yields.

2. Results and discussion

Chiral tridentate aminophenol ligands **3** can be easily be obtained by Mannich reaction[8] of cresol, paraformaldehyde, and (*S*)-**1**[9] followed by a deprotection step[7] (Scheme 1). These ligands are stable in air.

To investigate the catalytic properties of these two ligands, the asymmetric addition of diethylzinc to benzaldehyde was first carried out (Table 1). The tridentate aminophenol ligand **3a** was chosen for the initial experiments (Table 1, entries 1–8). The solvent played an important role in the enantioselective process (Table 1, entries 1–4). Toluene or toluene/hexane (1:1, v/v) gave the best results with 98%, 96% yields and 96%, 95% ee, respectively (Table 1, entries 1 and 2). The presence of CH_2Cl_2 or THF lowered the ee value of the resulting alcohol (Table 1, entries 3 and 4). Therefore, toluene was selected as the reaction solvent in the following reactions. Optimization of the reaction temperature indicated that room temperature favored a higher ee (Table 1, entries 1 and 5–7). On the other hand, in the presence of 5 mol % of **3a** the ee value of the resulting alcohol decreases (Table 1, entry 8). The reaction conditions of entry 1 were chosen as the optimal conditions for the following reactions. We also investigated the catalytic properties of **3b**. Under the reaction condition optimized for **3a**, the ethylation using **3b** providing 53% ee was quite slow, and 16% of the starting benzaldehyde remained unreacted after 18 h (Table 1, entry 5).

With the above optimal results, ligand **3a** was further used in the asymmetric addition of diethylzinc to other aromatic aldehydes (Table 2, entries 2–13). Fortunately, **3a** showed excellent enantioselectivity of >93% ee for various tested naphthaldehydes and *para*-, *meta*-, and *ortho*-substituted benzaldehydes, except *ortho*-chloro and *ortho*-bromo benzaldehydes. Usually it is assumed that the diethylzinc addition involves a transition state, which is a Zn-complex containing the corresponding ligand and the coordinated carbonyl compound.[2c,10] A higher electronegative substitution at the *ortho*-position of benzaldehyde would have a great influence on the coordination of the carbonyl compound to the Zn center possibly due to the electrostatics in this complex. Therefore, *ortho*-chloro or *ortho*-bromo substitution has

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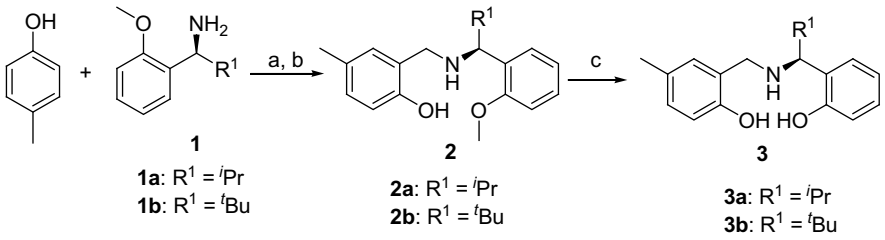
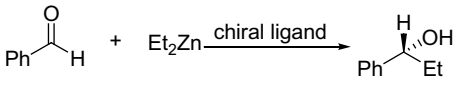


Scheme 1. Synthesis of chiral tridentate aminophenol ligands **3**. Reagents and conditions: (a) paraformaldehyde, LiCl/EtOH, reflux, 20 h; (b) $NH_2OH{\cdot}HCl$/MeOH, two steps, 55% overall yield; (c) $AlBr_3$/dry toluene, 0 °C, 50 h, 92%.

Table 1
Enantioselective addition of diethylzinc to benzaldehyde catalyzed by chiral ligands **3a**–**b**[a]



Entry	Ligand	Reaction conditions	Yield[b] (%)	ee[c,d] (%)
1	**3a**	Toluene, rt, 3 h	98	96 (*R*)
2	**3a**	Toluene/hexane, rt, 3 h	96	95 (*R*)
3	**3a**	CH_2Cl_2, rt, 14 h	82	88 (*R*)
4	**3a**	THF, rt, 24 h	10	3 (*R*)
5	**3a**	Toluene, 60 °C, 2 h	97	92 (*R*)
6	**3a**	Toluene, 0–5 °C, 7 h	90	94 (*R*)
7	**3a**	Toluene, −20 °C, 48 h	—	—
8[e]	**3a**	Toluene, rt, 3 h	98	91 (*R*)
9	**3b**	Toluene, rt, 18 h	78	53 (*R*)

[a] Molar ratio PhCHO/Et_2Zn/chiral ligand **3** = 1:1.2:0.1.
[b] Isolated yields.
[c] Based on HPLC analysis using Chiralcel OB-H.
[d] The configuration of the main enantiomer was assigned according to the value of the specific rotation.
[e] In the presence of 5 mol % of **3a**.

Table 2
Enantioselective addition of diethylzinc to aldehydes catalyzed by the chiral ligand **3a**[a]

Entry	Aldehyde (R^2CHO)	Time (h)	Yield[b] (%)	ee[h] (%)
1	C_6H_5CHO	3	98	96[c] (*R*)
2	*p*-$NO_2C_6H_4CHO$	3	80	93[f] (*R*)
3	*p*-ClC_6H_4CHO	3	98	94[d] (*R*)
4	*p*-BrC_6H_4CHO	3	95	93[d] (*R*)
5	*p*-MeC_6H_4CHO	3	97	98[d] (*R*)
6	*m*-$NO_2C_6H_4CHO$	3	87	93[f] (+)
7	*m*-ClC_6H_4CHO	3	95	94[c] (*R*)
8	*m*-MeC_6H_4CHO	3	92	96[c] (*R*)
9	*o*-ClC_6H_4CHO	3	92	80[c] (*R*)
10	*o*-BrC_6H_4CHO	3	93	60[c] (*R*)
11	*o*-MeC_6H_4CHO	3	95	96[c] (*R*)
12	α-Naphthaldehyde	2	93	95[e] (*R*)
13	β-Naphthaldehyde	2	97	96[e] (*R*)
14	2-Furaldehyde	2	96	85[f] (*R*)
15	2-Thiophenealdehyde	2	98	92[f] (*R*)
16	$C_6H_5CH_2CH_2CHO$	3	81	95[e] (*R*)
17	*E*-$C_6H_5CH{=}CHCHO$	3	98	94[e] (*R*)
18	*n*-$C_9H_{19}CHO$	4	82	92[g] (*R*)

[a] Molar ratio aldehyde/Et_2Zn/chiral ligand **3a** = 1:1.2:0.1; reaction conditions: toluene, rt.
[b] Isolated yields.
[c] Based on HPLC analysis using Chiralcel OB-H.
[d] Based on HPLC analysis using Chiralcel OJ.
[e] Based on HPLC analysis using Chiralcel OD-H.
[f] Based on HPLC analysis of its benzoate derivative using Chiralcel AD-H.
[g] Based on HPLC analysis of its benzoate derivative using Chiralcel OD-H.
[h] The configuration of the main enantiomer was assigned according to the value of the specific rotation.

an electrostatic effect in this complex besides steric hindrance while *ortho*-methyl substitution has only steric hindrance, resulting in the difference of the substitution effect on the ee value (80% ee for *ortho*-chlorobenzaldehyde, 60% ee for *ortho*-bromobenzaldehyde, and 96% ee for *ortho*-methylbenzaldehyde). The heterocyclic aromatic aldehydes, 2-furaldehyde and 2-thiophenealdehyde provided (*R*)-1-furyl-1-propanol (96% yield, 85% ee) and (*R*)-1-thienyl-1-propanol (98% yield, 92% ee) in good to excellent enantioselectivity (Table 2, entries 13 and 14). It is known that in the diethylzinc addition reaction, the enantioselectivity is usually much lower for aliphatic and α,β-unsaturated aldehydes than the identical reaction with aromatic aldehydes. Compound **3a** was next examined in the addition of diethylzinc to these more challenging substrates. Apparently, excellent enantioselectivities were observed with 92–95% ee (Table 2, entries 15–17). In comparison with other tridentate ligands[5] (Fig. 1), the following features of the ligand **3a** are noted: (1) For aromatic aldehydes, ligand **3a** displays stereoselectivities of similar magnitude as ligand **6**,[5f] and higher than ligands **4**,[5a] **5**,[5b] **7**,[5c] and **8**;[5g] (2) for aliphatic (entries

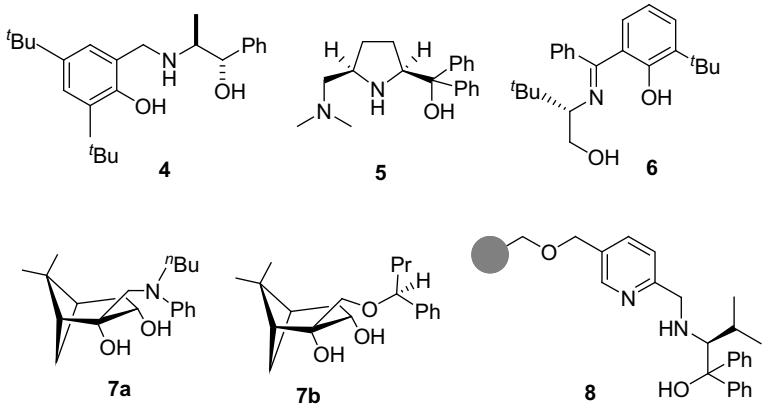
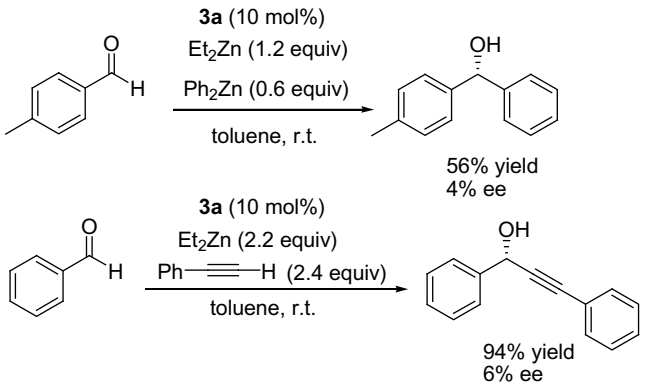


Figure 1.

15 and 17) and α,β-unsaturated (entry 16) aldehydes, ligand **3a** (95% ee, 92% ee, and 94% ee) shows higher enantioselecitivities than those of ligands **5**[5b] and **6**[5f] (70–83% ee); (3) the catalytic activities of ligand **3a** appear to be higher than the other tridentate ligands since the aldehydes required only 2–4 h at room temperature for complete conversion.

The catalytic properties of ligand **3a** were also examined for the enantioselective additions of diphenylzinc to *p*-tolualdehyde and phenylacetylene to benzaldehyde to provide the corresponding alcohols in moderate to high yields but with only 4% and 6% ee, respectively (Scheme 2).



Scheme 2. Phenylation of *p*-tolualdehyde and phenylethynylation of benzaldehyde using tridentate ligand **3a**.

The currently accepted mechanism for the addition of dialkylzinc to aldehydes[2c,10] has been reviewed and applied to the present system. In analogy to that established by Noyori and Yamakawa[10c] for β-amino alcohol, an O,N,O-chelating six/six bicyclic zinc-complex **A** is formed initially by the reaction of aminophenol (*S*)-**3a** with diethylzinc. Once a new molecule of diethylzinc and aldehyde coordinated, there were four possible forms of the 6/4/4 tricyclic transition states (**B**–**E**) (Fig. 2). The transition states of the type **D** and **E** should be less likely because of the increased steric hindrance between the ^{i}Pr group and the O–Zn–O–Zn ring structure. Between the transition states of the type **B** and **C**, the most energetically favorable should be type **B**, in which the aromatic ring of the benzaldehyde is oriented far from the hindered ligand 'cage'; (*R*)-alcohol is thus preferentially formed.

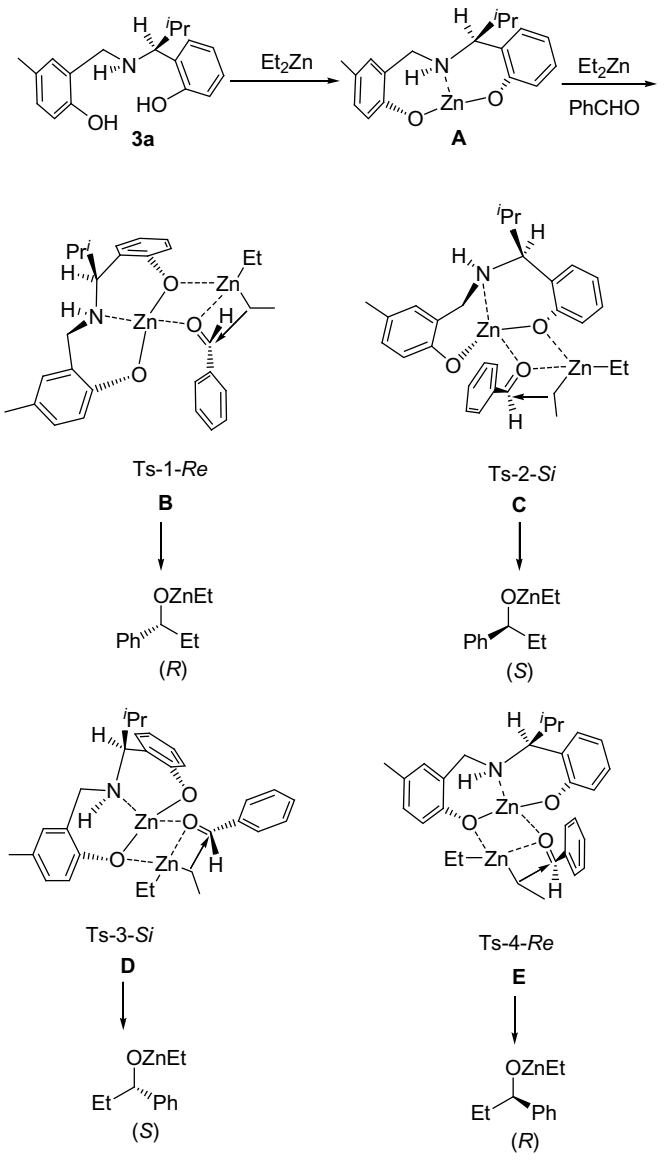


Figure 2.

3. Conclusions

In conclusion, we have prepared a new chiral tridentate aminophenol ligand **3a** for the enantioselective addition of diethylzinc to aldehydes. This tridentate aminophenol ligand provides good to excellent yields and enantioselectivities in the reactions of diethylzinc with a broad range of aromatic, aliphatic, and unsaturated aldehydes.

4. Experimental

^{1}H NMR spectra were recorded on Bruker AC300 or DPX400 MHz in Molecular Analysis and Life Science Center (Saitama University). The chemical shifts were reported in ppm downfield from Me_4Si in $CDCl_3$ solution and the coupling constants were given in Hertz. IR spectra were recorded on JASCO FT/IR 400. Enantiomeric excess determination was carried out using a set of JASCO LC 900 series with chiral columns. Optical rotations were measured with a JASCO DIP-370 polarimeter. Melting points were determined with a Mitamura Riken Kogyo MEL-TEMP instrument and are reported uncorrected. All commercially available reagents were purchased at the highest quality and were purified by distillation when necessary. Hexane and toluene were distilled and stored on sodium wire before use.

2-(((*S*)-1-(2-Methoxyphenyl)-2-methylpropylamino)methyl)-4-methylphenol (*S*)-**2a** and 2-(((*S*)-1-(2-methoxyphenyl)-2,2-dimethylpropylamino)methyl)-4-methylphenol (*S*)-**2b** were synthesized according to a literature procedure.[8]

4.1. Characterization of 2-(((*S*)-1-(2-methoxyphenyl)-2-methylpropylamino)methyl)-4-methylphenol (*S*)-2a

A yellow oil. $[\alpha]_D^{23} = -18.6$ (*c* 0.582, $CHCl_3$). Enantiomeric purity >99% ee was determined by HPLC analysis (CHIRALCEL OJ, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector) at retention time: *t* = 16.59 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.25 (m, 1H, Ar), 7.05 (d, *J* = 7.2 Hz, 1H, Ar), 6.95–6.90 (m, 3H, Ar), 6.75 (d, *J* = 8.4 Hz, 1H, Ar), 6.61 (s, 1H, ArCH_2), 3.81 (s, 3H, ArOCH_3), 3.69 (d, *J* = 13.6 Hz, 1H, ArC*H*), 3.54 (d, *J* = 13.6 Hz, 1H, ArCH_2), 3.46 (d, *J* = 8.8 Hz, 1H, ArCH_2), 2.19 (s, 3H, ArCH_3), 2.14–2.10 (m, 1H, $(CH_3)_2CH$), 1.09 (d, *J* = 6.4 Hz, 3H, $(CH_3)_2CH$), 0.71 (d, *J* = 6.8 Hz, 3H, $(CH_3)_2CH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (Ar, *C*OCH3),

156.0 (Ar, COH), 129.8 (Ar, CH), 128.9 (Ar, C), 128.8 (Ar, CH), 128.2 (Ar, C), 127.7 (Ar, C), 122.8 (Ar, CH), 120.5 (Ar, CH), 115.9 (Ar, CH), 110.7 (Ar, CH), 55.2 (OCH_3), 50.8 (ArCH), 32.2 ($(CH_3)_2CH$), 20.6 ($ArCH_3$), 20.3 ($(CH_3)_2CH$), 20.3 ($(CH_3)_2CH$). IR (neat): 3349, 2956, 2923, 2871, 1829, 1792, 1771, 1717, 1684, 1671, 1652, 1635, 1617, 1599, 1576, 1520, 1419, 1397, 1362, 1338, 1084, 893, 815, 768 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.11; H, 8.48; N, 4.46.

4.2. Characterization of 2-(((*S*)-1-(2-methoxyphenyl)-2,2-dimethylpropylamino)methyl)-4-methylphenol (*S*)-2b

A white solid. Mp: 142–144 °C. $[\alpha]_D^{23} = +6.6$ (*c* 0.696, $CHCl_3$). Enantiomeric purity >99% ee was determined by HPLC analysis (CHIRALCEL OJ, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector) at retention time: *t* = 14.13 min. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.18 (m, 2H, Ar), 7.00–6.90 (m, 3H, Ar), 6.78 (d, *J* = 8.4 Hz, 1H, Ar), 6.63 (s, 1H, Ar), 4.20 (s, 1H, ArCH), 3.79 (s, 1H, $ArOCH_3$), 3.67 (dd, *J* = 13.6 Hz, *J* = 33.6 Hz, 1H, $ArCH_2$), 3.53 (d, *J* = 13.6 Hz, 1H, $ArCH_2$), 2.19 (s, 3H, $ArCH_3$), 0.94 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5 (Ar, $COCH_3$), 155.7 (Ar, COH), 128.9 (Ar, C), 128.8 (Ar, CH), 128.2 (Ar, CH), 127.9 (Ar, C), 126.8 (Ar, CH), 123.0 (Ar, C), 120.3 (Ar, CH), 115.9 (Ar, CH), 110.6 (Ar, CH), 61.7 (ArCH), 55.3 ($ArOCH_3$), 51.2 ($ArCH_2$), 35.2 ($(CH_3)_3C$), 28.2 ($ArCH_3$), 26.6 ($(CH_3)_3C$), 20.3 ($(CH_3)_3C$). IR (KBr): 3306, 2931, 2870, 1868, 1844, 1792, 1771, 1733, 1717, 1684, 1670, 1652, 1635, 1598, 1558, 1540, 1521, 1474, 1457, 1419, 1339, 1291, 1187, 1125, 1056, 974, 881, 753 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47. Found: C, 76.32; H, 8.76; N, 4.13.

Chiral tridentate aminophenol ligands (*S*)-**3a** and (*S*)-**3b** were synthesized according to a literature procedure.[7]

4.3. Characterization of 2-((*S*)-1-(2-hydroxy-5-methylbenzylamino)-2-methylpropyl)phenol (*S*)-3a

A white solid. Mp: 44–46 °C. $[\alpha]_D^{23} = -19.0$ (*c* 0.4, $CHCl_3$). Enantiomeric purity >99% ee was determined by HPLC analysis (CHIRALCEL OJ, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector) at retention time: *t* = 19.32 min. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18–7.14 (m, 1H, Ar), 6.96–6.91 (m, 2H, Ar), 6.84–6.73 (m, 2H, Ar), 6.72 (d, *J* = 8.4 Hz, 1H, Ar), 3.85 (d, *J* = 13.2 Hz, 1H, ArCH), 3.55 (d, *J* = 13.2 Hz, 1H, $ArCH_2$), 3.45 (d, *J* = 7.2 Hz, 1H, $ArCH_2$), 2.23 (s, 3H, $ArCH_3$), 2.05–2.01 (m, 1H, $(CH_3)_2CH$), 0.98 (d, *J* = 6.8 Hz, 3H, $(CH_3)_2CH$), 0.80 (d, *J* = 6.8 Hz, 3H, $(CH_3)_2CH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0 (Ar, COH), 152.7 (Ar, COH), 131.2 (Ar, C), 130.2 (Ar, C), 129.5 (Ar, CH), 129.3 (Ar, CH), 128.3 (Ar, CH), 124.2 (Ar, CH), 124.0 (Ar, C), 119.0 (Ar, CH), 116.5 (Ar, CH), 115.6 (Ar, CH), 68.8 (ArCH), 48.4 ($ArCH_2$), 33.2 ($(CH_3)_2CH$), 20.4 ($ArCH_3$), 19.9 ($(CH_3)_2CH$), 19.3 ($(CH_3)_2CH$). IR (KBr): 2960, 2923, 2871, 1868, 1844, 1829, 1792, 1771, 1733, 1698, 1684, 1652, 1635, 1616, 1558, 1540, 1507, 1456, 1078, 816, 754 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.53; H, 8.25; N, 4.69.

4.4. Characterization of 2-((*S*)-1-(2-hydroxy-5-methylbenzylamino)-2,2-dimethylpropyl)phenol (*S*)-3b

A white solid. Mp: 63–65 °C. $[\alpha]_D^{23} = -22.5$ (*c* 0.516, $CHCl_3$). Enantiomeric purity >99% ee was determined by HPLC analysis (CHIRALCEL OJ, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector) at retention time: *t* = 17.49 min. ^1H NMR (400 MHz, $CDCl_3$): δ 7.11–7.07 (m, 1H, Ar), 6.89–6.83 (m, 2H, Ar), 6.78–6.70 (m, 3H, Ar), 6.65 (d, *J* = 4.0 Hz, 1H, Ar), 3.78 (d, *J* = 12.8 Hz, 1H, ArCH), 3.44 (d, *J* = 12.8 Hz, 1H, $ArCH_2$), 3.36 (s, 1H, $ArCH_2$), 2.15 (s, 3H, $ArCH_3$), 0.85 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9 (Ar, COH), 152.5 (Ar, COH), 131.5 (Ar, CH), 129.6 (Ar, CH), 129.4 (Ar, C), 128.4 (Ar, C), 124.0 (Ar, C), 118.4 (Ar, CH), 116.7 (Ar, CH), 115.5 (Ar, CH), 65.9 (ArCH), 48.4 ($ArCH_2$), 35.9 ($(CH_3)_3C$), 27.0 ($ArCH_3$), 20.4 ($(CH_3)_3C$), 15.2 ($(CH_3)_3C$). IR (KBr): 2954, 2867, 2954, 2867, 1942, 1918, 1868, 1844, 1828, 1792, 1771, 1749, 1733, 1717, 1698, 1684, 1671, 1652, 1635, 1590, 1558, 1540, 1473, 1366, 1223, 1151, 1122, 1106, 1080, 1035, 943, 906, 816 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.03; H, 8.42; N, 4.53.

4.5. Asymmetric addition of diethylzinc to aldehydes

4.5.1. General procedure for the enantioselective addition of diethylzinc to aldehydes catalyzed by chiral ligands

Diethylzinc (1.2 ml, 1.0 M solution in hexane) was added to a stirred solution of chiral ligand (0.1 mmol) in toluene (1.5 ml) under N_2 at room temperature. After stirring for 1 h, a solution of aldehyde (1 mmol) in toluene (3.0 ml) was added dropwise. The resulting mixture was monitored by TLC and when no more trace of the aldehyde was detected, the reaction mixture was quenched by saturated NH_4Cl solution. The mixture was extracted three times with ethyl acetate. The combined extracts were dried with anhydrous Na_2SO_4. After filtering and concentration, the residue was purified by TLC of silica gel to give the enantiomerically enriched alcohol. The ee values of the alcohol were determined by chiral HPLC analysis.

4.5.2. (*R*)-1-Phenyl-1-propanol

98% isolated yield. 96% ee determined by HPLC analysis (Chiralcel OB-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: *t* = 14.47 min ((*S*)-isomer: *t* = 12.52 min). $[\alpha]_D^{23} = +42.5$ (*c* 0.49, $CHCl_3$) (lit.[5e] $[\alpha]_D^{29} = +41.9$ (*c* 1.00, $CHCl_3$), 96% ee for (*R*)). ^1H NMR (400 MHz, $CDCl_3$): δ 7.27–7.16 (m, 5H), 4.76 (t, *J* = 6.4 Hz, 1H), 2.01 (s, 1H), 1.77–1.59 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 128.3, 127.4, 125.9, 75.9, 31.8, 10.1.

4.5.3. (*R*)-1-(4-Nitrophenyl)-1-propanol

80% isolated yield. 93% ee determined by HPLC analysis of its benzoate (Chiralcel AD-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: *t* = 19.35 min ((*S*)-isomer: *t* = 42.16 min). $[\alpha]_D^{23} = +26.8$ (*c* 0.32, $CHCl_3$) (lit.[6p] $[\alpha]_D^{16} = -15.2$ (*c* 1.52, $CHCl_3$), 47% ee). ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 4.75 (t, *J* = 6.4 Hz, 1H), 1.81–1.77 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 147.2, 126.6, 123.6, 74.8, 32.1, 9.7.

4.5.4. (*R*)-1-(4-Cholorophenyl)-1-propanol

98% isolated yield. 94% ee determined by HPLC analysis (Chiralcel OJ column, 3% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: *t* = 34.31 min ((*S*)-isomer: *t* = 32.58 min). $[\alpha]_D^{23} = +36.0$ (*c* 0.8, $CHCl_3$) (lit.[6e] $[\alpha]_D^{25} = +37.3$ (*c* 1.57, $CHCl_3$), 96% ee for (*R*)). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 4.55 (t, *J* = 6.4 Hz, 1H), 2.12 (s, 1H), 1.80–1.66 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 133.0, 128.4, 127.3, 75.2, 31.9, 9.9.

4.5.5. (*R*)-1-(4-Bromophenyl)-1-propanol

95% isolated yield. 93% ee determined by HPLC analysis (Chiralcel OJ column, 3% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: *t* = 40.05 min ((*S*)-isomer: *t* = 36.74 min). $[\alpha]_D^{23} = +15.0$ (*c* 0.894, benzene) (lit.[6j] $[\alpha]_D^{25} = +15.8$ (*c* 1.49, benzene), 90.3% ee for (*R*)). ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.55 (t, *J* = 6.4 Hz, 1H), 2.03 (s, 1H), 1.79–1.68 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 131.4, 127.7, 121.1, 75.2, 31.9, 9.9.

4.5.6. (*R*)-1-4-Tolyl-1-propanol

97% isolated yield. 98% ee determined by HPLC analysis (Chiralcel OJ column, 3% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 34.82 min ((*S*)-isomer: t = 32.30 min). $[\alpha]_D^{23}$ = +41.2 (*c* 0.432, benzene) (lit.[11] $[\alpha]_D$ = +39.2 (*c* 5, benzene), 96% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.52 (t, J = 6.4 Hz, 1H), 2.33 (s, 3H), 2.00 (s, 1H), 1.81–1.69 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 137.0, 129.0, 125.9, 75.8, 31.7, 21.1, 10.1.

4.5.7. (3-Nitrophenyl)-1-propanol

87% isolated yield. 93% ee determined by HPLC analysis of its benzoate (Chiralcel AD-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t_{major} = 15.63 min and t_{minor} = 19.32 min. $[\alpha]_D^{23}$ = +31.3 (*c* 0.16, $CHCl_3$) (lit.[6p] $[\alpha]_D^{16}$ = −28.3 (*c* 1.35, $CHCl_3$), >99% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 4.74 (t, J = 6.4 Hz, 1H), 1.85–1.76 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 146.7, 132.1, 129.3, 122.3, 120.9, 74.7, 32.1, 9.7.

4.5.8. (*R*)-1-(3-Cholorophenyl)-1-propanol

95% isolated yield. 94% ee determined by HPLC analysis (Chiralcel OB-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 13.63 min ((*S*)-isomer: t = 12.10 min). $[\alpha]_D^{23}$ = +34.5 (*c* 0.77, $CHCl_3$) (lit.[6e] $[\alpha]_D^{25}$ = +32.1 (*c* 1.30, $CHCl_3$), 94% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.28–7.18 (m, 3H), 4.55 (t, J = 6.4 Hz, 1H), 2.17 (s, 1H), 1.80–1.68 (m, 2H), 0.90 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 134.3, 129.6, 127.5, 126.1, 124.1, 75.3, 31.9, 9.9.

4.5.9. (*R*)-1-3-Tolyl-1-propanol

92% isolated yield. 96% ee determined by HPLC analysis (Chiralcel OB-H column, 5% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 16.63 min ((*S*)-isomer: t = 14.25 min). $[\alpha]_D^{23}$ = +35.6 (*c* 0.91, $CHCl_3$) (lit.[6e] $[\alpha]_D^{25}$ = +37.9 (*c* 1.76, $CHCl_3$), 95% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, J = 7.6 Hz, 1H), 7.04–6.99 (m, 3H), 4.44 (t, J = 6.4 Hz, 1H), 2.27 (s, 3H), 2.02 (s, 1H), 1.75–1.61 (m, 2H), 0.82 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 137.9, 128.2, 128.1, 126.6, 123.0, 75.9, 31.8, 21.4, 10.2.

4.5.10. (*R*)-1-(2-Cholorophenyl)-1-propanol

92% isolated yield. 80% ee determined by HPLC analysis (Chiralcel OB-H column, 3% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 17.69 min ((*S*)-isomer: t = 15.97 min). $[\alpha]_D^{23}$ = +44.4 (*c* 0.69, $CHCl_3$) (lit.[6p] $[\alpha]_D^{16}$ = −50.2 (*c* 2.10, $CHCl_3$), 92% ee for (*S*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.32–7.25 (m, 2H), 7.20–7.16 (m, 1H), 5.04 (dd, J = 4.8 Hz, J = 7.6 Hz, 1H), 2.24 (s, 1H), 1.85–1.68 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 131.9, 129.3, 128.3, 127.1, 126.9, 71.9, 30.4, 10.0.

4.5.11. (*R*)-1-(2-Bromophenyl)-1-propanol

93% isolated yield. 60% ee determined by HPLC analysis (Chiralcel OB-H column, 2% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 23.51 min ((*S*)-isomer: t = 21.84 min). $[\alpha]_D^{23}$ = +35.5 (*c* 0.72, benzene) (lit.[12] $[\alpha]_D^{20}$ = +54.2 (*c* 2.46, benzene), 85% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.49 (m, 2H), 7.34–7.30 (m, 1H), 7.13–7.09 (m, 1H), 4.99 (t, J = 5.6 Hz, 1H), 2.16 (s, 1H), 1.87–1.64 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 132.6, 128.7, 127.6, 127.4, 122.1, 74.1, 30.5, 10.0.

4.5.12. (*R*)-1-2-Tolyl-1-propanol

96% isolated yield. 96% ee determined by HPLC analysis (Chiralcel OB-H column, 5% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 16.08 min ((*S*)-isomer: t = 14.16 min). $[\alpha]_D^{23}$ = +65.2 (*c* 0.77, benzene) (lit.[11] $[\alpha]_D$ = +58.5 (*c* 2, benzene), >99% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.6 Hz, 1H), 7.16–7.03 (m, 3H), 4.76 (t, J = 6.4 Hz, 1H), 2.25 (s, 3H), 1.81 (s, 1H), 1.70–1.63 (m, 2H), 0.89 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 134.6, 130.3, 127.1, 126.2, 125.2, 72.0, 30.9, 19.0, 10.3.

4.5.13. (*R*)-1-(α-Naphthyl)-1-propanol

93% isolated yield. 95% ee determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 35.46 min ((*S*)-isomer: t = 24.42 min). $[\alpha]_D^{23}$ = +49.7 (*c* 0.58, $CHCl_3$) (lit.[12] $[\alpha]_D^{20}$ = +52.6 (*c* 2.55, $CHCl_3$), 93.5% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.48–7.43 (m, 3H), 5.35 (t, J = 7.2 Hz, 1H), 2.07 (s, 1H), 2.01–1.86 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 133.8, 130.5, 128.9, 127.8, 125.9, 125.5, 125.4, 123.2, 122.9, 72.6, 31.1, 10.5.

4.5.14. (*R*)-1-(β-Naphthyl)-1-propanol

97% isolated yield. 96% ee determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 24.01 min ((*S*)-isomer: t = 21.25 min). $[\alpha]_D^{23}$ = +27.0 (*c* 0.762, benzene) (lit.[12] $[\alpha]_D^{20}$ = +27.5 (*c* 3.80, benzene), 96.1% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 3H), 7.65 (s, 1H), 7.40–7.35 (m, 3H), 4.63 (t, J = 6.4 Hz, 1H), 2.08 (s, 1H), 1.83–1.70 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 133.2, 132.9, 128.2, 127.9, 127.6, 126.0, 125.7, 124.7, 124.1, 76.0, 31.7, 10.1.

4.5.15. (*R*)-1-Furyl-1-propanol

96% isolated yield. 85% ee determined by HPLC analysis of its benzoate (Chiralcel AD-H column, 2% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 13.45 min ((*S*)-isomer: t = 15.39 min). $[\alpha]_D^{23}$ = +18.5 (*c* 0.876, $CHCl_3$) (lit.[5e] $[\alpha]_D^{20}$ = +25.9 (*c* 2.10, $CHCl_3$), 90% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.28 (m, 1H), 6.25–6.24 (m, 1H), 6.15–6.14 (m, 1H), 4.51 (t, J = 6.8 Hz, 1H), 2.14 (s, 1H), 1.85–1.73 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 141.8, 110.0, 105.8, 69.1, 28.6, 9.9.

4.5.16. (*R*)-1-Thienyl-1-propanol

98% isolated yield. 92% ee determined by HPLC analysis of its benzoate (Chiralcel AD-H column, 2% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 15.15 min ((*S*)-isomer: t = 20.03 min). $[\alpha]_D^{23}$ = +23.9 (*c* 0.876, $CHCl_3$) (lit.[5e] $[\alpha]_D^{20}$ = +26.4 (*c* 2.20, $CHCl_3$), 95% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.20 (m, 1H), 6.94–6.92 (m, 2H), 4.76 (t, J = 6.8 Hz, 1H), 2.65 (s, 1H), 1.89–1.77 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 126.4, 124.3, 123.6, 71.5, 32.1, 10.0.

4.5.17. (*R*)-1-Phenyl-3-pentanol

81% isolated yield. 95% ee determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 18.70 min ((*S*)-isomer: t = 28.69 min). $[\alpha]_D^{23}$ = −21.1 (*c* 0.114, EtOH) (lit.[5e] $[\alpha]_D^{29}$ = −23.4 (*c* 1.00, EtOH), 81% ee for (*R*), lit.[13] $[\alpha]_D$ = −21.2 (*c* 7.72, EtOH), 94% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.17 (m, 5H), 3.59–3.53 (m, 1H), 2.84–2.77 (m, 1H), 2.71–2.64 (m, 1H), 1.85–1.66 (m, 2H), 1.59–1.46 (m, 2H), 1.26 (s, 1H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 128.4, 125.8, 72.7, 38.6, 32.1, 30.3, 9.8.

4.5.18. (*R*)-(*E*)-1-Phenylpent-1-en-3-ol

98% isolated yield. 94% ee determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 19.20 min ((*S*)-isomer: t = 30.03 min). $[\alpha]_D^{23} = +7.1$ (c 0.764, $CHCl_3$) (lit.[5e] $[\alpha]_D^{28} = +6.1$ (c 1.01, $CHCl_3$), 75% ee for (*R*)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.36 (m, 2H), 7.32–7.28 (m, 2H), 7.24–7.20 (m, 1H), 6.55 (d, J = 15.6 Hz, 1H), 6.20 (dd, J = 6.4 Hz, J = 15.6 Hz, 1H), 4.19 (q, J = 6.4 Hz, 1H), 1.69–1.60 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 132.3, 130.3, 128.5, 127.5, 126.4, 74.3, 30.2, 9.7.

4.5.19. (*R*)-3-Dodecanol[6o]

82% isolated yield. 92% ee determined by HPLC analysis of its benzoate (Chiralcel OD-H column, 2% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 10.96 min ((*S*)-isomer: t = 9.60 min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.49–3.42 (m, 1H), 1.60–1.20 (m, 18H), 0.99–0.79 (m, 6H).

4.5.20. (*R*)-(4-Methylphenyl)phenylmethanol[14]

56% isolated yield. 4% ee determined by HPLC analysis (Chiralcel OB-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 28.51 min ((*S*)-isomer: t = 47.31 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.23 (m, 7H), 7.12–7.11 (m, 2H), 5.36 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 139.4, 139.3, 137.1, 129.1, 128.3, 127.3, 127.2, 127.1, 79.7, 21.2.

4.5.21. (*S*)-1,3-Diphenyl-prop-2-yn-1-ol[7b]

94% isolated yield. 6% ee determined by HPLC analysis (Chiralcel OB-H column, 10% IPA in hexane, 0.5 ml/min, 254 nm UV detector). Retention time: t = 52.33 min ((*R*)-isomer: t = 59.83 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 2H), 7.46–7.19 (m, 8H), 5.64 (s, 1H), 2.81 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 131.7, 128.6, 128.5, 128.3, 128.2, 126.7, 122.4, 88.8, 86.5, 64.9.

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