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Asymmetric diethylzinc addition and phenyl transfer to aldehydes using chiral *cis*-cyclopropane-based amino alcohols

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Abstract—A new series of amino alcohols with a chiral cyclopropane backbone have been developed and used in the catalytic asymmetric diethylzinc addition and phenyl transfer to various types of aldehydes. These cyclopropane-based chiral amino alcohols show high enantioselectivity in the addition of organozincs to aromatic and aliphatic aldehydes. For diethylzinc addition to aromatic and aliphatic aldehydes, up to 97% ee and 93% ee are obtained, respectively. For the phenyl transfer to aromatic aldehydes, the best enantioselectivity was 89% ee.

1. Introduction

Cyclopropane is a fascinating subunit in organic synthesis.[1] The smallest cycloalkane often acts as a basic structural unit in a wide range of naturally occurring compounds[2] and the prepared unnatural products.[3] In these compounds, probably the best known cyclopropane-containing examples are the pyrethroid compounds, which are effective insecticides.[4] Cyclopropanes have also been used as versatile synthetic intermediates for the synthesis of more functionalized cycloalkanes and acyclic compounds.[5] Therefore, considerable efforts have been made to develop efficient methods for the synthesis of cyclopropane-related compounds, especially the enantioselective synthesis of cyclopropane.[6] A large variety of structurally diverse chiral cyclopropane compounds have already been prepared and applied extensively for many areas, but in asymmetric catalysis, cyclopropane skeletons have received relatively little attention and have rarely been used as chiral ligands for asymmetric reactions. So far only a few chiral cyclopropane-based ligands **1**–**4** have been reported (Fig. 1).[7]

In 1979, Colleuille et al. developed the first chiral cyclopropane-based ligand **1**.[7a] Using the cyclopropyl-based diphosphine **1** as a chiral ligand in the rhodium-catalyzed hydrogenation of dehydroamino acids, the corresponding reduction product can be obtained in 23% ee. In 1992, another chiral ligand **2** with a cyclopropane ring as a chiral backbone was reported by Minami et al.[7b] In the presence of catalyst Pd–**2**, an asymmetric allylic alkylation was carried out with 61% ee. Most recently, Molander et al. developed the chiral ligands **3** and **4**, and used them in the palladium-catalyzed allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate, the corresponding product can be obtained in high yield and with good enantioselectivity (up to 93% ee). They also found that the ligands based on *trans*-cyclopropane ring and metal would form a dimeric complex with a bridging ligand, which has been proven by the X-ray crystal structure of the complex from ligand **1** and $PdCl_2$.[7c] Dimeric or a mixture of a monomeric nonchelate catalyst has a high fluxional environment that subsequently leads to lower enantioselectivity. However, *cis*-ligands did chelate without forming dimers. The results showed that *cis*-cyclopropane-based ligand should have a better chelating capability.

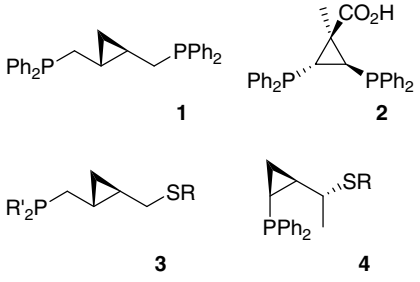

Figure 1. Chiral cyclopropane-based ligand.

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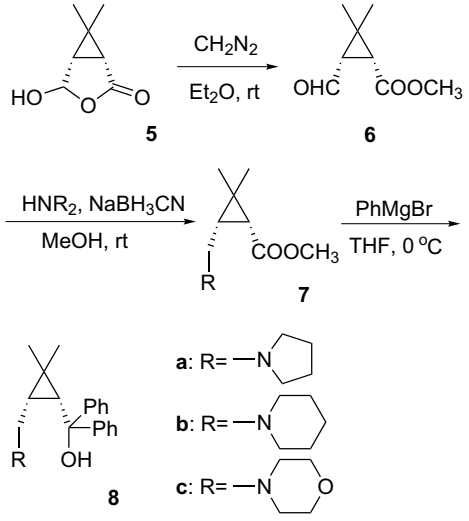
Based on these results, we designed and synthesized a new type of 1,4-aminoalcohol ligand with *cis*-cyclopropane as a chiral backbone, and have recently presented preliminary results on the addition of diethylzinc to aromatic aldehydes catalyzed by these amino alcohols.[8,9] Herein, the full results on the enantioselective diethylzinc addition to aromatic and aliphatic aldehydes with enantiopure cyclopropane-based amino alcohol ligands are provided.

Although the reaction of the asymmetric addition of an ethylzinc reagent to aldehydes has been well studied in recent years, the enantioselective addition of diphenylzinc to aldehydes is still challenging because the rapid competitive uncatalyzed phenylation leads to the undesired background reaction. Only a few results with high ee values have been reported.[10] Due to the importance of the resulting chiral diarylmethanols as intermediates for the synthesis of biologically and pharmaceutically active compounds,[10r] we herein report our main efforts towards the enantioselective phenyl transfer to aldehydes.

2. Results and discussion

Cyclopropane-based amino alcohol ligands were prepared from commercially available (1*R*,5*S*)-4-hydroxy-6,6-dimethyl-3-oxa-bicyclo-[3.1.0]hexan-2-one **5** in three simple steps, which is a key intermediate from pyrethroid insecticide and is quite inexpensive (Scheme 1).[4] Compound **5** reacted with diazomethane in diethyl ether to quantitatively give aldehydoester **6**. Subsequent reductive amination of **6** by $NaBH_3CN$ and secondary amines in methanol afforded a series of *cis*-cyclopropane aminoesters **7a**–**c** in 90–95% yield. A small amount of HCl can accelerate this reaction. In this reaction, when the temperature is above 35 °C, *trans*-cyclopropane aminoesters can be formed as a side product. Therefore, controlling the reaction temperature is very important. Aminoesters **7a**–**c** reacted with Grignard reagent at −15 °C to afford a series of aminoalcohol ligands **8a**–**c**. The ee values of **8a**–**c** are 98–99%. By recrystallization, the ee values of **8a**–**c** can be slightly improved.



Scheme 1. Synthesis of aminoalcohol ligands.

We succeeded in obtaining single crystals of ligand **8b** and **8c**, both of which were characterized by X-ray crystallographic analysis. The absolute configurations of **8b** and **8c** were assigned as (1*R*,3*S*) by their crystal structure (Figs. 2 and 3). This is identical with the configuration of the starting material **5**. The –OH group and N atom are situated at the same side of cyclopropane backbone, and the

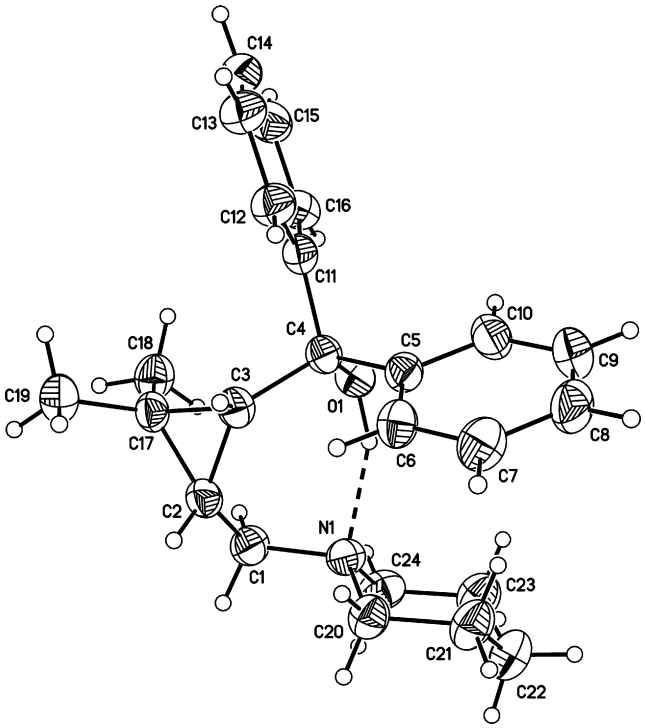


Figure 2. ORTEP diagram of amino alcohol (1*R*,3*S*)-**8b**.

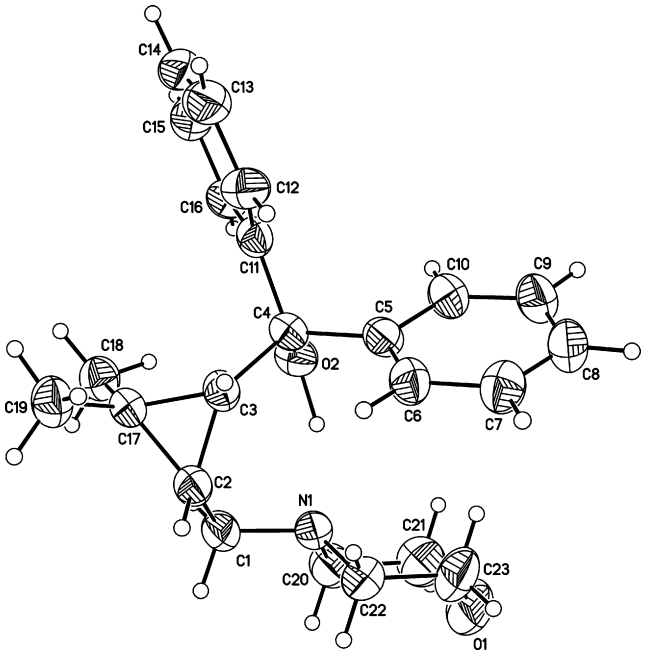
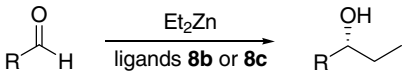


Figure 3. ORTEP diagram of amino alcohol (1*R*,3*S*)-**8c**.

hydrogen bond was observed in C–O–H···N–C (2.7 Å) to form a seven-membered ring. This clearly indicated that a metal can easily chelate to both of the groups despite highly rigid cyclopropane backbone.

At first, the diethylzinc addition to aromatic and aliphatic aldehydes was attempted with enantiopure cyclopropane-based amino alcohol ligands. Screening of ligands **8**, **8b** and **8c** demonstrated the best enantioselectivity. As shown in Table 1, in all cases, the aldehydes were completely consumed after 48 h under the reaction conditions. As shown by entries 1–14, the addition of diethylzinc to aromatic aldehydes proceeded in high yields and with enantioselectivities in the range of 95–97% ee. Compared with the cases of aromatic aldehydes, ligands **8b** and **8c** give lower selectivity in the ethylation of aliphatic and α,β-unsaturated aldehydes (Table 1, entries 15–26). For linear aldehydes, the catalyst displayed moderate enantioselectivity (entries 15–26). The best 93% ee was obtained with cyclohexanecarbaldehyde (entries 25–26). This is an encouraging result for generally poor selectivity in the addition to aliphatic aldehyde.

Table 1. Diethylzinc addition to aromatic aldehydes and aliphatic by using ligands **8b** and **8c**[a]



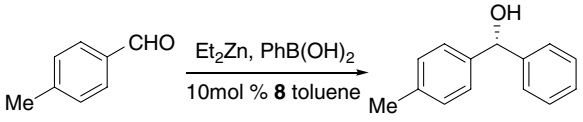
Entry	Aldehyde	Ligand	Yield[b] (%)	ee[c] (%)
1	Benzaldehyde	**8b**	87	96
2		**8c**	90	96
3	2-$MeOC_6H_4CHO$	**8b**	90	95
4		**8c**	88	95
5	3-$MeOC_6H_4CHO$	**8b**	93	95
6		**8c**	92	96
7	4-$MeOC_6H_4CHO$	**8b**	89	96
8		**8c**	90	96
9	2-ClC_6H_4CHO	**8b**	65	90
10		**8c**	60	94
11	4-ClC_6H_4CHO	**8b**	77	96
12		**8c**	80	96
13	1-Naphthaldehyde	**8b**	94	96
14		**8c**	93	97
15	*n*-Hexanal	**8b**	88	70
16		**8c**	82	65
17	*n*-Pentanal	**8b**	75	72
18		**8c**	82	66
19	*n*-Heptanal	**8b**	66	72
20		**8c**	70	66
21	*n*-Nonanal	**8b**	88	66
22		**8c**	82	61
23	*trans*-Cinnamaldehyde	**8b**	83	75
24		**8c**	85	72
25	Cyclohexanecarbaldehyde	**8b**	92	93
26		**8c**	90	93

[a] Reaction conditions: Et_2Zn (220 mol %), ligand (10 mol %), hexane as a solvent, −15 °C, 48 h.
[b] Isolated yield after flash chromatography.
[c] For aromatic alcohols, determined by HPLC analysis on a chiral Daicel OD-H column or by GC analysis on a chiral cyclodextrin capillary column; for aliphatic alcohols, determined by HPLC analysis of the corresponding 3,5-dinitrobenzoate of alcohol products on the Chiral Daicel OD-H column. Absolute configuration of major enantiomer was assigned as (*R*)-configuration by the comparison of specific rotation with literature data.

After our work on the diethylzinc addition to aromatic and aliphatic aldehydes had been finished, we turned our attention to the phenyl transfer to the aldehydes. In order to obtain excellent enantioselectivity in the addition of diphenylzinc to aldehydes, it is a key point to reduce the undesired background reaction from the rapid competitive uncatalyzed phenylation. Bolm et al. found that less active ethylphenylzinc can be used as a phenyl transfer reagent and suppress the undesired background reaction, and excellent enantioselectivity was realized.[10e] The ethylphenylzinc can easily be prepared by mixing diphenylzinc and diethylzinc, or alternatively by mixing arylboronic acids with diethylzinc. The latter method is a better choice, as it avoids using expensive and highly active diphenylzinc, and arylzinc reagent can easily be prepared by this method.

In exploring this reaction, ligands **8a**–**c** were screened for the phenylation of 4-methylbenzaldehyde by using the ethylphenylzinc reagent. First, the phenylzinc reagent was prepared from phenylboronic acid and diethylzinc in toluene at 60 °C for 12 h according to Bolm's protocol,[12d] then 10 mol % of **8** and a polyether (DiMPEG) were added into the mixture. Subsequently 4-methylbenzaldehyde was injected. As shown in Table 2, the phenyl transfer to 4-methylbenzaldehyde proceeded smoothly at 20 °C in 12 h with **8c** as the chiral ligand to give diarylmethanol in 90% yield but only in 72% ee (Table 2, entry 1). The same as in the case of diethylzinc addition to aldehydes, the reaction temperature is especially important for high enantioselectivity. When the temperature was lowered to 0 and −20 °C, a clear improvement in the enantioselectivity was obtained (Table 2, entry 1 vs entries 2 and 3) and the corresponding ee increased to 85%. When the temperature continued to be

Table 2. Enantioselective phenyl transfer to 4-methylbenzaldehyde using ligands **8a**–**c**[a]



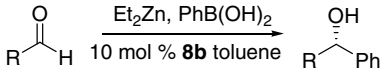
Entry	Ligands	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)
1	**8c**	20	12	90	72
2	**8c**	0	12	91	81
3	**8c**	−20	48	86	85
4	**8c**	−30	48	85	84
5[d]	**8c**	−20	48	88	79
6[e]	**8c**	−20	48	88	82
7	**8b**	−20	48	85	87
8	**8a**	−20	48	86	81

[a] Conditions: 2 equiv of $PhB(OH)_2$ and 6 equiv of Et_2Zn were used with respect to ArCHO.
[b] Isolated yield.
[c] Determined by HPLC analysis using a chiral column (Daicel Chiralcel OD-H; hexane/*i*-PrOH = 90:10), and the absolute configuration of the major enantiomer was assigned as (*R*) by the comparison of elution order on HPLC with the reported value.
[d] No DiMPEG was added.
[e] The ligand was pretreated with Et_2Zn.

lowered to −30 °C, the ee remained nearly the same (Table 2, entry 3 vs entry 4). According to the results reported by Ito, Katsuki and Uang et al., the use of DiMPEG as an additive deteriorated the enantioselectivity.[10g–i] Conversely, in our case, the use of DiMPEG as an additive improved enantioselectivity. When the reaction was carried out with DiMPEG, the ee increased from 79% to 84% (Table 2, entries 3 and 5). To optimize the reaction conditions, we also pretreated **8c** with Et_2Zn, which has been found to improve enantioselectivity.[10i] However, in our case, the ee value decreased slightly from 85% to 82% (Table 2, entry 3 vs entry 6). Under the optimized conditions, ligands **8a** and **8b** were examined in the same reaction. Ligand **8b** afforded the best 87% ee with 85% yield (Table 2, entry 7).

Under the optimized reaction conditions, various aromatic aldehydes were studied for the phenylation with 10 mol % of **8b** at −20 °C. High yields and good enantiomeric excesses in the range of 72–89% ee were accomplished with these aromatic aldehydes (Table 3). Electron-deficient and electron-rich aromatic aldehydes demonstrated different enantioselectivity in this reaction. Generally, electron-rich aromatic aldehydes showed the high enantioselectivity. 2-Methoxybenzaldehyde gave the best enantioselectivity at 89% ee (Table 3, entry 4).

Table 3. Enantioselective phenyl transfer to aromatic aldehydes using ligand **8b**[a]



Entry	Aldehyde	Yield[b] (%)	ee[c] (%)
1	2-BrC_6H_4CHO	83	79
2	3-BrC_6H_4CHO	82	83
3	2-ClC_6H_4CHO	90	72
4	2-$MeOC_6H_4CHO$	88	89
5	*trans*-Cinnamaldehyde	87	84
6	1-Naphthaldehyde	80	88
7	2-Naphthaldehyde	85	79

[a] Conditions: 2 equiv of $PhB(OH)_2$ and 6 equiv of Et_2Zn were used with respect to ArCHO, toluene as solvent, −20 °C, 48 h.
[b] Isolated yield.
[c] Determined by HPLC on a chiral column (Daicel Chiralcel OD-H), and the absolute configuration of the major enantiomer was assigned as (*R*) by the comparison of elution order of HPLC with the reported value.

3. Conclusions

In conclusion, a new type of *cis*-cyclopropane-based amino alcohol ligands has been developed. The ligands promoted the addition of diethylzinc and phenylzinc reagents to aromatic and aliphatic aldehydes under mild conditions to afford the corresponding secondary alcohols in high yield with moderate to excellent enantioselectivity. These results showed that the chiral cyclopropane-based ligand is promising in asymmetric catalysis and deserves more attention. Research on the synthesis of other chiral cyclopropane-based ligands and their application in other types of asymmetric reactions is being carried out in this laboratory and will be reported in due course.

4. Experimental

4.1. General

Melting points were determined using a Yanagimoto apparatus and are uncorrected. The optical rotations were measured with Perkin–Elmer PE-341 polarimeter. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker 500 MHz. All chemical shifts are quoted in parts per million relative to tetramethylsilane (δ, 0.00 ppm), and coupling constants (J) are measured in Hertz. Mass spectra were recorded on an Agilent instrument using the TOFMS technique. Infrared spectra were recorded using a Bruker Tensor 27 spectrometer. The reactions were carried out under nitrogen or argon using Schlenk technique when necessary. High Performance Liquid Chromatography was conducted on Agilent 1100 using chiral column Diacel Chiralcel OD-H. Gas Chromatography was conducted on Lu-Nan 6800 series with FID detector using chiral column CYCLODEX-B, 30 m × 0.25 mm I.D. (Agilent Technologies, USA). Retention time is given in minutes.

4.2. (1*R*,3*S*)-Methyl 3-formyl-2,2-dimethylcyclopropanecarboxylate 6

(1*R*,5*S*)-4-Hydroxy-6,6-dimethyl-3-oxa-bicyclo[3.1.0]-hexan-2-one **5** (2.84 g, 20 mmol) was dissolved in a mixture of 30 mL of Et_2O and 5 mL of MeOH. This solution was cooled to 0 °C and a solution of diazomethane in ether was added slowly with stirring, until the solution stopped bubbling and the color of the solution remained yellow. The solution was slowly allowed to warm to room temperature without additional heating. The reaction mixture was concentrated under reduced pressure. The crude product was passed through a silica gel column (hexane/ethyl acetate = 6/1) to afford **6** as a colorless oil (2.9 g, 93% yield). $[\alpha]_D^{18} = -73.4$ (*c* 0.99, $CHCl_3$); IR (neat) 2957, 1731, 1701, 1439, 1379, 1200, 1137, 1119, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (s, 3H), 1.55 (s, 3H), 1.83–1.86 (m, 1H), 2.12 (d, 1H, $J = 9.5$ Hz), 3.71 (s, 3H), 9.75 (d, 1H, $J = 9.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.5, 28.3, 29.8, 36.1, 40.9, 52.2, 170.4, 200.4; HRMS (TOF): m/z calcd for $C_8H_{13}NO_3$ $[M+H]^+$: 157.0865, found: 157.0865.

4.3. General procedure for the preparation of *cis*-cyclopropane aminoesters from *cis*-cyclopropane aldehydoester

To a solution of 60 mmol of a secondary amine in 50 mL of methanol was added 4 mL (20 mmol) of 5 M HCl–methanol, followed by 3.12 g (20 mmol) of **6** and 1 g (16 mmol) of $NaBH_3CN$. The resulting solution was stirred at room temperature for 16 h. Concentrated HCl was then added until pH <2, and the methanol was removed under reduced pressure. The residue was taken up in 15 mL of water and extracted with three 20 mL portions of ether. The aqueous solution was brought to pH >10 with 20% NaOH (aq), and extracted with ether (5 × 15 mL). The combined extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give **7a–c** with 90–95% yields.

4.3.1. (1*R*,3*S*)-Methyl 2,2-dimethyl-3-((pyrrolidin-1-yl)-methyl)cyclopropanecarboxylate 7a. Dense oil, $[\alpha]_D^{18} = -4.3$ (*c* 1.62, EtOH); IR (neat) 2952, 2782, 1729, 1437, 1383, 1355, 1175, 1140, 1088, 852 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 3H), 1.23 (s, 3H), 1.30–1.34 (br s, 4H), 1.53 (d, 1H, $J = 9.0$ Hz), 1.77 (br s, 4H), 2.52 (br s, 1H), 2.71–2.75 (m, 1H), 2.85–2.89 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.5, 23.4, 25.1, 28.5, 28.7, 32.4, 50.0, 51.1, 53.9, 172.2; HRMS (TOF): *m*/*z* calcd for $C_{12}H_{22}NO_2$ $[M+H]^+$: 212.1651, found: 212.1642.

4.3.2. (1*R*,3*S*)-Methyl 2,2-dimethyl-3-((piperidin-1-yl)-methyl)cyclopropanecarboxylate 7b. Dense oil, $[\alpha]_D^{18} = -7.1$ (*c* 0.98, $CHCl_3$); IR (neat) 2935, 2854, 1729, 1437, 1375, 1174, 1153, 1133, 1089, 849 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 3H), 1.21 (s, 3H), 1.26–1.28 (m, 1H), 1.43 (br s, 2H), 1.52 (d, 1H, $J = 9.0$ Hz), 1.58 (br s, 4H), 2.40 (br s, 4H), 2.58–2.62 (m, 1H), 2.71–2.74 (m, 1H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.5, 24.4, 25.0, 26.1, 28.5, 28.7, 31.3, 51.1, 53.3, 54.2, 172.1; HRMS (TOF): *m*/*z* calcd for $C_{13}H_{24}NO_2$ $[M+H]^+$: 226.1807, found: 226.1810.

4.3.3. (1*R*,3*S*)-Methyl 2,2-dimethyl-3-(morpholinomethyl)-cyclopropanecarboxylate 7c. Dense oil, $[\alpha]_D^{18} = +15.4$ (*c* 0.88, $CHCl_3$); IR (neat) 2952, 2854, 1727, 1456, 1374, 1177, 1117, 1087, 1010, 866 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 3H), 1.22 (s, 3H), 1.24–1.27 (m, 1H), 1.54 (d, 1H, $J = 9.0$ Hz), 2.47 (br s, 4H), 2.64–2.68 (m, 1H), 2.74–2.78 (m, 1H), 3.64 (s, 3H), 3.70 (br s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.5, 25.0, 28.4, 28.7, 30.7, 51.1, 52.9, 53.4, 67.1, 172.0; HRMS (TOF): *m*/*z* calcd for $C_{12}H_{22}NO_3$ $[M+H]^+$: 228.1600, found: 228.1589.

4.4. General procedure for the synthesis of *cis*-cyclopropane aminoalcohol 8a–c

Magnesium (0.6 g, 25.0 mmol) was added to 20 mL of anhydrous THF. A solution of bromobenzene (3.14 g, 20 mmol in 10 mL of THF) was added dropwise into the above mixture. Once the reaction began, the rest of the bromobenzene solution was added at a rate that maintained a gentle reflux. When the addition of the bromobenzene solution was complete, the mixture was refluxed for 20 min, and was then cooled to −15 °C. Compound **7** (5 mmol) was dissolved in 5 mL of anhydrous THF and added to the prepared Grignard mixture. After the solution of compound **7** had been added, the resulting mixture was stirred at room temperature for an additional 12 h. The reaction was quenched with saturated NH_4Cl (aq), and the mixture was extracted several times with Et_2O. The organic phases were combined, dried over $MgSO_4$ and concentrated under reduced pressure. The residual yellow solid was purified by flash chromatography (hexane/ethyl acetate = 1/2) to yield **9a**–**b** as colorless crystals.

4.4.1. ((1*R*,3*S*)-2,2-Dimethyl-3-((pyrrolidin-1-yl)methyl)-cyclopropyl)diphenylmethanol 8a. Colorless needles, mp 112–113 °C; $[\alpha]_D^{18} = +14.1$ (*c* 1.51, $CHCl_3$); IR (KBr) 3370, 2949, 1446, 1371, 1346, 1319, 1278, 1184, 1090, 1066, 1032, 956, 876, 768, 748, 700, 636 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.91 (s, 3H), 0.92–1.02 (m, 1H), 1.22 (s, 3H), 1.61–1.64 (m, 2H), 1.65–1.74 (m, 3H), 2.40–2.91 (m, 5H), 2.93–2.95 (m, 1H), 7.09–7.16 (m, 2H), 7.22–7.28 (m, 4H), 7.50–7.56 (m, 4H), 8.09(br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.5, 20.1, 23.3, 26.5, 30.1, 38.3, 51.3, 52.9, 125.3, 125.7, 125.9, 127.6, 127.7, 149.1, 152.1; HRMS (TOF): *m*/*z* calcd for $C_{23}H_{30}NO$ $[M+H]^+$: 336.2327, found: 336.2322.

4.4.2. ((1*R*,3*S*)-2,2-Dimethyl-3-((piperidin-1-yl)methyl)-cyclopropyl)diphenylmethanol 8b. Colorless needles, mp 162–163 °C; $[\alpha]_D^{18} = +167.6$ (*c* 0.82, $CHCl_3$); IR (KBr) 3420, 2937, 1444, 1370, 1305, 1194, 1124, 1097, 1062, 1028, 1010, 985, 881, 773, 750, 700, 636 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (s, 3H), 1.00–1.05 (m, 1H), 1.16 (s, 3H), 1.20–1.37 (m, 6H), 1.84 (d, 1H, $J = 9.0$ Hz), 2.46–2.61 (m, 6H), 7.09–7.14 (m, 2H), 7.22–7.26 (m, 4H), 7.52–7.60 (m, 4H), 7.78 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.4, 20.0, 24.1, 25.1, 25.3, 30.3, 37.3, 53.5, 54.7, 125.63, 125.66, 125.74, 127.5, 127.8, 149.3, 151.9; HRMS (TOF): *m*/*z* calcd for $C_{24}H_{32}NO$ $[M+H]^+$: 350.2484, found: 350.2479.

4.4.3. ((1*R*,3*S*)-2,2-Dimethyl-3-(morpholinomethyl)cyclopropyl)diphenylmethanol 8c. Colorless needles, mp 156–157 °C; $[\alpha]_D^{18} = +158.5$ (*c* 0.93, $CHCl_3$); IR (KBr) 3430, 2822, 1449, 1371, 1299, 1272, 1192, 1113, 1070, 1031, 1014, 920, 864, 778, 752, 706, 637 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 3H), 0.93–1.05 (m, 1H), 1.17 (s, 3H), 1.88 (d, 1H, $J = 9.0$ Hz), 2.35 (br s, 2H), 2.52 (br s, 2H), 2.56–2.60 (m, 1H), 2.65–2.69 (m, 2H), 3.30 (b, 2H), 3.48–3.52 (m, 2H), 7.11–7.15 (m, 2H), 7.24–7.27 (m, 4H), 7.51–7.61 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.3, 20.1, 24.5, 30.3, 37.1, 52.6, 54.6, 66.2, 125.4, 125.6, 125.8, 126.2, 127.7, 127.9, 148.9, 151.6; HRMS (TOF): *m*/*z* calcd for $C_{23}H_{30}NO_2$ $[M+H]^+$: 352.2277, found: 352.2272.

4.5. X-ray crystal structure data for (1*R*,3*S*)-8b and 8c

Compound **8b**: $C_{24}H_{31}NO$, $M_r = 349.50$, triclinic, *P*1, $a = 6.1917(12)$, $b = 8.8540(18)$, $c = 9.7155(19)$ Å; $\alpha = 92.53(3)°$, $\beta = 95.90(3)°$, $\gamma = 105.29(3)°$; $V = 509.63(17)$ Å^3; $2.39° < 2\theta < 27.64°$; $\rho_{calc} = 1.273$ g cm^{-3}, $Z = 1$, $F(000) = 190$; Final $R_1 = 0.0524$, $wR_2 = 0.1447$, all data, $R_1 = 0.0642$, $wR_2 = 0.1550$.

Compound **8c**: $C_{23}H_{29}NO_2$, $M_r = 351.47$, triclinic, *P*1, $a = 6.2009(12)$, $b = 8.7144(17)$, $c = 9.6164(19)$ Å; $\alpha = 92.38(3)°$, $\beta = 98.64(3)°$, $\gamma = 104.91(3)°$; $V = 494.70(17)$ Å^3; $2.15° < 2\theta < 27.45°$; $\rho_{calc} = 1.180$ g cm^{-3}, $Z = 1$, $F(000) = 190$; Final $R_1 = 0.0473$, $wR_2 = 0.1270$, all data, $R_1 = 0.0712$, $wR_2 = 0.1398$.

CCDC-618048 and CCDC-618049 contain the supplementary crystallographic data for **8b** and **8c**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the CCDC, Cambridge, CB21EZ, UK; fax: (+44)-1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk].

4.6. General procedure for diethylzinc addition to aldehydes

The chiral ligand (0.1 mmol) was dissolved in hexane (3 mL), cooled to −15 °C, and diethylzinc (1.5 mL of 1.5 M of toluene solution, 2.2 mmol) was injected. After the mixture was stirred for 20 min, benzaldehyde (0.1 g, 1 mmol) was added dropwise via a syringe, and the mixture stirred for the corresponding reaction time under N_2. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (10 mL). The mixture was then extracted with Et_2O (3×15 mL). The combined organic phases were dried and concentrated in vacuo. The crude products were purified by flash column chromatography (hexane/EtOAc). The ee values of the alcohol products were determined by HPLC on a Chiralcel OD-H column (*i*-PrOH/hexane) or by GC analysis on a chiral cyclodextrin capillary column. The absolute configuration of the major enantiomer was assigned by the comparison of optical rotation with literature data.

4.6.1. (*R*)-1-Phenyl-1-propanol. $[\alpha]_D^{26} = +40.3$ (*c* 1.21, $CHCl_3$). {lit.[11a] $[\alpha]_D = -33.0$ (*c* 3.35, $CHCl_3$) for 80% ee (*S*)}; 96% ee (*R*) by HPLC analysis (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1.0 mL/min, 254 nm UV detection), $t_R = 8.4$ min for (*R*) and $t_R = 13.2$ min for (*S*).

4.6.2. (*R*)-1-(2-Methoxyphenyl)-1-propanol. $[\alpha]_D^{26} = +23.7$ (*c* 1.40, $CHCl_3$). {lit.[11b] $[\alpha]_D = +44.6$ (*c* 0.451, toluene) for 78% ee (*R*)}; 95% ee (*R*) by GC analysis (CYCLODEX-B column, $N_2 = 1.0$ mL/min, DET = 250 °C, INJ = 240 °C, OVEN = 160 °C), $t_R = 11.7$ min for (*S*) and $t_R = 13.3$ min for (*R*).

4.6.3. (*R*)-1-(3-Methoxyphenyl)-1-propanol. $[\alpha]_D^{26} = +40.3$ (*c* 1.21, $CHCl_3$). {lit.[11b] $[\alpha]_D = +23.3$ (*c* 0.498, benzene) for 81% ee (*R*)}; 95% ee (*R*) by HPLC analysis (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1 mL/min, 254 nm UV detection), $t_R = 16.0$ min for (*R*) and $t_R = 19.8$ min for (*S*).

4.6.4. (*R*)-1-(4-Methoxyphenyl)-1-propanol. $[\alpha]_D^{26} = +38.9$ (*c* 1.23, $CHCl_3$). {lit.[11b] $[\alpha]_D = +28.5$ (*c* 0.534, benzene) for 83% ee (*R*)}; 96% ee (*R*) by HPLC analysis (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1.0 mL/min, 254 nm detection), $t_R = 10.7$ min for (*R*) and $t_R = 12.9$ min for (*S*).

4.6.5. (*R*)-1-(2-Chlorophenyl)-1-propanol. $[\alpha]_D^{26} = +42.5$ (*c* 1.62, $CHCl_3$). {lit.[11c] $[\alpha]_D = +37.1$ (*c* 4, $CHCl_3$) for 79% ee (*R*)}; 95% ee (*R*) by GC analysis (CYCLODEX-B column, $N_2 = 1.0$ mL/min, DET = 250 °C, INJ = 240 °C, OVEN = 160 °C), $t_R = 12.0$ min for (*R*) and $t_R = 12.8$ min for (*S*).

4.6.6. (*R*)-1-(4-Chlorophenyl)-1-propanol. $[\alpha]_D^{26} = +30.6$ (*c* 2.08, $CHCl_3$). {lit.[11b] $[\alpha]_D = +19.8$ (*c* 0.479, benzene) for 82% ee (*R*)}; 96% ee (*R*) by HPLC analysis (Chiralcel OD-H column, hexane/2-propanol = 97/3, 1.0 mL/min, 254 nm UV detection), $t_R = 7.4$ min for (*S*) and $t_R = 7.8$ min for (*R*).

4.6.7. (*R*)-1-(1-Naphthalenyl)-1-propanol. $[\alpha]_D^{26} = +60.3$ (*c* 1.11, $CHCl_3$). {lit.[11b] $[\alpha]_D = +61.1$ (*c* 0.442, benzene) for 77% ee (*R*)}; 97% ee (*R*) by HPLC analysis (Chiralcel OD-H column, hexane/2-propanol = 80/20, 1.0 mL/min, 254 nm UV detection), $t_R = 6.4$ min for (*S*) and $t_R = 10.9$ min for (*R*).

4.6.8. (*R*)-Heptan-3-ol. $[\alpha]_D^{26} = -4.9$ (*c* 0.68, $CHCl_3$). {lit.[11d] $[\alpha]_D = +5.8$ (*c* 0.442, $CHCl_3$) for 95% ee (*S*)}; 72% ee (*R*) by HPLC analysis of the corresponding derivative 3,5-dinitrobenzoate by OD-H column (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1.0 mL/min, 254 nm UV detection), $t_R = 10.2$ min for (*S*) and $t_R = 11.4$ min for (*R*).

4.6.9. (*R*)-Octan-3-ol. $[\alpha]_D^{26} = -6.5$ (*c* 0.80, $CHCl_3$). {lit.[11e] $[\alpha]_D = -8.9$ (*c* 6.12, $CHCl_3$) for 98% ee (*R*)}; 70% ee (*R*) by HPLC analysis of the corresponding derivative 3,5-dinitrobenzoate by OD-H column (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1.0 mL/min, 254 nm UV detection), $t_R = 11.3$ min for (*S*) and $t_R = 12.6$ min for (*R*).

4.6.10. (*R*)-Nonan-3-ol. $[\alpha]_D^{26} = -9.0$ (*c* 0.68, $CHCl_3$). {lit.[11f] $[\alpha]_D = +9.1$ (*c* 7.2, $CHCl_3$) for 88% ee (*S*)}; 72% ee (*R*) by HPLC analysis of the corresponding derivative 3,5-dinitrobenzoate by OD-H column (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1.0 mL/min, 254 nm UV detection), $t_R = 9.5$ min for (*S*) and $t_R = 10.6$ min for (*R*).

4.6.11. (*R*)-Undecan-3-ol. $[\alpha]_D^{26} = -6.3$ (*c* 0.41, $CHCl_3$). {lit.[11g] $[\alpha]_D = +5.2$ (*c* 1, $CHCl_3$) for 84% ee (*S*)}; 66% ee (*R*) by HPLC analysis of the corresponding derivative 3,5-dinitrobenzoate by OD-H column (Chiralcel OD-H column, hexane/2-propanol = 95/5, 1.0 mL/min, 254 nm UV detection), $t_R = 8.6$ min for (*S*) and $t_R = 9.6$ min for (*R*).

4.6.12. (*R*)-(*E*)-1-Phenylpent-1-en-3-ol. $[\alpha]_D^{26} = +18.4$ (*c* 0.61, $CHCl_3$). {lit.[11g] $[\alpha]_D = -13.2$ (*c* 2.1, Et_2O) for 48% ee (*S*)}; 75% ee (*R*) by HPLC analysis (Chiralcel OD-H column, hexane/2-propanol = 90/10, 1.0 mL/min, 254 nm UV detection), $t_R = 7.6$ min for (*R*) and $t_R = 11.4$ min for (*S*).

4.6.13. (*R*)-1-Cyclohexylpropan-1-ol. $[\alpha]_D^{26} = +5.4$ (*c* 0.61, $CHCl_3$). {lit.[11g] $[\alpha]_D = -3.1$ (*c* 0.47, $CHCl_3$) for 89% ee (*S*)}; 93% ee (*R*) by HPLC analysis of the corresponding derivate of 3,5-dinitrobenzoate by OD-H column (Chiralcel OD-H column, hexane/2-propanol = 98/2, 1.0 mL/min, 254 nm UV detection), $t_R = 31.7$ min for (*S*) and $t_R = 33.7$ min for (*R*).

4.7. General procedure for phenyl transfer reaction

A flame dried Schlenk tube containing toluene (2 mL), phenylboronic acid (122 mg, 1 mmol), and diethylzinc (3.0 mmol, 1.5 M solution in toluene) was heated at 60 °C for 12 h. After the flask was cooled to room temperature, the mixture was added into another flask containing **9c** (17.5 mg, 0.05 mmol) and DiMPEG (0.1 g, 0.05 mmol) in toluene (1 mL), and was stirred for 15 min. It was cooled to −20 °C, and a solution of 4-tolualdehyde (60 mg,

0.5 mmol) in toluene (1 mL) was added with stirring. After 48 h at −20 °C, the reaction was quenched with saturated aqueous ammonium chloride and then extracted with Et_2O (3 × 10 mL). The combined organic phases were dried and concentrated in vacuo. The crude products were purified by flash column chromatography (hexane/EtOAc = 1/6). The ee values of the alcohol products were determined by HPLC on a Chiralcel OD-H column. The absolute configuration of the major enantiomer was assigned as *R* by the comparison of elution order of HPLC with the reported value.

4.7.1. (*R*)-Phenyl(*p*-tolyl)methanol.[12] Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 90/10, 1 mL/ min. t_R = 9.5 min (*S*), 10.4 min (*R*); 87% ee.

4.7.2. (*R*)-(2-Bromophenyl)(phenyl)methanol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 90/10, 1 mL/ min. t_R = 9.6 min (*R*), 14.0 min (*S*); 79% ee.

4.7.3. (*R*)-(3-Bromophenyl)(phenyl)methanol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 90/10, 1 mL/ min. t_R = 11.7 min (*S*), 13.2 min (*R*); 83% ee.

4.7.4. (*R*)-(2-Chlorophenyl)(phenyl)methanol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 90/10, 1 mL/ min. t_R = 9.1 min (*R*), 11.5 min (*S*); 72% ee.

4.7.5. (*R*)-(2-Methoxyphenyl)(phenyl)methanol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 98/2, 1 mL/ min. t_R = 47.6 min (*S*), 56.9 min (*R*); 89% ee.

4.7.6. (*R*)-(Naphthalen-1-yl)(phenyl)methanol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 70/30, 1 mL/ min. t_R = 7.2 min (*S*), 14.8 min (*R*); 88% ee.

4.7.7. (*R*)-(Naphthalen-2-yl)(phenyl)methanol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 90/10, 1 mL/ min. t_R = 16.7 min (*S*), 20.2 min (*R*); 72% ee.

4.7.8. *E*-(*R*)-1,3-Diphenylprop-2-en-1-ol. Chiralcel OD-H, UV 225 nm, hexane/2-propanol = 90/10, 1 mL/ min. t_R = 17.4 min (*R*), 22.6 min (*S*); 72% ee.

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