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Chiral C_2-symmetric 2,4-disubstituted azetidines as chiral ligands in the addition of diethylzinc to aldehydes

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Abstract

Chiral C_2-symmetric 2,4-disubstituted azetidine derivatives having a β-amino alcohol moiety have been successfully synthesized and their stereoselective catalytic abilities have been examined in the asymmetric addition of diethylzinc to aldehydes in hexane. When *N*-(2,2-diphenyl-2-hydroxyethyl)-(*S*,*S*)-2,4-bis(methoxymethyl)azetidine **12** was used as a catalytic chiral ligand, the production of *sec*-alcohols having an *S*-absolute configuration could be achieved in high chemical yields (92–99%) and high enantiomeric excesses (83–93% for arylaldehydes and 63–65% for aliphatic aldehydes). For some arylaldehydes, the enantioselectivities are higher than the corresponding chiral C_2-symmetric 2,5-disubstituted pyrrolidine ligands. However, when the chiral C_2-symmetric azetidine derivatives **13** and **14**, which have bulky substituents on the 2,4-positions were used as the chiral ligands under the same reaction conditions, the enantiomeric excesses of the corresponding *sec*-alcohols decreased to 20–30%.

1. Introduction

High efficiencies of C_2-symmetric chiral reagents, including auxiliaries and catalyst ligands, in asymmetric induction have attracted much attention in asymmetric synthesis.[1] Previously, we reported chiral C_2-symmetric 2,5-disubstituted pyrrolidine derivatives as chiral catalyst ligands in the reaction of diethylzinc with arylaldehydes.[2] Very high yields and very high enantioselectivities have been achieved in this asymmetric addition reaction.[3] The relatively rigid C_2-symmetric five-membered ring structure is considered to be the determining factor for those ligands being so effective in asymmetric catalytic reactions. According to this point of view, we tried to design and synthesize some novel chiral ligands which have C_2-symmetric four-membered rings since the backbone of a four-membered ring is totally rigid, and consequently higher enantiomeric excesses (ees) might be achieved. Based on this concept, we have started to synthesize some chiral C_2-symmetric azetidine β-amino alcohols and have used them as chiral ligands for catalytic asymmetric reactions.

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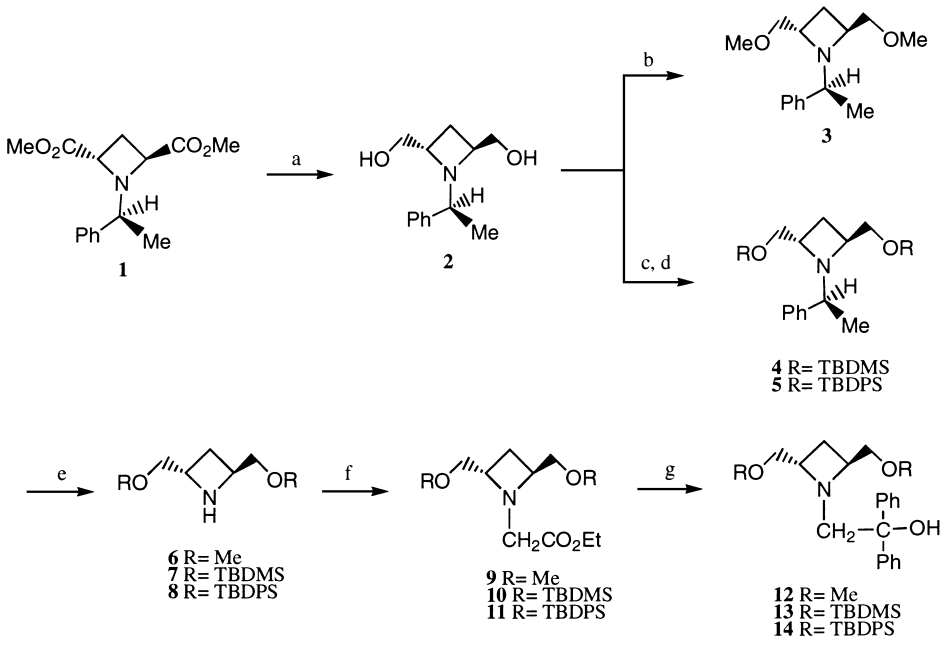
2. Results and discussion

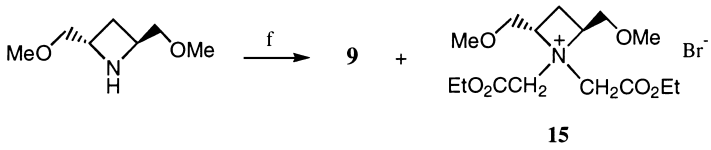
The optically active azetidine 2,4-dicarboxylic acid ester **1** could be synthesized by a similar method to that reported for the preparation of chiral C_2-symmetric pyrrolidine 2,5-dicarboxylic acid ester[4,5] and its diol **2** could be easily obtained as the key intermediate by reduction with lithium aluminum hydride in THF. Thus, we can readily introduce a Me group, a TBDMS group (*tert*-butyldiphenylsilyl) or a TBDPS group (*tert*-butyldiphenylsilyl) on the 2,4-position of the azetidine ring, respectively, to obtain the compounds **3**, **4** and **5** (Scheme 1).



Scheme 1. Conditions: (a) $LiAlH_4$, THF, reflux, 5 h; 96%. (b) MeI, NaH, THF, rt-reflux, 89%. (c) TBDMSCl, imidazole, CH_2Cl_2, rt 30 h; 76%. (d) TBDPSCl, imidazole, CH_2Cl_2, rt 30 h; 86%. (e) H_2, $Pd(OH)_2$, MeOH; 80% for **6**, 90% for **7** and 90% for **8**. (f) $BrCH_2CO_2Et$, K_2CO_3, MeCN, 0°C–rt 24 h; 50% for **9**, 99% for **10** and 90% for **11**. (g) PhMgBr, THF, 0°C, 12 h; 75% for **12**, 85% for **13** and 70% for **14**

The chiral auxiliary (2-phenethyl group) can be removed by catalytic hydrogenation over $Pd(OH)_2$/C (20%) to give the corresponding chiral C_2-symmetric 2,4-disubstituted azetidines **6**, **7** and **8**, which were subsequently treated with ethyl α-bromoacetate and then a Grignard reagent to afford the desired β-amino alcohols **12**, **13** and **14**. All those synthetic reactions are very similar to the synthesis of the corresponding 2,5-disubstituted pyrrolidine derivatives.[3] Only in the preparation of *N*-(ethoxycarbonylmethyl)-(*S*,*S*)-2,4-bis(methoxymethyl)azetidine **9**, is the reaction somewhat different from the corresponding 2,5-disubstituted pyrrolidine case. The yield of **9** is 50%, with the formation of *N*,*N*-bis(ethoxycarbonylmethyl)-(*S*,*S*)-2,4-bis(methoxymethyl)azetidinium bromide **15** in 12% yield as a by-product (Scheme 2). However, after carefully re-examining our previous results,[3] we confirmed that the formation of the corresponding pyrrolidinium bromide could not be observed at all in the preparation of the corresponding *N*-(ethoxycarbonylmethyl)-(*R*,*R*)-2,5-bis(methoxymethyl)pyrrolidine.[3] This result strongly suggests that the nitrogen atom in the four-membered rings has higher nucleophilicity than that in the five-membered rings; thus the tertiary amine could further react with another ethyl α-bromoacetate to afford the ammonium salt.

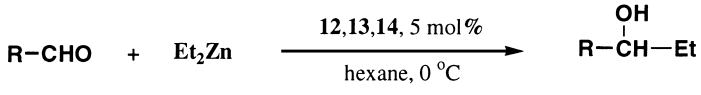
It is well known that the reaction of aldehydes with diethylzinc giving the corresponding *sec*-alcohols takes place in the presence of a catalytic amount of β-amino alcohol.[6] Excellent chiral inductions



Scheme 2.

including asymmetric amplifications by use of chiral β-amino alcohols in this reaction have been reported.[7] Now this interesting reaction has been widely utilized for the examination of the efficiencies of chiral ligands.

In order to clarify the chiral induction abilities of these interesting C_2-symmetric azetidine derivatives and the differences between the four-membered ring and five-membered ring, we examined the asymmetric addition reaction of diethylzinc with arylaldehydes and aliphatic aldehydes in the presence of catalytic amounts (4 mol%) of chiral β-amino alcohols **12**, **13** and **14**. The results are summarized in Table 1. The ees of the products were determined by HPLC analysis using a chiral stationary-phase column (Chiralcel OD and OJ) and the absolute configurations of the major enantiomers were assigned according to the sign of their specific rotations.[8,9] As shown in Table 1, high yields and high ees could be achieved by using the chiral C_2-symmetric β-amino alcohol **12**. For some arylaldehydes, the ees are higher than the corresponding chiral C_2-symmetric 2,5-disubstituted pyrrolidine cases. For example, in the case of *p*-chlorobenzaldehyde, the ee of the product is only 76% in the presence of 5 mol% of *N*-(2,2-diphenyl-2-hydroxyethyl)-(*R*,*R*)-2,5-bis(methoxymethyl)pyrrolidine.[2] But, using the azetidine derivative, the ee can reach 92% (Table 1). Even in the presence of 0.8 mol% of **12**, similar results could be obtained under the same reaction conditions. On the other hand, for the aliphatic aldehydes the ees decreased to 63–65%. This is simply due to the phenyl group being larger than the normal aliphatic group. The bulky substrates usually give higher stereoselectivity. However, when the chiral C_2-symmetric azetidine derivatives having bulky substituents on the 2,4-position were used as the chiral ligands under the same reaction conditions, the ees of the corresponding *sec*-alcohols decreased to 20–30%. A similar tendency has also been observed in the same addition reaction using chiral C_2-symmetric 2,5-disubstituted pyrrolidine derivatives as the chiral ligands.[2] It is common knowledge that higher stereoselectivity can be achieved by introduction of sterically bulky substituents into the chiral ligands or auxiliaries. However, our results showed that this is not always the case. This result suggests that the flexible methoxy group on the side chain of **12** may provide an additional coordination to the β-amino alcohol-chelated zinc atom[7,10] and this totally rigid chiral Lewis acid affects the highly stereoselective addition reaction,[3] whereas the sterically bulky group on the 2,4-position would impede this kind of coordination and influence both the approach of aldehyde and reaction transition state which may cause the decrease of the enantioselectivity.

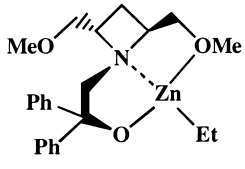


Based on these results, we illustrate the possible active species of **12** and the corresponding five-membered β-amino alcohol in the above mentioned asymmetric addition reaction in Fig. 1 in which complex A and complex B represent the chiral Lewis acids for the asymmetric reaction. We believe the two active species are very similar. The only difference between them is the backbone structure of the azetidine and pyrrolidine ring. The totally rigid azetidine complex A is responsible for the slightly better chiral induction compared to the pyrrolidine case. In order to verify this speculation, we also tried to synthesize the chiral C_2-symmetric 2,6-disubstituted six-membered ring according to the literature.[5] However, the separation of these diastereoisomers was very difficult. Until now, we could not obtain the enantiomerically pure C_2-symmetric 2,6-disubstituted piperidine.

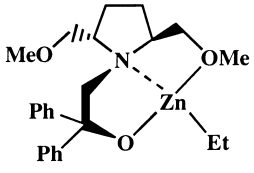
Table 1
Asymmetric addition reaction of diethylzinc with aldehydes in the presence of 5 mol% chiral C_2-symmetric 2,4-disubstituted azetidines **12**, **13**, and **14**

R	Cat.	Yield (%)[a]	ee (%)[b]	absolute configuration
Ph	**12**	99	92	S
p-MePh	**12**	95	83	S
p-ClPh	**12**	92	92	S
p-BrPh	**12**	94	93	S
1-Naphthyl	**12**	97	86	S
n-C_4H_9	**12**	94	65	S
Ph-CH=CH	**12**	86	63	S
Ph	**13**	96	20	S
p-MePh	**13**	96	20	S
p-ClPh	**13**	86	18	S
p-MeOPh	**13**	72	18	S
p-MePh	**14**	90	20	S
p-ClPh	**14**	86	26	S

[a] Isolated Yields; [b] Determined by chiral HPLC.



Complex A



Complex B

Figure 1.

In conclusion, we have found that the totally rigid C_2-symmetric four-membered ring is a good potential chiral unit for the catalytic asymmetric induction reaction. Efforts are underway to elucidate the mechanistic details of why *N*-(2,2-diphenyl-2-hydroxyethyl)-(*S*,*S*)-2,4-bis(methoxymethyl)azetidine **12** is such an effective catalyst ligand.

3. Experimental

Mps were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined in a solution of $CHCl_3$ and methanol at 20°C by using a Perkin–Elmer 241 MC digital polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. ^1H NMR spectra were determined for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard on a Bruker AMX-300 spectrometer; *J* values are in hertz. IR spectra were determined by a Perkin–Elmer 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument. High resolution mass spectra were recorded on a Finnigan MA+ instrument. All solid compounds reported in this paper gave satisfactory CHN

microanalyses with an Italian Carlo-Erba 1106 analyzer. Compounds **1**, **2**, **3** and **6** were prepared according to the literature.[4,5]

3.1. Preparation of (S,S)-2,4-bis[(tert-butyldimethylsiloxy)methyl]-N-[(S)-1-phenylethyl]azetidine **4**

To a solution of **2** (260 mg, 1.18 mmol) and imidazole (160 mg, 2.36 mmol) in dichloromethane (30 ml) was added *tert*-butyldimethylsilyl chloride (356 mg, 2.36 mmol) and the reaction mixture was stirred for 36 h at room temperature. The mixture was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **4** as a colorless oil (eluent: ethyl acetate:petroleum ether=1:10). Yield: 400 mg, 76%; $[\alpha]_D$ −60.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (6H, s, SiMe), 0.10 (6H, s, SiMe), 0.96 (18H, s, Me_3C), 1.12 (3H, d, *J*=6.2, Me), 2.12 (2H, t, *J*=7.0), 3.50–3.70 (6H, m), 4.00–4.20 (1H, q, *J*=6.2), 7.10–7.50 (5H, m, Ar); [HRMS (EI) found: 449.3157 (M^+); $C_{25}H_{47}NO_2Si_2$ requires: 449.3145].

3.2. Preparation of (S,S)-2,4-bis[(tert-butyldiphenylsiloxy)methyl]-N-[(S)-1-phenylethyl]azetidine **5**

This compound was prepared in the same manner as that described above. Yield: 658 mg, 86%; $[\alpha]_D$ +20.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (18H, s, Me_3C), 1.12 (3H, d, *J*=6.2, Me), 2.02 (2H, t, *J*=7.0), 3.10 (2H, dd, *J*=10.4, 3.8), 3.45 (2H, dd, *J*=10.4, 6.3), 3.70–3.85 (2H, m), 3.90 (1H, q, *J*=6.2), 7.00–7.10 (3H, m, Ar), 7.15–7.22 (2H, m, Ar), 7.30–7.50 (12H, m, Ar), 7.51–7.70 (8H, m, Ar); [HRMS (EI) found: 697.3756 (M^+); $C_{45}H_{55}NO_2Si_2$ requires: 697.3771].

3.3. Preparation of (S,S)-2,4-bis[(tert-butyldimethylsiloxy)methyl]azetidine **7**

To a solution of **4** (390 mg, 0.87 mmol) in methanol (40 ml) was added $Pd(OH)_2/C$ (20%, 100 mg) and the reaction mixture was stirred at room temperature for 64 h under a hydrogen atmosphere. The solvent was removed under reduced pressure and the residue was used for the next reaction without purification. Yield: 273 mg, 90%; $[\alpha]_D$ −1.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (12H, s, SiMe), 0.96 (18H, s, Me_3C), 2.16 (2H, t, *J*=7.0), 2.61 (1H, br, s, NH), 3.70–3.85 (4H, m), 3.90 (2H, m); [HRMS (EI) found: 345.2536 (M^+); $C_{17}H_{39}NO_2Si_2$ requires 345.2519].

3.4. Preparation of (S,S)-2,4-bis[(tert-butyldiphenylsiloxy)methyl]azetidine **8**

This compound was prepared in the same manner as that described above. Yield: 273 mg, 90%; $[\alpha]_D$ +3.5 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (18H, s, Me_3C), 2.20 (2H, t, *J*=7.0), 2.70 (1H, br, s, NH), 3.70–3.85 (4H, m), 3.90 (2H, m), 7.30–7.50 (12H, m, Ar), 7.51–7.70 (8H, m, Ar); [HRMS (EI) found: 593.3155 (M^+); $C_{37}H_{47}NO_2Si_2$ requires: 593.3145].

3.5. Preparation of N-(ethoxycarbonylmethyl)-(S,S)-2,4-bis(methoxymethyl)azetidine **9**

To a solution of **6** (300 mg, 2.10 mmol) and potassium carbonate (428 mg, 3.10 mmol) in acetonitrile (30 ml) was added ethyl α-bromoacetate (380 mg, 0.25 ml, 2.28 mmol) and the reaction mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the residue was extracted with ether (3×30 ml). The organic layer was washed with water, brine and dried over $NaSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **9** as a colorless oil (eluent: ethyl acetate:petroleum ether=1:1). Yield: 230 mg, 50%; $[\alpha]_D$ −70.2 (*c* 0.64, $CHCl_3$); IR (neat) ν 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (3H, t, *J*=7.1, Me),

2.06 (2H, t, *J*=7.1), 3.36 (6H, s, OMe), 3.42 (1H, d, *J*=17.3), 3.48 (2H, dd, *J*=10.4, 4.0), 3.54 (2H, dd, *J*=10.4, 6.3), 3.63 (1H, d, *J*=17.3), 3.72–3.83 (2H, m), 4.20 (2H, q, *J*=7.1); [HRMS (EI) found: 231.1459 (M^+); $C_{11}H_{21}NO_4$ requires: 231.1471].

3.6. Preparation of N-*(ethoxycarbonylmethyl)-(*S,S*)-2,4-bis[(*tert*-butyldimethylsiloxy)methyl]azetidine **10**

To a solution of **7** (250 mg, 0.74 mmol) and potassium carbonate (112 mg, 0.80 mmol) in acetonitrile (30 ml) was added ethyl α-bromoacetate (124 mg, 0.74 mmol) and the reaction mixture was stirred at room temperature for 38 h. The solvent was removed under reduced pressure and the residue was extracted with ethyl acetate. The organic layer was washed with water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **10** as a colorless oil (eluent: ethyl acetate:petroleum ether=1:10). Yield: 319 mg, 99%; $[\alpha]_D$ −28.1 (*c* 1.25, $CHCl_3$); IR (neat) ν 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (6H, s, SiMe), 0.10 (6H, s, SiMe), 0.96 (18H, s, Me_3C), 1.28 (3H, t, *J*=5.9, Me), 2.02 (2H, t, *J*=7.0), 3.40 (1H, d, *J*=18.0), 3.50–3.73 (4H, m, CH_2), 3.67 (1H, d, *J*=18.0), 4.00–4.20 (4H, m); [HRMS (EI) found: 431.2870 (M^+); $C_{21}H_{45}NO_4Si_2$ requires: 431.2887].

3.7. Preparation of N-*(ethoxycarbonylmethyl)-(*S,S*)-2,4-bis[(*tert*-butyldiphenylsiloxy)methyl]azetidine **11**

This compound was prepared in the same manner as that described above. Yield: 273 mg, 90%; $[\alpha]_D$ +12.2 (*c* 1.0, $CHCl_3$); IR (neat) ν 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (18H, s, Me_3C), 1.32 (3H, t, *J*=5.9, Me), 2.14 (2H, t, *J*=7.0), 3.40 (1H, d, *J*=18.0), 3.50–3.73 (4H, m, CH_2), 3.67 (1H, d, *J*=18.0), 4.00–4.20 (4H, m), 7.30–7.50 (12H, m, Ar), 7.51–7.70 (8H, m, Ar); [HRMS (EI) found: 679.3502 (M^+); $C_{41}H_{53}NO_4Si_2$ requires: 679.3513].

3.8. Preparation of N-*(2,2-diphenyl-2-hydroxyethyl)-(*S,S*)-2,4-bis(methoxymethyl)azetidine **12**

To a solution of phenylmagnesium bromide prepared from the reaction of bromobenzene (1.5 g, 9.55 mmol) and magnesium (250 mg, 10.42 mmol) in THF (10 ml) was added **9** (220 mg, 0.95 mmol) at 0°C and the reaction mixture was stirred for 24 h. The reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ether (3×25 ml). The organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **12** as a colorless oil (eluent: ethyl acetate:petroleum ether=1:3). Yield: 242 mg, 75%; $[\alpha]_D$ −16.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.02 (2H, t, *J*=7.0), 3.12 (1H, d, *J*=13.6), 3.17–3.26 (4H, m, CH_2), 3.30 (6H, s, OMe), 3.40–3.60 (2H, m), 3.75 (1H, d, *J*=13.6), 5.40 (1H, br, s, OH), 7.10–7.30 (6H, m, Ar), 7.40–7.50 (4H, m, Ar); [HRMS (EI) found: 341.1979 (M^+); $C_{21}H_{27}NO_3$ requires: 341.1991].

3.9. Preparation of N-*(2,2-diphenyl-2-hydroxyethyl)-(*S,S*)-2,4-bis[(*tert*-butyldimethylsiloxy)methyl]-azetidine **13**

This compound was prepared in the same manner as that described above. Yield: 437 mg, 85%; $[\alpha]_D$ −11.0 (*c* 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (12H, s, SiMe), 0.96 (18H, s, Me_3C), 2.02 (2H, t, *J*=7.0), 3.12 (1H, d, *J*=13.6), 3.20–3.50 (6H, m, CH_2), 3.85 (1H, d, *J*=13.6), 5.40 (1H, br, s, OH),

7.10–7.40 (6H, m, Ar), 7.40–7.60 (4H, m, Ar); [HRMS (EI) found: 523.3315 (M^+-H_2O); $C_{31}H_{49}NO_2Si_2$ requires: 523.3302].

3.10. *Preparation of* N-*(2,2-diphenyl-2-hydroxyethyl)-(*S,S*)-2,4-bis[(*tert*-butyldiphenylsiloxy)methyl]-azetidine **14**

This compound was prepared in the same manner as that described above. Yield: 525 mg, 70%; $[\alpha]_D$ +22.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (18H, s, Me_3C), 2.12 (2H, t, *J*=7.0), 3.16 (1H, d, *J*=13.8), 3.20–3.60 (6H, m, CH_2), 3.85 (1H, d, *J*=13.8), 5.40 (1H, br, s, OH), 7.10–7.40 (6H, m, Ar), 7.40–7.52 (16H, m, Ar), 7.53–7.70 (8H, m, Ar); [HRMS (EI) found: 789.4029 (M^+); $C_{51}H_{59}NO_3Si_2$ requires: 789.4033].

3.11. *The formation of* N,N-*bis(ethoxycarbonylmethyl)-(*S,S*)-2,4-bis(methoxymethyl)azetidinium bromide **15**

This compound was obtained in the preparation of **9**. Yield: 90 mg, 12%; $[\alpha]_D$ +1.5 (*c* 0.95, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (6H, t, *J*=7.1, Me), 2.05 (1H, dt, *J*=14.7, 7.1), 2.13 (1H, dt, *J*=14.7, 7.1), 3.00–3.20 (1H, m), 3.18 (3H, s, OMe), 3.46 (3H, s, OMe), 3.45–3.60 (2H, m, CH_2), 3.66 (4H, d, *J*=1.3, CH_2), 3.56–3.80 (2H, m, CH_2), 4.18 (4H, q, *J*=7.1, CH_2), 4.31 (1H, m); MS (EI) *m/z* 397, 399 (M^+); [HRMS (EI) found: 397.1307 (M^+); $C_{15}H_{28}BrNO_6$ requires: 397.1300].

Typical reaction procedure: to a suspension of β-amino alcohol **12** (8.5 mg, 0.025 mmol) in hexane (1.0 ml), diethylzinc (1.1 mmol, 1.1 ml of 1 M hexane solution) was added at 0°C. After stirring for 0.5 h, benzaldehyde (53 mg, 1.0 mmol) was added and the reaction mixture was stirred for 24 h at 0°C. The reaction was quenched by 3% HCl aqueous solution and the organic product was extracted with ethyl acetate. The extract was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by silica gel TLC to give the optically active 1-phenylpropanol (67 mg, 99%).

Acknowledgements

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