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Tetrahedron: *Asymmetry* 16 (2005) 2039–2043

Asymmetric synthesis of 1,4-amino alcohol ligands with a norbornene backbone for use in the asymmetric diethylzinc addition to benzaldehyde

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Received 8 April 2005; accepted 18 April 2005
Available online 23 May 2005

Abstract—The asymmetric synthesis of *cis*-1,4-amino alcohols with a norbornene backbone was performed starting with (2*S*,3*R*)-(−)-*cis*-hemiester **2** (98% ee). Chemoselective amination with NH_4OH and HMPTA followed by LAH reduction afforded **5** and **7**, respectively. Amido ester **6** was transformed into chiral ligand **9** with Grignard reaction followed by LAH reduction. The chiral ligands **5**, **7**, and **9** were subjected to asymmetric diethylzinc addition to examine their effectiveness as chiral catalysts. Among these, chiral ligand **7** exhibited the highest enantioselectivity (88% ee).

1. Introduction

Amino alcohols are versatile chiral building blocks for organic synthesis[1] and have also been used extensively as chiral auxiliaries[2] or ligands in asymmetric synthesis.[3] In particular, the formation of C–C bonds has always been one of the most challenging areas in organic synthesis. Among these, the enantioselective addition of diethylzinc to aldehydes in the presence of chiral ligands was first reported by Noyori et al.[4] Although different types of chiral ligands, such as diamines,[5] diols,[6] aminothiols,[7] and aminosulfides,[7] were used in this reaction, amino alcohols are the most common type of ligands among them. Chiral 1,2-aminoalcohols are widely used in diethylzinc addition reactions, however, there are only just a few examples of chiral 1,4-amino alcohols used in this reaction.[1,8–12] 1,4-Amino alcohols have more flexible structures with respect to 1,2-amino alcohols for complexation with various types of metals and thus may form more stable and selective catalysts in the reaction. This prompted us to develop new chiral 1,4-amino alcohols including a norbornene backbone and study their use in the alkylation of benzaldehyde by diethylzinc.

2. Asymmetric synthesis of 1,4-amino alcohols with a norbornene backbone

In our synthetic strategy, *cis*-monoester (−)-**2** was chosen as the homochiral starting compound for the construction of a norbornene backbone. Bolm et al.[13] have recently reported a highly efficient method for the enantioselective desymmetrizaton of *meso*-anhydrides via an alkaloid-mediated opening with methanol. Quinine and quinidine are used as the chiral directing agents and both enantiomers of the corresponding *cis*-monoester can be obtained with very high enantiomeric excesses (up to 99% ee) and chemical yield.

Quinine-mediated desymmetrization of anhydride **1** with methanol resulted in *cis*-monoester (−)-**2** with a high enantiomeric excess (98% ee) (Scheme 1). Monoester (−)-**2** was then reacted with *p*-bromophenol via DCC coupling method to produce corresponding diester **3**, which was then analyzed by HPLC for enantiomeric excess determination.

In our synthetic route, the carboxylic acid group of monoester (−)-**2** was chemoselectively activated with ethyl chloroformate and then reacted with NH_4OH to afford the corresponding *cis*-monoester amide **4** with a yield of 82%. One of the target *cis*-1,4-unsubstituted amino alcohol derivatives **5** was obtained by subsequent $LiAlH_4$ reduction of **4** in ether with 73% yield.

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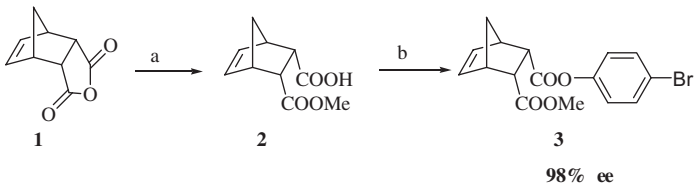
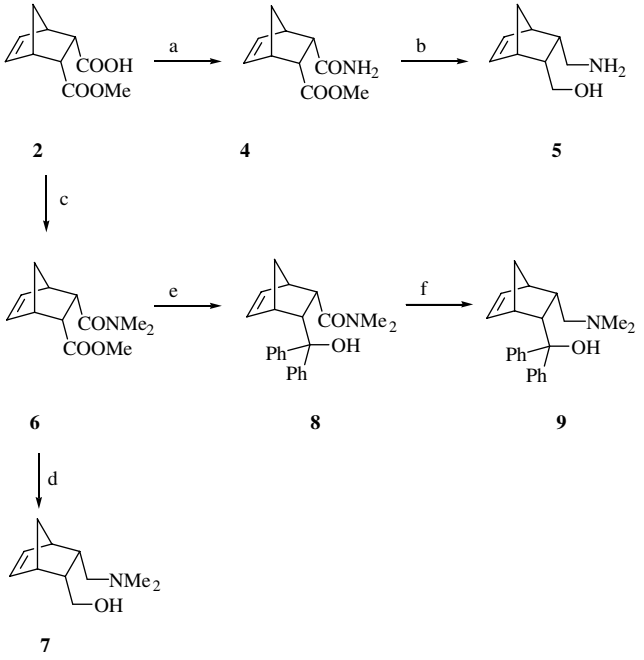
doi:10.1016/j.tetasy.2005.04.019



Scheme 1. Reagents and conditions: (a) quinine, MeOH, toluene/CCl_4, −55 °C; (b) 4-bromophenol, DCC, DMAP, CH_2Cl_2.

Substitution on norbornene based *cis*-1,4-amino alcohol nitrogen and methylene bearing hydroxy group would presumably cause an impact on the catalytic activity of the resulting chiral ligands used in the asymmetric addition of diethylzinc to benzaldehyde. In the synthesis of sterically and electronically modified chiral ligands, monoester (−)-**2** was reacted with hexamethylphosphorus triamide, which transformed the carboxylic acid group into corresponding *N*,*N*-dimethyl amide derivative **6** with a yield of 88%.[14] Subsequent reduction of **6** by $LiAlH_4$ in ether afforded the *N*,*N*-dimethyl substituted *cis*-1,4-amino alcohol type chiral ligand **7** with a yield of 90%. Using a Grignard method, the ester group of **6** was functionalized with phenylmagnesium bromide giving diphenyl substituted derivative **8**. The reduction of the *N*,*N*-dimethyl amide function was accomplished by $LiAlH_4$ in ether to afford chiral ligand **9** with a yield of 94% (Scheme 2).



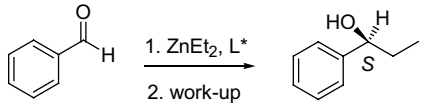
Scheme 2. Reagents and conditions: (a) (i) $ClCO_2Et$, TEA, THF, (ii) NH_4OH; (b) $LiAlH_4$, Et_2O, reflux; (c) HMPTA, benzene, reflux; (d) $LiAlH_4$, Et_2O, reflux; (e) (i) PhBr, Mg, Et_2O, (ii) 1 M HCl; (f) $LiAlH_4$, Et_2O, reflux.

The absolute configurations of (−)-**5**, (+)-**7**, and (−)-**9** were determined as (2*S*,3*R*) by comparing specific rotation signs determined at equal concentration in the same solvent with *cis*-monoester (+)-**2**, which had been reported in the literature.[13,15] Since transformation of *cis*-monoester (−)-**2** to chiral ligands **5**, **7**, and **9** has no effect on the stereocenters of the norbornene backbone, the absolute configuration of each ligand was not changed during transformation reactions.

3. Enantioselective addition of diethylzinc to benzaldehyde using 5, 7, and 9

The catalytic properties of the three new chiral 1,4-amino alcohols **5**, **7**, and **9** were explored in asymmetric diethylzinc addition to benzaldehyde. The results are summarized in Table 1.

Table 1. Asymmetric diethylzinc addition to benzaldehyde using norbornene based 1,4-aminoalcohol catalysts



L* = **5**, **7**, **9**

Entry	Ligand[a]	Yield (%)[b]	ee (%)[c]
1	**5**	15	53
2	**7**	98	82
3	**9**	97	49

[a] 10 mol % of chiral catalysts were used. Toluene was used as solvent. All reactions were done at 0 °C.
[b] Yields were calculated after column chromatography.
[c] Enantiomeric ratios were determined by HPLC analysis using a chiral column. The major product has an (*S*)-configuration.

All the ligands exhibited acceptable enantioselectivities (up to 82% ee) and afforded 1-phenylpropanol in good yields (up to 98%). The best result was obtained with amino alcohol **7**, which has dimethyl substituents on the nitrogen atom (entry 2). Catalysts without any substituent on the nitrogen and hydroxymethylene carbon **5** and with dimethyl and diphenyl substituents on nitrogen and hydroxymethylene carbon **9**, respectively (entries 1 and 3) gave the products with lower ee values. These results prompted us toward the investigation of the conditions to improve the enantioselectivity of chiral catalyst **7**. For this purpose, the temperature and solvent dependence enantioselectivity of chiral ligand **7** was explored.

The asymmetric diethylzinc addition reaction was carried out in toluene with 10 mol % of chiral catalyst **7** at −10 and at 20 °C and compared with the result given in Table 1 (entry 2). At −10 °C, catalyst **7** gave 76% ee and afforded 1-phenylpropanol with a yield of 67%. Both the enantioselectivity and the chemical yield were lower than entry 2. When the temperature was raised

up to 20 °C, no chemical yield change was observed. The enantioselectivity decreased as in the former case (75% ee). We also examined the effect of solvent using hexane, DCM, and THF. All the results are given in Table 2. The reactions were carried out at the optimized temperature 0 °C and among the solvents, the best result was obtained in hexane (88% ee) (Table 2, entry 2). We obtained very low ee with DCM and THF with 30% and 59% ee, respectively (entries 3 and 4).

Table 2. The effect of solvent on the enantioselectivity of chiral ligand **7**

Entry[a]	Solvent	Yield (%)[b]	ee (%)[c]
1	Toluene	98	82
2	Hexane	98	88
3	DCM	5	30
4	THF	15	59

[a] 10 mol % of chiral catalyst was used. All reactions were done at 0 °C.
[b] Yields were calculated after column chromatography.
[c] Enantiomeric ratios were determined by HPLC analysis using a chiral column. The major product has *S* configuration.

4. Conclusion

We have synthesized a series of chiral norbornene-based 1,4-amino alcohols (2*S*,3*R*)-**5**, (2*S*,3*R*)-**7**, and (2*S*,3*R*)-**9**. These compounds were used as ligands in the asymmetric diethylzinc addition to benzaldehyde. Ligand (2*S*,3*R*)-**7** showed the best enantioselectivity over the others. We optimized the asymmetric diethylzinc addition condition. All the ligands directed the catalytic process toward the formation of (1*S*)-1-phenylpropanol.

5. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker Spectrospin Avance DPX 400 spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane. Apparent splittings are given in all cases. Infrared spectra were obtained from KBr pellets on a Mattson 1000 FT-IR spectrophotometer. Mass spectra were recorded on a Varian MAT 212. Melting points are uncorrected. Optical rotations were measured in a 1 dm cell using a Bellingham and Stanley P20 polarimeter at 20 °C. HPLC measurements were performed with ThermoFinnigan Spectra System instrument. Separations were carried out on Chiralcel OD-H analytical column (250 × 4.60 mm) with hexane/2-propyl alcohol as eluent. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2-mm silica gel 60 F_{254} analytical aluminum plates.

5.1. Synthesis of (2*S*,3*R*)-3-methoxycarbonylbicyclo-[2.2.1]hept-5-ene-2-carboxylic acid 2

MeOH (1.48 mL, 36 mmol) was added dropwise to a stirred solution of the *meso*-anhydride **1** (2.00 g, 12 mmol) and quinine (4.35 g, 13 mmol) in a 1:1 mixture of toluene (120 mL) and carbon tetrachloride (120 mL) at −55 °C under argon. The reaction mixture was stirred at this temperature for 60 h. Subsequently, the resulting clear solution was concentrated in vacuo to dryness and the resulting residue dissolved in ethyl acetate. The ethyl acetate solution was washed with 2 M HCl, and after phase separation, followed by extraction of aqueous phase with ethyl acetate and the organic layer dried over $MgSO_4$ was filtered, and concentrated providing the monoester **2** (2.17 g, 92%). $[\alpha]_D^{20} = -7.8$ (*c* 4.0, CCl_4), lit.[15,16] $[\alpha]_D^{20} = -7.9$ (*c* 4.8, CCl_4); mp 75–78 °C, lit.[15,16] 74 °C (racemic); ^{1}H NMR: δ 6.26 (dd, $J = 2.96$, 5.50 Hz, 1H), 6.16 (dd, $J = 2.94$, 5.53 Hz, 1H), 3.54 (s, 3H), 3.28 (dd, $J = 3.22$, 10.14 Hz, 1H), 3.22 (dd, $J = 3.13$, 10.15 Hz, 1H), 3.14 (br s, 1H), 3.11 (br s, 1H), 1.43 (dt, $J = 1.56$, 8.67 Hz, 1H), 1.28 (d, $J = 8.69$ Hz, 1H); ^{13}C NMR: δ 177.8, 173.1, 135.6, 134.4, 51.6, 48.8, 48.2, 47.9, 46.6, 46.1.

To recover the quinine, the acidic aqueous phase was neutralized with Na_2CO_3 and extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered. Evaporation of the solvent yielded the quinine almost quantitatively.

5.2. Synthesis of (2*S*,3*R*)-2-(4-bromophenoxy)-3-methoxycarbonylbicyclo[2.2.1]hept-5-ene 3

4-Bromophenol (0.088 g, 0.51 mmol) and monoester **2** (0.100 g, 0.51 mmol) were dissolved in CH_2Cl_2 (5 mL) at 0 °C under argon. Then, DCC (0.105 g, 0.51 mmol) and DMAP (0.016 g, 0.13 mmol) were added simultaneously at 0 °C. The mixture was stirred overnight at room temperature. DCC precipitated as dicyclohexylurea. The mixture was filtered and filtrate washed first with 5% HOAc, then 1 M NaOH and finally brine. The organic phase was dried over $MgSO_4$ and evaporation of the solvent afforded the compound **3** (0.16 g, 89%). HPLC-analysis of the methyl 4-bromophenyl diester: Chiralcel OD-H at room temperature, *n*-hexane/2-propanol = 98:2, 0.5 mL/min, 254 nm, $t_1 = 20.3$ min (major), $t_2 = 23.2$ min (minor); ^{1}H NMR: δ 7.37 (d, $J = 8.72$ Hz, 2H), 6.92 (d, $J = 8.71$ Hz, 2H), 6.32 (dd, $J = 2.91$, 5.39 Hz, 1H), 6.15 (dd, $J = 2.92$, 5.41 Hz, 1H), 3.55 (s, 3H), 3.39 (s, 2H), 3.20 (s, 1H), 3.17 (s, 1H), 1.40 (d, $J = 8.70$ Hz, 1H), 1.33 (d, $J = 8.61$, 1H); ^{13}C NMR: δ 173.0, 171.2, 150.3, 135.9, 135.0, 132.7, 123.8, 119.0, 52.2, 49.1, 48.7, 48.5, 47.2, 46.6.

5.3. Synthesis of (2*S*,3*R*)-2-carboxamido-3-methoxycarbonylbicyclo[2.2.1]hept-5-ene 4

Ethylchloroformate (0.97 mL, 10.2 mmol) was added to a mixture of monoester **2** (2.00 g, 10.2 mmol) dissolved in dry THF (15 mL) and triethylamine (1.42 mL, 10.2 mmol) over a period of 5 min at −7 °C. The resultant mixture was stirred for an additional 30 min at −7 °C and then the mixture filtered, and the cake washed with THF (3 × 5 mL). NH_4OH (3 mL) was added to the filtrate in one portion and the mixture stirred for 1 h at 10 °C, afterwards the mixture was concentrated. The solid residue was dissolved in CH_2Cl_2 and washed with 1 M HCl. The organic phase was dried over

$MgSO_4$ and the solvent evaporated. The crude product was purified by column chromatography (5% MeOH/95% $CHCl_3$) to give compound **4** (1.63 g, 82%). $[\alpha]_D^{20} = -2.5$ (*c* 2.77, MeOH); mp 130–131 °C; IR (KBr): 3325, 3198, 1738, 1671 cm^{-1}; ^1H NMR: δ 6.45 (dd, $J = 3.04$, 5.44 Hz, 1H), 6.11 (dd, $J = 2.97$, 5.48 Hz, 1H), 5.54 (s, 2H), 3.54 (s, 3H), 3.23 (dd, $J = 3.04$, 10.45 Hz, 1H), 3.18 (dd, $J = 2.83$, 10.49 Hz, 1H), 3.07 (m, 2H), 1.44 (d, $J = 8.61$ Hz, 1H), 1.28 (d, $J = 8.59$, 1H); ^{13}C NMR: δ 174.3, 173.6, 137.0, 133.3, 51.5, 49.8, 49.3, 49.0, 47.2, 45.7.

5.4. Synthesis of (2*S*,3*R*)-2-aminomethyl-3-hydroxymethylbicyclo[2.2.1]hept-5-ene 5

To a suspension of $LiAlH_4$ (0.11 g, 3.0 mmol) in dry THF (10 mL) was added a solution of amido ester **4** (0.20 g, 1.0 mmol) in THF (5 mL) at a rate, which maintained gentle reflux. The mixture was then refluxed for 1 day and hydrolized by the cautious addition of water and 15% NaOH solution. The fine white precipitate which formed was washed with ether and discarded. The filtrate was concentrated and purified by column chromatography (8% MeOH/2% NH_4OH/90% $CHCl_3$) to afford compound **5** (1.11 g, 73%). $[\alpha]_D^{20} = -8.9$ (*c* 0.56, MeOH); mp 102–104 °C; IR (KBr): 3378, 3077, 2665, 1608 cm^{-1}; ^1H NMR: δ 6.06 (dd, $J = 3.00$, 5.39 Hz, 1H), 6.02 (dd, $J = 2.39$, 5.80 Hz, 1H), 3.74 (br s, 2H), 3.55 (dd, $J = 3.23$, 11.61 Hz, 1H), 3.32 (t, $J = 11.42$ Hz, 1H), 2.98 (dd, $J = 2.57$, 11.76 Hz, 2H), 2.77 (t, $J = 1.42$ Hz, 2H), 2.56–2.60 (m, 1H), 2.44 (t, $J = 11.95$ Hz, 1H), 2.28–2.35 (m, 1H), 1.40 (d, $J = 1.83$ Hz, 1H), 1.39 (d, $J = 1.87$ Hz, 1H); ^{13}C NMR: δ 135.3, 134.4, 63.2, 49.8, 47.6, 46.9, 46.2, 44.5, 42.2; HRMS calcd for $C_9H_{16}NO$ $(M+H)^+$, 154.1232. Found 154.1240.

5.5. Synthesis of (2*S*,3*R*)-2-(*N*,*N*-dimethylcarboxamido)-3-methoxycarbonylbicyclo[2.2.1]hept-5-ene 6

To the solution of monoester **2** (2.00 g, 10.2 mmol) in benzene (5 mL) was added hexamethylphosphorus triamide (1.85 mL, 5.1 mmol) at a rate which maintained reflux of the reaction. After 2 h, the resulting cloudy solution was allowed to cool to room temperature and a saturated $NaHCO_3$ solution was added. The aqueous layer was extracted with DCM. The organic solutions were combined, dried over $MgSO_4$, and concentrated to give compound **6** (2.01 g, 88%). $[\alpha]_D^{20} = -35.7$ (*c* 1.16, $CHCl_3$); mp 78–79 °C; IR (KBr): 2998, 1742, 1637 cm^{-1}; ^1H NMR: δ 6.30 (dd, $J = 3.03$, 5.34 Hz, 1H), 6.12 (dd, $J = 2.93$, 5.39 Hz, 1H), 3.52 (s, 3H), 3.35 (dd, $J = 3.16$, 9.91 Hz, 1H), 3.19 (dd, $J = 3.48$, 9.92 Hz, 1H), 3.12 (s, 1H), 3.04 (s, 1H), 2.95 (s, 3H), 2.81 (s, 3H), 1.38 (d, $J = 8.5$ Hz, 1H), 1.27 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR: 173.3, 172.4, 136.6, 133.9, 51.9, 49.2, 48.9, 47.3, 47.0, 46.9, 37.3, 36.0; HRMS calcd for $C_{12}H_{18}NO_3$ $(M+H)^+$, 224.1287. Found 224.1277.

5.6. Synthesis of (2*S*,3*R*)-2-dimethylaminomethyl-3-hydroxymethylbicyclo[2.2.1]hept-5-ene 7

To a suspension of $LiAlH_4$ (0.26 g, 6.72 mmol) in anhydrous ether (1 mL) was added a solution of amido ester **6** (0.50 g, 2.24 mmol) in dry THF (5 mL) at a rate, which maintained gentle reflux. The mixture was then refluxed for 3 h and hydrolized by the cautious addition of water and 15% NaOH solution. The fine white precipitate, which formed was washed with ether and discarded. The filtrate was concentrated to give amino alcohol **7** (0.37 g, 90%). $[\alpha]_D^{20} = +15.1$ (*c* 1.16, MeOH); mp 90–92 °C; IR (KBr): 3131, 2959, 2361, 1507 cm^{-1}; ^1H NMR: δ 5.98 (m, 2H), 3.43 (dd, $J = 2.12$, 11.61 Hz, 1H), 3.13 (t, $J = 11.32$ Hz, 1H), 2.64 (s, 1H), 2.61 (s, 1H), 2.42 (m, 2H), 2.24 (t, $J = 12.49$ Hz, 1H), 2.16 (s, 6H), 2.03 (dd, $J = 1.79$, 12.42 Hz, 1H), 1.33 (m, 2H); ^{13}C NMR: δ 135.8, 134.8, 63.5, 61.0, 50.4, 48.0, 47.3, 46.5, 45.6, 40.2; HRMS calcd for $C_{11}H_{20}NO$ $(M+H)^+$, 182.1546. Found 182.1550.

5.7. Synthesis of (2*S*,3*R*)-2-(*N*,*N*-dimethylcarboxamido)-3-(diphenylhydroxymethyl)-bicyclo[2.2.1]hept-5-ene 8

Bromobenzene (3.2 g, 20.4 mmol) was dissolved in 10 mL of anhydrous diethyl ether and put into the addition funnel. This solution was added to magnesium (0.6 g, 25.0 mmol) turnings. Once the reaction had begun, the rest of the bromobenzene solution was added dropwise at a rate that maintained gentle reflux. When the addition of the bromobenzene solution was complete, the mixture was refluxed for 20 min. Compound **6** (1.51 g, 6.78 mmol) was dissolved in 15 mL of anhydrous diethyl ether and added to the prepared Grignard mixture. After all of compound **6** solution had been added, the reaction mixture was refluxed for 2 h. The resultant mixture was poured into the mixture of ice (25 g) and 3 M H_2SO_4 (30 mL). The organic phase was washed with 5% $NaHCO_3$ and then brine. This was dried over $MgSO_4$, the solvent evaporated and the crude product purified by column chromatography (5% MeOH, 95% $CHCl_3$) to give compound **8** (1.96 g, 83%). $[\alpha]_D^{20} = +8.3$ (*c* 0.7, $CHCl_3$); mp 203–204 °C; IR (KBr): 3479, 3217, 1605 cm^{-1}; ^1H NMR: 7.45–7.50 (m, 4H), 7.16–7.21 (m, 4H), 7.02–7.08 (m, 2H), 6.53 (dd, $J = 3.40$, 5.20 Hz, 1H), 5.87 (dd, $J = 3.00$, 5.42 Hz, 1H), 3.56 (dd, $J = 3.22$, 9.58 Hz, 1H), 3.46 (dd, $J = 2.56$, 9.57 Hz, 1H), 2.86 (s, 1H), 2.84 (s, 3H), 2.56 (s, 1H), 2.30 (s, 3H), 1.29 (s, 2H); ^{13}C NMR: 175.3, 150.8, 148.5, 138.8, 131.0, 128.2, 128.1, 128.0, 126.4, 126.3, 126.2, 78.1, 58.7, 50.5, 47.8, 46.4, 45.1, 38.5, 36.4; HRMS calcd for $C_{23}H_{26}NO_2$ $(M+H)^+$, 348.1964. Found 348.1977.

5.8. Synthesis of (2*S*,3*R*)-2-(dimethylaminomethyl)-3-(diphenylhydroxymethyl)bicyclo[2.2.1]hept-5-ene 9

To a suspension of $LiAlH_4$ (0.033 g, 0.86 mmol) in anhydrous ether (10 mL) was added a solution of amide alcohol **8** (0.15 g, 0.43 mmol) in dry THF (5 mL) at a rate, which maintained gentle reflux. The mixture was then refluxed for 3 h and hydrolized by the cautious addition of water and 15% NaOH solution. The fine white precipitate which formed was washed with ether and discarded. The filtrate was concentrated to give amino alcohol **9** (0.135 g, 94%). $[\alpha]_D^{20} = -17.8$ (*c* 0.56, MeOH); mp 133–136 °C; IR (KBr): 3528, 1976, 1653 cm^{-1}; ^1H NMR: 7.55 (d, $J = 7.72$ Hz, 2H), 7.39

(d, $J = 7.73$ Hz, 2H), 7.27 (m, 4H), 7.15 (m, 2H), 6.33 (m, 2H), 3.53 (dd, $J = 2.67$, 9.85 Hz, 1H), 3.06 (br s, 1H), 2.75 (m, 1H), 2.35 (br s, 1H), 2.13 (t, $J = 10.65$ Hz, 1H), 1.98 (s, 6H), 1.89 (dd, $J = 4.14$, 12.78 Hz, 1H), 1.39 (br s, 2H); ^{13}C NMR: 149.3, 148.7, 137.4, 135.7, 128.1, 127.9, 126.4, 125.9, 125.3, 79.6, 60.6, 52.2, 50.6, 47.3, 46.6, 45.8, 42.8; HRMS calcd for $C_{23}H_{28}NO$ $(M+H)^+$, 334.2172. Found 334.2161.

5.9. General procedure for diethylzinc addition reactions

The ligand (0.05 mmol) was dissolved in hexane (or toluene) (3 mL) at room temperature under an argon atmosphere and diethyl zinc (1.0 mmol, 1 M in hexane) then added to this solution. The mixture was stirred for 30 min and then cooled to 0 °C. Benzaldehyde (0.5 mmol) was added to the mixture and the reaction mixture stirred for 48 h at 0 °C. After adding 1 M HCl (10 mL), it was extracted with ethyl acetate (25 mL). Then the organic phase was dried over $MgSO_4$ and the solvent evaporated to give the corresponding alcohol. HPLC-analysis of 1-phenyl-1-propanol: Chiralcel OD-H at room temperature, *n*-hexane/2-propanol = 98:2, 1.0 mL/min, 254 nm, $t_1 = 26.3$ min (*R*), $t_2 = 31.5$ min (*S*).

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