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Amino alcohols with the bicyclo[3.3.0]octane scaffold as ligands for the catalytic enantioselective addition of diethylzinc to aldehydes

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Abstract—Amino alcohols with the bicyclo[3.3.0]octane framework were synthesized, characterized and used as chiral ligands for the addition of diethylzinc to aldehydes. Quantitative yields and enantiomeric excesses of up to 92% were obtained in the ethylation reactions.

1. Introduction

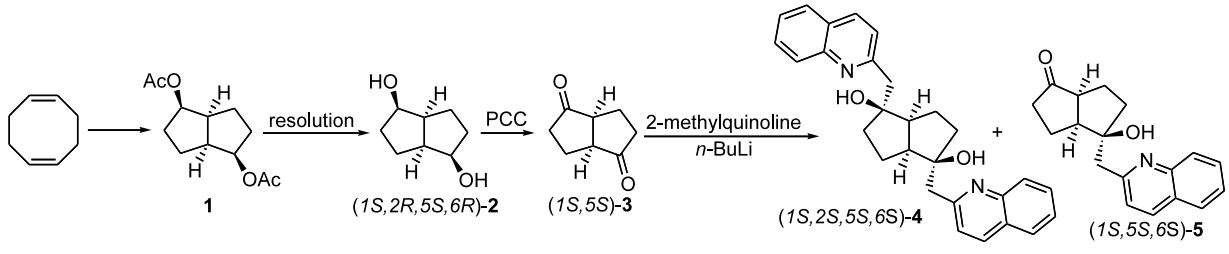
The design and synthesis of chiral ligands for catalytic asymmetric synthesis continues to attract great interest. Of the chiral ligands reported, amino alcohols have proven to be highly efficient chiral ligands for a variety of asymmetric processes, particularly, the enantioselective addition of diethylzinc to benzaldehyde[1,2] discovered by Oguni and Omi.[3]

A convenient method for the preparation of chiral amino alcohols is the nucleophilic addition of *N*-functionalized organolithium compounds to readily available chiral ketones, such as (+)-camphor, (−)-fenchone, and (−)-menthone. Amino alcohols of this type were found to be very effective ligands in the enantioselective addition of diethylzinc to aryl aldehydes.[4] Obviously, the origin of the stereoselectivity in this reaction derives from the rigidity of the chiral ketone framework.

Herein, we report studies into the synthesis of chiral amino alcohols with a bicyclo[3.3.0]octane framework and their use as ligands for the enantioselective addition of diethylzinc to aldehydes. To the best of our knowledge, there is no report on the synthesis of chiral ligands or auxiliaries with the bicyclo[3.3.0]octane framework and their application in asymmetric reactions.

2. Results and discussion

Firstly, we required a bicyclo[3.3.0]octane bearing a ketone moiety, such as compound **3** (Scheme 1), which could be used as a starting material in the synthesis of the target amino alcohols. As shown in Scheme 1, enantiomerically pure diketone **3** was prepared from 1,5-cyclooctadiene in three steps, involving palladium chloride-mediated transannular cyclization,[5] enzymatic



Scheme 1. Synthesis of ligands **4** and **5**.

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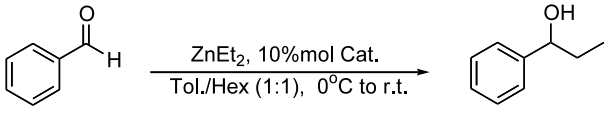
resolution[6] and PCC oxidation according to minor modifications of our previous report and improvement of the e.e. of diol **2**. Thus, 2-methylquinoline was first lithiated with equimolar *n*-BuLi, followed by trapping with diketone **3** to produce the bis-amino alcohol (1*S*,2*S*,5*S*,6*S*)-**4** and the mono-amino alcohol (1*S*,5*S*,6*S*)-**5**. Their relative configurations were confirmed by ^{1}H NMR analyses and observed NOE effects (see Section 4).

Ligands (1*S*,2*S*,5*S*,6*S*)-**4** and (1*S*,5*S*,6*S*)-**5** were then used as catalysts in the addition of diethylzinc to benzaldehyde under the standard conditions (0°C to rt; 10% mol catalyst; toluene/*n*-hexane mixture (1:1) as the solvent) (Scheme 2). The results are shown in Table 1.



Scheme 2.

Table 1. Enantioselective addition of diethylzinc to benzaldehyde catalyzed by **4** and **5**

Entry	Ligand	Yield (%)[a]	E.e. (%)[b]	Conf.[c]
1	(1*S*,2*S*,5*S*,6*S*)-**4**	74	7	*R*
2	(1*S*,5*S*,6*S*)-**5**	100	76	*R*

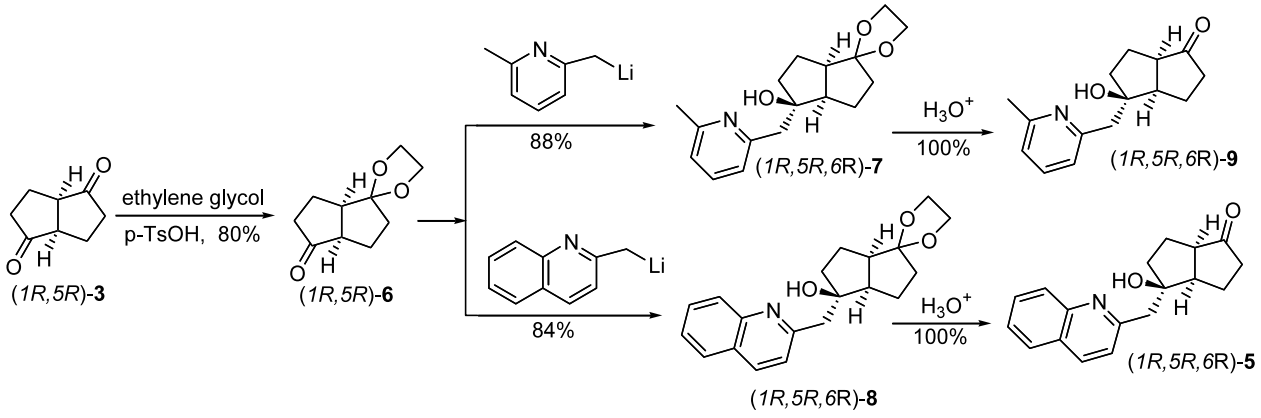
[a] Isolated yield.
[b] Determined by chiral HPLC analyses.
[c] Determined by the sign of the specific rotation.

Surprisingly, unlike many C_2-symmetric ligands which proved effective in asymmetric reactions,[7] bis-amino alcohol (1*S*,2*S*,5*S*,6*S*)-**4** only produced low enantioselectivity (7% e.e., entry 1). In contrast, mono-amino alcohol (1*S*,5*S*,6*S*)-**5** was more efficient to catalyze this reaction (entry 2), providing the product with 76% e.e. in quantitative yield. At the time of writing we are unsure why the e.e. was so low when (1*S*,2*S*,5*S*,6*S*)-**4** was used as ligand in this reaction. We speculate that the stereostructure and conformation of the bicyclo[3.3.0]octane framework of (1*S*,2*S*,5*S*,6*S*)-**4** and (1*S*,5*S*,6*S*)-**5** are different which results in the drastic difference in enantioselectivity. Detailed studies to address this problem will be conducted in due course.

We then turned our attention to other mono-amino alcohols with the bicyclo[3.3.0]octane skeleton. As shown in Scheme 3, diketone (1*R*,5*R*)-**3** was first monoprotected as mono-ketal (1*R*,5*R*)-**6**, then treated with 2,6-lutidine lithium and 2-methylquinoline lithium respectively to provide ligand (1*R*,5*R*,6*R*)-**7** and (1*R*,5*R*,6*R*)-**8** which were deprotected to afford (1*R*,5*R*,6*R*)-**9** and (1*R*,5*R*,6*R*)-**5**.

The effects of ligands **5**, **7**, **8** and **9** in the addition of diethylzinc to aryl aldehydes were then tested under the reaction conditions depicted in Scheme 2. The results are summarized in Table 2.

The ketal-protected ligands (1*R*,5*R*,6*R*)-**7** and (1*R*,5*R*,6*R*)-**8** induced moderate enantioselectivities (78 and 63% e.e., entries 1 and 2) in the addition of diethylzinc to benzaldehyde, while the amino alcohols (1*R*,5*R*,6*R*)-**9** and (1*R*,5*R*,6*R*)-**5**, with an unmasked carbonyl function, proved to be more effective. The best result was obtained when (1*R*,5*R*,6*R*)-**9** was used as catalyst (92% e.e., entry 3). Thus, (1*R*,5*R*,6*R*)-**9** was used to catalyse the addition of diethylzinc to a number of structurally different aldehydes. As far as aromatic aldehydes are concerned, it can be seen from entries 5–11 that the enantiomeric excesses remained at the 90% level irrespective of the presence of electron-donating and electron-withdrawing groups. However, with aliphatic aldehydes, the enantioselectivities were moderate (entry 12), or worse (entries 13 and 14). One point worthy of mention is that when the catalyst was (1*R*,5*R*,6*R*)-**5** (Table 2, entry 4) instead of its enantiomer (1*S*,5*S*,6*S*)-**5** (Table 1, entry 2), the configuration of the phenylpropan-1-ol product switched from *R* to *S*. It is well known that obtaining chiral materials in both enantiomeric forms from common starting materials is one of the key requirements in asymmetric reactions.[8] Thus, it is of interest to note that with both (1*R*,5*R*,6*R*)-**5** and (1*S*,5*S*,6*S*)-**5** in hand, it is possible to obtain both enantiomers of the chiral products.



Scheme 3. Syntheses of amino alcohols **5**, **7**–**9**.

Table 2. Enantioselective addition of diethylzinc to aldehydes catalyzed by **5**, **7–9**

Entry	RCHO	Catalyst	Yield (%)[a]	E.e. (%)[b]	Conf.[c]
1	Benzaldehyde	(1*R*,5*R*,6*R*)-**7**	96	78	*S*
2	Benzaldehyde	(1*R*,5*R*,6*R*)-**8**	92	63	*S*
3	Benzaldehyde	(1*R*,5*R*,6*R*)-**9**	100	**92**	*S*
4	Benzaldehyde	(1*R*,5*R*,6*R*)-**5**	100	83	*S*
5	*p*-Tolualdehyde	(1*R*,5*R*,6*R*)-**9**	100	**91**	*S*
6	*p*-Chlorobenzaldehyde	(1*R*,5*R*,6*R*)-**9**	84	**91**	*S*
7	*p*-Anisaldehyde	(1*R*,5*R*,6*R*)-**9**	100	**91**	*S*
8	*o*-Anisaldehyde	(1*R*,5*R*,6*R*)-**9**	95	**90**	*S*
9	3,4-Dimethoxybenzaldehyde	(1*R*,5*R*,6*R*)-**9**	88	**92**	*S*
10	1-Naphthaldehyde	(1*R*,5*R*,6*R*)-**9**	100	**89**	*S*
11	2-Naphthaldehyde	(1*R*,5*R*,6*R*)-**9**	100	**91**	*S*
12	Cyclohexanecarboxaldehyde	(1*R*,5*R*,6*R*)-**9**	80	70[d]	*S*
13	*trans*-Cinnamaldehyde	(1*R*,5*R*,6*R*)-**9**	100	51	*S*
14	Heptanal	(1*R*,5*R*,6*R*)-**9**	60	14[e]	*S*

[a] Isolated yield.
[b] Determined by chiral HPLC analysis.
[c] Determined by the sign of the specific rotation.
[d] Determined by comparison of the specific roation with that reported in the literature, see Ref. 9.
[e] Determined by comparison of the specific roation with that reported in the literature, see Ref. 10.

3. Conclusion

In summary, a new category of chiral amino alcohol, with the bicyclo[3.3.0]octane framework has been synthesized, and used as ligands for the enantioselective addition of diethylzinc to aldehydes. The bis-amino alcohol ligand (1*S*,2*S*,5*S*,6*S*)-**4** only provided the product with low e.e. On the other hand, the mono-amino alcohol ligands **5–9** proved to be more efficient as catalysts for this reaction. Studies to elaborate the effect of the unmasked carbonyl function of ligands **5** and **9** will be published in due course. Further work to extend the use of these amino alcohol ligands to other asymmetric reactions is now in progress.

4. Experimental

4.1. General

Melting points were uncorrected. Optical rotations were measured on a Perkin–Elmer 241MC polarimeter. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ on 300 and 75 MHz FT-spectrometers, respectively, using $SiMe_4$ as the internal reference. IR spectra were recorded on a Bio-Rad FTS-185 IR spectrometer. Mass spectra were recorded by the EI method, and HRMS were measured on a Finnigan MAT-8430 mass spectrometer. Elemental analyses were performed on Heraeus Rapid-CHNO. Enantiomeric excess (e.e.) determination was carried out using HPLC with Chiralcel OD, AS, AD, OJ columns. The silica gel used for flash chromatography was 300–400 mesh. All solvents were dried by standard methods. Unless otherwise noted, commercially available reagents were used without further purification.

4.2. (1*S*,2*S*,5*S*,6*S*)-2,6-Di-(quinolin-2-ylmethyl)-bicyclo-[3.3.0]octan-2,6-diol, 4 and (1*S*,5*S*,6*S*)-6-hydroxy-6-(quinolin-2-ylmethyl)-bicyclo[3.3.0]octan-2-one, 5

To a 100 mL flame-dried three-necked flask under an argon atmosphere were added 2-methylquinoline (0.4 mL, 3 mmol) and anhydrous ether (10 mL). This solution was cooled to 0°C and 1.6 M *n*-BuLi solution in *n*-hexane (1.9 mL) was added dropwise. After 15 min, the ice bath was removed and stirring was continued for 1 h at rt. Then, the system was cooled to 0°C again and a solution of diketone (1*S*,5*S*)-**3** (138 mg, 1 mmol) in 10 mL anhydrous ether was added dropwise. The mixture was stirred for 10 h and 10 mL saturated aqueous NH_4Cl solution was added to quench the reaction. The ether layer was separated, and the water layer was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine and dried over with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography to give (1*S*,2*S*,5*S*,6*S*)-**4** (211 mg, 49.7%) and (1*S*,5*S*,6*S*)-**5** (52 mg, 19.6%).

(1*S*,2*S*,5*S*,6*S*)-4: mp 150°C; $[\alpha]_D^{20}=+53.1$ (*c* 1.40 $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ ppm): 1.19 (m, 2H), 1.50 (m, 2H), 1.66–1.85 (m, 4H), 2.65 (m, 2H), 3.18 (s, 4H), 6.00–6.20 (br, 2H), 7.44 (d, $J=8.55$ Hz, 2H), 7.53 (t, $J=7.33$ Hz, 2H), 7.72 (m, 2H), 7.81 (d, $J=8.56$ Hz, 2H), 8.12 (m, 4H). ^{13}C NMR ($CDCl_3$, δ ppm): 20.52, 43.45, 46.10, 53.24, 80.20, 123.11, 126.13, 126.77, 127.53, 128.14, 129.74, 136.59, 146.39, 160.58. FT-IR (KBr): 3403, 3062, 2967, 1577, 758. EIMS (*m*/*z*, %): 424 (M^+, 1.42), 406 (M^+-H_2O, 2.59), 170 (10.13), 144 (16.11), 143 (100.00), 142 (14.73), 128 (9.58), 116 (8.97), 115 (14.46), 43 (16.26). HRMS calcd for $C_{28}H_{28}N_2O_2$ (M^+): 424.2157. Found: 424.2188. Anal. calcd for $C_{28}H_{28}N_2O_2$: C, 79.22; H, 6.65; N, 6.60. Found: C, 78.83; H, 6.57; N, 6.47.

(1*S*,5*S*,6*S*)-5: mp 102°C; $[\alpha]_D^{20}=+147.6$ (*c* 0.65 $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ ppm): 1.50 (m, 1H), 1.65 (m, 1H), 1.90 (m, 4H), 2.20 (m, 1H), 2.46 (m, 2H), 2.61 (m, 1H), 2.95 (d, $J=14.97$ Hz, 1H), 3.29 (d, $J=14.97$ Hz, 1H), 6.00 (br, 1H), 7.20 (d, $J=8.37$ Hz, 1H), 7.45 (m, 1H), 7.60 (m, 1H), 7.70 (d, $J=8.13$ Hz, 1H), 7.90 (d, $J=8.42$

Hz, 1H), 8.10 (d, $J=8.38$ Hz, 1H). FT-IR (KBr): 3294, 2942, 1733, 1139, 832, 753. EIMS (m/z, %): 281 (M^+, 1.80), 263 (M^+-H_2O, 1.21), 199 (8.10), 198 (6.98), 185 (10.27), 170 (14.45), 144 (7.15), 143 (100.00), 128 (7.60), 115 (10.71). HRMS m/z calcd for $C_{18}H_{19}NO_2$: 281.1416. Found: 281.1404.

The relative configurations of **4** and **5** are shown in Fig. 1 and were confirmed by NOE effects. As far as **4** is concerned, it should be C_2-symmetric according to ^{1}H NMR analyses. The relative configuration is that shown in Fig. 1 confirmed by the existence of NOE effects between the benzylic hydrogen H_1 and the bridgehead hydrogen H_2. The relative configuration of **5** can also been confirmed by the existence of NOE effects between the benzylic hydrogen H_4 and the bridgehead hydrogen H_3.

4.3. (1*R*,5*R*)-Bicyclo[3.3.0]octan-2,6-dione monoethylene ketal, 6[11]

(1*R*,5*R*)-Bicyclo[3.3.0]octan-2,6-dione **3** (1.9 g, 13.7 mmol), ethylene glycol (0.84 mL, 15.1 mmol) and *p*-toluenesulfonic acid monohydrate (261 mg, 1.37 mmol) were added to toluene (120 mL). The solution was heated under reflux for 8 h while removing the water azeotropically. Then, saturated aqueous $NaHCO_3$ solution was added to stop the reaction after the mixture was cooled to rt. The mixture was extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with brine and dried over with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and purification by flash chromatography gave (1*R*,5*R*)-**6** (1.57 g, 80.2%); $[\alpha]_D^{20}=-160.0$ (*c* 1.35 $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ ppm): 1.75 (m, 4H), 2.00 (m, 2H), 2.28 (m, 2H), 2.73 (m, 2H), 3.97 (m, 4H). FT-IR (film): 2964, 1737, 1162, 1118. EIMS (m/z, %): 100 (61.82), 99 (100.00), 86 (35.37), 55 (16.04), 53 (12.81), 43 (10.26), 42 (21.78), 41 (16.24).

4.4. (1*R*,5*R*,6*R*)-6-Hydroxy-6-(6-methylpyridin-2-ylmethyl)-bicyclo[3.3.0]octan-2-one ethylene ketal, 7

Prepared from (1*R*,5*R*)-**6** (728 mg, 4.0 mmol), 2,6-lutidine (0.7 mL, 6.0 mmol), and 1.6 M *n*-BuLi solution in *n*-hexane (3.75 mL, 6.0 mmol) in a similar way as described in Section 4.2 to give **7** as an oil (972 mg, 84%); $[\alpha]_D^{20}=-26.2$ (*c* 1.10 $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ ppm): 1.45 (m, 2H), 1.50–1.90 (m, 6H), 2.30 (m, 1H), 2.40 (m, 1H), 2.50 (s, 3H), 2.90 (s, 2H), 3.90 (m, 4H), 6.95 (d, $J=7.60$ Hz, 1H), 7.00 (d, $J=7.70$ Hz, 1H), 7.50 (t, $J=7.70$ Hz, 1H). FT-IR (film): 3338, 3065, 2955, 1595, 1579, 1108, 796. EIMS (m/z, %): 272 (M^+–OH, 15.44), 244 (10.14), 186 (8.19), 172 (11.08), 107 (56.42), 99 (9.89), 55 (6.98), 41 (7.87). HRMS m/z calcd for $C_{17}H_{23}NO_3$: 289.1678. Found: 289.1698. Anal. calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.30; H, 7.73; N, 4.83%.

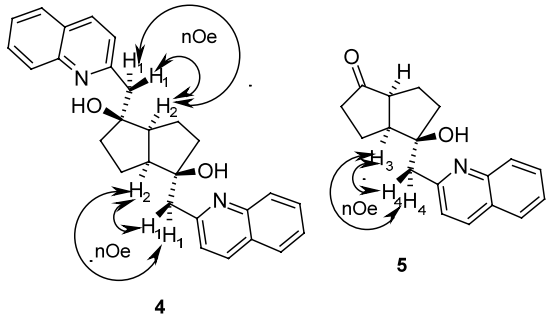


Figure 1.

4.5. (1*R*,5*R*,6*R*)-6-Hydroxy-6-(quinolin-2-ylmethyl)-bicyclo[3.3.0]octan-2-one ethylene ketal, 8

Prepared from (1*R*,5*R*)-**6** (546 mg, 3.0 mmol), 2-methylquinoline (0.43 mL, 4.5 mmol), and 1.6 M *n*-BuLi solution in *n*-hexane (2.8 mL, 4.5 mmol) in a similar way as described in Section 4.2 to give **8** as a pale yellow solid (796 mg, 88%); $[\alpha]_D^{20}=-14.6$ (*c* 0.85 $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ ppm): 1.38 (m, 1H), 1.40–1.85 (m, 7H), 2.38 (m, 2H), 3.05 (s, 2H), 3.80 (m, 4H), 5.80 (br, 1H), 7.25 (t, $J=7.60$ Hz, 1H), 7.50 (t, $J=8.0$ Hz, 1H), 7.70 (m, 1H), 7.80 (d, $J=8.1$ Hz, 1H), 8.06 (d, $J=8.4$ Hz, 1H), 8.12 (d, $J=8.3$ Hz, 1H). FT-IR (film): 3345, 3061, 2957, 1600, 1111, 828. EIMS (m/z, %): 325 (M^+, 2.05), 143 (100.00), 115 (17.65), 100 (19.17), 99 (33.79), 86 (15.83), 55 (17.42), 42 (19.62), 41 (18.64). HRMS m/z calcd for $C_{20}H_{23}NO_3$: 325.1678. Found: 325.1688. Anal. calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.77; H, 7.01; N, 4.25%.

4.6. (1*R*,5*R*,6*R*)-6-Hydroxy-6-(6-methylpyridin-2-ylmethyl)-bicyclo[3.3.0]octan-2-one, 9

Compound (1*R*,5*R*,6*R*)-**7** (583 mg, 2.02 mmol), 5% HCl (4.0 mL) and acetone (2.0 mL) were added into 25 mL THF. The solution was stirred at rt for 5 h. THF was evaporated under reduced pressure. Then, saturated aqueous $NaHCO_3$ solution was added to neutralize the mixture. The mixture was extracted with ethyl acetate. The combined organic layer was washed with water and brine and dried over with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and purification by flash chromatography gave (1*R*,5*R*,6*R*)-**9** as a white solid; mp 69°C; $[\alpha]_D^{20}=-145.7$ (*c* 2.45 $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ ppm): 1.50 (m, 2H), 1.90 (m, 4H), 2.18 (m, 1H), 2.35 (m, 2H), 2.45 (s, 3H), 2.55 (m, 1H), 2.70 (d, $J=14.6$ Hz, 1H), 3.00 (d, $J=14.5$ Hz, 1H), 6.80 (d, $J=7.6$ Hz, 1H), 6.90 (d, $J=7.7$ Hz, 1H), 7.45 (t, $J=7.7$ Hz, 1H). FT-IR (KBr): 3268, 2946, 1732, 1594, 1154, 749. EIMS (m/z, %): 228 (M^+–OH, 3.53), 163 (9.47), 149 (8.82), 134 (11.76), 107 (100.00), 79 (8.40), 77 (8.74), 65 (9.24), 41 (12.06). HRMS m/z calcd for $C_{15}H_{19}NO_2$: 245.1416. Found: 245.1413.

4.7. (1*R*,5*R*,6*R*)-6-Hydroxy-6-(quinolin-2-ylmethyl)-bicyclo[3.3.0]octan-2-one, 5

Prepared from (1*R*,5*R*,6*R*)-**8** in a similar manner to that described in Section 4.6; $[\alpha]_D^{20}=-145.6$ (*c* 2.45 $CHCl_3$).

4.8. General procedure for the asymmetric addition of diethylzinc to arylaldehydes

To a solution of ligand (1*R*,5*R*,6*R*)-**9** (0.10 mmol) in toluene (2 mL) and hexane (2 mL) at 0°C was added 15% w/w solution of diethylzinc in hexane (2.3 mL, 2.0 mmol). After stirring for 30 min at 0°C, freshly distilled benzaldehyde (1.0 mmol) was added. The reaction mixture was stirred for 4 h at 0°C, then allowed to warm to room temperature gradually with stirring for 24 h. After the addition of 1N HCl (10 mL), the phases were separated. The aqueous layer was extracted with ethyl acetate (3×5 mL). The combined organic layer was washed with brine and dried over with anhydrous Na_2SO_4. After purification by flash chromatography, the enantiomeric excess of the product was determined by chiral HPLC analysis.

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