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Enantioselective Addition of Diethylzinc to Benzaldehyde Catalyzed by Chiral Titanate Complexes with Helical Ligands

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Abstract: *Enantioselective alkylation of benzaldehyde with Et_2Zn has been studied. This reaction is catalyzed by helical titanium complexes of tetradentate ligands and has been found to give good to excellent enantioselectivities.* © 1997 Elsevier Science Ltd.

The asymmetric addition of dialkylzinc reagents to aldehydes is one of the most widely studied carbon-carbon bond forming reactions. A variety of catalysts have been employed which facilitate this process with high enantioselectivity.[1] While many of these systems rely on zinc catalysts coordinated to amino alcohol ligands,[1] the TADDOLs ligand of Seebach[2] and the chiral sulfonamide ligands designed by Yoshioka[3] and applied to the synthesis of complex secondary alcohols by Knochel,[4a-h] are examples of titanium based catalysts. They have proven to be very useful and to give high enantioselectivities at low catalyst loadings.

We have been interested in the development of new early metal Lewis acid catalysts for the addition of dialkyl zinc reagents to carbonyl groups. Recently, we reported a helical titanium complex which facilitates the asymmetric addition of diethylzinc to aromatic and α,β-unsaturated aldehydes.[5] The titanium complexes of these ligands are envisioned to have deep chiral pockets and to coordinate the substrate in a very specific manner allowing high enantioselectivity. Herein we disclose the detailed procedure for the synthesis of these ligands and the results of their use in the catalytic asymmetric alkylation of benzaldehyde.

Results and Discussion: We have designed ligands based on the phenol and sulfonamide groups because phenoxides are known to form strong bonds to group IV transition metals and sulfonamides are both acidic (pKa ~ 10) and very robust. Figure 1 shows two families of ligands which vary in their steric and electronic properties. The ligands employ either *trans*-1,2-diaminocyclohexane or 1,2-diphenylethylene diamine as the chiral backbones. The ligands **1-3** and **9-11** were synthesized in the Zhang group by condensation of chiral amines with substituted hydroxy benzene sulfonyl chlorides. The sulfonyl chlorides are easily prepared from chlorosulfonation of the halogenated phenols. The ligands **1** and **4-8** were made by the Walsh group. Unlike phenols with electron withdrawing halogen groups, chlorosulfonation of the alkyl substituted phenols proved unsuccessful. In the preparation of ligands **4-8**,

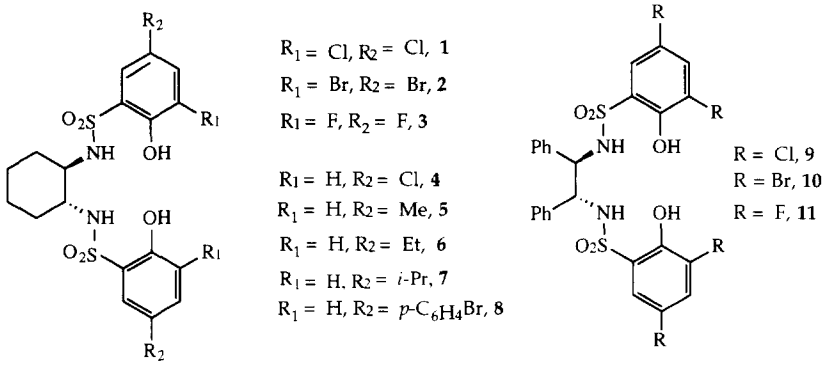


Figure 1

it was necessary to protect the phenol in order to synthesize the sulfonyl chlorides (Figure 2).

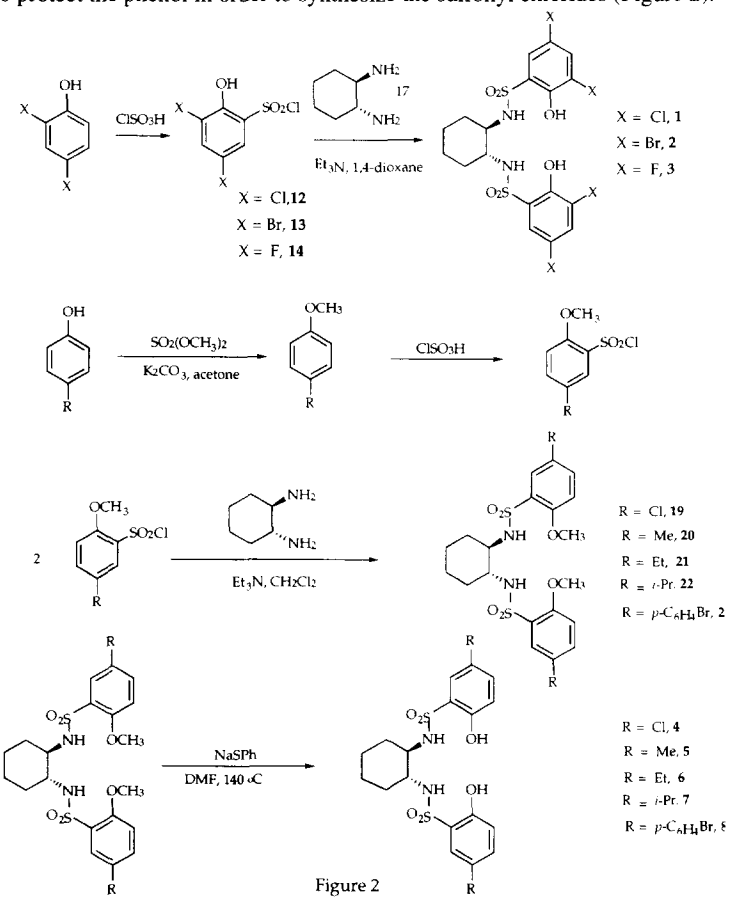


Figure 2

The synthesis of the anisols from the phenols was accomplished using dimethyl sulfate and potassium carbonate. Chlorosulfonation was easily performed with an excess of chlorosulfonic acid between 0 °C and

room temperature supplying the sulfonyl chlorides. Formation of the protected sulfonamide ligands was achieved by combining the sulfonyl chlorides with the diamine and an excess of triethyl amine. The final step involved deprotection with sodium hydride and thiophenol in DMF. All of these reactions were very clean and we found that it was only necessary to purify the final product, which was done using standard column chromatography on silica gel.

We have changed the procedure[6] for the resolution of 1,2-diaminocyclohexane by using *trans*-1,2-diaminocyclohexane **17** instead of the mixture of *meso* and *trans*-1,2-diaminocyclohexane (Figure 3). The resolution is simple, efficient and provides the diamine in high enantiomeric excess. Addition of the racemic diamine to a boiling aqueous solution of L-tartaric acid provides a homogeneous solution which, upon cooling forms white crystals of the tartrate salt **15**. Filtration of the resolved diamine gave optically pure material (% ee was determined by HPLC using a reported method[6]). The tartrate salt is then converted to the hydrochloride salt **16** which is subsequently treated with concentrated NaOH/KOH to liberate the free chiral diamine **17**. The optically pure (1R,2R)-(+)-1,2-diphenylethylene diamine was made according to a literature procedure.[7]

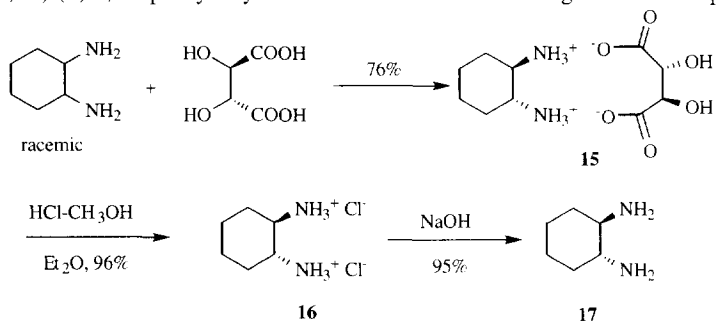


Figure 3

Many highly enantioselective enzymatic reactions occur in a deeply embedded active site. Substrates enter into this chiral pocket and interact with the active site through multipoint interactions. In contrast, most synthetic systems are composed of a metal center bonded to a chiral ligand or ligands. A problem frequently encountered in these systems, however, is that the chirality of the ligand is often distant from the available coordination site to which the substrate binds. In principle, catalysts designed with deep chiral pockets will show higher enantioselectivities in asymmetric reactions. Inspired by the helical structure of DNA and α-helical polypeptides, we have designed chiral ligands that can form helical asymmetric Lewis acid.

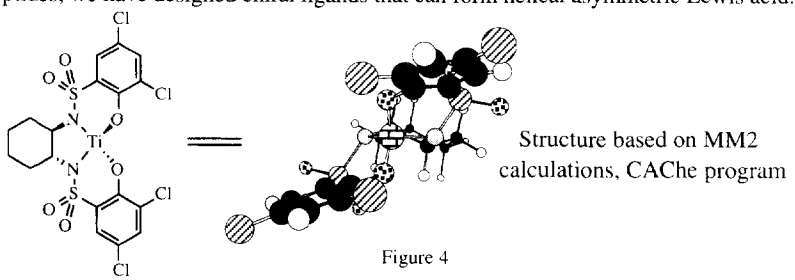
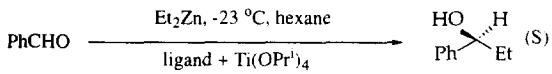


Figure 4

These compounds function as catalysts and have been found to facilitate asymmetric alkylation of aldehydes.[5] Likewise, helical catalysts such as Yamamoto's substituted binaphthol systems[8] and Wulff's vaulted biaryl complexes,[9] have also been shown to be highly enantioselective catalysts.

Table 1. Results of the enantioselective addition of Et_2Zn to benzaldehyde catalyzed by titanate complexes with chiral tetradentate ligands[a]



entry	Ligand	Yield[b]	%ee[b]
1	**1**	98	99
2	**2**	100	92
3	**3**	47	91
4	**4**	14	45
5	**5**	53	28
6	**6**	27	73
7	**7**	10	72
8	**8**	67	44
9	**9**	100	74 (R)
10	**10**	100	63 (R)
11	**11**	61	16 (R)

[a] Reaction condition: The ligand (0.20 mmol) (**1-8** from (1R,2R)-(-)-1,2-diamnocyclohexane or **9-11** from (1R, 2R)-(+)-1,2-diphenylethylene diamine) and $Ti(OPr^i)_4$ (1.4 mmol) were refluxed for 1h in dry hexane. Et_2Zn (1.0 M in hexane, 1.8 mmol) and benzaldehyde (1.0 mmol) were added at -23 °C. After for 4 hrs the reaction was quenched with 1 M HCl. [b]Isolated yield, % ee's were determined by HPLC using a CHIRALCEL OD column or by GC using a β-DEX column.

The key features of our ligand system are that the phenolic and sulfonamide groups bind tightly to the metal and encapsulating it in a chiral environment. As can be seen in Figure 4, the phenolic rings are the cleft-defining groups. They function by defining a rigid environment which controls the binding and orientation of the aldehyde substrates in the asymmetric process. Because of the facile synthesis of the ligands, we have been able to systematically vary the properties of the catalyst by changing the substituents on the ligands.

The results of our study are listed in Table 1. We have examined the asymmetric alkylation reaction with several chiral tetradentate ligands which vary in their steric and electronic properties. Up to 99% ee has been achieved in the addition reaction catalyzed by titanium complexes of these ligands. Additionally, we have performed preliminary experiments to probe the mechanism of this useful asymmetric process. Using ^1H NMR spectrometry in combination with an investigation of the correlation between ligand enantiopurity and ee of the product alcohol, we have determined that the catalyst is monomeric.

There have been several mechanisms proposed for the addition of diethylzinc to aldehydes. Based on our experimental findings and related mechanistic studies by Seebach,[2] Yoshioka[3] and Knochel,[4a-h] we propose a following model to explain our results (Figure 5).

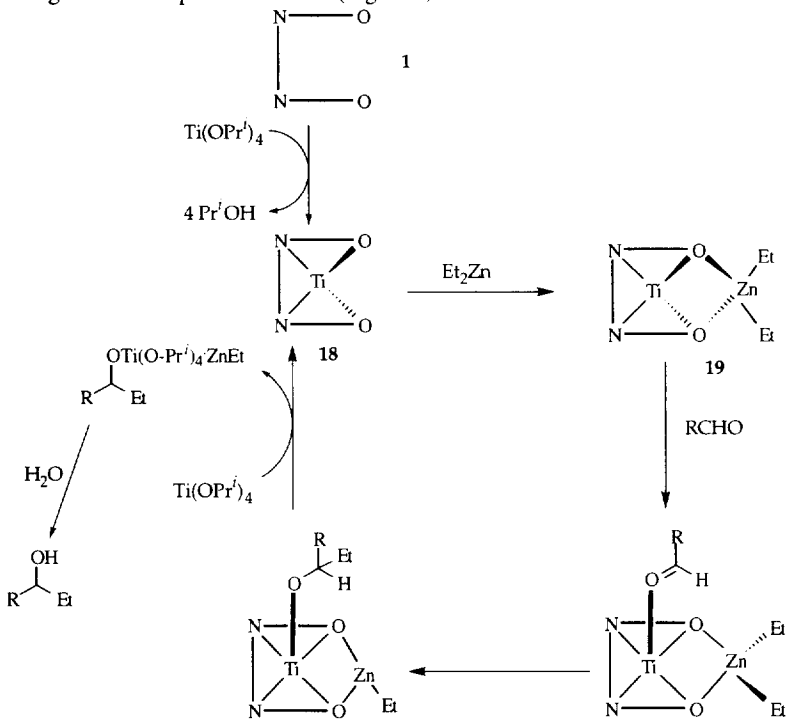


Figure 5. A Proposed Mechanism for Asymmetric Alkyaltion

The first step involves exchange of the sulfonamide ligand **1** with the titanium bound alkoxides producing isopropanol and the chiral catalyst (**18**), and the monomeric species **18** is thought to be followed by the formation of a the highly ordered phenoxide bridged heterobimetallic complex (**19**).[4g] We[5] and others[2-4] have found that the catalytic addition of diethylzinc to aldehydes is a slow process in the absence of excess Ti(OPr^i)$_4$. In order to accelerate the reaction, 1.2 equivalents of Ti(OPr^i)$_4$ are used in many systems. It is rationalized that the role of excess Ti(OPr^i)$_4$ is to remove the chiral alkoxide from the titanium catalyst by forming the bimetallic complex R'OZnEt·Ti(OPr^i)$_4$

It is also known that Ti(OPr^i)$_4$ is sufficiently Lewis acidic to catalyze the addition of diethylzinc to aldehydes. Thus, there is a competition between the more Lewis acidic, chiral titanium complex and the less

Lewis acidic, but more prevalent, achiral $Ti(OPr^i)_4$. Therefore, reaction conditions must be chosen carefully in order to maximize the enantioselectivity while shutting down catalysis by $Ti(OPr^i)_4$. The catalytic activity of $Ti(OPr^i)_4$ decreases significantly at lower temperatures. To further reduce catalysis by $Ti(OPr^i)_4$ the reaction was performed at a temperature lower than -20°C.

To examine the possibility of oligerimazation of the catalyst in solution, we varied the enantiopurity of the ligand employed in the asymmetric alkylation reaction and measured the ee's of the 1-phenyl-1-propanol produced. Aggregation of the catalyst would be expected to exhibit a non-linear relationship between the optical purity of the ligand and the enantiomeric excess of the product.[10] We found that variation in the enantiopurity of the ligand **1** directly correlated with the enantiomeric excess of the chiral alcohol as illustrated in Figure 6. This result indicates that the catalytically active species is monomeric. Additional information about the proposed catalyst was gained using NMR spectrometry. After mixing equimolar amounts of ligand **1** and $Ti(OPr^i)_4$, the ^1H NMR spectrum shows a clean pattern of two sets of aromatic protons (δ = 7.56 ppm, d, J = 2.6 Hz, 2H; δ = 7.45 ppm, d, J = 2.6 Hz, 2H), which correspond to the aromatic protons. Unlike the ^1H NMR spectrum of the free ligand, that for the titanium complex does not show resonances for the phenolic OH and sulfonamide NH groups which is consistent with the formation of the desired tetradentate complex and isopropanol (identified by NMR). These results suggest that the ligand binds to Ti(IV) in a tetradentate fashion and that the monomeric species **18**, that plays a role in this catalytic system. Interestingly, no change in the aromatic region of the ^1H NMR spectrum was observed when the ratio of $Ti(OPr^i)_4$ to **1** is increased to 7:1. The excess $Ti(OPr^i)_4$, which is present in the catalytic process, does not appear to change the structure **18**.

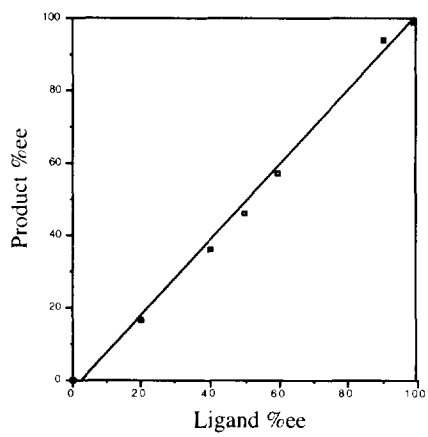
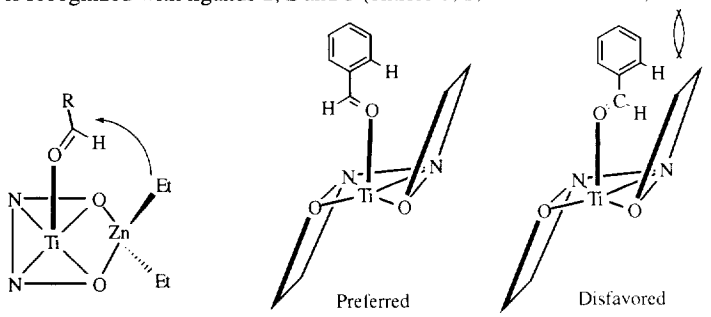


Figure 6. Nonlinear effect study (Ligand **1**)

Based on our proposed mechanism, the enantioselectivity is determined when the ethyl group is transferred from zinc to the carbonyl carbon intramolecularly. In the bimetallic complex **19**, the cliffs formed by the two benzene rings are suitable to control enantioselectivity (Figure 7). During the reaction process, one of the axial positions is occupied by an aldehyde. The Lewis acidity of the titanium center activates the substrate and accelerates the reaction. The two arene rings of the ligand generate a chiral environment which

limits the free rotation of the substrates; thus, the *Re* and *Si* faces of benzaldehyde are differentiated (Figure 7). The orientation of benzaldehyde is well controlled with ligand **1** that the ethyl group can be transferred only to the *Si* face of the substrate. The unfavored interaction between the rigid wall and benzaldehyde makes it impossible for the ethyl group to be transferred to the *Re* face. Thus, only S-enantiomer is produced and high enantioselectivity is recognized with ligands **1**, **2** and **3** (entries 1, 2, and 3 in Table 1).



Ethyl group is delivered from the front

Figure 7

Differences in the ligand structures strongly influence the reactivity and enantioselectivity of the catalyst (Table 1). For example, replacement of the chlorides in ligand **1** with bromides (**2**) and fluoride (**3**) result in a slight decrease the enantiometic excess of the product (entries **1** to **3**). Substitution of the 1,2-diphenylethylene diamine for the *trans*-1,2-diaminocyclohexane resulted in larger drop in the enantioselectivity (entries 1-3 vs. entries 9-11). Although, the same trend is observed, with the chloride based ligand being the most selective (ee% : **1>2>3**; and **9>10>11**), we are unable to rationalize the large drop in ee with the fluoride based ligand **11**. One possible explanation for the greater enantioselectivities of the cyclohexane based ligands is that the different diamines give complexes which have slightly different conformations. This could alter the orientation of aromatic cliffs, changing the shape of the chiral pocket.

Changes in the substitution pattern at the 3-position also have a large effect on the enantioselectivity and the efficiency of the catalyst. For example, on changing the 3-substituent in **1** from Cl to H (**4**) results in a large decrease in the enantioselectivity. Additionally, the productivity of the catalyst, as measured through the percent conversion, is significantly lower. It is expected that the ligands **1-3**, which have more electron withdrawing groups on the aromatic rings, render the catalysts more Lewis acidic than the complex derived from ligand **4**. Therefore, it is not surprising that the catalyst derived from **4** is not as effective in this ligand accelerated process. Additionally, substitution in the 3 and 5-positions (ligands **1-3**) provide more steric hindrance on the aromatic cliffs than the substitution in the 5-position alone (ligands **4-8**). This increased steric bulk appears to play a crucial role in orienting the coordinated benzaldehyde in the aromatic cliff. Furthermore, the size of the substituent in the 5 position effects the enantioselectivity of the ethyl group transfer. There is a notable change in enantioselectivity on going from the methyl derivative (**5**) to ethyl derivative (**6**). However, ligands **6** and **7** give essentially the same ee. In the 4-bromophenyl derivative, the

enantioselectivity again drops. Of the ligands employed in this study, **1** is the most effective and the easiest to synthesize, requiring only one step from commercially available materials.

In conclusion, we have designed and synthesized several tetradentate helical ligands. The titanium complexes of these ligands are effective catalysts for asymmetric alkylation reaction, in some cases giving very high enantioselectivities. Mechanistic studies reveal that the catalyst readily forms from titanium tetraisopropoxide and the ligand and that there is no need for removal of the liberated isopropanol. Additionally, correlation of the ligand enantiopurity with the enantiomeric excess of the product indicate that the catalyst composed of ligand **1** is a monomeric species during the asymmetric process. We are continuing our mechanistic work in this area as well as the application of helical Lewis acid catalysts to other asymmetric processes.

Experimental Section

General Considerations. Unless otherwise indicated, all reactions were carried out under nitrogen. THF and ether were freshly distilled from sodium benzophenone ketyl. Toluene and 1,4-dioxane were freshly distilled from sodium. Dichloromethane and hexane were freshly distilled from CaH_2. Methanol was distilled from magnesium and CaH_2. Reactions were monitored by thin-layer chromatography (TLC) analysis. Column chromatography was performed using EM silica gel 60 (230-400 mesh). Diethylzinc (1.0 M in hexane) was available from Aldrich Co., and used directly. Titanium(IV) isopropoxide was stored under nitrogen. Aldehydes were distilled before use.

^1H NMR were recorded on Bruker ACE 200, WP 200, AM 300 and WM 360 spectrometers at Penn. State University or a Varian Gemini 2000-BB 200 MHz or Unity 500 MHz at SDSU. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 7.26 ppm). ^{13}C and ^1H NMR spectra were recorded on Bruker AM 300 and WM 360 or Varian 200 or 500 spectrometers with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm). Optical rotation was obtained on a Perkin-Elmer 241 polarimeter. MS spectra were recorded on a KRATOS mass spectrometer MS 9/50 for LR-EI and HR-EI. GC analysis were carried on Helwett-Packard 5890 gas chromatograph with a 30-m Supelco β-DEX™ column. HPLC analysis were carried on Waters™ 600 chromatograph with a 25-cm CHIRALCEL OD column.

General Procedure for the Synthesis of Ligands 1-3

(1R,2R)-(+)-1,2-(3,3',5,5'-Tetrachloro-2,2'-dihydroxydibenzenesulfonamido) cyclohexane **1**:[11] (1R,2R)-(-)-1,2-Diaminocyclohexane **17** (3.43 g, 30.0 mmol) was dissolved in 1,4-dioxane (100 mL) and Et_3N (83.7 mL, 601 mmol) was added. This solution was added in one portion to a solution of 3,5-dichloro-2-hydroxybenzenesulfonyl chloride **12** (15.6 g, 59.8 mmol) in 1,4-dioxane (100 mL). The reaction mixture was stirred at room temperature overnight. The solution was diluted with ether (200 mL), washed with 10% HCl (2 x 100 mL) and water (100 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was recrystallized from CH_2Cl_2-hexane to give a white crystal (10.9 g, **1**, 64.5% yield).

^1H NMR ($CDCl_3$) δ 8.08 (s, 2H), 7.65 (d, J = 2.7 Hz, 2H), 7.56 (d, J = 3.2 Hz, 2H), 5.29 (d, J = 36.6 Hz, 2H), 2.90-2.87 (m, 2H), 1.88 (d, J = 12.0 Hz, 2H), 1.65 (d, J = 6.5 Hz, 2H), 1.28-1.17 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 148.5, 134.4, 127.1, 125.5, 123.9, 57.3, 33.3, 24.2; Mass Spectrum (EI) m/z (Relative Intensity)

562 (M^+, 3), 337 (8), 322 (2), 303 (2), 96 (100); Exact Mass for $C_{18}H_{18}Cl_4N_2O_6S_2$: Calc. 561.9360, Found 561.9359; $[\alpha]^{20}_D = +13.8°$ (c = 1, ethanol).

(1R,2R)-(+)-1,2-(3,3',5,5'-Tetrabromo-2,2'-dihydroxydibenzenesulfonamido) cyclohexane **2**: Yield: 83%; White Solid; ^1H NMR ($CDCl_3$) δ 8.24 (s, 2H), 7.83 (m, 4H), 5.49 (d, J = 6.6 Hz, 2H), 2.92 (s, 2H), 1.91 (d, J = 12.6 Hz, 2H), 1.66 (d, J = 8.3 Hz, 2H), 1.26 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 151.5, 140.3, 131.4, 129.5, 114.0, 112.1, 57.5, 33.2, 24.6; Mass Spectrum (EI) m/z (Relative Intensity) 742 (M^+, 2), 427 (7), 96 (100); Exact Mass for $C_{18}H_{18}Br_4N_2O_6S_2$: Calc. 737.7342, Found 737.7397; $[\alpha]^{20}_D = +13.7°$ (c = 1, ethanol).

(1R,2R)-(+)-1,2-(3,3',5,5'-Tetrafluoro-2,2'-dihydroxydibenzenesulfonamido) cyclohexane **3**: Yield: 68%; White Solid; ^1H NMR ($CDCl_3$) δ 8.12 (br, 2H), 7.28-7.25 (m, 2H), 7.11-7.06 (m, 2H), 5.46 (d, J = 6.7 Hz, 2H), 2.90 (br, 2H), 1.90-1.87 (m, 4H), 1.26-1.16 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 156.3 (d, J = 0.13 Hz), 154.1 (d, J = 0.15 Hz), 153.2 (d, J = 0.15 Hz), 151.0 (d, J = 0.16 Hz), 129.8, 140.6, 57.5, 30.1, 24.6; Mass Spectrum (EI) m/z (Relative Intensity) 498 (M^+, 33), 305 (100), 288 (6), 96 (27); Exact Mass for $C_{18}H_{18}F_4N_2O_6S_2$: Calc. 498.0542, Found 498.0495; $[\alpha]^{20}_D = +10.7°$ (c = 1, ethanol).

General Procedure for the Chlorosulfonation of Substituted Anisols

2-Hydroxy-5-chlorobenzene sulfonyl chloride: To a flask containing 40.07 g (0.345 mol) of chlorosulfonic acid at 0 °C was added 9.85 g (0.0691mol) of *p*-chloroanisol dropwise over 5 min with stirring. After the addition the mixture was allowed to warm to ambient temperature and the progress of the reaction followed by TLC. After 3 h the *p*-chloroanisol had been consumed as judged by TLC. The reaction mixture was then carefully added to 125 g of ice. The aqueous solution was extracted twice with 50 mL of CH_2Cl_2 and the organic layers combined, dried over magnesium sulfate, and filtered. The solvent was evaporated under reduced pressure to give 12.31 g (0.05085 mol, 74 %) of product. The sulfonyl chloride was judged pure by ^1H NMR spectrometry and was used without further purification.

5-Chloro-2-methoxybenzene sulfonyl chloride: ^1H NMR (200 MHz, $CDCl_3$) δ 7.95 (d, J=2.7 Hz, 1H, CH) , 7.64 (dd, J= 8.9 Hz, J=2.7 Hz, 1H, CH), 7.08 (d, J= 8.9 Hz, 1H, CH), 4.06 (s, 3H, CH_3), ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.9, 137.0, 132.5, 129.3, 125.5, 114.7, 56.9 ppm; IR (KBr) 3495, 3424, 3107, 1590, 1561, 1496, 1396, 1373, 1273, 1179, 1114, 1002, 891, 832, 703, 650, 585, 521 cm^{-1}; mp 100-102.5 °C.

2-Methoxy-5-methylbenzene sulfonyl chloride: ^1H NMR (200 MHz, $CDCl_3$) δ 7.76 (d, J=3.1 Hz, 1H, CH), 7.35 (dd, J= 8.9 Hz, J=3.1 Hz, 1H, CH), 7.02 (d, J= 8.9 Hz, 1H, CH), 4.03 (s, 3H, CH_3), 2.37 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.3.137.8, 131.4, 130.1, 129.7, 113.2, 56.6, 20.2 ppm; IR (KBr) 3495, 3401, 2355, 1608, 1561, 1502, 1367, 1290, 1259, 1173, 1067, 1014, 885, 820, 585, 532 cm^{-1}; mp 76-79 °C.

5-Ethyl-2-methoxybenzene sulfonyl chloride: ^1H NMR (200 MHz, $CDCl_3$) δ 7.79 (d, J = 2.4 Hz, 1H, CH), 7.53 (dd, J = 2.4, J = 8.6 Hz,1H, CH), 7.06 (d, J = 8.6 Hz, 1H, CH), 4.05 (s, 3H, CH_3), 2.68 (q, J = 8.0 Hz, 2H, CH_2), 1.26 (t, J = 8.0 Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.5, 136.7, 136.5, 131.5, 128.7, 113.3, 56.59, 27.67, 15.35 ppm; IR (KBr) 3020, 2972, 2842, 1607, 1568, 1504, 1461, 1360, 1290, 1260, 1167, 1066, 1013, 866, 831, 721, 688 cm^{-1}; mp 59.5 - 61 ^{0}C.

5-Isopropyl-2-methoxybenzene sulfonyl chloride: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.79 (d, J=2.4 Hz, 1H, CH), 7.54 (dd, J= 8.7 Hz, J= 2.4 Hz, 1H, CH), 7.05 (d, J= 8.7 Hz, 1H, CH), 4.04 (s, 3H, CH_3), 2.94 (sep, J=6.8 Hz, 1H, CH), 1.23 (d, J=6.8 Hz, 6H, CH_3) ppm, $^{13}C\{^1H\}$NMR ($CDCl_3$) δ 155.4, 141.2, 135.3, 131.5, 127.3, 113.3, 56.6, 33.2, 23.8 ppm; IR (KBr) 3460, 2966, 2860, 1567, 1519, 1501, 1462, 1362, 1284, 1260, 1172, 1059, 1015, 826, 724, 673, 595, 544 cm^{-1}; mp 63.5-65.5 °C.

2-Methoxy-5-(4-bromophenyl)benzene sulfonyl chloride: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.11 (s, 3H, OCH_3), 7.20 (d, 1H, J = 8.7 Hz), 7.40 (d, 2H, J = 8.7Hz), 7.59 (d, 2H, J = 8.7Hz), 7.86 (d, 1H, J = 8.7 Hz), 8.15 (s, 1H) $^{13}C\{^1H\}$NMR ($CDCl_3$) 200 MHz δ (in ppm) 113.8, 122.2, 127.9, 128.4, 132.3, 132.6, 135.3, 137.2, 156.8, IR (KBr) 2935, 1605, 1482,1356, 1282, 1174, 1078, 1010.0, 811, 702, 607, 556, 534 cm^{-1}.

General Procedure for the Synthesis 19-22

The L-tartrate salt **15** (2.07g, 7.85 mmol) was stirred with 20 mL of CH_2Cl_2 at 0 °C and 2M NaOH (43 mL) was added. To this biphasic reaction mixture was slowly added 5-chloro-2-methoxybenzenesulfonyl chloride (3.61 g, 14.92 mmol) with stirring. The reaction mixture was allowed to react for 1 h at ambient temperature, at which time TLC analysis of the reaction mixture indicated that the reaction was complete. The reaction mixture was acidified with 91 mL of 1M $NaHSO_4$ followed by addition of 50 mL of ethyl acetate to dissolve precipitate. The aqueous layer was extracted two times with 20 mL of ethyl acetate and the organic layers were combined, dried over magnesium sulfate, filtered to give a clear solution, and the solvent was removed under reduced pressure to provide 3.8g of **19** (6.00 mmol, 92 %).

Data for **19**: White solid, mp 221.5-224 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 2.6 Hz, 2H, CH), 7.51 (dd, J= 8.8 Hz, J= 2.6 Hz, 2H, CH), 6.98, (d, J= 8.8 Hz, 2H, CH), 5.13 (s(br), 2H, NH), 3.98 (s, 6H, CH_3), 2.36 (m, 2H, CH), 1.90 (m, 2H, CH), 1.60 (m, 4H, CH) , 1.57 (m, 2H, CH) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 154.9, 134.2, 129.6, 128.9, 125.4, 113.6, 57.1, 56.8, 33.4, 24.1 ppm; IR (KBr) 3261, 3093, 2939, 2855, 1588, 1579, 1564, 1468, 719 cm^{-1}; $[\alpha]^{20}_D$ = -2.98° (c=0.08, methylene chloride).

Data for **20**: White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J=2.2 Hz, 2H, CH), 7.34 (dd, J= 8.4 Hz, J=2.2 Hz, 2H, CH), 6.93 (d, J= 8.4 Hz, 2H, CH), 5.20 (s, 2H, NH), 3.95 (s, 6H, CH_3), 2.56 (m, 2H, CH), 2.35 (s, 6H, CH_3), 1.93 (m, 4H, CH), 1.60 (m, 4H, CH) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 154.2, 135.0, 130.3, 129.8, 126.8, 112.0, 56.9, 56.4, 33.1, 24.1, 20.3 ppm; IR (KBr) 3284, 2929, 1608, 1501, 1318, 1282, 1254, 1162, 1072, 1021, 926, 818, 724, 694, 612, 540 cm^{-1} ; mp 65.5-68°C; $[\alpha]^{20}_D$ = -2.00° (c=0.083, methylene chloride).

Data for **21**: ^{1}HNMR (200 MHz, $CDCl_3$) δ 7.71 (m, 2H, CH), 7.37 (m, 2H, CH), 6.96 (m, 2H, CH), 5.19 (s, 2H, NH), 3.95 (s, 6H, CH_3), 2.73 (m, 2H, CH), 2.68 (q, J = 3.05 Hz, 4H, CH_2), 1.99 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.24 (t, J = 3.05 Hz, 6H, CH_3), 1.11 (m, 4H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 154.3, 136.2, 133.8, 129.2,126.9, 112.1, 56.9, 56.3, 33.0, 27.7, 24.0, 15.5 ppm; IR (KBr) 3297, 2954, 2932, 2862, 1607, 1575, 1495, 1456, 1326, 1281, 1161, 1070, 1020, 900, 823, 692, 598 cm^{-1}; mp 106 - 108 °C; $[\alpha]^{20}_D$ -1.58 (c=0.08,CH_2Cl_2).

Data for **22**: ^{1}HNMR (200 MHz, $CDCl_3$) δ (ppm) 1.11 (m, 4H, CH_2) 1.56 (q, 2H, CH_2), 1.96 (q, 2H, CH_2), 2.78 (t, 2H, CH), 4.14 (s,6H, CH_3), 5.21 (d, 2H, NH, J = 4.9 Hz), 7.12 (d, 2H, J = 8.7

Hz), 7.49 (d, 4H, J = 2.2 Hz), 7.61 (d, 4H, J = 2.2 Hz), 7.75 (dd, 2H, J = 8.7 Hz), 8.10 (d, 2H, J = 2.2 Hz), $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ (ppm) 154.4, 141.0, 132.4, 128.0, 112.1, 56.9, 56.4, 33.1, 30.9, 24.1, 23.9, 23.8 ppm, IR (KBr) 3273, 2935, 2857, 1604 and 1481, 1336, 1274, 1162, 1075, 1016, 900, 812, 705, 591, 504 cm^{-1}, mp=137-140°C, $[\alpha]^{20}_{D}$=+1.25 (c=0.075, CH_2Cl_2).

General Procedure for the Synthesis of Ligands 4-8

Sodium hydride (2.84 g, 71.0 mmol) was slowly added to a stirring solution of dimethyl formamide (12 mL). Thiophenol (7.50 mL,71.0 mmol) was then carefully added to this heterogenous mixture in a dropwise fashion and the solution was stirred until gas evolvution ceased (15 min). The protected ligand **19** (3.64 g, 7.1 mmol) was added and the mixture was heated to 160 °C for 4 hrs. At this time a TLC was taken which indicated the reaction was complete. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with 30 mL of 1M H_2SO_4. The organic layer was washed four times with 30 mL of water. The resulting organic layer was dried with magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. Column chromotograpy on silica gel (1:1 ethyl acetate : hexane) gave 1.91 g (3.91 mol, 55 %) of product.

(1R,2R)-(+)-1,2-(5,5'-Dichloro-2,2'-dihydroxydibenzenesulfonamido) cyclohexane **4**: White Solid; ^{1}H NMR (Acetone-d_6) δ 9.65 (br, 2H), 7.55 (d, J = 2.6 Hz, 2H), 7.34 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.36 (s, 2H), 2.89 (br, 2H), 1.95-1.90 (m, 2H), 1.73-1.67 (m, 2H), 1.20-1.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 153.2, 135.2, 128.0, 125.5, 124.9, 120.3, 57.1, 33.2, 24.2; Mass Spectrum (EI) m/z (Relative Intensity) 494 (M^+, 5), 303 (9), 96 (100); Exact Mass for $C_{18}H_{20}N_2O_6S_2Cl_2$: Calc. 494.0140, Found 494.0140; $[\alpha]^{20}_{D}$ = +16.3° (c = 0.72, acetone).

(1R,2R)-(+)-1,2-(5,5'-Dimethyl-2,2'-dihydroxydibenzenesulfonamido) cyclohexane **5**: White Solid; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.37 (s, 2H), 7.45 (d, J = 2.6 Hz, 2H), 7.26 (dd, J_1 = 2.6 Hz, J_2 = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.88 (br, 2H), 2.76 (br, 2H), 2.32 (s, 6H), 1.86 (br, 2H), 1.60 (br, 2H), 1.17-1.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 152.3, 136.1, 130.2, 128.4, 122.7, 118.3, 56.7, 32.3, 24.0, 20.2; Mass Spectrum (EI) m/z (Relative Intensity) 454 (M^+, 10), 283 (7), 96 (100); Exact Mass for $C_{20}H_{26}N_2O_6S_2$: Calc. 454.1232, Found 454.1218; $[\alpha]^{20}_{D}$ = +24.0° (c = 1.55, acetone).

(1R,2R)-(+)-1,2-(5,5'-Diethyl-2,2'-dihydroxy dibenzenesulfonamido)cyclohexane **6**: White Solid; ^{1}H NMR ($CDCl_3$) δ 8.48 (br, 2H), 7.51 (d, J = 2.2 Hz, 2H), 7.26 (dd, J_1 = 2.2 Hz, J_2 = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 5.42 (d, J = 5.8 Hz, 2H), 2.84 (br, 2H), 2.58 (q, J = 7.6 Hz, 4H), 1.84 (d, J = 16.0 Hz, 2H), 1.60 (br, 2H), 1.26-1.12 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 152.2, 136.3, 134.6, 127.2, 122.8, 118.0, 56.5, 32.3, 27.4, 23.8, 15.1; Mass Spectrum (EI) m/z (Relative Intensity) 482 (M^+, 5), 297 (6), 279 (1), 96 (100); Exact Mass for $C_{22}H_{30}N_2O_6S_2$: Calc. 482.1545, Found 482.1564; $[\alpha]^{20}_{D}$ = -4.88° (c = 1.71, acetone).

(1R,2R)-(+)-1,2-(5,5'-Di-*iso*-propyl-2,2'-dihydroxy dibenzenesulfonamido)cyclohexane **7**: White Solid; ^{1}H NMR ($CDCl_3$) δ 8.46 (br, 2H), 7.50 (d, J = 2.0 Hz, 2H), 7.32 (dd, J_1 = 2.2 Hz, J_2 = 8.4 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 5.24 (d, J = 6.2 Hz, 2H), 2.92-2.82 (m, 4H), 1.84 (d, J = 12.2 Hz, 2H), 1.60 (d, J = 6.4 Hz, 2H), 1.30-1.07 (m, 16H); Mass Spectrum (EI) m/z (Relative Intensity) 510 (M^+, 1), 313 (6), 268 (4), 96 (100); $[\alpha]^{20}_{D}$ = +22.8° (c = 1.34, acetone).

(1R,2R)-(+)-1,2-[5,5'-Di-(4-bromophenyl)-2,2'-dihydroxy dibenzenesulfonamido]cyclohexane **8**: Yellow Solid; ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 2.4 Hz, 2H), 7.68 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 2H), 7.60 (s, 8H), 7.06 (d, J = 8.8 Hz, 2H), 5.62 (s, 2H), 3.10-3.04 (m, 2H), 2.10-2.04 (m, 2H), 1.86-1.80 (m, 2H), 1.24-1.14 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 154.3, 137.8, 133.8, 132.9, 132.1, 128.3, 126.5, 123.7, 121.9, 119.5, 56.9, 33.3, 24.2; Mass Spectrum (EI) m/z (Relative Intensity) 733 (M^+-1, 6), 425 (2), 380 (2), 296 (2), 96(100); $[\alpha]^{20}_D$ = +7.1° (c = 1.17, acetone).

(1R,2R)-(+)-1,2-(3,3',5,5'-Tetrachloro-2,2'-dihydroxydibenzenesulfonamido)-1,2-diphenylethane **9**: (1R,2R)-(+)-1,2-Diphenylethylene diamine (0.86 g, 4.05 mmol) was dissolved in dry 1,4-dioxane (20 mL) and Et_3N (11.3 mL, 81.0 mmol) was added. This solution was added in one portion to a solution of 3,5-dichloro-2-hydroxybenzenesulfonyl chloride **12** (2.12 g, 8.10 mmol) in 1,4-dioxane (20 mL) at room temperature. Stirring was continued overnight and CH_2Cl_2 (60 mL) was added. The mixture was washed with 10% HCl (2 x 20 mL) and water (20 mL), dried over Na_2SO_4 and concentrated. The crude product was recrystallized from CH_2Cl_2-hexane to give a white crystal (1.59 g, **9**, 59% yield). ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 4H), 6.97 (m, 6H), 6.80 (m, 4H), 4.65 (s, 2H); ^{13}C NMR ($CDCl_3$) δ(ppm) 148.5, 134.4, 133.9, 128.5, 128.2, 127.3, 127.1, 126.2, 124.8, 123.4, 62.6; Mass Spectrum (CI) m/z (Relative Intensity) 330 (M^+/2, 100), 106 (46); Exact Mass for $C_{13}H_{10}Cl_2NO_3S$ (M^+/2): Calc. 329.9758, Found 329.9775; $[\alpha]^{20}_D$ = +123.6° (c = 1, acetone).

(1R,2R)-(+)-1,2-(3,3',5,5'-Tetrabromo-2,2'-dihydroxydibenzenesulfonamido)-1,2-diphenylethane **10:** Yield: 55%; White Solid; ^{1}H NMR (200 MHz, Acetone-d_6) δ 7.58 (d, J = 2.4 Hz, 2H), 7.36 (d, J = 2.4 Hz, 2H), 7.02-6.91 (m, 10H), 4.73 (s, 2H); ^{13}C NMR (DMSO) δ 150.9, 139.8, 136.9, 131.1, 128.9, 128.6, 128.5, 128.3, 113.4, 111.7, 63.5; Mass Spectrum (EI) m/z (Relative Intensity) 420 (M^+/2, 31), 106 (100), 79 (6); Exact Mass for $C_{13}H_{10}Br_2NO_3S$ (M^+/2): Calc. 417.8749, Found 417.8729; $[\alpha]^{20}_D$ = +152.1° (c = 0.24, acetone).

(1R,2R)-(+)-1,2-(3,3',5,5'-Tetrafluoro-2,2'-dihydroxydibenzenesulfonamido)-1,2-diphenylethane **11:** Yield: 67%; White Solid; ^{1}H NMR (Acetone-d_6) δ 9.22 (s, 2H), 7.54 (d, J = 6.1 Hz, 2H), 7.07-7.01 (m, 6H), 6.95-6.89 (m, 8H), 4.74 (d, J = 2.3 Hz, 2H), 2.87 (s, 2H); ^{13}C NMR (DMSO) δ 154.8, 153.6, 150.0, 148.7, 139.6, 138.1, 129.6, 127.0, 110.1, 108.0, 62.5; Mass Spectrum (EI) m/z (Relative Intensity) 596 (M^+, 0.1), 298 (45), 145 (10), 106 (100), 79 (7); Exact Mass for $C_{13}H_{10}F_2NO_3S$ (M^+/2): Calc. 298.0349, Found 298.0340; $[\alpha]^{20}_D$ = +131.0° (c = 1, acetone).

General Procedure for the Synthesis of 12-14[12]

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride **12**: 2,4-Dicholorophenol (24.0 g, 0.147 mol) was added dropwise to cholorosulfonic acid (50 mL, 0.752 mol) at 0°C. After addition, the mixture was stirred at room temperature overnight. The reaction mixture was poured into ice (100 g) and the precipitate was collected and washed with ice water. Recrystallization from CH_2Cl_2 gave white needles (25.1 g, **12**, 65% yield). ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1H), 7.79 (d, J = 2.5 Hz, 1H), 7.73 (d, J = 2.5 Hz, 1H).

3,5-Dibromo-2-hydroxybenzenesulfonyl chloride **13**: Yield: 87%; White Solid, ^{1}H NMR ($CDCl_3$) δ 8.00 (d, J = 1.5 Hz, 1H), 7.96 (d, J = 1.7 Hz, 1H).

3,5-Difluoro-2-hydroxybenzenesulfonyl chloride **14**: Yield: 37%; White Solid; ^{1}H NMR ($CDCl_3$) δ(ppm) 7.73-7.71 (m, 1H), 7.44-7.39 (m, 1H).

Synthesis of Chiral 1,2-Diaminocyclohexane

(1R,2R)-(+)-1,2-Diaminoniumcyclohexane L-Tartrate Salt **15**: L-Tartaric acid (100.0 g, 0.666 mol) was dissolved in H_2O (270 mL). The solution was heated to 90°C. (±)-*trans*-1,2-Diaminocyclohexane (80.0 mL, 0.666 mmol) was added dropwise. When white precipitate appeared, hot water was added to keep the solution clear. The final volume of the solution was about 1000 mL. The clear solution was then gradually cooled to room temperature and stood overnight in a refrigerator. The crystals were filtered out, washed with ice water (70 mL) and methanol (80 mL), and dried under vacuum, affording a white solid (66.5 g, >99.9 % d.e.,[6] 37.3% yield)

(1R,2R)-1,2-Diaminoniumcyclohexane dichloride salt **16:** (1R,2R)-(+)-1,2-Diaminoniumcyclohexane L-tartrate salt **15** (10 g, 37.8 mmol) was dissolved in a minimum amount of 10% HCl in methanol. To this solution was added ether dropwise until a white precipitate appeared. The precipitate was filtered and dried under vacuum (6.9 g, 96% yield).

(1R,2R)-(-)-1,2-Diaminocyclohexane **17**: (1R,2R)-1,2-Diaminoniumcyclohexane dichloride salt **16** (6.9 g, 37 mmol) was dissolved in a minimum amount of saturated NaOH solution. KOH pellets were added to remove water. The mixture was extracted with ether (2 x 150 mL). The organic layer was separated and filtered. Solvent was removed under vacuum to give a colorless oil, which became a solid on standing (39 g, 95% yield).

General Procedure of the Addition of Dialkylzinc to Aldehydes

A chiral ligand (0.20 mmol) was added to dry hexane (50 mL) and titanium (IV) isopropoxide (0.42 mL, 1.4 mmol) was added under N_2. The mixture was heated at reflux for 1 hour. After the flask was cooled to -23°C, dialkylzinc (1.8 mmol) was added followed by aldehyde (1.0 mmol). Stirring was continued at -23°C for 4 hours. 1 M HCl (10 mL) was added and the mixture was extracted with ether (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was analyzed by GC, or the purified product after chromatography (silica gel, CH_2Cl_2) was analyzed by HPLC or GC with chiral columns.

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