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Synthesis of a Schiff's base chiral ligand with a trifluoromethyl carbinol moiety

Yasser Samir Sokeirik, Masaaki Omote, Kazuyuki Sato, Itsumaro Kumadaki and Akira Ando*

Faculty of Pharmaceutical Sciences, 45-1, Nagaotoge-cho, Hirakata 573-0101, Japan

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Abstract—A Schiff's base ligand with a trifluoromethyl carbinol moiety was synthesized, and a structure of the active complex for asymmetric induction on the reaction of diethylzinc with aldehydes is proposed.

1. Introduction

Chiral Schiff bases have been used as a unique class of chiral ligands, and their metal complexes are used for asymmetric Diels–Alder reactions, cyanosilylation of aldehydes, cyclopropanations, and so on.[1] On the other hand, we have reported a new axially dissymmetric ligand with two trifluoromethyl (CF_3) carbinol moieties.[2] A CF_3 group exhibits a large steric effect on an adjacent center,[3] and the hydroxy group of a CF_3 carbinol moiety could be superior to other aliphatic hydroxy groups in binding to metals due to its higher acidity and stability against elimination, racemization, or oxidation.[2]

Our new project was to synthesize another asymmetric tridentate Schiff's base ligand **1a**, which has one stereogenic center based on a trifluoromethyl carbinol moiety, and examine the activity as a chiral ligand for asymmetric reactions (Fig. 1).

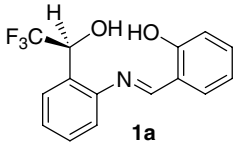

Figure 1. New Schiff's base ligand with a trifluoromethyl carbinol moiety.

* Corresponding author. Tel.: +81 72 866 3140; fax: +81 72 850 7020; e-mail: aando@pharm.setsunan.ac.jp

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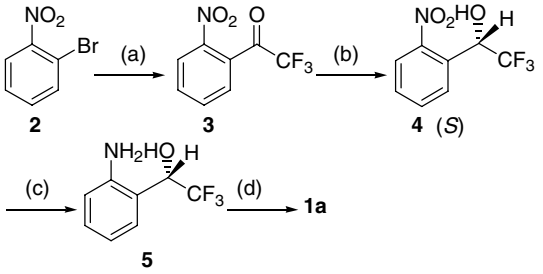
2. Results and discussion

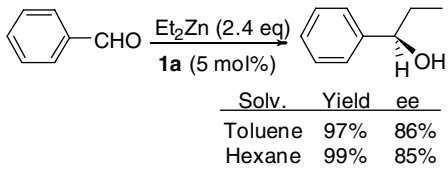
The synthesis of **1a** and its related compounds was accomplished according to Scheme 1.



Scheme 1. Synthesis of **1a**. Reagents and conditions: (a) *n*-BuLi, $CF_3COOC_2H_5$, THF, −100 °C; (b) Catecholborane, (*R*)-CBS catalyst 10 mol %, toluene, −60 °C; (c) H_2/Pd–C, MeOH; (d) salicylaldehyde derivatives, $MgSO_4$, dry EtOH.

The synthesis started with commercially available *o*-bromonitrobenzene **2**. The CBS reduction of **3** to **4** proceeded smoothly to give up to 97% ee. Amino alcohol **5** obtained by the reduction was recrystallized from toluene to give enantiomerically pure **5**. The absolute configuration was determined to be (*S*) by the deamination of **5** to the alcohol and comparison of the sign already rotation with that previously reported.[4] The condensation of **5** with salicylaldehyde afforded the desired Schiff bases **1a**.

To evaluate the catalytic activity of **1a** as a ligand, we examined the typical addition reaction of diethylzinc to an aldehyde, as shown in Scheme 2.



Solv.	Yield	ee
Toluene	97%	86%
Hexane	99%	85%

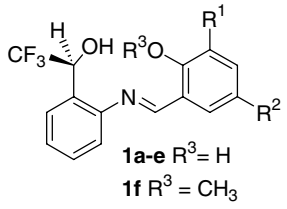
Scheme 2. Asymmetric addition of diethylzinc to benzaldehyde.

The reaction proceeded in non-polar solvents, but did not in polar solvents such as THF, diethyl ether, or methylene chloride. Hexane took a longer reaction time than toluene, but gave a cleaner reaction and proved much easier to be evaporated than toluene.

Next, we have introduced a few substituents onto the salicylaldehyde part, and their activities for the addition reaction of diethylzinc were then examined (see Table 1).

Table 1. Effect of substituents on the activity

Ligand	R^1	R^2	Yield (%)	ee
1a	H	H	87	86
1b	*t*-Bu	*t*-Bu	NR	—
1c	*t*-Bu	H	NR	—
1d	CH_3	H	20	Racemic
1e	H	*t*-Bu	92	83
1f	H	H	78	40



The substituents *ortho* to the phenolic hydroxy group led to a loss of the catalytic activity (**1b**, **1c**, or **1d**). No reaction was observed for **1b** or **1c** from 0 °C to room temperature, while in the case of **1d**, a slow reaction proceeded at room temperature leading to a racemic product in a low yield. Substitution at the *para*-position of the hydroxy group as in **1e** did not show any decrease in activity (83% ee).

Next, we examined the activity of ligand **1a** with various types of aldehydes. The results are shown in Table 2.

Ligand **1a** showed moderate to high ee for aromatic aldehydes (entries 1–6), while low ee for an aliphatic aldehyde (entry 7). The ee of this reaction is comparable to that using our previous axially dissymmetric ligands,[2] while this needs no titanium tetraisopropoxide. The ee is better than that of SALEN ligand, 10 mol % of which was used to give 77% ee.[6]

We then became interested in the mechanism of the reaction catalyzed by ligand **1a**. First, we examined whether chiral amplification would be observed or not, when **1a** with low ee was used. Plotting the ee of the product versus the ee of **1a** showed a non-linear relationship with a moderate enantiomeric amplification (25% ee of the ligand gives 46% ee of the product) (Fig. 2). This suggests that the ligand might not work in a simple monomeric form but in a dimeric form, as Noyori's model of enantiomeric amplification.[7]

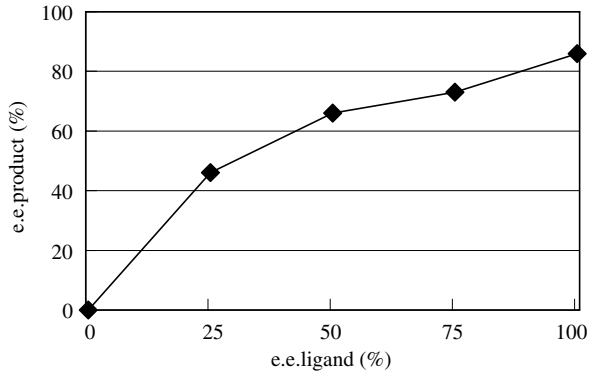


Figure 2. Examination of chiral amplification.

Katagiri et al. have synthesized a series of fluorinated amino alcohols and evaluated activities as chiral ligands using addition reactions of diethylzinc. They proposed that the ligands might act in an aggregated form.[8] To examine whether this was true for our ligand, we plotted the effect of the concentration of the ligand on the ee and the yield of the product (Fig. 3). The concentration of **1a** has a slight effect on the ee of the product, which is different to Katagiri's findings. We think that our catalyst must work as a well defined dimeric complex.

Table 2. Reaction of various aldehydes

Entry	Aldehyde	Solvent	Time (h)	Yield (%[a])	ee[b] (abs. config.[c])
1	*p*-Cl–C_6H_4CHO	Hexane	24	91	81 (*R*)
2	*o*-Cl–C_6H_4CHO	Hexane	36	83	77 (*R*)
3	*o*-F–C_6H_4CHO	Hexane	24	86	89 (*R*)
4	*p*-CH_3–C_6H_4CHO	Hexane	36	96	77 (*R*)
5	*p*-$(CH_3)_2CH$–C_6H_4CHO	Hexane	36	83	78 (*R*)
6	*p*-CH_3OCO–C_6H_4CHO	Hexane–toluene	24	88	75 (*R*)
7	$C_6H_5CH_2CH_2CHO$	Hexane	48	76	12 (*R*)

[a] Isolated yields.
[b] Determined by chiral GC.
[c] Determined by the sign of rotation.[5]

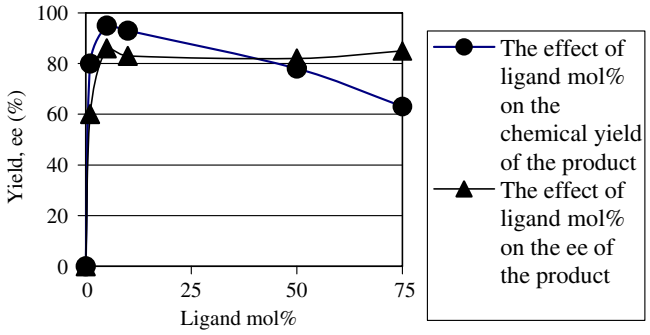


Figure 3. Effect of concentration of ligand.

To estimate the structure of our complex, we examined a high resolution MS/ESI for the complex formed from **1a** and diethylzinc. Interestingly, we were able observe a peak that might be due to one of two structures illustrated in Figure 4 with the peak of free **1a**.

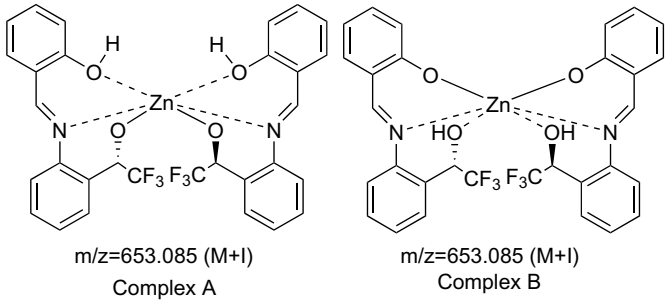


Figure 4. Structures of zinc complex of **1a** estimated by MS/ESI.

The ^{13}C NMR indicated a big shift for the carbinol carbon from 67 to 82 ppm indicating that it was strongly affected by complex formation, while a small shift was observed for both the phenolic and imino carbons (162 to 168 and 164 to 172 ppm, respectively). These results suggest that zinc is strongly bound to the carbinol oxygens and is weakly coordinated to phenolic ones, namely, the complex must be complex A. The ^{19}F NMR showed a shift from 15.2 to 10.2 ppm for the CF_3 fluorine by the complex formation with diethylzinc. To confirm the formation of this complex, MS/ESI of the complex of **1f** derived from *o*-anisaldehyde was also examined. We could identify a similar complex (see Fig. 5).

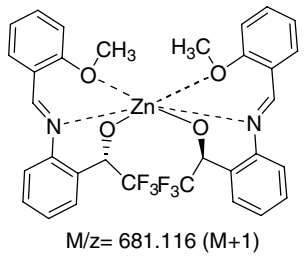


Figure 5. Structures of zinc complex of **1f** estimated by MS/ESI.

From this result, we can conclude that the two trifluoromethyl carbinol oxygens coordinate with a zinc atom to form a complex.[9] These results are consistent with Katagiri's report, which suggests coordination of the trifluoromethyl carbinol oxygen with zinc. This complex must be the active complex, since it was the only complex detected by ^{13}C and ^{19}F NMR. The asymmetric induction by **1f** seems to support this speculation.

Furthermore, the above speculation was supported by the following observations. The zinc complex from (*S*)-**1a** of 25% ee showed two peaks in ^{19}F NMR at 10.4 and 10.7 ppm in a ratio of 1:1.44. The former peak must be attributed to the homodimeric zinc complex, Zn((*S*)-**1a**)$_2$ or Zn((*R*)-**1a**)$_2$, and the latter the heterodimeric complex, Zn((*R*)-**1a**)((*S*)-**1a**). If the former were much more stable than the latter, only the former peak would be observed. If the latter were more stable, the peak ratio would be 1:3. The peak ratio 1:1.44 means that about 60% of the heterodimer was formed. The mixture of 25% ee contains 37.5% of (*R*)-**1a**, and a half of heterodimeric complex, 30% is this isomer. Thus, 30% of (*R*)-**1a** is used as the heterodimeric complex and 7.5% as in homodimeric complex, showing that the heterodimeric complex is more stable than the homodimeric complex. The complex formed from racemic **1a** showed the latter peak with a trace of the former. The heterodimeric complex accelerates the reaction less than the homodimeric complex. We believe this is the reason why a small enantiomeric amplification was observed when 25% ee of (*S*)-**1a** was used.

3. Conclusion

In conclusion, we have synthesized a new Schiff base ligand with a chiral trifluoromethyl carbinol moiety. The enantiomeric excess of the reaction of diethylzinc with an aldehyde in the presence of this ligand seems to be the highest among the ligands with iminoalcohol moieties. This ligand does not require titanium tetraisopropoxide, as in the case of BINOL. We were able to estimate the active complex of this ligand to contain two moles of chiral ligand and one zinc atom. This would help understanding of the reactions catalyzed by chiral ligands and open the door for many applications of this type of simple Schiff's base ligand.

4. Experimental

4.1. Synthesis of (*S*)-1-(2-aminophenyl)-2,2,2-trifluoroethanol 5

4.1.1. 2,2,2-Trifluoro-1-(2-nitrophenyl)ethanone 3. To a solution of 2-bromonitrobenzene (5.00 g, 24.8 mmol) in THF (120 mL) at −100 °C was added *n*-BuLi in hexane (1.58 M, 17.2 mL, 27.2 mmol) in 45 min. The resulting mixture was stirred for an additional 1 h at the same temperature. To this solution was added ethyl trifluoroacetate (3.24 mL, 27.2 mmol) in 20 min, and the resulting mixture kept at this temperature under stirring for an additional 6 h. The mixture was quenched with 2 M HCl (50 mL), and the whole mixture extracted with Et_2O. The Et_2O layer was dried over $MgSO_4$, and evaporated under vacuum to give an oily black mass, which was purified by column

chromatography (SiO_2, 5% Et_2O in hexane) to give **3** (2.82 g, 52%). A pale yellow oil. ^1H NMR ($CDCl_3$) δ: 8.33 (1H, d, $J = 8.3$ Hz), 7.91 (1H, t, $J = 7.3$ Hz), 7.84 (1H, dt, $J = 7.3$, 1.0 Hz), 7.58–7.55 (1H, d, $J = 7.9$ Hz). ^{19}F NMR ($CDCl_3$) δ (from $C_6H_5CF_3$): −12.85 (3F, s). IR (neat) cm^{-1}: 1748.

4.1.2. (*S*)-2,2,2-Trifluoro-1-(2-nitrophenyl)ethanol 4. To a stirred suspension of (*R*)-5,5-diphenyl-2-methyl-3,4-propano-1,3,2-oxazaborolidine (124 mg) in dry toluene (20 mL) was added catecholborane (1.01 mL), and the reaction mixture was stirred for 1 h at room temperature. The mixture was cooled to −85 °C, and **3** (1.00 g) in dry toluene (10 mL) was added in 1 h. The mixture was warmed up to −65 °C and kept stirring for 12 h. The reaction mixture was quenched with a cold mixture of 10% NaOH (20 mL) and 30% H_2O_2 (10 mL) and the whole mixture was stirred for 3 h at room temperature. The organic phase was separated, and the aqueous phase extracted with Et_2O. The combined organic phase was dried over $MgSO_4$, and evaporated under vacuum to give the crude product, which was purified by column chromatography (SiO_2, 20% Et_2O in hexane) to give **4** (898 mg, 89%) as a yellow oil in ee up to 95% by chiral GC. $[\alpha]_D^{15} = +154.2$ (*c* 0.98, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 8.00 (1H, dd, $J = 7.8$, 1.5 Hz), 7.97 (1H, d, $J = 7.8$ Hz), 7.75–7.70 (1H, m), 7.61–7.54 (1H, m), 6.25 (1H, q, $J = 6.5$ Hz), 3.55 (1H, s, disappeared with D_2O). ^{19}F NMR ($CDCl_3$) δ: −14.55 (3F, d, $J = 7.5$ Hz). IR (neat) cm^{-1}: 3550.

4.1.3. (*S*)-1-(2-Aminophenyl)-2,2,2-trifluoroethanol 5. A solution of **4** (500 mg) in MeOH (30 mL) was shaken under an atmospheric pressure of H_2 in the presence of 10% Pd–C (50 mg) for 4 h. After the catalyst was filtered off, the filtrate was concentrated under vacuum to afford a solid material, which was recrystallized from toluene to give **5** (371 mg, 85%) as colorless needles. Mp 143–145 °C. $[\alpha]_D^{20.5} = +32.7$ (*c* 1.40, CH_3OH). ^1H NMR (DMSO) δ: 7.19–7.17 (1H, d, $J = 7.3$ Hz), 7.07–7.04 (1H, t, $J = 7.3$ Hz), 6.76–6.59 (3H, m), 5.07 (1H, s, disappeared with D_2O), 4.67 (2H, s, disappeared with D_2O). ^{19}F NMR (DMSO) δ: −14.51 (3F, d, $J = 7.6$ Hz). IR (KBr) cm^{-1}: 3412, 3340, 3200. MS *m*/*z*: 191 (M^+). HRMS Calcd for $C_8H_8F_3NO$: 191.0558 (M^+). Found: 191.0563.

4.2. General procedure for preparation of chiral Schiff's base ligands 1

Aminoalcohol **5** (1 equiv) was dissolved in dry MeOH, and anhydrous $MgSO_4$ (excess) and the corresponding salicylaldehyde (1.1 equiv) added. The mixture was stirred for an appropriate time followed by TLC. After the reaction was completed, $MgSO_4$ was filtered off, and the solvent was evaporated under vacuum. The resulting Schiff's base was purified as follows.

4.2.1. (*S*,*E*)-2-((2-(2,2,2-Trifluoro-1-hydroxyethyl)-phenylimino)methyl)phenol 1a. The reaction time was 4 h. The product was recrystallized from hexane–Et_2O to give a yellow solid. Yield 93%. Mp 115–117 °C. $[\alpha]_D^{20.5} = -159.5$ (*c* 1.10, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 12.58 (1H, s, disappeared with D_2O), 7.99 (1H, s), 7.64 (1H, d, $J = 7.8$ Hz), 7.13–7.04 (4H, m), 7.01–6.95 (3H, m), 6.59 (1H, d, $J = 7.8$ Hz), 5.38–5.32 (1H, q, $J = 6.5$ Hz), 2.40 (1H, s, disappeared with D_2O). ^{13}C NMR ($CDCl_3$–toluene d_8) δ: 76.76 (q, $J = 32$ Hz), 117.56, 118.70, 119.3, 119.45, 125.13 (q, $J = 280$ Hz), 127.04, 128.38, 130.33, 132.83, 133.84, 137.51, 147.77, 161.33, 164.68. ^{19}F NMR ($CDCl_3$–toluene d_8) δ: −14.51 (3F, d, $J = 7.6$ Hz). IR (KBr) cm^{-1}: 3412, 1622. MS *m*/*z*: 295 (M^+). HRMS Calcd for $C_{15}H_{12}F_3NO_2$: 295.0820 (M^+). Found: 295.0828.

4.2.2. (*S*,*E*)-2,4-Di-*tert*-butyl-6-((2-(2,2,2-trifluoro-1-hydroxyethyl)phenylimino)methyl)phenol 1b. The reaction time was 18 h. The product was purified by flash column chromatography (SiO_2, 5% Et_2O in hexane) to give a yellow oil. Yield 75%. $[\alpha]_D^{20.5} = -162.0$ (*c* 1.41, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 12.83 (1H, s, disappeared with D_2O), 8.44 (1H, s), 7.64 (1H, d, $J = 7.8$ Hz), 7.41 (1H, d, $J = 2.4$ Hz), 7.36 (1H, dd, $J = 7.8$, 1.5 Hz), 7.26 (1H, dd, $J = 7.8$, 1.5 Hz), 7.15 (1H, d, $J = 2.4$ Hz), 6.98 (1H, dd, $J = 7.8$, 1.0 Hz), 5.35 (1H, q, $J = 6.5$ Hz), 2.40 (1H, s, disappeared with D_2O), 1.56 (9H, s), 1.14 (9H, S). ^{19}F NMR ($CDCl_3$–toluene d_8) δ: −14.51 (3F, d, $J = 7.6$ Hz). MS *m*/*z*: 407 (M^+). HRMS Calcd for $C_{23}H_{28}F_3NO_2$: 407.2072 (M^+). Found: 407.2078.

4.2.3. (*S*,*E*)-2-*tert*-Butyl-6-((2-(2,2,2-trifluoro-1-hydroxyethyl)phenylimino)methyl)phenol 1c. The reaction time was 12 h. The product was purified by flash column chromatography (SiO_2, 5% Et_2O in hexane) to give a yellow oil. Yield 82%. $[\alpha]_D^{20.5} = -180.2$ (*c* 1.03, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 13.02 (1H, s, disappeared with D_2O), 8.45 (1H, s), 7.62 (1H, d, $J = 7.8$ Hz), 7.40–7.34 (2H, m), 7.28 (1H, t, $J = 7.8$ Hz), 7.18 (1H, t, $J = 7.8$ Hz), 7.00 (1H, d, $J = 7.8$ Hz), 6.82 (1H, t, $J = 7.8$ Hz), 5.56 (1H, q, $J = 6.8$ Hz), 2.89 (1H, s, disappeared with D_2O), 1.34 (9H, s). ^{19}F NMR ($CDCl_3$–toluene d_8) δ: −14.69 (3F, d, $J = 6.3$ Hz). MS *m*/*z* 351 (M^+). HRMS Calcd for $C_{19}H_{20}F_3NO_2$: 351.1446 (M^+). Found: 351.1447.

4.2.4. (*S*,*E*)-2-Methyl-6-((2-(2,2,2-trifluoro-1-hydroxyethyl)phenylimino)methyl)phenol 1d. The reaction time was 4 h. The product was recrystallized from hexane–Et_2O to give yellow crystals. Yield 81%. Mp 95–97 °C. $[\alpha]_D^{20.5} = -208.3$ (*c* 1.70, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: ^1H NMR ($CDCl_3$) δ: 12.69 (1H, s, disappeared with D_2O), 8.52 (1H, s), 7.71 (1H, d, $J = 7.3$ Hz), 7.45 (1H, t, $J = 7.3$ Hz), 7.37 (1H, t, $J = 7.3$ Hz), 7.31–7.23 (2H, m), 7.08 (1H, d, $J = 7.3$ Hz), 6.88 (1H, t, $J = 7.3$ Hz), 5.62 (1H, q, $J = 6.5$ Hz), 2.87 (1H, s, disappeared with D_2O), 2.33 (3H, s). ^{19}F NMR ($CDCl_3$) δ: −14.51 (3F, d, $J = 7.6$ Hz). MS *m*/*z*: 309 (M^+). HRMS Calcd for $C_{16}H_{14}F_3NO_2$: 309.0977 (M^+). Found: 309.0967.

4.2.5. (*S*,*E*)-4-*tert*-Butyl-2-((2-(2,2,2-trifluoro-1-hydroxyethyl)phenylimino)methyl)phenol 1e. The reaction time was 4 h. The product was recrystallized from hexane–Et_2O to give a yellow solid. Yield 86%. Mp 139–142 °C. $[\alpha]_D^{20.5} = -212.8$ (*c* 1.21, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 12.34 (1H, s, disappeared with D_2O), 8.54 (1H, s), 7.72 (1H, d, $J = 7.8$ Hz), 7.50–7.44 (2H, m), 7.41–7.35 (2H, m), 7.09 (1H, dd, $J = 7.8$, 1.0 Hz), 6.98 (1H, d, $J = 8.7$ Hz), 5.62 (1H, q, $J = 6.4$ Hz), 2.83 (1H, s, dis-

appeared with D_2O), 1.33 (9H, s). ^{19}F NMR ($CDCl_3$–toluene d_8) δ: −14.72 (3F, d, $J = 6.2$ Hz). IR (KBr) cm^{-1}: 3415, 1620. MS m/z: 351 (M^+). HRMS Calcd for $C_{19}H_{20}F_3NO_2$: 351.1446 (M^+). Found: 351.1447.

4.2.6. (*S*,*E*)-2,2,2-Trifluoro-1-(2-(2-methoxy-benzylidene-amino)phenyl)ethanol 1f. A solution of **5** (100 mg, 0.52 mmol) and 72 mg (0.52 mmol) of *o*-anisaldehyde in dry toluene was refluxed under Dean and Stark condenser for 4 h with continuous removal of water. The resulting Schiff's base was kept in 2 mL dry toluene and used as stock solution, MS m/z: 309 (M^+). HRMS Calcd for $C_{16}H_{14}F_3NO_2$: 309.0977 (M^+). Found: 309.0984.

4.3. General procedure for the reaction of Et_2Zn with aldehyde

To a solution of the Schiff's base catalyst (0.034 mmol) in dry solvent (5 mL) was added Et_2Zn (1.62 mL of 1 M solution in hexane, 1.62 mmol). The mixture was stirred for 1 h at room temperature and then cooled to 0 °C. The appropriate aldehyde (0.68 mmol) was added slowly at this temperature. The mixture was kept stirring at this temperature and followed by GLC. After the reaction was completed, the mixture was quenched with 2 M HCl. The product was extracted with an appropriate solvent and purified by flash column chromatography. The ee was checked by chiral GC. The results shown in Table 2 were obtained.

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9. This complex was not formed when either half or 1 equiv of diethylzinc was used. It only formed in the presence of a large excess of diethylzinc.