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Asymmetric addition of diethylzinc to aromatic aldehydes by chiral ferrocene-based catalysts

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Abstract

A series of chiral C_1- and C_2-symmetric ferrocenyl Schiff bases (**1a**–**c**), ferrocenyl aminoalcohols (**2a**), ferrocenylphosphinamides (**2b**–**c**), 1,1′-ferrocenyl-diol (**3**), and 1,1′-ferrocenyl-disulfonamide (**4**) were prepared and employed as base catalysts or as ligand for titanium(IV) complexes in the asymmetric addition of diethylzinc to aromatic aldehydes. High enantioselectivity up to almost 100% ee was achieved for the alkylation of benzaldehyde and *p*-methoxybenzaldehyde with **1** or **3**. In contrast, however, the β-aminoalcohol (**2a**) and phosphinamides (**2b** and **c**) that are ubiquitous classes of base catalysts for this reaction proved inefficient in our hands, regardless of the types of substrates or reaction conditions. Comparative studies show that there exist various reaction parameters governing not only chemical yields but also optical yields. These include steric and electronic environment of the substrate, the solvent, the reaction temperature, and the nature of the ferrocene moieties. © 2002 Published by Elsevier Science B.V.

Keywords: Chiral ferrocenes; Diethylzinc; Asymmetric addition; Aldehydes

1. Introduction

The catalytic asymmetric addition of diorganozinc to various aldehydes is an important method for the preparation of optically active secondary alcohols, and has thus attracted a great deal of interest since the first report in 1984 by Oguni who used (*S*)-leucinol, a β-amino alcohol, as base catalyst [1,2]. Upon examination of literature, it is now well established that enantioselectivity can be accomplished either by Lewis base catalysis or Lewis acid catalysis. Consequently there now exist an array of chiral functionalities that have been successfully used either as base catalysts or as ligands for transition metal complexes. These include the well-known β-amino alcohols [3], β-imino alcohol [4], piperazine [5], oxazaborolidine [6], aminothiolate [7], aminothiols [8], aminothioester [9], diols [10], disulfonamides [11], diphosphoramides [12], amino acid derivatives [13], and ferrocene-based amino alcohols [14].

Following the lead by others, and motivated by our continuing effort to design a new series of chiral ferrocenes for use in asymmetric catalysis [15], we have attempted the preparation of some new chiral ferrocenes such as those shown in Schemes 1 and 2 and investigated their efficiency as base catalysts or as ligand for titanium complexes. In this paper their synthesis, characterization including X-ray crystallographic analysis, and application to asymmetric catalytic addition of diethylzinc to aldehydes are presented.

2. Results and discussion

2.1. Synthesis

The synthetic strategies and reaction conditions adopted in this work are described in Schemes 1 and 2. Scheme 1 shows the synthetic routes leading to the formation of ferrocenyl Schiff bases (**1a**–**c**) and ferro-

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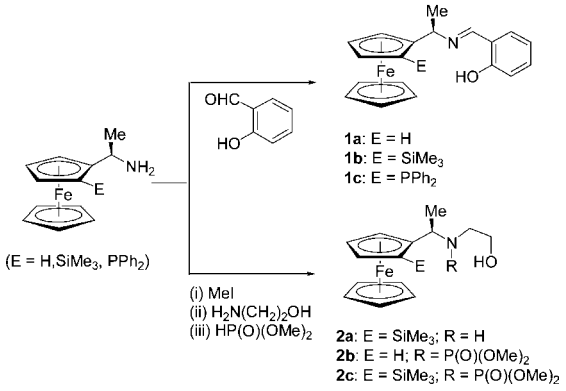
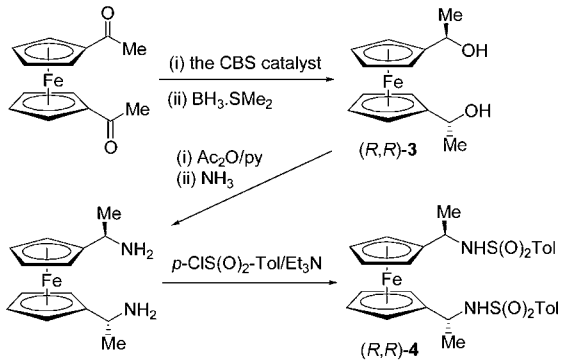
cenylaminoalcohols (**2a**–**c**) to be used as base catalysts. Their synthesis requires initially the preparation and the resolution of chiral template, *N*,*N*-dimethyl-1-ferrocenylethylamine (FA) reported by Ugi and coworkers [16]. Ortholithiation of (*R*)-FA followed by electrophilic substitution with Me_3SiCl and Ph_2PCl produces corresponding *ortho* substituted derivatives with



Scheme 1.



Scheme 2.

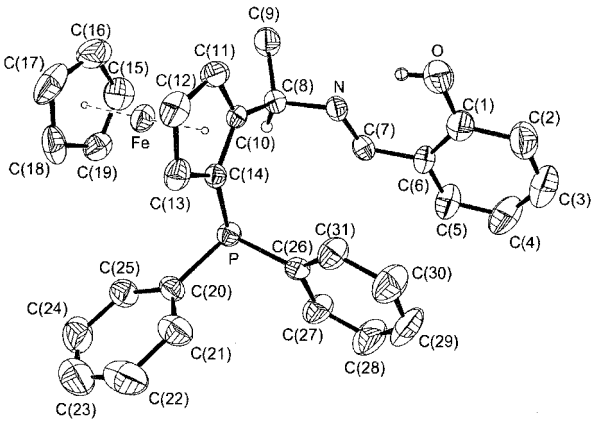


Fig. 1. The X-ray crystal structure of (*R*,*S*)-**1c**. Selected distances (Å) and angles (°): C(6)–C(7) 1.453(5), C(7)–N 1.268(4), *N*–C(8) 1.466(4), P–C(14) 1.821(4), P–C(20) 1.832(4), P–C(26) 1.845(4), C(6)–C(7)–N 122.5(4), C(7)–N–C(8) 119.9(3), C(14)–P–C(20) 101.2(2), C(14)–P–C(26) 102.7(2), C(20)–P–C(26) 100.2(2).

Table 1
Crystal data and structure refinement parameters for (*R*,*S*)-**1c** and (*S*,*R*)-**2c**

	(*R*,*S*)-**1c**	(*S*,*R*)-**2c**
Empirical formula	$C_{31}H_{28}FeNOP$	$C_{19}H_{32}FeNO_4PSi$
Molecular weight	517.36	453.37
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	13.212(1)	7.8713(9)
b (Å)	13.354(1)	11.1017(7)
c (Å)	15.5670(9)	25.566(2)
β (°)	105.642(6)	
V (Å^3)	2644.9(4)	2234.1(3)
Z	4	4
D_{calc} (g cm^{-3})	1.299	1.348
μ (cm^{-1})	6.54	8.23
Crystal size (mm)	$0.30\times0.35\times0.40$	$0.45\times0.45\times0.50$
$2\theta_{max}$ (°)	50.96	50.94
Unique reflections	4905	2394
Observed ($I>2\sigma I$)	1752	1999
Parameters	317	245
R_1	0.048	0.34
wR_2	0.078	0.101
Largest difference peak and hole (e Å^{-3})	0.28	0.52

(*R*,*S*)-configuration. These compounds are further converted to the primary amines $(C_5H_5)Fe(C_5H_4E)$-$CH(Me)NH_2$ ($E = SiMe_3$, PPh_2) via acetylation with aceticanhydride followed by amination with liquid ammonia [17].

Simple condensation reaction of salicylaldehyde with (*R*)-$(C_5H_5)Fe[C_5H_4CH(Me)NH_2]$ leads to the formation of (*R*)-**1a**, and the same reaction with (*R*,*S*)-$(C_5H_5)Fe[C_5H_3$-1-$CH(Me)NH_2$-2-$SiMe_3]$ and (*R*,*S*)-$(C_5H_5)Fe[C_5H_3$-1-$CH(Me)NH_2$-2-$PPh_2]$ to (*R*,*S*)-**1b**, and (*R*,*S*)-**1c**, respectively. Their structural confirmation comes from various techniques such as elemental analysis, NMR spectroscopy, and mass spectrometry. For instance, the ^{1}H-NMR spectra confirm the presence of the hydroxy group appearing as a singlet in the region 7.81–8.34 ppm, and the imino aldehydic proton as a broad signal at 13.06–13.80 ppm. The presence of strong infrared C=N stretching bands at around 1625 cm^{-1} further confirms their structures. As for (*R*,*S*)-**1c**, the ^{31}P-NMR spectrum exhibits the expected singlet at -23.10 ppm. In addition, its X-ray crystal structure is shown in Fig. 1, and crystal data in Table 1.

The preparation of **2a**–**c** simply takes advantage of the fact that the NH_2 group in the starting compound with a suitable leaving group such as trimethylammonium undergoes nucleophilic substitution in a stereotentive SN1-type reaction leading to complete retention of configuration [16a,18]. Thus, treatment of the primary amine (*S*)-$(C_5H_5)Fe[C_5H_4CH(Me)NH_2]$ with an equimolar amount of MeI followed by the reaction

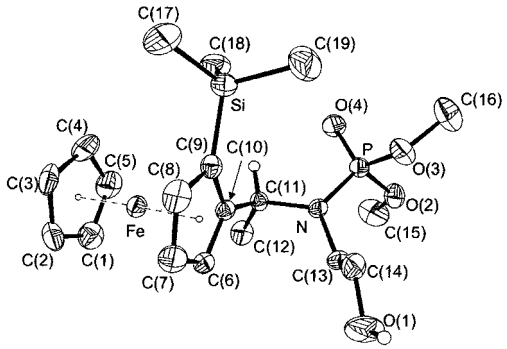


Fig. 2. The X-ray crystal structure of (*S*,*R*)-**2c**. Selected distances (Å) and angles (°): N–C(11) 1.497(6), N–C(13) 1.471(6), N–P 1.615(4), P–O(4) 1.467(4), P–O(2) 1.571(4), P–O(3) 1.568(4), C(11)–N–C(13) 117.6(5), C(13)–N–P 119.8(3), C(11)–N–P 122.2(3), O(4)–P–N 113.7(2), O(3)–P–N 105.1(2), O(2)–P–N 108.3(2).

with 2-aminoethanol resulted in the corresponding aminoalcohol. The ortholithiation with BuLi followed by treatment with trimethylsilyl chloride yields (*S*,*R*)-**2a**. Further substitution at the resulting secondary amine group with $HP(O)(OMe)_2$ leads to the formation of the ferrocenylphosphinamides (*S*,*R*)-**2c**.

The NMR patterns are straightforward and reveal the signals expected for their structures. For example, ^{31}P-NMR spectra of (*S*)-**2b** and (*S*,*R*)-**2c** confirm the presence of phosphinamide, and a more definitive evidence comes from the X-ray crystal structure of (*S*,*R*)-**2c** shown in Fig. 2. Its crystal data are listed in Table 1.

Scheme 2 describes the synthetic routes to the synthesis of (*R*,*R*)-**3** and (*R*,*R*)-**4**. Both routes employ essentially the Friedel–Crafts acylation of ferrocene followed by the well-established CBS reduction with (*S*)-2-methyl-CBS-oxazaborolidine. By this method the previously known (*R*,*R*)-**3** is obtained in an almost quantitative yield ($\sim$93%) with enantioselectivity of 98% ee [19]. The formation of (*R*,*R*)-**4** can be accomplished in high yield (86%) from the reaction of *p*-toluenesulfonyl chloride with (*R*,*R*)-ferrocenyl-1,1′-diamine which is produced from the acetylation of (*R*,*R*)-**3** followed by amination.

2.2. Catalysis

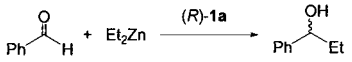
2.2.1. Base catalysis

Since benzaldehyde is one of the most extensively studied substrates in the enantioselective addition of diethylzinc to aldehydes, we employed this substrate to find the optimum reaction parameters such as the relative amount of catalyst, the solvent, and the reaction temperature.

Table 2 shows the results of our initial investigation. With (*R*)-**1a** as a base catalyst, both the highest chemical and optical yields are obtained with the combination of the substrate, Et_2Zn, and the catalyst in an 1:3:0.1 molar ratio in toluene at 0 °C (entry 3). Other solvents such as CH_2Cl_2, THF, and Et_2O give poor to zero enantiomeric excesses (entries 4–6). Changing the reaction temperature below or above 0 °C affects adversely both the conversion and the enantiomeric excess (entries 7 and 8). Here it is worth noting the reversal of the absolute configuration of the product on cooling the temperature below 0 °C.

As might be expected, structural and stereochemical modification of the catalyst affects significantly both the conversion and the enantiomeric excess as revealed in Table 3. For instance, the conversion is retarded on substitution with a bulkier group at the *ortho* position of the ferrocene moiety. Thus, of the three catalysts **1a**–**c**, the highest conversion is achieved with **1a** which is sterically the least crowded (entry 1 vs. entries 3 and 5). As far as the enantiomeric excess is concerned, however, **1c** is the choice of preference, which gives 94% ee under the standard set of reaction conditions (entry 5). Here, a cooperative interaction of diphenylphosphine with zinc in the zincate intermediate may be accounted for the elevated ee% although the exact role of phosphine is hard to know. Stereochemically, a

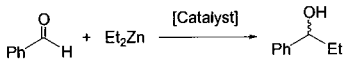
Table 2
Optimization of asymmetric addition of diethylzinc to benzaldehyde catalyzed by (*R*)-**1a** [a]



Entry	[sub]/[Zn]/[cat]	Solvent	Temperature (°C)	Yield (%)	% ee	Configuration
1	1.0/2.0/0.05	Toluene	0	79	18	*S*
2	1.0/3.0/0.05	toluene	0	99	28	*S*
3	1.0/3.0/0.1	toluene	0	100	70	*S*
4	1.0/3.0/0.1	CH_2Cl_2	0	32	18	*S*
5	1.0/3.0/0.1	THF	0	0	0	–
6	1.0/3.0/0.1	Ether	0	67	30	*S*
7	1.0/3.0/0.1	Toluene	RT	100	10	*S*
8	1.0/3.0/0.1	Toluene	−10	51	18	*R*

[a] The stoichiometric amounts of Et_2Zn and PhCHO are 1.4 and 0.47 mmol, respectively.

Table 3
The effects of catalyst on enantioselectivity of the addition of Et_2Zn to PhCHO [a]

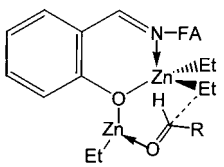


Entry	Catalyst	Condition [b]	Yield (%)	% ee	Configuration
1	(*R*)-**1a**	A	100	70	*S*
2		B	71	74	*S*
3	(*R*,*S*)-**1b**	A	63	44	*S*
4		B	47	52	*S*
5	(*R*,*S*)-**1c**	B	40	98	*S*
6	(*S*,*R*)-**2a**	A	55	36	*R*
7	(*S*)-**2b**	A	53	5	*R*
8	(*S*,*R*)-**2c**	A	50	25	*R*

[a] The reaction was run under the same conditions as described in entry 3, Table 2.
[b] Experimental details for conditions A and B are described in Section 4.

matching combination of central and planar chirality in the catalyst for a given product configuration seems to be (*S*,*R*) or (*R*,*S*) as judged from the observations that both (*R*,*S*)-**1b** and (*R*,*S*)-**1c** give the same product configuration (*S*) as (*R*)-**1a** (entries 1, 3, and 5), while the catalysts with the (*S*,*R*) combination give the product with an opposite configuration (entries 6–8). It is rather disappointing to find that the β-aminoalcohol (**2a**) and the phosphinamide catalyts **2b** and **c** give even lower enantiomeric excesses than their iminoalcohol counterpart **1a**–**c**. This may prove that the presence of a β-aminoalcohol moiety in the catalyst as a structural prerequisite for high enantioslectivity is ungrounded.

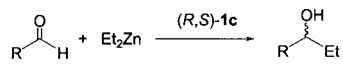
An additional feature of Table 3 is that the catalyst, when it is made pre-formed (condition B), works better to give higher enantiomeric excess than when it is used in situ (condition A) (entries 1 and 3 vs. entries 2 and 4). These same observations had already been made by others [14b] and may be explained partly in terms of the increased Lewis acidity of the pre-formed zinc catalyst, which makes the attack of incoming aldehyde to diethylzinc more effective. In fact, chiral Lewis bases are known to activate diorganozincs by coordinating to the zinc atom and by forming chiral zincate of the type R_2Zn-B which, due to the enhanced nucleophilicity of organo moiety of chiral zincate, adds to aldehydes in an enantioselective fashion (vide infra).



Having established the optimum reaction conditions and found that (*R*,*S*)-**1c** exhibits the highest enantioselectivity, we proceeded to the reactions of a series of aromatic aldehydes employing (*R*,*S*)-**1c** as catalyst. The results are listed in Table 4.

Very high enantiomeric excesses are accomplished for the alkylation of benzaldehyde and *p*-methoxybenzaldehyde (entries 1 and 2). These values are comparable with those obtained with the well-known catalysts in the literature [1,3–14]. With this catalyst even higher enantiomeric excess is obtained at temperature below 0 °C (entries 1 and 2). In addition, no change in the product configuration is observed regardless of the types of substrate. For the comparative purposes, it can be stated as a rule of thumb that any substitution at the aromatic ring lowers the ee% value as compared with the parent benzaldehyde. Further, both electronic and steric factors of the substrate affect apparently the enantiomeric excess. For instance, *o*- and *p*-methoxyaldehydes provide representative examples (entries 3 and 4). While the former leads to higher ee% than the latter (84% ee vs. 22% ee), the trend in the chemical yields is reversed (30% vs. 95%). A possible explanation for the lower ee% with *o*-methoxybenzaldehyde may be given in terms of the fact that the strong

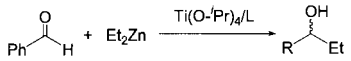
Table 4
Base-catalyzed asymmetric addition of diethylzinc to various aldehydes catalyzed by (*R*,*S*)-**1c** [a]



Entry	R	Yield (%)	% ee	Configuration
1	Ph	40	98	*S*
2	*p*-$MeOC_6H_4$	30	84	*S*
3	*o*-$MeOC_6H_4$	95	22	*S*
4	*p*-ClC_6H_4	100	14	*S*
5	*trans*-PhCH=CH	97	72	*S*
6	1-Naphthyl	85	24	*S*
7	2-Naphthyl	100	36	*S*

[a] Reactions were carried out under the condition B described in Section 4.

Table 5
Optimization of Ti-catalyzed asymmetric alkylation of PhCHO



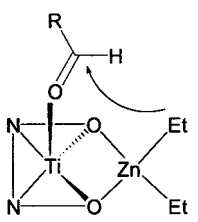
Entry	[sub]/[Zn]/[L]	L [a]	Solvent	Temperature (°C)	Yield (%)	% ee	Configuration
1	1.0/2.0/0.1	**3**	Toluene	RT	39	28	*R*
2	1.0/2.0/0.15	**3**	Toluene	RT	62	30	*R*
3	1.0/2.0/0.2	**3**	Toluene	RT	97	34	*R*
4	1.0/3.0/0.2	**3**	Toluene	RT	89	96	*R*
5			Toluene	0	70	96	*R*
6			THF	RT	76	22	*S*
7			THF	0	49	70	*S*
8			CH_2Cl_2	RT	95	6	*R*
9	1.0/2.0/0.2	**4**	Toluene	RT	23	72	*S*
10	1.0/2.0/0.15	**4**	Toluene	RT	39	80	*S*
11	1.0/2.0/0.2	**4**	Toluene	RT	45	52	*S*
12	1.0/3.0/0.15	**4**	Toluene	RT	100	84	*S*
13			Toluene	0	92	90	*S*
14			Toluene	−10	83	96	*S*
15			CH_2Cl_2	RT	42	4	*S*
16	1.0/3.0/0.2	**4**	Toluene	RT	100	58	*S*

[a] The absolute configuration of both **3** and **4** is (*R*,*R*).

steric hindrance of *ortho*-substituents weakens the coordination of the substrate to the catalyst thus lowering influence of the chiral environment of the catalyst on the orientation of the substrate [10c]. Similar observations are also made in the reaction of naphthaldehydes: namely, higher enantioselectivity and lower conversion with hindered aldehydes (entries 7 and 8). When only the electronic effects are taken into consideration, electron-donating substituents (i.e. methoxy, allyl) result in both higher conversion and enantioselectivity than electron-withdrawing groups (entries 3, 5, and 6).

2.2.2. Acid catalysis

In Lewis acid catalysis, aldehydes are activated initially by coordinating to the metal such as titanium. The electrophilicity of aldehyde is thus enhanced enough to be attacked by diorganozinc from one enantioface of the aldehydes. The Lewis acidity may be further increased by the presence of the electron-withdrawing ligands such as sulfonamide, as may be deduced from the structure of a reaction intermediate suggested to be present in the catalytic cycle (vide infra) [11e].



Based on this rationale, it is tempting to investigate the efficiency of (*R*,*R*)-**3** and (*R*,*R*)-**4** as chiral ligands for titanium(IV) complexes.

Again, through optimization of various reaction parameters, both ligands proved to be highly efficient for the target reaction as shown in Table 5 (entries 4 and 14). The two ligands possessing the same absolute configurations lead to opposite product configurations. Here, as in the case of base catalysis, the choice of solvent is toluene to guarantee high enantiomeric excess. In other solvents both chemical and optical yields drop significantly, and in the case of THF reversal in the product configuration is accompanied (entries 6 and 7). As expected, lowering the reaction temperature causes increase in ee% with a concomitant drop in the chemical yield, yet enantioselectivity seems to be more tolerable toward a change in the reaction temperatures (entries 4, 5, and 12–14).

Table 6 shows the results of Ti-catalyzed asymmetric alkylation of various aromatic aldehydes employing (*R*,*R*)-**3** and (*R*,*R*)-**4** as ligands. Very high enantioselectivity is achieved for the reaction of benzaldehyde and *p*-methoxybenzaldehyde reaching as high as 100% ee (entries 1–4). These values are ranked among the highest in the literature [10–12].

Of the two ligands, the disulfonamide (*R*,*R*)-**4** gives higher % ee values throughout all substrates investigated. Here again, any substitution at the aromatic ring of benzaldehyde drops the % ee values significantly regardless of the steric or electronic nature of the substituent. When the comparison is made among the

substrates, those bearing the electron-donating group exhibit slightly higher enantioselectivity than their electron-withdrawing counterparts (entries 3 and 4 vs. entries 7 and 8). This is because the substrate carrying the electron-donating group bounds through oxygen more tightly to the Lewis acidic titanium center, thus chiral environment of the catalyst becoming more influential. Steric factors also play a role, which can be seen from the reactions of *p*- and *o*-methoxybenzaldehydes (entries 3 and 4 vs. 5 and 6). The same reasoning provided in the case of base catalysis (vide supra) may be applied in the acid catalysis as well. In the same vein, the sterically less-hindered 2-naphthaldehyde gives slightly higher enantioselectivity than the sterically more demanding 1-naphthaldehyde (entries 11 and 13 vs. entries 12 and 14).

3. Conclusions

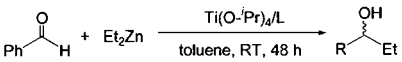
We have prepared a series of C_1- and C_2-symmetric ferrocene-based chiral compounds such as Schiff bases (**1a**–**c**), aminoalcohols (**2a**–**c**), ferrocenyl-1,1′-diol (**3**), and ferrocenyl-1,1′-disulfoanamide (**4**) and used them as base catalysts or as ligands for titanium complexes in the enantioselective addition of diethylzinc to aromatic aldehydes. Except for **2a**–**c**, all these compounds prove excellent for the alklylation of benzaldehyde and *p*-methoxybenzaldehyde to give high ee% values that are comparable to or in some instances even higher than those obtained with the well-known catalysts in the literature. Comparative studies show that there exist various reaction parameters governing not only chemical yields but also optical yields. These include steric and electronic environment of the substrate, the solvent, the reaction temperature, and the nature of the ferrocene moieties.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of Ar or N_2 using Schlenk techniques. Solvents were purified by standard methods and were freshly distilled prior to use. All commercial reagents were used as received unless otherwise mentioned. Microanalyses were performed by the Center for Instrumental Analysis, Kyungpook National University. Melting points were measured using a electrothermal model IA 9100 digital melting point apparatus and are reported without correction. ^{1}H- and ^{31}P-NMR spectra were recorded in a Varian Unity Plus spectrometer operating at 400 and 121.5 MHz, respectively. ^{1}H shifts are reported relative to internal Me_4Si and ^{31}P shifts relative to 85% H_3PO_4. High-resolution mass spectra (HRMS) were obtained by using a Micromass Quattro II GC8000 series model with electron energy of 20 or 70 eV. Optical rotations were measured on a JASCO DIP-360 digital polarimeter at ambient temperature. IR spectra were run in a Mattson FT-IR Galaxy 6030E spectrophotometer and Nicolet Magna-IR 550 spectrophotometer. HPLC analyses were performed in a Waters 600E type instrument equipped with a chiral column (chiralcel OD, Daicel Chemical Industries) and

Table 6
Ti-catalyzed asymmetric alkylation of aromatic aldehydes [a]



Entry	R	L	Yield(%)	% ee	Configuration
1	Ph	**3**	89	96	*R*
2		**4**	83	96	*S*
3	*p*-$MeOC_6H_4$	**3**	99	46	*R*
4		**4**	96	100	*S*
5	*o*-$MeOC_6H_4$	**3**	99	12	*R*
6		**4**	96	20	*S*
7	*p*-ClC_6H_4	**3**	99	8	*R*
8		**4**	25	18	*S*
9	*trans*-PhCH=CH	**3**	99	4	*S*
10		**4**	89	44	*S*
11	1-Naphthyl	**3**	98	6	*S*
12		**4**	100	22	*R*
13	2-Naphthyl	**3**	100	6	*S*
14		**4**	100	24	*R*

[a] [Sub]/[Zn]/[(*R*,*R*)-**3**] = 1.0/3.0/0.2; [Sub]/[Zn]/[(*R*,*R*)-**4**] = 1.0/3.0/0.15.

UV detector for determining the optical purity of the products. The absolute configuration of the products was assigned by comparing the sign of optical rotation values with literature data [3m].

4.2. Structure determinations

Crystal data and details of the structural analysis are tabulated in Table 1. Intensity data were collected at room temperature with CAD4 diffractometer using monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Lorentz and polarization reflections were applied and absorption corrections made with 3Ψ scans. The structures solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97 [20]. The R values are defined as $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR_2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions.

4.3. Materials

N,*N*-Dimethyl-1-ferrocenylethylamine (FA) [16], (*R*)-1-ferrocenylethylamine [16c], (*R*)-*N*,*N*,dimethyl-1-[(*S*)-2-(trimethylsilyl)ferrocenyl]ethylamine [17b], (*R*)-1-[(*S*)-2-(trimethylsilyl)ferrocenyl]ethylamine [17b], (*R*)-*N*,*N*,dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]-ethylamine [17b], (*R*)-1-[(*S*)-2-(diphenylphosphino)-ferrocenyl]ethylamine [17b],. (*S*)-2-(1-ferrocenylethylamino)ethanol [19] were prepared according to the literature methods.

4.4. (R)-2-[(1-Ferrocenylethylimino)methyl]phenol ((R)-**1a**)

Salicylaldehyde (1.4 ml, 13 mmol) was added to (*R*)-1-ferrocenylethylamine (3.0 g, 13 mmol) dissolved in EtOH (30 ml). The solution was stirred for 2 h under reflux. After cooling the reaction mixture to room temperature (r.t.), the solvent was removed to leave a dark residue which was chromatographed on silica gel with a mixture of hexane and Et_2O (9:1) as an eluent. The single orange band was collected to give orange crystals after recrystallization from Et_2O. Yield: 3.9 g, 90%. M.p.: 134–135 °C. $[\alpha]_D^{20} = -25.3$ ($c = 0.01$, $CHCl_3$). $\nu_{C=N}$ (KBr, cm^{-1}): 1625 (s). ^{1}H-NMR ($CDCl_3$): 1.57 (d, $J = 6.6$ Hz, 3H, CH_3), 4.09, 4.15 (AB, 4H, C_5H_4), 4.16 (s, 5H, C_5H_5), 4.30 (q, $J = 6.5$ Hz, 1H, CH), 6.87–7.35 (m, 4H, C_6H_4), 8.34 (s, 1H, OH), 13.80 (br, 1H, N = CH). MS; m/z (%): 333 (81, [M^+]), 213 (100), 176 (41), 121 (49). Anal. Calc. for $C_{19}H_{19}FeNO$: C, 68.49; H, 5.75; N, 4.20. Found: C, 68.46; H, 5.74; N, 4.17%.

4.5. (R)-2-{1-[(S)-2-(Trimethylsilyl)ferrocenylethylimino]methyl}phenol ((R,S)-**1b**)

The title compound was prepared in the same manner as described above for (*R*)-**1a** by simply replacing (*R*)-1-ferrocenylethylamine with (*R*)-1-[(*S*)-2-(trimethylsilyl)ferrocenyl]ethylamine (1.4 g, 4.7 mmol). The product was obtained as orange crystals after recrystallization from hexane. Yield: 1.8 g, 96%. M.p.: 110–112 °C. $[\alpha]_D^{20} = -115.9$ ($c = 0.01$, $CHCl_3$). $\nu_{C=N}$ (KBr, cm^{-1}): 1625 (m). ^{1}H-NMR ($CDCl_3$): 0.19 (s, 9H, $Si(CH_3)_3$), 1.67 (d, $J = 6.9$ Hz, 3H, CH_3), 4.13, 4.39, 4.42 (3H, C_5H_3), 4.16 (s, 5H, C_5H_5), 4.75 (q, $J = 6.8$ Hz, 1H, CH), 6.77–7.27 (m, 4H, C_6H_4), 7.97 (s, 1H, OH), 13.71 (br, 1H, N=CH). MS; m/z (%): 405 (69, [M^+]), 285 (100), 73 (39). Anal. Calc. for $C_{22}H_{27}FeNOSi$: C, 65.18; H, 6.71; N, 3.46. Found: C, 65.59; H, 6.86; N, 3.37%.

4.6. (R)-2-{1-[(S)-2-(Diphenylphosphino)-ferrocenylethylimino]methyl}phenol ((R,S)-**1c**)

The title compound was prepared in the same manner as described above for (*R*)-**1a** by replacing (*R*)-1-ferrocenylethylamine with (*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (1.0 g, 2.4 mmol). Recrystallization from Et_2O gave orange crystals. Yield: 1.1 g, 88%. M.p.: 154–155 °C. $[\alpha]_D^{20} = -9.3$ ($c = 0.01$, $CHCl_3$). $\nu_{C=N}$ (KBr, cm^{-1}): 1625 (s). ^{1}H-NMR ($CDCl_3$): 1.62 (d, $J = 6.5$ Hz, 3H, CH_3), 3.67, 4.26, 4.51 (3H, C_5H_3), 4.01 (s, 5H, C_5H_5), 4.64 (q, $J = 7.4$ Hz, 1H, CH), 6.53–7.45 (m, 14H, C_6H_5 and C_6H_4), 7.81 (s, 1H, OH), 13.06 (br, 1H, N=CH). ^{31}P-NMR ($CDCl_3$): −23.10 (s). MS; m/z (%): 517 (82, [M^+]), 452 (89), 398 (100), 212 (46). Anal. Calc. for $C_{31}H_{28}FeNOP$: C, 71.97; H, 5.45; N, 2.71. Found: C, 71.62; H, 5.50; N, 2.64%.

4.7. (S)-2-1-[(R)-2-Trimethylsilyl]-ferrocenylethylaminoethanol ((S,R)-**2a**)

The title compound was prepared in the same manner as described above for (*S*)-2-(1-ferrocenylethylamino)ethanol by simply replacing (*S*)-*N*,*N*,*N*-trimethyl-1-ferrocenylethylammonium iodide with (*S*)-*N*,*N*,*N*-trimethyl-1-[(*R*)-2-(trimethylsilyl)ferrocenylethyl]ammonium iodide (8.00 g, 17.0 mmol). The product was obtained as a yellow solid. Yield: 5.00 g, 85%. M.p.: 93–94 °C. $[\alpha]_D^{20} = -19$ ($c = 0.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.29 (s, 9H, $(CH_3)_3Si$), 1.48 (d, 3H, $J = 6.5$ Hz, CH_3), 2.59–2.71 (m, 2H, CH_2OH), 3.53 (t, $J = 5.1$ Hz, 2H, CH_2N), 3.70 (q, 1H, CH), 4.05, 4.28 and 4.36 (3H, C_5H_3), 4.10 (s, 5H, C_5H_5). HRMS; m/z (%): Calc. for $C_{17}H_{27}ONSiFe$: 345.1211 [M^+]. Found: 345.1212.

4.8. N-(O,O-Dimethylphosphoryl)-(S)-2-(1-ferrocenylethylamino)ethanol ((S)-2b)

To an ice-cold stirred solution of (*S*)-2-(1-ferrocenylethylamino)ethanol (4.00 g, 14.6 mmol), dimethyl phosphite (1.61 ml, 17.5 mmol), and Et_3N (2.44 ml, 17.5 mmol) in CH_2Cl_2 (30 ml) was added dropwise CCl_4 (2.96 ml, 30.7 mmol). The resulting solution was allowed to slowly warm to r.t. and then stirred for 5 h, after which time the mixture was quenched with aq. NH_4Cl. The organic layer was separated, dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (eluent: EtOAc–CH_3CN, 1:1) to afford orange crystals after crystallization from Et_2O. Yield: 3.50 g, 60%. M.p. 105–106 °C. $[\alpha]_D^{20} = +143$ ($c = 0.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 1.51 (d, $J = 6.7$ Hz, 3H, CH_3), 2.90–3.02 (m, 3H, CH_2N) 3.07 (t, $J = 5.6$ Hz, 1H, OH), 3.27–3.38 (m, 2H, CH_2OH), 3.73 (d, $J = 4.4$ Hz, 3H, OCH_3), 3.76 (d, $J = 4.4$ Hz, 3H, OCH_3), 4.59 (q, 1H, CH), 4.16 and 4.30 (AB, 4H, C_5H_4), 4.13 (s, 5H, C_5H_5). ^{31}P-NMR ($CDCl_3$): 15.3 (s). HRMS; *m*/*z* (%): Calc. for $C_{16}H_{24}O_4NFe$: 381.0792 [M^+]. Found: 381.0793.

4.9. N-(O,O-Dimethylphosphoryl)-(S)-2-1-[(R)-2-tri-methylsilyl]ferrocenylethylaminoethanol ((S,R)-2c)

The title compound was prepared in the same manner as described above for (*S*)-**2b** by replacing (*S*)-2-(1-ferrocenylethylamino)ethanol with (*S*,*R*)-**2a** (3.00 g, 8.69 mmol). The product was obtained as orange crystals. Yield: 2.22 g, 58%. M.p.: 153–154 °C. $[\alpha]_D^{20} = +56$ ($c = 0.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.31 (s, 9H, $SiMe_3$), 1.50 (d, $J = 5.7$ Hz, 3H, CH_3), 2.14 (t, $J = 5.8$ Hz, 1H, OH), 2.92–2.98 (m, 2H, CH_2N), 3.06–3.14 (m, 2H, CH_2OH), 3.72 (d, $J = 3.6$ Hz, OCH_3), 3.74 (d, $J = 3.6$ Hz, OCH_3), 4.74 (qt, 1H, CH), 4.45–4.15 (ABC, 3H, C_5H_3), 4.16 (s, 5H, C_5H_5). ^{31}P-NMR ($CDCl_3$): 19.3 (s). HRMS; *m*/*z* (%): Calc. for $C_{19}H_{32}O_4NSiPFe$: 453.1188 [M^+]. Found: 453.1188.

4.10. (R,R)-1,1′-Bis(1-ferrocenylethanol) ((R,R)-3)

The title compound was obtained according to the literature method with a slight modification [19]. The (*S*)-2-methyl-CBS-oxazaborolidine catalyst (3.3 g, 12 mmol) was dissolved in THF (30 ml) and cooled to 0 °C. From a syringe charged with borane dimethylsulfide (BMS) (1 M in THF, 40 ml) 20% of the final amount (8 ml) was added to the catalyst solution. After stirring 5 min, the remaining BMS and a solution of the diacetylferrocene (5.4 g, 20 mmol) in THF (50 ml) was added simultaneously within 20 min. The red color of ketone turned to yellow on reduction. After 15 min at 0 °C, the excess BMS was quenched by dropwise addition of MeOH (20 ml; caution: gas evolution!). After the methanolysis had ceased, the mixture was poured into saturated aq. NH_4Cl (250 ml) and extracted with CH_2Cl_2. The organic layer was washed with water (100 ml). The solvents were evaporated to leave a yellow solid which was purified by column chromatography on silica gel with a mixture of hexane and Et_2O (1:1) as an eluent. Yield: 5.1 g, 93%. M.p.: 68–69 °C. $[\alpha]_D^{20} = -51.1$ ($c = 0.01$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 1.40 (d, $J = 6.4$ Hz, 6H, CH_3), 4.12–4.19 (m, 8H, C_5H_4), 4.65 (qt, $J = 6.4$ Hz, 2H, CH). MS; *m*/*z* (%): 274 (51, [M^+]), 256 (46), 164 (100), 92 (76), 91 (62). Anal. Calc. for $C_{14}H_{18}O_2Fe$: C, 61.34; H, 6.62. Found: C, 61.04; H, 6.57%.

4.11. (R,R)-1,1′-Bis(1-ferrocenylethylamine)

The diol (*R*,*R*)-**2** was converted to the title compound as follows: (*R*,*R*)-1,1′-bis(1-ferrocenylethyl acetate) (2.0 g, 5.6 mmol) prepared according to the literature method [20] was dissolved in MeOH (20 ml) saturated with NH_3 (40 ml) in an autoclave at −30 °C. The reaction mixture was stirred for 10 h at 100 °C, after which the mixture was cooled to r.t. The unreacted NH_3 was released and the remaining solution treated with dilute aq. NaOH. The organic layer was extracted with Et_2O, the solvents dried over anhydrous $MgSO_4$, and evaporated to dryness to give a brown oil. Yield: 1.3 g, 86%. $[\alpha]_D^{20} = -33.3$ ($c = 0.01$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 1.33 (d, $J = 6.5$ Hz, 6H, CH_3), 1.80 (s, 4H, NH_2), 3.81 (qt, $J = 7.0$ Hz, 2H, CH), 4.10–4.13 (m, 8H, C_5H_4). MS; *m*/*z* (%): 272 (29, [M^+]), 255 (100), 240 (39), 228 (33). HRMS; *m*/*z* (%): Calc. for $C_{14}H_{20}N_2Fe$: 272.1754 [M^+]. Found: 272.0976.

4.12. (R,R)-1,1′-Bis[N-(1-ferrocenylethyl)-4-methylbenzenesulfonamide] ((R,R)-3)

p-Toluenesulfonyl chloride (2.8 g, 15 mmol) in CH_2Cl_2 (20 ml) was added to a solution of (*R*,*R*)-1,1′-bis(1-ferrocenylethylamine) (2.0 g, 7.4 mmol) and Et_3N (2.6 g, 26 mmol) in CH_2Cl_2 (30 ml) at −30 °C. After stirring for 10 h at r.t., the reaction mixture was extracted with CH_2Cl_2. The solvent was dried over anhydrous $MgSO_4$ and concentrated to about 2 ml to be chromatographed on silica gel (eluent: hexane and Et_2O, 1:2). A yellow solid was obtained after usual work-up. Yield: 2.5 g, 59%. M.p.: 162–164 °C. $[\alpha]_D^{20} = -27.7$ ($c = 0.01$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 1.29 (d, $J = 6.8$ Hz, 6H, $CHCH_3$), 2.44 (s, 6H, $PhCH_3$), 3.91–4.10 (m, 8H, C_5H_4), 4.15–4.22 (m, 2H, CH), 4.93 (d, $J = 7.6$ Hz, 2H, NH), 7.33 (d, $J = 8.4$ Hz, 4H, C_6H_2), 7.83 (d, $J = 8.4$ Hz, 4H, C_6H_2). MS; *m*/*z* (%): 580 (23, [M^+]), 396 (30), 91 (100), 65 (31). Anal. Calc. for $C_{28}H_{32}N_2O_4S_2Fe$: C, 57.93; H, 5.56; N, 4.83; S, 10.05. Found: C, 58.18; H, 5.59; N, 4.60; S, 10.29%.

4.13. General procedure for base catalysis

4.13.1. Condition A

A toluene solution (1.0 ml) of the base catalyst **1** (0.047 mmol, 10 mol%) was prepared. After stirring the solution for 10 min at ambient temperature, 30 molar excess of diethylzinc (1.4 ml, 1.4 mmol) was added to the solution. Stirring was continued for additional 30 min. The resulting solution was cooled to 0 °C to which benzaldehyde (0.048 ml, 0.47 mmol) was added. The reaction mixture was stirred further for 48 h at 0 °C, quenched with 5% HCl, and extracted with Et_2O. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. The oily residue was passed through a short silica gel column to remove catalyst using a 95:5 hexane–EtOAc mixture as an eluent.

4.13.2. Condition B

A 1:1 mixture of diethylzinc (0.047 ml, 0.047 mmol, 1 M solution in hexane) and the base catalyst **1** (0.047 mmol, 10 mol%) in toluene (1 ml) was prepared. The solution was stirred for 30 min at ambient temperature, after which was cooled to 0 °C and treated with diethylzinc (1.4 ml, 1.4 mmol) and benzaldehyde (0.048 ml, 0.47 mmol). The reaction mixture was further stirred for 48 h at this temperature. Quenching with 5% HCl followed by extraction with Et_2O, drying over anhydrous $MgSO_4$, and column chromatogrpahic separation gave the product.

4.14. General procedure for acid catalysis

To a solution of (*R*,*R*)-**2** (0.084 mmol, 20 mol%) in toluene (2.0 ml) was added titanium(IV) isopropoxide (0.19 g, 0.66 mmol) at ambient temperature. After stirring the solution for 30 min, the reaction mixture was cooled to 0 °C. Diethylzinc (1.4 ml, 1.4 mmol, 1 M solution in hexane) and benzaldehyde (0.048 ml, 0.47 mmol) was added and the reaction mixture was further stirred for 48 h at ambient temperature. The reaction was quenched with 5% HCl and the product obtained after usual work-ups as described above.

4.15. HPLC conditions for enantiomeric separation of chiral alcohols

All products were eluted with a mixture of hexane and 2-propanol (98:2) at 1.0 ml min^{-1} using UV detector at 254 nm.

*1-Phenyl-1-propanol (**a**).* (*R*)-**a**: $t_R = 13.0$ min; (*S*)-**a**: $t_R = 15.1$ min.

*1-(p-Methoxyphenyl)-1-propanol (**b**).* (*R*)-**b**: $t_R = 16.2$ min; (*S*)-**b**: $t_R = 19.1$ min.

*1-(o-Methoxyphenyl)-1-propanol (**c**).* (*R*)-**c**: $t_R = 11.7$ min; (*S*)-c: $t_R = 12.8$ min.

*1-(p-Chlorophenyl)-1-propanol (**d**).* (*R*)-**d**: $t_R = 11.3$ min; (*S*)-**d**: $t_R = 10.4$ min.

*(E)-1-Phenyl-1-(3-pentenol) (**e**).* (*R*)-**e**: $t_R = 11.9$ min; (*S*)-**e**: $t_R = 19.4$ min.

*1-(1-Naphthyl)-1-propanol (**f**).* (*R*)-**f**: $t_R = 19.2$ min; (*S*)-**f**: $t_R = 12.5$ min.

*1-(2-Naphthyl)-1-propanol (**g**).* (*R*)-**g**: $t_R = 23.8$ min; (*S*)-**g**: $t_R = 21.9$ min.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172446 and 172447 for compounds (*R*,*S*)-**1c** and (*S*,*R*)-**2c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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