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Synthesis of new chiral ferrocenyl P,N-ligands with a benzoxazole ring and their application in Ag-catalyzed asymmetric [3+2] cycloaddition

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ABSTRACT

New chiral ferrocenyl P,N-ligands with a benzoxazole ring as the *N*-donor group have been synthesized from 2-aminophenol through a three-step transformation and successfully employed in the Ag-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with electron-deficient alkenes. High diastereoselectivities, excellent enantioselectivities, and good yields have been achieved for a variety of substrates, demonstrating the potential of these new P,N-ligands in asymmetric catalysis.

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Asymmetric catalysis is one of the most powerful methods for the preparation of enantiomerically pure compounds. In this context, a number of metal complexes with hybrid chiral P,N-ligands bearing an oxazoline as the *N*-donor group have been recognized as powerful catalysts in a variety of asymmetric catalytic reactions such as hydrogenation, allylic alkylation, and so on.[1] In sharp contrast, few chiral P,N-ligands with an oxazole/benzoxazole ring as the *N*-donor moiety have been found to be efficient in catalytic asymmetric reactions presumably due to the lack of α-central chirality close to the *N*-donor atom as that in oxazoline ligands (Fig. 1).[2] However, the increased rigidity caused by the presence of a benzoxazole ring in the ligand backbone may be advantageous in some cases to create an efficient chiral environment around the central metal. The most important task for the development of an efficient chiral phosphine–benzoxazole ligand should be to search for an appropriate chiral skeleton.

In our recent Letter, we have developed a series of chiral P,N-ligands based on chiral 1-ferrocenylethylamine skeleton. These ligands displayed excellent enantio-induction in the Pd-catalyzed asymmetric allylic alkylation,[3] Ru-catalyzed asymmetric cyclopropanation,[4] Cu-catalyzed asymmetric propargylic amination,[5] Cu-catalyzed asymmetric [3+3] cycloaddition,[6] and so on.[7] The success of these ligands in asymmetric catalysis demonstrated the potential of 1-ferrocenylethylamine as the chiral ligand backbone. As an effort toward further exploration of the application of this chiral skeleton in asymmetric catalysis,[8] herein, we report the synthesis of a new type of chiral P,N-ligands with a benzoxazole ring as the *N*-donor moiety from 1-ferrocenylethylamine derivatives, which were found to be highly effective in the Ag(I)-catalyzed asymmetric [3+2] cycloaddition of azomethine ylides with some electron-deficient alkenes.

Chiral phosphine–benzoxazole ligands **1a**–**b** were synthesized from 2-aminophenol according to the procedure shown in Scheme 1. Initially, 2(3*H*)-benzoxazolethione (**3**) was prepared as a white needle in 82% yield by the reaction of 2-aminophenol with CS_2 in refluxing aqueous EtOH for 3 h.[9] The treatment of 2(3*H*)-benzoxazolethione with $POCl_3$ and PCl_5 in CH_2Cl_2 at room temperature generated 2-chlorobenzoxazole **4** as a colorless oil in 60% yield.[10] Finally, 2-chlorobenzoxazole **4** was converted into the desired phosphine–benzoxazole ligands **1a**–**b**[11] in high yields by the reaction with chiral phosphine–amine intermediates, (R_c,S_p)-PPFNHR,[12] under the basic condition.

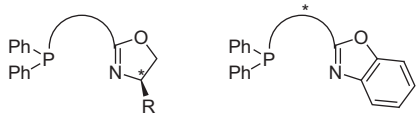

Figure 1. Structure of *P*-oxazoline and *P*-benzoxazole ligands.

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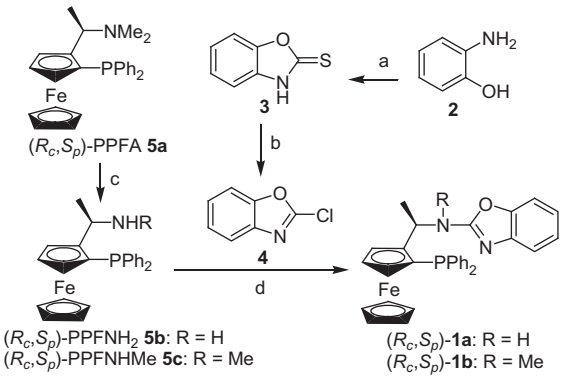
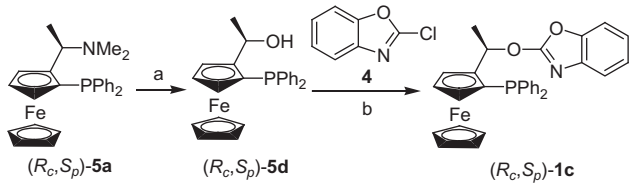


Scheme 1. Synthesis of chiral ferrocenyl P,N-ligands (R_c,S_a)-**1a**–**b**. Reagents and conditions: (a) KOH, EtOH/H_2O (5/1), refluxing, 3 h; (b) $POCl_3$/PCl_5, CH_2Cl_2, rt, 12 h; (c) Ac_2O, 110 °C, NH_3 or $MeNH_2$, MeOH, 80 °C; (d) *i*-Pr_2NEt, DMF, rt; −50 °C, 12 h.



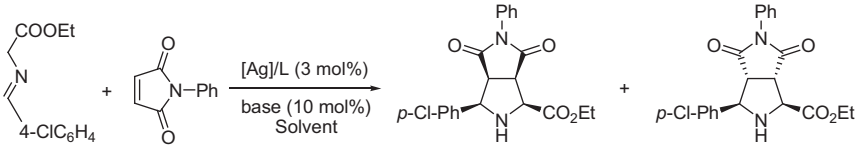
Scheme 2. Synthesis of chiral ferrocenyl *P*,*N*-ligand (R_c,S_a)-**1c**. Reagents and conditions: (a) Ac_2O, 110 °C, 3 h, and then $LiAlH_4$, THF, reflux for 12 h; (b) *n*-BuLi, Et_2O, and then reflux for 12 h.

For a comparison, (R_c,S_p)-**1c** with a oxygen linker was also prepared in a similar procedure as shown in Scheme 2.

With these newly developed ferrocenyl phosphine–benzoxazole ligands in hand, we then examined their efficiency in the Ag-catalyzed asymmetric [3+2] cycloaddition of azomethine with *N*-phenylmaleimide.[13] Initially, the cycloaddition of *N*-(4-chlorobenzylidene)glycine ethyl ester (**6a**) with *N*-phenylmaleimide **7** was selected as a model reaction. The reaction was performed in Et_2O at rt in the presence of a catalytic amount of Et_3N (10 mol %) and the catalyst (3 mol %) in situ prepared from silver salts and 1.1 equiv of ferrocenyl phosphine–benzoxazole ligands **1a**–**c**,[14] and the results are summarized in Table 1. In comparison with ligand **1a** bearing a N–H proton, ligand **1b** with a *N*-methyl substituent showed significantly improved enantioselectivity in this model reaction, giving the *endo*-cycloadduct **8a** in good diastereoselectivity (95/5) with enantioselectivity of up to 95% ee (entry 1 vs entry 2). With (R_c,S_p)-**1c** as ligand, the reaction gave the cycloadducts in slightly decreased enantioselectivity (87% ee) but with the same configuration as that obtained with (R_c,S_p)-**1a** (entry 3). This result suggested that in this class of P,N-ligands, the N-atom in the benzoxazole ring rather than the one directly attached to the stereogenic carbon center is the actual *N*-donor atom. The reaction proved to be highly sensitive to the catalyst precursors. Thus, the use of AgOTf and $AgBF_4$ resulted in dramatically decreased enantioselectivities (entries 4 and 5). The nature of the solvent has some influence on the conversion, diastereoselectivity, and enantioselectivity (entries 6–9). Further work on the screening of various bases indicated that Et_3N was the best choice (entries 10–13). The reaction temperature had some impact on the reactivity and enantioselectivity, and the reaction performed at lower temperatures tended to give better enantioselectivity (entries 14–17). When the reaction temperature was carried out at −20 °C, up to 98% ee was achieved (entry 17).

Under the optimized reaction conditions, the scope of the present catalytic system in the 1,3-dipolar cycloaddition was carried

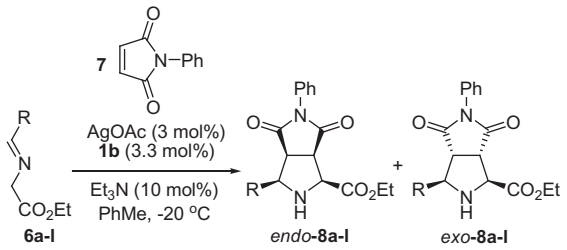
Table 1
Catalytic asymmetric [3+2] cycloaddition reaction of *N*-(4-chlorobenzylidene)glycine ethyl ester **6a** with *N*-phenylmaleimide **7**[a]



Entry	Ligand	Ag salt	Base	Solvent	Temperature	Yield[b] (%)	*Endo*/*exo*[c]	Ee (%)[d]
1	**1a**	AgOAc	Et_3N	Toluene	rt	85	>95/5	50
2	**1b**	AgOAc	Et_3N	Toluene	rt	93	95/5	95
3	**1c**	AgOAc	Et_3N	Toluene	rt	90	>95/5	87
4	**1b**	AgOTf	Et_3N	Toluene	rt	97	90/10	27
5	**1b**	$AgBF_4$	Et_3N	Toluene	rt	82	92/8	64
6	**1b**	AgOAc	Et_3N	CH_2Cl_2	rt	93	90/10	97
7	**1b**	AgOAc	Et_3N	THF	rt	93	93/7	74
8	**1b**	AgOAc	Et_3N	CH_3CN	rt	78	95/5	97
9	**1b**	AgOAc	Et_3N	Et_2O	rt	92	93/7	95
10	**1b**	AgOAc	––	Toluene	rt	94	95/5	93
11	**1b**	AgOAc	*i*-Pr_2NEt	Toluene	rt	92	>95/5	95
12	**1b**	AgOAc	DBU	Toluene	rt	87	>95/5	31
13	**1b**	AgOAc	DABCO	Toluene	rt	91	95/5	94
14	**1b**	AgOAc	Et_3N	Toluene	40	94	95/5	94
15	**1b**	AgOAc	Et_3N	Toluene	0	93	95/5	96
16[e]	**1b**	AgOAc	Et_3N	Toluene	−10	89	>95/5	97
17[f]	**1b**	AgOAc	Et_3N	Toluene	−20	94	>95/5	98

[a] Reactions were performed in 3 mL of solvent with 0.5 mmol of substrate **6a**, 10 mol % of base additives, and 3 mol % of catalyst prepared in situ from Ag salts and 1.1 equiv of ligand at indicated temperature for 2 h.
[b] Isolated yields.
[c] *Endo*/*exo*-ratio was determined by ^1H NMR.
[d] Enantiomeric excesses were determined by chiral HPLC.
[e] Reaction time, 6 h.
[f] Reaction time, 12 h.

Table 2
Catalytic asymmetric [3+2] cycloaddition of imino esters **6a–l** with *N*-phenylmaleimide **7**[a]



Entry	Substrate (R)	Yield[b] (%)	*Endo/exo* [c]	ee[d] (%)
1	**6a**: 4-ClC_6H_4	94	95/5	98
2	**6b**: 3-ClC_6H_4	94	>95/5	95
3	**6c**: 2-ClC_6H_4	92	>95/5	98
4	**6d**: Ph	90	>95/5	97
5	**6e**: 4-FC_6H_4	89	94/6	98
6	**6f**: 4-$CF_3C_6H_4$	87	94/6	97
7	**6g**: 4-BrC_6H_4	94	>95/5	95
8	**6h**: 4-MeC_6H_4	85	92/8	>99
9	**6i**: 4-$MeOC_6H_4$	80	90/10	98
10	**6j**: 1-Naphthyl	85	95/5	98
11	**6k**: 2-Thienyl	75	>95/5	88
12	**6l**: Cyclohexyl	80	93/7	91

[a] Reactions were performed in 3 mL of toluene with 0.5 mmol of substrate **6a–j**, 10 mol % of Et_3N, and 3 mol % of catalyst prepared in situ from AgOAc and 1.1 equiv of **1b** at −20 °C for 12 h.
[b] Isolated yields.
[c] *Endo*/*exo*-ratio was determined by ^1H NMR.
[d] Enantiomeric excesses were determined by chiral HPLC.

out. As shown in Table 2, various imino esters **6a–i** prepared from various substituted benzaldehydes reacted with *N*-phenylmaleimide **7** to give the corresponding *endo*-adducts **8a–i** in high yields and good to perfect enantioselectivities (95 to >99% ee) (entries 1–9). The results disclosed that the electronic property of the substituent on the phenyl ring had little effect in the enantioselectivities, but had some influence on the diastereoselectivities (entries 1, 4–9). The substrates bearing an electron-withdrawing substituent tended to give higher diastereoselectivities than those with an electron-donating group (entries 8 and 9 vs entries 5–7). An azomethine ylide derived from 1-naphthylaldehyde also proved to be a suitable substrate in this transformation, producing *endo*-cycloadduct in 98% ee (entry 10). 2-Thienyl substrate **6k** was also efficient, giving *endo*-cycloadduct in 88% ee (entry 11). More importantly, the presence of catalytic system showed good reactivity for alkyl substituted substrate **6l**, giving *endo*-cycloadduct in 91% ee (entry 12).

To further extend the scope of this catalytic system, the scope and generality of this catalytic system with regard to iminoesters and dipolarophiles were also investigated (Fig. 2). The present catalytic system is remarkably tolerant and remains high in reactivity for azomethine ylides derived from amino esters other than glycinate. Thus, under the optimized reaction conditions, the azomethine ylide derived from phenylalanine successfully reacted with *N*-phenylmaleimide **7**, leading to perfect *endo*-selectivities (>95/5) and excellent enantioselectivities (96% ee). A variety of other dipolarophiles was also subjected to this reaction. With *N*-methylmaleimide, high *endo*-selectivity (*endo*/*exo* >95/5) and good enantioselectivity (94% ee) were achieved. However, for dimethyl maleate and *tert*-butyl arcylate, the present catalytic system proved to be less efficient, displaying very low enantioselectivity.

In conclusion, we have developed a new family of chiral ferrocenyl P,N-ligands with a benzoxazole fragment through an efficient and simple synthesis route. These ligands were evaluated in the Ag(I)-catalyzed asymmetric [3+2] cycloaddition of azomethine

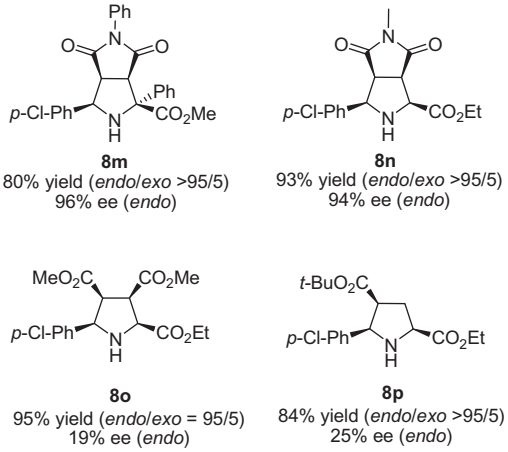


Figure 2. Cycloadducts of the reaction between imino esters with other dipolarophiles.

ylides with various electronic-deficient alkenes, in which high *endo*-selectivities and good to excellent enantioselectivities (up to >99% ee) were achieved. Further applications of these new ligands in other type of asymmetric reactions are in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.05.003.

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11. *Selected physical and spectral data for* (R_c, S_p)-**1a**: yellow solid; mp: 120–124 °C; $[\alpha]_D^{25}$: −304.6 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (d, *J* = 6.4 Hz, 3H), 3.79 (s, 1H), 4.02 (s, 5H), 4.30 (s, 1H), 4.50 (s, 1H), 5.11–5.15 (m, 1H), 5.71 (br, 1H), 6.94–6.98 (m, 1H), 7.06–7.13 (m, 7H), 7.32–7.35 (m, 4H), 7.48–7.52 (m, 2H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −24.6; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 48.9 (d, *J* = 4.1 Hz), 69.2, 69.9, 70.2 (d, *J* = 4.4 Hz), 72.1 (d, *J* = 4.2 Hz), 95.1, 108.5, 116.2, 120.4, 123.5, 128.0, 128.1, 128.2, 129.1, 132.6 (d, *J* = 18.8 Hz), 134.9 (d, *J* = 20.6 Hz), 136.6 (d, *J* = 7.6 Hz), 138.7 (d, *J* = 8.3 Hz), 143.1, 148.3, 160.4; HRMS (*m*/*z*) calcd for $C_{31}H_{27}FeN_2OP$: 530.1210, found: 530.1209.
Selected physical and spectral data for (R_c, S_p)-**1b**: yellow needle; mp: 154–156 °C; $[\alpha]_D^{25}$: −364.1 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.76 (s, 1H), 4.13 (s, 5H), 4.32 (s, 1H), 4.50 (s, 1H), 5.81–5.83 (m, 1H), 6.81–6.86 (m, 4H), 6.89–6.93 (m, 1H), 7.00–7.09 (m, 3H), 7.28–7.30 (m, 4H), 7.44–7.48 (m, 2H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −25.7; ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 28.6, 51.4 (d, *J* = 8.9 Hz), 68.7, 69.9 (d, *J* = 3.5 Hz), 70.0, 72.1 (d, *J* = 4.5 Hz), 77.8 (d, *J* = 10.2 Hz), 91.9, 92.1, 108.3, 115.7, 119.5, 123.3, 127.6 (d, *J* = 7.2 Hz), 128.0 (d, *J* = 17.4 Hz), 128.1, 128.7, 132.5, 132.7, 134.4, 134.6, 136.8 (d, *J* = 9.9 Hz), 137.8 (d, *J* = 9.5 Hz), 143.5, 148.6, 161.0. HRMS (*m*/*z*) calcd for $C_{32}H_{29}FeN_2OP$: 544.1367, found: 544.1367.
Selected physical and spectral data for (R_c, S_p)-**1c**: yellow solid; mp: 196–198 °C; $[\alpha]_D^{25}$: −346.6 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (d, *J* = 7.2 Hz, 3H), 3.81 (s, 1H), 4.17 (s, 5H), 4.43 (s, 1H), 4.83 (s, 1H), 5.91–5.93 (m, 1H), 6.68–6.93 (m, 9H), 7.29–7.48 (m, 5H); ^{31}P NMR (162 MHz, $CDCl_3$): δ −26.4; ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 48.6 (d, *J* = 8.0 Hz), 69.0, 70.1 (d, *J* = 3.5 Hz), 70.7, 72.7 (d, *J* = 4.5 Hz), 77.8 (d, *J* = 10.2 Hz), 89.8, 90.1, 109.5, 109.7, 121.3, 122.7, 127.4 (d, *J* = 6.9 Hz), 127.8, 128.0 (d, *J* = 7.6 Hz), 129.1, 131.9 (d, *J* = 20 Hz), 134.7 (d, *J* = 20 Hz), 136.4 (d, *J* = 9.1 Hz), 136.8 (d, *J* = 9.2 Hz), 142.3, 152.7. HRMS (*m*/*z*) calcd for $C_{31}H_{26}FeNO_2P$: 531.1051, found: 531.1047.
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14. *General procedure for catalytic asymmetric 1,3-dipolar cycloadditon of azomethine ylides.* Under nitrogen atmosphere, a solution of AgOAc (0.015 mmol) and ligand **1b** (0.0165 mmol) in 3 mL of toluene was stirred at room temperature for 1 h. The solution was cooled to −20 °C, and then added imino esters (0.5 mmol), Et_3N (7.5 μL, 0.05 mmol), and *N*-phenylmaleimide **7** (0.6 mmol) successively. After 12 h, the mixture was passed through a short column of silica gel and the diastereometric ratio (*endo*/*exo*) was determined by the NMR spectroscopic analysis of the crude product. The residue was then purified by column chromatography on silica gel, and was submitted to ee analysis by HPLC with a chiral column.