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The application of chiral phosphine-Schiff base type ligands in silver(I)-catalyzed asymmetric vinylogous Mannich reaction of aldimines with trimethylsiloxyfuran

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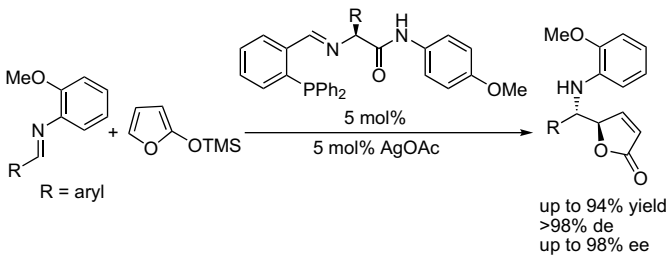
ABSTRACT

Catalytic asymmetric vinylogous Mannich (AVM) reactions of readily available aldimines with trimethylsiloxyfuran in the presence of catalytic amount of AgOAc and chiral phosphine-Schiff base type ligands are described, affording the corresponding products in up to 91% yield, *anti*/*syn* >99:1 and 81% ee.

1. Introduction

The reaction of silyloxyfuran with imines, nitrones or iminium ions has already been reported by several research groups.[1] Such Mannich-type reaction is one of the most important methods for the synthesis of β-amino carbonyls and their derivatives, which can be found in a large number of biologically active natural products.[2] Recently, several elegant catalytic systems have been applied in asymmetric vinylogous Mannich (AVM) reactions. For example, Martin and Lopez reported the first catalytic asymmetric addition of trialkylsilyloxyfurans to aldimines in 1999.[3] Later, Hoveyda and Snapper have developed a silver(I)-based catalyst, leading to the product of AVM reaction in excellent diastereo- and enantioselectivity.[4] In particular, the use of 2-methyloxyphenyl group as aldimine substituent was essential for achieving good enantioselectivities in AVM reaction (Scheme 1). Moreover, Carretero et al. reported an AVM reaction which relied on the use of *N*-(2-thienyl)-sulfonylimines as substrates.[5] A bifunctional thiourea catalyst promoted AVM reaction was developed by Chen et al. in 2007.[6] Very recently, a chiral Brønsted acid-catalyzed approach to this AVM reaction was achieved by Akiyama et al.[7] and Schneider's group,[8] respectively. Aside from these pioneering investigations, the exploration of new catalytic systems in AVM reaction is still a main challenge at the present stage.



Scheme 1. Previous research in AVM reaction and our approach.

Previous research has disclosed that aldimine substrates having 2-methyloxyphenyl group is essential to give the AVM product in high yield and good enantioselectivity in this catalytic system through a bidentate chelation with the chiral metal complex (Scheme 1).[4] Herein, we wish to report a novel and efficient silver(I)-catalyzed AVM procedure, which relies on the use of chiral phosphine-Schiff base type ligands developed in our group. Furthermore, this paper will reveal that the AVM reaction of aldimines **1**, which do not possess 2-methyloxyphenyl group, with siloxyfuran **2** can proceed smoothly to give the corresponding products **3** in good yields and moderate to good enantioselectivities in the presence of phosphine-Schiff base type ligand and AgOAc under mild reaction conditions (Scheme 1).

2. Results and discussion

We initially utilized a moderate Lewis acid AgOAc (10 mol %)[9] combined with chiral phosphine-Schiff base type ligands **L1–L11** (11 mol %) prepared from the reaction of salicylaldehyde as well as their analogs with (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine[10] (Fig. 1) as the catalysts and the AVM reaction of readily available aldimine **1a** (0.2 mmol) with siloxyfuran **2** (0.36 mmol) as a model reaction in tetrahydrofuran (THF) containing 0.36 mol of ^{i}PrOH (1.8 equiv) to develop the optimal reaction conditions and the results of these experiments are summarized in Table 1. It was

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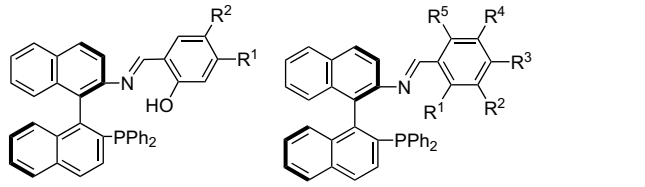
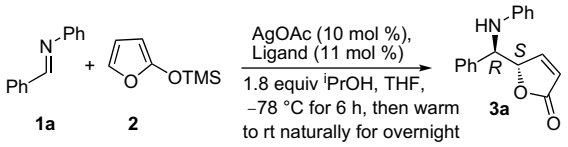


L1: R^1 = OMe, R^2 = H
L2: R^1 = H, R^2 = Me

L3: R^1 = H, R^2 = H, R^3 = H, R^4 = H, R^5 = H
L4: R^1 = Cl, R^2 = H, R^3 = Cl, R^4 = H, R^5 = H
L5: R^1 = Cl, R^2 = H, R^3 = H, R^4 = H, R^5 = Cl
L6: R^1 = Cl, R^2 = Cl, R^3 = H, R^4 = H, R^5 = H
L7: R^1 = F, R^2 = H, R^3 = H, R^4 = H, R^5 = H
L8: R^1 = Br, R^2 = H, R^3 = H, R^4 = H, R^5 = H
L9: R^1 = CF_3, R^2 = H, R^3 = H, R^4 = H, R^5 = H
L10: R^1 = OMe, R^2 = H, R^3 = OMe, R^4 = H, R^5 = H
L11: R^1 = OBn, R^2 = ^{t}Bu, R^3 = H, R^4 = ^{t}Bu, R^5 = H

Figure 1. Chiral phosphine-Schiff base type ligands **L1**–**L12**.

Table 1
Optimization of chiral ligands for the AVM reaction of aldimine **1a** and siloxyfuran **2**



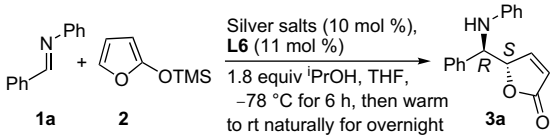
Entry[a]	Ligand	Yield[b] (%)	dr (*anti*/*syn*)[c]	ee[d] (%)	Absolute Configuration[e]
		3a	**3a**	**3a**	
1	**L1**	53	99:1	35	*R*,*S*
2	**L2**	50	99:1	33	*R*,*S*
3	**L3**	73	99:1	23	*R*,*S*
4	**L4**	70	99:1	65	*R*,*S*
5	**L5**	69	99:1	17	*R*,*S*
6	**L6**	80	99:1	70	*R*,*S*
7	**L7**	81	99:1	63	*R*,*S*
8	**L8**	78	99:1	70	*R*,*S*
9	**L9**	77	99:1	70	*R*,*S*
10	**L10**	75	99:1	60	*R*,*S*
11	**L11**	73	99:1	8	*R*,*S*

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.36 mmol), ^{i}PrOH (0.36 mmol), AgOAc (10 mol %), ligand (11 mol %), THF (1.0 mL), and the reaction was carried out at −78 °C to rt for 24 h.
[b] Isolated yield after column chromatography.
[c] Determined by analysis of 300 MHz ^{1}H NMR spectra.
[d] Determined by chiral HPLC analysis; see Supplementary data for the details.
[e] Determined by the X-ray diffraction.

found that the corresponding AVM product **3a** was obtained in 53% yield and 35% ee as *anti*-configuration as the major diastereomer (dr=99:1) in the presence of **L1** (Table 1, entry 1). Using **L2** as a ligand[11] combined with AgOAc afforded **3a** in 50% yield and 33% ee (dr=99:1) (Table 1, entry 2). After investigating the phosphine-Schiff base type ligand **L3**, which do not have a phenolic hydroxy group, we found that **3a** was produced in 73% yield and 23% ee (dr=99:1), indicating that this type of phosphine-Schiff base ligands has higher catalytic ability (Table 1, entry 3). Then, it was found that chiral phosphine-Schiff base ligands **L4**–**L11** having electron-withdrawing group or electron-donating group at 2-position of benzene ring gave the better results (Fig. 1) (Table 1, entries 4–10). As for the phosphine-Schiff base ligand **L5** having a 2,6-disubstituted benzene ring, product **3a** was produced in 69% yield and only 17% ee (dr=99:1) (Table 1, entry 5). As for the sterically bulky chiral phosphine-Schiff base ligand **L11** bearing electron-donating 3,5-di-*tert*-butyl groups on the benzene ring, the product **3a** was obtained in 73% yield and only 8% ee (dr=99:1) under identical conditions (Table 1, entry 11). Among the ligands examined, chiral phosphine-Schiff base ligand **L6** possessing two electron-withdrawing groups at 2- and 3-positions of benzene ring gave the best result, affording **3a** in 80% yield and 70% ee (dr=99:1) (Table 1, entry 6).

With the best chiral phosphine-Schiff base ligand being identified, we next carried out silver(I)-**L6** catalyzed AVM reaction of **1a** with **2** in different solvents with a variety of silver(I) salts. The results are outlined in Table 2. When the reaction was carried out in CH_2Cl_2 and toluene, **3a** was obtained in 87% and 85% yield as well as 66% and 67% ee, respectively (Table 2, entries 2 and 3). Solvents such as Et_2O, CH_3CN, and 1,4-dioxane are not suitable to this reaction, providing **3a** in lower yields and ee's even raising the reaction temperature to −20 °C (Table 2, entries 1, 4, and 5). Therefore, the best conditions are to carry out the reaction in THF at −78 °C to room temperature for 24 h. The decrease in yields, diastereoselectivities (from 60:40 to 75:25), and enantioselectivities was also observed when other silver(I) salts such as AgOTf, AgOTFA, and $AgClO_4$ were applied instead of AgOAc in this reaction (Table 2, entries 6–8).

Table 2
Effect of solvents and silver salts on the AVM reaction of aldimine **1a** and siloxyfuran **2**



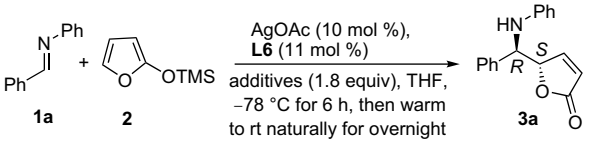
Entry[a]	Solvent	Silver salt	Yield[b] (%)	dr (*anti*/*syn*)[c]	ee[d] (%)	Absolute Configuration[e]
			3a	**3a**	**3a**	
1	Et_2O	AgOAc	50	99:1	62	*R*,*S*
2	Toluene	AgOAc	87	99:1	66	*R*,*S*
3	CH_2Cl_2	AgOAc	85	99:1	67	*R*,*S*
4	CH_3CN	AgOAc	21	90:10	66	*R*,*S*
5[f]	Dioxane	AgOAc	36	99:1	43	*R*,*S*
6	THF	AgOTf	38	75:25	38	*R*,*S*
7	THF	AgOTFA	30	60:40	30	*R*,*S*
8	THF	$AgClO_4$	37	65:35	37	*R*,*S*

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.36 mmol), ^{i}PrOH (0.36 mmol), silver salt (10 mol %), **L6** (11 mol %), solvent (1.0 mL), and the reaction was carried out at −78 °C to rt for 24 h.
[b] Isolated yield after column chromatography.
[c] Determined by analysis of 300 MHz ^{1}H NMR spectra.
[d] Determined by chiral HPLC analysis; see Supplementary data for the details.
[e] Determined by the X-ray diffraction.
[f] The reaction was carried out at −20 °C to rt for 24 h.

Previous studies have revealed that additives, even small amounts of simple achiral compounds, often played an important role in the enhancement of the reactivity and enantioselectivity.[8,12] The optimization studies on the effects of different additives were performed and the results of these experiments are summarized in Table 3. When the reaction was carried out without any additive, the desired product **3a** was obtained in 49% yield and 51% ee after stirring for 48 h from −78 °C to room temperature (Table 3, entry 1).[13] Adding EtOH, ^{t}BuOH, and 1,2-cyclohexanediol into the reaction system afforded **3a** in higher yields and enantioselectivities under identical conditions (Table 3, entries 2–4). We also examined (−)-menthol, 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), which is known to accelerate the reaction rate and enantioselectivity in some cases,[14] CF_3CH_2OH, diphenylmethanol, and triphenylmethanol in this AVM reaction and found that similar results were achieved (Table 3, entries 5–9). Gratifyingly, when phenylmethanol (BnOH) was used as an additive, the desired product **3a** was attained in 85% yield and 79% ee (Table 3, entry 10). Therefore, various phenylmethanol derivatives combined with AgOAc and ligand **L6** were screened for the reaction. However, it was found that

(4-nitrophenyl)methanol, (4-methoxyphenyl)methanol, and pyridin-2-ylmethanol are less effective in both of the yield and ee than those of phenylmethanol under identical conditions (Table 3, entries 11–13). Silica gel could also accelerate the reaction rate, but did not improve the enantioselectivity of **3a** (Table 3, entry 14). $NaBAr_F$ [sodium tetrakis(3,5-bistrifluoromethylphenylborate)], which has been successfully used in several asymmetric catalysis,[15] was examined in this reaction as an additive, producing **3a** in 81% yield and 77% ee (Table 3, entry 15).

Table 3
Optimization of reaction conditions of aldimine **1a** and siloxyfuran **2**

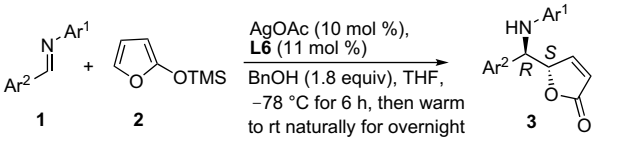


Entry[a]	Additive	Time (h)	Yield[b] (%)	dr (*anti*/*syn*)[c]	ee[d] (%)	Absolute Configuration[e]
			3a	**3a**	**3a**	
1	—	48	49	95:5	51	*R*,*S*
2	EtOH	24	77	95:5	59	*R*,*S*
3	^{t}BuOH	24	79	99:1	65	*R*,*S*
4	1,2-Cyclohexanediol	24	73	99:1	71	*R*,*S*
5	(−)-Menthol	24	67	99:1	69	*R*,*S*
6	HFIP	24	66	99:1	66	*R*,*S*
7	CF_3CH_2OH	24	75	99:1	75	*R*,*S*
8	Diphenylmethanol	24	81	99:1	65	*R*,*S*
9	Triphenylmethanol	24	50	95:5	65	*R*,*S*
10	Phenylmethanol	24	85	99:1	79	*R*,*S*
11	(4-Nitrophenyl)-methanol	24	35	95:5	63	*R*,*S*
12	(4-Methoxyphenyl)-methanol	24	61	99:1	70	*R*,*S*
13	Pyridin-2-yl-methanol	48	25	90:10	53	*R*,*S*
14[f]	Silica gel	8	85	99:1	71	*R*,*S*
15[g]	$NaBAr_F$	24	81	99:1	77	*R*,*S*

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.36 mmol), additives (0.36 mmol), AgOAc (10 mol %), **L6** (11 mol %), THF (1.0 mL), and the reaction was carried out at −78 °C to rt for 24 h.
[b] Isolated yield after column chromatography.
[c] Determined by analysis of 300 MHz ^{1}H NMR spectra.
[d] Determined by chiral HPLC analysis; see Supplementary data for the details.
[e] Determined by the X-ray diffraction.
[f] The reaction was carried out with 50 mg of silica gel.
[g] The reaction was carried out with 11 mol % of $NaBAr_F$.

Under these optimum conditions, that is, use of 10 mol % of AgOAc, 11 mol % of chiral ligand **L6**, and 1.8 equiv of phenylmethanol (BnOH) as the additive, we next examined the generality of this reaction with various aldimines **1**, which do not possess 2-methyloxyphenyl group, with siloxyfuran **2** and the results are summarized in Table 4. Aldimines **1b** having a 4-nitro substituent on the phenyl ring of Ar^1 gave the corresponding AVM product **3b** in 51% yield and 38% ee (Table 4, entry 1). In most cases, the corresponding AVM adducts **3c–i** were formed in good yields and good diastereoselectivities as well as moderate to good enantioselectivities (Table 4, entries 2–8). When ligands **L8** and **L9** were used in this reaction under the optimized conditions, the achieved enantiomeric excesses of adduct **3h** were lower than that of **L6** (Table 4, entries 7, 9, and 10). Only using aldimine **1g** having 2,4-dimethoxy group on the benzene ring of Ar^2 afforded **3g** in 75:25 diastereoselectivity, presumably due to the electronic effect (Table 4, entry 6). The highest ee was achieved using aldimine **1h** having 2,4-dichloro groups on the benzene ring of Ar^2 to give the adduct **3h** in 81% ee and 80% yield (dr=99:1) (Table 4, entry 8). Their structures were determined by ^{1}H and ^{13}C NMR spectroscopy and HRMS or microanalyses, and the enantiomeric excesses were analyzed by chiral HPLC (see Supplementary data). The absolute configuration of **3** was determined as (*R*,*S*)-configuration by X-ray diffraction of **3e** containing a bromine atom on the benzene ring.[16] The ORTEP drawing of **3e** is shown in Figure 2 and the CIF data of **3e** are presented in Supplementary data.[17]

Table 4
Scope and limitations of AVM reaction of aldimine **1** and siloxyfuran **2**



Entry[a]	Aldimine **1** (Ar^1/Ar^2)	Yield[b] (%)	dr (*anti*/*syn*)[c]	ee[d] (%)	Absolute Configuration[e]
		3	**3**	**3**	
1	**1b** (4-$NO_2C_6H_4$/C_6H_5)	**3b**, 51	99:1	38	*R*,*S*
2	**1c** (4-$MeOC_6H_4$/C_6H_5)	**3c**, 56	99:1	62	*R*,*S*
3	**1d** (3-$CF_3C_6H_4$/C_6H_5)	**3d**, 90	99:1	65	*R*,*S*
4	**1e** (4-BrC_6H_4/4-BrC_6H_4)	**3e**, 78	99:1	65[e]	*R*,*S*
5	**1f** (4-BrC_6H_4/2-$CF_3C_6H_4$)	**3f**, 85	99:1	55	*R*,*S*
6	**1g** (4-BrC_6H_4/2,4-$(MeO)_2C_6H_3$)	**3g**, 81	75:25	80	*R*,*S*
7	**1h** (C_6H_5/2,4-$Cl_2C_6H_3$)	**3h**, 80	99:1	81	*R*,*S*
8	**1i** (C_6H_5/4-$NO_2C_6H_4$)	**3i**, 91	99:1	59	*R*,*S*
9[f]	**1h** (C_6H_5/2,4-$Cl_2C_6H_3$)	**3h**, 83	99:1	73	*R*,*S*
10[g]	**1h** (C_6H_5/2,4-$Cl_2C_6H_3$)	**3h**, 85	99:1	75	*R*,*S*

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.36 mmol), BnOH (0.36 mmol), AgOAc (10 mol %), **L6** (11 mol %), THF (1.0 mL), and the reaction was carried out at −78 °C to rt for 24 h.
[b] Isolated yield after column chromatography.
[c] Determined by analysis of 300 MHz ^{1}H NMR spectra.
[d] Determined by chiral HPLC analysis; see Supplementary data for the details.
[e] The absolute configuration was determined by X-ray crystallographic analysis.
[f] Ligand **L8** was used under optimized conditions instead of **L6**.
[g] Ligand **L9** was used under optimized conditions instead of **L6**.

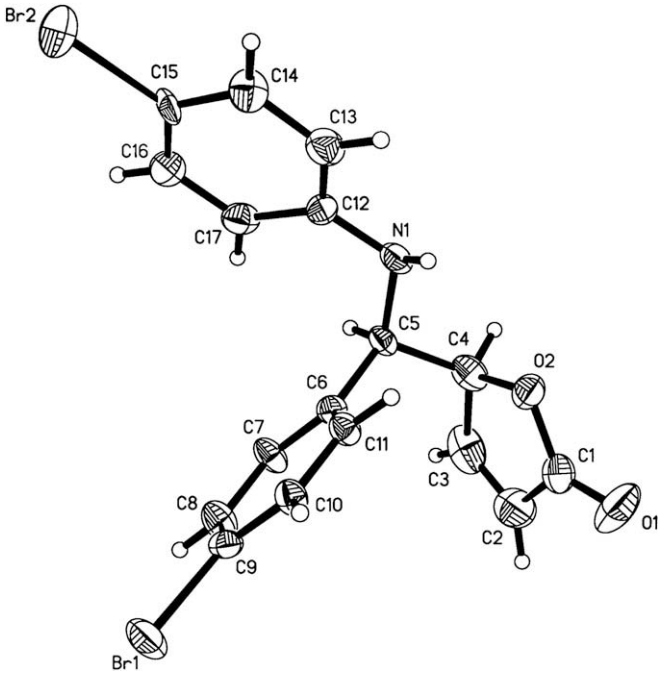
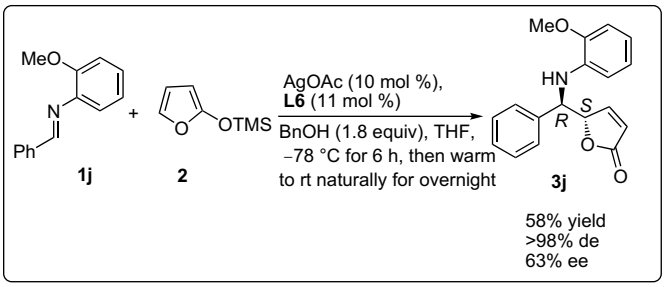


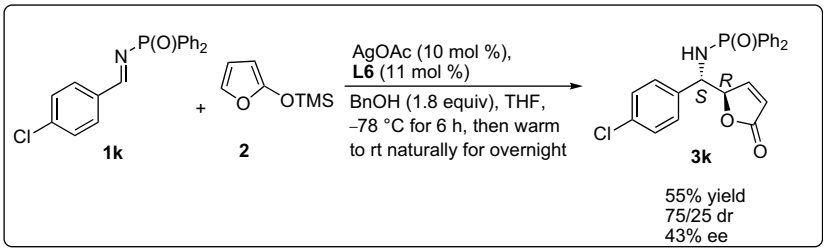
Figure 2. ORTEP drawing of **3e**.

Then we applied our newly developed catalytic system into the previously reported AVM reaction, which used the substrate bearing an *o*-anisidine *N*-aryl group.[4] The adduct **3j** was obtained in 58% yield and 63% ee, less effective than the catalytic system developed by Hoveyda et al. (Scheme 2).



Scheme 2. AVM reaction of the substrate that bears an *o*-anisidine *N*-aryl group.

Since *N*-diphenylphosphinoyl group could be easily removed under acidic conditions,[19] we next applied our catalytic system into the AVM reaction of the *N*-diphenylphosphinoylimine **1k** with siloxyfuran **2** under the optimized reaction conditions. It was found that this AVM reaction could also give the corresponding adduct **3k** in 55% yield with moderate enantio- and diastereoselectivity (43% ee and 75:25 dr, Scheme 3).



Scheme 3. AVM reaction of the *N*-diphenylphosphinoylimine **1k** and siloxyfuran **2**.

In summary, we have developed a new catalytic AVM reaction system applicable to aldimines, which do not possess 2-methyloxyphenyl group and siloxyfuran using a chiral phosphine-Schiff base ligand/AgOAc/BnOH combination.[18] The catalytic system reported here afforded AVM product **3** in up to 91% yield and 81% ee. The addition of phenylmethanol (BnOH) is important to achieve better yield and diastereoselectivity as well as enantioselectivity. Current efforts are in progress to extend this chiral phosphine-Schiff base ligand/AgOAc/BnOH combination to other catalytic enantioselective reactions in our laboratory.

3. Experimental section

3.1. General remarks

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in hertz. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN and 1,2-dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

3.2. General procedure of the preparation of chiral phosphine-Schiff base type ligands L1–L11

To a solution of (*R*)-(−)-2-(diphenylphosphino)-1,1′-binaphthyl-2′-amine[10,11] (227 mg, 0.5 mmol) in absolute ethanol (4.0 mL) was added salicylaldehydes (0.5 mmol) or benzaldehydes (0.5 mmol) at room temperature and the reaction mixture was stirred under reflux overnight. After cooling to room temperature, precipitates settled out, which were filtered to give the corresponding phosphine-salen type ligands and phosphine-Schiff base type ligands **L1**–**L11** as yellow solids.

*3.2.1. (R,E)-2-((2′-(Diphenylphosphino)-1,1′-binaphthyl-2-ylimino)methyl)-5-methoxyphenol (**L1**)*

A yellow solid; this is a known compound.[11] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.74 (s, 3H, CH_3), 6.21 (s, 1H, ArH), 6.34 (d, *J*=8.4 Hz, 1H, ArH), 6.89–7.28 (m, 12H, ArH), 7.38–7.51 (m, 4H, ArH), 7.91–7.95 (m, 4H, ArH), 8.05 (d, *J*=8.7 Hz, 1H, ArH), 8.21 (s, 1H, CH), 12.30 (s, 1H, OH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −17.39. $[\alpha]_D^{20}$ +136 (*c* 0.35, $CHCl_3$).

*3.2.2. (R,E)-2-((2′-(Diphenylphosphino)-1,1′-binaphthyl-2-ylimino)methyl)-4-methylphenol (**L2**)*

A yellow solid; this is a known compound.[11] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.23 (s, 3H, CH_3), 6.68 (d, *J*=8.4 Hz, 1H, ArH), 6.82–7.52 (m, 20H, ArH), 7.94–7.96 (m, 3H, ArH), 8.06 (d, *J*=9 Hz, 1H, Ar), 8.24 (s, 1H, CH), 11.55 (s, 1H, OH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −17.40. $[\alpha]_D^{20}$ +178 (*c* 0.25, $CHCl_3$).

*3.2.3. (R,E)-N-Benzylidene-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L3**)*

A yellow solid; this is a known compound.[11] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.67 (d, *J*=8.1 Hz, 1H, ArH), 6.93–7.56 (m, 21H, ArH), 7.74 (d, *J*=7.8 Hz, 1H, ArH), 7.80 (d, *J*=8.7 Hz, 1H, ArH), 7.87–7.90 (m, 3H, ArH), 8.16 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −17.70. $[\alpha]_D^{20}$ +191 (*c* 0.25, $CHCl_3$).

*3.2.4. (R,E)-N-(2,4-Dichlorobenzylidene)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L4**)*

A yellow solid; this is a known compound.[11] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.90–7.53 (m, 20H, ArH), 7.72–7.91 (m, 4H, ArH), 8.02 (d, *J*=8.7 Hz, 1H, ArH), 8.52 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.89. $[\alpha]_D^{20}$ +335 (*c* 0.25, $CHCl_3$).

*3.2.5. (R,E)-N-(2,6-Dichlorobenzylidene)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L5**)*

A yellow solid; this is a known compound.[11] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.92–7.06 (m, 2H, ArH), 7.09–7.21 (m, 10H, ArH), 7.22–7.48 (m, 9H, ArH), 7.75–7.92 (m, 3H, ArH), 8.03 (d, *J*=9.0 Hz, 1H, ArH), 8.22 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.66. $[\alpha]_D^{20}$ +291 (*c* 0.2, $CHCl_3$).

*3.2.6. (R,E)-N-(2,3-Dichlorobenzylidene)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L6**)*

A yellow solid; this is a known compound.[11] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.92–7.51 (m, 19H, ArH), 7.69–7.93 (m, 5H, ArH), 8.04 (d, *J*=8.7 Hz, 1H, ArH), 8.50 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.63. $[\alpha]_D^{20}$ +392 (*c* 0.2, $CHCl_3$).

*3.2.7. (R,E)-2′-(Diphenylphosphino)-N-(2-fluorobenzylidene)-1,1′-binaphthyl-2-amine (**L7**)*

A yellow solid, mp 75–78 °C. IR (CH_2Cl_2): ν 3052, 3007, 1612, 1581, 1502, 1485, 1458, 1433, 1300, 1279, 1265, 1238, 1216, 1149, 1096, 1026, 964 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.89–

7.48 (m, 22H, ArH), 7.82–7.92 (m, 3H, ArH), 8.02 (d, 1H, *J*=8.4 Hz, ArH), 8.48 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.65. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −121.94. MS (EI) *m*/*e* 559 [M^+] (20.9), 438 (39.5), 437 (100), 359 (2.9), 326 (3.8), 281 (11.5), 183 (3.1), 179 (3.2), 109 (2.0). HRMS (EI) calcd for $C_{39}H_{27}FNP$ (M+H^+): 559.1865, found: 559.1863. $[\alpha]_D^{20}$ +156.8 (*c* 0.75, CH_2Cl_2).

*3.2.8. (R,E)-N-(2-Bromobenzylidene)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L8**)*

A yellow solid, mp 76–78 °C. IR (CH_2Cl_2): ν 3052, 1610, 1585, 1561, 1502, 1479, 1433, 1265, 1195, 1024, 965 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.93–7.44 (m, 22H, ArH), 7.84–7.94 (m, 3H, ArH), 8.04 (d, 1H, *J*=8.4 Hz, ArH), 8.53 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.64. MS (EI) *m*/*e* 619 [M^+] (6.3), 621 (6.9), 540 (5.8), 438 (35.6), 437 (100), 357 (3.7), 281 (9.3), 183 (3.1), 77 (3.1). HRMS (EI) calcd for $C_{39}H_{27}BrNP$ (M+H^+): 619.1064, found: 619.1067. $[\alpha]_D^{20}$ +232.7 (*c* 0.85, CH_2Cl_2).

*3.2.9. (R,E)-2′-(Diphenylphosphino)-N-(2-(trifluoromethyl)-benzylidene)-1,1′-binaphthyl-2-amine (**L9**)*

A yellow solid, mp 85–88 °C. IR (CH_2Cl_2): ν 3053, 1617, 1586, 1575, 1502, 1480, 1433, 1313, 1277, 1169, 1124, 1059, 1034, 967 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 6.88–7.57 (m, 22H, ArH), 7.85–7.94 (m, 3H, ArH), 8.06 (d, 1H, *J*=8.4 Hz, ArH), 8.56 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.70. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −57.51. MS (EI) *m*/*e* 609 [M^+] (11.7), 438 (38.3), 437 (100), 357 (4.1), 281 (10.0), 250 (3.8), 218 (5.2), 179 (4.2), 77 (3.8). HRMS (EI) calcd for $C_{40}H_{27}F_3NP$ (M+H^+): 609.1833, found: 609.1830. $[\alpha]_D^{20}$ +160.9 (*c* 0.50, CH_2Cl_2).

*3.2.10. (R,E)-N-(2,4-Dimethoxybenzylidene)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L10**)*

A yellow solid, mp 79–82 °C. IR (CH_2Cl_2): ν 3459, 3381, 3052, 3001, 2964, 2938, 2837, 1677, 1601, 1586, 1504, 1463, 1434, 1421, 1306, 1290, 1273, 1209, 1159, 1117, 1031, 966 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.65 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 6.28–6.29 (m, 2H, ArH), 6.94–7.48 (m, 19H, ArH), 7.82–7.90 (m, 3H, ArH), 8.00 (d, 1H, *J*=8.4 Hz, ArH), 8.55 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.56. MS (EI) *m*/*e* 601 [M^+] (17.5), 570 (6.4), 438 (37.3), 437 (100), 416 (5.0), 357 (5.0), 301 (11.6), 281 (9.9), 183 (4.4). HRMS (EI) calcd For $C_{41}H_{32}NO_2P$ (M+H^+): 601.2171, found: 601.2177. $[\alpha]_D^{20}$ +172.5 (*c* 0.65, CH_2Cl_2).

*3.2.11. (R,E)-N-(2-(Benzyloxy)-3,5-di-tert-butylbenzylidene)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-amine (**L11**)*

A yellow solid (mixtures of *E*- and *Z*-isomers), mp 88–91 °C. IR (CH_2Cl_2): ν 3474, 3378, 3052, 2961, 2868, 1686, 1619, 1585, 1498, 1478, 1435, 1362, 1264, 1202, 1163, 1116, 1014, 964 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.03 (s, 9H, CH_3), 1.39 (s, 9H, CH_3), 4.52 (d, 1H, *J*=12.3 Hz, CH_2), 4.68 (d, 1H, *J*=12.3 Hz, CH_2), 6.75–7.41 (m, 20H, ArH), 7.82–7.90 (m, 4H, ArH), 8.43 (s, 1H, CH). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ −12.80, −12.25. MS (EI) *m*/*e* 759 [M^+] (10.5), 669 (54.2), 668 (100), 468 (9.2), 453 (11.7), 437 (62.6), 281 (7.9), 201 (9.5), 91 (47.5). HRMS (EI) calcd for $C_{54}H_{50}NOP$ (M+H^+): 759.3630, found: 759.3636. $[\alpha]_D^{20}$ +159.0 (*c* 0.25, CH_2Cl_2).

3.3. General procedure for the reaction of aldimine 1 with siloxyfuran 2 in the presence of AgOAc and chiral phosphine-Shiff base ligand L6

The procedure of AVM reaction was performed according to the method stated in Snapper and Hoveyda's report.[4] AgOAc (0.02 -mmol) and chiral phosphine-Shiff base ligand **L6** (0.022 mmol) were added into a Schlenk tube and then THF (0.5 mL) was added into the reaction vessel. The resulting solution was allowed to stir for 30 min at room temperature. A solution of aldimine **1** (0.20 mmol) in THF (0.5 mL) was added followed by phenylmethanol (0.36 mmol). Siloxyfuran **2** (0.36 mmol) was added when the mixture was cooled to −78 °C, and the reaction mixture was stirred at −78 °C for 6 h then the reaction solution was warmed to room temperature naturally and stirred overnight. The reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (2 mL). After stirring for 15 min at room temperature, the mixture was extracted by Et_2O, washed with brine, and the organic layer was dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2) to give the corresponding product **3**.

*3.3.1. (S)-5-((R)-Phenyl(phenylamino)methyl)furan-2(5H)-one (**3a**)*

A pale yellow solid; this is a known compound.[18] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.38 (1H, d, *J*=6.4 Hz, NH), 4.84 (1H, dd, *J*=4.4, 6.4 Hz, CH), 5.41 (1H, ddd, *J*=1.2, 2.0, 4.4 Hz, CH), 6.04 (1H, dd, *J*=2.0, 6.0 Hz, CH), 6.54 (2H, d, *J*=7.6 Hz, ArH), 6.70 (1H, t, *J*=8.0 Hz, ArH), 7.10 (2H, dd, *J*=7.6, 8.0 Hz, ArH), 7.24–7.31 (5H, m, ArH), 7.34 (1H, dd, *J*=1.2, 6.0 Hz, CH). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=80:20, 1.0 mL/min, 254 nm, t_{major}=19.52 min, t_{minor}=27.20 min; $[\alpha]_D^{20}$ −108.2 (*c* 0.65, CH_2Cl_2), 79% ee).

*3.3.2. (S)-5-((R)-(4-Nitrophenylamino)(phenyl)methyl)furan-2(5H)-one **3b***

A yellow solid, mp 152–155 °C. IR (CH_2Cl_2): ν 3361, 3301, 3071, 3019, 2970, 2925, 2346, 1742, 1599, 1528, 1502, 1477, 1365, 1322, 1303, 1229, 1217, 1197, 1159, 1111, 1025, 899 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.99 (dd, 1H, *J*=7.2, 3.6 Hz, CH), 5.21 (d, 1H, *J*=4.2 Hz, NH), 5.51 (dd, *J*=3.6, 1.8 Hz, CH), 6.10 (dd, *J*=5.7, 2.1 Hz, CH), 6.53 (d, 2H, *J*=9.3 Hz, ArH), 7.29–7.41 (m, 6H, ArH+CH), 8.02 (d, 2H, *J*=9.0 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 58.9, 84.3, 113.9, 119.2, 123.4, 124.0, 128.8, 129.2, 144.3, 145.3, 147.7, 152.9, 171.7. MS (EI) *m*/*e* 310 [M^+] (6.9), 228 (15.6), 227 (100), 181 (36.9), 180 (9.1), 173 (12.7), 117 (15.5), 103 (10.5), 76 (11.0). HRMS (EI) calcd for $C_{17}H_{14}N_2O_4$ (M+H^+): 310.0954, found: 310.0956. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=80:20, 0.7 mL/min, 230 nm, t_{minor}=17.33 min, t_{major}=20.33 min; $[\alpha]_D^{20}$ −29.5 (*c* 0.50, CH_2Cl_2), 38% ee).

*3.3.3. (S)-5-((R)-(4-Methoxyphenylamino)(phenyl)methyl)-furan-2(5H)-one **3c***

A white solid; this is a known compound.[3] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.68 (3H, s, CH_3), 4.12 (1H, br, NH), 4.77 (1H, d, *J*=3.0 Hz, CH), 5.41 (1H, d, *J*=1.8 Hz, CH), 6.04 (1H, dd, *J*=1.2, 5.7 Hz, CH), 6.51 (2H, d, *J*=9.0 Hz, ArH), 6.69 (2H, d, *J*=9.0 Hz, ArH), 7.25–7.30 (5H, m, ArH), 7.35 (1H, d, *J*=5.7 Hz, CH). Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (hexane/*i*PrOH=90:10, 0.7 mL/min, 214 nm, t_{major}=126.58 min, t_{minor}=151.22 min; $[\alpha]_D^{20}$ −55.6 (*c* 0.65, CH_2Cl_2), 62% ee).

*3.3.4. (S)-5-((R)-Phenyl(3-(trifluoromethyl)phenylamino)-methyl)furan-2(5H)-one (**3d**)*

A yellow solid, mp 127–132 °C. IR (CH_2Cl_2): ν 3726, 3368, 3016, 2970, 2925, 2840, 2346, 1740, 1600, 1518, 1438, 1365, 1350, 1229, 1217, 1160, 1105, 900 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.66 (d, 1H, *J*=6.9 Hz, NH), 4.89 (dd, 1H, *J*=7.5, 4.2 Hz, CH), 5.45 (t, 1H, *J*=3.6 Hz, CH), 6.07 (dd, 1H, *J*=6.0, 1.5 Hz, CH), 6.67 (dd, 1H, *J*=6.0, 1.8 Hz, ArH), 6.79 (s, 1H, ArH), 6.92 (d, 1H, *J*=7.8 Hz, CH), 7.18 (t, 1H, *J*=7.5 Hz, ArH), 7.28–7.38 (m, 6H, ArH+CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 59.0, 84.8, 110.3 (q, *J*=3.9 Hz), 114.9 (q, *J*=4.1 Hz), 116.6, 123.5, 124.0 (q, *J*=256 Hz), 127.0, 128.6, 129.0, 129.5, 129.7, 131.3 (q, *J*=32.1 Hz), 135.9, 146.2, 152.6, 172.0. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −68.49. MS (EI) *m*/*e* 333 [M^+] (0.7), 251 (16.3), 250 (100), 173 (2.7), 172 (22.2), 145 (30.6), 127 (1.6), 125 (2.1), 77 (5.9). HRMS

(EI) calcd for $C_{18}H_{14}F_3NO_2$ (M+H$^+$): 333.0977, found: 333.0981. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexane/*i*PrOH=90:10, 0.7 mL/min, 230 nm, t_{minor}=8.63 min, t_{major}=13.28 min; $[\alpha]_D^{20}$ −80.8 (*c* 2.10, CH_2Cl_2), 65% ee).

3.3.5. (S)-5-((R)-(4-Bromophenyl)(4-bromophenylamino)-methyl)furan-2(5H)-one (**3e**)

A pale yellow solid, mp 147–152 °C. IR (CH_2Cl_2): *ν* 3371, 3032, 2970, 2925, 2372, 2351, 1744, 1594, 1489, 1366, 1229, 1217, 1160, 1092, 1073, 1010, 901 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 4.44 (1H, d, *J*=6.9 Hz, NH), 4.78 (1H, dd, *J*=0.9, 6.9 Hz, CH), 5.43 (1H, ddd, *J*=0.9, 1.2, 1.8 Hz, CH), 6.09 (1H, dd, *J*=1.8, 6.0 Hz, CH), 6.40 (2H, d, *J*=9.0 Hz, ArH), 7.15–7.21 (4H, m, ArH), 7.34 (1H, dd, *J*=1.2, 6.0 Hz, CH), 7.46 (2H, d, *J*=8.4 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 58.8, 84.5, 110.6, 115.5, 122.4, 123.6, 128.8, 131.9, 132.0, 135.1, 144.6, 152.4, 171.8. MS (EI) *m*/*e* 421 [M$^+$] (2.6), 343 (7.0), 342 (47.2), 340 (100), 338 (50.8), 184 (15.8), 115 (10.8), 89 (10.2), 76 (17.0). HRMS (EI) calcd for $C_{17}H_{13}Br_2NO_2$ (M+H$^+$): 420.9313, found: 420.9308. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=80:20, 1.0 mL/min, 254 nm, t_{minor}=21.62 min, t_{major}=32.03 min; $[\alpha]_D^{20}$ −111.2 (*c* 2.15, CH_2Cl_2), 62% ee).

3.3.6. (S)-5-((R)-(4-Bromophenylamino)(2-(trifluoro-methyl)phenyl)methyl)furan-2(5H)-one (**3f**)

A pale yellow oil. IR (CH_2Cl_2): *ν* 3376, 3098, 2954, 2925, 2854, 1764, 1697, 1594, 1491, 1453, 1401, 1310, 1276, 1251, 1164, 1118, 1074, 1036, 901 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 4.45 (d, 1H, *J*=6.6 Hz, NH), 5.32 (dd, 1H, *J*=7.8, 2.1 Hz, CH), 5.49 (d, 1H, *J*=2.1 Hz, CH), 6.09 (d, 1H, *J*=3.9 Hz, CH), 6.48 (d, 2H, *J*=8.1 Hz, ArH), 7.20 (d, 2H, *J*=8.1 Hz, ArH), 7.38–7.45 (m, 2H, ArH), 7.51–7.62 (m, 2H, ArH), 7.71 (d, 1H, *J*=6.9 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 54.6, 84.0, 110.9, 115.7, 123.7, 124.3 (q, *J*=270 Hz), 126.6 (q, *J*=5.3 Hz), 127.9, 128.2 (q, *J*=30 Hz), 128.7, 132.7, 135.4, 144.3, 152.3, 171.7. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): *δ* −62.80. MS (EI) *m*/*e* 411 [M$^+$] (4.7), 331 (15.3), 330 (89.3), 328 (100), 310 (56.8), 308 (58.8), 229 (39.6), 134 (16.9), 76 (24.9). HRMS (EI) calcd for $C_{18}H_{13}BrF_3NO_2$ (M+H$^+$): 411.0082, found: 411.0084. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=90:10, 0.7 mL/min, 230 nm, t_{minor}=21.33 min, t_{major}=30.93 min; $[\alpha]_D^{20}$ −65.5 (*c* 0.70, CH_2Cl_2), 55% ee).

3.3.7. (S)-5-((R)-(4-Bromophenylamino)(2,4-dimethoxy-phenyl)methyl)furan-2(5H)-one (**3g**)

A pale yellow oil. IR (CH_2Cl_2): *ν* 3727, 3375, 3025, 2970, 2840, 2346, 1744, 1605, 1591, 1502, 1455, 1365, 1293, 1263, 1229, 1216, 1207, 1158, 1090, 1034, 898 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 3.75 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.56 (d, 1H, *J*=8.4 Hz, NH), 4.89 (t, 0.6H, *J*=1.5 Hz, CH, NH), 5.16 (dd, 1H, *J*=8.1, 4.2 Hz, CH), 5.48 (t, 1H, *J*=1.8 Hz, CH), 5.99 (dd, 1H, *J*=5.4, 1.8 Hz, CH), 6.16 (dd, 0.3H, *J*=7.8, 1.8 Hz, CH), 6.37–6.44 (m, 4H, ArH), 7.07 (d, 1H, *J*=8.4 Hz, ArH), 7.13 (d, 2H, *J*=8.7 Hz, ArH), 7.40 (dd, 1H, *J*=5.7, 1.2 Hz, CH), 7.55 (dd, 0.3H, *J*=5.7, 1.2 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 52.7, 55.2, 55.4, 84.4, 98.4, 104.5, 109.7, 115.2, 115.7, 121.5, 122.6, 128.5, 131.8, 145.2, 153.3, 157.6, 160.6, 172.5. MS (EI) *m*/*e* 403 [M$^+$] (0.7), 323 (18.0), 322 (99.2), 321 (20.4), 320 (100), 233 (12.1), 149 (14.8), 121 (12.9), 77 (6.1). HRMS (EI) calcd for $C_{19}H_{18}BrNO_4$ (M+H$^+$): 403.0419, found: 403.0424. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=90:10, 0.7 mL/min, 230 nm, t_{minor}=44.13 min, t_{major}=67.98 min; $[\alpha]_D^{20}$ −100.1 (*c* 2.65, CH_2Cl_2), 80% ee).

3.3.8. (S)-5-((R)-(2,4-Dichlorophenyl)(phenylamino)methyl)-furan-2(5H)-one (**3h**)

A pale yellow oil. IR (CH_2Cl_2): *ν* 3377, 3089, 3054, 2924, 2847, 2320, 1753, 1602, 1561, 1504, 1470, 1453, 1384, 1316, 1229, 1217, 1158, 1103, 1043, 993 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 4.65 (d, 1H, *J*=8.1 Hz, NH), 5.40 (dd, 1H, *J*=5.4, 3.3 Hz, CH), 5.55 (t, 1H, *J*=1.5 Hz, CH), 6.03 (dd, 1H, *J*=6.0, 2.1 Hz, CH), 6.50 (d, 2H, *J*=7.5 Hz, ArH), 6.72 (t, 1H, *J*=7.2 Hz, Ar), 7.09–7.19 (m, 3H, ArH), 7.32 (d, 1H, *J*=8.4 Hz, ArH), 7.37 (d, 1H, *J*=2.1 Hz, Ar), 7.52 (dd, 1H, *J*=5.7, 1.2 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 54.8, 83.9, 113.5, 118.9, 123.5, 127.9, 129.3, 129.4, 129.6, 132.2, 133.9, 134.7, 145.1, 151.9, 171.8. MS (EI) *m*/*e* 333 [M$^+$] (2.0), 254 (11.1), 252 (63.2), 250 (100), 214 (10.9), 152 (5.5), 104 (24.2), 93 (3.6), 77 (38.5). HRMS (EI) calcd for $C_{17}H_{13}Cl_2NO_2$ (M+H$^+$): 333.0323, found: 333.0318. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=80:20, 1.0 mL/min, 254 nm, t_{minor}=16.36 min, t_{major}=24.32 min; $[\alpha]_D^{20}$ −103.5 (*c* 1.05, CH_2Cl_2), 81% ee).

3.3.9. (S)-5-((R)-(4-Nitrophenyl)(phenylamino)methyl)-furan-2(5H)-one (**3i**)

A yellow oil. IR (CH_2Cl_2): *ν* 3378, 3107, 3053, 2923, 2847, 1929, 1759, 1602, 1519, 1437, 1347, 1319, 1278, 1254, 1160, 1104, 1045, 993 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 4.56 (1H, d, *J*=7.2 Hz, NH), 4.95 (1H, dd, *J*=3.6, 7.2 Hz, CH), 5.48 (1H, ddd, *J*=1.6, 2.0, 3.6 Hz, CH), 6.09 (1H, dd, *J*=2.0, 5.6 Hz, CH), 6.52 (2H, d, *J*=8.8 Hz, ArH), 6.74 (1H, t, 7.6 Hz, ArH), 7.12 (2H, dd, *J*=7.6, 8.8 Hz, ArH), 7.41 (1H, dd, *J*=1.6, 5.6 Hz, CH), 7.51 (2H, d, *J*=8.4 Hz, ArH), 8.17 (2H, d, *J*=8.4 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 58.9, 84.3, 113.7, 119.0, 123.5, 123.9, 128.4, 129.3, 144.3, 145.1, 147.7, 152.5, 171.6. MS (EI) *m*/*e* 310 [M$^+$] (7.0), 228 (15.5), 227 (100), 181 (42.3), 180 (17.5), 168 (7.7), 115 (7.3), 93 (12.7), 77 (24.3). HRMS (ESI) calcd for $C_{17}H_{14}N_2O_4$ (M+H$^+$): 310.0954, found: 310.0952. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexane/*i*PrOH=80:20, 1.0 mL/min, 230 nm, t_{minor}=18.38 min, t_{major}=24.23 min; $[\alpha]_D^{20}$ −92.7 (*c* 2.00, CH_2Cl_2), 59% ee).

3.3.10. (S)-5-((R)-(2-Methoxyphenylamino)phenylmethyl)-furan-2(5H)-one (**3j**)

A pale yellow solid, mp 143–146 °C. IR (CH_2Cl_2): *ν* 3416, 3063, 2938, 2835, 1762, 1600, 1512, 1455, 1430, 1340, 1245, 1222, 1157, 1132, 1105, 1026, 896 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 3.87 (s, 3H, CH_3), 4.85 (d, 1H, *J*=3.6 Hz, NH), 4.93 (d, 1H, *J*=5.1 Hz, CH), 5.45 (t, 1H, *J*=2.1 Hz, CH), 6.11 (dd, 1H, *J*=5.1, 1.5 Hz, CH), 6.37 (dd, 1H, *J*=5.1, 1.5 Hz, CH), 6.63–6.78 (m, 3H, ArH), 7.26–7.34 (m, 5H, ArH), 7.39 (dd, 1H, *J*=5.1, 1.5 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): *δ* 55.5, 59.2, 85.4, 109.5, 111.3, 117.7, 120.9, 123.2, 127.1, 128.2, 128.8, 135.9, 137.1, 147.0, 153.0, 172.3. MS (EI) *m*/*e* 295 [M$^+$] (2.6), 213 (17.0), 212 (100), 196 (17.5), 134 (1.1), 120 (33.6), 115 (7.3), 91 (17.5), 77 (9.7). HRMS (ESI) calcd for $C_{17}H_{14}N_2O_4$ (M+H$^+$): 295.1208, found: 295.1207. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=80:20, 1.0 mL/min, 254 nm, t_{major}=26.62 min, t_{minor}=47.77 min; $[\alpha]_D^{20}$ −85.8 (*c* 0.75, CH_2Cl_2), 63% ee).

3.3.11. (R)-5-((S)-{4-Chlorophenyl-(diphenylphosphinoylamino)}-methyl)-(5H)-furan-2-one (**3k**)

A white solid; this is a known compound.[20] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *δ* 4.31 (dd, 1H, *J*=9.6, 6.6 Hz, NH), 4.54 (ddd, 1H, *J*=3.6, 3.6, 10.8 Hz, CH), 5.56 (s, 1H, CH), 5.90 (d, 1H, *J*=5.7 Hz, CH), 7.05 (d, 2H, *J*=8.4 Hz, ArH), 7.21 (d, 2H, *J*=8.4 Hz, ArH), 7.36–7.54 (m, 7H, ArH and CH), 7.69 (dd, 2H, *J*=12.0, 7.8 Hz, ArH), 7.82 (dd, 2H, *J*=12.0, 7.8 Hz, ArH). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/*i*PrOH=90:10, 0.7 mL/min, 214 nm, t_{major}=24.15 min, t_{minor}=32.21 min; $[\alpha]_D^{20}$ +13.5 (*c* 2.00, $CHCl_3$), 43% ee).

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Supplementary data

Spectroscopic data of the compounds shown in Tables 1–4 and the detailed descriptions of experimental procedures. This material is available free of charge via the Internet at the Website. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.05.080.

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