Tetrahedron 69 (2013) 8777–8784

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New silver(I)–monophosphine complex derived from chiral Ar-BINMOL: synthesis and catalytic activity in asymmetric vinylogous Mannich reaction

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ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form 13 July 2013
Accepted 22 July 2013
Available online 11 August 2013

Keywords:
Silver
Ar-BINMOL
Phosphine
Vinylogous Mannich reaction
Asymmetric catalysis

ABSTRACT

A new family of C_2-axially chiral monophosphines (Ar-NNPs) from Ar-BINMOLs was developed for silver-catalyzed asymmetric vinylogous Mannich reaction of (furan-2-yloxy)trimethylsilane with aromatic aldimines. It was found that the enantioselective vinylogous Mannich-type reactions of trimethylsiloxyfuran with aldimines are catalyzed efficiently by silver(I) complexes of the Ar-BINMOL-derived chiral monophosphine. This procedure displays wide aldimine versatility, excellent yields (up to 99% isolated yields), moderate to good enantioselectivity (up to 78%ee) and exceptional diastereoselectivity (>99:1 dr) in most cases examined. The molecular structure of silver–monophosphine complex was confirmed by X-ray analysis and revealed that the benzyl group on chiral monophosphine provided dual function with weak silver–π/π–π stacking and steric repulsion to favour the diastereoselective *Re*-nucleophilic addition of siloxyfuran to imine.

1. Introduction

During the past decade, intense research efforts have been devoted to develop effective catalyst systems using new ligands and related silver complex.[1] Especially, the chiral silver complexes have been recognized as attractive and privileged catalysts in many organic reactions to prepare important optically active molecules.[2] Whilst many elegant methods have been established for the preparation of the silver–phosphine complex, its successful implementation in asymmetric catalysis is rather limited in comparison to that of other transition metals, such as palladium, rhodium, etc. New silver–phosphine complex with specific catalytic behaviours and good enantioselective induction could be constructed and controlled by chiral phosphine. However, synthesizing such chiral phosphine with good catalytic activity is still a great challenge. In this context, we became interested in the synthesis of chiral phosphine ligands and its potential application as a key element in the preparation of functional γ-butenolides through silver-catalyzed vinylogous Mannich-type reaction.

Functional and optically pure five-membered γ-butenolides are valuable intermediates in organic synthesis and also are the structural motifs frequently found in many natural products.[3] Among the known synthetic methods to highly functionalized γ-butenolides bearing amino groups, the Lewis acid-catalyzed vinylogous Mannich-type reaction of trimethylsiloxyfuran is considered to be one of the most efficient synthetic approaches.[4] However, the synthesis of optically pure γ-butenolides through asymmetric vinylogous Mannich-type reaction has limited exploration.[3–5] The first asymmetric vinylogous Mannich-type reaction of trimethylsiloxyfuran catalyzed by titanium complex was reported by Martin and Lopez in 1999, in which both the enantioselectivities and yields were only moderate (up to 54%ee).[6] The development of effective chiral catalyst system for the enantioselective synthesis of γ-butenolide derivatives has been realized as an important topic since then.[7–10] Among these catalyst systems, silver–phosphine complexes containing Schiff base or oxazoline moiety were proved to be powerful chiral catalysts in the asymmetric vinylogous Mannich-type reaction of trimethylsiloxyfuran. For example, in 2006, Hoveyda and coworkers reported a highly efficient and practical method for catalytic asymmetric vinylogous Mannich reactions of trimethylsiloxyfuran and 2-aminophenol-derived imines.[8] With the similar type of amino acid-derived chiral phosphine containing Schiff base motif, Hoveyda

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http://dx.doi.org/10.1016/j.tet.2013.07.105

and co-workers have also found that various imines could be suitable substrates in the silver-catalyzed vinylogous Mannich reactions.[9] Recently, Shi and co-workers reported an asymmetric synthesis of γ-butenolide derivatives through silver-catalyzed vinylogous Mannich reactions of versatile imines in the presence of axial chiral phopshine–oxazoline ligands.[10]

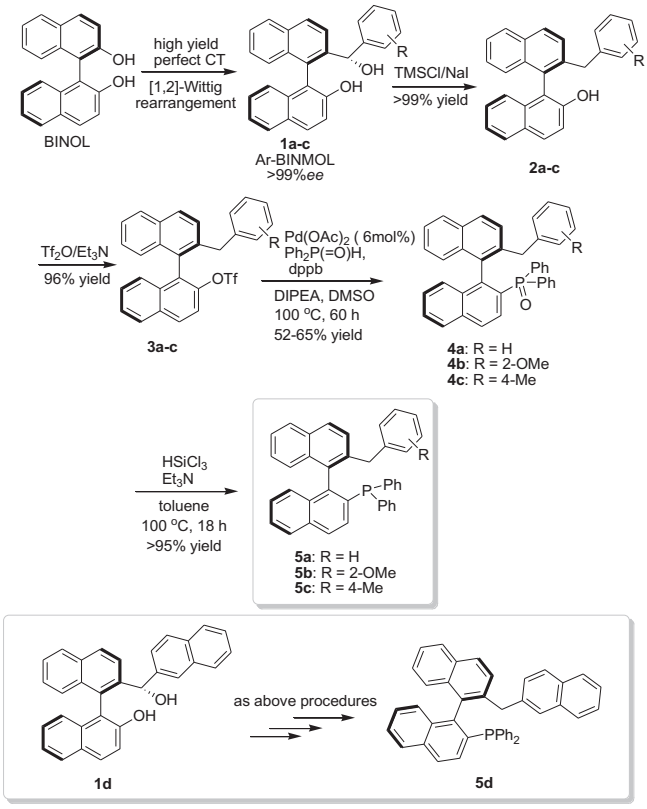
The work of Hoveyda,[8,9] Shi[10] and Zanardi[7h] was significant because it showed that the chiral phosphine ligands having an additional nitrogen group are essential to give the vinylogous Mannich adducts in good enantioselectivity. This led us to explore the effectiveness of BINOL (1,1′-binaphthalene-2,2′-diol)-derived or BINAP (2,2′-bis(diphenylphophino)-1,1′-binaphthyl)-like monophosphines in asymmetric vinylogous Mannich reaction. To the best of our knowledge, the enantioselective activity of simple monophosphines lack of additional heteroatom on this ligand has not been explored. In addition, although enormous research efforts have been interested in the synthesis of chiral ligands,[11] the development of new chiral phosphine ligands with good enantioselectivity remains a vital challenge in catalytic asymmetric reactions. Herein, we report the facile synthesis of novel axially chiral monophosphine ligands for asymmetric vinylogous Mannich reactions. This work reveals that the silver-catalyzed asymmetric vinylogous Mannich reaction of trimethylsiloxyfuran with aldimines can proceed smoothly to give the corresponding γ-butenolide derivatives in moderate to good enantioselectivity in the presence of the simple chiral monophosphine under mild conditions.

2. Results and discussion

We initiated our studies by synthesizing a novel axially monophosphine from our Ar-BINMOL (1,1′-binaphthalene-2-α-arylmethanol-2′-ol) ligand that is prepared from C_2 axial 1,1′-binaphthalene-2,2′-diol (BINOL) through [1,2]-Wittig rearrangement reaction.[12] We have identified that the [1,2]-Wittig rearrangement was a practical procedure for the construction of novel diol ligands with both axial and sp^3 central chirality that could act as efficient chiral ligands in various transformations.[13] Because of the established importance and interesting effect of the rotatable benzyl group on this type of chiral compounds in asymmetric catalysis,[14] it has become necessary to consider the preparation of Ar-BINMOL-derived chiral monophosphine.

As shown in Scheme 1, the axially chiral monophosphine ligands **5** were prepared in four steps easily from the available starting Ar-BINMOLs.[12,13e,14] The deoxygenation of secondary alcohol was carried out successfully in the presence of large amount of TMSCl (6 equiv) and NaI (6 equiv), which led to the intermediate **2** in excellent yields. Treatment of **2** with trifluoromethanesulfonic anhydride (Tf_2O) and triethylamine afforded, in almost quantitative yield, the corresponding products **3a**–**c** that was then submitted to palladium-catalyzed cross coupling of **3** and diphenylphosphite under the reported conditions.[15]

The desired chiral phosphites **4a**–**d** then underwent reduction on treatment with $HSiCl_3$ (5 equiv) and triethylamine (6 equiv) in toluene at 100 °C for 18 h to furnish Ar-BINMOL-derived chiral monophosphines **5a**–**d** (Ar-NNPs) in excellent yields (>95%). Notably, these monophosphines **5a**–**d** exhibit good air stability. The stereochemical identify of Ar-NNPs **5** was verified by an X-ray crystal structure determination of monophosphine **5a**. As shown in Fig. 1, although there is no any functional heteroatom-based group excluding the phosphine centre, this chiral phosphine is suggested to be BINAP-like monophosphine. This structure or conformation of Ph-NNP **5a** {Ph-NNP: (*R*)-(1-(2-benzylnaphthalen-1-yl)naphthalen-2-yl)diphenylphosphine} is interesting since the aromatic ring of rotatable benzyl group can provide possible aromatic interactions between catalyst system and substrate to enhance the enantioselective induction.



Scheme 1. The synthesis of novel Ar-BINMOL-derived monophosphines (Ar-NNPs).

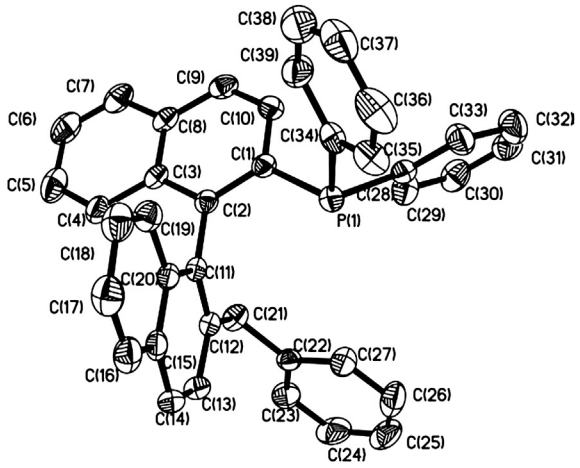
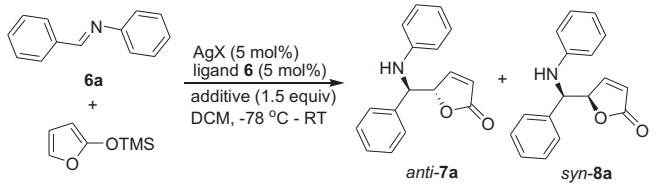


Fig. 1. Crystal structure of chiral monophosphine ligand **5a** (Ph-NNP), hydrogen atoms have been omitted for clarity (CCDC 918256).

Subsequently, we began to evaluate the activity of enantioselective induction of the novel chiral ligands **5** in silver-catalyzed vinylogous Mannich-type reaction of trimethylsiloxyfuran with aldimines. As the data summarized in Table 1 illustrated, among these simple chiral monophosphines **5a**–**d** of Scheme 1, ligand **5a** (Ph-NNP) exhibited the best catalytic performance in term of enantioselectivity (76%ee) and isolated yield (entries 1–4). Comparably, the use of classic and famous bisphosphine, (*R*)-BINAP [(*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl], resulted in the formation of **7a** in only 64%ee and 90% yield (entry 5), which showed the novel chiral monophosphine **5a** gave better enantioselective induction in this reaction than that of (*R*)-BINAP (ee: 76%

vs 64%, and yield: 99% vs 90%, respectively). Similarly to previous studies,[7,8,16] it was revealed that *i*-PrOH played important role in the asymmetric transformations of siloxyfurans (entries 1 and 6). Then the positive effect of *i*-PrOH promoted us to investigate other alcohols as additives in this reaction. Furthermore, the effect of second metal catalyst and other silver salts on the enantioselectivity of chiral monophosphine ligand **5a** was also studied. Table 1 illustrates representative results of the additives and various metal catalysts (entries 6–19). Unfortunately, the improvement of enantioselectivity in this reaction was unsuccessful under these conditions. Initially, the use of $AgClO_4$, Ag_2O and AgOTf instead of AgOAc led to the formation of desired product **7a** in low to moderate yields (46–89% yield) and poorer enantioselectivities and diastereoselectivities (entries 7–9, for AgOTf, 58:42 dr, no enantioselectivity).

Table 1
Effect of chiral ligands and additive for the asymmetric vinylogous Mannich-type reaction of trimethylsiloxyfuran with aldimine **6a**[a]



Entry	AgX	Ligand	Additive	Yield[b] (%)	dr[c] **7a**/**8a**	ee[d]/%
1	AgOAc	**5a**	*i*-PrOH	99	>99:1	76
2	AgOAc	**5b**	*i*-PrOH	97	>99:1	65
3	AgOAc	**5c**	*i*-PrOH	92	>99:1	66
4	AgOAc	**5d**	*i*-PrOH	95	>99:1	74
5	AgOAc	BINAP	*i*-PrOH	90	99:1	64
6[e]	AgOAc	**5a**	—	77	>99:1	44
7[e]	$AgClO_4$	**5a**	—	89	66:34	0
8	Ag_2O	**5a**	*i*-PrOH	46	99:1	55
9	AgOTf	**5a**	*i*-PrOH	88	58:42	0
10	AgOAc	**5a**	HMDS	91	>99:1	74
11	AgOAc	**5a**	EtOH	89	99:1	74
12	AgOAc	**5a**	MeOH	92	98:2	68
13	AgOAc	**5a**	BnOH	93	99:1	73
14	AgOAc	**5a**	$PhNH_2$	95	>99:1	71
15[f]	AgOAc	**5a**	*i*-Pr_2NH	46	61:39	65
16	AgOAc	**5a**	BSA[g]	28	65:35	0
17	AgOAc	**5a**	$Cu(OAc)_2$	97	99:1	75
18	AgOAc	**5a**	$Cu(OTf)_2$	95	77:23	0
19	AgOAc	**5a**	H_2O	94	99:1	74
20	AgOAc	**5a**	TBAF[h]	Trace	—	—

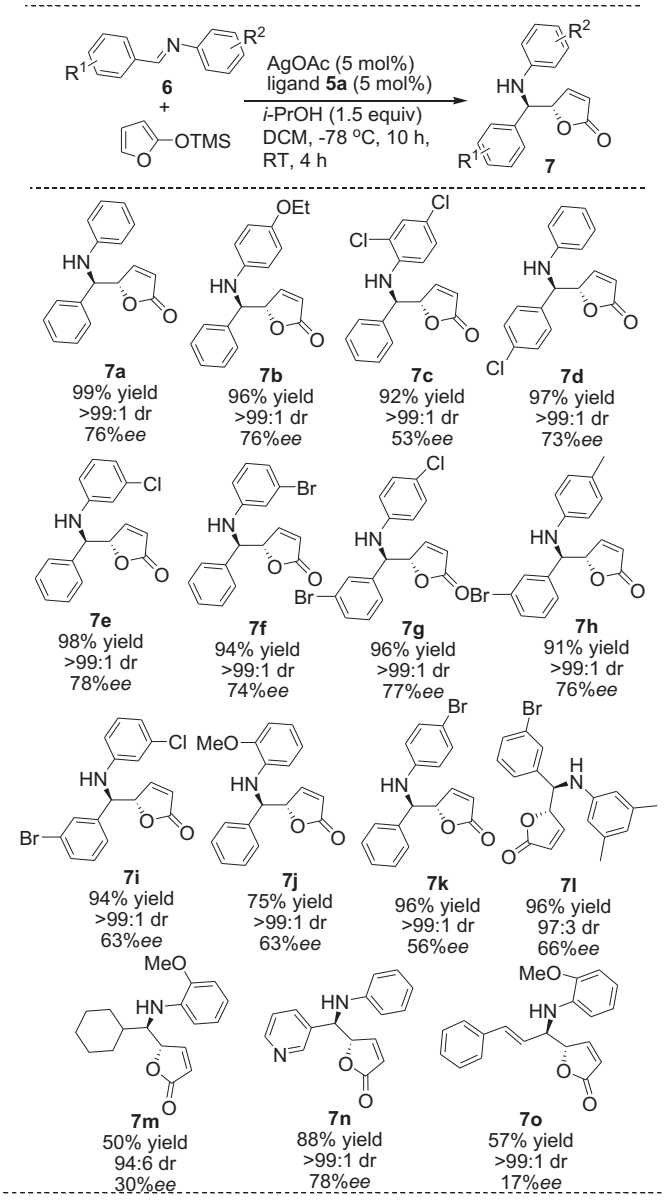
[a] Reaction conditions: **6a** (0.25 mmol), trimethylsiloxyfuran (1.5 equiv), additive (1.5 equiv), AgX (5 mol %), ligand (5 mol %), DCM (1.8 mL), and the reaction was carried out at −78 °C to rt for 18 h.
[b] Isolated yield after chromatography.
[c] Determined by ^1H NMR and confirmed by chiral HPLC and GC/MS.
[d] The enantiomeric excess of **7a** was determined by chiral HPLC analysis.
[e] No addition of any additives.
[f] Both the enantiomeric excess of **7a** and **8a** are 65%ee.
[g] BSA is trimethylsilyl *N*-trimethylsilylacetimidate.
[h] TBAF is tetrabutylammonium fluoride.

Except *i*-PrOH, the use of various primary alcohols as additive, such as MeOH, EtOH, BnOH, also led to excellent isolated yield and promising enantioselectivity (entries 11–13, 68–75%ee). Interestingly, HMDS (hexamethyldisilazane) was also a good additive that gave the desired product **7a** in 91% yield and 74%ee. Thus the role of different amines or organosilicon compound (BSA) was then investigated in this reaction. Similarly, aniline gave the same level of enantioselectivity and diastereoselectivity as well as isolated yield (entry 14, 75%ee). However, the secondary amine, diisopropylamine, inhibited this reaction as both the yield and diastereoselectivity were low (entry 15, 46% yield, 61:39 dr). Different from HMDS, trimethylsilyl *N*-trimethylsilylacetimidate (BSA) disturbed the enantioselective induction of chiral phosphine ligand **5a** in this reaction, in which almost no enantioselectivity and low yield of **7a** was detected (entry 16). It should be also noted that the introduction of $Cu(OAc)_2$ as a co-catalyst, resulted in excellent enantioselectivity (75%ee) for the adduct **7a**, while the enantioselectivity and diastereoselectivity is low when $Cu(OTf)_2$ was used in this reaction (entries 17 and 18). Luckily, the addition of water in this silver–phosphine catalyst system also led to good yield and enantioselectivity (entry 19). However, the use of classic desilylation reagent, TBAF (tetrabutylammonium fluoride), led to almost no reaction (entry 20). These results showed that the effect of a hydrogen donor as an additive in the catalytic asymmetric Mannich reaction is pronounced in both the conversion and enantioselectivity.[16]

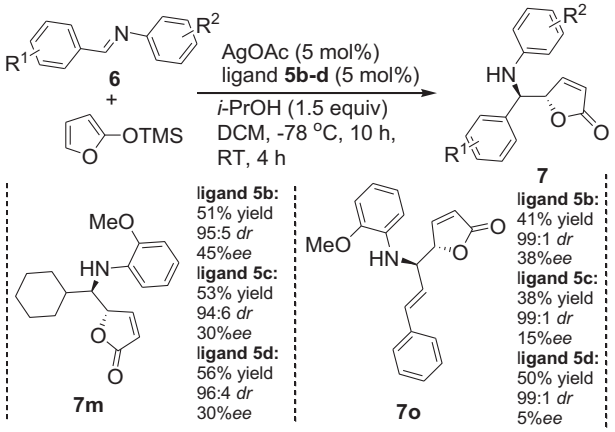
In light of above findings, we next examined the generality of this vinylogous Mannich-type reaction with various simple aldimines and trimethylsiloxyfuran under the optimized conditions. As shown in Scheme 2, various aldimines can be used in this reaction in the presence of the Ar-BINMOL-derived monophosphine ligand **5a**. Whereas the vinylogous Mannich-type reaction of aldimines with 2-methoxyphenyl group results in moderate yield of **7j**, most of reactions proceed to >90% isolated yields and afford a single diastereomer (>99:1) as well as moderate to good enantioselectivities (**7a**–**l**). Then, to enlarge the scope of this silver–**5a** complex-catalyzed vinylogous Mannich-type reaction, we investigated the reactivity of alkyl aldehyde and 2-methoxybenzenamine -derived aldimine **6m** (*N*-(cyclohexylmethylene)-2-methoxybenzenamine) and cinnamaldehyde-derived aldimine **6o** *N*-(3-phenylallylidene)benzenamine in this reaction. Unfortunately, these types of substrate are not suitable for the present silver–monophosphine-catalyzed vinylogous Mannich-type reaction of trimethylsiloxyfuran with **6m** and **6o** (17–30%ee). Even other Ar-NNPs (monophosphines **5b**–**d**) gave better enantioselectivities (Scheme 3, **7m** and **7o**) in comparison to that of Ph-NNP **5a**, we observed that the use of these monophosphines as the chiral ligands in silver-catalyzed vinylogous Mannich reaction of alkyl imine was not satisfied because of moderate yields (38–56%) and low to moderate enantioselectivities (5–45%ee). As an explain for the pronounced difference in these substrates, the possible non-covalent interactions, including hydrogen bonding and aromatic π–π stacking, between catalyst and substrate would play important role in the enantioselective vinylogous Mannich reaction. Fortunately, the conversion of heterocyclic aldimine, such as **6n** (*N*-(pyridin-3-ylmethylene)benzenamine), was excellent to give the corresponding product **7n** in 88% isolated yield and 78%ee as well as excellent diastereoselectivity (>99:1 dr). Although the enantioselective induction of chiral monophosphines (Ar-NNPs) is not perfect, these reaction results described here indicate that the simple and axially chiral monophosphine without other heteroatom-based groups for additional binding site is also a promising type of chiral ligand to give enantioselective induction in this reaction.

To illustrate the mechanistic rationale for the Ag-catalyzed vinylogous Mannich-type reaction, electrospray ionization mass spectrometry (ESI-MS) was carried out for determination of possible silver(I)–phosphine complex (Fig. S1–4, see Supplementary data). ESI(+)-MS was able to intercept the key silver complex, Ag with one or two phosphine ligand **5a** of *m*/*z* 635.15 $[Ag+Ph\text{-}NNP]^+$ and *m*/*z* 1164.78 or 1164.82 $[2Ag+Ph\text{-}NNP+H]^+$, respectively (Fig. 2, and also see Supplementary data).

In addition, the molecular structure of silver–**5a** (Ph-NNP) complex is confirmed by X-ray analysis and depicted in Fig. 3. The structure of silver–**5a** (Ph-NNP) complex represents a unique binding mode for planar silver-linked acetate and reflects acetate anion is important in the silver complex, in which the silver atom is essentially four-coordinated by the phosphine atom, two oxygen



Scheme 2. Ag-catalyzed asymmetric vinylogous Mannich-type reaction of trimethylsiloxyfuran and aldimines.



Scheme 3. Ag-catalyzed asymmetric vinylogous Mannich-type reaction of trimethylsiloxyfuran and aldimines.

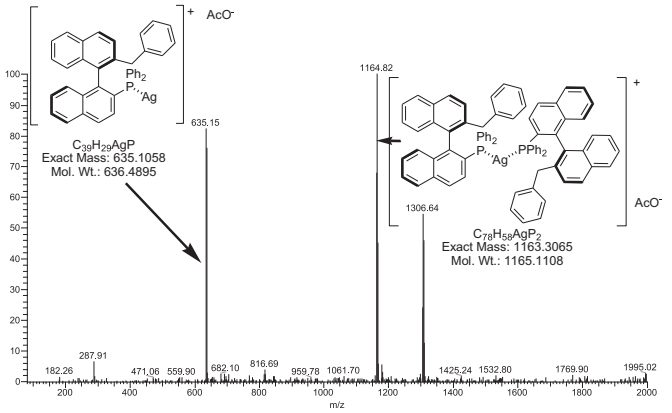


Fig. 2. ESI(+)-MS for the vinylogous Mannich reaction mixtures of AgOAc, imine **6a**, *i*-PrOH, 2-(trimethylsilyloxy)furans and monophosphine ligand **5a** (Ph-NNP) in DCM.

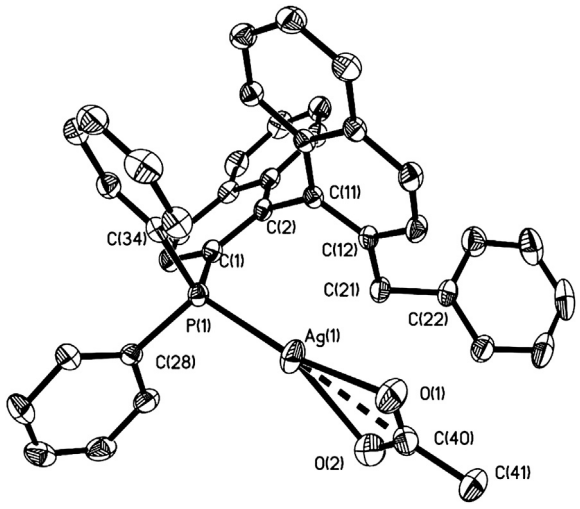


Fig. 3. Crystal structure of chiral silver–**5a** monophosphine complex, hydrogen atoms have been omitted for clarity (CCDC 925867).

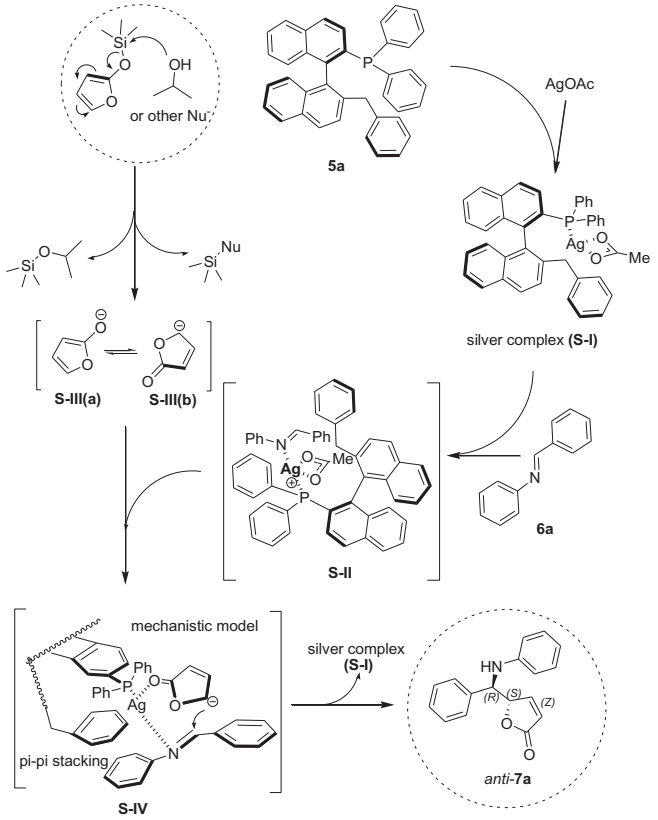
atoms and one central carbon atom of acetate anion. Important bond lengths and angles of the silver complex are listed in Table 2 and reveal the distance of silver atom and two oxygen of acetate is significantly different. The interaction between acetate silver–phosphine-linked aromatic ring and the benzyl group-linked naphthyl ring looks repulsive, and a promising and positive splay angle clearly supports this observation. The large cavity between parallel aromatic rings may be beneficial to the interaction of silver with aldimine or trimethylsiloxyfuran, which guarantees the selective addition of trimethylsiloxyfuran to aldimine.

Table 2
Selected bond lengths (Å) and angles (°) for silver–**5a** (Ph-NNP)

Bond lengths (Å)		Bong angles (°)	
Ag(1)–O(1)	2.203(4)	O(1)–Ag(1)–P(1)	167.36(14)
Ag(1)–O(2)	2.568(6)	O(1)–Ag(1)–O(2)	54.17(19)
Ag(1)–P(1)	2.3553(9)	P(1)–Ag(1)–O(2)	136.89(13)
P(1)–C(34)	1.818(4)	P(1)–Ag(1)–C(40)	163.65(19)
P(1)–C28	1.827(3)	O(2)–Ag(1)–C(40)	27.2(2)
P(1)–C(1)	1.834(4)	C(34)–P(1)–C(28)	104.88(17)
C(1)–C(2)	1.378(5)	C(34)–P(1)–C(1)	103.59(17)
C(2)–C(11)	1.513(4)	C(28)–P(1)–C(1)	105.04(16)
C(11)–C(12)	1.384(5)	C(34)–P(1)–Ag(1)	116.81(13)
C(12)–C(21)	1.520(5)	C(28)–P(1)–Ag(1)	107.87(12)
C(21)–C(22)	1.503(6)	C(1)–P(1)–Ag(1)	117.41(11)
C(40)–C(41)	1.533(8)	C(12)–C(21)–C(22)	114.2(3)

The electronic UV–vis spectra of monophosphine ligand **5a** and its silver complex show a major π–π* transition at about 236 nm due to naphthyl groups (see Supplementary data, Fig. S5). Upon the molecular interaction between silver–**5a** complex and substrate, different changes in UV–vis absorption peak appear to be assigned to the possible π–π stacking of aromatic rings. Especially for the addition of aldimine **6a**, naphthyl π–π* transition has red-shifted by 27 nm, while the use of trimethylsiloxyfuran resulted in slightly blue-shifted by 6 nm. Similarly, in fluorescence emission (FL) spectra of the silver complex and the reaction mixture (see Supplementary data, Fig. S6), the emission band (λ_{max}=258 and 310 nm) of silver–**5a** complex dramatically decreased due to the intermolecular interaction between **6a** and silver–**5a** complex.

Thus on the basis of reaction data and spectroscopy analysis, we proposed a preliminary mechanistic process for Ag/Ph-NNP **5a** complex-catalyzed vinylogous Mannich-type reaction in Scheme 4. As shown in Scheme 4, the interaction of phosphine ligand **5a** and silver salt led to the formation of silver–**5a** complex (**S-I**). And then the silver complex could activate the electrophilic activity of aldimine by silver–nitrogen coordination (**S-II**). Meanwhile, the formation of intermediate **S-III** was facilitated by desilylation with aid of the *i*-PrOH or other nucleophilic reagent. The key feature in our catalyst system that is different from bidentate N,P-ligand maybe exist a possible steric repulsion and aromatic interaction[17] between substrate (aromatic imine) and silver–phosphine complex, in which the benzyl group on chiral monophosphine provides possibly dual function with weak silver–π/π–π stacking[18] and steric repulsion to favour the diastereoselective *Re*-nucleophilic addition of siloxyfuran to imine.



Scheme 4. Proposed mechanistic process for Ag-catalyzed vinylogous Mannich-type reaction.

3. Conclusions

In summary, we have reported a simple procedure for the synthesis of a new family of axially chiral monophosphines derived from chiral Ar-BINMOLs. The novel and air-stable monophosphines (Ar-NNPs) featured with single phosphine-based binding site and an additional benzyl group was synthesized in gram scale in high yields. Furthermore, we evaluated the enantioselective activity of these chiral monophosphines in asymmetric vinylogous Mannich-type reaction. The enantioselective Ag-catalyzed vinylogous Mannich-type reaction of trimethylsiloxyfuran with aldimines was proved to a practical and efficient procedure in the presence of chiral monophosphine, as the reaction proceed with excellent yields (up to 99% isolated yields) and exceptional diastereoselectivity (>99:1 dr). The enantiomeric excesses of desired γ-butenolide derivatives were also promising and could reach moderate to good level (up to 89:11 er), which offered a simple and unprecedented example that axially chiral monophosphine without additional heteroatom-donating group could exhibit good enantiocontrol and high catalytic performances in silver-catalyzed asymmetric vinylogous Mannich-type reaction. Further modification of the new axially chiral monophosphine ligands for stereoselective vinylogous Mannich-type reaction and other transformations to the synthesis of useful molecules is the focus of our ongoing studies in the near future.

4. Experimental section

4.1. General

Flash column chromatography was performed over silica (200–300 mesh). ^{1}H NMR, and ^{13}C NMR were recorded at 400 and 100 MHz, respectively, on Advance (Bruker) 400 MHz Nuclear Magnetic Resonance Spectrometer, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel; F_{254} TLC plates and visualized with ultraviolet light. HPLC was carried out with a Waters 2695 Millennium system equipped with a photodiode array detector. EI and CI mass spectra were performed on a Trace DSQ GC/MS spectrometer. Data are reported in the form of (*m*/*z*). The substrates including *i*-butyllithium were commercial available and used directly. The Ar-BINMOLs **1** and most of products **7** were known and confirmed by usual spectral methods (^{1}H NMR, ^{13}C NMR, IR). The ESI-MS analysis of the samples was operated on an LCQ advantage mass spectrometer (Thermo-Fisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). DCM was dried and distilled over CaH_2. THF and Et_2O were distilled from sodium benzophenone ketyl. X-ray diffraction: data sets were collected with Bruker APEX DUO and Bruker APEX-II CCD diffractometers. Programs used: data collection Bruker APEX2,[19a] data reduction Bruker SAINT, absorption correction for multi-scan, structure solution SHELX-97,[19b] structure refinement SHELXL-97,[19b] graphics Bruker SHELXTL.[19b]

4.2. General procedure for the synthesis of ligands 5a–d

4.2.1. Typical procedure for the synthesis of ***2****.* To a solution of **1a** (7.52 g, >99%ee, 20 mmol) and NaI (17.8 g, 120 mmol) in dry acetonitrile (100 mL) was added TMSCl (10.3 mL, 120 mmol) at room temperature under Argon atmosphere. After the addition, the solution was allowed to stir at room temperature overnight. Then saturated sodium thiosulfate solution was added until the mixture turned colourless. The resultant mixture was extracted with EtOAc, and washed with water and saturated NaCl solution. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (hexanes/ethyl acetate=5:1) to give **2a**[14] (7.13 g, >99% yield).

*4.2.1.1. (R)-2′-(2-Methoxybenzyl)-[1,1′-binaphthalen]-2-ol (****2b****).* Yield 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.96 (dd,

J=7.2, 2.8 Hz, 1H), 7.93–7.89 (m, 3H), 7.49–7.43 (m, 2H), 7.40 (dd, *J*=8.8, 2.4 Hz, 1H), 7.38–7.34 (m, 1H), 7.30–7.24 (m, 3H), 7.20 (t, *J*=8.0 Hz, 1H), 7.06 (d, *J*=8.8 Hz, 1H), 6.97 (d, *J*=7.2 Hz, 1H), 6.87–6.79 (m, 2H), 5.19 (s, 1H), 3.84 (dd, *J*=20.0, 4.0 Hz, 2H), 3.65 (d, *J*=3.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=171.2 (EtOAc: CO), 157.3, 151.1, 140.2, 133.8, 133.2, 132.6, 131.2, 129.8, 129.1, 128.9, 128.6, 128.5, 128.0, 128.0, 127.6, 127.5, 126.7, 126.5, 125.8, 125.6, 124.8, 123.3, 120.4, 117.7, 110.4, 60.4 (EtOAc: CH_2), 55.1, 34.1, 21.0 (EtOAc: $COCH_3$), 14.2 (EtOAc: CH_3) ppm; IR (neat): 3416, 3050, 2838, 1693, 1595, 1493, 1462, 1377, 1244, 1167, 1142, 1111, 1049, 1028, 943, 816, 748, 708, 681, 663, 619 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}NaO_2$ [M+Na]$^+$: 413.1512; Found: 413.1514.

*4.2.1.2. (R)-2′-(4-Methylbenzyl)-[1,1′-binaphthalen]-2-ol (**2c**).* Yield 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.90 (d, *J*=8.8 Hz, 1H), 7.88–7.84 (m, 3H), 7.46 (d, *J*=8.4 Hz, 1H), 7.42 (t, *J*=7.2 Hz, 1H), 7.32–7.28 (m, 2H), 7.25–7.21 (m, 2H), 7.18 (d, *J*=6.4 Hz, 1H), 6.99 (d, *J*=8.4 Hz, 1H), 6.92 (d, *J*=8.0 Hz, 2H), 6.79 (d, *J*=7.6 Hz, 2H), 4.70 (s, 1H), 3.70 (dd, *J*=16.8, 15.6 Hz, 2H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.1, 140.6, 137.2, 135.4, 133.6, 133.1, 132.6, 129.9, 129.2, 129.0, 128.9, 128.9, 128.6, 128.2, 128.1, 126.9, 126.6, 125.9, 125.7, 124.6, 123.4, 117.4, 117.2, 39.1, 20.9 ppm; IR (neat): 3530, 3483, 3053, 1616, 1595, 1512, 1468, 1333, 1202, 1167, 1140, 1126, 1022, 974, 847, 816, 762, 750, 679, 663, 625 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}NaO$ [M+Na$^+$]: 397.1563; Found: 397.1569.

*4.2.1.3. (R)-2′-(Naphthalen-2-ylmethyl)-[1,1′-binaphthalen]-2-ol (**2d**).* Yield 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.93–7.85 (m, 4H), 7.69 (d, *J*=8.4 Hz, 1H), 7.58 (d, *J*=4.0 Hz, 2H), 7.51–7.47 (m, 1H), 7.44–7.38 (m, 1H), 7.36 (t, *J*=3.6 Hz, 2H), 7.31–7.24 (m, 5H), 7.19–7.14 (m, 1H), 7.02 (dd, *J*=17.2 Hz, 2H), 4.74 (s, 1H), 3.88 (d, *J*=6.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.0, 140.0, 137.6, 133.5, 133.3, 133.1, 132.6, 131.8, 130.0, 129.2, 129.0, 128.9, 128.2, 128.0, 127.8, 127.5, 127.4, 126.9, 126.6, 125.9, 125.7, 125.1, 124.5, 123.4, 117.4, 117.1, 39.7 ppm; IR (neat): 3517, 3053, 2856, 2924, 1620, 1595, 1506, 1468, 1435, 1379, 1310, 1269, 1202, 1171, 1142, 1126, 937, 901, 891, 858, 812, 787, 744, 642, 619 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{22}NaO$ [M+Na]$^+$: 433.1563; Found: 433.1575.

*4.2.2. Typical procedure for the synthesis of **3**.* A single necked flask charged with a solution of **2a** (5.4 g, 15 mmol) and Et_3N (4.55 g, 6.3 mL, 45 mmol) in CH_2Cl_2 (50 mL) was cooled to −78 °C, and Tf_2O (5.07 g, 5.73 mL, 18 mmol) was added dropwise. Then the resulting mixture was warmed to 0 °C for 2 h. After removal of the solvent under vacuum, the resulting thick residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate=10:1, v/v) to afford the desired product **3a** as a white solid (7.08 g, >96% yield).

*4.2.2.1. (R)-2′-Benzyl-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (**3a**).* Yield 98%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.04 (d, *J*=9.2 Hz, 1H), 7.93 (dd, *J*=10.0, 8.4 Hz, 2H), 7.87 (d, *J*=8.0 Hz, 1H), 7.56 (d, *J*=9.2 Hz, 1H), 7.50 (t, *J*=7.6 Hz, 1H), 7.44–7.40 (m, 2H), 7.30–7.23 (m, 2H), 7.20–7.18 (m, 1H), 7.11–7.05 (m, 4H), 6.89 (d, *J*=2.0 Hz, 1H), 6.87 (s, 1H), 3.77 (dd, *J*=54.4, 15.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.2, 140.1, 138.5, 133.6, 132.9, 132.5, 132.2, 130.6, 129.4, 129.3, 129.2, 128.8, 128.2, 128.0, 127.9, 127.7, 127.1, 126.9, 126.5, 126.1, 126.0, 125.6, 119.5, 39.8 ppm; IR (neat): 3059, 2926, 2856, 1596, 1508, 1495, 1418, 1248, 1207, 1171, 1138, 1065, 1028, 939, 864, 831, 808, 775, 744, 717, 698, 677, 631, 604 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{19}F_3NaO_3S$ [M+Na]$^+$: 515.0899; Found: 515.0913.

*4.2.2.2. (R)-2′-(2-Methoxybenzyl)-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (**3b**).* Yield 96%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.02 (d, *J*=8.8 Hz, 1H), 7.94 (d, *J*=8.0 Hz, 1H), 7.88 (t, *J*=11.2 Hz, 2H), 7.55 (d, *J*=8.8 Hz, 1H), 7.52–7.48 (m, 1H), 7.41 (t, *J*=8.8 Hz, 2H), 7.30–7.21 (m, 3H), 7.08–7.05 (m, 2H), 6.81 (d, *J*=7.6 Hz, 1H), 6.71–6.65 (m, 2H), 3.78 (dd, *J*=33.6, 16.0 Hz, 2H), 3.51 (d, *J*=2.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=219.2, 157.3, 145.3, 138.7, 133.7, 132.9, 132.5, 132.1, 130.9, 130.4, 129.6, 129.0, 128.6, 128.3, 128.1, 127.9, 127.8, 127.4, 127.2, 127.0, 126.2, 126.1, 125.4, 120.2, 119.5, 110.0, 55.0, 33.7 ppm; IR (neat): 3060, 3002, 2906, 2835, 1597, 1506, 1489, 1460, 1416, 1244, 1204, 1159, 1138, 1105, 1032, 970, 951, 943, 866, 831, 812, 754, 702, 673, 629, 615 cm^{-1}; HRMS (ESI) calcd For $C_{29}H_{21}F_3NaO_4S$ [M+Na$^+$]: 545.1005; Found: 545.1012.

*4.2.2.3. (R)-2′-(4-Methylbenzyl)-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (**3c**).* Yield 98%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.04 (d, *J*=9.2 Hz, 1H), 7.95 (d, *J*=8.0 Hz, 1H), 7.92 (d, *J*=8.8 Hz, 1H), 7.88 (d, *J*=8.4 Hz, 1H), 7.56 (dd, *J*=8.8, 2.4 Hz, 1H), 7.54–7.50 (m, 1H), 7.44–7.40 (m, 2H), 7.31–7.20 (m, 3H), 7.08 (dd, *J*=8.4, 2.8 Hz, 1H), 6.90 (d, *J*=7.6 Hz, 2H), 6.78 (d, *J*=7.6 Hz, 2H), 3.73 (dd, *J*=55.6, 15.6 Hz, 2H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.1, 138.8, 136.9, 135.4, 133.6, 132.8, 132.4, 132.1, 130.5, 129.4, 129.2, 129.0, 128.8, 128.6, 128.2, 127.9, 127.8, 127.6, 127.0, 126.9, 126.3, 126.0, 125.5, 119.4, 39.3, 20.9 ppm; IR (neat): 3060, 2931, 1609, 1510, 1414, 1246, 1215, 1140, 1065, 1030, 964, 939, 868, 833, 806, 754, 673, 631, 615 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{21}F_3NaO_3S$ [M+Na$^+$]: 529.1056; Found: 529.1057.

*4.2.2.4. (R)-2′-(Naphthalen-2-ylmethyl)-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (**3d**).* Yield 97%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.04 (dd, *J*=8.8, 2.4 Hz, 1H), 7.93–7.87 (m, 3H), 7.70–7.68 (m, 1H), 7.58–7.54 (m, 3H), 7.49–7.40 (m, 3H), 7.39–7.34 (m, 2H), 7.28–7.25 (m, 2H), 7.19 (d, *J*=4.0 Hz, 2H), 7.13–7.04 (m, 2H), 4.00 (dd, *J*=15.6, 6.0 Hz, 1H), 3.86 (dd, *J*=15.6, 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.2, 138.4, 137.5, 133.7, 133.6, 132.9, 132.5, 132.3, 132.0, 130.7, 129.5, 129.4, 129.0, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.1, 126.9, 126.5, 126.1, 125.9, 125.7, 125.3, 119.6, 40.1 ppm; IR (neat): 3060, 2912, 1615, 1508, 1414, 1246, 1232, 1213, 1171, 1151, 1138, 1065, 937, 868, 831, 812, 768, 754, 744, 673, 662, 631, 613 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{21}F_3NaO_3S$ [M+Na$^+$]: 565.1056; Found: 565.1073.

*4.2.3. Typical procedure for the synthesis of **4**.* To a Schlenk flask charged with **3a** (4.92 g, 10 mmol), diphenylphosphine oxide (4.04 g, 20 mmol), $Pd(OAc)_2$ (0.112 g, 0.5 mmol) and dppb (0.213 g, 0.5 mmol) in DMSO (45 mL) was added DIEA (5.15 g, 7.0 mL, 40 mmol) under argon. The resulting mixture was stirred at 100 °C for 60 h. Then the mixture was cooled to room temperature, diluted with EtOAc (100 mL), washed with water (40 mL×3), brine (50 mL), successively. The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated, and the crude residue was filtrated through a short silica gel column and flushed with petroleum ether/ethyl acetate (3:1, v/v). The filtrate was concentrated under reduce pressure, and a yellow solid **4a** (3.54 g, 65% yield) was obtained and used for the next step without further purification.

To a dried Schlenk flask charged with the above product (2.72 g, 5 mmol) in dry toluene (100 mL), Et_3N (3.54 g, 4.96 mL, 35 mmol) and $HSiCl_3$ (3.38 g, 2.53 mL, 25 mmol) were added successively under argon at 0 °C. The resulting mixture was stirred at 100 °C for 18 h. After cooled to 0 °C, diluted by Et_2O (50 mL), quenched with saturated Na_2CO_3 solution, the mixture was filtered by a short Celite column, and washed with Et_2O (30 mL×3). The filtrate was dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate=20:1, v/v) to afford the desired product **5a** as a white solid (2.51 g, >95% yield).

*4.2.3.1. (R)-(2′-Benzyl-[1,1′-binaphthalen]-2-yl)diphenylphosphine (**5a**).* Yield 95%; white solid; mp: 199–200 °C; ^{1}H NMR

(400 MHz, $CDCl_3$): δ=7.90–7.80 (m, 4H), 7.49–7.44 (m, 2H), 7.32–7.28 (m, 4H), 7.25–7.23 (m, 3H), 7.19 (t, J=8.0 Hz, 3H), 7.13 (t, J=7.2 Hz, 2H), 7.08–6.97 (m, 6H), 6.83 (t, J=7.6 Hz, 3H), 3.51 (dd, J=21.2, 16.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.6, 144.3, 140.4, 138.1, 137.4, 137.3, 135.5, 135.4, 135.3, 133.7, 133.7, 133.5, 133.5, 133.2, 133.0, 132.9, 131.9, 130.5, 129.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.3, 127.0, 126.9, 126.6, 126.5, 125.8, 125.1, 39.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ=−14.40 ppm; IR (neat): 3050, 1495, 1479, 1433, 1024, 961, 866, 829, 820, 808, 762, 744, 717, 692, 633, 619 cm^{-1}; HRMS (ESI) calcd for $C_{39}H_{29}NaP$ $[M+Na]^+$: 551.1899; Found: 551.1892. HPLC with a Chiralcel OD-H column (λ=254 nm; eluent: Hexane/Isopropanol=95:5; Flow rate: 0.8 mL/min; t_{major}=5.399 min; ee %=99.9%).

*4.2.3.2. (R)-(2′-(2-Methoxybenzyl)-[1,1′-binaphthalen]-2-yl)diphenylphosphine (**5b**).* Yield 96%; white solid; mp: 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.88–7.80 (m, 4H), 7.48 (dd, J=8.8, 2.8 Hz, 1H), 7.45–7.41 (m, 1H), 7.28–7.22 (m, 7H), 7.19–7.16 (m, 3H), 7.12 (t, J=7.2 Hz, 2H), 7.05 (t, J=7.6 Hz, 3H), 6.95 (t, J=7.6 Hz, 1H), 6.79 (d, J=8.8 Hz, 1H), 6.73 (d, J=7.2 Hz, 1H), 6.67–6.63 (m, 2H), 3.59 (dd, J=30.8, 15.6 Hz, 2H), 3.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=157.5, 145.0, 144.7, 138.1, 137.9, 137.7, 137.6, 135.7, 135.6, 135.4, 133.9, 133.7, 133.6, 133.4, 133.2, 133.0, 131.9, 131.3, 130.6, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 127.2, 126.9, 126.6, 126.2, 125.6, 124.9, 120.2, 110.1, 55.0, 33.9 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ=−14.20 ppm; IR (neat): 3042, 2931, 2828, 1590, 1486, 1467, 1428, 1242, 1151, 1113, 1049, 1016, 816, 746, 687, 629 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{31}NaOP$ $[M+Na]^+$: 581.2005; Found: 581.2008.

*4.2.3.3. (R)-(2′-(4-Methylbenzyl)-[1,1′-binaphthalen]-2-yl)diphenylphosphine (**5c**).* Yield 98%; white solid; mp: 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.95–7.86 (m, 4H), 7.54–7.50 (m, 2H), 7.37–7.24 (m, 10H), 7.19 (t, J=7.6 Hz, 2H), 7.10 (t, J=7.2 Hz, 2H), 7.04 (t, J=7.6 Hz, 1H), 6.95–6.88 (m, 3H), 6.77 (d, J=8.0 Hz, 2H), 3.54 (dd, J=21.2, 15.6 Hz, 2H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.8, 144.5, 138.4, 137.8, 137.7, 137.6, 137.4, 135.8, 135.7, 135.5, 135.4, 135.3, 133.9, 133.8, 133.8, 133.7, 133.6, 133.5, 133.2, 133.1, 132.0, 130.6, 129.5, 129.0, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 127.9, 127.5, 127.0, 126.8, 126.6, 125.9, 125.2, 39.4, 21.1 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ=−14.34 ppm; IR (neat): 3044, 1510, 1479, 1433, 1258, 1180, 1117, 1090, 1022, 860, 839, 816, 798, 789, 775, 743, 696, 633, 621, 613 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{31}NaP$ $[M+Na]^+$: 565.2056; Found: 565.2046.

*4.2.3.4. (R)-(2′-(Naphthalen-2-ylmethyl)-[1,1′-binaphthalen]-2-yl)diphenylphosphine (**5d**).* Yield 96%; white solid; mp: 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.99–7.88 (m, 4H), 7.77–7.76 (m, 1H), 7.62–7.58 (m, 3H), 7.51–7.47 (m, 1H), 7.43–7.22 (m, 15H), 7.15 (d, J=6.4 Hz, 2H), 7.10–7.05 (m, 2H), 6.97 (s, 1H), 3.78 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.7, 144.3, 137.9, 137.7, 137.7, 137.6, 137.5, 135.7, 135.6, 135.6, 135.6, 133.8, 133.8, 133.7, 133.6, 133.5, 133.4, 133.1, 133.1, 132.0, 132.0, 130.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.0, 126.7, 126.5, 125.9, 125.7, 125.2, 40.0 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ=−14.39 ppm; IR (neat): 3060, 2970, 2860, 1506, 1477, 1433, 1259, 1155, 1113, 1090, 1069, 1024, 866, 858, 812, 771, 741, 694, 644, 629, 611 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{32}P$ $[M+H]^+$: 579.2236; Found: 579.2231.

4.3. General procedure for the silver/Ph-NNP 5a complex-catalyzed asymmetric vinylogous Mannich reactions with 2-(trimethylsilyloxy)-furan

To a dried Schlenk flask charged with AgOAc (2.2 mg, 0.0125 mmol) and chiral phosphine ligand **5a** (6.6 mg, 0.0125 mmol), was added freshly distilled CH_2Cl_2 (1.0 mL) under argon. The resulting mixture was stirred for 30 min at room temperature, and then imine **6a** (0.25 mmol) in CH_2Cl_2 (0.8 mL) was added to the mixture followed by isopropanol (28 μL) and 2-(trimethylsilyloxy)furan (61.2 μL, 0.375 mmol) when the mixture was cooled to −78 °C. And the reaction mixture was stirred at −78 °C for 10 h and the resulted mixture was also warmed to room temperature for the next 4 h. The reaction was quenched by the addition of saturated aqueous solution of $NaHCO_3$. After stirring for 15 min at room temperature, the mixture was extracted with CH_2Cl_2, washed with brine, and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and residue was purified by flash column chromatography to give the corresponding product **7a** (65.6 mg, 99% yield, 76%ee).

*4.3.1. (S)-2-((R)-Phenyl(phenylamino)methyl)furan-3(2H)-one (**7a**).* Yield 99%; white solid; mp: 129–132 °C; $[\alpha]_D^{20}$ −106.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.37–7.25 (m, 6H), 7.12 (t, J=7.2 Hz, 2H), 6.72 (t, J=7.2 Hz, 1H), 6.57 (d, J=7.6 Hz, 2H), 6.05 (dd, J=5.6, 2.0 Hz, 1H), 5.44 (dd, J=4.0, 2.0 Hz, 1H), 4.86 (d, J=4.0 Hz, 1H), 4.44 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=172.4, 153.2, 146.0, 136.9, 129.3, 128.9, 128.3, 127.2, 123.2, 118.6, 114.0, 85.2, 59.4 ppm; IR (neat): 3408, 3357, 1749, 1601, 1508, 1497, 1452, 1312, 1248, 1161, 1105, 1043, 932, 905, 810, 754, 725, 694, 611 cm^{-1}; MS (ESI): *m*/*z*: 266 $[M+H]^+$; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (λ=254 nm; eluent: Hexane/Isopropanol=80:20; Flow rate: 1.0 mL/min; t_{major}=23.335 min, t_{minor}=33.090 min; ee %=76%).

Acknowledgements

Financial support by the National Natural Science Foundation of China (NSFC, Nos. 21173064 and 51203037), Program for Excellent Young Teachers in Hangzhou Normal University (HNUEYT, JTAS 2011-01-014) and Zhejiang Provincial Natural Science Foundation of China (Q12B020037), is appreciated. X.L.W. thank Prof. G.Q. Lai, Prof. J.X. Jiang, Dr. Y. Deng, Ms. F.E. Zhu, Dr. K.Z. Jiang and Dr. C.Q. Sheng of HZNU for X-ray crystallographic, NMR, IR and ESI-MS measurements.

Supplementary data

Supplementary data of general remarks and the procedure of the synthetic reaction, NMR data diagrams for all the products 2–**7**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.07.105.

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