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Novel chiral sulfinamide phosphines: valuable precursors to chiral β-aminophosphines

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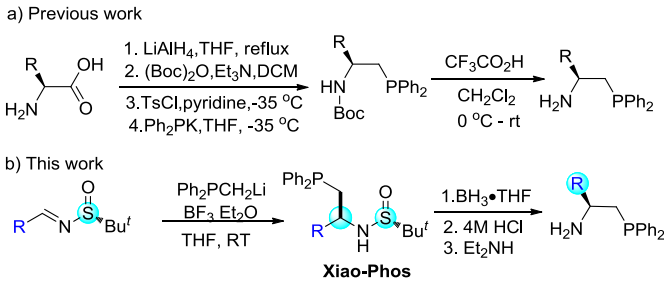
ABSTRACT

Starting from commercially available aldehyde and chiral *tert*-butanesulfinamide, a series of chiral sulfinamide phosphines (**Xiao-Phos**) were synthesized via a two-step condensation-nucleophilic addition procedure. In most cases, nucleophilic addition of the *N*-*tert*-butanesulfinyl imine with diphenyl methyl phosphonic lithium showed high diastereoselectivity (d.r>20:1) with BF_3 as additives. Following removal of the chiral auxilliary, an important class of ligands i.e chiral β-aminophosphines and its derivatives were obtained in high yields using this approach.

1. Introduction

In the past two decades, the asymmetric nucleophilic catalysis has been developed into one of the most powerful and efficient tool for the preparation of chiral organic molecules. Compared with similarly substituted amine catalysts, phosphines displayed unique catalytic activities because of their weaker basicity and stronger nucleophilicity.[1] Phosphine-promoted catalytic processes, particularly asymmetric reactions that are catalyzed by chiral phosphines have emerged as a powerful approach to structurally diverse and synthetically valuable optically active organic building blocks,[2] which has attracted enormous attention in recent years.

The development of novel chiral phosphine catalysts is one of the most attractive and practical aspects in organocatalysis. Very recently, our group has developed a new type of chiral sulfinamide monophosphine ligands (**Ming-Phos**), which performed well in the enantioselective gold-catalyzed cycloaddition reaction of 2-(1-alkynyl)-alk-2-en-1-ones with nitrones. Both enantiomers of the products could be obtained in good yields and with excellent diastereo- and enantioselectivity by the use of gold complexes derived from two diastereomers of Ming-Phos. The Ming-Phos ligands could be easily prepared in good yields from inexpensive, commercially available chiral *tert*-butylsulfinamide via a two-step condensation-nucleophilic addition procedure.[3] It was well known that chiral β-aminophosphines represent one of the most attractive chiral phosphines, which have been widely utilized as nucleophilic catalysts[4] or chiral ligands[5] in a broad spectrum of useful organic transformations. However, only a few methods for the efficient synthesis of β-aminophosphines have been developed and the one from natural amino acids is the most commonly used one method (Scheme 1a).[6] Very recently, we designed a novel type of chiral β-sulfinamide phosphines, structured as **Xiao-Phos**, which could be obtained by using commercially available aldehyde and diphenyl methyl phosphonic lithium.[7] We envisaged that an important class of ligands i.e. chiral β-aminophosphines could be



Scheme 1. Synthesis of chiral β-aminophosphines.

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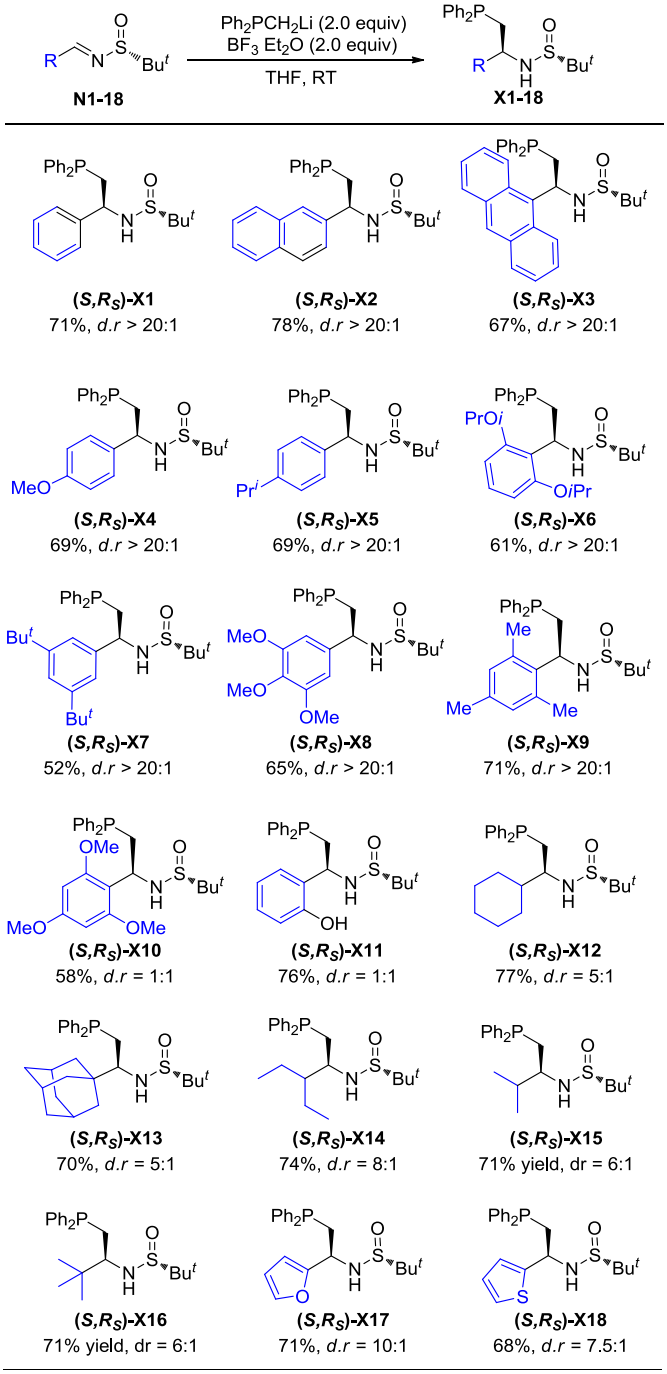
obtained via the removal of the chiral auxilliary (Scheme 1b). Herein, we report our efforts for the synthesis of Xiao-Phos and the success of removal of the ^{t}BuSO auxilliary group.

2. Results and discussion

Our initial attempts for the preparation of Xiao-Phos started from readily available benzaldehyde and chiral *tert*-butanesulfinamide (Scheme 2). The corresponding imine **N1** was obtained in excellent yield when the reaction was performed at 60 °C in the presence of titanium tetraisopropanolate as Lewis acid.[8] Treatment of Ph_2PMe with *n*-BuLi in the presence of TMEDA at room temperature would produce a solution of Ph_2PCH_2Li in THF according to reported procedure,[9] which would undergo nucleophilic addition to chiral (R_S)-sulfinimine **N1** at −78 °C, furnishing the desired product **X1** in 71% yield with 5:1 dr (Table 1, entry 1). The absolute configurations of **(*S, R*$_S$)-X1** was established by single-crystal X-ray diffraction analysis.[10] Solvent screening was subsequently performed and THF was found to be the best solvent. Other solvents such as Et_2O, toluene, DME and dioxane didn't bring significant improvement in diastereoselectivity. When the reaction was carried out at room temperature, the corresponding product could be obtained in 70% yields with 10:1 dr (Table 1 entry 6). Notably, the addition of $BF_3\cdot Et_2O$ (2.0 equiv) to the reaction system could remarkably improve the diastereoselectivity to >20:1 dr (Table 1 entry 7).

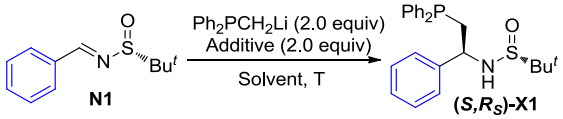


Scheme 2. Synthesis of chiral β-sulfinamide phosphines **X1**–**X18**.

Having established the optimal reaction conditions for the synthesis of chiral sulfinamide phosphines **(*S, R*$_S$)-X1**, we next focused on the substrate scope of this transformation. Chiral sulfinyl imines **N2**–**N18** were easily prepared by the condensation of *tert*-butanesulfinamide with the corresponding aldehydes according to the reported procedure. With these imines in hand, the scope of nucleophilic addition of Ph_2PCH_2Li to these substrates was subsequently investigated under identified reaction conditions and the results are outlined in Scheme 2. As demonstrated in Scheme 2, the nucleophilic addition of Ph_2PCH_2Li with chiral sulfinyl imines **N1**–**N18** is pretty general and practically useful method for the preparation of a range of functionalized chiral sulfonamide phosphine **X1**–**X18**. Chiral sulfinyl imines derived from aromatic aldehydes with various substituents at different position of phenyl ring generally exhibited high diastereoselectivities (d.r>20) with moderate isolated yields (***S, Rs*)-X1**–**X9** except the sulfinyl imines **N10**–**N11**, which give the corresponding **X10**–**X11** with a 1: 1 ratio of two diastereoisomers. The additions to chiral sulfinyl imines derived from aliphatic aldehydes as well as heteroaromatic aldehyde such as furan-2-carbaldehyde and thiophene-2-carbaldehyde showed acceptable diastereoselectivities (d.r=5: 1–10:1), delivered the corresponding (***S, Rs*)-X12**–**X18** in good yields, albeit that in some cases two diastereomers are not easily separated by the flash column chromatography.

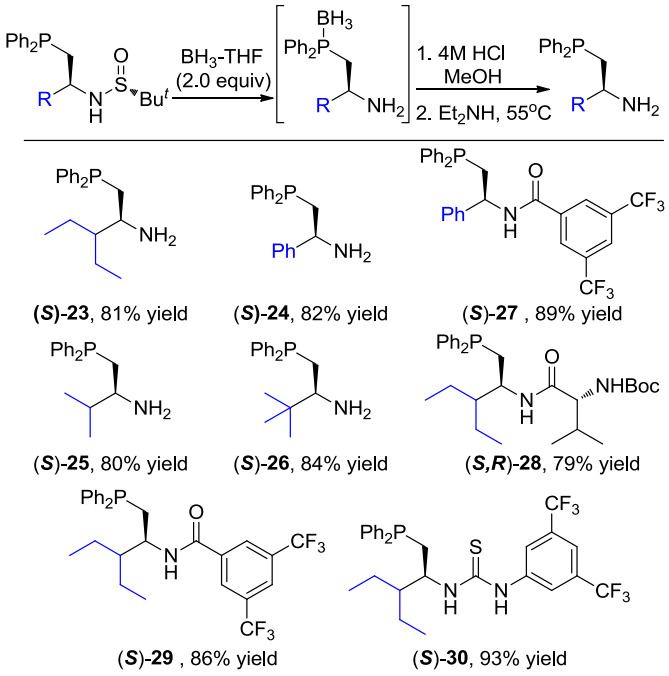
Synthetic applications of our novel designed chiral β-sulfinamide phosphines (**Xiao-Phos**) for synthesis of various types of chiral β-aminophosphines and its derivatives have been showcased by the selective transformations of the representative Xiao-Phoses **X1**, **X14**, **X15** and **X16** (Scheme 3). The attempts to direct removal of the ^{t}BuSO auxilliary group under acid conditions (4M HCl/MeOH) failed, which led to the oxidation of the phosphine. Thus, we then decided to protect the phosphine with the use of borane in THF. The structure of BH_3-protected intermediate was confirmed after isolating representative **(*S, R*$_S$)-X1-BH$_3$** through column chromatography on silica gel (hexane/ethyl acetate=3:1, quantitative yield). H

Table 1
Solvent and additive effect on the yield and diastereomeric ratios



Entry[a]	T (°C)	Additive (2.0 equiv)	Solvent	Yield[b]	d.r.[c]
1	−78	—	THF	71%	5:1
2	−78	—	Et_2O	65%	5:1
3	−78	—	Toluene	67%	4.2:1
4	−78	—	DME	46%	4.4:1
5	−78	—	Dioxane	58%	3:1
6	RT	—	THF	72%	10:1
7	RT	$BF_3\cdot Et_2O$	THF	71%	20:1

[a] The reaction was conducted using **N1**(1.5 mmol), Ph_2PCH_2Li(3.0 mmol).
[b] Isolated yield.
[c] The d.r was determined by the ^{1}H NMR analysis.



Scheme 3. Synthesis of chiral β-aminophosphines and derivatives.

NMR, ^{31}P NMR and HRMS-ESI spectra of **(*S, R*$_S$)-X1-BH$_3$** revealed that only *P*-adduct was formed in the presence of 2.0 equiv of BH_3. In some case, after borane protection, the two diastereoisomers could be more easily separated by the column chromatography. The chiral auxiliary the *tert*-butyl sulfinyl group in chiral sulfinamide phosphines (**Xiao-Phos**) could be readily removed under acid conditions (4M HCl) and the corresponding chiral β-aminophosphines (***S***)-**23**–**26** could be obtained in high yields after deprotection of borane by treatment with the diethylamine without loss of the chirality information. These chiral β-aminophosphines are valuable platform precursors for synthesis of other types of valuable functionalized chiral phosphine catalysts. For examples, β-amidephosphines (***S***)-**27**, (***S, R***)-**28**, and (***S***)-**29** could be obtained from the corresponding chiral β-aminophosphines by reacting with acids or chiral amino acid. The useful β-thiourearphosphine (***S***)-**30** could be also produced in 93% yield by treatment with isothiocyanate under mild conditions.

3. Conclusions

In summary, we developed a novel method for the synthesis of useful chiral β-aminophosphines and its derivatives from commercially available aldehyde and chiral *tert*-butane-sulfinamide and diphenyl methyl phosphine. A series of chiral β-sulfinamide phosphines (**Xiao-Phos**) were synthesized in good yields with moderate to high diastereoselectivity via a two-step condensation-nucleophilic addition procedure. These chiral sulfinamide phosphines (**Xiao-Phos**) were valuable precursors for the synthesis of chiral β-aminophosphines and its derivatives. Other applications of Xiao-Phos as well as β-aminophosphines and its derivatives in asymmetric reactions are underway in our laboratory and will be reported in due course.

4. Experimental section

4.1. General

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{31}P NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d_3. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ=0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ=77.00 ppm). The data is being reported as (s=singlet, d=doublet, t=triplet, m=multiplet or unresolved, br=broad signal, coupling constant(s) in Hz, integration). Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer.

Tetrahydrofuran (THF) was dried with sodium benzophenone and distilled before use; Ph_2PCH_3 was purchased from Acros Company.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200–400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

4.2. General procedure for the preparation of imines N1-18[7,8]

A round bottom flask was charged with a solution of chiral *tert*-butanesulfinamide (11 mmol) and aldehyde (10 mmol) in THF (20 mL) followed by the addition of isopropyl titanate (15 mmol). The reaction mixture was stirred until completion of aldehyde as indicated by TLC. The reaction was then quenched with water, diluted with EtOAc and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by silica gel column chromatography using Petroleum Ether/AcOEt as an eluent to give the desired product in 58–95% yields.

4.3. General procedure for the synthesis of Xiao-Phos

Boron trifluoride diethyl etherate (3.0 mmol) was added to the solution of the imine **N** (1.5 mmol) in dry THF (10 mL), a solution of diphenyl methyl phosphonic lithium (3.0 mmol) that containing TMEDA (3.0 mmol) in THF was slowly added at room temperature. The mixture was stirred until completion of imine as indicated by TLC, followed by hydrolysis with 10 mL of water and diluted with EtOAc. The organic layer was separated, the aqueous phase was extracted three times with EtOAc (3×10 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. The product was purified by a flash chromatography to afford product.

4.3.1. Compound ***(S, R$_S$)-X1****.* $[\alpha]_D^{20}$= −28.4 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2863, 1494, 1264, 1047, 915, 735; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.36–7.28 (m, 7H), 7.27–7.25 (m, 6H), 4.48–4.41 (m, 1H), 3.63 (d, *J*=4.4 Hz, 1H), 2.89 (dd, *J*=13.8, 6.8 Hz, 1H), 2.50 (dd, *J*=13.8, 8.0 Hz, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.08 (d, $J_{C,P}$=44 Hz), 138.10 (d, $J_{C,P}$=12.9 Hz), 137.51 (d, $J_{C,P}$=13 Hz), 132.78 (d, $J_{C,P}$=5.8 Hz), 132.59 (d, $J_{C,P}$=5.8 Hz), 128.79, 128.62, 128.60, 128.54 (d, $J_{C,P}$=2.3 Hz), 128.35 (d, $J_{C,P}$=6.7 Hz), 128.04, 127.12 (d, $J_{C,P}$=1 Hz), 57.56 (d, $J_{C,P}$=19 Hz), 56.02, 37.47 (d, $J_{C,P}$=14 Hz), 22.52; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −24.00 ppm. ESI-MS calcd for $C_{24}H_{29}NOPS$: *m/z* (%): 410.1702 ($M+H^+$), found: 410.1687.

4.3.2. Compound ***(S, R$_S$)-X2****.* $[\alpha]_D^{20}$= −26.6 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2958, 1433, 1035, 892, 801, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.75 (m, 3H), 7.70 (s, 1H), 7.46–7.39 (m, 5H), 7.36–7.27 (m, 5H), 7.21–7.18 (m, 3H), 4.66–4.59 (m, 1H), 3.71 (d, *J*=4.3 Hz, 1H), 2.98 (dd, *J*=13.8, 6.8 Hz, 1H), 2.62 (dd, *J*=13.8, 8.0 Hz, 1H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.25 (d, $J_{C,P}$=4.4 Hz), 138.02 (d, $J_{C,P}$=12.7 Hz), 137.52 (d, $J_{C,P}$=12.9 Hz), 133.13 (d, $J_{C,P}$=5.8 Hz), 132.83

(d, $J_{C,P}$=3.1 Hz), 132.64(d, $J_{C,P}$=3.5 Hz), 128.81, 128.62, 128.55, 128.32 (d, $J_{C,P}$=6.7 Hz), 128.02, 126.40 (d, $J_{C,P}$=1.1 Hz), 126.11(d, $J_{C,P}$=9.9 Hz), 124.77, 57.73 (d, $J_{C,P}$=19.6 Hz), 56.08, 37.16 (d, $J_{C,P}$=14.4 Hz), 22.56; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.88 ppm. ESI-MS calcd for $C_{28}H_{31}NOPS$: *m*/*z* (%): 460.1858 ($M+H^+$), found: 460.1827.

4.3.3. Compound ***(S, R$_S$)-X3***. $[\alpha]_D^{20}$= −11.6 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 3053, 1433, 1067, 925, 885, 132; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J*=8.6 Hz, 1H), 8.29 (s, 1H), 8.00 (d, *J*=8.8 Hz, 1H), 7.94–7.90 (m, 2H), 7.45–7.30 (m, 9H), 7.04–7.01 (m, 1H), 6.92–6.90 (m, 4H), 6.19–6.14 (m, 1H), 3.96 (s, 1H), 3.31–3.23 (m, 2H),1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.94 (d, J_{CP}=12.6 Hz), 136.71 (d, J_{CP}=13.2 Hz), 132.70 (d, J_{CP}=23.8 Hz), 132.47 (d, J_{CP}=22.2 Hz), 131.91, 131.25, 129.87, 128.99 (d, J_{CP}=4.0 Hz), 128.52, 128.51 (d, J_{CP}=10.6 Hz), 128.35, 127.77 (d, J_{CP}=7.2 Hz), 126.44, 125.84, 125.21, 124.89, 124.42, 123.55, 56.03, 51.09 (d, J_{CP}=23.3 Hz), 35.57 (d, J_{CP}=10.4 Hz), 22.78; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −22.62 ppm. ESI-MS calcd for $C_{32}H_{32}NNaOPS$: *m*/*z* (%): 532.1834 ($M+Na^+$), found: 532.1789.

4.3.4. Compound ***(S, R$_S$)-X4***. $[\alpha]_D^{20}$= −26.9 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2954, 1610, 1512, 1434, 1247, 1178, 1050, 830, 738, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.35–7.26 (m, 8H), 7.19 (d, *J*=2.1 Hz, 2H), 4.44–4.38 (m, 1H), 3.78 (s, 3H), 3.56 (m, 1H), 2.92–2.87 (m, 1H), 2.50–2.44 (m, 1H), 2.45 (s, 3H),1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.28, 138.28 (d, J_{CP}=12.9 Hz), 137.53 (d, J_{CP}=12.9 Hz), 134.09 (d, J_{CP}=4.3 Hz), 132.85 (d, J_{CP}=11.9 Hz), 132.66 (d, J_{CP}=11.9 Hz), 128.83, 128.64, 128.54 (d, J_{CP}=4.8 Hz), 128.39, 128.32, 113.98, 56.94 (d, J_{CP}=19.8 Hz), 55.94, 55.20, 37.32 (d, J_{CP}=13.9 Hz), 22.57; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.94 ppm. ESI-MS calcd for $C_{25}H_{31}NO_2PS$: *m*/*z* (%): 440.1768 ($M+H^+$), found: 440.1804.

4.3.5. Compound ***(S, R$_S$)-X5***. $[\alpha]_D^{20}$= −24.8 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2955, 1433, 1047, 903, 828, 792, 741; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.33–7.24 (m, 8H), 7.21–7.12 (m, 4H), 4.48–4.42 (m, 1H), 3.60 (d, *J*=4.4 Hz, 2H), 2.89–2.83 (m, 2H), 2.51 (d, *J*=13.8, 7.8 Hz, 1H), 1.22 (d, *J*=6.9 Hz, 6H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.54, 139.44 (d, J_{CP}=4.3 Hz), 138.13 (d, J_{CP}=13.0 Hz), 137.82(d, J_{CP}=12.7 Hz), 132.81 (d, J_{CP}=10.1 Hz), 132.62 (d, J_{CP}=9.7 Hz), 128.61 (d, J_{CP}=15.6 Hz), 128.52 (d, J_{CP}=6.6 Hz), 127.03, 126.66, 57.41 (d, J_{CP}=23.6 Hz), 56.01, 37.43 (d, J_{CP}=14.1 Hz), 33.70, 23.87 (d, J_{CP}=1.0 Hz), 22.57; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.77 ppm. ESI-MS calcd for $C_{27}H_{35}NOPS$: *m*/*z* (%): 452.2171 ($M+H^+$), found: 452.2134.

4.3.6. Compound ***(S, R$_S$)-X6***. $[\alpha]_D^{20}$= −7.5 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2974, 1591, 1465, 1384, 1239, 1111, 1052, 906; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.37–7.30 (m, 3H), 7.24–7.22 (m, 2H), 7.18–7.16 (m, 3H), 7.10–7.06 (m, 1H), 6.43 (dd, *J*=13.0, 8.3 Hz, 2H), 5.24–5.16 (m, 1H), 4.79 (d, *J*=10.6 Hz, 1H), 4.62–4.56 (m, 1H), 4.39–4.33 (m, 1H), 3.13–3.08 (m, 1H), 2.90–2.83 (m, 1H), 1.37 (d, *J*=6.0 Hz, 3H), 1.31 (d, *J*=6.0 Hz, 3H), 1.10–1.03 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.20, 154.90, 139.42 (d, J_{CP}=13.3 Hz), 139.02 (d, J_{CP}=14.4 Hz), 133.06 (d, J_{CP}=19.2 Hz), 132.36 (d, J_{CP}=18.3 Hz), 128.39, 128.24 (d, J_{CP}=12.3 Hz), 128.25, 128.08, 121.12 (d, J_{CP}=6.2 Hz), 106.64, 105.03, 70.96, 69.20, 56.02, 51.46 (d, J_{CP}=17.6 Hz), 36.06 (d, J_{CP}=13.7 Hz), 22.73, 22.51, 22.22; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −21.87 ppm. ESI-MS calcd for $C_{30}H_{41}NO_3PS$: *m*/*z* (%): 526.2539 ($M+H^+$), found: 526.2530.

4.3.7. Compound ***(S, R$_S$)-X7***. $[\alpha]_D^{20}$= −17.4 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2951, 1599, 1475, 1361, 1248, 1059, 876, 737, 605; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 7H), 7.23–7.20 (m, 4H), 7.10 (d, *J*=1.7 Hz, 2H), 4.55–4.49 (m, 1H), 3.66 (d, *J*=3.0 Hz, 1H), 2.87 (dd, *J*=14.4, 6.0 Hz, 1H), 2.54 (dd, *J*=13.8, 8.2 Hz, 1H), 1.27 (s, 18H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.91, 114.14 (d, J_{CP}=3.7 Hz), 138.36 (d, J_{CP}=13.2 Hz), 138.08 (d, J_{CP}=12.9 Hz), 132.83, 132.64, 128.62, 128.50, 128.43, 128.26 (d, J_{CP}=6.9 Hz), 121.95, 121.34, 57.77 (d, J_{CP}=20.7 Hz), 55.97, 37.35 (d, J_{CP}=14.3 Hz), 34.81, 22.68; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.40 ppm. ESI-MS calcd for $C_{32}H_{45}NOPS$: *m*/*z* (%): 522.2954 ($M+H^+$), found: 522.2949.

4.3.8. Compound ***(S, R$_S$)-X8***. $[\alpha]_D^{20}$= −11.6 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 1592, 1508, 1460, 1327, 1236, 1121, 1044, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.35–7.26 (m, 8H), 6.47 (s, 2H), 4.48–4.42 (m, 1H), 3.80 (s, 3H), 3.79 (s, 6H), 3.64 (d, *J*=3.8, 1H), 2.85 (dd, *J*=13.8, 6.4 Hz, 1H), 2.53 (dd, *J*=13.8, 8.1 Hz, 1H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.14, 137.96, 137.83, 137.75 (d, $J_{C,P}$=12.3 Hz), 137.44, 137.40, 132.88 (d, $J_{C,P}$=19.6 Hz), 132.54 (d, $J_{C,P}$=19.0 Hz), 128.72, 128.53 (d, $J_{C,P}$=6.7 Hz), 128.30, 104.08, 60.72, 57.94 (d, $J_{C,P}$=21.0 Hz), 56.06, 56.00, 37.14 (d, $J_{C,P}$=4.4 Hz), 22.56; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.71 ppm. ESI-MS calcd for $C_{27}H_{34}NNaO_4PS$: *m*/*z* (%): 522.1838 ($M+Na^+$), found: 522.1819.

4.3.9. Compound ***(S, R$_S$)-X9***. $[\alpha]_D^{20}$= −25.6 (*c*=0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.48–7.44 (m, 2H), 7.38–7.33 (m, 3H), 7.28–7.22 (m, 5H), 6.73 (s, 2H), 4.96–4.90 (m, 1H), 3.51–3.46 (m, 1H), 2.98 (dd, *J*=13.8, 7.2 Hz, 1H), 2.65 (dd, *J*=13.8, 8.6 Hz, 1H), 2.45 (s, 3H), 2.22 (s, 3H), 1.98 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.28, 138.28 (d, J_{CP}=12.9 Hz), 137.53 (d, J_{CP}=12.9 Hz), 134.09 (d, J_{CP}=4.3 Hz), 132.85 (d, J_{CP}=11.9 Hz), 132.66 (d, J_{CP}=11.9 Hz), 128.83, 128.64, 128.54 (d, J_{CP}=4.8 Hz), 128.39, 128.32, 113.98, 57.04, 56.85, 55.94, 55.20, 37.32 (d, J_{CP}=13.9 Hz), 55.57; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.33 ppm. ESI-MS calcd for $C_{27}H_{35}NOPS$: *m*/*z* (%): 452.2171 ($M+H^+$), found: 452.2147.

4.3.10. Compound ***(S, R$_S$)-X10***. $[\alpha]_D^{20}$= +8.2 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2955, 1592, 1455, 1433, 1204, 11,476, 1113, 1062, 949, 731, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.37–7.30 (m, 5H), 7.29–7.24 (m, 3H), 6.05 (s, 2H), 5.03–4.94 (m, 1H), 4.61 (d, *J*=10.9 Hz, 1H), 3.76 (s, 9H), 2.85 (dd, *J*=13.8, 9.4 Hz, 1H), 2.49–2.43 (m, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.37, 139.25 (d, J_{CP}=13.3 Hz), 138.95 (d, J_{CP}=13.9 Hz), 132.98 (d, J_{CP}=19.2 Hz), 132.50 (d, J_{CP}=18.5 Hz), 128.30, 128.22 (d, J_{CP}=2.7 Hz), 128.16 (d, J_{CP}=2.2 Hz), 128.08, 112.13 (d, J_{CP}=5.4 Hz), 91.10, 55.79, 55.52, 55.19, 51.01 (d, J_{CP}=18.5 Hz), 35.93 (d, J_{CP}=13.7 Hz), 22.46; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −22.02 ppm. ESI-MS calcd for $C_{27}H_{35}NO_4PS$: *m*/*z* (%): 500.2019 ($M+H^+$), found: 500.2021.

4.3.11. Compound ***(R, R$_S$)-X10***. $[\alpha]_D^{20}$= −15.8 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2950, 1591, 1454, 1203, 1147, 1110, 1060, 949, 812, 738, 696, 588; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 2H), 7.35–7.29 (m, 5H), 7.25–7.16 (m, 5H), 6.86 (dd, *J*=6.9, 2.2 Hz, 1H), 6.68–6.60 (m, 2H), 6.07 (dd, *J*=7.6, 1.6 Hz, 1H), 5.99 (s, 2H), 5.07–5.02 (m, 1H), 4.60 (d, *J*=10.3 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 6H), 3.07–3.02 (m, 1H), 2.91 (dd, *J*=13.2, 11.0 Hz, 1H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.42, 139.15 (d, J_{CP}=12.9 Hz), 138.30 (d, J_{CP}=13.2 Hz), 132.86 (d, J_{CP}=14.7 Hz), 132.67 (d, J_{CP}=14.8 Hz), 128.30, 128.19 (d, J_{CP}=6.6 Hz), 127.91, 127.90 (d, J_{CP}=9.9 Hz), 126.49, 110.54 (d, J_{CP}=2.5 Hz), 91.14, 55.80, 55.69, 55.15, 50.92 (d, J_{CP}=22.8 Hz), 36.72 (d, J_{CP}=13.3 Hz), 22.40; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −22.39 ppm. ESI-MS calcd for $C_{27}H_{35}NO_4PS$: *m*/*z* (%): 500.2019 ($M+H^+$), found: 500.2017.

4.3.12. Compound ***(S, R$_S$)-X12***. $[\alpha]_D^{20}$= +30.7 (*c*=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2923, 1433, 1055, 907, 733; ^{1}H NMR (400 MHz, C_6D_6) δ 7.49–7.44 (m, 4H), 7.14–7.04 (m, 6H), 3.44(d, *J*=8.6 Hz, 1H), 3.31–3.24 (m, 1H), 2.31–2.18 (m, 2H), 1.90–1.83 (m, 1H), 1.66–1.50 (m, 5H), 1.25–1.17 (m, 1H), 1.10 (s, 9H), 1.06–0.99 (m, 3H), 0.96–0.86 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.97 (d, $J_{C,P}$=14.2 Hz), 139.09 (d, $J_{C,P}$=15.4 Hz), 133.68 (d, $J_{C,P}$=19.9 Hz), 129.09, 128.81

(d, $J_{C,P}$=6.8 Hz), 128.72 (d, $J_{C,P}$=6.1 Hz), 128.51, 60.14 (d, $J_{C,P}$=13.3 Hz), 56.05, 43.81 (d, $J_{C,P}$=6.7 Hz), 33.11 (d, $J_{C,P}$=13.7 Hz), 29.22, 28.17, 26.74, 26.52 (d, $J_{C,P}$=7.9 Hz), 22.78 (d, $J_{C,P}$=0.9 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ= −9.10 ppm. ESI-MS calcd for $C_{24}H_{35}NOPS$: m/z (%): 416.2171 ($M+H^+$), found: 416.2173.

4.3.13. Compound ***(S, R_S)-X13***. $[\alpha]_D^{20}$= +67.6 (c=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2899, 1433, 1044, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.44 (m, 2H), 7.36−7.27 (m, 8H), 3.42 (d, J=7.9 Hz, 1H), 2.82−2.74 (m, 1H), 2.55−2.50 (m, 1H), 1.98−1.91 (m, 4H), 1.76−1.44 (m, 12H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.00 (d, J_{CP}=13.9 Hz), 137.65 (d, J_{CP}=15.7 Hz), 133.94 (d, J_{CP}=20.2 Hz), 131.91 (d, $J_{C,P}$=17.9 Hz), 129.14, 128.50 (d, J_{CP}=7.2 Hz), 128.33 (d, $J_{C,P}$=5.7 Hz), 127.98, 63.46 (d, $J_{C,P}$=11.6 Hz), 57.10, 38.81, 36.86 (d, $J_{C,P}$=5.8 Hz), 36.77, 32.11 (d, $J_{C,P}$=13.1 Hz), 28.28, 23.27 (d, $J_{C,P}$=3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ= −22.65 ppm. ESI-MS calcd for $C_{28}H_{39}NOPS$: m/z (%): 468.2428 ($M+H^+$), found: 468.2487.

4.3.14. Compound ***(S, R_S)-X14***. $[\alpha]_D^{20}$= +25.7 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 2956, 1495, 1237, 1042, 903, 828, 756; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 4H), 7.35−7.27 (m, 6H), 3.46−3.36 (m, 1H), 3.26 (d, J=8.0 Hz, 1H), 2.24−2.21 (m, 1H), 1.69−1.59 (m, 2H), 1.54−1.40 (m, 1H), 1.36−1.20 (m, 1H), 1.16 (s, 9H), 0.88 (t, J=7.5 Hz, 3H), 0.78 (t, J=7.5 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ= −22.27 ppm ^{13}C NMR (125 MHz, CDCl3) δ 138.54 (d, $J_{C,P}$=62.5 Hz), 138.19 (d, $J_{C,P}$=15 Hz), 133.06 (d, $J_{C,P}$=20 Hz), 132.18 (d, $J_{C,P}$=18.75 Hz), 128.77, 128.4 (d, $J_{C,P}$=3.75 Hz), 128.35 (d, $J_{C,P}$=3.75 Hz), 56.11, 56.08, 56.00, 46.78 (d, $J_{C,P}$=6.25 Hz), 31.98 (d, $J_{C,P}$=13.75 Hz), 22.51, 22.50, 22.31, 21.57, 12.01, 11.82. ESI-MS calcd for $C_{23}H_{34}NNaOPS$: m/z (%): 426.1997 ($M+H^+$), found: 426.1991.

4.3.15. Compound ***(S, R_S)-X15***. $[\alpha]_D^{20}$= +32.3 (c=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2956, 1491, 1251, 1048, 913, 838, 782; ^{1}H NMR (400 MHz, C_6D_6) δ 7.47−7.43 (m, 4H), 7.16−7.03 (m, 6H), 3.34−3.24 (m, 2H), 2.25−2.16 (m, 3H), 1.09 (s, 9H), 0.87 (d, J=6.8 Hz, 3H), 0.72 (d, J=6.9 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 139.79 (d, $J_{C,P}$=13.9 Hz), 139.10 (d, $J_{C,P}$=15.3 Hz), 133.62 (d, $J_{C,P}$=19.8 Hz), 132.66 (d, $J_{C,P}$=18.3 Hz), 129.08, 128.81(d, $J_{C,P}$=6.9 Hz), 128.74 (d, $J_{C,P}$=6.2 Hz), 128.55, 60.41,56.02, 33.44(d, $J_{C,P}$=6.9 Hz), 32.24(d, $J_{C,P}$=13.85 Hz), 22.69, 18.27, 17.32; ^{31}P NMR (162 MHz, C_6D_6) δ= −9.05 ppm. ESI-MS calcd for $C_{21}H_{31}NOPS$: m/z (%): 376.1858 ($M+H^+$), found: 376.1859.

4.3.16. Compound ***(S, R_S)-X16***. $[\alpha]_D^{20}$= +29.3 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 2968, 1481, 1271, 1028, 903, 848, 762; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (ddd, J=7.3, 4.8, 1.9 Hz, 2H), 7.38−7.25 (m, 8H), 3.33 (d, J=7.5 Hz, 1H), 3.09−2.75 (m, 1H), 2.46 (ddd, J=13.8, 4.9, 1.9 Hz, 1H), 2.00 (ddd, J=14.0, 10.6, 4.8 Hz, 1H), 1.26 (s, 9H), 0.91 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.79 (d, $J_{C,P}$=13.5 Hz), 137.69 (d, $J_{C,P}$=15 Hz), 134.96 (d, $J_{C,P}$=20 Hz), 131.84 (d, $J_{C,P}$=17.5 Hz), 129.16, 128.49 (d, $J_{C,P}$=7.5 Hz), 128.32 (d, $J_{C,P}$=5 Hz), 127.98, 63.06, 62.97, 56.96, 35.32 (d, $J_{C,P}$=6.25 Hz), 33.8 (d, $J_{C,P}$=13.75 Hz), 26.80, 23.13 (d, $J_{C,P}$=5 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ= −22.24 ppm. ESI-MS calcd for $C_{22}H_{33}NOPS$: m/z (%): 390.1942 ($M+H^+$), found: 390.1949.

4.3.17. Compound ***(S, R_S)-X17***. $[\alpha]_D^{20}$= −7.2 (c=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2956, 1482, 1176, 1039, 895, 743, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.36 (m, 4H), 7.34−7.30 (m, 7H), 6.30−6.27 (m, 2H), 4.53−4.45 (m, 1H), 3.56 (d, J=7.5 Hz, 1H), 2.78 (dd, J=13.9, 7.6 Hz, 1H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.28 (d, J_{CP}=5.4 Hz), 142.21, 137.80 (d, J_{CP}=2.2 Hz), 137.67 (d, J_{CP}=2.0 Hz), 132.77 (d, J_{CP}=17.0 Hz), 132.57 (d, J_{CP}=16.8 Hz), 128.74, 128.71, 128.52 (d, J_{CP}=6.5 Hz), 128.46 (d, J_{CP}=6.6 Hz), 110.24, 107.52 (d, J_{CP}=1.6 Hz), 56.23, 52.43 (d, J_{CP}=19.8 Hz), 35.11 (d, J_{CP}=14.4 Hz), 22.41; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.44 ppm. ESI-MS calcd for $C_{22}H_{27}NO_2PS$: m/z (%): 400.1495 ($M+H^+$), found: 400.1483.

4.3.18. Compound ***(S, R_S)-X18***. $[\alpha]_D^{20}$= −26.8 (c=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2957, 2865, 1433, 1382, 1067, 817, 739, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.42 (m, 2H), 7.35−7.29 (m, 5H), 7.22 (d, J=4.8 Hz, 2H), 7.02 (d, J=3.2 Hz, 1H), 6.93−6.91 (m, 1H), 4.77−4.71 (m, 1H), 3.66 (d, J=4.7 Hz, 1H), 2.94 (dd, J=13.8, 6.8 Hz, 1H), 2.59 (dd, J=13.8, 7.8 Hz, 1H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.94 (d, J_{CP}=18.7 Hz), 137.91 (d, J_{CP}=12.6 Hz), 137.40 (d, J_{CP}=12.9 Hz), 132.82 (d, J_{CP}=3.2 Hz), 132.63 (d, J_{CP}=3.5 Hz), 128.86, 128.64, 128.62 (d, J_{CP}=9.6 Hz), 128.45 (d, J_{CP}=6.7 Hz), 126.71, 125.75 (d, J_{CP}=1.7 Hz), 125.26, 56.18, 53.51 (d, J_{CP}=20.4 Hz), 38.30 (d, J_{CP}=14.1 Hz), 22.53; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −23.78 ppm; ESI-MS calcd for $C_{22}H_{26}NNaOPS_2$: m/z (%): 438.1086 ($M+H^+$), found: 438.1075.

4.4. General procedure for the synthesis of Xiao-Phos variants (*S*, R_S)-X11 and (*R*, R_S)-X11

A solution of diphenyl methyl phosphonic lithium (4.5 mmol) that containing TMEDA (4.5 mmol) in THF was added very slowly to the solution of the imine **N11** (337.5 mg, 1.5 mmol) in dry THF (10 mL) at room temperature. The mixture was stirred until completion of the imine as indicated by TLC, followed by hydrolysis with 10 mL of water and diluted with EtOAc. The organic layer was separated, the aqueous phase was extracted three times with EtOAc (3×10 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo to afford two diastereoisomers mixture, which should not be isolated by column chromatography.

Et_3N (15.0 mmol) was added to the above mixture solution in dry CH_2Cl_2 (10 mL) containing **(*R*, R_S)-X11** and **(*S*, R_S)-X11** and the mixture was stirred at room temperature for 5 min, and then the corresponding $^iPr_3SiCl$ reagent was slowly added. The reaction mixture was then stirred until completion of **X11** as indicated by TLC, followed by quenching with 10 mL of water. The aqueous phase was separated and extracted three times with 20 mL of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. The product was purified by chromatography to afford two diastereomers in 90% yield.

TBAF (1.2 equiv) was added slowly to the solution of **(*S*, R_S)-isomer** or in dry THF (10 mL) and the mixture was stirred at room temperature until completion of material as indicated by TLC, followed by washing with 10 mL of water. The aqueous phase was separated and extracted three times with 20 mL of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. Pure **(*S*, R_S)-X11** could be obtained in 91% isolated yield. The corresponding (***R*, R_S**)-**X11** could be also obtained in 93% yield using the same procedure.

4.4.1. Compound ***(S, R_S)-X11***. $[\alpha]_D^{20}$= +30.6 (c=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2955, 1457, 1258, 1034, 917, 870, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.51−7.46 (m, 2H), 7.35−7.30 (m, 5H), 7.27−7.26 (m, 3H), 6.86 (dd, J=6.9, 2.2 Hz, 1H), 6.68−6.60 (m, 2H), 6.07 (dd, J=7.6, 1.6 Hz, 1H), 5.34 (d, 5.34 Hz, 1H), 4.31−4.23 (m, 1H), 3.08 (m, 1H), 2.37−2.32 (m, 1H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.66, 138.66, 138.65 (d, $J_{C,P}$=27 Hz), 132.97 (d, $J_{C,P}$=19.5 Hz), 132.44 (d, $J_{C,P}$=18.4 Hz), 129.01, 128.65, 128.43, 128.37 (d, $J_{C,P}$=3.0 Hz), 128.32, 7.87 (d, $J_{C,P}$=6.6 Hz), 127.14, 118.86, 116.77, 61.85 (d, $J_{C,P}$=17.4 Hz), 56.76, 36.12 (d, $J_{C,P}$=14.1 Hz), 22.71; ^{31}PNMR (162 MHz, $CDCl_3$) δ= −21.40 ppm. ESI-MS calcd for $C_{24}H_{29}NO_2PS$: m/z (%): 426.1651 ($M+H^+$), found: 426.1717.

4.4.2. Compound ***(R, R_S)-X11***. $[\alpha]_D^{20}$= −77.8 (c=0.50, $CHCl_3$). IR (neat) ν (cm^{-1}) 2957, 1598, 1456, 1367, 1282, 1044, 857, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.45−7.40 (m, 2H), 7.31−7.17 (m,

8H), 7.03–6.98 (m, 2H), 6.76–6.73 (m, 2H), 4.90 (t, J=4.4 Hz, 1H), 4.61–4.55 (m, 1H), 2.86–2.80 (s, 1H), 2.75–2.69 (s, 1H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.11, 137.44 (d, $J_{C,P}$=11.0 Hz), 137.06 (d, $J_{C,P}$=11.4 Hz), 132.91 (d, $J_{C,P}$=18.9 Hz), 132.74 (d, $J_{C,P}$=18.8 Hz), 129.03, 128.77, 128.57, 128.50, 128.35 (d, $J_{C,P}$=6.9 Hz), 126.00 (d, $J_{C,P}$=5.0 Hz), 119.43, 116.52, 56.06, 55.85(d, $J_{C,P}$=18.2 Hz), 36.21 (d, $J_{C,P}$=15.1 Hz), 22.53; ^{31}P NMR (162 MHz, $CDCl_3$) δ= −24.21 ppm. ESI-MS calcd for $C_{24}H_{29}NO_2PS$: m/z (%): 426.1651 ($M+H^+$), found: 426.1712.

4.5. General procedure for the synthesis of chiral β-aminophosphines from Xiao-Phos

BH_3-THF(2.0 equiv) was added slowly to the solution of corresponding Xiao-Phos in dry THF at −30 °C and the mixture was stirred for 2 h at −30 °C until completion of material as indicated by TLC followed by washing with 10 mL of water. The aqueous phase was separated and extracted three times with 20 mL of EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. 4M HCl (2.0 equiv) was added slowly to the solution of the above residue in MeOH and the reaction mixture was stirred at room temperature for 3 h until completion of material as indicated by TLC followed by washing with aq $NaHCO_3$ and 10 mL aq brine water. The organic layers was separated and extracted three times with 20 mL EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. Et_2NH (2.0 mL) was added slowly to the above residue and the mixture was stirred at 55 °C for 6 h under the protection of N_2 until completion of material as indicated by TLC. The reaction mixture was dried in vacuo and residue was directly purified by chromatography to afford chiral β-aminophosphines. The yield of **(*S*)-23** is 80%, **(*S*)-24** is 82%, **(*S*)-25** is 80%, **(*S*)-26** is 84%.

For synthesis of **(*S, R*$_S$)-X1-BH$_3$.** $[\alpha]_D^{20}$= −19.4 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 2893, 1484, 1194, 1087, 905, 715;^{1}H NMR (500 MHz, CDCl3) δ 7.73–7.64 (m, 2H), 7.55–7.49 (m, 2H), 7.49–7.36 (m, 4H), 7.31 (td, J=7.4, 1.7 Hz, 2H), 7.28 (d, J=1.6 Hz, 1H), 7.24–7.14 (m, 3H), 4.82 (ddt, J=10.9, 7.4, 5.6 Hz, 1H), 3.91 (d, J=5.1 Hz, 1H), 3.10 (ddd, J=14.7, 10.3, 7.6 Hz, 1H), 2.77 (ddd, J=14.7, 11.8, 5.7 Hz, 1H), 1.36–1.11 (m, 3H), 1.06 (s, 9H); ^{31}P NMR (200 MHz, $CDCl_3$) δ 12.37(d, $J_{B,P}$=44.0 Hz); ^{13}C NMR (125 MHz, CDCl3) δ 140.79(d, $J_{C,P}$=8.75 Hz), 132.18, 132.13, 132.11, 132.06, 131.38(d, $J_{C,P}$=2.5 Hz), 131.20(d, $J_{C,P}$=2.5 Hz), 129.56, 129.11, 129.04, 128.96, 128.92, 128.81, 128.73, 128.64, 128.48, 128.25, 127.55, 56.36(d, $J_{C,P}$=2.5 Hz), 56.12, 34.41(d, $J_{C,P}$=33.75 Hz), 22.49; ESI-MS calcd for $C_{24}H_{31}BNNaOPS$: m/z (%): 446.1862 ($M+Na^+$), found: 446.1849.

Chiral β-aminophosphines ***(S)-27*–*(S)-30*** were prepared from the methods reported in the literature,[11] while ***(S)-25*** were characterized by comparison of their physical and spectroscopic data with the reported in the literature.[12]

4.5.1. Compound ***(S)-23***. $[\alpha]_D^{20}$= +33.9 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 2951, 1475, 1298, 1059, 917, 824, 769; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (ddd, J=7.4, 4.8, 1.5 Hz, 2H), 7.41 (ddd, J=8.7, 7.3, 1.6 Hz, 2H), 7.36–7.28 (m, 6H), 2.87 (tt, J=9.6, 3.7 Hz, 1H), 2.28 (dt, J=13.6, 3.5 Hz, 1H), 2.01–1.91 (m, 1H), 1.43–1.31 (m, 3H), 1.31–1.22 (m, 3H), 1.22–1.15 (m, 1H), 0.83 (t, J=7.4 Hz, 3H), 0.79 (t, J=7.4 Hz, 3H); ^{31}PNMR (200 MHz, $CDCl_3$) δ= −21.13 ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.35, 139.26, 138.22, 138.12, 133.29, 133.13, 132.52, 132.37, 128.85, 128.49, 128.42 (d, $J_{C,P}$=3.8 Hz), 128.34 (d, $J_{C,P}$=3.8 Hz), 49.78, 49.67, 48.18, 48.12, 34.96, 34.87, 22.18, 21.45, 12.04, 12.02; ESI-MS calcd for $C_{19}H_{27}NP$: m/z (%): 300.1876 ($M+H^+$), found: 300.1871.

4.5.2. Compound ***(S)-24***. $[\alpha]_D^{20}$= +46.8 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 3200, 2957, 1456, 1372, 1282, 1044, 857, 750; ^{1}H NMR (500 MHz, CDCl3) δ 7.57–7.42 (m, 4H), 7.42–7.32 (m, 10H), 7.30–7.22 (m, 1H), 4.06 (ddd, J=9.1, 7.6, 4.9 Hz, 1H), 2.65–2.56 (m, 1H), 2.54–2.40 (m, 1H), 1.87 (s, 2H); ^{31}P NMR (200 MHz, CDCl3) δ= −21.75 ppm; ^{13}C NMR (125 MHz, CDCl3) δ 146.60, 146.55, 138.82 (d, $J_{C,P}$=12.5 Hz), 138.12 (d, $J_{C,P}$=12.5 Hz), 133.13 (d, $J_{C,P}$=20 Hz), 132.69 (d, $J_{C,P}$=18.75 Hz), 128.91, 128.63, 128.59, 128.58, 128.56, 128.50, 127.27, 126.23, 53.83, 53.76 (d, $J_{C,P}$=16.25 Hz), 40.12 (d, $J_{C,P}$=15 Hz); ESI-MS calcd for $C_{19}H_{27}NP$: m/z (%): 305.1333 ($M+H^+$), found: 305.1127.

4.5.3. Compound ***(S)-26***. $[\alpha]_D^{20}$= +24.1 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 3180, 2980, 1372, 1272, 1084, 897, 790; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.22 (m, 3H), 7.21–7.13 (m, 3H), 2.41–2.32 (m, 2H), 1.68 (ddd, J=13.8, 11.4, 4.7 Hz, 1H), 1.29 (s, 2H), 0.77 (s, 9H); ^{31}P NMR (200 MHz, $CDCl_3$) δ= −19.46 ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.68 (d, $J_{C,P}$=12.5 Hz), 137.60 (d, $J_{C,P}$=15 Hz), 133.34 (d, $J_{C,P}$=20 Hz), 132.03 (d, $J_{C,P}$=6.25 Hz), 128.83, 128.32 (d, $J_{C,P}$=6.25 Hz), 128.19 (d, $J_{C,P}$=7.5 Hz), 127.97, 57.47 (d, $J_{C,P}$=12.5 Hz), 34.74 (d, $J_{C,P}$=6.25 Hz), 32.47 (d, $J_{C,P}$=10 Hz), 25.75; ESI-MS calcd for $C_{18}H_{25}NP$: m/z (%): 286.3708 ($M+H^+$), found: 286.3711.

4.5.4. Compound ***(S)-27***. $[\alpha]_D^{20}$= +15 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 3108, 2951, 1680, 1059, 917, 824, 769; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J=19.6 Hz, 3H), 7.59–7.49 (m, 2H), 7.48–7.39 (m, 2H), 7.40–7.32 (m, 10H), 7.31–7.25 (m, 1H), 7.16 (dt, J=27.0, 7.2 Hz, 1H), 6.73 (d, J=7.4 Hz, 1H), 5.46–5.34 (m, 1H), 2.88 (dd, J=14.1, 9.5 Hz, 1H), 2.71 (dd, J=14.1, 5.5 Hz, 1H); ^{19}F NMR (282 MHz, CDCl3) δ= −62.79 ppm; ^{31}P NMR (200 MHz, CDCl3) δ= −22.81 ppm; ^{13}C NMR (125 MHz, CDCl3) δ 163.63, 141.94 (d, $J_{C,P}$=6.25 Hz), 137.78 (d, $J_{C,P}$=12.5 Hz), 137.48 (d, $J_{C,P}$=12.5 Hz), 136.16, 133.06, 132.90, 132.71, 132.56, 131.95 (d, $J_{C,F}$=33.75 Hz), 130.59, 130.51, 130.47, 130.39, 129.26, 128.99, 128.88, 128.78 (d, $J_{C,P}$=7.5 Hz), 128.70 (d, $J_{C,P}$=7.5 Hz), 127.90, 127.28 (d, $J_{C,P}$=2.5 Hz), 126.40, 125.86, 124.99, 124.96, 124.93, 122.88 (q, $J_{C,F}$=271.25 Hz), 53.01 (d, $J_{C,P}$=16.5 Hz), 35.91(d, $J_{C,P}$=16.5 Hz); ESI-MS calcd for $C_{29}H_{22}F_6NNaOP$: m/z (%): 568.1258 ($M+Na^+$), found: 568.1235.

4.5.5. Compound ***(S, R)-28***. $[\alpha]_D^{20}$= +22.6 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 2959, 1680, 1582, 1382, 1275, 1046, 808, 723, 699; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.43 (ddd, J=7.4, 4.9, 1.5 Hz, 2H), 7.40–7.31 (m, 6H), 5.85 (d, J=7.4 Hz, 1H), 4.93 (d, J=6.5 Hz, 1H), 4.30–4.06 (m, 1H), 3.96–3.62 (m, 1H), 2.29–2.23 (m, 2H), 2.20–2.09 (m, 1H), 1.47 (s, 9H), 1.39 (ddd, J=9.7, 7.4, 3.8 Hz, 1H), 1.31 (dt, J=21.1, 6.8 Hz, 1H), 1.26–1.15 (m, 2H), 0.94 (d, J=6.8 Hz, 3H), 0.87 (d, J=6.8 Hz, 3H), 0.83 (dt, J=10.8, 7.4 Hz, 6H); ^{31}P NMR (200 MHz, CDCl3) δ= −23.30 ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.60, 155.83, 138.61 (d, $J_{C,P}$=15 Hz), 138.26 (d, $J_{C,P}$=12.5 Hz), 133.01 (d, $J_{C,P}$=20 Hz), 132.73 (d, $J_{C,P}$=18.75 Hz), 130.65, 128.76 (d, $J_{C,P}$=8.75 Hz), 128.60, 128.55, 128.48, 79.77, 60.19, 48.45 (d, $J_{C,P}$=15 Hz), 45.18 (d, $J_{C,P}$=6.25 Hz), 42.81, 31.68 (d, $J_{C,P}$=13.75 Hz), 30.47, 28.33, 22.48, 21.80, 19.40, 17.70, 11.71, 11.66; ESI-MS calcd for $C_{28}H_{43}N_2NaO_3P$: m/z (%): 521.2904 ($M+H^+$), found: 521.2915.

4.5.6. Compound ***(S)-29***. $[\alpha]_D^{20}$= +13.4 (c=0.33, $CHCl_3$). IR (neat) ν (cm^{-1}) 2957, 2865, 1433, 1382, 1067, 817, 739, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J=8.5 Hz, 3H), 7.48–7.44 (m, 2H), 7.43–7.39 (m, 2H), 7.33–7.17 (m, 6H), 5.88 (d, J=9.0 Hz, 1H), 4.64–4.29 (m, 1H), 2.52–2.29 (m, 2H), 1.64 (m, 1H), 1.51–1.37 (m, 3H), 1.36–1.26 (m, 1H), 0.90 (td, J=7.3, 0.8 Hz, 6H); ^{31}P NMR (200 MHz, $CDCl_3$) δ= −22.98 ppm; 19F NMR (282 MHz, CDCl3) δ= −62.77 ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.69, 138.21 (d, $J_{C,P}$=13.75 Hz), 138.05 (d, $J_{C,P}$=12.5 Hz), 136.61, 132.84 (d, $J_{C,P}$=8.75 Hz), 132.69 (d, $J_{C,P}$=7.5 Hz), 131.93 (q, $J_{C,F}$=32.5 Hz), 128.98, 128.90, 128.67(d, $J_{C,P}$=3.75 Hz), 128.62(d, $J_{C,P}$=3.75 Hz), 127.05 (d, $J_{C,F}$=3.75 Hz), 124.76 (dd, $J_{C,F}$=7.5, 3.8 Hz), 122.91 (q, $J_{C,F}$=273 Hz), 50.28 (d, $J_{C,P}$=13.75 Hz), 45.67 (d, $J_{C,P}$=7.5 Hz), 31.21 (d, $J_{C,P}$=15 Hz),

22.20, 22.02, 11.55, 11.40; ESI-MS calcd for $C_{28}H_{28}F_6NNaOP$: *m*/*z* (%): 562.1705 ($M+Na^+$), found: 562.1703.

4.5.7. Compound ***(S)-30***. $[\alpha]_D^{20}$= −6.9 (*c*=0.33, $CHCl_3$). IR (neat) *ν* (cm^{-1}) 2959, 1582, 1453, 1382, 1262, 1046, 817, 739, 695; ^1H NMR (500 MHz, $CDCl_3$) *δ* 8.67 (s, 1H), 7.68 (d, *J*=9.1 Hz, 3H), 7.54–7.41 (m, 4H), 7.38–7.30 (m, 6H), 6.32 (s, 1H), 4.84 (s, 1H), 2.47 (dd, *J*=14.1, 3.9 Hz, 1H), 2.37 (dd, *J*=14.0, 8.8 Hz, 1H), 1.74 (d, *J*=36.9 Hz, 2H), 1.44–1.19 (m, 4H), 0.88 (dt, *J*=14.3, 7.3 Hz, 6H); ^{31}P NMR (200 MHz, CDCl3) *δ*= −24.09 ppm; ^{19}F NMR (282 MHz, CDCl3) *δ*= −63.02 ppm; ^{13}C NMR (125 MHz, CDCl3) *δ* 179.61, 138.77, 137.67 (d, $J_{C,P}$=10 Hz), 132.96 (d, $J_{C,P}$=18.75 Hz), 132.66(d, $J_{C,P}$=18.75 Hz), 129.02 (d, $J_{C,P}$=18.75 Hz), 128.64 (d, $J_{C,P}$=6.25 Hz), 123.21, 122.78 (d, $J_{C,P}$=271.25 Hz), 118.95, 118.92, 118.89, 55.02 (d, $J_{C,P}$=15 Hz), 44.94, 30.68, 22.45, 11.70, 11.51; ESI-MS calcd for $C_{28}H_{30}F_6N_2SP$: *m*/*z* (%): 571.1766 ($M+H^+$), found: 571.1761.

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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.tet.2015.12.002.

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