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BABIPhos Family of Biaryl Dihydrobenzooxaphosphole Ligands for Asymmetric Hydrogenation

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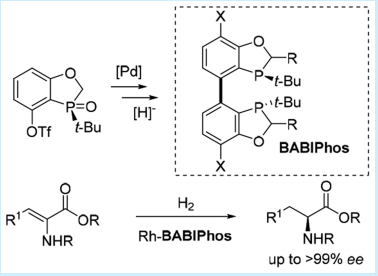
Supporting Information

ABSTRACT: Novel bidentate phosphine ligands **BABIPhos** featuring a biaryl bis-dihydrobenzooxaphosphole core are presented. Their synthesis was achieved via Pd-catalyzed reductive homocoupling of dihydrobenzooxaphosphole aryl triflates. An efficient route toward various analogues was also established, giving access to phosphines with different electronic and steric properties. The newly obtained ligands demonstrated high efficiency and selectivity in Rh-catalyzed asymmetric hydrogenation of di- and trisubstituted enamides. This new class of ligands is complementary to previously described bidentate benzooxaphosphole ligands **BIBOP**.



The development of chiral ligands remains a central theme in homogeneous asymmetric catalysis. Since the discovery of BINAP,[1] numerous atropisomeric phosphine ligands based on a biaryl backbone have been developed and established as key tools in asymmetric hydrogenation and other catalytic transformations (Figure 1A).[2] Advances in this area are focused on modification

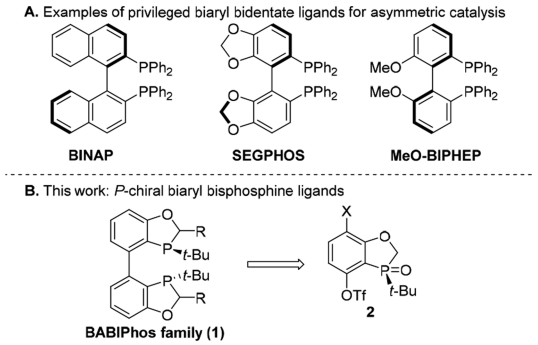


Figure 1. Bidentate biaryl phosphine ligands.

of a chiral biaryl skeleton for fine-tuning of the steric and electronic properties of the ligand, as well as its dihedral angle. We have envisioned that shifting chirality from a biaryl axis into phosphorus atom can offer a complementary mode of stereo-induction around the metal center while preserving the rigidity of the transition state due to the biaryl architecture of the ligand. Given our recent success in development of chiral ligands based on a benzooxaphosphole core,[3] we were naturally interested in further expanding our library with biaryl bidentate phosphorus ligands (Figure 1B). Herein, we report a new series of *P*-chiral bidentate biaryl dihydrobenzooxaohosphole (**BABIPhos**) ligands possessing an achiral biaryl backbone and their application in asymmetric hydrogenation of functionalized di- and trisubstituted alkenes.

To access this class of ligands, we aimed to developed transition-metal catalyzed reductive homocoupling of aryl triflate **2** to construct a biaryl backbone.[4,5] Notably, bidentate biaryl ligands are traditionally obtained by introduction of a phosphine moiety into preformed bis-functionalized biaryl derivatives.[2] Thus, under Pd-catalyzed homocoupling conditions using sterically hindered *o*-Tol_3P ligand **2a** can be converted to the desired biaryl phosphine oxide, albeit in low conversion and with poor selectivity (Table 1, entry 1). Hydrolysis and reduction of the triflate group were the major observed side reactions. Notably, high temperature (140 °C) was required to initiate the homocoupling. Screening of the ligands revealed that biaryl monodentate ligands XPhos or BI-DIME[6] provided full conversion and minimized byproduct formations (entries 2 and 4). More sterically hindered ligands, such as *t*-BuXPhos or Me-BIDIME, were less effective (entries 3 and 5). In general, bidentate ligands did not promote homocoupling (entries 6 and 7), with the exception of DTBPF (entry 8), which provided excellent conversion. However, in this case, purification of the dimeric phosphine oxide from the reaction mixture was found to be challenging. The presence of an external halide source proved to be crucial, as only traces of product were observed without any additives (entry 9). Tetraethylamonium iodide was identified as an optimal salt leading to the clean formation of the product

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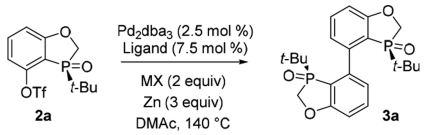
Table 1. Optimization of Reductive Homocoupling of 2a[a]



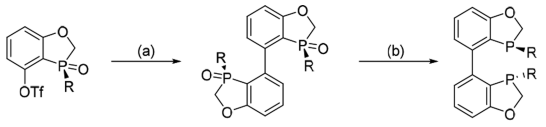
entry	ligand	MX	% 2a[b]	% 3a[b]
1	*o*-Tol$_3$P	KBr	41	40
2	XPhos	KBr	0	81
3	*t*-BuXPhos	KBr	56	5
4	BI-DIME	KBr	0	83
5	Me-BI-DIME	KBr	6	78
6	BINAP	KBr	56	1
7	DPPF	KBr	68	0
8	DTBPF	KBr	0	92
9	BI-DIME	none	80	7
10	BI-DIME	*n*-Bu$_4$NBr	0	49
11	BI-DIME	Et$_4$NI	0	90

[a]Conditions: **2a** (1 equiv), Pd_2dba_3 (2.5 mol %), Ligand (7.5 mol %), MX (2 equiv), Zn dust (3 equiv), DMAc, 140 °C, 3h. [b]Relative HPLC integration of **2a**, **3a**, and other side products.

(entry 11). Importantly, Zn dust was found to be essential, as only traces of product were observed if Zn mesh was used.

Using the optimized reaction conditions (Table 1, entry 11), aryl triflate **2a** was converted to the corresponding dimeric phosphine oxide in 78% yield after crystallization (Scheme 1).

Scheme 1. Synthesis of BABIPhos Ligands[a]

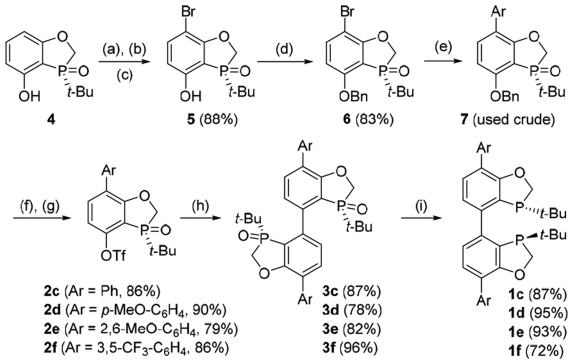


[a]Conditions: (a) **2a** (1 equiv), $Pd_2(dba)_3$ (2.5 mol %), BI-DIME (7.5 mol %) or XPhos (7.5 mol %), Et$_4$NI (2 equiv), Zn (3 equiv), DMAc, 140 °C; (b) $(Me_2HSi)_2O$ (3 equiv), Ti(O-*i*-Pr)$_4$ (2.3 equiv), THF, 65 °C.

Reduction of this product furnished the desired bis-phosphine **1a** (**BABIPhos**) in high yield. Additionally, analogous bis-benzooxaphosphole **1b** bearing a less hindered phenylphosphine moiety was obtained following this route.

In order to expand the newly discovered family of phosphines, an efficient route for the synthesis of aryl triflates **2** possessing substitution at the C7 positions has been developed next (Scheme 2). The route commenced with the synthesis of aryl bromide **5** via bromination of common intermediate **4**[6] after protection of phenol with bulky TBDPS group in order to avoid bromination at the C5 position. Further protecting group manipulations led to the benzyl-protected aryl bromide **6**. Its subsequent derivatization by Suzuki cross-coupling with various boronic acids delivered a series of benzooxaphosphole oxides **7** bearing an extended aryl backbone. These intermediates were then converted to the corresponding aryl triflates **2c–f** in high yields. The developed Pd-catalyzed reductive homocoupling was effective regardless of the electronic nature of C7-substituents of

Scheme 2. Synthesis of C7,C7′-Substituted BABIPhos Analogues[a]

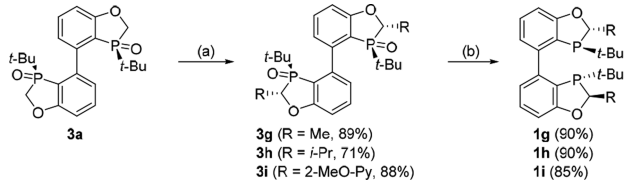


[a]Conditions: (a) TBDPSCl (1.1 equiv), Et$_3$N (1.3 equiv), DMAP (5 mol %), THF, rt, 88%; (b) NBS (1.03 equiv), CH_3CN, rt, quant; (c) TBAF (0.63 equiv), THF, rt; 83%; (d) BnBr (1.05 equiv), K_2CO_3 (1.2 equiv), DMF, rt, quant; (e) $ArB(OH)_2$ (1.2 equiv), $PdCl_2(PPh_3)_2$ (2 mol %), Na_2CO_3 (2.4 equiv), dioxane/water, 80 °C; (f) Pd/C (10 wt %), H_2 (300 psi), MeOH, rt; (g) $PhNTf_2$ (1.1 equiv), Et$_3$N (2.0 equiv), CH_2Cl_2, rt; (h) $Pd_2(dba)_3$ (2.5 mol %), XPhos (7.5 mol %), KBr (2 equiv), Zn (3 equiv), DMAc, 140 °C; (i) $(Me_2HSi)_2O$ (3 equiv), Ti(O-*i*-Pr)$_4$ (2.3 equiv), THF, 65 °C.

the aryl triflates and the desired biaryls **3c–f** were isolated in 78–96% yields. Finally, phosphine oxide reduction completed the synthesis of bis-benzooxaphospholes **1c–f** of different electronic nature. It is noteworthy that this newly developed strategy for the synthesis of modified triflates **2** opens avenue for expansion not only **BABIPhos** ligands' library but also related families of previously disclosed ligands, such as **BIBOP**, **BI-DIME**, and other benzooxaphosphole series.[3]

Furthermore, various C2,C2′-substituted BABIPhos analogues could be easily accessed by modification of the parent phosphine oxide **3a** via a deprotonation/alkylation strategy previously employed for the synthesis of various benzooxaphosphole ligands, such as **POP**, **BoQPhos**, and **JoshPhos**.[7] Gratifyingly, this procedure was also suitable for the synthesis of modified bis-benzooxapospholes **1g–i** allowing for further modulation of steric properties around the phosphorus atom of the ligands (Scheme 3).

Scheme 3. Synthesis of C2,C2′-Substituted BABIPhos Analogues[a]



[a]Conditions: (a) LDA (2.5 equiv), RX (2.5 equiv; MeI for **3g**, *i*-PrI for **3h**, 2-methoxy-6-(phenylsulfonyl)pyridine for **3i**), THF, −78 °C to rt; (b) $(Me_2HSi)_2O$ (3 equiv), Ti(O-*i*-Pr)$_4$ (2.3 equiv), THF, 65 °C.

To gain information on the coordination ability of the newly obtained bisphosphines, complex [Rh(*S*,*S*)-BABIPhos)(NBD)]-BF_4 was synthesized (Figure 2). As predicted, BABIPhos binds to the Rh center though both phosphorus atoms form a seven-membered ring chelate. Notably, the distance between Rh and P atoms as well as the P–Rh–P angle are similar to those described for analogous [Rh((*R*)-BINAP)(NBD)]BF_4.[8] On the other

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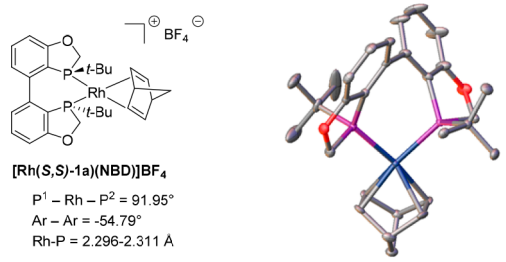
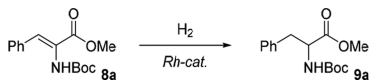


Figure 2. X-ray structure of [Rh((*S*,*S*)-**1a**)(NBD)]BF_4 complex.

hand, the biaryl dihedral angle is considerably smaller in the case of the BABIPhos-containing complex, compared to that of BINAP-based analogue, which creates a more rigid environment around the metal center and can potentially lead to unique catalytic properties of the complex.

Encouraged by the structural features of the **BABIPhos**–Rh complex, we were intrigued to test its catalytic abilities. For that purpose, we selected hydrogenation of enamides, as this transformation became a measure for efficiency of emerging ligands,[9] including the ones developed by our laboratories.[3a,7a] Therefore, trisubstituted enamide **8a** was subjected to hydrogenation in the presence of $Rh(NBD)_2BF_4$ and newly obtained ligands (Table 2). Gratifyingly, employment of parent **BABIPhos** ligand (**1a**) led to an excellent reactivity and selectivity of the reaction delivering the desired α-amino acid derivative **9a** in >99% ee (entry 1). In comparison, reaction in the presence of analogous ligand (**1b**) possessing phenyl phosphine moiety yielded the product as a racemic mixture (entry 2),

Table 2. Screen of Reaction Conditions for Rh-Catalyzed Asymmetric Hydrogenation of Enamides[a]



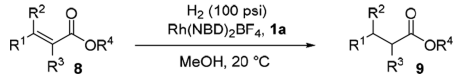
entry	[Rh]	ligand	solvent	*t* (°C); [H_2] (psi)	**9a:8a**	er
1	$Rh(NBD)_2BF_4$	**1a**	MeOH	20; 100	>99:1	>99.5:0.5
2	$Rh(NBD)_2BF_4$	**1b**	MeOH	20; 100	>99:1	48:52
3	$Rh(NBD)_2BF_4$	**1c**	MeOH	20; 100	>99:1	99.1:0.9
4	$Rh(NBD)_2BF_4$	**1d**	MeOH	20; 100	>99:1	99.5:0.5
5	$Rh(NBD)_2BF_4$	**1e**	MeOH	20; 100	>99:1	>99.5:0.5
6	$Rh(NBD)_2BF_4$	**1f**	MeOH	20; 100	>99:1	99.3:0.7
7	$Rh(NBD)_2BF_4$	**1g**	MeOH	20; 100	58:42	76:24
8	$Rh(NBD)_2BF_4$	**1h**	MeOH	20; 100	20:80	75:25
9	$Rh(NBD)_2BF_4$	**1i**	MeOH	20; 100	>99:1	50:50
10	$Rh(COD)_2BF_4$	**1a**	MeOH	20; 100	>99:1	>99.5:0.5
11	$Rh(NBD)_2OTf$	**1a**	MeOH	20; 100	>99:1	>99.5:0.5
12	$Rh(NBD)_2BF_4$	**1a**	DCM	20; 100	>99:1	>99.5:0.5
13	$Rh(NBD)_2BF_4$	**1a**	THF	20; 100	>99:1	>99.5:0.5
14	$Rh(NBD)_2BF_4$	**1a**	MeOH	20; 50	>99:1	>99.5:0.5
15	$Rh(NBD)_2BF_4$	**1a**	MeOH	20; 400	>99:1	>99.5:0.5
16	$Rh(NBD)_2BF_4$	**1a**	MeOH	60; 100	>99:1	99.2:0.8

[a]Conditions: **8a** (1 equiv), $Rh(NBD)_2BF_4$ (1 mol %), ligand (1 mol %), solvent (0.1 M).

indicating the importance of the *t*-Bu substituent on the phosphorus atom for stereoinduction. Testing of ligands **1c–f** revealed that reactivity and selectivity of the reduction is independent of the electronic nature of biaryl backbone, as in all cases high performance was observed (entries 3–6). The ligands possessing C2,C2′-substitution were not suitable for this transformation as loss of reactivity and/or selectivity was noted in these reactions (entries 7–9). To further verify the robustness of Rh–BABIPhos catalytic system, other reaction parameters were quickly examined. The reaction was equally efficient with different Rh-sources (entries 10 and 11), in several solvents (entries 12 and 13), and under various hydrogen pressure (entries 14 and 15). A slight decrease of enantioselectivity was found only under temperatures higher than 60 °C (entry 16).[10]

Hydrogenation of various trisubstituted enamides in the presence of 1 mol % of Rh–BABIPhos catalyst was investigated next (Table 3). Thus, different 2-amino-3-phenyl acrylates were

Table 3. Rh-Catalyzed Asymmetric Hydrogenation of Trisubstituted Enamides[a]



entry	R^1	R^2	R^3	R^4		ee (%)	yield (%)
1	Ph	H	NHBoc	Me	**9a**	>99	98
2	Ph	H	NHCbz	Me	**9b**	98	85
3	Ph	H	NHAc	Me	**9c**	>99	98
4	Ph	H	NHAc	Et	**9d**	99	98
5	Ph	H	NHAc	H	**9e**	98	90
6	Me	H	NHCbz	Me	**9f**	99	92
7	*p*-MeO-C_6H_4	H	NHAc	Me	**9g**	>99	97
8	*p*-CF_3-C_6H_4	H	NHBoc	Me	**9h**	>99	99
9	3-furyl	H	NHBoc	Me	**9i**	>99	74
10	3-benzothiophenyl	H	NHBoc	Me	**9j**	>99	99
11	Ph	NHAc	H	Et	**9k**	82	98
12	Me	NHAc	H	Me	**9l**	90	83

[a]Conditions: **8** (1 equiv), $Rh(NBD)_2BF_4$ (1 mol %), BABIPhos (**1a**) (1 mol %), MeOH, 100 psi of H_2, 20 °C.

successfully converted to α-amino acid derivatives in high yields and >98% ee, regardless of the protecting group on nitrogen (entries 1–3) or the nature of the ester (entry 4). The hydrogenation of acid-containing analogue **8e** was also efficient, although a slight decrease of enantioselectivity (98% ee) was observed. Notably, Rh-catalyzed hydrogenation of this substrate in the presence of (*S*)-BINAP gave the product in 84% enantiopurity.[1] Additionally, different substitution of the double bond is well tolerated, including alkyl (**8f**), electron-rich (**8g**), electron-deficient (**8h**) aryl, and heteroaryl (**8i,j**) groups. The reduction of 3,3-disubstituted acrylate derivatives leading to β-amino acid analogues gave the desired products **9k** and **9l** in good yield and moderate selectivity.

The generality of this system was further confirmed by hydrogenation of disubstituted enamides **10** (Scheme 4). High yields and enantioselectivities were achieved under standard reaction conditions for both phenyl- (**10a**) and naphthyl-substituted (**10b**) substrates.

In order to streamline selection between benzooxaphosphole based ligands, the catalytic properties of **BABIPhos** were compared to those of another dimeric ligand **BIBOP**, for

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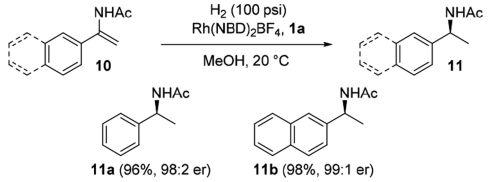
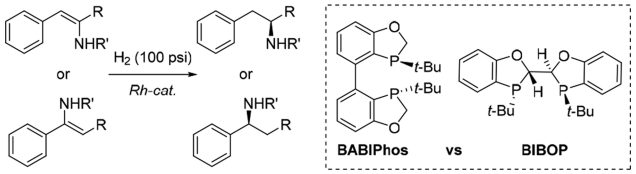
Scheme 4. Rh-Catalyzed Asymmetric Hydrogenation of Disubstituted Enamides[a]



[a]Conditions: **10** (1 equiv), $Rh(NBD)_2BF_4$ (1 mol %), BABIPhos (**1a**) (1 mol %), MeOH, 100 psi of H_2, 20 °C.

which highly enantioselective hydrogenation of enamides was previously reported (Table 4).[3a] It was found that **BABIPhos**

Table 4. Comparison between BABIPhos and BIBOP in Rh-Catalyzed Asymmetric Hydrogenation of Enamides[a]



entry	substrate	ligand	er
1	**8a**	**1a**	99.7:0.3
2	**8a**	BIBOP	96.5:3.5
3	**8k**	**1a**	91:9
4	**8k**	BIBOP	97:3
5	**10a**	**1a**	98:2
6	**10a**	BIBOP	96:4

[a]Conditions: **8** or **10** (1 equiv), $Rh(NBD)_2BF_4$ (1 mol %), ligand (1 mol %), MeOH, 100 psi of H_2, 20 °C.

(**1a**) is the ligand of choice for reduction of 2-amino acrylate **8a**, giving access to the corresponding α-amino acid in 99.7:0.3 er versus 96.5:3.5 er in the case of hydrogenation with **BIBOP** under identical reaction conditions (entry 1 and 2). On the other hand, **BIBOP** outperformed **BABIPhos** in reduction of 3-amino acrylate **8k** (entry 3 vs 4). In case of disubstituted enamide **10a**, only slight advantage of **BABIPhos** over **BIBOP** was found with both ligands delivering synthetically useful results (entries 5 and 6).

In conclusion, a novel family of dimeric biaryl ligands based on a rigid benzooxaphosphole core (**BABIPhos**) has been disclosed. Palladium-catalyzed reductive homocoupling of aryl triflates was adopted for sterically demanded benzooxaphospholes, giving straightforward access to biaryl bisphosphines oxides and subsequently to the corresponding bisphosphine ligands. High catalytic performance of these ligands was showcased in Rh-catalyzed hydrogenation of alkenes, thus demonstrating high potential of these ligands for enantioselective catalysis. Applications of this new set of bisphosphine ligands to other catalytic reactions are currently under investigation and will be disclosed in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00139.

Experimental procedures, NMR spectra, HPLC chromatograms (PDF)

Accession Codes

CCDC 1816605 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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