Biaryls

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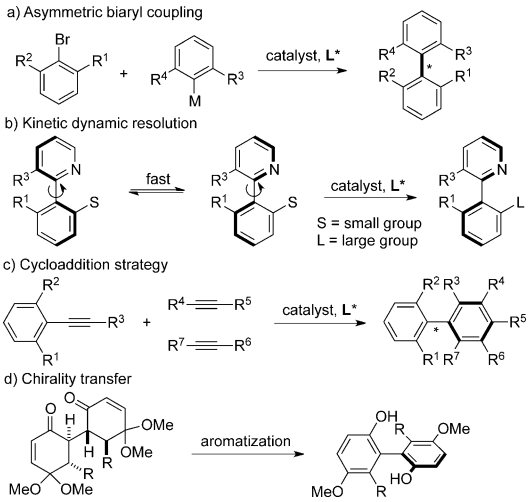
Enantioselective Synthesis of Atropisomeric Vinyl Arene Compounds by Palladium Catalysis: A Carbene Strategy

*Jia Feng[+], Bin Li[+], Yun He, and Zhenhua Gu**

Abstract: *An efficient palladium-catalyzed asymmetric synthesis of axially chiral vinyl arenes from aryl bromides and hydrazones is reported. The products were easily oxidized to axially chiral biaryl compounds, and the phosphine oxides were readily reduced to phosphine ligands.*

Atropisomeric molecules exhibit an axis of chirality because of the inhibited bond rotations, and are significantly different from stereogenic atoms with four different substituents. Represented by 1,1′-bi-2-naphthol (BINOL), biaryl axially chiral compounds became one of the most successful chiral chiral ligands in organic synthesis. Natural enantiopure atropisomers such as vancomycin and (−)-steganone have significant biological activities, thus increasing the scientific interest in axially chiral compounds.

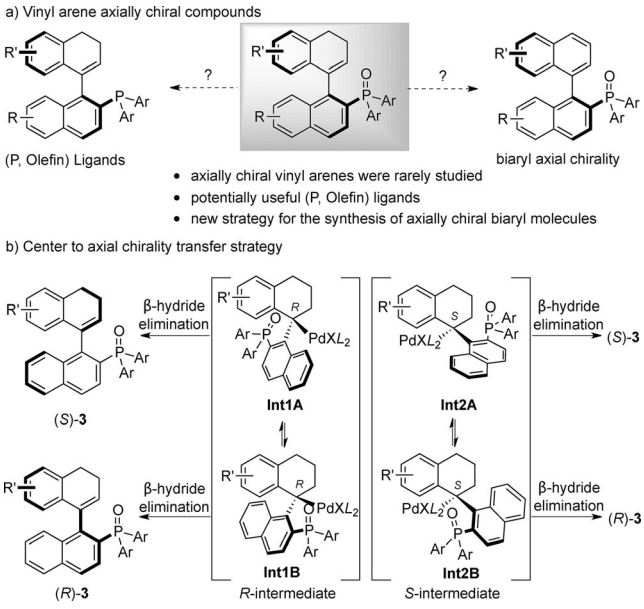
A straight forward way to synthesize axially chiral biaryl compounds[1] is the coupling of two arenes by either oxidative dimerization or cross-coupling (Scheme 1 a). Representative contributions come from the groups of Brussee,[2] Smrčina, Kočovský,[3] Gong,[4] Hayashi,[5] Espinet,[6] Buchwald,[7] Lin,[8] and Tang,[9] as well as others.[10] The groups of Fernández and Lassaletta, and Stoltz prepared a class of useful chiral 1-arylisoquinoline derivatives by palladium-catalyzed kinetic dynamic resolution (KDR; Scheme 1 b).[11] The groups of Miller, Akiyama, You, and Colobert developed direct asymmetric C–H halogenation or olefination reactions for the construction of axially chiral compounds with good to excellent enantioselectivity.[12] A bond-cleavage KDR strategy for the synthesis of axial compounds from small-ring-bridged biaryls was used by the groups of Bringmann, Clayden, and Hayashi.[13–15] Transition metal catalyzed [2+2+2] cycloadditions have been proven as useful ways for the synthesis of atropisomeric molecules (Scheme 1 c).[16] Additionally atropisomeric molecules could also be accessed by chirality transfer aromatization reactions from chiral compounds with stereogenic atoms (Scheme 1 d).[17,18]



Scheme 1. Catalytic asymmetric synthesis of axially chiral compounds.

Although these achievements are important, catalytic asymmetric synthesis of atropisomeric compounds is still in its infancy. The tedious preparation of multisubstituted and hindered aryl (pseudo)halides or organometallic reagents hampered the progress in the area of biaryl cross-coupling. Thus, the development of new versatile methods using easily available materials to access synthetically valuable atropisomeric compounds is urgent and challenging.

During a survey on the synthesis of axially chiral molecules, it was found that axially chiral vinyl arenes were rarely studied (Scheme 2 a). The axially chiral C=C bond might act as a new class of ligands, such as (P, Olefin) ligands.



Scheme 2. The synthesis of axially chiral vinyl arenes.

[*] J. Feng,[+] B. Li,[+] Y. He, Prof. Dr. Z. Gu
Department of Chemistry
University of Science and Technology of China
96 Jinzhai Road, Hefei, Anhui 230026 (China)
E-mail: zhgu@ustc.edu.cn
[+] These authors contributed equally to this work.

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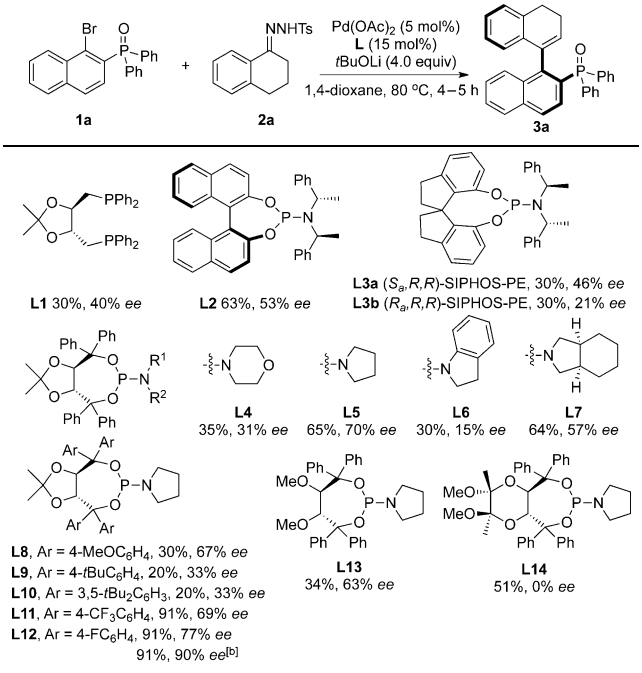
Furthermore, it would provide a new protocol for the synthesis of biaryl atropisomers after aromatization. We reasoned that β-hydride elimination of a quaternary carbon atom bearing a C–Pd bond would form vinyl arene compounds. The challenge is that both the *R*- and *S*-configured intermediates have two conformers, wherein **Int1A** and **Int2A** give (*S*)-**3**, and **Int1B** and **Int2B** give (*R*)-**3** (Scheme 2b). The palladium/carbene-involved insertion, migration, and β-hydride elimination process,[19] which was extensively studied for the synthesis of multisubstituted alkenes by the groups of van Vranken,[20] Barluenga and Valdés,[21] and Wang,[22] as well as others,[23] provides an ideal model to realize our hypothesis. However, to our knowledge there is no catalytic asymmetric study on this C=C formation reaction. Herein we report an asymmetric palladium-catalyzed synthesis of axially chiral vinyl arenes from aryl bromides and hydrazones, which are easily obtained on large scale with versatile functionalities.

The primary screening with **1a** and **2a** as substrates indicated that 1,4-dioxane and *t*BuOLi were the optimum solvent and base (Table 1). The reaction with (*R*)-DIOP (**L1**) as the ligand afforded **3a** in only 40% *ee*. The use of the ligands **L2**, **L3a**, and **L3b** did not result in satisfactory selectivity. TADDOL-based phosphoramidites proved to be a class of promising ligands, and by examination of the substituents on N, the pyrrolidine moiety (**L5**) was superior to others, such as morpholine (**L4**), indoline (**L6**), *cis*-octahydro-1*H*-isoindole (**L7**), and other acyclic amines. Inspired by these findings, further screening focused on the modification of pyrrolidine-based phosphoramidites. Replacing the phenyl ring with electron-rich aryls (**L8**–**L10**) decreased the catalytic activity. Furthermore, the enantioselectivity declined to around 30% when the bulky ligands **L9** and **L10** were used. The introduction of an electron-withdrawing trifluoromethyl group onto the ligand (**L11**) substantially improved the catalytic activity, and the yield increased to 91%. Pleasingly, the *p*-fluorophenyl-derived ligand **L12** proved superior to others, and the enantioselectivity increased to 77%. The increased catalytic activity of Pd/**L12** allowed the reaction to be performed at 50 °C, and as a result the *ee* value increased to 90%. The evaluation of other ligands, such as **L13** and **L14**, showed that the 1,3-dioxolane skeleton is critical for both highly catalytic activity and selectivity.

Firstly we tested the generality regarding different substituted diaryl phosphine oxides (Table 2). The reaction with either electron-donating or electron-withdrawing groups at the *para*-position of the phenyl rings proceeded uneventfully with excellent yields and enantioselectivity (**3b**–**f**). Notably, a longer reaction time was required when the phenyl ring bears a bulky substituent (**3c** and **3d**). Both the *meta*-methoxyphenyl and *meta*-methylphenyl phosphine oxides (**3g** and **3h**), and the disubstituted phenyl phosphine oxides (**3i** and **3j**) worked smoothly to give the corresponding products in 87–91% *ee*. Both β- and α-naphthyl phosphine oxides readily underwent the coupling reaction to deliver **3k** and **3l**, respectively, in excellent enantioselectivity, albeit the one with the bulkier α-naphthyl phosphine oxide resulted in a lower relative yield.

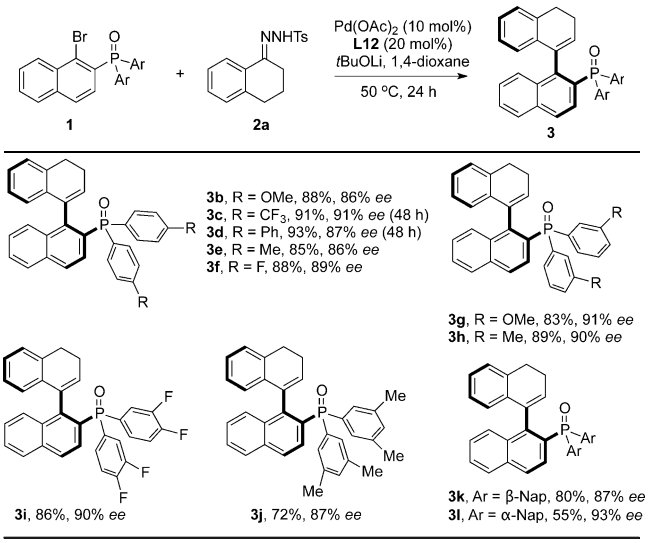
The reactions of both 7- and 6-subsituted tetralone-derived hydrazones smoothly furnished the products in decent yields and excellent *ee* values (Table 3; **3m**–**q**). 5-Methoxyl-1-tetralone-derived hydrazone was a good substrate, and it readily reacted with 2-bromonaphthylenes to deliver the products in up to 97% *ee* (**3r**–**t**). We were pleased to see that 4,4-disubstituted hydrazones were compatible

Table 1: Optimization of reaction conditions.[a]



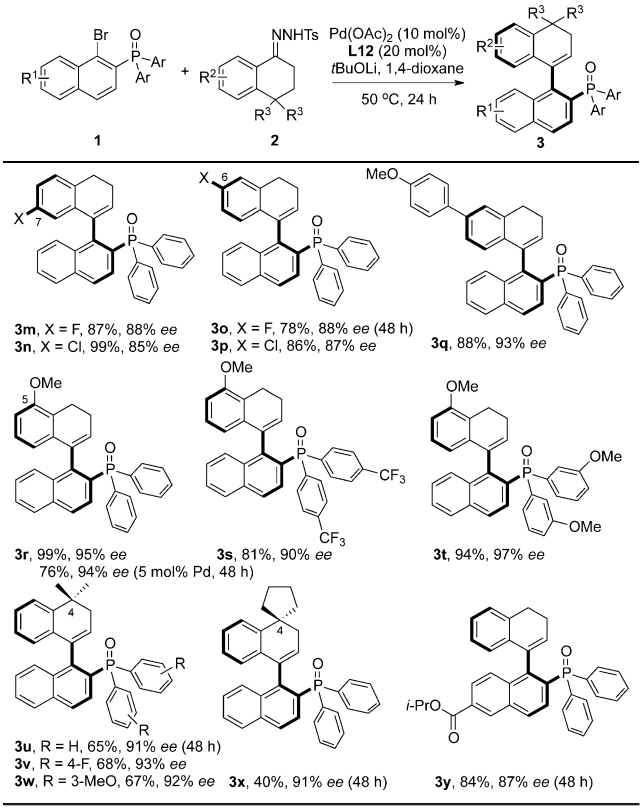
[a] The reaction was conducted with **1a** (0.20 mmol, 1.0 equiv) and **2a** (3.0 equiv). Yield is that of the isolated product. The *ee* values were determined by HPLC analysis using a chiral stationary phase. [b] The reaction was conducted with **2a** (1.5 equiv), $Pd(OAc)_2$ (10 mol %), **L12** (20 mol %), LiO*t*Bu (2.5 equiv) at 50 °C for 24 h. Ts = 4-toluenesulfonyl.

Table 2: Substrate scope with respect to the phosphine oxides.[a]

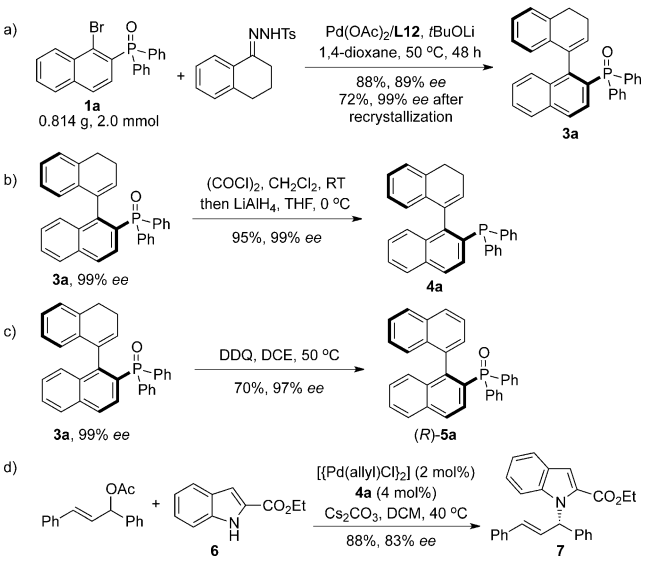


[a] For details see the Supporting Information. Yield is that of the isolated product. The *ee* values were determined by HPLC analysis using a chiral stationary phase.

Table 3: Substrate scope.[a]



[a] For details see Supporting Information. Yield is that of the isolated product. The *ee* values were determined by HPLC analysis using a chiral stationary phase.

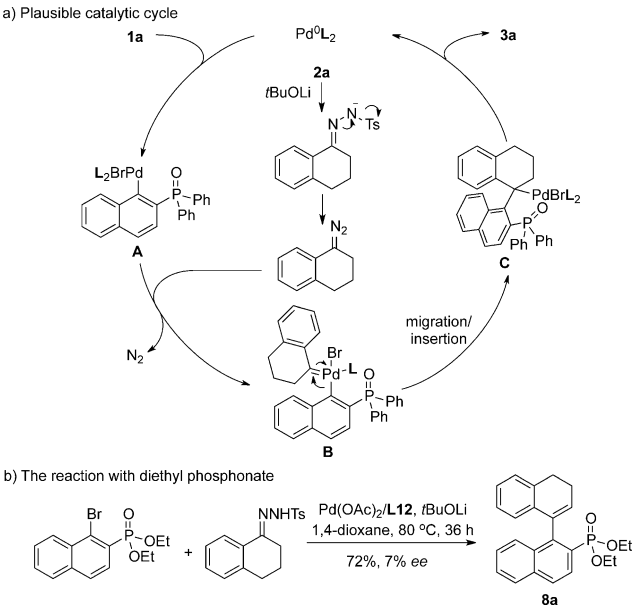


Scheme 3. Transformations and application. DCE = 1,2-dichloroethane, DCM = dichloromethane, DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone, THF = tetrahydrofuran.

substrates, where the quaternary carbon center did not affect the enantioselectivity (**3u**–**x**). Cheerfully, 6-isopropoxycarbonyl-(1-bromonaphthalen-2-yl)-diphenylphosphine oxide displayed good reactivity, and the corresponding reactions gave excellent results in both yield and selectivity (**3y**).

The scalability of this reaction was evaluated by performing the reaction with 2.0 mmol of **1a**. The reaction gave 88% yield and 89% *ee* of **3a**, and the *ee* value was further improved by recrystallization (Scheme 3a).[25] Gratifying, the phosphine oxide could be readily reduced under mild reaction conditions with excellent yield and *ee* value (Scheme 3b). In the presence of DDQ, **3a** was easily aromatized to the biaryl atropisomer (*R*)-**5a** with a high *ee* value, thus the absolute configuration was determined by comparison of the optical rotation of (*R*)-**5a** with the reported data (Scheme 3c). The utility of (P, Olefin) ligands[24] was primarily demonstrated by a benchmark asymmetric allylation reaction between (*E*)-1,3-diphenylallyl acetate and the indole **6**. In the presence of Pd/**4a** (1:1), the reaction afforded the N-allylation product **7** in 88% yield and 83% *ee* (Scheme 3d).[26]

A catalytic cycle is proposed (Scheme 4a). The oxidative addition of Pd^0 with **1a** would give **A**, which reacts with the diazo compound (generated in situ from hydrazones in the presence of *t*BuOLi) to afford the carbene-coordinated complex **B**. Migration/insertion of **B** affords a quaternary carbon center bearing a C–Pd bond, and delivers the final product by β-hydride elimination. It is possible that the



Scheme 4. Plausible catalytic cycle.

enantioselectivity was partially affected by the π–π interaction of the phenyl ring of the phosphine oxide with the tetrahydronaphthalene moiety in either **B** or **C**, since a control reaction with diethyl phosphonate as a substrate gave **8a** in 7% *ee* (Scheme 4b).

In conclusion, we have reported a palladium-catalyzed asymmetric synthesis of axially chiral 1-vinylnaphthalen-2-yl phosphine oxides from aryl bromides and hydrazones. The use of carbene precursors as coupling partners resulted in mild reaction conditions and thus a broad functional-group tolerance.

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Keywords: biaryls · chirality · enantioselectivity · hydrazones · palladium

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