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Pd(II)-Catalyzed P(O)R^{1}R^2-Directed Asymmetric C−H Activation and Dynamic Kinetic Resolution for the Synthesis of Chiral Biaryl Phosphates

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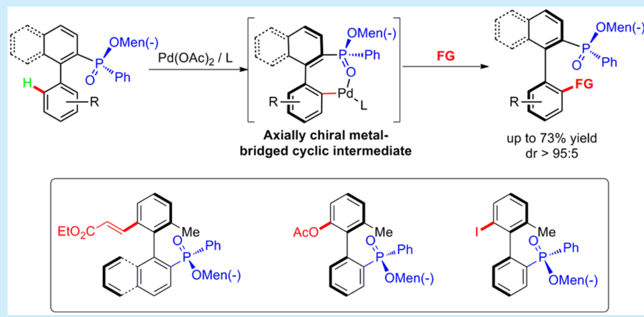
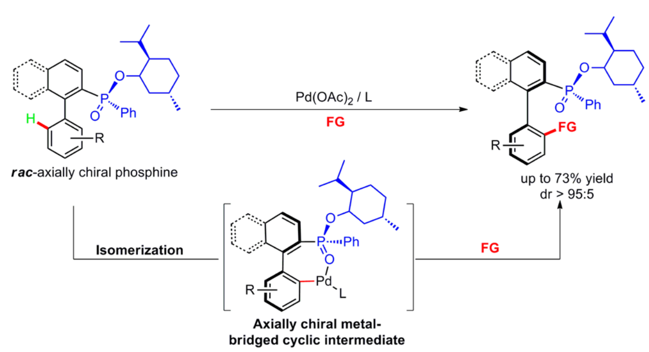
Supporting Information

ABSTRACT: An efficient method of Pd(II)-catalyzed P(O)-R^{1}R^2-directed asymmetric C−H activation and dynamic kinetic resolution for synthesis of chiral phosphinate ligands has been performed and exhibits a wide scope of substrates and an excellent diastereomeric ratio (>95:5).



In many transition metal-catalyzed asymmetric transformations, axially chiral phosphine-based ligands play indispensable roles.[1] The extent to which they can be utilized in these endeavors depends on the efficient and selective chemical methods for their construction. Consequently, researchers have devoted tremendous efforts over the past decades to synthesize these kinds of chiral auxiliaries that possess novel electronic, steric properties, as well as functional groups.[2] The most commonly used method involves optically pure substrates such as binaphthol and others afforded directly by phosphorization.[3] Transition metal-catalyzed asymmetric cross-coupling with two aryl compounds also provides an efficient pathway.[4] Moreover, the kinetic resolution is also the main route for preparation of axially chiral phosphine-based ligands.[5] However, this procedure is limited to a maximum theoretical yield of 50%. Many efforts have been devoted to overcome this limitation and to afford compounds with the same high enantiomeric purity but with much improved yields. Recently, a new method of dynamic kinetic resolution (DKR) of biaryl atropisomers, which occur in tandem with *in situ* racemization and resolution, provides one of the most convenient and efficient approaches to a wide range of enantiomerically enriched molecules.[6] The dynamic kinetic resolution of biaryl atropisomers through rhodium-catalyzed atropoenantioselective alkylation of 2-(1-naphthyl)-3-methylpyridine was first applied in 2000 by the Murai group.[6b] Ten years later, Miller developed a dynamic kinetic resolution of biaryl atropisomers via peptide-catalyzed asymmetric bromination and delivered chiral nonracemic biaryl compounds with excellent enantioselectivity and good yields.[6c] In 2013, two groups of Stoltz and Lassaletta achieved simultaneous but independent asymmetric synthesis of axially chiral heterobiaryls via dynamic kinetic asymmetric transformation of the racemic prefunctionalized (naphthyl)quinoline derivatives.[6d,e] Very recently, Colobert first reported the synthesis of axially chiral biaryls through sulfoxide-directed asymmetric C−H activation and dynamic kinetic resolution.[6f−h] Here in, we disclose the first example of Pd(II)-catalyzed P(O)R^{1}R^2-directed asymmetric C−H alkenylation, acetoxylation, and iodization through dynamic kinetic resolution for the synthesis of various axially chiral phosphine oxide compounds (Scheme 1), which proved easier when converting the corresponding axially chiral phosphine auxiliary by hydrogen reduction of silicide. Compared with our previous reports of Pd(II)-catalyzed the optically pure chiral [1,1′-binaphthalen]-2-yldiphenylphosphine oxide directed C−H functionalization to

Scheme 1. Pd(II)-Catalyzed C−H Activation/Dynamic Kinetic Resolution for Synthesis Chiral Biaryl Phosphates



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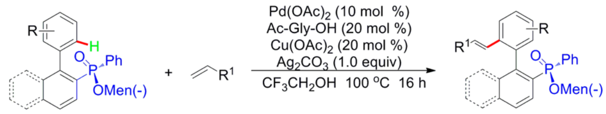
synthesize different axially chiral phosphine-based ligands.[7] This method demonstrated a wide substrate scope and the excellent diastereomeric ratio (>95:5) under higher reaction temperatures. The products contained both the axially chirality and P-stereogenic center, which are difficult to obtain in former P(O)R2-directed C−H activation reactions. Furthermore, chiral $P(O)R^1R^2$ acts not only as the directing group but also serves to facilitate the composition of the product in a useful manner.

We initially chose the easily available enantiopure menthyl phenylphosphate group as the directing group for C−H olefination. We synthesized the axially racemic substrate (*S*)-(−)-menthyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl)-phosphinate **1a** (see the Supporting Information)[8] and examined the asymmetric C−H olefination[9] between **1a** and ethyl acrylate (**2a**). To our delight, the desired product **3a** was obtained in 58% yield with an excellent diastereomeric ratio (>95:5) under our previous conditions (entry 1; for detailed studies, see the Supporting Information). Encouraged by this result, we further optimized the reaction conditions. Solvents screening showed that the CF_3CH_2OH is still the best choice. The influence of the oxidants was further examined; $Cu(OAc)_2$, Ag_2CO_3, $AgNO_3$, and $PhI(OAc)_2$ could effectively promote the reaction and $Cu(OAc)_2$ shows the best results. Finally, the combination of Ag_2CO_3 (1.0 equiv) and $Cu(OAc)_2$ (20 mol %) was found optimal and gave **3a** in 73% yield and >95:5 dr. Subsequently, we carried out evaluations of other amino acids, but relatively lower yields were obtained. Other Pd sources, such as $Pd(TFA)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(NO_3)_2$, and $Pd(acac)_2$, could also promote this reaction, and when $Pd(acac)_2$ was used, the desired product **3a** was also obtained with the best result. Finally, when we selected the relatively cheaper $Pd(OAc)_2$ as the catalyst, the optimized reaction conditions are as follows: $Pd(OAc)_2$ (10 mol %) as the catalyst, Ac-Gly-OH (20 mol %) as the ligand, and Ag_2CO_3 (1.0 equiv) and $Cu(OAc)_2$ (20 mol %) as the oxidants in CF_3CH_2OH at 100 °C for 16 h.

With the optimized reaction conditions in hand, we examined the scope of different substituted axially racemic (*S*)-(−)-menthyl phenylphosphinate derivatives and various acrylates (Table 1). We focused first on the investigation of various acrylates using (*S*)-(−)-menthyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl)phosphinate **1a** as a substrate (Table 1, entries 1−8). We were pleased to find that different olefins such as methyl, butyl, and benzyl acrylates, phenyl vinyl sulfone, alkenyl phosphate, and acrolein were compatible with the reaction and the corresponding products were afforded in moderate to good yields with excellent diastereomeric ratios (all >95:5). Furthermore, a variety of axially racemic (*S*)-(−)-menthyl phenylphosphinate derivatives[10] bearing substituents in position 2′ were taken into the reaction (Table 1, entries 9−11). All the substrates were subjected to the C−H alkenylation with ethyl acrylate and the corresponding coupling products **3ba**−**3da** were isolated in moderate to good yields showing excellent diastereoselectivity. The axially racemic (*S*)-(−)-menthyl (2′,3′-dimethyl-[1,1′-biphenyl]-2-yl)(phenyl)-phosphinate **1e** was also examined and gave the alkenylation product **3ea** in 60% yield and excellent diastereoselectivity (dr >95:5). Finally, the substrates with a substituent at position 6 could also go through C−H alkenylation with good yield and show excellent diastereoselectivity, a little of di-ortho-alkenylated products were also observed in these reactions (Table 1, entries 13 and 14). Moreover, we also tried to synthesize axially racemic ortho trisubstituted substrates, but we produced the chiral ones.

Table 1. Pd(II)-Catalyzed C−H Activation/DKR[a]

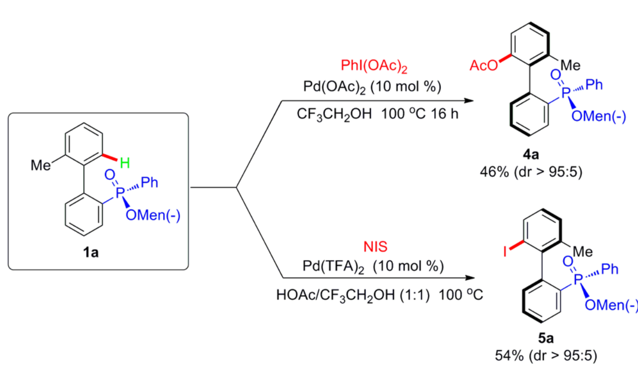


entry	product	yield[b]	dr[c]	entry	product	yield[b]	dr[c]
1	**3aa**	73%	> 95:5	8	**3ah**	27%	> 95:5
2	**3ab**	69%	> 95:5	9	**3ba**	42%	> 95:5
3	**3ac**	62%	> 95:5	10	**3ca**	69%	> 95:5
4	**3ad**	53%	> 95:5	11	**3da**	54%	> 95:5
5	**3ae**	60%	> 95:5	12	**3ea**	60%	> 95:5
6	**3af**	31%	> 95:5	13	**3fa**	63%	> 95:5
7	**3ag**	62%	> 95:5	14	**3ga**	72% (m/d = 6:1)	> 95:5

[a]Reaction conditions: 0.2 mmol of **1**, 0.6 mmol of **2**, 10 mol % $Pd(OAc)_2$, 20 mol % Ac-Gly-OH, 20 mol % $Cu(OAc)_2$, and 0.2 mmol of Ag_2CO_3 in CF_3CH_2OH (2.0 mL) under air atmosphere. [b]Isolated yields. [c]Determined by ^1H NMR and ^{31}P NMR.

Next, we turned our attention to asymmetric C−H functionalization with other reagents. (Scheme 2)[11,12] When (*S*)-(−)-menthyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl) phosphinate **1a** was subjected to the C−H acetoxylation with $PhI(OAc)_2$ under 10 mol % $Pd(OAc)_2$ in CF_3CH_2OH at 100 °C for 16 h, the desired acetoxylated product **4a** was obtained in 46% yield with excellent diastereomeric ratio (dr >95:5).

Scheme 2. Asymmetric C−H Acetoxylation and Iodization/KDR



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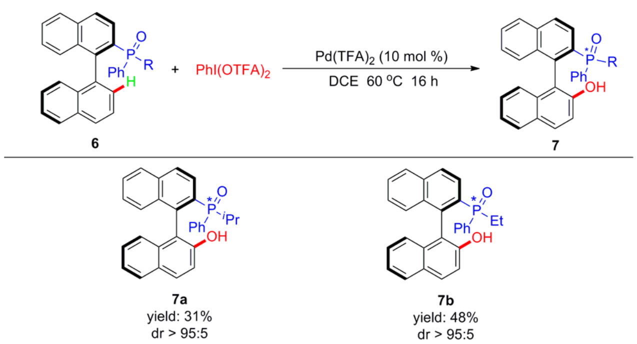
Moreover, the product can be further transformed into the chiral P,O-ligand. Delightedly the iodization also carried out smoothly in this transformation, and the desired product of **5a** could be acquired in 54% yield with excellent diastereomeric ratio (dr >95:5).

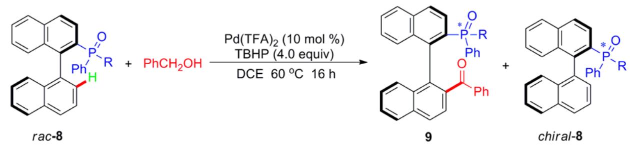
Encouraged by the efficiency of this diastereoselective alkenylation, acetoxylation, and iodization reactions, we subsequently focused on proving a more general character of such an original asymmetric C−H activation. Aiming to construct synthetically useful axially chiral scaffolds, we wished to extend this methodology to the hydroxylation reaction.[13] However, our efforts produced only trace amounts of the hydroxylation product under our previous hydroxylation reaction conditions when **1a** was used as the substrate. Then, we tried to replace the menthyl group by alkyl with alkyl lithium in order to synthesize axially racemic (*R*)-alkyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl)phosphine oxides but failed. This impelled us to speculate on the possibility that conditions could be developed to acquire the chiral hydroxylation product. Combing the axially chiral substrates induced the kinetic resolution with C−H activation provided a conceivable alternative, because we could obtain different two axially chiral phosphine oxide ligands via one step. To the best of our knowledge, this strategy has never been demonstrated. Indeed, when we used the axially chiral substrates (*R*)-isopropyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl)phosphine oxide (**6a**) and (*R*)-ethyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl)-phosphine oxide (**6b**) to the C−H hydroxylation, the corresponding products of **7a** and **7b** were obtained with good yields and excellent diastereoselectivity, but the starting material disappeared under the reaction conditions (Scheme 3).

Scheme 3. Asymmetric C−H Hydroxylation/KR



In addition to the hydroxylation, we attempted to extend the kinetic resolution (*R*)-alkyl (2′-methyl-[1,1′-biphenyl]-2-yl)-(phenyl)phosphine oxides through C−H acylation (Table 2).[14] As we expected, reactions were carried out smoothly in terms of highest diastereoselectivity and good yields for both of the products (**9a**,[15] **9b**) and recovered starting materials (**8a**, **8b**) (notably, the dr of substrate **8b** is 1:1.7, so the yield of product **8b** is lower and the yield of recovered starting material **8b** is greater than 50% with excellent dr >95:5) when we use (*R*)-*tert*-butyl (2′-methyl-[1,1′-biphenyl]-2-yl)(phenyl)phosphine oxide (**8a**) and (*R*)-isopropyl-butyl (2′-methyl-[1,1′-biphen-yl]-2-yl)(phenyl) phosphine oxide (**8b**) as substrates. Desired products of **9c** and **9d** were obtained in moderate yields with excellent diastereoselectivity and the recovered starting materials **8c**, **8d** in good yields with moderate diastereoselectivity, which indicated that the activity of these two directing groups is worse than −P(O)^{t}BuPh and −P(O)^{i}PrPh. The

Table 2. Pd(II)-Catalyzed C−H Acylation/KR[a]



		9		chiral-8	
entry	R	yield[b]	dr[c]	yield[b]	dr[c]
1	R = ^{t}Bu	**9a**, 36%	>95.5	**8a**, 25%	>95:5
2	R = ^{i}Pr	**9b**, 22%	>95.5	**8b**, 55%	>95:5
3	R = ^{n}Bu	**9c**, 20%	>95.5	**8c**, 56%	80:20
4	R = Et	**9d**,18%	>95.5	**8d**, 52%	80:20

[a]Reaction conditions: 0.3 mmol of **5**, 0.75 mmol of $PhCH_2OH$, 10 mol % $Pd(TFA)_2$, 1.2 mmol of TBHP (70% aqueous solution) in DCE (1.5 mL) under air atmosphere. [b]Isolated yields. [c]Determined by ^{1}H NMR and ^{31}P NMR.

additional key advantage the strategy presented herein relies on the character of the $P(O)R^1R^2$ directing group, which paves the way toward a general application of the transformation to phosphine-based ligands (for example, alkene-phosphine hybride ligands, P,O-ligands).

Summit

In summary, a novel atroposelective mild C−H activation occurring through dynamic kinetic resolution and kinetic resolution toward the synthesis of alkenylation, acetoxylation, iodization, hydroxylation, and acylation atropisomeric biaryls or chiral phosphine oxides isomers represents a rare example of a C−H activation-based asymmetric strategy enabling axial stereocontrol or formation of central chirality on the phosphorus atom.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) CCDC 1045456 (**9a**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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