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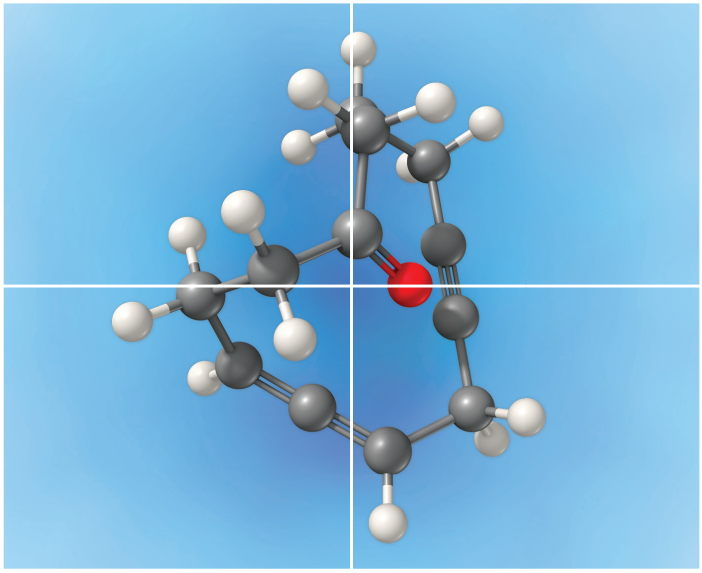

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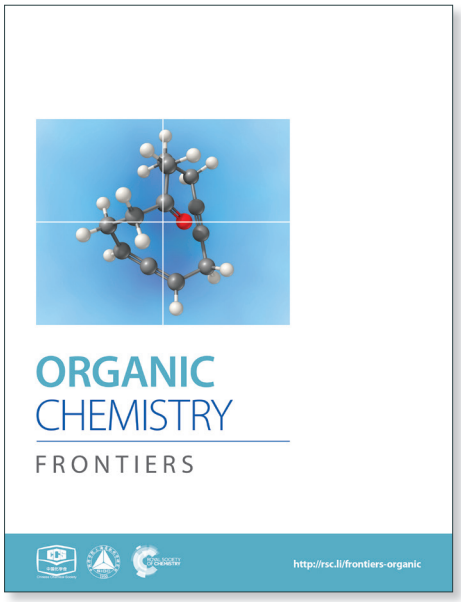

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Highly Enantioselective Oxidative Tandem Cyclization Reaction: Chiral Ligand and Anion Cooperatively Control Stereoselectivity

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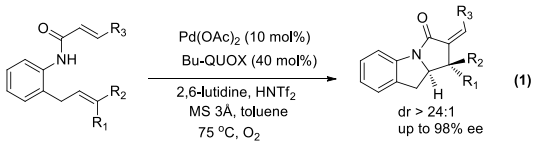
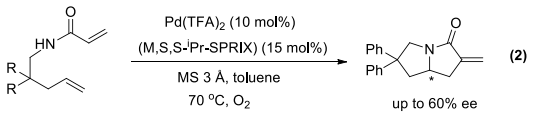
ABSTRACT: The unprecedented combination of a palladium(II) complex with a chiral Bu-QUOX ligand and a chiral phosphoric acid enables the highly efficient asymmetric oxidative tandem cyclization of N-(2,2-disubstituted hex-5-en-1-yl)acrylamides, providing a straightforward method to access chiral 6,5-bicyclic aza-heterocycles in moderate to good yields and with excellent enantioselectivities.

The palladium(II)-catalyzed alkene functionalization via nucleopalladation of the carbon-carbon double bond has enabled numerous transformations, providing efficient entries to diverse families of either oxygenous or N-containing molecules, in particular, heterocycles.[1] However, asymmetric Pd(II)-catalyzed functionalization of alkenes[2] has met with much less success than chiral palladium(0) complex-catalyzed enantioselective reactions.[3] The limited number of chiral ligands compatible with oxidizing conditions,[4,5] which are mostly required in Pd(II)-catalysis, has been considered one of key factors to surpass the reality of highly enantioselective Pd(II)-catalyzed functionalization of alkenes.

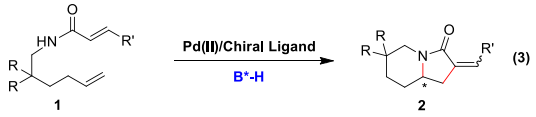
The palladium(II)-catalyzed enantioselective tandem Wacker-type oxidation/cyclization reactions are capable of directly generating complex polycyclic products, which have been commonly incorporated in natural alkaloids as core structural elements.[6] Sasai established the first highly enantioselective Pd(II)-catalyzed oxidative tandem cyclization reactions of alkenyl alcohols affording bicyclic products with excellent levels of enantioselectivity (up to 95% ee).[6e] Yang and coworkers accomplished a Pd(II)-catalyzed enantioselective oxidative tandem reaction of nitrogen atom-based nucleophiles using readily available (-)-sparteine as a chiral ligand, generating dihydro-1H-pyrrolo[1,2-a]indol-3(2H)-one derivatives in good yields and high enantioselectivities.[6f] Thereafter, the same group further improved the reaction by using Bu-Quox as a chiral ligand (Scheme 1, eq. 1).[6g] Recently, Sasai presented a Pd(II)-SPRIX-catalyzed enantioselective cascade intramolecular C-N/C-C bond formation reaction of N-(2,2-disubstiuted pent-4-en-1-yl)acrylamides for the synthesis of tetrahydro-1H-pyrrolizin-3(2H)-ones in good yields, but with moderate enantioselectivities (Scheme 1, eq. 2).[6i] In contrast to these well-established methods available to access fused 5,5-bicyclic N-containing skeletons, the Pd(II)-catalyzed enantioselective oxidative tandem cyclization reaction has much less been developed for generation of fused 6,5-bicyclic aza-heterocycles.

Scheme 1. Palladium(II) catalyzed enantioselective oxidative tandem cyclization to access fused 5,5-bicyclic nitrogenous skeletons



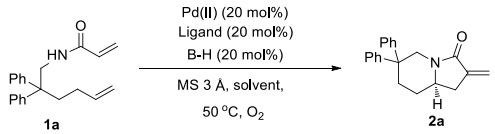


This work: Asymmetric oxidative tandem cyclization reaction to acess fused 6,5-bicyclic heterocycles



Recently, the combination of metal catalysis with organocatalysis has been a robust strategy for the creation of enantioselective transformations.[7] In particular, chiral Brønsted acids have been found to be highly compatible with palladium catalysts.[8,9] Notably, the use of chiral phosphoric acid alone was able to control the stereoselectivity in some typical Pd(II) catalyzed reactions.[8] Thus, we envisioned that the use of chiral phosphoric acid as a co-catalyst would be able to modulate the enantioselectivity of the palladium(II)-catalyzed tandem Wacker-type oxidation/cyclization reactions. Herein, we describe a highly enantioselective Wacker-type oxidative transformation catalyzed by a chiral palladium(II) complex and a chiral phosphoric acid, providing a straightforward entry to chiral 6,5-bicyclic heterocycles (eq. 3).

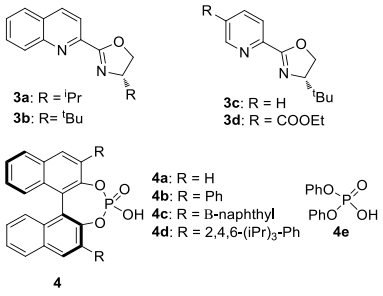
Table 1. Optimizing Reaction Conditions[a]



Entry	Ligand	B-H	Yield (%)[b]	Er[c]
1	**3a**	(S)-**4a**	21	77.5:22.5
2	**3b**	(S)-**4a**	25	79.5:20.5
3	**3c**	(S)-**4a**	27	75:25
4	**3d**	(S)-**4a**	29	72.5:27.5
5	**3b**	(S)-**4b**	42	93.5:6.5
6	**3b**	(S)-**4c**	38	93:7
7	**3b**	(S)-**4d**	43	97.5:2.5
8	**3b**	(*R*)-**4d**	37	92:8
9	**3b**	(S)-**4e**	42	75:25
10	**3b**	PhCOOH	10	66.5:33.5
11	**3b**	p-TSA	45	86:14
12	**3b**	(S)-**4d**	35	85:15[d]
13	**3b**	(S)-**4d**	50	98:2[e]
14	**3b**	(S)-**4d**	40	86.5:13.5[e,f]
15	**3b**	(S)-**4d**	38	96.5:3.5[e,g]
16	**3b**	--	24	92:8[e]

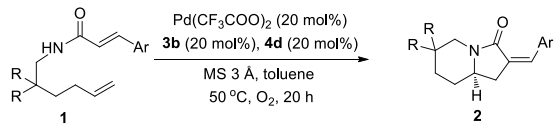
[a] Unless indicated otherwise, the reaction of **1a** (0.1 mmol) was carried out in toluene (1 mL) at 50 °C in the presence of $Pd(OAc)_2$ (20 mol %), Ligand (20 mol %), Brønsted acid (20 mol%) and 3 Å (50 mg) under O_2 (balloon) for 20 h. [b] Isolated yield. [c] Determined by HPLC. [d] $Pd(MeCN)_4(BF_4)_2$ was used. [e] $Pd(CF_3COO)_2$ was used. [f] The solvent was 1,4-dixone. [g] The solvent was chlorobenzene.

Figure 1. Ligand and phosphoric acid derivatives surveyed.



Our initial study began with a reaction of N-(2,2-diphenylhex-5-en-1-yl)acrylamide **1a** in the presence of 20 mol% $Pd(OAc)_2$, 20 mol% ^{i}Pr-quinolineoxazoline **3a** and 20 mol% of a phosphoric acid **4a** along with 3 Å MS and molecular oxygen (balloon) as the sole oxidant in toluene at 50 °C for 20 h (Table 1, entry 1). To our delight, the desired product was isolated in 21% yield with a promising enantiomeric ratio of 77.5:22.5. It should be noted that a small amount of side product was formed and 65% of starting material **1a** was recovered.

Table 2. Scope of substrate[a]



Entry	**2**	R	Ar	Yield(%)[b]	Er[c]
1	**2b**	Ph	Ph	52	96:4
2	**2c**	Ph	2-ClC_6H_4	48	95:5
3	**2d**	Ph	3-FC_6H_4	55	92:8
4	**2e**	Ph	4-MeC_6H_4	39	94:6
5	**2f**	Ph	4-$OMeC_6H_4$	56	96:4
6	**2g**	Ph	4-FC_6H_4	55	93:7
7	**2h**	Ph	4-ClC_6H_4	51	94.5:5.5
8	**2i**	Ph	4-$NO_2C_6H_4$	48	95:5[d]
9	**2j**	Ph	3,4,5-$OMeC_6H_2$	65	93:7
10	**2k**	Me	Ph	57	92.5:7.5
11	**2l**	-C_4H_8-	Ph	60	91:9
12	**2m**	-C_5H_{10}-	Ph	54	92:8
13	**2n**	--	--[e]	51	92.5:7.5

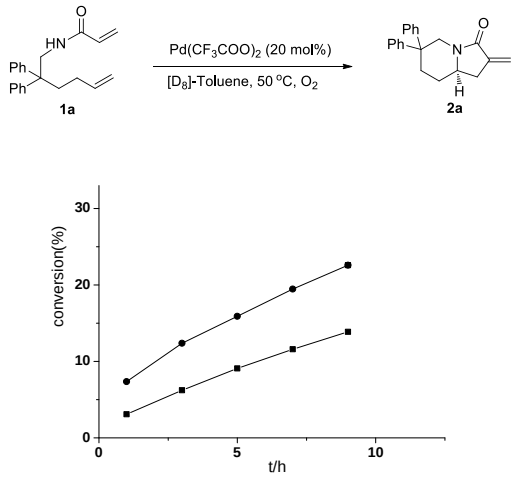
[a] Unless indicated otherwise, the reaction of **1** (0.1 mmol) was carried out in toluene (1 mL) at 50 °C in the presence of $Pd(CF_3COO)_2$ (20 mol %), **3b** (20 mol %), **4d** (20 mol%) and 3 Å (50 mg) under O_2 (balloon) for 20 h. [b] Isolated yield. [c] Determined by HPLC. [d] The reaction time was 36 h. [e] The substrate was N-(2,2-diphenylpent-4-en-1-yl)acrylamide and $Pd(OAc)_2$ was used at 25 °C.

A further improvement in both yield (25%) and enantioselectivity (79.5:20.5) could be achieved upon exploiting **3b** as a ligand (Table 1, entries 2-4). Next, various chiral phosphoric acids **4b-4d** derived from 3,3′-disubstituted BINOLs were evaluated (entries 5-7). Among them, (*S*)-trip-PA **4d** turned out to be the preeminent catalyst and was able to provide **2a** with 43% yield and 97.5:2.5 er. Notably, the use of (*R*)-trip-PA as a co-catalyst gave a lower yield and enantioselectivity than its enantiomer **4d**, suggesting that (*S*)-trip-PA acts as a matched cocatalyst (entry 8 vs 7). Although the acidity of achiral Bronsted acids, to some degree, affected the reaction performance, none of them was able to provide better results than chiral PA **4d** (entries 9-11 vs 7). The palladium (II) source also exerted great impact on the stereochemical outcomes (entries 7, 12-13). When $Pd(CF_3COO)_2$ was used, the cyclic product **2a** was generated with 50% yield and 98:2 er (entry 13). Conducting the reaction in other solvents was unable to enhance either the yield or the enantioselectivity (entries 14-15). Significantly, both yield (24%) and enantioselectivity (92:8) were diminished when chiral ligand **3b** was used alone

(entry 16), suggesting that the synergistic effect exists between the chiral ligand and phosphate.

With the optimal conditions in hand, the generality and the substrate scope of the enantioselective oxidative tandem cyclization reaction were explored. When N-(2,2-diphenylhex-5-en-1-yl)cinnamamide **1b** was employed under the optimized conditions, the target product **2b** was delivered in 52% yield with 96:4 er. Substrates **1c-1j** with different substituents at phenyl group of cinnamamide were able to undergo the oxidative tandem cyclization reaction to give the corresponding **2c-2j** in moderate to good yields with high levels of enantioselectivities (entries 2-9). Basically, the electron feature of substituents exerts obvious effect on the reaction performance (entries 4-8) while the substitution pattern of cinnamamide moiety has little influence on the stereoselectivity (entry 2 *vs* 7 and 3 *vs* 6). A fairly good yield (65%) and high enantioselectivity (93:7 er) were obtained for highly electronically rich **2j** substituted with methoxy at 3-, 4-, 5-positions, respectively (entry 9). The replacement of sterically bulky *γ*-diphenyl substituents of **1b** with *γ*-dimethyl groups, as shown in **1k**, was also allowed to produce the corresponding product **2k** in a good yield (57%) and a high enantioselectivity (92.5:7.5 er, entry 10). Both cyclopentyl and cyclohexyl substituted substrates (**1l** and **1m**) underwent the reaction smoothly to deliver the corresponding products **2l** and **2m** in good yields and high enantioselectivities, respectively (entries 11 and 12). Moreover, N-(2,2-diphenylpent-4-en-1-yl)acrylamide could also be tolerated and afforded **2n** in a 51% yield and with 92.5:7.5 er by using

Figure 2. Kinetic studies on the oxidative tandem cyclization reaction catalyzed by 20 mol% Ligand 3b and 20 mol% 4d (●),and by 20 mol% Ligand 3b (◆).

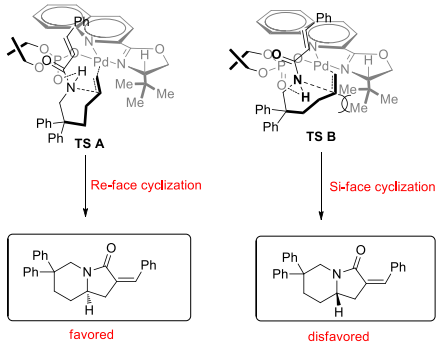


$Pd(OAc)_2$ as a precatalyst at 25 °C (entries 13).

To gain insight into the reaction process, we investigated the kinetics of the cascade reaction. As shown in Figure 2, the chiral palladium(II) complex of ligand **3b** was able to catalyze the oxidative tandem cyclization reaction alone, but in the presence of the chiral phosphoric acid **4d**, the reaction proceeded even faster. This observation, together with the difference in the enantioselectivity (entry 13 vs 16, Table 1), strongly suggested that the synergistic effect of the chiral ligand and Brønsted acid played important role in the enantioselective catalysis.

To found out the palladium species in the catalysis, a high-resolution mass spectrometry (HRMS) analysis of a reaction mixture of palladium complex with **3b** and **4d** was conducted.[10] The result showed that an anion exchange occurred between one molecule of chiral phosphoric acid **4d** and $Pd(CF_3COO)_2$, which coordinated to one molecule of chiral ligand **3b**, leading to the formation of the catalytically active

Scheme 3. The Proposed Tranisition-state mode to Account for the Stereochemistry.



palladium(II) complex possessing both a chiral ligand and a chiral phosphate.[8a,8b,9] On the basis of this fact and the experimental observations, a transition-state model was proposed. As shown in Scheme 3, the alkene coordinates to the Pd(II) and cinnamamide was activated by hydrogen bonding interaction with phosphoric acid.[11] The formation of TS-A is favored and leads to a *Re*-face cyclization because the orientation of the vinyl group of the substrate is sterically matched with the chiral environment of **3b**. In contrast, the *Si*-face cyclization via TS-B is disfavored due to the steric repulsion between the vinyl moiety of substrate and the *tert*-butyl group of **3b**.

In summary, we have demonstrated that the combined use of a palladium(II) complex of chiral Bu-QUOX ligand and a chiral phosphoric acid enabled a highly enantioselective oxidative cascade cyclization reaction of N-(2,2-disubstituted hex-5-en-1-yl)acrylamides, providing a straightforward method to access chiral 6,5-bicyclic aza-heterocycles in moderate yields and with excellent enantioselectivities. A synergistic effect between the ligand and counterion was found in the catalysis. The chiral ligand and anion cooperatively control the stereoselectivity. The findings suggest that the combined catalysts of chiral Pd(II) complex and chiral Brønsted acid might be amenable to the development of other asymmetric catalytic oxidative reactions.

Acknowledgment

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(10) The details of HRMS data was described in the Supporting Information.

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