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Pd-catalyzed oxidative homo-coupling of acrylates and aromatic alkenes for the conjugated diene synthesis

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ABSTRACT

We developed a bidentate monoanionic nitrogen ligand that was effective in the Pd-catalyzed oxidative homo-coupling reaction of acrylates and aromatic alkenes. In the presence of Pd(OAc)$_2$/ligand several conjugated dienes were obtained in good yields with high stereoselectivities.

Conjugated diene fragments are widely distributed in many natural compounds, optical materials and pharmaceuticals [1]. Accordingly, diene syntheses attract considerable research interest. Pd-catalyzed C—H bond activation is a very powerful tools for C—C bond formation [2]. This method provides a straightforward and atom-economical strategy for synthesizing compounds. However, simple alkenes are not widely used to prepare dienes. Given the intrinsically poor activity of the ester group in coordinating with the metal center, the alkenyl C—H bond is difficult to activate [3]. In 2004, Ishii et al. reported the first example of the oxidative cross-coupling reaction of acrylates with vinyl carboxylates under a Pd(OAc)$_2$/HPMoV/O$_2$ system (Scheme 1a) [4]. In 2009, Loh et al. developed an efficient method for the Pd-catalyzed oxidative cross-coupling reaction of simple olefins with acrylates (Scheme 1b) [5]. In 2015, Wen et al. reported the feasibility Pd-catalyzed homodehydrogenation coupling reaction of aromatic alkenes (Scheme 1c) [6]. However, in Loh and Wen's systems, the use of 20 mol% Pd(OAc)$_2$ catalyst achieves good yields, and decreased Pd(OAc)$_2$ amount to 10 mol%, leads to relatively low yield. Very recently, Lin and Feng et al. reported an elegant synthesis of 1,3-dienes from terminal alkenes via 1,4-palladium migration/Heck sequence [7].

In a previous communication, we reported the palladium-catalyzed oxidative Heck reaction of simple arenes without directed groups [8]. In such work, we found that a bidentate monoanionic nitrogen ligand 2-OH-1,10-phen/Pd(OAc)$_2$ more effectively catalyzed the oxidative Heck reaction of arenes than did 1,10-phen/Pd(OAc)$_2$. We believed that the complex of 2-OH-1,10-phen with Pd(OAc)$_2$ only contained one acetate anion on the Pd atom. Given that the binding ability of the acetic anion to Pd is not strong, a palladium intermediate with a vacant coordination site can be generated with relative ease and act as a catalyst for the C—H bond cleavage of simple arenes. On the basis of the design, we used bidentate monoanionic nitrogen ligands in the Pd-catalyzed oxidative homo-coupling reaction of acrylates and aromatic alkenes.

To evaluate the feasibility of the homo-coupling reaction, we chose *n*-butyl acrylate as the substrate and 5 mol% of Pd(OAc)$_2$ as catalyst (Table 1). First, we used 1.0 equivalent Ag$_2$CO$_3$ as oxidant in 1,4-dioxane at 140 °C to conduct the reaction without the ligand, but no product was formed (entry 1). Adding 2-OH-1,10-phen (**L1**) led to a 21% product yield (entry 2). By contrast, the use of 1,10-phen (**L2**) totally inhibited the progress of reaction with no formation of the desired product (entry 3). The 2-OH-1,1′-bipyridine (**L3**) with a similar structure to that of **L1** exhibited low catalytic activity (14% yield, entry 4). Interestingly, the use of 2-OH-4,4′-*t*Bu-1,1′-bipyridine (**L4**) significantly increased the product yield to 72% (entry 5). We assumed that the presence of a *t*-butyl group in **L4** can increase the solubility of the generated Pd/**L4** complex relative to that of Pd/**L1** in reaction. Other nitrogen ligands (**L5**–**L7**) [9] were also tested in reaction but did not attain improved results (entries 6–8). The survey of oxidants showed that silver salt

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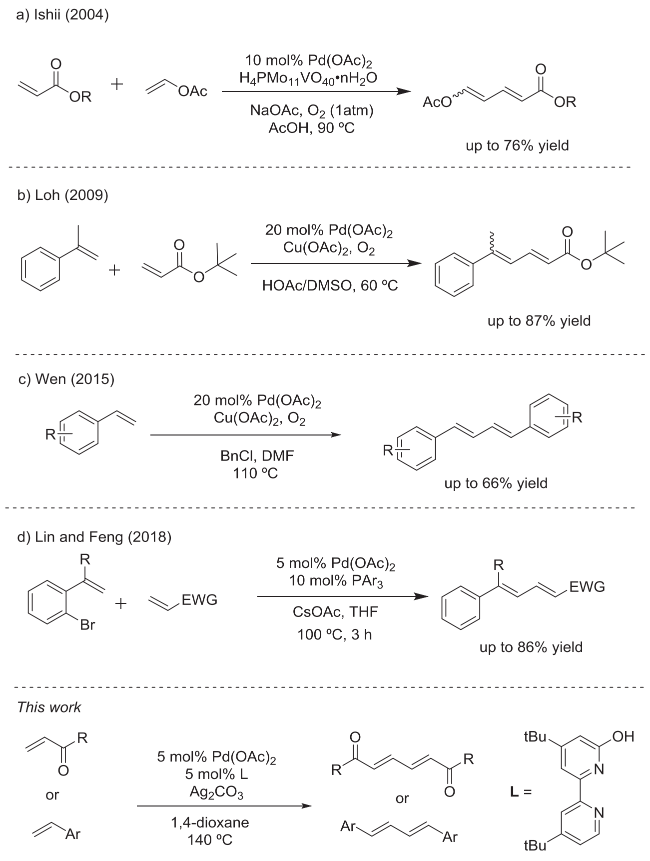
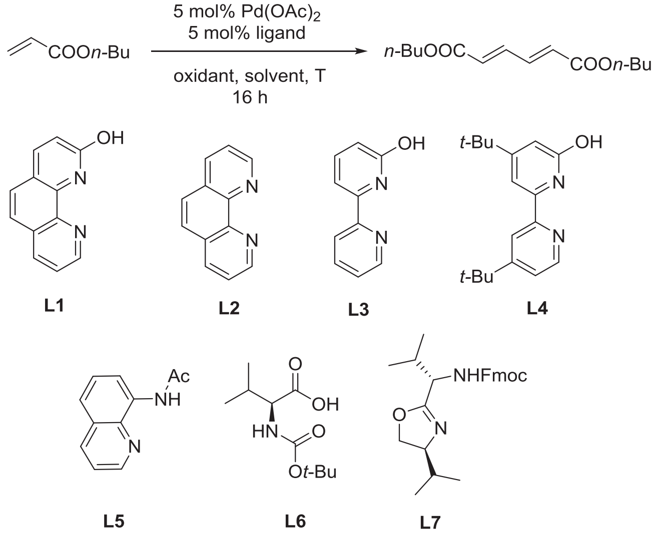


Scheme 1. Pd-catalyzed simple alkenes to form conjugated dienes.

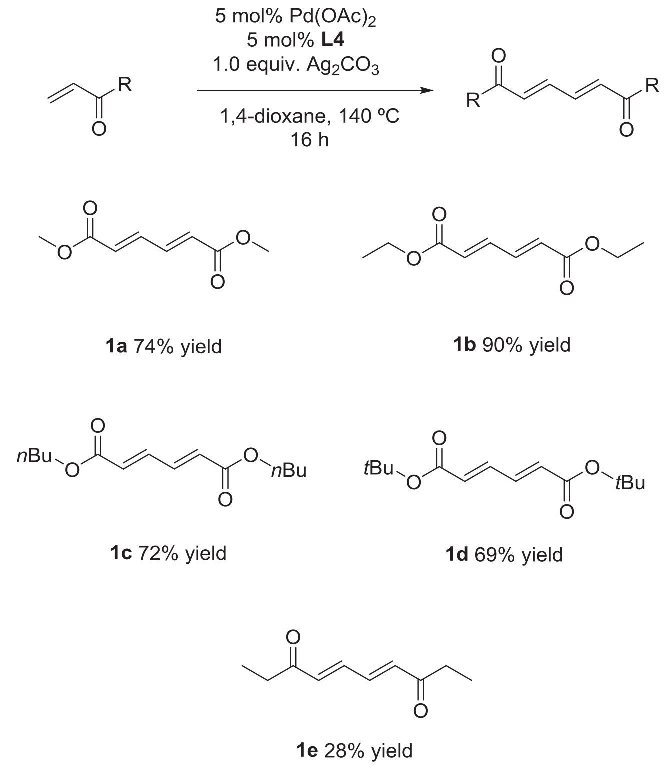
Table 1
Optimization of reaction conditions.[a]



Entry	Ligand	Oxidant (equiv.)	Solvent	T(°C)	Yield[b](%)
1	/	Ag_2CO_3 (1.0)	Dioxane	140	n. p[c]
2	**L1**	Ag_2CO_3 (1.0)	Dioxane	140	21
3	**L2**	Ag_2CO_3 (1.0)	Dioxane	140	n. p.
4	**L3**	Ag_2CO_3 (1.0)	Dioxane	140	14
5	**L4**	Ag_2CO_3 (1.0)	Dioxane	140	75 (72[d])
6	**L5**	Ag_2CO_3 (1.0)	Dioxane	140	n. p.
7	**L6**	Ag_2CO_3 (1.0)	Dioxane	140	n. p.
8	**L7**	Ag_2CO_3 (1.0)	Dioxane	140	n. p.
9	**L4**	AgOAc (1.0)	Dioxane	140	60
10	**L4**	Ag_2CO_3 (2.0)	Dioxane	140	66
11	**L4**	Ag_2O (1.0)	Dioxane	140	n. p.
12	**L4**	AgTFA (1.0)	Dioxane	140	n. p.
13	**L4**	Cu_2CO_3 (1.0)	Dioxane	140	15
14	**L4**	Ag_2CO_3 (1.0)	dioxane	150	55
15	**L4**	Ag_2CO_3 (1.0)	Dioxane	120	50
16	**L4**	Ag_2CO_3 (1.0)	DME	140	35
17	**L4**	Ag_2CO_3 (1.0)	CH_3CN	140	n. p.
18	**L4**	Ag_2CO_3 (1.0)	DMF	140	9
19	**L4**	Ag_2CO_3 (1.0)	DMA	140	27

[a] All the reactions were conducted with 0.40 mmol of alkenes in 2.0 mL of solvent.
[b] Yields were determined by 1H NMR analysis of the crude product using CH_2Br_2 as the internal standard.
[c] n. p. = no product.
[d] Isolated yields.

Table 2
Pd-catalyzed oxidative homo-coupling of acrylates.[a,b]



[a]All the reactions were conducted with 0.40 mmol of alkenes in 2.0 mL of solvent.
[b]Isolated yields.

was more effective than copper salt containing OAc$^-$ or CO$_3^{2-}$ (entries 9–13). We also found that neither higher nor lower reaction temperatures were beneficial for the reaction yield (entries 14 and 15). Finally, various solvents, such as DME, CH_3CN, and DMF were screened (entries 16–19), but no further improvement was achieved.

Under the obtained optimized conditions, the scope of several acrylates was investigated (Table 2). Ethyl acrylate, methyl acrylate, and *n*-butyl acrylate provided the expected products in moderate to good yields. However, the reaction of buten-2-one led to 28% yield. We next examined the reaction of aromatic alkenes under the reaction conditions in Table 3. The reaction of styrene provided 51% of the desired product at 140 °C. Substituents at