Dual Catalysis

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Chiral Primary Amine/Palladium Dual Catalysis for Asymmetric Allylic Alkylation of β-Ketocarbonyl Compounds with Allylic Alcohols

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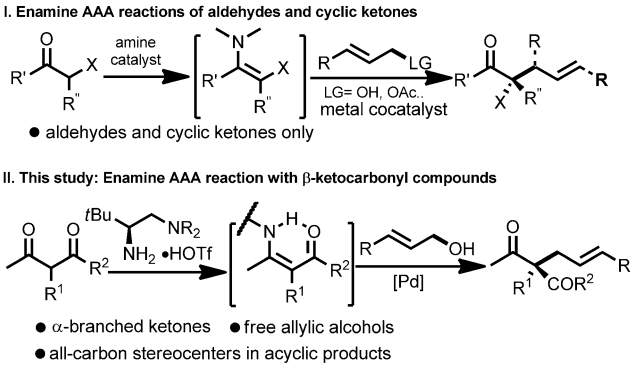
Abstract: *An efficient dual catalytic system composed of a chiral primary amine and a palladium complex was developed to promote the direct asymmetric allylic alkylation (AAA) of β-ketocarbonyl compounds. In particular, the synergistic dual catalytic system enabled the AAA reaction of challenging acyclic aliphatic ketones, such as β-ketocarbonyl compounds and 1,3-diketones.*

Transition-metal-catalyzed asymmetric allylic alkylation (AAA) reactions serve as a versatile and powerful tool for enantioselective C–C bond formation.[1] One of the most recent developments along this line are enamine-based AAA reactions. As versatile nucleophilic synthons and catalytic intermediates, enamines, either preformed or generated in situ, have long been investigated for allylic alkylation reactions.[2] The merging of aminocatalysis, an iconic form of organocatalysis, with transition-metal catalysis has enabled asymmetric allylic alkylation reactions of simple aldehydes and ketones (Scheme 1 I), for which the typical enolate-based approaches were generally less effective owing to the requirement of a stoichiometric base as well as associated issues with racemization and side pathways.[3–5] Córdova first introduced the dual amine/palladium-catalyzed allylic alkylation with aldehydes and cyclic ketones in 2006.[4e] Later on, the synergistic amine–transition-metal-catalyzed asymmetric allylic alkylation was extended to α-branched aldehydes through elegant contributions from the research groups of List and Carreira.[4a,d] Despite these advances, acyclic ketones remained elusive substrates for this reaction.

The direct use of free allylic alcohols in AAA reactions has attracted much attention owing to the high reaction economy. However, free allylic alcohols are normally sluggish substrates requiring higher reaction temperatures or additional activators for the generation of the active π-allyl intermediates; hence, most such reactions have been limited to achiral transformations.[6] Transition-metal-catalyzed AAA reactions with allylic alcohols under mild conditions are still rare.[2c,6a,7] On the other hand, β-ketocarbonyl compounds are versatile synthetic intermediates for the synthesis of natural and bioactive products, and the development of stereoselective transformations of β-ketocarbonyl compounds is of long-standing interest in organic chemistry. Although the creation of quaternary carbon stereocenters with cyclic β-ketocarbonyl compounds by AAA reactions has been well documented by Trost and co-workers and others,[1e,5e,8] asymmetric allylic alkylation with acyclic β-ketocarbonyl compounds remains an unaddressed issue in this field.[1e,8a,c,9] In particular, the successful combination of simple allylic alcohols and acyclic β-ketocarbonyl compounds has not been reported previously. Herein, we describe an unprecedented asymmetric allylic alkylation of acyclic β-ketocarbonyl compounds with free allylic alcohols under mild conditions (Scheme 1 II). The reaction was enabled by a synergistic combination of our developed chiral primary amine and palladium catalyst[10] and features the enantioselective construction of quaternary stereocenters with challenging acyclic aliphatic ketones, such as β-ketocarbonyl compounds and 1,3-diketones.



Scheme 1. Strategies and scope of enamine AAA reactions. LG = leaving group, Tf = trifluoromethanesulfonyl.

Our initial investigation was performed with *tert*-butyl 2-methyl-3-oxobutanoate (**1a**, 0.15 mmol), cinnamyl alcohol (**2a**, 0.1 mmol), [{Pd(allyl)Cl}$_2$] (5 mol%), PPh_3 (20 mol%), and the primary amine **4a** (20 mol%) in CH_3CN (0.5 mL) for 36 h at 40 °C. We obtained the desired product in excellent yield and with a moderate *ee* value (Table 1, entry 1). The two most commonly used palladium-catalyst precursors were tested next, but none of the desired product was formed (Table 1, entries 2 and 3). We then investigated other primary–tertiary-diamine catalysts (Table 1, entries 4–12) and found that *tert*-leucine-derived primary-tertiary diamines gave the best results (Table 1, entries 4–9); other primary-amine catalysts gave inferior results or were even inert for the reaction (Table 1, entries 10–12). We synthesized a series of primary–tertiary diamines with the *tert*-leucine skeleton with variations in the tertiary-amine moiety. It was found that the steric encumbrance of the tertiary-amine moiety significantly

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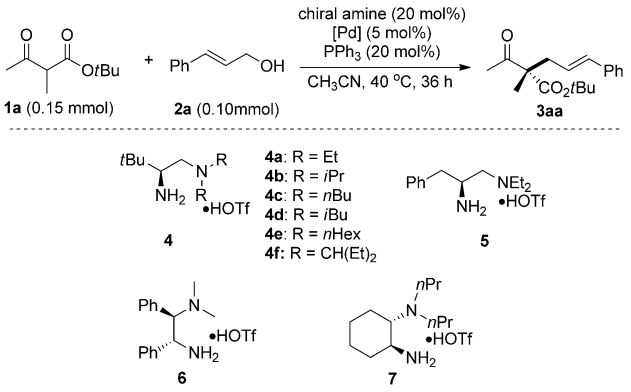
Table 1: Screening and optimization.

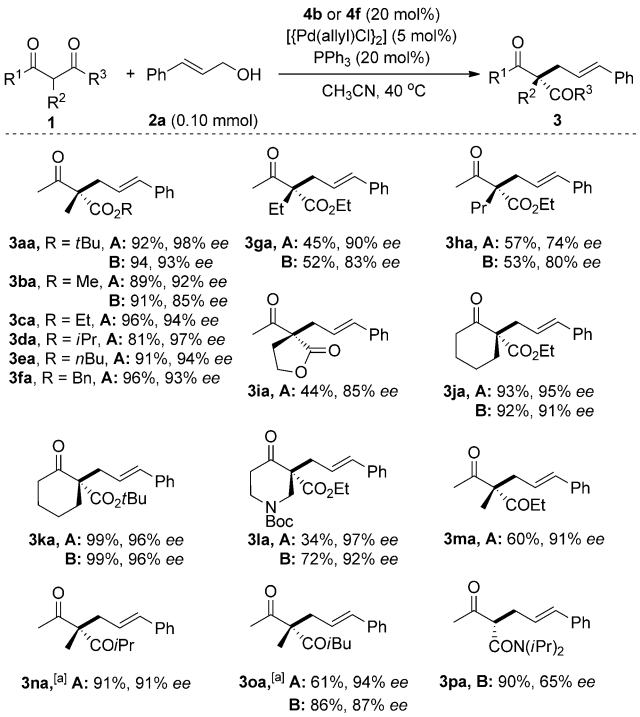


Entry	[Pd] source	Amine	Yield [%][a]	*ee* [%]
1	$[\{Pd(allyl)Cl\}_2]$	**4a**	90	54
2	$Pd(PPh_3)_4$	**4a**	n.r.	
3	$Pd_2(dba)_3$	**4a**	trace	n.d.
4	$[\{Pd(allyl)Cl\}_2]$	**4b**	94	93
5	$[\{Pd(allyl)Cl\}_2]$	**4c**	88	62
6	$[\{Pd(allyl)Cl\}_2]$	**4d**	92	88
7	$[\{Pd(allyl)Cl\}_2]$	**4e**	94	70
8	$[\{Pd(allyl)Cl\}_2]$	**4f**	25[b]	>99
9	$[Pd(allyl)Cl]_2$	**4f**	92[c]	98
10	$[\{Pd(allyl)Cl\}_2]$	**5**	n.r.	
11	$[\{Pd(allyl)Cl\}_2]$	**6**	83	14
12	$[\{Pd(allyl)Cl\}_2]$	**7**	n.r.	
13	$[\{Pd(allyl)Cl\}_2]$	–	trace	n.d.
14	–	**4b**	n.r.	
15	$[\{Pd(allyl)Cl\}_2]$	**4b**[d]	n.r.	

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.10 mmol), chiral amine (20 mol%), Pd precursor (5 mol%), PPh_3 (20 mol%), CH_3CN (0.5 mL), 40°C, 36 h. [b] Reaction time: 40 h. [c] The reaction was carried out with 3 equivalents of ketoester **1a**, and the reaction time was extended to 72 h. [d] The reaction was carried out without the conjugate acid HOTf. dba = dibenzylideneacetone, n.r. = no reaction, n.d. = not determined.

influenced the enantioselectivity of the reaction to form the desired product. With bulkier substituents, improved enantioselectivity was observed (Table 1, entries 4–8); optimal results were obtained with the isopropyl-substituted catalyst **4b** and pentan-3-yl-substituted catalyst **4f** (Table 1, entries 4 and 8). In the presence of **4b**, the reaction gave **3aa** in 94% yield with 93% *ee* (Table 1, entry 4), whereas the more sterically hindered catalyst **4f** gave the product with >99% *ee*, albeit at the expense of catalytic activity (25% yield; Table 1, entry 8). In this case, when the reaction time was prolonged and the ratio of **1a** to **2a** was increased to 3:1, the product was formed in 92% yield with 98% *ee* (Table 1, entry 9). Control experiments revealed that the reaction did not proceed with either a palladium catalyst or a primary-amine catalyst alone (Table 1, entries 13 and 14). The conjugated acid TfOH was also essential for this reaction (Table 1, entry 15). Mechanistically, it is known that TfOH could expedite the formation of the enamine intermediate,[10] and it may also facilitate the formation of the π-allyl intermediate in this context.[11]

Having optimized the reaction conditions, we first examined the functional-group tolerance of the reaction with a variety of β-ketocarbonyl compounds. The identified catalysts **4b** and **4f** were both examined in a few selected cases. Different ester moieties of various sizes were generally tolerated to give the desired adducts in good yields with excellent enantioselectivity (Scheme 2, products **3aa–fa**). The catalyst **4b** showed higher reactivity with substrates **1a** and **1b**. On the other hand, better enantioselectivity was generally obtained with catalyst **4f** (products **3aa** and **3ba**). Bulky α-substituents were found to lead to reduced reactivity and enantioselectivity (Scheme 2, products **3ga** and **3ha**), and the less bulky catalyst **4b** was preferable for the substrate with a bulky propyl substituent (**3ha**). Cyclic β-ketoesters were also tolerated and transformed into the desired products **3ja** and **3ka** with high enantioselectivity and reactivity. A piperidone-derived substrate was also used in the reaction to give the desired product **3la** with 97 and 92% *ee* under the two sets of optimal conditions. Even the β-diketone substrate **1m**, once regarded as an challenging substrate for the transition-metal-catalyzed AAA reaction owing to the steric and electronic similarities of the two keto moieties, was compatible with our primary–tertiary diamine/palladium catalytic system and was converted into the desired product **3ma** in 60% yield with 91% *ee*. When the bulkiness of one keto moiety was increased, the enantioselectivity was not affected, and the desired products **3na** and **3oa** were obtained in good yield with high enantioselectivity. Notably, a α-

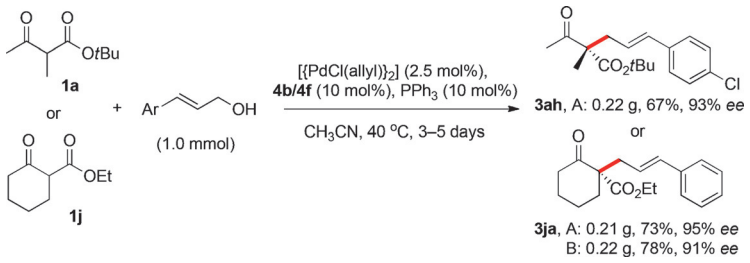


Scheme 2. Scope of the reaction with respect to the β-ketocarbonyl substrate (**1a–p**). Method **A**: The reaction was performed with **1** (0.30 mmol), **2a** (0.10 mmol), **4f** (20 mol%), $[\{PdCl(allyl)\}_2]$ (5 mol%), and PPh_3 (20 mol%) in CH_3CN (0.5 mL) at 40°C for 72 h. Method **B**: The reaction was performed with **1** (0.15 mmol), **2a** (0.10 mmol), **4b** (20 mol%), $[\{PdCl(allyl)\}_2]$ (5 mol%), and PPh_3 (20 mol%) in CH_3CN (0.5 mL) at 40°C for 36 h. [a] Reaction time: 96 h. Bn = benzyl, Boc = *tert*-butoxycarbonyl.

nonsubstituted β-ketoamide was also tested, and the desired monoalkylation product **3pa** was obtained in high yield with 65% *ee* (Scheme 2). Asymmetric allylic alkylation reactions with such compounds have not succeeded previously.[6a,f]

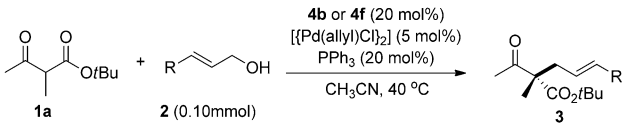
We then set out to explore the scope of the AAA reaction with regard to the allylic-alcohol component. A range of cinnamyl alcohols bearing either electron-donating or electron-withdrawing groups at the *ortho*, *meta*, or *para* position of the arene moiety participated in the allylic alkylation of *tert*-butyl 2-methyl-3-oxobutanoate (**1a**) to furnish the desired products in good to high yield with excellent enantioselectivity (Table 2, entries 1–9, products **3ab**–**aj**). A 2-naphthyl-substituted allylic alcohol was also applicable and was converted into the expected product in 87% yield with 98% *ee* (Table 2, entry 10). Cinnamylic alcohols incorporating heteroarenes were also proved to be good substrates and were converted into the corresponding products in moderate yield with excellent enantioselectivity (Table 2, entries 11 and 12). The aliphatic allylic alcohols prop-2-en-1-ol was also tested, and the desired product was obtained in 51% yield with 86% *ee* in 12 h. Secondary allylic alcohols, such as 2-cyclohexen-1-ol and 4-phenyl-2-butenol, showed very low reactivity, probably as a result of the inertness of these allylic alcohols toward the formation of a π-allyl intermediate, and they could be recovered quantitatively after treatment under the present conditions.[12]

To evaluate the practicality of the present method, we performed a large-scale synthesis with both acyclic and cyclic β-ketoesters **1a** and **1j** in the presence of only 10 mol% of **4b** or **4f** and 2.5 mol% of [{PdCl(allyl)}$_2$]. Comparable results were obtained with a prolonged reaction time (Scheme 3).



Scheme 3. Gram-scale experiments with **1a** and **1j**.

Table 2: Scope of the reaction with respect to the allylic alcohol (**2a**–**n**).



Entry	R	Product	Method	Yield [%]	*ee* [%]
1	4-$CH_3C_6H_4$	**3ab**	**A**	74	97
			B	64	93
2	4-$CH_3OC_6H_4$	**3ac**	**A**	96	96
			B	96	93
3	4-*t*BuC_6H_4	**3ad**	**A**	61	97
			B	99	92
4	3-$CH_3OC_6H_4$	**3ae**	**A**	71	98
			B	92	93
5	2-$CH_3OC_6H_4$	**3af**	**A**	92	98
			B	96	90
6	4-FC_6H_4	**3ag**	**A**	91	97
			B	89	93
7	4-ClC_6H_4	**3ah**	**A**	91	97
			B	75	94
8	3-FC_6H_4	**3ai**	**A**	87	98
			B	91	93
9	2-FC_6H_4	**3aj**	**A**	72	98
			B	34	92
10	2-naphthyl	**3ak**	**A**	87	98
			B	95	93
11	2-furyl	**3al**	**A**	42	97
			B	92	90
12	2-thiophenyl	**3am**	**B**	59	91
13[b]	H	**3an**	**B**	51	86

[a] Method **A**: **1a** (0.30 mmol), **2** (0.10 mmol), **4f** (20 mol%), [{PdCl(allyl)}$_2$] (5 mol%), PPh_3 (20 mol%), CH_3CN (0.5 mL), 40°C, 72 h. Method **B**: **1a** (0.15 mmol), **2** (0.10 mmol), **4b** (20 mol%), [{PdCl(allyl)}$_2$] (5 mol%), PPh_3 (20 mol%), CH_3CN (0.5 mL), 40°C, 36 h. [b] Reaction time: 12 h. The *ee* value of the desired product was determined after one-step transformation into **3aa** through olefin cross-metathesis (see the Supporting Information).

On the basis of a previous report,[8d] the absolute configuration of the newly formed quaternary stereocenter was assigned to be *S*.[10,13] Accordingly, *Si*-facial attack of the π-allylpalladium complex on the enamine intermediate can be proposed to account for the observed stereoinduction (Figure 1). In this mode, steric effects play a key role in channeling the attack of the π-allylpalladium species, for which a notable H-bonding site is lacking. The observed effect of bulky substituents on the tertiary amino moiety is clearly in support of this steric model (Table 1). Besides serving as a steric directing group, the protonated tertiary amine also participates in intramolecular H-bonding, as previously verified,[14] and results in a restricted conformation, which is also beneficial for stereoselectivity.

In summary, we have developed a highly enantioselective allylic alkylation of β-ketocarbonyl compounds with simple allylic alcohols by merging primary–tertiary-diamine and palladium catalysis. The reaction features the versatile enantioselective construction of a quaternary stereocenter in an acyclic compound under rather mild conditions. The synergistic combination of chiral primary–tertiary-diamine and transition-metal catalysis enables unprecedented asymmetric allylation reactions of acyclic aliphatic ketones,

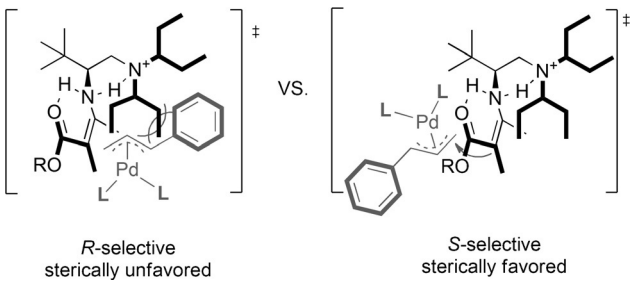


Figure 1. Proposed transition state for the *S*-selective AAA reactions.

including challenging aliphatic β-ketocarbonyl compounds and 1,3-diketones.

Experimental Section

General procedure: *tert*-Butyl 2-methyl-3-oxobutanoate (**1a**, 0.15 or 0.30 mmol), cinnamyl alcohol (**2a**, 0.1 mmol), [{Pd(allyl)Cl}$_2$] (5 mol%), PPh_3 (20 mol%), and a primary amine (**4b** or **4f**, 20 mol%) were placed in a flame-dried Schlenk tube equipped with a magnetic stir bar, and the mixture was diluted with anhydrous CH_3CN (0.5 mL) and then degassed 3 times by a standard freeze–thaw method. The mixture was stirred at 40 °C for 36 or 72 h. The solvent was then removed, and the residue was purified by silica-gel chromatography (5% EtOAc in petroleum ether) to give **3aa** as a colorless oil. The *ee* value was determined by HPLC (OJ-H column).

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Keywords: allylic alcohols · asymmetric allylic alkylation · chiral primary amines · palladium · β-ketocarbonyl compounds

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