Synthetic Methods

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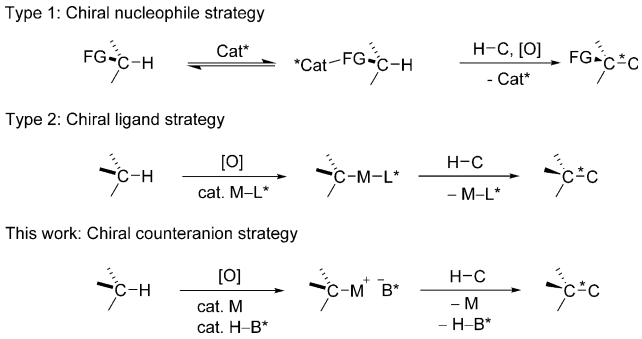
Chiral Counteranion Strategy for Asymmetric Oxidative C(sp^3)–H/C(sp^3)–H Coupling: Enantioselective α-Allylation of Aldehydes with Terminal Alkenes**

*Pu-Sheng Wang, Hua-Chen Lin, Yu-Jia Zhai, Zhi-Yong Han, and Liu-Zhu Gong**

Abstract: *The first enantioselective α-allylation of aldehydes with terminal alkenes has been realized by combining asymmetric counteranion catalysis and palladium-catalyzed allylic C–H activation. This method can tolerate a wide scope of α-branched aromatic aldehydes and terminal alkenes, thus affording allylation products in high yields and with good to excellent levels of enantioselectivity. Importantly, the findings suggest a new strategy for the future creation of enantioselective C–H/C–H coupling reactions.*

Carbon–carbon bond formation is unarguably the basis for building up structurally complex molecules.[1] Among various means of forging carbon–carbon bonds,[2] the direct oxidative coupling of two different C–H bonds, now known as cross-dehydrogenative coupling (CDC),[3] turns out to be one of most appealing synthetic alternatives to conventional coupling procedures, which mostly rely on the use of prefunctionalized starting materials. Over the last decade, CDC reactions have proven adequate with a range of nucleophiles and oxidants, and are capable of accommodating a variety of functional groups.[3] Although endeavors toward direct catalytic enantioselective CDC reactions for the construction of carbon–carbon bonds have been reported in recent years,[4] successful protocols are still rather limited.

Basically, the general strategies for stereochemical control in asymmetric C–H/C–H coupling reactions can be categorized into two main types (Scheme 1): one is the chiral nucleophile strategy,[4a–g] wherein the nucleophile is reversibly bonded to a chiral Lewis acid or organocatalyst and controls the stereochemistry during the reaction with electrophiles. The other relies on the use of chiral ligands[4h] which can coordinate to transition-metal catalysts to enantioselectively control C–H activation or (and) the bond-forming events. Herein, we introduce the use of a chiral counteranion strategy to control the stereochemistry of C(sp^3)–H/C(sp^3)–H oxidative coupling reactions, thus enabling the first enantioselective α-allylation of aldehydes with terminal alkenes.



Scheme 1. General strategies for asymmetric oxidative C–H/C–H coupling reactions.

Recently, the use of chiral anions to control stereochemistry in asymmetric catalysis has received a great deal of attention,[5] thus leading to the appearance of exciting new modes of reactivity or selectivity and thereby enabling the discovery of highly stereoselective transformations. Encouraged by our previous studies on chiral counteranion controlled asymmetric allylic alkylation[6] and palladium-catalyzed allylic C–H-activation-based olefination,[7] we hypothesized that chiral counteranion catalysis might provide a new strategy to realize asymmetric allylic C–H alkylation, as a showcase for chiral counteranion controlled enantioselective C–H/C–H oxidative coupling reaction. Although palladium-catalyzed allylic C–H-activation-based carbon–carbon bond formation reactions have been well established,[8] the asymmetric versions have met with little success until Trost and co-workers reported a chiral phosphine ligand promoted palladium-catalyzed allylic C–H activation.[4h,9] We proposed that in the presence of palladium(0), an oxidant, and a chiral phosphoric acid, olefins bearing allylic C–H bonds could be oxidized to generate the π-allyl palladium phosphate complex **I** (Scheme 2), which was a critical intermediate for stereoselective allylic alkylation with an enamine, via the transition-state **TS-1**, as demonstrated by List and co-workers,[10] leading to the formation of an optically active allylation product. As a consequence, we believed that the combined catalytic system[10,11] of palladium(0), amine, and chiral phosphoric acid would enable asymmetric α-allylation of aldehydes[12] with terminal alkenes under oxidizing conditions.

The enolizable aldehydes are highly reactive and thus able to participate in many side reactions, such as dehydrogenation[13] and C–C bond cleavage[14] under oxidizing conditions,

[*] P.-S. Wang, H.-C. Lin, Y.-J. Zhai, Z.-Y. Han, Prof. Dr. L.-Z. Gong
Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry
University of Science and Technology of China
Hefei, 230026 (China)
E-mail: gonglz@ustc.edu.cn
Prof. Dr. L.-Z. Gong
Collaborative Innovation Center of Chemical Science and Engineering, Tianjin (China)

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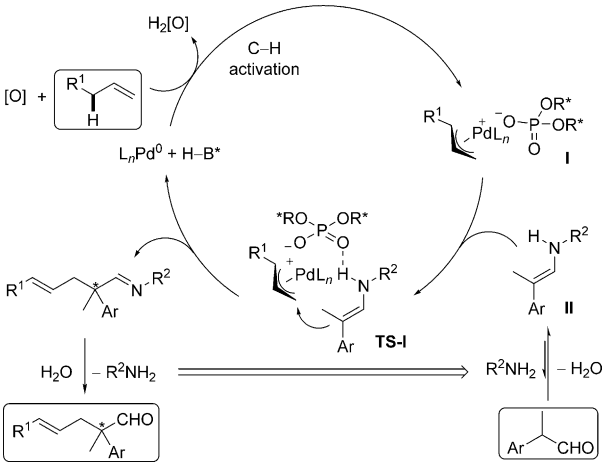
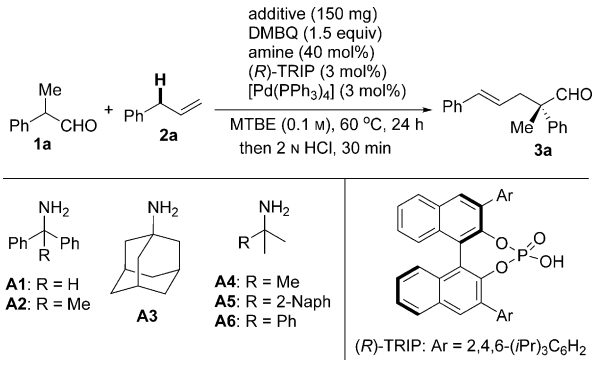


Scheme 2. Design of C–H-activation-based asymmetric α-allylation of aldehydes with terminal alkenes by using chiral counteranion strategy.

so to accomplish the desired oxidative cross-coupling reaction, a bulky and mild oxidant [2,6-dimethylbenzoquinone (DMBQ)] which has demonstrated utility in a number of oxidation reactions,[4h, 8c] was used in the reaction. Thus, the validation of the hypothesis for the proposed asymmetric α-allylation of aldehydes with terminal alkenes started with a reaction of 2-phenylpropanal (**1a**) and allylbenzene (**2a**) by using DMBQ as the oxidant in the presence of $[Pd(PPh_3)_4]$ (3 mol%), (*R*)-TRIP[15] (3 mol%), and an achiral amine (40 mol%) at 60°C (Table 1). Disappointingly, only trace amounts of the oxidative coupling product **3a** were detected when the diphenylmethanamine **A1**, which was the best cocatalyst in the asymmetric allylic alkylation of allylic alcohols and aldehydes,[10b] was used (entry 1). The desired reaction failed to occur under the oxidizing conditions, probably stemming from the fact that the diphenylmethanamine was easily oxidized into the corresponding diphenylmethanimine[16] and thereby lost the capacity to activate the aldehyde. Indeed, a small amount of benzophenone produced from the hydrolysis of diphenylmethanimine was detected by GC-MS (see the Supporting Information). Thus, a variety of hard-to-oxidize achiral primary amines bearing quaternary carbon atoms were subsequently evaluated (entries 2–6). To our delight, these reactions proceeded smoothly to afford the desired **3a** in much enhanced yields and in particular, the cumylamine **A6** gave the best results in terms of both yield and enantioselectivity (entry 6). Notably, the addition of desiccants to the reaction system had obvious effects on the performance of the reaction (entries 7–10). For instance, the presence of either $MgSO_4$ or 5 Å molecular sieves led to a decrease in the yield but maintained the enantioselectivity (entries 7 and 8). In contrast, the enhanced yield and enantioselectivity (74%, 90% *ee*) were obtained upon using 3 Å molecular sieves as an additive (entry 10).

Under the optimized reaction conditions, we next explored the substrate scope with respect to the aldehydes (Table 2). A wide range of 2-aryl propinonaldehydes bearing either electron-donating or electron-withdrawing groups was nicely tolerated (entries 1–10), thus giving rise to the desired allylation products in moderate to good yields and with high

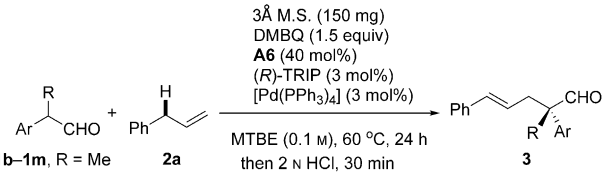
Table 1: Screening of catalysts and optimization of the reaction conditions.[a]

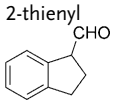


Entry	Amine	Additive	Conv. [%][b]	Yield [%][b]	*ee* [%][c]
1	**A1**	–	65	3	–
2	**A2**	–	67	32	60
3	**A3**	–	96	78	30
4	**A4**	–	96	83	65
5	**A5**	–	94	35	85
6	**A6**	–	86	67	85
7	**A6**	$MgSO_4$	87	47	85
8	**A6**	5 Å M.S.	80	49	84
9	**A6**	4 Å M.S.	96	79	82
10	**A6**	3 Å M.S.	92	74(72[d])	90

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Pd(PPh_3)_4]$ (3 mol%), (*R*)-TRIP (3 mol%), amine (40 mol%), DMBQ (1.5 equiv), additive (150 mg), MTBE (2 mL), 60°C, 24 h, under Ar. [b] Based on ^{1}H NMR analysis of the crude reaction mixture using benzyl benzoate as an internal standard. [c] The *ee* value was determined by HPLC and the absolute configuration was assigned by comparing the optical rotation with the literature value.[10, 12] [d] Yield of isolated product. M.S. = molecular sieves, MTBE = *tert*-butyl methyl ether.

Table 2: Scope with respect to the aldehydes.[a]



Entry	Ar	1	3	Yield [%][b]	*ee* [%][c]
1	4-MeC_6H_4	**1b**	**3b**	65	88
2	4-PhC_6H_4	**1c**	**3c**	90	87
3	4-$MeOC_6H_4$	**1d**	**3d**	73	84
4	4-ClC_6H_4	**1e**	**3e**	89	74
5	4-$CF_3C_6H_4$	**1f**	**3f**	85	67
6	3-MeC_6H_4	**1g**	**3g**	79	89
7	3-$MeOC_6H_4$	**1h**	**3h**	75	86
8	3-ClC_6H_4	**1i**	**3i**	81	78
9	2-FC_6H_4	**1j**	**3j**	51	81
10	6-tetralinyl	**1k**	**3k**	85	88
11	2-naphthyl	**1l**	**3l**	85	87
12	2-thienyl	**1m**	**3m**	34	90
13		**1n**	**3n**	38	85

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), $[Pd(PPh_3)_4]$ (3 mol%), (*R*)-TRIP (3 mol%), **A6** (40 mol%), DMBQ (1.5 equiv), 3 Å MS(150 mg), MTBE (2 mL), 60°C, 24 h, under Ar. [b] Yield of isolated product. [c] Determined by HPLC.

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levels of enantioselectivity (up to 90% *ee*). Basically, 2-aryl propinonaldehydes containing electron-donating substituents at the *para* position appeared to deliver higher enantioselectivities than those with electron-withdrawing groups (entries 1–3 versus 4 and 5). A similar trend in the stereoselectivity was also observed for the *meta*-substituted 2-aryl propinonaldehydes (entries 6 and 7 versus 8). Although 2-(2-fluorophenyl) propinonaldehyde was seemingly less reactive, the enantioselectivity remained to be high (entry 9). A 3,4-disubstited 2-(6-tetralinyl) propinonaldehyde (**1k**), underwent a clean allylation reaction with **2a** in high yield and with 88% *ee* (entry 10). Using 2-naphthyl propinonaldehyde in the asymmetric allylation afforded **3l** in 85% yield and 87% *ee* (entry 11). Notably, 2-thienyl propinonaldehyde also participated in the allylation reaction with excellent enantioselectivity (90% *ee*), but gave a much lower yield (entry 12). Moreover, a 2,3-dihydro-1-indanone-derived aldehyde was also a suitable substrate and furnished the allylation product with high enantiomeric excess, but in moderate yield (entry 13).

Finally, the generality for terminal alkenes was examined under the optimized reaction conditions (Table 3). Significantly, the protocol was amenable to a wide range of unactivated allylarenes. In general, the enantioselectivity was not significantly affected by the electronic nature and substitution pattern of the arene moiety. Thus, the allylarenes examined were all able to provide high stereochemical outcomes ranging from 84 to 90% *ee*. However, the reactivity appeared to be greatly influenced by the aryl substituent. For instance, the reaction with allylbenzenes substituted with an electron-deficient or an alkyl substituent at the *para* position of benzene ring proceeded smoothly under the optimal reaction conditions (entries 1, 3, and 4). In contrast, the substrates possessing a strongly electron-donating group or a chloride *para* to the allyl moiety showed a slightly lower reactivity and, consequently, an elevated reaction temperature was required to provide a good yield (entry 2 or 5). Moreover, the allylation reaction with *meta*-substituted allylbenzenes also required a reaction temperature of 80°C, together with the use of more of the catalyst to ensure a good conversion (entries 6–9). Both 2-allylnaphthalene and 3-allylthiophene were compatible with the optimal reaction conditions, thus delivering the desired products in good yields and with high enantioselectivities (entries 10 and 11). Furthermore, a 1,4-diene was also able to afford the alkylation product in good yield and enantioselectivity (entry 12).

In conclusion, we have established a highly enantioselective α-allylation reaction of aldehydes with terminal alkenes by combining asymmetric counteranion catalysis and palladium-catalyzed allylic C–H activation. A wide variety of α-branched aromatic aldehydes and terminal alkenes were able to undergo the C–H-activation-based asymmetric allylic alkylation to afford good to excellent enantioselectivity. More importantly, this work actually demonstrates a general strategy for enantioselective functionalization of inactive C–H bonds and will provide an alternative platform for the creation of new enantioselective C–H/C–H coupling reactions.

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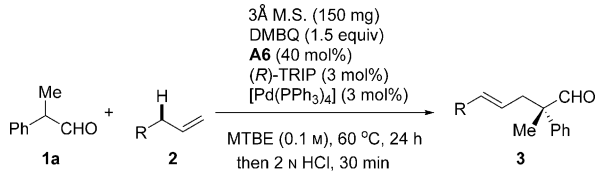
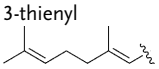
Table 3: Scope with respect to the alkenes.[a]



Entry	R	2	3	Yield [%][b]	*ee* [%][c]
1	4-*t*BuC$_6$H$_4$	**2b**	**3o**	90	90
2[d,e]	4-MeOC$_6$H$_4$	**2c**	**3p**	79	90
3	4-CO$_2$MeC$_6$H$_4$	**2d**	**3q**	83	86
4	4-CF$_3$C$_6$H$_4$	**2e**	**3r**	61	80
5[e]	4-ClC$_6$H$_4$	**2f**	**3s**	60	84
6[d,e]	3-MeC$_6$H$_4$	**2g**	**3t**	64	88
7[d,e]	3-MeOC$_6$H$_4$	**2h**	**3u**	50	88
8[d,e]	3-ClC$_6$H$_4$	**2i**	**3v**	54	87
9[d,e]	3-CO$_2$MeC$_6$H$_4$	**2j**	**3w**	60	86
10	2-naphthyl	**2k**	**3x**	47	88
11	3-thienyl	**2l**	**3y**	57	90
12[d]		**2m**	**3z**	70[f]	85

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Pd(PPh$_3$)$_4$ (3 mol%), (*R*)-TRIP (3 mol%), **A6** (40 mol%), DMBQ (1.5 equiv), 3 Å M.S. (150 mg), MTBE (2 mL), 60°C, 24 h, under Ar. [b] Yield of the isolated product. [c] Determined by HPLC. [d] [Pd(PPh$_3$)$_4$] (6 mol%), (*R*)-TRIP (6 mol%), **A6** (80 mol%). [e] The reaction was conducted at 80°C. [f] *E*/*Z* = 3.3:1; determined by ^{1}H NMR spectroscopy.

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