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Palladium-catalysed α and β C–H allylation of aryl alkenes†Yilei Liao,^{†,a} Xiandie Zhang,^{†,a} Xiaoli Li,^a Xiuying Liu,^a Jiakai Chen,^a Chao Shen,^{*b}
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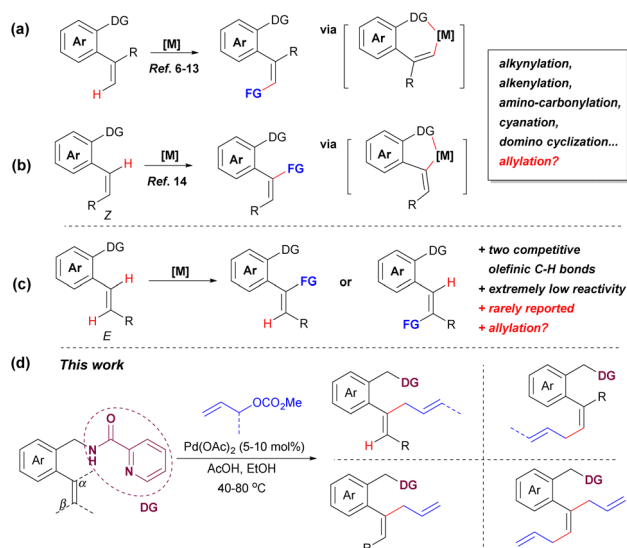
Remarkable progress has been made on chelation-assisted α and β C–H functionalization of aryl alkenes; however, there is no report on C–H allylation reactions. This work focuses on the first α and β C–H allylation of aryl alkenes using allyl carbonates to produce linear and branched 1,4-dienes enabled by chelation-assistance of pyridine-2-carboxamide, simply performed with Pd(OAc)₂/AcOH in ethanol. This operationally simple protocol exhibited wide functionality tolerance and broad substrate scope and enabled successful gram-scaled preparation.

Introduction

Chelation-assisted C–H functionalization represents a powerful strategy toward structural complexity from simple raw feedstocks. Among them, olefinic C–H functionalization has attracted remarkable attentions, which provide regio- and stereo-selective synthesis of olefinic derivatives such as 1,3-dienes, 1,4-dienes, and enynes.^{1–3} These chelation-assisted alkenyl C–H functionalizations proceed by *endo*- or *exo*-metallocycle intermediates, generally using 1,1-disubstituted alkenes² and disubstituted *Z*-alkenes³ as the substrates, with the other possible reaction sites blocked (Scheme 1a). To the best of our knowledge, although C–H functionalization of *Z*-alkenes by *exo*-metallocycle has shown remarkable progress,³ chelation-assisted α C–H functionalization of *E*-alkenes (including *E*-styrenes) bearing two competitive C–H bonds through *exo*-cyclometallation remains unexplored.

Aryl alkenes are widely occurring and show extensive applications in material and pharmaceutical science.⁴ Significant

progress has been made on chelation-assisted olefinic C–H functionalization of aryl alkenes.^{5–13} The well-defined one is the β C–H functionalization of aryl alkenes by *endo*-metallocycles, including C–H alkylation, alkenylation, cyanation and amino-carbonylation (Scheme 1a).^{6–13} However, α C–H functionalization of aryl alkenes has attracted very limited attention, and the reported methods not only restricted to C–H alkenylation reactions but also employed only (*Z*)-configured aryl alkenes¹⁴ or plain styrenes (Scheme 1b).^{12a} For example, Engle^{14a} and our group^{14b} simultaneously reported on (asymmetric) α C–H alkenylation of aryl alkenes, affording (axially chiral) aryl dienes. In stark contrast, α C–H functionalization of *E*-aryl alkenes is rarely reported due to the more difficult

Scheme 1 Chelation-assisted α and β C–H allylation of aryl alkenes.

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exo-cyclometallation and the existence of two competitive C–H bonds.¹⁵ Moreover, although remarkable progress has been made on olefinic C–H allylation of simple alkenes,¹⁶ there is no report on α or β C–H allylation of aryl alkenes (Scheme 1a–c).

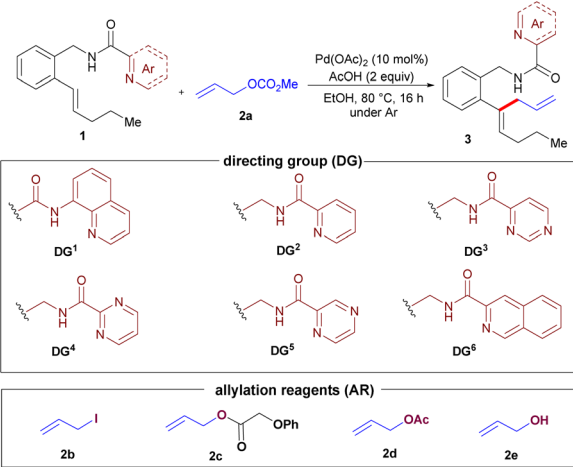
Development of α C–H allylation of (*E*)- and (*Z*) configured styrenes is highly desirable not only for the synthetic diversity to giving skipped diene products with complementary *E/Z* selectivity but also for providing in-depth mechanistic insight into C–H cyclometallation.^{1–3} With our ongoing interest in olefinic C–H functionalization,^{2i–o,3e–f,14b,15} herein, we report on the first chelation-assisted α and β C–H allylation of various styrenes, affording linear and branched skipped dienes and even triene in excellent *E/Z* ratio selectivity (Scheme 1d).

Results and discussion

Based on our previous reports,^{12a,15} we herein turned to examine the C–H allylation of *trans*-styrene bearing a *N,N* bidentate-chelation directing group (**DG**^{1–6}). Although styrene **1** bearing Daugulis's 8-aminoquinoline (**DG**¹)¹⁷ led to no reaction with allyl carbonate **2a** (Table 1, entry 1), the substrate bearing pyridine-2-carboxamide (**DG**²)¹⁸ afforded α C–H allylation product **3a** in 77% yield, simply in the presence of 10 mol% Pd(OAc)₂ and 2.0 equivalent AcOH in EtOH at 80 °C (entry 2). Aryl alkene bearing pyrimidine-4-carboxamide (**DG**³) led to comparable results (entry 3). Other nitrogen heterocycle carboxamide such as pyrimidine-2-carboxamide (**DG**⁴), pyrazinamide (**DG**⁵) and isoquinoline-3-carboxamide (**DG**⁶) were also examined, demonstrating that **DG**² was the best one (entries 4–6). Using PivOH instead of AcOH led to a 63% yield (entry 7). The reaction without carboxylic acid only afforded a trace product, exhibiting a carboxylate-assisted C–H activation event (entry 8). The reaction was unsuccessful using H₂O as a solvent, however, H₂O/MeOH still led to a 53% yield to demonstrate its robustness (entries 9 and 10). Some other allylation reagents (**AR**) were also examined in such C–H allylation reactions. While allyl iodide **2b** and allyl alcohol **2e** afforded no reaction, allyl carboxylates **2c** and **2d** gave moderate yields (entries 11–14).

With the optimized conditions in hand, C–H allylation between various *trans*-styrenes **1** and allyl carbonates **2** were examined (Table 2). *meta*- and *para*-Substitutes such as F, OMe, CF₃, and Me were all well tolerated, affording aryl 1,4-dienes in 49–77% yields (**3a–3h**). Styrene bearing longer aliphatic chains such as pentyl afforded **3i** in 59% yield. However, changing propyl to methyl and phenyl groups decreased the product yield to 33% (**3j**) and 23% (**3k**), respectively. Substrates bearing dimethoxy phenyl and naphthyl also gave **3l** and **3m** in good yields. Secondary amine-derived amide still converted well to give **3n** in 66% yield. Unfortunately, neither aniline nor phenylethylamine derivatives showed reactivity, exhibiting the difficult formation of five- and seven-membered palladacycle. Notably, branched allyl carbonate **2f**

Table 1 Evaluation and optimization of the reaction^{a,b}



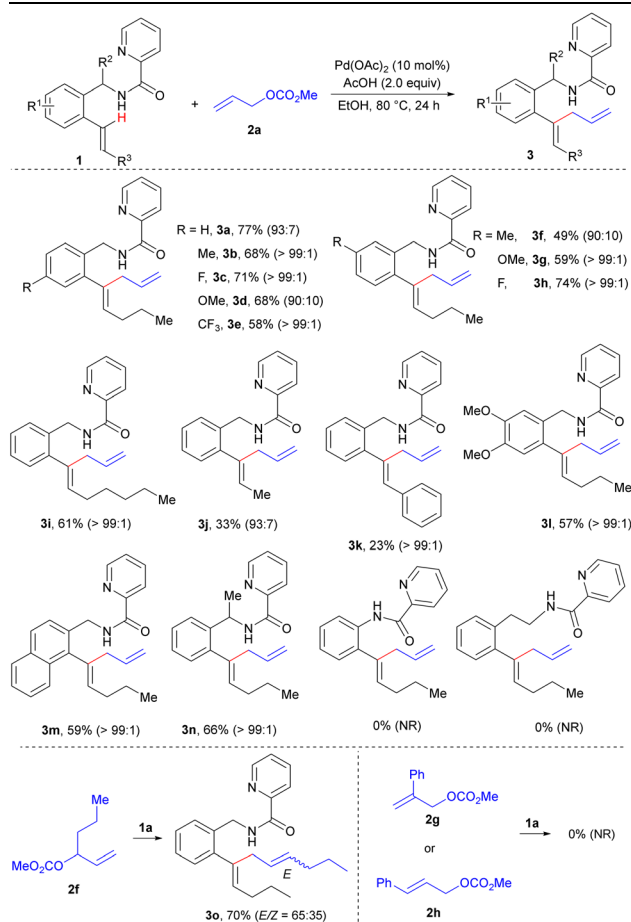
Entry	DG	AR	Additive	Yield ^b (%)
1	1	2a	AcOH	0
2	2	2a	AcOH	77
3	3	2a	AcOH	73
4	4	2a	AcOH	31
5	5	2a	AcOH	65
6	6	2a	AcOH	46
7	2	2a	PivOH	63
8	2	2a	—	<5
9 ^c	2	2a	AcOH	<5
10 ^d	2	2a	AcOH	53
11	2	2b	AcOH	0
12	2	2c	AcOH	52
13	2	2d	AcOH	51
14	2	2e	AcOH	0

^a Reaction conditions: **1** (0.15 mmol, 1 equiv.), **2a** (0.6 mmol, 4 equiv.), Pd(OAc)₂ (10 mol%), AcOH (2 equiv.), in EtOH (0.1 M) at 80 °C, for 24 h. ^b *E/Z* ratios of the isomer given in parentheses were determined by ¹H NMR analysis. ^c Using H₂O as a solvent. ^d Using MeOH/H₂O as a solvent.

also reacted well to give rise to **3o** in 70% yield with 65 : 35 *E/Z* ratio selectivity. However, other allyl carbonates from 2-phenyl prop-2-en-1-ol (**2g**) and cinnamyl alcohol (**2h**) exhibited no reactivity.

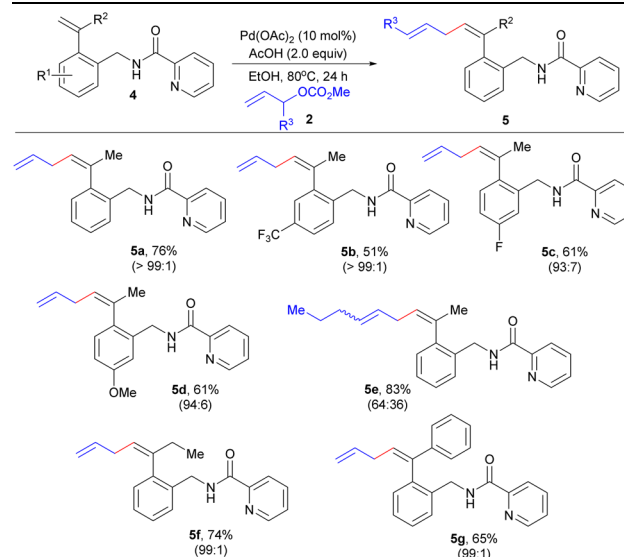
After that, we turned to examine the β C–H allylation of aryl alkenes **4** also bearing pyridine-2-carboxamide (**DG**²) (Table 3). Under the optimal conditions, styrenes bearing F, CF₃ and OMe were converted smoothly to afford 1,4-dienes **5a–5d** in 51–76% yields. Notably, branched allyl carbonate **2f** reacted well to give diene product **5e** in 83% yield. Aryl alkenes **4** bearing phenyl or ethyl at the α position reacted successfully to afford **5f** and **5g** in 74% and 65% yields, respectively, with excellent *E/Z* ratio selectivity.

Next, we investigated the reaction of *Z*-configured aryl alkene **6** and plain styrene **8** under optimal conditions. While *Z*-styrene gave rise to α C–H allylation product **7** in 66% yield with 93 : 7 *E/Z* ratio selectivity (Scheme 2a), plain styrene **8** afforded triene product **9** in 51% yield with >99 : 1 *E/Z* ratio selectivity (Scheme 2b).¹⁹

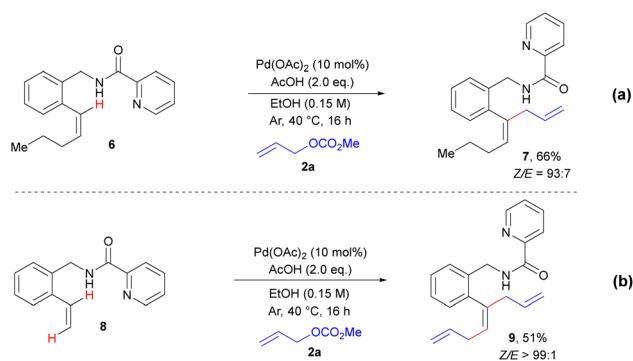
Table 2 Pd-catalysed α C–H allylation of *E*-styrenes^{a,b}

^a Reactions conditions: **1** (0.15 mmol, 1 equiv.), **2** (0.6 mmol, 4 equiv.), Pd(OAc)₂ (10 mol%), AcOH (2 equiv.), in EtOH (0.1 M) at 80 °C, for 24 h. ^b Isolated yields; *E/Z* ratios of the isomers given in parentheses were determined by ¹H NMR analysis.

To explore the mechanism of this C–H allylation of styrenes, controlled reactions were performed as described in Scheme 3. If *E*-styrene **1a** was subjected to the optimal conditions with EtOD (0.1 M), 97% deuterium incorporation was observed with 81% recovery, exhibiting the α C–H activation to be facile and reversible (Scheme 3a). If the same reaction was conducted in the presence of allyl carbonate **2a**, 38% product yield and 50% recovery of **1a** without deuterium incorporation were observed, which demonstrated a much faster olefin insertion to outcompete the C–H activation step (Scheme 3b). Allylation product **3a** was obtained in 38% yield with 0% deuterium incorporation, exhibiting a direct **2a** insertion followed by liberation of CO₂ and MeOH.^{3f,16} An intermolecular competition experiment between **6** and **1a** was conducted to give the product **7** in 40% yield and **3a** in trace amount, exhibiting a much higher reactivity of *Z*-styrene to outcompete *E*-styrene, also exhibiting a more difficult formation of *exo*-metallocycle with *E*-alkenes (Scheme 3c).¹⁵ Aliphatic *E*-alkene **10** was also examined, and only a trace product was detected under optimal conditions (Scheme 3d). Benzyl amide **11** led to no

Table 3 Pd-catalysed β C–H allylation of styrenes^{a,b}

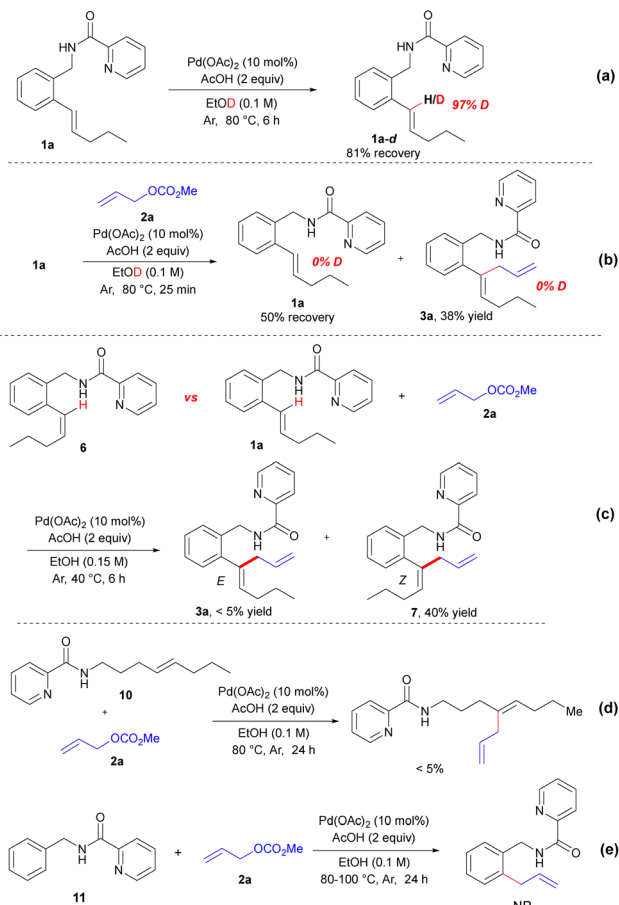
^a Reactions conditions: **4** (0.15 mmol, 1 equiv.), **2** (0.6 mmol, 4 equiv.), Pd(OAc)₂ (10 mol%), AcOH (2 equiv.), in EtOH (0.1 M) at 80 °C, for 24 h. ^b Isolated yields; *Z/E* ratios of the isomers given in parentheses were determined by ¹H NMR analysis.

Scheme 2 α and β C–H allylation of *Z*- and plain styrenes.

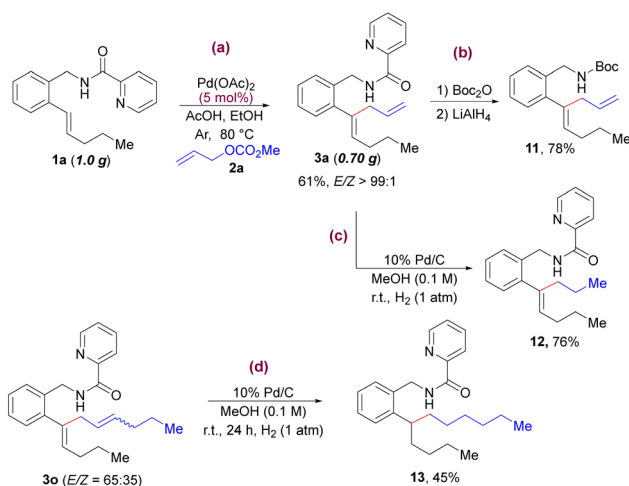
aromatic C–H allylation, exhibiting the difficult formation of five-membered palladacycle (Scheme 3e).²⁰

Gram-scaled preparation of **3a** was successful using 5 mol% Pd(OAc)₂ to demonstrate the robustness and practicality of this method (Scheme 4a). The directing group was readily removed by *N*-Boc protection followed by reduction with LiAlH₄, providing NHBoc benzylamine **11** in 78% yield (Scheme 4b). Terminal alkene of 1,4-diene **3a** was selectively reduced to give alkene **12** in 76% yield by using 10% Pd/C under hydrogen (1 atm) (Scheme 4c). Notably, two olefin moieties in **3o** were completely reduced to afford branched alkane **13** in 45% yield (Scheme 4d).

Based on previous reports¹⁶ and experiment results, a plausible catalytic cycle is proposed in Scheme 5. Coordination between the substrate and metal occurred to give a π -olefin palladium complex **I**, which then formed a six-membered pal-

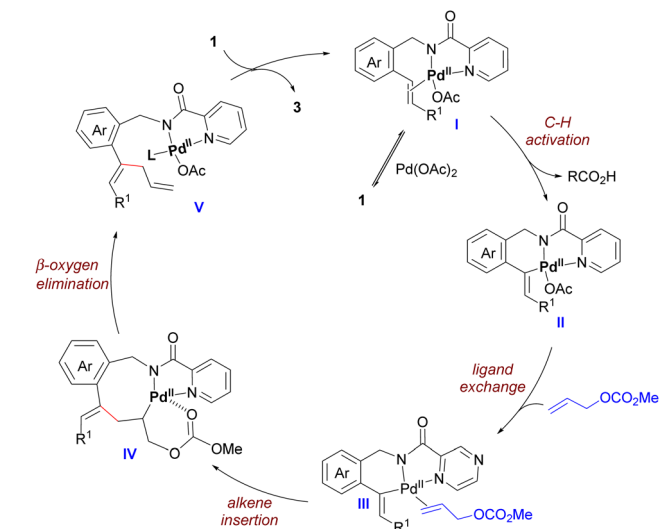


Scheme 3 Controlled experiments.



Scheme 4 Gram-scaled synthesis and derivation.

ladacycle **II** by a reversible α -C–H activation. Ligand exchange by allyl carbonate coordination and alkene insertion took place to afford an eight-membered palladacycle **IV**. Finally, β -oxygen elimination occurred to produce aryl 1,4-diene **3**.



Scheme 5 Proposed mechanism.

Conclusions

In conclusion, we have developed *N,N*-bidentate-chelation assisted α and β C–H allylation of *E*- and *Z*-configured aryl alkenes, as well as α -substituted styrenes and plain styrenes, producing linear and branched 1,4-dienes and 1,4,7-triene with excellent *Z/E* ratio selectivity. The operationally simple protocol showed a broad substrate scope and enabled gram-scaled preparation. This method is anticipated to exhibit wide applications in multifarious organic synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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