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COMMUNICATION

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Palladium-catalyzed decarboxylative coupling of α,β-unsaturated carboxylic acids with aryl tosylates

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We report a general method for selective cross-coupling of α,β-unsaturated carboxylic acids with aryl tosylates enabled by versatile Pd(II) complexes. This method features the general cross-coupling of ubiquitous α,β-unsaturated carboxylic acids by decarboxylation. The transformation is characterized by its operational simplicity, the use of inexpensive, air-stable Pd(II) catalysts, scalability and wide substrate scope. The reaction proceeds with high *trans* selectivity to furnish valuable (*E*)-1,2-diarylethenes.

KEYWORDS
aryl tosylates, decarboxylative coupling, palladium-catalyzed, synthesis of *trans*-vinylarene, α,β-unsaturated carboxylic acids

1 | INTRODUCTION

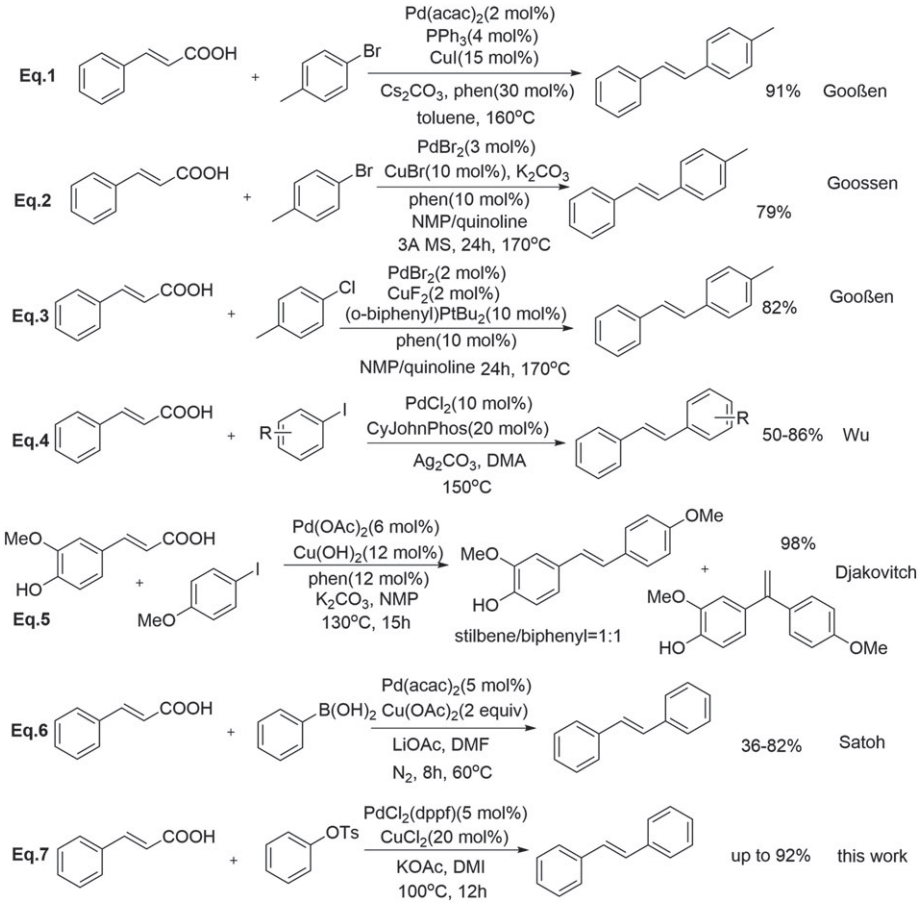
Transition metal-catalyzed oxidative cross-coupling reactions[1–5] are powerful tools for the formation of carbon–carbon bonds to prepare complex and diverse aromatic compounds, which remains a significant challenge in organic synthesis. Such methods represent environmentally benign and atom-economical alternatives to traditional coupling transformations,[5–10] which require the use of two pre-functionalized starting materials. Several recent elegant and successful transformations[11–15] have been developed for the preparation of aromatic compounds via transition metal-catalyzed oxidative cross-coupling. Among those transformations, Rh-, Ru-, Cu- and Pd-catalyzed direct oxidative cross-coupling reactions[16] have been extensively studied due to their high efficiency. Although continuing efforts have been devoted to develop efficient transformations for the synthesis of aromatic compounds, oxidative coupling of aromatic compounds is still highly favorable.

(*E*)-1,2-Diarylethene motif-containing compounds are prevalent in synthetic and natural products with a wide spectrum of applications. (*E*)-1,2-Diarylethene scaffolds have received a great deal of attention from biology and synthetic chemistry researchers in the past decade because of their wide-ranging spectrum of biological activities and broad applications in various fields of research. In addition, (*E*)-1,2-diarylethenes are also considered as important building blocks in synthetic dyes and molecules used in organic light-emitting diodes and liquid crystals.[17–20] Traditional syntheses of this substructure, such as Wittig or Julia olefinations,[21,22] Pd-catalyzed Heck-type coupling[23–27] and some reduction and condensation methods using suitable substrates,[28–30] are waste-intensive, limited in scope and/or require multistep syntheses of starting materials.

Transition metal-catalyzed alkenylation with aryl (pseudo)halide arguably represents an efficient and step-economical strategy for the assembly of (*E*)-1,2-diarylethenes. The selective synthesis of diarylalkenes from widely available aryl (pseudo)halides by Heck-type reactions would be a welcome alternative.[31,32] However, electronic and steric factors usually determine the regiochemical outcome of the carbopalladation for simple hydrocarbons, so that 1,1-diarylalkenes are obtained from styrenes.[33–35] As a result of the wealth of methods for their preparation, cinnamic acids are alternative attractive starting materials and more widely available in greater structural diversity than styrenes. In Heck coupling reactions with aryl (pseudo)halides, the carboxylate group

should direct the carbopalladation into its β-position, thereby leading to the intermediate formation of diarylacrylic acids. Their *in situ* conversion into the desired 1,2-diarylalkenes might be accomplished by an added silver or copper decarboxylation catalyst. This catalyst combination is known to effectively promote decarboxylative cross-coupling with formation of (*E*)-1,2-diarylalkenes.[36–38]

Based on pioneering studies by Gooßen *et al.*,[39] tremendous progress has been made in palladium-catalyzed decarboxylative cross-coupling with cinnamic acids. $Pd(acac)_2$/CuI-catalyzed decarboxylative coupling of 1-bromo-4-methylbenzene and cinnamic acid with the assistance of PPh_3 and phen at 160°C was achieved in a yield of 91% (Scheme 1, equation (1)). Following this significant lead, extensive efforts have been made in the development of more active and selective transition metal catalytic systems. Goossen *et al.*[40] accomplished similar $PdBr_2$/CuBr-catalyzed decarboxylative reaction under ligand-free conditions at 170°C in a 79% yield (Scheme 1, equation (2)). In 2008, Gooßen's group[41] reported the first decarboxylative coupling of cinnamic acid with 1-chloro-4-methylbenzene. A yield of 82% of (*E*)-1-methyl-4-styrylbenzene was obtained under catalysis of $PdBr_2/CuF_2$ with (*o*-biphenyl)$PtBu_2$ at 170°C (Scheme 1, equation (3)). Wu *et al.*[36] then reported the efficient decarboxylation of cinnamic acid with aryl iodide catalyzed by a combination of palladium chloride and CyJohnPhos in the presence of Ag_2CO_3 as an additive with good functional-group tolerance (Scheme 1, equation (4)). Recently, Djakovitch *et al.*[42] described a decarboxylative coupling of electron-rich cinnamic acid with electron-rich aryl iodide to afford corresponding stilbenes and isomerized biaryls (Scheme 1, equation (5)). Despite these indisputable advances, the catalysis was severely limited to rather harsh reaction conditions (130–170°C). A notable elegant exception was developed by Satoh and co-workers,[43] which indicated the potential of the replacement of aryl halides with arylboronic acids. The cinnamic acids possessing a hydroxyl group undergo direct decarboxylative arylation under $Pd(acac)_2$/$Cu(OAc)_2$ catalysis with LiOAc to form hydroxylated stilbenes in 36–82% yields via oxidative Mizoroki–Heck reaction (Scheme 1, equation (6)). There is still much room for improvement, particularly in terms of substrate scope and catalytic efficiency with new coupling partners.



SCHEME 1 Pd-catalyzed decarboxylative cross-coupling of cinnamic acids with various coupling partners

Oxygen-based electrophiles have frequently been employed as (pseudo)aryl halides in transition metal-catalyzed coupling reactions because they are easily prepared from phenol derivatives, which are inexpensive and readily accessible compared to aryl halides.[44–48] The use of phenol derivatives instead of halides reduces the production of halide waste, thus lowering the environmental impact of the cross-coupling process. Furthermore, the use of phenol derivatives may exhibit orthogonal reactivity to aryl halides. Among them, aryl tosylates are inexpensive compared with the corresponding nonaflates and triflates and are therefore desirable alternative precursors for cross-coupling reactions. Moreover, aryl tosylates are easy to handle because of their high hydrolytic stability and crystallinity.[49–52] Based on our efforts in transition metal-catalyzed cross-coupling research and considering our further interest in exploring the new-type synthetic methodology towards cross-coupling,[53–57] herein we report a successful attempt for the synthesis of stilbenes using C–O electrophiles by decarboxylative coupling using a combination of $PdCl_2$(dppf) and $CuCl_2$ in DMI (1,3-dimethylimidazolidinone) under mild conditions (Scheme 1, equation (7)).

2 | RESULTS AND DISCUSSION

We commenced our investigation with the substrates cinnamic acid and phenyl tosylate in DMI using KOAc as a base. To our delight, the desired decaboxylative coupling product was formed in 60% yield by using $Pd(OAc)_2$ as the catalyst and $CuCl_2$ as the co-catalyst (Table 1, entry 1). The screening of various commercially available palladium salts, such as $PdCl_2$, PdI_2, $Pd(TFA)_2$, $PdCl_2(MeCN)_2$, $PdCl_2(PhCN)_2$, $PdCl_2$ $(PPh_3)_3$ and $PdCl_2$(dppf), revealed that $PdCl_2$(dppf) was the optimal catalyst and showed the highest reactivity, giving the product (*E*)-1,2-diphenylethene in 89% yield (Table 1, entries 2–8). Other Pd(0)-based catalysts were ineffective or less efficient for this transformation. Other copper salts were also tested in the reaction, and the effects were inferior to that of $CuCl_2$ (Table 1, entries 11–16). Some highly valent oxidants, such as $PhI(OAc)_2$ and $K_2S_2O_8$, could not give the desired product (Table 1, entries 17 and 18). A control experiment showed that $PdCl_2$(dppf) and $CuCl_2$ were essential for the amination reaction (Table 1, entries 19 and 20). Further optimization results for bases and solvents are in the supporting information.

With the optimized reaction conditions in hand, we then turned our attention to the investigation of substrate scope. First, with phenyl tosylate as the substrate, we tested the scope of the reaction with a representative set of decorated cinnamic acids. As evident from Table 2, substrates

TABLE 1 Decarboxylative coupling of cinnamic acids with phenyl tosylates with various catalysts and co-catalysts[a]

Entry	Catalyst	Co-catalyst	Yield (%)[b]
1	$Pd(OAc)_2$	$CuCl_2$	60
2	$PdCl_2$	$CuCl_2$	57
3	PdI_2	$CuCl_2$	36
4	$Pd(TFA)_2$	$CuCl_2$	65
5	$PdCl_2(MeCN)_2$	$CuCl_2$	77
6	$PdCl_2(PhCN)_2$	$CuCl_2$	71
7	$PdCl_2(PPh_3)_3$	$CuCl_2$	80
8	**$PdCl_2$(dppf)**	**$CuCl_2$**	**89**
9	$Pd(PPh_3)_4$	$CuCl_2$	14
10	$Pd_2(dba)_3$	$CuCl_2$	21
11	$PdCl_2$(dppf)	$Cu(OAc)_2$	85
12	$PdCl_2$(dppf)	$CuBr_2$	78
13	$PdCl_2$(dppf)	$Cu(OTf)_2$	81
14	$PdCl_2$(dppf)	CuCl	8
15	$PdCl_2$(dppf)	CuBr	18
16	$PdCl_2$(dppf)	Cu_2O	15
17	$PdCl_2$(dppf)	$PdI(OAc)_2$	—
18	$PdCl_2$(dppf)	Ag_2CO_3	—
19	$PdCl_2$(dppf)	—	—
20	—	$CuCl_2$	—

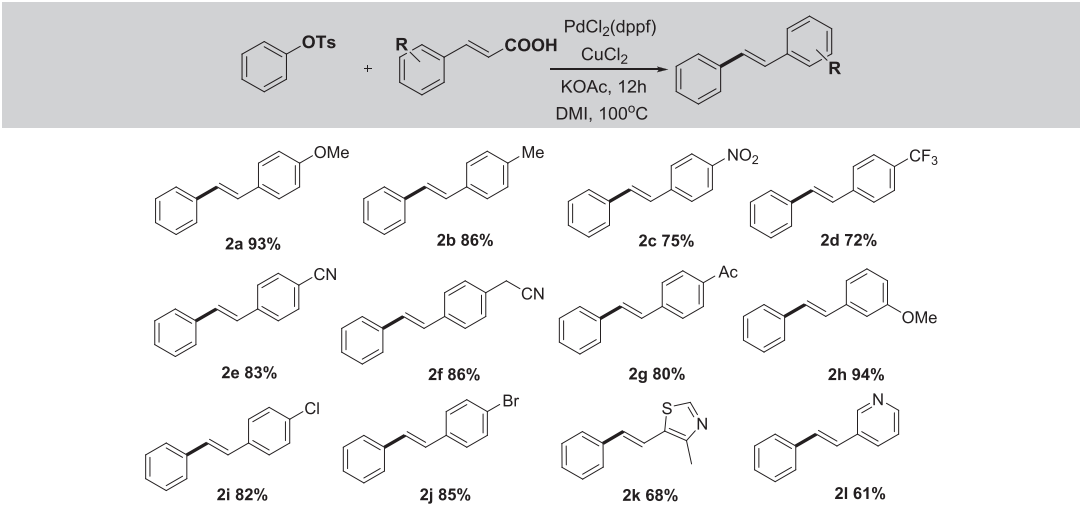
[a]Reaction conditions: cinnamic acids (1.0 mmol), phenyl tosylates (1.1 mmol), catalyst (5 mol%), co-catalyst (20 mol%), KOAc (2.0 mmol), DMI (2 ml), 100°C, 12 h.

[b]Isolated yields.

bearing both electron-rich and electron-poor groups on the aromatic ring were well tolerated in this process, resulting in the corresponding alkenylated products with good to outstanding yields (Table 2, 2**a**–2**g**). The reaction proceeded well with substrates bearing *meta*-methoxy substituents, thus giving the products in 94% yield (Table 2, 2**h**). It is noteworthy that the reactions of 4-chlorocinnamic acid or 4-bromocinnamic acid with phenyl tosylate all efficiently proceeded to form the decarboxylative products, with the halogen substituents untouched during the reactions, which renders the coupling products good candidates for further transformations such as transition metal-catalyzed functionalization of the carbon–halogen bond (Table 2, 2**i** and 2**j**). Heteroaryl-substituted carboxylic acids led to a slightly lower yield of the desired products (Table 2, 2**k** and 2**l**).

After achieving the alkenylation of various cinnamic acids with phenyl tosylates, we further investigated the direct reaction of various aryl tosylates under similar reaction conditions (Tables 3–5). The reaction of electron-rich 4-methoxycinnamic acid worked well with

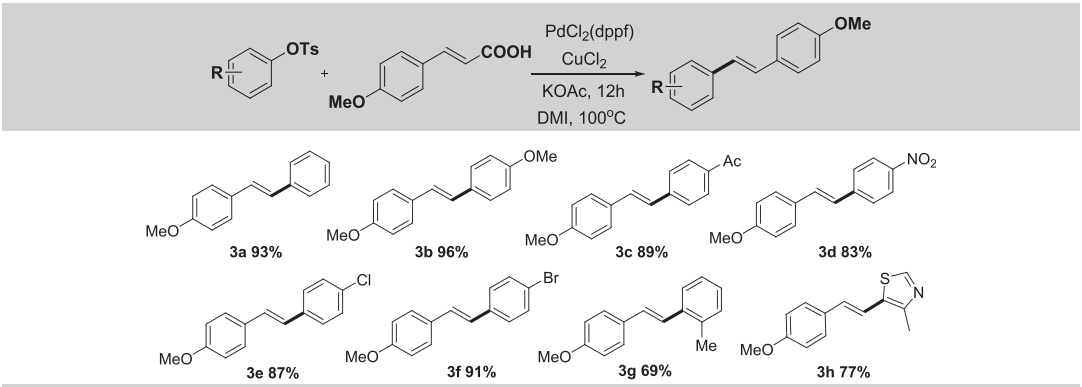
TABLE 2 Scope of decarboxylative coupling with phenyl tosylates and various cinnamic acids[a,b]



[a]Reaction conditions: cinnamic acids (1.0 mmol), phenyl tosylates (1.1 mmol), $PdCl_2$(dppf) (5 mol%), $CuCl_2$ (20 mol%), KOAc (2.0 mmol), DMI (2 ml), 100°C, 12 h.

[b]Isolated yields.

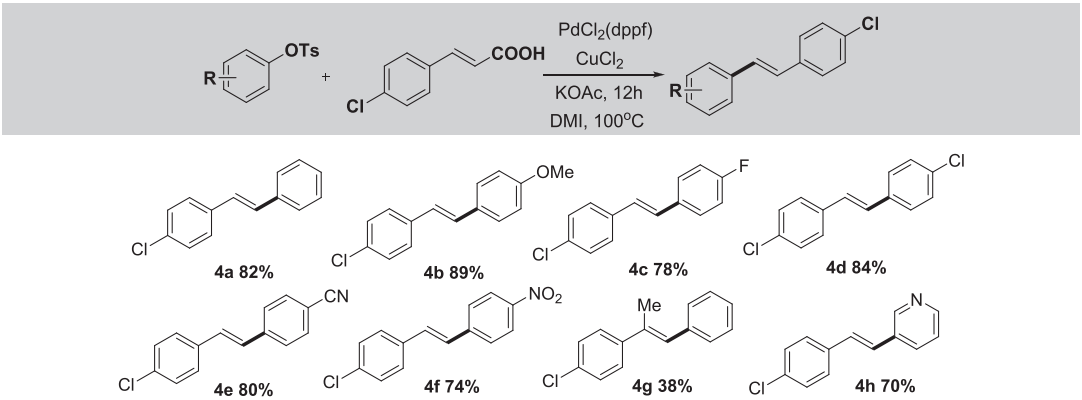
TABLE 3 Scope of decarboxylative coupling with various aryl tosylates and 4-methoxycinnamic acids[a,b]



[a]Reaction conditions: 4-methoxycinnamic acids (1.0 mmol), aryl tosylates (1.1 mmol), $PdCl_2$(dppf) (5 mol%), $CuCl_2$ (20 mol%), KOAc (2.0 mmol), DMI (2 ml), 100°C, 12 h.

[b]Isolated yields.

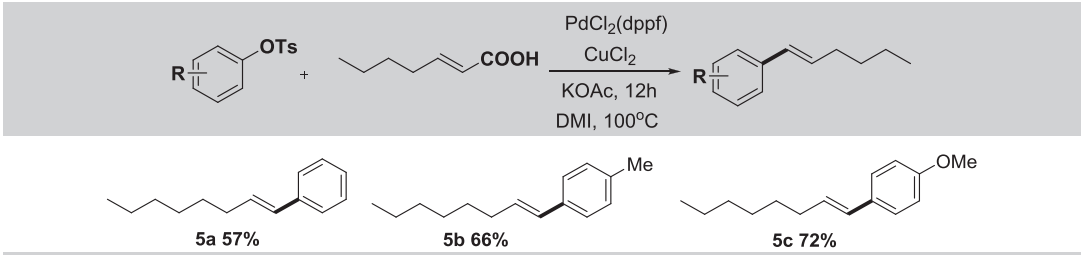
TABLE 4 Scope of decarboxylative coupling with various aryl tosylates and 4-chlorocinnamic acids[a,b]



[a]Reaction conditions: 4-chlorocinnamic acids (1.0 mmol), aryl tosylates (1.1 mmol), $PdCl_2$(dppf) (5 mol%), $CuCl_2$ (20 mol%), KOAc (2.0 mmol), DMI (2 ml), 100°C, 12 h.

[b]Isolated yields.

TABLE 5 Scope of decarboxylative coupling with various aryl tosylates and (*E*)-hept-2-enoic acid[a,b]



[a]Reaction conditions: (*E*)-hept-2-enoic acid (1.0 mmol), aryl tosylates (1.1 mmol), $PdCl_2$(dppf) (5 mol%), $CuCl_2$ (20 mol%), KOAc (2.0 mmol), DMI (2 ml), 100°C, 12 h.

[b]Isolated yields.

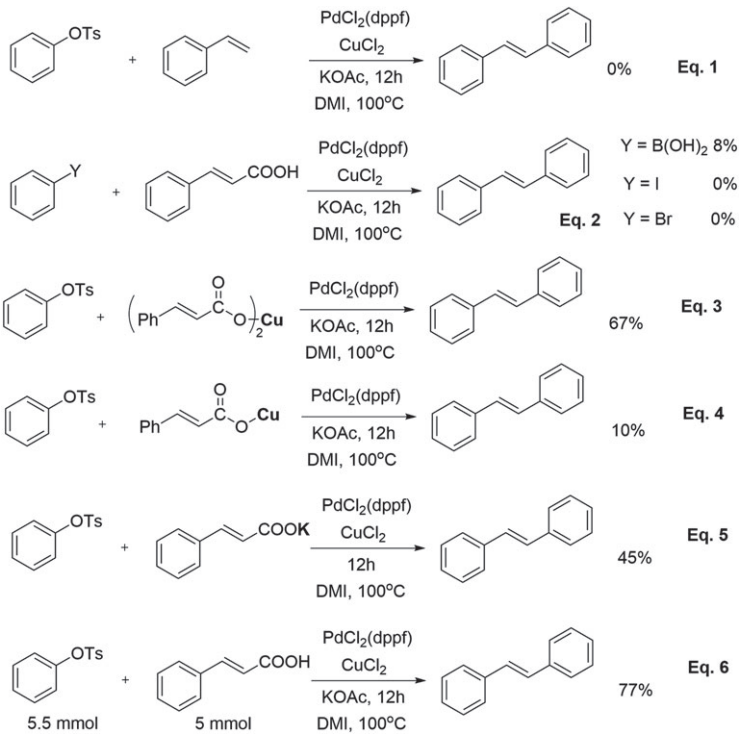
a series of *para*-substituted phenyl tosylates, proceeding smoothly under the same reaction conditions as shown above, thus affording the corresponding alkenylation products in good yields (Table 3, 3**b**–3**f**). In general, the substrates with electron-donating groups on the aromatic ring gave slightly higher yields. Interestingly, when phenyl tosylate bears an bromo substituent, the (*E*)-1-bromo-4-(4-methoxystyryl)benzene compound could be synthesized (Table 3, 3**f**), which suggests the mildness of our protocol since, in previous transition metal-catalyzed protocols, the bromo substituent could not be tolerated. The sterically hindered *ortho*-substituted phenyl tosylate also coped with this reaction condition, although with lower yield (Table 3, 3**g**). For the substrate with thiazolyl, the alkenylation product could be obtained in a yield of 77% (Table 3, 3**h**).

In addition to the 4-methoxycinnamic acid derived from 4-methoxybenzaldehyde, the 4-chlorocinnamic acid derived from 4-chlorobenzaldehyde is also a suitable substrate (Table 4, 4**a**–4**h**). Diverse aryl tosylates with electron-withdrawing and electron-donating groups can undergo the reaction smoothly, with the corresponding products isolated in modest to good yields (Table 4, 4**b**–4**f**). However, when a methyl group was installed on the β-carbon of cinnamic acid, corresponding product was obtained and the yield dropped to 38% (Table 4, 4**g**). Some heterocycles are also compatible with our conditions, with (*E*)-3-(4-chlorostyryl)pyridine being produced in good yield (Table 4, 4**h**). No detection of 1,1-isomers was observed in all these cases.

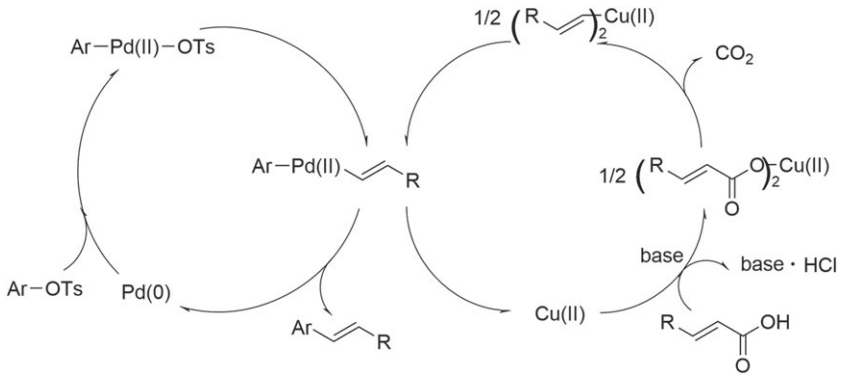
Notably, in addition to cinnamic acids, aliphatic α,β-unsaturated carboxylic acids could also be converted to the corresponding alkylvinylarenes in moderate yields (Table 5, 5**a**–5**c**). Aliphatic tosylates such as benzyl trifluoroborate and cyclopropyl tosylate were investigated; however, no desired products were obtained. Furthermore, no isomerization has been observed in these transformations.

We commenced the study with a series of control reactions to identify the characteristics of this transformation. As shown in Scheme 2, when cinnamic acid was replaced by styrene, only a complicated reaction mixture of unidentified products was obtained under optimum reaction conditions (Scheme 2, equation (1)). When the reaction was conducted with iodobenzene/bromobenzene/phenylboronic acid, the formation of (*E*)-1,2-diphenylethene was completely inhibited (Scheme 2, equation (2)). This indicated that phenyl tosylate was much more reactive than iodobenzene, bromobenzene and phenylboronic acid under our reaction conditions. (Cinnamoyloxy)copper, which was easily prepared using $CuCl_2$ and cinnamate acid, could react with phenyl tosylate smoothly without the addition of co-catalyst ($CuCl_2$), indicating that (cinnamoyloxy)copper might be involved in this catalytic cycle (Scheme 2, equation (3)). Then (cinnamoyloxy)copper(I) was also prepared to investigate the reaction with phenyl tosylate, and only 10% yield of (*E*)-1,2-diphenylethene was obtained (Scheme 2, equation (4)). Furthermore, when Cu(II) was replaced by Cu(I) based on the standard conditions, we found the desired yields decreased sharply, which indicated that the transformation was more likely via a Cu(I)-catalyzed pathway (Table 1, entries 11–16). Moreover, when cinnamic acid was replaced with potassium cinnamate, the decarboxylative coupling with phenyl tosylate could afford desired product in the absence of KOAc in a yield of 45% (Scheme 2, equation (5)). Finally, the decarboxylative coupling of both aryl tosylates and cinnamic acids was scalable on the gram scale, which showed the potential of our palladium-catalyzed methods in industrial application (Scheme 2, equation (6)).

On the basis of our results and previous reports of coupling reactions with aryl tosylates, we propose the reaction mechanism shown in Scheme 3. α,β-Unsaturated carboxylic acids react with copper(II) species to give the (*E*)-3-arylacrylate copper(II) complex A through ligand-exchange with the assistance of base, and then (*E*)-(arylvinyl)copper complex B is formed through decarboxylation steps. The combination of $PdCl_2$(dppf) and KOAc generates the active [Pd(0)] catalyst which



SCHEME 2 Control experiments and scalability



SCHEME 3 Possible mechanism for cross-coupling

undergoes oxidative addition into the Ar&bond;OTs bond to give the arylpalladium(II) complex C. Organocopper complex B reacts with the arylpalladium complex C via transmetallation to afford arylarylvinylpalladium (II) complex D and regenerate copper(II) species. Finally the desired coupled product is formed through reductive elimination, and during the last step the active [Pd(0)] species is regenerated to complete the catalytic cycle.

3 | CONCLUSIONS

We have developed an operationally simple and efficient method of palladium/copper co-catalyzed decarboxylative coupling reactions towards the regioselective synthesis of (*E*)-1,2-diarylethenes from α,β-unsaturated carboxylic acids and aryl tosylates. Using simple and readily available metal reagents like $PdCl_2$(dppf) as catalyst (5 mol%) and $CuCl_2$ as co-catalyst (10 mol%), the successful construction of new aryl–vinyl bond in the decarboxylative process was achieved via the selective cleavage of C&bond;C/C&bond;O bonds. We anticipate that this cross-coupling approach via a Pd/Cu-catalyzed pathway might offer access to several styrene compounds in the synthesis of functionalized materials, complex molecules and pharmaceuticals.

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SUPPORTING INFORMATION

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