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# Facile access to 2,2-diaryl 2*H*-chromenes through a palladium-catalyzed cascade reaction of *ortho*-vinyl bromobenzenes with *N*-tosylhydrazones†

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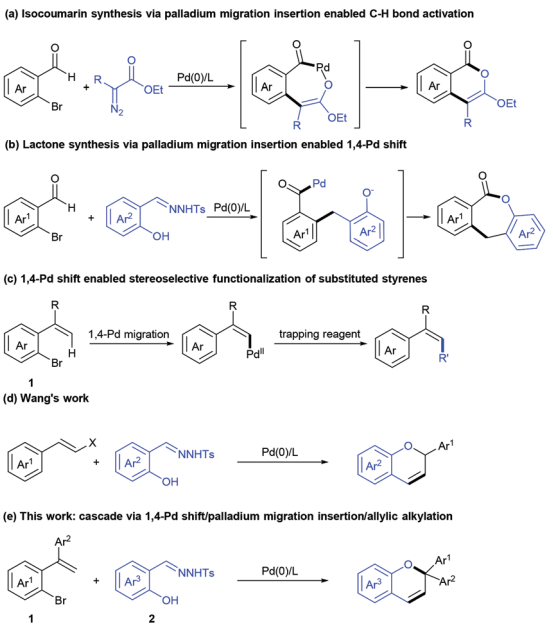
**A palladium-catalyzed cascade reaction of *ortho*-vinyl bromobenzenes with *N*-tosylhydrazones has been developed, which provides a facile approach to 2,2-disubstituted 2*H*-chromenes. The migration of palladium from the aryl to vinyl position is crucial, as the *in situ* produced vinyl palladium intermediate could further react with diazo compounds to generate the reactive species for the sequential annulation.**

## Introduction

Palladium-catalyzed cross-coupling reactions using diazo compounds as coupling reagents are versatile for the construction of new chemical bonds.[1] Among them, the reaction of appropriate organic halides with diazo compounds has been established as a powerful alternative approach to generate an $\eta^3$-allylpalladium intermediate to further participate in Tsuji–Trost-type allylic alkylations.[2,3] As part of our continuing research interest in diazo chemistry,[4] we have recently demonstrated a strategy on bridging C–H activation of aldehyde enabled by migratory insertion of a palladium carbene intermediate.[5] In this specific reaction, the oxygen atom of the carbonyl group in the diazo compound could be considered as a tethered nucleophile. After a sequence of C–H activation/reductive elimination, products bearing an isocoumarin scaffold could be obtained (Scheme 1a). Consequently, we have further applied such a strategy for seven-membered lactone synthesis.[5d] This time tosylhydrazones with an *ortho*-phenol tether were employed as the diazo precursors (Scheme 1b). According to deuterium labeling experiments and DFT calculations, a pathway involving palladium carbene migratory insertion enabled 1,4-palladium shift[6,7] was proposed.

Recently, *ortho*-vinyl bromobenzenes **1** have been demonstrated to be competent substrates to undergo the 1,4-palladium shift from the aryl to vinyl position. Based on this reaction mode, several elegant transformations have been discovered by Lin and Feng (Scheme 1c).[7c–g] Wang and coworkers found that **1** could react with (trimethylsilyl)diazomethane in the presence of a palladium catalyst to give 1*H*-indenes in a straightforward manner.[8] Inspired by these remarkable advances, and as a consequent study on our research interests in palladium carbene-participated 1,4-palladium shift, we wondered whether the reaction of **1** with tosylhydrazone **2** could




**Scheme 1** Merging the 1,4-Pd shift with migratory insertion of a palladium carbene intermediate.

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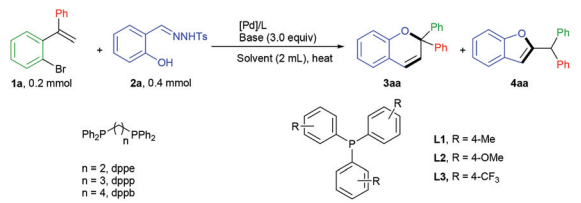
offer a facile approach to 2,2-diarylsubstituted 2*H*-chromene, which has potential applications in the area of photochromic materials.[9,10] It is worthwhile to mention that Wang has reported an elegant work on 2*H*-chromene synthesis by the reaction of vinyl bromide with tosylhydrazone **2** (Scheme 1d), in which there were no examples of 2,2-disubstituted 2*H*-chromene preparation.[11,12] Herein we describe our recent endeavor towards this goal, which could be considered as a rare example of cascade reactions on 1,4-palladium shift and Tsuji–Trost-type allylic alkylation involving a palladium carbene intermediate, and further complement Wang's work on 2*H*-chromene synthesis (Scheme 1e).

## Results and discussion

We initiated our investigation by performing the reaction of aryl bromide **1a** and *N*-tosylhydrazone **2a** using $[Pd(allyl)Cl]_2$ as the palladium source and dppb (1,4-bis(diphenylphosphanyl)butane) as the ligand. To our delight, the anticipated reaction indeed occurred with $K_2CO_3$ as the base in THF at 110 °C, and product **3aa** was isolated in 46% yield, along with a trace amount of isomer **4aa** (Table 1, entry 1). A variety of mono- and bidentate phosphine ligands proved to be less efficient, providing **3aa** in lower yields and lower conversion rates (entries 2–7). Testing the effects of solvents revealed that 2-MeTHF was the most effective for this transformation, resulting in an increase of the yield of **3aa** to 52% (entry 10). Increasing the loading of the catalyst led to a full conversion of **1a**, and **3aa** was obtained in 79% yield upon isolation (entry 12). A brief examination of the effects of the base showed that $K_2CO_3$ was still the best choice. Other palladium precatalysts were also examined but delivered unsatisfactory yields except $[Pd(cinnamyl)Cl]_2$. Finally, control experiments showed that the palladium source, ligand and base were all crucial for the reaction to occur.

With the optimized reaction conditions in hand (Table 1, entry 12), a variety of *N*-tosylhydrazones, easily prepared from the corresponding aldehydes, were employed to investigate the substrate scope of this reaction. As seen from the results presented in Scheme 2, aromatic *N*-tosylhydrazones bearing Me, OMe, OTBS, F, Cl, or COOMe substituents are all suitable substrates for this reaction, giving the corresponding products in moderate to good yields (**3aa–3am**), thus indicating that the reaction is compatible with both electron-withdrawing and electron-donating groups as aromatic substituents. On the other hand, the reactions with *ortho* substituted tosylhydrazones also succeeded to afford the corresponding cyclized products (**3al** and **3am**), which revealed that the method shows good tolerance to steric hindrance effects. However, naphthyl *N*-tosylhydrazone **2m** gave the products with low regioselectivity with **4am** as the major product. Hydrazones derived from estrone and methyl tyrosinate could also provide the desired products with good yields and chemoselectivities (**3an** and **3ao**). The structure of **3ac** was further established by X-ray diffraction.

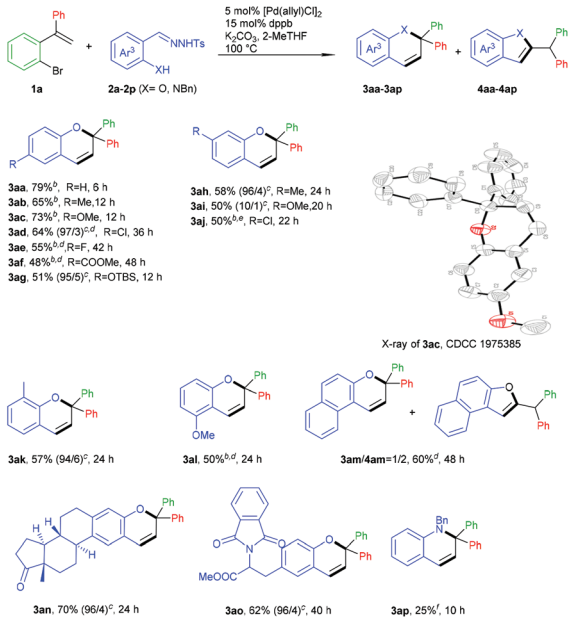
**Table 1** Optimization of reaction conditions[a]



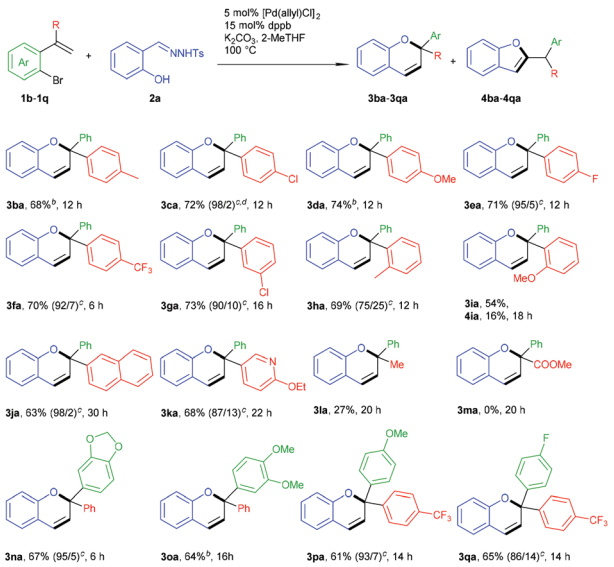

| Entry | [Pd]/L | *T*/°C | Solvent | Base | [%][b] 1a | 3aa | 4aa |
|---|---|---|---|---|---|---|---|
| 1 | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppb | 110 | THF | $K_2CO_3$ | 16 | 51(46)[c] | 3 |
| 2 | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppe | 110 | THF | $K_2CO_3$ | 21 | 25 | 1 |
| 3 | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppp | 110 | THF | $K_2CO_3$ | 43 | 15 | <1 |
| 4 | 2.5 mol% $[Pd(allyl)Cl]_2$/15 mol% $PPh_3$ | 110 | THF | $K_2CO_3$ | 34 | 29 | <1 |
| 5 | 2.5 mol% $[Pd(allyl)Cl]_2$/15 mol% **L1** | 110 | THF | $K_2CO_3$ | 32 | 35 | <1 |
| 6 | 2.5 mol% [Pd(allyl)Cl]2/15 mol% **L2** | 110 | THF | $K_2CO_3$ | 23 | 38 | <1 |
| 7 | 2.5 mol% $[Pd(allyl)Cl]_2$/15 mol% **L3** | 110 | THF | $K_2CO_3$ | 39 | 27 | <1 |
| 8 | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppb | 100 | THF | $K_2CO_3$ | 27 | 50 | 3 |
| 9 | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppb | 100 | Dioxane | $K_2CO_3$ | 13 | 36 | <1 |
| 10 | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppb | 100 | 2-MeTHF | $K_2CO_3$ | 35 | 52 | 3 |
| 11[d] | 2.5 mol% $[Pd(allyl)Cl]_2$/7.5 mol% dppb | 100 | 2-MeTHF | $K_2CO_3$ | 11 | 43 | 3 |
| 12 | 5 mol% $[Pd(allyl)Cl]_2$/15 mol% dppb | 100 | 2-MeTHF | $K_2CO_3$ | 0 | 87(79)[c,e] | 8 |
| 13 | 5 mol% $[Pd(allyl)Cl]_2$/15 mol% dppb | 100 | 2-MeTHF | CsF | 16 | 36 | <1 |
| 14 | 5 mol% $[Pd(allyl)Cl]_2$/15 mol% dppb | 100 | 2-MeTHF | $K_3PO_4$ | 0 | 68 | <1 |
| 15 | 10 mol% $Pd(OAc)_2$/15 mol% dppb | 100 | 2-MeTHF | $K_2CO_3$ | 0 | 59 | 2 |
| 16 | 5 mol% $[Pd(cinnamyl)Cl]_2$/15 mol% dppb | 100 | 2-MeTHF | $K_2CO_3$ | 0 | 79(78)[c,e] | 2 |

[a] The reaction was carried out for 20 h. [b] Determined by $^1H$ NMR using *N*,*N*-dimethylpyridin-4-amine as an internal standard. [c] Yield of the isolated product. [d] *n*-$Bu_4NBr$ (0.02 mmol) was added. [e] The reaction was completed in 6 h.

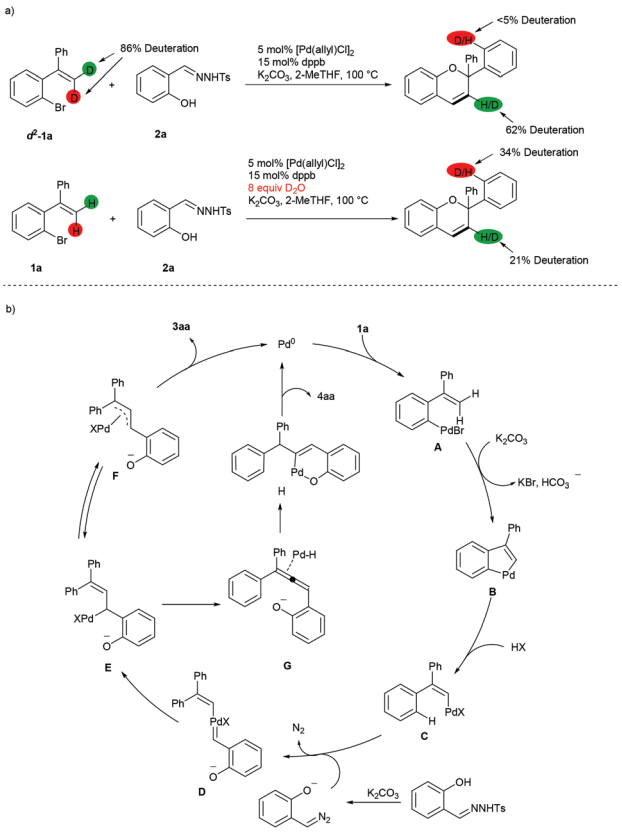



**Scheme 2** Substrate scope of *N*-tosylhydrazones. [a] Reaction conditions: Table 1, entry 12; yield of the isolated product. [b] Isolated as a pure isomer, the ratio of **3**/**4** > 15/1. [c] Isolated as an inseparable mixture of **3** and **4** with the ratio shown in parentheses. [d] 5 mol% [Pd(cinnamyl)Cl]$_2$ replaced 5 mol% [Pd(allyl)Cl]$_2$. [e] 10 mol% [Pd(cinnamyl)Cl]$_2$ and 30 mol% dppb were used. [f] Reaction conditions: 5 mol% $Pd(PPh_3)_2Cl_2$, dioxane (0.1 M), 300 mol% $K_2CO_3$, 100 °C, 10 h.



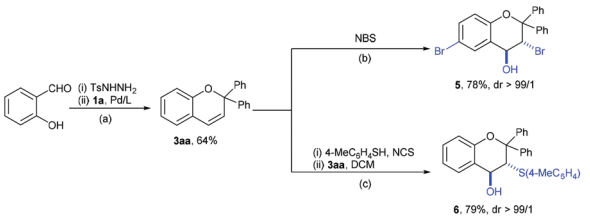

**Scheme 3** Substrate scope of *ortho*-vinyl bromobenzenes. [a] Reaction conditions: Table 1, entry 12; yield of the isolated product. [b] The ratio of **3**/**4** > 15/1. [c] Isolated as an inseparable mixture of **3** and **4** with the ratio in parentheses. [d] 5 mol% of [Pd(cinnamyl)Cl]$_2$ was used as the precatalyst.

Next, the scope of *ortho*-vinyl bromobenzenes **1** was evaluated (Scheme 3). If the R group was a phenyl ring, a series of substituents on the *meta*- or *para*-position, including Me, OMe, $CF_3$, Cl, and F, were all compatible, giving the corresponding products in moderate to good yields with high selectivity. The shift of substituents to the *ortho*-position led to reduced selectivity, presumably due to the steric effects (**3ha** and **3ia**). It is noteworthy that substrates with the phenyl ring replaced by a naphthyl or 3-pyridinyl group were also identified to be suitable for the current reaction, delivering the products with moderate yields and good selectivity (**3ja** and **3ka**). Replacement of the phenyl ring R with a methyl or ester group shut down the selectivity. The transformation efficiency was diminished due to other unidentified side reactions (**3la** and **3ma**), indicating a significant influence of the R groups on the reaction. Bromides bearing different substituents on both aromatic rings were viable substrates. They could react with *N*-tosylhydrazone **2a** to afford the corresponding products in moderate yields and with good selectivities (**3pa** and **3qa**).




**Scheme 4** Deuterium labeling experiments and the plausible reaction pathway.

To understand the mechanistic details of this cascade reaction, several deuterium labeling experiments were carried out (Scheme 4a). First, the reaction of the deuterated arylbromide ***d*$_2$-1a** under standard reaction conditions gave the corresponding products with a low incorporation of deuterium at the *ortho*-position of the phenyl ring and 62% incorporation of deuterium at the double bond carbon. Second, we tested the reaction with **1a** by adding 8 equiv. of $D_2O$, and found 34% incorporation of deuterium at the *ortho*-position of the phenyl ring and 21% incorporation of deuterium at the double bond




**Scheme 5** Derivatizations of 2*H*-chromene **3aa**. Reaction conditions: (a) (i) Salicylaldehyde (10 mmol), $TsNHNH_2$ (10 mmol), 2-MeTHF (30 mL), rt, 2 h, (ii) $[Pd(allyl)Cl]_2$ (0.25 mmol), dppb (0.75 mmol), $K_2CO_3$ (15 mmol), **1a** (5 mmol), 2-MeTHF (20 mL), 100 °C, 20 h; (b) **3aa** (0.2 mmol), NBS (0.6 mmol), acetone/$H_2O$ (2 mL/0.4 mL), rt, 16 h; (c) (i) 4-$MeC_6H_4SH$ (0.4 mmol), NCS (0.4 mmol), DCM (3 mL), 0 °C, 30 min, (ii) **3aa** (0.2 mmol), 0 °C–rt, 2 h.

carbon. On the basis of these observations and the previous studies,[7] a plausible reaction pathway of this reaction is outlined in Scheme 4b. As shown, the reaction is supposed to start with the oxidative addition of *ortho*-vinyl bromobenzene **1a** to generate $Pd^{II}$ species **A**, which undergoes a C–H activation step and furnishes five-membered palladacycle **B**.[13] Then protonation of the palladacycle occurs to generate intermediate **C**, accomplishing the 1,4-palladium shift from the aryl to vinyl position. During this process, the proton concentration in the reaction medium is relatively high as a consequence of base-assisted *N*-tosylhydrazone decomposition, which probably results in low deuterium incorporation ratios at the *ortho*-position of the phenyl ring in the deuterium labeling experiment. **C** reacts with diazo substrate **2a** to form $Pd^{II}$ carbene species **D**, followed by migratory insertion to give $\eta^1$-allylpalladium intermediate **E**, which exists in a fast equilibrium with $\eta^3$-allylpalladium species **F**. **E** may also undergo a β-hydrogen elimination to afford intermediate **G**[14] with the palladium hydride species coordinating with the allene skeleton. Reinsertion of the palladium hydride species to the double bond in **G** gives rise to intermediate **H**. Finally, the product **3aa** is formed through an intramolecular Tsuji–Trost-type allylic substitution; meanwhile the isomer **4aa** is obtained as a result of reductive elimination of intermediate **H**.

A one-pot, three-component, two-step reaction of salicylaldehyde, 4-methylbenzenesulfonohydrazide and *ortho*-vinyl bromobenzene **1a** was conducted on a gram scale, and the target 2*H*-chromene **3aa** was obtained in 64% overall yield. Further experiments on the transformations of **3aa** were performed (Scheme 5). As can be seen, the double bond in **3aa** could be difunctionalized smoothly through simple manipulations.[15]

## Conclusions

We have developed an efficient palladium-catalyzed cascade reaction of *ortho*-vinyl bromobenzenes and *ortho*-hydroxybenzenesulfonohydrazide to access 2,2-disubstituted 2*H*-chromenes. This protocol proceeds through a sequence of 1,4-palladium migration, carbene migratory insertion and regioselective allylic substitution. The merging of the palladium carbene migratory insertion chemistry with the 1,4-palladium shift has offered a new way to generate an $\eta^3$-allylpalladium intermediate, which further provides new opportunities to expand the scope of Tsuji–Trost-type allylic alkylations.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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