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Palladium-Catalyzed Cascade Reaction of *o*-Bromobenzaldehydes with *N*-Sulfonylhydrazones: An Efficient Approach to the Naphthalene Skeleton

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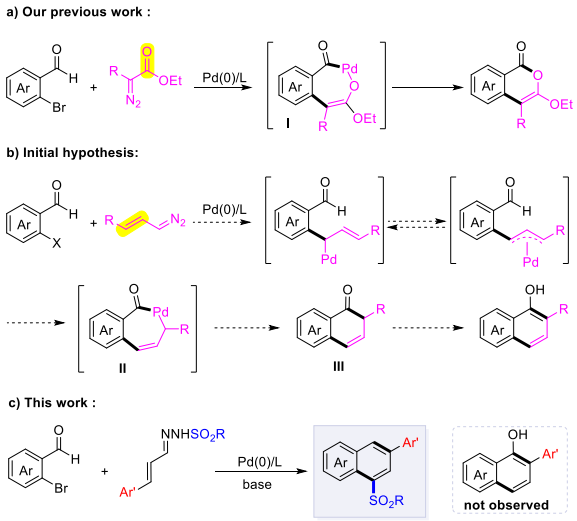
Abstract. A new strategy for the construction of the naphthalene backbone is described. The reaction essentially starts from two simple aldehydes. The key step is enabled by a palladium–carbene migratory insertion. After that, a sequence of reversible allylic alkylation and intramolecular condensation takes place to give the substituted naphthalene derivatives. Additional manipulations on the sulfonyl group in the product via palladium-catalyzed Kumada coupling were also investigated.

Keywords: Palladium carbene; migratory insertion; naphthalene; Kumada coupling

Cascade reactions are considered as powerful methods to construct structurally complex molecules from simple and readily available feedstocks, while omitting tedious procedures to isolate synthetic intermediates, thus rendering it economic and environmentally benign.[1] Diazo compounds are easily accessible, possessing tunable reactivity. They are often employed as carbene precursors to participate in a range of classical transformations.[2] As demonstrated by the seminal work of van Vranken, Barluenga, Wang, and others, diazo compounds have also proved to be versatile in a variety of transition-metal-catalyzed cross-coupling reactions.[3,4]

Recently, we have reported a palladium-catalyzed intermolecular acylation of aryl diazo esters with *o*-bromobenzaldehydes, in which diazo esters act as modular three-atom units to build up the key seven-membered palladacycles **I** (Scheme 1a).[5] To test the synthetic potential of this concept, we envisioned that replacement of carbonyl group with proper C-C double bond may give a seven-membered carbopalladacyle **II**, which upon reductive elimination would afford a transient ketone **III**. Aromatization of **III** would lead to the formation of final product naphthalen-1-ol (Scheme 1b). In this communication, we would like to describe our efforts toward this goal which leads to an unexpected discovery of a cascade reaction of *o*-bromobenzaldehydes with *α*, *β*-unsaturated *N*-sulfonylhydrazones enabled by migratory insertion of palladium carbene. This reaction is efficient for the synthesis of a range of naphthyl sulfones and the expected naphthalen-1-ol is not observed (Scheme 1c). Naphthalene unit is an ubiquitous skeleton in chemical and pharmaceutical industries as well as optical and electronic materials.[6] Compared with the existing methods on build up the naphthalene backbone,[7] the current work uses simple aldehydes as the reactants, giving the corresponding substituted naphthalenes in complete regioselectivity with relatively broad substrates scope, thus making this strategy unique and attractive.



Scheme 1. Palladium Carbene Enabled Annulations.

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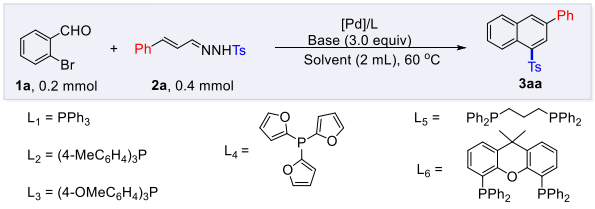
To begin our study, we chose readily available *o*-bromobenzaldehyde **1a** and *N*-tosylhydrazone **2a** as model substrates. The reaction was initially carried out in DMF at 60 °C for 24 h using $Pd_2dba_3{\cdot}CHCl_3/PPh_3$ as the precatalyst, K_2CO_3 as base (Table 1, entry 1). After careful analysis of the reaction mixture, naphthyl sulfone **3aa** was isolated in 9% yield, and the designed naphthalene-1-ol was not observed. Further inspection of the reaction conditions revealed that solvent had a notable effect on the reaction yield. Trace amount of product isolated when DMF was replaced by toluene, DMSO or chloroform (Table 1, entries 2-4). Continuing evaluation of the reaction medium led to identify that MeCN was the best choice of solvent, and **3aa** was obtained in 48% yield (Table 1, entry 6). A brief examination of the effects of base showed that K_2CO_3 was superior to others (Table 1, entries 6-11). Subsequently, several palladium precatalysts combined with different phosphine ligands were also tested. When the reaction was carried out in presence of $[Pd(allyl)Cl]_2$ and PPh_3 for 6 h, and product **3aa** could be isolated in 77% yield (Table 1, entry 14). $Pd(PPh_3)_4$ could also catalyze this reaction efficiently (Table 1, entry 13).

Table 1. Optimization of Reaction Conditions[a]



$L_1 = PPh_3$

$L_2 = (4\text{-}MeC_6H_4)_3P$

$L_3 = (4\text{-}OMeC_6H_4)_3P$

L_4 =

L_5 = Ph_2P PPh_2

L_6 = PPh_2 PPh_2

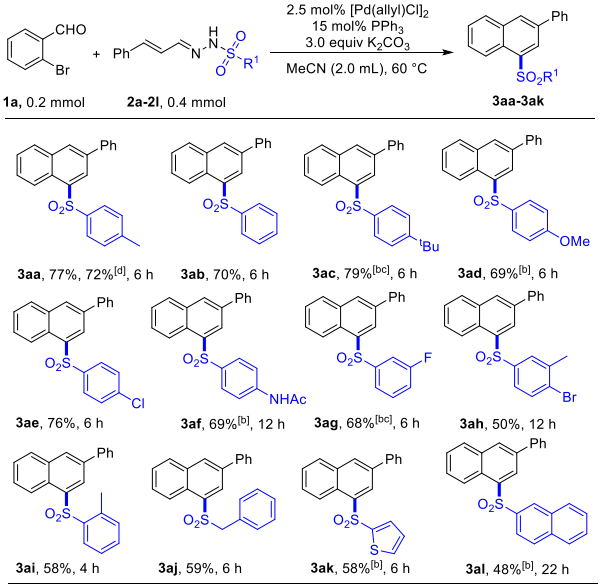
Entry	[Pd]	L	Solvent	Base	Yield [%][b]
1	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	DMF	K_2CO_3	9
2	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	toluene	K_2CO_3	trace
3	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	DMSO	K_2CO_3	7
4	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	$CHCl_3$	K_2CO_3	trace
5	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	THF	K_2CO_3	22
6	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	MeCN	K_2CO_3	48
7	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	MeCN	Na_2CO_3	6
8[c]	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	MeCN	Na_2CO_3	21
9	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	MeCN	Cs_2CO_3	13
10	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	MeCN	K_3PO_4	12
11	2.5 mol% $Pd_2dba_3{\cdot}CHCl_3$	15 mol% L_1	MeCN	^{t}BuOLi	34
12	5 mol% $Pd(OAc)_2$	15 mol% L_1	MeCN	K_2CO_3	53
13	5 mol% $Pd(PPh_3)_4$	-	MeCN	K_2CO_3	75
14[d]	2.5 mol% $[Pd(allyl)Cl]_2$	15 mol% L_1	MeCN	K_2CO_3	77
15	5 mol% $Pd(MeCN)_2Cl_2$	15 mol% L_1	MeCN	K_2CO_3	47
16	2.5 mol% $[Pd(allyl)Cl]_2$	15 mo% L_2	MeCN	K_2CO_3	72
17	2.5 mol% $[Pd(allyl)Cl]_2$	15 mo% L_3	MeCN	K_2CO_3	73
18	2.5 mol% $[Pd(allyl)Cl]_2$	15 mol% L_4	MeCN	K_2CO_3	11
19	2.5 mol% $[Pd(allyl)Cl]_2$	7.5 mol% L_5	MeCN	K_2CO_3	5
20	2.5 mol% $[Pd(allyl)Cl]_2$	7.5 mol% L_6	MeCN	K_2CO_3	trace

[a]The reaction was carried out for 24 h. [b]Isolated yield. [c]$BnNEt_3Cl$ (0.2 mmol) was added. [d]The reaction was completed in 6 h.

Other palladium sources including $Pd(OAc)_2$ and $Pd(MeCN)_2Cl_2$ proved to be less efficient for the current transformation (Table 1, entries 11 and 14). Then a variety of mono- and bidentate phosphine ligands were verified, and the yields of **3aa** were not improved. Finally, control experiments showed that the palladium catalyst, the ligand, and the base were all crucial for the reaction to occur.

With the optimized reaction conditions in hand (Table 1, entry 14), we examined the scope of this reaction by variation of the sulfonyl groups in hydrazones. The results are summarized in Scheme 2. The reactions of hydrazones bearing substituents on the benzene ring could be varied and both electron-withdrawing groups (F, Cl, and Br) and electron-donating groups (Me, OMe and NHAc) all proceeded efficiently to lead to the corresponding products in moderate to good yields. It is noteworthy that benzyl hydrazone, naphthyl hydrazone and thienyl hydrazine were also identified as suitable substrates for the reaction, delivering the products in moderate yields. In order to test the practicality of the current catalytic system, the reaction was carried out on gram-scale for **1a** (6 mmol, 1.11 g), and the desired product **3aa** was afforded in 72% yield (1.55 g).

Scheme 2. Substrate scope of substituted *N*-sulfonyl hydrazones.[a]



[a]Reaction conditions: Table 1, entry 13. [b]0.5 mmol hydrazone **2** were employed. [c]5 mol% $[Pd(allyl)Cl]_2$ and 30 mol% PPh_3 were added. [d]The reaction was carried out on 6 mmol scale.

Next the scope of the aldehydes and *N*-tosylhydrazones with different substituents on the aromatic rings were evaluated (Scheme 3). With respect to *o*-bromo benzaldehyde, a series of substituents, including Me, OMe, OTs, Cl, Br on the phenyl ring were all compatible, giving the corresponding products in moderate to good yields (**5da-5ha**). The structure of **5ca** was further established by X-ray diffraction.[8] The toleration of halide groups may offer new opportunity for further transition metal-catalyzed cross coupling reactions. A set of *N*-tosylhydrazones with different substituents and functional groups, including substituted aromatics and heteroaromatic ring, could react smoothly with benzaldehyde **1a** to afford the corresponding naphthyl sulfone in moderate to good yields. Substituents on *para*, *ortho*, *meta*-position of

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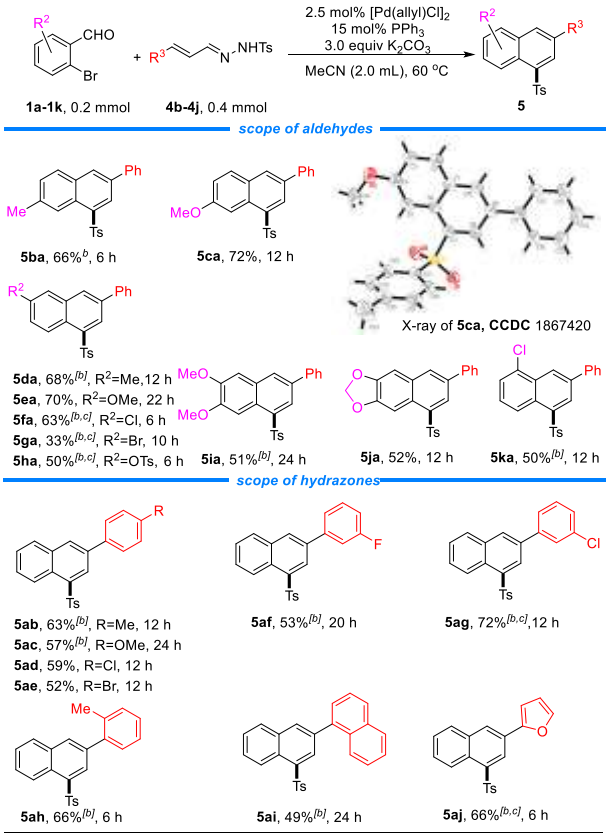
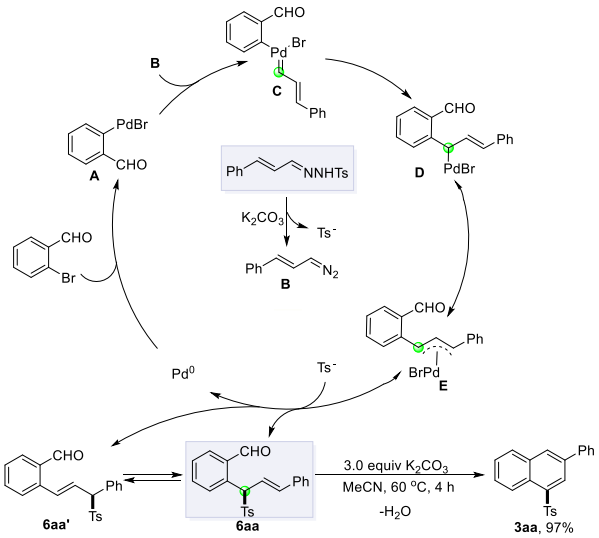
the phenyl ring were all tolerated. Furanyl-substituted and naphthyl-substituted *N*-tosylhydrazones were also participated in the transformation, providing the products in 66% and 49% yields respectively.

Scheme 3. Substrate scope of aldehydes and *N*-tosylhydrazones [a]

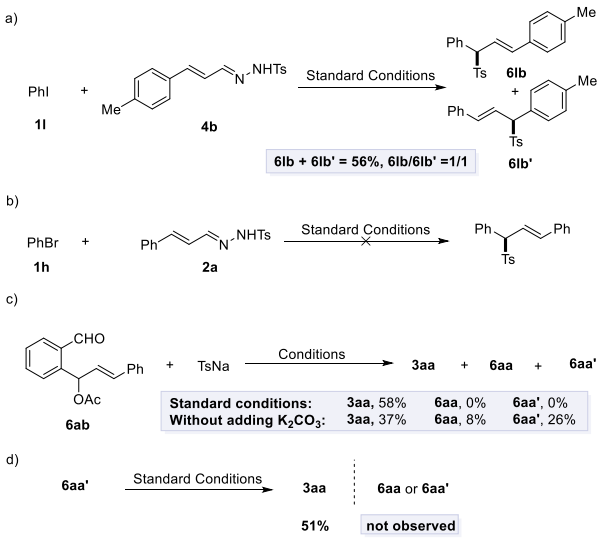


[a]Reaction conditions: Table 1, entry 13. [b]0.5 mmol hydrazone **2** were employed. [c]5 mol% $[Pd(allyl)Cl]_2$ and 30 mol% PPh_3 were added.

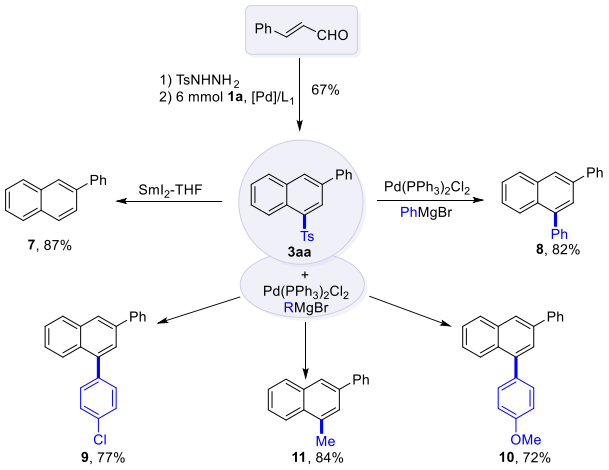
According to previous reports[9] and the results obtained here, a plausible catalytic cycle for current transformation for 2-sulfonylnaphthalene synthesis could be envisioned (Scheme 4). As depicted, the reaction is supposed to start with the oxidative addition of low valent palladium catalyst to *o*-bromobenzaldehyde **1a**. The resulting palladium(II) species **A** would further react with *α*, *β*-unsaturated diazo compound **B** to give palladium carbene intermediate **C**. Migratory insertion of **C** would eventually afford η^1-allylpalladium intermediate **D**, which may exist as a fast equilibrium with η^3-allylpalladium species **E**. Diazo compound **B** was generated *in situ* via Bamford-Stevens reaction[10] of *N*-tosylhydrazone **2a** with K_2CO_3. At the meantime, one equivalent of sulfinate anion would be released. It is worthwhile to mention that Liang and coworkers have reported a palladium-catalyzed allyl sulfone synthesis through the reaction of aryl iodides and *N*-sulfonylhydrazone.[9h] Under the current conditions, the reaction of phenyl iodide **1l** with *N*-tosylhydrazone **4b** gave the corresponding allyl sulfones as a mixture of regio isomers in a ratio of 1:1 (Scheme 5a). Interestingly, the corresponding allyl sulfone could not be observed from the reaction of phenyl bromide with *N*-tosylhydrazones (Scheme 5b). According to the structure of the product obtained, we could conclude that sulfone **6aa**, which was generated through the reaction of sulfinate anion with intermediate **E**, would further undergo intramolecular Aldol type condensation, giving **3aa** ultimately. A separate experiment revealed that treatment of sulfone **6aa** with 3 equivalent of K_2CO_3 in MeCN led to the formation of **3aa** in nearly quantitative yield. The exact reason to explain the complete regioselectivity is not clear at the current stage. But one could envision that the formyl group on the phenyl ring is the key for the reactivity and regioselectivity. It could not only activate phenyl bromide to facilitate elementary step of oxidative addition, but also make the carbenic carbon atom in **E** slightly more electrophilic. Thus the sulfinate anion would add to this carbon center more selectively. Base triggered Aldol condensation of sulfone **6aa** for the formation of thermodynamically stable 2-sulfonylnaphthalene **3aa** might be decisive for the observed regioselectivity. To verify this assumption, we have prepared allyl acetate **6ab** and subjected it to the reaction with sodium 4-methylbenzenesulfinate (TsNa) under standard conditions, the naphthyl sulfone **3aa** was isolated in 58% yield. The corresponding allyl sulfone **6aa** and its regioisomer **6aa**' were not observed. If the reaction was carried out under otherwise identical conditions but without the addition of K_2CO_3 (Scheme 5c, for details on the procedure see SI), besides **3aa**, allyl sulfone **6aa** and its region isomer **6aa**' were obtained in 8% and 26% yields, respectively. Notably, the reaction of **6aa** under standard conditions also gave **3aa** in 51% isolated yield (Scheme 5d). Taken all these data together, we believe that the sulfonylation of intermediate **E** is reversible, and the formation of thermal dynamically stable **3aa** is the driving force to make **6aa**' convert to its regioisomer **6aa** under optimized conditions.



Scheme 4. Plausible reaction pathway. Ligands were omitted for clarity.



Scheme 5. Control experiments.



Scheme 6. Synthetic manipulations on **3aa**.

To further demonstrate the operational simplicity, a one-pot, three-component, two-step reaction of cinnamaldehyde with tosyl hydrazide and *o*-bromobenzaldehyde was carried out in 6 mmol scale, and the target naphthalene **3aa** was obtained in 67% overall yield. Molecules containing aryl sulfone motif often exhibit unique biological and chemical properties,[11] and the sulfonyl groups are valuable for other reactions, for example, serve as useful precursors for C-C bond formation via fragment coupling or Julia olefination. Representative downstream transformations of the products were conducted (Scheme 6). As can be seen, the sulfonyl group could be removed with an excess amount of SmI_2-THF under mild conditions,[12] and 2-phenylnaphthalene **7** was obtained in high yield. Furthermore, **3aa** has also proved to a good electrophile to participate in palladium-catalyzed Kumada coupling reactions.[13] As such, **3aa** could react with a variety of Grignard reagents in presence of catalytic amount of $Pd(PPh_3)_2Cl_2$. Thus, the tosyl group on the naphthalene ring was converted to other functionalities with ease (**8-11**, Scheme 6). It is worthwhile to mention that the possible coupling by-product tolyl group was not observed from the reaction mixture.

In conclusion, we have reported a palladium-catalyzed cascade reaction for the synthesis of naphthyl sulfones from *o*-bromobenzaldehydes and *N*-sulfonylhydrazones. The reaction goes through a sequence of palladium–carbene migratory insertion/allylic alkylation and base-promoted aldol condensation. Compared with previous work reported in the literature, the retrosynthetic orthogonality of current strategy to construct naphthalene backbone is remarkable. As shown by mechanistic studies, the sulfonylation of the allylpalladium intermediate is reversible. The formation of a thermodynamically stable naphthalene ring renders the whole process regioselective. Additional experiments have uncovered an efficient palladium-catalyzed Kumada coupling of naphthyl sulfones with Grignard reagents.

Experimental Section

An oven-dried Schlenk tube under argon atmosphere was charged with *o*-bromo aryl formaldehydes **1** (0.2 mmol, 1.0 equiv), arylvinyl N-tosylhydrazones **2** (0.4 mmol or 0.5 mmol, 2.0 equiv or 2.5 equiv), $[Pd(allyl)Cl]_2$ (2.5 mol% or 5.0 mol%), PPh_3 (15 mol% or 30 mol%), K_2CO_3 (0.60 mmol, 3.0 equiv), and CH_3CN (2 mL). The mixture was stirred at 60 °C and the progress of the reaction was monitored by TLC. Upon completion, the resulting mixture was cooled to room temperature and filtered through Celite with EtOAc as the eluent. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the products.

Acknowledgements

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