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Palladium-Catalyzed Desulfitative Cross-Coupling Reaction of Sodium Sulfinates with Propargylic Carbonates

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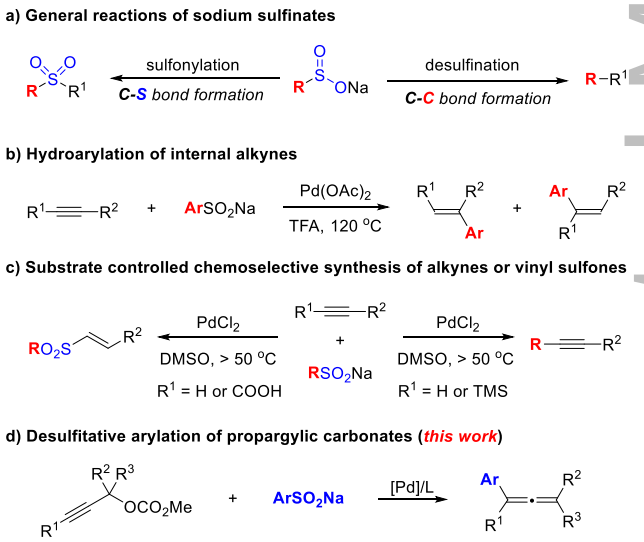
Abstract. Desulfitative cross-coupling of propargylic carbonates with sodium sulfinates has been observed. The reaction exhibited good functional group compatibility affording allenes as a single product. Potential anticancer activities of these allene products were also studied.

Keywords: Desulfitative; Cross-Coupling; Sodium Sulfinates; Allenes

Transition metal-catalyzed cross-coupling reactions are important methodologies in organic synthesis.[1] In particular, palladium-catalyzed carbon-carbon and carbon-heteroatom bonds formation have been widely used in the construction of natural products and biologically active molecules.[2] Recently, much attention has been paid to the desulfitative coupling for the construction of C-C bonds from sodium arylsulfinates, which were frequently used for sulfonylation and sulfuration reactions (Scheme 1a).[3] Sodium arylsulfinates are also used as aryl donors to react with alkenes,[4] alkynes,[5] heteroarenes,[6] benzyl chlorides,[7] aryl triflates,[8] nitriles,[9] and so on.[10] In 2003, Deng and co-workers reported a palladium-catalyzed desulfitative hydroarylation of alkynes with good regio- and stereoselectivity (Scheme 1b).[5a] Later, Jiang and co-workers described an efficient palladium-catalyzed coupling of sodium sulfinates and alkynes for the selective synthesis of vinyl sulfones and unsymmetrical internal alkynes (Scheme 1c).[5b]

Allenes are useful building blocks for the synthesis of pharmaceuticals, natural products, and functional materials.[11,12] Some methods toward efficient synthesis of different types of allenes have been successfully developed.[13] Transition metal-catalyzed coupling of propargylic compounds with organometallic reagents[14] such as organoboronic reagents,[15] Grignard reagents,[16] and organozinc reagents[17] is one of the most useful and efficient methodology to synthesize allenes.[18] However, some organometallic reagents are unstable, expensive, and toxic. To the best of our knowledge, there is no literature reported to date in which sodium arylsulfinates are used in the coupling reaction with propargylic carbonates to afford allenes (Scheme 1d). The developed methodology discussed in this manuscript offered a new alternative for arylation due to the advantages, such as remarkable stability, easy-handiness for workup, low cost, and simple preparation from their corresponding sulfonyl chlorides.

Scheme 1. Transition metal-catalyzed coupling reactions with sodium sulfinates



We began the study with propargylic carbonate **1a** and sodium *p*-toluenesulfinate **2a** as the model substrates to identify the best ligand for the reaction at 50 °C (Table 1). Triphenylphosphine (**L1**) was initially employed as the ligand but the desired desulfitative product allene **5aa** was not formed. Instead, 4% of 1,2-allenyl sulfone **3aa** and 53% of propargylic sulfone **4aa** were observed (Entry 1). Tri(*o*-tolyl)phosphine (**L2**) did not give any products. Tri(*m*-tolyl)phosphine (**L3**) and tri(*p*-tolyl)phosphine (**L4**) also preferred to give sulfone **4aa** as the major product (Entries 3 and 4). Electron-deficient ligand, tris[3,5-bis(trifluoromethyl)phenyl]phosphine **L5**, failed to

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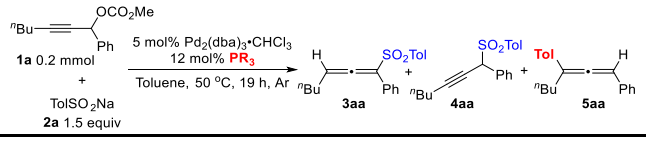
give the desired product (Entry 5). We were pleased to find the electron-rich ligand, tris[2,6-bis(methoxy)phenyl]phosphine (**L6**), could afford the desulfitative allene product **5aa** in 56% yield with an excellent selectivity (Entry 6). The more electron-rich ligand tris[2,4,6-(trimethoxy)phenyl]phosphine (**L7**) also offered single product **5aa**, however, the yield was lower (27%, entry 7). Tri(cyclohexyl) phosphine (**L8**) failed to give any products (Entry 8).

Table 1. Ligand Screening[a]



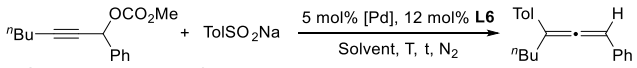
Entry	R	Yield (%) 3aa	4aa	5aa	3/4/5	Recovery (%)
1	Ph (**L1**)	4	53	/	1:13.2:/	trace
2	2-MeC_6H_4 (**L2**)	/	/	/	N/A	80
3	3-MeC_6H_4 (**L3**)	5	51	/	1:10:/	trace
4	4-MeC_6H_4 (**L4**)	11	52	/	1:13.2:/	trace
5	3,5-$(CF_3)_2C_6H_3$ (**L5**)	/	/	/	N/A	72
6	2,6-$(MeO)_2C_6H_3$ (**L6**)	/	/	56	/:/:1	35
7	2,4,6-$(MeO)_3C_6H_2$ (**L7**)	/	/	27	/:/:1	56
8	Cy (**L8**)	/	/	/	N/A	quant.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Pd_2(dba)_3$·$CHCl_3$ (5 mol%), PR_3 (12 mol%) in anhydrous toluene (1.0 mL) was stirred at 50 °C for 19 h. The yields of **3aa**, **4aa** and **5aa** were determined by ^{1}H NMR analysis.

Among the solvents surveyed, the reaction in dioxane resulted in 23% yield (Table 2, entry 2). While no better results was observed in DCE, DMF, and MeCN (Table 2, entries 3-5). The yield was slightly improved to 62% when THF was used as solvent with 22% recovery of **1a** (Table 2, entry 6). The yield of **5aa** was improved to 71% with the reaction being conducted at 60 °C (Table 2, entry 7). After further screening of palladium catalysts, we found $[Pd(allyl)Cl]_2$ was the most efficient, yielding 81% of **5aa** (Table 2, entry 10). Thus, optimal conditions have been defined as 5 mol% of $[Pd(allyl)Cl]_2$ and 12 mol% of **L6** in toluene at 60 °C under N_2 atmosphere.

With the optimal reaction conditions in hand, we next examined the scope of the desulfitative coupling process. As shown in Table 3, a wide range of propargylic carbonates with different substituents at different positions reacted smoothly with sodium *p*-toluenesulfinate **2a** forming the corresponding allene products with decent yields. The reaction is amenable to both electron-withdrawing and electron-donating aryl groups. Various functional groups, including halides (**5ba**, **5ca**, **5da**, **5sa**, and **5ta**), ester (**5fa**), cyano (**5ga**), and carbonate (**5ka**) are well tolerated in the 2-alkynylic carbonates. There is no obvious influence of the steric effect since substrates bearing the methyl group at the *o*-, *m*-, and *p*-position of the phenyl group all afforded the desired products with good yields (**5ha**, **5ia**, and **5ja**). The reaction also afforded corresponding allene products with good efficiency when Ar group was biphenyl (**5la**) or naphthyl (**5ma**).

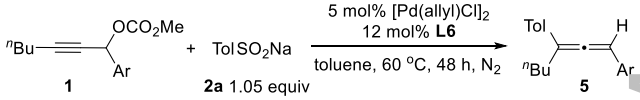
Table 2. Further optimization of reaction parameters[a]



Entry	[Pd]	solvent	T (°C)	t (h)	MMR yield of **5aa** (%)	Recovery of **1a** (%)
1	$Pd_2(dba)_3$•$CHCl_3$	Toluene	50	19	56	35
2	$Pd_2(dba)_3$•$CHCl_3$	Dioxane	50	19	23	71
3	$Pd_2(dba)_3$•$CHCl_3$	DCE	50	19	trace	70
4	$Pd_2(dba)_3$•$CHCl_3$	DMF	50	19	21	10
5	$Pd_2(dba)_3$•$CHCl_3$	MeCN	50	19	13	69
6	$Pd_2(dba)_3$•$CHCl_3$	THF	50	19	62	22
7[b]	$Pd_2(dba)_3$•$CHCl_3$	Toluene	60	40	71	12
8[b]	$Pd(OAc)_2$	Toluene	60	42	11	76
9[b]	$Pd_2(dba)_3$	Toluene	60	42	60	9
10[b]	$[Pd(allyl)Cl]_2$	Toluene	60	42.5	81	7

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Pd] (5 mol%), **L6** (12 mol%) in anhydrous toluene (1.0 mL). The yield of **5aa** was determined by ^{1}H NMR analysis. [b] **2a** (1.05 equiv).

Table 3. Scope of propargylic carbonates[a]



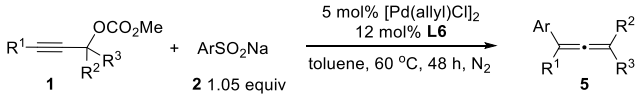
Entry	Ar, **1**	Yield of **5** (%)
1	Ph (**1a**)	78 (**5aa**)
2	4-FC_6H_4 (**1b**)	72 (**5ba**)
3	4-ClC_6H_4 (**1c**)	72 (**5ca**)
4[b]	4-BrC_6H_4 (**1d**)	70 (**5da**)
5[b]	3-BrC_6H_4 (**1s**)	73 (**5sa**)
6[b,c]	2-BrC_6H_4 (**1t**)	60 (**5ta**)
7	3-MeOC_6H_4 (**1e**)	86 (**5ea**)
8[b]	4-$MeO_2C$$C_6H_4$ (**1f**)	73 (**5fa**)
9	4-NCC_6H_4 (**1g**)	70 (**5ga**)
10	2-MeC_6H_4 (**1h**)	77 (**5ha**)
11	3-MeC_6H_4 (**1i**)	71 (**5ia**)
12	4-MeC_6H_4 (**1j**)	68 (**5ja**)
13	2-$MeO_2C$$C_6H_4$ (**1k**)	65 (**5ka**)
14	4-PhC_6H_4 (**1l**)	69 (**5la**)
15	1-Naphthyl (**1m**)	69 (**5ma**)

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.21 mmol), $[Pd(allyl)Cl]_2$ (5 mol %), **L6** (12 mol %), and toluene (1 mL) at 60 °C for 48 h, yield for isolated products. [b] $[Pd(allyl)Cl]_2$ (10 mol %) and **L6** (24 mol %) were used. [c] 21% of **1t** recovery by using 14 μL CH_2Br_2 as internal standard.

Next, we turned our attention to the scope of the R^1 group (Table 4). Alkyl groups with different functional groups, such as halide (**5na**), cyano (**5pa**), and silyl-protected alcohol (**5qa**) were well tolerated in this transformation. Not only secondary propargylic carbonates, tertiary propargylic carbonate **1r** was also working well affording the corresponding tetrasubstituted allene **5ra**. Sodium *p*-fluorosulfinate

2b reacted smoothly affording allene product **5ab** with 78% yield. Finally, sodium 1-naphthylsulfinate **2c** could also work to afford **5ac** in 82% yield.

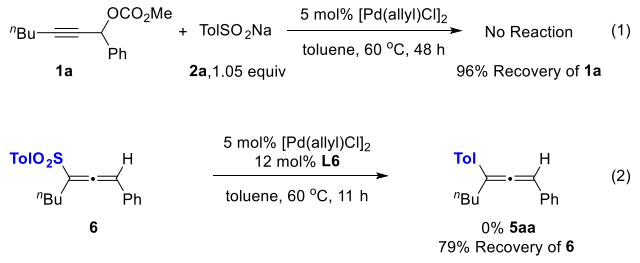
Table 4. Scope of propargylic carbonates with sodium sulfinates[a]



Entry	(*Ra*)-**1**			Ar	Yield of **5** (%)
	R^1	R^2	R^3		
1[b]	-$(CH_2)_4$**Cl**	Ph	H (**1n**)	Tol (**2a**)	67 (**5na**)
2[c]	-$(CH_2)_2$**^{i}Pr**	Ph	H (**1o**)	Tol (**2a**)	73 (**5oa**)
3[d]	-$(CH_2)_3$**CN**	Ph	H (**1p**)	Tol (**2a**)	56 (**5pa**)
4	-$(CH_2)_3$**OTBS**	Ph	H (**1q**)	Tol (**2a**)	73 (**5qa**)
5[e,f]	^{n}C_6H_{13}	CH_3	CH_3 (**1r**)	Tol (**2a**)	59 (**5ra**)
6	^{n}Bu	Ph	H (**1a**)	4-FC_6H_4 (**2b**)	78 (**5ab**)
7[g]	^{n}Bu	Ph	H (**1a**)	1-Naphthyl (**2c**)	82 (**5ac**)

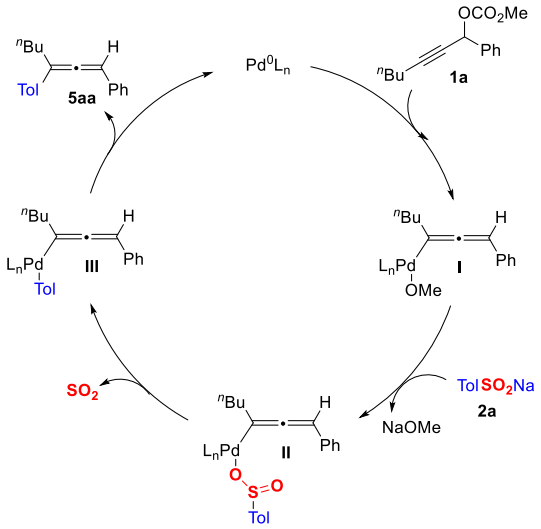
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.21 mmol), $[Pd(allyl)Cl]_2$ (5 mol %), **L6** (12 mol %), and toluene (1 mL) at 60 °C for 48 h, yield for isolated products. [b] The reaction time is 48.7 h. [c] The reaction time is 66 h. [d] The reaction time is 54 h. [e] Reaction at 80 °C. f) 17% of **1r** recovery by using 14 μL CH_2Br_2 as internal standard. [g] **2c** (2.0 equiv).

To gain further insight into the mechanism, we carried out some control experiments. First, we set up a reaction without any ligand and 96% of **1a** was recovered without forming any desired product (eq. 1). The result suggests that the ligand **L6** plays an important role in this process for both the reactivity and selectivity. When the normal coupling product sulfone **6** was subjected to the standard conditions, no desulfitative product **5aa** was observed, indicating sulfone **6** was not the intermediate (eq. 2).



A possible mechanism is proposed in Scheme 2. Pd(0) would undergo S_N2'-type oxidative addition with propargylic carbonate **1a** to give the allenylic palladium methoxide intermediate **I**, which would undergo ligand exchange with the sodium sulfinate **2a** to form the intermediate **II**. Desulfitation of intermediate **II** would afford intermediate **III**. Subsequent reductive elimination would furnish the product **5aa** and regenerate the catalytically active palladium(0) catalyst.

Scheme 2. Proposed Mechanism



Finally, we were intrigued by the potential biological activities of these newly synthesized allene products, so their cytotoxicities against A549 human lung cancer cells were measured by using the sulforhodamine B (SRB) assay. As shown in Figure 1A, most of the tested compounds significantly inhibited

A)

Compound	IR (%)[a]	Compound	IR (%)[a]
5ea	73.0 ± 1.4	**5ma**	76.8 ± 1.7
5fa	76.3 ± 2.4	**5na**	75.1 ± 3.5
5ha	81.7 ± 1.1	**5pa**	65.9 ± 2.2
5ia	66.9 ± 5.2	**5qa**	70.8 ± 1.8
5ja	75.1 ± 4.5	**5ra**	73.9 ± 6.6
5ka	87.7 ± 0.2	**Taxol**[b]	62.0 ± 0.8

[a] Inhibitory rate of cellular growth at 100 μM (**5ea** - **5ra**) or 25 nM (Taxol). [b] Taxol was used as a positive control.

B)

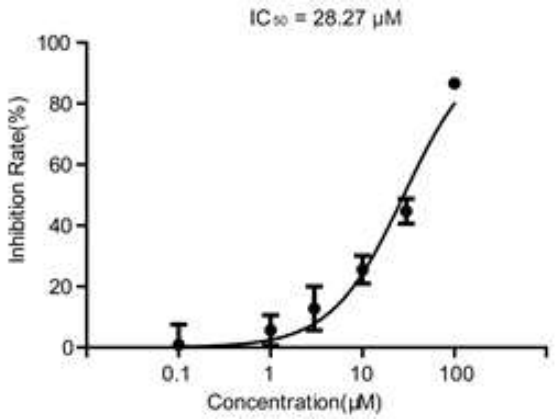


Figure 1. A) Cytotoxicity against A549 human lung cancer cells; B) **5ka** inhibited the proliferation of A549 cells in a dose-dependent manner.

the growth of A549 cells at 100 μM. Among them, **5ka** showed the most potent activity with an IC_{50} of 28.27 μM (Figure 1B).

In summary, we have developed a new approach, i.e., desulfitative coupling of sodium sulfinates with propargylic carbonates, for the synthesis of allenes. Excellent selectivity was achieved by using an electron-rich and bulky phosphine ligand. The reaction exhibits good substrate scope and functional group compatibility. A preliminary biological study found that some of these allene products exhibited significant anticancer activity. Further studies related to this topic are in progress in our laboratory.

Experimental Section

General Procedure for Palladium-Catalyzed Desulfitative Cross-Coupling Reaction of Sodium Sulfinates with Propargylic Carbonates

To an oven-dried 4 mL vial were added $[Pd(allyl)Cl]_2$ (3.6 mg, 0.01 mmol), **L6** (10.6 mg, 0.024 mmol), $TolSO_2Na$ (37.8 mg, 0.21 mmol), **1a** (49.1 mg, 0.2 mmol), and anhydrous toluene (1 mL) under the N_2 atmosphere. The vial was capped and the resulting mixture was stirred at 60 °C for 48 h in reaction block. The reaction mixture was filtered through a short column of silica gel (3.5 cm) eluted with ethyl acetate (13 mL), and concentrated. The residue was purified by column chromatography on silica gel to afford **5aa**.

Acknowledgements

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Palladium-Catalyzed Desulfitative Cross-Coupling Reaction of Sodium Sulfinates with Propargylic Carbonates

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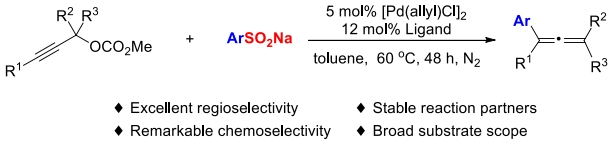

- Excellent regioselectivity
- Remarkable chemoselectivity
- Stable reaction partners
- Broad substrate scope