



Phenoxide-mediated Sonogashira coupling of trimethylsilylalkynes and aryl iodides: practical synthesis of phenolic-hydroxy-substituted diarylethyne and 1,4-diarylbutadiynes

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ABSTRACT

We successfully synthesized phenolic-hydroxy-substituted diarylethyne and 1,4-diarylbutadiynes from trimethylsilylalkynes and aryl iodides via silyl-group-migration-induced deprotection of alkynes and the usual Sonogashira coupling. The phenol moiety, which works as a desilylating agent, can be attached to any position in the coupling partner. This improvement for Sonogashira coupling would be highly effective, especially when the coupling partner has a phenol moiety. Additionally, the stability of the migrated silyl moiety on the ethynylation of 2-iodophenol is discussed.

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Sonogashira coupling¹ is a fundamental and important reaction for the synthesis of aryl acetylene derivatives, which in turn can be applied for preparing organic and polymeric materials,² and bioactive compounds.³ Among the various applications of this reaction,⁴ coupling with silylalkynes has been actively developed,^{5–8} for the main reason that isolation of the unstable terminal alkyne intermediates is not required. This reaction involves desilylation by Cl[−] ions in a polar solvent,⁵ *sec*-amines,^{5h,6} oxygen nucleophiles such as alkoxides, siloxides, and hydroxides,⁷ or fluoride reagents,^{5b,8} followed by the usual Sonogashira coupling.

Phenolic-hydroxy-substituted diarylethyne and 1,4-diarylbutadiynes have the basic structure of liquid crystals, and they are synthetic intermediates for polycyclic antibiotics and functional polymers. These phenolic compounds with an alkyne functionality are synthesized frequently via Sonogashira coupling.^{3,9} However, the hydroxy group tends to undergo undesired reactions such as *O*-arylation;¹⁰ in particular, the *ortho* hydroxy group undergoes intramolecular cyclization to afford benzofuran.¹¹

To solve these problems, we supposed that if the silyl group on an alkyne migrates to the phenol moiety, Sonogashira coupling can be carried out without the risk of the aforementioned undesired reactions. Recently, inspired by Mukaiyama's report,¹² we developed the monoarylation of 1,3-bis(trimethylsilyl)butadiyne via monode-

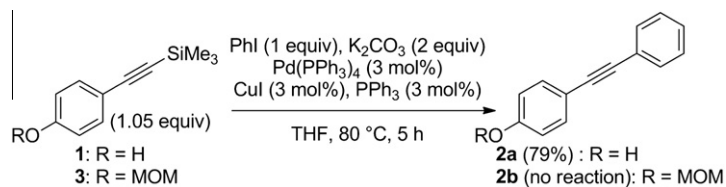
silylation by a phenoxide, on the basis of the above mentioned supposition.¹³ In this Letter, we present the efficient syntheses of hydroxyl-substituted diarylethyne and 1,4-diarylbutadiynes by silyl migration and Sonogashira coupling.

To verify the effectiveness of phenols as desilylating agents, we carried out Sonogashira coupling using 4-(trimethylsilylethynyl)phenol **1** and MOM-protected phenol **3**. Trimethylsilylethynylbenzene **1** or **3** (1.05 equiv) was treated with iodobenzene (1 equiv), Pd(PPh₃)₄ (3 mol %), CuI (3 mol %), PPh₃ (3 mol %), and K₂CO₃ (2 equiv) in THF, and the mixture was heated to 80 °C. Under these conditions, the one-pot Sonogashira coupling of **3** did not give the desired product (no conversion), but the reaction with **1** proceeded to afford the product in 79% yield (Scheme 1).

This protocol could also be applied to the synthesis of various diarylacetylenes, by the coupling of **1** with various aryl iodides. The results are summarized in Table 1. The electron-donating 4-(1-hexyloxy)iodobenzene **4b** and electron-withdrawing 4-nitroiodobenzene **4c** underwent the coupling smoothly to afford the desired products in 82% (entry 2) and 76% yields (entry 3), respectively. However, 4-iodobromobenzene **4d** was alkynylated only at the iodide position, and the Br–C bond was not cleaved (entry 4). 3-Trimethylsilyliodobenzene **4e** was converted into diarylacetylene **2e** in 64% yield, and the desilylated product **2a** was not detected in the crude mixture by ¹H NMR (entry 5).¹⁴ The proposed protocol could be extended to diarylbutadiyne derivatives as well, under the same conditions. 4-(Trimethylsilylbutadiynyl)phenol **5** was coupled with iodobenzene **4a** to give the desired product in quantita-

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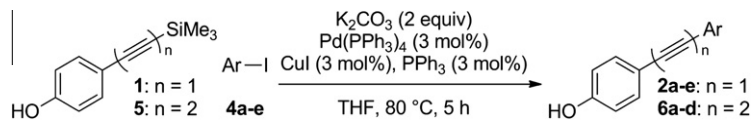
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Scheme 1. Sonogashira coupling with unprotected and protected trimethylsilylalkynylphenol.

Table 1

Scope of coupling 4-(trimethylsilylalkynyl)phenol **5** and various aryl iodides

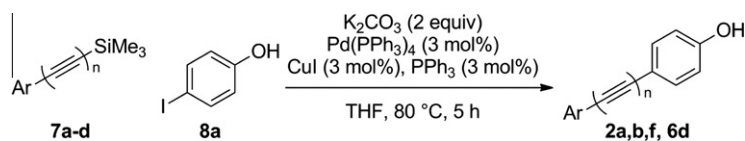


Entry	<i>n</i>	Ar-I	Yield (%)
1	1		79 (2a)
2	1		82 (2b)
3	1		76 (2c)
4	1		95 (2d)
5	1		64 (2e) ^a
6	2		Quant (6a)
7	2		68 (6b)
8	2		97 (6c)
9	2		64 (6d)

^a The desilylated product **2a** was not detected in the crude mixture by ¹H NMR.

Table 2

Scope of coupling 4-iodophenol with various aryltrimethylsilylalkynes



Entry	$\text{Ar-C}\equiv\text{C-SiMe}_3$	Yield (%)
1		63 (2a)
2		81 (2b)
3		Quant (2f)
4		99 (6d)

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