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Copper(II) Triflate-Catalyzed Nucleophilic Substitution of Propargylic Acetates with Enoxysilanes. A Straightforward Synthetic Route to Polysubstituted Furans

Zhuang-ping Zhan,[a,*] Shao-pei Wang,[a] Xu-bin Cai,[a] Hui-juan Liu,[a] Jing-liang Yu,[a] and Yuan-yuan Cui[a]

[a] Department of Chemistry and The Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, People's Republic of China
Phone: (+86)-592-2180-318; fax: (+86)-592-2180-318; e-mail: zpzhan@xmu.edu.cn

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Abstract: A novel and efficient procedure for the synthesis of γ-alkynyl ketones by the nucleophilic substitution of propargylic acetates with enoxysilanes in the presence of a catalytic amount of Copper(II) triflate, has been developed. The substitution reaction can be followed by a 4-toluenesulfonic acid-catalyzed cyclization without purification of the γ-alkynyl ketone intermediates, offering a straightforward synthetic route to polysubstituted furans.

Keywords: copper(II) triflate; enoxysilanes; furans; nucleophilic substitution; propargylic acetates

Because the alkyne moiety offers a handle for transformation into various other functional groups,[1] the propargylic substitution reactions have became an important and powerful tool for the construction of complex molecules.[2] Reactions of this type have been traditionally carried out using the Nicholas reaction but with some drawbacks: more than a stoichiometric amount of $[Co_2(CO)_8]$ is required, and several steps are necessary to obtain the propargylic product from propargylic alcohols *via* cationic propargylic complexes $[Co_2(CO)_6(propargyl)]^+$.[3,4] Some transition metal complexes were employed as efficient catalysts for the propargylic substitution reactions of propargylic alcohols with nucleophiles,[2a,b,5] where most of the nucleophiles were heteroatom-centered such as alcohols, thiols, amides and so on; In contrast, carbon-centered nucleophiles were unfortunately limited to allylsilanes for the construction of sp^3–sp^3 C–C bonds in the reaction.[2b,5h] Recently, Matsuda and coworkers[6] reported that iridium complex [Ir(cod)-$\{P(OPh)_3\}_2$]OTf serves as a catalyst for the transformation to γ-alkynyl ketones by the coupling of propargylic esters with enoxysilanes. Nishibayashi's team[7] also described an efficient coupling of propargylic alcohols with ketones for the formation of γ-alkynyl ketones and the straightforward synthesis of substituted furans in the presence of catalytic amounts of a ruthenium catalyst. However, with this method, propargylic alcohols bearing a terminal alkyne group are the exclusive applicable substrates. Even so, the peculiarity and high cost of such catalysts make a barrier to their large-scale use. Therefore, the development of a general, efficient, cheap and readily available catalyst for the formation of γ-alkynyl ketones by propargylic substitution reaction is of significance.

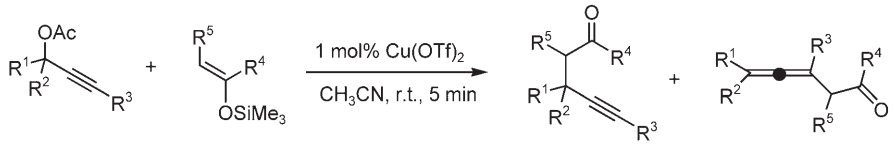
Recently, we have developed a highly efficient iron(III)- or bismuth(III)-catalyzed propargylic substitution of propargylic alcohols or acetates with various heteroatom- and carbon-centered nucleophiles,[8] where the allylsilane as the carbon-centered nucleophile is the exclusive example for the construction of sp^3–sp^3 C–C bonds. Naturally we attempted to extend the scope of carbon-centered nucleophiles from allylsilanes to ketones or enoxysilanes for the formation of γ-alkynyl ketones. $Cu(OTf)_2$, as an efficient Lewis acid catalyst, has been widely used in organic synthesis.[9] So we employed $Cu(OTf)_2$ to catalyze the reaction of propargylic acetates with ketones, but the starting materials were recovered intact, probably due to the weak nucleophilicity of the α-C of the ketones. Gratifyingly, when using enoxysilanes instead of ketones as the carbon-centered nucleophiles, the reaction proceeded rapidly in the presence of 1 mol% $Cu(OTf)_2$ and efficiently afforded the corresponding γ-alkynyl ketones in high yields. Herein we report the successful results and scope of the reaction, and that this CuII)-catalyzed reaction allows for the straightforward synthesis of polysubstituted furans.

The reaction of propargylic acetate **1a** and enoxysilane **2a** was first carried out employing $Cu(OTf)_2$ as the catalyst. γ-Alkynyl ketone **3aa** was obtained in 87% isolated yield at room temperature within just 5 min in the presence of 1 mol% $Cu(OTf)_2$. Anhydrous iron(III) chloride is also an efficient catalyst for this transformation but the practical loading of catalyst should be not less than 5 mol% (Table 1, entry 1), while bismuth(III) chloride proved to be inefficient in the propargylic substitution and product **3aa** or **4aa** was not detected. Reaction of propargylic alcohol **1a-OH** with **2a** catalyzed by $Cu(OTf)_2$ was also tested and the propargylic substitution did not proceed. The reason may rest on the fact that the hydroxy function is not an active leaving group. With these conditions in hand, various propargylic acetates were treated with the enoxysilane **2a** in the presence of 1 mol% $Cu(OTf)_2$ and all the reactions gave the desired coupling products in moderate to high yields. Typical results are summarized in Table 1. The reaction proceeded smoothly without exclusion of moisture or air from the reaction mixture. Both electron-donating and electron-withdrawing aromatic substrates (**1k–m**) reacted smoothly with enoxysilane **2a** affording the corresponding alkylated products in high yields (Table 1, entries 11–13). Functional groups, such as chloro, cyano and methoxy in the substrates did not affect the course of the construction of carbon-carbon bonds, but the electron-withdrawing substrates require relatively longer times for completion (Table 1, entry 12). Variation in the alkyne substituents from an aryl to an *n*-Bu, trimethylsilyl, or H (**1a–c, 1g**) is well tolerated. This is in sharp contrast to the Ru-catalyzed substitution[7] where the substrates were limited to propargylic alcohols bearing a terminal alkyne group. Coupling of secondary benzylic propargylic acetates with **2a** was completed at room temperature within 5 min furnishing corresponding substitution products in 81–88% yields (Table 1, entries 1–3, 7, 11–13). However, the secondary aliphatic propargylic acetate ($R^1=CH_3$, $R^2=H$, $R^3=Ph$) **1i** did not react at all with **2a**. And the starting **1i** and **2a** were recovered intact. The desired transformation was accomplished by using corresponding phosphate **1iP** as the substrate under forcing conditions, with low yield (Table 1, entry 9). The primary aliphatic propargylic phosphate **1jP** did not undergo the substitution even under fierce reaction conditions (Table 1, entry 10). On the other hand, tertiary aliphatic propargylic acetates allow for the construction of sp^3–sp^3 C–C bonds in high yields (Table 1, entries 4 and 5). The experimental results suggest a mechanism through the formation of propargylic cation intermediate. Instability of the propargylic cation intermediate clearly made the substitution reaction less favorable. Unfortunately, the allenyl isomer was concomitantly formed in 37% yield in the example of the more hindered substrate **1h** which has two phenyl groups on the propargylic carbon (Table 1, entry 8). This result implies that the regioselectivity of this substitution is crucially affected by the steric bulkiness at the electrophilic site. It is noteworthy that the corresponding γ-alkynyl ketones were obtained in good yields in the examples involving the substrates **1d** and **1e** which have alkyl groups on the propargylic carbon, and the elimination product enynes **5d** and **5e** were not observed in the reaction (Table 1, entries 4 and 5), while in the Ir-catalyzed procedure,[6] enynes **5d** and **5e** were obtained as the major products at 25 °C. Furthermore, the copper(II)-catalyzed substitution proceeded completely in 5 min. Compared with the existing methodologies[6,7] where several hours were required for complete transformation, our procedure needs much lower reaction times. The results exhibit the superiority of $Cu(OTf)_2$ as the catalyst in this type reaction.

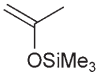
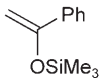
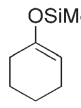
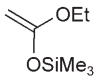
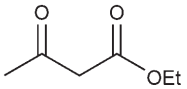
With these preliminary results available, the scope of the nucleophiles in this reaction was investigated. Enoxysilanes **2b**, **2c** and **2d** proved to be efficient for the present transformation as well. The regioselectivity that preferred the propargylic products **3** was retained in examples involving **2b** as the nucleophile (Table 1, entries 14–18). Allenyl isomer **4hb** (**3hb**:**4hb** = 38:52) was concomitantly formed only in the reaction of the sterically encumbered substrate **1h** (Table 1, entry 19). In the cases involving **2c** as nucleophile, the ratio of the products **3** and **4** was obviously affected by the steric bulkiness of the propargylic acetates. γ-Alkynyl ketones **3** were the sole products in the reactions of secondary propargylic acetates **1c, 1g**, and no allenyl isomers were detected (Table 1, entries 20 and 24). But, on changing the substrates to tertiary propargylic acetates **1d**, **1e** and **1f**, the yields of substitution products **3** decreased and the allenyl isomers **4** were respectively obtained in 33, 41, 15% yields (Table 1, entries 21–23). Especially, the allenyl isomer **4hc** was isolated as the sole product in 87% yield in the reaction of **1h** with **2c** (Table 1, entry 25). Ketene acetal **2d** retained the preferential formation of **4hd** in reaction with **1h** (Table 1, entry 27). Steric bulkiness at the nucleophilic site seems to be advantageous for the formation of **4**. In addition, β-diketone ester **2e** can be directly used for the propargylic substitution giving the corresponding alkylated products in good yields (Table 1, entries 28 and 29).

The $Cu(OTf)_2$-catalyzed propargylic substitution allows for the straightforward synthesis of tri- or tetrasubstituted furans by sequential cyclization reaction of γ-alkynyl ketone intermediates. The mixture of secondary propargylic acetates **1**, enoxysilanes **2**, and 1 mol% $Cu(OTf)_2$ was simply stirred in acetonitrile. Upon completion of the reaction, the solvent acetonitrile was removed under vacuum, followed by the addition of toluene and a stoichiometric amount of 4-

Table 1. $Cu(OTf)_2$-catalyzed substitution of propargylic acetates **1** with nucleophiles **2**.[a]



1 **2** **3** **4**

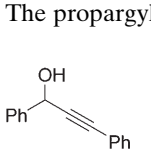
Entry	Enoxysilane	Substrate R^1; R^2; R^3	Product	Isolated yield [%] **3**	**4**
1		**1a**: Ph; H; Ph	**aa**[b,c]	87	0
2		**1b**: Ph; H; *n*-Bu	**ba**	81	0
3		**1c**: Ph; H; TMS	**ca**	88	0
4		**1d**: CH_3; CH_3; Ph	**da**	91	0
5		**1e**: -$(CH_2)_5$-; Ph	**ea**	80	0
6		**1f**: Ph; CH_3; Ph	**fa**	81	0
7	**2a** 	**1g**: Ph; H; H	**ga**	82	0
8		**1h**: Ph; Ph; Ph	**ha**	53	37
9		**1i**: CH_3; H; Ph	**ia**	0 (36)[d]	0
10		**1j**: H; H, Ph	**ja**	0 (0)[e]	0
11		**1k**: 4-Cl-C_6H_4; H; *n*-Bu	**ka**	85	0
12		**1l:** 4-CN-C_6H_4; H; *n*-Bu	**la**	78[f]	0
13		**1m**: 2-MeO-C_6H_4; H; *n*-Bu	**ma**	89	0
14		**1a**: Ph; H; Ph	**ab**	88	0
15		**1b**: Ph; H; *n*-Bu	**bb**	93	0
16	**2b** 	**1c**: Ph; H; TMS	**cb**	92	0
17		**1d**: CH_3;CH_3; Ph	**db**	96	0
18		**1g**: Ph; H; H	**gb**	84	0
19		**1h**: Ph; Ph; Ph	**hb**	38	52
20		**1c**: Ph; H; TMS	**cc**	93[g]	0
21		**1d**: CH_3;CH_3; Ph	**dc**	55	33
22		**1e**: -$(CH_2)_5$-; Ph	**ec**	46	41
23	**2c** 	**1f**: Ph; CH_3; Ph	**fc**	75 [h]	15
24		**1g**: Ph; H; H	**gc**	89[i]	0
25		**1h**: Ph; Ph; Ph	**hc**	0	87
26		**1a**: Ph; H; Ph	**ad**	57	0
27	**2d** 	**1h**: Ph; Ph; Ph	**hd**	43	46
28		**1a**: Ph; H; Ph	**ae**	85[j]	0
29	**2e** 	**1b**: Ph; H; *n*-Bu	**be**	72[k]	0

[a] The reactions of **1** (0.5 mmol) with **2** (1.5 mmol) were carried out in the presence of $Cu(OTf)_2$ (0.005 mmol) in CH_3CN (1.0 mL) at room temperature for 5 min.

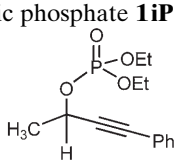
[b] 1 mol% $FeCl_3$ as the catalyst, overnight at room temperature, but still the reaction was incomplete leading to an 32% yield of product **3aa**.

[c] 5 mol% $FeCl_3$ as the catalyst, 5 min at room temperature, 85% isolated yield of **3aa**.

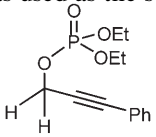
[d] The propargylic phosphate **1iP** was used as the substrate, at 60 °C for 15 min.



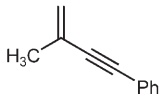
1a-OH



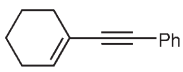
1iP



1jP



5d



5e

[e] The propargylic phosphate **1jP** was used as the substrate, at 60 °C for 12 h.

[f] At room temperature, 30 min.

[g] Two diastereoisomers were formed with the isomer ratio of 1.8:1.

[h] Two diastereoisomers were formed with the isomer ratio of 1.5:1.

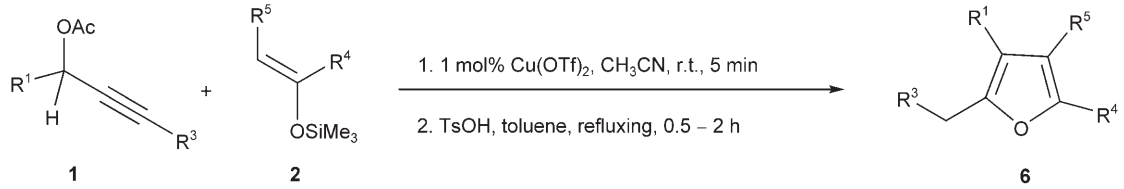
[i] Two diastereoisomers were formed with the isomer ratio of 1.5:1.

[j] Two diastereoisomers were formed with the isomer ratio of 1.6:1.

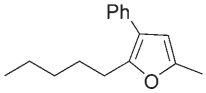
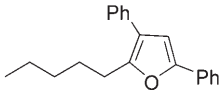
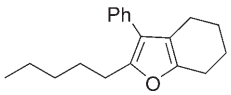
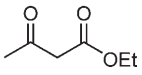
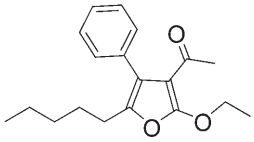
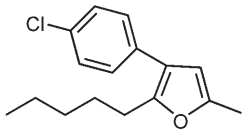
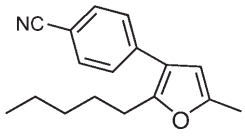
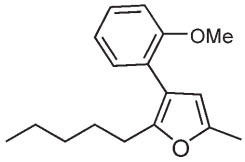
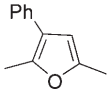
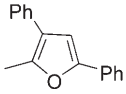
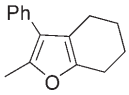
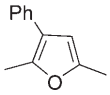
[k] Two diastereoisomers were formed with the isomer ratio of 1.5:1.

toluenesulfonic acid (TsOH). Highly substituted furans were conveniently furnished in good yields within no more than 2 h under refluxing conditions (Table 2). Reactions of enoxysilane **2a** with various

Table 2. Synthesis of substituted furans from propargylic acetates **1** and enoxysilanes **2**.[a]



1 2 6

Entry	Substrate	Enoxysilane	Time [h]	Product	Isolated yield [%]
1		**2a:** R^4 = Me; R^5 = H	0.5	**6ba** 	77
2		**2b:** R^4 = Ph; R^5 = H	1.0	**6bb** 	80
3	**1b:** R^1 = Ph; R^3 = *n*-Bu	**2c:** R^4 = R^5 = -$(CH_2)_4$-	1.0	**6bc** 	81
4		**2e:** 	1.0	**6be** 	65
5	**1k:** R^1 = 4-Cl-C_6H_4; R^3 = *n*-Bu	**2a:** R^4 = Me; R^5 = H	0.5	**6ka** 	75
6	**1l:** R^1 = 4-CN-C_6H_4; R^3 = *n*-Bu	**2a:** R^4 = Me; R^5 = H	2.0	**6la** 	70
7	**1m:** R^1 = 2-MeO-C_6H_4; R^3 = *n*-Bu	**2a:** R^4 = Me; R^5 = H	0.5	**6ma** 	85
8		**2a:** R^4 = Me; R^5 = H	1.0	**6ga** 	75
9	**1g:** R^1 = Ph; R^3 = H	**2b:** R^4 = Ph; R^5 = H	2.0	**6gb** 	78
10		**2c:** R^4 = R^5 = -$(CH_2)_4$-	2.0	**6gc** 	76
11	**1c:** R^1 = Ph; R^3 = TMS	**2a:** R^4 = Me; R^5 = H	1.0	**6ga** 	82

[a] The solution of propargylic acetates **1** (0.5 mmol), enoxysilanes **2** (1.5 mmol) and $Cu(OTf)_2$ (0.005 mmol) was stirred in CH_3CN at room temperature for 5 min. Acetonitrile was then removed, followed by the addition of TsOH (0.5 mmol) and toluene (6.0 mL). Cyclization proceeds under reflux for 0.5–2.0 h.

propargylic acetates afforded the corresponding 2,3,5-trisubstituted furans in high yields (Table 2, entries 1, 5–8, 11). Functional groups such as chloro, cyano and methoxy in the substrates were tolerated in the PTSA-catalyzed cyclization, which allows an access to other functionalized furans. When **2b** displaced **2a**, good results were also gained under the same conditions (Table 2, entries 2 and 9). Starting with enoxylsilane **2c** and propargylic acetates **1b**, **1g**, tetra-substituted furans were isolated in 81 and 76% yields, respectively (Table 2, entries 3 and 10). The trimethylsilyl group cannot be tolerated under the acidic condition and so the same product was obtained in the examples involving **1c** and **1g** (Table 2, entries 8 and 11). Treatment of propargylic acetate **1b** with β-diketone ester **2e** gave the 3-acetylated tetra-substituted **6be** in moderate yield (Table 2, entry 4). Regioisomers of furans were not observed in all cases. In the sequential process, the intermediates γ-alkynyl ketones obtained by the coupling of propargylic acetates with nucleophiles in the first step, can be directly used for the next cyclization without purification, which would lessen the yield loss of the furan products. Nishibayashi's team[7d] reported novel ruthenium- and platinum-catalyzed sequential reactions to afford the corresponding tri- and tetra-substituted furans by the direct use of propargylic alcohols as substrates and ketones as carbon-centered nucleophiles under N_2, but the substrates were limited to propargylic alcohols bearing a terminal alkyne group and the reaction required rather long times for completion. In contrast, propargylic acetates bearing both terminal alkyne group and internal alkyne group are available, and the reaction proceeded much more rapidly without inert gases protection. Even though more active enoxysilanes of ketones as nucleophiles were required in our procedure.

Notably, starting from **1b** and enoxysilane **2f**, after substitution and annulation, we can finally obtain a symmetrical oligomer **6bf** containing two furan moieties (Scheme 1). The photophysical properties of **6bf** were briefly examined. The oligomer exhibits very bright emission in the purple light region with high fluorescence quantum yields (Φ_f) in CH_2Cl_2 and EtOAc, but a relatively lower quantum yield in $CHCl_3$ (Table 3). The emission spectrum shows the vibronic fine structure of **6bf**. Importantly, this oligomer bears a long chain aliphatic moiety which increases the solubility for the convenience of processing leading to devices for optoelectronic investigations. Syntheses of analogous oligomers by the $Cu(OTf)_2$-catalyzed substitution/cyclization sequential process and their potential optoelectronic applications are currently on-going in our laboratory.

In summary, a novel and efficient procedure for the synthesis of γ-alkynyl ketones by the substitution reaction of propargylic acetates with enoxysilanes catalyzed by 1 mol% $Cu(OTf)_2$, has been developed. The reaction is completed rapidly within a very short time under mild conditions and air or moisture is tolerant. Propargylic acetates bearing terminal alkyne group or internal alkyne group are readily available. Such relevant advantages make our procedure an appealing alternative to current available methods to γ-alkynyl ketones. Additionally, the $Cu(OTf)_2$-catalyzed substitution reaction is followed by a TsOH-accelerated cyclization without purification of the γ-alkynyl ketone intermediates, offering a straightforward synthetic route to tri- or tetra-substituted furans.

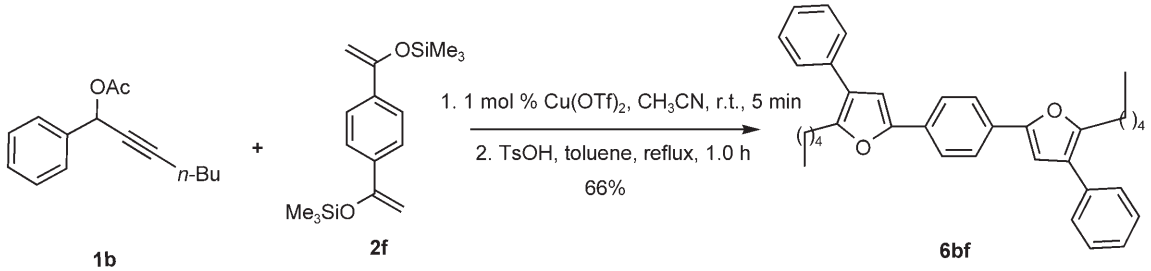
Experimental Section

Typical Procedure for the Synthesis of γ-Alkynyl Ketones

To a 5-mL flask, propargylic acetate **1a** (0.5 mmol, 0.125 g), enoxysilane **2a** (1.5 mmol, 0.195 g), CH_3CN (1.0 mL), and $Cu(OTf)_2$ (0.005 mmol, 0.002 g) were successively added, the reaction mixture was stirred at room temperature, and monitored periodically by TLC. After 5 min, the reaction was completed, the solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified

Table 3. Photophysical properties of **6bf**.

Solvent	λ_{max} [nm]	λ_{em} [nm]	Φ_f
CH_2Cl_2	346	377, 396	0.61
EtOAc	342	371, 391	0.64
$CHCl_3$	346	377, 396	0.16



1b 2f 6bf

Scheme 1.

by silica gel column chromatography (EtOAc/hexane) to afford corresponding γ-alkynyl ketone **3aa**; yield: 0.108 g (87%).

Typical Procedure for the Synthesis of Substituted Furans

To a 10-mL flask, propargylic acetate **1b** (0.5 mmol, 0.115 g), enoxysilane **2a** (1.5 mmol, 0.195 g), CH_3CN (1.0 mL) and $Cu(OTf)_2$ (0.005 mmol, 0.002 g) were successively added, the reaction mixture was stirred at room temperature, and monitored periodically by TLC. Upon reaction completion, the solvent CH_3CN was removed under reduced pressure by an aspirator, followed by the addition of toluene (6.0 mL) and a stoichiometric amount of 4-toluenesulfonic acid (0.5 mmol, 0.086 g). The reaction was heated to reflux and monitored by TLC. When completed, toluene was concentrated under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (hexane) to afford the corresponding substituted furan **6ba**; yield: 0.088 g (77%).

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