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Copper-catalyzed propargylic C–H functionalization for allene syntheses†

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Allenenitriles bearing different synthetically versatile functional groups have been prepared smoothly from 5-alkynyl fluorosulfonamides in decent yields with an excellent chemo- and regio-selectivity under redox neutral conditions. The resulting allenenitriles can be readily converted to useful functionalized heterocycles. Based on mechanistic study, it is confirmed that this is the first example of radical-based non-activated propargylic C–H functionalization for allene syntheses.

Introduction

Cross coupling reactions represent one of the most straightforward strategies for the construction of complex molecules.[1] As one important class of substrates, the transformations of propargylic compounds are attracting more and more interest.[2] In the past few decades, catalytic couplings of propargylic alcohol derivatives with organometallic reagents have been established as an effective and very reliable way to synthesize functionalized alkynes[3,4] or allenes[5,6] either *via* a two-electron or one-electron process (Fig. 1A). However, all these methods apply propargylic alcohol derivatives with an appropriate leaving group. In contrast, direct functionalization of the inert propargylic C–H bonds would provide a straightforward and atom economic approach. In this area, preparation of alkynes has been realized *via* the Kharasch–Sosnovsky-Type reaction,[7] intramolecular or intermolecular nitrene insertion,[8] and coordination-directed deprotonation[9] (Fig. 1B). Recently Liu *et al.* reported the benzylic C–H activation of 1-aryl-2-alkynes for arylallene syntheses.[10] We envisioned a strategy of 1,5-hydrogen atom transfer[11] for the generation of a propargylic radical, which would be in rapid resonance with an allenyl radical. Trapping with an appropriate reagent would afford alkynes or allenes (Fig. 1C). Such a protocol for selective allene syntheses faces three challenges: (1) the more reactive C≡C bonds may cause undesired transformations such as radical cyclization that complicates the target reaction, (2) the selectivity issue of propargylic radicals *vs.* allenyl radicals to form either alkyne[7,12] or allene products, and (3) a matched trapping reagent. Allenenitriles could be prepared though the corresponding Wittig reaction,[13] S_N2'-type substitution of the *in situ* generated propargylic phosphates,[14] cross coupling of propargylic substrates,[6f,15] and difunctionalization of 1,3-enynes.[16] Herein, we wish to report our results on copper-catalyzed cyanation of non-activated propargylic C–H bonds, affording di- or tri-substituted allenenitriles bearing an attractive remote sulfonamide in decent yields with an excellent chemo- and regio-selectivity tolerating many synthetically versatile functionalities (Fig. 1D).

Results and discussion

We began our investigation with fluorosulfonamide[17,18] **1a** and TMSCN[15b,16] in the presence of $Cu(CH_3CN)_4PF_6$ (ref. [19]) and

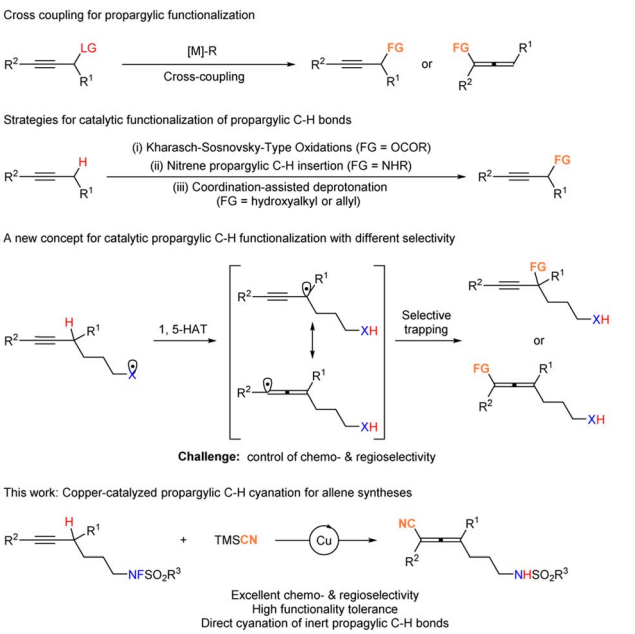

Fig. 1 Catalytic functionalization of propargylic compounds.

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ligand **L1** in DCE at 30 °C. To our delight, 17% yield of desired allenenitrile **2a** was obtained with 70% recovery of **1a** (Table 1, entry 1). Then, attention was focused on the solvent effect (Table 1, entries 2–8): the reaction in CH_3CN for 24 h could deliver a much better yield of **2a** of 75%, with only 12% recovery of **1a**. By extending the reaction time to 30 hours, **1a** could be converted completely, affording **2a** in 83% yield (Table 1, entry 9), and the formation of isomeric alkyne product **3a** was not observed. When $Cu(CH_3CN)_4BF_4$ was used instead of $Cu(CH_3CN)_4PF_6$, the yield of **2a** dropped to 61%, with 10% recovery of **1a**. This may be attributed to the stronger coordinating ability of BF_4^- than that of PF_6^-,[20] which led to a lower catalytic activity. Further screening of other copper catalysts and ligands (Table 1, entries 11–17), didn't give any better results, indicating that $Cu(CH_3CN_4)PF_6$ and **L1** are optimal.

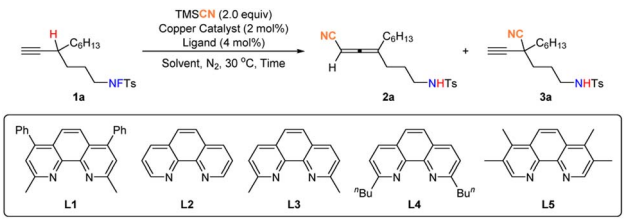
With the optimized conditions in hand, we set out to explore the scope of this propargylic C–H cyanation reaction. As shown in Fig. 2, a variety of fluorosulfonamides bearing a highly sensitive terminal alkyne could be converted to trisubstituted allenes exclusively in decent yields. The R^1 group may be alkyl, cycloalkyl, chloroalkyl, or methoxyalkyl, and **2a–2f** were furnished in 77–83% yields. In addition, terminal olefin and differently substituted benzyl groups, such as halide atoms (F, Cl, and Br), methoxy, and trifluoromethyl may be tolerated, affording **2g–2m** in 67–76% yields, and the related allyl or benzyl cyanation products were not formed, indicating a perfect chemoselectivity. Furthermore, important heteroaryl groups including thiophene and pyridine are compatible, affording heteraryl-containing products **2n** and **2o** in 66% and 55% yields.

Compared to the alkyl-substituted substrates, the reaction of the substrate with R^1 being phenyl proceeded more smoothly, affording **2p** in 83% yield. The scope could be further expanded to internal alkynes to prepare tetrasubstituted allenes **2q–2u** in 58–82% yields after adjusting the reaction conditions slightly. Besides, the R^3 group with synthetic versatile functional groups such as acetyl, ester, cyano, nitro, and iodo groups were all intact under the optimal mild reaction conditions (**2v–2aa**, 66–76% yields). The cyanation reaction could be smoothly implemented for the modification of drug molecules, providing allenenitriles **2ab** and **2ac** in satisfactory yields. Finally, the reaction may be easily scaled up to the gram-scale (**2a**), demonstrating the practicality of the protocol.

Moreover, substrates **1ad**, **1ae**, and **1af** were prepared on purpose to check the possibility of 1,4-, 1,6-, or even 1,7-HAT: the reaction of **1ad** was complicated (Fig. 3A); the reaction of **1ae** underwent 1,6-HAT to result in allenenitrile **2ae** in 60% yield with an excellent regioselectivity (Fig. 3B); the reaction of **1af** still gave the 1,5-HAT non-allene product **5** in a poor yield (Fig. 3C). Thus, 1,4-HAT and 1,7-HAT do not work while 1,6-HAT works.

Such highly functionalized allenes show great synthetic potential (Fig. 4): **2a** may undergo conjugate addition exclusively under a set of mild conditions to afford nitrile **6** bearing a tetrahydropyridine in 88% yield; **2a** could also be cyclized with

Table 1 Optimization of the reaction conditions[a]



Entry	Solvent	Copper catalyst	Ligand	Time (h)	Yield of **2a**[b] (%)	Recovery of **1a**[b] (%)
1	DCE	$Cu(CH_3CN)_4PF_6$	**L1**	24	17	70
2	Toluene	$Cu(CH_3CN)_4PF_6$	**L1**	24	10	67
3	Ethyl acetate	$Cu(CH_3CN)_4PF_6$	**L1**	24	29	35
4	MTBE	$Cu(CH_3CN)_4PF_6$	**L1**	24	13	56
5	THF	$Cu(CH_3CN)_4PF_6$	**L1**	24	13	24
6	Dioxane	$Cu(CH_3CN)_4PF_6$	**L1**	24	38	17
7	DMF	$Cu(CH_3CN)_4PF_6$	**L1**	24	44	—
8	CH_3CN	$Cu(CH_3CN)_4PF_6$	**L1**	24	75	12
9	CH_3CN	$Cu(CH_3CN)_4PF_6$	**L1**	30	83	—
10	CH_3CN	$Cu(CH_3CN)_4BF_4$	**L1**	36	61	10
11	CH_3CN	CuCN	**L1**	36	69	—
12	CH_3CN	CuOAc	**L1**	36	66	—
13	CH_3CN	CuTc	**L1**	36	61	—
14	CH_3CN	$Cu(CH_3CN)_4PF_6$	**L2**	36	49	47
15	CH_3CN	$Cu(CH_3CN)_4PF_6$	**L3**	36	75	7
16	CH_3CN	$Cu(CH_3CN)_4PF_6$	**L4**	36	71	5
17	CH_3CN	$Cu(CH_3CN)_4PF_6$	**L5**	36	3	67

[a] All reactions were run on a 0.1 mmol scale in solvent (1 mL) at 30 °C under a nitrogen atmosphere. [b] Determined by ^1H NMR analysis with CH_3NO_2 as the internal standard.

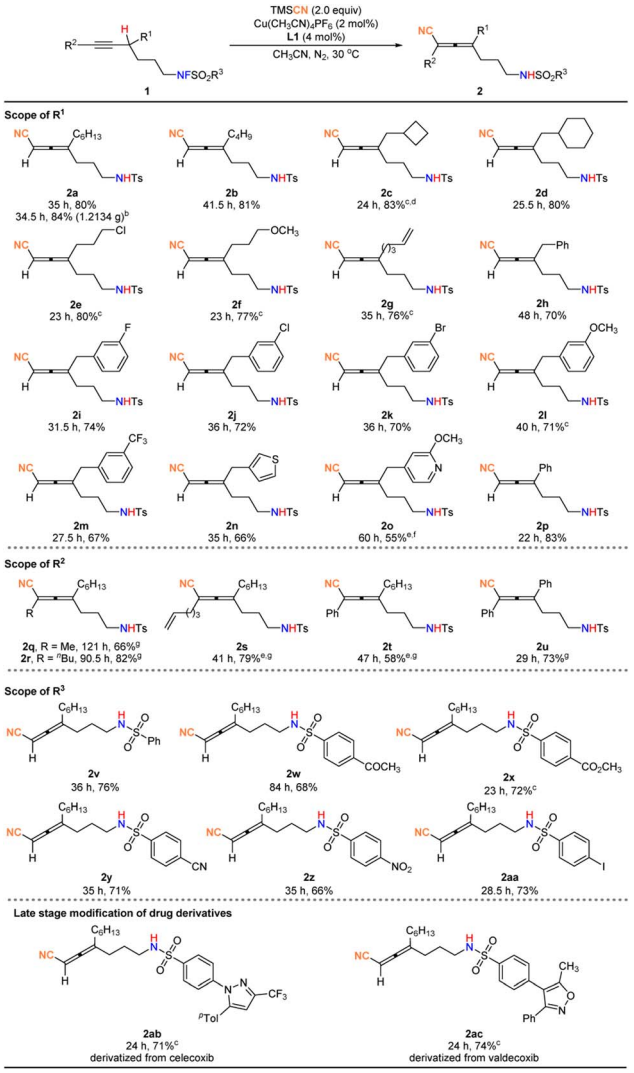


Fig. 2 Scope. [a]Reaction conditions: **1** (0.5 mmol), TMSCN (1.0 mmol), $Cu(CH_3CN)_4PF_6$ (2 mol%), and **L1** (4 mol%) in CH_3CN (5 mL) at 30 °C. [b]Reaction on a 4.0 mmol scale. [c]$Cu(CH_3CN)_4PF_6$ (4 mol%), **L1** (8 mol%). [d]The product was a mixture of **2c** and its isomer **2g** (**2c**/**2g** = 97/3), originated from the starting material **1c** (**1c**/**1g** = 96/4). [e]Reaction on a 0.2 mmol scale. [f]Additional $Cu(CH_3CN)_4PF_6$ (2 mol%) and **L1** (4 mol%) were added to the reaction mixture after stirring for 36 h. [g]$Cu(CH_3CN)_4PF_6$ (10 mol%), **L2** (20 mol%).

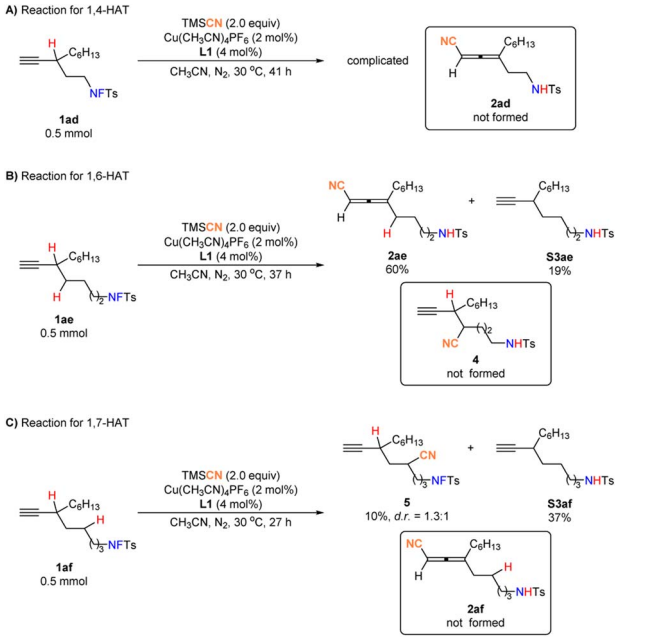


Fig. 3 The reactions for 1,*n*-HAT ($n \neq 5$).

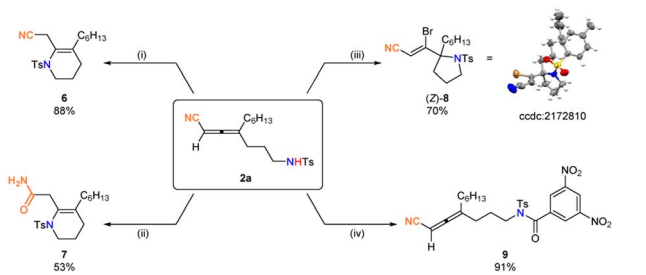


Fig. 4 Transformations of products. Reaction conditions: (i) Cs_2CO_3 (1.0 equiv.), CH_3CN, rt, 17 h. (ii) NaOH (2.0 equiv.), H_2O_2 (4.0 equiv.), EtOH, 80 °C, 7 h. (iii) NBS (1.2 equiv.), DCM/THF = 4/1, rt, 23 h. (iv) 3,5-Dinitrobenzoyl chloride (1.2 equiv.), DMAP (0.1 equiv.), Et_3N (1.5 equiv.), rt, 4 h.

the nitrile group being hydrolyzed to afford amide **7** in 53% yield with NaOH and H_2O_2; NBS promoted electrophilic bromocyclization[21] of **2a** would afford stereodefined brominated alkenenitrile (*Z*)-**8** bearing a tetrahydropyrrole ring in 70% yield with an excellent stereoselectivity, which has been clearly identified by X-ray analysis. The amine functionality could also be easily modified to afford the corresponding *N*-tosylbenzamide **9** in an excellent yield.

In addition, we found with R^1 being H, both reactions of **1ag** and **1ah** delivered a mixture of allene **2** and alkyne **3**. However, the reactions of substrates with R^1 being a non-H substituent, all afforded the allenenitriles **2** exclusively (Fig. 5A). Thus, we reasoned that the steric effect of R^1 is critical for the observed regioselectivity. To unveil the mechanism, a set of experiments were conducted. Initially, BHT was employed as a radical trapping reagent in the reaction of **1a**: the formation of **2a** was inhibited gradually with the increase of BHT (Fig. 5B), suggesting a possible radical pathway. To further confirm the existence of any radical intermediates, the reaction of **1ag** was conducted under an oxygen atmosphere: the cyanation was inhibited completely, and alkynone **10** was isolated in 27% yield, which couldn't be afforded by the direct oxidation of amine **S3ag**, confirming the existence of propargylic radical intermediates[22] (Fig. 5C). Finally, we investigated the reaction rate of **1a**/**1a**-*d* to **2a** by NMR monitoring (see the ESI†), showing that the primary kinetic isotope effect (KIE) was 1.5 (Fig. 5D).

On the basis of these experiments, a catalytic cycle involving radical intermediates has been proposed (Fig. 6): firstly, the LCu^{I} species would reduce the N–F bond of **1** to produce the $LCu^{II}F$ species and the *N*-centered radical **Int 1**. Then **Int 1** undergoes a radical 1,5-HAT process to generate the resonance hybrid of propargylic/allenyl radical **Int 2**, and the $LCu^{II}F$

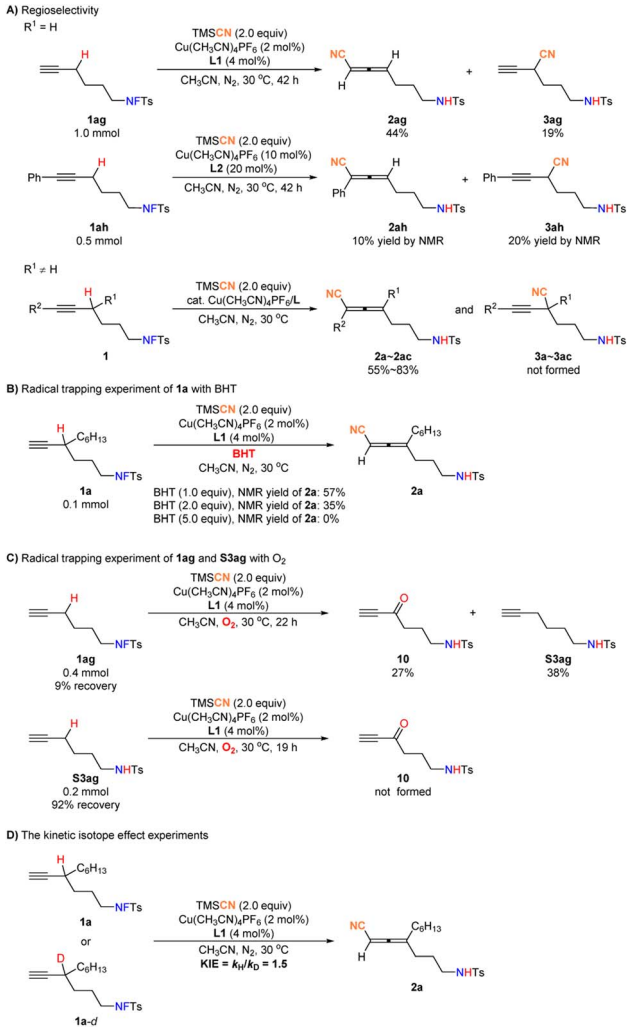


Fig. 5 Regioselectivity and mechanistic studies.

species is converted to the $LCu^{II}CN$ species by ligand exchange with TMSCN. Subsequently, the allenyl radical, one of the resonance structures of **Int 2** with less steric hindrance would

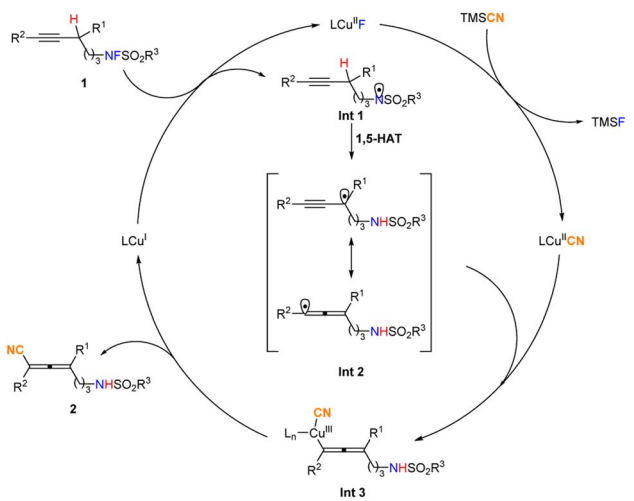


Fig. 6 Proposed mechanism.

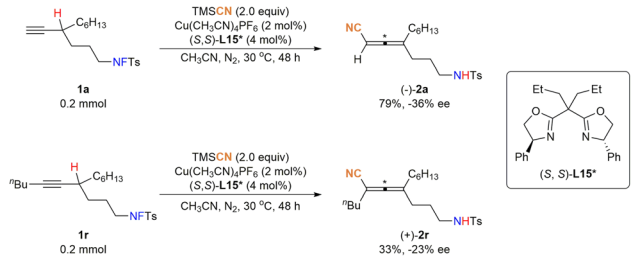


Fig. 7 Preliminary results of catalytic asymmetric propargylic C–H cyanation.

be selectively trapped by the $LCu^{II}CN$ species to afford the allenyl $LCu^{III}CN$ species **Int 3**. Reductive elimination would deliver the desired allene **2** and regenerate the catalytically active LCu^{I} species.

With this approach in hand, we also attempted the enantioselective reaction with different chiral bis(oxazoline) and pyrine-oxazoline ligands. After a series of efforts (for details see Table S6 in the ESI†), the reaction of fluorosulfonamide **1a** by using (*S*,*S*)-**L15*** gave (−)-**2a** in 79% yield and −36% ee. Furthermore, non-terminal alkyne **1r** was also subjected to such conditions, which delivered (+)-**2r** in 33% yield and −23% ee (Fig. 7).

In summary, we have developed the first example of 1,5-HAT-based propargylic C–H activation, providing a highly chemo- and regioselective approach for the construction of allenenitriles, featuring great functionality compatibility. The resulting products may be readily converted to different functionalized heterocycles. Mechanistic studies support the catalytic cycle of Cu^{I}/Cu^{III} involving a propargylic radical and allenyl radical. Further studies on other types of 1,5-HAT based propargylic C–H functionalization for allene syntheses and further investigations on the asymmetric version of this propargylic C–H cyanation are ongoing in our laboratory.

Data availability

All detailed procedures, characterization data, and spectra are available in the ESI.†

Author contributions

S. M., X. W. and D. Z. designed the experiments. D. Z., J. F., Y. S and Y. H performed the experiments. D. Z. and S. M. wrote the manuscript. D. Z., C. F. and S. M. checked the experimental data.

Conflicts of interest

The authors declare no competing interests.

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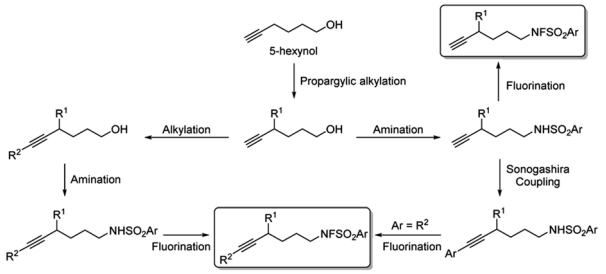

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