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Copper-Catalyzed Trifluoromethylation of Vinylsiloxanes

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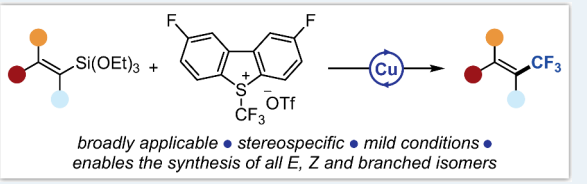
ABSTRACT: Trifluoromethylated alkenes are shown to be readily synthesized from the corresponding vinylsiloxanes using a simple copper-catalyzed trifluoromethylation with Umemoto's reagent II. Upon simple activation with tetrabutylammonium triphenyldifluorosilicate in the presence of Kubas' salt and without an additional exogenous ligand, they were indeed found to be easily trifluoromethylated with high levels of stereospecificity. In addition to a broad substrate scope and mild reaction conditions, this route to trifluoromethylated alkenes enables the synthesis of all *E*, *Z*, and branched isomers.



KEYWORDS: *copper catalysis, trifluoromethylation, trifluoromethylated alkenes, vinylsiloxanes, Umemoto's reagent*

INTRODUCTION

In addition to being valuable and emerging building blocks participating in a variety of transformations[1] enabling the synthesis of a variety of fluorinated molecules, trifluoromethylated alkenes have also found major applications as agrochemicals and in medicinal chemistry, due to the unique properties brought by this moiety. The most iconic examples are the synthetic pyrethrinoid insecticides λ-cyhalothrin **1** or tefluthrin **2** commonly utilized for crop protection (Figure 1A). In medicinal chemistry, representative examples include panomifene **3**, a tamoxifen analogue with an antiestrogenic activity, Pfizer's EGRF inhibitor **4**,[2] as well as Fludelone **5**, a trifluorinated epothilone B analogue with enhanced metabolic stability and increased antitumor activity (Figure 1B).[3]

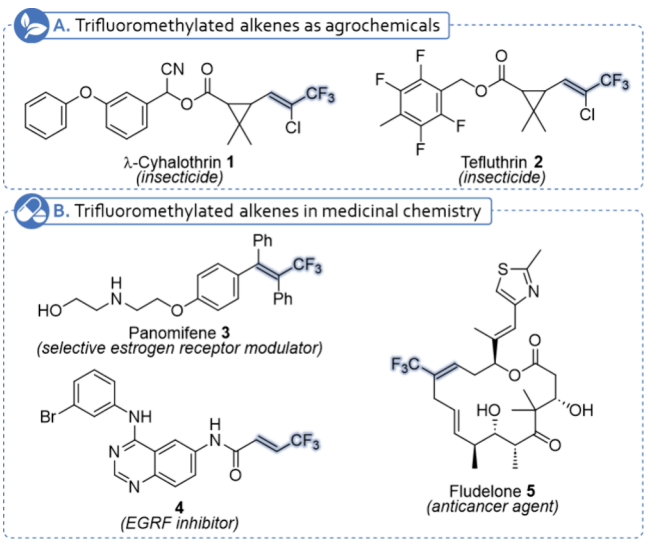


Figure 1. Representative trifluoromethylated alkenes in agrochemicals and drugs.

Despite their apparent simplicity, the synthesis of trifluoromethylated alkenes **6** is, to date, still far from being a trivial task (Figure 2A). Classical approaches relying on Horner−Wadsworth−Emmons,[4] Julia−Kocienski,[5] and other related[6] olefination reactions of aldehydes **7** indeed suffer from limited stereoselectivity in most cases, in addition to being inefficient with ketones. While appealing, alternative strategies based on the direct trifluoromethylation of alkenes **8**[7] or hydro-

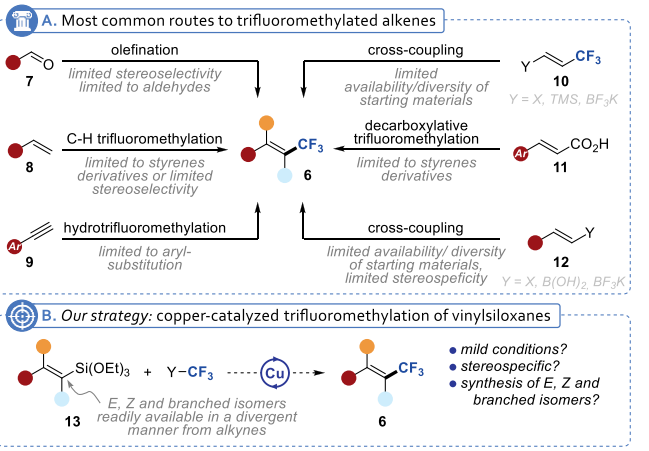


Figure 2. Previous routes to trifluoromethylated alkenes and our strategy.

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trifluoromethylation of terminal alkynes **9**[8] have also important inherent limitations, in terms of stereoselectivity or scope, since they mostly afford monosubstituted trifluoromethylated alkenes, when this single substituent is not limited to being an aromatic group.[9] Another route that has been investigated relies on cross-coupling reactions involving functionalized trifluoromethylpropene partners **10**:[10] if relatively efficient, the diversity and degree of substitution of such starting materials is quite narrow, hence limiting the synthetic usefulness of this approach. The same holds true for decarboxylative cross-coupling reactions with acrylic acids derivatives **11** which are moreover limited to the synthesis of aryl-substituted trifluoromethylated alkenes.[11,12]

The best option actually lies in the cross-coupling of prefunctionalized alkenes **12** and trifluoromethylating agents. A variety of coupling partners **12** including vinyl halides[13] and sulfonates,[14] vinylboronic acids,[15] and potassium trifluoroborates[16] have indeed been reported over the years for the synthesis of trifluoromethylated alkenes but major limitations in terms of efficiency, generality (e.g., restriction to an aryl substituent), possible substitution patterns, and stereochemistry remain when the stereospecificity of the trifluoromethylative cross-coupling is not an issue. Therefore, a more-general, versatile, and robust access to trifluoromethylated alkenes enabling the stereoselective synthesis of all possible isomers remains elusive, despite its high interest, especially for the pharmaceutical and agrochemical industries.

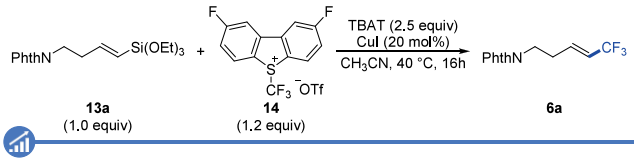
Based on our combined interests in copper catalysis, trifluoromethylations,[17] and vinylsiloxanes,[18] we envisioned that an interesting alternative that might address most of the current limitations met with the synthesis of trifluoromethylated alkenes **6** could rely on a copper-catalyzed trifluoromethylation of vinylsiloxanes **13** (Figure 2B), Hartwig's copper-mediated trifluoromethylation of arylsiloxanes moreover supporting this working hypothesis.[19] Provided that conditions enabling a stereospecific cross-coupling with a suitable trifluoromethylating agent could be developed, such reagents might indeed prove optimal since they can be readily obtained by hydrosilylation of the corresponding terminal alkynes with excellent levels of regioselectivities and stereoselectivities and in a divergent manner.[20]

RESULTS AND DISCUSSION

With this goal in mind, nonactivated *E*-vinylsiloxane **13a** was selected as a model substrate to first test the feasibility of our working hypothesis. Commercially available Umemoto's reagent II **14** was selected as the trifluoromethylating agent due to its ability to act both as an electrophilic and radical trifluoromethyl source and to participate in oxidative additions as well.

Our first trial, based on the use of tetrabutylammonium triphenyldifluorosilicate (TBAT) to activate the starting siloxane and 20 mol % copper(I) iodide as the catalyst without an additional ligand in acetonitrile at 40 °C for 16 h gratifyingly gave the desired trifluoromethylated alkene **6a** in 61% ^{1}H NMR yield and as a single *E* isomer (Table 1, entry 1), therefore validating our working hypothesis. Decreasing or increasing the loading of copper(I) iodide did not positively affect the reaction outcome (Table 1, entries 2 and 3) and a control experiment revealed the crucial role of copper for the reaction to proceed since not a trace of **6a** could be detected in the absence of copper(I) iodide (Table 1, entry 4). A slight increase to 1.5 equiv of Umemoto's reagent II **14** was found

Table 1. Optimization of the Reaction Conditions



entry	variations from reaction conditions	yield[a] (%)
1	none	61
2	10 mol % of CuI	57
3	30 mol % of CuI	53
4	no CuI	0
5	1.5 equiv of **14**	65
6	2.0 equiv of **14**	55
7	1.5 equiv of **14**, at 25 °C	59
8	1.5 equiv of **14**, at 60 °C	58
9	$Cu(CH_3CN)_4PF_6$ instead of CuI 1.5 equiv of **14**	65 (61)

[a] ^{1}H NMR yields using 3,3′-bis(trifluoromethyl)benzophenone as an internal standard. Isolated yield between parentheses.

optimal (Table 1, entries 5 and 6) and the trifluoromethylation was shown to be best performed at 40 °C (Table 1, entries 7 and 8). Finally, replacing copper(I) iodide by Kubas' salt ($Cu(CH_3CN)_4PF_6$) led to a cleaner reaction mixture and a much easier purification of trifluoromethylated alkene **6a** which could be isolated in 61% yield (Table 1, entry 9).

With these optimized conditions in hands, we next moved to the study of the scope and limitations of this copper-catalyzed trifluoromethylation starting from a series *E*-vinylsiloxanes *E*-**13**, compounds that are readily available, on a large scale, using a regioselective and stereoselective hydrosilylation of the corresponding terminal alkynes with Markó's catalyst.[20a−c] As highlighted with results collected in Figure 3, the copper-catalyzed trifluoromethylation of these siloxanes *E*-**13** was found to be quite efficient and general, the corresponding *E* trifluoromethylated alkenes **6a−6j** being obtained in fair to good isolated yields and, most importantly, as single *E* isomers,

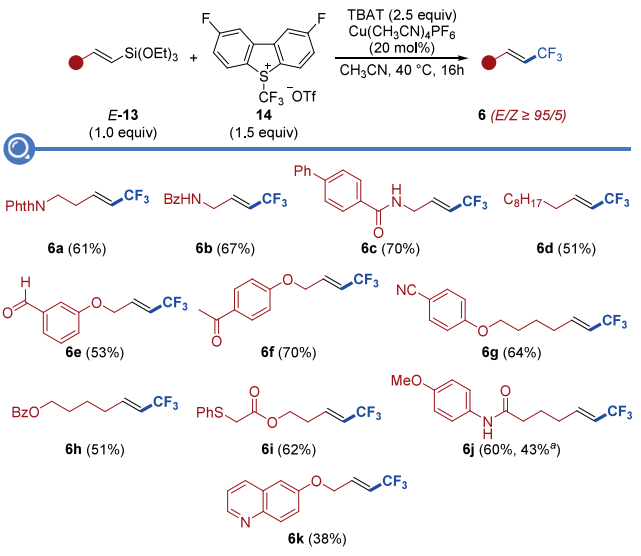


Figure 3. Scope of copper-catalyzed trifluoromethylation of *E*-vinylsiloxanes. The superscripted "*a*" inside the figure indicates that the reaction was performed on a gram scale.

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the trifluoromethylation being fully stereospecific. A variety of functional groups are tolerated, such as protected amines (**6a**), amides (**6b**,**6c**,**6j**), ethers (**6e**−**6g**,**6j**), esters (**6h**,**6i**), thioethers (**6i**), nitriles (**6g**), ketones (**6f**), and even an aldehyde (**6e**). Importantly, a substrate containing a strongly coordinating quinoline group can be tolerated (**6k**), even if its trifluoromethylation proceeded with reduced efficiency. As notes, the lower isolated yields obtained in some cases, such as for **6d** for instance, can be attributed to the high volatility and low saturation vapor pressures, and the trifluoromethylation can be readily performed on a gram scale, as highlighted with the synthesis of **6j** starting from a gram of the corresponding siloxane.

We then logically turned our attention to the more challenging synthesis of *Z* trifluoromethylated alkenes, compounds that can hardly be prepared with synthetically useful levels of stereoselectivity except using a *Z*-selective cross-metathesis with an excess of *Z*-1,1,1,4,4,4-hexafluoro-2-butene.[21,22] An alternative option based on cross-coupling with a readily available trifluoromethylating agent would be much more appealing but was not met with success so far due to a lack of stereospecificity and/or isomerization under the reaction conditions. Based on these considerations and motivated by the success met with our copper-catalyzed trifluoromethylation of *E*-vinylsiloxanes, we therefore next focused our efforts on its extension to their *Z* isomers *Z*-**13**, readily obtained by a *Z*-selective hydrosilylation using a remarkably efficient cyclometalated rhodium(III) triazolylidene complex developed by Jiménez and Pérez-Torrente.[20d] To our delight, and as shown in Figure 4, our copper-catalyzed

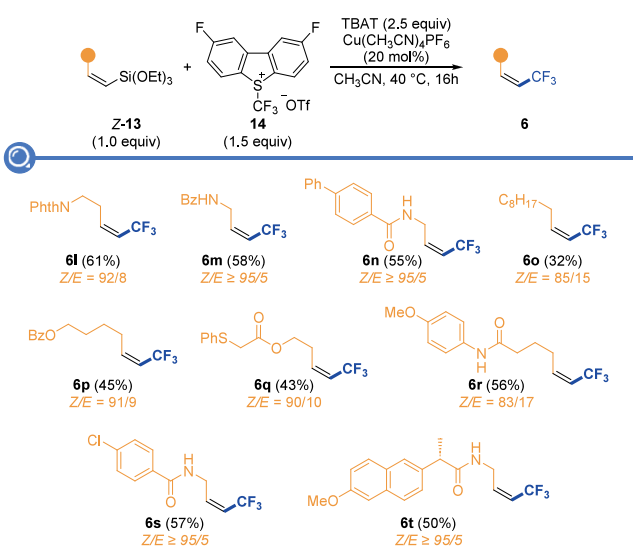

Figure 4. Scope of copper-catalyzed trifluoromethylation of *Z*-vinylsiloxanes.

trifluoromethylation could be readily extended to the synthesis of *Z* trifluoromethylated alkenes **6l**−**6t**, which could be obtained in fair to moderate yields and with excellent or synthetically useful levels of stereoselectivity. Indeed, and for some unclear reasons, while a fully stereospecific cross-coupling occurred with some substrates, an erosion of the *Z*/*E* ratio was observed with others which gave the corresponding *Z* trifluoromethylated alkenes with lower, but still acceptable *Z*/*E* ratios ranging from 83/17 to 92/8. As in the previous case, a range of functional groups were tolerated, and it is worth mentioning that an aryl chloride (**6s**) was left untouched, leaving opportunities for further derivatization by cross-coupling, and that Naproxen derivative **6t** could be obtained as a single *Z* isomer and in 50% yield.

A final extension to the trifluoromethylation of branched vinylsiloxanes *α*-**13**, compounds that can also be prepared from the corresponding terminal alkynes via a Markonikov hydrosilylation with a cationic ruthenium catalyst developed by the Trost group, was then briefly envisioned.[20e,f] As shown in Figure 5, the copper-catalyzed trifluoromethylation of these

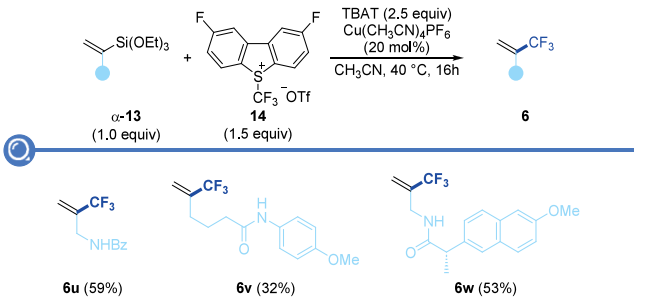

Figure 5. Scope of copper-catalyzed trifluoromethylation of branched (*α*) vinylsiloxanes.

branched vinylsiloxanes *α*-**13** is also operative and provides an efficient entry to branched trifluoromethylated alkenes such as **6u**, **6v** or **6w**, further highlighting the applicability and robustness of our process.

As an important technical note that might be of importance for further studies with aliphatic trifluoromethylated alkenes, their configuration can be unambiguously assigned based on their chemical shift in ^{19}F-NMR. As shown in Figure 6, and in

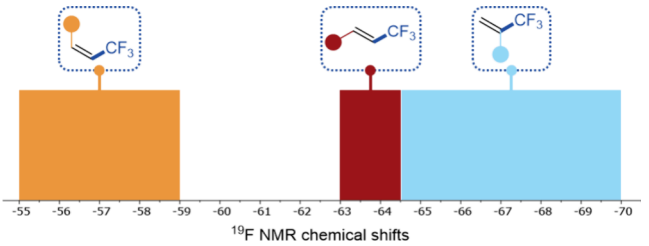

Figure 6. Structural and stereochemical assignment of aliphatic trifluoromethylated alkenes on the basis of ^{19}F-NMR.

agreement with values previously reported in the literature, *Z* trifluoromethylated alkenes are characterized by a signal appearing between −55 and −59 ppm, while signals in the ranges of −63 to −64.5 ppm and −64.5 to −70 ppm are characteristic of their *E* and branched (*α*) isomers, respectively.

Regarding the mechanism associated with this copper-catalyzed cross-coupling between vinylsiloxanes **13** and Umemoto's reagent II **14**, three possibilities can reasonably be envisioned. The first one would imply a catalytic cycle relying on a transmetalation with **13**—subsequent to its activation with TBAT—[23] and an oxidative addition with **14** involving copper(I) and copper(III) intermediates (not shown). Despite the evidence for the generation of trifluoromethylcopper(III) complexes and their relevance in trifluoromethylation reactions,[24] the intermediacy of such a species in our case is rather unlikely in the absence of strongly donating ligands and under catalytic conditions. Alternatively,

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a trifluoromethyl radical species could be generated upon single electron reduction of **14** with the copper(I) catalyst and its radical addition to **13**, followed by oxidation and elimination of a silyl moiety could account for the overall trifluoromethylation (not shown). This copper(I)/copper(II) catalytic cycle is however in agreement neither with the requirement for the activation of **13** with a source of fluoride for the reaction to occur nor with the regioselectivities and stereoselectivities observed. It might however account for the minor loss of stereoselectivity observed in some cases and might thus be a competing mechanism. The last and most probable option, shown in Figure 7, involves a transmetalation

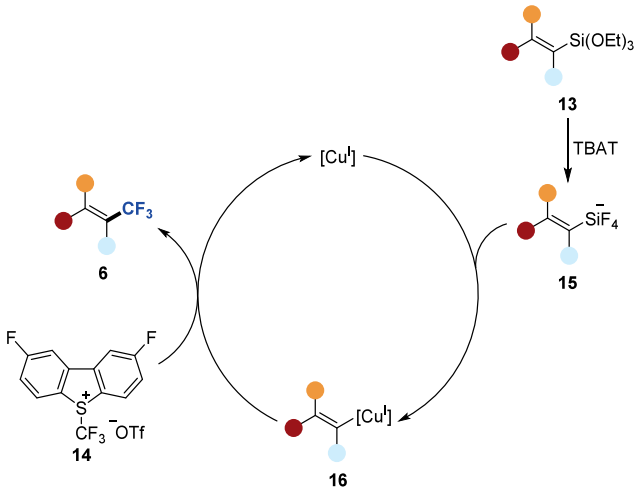

Figure 7. Proposed catalytic cycle for the copper-catalyzed trifluoromethylation of vinylsiloxanes with Umemoto's Reagent II.

of the copper(I) catalyst with in-situ-generated vinylfluorosilane species **15**, yielding an intermediate nucleophilic vinylcopper(I) intermediate **16**, which would next be trapped by Umemoto's reagent II **14**, acting as an electrophilic trifluoromethylation agent, generating the desired trifluoromethylated alkene **6** and closing the catalytic cycle. As a note, the use of one equivalent of TEMPO under our standard reaction conditions had a dramatic impact on the trifluoromethylation of **13a**, which was formed with 7% ^{1}H NMR yield instead of 65%. While this could be in favor of a radical mechanism, this might however be better attributed to the well-established oxidation of copper(I) complexes by TEMPO[25] which would, overall, shut down the whole catalytic cycle and, hence, inhibit the trifluoromethylation.

CONCLUSIONS

In conclusion, we have developed a novel, robust, and efficient entry to trifluoromethylated alkenes based on a copper-catalyzed electrophilic trifluoromethylation of vinylsiloxanes with Umemoto's reagent II. Compared to previously reported synthesis of trifluoromethylated alkenes, our procedure enables the synthesis of all *E*, *Z*, and branched isomers with, in most cases, high levels of stereospecificity. The main advantages of this procedure, which should facilitate and expedite the synthesis of trifluoromethylated alkenes, include its broad scope and functional group tolerance, the use of a simple copper(I) catalyst, Kubas' salt, under ligandless conditions, as well as the availability of all isomers of the starting vinylsiloxanes that can be readily prepared by divergent hydrosilylations of the corresponding terminal alkynes. These studies moreover further highlight the strong potential of vinylsiloxanes as coupling partners in copper-catalyzed cross-coupling reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.5c07064.

Experimental procedures, characterization, copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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