Recent progress in the trifluoromethylation of alkenes with Togni's reagents

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Abstract
Recent progress in the trifluoromethylation of alkenes with Togni's reagents is reviewed. Seven approaches to the trifluoromethylation of alkenes are summarized: (i) oxytrifluoromethylation, (ii) aminotrifluoromethylation, (iii) allylic trifluoromethylation, (iv) cyanotrifluoromethylation, (v) trifluoromethylazidation, (vi) carbotrifluoromethylation, and (vii) trifluoromethylation-rearrangement.

Keywords: Trifluoromethylation, alkenes, Togni's reagents, allylic, rearrangement

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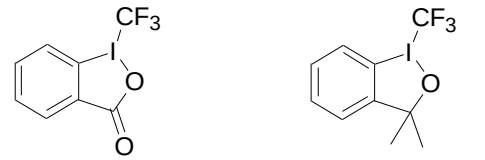
1. Introduction

The trifluoromethyl group is valuable in the fields of pharmaceuticals, agrochemicals, and material sciences.[1] Molecules with a CF_3 group have attracted great interest since the

trifluoromethyl group can dramatically enhance their metabolic and chemical stability and lipophilicity.[2,3] Hence, introduction of the trifluoromethyl group into alkenes has already become one of the hottest topics in pharmaceutical and agrochemical research.[4-9]

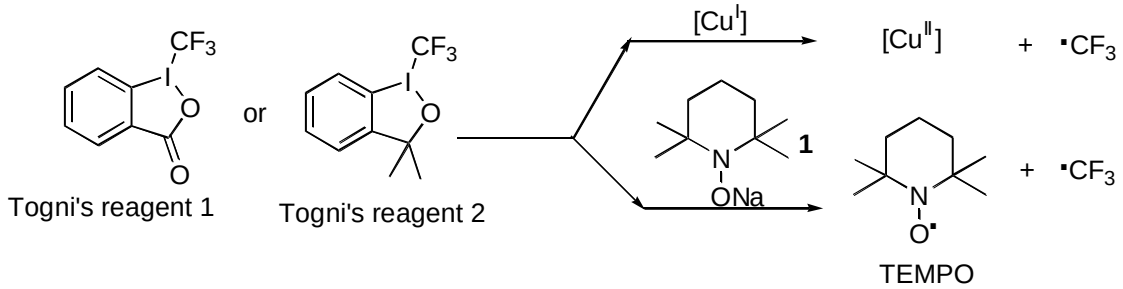
Several years ago, Togni and co-workers[10] reported a conceptually new family of formally electrophilic CF_3 transfer reagents based on a cyclic hypervalent iodine(III) core, the most successful ones being Togni's reagents 1 and 2 (Scheme 1). These reagents are employed in the trifluoromethylation of phosphorus-, carbon- and oxygen-centered nucleophiles such as phosphines,[11] α-nitro- and β-keto-esters,[12,13] phosphorothioates,[14] aromatics,[15] alcohols,[16] sulfonic acids,[17] hydrogen phosphates,[18] aldehydes,[19] phenols,[20] arylboronic acids,[21] and quinones[22].



Scheme 1

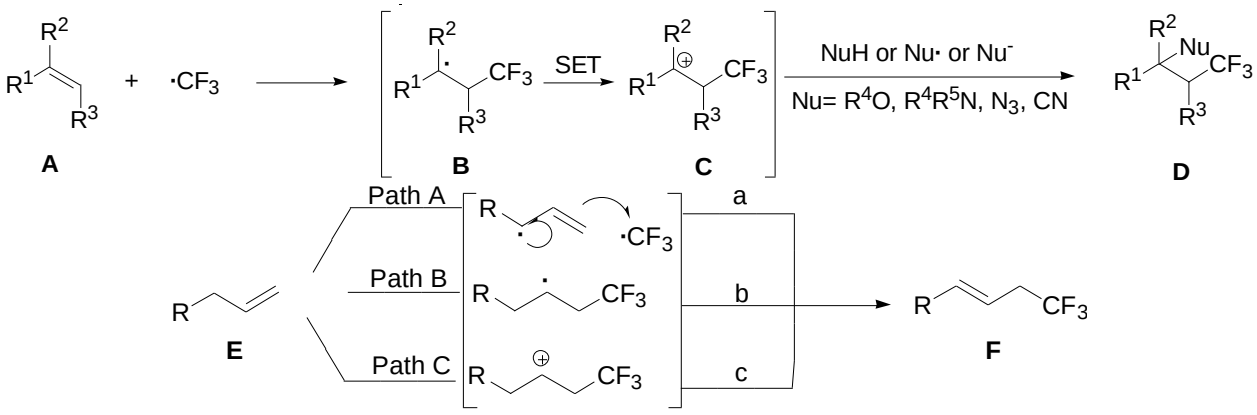
This review provides an overview of trifluoromethylation of alkenes with Togni's reagents over the period from 2011 to the present. Several approaches will be reviewed. These can be divided into (i) oxytrifluoromethylation, (ii) aminotrifluoromethylation, (iii) allylic trifluoromethylation, (iv) cyanotrifluoromethylation, (v) trifluoromethylazidation, (vi) carbotrifluoromethylation, and (vii) trifluoromethylation-rearrangement.

In 2011, the groups of Buchwald[23] and Wang[24] showed that Togni's reagents can be used as a clean source of the CF_3 radical for the trifluoromethylation of alkenes. These trifluoromethylations rely on Cu(I) catalysis, and experimental evidence for the involvement of free CF_3 radicals was provided (Scheme 2). Based on these results, Li and Studer[25] used the readily available sodium aminoalkoxide **1** as a single-electron-transfer (SET) reagent for the reduction of Togni's reagents to generate the CF_3 radical along with the corresponding persistent TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) radical.



Scheme 2

A proposed mechanism for this trifluoromethylation reaction is depicted in Scheme 3. Reaction of Togni's reagents with a copper catalyst generates a CF_3 radical (Scheme 2),[23,24] followed by radical addition and single-electron oxidation to give intermediate **C**.[26] Subsequent trapping of the carbocation **C** with a nucleophile leads to the desired product **D**. It is assumed that trifluoromethylation of olefin substrate **E** might be achieved using a copper-based strategy involving the generation of an allylic radical and a subsequent CF_3 transfer (Scheme 3, Path A).[27-29] Alternatively, if Togni's reagent 1 could be used as an electrophilic CF_3·equivalent, the final product **F** may be generated through an atom transfer radical addition type pathway (Scheme 3, Path B).[30] Finally, an electrophilic trifluoromethylation proceeding *via* a cationic intermediate may also be viable (Scheme 3, Path C).



Scheme 3

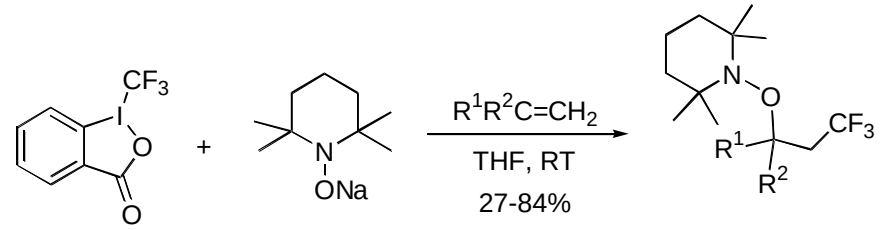
CAUTION! Togni's reagents were reported to be explosive, and should only be handled with the appropriate knowledge and safety measures.[31] Togni's reagent 1, which showed a decomposition energy of 502 J/g in the DSC-measurement, is dangerously explosive and may only be transported by approval of the national competent authority. Another critical property of Togni's reagent 1 is the fast combustion when ignited. The substance vaporizes quickly without flame when ignited with a match corresponding to a combustion factor BZ6 which is the same classification as that of black powder.[31] Togni's reagent 2 produces a melting signal with an onset at 77 °C followed by a decomposition with a strong exotherm of 790 J/g with an onset at 135 °C and a maximum heat flow of 6 W/g in an aluminum pan with pierced lid.[31]

2. Trifluoromethylation of Alkenes with Togni's Reagents

2.1. Oxytrifluoromethylation

Recently, an easy-to-conduct, transition-metal-free trifluoromethylaminoxylation of alkenes using the commercially available Togni's reagent 1 was developed by Li and Studer (Scheme 4).[25] Styrene and styrene derivatives were readily oxytrifluoromethylated and the corresponding

products **2** were isolated in good yields. A side product in these radical trifluoromethylations was $TEMPOCF_3$ resulting from the direct trapping of the CF_3 radical with TEMPO.



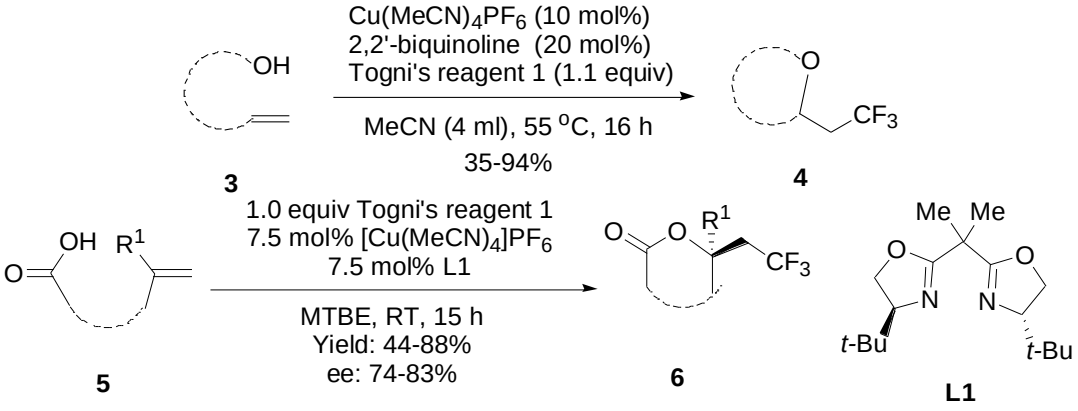
Togni's reagent 1 **1** **2**

R^1 = Ph, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, β-naphthyl, C_6F_5, $Ph(CH_2)_2$, $Ph(CH_2)_3$, $Br(CH_2)_3$, $HO(CH_2)_4$, CO_2CH_3, BuO, CH_3CH_2

R^2 = H, CH_3, CH_3CH_2

Scheme 4

In 2012 and 2013, Buchwald and co-workers[26,32] reported a simple and mild method for the oxytrifluoromethylation of unactivated alkenes bearing a hydroxy or carboxylic group in the presence of Togni's reagent 1 and a catalytic amount of $[(MeCN)_4Cu]PF_6$ (Scheme 5). A series of unsaturated aliphatic and aromatic carboxylic acids or alcohols were found to undergo the desired transformation to give the corresponding trifluoromethylated lactones or cyclic ethers in good yields and useful enantiomeric excesses.



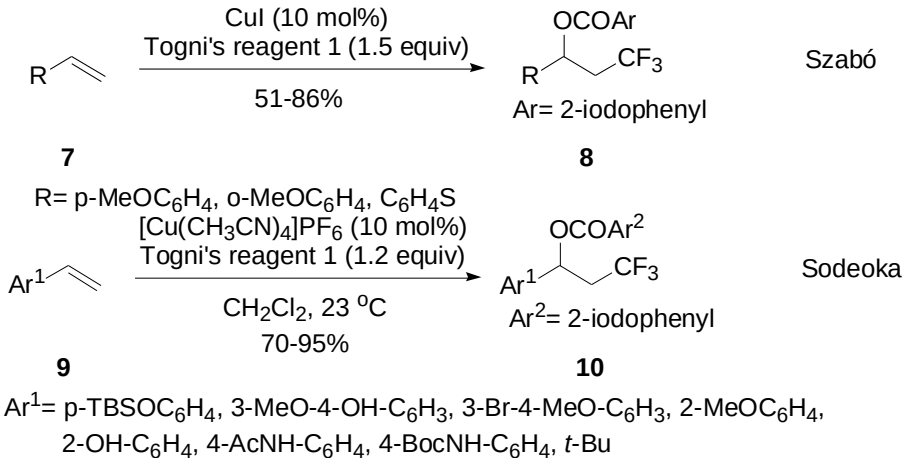
5 **6** **L1**

R^1= Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, $CH_3COC_6H_4$, 3-Thiophene

Scheme 5

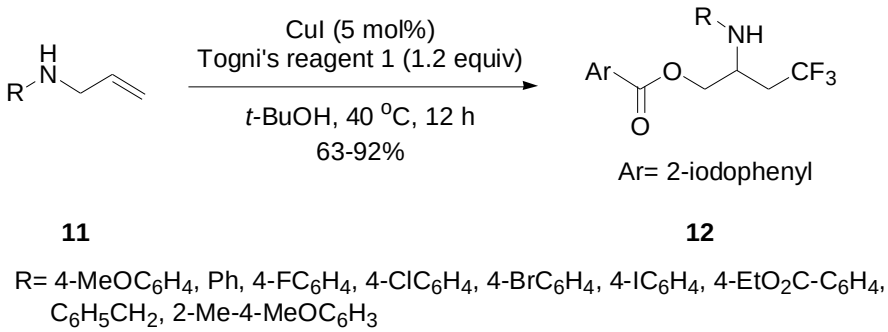
A mild and convenient method for the efficient oxytrifluoromethylation of unactivated alkenes based on a copper-catalyzed oxidative difunctionalization strategy was developed by the research groups of Szabó and Sodeoka in 2012 (Scheme 6).[33,34] Szabó *et al.* showed that alkenes undergo smooth addition reactions with Togni's reagent 1 using CuI as catalyst.[32] The reaction proceeds with higher yield, high regioselectivity and more cleanly for electron-rich styrenes.

Vinyl sulfide substrates reacted similarly to styrenes to give the expected trifluoromethyl benzoate products. Sodeoka and co-workers[34] showed that oxytrifluoromethylation reaction of styrene derivatives was achieved with high efficiency in the presence of $[(MeCN)_4Cu]PF_6$ catalyst and Togni's reagent 1. Oxytrifluoromethylation of styrene derivatives bearing an oxygen atom or no heteroatom on a phenyl ring and N-protected aniline derivatives proceeded smoothly to give the corresponding products in high yields.



Scheme 6

In 2013, Sodeoka's group[35] reported copper-catalyzed N-migratory oxytrifluoromethylation reactions of allylamine derivatives in the presence of Togni's reagent 1 in *t*-BuOH (Scheme 7). N-Migratory oxytrifluoromethylation products, which are potentially useful intermediates for the synthesis of bioactive compounds, were obtained in 63-92 % yield.

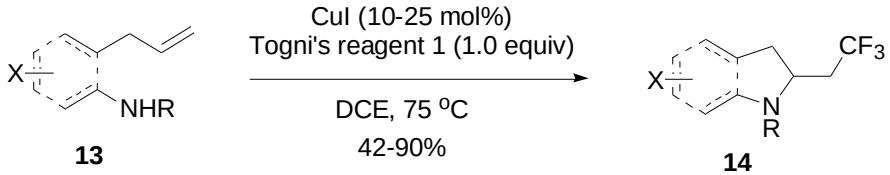


Scheme 7

2.2. Aminotrifluoromethylation

In 2013, Liu and co-workers[36] reported intramolecular aminotrifluoromethylation of unactivated alkenes (from free amines to various protected amines) in the presence of Togni's reagent 1 with

CuI catalyst (Scheme 8). This method provides access to the synthesis of trifluoromethylated pyrrolidines or indolines in good to excellent yields.

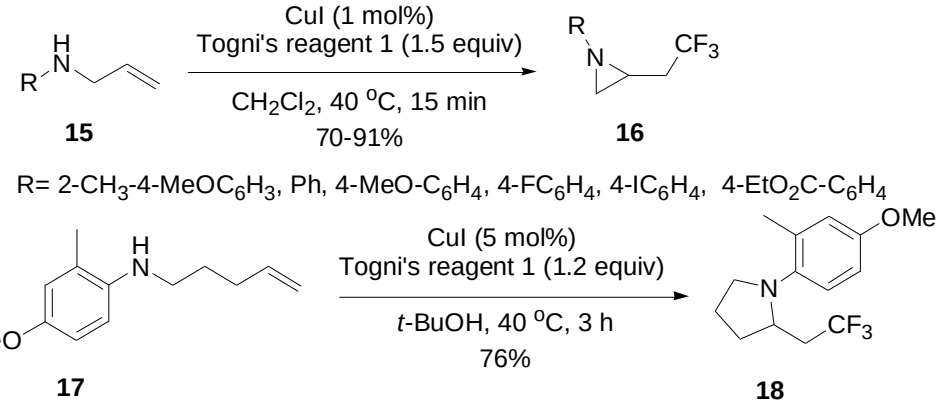


13 **14**

X= H, Cl, Me, MeO, F, Br, CN,
R= Ts, Bs, Ms, Ns, 4-$MeOC_6H_4SO_2$, H

Scheme 8

Copper-catalyzed aminotrifluoromethylation of alkenyl amine derivatives for the generation of various pyrrolidine or aziridine derivatives was developed by Sodeoka and co-workers in 2013 (Scheme 9).[35] In the aminotrifluoromethylation, reactions of substrates bearing an electron-donating group on the aniline ring were faster than those of substrates with an electron-withdrawing group. Without a substituent on the aromatic ring the yield was somewhat lower (70 %), although the reaction still proceeded smoothly. Encouraged by these results, the aminotrifluoromethylation of the 4-methoxy-*N*-pentenylaniline derivative **17** was also attempted, and the pyrrolidine derivative **18** was obtained in 76 % yield.



15 **16**

R= 2-CH_3-4-$MeOC_6H_3$, Ph, 4-MeO-C_6H_4, 4-FC_6H_4, 4-IC_6H_4, 4-EtO_2C-C_6H_4

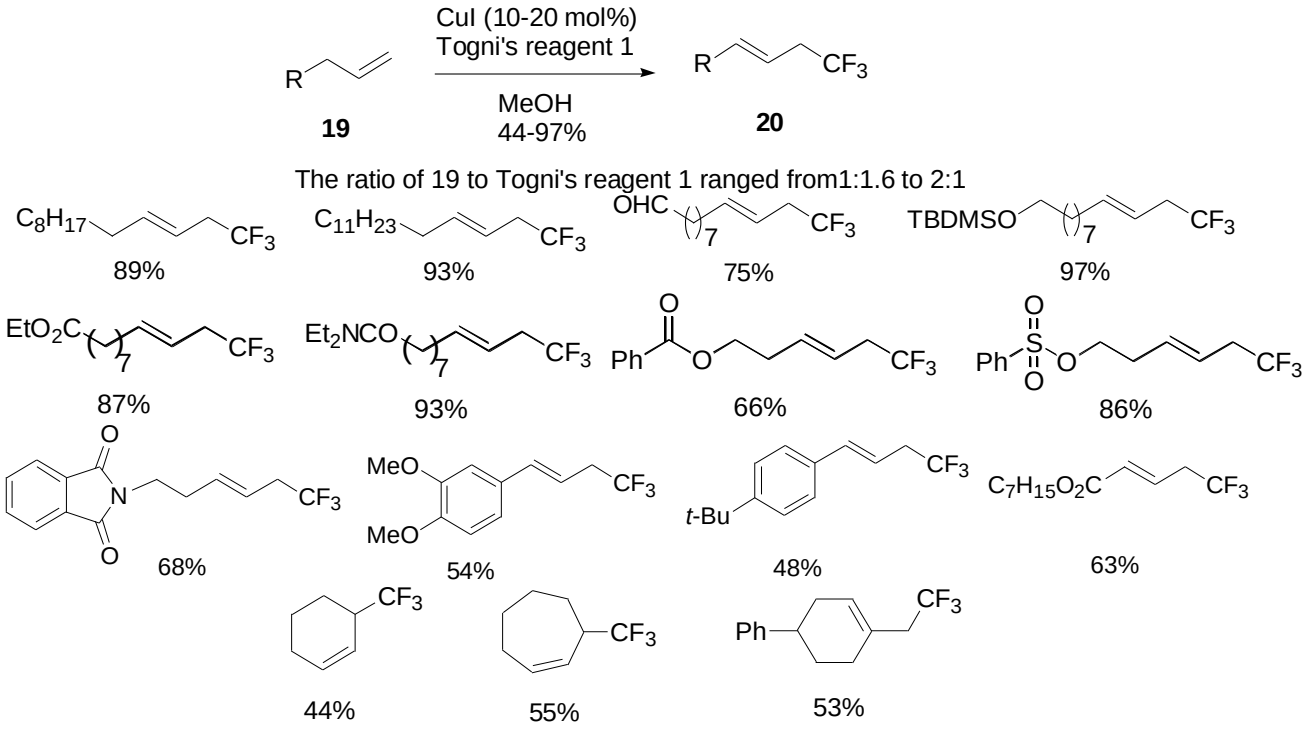
17 **18**

Scheme 9

2.3. Allylic trifluoromethylation

In 2011 a CuCl-catalyzed allylic trifluoromethylation reaction, which provides a general and straightforward way to synthesize allylic trifluoromethylated compounds under mild conditions, was developed by Wang and co-workers (Scheme 10).[24] The simple alkenes, aliphatic aldehyde group, and *tert*-butyldimethylsilyl (TBDMS) ether protecting group were tolerated in the reaction, with the desired product being obtained in excellent yield. Other linear allylic trifluoromethylated compounds were obtained in 48-93% yield, when terminal olefins bearing ester, amide, benzoate, benzenesulfonate, phthalimide functional groups and an aromatic moiety were employed as substrates. Cyclohexene, cycloheptene and a substrate featuring an exocyclic

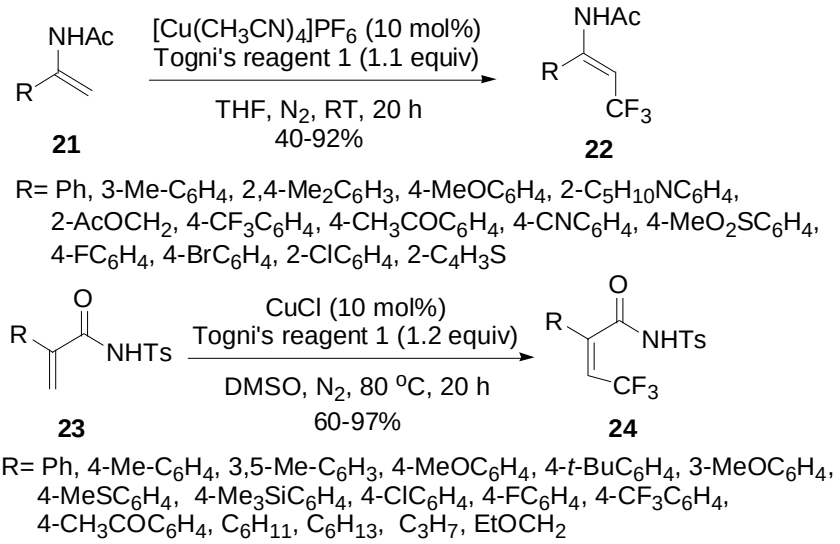
double bond at the cyclohexyl ring were also tested with Togni's reagent 1, affording the corresponding trifluoromethylated cycloalkene and CF_3-containing cyclohexane derivative in acceptable yields (44-55%).



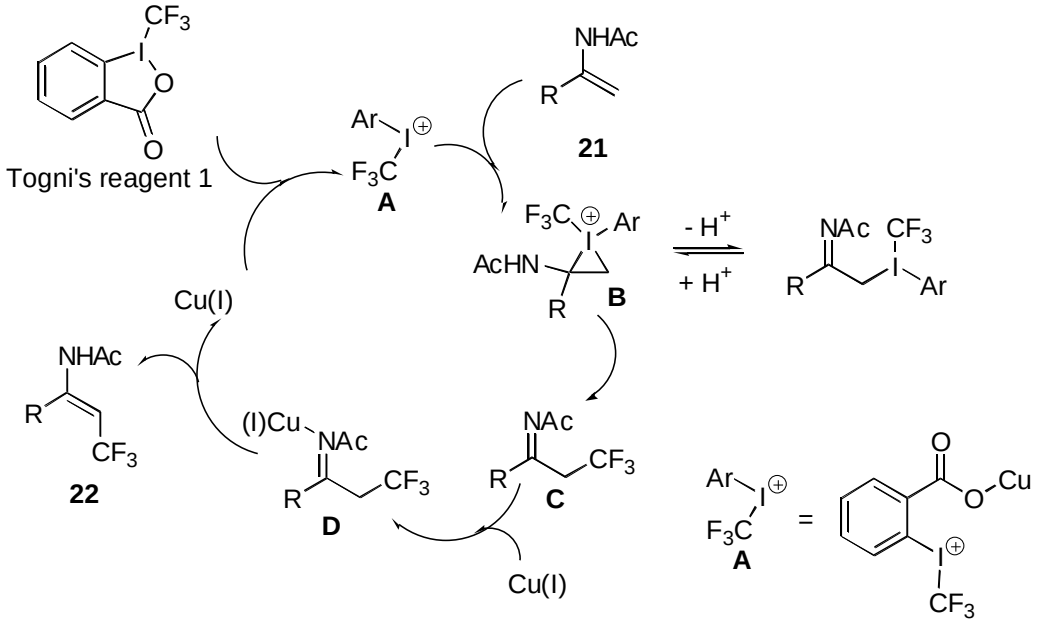
Scheme 10

In addition, Loh's group[37,38] developed olefinic trifluoromethylation of enamides and C-H trifluoromethylation of electron-deficient alkenes by taking advantage of neighboring directing groups with Togni**'**s reagent 1 in the presence of $[(MeCN)_4Cu]PF_6$ or CuCl as catalyst (Scheme 11). The reactions tolerated a wide variety of substrates with both electron-donating and electron-withdrawing substituents to produce the desired trifluoromethylation products in moderate to excellent yields.

On the basis of experimental results and related precedent, the reaction mechanism proposed is as depicted in Scheme 12. The reactive intermediate **A**, arising from the reaction between Togni's reagent 1 and Cu(I), reacts with enamide to produce the iodo(III) cyclopropane **B**,[39,40] which is expected to be in equilibrium with the corresponding α-iodo(III) imine. Subsequent reductive elimination from **B** generates the α-trifluoromethyl imine intermediate **C**, which can react *via* two divergent routes depending on the solvent and catalyst used. Using the CuCl–methanol system, the imine intermediate is sequestered by the methanol solvent to form the N-acyl-β-trifluoromethyl enamines **22**, while with the $Cu(MeCN)_4PF_6$–THF system, intermediate **C** goes on to form complex **D**, with the nitrogen bound to the Lewis acidic Cu(I) catalyst, which in turn induces α-proton elimination or transfer to deliver the final olefinic trifluoromethylation product.



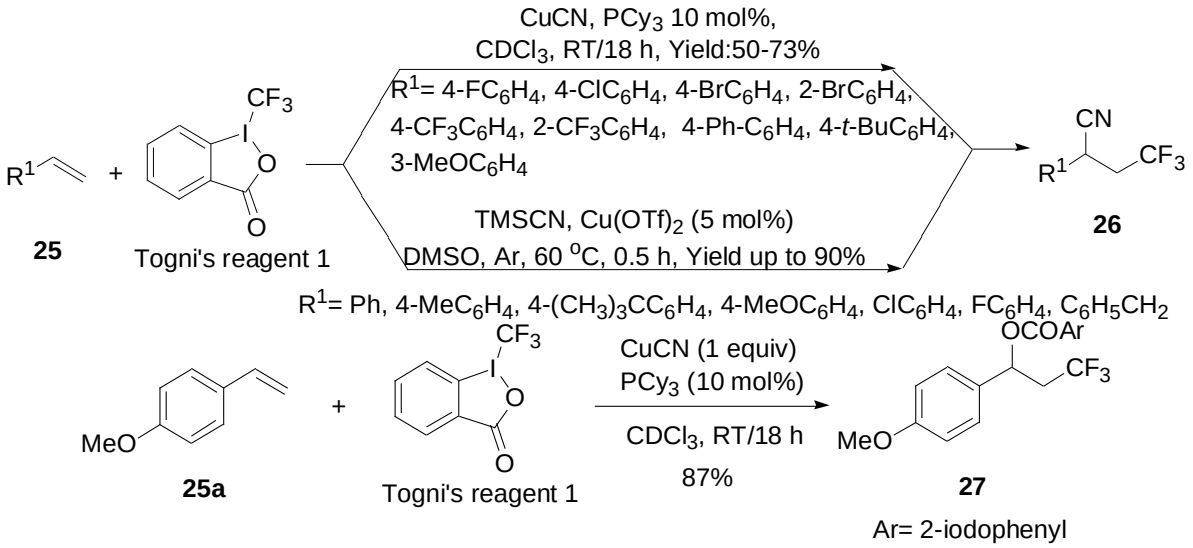
Scheme 11



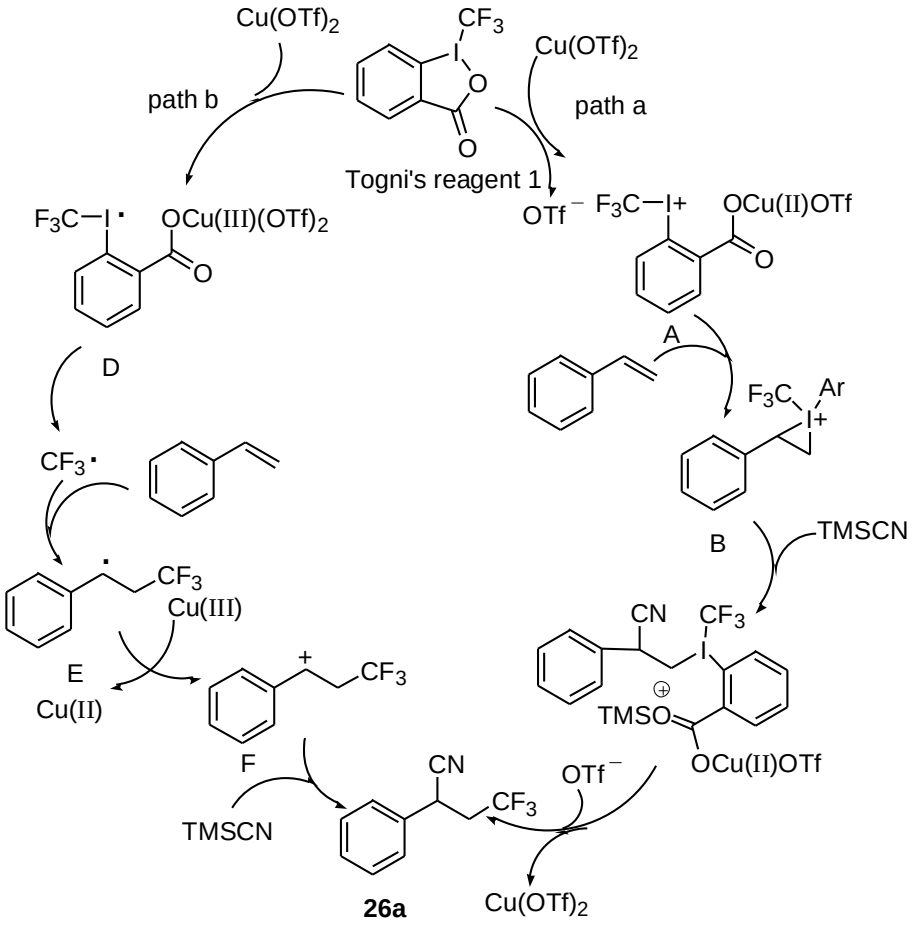
Scheme 12

2.4. Cyanotrifluoromethylation

Szabó and co-workers[41] reported that under appropriate reaction conditions CuCN in combination with Togni's reagent 1 is suitable for selective introduction of the CF_3 and CN groups to styrenes, thus creating two C−C bonds in a single addition reaction (Scheme 13). Styrenes with an electron withdrawing group proved to be particularly useful substrates for cyanotrifluoromethylation. However, the reaction of styrenes **25a** under the standard reaction conditions afforded oxytrifluoromethylated product **27** in 87% yield.



Scheme 13

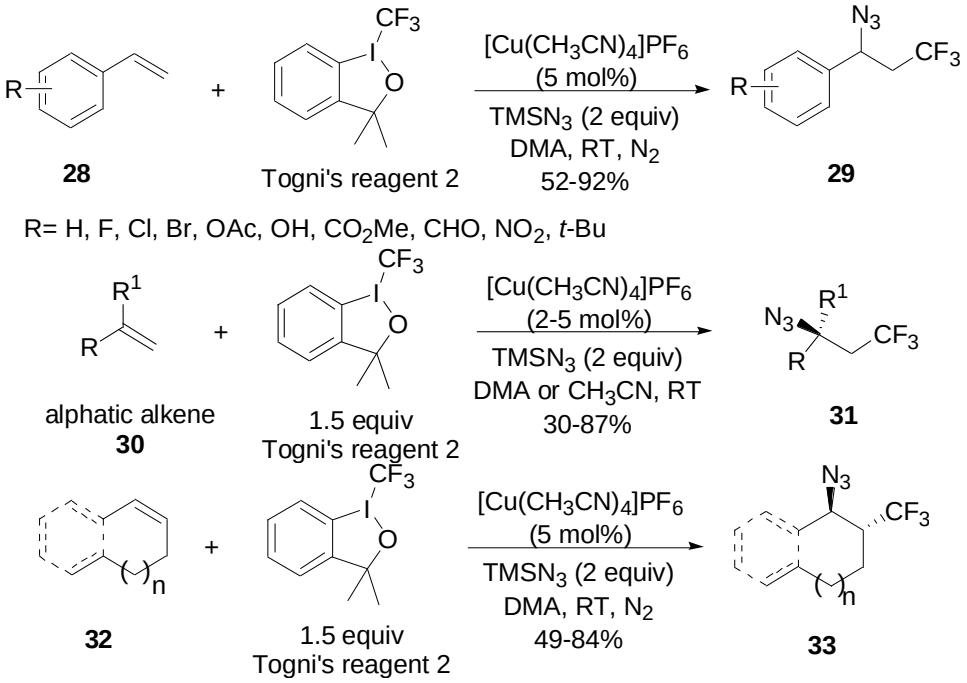


Scheme 14

On the other hand, Liang *et al.* reported the $Cu(OTf)_2$-catalyzed intermolecular cyanotrifluoromethylation of alkenes based on the difunctionalization strategy.[42] In most cases, alkenes **25** proceeded smoothly to transform into the cyanotrifluoromethylation products **26** in moderate to good yields, and the substrates bearing electron-donating groups gave higher yields than those containing electron-withdrawing groups on the aromatic rings. A possible mechanism for cyanotrifluoromethylation of alkenes with Togni's reagent 1 is shown in Scheme 14.[42]

2.5. Trifluoromethylazidation

Liu and co-workers reported that a novel copper-catalyzed intermolecular trifluoromethylazidation of alkenes delivered vicinal CF_3-substituted alkyl azides in one step, when the less reactive Togni's reagent 2 is employed as a CF_3 source (Scheme 15).[43] Substrates **28**, having various substituents (R) on the aromatic ring, including electron-donating and electron-withdrawing groups, were tolerated under the reaction conditions to give the desired products **29** in good yields. A range of 1,1-dialkyl-substituted alkenes **30** or cyclic substrates from five- to eight-membered rings **32** were suitable for this trifluoromethylazidation reaction and gave the tertiary alkyl azides **31** or the trifluoromethylated cyclic organoazides **33** in good yields.

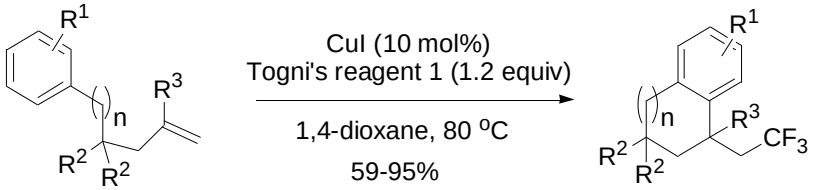


Scheme 15

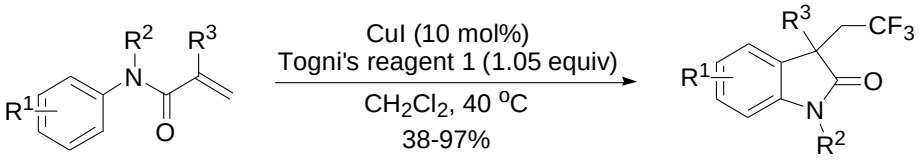
2.6. Carbotrifluoromethylation

In 2013, Sodeoka and co-workers reported the copper-catalyzed carbotrifluoromethylation of simple C=C bonds using the Cu(I)/Togni's reagent 1 system (Scheme 16).[44] These reactions provide trifluoromethylated carbocycles and heterocycles in good yields. In addition, carbo-

trifluoromethylation of acryloanilide derivatives with the combination of CuI and Togni's reagent 1 affording oxindole derivatives bearing a 3-trifluoroethyl group in 38-95% yields under mild conditions has also been developed by the same group (Scheme 17).[45]

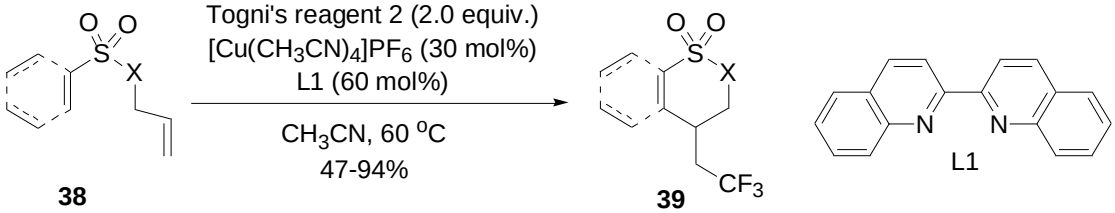


Scheme 16



Scheme 17

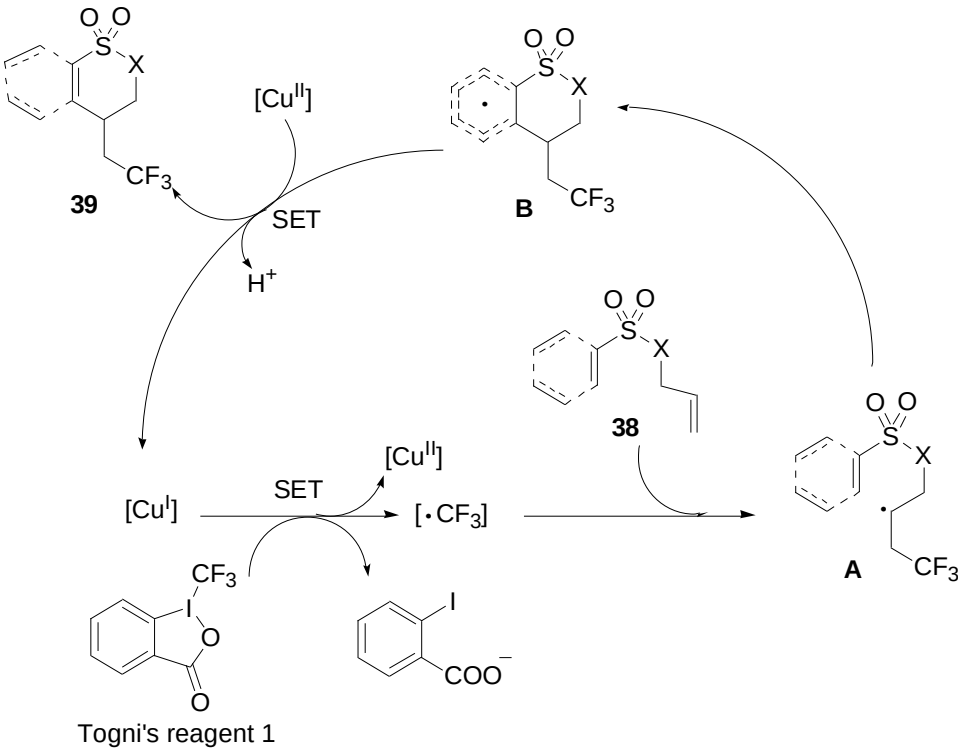
In 2013, Shi's group developed a practical and efficient method of trifluoromethylation to construct medicinally significant 1,2-benzothiazinane dioxide derivatives in fair to excellent yields under mild conditions employing Togni's reagent 2 with $[(MeCN)_4Cu]PF_6$ catalyst (Scheme 18).[46]



Ar = *p*-MeC_6H_4, Ph, *p*-$MeOC_6H_4$, *p*-BrC_6H_4, *p*-$O_2NC_6H_4$, o-MeC_6H_4, *m*-MeC_6H_4, 2-thienyl, 3-pyridyl
X = N-*i*Pr, N-Et, N-Me, N-H, N-$(CH_2)_2OH$, N-$(CH_2)_2Br$, N-$(CH_2)_2NHTs$, N-SO_2Ph, CH_2

Scheme 18

A possible mechanism for carbotrifluoromethylation of alkenes with Togni**'**s reagent **1** is shown in Scheme 19. First, a single-electron transfer (SET) takes place from Cu(I) catalyst to togni reagent **1** to generate a Cu(II) complex and a trifluoromethyl radical species, which reacts with the alkene of substrate **38** to form a radical intermediate **A**, followed by a cyclization with the sulfonylbenzene ring to give another radical intermediate **B**. After aromatization, the trifluoromethylated cyclization product **39** is formed.



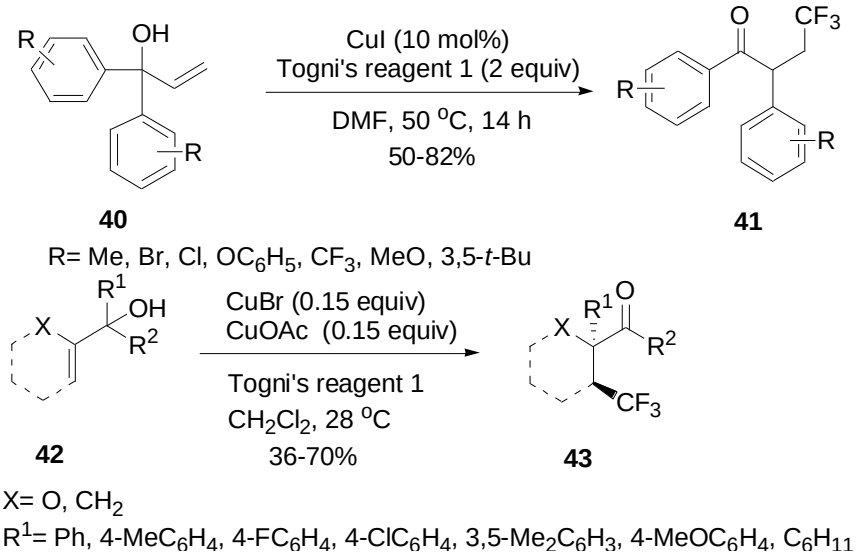
Scheme 19

2.7. Trifluoromethylation-rearrangement

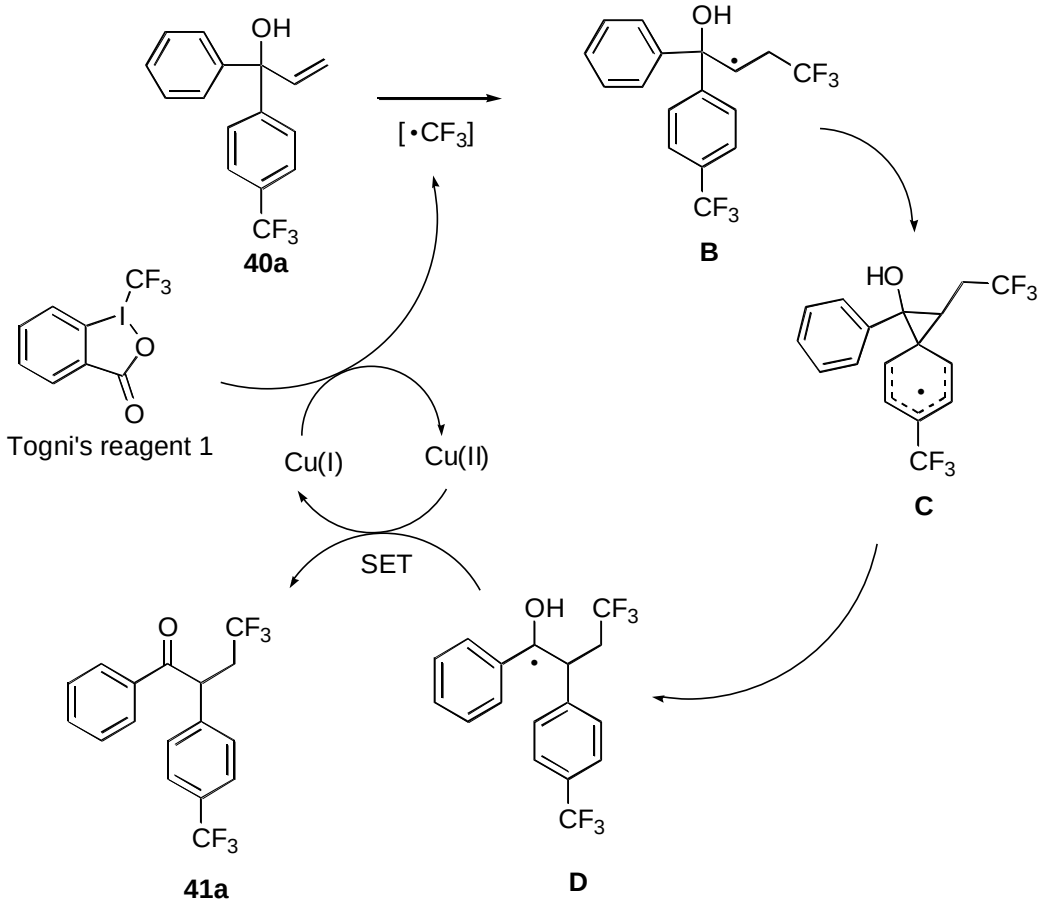
In 2013, Wu's group[47] reported a novel trifluoromethylation-rearrangement reaction of allylic alcohols employing Togni's reagent 1 with CuI as catalyst. Similar reactions have later been reported by Tu and co-workers.[48] These methods enable the construction of both C_{sp3}-CF_3 bonds and a quaternary carbon center. A wide variety of β-trifluoromethyl α-aryl ketones with different substituents can be easily prepared under mild conditions (Scheme 20).

To gain further understanding about the migration step, Wu's group conducted computational studies using **40a** as a model compound (Scheme 21). The calculation indicated that the *para*-trifluoromethylphenyl group migrates preferentially over the phenyl group when radical intermediate B is involved. Moreover, the preferential migratory aptitudes of non-*ortho*-substituted aryl groups over *ortho*-substituted ones were also reproduced, with the migration occurring *via* radical intermediate **B**. Therefore, a simplified catalytic cycle for the rearrangement is proposed (Scheme 21). A CF_3 radical, presumably arising from the Togni's

reagent **1** and Cu^{I}, reacts with alkene **40a** to generate radical B. Subsequent migration of the



Scheme 20



Scheme 21

electron-deficient aryl group *via* spiro[2,5]octadienyl radical **C** produces intermediate **D**. Single-electron transfer (SET) between Cu^{II} and D delivers the desired product 41a with concomitant loss of a proton, and regenerates the active copper(I) species. When *ortho* substituent(s) are present on one of two aryl groups in 40a, the migration of the non-*ortho*-substituted aryl group might be more favorable, generating a sterically less congested radical **C**.

3. Conclusions

In summary, due to the great importance of the CF_3-containing compounds in pharmaceutical and agrochemical industries, much attention has been focused on the trifluoromethylation of alkenes with Togni's reagents for the construction of C–CF_3 bond in recent years. In this review, we classified trifluoromethylation reactions under seven headings: oxytrifluoromethylation, aminotrifluoromethylation, allylic trifluoromethylation, cyanotrifluoromethylation, trifluoro-methylazidation, carbotrifluoromethylation and trifluoromethylation-rearrangement. Most of the newly developed methods facilitate convenient trifluoromethylation of alkenes under mild conditions with high regioselectivity and in good to excellent yield. With the rapid development of new chemistry in recent years, new and effective approaches to the trifluoromethylation of alkenes with Togni's reagents can be expected.

4. Acknowledgement

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