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Synthesis and further use of SF_5-alkynes as platforms for the design of more complex SF_5-containing products.

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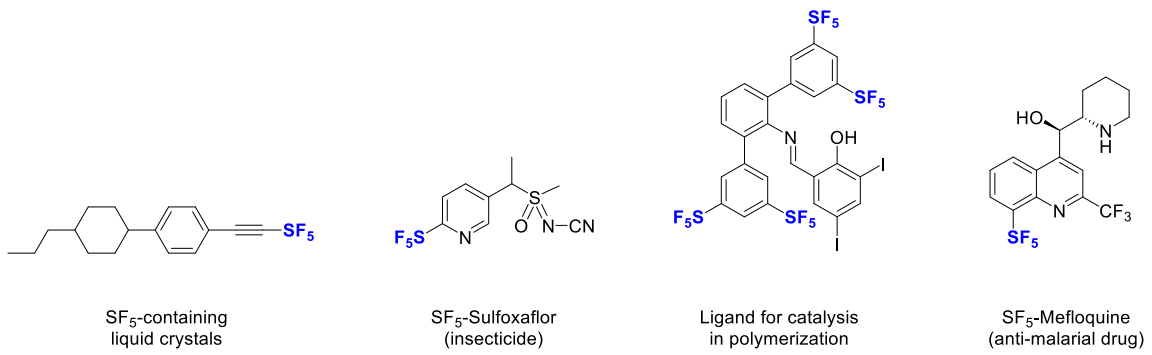
1 Introduction

Pentafluorosulfanyl group is known as an emerging fluorinated group, it has been reported for the first time in 1960, and then remained an exotic fluorinated group for years, but nowadays this group is rising in interest and many groups and companies start to investigate this fluorinated motif in more depth. Indeed, SF_5 is known as a "super CF_3", gathering and magnifying the benefits of CF_3 that are a large volume, a high electronegativity and a high lipophilicity, which are highly valuable properties for drugs development. Several general reviews on the synthesis and use of SF_5 compounds have been published recently.[1–6] In parallel, a few applications of SF_5-containing molecules has begun to appear in materials science,[7,8] drug design[9] or crop protection[10] (Scheme 1), but innovation remains highly dependent on the synthetic methods available to introduce SF_5 in organic molecules. In this report, we turned our attention more specifically to SF_5-alkynes, from their synthesis to applications.



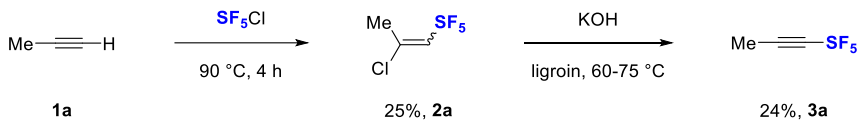
Scheme 1 : Selected examples of applications of SF_5 containing molecules

2 Synthesis of SF_5-alkynes

2.1 By means of SF_5Cl

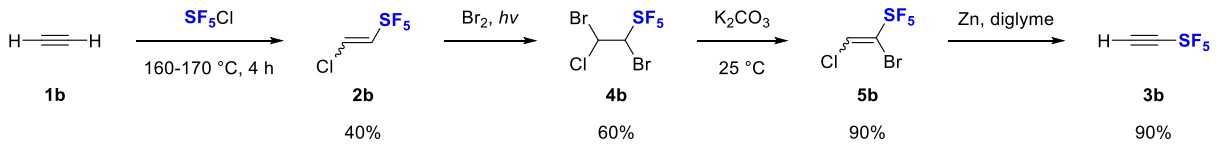
Pentafluorosulfanyl chloride (SF_5Cl) is a commercially available gas and the most frequently used reagent to functionalize aliphatic compounds with an SF_5 group.[11] Moreover, a convenient synthesis of this gas has been reported recently starting from molecular sulfur, potassium fluoride and trichloroisocyanuric acid as oxidant; SF_5Cl can be stored and used in hexanes solution.[12,13] SF_5Cl adds to C=C or C≡C bonds under thermal, photochemical, or chemical activation; this latter activation being essentially conducted with the aid of Et_3B.

Thermal reaction of an acetylene with SF_5Cl led regioselectively to the corresponding SF_5-chloro-olefin in relatively low yield. The subsequent dehydrohalogenation reaction is of great interest because it yields a polarized SF_5-alkyne. In 1961, Case and co-workers reported the first example of SF_5-alkyne by HCl elimination in basic conditions, which produced the SF_5-propyne **3a** in a low 6% overall yield (Scheme 2).[14] Unfortunately this sequence was not applicable to other substrates.



Scheme 2 : Addition reaction of SF_5Cl onto propyne and subsequent dehydrochloration

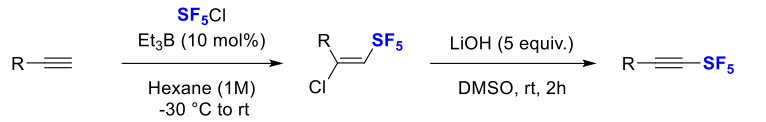
In 1964, Hoover and Coffman described a four-step strategy through initial thermal addition of SF_5Cl onto acetylene (Scheme 3).[15] Next, the photochemical addition of bromine on the chloro SF_5-olefin **2b**, followed by base-mediated dehydrobromination afforded olefin **5b** as a mixture of isomers. A final step of reduction with zinc led to SF_5-acetylene **3b** in high yield albeit with a low 11% overall yield.



Scheme 3: Synthesis of SF_5-acetylene.

At that time, the harsh thermal conditions appeared as a strong limitation to diversify easily the scope of SF_5-alkynes in decent yields. A revolution appeared in 2002, when Dolbier reported an easy and practical radical activation procedure based on Et_3B-catalyzed addition of SF_5Cl to terminal alkynes in hexane (Scheme 4).[16–19] The reaction proceeded smoothly at low temperature and provided the *trans*-1,2-addition products **2c-h** in high yields for alkylacetylenes and moderate yields with arylacetylenes. When intermediates **2** were treated with an excess of lithium hydroxide in DMSO, HCl

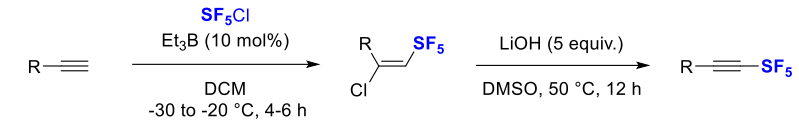
elimination occurred and delivered the corresponding SF_5-alkynes **3c-g** in moderate to high yields, depending on the substitution pattern of alkynes.



R = Ph, **1c**	49%, **2c**	93%, **3c**
CH_2Bn, **1d**	-	43%, **3d** (over 2
p-tolyl, **1e**	50%, **2e**	steps)
p-anisyl, **1f**	68%, **2f**	88%, **3e**
n-butyl, **1g**	90%, **2g**	85%, **3f**
n-hexyl, **1h**	94%, **2h**	67%, **3g**
		-

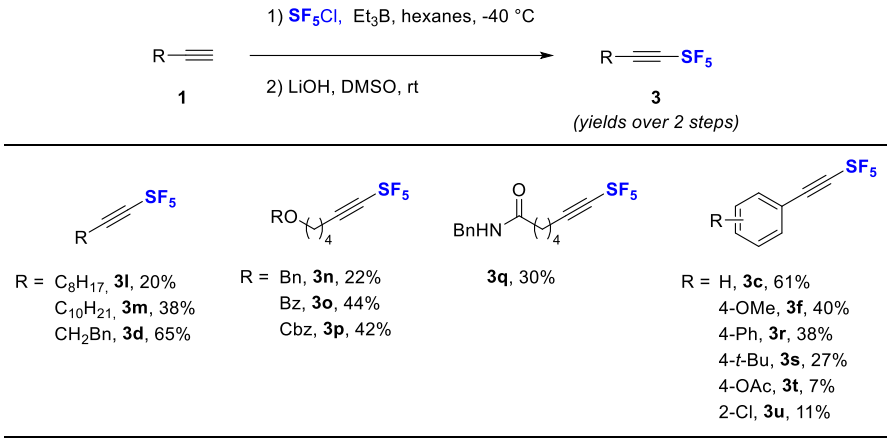
Scheme 4: Dolbier's procedure for the synthesis of SF_5-alkynes

This two-step strategy was also used by Röschenthaler and co-workers to synthesize liquid crystalline compounds with a terminal SF_5-substituted acetylene moiety **3i-k** (Scheme 5).[20,21] In this case, hexane was replaced by dichloromethane and the reaction mixture was maintained at -20 °C for the SF_5-addition step. The subsequent elimination step with 5 equivalents of LiOH required higher temperature (50 °C) and longer reaction time (12 h) compared to Dolbier's procedure showed in Scheme 4. In 2019, the Dolbier's method was illustrated by Paquin in relatively low overall yields (Scheme 6).[22]



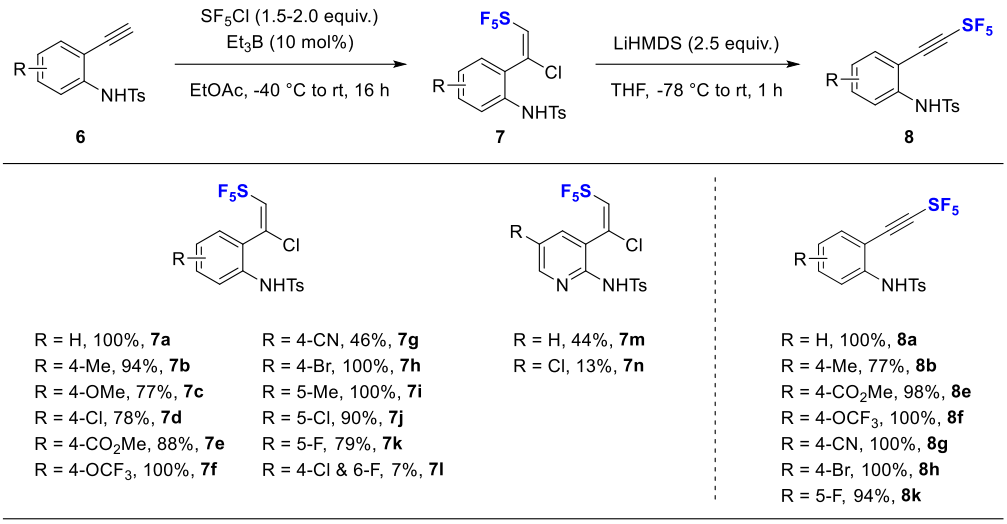
1i	*n*-C_3H_7	92%, **2i**	65%, **3i**
1j	*n*-C_3H_7	83%, **2j**	70%, **3j**
1k	*n*-C_5H_{11}	86%, **2k**	72%, **3k**

Scheme 5: Synthesis of liquid crystals containing a SF_5-alkyne



Scheme 6: Synthesis of various SF_5-alkynes using Dolbier's procedure

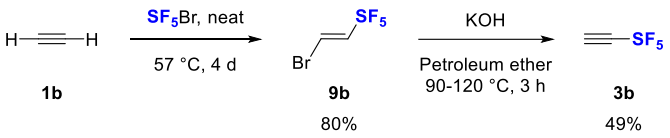
In 2021, Bizet and co-workers modified the original Dolbier's method with 2-ethynyl aniline substrates **6** by performing the radical addition of SF_5Cl in ethyl acetate, which gave the corresponding adducts **7** in high yields. Moreover, they developed a new elimination protocol for the synthesis of SF_5-alkynes by using an excess of LiHMDS at -78 °C, affording SF_5 2-ethynyl aniline derivatives **8** in high yields. These conditions proved to be tolerant to sensitive functional groups such as ester, nitrile, or halogens (Scheme 7).[23]



Scheme 7 : Synthesis of SF_5-alkynes derived from 2-ethynyl anilines

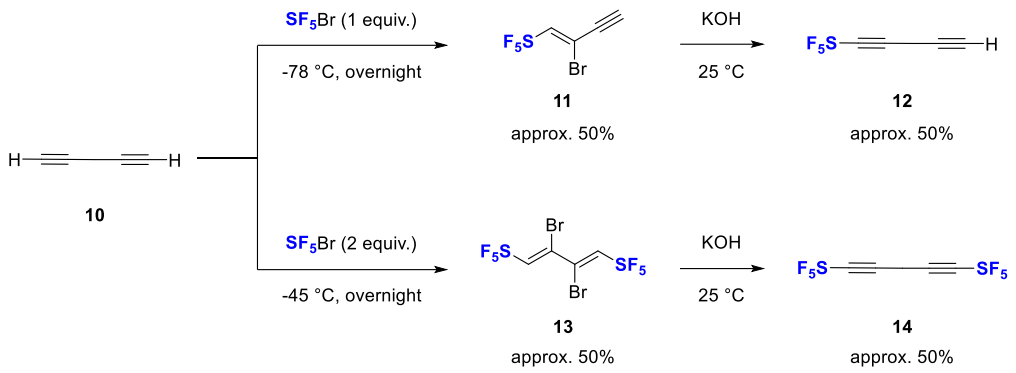
2.2 By means of SF_5Br

SF_5Br is much more reactive than SF_5Cl. However, one big limitation is that this gas is not commercially available nor easily manufactured. Nevertheless, it has been used in reactions with alkenes or functionalized double bond systems providing vicinal bromo-pentafluorosulfanyl alkanes, which illustrated the compatibility of the reagent with several functional groups, although the reagent is less selective compared to SF_5Cl. Like its chlorinated analogue, SF_5Br was used for addition onto different alkynes. Gard, Shreeve and co-workers improved the previous works of Case and Hoover and develop a straightforward synthesis by using of SF_5Br instead of SF_5Cl. In that case, the dehydrobromination was more efficient and gave the SF_5-acetylene **3b** in 39% overall yield (Scheme 8).[24,25]



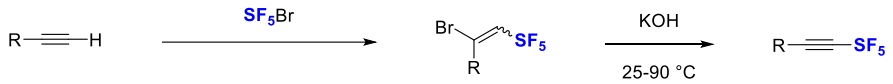
Scheme 8 : Alternative synthesis of SF_5-acetylene with SF_5Br

This methodology is not limited to acetylene but could be extended to diversely substituted alkynes [26–31] or diacetylenes [32,33]. Firstly, when diacetylene **10** reacted neat with one equivalent of SF_5Br at -78 °C, it gave the mono-SF_5 adduct **11** in 50% yield, while the di-SF_5 adduct **13** was formed with two equivalents of SF_5Br at -45 °C. Treatment with KOH at 25 °C delivered the mono- or disubstituted SF_5 diacetylenes **12** & **14**, in approximatively 50% yield in both cases (Scheme 9).



Scheme 9 : Synthesis of SF_5-diacetylenes using SF_5Br

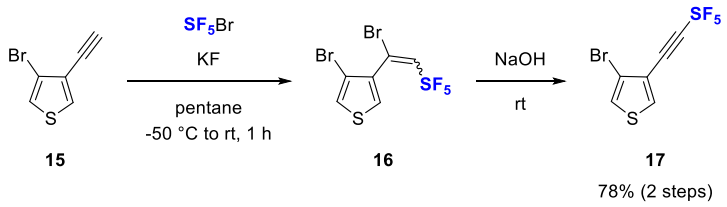
Similarly, addition reaction of SF_5Br onto several substituted alkynes has been reported and it was shown that the SF_5Br can react with electron deficient alkynes (**1w-y**) thanks to thermal activation to give the corresponding 2-bromo-1-SF_5-alkenes **9** in moderate to good yields. Few SF_5-alkynes **3** were obtained in good yields by dehydrobromination with KOH (Scheme 10).[26–31]



R = Si(*i*-Pr)$_3$, **1v**	Freon 113, -35 °C, 3 h	n.d., **9v**	95%, **3v**
Me, **1a**	neat, rt, 12 h	30%, **9a**	
CF_3, **1w**	neat, 80 °C, 2 d	80%, **9w** (33:67 *E*:*Z*)	65%, **3w** over 2 steps
SF_5, **1x**	neat, 105 °C, 3 h	75%, **9x**	64%, **3x**
CO_2Et, **1y**	Freon 113, 40-65 °C, 2 d	70%, **9y** (95:5)	

Scheme 10 : Synthesis of SF_5-alkynes by bromopentafluorosulfanylation reaction and HBr elimination

In the 80s and 90s, Seppelt and Berry used these alkynes for coordination chemistry of nickel [34] or cobalt [35–37] complexes. More recently, in 2006, polymer chemists became interested in SF_5 alkynes as monomer precursor and SF_5-ethynylthiophene **17** was synthesized with an excellent 78% yield over two steps with the use of NaOH for the dehydrobromination step; thus expanding the scope of alkynes to those featuring heteroaromatic substituents (scheme 11).[38]



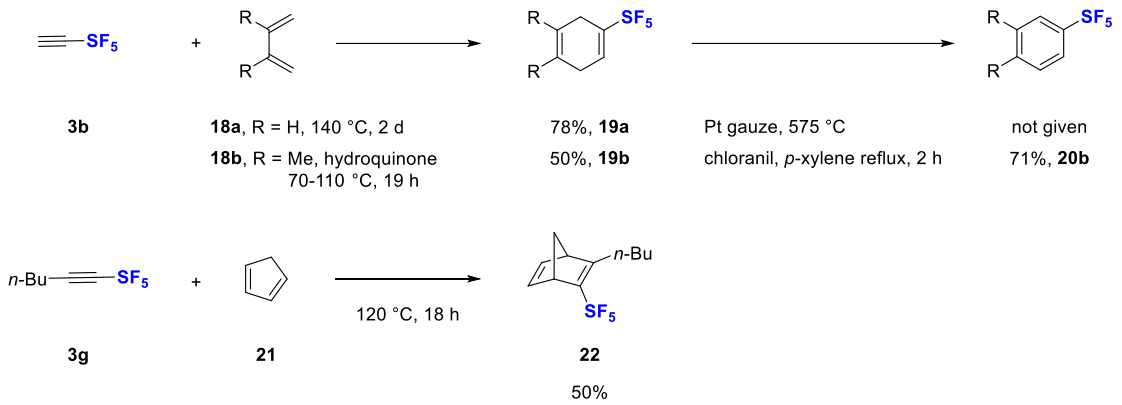
Scheme 11 : Synthesis of SF_5-ethynylthiophene

3 Cycloaddition reactions with SF_5-alkynes

3.1 SF_5-alkynes in Diels-Alder cycloadditions

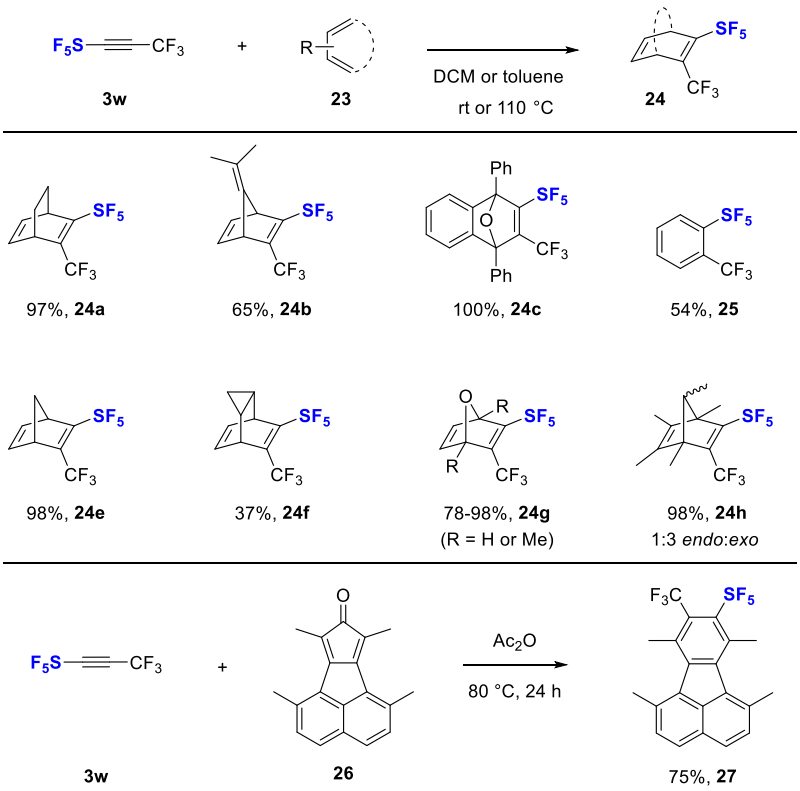
The common "normal" electron demand Diels–Alder reaction takes place by HOMO/LUMO interactions between an electron-rich diene and an electron-deficient dienophile. The SF_5 motif, which is a strong electron-withdrawing group makes SF_5-alkynes good electron-deficient dienophiles for such reaction.[1,2] The group of Dolbier has largely contributed to the use of SF_5 alkynes as dienophiles in [4+2] cycloaddition reactions. For instance, SF_5-acetylene **3b** reacted with butadiene **18a** or 2,3-dimethylbuta-1,3-diene **18b**, to give SF_5-substituted cyclohexa-1,4-dienes **19** in moderate to good

yields. These intermediates **19** could give SF_5-substituted benzenes **20** after aromatizing dehydrogenation either over platinum gauze at 575 °C or by refluxing with chloranil in *p*-xylene.[15] When *n*-Bu substituted SF_5-alkyne **3g** was heated with cyclopentadiene **21** at 120 °C for 5 h, the norbornadiene derivative **22** was obtained in 50% yield (Scheme 12).[39]



Scheme 12 : Diels-Alder reactions of SF_5-alkynes with 1,3-dienes

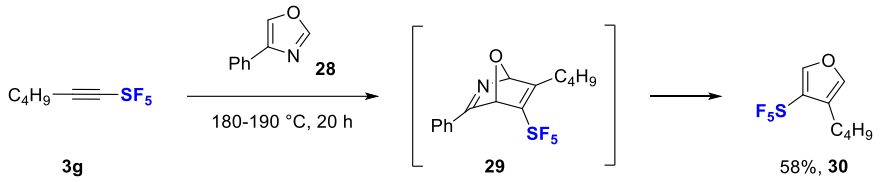
The electron-deficient alkyne **3w** was successfully used as versatile dienophile in [4+2] Diels-Alder cycloaddition with a series of cyclic 1,3-dienes **23** (scheme 13). The reactions occurred in DCM at room temperature or in refluxing toluene and provided the corresponding cycloadducts **24** in high yields in most cases. Starting from pyranone **23d** as diene, the corresponding cycloadduct **24d** was not stable to be isolated and instead the reaction yielded 1-SF_5-2-CF_3-benzene **25** after elimination of CO_2 in a spontaneous retro-Diels-Alder reaction. Similarly, the diene **26** was reacted with the SF_5-alkyne **3w** to yield the fluoranthene **27** in 75% yield.[31]



Scheme 13 : Diels–Alder reactions of $F_3C–C≡C–SF_5$ with cyclic 1,3-dienes

3.2 SF_5-alkynes in hetero-Diels-Alder reactions

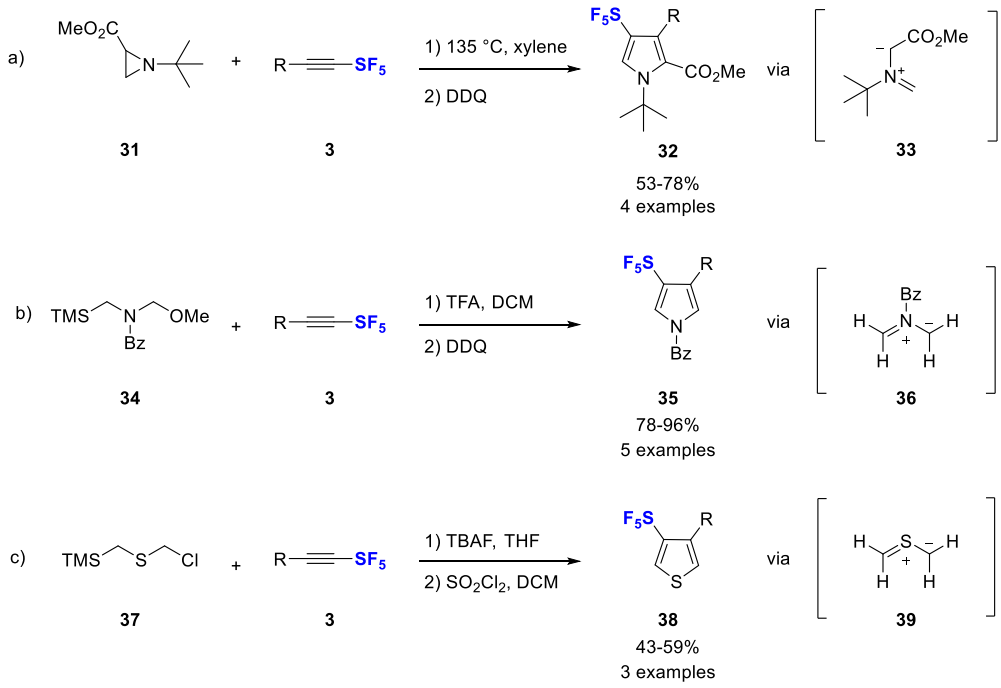
The preparation of SF_5-substituted heterocycles from SF_5-alkynes is scarce in the literature and only one example of hetero-Diels-Alder reaction has been described by Dolbier. The 3-butyl-4-SF_5-furan **30** was obtained in 58% yield following a tandem Diels-Alder/retro-Diels-Alder sequence between SF_5-hexyne **3g** and 4-phenyloxazole **28** (scheme 14).[17,39]



*Scheme 14 : Synthesis of 4-SF_5-furan derivative **30***

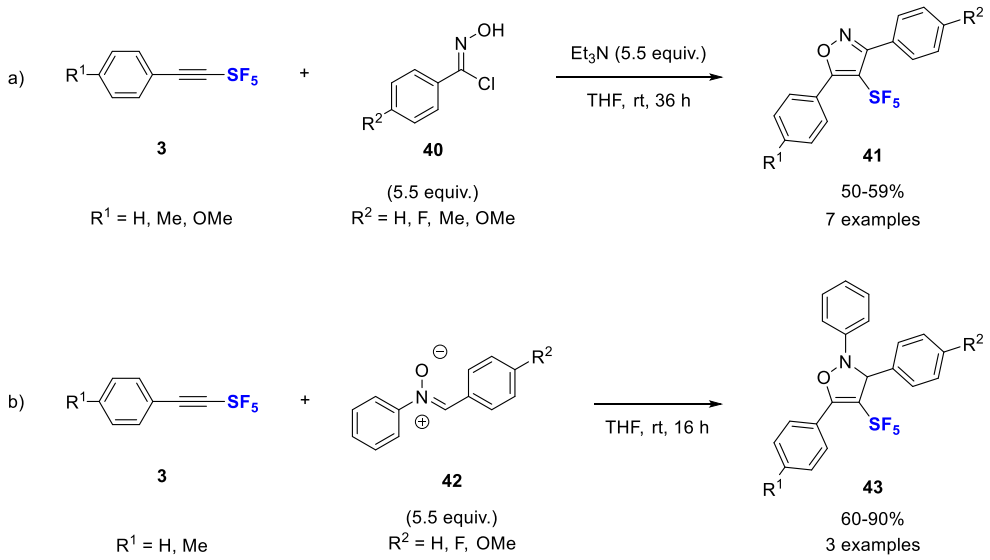
3.3 SF_5-alkyne in 1,3 dipolar cycloadditions

The group of Dolbier also studied the formation of nitrogen-containing heterocycles from SF_5-alkynes using 1,3-dipolar cycloaddition reactions. Reaction of *tert*-butyl aziridine **31** at high temperature generated the intermediate azomethine ylide **33**, which reacted with SF_5-alkyne **3** to yield SF_5-pyrroles **32** after oxidation with DDQ (scheme 15a).[18] Few years later, a similar strategy was used using another azomethine ylide precursor **34**, which was activated in softer conditions at room temperature with TFA and afforded SF_5-pyrroles **35** in high yields (scheme 15b).[40] This method has been extended to the synthesis of SF_5-thiophenes **38**, using SO_2Cl_2 in a second step to re-aromatize the dihydrothiophene to thiophene in moderate yields (scheme 15c).



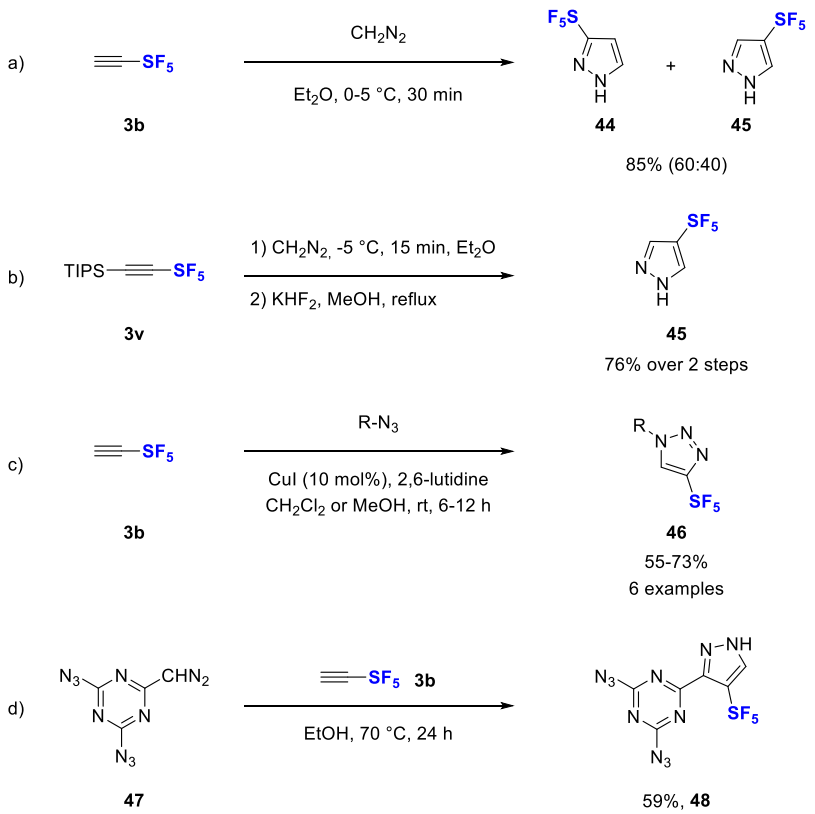
Scheme 15 : Synthesis of SF_5-substituted pyrroles and thiophenes by 1,3-dipolar cycloadditions

Aryl SF_5-alkynes **3** proved to be suitable substrates in 1,3-dipolar cycloadditions for the synthesis of 4-SF_5-isoxazoles **41** and isooxazolines **43**, by reaction with benzohydroxyiminoyl chlorides **40** and *N*-benzylidene aniline *N*-oxides **42**, respectively (scheme 16).[19,41]



Scheme 16 : Preparation of 4-SF_5-isoxazoles and isooxazolines via 1,3-dipolar cycloadditions

The synthesis of SF_5 pyrazoles **44** and **45** and triazoles **46** was reported by Shreeve and co-workers, using diazomethane or "click" chemistry process with azide, for applications in materials science.[42,43] The addition of diazomethane to SF_5-acetylenes led to a 3:2-mixture of 3- and 4-SF_5-pyrazoles **44** and **45**,[15] while the single regioisomer **45** was obtained from the triisopropylsilyl (TIPS) derivative **3v** in excellent yields (scheme 17a-b).[44] The Huisgen cycloaddition was successfully applied to SF_5-acetylene and delivered triazole **46** in good yields (scheme 17c). Interestingly, the 2,4-diazido-6-diazomethyl-1,3,5-triazine **47** was heated with SF_5-acetylene **3b** in ethanol to give selectively the pyrazole **48** in 59% yield, while the two azido groups remained unreactive under these conditions (scheme 17d).



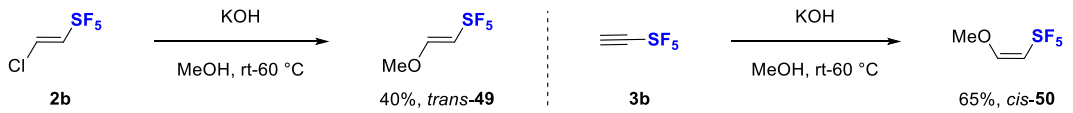
Scheme 17 : Synthesis of SF_5-pyrazoles and triazoles

4 Nucleophilic additions onto SF_5-alkynes

SF_5-Substituted alkynes are highly polarized as a result of the strong electron-withdrawing property of the SF_5 that renders the β-carbon of the alkyne a highly reactive site for nucleophilic additions. However, for intramolecular process, the reaction can take place of the α-carbon driven by the formation of 5-membered heteroaromatics.

4.1 Synthesis of *cis*- and *trans*-1-SF_5-2-methoxy-ethene

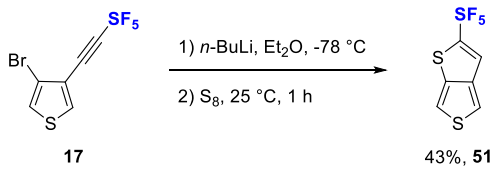
In 1964, Hoover and co-workers described the first reaction involving a SF_5-alkyne to form an enol-ether.[15] Interestingly, they observed that treatment of 2-chloro-1-SF_5-ethene **2b** with MeOH and KOH gave exclusively *trans*-1-SF_5-2-methoxyethene **49** in 40% yield by nucleophilic substitution of the chlorine atom by a methoxy group under basic conditions. On the other hand, the reaction of SF_5-acetylene **3b** in similar conditions provided mainly the opposite *cis*-isomer **50** in 65% yield with small amount of the *trans*-isomer **49** (scheme 18).



Scheme 18 : Synthesis of trans- and cis-1-SF_5-2-methoxy-ethenes

4.2 Synthesis of SF_5-substituted thienothiophene

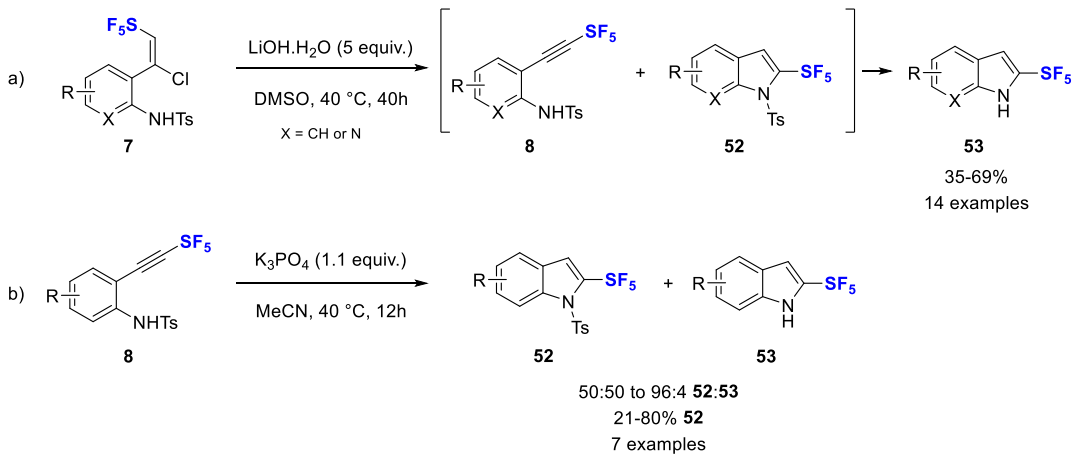
The SF_5-ethynylthiophene **17**, depicted earlier in the text (see scheme 11), was engaged in halogen-lithium exchange using *n*-BuLi at -78 °C. Then, treatment with elemental sulfur gave the SF_5-substituted thienothiophene **51** in 43% yield (scheme 19).[38]



Scheme 19 : Synthesis of SF_5-substituted thienothiophene

4.3 Synthesis of 2-SF_5-(aza)indoles via intramolecular cyclization

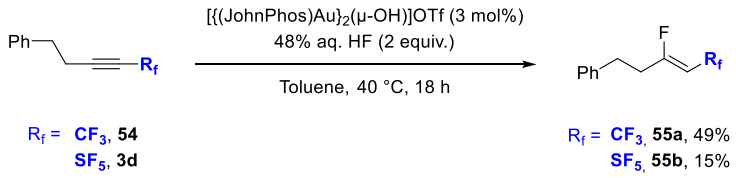
Recently, the synthesis of 2-SF_5-indoles **53** was developed by Bizet and co-workers starting from 2-ethynylaniline derivatives following a one-pot telescoped procedure.[23] Interestingly, it was shown that by treatment of **7** in classical basic conditions using an excess of LiOH in DMSO, the HCl elimination took place to form **8** but this step was rapidly followed by 5-*endo*-dig cyclization (**52**) and *N*-tosyl deprotection affording 2-SF_5-(aza)indoles **53** in moderate to good and reproducible yields (Scheme 20a). The synthesis was then decomposed stepwise and K_3PO_4 was identified as a suitable base to transform selectively **8** into **52**. Noteworthy, with electron-withdrawing substituents R, some non-negligible amount of unprotected indole **53** was also formed (Scheme 20b).



Scheme 20 : Synthesis of 2-SF_5-(aza)indoles via a base-mediated 5-endo-dig cyclization

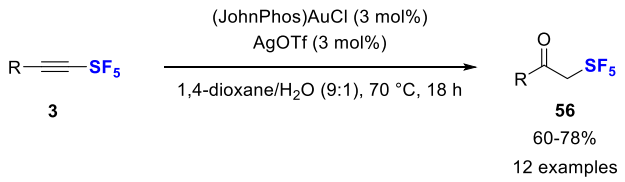
4.4 Hydrofunctionalization of SF_5 alkynes

The gold-catalyzed hydrofluorination of SF_5-alkyne has been reported on a single example obtained in a low 15% yield (**55b**), which is much lower than the 49% yield obtained for the CF_3-analog **55a**.[45] The bulkiness of the SF_5 compared to the CF_3 was proposed to explain the lower reactivity of **3d** in these conditions (Scheme 21).



Scheme 21 : Gold-catalyzed hydrofluorination of R_f-alkynes

In contrast, gold-catalyzed hydration of SF_5-alkynes was much more efficient and delivered α-SF_5 ketones **56** in yields ranging from 60 to 78% both from aromatic and aliphatic substrates (Scheme 22).[22]



Scheme 22 : Gold-catalyzed hydration of SF_5-alkynes

5 Conclusion

Over the past sixty years, the synthetic access to variously decorated SF_5-containing compounds has remained a highly challenging task. Within the past few years, the synthesis of SF_5-alkynes has been significantly improved making a strong new impulse to the development of small SF_5-building blocks. A wider scope of SF_5-alkynes was synthesized and the application of these alkynes in synthetic transformations has been discussed in this article. In the coming years, many applications of SF_5-small molecules are expected in various fields such as crop science, drug discovery or materials science. Development of new synthetic methods is always timely and relevant to bring molecular complexity a step further. This topic of synthetic organofluorine chemistry is rising and many innovative discoveries are expected in near future.

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