Journal of Fluorine Chemistry 243 (2021) 109734

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Electron donor-acceptor (EDA)-complex enabled SF_5Cl addition on alkenes and alkynes

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ARTICLE INFO

Keywords:
Pentafluorosulfanyl substituent
Chloropentafluorosulfanylation
(EDA)-complexes
Radical addition
Visible-light activation

ABSTRACT

A new method for the addition of SF_5Cl on unsaturated compounds was developed, based on the use of an electron donor-acceptor (EDA)-complex and visible light irradiation. The reaction does not require the presence of oxygen to proceed, compared to the most-common SF_5Cl addition protocols. A total of 19 examples of alkenes and alkynes were performed, with yields ranging from 31 % to 86 %.

1. Introduction

In the past decades, the pentafluorosulfanyl ($-SF_5$) substituent has attracted more and more attention due to its unique properties. Often referred to as a "super CF_3", the SF_5 group shows similar but enhanced properties when compared to the trifluoromethyl moiety [1]. While the SF_5 group is bulkier and more chemically and thermally stable than its trifluoromethylated analogue [2], it also induces a stronger dipole moment (3.44 D for $PhSF_5$ vs. 2.60 D for $PhCF_3$), has a higher electron-withdrawing capacity ($\sigma_p = 0.68$ vs 0.53 for CF_3) as well as a greater lipophilicity ($\pi_p = 1.50$ vs. 0.88 for CF_3) [3]. These unique properties account for the increasing occurrence of the pentafluorosulfanyl substituent in many fields of organic chemistry, including medicinal chemistry [4], agrochemistry [5] and material sciences [6].

While the interest toward the SF_5 group is increasing, the synthetic methods to introduce it into organic molecules remain rare. In order to incorporate the SF_5 moiety on aliphatic substrates, Dolbier's protocol for the radical addition of SF_5X (X = Cl, Br) on unsaturated compounds, using Et_3B as the radical initiator, has emerged as the most versatile one (Scheme 1A, top) [7]. This method allows the synthesis of a wide range of aliphatic pentafluorosulfanylated compounds with high yields and without the need for special apparatus such as microreactors or autoclaves. It has shown to be compatible with functional groups such as allylsilanes [8], in addition of being useful for the synthesis of a wide range of SF_5-containing building blocks of interest [9]. However, the use of Et_3B represents a drawback to the reaction. Et_3B being air-unstable and pyrophoric, its use in the laboratory can be challenging, or may necessitate the use of special apparatus [10]. Moreover, the quality and the concentration of Et_3B commercial solutions can largely vary between suppliers, therefore limiting the reproducibility of the reactions. In order to address these issues, we recently reported an alternative reaction to the Dolbier's method, using air-stable amine-borane complexes as radical initiators (Scheme 1A, bottom) [11]. This allowed the SF_5Cl radical addition on several alkenes and alkynes without the use of Et_3B. Nonetheless, the reaction still requires the presence of oxygen for the initiation of the radical chain, a parameter that can be hard to control. Indeed, in 2016, Curran and coworker reported a kinetic theory regarding the use of the Et_3B/O_2 system as a radical initiator [12]. While some reactions can be easily initiated with Et_3B and small or limited amount of oxygen, some other Et_3B-initiated processes necessitate a large excess of oxygen to either initiate, or simply keep running. This difference can be explained by the autooxidation mechanism of Et_3B, in competition with the desired chain-propagation reaction [13]. In a low-oxygen system, all the steps in the target chain must be faster than the autooxidation chain. The latter is therefore overrun by the desired radical chain reaction. Since the reaction of alkyl radicals with oxygen are typically fast, a low concentration in oxygen can favor the reaction of ethyl radical $Et^{\bullet}$ with the desired substrate rather than O_2, thus favoring the desired reaction. It is likely the case with Dolbier's protocol for the SF_5Cl addition on unsaturated compounds, since only 10 mol% of Et_3B and the residual air in solvent is sufficient for the reaction to occur. In contrast, with the high-oxygen reaction, the autooxidation of Et_3B is more productive than the target chain reaction, resulting in the need of a high amount of Et_3B and large excess of oxygen for the desired reaction

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https://doi.org/10.1016/j.jfluchem.2021.109734
Received 14 December 2020; Received in revised form 13 January 2021; Accepted 13 January 2021
Available online 19 January 2021

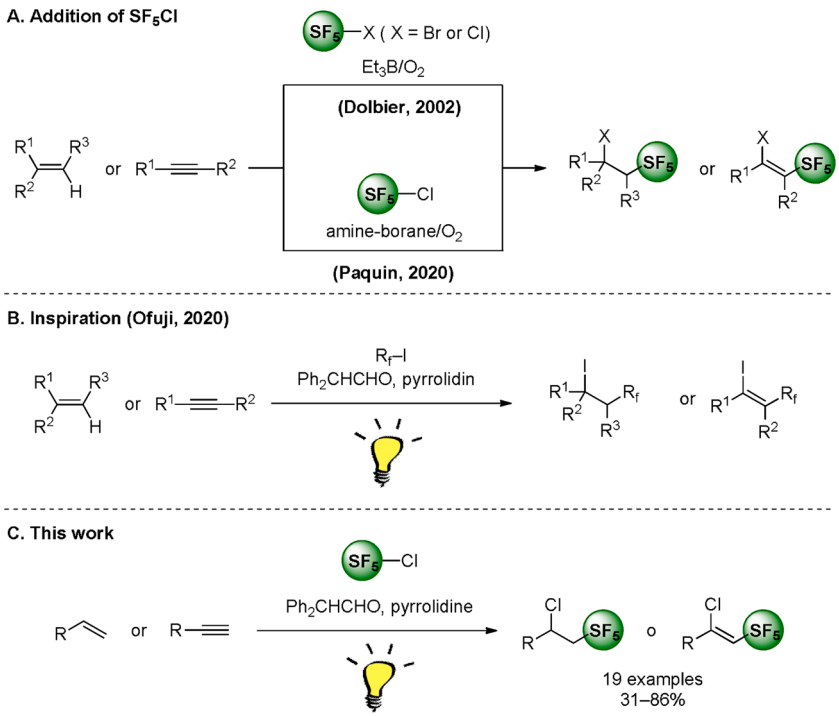
to occur. The efficiency of Et_3B/O_2 initiated reactions is therefore highly dependant on the concentration of oxygen in the reaction, as well as the free-radical reaction itself.

In a similar vein, we sought to develop new synthetic protocols for the incorporation of the SF_5-moiety on aliphatic derivatives, without having to rely on an oxygen-based initiation step. In order to do so, we got inspired by a recent report from Ofuji's group, in which they performed the photocatalyzed perfluoroalkylation of various olefins and alkynes, using an electron donor-acceptor (EDA)-complex as the photocatalyst (Scheme 1B) [14]. EDA-complexes have proven successful activators or photocatalysts in many perfluoroalkylation reactions [15]. These complexes represent a useful tool for perfluoroalkylation reactions, since they are environmentally benign, compared to the use of metal-based photocatalysts, and provide mild-reaction conditions to yield the desired perfluoroalkylated derivatives. They are formed *in situ* through halogen-bonding of R_f–I reagents and Lewis bases such as amines, alcohols, thiols, etc., and upon light activation, these complexes can form the desired R_f radical species ($R_f^{\bullet}$) [16]. We therefore hypothesized that this type of reaction could be applied to the use of SF_5Cl instead of R_f–I, in order to obtain the pentafluorosulfanylated derivatives. Herein, we report the first EDA-complex promoted SF_5Cl addition on unsaturated compounds (Scheme 1C).

2. Results and discussion

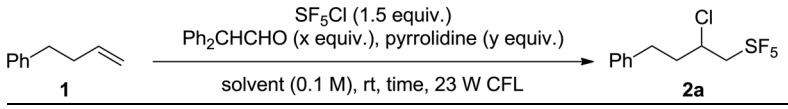
4-Phenyl-1-butene (**1**) was chosen as the model substrate for the optimization, and was submitted to similar reaction conditions reported in Ofuji's article, *i.e.*, 1.5 equivalent of SF_5Cl (instead of 1.1 equivalent of the R_f–I reagent), 10 mol% of diphenylacetaldehyde and pyrrolidine, in dichloromethane at room temperature for 16 h with a 23 W light bulb irradiation (entry 1). To our delight, a 90 % NMR yield of the desired compound **2a** was obtained. The reaction was then performed with other solvents (THF, Et_2O, MeCN, toluene, EtOAc, 1,4-dioxane and hexane), but none of them yielded the desired product in higher yield (data not shown). When trying to decrease the reaction time from 16 to 3 h, a lower conversion of 22 % was observed and only traces amount of the desired compound were obtained (entry 2). Finally, some control tests were performed in order to demonstrate that all the components of the system are necessary for the desired pentafluorosulfanylation to occur. Therefore, the reaction was performed without light activation (entry 3), without the presence of the aldehyde (entry 4) or the amine (entry 5) and with only light as the initiator (entry 6). In all cases, low conversions were obtained, and the final compound could not be detected in the reaction mixture. It was not possible to identify any side-product resulting from the low conversion, therefore, the conversion was attributed to degradation products. The reaction conditions described in entry 1 were chosen as the optimal one.

We next performed the reaction on an alkyne substrate, *i.e.*, benzylpropargyl ether (**3**) (Table 2, entry 1), with the previously chosen optimal conditions (Table 1, entry 1). Surprisingly, a low yield of 5% of the desired product was obtained. The reaction was therefore optimized, and the results are presented in Table 2. First, MeCN, dichloroethane and Et_2O were used as the solvent in the reaction, but none of these solvents significantly improved the yield of the reaction (entries 2–4). In the case of DCE (entry 3), a low yield of 14 % was obtained, and the conversion of 90 % was attributed mainly to degradation. When the number of equivalents of SF_5Cl was increased from 1.5 to 3, slightly higher yields of **4a** were obtained in all tested solvents (entries 6–8), with the exception of Et_2O, in which a full conversion and a good yield of 69 % were obtained (entry 5). These results tend to show that increasing the initial amount of SF_5Cl might have helped having more of the gaseous SF_5Cl in solution, therefore increasing the conversion and yield. While diluting or concentrating the reaction did not prove beneficial (entries 9–10), changing the number of equivalents of the diphenylacetaldehyde and pyrrolidine proved to strongly affect the reaction (entries 11–14). Indeed, when the number of equivalents of both aldehyde and amine were increased, no conversion was observed (entries 11–12), while reducing the catalytic amounts to 5 mol% led to the moderate yield of 47 % (entry 13). Moreover, when changing the diphenylacetaldehyde/pyrrolidine ratio in favor of the pyrrolidine, no final compound was detected in the reaction mixture (entry 14). Finally, the reaction time was optimized (entries 15–18), and 16 h proved optimal with a 71 % NMR yield (entry 17). Therefore, these reaction conditions were chosen as the optimal ones for the evaluation of the scope of



Scheme 1. Previous and present works on the SF_5Cl radical addition on unsaturated compounds.

Table 1
Optimization of the SF_5Cl addition on 4-phenyl-1-butene 1.



1 2a

Entry	Solvent	x equiv.	y equiv.	time (h)	Conversion (%)[a]	Yield (%)[a]
1	**CH_2Cl_2**	**0.1**	**0.1**	**16**	**100**	**90 (78)**[b]
2	CH_2Cl_2	0.1	0.1	3	22	traces
3	CH_2Cl_2	0.1	0.1	16	36	0[c]
4	CH_2Cl_2	0	0.1	16	37	0
5	CH_2Cl_2	0.1	0	16	26	0
6	CH_2Cl_2	0	0	16	32	0

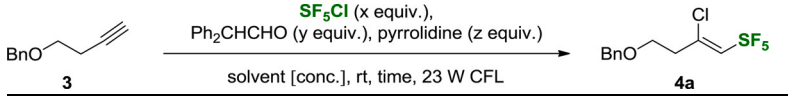
[a] Estimated by ^1H and ^{19}F NMR using 2-fluoro-4-nitrotoluene as an internal standard.
[b] Isolated yield.
[c] Reaction performed without light activation.

alkynes.

With the optimized conditions in hand, a series of alkenes and alkynes were submitted to the reaction. First, the alkene scope is depicted in Scheme 2. Both the isolated yields and the NMR yields are shown, since it was observed that in a few cases, purification proved problematic, leading to considerably lower isolated yields than the NMR ones. For example, a 90 % NMR yield of the model substrate **2a** was obtained, but only 78 % could be isolated from the reaction mixture. The reaction leads to several unidentified side products, which rendered some purifications laborious. First, a series of aromatic esters were submitted to the reaction conditions. The vinyl benzoate addition product **2b** led to an excellent NMR yield of 88 % and a moderate isolated yield of 66 %. When the aliphatic chain was increased such as with substrate **2c**, the same yield of 88 % was obtained by NMR analysis, but the purification step proved easier and a good isolated yield of 81 % was obtained. Next, the electronic nature of the phenyl group was varied, either with an electron-donating group such as methoxy (**2d**) or an electron-withdrawing substituent such as fluorine (**2e**), and no particular effect on the yield was observed, since these products were obtained in 78 % and 69 % isolated yields respectively. When the reaction was performed with the 2-naphtoate derivative, compound **2f** was isolated with a moderate yield of 48 %. The use of an aliphatic ester led to a similar NMR yield of 78 %, but purification proved particularly problematic with that substrate, and only 31 % of product **2g** could be isolated. When the reaction was performed on allyl benzyl ether, a moderate yield of 56 % of compound **2h** was obtained. Interestingly, two styrene derivatives *i.e.*, styrene and *tert-butyl* styrene were tolerated in the reaction, and afforded compounds **2i** and **2j** with 52 % and 46 % yield respectively. Styrene derivatives have shown to polymerize in SF_5Cl radical additions, but this did not prove to be a problem in our conditions, since no sign of polymerization was detected in the crude reaction mixture [11]. Moreover, several aliphatic derivatives were also investigated in our (EDA)-complex enabled SF_5Cl addition. When 9-decen-1-ol was tested in the reaction, an excellent NMR yield of 90 % was obtained, but the final compound **2k** could not be isolated from the reaction mixture. Nonetheless, this result is of interest, considering that free alcohols are not tolerated in the Et_3B-initiated SF_5Cl addition [7]. When the alcohol group was next protected with an acetate group, a NMR yield of 74 % was obtained, and 53 % of the product 2**l** was isolated. Finally, the bromine-containing aliphatic derivative **2m** was also tolerated in the reaction condition, with a 74 % NMR yield and a 51 % isolated yield.

Some compounds proved unproductive in our EDA-complex mediated SF_5Cl. First, methyl acrylate was tested in the reaction, and derivative **2n** could not be detected in the reaction mixture. A similar result was obtained when *N*-allylaniline was submitted to the reaction conditions, since no trace of compound **2o** could be detected. These results are not surprising, considering that these substrates are also not tolerated in Dolbier's protocol for the addition of SF_5Cl [7]. However, the acid

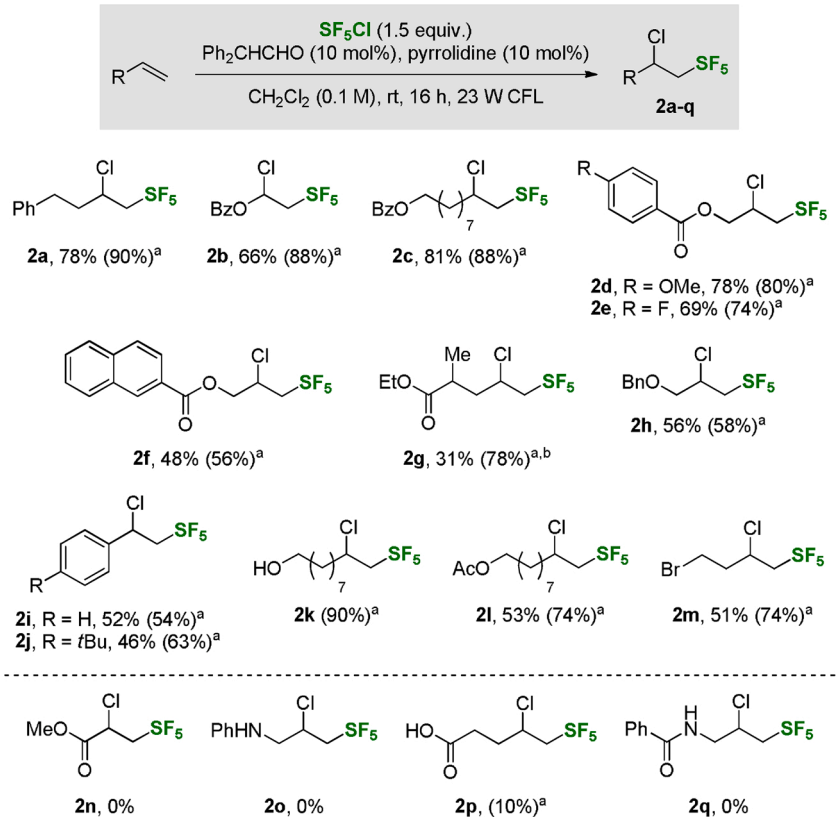
Table 2
Optimization of the SF_5Cl addition on benzylpropargyl ether 3.



3 4a

Entry	Solvent	[Conc.] (M)	x equiv.	y equiv.	z equiv.	Time (h)	Conversion (%)[a]	Yield (%)[a]
1	CH_2Cl_2	0.1	1.5	0.1	0.1	18	6	5
2	MeCN	0.1	1.5	0.1	0.1	18	0	0
3	DCE	0.1	1.5	0.1	0.1	18	90	14
4	Et_2O	0.1	1.5	0.1	0.1	18	10	8
5	Et_2O	0.1	3.0	0.1	0.1	18	100	69
6	dioxane	0.1	3.0	0.1	0.1	18	57	32
7	THF	0.1	3.0	0.1	0.1	18	60	25
8	EtOAc	0.1	3.0	0.1	0.1	18	30	13
9	Et_2O	0.05	3.0	0.1	0.1	18	64	29
10	Et_2O	0.4	3.0	0.1	0.1	18	32	14
11	Et_2O	0.1	3.0	0.2	0.2	18	0	0
12	Et_2O	0.1	3.0	1	1	18	0	0
13	Et_2O	0.1	3.0	0.05	0.05	18	63	47
14	Et_2O	0.1	3.0	0.1	1	18	0	0
15	Et_2O	0.1	3.0	0.1	0.1	4	95	45
16	Et_2O	0.1	3.0	0.1	0.1	6	96	66
17	**Et_2O**	**0.1**	**3.0**	**0.1**	**0.1**	**16**	**100**	**71**
18	Et_2O	0.1	3.0	0.1	0.1	24	100	54

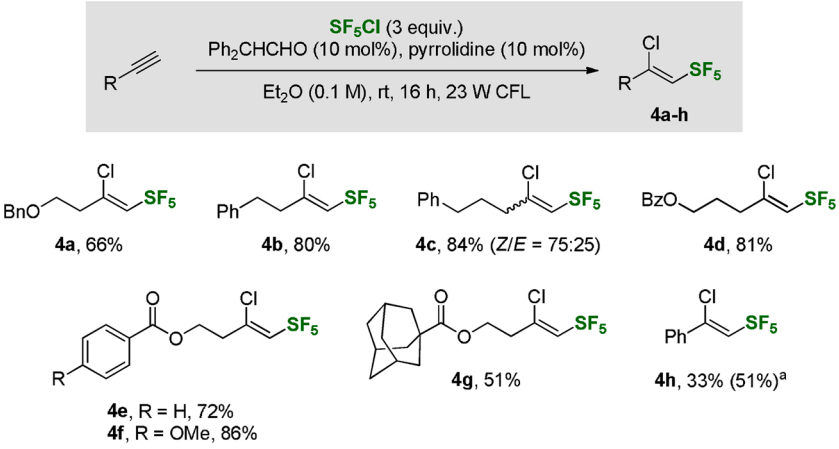
[a] Estimated by ^1H and ^{19}F NMR using 2-fluoro-4-nitrotoluene as an internal standard.



Scheme 2. Alkene scope of the EDA-complex mediated SF_5Cl addition. Unless noted otherwise, isolated yields are reported. [a]Yield estimated by ^{19}F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard. [b]51:49 diastereoisomeric mixture.

derivative **2p** was only obtained in 10 % NMR yield in our method even though this substrate can be easily obtained in the Et_3B-mediated protocol [17]. This result may be due to an acid-base reaction between the substrate and pyrrolidine, which almost shut down the activation step. Moreover, the amide derivative **2q** could also not be obtained with our reaction conditions, while amides are tolerated in Dolbier's protocol [18]. At the moment, we hypothesized that the reason for this result might come from a competition between the amide and the enamine in the formation of the EDA-complex though more elaborate experiments are required in order to confirm this hypothesis.

Next, a series of alkynes were submitted in the optimized reaction conditions (Scheme 3). In general, alkyne substrates led to slightly higher yields than the alkenes, and no sign of side reactions complicated the purification step. The model substrate benzyl 3-butynyl ether led to 66 % of compound **4a**. When 4-phenyl-1-butyne and 5-phenyl-1-pentyne were submitted to the reaction conditions, compounds **4b** and **4c** were obtained in good yields, respectively 80 % and 84 %. Surprisingly, compound **4c** was obtained as a stereoisomeric mixture (Z/E = 75:25). This compound is the only one who did not show a complete stereoselectivity in favor of the Z isomer in the reaction, and the reason for that remains unclear. The presence of the E isomer in the SF_5Cl radical addition on alkynes has, to the best of our knowledge, never been reported in the literature. The ester derivative **4d** was also obtained in a good yield of 81 %, as well as the derivative with a one-carbon smaller aliphatic chain **4e**, which was obtained with a 72 % yield. Moreover, adding an electron-donating substituent on the phenyl ring proved



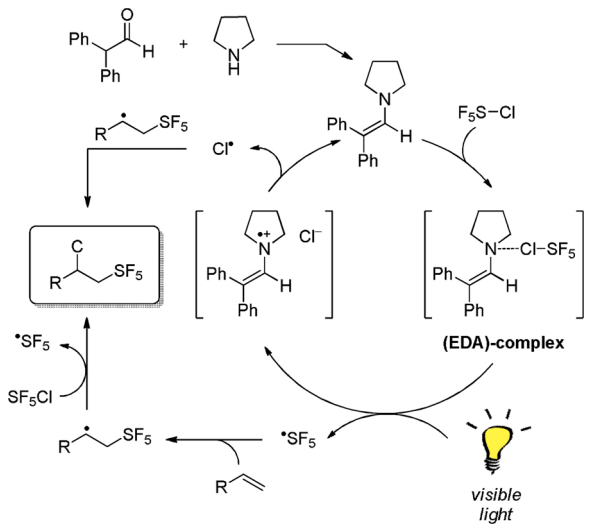
Scheme 3. Alkyne scope of the EDA-complex mediated SF_5Cl addition. Unless noted otherwise, isolated yields are reported. [a]Yield estimated by ^{19}F NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.

beneficial to the reaction, since compound **4f** could be obtained with an 86 % yield. A moderate yield of 51 % was afforded with the adamantane-containing ester derivative **4g**. Finally, the (EDA)-complex enabled SF_5Cl addition was performed on phenylacetylene. The formation of the desired compound **4h** has been shown to be in competition with the formation of the 2:1 addition product in Dolbier's protocol [7]. However, in our reaction conditions, no sign of the 2:1 addition product was detected, and the desired compound **4h** could be afforded with a 51 % NMR yield and a 33 % isolated yield. The difference between the NMR and the isolated yield was attributed to the volatility of compound **4h**.

A plausible mechanism, based on Ofuji and coworkers' work [14], for the (EDA)-complex SF_5Cl addition on olefins and alkynes is depicted in Scheme 4. We hypothesized that the SF_5Cl addition would undergo a similar pathway than with the perfluoroalkylated reagents. First, following the formation of the enamine from the reaction between 2, 2-diphenylacetaldehyde and pyrrolidine, the (EDA)-complex could be formed through halogen-bonding of the chlorine atom from SF_5Cl and the nitrogen atom of the enamine. Upon light irradiation, the (EDA)--complex would next collapse to generate the desired radical species $SF_5^{\bullet}$, the radical cationic enamine and the chlorine anion. The starting enamine could be regenerated by the expulsion of a chlorine radical $Cl^{\bullet}$, while the $SF_5^{\bullet}$ could add on the alkene to generate the pentafluorosulfanylated radical intermediate. The latter could either combine with the $Cl^{\bullet}$ generated for the recovery of the starting enamine, or propagate the reaction by the activation of another SF_5Cl equivalent, therefore leading to a free-radical mechanism. While more studies need to be performed to further increase our understanding of the reaction mechanism, and possibly exclude one of the two plausible pathways, it is still noteworthy that no oxygen is involved in the mechanism, which represents an advantage compared to both the Et_3B and the DICAB-initiated SF_5Cl additions on alkenes and alkynes [7,11].

3. Conclusion

In conclusion, we have reported the first (EDA)-complex mediated SF_5Cl addition on unsaturated compounds. A total of 19 examples were performed, with yields going from 31 % to 86 %. Functional groups such as ethers, esters, alcohols and bromine were tolerated in the reaction, while methyl acrylate, acid derivatives and nitrogen-containing functional groups did not afford the desired SF_5Cl addition products. Alkyne derivatives showed to be slightly superior to alkenes substrates. Overall, this method represents an oxygen-free alternative to the most common SF_5Cl addition reaction conditions.



Scheme 4. Proposed mechanism for the (EDA)-complex mediated SF_5Cl addition on unsaturated compounds.

4. Experimental

4.1. General information

All reactions were carried out under an argon atmosphere with dry solvents. All commercially available compounds were used as received. SF_5Cl was purchased at SynQuest Labs inc. and was condensed at a known concentration in hexanes. This solution was then used for the SF_5Cl additions and could be stored for several months in a -35 °C freezer. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Silicycle silica gel 60 Å F254 TLC plates, and visualized under UV or by staining with potassium permanganate. Flash column chromatography was carried out on Silicycle silica gel 60 Å, 230–400 mesh. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ at room temperature using an Agilent DD2 500 or a Varian Inova 400 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield of tetramethylsilane and are respectively referenced to tetramethylsilane (δ =0.00 ppm) and residual solvent (δ =77.16 ppm). For ^{19}F NMR, calibration was performed using a unified scale [19]. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, m = multiplet, bs = broad signal. High-resolution mass spectra were obtained on a LC/MS–TOF Agilent 6210 using electrospray ionization (ESI). GC–MS analyses were performed on a Thermo Trace ULTRA GCMS equipped with an Agilent J&W HP-1 capillary column, an ITQ 900 mass selective detector (EI) or (CI) using the following method: 40 °C for 1 min then 10 °C/min until 330 °C. Infrared spectra were recorded using an ABB MB3000 FT-IR spectrometer. The melting points (m.p.) were recorded on a MPA100 apparatus using the following method: 40 °C–200 °C at 2 °C/min.

4.2. Synthesis of the starting material

4.2.1. Dec-9-en-1-yl benzoate

Following the procedure described by Kang and coworkers [20], dec-9-en-1-ol (0.58 mL, 3.28 mmol, 2 equiv.) was added to a solution of benzoic acid (200 mg, 1.64 mmol, 1 equiv.) in dry dichloromethane (3.6 mL, 0.45 M) at room temperature under argon. 4-Dimethylaminopyridine (20 mg, 0.16 mmol, 0.1 equiv.) was then added, and the reaction mixture was cooled to 0 °C and stirred for 15 min. *N, N'*-dicyclohexylcarbodiimide (676 mg, 3.28 mmol, 2 equiv.) was then added, and the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was next filtrated, and the filtrate was concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel using hexane/dichloromethane (70:30) as the eluent to afford the title compound as a colorless oil (413.7 mg, 1.59 mmol, 97 %).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06 – 8.02 (m, 2 H), 7.58 – 7.52 (m, 1 H), 7.47 – 7.40 (m, 2 H), 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H), 4.99 (ddt, J = 17.1, 2.2, 1.6 Hz, 1 H), 4.93 (ddt, J = 10.2, 2.3, 1.2 Hz, 1 H), 4.31 (t, J =6.7 Hz, 2 H), 2.13 – 1.92 (m, 2 H), 1.84 – 1.66 (m, 2 H), 1.49 – 1.17 (m, 10 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.7, 139.2, 132.8, 130.5, 129.5, 128.3, 114.2, 65.1, 33.8, 29.4, 29.2, 29.0, 28.9, 28.7, 26.0; HRMS-ESI (+) *m/z* calcd for $C_{17}H_{25}O_2$ $[M+H]^+$ 261.1849 found 261.1859; IR (ATR, Diamond): ν (cm^{-1}) = 2926, 2854, 1718, 1452, 1269, 1111, 993, 708.

4.2.2. Allyl 4-methoxybenzoate

Following the procedure described by Mereddy and coworkers [21], Na_2CO_3 (418 mg, 3.94 mmol, 3 equiv.) was added to a solution of 4-methoxybenzoic acid (200 mg, 1.31 mmol, 1 equiv.) in dry DMSO (3.3 mL, 0.4 M). The reaction mixture was stirred at room temperature for 15 min before allyl bromide (0.11 mL, 1.31 mmol, 1 equiv.) was added. The reaction was stirred for 2 h at room temperature. Water was then added, and the mixture was extracted with Et_2O (3x) and washed with a saturated solution of $NaHCO_3$. The organic layers were combined,

dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was next purified by flash chromatography on silica gel using hexane/EtOAc (90:10) as the eluent to afford the title compound as a colorless oil (178.4 mg, 0.93 mmol, 71 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06 – 7.97 (m, 2 H), 6.96 – 6.87 (m, 2 H), 6.04 (ddt, J = 17.2, 10.5, 5.6 Hz, 1 H), 5.40 (dq, J = 17.2, 1.6 Hz, 1 H), 5.28 (dq, J = 10.4, 1.3 Hz, 1 H), 4.80 (dt, J = 5.6, 1.5 Hz, 2 H), 3.86 (s, 3 H). Analytical data were identical to those previously reported [22].

4.2.3. Allyl 4-fluorobenzoate

Following the procedure described by Mereddy and coworkers [21], Na_2CO_3 (454 mg, 4.28 mmol, 3 equiv.) was added to a solution of 4-fluorobenzoic acid (200 mg, 1.43 mmol, 1 equiv.) in DMSO (3.6 mL, 0.4 M). The reaction mixture was stirred at room temperature for 15 min before allyl bromide (0.12 mL, 1.43 mmol, 1 equiv.) was added. The reaction was stirred for 2 h at room temperature. Water was then added, and the mixture was extracted with Et_2O (3x) and washed with a saturated solution of $NaHCO_3$. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was next purified by flash chromatography on silica gel using hexane/EtOAc (90:10) as the eluent to afford the title compound as a colorless oil (185.6 mg, 1.03 mmol, 72 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.11 – 8.05 (m, 2 H), 7.15 – 7.07 (m, 2 H), 6.04 (ddt, J = 17.2, 10.5, 5.7 Hz, 1 H), 5.41 (dq, J = 17.2, 1.5 Hz, 1 H), 5.30 (dq, J = 10.5, 1.3 Hz, 1 H), 4.82 (dt, J = 5.7, 1.4 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.8 (d, J =253.7 Hz), 165.3, 132.2 (d, J =9.3 Hz), 132.1, 126.4 (d, J =3.0 Hz), 118.4, 115.5 (d, J =22.0 Hz), 65.7; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = -105.61 – -105.76 (m, 1 F); GC–MS (CI) [23]: m/z calcd for $C_{10}H_{10}FO_2$ $[M+H]^+$ 181.07 found 181.00; IR (ATR, Diamond): ν (cm^{-1}) = 3084, 2947, 1720, 1508, 1263, 1236, 852, 766.

4.2.4. Allyl 2-naphthoate

Following the procedure described by Mereddy and coworkers [21], Na_2CO_3 (369 mg, 3.48 mmol, 3 equiv.) was added to a solution of 2-naphthoic acid (200 mg, 1.16 mmol, 1 equiv.) in DMSO (2.9 mL, 0.4 M). The reaction mixture was stirred at room temperature for 15 min before allyl bromide (0.10 mL, 1.16 mmol, 1 equiv.) was added. The reaction was stirred for 2 h at room temperature. Water was then added, and the mixture was extracted with Et_2O (3x) and washed with a saturated solution of $NaHCO_3$. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was next purified by flash chromatography on silica gel using hexane/EtOAc (95:5) as the eluent to afford the title compound as a colorless oil (226 mg, 1.06 mmol, 91 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.66 – 8.59 (m, 1 H), 8.09 (dd, J = 8.6, 1.7 Hz, 1 H), 7.99 – 7.93 (m, 1 H), 7.91 – 7.85 (m, 2 H), 7.62 – 7.57 (m, 1 H), 7.56 – 7.52 (m, 1 H), 6.10 (ddt, J = 17.2, 10.5, 5.7 Hz, 1 H), 5.46 (dq, J = 17.2, 1.6 Hz, 1 H), 5.33 (dq, J = 10.4, 1.3 Hz, 1 H), 4.90 (dt, J = 5.6, 1.4 Hz, 2 H). Analytical data were identical to those previously reported [24].

4.2.5. Dec-9-en-1-yl acetate

The title compound was prepared as previously reported [11].

4.2.6. ((But-3-yn-1-yloxy)methyl)benzene

Following the procedure described by Yamada and coworkers [25], sodium hydride (79,3 mg, 60 % in mineral oil, 1.98 mmol, 1 equiv.), tetrabutylammonium iodide (60.9 mg, 0.165 mmol, 8 mol%), and benzyl bromide (0.283 mL, 2.38 mmol, 1.2 equiv.) were added to a solution of 3-butyn-1-ol (0.150 mL, 1.98 mmol 1 equiv.) in THF (1.6 mL, 1.2 M) at 0 °C. The resulting solution was stirred at 25 °C for 18 h, quenched with sat. NH_4Cl aq., and extracted with Et_2O (3×). A combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using hexane/EtOAc (5:1) as the eluent to give the title compound as a pale yellow oil in quantitative yield (32 mg, 1.98 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.35 – 7.28 (m, 5 H), 4.57 (s, 2 H), 3.60 (t, J = 6.8 Hz, 2 H), 2.50 (dt, J = 2.8, 6.8 Hz, 2 H), 1.98 (t, J = 2.8 Hz, 1 H). Analytical data were identical to those previously reported [26].

4.2.7. Pent-4-yn-1-yl benzoate

Following the procedure described by Gilmour and coworkers [27], pent-4-yl-1-ol (0.93 mL, 10 mmol, 1 equiv.) and benzoyl chloride (1.3 mL, 11 mmol, 1.1 equiv.) were dissolved in Et_2O (15 mL, 0.67 M). Et_3N (1.5 mL, 11 mmol, 1.1 equiv.) was added slowly and the reaction mixture was stirred for 24 h. The reaction mixture was diluted with EtOAc and H_2O, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the crude mixture was purified by flash chromatography on silica gel using hexane/EtOAc (98:2) as the eluent to afford the title compound as a colorless oil (1.3 g, 7.3 mmol, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.06 – 8.03 (m, 2 H), 7.58 – 7.54 (m, 1 H), 7.46 – 7.42 (m, 2 H), 4.43 (t, J =6.3 Hz, 2 H), 2.39 (td, J = 7.0, 2.7 Hz, 2 H), 2.04 – 1.98 (m, 3 H). Analytical data were identical to those previously reported [28, 29].

4.2.8. But-3-yn-1-yl benzoate

Following the procedure described by Gilmour and coworkers [27], but-3-yl-1-ol (0.38 mL, 5.0 mmol, 1 equiv.) and benzoyl chloride (0.87 mL, 7.5 mmol, 1.5 equiv.) were dissolved in Et_2O (15 mL, 0.3 M). Et_3N (1.0 mL, 7.5 mmol, 1.5 equiv.) was added slowly, and the reaction mixture was stirred for 15 h. The reaction mixture was diluted with EtOAc and H_2O, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the crude mixture was purified by flash chromatography on silica gel using hexane/EtOAc (98:2) as the eluent to afford the title compound as a colorless oil (0.40 g, 2.3 mmol, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.08 – 8.05 (m, 2 H), 7.59 – 7.55 (m, 1 H), 7.47 – 7.43 (m, 2 H), 4.43 (t, J =6.8 Hz, 2 H), 2.68 (td, J = 6.8, 2.7 Hz, 2 H), 2.03 (t, J =2.6 Hz, 1 H). Analytical data were identical to those previously reported [22].

4.2.9. But-3-yn-1-yl 4-methoxybenzoate

Following the procedure described by Gilmour and coworkers [27], but-3-yl-1-ol (0.38 mL, 5.0 mmol, 1 equiv.) and 4-methoxy benzoyl chloride (1.0 mL, 7.5 mmol, 1.5 equiv.) were dissolved in Et_2O (15 mL, 0.3 M). Et_3N (1.0 mL, 7.5 mmol, 1.5 equiv.) was added slowly, and the reaction mixture was stirred for 24 h. The reaction mixture was diluted with EtOAc and H_2O, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the crude mixture was purified by flash chromatography on silica gel using hexane/EtOAc (20:1) as the eluent to afford the title compound as a white solid (0.67 g, 3.1 mmol, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.08 – 8.03 (m, 2 H), 6.94 – 6.91 (m, 2 H), 4.40 (t, J =6.3 Hz, 2 H), 3.87 (s, 3 H), 2.66 (td, J = 7.1, 2.7 Hz, 2 H), 2.03 – 2.02 (m, 1 H). Analytical data were identical to those previously reported [22].

4.2.10. But-3-yn-1-yl adamantane-1-carboxylate

Following the procedure described by Potkin and coworkers [30], anhydrous pyridine (0,28 mL, 3.5 mmol, 1.2 equiv.) was added to a solution of 1-adamantoyl chloride (0.60 mg, 3.0 mmol, 1 equiv.) and but-3-yn-1-ol (0,23 mL, 3.0 mmol, 1 equiv.) in 70 mL of dry diethyl ether. The mixture was allowed to stir at room temperature for 24 h. The precipitate of pyridine hydrochloride was filtered off and washed with 30 mL of diethyl ether; the combined filtrates were washed with H_2O and saturated aqueous solution of sodium hydrogen carbonate. The ethereal solution was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography using 100 % hexane as the eluent to afford 73 % (0,50 g, 2.19 mmol) of the expected product as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.16 (t,

J =6.8 Hz, 2 H), 2.54 – 2.50 (m, 2 H), 2.02 – 1.98 (m, 4 H), 1.90 (d, *J* =3.0 Hz, 6 H), 1.73 – 1.70 (m, 6 H). Analytical data were identical to those previously reported [30].

4.3. General procedure for the SF_5Cl addition on alkenes

To a sealable microwave vial containing the alkene (1 equiv.) under argon was added a solution of 2,2-diphenylacetaldehyde (0.1 equiv.) in dry dichloromethane (0.1 M). Pyrrolidine (0.1 equiv.) was then added, and the reaction vial was sealed before SF_5Cl (1.5 equiv.) was added to the reaction mixture. The reaction was stirred at room temperature for 16 h under 23 W CFL lamp irradiation. The reaction was then quenched with a saturated solution of $NaHCO_3$. The phases were separated, and the organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel.

4.3.1. (2-Chloro-4-phenylbutyl)pentafluoro-λ^6-sulfane (2a)

4-phenyl-1-butene (50 mg, 0.38 mmol), 2,2-diphenylacetaldehyde (7 µL, 0.038 mmol), pyrrolidine (3 µL, 0.038 mmol), SF_5Cl (1.38 M in hexane, 0.41 mL, 0.57 mmol) and dichloromethane (3.8 mL) were engaged in general procedure to afford the title compound as a colorless oil (87.5 mg, 0.30 mmol, 78 %) after purification by flash chromatography using hexane/EtOAc (98:2) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.33 – 7.29 (m, 2 H), 7.26 – 7.17 (m, 3 H), 4.30 (dtd, *J* = 9.6, 6.3, 3.3 Hz, 1 H), 4.09 – 3.97 (m, 1 H), 3.96 – 3.83 (m, 1 H), 2.98 – 2.89 (m, 1 H), 2.79 (ddd, *J* = 13.8, 8.9, 7.4 Hz, 1 H), 2.32 – 2.20 (m, 1 H), 2.04 (dtd, *J* = 14.3, 9.3, 4.9 Hz, 1 H); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 84.8 – 79.9 (m, 1 F), 66.4 (dt, *J* = 146.5, 8.1 Hz, 4 F). Analytical data were identical to those previously reported [31].

4.3.2. 1-Chloro-2-(pentafluoro-λ^6-sulfanyl)ethyl benzoate (2b)

Vinyl benzoate (50 mg, 0.34 mmol), 2,2-diphenylacetaldehyde (6 µL, 0.034 mmol), pyrrolidine (3 µL, 0.034 mmol), SF_5Cl (1.48 M in hexane, 0.34 mL, 0.51 mmol) and dichloromethane (3.4 mL) were engaged in general procedure to afford the tittle compound as a colorless oil (68.8 mg, 0.22 mmol, 66 %) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.09 – 8.05 (m, 2 H), 7.67 – 7.62 (m, 1 H), 7.52 – 7.47 (m, 2 H), 7.14 (dd, *J* = 9.8, 2.1 Hz, 1 H), 4.48 – 4.38 (m, 1 H), 4.25 – 4.17 (m, 1 H); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 81.4 – 80.1 (m, 1 F), 66.7 (dt, *J* = 147.2, 8.1 Hz, 4 F). Analytical data were identical to those previously reported [11].

4.3.3. 9-Chloro-10-(pentafluoro-λ^6-sulfanyl)decyl benzoate (2c)

Dec-9-en-1-yl benzoate (100 mg, 0.38 mmol), 2,2-diphenylacetaldehyde (7 µL, 0.038 mmol), pyrrolidine (3 µL, 0.038 mmol), SF_5Cl (1.18 M in hexane, 0.49 mL, 0.58 mmol) and dichloromethane (3.8 mL) were engaged in general procedure to afford the title compound as a colorless oil (132.6 mg, 0.31 mmol, 81 %) after purification by flash chromatography using hexane/CH_2Cl_2 (70:30) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.08 – 7.98 (m, 2 H), 7.59 – 7.51 (m, 1 H), 7.47 – 7.40 (m, 2 H), 4.41 – 4.22 (m, 3 H), 4.04 – 3.95 (m, 1 H), 3.95 – 3.82 (m, 1 H), 1.98 – 1.82 (m, 1 H), 1.84 – 1.66 (m, 3 H), 1.62 – 1.51 (m, 1 H), 1.50 – 1.41 (m, 3 H), 1.40 – 1.29 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.7, 132.8, 130.5, 129.5, 128.3, 77.0 (p, *J* =13.1 Hz), 65.0, 55.8 (p, *J* =4.3 Hz), 37.5, 29.2, 29.1, 28.69, 28.68, 26.0, 25.9; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 84.9 – 80.5 (m, 1 F), 66.2 (dt, *J* = 146.4, 8.1 Hz, 4 F); HRMS-ESI (+) *m/z* calcd for $C_{17}H_{25}ClF_5O_2S$ $[M+H]^+$ 423.1202 found 423.1178; IR (ATR, Diamond): ν (cm^{-1}) = 2932, 2858, 1717, 1273, 1111, 1070, 839, 710.

4.3.4. 2-Chloro-3-(pentafluoro-λ^6-sulfanyl)propyl 4-methoxybenzoate (2d)

Allyl 4-methoxybenzoate (87.1 mg, 0.45 mmol), 2,2-diphenylacetaldehyde (8 µL, 0.045 mmol), pyrrolidine (4 µL, 0.045 mmol), SF_5Cl (1.18 M in hexane, 0.58 mL, 0.68 mmol) and dichloromethane (4.5 mL) were engaged in general procedure to afford the title compound as a colorless oil (124.7 mg, 0.35 mmol, 78 %) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.02 – 7.97 (m, 2 H), 6.97 – 6.93 (m, 2 H), 4.73 – 4.64 (m, 1 H), 4.58 (dd, *J* = 11.9, 5.1 Hz, 1 H), 4.52 (dd, *J* = 11.9, 5.7 Hz, 1 H), 4.22 – 4.12 (m, 1 H), 4.08 – 3.97 (m, 1 H), 3.88 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.4, 163.9, 131.9, 121.3, 113.9, 73.4 (p, *J* =14.9 Hz), 65.7, 55.5, 52.3 (p, *J* =4.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 86.9 – 72.9 (m, 1 F), 66.8 (dt, *J* = 146.8, 7.9 Hz, 4 F); HRMS-ESI (+) *m/z* calcd for $C_{11}H_{13}ClF_5O_3S$ $[M+H]^+$ 355.0189 found 355.0209; IR (ATR, Diamond): ν (cm^{-1}) = 2972, 2843, 1717, 1605, 1254, 1167, 816, 766.

4.3.5. 2-Chloro-3-(pentafluoro-λ^6-sulfanyl)propyl 4-fluorobenzoate (2e)

Allyl 4-fluorobenzoate (50 mg, 0.28 mmol), 2,2-diphenylacetaldehyde (5 µL, 0.028 mmol), pyrrolidine (2 µL, 0.028 mmol), SF_5Cl (1.18 M in hexane, 0.35 mL, 0.42 mmol) and dichloromethane (2.8 mL) were engaged in general procedure to afford the title compound as a colorless oil (65.2 mg, 0.19 mmol, 69 %) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.10 – 8.03 (m, 2 H), 7.18 – 7.13 (m, 2 H), 4.75 – 4.66 (m, 1 H), 4.58 (dd, *J* = 5.3, 2.1 Hz, 2 H), 4.21 – 4.10 (m, 1 H), 4.09 – 3.99 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.0 (d, *J* =315.8 Hz), 165.2, 132.4 (d, *J* =9.5 Hz), 125.3 (d, *J* =3.0 Hz), 115.9 (d, *J* =22.0 Hz), 73.3 (p, *J* =15.0 Hz), 66.1, 52.2 (p, *J* =4.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.1 – 80.3 (m, 1 F), 66.8 (dt, *J* = 146.7, 7.9 Hz, 4 F), -104.1 – -104.3 (m, 1 F); GC–MS (CI) [19]: *m/z* calcd for $C_{10}H_{10}ClF_6O_2S$ $[M+H]^+$ 343.00 found 343.07; IR (ATR, Diamond): ν (cm^{-1}) = 1726, 1603, 1508, 1261, 1119, 1090, 818, 638.

4.3.6. 2-Chloro-3-(pentafluoro-λ^6-sulfanyl)propyl 2-naphthoate (2f)

Allyl 2-naphthoate (100 mg, 0.47 mmol), 2,2-diphenylacetaldehyde (8 µL, 0.047 mmol), pyrrolidine (4 µL, 0.047 mmol), SF_5Cl (1.18 M in hexane, 0.60 mL, 0.71 mmol) and dichloromethane (4.7 mL) were engaged in general procedure to afford the title compound as a colorless oil (85.3 mg, 0.23 mmol, 48 %) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.68 – 8.53 (m, 1 H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1 H), 8.01 – 7.96 (m, 1 H), 7.93 – 7.88 (m, 2 H), 7.63 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1 H), 7.58 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1 H), 4.80 – 4.72 (m, 1 H), 4.70 – 4.55 (m, 2 H), 4.28 – 4.16 (m, 1 H), 4.16 – 4.01 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.8, 135.8, 132.4, 131.6, 129.5, 128.7, 128.5, 127.9, 126.9, 126.2, 125.0, 73.4 (p, *J* =14.8 Hz), 66.1, 52.2 (p, *J* =4.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.9 – 79.9 (m, 1 F), 66.8 (dt, *J* = 146.7, 7.9 Hz, 4 F); HRMS-ESI (+) *m/z* calcd for $C_{14}H_{13}ClF_5O_2S$ $[M+H]^+$ 375.0239 found 375.0259; IR (ATR, Diamond): ν (cm^{-1}) = 3063, 2974, 1720, 1277, 1194, 1130, 818, 638.

4.3.7. Ethyl 4-chloro-2-methyl-5-(pentafluoro-λ^6-sulfanyl)pentanoate (2 g)

Ethyl 2-methylpent-4-enoate (50 mg, 0.35 mmol), 2,2-diphenylacetaldehyde (6 µL, 0.035 mmol), pyrrolidine (3 µL, 0.035 mmol), SF_5Cl (1.48 M in hexane, 0.36 mL, 0.53 mmol) and dichloromethane (3.5 mL) were engaged in general procedure to afford the title compound as a colorless oil (33.3 mg, 0.11 mmol, 31 %) in a 51:49 diastereoisomeric mixture after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.51 – 4.43 (m, 1H, dia a), 4.42 – 4.34 (m, 0.95H, dia b), 4.17 (app. p, *J* =7.1 Hz, 3.90H, dia a + b), 4.08 – 3.97 (m, 2H, dia a), 3.97 – 3.84 (m, 1.90H, dia b), 2.91 – 2.81 (m, 1H, dia a), 2.80 – 2.72 (m, 0.95H, dia b), 2.35 (ddd, *J* = 13.8, 10.7, 2.7 Hz, 0.95H, dia a), 2.23 – 2.12 (m, 1H, dia a), 2.05 – 1.94 (m, 0.95H, dia b), 1.68 (ddd, *J* = 14.3, 11.0, 3.2 Hz, 1H, dia a), 1.27 (td, *J* = 7.1, 1.5 Hz, 5.85H, dia a + b), 1.24 (d, *J* =7.2 Hz, 3H, dia a), 1.22 (d, *J* =7.0 Hz, 2.85H, dia b); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.7 – 82.0 (m, 1.95 F, dia a + b), 66.6 (dt, *J* = 147.1, 8.2 Hz, 4 F, dia a), 66.5 (dt, *J* = 146.5, 8.2 Hz, 3.8 F, dia b). Analytical data were identical to

those previously reported [32].

4.3.8. (3-(Benzyloxy)-2-chloropropyl)pentafluoro-λ^6-sulfane (2 h)

((allyloxy)methyl)benzene (50 mg, 0.34 mmol), 2,2-diphenylacetaldehyde (6 μL, 0.034 mmol), pyrrolidine (3 μL, 0.034 mmol), SF_5Cl (1.48 M in hexane, 0.34 mL, 0.51 mmol) and dichloromethane (3.4 mL) were engaged in general procedure to afford the title compound as a colorless oil (58.5 mg, 0.19 mmol, 56 %) after purification by flash chromatography using hexane/CH_2Cl_2 (80:20) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 – 7.34 (m, 2 H), 7.36 – 7.29 (m, 3 H), 4.59 (s, 2 H), 4.47 (ddt, J = 7.8, 6.7, 4.4 Hz, 1 H), 4.31 – 4.23 (m, 1 H), 3.92 – 3.81 (m, 1 H), 3.76 (dd, J = 10.5, 4.6 Hz, 1 H), 3.60 (dd, J = 10.4, 6.7 Hz, 1 H); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 84.1 – 81.6 (m, 1 F), 66.6 (dt, J = 146.8, 8.1 Hz, 4 F). Analytical data were identical to those previously reported [33].

4.3.9. (2-Chloro-2-phenylethyl)pentafluoro-λ^6-sulfane (2i)

Styrene (51 mg, 0.49 mmol), 2,2-diphenylacetaldehyde (8 μL, 0.049 mmol), pyrrolidine (4 μL, 0.049 mmol), SF_5Cl (1.48 M in hexane, 0.50 mL, 0.73 mmol) and dichloromethane (4.9 mL) were engaged in general procedure to afford the title compound as a colorless oil (68 mg, 0.25 mmol, 52 %) after purification by flash chromatography using 100 % hexane as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.41 – 7.37 (m, 5 H), 5.36 (t, J =6.8 Hz, 1 H), 4.36 – 4.24 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 138.5, 129.4, 129.1, 126.9, 56.4, 56.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 84.3 – 79.5 (m, 1 F), 66.4 (dt, J = 147.4, 8.1 Hz, 4 F). GC–MS (EI) [19]: m/z calcd for $C_8H_8ClF_5S$ $[M]^+$ 266.00 found 266.13; IR (ATR, Diamond): ν (cm^{-1}) = 2930, 1458, 1184, 949, 876, 849, 816, 694.

4.3.10. (2-(4-(tert-butyl)phenyl)-2-chloroethyl)pentafluoro-λ^6-sulfane (2 j)

1-(*tert*-butyl)-4-vinylbenzene (50 mg, 0.31 mmol), 2,2-diphenylacetaldehyde (6 μL, 0.031 mmol), pyrrolidine (3 μL, 0.031 mmol), SF_5Cl (1.18 M in hexane, 0.40 mL, 0.47 mmol) and dichloromethane (3.1 mL) were engaged in general procedure to afford the title compound as a yellow oil (46 mg, 0.14 mmol, 46 %) after purification by flash chromatography using 100 % hexane as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.42 – 7.40 (m, 2 H), 7.32 – 7.30 (m, 2 H), 5.37 – 5.34 (m, 1 H), 4.33 – 4.23 (m, 2 H), 1.31 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 152.6, 135.4, 126.5, 126.0, 56.4, 56.3, 56.2, 34.7, 31.2; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 82.3 – 82.0 (m, 1 F), 66.3 (dt, J = 147.2, 7.8 Hz, 4 F). GC–MS (EI) [19]: m/z calcd for $C_8H_8ClF_5S$ $[M]^+$ 322.06 found 322.27; IR (ATR, Diamond): ν (cm^{-1}) = 2966, 1396, 1202, 1109, 879, 816, 783, 679.

4.3.11. 9-Chloro-10-(pentafluoro-λ^6-sulfanyl)decyl acetate (2l)

Dec-9-en-1-yl acetate (50 mg, 0.25 mmol), 2,2-diphenylacetaldehyde (4 μL, 0.025 mmol), pyrrolidine (2 μL, 0.025 mmol), SF_5Cl (1.48 M in hexane, 0.26 mL, 0.38 mmol) and dichloromethane (2.5 mL) were engaged in general procedure to afford the title compound as a colorless oil (48.7 mg, 0.13 mmol, 53 %) after purification by flash chromatography using hexane/EtOAc (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.38 – 4.32 (m, 1 H), 4.06 (t, J =6.8 Hz, 2 H), 4.03 – 3.96 (m, 1 H), 3.95 – 3.84 (m, 1 H), 2.05 (s, 3 H), 1.97 – 1.82 (m, 1 H), 1.79 – 1.68 (m, 1 H), 1.67 – 1.50 (m, 3 H), 1.49 – 1.44 (m, 1 H), 1.38 – 1.25 (m, 8 H); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 84.8 – 79.7 (m, 1 F), 66.2 (dt, J = 146.4, 8.1 Hz, 4 F). Analytical data were identical to those previously reported [7b].

4.3.12. (4-Bromo-2-chlorobutyl)pentafluoro-λ^6-sulfane (2 m)

4-Bromobut-1-ene (53 mg, 0.39 mmol), 2,2-diphenylacetaldehyde (7 μL, 0.039 mmol), pyrrolidine (3 μL, 0.039 mmol), SF_5Cl (1.48 M in hexane, 0.40 mL, 0.58 mmol) and dichloromethane (3.9 mL) were engaged in general procedure to afford the title compound as a colorless oil (59 mg, 0.20 mmol, 51 %) after purification by flash chromatography using hexane/Et_2O (96:4) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.64 – 4.59 (m, 1 H), 4.12 – 4.05 (m, 1 H), 3.96 – 3.88 (m, 1 H), 3.61 – 3.59 (m, 2 H), 2.45–2.51 (m,1 H), 2.27 – 2.17 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 39.7, 30.3, 29.7, 28.6; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.2 – 82.0 (m, 1 F), 66.8 (dt, J = 146.7, 8.2 Hz, 4 F); GC–MS (EI) [19]: m/z calcd for $C_4H_7BrClF_5S$ $[M]^+$ 295.91 found 296.20; IR (ATR, Diamond): ν (cm^{-1}) = 2932, 1493, 1448, 1084, 837, 754, 696, 652.

4.4. General procedure for the SF_5Cl addition on alkynes

To a sealable microwave vial containing the alkyne (1 equiv.) under argon was added a solution of 2,2-diphenylacetaldehyde (0.1 equiv.) in dry diethyl ether (0.1 M). Pyrrolidine (0.1 equiv.) was then added, and the reaction vial was sealed before SF_5Cl (3.0 equiv.) was added to the reaction mixture. The reaction was stirred at room temperature for 16 h under 23 W CFL lamp irradiation. The reaction was then quenched with a saturated solution of $NaHCO_3$. The phases were separated, and the organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel.

4.4.1. (Z)-(4-(benzyloxy)-2-chlorobut-1-en-1-yl)pentafluoro-λ^6-sulfane (4a)

((but-3-yn-1-yloxy)methyl)benzene (23 mg, 0.14 mmol), 2,2-diphenylacetaldehyde (2 μL, 0.014 mmol), pyrrolidine (1 μL, 0.014 mmol), SF_5Cl (1.38 M in hexane, 0.30 mL, 0.42 mmol) and diethyl ether (1.4 mL) were engaged in general procedure to afford the title compound as a colorless oil (30 mg, 0.09 mmol, 66 %) after purification by flash chromatography using hexane/Et_2O (97:3) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.37 – 7.29 (m, 5 H), 6.69 (d, J =7.2 Hz, 1 H), 4.53 (s, 2 H), 3.87 (s, 3 H), 3.73 (t, J = 6.7, 2 H), 3.04 – 3.02 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 144.1 (q, J = 6.3), 138.5 (q, J = 21.4), 137.8, 128.4, 127.7, 127.5, 73.0, 66.5, 36.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.0 – 81.7 (m, 1 F), 67.8 (dd, J = 151.5, 8.3 Hz, 4 F). HRMS-ESI (+) m/z calcd for $C_{11}H_{13}ClF_5OS$ $[M+H]^+$ 322.0281 found 322.0278; IR (ATR, Diamond): ν (cm^{-1}) = 2957, 2897, 1443, 1246, 1057, 831, 754, 689.

4.4.2. (Z)-(2-chloro-3-phenylprop-1-en-1-yl)pentafluoro-λ^6-sulfane (4b)

4-phenyl-1-butyne (18 mg, 0.14 mmol), 2,2-diphenylacetaldehyde (2 μL, 0.014 mmol), pyrrolidine (1 μL, 0.014 mmol), SF_5Cl (1.48 M in hexane, 0.28 mL, 0.41 mmol) and diethyl ether (1.4 mL) were engaged in general procedure to afford the title compound as a colorless oil (33 mg, 0.11 mmol, 80 %) after purification by flash chromatography using 100 % hexane as the eluent.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.33 – 7.30 (m, 2 H), 7.25 – 7.20 (m, 3 H), 6.64 (p, J =8.2 Hz, 1 H), 2.98 – 2.91 (m, 4 H); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 85.2 – 82.7 (m, 1 F), 67.3 (dd, J = 151.5, 8.2 Hz, 4 F). Analytical data were identical to those previously reported [11].

4.4.3. (Z),(E)-(2-chloro-5-phenylpent-1-en-1-yl)pentafluoro-λ^6-sulfane (4c)

4-phenyl-1-pentyne (29 mg, 0.20 mmol), 2,2-diphenylacetaldehyde (4 μL, 0.020 mmol), pyrrolidine (2 μL, 0.020 mmol), SF_5Cl (1.48 M in hexane, 0.40 mL, 0.60 mmol) and diethyl ether (2.0 mL) were engaged in general procedure to afford the title compound as a mixture of inseparable (*Z*) and (*E*) products (75:25) as a yellow oil (51 mg, 0.17 mmol, 84 %) after purification by flash chromatography using 100 % hexane as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) (*Z*):(*E*): δ (ppm) = 7.45–7.46 (m, 1 H), 7.30 – 7.28 (m, 2 H), 7.22 – 7.17 (m, 3 H), 6.77 (p, J =9.3 Hz, 1 H), 6.62 (p, J =8.3 Hz, 1 H), 2.90 (t, J =5.7 Hz, 2 H), 2.84 (t, J =6.3 Hz, 2 H), 2.72 (t, J =7.8 Hz, 2 H), 2.67 (t, J =7.7 Hz, 2 H), 2.00 – 1.95 (m, 2 H), 1.94 – 1.88 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 140.9, 137.2, 137.1, 129.8, 129.4, 128.4, 128.3,

126.5, 126.1, 125.0, 35.5, 35.0, 29.5, 28.8, 22.4; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 88.0 – 85.1 (m, 1 F), 84.5 – 80.1 (m, 1 F), 67.4 (dd, J = 151.4, 8.4 Hz, 4 F), 67.3 (dd, J = 150.1, 9.4 Hz, 4 F). GC–MS (EI) [19]: *m/z* calcd for $C_{11}H_{12}ClF_5S$ $[M]^+$ 306.03 found 305.93; IR (ATR, Diamond): ν (cm^{-1}) = 2930, 1497, 1454, 1088, 887, 829, 716, 698.

4.4.4. (Z)-4-chloro-5-(pentafluoro-λ^6-sulfanyl)pent-4-en-1-yl benzoate (4d)

Pent-4-yn-1-yl benzoate (20 mg, 0.10 mmol), 2,2-diphenylacetaldehyde (2 μL, 0.010 mmol), pyrrolidine (1 μL, 0.010 mmol), SF_5Cl (1.48 M in hexane, 0.21 mL, 0.30 mmol) and diethyl ether (1.0 mL) were engaged in general procedure to afford the title compound as a colorless oil (28 mg, 0.08 mmol, 81 %) after purification by flash chromatography using hexane/Et_2O (95:5) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.05 – 8.03 (m, 2 H), 7.59 – 7.56 (m, 1 H), 7.45 (td, J = 7.8, 1.5 Hz, 2 H), 6.66 (p, J =8.2 Hz, 1 H), 4.38 (td, J = 6.1, 1.5 Hz, 2 H), 2.90 (t, J =7.7 Hz, 2 H), 2.17 – 2.11 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.4, 137.6, 137.5, 137.3, 133.0, 129.9, 129.5, 128.4, 63.5, 32.9, 26.5; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.2 – 81.9 (m, 1 F), 67.3 (dd, J = 151.1, 8.4 Hz, 4 F). HRMS-ESI (+) *m/z* calcd for $C_{12}H_{13}ClF_5O_2S$ $[M+H]^+$ 351.0239 found 351.0247; IR (ATR, Diamond): ν (cm^{-1}) = 3078, 2964, 1718, 1452, 1269, 835, 708, 640.

4.4.5. (Z)-3-chloro-4-(pentafluoro-λ^6-sulfanyl)but-3-en-1-yl benzoate (4e)

But-3-yn-1-yl benzoate (19 mg, 0.11 mmol), 2,2-diphenylacetaldehyde (2 μL, 0.011 mmol), pyrrolidine (1 μL, 0.011 mmol), SF_5Cl (1.48 M in hexane, 0.22 mL, 0.33 mmol) and diethyl ether (1.1 mL) were engaged in general procedure to afford the title compound as a colorless oil (27 mg, 0.08 mmol, 72 %) after purification by flash chromatography using hexane/Et_2O (98:02) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.03 (dd, J =8.4 Hz, 1.3 Hz, 2 H), 7.63 – 7.51 (m, 1 H), 7.45 (m, 2 H), 6.77 (p, J =8.2 Hz, 1 H), 4.61 (t, J =6.2 Hz, 2 H), 3.19 (t, J =6.5 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.2, 133.2, 129.6, 128.4, 60.8, 35.1, 30.3, 29.7; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 83.2 – 81.9 (m, 1 F), 67.3 (dd, J = 151.3, 8.2 Hz, 4 F). GC–MS (CI) [19]: *m/z* calcd for $C_{11}H_{11}ClF_5O_2S$ $[M+H]^+$ 337.00 found 336.93; IR (ATR, Diamond): ν (cm^{-1}) = 2932, 1718, 1452, 1269, 1117, 839, 708, 642.

4.4.6. (Z)-3-chloro-4-(pentafluoro-λ^6-sulfanyl)but-3-en-1-yl 4-methoxybenzoate (4f)

But-3-yn-1-yl 4-methoxybenzoate (23 mg, 0.11 mmol), 2,2-diphenylacetaldehyde (2 μL, 0.011 mmol), pyrrolidine (1 μL, 0.011 mmol), SF_5Cl (1.48 M in hexane, 0.23 mL, 0.33 mmol) and diethyl ether (1.1 mL) were engaged in general procedure to afford the title compound as a yellow solid (35 mg, 0.1 mmol, 86 %) after purification by flash chromatography using hexane/Et_2O (95:5) as the eluent. m.p. = 53.3–54.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, J =7.6 Hz, 2 H), 6.93 (d, J =7.5 Hz, 2 H), 6.76 (p, J =8.1 Hz, 1 H), 4.57 (td, J = 6.2, 1.4 Hz, 2 H), 3.87 (s, 3 H), 3.17 (t, J =6.2 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.9, 163.5, 131.6, 113.7, 60.5, 55.4, 35.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 82.9 – 81.6 (m, 1 F), 67.7 (dd, J = 151.5, 8.2 Hz, 4 F). HRMS-ESI (+) *m/z* calcd for $C_{12}H_{13}ClF_5O_3S$ $[M+H]^+$ 367.0189 found 367.0196 ; IR (ATR, Diamond): ν (cm^{-1}) = 3080, 2903, 1717, 1512, 1252, 1097, 818, 717.

4.4.7. (Z)-3-chloro-4-(pentafluoro-λ^6-sulfanyl)but-3-en-1-yl adamantane-1-carboxylate (4 g)

But-3-yn-1-yl adamantane-1-carboxylate (27 mg, 0.11 mmol), 2,2-diphenylacetaldehyde (2 μL, 0.011 mmol), pyrrolidine (1 μL, 0.011 mmol), SF_5Cl (1.48 M in hexane, 0.23 mL, 0.33 mmol) and diethyl ether (1.1 mL) were engaged in general procedure to afford the title compound as a colorless oil (22 mg, 0.06 mmol, 51 %) after purification by flash chromatography using 100 % hexane as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.73 (p, J =8.1 Hz, 1 H), 4.32 (t, J = 6.2, 2 H), 3.04 (t, J = 6.1, 2 H), 2.02 – 2.00 (m, 3 H), 1.87 (d, J = 2.9, 6 H), 1.74 – 1.67 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = δ 177.3, 139.1, 139.0, 59.9, 40.7, 38.6, 36.4, 34.8, 34.7, 27.8; ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 82.8 – 81.5 (m, 1 F), 67.6 (dd, J = 151.4, 8.2 Hz, 4 F). GC–MS (CI) [19]: *m/z* calcd for $C_{15}H_{21}ClF_5O_2S$ $[M+H]^+$ 395.08 found 395.27; IR (ATR, Diamond): ν (cm^{-1}) = 2907, 2854, 1726, 1454, 1230, 1074, 825, 717.

4.4.8. (Z)-(2-chloro-2-phenylvinyl)pentafluoro-λ^6-sulfane (4 h)

Phenylacetylene (32 mg, 0.31 mmol), 2,2-diphenylacetaldehyde (6 μL, 0.031 mmol), pyrrolidine (2 μL, 0.031 mmol), SF_5Cl (1.18 M in hexane, 0.53 mL, 0.93 mmol) and diethyl ether (3.1 mL) were engaged in general procedure to afford the title compound as a colorless oil (27 mg, 0.10 mmol, 33 %) after purification by flash chromatography using 100 % hexane as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.43 – 7.39 (m, 3 H), 7.37 – 7.34 (m, 2 H), 6.93 (p, J =7.6 Hz, 1 H); ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) = 81.9 – 80.6 (m, 1 F), 69.0 (dd, J = 152.9, 7.6 Hz, 4 F). Analytical data were identical to those previously reported [11].

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgments

We acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), OmegaChem and Université Laval.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfluchem.2021.109734.

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