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Fang-Fang Feng, Jun-An Ma, Dominique Cahard. Radical 1,5-Chloropentafluorosulfanylation of Unactivated Vinylcyclopropanes and Transformation into  $\alpha$ -SF 5 Ketones. *Journal of Organic Chemistry*, In press, 10.1021/acs.joc.1c01886 . hal-03357178

**HAL Id: hal-03357178**

**<https://hal.science/hal-03357178v1>**

Submitted on 30 Sep 2021

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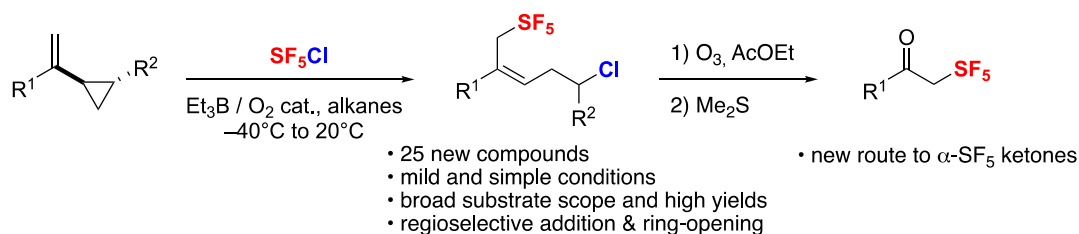
# Radical 1,5-Chloropentafluorosulfanylation of Unactivated Vinylcyclopropanes and Transformation into $\alpha$ -SF<sub>5</sub> Ketones

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Supporting Information Placeholder

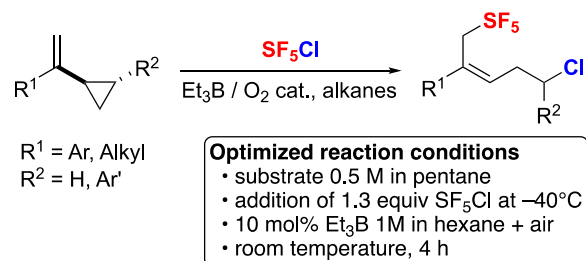


**ABSTRACT:** The radical 1,5-chloropentafluorosulfanylation of vinyl cyclopropanes (VCPs) initiated by Et<sub>3</sub>B/O<sub>2</sub> affords allylic pentafluorosulfanyl / homoallylic chloride products through ring-strain release of the cyclopropane. The VCP substitution pattern was investigated. The utility of this reaction was illustrated in post-transformation of the C=C bond by ozonolysis giving access to valuable  $\alpha$ -SF<sub>5</sub> carbonyl compounds.

Vinyl cyclopropane (VCP) is an all-carbon multifaceted scaffold of great interest for the installation of elements and a diversity of functional groups in straightforward synthetic transformations.<sup>1</sup> The substitution pattern of VCPs strongly impacts the reactivity and reaction possibilities with nucleophilic, electrophilic or radical partners. Activated VCPs, which typically feature two geminal electron-withdrawing substituents (EWS) on the cyclopropane ring to ease ring-opening reactions, react with the aid of transition-metal catalysts to form zwitterionic  $\pi$ -allylmetal intermediates that subsequently engage in allylic substitutions, addition reactions or cycloaddition reactions.<sup>2</sup> In sharp contrast, unactivated VCPs lacking EWS less favourably form 1,3-dipoles in the presence of metal catalysts and prefer to undergo oxidative addition to form a metallacycle intermediate for subsequent annulation reactions.<sup>3</sup> Unactivated VCPs, as five-carbon synthons, were explored in a number of transition-metal catalyzed 1,5-difunctionalization reactions, *e.g.* Ni-catalyzed silaboration,<sup>4</sup> Fe-catalyzed hydroboration,<sup>5</sup> Fe-catalyzed dicarbofunctionalization,<sup>6</sup> Rh-catalyzed nitrene-transfer,<sup>7</sup> Cu-catalyzed cyanotrifluoromethylation,<sup>8</sup> Au-catalyzed hydroamination,<sup>9</sup> and Ir-catalyzed bromotrichloromethylation.<sup>10</sup> In addition, an organocatalytic (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B-catalyzed ionic hydrosilylation<sup>11</sup> and a visible-light-promoted hydrotrifluoromethylation<sup>12</sup> have been developed. In mechanistic studies, the VCP scaffold is widely used as radical probe but the 1,5-difunctionalized products are clearly not central to the research works.<sup>13</sup> Remote 1,5-difunctionalization of unactivated VCPs with concomitant creation of a C–S bond has been reported in 1974 by reaction of arylsulfenyl chloride

with VCPs through a carbonium ion intermediate<sup>14</sup> and recently in 2020 in a photo-mediated organocatalytic radical 1,5-trifluoromethylthio-sulfonylation.<sup>15</sup> Other examples of C–S bond formation starting from the VCP motif could be found in mechanistic studies of various reactions exploiting VCPs as radical probes.<sup>16</sup> In order to increase the diversity of sulfur-containing products accessible from VCPs, we herein report that exposure of unactivated VCPs to pentafluorosulfanyl chloride under metal-free conditions in the presence of a radical initiator resulted in an efficient, atom-economic 1,5-chloropentafluorosulfanylation reaction (Scheme 1).

**Scheme 1. Radical pentafluorosulfanylation of VCPs.<sup>a</sup>**



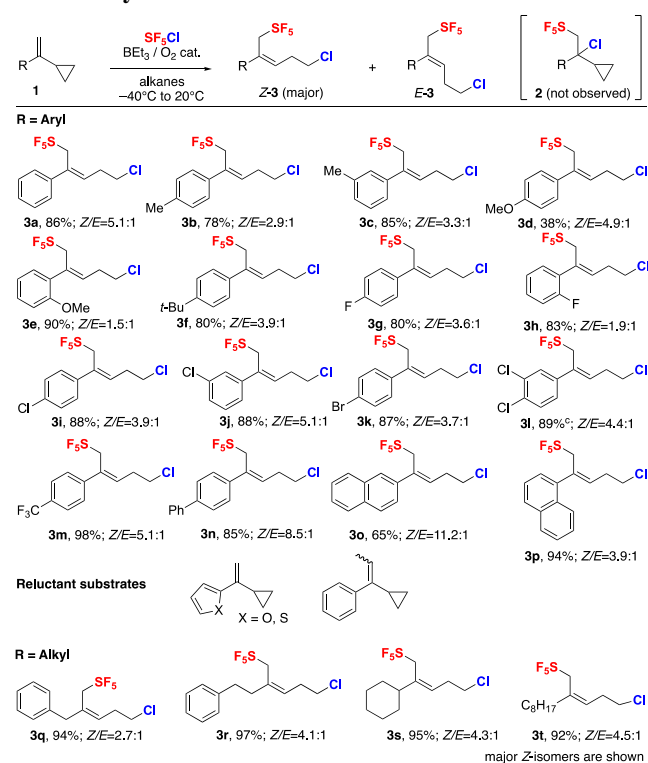
<sup>a</sup> See the experimental section for detailed procedures.

Our choice for the fluorine-containing SF<sub>5</sub> motif was motivated by its emerging position in the ever more vibrant field of organofluorine chemistry. Indeed, the incremental progress of the SF<sub>5</sub> chemistry has demonstrated that installation of a SF<sub>5</sub>

group on an organic molecule deeply influences its chemical and physical properties (reactivity, metabolic stability, membrane permeability, aqueous solubility, pKa, Log *D*, ...).<sup>17</sup> Nevertheless, the number of SF<sub>5</sub>-containing molecules is still rather small and a particular focus is given to SF<sub>5</sub>-substituted (hetero)aromatics<sup>18</sup> while aliphatic SF<sub>5</sub> derivatives are less investigated.<sup>19</sup> In this context, expanding the chemical space of SF<sub>5</sub>-containing aliphatic compounds offers wide opportunities. Specifically, we have used pentafluorosulfanyl chloride in a radical chain addition process to VCPs in the presence of the couple Et<sub>3</sub>B/O<sub>2</sub> as a catalytic initiator.

SF<sub>5</sub>Cl is a colorless gas (Bp -21°C) commercially available from rare suppliers or prepared in the lab according to a recent procedure.<sup>20</sup> It can be easily condensed in hexane and the solutions are kept in a freezer for weeks. Since the demonstration by Dolbier and Ait-Mohand in 2002 that Et<sub>3</sub>B/O<sub>2</sub> acts as an efficient SF<sub>5</sub> radical initiator, the method has become prevalent in the free radical chain addition of SF<sub>5</sub>• to unsaturations.<sup>21a-c</sup> Note that the combination Et<sub>3</sub>B/O<sub>2</sub> also served in the transfer of pyridine tetrafluorosulfanyl chloride to alkenes and alkynes,<sup>21d</sup> albeit it was later demonstrated that these precise reactions performed spontaneously without catalyst.<sup>21e</sup> It is therefore only natural that we carried out our study with the couple Et<sub>3</sub>B/O<sub>2</sub> keeping in mind to evaluate the requirement of it. By selecting the unactivated VCPs **1** as substrates, which feature the vinyl group as radical accepting group and an aryl or an alkyl substituent as radical stabilizing group, we anticipated that one issue would be the participation or not of the cyclopropane ring to the chain process; in other words, either the 1,2-addition product **2** or the 1,5-addition product **3** could possibly formed (Scheme 2).

### Scheme 2. Scope I of the pentafluorosulfanylation of VCPs: vinyl substituent effect.<sup>a,b</sup>

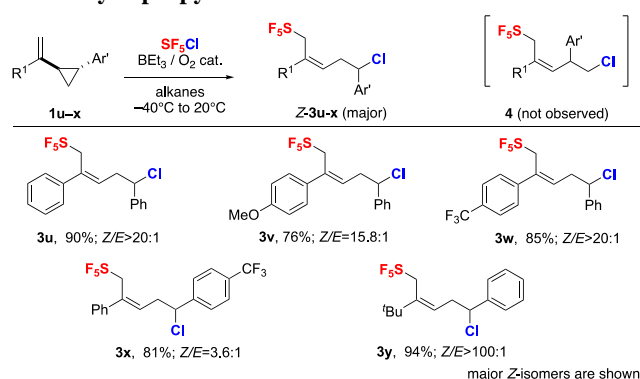


<sup>a</sup> See experimental section for detailed procedures. <sup>b</sup> Z/E ratios were determined on crude reaction mixtures. <sup>c</sup> Two equivalents of SF<sub>5</sub>Cl were required to reach full conversion.

The experiments demonstrated the obtention of **3** as single regioisomer with Z/E ratios depending on the substitution pattern of substrates **1**. The Z-isomer was assigned as the major isomer by 2D NOESY NMR of product **3n** and X-ray crystal analysis of product **3o**.<sup>22</sup> Consistently, high yields were achieved with the variously substituted phenyl groups in **3a-p** with one exception (**3d** was obtained in 38% yield). Halogens (F, Cl, Br), alkyls (Me, *t*-Bu), aryl (Ph, Naphth), EDG and EWG groups (MeO, CF<sub>3</sub>) at different ring positions are compatible with the reaction conditions. Nevertheless, we identified reluctant substrates that are heteroaryl-containing VCPs as well as a VCP featuring a trisubstituted olefin moiety (Scheme 2). In the cases of 2-furyl- and 2-thiophenyl-derived VCPs, the substrates were fully consumed yet not in the expected allylic SF<sub>5</sub> products. The reaction conditions were modified, in particular by using other solvents. In ethyl acetate, two major products were identified resulting in 1,5-acetylchlorination and 1,5-chlorofluorination. The required acetyl radical was generated by homolytic cleavage of EtOAc and the fluorine radical was formed together with SF<sub>4</sub> (detected by <sup>19</sup>F NMR) during the decomposition of SF<sub>5</sub> radical. Possibly, the Lewis acidity of triethylborane was an issue for these heteroaryl substrates. Alkyl-substituted VCPs gave even higher yields (92-97%) in 1,5-chloropentafluorosulfanylated products **3q-t** (Scheme 2). The explanation could be that the tertiary radical intermediates are less stabilized than the benzylic radical issued of aryl substituted VCPs and thus they more easily promote the radical-mediated cyclopropane ring-opening reaction affording the homoallylic primary radical (see later in the text Scheme 4).

A further scope investigation was carried out with disubstituted *trans*-cyclopropyl VCPs. Here again the regioselective 1,5-addition products were isolated as sole products; moreover, the cyclopropane ring-opening furnished specifically products **3u-x** without trace of isomers **4** as certified by COSY NMR (Scheme 3 and SI). As previously noticed with alkyl VCPs **3q-t**, addition product **3y** was obtained in an excellent 94% yield, and furthermore with a total diastereoselectivity for the Z isomer.

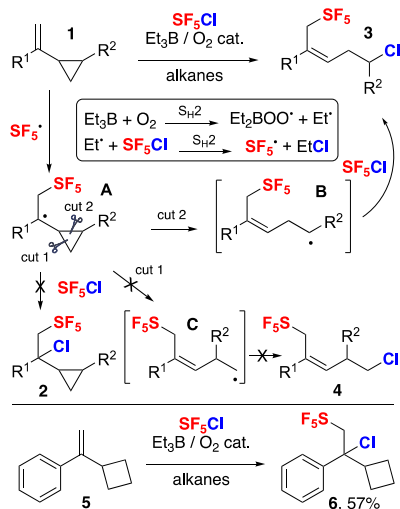
### Scheme 3. Scope II of the pentafluorosulfanylation of VCPs: cyclopropyl substituent effect.<sup>a,b</sup>



<sup>a</sup> See experimental section for detailed procedures. <sup>b</sup> Z/E ratios were determined on crude reaction mixtures.

From a mechanistic point of view, triethylborane underwent a homolytic substitution ( $S_H2$ ) reaction with triplet  $O_2$  from which an ethyl radical was liberated. When in contact with  $SF_5Cl$ ,  $Et^\cdot$

#### Scheme 4. Mechanistic suggestions.



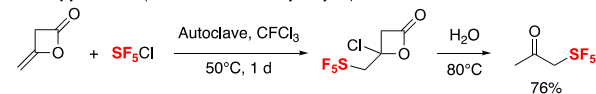
caused the  $S_H2$  to produce the radical  $SF_5^\cdot$  and  $EtCl$  (Scheme 4). VCPs reacted regioselectively at the vinyl group with  $SF_5^\cdot$  to furnish the cyclopropylcarbinyl radical **A** and further ring-opening by  $\beta$ -homolytic fission and strain release rearrangement to give **B**, which propagates the chain process by  $S_H2$  with  $SF_5Cl$  and production of compound **3**. The reverse reaction that releases the double bond was slower than the ring-opening and  $\beta$ -fragmentation of the pentafluorothyl radical was not a limitation. Since the release of strain from the cyclopropane ring is thermodynamically highly favorable, product **2** resulting in a 1,2-addition onto the vinyl function was not observed. For substrates featuring a  $R^2$  substituent on the cyclopropane moiety, two regioisomers could potentially be obtained: **3** via the secondary alkyl radical **B** and **4** via the primary alkyl radical **C**. The greater stability of **B** is responsible for the unique formation of addition product **3** (Scheme 4). In the absence of  $Et_3B/O_2$ , no spontaneous reaction took place. Regarding the diastereoselectivity, the ratio  $Z/E$  was dictated by the conformation of the intermediate cyclopropylcarbinyl radical **A** and varies with the VCP substitution pattern.<sup>23</sup> Application of the chloropentafluorosulfanylation to homologous vinylcyclobutane was somehow successful; however, while both the vinyl and the cyclopropane participate in the 1,5-difunctionalization of VCP, the cyclobutane ring in homologous vinylcyclobutane **5** was not altered and the 1,2-addition product **6** was isolated as single reaction product (Scheme 4).

The potential of  $\alpha$ - $SF_5$  carbonyl compounds, for instance in enolate chemistry, has not yet been explored in details because of the paucity of synthetic methods to reach these structures. Pioneering works by Seppelt consisted of  $SF_5Cl$  addition onto diketene and hydrolysis of the intermediate<sup>24a</sup> or on ketene followed by a Friedel-Crafts reaction (Scheme 5).<sup>24b</sup> The  $Et_3B$ -catalyzed addition of  $SF_5Cl$  onto enol acetates of acetone by Dolbier<sup>24c</sup> or of acetophenone by Welch<sup>24d</sup> gave after hydroly-

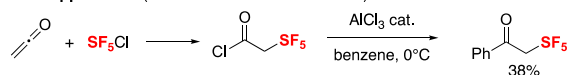
sis the corresponding  $\alpha$ - $SF_5$  ketones. Among the most recent approaches toward  $\alpha$ - $SF_5$  ketones, one can cite the gold-catalyzed hydration of  $SF_5$ -alkynes described by Paquin<sup>24e</sup> and the direct pentafluorosulfanylation of diazo compounds in the presence of tripotassium phosphate by Qing (Scheme 5).<sup>24f</sup> We assumed that allylic pentafluorosulfanyl products **3** would be precursors

#### Scheme 5. Preparation of $\alpha$ - $SF_5$ ketones: State-of-the-art and our approach by ozonolysis.<sup>a</sup>

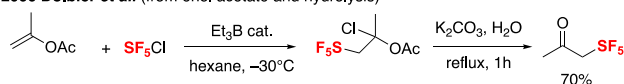
1979 Seppelt *et al.* (from diketene and hydrolysis)



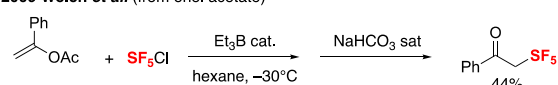
1990 Seppelt *et al.* (from ketene and Friedel-Crafts)



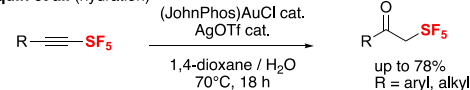
2006 Dolbier *et al.* (from enol acetate and hydrolysis)



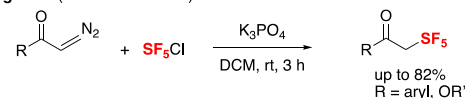
2009 Welch *et al.* (from enol acetate)



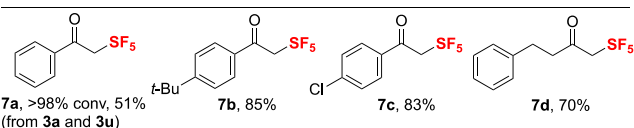
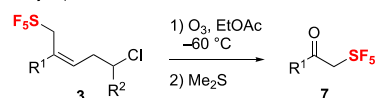
2019 Paquin *et al.* (hydration)



2021 Qing *et al.* (direct introduction)



Our approach (ozonolysis)



<sup>a</sup> See experimental section for detailed procedures.

of  $\alpha$ - $SF_5$  ketones through ozonolysis. Indeed, aryl and aliphatic ketones **7a-d** were easily obtained by ozonolysis in ethyl acetate with reductive workup (Scheme 5). The transformation was clean and quantitative from **3a** and **3u** affording the same ketone **7a** albeit in a moderate yield due to its volatility. Other  $\alpha$ - $SF_5$  ketones with higher molecular weights were isolated in 70–85% yields. Notably, this transformation is the first evidence of compatibility of aliphatic  $SF_5$  derivatives with ozone.

In conclusion, we have carried out the radical 1,5-chloropentafluorosulfanylation of vinyl cyclopropanes by means of a stock solution of  $SF_5Cl$  and the catalytic combination  $Et_3B/O_2$ . Novel allylic pentafluorosulfanyl derivatives were prepared in high yields. Because the activation step is metal-free, catalytic in radical initiator and the 1,5-addition is obviously fully atom-economical, this process fulfills the key ideals of modern synthetic chemistry. Remarkably, a new

synthetic strategy for the construction of  $\alpha$ -SF<sub>5</sub> ketones has been established. The key elements of this cutting-edge research in organofluorine compounds contributes to the flourishing chemistry of the emerging SF<sub>5</sub> motif.

## EXPERIMENTAL SECTION

All experiments were conducted under a fume-hood. Analytical thin-layer chromatographies were performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm) and/or chemical staining with a *p*-anisaldehyde or KMnO<sub>4</sub> solution. Column chromatographies were performed with silica gel (0.040-0.060 nm). NMR spectra were recorded on a Bruker DXP 300 instrument at 300 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C and 282 MHz for <sup>19</sup>F in CDCl<sub>3</sub> at room temperature unless otherwise stated. Chemical shifts ( $\delta$ ) were quoted in parts per million (ppm) relative to the residual peak of CHCl<sub>3</sub> ( $\delta_{\text{H}} = 7.26$  ppm and  $\delta_{\text{C}} = 77.16$  ppm) and internal standard CFC1<sub>3</sub> ( $\delta_{\text{F}} = 0.00$  ppm). Spectra are reported as follows: chemical shift  $\delta$  (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets q = quartet, p = pentet, m = multiplet and dm = doublet of multiplet), integration and coupling constant. Infrared spectra were recorded on a PerkinElmer Spectrum 100. High-resolution mass spectra (HRMS) were recorded on a JEOL AccuTof 4G with GC HP Agilent 7890. Commercially available chemicals were obtained from Fisher scientific, Sigma Aldrich, Alfa Aesar, TCI, Fluorochem and used as received unless otherwise stated. Tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), and toluene were distilled from sodium / benzophenone prior to use; CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub>.

### Synthesis of vinylcyclopropanes

Vinylcyclopropanes **1a-p** were prepared in a two-step sequence according to reported procedures.<sup>25a,b</sup> Vinylcyclopropanes **1q-t** were prepared in a two-step sequence according to a reported procedure.<sup>26</sup> Vinylcyclopropanes **1u-y** were prepared in a two-step sequence according to a reported procedure.<sup>27</sup> All vinylcyclopropanes **1a-k** and **1m-t**, **1u**, **1v**, **1x** and **1y** are known compounds for which analytical data are identical to those reported in the literature. **1a** CAS [825-76-3],<sup>25b</sup> **1b** CAS [15620-28-7],<sup>25b</sup> **1c** CAS [2374777-09-8],<sup>25b</sup> **1d** CAS [829-17-4],<sup>25b</sup> **1e** CAS [1355988-71-4],<sup>25b</sup> **1f** CAS [933054-41-2],<sup>25b</sup> **1g** CAS [827-87-2],<sup>25b</sup> **1h** CAS [2414140-70-6],<sup>25b</sup> **1i** CAS [1009-33-2],<sup>25b</sup> **1j** CAS [2417453-22-4],<sup>25b</sup> **1k** CAS [65322-32-9],<sup>25b</sup> **1m** CAS [1028387-07-6],<sup>25b</sup> **1n** CAS [949090-83-9],<sup>25b</sup> **1o** CAS [155337-96-5],<sup>25b</sup> **1p** CAS [418763-99-2],<sup>25b</sup> **1q** CAS [25522-55-8],<sup>26</sup> **1r** CAS [473441-75-7],<sup>26</sup> **1s** CAS [1028387-17-8],<sup>26</sup> **1t** CAS [1185742-70-4],<sup>26</sup> **1u** CAS [50990-42-6],<sup>27</sup> **1v** CAS [2135721-72-9],<sup>27</sup> **1x** CAS [2304809-66-1],<sup>27</sup> **1y** CAS [2381228-04-0].<sup>27</sup> Vinylcyclopropanes **1l** and **1w** are new compounds.

*1,2-Dichloro-4-(1-cyclopropylvinyl)benzene (1l)*: Colorless oil after column chromatography with petroleum ether / ethyl acetate 30:1 ( $R_f = 0.5$ ), 75% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (dd,  $J = 1.9, 0.6$  Hz, 1H), 7.54 – 7.31 (m, 2H), 5.30 (d,  $J = 0.6$  Hz, 1H), 5.00 (dd,  $J = 1.3, 0.7$  Hz, 1H), 1.74 – 1.43 (m, 1H), 0.97 – 0.74 (m, 2H), 0.68 – 0.43 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  147.3, 141.7, 132.3, 131.4, 130.1, 128.1, 125.5, 110.8, 15.5, 6.8. HRMS (EI)  $m/z$ :  $M^{+}$  Calcd for C<sub>11</sub>H<sub>11</sub>Cl<sub>2</sub> 212.0160; Found 212.0158.

*trans-1-(1-(2-Phenylcyclopropyl)vinyl)-4-(trifluoromethyl)benzene (1w)*: Colorless oil after column

chromatography with petroleum ether / ethyl acetate 30:1 ( $R_f = 0.4$ ), 80% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (q,  $J = 8.4$  Hz, 4H), 7.42 (t,  $J = 7.4$  Hz, 2H), 7.32 (d,  $J = 7.0$  Hz, 1H), 7.28 – 7.19 (m, 2H), 5.55 (s, 1H), 5.26 (s, 1H), 2.21 – 1.87 (m, 2H), 1.52 (dt,  $J = 8.8, 5.6$  Hz, 1H), 1.42 (dt,  $J = 8.7, 5.5$  Hz, 1H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -63.0. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  147.4, 144.7 (d,  $J = 1.5$  Hz), 142.3, 129.9 (t,  $J = 32.4$  Hz), 128.7, 126.5, 126.1, 125.8, 125.4 (q,  $J = 3.8$  Hz), 124.4 (d,  $J = 271.8$  Hz), 111.6, 27.9, 26.6, 15.9. HRMS (EI)  $m/z$ :  $M^{+}$  Calcd for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub> 288.1126; Found 288.1129.

### General procedure for the reaction of vinylcyclopropanes **1** with SF<sub>5</sub>Cl

To a vial (10 mL) equipped with a stirring bar was added vinylcyclopropane **1** (0.5 mmol), and pentane (1.0 mL). The vial was then sealed. The mixture was stirred at -40°C, and a solution of SF<sub>5</sub>Cl in hexane 0.5–0.7 M (0.76 mmol, 1.34 equiv) was added. Air was added into the system with a syringe. Then, Et<sub>3</sub>B 1M in hexane (0.05 mmol, 0.1 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. Upon completion of the reaction (monitoring by TLC), the mixture was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired products **3**, which are all new compounds.

(*Z*)-(5-chloro-2-phenylpent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**Z-3a**) and (*E*)-(5-chloro-2-phenylpent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**E-3a**): Yellow liquid after column chromatography with petroleum ether / ethyl acetate 20:1 ( $R_f = 0.3$ ). Yield (131.9 mg, 0.43 mmol, 86%, mixture of E/Z isomers 5.1:1 for the 0.5 mmol, 72.04 mg scale) and (1.306 g, 42.6 mmol, 85.4%, mixture of E/Z isomers 5.2:1 for the 50 mmol, 720.47 mg scale). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.16 (m, 4.54H), 7.16 – 7.05 (m, 0.36H), 5.99 (t,  $J = 7.3$  Hz, 0.76H), 5.91 (t,  $J = 7.1$  Hz, 0.17H), 4.67 (p,  $J = 7.6$  Hz, 1.61H), 4.49 (p,  $J = 7.7$  Hz, 0.36H), 3.55 (t,  $J = 6.5$  Hz, 1.61H), 3.40 (t,  $J = 6.6$  Hz, 0.34H), 2.68 (q<sub>app</sub>,  $J = 6.8$  Hz, 1.62H), 2.45 (q<sub>app</sub>,  $J = 6.7$  Hz, 0.37H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  84.3 – 81.2 (m, 1F), 66.4 (dm,  $J = 145.0, 3.35$ F), 64.5 (dm,  $J = 146.6, 0.65$ F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  140.5 (Z), 137.4 (E), 135.7 (E), 135.2 (Z), 134.4 (E) (p,  $J = 2.2$  Hz), 133.52 (Z) (p,  $J = 2.0$  Hz), 128.7 (Z), 128.6 (E), 128.5 (E), 128.1 (Z), 128.0 (E), 126.6 (Z), 79.3 (E) (p,  $J = 12.4$  Hz), 70.48 (Z) (p,  $J = 13.1$  Hz), 43.5 (E), 43.3 (Z), 32.3 (Z+E). IR (ATR):  $\nu_{\text{max}} = 3030, 2964, 1692, 1599, 1495, 1447, 1298, 811, 775, 695, 645, 593, 563, 546$  cm<sup>-1</sup>. HRMS (EI)  $m/z$ :  $M^{+}$  Calcd for C<sub>11</sub>H<sub>12</sub>ClF<sub>5</sub>S 306.0268; Found 306.0284.

(*Z*)-(5-chloro-2-(*p*-tolyl)pent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**Z-3b**) and (*E*)-(5-chloro-2-phenylpent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**E-3b**): Yellow liquid after column chromatography with petroleum ether / ethyl acetate 20:1 ( $R_f = 0.3$ ), 125.1 mg (0.39 mmol), 78% yield, mixture of E/Z isomers (2.9:1). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 – 7.10 (m, 1.59H), 7.14 – 7.03 (m, 2H), 6.99 (d,  $J = 8.1$  Hz, 0.57H), 5.97 (t,  $J = 7.4$  Hz, 0.74H), 5.89 (t,  $J = 7.1$  Hz, 0.26H), 4.66 (p,  $J = 7.6$  Hz, 1.49H), 4.48 (p,  $J = 7.7$  Hz, 0.54H), 3.55 (t,  $J = 6.5$  Hz, 1.47H), 3.40 (t,  $J = 6.6$  Hz, 0.53H), 2.67 (q<sub>app</sub>,  $J = 6.8$  Hz, 1.51H), 2.46 (q<sub>app</sub>,  $J = 6.8$  Hz, 0.60H), 2.26 (s, 3H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  84.1 – 80.2 (m, 1F), 66.4 (dm,  $J = 143.0$  Hz, 3.01F), 64.4 (dm,  $J = 143.3$  Hz, 1.03F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  138.0, 137.8, 137.7, 135.4, 134.5, 134.4, 134.4 (p,  $J = 2.2$  Hz), 133.4 (p,  $J = 2.6$  Hz), 129.4, 129.3, 128.3, 126.4, 79.4 (p,  $J = 12.2$  Hz), 70.5 (p,  $J = 13.1$  Hz), 43.6,

43.3, 32.4, 32.4, 21.3, 21.1. **HRMS** (API<sup>+</sup>) *m/z*: M<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>ClF<sub>5</sub>S 320.0425; Found 320.0420.

(*Z*)-(5-chloro-2-(*m*-tolyl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3c**) and (*E*)-(5-chloro-2-(*m*-tolyl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3c**): Yellow liquid after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.3), 137.0 mg (0.43 mmol), 85% yield, mixture of *E/Z* isomers 3.3:1. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.23 – 7.09 (m, 1H), 7.10 – 6.99 (m, 2.48H), 6.97 – 6.82 (m, 0.53H), 5.98 (t, J = 7.4 Hz, 0.74H), 5.90 (t, J = 7.1 Hz, 0.25H), 4.66 (p, J = 7.6 Hz, 1.53H), 4.49 (p, J = 7.7 Hz, 0.52H), 3.55 (t, J = 6.5 Hz, 1.51H), 3.40 (t, J = 6.6 Hz, 0.49H), 2.68 (q, J = 6.8 Hz, 1.54H), 2.46 (q, J = 6.8 Hz, 0.54H), 2.27 (s, 3H). **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ 83.8 – 81.0 (m, 1F), 66.3 (dm, J = 145.1 Hz, 3.08F), 64.5 (dm, J = 144.8 Hz, 0.93F). **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, CDCl<sub>3</sub>) δ 140.5, 138.4, 138.2, 137.4, 135.5, 134.9, 134.5 (p, J = 2.4 Hz), 133.7 (p, J = 2.6 Hz), 129.0, 128.9, 128.8, 128.6, 128.4, 127.4, 125.6, 123.6, 79.3 (p, J = 12.0 Hz), 70.5 (p, J = 13.3 Hz). **HRMS** (EI) *m/z*: M<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>ClF<sub>5</sub>S 320.0425; Found 320.0419.

(*Z*)-(5-chloro-2-(4-methoxyphenyl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3d**) and (*E*)-(5-chloro-2-(4-methoxyphenyl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3d**): Yellow solid after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.2), 64.0 mg (0.19 mmol), 38% yield, mixture of *E/Z* isomers 4.9:1. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.24 (m, 1.61H), 7.18 – 7.08 (m, 0.39H), 7.00 – 6.84 (m, 2.07H), 6.03 (t, J = 7.4 Hz, 0.85H), 5.97 (t, J = 7.1 Hz, 0.15H), 4.75 (p, J = 7.6 Hz, 1.67H), 4.76 (p, J = 7.5 Hz, 0.47H), 3.83 (s, 0.66H), 3.82 (s, 2.23H), 3.67 (t, J = 6.5 Hz, 1.56H), 3.52 (t, J = 6.6 Hz, 0.38H), 2.78 (q, J = 6.8 Hz, 1.62H), 2.58 (q, J = 6.8 Hz, 0.39H). **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ 85.8 – 79.1 (m, 1F), 66.4 (dm, J = 143.0 Hz, 3.30F), 64.4 (dm, J = 146.5 Hz, 0.68F). **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, CDCl<sub>3</sub>) δ 159.5, 159.2, 135.2 (p, J = 2.2 Hz), 133.6, 132.9 (p, J = 2.5 Hz), 129.6, 127.6, 114.0, 113.9, 79.2 (q, J = 12.3 Hz), 70.5 (q, J = 13.2 Hz), 55.3, 55.3, 43.5, 43.3, 32.4, 32.3. **HRMS** (EI) *m/z*: M<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>ClF<sub>5</sub>OS 336.0374; Found 336.0376.

(*Z*)-(5-chloro-2-(2-methoxyphenyl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3e**) and (*E*)-(5-chloro-2-(2-methoxyphenyl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3e**): Yellow oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.2), 151.5 mg (0.45 mmol), 90% yield, mixture of *E/Z* isomers 1.5:1. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.34 (dddd, J = 8.2, 7.4, 4.6, 1.8 Hz, 1H), 7.25 – 7.10 (m, 1H), 7.07 – 6.86 (m, 2H), 6.05 (t, J = 7.2 Hz, 0.41H), 5.94 (t, J = 7.3 Hz, 0.59H), 4.93 (p, J = 8.0 Hz, 1.24H), 4.71 (p, J = 8.1 Hz, 0.77H), 3.84 (s, 1.76H), 3.83 (s, 1.19H), 3.67 (t, J = 6.7 Hz, 1.20H), 3.52 (t, J = 6.7 Hz, 0.81H), 2.80 (q, J = 6.9 Hz, 1.20H), 2.51 (q, J = 6.9 Hz, 0.8H). **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ 86.4 – 80.6 (m, 1F), 66.9 (dm, J = 143.1, 2.46F), 64.5 (dm, J = 144.4, 1.58F). **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, CDCl<sub>3</sub>) δ 156.6, 156.4, 136.4, 132.9 (p, J = 2.7 Hz), 132.2 (p, J = 2.6 Hz), 131.4, 131.3, 130.0, 129.6, 129.5, 125.5, 121.1, 120.6, 111.0, 110.6, 78.1 (p, J = 11.6 Hz), 70.8 (p, J = 12.5 Hz), 55.4, 43.5, 43.2, 32.5, 32.0. **HRMS** (EI) *m/z*: M<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>ClF<sub>5</sub>OS 336.0374; Found 336.0377.

(*Z*)-(2-(4-(*tert*-butyl)phenyl)-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3f**) and (*E*)-(2-(4-(*tert*-butyl)phenyl)-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3f**): Yellow oil after column chromatography with petrole-

um ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.3), 156.0 mg (0.43 mmol), 86% yield, mixture of *E/Z* isomers 3.9:1. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.38 (m, 2H), 7.39 – 7.29 (m, 1.70H), 7.22 – 7.12 (m, 0.41H), 6.13 (t, J = 7.4 Hz, 0.81H), 6.04 (t, J = 7.1 Hz, 0.19H), 4.81 (p, J = 7.6 Hz, 1.61H), 4.63 (p, J = 7.7 Hz, 0.41H), 3.68 (t, J = 6.5 Hz, 1.62H), 3.55 (t, J = 6.6 Hz, 0.38H), 2.82 (q, J = 6.8 Hz, 1.65H), 2.62 (q, J = 6.8 Hz, 0.48H), 1.38 (s, 2.49H), 1.37 (s, 6.63H). **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ 84.2 – 80.8 (m, 1F), 66.3 (dm, J = 145.3, 3.16F), 64.4 (dm, J = 143.8, 0.81F). **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, CDCl<sub>3</sub>) δ 151.2, 151.0, 137.5, 135.5, 134.5, 134.3 (p, J = 2.5 Hz), 133.3 (p, J = 2.6 Hz), 128.1, 126.2, 125.7, 125.5, 79.3 (p, J = 12.3 Hz), 70.5 (p, J = 13.2 Hz), 43.6, 43.4, 34.7, 34.7, 32.5, 32.4, 31.4. **HRMS** (EI) *m/z*: M<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>ClF<sub>5</sub>S 362.0894; Found 362.0899.

(*Z*)-(2-(2-(4-fluorophenyl)pent-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3g**) and (*E*)-(2-(2-(4-fluorophenyl)pent-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3g**): Yellow liquid after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.2), 129.9 mg (0.40 mmol), 80% yield, mixture of *E/Z* isomers 3.6:1. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.27 (m, 1.60H), 7.25 – 7.14 (m, 0.51H), 7.08 (td, J = 8.7, 7.0 Hz, 2H), 6.15 – 5.96 (m, 1H), 4.75 (p, J = 7.6 Hz, 1.59H), 4.58 (p, J = 7.6 Hz, 0.49H), 3.68 (t, J = 6.4 Hz, 1.53H), 3.53 (t, J = 6.5 Hz, 0.49H), 2.79 (q, J = 6.7 Hz, 1.58H), 2.54 (q, J = 6.7 Hz, 0.52H). **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ 86.5 – 77.8 (m, 1F), 66.4 (dm, J = 143.8 Hz, 3.13F), 64.6 (dm, J = 145.0 Hz, 0.86F), -114.2, -114.7. **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, CDCl<sub>3</sub>) δ 162.6 (d, J = 247.4 Hz), 162.4 (d, J = 247.6 Hz), 136.7, 136.2, 135.3, 133.5 (p, J = 2.5 Hz), 130.3 (p, J = 2.6 Hz), 130.3 (d, J = 8.1 Hz), 128.3 (d, J = 8.1 Hz), 115.7 (d, J = 21.6 Hz), 115.7 (d, J = 21.6 Hz), 79.2 (p, J = 12.6 Hz), 70.6 (p, J = 13.5 Hz), 43.4, 43.3, 32.3. **HRMS** (EI) *m/z*: M<sup>+</sup> Calcd for C<sub>11</sub>H<sub>11</sub>ClF<sub>6</sub>S 324.0174; Found 324.0177.

(*Z*)-(2-(2-(fluorophenyl)pent-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3h**) and (*E*)-(2-(2-(fluorophenyl)pent-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3h**): Colorless oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.2), 135.6 mg (0.42 mmol), 83% yield, mixture of *E/Z* isomers 1.9:1. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.39 – 6.85 (m, 4H), 6.04 (t, J = 7.2 Hz, 0.36H), 5.93 (t, J = 7.3 Hz, 0.62H), 4.71 (p, J = 8.0 Hz, 1.30 H), 4.53 (p, J = 7.7 Hz, 0.72 H), 3.57 (t, J = 6.5 Hz, 1.28 H), 3.43 (t, J = 6.6 Hz, 0.72 H), 2.70 (q<sub>app</sub>, J = 6.7 Hz, 1.28 H), 2.40 (q<sub>app</sub>, J = 6.7 Hz, 0.72 H). **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ 83.9 – 80.7 (m, 1F), 66.7 (dm, J = 144.6 Hz, 2.61 F), 65.0 (dm, J = 145.2 Hz, 1.40F), -114.80, -116.55. **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, CDCl<sub>3</sub>) δ 159.9 (d, J = 246.4 Hz), 159.8 (d, J = 246.7 Hz), 138.1, 131.2 (d, J = 3.6 Hz), 131.1 (d, J = 3.7 Hz), 130.2 (d, J = 8.4 Hz), 129.9 (d, J = 8.5 Hz), 129.6 (t, J = 2.9 Hz), 128.9 (t, J = 2.7 Hz), 128.7, 128.5, 124.7 (d, J = 3.4 Hz), 124.5, 124.4 (d, J = 3.5 Hz), 116.1 (d, J = 22.2 Hz), 115.8 (d, J = 22.4 Hz), 79.30 – 77.83 (m), 71.45 – 70.31 (m), 43.2, 43.0, 32.6, 32.0. **HRMS** (CI<sup>+</sup>) *m/z*: M<sup>+</sup> Calcd for C<sub>11</sub>H<sub>11</sub>ClF<sub>6</sub>S 324.0174; Found 324.0170.

(*Z*)-(2-(4-(chlorophenyl)pent-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3i**) and (*E*)-(2-(4-(chlorophenyl)pent-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3i**): Yellow liquid after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.3), 150.3 mg (0.44 mmol), 88% yield, mixture of *E/Z* isomers 3.9:1. **<sup>1</sup>H**



(E) m/z: M<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>ClF<sub>5</sub>S 356.0425; Found 356.0418. A crystal was grown from a solution of **3o** in DCM and petroleum ether by slow evaporation. X-Ray analysis is available from CCDC.<sup>22</sup> <sup>1</sup>H and <sup>19</sup>F NMR data of pure **Z-3o** were recorded.

(Z)-(5-chloro-2-(naphthalen-1-yl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3p**) and (E)-(5-chloro-2-(naphthalen-1-yl)pent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3p**): Yellow oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.3), 167.7 mg (0.47 mmol), 94% yield, mixture of E/Z isomers 4.0:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.05 – 7.83 (m, 2.25H), 7.80 – 7.68 (m, 0.83H), 7.65 – 7.50 (m, 3H), 7.44 (d, J = 7.2 Hz, 1H), 6.41 (t, J = 7.1 Hz, 0.78H), 6.10 (t, J = 7.4 Hz, 0.21H), 5.01 – 4.78 (m, 1.17H), 4.80 – 4.59 (m, 0.83H), 3.73 (t, J = 6.3 Hz, 0.43H), 3.48 (t, J = 6.5 Hz, 1.57H), 2.95 (q, J = 6.7 Hz, 0.42H), 2.39 (qd, J = 6.7, 3.7 Hz, 1.58H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 84.3 – 79.8 (m, 1F), 66.8 (dm, J = 143.2 Hz, 0.81F), 65.1 (dm, J = 143.8 Hz, 3.22F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 139.0, 138.5, 138.4, 134.9, 134.1, 134.0, 132.58 (p, J = 2.4 Hz), 132.2 (p, J = 2.7 Hz), 131.0, 130.7, 129.0, 128.9, 128.7, 128.5, 127.1, 126.7, 126.6, 126.5, 126.1, 126.0, 125.5, 125.4, 124.9, 124.7, 79.1 (p, J = 12.7 Hz), 72.8 (p, J = 13.1 Hz), 43.3, 32.7, 32.3. HRMS (EI) m/z: M<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>ClF<sub>5</sub>S 356.0425; Found 356.0439.

(Z)-(2-benzyl-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3q**) and (E)-(2-benzyl-5-chloropent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3q**): Yellow oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.4), 150.8 mg (0.47 mmol), 94% yield, mixture of E/Z isomers 2.7:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.49 – 6.32 (m, 3H), 6.27 (td, J = 8.6, 7.9, 1.5 Hz, 2H), 4.97 (t, J = 7.1 Hz, 0.71H), 4.89 (t, J = 7.3 Hz, 0.28H), 3.29 (p, J = 7.5 Hz, 0.47H), 3.22 (p, J = 7.5 Hz, 1.54H), 2.79 – 2.64 (m, 4H), 1.86 (q, J = 6.8 Hz, 1.43H), 1.75 (q, J = 6.8 Hz, 0.56H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 85.4 – 80.3 (dm, J = 142.2 Hz, 1F), 66.4 (dm, J = 143.7 Hz, 1.1F), 64.2 (dm, J = 143.7 Hz, 2.93F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 138.2, 137.9, 134.9, 133.7, 132.4 (p, J = 2.3 Hz), 132.3 (p, J = 2.3 Hz), 129.2, 129.0, 128.9, 128.8, 127.0, 126.9, 76.8 (p, J = 12.7 Hz), 70.0 (p, J = 13.5 Hz), 43.5, 43.4, 35.6, 31.7, 31.6. HRMS (EI) m/z: M<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>ClF<sub>5</sub>S 320.0425; Found 320.0431.

(Z)-(5-chloro-2-phenethylpent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3r**) and (E)-(5-chloro-2-phenethylpent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3r**): Colorless oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.4), 162.4 mg (0.49 mmol), 97% yield, mixture of E/Z isomers 4.1:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.17 – 6.04 (m, 2H), 6.04 – 5.88 (m, 3H), 4.46 (m, 1H), 3.06 (p, J = 8.0 Hz, 0.41H), 2.93 (p, J = 8.1 Hz, 1.64H), 2.29 (t, J = 6.5 Hz, 0.44H), 2.17 (t, J = 6.7 Hz, 1.58H), 1.63 – 1.44 (m, 2H), 1.42 – 1.16 (m, 4H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 84.6 – 81.0 (m, 1F), 65.7 (dm, J = 142.3 Hz, 0.79F), 63.9 (dm, J = 143.4 Hz, 3.20F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 140.9, 140.8, 134.8, 132.5 (p, J = 2.3 Hz), 131.9 (p, J = 2.5 Hz), 128.6, 128.6, 128.5, 128.5, 126.4, 126.3, 77.5 (t, J = 12.4 Hz), 71.0 (t, J = 13.1 Hz), 43.3, 43.2, 38.2, 34.6, 34.2, 31.7, 31.5, 31.4. HRMS (EI) m/z: M<sup>+</sup> Calcd for C<sub>13</sub>H<sub>16</sub>ClF<sub>5</sub>S 334.0581; Found 334.0584.

(Z)-(5-chloro-2-cyclohexylpent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3s**) and (E)-(5-chloro-2-cyclohexylpent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3s**): Colorless oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub>

= 0.4), 148.4 mg (0.48 mmol), 95% yield, mixture of E/Z isomers 4.3:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.84 – 5.51 (m, 1H), 4.32 (p, J = 8.0 Hz, 1.53H), 4.21 (p, J = 8.1 Hz, 0.39H), 3.63 – 3.45 (m, 2H), 2.72 – 2.54 (m, 2H), 2.49 – 2.34 (m, 0.21H), 2.02 (m, 0.89H), 1.89 – 1.57 (m, 5H), 1.39 – 1.04 (m, 5H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 85.2 – 80.3 (m, 1F), 65.7 (dm, J = 142.9 Hz, 3.24F), 63.5 (dm, J = 144.0 Hz, 0.75F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 138.4 (p, J = 2.1 Hz), 137.6 (p, J = 1.9 Hz), 134.0, 129.5, 75.4 (t, J = 13.0 Hz), 71.3 (p, J = 12.7 Hz), 43.9, 43.6, 43.6, 40.8, 32.8, 31.6, 31.5, 31.1, 26.9, 26.8, 26.3, 26.1. HRMS (EI) m/z: M<sup>+</sup> Calcd for C<sub>11</sub>H<sub>18</sub>ClF<sub>5</sub>S 312.0738; Found 312.0732.

(Z)-(2-(3-chloropropylidene)decyl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3t**) and (E)-(2-(3-chloropropylidene)decyl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3t**): Yellow oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.4), 157.3 mg (0.46 mmol), 92% yield, mixture of E/Z isomers 4.5:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.66 (t, J = 7.1 Hz, 1H), 4.45 – 4.14 (m, 2H), 3.56 (m, 2H), 2.59 (m, 2H), 2.37 – 2.07 (m, 2H), 1.45 – 1.14 (m, 12H), 1.01 – 0.63 (m, 3H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 82.9 (m, 1F), 65.9 (dm, J = 142.5 Hz, 0.73F), 63.7 (dm, J = 143.3, 3.25F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 133.9 (p, J = 2.2 Hz), 133.7, 132.9 (p, J = 2.1 Hz), 77.6 (p, J = 12.5 Hz), 71.0 (p, J = 13.1 Hz), 43.5, 43.4, 36.6, 32.0, 31.6, 31.5, 29.8, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 28.2, 28.0, 22.8, 14.2. HRMS (EI) m/z: M<sup>+</sup> Calcd for C<sub>13</sub>H<sub>24</sub>ClF<sub>5</sub>S 342.1207; Found 342.1214.

(Z)-(2-(3-chloropropylidene)decyl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3u**) and (E)-(2-(3-chloropropylidene)decyl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3u**): Yellow oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.4), 172.3 mg (0.45 mmol), 90% yield, mixture of E/Z isomers > 20:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.27 (m, 9.76H), 7.16 (m, 0.16H), 6.18 (t, J = 7.4 Hz, 0.91H), 6.08 (t, J = 7.2 Hz, 0.06H), 5.10 (dd, J = 8.1, 5.9 Hz, 0.91H), 4.97 (dd, J = 7.7, 6.3 Hz, 0.08H), 4.76 (p, J = 7.5 Hz, 1.85H), 4.62 (p, J = 7.6 Hz, 0.12H), 3.38 – 3.02 (m, 1.85H), 3.02 – 2.82 (m, 0.13H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 84.3 – 80.4 (m, 1F), 66.5 (dm, J = 145.1 Hz, 3.86F), 64.7 (dm, J = 146.5 Hz, 0.15F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 140.8, 140.7, 140.6, 137.5, 135.2, 134.6, 133.6 (p, J = 2.6 Hz), 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 79.3 (d, J = 13.1 Hz), 70.5 (p, J = 13.3 Hz), 62.3, 62.1, 39.8, 39.6. HRMS (CI<sup>+</sup>) m/z: M<sup>+</sup> Calcd for C<sub>17</sub>H<sub>16</sub>ClF<sub>5</sub>S 382.0581; Found 382.0580.

(Z)-(5-chloro-2-(4-methoxyphenyl)-5-phenylpent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**Z-3v**) and (E)-(5-chloro-2-(4-methoxyphenyl)-5-phenylpent-2-en-1-yl)pentafluoro-λ<sup>6</sup>-sulfane (**E-3v**): Yellow oil after column chromatography with petroleum ether / ethyl acetate 20:1 (R<sub>f</sub> = 0.4), 156.0 mg (0.38 mmol), 76% yield, mixture of E/Z isomers 15.8:1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.16 (m, 5H), 7.15 – 7.05 (m, 1.86H), 6.89 (d, J = 8.7 Hz, 0.17H), 6.83 – 6.67 (m, 2H), 5.90 (t, J = 7.4 Hz, 0.89H), 5.83 (t, J = 7.1 Hz, 0.08H), 4.44 – 4.31 (m, 0.91H), 4.82 – 4.71 (m, 0.09H), 4.64 – 4.44 (m, 1.82H), 4.38 (q, J = 7.7 Hz, 0.16H), 3.67 (s, 0.45H), 3.67 (s, 2.50H), 3.08 – 2.78 (m, 1.84H), 2.81 – 2.62 (m, 0.16H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 85.7 – 79.8 (m, 1F), 66.5 (dm, J = 143.3 Hz, 0.24F), 64.6 (dm, J = 144.9 Hz, 0.24F). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 159.6, 159.2, 140.8, 140.8, 134.7, 134.1 (p, J = 2.6 Hz), 133.2, 132.9 (p, J = 2.6 Hz), 129.6, 128.9, 128.7, 128.6, 127.7, 127.0, 127.0, 114.1, 114.0, 79.5 (p, J = 12.3 Hz), 70.6 (p, J = 13.0 Hz), 62.3, 62.2, 55.3, 55.2, 39.7, 39.6.



**HRMS** (EI) *m/z*:  $M^{++}$  Calcd for  $C_{18}H_{18}ClF_5OS$  412.0687; Found 412.0692.

(*Z*)-(5-chloro-5-phenyl-2-(4-(trifluoromethyl)phenyl)pent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**Z-3w**) and (*E*)-(5-chloro-5-phenyl-2-(4-(trifluoromethyl)phenyl)pent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**E-3w**): Colorless oil after column chromatography with petroleum ether / ethyl acetate 20:1 ( $R_f$  = 0.4), 190.6 mg (0.43 mmol), 85% yield, mixture of *E/Z* isomers > 20:1.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.66 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.28 (m, 7H), 6.30 – 6.07 (m, 1H), 5.09 (dd, *J* = 8.1, 5.8 Hz, 0.96H), 4.97 (dd, *J* = 7.5, 6.3 Hz, 0.05H), 4.85 – 4.62 (m, 1.93H), 4.64 – 4.45 (m, 0.09H), 3.30 – 2.98 (m, 1.94H), 2.96 – 2.76 (m, 0.08H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ )  $\delta$  83.7 – 80.7 (m, 1F), 66.7 (dm, *J* = 142.8 Hz, 3.96F), 65.4 (dd, *J* = 143.8 Hz, 0.08F), –63.0, –63.1.  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  144.1, 140.6, 136.4, 132.7 (t, *J* = 2.7 Hz), 130.2 (q, *J* = 32.6 Hz), 129.0, 128.9, 127.0, 127.0, 125.7 (q, *J* = 3.8 Hz), 124.2 (d, *J* = 272.0 Hz), 70.1 (p, *J* = 14.0 Hz), 61.8, 39.8. **HRMS** (EI) *m/z*:  $M^{++}$  Calcd for  $C_{18}H_{15}ClF_8S$  450.0455; Found 450.0461.

(*Z*)-(5-chloro-2-phenyl-5-(4-(trifluoromethyl)phenyl)pent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**Z-3x**) and (*E*)-(5-chloro-5-phenyl-2-(4-(trifluoromethyl)phenyl)pent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**E-3x**): Colorless oil after column chromatography with petroleum ether / ethyl acetate 20:1 ( $R_f$  = 0.4), 182.46 mg (0.41 mmol), 81% yield, mixture of *E/Z* isomers 3.6:1.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.71 (d, *J* = 8.1 Hz, 1.58H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.38 (m, 5H), 7.19 – 6.97 (m, 0.49H), 6.13 (t, *J* = 7.3 Hz, 0.75H), 6.04 (t, *J* = 7.2 Hz, 0.22H), 5.09 (dd, *J* = 8.2, 5.7 Hz, 0.73H), 4.95 (t, *J* = 7.0 Hz, 0.25H), 4.76 (p, *J* = 7.5 Hz, 1.49H), 4.59 (p, *J* = 7.6 Hz, 0.47H), 3.25 – 2.99 (m, 1.48H), 3.01 – 2.76 (m, 0.52H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ )  $\delta$  146.2 – 142.7 (m), 129.0 (dm, *J* = 143.4 Hz, 3.11F), 127.1 (dm, *J* = 144.3 Hz, 0.86F), –63.1.  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  144.7 (q, *J* = 1.4 Hz), 144.6 (q, *J* = 1.4 Hz), 140.4, 137.3, 135.2 (p, *J* = 2.5 Hz), 134.3, 134.1 (p, *J* = 2.7 Hz), 133.9, 131.0 (q, *J* = 32.6 Hz), 130.7 (q, *J* = 32.6 Hz), 128.8, 128.7, 128.4, 128.3, 128.1, 127.5, 126.6, 126.0 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 3.5 Hz), 124.0 (d, *J* = 272.3 Hz), 118.6, 79.2 (p, *J* = 12.7 Hz), 70.5 (p, *J* = 13.5 Hz), 61.0 (p, *J* = 4.5 Hz), 39.6, 39.5. **HRMS** (EI) *m/z*:  $M^{++}$  Calcd for  $C_{18}H_{15}ClF_8S$  450.0455; Found 450.0464.

(*Z*)-(2-(tert-butyl)-5-chloro-5-phenylpent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**Z-3y**) and (*E*)-(2-(tert-butyl)-5-chloro-5-phenylpent-2-en-1-yl)pentafluoro- $\lambda^6$ -sulfane (**E-3y**): Colorless oil after column chromatography with petroleum ether / ethyl acetate 30:1 ( $R_f$  = 0.6), 169.7 mg (0.47 mmol), 94% yield, mixture of *E/Z* isomers > 100:1.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.51 – 6.95 (m, 5H), 5.81 (t, *J* = 7.2 Hz, 1H), 4.82 (dd, *J* = 8.1, 5.9 Hz, 1H), 4.23 (pd, *J* = 7.8, 2.2 Hz, 2H), 3.05 – 2.58 (m, 2H), 1.00 (s, 9H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ )  $\delta$  85.4 – 81.2 (m, 1F), 65.9 (dm, *J* = 143.1 Hz, 4F).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  141.2, 140.5 (p, *J* = 1.9 Hz), 131.4, 128.8, 128.6, 127.0, 69.6 (p, *J* = 13.7 Hz), 62.6, 39.6 (p, *J* = 2.2 Hz), 36.8, 30.3. **HRMS** (EI) *m/z*:  $M^{++}$  Calcd for  $C_{15}H_{20}ClF_5S$  362.0894; Found 362.0898.

(2-chloro-2-cyclobutyl-2-phenylethyl)pentafluoro- $\lambda^6$ -sulfane (**6**): Colorless oil after column chromatography with petroleum ether/ethyl acetate 20:1 ( $R_f$  = 0.6), 91.4 mg (0.29 mmol), 57% yield.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.57 – 7.46 (m, 2H), 7.45 – 7.27 (m, 3H), 4.36 (pd, *J* = 8.2, 3.7 Hz, 2H), 3.51 – 3.14 (m, 1H), 2.50 – 2.00 (m, 3H), 2.02 – 1.71 (m, 3H).  $^{19}F$  NMR

(282 MHz,  $CDCl_3$ )  $\delta$  87.1 – 79.4 (m, 1F), 69.9 (dm, *J* = 148.1 Hz, 4F).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  139.4, 128.3, 128.2, 126.8, 78.7 (p, *J* = 11.1 Hz), 44.1, 24.9, 23.9, 16.6. **HRMS** ( $CI^+$ ) *m/z*:  $M^{++}$  Calcd for  $C_{12}H_{14}ClF_5S$  320.0425; Found 320.0420.

**Ozonolysis: Access to  $\alpha$ -SF<sub>5</sub> ketones.**<sup>28</sup>

Typical experiment: Compound **3a** (123.1 mg, 0.5 mmol, 1equiv) was dissolved in ethyl acetate (20 mL), and the solution was cooled to -60 °C. The solution was sparged with ozone for 10 min, and sparged with nitrogen for 10 min. Dimethylsulfide (10 mmol, 20 equiv) was added, and the reaction was allowed to stir for 10 hours while warming gradually to room temperature. The solvent was removed in vacuo. The ketone compound was purified by flash silica chromatography ( $R_f$  = 0.25, petroleum ether/ethyl acetate 20:1) to afford the product **7a** quantitatively as evaluated by  $^{19}F$  NMR. However, due to high volatility of **7a**, yields vary in the range 50–85% in repeated experiments.

All 2-(pentafluoro- $\lambda^6$ -sulfanyl) ketones **7a-d** are known compounds for which analytical data are identical to those reported in the literature. **7a** CAS [129421-48-3],<sup>24e</sup> **7b** CAS [2310325-34-7],<sup>24e</sup> **7c** CAS [2669730-32-7],<sup>24f</sup> **7d** CAS [2310325-24-5].<sup>24e</sup>

## ASSOCIATED CONTENT

### Supporting Information

The material is available free of charge via the Internet at <http://pubs.acs.org>.

Copies of  $^1H$ ,  $^{19}F$  and  $^{13}C\{^1H\}$  NMR spectra of the products (pdf).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## ACKNOWLEDGMENT

Our research was supported by the Centre National de la Recherche Scientifique CNRS, Normandy University, Labex SynOrg (ANR-11-LABX-0029), the graduate school for research XL-Chem (ANR-18-EURE-0020 XL CHEM) and the Région Normandie. F-F. F. is grateful to the French ministry of foreign affairs for an Eiffel excellence doctorate scholarship.

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