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Markovnikov-Type Hydrotrifluoromethylchalcogenation of Unactivated Terminal Alkenes with [Me₄N][XCF₃] (X = S, Se) and TfOH

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Abstract: The first Markovnikov-type hydrotrifluoromethylselenolation of unactivated terminal alkenes with the readily accessible [Me₄N][SeCF₃] reagent and the superacid TfOH is reported. The reaction proceeded at room temperature under catalyst- and additive-free conditions to give the branched trifluoromethylselenolated products in good yields. This protocol is also applicable to the Markovnikov-type hydrotrifluoromethylthiolation of unactivated terminal alkenes using [Me₄N][SCF₃]/TfOH, but not to the hydrotrifluoromethoxylation with CsOCF₃/TfOH under the same conditions. The successful hydrotrifluoromethylselenolation and hydrotrifluoromethylthiolation showed simplicity and high regioselectivity, taming the sensitive −XCF₃ (X = S, Se) anions with TfOH, and offered a convenient method for the straightforward synthesis of branched trifluoromethyl selenoethers and thioethers from unactivated alkenes.

Keywords: hydrotrifluoromethylselenolation; hydrotrifluoromethylthiolation; Markovnikov-type; terminal alkene; superacid

1. Introduction

Over the past few decades, fluorinated compounds have attracted great attention in various fields ranging from materials to life sciences because of their unique properties imparted by fluorine [1]. Recently, the special stereoelectronic and physicochemical properties originating from the association of the trifluoromethyl (CF₃) moiety with chalcogens (e.g., oxygen, sulfur and selenium) have been well documented [2–13]. The OCF₃ and SCF₃ groups possess strong electronegativity, considerable steric hindrance, and high lipophilicity, which can significantly change the bioactivity of a molecule [2–10]. The least-studied SeCF₃ group represents another important functionality, exhibiting a valuable stereoelectronic nature and lipophilicity, and has immense potential to modulate the potency of agrochemicals and pharmaceuticals [11–13]. It is well known that selenium (Se) is an essential trace element in the human body, constituting the crucial parts of antioxidant enzymes that protect cells against the effects of free radicals that are produced during normal oxygen metabolism [14–18]. Although selenium substances have shown very useful biological activities and have been widely utilized in drug design and development [14–18], to our knowledge, the uses of SeCF₃-containing compounds have rarely been explored in comparison with those non-fluorinated analogues. This may be attributed to the lack of structural diversity, sufficient synthetic methods, and imperative biological investigation of the trifluoromethylselenolated compounds [2–13]. Thus, continuously developing efficient approaches for the construction of different types of SeCF₃-containing organic scaffolds for future function studies is highly sought-after.
To date, there have been two major strategies for the synthesis of SeCF$_3$-substituted molecules: indirect and direct approaches [19–36]. The indirect method comprises the trifluoromethylation of selenols, diselenides, and selenocyanates with diverse CF$_3$ transfer reagents, including CF$_3$SO$_2$Na/oxidant, TMSCF$_3$/fluoride, HCF$_3$/base, CF$_3$I/TDAE (tetrakis(dimethylamino)ethylene), and so on. However, these reactions suffer from harsh conditions, low efficiency, poor functional group tolerance, narrow substrate scope, and/or toxicity and pre-functionalization of starting materials, which limit their practical applications [19–27]. Notably, the direct trifluoromethylselenolation offers an elegant way to the C-SeCF$_3$ bond formation by using elaborate SeCF$_3$ reagents, such as CuSeCF$_3$, Hg(SeCF$_3$)$_2$, [(bpy)[Cu(SeCF$_3$)]$_2$, AgSeCF$_3$, [Me$_4$N][SeCF$_3$], ClSeCF$_3$, and TsSeCF$_3$ [28–47]. Among these reagents, [Me$_4$N][SeCF$_3$] is thermally stable, non-volatile, easy to handle, and readily accessible, and has become one of the most important SeCF$_3$ sources by far [48]. It has been reported that reactions of [Me$_4$N][SeCF$_3$] with organic halides, aryl diazonium salts, diarylidenonium triflates, α-diazo carbonyls, boronic acids and their esters, terminal alkynes, electron-rich (hetero)arenes, carboxylic acids, 1,3-dicarbonyls and alcohols under transition-metal-catalyzed or -free conditions provide the corresponding trifluoromethyl selenoethers in excellent yields [37–47]. The results have demonstrated a broad prospect of application of [Me$_4$N][SeCF$_3$] in the direct trifluoromethylselenolation of various structurally diversified molecules.

The carbon–carbon double bond (C = C) is one of the most useful and versatile functional groups in organic chemistry [49–53]. It serves as a central functionality for a wide variety of reactions. Hydrofluoroalkylation of alkenes constitutes a challenging task because of the difficulties of taming the elusive fluorooalkylation reagents with hydrogen sources [54–65]. By using CF$_3$SH, electrophilic “SCF$_3$” reagents, and trifluoromethanesulfonic anhydride (Tf$_2$O), the respective hydrotrifluoromethylthiolation of alkenes has been successfully accomplished [66–70]. However, the homologous hydrotrifluoromethylselenolation of unactivated alkenes has not been achieved despite sulfur and selenium being the elements of the same main group [13,71–73]. Encouraged by the fact that the readily available [Me$_4$N][SeCF$_3$] salt is compatible with a superacid in the reactions with α-diazo carbonyls [43], we investigated in this article the hydrotrifluoromethylselenolation of alkenes with [Me$_4$N][SeCF$_3$] in the presence of a strong acid. It was pleasing to find that reactions of unactivated terminal alkenes with [Me$_4$N][SeCF$_3$] and trifluoromethanesulfonic acid (TfOH) under catalyst- and additive-free conditions formed the secondary alkyl trifluoromethyl selenoethers in good yields.

2. Results and Discussions

Initially, 4-(but-3-en-1-yl)-1,1′-biphenyl (1a) was chosen as a model substrate to optimize the reaction conditions for hydrotrifluoromethylselenolation with an acid. It was found that reaction of [Me$_4$N][SeCF$_3$] (1.5 equiv) with a mixture of 1a and TfOH (1.5 equiv) in dichloromethane at room temperature under a nitrogen atmosphere for 6 h gave (4-((1,1′-biphenyl)-4-yl)butan-2-yl)(trifluoromethyl)selane (3a) in 45% yield (Table 1, entry 1). Using the commonly used acids such as CF$_3$CO$_2$H, concentrated H$_2$SO$_4$ (98%), anhydrous HCl, 85% H$_3$PO$_4$ (aq), Et$_3$N•3HF, Et$_3$O•HBF$_4$ (85%), TsOH•H$_2$O, and (CF$_3$SO$_2$)$_2$NH instead of TfOH led to no formation of 3a (Table 1, entries 2–9). These results suggested that TfOH was a better acid than other tested acids for the hydrotrifluoromethylselenolation. The choice of solvent also had an influence on the reaction. Treatment of 1a and TfOH with [Me$_4$N][SeCF$_3$] in 1.2-dichloroethane, toluene, chlorobenzene, and 1,1,2-trichloro-1,2,2-trifluoroethane (CFCl$_2$CF$_2$Cl) under the same conditions provided 3a with 19–37% yields (Table 1, entries 10–13). If the reaction was run in acetonitrile or (CF$_3$)$_2$CHOH, no desired product was formed (Table 1, entries 14–15). It seemed that the polar solvents were ineffective for the transformation, as they likely trapped the proton of TfOH and reduced the acidity of TfOH. Moreover, the reaction time could be shortened. Reaction of 1a and TfOH (1.5 equiv) with [Me$_4$N][SeCF$_3$] (1.5 equiv) at room temperature for 3 h furnished 3a in 48% yield, which was comparable to that obtained for 6 h (Table 1, entry 16). In addition, the reactant ratios had an interesting effect on the hydrotrifluoromethylselenolation. Reducing the equivalents of TfOH from 1.5 to 1.0 equiv in the
were employed to probe the substrate scope of the reaction (Scheme 1). To our delight, a range of 2 (Table 1, entries 18–21). Remarkably, if 1a (2 equiv) reacted with TfOH (1.0 equiv) and [Me₄N][SeCF₃] (2 equiv) at room temperature under N₂ for 3 h, 3a was formed in 83% yield (79% isolated yield) (Table 1, entry 22). Furthermore, the reaction at room temperature was preferable as either elevating or lowering the temperature decreased the yield of 3a (Table S3 (see Supporting Information)). Addition of gold, copper, and silver salts as Lewis acids to the reaction mixtures of 1a, [Me₄N][SeCF₃] (1.5 equiv), and TfOH (1.0 equiv) did not promote the production of 3a (see Table S6). It was noteworthy that from the above successful hydrotrifluoromethylselenolations, branched trifluoromethyl selenoether was isolated rather than the linear isomer, showing excellent regioselectivity of the reaction.

Table 1. Hydrotrifluoromethylselenolation of 1a with [Me₄N][SeCF₃] and an acid.

| Entry | Solvent          | Acid             | 1a:2a:Acid | Time (h) | Yields (3a, %) b |
|-------|------------------|------------------|------------|----------|-----------------|
| 1     | CH₂Cl₂           | TfOH             | 1:1.5:1.5  | 6        | 45              |
| 2     | CH₂Cl₂           | CF₃COOH          | 1:1.5:1.5  | 6        | 0               |
| 3     | CH₂Cl₂           | conc. H₂SO₄      | 1:1.5:1.5  | 6        | 0               |
| 4     | CH₂Cl₂           | anhydrous HCl    | 1:1.5:1    | 3        | 0               |
| 5     | CH₂Cl₂           | H₃PO₄ (85%)      | 1:1.5:1.5  | 6        | 0               |
| 6     | CH₂Cl₂           | Et₃N•3HF         | 1:1.5:1.5  | 6        | 0               |
| 7     | CH₂Cl₂           | Et₂O•HBF₄ (85%)  | 1:1.5:1.5  | 6        | 0               |
| 8     | CH₂Cl₂           | TsOH•H₂O         | 1:1.5:1.5  | 6        | 0               |
| 9     | CH₂Cl₂           | (CF₃SO₂)₂NH      | 1:1.5:1.5  | 6        | 0               |
| 10    | CHCl₂CH₂Cl       | TfOH             | 1:1.5:1.5  | 6        | 33              |
| 11    | toluene          | TfOH             | 1:1.5:1.5  | 6        | 19              |
| 12    | PhCl             | TfOH             | 1:1.5:1.5  | 6        | 37              |
| 13    | C₂F₅C₄FCl        | TfOH             | 1:1.5:1.5  | 6        | 24              |
| 14    | MeCN             | TfOH             | 1:1.5:1.5  | 6        | 0               |
| 15    | (CF₃)₂CHOH       | TfOH             | 1:1.5:1.5  | 6        | 0               |
| 16    | CH₂Cl₂           | TfOH             | 1:1.5:1.5  | 3        | 48              |
| 17    | CH₂Cl₂           | TfOH             | 1:1.5:1    | 3        | 71 (68)         |
| 18    | CH₂Cl₂           | TfOH             | 1:1.5:2    | 6        | 15              |
| 19    | CH₂Cl₂           | TfOH             | 1:2:1      | 3        | 57              |
| 20    | CH₂Cl₂           | TfOH             | 1:1:1      | 3        | 39              |
| 21    | CH₂Cl₂           | TfOH             | 1.5:1:1    | 3        | 42              |
| 22    | CH₂Cl₂           | TfOH             | 2:2:1      | 3        | 83 (79)         |

*a Reaction conditions: To a solution of 1a (0.2, 0.3, or 0.4 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.2, 0.3, or 0.4 mmol) in CH₂Cl₂ (1 mL), followed by addition of [Me₄N][SeCF₃] (0.2, 0.3, or 0.4 mmol) within 1 min, at room temperature under N₂. b The yields were determined by HPLC using pure (4-[(1,1′-biphenyl)-4-yl]butan-2-yl)(trifluoromethyl)selenane (3a) as an external standard (t_R = 11.85 min, λ_max = 253 nm, water/methanol (v/v = 10:90)). Isolated yield is depicted in the parenthesis.

Next, the combinations of 1 (2 equiv)/TfOH (1.0 equiv)/[Me₄N][SeCF₃] (2 equiv)/CH₂Cl₂/r.t./3 h and 1 (1.0 equiv)/TfOH (1.0 equiv)/[Me₄N][SeCF₃] (1.5 equiv)/CH₂Cl₂/r.t./3 h (Table 1, entries 17 and 22) were employed to probe the substrate scope of the reaction (Scheme 1). To our delight, a range of but-3-en-1-ylarenes with functional groups such as F, Cl, Br, I, CF₃, NO₂, t-Bu, CH₃, and OCH₃ on the aryl rings were favorably converted to form the corresponding Markownikov-type hydrotrifluoromethylselenolated products (3a–m) under the two standard conditions in good yields. The position of the substituents on the aryl groups of but-3-en-1-ylarenes probably had an influence...
on the hydrotrifluoromethylselenolation as the reactions of alkenes with either electron-donating or withdrawing para-substituents on the aryl functionalities (e.g., 3g and 3j) gave higher yields than those of the substrates bearing ortho- and/or meta-substitution of the same groups on the aryl moieties (e.g., 3h, 3k, and 3l). The reasons for these differences remained unclear. Treatment of 2-(but-3-en-1-yl)naphthalene (1n) with [Me₄N][SeCF₃] and TfOH under the two standard conditions formed 3n in 75% and 52% yields, respectively. The non-substituted but-3-en-1-ylbenzene (1o) and hex-5-en-1-ylbenzene (1p) reacted similarly with [Me₄N][SeCF₃] and TfOH to afford the branched trifluoromethyl selenoethers in 20–54% yields. It should be mentioned that the assembly of 1 (2 equiv)/TfOH (1.0 equiv)/[Me₄N][SeCF₃] (2 equiv)/CH₂Cl₂/r.t./3 h provided higher yields of the desired products than that of 1 (1.0 equiv)/TfOH (1.0 equiv)/[Me₄N][SeCF₃] (1.5 equiv)/CH₂Cl₂/r.t./3 h in most cases, suggesting that the use of excess alkenes was beneficial for promotion of the reaction. Unfortunately, the activated alkenes (e.g., styrene and 4-vinyl-1,1′-biphenyl), internal alkenes (e.g., cyclohexene (1q) and (E)-tetradec-7-ene), and geminal disubstituted alkenes (e.g., (3-methylbut-3-en-1-yl)benzene (1r) and (3-bromobut-3-en-1-yl)benzene reacted with [Me₄N][SeCF₃] and TfOH under the standard conditions to give complicated mixtures, in which the pure products were not isolated even though the ¹⁹F NMR analysis of the reaction mixtures showed the formation of the corresponding desired products.

Scheme 1. Hydrotrifluoromethylselenolation of unactivated terminal alkenes with [Me₄N][SeCF₃] and TfOH. a Reaction conditions: To a solution of 1 (0.4 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.2 mmol) and [Me₄N][SeCF₃] (0.3 mmol). Isolated yields. b The same reaction was run with 1 (0.2 mmol), TfOH (0.2 mmol) and [Me₄N][SeCF₃] (0.3 mmol). Isolated yields. c ¹⁹F NMR yields.

Since the −SCF₃ and −OCF₃ anions have similar reactivities to that of the −SeCF₃ anion, the analogous hydrotrifluoromethylthiolation and hydrotrifluoromethoxylation of unactivated terminal alkenes with the nucleophilic SCF₃ and OCF₃ reagents in the presence of a superacid were also examined. Encouragingly, the straightforward reactions of 1a and TfOH with [Me₄N][SCF₃] under the two standard conditions that were used for the hydrotrifluoromethylselenolation of alkene with [Me₄N][SeCF₃] gave...
the expected branched hydrotrifluoromethylthiolated product (4a) in 48% and 33% yield, respectively (Scheme 2). By this method, a series of unactivated terminal alkenes, such as 1d, 1e, 1g, 1i, 1j, 1n, and 1o, were readily transformed, affording the corresponding products (4b–h) in 16–49% yields. These yields were generally lower than those of the homologous trifluoromethylselenolated products, which might be caused by the poorer nucleophilicity of the −SCF3 anion than the −SeCF3 anion in [Me4N][XCF3] salts. Moreover, because products 4e and 4f had very similar polarity to the alkenes and could not be fully separated from the starting alkenes by column chromatography and preparative TLC plate, they were finally obtained with much lower isolated yields (19–21%) than the 19F NMR yields (48–49%). Nonetheless, reactions of alkene (1a) with CsOCF3 and TfOH under the standard or modified conditions did not form the hydrotrifluoromethoxylated product (see Supplementary Materials), which was determined by 19F NMR analysis of the reaction mixtures. These observations implied that the −SeCF3 anion is a more suitable reagent than the −SCF3 and −OCF3 anions for the hydrotrifluoromethylchalcogenation of unactivated terminal alkenes in the presence of a superacid.

Scheme 2. Hydrotrifluoromethylthiolation of unactivated terminal alkenes with [Me4N][SCF3] and TfOH. a Reaction conditions: To a solution of 1 (0.4 mmol) in CH2Cl2 (1 mL) was added a solution of TfOH (0.2 mmol) in CH2Cl2 (1 mL), followed by addition of [Me4N][SCF3] (0.3 mmol) within 1 min. The mixture was reacted at room temperature under N2 for 3 h. Isolated yields. b The same reaction was run with 1 (0.2 mmol), TfOH (0.2 mmol) and [Me4N][SCF3] (0.3 mmol). Isolated yields. c 19F NMR yields.

It should be noted that the charging sequence of alkene, [Me4N][SeCF3], and TfOH significantly affected the hydrotrifluoromethylselenolation (Table 2). Addition of [Me4N][SeCF3] (2 equiv) to a solution of 1a (2 equiv) and TfOH in CH2Cl2 that was pre-mixed at room temperature for 1 min or 1 h provided 3a in 83% or 65% yield, respectively, under the standard conditions. If a solution of TfOH in CH2Cl2 was introduced into a mixture of [Me4N][SeCF3] (2 equiv) and 1a (2 equiv) that was pre-mixed in CH2Cl2 at room temperature under N2 for 1 min or 1 h, 3a was obtained in 47% or 40% yield, respectively. Surprisingly, if a solution of 1a (2 equiv) in CH2Cl2 was treated with a mixture of [Me4N][SeCF3] (2 equiv) and TfOH that was pre-mixed in CH2Cl2 at room temperature under N2 for 1 min or 1 h, no desired product was formed. When a combination of 1a (1.0 equiv)/TfOH (1.0 equiv)/[Me4N][SeCF3] (1.5 equiv) was used instead of 1a (2.0 equiv)/TfOH (1.0 equiv)/[Me4N][SCF3] (2.0 equiv) for the reactions, similar results were also observed (Table 2). These results demonstrated that pre-activation of 1a by TfOH was very essential for the hydrotrifluoromethylselenolation of 1a with [Me4N][SeCF3], whereas pre-treatment of [Me4N][SeCF3] with TfOH led to complete failure of the reaction. Since pre-mixing 1a with TfOH for 1 h gave a lower yield of 3a (65% or 11%) than that (83% or 71%) for 1 min, the longer pre-treatment of 1a and TfOH might harm the subsequent hydrotrifluoromethylselenolation,
which was likely attributed to the decay of the key reactive intermediates. Furthermore, the $^1$H and $^{19}$F NMR analysis of a reaction mixture of 1a and TiOH in the absence of [Me$_4$N][SeCF$_3$] showed the fast conversion of 1a and formation of an alkyl triflate (Figures S13–S24 (see Supplementary Materials)), but the similar measurement of a mixture of [Me$_4$N][SeCF$_3$] and TiOH in the absence of 1a revealed a very complicated system (Figures S1–S12 (see Supplementary Materials)). These outcomes might explain in part the distinct results of the reactions with different charging sequences under the standard conditions.

### Table 2. The effects of charging sequence on the reaction.

| Method | Yield (3a, %)$^a$ | Yield (3a, %)$^b$ |
|--------|------------------|------------------|
| Method A | 83$^c$, 65$^d$ | 71$^c$, 11$^d$ |
| Method B | 47$^c$, 40$^d$ | 45$^c$, 42$^d$ |
| Method C | 0$^c$, 0$^d$ | 0$^c$, 0$^d$ |

$^a$ Reaction conditions: 1a (0.4 mmol), [Me$_4$N][SeCF$_3$] (0.4 mmol), TiOH (0.2 mmol), CH$_2$Cl$_2$ (2 mL), rt, 3 h, N$_2$. The yields were determined by HPLC using 3a as an external standard ($t_R = 11.85$ min, $\lambda_{max} = 253$ nm, water/methanol ($\nu\psi = 10:90$)).  

$^b$ Reaction conditions: 1a (0.2 mmol), [Me$_4$N][SeCF$_3$] (0.3 mmol), TiOH (0.2 mmol), CH$_2$Cl$_2$ (2 mL), rt, 3 h, N$_2$. The yields were determined by HPLC using 3a as an external standard ($t_R = 11.85$ min, $\lambda_{max} = 253$ nm, water/methanol ($\nu\psi = 10:90$)). Method A: To a solution of 1a and TiOH in CH$_2$Cl$_2$ (2 mL) was added [Me$_4$N][SeCF$_3$]. Method B: To a mixture of 1a and [Me$_4$N][SeCF$_3$] in CH$_2$Cl$_2$ (1 mL) was added a solution of TiOH in CH$_2$Cl$_2$ (1 mL). Method C: To a mixture of [Me$_4$N][SeCF$_3$] and TiOH in CH$_2$Cl$_2$ (1 mL) was added a solution of 1a in CH$_2$Cl$_2$ (1 mL).  

The two reactants were premixed for 1 h before addition of the third one.  

On the basis of the above observations, a plausible reaction mechanism for the TiOH-mediated hydrotrifluoromethylselenolation of unactivated terminal alkene was suggested in Scheme 3. First, Markovnikov-type protonation of the carbon–carbon double bond of alkene at the terminal carbon site forms a relatively stable alkyl cation intermediate (5), which is combined with the $^{-}$OTf anion to yield a secondary alkyl triflate (6). Then, nucleophilic attack of 6 by the free $^{-}$SeCF$_3$ anion generates the final product (3) (path a). Alternatively, direct trifluoromethylselenolation of the secondary carbon cation (5) upon its formation by $^{-}$SeCF$_3$ can also form the desired product (path b). Path a could be the most plausible process in the reactions according to the NMR experiments (Figures S13–S24) if alkene was pre-mixed with TiOH before addition of [Me$_4$N][SeCF$_3$]. Nevertheless, the in situ generation of HSeCF$_3$ from metathesis of [Me$_4$N][SeCF$_3$] and TiOH followed by addition of HSeCF$_3$ to the carbon–carbon double bond of alkene could be excluded (path c) as the reactions of 1a with mixtures of [Me$_4$N][SeCF$_3$] and TiOH that were pre-mixed at room temperature for some time gave no hydrotrifluoromethylselenolated product (Table 2).

### Scheme 3. A proposed reaction mechanism for TiOH-mediated hydrotrifluoromethylselenolation of unactivated terminal alkene.
3. Materials and Methods

3.1. General Information

All reactions were carried out under a nitrogen atmosphere unless otherwise specified. The NMR spectra were recorded in CDCl$_3$ on a 500 (for $^1$H), 471 (for $^{19}$F), and 126 MHz (for $^{13}$C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm) for $^1$H NMR and PhOCH$_3$F (58.0 ppm) or PhOCF$_3$ (63.0 ppm) for $^{19}$F NMR as an internal or external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 µm, 4.6 × 250 mm), and the HPLC yields of the product were determined by using the corresponding pure compound as the external standard. MS experiments were performed on a TOF-Q ESI or EI instrument. Reagents [Me$_4$N][SeCF$_3$] (2a), [Me$_4$N][SeCF$_3$] (2b), and CsOCF$_3$ were synthesized according to the literature [74,75]. Substrates 1a–f [76], 1g–1h [77], 1i–1l [76], 1m–1n [78], and 1p–1r [78] were synthesized according to the literature. Solvents were dried before use according to the literature [79]. Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

3.2. General Procedure for Hydrotrifluoromethylselenolation of Unactivated Terminal Alkenes

Under a nitrogen atmosphere, a Schlenk tube was charged with 1 (0.4 or 0.2 mmol) and CH$_2$Cl$_2$ (1 mL) with stirring. A solution of TfOH (0.2 mmol) in CH$_2$Cl$_2$ was added, followed by addition of [Me$_4$N][SeCF$_3$] (2a, 0.4 or 0.3 mmol) within 1 min. The mixture was reacted at room temperature under N$_2$ for 3 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoromethylselenolated products (3).

(4-[[1,1′-Biphenyl]-4-yl]butan-2-yl)(trifluoromethyl)selenane (3a)

Yellow oil, 59.4 mg (79%), 1a:[Me$_4$N][SeCF$_3$]:TfOH = 2:2:1) and 50.8 mg (68%, 1a:[Me$_4$N][SeCF$_3$]:TfOH = 1:1:5:1), petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J$ = 8.1 Hz, 2H), 7.57 (d, $J$ = 7.8 Hz, 2H), 7.47 (t, $J$ = 7.7 Hz, 2H), 7.37 (t, $J$ = 7.9 Hz, 1H), 7.30 (d, $J$ = 8.0 Hz, 2H), 3.59 (m, 1H), 2.89–2.79 (m, 2H), 2.19–2.03 (m, 2H), 1.68 (d, $J$ = 6.9 Hz, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ –31.9 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.0, 140.0, 139.2, 128.9, 128.8, 127.3, 127.2, 127.0, 123.2 (q, $J$ = 331.1 Hz), 39.5, 39.2, 33.4, 23.1. IR (KBr): 2985, 2975, 2950, 2927, 2855, 1851, 1564, 1520, 1487, 1450, 1409, 1383, 1260, 1212, 1098, 1008, 838, 761, 738, 697, 598, 550, 507 cm$^{-1}$. HRMS-ESI (m/z) calcd. for C$_{27}$H$_{19}$F$_2$Se ([M + H]$^+$): 359.0520; found: 359.0511.

(4-(4-Fluorobiphenyl)butan-2-yl)(trifluoromethyl)selenane (3b)

Yellow oil, 25.8 mg (43%, 1b:[Me$_4$N][SeCF$_3$]:TfOH = 2:2:1) and 23.4 mg (39%, 1b:[Me$_4$N][SeCF$_3$]:TfOH = 1:1:5:1), petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J$ = 8.3 Hz, 2H), 7.07 (d, $J$ = 8.3 Hz, 2H), 3.50 (m, 1H), 2.78–2.68 (m, 2H), 2.09–1.93 (m, 2H), 1.62 (d, $J$ = 7.0 Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ –32.0 (s, 3F), –117.2 (m, 1F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.5 (d, $J$ = 244.5 Hz), 136.4 (d, $J$ = 3.3 Hz), 129.7 (d, $J$ = 7.8 Hz), 123.1 (q, $J$ = 330.8 Hz), 115.3 (d, $J$ = 21.1 Hz), 39.3, 39.2, 32.9, 23.0. IR (KBr): 3041, 2927, 2856, 1602, 1511, 1455, 1383, 1259, 1224, 1157, 1098, 1016, 827, 760, 738, 543 cm$^{-1}$. HRMS-ESI (m/z) calcd. for C$_{11}$H$_{12}$F$_4$Se: 294.0100; found: 294.0109.

(4-(4-Chlorobiphenyl)butan-2-yl)(trifluoromethyl)selenane (3c)

Yellow oil, 49.3 mg (78%, 1c:[Me$_4$N][SeCF$_3$]:TfOH = 2:2:1) and 36.0 mg (57%, 1c:[Me$_4$N][SeCF$_3$]:TfOH = 1:1:5:1), petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J$ = 8.4 Hz, 2H), 7.12 (d, $J$ = 8.3 Hz, 2H), 3.50 (m, 1H), 2.79–2.69 (m, 2H), 2.09–1.94 (m, 2H), 1.62 (d, $J$ = 6.9 Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ –32.0 (s, 3F). $^{13}$C NMR
(126 MHz, CDCl₃) δ 139.3, 132.0, 129.7, 128.7, 123.1 (q, J = 331.3 Hz), 39.2, 39.1, 33.0, 23.0. IR (KBr): 3084, 3028, 2927, 2856, 1895, 1731, 1598, 1493, 1455, 1408, 1383, 1290, 1279, 1260, 1232, 1214, 1096, 1035, 1016, 832, 818, 807, 778, 738, 715, 672, 663, 631, 523 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₀H₁₂Cl ([M – SeCF₃]⁺): 167.0622; found: 167.0624.

(4-(4-Bromophenyl)butan-2-yl)(trifluoromethyl)selane (3d)

Yellow oil, 58.3 mg (81%, 1d:[Me₄N][SeCF₃]:TfOH = 2:2:1) and 43.2 mg (60%, 1d:[Me₄N][SeCF₃]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 3.50 (m, 1H), 2.78–2.68 (m, 2H), 2.09–1.93 (m, 2H), 1.62 (d, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 129.8, 131.6, 130.1, 123.1 (q, J = 331.2 Hz), 120.0, 39.2, 39.0, 33.1, 23.0. IR (KBr): 3025, 2961, 2926, 2863, 1489, 1454, 1405, 1383, 1278, 1260, 1214, 1097, 1074, 1012, 960, 897, 828, 813, 802, 770, 738, 711, 654, 634, 605, 515 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃Br²⁴Se: 353.9299; found: 353.9307.

(4-(4-Iodophenyl)butan-2-yl)(trifluoromethyl)selane (3e)

Yellow oil, 69.3 mg (85%, 1e:[Me₄N][SeCF₃]:TfOH = 2:2:1) and 43.2 mg (53%, 1e:[Me₄N][SeCF₃]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 3.49 (m, 1H), 2.76–2.67 (m, 2H), 2.08–1.93 (m, 2H), 1.62 (d, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 140.5, 137.6, 130.5, 123.1 (q, J = 331.2 Hz), 91.3, 39.2, 39.0, 33.2, 23.0. IR (KBr): 3019, 2960, 2925, 2854, 1485, 1454, 1401, 1382, 1291, 1275, 1260, 1213, 1202, 1097, 1063, 1035, 1007, 897, 826, 799, 766, 738, 709, 512 cm⁻¹. HRMS-ESI (m/z) calcd. for C₉H₁₂I₂Se ([M – CF₃]⁺): 337.9196; found: 337.9198.

(Trifluoromethyl)(4-(4(trifluoromethyl)phenyl)butan-2-yl)selane (3f)

Yellow oil, 42.0 mg (60%, 1f:[Me₄N][SeCF₃]:TfOH = 2:2:1) and 30.1 mg (43%, 1f:[Me₄N][SeCF₃]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.51 (m, 1H), 2.89–2.79 (m, 2H), 2.13–1.98 (m, 2H), 1.64 (d, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 145.0, 128.7, 128.6 (q, J = 32.4 Hz), 125.5 (q, J = 3.8 Hz) 124.3 (q, J = 275.1 Hz), 123.1 (q, J = 330.8 Hz), 39.2, 38.9, 33.5, 23.0. IR (KBr): 2958, 2929, 2858, 1620, 1456, 1419, 1384, 1327, 1165, 1117, 1095, 1068, 1019, 899, 840, 823, 738, 650, 633, 599 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₂F₆²⁴Se: 344.0068; found: 344.0061.

(4-(4-Nitrophenyl)butan-2-yl)(trifluoromethyl)selane (3g)

Yellow oil, 46.4 mg (71%, 1g:[Me₄N][SeCF₃]:TfOH = 2:2:1) and 28.1 mg (43%, 1g:[Me₄N][SeCF₃]:TfOH = 1:1.5:1), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.50 (m, 1H), 2.94–2.84 (m, 2H), 2.14–2.00 (m, 2H), 1.64 (d, J = 6.9 Hz, 3H). ¹³F NMR (471 MHz, CDCl₃) δ −32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 148.7, 146.7, 129.2, 123.9, 123.0 (q, J = 331.1 Hz), 39.0, 38.7, 33.6, 23.0. IR (KBr): 3112, 3080, 2950, 2929, 2856, 2453, 2217, 1927, 1727, 1602, 1520, 1495, 1455, 1384, 1347, 1319, 1289, 1236, 1263, 1180, 1098, 1035, 1016, 973, 891, 858, 848, 806, 768, 747, 738, 698, 660, 647, 632, 619, 513 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₁H₁₃F₃NO₂Se ([M + H]⁺): 328.0058; found: 328.0060.

(4-(2-Nitrophenyl)butan-2-yl)(trifluoromethyl)selane (3h)

Yellow oil, 37.3 mg (57%, 1h:[Me₄N][SeCF₃]:TfOH = 2:2:1) and 21.6 mg (33%, 1h:[Me₄N][SeCF₃]:TfOH = 1:1.5:1), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.40–7.36 (m, 2H), 3.60 (m, 1H), 3.11–2.98 (m, 2H), 2.14–2.03 (m, 2H), 1.66 (d, J = 7.0 Hz, 3H). ¹³F NMR (471 MHz, CDCl₃) δ −32.1 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 149.2, 136.1, 133.2, 132.0,
127.5, 125.0, 123.1 (q, J = 330.5 Hz), 39.5, 38.5, 31.3, 22.8. IR (KBr): 3069, 2964, 2928, 2856, 1611, 1579, 1527, 1481, 1457, 1383, 1348, 1281, 1231, 1215, 1099, 959, 861, 813, 787, 739, 702, 667 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃NO₂Se: 321.0045; found: 321.0039.

(4-(4-(Tert-butyl)phenyl)butan-2-yl)(trifluoromethyl)selane (3i)

Yellow oil, 45.3 mg (67%, 1i:[Me₄N][SeCF₃]:TiOH = 2:2:1) and 33.8 mg (50%, 1i:[Me₄N][SeCF₃]:TiOH = 1:1:5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.55 (m, 1H), 2.79–2.69 (m, 2H), 2.12–1.96 (m, 2H), 1.64 (d, J = 6.9 Hz, 3H), 1.32 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ −32.0 (s, 3F). ¹⁹F NMR (471 MHz, CDCl₃) δ −32.0 (s, 3F). IR (KBr): 3183, 3024, 2964, 1517, 1457, 1412, 1394, 1382, 1364, 1269, 1234, 1215, 1039, 1035, 1019, 829, 815, 738, 569 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₅H₂₁F₃Se: 332.0820; found: 332.0816.

(4-(p-Tolyl)butan-2-yl)(trifluoromethyl)selane (3j)

Yellow oil, 46.2 mg (78%, 1j:[Me₄N][SeCF₃]:TiOH = 2:2:1) and 29.6 mg (50%, 1j:[Me₄N][SeCF₃]:TiOH = 1:1:5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.12–7.08 (m, 4H), 3.53 (m, 1H), 2.78–2.68 (m, 2H), 2.33 (s, 3H), 2.10–1.94 (m, 2H), 1.63 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 137.7, 135.7, 129.2, 128.3, 123.2 (q, J = 330.5 Hz), 39.4, 39.3, 33.2, 23.0, 21.0. IR (KBr): 3048, 3020, 2925, 2859, 1516, 1454, 1381, 1260, 1214, 1097, 1022, 830, 807, 738, 543 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃Se: 290.0351; found: 290.0349.

(4-(o-Tolyl)butan-2-yl)(trifluoromethyl)selane (3k)

Yellow oil, 30.2 mg (51%, 1k:[Me₄N][SeCF₃]:TiOH = 2:2:1) and 34.3 mg (58%, 1k:[Me₄N][SeCF₃]:TiOH = 1:1:5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.16–7.14 (m, 4H), 3.60 (m, 1H), 2.82–2.70 (m, 2H), 2.32 (s, 3H), 2.06–1.92 (m, 2H), 1.67 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −32.1 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 139.1, 135.8, 130.4, 128.8, 126.3, 126.1, 123.1 (q, J = 330.2 Hz), 39.8, 38.1, 31.2, 23.0, 19.2. IR (KBr): 3066, 3018, 2958, 2928, 2869, 1605, 1493, 1459, 1382, 1265, 1222, 1098, 1012, 754, 739 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃Se: 290.0351; found: 290.0345.

(4-(m-Tolyl)butan-2-yl)(trifluoromethyl)selane (3l)

Yellow oil, 33.7 mg (57%, 1l:[Me₄N][SeCF₃]:TiOH = 2:2:1) and 26.1 mg (44%, 1l:[Me₄N][SeCF₃]:TiOH = 1:1:5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.20 (t, J = 7.5 Hz, 1H), 7.04–6.99 (m, 3H), 3.54 (m, 1H), 2.79–2.69 (m, 2H), 2.35 (s, 3H), 2.12–1.96 (m, 2H), 1.64 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.8, 138.1, 129.2, 128.4, 126.9, 125.4, 123.2 (q, J = 330.4 Hz), 39.5, 39.2, 33.6, 23.1, 21.4. IR (KBr): 3023, 2966, 2925, 2860, 1610, 1591, 1489, 1455, 1382, 1355, 1213, 1098, 882, 783, 738, 719, 699 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃Se: 290.0351; found: 290.0357.

(4-(4-Methoxyphenyl)butan-2-yl)(trifluoromethyl)selane (3m)

Yellow oil, 33.7 mg (78%, 1m:[Me₄N][SeCF₃]:TiOH = 2:2:1) and 26.1 mg (57%, 1m:[Me₄N][SeCF₃]:TiOH = 1:1:5:1), a mixture of petroleum ether and ethyl acetate (80:1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 3.52 (m, 1H), 2.76–2.66 (m, 2H), 2.09–1.93 (m, 2H), 1.63 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 158.1, 132.9, 129.3, 123.1 (q, J = 331.0 Hz), 114.0, 55.3, 39.4, 39.4, 32.7, 23.1. IR (KBr): 3032, 2991, 2954, 2928, 2855, 2837, 1613, 1584, 1513, 1456, 1382, 1301, 1248, 1178, 1098, 1038, 827, 809, 750, 738, 552, 519 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₃H₂₁F₃Se: 332.0820; found: 332.0816.
(4-(Naphthalen-2-yl)butan-2-yl)(trifluoromethyl)selane (3n)

Yellow oil, 49.8 mg (75%, 1n:[Me4N][SeCF3]:TfOH = 2:2:1) and 34.5 mg (52%, 1n:[Me4N][SeCF3]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, CDCl3) δ 7.83–7.79 (m, 3H), 7.64 (s, 1H), 7.49–7.43 (m, 2H), 7.33 (dd, J = 8.4 Hz, 1.1 Hz, 1H), 3.57 (m, 1H), 2.99–2.90 (m, 2H), 2.22–2.06 (m, 2H), 1.66 (d, J = 6.9 Hz, 3H). ^19F NMR (471 MHz, CDCl3) δ −31.9 (s, 3F). ^13C NMR (126 MHz, CDCl3) δ 138.3, 133.6, 132.1, 128.1, 127.6, 127.4, 127.0, 126.6, 126.1, 125.4, 123.2 (q, J = 330.9 Hz), 39.4, 39.0, 33.8, 23.1. IR (KBr): 3054, 3015, 2958, 2924, 2853, 1633, 1601, 1509, 1454, 1382, 1261, 1242, 1201, 1097, 1019, 960, 888, 853, 817, 746, 738 cm^-1. HRMS-EI (m/z) calcd. for C_{19}H_{12}F_{3}Se: 326.0351; found: 326.0352.

(4-Phenylbutan-2-yl)(trifluoromethyl)selane (3o).

Yellow oil, 23.1 mg (41%, 1o:[Me4N][SeCF3]:TfOH = 2:2:1) and 11.3 mg (20%, 1o:[Me4N][SeCF3]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, CDCl3) δ 7.30 (t, J = 7.6 Hz, 2H), 7.23–7.19 (m, 3H), 3.53 (m, 1H), 2.82–2.73 (m, 2H), 2.13–1.97 (m, 2H), 1.63 (d, J = 6.9 Hz, 3H). ^19F NMR (471 MHz, CDCl3) δ −32.0 (s, 3F). ^13C NMR (126 MHz, CDCl3) δ 140.8, 128.5, 128.4, 126.2, 123.1 (q, J = 330.5 Hz), 39.4, 39.2, 33.7, 23.0 [43,46].

(6-Phenylhexan-2-yl)(trifluoromethyl)selane (3p).

Yellow oil, 33.5 mg (54%, 1p:[Me4N][SeCF3]:TfOH = 2:2:1) and 21.1 mg (34%, 1p:[Me4N][SeCF3]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, CDCl3) δ 7.30 (t, J = 7.60 Hz, 2H), 7.21–7.18 (m, 3H), 3.55 (m, 1H), 2.64 (t, J = 7.7 Hz, 2H), 1.84–1.70 (m, 2H), 1.69–1.63 (m, 1H), 1.58 (d, J = 6.9 Hz, 3H), 1.52–1.44 (m, 2H). ^19F NMR (471 MHz, CDCl3) δ −32.3 (s, 3F). ^13C NMR (126 MHz, CDCl3) δ 142.3, 128.4, 128.3, 125.8, 123.2 (q, J = 330.8 Hz), 39.9, 37.4, 35.7, 31.0, 27.1, 22.9. IR (KBr): 3084, 3064, 3028, 2932, 2859, 1604, 1497, 1454, 1382, 1205, 1099, 1030, 909, 747, 738, 699 cm^-1. HRMS-EI (m/z) calcd. for C_{21}H_{17}F_{3}Se: 304.0507; found: 304.0502.

3.3. General Procedure for Hydrotrifluoromethylthiolation of Unactivated Terminal alkenes

Under a nitrogen atmosphere, a Schlenk tube was charged with 1 (0.4 or 0.2 mmol) and CH_{2}Cl_{2} (1 mL) with stirring. A solution of TfOH (0.2 mmol) in CH_{2}Cl_{2} was added, followed by addition of [Me4N][SCF3] (2b, 0.4 or 0.3 mmol) within 1 min. The mixture was reacted at room temperature under N_{2} for 3 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoromethylthiolated products (4).

(4-[(1,1’-Biphenyl)-4-yl]butan-2-yl)(trifluoromethyl)sulfane (4a)

Yellow oil, 29.8 mg (48%, 1a:[Me4N][SCF3]:TfOH = 2:2:1) and 20.5 mg (33%, 1a:[Me4N][SCF3]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, CDCl3) δ 7.59 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 2H), 7.35 (m, 1H), 3.28–3.27 (m, 2H), 2.86–2.77 (m, 2H), 2.05–1.93 (m, 2H), 1.50 (d, J = 6.9 Hz, 3H). ^19F NMR (471 MHz, CDCl3) δ −38.8 (s, 3F). ^13C NMR (126 MHz, CDCl3) δ 140.9, 140.0, 139.2, 131.2 (q, J = 305.9 Hz), 128.8, 128.9, 127.3, 127.1, 127.0, 40.7, 38.5, 32.5, 22.5. IR (KBr): 3081, 3057, 3029, 2966, 2928, 2859, 1602, 1520, 1487, 1451, 1409, 1393, 1298, 1264, 1247, 1146, 1116, 1040, 1008, 965, 912, 838, 761, 732, 697, 642, 586, 553, 510 cm^-1. HRMS-EI (m/z) calcd. for C_{19}H_{17}F_{3}S: 310.1003; found: 310.1006.

(4-(4-Bromophenyl)butan-2-yl)(trifluoromethyl)sulfane (4b)

Yellow oil, 23.7 mg (38%, 1d:[Me4N][SCF3]:TfOH = 2:2:1) and 25.0 mg (40%, 1d:[Me4N][SCF3]:TfOH = 1:1.5:1), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, CDCl3) δ 7.42 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 3.29 (m, 1H), 2.77–2.68 (m, 2H), 1.98–1.86 (m, 2H), 1.46 (d, J = 6.9 Hz, 3H). ^19F NMR (471 MHz, CDCl3) δ −38.9 (s, 3F). ^13C NMR (126 MHz, CDCl3) δ 139.8, 131.6, 131.1 (q, J = 305.9 Hz), 130.1, 120.0, 40.5, 38.3, 32.2, 22.5. IR (KBr): 3026, 2966, 2929,
(4-(4-Iodophenyl)butan-2-yl)(trifluoromethyl)sulfane (4c)

Yellow oil, 34.6 mg (48%, 1e:[Me₄N][SCF₃]:TfOH = 2:2:1) and 33.8 mg (47%, 1e:[Me₄N][SCF₃]:TfOH = 1:1:5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 3.29 (m, 1H), 2.76–2.67 (m, 1H), 1.98–1.86 (m, 2H), 1.46 (d, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 140.5, 137.6, 131.1 (q, J = 306.0 Hz), 130.5, 91.2, 40.5, 38.3, 32.3, 22.5. IR (KBr): 3068, 3021, 2965, 2928, 2857, 1898, 1640, 1588, 1486, 1455, 1402, 1383, 1354, 1297, 1280, 1235, 1148, 1115, 1062, 1041, 1007, 961, 898, 826, 801, 756, 710, 631, 519 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₁H₁₂F₃BrS: 359.9656; found: 359.9660.

(4-(4-Nitrophenyl)butan-2-yl)(trifluoromethyl)sulfane (4d)

Yellow oil, (26.8 mg (48%, 1g:[Me₄N][SCF₃]:TfOH = 2:2:1), 48%; 23.4 mg (1g:[Me₄N][SCF₃]:TfOH = 1:1:5:1), 42%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 3.30 (m, 1H), 2.94–2.83 (m, 2H), 2.01–1.94 (m, 2H), 1.49 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 148.6, 146.7, 131.0 (q, J = 306.5 Hz), 129.2, 123.9, 40.5, 37.9, 32.8, 22.5. IR (KBr): 3080, 2928, 2855, 2447, 1916, 1687, 1601, 1520, 1495, 1456, 1384, 1347, 1295, 1112, 1041, 1016, 901, 858, 848, 806, 756, 748, 698, 633, 519 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₁H₁₂F₃NO₂S: 279.0541; found: 279.0538.

(4-(4-Tert-butyl)phenyl)butan-2-yl)(trifluoromethyl)sulfane (4e)

Yellow oil, 12.2 mg (21%, 1i:[Me₄N][SCF₃]:TfOH = 2:2:1) and 9.3 mg (16%, 1i:[Me₄N][SCF₃]:TfOH = 1:1:5:1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 3.33 (m, 1H), 2.78–2.69 (m, 2H), 1.99–1.88 (m, 2H), 1.47 (d, J = 6.9 Hz, 3H), 1.32 (s, 9H). ¹⁹F NMR (471 MHz, CDCl₃) δ −38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.0, 137.8, 131.2 (q, J = 306.3 Hz), 128.0, 125.4, 40.8, 38.5, 34.4, 32.3, 31.4, 22.4. IR (KBr): 3057, 3025, 2965, 2929, 2858, 1645, 1512, 1461, 1415, 1395, 1382, 1364, 1269, 1150, 1116, 1043, 1020, 900, 829, 814, 756, 645, 570 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₅H₂₂F₃S ([M + H]+): 291.1380; found: 291.1389.

(4-(p-Toly)butan-2-yl)(trifluoromethyl)sulfane (4f)

Yellow oil, (9.4 mg (1j:[Me₄N][SCF₃]:TfOH = 2:2:1), 19%; 7.9 mg (1j:[Me₄N][SCF₃]:TfOH = 1:1:5:1), 16%), petroleum ether as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.31 (m, 1H), 2.77–2.68 (m, 2H), 2.33 (s, 3H), 1.99–1.86 (m, 2H), 1.46 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 137.7, 135.7, 131.2 (q, J = 306.5 Hz), 129.2, 128.3, 40.6, 38.6, 32.4, 22.5, 21.0. IR (KBr): 3191, 2965, 2927, 2854, 1739, 1660, 1632, 1516, 1464, 1411, 1378, 1261, 1100, 1020, 865, 800, 756, 703 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₁H₁₂F₃S: 248.0847; found: 248.0841.

(4-(Naphthalen-2-yl)butan-2-yl)(trifluoromethyl)sulfane (4g)

Yellow oil, 26.1 mg (46%, 1n:[Me₄N][SCF₃]:TfOH = 2:2:1) and 22.7 mg (40%, 1n:[Me₄N][SCF₃]:TfOH = 1:1:5:1), petroleum ether as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.83–7.79 (m, 3H), 7.64 (s, 1H), 7.49–7.43 (m, 2H), 7.34 (dd, J = 8.4, 1.6 Hz, 1H), 3.35 (m, 1H), 2.99–2.89 (m, 2H), 2.11–1.98 (m, 2H), 1.50 (d, J = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ −38.8 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 138.3, 133.6, 132.1, 131.2 (q, J = 306.5 Hz), 128.2, 127.7, 127.5, 127.0, 126.6, 126.1, 125.4, 40.7, 38.4, 33.0, 22.5. IR (KBr): 3055, 3021, 2927, 2855, 1635, 1601, 1509, 1455, 1382, 1351, 1298, 1271, 1247, 1146, 1117, 1044, 1019, 961, 910, 889, 853, 817, 747 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₂H₁₅F₃S: 284.0847; found: 284.0841.
4. Conclusions

In summary, we have developed a convenient method for Markovnikov-type hydrotrifluoromethylselenolation of aliphatic terminal alkenes with [Me₄N][SeCF₃] and TfOH. The reaction proceeded smoothly at room temperature and furnished the branched trifluoromethylselenolated products in good yields. This protocol was also applicable to the Markovnikov-type hydrotrifluoromethylthiolation of unactivated terminal alkenes using [Me₄N][SCF₃] and TfOH, which exhibited relatively poorer reactivity than that of [Me₄N][SeCF₃] under the two standard conditions. Nevertheless, reactions of alkene with CsOCF₃ and TfOH under the same conditions did not form the hydrotrifluoromethoxylated product. The successful hydrotrifluoromethylselenolation and hydrotrifluoromethylthiolation reactions featured simplicity, convenience, and high regioselectivity, taming the sensitive −XCF₃ (X = Se, S) anions with TfOH, and represented the first synthesis of Markovnikov-type alkyl trifluoromethyl selenoethers and thioethers from unactivated terminal alkenes. Application of [Me₄N][SeCF₃] as a viable SeCF₃ source for bifunctionalization of simple alkenes is currently under way in our laboratory.

Supplementary Materials: The brief description of screening the optimal reaction conditions, general procedures for hydrotrifluoromethylchalcogenation of unactivated terminal alkenes with [Me₄N][XCF₃] (X = S, Se), and TfOH, control experiments for mechanistic insights, characterization data, and NMR spectra of the products (PDF) are available online.

Author Contributions: J.S.: literature search, performing the experiments, figures and data collection, data analysis and interpretation, and writing the draft of the manuscript. C.-P.Z.: substantial contributions to the conception and design of the work, manuscript writing, and final approval of the version to be published. The authors agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Wuhan University of Technology and the “Hundred Talent” Program of Hubei Province (China).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kirsch, P. Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications, 2nd ed.; Wiley-VCH: Wernheim, Germany, 2013.
2. Shao, X.; Xu, C.; Lu, L.; Shen, Q. Shelf-Stable Electrophilic Reagents for Trifluoromethylthiolation. Acc. Chem. Res. 2015, 48, 1227–1236. [CrossRef] [PubMed]
3. Xu, X.-H.; Matsuzaki, K.; Shibata, N. Synthetic Methods for Compounds Having CF₃-S Units on Carbon by Trifluoromethylation, Trifluoromethylthiolation, Trifylation, and Related Reactions. Chem. Rev. 2015, 115, 731–764. [CrossRef] [PubMed]
4. Barata-Vallejo, S.; Bonesi, S.; Postigo, A. Late Stage Trifluoromethylthiolation Strategies for Organic Compounds. Org. Biomol. Chem. 2016, 14, 7150–7182. [CrossRef] [PubMed]
5. Tlili, A.; Toulgoat, F.; Billard, T. Synthetic Approaches to Trifluoromethoxy-Substituted Compounds. Angew. Chem. Int. Ed. 2016, 55, 11726–11735. [CrossRef] [PubMed]
6. Zhang, X.; Tang, P. Recent Advances in New Trifluoromethoxylation Reagents. Sci. China Chem. 2019, 62, 525–532. [CrossRef]
7. Song, H.-X.; Han, Q.-Y.; Zhao, C.-L.; Zhang, C.-P. Fluoroalkylation Reactions in Aqueous Media: A Review. Green Chem. 2018, 20, 1662–1731. [CrossRef]
8. Hardy, M.A.; Chachignon, H.; Cahard, D. Advances in Asymmetric Di-and Trifluoromethylthiolation, and Di- and Trifluoromethoxylation Reactions. Asian J. Org. Chem. 2019, 8, 591–609. [CrossRef]
9. Wu, S.; Song, H.-X.; Zhang, C.-P. Fluoroalkylation of Diazo Compounds with Diverse R₃Sn Reagents. Chem. Asian J. 2020, 15, 1660–1677. [CrossRef]
10. Han, Z.-Z.; Zhang, C.-P. Fluorination and Fluoroalkylation Reactions Mediated by Hypervalent Iodine Reagents. Adv. Synth. Catal. 2020. [CrossRef]
11. Tlili, A.; Ismalaj, E.; Glenadel, Q.; Ghiazza, C.; Billard, T. Synthetic Approaches to Trifluoromethylselenolated Compounds. *Chem. Eur. J.* 2018, 24, 3659–3670. [CrossRef]
12. Ghiazza, C.; Billard, T.; Tlili, A. Merging Visible-Light Catalysis for the Direct Late-Stage Group-16-Trifluoromethyl Bond Formation. *Chem. Eur. J.* 2019, 25, 6482–6495. [CrossRef] [PubMed]
13. Ghiazza, C.; Monnereau, C.; Khrouz, L.; Medebielle, M.; Billard, T.; Tlili, A. New Avenues in Radical Trifluoromethylselenylation with Trifluoromethyl Tolueneselenosulfonate. *Synlett* 2019, 30, 777–782. [CrossRef]
14. Peeler, J.C.; Weerapana, E. Chemical Biology Approaches to Interrogate the Selenoproteome. *Acc. Chem. Res.* 2019, 52, 2832–2840. [CrossRef] [PubMed]
15. Robberecht, H.; De Bruyne, T.; Davioud-Charvet, E.; Mackrill, J.; Hermans, N. Selenium Status in Elderly People: Longevity and Age-Related Diseases. *Curr. Pharm. Design* 2019, 25, 1694–1706. [CrossRef]
16. Rayman, M.P. Selenium and Human Health. *Lancet* 2012, 379, 1256–1268. [CrossRef]
17. Weekley, C.M.; Harris, H.H. Which Form is That? The Importance of Selenium Speciation and Metabolism in the Prevention and Treatment of Disease. *Chem. Soc. Rev.* 2013, 42, 8870–8894. [CrossRef]
18. Misra, S.; Boylan, M.; Selvam, A.; Spallholz, J.E.; Björnstedt, M. Redox-Active Selenium Compounds—From Toxicity and Cell Death to Cancer Treatment. *Nutrients* 2015, 7, 3536–3556. [CrossRef]
19. Ma, J.-J.; Yi, W.-B.; Lu, G.-P.; Cai, C. Trifluoromethylation of Thiophenols and Thiols with Sodium Trifluoromethanesulfinate and Iodine Pentoxide. *Catal. Sci. Technol.* 2016, 6, 417–421. [CrossRef]
20. Billard, T.; Langlois, B.R. A New Simple Access to Trifluoromethyl Thioethers or Selenoethers from Trifluoromethyl Trimethylsilane and Disulfides or Diselenides. *Tetrahedron Lett.* 1996, 37, 6865–6868. [CrossRef]
21. Billard, T.; Large, S.; Langlois, B.R. Preparation of Trifluoromethyl Sulfinates or Seleninates from Trifluoromethyl Trimethylsilyl and Thiocyanates or Selenocyanates. *Tetrahedron Lett.* 1997, 38, 65–68. [CrossRef]
22. Large, S.; Roques, N.; Langlois, B.R. Nucleophilic Trifluoromethylation of Carbonyl Compounds and Disulfides with Trifluoromethane and Silicon-Containing Bases. *J. Org. Chem.* 2000, 65, 8848–8856. [CrossRef] [PubMed]
23. Potash, S.; Rozen, S. General Synthesis of Trifluoromethyl Selenides Utilizing Selenocyanates and Fluoroform. *J. Org. Chem.* 2014, 79, 11205–11208. [CrossRef] [PubMed]
24. Pooput, C.; Medebielle, M.; Dolbier Jr., W. R. A New and Efficient Method for the Synthesis of Trifluoromethylthio- and Selenoethers. *Org. Lett.* 2004, 6, 301–303. [CrossRef]
25. Pooput, C.; Dolbier, W.R., Jr.; Medebielle, M. Nucleophilic Perfluoroalkylation of Aldehydes, Ketones, Imines, Disulfides, and Diselenides. *J. Org. Chem.* 2006, 71, 3564–3568. [CrossRef] [PubMed]
26. Cherkupally, P.; Beier, P. Alkoxide-Induced Nucleophilic Trifluoromethylation Using Diethyl Trifluoromethylphosphonate. *Tetrahedron Lett.* 2010, 51, 252–255. [CrossRef]
27. Blond, G.; Billard, T.; Langlois, B.R. New Stable Reagents for the Nucleophilic Trifluoromethylation. Part 4: Trifluoromethylation of Disulfides and Diselenides with Hemiaminals of Trifluorooctaldehyde. *Tetrahedron Lett.* 2001, 42, 2473–2475. [CrossRef]
28. Kondratenko, N.V.; Kolomeytsev, A.A.; Popov, V.I.; Yakugolskii, L.M. Synthesis and Reactions of Trifluoromethylthio(seleno)- and Pentfluoroacylithio(seleno)-Copper. *Synthesis* 1985, 1985, 667–669. [CrossRef]
29. Feldhoff, R.; Haas, A.; Lieb, M. Darstellung und Eigenschaften Trifluormethyl- und Trifluormethylchalcogenyl-Substituierter Adamantane. *J. Fluorine Chem.* 1994, 67, 245–251. [CrossRef]
30. Chen, C.; Hou, C.; Wang, Y.; Hor, T.S.A.; Weng, Z. Copper-Catalyzed Trifluoromethylselenolation of Aroyl and Alkyl Halides: The Silver Effect in Transmetalation. *Org. Lett.* 2014, 16, 524–527. [CrossRef]
31. Zhang, M.; Weng, Z. Palladium-Catalyzed Tandem Synthesis of 2-Trifluoromethylthio(seleno)-Substituted Benzofused Heterocycles. *Org. Lett.* 2019, 21, 5838–5842. [CrossRef]
32. Glenadel, Q.; Ismalaj, E.; Billard, T. Benzylltrifluoromethyl (or Fluoroalkyl) Selenide: Reagent for Electrophilic Trifluoromethylation (or Fluoroalkylation) Selenolations. *J. Org. Chem.* 2016, 81, 8268–8275. [CrossRef] [PubMed]
33. Ghiazza, C.; Debrauwer, V.; Monnereau, C.; Khrouz, L.; Medebielle, M.; Billard, T.; Tlili, A. Visible-Light-Mediated Metal-Free Synthesis of Trifluoromethylselenolated Arenes. *Angew. Chem. Int. Ed.* 2018, 57, 11781–11785. [CrossRef] [PubMed]
34. Chen, X.-L.; Zhou, S.-H.; Lin, J.-H.; Deng, Q.-H.; Xiao, J.-C. Difluorocarbene-Derived Trifluoromethylselenolation of Benzyl Halides. *Chem. Commun.* 2019, 55, 1410–1413. [CrossRef] [PubMed]
35. Dix, S.; Jakob, M.; Hopkinson, M.N. Deoxytrifluoromethylthiolation and Selenylation of Alcohols by Using Benzothiazolum Reagents. *Chem. Eur. J.* 2019, 25, 7635–7639. [CrossRef] [PubMed]

36. Modak, A.; Pinter, E.N.; Cook, S.P. Copper-Catalyzed, N-Directed Csp³-H Trifluoromethylthiolation (-SCF₃) and Trifluoromethylselenolation (-SeCF₃). *J. Am. Chem. Soc.* 2019, 141, 18405–18410. [CrossRef] [PubMed]

37. Lefebvre, Q.; Pluta, R.; Rueping, M. Copper Catalyzed Oxidative Coupling Reactions for Trifluoromethylselenolations - Synthesis of R-SeCF₃ Compounds Using Air Stable Tetramethylammonium Trifluoromethylselenolate. *Chem. Commun.* 2015, 51, 4394–4397. [CrossRef] [PubMed]

38. Aufiero, M.; Sperger, T.; Tsang, A.S.K.; Schoenebeck, F. Highly Efficient C-SeCF₃ Coupling of Aryl Iodides Enabled by an Air-Stable Dinuclear Pd² Catalyst. *Angew. Chem., Int. Ed.* 2015, 54, 10322–10326. [CrossRef] [PubMed]

39. Matheis, C.; Wagner, V.; Goossen, L.J. Sandmeyer-Type Trifluoromethylthiolation and Trifluoromethylselenolation of (Hetero)Aromatic Amines Catalyzed by Copper. *Chem. Eur. J.* 2016, 22, 79–82. [CrossRef]

40. Matheis, C.; Krause, T.; Bragoni, V.; Goossen, L.J. Trifluoromethylthiolation and Trifluoromethylselenolation of α-Diazo Esters Catalyzed by Copper. *Chem. Eur. J.* 2016, 22, 12270–12273. [CrossRef]

41. Fang, W.-Y.; Dong, T.; Han, J.-B.; Zha, G.-F.; Zhang, C.-P. Expeditious Trifluoromethylthiolation and Trifluoromethylselenolation of Alkynyl(phenyl)iodoniums by [XCF₃]⁺ (X = S, Se) Anions. *Org. Biomol. Chem.* 2016, 14, 11502–11509. [CrossRef]

42. Han, J.-B.; Dong, T.; Vicic, D.A.; Zhang, C.-P. Nickel-Catalyzed Trifluoromethylselenolation of Aryl Halides Using the Readily Available [Me₄N][SeCF₃] Salt. *Org. Lett.* 2017, 19, 3919–3922. [CrossRef] [PubMed]

43. Dong, T.; He, J.; Li, Z.-H.; Zhang, C.-P. Catalyst- and Additive-Free Trifluoromethylselenolation with [Me₄N][SeCF₃]. *ACS Sustainable Chem. Eng.* 2018, 6, 1327–1335. [CrossRef]

44. Han, Q.-Y.; Zhao, C.-L.; Dong, T.; Shi, J.; Tan, K.-L.; Zhang, C.-P. Metal-Free Oxidative Trifluoromethylselenolation of Electron-Rich (Hetero)arenes with the Readily Available [Me₄N][SeCF₃] Reagent. *Org. Chem. Front.* 2019, 6, 2732–2737. [CrossRef]

45. Han, Q.-Y.; Tan, K.-L.; Wang, H.-N.; Zhang, C.-P. Organic Photoredox-Catalyzed Decarboxylative Trifluoromethylselenolation of Aliphatic Carboxylic Acids with [Me₄N][SeCF₃]. *Org. Lett.* 2019, 21, 10013–10017. [CrossRef]

46. Tan, K.-L.; Dong, T.; Zhang, X.-Q.; Zhang, C.-P. Oxidative Trifluoromethylselenolation of 1,3-Dicarboxyls with [Me₄N][SeCF₃]. *Org. Biomol. Chem.* 2020, 18, 1769–1779. [CrossRef]

47. Wu, S.; Jiang, T.-H.; Zhang, C.-P. CaCl₂-Promoted Dehydroxytrifluoromethylselenolation of Alcohols with [Me₄N][SeCF₃]. *Org. Lett.* 2020, 22, 6016–6020. [CrossRef]

48. Tyrra, W.; Naumann, D.; Yagupolskii, Y.I. Stable Trifluoromethylselenenates(0). [A]SeCF₃ - Synthesis, Characterizations and Properties. *J. Fluorine Chem.* 2003, 123, 183–187. [CrossRef]

49. Petrone, D.A. Stereoselective Heterocycle Synthesis via Alkene Difunctionalization. Springer International Publishing: Cham, Switzerland, 2018.

50. Kissin, Y.V. *Alkene Polymerization Reactions with Transition Metal Catalysts*; Studies in Surface Science and Catalysis 173; Elsevier Academic Press: Waltham, MA, USA, 2007.

51. Zhao, H.-P.; Liang, G.-C.; Nie, S.-M.; Lu, X.; Pan, C.-X.; Zhong, X.-X.; Su, G.-F.; Mo, D.-L. Metal-Free Trifluoromethylthiolation of Unactivated Alkenes via Alkene Difunctionalization. *Angew. Chem. Int. Ed.* 2013, 52, 2198–2202. [CrossRef] [PubMed]

52. Ma, X.-P.; Nong, C.-M.; Zhao, J.; Lu, X.; Liang, C.; Mo, D.-L. Yb(OTf)₃-Catalyzed Cycloadition[3,3]-Rearrangement of N-Vinyl-α,β-Unsaturated Ketonitriles with Methylencyclopropanes: Stereoselective Synthesis of Nine-Membered Nitrogen Heterocycles. *Adv. Synth. Catal.* 2020, 362, 478–486. [CrossRef]

53. Zhang, Y.; Briski, J.; Zhang, Y.; Rendy, R.; Klumpp, D.A. Supercacid-Catalyzed Reactions of Olefinic Pyrazines: An Example of Anti-Markovnikov Addition Involving Superelectrophiles. *Org. Lett.* 2005, 7, 2505–2508. [CrossRef]

54. Wu, X.; Chu, L.; Qing, F.-L. Silver-Catalyzed Hydrotrifluoromethylation of Unactivated Alkenes with CF₃SiMe₃. *Angew. Chem. Int. Ed.* 2013, 52, 2198–2202. [CrossRef] [PubMed]

55. Mizuta, S.; Verhoog, S.; Engle, K.M.; Khotavivattana, T.; O’Duill, M.; Wheelhouse, K.; Rassias, G.; Mdebielle, M.; Gouverneur, V. Catalytic Hydrotrifluoromethylation of Unactivated Alkenes. *J. Am. Chem. Soc.* 2013, 135, 2505–2508. [CrossRef] [PubMed]
56. Zhu, L.; Wang, L.-S.; Li, B.; Fu, B.; Zhang, C.-P.; Li, W. Operationally Simple Hydrotrifluoromethylation of Alkenes with Sodium Triflate Enabled by Ir Photoredox Catalysis. Chem. Commun. 2016, 52, 6371–6374. [CrossRef] [PubMed]

57. Straathof, N.J.W.; Cramer, S.E.; Hessel, V.; Noël, T. Practical Photocatalytic Trifluoromethylation and Hydrotrifluoromethylation of Styrenes in Batch and Flow. Angew. Chem. Int. Ed. 2016, 55, 15549–15553. [CrossRef]

58. Lonca, G.H.; Ong, D.Y.; Tran, T.M.H.; Tejo, C.; Chiba, S.; Gagosz, F. Anti-Markovnikov Hydrofunctionalization of Alkenes: Use of a Benzyl Group as a Traceless Redox-Active Hydrogen Donor. Angew. Chem. Int. Ed. 2017, 56, 11440–11444. [CrossRef]

59. Zhang, W.; Zou, Z.; Wang, Y.; Wang, Y.; Liang, Y.; Wu, Z.; Zheng, Y.; Pan, Y. Leaving Group Assisted Strategy for Photoinduced Fluoroalkylations Using N-Hydroxybenzimidoyl Chloride Esters. Angew. Chem. Int. Ed. 2019, 58, 624–627. [CrossRef] [PubMed]

60. Ma, G.; Wan, W.; Li, J.; Hu, Q.; Jiang, H.; Zhu, S.; Wang, J.; Hao, J. Efficient Regioselective Hydrodifluoromethylation of Unactivated Alkenes with TMSCF₂CO₂Et at Ambient Temperature. Chem. Commun. 2014, 50, 9749–9752. [CrossRef]

61. Yu, C.; Iqbal, N.; Park, S.; Cho, E.J. Selective Difluoroalkylation of Alkenes by Using Visible Light Photoredox Catalysis. Chem. Commun. 2014, 50, 12884–12887. [CrossRef]

62. Huang, W.; Chen, W.; Wang, G.; Li, J.; Cheng, X.; Li, G. Thiyl-Radical-Catalyzed Photoreductive Hydrodifluoroacetamidation of Alkenes with Hantzsch Ester as a Multifunctional Reagent. ACS Catal. 2016, 6, 7471–7474. [CrossRef]

63. Nie, X.; Cheng, C.; Zhu, G. Palladium-Catalyzed Remote Aryldifluoroalkylation of Alkenyl Aldehydes. Angew. Chem. Int. Ed. 2017, 56, 1898–1902. [CrossRef]

64. Wang, H.; Jui, N.T. Catalytic Defluoroalkylation of Trifluoromethylaromatics with Unactivated Alkenes. J. Am. Chem. Soc. 2018, 140, 163–166. [CrossRef] [PubMed]

65. Yu, J.; Lin, J.-H.; Cao, Y.-C.; Xiao, J.-C. Visible-Light-Induced Radical Hydrodifluoromethylation of Alkenes. Org. Chem. Front. 2019, 6, 3580–3583. [CrossRef]

66. Barthelemy, A.-L.; Magnier, E.; Dagousset, G. Direct Trifluoromethylthiolation Reactions Involving Radical Processes. Synthesis 2018, 50, 4765–4776.

67. Harris, J.F., Jr.; Stacey, F.W. The Free Radical Addition of Trifluoromethanethiol to Fluoroölefins. J. Am. Chem. Soc. 1961, 83, 840–845. [CrossRef]

68. Yang, T.; Lu, L.; Shen, Q. Iron-Mediated Markovnikov-Selective Hydro-Trifluoromethylthiolation of Unactivated Alkenes. Chem. Commun. 2015, 51, 5479–5481. [CrossRef] [PubMed]

69. Shao, X.; Hong, X.; Lu, L.; Shen, Q. Cobalt-Catalyzed Hydro-Difluoromethylthiolation/Hydro-Trifluoromethylthiolation of Unactivated Alkenes. Tetrahedron 2019, 75, 4156–4166. [CrossRef]

70. Ouyang, Y.; Xu, X.-H.; Qing, F.-L. Hydrotrifluoromethylthiolation of Unactivated Alkenes and Alkynes with Trifluoromethanesulfonic Anhydride through Deoxygenative Reduction and Photoredox Radical Processes. Angew. Chem. Int. Ed. 2019, 58, 18508–18512. [CrossRef]

71. Ghiazza, C.; Ghiazza, C.; Tili, A.; Billard, T. Trifluoromethyllyselonelation and Fluoroalkyllyselonelation of Alkenes by Electrophilic Addition. Eur. J. Org. Chem. 2017, 3812–3814. [CrossRef]

72. Ghiazza, C.; Khouz, L.; Monneron, C.; Billard, T.; Tili, A. Visible-Light Promoted Fluoroalkyllyselonelation: Toward the Reactivity of Unsaturated Compounds. Chem. Commun. 2018, 54, 9909–9912. [CrossRef]

73. Zhang, B.-S.; Gao, L.-Y.; Zhang, Z.; Wen, Y.-H.; Liang, Y.-M. Three-Component Difluoroalkylation and Trifluoromethylthiolation of Alkenes. Chem. Commun. 2018, 54, 1185–1188. [CrossRef]

74. Roesky, H.W. Efficient Preparations of Fluorine Compounds; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013.

75. Qi, X.-X.; Chen, P.-H.; Liu, G.-S. Catalytic Oxidative Trifluoromethoxylation of Allylic C-H Bonds Using a Palladium Catalyst. Angew. Chem. Int. Ed. 2017, 56, 9517–9521. [CrossRef] [PubMed]

76. Liu, R.; Lu, Z.-H.; Hu, X.-H.; Li, J.-L.; Yang, X.-J. Monocarboxylation and Intramolecular Coupling of Butenylated Arenes via Palladium-Catalyzed C–H Activation Process. Org. Lett. 2015, 17, 1489–1492. [CrossRef] [PubMed]

77. Brown, L.J.; Brown, R.C.D.; Raja, R. Heterogenisation of Ketone catalysts within Mesoporous Supports for Asymmetric Epoxidation. RSC Adv. 2013, 3, 843–850. [CrossRef]
78. Meng, Q.-Y.; Schirmer, T.E.; Katou, K.; König, B. Controllable Isomerization of Alkenes by Dual Visible-Light-Cobalt Catalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 5723–5728. [CrossRef] [PubMed]

79. Armarego, W.L.F.; Chai, C.L.L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth Heinemann: Oxford, UK, 2003.

**Sample Availability:** Samples of the compounds 2a–b, CsOCF3, 1a–r, 3a–p, and 4a–h are available from the authors.

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