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Fluoride-induced coupling of perfluoroketene dithioacetals with silyl alkynes: A way towards new polyfunctionalized trifluoromethyl building blocks☆

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Dedicated to Professor Kenji Uneyama, in honor of his ACS Award for creative work in fluorine chemistry.

Abstract

Under fluoride activation, the vinyl fluorine of perfluoroketene dithioacetal may be substituted by silylated nucleophiles. Using silyl alkynes, a formal transition metal free sila-Sonogashira cross-coupling reaction occurred. The resulting enynes were hydrolyzed giving new polyfunctional trifluoromethyl building blocks.

Keywords: Ketene dithioacetal; Cross-coupling; Sila-Sonogashira; Fluorine substitution; Silyl alkynes; Trifluoromethyl building blocks

1. Introduction

Perfluoroketene dithioacetals **1** [1] are simple and versatile building blocks. Most of applications we have reported so far were a consequence of the easy substitution of the vinylic fluorine atom by an enolate to give, after acid hydrolysis, an α-trifluoromethyl γ-keto thiolester [2] or α-trifluoromethyl succinic derivatives [3], which can be derivatized towards various types of trifluoromethyl heterocycles [4], a class of compounds of great interest. Whereas, conversion of **1** into γ-keto derivatives using potassium ketone enolate works very well (Scheme 1), similar reaction with potassium or lithium ethyl acetate enolate failed, the enolate being unreactive at low temperature and its decomposition at room temperature leading to a quantitative conversion of the substrate into the ethoxide substituted analogue (Scheme 1). A first possibility to overcome this difficulty was to use enediolates as reagents [5]. A second one, more efficient, was to use a silylated precursor of ethyl acetate enolate which, under smooth fluoride activation and hydrolysis of ketene dithioacetal intermediate, gave the expected α-trifluoromethyl succinic derivative in high yield (Scheme 1) [3].

This result prompted us to study an extension of this chain reaction (Scheme 2) to other silyl nucleophiles, using substrate **2** as a model. Even if the reaction concept can be applied to O-silyl derivatives like silyl ethers and enol silyl ethers [6], the practical interest of these reagents is limited since the reaction works very well with alkoxides or ketone enolates. C-silyl nucleophiles were more attractive because the *a priori* required reaction conditions would be much milder than those using a classical organometallic reagent. We report here on cross-coupling reactions of the substrate **2** with C-silyl nucleophiles under fluoride activation, with a special interest for silyl alkyne reagents, which exhibit interesting reactivity on acid hydrolysis.

☆ Fluorinated ketene dithioacetals. Part 14. For part 13, see Sotoca et al. [E. Sotoca, J.-P. Bouillon, S. Gil, M. Parra, C. Portella, Tetrahedron 61 (2005) 4395–4402].

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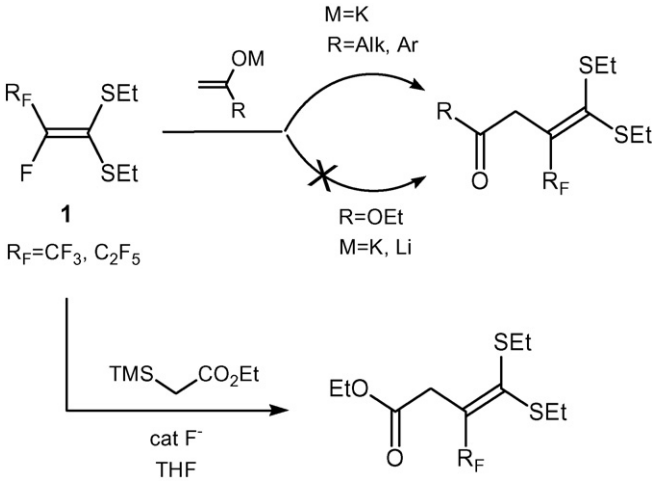


Scheme 1.

2. Results and discussion

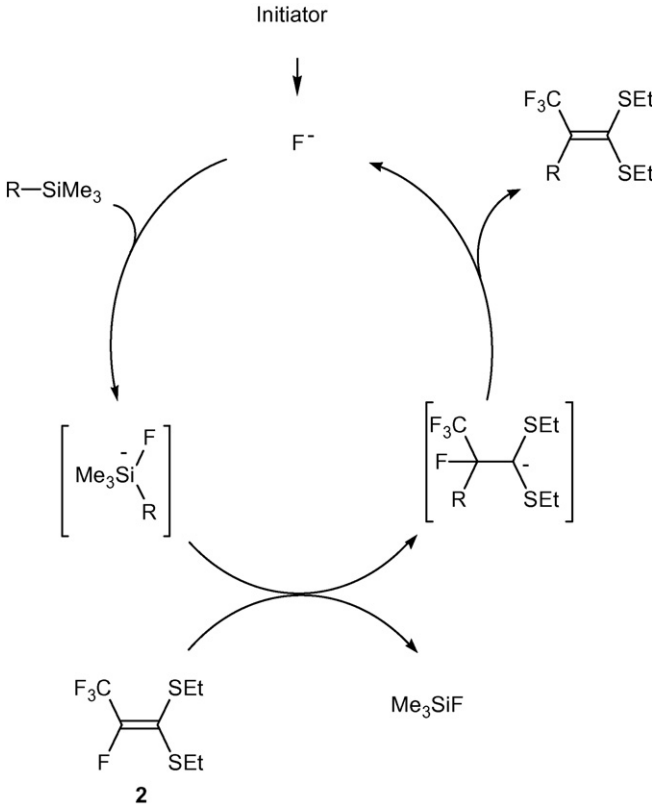
Reaction of compound **2** with various commercially available silyl reagents, in the presence of 10% molar equivalent of tetramethylammonium fluoride (TMAF), gave variable results (Table 1). Benzyltrimethylsilane reacted smoothly to give effectively the expected coupling product **3** in 73% isolated yield (entry 1). Reaction with allyltrimethylsilane was more problematic. Depending on the fluoride initiator and solvent, either no reaction (entries 2 and 3) or partial conversion was observed. The corresponding allyl product **4** could be isolated in moderate yield using TMAF and acetonitrile (ACN) as solvent (entry 4). Vinyltrimethylsilane and trimethylsilylcyanide failed to give coupling reaction (entries 5 and 6).

We then turned our attention to silylalkynes. Transition metal catalyzed cross coupling of terminal alkynes with aryl or vinyl halides, the Sonogashira reaction [7], has been extended to silyl alkynes [8]. Our aim was to perform a sila-Sonogashira type reaction between silyl alkynes and the fluorovinyl substrate **2** without transition metal, under simple fluoride initiation. This type of coupling was exemplified with polyfluorinated aromatics [9], but was never reported, to our knowledge, with fluorovinyl derivatives. Functionalized silyl alkynes bearing an ester or a ketone function failed to give any modification of the starting material (entries 7 and 8). In contrast, complete conversion occurred when a mixture of **2** and phenyl(trimethylsilyl)acetylene is activated by a catalytic amount of TMAF in THF at room temperature, giving the coupling product **5** in 78% isolated yield (entry 9).

Coupling of (trimethylsilyl)acetylene was then attempted. Surprisingly, using an equimolar mixture of reactants, the only compound we were able to fully characterize was the 1/2 coupling product **6**, isolated in 10% yield. This indicates that once the ''normal'' coupling has taken place, fluoride is basic enough to deprotonate the terminal alkyne moiety, allowing the chain process to evolve (Scheme 3). Fluoride activation of Pd or Pd/Cu catalyzed coupling between terminal alkynes and organic halides has been recently reported [10]. In our case, the CF_3 substituent probably enhances the acidity of terminal alkyne moiety resulting from the first coupling. When **2** was reacted with 0.5 equivalent of (trimethylsilyl)acetylene, the yield of **6** increased to 35%, but the conversion remained incomplete (70%). This reaction produced a deep-dark unidentified by-product (*vide infra*). We assumed that the reaction could be improved using bis(trimethylsilyl)acetylene in a 1/2 ratio with **2**. The yield of **6** was indeed increased, but to a moderate extent (44%), for similar reasons.

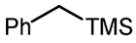
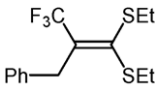
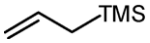
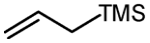
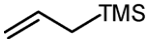
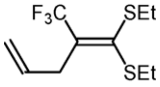
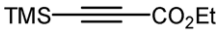
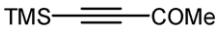
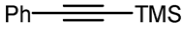
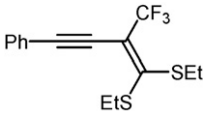
Reactions with both (trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene gave, beside the bis(coupling) product **6**, a deep-dark compound **X** not yet fully characterized [11]. This compound, obtained after washing the silica gel column with ether, is highly soluble in this solvent and soluble in hexane. After high dilution in ether, the color turned to red. For the moment, it seems to be a highly conjugated oligomeric or polymeric compound. Further investigations are foreseen for both characterization of this compound and optimization of the selectivity of the reaction.

Most often, the condensation product prepared so far by substitution of the vinylic fluorine of **1** by an enolate was converted into a thiolester by acid hydrolysis. The new alkyne derived coupling products reported here exhibit two conjugated protonation sites, and their acid hydrolysis was not expected to be a trivial reaction. Indeed, none of the alkyne derivatives **5** and **6** gave, on acid hydrolysis, the product derived from a simple reaction of the dithioacetal moiety. Compound **5** was converted into the 1,3-diketo derivative **7** on treatment with hot trifluoroacetic acid–water 9:3. This transformation is due to a



Scheme 2.

Table 1
Fluoride activated cross coupling of some C-silyl compounds

Entry	R-TMS	Solvent	Initiator[a]	Conversion (%)[b]	Product	Yield (%)[c]
1		THF	TMAF	100		73
2		THF	TMAF	0	–	–
3		DME	CsF	0	–	–
4		ACN	TMAF	67		38
5		THF	TMAF	0	–	–
6	TMSCN	THF	TMAF	0[d]	–	–
7		THF	TMAF	0	–	–
8		THF	TMAF	0	–	–
9		THF	TMAF	100		78

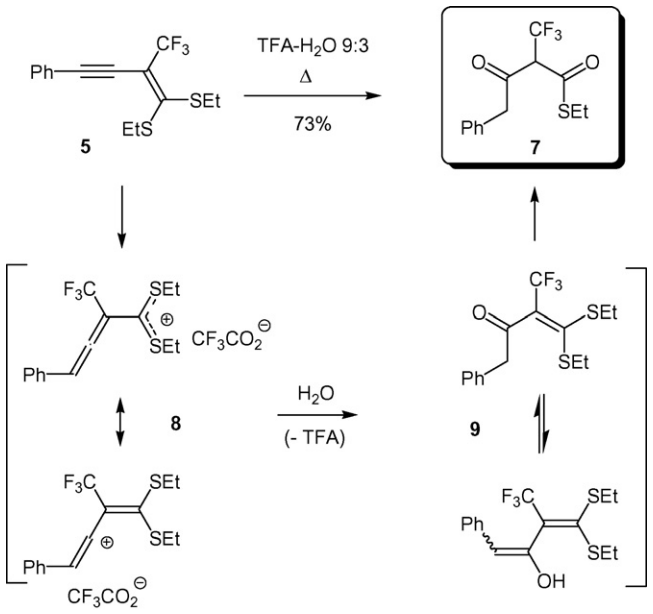
[a] 0.1 equiv.
[b] 1 h reaction at room temperature.
[c] Isolated yield.
[d] Partial decomposition (<15%) of starting material occurred on heating with CsF (1.0 equiv.) in DMF or DMSO.

conjugate protonation leading to the delocalized intermediate cation **8** (Scheme 4). This intermediate traps water selectively at the β-carbon, leading to the acyl intermediate **9** which is further hydrolyzed into thiolester **7**.

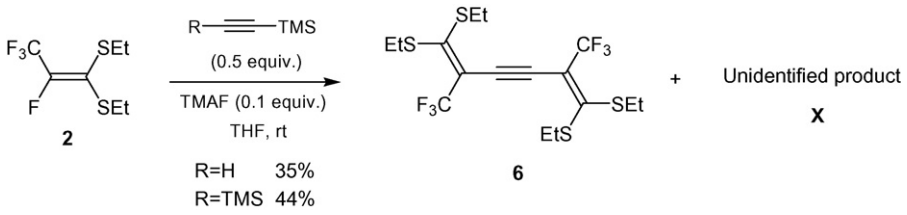
To confirm this mechanism, **5** was reacted with refluxing anhydrous trifluoroacetic acid. A minor amount of compound **10**, corresponding to the trapping of the intermediate **8** by ethanethiol (probably produced by degradation), was characterized. Finally, reacting **5** in anhydrous trifluoroacetic acid containing one equivalent of *n*-hexanethiol gave quantitatively the corresponding thioenol derivative **11** (Scheme 5).

The acid hydrolysis of the dienyne type compound **6** gave interesting results. Treatment of **6** during 2 h at 75 °C in a mixture trifluoroacetic acid–water 9:3 led to a new and unexpected compound, the thiophene derivative **12**, in high yield (88%). Such a compound can be explained by a similar first conjugated protonation, with a subsequent intramolecular trapping of the intermediate **13** by sulfur and then S-dealkylation (Scheme 6). The resulting compound **14** is further hydrolyzed into the final substituted 3-trifluoromethyl thiophene derivative **12**.

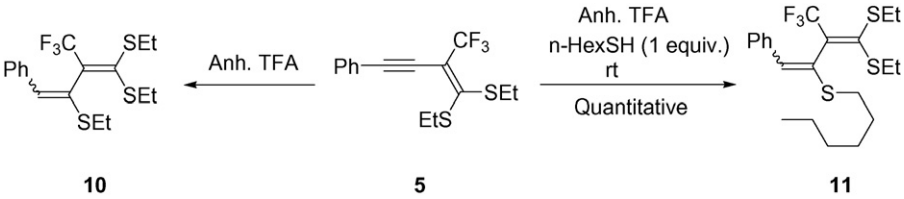
This reaction path was confirmed in a way similar to the previous one: using anhydrous trifluoroacetic acid, the reaction



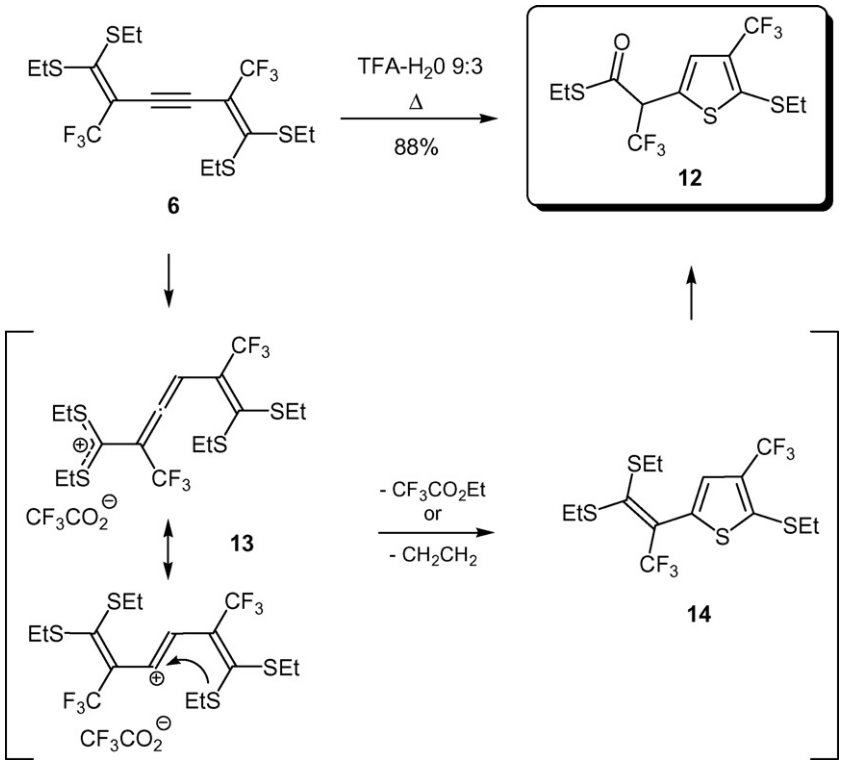
Scheme 4.



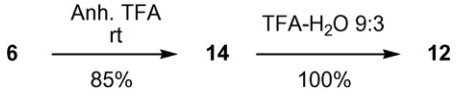
Scheme 3.



Scheme 5.



Scheme 6.



Scheme 7.

stopped at the compound **14** which was isolated in 85% yield. Its reaction with trifluoroacetic acid–water 9:3 led quantitatively to the corresponding thiol ester **12** (Scheme 7).

3. Conclusion

C-silyl nucleophiles, more particularly silyl alkynes, react in very mild conditions with perfluoroketene dithioacetal **2**, via a chain process initiated by tetramethylammonium fluoride. This reaction can be viewed as a transition metal free sila-Sonogashira cross-coupling reaction between a silyl alkyne and a fluorovinyl substrate. The enyne type compounds **5** and **6** undergo an interesting acid hydrolysis pathway via a totally selective conjugate protonation.

The coupling products and their hydrolysis products are further examples contributing to the versatility of the very simple building block **2**.

4. Experimental

4.1. General remarks

Melting points are uncorrected. FT-IR spectra were recorded on a MIDAC Corporation Spectrafile IR^{TM} apparatus. ^{1}H, ^{13}C and ^{19}F spectra were recorded on a Bruker AC-250 in $CDCl_3$ as the solvent. Tetramethylsilane ($\delta = 0.00$) or $CHCl_3$ ($\delta = 7.27$) were used as internal standards for ^{1}H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F NMR spectra. MS data were obtained on a Trace MS Thermoquest apparatus (GCMS) at 70 eV in the electron impact mode. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. All reactions were monitored by GCMS. Silicagel Merck 9385 (40–63 μm) was used for flash chromatography. Tetramethylammonium fluoride (TMAF) was dried for 5 h by heating at 200 °C under reduced pressure. Perfluoroketene dithioacetal **2** was prepared according to Ref. [1].

4.2. Typical fluoride activated cross-coupling procedure

To a suspension of anhydrous TMAF (16 mg, 0.1 equiv.) in dry THF (10 mL) were added perfluoroketene dithioacetal **2**

(0.40 g, 1.7 mmol), then benzyltrimethylsilane (0.39 mL, 2.0 mmol). The suspension was stirred for 1 h at room temperature, under argon atmosphere. The resulting mixture was washed with brine (8 mL) and the aqueous phase was extracted twice with ether (2× 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by silica gel column chromatography (eluent:petroleum ether/AcOEt (97/3)) to give the cross-coupling product **3** as an oil (0.38 g; yield: 73%).

*4.2.1. 1,1-Bis(ethylsulfanyl)-3-phenyl-2-trifluoromethylprop-1-ene (**3**)*

^{1}H NMR: δ = 1.25 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3CH_2S), 1.28 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3CH_2S), 2.85 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2S), 2.89 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2S), 4.07 (s, 2H, PhCH_2), 7.1–7.4 (m, 5H, Ph). ^{13}C NMR: δ = 14.7 (CH_3CH_2S), 15.0 (CH_3CH_2S), 27.9 (CH_2S), 28.8 (CH_2S), 37.7 (q, $^3J_{C,F}$ = 2.0 Hz, PhCH_2), 123.3 (q, $^1J_{C,F}$ = 276.5 Hz, CF_3), 126.3 (*CH* Ph), 127.9 (2× *CH* Ph), 128.5 (2× *CH* Ph), 135.6 (q, $^2J_{C,F}$ = 27.5 Hz, CF_3C=), 138.2 (C_q Ph), 143.8 (q, $^3J_{C,F}$ = 3.0 Hz, $(EtS)_2C$=). ^{19}F NMR: δ = −55.9 (s). IR (film) ν = 3030, 2968, 2928, 1561, 1453, 1300, and 1126 cm^{-1}; MS: *m/z* (%) = 306 [M^+], 277, 215, 195, 151, 91 (100). Anal. Calcd. for $C_{14}H_{17}F_3S_2$: C, 54.88; H, 5.59; found: C, 55.27; H, 5.49.

*4.2.2. 1,1-Bis(ethylsulfanyl)-2-trifluoromethylpenta-1,4-diene (**4**)*

It is prepared according to a similar procedure from TMAF (20 mg, 0.21 mmol), perfluoroketene dithioacetal **2** (0.50 g, 2.1 mmol) and allyltrimethylsilane (0.41 mL, 2.6 mmol). The crude was distilled under reduced pressure using a Büchi Kugelrohr apparatus to give the starting compound **2** (165 mg, conversion: 67%) and the desired product **4** as an oil (208 mg, yield: 38%).

Bp 100–115 °C/10 mbar. ^{1}H NMR: δ = 1.24 (t, $^3J_{H,H}$ = 7.3 Hz, CH_3CH_2S), 1.25 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3CH_2S), 2.82 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2S), 2.86 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2S), 3.42 (dm, $^3J_{H,H}$ = 5.8 Hz, 2H, CH_2CH=CH_2), 5.0–5.1 (m, 2H, CH_2CH=CH_2), 5.7–5.9 (m, 1H, CH_2CH=CH_2). ^{13}C NMR: δ = 14.6 (CH_3CH_2S), 15.1 (CH_3CH_2S), 27.6 (CH_2S), 28.7 (CH_2S), 36.0 (q, $^3J_{C,F}$ = 2.0 Hz, CH_2CH=CH_2), 116.2 (CH_2CH=CH_2), 123.2 (q, $^1J_{C,F}$ = 276.4 Hz, CF_3), 133.7 (CH_2CH=CH_2), 134.9 (q, $^2J_{C,F}$ = 26.2 Hz, CF_3C=), 142.7 (q, $^3J_{C,F}$ = 3.0 Hz, $(EtS)_2C$=). ^{19}F NMR: δ = −56.7 (s). IR (film): ν = 2980, 2929, 1562, 1298, 1159, 1128 cm^{-1}; MS: *m/z* (%) = 257 [*M* + 1], 227, 195, 165 (100), 139.

*4.2.3. 1,1-Bis(ethylsulfanyl)-4-phenyl-2-trifluoromethylbut-1-en-3-yne (**5**)*

It is prepared according to a similar procedure from TMAF (4 mg, 0.04 mmol), perfluoroketene dithioacetal **2** (0.10 g, 0.4 mmol) and phenyltrimethylsilylacetylene (0.13 mL, 0.6 mmol). The crude was purified by silica gel column chromatography (eluent:petroleum ether/AcOEt (99/1)) to give the cross-coupling product **5** as an oil (105 mg, yield: 78%).

^{1}H NMR: δ = 1.33 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3CH_2S), 1.37 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3CH_2S), 2.95 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, CH_2S), 3.07 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, CH_2S), 7.3–7.6 (m, 5H, Ph). ^{13}C NMR: δ = 14.8 (CH_3CH_2S), 14.9 (CH_3CH_2S), 28.9 (CH_2S), 30.3 (CH_2S), 83.8 (q, $^3J_{C,F}$ = 3.0 Hz, PhC*C*), 100.4 (Ph*C*C), 116.7 (q, $^2J_{C,F}$ = 33.7 Hz, CF_3C=), 121.2 (q, $^1J_{C,F}$ = 274.9 Hz, CF_3), 122.6 (C_q Ph), 128.4 (2× *CH* Ph), 131.4 (2× *CH* Ph), 128.8 (*CH* Ph), 153.6 (q, $^3J_{C,F}$ = 2.0 Hz, $(EtS)_2C$=). ^{19}F NMR: δ = −56.9 (s). Calcd. for $C_{14}H_{17}F_3S_2$: C, 56.94; H, 4.78; S, 20.27; found: C, 57.21; H, 5.09; S, 20.20.

*4.2.4. 1,1,6,6-Tetrakis(ethylsulfanyl)-2,5-bis(trifluoromethyl)-hexa-1,5-dien-3-yne (**6**)*

It is prepared according to a similar procedure from TMAF (6 mg, 0.06 mmol), perfluoroketene dithioacetal **2** (0.30 g, 1.3 mmol) and bis(trimethylsilyl)acetylene (0.15 mL, 0.6 mmol). The reaction mixture was stirred for 10 h at room temperature, under argon atmosphere. After usual work-up, the crude was purified by silica gel column chromatography (eluent:petroleum ether/AcOEt (95/5)) to give the starting compound **2** (78 mg, conversion: 74%) and the desired product **6** as an oil (120 mg, yield: 44%).

^{1}H NMR: δ = 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3CH_2S), 1.31 (t, $^3J_{H,H}$ = 7.4 Hz, 6H, CH_3CH_2S), 2.95 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, CH_2S), 3.03 (q, $^3J_{H,H}$ = 7.4 Hz, 4H, CH_2S). ^{13}C NMR: δ = 14.8 (CH_3CH_2S), 14.9 (CH_3CH_2S), 29.2 (CH_2S), 30.4 (CH_2S), 94.4 (C_q acetylenic), 116.1 (q, $^2J_{C,F}$ = 34.0 Hz, CF_3C=), 121.2 (q, $^1J_{C,F}$ = 275.3 Hz, CF_3), 155.2 ($(EtS)_2C$=). ^{19}F NMR: δ = −56.8 (s). MS: *m/z* (%) = 454 (M^+, 100), 396, 336. HRMS (ESI+) Calcd. for $C_{16}H_{21}O_2F_6S_4$ [*M* + H] + 455.0430; found: 455.0422.

4.3. Reactions of coupling products with TFA

*4.3.1. S-Ethyl 3-oxo-4-phenyl-2-trifluoromethylbutanthioate (**7**)*

To compound **5** (65 mg, 0.2 mmol) were added trifluoroacetic acid (TFA, 153 μL, 2.0 mmol) and water (12 μL, 0.7 mmol). The mixture was heated at 70–75 °C for 2 h. After cooling at 0 °C, the excess of TFA was neutralized with a saturated aqueous solution of $NaHCO_3$ (∼1.0 mL). The aqueous phase was extracted twice with dichloromethane (2× 3 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude was purified by silica gel column chromatography (eluent:petroleum ether/AcOEt (95/5)) to give the desired product **7** as an oil (42 mg, yield: 73%.).

^{1}H NMR: δ = 1.29 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3CH_2S), 2.99 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, CH_2S), 3.88 (d, $^2J_{H,H}$ = 16.0 Hz, 1H, PhCH_2), 3.96 (d, $^2J_{H,H}$ = 16.0 Hz, 1H, PhCH_2), 4.52 (q, $^3J_{H,F}$ = 8.0 Hz, 1H, CF_3CH), 7.1–7.4 (m, 5H, Ph). ^{13}C NMR: δ = 14.0 (CH_3CH_2S), 24.7 (CH_2S), 49.3 (PhCH_2), 67.2 (q, $^2J_{C,F}$ = 26.3 Hz, CF_3CH), 121.5 (q, $^1J_{C,F}$ = 281.5 Hz, CF_3), 127.8 (*CH* Ph), 129.0 (*CH* Ph), 129.7 (*CH* Ph), 131.7 (C_q Ph), 186.5 (CO), 193.1 (CO). ^{19}F NMR: δ = −64.0 (d, $^3J_{H,F}$ = 8.0 Hz). LC–MS (ES^-): *m/z* (%) = 289 [$M - 1$]$^-$, 243 (100), 227, 217. HRMS (ESI+) Calcd. for $C_{13}H_{13}O_2F_3SNa$ [M + Na]$^+$: 313.0486; found: 313.0482.

*4.3.2. 1,1-Bis(ethylsulfanyl)-3-hexylsulfanyl-4-phenyl-2-trifluoromethylbuta-1,3-diene (**11**)*

Compound **5** (165 mg, 0.52 mmol) was added to *n*-hexanethiol (68 mg, 0.58 mmol) and anhydrous TFA (2.5 mL). The resulting mixture was stirred for 2 h at room temperature. TFA was then evaporated under reduced pressure and the resulting oil was immediately purified by silica gel column chromatography (eluent:petroleum ether) to give compound **11** (227 mg, yield: 100%), as a 1:2.6 mixture of stereoisomers.

Major isomer: ^{1}H NMR: δ = 0.8–0.9 (m, 3H), 1.10 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, *CH*$_3$CH$_2$S), 1.19 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, *CH*$_3$CH$_2$S), 1.1–1.3 (m, 8H, 4× CH$_2$), 2.5–3.0 (m, 6H, 3× CH$_2$), 6.73 (s, 1H, PhC*H*=), 7.1–7.3 (m, 5H, Ph). ^{13}C NMR: δ = 14.5 (CH$_3$), 15.4 (CH$_3$), 15.7 (CH$_3$), 23.0 (CH$_2$), 28.4 (CH$_2$), 29.1 (CH$_2$), 29.8 (CH$_2$), 31.8 (CH$_2$), 31.9 (CH$_2$), 32.9 (CH$_2$), 122.5 (q, $^1J_{C,F}$ = 274.0 Hz, CF$_3$), 127.9 (2× CH Ph), 128.3 (2× CH Ph), 128.8 (CH Ph), 129.9 (C$_q$), 132.0 (C$_q$), 132.6 (C$_q$), 136.1 (Ph*CH*), 147.2 (C$_q$). ^{19}F NMR: δ = −55.0 (s). Anal Calcd. for $C_{21}H_{29}F_3S_3$: C, 58.03; H, 6.73; found: C, 57.94; H, 6.94.

Minor isomer: Selected data: ^{1}H NMR: δ = 6.39 (s, 1H, PhC*H*=). ^{19}F NMR: δ = −55.9 (s).

*4.3.3. S-Ethyl 2-(2′-ethylsulfanyl-3′-trifluoromethylthiophen-5′-yl)-3,3,3-trifluoropropanethioate (**12**)*

A similar procedure was applied to compound **6** (100 mg, 0.2 mmol), treated with TFA (153 μL, 2.0 mmol) and water (12 μL, 0.7 mmol). The crude was purified by silica gel column chromatography (eluent:petroleum ether/AcOEt (95/5)) to give the desired product 12 as an oil (67 mg, yield: 88%).

^{1}H NMR: δ = 1.30 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, *CH*$_3$CH$_2$S), 1.35 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, *CH*$_3$CH$_2$S), 2.99 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, *CH*$_2$S), 3.00 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, *CH*$_2$S), 4.65 (q, $^3J_{H,F}$ = 8.0 Hz, 1H, CF$_3$*CH*), 7.22 (s, 1H, H-4′). ^{13}C NMR: δ = 14.0 (*CH*$_3$CH$_2$S), 14.3 (*CH*$_3$CH$_2$S), 24.7 (*CH*$_2$S), 32.2 (*CH*$_2$S), 57.4 (q, $^2J_{C,F}$ = 29.4 Hz, CF$_3$*CH*), 121.7 (q, $^1J_{C,F}$ = 271.8 Hz, CF$_3$), 122.3 (q, $^1J_{C,F}$ = 282.1 Hz, CF$_3$), 128.4 (q, $^3J_{C,F}$ = 2.7 Hz, CH), 130.3 (*C*$_q$), 131.2 (q, $^2J_{C,F}$ = 34.1 Hz, CF$_3$*C*=), 141.7 (q, $^3J_{C,F}$ = 2.1 Hz, *C*$_q$), 190.0 (CO). ^{19}F NMR: δ = −67.8 (d, $^3J_{H,F}$ = 8.0 Hz, 3F, *CF*$_3$CH), −58.4 (s, 3F, *CF*$_3$C=). IR (film): ν = 2972, 2932, 1683, 1450, and 1126 cm^{-1}; LC–MS (ES$^-$): *m*/*z* (%) = 381 [*M* − 1]$^-$ (100). HRMS (ESI$^-$) Calcd. for $C_{12}H_{12}F_6OS_3$–H$^+$: 380.9876; found: 380.9887.

*4.3.4. 5-(1,1-Bis(ethylsulfanyl)-3,3,3-trifluoroprop-1-en-2-yl)-2-(ethylsulfanyl)-3-(trifluoromethyl) thiophene (**14**)*

Compound **6** (155 mg, 0.34 mmol) was added to anhydrous TFA (2.5 mL) under nitrogen and the resulting mixture was stirred overnight at room temperature. The excess of TFA was then evaporated under reduced pressure and the resulting oil was purified by silica gel TLC (eluant:petroleum ether) to give compound **14** as an oil (122 mg, yield: 85%.).

^{1}H NMR: δ = 1.33 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, *CH*$_3$CH$_2$S), 1.44 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, *CH*$_3$CH$_2$S), 1.46 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, *CH*$_3$CH$_2$S), 2.92 (q, $^3J_{H-H}$ = 7.3 Hz, 2H, *CH*$_2$S), 3.04 (q, $^3J_{H-H}$ = 7.3 Hz, 2H, *CH*$_2$S), 3.08 (q, $^3J_{H-H}$ = 7.3 Hz, 2H, *CH*$_2$S), 7.09 (1H, s, *CH* thiophène). ^{13}C NMR: δ = 14.3 (*CH*$_3$CH$_2$S), 14.7 (*CH*$_3$CH$_2$S), 14.8 (*CH*$_3$CH$_2$S), 28.7 (*CH*$_2$S), 29.8 (*CH*$_2$S), 32.3 (*CH*$_2$S), 121.7 (q, $^1J_{C,F}$ = 274.0 Hz, CF$_3$), 121.9 (q, $^1J_{C,F}$ = 270.0 Hz, CF$_3$), 125.4 (q, $^2J_{C,F}$ = 32.0 Hz, CF$_3$*C*=), 128.6 (CH), 131.2 (q, $^2J_{C,F}$ = 34.0 Hz, CF$_3$*C*=), 136.9 (*C*$_q$), 140.3 (*C*$_q$), 152.6 (*C*$_q$). ^{19}F NMR: δ = −58.1 (s), −55.7 (s). MS: *m*/*z* (%) = 426, 367 (100), 338.

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[11] NMR data of unidentified by-product **X**: ^{1}H NMR: δ = 1.0–1.6 (brs), 2.6–3.6 (brs). ^{13}C NMR: δ = 14.5–15.5 (brs), 29.5–30.5 (brs). ^{19}F NMR: δ = −56.4 to −57.0 (brs).