

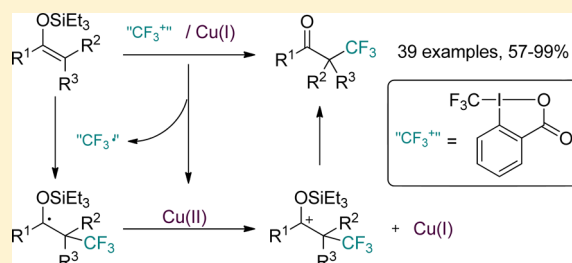
Synthesis of α -Trifluoromethyl Ketones via the Cu-Catalyzed Trifluoromethylation of Silyl Enol Ethers Using an Electrophilic Trifluoromethylating Agent

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S Supporting Information

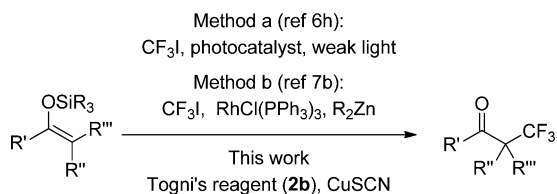
ABSTRACT: A method has been developed for the synthesis of α -trifluoromethyl ketones via the Cu-catalyzed trifluoromethylation of silyl enol ethers with an electrophilic trifluoromethylating agent, which produces a trifluoromethyl radical.



INTRODUCTION

Organofluorine compounds are widely used in agrochemicals, pharmaceuticals and functional materials because of the unique properties associated with the introduction of fluorine atoms, such as enhanced lipophilicity, binding selectivity, and metabolic stability.^{1,2} In recent years, a large number of methods have been developed for the incorporation of CF_3 groups into suitably activated parent molecules.³ Among them, the synthesis of α - CF_3 -substituted carbonyl compounds represents an important transformation.⁴ The α - CF_3 -substituted ketones can be synthesized from enolates or their equivalents, alkenes, and other substrates by the reactions with electrophilic and radical trifluoromethylating reagents.^{4–7} In 1994, Umemoto et al.^{5b} reported the development of procedure for the trifluoromethylation of reactive enolate anions, which is a reaction mediated by an organoboron ester. In 2012, Grushin et al.⁴ developed a method for the nucleophilic trifluoromethylation of α -halogenated ketones, and Xiao⁶ⁱ and Maiti^{6k} recently reported the synthesis of α - CF_3 -substituted carbonyl compounds from olefins. In 2011, MacMillan et al.^{6h} successfully generated α - CF_3 -substituted carbonyl compounds by visible-light photocatalyst. In this particular report, gaseous trifluoromethyl iodide was used as the trifluoromethylating agent, which limited the practical appeal of this procedure. From a practical perspective, the development of a solid trifluoromethylating source would be desirable, although more expensive.⁸ Compared to the synthesis of α - CF_3 -substituted β -ketoesters by electrophilic trifluoromethylation,⁹ the synthesis of α - CF_3 -substituted ketones by electrophilic trifluoromethylating agents is more challenging (Scheme 1). In Xiao's work,⁶ⁱ an electrophilic trifluoromethylation reagent was used to generate a trifluoromethyl radical. Inspired by this work, we envisaged that the reaction of a suitably substituted silyl enol ether with an electrophilic trifluoromethylating agent under redox

Scheme 1. Comparison with Highly Related Reference Methods

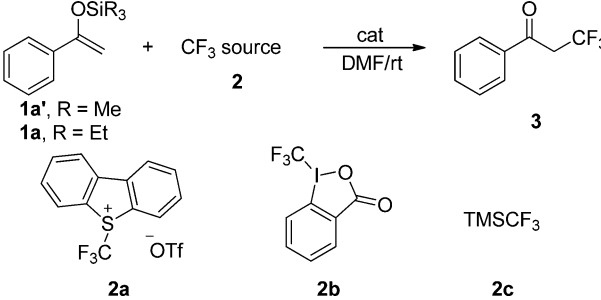


conditions would provide access to α - CF_3 ketones in good yield. The reaction will be beneficial and practical because it has a wide scope of substrates with no requirement for gaseous starting materials, strong bases (such as lithium diisopropylamide, LDA), or conditions of a very low temperature.

RESULTS AND DISCUSSION

The reaction of **1a'** with Umemoto's electrophilic reagent **2a** in the presence of a copper catalyst in DMF at room temperature was initially selected as a model reaction to identify the optimum conditions for the transformation. Among the copper salts screened for this reaction, CuI provided the best results in terms of the yield (55%) of desired ketone product (Table 1, entries 1–4). The yield of the product was increased significantly to 81% when Togni's reagent **2b** was used as the trifluoromethylating agent (Table 1, entry 5). Various different copper salts were then screened in conjunction with Togni's reagent, and the results revealed that CuSCN gave the best yield of α - CF_3 ketone (Table 1, entries 5–13). These conditions were then applied to ethyl-substituted **1a** instead of **1a'**, and the yield was improved to 95% (Table 1, entry 14).

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Table 1. Screening of Reaction Conditions^a


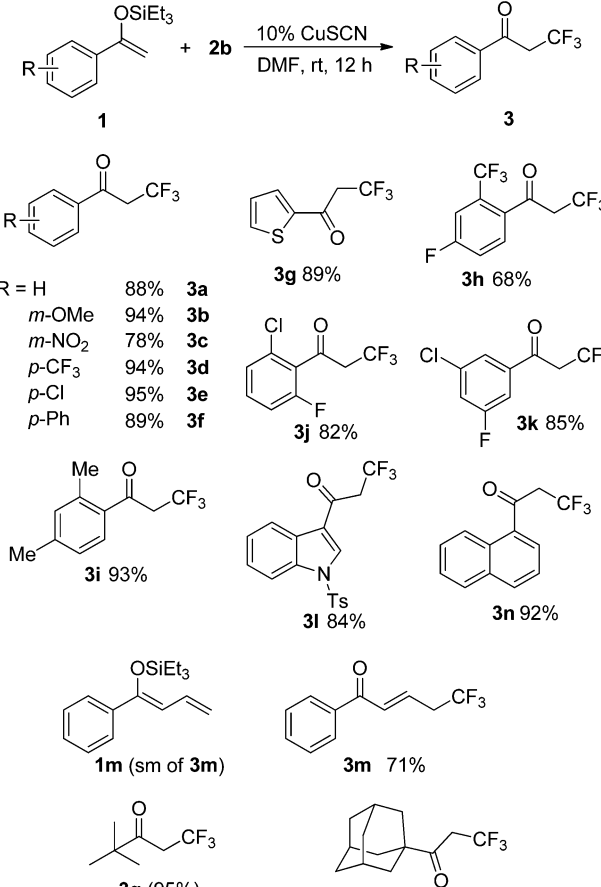
entry	1	2	cat.	yield ^b (%)
1	1a'	2a	CuI	55
2	1a'	2a	CuCl	31
3	1a'	2a	CuOAc	14
4	1a'	2a	Cu(PF ₄)(MeCN) ₄	10
5	1a'	2b	CuI	81
6	1a'	2b	CuCl	83
7	1a'	2b	CuOAc	18
8	1a'	2b	Cu(PF ₄)(MeCN) ₄	45
9	1a'	2b	CuBr	73
10	1a'	2b	CuTc ^c	32
11	1a'	2b	CuSCN	89
12	1a'	2b	Cu(OAc) ₂	15
13	1a'	2b	Cu(OTf) ₂	27
14	1a	2b	CuSCN	95
15 ^d	1a	2b	CuSCN	0
16 ^e	1a	2b	CuSCN	42
17 ^f	1a	2c	—	35

^aGeneral conditions: silyl enol ether **1a'** or **1a** (0.2 mmol), CF₃ source (0.3 mmol), copper salt (0.02 mmol), DMF (2 mL), under nitrogen atmosphere, rt, 12 h. ^bYield based on ¹⁹F NMR. ^cCuTc is copper(I) thiophene-2-carboxylate. ^dWith MeCN as solvent. ^eWith MeOH as solvent; ^fReaction conditions: **1a** (0.2 mmol), **2c** (0.8 mmol), PhI(OAc)₂ (0.4 mmol), DMF (2 mL), under nitrogen atmosphere, rt, 12 h.

The use of other solvents, such as MeCN or MeOH, led to no reaction or a low yield of the desired product (Table 1, entries 15 and 16). It is noteworthy that when the reaction was conducted in the presence of the nucleophilic trifluoromethyl reagent **2c** (i.e., Ruppert–Prakash reagent) using PhI(OAc)₂ as an oxidant, the desired product was formed in a low yield of only 35% (Table 1, entry 17).

With the optimal conditions in hand, we proceeded to evaluate the scope of the reaction using a wide variety of different nonsubstituted silyl enol ethers (Table 2). The presence of an electron-donating (**3b**, **3f**, **3i**) or electron-withdrawing (**3c–e**, **3h**, **3j**, **3k**) substituent on the aromatic ring was well tolerated under the optimized conditions, especially *ortho*-substituents (**3h**, **3i**, **3j**). Heterocyclic compounds also reacted smoothly under the optimized conditions to give the corresponding α -trifluoromethylated products in good yields (e.g., **3g**, 89% and **3l**, 84%). The presence of a naphthyl moiety was also well tolerated (**3n**), and the conjugated diene **1m** gave the terminal addition product **3m** exclusively in 71% yield. These conditions were applicable for synthesis of aliphatic ketones **3q** and **3r**.

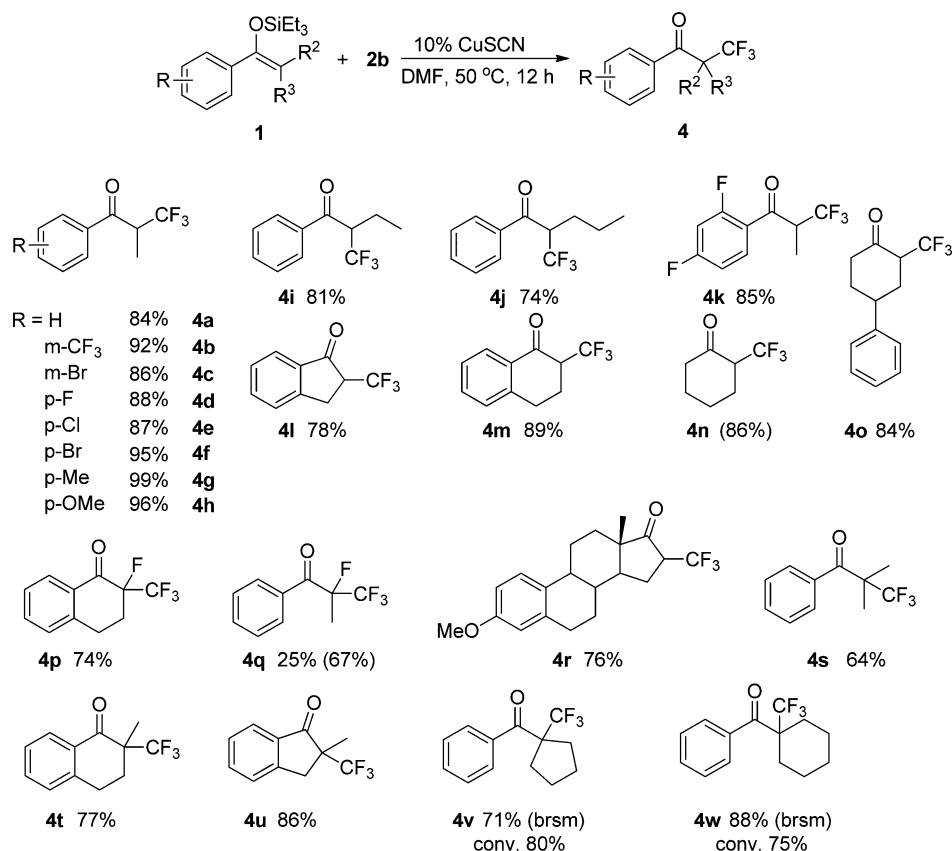
To extend the scope of the substrates, we also examined the application of the optimized conditions to substituted silyl enol ethers (Table 3). Unfortunately, our initial efforts in this regard resulted in a poor conversion when the reaction was conducted

Table 2. Reactions with Nonsubstituted Silyl Enol Ethers^a


Product	Yield (%)
3a (R = H)	88%
3b (R = <i>m</i> -OMe)	94%
3c (R = <i>m</i> -NO ₂)	78%
3d (R = <i>p</i> -CF ₃)	94%
3e (R = <i>p</i> -Cl)	95%
3f (R = <i>p</i> -Ph)	89%
3g (thiophene)	89%
3h (2-fluorophenyl)	68%
3i (2,4-dimethylphenyl)	93%
3j (2-chloro-4-fluorophenyl)	82%
3k (2-chloro-4-fluorophenyl)	85%
3l (1-(2-thienyl)ethyl)	84%
3m (conjugated diene)	71%
3n (naphthyl)	92%
3o (cyclohexyl)	80%
3p (cyclohexyl)	80%
3q (aliphatic ketone)	95%
3r (aliphatic ketone)	80%

^aReaction conditions: **1** (0.5 mmol), **2b** (0.75 mmol), CuSCN (0.05 mmol), DMF (5 mL), under nitrogen atmosphere, rt, 12 h. Isolated yield is shown, and yields based on ¹⁹F NMR spectroscopy are in parentheses.

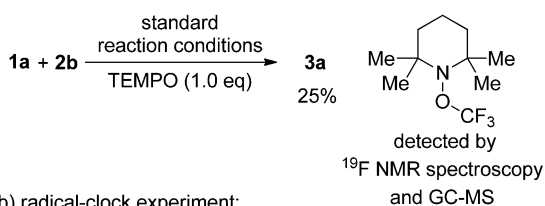
at room temperature, most likely because of negative steric and electronic effects. To overcome these issues, the reaction temperature was increased to 50 °C, which led to an increase in the yield of the desired product **4a** to 84%. With these new conditions in hand, we proceeded to investigate the α -trifluoromethylation of a range of other silyl enol ether substrates at 50 °C (Scheme 2). A variety of different substituted aromatic compounds reacted smoothly under the optimized conditions, including those bearing electron-donating (**4g,h**) and electron-withdrawing (**4b–f,k**) substituents on the aromatic moiety, which gave the corresponding products in high yields (85–99%). The presence of an ethyl (**4i**) or propyl (**4j**) substituent on double bond was also well tolerated. Notably, several cyclic (**4m,l**) and aliphatic (**4n,o**) compounds also underwent the trifluoromethylation reaction to give the corresponding products in good yield (78–89%). Interestingly, the application of the optimized conditions to a silyl enol ether bearing a fluorine atom on the double bond provided access to the corresponding α -F- α -CF₃-substituted carbonyl compound in good yield (**4p**, 74%). Although the ¹⁹F NMR yield for compound **4q** was 67%, the isolated yield was much lower at 25%. This low yield was attributed to the higher volatility of **4q**, which would have led to significant losses during its purification. With respect to its general application as a synthetic method for the α -trifluoromethylation of ketones

Table 3. Reactions with Substituted Silyl Enol Ethers^a

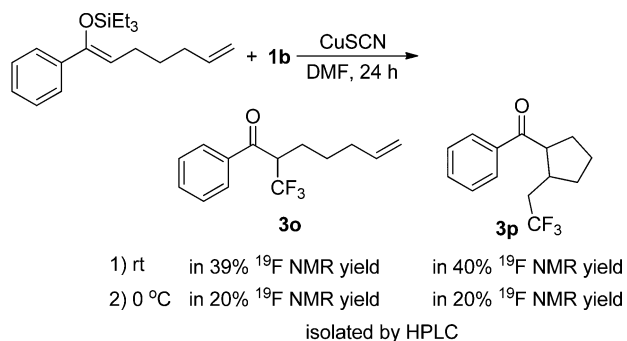
^aReaction conditions: **1** (0.5 mmol), **2b** (0.75 mmol), CuSCN (0.05 mmol), DMF (5 mL), at a nitrogen atmosphere, 50 °C, 12 h; Isolated yields are showed and yields based on ¹⁹F NMR spectroscopy are in parentheses.

Scheme 2. Mechanistic Experiments

a) evidence in support of a radical pathway:



b) radical-clock experiment:



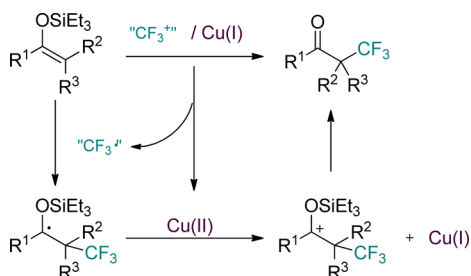
and silyl enol ethers, it is important to note that this method also allows for the synthesis of compounds containing a CF₃-substituted quaternary carbon center, which can be difficult to access using the previously published procedures.¹⁰ In this study, we have successfully prepared several compounds (**4s–w**) containing a CF₃-substituted quaternary carbon center in

moderate to high yields (64–88%). The presence of bulky substituents on the double bond of the silyl enol ether led to large steric effects, which made it difficult for the addition of CF₃ to take place and resulted in the incomplete conversion of the silyl enol ethers and lower than expected isolated yields of **4v** (71%) and **4w** (88%) based on recovered starting material. Furthermore, the trifluoromethylation of methylated estrone using this method gave the product **4r** in 76% yield, which was higher than the yield reported using Umemoto's method (44%).^{5b}

A preliminary investigation of the reaction mechanism suggested that the reaction most likely involved a CF₃ radical. The ¹⁹F NMR yield of the α-CF₃-substituted ketone (**3a**) was reduced from 95 to 25% when the reaction was conducted under the optimized conditions in the presence of TEMPO (Scheme 2). Furthermore, TEMPO-CF₃ was detected in the reaction mixture by ¹⁹F NMR spectroscopy and GC–MS. A radical-clock experiment was also conducted and confirmed the existence of a CF₃ radical in the reaction mixture which was captured by both of the double bonds. In this experiment, the CF₃ product was formed in a total yield of 80% by ¹⁹F NMR spectroscopy (**3o**:**3p** = 1:1). It was not possible to separate compounds **3o** and **3p** by flash column chromatography, and the compounds were therefore isolated by preparative HPLC. The reactivity of the substituted enol form of the alkene toward the addition of the CF₃ radical was close to that of a terminal alkene. A reduction in the reaction temperature from 25 to 0 °C, however, resulted in a decrease in the total yield to 40%, although the ratio of **3o**:**3p** was still 1:1 (Scheme 2).

Based on these experimental results, we propose that the copper(I)-mediated trifluoromethylation of silyl enol ethers might proceed via the mechanism shown in Scheme 3. Briefly,

Scheme 3. Proposed Mechanism



the reaction of copper(I) with Togni's reagent would produce the CF_3 radical with concomitant oxidation of copper(I) to copper(II). The CF_3 radical would then add to silyl enol ether **1** to give radical intermediate **5**, which would be oxidized by copper(II) to give cationic intermediate **6** together with the regeneration of copper(I). It is known that Cu(II) is effective in the oxidation of such radicals.^{6b} Finally, the loss of the silyl group of **6** would produce the α - CF_3 -substituted ketone.

In conclusion, we have developed an efficient and general method for the synthesis of α - CF_3 -substituted ketones under mild conditions via the reaction of silyl enol ethers with an electrophilic trifluoromethylating reagent (i.e., Togni's reagent II) in the presence of CuSCN. This newly developed method exhibited good functional group tolerance and substrate applicability and could also be used to construct CF_3 -substituted quaternary carbon centers. Given the mild conditions and broad substrate scope of this protocol, we envisage that it will be widely used by synthetic chemists working in the fields of medicinal and agrochemical research.

EXPERIMENTAL SECTION

General Experimental Details. DMF were purified by distillation over CaH_2 . Silyl enol ethers was synthesized according to the method reported by Shreeve.¹¹ NMR spectra were obtained on 300 or 400 MHz spectrometers and recorded at 25 °C. Chemical shifts for ^1H NMR spectra are reported in ppm downfield from TMS, chemical shifts for ^{13}C NMR spectra are recorded in ppm relative to internal chloroform (δ 77.0 ppm for ^{13}C), and chemical shifts for ^{19}F NMR are reported in ppm downfield from fluorotrichloromethane (CFCl_3). Coupling constants (J) are reported in hertz. The terms m, s, d, t, and q refer to multiplet, singlet, doublet, triplet, and quartet, respectively. ^{13}C NMR was broad-band decoupled from hydrogen nuclei. Infrared spectra (IR) were recorded with an infrared spectrometer; absorbance frequencies are given at maximum intensity in cm^{-1} . The mass analyzer type used for the HRMS is time-of-flight mass spectrometry (TOF-MS) or Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). Column chromatography was performed using silica gel (mesh 300–400).

General Procedure of Trifluoromethylation of Silyl Enol Ethers. A 10 mL Schlenk tube was charged with a stir bar, Togni's reagent **2b** (0.3 or 0.75 mmol), and CuSCN (0.02 or 0.05 mmol) under N_2 atmosphere. To the mixture were added silyl enol ethers (0.2 or 0.5 mmol) and DMF (2 or 5 mL). The mixture was stirred at room temperature or 50 °C for 12 h. Then, 4 or 10 mL water was added, the resulting mixture was extracted with DCM (2 or 5 mL $\times$ 3), and the organic extracts were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a hexane/DCM mixture as eluent.

3,3,3-Trifluoro-1-phenylpropan-1-one (3a).⁴ Triethyl((1-phenylvinyl)oxy)silane (46.8 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 88% yield (33 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.78 (q, J = 10.2 Hz, 2H), 7.48–7.51 (m, 2H), 7.60–7.64 (m, 1H), 7.91–7.93 (m, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.1 (t, J = 10.2 Hz).

3,3,3-Trifluoro-1-(3-methoxyphenyl)propan-1-one (3b).⁴ Triethyl((1-(3-methoxyphenyl)vinyl)oxy)silane (52.8 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an oil in 94% yield (40.8 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.76 (q, J = 10.2 Hz, 2H), 3.83 (s, 3H), 7.13–7.16 (m, 1H), 7.36–7.40 (m, 1H), 7.44–7.46 (m, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.2 (t, J = 10.2 Hz).

3,3,3-Trifluoro-2-methyl-1-(3-nitrophenyl)propan-1-one (3c).⁶¹ Triethyl((1-(3-nitrophenyl)vinyl)oxy)silane (55.8 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 78% yield (36.4 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.86 (q, J = 10.2 Hz, 2H), 7.74 (t, J = 7.9, 8.3 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.73 (s, 1H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.0 (t, J = 10.2 Hz).

3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1-one (3d).⁶¹ triethyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane (151.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), DMF (5 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 94% yield (121 mg); ^1H NMR (CDCl_3 , 400 MHz): δ = 3.81 (q, J = 10.0 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 42.6 (q, J = 29.1 Hz), 123.6 (q, J = 273 Hz), 123.9 (q, J = 277.2 Hz), 126.3 (q, J = 3.3 Hz), 128.3, 135.7 (q, J = 32.8 Hz), 138.6, 189.1; ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.1 (t, J = 10.0 Hz, 3F), –63.4 (s, 3F); IR (neat) ν/cm^{-1} : 2954, 1705, 1328, 1137, 1064; EI-MS m/z : 256 (6.45), 173 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_6\text{OF}_6$ (M^+) 256.0323, found 256.0321.

1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one (3e).⁴ ((1-(4-chlorophenyl)vinyl)oxy)triethylsilane (53.6 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 95% yield (42 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.75 (q, J = 9.5 Hz, 2H), 7.46 (d, J = 7.1 Hz, 2H), 7.85 (d, J = 7.1 Hz, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.1 (t, J = 9.5 Hz).

1-([1,1'-Biphenyl]-4-yl)-3,3,3-trifluoropropan-1-one (3f).⁴ ((1-([1,1'-Biphenyl]-4-yl)vinyl)oxy)triethylsilane (62 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 89% yield (47.2 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.81 (q, J = 10.2 Hz, 2H), 7.41–7.49 (m, 3H), 7.61–7.63 (m, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 8.6 Hz, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.0 (t, J = 10.2 Hz).

3,3,3-Trifluoro-1-(thiophen-2-yl)propan-1-one (3g).⁴ Triethyl((1-(thiophene-2-yl)vinyl)oxy)silane (48 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), NS DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 89% yield (29.6 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.69 (q, J = 10.0 Hz, 2H), 7.15–7.17 (m, 1H), 7.70–7.74 (m, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –62.0 (t, J = 10.0 Hz).

3,3,3-trifluoro-1-(4-fluoro-2-(trifluoromethyl)phenyl)propan-1-one (3h). Triethyl((1-(4-fluoro-2-(trifluoromethyl)phenyl)vinyl)oxy)silane (160.1 mg, 0.5 mmol), Togni's reagent (239

mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an oil in 68% yield (93 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 3.66 (q, *J* = 9.8 Hz, 2H), 7.31–7.36 (m, 1H), 7.43–7.46 (m, 1H), 7.49–7.53 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 46.1 (q, *J* = 29.0 Hz), 115.1 (dq, *J* = 25.2, 5.3 Hz), 119.1 (d, *J* = 21.3 Hz), 122.4 (q, *J* = 273.9 Hz), 123.2 (q, *J* = 277 Hz), 130.2, 130.3, 134.2, 163.5 (d, *J* = 254.9 Hz), 191.9. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –58.5 (s, 3F), –62.4 (t, *J* = 9.8 Hz, 3F), –105.29 to –105.21 (m, 1F); IR (neat) ν /cm^{–1}: 2950, 1724, 1316, 1143, 1054. EI-MS *m/z*: 274 (4.96), 191 (100). HRMS (EI): calcd for C₁₀H₉OF₃ (M⁺) 274.0229, found 274.0228.

1-(2,4-Dimethylphenyl)-3,3,3-trifluoropropan-1-one (3i).⁴ ((1-(2,4-Dimethylphenyl)vinyl)oxy)triethylsilane (52.4 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an oil in 93% yield (40.2 mg); ¹H NMR (CDCl₃, 400 MHz): δ = 2.36 (s, 3H), 2.52 (s, 3H), 3.73 (q, *J* = 10.1 Hz, 2H), 7.09–7.10 (m, 2H), 7.52–7.56 (m, 1H); ¹⁹F NMR (CDCl₃, 376 MHz): δ = –62.5 (t, *J* = 10.1 Hz).

1-(2-Chloro-6-fluorophenyl)-3,3,3-trifluoropropan-1-one (3j). ((1-(2-Chloro-6-fluorophenyl)vinyl)oxy)triethylsilane (143.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an oil in 82% yield (98 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 3.68 (q, *J* = 10.1 Hz, 2H), 7.04–7.09 (m, 1H), 7.23–7.25 (m, 1H), 7.34–7.40 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 47.6 (q, *J* = 28.9 Hz), 114.7 (d, *J* = 21.4 Hz), 123.2 (q, *J* = 277 Hz), 126.2, 127.1, 131.4, 132.4, 159.3 (d, *J* = 251.8 Hz), 189.3. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –62.5 (t, *J* = 10.1 Hz, 3F), –113.42 to –113.48 (m, 1F). IR (neat) ν /cm^{–1}: 2942, 1725, 1372, 1138, 1102. EI-MS *m/z*: 240 (25.85), 157 (100). HRMS (EI): calcd for C₉H₅OF₄Cl (M⁺) 239.9965, found 239.9969.

1-(3-Chloro-5-fluorophenyl)-3,3,3-trifluoropropan-1-one (3k). ((1-(3-Chloro-5-fluorophenyl)vinyl)oxy)triethylsilane (143.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an oil in 85% yield (101 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 3.78 (q, *J* = 9.8 Hz, 2H), 7.35–7.38 (m, 1H), 7.51–7.54 (m, 1H), 7.69 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 42.3 (q, *J* = 29.0 Hz), 113.7 (d, *J* = 22.9 Hz), 121.7 (d, *J* = 24.4 Hz), 123.5 (q, *J* = 277.7 Hz), 124.5 (d, *J* = 3.0 Hz), 136.1 (d, *J* = 10.0 Hz), 138.3, 162.7 (d, *J* = 253.3 Hz), 187.4. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –62.6 (t, *J* = 9.8 Hz, 3F), –108.8 (t, *J* = 8.0 Hz, 1F). IR (neat) ν /cm^{–1}: 2948, 1709, 1372, 1130, 1108. EI-MS *m/z*: 240 (45.9), 157 (100). HRMS (EI): calcd for C₉H₅OF₄Cl (M⁺) 239.9965, found 239.9966.

3,3,3-Trifluoro-1-(1-tosyl-1H-indol-3-yl)propan-1-one (3l). 1-Tosyl-3-((1-(triethylsilyl)oxy)vinyl)-1H-indole (213.8 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an solid in 84% yield (159 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 2.37 (s, 3H), 3.74 (q, *J* = 9.5 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.36–7.41 (m, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.93–7.95 (m, 1H), 8.27 (s, 1H), 8.32–8.34 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 21.6, 43.8 (q, *J* = 27.7 Hz), 113.1, 120.7, 123.1, 123.9 (q, *J* = 277.5 Hz), 125.2, 126.3, 127.1, 127.2, 130.4, 132.9, 134.1, 134.8, 146.3, 184.7. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –61.8 (t, *J* = 9.5 Hz). IR (neat) ν /cm^{–1}: 2985, 1667, 1539, 1389, 1146. EI-MS *m/z*: 381 (5.08), 105 (100). HRMS (EI): calcd for C₁₈H₁₄NO₃F₃S (M⁺) 381.0647, found 381.0651.

(E)-5,5,5-Trifluoro-1-phenylpent-2-en-1-one (3m). Triethyl-((1-phenylbuta-1,3-dien-1-yl)oxy)silane (130.2 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column

chromatography and isolated as an solid in 71% yield (76 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 3.06–3.16 (m, 2H), 6.84–6.92 (m, 1H), 7.09 (d, *J* = 15.1 Hz, 1H), 7.46–7.51 (m, 2H), 7.57–7.61 (m, 1H), 7.94 (d, *J* = 7.4 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 37.1 (q, *J* = 30.5 Hz), 125.2 (q, *J* = 277.5 Hz), 128.6, 128.7, 131.4, 133.3, 134.6 (q, *J* = 3.8 Hz), 137.1, 189.5. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –65.3 (t, *J* = 10.2 Hz). IR (neat) ν /cm^{–1}: 2946, 1676, 1621, 1578, 1057. EI-MS *m/z*: 214 (22.99), 105 (100). HRMS (EI): calcd for C₁₁H₉OF₃ (M⁺) 214.0605, found 214.0610.

3,3,3-Trifluoro-1-(naphthalen-1-yl)propan-1-one (3n).⁶ⁱ Triethyl-((1-(naphthalen-2-yl)vinyl)oxy)silane (56.8 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as an oil in 92% yield (43.8 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 3.88 (q, *J* = 10.1 Hz, 2H), 7.46–7.50 (m, 1H), 7.53–7.57 (m, 1H), 7.59–7.64 (m, 1H), 7.81–7.88 (m, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 8.71 (d, *J* = 8.6 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz): δ = –61.9 (t, *J* = 10.1 Hz).

1-Phenyl-2-(trifluoromethyl)hept-6-en-1-one (3o). Triethyl-((1-phenylhepta-1,6-dien-1-yl)oxy)silane (151.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 24 h. The compound was separated by HPLC. Oil. ¹H NMR (CDCl₃, 400 MHz): δ = 1.35–1.43 (m, 2H), 1.86–1.92 (m, 1H), 2.02–2.15 (m, 3H), 4.16–4.22 (m, 1H), 4.93–4.99 (m, 2H), 5.67–5.74 (m, 1H), 7.49–7.53 (m, 2H), 7.61–7.65 (m, 1H), 7.95–7.97 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 26.2, 26.3, 33.4, 49.2 (q, *J* = 26.1 Hz), 115.4, 124.9 (q, *J* = 28.1 Hz), 128.5, 128.9, 134.0, 136.8, 137.4, 194.4. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –66.2 (d, *J* = 8.2 Hz). IR (neat) ν /cm^{–1}: 3077, 2926, 1693, 1597, 1459, 1262. EI-MS *m/z*: 256 (14.95), 105 (100). HRMS (EI): calcd for C₁₄H₁₅OF₃ (M⁺) 256.1075, found 256.1079.

Phenyl(2-(2,2,2-trifluoroethyl)cyclopentyl)methanone (3p). Triethyl-((1-phenylhepta-1,6-dien-1-yl)oxy)silane (151.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at room temperature for 24 h. The compound was separated by HPLC. Oil. ¹H NMR (CDCl₃, 400 MHz): δ = 1.65–1.76 (m, 1H), 1.80–1.90 (m, 2H), 1.93–2.08 (m, 3H), 2.17–2.29 (m, 1H), 2.28–2.39 (m, 1H), 2.40–2.49 (m, 1H), 3.92–3.99 (m, 1H), 7.43–7.49 (m, 2H), 7.54–7.59 (m, 1H), 7.91–7.97 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 23.5, 30.1, 31.6, 34.3 (q, *J* = 27.9 Hz), 37.4, 47.7, 127.2 (q, *J* = 277.3 Hz), 128.2, 128.7, 133.0, 137.1, 202.2. ¹⁹F NMR (CDCl₃, 376 MHz): δ = –64.8 (t, *J* = 10.9 Hz). IR (neat) ν /cm^{–1}: 3062, 2961, 1679, 1597, 1448, 1256. EI-MS *m/z*: 256 (14.95), 105 (100). HRMS (EI): calcd for C₁₄H₁₅OF₃ (M⁺) 256.1075, found 256.1079.

1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-3,3,3-trifluoropropan-1-one (3r).^{6h} ((1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)vinyl)oxy)triethylsilane (58.4 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at room temperature for 12 h. The compound was purified by column chromatography and isolated as a solid in 80% yield (39 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 1.64–1.82 (m, 12H), 2.07 (s, 3H), 3.27 (q, *J* = 10.8 Hz, 2H). ¹⁹F NMR (CDCl₃, 376 M): δ = –62.2 (d, *J* = 10.8 Hz).

3,3,3-Trifluoro-2-methyl-1-phenylpropan-1-one (4a).^{5c} Triethyl-((1-phenylprop-1-en-1-yl)oxy)silane (49.6 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 84% yield (34 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 1.46 (d, *J* = 7.1 Hz, 3H), 4.19–4.27 (m, 1H), 7.47–7.51 (m, 2H), 7.59–7.61 (m, 1H), 7.92–7.95 (m, 2H). ¹⁹F NMR (CDCl₃, 376 MHz): δ = –68.3 (d, *J* = 8.1 Hz).

3,3,3-Trifluoro-2-methyl-1-(3-(trifluoromethyl)phenyl)propan-1-one (4b). Triethyl-((1-(3-(trifluoromethyl)phenyl)prop-1-en-1-yl)oxy)silane (158.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was

purified by column chromatography and isolated as an oil in 92% yield (124 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.47 (d, J = 7.0 Hz, 3H), 4.18–4.29 (m, 1H), 7.65 (t, J = 7.8, 7.9 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.17 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.6, 44.7 (q, J = 26.8 Hz), 123.6 (q, J = 272.4 Hz), 125.1 (q, J = 280.5 Hz), 125.5 (q, J = 3.7 Hz), 129.8, 130.5 (q, J = 3.7 Hz), 131.8, 131.9 (q, J = 33.3 Hz), 136.4, 193.3. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –63.0 (s, 3F), –68.2 (d, J = 6.8 Hz). IR (neat) ν/cm^{-1} : 2958, 1702, 1332, 1135, 1075. EI-MS m/z : 270 (0.43), 173 (100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_8\text{OF}_6$ (M^+) 270.0479, found 270.0475.

1-(3-Bromophenyl)-3,3,3-trifluoro-2-methylpropan-1-one (4c). ((1-(3-Bromophenyl)prop-1-en-1-yl)oxy)triethylsilane (163.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 86% yield (121 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.46 (d, J = 7.2 Hz, 3H), 4.13–4.21 (m, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 8.06 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.7, 44.7 (q, J = 26.8 Hz), 123.5, 125.2 (q, J = 280.5 Hz), 127.2, 130.6, 131.8, 137.0, 137.6, 193.3. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –68.6 (d, J = 7.9 Hz). IR (neat) ν/cm^{-1} : 2953, 1698, 1422, 1266, 1135. EI-MS m/z : 280 (6.05), 183 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{OF}_3\text{Br}$ (M^+) 279.9711, found 279.9714.

3,3,3-Trifluoro-1-(4-fluorophenyl)-2-methylpropan-1-one (4d). Triethyl((1-(4-fluorophenyl)prop-1-en-1-yl)oxy)silane (133.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 88% yield (97 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.45 (d, J = 7.1 Hz, 3H), 4.14–4.22 (m, 1H), 7.13–7.18 (m, 2H), 7.95–7.99 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.5, 44.3 (q, J = 26.4 Hz), 116.1 (d, J = 21.8 Hz), 125.2 (q, J = 280.3 Hz), 131.4 (d, J = 9.3 Hz), 132.1, 166.2 (d, J = 257 Hz), 192.8. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –68.3 (d, J = 8.2 Hz, 3F), –103.3 to –103.4 (m, 1F). IR (neat) ν/cm^{-1} : 2955, 1664, 1463, 1135, 852. EI-MS m/z : 220 (6.34), 123 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{OF}_4$ (M^+) 220.0511, found 220.0512.

1-(4-Chlorophenyl)-3,3,3-trifluoro-2-methylpropan-1-one (4e). ((1-(4-Chlorophenyl)prop-1-en-1-yl)oxy)triethylsilane (56.4 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as a solid in 87% yield (41 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.45 (d, J = 7.0 Hz, 3H), 4.13–4.21 (m, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –68.2 (d, J = 8.2 Hz).

1-(4-Bromophenyl)-3,3,3-trifluoro-2-methylpropan-1-one (4f). ((1-(4-Bromophenyl)prop-1-en-1-yl)oxy)triethylsilane (163 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 95% yield (132.4 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.44 (d, J = 7.0 Hz, 3H), 4.13–4.21 (m, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.7, 44.5 (q, J = 26.4 Hz), 125.3 (q, J = 280.5 Hz), 129.6, 130.2, 132.4, 134.6, 193.6. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –68.3 (d, J = 8.1 Hz). IR (neat) ν/cm^{-1} : 2963, 1690, 1404, 1272, 1111. EI-MS m/z : 280 (6.05), 183 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{OF}_3\text{Br}$ (M^+) 279.9711, found 279.9708.

3,3,3-Trifluoro-2-methyl-1-(*p*-tolyl)propan-1-one (4g). Triethyl((1-(*p*-tolyl)prop-1-en-1-yl)oxy)silane (131.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 99% yield (107 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.46 (d, J = 7.0 Hz, 3H), 2.42 (s, 3H), 4.18–4.28 (m, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.7, 21.6, 44.1 (q, J = 26.4 Hz), 125.4 (q, J = 279.5 Hz), 128.7, 129.6, 133.2, 145.0, 194.0. ^{19}F NMR (CDCl_3 , 376 MHz):

δ = –68.7 (d, J = 9.9 Hz). IR (neat) ν/cm^{-1} : 2953, 1690, 1411, 1229, 1134. EI-MS m/z : 216 (11.53), 119 (100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_{11}\text{OF}_3$ (M^+) 216.0762, found 216.0767.

3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-methylpropan-1-one (4h). Triethyl((1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)silane (55.6 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 96% yield (44.4 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.46 (d, J = 7.0 Hz, 3H), 3.89 (s, 3H), 4.15–4.23 (m, 1H), 6.97 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.7, 43.9 (q, J = 27 Hz), 55.6, 114.1, 125.4 (q, J = 283 Hz), 128.7, 130.9, 164.2, 192.8. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –68.7 (d, J = 7.9 Hz). IR (neat) ν/cm^{-1} : 2953, 1682, 1463, 1132, 846. EI-MS m/z : 232 (13.95), 135 (100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{F}_3$ (M^+) 232.0711, found 232.0712.

1-Phenyl-2-(trifluoromethyl)butan-1-one (4i). Triethyl((1-phenylbut-1-en-1-yl)oxy)silane (131.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 81% yield (88 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 0.94 (t, J = 7.4 Hz, 3H), 1.93–1.97 (m, 1H), 2.06–2.11 (m, 1H), 4.06–4.16 (m, 1H), 7.47–7.51 (m, 2H), 7.59–7.63 (m, 1H), 7.93–7.96 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.5, 20.4, 50.7 (q, J = 24.9 Hz), 125.0 (q, J = 280.3 Hz), 128.5, 128.8, 133.9, 136.9, 194.5. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –66.2 (d, J = 8.2 Hz). IR (neat) ν/cm^{-1} : 2977, 1690, 1449, 1254, 1168. EI-MS m/z : 216 (18.83), 105 (100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_{11}\text{OF}_3$ (M^+) 216.0762, found 216.0764.

1-Phenyl-2-(trifluoromethyl)pentan-1-one (4j). Triethyl((1-phenylpent-1-en-1-yl)oxy)silane (55.3 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 74% yield (34 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 0.89 (t, J = 7.5 Hz, 3H), 1.26–1.36 (m, 2H), 1.78–1.88 (m, 1H), 2.02–2.12 (m, 1H), 4.13–4.24 (m, 1H), 7.47–7.51 (m, 2H), 7.59–7.63 (m, 1H), 7.93–7.95 (m, 2H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –66.3 (d, J = 8.2 Hz).

1-(2,4-Difluorophenyl)-3,3,3-trifluoro-2-methylpropan-1-one (4k). ((1-(2,4-Difluorophenyl)prop-1-en-1-yl)oxy)triethylsilane (142.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 85% yield (101 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.44 (d, J = 7.2 Hz, 3H), 4.10–4.18 (m, 1H), 6.86–6.92 (m, 1H), 6.97–7.01 (m, 1H), 7.87–7.92 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 11.1, 49.1 (dq, J = 26.3, 8.6 Hz), 105.1 (dd, J = 26.8, 25.8 Hz), 113.0 (dd, J = 21.5, 3.2 Hz), 121.5, 125.3 (q, J = 279.9 Hz), 133.5 (dd, J = 10.8, 3.8 Hz), 162.4 (dd, J = 256.6, 12.4 Hz), 166.5 (dd, J = 259, 12.4 Hz), 191.5. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –69.0 (d, J = 7.9 Hz, 3F), –100.20 to –100.25 (m, 1F), –100.56 to –100.59 (m, 1F). IR (neat) ν/cm^{-1} : 2956, 1698, 1464, 1173, 978. EI-MS m/z : 238 (3.45), 141 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_7\text{OF}_5$ (M^+) 238.0417, found 238.0412.

2-(Trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one (4l). 5c ((1*H*-Inden-3-yl)oxy)triethylsilane (49.2 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as a solid in 78% yield (31 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 3.28–3.35 (m, 1H), 3.37–3.47 (m, 2H), 7.39–7.43 (m, 1H), 7.49–7.51 (d, J = 7.8 Hz, 1H), 7.62–7.66 (m, 1H), 7.78–7.81 (d, J = 7.9 Hz, 1H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –67.8 (d, J = 9.5 Hz).

2-(Trifluoromethyl)-3,4-dihydronaphthalen-1(2*H*)-one (4m). 5c ((3,4-Dihydronaphthalen-1-yl)oxy)triethylsilane (52.1 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as a solid in 89% yield (38 mg). ^1H NMR (CDCl_3 , 400 MHz):

δ = 2.23–2.31 (m, 1H), 2.45–2.51 (m, 1H), 3.04–3.10 (m, 2H), 3.22–3.28 (m, 1H), 7.25 (d, J = 7.8 Hz, 1H), 7.30–7.34 (m, 1H), 7.48–7.52 (m, 1H), 8.04 (d, J = 8.3 Hz, 1H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –67.6 (d, J = 9.5 Hz).

4-Phenyl-2-(trifluoromethyl)cyclohexanone (4o). Triethyl((3-(trifluoromethyl)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane (144.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as a solid in 84% yield (102 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.94–2.09 (m, 2H), 2.24–2.29 (m, 1H), 2.47–2.61 (m, 3H), 3.10–3.14 (m, 1H), 3.27–3.31 (m, 1H), 7.22–7.27 (m, 3H), 7.31–7.35 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 34.4, 34.5, 42.1, 42.4, 53.3 (q, J = 25.7 Hz), 124.6 (q, J = 278.8 Hz), 126.8, 127.3, 129.0, 143.2, 200.2. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –69.2 (d, J = 8.2 Hz). IR (neat) ν/cm^{-1} : 2960, 1720, 1496, 1391, 1061. EI-MS m/z : 242 (50.93), 104 (100). HRMS (EI): calcd for $\text{C}_{13}\text{H}_{13}\text{OF}_3$ (M^+) 242.0918, found 242.0920.

2-Fluoro-2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one (4p). Triethyl((2-fluoro-3,4-dihydronaphthalen-1-yl)oxy)silane (139.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as a solid in 74% yield (86 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 2.60–2.70 (m, 2H), 3.18–3.22 (m, 2H), 7.31 (d, J = 7.8 Hz, 1H), 7.37–7.41 (m, 1H), 7.56–7.61 (m, 1H), 8.09 (d, J = 7.9 Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 24.2 (d, J = 7 Hz), 28.5 (d, J = 22.6 Hz), 90.5 (dq, J = 194.6, 31.2 Hz), 122.1 (qd, J = 28.5, 28.8 Hz), 127.5, 128.6, 128.8, 130.6, 134.9, 142.6, 186.3 (d, J = 20.3 Hz). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –77.5 (d, J = 9.5 Hz, 3F), –172.79 to –172.92 (m, 1F). IR (neat) ν/cm^{-1} : 2950, 1708, 1326, 1175, 953. EI-MS m/z : 232 (33.38), 118 (100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_8\text{OF}_4$ (M^+) 232.0511, found 232.0514.

2,3,3,3-Tetrafluoro-2-methyl-1-phenylpropan-1-one (4q). Triethyl((2-fluoro-1-phenylprop-1-en-1-yl)oxy)silane (133.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 25% yield (27 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.87 (d, J = 22.6 Hz, 3H), 7.46–7.51 (m, 2H), 7.60–7.65 (m, 1H), 8.02–8.06 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 18.9 (dq, J = 22.1, 1.5 Hz), 97.4 (dq, J = 202.2, 30.5 Hz), 122.0 (qd, J = 285.4, 29.0 Hz), 128.5, 130.0, 133.8, 134.1, 193.4 (d, J = 25.2 Hz). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –78.6 (d, J = 7.9 Hz, 3F), –165.48 to –165.59 (m, 1F). IR (neat) ν/cm^{-1} : 2958, 1697, 1301, 1200, 1108. EI-MS m/z : 220 (0.93), 105 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{OF}_4$ (M^+) 220.0511, found 220.0509.

(13S)-3-Methoxy-12,13-methyl-16-(trifluoromethyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17-(14H)-one (4r). Triethyl((3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)silane (199.3 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as a solid in 76% yield (134 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 0.96 (s, 3H), 1.42–1.70 (m, 5H), 1.92–2.02 (m, 3H), 2.24–2.29 (m, 2H), 2.38–2.41 (m, 1H), 2.88–2.91 (m, 2H), 3.18–3.29 (m, 1H), 3.77 (s, 3H), 6.63–6.64 (m, 1H), 6.69–6.73 (m, 1H), 7.16–7.19 (m, 1H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –66.2 (d, J = 10.9 Hz).

3,3,3-Trifluoro-2,2-dimethyl-1-phenylpropan-1-one (4s). Triethyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (131.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 64% yield (69 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.54 (s, 6H), 7.38–7.42 (m, 2H), 7.46–7.50 (m, 1H), 7.60–7.63 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 20.7 (q, J = 2.9 Hz), 53.3 (q, J = 26.7 Hz), 126.8 (q, J = 282.3 Hz), 127.7, 128.2, 131.5, 138.1, 200.7. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –72.7 (s). IR (neat) ν/cm^{-1} :

ν/cm^{-1} : 2954, 1689, 1474, 1263, 1127. EI-MS m/z : 216 (0.26), 105 (100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_{11}\text{OF}_3$ (M^+) 216.0762, found 216.0765.

2-Methyl-2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one (4t). Triethyl((2-methyl-3,4-dihydronaphthalen-1-yl)oxy)silane (54.9 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 77% yield (35 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.43 (s, 3H), 2.11–2.18 (m, 1H), 2.39–2.47 (m, 1H), 3.04–3.06 (m, 2H), 7.22–7.25 (m, 1H), 7.30–7.34 (m, 1H), 7.47–7.51 (m, 1H), 8.05 (d, J = 7.4 Hz, 1H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –73.1 (s).

2-Methyl-2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one (4u). Triethyl((2-methyl-1H-inden-3-yl)oxy)silane (52.1 mg, 0.2 mmol), Togni's reagent (95.6 mg, 0.3 mmol), CuSCN (2.42 mg, 0.02 mmol), and DMF (2 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 86% yield (37 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.49 (s, 3H), 3.02 (d, J = 17.6 Hz, 1H), 3.56 (d, J = 17.6 Hz, 1H), 7.40–7.45 (m, 1H), 7.47–7.49 (m, 1H), 7.63–7.68 (m, 1H), 7.79–7.81 (m, 1H). ^{19}F NMR (CDCl_3 , 376 MHz): δ = –73.8 (s).

Phenyl(1-(trifluoromethyl)cyclopentyl)methanone (4v). (Cyclopentylidene(phenyl)methoxy)triethylsilane (144.2 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 71% yield (69 mg, brsm). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.62–1.67 (m, 2H), 1.72–1.78 (m, 2H), 2.24–2.31 (m, 2H), 2.46–2.53 (m, 2H), 7.40–7.44 (m, 2H), 7.50–7.54 (m, 1H), 7.82 (d, J = 7.9 Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 26.2, 32.8 (q, J = 1.5 Hz), 64.1 (q, J = 24.2 Hz), 127.1 (q, J = 281.8 Hz), 129.2 (q, J = 2.3 Hz), 128.1, 132.3, 136.7, 198.5. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –68.5 (s). IR (neat) ν/cm^{-1} : 2966, 1682, 1447, 1240, 1159. EI-MS m/z : 242 (0.71), 105 (100). HRMS (EI): calcd for $\text{C}_{13}\text{H}_{13}\text{OF}_3$ (M^+) 242.0918, found 242.0922.

Phenyl(1-(trifluoromethyl)cyclohexyl)methanone (4w). (Cyclohexylidene(phenyl)methoxy)triethylsilane (151.1 mg, 0.5 mmol), Togni's reagent (239 mg, 0.75 mmol), CuSCN (6.05 mg, 0.05 mmol), and DMF (5 mL) were used. The mixture was stirred at 50 °C for 12 h. The compound was purified by column chromatography and isolated as an oil in 88% yield (85 mg, brsm). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.04–1.12 (m, 2H), 1.15–1.23 (m, 1H), 1.57–1.70 (m, 5H), 2.59–2.63 (m, 2H), 7.40–7.44 (m, 2H), 7.48–7.52 (m, 1H), 7.67–7.69 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 21.9, 24.9, 28.7 (q, J = 1.9 Hz), 57.2 (q, J = 22.9 Hz), 126.1 (q, J = 283.2 Hz), 127.6, 128.2, 131.5, 139.4, 200.9. ^{19}F NMR (CDCl_3 , 376 MHz): δ = –71.2 (s). IR (neat) ν/cm^{-1} : 2943, 1687, 1457, 1246, 1002. EI-MS m/z : 256 (1.82), 105 (100). HRMS (EI): calcd for $\text{C}_{14}\text{H}_{15}\text{OF}_3$ (M^+) 256.1075, found 256.1073.

■ ASSOCIATED CONTENT

● Supporting Information

Copies of ^1H , ^{13}C , and ^{19}F NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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