

Metal-Free Oxidative Trifluoromethylthiolation of Terminal Alkynes with CF₃SiMe₃ and Elemental Sulfur

Chao Chen[†], Lingling Chu[†] and Feng-Ling Qing^{*,†,‡}

[†]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 345 Lingling Lu, Shanghai 200032, China

[‡]College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

Email: flq@mail.sioc.ac.cn

SUPPORTING INFORMATION

Table of Contents

General Information.....	S2
Effect of Solvents.....	S2
Effect of Additives.....	S3
Preparation of Substrates.....	S3
General Procedure for Metal-free Oxidative Trifluoromethylthiolation of Terminal Alkynes with CF ₃ SiMe ₃ and Elemental Sulfur.....	S5
Experiments for Mechanistic Investigations.....	S15
NMR spectra of Product.....	S23

General Information

^1H NMR and ^{19}F NMR spectra (CFCl_3 as outside standard and low field is positive) were recorded on a Bruker AM300 spectrometer. ^{13}C NMR was recorded on a Bruker AM400 spectrometer. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm).

Unless otherwise noted, all reagents were obtained commercially and used without further purification. The purity of elemental sulfur used is 99.99%. THF and toluene were distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 and CH_3CN were distilled from CaH_2 immediately prior to use. DMF, DMSO and DMAC were distilled from CaH_2 under reduced pressure and stored over 4 Å molecular sieves under nitrogen. Spray-dried KF was dried at 200 °C for 12 h under vacuum prior to use. Substrates **1d**,¹ **1n**,² and **1q**³ were prepared according to literature procedures. Other substrates were purchased from commercial sources (Aldrich, Acros, Alfa, and TCI). Reactions were performed under an atmosphere of nitrogen or air using glassware that was flame-dried under vacuum.

Effect of Solvents

Table S1. Screening of Solvents.^a



entry	solvent [0.05M]	yield of 2a (3a) ^b
1	DMF	92% (/)

(1) Hongbin Li, Jeffrey L. Petersen, and Kung K. Wang. *J. Org. Chem.*, **2001**, 66, 7804.

(2) Tang, Y.; Zhou, Z.; Ogawa, K.; Lopez, G. P.; Schanze, K. S.; Whitten, D. G. *Langmuir* **2009**, 25, 21.

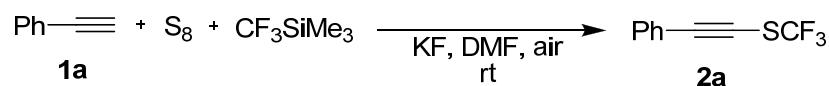
(3) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, 53, 2489.

2	DMAC	57% (/)
3	CH ₃ CN	12% (/)
4	DCM	/ (/)
5	THF	/ (/)
6	DMSO	/ (/)
7	toluene	/ (/)

^a Reaction conditions: **1a** (0.2 mmol), S₈ (6.0 equiv), CF₃SiMe₃ (5.0 equiv), KF (3.0 equiv), solvent (4 mL), room temperature, 6 h, under air. ^b Yields determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard. Abbreviations: DMF, dimethylformamide; DMAC, dimethylacetamide.

Effect of Additives

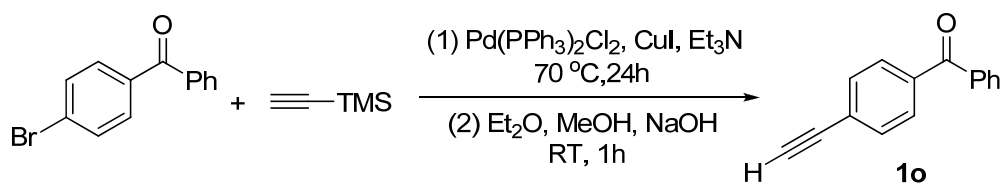
Table S2. Effect of Additives on Oxidative Trifluoromethylthiolation of Phenylacetylene **1a with CF₃SiMe₃ and Elemental Sulfur ^a**



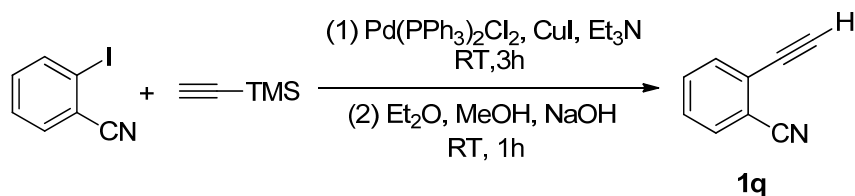
entry	additive	yield of 2a (%)
1	ambient light	92
2	dark	97
3	TEMPO (3 equiv)	79
4	Hydroquinone (20 mol %)	79
5	1,4-Dinitrobenzene (20 mol %)	73

^a Reaction conditions: **1a** (0.2 mmol), S₈ (6.0 equiv), CF₃SiMe₃ (5.0 equiv), KF (2.0 equiv), DMF (4 mL), additives, room temperature, 6 h, under air. ^b Yields determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard.

Preparation of Substrates



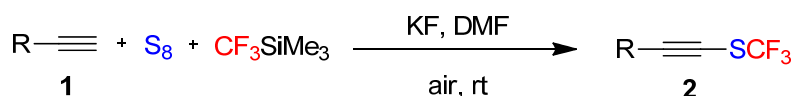
To a mixture of (4-bromophenyl)(phenyl)methanone (2.13 g, 8.00 mmol), $\text{Pd(PPh}_3)_2\text{Cl}_2$ (0.281g, 0.40 mmol), and CuI (0.107g, 0.56 mmol) in 30 mL of triethylamine, (trimethylsilyl)acetylene (0.865 g, 8.80 mmol) was added, and the mixture was stirred at 70°C for 24h. The reaction mixture was cooled to room temperature, diluted with diethyl ether, quenched with saturated NH_4Cl , and the aqueous layer was extracted with Et_2O (3 times). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated to afford the crude product, to which was added diethyl ether (20 mL), methanol (20 mL), and 10% sodium hydroxide solution (10 mL). The resulting mixture was stirred at rt for 1h, and neutralized with a 1 M HCl solution. The organic layer was washed with water and brine, dried over sodium sulfate, and concentrated. The resulting residue was purified by flash column chromatography (silica gel, Petroleum ether/ Ethyl acetate=10:1, R_f =0.40), and the title compound **1o** was obtained as a light red solid (1.26 g, two steps: 76% yield). ^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.80-7.75 (m, 4H), 7.63-7.51 (m, 3H), 7.50-7.46 (m, 2H), 3.25 (s, 1H). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 195.88, 137.43, 137.25, 132.65, 131.99, 129.99, 129.94, 128.39, 126.26, 82.82, 80.13. IR (ATR): ν_{max} 3288.31, 1659.11, 1601.43, 1446.93, 1285.23, 1273.34, 924.00, 853.67, 699.75 cm^{-1} . MS (EI): m/z (%) 206 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{10}\text{O}$: 206.0732; Found: 206.0734.



To a mixture of 2-iodobenzonitrile (2.29 g, 10.00 mmol), $\text{Pd(PPh}_3)_2\text{Cl}_2$ (0.211 g, 0.30

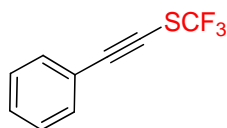
mmol), and copper(I) iodide (0.096 g, 0.50 mmol) in 30 mL of triethylamine, (trimethylsilyl)acetylene (1.08 g, 11.00 mmol) was added, and the mixture was stirred at rt for 3 h. The reaction mixture was diluted with diethyl ether, quenched with saturated NH₄Cl, and the aqueous layer was extracted with Et₂O (3 times). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated to afford the crude product, to which was added diethyl ether (20 mL), methanol (20 mL), and 10% sodium hydroxide solution (10 mL). The resulting mixture was stirred at rt for 1 h, and neutralized with a 1 M HCl solution. The organic layer was washed with water and brine, dried over sodium sulfate, and concentrated. The resulting residue was purified by flash column chromatography (silica gel, Petroleum ether/ Ethyl acetate=5:1, R_f=0.45), and the title compound **1q** was obtained as a light red solid (1.10 g, two steps: 87% yield). ¹H NMR (300 MHz, CDCl₃, 293K, TMS): δ ppm 7.68-7.54 (m, 3H), 7.48-7.43 (m, 1H), 3.49 (s, 1H). ¹³C NMR (100.7 MHz, CDCl₃, 293K, TMS): δ ppm 133.01, 132.68, 132.41, 128.99, 125.94, 117.24, 115.87, 83.80, 79.58. IR (ATR): ν_{max} 3243.33, 2228.41, 1480.35, 910.32, 761.72, 733.44, 683.29 cm⁻¹. MS (EI): *m/z* (%) 127 (100). HRMS: Calculated for C₉H₅N: 127.0422; Found: 127.0421.

General Procedure for the Metal-free Oxidative Trifluoromethylthiolation of Terminal Alkynes with CF₃SiMe₃ and Elemental Sulfur (0.2 mmol Scale)



In a glove box, KF (0.4 mmol, 24 mg) and S₈ (1.2 mmol, 39 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum and taken out. The vial was evacuated and then refilled with dry air for three times. DMF (4.5 mL) was added and the mixture was stirred at room temperature for 30 minutes. Terminal alkyne **1** (0.2 mmol) was then added to the mixture, followed by addition of CF₃SiMe₃ (1.0 mmol, 0.15 mL). The resulting orange-yellow reaction mixture

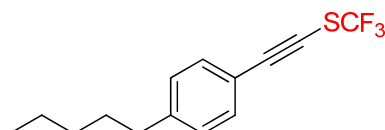
was stirred at room temperature for 6 h. The reaction solution was quenched with water and extracted with diethyl ether, and the organic layer was washed with brine, dried with Na₂SO₄ and concentrated. The resulting residue was purified by flash column chromatography using petroleum ether and dichloromethane as fluent solvent.



2a

(Phenylethynyl)(trifluoromethyl)sulfane 2a:

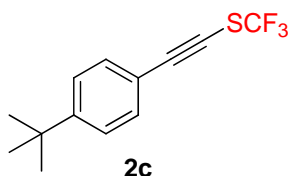
2a was obtained as a light yellow oil in 74% yield (R_f = 0.80 in petroleum ether). ¹H NMR (300 MHz, CDCl₃, 293K, TMS): δ ppm 7.51-7.48 (m, 2H), 7.39-7.33 (m, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -44.07 (s, 3F). ¹³C NMR (100.7 MHz, CDCl₃, 293K, TMS): δ ppm 132.18, 129.70, 128.45, 128.12 (q, J = 313.4 Hz), 121.573, 101.28 (d, J = 1.5 Hz), 66.67 (q, J = 4.5 Hz). IR (ATR): ν_{\max} 2927.19, 2854.73, 2179.79, 1488.05, 1443.73, 1161.97, 1105.59, 755.54, 688.17cm⁻¹. MS (EI): m/z (%) 202 (100). HRMS: Calculated for C₉H₅F₃S: 202.0064; Found: 202.0067.



2b

((4-pentylphenyl)ethynyl)(trifluoromethyl)sulfane 2b

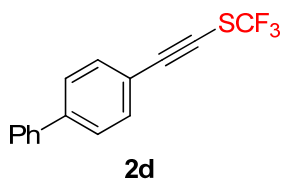
2b was obtained as a yellow oil in 83% yield (R_f = 0.80 in petroleum ether). ¹H NMR (300 MHz, CDCl₃, 293K, TMS): δ ppm 7.41 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 1.65-1.55 (m, 2H), 1.34-1.27 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -44.26 (s, 3F). ¹³C NMR (100.7 MHz, CDCl₃, 293K, TMS): δ ppm 145.26, 132.32, 128.57, 128.14 (q, J = 313.4 Hz), 118.64, 101.55, 65.79 (q, J = 4.5 Hz), 35.92, 31.37, 30.81, 22.47, 13.96. IR (ATR): ν_{\max} 2958.60, 2930.93, 1508.05, 1159.26, 1104.94cm⁻¹. MS (EI): m/z (%) 272, 215 (100). HRMS: Calculated for C₉H₅F₃S: 272.0847; Found: 272.0843.



((4-*tert*-Butylphenyl)ethynyl)(trifluoromethyl)sulfane 2c

2c was obtained as a colorless oil in 85% yield ($R_f = 0.80$ in petroleum ether).

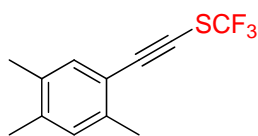
^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.43 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 1.31 (s, 9H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.2 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 153.35, 132.19, 128.17 (q, $J = 313.4$ Hz), 125.49, 118.51, 101.53, 65.84 (q, $J = 4.5$ Hz), 34.92, 31.05. IR (ATR): ν_{max} 2965.94, 2176.92, 1504.11, 1159.25, 1103.21, 834.84, 757.34 cm^{-1} . MS (EI): m/z (%) 258, 243 (100). HRMS: Calculated for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{S}$: 258.0690; Found: 258.0691.



(Biphenyl-4-ylethynyl)(trifluoromethyl)sulfane 2d

2d was obtained as a white crystal in 91% yield ($R_f = 0.70$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.57-7.52 (m, 6H), 7.43 (t, $J = 5.7$ Hz, 2H), 7.37-7.33 (m, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.6 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 142.55, 139.99, 132.74, 128.97, 128.19 (q, $J = 312.6$ Hz), 128.01, 127.15, 127.11, 120.36, 101.29, 67.31 (q, $J = 4.5$ Hz). IR (ATR): ν_{max} 3032.94, 2929.22, 2175.83, 1601.06, 1486.46, 1156.89, 1106.95, 908.15, 840.57, 763.29, 735.03 cm^{-1} . MS (EI): m/z (%) 278, 209 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_9\text{F}_3\text{S}$: 278.0377; Found: 278.0373. Anal. Calcd for $\text{C}_{15}\text{H}_9\text{F}_3\text{S}$: C, 64.74; H, 3.26. Found: C, 64.82; H, 3.60.

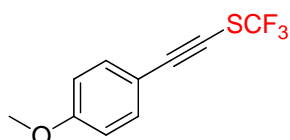


2e

((Trifluoromethyl)((2,4,5-trimethylphenyl)ethynyl)sulfane 2e

2e was obtained as a pale yellow solid in 61% yield (R_f = 0.85 in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.22 (s, 1H), 6.98 (s, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.6 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 138.90, 138.74, 133.93, 133.56, 131.01, 128.21 (q, J = 312.6 Hz), 118.54, 100.73, 68.74 (q, J = 3.7 Hz), 19.77, 19.74, 18.93. IR (ATR): ν_{max} 2924.22, 2165.82, 1503.44, 1454.55, 1180.84, 1157.66, 1105.73, 874.92 cm^{-1} . MS (EI): m/z (%) 244 (100). HRMS: Calculated for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{S}$: 244.0534; Found: 244.0533.

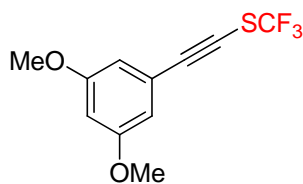


2f

((4-Methoxyphenyl)ethynyl)(trifluoromethyl)sulfane 2f

2f was obtained as a pale yellow oil in 50% yield (R_f = 0.60 in petroleum ether/dichloromethane=6:1).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.46 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.3 Hz, 2H), 3.82 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.5 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 160.88, 134.34, 128.15 (q, J = 313.4 Hz), 114.09, 113.50, 101.47, 65.11 (q, J = 4.5 Hz), 55.29. IR (ATR): ν_{max} 2841.48, 2175.03, 1604.88, 1510.18, 1153.67, 1102.61, 832.48 cm^{-1} . MS (EI): m/z (%) 232, 163 (100). HRMS: Calculated for $\text{C}_{10}\text{H}_7\text{F}_3\text{OS}$: 232.0170; Found: 232.0168.

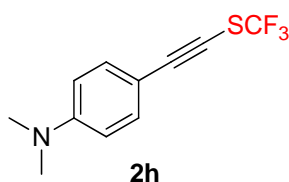


2g

((3,5-Dimethoxyphenyl)ethynyl)(trifluoromethyl)sulfane 2g

2g was obtained as a pale yellow oil in 71% yield ($R_f = 0.20$ in petroleum ether).

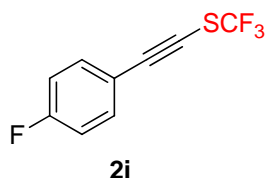
^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 6.63 (d, $J = 2.1$ Hz, 2H), 6.49 (t, $J = 2.1$ Hz, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.0 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 160.59, 128.12 (q, $J = 313.3$ Hz), 122.69, 109.80, 103.15 (d, $J = 1.5$ Hz), 101.35, 66.24 (q, $J = 4.5$ Hz), 55.39. IR (ATR): ν_{max} 2961.53, 2938.52, 2179.74, 1597.60, 1456.54, 1421.45, 1332.90, 1156.55, 1103.24, 837.17, 678.69 cm^{-1} . MS (EI): m/z (%) 262 (100). HRMS: Calculated for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_2\text{S}$: 262.0275; Found: 262.0274.



***N,N*-dimethyl-4-((trifluoromethylthio)ethynyl)aniline 2h**

2h was obtained as a white solid in 45% yield ($R_f = 0.20$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.39 (d, $J = 9.0$ Hz, 2H), 6.61 (d, $J = 9.0$ Hz, 2H), 3.00 (s, 6H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -45.1 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 151.13, 134.37, 128.20 (q, $J = 313.3$ Hz), 111.43, 107.70, 103.15 (d, $J = 1.5$ Hz), 63.87 (q, $J = 4.4$ Hz), 40.01. IR (ATR): ν_{max} 2924.40, 2159.42, 1604.45, 1524.99, 1373.62, 1179.95, 1132.81, 1105.37, 907.77, 733.50 cm^{-1} . MS (EI): m/z (%) 245, 176 (100). HRMS: Calculated for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{NS}$: 245.0486; Found: 245.0488.

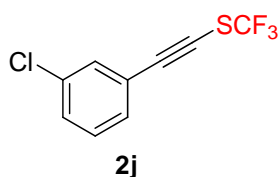


((4-Fluorophenyl)ethynyl)(trifluoromethyl)sulfane 2i

2i was obtained as a pale yellow oil in 84% yield ($R_f = 0.80$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.49 (dd, $J_1 = 8.8$ Hz, $J_2 = 5.2$ Hz, 2H),

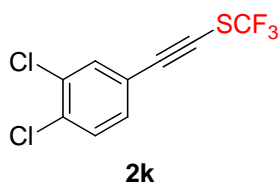
7.04 (t, $J = 8.8$ Hz, 2H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -45.1 (s, 3F), -109.3 (s, 1F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 163.40 (d, $J = 253.6$ Hz), 134.48 (d, $J = 9.0$ Hz), 128.08 (q, $J = 313.3$ Hz), 117.66 (d, $J = 3.7$ Hz), 115.87 (d, $J = 22.5$ Hz), 100.20, 66.64 (q, $J = 4.5$ Hz). IR (ATR): ν_{max} 2180.77, 1600.97, 1508.01, 1241.52, 1157.52, 1103.07, 836.20 cm^{-1} . MS (EI): m/z (%) 220, 151 (100). HRMS: Calculated for $\text{C}_9\text{H}_4\text{F}_4\text{S}$: 219.9970; Found: 219.9966.



((3-Chlorophenyl)ethynyl)(trifluoromethyl)sulfane 2j

2j was obtained as a pale yellow oil in 81% yield ($R_f = 0.90$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.47 (t, $J = 1.8$ Hz, 1H), 7.38-7.35 (m, 2H), 7.30-7.25 (m, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.7 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 134.38, 131.81, 130.09, 129.92, 129.67, 127.97 (q, $J = 313.3$ Hz), 123.14, 99.74 (d, $J = 1.5$ Hz), 68.31 (q, $J = 3.8$ Hz). IR (ATR): ν_{max} 2927.12, 1591.65, 1561.51, 1473.86, 1161.76, 1103.67, 915.58, 784.12 cm^{-1} . MS (EI): m/z (%) 236, 167 (100). HRMS: Calculated for $\text{C}_9\text{H}_4\text{ClF}_3\text{S}$: 235.9674; Found: 235.9675.

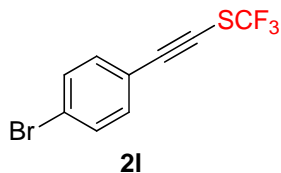


((3,4-Dichlorophenyl)ethynyl)(trifluoromethyl)sulfane 2k

2k was obtained as a white solid in 56% yield ($R_f = 0.80$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.56 (d, $J = 1.6$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.29 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.5 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 134.34, 133.59, 132.87, 131.05, 130.56, 127.85 (q, $J = 313.4$ Hz), 121.33, 98.82, 69.30 (q, $J = 4.5$ Hz). IR (ATR): ν_{max} 2926.77, 1475.83, 1462.50, 1163.90, 1130.53, 1103.84, 845.61 cm^{-1} . MS (EI): m/z

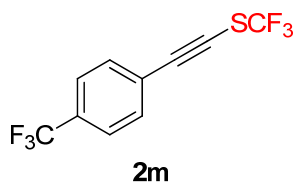
(%) 270, 201 (100). HRMS: Calculated for C₉H₃Cl₂F₃S: 269.9285; Found: 269.9283.



((4-Bromophenyl)ethynyl)(trifluoromethyl)sulfane 2l

2l was obtained as a pale yellow solid in 44% yield (R_f = 0.80 in petroleum ether).

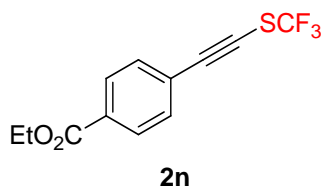
¹H NMR (300 MHz, CDCl₃, 293K, TMS): δ ppm 7.49 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -43.8 (s, 3F). ¹³C NMR (100.7 MHz, CDCl₃, 293K, TMS): δ ppm 133.52, 131.86, 127.99 (q, J = 313.0 Hz), 124.31, 120.48, 100.23, 68.18 (q, J = 4.3 Hz). IR (ATR): ν_{\max} 2926.59, 1585.23, 1485.27, 1160.67, 1099.48, 1071.38, 1011.85, 823.31 cm⁻¹. MS (EI): m/z (%) 280, 282 (100). HRMS: Calculated for C₉H₄BrF₃S: 279.9139; Found: 279.9167.



(Trifluoromethyl)((4-(trifluoromethyl)phenyl)ethynyl)sulfane 2m

2m was obtained as a colorless oil in 74% yield (R_f = 0.85 in petroleum ether).

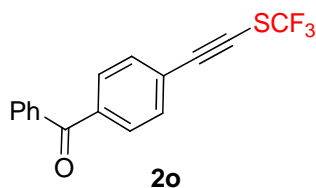
¹H NMR (300 MHz, CDCl₃, 293K, TMS): δ ppm 7.62 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 9.0 Hz, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -43.6 (s, 3F), -63.5 (s, 3F). ¹³C NMR (100.7 MHz, CDCl₃, 293K, TMS): δ ppm 132.03, 131.20 (q, J = 33.0 Hz), 127.90 (q, J = 313.3 Hz), 125.40 (q, J = 3.7 Hz), 125.20 (d, J = 1.5 Hz), 123.62 (q, J = 272.8 Hz), 99.77, 69.73 (q, J = 4.5 Hz). IR (ATR): ν_{\max} 2931.64, 1616.60, 1404.90, 1324.58, 1166.46, 1130.04, 1102.52, 1067.28, 841.65 cm⁻¹. MS (EI): m/z (%) 270, 201 (100). HRMS: Calculated for C₁₀H₄F₆S: 269.9938; Found: 269.9936.



Ethyl 4-((trifluoromethylthio)ethynyl)benzoate 2n

2n was obtained as a yellow oil in 71% yield ($R_f = 0.60$ in petroleum ether).

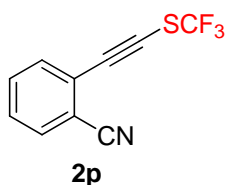
^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 8.01 (d, $J = 8.7$ Hz, 2H), 7.52 (d, $J = 8.7$ Hz, 2H), 4.37 (q, $J = 6.9$ Hz, 2H), 1.39 (t, $J = 6.9$ Hz, 3H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.7 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 165.66, 131.59, 131.03, 129.49, 127.95 (q, $J = 313.1$ Hz), 125.80, 100.49, 69.85 (q, $J = 3.7$ Hz), 61.26, 14.19. IR (ATR): ν_{max} 2984.45, 1723.30, 1606.70, 1288.19, 1275.31, 1177.45, 1101.55, 1020.14, 857.94, 767.95 cm^{-1} . MS (EI): m/z (%) 274, 229 (100). HRMS: Calculated for $\text{C}_{12}\text{H}_9\text{F}_3\text{O}_2\text{S}$: 274.0275; Found: 274.0278.



Phenyl(4-((trifluoromethylthio)ethynyl)phenyl)methanone 2o

2o was obtained as a a yellow solid in 55% yield ($R_f = 0.70$ in petroleum ether/dichloromethane=1:1).

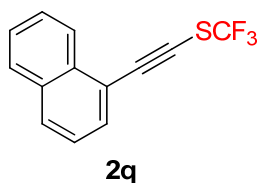
^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.81-7.78 (m, 4H), 7.64-7.59 (m, 3H), 7.652-7.48 (m, 2H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.6 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 195.71, 137.98, 137.09, 132.77, 131.63, 130.23, 129.99, 128.43, 127.95 (q, $J = 313.3$ Hz), 125.47, 100.47, 70.09 (q, $J = 4.5$ Hz). IR (ATR): ν_{max} 2926.95, 1661.83, 1600.24, 1447.91, 1275.16, 1177.54, 1102.50, 923.89, 698.63 cm^{-1} . MS (EI): m/z (%) 306. HRMS: Calculated for $\text{C}_{16}\text{H}_9\text{F}_3\text{OS}$: 306.0326; Found: 306.0322.



2-((Trifluoromethylthio)ethynyl)benzonitrile 2p

2p was obtained as a light yellow oil in 75% yield ($R_f = 0.30$ in petroleum ether/dichloromethane=3:1).

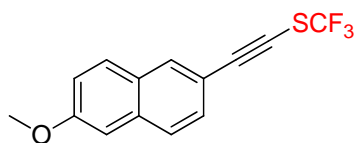
^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.68 (d, $J = 7.8$ Hz, 1H), 7.64-7.59 (m, 2H), 7.54-7.47 (m, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.1 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 132.82, 132.54, 132.53, 129.60, 127.75 (q, $J = 313.9$ Hz), 125.18, 116.75, 115.27, 97.24 (d, $J = 1.5$ Hz), 74.25 (q, $J = 4.4$ Hz). IR (ATR): ν_{max} 2927.22, 2231.64, 1479.58, 1445.40, 1160.77, 1101.62, 760.34 cm^{-1} . MS (EI): m/z (%) 227, 158 (100). HRMS: Calculated for $\text{C}_{10}\text{H}_4\text{F}_3\text{NS}$: 227.0017; Found: 227.0020.



(Naphthalen-1-ylethynyl)(trifluoromethyl)sulfane 2q

2q was obtained as a colorless oil in 80% yield ($R_f = 0.75$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 8.23 (d, $J = 8.1$ Hz, 1H), 7.86 (t, $J = 8.1$ Hz, 2H), 7.72 (dd, $J_1 = 7.2$ Hz, $J_2 = 0.9$ Hz, 1H), 7.62-7.49 (m, 2H), 7.44-7.39 (m, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.9 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 133.42, 133.09, 131.64, 130.32, 128.42, 128.21 (q, $J = 313.3$ Hz), 127.38, 126.73, 125.71, 125.08, 119.13, 99.68, 71.18 (q, $J = 4.5$ Hz). IR (ATR): ν_{max} 3060.42, 1508.20, 1158.39, 1103.11, 798.35, 771.03 cm^{-1} . MS (EI): m/z (%) 252, 183 (100). HRMS: Calculated for $\text{C}_{13}\text{H}_7\text{F}_3\text{S}$: 252.02214; Found: 252.0222.

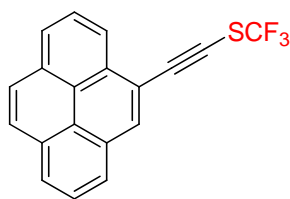


2r

((6-Methoxynaphthalen-2-yl)ethynyl)(trifluoromethyl)sulfane 2r

2r was obtained as a white solid in 45% yield ($R_f = 0.35$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.94 (s, 1H), 7.68-7.63 (m, 2H), 7.47-7.44 (m, 1H), 7.17-7.07 (m, 1H), 7.06 (d, $J = 2.1$ Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.2 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 159.01, 135.02, 132.92, 129.62, 128.97, 128.27 (q, $J = 313.1$ Hz), 128.24, 127.05, 119.80, 116.33, 105.87, 102.10, 66.10 (q, $J = 4.3$ Hz), 55.35. IR (ATR): ν_{max} 2967.13, 2163.44, 1622.41, 1483.09, 1271.64, 1161.54, 1030.84, 734.32 cm^{-1} . MS (EI): m/z (%) 282, 213 (100). HRMS: Calculated for $\text{C}_{14}\text{H}_9\text{F}_3\text{OS}$: 282.0326; Found: 282.0324.

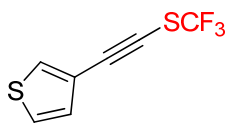


2s

(Pyren-4-ylethynyl)(trifluoromethyl)sulfane 2s

2s was obtained as an orange-yellow solid in 74% yield ($R_f = 0.70$ in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 8.27 (d, $J = 9.3$ Hz, 1H), 8.08 (d, $J = 7.2$ Hz, 2H), 8.00-7.83 (m, 6H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.8 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 132.65, 132.10, 130.92, 130.68, 129.98, 128.83, 128.78, 128.37 (q, $J = 313.4$ Hz), 126.92, 126.26, 125.97, 125.89, 124.64, 124.18, 123.99, 123.81, 115.37, 100.80, 71.52 (q, $J = 4.5$ Hz). IR (ATR): ν_{max} 3044.90, 2171.32, 1594.11, 1153.70, 1099.37, 844.79, 714.73 cm^{-1} . MS (EI): m/z (%) 326, 256 (100). HRMS: Calculated for $\text{C}_{19}\text{H}_9\text{F}_3\text{S}$: 326.0377; Found: 326.0381.

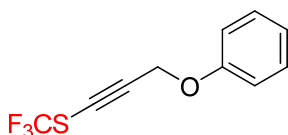


2t

3-((Trifluoromethylthio)ethynyl)thiophene 2t

2t was obtained as a yellow oil in 72% yield (R_f = 0.80 in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.65-7.63 (m, 1H), 7.32-7.29 (m, 1H), 7.19-7.17 (m, 1H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.14 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 132.09, 130.08, 128.01 (q, J = 313.4 Hz), 125.71, 120.67, 96.37, 66.50 (q, J = 4.4 Hz). IR (ATR): ν_{max} 2926.98, 2170.08, 1358.54, 1158.93, 1103.83, 783.81 cm^{-1} . MS (EI): m/z (%) 208, 163 (100). HRMS: Calculated for $\text{C}_7\text{H}_3\text{F}_3\text{S}_2$: 207.9628; Found: 207.9624.

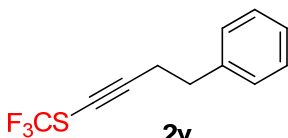


2u

(3-Phenoxyprop-1-ynyl)(trifluoromethyl)sulfane 2u

2u was obtained as a yellow liquid in 57% yield (R_f = 0.50 in petroleum ether).

^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.34-7.28 (m, 2H), 7.04-6.94 (m, 3H), 4.85 (s, 2H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -43.7 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 157.30, 129.55, 127.91 (q, J = 313.3 Hz), 121.81, 114.88, 98.60, 66.56 (q, J = 4.4 Hz), 56.43. IR (ATR): ν_{max} 2918.53, 1599.44, 1589.45, 1495.40, 1214.85, 1103.41, 753.15, 690.15 cm^{-1} . MS (EI): m/z (%) 232, 139 (100), 163 (100). HRMS: Calculated for $\text{C}_{10}\text{H}_7\text{F}_3\text{OS}$: 232.0170; Found: 232.0167.



2v

(4-Phenylbut-1-yn-1-yl)(trifluoromethyl)sulfane 2v

2v was obtained as a yellow liquid in 21% yield (R_f = 0.80 in petroleum ether).

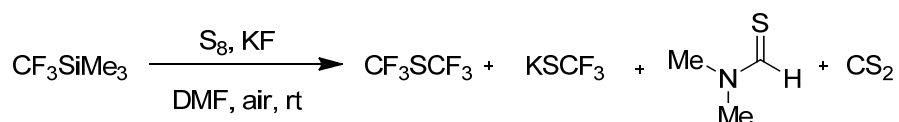
^1H NMR (300 MHz, CDCl_3 , 293K, TMS): δ ppm 7.31-7.28 (m, 2H), 7.24-7.19 (m, 3H),

2.86 (t, $J = 7.2$ Hz, 2H), 2.66 (t, $J = 7.2$ Hz, 2H). ^{19}F NMR (282 MHz, CDCl_3): δ ppm -44.5 (s, 3F). ^{13}C NMR (100.7 MHz, CDCl_3 , 293K, TMS): δ ppm 139.82, 128.45, 128.40 (q, $J = 310.3$ Hz), 128.38, 126.50, 102.94, 57.90 (q, $J = 4.5$ Hz), 34.33, 22.36. IR (ATR): ν_{max} 2927.27, 1454.53, 1156.40, 1106.93, 698.16 cm^{-1} . MS (EI): m/z (%) 230 (100). HRMS: Calculated for $\text{C}_{11}\text{H}_9\text{F}_3\text{S}$: 230.0377; Found: 230.0375.

Experiments for Mechanistic Investigations

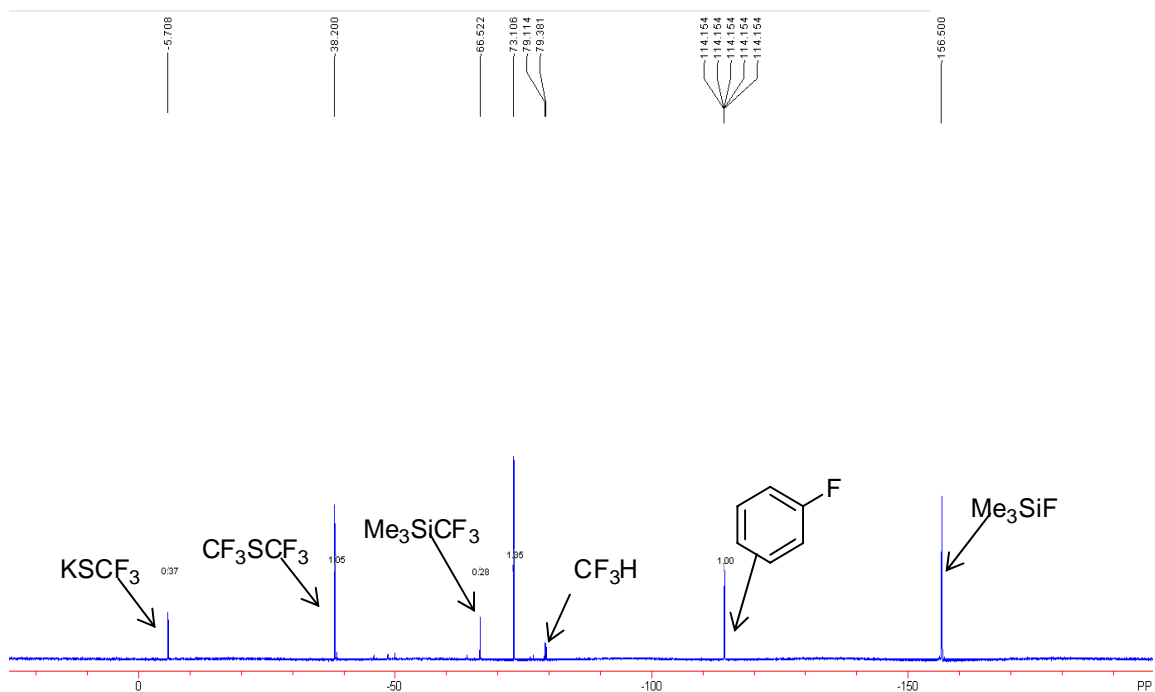
1. Control experiments

(1-a):

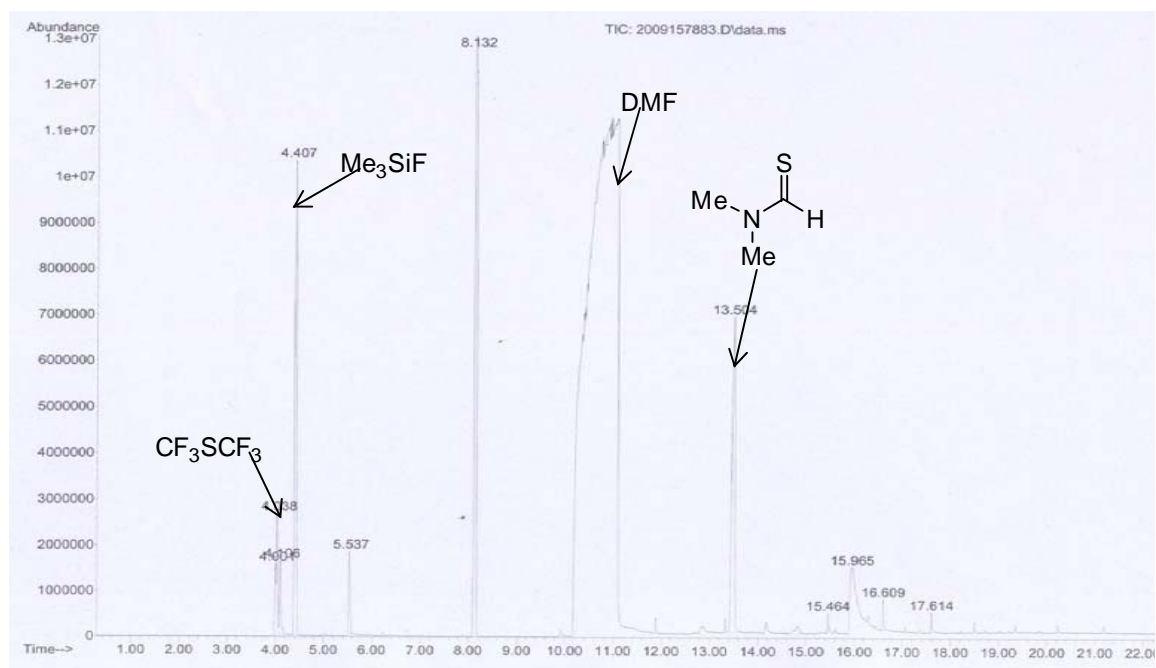


In a glove box, KF (0.4 mmol, 24mg) and S_8 (1.2 mmol, 39mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum and taken out. The vial was evacuated and then refilled with dry air for three times. DMF (4.5 mL) and fluorobenzene (0.6 mmol, 56 μL) were added and the mixture was stirred at room temperature for 30 min. CF_3SiMe_3 (1.0 mmol, 0.15mL) was then added to the mixture. The resulting reaction mixture was stirred at room temperature for a certain period of time. This sample was then analyzed by GC and ^{19}F NMR.

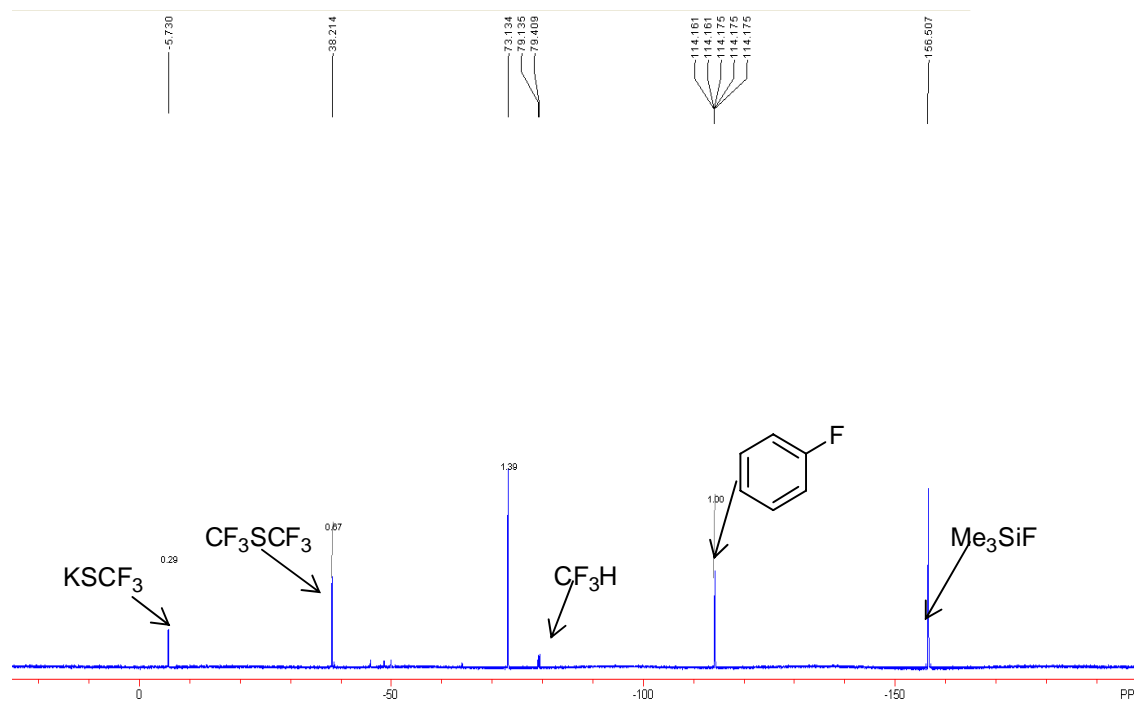
^{19}F NMR spectrum (10 min):



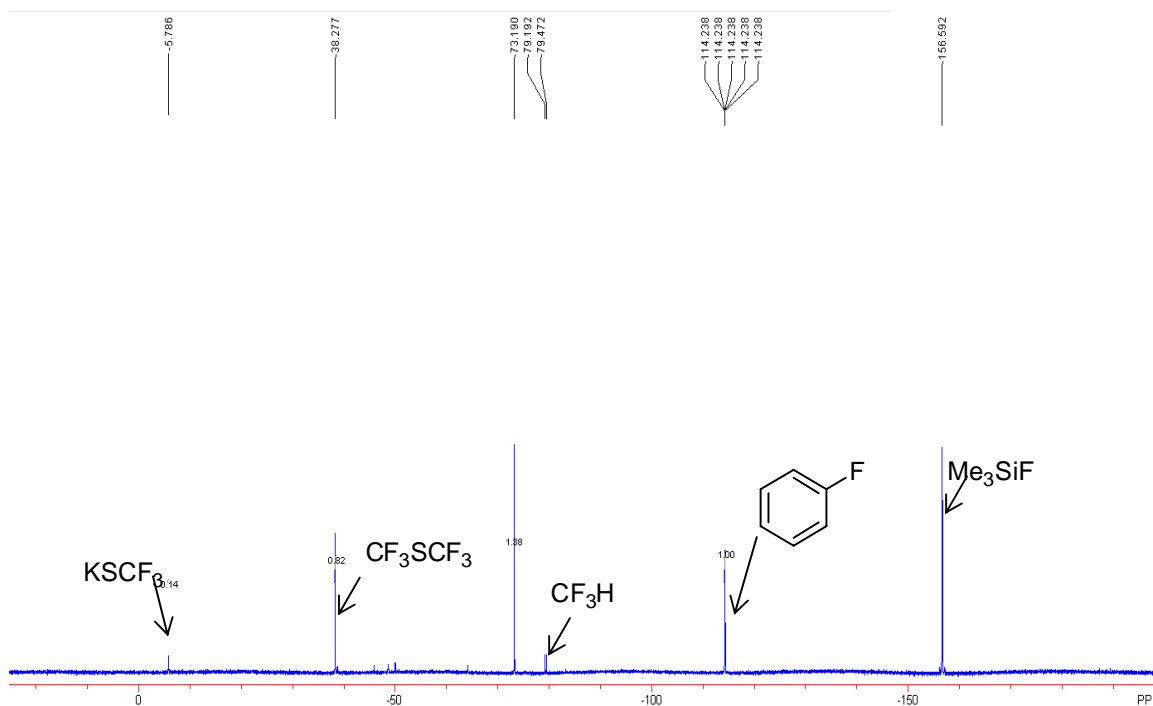
GC-MS analysis (10 min):



^{19}F NMR spectrum (25 min):



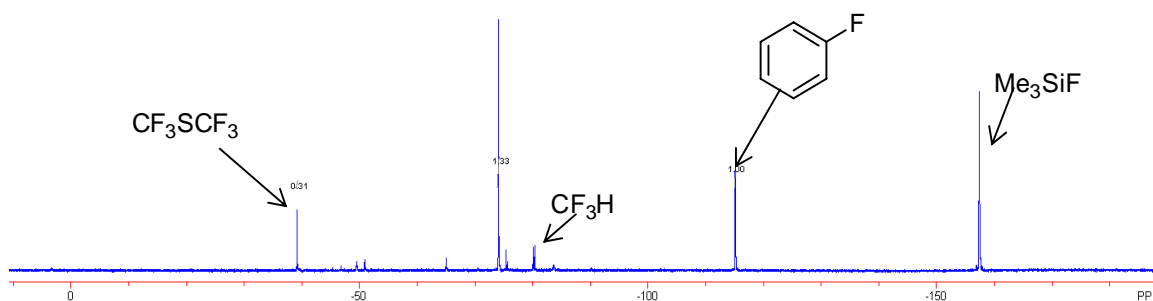
^{19}F NMR spectrum (40 min):



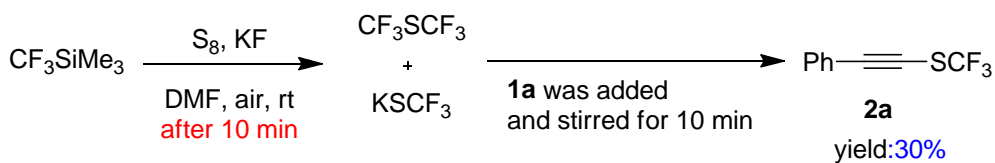
¹⁹F NMR spectrum (60 min):



KSCF₃ was decomposed completely

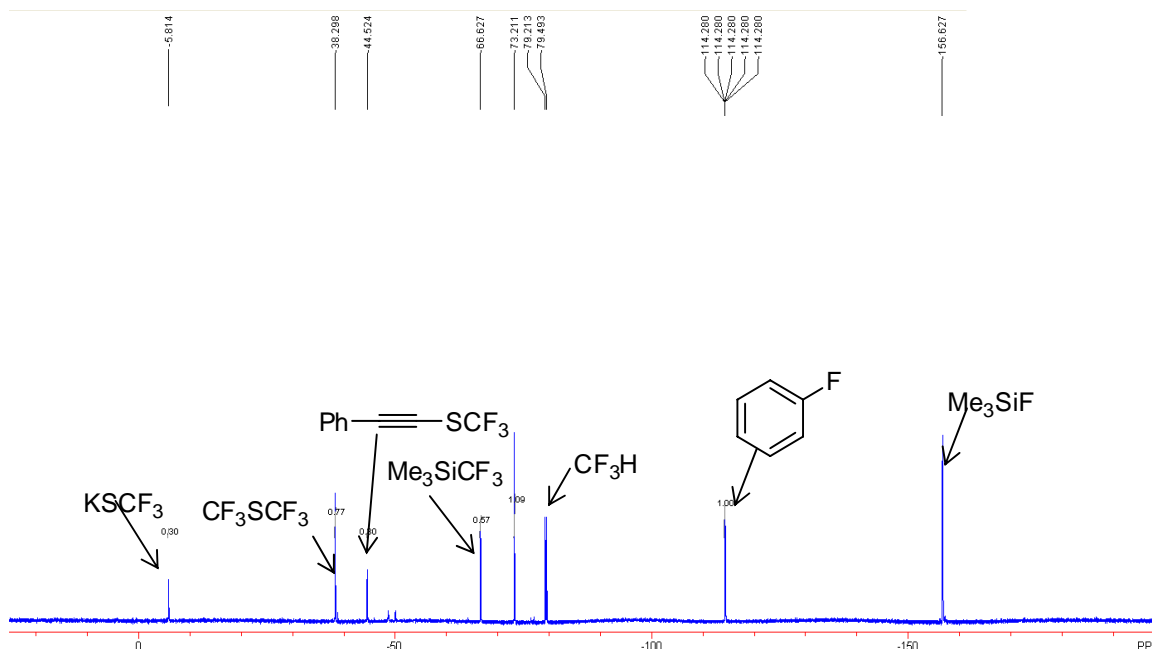


(1-b):

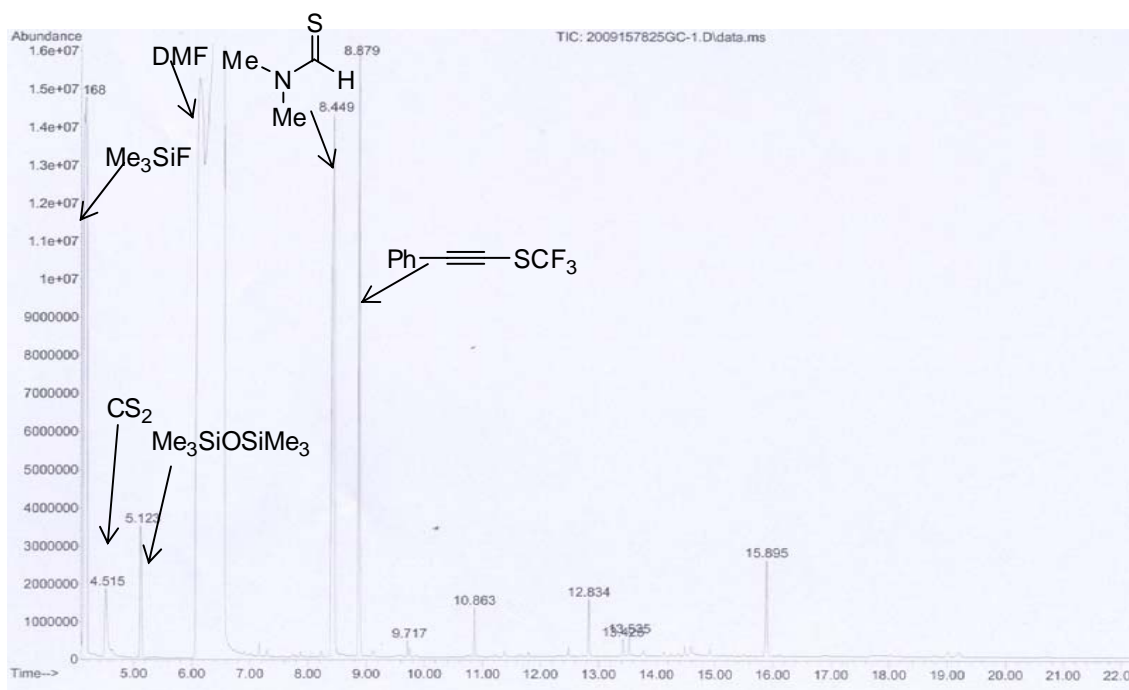


In a glove box, KF (0.4 mmol, 24mg) and S₈ (1.2 mmol, 39mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum and taken out. The vial was evacuated and then refilled with dry air for three times. DMF (4.5 mL) and fluorobenzene (0.6 mmol, 56μL) were added and the mixture was stirred at room temperature for 30 min. CF₃SiMe₃ (1.0 mmol, 0.15mL) was then added to the mixture. The resulting reaction mixture was stirred at room temperature for 10 min. Terminal alkyne **1a** was then added, and the reaction mixture was stirred at room temperature for another 10 min. This sample was then analyzed by GC and ¹⁹F NMR, and the yield was determined by ¹⁹F NMR.

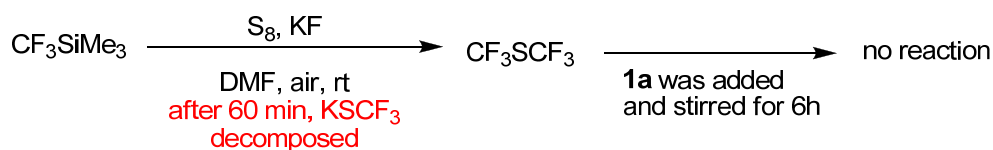
¹⁹F NMR spectrum:



GC-MS analysis:

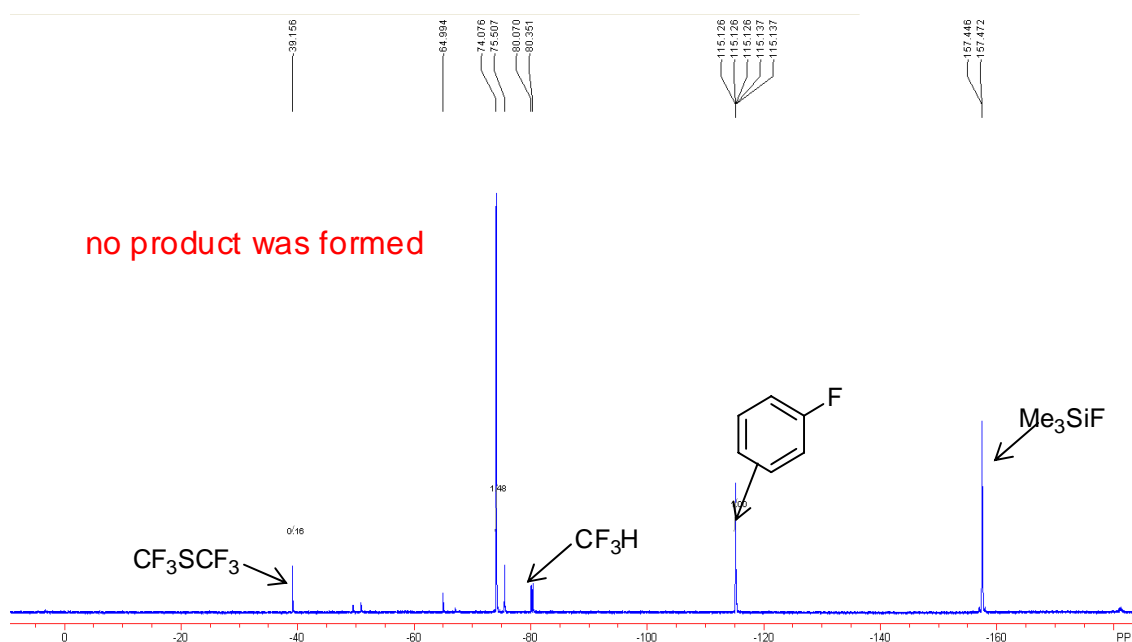


(1-c):

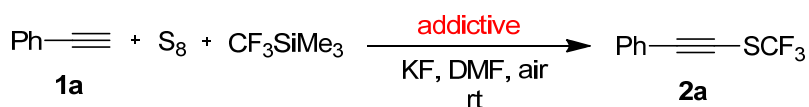


In a glove box, KF (0.4 mmol, 24mg) and S₈ (1.2 mmol, 39mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum and taken out. The vial was evacuated and then refilled with dry air for three times. DMF (4.5 mL) and fluorobenzene (0.6 mmol, 56μL) were added and the mixture was stirred at room temperature for 30 min. CF₃SiMe₃ (1.0 mmol, 0.15mL) was then added to the mixture. The resulting reaction mixture was stirred at room temperature for 60 min. Terminal alkyne **1a** was then added, and the reaction mixture was stirred at room temperature for another 6h. This sample was then analyzed by GC and ¹⁹F NMR, and the yield was determined by ¹⁹F NMR.

¹⁹F NMR spectrum:



2. Radical inhibition experiments



entry	additive	yield of 2a (%)
1	TEMPO (3 equiv)	79
2	Hydroquinone (20 mol %)	79
3	1,4-Dinitrobenzene (20 mol %)	73

In a glove box, KF (0.4 mmol, 24mg), S₈ (1.2 mmol, 39mg), and TEMPO (0.6 mmol, 97mg) or hydroquinone (0.04mmol, 4.5mg) or 1, 1-dibenzenethene (0.04 mmol, 6.8mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum and taken out. The vial was evacuated and then refilled with dry air for three times. DMF (4.5 mL) was added and the mixture was stirred at room temperature for 30 min. Terminal alkyne **1a** (0.2 mmol, , 24μl) was then added to the mixture, followed by addition of CF₃SiMe₃ (1.0 mmol, 0.15mL). The resulting reaction mixture was stirred at room temperature for 6h. This sample was then analyzed by GC

and ^{19}F NMR, and the yield was determined by ^{19}F NMR. Fluorobenzene (0.6 mmol, 56 μL) was added as an internal standard. The sample was analyzed by ^{19}F NMR, and the yield was determined by ^{19}F NMR.

