Supporting Information

Thioether-Functionalized Trifluoromethyl-alkynes, 1, 3-Dienes and Allenes: Divergent Synthesis from Reaction of 2-Trifluoromethyl-1, 3-Conjugated Enynes with Sulfur Nucleophiles

Huayu Cheng, Xiaofan Zhou, Anjing Hu, Shiteng Ding, Yimo Wang, Yuanjing Xiao* and Junliang Zhang*

Department of Chemistry, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200241, P. R. China, Fax: (+86)-21-54345471

E-mail: yjxiao@chem.ecnu.edu.cn, jlzhang@chem.ecnu.edu.cn
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1. General information.

$^1$H NMR spectra, $^{13}$C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl$_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out under an atmosphere of Argon in flame-dried glassware with magnetic stirring, CH$_2$Cl$_2$ (DCM), CH$_3$CN, DMSO, DMF, chlorobenzene were freshly distilled from CaH$_2$; Et$_2$O, MTBE (methyl tert-butyl ether), toluene and THF was freshly distilled from sodium metal prior to use. Chloroform (CHCl$_3$) was freshly distilled from phosphorous pentoxide (P$_2$O$_5$) prior to use. 2- trifluoromethyl 1,3-enynes 1 and 2-methyl 1,3-enynes 1z were prepared in good yields according to the literature.$^{[1]}$
2. Table S1. Screening results of reaction conditions.\[a\]

![Diagram of reaction](image)

| Entry | Base (equiv) | Solvent | 2a (equiv) | 3aa [%]<sup>b</sup> | 4aa [%]<sup>b</sup> | 5aa [%]<sup>b</sup> |
|-------|-------------|---------|------------|-------------------|-----------------|-----------------|
| 1     | --          | Toluene | 1.5        | -                 | -               | -               |
| 2     | Et<sub>3</sub>N(0.5) | Toluene | 1.5        | 70                | 13              | 5               |
| 3     | Et<sub>3</sub>N(2.0) | Toluene | 1.5        | 75                | 11              | 7               |
| 4     | Et<sub>3</sub>N(2.0) | Toluene | 3.0        | 77                | 8               | 5               |
| 5     | Et<sub>3</sub>N(2.0) | ether   | 1.5        | 82(77)            | 8               | 3               |
| 6     | Et<sub>3</sub>N(1.0) | ether   | 1.5        | 78                | 9               | 10              |
| 7     | TMG(2.0)    | ether   | 1.5        | 15                | 48              | 8               |
| 8     | DBU(2.0)    | ether   | 1.5        | 29                | 62              | 10              |
| 9     | DIEA(2.0)   | ether   | 1.5        | 39                | 21              | 6               |
| 10    | DMAP(2.0)   | ether   | 1.5        | 74                | 22              | 1               |
| 11    | BDMA(2.0)   | ether   | 1.5        | 35                | 1               | 17              |
| 12    | “Bu<sub>4</sub>N(2.0) | ether | 1.5        | 34                | 1               | 7               |
| 13    | Et<sub>3</sub>N(2.0) | DCM   | 1.5        | 43                | 16              | 8               |
| 14    | Et<sub>3</sub>N(2.0) | THF   | 1.5        | 64                | 21              | 5               |
| 15    | Et<sub>3</sub>N(2.0) | MeCN  | 1.5        | 21                | 45              | 7               |
| 16    | Et<sub>3</sub>N(2.0) | DMF   | 1.5        | 13                | 61              | 3               |
| 17    | Et<sub>3</sub>N(2.0) | DMSO  | 1.5        | 12                | 72              | 3               |
| 18    | Et<sub>3</sub>N(2.0) | MeOH  | 1.5        | 30                | 54              | 11              |
| 19    | Et<sub>3</sub>N(2.0) | EtOH  | 1.5        | 20                | 66              | 1               |
| 20    | Et<sub>3</sub>N(2.0) | DMSO  | 1.2        | 5                 | 77              | 1               |
We initiated this project using enyne 1a and 4-methyl-thiophenol 2a as model substrates for screening reaction conditions. Under base free conditions, no reaction occurred (Table 1 entry 1), the result prompted us to test base as additives. Considering that the replacement of the alkaline metal ion with ammonium cation formed by deprotonation of hydrosulfuryl of thiophenol will weaken the metalfluorine interaction, thus suppress the defluorination process, we choose organic base such as tertiary amine for reaction screening. A series of commonly used tertiary amine such as Et₃N, nBu₄N, DBU, DIEA, and DMAP at room temperatures in various solvents were investigated. Nucleophilic addition pattern relied heavily on the solvent and base used. The combination of Et₃N as base and ether as solvent was found to be the optimal reaction conditions for 1,2–nucleophilic addition pattern, and functionalized alkyne 3aa could be obtained in 77% isolated yield (Table 1 entry 5). Interestingly, simply use DMSO instead of ether as solvent invert the regioselectivity to 3,4–nucleophilic addition pattern, and functionalized 1,3-diene 4aa could be obtained in 80% isolated yield (Table 1 entry 21).
3. General procedure for the synthesis of thioether-functionalized trifluoromethyl-alkynes 3

To the solution of 2-trifluoromethyl 1,3-conjugated enynes 1 (1.0 mmol), thiophenol 2 (1.5 mmol) in toluene (5.0 mL) under nitrogen at room temperature was added Et$_3$N (2.0 mmol), the reaction was stirred at room temperature for 24 h. After 1 was completely consumed, which was determined by TLC analysis, the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 1:0~5:1) to give the desired 3.

77% isolated yield. Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.48 – 7.25 (m, 5H), 7.37 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 3.56 – 3.39 (m, 1H), 3.33 (dd, J = 13.4, 4.0 Hz, 1H), 3.12 (dd, J = 13.3, 10.5 Hz, 1H), 2.32 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.65, 131.95, 131.70, 130.44, 130.02, 128.69, 128.20, 124.57 (q, J = 280.9 Hz), 122.05, 85.66, 81.02 (d, J = 3.3 Hz), 39.24 (q, J = 30.0 Hz), 34.16, 21.03. $^{19}$F NMR (283 MHz, CDCl$_3$) δ -70.59. MS (70 eV): m/z (%): 320 (M$^+$, 45.55), 137 (100). HRMS(EI) calcd for C$_{18}$H$_{15}$F$_3$S : 320.0847, found: 320.0842.
75\% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 – 7.34 (m, 4H), 7.11 (d, $J = 7.9$ Hz, 2H), 6.98 (t, $J = 8.7$ Hz, 2H), 3.51 – 3.39 (m, 1H), 3.32 (dd, $J = 13.4$, 4.0 Hz, 1H), 3.11 (dd, $J = 13.4$, 10.5 Hz, 1H), 2.31 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.73 (d, $J = 250.0$ Hz), 137.66, 133.90 (d, $J = 8.4$ Hz), 131.65, 130.42, 130.02, 124.52 (q, $J = 280.8$ Hz), 118.12 (d, $J = 3.5$ Hz), 115.50 (d, $J = 22.1$ Hz), 84.63, 80.79 (d, $J = 2.1$ Hz), 39.25 (q, $J = 30.1$ Hz), 34.06, 21.00. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.60, -110.11. MS (70 eV): m/z (%): 338 (M$^+$, 36.12), 141 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$F$_4$S: 338.0752, found: 338.0750.

57\% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 7.8$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 3.50 – 3.41 (m, 1H), 3.32 (dd, $J = 13.4$, 3.6 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.31 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.68, 134.79, 133.16, 131.65, 130.35, 130.02, 128.54, 124.46 (q, $J = 280.9$ Hz), 120.50, 84.58, 82.06 (q, $J = 6.3$, 3.0 Hz), 39.31 (q, $J = 30.0$ Hz), 34.00, 21.00. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.52. MS (70 eV): m/z (%): 354 (M$^+$, 25.12), 137 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$F$_3$ClS: 354.0457, found: 354.0458.
89% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 3.50-3.40 (m, 1H), 3.32 (dd, $J = 13.5$, 3.9 Hz, 1H), 3.11 (dd, $J = 13.4$, 10.5 Hz, 1H), 2.29 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.63, 133.33, 131.61, 131.44, 130.35, 130.00, 124.42 (q, $J = 280.9$ Hz), 123.02, 120.93, 84.63, 82.24 (q, $J = 3.2$ Hz), 39.33 (q, $J = 30.0$ Hz), 33.93, 20.97. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.45. MS (70 eV): m/z (%): 398 (M$^+$, 52.65), 137 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$F$_3$BrS: 397.9952, found: 397.9962.

This compound has the same polarity as corresponding allene and can’t be separated with each other, we can’t get it’s pure spectrum.

33% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.58 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 3.52 – 3.42 (m, 1H), 3.34 (dd, $J = 13.5$, 4.0 Hz, 1H), 3.13 (dd, $J = 13.4$, 10.5 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 155.44, 137.72, 136.64, 132.04, 131.72, 130.37, 130.05, 125.79, 124.50 (q, $J = 280.8$ Hz), 122.86, 85.30, 82.41 (q, $J = 2.7$ Hz), 39.34 (q, $J = 30.2$ Hz), 34.10, 21.06, 11.85. $^{19}$F NMR (471 MHz, CDCl$_3$) δ
-70.54. MS (70 eV): m/z (%): 362 (M⁺, 27.84), 43 (100). HRMS(EI) calcd for C_{20}H_{17}NOF_{3}S: 362.0952, found: 362.0938.

53% isolated yield. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H), 3.57-3.47 (m, 1H), 3.34 (dd, J = 13.5, 4.0 Hz, 1H), 3.13 (dd, J = 13.5, 10.5 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.39, 137.77, 131.88, 131.72, 130.24, 130.05, 130.00, 129.34, 126.64, 124.39 (q, J = 280.9 Hz), 84.90, 84.01 (q, J = 3.3 Hz), 52.23, 39.40 (q, J = 30.1 Hz), 33.96, 21.03. ¹⁹F NMR (471 MHz, CDCl₃) δ -70.47. MS (70 eV): m/z (%): 378 (M⁺, 19.72), 191 (100). HRMS(EI) calcd for C_{20}H_{17}NO_{2}F_{3}S: 378.0901, found: 378.0899.

61% isolated yield. Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.55 – 6.50 (m, 1H), 3.82 – 3.71 (m, 2H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ -62.20. ¹⁹F NMR (282 MHz, CDCl₃) δ -62.00. MS (70 eV): m/z (%): 365 (M⁺, 100), 365 (100). HRMS(EI) calcd for C_{18}H_{14}NO_{2}F_{3}S: 365.0697, found: 365.0698.
66% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.37 (d, $J$ = 7.8 Hz, 2H), 7.31 (d, $J$ = 7.8 Hz, 2H), 7.12 (d, $J$ = 7.8 Hz, 2H), 7.11 (d, $J$ = 7.8 Hz, 2H), 3.50 - 3.39 (m, 1H), 3.33 (dd, $J$ = 13.3, 3.6 Hz, 1H), 3.11 (dd, $J$ = 12.9, 10.8 Hz, 1H), 2.34 (d, $J$ = 11.6 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.85, 137.61, 131.84, 131.68, 130.52, 130.01, 128.96, 124.61 (q, $J$ = 281.0 Hz), 118.99, 85.78, 80.29 (q, $J$ = 3.3 Hz), 39.22 (q, $J$ = 30.1 Hz), 34.23, 21.48, 21.05. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.65. MS (70 eV): m/z (%): 334 (M$^+$, 34.37), 137 (100). HRMS(EI) calcd for C$_{19}$H$_{17}$F$_3$S : 334.1003, found: 334.0999.

53% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ7.37 (d, $J$ = 7.7 Hz, 2H), 7.35 (d, $J$ = 8.3 Hz, 2H), 7.12 (d, $J$ = 7.7 Hz, 2H), 6.82 (d, $J$ = 8.3 Hz, 2H), 3.79 (s, 3H), 3.52 – 3.39 (m, 1H), 3.32 (dd, $J$ = 13.4, 3.5 Hz, 1H), 3.16 – 3.02 (m, 1H), 2.32 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.88, 137.56, 133.41, 131.61, 130.56, 129.99, 124.64 (q, $J$ = 280.8 Hz), 114.13, 113.82, 85.58, 79.58 (q, $J$ = 3.2 Hz), 55.24, 39.21 (q, $J$ = 29.9 Hz), 34.23, 21.02. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.65. MS (70 eV): m/z (%): 350 (M$^+$,18.47), 137 (100). HRMS(EI) calcd for C$_{19}$H$_{17}$F$_3$OS : 350.0952, found: 350.0948.
70% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.49 – 7.38 (m, 4H), 7.30 (dd, $J = 14.3$, 6.9 Hz, 3H), 6.99 (t, $J = 8.5$ Hz, 2H), 3.45 (d, $J = 1.4$ Hz, 1H), 3.30 (dd, $J = 13.4$, 2.5 Hz, 1H), 3.11 (dd, $J = 12.4$, 11.3 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.48 (d, $J = 248.2$ Hz), 134.01 (d, $J = 8.2$ Hz), 131.90 (s), 129.21, 128.80, 128.25, 124.50 (q, $J = 280.8$ Hz), 121.90, 116.36 (d, $J = 21.9$ Hz), 85.91, 80.78 (q, $J = 2.7$ Hz), 39.28 (q, $J = 30.1$ Hz), 34.62. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.55, -113.48. MS (70 eV): m/z (%): 324 (M$^+$,45.92), 141 (100). HRMS(EI) calcd for C$_{17}$H$_{12}$F$_4$S : 324.0596, found: 324.0593.

80% isolated yield. Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.2$ Hz, 4H), 7.39 – 7.27 (m, 5H), 3.57 – 3.46 (m, 1H), 3.38 (dd, $J = 13.5$, 4.0 Hz, 1H), 3.20 (dd, $J = 13.4$, 10.5 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 133.48, 132.87, 132.22, 131.90, 129.37, 128.83, 128.26, 124.43 (q, $J = 280.9$ Hz), 121.81, 85.99, 80.63 (q, $J = 3.2$ Hz), 39.33 (q, $J = 30.2$ Hz), 33.70. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.60. MS (70 eV): m/z (%): 340 (M$^+$,31.44), 157 (100). HRMS(EI) calcd for C$_{17}$H$_{12}$F$_3$ClS : 340.0300, found: 340.0298.
Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 7.5$ Hz, 2H), 7.35-7.27 (m, 5H), 3.54 – 3.45 (m, 1H), 3.35 (dd, $J = 13.5$, 3.8 Hz, 1H), 3.17 (dd, $J = 13.2$, 10.6 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 133.59, 132.30, 132.29, 131.90, 128.83, 128.26, 124.42 (q, $J = 280.9$ Hz), 121.78, 121.37, 86.01, 80.60 (q, $J = 3.2$ Hz), 39.34 (q, $J = 30.2$ Hz), 33.49. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.60. MS (70 eV): m/z (%): 384 (M$^+$, 64.44), 128 (100). HRMS(EI) calcd for C$_{17}$H$_{12}$F$_3$BrS : 383.9795, found: 383.9792.

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.8$ Hz, 2H), 7.47 – 7.42 (m, 2H), 7.33 – 7.29 (m, 3H), 6.85 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 3.46-3.37 (m, 1H), 3.26 (dd, $J = 13.4$, 4.0 Hz, 1H), 3.05 (dd, $J = 13.4$, 10.5 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.77, 134.72, 131.95, 128.69, 128.22, 124.59 (q, $J = 280.9$ Hz), 124.21, 122.09, 114.86, 85.66, 81.10 (q, $J = 3.2$ Hz), 55.29, 39.22 (q, $J = 30.0$ Hz), 35.26. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -70.52. MS (70 eV): m/z (%): 336 (M$^+$, 67.43), 153 (100). HRMS(EI) calcd for C$_{17}$H$_{12}$F$_3$S : 336.0796, found: 336.0792.

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69% isolated yield. Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.5$ Hz, 2H), 7.35 – 7.27 (m, 5H), 6.61 (d, $J = 8.5$ Hz, 2H), 3.75 (s, 2H), 3.48 – 3.33 (m, 1H), 3.20 (dd, $J = 13.3$, 4.0 Hz, 1H), 2.99 (dd, $J = 13.2$, 10.6 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.91, 135.28, 131.96, 128.64, 128.22, 124.65 (q, $J = 280.8$ Hz), 122.16, 120.82, 115.66, 85.49, 81.30 (q, $J = 3.2$ Hz), 39.02 (q, $J = 29.8$ Hz), 35.68. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -70.44. HRMS(ESI) calcd for C$_{17}$H$_{15}$F$_3$SN [M+H$^+$]: 322.0872, found: 322.0878.

4. General procedure for the synthesis of products 4

To the solution of 2-trifluoromethyl 1,3-conjugated enynes 1 (1.0 mmol), thiophenol 2 (1.1 mmol) in DMSO (5.0 mL) under nitrogen at room temperature was added Et$_3$N (2.0 mmol), the reaction was stirred at room temperature for 24 h. After 1 was completely consumed, which was determined by TLC analysis, water (15 mL) was added to reaction mixture and extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography on silica gel (petroleum ether: ethyl acetate = 1:0~5:1) to give the desired 4.
80% isolated yield. Colorless solid. Mp 38.5-40.6 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 – 7.21 (m, 7H), 7.17 (d, $J$ = 8.1 Hz, 2H), 6.91-6.96 (m, 1H), 5.78 (s, 1H), 5.36 (s, 1H), 2.37 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.48, 135.55, 135.45, 135.02 (q, $J$ = 31.9 Hz), 133.62, 130.45, 129.91, 128.87, 128.70, 128.30, 127.85, 125.42 (q, $J$ = 4.4 Hz), 122.43 (q, $J$ = 275.7 Hz), 21.18. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -63.92. MS (70 eV): m/z (%): 320 (M$^+$, 100), 320 (100). HRMS(EI) calcd for C$_{18}$H$_{15}$F$_3$S : 320.0847, found: 320.0848.

77% isolated yield. Colorless solid. Mp 31.9-34.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (d, $J$ = 8.0 Hz, 2H), 7.26 (dd, $J$ = 8.6, 5.5 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 6.92 (dd, $J$ = 8.7 Hz, 5.5 Hz, 2H), 6.84 (s, 1H), 5.75 (s, 1H), 5.32 (s, 1H), 2.31 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.17 (d, $J$ = 248.5 Hz), 138.60, 134.91 (q, $J$ = 31.6 Hz), 134.03, 133.69, 131.61 (d, $J$ = 3.4 Hz), 130.42, 130.35, 129.94, 128.67, 125.57 (q, $J$ = 4.7 Hz), 122.38 (q, 275.5 Hz), 115.28 (d, $J$ = 21.5 Hz), 21.10. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.88, -113.02. MS (70 eV): m/z (%): 338(M$^+$, 100), 137 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$Fs : 338.0752, found: 338.0753.
77% isolated yield. Colorless solid. Mp 41.7-43.8 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, $J$ = 8.0 Hz, 2H), 7.27 – 7.19 (m, 4H), 7.16 (d, $J$ = 7.7 Hz, 2H), 6.77 (s, 1H), 5.79 (s, 1H), 5.36 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.78, 134.86 (q, $J$ = 31.6 Hz), 133.94, 133.89, 133.54, 133.16, 131.63, 129.99, 129.84, 128.49, 128.38, 125.75 (q, $J$ = 4.7 Hz), 122.30 (q, $J$ = 275.6 Hz), 21.17. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.98. MS (70 eV): m/z (%): 354(M$^+$, 100). HRMS(EI) calcd for C$_{18}$H$_{14}$F$_3$ClS : 354.0457, found: 354.0458.

94% isolated yield. Colorless solid. Mp 44.5-45.8 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39 (t, $J$ = 8.5 Hz, 2H), 7.40(t, $J$ = 8.5 Hz, 2H), 7.18 (d, $J$ = 7.6 Hz, 4H), 6.77 (s, 1H), 5.82 (s, 1H), 5.39 (s, 1H), 2.37 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.80, 134.85 (q, $J$ = 31.6 Hz), 134.39, 133.93, 133.07, 131.83, 131.44, 130.11, 130.00, 128.32, 125.77 (q, $J$ = 4.7 Hz), 122.27 (q, $J$ = 275.6 Hz), 121.76), 21.18. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.89. MS (70 eV): m/z (%): 398(M$^+$, 97.08), 400 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$F$_3$BrS : 397.9952, found: 397.9949.
91% isolated yield. *E/Z* = 2.8:1

Major isomer. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H), 7.15(d, $J = 8.0$ Hz, 2H), 7.16 (s, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 5.97 (s, 1H), 5.91 (s, 1H), 2.31 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 139.98 (s), 137.33, 136.53 (q, $J = 29.8$ Hz), 134.99, 131.66, 131.63, 130.20, 130.04, 129.84, 129.28, 124.93 (q, $J = 5.2$ Hz), 122.51 (q, $J = 275.1$ Hz), 118.52, 111.36, 20.84. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.50. MS (70 eV): m/z (%): 345 (M$^+$, 100). HRMS(EI) calcd for C$_{19}$H$_{14}$NF$_3$S: 345.0799, found: 345.0793.

Minor isomer. Colorless solid. Mp 82.3-84.1 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.58 (s, 1H), 5.89 (s, 1H), 5.48 (s, 1H), 2.37 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 140.03, 139.50, 135.85, 134.78 (q, $J = 32.1$ Hz), 134.56, 131.99, 130.23, 129.82, 128.90, 127.34, 126.47 (q, $J = 4.8$ Hz), 122.09 (q, $J = 275.5$ Hz), 118.66, 110.71, 21.22. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -64.09. MS (70 eV): m/z (%): 345 (M$^+$, 100). HRMS(EI) calcd for C$_{19}$H$_{14}$NF$_3$S: 345.0799, found: 345.0793.

89% isolated yield. *E/Z* = 1.8:1

Major isomer. Colorless solid. Mp 53.3-55.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.24 (s, 1H), 7.18 (d, $J = 8.2$ Hz, 2H),
7.10 (d, J = 8.2 Hz, 2H), 5.98 (d, J = 1.8 Hz, 1H), 5.91 (s, 1H), 2.61 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 197.21, 140.16, 137.06, 136.78 (q, J = 29.7 Hz), 136.28, 136.27, 136.26, 130.35, 130.03, 129.80, 129.74, 129.74, 124.52 (q, J = 5.2 Hz), 122.65 (q, J = 275.2 Hz), 26.42, 20.87. 

Minor isomer. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 5.84 (s, 1H), 5.43 (s, 1H), 2.56 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 197.39, 140.18, 139.17, 135.79, 134.97 (q, J = 31.9 Hz), 134.26, 131.81, 130.13, 128.62, 128.34, 127.88, 126.12 (q, J = 4.9 Hz), 122.22 (q, J = 275.4 Hz), 26.53, 21.24. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -64.01. MS (70 eV): m/z (%): 362 (M$^+$, 100). HRMS(EI) calcd for C$_{20}$H$_{17}$OF$_3$S: 362.0952, found: 362.0949.

84% isolated yield. E/Z =1.2:1

Major isomer. Colorless solid. Mp 54.6-56.0 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.02 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.19 (s, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 5.93 (d, J = 1.5 Hz, 1H), 5.87 (s, 1H), 3.90 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.61, 140.11, 137.08, 136.89 (q, J =29.7 Hz), 136.48 (d, J = 1.1 Hz), 130.23, 130.07, 129.95, 129.86, 129.61, 129.56, 129.31, 124.51 (q, J = 5.2 Hz), 122.73 (q, J = 275.2 Hz), 52.09, 20.98. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.47. MS (70 eV): m/z (%): 378 (M$^+$, 100). HRMS(EI) calcd for C$_{20}$H$_{17}$NO$_2$F$_3$S: 378.0901, found: 378.0904.

Minor isomer. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.94 (d, J = 8.5 Hz, 2H),
7.39 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.75 (s, 1H), 5.84 (d, J = 1.2 Hz, 1H), 5.44 (d, J = 1.1 Hz, 1H), 3.89 (s, 3H), 2.36 (s, 3H). 1H NMR (500 MHz, CDCl₃) δ = 8.20 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.17 (s, 1H), 7.08 (d, J = 7.8 Hz, 2H), 5.96 (d, J = 1.5 Hz, 1H), 5.92 (s, 1H), 2.30 (s, 3H). 13C NMR (125 MHz, CDCl₃) δ 146.99, 142.10, 137.59, 136.61 (q, J = 29.7 Hz), 134.54, 132.54, 130.43, 130.39, 130.36, 130.00, 129.27, 125.26 (q, J = 4.5 Hz), 123.34, 122.59 (q, J = 275.4 Hz), 21.02. 19F NMR (471 MHz, CDCl₃) δ -63.59. MS (70 eV): m/z (%): 365 (M⁺, 100). HRMS(EI) calcd for C₂₀H₁₇NO₂F₃S : 378.0901, found: 378.0898.

94% isolated yield. E/Z = 4:1

Major isomer. Colorless solid. Mp 30.3-32.2 °C. 1H NMR (500 MHz, CDCl₃) δ 8.20 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.17 (s, 1H), 7.08 (d, J = 7.8 Hz, 2H), 5.96 (d, J = 1.5 Hz, 1H), 5.92 (s, 1H), 2.30 (s, 3H). 13C NMR (125 MHz, CDCl₃) δ 146.99, 142.10, 137.59, 136.61 (q, J = 29.7 Hz), 134.54, 132.54, 130.43, 130.39, 130.36, 130.00, 129.27, 125.26 (q, J = 4.5 Hz), 123.34, 122.59 (q, J = 275.4 Hz), 21.02. 19F NMR (471 MHz, CDCl₃) δ -63.59. MS (70 eV): m/z (%): 365 (M⁺, 100). HRMS(EI) calcd for C₁₈H₁₄NO₂F₃S : 365.0697, found: 365.0695.

Minor isomer. Colorless solid. Mp 41.8-43.6 °C. 1H NMR (500 MHz, CDCl₃) δ 8.10 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.57 (s, 1H), 5.93 (s, 1H), 5.53 (s, 1H), 2.38 (s, 3H). 13C NMR (125 MHz, CDCl₃) δ 146.50, 142.09, 139.73, 136.95, 135.13 (q, J = 32.3 Hz), 134.76, 130.35, 129.01, 128.81, 127.16, 126.71 (q, J = 4.7 Hz), 123.60, 122.09 (q, J = 275.5 Hz), 21.29. 19F NMR (471 MHz, CDCl₃) δ -64.14. MS (70 eV): m/z (%): 365 (M⁺, 100). HRMS(EI) calcd for C₁₈H₁₄NO₂F₃S : 365.0697, found: 365.0699.
80% isolated yield. Colorless solid. Mp 53.4-55.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.92 (s, 1H), 5.71 (s, 1H), 5.29 (s, 1H), 2.29 (d, $J = 11.4$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.25, 137.92, 136.25, 135.12 (q, $J = 31.4$ Hz), 133.36, 132.56, 129.82, 129.16, 129.02, 129.00, 128.67, 125.12 (q, $J = 4.7$ Hz), 122.48 (q, $J = 275.7$ Hz), 21.13, 21.09. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.72. MS (70 eV): m/z (%): 334 (M$^+$, 100), 137 (100). HRMS (EI) calcd for C$_{19}$H$_{17}$F$_3$S : 334.1003, found: 334.1000.

89% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (d, $J = 7.4$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.5$ Hz, 2H), 6.96 (s, 1H), 6.82 (d, $J = 8.0$ Hz, 2H), 5.75 (s, 1H), 5.31 (s, 1H), 3.80 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.37, 138.13, 136.49, 135.17 (q, $J = 31.0$ Hz), 133.17, 130.21, 129.79, 129.40, 128.02, 127.31, 124.98 (q, $J = 4.8$ Hz), 122.49 (q, $J = 275.4$ Hz), 113.74, 55.21, 21.16. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.88. MS (70 eV): m/z (%): 350 (M$^+$, 96.43), 137 (100). HRMS (EI) calcd for C$_{19}$H$_{17}$F$_3$OS : 350.0952, found: 350.0947.
86% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 (dd, $J$ = 7.9, 5.7 Hz, 2H), 7.39-7.24 (m, 5 H), 7.07 (t, $J$ = 8.5 Hz, 2H), 6.99 (s, 1H), 5.79 (s, 1H), 5.33 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.86 (d, $J$ = 249.0 Hz), 136.35, 135.67 (d, $J$ = 8.4 Hz), 135.18, 134.85 (q, $J$ = 31.5 Hz), 130.00, 128.74, 128.36, 128.08, 127.71 (d, $J$ = 3.3 Hz), 125.54 (q, $J$ = 4.7 Hz), 122.36 (q, $J$ = 275.5 Hz), 116.25 (d, $J$ = 22.0 Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.85, -112.41. MS (70 eV): m/z (%): 324 (M$^+$, 92.23), 128 (100). HRMS (EI) calcd for C$_{17}$H$_{12}$F$_4$S: 324.0596, found: 324.0587.

85% isolated yield. Colorless solid. Mp 32.3-33.7 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, $J$ = 8.3 Hz, 2H), 7.27 - 7.36 (m, 7H), 7.07 (s, 1H), 5.79 (s, 1H), 5.35 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 137.81, 135.07, 134.73 (q, $J$ = 31.5 Hz), 134.33, 134.25, 131.30, 129.26, 129.12, 128.81, 128.41, 128.24, 125.66 (q, $J$ = 4.8 Hz), 122.31 (q, $J$ = 275.6 Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.87. MS (70 eV): m/z (%): 340 (M$^+$, 94.58), 128 (100). HRMS (EI) calcd for C$_{17}$H$_{12}$F$_3$ClS: 340.0300, found: 340.0294.
94% isolated yield. Colorless solid. Mp 34.5-36.8 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 (d, $J = 8.1$ Hz, 2H), 7.40 – 7.24 (m, 7H), 7.09 (s, 1H), 5.79 (s, 1H), 5.36 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 138.10, 135.00, 134.64 (d, $J = 31.5$ Hz), 134.31, 132.15, 132.00, 128.82, 128.79, 128.38, 128.24, 125.66 (q, $J = 4.8$ Hz), 122.35, 122.30 (q, $J = 275.7$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.88. MS (70 eV): m/z (%): 384 (M$^+$, 61.37), 128 (100). HRMS(EI) calcd for C$_{17}$H$_{12}$F$_3$BrS : 383.9795, found: 383.9789.

78% isolated yield. Colorless solid. Mp 32.8-34.7 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.5$ Hz, 2H), 7.38 – 7.21 (m, 5H), 6.92 (d, $J = 8.5$ Hz, 2H), 6.84 (s, 1H), 5.82 (s, 1H), 5.36 (s, 1H), 3.85 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 160.12, 135.99, 135.48, 135.09 (d, $J = 31.5$ Hz), 133.96, 131.29, 128.62, 128.26, 127.71, 125.44 (q, $J = 4.8$ Hz), 122.69, 122.41 (q, $J = 275.6$ Hz), 114.71, 55.27. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.94. MS (70 eV): m/z (%): 336 (M$^+$, 100), 336 (100). HRMS(EI) calcd for C$_{18}$H$_{15}$OF$_3$S : 336.0796, found: 336.0789.
65% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40-7.20 (m, 5H), 7.30 (d, $J$ = 7.5 Hz, 2H), 6.75 (s, 1H), 6.68 (d, $J$ = 7.9 Hz, 2H), 5.84 (s, 1H), 5.39 (s, 1H), 3.83 (brs, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.28, 136.34, 135.64, 135.19 (q, $J$ = 31.5 Hz), 132.45, 132.09, 128.52, 128.19, 125.48, 125.39 (q, $J$ = 4.8 Hz), 122.44 (q, $J$ = 275.5 Hz), 119.19, 115.52. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.84. HRMS(ESI) calcd for C$_{17}$H$_{15}$F$_3$SN [M+H$^+$]: 322.0872, found: 322.0873.

84% isolated yield. Colorless solid. Mp 53.8-55.7 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J$ = 8.9 Hz, 2H), 7.49 (d, $J$ = 8.9 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 7.34 (s, 1H), 5.84 (d, $J$ = 1.0 Hz, 1H), 5.51 (d, $J$ = 1.1 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.50, 143.40, 143.30, 134.49 (q, $J$ = 31.5 Hz), 134.45, 130.19, 128.97, 128.92, 128.56, 126.18 (q, $J$ = 4.8 Hz), 125.68, 123.93, 122.18 (q, $J$ = 275.5 Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.74. MS (70 eV): m/z (%): 351 (M$^+$, 54.70), 128 (100). HRMS(EI) calcd for C$_{17}$H$_{12}$NO$_2$F$_3$S: 351.0541, found: 351.0536.
5. Table S2. Screening results of reaction conditions.\textsuperscript{[a]}

\begin{table}
\centering
\begin{tabular}{cccc}
\hline
Entry & Solvent\textsuperscript{[c]} & Base & \(3\text{gh}[^{[b]}]\) & \(5\text{gh}[^{[b]}]\) \\
\hline
1 & MeOH & TMEDA & 33 & 59 \\
2 & Toluene & TMEDA & 69 & 22 \\
3 & CHCl\(_3\) & TMEDA & 65 & 29 \\
4 & MTBE & TMEDA & 53 & 27 \\
5 & DMSO & TMEDA & 52 & 47 \\
6 & DMSO/MeOH & TMEDA & 23 & 60 \\
7 & DMSO/CHCl\(_3\) & TMEDA & 19 & 80(75) \\
8 & DMSO/CHCl\(_3\) & Et\(_3\)N & 26 & 71 \\
9 & DMSO/CHCl\(_3\) & pyridine & 50 & 42 \\
10 & DMSO/CHCl\(_3\) & DMAP & 31 & 26 \\
11 & DMSO/CHCl\(_3\) & Diisopropylamine & 22 & 73 \\
12 & DMSO/CHCl\(_3\) & DIEA & 48 & 43 \\
13 & DMSO/CHCl\(_3\) & BDMA & 44 & 46 \\
14\textsuperscript{[d]} & DMSO/CHCl\(_3\) & TMEDA & 18 & 78 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{[a]} Reaction conditions: enyne \(1\text{g}\) (0.32 mmol), benzyl mercaptan \(2\text{h}\) (0.2 mmol) Slovent (2.0 mL), Base (10\% mol), RT, \(\text{N}_2\), 24 h; \textsuperscript{[b]} Determined by \(^{1}\text{H} \text{NMR}\) of the reaction mixture containing CH\(_2\)Br\(_2\) as an internal standard; \textsuperscript{[c]} co-solvent (\(v : v\) = 1:1); \textsuperscript{[d]} the reaction was carried out at 0\(^\circ\)C; DIEA= N,N-Diisopropylethylamine; DMAP: S23
6. General procedure for the synthesis of thioether-functionalized trifluoromethyl-allenes 5

To the solution of benzyl mercaptan 2 (1.0 mmol) in DMSO/CHCl₃ (V:V = 1:1, 5.0 mL) under nitrogen at room temperature was added TMEDA (0.1 mmol), then added 2-trifluoromethyl 1,3-conjugated enynes 1 (1.6 mmol), the reaction was stirred at room temperature for 4 h. After 2 was completely consumed, which was determined by TLC analysis, water (2.0 mL) was added and the reaction mixture was extracted with ethyl acetate (3x4.0 mL). The combined organic extracts were washed with brine (4.0 mL) and dried over MgSO₄. After filtration and evaporation, the residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 100:0~50:1) to give the desired 5.

75 % isolated yield. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.39 – 7.18 (m, 5H), 6.78 (q, J = 3.1 Hz, 1H), 3.95 (s, 3H), 3.77 (d, J = 13.5 Hz, 1H), 3.73 (d, J = 13.5 Hz, 1H), 3.32 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 206.05 (q, J = 3.7 Hz), 166.36, 137.09, 136.04, 130.15, 130.02, 128.78, 128.47, 127.37, 127.16, 122.73 (q, J = 275.3 Hz), 101.72, 101.14 (q, J = 33.8 Hz), 52.07, 35.99, 27.65. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.51. HRMS (ESI) calcd for C₂₀H₁₇F₃NaO₂S : 401.0794, found: 401.0810
52 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 – 7.03 (m, 9H), 6.70 (q, $J = 3.0$ Hz, 1H), 3.73 (d, $J = 13.5$ Hz, 1H), 3.69 (d, $J = 13.5$ Hz, 1H), 3.26 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.42 (q, $J = 3.6$ Hz), 137.23, 134.46, 129.89, 129.23, 128.87, 128.73, 128.56, 127.25, 122.86 (q, $J = 273.4$ Hz), 101.50, 100.97 (q, $J = 34.0$ Hz), 36.10, 27.79. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.71. MS (70 ev): m/z (%): 354 (M$^+$,0.17), 91(100). HRMS (EI) calcd for C$_{18}$H$_{14}$F$_3$ClS: 354.0457, found: 354.0459.

71 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.33 – 7.23 (m, 5H), 6.74 (q, $J = 2.8$ Hz, 1H), 3.76 (d, $J = 13.5$ Hz, 1H), 3.72 (d, $J = 13.5$ Hz, 1H), 3.30 (dd, $J = 2.3$, 0.8 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.13 (q, $J = 3.7$ Hz), 136.97, 136.25, 132.60, 128.73, 128.50, 127.91, 127.23, 122.55 (q, $J = 275.4$ Hz), 118.38, 111.87, 101.97 (q, $J = 34.2$ Hz), 101.37, 36.18, 27.58. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.57. HRMS (ESI) calcd for C$_{19}$H$_{14}$F$_3$NNaS: 368.0691, found: 368.0698.

63 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.34 – 7.24 (m, 5H), 6.79 (q, $J = 3.0$ Hz, 1H), 3.77 (d, $J = 13.5$ Hz, 1H), 3.72 (d, $J = 13.5$ Hz, 1H), 3.40 – 3.25 (m, 2H), 2.62 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.11 (d, $J = 3.9$ Hz), 197.11, 137.05, 136.76, 136.16, 128.91,
128.77, 128.46, 127.55, 127.16, 122.69 (d, J = 275.2 Hz), 101.65 , 101.14 (d, J = 33.8 Hz), 35.97, 27.59, 26.49. $^{19}$F NMR (500 MHz, CDCl$_3$) δ -62.51. HRMS (ESI) calcd for C$_{20}$H$_{17}$F$_3$NaOS: 385.0844, found: 385.0851

77 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.43 – 7.14 (m, 5H), 6.78 (q, J = 2.7 Hz, 1H), 3.76 (d, J = 13.5 Hz, 1H), 3.72 (d, J = 13.5 Hz, 1H), 3.31 (d, J = 1.5 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.50 (q, J = 3.7 Hz), 147.53, 138.28, 137.00, 128.80, 128.58, 128.09, 127.32, 124.25, 122.56 (q, J = 275.3 Hz), 102.18 (q, J = 34.4 Hz), 101.11, 36.28, 27.57. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.58. HRMS (ESI) calcd for C$_{18}$H$_{14}$F$_3$NNaO$_2$S: 388.0590, found: 388.0591.

80 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18-8.13 (m, 2H), 7.68-7.65 (m, 1H), 7.58-7.53 (m, 1H), 7.33 – 7.23 (m, 5H), 6.79 (q, J = 2.8 Hz, 1H), 3.77 (d, J = 13.5 Hz, 1H), 3.73 (d, J = 13.5 Hz, 1H), 3.37 – 3.22 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 205.69 (q, J = 3.8 Hz), 148.65, 137.03, 133.44, 133.00, 129.91, 128.81, 128.56, 127.28, 123.20, 122.57 (q, J = 275.3 Hz), 122.14, 102.27 (q, J = 34.2 Hz), 100.95, 36.21, 27.62. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.66. HRMS (ESI) calcd for C$_{18}$H$_{14}$F$_3$NNaO$_2$S: 388.0590, found: 388.0594.
56 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.35 – 7.22 (m, 5H), 6.77 (q, 2.7 Hz, 1H), 3.77 (d, $J = 13.5$ Hz, 1H), 3.73 (d, $J = 13.5$ Hz, 1H), 3.35 – 3.26 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.95 (q, $J = 3.8$ Hz), 137.16, 135.23, 130.52 (q, $J = 32.6$ Hz), 128.87, 128.60, 127.74, 127.31, 125.96 (q, $J = 3.8$ Hz), 123.89 (q, $J = 272.1$ Hz), 123.71 (q, $J = 275.1$ Hz), 101.67 (q, $J = 34.2$ Hz), 101.50, 36.22, 27.71. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.59, -62.61. MS(70 ev): m/z(%): 388(M$^+$,4.67),91(100). HRMS(EI) calcd for C$_{19}$H$_{14}$F$_6$S: 388.0720, found: 388.0718.

73 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.23 (d, $J = 8.8$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.80 (q, $J = 2.9$ Hz, 1H), 3.73 (d, $J = 13.5$ Hz, 1H), 3.69 (d, $J = 13.4$ Hz, 1H), 3.31 (d, $J = 2.5$ Hz, 2H), 2.33 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.48 (q, $J = 3.8$ Hz), 147.48, 138.30, 136.99, 133.84, 129.23, 128.67, 128.06, 124.20, 122.56 (q, $J = 275.3$ Hz), 102.19 (q, $J = 34.2$ Hz), 101.06, 35.92, 27.46, 20.98. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.58. HRMS (ESI) calcd for C$_{19}$H$_{16}$F$_3$NNaO$_2$S: 402.0746, found: 402.0748.
65 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, $J$ = 8.8 Hz, 2H), 7.47 (d, $J$ = 8.8 Hz, 2H), 7.38-7.34 (m, 1H), 7.32–7.28 (m, 1H), 7.24 – 7.17 (m, 2H), 6.80 (q, $J$ = 2.8 Hz, 1H), 3.88 (d, $J$ = 13.6 Hz, 1H), 3.83 (d, $J$ = 13.6 Hz, 1H), 3.42 – 3.36 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.45 (q, $J$ = 3.7 Hz), 147.47, 138.16, 134.92, 133.93, 130.56, 129.81, 128.72, 128.08, 126.86, 124.16, 122.52 (q, $J$ = 275.4 Hz), 102.19 (q, $J$ = 34.4 Hz), 101.28, 33.91, 28.09. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.60. HRMS(ESI) calcd for C$_{18}$H$_{13}$ClF$_3$NNaO$_2$S: 422.0200, found: 422.0201

63 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.25 (d, $J$ = 8.7 Hz, 2H), 7.49 (d, $J$ = 8.7 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 7.20 (d, $J$ = 8.4 Hz, 2H), 6.86 (q, $J$ = 2.8 Hz, 1H), 3.74 (d, $J$ = 13.7 Hz, 1H), 3.70 (d, $J$ = 13.7 Hz, 1H), 3.31 (d, $J$ = 1.3 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.49 (q, $J$ = 3.7 Hz), 147.62, 138.15, 135.57, 133.15, 130.12, 128.75, 128.10, 124.28, 122.52 (q, $J$ = 275.4 Hz), 102.07 (q, $J$ = 34.4 Hz), 101.17, 35.66, 27.64. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.71. HRMS (ESI) calcd for C$_{18}$H$_{13}$ClF$_3$NNaO$_2$S: 422.0200, found: 422.0206
80 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.23 (d, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 6.76 (q, $J = 2.7$ Hz, 1H), 3.70 (d, $J = 13.7$ Hz, 1H), 3.66 (d, $J = 13.7$ Hz, 1H), 3.28 (d, $J = 2.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.51 (q, $J = 3.6$ Hz), 147.67, 138.16, 136.11, 131.75, 130.49, 128.13, 124.32, 122.54 (q, $J = 273.6$ Hz), 121.27, 102.11 (q, $J = 34.5$ Hz), 101.20, 35.78, 27.67. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.53. HRMS(ESI) calcd for C$_{18}$H$_{13}$BrF$_3$NNaO$_2$S: 465.9695, found: 465.9695.

80 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.7$ Hz, 2H), 7.21 (dd, $J = 8.5$, 5.4 Hz, 2H), 6.97 (t, $J = 8.6$ Hz, 2H), 6.80 (q, $J = 2.7$ Hz, 1H), 3.73 (d, $J = 13.6$ Hz, 1H), 3.69 (d, $J = 13.6$ Hz, 1H), 3.29 (t, $J = 2.2$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.47 (q, $J = 3.7$ Hz), 161.92 (d, $J = 246.2$ Hz), 147.55, 138.18, 132.72 (d, $J = 3.3$ Hz), 130.38, 130.31, 128.08, 124.24, 122.52 (q, $J = 275.3$ Hz), 115.44 (d, $J = 21.4$ Hz), 102.06 (q, $J = 34.4$ Hz), 101.13, 35.50, 27.55. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.62, -114.83. HRMS(ESI) calcd for C$_{18}$H$_{13}$F$_4$NNaO$_2$S: 406.0495, found: 406.0499
81 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.21 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.8$ Hz, 2H), 7.16 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 6.79 (q, $J = 2.7$ Hz, 1H), 3.78 (s, 3H), 3.71 (d, $J = 13.4$ Hz, 1H), 3.67 (d, $J = 13.4$ Hz, 1H), 3.32 – 3.29 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.49 (q, $J = 3.7$ Hz), 158.79, 147.51, 138.29, 129.88, 128.85, 128.06, 124.20, 122.57 (q, $J = 275.3$ Hz), 113.93, 102.26 (q, $J = 34.2$ Hz), 101.05, 55.15, 35.69, 27.46. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.57. HRMS (ESI) calcd for C$_{19}$H$_{16}$F$_3$NaO$_3$S: 418.0695, found: 418.0698

81 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.79 (q, $J = 2.7$ Hz, 1H), 3.79 – 3.61 (m, 2H), 3.74 (d, $J = 13.4$ Hz, 1H), 3.70 (d, $J = 13.4$ Hz, 1H), 3.33 (d, $J = 1.7$ Hz, 2H), 1.31 (s, 9H). $^{13}$C NMR (125MHz, CDCl$_3$) $\delta$ 206.62 (q, $J = 3.8$ Hz), 150.39, 147.54, 138.34, 133.90, 128.48, 128.10, 125.52, 124.26, 122.59 (q, $J = 275.3$ Hz), 102.28 (q, $J = 34.2$ Hz), 101.09, 35.87, 34.45, 31.24, 27.68. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.57. HRMS(ESI) calcd for C$_{22}$H$_{22}$F$_3$NaO$_2$S: 444.1216, found: 444.1226
81 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J$ = 8.7 Hz, 2H), 7.50 (d, $J$ = 8.7 Hz, 2H), 6.84 (s, 2H), 6.82 (q, $J$ = 2.9 Hz, 1H), 3.84 (d, $J$ = 11.4 Hz, 1H), 3.81 (d, $J$ = 11.4 Hz, 1H), 3.52 (t, $J$ = 2.5 Hz, 2H), 2.35 (s, 6H), 2.26 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.44 (q, $J$ = 3.6 Hz), 147.53, 138.27, 136.91, 136.90, 129.75, 129.05, 128.07, 124.20, 122.63 (q, $J$ = 275.5 Hz), 102.64 (q, $J$ = 34.0 Hz), 101.19, 31.75, 29.65, 20.82, 19.42. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.65.

HRMS (ESI) calcd for C$_{21}$H$_{20}$F$_3$NNaO$_2$:430.1059, found: 430.1062

71 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J$ = 8.5 Hz, 2H), 7.46 (d, $J$ = 8.8 Hz, 2H), 7.34 (d, $J$ = 2.2 Hz, 1H), 7.24 (d, $J$ = 8.2 Hz, 1H), 7.18 (d, $J$ = 8.2 Hz, 1H), 6.80 (q, $J$ = 2.9 Hz, 1H), 3.83 (d, $J$ = 13.7 Hz, 1H), 3.79 (d, $J$ = 13.7 Hz, 1H), 3.40 – 3.36 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.45, 147.52, 138.05, 134.62, 133.75, 133.63, 131.28, 129.58, 128.08, 127.17, 124.19, 122.48 (q, $J$ = 275.6 Hz), 102.06 (q, $J$ = 34.4 Hz), 101.34, 33.37, 28.15. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.71. HRMS (ESI) calcd for C$_{18}$H$_{12}$Cl$_2$F$_3$NNaO$_2$: 455.9810, found: 455.9811
78 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.21 (d, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 6.79 (q, $J = 2.8$ Hz, 1H), 3.42 (d, $J = 2.5$ Hz, 2H), 2.62 – 2.53 (m, 2H), 1.23 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.49 (q, $J = 3.8$ Hz), 147.55, 138.34, 128.07, 124.20, 122.61 (q, $J = 272.5$ Hz), 102.39 (q, $J = 34.2$ Hz), 100.99, 28.10, 26.11, 14.13. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.70. HRMS (ESI) calcd for C$_{13}$H$_{12}$F$_3$NNaO$_2$S: 326.0433, found: 326.0432.

62 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.8$ Hz, 2H), 6.76 (q, $J = 2.9$ Hz, 1H), 3.42 (d, $J = 2.9$ Hz, 2H), 1.33 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.51 (q, $J = 3.4$ Hz), 147.51, 138.32, 128.16, 124.17, 122.69 (q, $J = 275.1$ Hz), 102.75 (q, $J = 34.3$ Hz), 101.32, 43.20, 30.65, 24.90. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.01. HRMS (ESI) calcd for C$_{15}$H$_{16}$F$_3$NNaO$_2$S: 354.0746, found: 354.0754.

65 % isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 6.78 (q, $J = 2.8$ Hz, 1H), 3.43 (d, $J = 2.7$ Hz, 2H), 2.70 – 2.61 (m, 1H), 1.98 – 1.84 (m, 2H), 1.78 – 1.65 (m, 2H), 1.61 – 1.51 (m, 1H), 1.38 – 1.07 (m, 5H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.51 (q, $J = 3.6$ Hz), 147.48, 138.40,
128.08, 124.12, 122.63 (q, J = 275.3 Hz), 102.77 (q, J = 34.2 Hz), 101.01, 43.69, 33.12, 33.08, 26.60, 25.94, 25.85, 25.57. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -62.72. HRMS (ESI) calcd for C$_{17}$H$_{19}$F$_3$NNaO$_2$S: 380.0905, found: 380.0903.

7. Derivatizations of alkyne 3aa, 1,3-diene 4aa and allene 5eh, 5hh

(1) Synthesis of diiodic compound 6

Under N$_2$, to a solution of 3aa (0.5 mmol, 160 mg) in toluene (2.0 mL) was added I$_2$ (0.5 mmol, 127 mg) at room temperature. The reaction mixture was stirred for 12 h, saturated Na$_2$S$_2$O$_3$ (5.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography (silica gel, PE) to afford 6 (143 mg, 50% yield) as a colorless solid.

![Diagram of 6](image)

50% isolated yield. Colorless solid. Mp 35.1-37.2 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.21 – 7.06 (m, 7H), 6.91 (d, J = 7.6 Hz, 2H), 4.88 – 4.77 (m, 1H), 3.64 (dd, J = 10.1, 2.6 Hz, 1H), 3.51 (dd, J = 10.8 Hz, 1H), 2.22 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 149.89, 142.64, 138.55, 133.85, 129.43, 129.21, 128.25, 127.99, 127.73, 124.18 (q, J = 283.9 Hz), 96.61, 52.37 (q, J = 27.6 Hz), 21.12, 3.18. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -66.71. HRMS(ESI) calcd for C$_{18}$H$_{15}$F$_3$IS [M-I$^-$]: 446.9886, found: 446.9892.
(2) Synthesis of β-iodo alkenyl sulfides 7

Under N$_2$, to a solution of 3aa (0.2 mmol, 64 mg) in toluene (2.0 mL) was added NIS (0.6 mmol, 135 mg) at room temperature. The reaction was monitored through TLC (hexanes). After stirring for 12 h, saturated Na$_2$S$_2$O$_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography (silica gel, PE) to afford 7 (86 mg, 96% yield, E/Z = 2:3) as a colorless oil.

96% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ [7.22– 6.84 (m, 9H)], [6.01 (s, 0.38H, 5.80 (s, 0.38H), 5.34 (s, 0.58H)], [2.20 (s, 1.1H), 2.1 8(s, 1.8H)]. $^{13}$C NMR (125 MHz, CDCl$_3$) δ (152.94, 148.00), [140.33 (q, J = 32.1 Hz), 140.19 (q, J = 31.7 Hz)], (141.13, 138.48), (138.20, 136.10), 134.69, (133.47, 129.55), (129.30, 129.22), (128.92, 128.68), (128.09, 127.72), (127.56, 127.40), [124.85 (q, J = 4.3 Hz), 124.38 (q, J = 4.5 Hz)], [122.26 (q, J = 275.5 Hz), 122.07 (q, J = 276.0 Hz)], (82.87, 82.13), (21.09, 21.06). $^{19}$F NMR (471 MHz, CDCl$_3$) δ (-63.35, -64.33). MS (70 eV): m/z (%): 446 (M$^+$, 56.93), 123 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$IF$_3$S : 445.9813, found: 445.9810

(3) Synthesis of β-bromo alkenyl sulfides 8

Under N$_2$, to a solution of 3aa (0.2 mmol, 64 mg) in toluene (2.0 mL) was added NBS (0.6 mmol, 106 mg) at room temperature. The reaction
was monitored through TLC (hexanes). After stirring for 12 h, saturated Na$_2$S$_2$O$_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography (silica gel, PE) to afford 8 (78 mg, 98% yield, E/Z = 10:1) as a colorless oil.

![Chemical Structure](image)

98% isolated yield. Colorless solid. Mp 47.2-49.0 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ [7.25-7.13 (m, 5H)], [7.07 (d, J = 8.1 Hz, 0.2H)], [7.01 (d, J = 8.1 Hz, 1.8H)], [6.89 (d, J = 7.9 Hz, 1.8H)], [6.85 (d, J = 7.9 Hz, 0.2H)], [6.14 (d, J = 1.1 Hz, 0.9H)], [5.67 (d, J = 1.1 Hz, 0.1H)], [5.36 (d, J = 1.3 Hz, 0.9H)], [5.87 (d, J = 1.3 Hz, 0.9H)], [2.20 (s, 2.7H)], [2.19 (s, 0.3H)]. $^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.08, 138.05, 138.03, 137.63, 129.66, 129.46, 129.39, 129.21, 128.68, 128.12, 127.69, 125.81, 122.15, 109.36, 21.06. $^{19}$F NMR (471 MHz, CDCl$_3$) δ (-63.99, -64.86). MS (70 eV): m/z (%): 398 (M$^+$, 53.32), 228 (100). HRMS(EI) calcd for C$_{18}$H$_{14}$BrF$_3$S: 397.9952, found: 397.9954.

(4) Synthesis of cycloaddition product

Under N$_2$, 4aa (0.3 mmol, 96 mg) and N-phenyl-Maleimidein (0.6 mmol, 104 mg) in PhCl (4 mL) was heated at 150 °C in a sealed tube for 48 h. The reaction solvent was removed under reduced pressure and residue was purified by column chromatography (silica gel, PE:EA =
20:1) to afford the desired product 9 (92 mg, 62%, dr = 8:1) as a colorless solid.

\[
\text{Me} \hspace{1cm} \text{Ph} \hspace{1cm} \text{O} \\
\text{F}_3 \hspace{1cm} \text{C} \hspace{1cm} \text{N-Ph} \hspace{1cm} \text{O} \\
\text{9}
\]

62% isolated yield. Colorless solid. Mp 137.2-139.2 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.20 (m, 6H), 7.16 (d, \(J = 8.0\) Hz, 2H), 7.08 (d, \(J = 7.9\) Hz, 2H), 6.85 (d, \(J = 7.6\) Hz, 2H), 6.42 – 6.38 (m, 2H), 4.11 (d, \(J = 6.9\) Hz, 1H), 3.45 – 3.36 (m, 1H), 3.30 (dd, \(J = 9.0, 7.2\) Hz, 1H), 3.20 (dd, \(J = 19.0, 2.7\) Hz, 1H), 3.10 (dd, \(J = 19.4, 11.4\) Hz, 1H), 2.37 (s, 3H). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -59.43. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 177.28, 175.15, 142.43 (d, \(J = 2.4\) Hz), 139.67, 134.89, 134.78, 130.93, 130.03, 128.89, 128.86, 128.76, 128.52, 128.12, 126.11, 125.79, 124.32 (q, \(J = 30.0\) Hz), 123.66 (q, \(J = 275.6\) Hz), 45.38, 36.45, 22.31 (q, \(J = 3.3\) Hz), 21.16, 0.95. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -59.43. HRMS(ESI) calcd for C\(_{28}\)H\(_{22}\)F\(_3\)NNaO\(_2\)S [M+H\(^+\)]: 516.1216, found: 516.1224.

(5) Synthesis of alkenyl sulfides 10

Under N\(_2\), to a solution of 4-4aa (0.5 mmol, 160 mg) in DMSO (4.0 mL) was added BnNH\(_2\) (1.0 mmol, 107 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 5:1). After stirring for 12 h, water (15 mL) was added to reaction mixture and extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash
column chromatography on silica gel (silica gel, PE:EA = 5:1) to afford 
10 (169 mg, 86% yield) as a colorless oil.

86% isolated yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.16 (m, 
10H), 7.08 (d, $J$ = 7.9 Hz, 2H), 6.94 (d, $J$ = 6.7 Hz, 2H), 3.74 (s, 2H), 3.51 (s, 2H), 
3.44 (s, 2H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 146.87, 139.69, 138.98, 
137.57, 134.39, 129.83, 128.40, 128.38, 128.07, 127.85, 127.58, 127.53 (d, $J$ = 27.6 
Hz), 127.06, 126.46, 124.31 (d, $J$ = 276.2 Hz), 53.03, 46.74 (d, $J$ = 2.2 Hz), 37.37, 
21.16. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -57.57. HRMS(ESI) calcd for C$_{25}$H$_{25}$F$_3$NS 
[M+H$^+$]: 428.1654, found: 428.1658.

(6) Synthesis of 3-bromo-thiophene derivative 11

Under N$_2$, to a solution of 5eh (0.2 mmol, 69 mg) in toluene (2.0 mL) 
was added NBS (0.6 mmol, 107 mg) at room temperature. The reaction 
was monitored through TLC (petroleum ether: ethyl acetate = 20:1). After 
stirring for 4 h, saturated Na$_2$S$_2$O$_3$ (2.0 mL) solution was added then 
stirring for 10 min until the reaction mixture turn to colorless, then 
exttracted with ethyl acetate (3×5 mL). Organic layers were combined and 
evaporated to get crude residue which was purified through flash column 
chromatography silica gel (petroleum ether: ethyl acetate = 100:1~50:1)) 
to afford 11 (54 mg, 81% yield) as a colorless solid.
81% isolated yield. White solid; Mp 92.8-94.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (s, 1H), 7.76 (d, $J = 8.7$ Hz, 2H), 7.73 (d, $J = 8.6$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 139.47, 136.36, 132.40, 132.05 (q, $J = 35.0$ Hz), 129.94, 128.28 (q, $J = 5.1$ Hz), 120.76 (q, $J = 270.8$ Hz), 118.18, 112.69, 106.06. $^{19}$F NMR (471MHz, CDCl$_3$) $\delta$ -62.53. MS(70 ev): m/z(%): 331(M$^+$, 99.39), 333(100). HRMS (EI) calcd for C$_{12}$H$_5$F$_3$NBrS: 330.9278, found: 330.9274.

(7) Synthesis of 3-iodo-thiophene derivative 12

Under N$_2$, to a solution of 5hh (0.2 mmol, 69 mg) in toluene (2.0 mL) was added NIS (0.6 mmol, 135 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 20:1). After stirring for 4 h, saturated Na$_2$S$_2$O$_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turn to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography silica gel (petroleum ether: ethyl acetate = 100:1~50:1)) to afford 12 (63 mg, 79% yield) as a yellow solid.
isolated yield. Yellow solid. Mp 110.2-112.8 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, $J$ = 8.8 Hz, 2H), 7.95 (s, 1H), 7.74 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 147.93, 143.27, 140.04, 135.19 (q, $J$ = 34.5 Hz), 130.88, 129.55 (q, $J$ = 5.3 Hz), 123.84, 120.86 (q, $J$ = 271.2 Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -60.44. MS (70 ev): m/z(%): 399(M$^+$, 100), 399(100). HRMS (EI) calcd for C$_{11}$H$_5$IF$_3$NO$_2$S: 398.9038, found: 398.9041.

(8) Synthesis of 3-bromo-thiophene derivative 13

Under N$_2$, to a solution of 5eh (0.2 mmol, 69 mg) in toluene (2.0 mL) was added NBS (0.6 mmol, 107 mg) at room temperature. The reaction was monitored through TLC (petroleum ether: ethyl acetate = 20:1). After stirring for 12 h, saturated Na$_2$S$_2$O$_3$ (2.0 mL) solution was added then stirring for 10 min until the reaction mixture turned to colorless, then extracted with ethyl acetate (3×5 mL). Organic layers were combined and evaporated to get crude residue which was purified through flash column chromatography silica gel (petroleum ether: ethyl acetate = 100:1~50:1)) to afford 13 (59 mg, 84% yield) as a colorless solid.

84% isolated yield. White solid. Mp 108.3-110.9 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, $J$ = 8.3 Hz, 2H), 7.91 (s, 1H), 7.81 (d, $J$ = 8.6 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 147.92, 139.14, 138.28, 132.33 (q, $J$ = 35.0 Hz), 130.29, 128.48 (q, $J$ = 5.2 Hz), 123.97, 120.80 (q, $J$ = 268.8Hz), 106.53. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -61.18.
MS(70 ev): m/z(%): 351(M⁺, 39.03), 99(100). HRMS(EI) calcd for C₁₁H₅Br₃NO₂S: 350.9176, found: 350.9181.

8. Reference:

[1] Q. Zeng, L. Zhang, J. Yang, B. Xu, Y. Xiao and J. Zhang, *Chem. Commun.*, **2014**, *50*, 4203.

[2] K. Uneyama, T. Katagiri, H. Amii, *Acc. Chem. Res.* **2008**, *41*, 817–829.

9. X-ray structures for 1,3-diene 4ag and diiodic compounds 6

*Figure 1.* ORTEP depiction of compound 4ag, CCDC1867549

*Figure 2.* ORTEP depiction of compound 6, CCDC1860794
$\text{f1 (ppm)}$
The image shows a chemical structure labeled as 3ac, along with a corresponding NMR spectrum. The spectrum includes peaks at various ppm values, indicated by the numbers next to the corresponding chemical shifts.
major isomer of 4ea
major isomer of 4ea
minor isomer of 4ea
major isomer of 4fa
major isomer of 4fa

-63.417 ppm
minor isomer of 4fa
minor isomer of 4fa
major isomer of 4ga

CO₂Me

f1 (ppm)
major isomer of 4ga

$\delta_{1} (\text{ppm}) = -63.473$
minor isomer of 4ga
minor isomer of 4ga
major isomer of 4ha
minor isomer of 4ha
minor isomer of 4ha
The image shows a chemical structure labeled as 4ia. The structure contains multiple functional groups, including a thiophene ring, a phenyl ring with a Me group, and other substituents. The graph displays a peak at around -63.723 ppm on the f1 axis. The x-axis is labeled as 'f1 (ppm)' and ranges from 0 to -210 ppm.
The image contains a chemical structure labeled as 4ac, along with a set of chemical shifts in ppm. The chemical shifts listed are as follows:

- 137.81
- 135.07
- 134.86
- 134.61
- 134.43
- 134.25
- 131.30
- 129.26
- 129.12
- 128.81
- 128.41
- 128.24
- 125.72
- 125.68
- 125.60
- 125.40
- 121.21
- 119.02

These chemical shifts correspond to the peaks observed in the NMR spectrum.
$\Delta f_1$ (ppm) $\approx -62.508$
$\text{f1 (ppm)}$
-62.583
-62.581
$\text{f1 (ppm)}$

-62.602
$f_1$ (ppm)
\[ \text{f1 (ppm)} \]

![Chemical Structure](image)
