The Facile Synthesis of α-trifluoromethylthio Phosphonium Ylides with a Constrained Trifluoromethylthiooxide via Proton-Transfer Procedure

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1. General information

$^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded with JEOL AL - 600 MHz, AL - 400 MHz and AL - 300 MHz spectrometer. CDCl$_3$ was selected as the solvent and residual proton resonance of CDCl$_3$ was referenced using the 7.26 ppm in $^1$H NMR and 77.16 ppm in $^{13}$C NMR. Data are reported in the following order: multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and Coupling constants ($J$) are in Hertz (Hz). HRMS were recorded on a high-resolution mass spectrometer in the EI or ESI mode. IR spectra was recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

Materials: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents were purified by solvent purification system. Reactions were performed under an atmosphere of N$_2$ using glassware that was flame-dried under vacuum. n-BuLi was purchased from Energy (1,6 M in hexane). AgSCF$_3$ and compounds A$_1$, A$_2$, A$_3$, A$_4$, A$_5$ were prepared following the literature.
2. Synthesis of compound A

A 200 mL round-bottomed flask charged with 1-adamantanemethanol (4.5 mmol, 686 mg), N-trifluoromethylthiosaccharin (5.9 mmol, 1.65 g), and Et3N (10.4 mmol, 1.5 mL) was added DCM (90 mL). The mixture was stirred at room temperature for 10 min. The mixture was concentrated to (15 mL). The resulting mixture was then purified by flash column chromatography (Eluent: pentane) to give trifluoromethyl substituted thioperoxide A as a colorless liquid in 87% yield.

\[ OSCF_3 \]

\[^1\text{H} \text{NMR (400 MHz, CHLOROFORM-D)} \delta 2.23 (s, 3H), 1.82 (s, 6H), 1.62 (q, J = 12.4 Hz, 6H). \]
\[^13\text{C} \text{NMR (101 MHz, CHLOROFORM-D)} \delta 130.69 (q, J = 312.5 Hz), 83.10, 41.60, 35.88, 31.41. \]
\[^19\text{F} \text{NMR (283 MHz, CHLOROFORM-D)} \delta -52.50 (s). \]

IR (FTIR): \(\nu = 2912, 2856, 1456, 1117, 1047, 892, 798 \text{ cm}^{-1}\).


3. Studies of compound Ph_3P=CHSCF_3 by trifluoromethylthiolated of methylenetriphenylphosphorane

Initial observation of Ph_3P=CHSCF_3. To a solution of Methyltriphenylphosphonium bromide (71.4 mg, 0.2 mmol) in THF (2 mL) was added n-BuLi (1.6 M in hexane, 125 \mu L, 0.2 mmol) at -78 \degree C, and stirred for 1 h. Then trifluoromethylthiolation reagent A – A5 (0.1 mmol) was added to the reaction mixture independently. The mixture was allowed to warm to 30 \degree C and stirred for 4 h. As shown in Figure S1, a strong signal at around \(\delta = -52.6 \text{ ppm} \) was observed by \(^{19}\text{F} \text{NMR spectroscopy at room temperature using reagent A5 and A (1.0 equiv) as the trifluoromethylthiolating reagents (5, 6). When A1 to A4 was used as the functional reagent, no change was occurred (Figure S1, 1 – 4).}

![Diagram of reactions](image)

\(\text{Ph}CF_3\)

\(\text{Ph}P=\text{CH}_2 + \text{SCF}_3\text{” reagent A1} \)

\(\text{Ph}P=\text{CH}_2 + \text{SCF}_3\text{” reagent A2} \)

\(\text{Ph}P=\text{CH}_2 + \text{SCF}_3\text{” reagent A3} \)

\(\text{Ph}P=\text{CH}_2 + \text{SCF}_3\text{” reagent A4} \)

\(\text{Ph}P=\text{CH}_2 + \text{SCF}_3\text{” reagent A5} \)

\(\text{Ph}P=\text{CH}_2 + \text{SCF}_3\text{” reagent A} \)

\(\text{Figure S1} \) \(^{19}\text{F} \text{NMR of the mixture of methylenetriphenylphosphorane with “SCF}_3\text{” reagents A - A5}\)
The identification and reactivity of Ph₃P=CHSCF₃. In order to further affirm the new intermediate was our trifluoromethylthiolated ylide, aldehyde was added into the mixture in one-pot, ¹⁹F NMR spectra was recorded for different hours. As we can see the peak at -52.6 ppm decreased quickly in 10 min, and two new signals at -43.2 ppm emerged, which is exactly the same signal of the corresponding trifluoromethylthiolated olefin products (Figure S2). Prolonging the reaction time, the intermediate was almost consumed completely. The above information obviously indicated that compound Ph₃P=CHSCF₃ was produced and can finish Wittig reaction smoothly. It should be noted that compound Ph₃P=CHSCF₃ was not stable enough to be separated because of its high activity.

![Figure S2](image)

**Figure S2.** ¹⁹F NMR spectrum of the mixture of Ph₃P=CHSCF₃ and 1-Naphthaldehyde in THF
4. General procedure for the synthesis of compound 2b-2d

Phosphonium ylide (0.2 mmol) was added to a dry seal tube. The tube was evacuated and backfilled with pure N₂ for 3 times. DCM (2 mL) was added, then “SCF₃” reagent A (0.2 mmol) was added, the reaction was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a 5:1 mixture of Petroleum ether/EtOAc as an eluent to provide the trifluoromethylthiolated ylides 2b, 2c, 2d.

![Diagram of the reaction](image)

**2b** methyl 2-((trifluoromethyl)thio)-2-(triphenyl-λ₅-phosphanylidene)acetate 2b was obtained as white solid in 90% yield; R₆(PE/EA=5:1)=0.54. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.60 (m, 9H), 7.49 (m, 6H), 3.67 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 134.01 (d, J = 9.5 Hz), 132.43 (d, J = 2.6 Hz), 128.77 (d, J = 12.4 Hz). ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -49.53 (d, J = 440.3 Hz). ³¹P NMR (243 MHz, CHLOROFORM-D) δ 29.47 (s). HRMS (ESI) calcd for C₂₂H₁₈F₃O₂PS (M+H)+ 435.0790, found 435.0788. MP: 164.2 - 165.7 °C.

**2c** ethyl 2-((trifluoromethyl)thio)-2-(triphenyl-λ₅-phosphanylidene)acetate 2c was obtained as white solid in 92% yield; R₆(PE/EA=5:1)=0.54. ¹H NMR (600 MHz, CHLOROFORM-D) δ 7.64 – 7.53 (m, 9H), 7.51 – 7.43 (m, 6H), 4.43 – 3.58 (m, 2H), 1.70 – 0.96 (m, 3H). ¹³C NMR (151 MHz, CHLOROFORM-D) δ 133.94 (d, J = 9.6 Hz), 132.34 (d, J = 1.6 Hz), 128.67 (d, J = 12.4 Hz), 126.21 (m), 59.51 (m), 14.08 (m). ¹⁹F NMR (565 MHz, CHLOROFORM-D) δ -49.51 (d, J = 379.6 Hz). ³¹P NMR (243 MHz, CHLOROFORM-D) δ 29.60 (s). HRMS (ESI) calcd for C₂₃H₂₀F₃O₂PS (M+H)+ 449.0946, found 449.0941. MP: 165. – 166.4 °C.

**2d** 2-((trifluoromethyl)thio)-2-(triphenyl-l₅-phosphanylidene)acetonitrile 2d was obtained as white solid in 60% yield; R₆(PE/EA=5:1)=0.35. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.71 – 7.61 (m, 9H), 7.56 (m, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 134.08 (d, J = 9.7 Hz), 133.57 (d, J = 2.3 Hz), 129.30 (d, J = 12.5 Hz), 126.58 (d, J = 25.6 Hz), 123.72 (d, J = 92.3 Hz). ¹⁹F NMR (283 MHz, CHLOROFORM-D) δ -49.08 (s). ³¹P NMR (243 MHz, CHLOROFORM-D) δ 30.41 (s). HRMS (ESI) calcd for C₂₁H₁₅F₃NPS (M+H)+ 402.0688, found 402.0685. MP: 161.5 – 162 °C.
5. **Table S1. Optimization of Wittig-Horner reaction conditions**

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<th>Entry</th>
<th>SCF₃ reagent</th>
<th>Base</th>
<th>T°C</th>
<th>Solvent</th>
<th>Yield of 4aa (%) b</th>
<th>Z/E b</th>
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<td>A1-A4</td>
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<tr>
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<td>A5</td>
<td>n-BuLi</td>
<td>-78 to rt</td>
<td>THF</td>
<td>69</td>
<td>80:20</td>
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<tr>
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<td>A</td>
<td>n-BuLi</td>
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<td>THF</td>
<td>98 (96)c</td>
<td>80:20</td>
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<tr>
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<td>THF</td>
<td>50</td>
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<td>THF</td>
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<chem>
\[
\begin{align*}
\text{3a} & \xrightarrow{\text{R-SCF₃, A - A5}} \text{50 °C, 12 h} & \text{4aa}
\end{align*}
\]

a Reaction conditions: preparation of the phosphonium ylide: methyltriphenylphosphonium bromide (0.2 mmol), base (0.2 mmol), solvent; A - A5 (0.2 mmol) was added dropwise to the reaction mixture, 30°C, 4 h. then aldehyde (0.17 mmol) was added, 50°C, 12 h. b Yields and Z/E ratio were determined by 19F-NMR using trifluoromethylbenzene as an internal standard. c Value in parentheses refers to isolated yield.
6. Typical procedures for the synthesis of compound 4

Methyltriphenylphosphonium bromide (71.4 mg, 0.2 mmol, 1.2 equiv) was added to a dry Seal tube. The tube was evacuated and backfilled with pure N₂ for 3 times. THF (2 mL) was added with syringe and the solution was cooled to -78 °C, then n-BuLi (1.6 M in hexane, 125 μL, 0.2 mmol, 1.2 equiv) was added, the mixture was allowed to stirred for 1 h. “SCF₃” reagent A (52.0 mg, 0.2 mmol, 1.2 equiv) was added, the reaction was stirred for additional 4 h at 30°C. With the prepared trifluoromethylthiolated phosphonium ylides in hand, aldehydes (0.17 mmol, 1 equiv) was added in situ. The reaction mixture was stirred at corresponding temperature. The reaction was monitored by TLC. After completed the reaction, the reaction was treated with H₂O and extracted three times with EtOAc. The combined organic layers were dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography to give the products.

**Analytic Data for products**

![Image of compound 4aa](image)

**(2-(Naphthalen-1-yl)vinyl)(trifluoromethyl)sulfane 4aa** was obtained as colorless oil in 96% yield (Z:E = 80:20, 41.5 mg); Rₜ(n-pentane)=0.80. NMR of the major isomer: ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.98 – 7.94 (m, 1H), 7.93 – 7.90 (m, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 10.1 Hz, 1H), 7.42 (d, J = 7.1 Hz, 1H), 6.72 (d, J = 10.0 Hz, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 133.70, 132.21, 131.18, 130.95, 129.85 (q, J = 307.6 Hz), 129.16, 128.77, 126.67, 126.41, 126.36, 125.23, 124.26, 117.40 (q, J = 3.2 Hz). ¹⁹F NMR (283 MHz, CHLOROFORM-D) δ -43.21 (s). HRMS (ESI) calcd for C₁₃H₉F₃S [M]+: 254.0377; found, 254.0374.

![Image of compound 4ab](image)

**(2-(Naphthalen-2-yl)vinyl)(trifluoromethyl)sulfane 4ab** was obtained as white solid in 82% yield (Z:E = 84:16, 35.4 mg); Rₜ(n-pentane)=0.80. NMR of the major isomer: ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.89 – 7.81 (m, 3H), 7.78 (s, 1H), 7.50 (m, 3H), 7.00 (d, J = 10.5 Hz, 1H), 6.49 (d, J = 10.5 Hz, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 133.25, 132.97, 132.70, 132.35, 129.72 (q, J = 307.9 Hz), 128.39, 128.37, 128.29, 127.81, 126.82, 126.71, 126.25, 114.36 (q, J = 3.6 Hz). ¹⁹F NMR (283 MHz, CHLOROFORM-D) δ -43.00 (s). HRMS (ESI) calcd for C₁₃H₉F₃S [M]+: 254.0377; found, 254.0372.

![Image of compound 4ac](image)

**Styryl(trifluoromethyl)sulfane 4ac** was obtained as light yellow oil in 81% yield (Z:E = 83:17, 28.1 mg); Rₜ(n-pentane)=0.82. NMR of the major isomer: ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.29 (m, 5H), 6.85 (d, J = 10.4 Hz, 1H), 6.40 (d, J = 10.4 Hz, 1H). ¹³C NMR (151 MHz, CHLOROFORM-D) δ 129.72 (q, J = 307.9 Hz), 128.39, 128.37, 128.29, 127.81, 126.82, 126.71, 126.25, 114.36 (q, J = 3.6 Hz). ¹⁹F NMR (283 MHz, CHLOROFORM-D) δ -43.00 (s). HRMS (ESI) calcd for C₁₃H₉F₃S [M]+: 254.0377; found, 254.0372.
CHLOROFORM-D) δ 135.17, 132.32, 129.67 (q, $J = 307.8$ Hz), 128.79, 128.71, 128.39, 114.01 (q, $J = 3.0$ Hz). $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -42.81(s). HRMS (ESI) calcd for C$_9$H$_7$F$_3$S $[M]^+$: 204.0221; found, 204.0220.

(4-methylstyryl)( trifluoromethyl)sulfane 4ad was obtained as colorless oil in 80% yield ($Z:E$=84:16, 29.7 mg); R$_f$(n-pentane)=0.82. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 10.5$ Hz, 1H), 6.34 (d, $J = 10.4$ Hz, 1H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 138.46, 132.46, 132.40, 129.73 (q, $J = 307.7$ Hz), 129.39, 128.78, 112.89 (q, $J = 3.5$ Hz), 21.42. $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -43.15 (s). HRMS (ESI) calcd for C$_{10}$H$_9$F$_3$S $[M]^+$: 218.0377; found, 218.0379.

(4-isopropylstyryl)( trifluoromethyl)sulfane 4ae was obtained as colorless oil in 83% yield ($Z:E$=84:16, 34.7 mg); R$_f$(n-pentane)=0.82. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 10.5$ Hz, 1H), 6.35 (d, $J = 10.5$ Hz, 1H), 2.94 (m, 1H), 1.28 (d, $J = 7.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 149.37, 132.40, 129.74 (q, $J = 307.7$ Hz), 128.91, 127.06, 126.79, 112.87 (q, $J = 3.5$ Hz), 34.11, 23.97. $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -43.17 (s). HRMS (ESI) calcd for C$_{12}$H$_{13}$F$_3$S $[M]^+$: 246.0690; found, 246.0688.

(4-methoxystyryl)( trifluoromethyl)sulfane 4af was obtained as pale yellow oil in 68% yield ($Z:E$=78:22, 27.1 mg); R$_f$(n-pentane/EA 10:1)=0.74. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.31 (d, $J = 7.4$ Hz, 2H), 6.93 (d, $J = 7.4$ Hz, 2H), 6.80 (d, $J = 10.4$ Hz, 1H), 6.27 (dd, $J = 10.4, 1.4$ Hz, 1H), 3.84 (s, 3H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 159.62, 132.42, 130.36, 129.74 (q, $J = 307.5$ Hz), 127.86, 114.09, 111.38 (q, $J = 3.3$ Hz), 55.42. $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -43.16 (s). HRMS (ESI) calcd for C$_{10}$H$_9$F$_3$OS $[M]^+$: 234.0326; found, 234.0328.

(4-methoxystyryl)( trifluoromethyl)sulfane 4ag was obtained as white solid in 83% yield ($Z:E$=86:14, 31.1 mg); R$_f$(n-pentane/EA 10:1)=0.45. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (d, $J = 7.8$ Hz, 2H), 6.85 (d, $J = 7.8$ Hz, 2H), 6.78 (d, $J = 10.4$ Hz, 1H), 6.26 (dd, $J = 10.4, 0.9$ Hz, 1H), 5.15 (s, 1H). $^{13}$C NMR (101 MHz, CHLOROFORM-D)
\[ \delta 155.61, 132.31, 130.59, 129.71 \text{ (q, } J = 307.7 \text{ Hz), 128.12, 115.60, 111.57 \text{ (q, } J = 3.4 \text{ Hz).} \]

$^{19}$F NMR (283 MHz, CHLOROFORM-D) \( \delta -43.19 \) (s). HRMS (ESI) calcd for C$_9$H$_7$F$_3$OS [M]$^+$: 220.0170; found, 220.0169. MP: 52.2 – 54.7 °C.

(2-(1,1'-biphenyl)-4-ylvinyl)(trifluoromethyl)sulfane 4ah was obtained as white solid in 91% yield (Z:E=82:18, 43.3 mg); R$_f$(n-pentane)=0.77. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) \( \delta 7.69 – 7.65 \) (m, 4H), 7.51 – 7.40 (m, 5H), 6.91 (d, \( J = 10.5 \text{ Hz, } 1H \)), 6.47 (d, \( J = 10.5 \text{ Hz, } 1H \)). $^{13}$C NMR (101 MHz, CHLOROFORM-D) \( \delta 141.11, 140.41, 134.11, 131.89, 129.68 \text{ (q, } J = 307.9 \text{ Hz), 129.30, 129.01, 127.77, 127.32, 127.17, 125.09, 113.88 \text{ (q, } J = 3.3 \text{ Hz).} \)

$^{19}$F NMR (376 MHz, CHLOROFORM-D) \( \delta -45.49 \) (s). HRMS (ESI) calcd for C$_{15}$H$_{11}$F$_3$S [M]+$^+$: 280.0534; found, 280.0529.

(4-bromostyryl)(trifluoromethyl)sulfane 4ai was obtained as colorless oil in 98% yield (Z:E=79:21, 47.0 mg); R$_f$(n-pentane)=0.60. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) \( \delta 7.51 \) (dd, \( J = 8.4, 1.4 \text{ Hz, } 1H \)), 7.20 (d, \( J = 8.4 \text{ Hz, } 1H \)), 6.77 (d, \( J = 10.4 \text{ Hz, } 1H \)), 6.43 (dd, \( J = 10.5, 1.2 \text{ Hz, } 1H \)). $^{13}$C NMR (101 MHz, CHLOROFORM-D) \( \delta 134.01, 131.89, 131.21, 130.30, 129.50 \text{ (q, } J = 308.0 \text{ Hz), 122.45, 114.92 \text{ (q, } J = 3.4 \text{ Hz).} \)$

$^{19}$F NMR (283 MHz, CHLOROFORM-D) \( \delta -42.93 \) (s). HRMS (ESI) calcd for C$_{9}$H$_{6}$BrF$_3$S [M]+$^+$: 281.9326; found, 281.9327.

(4-chlorostyryl)(trifluoromethyl)sulfane 4aj was obtained as colorless oil in 99% yield (Z:E=74:26, 40.1 mg); R$_f$(n-pentane)=0.60. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) \( \delta 7.29 \) (dd, \( J = 8.4 \text{ Hz, } 2H \)), 7.19 (d, \( J = 8.4 \text{ Hz, } 2H \)), 6.71 (d, \( J = 10.5 \text{ Hz, } 1H \)), 6.34 (d, \( J = 10.5 \text{ Hz, } 1H \)). $^{13}$C NMR (101 MHz, CHLOROFORM-D) \( \delta 134.25, 133.58, 131.20, 130.05, 129.53 \text{ (q, } J = 307.7 \text{ Hz), 128.94, 114.77 \text{ (q, } J = 3.6 \text{ Hz).} \)$

$^{19}$F NMR (283 MHz, CHLOROFORM-D) \( \delta -42.94 \) (s). HRMS (ESI) calcd for C$_{9}$H$_{6}$ClF$_3$S [M]+$^+$: 237.9831; found, 237.9828.

(4-nitrostyryl)(trifluoromethyl)sulfane 4ak was obtained as pale yellow oil in 99% yield (Z:E=75:25, 41.9 mg); R$_f$(n-pentane/EA 10:1)=0.30. $^1$H NMR (400 MHz, CHLOROFORM-D) \( \delta 8.24 \) (d, \( J = 8.8 \text{ Hz, } 2H \)), 7.48 (d, \( J = 8.8 \text{ Hz, } 2H \)), 6.88 (d, \( J = 10.7 \text{ Hz, } 1H \)), 6.64 (d, \( J = 10.7 \text{ Hz, } 1H \)). $^{13}$C NMR (101 MHz, CHLOROFORM-D) \( \delta 147.08, 141.34, 129.70, 129.42, 129.19 \text{ (q, } J = \))
4-(2-((trifluoromethyl)thio)vinyl)benzonitrile 4al was obtained as yellow oil in 91% yield (Z:E=88:12, 35.4 mg); Rf(n-pentane/EA 10:1)=0.33. NMR of the major isomer: 1H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 10.7 Hz, 1H), 6.59 (d, J = 10.7 Hz, 1H). 13C NMR (101 MHz, CHLOROFORM-D) δ 139.43, 132.44, 130.13, 129.21, 129.21 (d, J = 308.3 Hz), 118.57, 117.99 (q, J = 3.5 Hz), 111.71. 19F NMR (376 MHz, CHLOROFORM-D) δ -45.17 (s). HRMS (ESI) calcd for C9H6F3NO2S [M]+: 249.0071; found, 249.0072.

Methyl-4-(2-((trifluoromethyl)thio)vinyl)benzoate 4am was obtained as white solid in 92% yield (Z:E=86:14, 41.1 mg); Rf(n-pentane/EA 10:1)=0.46. NMR of the major isomer: 1H NMR (400 MHz, CHLOROFORM-D) δ 8.04 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 10.6 Hz, 1H), 6.51 (d, J = 10.6 Hz, 1H), 3.92 (s, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 166.58, 139.43, 130.93, 129.93, 129.67, 129.44 (q, J = 307.9 Hz), 128.62, 116.55 (q, J = 3.7 Hz), 52.29. 19F NMR (376 MHz, CHLOROFORM-D) δ -45.17 (s). HRMS (ESI) calcd for C11H9F3O2S [M]+: 262.0275; found, 262.0278.

(3-bromostyryl)(trifluoromethyl)sulfane 4an was obtained as yellow oil in 65% yield (Z:E=80:20, 31.2 mg); Rf(n-pentane)=0.60. NMR of the major isomer: 1H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (s, 1H), 7.44 (td, J = 5.1, 2.1 Hz, 1H), 7.26 (d, J = 5.1 Hz, 2H), 6.76 (d, J = 10.6 Hz, 1H), 6.46 (d, J = 10.6 Hz, 1H). 13C NMR (101 MHz, CHLOROFORM-D) δ 137.12, 131.66, 131.33, 130.69, 130.20, 129.48 (q, J = 307.9 Hz), 127.19, 122.83, 115.86 (q, J = 3.6 Hz). 19F NMR (376 MHz, CHLOROFORM-D) δ -45.32 (s). HRMS (ESI) calcd for C9H6BrF3S [M]+: 281.9326; found, 281.9325.

(2-bromostyryl)(trifluoromethyl)sulfane 4ao was obtained as colorless oil in 99% yield (Z:E=75:25, 47.5 mg); Rf(n-pentane)=0.60. NMR of the major isomer: 1H NMR (400 MHz, CHLOROFORM-D) δ 7.63 (d, J = 8.3 Hz, 1H), 7.34 (m, 2H), 7.23 – 7.15 (m, 1H), 7.00 (d, J = 10.4 Hz, 1H), 6.54 (d, J = 10.4 Hz, 1H). 13C NMR (101 MHz, CHLOROFORM-D) δ 135.11,
133.16, 132.17, 129.94, 129.66, 129.60 (q, \( J = 308.0 \) Hz), 127.40, 123.93, 116.75 (q, \( J = 308.0 \) Hz), 127.40, 123.93, 116.75 (q, \( J = 3.5 \) Hz).

\(^{19}\)F NMR (283 MHz, CHLOROFORM-D) \( \delta -42.73 \) (s). HRMS (ESI) calcd for \( C_{9}H_{6}BrF_{3}S \) \([M]^{+}: 281.9326\); found, 281.9326.

(2-nitrostyryl)(trifluoromethyl)sulfane 4ap was obtained as pale yellow oil in 82% yield (Z:E=66:34, 34.7 mg); \( R_{f}(n\text{-pentane})=0.34 \). NMR of the major isomer: \(^1\)H NMR (400 MHz, CHLOROFORM-D) \( \delta 8.13 \) (d, \( J = 8.2 \) Hz, 1H), 7.66 (t, \( J = 7.7 \) Hz, 1H), 7.53 (t, \( J = 8.1 \) Hz, 1H), 7.46 (d, \( J = 7.4 \) Hz, 1H), 7.29 (d, \( J = 10.2 \) Hz, 1H), 6.60 (d, \( J = 10.2 \) Hz, 1H). \(^{13}\)C NMR (101 MHz, CHLOROFORM-D) \( \delta 147.39, 134.0, 133.64, 130.93, 130.54, 129.51, 129.49 \) (q, \( J = 308.0 \) Hz), 125.29, 117.60 (q, \( J = 3.1 \) Hz). \(^{19}\)F NMR (283 MHz, CHLOROFORM-D) \( \delta -42.26 \) (s).

HRMS (ESI) calcd for \( C_{9}H_{6}F_{3}NO_{2}S \) \([M]^{+}: 249.0071\); found, 249.0074.

2-(2-((trifluoromethyl)thio)vinyl)benzo[b]thiophene 4aq was obtained as white solid in 68% yield (Z:E=82:18, 30.1 mg); \( R_{f}(n\text{-pentane})=0.85 \). NMR of the major isomer: \(^1\)H NMR (400 MHz, CHLOROFORM-D) \( \delta 7.85 – 7.82 \) (m, 1H), 7.77 – 7.79(m 1H), 7.40 – 7.36 (m, 2H), 7.33 (s, 1H), 7.07 (d, \( J = 10.1 \) Hz, 1H), 6.41 (d, \( J = 10.2 \) Hz, 1H). \(^{13}\)C NMR (101 MHz, CHLOROFORM-D) \( \delta 139.59, 138.87, 138.16, 130.97 \) (t, \( J = 308.7 \) Hz), 127.51, 126.85, 125.44, 124.90, 124.09, 122.36, 113.28 (d, \( J = 3.4 \) Hz). \(^{19}\)F NMR (283 MHz, CHLOROFORM-D) \( \delta -42.43 \) (s).

HRMS (ESI) calcd for \( C_{11}H_{7}F_{3}S_{2} \) \([M]^{+}: 259.9941\); found, 259.9944.

(4-phenylbut-1-en-1-yl)(trifluoromethyl)sulfane 4ar was obtained as colorless oil in 35% yield (Z:E= 50:50, 13.8 mg); \( R_{f}(n\text{-pentane})=0.88 \). NMR of the major isomer: \(^1\)H NMR (400 MHz, CHLOROFORM-D) \( \delta 7.32 \) (d, \( J = 7.2 \) Hz, 1H), 7.31 (d, \( J = 7.6 \) Hz, 1H), 7.26 – 7.16 (m, 3H), 6.33 – 6.05 (m, 2H), 2.78 – 2.72 (m, 2H), 2.59 – 2.49 (m, 2H). \(^{13}\)C NMR (101 MHz, CHLOROFORM-D) \( \delta 140.75, 138.83, 129.75 \) (d, \( J = 307.0 \) Hz), 128.56, 128.5, 126.29, 113.69 (d, \( J = 2.8 \) Hz), 34.74, 30.91. \(^{19}\)F NMR (283 MHz, CHLOROFORM-D) \( \delta -43.08 \) (s). HRMS (ESI) calcd for \( C_{11}H_{11}F_{3}S \) \([M]^{+}: 232.0534\); found, 232.0536.

3E-4-phenylbuta-1,3-dien-1-yl)(trifluoromethyl)sulfane 4as was obtained as colorless oil in 85% yield (Z:E= 61:39, 33.3 mg); \( R_{f}(n\text{-pentane})=0.85 \). NMR of the major isomer: \(^1\)H NMR (400 MHz, CHLOROFORM-D) \( \delta 7.47 \) (d, \( J = 7.3 \) Hz, 2H), 7.40 – 7.35 (m, 3H), 7.10 (dd, \( J = 15.3, 11.1 \) Hz,
1H), 6.78 – 6.72 (m, 2H), 6.17 (d, J = 9.5 Hz, 1H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 137.39, 136.43, 129.61 (q, J = 307.5 Hz), 128.91, 128.79, 128.08, 127.10, 126.95, 122.94, 112.63 (q, J = 2.8 Hz). $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -42.26 (s). HRMS (ESI) calcd for C$_{11}$H$_9$F$_3$S [M]+: 230.0377; found, 230.0373.

((4-phenylcyclohexylidene)methyl)(trifluoromethyl)sulfane 4at was obtained as colorless oil in 42% yield (19.4 mg); R$_f$(n-pentane)=0.76. $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.31 (t, J = 7.5 Hz, 2H), 7.25 – 7.19 (m, 3H), 5.91 (s, 1H), 3.09 (d, J = 14.7 Hz, 1H), 2.76 (t, J = 12.2 Hz, 1H), 2.55 (d, J = 13.7 Hz, 1H), 2.41 – 2.29 (m, 1H), 2.13 – 2.04 (m, 3H), 1.66 – 1.53 (m, 2H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 155.07, 146.00, 130.03 (q, J = 306.9 Hz), 128.61, 126.92, 126.42, 103.63 (q, J = 2.0 Hz), 44.14, 36.67, 35.31, 34.43, 30.50. $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -43.02 (s). HRMS (ESI) calcd for C$_{14}$H$_{15}$F$_3$S [M]+: 272.0847; found, 272.0851.

(2-(4-nitrophenyl)prop-1-en-1-yl)(trifluoromethyl)sulfane 4au was obtained as pale yellow oil in 65% yield (Z:E = 55:45, 29 mg); R$_f$(n-pentane/EA 10:1)=0.30. NMR of the major isomer: $^1$H NMR (400 MHz, CHLOROFORM-D) δ 8.22 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 6.57 (s, 1H), 2.23 (s, 3H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 146.87, 146.11, 143.44, 129.55 (q, J = 3.0 Hz), 25.43. $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -42.75 (s). HRMS (ESI) calcd for C$_{10}$H$_8$F$_3$NO$_2$S [M]+: 263.0228; found, 263.0226.

(Z)-(1-(naphthalen-1-yl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ea was obtained as colorless oil in 37% yield (17.0 mg); R$_f$(n-pentane)=0.78. $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.89 – 7.85 (m, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.52 (m, 2H), 7.54 – 7.50 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.33 (s, 1H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 135.35, 133.45, 133.21, 131.47, 129.74 (d, J = 308.9 Hz), 128.62, 128.56, 127.59, 127.37, 126.38, 126.15, 125.23, 124.59, 25.86. $^{19}$F NMR (283 MHz, CHLOROFORM-D) δ -37.97 (s). HRMS (ESI) calcd for C$_{14}$H$_{13}$F$_3$S [M]+: 268.0534; found, 268.0533.

(E)-(1-(naphthalen-1-yl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ea’ was obtained as colorless oil in 32% yield (14.0 mg); R$_f$(n-pentane)=0.82. $^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.92
- 7.86 (m, 2H), 7.84 (d, J = 8.3 Hz, 1H), 7.59 (s, 1H), 7.57 – 7.51 (m, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 2.18 (s, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 141.09, 133.65, 133.12, 131.40, 130.35 (q, J = 308.8 Hz), 128.76, 128.68, 126.86, 126.69, 126.60, 126.34, 125.32, 124.63, 21.89. 19F NMR (283 MHz, CHLOROFORM-D) δ -40.56 (s). HRMS (ESI) calcd for C14H11F3S [M]+: 268.0534; found, 268.0531.

![Image](image1)

(1-(4-methoxyphenyl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ef was obtained as colorless oil in 85% yield (Z:E = 63:37, 35.8 mg); Rf (n-pentane/EA 10:1) = 0.56. NMR of the major isomer: 1H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.86 (s, 1H), 3.83 (s, 3H), 2.32 (s, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 159.45, 137.75, 130.81, 129.95 (q, J = 309.5 Hz), 128.20, 121.63, 113.73, 55.39, 27.10. 19F NMR (283 MHz, CHLOROFORM-D) δ -38.29 (s). HRMS (ESI) calcd for C11H11F3OS [M]+: 248.0483; found, 248.0485.

![Image](image2)

(1-(4-bromophenyl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ei was obtained as colorless oil in 89% yield (Z:E = 62:38, 44.8 mg); Rf (n-pentane) = 0.86. NMR of the major isomer: 1H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.83 (s, 1H), 2.33 (s, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 136.75, 134.50, 131.53, 130.90, 129.69 (q, J = 309.3 Hz), 125.00, 122.19, 26.96. 19F NMR (283 MHz, CHLOROFORM-D) δ -38.07 (s). HRMS (ESI) calcd for C10H8BrF3S [M]+: 295.9482; found, 295.9483.

![Image](image3)

(E)-(2-(4-bromophenyl)-1-phenylvinyl)(trifluoromethyl)sulfane 4fi was obtained as colorless oil in 20% yield (12.3 mg); Rf (n-pentane) = 0.84. 1H NMR (400 MHz, CHLOROFORM-D) δ 7.38 – 7.31 (m, 5H), 7.28 (d, J = 8.5 Hz, 2H), 7.20 (s, 1H), 6.88 (d, J = 8.5 Hz, 2H). 13C NMR (101 MHz, CHLOROFORM-D) δ 139.46, 137.50, 134.30, 131.64, 131.06, 129.49, 129.02, 128.98, 128.91, 122.72. 19F NMR (283 MHz, CHLOROFORM-D) δ -40.81 (s). HRMS (ESI) calcd for C15H10BrF3S [M]+: 357.9639; found, 357.9635.
7. References

8. Copies of $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra of the products.

$^1$H NMR spectrum of A in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of A in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of A in CDCl$_3$ (283 MHz)

$^1$H NMR spectrum of 2b in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 2b in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 2b in CDCl$_3$ (565 MHz)
$^{31}$P NMR spectrum of 2b in CDCl$_3$ (243 MHz)

$^1$H NMR spectrum of 2c in CDCl$_3$ (600 MHz)
$^{13}$C NMR spectrum of 2c in CDCl$_3$ (151 MHz)

$^{19}$F NMR spectrum of 2c in CDCl$_3$ (565 MHz)
$^3$P NMR spectrum of 2c in CDCl$_3$ (243 MHz)

$^1$H NMR spectrum of 2d in CDCl$_3$ (400 MHz)
\(^{13}\)C NMR spectrum of 2d in CDCl\(_3\) (101 MHz)

\(^{19}\)F NMR spectrum of 2d in CDCl\(_3\) (283 MHz)
$^{31}$P NMR spectrum of 2d in CDCl$_3$ (243 MHz)

$^1$H NMR spectrum of 4aa in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4aa in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4aa in CDCl$_3$ (283 MHz)
$^1$H NMR spectrum of 4ab in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ab in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4ab in CDCl$_3$ (283 MHz)

$^1$H NMR spectrum of 4ac in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4ac in CDCl$_3$ (151 MHz)

$^{19}$F NMR spectrum of 4ac in CDCl$_3$ (283 MHz)
$^1$H NMR spectrum of 4ad in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ad in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4ad in CDCl₃ (283 MHz)

$^1$H NMR spectrum of 4ae in CDCl₃ (400 MHz)
$^{13}$C NMR spectrum of 4ae in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4ae in CDCl$_3$ (283 MHz)
$^1$H NMR spectrum of 4af in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4af in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4af in CDCl$_3$ (283 MHz)

$^1$H NMR spectrum of 4ag in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of $4ag$ in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of $4ag$ in CDCl$_3$ (4283 MHz)
$^1$H NMR spectrum of 4ah in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ah in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4ah in CDCl$_3$ (376 MHz)

$^1$H NMR spectrum of 4ai in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4ai in CDCl$_3$ (101 MHz)

$^{13}$F NMR spectrum of 4ai in CDCl$_3$ (283 MHz)
$^1$H NMR spectrum of 4aj in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4aj in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4aj in CDCl$_3$ (283 MHz)

$^1$H NMR spectrum of 4ak in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4ak in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4ak in CDCl$_3$ (565 MHz)
$^1$H NMR spectrum of 4a1 in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4a1 in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4al in CDCl$_3$ (376 MHz)

$^{1}$H NMR spectrum of 4am in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4am in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4am in CDCl$_3$ (376 MHz)
$^1$H NMR spectrum of 4an in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4an in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4an in CDCl₃ (376 MHz)

$^1$H NMR spectrum of 4ao in CDCl₃ (400 MHz)
$^{13}$C NMR spectrum of 4ao in CDCl$_3$ (101 MHz)

$^9$F NMR spectrum of 4ao in CDCl$_3$ (283 MHz)
$^1$H NMR spectrum of 4ap in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ap in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4ap in CDCl$_3$ (283 MHz)

$^1$H NMR spectrum of 4aq in CDCl$_3$ (400 MHz)
$\text{\textsuperscript{13}C NMR spectrum of 4aq in CDCl}_3$ (101 MHz)

$\text{\textsuperscript{19}F NMR spectrum of 4aq in CDCl}_3$ (283 MHz)
$^1$H NMR spectrum of 4ar in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ar in CDCl$_3$ (101 MHz)
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$^{19}$F NMR spectrum of 4as in CDCl$_3$ (283 MHz)
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$^{13}$C NMR spectrum of 4at in CDCl$_3$ (101 MHz)
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$^1$H NMR spectrum of 4au in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4au in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4au in CDCl$_3$ (283 MHz)
$^{1}$H NMR spectrum of 4ea in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ea in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4ea in CDCl$_3$ (283 MHz)

$^1$H NMR spectrum of 4ea' in CDCl$_3$ (400 MHz)
$^{13}$C NMR spectrum of 4ea in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4ea in CDCl$_3$ (283 MHz)
$^{1}$H NMR spectrum of 4ef in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4ef in CDCl$_3$ (101 MHz)
\(^{19}\)F NMR spectrum of 4ef in CDCl\(_3\) (283 MHz)

\(^1\)H NMR spectrum of 4ei in CDCl\(_3\) (400 MHz)
$^{13}$C NMR spectrum of 4ei in CDCl$_3$ (101 MHz)

$^{19}$F NMR spectrum of 4ei in CDCl$_3$ (283 MHz)
$^1$H NMR spectrum of 4fi in CDCl$_3$ (400 MHz)

$^{13}$C NMR spectrum of 4fi in CDCl$_3$ (101 MHz)
$^{19}$F NMR spectrum of 4f in CDCl$_3$ (283 MHz)
9. X-ray single crystallographic data of compound 2b

The trifluoromethylthiolated phosphonium ylide 2b was recrystallized from a solution in DCM/PE. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 1914419).

Table 1 Crystal data and structure refinement for compound 2b.

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Final R indexes [I>=2\sigma (I)] R_1 = 0.0404, wR_2 = 0.1350
Final R indexes [all data] R_1 = 0.0437, wR_2 = 0.1407
Largest diff. peak/hole / e Å^{-3} 0.57/-0.48