Supporting Information

for

Metal-free visible-light-enabled vicinal trifluoromethyl dithiolation of unactivated alkenes

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Full experimental details, compound characterization, and copies of NMR spectra
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I. General methods

All reactions were performed in flame-dried glassware with equipped with a magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and were used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was done using silica gel (silica gel 60 F254). TLC plates were analyzed by exposure to ultraviolet (UV) light. NMR experiments were performed using a Bruker AVANCE III-400 or 500 spectrometer and carried out in deuterochloroform (CDCl₃). ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz, respectively. ¹⁹F NMR spectra were recorded at 376 MHz or 470 MHz. Chemical shifts are reported as δ values relative to internal TMS (δ 0.00 for ¹H NMR), chloroform (δ 7.26 for ¹H NMR), chloroform (δ 77.00 for ¹³C NMR). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; coupling constants (J) are reported in hertz (Hz). Melting points were uncorrected. Infrared spectra were obtained on an agilent Cary630. HRMS were recorded on a Bruker microTOF-Q111. GC–MS spectra were performed on a Shimadzu QP2010 (EI source).

In a general experiment, 10 W blue LEDs (465 nm) were used as a blue light source. A borosilicate glass tube was used as a reaction tube. We have not used any filters. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were carried out under argon. Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C). Cap with septum: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)
II. Synthesis of starting materials

Substrates 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1j, 1k, and 1m were prepared according to the literature [1-5]. Substrates 1h and 1l, were purchased from commercial sources (Alfa, TCI, Energy and Macklin) and used as received.

Procedure for the synthesis of N-(trifluoromethylthio)phthalimide (3)[6]

Under argon, dried CH$_3$CN (40 mL) was added to a mixture of N-bromophthalimide (5.2 g, 23 mmol), AgSCF$_3$ (6.25 g, 30 mmol) in a 100 mL round-bottomed flask. The mixture was stirred at room temperature for 3 h and then the solvent was evacuated under rotary evaporator. Before filtering the residue through a short plug of Celite, CH$_2$Cl$_2$ (20 mL) was added. Then, the filter residue was evacuated again under reduced pressure to obtain the target compound as a white solid (5.3 g, 93%). N-(trifluoromethylthio)phthalimide (3) $^1$H NMR (500 MHz, chloroform-d) $\delta$ 8.02 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.87 (dd, $J = 5.5$, 3.1 Hz, 2H). $^{19}$F NMR (471 MHz, chloroform-d) $\delta$ $-$48.89.
### III. Optimization of the reaction conditions

#### Table S1. Optimization of solvent

| Entry | Solvent | Yield of 4c (%) |
|-------|---------|----------------|
| 1     | MeCN    | 16             |
| 2     | Acetone | n.r.           |
| 3     | DMA     | n.r.           |
| 4     | EA      | 3              |
| 5     | DCM     | 1              |
| 6     | THF     | n.r.           |
| 7     | DMF     | 8              |
| 8     | DMSO    | 20             |
All reactions were carried out with 1a (0.1 mmol, 1 equiv), 2a (0.1 mmol, 1 equiv), 3 (1.2 equiv), K₂HPO₄ (2 equiv), photocatalyst 4CzIPN (2 mol %) in solvent (1.0 mL) at rt under Ar and 60 W blue LEDs.

Crude yields were determined by ¹⁹F NMR using trifluoromethoxybenzene as internal standard.

**Table S2. Optimization of base**

| Entry | Base         | Yield of 4c[b](%): |
|-------|--------------|--------------------|
| 1     | LiOAc        | n.r.               |
| 2     | K₂HPO₄       | 25                 |
| 3     | KOOCH        | n.r.               |
| 4     | KF           | n.r.               |
| 5     | K₃PO₄       | 21                 |
| 6     | K₂CO₃       | trace              |
| 7     | Et₃CN        | n.r.               |
| 8     | NaH₂PO₄      | 20                 |

[a] All reactions were carried out with 1a (0.1 mmol, 1 equiv), 2a (0.1 mmol, 1 equiv), 3 (1.2 equiv), photocatalyst 4CzIPN (2 mol %) in DMSO (1.0 mL) at rt under Ar and 60 W blue LEDs.

[b] Crude yields were determined by ¹⁹F NMR using trifluoromethoxybenzene as internal standard.
Table S3. Optimization of the light source <sup>a</sup>

| Entry | Light source | Yield of 4c <sup>b</sup>(%) |
|-------|--------------|----------------------------|
| 1     | CFL          | n.r.                       |
| 2     | 10 W         | 32                         |
| 3     | 30 W         | 17                         |
| 4     | 60 W         | 21                         |
| 5     | 90 W         | 14                         |

[a] All reactions were carried out with 1a (0.1 mmol, 1 equiv), 2a (0.1 mmol, 1 equiv), 3 (1.2 equiv), K₂HPO₄ (2 equiv), photocatalyst 4CzIPN (2 mol %) in DMSO (1.0 mL) at rt under Ar and LEDs.

[b] Crude yields were determined by <sup>19</sup>F NMR using trifluoromethoxybenzene as internal standard.

Table S4. Optimization the amount of base <sup>a</sup>

| Entry | K₂HPO₄ ( eq ) | Yield of 4c <sup>b</sup>(%) |
|-------|---------------|----------------------------|
| 1     | 0             | 0                          |
| 2     | 0.1           | 53                         |
| 3     | 0.2           | 52                         |
| 4     | 1             | 39                         |
| 5     | 2             | 32                         |
| 6     | 3             | 28                         |
[a] All reactions were carried out with 1a (0.1 mmol, 1 equiv), 2a (0.1 mmol, 1 equiv), 3 (1.2 equiv), K₂HPO₄, photocatalyst 4CzIPN (2 mol %) in DMSO (1.0 mL) at rt under Ar and 10 W blue LEDs.

[b] Crude yields were determined by ¹⁹F NMR using trifluoromethoxybenzene as internal standard.

Table S5. Optimization of the amount of 2a and 3

| Entry | 3 (eq) | 2a   | Yield of 4c [b](%) |
|-------|--------|------|-------------------|
| 1     | 1.5    | 1    | 68                |
| 2     | 1.5    | 0.8  | 60                |
| 3     | 1.2    | 0.8  | 65                |
| 4     | 2      | 1    | 60                |
| 5     | 1      | 1    | 34                |

[a] All reactions were carried out with 1a (0.1 mmol, 1 equiv), 2a, 3, K₂HPO₄ (10 mol %), photocatalyst 4CzIPN (2 mol %) in DMSO (1.0 mL) at rt under Ar and 10 W blue LEDs.
[b] Crude yields were determined by ¹⁹F NMR using trifluoromethoxybenzene as internal standard.

IV. Experimental procedures

General procedure

Under argon, 4CzIPN (2 mol %) and N-(trifluoromethylthio)phthalimide (3, 1.5 equiv), 1a (0.2 mmol, 1 equiv), 2a (0.2 mmol, 1 equiv), and K₂HPO₄ (10 mol %) were dissolved in dried DMSO (2 mL) at room temperature. After that, the tube was exposed to 10 W blue LEDs and the mixture was stirred at room temperature for about 24 h until the reaction was completed as monitored by TLC analysis. Then, the reaction solution was poured into 10 mL of water. The aqueous phase was extracted with EA (3 × 15 mL). The combined organic phases were washed with 15 mL of water and 15 mL of brine. After drying over Na₂SO₄ and removal of the solvent in vacuo, the crude products were directly purified by flash chromatography on silica gel to give the desired product.
V. Mechanistic investigations

The GC–MS of the reaction mixture
VI. Characterization data

4,4,5,5-Tetramethyl-2-(2-(phenylthio)-3-((trifluoromethyl)thio)propyl)-1,3,2-dioxaborolane (4a)

Following the general procedure, 4a was purified by silica gel chromatography (EA/PE = 1/80); 52.9 mg (70%); yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51 – 7.45 (m, 2H), 7.36 – 7.28 (m, 3H), 3.56-3.49 (m, J = 7.5, 5.6 Hz, 1H), 3.18 (dd, J = 13.4, 5.4 Hz, 1H), 3.03 (dd, J = 13.4, 7.6 Hz, 1H), 1.36 (dd, J = 15.9, 6.9 Hz, 1H), 1.28 (s, 12H), 1.20 (dd, J = 15.9, 7.9 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 133.5, 132.9, 131.1 (q, J = 306.2 Hz), 129.0, 127.9, 83.7, 44.8, 36.6 (q, J = 1.8 Hz), 24.8, 24.8, 16.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -40.88.

HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{16}$H$_{22}$BF$_3$NaO$_2$S$_2$ 401.0998; found 401.0998.

2-(2-((4-(tert-Butyl)phenyl)(thio))-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)

Following the general procedure, 4b was purified by silica gel chromatography (EA/PE = 1/80); 52.1 mg (60%); yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.38 (m, 2H), 7.37 – 7.30 (m, 2H), 3.56 – 3.37 (m, 1H), 3.18 (dd, J = 13.3, 5.6 Hz, 1H), 3.04 (dd, J = 13.4, 7.4 Hz, 1H), 1.39 – 1.33 (m, 1H), 1.31 (s, 9H), 1.28 (s, 12H), 1.25 – 1.16 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.4, 133.8, 131.1 (q, J = 306.3 Hz), 128.9, 126.1, 83.6, 44.9, 36.6 (q, J = 2.0 Hz), 34.6, 31.2, 30.9, 24.8, 24.8, 16.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -40.85.

HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{20}$H$_{30}$BF$_3$NaO$_2$S$_2$ 457.1625; found 457.1626.

4,4,5,5-Tetramethyl-2-(2-(p-tolylthio)-3-((trifluoromethyl)thio)propyl)-1,3,2-dioxaborolane (4c)

Following the general procedure, 4c was purified by silica gel chromatography (EA/PE = 1/80); 53.3 mg (68%); yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 3.51 – 3.38 (m, 1H), 3.15 (dd, J = 13.3, 5.6 Hz, 1H), 3.02 (dd, J = 13.3, 7.4 Hz, 1H), 2.34 (s, 3H), 1.33 (dd, J = 15.9, 7.0 Hz, 1H), 1.28 (s, 12H), 1.18 (dd, J = 16.0, 8.0 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.2, 134.1, 131.1 (q, J = 306.4 Hz), 129.8, 128.9, 83.6, 45.0, 36.6 (q, J = 1.8 Hz), 24.8, 24.8, 21.1, 16.7. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -40.88. HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{17}$H$_{24}$BF$_3$NaO$_2$S$_2$ 416.1155; found 415.1152.
2-(2-((4-Bromophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)

Following the general procedure, 4d was purified by silica gel chromatography (EA/PE = 1/80); 52.9 mg (58%); yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 3.54 – 3.44 (m, 1H), 3.16 (dd, $J = 13.5$, 5.6 Hz, 1H), 3.03 (dd, $J = 13.5$, 7.5 Hz, 1H), 1.36 (dd, $J = 16.0$, 6.9 Hz, 1H), 1.27 (s, 12H), 1.19 (dd, $J = 16.0$, 8.0 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 134.9, 134.5, 131.0(q, $J = 306.2$ Hz), 132.2, 122.3, 83.7, 45.1, 36.6 (q, $J = 1.9$ Hz), 24.8, 24.8, 16.8. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -40.85. HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{16}$H$_{21}$BBrF$_3$NaO$_2$S$_2$ 479.0104; found 479.0103.

2-(2-((3,5-Dichlorophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(4e)

Following the general procedure, 4e was purified by silica gel chromatography (EA/PE = 1/80); 57.9 mg (65%); yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33 (d, $J = 1.9$ Hz, 2H), 7.27 – 7.24 (m, 1H), 3.62 – 3.55 (m, 1H), 3.21 (dd, $J = 13.7$, 5.4 Hz, 1H), 3.07 (dd, $J = 13.7$, 7.7 Hz, 1H), 1.40 (dd, $J = 16.1$, 6.8 Hz, 1H), 1.27 (d, $J = 2.4$ Hz, 12H), 1.21 (dd, $J = 16.1$, 7.9 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.4, 135.2, 130.9 (q, $J = 306.5$ Hz), 129.8, 127.6, 83.9, 45.0, 36.6 (q, $J = 1.6$ Hz), 24.8, 16.8. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -40.79. HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{16}$H$_{20}$BCl$_2$F$_3$NaO$_2$S$_2$ 469.0219; found 469.0220.

2-(2-((2-Fluorophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f)

Following the general procedure, 4f was purified by silica gel chromatography (EA/PE = 1/80); 43.6 mg (55%); yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53-7.46 (m, 1H), 7.34 – 7.28 (m, 1H), 7.17 – 7.04 (m, 2H), 3.64-3.54 (m, 1H), 3.19 (dd, $J = 13.6$, 5.2 Hz, 1H), 3.04 (dd, $J = 13.6$, 7.6 Hz, 1H), 1.36 (dd, $J = 16.0$, 7.3 Hz, 1H), 1.25 (s, 12H), 1.21 (dd, $J = 16.1$, 7.4 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 162.7 (d, $J = 246.8$ Hz), 136.1, 131.0 (q, $J = 306.3$ Hz), 130.4 (d, $J = 8.0$ Hz), 124.6 (d, $J = 4.0$ Hz), 119.9 (d, $J = 18.4$ Hz), 116.0 (d, $J = 23.1$ Hz), 83.7, 44.3 (q, $J = 1.8$ Hz), 36.6, 24.8, 24.8, 16.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -40.94, -106.54, -106.63 (m, 3H, J = 7.6, 0.4 Hz). HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{16}$H$_{22}$BF$_3$NaO$_2$S$_2$ 419.0904; found 419.0902.
Following the general procedure, 4g was purified by silica gel chromatography (EA/PE = 1/80); 56.0 mg (68%); yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.44 – 7.37\) (m, 2H), 7.32-7.27 (m, 2H), 3.55 – 3.43 (m, 1H), 3.15 (dd, \(J = 13.5, 5.6\) Hz, 1H), 3.03 (dd, \(J = 13.4, 7.4\) Hz, 1H), 1.35 (dd, \(J = 16.0, 6.9\) Hz, 1H), 1.27 (s, 12H), 1.18 (dd, \(J = 15.9, 8.0\) Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 134.8, 134.2, 131.4, 131.0\) (q, \(J = 306.3\) Hz), 129.2, 83.7, 45.2, 36.5 (q, \(J = 1.9\) Hz), 24.8, 24.8, 16.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -40.88\). HRMS(ESI) m/z: [M] calcld for C\(_{16}\)H\(_{22}\)BClF\(_3\)O\(_2\)S\(_2\) 413.0789; found 413.0789.

Following the general procedure, 5a was purified by silica gel chromatography (EA/PE = 1/80); 67.7 mg (78%); colourless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.01 – 7.92\) (m, 2H), 7.49 – 7.38 (m, 4H), 7.34-7.29 (m, \(J = 4.0, 1.7\) Hz, 3H), 4.37 (t, \(J = 6.2\) Hz, 2H), 3.32-3.24 (m, 1H), 3.21 (dd, \(J = 13.6, 5.3\) Hz, 1H), 2.94 (dd, \(J = 13.5, 8.3\) Hz, 1H), 2.21 – 2.08 (m, 1H), 2.06 – 1.92 (m, 2H), 1.72 – 1.61 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 165.7, 139.4, 133.3, 132.2, 130.9\) (q, \(J = 306.4\) Hz), 130.9, 129.2, 128.7, 128.6, 128.1, 64.5, 48.1, 35.0 (q, \(J = 1.8\) Hz), 29.2, 26.1. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta -40.84\). HRMS(ESI) m/z: [M + Na]\(^+\) calcld for C\(_{19}\)H\(_{18}\)ClF\(_3\)NaO\(_2\)S\(_2\) 457.0281; found 457.0279.
5-(Phenythio)-6-((trifluoromethyl)thio)hexyl 4-methylbenzoate (5b)

Following the general procedure, 5b was purified by silica gel chromatography (EA/PE = 1/80); 56.5 mg (66%); colourless oil. 1H NMR (400 MHz, CDCl3) δ 7.97 – 7.90 (m, 2H), 7.47 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 7.26-7.21 (m, 2H), 4.32 (t, J = 6.0 Hz, 2H), 3.33 – 3.20 (m, 1H), 3.17 (dd, J = 13.4, 5.2 Hz, 1H), 2.94 (dd, J = 13.4, 8.1 Hz, 1H), 2.40 (s, 3H), 1.96 – 1.72 (m, 4H), 1.71 – 1.56 (m, 2H). 13C NMR (126 MHz, CDCl3) δ 166.6, 143.5, 133.2, 132.6, 130.9 (q, J = 306.4 Hz), 129.5, 129.1, 129.0, 127.6, 64.4, 48.3, 35.0 (q, J = 1.8 Hz), 32.3, 28.4, 23.4, 21.6. 19F NMR (376 MHz, CDCl3) δ -40.87. HRMS(ESI) m/z: [M + Na]+ calcd for C23H23F3NaO2S2 451.0984; found 451.0983

4-(Phenythio)-5-((trifluoromethyl)thio)pentyl 3,5-dimethylbenzoate (5c)

Following the general procedure, 5c was purified by silica gel chromatography (EA/PE = 1/80); 61.6 mg (72%); colourless oil. 1H NMR (400 MHz, CDCl3) δ 7.66 (s, 2H), 7.48 – 7.41 (m, 2H), 7.33-7.28 (m, 3H), 7.20 (s, 1H), 4.36 (t, J = 6.2 Hz, 2H), 3.35-3.26 (m, 1H), 3.21 (dd, J = 13.5, 5.3 Hz, 1H), 2.96 (dd, J = 13.5, 8.2 Hz, 1H), 2.36 (s, 6H), 2.23 – 2.09 (m, 1H), 2.08 – 1.91 (m, 2H), 1.75 – 1.59 (m, 1H). 13C NMR (126 MHz, CDCl3) δ 166.9, 138.0, 134.6, 133.3, 132.2, 130.9 (q, J = 306.4 Hz), 130.0, 129.2, 128.1, 127.3, 64.1, 48.1, 35.0 (q, J = 2.1 Hz), 29.2, 26.1, 21.1. 19F NMR (376 MHz, CDCl3) δ -40.85. HRMS(ESI) m/z: [M + Na]+ calcd for C23H23F3NaO2S2 451.0984; found 451.0980.

5-(Phenythio)-6-((trifluoromethyl)thio)hexyl 2-naphthoate (5d)

Following the general procedure, 5d was purified by silica gel chromatography (EA/PE = 1/80); 62.2 mg (67%); colourless oil. 1H NMR (500 MHz, CDCl3) δ 8.63 (s, 1H), 8.10-8.06 (m, 1H), 7.98-7.04 (m, 1H), 7.91-7.86 (m, 2H), 7.62-7.52 (m, 2H), 7.48-7.43 (m, 2H), 7.36 – 7.27 (m, 3H), 4.42 (t, J = 6.3 Hz, 2H), 3.32-3.25 (m, 1H), 3.20 (dd, J = 13.5, 5.2 Hz, 1H), 2.97 (dd, J = 13.5, 8.2 Hz, 1H), 1.98 – 1.79 (m, 4H), 1.75 – 1.65 (m, 2H). 13C NMR (126 MHz, CDCl3) δ 166.7, 135.5, 133.1, 132.6, 132.5, 131.0, 131.0 (q, J = 306.4 Hz), 129.3, 129.2, 128.2, 128.1, 128.0, 127.7, 127.5, 126.6, 125.2, 64.7, 48.3, 35.0 (q, J = 1.8 Hz), 32.3, 28.4, 23.4. 19F NMR (471 MHz, CDCl3) δ -40.82. HRMS(ESI) m/z: [M + Na]+ calcd for C24H24F3NaO3S2 487.0984; found 487.0986.
(5-(3-Bromophenoxy)-1-((trifluoromethyl)thio)pentan-2-yl)(phenyl)sulfane(5e)

Following the general procedure, 5e was purified by silica gel chromatography (EA/PE = 1/80); 54.9 mg (61%); colourless oil. 1H NMR (500 MHz, CDCl3) δ 7.51 – 7.43 (m, 2H), 7.38 – 7.29 (m, 3H), 7.14 (t, J = 8.0 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.85 - 6.80 (m, 1H), 3.99 (t, J = 3.9 Hz, 2H), 3.35-3.25 (m, 1H), 3.20 (dd, J = 13.5, 5.4 Hz, 1H), 2.97 (dd, J = 13.5, 8.1 Hz, 1H), 2.20-2.09 (m, 1H), 2.07 – 1.92 (m, 2H), 1.80 – 1.63 (m, 1H). 13C NMR (126 MHz, CDCl3) δ 159.6, 133.3, 132.4, 130.9 (q, J = 306.5 Hz), 130.5, 129.2, 128.1, 123.8, 122.8, 117.7, 113.5, 67.5, 48.3, 35.1 (q, J = 1.8 Hz), 29.4, 26.5. 19F NMR (376 MHz, CDCl3) δ -40.87. HRMS(ESI) m/z: [M + Na]+ calcd for C18H18BrF3NaOS2 472.9827; found 472.9826.

2-Phenyl-3-((4-(phenylthio)-5-((trifluoromethyl)thio)pentyl)oxy)-4H-chromen-4-one(5f)

Following the general procedure, 5f was purified by silica gel chromatography (EA/PE = 1/10); 61.9 mg (65%); colourless oil. 1H NMR (400 MHz, CDCl3) δ 8.27 (dd, J = 8.0, 1.7 Hz, 1H), 8.13 – 8.04 (m, 2H), 7.72 – 7.66 (m, 1H), 7.57 – 7.48 (m, 4H), 7.44 – 7.38 (m, 3H), 7.36 – 7.27 (m, 3H), 4.12 – 4.07 (m, 2H), 3.31 – 3.20 (m, 1H), 2.11 – 1.99 (m, 1H), 1.97 – 1.81 (m, 2H), 1.65 – 1.56 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 175.1, 156.0, 155.3, 140.4, 133.4, 133.2, 132.6, 131.0 (q, J = 306.3 Hz), 131.0, 130.7, 129.1, 128.7, 128.4, 127.9, 125.8, 124.7, 124.2, 118.0, 72.0, 48.3, 35.1 (q, J = 2.3 Hz), 29.6, 27.5. 19F NMR (376 MHz, CDCl3) δ -40.92. HRMS(ESI) m/z: [M + Na]+ calcd for C27H23BrF3NaO3S2 539.0933; found 539.0930.

(4-(3-Methoxyphenoxy)-1-((trifluoromethyl)thio)butan-2-yl)(phenyl)sulfane(5g)

Following the general procedure, 5g was purified by silica gel chromatography (EA/PE = 1/40); 52 mg (67%); colourless oil. 1H NMR (500 MHz, CDCl3) δ 7.52 – 7.45 (m, 2H), 7.39 – 7.31 (m, 3H), 7.22 (t, J = 8.2 Hz, 1H), 6.58 - 6.53 (m, 2H), 6.50 (t, J = 2.4 Hz, 1H), 4.30 – 4.17 (m, 2H), 3.83 (s, 3H), 3.65-3.55 (m, 1H), 3.26 (dd, J = 13.6, 5.5 Hz, 1H), 3.11 (dd, J = 13.5, 7.9 Hz, 1H), 2.39-2.30 (m 1H), 2.07-1.98 (m, 1H). 13C NMR (126 MHz, CDCl3) δ 160.8, 159.8, 133.2, 132.4, 131.0 (q, J = 306.5 Hz), 129.9, 129.2, 128.1, 106.7, 106.5, 101.0, 64.7, 55.3, 45.6, 35.2 (q, J = 1.8 Hz), 32.5. 19F NMR (471 MHz, CDCl3) δ -40.90. HRMS(ESI) m/z: [M + Na]+ calcd for C19H19F3NaO3S2 461.0671; found 411.0670.
Phenyl(4-phenyl-1-((trifluoromethyl)thio)butan-2-yl)sulfane (5h)

Following the general procedure, 5h was purified by silica gel chromatography (EA/PE = 1/80); 53.4 mg (78%); colourless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.47 – 7.41\) (m, 2H), 7.36 – 7.28 (m, 5H), 7.24 – 7.19 (m, 3H), 3.26 – 3.13 (m, 2H), 3.01 – 2.93 (m, 2H), 2.88 – 2.77 (m, 1H), 2.22 – 2.09 (m, 1H), 1.92 – 1.80 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 140.8, 133.2, 132.5, 130.9\) (q, \(J = 306.5\) Hz), 129.2, 128.5, 128.4, 128.0, 126.2, 47.6, 35.1, 34.2, 32.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -40.91\). HRMS(ESI) m/z: [M + Na\(^+\)] calcd for C\(_{17}\)H\(_{17}\)F\(_3\)NaS\(_2\) 365.0616; found 365.0615.

(4-Methoxyphenyl)(4-phenyl-1-((trifluoromethyl)thio)butan-2-yl)sulfane (5i)

Following the general procedure, 5i was purified by silica gel chromatography (EA/PE = 1/80); 52.8 mg (71%); colourless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.44 – 7.40\) (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 3H), 6.90 – 6.86 (m, 2H), 3.82 (s, 3H), 3.13 (dd, \(J = 12.9, 5.6\) Hz, 1H), 3.08 – 3.01 (m, 1H), 3.01 – 2.91 (m, 2H), 2.88 – 2.79 (m, 1H), 2.12 – 2.03 (m, 1H), 1.87 – 1.77 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 160.1, 140.9, 136.4, 131.0\) (q, \(J = 306.4\) Hz), 128.5, 128.4, 126.1, 122.1, 114.7, 55.3, 48.3, 35.0 (q, \(J = 1.8\) Hz), 34.2, 32.9. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta -40.96\). HRMS(ESI) m/z: [M + Na\(^+\)] calcd for C\(_{18}\)H\(_{19}\)F\(_3\)NaOS\(_2\) 395.0721; found 395.0717.

2-(4-(Phenylthio)-5-((trifluoromethyl)thio)pentyl)isoindoline-1,3-dione (5j)

Following the general procedure, 5j was purified by silica gel chromatography (EA/PE = 1/80); 57.8 mg (68%); colourless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.88 – 7.82\) (m, 2H), 7.76 – 7.70 (m, 2H), 7.49 – 7.39 (m, 2H), 7.34 – 7.19 (m, 3H), 3.73 (t, \(J = 6.9\) Hz, 2H), 3.30 – 3.01 (m, 1H), 3.01 – 2.91 (m, 2H), 2.88 – 2.79 (m, 1H), 2.17 – 1.99 (m, 1H), 1.95 – 1.78 (m, 2H), 1.61 – 1.49 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 168.4, 134.0, 133.5, 132.2, 132.0, 130.9\) (q, \(J = 306.4\) Hz), 129.2, 128.1, 123.3, 48.2, 37.4, 35.0 (q, \(J = 2.1\) Hz), 29.9, 25.9. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta -40.94\). HRMS(ESI) m/z: [M + Na\(^+\)] calcd for C\(_{20}\)H\(_{18}\)F\(_3\)NNaO\(_2\)S\(_2\) 448.0623; found 448.0624.

5-(Phenylthio)-6-((trifluoromethyl)thio)hexyl 4-methylbenzenesulfonate (5k)

Following the general procedure, 5k was purified by silica gel chromatography (EA/PE = 1/8); 44.5 mg (48%); colourless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.3\) (d, \(J = 8.3\) Hz, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.29 (m, 5H), 4.05 (t, \(J = 6.0\) Hz, 2H), 3.21 – 3.06 (m, 2H), 2.96 – 2.81 (m, 1H), 2.44 (s, 3H), 1.82 – 1.61
(8R,9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-
dodecahydro-3H-cyclopenta[a]phenanthren-17-yl 10-(phenylthio)-11-
((trifluoromethyl)(thio)undecanoate (5I)

Following the general procedure, 5I was purified by silica gel chromatography (EA/PE = 1/40); 59.6 mg (45%); colourless oil. $\text{^1H NMR (400 MHz, CDCl}_3\) \delta 7.47 - 7.23 (m, 4H), 7.04 (d, $J = 10.2$ Hz, 1H), 6.23 (dd, $J = 10.1, 1.9$ Hz, 1H), 6.07 (t, $J = 1.6$ Hz, 1H), 4.64 - 4.55 (m, 1H), 3.29-3.20 (m, 1H), 3.16 (dd, $J = 13.4, 5.2$ Hz, 1H), 2.94 (dd, $J = 13.4, 8.1$ Hz, 1H), 2.53-2.43 (m, 1H), 2.40-2.35 (m, 1H), 2.30 (t, $J = 7.5$ Hz, 2H), 2.23 - 2.11 (m, 1H), 2.00 - 1.91 (m, 1H), 1.86 - 1.44 (m, 13H), 1.42 - 1.35 (m, 1H), 1.31 (s, 7H), 1.26 (s, 1H), 1.23 (s, 3H), 1.22-1.16 (m, 1H), 1.12 - 0.98 (m, 3H), 0.87 (s, 3H). $\text{^{13}C NMR (126 MHz, CDCl}_3\) \delta 186.3, 173.7, 168.8, 155.6, 132.9, 132.9, 131.0 (q, $J = 306.5$ Hz), 129.1, 127.8, 127.5, 123.9, 82.0, 52.1, 49.8, 48.3, 43.5, 42.7, 36.5, 35.3, 35.0 (q, $J = 1.7$ Hz), 34.4, 33.0, 32.7, 32.6, 29.2, 29.1, 29.0, 27.4, 26.6, 25.0, 23.6, 22.3, 18.7, 12.1. $\text{^{19}F NMR (376 MHz, CDCl}_3\) \delta -40.88. HRMS(ESI) m/z: [M + H]$^+$ calcd for C$_{37}$H$_{50}$F$_3$O$_9$S$_2$ 663.3148; found 663.3147.

(3aS,5S,6R,6aS)-5-((S)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro-
furo[2,3-d][1,3]dioxol-6-yl 4-(phenylthio)-5-((trifluoromethyl)(thio)pentanoate (5m)

Following the general procedure, 5m was purified by silica gel chromatography (EA/PE = 1/40); 80.6 mg (73%); colourless oil. $\text{^1H NMR (400 MHz, CDCl}_3\), the mixture of diastereomers} \delta 7.47-7.42 (m, 2H), 7.37 - 7.30 (m, 3H), 5.90-5.85 (m, 1H), 5.32-5.25 (m, 1H), 4.53-4.44 (m, 1H), 4.25-4.17 (m 2H), 4.12 - 4.00 (m, 2H), 3.35-3.25 (m,1H), 3.23-3.15(m,1H), 3.00-2.88 (m, 1H), 2.77-2.60 (m, 2H), 2.29 - 2.16 (m, 1H), 1.93 - 1.75 (m, 1H), 1.52 (s, 3H), 1.44-1.38 (m, 3H), 1.34-1.27 (m, 6H). $\text{^{19}F NMR (376 MHz, CDCl}_3\) \delta -40.92, -40.94. $\text{^{13}C NMR (126 MHz, CDCl}_3\), the mixture of diastereomers} \delta 171.26, 133.48 & 133.54, 131.99 & 131.70, 130.82 (q, $J=307.4$Hz), 130.80 (q, $J=307.4$Hz), 129.25, 128.33 & 128.23, 112.26, 109.35, 105.01, 83.27, 79.77 & 79.76, 76.22 & 76.21, 72.40 & 72.38, 67.28 & 67.26, 47.88, 35.14-34.98 (m, the carbon of $\alpha$-SCF$_3$), 31.43 & 31.35, 27.80 & 27.66, 26.84 & 26.83, 26.67, 26.14 & 26.13, 25.19 & 25.17. HRMS(ESI) m/z: [M + Na]$^+$ calcd for C$_{42}$H$_{51}$F$_3$NaO$_9$S$_2$ 575.1356; found 575.1349.
VII. Spectral data

4,4,5,5-Tetramethyl-2-(2-(phenylthio)-3-((trifluoromethyl)thio)propyl)-1,3,2-dioxaborolane (4a)
2-(2-((4-(tert-Butyl)phenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)
4,4,5,5-Tetramethyl-2-(2-(p-tolylthio)-3-((trifluoromethyl)thio)propyl)-1,3,2-dioxaborolane (4c)
2-(2-((4-Bromophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)
2-(2-((3,5-Dichlorophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(4e)
2-(2-((2-Fluorophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g)
2-(2-((4-Chlorophenyl)thio)-3-((trifluoromethyl)thio)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(4g)
4,4,5,5-Tetramethyl-2-(3-(phenylthio)-4-((trifluoromethylthio)butyl)-1,3,2-dioxaborolane(4h)
4-(Phenylthio)-5-((trifluoromethyl)thio)pentyl 4-chlorobenzoate (5a)
5-(Phenylthio)-6-((trifluoromethyl)thio)hexyl 4-methylbenzoate (5b)
4-(Phenylthio)-5-((trifluoromethyl)thio)penty1 3,5-dimethylbenzoate (5c)
5-(Phenylthio)-6-((trifluoromethyl)thio)hexyl 2-naphthoate (5d)
(5-(3-Bromophenoxy)-1-((trifluoromethyl)thio)pentan-2-yl)(phenyl)sulfane (5e)
2-Phenyl-3-((4-(phenylthio)-5-((trifluoromethyl)thio)pentyl)oxy)-4H-chromen-4-one (5f)
(4-(3-Methoxyphenoxy)-1-((trifluoromethyl)thio)butan-2-yl)(phenyl)sulfane (5g)
Phenyl(4-phenyl-1-((trifluoromethyl)thio)butan-2-yl)sulfane (5h)
(4-Methoxyphenyl)(4-phenyl-1-((trifluoromethyl)thio)butan-2-yl)sulfane (5i)
2-(4-(Phenylthio)-5-((trifluoromethyl)thio)pentyl)isoindoline-1,3-dione (5j)
5-(Phenylthio)-6-((trifluoromethyl)thio)hexyl 4-methylbenzenesulfonate (5k)
(8R,9S,10R,13S,14S)-10,13-dimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3H-cyclopenta[a]phenanthren-17-yl 10-(phenylthio)-11-((trifluoromethyl)thio)undecanoate (5l)
(3aS,5S,6R,6aS)-5-((S)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-(phenylthio)-5-((trifluoromethyl)thio)pentanoate (5m)
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