A highly efficient approach for the synthesis of novel trifluoroacetylated enaminones using DBU as a base

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1. General Information

All solvents and chemicals were obtained commercially and were used as received. Organic solvents were purified and dried by standard methods. All the reactions were performed in an oven-dried Schlenk flask under nitrogen atmosphere. Column chromatography was performed using silica gel (100-200 mesh). Analytical TLC were performed with Merck TLC aluminium sheet silica gel 60 F254 and visualized by either UV irradiation or by staining with I2. Crystal structure analysis was accomplished on single crystal X-ray diffractometer. The synthesized compounds were characterized with analytical techniques. All melting points were determined on Electro-thermal IA 9000 series digital melting point apparatus and are uncorrected. IR spectra were recorded in KBr and CHCl3 on a Perkin Elmer Spectrum RX-1 FT-IR spectrophotometer in the 4000-400 cm-1 range. 1H-NMR, 13C-NMR, 19F NMR of the compounds were recorded with Jeol JNM-ECX400P at 400 MHz, 100 MHz, and 376 MHz respectively. CDCl3 was used as solvent for characterization of compounds. All chemical shifts are reported in ppm and are referenced to tetramethylsilane using residual 1H or 13C signals of the deuterated solvents as internal standards. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br s = broad singlet), coupling constants in Hertz. HRMS (ESI) were recorded with a QTOF electrospray mass spectrometer.

2. General procedure for synthesis of enaminones 2(a-s)1

Enaminones 2(a-s) were easily prepared by the direct amination reaction from α-oxoketene dithioacetals2 (1 equiv.) and substituted/unsubstituted aromatic, aliphatic or cyclic amines (1.25 equiv.) refluxing in toluene at 120°C until starting material had been completely consumed (as determined by TLC) and was allowed to cool to room temperature. After the addition of water (20ml) mixture was extracted with ethyl acetate (3 × 20 mL) and organic layer was separated. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100-200 mesh size; EtOAc–hexane, 3%) and pure compound was identified as single (E)-stereoisomeric forms on the basis of previously reported findings in literature3.
Analytical data for the compounds 2(a-s)

The compound 2a-d, 2g-k, were reported in literature\(^3\)

\((E)-1-(4\text{-bromo} \text{phenyl})-3-(3\text{-fluorophenyl} \text{amino})-3\text{-methylthio} \text{prop-2-en-1-one}(2e)\)

![Chemical structure of 2e]

The compound was obtained as a light yellow solid; mp 96-98\(^0\)C; Yield: (0.48g) 80\%; IR (\(\nu_{max} \text{cm}^{-1}\)) (CHCl\(_3\)): 3448, 2926, 1585, 1438; \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta: 13.48 \text{ (br s, 1H, -NH)}, 7.69 \text{ (dd, } J = 6.1, 2.29 \text{Hz, 2H)}, 7.50 \text{ (dd, } J = 6.10, 2.29 \text{Hz, 2H)}, 7.28\text{-}7.23 \text{ (m, 1H), 7.03\text{-}7.00 \text{ (m, 2H), 6.88 \text{ (t, } J = 8.39 \text{Hz, 1H)}, 5.77 \text{ (s, 1H, vinylic CH)}, 2.39 \text{ (s, 3H, -SCH}_3\text{);} \text{ }\text{\textsuperscript{13}C NMR} (100 \text{ MHz, CDCl}_3) \delta: 184.90, 167.52, 163.94, 161.48, 139.95 \text{ (d, } J = 10.54), 138.70, 131.55, 130.28, 128.64, 125.75, 120.59, 113.22 \text{ (d, } J = 21.09), 112.21 \text{ (d, } J = 23.96 \text{Hz), 88.88 \text{ (vinylic CH), 14.81 (-SCH}_3\text{).} \text{HRMS} (\text{ESI}): m/z [M + H]^+ \text{ calcd for C}_{16}\text{H}_{13}\text{BrFNOS: 365.9963; found: 365.9952.}

\((E)-1-(4\text{-bromo} \text{phenyl})-3-(2\text{-fluorophenyl} \text{amino})-3\text{-methylthio} \text{prop-2-en-1-one}(2f)\)

![Chemical structure of 2f]

The compound was obtained as a light brown solid; mp 84-86\(^0\)C; Yield: (0.49g) 82\%; IR (\(\nu_{max} \text{cm}^{-1}\)) (CHCl\(_3\)): 3445, 2925, 1563, 1472; \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta: 13.26 \text{ (br s, 1H, -NH)}, 7.77 \text{ (d, } J = 8.39 \text{Hz, 2H)}, 7.55 \text{ (d, } J = 9.16 \text{Hz, 2H}), 7.43 \text{ (dd, } J = 9.40, 1 \text{H), 7.25\text{-}7.23 \text{ (m, 1H), 7.16 \text{ (dd, } J = 9.16 \text{Hz, 1H)}, 5.86 \text{ (s, 1H, vinylic CH), 2.44 \text{ (s, 3H, -SCH}_3\text{);} \text{ }\text{\textsuperscript{13}C NMR} (100 \text{ MHz, CDCl}_3) \delta: 185.08, 168.58, 157.76, 155.28, 138.68, 131.50, 128.74, 128.13 \text{ (d, } J = 7.67), 126.03 \text{ (d), 125.71, 124.12, 116.27 \text{ (d, } J = 20.13), 88.82 \text{ (vinylic CH), 14.75 (-SCH}_3\text{).} \text{HRMS} (\text{ESI}): m/z [M + H]^+ \text{ calcd for C}_{16}\text{H}_{13}\text{BrFNOS: 365.9963; found: 365.9960.}
(E)-1-(4-chlorophenyl)-3-(cyclohexylamino)-3-(methylthio)prop-2-en-1-one (2l)

The compound was obtained as a off white solid, mp 62-64°C; Yield: (0.53g) 90%; **IR** (ν<sub>max</sub> cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3430, 2929, 1560, 1468; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 11.89 (br s, 1H, -NH), 7.70 (d, J = 8.39 Hz, 2H), 7.28 (d, J = 8.39 Hz, 2H), 5.49 (s, 1H, vinylic CH), 3.56-3.52 (m, 1H), 2.39 (s, 3H, -SCH<sub>3</sub>), 1.93-1.90 (m, 2H), 1.72-1.69 (m, 2H), 1.53-1.49 (m, 2H), 1.37-1.26 (m, 3H), 1.17-1.12(m, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ: 183.3, 168.3, 139.1, 136.3, 128.3, 128.1, 127.6, 85.5 (vinylic CH), 52.9, 33.0, 25.3, 24.3, 14.2 (-SCH<sub>3</sub>). **HRMS (ESI) (M+H)<sup>+</sup>** Calcd for C<sub>16</sub>H<sub>20</sub>ClNOS: 310.1032, found 310.1020.

(E)-3-(cyclohexylamino)-3-(methylthio)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (2m)

The compound was obtained as a light yellow solid, mp 65-67°C; Yield: (0.52g) 89%; **IR** (ν<sub>max</sub> cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3434, 2927, 1559, 1475; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 11.95 (bs, 1H, -NH), 8.03 (s,1H), 7.93 (d, J = 7.63 Hz, 1H), 7.58 (d, J = 7.63 Hz, 1H), 7.44 (t, J = 7.63 Hz, 1H), 5.52 (s, 1H, vinylic CH), 3.60-3.54 (m, 1H), 2.41 (s, 3H, -SCH<sub>3</sub>), 1.94-1.91 (m, 2H), 1.73-1.70 (m, 2H), 1.58-1.51 (m, 2H), 1.39-1.30 (m, 2 H),1.18-1.13(m, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ: 182.77, 168.9, 141.4, 129.9, 128.6, 128.6, 128.0, 127.6, 126.7, 123.7, 85.63 (vinylic CH), 53.0, 32.9, 25.3, 24.2, 14.2 (-SCH<sub>3</sub>). **HRMS (ESI) (M+H)<sup>+</sup>** Calcd for C<sub>17</sub>H<sub>20</sub>F<sub>3</sub>NOS: 344.1296, found 344.1296.
(E)-3-(cyclohexylamino)-1-(4-methoxyphenyl)-3-(methylthio)prop-2-en-1-one (2n)

The compound was obtained as a light brown solid, mp 72-74°C; Yield: (0.51g) 85%; IR (νmax cm⁻¹) (CHCl₃): 3436, 2927, 1560, 1468; ¹H NMR (400 MHz, CDCl₃) δ: 11.78 (br s, 1H, -NH), 7.75 (d, J = 9.16 Hz, 2 H), 6.82 (d, J = 9.16 Hz, 2 H), 5.51 (s, 1H, vinylic CH), 3.76 (s, 1H, Ar-OCH₃), 3.55-3.50 (m, 1H), 2.39 (s, 3H, -SCH₃), 1.93-1.90 (m, 2H), 1.72-1.69 (m, 3H), 1.53-1.50 (m, 1H), 1.39-1.25 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ: 184.21, 167.34, 161.46, 133.32, 128.57, 113.35, 85.35 (vinylic CH), 55.27, 52.80, 33.19, 25.36, 24.36, 14.28 (-SCH₃). HRMS (ESI) (M+H)⁺ Calcd for C₁₇H₂₃NO₂S: 306.1527, found 306.1523.

(E)-3-(cyclohexylamino)-3-(methylthio)-1-(p-tolyl)prop-2-en-1-one (2o)

The compound was obtained as a light brown solid, mp 66-68°C; Yield: (0.52g) 86%; IR (νmax cm⁻¹) (CHCl₃): 3428, 2929, 1560, 1468; ¹H NMR (400 MHz, CDCl₃) δ: 11.98 (br s, 1H, -NH), 7.68 (d, J = 8.54Hz, 2H), 7.49 (d, J = 8.54Hz 2H), 5.52 (s, 1H, vinylic CH), 3.61-3.57 (m, 1H), 2.69 (s, 3H, Ar-CH₃), 2.44 (s, 3H, -SCH₃), 1.97-1.95 (m, 2H), 1.77-1.74 (m, 2H), 1.58-1.55 (m, 1H), 1.43-1.22 (m, 5 H). ¹³C NMR (100 MHz, CDCl₃): δ = 183.48, 167.34, 161.46, 139.35, 131.32, 128.32, 124.94, 85.44 (vinylic CH), 53.16, 32.91, 25.25, 24.28, 18.53, 14.2 (-SCH₃); HRMS (ESI) (M+H)⁺ Calcd for C₁₇H₂₀F₃NOS: 344.1296, found 344.1296.

(E)-1-(4-fluorophenyl)-3-(isopropylamino)-3-(methylthio)-2-en-1-one (2p)
The compound was obtained as light brown viscous material, Yield: (0.46g) 89%; IR ($\nu_{\text{max}}$ cm$^{-1}$) (CHCl$_3$): 3328, 2925, 1558, 1458; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 11.72 (br s, 1H, -NH), 7.77 (dd, $J = 6.10$ Hz, 2H), 7.18 (t, $J = 6.87$ Hz, 2H), 5.46 (s, 1H, vinylic CH), 3.88-3.79 (m, 1H), 2.35 (s, 3H, -SCH$_3$), 1.22 (d, $J = 6.10$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 183.44, 168.20, 146.65, 128.89 (J = 8.63 Hz), 128.03, 127.57, 114.98 (d, $J = 21.09$ Hz), 85.35 (vinyllic CH), 46.08, 23.18, 22.58, 14.19 (-SCH$_3$). HRMS (ESI) (M+H)$^+$ Calcd for C$_{13}$H$_{16}$FNOS: 254.1015, found: 254.1012.

$E$)-3-(methylthio)-3-(propylamino)-1-(3-trifluoromethyl)phenyl)prop-2-en-1-one(2q)

The compound was obtained as a pale yellow viscous material, Yield: (0.46g) 90%; IR ($\nu_{\text{max}}$ cm$^{-1}$) (CHCl$_3$): 3397, 2924, 1567, 1472; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 12.03 (br s, 1H, -NH), 8.10 (s, 1H), 8.01 d, $J = 7.63$Hz, 1H), 7.66 (d, $J = 7.63$Hz, 1H), 7.50 (t, $J = 8.01$Hz, 1H) 5.55 (s, 1H, vinylic CH), 3.38 (q, 2 H, -CH$_2$CH$_2$CH$_3$), 2.47 (s, 3H, -SCH$_3$), 1.75-1.638 (m, 2H, CH$_2$CH$_2$CH$_3$), 1.04 (t, $J = 7.63$Hz, 3H, -CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 183.14, 146.39, 130.05, 128.71, 128.06, 127.60, 126.92, 125.60, 123.78, 86.44 (vinyllic CH), 46.60(-CH$_2$CH$_2$CH$_3$), 22.661(-CH$_2$CH$_2$CH$_3$), 14.25 (-SCH$_3$), 11.42 (-CH$_3$). HRMS (ESI) (M+H)$^+$ Calcd for C$_{14}$H$_{18}$F$_3$NOS: 304.0983; found: 304.0975.
(E)-1-(4-fluorophenyl)-3-(methylthio)-3-(propylamino)prop-2-en-1-one(2r)

The compound was obtained as a yellow viscous material, Yield: (0.48g) 92%; IR (ν_{max} cm^{-1}) (CHCl₃): 3394, 2927, 1567, 1473; \(^1\)H NMR (400 MHz, CDCl₃) δ: 11.82 (br s, 1H, -NH), 7.83 (dd, J = 5.34 Hz, 3.81 Hz, 2H), 7.03 (t, J = 8.39 Hz, 2H), 5.55 (s, 1H, vinylic CH), 3.32 (q, 2H, -CH₂CH₂CH₃), 2.40 (s, 3H, -SCH₃), 1.72-1.63 (m, 2H, CH₂CH₂CH₃), 1.00 (t, J = 6.87 Hz, 3H, -CH₃). HRMS (ESI) (M+H)^+ Calcd for C₁₃H₁₆FNOS: 254.1015, found 254.1026.

(E)-1-(4-chlorophenyl)-3-(methylthio)-3-(propylamino)prop-2-en-1-one(2s)

The compound was obtained as a light yellow viscous material, Yield: (0.47g) 91%; IR (ν_{max} cm^{-1}) (CHCl₃): 3384, 2923, 1560, 1471; \(^1\)H NMR (400 MHz, CDCl₃) δ: 12.03 (br s, 1H, -NH), 7.86 (t, J = 6.96 Hz, 2H), 7.06 (t, J = 8.79 Hz, 2H), 5.50 (br s, 1H, vinylic CH), 3.36 (s, 2H, -CH₂CH₂CH₃), 2.47 (s, 3H, -SCH₃), 1.76-1.71 (m, 2H, CH₂CH₂CH₃), 1.01 (t, 3H, -CH₃); \(^1\)C NMR (100 MHz, CDCl₃) δ: 184.31, 168.92, 161.45, 133.21, 128.55, 113.33, 85.45 (vinylic CH), 45.60(-CH₂CH₂CH₃), 22.81(-CH₂CH₂CH₃), 14.21 (-SCH₃), 11.42 (-CH₃); HRMS (ESI) (M+H)^+ Calcd for C₁₃H₁₆ClNOS: 270.0719, found 270.0724.
2. General procedure for synthesis of trifluoroacetylated enaminones 3(a-s)

To a solution of enaminones 2 (1 equiv.) in DCE (5 ml) was added DBU (2 equiv.) under N₂ atmosphere. TFAA (2.5 equiv.) was added dropwise over 10 mins, keeping the temperature at 0°C. When addition was completed, the mixture was allowed to slowly warm up to room temperature and stirred for 2 hrs. Reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with aqueous NaHCO₃, then washed with dilute HCl and finally water was added. Compound was extracted by DCM and organic layer was dried over anhydrous Na₂SO₄. After concentrating by rotary evaporation, solid compound was obtained which was crystallized by ether/pentane (5%) to give pure compound 3.

Analytical data for the compounds 3(a-s)

\((E)-4,4,4\text{-trifluoro-2-}\text{((methylthio)(phenylamino)methylene)-1-phenylbutane-1,3-dione (3a)}\)

\[
\text{\includegraphics[width=0.3\textwidth]{3a.png}}
\]

The compound was obtained as a white solid, mp 87-89°C; Yield: (0.36 g) 90%; IR (\(\nu_{\text{max}} \text{cm}^{-1}\)) (KBr): 3418, 1721, 1616, 1521, 1446; \(^1\text{H NMR}\) (400 MHz, CDCl₃) \(\delta\): 13.20 (br s, 1H, -NH), 7.77 (d, \(\text{J} = 8.39\text{Hz}, 3\text{H}\)), 7.55 (d, \(\text{J} = 9.16\text{Hz}, 3\text{H}\)), 7.43 (dd, \(\text{J} = 8.39\text{Hz}, 1\text{H}\)), 7.22-7.11 (m, 3H), 2.44 (s, 3H, -SCH₃); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \(\delta\): 185.08, 174.77, 168.58, 157.76, 155.28, 138.68, 128.74, 127.55, 125.71, 124.08, 116.27(d, \(\text{J = 20.13}\)), 107.0, 14.75(-SCH₃) \(^{19}\text{F NMR}\) (376 MHz, CDCl₃): \(\delta\) -70.68 (s, 3F, COCF₃); HRMS (ESI) (M+H)⁺ Calcd for C₁₈H₁₄F₃NO₂S: 366.0775 found 366.0766.

\((E)-4,4,4\text{-trifluoro-2-}(((\text{methoxyphenyl})amino)(methylthio)methylene)-1-phenylbutane-1,3-dione (3b)\)

\[
\text{\includegraphics[width=0.3\textwidth]{3b.png}}
\]
The compound was obtained as a pale yellow solid, mp 91-93°C; Yield: (0.36g) 92%; IR(ν_{max} cm^{-1}) (KBr): 3422, 2926, 1722, 1619, 1520, 1448; ^1H NMR (400 MHz, CDCl3): 13.23 (br s, 1H, -NH), 7.88 (d, J=7.63Hz, 2H), 7.50 (d, J=7.63Hz, 1H), 7.42 (t, J=7.63Hz, 2H), 7.26 (d, J=9.16Hz, 2H), 6.86 (d, J=9.16Hz, 2H), 3.75 (s, 3H, Ar-OCH3), 1.75 (s, 3H, -SCH3); ^13C NMR (100 MHz, CDCl3) δ: 192.30, 174.52, 168.21, 158.73, 139.14, 133.26, 130.12, 129.30, 128.62, 125.89, 114.80, 109.13, 55.50, 17.17 (-SCH3).

(E)-4,4,4-trifluoro-1-(4-fluorophenyl)-2-((methylthio)(phenylamino)methylene)butane-1,3-dione(3c)

![Structure 3c]

The compound was obtained as off white solid, mp 90-92°C; Yield: (0.36g) 92%; IR(ν_{max} cm^{-1}) (KBr): 3442, 2925, 1725, 1621, 1562, 1460; ^1H NMR (400 MHz, CDCl3): 13.24 (br s, 1H, -NH), 7.97 (t, J=6.87Hz, 2H), 7.41 (d, J=6.87Hz, 4H), 7.31 (s, 1H), 7.14 (t, J=7.63Hz, 2H), 1.82 (s, 3H, -SCH3); ^13C NMR (100 MHz, CDCl3) δ: 207.08, 190.71, 174.54, 167.97, 137.39, 135.54, 131.92, 131.83, 129.73, 127.52, 124.37, 115.92, 115.71, 109.47, 17.18(-SCH3). ^19F NMR (376 MHz, CDCl3): δ -70.55 (s, 3F, COCF3), -76.00(s, 1F, F-Ar); HRMS (ESI) (M+H)^+ Calcd for C_{19}H_{16}F_{4}NO_{2}S: 396.0879 found 396.0875.

(E)-1-(4-chlorophenyl)-4,4,4-trifluoro-2-((methylthio)(phenylamino)methylene)butane-1,3-dione(3d)

![Structure 3d]

The compound was obtained as a white solid, mp 87-89°C; Yield: (0.35g) 90%; IR(ν_{max} cm^{-1}) (KBr): 3440, 2924, 1723, 1616, 1558, 1438; ^1H NMR (400 MHz, CDCl3): 13.18 (br s, 1H, -NH), 7.83 (d, J=8.39Hz, 2H), 7.39 (d, J=8.39Hz, 2H), 7.35 (s, 4H), 7.26-7.23 (m, 1H), 1.76(s, 3H, -
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 191.08, 174.81, 167.97, 139.80, 137.46, 137.34, 130.62, 129.78, 129.03, 127.60, 124.40, 118.63, 115.57, 109.32, 17.21 (-SCH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -70.84 (s, 3F, COCF$_3$); HRMS (ESI) (M+H)$^+$ Calcd for C$_{18}$H$_{13}$ClF$_3$NO$_2$S: 400.0384 found 400.0379.

(E)-1-(4-bromophenyl)-4,4,4-trifluoro-2-(((3-fluorophenylamino)(methylthio)methylene)butane-1,3-dione

The compound was obtained as a light yellow solid, mp 65-67$^\circ$C; Yield: (0.33g) 88%; IR($\nu$max cm$^{-1}$) (KBr): 3432, 2916, 1721, 1620, 1560, 1454; $^1$H NMR (400 MHz, CDCl$_3$): 13.49 (br s, 1H, -NH), 7.67 (d, $J$=9.16 Hz, 2H), 7.49 (d, $J$=9.16 Hz, 2H), 7.30-7.22 (m, 2H), 7.04-7.00 (m, 2H), 2.40 (s, 3H, -SCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 185.17, 174.04, 163.94, 161.48, 131.65, 130.49, 128.72, 120.61, 115.83, 112.27(d, 23.96) 108.15(d, 26.84), 14.87 (-SCH$_3$).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -70.29 (s, 3F, COCF$_3$), -75.78 (s, 1F, Ar-F); HRMS (ESI) (M+H)$^+$ Calcd for C$_{18}$H$_{12}$BrF$_4$NO$_2$S: 461.9786 found 461.9789

(E)-1-(4-bromophenyl)-4,4,4-trifluoro-2-(((2-fluorophenylamino)(methylthio)methylene)butane-1,3-dione

The compound was obtained as a white solid, mp 54-56 $^\circ$C; Yield: (0.33g) 89%; IR($\nu$max cm$^{-1}$) (KBr): 3422, 2924, 1721, 1620, 1558, 1458; $^1$H NMR (400 MHz, CDCl$_3$): 12.78 (br s, 1H, -NH), 8.18 (dd, $J$=7.63Hz, 1.53Hz, 3H), 7.18-7.06 (m, 5H), 2.39 (s, 3H, -SCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 185.37, 174.04, 153.93, 151.49, 131.61, 128.75, 126.75, 124.92, 121.96, 106.43, 14.82 (-SCH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -70.11 (s, 3F, COCF$_3$), -75.78 (s, 1F, Ar-F); HRMS (ESI) (M+H)$^+$ Calcd for C$_{18}$H$_{12}$BrF$_4$NO$_2$S: 461.9786 found 461.9786.

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(E)-4,4,4-trifluoro-1-(4-methoxyphenyl)-2-(methylthio)(phenylamino)methylene)butane-1,3-dione (3g)

The compound was obtained as a white solid, mp 90-92\(^0\)C; Yield: (0.35g) 89\%; IR\((\nu_{\text{max}} \text{ cm}^{-1})\) (KBr): 3428, 2922, 1723, 1620, 1560, 1454; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 12.06 (br s, 1H, -NH), 7.75 (d, \(J=8.89\)Hz, 2H), 7.64 (dd, \(J=8.77\)Hz, 4H), 7.54 (d, \(J=8.39\)Hz, 3H), 2.51 (s, 3H, Ar-OCH\(_3\)), 2.27 (s, 3H, -SCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 191.20, 176.03, 168.02, 163.59, 132.41, 131.67, 129.33, 113.72, 108.16, 55.42, 19.39 (-SCH\(_3\)), \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -70.56 (s, 3F, COCF\(_3\)); HRMS (ESI) (M+H\(^+\) Calcd for C\(_{19}\)H\(_{16}\)F\(_3\)N\(_3\)O\(_3\): 396.0879, found 396.0875

(E)-1cyclopropyl-4,4-trifluoro-2-((methylthio)(phenylamino)methylene)butane-1,3-dione (3h)

The compound was obtained as off white solid, mp 108-110\(^0\)C; Yield: (0.37g) 89\%; IR\((\nu_{\text{max}} \text{ cm}^{-1})\) (KBr): 3405, 2920, 1719, 1618, 1548, 1440; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.31 (s, 5H), 2.27 (s, 3H), 1.90-1.84 (m, 1H), 1.08 (t, \(J=3.05\)Hz, 2H), 0.88 (q, \(J=3.05\)Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 194.47, 156.49, 152.00, 137.85, 129.18, 127.69, 118.67, 117.45, 114.40, 22.56, 15.64, 11.77 (-SCH\(_3\)), \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -70.52 (s, 3F, COCF\(_3\)); HRMS (ESI) (M+H\(^+\) Calcd for C\(_{19}\)H\(_{16}\)F\(_3\)N\(_2\)O\(_2\): 330.0775, found 330.0770.
(E)-4,4,4-trifluoro-2-((methylthio)(phenylamino)methylene)-1-(thiophen-2-yl)butane-1,3-dione (3i)

The compound was obtained as alight yellow solid, mp 123-125°C; Yield: (0.35g) 88%; IR(ν max cm⁻¹) (KBr): 3425, 2928, 1725, 1622, 1452, 1460; ¹H NMR (400 MHz, CDCl₃): 12.20 (br s, 1H, -NH), 7.62 (dd, J=4.20Hz, 1H), 7.42-7.26 (m, 3H), 7.02 (t, J=4.20Hz, 2H), 6.84 (s, 1H), 6.63 (s, 1H), 2.35 (s, 3H, SCH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 187.91, 178.98, 165.86, 144.89, 136.42, 135.68, 135.28, 132.45, 130.22, 129.71, 128.42, 127.74, 116.65, 114.05, 109.70, 15.47 (SCH₃); ¹⁹F NMR (376 MHz, CDCl₃): δ -71.29 (s, 3F, COCF₃); HRMS (ESI) (M+H)⁺ Calcd for C₁₆H₁₂F₃N₂O₂S₂: 372.0340, found 372.0331.

(E)-4,4,4-trifluoro-2-(((4-methoxyphenyl)amino)(methylthio)methylene)-1-(thiophen-2-yl)butane-1,3-dione (3j)

The compound was obtained as off white solid, mp 111-113°C; Yield: (0.36g) 92%; IR(ν max cm⁻¹) (KBr): 3421, 2927, 1723, 1621, 1545, 1462; ¹H NMR (400 MHz, CDCl₃): 13.22 (br s, 1H, -NH), 7.88 (d, J=4.20Hz, 1H), 7.42 (t, J=4.39Hz, 2H), 7.26 (d, J=7.63Hz, 1H), 6.86 (d, J=9.16Hz, 3H), 3.75 (s, 3H, Ar-OCH₃), 2.10 (s, 3H, -SCH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 192.30, 174.98, 168.21, 158.73, 139.14, 133.26, 130.12, 129.30, 128.62, 125.89, 114.80, 109.13, 55.50, 17.17 (-SCH₃); ¹⁹F NMR (376 MHz, CDCl₃): δ -70.21 (s, 3F, COCF₃); HRMS (ESI) (M+H)⁺ Calcd for C₁₇H₁₄F₃NO₃S₂: 402.0445 found 402.0459.
(E)-1-(4-bromophenyl)-2-((cyclohexylamino)(methylthio)methylene)-4,4,4-trifluorobutane-1,3-dione(3k)

The compound was obtained as a white solid, mp 92-94\(^\circ\)C; Yield: (0.36g) 95\%; \textbf{IR}(\nu_{\text{max}} \text{cm}^{-1}) (KBr): 3432, 2931, 1725, 1682, 1542, 1438; \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\(_3\)): 12.06 (br s, 1H, -NH), 7.75 (d, J=8.89Hz, 2H), 7.64 (dd, J=8.77Hz, 1H), 7.54 (d, J= 8.39Hz, 1H), 3.68-3.62 (m, 1H), 2.27 (s, 3H, -SCH\(_3\)); \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\(_3\)) \(\delta\): 191.53, 184.71, 168.13, 131.86, 130.71, 128.64, 115.43, 107.66, 55.25, 33.38, 32.40, 24.29, 19.46 (-SCH\(_3\)), \textbf{\textsuperscript{19}F NMR} (376 MHz, CDCl\(_3\)): \(\delta\) -70.55 (s, 3F, CO\(_{CF_3}\)); \textbf{HRMS} (ESI) (M+H\(^+\) Calcd for C\(_{18}\)H\(_{19}\)BrF\(_3\)NO\(_2\)S: 450.0350, found 450.0341.

(E)-1-(4-chlorophenyl)-2-((cyclohexylamino)(methylthio)methylene)-4,4,4-trifluorobutane-1,3-dione(3l)

The compound was obtained as a white solid, mp 108-110\(^\circ\)C; Yield: (0.36g) 94\%; \textbf{IR}(\nu_{\text{max}} \text{cm}^{-1}) (KBr): 3448, 2933, 1726, 1654, 1574, 1460; \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\(_3\)): 12.07 (br s, 1H, -NH), 7.75 (t, J=8.39Hz, 2H), 7.35 (d, J=8.39Hz, 2H), 3.95 (s, 1H, -NH\textsubscript{CH}), 2.19 (s, 3H, -SCH\(_3\)), 1.90-1.87 (m, 3H), 1.74-1.72 (m, 2H), 1.57-1.55 (m, 1H), 1.46-1.24 (m, 4H); \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\(_3\)) \(\delta\): 191.17, 174.01, 167.94, 139.44, 137.82, 130.57, 128.83, 128.64, 128.44, 118.75, 115.88, 107.74, 55.21, 33.36, 24.95, 24.16, 19.43(-SCH\(_3\)). \textbf{\textsuperscript{19}F NMR} (376 MHz, CDCl\(_3\)): \(\delta\) -70.68 (s, 3F, CO\(_{CF_3}\)); \textbf{HRMS} (ESI) (M+H\(^+\) Calcd for C\(_{18}\)H\(_{19}\)ClF\(_3\)NO\(_2\)S: 406.0855, found 406.0853.
\((E)\)-2-((cyclohexylamino)(methylthio)methylene)-4,4,4-trifluoro-1-(3-trifluoromethyl)phenyl butane-1,3-dione (3m)

The compound was obtained as a white solid, mp 107-109^\circ{}C; Yield: (0.36g) 95\%; IR\((\nu_{\text{max}}\text{cm}^{-1})\) (KBr): 3448, 2930, 1725, 1622, 1562, 1460; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 12.03 (br s, 1H, -NH), 8.07 (s, 1H), 7.98 (d, \(J=7.63\text{Hz}\), 1H), 7.73 (d, \(J=7.63\text{Hz}\), 1H), 7.53 (d, \(J=8.01\text{Hz}\), 1H), 3.95 (s, 1H, -NHCH), 2.18 (s, 3H, -SCH\(_3\)), 1.90-1.87 (m, 2H), 1.76-1.73 (m, 2H), 1.58-1.55 (m, 1H), 1.48-1.24 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 190.89, 174.27, 168.08, 140.04, 132.29, 131.45, 129.28, 129.18, 125.78, 118.63, 115.61, 107.48, 55.32, 33.36, 24.95, 24.18, 19.40 (-SCH\(_3\)). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -62.61 (s, 3F, ArCF\(_3\)), -70.44 (s, 3F, COCF\(_3\)); HRMS (ESI) (M+H)\(^{+}\) Calcd for C\(_{18}\)H\(_{19}\)ClF\(_3\)NO\(_2\): 440.119, found 440.1116.

\((E)\)-2-((cyclohexylamino)(methylthio)methylene)-4,4,4-trifluoro-1-(4-methoxyphenyl)butane-1,3-dione (3n)

The compound was obtained as a white solid, mp 92-94\(^\circ\)C; Yield: (0.35g) 90\%; IR\((\nu_{\text{max}}\text{cm}^{-1})\) (KBr): 3442, 2930, 1720, 1623, 1566, 1458; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 12.22 (br s, 1H, -NH), 7.85 (dd, \(J=7.63\text{Hz}\), 2H), 6.90 (d, \(J=7.63\text{Hz}\), 1H), 3.84 (s, 3H, Ar-OCH\(_3\)), 2.25 (s, 3H, -SCH\(_3\)), 1.95 (s, 3H), 1.95 (s, 3H), 1.78 (s, 3H), 1.46-1.30 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 191.20, 174.02, 168.02, 163.59, 132.41, 131.67, 129.33, 113.72, 108.16, 55.42, 33.38, 25.00, 24.33, 19.40 (-SCH\(_3\)). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -70.51 (s, 3F, COCF\(_3\)); HRMS (ESI) (M+H)\(^{+}\) Calcd for C\(_{19}\)H\(_{22}\)F\(_3\)NO\(_3\): 402.1350, found 402.1341.
(E)-2-((cyclohexylamino)(methylthio)methylene)-4,4,4-trifluoro-1-(p-tolyl)butane-1,3-dione (3o)

The compound was obtained as a white solid, mp 90-92°C; Yield: (0.35g) 88%; IR(νmax cm⁻¹) (KBr): 3440, 2928, 1718, 1621, 1562, 1454; 12.21 (br s, 1H, -NH), 7.85 (dd, J=7.63Hz, 2H), 6.90 (d, J=7.63Hz, 2H), 2.49 (s, 3H, Ar-CH₃), 2.25 (s, 3H, -SCH₃), 1.95 (s, 3H), 1.95-1.60 (M, 5H), 1.48-1.30 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 191.36, 173.49, 168.08, 140.04, 132.29, 131.45, 129.28, 125.78, 122.61, 107.02, 55.08, 32.80, 25.59, 24.06, 22.30, 19.40(-SCH₃), ¹⁹F NMR (376 MHz, CDCl₃): δ -70.21(s, 3F, -COCF₃); HRMS (ESI) (M+H)+ Calcd for C₁₉H₂₂F₃N₂O₂S: 386.1401, found 386.1405.

(E)-4,4,4-trifluoro-1-(4-fluorophenyl)-2-((isopropylamino)(methylthio)methylene)butane-1,3-dione(3p)

The compound was obtained as a white solid, mp 58-60°C; Yield: (0.37g) 90%; IR(νmax cm⁻¹) (KBr): 3432, 2916, 1716, 1618, 1562, 1460; ¹H NMR (400 MHz, CDCl₃): 12.01 (br s, 1H, -NH), 7.90 (dd, J=9.16Hz, 2H), 7.11 (t, J=9.16Hz, 2H), 4.35-4.28 (m, 1H), 2.26 (s, 3 H, -SCH₃), 1.35 (d, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 190.91, 174.04, 168.16, 164.31, 131.83(d, J=9.58), 129.54, 115.71(d, J=13.42Hz), 107.39, 48.70, 23.45, 22.37, 19.31(-SCH₃), ¹⁹F NMR (376 MHz, CDCl₃): δ -70.90 (s, 3F, -COCF₃), -76.18 (s, 1F, F-Ar); HRMS (ESI) (M+H)+ Calcd for C₁₅H₁₅F₄NO₂S: 350.0838, found 350.0838.
**E)-4,4,4-trifluoro-2-((methylthio)(propylamino)methylene)-1-(3-(trifluoromethyl)phenyl)butane-1,3-dione(3q)**

The compound was obtained as a white solid, mp 60-62°C; Yield: (0.37g) 95%; IR($\nu_{\text{max}}$ cm$^{-1}$) (KBr): 3418, 2903, 1723, 1562, 1464; $^1$H NMR (400 MHz, CDCl$_3$): 11.95 (br s, 1H, -NH), 8.06 (s, 1H), 7.99 (d, $J$=7.63Hz, 2H), 7.74 (d, $J$=7.63Hz, 1H), 7.54 (d, $J$=7.63Hz, 1H), 3.58 (q, $J$ = 6.10Hz, 2H), 2.15 (s, 3H, -SCH$_3$), 1.74-1.65 (m, 2H), 1.00 (t, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 190.76, 174.42, 169.21, 140.03, 132.26, 129.21, 128.08, 125.77, 115.78, 107.67, 48.06, 23.14, 18.48 (-SCH$_3$), 11.29(-CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -63.73 (s, 3F, ArCF$_3$), 71.87 (s, 3F, -COCF$_3$); HRMS (ESI) (M+H)$^+$ Calcd for C$_{16}$H$_{15}$F$_6$NO$_2$S: 400.0806, found 400.0801.

**E)-4,4,4-trifluoro-1-(4-fluorophenyl)-2-((methylthio)(propylamino)methylene)butane-1,3-dione(3r)**

The compound was obtained as a white solid, mp 68-70°C; Yield: (0.39g) 95%; IR($\nu_{\text{max}}$ cm$^{-1}$) (KBr): 3416, 2906, 1716, 1628, 1560, 1462; $^1$H NMR (400 MHz, CDCl$_3$): 12.01 (br s, 1H, -NH), 7.86 (dd, $J$=5.34Hz, 3.05Hz, 2H), 7.06 (t, $J$=8.39Hz, 2H), 3.56 (t, $J$ = 6.13Hz, 2H), 2.18 (s, 3H, -SCH$_3$), 1.73-1.64 (m, 3H), 1.00 (t, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 190.86, 173.84, 169.39, 166.97, 164.43, 135.80, 131.89, 129.35, 115.78, 115.56, 107.99, 48.02, 23.12, 18.53(-SCH$_3$), 11.31(-CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -70.19 (s, 3F, COCF$_3$), -75.80 (s, 1F, F-Ar); HRMS (ESI) (M+H)$^+$ Calcd for C$_{15}$H$_{15}$F$_6$NO$_2$S: 350.0838, found 350.0832.
(E)-4,4,4-trifluoro-1-(4-chlorophenyl)-2-((methylthio)(propylamino)methylene)butane-1,3-dione(3s)

The compound was obtained as a white solid, mp 68-70°C; Yield: (0.38g) 94%; IR(νmax cm⁻¹) (KBr): 3412, 2908, 1718, 1630, 1562, 1464; ¹H NMR (400 MHz, CDCl₃) δ: 11.82 (br s, 1H, -NH), 7.83 (dd, J = 5.34Hz, 3.81 Hz, 2H), 7.03 (t, J = 8.39Hz, 2H), 3.32 (q, J = 6.87Hz, 6.10Hz, 2H), 2.40 (s, 3H, -SCH₃), 1.72-1.63 (m, 2H, CH₂CH₂CH₃), 1.00 (t, 3H, -CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 183.46, 173.84, 169.62, 165.29, 128.89, 127.97, 115.49, 108.82, 45.60(-CH₂CH₂CH₃), 22.69(-CH₂CH₂CH₃), 14.07 (-SCH₃), 11.31 (-CH₃); ¹⁹F NMR (376 MHz, CDCl₃): δ -70.05 (s, 3F, COCF₃). HRMS (ESI) (M+H)⁺ Calcd for C₁₅H₁₅ClF₃NO₂S: 366.0542, found 366.0549.
COPIES OF $^1H$, $^{13}C$ & $^{19}F$ NMR DATA
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$\text{H-NMR in CDCl}_3 (400MHz)$

$\text{C-NMR in CDCl}_3 (100MHz)$
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^{1}H$-NMR in CDCl$_3$ (400MHz)

$^{13}C$-NMR in CDCl$_3$ (100MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
2ο

$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (400MHz)
$^{1}$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
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$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^{19}\text{F-NMR in CDCl}_3$ (376 MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)
$^{13}$C-NMR in CDCl$_3$ (100MHz)

$^{19}$F-NMR in CDCl$_3$ (376MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^{19}$F-NMR in CDCl$_3$ (376MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
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$^{19}$F-NMR in CDCl$_3$ (376MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)
$^{13}$C-NMR in CDCl$_3$ (100MHz)

$^{19}$F-NMR in CDCl$_3$ (376MHz)
3h

$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^{19}$F-NMR in CDCl$_3$ (376MHz)
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\[^19\text{F}\text{-NMR in CDCl}_3\ (376\text{MHz})\]
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$^1$H-NMR in CDCl$_3$ (400MHz)

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$^{19}$F-NMR in CDCl$_3$ (376MHz)
$^1$H-NMR in CDCl$_3$ (400MHz)

$^{13}$C-NMR in CDCl$_3$ (100MHz)
$^{19}$F-NMR in CDCl$_3$ (376MHz)
X-ray Crystallographic Studies

Figure 1. ORTEP Structure of compound 3q

The intensity data for 3q (CCDC No: 1515192) was collected on an Oxford Xcalibur CCD diffractometer equipped with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The structures was solved using SIR-92 and refined by full matrix least square technique on F2 using the SHELXL-97 program within the Wingx software package.
Table 3. Crystallographic data and structure refinement for compounds 3q

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<td><strong>Final R indices [I&gt;2sigma(I)]^a,b</strong></td>
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<td><strong>R indices (all data)</strong></td>
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<td><strong>Extinction coefficient</strong></td>
<td>0.0072(8)</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.332 and -0.258 e.Å³</td>
</tr>
</tbody>
</table>
Reference


