### **Supporting Information**

# Efficient trifluoromethylation of $C(sp^2)$ -H functionalized $\alpha$ -oxoketene dithioacetals : route to regioselective synthesis of trifluoromethylated pyrazoles

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### **X-ray Crystallographic Studies**



Figure 1. ORTEP Structure of compound 31

The intensity data for 31 was collected on an Oxford Xcalibur CCD diffractometer equipped with graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K<sup>1</sup>. A multi-scan correction was applied. The structure was solved by the direct methods using SIR-92 and refined by full-matrix least-squares refinement techniques on  $F^2$  using SHELXL97<sup>2</sup>. The hydrogen atoms were placed into the calculated positions and included in the last cycles of the refinement. All calculations were done using Wingx software package<sup>3</sup>.

 Table 1. Crystal data and structure refinement for compound 31

Empirical formula	$C_{14}H_{11}F_{3}O_{2}S_{2}$
Formula weight	332.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>P</i> b c a
a	13.456(5) Å
b	10.034(5) Å
С	22.429(5) Å
α	90(5)°
β	90(5)°
γ	90(5)°
Volume	3028(2) Å <sup>3</sup>
Ζ	8
Density (calculated)	1.458 Mg/m <sup>3</sup>
Absorption coefficient	0.383 mm <sup>-1</sup>
F(000)	1360
Crystal size	0.22 x 0.20 x 0.18 mm <sup>3</sup>
Theta range for data collection	3.12 to 25.00°
Index ranges	$-16 \le h \le 15, -11 \le k \le 11, -21 \le l \le 26$
Reflections collected	9837
Independent reflections	2653 [R(int) = 0.0226]
Completeness to theta = $25.00^{\circ}$	99.8 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9342 and 0.9204
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2653 / 0 / 190
Goodness-of-fit on $F^2$	1.087
Final <i>R</i> indices [I>2sigma(I)] <sup>a, b</sup>	$R_1 = 0.0470, wR_2 = 0.1121$
<i>R</i> indices (all data)	$R_1 = 0.0583, wR_2 = 0.1175$
Largest diff. peak and hole	0.205 and -0.180 e.Å <sup>-3</sup>

<sup>a</sup> $R = \sum (\|Fo| - |Fc\|) / \sum |Fo|; {}^{b}wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ 



Figure 2. ORTEP drawings of compound 4i

The intensity data for was collected on an Oxford CCD diffractometer equipped with Xcalibur Sapphire diffraction measurement device graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K<sup>1</sup>. A multi-scan correction was applied. The structure was solved by the direct methods using SIR-92 and refined by full-matrix least-squares refinement techniques on  $F^2$  using SHELXL97<sup>2</sup>. The hydrogen atoms were placed into the calculated positions and included in the last cycles of the refinement. All calculations were done using Wingx software package<sup>3</sup>.

Empirical formula	$C_8H_9N_2F_3S$
Formula weight	222.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2/c
a	19.392(5) Å
b	12.369(5) Å
с	18.099(5) Å
α	90(5)°
β	110.204(5)°
γ	90(5)°
Volume	4074(2) Å <sup>3</sup>
Ζ	16
Density (calculated)	1.449 Mg/m <sup>3</sup>
Absorption coefficient	0.323 mm <sup>-1</sup>
<i>F</i> (000)	1824
Crystal size	0.22 x 0.21 x 0.20 mm <sup>3</sup>
Theta range for data collection	2.98 to 25.00°
Index ranges	$-21 \le h \le 23, -14 \le k \le 14, -21 \le l \le 21$
Reflections collected	24995
Independent reflections	6891 [R(int) = 0.0832]
Completeness to theta = $25.00^{\circ}$	95.9 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9382 and 0.9323
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	6891 / 2 / 523
Goodness-of-fit on $F^2$	1.041
Final <i>R</i> indices [I>2sigma(I)] <sup>a, b</sup>	$R_1 = 0.1116, wR_2 = 0.2682$
<i>R</i> indices (all data)	$R_1 = 0.2134, wR_2 = 0.3318$
Largest diff. peak and hole	0.417 and -0.278 e.Å <sup>-3</sup>

 Table 2. Crystallographic data and structure refinement for compounds 4i

<sup>a</sup> $R = \sum (\|Fo| - |Fc\|) / \sum |Fo|; {}^{b}wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ 

#### **References :**

- 1. CrysAlispro, Agilent Technologies, Version 1.171.34.49 (2011).
- 2. Sheldrick, G. M. Acta Cryst. 2008, A64, 112-122.
- 3. Farrugia, L.J. WinGX Version 1.80.05, *An integrated system of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data;* Department of Chemistry, University of Glasgow (1997-2009).

# General procedure for the synthesis of $\alpha$ -iodo substituted oxoketene dithioacetals (2a-l)

To a stirred solution of substituted oxoketene dithioacetal (1equiv.) in CHCl<sub>3</sub>, N-iodosuccinimide (1.2equiv.) was added portionwise at rt. Colour of the reaction mixture changes to dark brown. Reaction mixture was stirred at rt for 1hr. Progress of reaction was monitored by TLC. After consumption of starting material, solvent was evaporated and crude compound was directly purified by column chromatography using silica gel (100: 200 mesh) in n-Hexane to afford **2a-l** as pure compound.

#### Analytical data of α-iodo substituted oxoketene dithioacetals (2a-l)



**2-iodo-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (2a) :** The compound was obtained as a yellow viscous material, yield : (718 mg, 92%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.84 (d, *J* = 7.93 Hz, 1H), 7.79 (d, *J* = 7.93 Hz, 1H), 7.26 (d, *J* = 7.93 Hz, 3H), 2.45 (s, 3H, -SCH<sub>3</sub>), 2.13 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 185.3, 165.3, 142.2, 136.5, 129.0, 127.7, 95.2 (vinylic CI), 17.2 (-SCH<sub>3</sub>), 14.9 (-SCH<sub>3</sub>).



#### 1-(4-fluorophenyl)-2-iodo-3,3-bis(methylthio)prop-2-en-1-

**one (2b) :** The compound was obtained as a pale yellow liquid, yield : (706 mg, 93%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.86 (dd, *J* = 8.24, 2.75 Hz, 2H), 7.08 (t, *J* = 8.24, 2H), 2.41 (s, 3H,-SCH<sub>3</sub>), 2.07 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 189.0, 167.2, 164.6, 142.5, 132.4, 130.3, 116.0, 115.8, 96.7 (vinylic C-I), 19.3 (-SCH<sub>3</sub>), 17.3 (-SCH<sub>3</sub>).



1-(4-chlorophenyl)-2-iodo-3,3-bis(methylthio)prop-2-en-1-

one (2c) : The compound was obtained as a yellow liquid, yield : (698 mg, 94%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.81 (d, J = 8.70 Hz, 2H), 7.42 (d, J = 8.70 Hz, 2H),

2.45 (s, 3H, -SCH<sub>3</sub>), 2.11 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 189.2, 142.9, 140.1, 132.4, 131.0, 129.1, 96.4 (vinylic C-I), 19.3 (-SCH<sub>3</sub>), 17.3 (-SCH<sub>3</sub>).



one (2d) : The compound was obtained as a brown solid, yield : (643 mg, 91%) ; mp 50-52°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.74 (d, J = 8.70, 2H), 7.59 (d, J = 8.70, 2H), 2.46 (s, 3H, -SCH<sub>3</sub>), 2.12 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 189.4, 142.9, 132.8, 132.1, 131.1, 128.9, 96.4 (vinylic C-I), 19.3 (-SCH<sub>3</sub>), 17.3 (-SCH<sub>3</sub>).

1-(4-bromophenyl)-2-iodo-3,3-bis(methylthio)prop-2-en-1-



#### 2-iodo-3,3-bis(methylthio)-1-(4-

(trifluoromethyl)phenyl)prop-2-en-1-one (2e) : The compound was obtained as a pale yellow liquid, yield : (665 mg, 93%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.98 (d, *J* = 8.24, 2H), 7.72 (d, *J* = 8.24, 2H), 2.47 (s, 3H, -SCH<sub>3</sub>), 2.10 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 189.2, 143.8, 137.1, 134.8, 134.5, 129.9, 125.7, 124.8, 122.2, 95.8 (vinylic C-I), 19.3 (-SCH<sub>3</sub>), 17.4 (-SCH<sub>3</sub>).



Br' 1-(3-bromophenyl)-2-iodo-3,3-bis(methylthio)prop-2-en-1-one (2f) : The compound was obtained as a light yellow solid, yield : (665 mg, 94%) ; mp 54-56°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.91 (t, J = 1.83 Hz, 1H), 7.67 (dt, J = 7.79, 2.75, 1H), 7.57 (dq, J = 7.79, 2.75, 1H), 7.24 (t, J = 7.79, 1H), 2.37 (s, 3H, -SCH<sub>3</sub>), 2.05 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 188.9, 143.5, 136.3, 136.0, 132.3, 130.2, 128.2, 122.9, 96.0 (vinylic C-I), 19.3 (-SCH<sub>3</sub>), 17.3 (-SCH<sub>3</sub>).

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#### 2-iodo-3,3-bis(methylthio)-1-(3-(trifluoromethyl)phenyl)prop-

**2-en-1-one (2g) :** The compound was obtained as yellow liquid, yield : (644 mg, 90%) ; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 8.14 (s, 1H), 8.04 (d, *J* = 8.39, 1H), 7.81 (d, *J* = 7.63, 1H), 7.61 (t, *J* = 7.63, 1H), 2.48 (s, 3H, -SCH<sub>3</sub>), 2.10 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 189.0, 143.9, 134.8, 132.8, 131.5, 129.9, 129.3, 126.2, 124.9, 95.6 (vinylic C-I), 19.2 (-SCH<sub>3</sub>), 17.4 (-SCH<sub>3</sub>).



**2-iodo-3,3-bis(methylthio)-1-(p-tolyl)prop-2-en-1-one (2h) :** The compound was obtained as a yellow liquid, yield : (687 mg, 90%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.78 (d, J = 8.24, 2H), 7.25 (d, J = 8.24, 2H), 2.45 (s, 3H, -SCH<sub>3</sub>), 2.40 (s, 3H, Ar-CH<sub>3</sub>), 2.11 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 190.1, 144.7, 141.7, 131.3, 129.9, 129.4, 97.8 (vinylic C-I), 21.7 (Ar-CH<sub>3</sub>), 19.3 (-SCH<sub>3</sub>), 17.3 (-SCH<sub>3</sub>).



<sup>O</sup> **1-cyclopropyl-2-iodo-3,3-bis(methylthio)prop-2-en-1-one (2i) :** The compound was obtained as a yellow liquid, yield : (792 mg, 95%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.39 (s, 3H, SCH<sub>3</sub>), 2.25 (s, 3H, SCH<sub>3</sub>), 2.16-2.12 (m, 1H, cyclopropyl CH), 1.20-1.16 (m, 2H, cyclopropyl CH<sub>2</sub>), 1.01-0.96 (s, 2H, cyclopropyl CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 206.9, 200.4, 100.5 (vinylic C-I), 30.8 (cyclopropyl CH), 19.7 (-SCH<sub>3</sub>), 17.6 (-SCH<sub>3</sub>), 13.1 (cyclopropyl CH<sub>2</sub>).



S O 2-iodo-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (2j) : The compound was obtained as a yellow liquid, yield : (711 mg, 92%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.68 (d, J = 5.04 Hz, 1H), 7.61 (d, J = 4.58, 1H), 7.11(t, J = 4.58, 1H), 2.45 (s, 3H, -SCH<sub>3</sub>), 2.17 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 183.4, 143.2, 140.9, 135.2, 134.4, 128.3, 95.8 (vinylic C-I), 19.6 (-SCH<sub>3</sub>), 17.4 (-SCH<sub>3</sub>).



**1-(furan-2-yl)-2-iodo-3,3-bis(methylthio)prop-2-en-1-one (2k) :** The compound was obtained as a yellow liquid, yield : (722 mg, 91%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.63 (t, J = 1.83 Hz, 1H), 7.14 (d, J = 3.66 Hz, 1H), 6.54 (dd, J = 3.66, 1.83 Hz, 1H), 2.45 (s, 3H, -SCH<sub>3</sub>), 2.18 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.7, 149.7, 147.7, 144.2, 120.2, 112.6, 94.8 (vinylic C-I), 19.6 (-SCH<sub>3</sub>), 17.4 (-SCH<sub>3</sub>).



1-(benzofuran-2-yl)-2-iodo-3,3-bis(methylthio)prop-2-en-1-

**one (2l) :** The compound was obtained as a yellow viscous material, yield : (686 mg, 93%) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.68 (d, *J* = 7.79 Hz, 1H), 7.57 (d, *J* = 8.70 Hz, 1H), 7.48-7.44 (m, 2H) 7.29 (t, *J* = 7.79 Hz, 1H), 2.48 (s, 3H, -SCH<sub>3</sub>), 2.18 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 180.5, 156.2, 149.9, 145.2, 128.6, 126.9, 124.0, 123.4, 115.9, 112.5, 94.2 (vinylic C-I), 19.7 (-SCH<sub>3</sub>), 17.4 (-SCH<sub>3</sub>).

## Genereal procedure for synthesis of trifluoromethylated α-oxoketene dithioacetals (3a-l)

To a solution of compound **2** (1equiv.) in DMF, CuI (1.2equiv.) was added portionwise. After stirring for 5 minutes,  $FSO_2CF_2COOMe$  (1.5equiv.) was added dropwise at rt and reaction mass was heated to 90°C and stirred for 2-3hrs. Progress of reaction was monitored by TLC. After consumption of starting material **2**, crude was quinched with NH<sub>4</sub>OAc and extracted with EtOAc. Organic layer was washed with water. Combined organic layers were concentrated and crude was purified by column chromatography using 5% EtOAc: Hexane in silica gel(100:200) mesh to afford **3a-I** as pure compound. Analytical data of trifluoromethylated α-oxoketene dithioacetals (3a-l)



**3,3-bis(methylthio)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (3a) :** The compound was obtained as a light yellow solid, yield : (434 mg, 80%) ; mp 77-79°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2927, 1672 ; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.89 (d, J = 8.54, 2H), 7.59 (t, J = 7.32 Hz, 1H), 7.48 (t, J = 7.32, 2H), 2.44 (s, 3H, -SCH<sub>3</sub>), 2.16 (s, 3H, -SCH<sub>3</sub>) ; <sup>13</sup>C **NMR** (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 188.2, 151.2, 135.0, 132.2, 130.5, 129.2, 125.9, 122.2 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 17.2 (-SCH<sub>3</sub>), 16.9 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>11</sub>F<sub>3</sub>OS<sub>2</sub>: 293.0281, found 293.0282.



1-(4-fluorophenyl)-3,3-bis(methylthio)-2-(trifluoromethyl)prop-2-

**en-1-one (3b) :** The compound was obtained as a pale yellow viscous material, yield : (465 mg, 85%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2925, 1671 ; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.92 (dd, *J* = 8.24, 2.75 Hz, 2H), 7.15 (t, *J* = 8.24, 2H), 2.44 (s, 3H, -SCH<sub>3</sub>), 2.18 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 187.8, 167.5, 164.9, 150.8, 132.6, 131.8, 122.2 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 116.2, 116.0, 17.2 (-SCH<sub>3</sub>), 16.9 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>10</sub>F<sub>4</sub>OS<sub>2</sub>: 311.0187, found 311.0177.



1-(4-chlorophenyl)-3,3-bis(methylthio)-2-(trifluoromethyl)prop-2-

**en-1-one (3c) :** The compound was obtained as a yellow solid, yield : (463 mg, 84%) ; mp 50-52°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2927, 1685 ; <sup>1</sup>H **NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.83 (d, J = 8.24 Hz, 2H), 7.45 (d, J = 8.70 Hz, 2H), 2.44 (s, 3H, -SCH<sub>3</sub>), 2.17 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C **NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.1, 151.0, 140.4, 134.6, 130.4, 129.2, 122.0 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 17.2 (-SCH<sub>3</sub>), 17.0 (-SCH<sub>3</sub>); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>10</sub>ClF<sub>3</sub>OS<sub>2</sub>: 326.9892, found 326.9898.



#### 1-(4-bromophenyl)-3,3-bis(methylthio)-2-(trifluoromethyl)prop-

**2-en-1-one (3d) :** The compound was obtained as a light yellow viscous material, yield : (446 mg, 86%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2927, 1672 ; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.75 (d, *J* = 8.70, 2H), 7.62 (d, *J* = 8.70, 2H), 2.43 (s, 3H, -SCH<sub>3</sub>), 2.17 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 188.2, 151.2, 135.0, 132.2, 130.5, 129.2, 125.9, 122.2 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 17.2 (-SCH<sub>3</sub>), 16.9 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>10</sub>ClF<sub>3</sub>OS<sub>2</sub>: 370.9387, found 370.9381.



#### 3,3-bis(methylthio)-2-(trifluoromethyl)-1-(4-

(trifluoromethyl)phenyl)prop-2-en-1-one (3e) : The compound was obtained as a yellow solid, yield : (444 mg, 86%) ; IR ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2826, 1685 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) &: 7.99 (d, *J* = 8.24, 2H), 7.74 (d, *J* = 8.24, 2H), 2.45 (s, 3H,-SCH<sub>3</sub>), 2.16 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) &: 188.1, 152.0, 139.0, 135.1, 134.7, 131.0, 130.7, 129.2, 125.9, 124.8, 122.2, 122.0 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 17.2 (-SCH<sub>3</sub>), 17.0 (-SCH<sub>3</sub>); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>6</sub>OS<sub>2</sub>: 361.0155, found 361.0156.



1-(3-bromophenyl)-3,3-bis(methylthio)-2-(trifluoromethyl)prop-2-

**en-1-one (3f) :** The compound was obtained as a light yellow viscous material, yield : (441 mg, 85%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2925, 1670 ; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.04 (d, *J* = 1.53 Hz, 1H), 7.77 (d, *J* = 7.63, 1H), 7.71 (d, *J* = 7.63, 1H), 7.36 (t, *J* = 7.63, 1H), 2.45 (s, 3H, -SCH<sub>3</sub>), 2.17 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 187.8, 151.6, 138.0, 136.6, 131.8, 130.3, 127.6, 123.1, 122.2 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 17.2 (-SCH<sub>3</sub>), 16.9 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>10</sub>BrF<sub>3</sub>OS<sub>2</sub>: 370.9387, found 370.9389.



#### 3,3-bis(methylthio)-2-(trifluoromethyl)-1-(3-

(trifluoromethyl)phenyl)prop-2-en-1-one (3g) : The compound was obtained as a pale yellow solid, yield : (429 mg, 83%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2925, 1680 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 8.15 (s, 1H), 8.04 (d, *J* = 7.63, 1H), 7. 84 (d, *J* = 7.63, 1H), 7.63 (t, *J* = 8.01, 1H), 2.45 (s, 3H, -SCH<sub>3</sub>), 2.16 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) &: 187.8, 152.2, 136.8, 132.1, 131.7, 131.4, 130.8, 130.5, 130.1, 129.5, 125.6, 122.1 (vinylic C-CF<sub>3</sub>), 119.6 (vinylic CF<sub>3</sub>), 17.1 (-SCH<sub>3</sub>), 17.0 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>6</sub>OS<sub>2</sub>: 361.0155, found 361.0156.



3,3-bis(methylthio)-1-(p-tolyl)-2-(trifluoromethyl)prop-2-en-1-

one (3h): The compound was obtained as a yellow liquid, yield : (413 mg, 82%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2928, 1665 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.74 (d, *J* = 8.39, 2H), 7.21 (d, *J* = 7.63, 2H), 2.40 (s, 3H, -SCH<sub>3</sub>), 2.35 (s, 3H, Ar-CH<sub>3</sub>), 2.06 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 190.1, 144.7, 141.7, 131.3, 129.9, 129.4, 125.9, 122.4 (vinylic C-CF<sub>3</sub>), 119.4 (-CF<sub>3</sub>), 21.7 (Ar-CH<sub>3</sub>), 19.3 (-SCH<sub>3</sub>), 17.3 (-SCH<sub>3</sub>) ; HRMS (ESI) (M+H)<sup>+</sup> Calcd for C<sub>13</sub>H<sub>13</sub>F<sub>3</sub>OS<sub>2</sub>: 307.0438, found 307.0457.



(31) : The compound was obtained as a yellow liquid, yield : (491 mg, 86%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2884, 1692 ; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.36 (s, 6H, 2 x SCH<sub>3</sub>), 2.12-2.07 (m, 1H, cyclopropyl CH), 1.22-1.18 (m, 2H, cyclopropyl CH<sub>2</sub>), 1.05-1.00 (m, 2H, cyclopropyl CH<sub>2</sub>); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 198.9, 150.3, 122.4 (vinylic C-CF<sub>3</sub>), 119.7 (vinylic CF<sub>3</sub>), 22.5 (cyclopropyl CH), 17.3 (-SCH<sub>3</sub>), 12.7 (cyclopropyl CH<sub>2</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>9</sub>H<sub>11</sub>F<sub>3</sub>OS<sub>2</sub>: 257.0281, found 257.0280.



#### 3,3-bis(methylthio)-1-(thiophen-2-yl)-2-(trifluoromethyl)prop-2-en-1-

one (3j) : The compound was obtained as a yellow liquid, yield : (462 mg, 85%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2885, 1665 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.71 (d, J = 5.34 Hz, 1H), 7.60 (d, J = 3.81, 1H), 7.12 (t, J = 3.81, 1H), 2.43 (s, 3H, -SCH<sub>3</sub>), 2.22 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.4, 151.5, 143.4, 135.6, 134.1, 128.3, 122.2 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 17.4 (-SCH<sub>3</sub>), 16.9 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub>OS<sub>3</sub>: 298.9846, found 298.9839.



#### 1-(furan-2-yl)-3,3-bis(methylthio)-2-(trifluoromethyl)prop-2-en-1-one

(**3k**) : The compound was obtained as a yellow liquid, yield : (453 mg, 84%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 2878, 1655 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 7.64 (t, *J* = 1.83 Hz, 1H), 7.15 (d, *J* = 3.66 Hz, 1H), 6.55(q, *J* = 3.66, 1.83 Hz, 1H), 2.42 (s, 3H), 2.23 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) & 176.5, 152.6, 151.9, 147.9, 130.8, 130.4, 122.3 (vinylic C-CF<sub>3</sub>), 119.9 (-CF<sub>3</sub>), 112.7, 17.5 (-SCH<sub>3</sub>), 16.9 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 283.0074, found 283.0072.



1-(benzofuran-2-yl)-3,3-bis(methylthio)-2-(trifluoromethyl)prop-2-

**en-1-one (3l) :** The compound was obtained as a yellow solid, yield : (475 mg, 93%) ; **IR**  $(v_{max}cm^{-1})$  (CHCl<sub>3</sub>): 2925, 1656 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.70 (d, J = 8.24 Hz, 1H), 7.57 (d, J = 8.24 Hz, 1H), 7.48 (t, J = 8.24 Hz, 2H) 7.30 (t, J = 7.79 Hz, 1H), 2.46 (s, 3H), 2.23 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.3, 156.3, 153.5, 152.0, 128.9, 126.9, 124.1, 123.5, 122.4 (vinylic C-CF<sub>3</sub>), 119.5 (-CF<sub>3</sub>), 115.6, 112.5, 17.7 (-SCH<sub>3</sub>), 17.0 (-SCH<sub>3</sub>) ; **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>14</sub>H<sub>11</sub>F<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 333.0231, found 333.0230.

#### General procedure for the synthesis of trifluoromethylated 1*H*-pyrazoles (4a-l)

In an oven-dried RBF, hydrazine hydrate (1.5equiv.) was added to a solution of compound **3** (1equiv.) in EtOH and reaction mass was heated at 90°C for 2-3hrs. Progress of reaction was monitored by TLC. The reaction mixture was then cooled and solvent was evaporated. After that crude was purified by column chromatography using 20% ethyl acetate/hexane as eluent to afford the corresponding products **4a-1**.

#### 5.7.4.1 Analytical data of 3,4-dihydro-1*H*-quinazolin-2-ylidenes (4a-l)



#### 3-(methylthio)-5-phenyl-4-(trifluoromethyl)-1*H*-pyrazole (4a) :

The compound was obtained as light yellow solid, yield : (247 mg, 80%) ;mp 122-124°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3221, 2924 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.45 (s, 5H), 2.54 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 146.3, 146.1, 129.8, 128.7, 128.4, 128.1, 124.2, 121.5(*C*-CF<sub>3</sub>), 114.0, 108.7 (q, *J* = 32.5Hz, -CF<sub>3</sub>), 15.4 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -54.22 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>S: 259.0517, found 259.0515.



5-(4-fluorophenyl)-3-(methylthio)-4-(trifluoromethyl)-1*H*-pyrazole

(4b) : The compound was obtained as light yellow solid, yield : (252 mg, 81%) ; mp 112-114°C; IR ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3218, 2926 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.45 (dd, J = 8.70, 3.21 Hz, 2H), 7.12 (t, J = 8.70 Hz, .2H), 2.53 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.8, 162.3, 146.0, 145.4, 130.5, 124.4, 124.0, 121.3 (*C*-CF<sub>3</sub>), 116.0, 115.7, 109.0 (-CF<sub>3</sub>), 15.7 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -54.92 (s, 3F); HRMS (ESI) (M+H)<sup>+</sup> Calcd for C<sub>11</sub>H<sub>8</sub>F<sub>4</sub>N<sub>2</sub>S: 277.0422, found 277.0417.



5-(4-chlorophenyl)-3-(methylthio)-4-(trifluoromethyl)-1H-

pyrazole (4c) : The compound was obtained as light yellow solid, yield : (257 mg, 82%) ;

mp 120-122°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3216, 2925 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.20 (bs, 1H, *N*H), 7.36 (s, 4H), 2.50 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 146.1, 145.0, 136.0, 129.7, 128.9, 126.9, 124.0, 121.3(*C*-CF<sub>3</sub>), 118.7, 113.6, 109.1(-CF<sub>3</sub>), 15.9 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -53.91 (s, 3F); HRMS (ESI) (M+H)<sup>+</sup> Calcd for C<sub>11</sub>H<sub>8</sub>ClF<sub>3</sub>N<sub>2</sub>S: 293.0127, found 293.0126.



#### 5-(4-bromophenyl)-3-(methylthio)-4-(trifluoromethyl)-1H-

**pyrazole (4d)** : The compound was obtained as light yellow viscous material, yield : (254 mg, 80%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3219, 2925 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.41 (bs, 1H, *N*H), 7.53 (d, J = 7.79 Hz, 2H), 7.30 (d, J = 8.24 Hz, 2H), 2.50 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 131.9, 130.0, 128.9, 127.4, 125.5, 124.3, 15.9 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -53.22 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>11</sub>H<sub>8</sub>BrF<sub>3</sub>N<sub>2</sub>S: 336.9622, found 336.9620.



**F**<sub>3</sub>C **3-(methylthio)-4-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)-***1H*-pyrazole (4e) : The compound was obtained as light yellow solid, yield : (253 mg, 80%) ; mp 76-78°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3226, 2926 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.19 (bs, 1H, *N*H), 7.67 (d, J = 8.24 Hz, 2H), 7.59 (d, J = 7.33 Hz, 2H), 2.54 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 146.5, 144.4, 132.4, 131.8, 131.4, 128.9, 125.6, 124.1, 122.3, 121.3 (*C*-CF<sub>3</sub>), 109.2 (-CF<sub>3</sub>), 16.2 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -53.93 (s, 3F), -62.82 (s,3F, Ar-CF<sub>3</sub>); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>N<sub>2</sub>S: 327.0390, found 327.0385.



#### 5-(3-bromophenyl)-3-(methylthio)-4-(trifluoromethyl)-1H-

**pyrazole (4f) :** The compound was obtained as light yellow viscous material, yield : (257 mg, 81%) ; mp 104-106°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3219, 2925; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.84 (bs, 1H, *N*H), 7.58-7.52 (m, 2H), 7.37 (d, J = 7.33 Hz, 1H), 7.25 (d, J = 8.24 Hz, 1H), 2.49 (s,

3H, -SCH<sub>3</sub>); <sup>13</sup>C **NMR** (100 MHz, CDCl<sub>3</sub>) δ: 145.8, 144.7, 132.7, 131.3, 130.7, 130.1, 127.2, 124.0, 122.5, 121.3(*C*-CF<sub>3</sub>), 18.7, 109.6 (-CF<sub>3</sub>), 16.0 (-SCH<sub>3</sub>); <sup>19</sup>F **NMR** (376 MHz, CDCl<sub>3</sub>) δ: - 53.25 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>11</sub>H<sub>8</sub>BrF<sub>3</sub>N<sub>2</sub>S: 336.9622, found 336.9621.



#### 3-(methylthio)-4-(trifluoromethyl)-5-(3-

(trifluoromethyl)phenyl)-1*H*-pyrazole (4g) : The compound was obtained as light yellow solid, yield : (263 mg, 83%) ; mp 92-94°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3219, 2925 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 7.74 (s, 1H), 7.67 (t, *J* = 8.39 Hz, 2H), 7.54 (d, *J* = 8.39 Hz, 1H), 2.52 (s, 3H, -SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) & 146.4, 144.2, 131.9, 131.3, 130.0, 129.9, 129.2, 126.3, 125.3, 122.2, 121.3(*C*-CF<sub>3</sub>), 114.0, 109.7(-CF<sub>3</sub>), 16.1 (-SCH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) &: -53.81 (s, 3F), 62.84 (s, 3F, Ar-CF<sub>3</sub>); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>N<sub>2</sub>S: 327.0390, found 327.0382.



**CF**<sub>3</sub> **3-(methylthio)-5-(p-tolyl)-4-(trifluoromethyl)-1***H***-pyrazole 4h) <b>:** The compound was obtained as light yellow solid, yield : (223 mg, 72%) ; mp 128-130°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3233, 2927 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.87 (bs, 1H, *N*H), 7.32(d, *J* = 8.24 Hz, 2H), 7.21 (d, *J* = 8.24 Hz, 2H), 2.51 (s, 3H,-SCH<sub>3</sub>), 2.37 (s, 3H, Ar-CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 146.4, 146.2, 140.1, 129.4, 128.3, 125.0, 124.2, 121.5(*C*-CF<sub>3</sub>), 108.1(-CF<sub>3</sub>), 21.3 (Ar-CH<sub>3</sub>), 15.2 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -53.95 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>12</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>S: 273.0673, found 273.0664.

CF<sub>3</sub> **5-cyclopropyl-3-(methylthio)-4-(trifluoromethyl)-1***H*-pyrazole (4i) : The compound was obtained as a off white crystalline solid, yield : (230 mg, 76%) ; mp 116-118°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3174, 2920 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.30 (bs, 1H, *N*H), 2.46 (s, 3H,-SCH<sub>3</sub>), 2.01-1.93 (m, 1H,cyclopropyl CH), 1.02-0.97 (q, 2H, cyclopropyl CH<sub>2</sub>), 0.81-0.76 (q, 2H, cyclopropyl CH<sub>2</sub>) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.5, 144.7, 121.8 (*C*-CF<sub>3</sub>), 110.2 (q, J = 37.3 Hz, -CF<sub>3</sub>), 15.9 (-SCH<sub>3</sub>), 6.9 (cyclopropyl CH), 6.2 (cyclopropyl CH<sub>2</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -54.95 (s, 3F); HRMS (ESI) (M+H)<sup>+</sup> Calcd for C<sub>8</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>S: 223.0517, found 223.0521.

**3-(methylthio)-5-(thiophen-2-yl)-4-(trifluoromethyl)-1***H*-pyrazole (4j) **:** The compound was obtained as a viscous brown material, yield : (244 mg, 79%) ; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3459, 2923 ; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.38 (bs, 1H, *N*H), 7.28 (d, *J* = 5.04 Hz, 1H), 7.24 (d, *J* = 3.66 Hz, 1H), 6.98 (t, *J* = 4.58 Hz, 1H), 2.39 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 144.1, 141.7, 129.2, 128.5, 127.8, 127.4, 124.1, 121.4(*C*-CF<sub>3</sub>), 108.4 (-CF<sub>3</sub>), 15.9(-SCH<sub>3</sub>) ; <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -54.40 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>9</sub>H<sub>7</sub>F<sub>3</sub>N<sub>2</sub>S<sub>2</sub>: 265.0081, found 265.0082.

HN-N O CF3

**CF**<sub>3</sub> **5-(furan-2-yl)-3-(methylthio)-4-(trifluoromethyl)-1***H*-pyrazole (4k) : The compound was obtained as a off white crystalline solid, yield : (240 mg, 78%) ; mp 146-148°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3440, 2926 ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.05 (bs, 1H, *N*H), 7.45 (d, *J* = 1.83 Hz, 1H), 6.83 (d, *J* = 3.21 Hz, 1H), 6.50 (dd, *J* = 3.66, 1.83 Hz, 1H), 2.55 (s, 3H, -SCH<sub>3</sub>) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 146.5, 143.3, 141.8, 136.3, 124.1, 121.5 (*C*-CF<sub>3</sub>), 112.1, 111.4, 105.8 (q, *J* = 38.3 Hz, -CF<sub>3</sub>), 15.0 (-SCH<sub>3</sub>) ; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -54.60 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>9</sub>H<sub>7</sub>F<sub>3</sub>N<sub>2</sub>OS: 249.0309, found 249.0306.



#### 5-(benzofuran-2-yl)-3-(methylthio)-4-(trifluoromethyl)-1H-

**pyrazole (4l) :** The compound was obtained as a off white crystalline solid, yield : (241 mg, 77%) ; mp 178-180°C; **IR** ( $v_{max}$ cm<sup>-1</sup>) (CHCl<sub>3</sub>): 3420, 2924 ; <sup>1</sup>H NMR (400 MHz, DMSO-d<sup>6</sup>)  $\delta$ : 7.67 (d, J = 7.79 Hz, 1H), 7.56 (d, J = 8.24 Hz, 1H), 7.31 (t, J = 8.24 Hz, 1H) 7.24-7.21 (m, 2H), 2.49 (s, 3H,-SCH<sub>3</sub>) ; <sup>13</sup>C NMR (100 MHz, DMSO-d<sup>6</sup>)  $\delta$ : 154.2, 127.6,

125.8, 124.4, 123.6, 121.9 (*C*-CF<sub>3</sub>), 111.3, 106.7(-CF<sub>3</sub>), 14.7 (-SCH<sub>3</sub>) ; <sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ: -55.20 (s, 3F); **HRMS** (ESI) (M+H)<sup>+</sup> Calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>OS: 299.0466, found 299.0466.

### COPIES OF <sup>1</sup>H, <sup>13</sup>CNMR & HRMS DATA



















<sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)











2k <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)





2l <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)









Data File	SBNS318.d	Sample Name	SBNS318
Sample Type	Sample	Position	P2A3
Instrument Name	Instrument 1	User Name	Icmsdu-PC\admin
IRM Calibration Status Comment	s Success	DA Method	Default.m
Sample Group	In	ifo.	
Acquisition SW	6200 series TOF/6500 series		
Version	Q-TOF B.05.01 (B5125)		

ompound Table							
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula	
Cpd 7: C12 H11 F3 O S2	0.204	292.0209	C12 H11 F3 O S2	C12 H11 F3 O S2	-1.85	C12 H11 F3 O S2	



MFE MS Spectrum

0 5 2	Ср	d 7: (	C12 H	111	F3 C 293 111	52: - 0282 FB O	+ESI 2 S2]+H	MFE :	Spectr	rum (C	.148-0	).431	min) F	rag=1	35.0\	SBN	S318.	d	
1.5																			
1-	1																		
.5																			
0	Ļ	150	20	0 2	50	300	350	400	450	500	550	600	650	700	750	800	850	900	950

MFE MS Zoomed Spectrum

x10 <sup>5</sup>	Cpd 7: C12 H11 F3 O S2: +ESI MFE Spectrum (0.148-0.431 min) Frag=135.0V SBNS318.d
2-	([C12 H11 F3 O S2]+H)+
1.5	
1-	
0.5	315.0101 ([C12 H11 F3 O S2]+Na}+
0	1.         1.           260         265         270         275         280         285         290         295         300         305         310         325         330         335         340         345         350           Counts vs. Mass-to-Charge (m/z)

#### MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
293.0282	1	218569.19	C12 H11 F3 O S2	(M+H)+
294.0312	1	31013.34	C12 H11 F3 O S2	(M+H)+
295.025	1	20199.12	C12 H11 F3 O S2	(M+H)+
296.0267	1	2891.79	C12 H11 F3 O S2	(M+H)+
315.0101	1	12451.48	C12 H11 F3 O S2	(M+Na)+
316.0135	1	1928.45	C12 H11 F3 O S2	(M+Na)+
317.0083	1	1555.29	C12 H11 F3 O S2	(M+Na)+
318 009	1	155.1	C12 H11 F3 0 S2	(M+Na)+

---- End Of Report ----







Data File	SB-NS-348.d	Sample Name	SB-NS-348
Sample Type	Sample	Position	P2E8
Instrument Name	Instrument 1	User Name	lcmsdu-PC\admin
IRM Calibration Status Comment	Success	DA Method	Default.m
Sample Group	1	nfo.	



mpound Table						
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C12 H10 F4 O S2	0.202	310.0105	C12 H10 F4 O S2	C12 H10 F4 O S2	1.25	C12 H10 F4 O S2

.

Compound Label	m/z	RT	Algorithm	Mass
Cpd 2: C12 H10 F4 O S2	311.0177	0.202	Find by Molecular Feature	310.0105

MFE MS Spectrum



MFE MS Zoomed Spectrum

03	Cpd 2: C12 H10 F4 O S2: +ESI MFE Spectrum (0.163-0.297 min) Frag=135.0V SB-NS-348.d
7	311.0177 ([C12 H10 F⊈ O S2]+H)+
6	
5	
4	
3	
2	332.9971 ([C15 H9 F3 S2]+Na)+
1	

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
311.0177	1	7975.05	C12 H10 F4 O S2	(M+H)+
312.0213	1	1119.29	C12 H10 F4 O S2	(M+H)+
313.0155	1	843.83	C12 H10 F4 O S2	(M+H)+
332.9971	1	700.81	C15 H9 F3 S2	(M+Na)+

--- End Of Report ---










# <sup>13</sup>C-NMR in CDCl<sub>3</sub> (100MHz)













Sample	Position	0150
	10310011	PIF3
Instrument 1	User Name	Icmsdu-PC\admin
29.10.2014.m		
SURCESS	DA Method	Default.m
	Info.	
6200 series TOF/6500 series		
Q-TOF B.05.01 (B5125)		
	29.10.2014.m	29.10.2014.m DA Method Info. 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

# **Compound Table**

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C13 H10 F6 O S2	0.199	360.0083	C13 H10 F6 O S2	C13 H10 F6 O S2	-1.6	C13 H10 F6 O S2

5

Compound Label	m/z	RT	Algorithm	Mass
Cpd 3: C13 H10 F6 O S2	361.0156	0.199	Find by Molecular Feature	360.0083

# MFE MS Spectrum



#### MFE MS Zoomed Spectrum

x10 3	Cpd 3: C	13 H10	F6 O S	2: +ESI	MFE S	pectrun	n (0.151	-0.301	min) Fra	g=135	OV SB	-NS-380	).d	
8-						([C13 F	361.01 110 F6	56 O S2]+	H)+					
6-														
4 -														
2-														
0-	L													
	330	335	340	345	350 Co	unts vs.	. Mass-	365 to-Char	370 ge (m/z)	3/5	380	385	390	395

#### MS Spectrum Peak List

m/z		z Abund		Formula	Ion		
	361.0156	1	9403.09	C13 H10 F6 O S2	(M+H)+		
	362.0182	1	1485.17	C13 H10 F6 O S2	(M+H)+		





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Data File Sample Type	EXP-40 Sample	)8.d	Sample Name Position	EXP-408 P2E1 Icmedu-PC\admin		
Instrument Name	Instru	ment 1	Oser Name	Default m		
IRM Calibration Status Comment	Succe	5	DA Method	Debuicin		
Sample Group Acquisition SW 6200 Version Q-TO	series TOF/ DF B.05.01 (	In 6500 series 85125)	ifo.			
Compound Table			•			
		Marce	Formula	MFG Formula	(ppm)	DB Formula
Cpd 23: C12 H10 Br F3 O S2	0.196	369.9318	C12 H10 Br F3 O S2	C12 H10 Br F3 O S2	-2.5	C12 H10 Br F3 O S2
Compound Label	m/7	RT	Algorithm	Mass		
Cpd 23: C12 H10 Br F3 O S2	370.9389	0.196	Find by Molecular F	Feature 369.9318		
MFE MS Spectrum						
x10 3 Cpd 23: C12 H10	Br F3 O S2	: +ESI MFE Sp	ectrum (0.152-0.302 mi	n) Frag=135.0V EXP-408.d		
	3 ((C12 H10	72.9370 Br E3 O S21+H	+			
	([0121110					
5						
5						
3						
2						
1		ł				
0 150 200 2	50 300 3	50 400 450	500 550 600 650	700 750 800 850 900	950	
		Counts	vs. mass-to-Charge (in/	<i>2</i> )		
MFE MS Zoomed Spectrum	B. 53.0.0	DUEDIMEE O	octrum (0 152-0 302 mi	in) Frag=135.0V EXP-408.d		
x10 3 Cpd 23: C12 H10	Br F3 U S	372 8	370	ni) ridg toolor and		
7		([C12 H10 Br F	3 O S2]+H)+			
6						
5-						
4 -		11				
3-		11	392 92	216		
2		11	([C12 H10 Br F3	O S2]+Na)+		
1-			1			
340 345 35	355 36	0 365 370 3 Counts	375 380 385 390 3 vs. Mass-to-Charge (m.	95 400 405 410 415 42 /z)	425	
MS Spectrum Peak Lie	t					
m/z z Abund	For	mula	Ion			
		1110 0- 52 0 62	(M+H)+			

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1	6933.57	C12 H10 Br F3 O S2	(M+H)+
1	1170.93	C12 H10 Br F3 O S2	(M+H)+
1	8203.74	C12 H10 Br F3 O S2	(M+H)+
1	1207.36	C12 H10 Br F3 O S2	(M+H)+
1	739.39	C12 H10 Br F3 O S2	(M+H)+
1	508.03	C12 H10 Br F3 O S2	(M+Na)+
	1 1 1 1 1 1	1 6933.57 1 1170.93 1 8203.74 1 1207.36 1 739.39 1 508.03	1 6933.57 C12 H10 Br F3 O S2   1 1170.93 C12 H10 Br F3 O S2   1 8203.74 C12 H10 Br F3 O S2   1 1207.36 C12 H10 Br F3 O S2   1 739.39 C12 H10 Br F3 O S2   1 508.03 C12 H10 Br F3 O S2



<sup>13</sup>C-NMR in CDCl<sub>3</sub> (100MHz)





Data File	SB-NS-383.d	Sample Name	SB-NS-380
Sample Type	Sample	Position	P1F3
Instrument Name	Instrument 1	User Name	Icmsdu-PC\admin
Acq Method	29.10.2014.m		
IRM Calibration Status Comment	SUCCESS	DA Method	Default.m

Sample Group Acquisition SW Version

Info.

6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

#### **Compound Table**

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C13 H10 F6 O S2	0.199	360.0083	C13 H10 F6 O S2	C13 H10 F6 O S2	-1.6	C13 H10 F6 O S2

Compound Label	m/z	RT	Algorithm	Mass
Cpd 3: C13 H10 F6 O S2	361.0156	0.199	Find by Molecular Feature	360.0083

#### MFE MS Spectrum



# MFE MS Zoomed Spectrum



350 355 360 365 370 375 380 385 Counts vs. Mass-to-Charge (m/z) 390

# MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
361.0156	1	9403.09	C13 H10 F6 O S2	(M+H)+
362.0182	1	1485.17	C13 H10 F6 O S2	(M+H)+



3h <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)





#### Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	, DB Formula
Cpd 1: C13 H13 F3 O S2	0.215	306.0384	C13 H13 F3 O S2	C13 H13 F3 O S2	-7.94	C13 H13 F3 O S2

Compound Label	m/z	RT	Algorithm	Mass	
Cpd 1: C13 H13 F3 O S2	307.0457	0.215	Find by Molecular Feature	306.0384	
				2	

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#### MFE MS Spectrum



#### MFE MS Zoomed Spectrum

			307.0457				
4		([C13 H	113 FB O S2	]+H)+			
3							
2-							
1							

# MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
307.0457	1	45739.2	C13 H13 F3 O S2	(M+H)+
308.0496	1	6862.78	C13 H13 F3 O S2	(M+H)+
309.0411	1	4587.63	C13 H13 F3 O S2	(M+H)+
310.046	1	596.13	C13 H13 F3 O S2	(M+H)+

---- End Of Report ----



# <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)









#### **Compound Table**

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 27: C9 H11 F3 O S2	0.196	256.0207	C9 H11 F3 O S2	C9 H11 F3 O S2	-1.26	C9 H11 F3 O S2

Compound Label	m/z	RT	Algorithm	Mass	
Cpd 27: C9 H11 F3 O S2	257.028	0.196	Find by Molecular Feature	256.0207	
		anna.			2

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MFE MS Spectrum

0.75	]							•
1	-							
1.25	-							
1.5	-							
1.75	([C9 H11 F	0280 O S2]+H)+						
x10 5	Cpd 27: C9 H11 F	3 O S2: +ESI	MFE Spect	rum (0.142-0.57	5 min) Frag=1	35.0V SBN	IS368.d	

MFE MS Zoomed Spectrum

10 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	2	57.0280		, .		
1.75	([C9 H11	F: O S2]+F	1)+			
1.5						
1.25						
1-						
0.75						
0.5			2	79.0100		
0.25		li.	([C9 H11	F3 O SZJ+Na	3)+	
0	 	, <u> </u>				 -

#### MS Spectrum Peak List

e opean				
m/z	z	Abund	Formula	Ion
257.028	1	205398.03	C9 H11 F3 O S2	(M+H)+
258.0309	1	22227.01	C9 H11 F3 O S2	(M+H)+
259.0239	1	20336.6	C9 H11 F3 O S2	(M+H)+
260.0284	1	2383.76	C9 H11 F3 O S2	(M+H)+
279.01	1	6269.26	C9 H11 F3 O S2	(M+Na)+
280.0143	1	768.19	C9 H11 F3 O S2	(M+Na)+



<sup>13</sup>C-NMR in CDCl<sub>3</sub> (100MHz)







Data File	EXP361.d	Sample Name	EXP361
Sample Type	Sample	Position	P1E2
Instrument Name	Instrument 1	User Name	Icmsdu-PC\admin
IRM Calibration Status	Success -	DA Method	Default.m

IRM Calibration Status Comment

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

#### **Compound Table**

Mass	Formula	MFG Formula	(ppm)	DB Formula
197 297.97	67 C10 H9 F3 O S3	C10 H9 F3 O S3	0.17	C10 H9 F3 O S3
	Mass 197 297.97	r Mass Formula 197 297.9767 C10 H9 F3 0 S3	r Mass Formula MFG Formula 197 297.9767 C10 H9 F3 O S3 C10 H9 F3 O S3	r Mass Formula MFG Formula (ppm)   197 297.9767 C10 H9 F3 O S3 C10 H9 F3 O S3 0.17

Compound Label	m/z	RT	Algorithm	Mass
Cpd 4: C10 H9 F3 O S3	298.9839	0.197	Find by Molecular Feature	297.9767

#### MFE MS Spectrum



#### MFE MS Zoomed Spectrum

10 4 0	Cpd 4: C10 H9 F3 O S3: +ESI MFE Spectrum (0.142-0.375 min) Frag=135.0V EXP361.d
	298.0839
	([C10 H9 F3 O S3]+H)+
4	
3	
2	
1	
	Ш.,
0-	270 275 280 285 290 295 300 305 310 315 320 325 330 335

# MS Spectrum Peak List

m/z z Abund		z Abund Formula		Formula	Ion	
1	49916.02	C10 H9 F3 O S3	(M+H)+			
1	6201.3	C10 H9 F3 O S3	(M+H)+			
1	6972.59	C10 H9 F3 O S3	(M+H)+			
1	1003.5	C10 H9 F3 O S3	(M+H)+			
1	287.83	C10 H9 F3 O S3	(M+H)+			
	z 1 1 1 1 1	z Abund   1 49916.02   1 6201.3   1 6972.59   1 1003.5   1 287.83	z Abund Formula   1 49916.02 C10 H9 F3 O S3   1 6201.3 C10 H9 F3 O S3   1 6972.59 C10 H9 F3 O S3   1 1003.5 C10 H9 F3 O S3   1 287.83 C10 H9 F3 O S3			









3k

Data File Sample Type Instrument Name	SBNS 377.d Sample Instrument 1	Sample Name Position User Name	SBNS 377 P2-B6
IRM Calibration Status	Success	DA Method	Default.m

**IRM Calibration Status** Comment

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	O-TOF B.05.01 (B5125)	

Compound Label	RT	Mass	Formula	MFG Formula	(ppm)	DB Formula
Cpd 5: C10 H9 F3 O2 S2	0.226	281.9999	C10 H9 F3 O2 S2	C10 H9 F3 O2 S2	-1.12	C10 H9 F3 O2 S2

Compound Label	m/z	RT	Algorithm	Mass
Cpd 5: C10 H9 F3 O2 S2	283.0072	0.226	Find by Molecular Feature	281.9999

# MFE MS Spectrum

0.6 0.4 0.2

0



150 200 250 300 350 400 450 500 550 500 650 700 750 800 850 900 950 Counts vs. Mass-to-Charge (m/z)

# MFE MS Zoomed Spectrum



# MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
283.0072	1	1395088.25	C10 H9 F3 O2 S2	(M+H)+
284.0099	1	168605.67	C10 H9 F3 O2 S2	(M+H)+
285.004	1	132272.56	C10 H9 F3 O2 S2	(M+H)+
286.0064	1	14895.13	C10 H9 F3 O2 S2	(M+H)+
304,989	1	220674	C10 H9 F3 O2 S2	(M+Na)+
305,9918	1	26229.04	C10 H9 F3 O2 S2	(M+Na)+
306,9865	1	23123.41	C10 H9 F3 O2 S2	(M+Na)+
307,9901	1	2765.94	C10 H9 F3 O2 S2	(M+Na)+



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<sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)





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4a <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)



<sup>13</sup>C-NMR in CDCl<sub>3</sub> (100MHz)





4a

Data File	SB-NS-328.d	Sample Name	SB-NS-328
Sample Type	Sample	Position	P2C8
Instrument Name	Instrument 1	User Name	lcmsdu-PC\admin
IRM Calibration Status	Success	DA Method	Default.m
Comment			
Sample Group	Info.		
Acquisition SW	6200 series TOF/6500 series		
Version	Q-TOF B.05.01 (B5125)		

#### **Compound Table**

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 4: C11 H9 F3 N2 S	0.204	258.0442	C11 H9 F3 N2 S	C11 H9 F3 N2 S	-1.25	C11 H9 F3 N2 S

Compound Label	m/z	RT	Algorithm	Mass	
Cpd 4: C11 H9 F3 N2 S	259.0515	0.204	Find by Molecular Feature	258.0442	
•	1				3

#### MFE MS Spectrum



MFE MS Zoomed Spectrum

x10 4	Cpd 4: C11 H9 F3 N2 S: +ESI MFE Spectrum (0.151-0.334 min) Frag=135.0V SB-NS-328.d	
3.5	259.p515	
3	([C11 H9 F3 N2 S]+H)+	
2.5		
2		
1.5		
1-		
0.5		
0		
	230 235 240 245 250 255 260 265 270 275 280 285 290 Counts vs. Mass-to-Charge (m/z)	295

### **MS Spectrum Peak List**

m/z	z	Abund	Formula	Ion
259.0515	1	36040.07	C11 H9 F3 N2 S	(M+H)+
260.0543	1	4999.66	C11 H9 F3 N2 S	(M+H)+
261.0484	1	1928.92	C11 H9 F3 N2 S	(M+H)+
262.0542	1	204.75	C11 H9 F3 N2 S	(M+H)+





4b

Data File	SB-NS-360.d		Sample Name	SB-NS-360
Sample Type	Sample		Position	P2C3
Instrument Name	Instrument 1		User Name	Icmsdu-PC\admin
IRM Calibration Status Comment	Streess		DA Method	Default.m
Sample Group		Info.		
Acquisition SW	6200 series TOF/6500 series			
Version	Q-TOF B.05.01 (B5125)			

# **Compound Table**

Compound Label	RT	Mass	Formula	MFG Formula	(ppm)	DB Formula
Cpd 2: C11 H8 F4 N2 S	0.219	276.0345	C11 H8 F4 N2 S	C11 H8 F4 N2 S	-0.31	C11 H8 F4 N2 S

Compound Label	m/z	RT	Algorithm	Mass	
Cpd 2: C11 H8 F4 N2 S	277.0417	0.219	Find by Molecular Feature	276.0345	

#### MFE MS Spectrum

x10 4 1 -	Cpd 2:	C11 H	8 F4 N 277 1 H8 F	2 S: +  .0417 4 N2 S	ESI M	FE Sp	bectrur	m (0.1	67-0.3	51 mii	n) Frag=135	.0V S	B-NS-	360.d		
0.8		u														
0.6																
0.4	-															
0.2																
0	15	0 20	250	300	350	400 Co	450 ounts v	500 vs. Ma	550 ss-to-	600 Charg	650 700 e (m/z)	750	800	850	900	950

MFE MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion		
277.0417	1	10519.26	C11 H8 F4 N2 S	(M+H)+		
278.0453	1	1480.11	C11 H8 F4 N2 S	(M+H)+		
279.0394	1	601.3	C11 H8 F4 N2 S	(M+H)+		









Data File Sample Type Instrument Name IRM Calibration Status	SBNS- Samp Instru Succe	-372.d le ment 1	Sample Name Position User Name DA Method	SBNS-372 P2F2 Icmsdu-PC\admin Default.m		
Comment Sample Group Acquisition SW 620 Version Q-T	0 series TOF, OF B.05.01 (	Ir /6500 series B5125)	ıfo.		min Formula (ppm) DB Formula CI F3 N2 S -2.14 C11 H8 CI F3 N2 S 55 2 NS-372.d NS-372.d NS-372.d	
Compound Table Compound Label Cpd 6: C11 HB CI F3 N2 S	<b>RT</b> 0.204	Mass 292.0055	Formula C11 H8 CI F3 N2 S	MFG Formula C11 H8 CI F3 N2 S	MFG Diff (ppm) -2.14	DB Formula C11 H8 CI F3 N2 S
Compound Label Cpd 6: C11 H8 CI F3 N2 S	<b>m/z</b> 293.0126	<b>RT</b> 0.204	Algorithm Find by Molecular Fe	Mass Pature 292.0055	,	
MFE MS Spectrum x10 4 Cpd 6: C11 H8 Cl 3.5 ((C11 H8 2.5 - 2.5 - 1.5	F3 N2 S: + 293.0126 3 CI F3 N2 S 50 300 35	ESI MFE Specti 3]+H)+ 50 400 450 Counts v	rum (0.139-0.322 min) Fi	rag=135.0V SBNS-372.d 00 750 800 850 900 9	50	
MFE MS Zoomed Spectrum x10 4 Cpd 6: C11 H8 Cl 3.5 3 2.5 2 1.5 1 0.5	F3 N2 S: +	Counts v	s. mass-to-Charge (m/z) rum (0.139-0.322 min) Fi 293,0126 3 Cl #3 N2 S]+H)+	rag=135.0V SBNS-372.d		

# 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 Counts vs. Mass-to-Charge (m/z) MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
293.0126	1	37672.71	C11 H8 CI F3 N2 S	(M+H)+
294.0166	1	4994.9	C11 H8 CI F3 N2 S	(M+H)+
295.0096	1	14469.53	C11 H8 CI F3 N2 S	(M+H)+
296.0128	1	1875.03	C11 H8 CI F3 N2 S	(M+H)+
297.0116	1	729.36	C11 H8 CI F3 N2 S	(M+H)+



# 



4d



MFG Diff

(ppm)

-0.92

DB Formula C11 H8 Br F3 N2 S

0 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 Counts vs. Mass-to-Charge (m/z)

#### MFE MS Zoomed Spectrum



### MS Spectrum Peak List

m/z	z Abund		Formula	Ion	
336.9620	1	41064.77	C11 H8 Br F3 N2 S	(M+H)+	
337.9652	1	5446.67	C11 H8 Br F3 N2 S	(M+H)+	
338.9595	1	41900.1	C11 H8 Br F3 N2 S	(M+H)+	
339.9625	1	5446.27	C11 H8 Br F3 N2 S	(M+H)+	
340.9577	1	2330.67	C11 H8 Br F3 N2 S	(M+H)+	
341.9549	1	188.9	C11 H8 Br F3 N2 S	(M+H)+	



4e

# <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)









4f <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)



Data File SB-NS-409.d Sample Name SB-NS-409 Sample Type Sample Position P2A3 Instrument Name Instrument 1 User Name Icmsdu-PC\admin **IRM Calibration Status** Stuccess DA Method Default.m Comment Sample Group Info. Acquisition SW 6200 series TOF/6500 series Version Q-TOF B.05.01 (B5125) Compound Table MFG Diff Compound Label Cpd 6: C11 H8 Br F3 N2 MFG Formula C11 H8 Br F3 N2 S RT Formula C11 H8 Br F3 N2 S Mass (ppm) **DB Formula** 0.207 335.954 -0.92 C11 H8 Br F3 N2 S **Compound Label** m/z RT Algorithm Mass Cpd 6: C11 H8 Br F3 N2 S 336.9621 0.207 Find by Molecular Feature 335.9547 MFE MS Spectrum x10 4 Cpd 6: C11 H8 Br F3 N2 S: +ESI MFE Spectrum (0.150-0.467 min) Frag=135.0V SB-NS-409.d 338.9597 ([C11 H8 Br F3 N2 S]+H)+ 4 3.5 3 2.5 2 1.5 1 0.5 0 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 Counts vs. Mass-to-Charge (m/z) MFE MS Zoomed Spectrum x10 4 Cpd 6: C11 H8 Br F3 N2 S: +ESI MFE Spectrum (0.150-0.467 min) Frag=135.0V SB-NS-409.d 4 338.9597 ([C11 H8 Br F3 N2 S]+H)+ 3.5 3 2.5 2 1.5 1 0.5 0 305 310 315 320 325 330 335 340 345 350 Counts vs. Mass-to-Charge (m/z) 355 360 365 370 375 MS Spectrum Peak List z Abund Formula m/z Ion 336.9621 1 41064.77 C11 H8 Br F3 N2 S (M+H)+ 337.9652 1 5446.67 C11 H8 Br F3 N2 S (M+H)+ 338.9597 1 41900.1 C11 H8 Br F3 N2 S (M+H)+ 339.9625 1 5446.27 C11 H8 Br F3 N2 S 2330.67 C11 H8 Br F3 N2 S (M+H)+ 340.9577 1 (M+H)+ 341.9549 1 188.9 C11 H8 Br F3 N2 S (M+H)+

4f

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4g

# <sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)


SB-NS-416 Sample Name Data File SB-NS-416.d Sample Type Sample Position P1-A9 Instrument 1 User Name Instrument Name 06-06-2016 15:06:14 Acquired Time 29.10.2014.m Acq Method DA Method Default.m **IRM Calibration Status** Success Comment Info. Sample Group Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125) **Compound Table** MFG Diff Compound Label Cpd 1: C12 H8 F6 N2 S RT Mass Formula MFG Formula (ppm) **DB Formula** 326.0308 C12 H8 F6 N2 S C12 H8 F6 N2 S 1.22 C12 H8 F6 N2 S 11 **Compound Label** m/z RT Algorithm Mass Find by Molecular Feature 326.0308 Cpd 1: C12 H8 F6 N2 S 327.0382 11 MFE MS Spectrum x10 5 Cpd 1: C12 H8 F6 N2 S: +ESI MFE Spectrum (# 8-27) Frag=135.0V SB-NS-416.d 327.0382 ([C12 H8 F6 N2 S]+H)+ 4 3 2 1 0 150 200 250 300 350 400 450 500 550 600 650 700 750 800 Counts vs. Mass-to-Charge (m/z) MFE MS Zoomed Spectrum x10 5 Cpd 1: C12 H8 F6 N2 S: +ESI MFE Spectrum (# 8-27) Frag=135.0V SB-NS-416.d 327.0382 ([C12 H8 F6 N2 S]+H)+ 4 3 2 1 0 295 300 305 310 315 320 325 330 335 340 345 350 355 360 Counts vs. Mass-to-Charge (m/z) MS Spectrum Peak List z Abund Formula Ion m/z 327.0382 1 504488.09 C12 H8 F6 N2 S (M+H)+ (M+H)+ 328.0408 1 68466.58 C12 H8 F6 N2 S 329.0354 1 24271.75 C12 H8 F6 N2 S (M+H)+ (M+H)+

330.0367 1 ---- End Of Report ---- 3050.17 C12 H8 F6 N2 S



4h

4g

<sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)



Data File Sample Type Instrument Name

SB-NS-362.d Sample Instrument 1

Sample Name SB-NS-362 P2D7 User Name Icmsdu-PC\admin

Default.m

Position

DA Method

**IRM Calibration Status** Comment

Sample Group Acquisition SW Version

Info. 6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Success

**Compound Table** 

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C12 H11 F3 N2 S	0.203	272.0592	C12 H11 F3 N2 S	C12 H11 F3 N2 S	1.18	C12 H11 F3 N2 S

Compound Label	m/z	RT	Algorithm	Mass
Cpd 1: C12 H11 F3 N2 S	273.0664	0.203	Find by Molecular Feature	272.0592

### MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
273.0664	1	30955.35	C12 H11 F3 N2 S	(M+H)+
274.0699	1	4273.48	C12 H11 F3 N2 S	(M+H)+
275.0642	1	1961.88	C12 H11 F3 N2 S	(M+H)+

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<sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)



Data File Sample Type Instrument Name	SB NS 3 Sample Instrum	371.d ment 1	Sample Name Position User Name	SB NS 371 P2E9 Icmsdu-PC\admin
IRM Calibration Status Comment	Succes	S	DA Method	Default.m
Sample Group Acquisition SW 6200 Version 0-TC	series TOF/6 F B.05.01 (B	In 5500 series 35125)	fo.	
Compound Table	•			
Compound Table	RT	Mass	Formula	MFG Formula
Compound Table Compound Label Cpd 7: C8 H9 F3 N2 S	<b>RT</b> 0.219	Mass 222.0449	Formula C8 H9 F3 N2 S	MFG Formula C8 H9 F3 N2 S

### MFE MS Spectrum



MFG Diff

(ppm) -4.82 DB Formula C8 H9 F3 N2 S

### MFE MS Zoomed Spectrum

×10 5	Cpd 7	: C8 H9	F3 N2	S: +ES	MFE	Spectru	ım (0.16	62-0.39	6 min) F	Frag=10	00.0V S	B NS 3	71.d		
1						([C	223 8 H9 F3	.0521 3 N2 SJ	++1)+						
0.8															
0.6															
0.4															
0.2								Ι.							
0	190	195	200	205	210	215 Count	220 s vs. M	225 ass-to-0	230 Charge	235 (m/z)	240	245	250	255	

## MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
223.0521	1	107913.52	C8 H9 F3 N2 S	(M+H)+
224.0553	1	11598.36	C8 H9 F3 N2 S	(M+H)+
225.0498	1	5874.66	C8 H9 F3 N2 S	(M+H)+
226.0537	1	636.85	C8 H9 F3 N2 S	(M+H)+

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4j

<sup>1</sup>H-NMR in CDCl<sub>3</sub> (400MHz)



ersion	<b>SW</b> 6200 Q-T(	0 series TOF/ OF B.05.01 (B	Ir 6500 series 35125)	ifo.			
Compound	Table			•			
Compos	und Label	PT	Mass	Formula	MEG Formula	MFG Diff	DB Formula
Cpd 7:	C9 H7 F3 N2 S2	0.205	264.001	C9 H7 F3 N2 S2	C9 H7 F3 N2 S2	-2.91	C9 H7 F3 N2 S2
x10 4 Cpc	rum I 7: C9 H7 F3 N 265 ([C9 H7 F3	V2 S2: +ESI 0082 N2 S2]+H)	MFE Spectrum	n (0.158-0.342 min) Frag	g=135.0V SB-NS370.d		
IFE MS Spect x10 4 Cpc 2 1.5	rum 1 7: C9 H7 F3 N 265 ([C9 H7 F3	<b>12 S2: +ESI</b> ,0082 1 N2 S2]+H)	MFE Spectrum	n (0.158-0.342 min) Frag	g=135.0V SB-NS370.d		
IFE MS Spect x10 4 Cpc 2 - 1.5 - 1 -	rum 1 7: C9 H7 F3 N 265 ([C9 H7 F3	N2 S2: +ESI .0082 I N2 S2]+H)	MFE Spectrum	n (0.158-0.342 min) Frag	g=135.0V SB-NS370.d		
IFE MS Spect x10 4 Cpc 2 - 1.5 - 1 - 0.5 -	rum 17: C9 H7 F3 N 265 ([C9 H7 F3	<b>J2 S2: +ESI</b> ,0082 N2 S2]+H)	MFE Spectrun	n (0.158-0.342 min) Frag	g=135.0V SB-NS370.d		
IFE MS Spect x10 4 Cpc 2 1.5 1 0.5 0	rum 7: C9 H7 F3 N 265 ([C9 H7 F3 ([C9 H7 F3	N2 S2: +ESI .0082 N2 S2]+H) 0 300 35	MFE Spectrum	n (0.158-0.342 min) Fraç 500 550 600 650 7 5. Mass-to-Charge (m2)	9=135.0V SB-NS370.d	950	

4j

Sample Name Position

SB-NS370.d

Sample

SB-NS370 P1B6

U	235	240	245	250	255 Co	260 unts vs	265 Mass-	270 to-Char	275 ge (m/z	280	285	290	295	300
0														
0.5														
1	-													
1.5														
2					(	([C9 H7	265.008 F3 N2	2 S2]+H)	+					
x10 <sup>4</sup>	Cpu /. Cs	п/гэ	NZ 32.	TEOIN	IFE SP	ecuum	(0.156-	0.342 1	min) Fla	g=135.	00 30-	13370.	u	

Data File

Sample Type

m/z	z	Abund	Formula	Ion
265.0082	1	22043.51	C9 H7 F3 N2 S2	(M+H)+
266.0107	1	2720.37	C9 H7 F3 N2 S2	(M+H)+
267.0055	1	2392.42	C9 H7 F3 N2 S2	(M+H)+
268.0078	1	207.89	C9 H7 F3 N2 S2	(M+H)+

--- End Of Report ---



4k











## Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 5: C9 H7 F3 N2 O S	0.202	248.0233	C9 H7 F3 N2 O S	C9 H7 F3 N2 O S	-0.9	C9 H7 F3 N2 O S

2

,

Compound Label	m/z	RT	Algorithm	Mass
Cpd 5: C9 H7 F3 N2 O S	249.0306	0.202	Find by Molecular Feature	248.0233

## MFE MS Spectrum

0 -		2	49.03	306	·LON	pecut	.0) וווג	132-0	049 11	ari) Fr	ag-13	5.0V	SBIN	5-384	i.a	
1.2	([C	9 H7	-3 N2	0 S]+	H)+											
1																
D.8																
0.6																
).4 -																
).2																

MFE MS Zoomed Spectrum

x10 <sup>5</sup>	Cpd 5: C9 H7 F3 N2 O S: +ESI MFE Spectrum (0.132-0.649 min) Frag=135.0V SBNS-384.d
	249,0306
1.2	([C9 H7 F3 N2 O S]+H)+
1-	
0.8	
0.6	
0.4	
0.2	
0	
	220 225 230 235 240 245 250 255 260 265 270 275 280 285 Counts vs. Mass-to-Charge (m/z)

# MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
249.0306	1	141447.28	C9 H7 F3 N2 O S	(M+H)+
250.0334	1	15580.35	C9 H7 F3 N2 O S	(M+H)+
251.028	1	6658.76	C9 H7 F3 N2 O S	(M+H)+
252.0311	1	666.46	C9 H7 F3 N2 O S	(M+H)+

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Vata File Sample Type Enstrument Name	SB NS Sampl Instru	373.d e ment 1	Sample Name Position User Name	SB NS 373 P1E8 Icmsdu-PC\admin		
RM Calibration Statu: Comment	s Succe	S-Cole and	DA Method	Default.m		
Sample Group Acquisition SW Version	6200 series TOF Q-TOF B.05.01 (	In (6500 series (85125)	fo.			
Compound Table						
Compound Tuble		Maria	Formula	MFG Formula	(ppm)	DB Formula
Compound Label Cpd 2: C13 H9 F3 M	2 0 5 0.208	298.0394	C13 H9 F3 N2 O S	C13 H9 F3 N2 O S	-2.07	C13 H9 F3 N2 O S
				<u></u>		
			an and an and a second s	and a second		
Compound Label	m/z	RT	Algorithm	Mass		
Cpd 2: C13 H9 F3 N	2 O S 299.0466	6 0.208	Find by Molecular H	-eature 298.0394		
				and the construction of the second	2	
MFE MS Spectrum			(0 145 0 429 min) F	Frag=100 0V SB NS 373.d		
x10 4 Cpd 2: C13	H9 F3 N2 O S: 4	ESI MEE Spect	rum (0.145-0.429 mm) r	Tag-100.01 0B tto er ete		
3						
1 /1	299.0466 C13 H9 E3 N2 C	; ) S]+H)+				
2.5	299.0466 C13 H9 F3 N2 C	; ) S]+H)+				
2.5 ([	299.0466 C13 H9 F3 N2 C	; ) S]+H)+				
2.5 ([	299.0466 C13 H9 F3 N2 C	) S]+H)+				
2.5 (( 2- 1.5-	299.0466 C13 H9 F3 N2 C	; ) S]+H)+				
2.5 (( 2. 1.5- 1.	299.0466 C13 H9 F3 N2 C	; ) S]+H)+				
2.5. ([ 2- 1.5- 1-	299.0466 C13 H9 F3 N2 C	; ) S]+H)+				
2.5. (1 2- 1.5- 1- 0.5-	299.0466 C 13 H9 F3 N2 C	) S]+H)+				
2.5. (1 1.5- 1.5- 0.5- 0 150 2	299.0466 C13 H9 F3 N2 C	350 400 450 Counts	500 550 600 650 ys. Mass-to-Charge (m/	700 750 800 850 900	950	
2.5. (1 2.5. (1 1.5. 1.5. 0.5. 0.5. 0.5. 1.50 2	299.0466 (C 13 H9 F3 N2 C	350 400 450 Counts	500 550 600 650 vs. Mass-to-Charge (m/	700 750 800 850 900 (z)	950	
2.5. (1 2.5. (1 1.5. 1.5. 0.5. 0.5. 0.5. 150 2 MFE MS Zoomed Spect	299.0466 (C13 H9 F3 N2 C 00 250 300 trum	350 400 450 Counts	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min)	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13	299.0466 (C13 H9 F3 N2 C 00 250 300 trum	) S]+H)+ 350 400 450 Counts +ESI MFE Spec 299 046	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5. (I 2.5. (I 1.5. 1.5. 0.5. 0.5. 0.5. 150.2 MFE MS Zoomed Spect x10.4 [Cpd 2: C13]	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S:	350 400 450 Counts +ESI MFE Spec 299,046 ([C13 H9 F3 N2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 0	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S:	350 400 450 Counts +ESI MFE Spec 299.046 ([C13 H9 F3 N2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O SJ+H)+	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 C S:	350 400 450 Counts +ESI MFE Spec 299,046 ([C13 H9 F3 N2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2 1.5 1 1.5 1 1.5 2 MFE MS Zoomed Spect	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S:	350 400 450 Counts +ESI MFE Spec 299,046 ([C13 H9 F3 N2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+	700 750 800 850 900 z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2 1.5 1 2.5 2 1.5 1 2.5 2 1.5 1 2.5	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S:	350 400 450 Counts +ESI MFE Spec 299 046 ([C13 H9 F3 V2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 - 1 0.5 0 - 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 - 2 1.5 - 1 1.5 - 1	299.0466 (C13 H9 F3 N2 C 00 250 300 trum	350 400 450 Counts +ESI MFE Spec 299 D46 ([C13 H9 F3 N2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d	950	
2.5 (1 2.5 (1 1.5 - 1 0.5 - 0 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 - 2 1.5 - 1 0.5 - 1 0.	299.0466 (C13 H9 F3 N2 C 00 250 300 trum	350 400 450 Counts +ESI MFE Spec 299, D46 ([C13 H9 F3 V2	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0: ([C13 H9 F3 N2	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d 295 2 O S]+Na)+	950	
2.5 (1 2.5 (1 1.5 - 1 0.5 0 - 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 - 2 1.5 - 1 0.5 0	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S:	2 S]+H)+ 350 400 450 Counts +ESI MFE Spec 299 246 ([C13 H9 F3 N2 290 295 300	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ((C13 H9 F3 N) ((C13 H9 F3 N)	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d 295 2 O S]+Na)+ 325 330 335 340 345	950	·
2.5 (1 2.5 (1 1.5 - 1 0.5 0 - 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2 1.5 - 1 0.5 0 - 270 5	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S: 275 280 285	299 295 300 Counts	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ((C13 H9 F3 N) ((C13 H9 F3 N) 305 310 315 320 vs. Mass-to-Charge (m	700 750 800 850 900 z) Frag=100.0V SB NS 373.d 205 2 O S]+Na)+ 325 330 335 340 345 vz)	950	·
2.5. (1 2.5. (1 1.5. 1 0.5. 0 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5. 2 1.5. 1 0.5. 0 2.70 1 MS Spectrum Pe	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S: 2275 280 285 rak List	290 295 300 Counts	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ((C13 H9 F3 N) ((C13 H9 F3 N) 305 310 315 320 s vs. Mass-to-Charge (m	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d 295 2 O S]+Na)+ 325 330 335 340 345 /z)	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2 1.5 1 0.5 0 270 2 MS Spectrum Pe	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S: 275 280 285 ak List Abund Fc	2 SJ+H)+ 350 400 450 Counts +ESI MFE Spec 299 246 ([C13 H9 F3 V2 290 295 300 Counts rmula	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ((C13 H9 F3 N) ((C13 H9 F3 N) 305 310 315 320 vs. Mass-to-Charge (m	700 750 800 850 900 2) Frag=100.0V SB NS 373.d 205 2 O S]+Na)+ 325 330 335 340 345 vz)	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2 1.5 1 0.5 0 270 5 MS Spectrum Pee <u>m/z 299.0466 1</u>	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S: 275 280 285 ak List Abund F0 30043.73 C1	250 SJ+H)+ 350 400 450 Counts +ESI MFE Spec 299,046 ([C13 H9 F3 N2 290 295 300 Counts rmula 3 H9 F3 N2 O S	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ([C13 H9 F3 N] 305 310 315 320 s vs. Mass-to-Charge (m Ion (M+H)+	700 750 800 850 900 z) Frag=100.0V SB NS 373.d 205 2 O S]+Na)+ 325 330 335 340 345 vz)	950	
2.5 (1 2.5 (1 1.5 1 0.5 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 2 1.5 1 0.5 0 270 5 MS Spectrum Pe m/z 2 299.0466 1 300.0498 1	299.0466 (C13 H9 F3 N2 C 00 250 300 trum 275 280 285 ak List Abund F0 30043.73 (C1 4814.03 C1	2 S]+H)+ 350 400 450 Counts +ESI MFE Spec 299,046 ([C13 H9 F3 N2 290 295 300 Counts 1 1 290 295 300 Counts 1 1 1 1 1 1 1 1 1 1 1 1 1	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0: ([C13 H9 F3 N: 0 305 310 315 320 s vs. Mass-to-Charge (m [M+H)+ (M+H)+	700 750 800 850 900 z) Frag=100.0V SB NS 373.d 205 2 O S]+Na)+ 325 330 335 340 345 v(z)	950	
2.5 (1 2.5 (1 1.5 - 1 0.5 - 0 150 2 MFE MS Zoomed Spect x10 4 Cpd 2: C13 2.5 - 2 1.5 - 1 0.5 - 0 270 5 MS Spectrum Pe <u>m/z z 4</u> 300.0498 1 301.0446 1	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S: 275 280 285 <b>ak List</b> <b>Abund</b> F0 30043.73 C 1909.71 C1 1909.71 C1	2 S]+H)+ 350 400 450 Counts +ESI MFE Spec 299 246 ([C13 H9 F3 N2 ([C13 H9 F3 N2 O S 3 H9 F3 N2 O S 3 H9 F3 N2 O S	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ((C13 H9 F3 N) 305 310 315 320 vs. Mass-to-Charge (m Ion (M+H)+ (M+H)+ (M+H)+	700 750 800 850 900 (z) Frag=100.0V SB NS 373.d 295 2 O S]+Na)+ 325 330 335 340 345 (z)	950	
2.5. (1 2.5. (1 1.5. (1 0.5. (1) 0.5. (1) 0.5. (1) 0.5. (2) MFE MS Zoomed Spect x10 4 (Cpd 2: C13) 2.5. (2) 1.5. (1) 0.5. (2) 0.5. (2)	299.0466 (C13 H9 F3 N2 C 00 250 300 trum H9 F3 N2 O S: 275 280 285 ak List Abund F0 30043.73 C1 4814.03 C1 4814.03 C1 1909.71 C1 301.89 C1	2 SJ+H)+ 350 400 450 Counts +ESI MFE Spec 299 246 (C13 H9 F3 N2 290 295 300 Counts 19 F3 N2 0 S 3 H9 F3 N2 0 S 3 H9 F3 N2 0 S	500 550 600 650 vs. Mass-to-Charge (m/ trum (0.145-0.429 min) 6 O S]+H)+ 321.0 ((C13 H9 F3 N) ((C13 H9 F3 N) 305 310 315 320 s vs. Mass-to-Charge (m (M+H)+ (M+H)+ (M+H)+ (M+H)+ (M+H)+	700 750 800 850 900 [z] Frag=100.0V SB NS 373.d 295 2 O S]+Na)+ 325 330 335 340 345 [z]	950	

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