

## *Supplementary Information*

### An improved method for the preparation of 2-hydrazinylbenzo[*d*]thiazoles from benzo[*d*]thiazol-2-amines

Shahnaz Begum<sup>a,b</sup> & China Raju Bhimapaka<sup>\*a,b</sup>

<sup>a</sup> Department of Natural Products & Medicinal Chemistry

CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India

<sup>b</sup> Academy of Scientific and Innovative Research (AcSIR), CSIR-HRDC Campus,

Postal Staff College Area Sector 19, Kamla Nehru Nagar, Ghaziabad 201 002, Uttar Pradesh, India

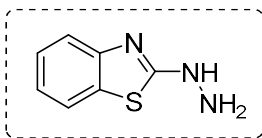
E-mail: chinaraju@iict.res.in

*Received 22 April 2024; accepted (revised) 22 May 2024*

|  |      |
|--|------|
| 1. Spectral data of compounds .....  | 3-5  |
| 2. Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR, ESI-Mass and HRMS Spectrums..... | 6-13 |
| 3. References.....   | .14  |

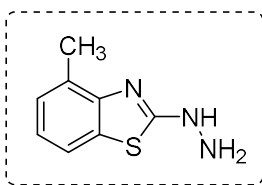
### Spectral data:

#### 2-Hydrazinylbenzo[d]thiazole (**3a**):<sup>1</sup>



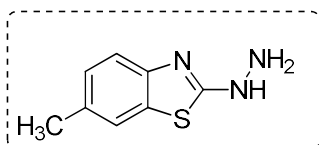
Yellowish solid (78%), m.p. 203-205 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.96 (s, 1H, NH), 7.66 (dd, *J* = 7.8, 0.8 Hz, 1H, aromatic), 7.33 (d, *J* = 7.6 Hz, 1H, aromatic), 7.20 (td, *J* = 7.8, 1.3 Hz, 1H, aromatic), 6.99 (td, *J* = 7.6, 1.1 Hz, 1H, aromatic), 4.99 (s, 2H, NH<sub>2</sub>) ppm. <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ 179.15, 158.39, 135.46, 130.65, 126.20, 125.66, 123.11 ppm. IR (KBr): 3225-3450 (NHNH<sub>2</sub>), 1622 (C-N), 1439 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 165 [M+H]<sup>+</sup>. HRMS (ESI): [M+H]<sup>+</sup> *m/z* calcd for C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>S = 166.0433, found = 166.0432.

#### 2-Hydrazinyl-4-methylbenzo[d]thiazole (**3b**):<sup>1</sup>



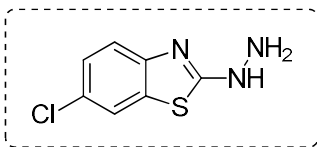
Yellowish brown solid (76%), m.p. 198-200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.94 (s, 1H, NH), 7.26-7.71 (m, 3H, aromatic), 4.82 (s, 2H, NH<sub>2</sub>), 2.45 (s, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 147.17, 135.09, 132.14, 123.91, 115.80, 112.67, 109.23, 17.24 ppm. IR (KBr): 3222-3449 (NHNH<sub>2</sub>), 1620 (C-N), 1439 (thiazole) cm<sup>-1</sup>, ESI-MS: *m/z* 179 [M+H]<sup>+</sup>. HRMS (ESI): [M+H]<sup>+</sup> *m/z* calcd for C<sub>8</sub>H<sub>10</sub>N<sub>3</sub>S = 180.0346, found = 180.0345.

#### 2-Hydrazinyl-6-methylbenzo[d]thiazole (**3c**):<sup>1</sup>



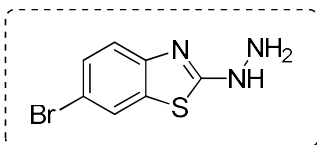
Pale green solid (69%), m.p. 167-169 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.92 (s, 1H, NH), 7.31-7.69 (m, 3H, aromatic), 4.83 (s, 2H, NH<sub>2</sub>), 2.83 (s, 3H, CH<sub>3</sub>) ppm. IR (KBr): 3220-3439 (NHNH<sub>2</sub>), 1638 (C-N), 1435 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 179 [M+H]<sup>+</sup>.

*2-Hydrazinyl-6-chlorobenzo[d]thiazole (3d):*<sup>1</sup>



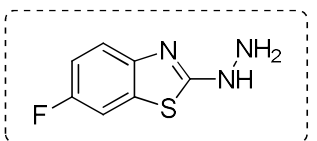
Brown solid (68%), m.p. 198-200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.90 (s, 1H, NH), 4.79 (s, 2H, NH<sub>2</sub>), 7.82-8.21 (m, 3H, aromatic) ppm. IR (KBr): 3218-3445 (NHNH<sub>2</sub>), 1624 (C-N), 1428 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 199 [M+H]<sup>+</sup>.

*2-Hydrazinyl-6-bromobenzo[d]thiazole (3e):*<sup>1</sup>



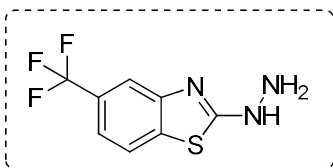
Yellowish brown solid (61%), m.p. 200-202 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.90 (s, 1H, NH), 7.63-7.93 (m, 3H, aromatic), 4.83 (s, 2H, NH<sub>2</sub>) ppm. IR (KBr): 3212-3449 (NHNH<sub>2</sub>), 1623 (C-N), 1451 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 244 [M+H]<sup>+</sup>.

*2-Hydrazinyl-6-fluorobenzo[d]thiazole (3f):*<sup>1</sup>



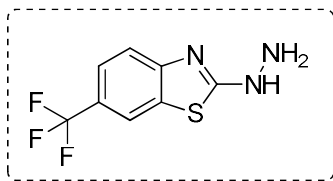
Greyish brown solid (70%); m.p. 204-206 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.94 (s, 1H, NH), 7.28-7.64 (m, 3H, aromatic), 4.83 (s, 2H, NH<sub>2</sub>) ppm. IR (KBr): 3200-3435 (NHNH<sub>2</sub>), 1631 (C-N), 1442 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 183 [M+H]<sup>+</sup>.

*2-Hydrazinyl-5-(trifluoromethyl)benzo[d]thiazole (3g):*<sup>1</sup>



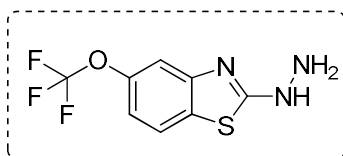
Brown solid (71%); m.p. 123-125 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.10 (s, 1H, NH), 7.32-7.70 (m, 3H, aromatic), 4.80 (s, 2H, NH<sub>2</sub>) ppm. IR (KBr): 3200-3440 (NHNH<sub>2</sub>), 1230-1580 (CF<sub>3</sub>), 1638 (C-N), 1432 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 233 [M+H]<sup>+</sup>.

*2-Hydrazinyl-6-(trifluoromethyl)benzo[d]thiazole (3h):*<sup>1</sup>



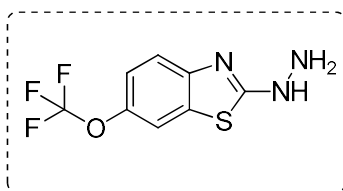
Brown solid (68%); m.p. 135-137 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.36 (s, 1H, NH), 7.96 (m, 1H, aromatic), 7.90 (m, 1H, aromatic), 7.27 (m, 1H, aromatic), 5.16 (s, 2H, NH<sub>2</sub>) ppm. IR (KBr): 3200-3440 (NHNH<sub>2</sub>), 1230-1570 (CF<sub>3</sub>), 1639 (C-N), 1430 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 233 [M+H]<sup>+</sup>.

*2-Hydrazinyl-5-(trifluoromethoxy)benzo[d]thiazole (3i):*<sup>1</sup>



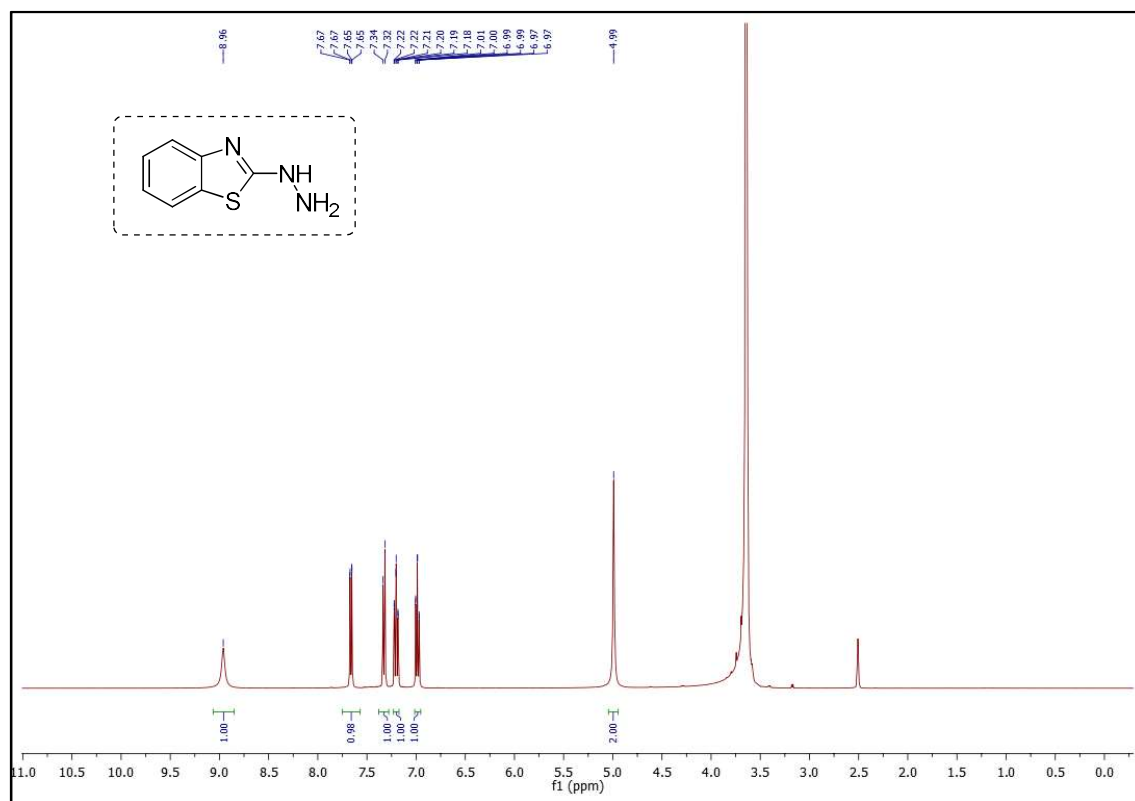
Colorless solid (69%); m.p. 231-233 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.36 (d, *J* = 8.4 Hz, 1H, aromatic), 6.58 (d, *J* = 1.5 Hz, 1H, aromatic), 6.54 (dd, *J* = 8.4, 2.4 Hz, 1H, aromatic), 3.96 (s, 2H, NH<sub>2</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>+DMSO-d<sub>6</sub>): δ 175.55, 152.87, 142.22, 131.79, 122.00, 119.29, 118.60, 114.76 ppm. IR (KBr): 3200-3435 (NHNH<sub>2</sub>), 1230-1565 (CF<sub>3</sub>), 1639 (C-N), 1428 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 249 [M+H]<sup>+</sup>. HRMS (ESI): [M+H]<sup>+</sup> *m/z* calcd for C<sub>8</sub>H<sub>7</sub>ON<sub>3</sub>F<sub>3</sub>S = 250.0256, found = 250.0261.

*2-Hydrazinyl-6-(trifluoromethoxy)benzo[d]thiazole (3j):*<sup>1</sup>

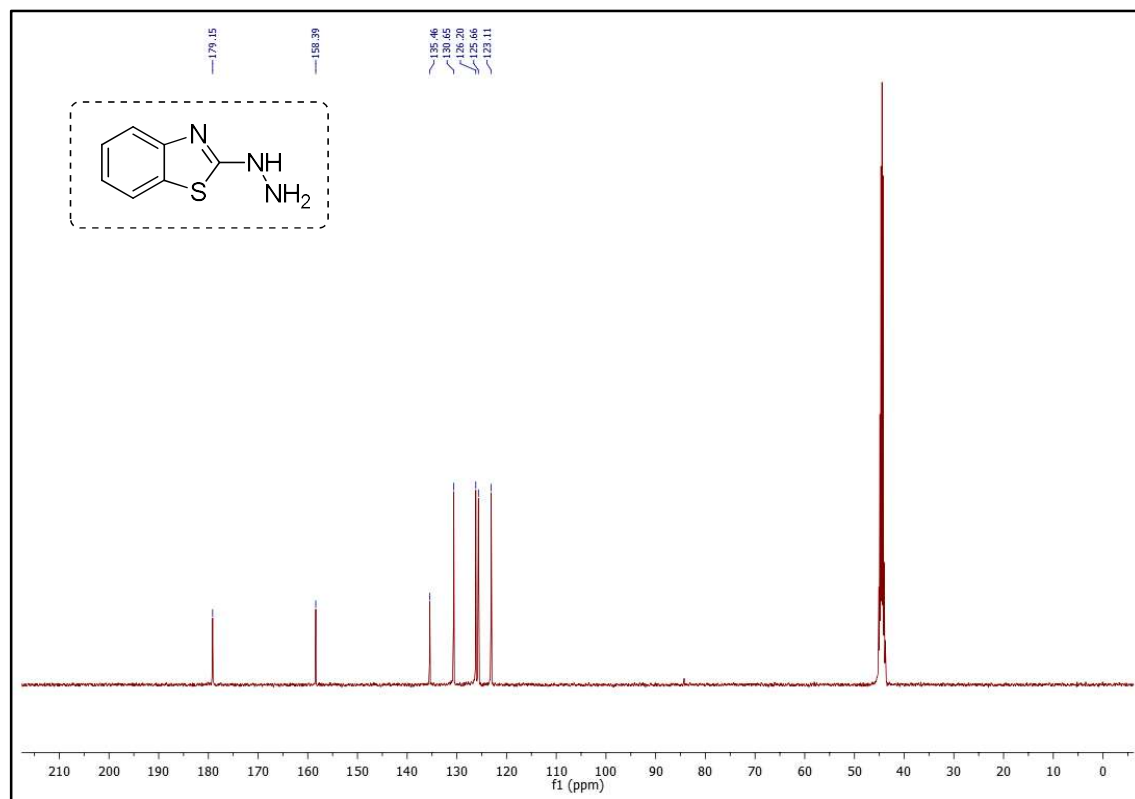


Colorless solid (73%); m.p. 205-207 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.32 (d, *J* = 8.4 Hz, 1H, aromatic), 6.54 (d, *J* = 1.5 Hz, 1H, aromatic), 6.50 (dd, *J* = 8.4, 2.4 Hz, 1H, aromatic), 3.92 (s, 2H, NH<sub>2</sub>) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 149.75, 148.76, 135.95, 121.38, 119.32, 117.51, 113.42, 107.06 ppm. IR (KBr): 3200-3435 (NHNH<sub>2</sub>), 1230-1565 (CF<sub>3</sub>), 1639 (C-N), 1428 (thiazole) cm<sup>-1</sup>. ESI-MS: *m/z* 249 [M+H]<sup>+</sup>. HRMS (ESI): [M+H]<sup>+</sup> *m/z* calcd for C<sub>8</sub>H<sub>7</sub>ON<sub>3</sub>F<sub>3</sub>S = 250.0256, found = 250.0262.

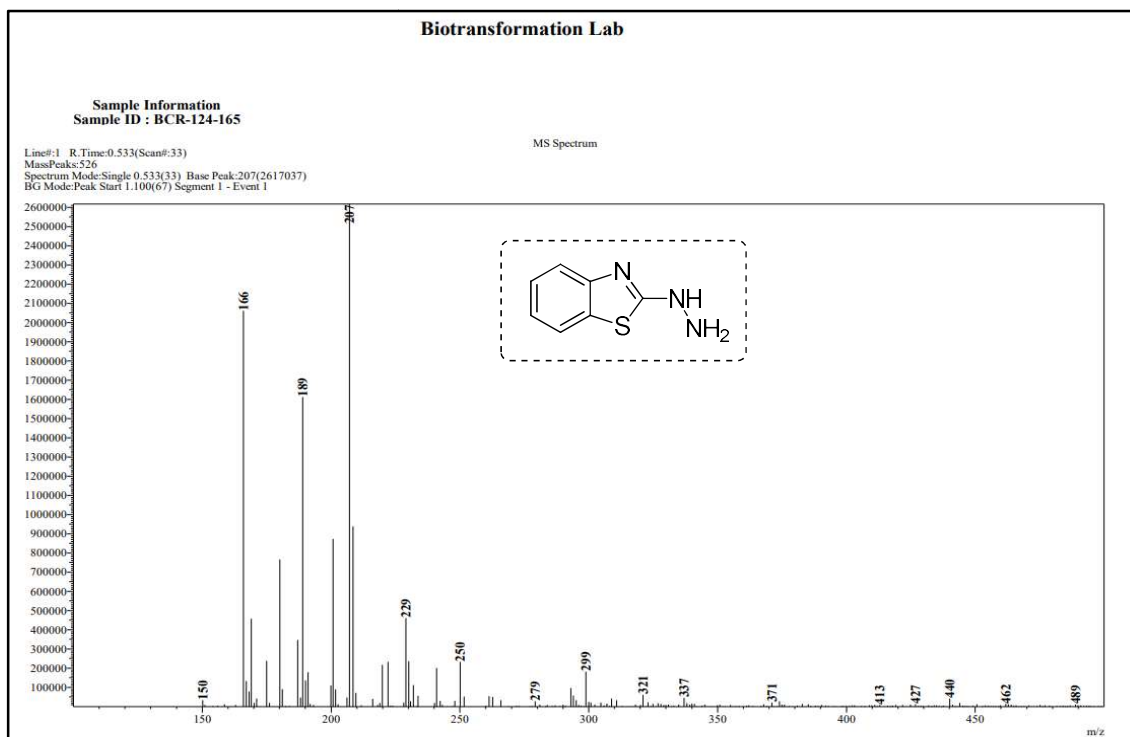
## Spectrum's of compounds



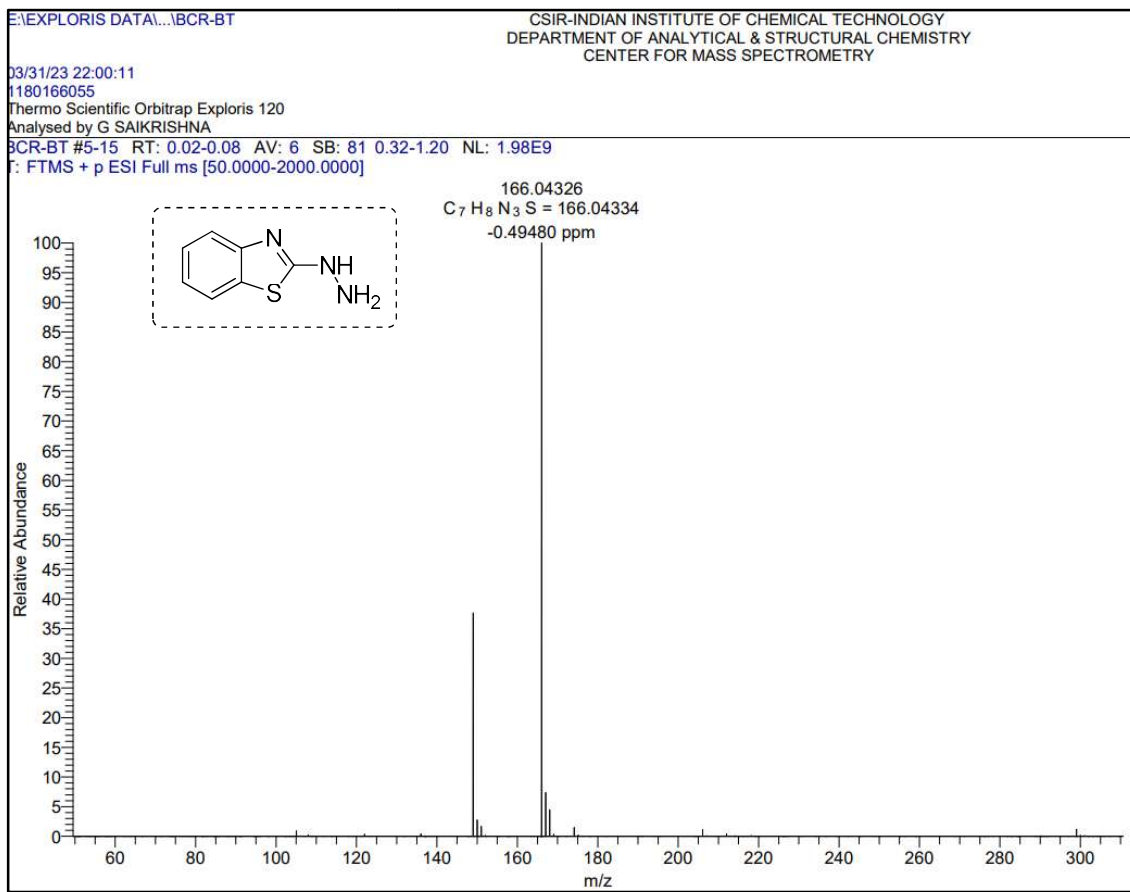
<sup>1</sup>H-NMR Spectrum of Compound 3a



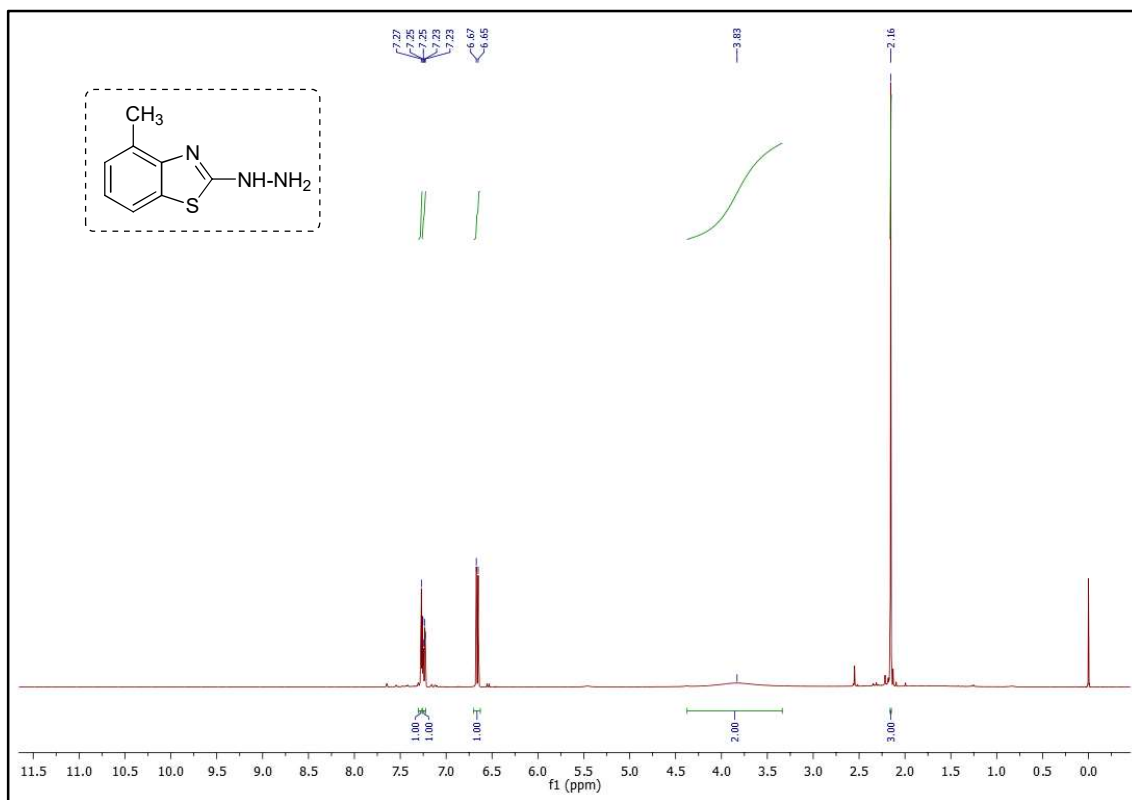
<sup>13</sup>C NMR Spectrum of compound 3a



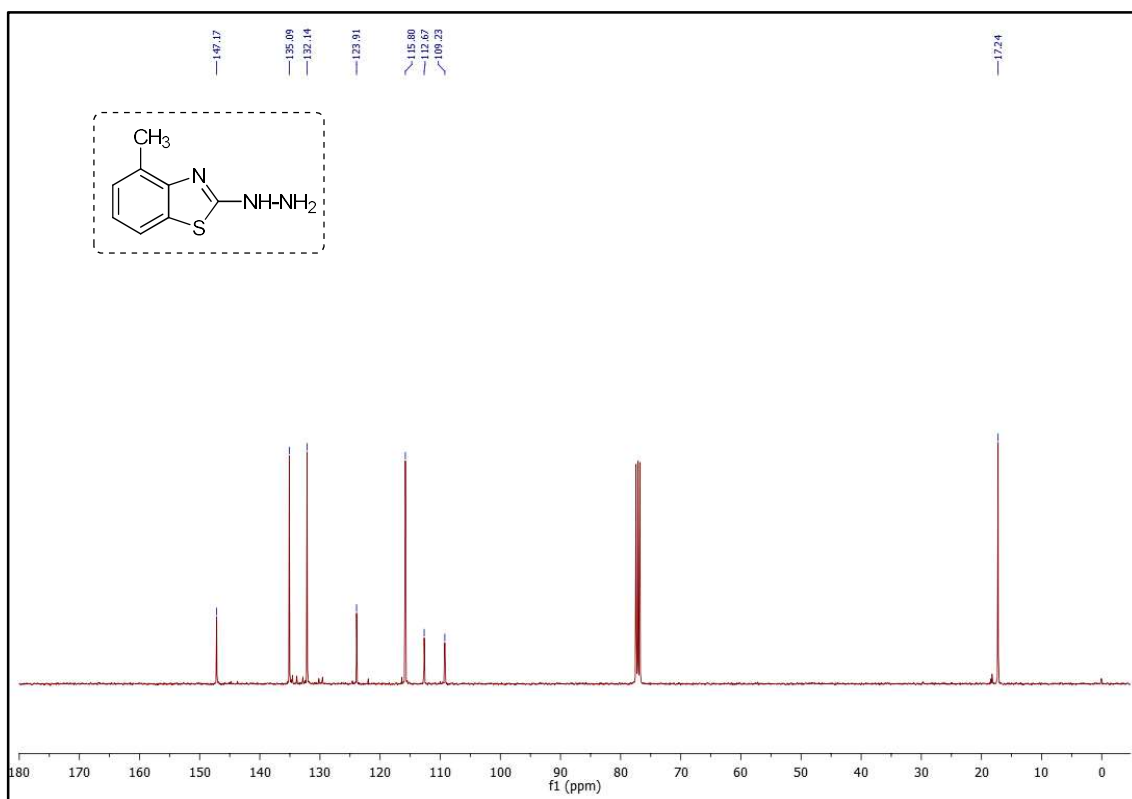
**Mass Spectrum of compound 3a**



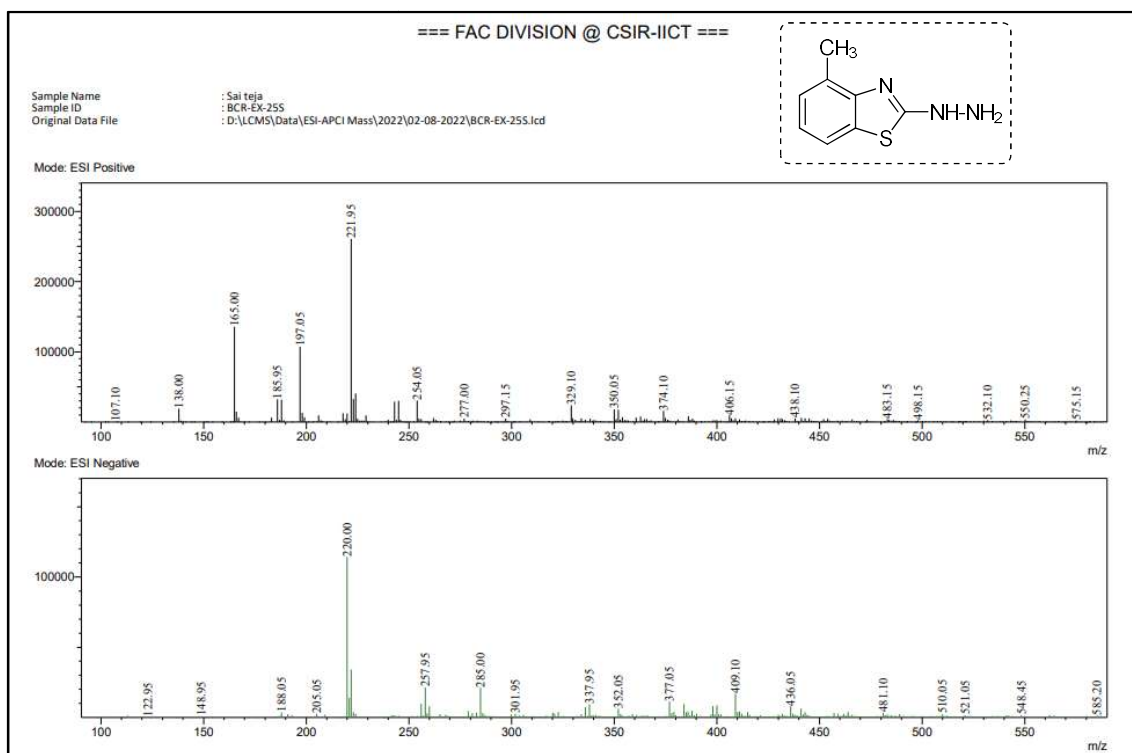
**HRMS of compound 3a**



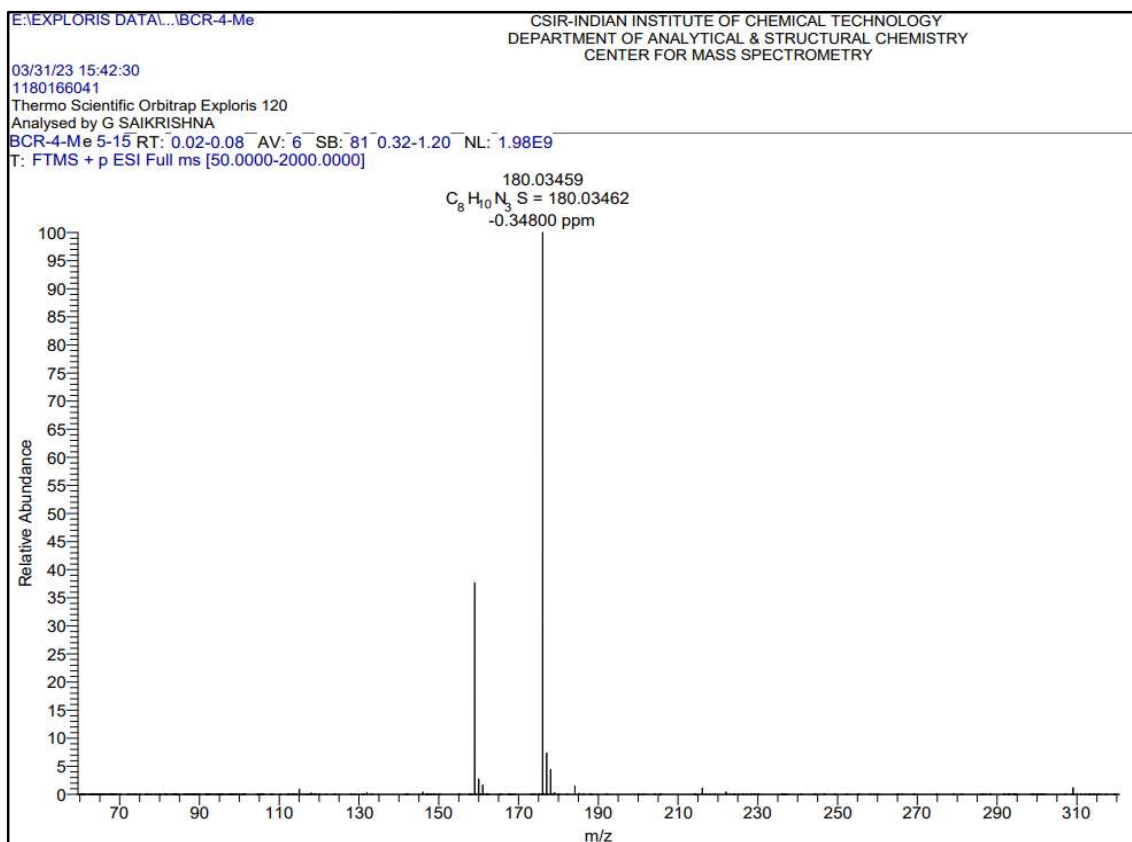
**<sup>1</sup>H-NMR Spectrum of Compound 3b**



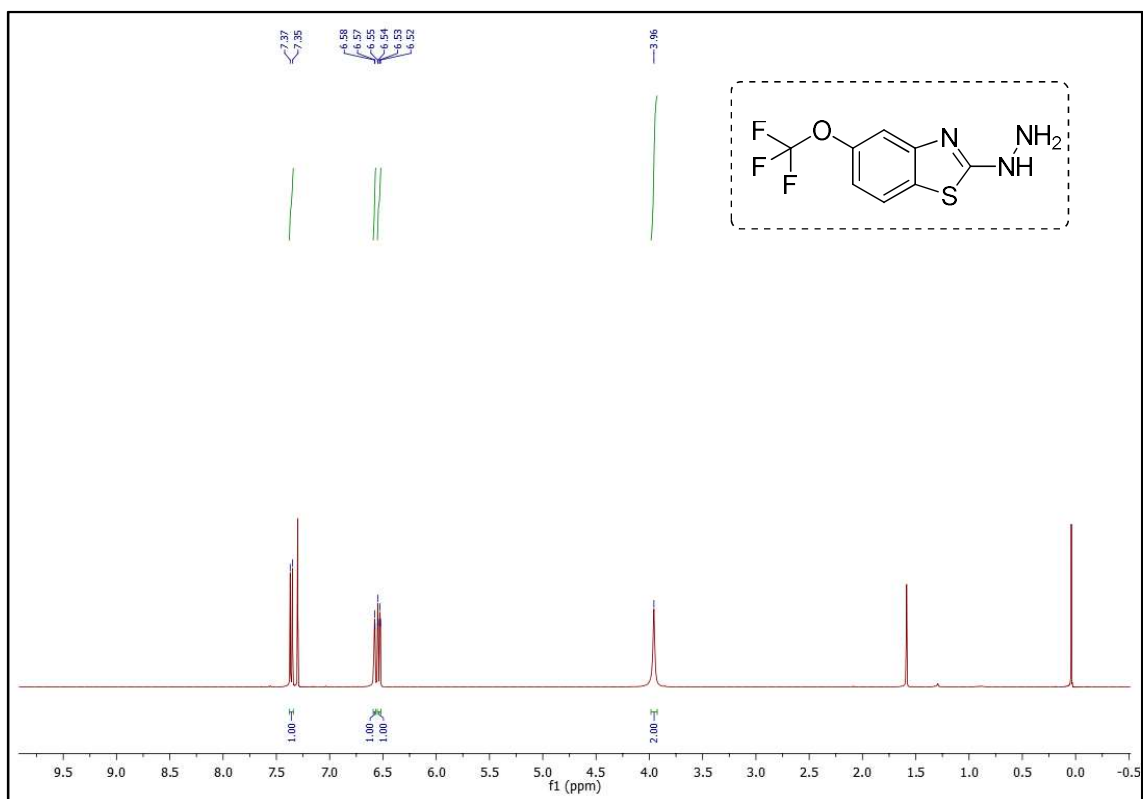
**<sup>13</sup>C NMR Spectrum of compound 3b**



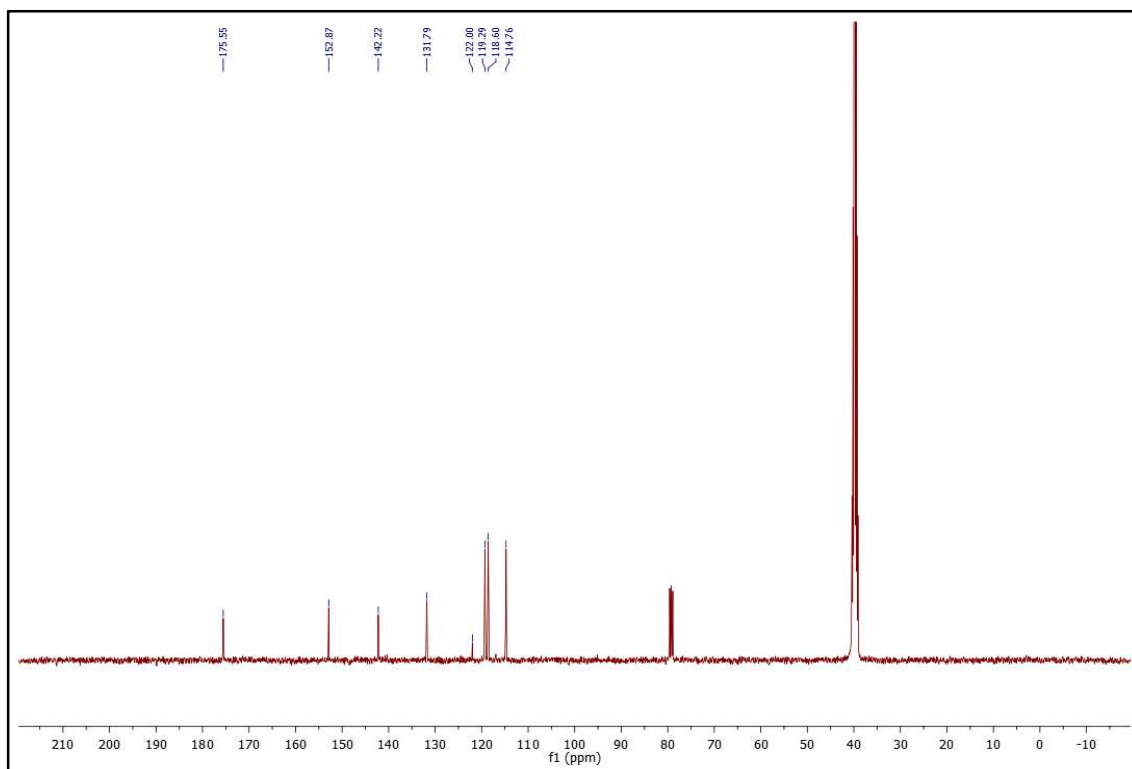
**Mass Spectrum of compound 3b**



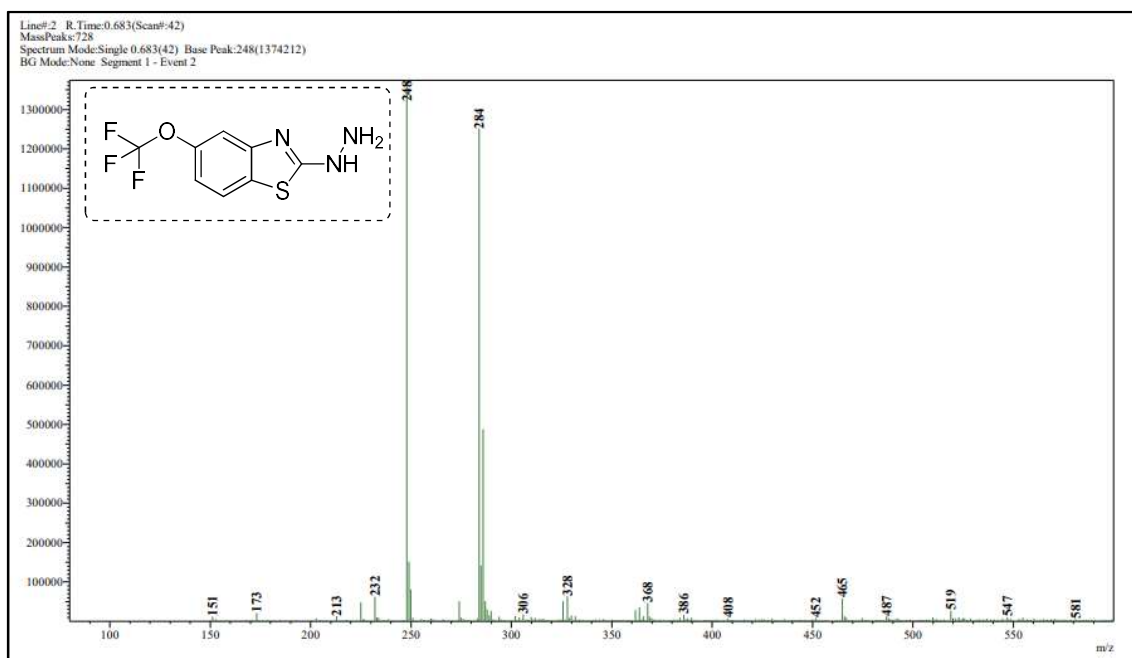
**HRMS of compound 3b**



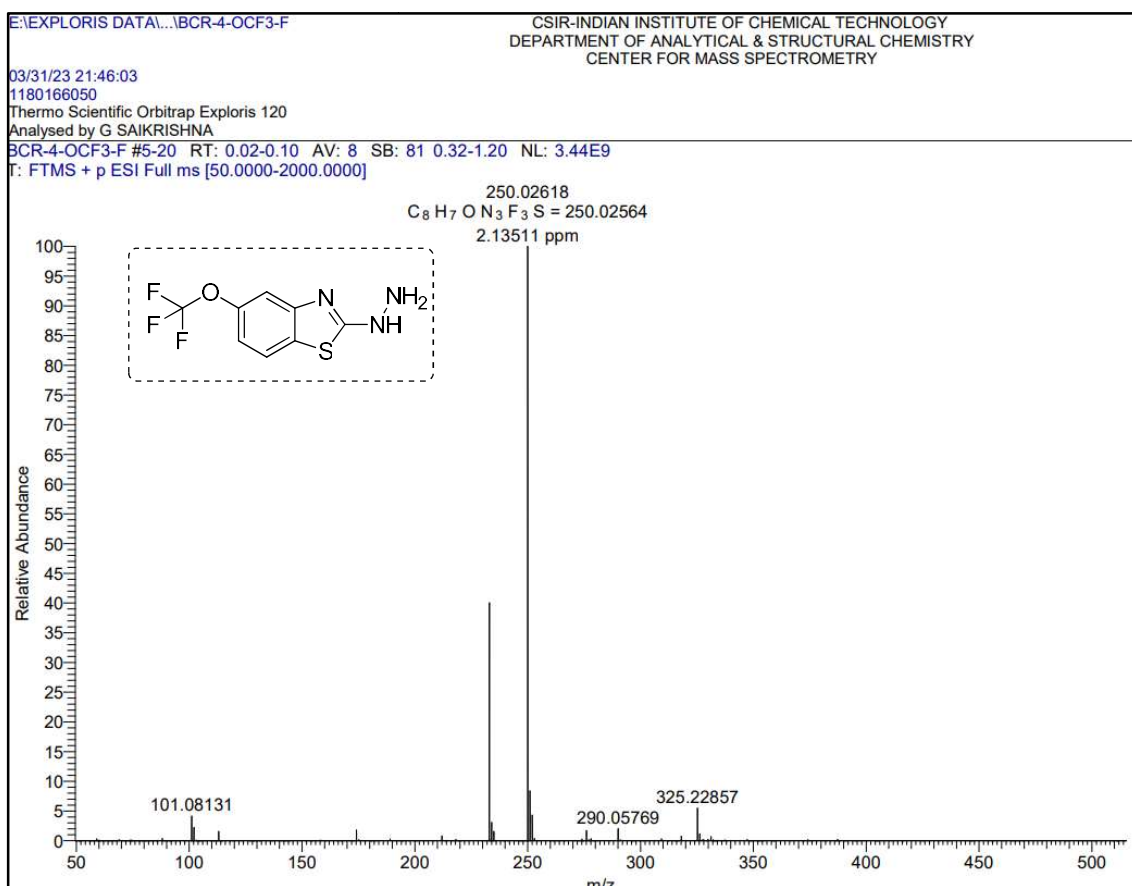
<sup>1</sup>H-NMR Spectrum of Compound 3i



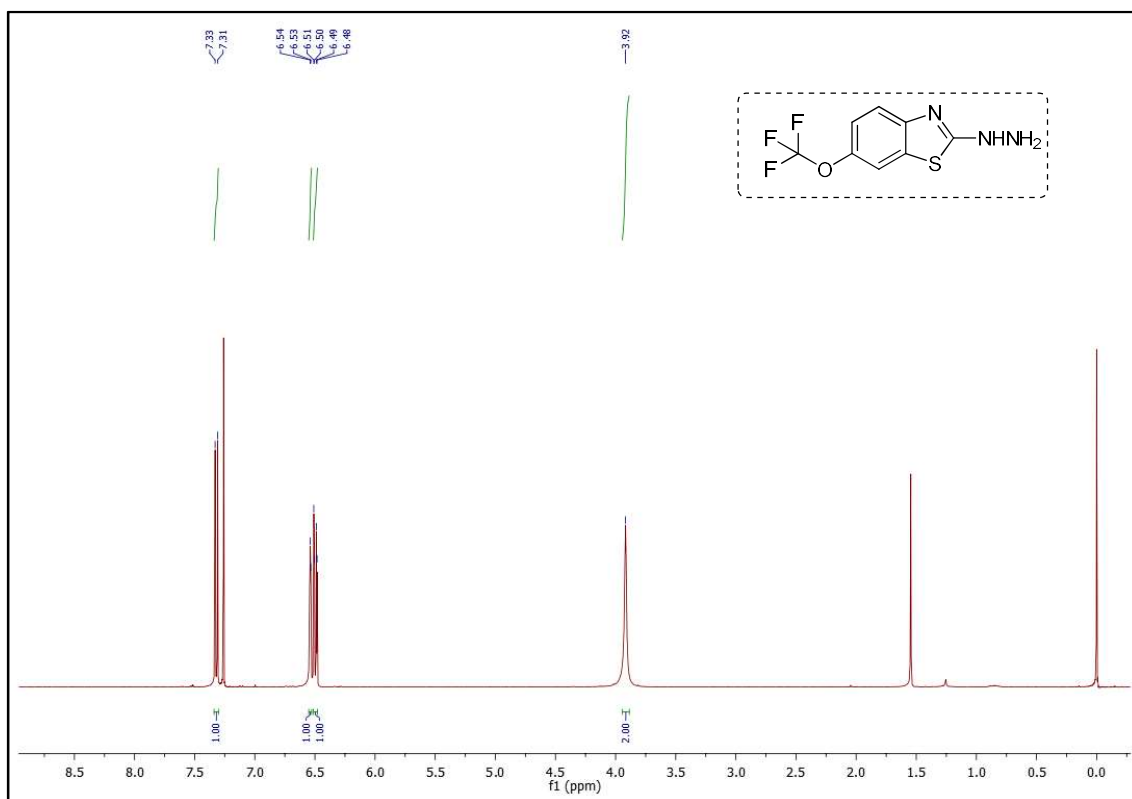
<sup>13</sup>C NMR Spectrum of compound 3i



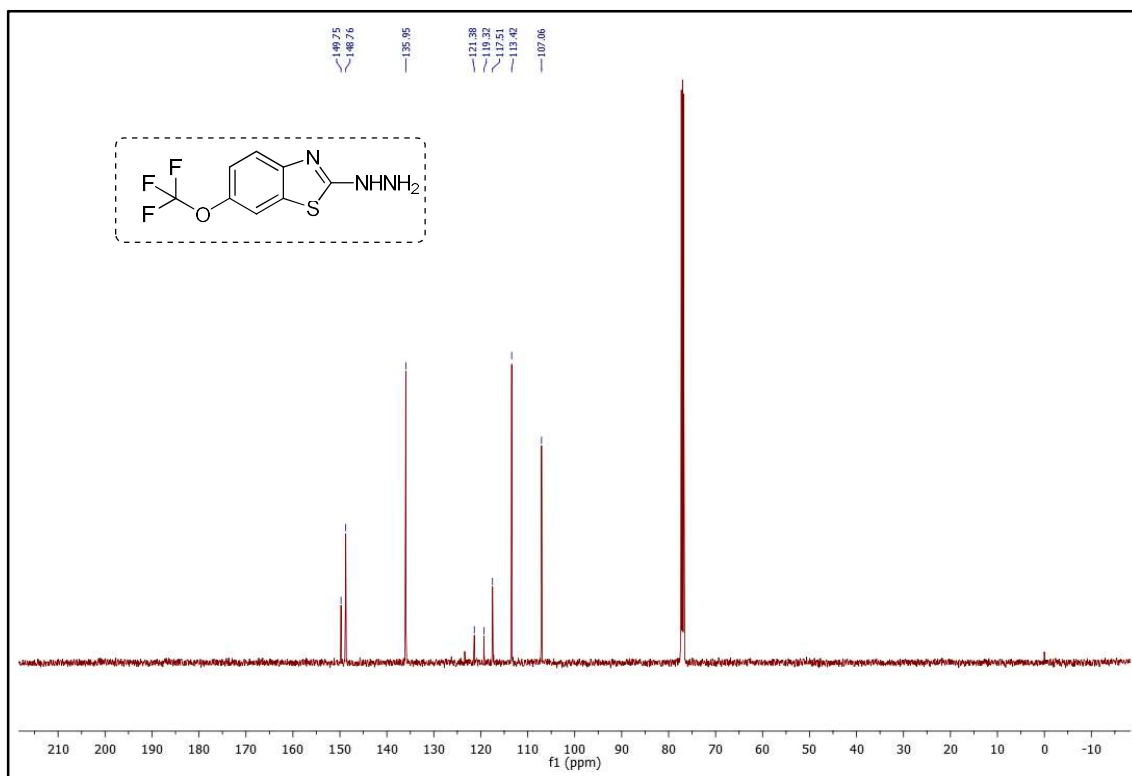
**Mass Spectrum of compound 3i**



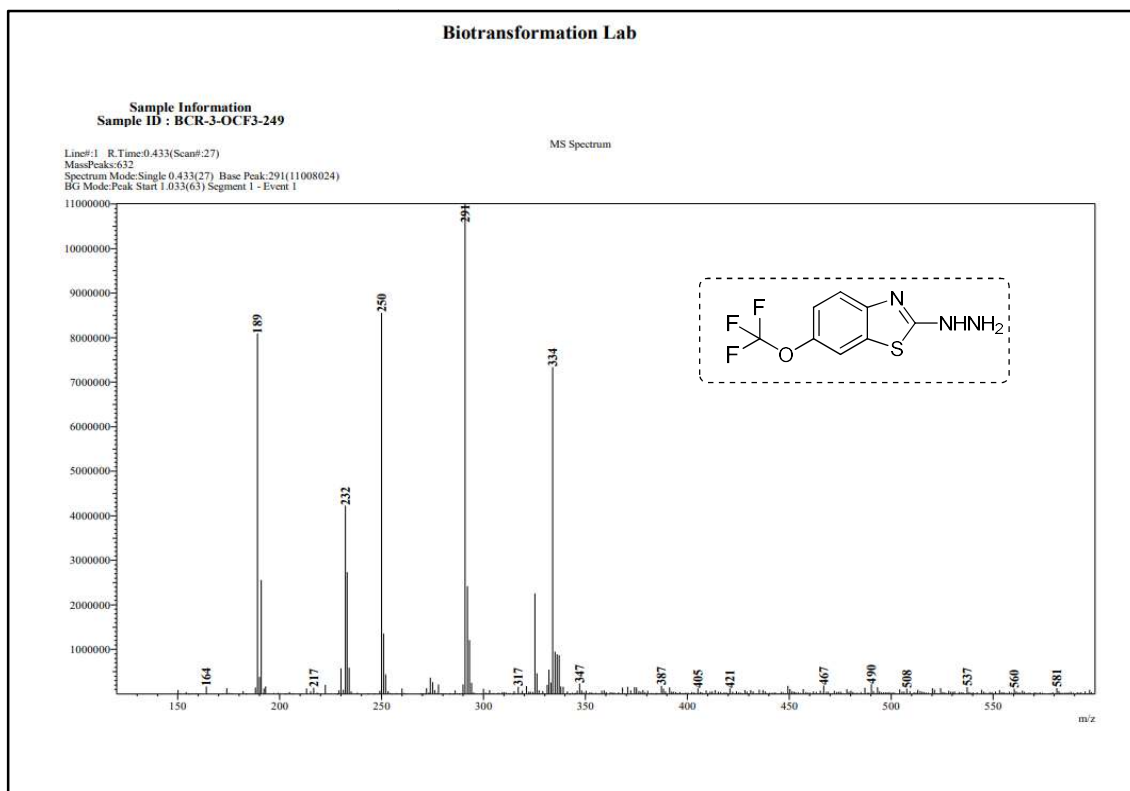
**HRMS of compound 3i**



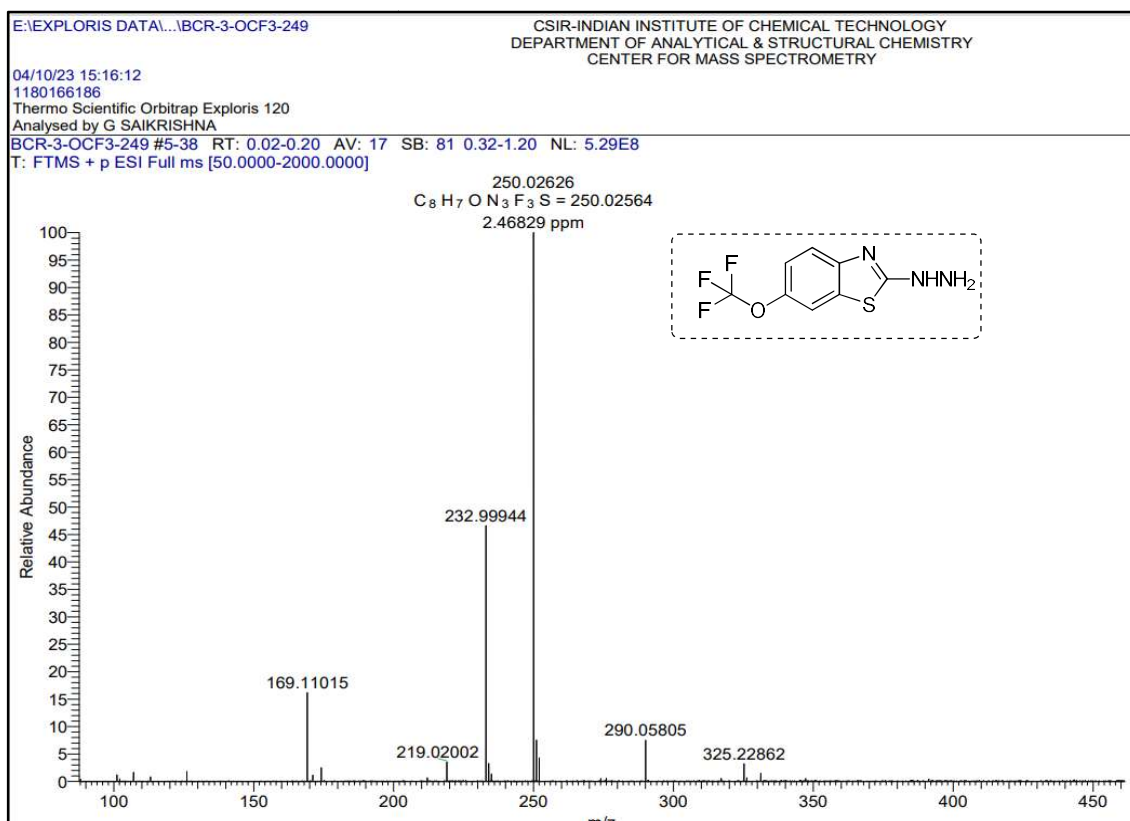
**<sup>1</sup>H-NMR Spectrum of Compound 3j**



**<sup>13</sup>C NMR Spectrum of compound 3j**



**Mass Spectrum of compound 3j**



**HRMS of compound 3j**

**References:**

1. Easmon J, Heinisch G, Hofmann J, Langer T, Grunicke H H, Fink J & Pürstinger G, *Eur. J. Med. Chem.*, 32 (1997) 397.