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	APT	33		APT	51		APT	69		APT	87				
	<sup>1</sup> H NMR	34		<sup>1</sup> H NMR	52		<sup>1</sup> H NMR	70		<sup>1</sup> H NMR	88				
7e	<sup>13</sup> C NMR	35	8d	<sup>13</sup> C NMR	53	9d	<sup>13</sup> C NMR	71	11e	<sup>13</sup> C NMR	89				
	APT	36		APT	54		APT	72		APT	90				
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<b>7</b> f	<sup>13</sup> C NMR	38	8e	<sup>13</sup> C NMR	56	9f	<sup>13</sup> C NMR	74	11f	<sup>13</sup> C NMR	92				
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11σ	<sup>13</sup> C NMR	95		<sup>1</sup> H NMR	105	130	<sup>13</sup> C NMR	115	14c	APT	125
115	APT	96	12c	<sup>13</sup> C NMR	106	150	APT	116		<sup>1</sup> H NMR	126
	<sup>1</sup> H NMR	97		APT	107		<sup>1</sup> H NMR	117	14d	<sup>13</sup> C NMR	127
11h 13	<sup>13</sup> C NMR	98		<sup>1</sup> H NMR	108	14a	<sup>13</sup> C NMR	118		APT	128
	APT	99	13a	<sup>13</sup> C NMR	109		APT	119		<sup>1</sup> H NMR	129
	<sup>1</sup> H NMR	100		APT	110		<sup>1</sup> H NMR	120	14e	<sup>13</sup> C NMR	130
12a	<sup>13</sup> C NMR	101		<sup>1</sup> H NMR	111	14b	<sup>13</sup> C NMR	121		APT	131
	APT	102	13b	<sup>13</sup> C NMR	112		APT	122		<sup>1</sup> H NMR	132
12h	<sup>1</sup> H NMR	103		APT	113	14c	<sup>1</sup> H NMR	123	15	<sup>13</sup> C NMR	133
120	<sup>13</sup> C NMR	104	13c	<sup>1</sup> H NMR	114	14c	<sup>13</sup> C NMR	124		APT	134

#### **Experimental part**

Solvents were purified and dried by standard methods. Melting points were determined with an electrothermal capillary melting point apparatus. <sup>1</sup>H NMR spectra were recorded with Agilent ProPulse 600 spectrometer (at 600 MHz for <sup>1</sup>H NMR, 151 MHz for <sup>13</sup>C NMR), Bruker 170 Avance 500 spectrometer (at 500 MHz for <sup>1</sup>H NMR, 126 MHz for <sup>13</sup>C NMR) and Varian Unity Plus 400 spectrometer (at 400 MHz for <sup>1</sup>H NMR, 101 MHz for <sup>13</sup>C NMR). Chemical shifts are reported in ppm relative to internal tetramethylsilane (TMS; for <sup>1</sup>H and <sup>13</sup>C). HRMS were recorded with Agilent 6224 TOF LC/MS.

#### General procedure for the synthesis of cyclic amidines 7

To a stirred solution of cyclic imidate **6a** (99.1 g, 1 mol, 1.1 eq.) in methanol (1 L) was added taurine (112.6 g, 0.9 mol, 1 eq.) and the resulting suspension was refluxed for two days. The reaction mixture was allowed cooling to room temperature and volatiles were removed under reduced pressure. The residue was triturated with MTBE (500 mL), filtered off, washed with MTBE ( $3 \times 400$  mL) and dried under reduced pressure to give amidine **7a** that was used in the next step without further purification.



#### 2-(pyrrolidin-2-ylideneamino)ethanesulfonic acid 7a

M.p. 271-273°C, a white powder, 173.0 g (purity 90%, yield 92.3%)

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  3.73-3.68 (m, 4H), 3.20 (t, *J* = 6.8 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.26-2.16 (m, 2H). <sup>13</sup>C NMR (150 MHz, D<sub>2</sub>O)  $\delta$  169.1 (C), 48.4 (CH<sub>2</sub>), 47.7 (CH<sub>2</sub>), 39.1 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 20.2 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S, 192.0569; found 192.0565.



#### 2-(2-azaspiro[4.5]decan-3-ylideneamino)ethanesulfonic acid 7b

M.p. 257-259°C, a white powder, 23.7g (yield 87.1%).

<sup>1</sup>H NMR (400 MHz, CF<sub>3</sub>COOD) δ 8.29-7.76 (m, 2H), 4.22-4.18 (m, 2H), 3.87-3.77 (m, 4H), 3.08-3.03 (m, 2H), 1.84-1.75 (m, 10H). <sup>13</sup>C NMR (126 MHz, CF<sub>3</sub>COOD) δ 168.8, 57.8, 49.7, 48.8, 42.1, 40.5, 38.5, 35.3, 34.8, 24.1, 21.8. HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S, 260.1195; found 260.1191.



#### 2-(piperidin-2-ylideneamino)ethanesulfonic acid 7c

M.p. 255-257°C, a white powder, 112.67 g (yield 94.1%)

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  3.62 (br.s, 2H), 3.42 (br.s, 2H), 3.18 (br.s, 2H), 2.59 (br.s, 2H), 1.81 (br.s, 4H). <sup>13</sup>C NMR (150 MHz, D<sub>2</sub>O)  $\delta$  163.6 (C), 48.2 (CH<sub>2</sub>), 41.5 (CH<sub>2</sub>), 36.9 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 20.3 (CH<sub>2</sub>), 17.5 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S, 206.0725; found 206.0723.



#### 2-(morpholin-3-ylideneamino)ethanesulfonic acid 7d

M.p. 273-275°C, a white powder, 94.23 g (yield 87.6%)

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  4.59 (s, 2H), 4.04 (t, *J* = 5.2 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.57 (t, *J* = 5.2 Hz, 2H), 3.24 (t, *J* = 6.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$ 



#### 2-((3,4-dihydroquinolin-2(1H)-ylidene)amino)ethanesulfonic acid 7e

M.p. 325-327°C, a white powder, 112.7 g (yield 93.7%)

<sup>1</sup>H NMR (400 MHz, CF<sub>3</sub>COOD) δ 9.78-9.64 (m, 1H), 8.64-8.43 (m, 1H), 7.55-7.42 (m, 4H), 4.46-4.42 (m, 2H), 3.99-3.94 (m, 2H), 3.32-3.21 (m, 4H). <sup>13</sup>C NMR (126 MHz, CF<sub>3</sub>COOD) δ 162.7 (C), 131.9 (C), 127.9 (CH), 127.7 (CH), 126.7 (CH), 123.5 (C), 117.2 (CH), 48.5 (CH<sub>2</sub>), 37.5 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S, 254.0725; found 254.0719.



#### 2-(azepan-2-ylideneamino)ethanesulfonic acid 7f

M.p. 271-274°C, a white powder, 107.6 g (yield 95.3%)

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  3.63 (t, *J* =6.4 Hz, 2H), 3.51-3.49 (m, 2H), 3.20 (t, *J* =6.8 Hz, 2H), 2.69-2.67 (m, 2H), 1.79-1.66 (m, 6H). <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O)  $\delta$  169.2 (C), 47.6 (CH<sub>2</sub>), 43.7 (CH<sub>2</sub>), 37.1 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S, 220.0882; found 220.0874.



#### 2-(azocan-2-ylideneamino)ethanesulfonic acid 7g

M.p. 286-289°C, a grey powder, 112.1 g (yield 93.9%)

<sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$  3.68 (t, *J* =6.50 Hz, 2H), 3.59 (t, *J* =5.5 Hz, 2H), 3.21 (t, *J* =6.5 Hz, 2H), 2.67 (t, *J* =6.0 Hz, 2H), 1.86-1.82 (m, 2H), 1.75-1.70 (m, 2H), 1.61-1.52 (m, 4H) <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O)  $\delta$  167.7 (C), 47.6 (CH<sub>2</sub>), 42.0 (CH<sub>2</sub>), 36.9 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 23.3 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S, 234.1038; found 234.1028.

#### General procedure for the synthesis of thiadiazine derivatives 8

Sulfonic acid **7a** (125.0 g, 0.65 mol, 1 eq.) was dissolved in POCl<sub>3</sub> (400 mL), then PCl<sub>5</sub> (135.4 g, 0.65 mol, 1 eq.) was added at 20°C. The resulting white suspension was stirred for 24 hours at 35°C. Upon completion, POCl<sub>3</sub> was removed under reduced pressure at the same temperature. The residue was triturated with MTBE (500 mL), filtered off and washed with MTBE (5×400 mL) to afford a crude sulfonyl chloride that was used in the next step without further purification. To a stirred suspension of the crude sulfonyl chloride (0.65 mol, 1 eq.) in dry CH<sub>3</sub>CN (1000 mL) was added in one portion DIPEA (180.6 g, 1.4 mol, 2.15 eq.) and the reaction mixture was stirred for 12 hours at room temperature (25°C). All volatiles were removed under reduced pressure leaving semi-oil residue. It was diluted with DCM (1 L), K<sub>2</sub>CO<sub>3</sub> (269.5 g, 1.95 mol, 3 eq.) and water (25 mL) were added. The reaction mixture was stirred for 2 hours at room temperature. Upon completion, inorganics were filtered off, and was washed with DCM (4×500 mL). Organic washings were combined and concentrated under reduced pressure (after evaporation of DCM at 10 Torr /30°C, excess of DIPEA was removed at 10 Torr /70°C) to give pure annulated thiadiazine **8a**.



# **3,6,7,8-tetrahydro-2H-pyrrolo[1,2-b][1,2,4]thiadiazine 4,4-dioxide 8a** M.p. 58-60°C, a beige powder, 94.6 g (yield 83.5%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.84-3.81 (m, 2H), 3.63 (t, *J* =6.8 Hz, 2H), 3.33 (t, *J* =6.0 Hz, 2H), 2.54-2.5 (m, 2H), 1.95-1.88 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  156.6 (C), 46.0 (CH<sub>2</sub>), 44.7 (CH<sub>2</sub>), 44.2 (CH<sub>2</sub>), 31.2 (CH<sub>2</sub>), 18.9 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S, 174.0463; found 174.0459.



# 2',3',6',8'-tetrahydrospiro[cyclohexane-1,7'-pyrrolo[1,2-b][1,2,4]thiadiazine] 4',4'-dioxide 8b

M.p. 98-103°C, a white solid 15.1 g (yield 91.1%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.82 (t, *J* =5.60 Hz, 2H), 3.41 (s, 2H), 3.35 (t, *J* =6.00 Hz, 2H), 2.39 (s, 2H), 1.44-1.36 (m, 10H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  156.5 (C), 54.0 (CH<sub>2</sub>), 46.4 (CH<sub>2</sub>), 45.3 (CH<sub>2</sub>), 43.5 (C), 37.8 (CH<sub>2</sub>), 34.8 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, 242.1089; found 242.1084.



#### 2,3,6,7,8,9-hexahydropyrido[1,2-b][1,2,4]thiadiazine 4,4-dioxide 8c

M.p. 68-70°C, a beige powder, 93.6 g (yield 93.4%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.85-3.82 (m, 2H), 3.49-3.46 (m, 2H), 3.42-3.39 (m, 2H), 2.36-2.33 (m, 2H), 1.81-1.75 (m, 2H), 1.71-1.65 (m, 2H) <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 151.7 (C), 44.9 (CH<sub>2</sub>), 44.3 (CH<sub>2</sub>), 42.4 (CH<sub>2</sub>), 32.9 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 20.9 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z:  $[M]^+$  calcd for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S, 188.0619; found 188.0616.



# 3,6,7,9-tetrahydro-2H-[1,4]oxazino[4,3-b][1,2,4]thiadiazine 4,4-dioxide 8d

M.p. 91°C, a white crystal, 97.1 g (yield 91.2%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  4.12 (s. 2H), 3.92-3.86 (m, 4H), 3.56-3.49 (m, 4H). <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$  147.8 (C), 68.4 (CH<sub>2</sub>), 64.9 (CH<sub>2</sub>), 45.4 (CH<sub>2</sub>), 45.0 (CH<sub>2</sub>), 40.8 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S, 190.0412; found 190.0404.



# 2,3,5,6-tetrahydro-[1,2,4]thiadiazino[2,3-a]quinoline 1,1-dioxide 8e

M.p. 126-128°C, yellow solid, 89.3 g (yield 79.1%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.54 (d, *J* =4.20 Hz, 1H), 7.29-7.25 (m, 2H), 7.16-7.12 (m, 1H), 3.96-3.93 (m, 2H), 3.77 (t, *J* =6.00 Hz, 2H), 2.81-2.78 (m, 2H), 2.60-2.57 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  151.1 (C), 132.7 (C), 130.3 (C), 128.2 (CH), 126.6 (CH), 124.9 (CH), 120.3 (CH), 47.2 (CH<sub>2</sub>), 43.2 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S, 236.0619; found 236.0615.



## 3,6,7,8,9,10-hexahydro-2H-[1,2,4]thiadiazino[2,3-a]azepine 4,4-dioxide 8f

M.p. 54-56°C, a beige powder, 101.8 g (yield 94.3%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.81 (t, *J* =6.0 Hz, 2H), 3.71-3.69 (m, 2H), 3.39 (t, *J* =6.4 Hz, 2H), 2.52-2.50 (m, 2H), 1.60 (br.s, 6H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  156.5 (C), 45.4 (CH<sub>2</sub>), 44.9 (CH<sub>2</sub>), 41.8 (CH<sub>2</sub>), 37.3 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S, 202.0776; found 202.0772.



#### 2,3,6,7,8,9,10,11-octahydro-[1,2,4]thiadiazino[2,3-a]azocine 4,4-dioxide 8g

M.p. 77-79°C, a brown oil, 87.7 g (yield 82.3%)

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.87-3.81 (m, 4H), 3.37 (t, *J* =7.5 Hz, 2H), 2.50-2.47 (m, 2H), 1.68-1.58 (m, 4H), 1.55-1.46 (m, 4H) <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  155.4 (C), 45.3 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 42.0 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S, 216.0932; found 216.0929.

#### General procedure for reductive cleavage of thiadiazine derivatives

To a stirred solution of thiadiazine derivative **8a** (34.8 g, 200 mmol, 1 eq.) in glacial acetic acid (150 mL) was added portion wise NaBH<sub>3</sub>CN (25.1 g, 400 mmol, 2 eq.) for 0.5 h keeping temperature below 30°C. The reaction mixture was stirred for 1h at 25°C-30°C, 1 h at 50°C, 21 h at 25°C. The reaction mixture was diluted with water (75 mL) and was cooled to 15°C. It was quenched with 50% aqueous NaOH till pH = 14 at 20°C. A precipitated solid was filtered off and washed with CHCl<sub>3</sub> (5×150 mL). The filtrate was extracted with CHCl<sub>3</sub> (4×200 mL), the combined organics were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure till dryness to afford a crude product **11a** that was purified by trituration with MTBE.



#### 1,2,7-thiadiazonane 1,1-dioxide 11a

M.p. 61°C, a white powder, 22.5 g (yield 63.1%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.74 (br.s, 1H), 3.33-3.13 (m, 5H), 2.94-2.92 (m, 2H), 2.68-2.67 (m, 2H), 1.62-1.54 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  52.9 (CH<sub>2</sub>), 49.5 (CH<sub>2</sub>), 45.0 (CH<sub>2</sub>), 43.4 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S, 178.0776; found 178.0772.



# 9-thia-8,12-diazaspiro[5.8]tetradecane 9,9-dioxide 11b

M.p. 129-133°C, a white solid, 3.3 g (yield 89.7%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 6.94 (br.s, 1H), 3.32 (br.s, 2H), 3.27 (br.s, 2H), 2.88 (br.s, 2H), 2.70 (br.s, 2H), 1.49-1.21 (m, 10H), 1.12-1.08 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 54.6 (CH<sub>2</sub>), 51.3 (CH<sub>2</sub>), 44.9 (CH<sub>2</sub>), 44.6 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 33.9 (C), 33.0 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 21.0 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S, 246.1402; found 246.1395.



#### 1,2,8-thiadiazecane 1,1-dioxide 11c

M.p. 98°C, a white powder, 14.3 g (yield 72.3%). Crude compound was purified by column chromatography (CHCl<sub>3</sub>/MeOH 90/10, SiO<sub>2</sub>) followed by triturating with MTBE ( $3 \times 80$  mL).

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) 6.74 (br.s, 1H), 3.18-3.15 (m, 2H), 3.09-3.08 (m, 2H), 2.95-2.92 (m, 2H), 2.59-2.57 (m, 2H), 2.27 (br.s, 1H), 1.58-1.43 (m, 6H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  47.9 (CH<sub>2</sub>), 44.7 (CH<sub>2</sub>), 43.3 (CH<sub>2</sub>), 41.8 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 20.4 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S, 192.0932; found 192.0924.



#### 1,5,4,8-oxathiadiazecane 5,5-dioxide 11d

M.p. 79°C, a white powder, 6.4 g (yield 67.1%). Crude compound was purified by column chromatography (first eluent  $CHCl_3/CH_3CN$ ,  $SiO_2$ , second eluent MTBE/MeOH 70/30,  $Al_2O_3$ ).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.02 (br.s, 1H), 3.52-3.48 (m, 4H), 3.26-3.23 (m, 2H), 3.15-3.12 (m, 2H), 3.01-2.97 (m, 2H), 2.75-2.72 (m, 2H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 71.2 (CH<sub>2</sub>), 68.6 (CH<sub>2</sub>), 51.1 (CH<sub>2</sub>), 47.4 (CH<sub>2</sub>), 44.3 (CH<sub>2</sub>), 43.6 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S, 194.0725; found 194.0726.



#### 3,4,5,6,7,8-hexahydro-1H-benzo[c][1,2,8]thiadiazecine 2,2-dioxide 11e

M.p. 154-157°C, a yellow powder, 4.8 g (yield 92.7%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.60 (d, *J* = 3.80 Hz, 1H), 7.19-7.15 (m, 2H), 7.04-7.01 (m, 1H), 3.36 (br.s, 1H), 3.09 (br.s, 2H), 2.99 (br.s, 2H), 2.69 (br.s, 2H), 2.19 (br.s, 2H), 1.69 (br.s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  138.5 (C), 131.2 (CH), 130.8 (C), 127.5 (CH), 124.3 (CH), 118.6 (CH), 45.9 (CH<sub>2</sub>), 43.5 (CH<sub>2</sub>), 41.9 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S, 240.0932; found 240.0927.



#### 1-thia-2,9-diazacycloundecane 1,1-dioxide 11f

M.p. 61°C, a white powder, 19.3 g (yield 87.5%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.66 (br.s, 1H), 3.13-3.07 (m, 4H), 2.93-2.91 (m, 2H), 2.60 (br.s, 2H), 2.00 (br.s, 1H), 1.43-1.41 (m, 8H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  50.2 (CH<sub>2</sub>), 46.7 (CH<sub>2</sub>), 44.7 (CH<sub>2</sub>), 41.6 (CH<sub>2</sub>), 27.9 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, 206.1089; found 206.1079.



#### 1-thia-2,10-diazacyclododecane 1,1-dioxide 11g

M.p. 68°C, a white powder, 27.1 g (yield 91.1%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.93 (br.s, 1H), 3.09 (br.s, 2H), 2.98 (br.s, 2H), 2.86 (br.s, 2H), 2.53 (br.s, 2H), 1.99 (br.s, 1H), 1.51-1.37 (m, 10H). <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$  50.7 (CH<sub>2</sub>), 46.4 (CH<sub>2</sub>), 42.9 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 25.0

(CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 23.5 (CH<sub>2</sub>), 23.4 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z:  $[M]^+$  calcd for C<sub>9</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S, 220.1245; found 220.1240.



#### 7-ethyl-1,2,7-thiadiazonane 1,1-dioxide 11h

Yellow oil, 13.2 g (yield 86.7%). The compound was prepared in a similar manner to that of **14a**.

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.63 (br.s, 1H), 3.26-3.21 (m, 4H), 2.73 (t, J = 6.0 Hz, 2H), 2.54-2.50 (m, 4H), 1.62-1.58 (m, 4H), 0.99 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  54.5 (CH<sub>2</sub>), 53.4 (CH<sub>2</sub>), 51.6 (CH<sub>2</sub>), 50.0 (CH<sub>2</sub>), 42.9 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 12.5 (CH<sub>3</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, 206.1089; found 206.1084.

#### General procedure for reducing thiadiazine derivatives

To a solution of annulated thiadiazine **8a** (34.8 g, 200 mmol) in MTBE (150 mL) was added dioxane/HCl till pH=1. The resulting white precipitate was filtered-off, washed with MTBE ( $3\times100$  mL) and dried under reduced pressure. The stirred solution of hydrochloride (200 mmol) in dry methanol (200 mL) was cooled to -10°C. NaBH<sub>4</sub> (15.1 g, 400 mmol, 2 eq.) was added portionwise to the reaction mixture and was stirred for 24 h. Upon completion, the reaction mixture was diluted with H<sub>2</sub>O (30 mL), stirred for 10 min and volatiles were evaporated under reduced pressure. The residue was triturated with CHCl<sub>3</sub> (200 mL) and filtered off. The residue was washed with CHCl<sub>3</sub> (3×100 mL). The combined washings were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to afford a crude **9a**.



# Hexahydro-1H-pyrrolo[1,2-b][1,2,4]thiadiazine 4,4-dioxide 9a

M.p. 68°C, a white powder, 32.3 g (yield 91.6%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 4.42-4.38 (m, 1H), 3.31-3.28 (m, 1H), 3.23-3.19 (m, 2H), 3.07-2.99 (m, 1H), 2.91-2.88 (m, 1H), 2.84-2.77 (m, 1H), 2.68-2.62 (m, 1H), 2.09-2.04 (m, 1H), 2.02-1.90 (m, 1H), 1.85-1.74 (m, 1H), 1.67-1.59 (m, 1H) <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 76.7 (CH), 45.2 (CH<sub>2</sub>), 45.2 (CH<sub>2</sub>), 44.0 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 21.3 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S, 176.0619; found 176.0613.



# Octahydropyrido[1,2-b][1,2,4]thiadiazine 4,4-dioxide 9c

M.p. 96°C, a white powder, 29.7 g (yield 86.7%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 4.31 (s, 1H), 3.29-3.26 (m, 1H), 3.12-2.97 (m, 4H), 2.90-2.88 (m, 2H), 1.69-1.61 (m, 3H), 1.51-1.41 (m, 3H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 71.3 (CH), 44.7 (CH<sub>2</sub>), 43.4 (CH<sub>2</sub>), 41.0 (CH<sub>2</sub>), 30.7 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 19.0 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S, 190.0776; found 190.0772.



# Hexahydro-1H-[1,4]oxazino[4,3-b][1,2,4]thiadiazine 4,4-dioxide 9d

M.p. 172°C, a white powder, 17.5 g (yield 93.1%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 4.20 (d, *J* =11.6 Hz, 1H), 3.85-3.82 (m, 1H), 3.71-3.68 (m, 1H), 3.59-3.50 (m, 2H), 3.31-2.25 (m, 2H), 3.08-2.94 (m, 5H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 70.0 (CH<sub>2</sub>), 69.9 (CH), 66.3 (CH<sub>2</sub>), 44.0 (CH<sub>2</sub>), 43.4 (CH<sub>2</sub>),

41.0 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z:  $[M]^+$  calcd for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S, 192.0569; found 192.0563.



#### Octahydro-1H-[1,2,4]thiadiazino[2,3-a]azepine 4,4-dioxide 9f

M.p. 81°C, a white powder, 17.9 g (yield 93.2%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  4.46-4.39 (m, 1H), 3.32-3.22 (m, 2H), 3.06-2.97 (m, 2H), 2.90-2.87 (m, 1H), 2.75-2.69 (m, 1H), 2.61-2.53 (m, 1H), 2.21-2.14 (m, 1H), 1.80-1.72 (m, 2H), 1.64-1.57 (m, 1H), 1.38-1.16 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  74.4 (CH), 46.7 (CH<sub>2</sub>), 43.8 (CH<sub>2</sub>), 41.6 (CH<sub>2</sub>), 34.8 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S, 204.0932; found 204.0927.

#### General procedure for the synthesis of tertiary salts 12

CH<sub>3</sub>I (49.7 g, 350 mmol, 7 eq.) was added to a stirring solution of **8a** (8.7 g, 50 mmol) in acetone (100 mL). The reaction mixture was refluxed for 3 h. After cooling to rt the precipitated solid was filtered off, washed with ether ( $3\times100$  mL) and dried under argon atmosphere to afford a pure quaternary salt **12a**. Compounds **12d** and **12e** were used in the next step without any characterization.



# 1-methyl-3,6,7,8-tetrahydro-2H-pyrrolo[1,2-b][1,2,4]thiadiazin-1-ium 4,4-dioxide iodide 12a

M.p. 215-217°C, a white powder, 12.7 g (yield 80.4%)

Elemental analysis: Calcd. for C<sub>7</sub>H<sub>13</sub>IN<sub>2</sub>O<sub>2</sub>S (316.16): C 26.59, H 4.14, I 40.14 N 8.86, O 10.12, S 10.14 Found: C 26.66, H 4.09, I 40.19 N 8.90, S 10.16.



# 1-methyl-2,3,6,7,8,9-hexahydropyrido[1,2-b][1,2,4]thiadiazin-1-ium 4,4-dioxide iodide 12b

M.p. 173°C, a white powder, 7.2 g (yield 72.9%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 4.33-4.29 (m, 2H), 4.26-4.22 (m, 2H), 3.71-3.67 (m, 2H), 3.33 (s, 3H), 2.92-2.88 (m, 2H), 1.84-1.76 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 165.6, 50.1, 43.9, 43.6, 42.5, 29.5, 20.6, 18.0. Elemental analysis: Calcd. for C<sub>8</sub>H<sub>15</sub>IN<sub>2</sub>O<sub>2</sub>S (330.19): C 29.10, H 4.58, I 38.43, N 8.48, O 9.69, S 9.71 Found: C 29.16, H 4.63, I 38.49, N 8.49, S 9.78.



# 1-methyl-3,6,7,8,9,10-hexahydro-2H-[1,2,4]thiadiazino[2,3-a]azepin-1-ium 4,4-dioxide iodide 12c

M.p. 158-161°C, a white powder, 6.3 g (yield 67.0%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  4.31-4.26 (m, 4H), 4.05-4.02 (m, 2H), 3.47 (s, 3H), 3.06-3.04 (m, 2H), 1.76-1.69 (m, 6H) <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  169.6 (C), 49.8 (CH<sub>2</sub>), 44.2 (CH<sub>2</sub>), 43.9 (CH<sub>3</sub>), 43.8 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>). Elemental analysis: Calcd. for C<sub>9</sub>H<sub>17</sub>IN<sub>2</sub>O<sub>2</sub>S (344.21): C 31.40, H 4.98, I 36.87, N 8.14, O 9.30, S 9.32 Found: C 31.37, H 5.04, I 36.92, N 8.17, S 9.28.

# General procedure for reductive cleavage of tertiary salts 12

To a stirred solution of **12a** (15.8 g, 50 mmol, 1 eq.) in glacial acetic acid (80 mL) was added portionwise NaBH<sub>3</sub>CN (12.6 g, 200 mmol, 4 eq.). The reaction mixture was stirred for 24 h at 80°C. The reaction mixture was diluted with water (40 mL) and allowed cooling to 20°C. It was quenched with 50% aqueous NaOH till pH=14 at 20°C. The precipitated solid was filtered off and washed with CHCl<sub>3</sub> (5×75 mL). The filtrate was extracted with CHCl<sub>3</sub> (3×70 mL), combined organics were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure till dryness to afford a pure *N*-Me azasultam **14a**.



## 7-methyl-1,2,7-thiadiazonane 1,1-dioxide 14a

Yellow oil, 9.0 g (yield 94.2%).

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.65 (br.s, 1H), 3.26-3.23 (m, 4H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.44 (m, 2H), 2.25 (s, 3H), 1.58 (m, 4H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  56.2 (CH<sub>2</sub>), 53.0 (CH<sub>2</sub>), 51.5 (CH<sub>2</sub>), 45.4 (CH<sub>3</sub>), 42.2 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S, 192.0932; found 192.0929.



## 8-methyl-1,2,8-thiadiazecane 1,1-dioxide 14b

M.p. 49-52°C, a white powder, 8.7 g (yield 96.1%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.45 (br.s, 1H), 3.25-3.22 (m, 2H), 3.09 (br.s, 2H), 2.66-2.64 (m, 2H), 2.34 (br.s, 2H), 2.15 (s, 3H), 1.49 (br.s, 6H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  52.7 (CH<sub>2</sub>), 52.5 (CH<sub>2</sub>), 49.3 (CH<sub>2</sub>), 42.9 (CH<sub>3</sub>), 42.1 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 20.7 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, 206.1089; found 206.1080.



## 9-methyl-1-thia-2,9-diazacycloundecane 1,1-dioxide 14c

M.p. 63-66°C, a white powder, 7.3 g (yield 92.7%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  6.50 (br.s, 1H), 3.19-3.17 (m, 2H), 3.06 (br.s, 2H), 2.65-2.63 (m, 2H), 2.38 (m, 2H), 2.09 (s, 3H), 1.40-1.34 (m, 8H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  53.7 (CH<sub>2</sub>), 53.3 (CH<sub>2</sub>), 50.3 (CH<sub>2</sub>), 41.4 (CH<sub>3</sub>), 40.0 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 20.9 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S, 220.1245; found 220.1235.



# 10-methyl-1-thia-2,10-diazacyclododecane 1,1-dioxide 14d

M.p. 68-71°C, a white powder, 7.8 g (yield 94.7%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.12 (br.s, 1H), 3.14 (br.s, 2H), 2.99 (br.s, 2H), 2.58 (br.s, 2H), 2.32 (br.s, 2H), 2.13 (s, 3H), 1.44-1.35 (m, 10H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 55.8 (CH<sub>2</sub>), 50.5 (CH<sub>2</sub>), 48.7 (CH<sub>2</sub>), 43.6 (CH<sub>3</sub>), 40.9 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 24.6 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>10</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S, 234.1402; found 234.1395.



# 8-methyl-1,5,4,8-oxathiadiazecane 5,5-dioxide 14e (purity 92%)

M.p. 105-109°C, a white powder, 4.7 g (yield 94.0%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.89 (br.s, 1H), 3.47-3.42 (m, 4H), 3.19 (br.s, 2H), 3.03 (br.s, 2H), 2.85-2.82 (br.s, 2H), 2.43 (br.s, 2H), 2.18 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  68.9 (CH<sub>2</sub>), 68.5 (CH<sub>2</sub>), 53.4 (CH<sub>2</sub>), 50.1 (CH<sub>2</sub>), 47.7 (CH<sub>2</sub>), 43.4 (CH<sub>2</sub>), 43.0 (CH<sub>3</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S, 208.0882; found 208.0874.

#### General procedure of reduction reaction of tertiary salts 12

The stirred solution of tertiary salt **12a** (25.3 g, 80 mmol, 1 eq.) in dry methanol (200 mL) was cooled to  $-10^{\circ}$ C. To the reaction mixture was added portionwise NaBH<sub>4</sub> (6.0 g, 160 mmol, 2 eq.) and was stirred for 24 h. The reaction mixture was diluted with H<sub>2</sub>O (20 mL), stirred for 10 min and volatiles were evaporated under reduced pressure. The residue was triturated with CHCl<sub>3</sub> (150 mL) and filtered off. The residue was washed with CHCl<sub>3</sub> (3×100 mL). The washings were collected, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to afford **13a**.



#### 1-methylhexahydro-1H-pyrrolo[1,2-b][1,2,4]thiadiazine 4,4-dioxide 13a

M.p. 96-99°C, a white powder, 13.3 g (yield 87.8%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.92-3.90 (m, 1H), 3.34-3.20 (m, 3H), 3.17-3.13 (m, 1H), 3.10-3.04 (m, 1H), 2.85-2.79 (m, 1H), 2.19 (s, 3H), 2.02-1.76 (m, 4H) <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  81.2 (CH), 53.5 (CH<sub>2</sub>), 46.1 (CH<sub>2</sub>), 45.7 (CH<sub>2</sub>), 38.8 (CH), 30.3 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S, 190.0776; found 190.0772.



M.p. 74-76°C, a white powder, 5.1 g (yield 91.1%)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.92 (s, 1H), 3.36-3.29 (m, 1H), 3.23-3.08 (m, 4H), 2.70-2.63 (m, 1H), 2.18 (s, 3H), 2.01-1.99 (m, 1H), 1.72-1.69 (m, 1H), 1.53-1.43 (m, 4H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  75.7 (CH), 53.3 (CH<sub>2</sub>), 44.9 (CH<sub>2</sub>), 42.8 (CH<sub>2</sub>), 39.4 (CH<sub>3</sub>), 28.2 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 18.2 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S, 204.0932; found 204.0929.



#### 1-methyloctahydro-1H-[1,2,4]thiadiazino[2,3-a]azepine 4,4-dioxide 13c

Yellow oil, 6.7 g (yield 84.6%)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  4.08-4.04 (m, 1H), 3.52-4.48 (m, 1H), 3.11-3.05 (m, 4H), 2.90-2.79 (m, 1H), 2.20 (s, 3H), 2.15-2.08 (m, 1H), 1.76-1.69 (m, 3H), 1.57-1.48 (m, 1H), 1.40-1.22 (m, 3H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  78.1 (CH), 52.9 (CH<sub>2</sub>), 45.8 (CH<sub>2</sub>), 43.3 (CH<sub>2</sub>), 37.4 (CH<sub>3</sub>), 32.4 (CH<sub>2</sub>), 30.9 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, 218.1089; found 218.1083.

#### Procedure for hydrolytic cleavage of tertiary salt 12a

Solid K<sub>2</sub>CO<sub>3</sub> (97 mg, 0.7 mmol, 2.2 eq) was added to the solution of tertiary salt **12a** (100 mg, 0.32 mmol, 1 eq.) in water (3 mL). The reaction mixture stirred at room temperature for 24h. It was extracted with CHCl<sub>3</sub> ( $3\times15$  mL), the combined extracts were dried under Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to afford **15**.



# 7-methyl-1,2,7-thiadiazonan-6-one 1,1-dioxide 15

M.p. 191°C, a white powder, 51 mg (yield 78.5%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  6.99 (t, *J* =5.50 Hz, 1H), 3.82-3.80 (m, 2H), 3.25-3.23 (m, 2H), 3.19-3.15 (m, 2H), 2.79 (s, 3H), 2.39-2.37 (m, 2H), 1.77-1.72 (m, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  173.6 (C), 51.0 (CH<sub>2</sub>), 45.9 (CH<sub>2</sub>), 41.8 (CH<sub>2</sub>), 32.9 (CH<sub>3</sub>), 29.4 (CH<sub>2</sub>), 27.3 (CH<sub>2</sub>). HRMS (ESI/TOF-Q) m/z: [M]<sup>+</sup> calcd for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S, 206.0725; found 206.0716.

#### X-ray experimental part

X-ray diffraction studies of compounds **11g** (C<sub>9</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S, H<sub>2</sub>O) and **15** (C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S) have been performed using the Bruker APEX II diffractometer (graphite monochromated MoK<sub> $\alpha$ </sub> radiation, CCD detector,  $\varphi$ - and  $\omega$ -scaning, 2 $\Theta_{max} = 50^{\circ}$ ). The structures were solved by direct method using SHELXTL package [1, 2]. Positions of the hydrogen atoms were located from electron density difference maps and refined using "riding" model with  $U_{iso} = nU_{eq}$  (n=1.5 for methyl group or n=1.2 for other hydrogen atoms) of the carrier atom.

Crystallographic data for **11g**:

The colourless crystals of **11g** are monoclinic. At 173 K a = 10.7318(3), b = 8.4291(3), c = 13.947(5) Å,  $\beta = 99.819(2)^{\circ}$ , V = 1243.22(7) Å<sup>3</sup>, M<sub>r</sub> = 238.34, Z = 4, space group  $P2_1/n$ , d<sub>calc</sub>= 1.273 g/cm<sup>3</sup>,  $\mu$ (MoK<sub> $\alpha$ </sub>) = 0.253 mm<sup>-1</sup>, F(000) = 520. Intensities of 15580 reflections (2190 independent, R<sub>int</sub>=0.022) were measured. Full-matrix least-squares refinement against F<sup>2</sup> in anisotropic approximation for non-hydrogen atoms

using 2190 reflections was converged to  $wR_2 = 0.097$  ( $R_1 = 0.038$  for 1855 reflections with F>4 $\sigma$ (F), S = 1.046). The final atomic coordinates, and crystallographic data for molecule **11g** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 2266969).

Crystallographic data for 15:

The colourless crystals of 15 are monoclinic. At 173 K a = 9.4126(2), b =9.9316(3), c = 10.3407(3) Å,  $\beta = 103.903(2)^{\circ}$ , V = 938.35(4) Å<sup>3</sup>,  $M_r = 206.26$ , Z = 4, space group  $P2_1/c$ ,  $d_{calc} = 1.460 \text{ g/cm}^3$ ,  $\mu(MoK_{\alpha}) = 0.323 \text{ mm}^{-1}$ , F(000) = 440. Intensities of 9961 reflections (1647 independent, R<sub>int</sub>=0.016) were measured. Full-matrix leastsquares refinement against  $F^2$  in anisotropic approximation for non-hydrogen atoms using 1647 reflections was converged to  $wR_2 = 0.086$  ( $R_1 = 0.032$  for 1507 reflections with F>4 $\sigma$ (F), S = 1.070). The final atomic coordinates, and crystallographic data for molecule 15 have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union CB2 1EZ, UK +44-1223-336033;Road, (fax: e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 2266968).

Reference:

- 1. Sheldrick GM (2015) Acta Crystallographica Section A Foundations and Advances, 71, 3–8
- 2. Sheldrick, G. M. (2015). Acta Crystallographica Section C, 71, 3-8



**Figure S1.** Molecular structure of compound **15** with the thermal displacements of non-hydrogen atoms at the 50% probability level.



**Figure S2.** Molecular structure of compound **11g** with the thermal displacements of non-hydrogen atoms at the 50% probability level.

lv17\_1







4.790

![](_page_25_Picture_0.jpeg)

![](_page_25_Picture_1.jpeg)

169.09

![](_page_25_Figure_2.jpeg)

48.42 47.67 39.05

30.62

20.17

S24

![](_page_25_Figure_3.jpeg)

Mqq	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	<del></del>
	File name: lv-17_C13.fid					Operator:			SF: 150.8301 MHz			NSC	: 0		PW:	: 3.09 use	c, RG: 60			SI: 65536	;
Date: 02-Jun-2022				Solvent:	d2o	SW: 37879 Hz				TE: 29	98 K	AQ: 0.87 sec, RD: 0.00 sec									

![](_page_26_Picture_0.jpeg)

![](_page_26_Picture_1.jpeg)

169.10

![](_page_26_Picture_2.jpeg)

48.43 47.68

39.07

30.63

ຶ<u>.</u> ອີ25

**7a** D<sub>2</sub>O

Mqq	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	1(		
	File name: lv-17_C13APT.fid					Operator: SF: 150.8329 MHz					NSC: 0			PW: 4.63	usec, RG:	60		SI: 13	31072		
Date: 02-Jun-2022 Solvent:				nt: d2o		SW: 390	)63 Hz		TE: 298 K			AQ: 0.87 s	ec, RD: 0.00	) sec							

![](_page_27_Figure_0.jpeg)

![](_page_27_Figure_1.jpeg)

![](_page_27_Figure_2.jpeg)

![](_page_27_Figure_3.jpeg)

lv-615.fid

11.630

![](_page_27_Picture_5.jpeg)

![](_page_27_Figure_6.jpeg)

![](_page_27_Figure_7.jpeg)

MAA	168.75 161.70 161.01 160.66		117.34 115.08 112.83 110.57		57.83 49.73 48.78	42.07 40.46 38.46 35.27 34.83 34.83 24.05 21.76	Sź	27
	lv-615_C13			=NSO <sub>3</sub> I 7b CF <sub>3</sub> CO	-I OD			
	180 170 160	150 140 130	20 110 100 90	80 70	60 50	40 30	20	######################################
<u>م</u>	File name: lv-615_C13	Operator: root	SF: 125.6429 MHz	NSC: 97	PW: 0.	00 usec, RG: 51200	20	SI: 131072
	Date: 28-Dec-2022	Solvent: TFA	SW: 32680 Hz	AQ: 1.5				

РРМ

![](_page_29_Figure_1.jpeg)

lv-18.fid

![](_page_29_Figure_3.jpeg)

**7c** D<sub>2</sub>O

![](_page_29_Figure_5.jpeg)

![](_page_30_Picture_0.jpeg)

48.20 41.48 36.86 26.14 17.48 17.48

.1.4

lv-18\_C13.fid

163.56

,SO₃H -==N --NH

![](_page_30_Figure_4.jpeg)

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Mdd	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	• • • •
	File name: lv-18_C13.fid					Operat	or:		SF: 150.8	8301 MHz		NSC	: 0		PW:	3.09 use	c, RG: 60			SI: 65536	
	Date: 02-Jun-2022				Solvent: d2o SW: 37879 Hz				TE: 298 K			AQ: 0.87 sec, RD: 0.00 sec									

![](_page_31_Picture_0.jpeg)

163.55

![](_page_31_Picture_2.jpeg)

lv-18\_C13APT.fid

![](_page_31_Picture_4.jpeg)

**7c** D<sub>2</sub>O

	190	180	170	160	150	140	130	120	110	100	90	80	70	0 60	50	40	30	20	10	
File name: lv-18_C13APT.fid					Operator:   SF: 150.8329 MHz					NSC: 0		PW: 4.63 usec, RG: 60					SI: 131072			
Date: 02-Jun-2022					Solve	nt: d2o			TE: 298 K		A	Q: 0.87 sec,	RD: 0.00 se	ec						

РРМ

![](_page_32_Picture_1.jpeg)

S31

lv-20

SO₃H NΗ

**7d** D<sub>2</sub>O

![](_page_32_Figure_5.jpeg)

![](_page_33_Picture_0.jpeg)

lv-20\_C13

160.44

![](_page_33_Picture_2.jpeg)

63.09 63.01 48.08 39.60 37.16

S32

![](_page_33_Figure_3.jpeg)

للفتري وتصادل والعناقر بارجيعه أأرج أرأر عور تنافعها أرجان الزين والبار معادرا وبالعراق فتسرر القادان والجامعية

200	180	160	140	120	100	80	60	40	20	0
File name: lv-	20_C13	Operator	: nmr	SF: 100.612	8 MHz	NSC: 175	PW	/: 0.00 usec, RG: 2	050	SI: 32768
Date: 08-Jun-2022		Solvent:	: D2O	SW: 26042	2 Hz	TE: 300 K	AQ:	1.26 sec, RD: 0.00	) sec	

![](_page_34_Picture_0.jpeg)

160.42

![](_page_34_Figure_3.jpeg)

39.58 37.16

S33

48.07

63.09 63.00

**7d** D<sub>2</sub>O

<u>200</u>	180	160	140	120	100	80	60	40	20	0	
File name: lv-20	_C13APT	Opera	ator: nmr	SF: 10	0.6128 MHz	NSC: 1326		PW: 0.00 usec	, RG: 2050	SI:	65536
Date: 09-Jun	-2022	Solv	ent: D2O	SW:	24038 Hz	TE: 300 K		AQ: 1.06 sec, R	D: 0.00 sec		

![](_page_35_Figure_0.jpeg)

![](_page_35_Figure_1.jpeg)

![](_page_35_Figure_2.jpeg)

![](_page_35_Figure_3.jpeg)
2dd	162.67 161.66 161.32 160.67	131.95 127.86 127.68 123.49	117.17 115.07 115.07 112.82 110.57			48.53 37.52	26.70 21.45	35
lv-488_C13								
				7e CF <sub>3</sub> COO	O₃H D			
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File name: lv-488_C13	Operator	r: root S	SF: 125.6429 MHz	NSC: 60	PW:	0.00 usec, RG: 5120	0	SI: 131072
Date: 28-Dec-2022	Solvent	t: TFA	SW: 32680 Hz	TE: 683 K	AQ: 1	1.57 sec, RD: 0.00 se	ec	









4.790

1.787 1.775 1.764 1.762 1.762 1.762 1.745 1.745 1.734 1.722 1.687 1.664

S37

 3.647
 3.647

 3.631
 3.631

 3.514
 3.514

 3.514
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 3.502
 3.502

 3.501
 3.501

 3.185
 2.691

 2.666
 2.666



lv-19\_C13

169.23





47.57 43.70 37.12 31.82 28.51 26.85 22.48 22.48

lv-19\_C13APT

169.23



**7f** D<sub>2</sub>O

Mdd	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	<del>,,,,,</del> ,
File name: lv-19_C13APT						0	perator: ro	oot		SF: 125	.6681 MHz	2	NSC	2: 330		PW:	0.00 used	c, RG: 512	200		SI: 6553	6
	Date: 05-Jun-2022 Solvent: D2O					20		SW: 3	32680 Hz		TE: 0	683 K		AQ: 1	1.57 sec,	RD: 0.00	sec					





lv-21



4.790



lv-21\_C13

167.70





lv-21\_C13APT

167.70

РРМ

2 D N



File name: lv-21_C13APT	Operator: root	SF: 125.6681 MHz	NSC: 60	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 01-Jun-2022	Solvent: D2O	SW: 32680 Hz	TE: 683 K	AQ: 1.57 sec, RD: 0.00 sec	





S43

lv-5-1





Mdd		156.53						45.95 44.68 44.17 39.51 33.51	<sup>68'81</sup> S4	5
	lv-5-1_C13APT	·								
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<u>ш</u>	File name: lv-5-1_C13APT		Operator: root	SF: 12	5.6681 MHz	NSC: 179		PW: 0.00 usec, RG: 51	200	SI: 65536
	 Date: 26-May-2022		Solvent: DMSO	SW:	32680 Hz	TE: 683 K		AQ: 1.57 sec, RD: 0.00	sec	



3.832 3.818 3.802

3.411 3.369 3.354 3.339

2.492 2.391

1.441 1.414 1.394 1.375 1.360









lv-4



8c DMSO-d6





Date: 26-May-2022 Solvent: DMSO SW: 32680 Hz TE: 683 K AQ: 0.78 sec, RD: 0.00 sec

PPM



151.67

44.79 44.31 39.52 39.52 22.90 20.85 22.90

lv-4\_C13APT



<sup>™</sup> 190 180 170 160 1	150 140 130 1	20 110 100 90	80 70	60 50 40 30 20 10	0
File name: Iv-4_C13APT	Operator: root	SF: 125.6681 MHz	NSC: 250	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 26-May-2022	Solvent: DMSO	SW: 32680 Hz	TE: 683 K	AQ: 1.57 sec, RD: 0.00 sec	



S52





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File name: lv-6_C13.fid					O	perator:		SF	: 150.8304	4 MHz		NSC: 0			PW: 3.0	)9 usec, R	G: 60		SI: 6	65536
	Date:	31-May-2	022		Solv	ent: dmso		ę	SW: 37879	) Hz		TE: 298 k	<		AQ: 0.87	sec, RD: 0	.00 sec			



68.42 64.87 45.43 44.95 40.80 39.95

S54

lv-6\_C13APT.fid

147.83



אר אר אר	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
	File name: lv-6_C13APT.fid					Ор	erator:		SF: 1	50.8333 N	1Hz	NS	C: 0		PW: 4	1.63 usec,	RG: 60		SI:	131072
		Date: 3	31-May-202	22		Solve	ent: dmso		SW	/: 39063 H	z	TE:	298 K		AQ: 0.8	7 sec, RD	: 0.00 sec			





S55

lv-527.fid



Date: 03-Oct-2022			Solvent: D	MSO	S	W: 32680 Hz	TE: 683 K	AQ: 0.7	78 sec, RD:	0.00 sec			
	: lv-527_C13		Operator:	root	SF:	125.6681 MHz	NSC: 96	PW: 0.	00 usec, R	G: 51200		SI:	131072
Iv-527_C	13	150		30 120		8	SO-d6	50	40	30		10	
Add		151.06	132.74	128.19 126.61 124.87 120.31				47.21	43.23 39.55 33.51	25.01	S	56	





S58

lv-3









156.45



lv-3\_C13.fid



8f DMSO-d6

Mdd	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
	File name: lv-3_C13.fid					Operat	or:		SF: 12	5.6926 M	Hz		NSC: 0			PW: 3.27	usec, RG	: 60		SI: 6	65536
	I	Date: 26-N	/lay-2022			Solvent:	dmso		SW:	31250 Hz	<u>.</u>	Т	E: 298 K		A	Q: 1.05 se	c, RD: 0.0	)0 sec			





S60

lv-3\_C13APT.fid



ד ד ד	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
	File name: lv-3_C13APT.fid				Oper	ator:	SF	: 125.692	5 MHz	NS	SC: 0		PW: 5.00	usec, RG	: 60			S	l: 131072		
	Date: 26-May-2022				Solvent	t: dmso		SW: 3289	5 Hz	TE:	298 K	A	Q: 1.95 se	ec, RD: 0.0	)0 sec		Autor	nated Pro	obe tuning	paramete	er





lv-2



8g DMSO-d6





lv-2\_C13

155.41



200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-2_C13 Ope					perator: ro	oot		SF: 12	5.6681 M⊦	lz	N	SC: 356		F	PW: 0.00 u	sec, RG:	51200		SI	: 131072
Dat	Date: 28-May-2022 Solvent: DMSO				ISO		SW:	32680 Hz		Т	E: 683 K		A	Q: 0.78 se	ec, RD: 0.	00 sec				



155.35



S63

lv-2\_C13APT



Mqq	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
	File nam	ne: lv-2_C	13APT		Op	perator: ro	ot		SF: 125.	6681 MHz		NSC	: 200		PW: (	0.00 usec	, RG: 512	00		SI: 65536
	Date:	28-May-2	022		Sc	olvent: DM	SO		SW: 32	2680 Hz		TE: 6	83 K		AQ: 1	.00 sec, F	RD: 0.00 s	ec		



44.69 43.44 30.97 30.65 24.88 24.88 24.88

71.28

lv-10\_C13.fid

210









Ě 11.0	10.0	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.	0
File name: Iv-9		Operator: nmr		SF: 400.13	00 MHz	NSC: 1	PW: 0.00 usec, RG: 25				SI: 32768
Date: 26-May-2022		Solvent: DMSC	)	SW: 822	4 Hz	TE: 300 K		AQ: 1.99 sec, RI	D: 0.00 sec		

1.73 1.00 0.95 0.88

1.08

0.85

0.92

76.71

45.19 45.16 44.00 39.95 31.73 31.73 21.27

lv-9\_C13.fid

200

	9c DMSO	H ⟩ -d6								
190 180 170 160	) 150 140 13	30 120 110 100	90 80	70 60 50	40 30 20	10 0				
File name: lv-9_C13.fid	Operator:	SF: 150.8304 MHz	NSC: 0	PW: 3.09 t	usec, RG: 60	SI: 65536				
Date: 26-May-2022	Solvent: dmso	SW: 37879 Hz	TE: 298 K	AQ: 0.87 sec, RD: 0.00 sec						

	Date: 26-May-2022	Solvent: dmso			SW: 39063 Hz			TE	E: 298 K	AQ: 0.87 sec, RD: 0.00 sec								
	File name: lv-9_C13AP	C	perator:		SF: 150.8333 MHz				NSC: 0	PW: 4.63 usec, RG: 60						SI: 131072		
PPM	200 190 180	170 160	150	140	130	120	<del></del> 110	100	90	80	70	60	50	40		30	20	 10
												et bilanen biadean antekenis Ar et antekenis antekenis						
	lv-9_C13APT.fid					ç		NH  O-d6										
MAA										76.71			45.18	45.17 44.01 39.96	31.73	ç	<sup>27.</sup> \$69	






S71

lv-11\_C13.fid

200

РРМ

	9d D	-NH SO-d6			
200 190 180 170	160 150 140	130 120 110 100	90 80 7	70 60 50 40 30 20	10 0
File name: lv-11_C13.fid	Operator:	SF: 150.8304 MHz	NSC: 0	PW: 3.09 usec, RG: 60	SI: 65536
Date: 26-May-2022	Solvent: dmso	SW: 37879 Hz	TE: 298 K	AQ: 0.87 sec, RD: 0.00 sec	





70.00 69.87 66.27

## lv-11\_C13APT.fid

9d DMSO-d6	

МЧЧ	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
File name: lv-11_C13APT.fid						Operator:		SF	: 150.8333	3 MHz		NSC: 0		PW	: 4.63 use	c, RG: 60		SI	l: 131072	
Date: 26-May-2022				S	Solvent: dms	0	ç	SW: 39063	Hz	-	TE: 298 K		AQ: 0	.87 sec, R	D: 0.00 sec					





Date: 26-May-2022	Solvent: DMSO	SW: 8224 Hz	TE: 300 K	AQ: 1.99 sec, RD: 0.00 sec	Parameter file, TOPSPINVersion 2.1



0=5,/	

9f DMSO-d6

46.74	43.79	41.55	40.01	34.79	31.32	30.01	22.99		

S74

ahtik an da Yiring kayorik			in philippen and a state of the		n a fall have a state of the st		nt personal programme and the second		an der fer der der der der der der der der der d	weekly Webster	n Water for Westersteine	and the state of the	i falan ya 1 kuto a bini ngina si ya ngi di ngina ngi		niyim
МЧЧ	130	120	110	100	90	80	70	60	50	40	30	20	10	0	<b>TT</b>
	File	name: lv8_C13	3	Operator:	nmr	SF	: 100.6128 MH	z	NSC: 367		PW: 0.00	usec, RG: 20	50	SI: 32768	
	Date	e: 30-May-2022		Solvent: [	DMSO		SW: 26042 Hz		TE: 300 K		AQ: 0.98	sec, RD: 0.00 s	sec		

74.40





6.737





28.71 28.55

lv-16\_C13



11a DMSO-d6

Mar N		Martal Martin	an de la filipada mangalan a kalan adalah di da da kalan da Mangalan da sana da sa	
di nation	ار بي علونيا	al a la surrena de la Il	a para da ante	and the second

PPM Mdd		190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-16_C13			Op	perator: nm	٦r	SF: 10	0.6128 MH	lz	NSC: 122		PW: 0.00	) usec, R	G: 2050				SI: 327	68			
Date: 03-Jun-2022			Sc	olvent: DM	so	SW:	26042 Hz		TE: 300 K		AQ: 0.98	sec, RD:	0.00 sec		Pa	rameter fil	e, TOPSP	INVersion	2.1		



lv-16\_C13APT



**11a** DMSO-d6

na kazi ka bahati mangalagi dan ban dalah saka kasin kasin ang mangilak basil akina si sinan kasik dan sa maj	ill, ak interest, die hij die siere en dies daar nie het daar is die state of antiskaar sendarie statie is aan	inter and and a faith the methodistic of the activity area for and providents. He are of the annual with the factor	h deer han he also he see the deer of the	ta de la pol <mark>e</mark> trica de a la site, de la plandel y secolar plane en red e de la plane e a dias de la site e de la
a in a participant a secular film a gla a secular participant a base of the participant of the grade of the secular participant of the s	under eine seine eine eine eine eine eine ein	lang na kalang manang manan	a philosophilic and the private physical basis	in filmer dan dit pulling ng hadina pananan daharapan dari baran karana di

≥ั่⊥	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
	File	name: Iv-1	6_C13APT		Operator:	nmr	SF: 100	0.6128 M⊦	lz	NSC: 357	P۱	V: 0.00 u	sec, RG: 20	50			SI: 65	5536		
	C	)ate: 03-Jur	n-2022		Solvent: D	OMSO	SW:	24038 Hz		TE: 300 K	AQ	: 1.36 se	c, RD: 0.00 s	sec	P	aramete	r file, TOPS	PINVersi	on 2.1	





6.938

2.880 2.696 2.499

3.321 3.274 1.490 1.416 1.396 1.396 1.319 1.319 1.301 1.301 1.230 1.230 1.230 1.230 1.230

МЧЧ	10.0	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0
File name: lv633-1		Operator:	root	SF: 499.6730	MHz	NSC: 1	PV	/: 0.00 usec, RG: 3	2	SI: 32768	
Date: 10-Nov-2022		Solvent: I	OMSO	SW: 8993	Hz	TE: 683 K	AQ:	1.82 sec, RD: 0.00 s	sec		

lv-	633	C1	3



File name: lv-633_C13	Operator: root	SF: 125.6429 MHz	NSC: 500	PW: 0.00 usec, RG: 51200	SI: 131072
Date: 12-Nov-2022	Solvent: DMSO	SW: 32680 Hz	TE: 683 K	AQ: 0.78 sec, RD: 0.00 sec	

0



PPM

Date: 12-Nov-2022

Solvent: DMSO



AQ: 1.00 sec, RD: 0.00 sec

lv-633\_C13APT

HN.S HN.S 9 N	Н					
11b DMSO-	d6					
200 180 1	60 140	120 100	80	60	40	20 0
File name: lv-633_C13APT	Operator: root	SF: 125.6429 MHz	NSC: 600	PW: 0.00	0 usec, RG: 51200	SI: 65536

TE: 683 K

SW: 32680 Hz





6.735

3.315 3.180 3.167 3.154 3.154 3.093 3.080 2.934 2.921 2.593 2.580

.948

500 465 454 426

58

584 553 535 512

567 494 271

11c DMSO-d6







lv-13\_C13



11c DMSO-d6

her for Langle for the	n galan na gana gana gana gana gana gana	and the state of the	t put an put to an data par	in a star of a star of the star	and a loss of the second second	arrighteninghallsagerent)	and a second	in the state of the second	and a start of the	an a	a a fa far fan de la compañsie de la compañsie La compañsie de la compañsie de	and the state of the second	elefters (all strengthed of	Disellation States, Cards	ter in e	and provide the second s	Arthursh Militan	the plates and the second s	alaa hahahahahahahah
Mdd	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
	File nan	ne: lv-13_0	C13		Operator: ı	root		SF: 125.	6681 MHz		NSC: 2	37		PW: 0.00	usec, RG:	51200		SI: 13	31072
	Date: 2	26-May-202	22		Solvent: D	MSO		SW: 3	2680 Hz		TE: 683	ЗК		AQ: 0.78 s	sec, RD: 0.	00 sec			





РРМ



lv-693\_C13.fid





lv-693\_C13APT.fid



210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20		10
File name: lv-693_C13APT.fid					Ope	erator:		SF: 1	50.8333 N	1Hz	N	SC: 0		PW	: 4.63 use	c, RG: 60			SI: 1	31072	
Date: 09-Dec-2022						Solve	nt: dmso		SW	': 39063 H	z	TE:	298 K		AQ: 0	.87 sec, R	D: 0.00 s	ec			







S88

lv-538.fid











6.662

РРМ



AQ: 1.05 sec, RD: 0.00 sec

lv-12\_C13.fid

Date: 26-May-2022

Solvent: dmso

	Q, Q HN <sup>-S</sup> (11 NH					
	I1f DMSO-d6					
S			allange and a state of the frequency for the state of the			
<u>}</u> 170 160 150 14 File name: Iv-12_C13.fid	0 130 120 Operator:	110 100 90 80   SF: 125.6926 MHz S	0 70 NSC: 0	60 50 40 PW: 3.27 usec, F	30 20 RG: 60	10 0 SI: 65536

SW: 31250 Hz

TE: 298 K





lv-12\_C13APT.fid

190

РРМ

HN-S HN-NH			
<b>11f</b> DMSO-d6			
ter fan de ferste fe De fjipper een terpe ferste ferste ferste een tereste een perste ferste geste spesiel ferste se 120 120 120 140 140 100 00	րները բուժում ոչ վարու անկ եներ բետ ոչ առեվ անհետել, ոչ փոսկել և միտուլ է դերերությեն, իստ էր Դրմ էս Դուլիսու են ու ու որ է երգնությունը հայտությունը հայտնությունը ու նարագույցությունը է է ու որ երգ ամիտոլի		
130 120 110 100 9		40 3	

File name: Iv-12_C13APT.fid	Operator:	SF: 125.6925 MHz	NSC: 0	PW: 5.00 usec, RG: 60	SI: 131072
Date: 26-May-2022	Solvent: dmso	SW: 32895 Hz	TE: 298 K	AQ: 1.95 sec, RD: 0.00 sec	Automated Probe tuning parameter



PPM										50.72 46.43	42.94 40.06 39.97	25.89	24.97 24.30 23.52 23.52 23.55 23.55	5	
	lv-1_C13.fid														
		0,0 HN <sup>-Š~</sup> (12	NH												
		<b>11g</b> DN	/ISO-d6												
	es life of state from the second s	i sana wa kuto di dan yao Bana si kata ya kuto kuto kuto kuto kuto kuto kuto kuto	kan, pana kay di ka asi mang dan bilan sa ang dan bilan sa ang dan bilan sa s		Mit de grades de se de si de de defenses ju	ten kit stondid keen, iden as en den k	dentere, burnelitere e norde i politik					- i kni vrate i klasti klast			
Mqq	170 160	) 150	140 130	120	110	100	90	80 70	60	50	40	30	20	10	0
	File name: lv-1_	C13.fid	Operator	:	SF	=: 150.8304 M	Hz	NSC: 0		P١	N: 3.09 usec	, RG: 60		SI: 655	536
	Date: 26-May-2	2022	Solvent: dr	nso	:	SW: 37879 Hz	z	TE: 298 K		AQ:	0.87 sec, RE	D: 0.00 sec			

PPM





## lv-1\_C13APT.fid



	150	140	130	120	110	100	90	80	7	0	60	50	40	30	20	10
File name: lv-1_C13APT.fid					Operator:		SF: 150.	8333 MHz		l	NSC: 0		PW: 4.63 us	sec, RG: 60		SI: 131072
Date: 26-May-2022				Solvent: dmso		SW: 3	9063 Hz		TI	E: 298 K		AQ: 0.87 sec,	RD: 0.00 sec			







lv-887-C13



5			54.48 53.41	51.59 49.95 42.87 40.01	28.63 25.92	<sup>47</sup> S99	
Iv-887-C13APT	HN-S 9 11h DMS	`Et SO-d6					
170 160 150 140	130 120 110		.0 <u>60</u> 	50 4		20 10	
File name: lv-887-C13APT	Operator: nmr	SF: 100.6128 MHz	NSC: 105		PW: 0.00 usec, RG	3: 2050	SI: 65536
Date: 28-Feb-2023	Solvent: DMSO	SW: 24038 Hz	TE: 300 K		AQ: 1.36 sec, RD: 0	).00 sec	





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169.44

50.15 49.99 44.66 40.08 33.60 18.59

<sup>ຊິອິ</sup>S101

lv-22\_C13



12a DMSO-d6

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erfelder bis å herre menninger, som belanser og de bis fra hinden for her her her her her her her her her he	<sup>16</sup> Maria a gerang managang kana kan kan kan kana managan kan kana kan merena managan kan kan kan kan kan kan k			
a har se la serie de serie An la serie de l	<mark>ll af te b</mark> ender strende stad af de stad de stad af de stad af de stad strende stad a stad de stad de stad de st	a kan a san a san ang ang ang ang ang ang ang ang ang a	nin heine als an	an de marte a la cata de la cata d

200	180	160 140		120 100		80	60	40	20	0
File name: lv-22_C13		Operator: nmr		SF: 100.6128 MHz		NSC: 91	PW: 0.00 usec, RG: 2050			SI: 32768
Date: 27-May-2022		Solvent: DM	ISO	SW: 26042 I	Hz	TE: 300 K	AQ: 0	.98 sec, RD: 0.00	sec	





lv-22\_C13APT

169.43



والمعالية ومطرف فستحج والتلا ومنطر الدائه والملا والملاز والم		A. A. M. Matthe	A and a state the set	and the feature of the second of the second
is da managen panagen panagen panagen panagen ber	a perior de la presenta de la presenta de la presenta de la recente de la presente	Allow well investigation of		din Halling polynomial Shirt Manu

Mqq	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-22_C13APT				Operator: nmr			SF: 100.6128 MHz			NSC: 455		PW: 0.00 usec, RG: 2050					SI:	65536		
Date: 27-May-2022				Solvent: I	DMSO		SW: 2	24038 Hz		TE: 30	00 K		AQ: 1.3	6 sec, RD:	0.00 sec					





S103

lv33









lv-23



12c DMSO-d6








Mad



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81.15



### lv-14\_C13APT



13a DMSO-d6

	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-14_C13APT						Operator	r: nmr		SF: 10	0.6128 MH	lz	NSO	C: 280		PW:	0.00 usec,	RG: 2050		:	SI: 65536
Date: 26-May-2022				Solvent:	DMSO		SW:	24038 Hz		TE:	300 K		AQ: 1	.06 sec, R	D: 0.00 sec	;				



Mad





	 Date: 31-May-2022	Solvent: dmso	SW: 32895 Hz	TE: 298 K	AQ: 1.95 sec, RD: 0.0	0 sec	Aut	tomated Probe to	uning parameter
1 1	180 170 160 150 File name: lv-25 APTC13.fid	140 130 Operator:	120 110 100 SF: 125.6925 MHz	) 90 80 NSC: 0	70 60 PW: 5.00 usec, RG:	50 60	40 3	30 20 SI: 13	10 0 1072
	Iv-25_APTC13.fid	13b	DM SO-d6		under van der Mite van de de la gege bede ei jewen stille de mit des de fer				nden gebenendekedennet det degte. di wa still perte energed
MAA					75.66	53.31 44.91	42.76 39.97 39.40	28.21 24.92 18.19	S113





78.09

52.95	45.79	43.29	39.56	37.41	32.35	30.90	CP9.05	51 <sup>2</sup>	5
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lv-26\_C13





אַ ב ג	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
File name: lv-26_C13					Operator: I	root		SF: 125.6	681 MHz		NSC: 4	400		PW: 0.00	0 usec, RG	: 51200		SI: 1	31072
Date: 28-May-2022				Solvent: D	MSO		SW: 32	680 Hz		TE: 68	3 K		AQ: 0.78	sec, RD: (	0.00 sec				

52.89	45.74	43.24	39.53	77 34

78.04

45.74	43.24	39.53	37.34	32.29	30.84	28.98	S <sup>R</sup>	16
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# lv-26\_C13APT





אַ ב	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	
File name: lv-26_C13APT					Operator:	root		SF: 125.6	681 MHz		NSC: 250	)	F	W: 0.00 us	ec, RG: 51	200		SI: 65536		
Date: 28-May-2022					Solvent: D	MSO		SW: 326	680 Hz		TE: 683 k	<b>〈</b>	А	Q: 1.00 sec	c, RD: 0.00	sec				



ЫЧ

56.23	52.96	51.47	45.35	42.16	39.55	28.19	24.51	S118
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lv-29-1\_C13



14a DMSO-d6

Мдд	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-29-1_C13					Operator: root		<b>SF</b> : 1	25.6681 MHz		NSC: 400		PW: 0.00	usec, RG: 51	1200		SI: 131072
Date: 28-May-2022				Solvent: DMSC	)	SV	V: 32680 Hz		TE: 683 K		AQ: 0.78 s	sec, RD: 0.00	) sec			



# lv-29-1\_C13APT

РРМ



14a DMSO-d6

≥ L L	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-29-1_C13APT						Ope	erator: root		SF:	: 125.6681	MHz	NS	SC: 300		PW: 0.	00 usec, R	G: 51200		SI: 6	35536
Date: 28-May-2022					Sol	vent: DMS(	S	S	SW: 32680	Hz	TE	: 683 K		AQ: 1.0	0 sec, RD	: 0.00 sec				



12.0



S120

lv-30



6.447



2 P P C



lv-30\_C13.fid





### lv-30\_APTC13.fid



190 180 170 1	60 150 14	0 130 120	110 100	90 80 70 60	50 40 30 20 10
File name: Iv-30_APTC13.fid	Operator:	SF: 125.6925 MHz	NSC: 0	PW: 5.00 usec, RG: 60	SI: 131072
Date: 31-May-2022	Solvent: dmso	SW: 32895 Hz	TE: 298 K	AQ: 1.95 sec, RD: 0.00 sec	Automated Probe tuning parameter

52.65 52.53 49.32 42.93 42.05 39.97 56.42 56.43 56.43 56.45



6.494



lv-31



14c DMSO-d6







lv-31\_C13



14c DMSO-d6

	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
File name: lv-31_C13					Operat	tor: root		SF: 12	25.6681 MH	Ηz	NSC	: 291		PW: 0.0	0 usec, RG	: 51200		SI: 13	31072
Date: 28-May-2022				Solven	nt: DMSO		SW	: 32680 Hz		TE: 6	83 K		AQ: 0.78	sec, RD: 0	0.00 sec				





lv-31\_C13APT





Mqq	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
	File nar	me: lv-31_(	C13APT		Oper	ator: root		SF:	NSC	: 267		PW: 0.0	0 usec, RG	: 51200		SI: 65536		
Date: 28-May-2022					Solve	ent: DMSO		SI	W: 32680 H	Z	TE: (	683 K		AQ: 1.00	) sec, RD: (	).00 sec		

7.117

3.318 3.140 2.996 2.996 2.134 2.134 2.134 2.134 2.134 2.134 2.134

lv-35



PPM

55.80	50.53	48.64	43.58	40.91	40.01	2618	24.57	23.11	22.80	<b>2</b> 2.38	127	7
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lv-35\_C13







# lv-35\_C13APT.fid



Mad No.	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
	File nar	ne: lv-35_C	13APT.fid		Op	perator:		SF: 150.83	333 MHz		NSC: 0		PW: 4	.63 usec, R0	G: 60		SI: 131072
	Da	te: 02-Jun-2	2022		Solv	ent: dmso		SW: 390	63 Hz		TE: 298 K		AQ: 0.87	' sec, RD: 0	.00 sec		



S129

lv-32.fid



14e DMSO-d6

					96.0				4.03 2.06 2.05 2.05	2:70		
Mqq	11.0	10.0	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0
	File name: lv-32.fic	k	Operator:		SF: 499.820	03 MHz	NSC: 0		PW: 12.40 u	sec, RG: 12		SI: 32768
	Date: 31-May-2022		Solvent: dmso		SW: 932	8 Hz	TE: 298 K		AQ: 1.72 sec,	RD: 0.00 sec		

6.886

PPM

68.93 68.51 53.44 50.09 47.72 43.40 42.95 39.56

S130

lv-32\_C13



14e DMSO-d6

	180	170	160	150	140	130	120	11	0	100	90	80	70	60	50	40	30	20	1	0	0	
	File r	name: Iv-32	2_C13_C1		Operat	or: root		S	SF: 125.6	681 MHz		NSC: 5120	0	P۷	V: 0.00 us	ec, RG: 51	200		SI	: 131072		
Date: 31-May-2022							t: DMSO			SW: 32	680 Hz		TE: 683 K	(	AC	): 0.78 sec	, RD: 0.00	sec				



lv-32\_C13\_C13APT



14e DMSO-d6

Mdd	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0
	Fil	e name: Iv	v-32_C13_	C13APT		Op	perator: roo	ıt	SF: 125.6681 MHz			N	SC: 5120		PW: (	).00 usec,	RG: 51200	)	SI:	65536
Date: 01-Jun-2022							olvent: DMS	30	ę	SW: 32680	Hz	Т	E: 683 K		AQ: 1	.57 sec, R	D: 0.00 se	с		





	File name: IV-41_AP1.fld	Operator:	SF: 125.6925 MHz	NSC: 0	PW:	5.00 usec, RG: 60			SI:	131072	
_		Onenten									
Mdd	190 180 170	160 150 14	) 130 120 11	) 100	90 80	70 60	50	40	30	20 10	0
		4 1 <b>4</b>	andra a haran.	·	- F. 1. 1. 1		In.				
17 <mark>11</mark> 1	fil fa gamat ya 10 filo gant fili biya, jima, iliya ha kwa fi su na su	per literation for department per period of the fight period period of the fight period period of the fight period of the figh	a tan di pada ana aka tina da da na na manana na manana na manana tan.	a filmende for her de service de service de la service La constant de la service d	) generative na Origen en antar A se sekan na on tate da andas	an taning ang ing ing ing ing ing ing ing ing ing i	ander over en		n de seu en la seu de la deservación de la seu de la deservación de la seu de la deservación de la seu de la de	ing the product of the first of	degrad tegetere a content
tak ni s	อเสดอด เป็นไป กระเบิด ไปของสาวได้เป็	աեռուտիտերիկեր	okalatoonala omatomoo noo oo oo tito n koo. It	kaun oo Modelle coo.	an udalar o barra	halilia a stan mandast	at al. the		and orbital states with the	Administration des Internation	.พ.ศ. 1. เมษ
			15 DMSO-d6								
			HN - <u>s</u>								
	lv-41_APT.fid		0 //								
										5134	
-	173.5						50.9	45. 39.	29.2	C101	