



## Supporting Information

for

### Base-promoted cascade recyclization of allomaltol derivatives containing an amide fragment into substituted 3-(1-hydroxyethylidene)tetronic acids

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## Analytical data for compounds 4a–t

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(3-oxo-2-phenethyl-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4a**). Pale yellow powder; yield 62% (0.25 g); mp 121–123°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.31 – 7.13 (m, 5H), 4.34 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.56–2.48 (m, 2H in DMSO), 2.46 (s, 3H), 2.14 (t, *J* = 11.8 Hz, 2H), 1.64 – 1.54 (m, 3H), 1.41 – 1.09 (m, 5H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 178.2, 175.5, 164.8, 138.1, 128.9, 128.3, 126.4, 98.7, 44.3, 44.0, 39.4, 32.6, 32.1, 24.7, 23.9, 21.9. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>23</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 396.1805; Found: 396.1801.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(3-oxo-2-phenethyl-8-oxa-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4b**). White powder; yield 59% (0.23 g); mp 161–163°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.32 – 7.13 (m, 5H), 4.37 (t, *J* = 7.3 Hz, 2H), 3.84 – 3.73 (m, 2H), 3.39 (t, *J* = 11.9 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.66 (s, 2H), 2.55–2.48 (m, 2H in DMSO), 2.46 (s, 3H), 1.27 – 1.17 (m, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 192.0, 178.3, 175.0, 164.9, 143.5, 138.1, 128.9, 128.2, 126.3, 98.6, 63.5, 43.9, 41.7, 38.8, 32.6, 32.3, 24.0. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 398.1598; Found: 398.1610.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(3-oxo-2-phenethyl-8-thia-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4c**). Pale yellow powder; yield 71% (0.29 g); mp 170–172°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.31 – 7.13 (m, 5H), 4.34 (t, *J* = 7.3 Hz, 2H), 2.81 – 2.64 (m, 5H), 2.58 – 2.55 (m, 2H), 2.47 – 2.40 (m, 6H), 1.66 – 1.56 (m, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 192.0, 178.4, 175.0, 164.7, 138.1, 128.9, 128.3, 126.3, 126.2, 98.7, 43.9, 43.5, 38.1, 32.5, 23.8, 23.6. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 414.1370; Found: 414.1361.

(*3E,5E*)-5-(2-(4-fluorophenethyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(*3H,5H*)-dione (**4d**). White powder; yield 56% (0.23 g); mp

134–136°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.97 (br. s, 1H), 7.24 – 7.13 (m, 2H), 7.11 – 6.99 (m, 2H), 4.29 (t,  $J$  = 7.6 Hz, 2H), 2.71 (t,  $J$  = 7.6 Hz, 2H), 2.55–2.48 (m, 2H in DMSO), 2.44 (s, 3H), 2.13 (d,  $J$  = 11.6 Hz, 2H), 1.68 – 1.50 (m, 3H), 1.43 – 1.03 (m, 5H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  192.2, 178.2, 175.4, 161.0 (d,  $J_{CF}$  = 242.0 Hz), 159.4, 145.9, 134.3, 134.3, 130.7 (d,  $J_{CF}$  = 8.0 Hz), 125.9, 114.9 (d,  $J_{CF}$  = 21.0 Hz), 98.7, 44.20, 44.0, 41.7, 32.1, 31.8, 24.7, 23.8, 21.9. HRMS (ESI-TOF)  $m/z$ : Calcd for  $\text{C}_{23}\text{H}_{25}\text{FNO}_5$  [M+H] $^+$  414.1711; Found: 414.1711.

(3*E*,5*E*)-5-(2-(4-chlorophenethyl)-3-oxo-8-oxa-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(3*H*,5*H*)-dione (**4e**). White powder; yield 67% (0.29 g); mp 96–98°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  9.52 (br. s, 1H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 7.21 (d,  $J$  = 8.0 Hz, 2H), 4.35 (t,  $J$  = 7.2 Hz, 2H), 3.85 – 3.74 (m, 2H), 3.38 (t,  $J$  = 12.1 Hz, 2H), 2.74 (t,  $J$  = 7.4 Hz, 2H), 2.67 (s, 2H), 2.45 (s, 3H), 2.07 (s, 2H), 1.25 (d,  $J$  = 12.9 Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  192.0, 178.4, 175.1, 164.9, 143.7, 137.3, 131.1, 130.9, 128.2, 126.3, 98.7, 63.6, 43.9, 41.8, 38.8, 32.4, 32.1, 23.9. HRMS (ESI-TOF)  $m/z$ : Calcd for  $\text{C}_{22}\text{H}_{23}\text{ClNO}_6$  [M+H] $^+$  432.1208; Found: 432.1205.

(3*E*,5*E*)-5-(2-(3-chlorophenethyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(3*H*,5*H*)-dione (**4f**). Pale yellow powder; yield 63% (0.27 g); mp 133–135°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  7.35 – 7.19 (m, 3H), 7.17 – 7.09 (m, 1H), 4.34 (t,  $J$  = 7.3 Hz, 2H), 2.75 (t,  $J$  = 7.2 Hz, 2H), 2.56–2.48 (m, 2H in DMSO), 2.46 (s, 3H), 2.13 (t,  $J$  = 12.1 Hz, 2H), 1.64 – 1.54 (m, 3H), 1.42 – 1.06 (m, 5H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  192.1, 178.2, 175.3, 164.6, 145.7, 140.7, 132.8, 130.0, 128.7, 127.7, 126.3, 126.0, 98.7, 44.2, 43.7, 32.2, 32.1, 24.6, 23.7, 21.9. HRMS (ESI-TOF)  $m/z$ : Calcd for  $\text{C}_{23}\text{H}_{25}\text{ClNO}_5$  [M+H] $^+$  430.1416; Found: 430.1434.

(*3E,5E*)-5-(2-(3-chlorophenethyl)-3-oxo-8-oxa-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(*3H,5H*)-dione (**4g**). White powder; yield 61% (0.26 g); mp 220-222°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 11.81 (br. s, 1H), 7.31 – 7.20 (m, 3H), 7.18 – 7.11 (m, 1H), 4.38 (t, *J* = 7.3 Hz, 2H), 3.85 – 3.73 (m, 2H), 3.38 (t, *J* = 12.1 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.66 (s, 2H), 2.56-2.48 (m, 2H in DMSO), 2.46 (s, 3H), 1.24 (d, *J* = 13.0 Hz, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 191.8, 178.4, 175.0, 164.8, 143.5, 140.8, 132.8, 130.0, 128.9, 127.7, 126.3, 98.6, 63.5, 43.7, 41.7, 38.8, 32.3, 23.8. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>22</sub>H<sub>23</sub>ClNO<sub>6</sub> [M+H]<sup>+</sup> 432.1208; Found: 432.1227.

(*3E,5E*)-5-(2-benzyl-3-oxo-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(*3H,5H*)-dione (**4h**). White powder; yield 72% (0.27 g); mp 145-147°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.32 – 7.14 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 2H), 5.41 (s, 2H), 2.68 (s, 2H), 2.39 (s, 3H), 2.17 – 2.02 (m, 2H), 1.66 – 1.56 (m, 3H), 1.47 – 1.33 (m, 3H), 1.33 – 1.25 (m, 1H), 1.24 – 1.09 (m, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 191.9, 178.21, 175.79, 164.59, 145.23, 136.61, 128.35, 127.19, 126.92, 126.36, 98.48, 45.56, 44.31, 31.86, 24.67, 23.62, 21.82. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>5</sub>: 382.1649; Found: 382.1639.

(*3E,5E*)-5-(2-benzyl-3-oxo-8-thia-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(*3H,5H*)-dione (**4i**). Pale yellow powder; yield 75% (0.30 g); mp 149-151°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.32 – 7.17 (m, 3H), 7.13 – 7.04 (m, 2H), 5.41 (s, 2H), 2.83 – 2.70 (m, 4H), 2.56 – 2.30 (m, 7H), 1.74 – 1.64 (m, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 191.6, 178.5, 175.3, 164.8, 143.3, 136.4, 128.4, 127.2, 127.0, 126.8, 126.6, 98.4, 45.6, 43.5, 37.9, 32.4, 23.7, 23.6. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>21</sub>H<sub>22</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 400.1213; Found: 400.1230.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-(2-methoxybenzyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4j**). Yellow powder; yield 70% (0.29 g); mp 164–166°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.25 – 7.14 (m, 1H), 6.97 – 6.87 (m, 2H), 6.86 – 6.75 (m, 1H), 5.26 (s, 2H), 3.72 (s, 3H), 2.65 (s, 2H), 2.39 (s, 3H), 2.21 – 2.03 (m, 2H), 1.63 (d, *J* = 12.1 Hz, 3H), 1.46 (d, *J* = 13.0 Hz, 2H), 1.39 – 1.25 (m, 2H), 1.25 – 1.12 (m, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 192.6, 177.5, 175.6, 164.5, 156.6, 146.8, 128.4, 127.4, 125.8, 124.1, 119.9, 110.6, 98.4, 55.1, 44.4, 43.0, 39.1, 32.1, 24.7, 23.8, 21.9. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>23</sub>H<sub>26</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 412.1755; Found: 412.1776.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-(3-methoxybenzyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4k**). Yellow powder; yield 67% (0.28 g); mp 87–89°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.17 (t, *J* = 7.8 Hz, 1H), 6.80 – 6.72 (m, 1H), 6.68 – 6.59 (m, 2H), 5.39 (s, 2H), 3.66 (s, 3H), 2.68 (s, 2H), 2.38 (s, 3H), 2.18 – 2.03 (m, 2H), 1.67 – 1.56 (m, 3H), 1.48 – 1.24 (m, 4H), 1.21 – 1.10 (m, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 191.7, 178.3, 175.7, 165.0, 159.1, 138.3, 129.5, 126.7, 119.0, 112.7, 112.5, 98.3, 54.9, 45.4, 44.2, 31.9, 24.7, 24.1, 21.8. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>23</sub>H<sub>26</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 412.1755; Found: 412.1755.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-(4-methylbenzyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4l**). White powder; yield 68% (0.27 g); mp 97–99°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.04 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 5.37 (s, 2H), 2.63 (s, 2H), 2.35 (s, 3H), 2.21 (s, 3H), 2.06 (t, *J* = 12.3 Hz, 2H), 1.66 – 1.53 (m, 4H), 1.41 – 1.26 (m, 4H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 191.6, 178.6, 175.8, 136.3, 133.8, 128.9, 127.2, 126.7, 119.3, 98.1, 45.0, 44.0, 31.9, 25.0, 24.7, 22.3, 21.8, 20.6. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>23</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 396.1805; Found: 396.1824.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-(3-methoxypropyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4m**). Pale yellow powder; yield 54% (0.19 g); mp 106–108°C.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.06 (br. s, 1H), 4.13 (t, *J* = 6.9 Hz, 2H), 3.27 (t, *J* = 6.1 Hz, 2H), 3.16 (s, 3H), 2.60 (s, 2H), 2.44 (s, 3H), 2.27 – 2.12 (m, 2H), 1.71 – 1.57 (m, 5H), 1.46 (d, *J* = 13.0 Hz, 2H), 1.41 – 1.14 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  192.8, 177.6, 175.5, 164.4, 153.9, 147.0, 125.1, 98.7, 69.4, 57.8, 44.4, 40.7, 32.0, 26.8, 24.6, 23.9, 21.9. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>19</sub>H<sub>26</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 364.1755; Found: 364.1775.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-(3-methoxypropyl)-3-oxo-8-thia-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4n**). Yellow powder; yield 58% (0.22 g); mp 151–153°C.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  4.15 (t, *J* = 6.7 Hz, 2H), 3.26 (t, *J* = 6.1 Hz, 2H), 3.15 (s, 3H), 2.76 (t, *J* = 13.9 Hz, 2H), 2.63 (s, 2H), 2.42 (s, 3H), 1.74 (d, *J* = 12.3 Hz, 2H), 1.70 – 1.56 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  192.5, 177.9, 175.0, 164.6, 145.1, 125.6, 98.7, 69.5, 57.8, 43.6, 40.7, 38.0, 32.5, 31.7, 26.8, 23.6. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>18</sub>H<sub>24</sub>NO<sub>6</sub>S [M+H]<sup>+</sup> 382.1319; Found: 382.1333.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(3-oxo-2-phenethyl-2-azaspiro[4.4]nonan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4o**). Pale yellow powder; yield 62% (0.24 g); mp 103–105°C.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.45 (br. s, 1H), 7.30 – 7.21 (m, 2H), 7.21 – 7.13 (m, 3H), 4.37 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.47 (s, 2H), 2.46 (s, 3H), 2.28 – 2.13 (m, 2H), 1.88 – 1.76 (m, 2H), 1.68 – 1.58 (m, 2H), 1.56 – 1.45 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  179.7, 175.1, 166.8, 164.6, 140.2, 138.3, 128.9, 128.2, 127.8, 126.2, 88.9, 43.6, 43.4, 39.6, 32.7, 32.2, 24.8, 21.9, 12.7. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 382.1649; Found: 382.1672.

(*3E,5E*)-5-(2-(3-chlorophenethyl)-3-oxo-2-azaspiro[4.4]nonan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(*3H,5H*)-dione (**4p**). Pale yellow powder; yield 67% (0.28 g); mp 110-112°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 9.77 (br. s, 1H), 7.36 – 7.18 (m, 3H), 7.18 – 7.11 (m, 1H), 4.39 (t, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.47 (s, 2H), 2.46 (s, 3H), 2.28 – 2.13 (m, 2H), 1.90 – 1.74 (m, 2H), 1.68 – 1.58 (m, 2H), 1.57 – 1.44 (m, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 192.2, 177.8, 175.3, 164.6, 140.7, 132.8, 130.0, 128.9, 127.8, 126.3, 125.2, 99.0, 49.0, 44.8, 43.7, 32.4, 25.0, 23.6. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>22</sub>H<sub>23</sub>CINO<sub>5</sub> [M+H]<sup>+</sup> 416.1259; Found: 416.1271.

(*3E,5E*)-5-(3,3-dimethyl-5-oxo-1-phenethylpyrrolidin-2-ylidene)-3-(1-hydroxyethylidene)furan-2,4(*3H,5H*)-dione (**4q**). White powder; yield 59% (0.21 g); mp 171-173°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.32 – 7.13 (m, 5H), 4.34 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.46 (s, 3H), 2.44 (s, 2H), 1.34 – 1.28 (m, 6H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 192.5, 177.9, 175.1, 164.6, 146.3, 138.0, 128.9, 128.3, 128.2, 126.3, 125.5, 99.0, 44.1, 43.7, 39.4, 32.6, 26.1, 23.7. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 356.1492; Found: 356.1487.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-(4-methoxyphenyl)-3-oxo-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4r**). Yellow powder; yield 37% (0.15 g); mp 190-192°C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 8.11 (br. s, 1H), 7.17 – 7.05 (m, 2H), 6.99 – 6.87 (m, 2H), 3.85-3.67 (m, 3H in H<sub>2</sub>O), 2.80 – 2.71 (m, 2H), 2.31 (s, 3H), 2.27 – 2.15 (m, 2H), 1.70 (d, *J* = 12.0 Hz, 4H), 1.46 – 1.29 (m, 2H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 194.8, 175.1, 164.4, 158.2, 130.7, 128.4, 127.5, 113.7, 113.5, 55.2, 44.9, 32.1, 25.19, 24.8, 22.2, 21.8. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 398.1598; Found: 398.1611.

(*3E,5E*)-3-(1-hydroxyethylidene)-5-(2-methyl-3-oxo-8-thia-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**4s**). Pale brown powder; yield 62% (0.20 g); mp 207-

209°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  3.26 (s, 3H), 2.75 (t,  $J = 12.9$  Hz, 2H), 2.64 (s, 2H), 2.58-2.35 (m, 4H), 2.43 (s, 3H), 1.79 (d,  $J = 12.6$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  193.2, 177.1, 175.2, 164.8, 147.0, 125.3, 98.5, 43.8, 37.9, 32.8, 32.6, 24.7, 23.6. HRMS (ESI-TOF)  $m/z$ : Calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}_5\text{S} [\text{M}+\text{H}]^+$  324.0900; Found: 324.0901.

*(3E,5E)-5-(2-cyclohexyl-3-oxo-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(3H,5H)-dione* and *(3E,5Z)-5-(2-cyclohexyl-3-oxo-2-azaspiro[4.5]decan-1-ylidene)-3-(1-hydroxyethylidene)furan-2,4(3H,5H)-dione* (mixture of E/Z isomers 5:1) (**4t**). White powder; yield 51% (0.19 g); mp 191-193°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.35 – 4.23 (m, 0.2H), 3.92 (t,  $J = 12.0$  Hz, 0.8H), 2.61 (s, 2H), 2.57 (s, 3H), 2.33 – 2.12 (m, 4H), 1.86 – 1.76 (m, 4H), 1.75 – 1.59 (m, 5H), 1.58 – 1.49 (m, 1H), 1.45 – 1.09 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  193.5, 193.2, 176.6, 176.4, 175.8, 150.7, 150.6, 125.4, 123.5, 99.2, 98.6, 60.6, 57.4, 45.4, 42.6, 41.3, 32.0, 31.6, 29.1, 25.7, 24.9, 24.8, 24.2, 23.9, 23.9, 23.9, 22.2, 21.8. HRMS (ESI-TOF)  $m/z$ : Calcd for  $\text{C}_{21}\text{H}_{29}\text{NO}_5 [\text{M}+\text{H}]^+$  374.1962; Found: 374.1969.

## Analytical data for compound 7

*(3E,5E)-3-(1-hydrazineylethylidene)-5-(3-oxo-2-phenethyl-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(3H,5H)-dione* (**7**). White powder; yield 71% (0.29 g); mp 199-201°C.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  12.11 (br. s, 1H), 7.30 – 7.12 (m, 5H), 5.72 (s, 2H), 4.47 (t,  $J = 7.5$  Hz, 2H), 2.68 (t,  $J = 7.7$  Hz, 2H), 2.56-2.48 (m, 2H in DMSO), 2.46 (s, 3H), 2.15 (t,  $J = 12.9$  Hz, 2H), 1.63 – 1.53 (m, 2H), 1.40 – 1.11 (m, 5H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  179.8, 175.3, 164.8, 140.4, 138.4, 129.0, 128.4, 128.3, 126.3, 88.98, 43.7, 43.5, 39.7, 32.8, 32.3, 24.9, 22.0, 12.8. HRMS (ESI-TOF)  $m/z$ : Calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_4 [\text{M}+\text{H}]^+$  410.2074; Found: 410.2092.

## Analytical data for compound 9

(*3E,5E*)-3-(1-((3-chlorobenzyl)amino)ethylidene)-5-(3-oxo-2-phenethyl-2-azaspiro[4.5]decan-1-ylidene)furan-2,4(*3H,5H*)-dione (**9**). White powder; yield 65% (0.34 g); mp 158–160°C.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.59 (s, 1H), 7.53 – 7.41 (m, 3H), 7.41 – 7.35 (m, 2H), 7.23 – 7.10 (m, 4H), 4.82 (d, *J* = 6.1 Hz, 2H), 4.42 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.57 (s, 3H), 2.54 (s, 2H), 2.16 (t, *J* = 12.9 Hz, 2H), 1.69 – 1.53 (m, 3H), 1.42 – 1.08 (m, 5H).  $^{13}\text{C}$  NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  175.7, 171.6, 139.4, 138.7, 138.7, 136.8, 136.6, 136.0, 134.0, 131.3, 129.4, 128.6, 128.4, 128.1, 127.9, 127.8, 126.7, 46.4, 44.3, 44.0, 33.3, 32.6, 25.2, 22.4, 14.8. HRMS (ESI-TOF) *m/z*: Calcd for C<sub>30</sub>H<sub>32</sub>CIN<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 519.2045; Found: 519.2051.