

**(2*S*,7*S*)-Dimethyl 2,7-*N,N'*-di[(4-nitrobenzoyl)amino]oct-4-enedioate (4)**

m.p. 90-92°C.  $[\alpha]_D^{22} +20.0^\circ$  ( $c = 0.21$ , CHCl<sub>3</sub>).  $\nu_{\max}$  (neat): 3365m, 3057w, 2957w, 2854w, 1728s, 1667s, 1602m, 1525s, 1487m, 1437m, 1348s, 1267m, 1227m, 1174w, 1157w, 1110w, 1014m, 974m, 869m, 874m, 737s, 718s cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.60-2.64 (m, 4H, H3, 6), 3.70 (s, 6H, OCH<sub>3</sub>), 4.88 (apparent q,  $J = 5.9$  Hz, 2H, H2, 7), 5.49-5.53 (m, 4H, H4, 5), 7.11 (bd,  $J = 7.4$  Hz, 2H, NH), 8.02 (d,  $J = 8.7$  Hz, 4H, H2', 6'), 8.21-8.29 (m, 4H, H3', 5'). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>):  $\delta$  35.0 (C3, 6), 52.8, 52.8 (C2, 7, OCH<sub>3</sub>), 123.8 (C3', 5'), 128.8, 128.9 (C2', 6', C4, 5), 139.2 (C1'), 149.9 (C4'), 165.2 (C1, 8), 172.1 (CONH). HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd for C<sub>24</sub>H<sub>25</sub>N<sub>4</sub>O<sub>10</sub> (M+H)<sup>+</sup> 529.1571, found: 529.1560;  $m/z$  calcd for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>NaO<sub>10</sub> (M+Na)<sup>+</sup> 551.1390, found:  $m/z$  551.1379.

**(2*S*,7*S*)-Dimethyl 2,7-*N,N'*-di[(4-nitrobenzoyl)amino]octanedioate (5)**

m.p. 117-119°. GC:  $t_R = 16.8$  min (GC column 30QC5/BPX5), 150°C for 1 min, 10°C min<sup>-1</sup> to 280°C for 6 min).  $\nu_{\max}$  (neat): 3304w, 2932w, 1740s, 1637s, 1603m, 1528s, 1438w, 1348m, 1265s, 1109w cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.39-1.54 (m, 4H, H4, 5), 1.74-2.04 (m, 4H, H3, 6), 3.81 (s, 6H, OCH<sub>3</sub>), 4.82 (dt,  $J = 7.3, 5.4$  Hz, 2H, H2, 7), 6.85 (bd,  $J = 7.4$  Hz, 2H, NH), 7.96 (d,  $J = 8.8$  Hz, 4H, H2', 6'), 8.28 (d,  $J = 8.7$  Hz, 4H, H3', 5'). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>):  $\delta$  24.7 (C4, 5), 32.4 (C3, 6), 52.7, 52.9 (C2, OCH<sub>3</sub>), 124.0 (C2', 6'), 128.5 (C3', 5'), 139.5 (C1'), 150.0 (C4'), 165.3, 172.8 (C1, 8, CONH). HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>NaO<sub>10</sub> (M+Na)<sup>+</sup> 553.1547, found: 553.1550.

**(2*S*)-Methyl 2-*N*-acetylaminohex-4-enoate (6)**

GC:  $t_R$  (*E/Z*) = 4.2 min, 4.4 min (GC column 30QC5/BPX5, 150°C for 1 min, 10°C min<sup>-1</sup> to 280°C for 6 min).  $\nu_{\max}$  (neat): 3284s, 2966w, 2954m, 2856w, 1747s, 1658s, 1547s, 1437s, 1375s, 1217m, 1142m, 1072w, 1016w, 968m, 848m cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.60 (dd,  $J = 6.3, 1.2$  Hz, 3H, H6), 1.95 (s, 3H, CH<sub>3</sub>CO), 2.36-2.44 (m, 2H, H3), 3.67 (s, 3H, OCH<sub>3</sub>), 4.55 (dt,  $J = 7.8$  Hz, 5.9 Hz, 1H, H2), 5.24 (m, 1H, H5), 5.49 (m, 1H, H4), 6.17 (bd,  $J = 6.4$  Hz, 1H, NH). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>):  $\delta$  18.1 (C6), 23.3 (CH<sub>3</sub>CO), 35.4 (C3), 52.1, 52.4 (C2, OCH<sub>3</sub>), 124.6, 130.2 (C4, 5), 169.7, 172.6 (C1, CONH). Mass Spectrum (ESI<sup>+</sup>, MeOH):  $m/z$  208.1 (M+Na)<sup>+</sup>, C<sub>9</sub>H<sub>15</sub>NNaO<sub>3</sub>.

**(2*S*,7*S*)-Dimethyl 2,7-*N,N'*-diacetylaminooct-4-enedioate (7)**

GC:  $t_R$  (*E/Z*) = 12.7 min, 12.8 min (GC column 30QC5/BPX5, 150°C for 1 min, 10°C min<sup>-1</sup> to 280°C for 6 min).  $[\alpha]_D^{22} +92.0^\circ$  ( $c = 0.004$ , CHCl<sub>3</sub>).  $\nu_{\max}$  (neat): 3286bm, 2956m, 2931m, 2856w, 1742s, 1659s, 1542m, 1438m, 1375m, 1267m, 1220m, 1138w, 1017w cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.04 (s, 6H, CH<sub>3</sub>CO), 2.40-2.50 (m, 4H, H3, 6), 3.74 (s, 6H, OCH<sub>3</sub>), 4.64-4.70 (m, 2H, H2, 7), 5.36-5.40 (m, 2H, H4, 5), 6.34 (bd,  $J = 7.2$  Hz, 2H, NH). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>):  $\delta$  23.1 (CH<sub>3</sub>CO), 35.1 (C3, 6), 51.7 (C2, 7), 52.6 (OCH<sub>3</sub>), 128.8 (C4, 5), 170.3, 172.6 (C1, 8, CONH). HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 337.1376, found: 337.1375.

**(2S,7S)-Dimethyl 2,7-*N,N'*-diacetylaminoctanedioate (8)**

GC:  $t_R$  = 14.4 min (GC column 30QC5/BPX5), 150°C for 1 min, 10°C min<sup>-1</sup> to 280°C for 6 min).  $\nu_{max}$  (neat): 3426bm, 3055w, 2932m, 2857w, 2360w, 1741s, 1666s, 1543w, 1438m, 1375w, 1266s, 1177w, 1120w, 896w, 738w, 702w cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.30-1.40 (m, 4H, H4, 5), 1.82-1.90 (m, 4H, H3, 6), 2.02 (s, 6H, CH<sub>3</sub>CO), 3.74 (s, 3H, OCH<sub>3</sub>), 4.56-4.63 (m, 2H, H2, 7), 6.16 (bd,  $J$  7.5 Hz, 2H, NH). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>):  $\delta$  23.3 (CH<sub>3</sub>CO), 24.7 (C4, 5), 32.3 (C3, 6), 52.0 (C2, 7), 52.5 (OCH<sub>3</sub>), 170.0, 173.1 (C1, 8, CONH). HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 339.1532, found: 339.1531.

**(2S)-Methyl 2-*N*-benzoylamino-5-methylhex-4-enoate (9)**

HPLC:  $t_R$  = 6.2 min (Chiralcel OJ column, 1.0 ml min<sup>-1</sup>, detection at 254 nm, 5% EtOH : 95% hexane).  $[\alpha]_D^{22}$  +53.0° ( $c$  = 1.19, CHCl<sub>3</sub>).  $\nu_{max}$  (neat): 3334m, 2953w, 1744s, 1645s, 1603w, 1580w, 1538s, 1489m, 1437m, 1353w, 1274w, 1211w, 1175w, 1095w, 1031w, 736w, 714w, 693w cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.61 (d,  $J$  = 0.5 Hz, 3H, CH<sub>3</sub>C=), 1.71 (d,  $J$  = 1.0 Hz, 3H, H6), 2.52-2.76 (m, 2H, H3), 3.77 (s, 3H, OCH<sub>3</sub>), 4.85 (dt,  $J$  = 7.7, 5.5 Hz, 1H, H2), 5.08 (m, 1H, H4), 6.65 (bd,  $J$  = 6.9 Hz, 1H, NH), 7.41-7.47 (m, 2H, H3', 5'), 7.51 (m, 1H, H4'), 7.76-7.79 (m, 2H, H2', 6'). <sup>13</sup>C n.m.r. (75 MHz, CDCl<sub>3</sub>):  $\delta$  18.0 (CH<sub>3</sub>C=), 26.0 (C6), 30.9 (C3), 52.5, 52.6 (C2, OCH<sub>3</sub>), 117.6 (C4), 127.2 (C2', 6'), 128.7 (C3', 5'), 131.8 (C4'), 134.3 (C5), 136.8 (C1'), 167.0, 172.8 (C1, CONH). HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd for C<sub>15</sub>H<sub>20</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 262.1443, found: 262.1441;  $m/z$  calcd for C<sub>15</sub>H<sub>19</sub>NNaO<sub>3</sub> (M+Na)<sup>+</sup> 284.1263, found: 284.1256.

**(2S)-Methyl 2-*N*-benzoylaminohex-4-enoate (10)**

$\nu_{max}$  (neat): 3337bm, 3057w, 2954m, 2856w, 1743s, 1652s, 1603w, 1580w, 1532s, 1488m, 1438m, 1360w, 1266s, 1217w, 1180w, 1116w, 1031m, 969w, 896w, 801w, 738s, 638w cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.66 (dd,  $J$  = 6.4, 1.4 Hz, 3H, H6), 2.52-2.66 (m, 2H, H3), 3.77 (s, 3H, OCH<sub>3</sub>), 4.82 (apparent dd,  $J$  = 7.6, 5.7 Hz, 1H, H2), 5.33 (m, 1H, H5), 5.63 (m, 1H, H4), 6.66 (bd,  $J$  = 7.0 Hz, 1H, NH), 7.43 (t,  $J$  = 7.0 Hz, 2H, H3', 5'), 7.50 (m, 1H, H4'), 7.78 (d,  $J$  = 7.1 Hz, 2H, H2', 6'). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>):  $\delta$  18.0 (C6), 35.4 (C3), 52.4, 52.5 (C2, OCH<sub>3</sub>), 124.5 (C5), 127.1 (C2', 6'), 128.6 (C3', 5'), 130.2 (C4), 131.7 (C4'), 134.1 (C1'), 166.9, 172.5 (C1, CONH). HRMS (ESI<sup>+</sup>, MeOH):  $m/z$  calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 248.1287, found: 248.1284;  $m/z$  calcd for C<sub>14</sub>H<sub>17</sub>NNaO<sub>3</sub> (M+Na)<sup>+</sup> 270.1106, found: 270.1098.

**(2S,7S)-Dimethyl 2,7-*N,N'*-dibenzoylaminoct-4-enedioate (12)**

m.p. 140-142°C. GC:  $t_R$  (*E/Z*) = 13.5, 13.9 min (GC column 30QC5/BPX5, 150°C for 1 min, 10°C min<sup>-1</sup> to 280°C for 6 min).  $[\alpha]_D^{22}$  +56.4° ( $c$  = 0.27, CHCl<sub>3</sub>).  $\nu_{max}$  (KBr): 3322bm, 2953m, 2358w, 1742s, 1644s, 1603w, 1580w, 1538m, 1488m, 1436m, 1267w, 1218m, 1027w, 973w, 802w, 736m cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.57-2.69 (m, 4H, H3, 6), 3.67 (s, 6H, OCH<sub>3</sub>), 4.85-4.98 (m, 2H, H2, 7), 5.49 (t,  $J$  = 4.1 Hz, 2H, H4, 5), 6.86 (bd,  $J$  = 7.4 Hz, 2H, NH), 7.40-7.44 (m, 4H, H3', 5'), 7.48-7.52 (m, 2H, H4'), 7.81-

7.83 (m, 4H, H2', 6'). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>): δ 35.2 (C3, 6), 52.5 (C2, 7), 52.6 (OCH<sub>3</sub>), 127.2 (C2', 6'), 128.7 (C3', 5'), 128.8 (C4, 5), 131.9 (C4'), 133.9 (C1'), 167.1, 172.4 (C1, 8, CONH). HRMS (ESI<sup>+</sup>, MeOH): m/z calcd for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 461.1689, found: 461.1695.

**(2*S*,7*S*)-Dimethyl 2,7-*N,N'*-dibenzoylaminooctanedioate (11)**

GC: *t*<sub>R</sub> = 17.2 min (GC: Column 30QC5/BPX5, 150°C for 1 min, 10°C min<sup>-1</sup> to 280°C for 6 min). *v*<sub>max</sub> (neat): 3055m, 2986w, 2955w, 1741s, 1662s, 1603w, 1580w, 1518m, 1486m, 1438s, 1359w, 1286s, 1182m, 1120m, 1028w, 896m cm<sup>-1</sup>. <sup>1</sup>H n.m.r. (300 MHz, CDCl<sub>3</sub>): δ 1.35-1.53 (m, 4H, H4, 5), 1.80-2.02 (m, 4H, H3, 6), 3.78 (s, 3H, OCH<sub>3</sub>), 4.82 (dt, *J* 7.4, 5.3 Hz, 2H, H2, 7), 6.73 (bd, *J* 7.7 Hz, 2H, NH), 7.40-7.49 (m, 6H, H3', 4', 5'), 7.78-7.82 (m, 4H, H2', 6'). <sup>13</sup>C n.m.r. (100 MHz, CDCl<sub>3</sub>): δ 24.9 (C4, 5), 32.6 (C3, 6), 52.5, 52.7 (C2, OCH<sub>3</sub>), 127.2 (C2', 6'), 128.6 (C3', 5'), 131.9 (C4'), 134.1 (C1'), 167.2, 173.2 (C1, 8, CONH). HRMS (ESI<sup>+</sup>, MeOH): m/z calcd for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>NaO<sub>6</sub> (M+Na)<sup>+</sup> 463.1845, found: 463.1842.