Supporting Information for

Total Synthesis and Stereochemical Revision of Relgro and 10'-Oxorelgro

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<td>HSQC Spectrum of compound 2a</td>
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Table 2. $^1$H chemical shifts* and coupling constants ($J_{H-H}$) for Natural product, Synthetic compounds 1, 1b, 2, and 2a (400 MHz) in CDCl$_3$

<table>
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<tr>
<th>Position</th>
<th>10'-Oxorelgro</th>
<th>10'-Oxorelgro</th>
<th>10'-Oxorelgro</th>
<th>(6'R,10'S)-Relgro</th>
<th>(6'S,10'S)-Relgro</th>
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<td>Natural product</td>
<td>Proposed (2)</td>
<td>Revised (2a)</td>
<td>Proposed (1)</td>
<td>Revised (1b)</td>
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<tr>
<td>2 -OH</td>
<td>11.50, s</td>
<td>11.47, s</td>
<td>11.46, s</td>
<td>11.52, s</td>
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<td>6.27 (d, $J = 2.7$)</td>
<td>6.26 (d, $J = 2.7$)</td>
<td>6.26 (d, $J = 2.5$)</td>
<td>6.26 (d, $J = 2.5$)</td>
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<tr>
<td>4 -OH</td>
<td>5.42, br s</td>
<td>5.58, br s</td>
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<td>6.23 (d, $J = 2.7$)</td>
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<td>6.22 (d, $J = 2.5$)</td>
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<td>1'-Ha</td>
<td>3.41 (t, $J = 12.5$)</td>
<td>3.40 (dt, $J = 2.6, 9.6$)</td>
<td>3.41 (dt, $J = 2.6, 9.5$)</td>
<td>3.40 (ddd, $J = 2.4, 9.8, 12.5$)</td>
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<td>1'-Hb</td>
<td>2.27 (dt, $J = 12.5, 9.0$)</td>
<td>2.26 (ddd, $J = 8.6, 9.6, 12.8$)</td>
<td>2.26 (ddd, $J = 8.5, 9.5, 12.9$)</td>
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<td>1.33-1.45, m</td>
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<td>1.33-1.44, m</td>
<td>1.35-1.46, m</td>
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<td>1.33-1.45, m</td>
<td>1.33-1.45, m</td>
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<td>4'-Ha</td>
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<td>4'-Hb</td>
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<tr>
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<td>-</td>
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<td>1.20 (d, $J = 6.1$)</td>
<td>1.20 (d, $J = 6.2$)</td>
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Multiplicities: s = singlet, br s = broad singlet, d = doublet, dd = doublet of a doublet, ddd = doublet of doublets of doublets, dt = doublet of triplets, t = triplet, m = multiplet. *The chemical shifts are in δ values (ppm) with reference to TMS. †couplings have been obtained with the help of extensive decoupling experiments.

Table 3. $^{13}$C chemical shifts* for Natural product, Synthetic compounds 1, 1b, 2, and 2a (400 MHz) in CDCl$_3$

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<td></td>
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<td>Proposed (2)</td>
<td>Revised (2a)</td>
<td>Proposed (1)</td>
<td>Revised (1b)</td>
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*The chemical shifts are in δ values (ppm)
\(^1\)H NMR spectrum of 9 (500 MHz, DMSO-\(d_6\))
$^{13}$C NMR spectrum of 9 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectrum of 10 (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 10 (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of 11 (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 11 (125 MHz, CDCl$_3$)
\(^1\text{H} \text{NMR spectrum of 12 (400 MHz, CDCl}_3\text{)}\)
$^{13}$C NMR spectrum of 12 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5 (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 5 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 13 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 13 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 14 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 14 (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of 15 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 15 (125 MHz, CDCl$_3$)
$\text{H NMR spectrum of 6 (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR spectrum of 6 (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of 4 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 4 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 16 (500 MHz, CDCl$_3$)
$\text{\(^{13}\)C NMR spectrum of 16 (100 MHz, CDCl}_3\)$
$^1$H NMR spectrum of 17 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 17 (100 MHz, CDCl$_3$)
\(^1\)H NMR spectrum of 1 (400 MHz, CDCl\(_3\))
$^{13}$C NMR spectrum of 1 (100 MHz, CDCl$_3$)
DQFCOSY spectrum of 1 (CDCl₃, 295 K, 400 MHz)
NOESY spectrum of 1 (CDCl$_3$, 295 K, 400 MHz)
HMBC spectrum of 1 (CDCl₃, 295 K, 400 MHz)
$^1$H NMR spectrum of 13a (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 13a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 14a (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 14a (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of 15a (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 15a (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of 6a (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 6a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 18 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 18 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 19 (500 MHz, CDCl$_3$)
$^1$H NMR spectrum of 19 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 20 (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 20 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 1a (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1a (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 13b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 13b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 14b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 14b (100 MHz, CDCl$_3$)
\(^1\)H NMR spectrum of 15b (500 MHz, CDCl\(_3\))
$^{13}$C NMR spectrum of 15b (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 6b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 6b (100 MHz, CDCl$_3$)
LC-LCMS Chromatogram of 6b
LC-LCMS Chromatogram of 6b
$^1$H NMR spectrum of 18a (500 MHz, CDCl$_3$)
$^1$C NMR spectrum of 18a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 19a (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 19a (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of 20a (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 20a (100 MHz, CDCl$_3$)
$^{1}$H NMR spectrum of 1b (400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1b (400 MHz, CDCl$_3$)
DQFCOSY spectrum of 1b (CDCl$_3$, 295 K, 400 MHz)
NOESY spectrum of 1b (CDCl₃, 295 K, 400 MHz)
HMBC spectrum of 1b (CDCl₃, 295 K, 400 MHz)
HSQC spectrum of 1b (CDCl₃, 295 K, 400 MHz)
\( \text{\(^1\)H NMR spectrum of 2a (400 MHz, CDCl}_3\)\)
$^{13}$C NMR spectrum of 2a (100 MHz, CDCl$_3$)
DQFCOSY spectrum of 2a (CDCl₃, 295 K, 400 MHz)
NOESY spectrum of 2a (CDCl₃, 295 K, 400 MHz)
HMBC spectrum of 2a (CDCl$_3$, 295 K, 400 MHz)
HSQC spectrum of 2a (CDCl$_3$, 295 K, 400 MHz)