Electronic Supporting Information of the Manuscript:

Highly Diastereoselective Oxidation of β-Thioglycosides: The 

d-exo-anomeric effect Paves the Way

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$^{13}$C-NMR (125 MHz, CDCl$_3$)


$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)

SI-7
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

Major diastereomer

$^{13}$C-NMR (100MHz, CDCl$_3$)

Major diastereomer
\( ^1H \)-NMR (400 MHz, CDCl3)

\( ^1C \)-NMR (100MHz, CDCl3)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100MHz, CDCl$_3$)

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$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100MHz, CDCl$_3$)
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1H-NMR (400 MHz, CDCl₃)
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$^1$H-NMR (300 MHz, CDCl$_3$)

SI-18
$^1$H-NMR (500 MHz, CDCl$_3$)

$^{13}$C-NMR (125 MHz, CDCl$_3$)
$^{1}H$-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100MHz, CDCl$_3$)

Major diastereomer
**H-NMR (400 MHz, CDCl3)**

Minor diastereomer

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<th>1.00</th>
<th>1.01</th>
<th>1.02</th>
<th>1.00</th>
<th>2.96</th>
<th>1.89</th>
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<td>3.00</td>
<td>3.01</td>
<td>3.02</td>
<td>3.03</td>
<td>3.04</td>
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<td>4.50</td>
<td>4.51</td>
<td>4.52</td>
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<td>4.54</td>
<td>4.55</td>
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**13C-NMR (100 MHz, CDCl3)**

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<tr>
<th>39.23</th>
<th>39.91</th>
<th>67.65</th>
<th>70.32</th>
<th>74.08</th>
<th>77.60</th>
<th>79.96</th>
<th>92.42</th>
<th>101.81</th>
<th>125.96</th>
<th>126.86</th>
<th>128.45</th>
<th>128.85</th>
<th>129.56</th>
<th>132.38</th>
<th>135.78</th>
<th>137.75</th>
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Minor diastereomer
$^1$H-NMR (400 MHz, CDCl$_3$)

![H-NMR Spectrum](image)

$^{13}$C-NMR (100 MHz, CDCl$_3$)

![C-NMR Spectrum](image)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100MHz, CDCl$_3$)
Table S1. Crystal data and structure refinement for compound 12R₈.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₃H₂₈O₅S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>416.51</td>
</tr>
<tr>
<td>Temperature</td>
<td>213(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 20.294(3) Å, b = 6.4701(8) Å, c = 15.4757(17) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90°, β = 96.306(4)°, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2019.7(4) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.370 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.193 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>888</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.45 x 0.15 x 0.15 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.15 to 25.22°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-17 ≤ h ≤ 24, -7 ≤ k ≤ 7, -13 ≤ l ≤ 18</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>10600</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3042 [R(int) = 0.0391]</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>Completeness to theta = 25.22°</td>
<td>95.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9714 and 0.9660</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3042 / 1 / 262</td>
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<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.170</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0598, wR2 = 0.1608</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0768, wR2 = 0.1720</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>-0.05(15)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.506 and -0.479 e.Å^{-3}</td>
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Table S2. Crystal data and structure refinement for compound 13R₈.

<table>
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<tr>
<th>Property</th>
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<tr>
<td>Empirical formula</td>
<td>C₂₉H₄₂O₁₂S₃</td>
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<td>Formula weight</td>
<td>678.81</td>
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<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.4931(8) Å</td>
</tr>
<tr>
<td></td>
<td>b = 11.5171(10) Å</td>
</tr>
<tr>
<td></td>
<td>c = 28.284(2) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90°, β = 91.379(4)°, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>3417.1(5) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.319 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.275 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1440</td>
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<tr>
<td>Crystal size</td>
<td>0.50 x 0.30 x 0.20 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.44 to 25.25°.</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12≤h≤11, -13≤k≤10, -33≤l≤33</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>39325</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9661 [R(int) = 0.0800]</td>
</tr>
<tr>
<td>Completeness to theta = 25.25°</td>
<td>98.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9471 and 0.9049</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix-block least-squares on F^2</td>
</tr>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F^2</td>
<td>0.994</td>
</tr>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0605, wR2 = 0.1574</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0843, wR2 = 0.1826</td>
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<td>Absolute structure parameter</td>
<td>0.06(3)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>1.136 and -1.068 e.Å^-3</td>
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**Table S3.** Crystal data and structure refinement for compound 19R_s.

<table>
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<tr>
<th>Property</th>
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<tr>
<td>Empirical formula</td>
<td>C_{17}H_{24}O_{10}S_{3}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>484.54</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2_1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 5.2270(6) Å, ( \alpha = 90^\circ )</td>
</tr>
<tr>
<td></td>
<td>b = 25.122(3) Å, ( \beta = 99.08^\circ )</td>
</tr>
<tr>
<td></td>
<td>c = 16.5667(18) Å, ( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>2148.2(4) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.498 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.397 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>1016</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.50 x 0.40 x 0.10 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.62 to 25.25°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-6 \leq h \leq 6, -30 \leq k \leq 29, -19 \leq l \leq 18</td>
</tr>
<tr>
<td>Reflections collected</td>
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</tr>
<tr>
<td>Description</td>
<td>Value/Details</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>-----------------------------------</td>
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<tr>
<td>Independent reflections</td>
<td>5111 ([R(\text{int}) = 0.0427])</td>
</tr>
<tr>
<td>Completeness to theta = 25.25°</td>
<td>98.3 %</td>
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<td>Absorption correction</td>
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<td>Max. and min. transmission</td>
<td>0.9614 and 0.8262</td>
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<td>Refinement method</td>
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<td>Final R indices ([I&gt;2\sigma(I)])</td>
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<td>Absolute structure parameter</td>
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<td>Largest diff. peak and hole</td>
<td>0.856 and -1.198 e(\text{Å}^{-3})</td>
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