Supplementary Information

for

Melioidosis Patient Serum-Reactive Synthetic Tetrasaccharides Bearing the Predominant Epitopes of Burkholderia pseudomallei and Burkholderia mallei O-Antigens

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### Supplementary results

**Table S1.** Unsuccessful attempts to epimerize tetrasaccharide 23.

<table>
<thead>
<tr>
<th>entry</th>
<th>oxidation reagents</th>
<th>solvent</th>
<th>temperature (°C)</th>
<th>yield (%)</th>
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<td>1</td>
<td>DMSO, PDCP, Et$_3$N</td>
<td>DCM</td>
<td>–10 to rt</td>
<td>nd$^a$</td>
</tr>
<tr>
<td>2</td>
<td>DMSO, PDCP, Et$_3$N</td>
<td>DCM</td>
<td>–78 to rt</td>
<td>nd$^b$</td>
</tr>
<tr>
<td>3</td>
<td>oxalyl chloride, DMSO, Et$_3$N</td>
<td>DCM</td>
<td>–78</td>
<td>nd$^b$</td>
</tr>
<tr>
<td>4</td>
<td>DMSO, Ac$_2$O</td>
<td>-</td>
<td>rt</td>
<td>nd$^b$</td>
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<tr>
<td>5</td>
<td>Dess-Martin periodinane</td>
<td>DCE</td>
<td>reflux</td>
<td>nd$^a$</td>
</tr>
</tbody>
</table>

$^a$Degradation of starting material.

$^b$No reaction.
NMR spectra
Supplementary Figure 1 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 18
Supplementary Figure 2 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 18
Supplementary Figure 3 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 18
Supplementary Figure 4 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 18
Supplementary Figure 5 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 15
Supplementary Figure 6 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 15
Supplementary Figure 7 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 15
Supplementary Figure 8 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 15
Supplementary Figure 9 | $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of allyl 3-tert-butyldimethylsilyl-4-O-levulinoyl-α-L-rhamnopyranoside
Supplementary Figure 10 | COSY NMR spectrum (CDCl₃, 400 MHz) of allyl 3-tert-butyldimethylsilyl-4-O-levulinoyl-α-L-rhamnopyranoside
Supplementary Figure 11 | $^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of allyl 3-tert-butyldimethylsilyl-4-O-levulinoyl-$\alpha$-L-rhamnopyranoside
Supplementary Figure 12 | HSQC NMR spectrum (CDCl₃, 400 MHz) of allyl 3-tert-butyldimethylsilyl-4-O-levulinoyl-α-L-rhamnopyranoside
Supplementary Figure 13 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 20
Supplementary Figure 14 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 20
Supplementary Figure 15 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 20
Supplementary Figure 16 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 20
Supplementary Figure 17 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 21
Supplementary Figure 18 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 21
Supplementary Figure 19 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 21
Supplementary Figure 20 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 21
Supplementary Figure 21 | $^1$H NMR spectrum (pyridine-d$_5$, 600 MHz) of compound 13
Supplementary Figure 22 | COSY NMR spectrum (pyridine-d$_5$, 600 MHz) of compound 13
Supplementary Figure 23 | $^{13}$C NMR spectrum (pyridine-d$_5$, 150 MHz) of compound 13
Supplementary Figure 24 | HSQC NMR spectrum (pyridine-d$_5$, 600 MHz) of compound 13
Supplementary Figure 25 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 22
Supplementary Figure 26 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 22
Supplementary Figure 27 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 22
Supplementary Figure 28 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 22
Supplementary Figure 29 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of para-methylphenyl 4-O-levulinoyl-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside
Supplementary Figure 30 | COSY NMR spectrum (CDCl\textsubscript{3}, 600 MHz) of \textit{para}-methylphenyl 4-\textit{O}-levulinoyl-2,3-\textit{O}-isopropylidene-1-thio-\textit{\alpha}-\textit{L}-rhamnopyranoside
Supplementary Figure 31 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of para-methylphenyl 4-O-levulinoyl-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside
Supplementary Figure 32 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of para-methylphenyl 4-O-levulinoyl-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside
Supplementary Figure 33 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 24
Supplementary Figure 34 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 24
Supplementary Figure 35 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 24
Supplementary Figure 36 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 24
Supplementary Figure 37 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of \textit{para}-methylphenyl 4-\textit{O}-levulinoyl-3-\textit{O}-\textit{para}-methoxybenzyl-1-thio-\textit{a}-\textit{L}-rhamnopyranoside
Supplementary Figure 38 | COSY NMR spectrum (CDCl₃, 600 MHz) of para-methylphenyl 4-O-levulinoyl-3-O-para-methoxybenzyl-1-thio-α-L-rhamnopyranoside
Supplementary Figure 39 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of para-methylphenyl 4-O-levulinoyl-3-O-para-methoxybenzyl-1-thio-α-L-rhamnopyranoside
Supplementary Figure 40 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of *para*-methylphenyl 4-O-levulinoyl-3-O-*para*-methoxybenzyl-1-thio-α-L-rhamnopyranoside
Supplementary Figure 41 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 25
Supplementary Figure 42 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 25
Supplementary Figure 43 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 25
Supplementary Figure 44 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 25
Supplementary Figure 45 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 26
Supplementary Figure 46 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 26
Supplementary Figure 47 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 26
Supplementary Figure 48 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 26
Supplementary Figure 49 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 12
Supplementary Figure 50 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 12
Supplementary Figure 51 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 12
Supplementary Figure 52 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 12
Supplementary Figure 53 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 27 (+10% of unknown inseparable impurity)
Supplementary Figure 54 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 27 (+ 10% of unknown inseparable impurity)
Supplementary Figure 55 | \(^{13}\)C NMR spectrum (CDCl$_3$, 150 MHz) of compound 27 (+ 10% of unknown inseparable impurity)
Supplementary Figure 56 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 27 (+ 10% of unknown inseparable impurity)
Supplementary Figure 57 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 28
Supplementary Figure 58 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 28
Supplementary Figure 59 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 28

Zoom of peaks 82.6 to 66.2 ppm
Supplementary Figure 60 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 28
Supplementary Figure 61 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of para-methylphenyl 4-O-levulinoyl-3-O-methyl-1-thio-α-L-rhamnopyranoside
Supplementary Figure 62 | COSY NMR spectrum (CDCl₃, 600 MHz) of para-methylphenyl 4-O-levulinoyl-3-O-methyl-1-thio-α-L-rhamnopyranoside
Supplementary Figure 63 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of para-methylphenyl 4-O-levulinoyl-3-O-methyl-1-thio-α-L-rhamnopyranoside
Supplementary Figure 64 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of $\text{para}$-methylphenyl 4-$\text{O}$-levulinoyl-3-$\text{O}$-methyl-1-thio-$\alpha$-L-rhamnopyranoside
Supplementary Figure 65 | ¹H NMR spectrum (CDCl₃, 600 MHz) of compound 29
Supplementary Figure 66 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 29
Supplementary Figure 67 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 29
Supplementary Figure 68 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 29
Supplementary Figure 69 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 10 (+ 12% of unknown inseparable impurity)
Supplementary Figure 70 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 10 (+ 12% of unknown inseparable impurity)
Supplementary Figure 71 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 10 (+ 12% of unknown inseparable impurity)

Zoom of peaks 82.7 to 66.1 ppm
Supplementary Figure 72 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 10 (+ 12% of unknown inseparable impurity)
Supplementary Figure 73 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 30
Supplementary Figure 74 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 30
Supplementary Figure 75 | $^{13}$C NMR spectrum (CDCl₃, 150 MHz) of compound 30

Zoom of peaks 82.8 to 66.3 ppm
Supplementary Figure 76 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 30
Supplementary Figure 77 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 32
Supplementary Figure 78 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 32
Supplementary Figure 79 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 32
Supplementary Figure 80 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 32
Supplementary Figure 81 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 33
Supplementary Figure 82 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 33
Supplementary Figure 83 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 33
Supplementary Figure 84 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 33
Supplementary Figure 85 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 34
Supplementary Figure 86 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 34
Supplementary Figure 87 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 34
Supplementary Figure 88 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 34
Supplementary Figure 89 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 35
Supplementary Figure 90 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 35
Supplementary Figure 91 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 35
Supplementary Figure 92 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 35
Supplementary Figure 93 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 36
Supplementary Figure 94 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 36
Supplementary Figure 95 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 36

Zoom of peaks 82.7 to 65.5 ppm
Supplementary Figure 96 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 36
Supplementary Figure 97 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 37
Supplementary Figure 98 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 37
Supplementary Figure 99 | ¹³C NMR spectrum (CDCl₃, 150 MHz) of compound 37

Zoom of peaks 82.7 to 65.2 ppm
Supplementary Figure 100 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 37
Supplementary Figure 101 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 38
Supplementary Figure 102 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 38
Supplementary Figure 103 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 38

Zoom of peaks 82.8 to 65.5 ppm
Supplementary Figure 104 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 38
Supplementary Figure 105 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 39
Supplementary Figure 106 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 39
Supplementary Figure 107 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 39

Zoom of peaks 82.8 to 65.2 ppm
Supplementary Figure 108 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 39
Supplementary Figure 109 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 40
Supplementary Figure 110 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 40
Supplementary Figure 111 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 40

$^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 40

[Image of the NMR spectrum with zoom on peaks 83.1 to 65.4 ppm]
Supplementary Figure 112 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 40
Supplementary Figure 113 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 31
Supplementary Figure 114 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 31
Supplementary Figure 115 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 31

Zoom of peaks 83.0 to 66.4 ppm
Supplementary Figure 116 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 31
Supplementary Figure 117 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 41
Supplementary Figure 118 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 41
Supplementary Figure 119 | $^1$H NMR spectrum (CDCl$_3$, 150 MHz) of compound 41
Supplementary Figure 120 | HSQC NMR spectrum (CDCl$_3$, 600 MHz) of compound 41
Supplementary Figure 121 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 42

Grease
Supplementary Figure 122 | COSY NMR spectrum (CDCl$_3$, 600 MHz) of compound 42
Supplementary Figure 123 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 42

Zoom of peaks 82.7 to 65.9 ppm
Supplementary Figure 124 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 42
Supplementary Figure 125 | $^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 43
Supplementary Figure 126 | COSY NMR spectrum (CDCl₃, 600 MHz) of compound 43
Supplementary Figure 127 | $^{13}$C NMR spectrum (CDCl$_3$, 150 MHz) of compound 43

Zoom of peaks 83.0 to 66.2 ppm
Supplementary Figure 128 | HSQC NMR spectrum (CDCl₃, 600 MHz) of compound 43
Supplementary Figure 129 | $^1$H NMR spectrum (D$_2$O, 600 MHz) of compound 8
Supplementary Figure 130 | COSY NMR spectrum (D$_2$O, 600 MHz) of compound 8
Supplementary Figure 131 | $^{13}$C NMR spectrum (D$_2$O, 150 MHz) of compound 8
Supplementary Figure 132 | HSQC NMR spectrum (D$_2$O, 600 MHz) of compound 8
Supplementary Figure 133 | Undecoupled HSQC NMR spectrum (D$_2$O, 600 MHz) of compound 8
Supplementary Figure 134 | $^1$H NMR spectrum (D$_2$O, 600 MHz) of compound 9
Supplementary Figure 135 | COSY NMR spectrum (D₂O, 600 MHz) of compound 9
Supplementary Figure 136 | $^{13}$C NMR spectrum (D$_2$O, 150 MHz) of compound 9
Supplementary Figure 137 | HSQC NMR spectrum (D₂O, 600 MHz) of compound 9
Supplementary references


