### **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.

entry	oxidation reagents	solvent	temperature (°C)	yield (%)
1	DMSO, PDCP, Et <sub>3</sub> N	DCM	-10 to rt	nd <sup>a</sup>
2	DMSO, PDCP, Et <sub>3</sub> N	DCM	-78 to rt	nd <sup>b</sup>
3	oxalyl chloride, DMSO, Et <sub>3</sub> N	DCM	-78	nd <sup>b</sup>
4	DMSO, Ac <sub>2</sub> O	-	rt	$\mathrm{nd}^b$
5	Dess-Martin periodinane	DCE	reflux	nd <sup>a</sup>
<b>D</b> 1				

<sup>a</sup>Degradation of starting material. <sup>b</sup>No reaction.







Supplementary Figure 2 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 18



Supplementary Figure 3 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 18



Supplementary Figure 4 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 18



Supplementary Figure 5 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 15



Supplementary Figure 6 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 15



Supplementary Figure 7 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 15



Supplementary Figure 8 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 15



Supplementary Figure 9 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of allyl 3-*tert*-butyldimethylsilyl-4-O-levulinoyl-α-L-rhamnopyranoside

Supplementary Figure 10 | COSY NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of allyl 3-*tert*-butyldimethylsilyl-4-*O*-levulinoyl-α-L-rhamnopyranoside





Supplementary Figure 11 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of allyl 3-*tert*-butyldimethylsilyl-4-*O*-levulinoyl-α-L-rhamnopyranoside



Supplementary Figure 12 | HSQC NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of allyl 3-*tert*-butyldimethylsilyl-4-*O*-levulinoyl-α-L-rhamnopyranoside



Supplementary Figure 13 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 20



Supplementary Figure 14 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 20



Supplementary Figure 15 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 20



Supplementary Figure 16 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 20



#### Supplementary Figure 17 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 21



Supplementary Figure 18 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 21



Supplementary Figure 19 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 21



Supplementary Figure 20 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 21



### Supplementary Figure 21 | <sup>1</sup>H NMR spectrum (pyridine-d<sub>5</sub>, 600 MHz) of compound 13



Supplementary Figure 22 | COSY NMR spectrum (pyridine-d<sub>5</sub>, 600 MHz) of compound 13



Supplementary Figure 23 | <sup>13</sup>C NMR spectrum (pyridine-d<sub>5</sub>, 150 MHz) of compound 13



Supplementary Figure 24 | HSQC NMR spectrum (pyridine-d<sub>5</sub>, 600 MHz) of compound 13



Supplementary Figure 25 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 22



Supplementary Figure 26 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 22



Supplementary Figure 27 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 22



Supplementary Figure 28 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 22

Supplementary Figure 29 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside







Supplementary Figure 31 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside





Supplementary Figure 32 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside



Supplementary Figure 33 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 24



Supplementary Figure 34 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 24


Supplementary Figure 35 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 24



Supplementary Figure 36 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 24

Supplementary Figure 37 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-3-*O-para*-methoxybenzyl-1-thio-α-L-rhamnopyranoside







Supplementary Figure 39 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-3-*O*-*para*-methoxybenzyl-1-thio-α-L-rhamnopyranoside









## Supplementary Figure 41 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 25



Supplementary Figure 42 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 25



Supplementary Figure 43 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 25



### Supplementary Figure 44 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 25



# Supplementary Figure 45 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 26



Supplementary Figure 46 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 26



Supplementary Figure 47 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 26



Supplementary Figure 48 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 26



Supplementary Figure 49 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 12



Supplementary Figure 50 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 12



Supplementary Figure 51 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 12



Supplementary Figure 52 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 12



Supplementary Figure 53 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 27 (+ 10% of unknown inseparable impurity)



Supplementary Figure 54 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 27 (+ 10% of unknown inseparable impurity)



Supplementary Figure 55 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 27 (+ 10% of unknown inseparable impurity)



Supplementary Figure 56 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 27 (+ 10% of unknown inseparable impurity)



### Supplementary Figure 57 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 28



Supplementary Figure 58 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 28



Supplementary Figure 59 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 28



Supplementary Figure 60 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 28

Supplementary Figure 61 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-3-*O*-methyl-1-thio-α-L-rhamnopyranoside







Supplementary Figure 63 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of *para*-methylphenyl 4-*O*-levulinoyl-3-*O*-methyl-1-thio-α-L-rhamnopyranoside









## Supplementary Figure 65 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 29



Supplementary Figure 66 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 29



## Supplementary Figure 67 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 29



Supplementary Figure 68 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 29



Supplementary Figure 69 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 10 (+ 12% of unknown inseparable impurity)



Supplementary Figure 70 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 10 (+ 12% of unknown inseparable impurity)


Supplementary Figure 71 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 10 (+ 12% of unknown inseparable impurity)



Supplementary Figure 72 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 10 (+ 12% of unknown inseparable impurity)



## Supplementary Figure 73 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 30







# Supplementary Figure 75 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 30



Supplementary Figure 76 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 30



Supplementary Figure 77 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 32



Supplementary Figure 78 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 32



Supplementary Figure 79 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 32



## Supplementary Figure 80 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 32



Supplementary Figure 81 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 33



Supplementary Figure 82 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 33



## Supplementary Figure 83 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 33



Supplementary Figure 84 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 33



## Supplementary Figure 85 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 34



Supplementary Figure 86 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 34



## Supplementary Figure 87 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 34



Supplementary Figure 88 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 34



## Supplementary Figure 89 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 35



Supplementary Figure 90 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 35



## Supplementary Figure 91 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 35



Supplementary Figure 92 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 35



Supplementary Figure 93 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 36



Supplementary Figure 94 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 36



#### Supplementary Figure 95 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 36



Supplementary Figure 96 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 36



Supplementary Figure 97 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 37



Supplementary Figure 98 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 37



Supplementary Figure 99 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 37



Supplementary Figure 100 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 37



## Supplementary Figure 101 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 38



Supplementary Figure 102 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 38



#### Supplementary Figure 103 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 38



Supplementary Figure 104 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 38



## Supplementary Figure 105 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 39



Supplementary Figure 106 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 39


#### Supplementary Figure 107 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 39



## Supplementary Figure 108 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 39



## Supplementary Figure 109 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 40



Supplementary Figure 110 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 40



## Supplementary Figure 111 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 40



Supplementary Figure 112 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 40



Supplementary Figure 113 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 31



Supplementary Figure 114 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 31



Supplementary Figure 115 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 31



Supplementary Figure 116 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 31



## Supplementary Figure 117 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 41



Supplementary Figure 118 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 41



Supplementary Figure 119 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 41



Supplementary Figure 120 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 41



### Supplementary Figure 121 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 42



Supplementary Figure 122 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 42



Supplementary Figure 123 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 42



Supplementary Figure 124 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 42



### Supplementary Figure 125 | <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 43



Supplementary Figure 126 | COSY NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 43



Supplementary Figure 127 | <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 150 MHz) of compound 43



## Supplementary Figure 128 | HSQC NMR spectrum (CDCl<sub>3</sub>, 600 MHz) of compound 43



## Supplementary Figure 129 | <sup>1</sup>H NMR spectrum (D<sub>2</sub>O, 600 MHz) of compound 8



Supplementary Figure 130 | COSY NMR spectrum (D<sub>2</sub>O, 600 MHz) of compound 8



Supplementary Figure 131 | <sup>13</sup>C NMR spectrum (D<sub>2</sub>O, 150 MHz) of compound 8



Supplementary Figure 132 | HSQC NMR spectrum (D<sub>2</sub>O, 600 MHz) of compound 8



Supplementary Figure 133 | Undecoupled HSQC NMR spectrum (D<sub>2</sub>O, 600 MHz) of compound 8







Supplementary Figure 135 | COSY NMR spectrum (D<sub>2</sub>O, 600 MHz) of compound 9



Supplementary Figure 136 | <sup>13</sup>C NMR spectrum (D<sub>2</sub>O, 150 MHz) of compound 9



Supplementary Figure 137 | HSQC NMR spectrum (D<sub>2</sub>O, 600 MHz) of compound 9

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