

## Supporting Information

### Highly Efficient *O*-Glycosylations with *p*-Tolyl Thioriboside and *p*-TolSOTf

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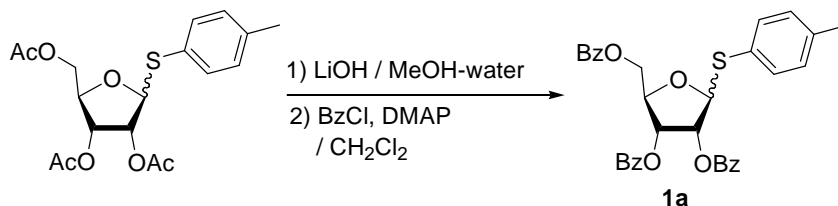
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**General Procedures and Methods:** All glassware was oven dried, assembled hot and cooled under a stream of nitrogen before use. Reactions with air sensitive materials were carried out by standard syringe techniques. Commercially available reagents were used as received without further purification. Thin layer chromatography was performed using 0.25 mm silica gel 60 plates visualizing at 254 nm, or developed with anisaldehyde solutions by heating with a hot-air gun. Specified products were purified by flash column chromatography using silica gel 60. IR absorptions were run on NaCl plates.  $^1\text{H}$  NMR spectral data were recorded at 300, 400 MHz instruments. The residual solvent signal was utilized as an internal reference  $\text{CDCl}_3$  (7.26).  $^{13}\text{C}$  NMR spectral data were recorded at 75, 100 MHz instruments. The residual solvent signal was utilized as an internal reference  $\text{CDCl}_3$  (77.23). For all NMR spectra,  $\delta$  values are given in ppm and  $J$  values in Hz.

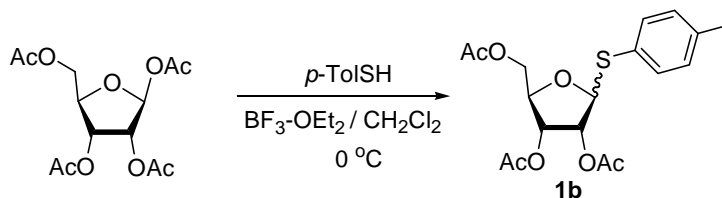
## Experimental Procedures

### *p*-Tolyl 2,3,5-tri-*O*-benzoyl-1-thio-D-ribofuranoside (**1a**).



To a stirred solution of a 1:6.6 mixture of *p*-tolyl 2,3,5-tri-*O*-acetyl-D-thioriboside (1.1 g, 2.88 mmol) in MeOH/water (10/1, 20 mL) was added LiOH (552 mg, 23.0 mmol). After 12h at rt, the reaction mixture was neutralized with 1N HCl and extracted with  $\text{CHCl}_3$ . The combined organic phase was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evap. *in vacuo* to provide the crude *p*-tolyl thioriboside. This was subjected to benzylation reaction with BzCl (14.4 mmol), DMAP (14.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) at 0 °C. The reaction mixture was quenched with aq. sat.  $\text{NaHCO}_3$ . The water phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phase was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 3:1) gave **1a** (1.63 g, 2.88 mmol, 100%). Data for **1a**:  $[\alpha]_{\text{D}}^{20} = -42.7$  (c 0.6 in  $\text{CHCl}_3$ ); IR (film) 1728, 1268, 1121  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.08-7.97 (m, 4H), 7.91-7.88 (m, 2H), 7.59-7.32 (m, 11H), 7.04 (d,  $J = 7.1$  Hz, 2H), 5.71 (t,  $J = 7.5$  Hz, 1H), 5.63 (t,  $J = 5.4$  Hz, 1H), 5.54 (d,  $J = 7.2$  Hz, 1H), 4.67-4.59 (m, 2H), 4.51-4.45 (m, 1H), 2.22 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 165.5, 165.3, 139.2, 134.8, 133.9, 133.7, 133.4, 132.9, 130.4, 130.1, 129.9, 129.7, 129.2, 129.1, 128.7, 128.7, 128.6, 127.1, 588.2, 80.6, 77.8, 74.5, 72.6, 64.5, 21.4; HRMS (ESI) Calcd. for  $\text{C}_{33}\text{H}_{28}\text{NaO}_7\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 591.1453; found: 591.1458.

### *p*-Tolyl 2,3,5-tri-*O*-acetyl-1-thio-D-ribofuranoside (**1b**).

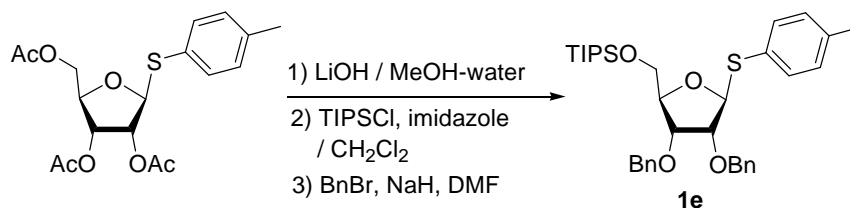


To a stirred solution of 1,2,3,5-tetra-*O*-acetyl-D-ribose (Fluka 1298919, 2.5 g, 7.86 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) at -78 °C was added *p*-TolSH (1.07 g, 8.64 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (5.5g, 39.3 mmol). The reaction mixture was stirred for 1h at 0 °C, and quenched with aq. sat.  $\text{NaHCO}_3$ . The water phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phase was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 3:1 to 1:1) gave the  $\alpha$ - and  $\beta$ -isomers with 1:6.6 ratio (2.4 g, 6.29 mmol, 80%). The  $\beta$ -isomer or a 1:6.6 mixture of *p*-tolyl 2,3,5-tri-*O*-acetyl-D-thioriboside was used in these studies.

$[\alpha]_{\text{D}}^{20} = -30.4$  (c 1.0 in  $\text{CHCl}_3$ ); IR (film) 1747, 1227, 1047  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 8.1$  Hz, 2H), 7.11 (d,  $J = 7.8$  Hz, 2H), 5.21 (m, 1H), 5.16 (d,  $J = 3.6$  Hz, 2H), 4.22-4.18 (m, 2H), 4.08 (m,

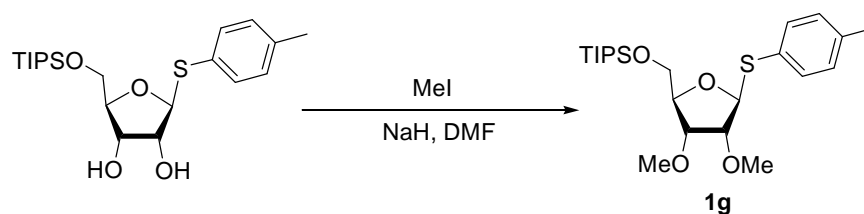
1H), 2.31 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.6, 169.8, 169.5, 138.9, 134.3, 129.9, 127.5, 88.0, 80.1, 73.7, 71.5, 63.6, 21.2, 20.8, 20.6; HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>22</sub>NaO<sub>7</sub>S (M+Na)<sup>+</sup>: 405.0984; found: 405.0986.

***p*-Tolyl 2,3-di-*O*-benzyl-1-thio-5-*O*-triisopropylsilyl-β-D-ribofuranoside (1e).**



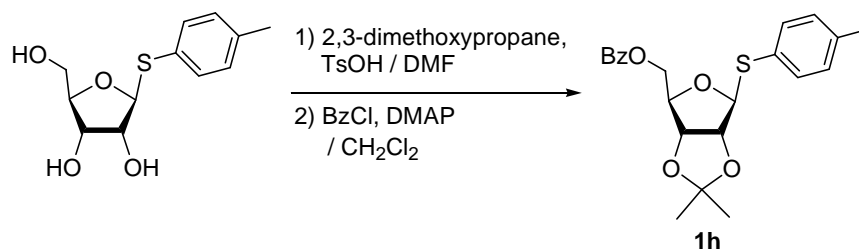
To a stirred solution of *p*-Tolyl 2,3,5-tri-*O*-acetyl-β-D-thioriboside (1.1 g, 2.88 mmol) in MeOH/water (10/1, 20 mL) was added LiOH (552 mg, 23.0 mmol). After 12h at rt, the reaction mixture was neutralized with 1N HCl and extracted with CHCl<sub>3</sub>. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo* to provide the crude *p*-tolyl thioriboside. This was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and TIPSCl (4.32 mmol) and imidazole (4.32 mmol) were added. After 12h, the reaction mixture was quenched with water. The water phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. The crude mixture was passed through SiO<sub>2</sub> plug to remove the salts. This was dissolved in DMF (20 mL). At 0 °C NaH (12.8 mmol) followed by BnBr (10.1 mmol) were added. After 1h, the reaction mixture was quenched with water. The water phase was extracted with Et<sub>2</sub>O. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/ethyl acetate = 5:1) gave **1e** (1.02 g, 1.73 mmol, 60%). Data for **1e**: [α]<sub>D</sub><sup>20</sup> = -19.9 (c 1.0 in CHCl<sub>3</sub>); IR (film) 2941, 1126, 772 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.32 (m, 12H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.37 (d, *J* = 4.2 Hz, 1H), 4.58-4.56 (m, 4H), 4.18 (dd, *J* = 4.4, 9.6 Hz, 1H), 4.06 (t, *J* = 4.8 Hz, 1H), 3.86 (t, *J* = 4.2 Hz, 1H), 3.72 (dd, *J* = 4.4, 10.8 Hz, 1H), 3.53 (dd, *J* = 5.6, 10.6 Hz, 1H), 2.33 (s, 3H), 1.09 (m, 3H), 1.04 (d, 3.2 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.0, 137.9, 137.7, 133.5, 129.8, 129.7, 128.8, 128.5, 128.3, 128.2, 128.0, 127.8, 88.8, 83.7, 80.2, 76.9, 72.2, 72.1, 63.6, 21.3, 18.2, 12.1; HRMS (ESI) Calcd. for C<sub>35</sub>H<sub>48</sub>NaO<sub>4</sub>SSi (M+Na)<sup>+</sup>: 615.2940; found: 615.2950.

***p*-Tolyl 2,3-di-*O*-methyl-1-thio-5-*O*-triisopropylsilyl-β-D-ribofuranoside (1g).**



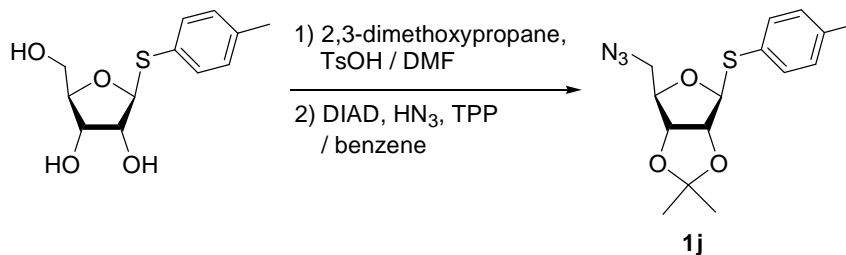
To a stirred solution of 5-*O*-Triisopropylsilyl-β-D-ribofuranoside (100 mg, 0.23 mmol) in DMF (1 mL) was added NaH (1.15 mmol), and MeI (2.3 mmol) at 0 °C. After 1h at 0 °C, the reaction mixture was quenched with water. The water phase was extracted with Et<sub>2</sub>O. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 5:1) gave **1g**. Data for **1g**: [α]<sub>D</sub><sup>20</sup> = -55.2 (c 1.0 in CHCl<sub>3</sub>); IR (film) 2941, 1644, 1124cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.27 (d, *J* = 4.8 Hz, 1H), 4.11-4.05 (m, 1H), 3.91 (t, *J* = 4.2 Hz, 1H), 3.80-3.73 (m, 2H), 3.58 (dd, *J* = 8.7 Hz, 10.5 Hz, 1H), 3.47 (s, 3H), 3.43 (s, 3H), 2.32 (s, 3H), 1.06 (m, 3H), 1.07 (s, 18H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.9, 133.2, 129.7, 88.2, 83.0, 82.9, 79.4, 63.7, 58.4, 57.9, 21.3, 18.1, 12.0; HRMS (ESI) Calcd. for C<sub>23</sub>H<sub>40</sub>NaO<sub>4</sub>SSi (M+Na)<sup>+</sup>: 463.2314; found: 463.2311.

***p*-Tolyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-1-thio- $\beta$ -D-ribofuranoside (**1h**).**



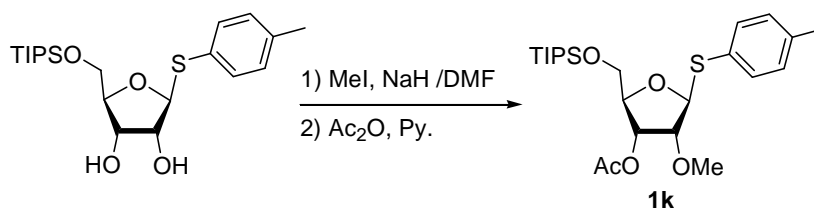
To a stirred solution of *p*-Tolyl thio- $\beta$ -D-ribofuranoside (200 mg, 0.78 mmol) in DMF (2 mL) at rt was added 2,3-dimethoxypropane (1.4 mmol) and TsOH (0.078 mmol). After 1h, the reaction mixture was quenched with aq. sat. NaHCO<sub>3</sub>. The water phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. This was subjected to a benzoylation reaction with BzCl (1.56 mmol) and DMAP (1.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). After 0.5h at 0 °C, the reaction mixture was quenched with water. The water phase was extracted with Et<sub>2</sub>O. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 5:1) gave **1h**. Data for **1h**:  $[\alpha]_D^{20} = -166.4$  (c 1.0 in CHCl<sub>3</sub>); IR (film) 1722, 1270, 1085 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (dd, *J* = 1.2, 3.2 Hz, 2H), 7.58 (t, *J* = 8.8 Hz, 1H), 7.47-7.40 (m, 4H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.56 (d, *J* = 0.6 Hz, 1H), 4.81 (s, 2H), 4.66 (m, 1H), 4.55 (m, 2H), 2.29 (s, 3H), 1.53 (s, 3H), 1.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.3, 138.1, 133.3, 132.8, 129.9, 128.5, 113.9, 92.7, 85.7, 84.6, 82.6, 64.7, 27.0, 25.6, 21.3; HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>24</sub>NaO<sub>5</sub>S (M+Na)<sup>+</sup>: 423.1242; found: 423.1250.

***p*-Tolyl 5-azido-5-deoxyl-2,3-*O*-isopropylidene-1-thio- $\beta$ -D-ribofuranoside (**1j**).**



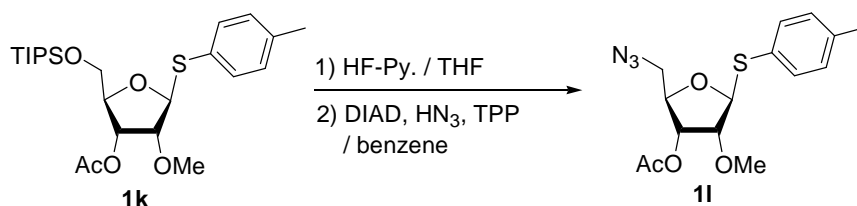
To a stirred solution of *p*-Tolyl thio- $\beta$ -D-ribofuranoside (200 mg, 0.78 mmol) in DMF (2 mL) at rt was added 2,3-dimethoxypropane (1.4 mmol) and TsOH (0.078 mmol). After 1h, the reaction mixture was quenched with aq. sat. NaHCO<sub>3</sub>. The water phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. This was dissolved in benzene (1 ml). Into the reaction mixture TPP (2.34 mmol), and DIAD (2.34 mmol), and HN<sub>3</sub> (~1.25 M, 2.34 mmol) were added. All volatiles were evaporated *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 8:1) gave **1j** (0.456 mmol, 75%). Data for **1j**:  $[\alpha]_D^{20} = -218.8$  (c 1.0 in CHCl<sub>3</sub>); IR (film) 2104, 1212, 1086 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (dd, *J* = 2.0, 6.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.48 (d, *J* = 2.4 Hz, 1H), 4.74 (dd, *J* = 2.0, 6.0 Hz, 1H), 4.63 (dd, *J* = 2.4, 6.4 Hz, 1H), 3.62 (dd, *J* = 6.8, 12.8 Hz, 1H), 3.52 (dd, *J* = 6.8, 12.4 Hz, 1H), 3.34 (s, 3H), 1.51 (s, 3H), 1.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.1, 132.5, 130.0, 129.6, 114.1, 92.6, 85.6, 85.3, 82.6, 52.9, 27.0, 25.5, 21.3; HRMS (ESI) Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>NaO<sub>3</sub>S (M+Na)<sup>+</sup>: 344.1045; found: 344.1041.

***p*-Tolyl 3-*O*-acetyl-2-*O*-methyl-1-thio-5-*O*-triisopropylsilyl- $\beta$ -D-ribofuranoside (**1k**).**



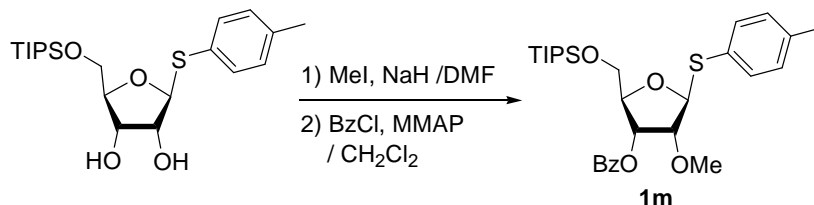
To a stirred solution of 5-*O*-Triisopropylsilyl- $\beta$ -D-ribofuranoside (100 mg, 0.23 mmol) in DMF-THF (4/1, 1 mL) was added NaH (1.15 mmol), and MeI (0.4 mmol) at -15 °C. After 1h at -15 °C, the reaction mixture was quenched with water. The water phase was extracted with Et<sub>2</sub>O. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. This was subjected to an acetylation reaction with Ac<sub>2</sub>O (1 mL) and Py. (1mL). After 6h, all volatiles were evaporated *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 5:1) gave **1k** (0.138 mmol, 60%). Data for **1k**:  $[\alpha]_D^{20} = -10.5$  (c 1.0 in CHCl<sub>3</sub>); IR (film) 1720, 1275 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.31 (t, *J* = 3.2 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 1H), 4.09 (dd, *J* = 3.6, 7.2 Hz, 1H), 3.81 (dd, *J* = 4.0, 10.4 Hz, 2H), 3.65 (dd, *J* = 4.2, 10.8 Hz, 1H), 3.40 (s, 3H), 2.32 (s, 3H), 2.10 (s, 3H), 1.08 (m, 3H), 1.06 (d, *J* = 4.8 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.5, 138.1, 133.4, 129.9, 129.8, 88.7, 83.8, 82.8, 72.3, 64.0, 59.3, 21.4, 21.1, 18.2, 12.1; HRMS (ESI) Calcd. for C<sub>24</sub>H<sub>40</sub>NaO<sub>5</sub>SSi (M+Na)<sup>+</sup>: 491.2263; found: 491.2268.

***p*-Tolyl 3-*O*-acetyl-5-azido-5-deoxy-2-*O*-methyl-1-thio- $\beta$ -D-ribofuranoside (**1l**).**



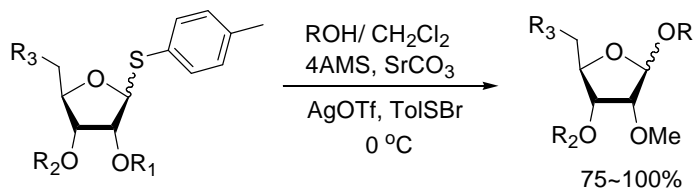
To a stirred solution of *p*-Tolyl 3-*O*-acetyl-2-*O*-methyl-1-thio-5-*O*-triisopropylsilyl- $\beta$ -D-ribofuranoside (**1k**) (200 mg, 0.427 mmol) in THF (1.5 mL) was added HF-Py (0.1 mL) at 0 °C. After 1h, the reaction was quenched with aq. sat. NaHCO<sub>3</sub>. The water phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 1:1) gave *p*-tolyl 3-*O*-acetyl-2-*O*-methyl-1-thio- $\beta$ -D-ribofuranoside. This was dissolved in benzene (1 ml). Into the reaction mixture TPP (1.28 mmol), and DIAD (1.28 mmol), and HN<sub>3</sub> (~1.25 M, 1.28 mmol) which was generated according to *Org. React.* **1947**, *3*, 327, were added. All volatiles were evaporated *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 5:1) gave **1l** (0.342 mmol, 80%). Data for **1l**:  $[\alpha]_D^{20} = -33.0$  (c 1.0 in CHCl<sub>3</sub>); IR (film) 2103, 1744, 1650 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.21 (d, *J* = 2.8 Hz, 1H), 5.01 (t, *J* = 4.0 Hz, 1H), 4.16 (dd, *J* = 4.8, 8.8 Hz, 1H), 3.82 (t, *J* = 5.6 Hz, 1H), 3.47-3.41 (m, 2H), 3.40 (s, 3H), 2.34 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 138.6, 133.6, 130.0, 128.9, 89.0, 82.4, 81.1, 72.57, 59.1, 52.8, 21.3, 20.9; HRMS (ESI) Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>NaO<sub>4</sub>S (M+Na)<sup>+</sup>: 360.0994; found: 360.0994.

***p*-Tolyl 3-*O*-benzoyl-2-*O*-methyl-1-thio-5-*O*-triisopropanylsilyl- $\beta$ -D-ribofuranoside (**1m**).**



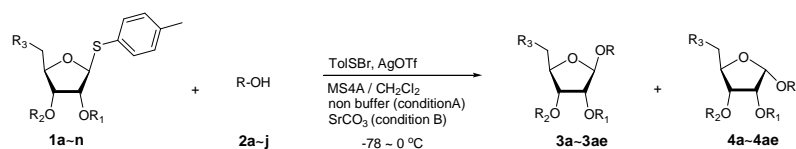
To a stirred solution of 5-*O*-Triisopropylsilyl- $\beta$ -D-ribofuranoside (100 mg, 0.23 mmol) in DMF-THF (4/1, 1 mL) was added NaH (1.15 mmol), and MeI (0.4 mmol) at -15 °C. After 1h at -15 °C, the reaction mixture was quenched with water. The water phase was extracted with Et<sub>2</sub>O. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. This was subjected to a benzylation reaction with BzCl (0.4 mmol) and DMAP. (0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). After 0.5h, the reaction mixture was quenched with water. The water phase was extracted with Et<sub>2</sub>O. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evap. *in vacuo*. Purification by silica gel chromatography (hexanes/EtOAc = 5:1) gave **1m**. Data for **1m**:  $[\alpha]_D^{20} = -14.4$  (c 1.0 in CHCl<sub>3</sub>); IR (film) 1725, 1270, 1114 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50-7.41 (m, 4H), 7.13 (d, *J* = 6.8 Hz, 2H), 5.78 (dd, *J* = 2.7 Hz, = 4.8 Hz, 1H), 5.28 (d, *J* = 6.9 Hz, 1H), 4.27 (dd, *J* = 3.9 Hz, = 6.9 Hz, 1H), 3.97-3.98 (m, 2H), 3.75 (dd, *J* = 4.5 Hz, = 11.1 Hz, 1H), 3.43 (s, 3H), 3.35 (s, 3H), 1.11 (m, 3H), 1.10 (s, 18H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  166.0, 138.1, 133.7, 133.4, 133.4, 130.0, 129.9, 129.8, 128.6, 88.8, 84.1, 82.9, 72.7, 64.0, 59.2, 21.3, 18.2, 12.1; HRMS (ESI) Calcd. for C<sub>29</sub>H<sub>42</sub>NaO<sub>5</sub>SSi (M+Na)<sup>+</sup>: 553.2420; found: 553.2431.

### General procedure for AgOTf/TolSBr promoted glycosylation



To a stirred solution of donor (0.12 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added 4Å MS (2 times the weight of donor), R<sub>1</sub>OH (0.06 mmol), SrCO<sub>3</sub> (0.24 mmol), AgOTf (0.12 mmol). The reaction mixture was stirred at rt for 15 min and cooled to 0 °C. *p*-TolSBr (2.0 M in 1,2-dichloroethane, 60  $\mu$ L, 0.12 mmol) was added. The reaction mixture was stirred at 0 °C for 1~15 min and quenched with Et<sub>3</sub>N (0.3 mmol). Filtration, evaporation gave the crude product. Purified by silica gel chromatography (hexane/EtOAc) gave the desired product(s).

*p*-TolSBr was generated by mixing (*p*-TolS)<sub>2</sub> (1 mmol) and Br<sub>2</sub> (1mmol) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (1 mL).



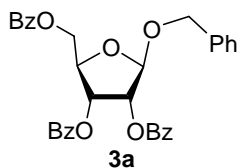
Entry	Donor	Acceptor	Temperature (°C)	Condition	Major Product	Yield(%)	$\alpha/\beta$ Selectivity (4/3)
1 2	 <b>1a:</b> R <sub>1</sub> , R <sub>2</sub> = Bz, R <sub>3</sub> = OBz <b>1b:</b> R <sub>1</sub> , R <sub>2</sub> = Ac, R <sub>3</sub> = OAc		-78-0	A	 <b>3a:</b> R <sub>1</sub> , R <sub>2</sub> = Bz, R <sub>3</sub> = OBz <b>3b:</b> R <sub>1</sub> , R <sub>2</sub> = Ac, R <sub>3</sub> = OAc	98 98	0/1 0/1
3	 <b>1a</b>		-78-0	A	 <b>3c</b>	100	0/1
4 5	 <b>1a</b>	 <b>2c:</b> R = Boc <b>2d:</b> R = Fomc	-78-0	B	 <b>3d:</b> R = Boc <b>3e:</b> R = Fomc	95 98	0/1 0/1
6 7 8	 <b>1a:</b> R <sub>3</sub> = OBz <b>1c:</b> R <sub>3</sub> = OTIPS <b>1d:</b> R <sub>3</sub> = N <sub>3</sub>	 <b>2e</b>	0	B	 <b>3f:</b> R <sub>3</sub> = OBz <b>3g:</b> R <sub>3</sub> = OTIPS <b>3h:</b> R <sub>3</sub> = N <sub>3</sub>	98 95 85	0/1 0/1 0/1
9 10 11	 <b>1e:</b> R <sub>1</sub> , R <sub>2</sub> = Bn, R <sub>3</sub> = OBn <b>1f:</b> R <sub>1</sub> , R <sub>2</sub> = Bn, R <sub>3</sub> = OTIPS <b>1g:</b> R <sub>1</sub> , R <sub>2</sub> = Me, R <sub>3</sub> = OTIPS		0	B	 <b>4i:</b> R <sub>1</sub> , R <sub>2</sub> = Bn, R <sub>3</sub> = OBn <b>4j:</b> R <sub>1</sub> , R <sub>2</sub> = Bn, R <sub>3</sub> = OTIPS <b>4k:</b> R <sub>1</sub> , R <sub>2</sub> = Me, R <sub>3</sub> = OTIPS	90 75 78	6.6/1 6.0/1 5.0/1
12 13 14	 <b>1h:</b> R <sub>3</sub> = OBz <b>1i:</b> R <sub>3</sub> = OTIPS <b>1j:</b> R <sub>3</sub> = N <sub>3</sub>		0	B	 <b>3l:</b> R <sub>3</sub> = OBz <b>3m:</b> R <sub>3</sub> = OTIPS <b>3n:</b> R <sub>3</sub> = N <sub>3</sub>	95 85 80	1/1.1 1/1.1 1/1.1
15 16 17 18	 <b>1k:</b> R <sub>2</sub> = Ac, R <sub>3</sub> = OTIPS <b>1l:</b> R <sub>2</sub> = Ac, R <sub>3</sub> = N <sub>3</sub> <b>1m:</b> R <sub>2</sub> = Bz, R <sub>3</sub> = OTIPS <b>1n:</b> R <sub>2</sub> = Bz, R <sub>3</sub> = N <sub>3</sub>		0	B	 <b>3o:</b> R <sub>2</sub> = Ac, R <sub>3</sub> = OTIPS <b>3p:</b> R <sub>2</sub> = Ac, R <sub>3</sub> = N <sub>3</sub> <b>3q:</b> R <sub>2</sub> = Bz, R <sub>3</sub> = OTIPS <b>3r:</b> R <sub>2</sub> = Bz, R <sub>3</sub> = N <sub>3</sub>	85 90 85 90	1/3.0 1/3.0 1/5.5 1/5.5
19 20 21	 <b>1a:</b> R <sub>3</sub> = OBz <b>1c:</b> R <sub>3</sub> = OTIPS <b>1d:</b> R = N <sub>3</sub>	 <b>2f</b>	0	B	 <b>3s:</b> R <sub>3</sub> = OBz <b>3t:</b> R <sub>3</sub> = OTIPS <b>3u:</b> R = N <sub>3</sub>	90 80 90	0/1 0/1 0/1

Continue

Entry	Donor	Acceptor	Temperature (°C)	Condition	Major Product	Yield(%)	$\alpha/\beta$ Selectivity (4/3)
22 23 24 25	<p> <b>1k:</b> R<sub>2</sub> = Ac, R<sub>3</sub> = OTIPS  <b>1l:</b> R<sub>2</sub> = Ac, R<sub>3</sub> = N<sub>3</sub>  <b>1m:</b> R<sub>2</sub> = Bz, R<sub>3</sub> = OTIPS  <b>1n:</b> R<sub>2</sub> = Bz, R<sub>3</sub> = N<sub>3</sub> </p>	<p><b>2f</b></p>	0	B	<p> <b>3v:</b> R<sub>2</sub> = Ac, R<sub>3</sub> = OTIPS (<math>\alpha/\beta</math> = 1/2.5)  <b>3w:</b> R<sub>2</sub> = Ac, R<sub>3</sub> = N<sub>3</sub> (<math>\alpha/\beta</math> = 1/2.5)  <b>3x:</b> R<sub>2</sub> = Bz, R<sub>3</sub> = OTIPS (<math>\alpha/\beta</math> = 1/5.5)  <b>3y:</b> R<sub>2</sub> = Bz, R<sub>3</sub> = N<sub>3</sub> (<math>\alpha/\beta</math> = 1/5.5) </p>	80 85 80 87	1/2.5 1/2.5 1/5.5 1/5.5
26	<p><b>1a</b> <math>\alpha : \beta = 1 : 6.6</math></p>	<p><b>2g</b></p>	0	B	<p><b>3z</b></p>	90	0/1
27 28	<p> <b>1k:</b> R<sub>2</sub> = Bz, R<sub>3</sub> = OTIPS  <b>1l:</b> R<sub>2</sub> = Ac, R<sub>3</sub> = N<sub>3</sub> </p>	<p><b>2h</b></p>	0	B	<p> <b>3aa:</b> R<sub>2</sub> = Bz, R<sub>3</sub> = OTIPS  <b>3ab:</b> R<sub>2</sub> = Ac, R<sub>3</sub> = N<sub>3</sub> </p>	80 85	1/2.5 1/5.5
29	<p><b>1k</b></p>	<p><b>2i</b></p>	0	B	<p><b>3ac</b></p>	85	1/2.5
30	<p><b>1f</b></p>	<p><b>2a</b></p>	0	B	<p><b>4ad</b></p>	85	1/2.5
31	<p><b>1b</b></p>	<p><b>2j</b></p>	0	B	<p><b>3ae</b></p>	90	0/1

## Compound Data

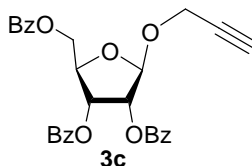
### Benzyl 2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranoside (**3a**).



**3a** ( $\beta$  isomer):  $[\alpha]_D^{20} = +4.0$  (c 0.5 in CHCl<sub>3</sub>); IR (film) 1720, 1130cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (dd,  $J = 8.4, 12.0$  Hz, 4H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.50 (t,  $J = 7.6$  Hz, 2H), 7.42 (t,  $J = 8.0$  Hz, 2H), 7.32 (m, 9H), 5.93 (t,  $J = 6.0$  Hz, 1H), 5.77 (d,  $J = 4.8$  Hz, 1H), 5.35 (s, 1H), 4.81 (d,  $J = 12.0$  Hz, 1H), 4.76-4.71 (m, 2H), 4.59 (d,  $J = 12.0$  Hz, 1H), 4.55 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 165.6, 165.5, 137.0, 133.7, 133.6, 133.3, 130.0, 130.0, 129.8, 129.4, 129.1, 128.7, 128.57, 128.2, 128.1, 104.7, 79.3, 75.8, 72.6, 69.9, 64.9; HRMS (ESI) Calcd. for C<sub>33</sub>H<sub>28</sub>NaO<sub>8</sub> (M+Na)<sup>+</sup>: 575.1682; found: 575.1691.

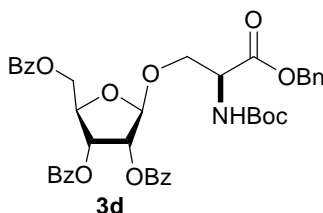


**Propargyl 2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranoside (3c).**



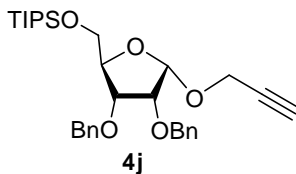
**3c** ( $\beta$  isomer):  $[\alpha]_D^{20} = +10.0$  (c 0.6 in  $\text{CHCl}_3$ ); IR (film) 1726, 1650, 1269  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09-8.02 (m, 4H), 7.89-7.86 (m, 2H), 7.62-7.48 (m, 3H), 7.43 (dd,  $J = 7.5$  Hz, 15.3 Hz, 4H), 7.31 (t,  $J = 7.8$  Hz, 2H), 5.91 (dd,  $J = 4.8, 6.9$  Hz, 1H), 5.75 (d,  $J = 4.5$  Hz, 1H), 5.49 (s, 1H), 4.75 (m, 1H), 4.71 (d,  $J = 3.9$  Hz, 1H), 4.56-4.50 (m, 1H), 4.30 (dd,  $J = 1.2, 2.4$  Hz, 1H), 2.45 (t,  $J = 2.4$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 165.6, 165.4, 133.8, 133.6, 133.4, 130.1, 130.0, 129.8, 129.1, 128.7, 128.7, 128.6, 103.5, 79.5, 78.5, 75.7, 75.5, 72.3, 64.6, 54.8; HRMS (ESI) Calcd. for  $\text{C}_{29}\text{H}_{24}\text{NaO}_8$  ( $\text{M}+\text{Na}$ ) $^+$ : 523.1369; found: 523.1364.

**3-(2,3,5-tri-*O*-Benzoyl- $\beta$ -D-ribofuranosyloxy)-2-tert-butoxycarbonylamino-propionic acid benzyl ester (3d).**



**3d** ( $\beta$  isomer):  $[\alpha]_D^{20} = +61.2$  (c 0.3 in  $\text{CHCl}_3$ ); IR (film) 1726, 1268, 1111  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02-7.97 (m, 4H), 7.89-7.86 (m, 2H), 7.60-7.48 (m, 3H), 7.44-7.29 (m, 1H), 5.66 (d,  $J = 4.8$  Hz, 1H), 5.59 (t,  $J = 5.1$  Hz, 1H), 5.48 (d,  $J = 8.7$  Hz, 1H), 5.25 (s, 1H), 5.24 (s, 2H), 4.68 (dd,  $J = 6.9, 11.7$  Hz, 1H), 4.57 (d,  $J = 18.7$  Hz, 1H), 4.50-4.37 (m, 2H), 4.29 (dd,  $J = 2.4, 9.9$  Hz, 1H), 3.78 (dd,  $J = 3.3, 10.2$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 166.2, 165.5, 160.9, 155.7, 135.5, 133.8, 133.6, 133.4, 130.0, 130.0, 129.8, 129.2, 129.0, 128.8, 128.7, 128.6, 106.2, 80.4, 79.4, 77.6, 77.4, 77.2, 76.8, 75.5, 73.1, 68.8, 67.7, 65.9, 54.0; HRMS (ESI) Calcd. for  $\text{C}_{41}\text{H}_{41}\text{NNaO}_{12}$  ( $\text{M}+\text{Na}$ ) $^+$ : 762.2526; found: 762.2531.

**Propargyl 2,3-di-*O*-benzyl-5-*O*-triisopropylsilyl- $\alpha$ -D-ribofuranoside (4j).**

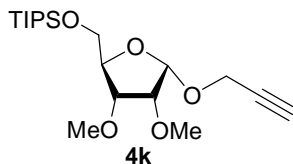


**4j** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +109.0$  (c 0.3 in  $\text{CHCl}_3$ ); IR (film) 1210  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.28 (m, 10H), 5.30 (d,  $J = 4.8$  Hz, 1H), 4.76-4.62 (m, 4H), 4.40 (d,  $J = 2.4$  Hz, 2H), 4.17 (dd,  $J = 3.6, 6.0$  Hz, 1H), 3.95 (dd,  $J = 2.8, 6.8$  Hz, 1H), 3.82 (dd,  $J = 4.4, 6.4$  Hz, 1H), 3.64-3.56 (m, 2H), 2.40 (t,  $J = 2.4$  Hz, 1H), 0.96 (m, 3H), 0.95 (d,  $J = 2.4$  Hz, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 138.0, 128.6, 128.5, 128.35, 128.2, 128.0, 127.8, 98.9, 84.6, 79.9, 78.0, 75.4, 74.3, 72.7, 72.4, 63.9, 54.4, 18.1, 12.0; HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{44}\text{NaO}_5\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 547.2856; found: 547.2851.

**3j** ( $\beta$  isomer):  $[\alpha]_D^{20} = +11.0$  (c 0.1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.28 (m, 10H), 5.22 (s, 1H), 4.65 (dd,  $J = 11.6, 34.4$  Hz, 2H), 4.51 (dd,  $J = 12.0, 22.0$  Hz, 2H), 4.22 (m, 2H), 3.92 (d,  $J = 4.0$  Hz, 1H), 3.85 (dd,  $J = 3.6, 10.8$  Hz, 1H), 3.76 (dd,  $J = 3.6, 11.2$  Hz, 1H), 2.40 (t,  $J = 2.4$  Hz, 1H), 1.06 (m, 3H),

1.07 (s, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.8, 137.3, 128.6, 128.6, 128.3, 128.1, 128.0, 103.1, 82.7, 80.1, 74.6, 72.7, 72.5, 63.5, 54.2, 18.2, 12.1; HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{44}\text{NaO}_5\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 547.2856; found: 547.2855

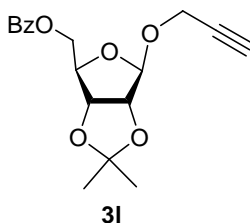
**Propargyl 2,3-di-*O*-methyl-5-*O*-triisopropylsilyl- $\alpha$ -D-ribofuranoside (4k).**



**4k** ( $\alpha$  isomer):  $[\alpha]_{\text{D}}^{20} = +33.0$  (c 0.4 in  $\text{CHCl}_3$ ); IR (film) 1463, 1107, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.37 (d,  $J = 4.4$  Hz, 1H), 4.36 (d,  $J = 2.4$  Hz, 1H), 4.18 (m, 1H), 3.87 (dd,  $J = 2.0, 6.4$  Hz, 1H), 3.83-3.78 (m, 2H), 3.69 (dd,  $J = 4.8, 10.4$  Hz, 1H), 3.49 (s, 3H), 3.44 (s, 3H), 1.03 (m, 3H), 1.06 (s, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  98.4, 84.0, 81.0, 79.6, 78.6, 74.4, 64.4, 59.0, 54.3, 18.2, 12.1; HRMS (ESI) Calcd. for  $\text{C}_{19}\text{H}_{36}\text{NaO}_5\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 395.2230; found: 395.2231.

**3k** ( $\beta$  isomer):  $[\alpha]_{\text{D}}^{20} = +11.0$  (c 0.1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.23 (s, 1H), 4.26 (m, 2H), 4.05 (m, 2H), 3.83 (m, 3H), 3.51 (d,  $J = 1.5$  Hz, 3H), 3.43 (d,  $J = 1.8$  Hz, 3H), 2.36 (s, 1H), 1.08 (m, 3H), 1.09 (s, 18H); HRMS (ESI) Calcd. for  $\text{C}_{19}\text{H}_{36}\text{NaO}_5\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 395.2230; found: 395.2236.

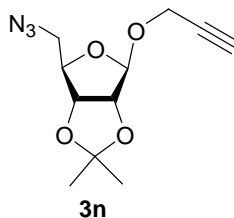
**Propargyl 5-*O*-benzoyl-2,3-*O*-isopropylidene- $\beta$ -D-ribofuranoside (3l).**



**3l** ( $\beta$  isomer):  $[\alpha]_{\text{D}}^{20} = +39.0$  (c 1.0 in  $\text{CHCl}_3$ ); IR (film) 1651, 1272, 1097  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (m, 2H), 5.57 (m, 2H), 7.45 (m, 2H), 5.36 (s, 3H), 4.76 (dd,  $J = 6.0, 19.8$  Hz, 1H), 4.57 (t,  $J = 6.9$  Hz, 1H), 4.37 (dd,  $J = 1.5$  Hz, 6.9 Hz, 2H), 4.23 (d,  $J = 2.4$  Hz, 2H), 2.42 (t,  $J = 2.7$  Hz, 1H), 1.52 (s, 3H), 1.35 (s, 3H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 133.4, 130.0, 129.9, 128.7, 113.0, 106.7, 85.6, 85.0, 82.0, 78.8, 75.1, 65.2, 54.4, 26.6, 25.2; HRMS (ESI) Calcd. for  $\text{C}_{18}\text{H}_{20}\text{NaO}_6$  ( $\text{M}+\text{Na}$ ) $^+$ : 355.1158; found: 355.1170.

**4l** ( $\alpha$  isomer):  $[\alpha]_{\text{D}}^{20} = -60.0$  (c 0.4 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (m, 2H), 7.58 (m, 1H), 7.46 (m, 2H), 5.31 (d,  $J = 4.8$  Hz, 1H), 4.79 (dd,  $J = 4.5$  Hz, 6.9 Hz, 1H), 4.71 (dd,  $J = 2.7, 7.2$  Hz, 1H), 4.54-4.44 (m, 3H), 4.38 (t,  $J = 2.7$  Hz, 2H), 2.40 (t,  $J = 2.4$  Hz, 1H), 1.61 (s, 3H), 1.38 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 133.5, 129.9, 128.7, 116.0, 99.9, 81.0, 81.0, 74.9, 64.7, 55.2, 26.2, 26.0; HRMS (ESI) Calcd. for  $\text{C}_{18}\text{H}_{20}\text{NaO}_6$  ( $\text{M}+\text{Na}$ ) $^+$ : 355.1158; found: 355.1162.

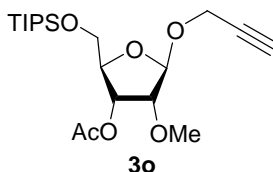
**Propargyl 5-azido-5-deoxy-2,3-*O*-isopropylidene- $\beta$ -D-ribofuranoside (3n).**



**3n** ( $\beta$  isomer):  $[\alpha]_D^{20} = +78.4$  (c 0.5 in  $\text{CHCl}_3$ ); IR (film) 2102, 1077  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.30 (s, 1H), 4.65 (dd,  $J = 6.0$  Hz, 18.9 Hz, 2H), 4.32 (t,  $J = 7.2$  Hz, 1H), 4.26 (dd,  $J = 1.2, 2.4$  Hz, 1H), 4.24 (dd,  $J = 1.2, 2.1$  Hz, 1H), 3.46 (dd,  $J = 7.8, 12.6$  Hz, 1H), 3.30 (dd,  $J = 6.9, 12.6$  Hz, 1H), 2.46 (m, 1H), 1.50 (s, 3H), 1.33 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  113.1, 107.1, 85.9, 85.4, 82.2, 75.2, 54.8, 53.8, 26.6, 25.1; HRMS (ESI) Calcd. for  $\text{C}_{11}\text{H}_{15}\text{N}_3\text{NaO}_4$  ( $\text{M}+\text{Na}$ ) $^+$ : 276.0960; found: 276.0960.

**4n** ( $\alpha$  isomer):  $[\alpha]_D^{20} = -16.0$  (c 0.3 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.23 (d,  $J = 4.8$  Hz, 1H), 4.73 (dd,  $J = 4.8, 7.2$  Hz, 1H), 4.55 (dd,  $J = 3.6$  Hz, 7.2 Hz, 1H), 4.32 (dd,  $J = 2.4, 4.2$  Hz, 2H), 4.27 (m, 1H), 3.55 (dd,  $J = 4.0, 13.2$  Hz, 1H), 3.36 (dd,  $J = 4.4, 16.0$  Hz, 1H), 2.39 (t,  $J = 2.4$  Hz, 1H), 1.55 (s, 3H), 1.33 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  116.2, 99.8, 81.2, 81.2, 80.6, 75.0, 55.1, 52.6, 26.2, 26.0; HRMS (ESI) Calcd. for  $\text{C}_{11}\text{H}_{15}\text{N}_3\text{NaO}_4$  ( $\text{M}+\text{Na}$ ) $^+$ : 276.0960; found: 276.0962.

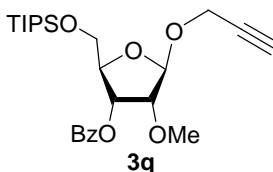
**Propargyl 3-O-acetyl-2-O-methyl-5-O-triisopropylsilyl- $\beta$ -D-ribofuranoside (3o).**



**3o** ( $\beta$  isomer):  $[\alpha]_D^{20} = -29.2$  (c 0.3 in  $\text{CHCl}_3$ ); IR (film) 1720, 1210  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.23 (m, 1H), 5.21 (s, 1H), 4.26 (m, 2H), 4.19 (dd,  $J = 4.8, 10.2$  Hz, 1H), 3.96 (m, 2H), 3.80 (t,  $J = 4.8$  Hz, 1H), 3.42 (s, 3H), 2.43 (t,  $J = 2.4$  Hz, 1H), 2.11 (s, 3H), 1.08 (m, 3H), 1.05 (d,  $J = 4.2$  Hz, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 103.2, 83.0, 79.1, 74.8, 73.3, 64.3, 59.0, 54.6, 21.0, 18.1, 12.1; HRMS (ESI) Calcd. for  $\text{C}_{20}\text{H}_{36}\text{NaO}_6\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 423.2179; found: 423.2179.

**4o** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +78.6$  (c 0.1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.40 (d,  $J = 4.2$  Hz, 1H), 5.33 (dd,  $J = 2.1, 6.6$  Hz, 1H), 4.37 (t,  $J = 2.7$  Hz, 2H), 4.13 (d,  $J = 2.4$  Hz, 1H), 3.98-3.89 (m, 2H), 3.82 (dd,  $J = 2.7$  Hz, 10.8 Hz, 1H), 3.46 (s, 3H), 2.39 (t,  $J = 2.1$  Hz, 1H), 2.14 (s, 3H), 1.12 (m, 3H), 1.06 (d,  $J = 4.5$  Hz, 18H); HRMS (ESI) Calcd. for  $\text{C}_{20}\text{H}_{36}\text{NaO}_6\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 423.2179; found: 423.2183.

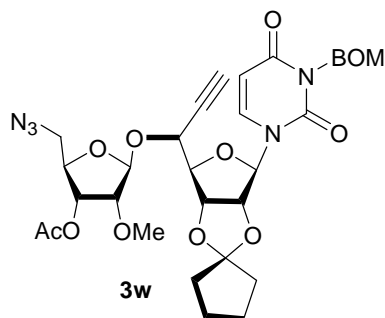
**Propargyl 3-O-benzoyl-2-O-methyl-5-O-triisopropylsilyl- $\beta$ -D-ribofuranoside (3q).**



**3q** ( $\beta$  isomer):  $[\alpha]_D^{20} = -27.6$  (c 0.5 in  $\text{CHCl}_3$ ); IR (film) 2942, 1726, 1274  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.2$  Hz, 2H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 1H), 5.47 (t,  $J = 5.2$  Hz, 1H), 5.29 (d,  $J = 2.0$  Hz, 1H), 4.38 (dd,  $J = 4.8, 18.0$  Hz, 1H), 4.30 (t,  $J = 3.2$  Hz, 2H), 4.09 (dd,  $J = 1.6, 4.8$  Hz, 1H), 3.87 (t,  $J = 4.8, 2\text{H}$ ), 2.44 (t,  $J = 2.4$  Hz, 1H), 1.10 (m, 3H), 1.05 (s, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 133.4, 130.1, 129.9, 128.6, 103.6, 83.2, 82.5, 79.2, 74.9, 73.8, 64.4, 59.1, 54.7, 18.1, 12.1; HRMS (ESI) Calcd. for  $\text{C}_{25}\text{H}_{38}\text{NaO}_6\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 485.2335; found: 485.2328.

**4q** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +60.0$  (c 0.2 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 8.0$  Hz, 2H), 7.55 (t,  $J = 7.2$  Hz, 1H), 7.43 (t,  $J = 8.0$  Hz, 2H), 5.61 (dd,  $J = 1.6, 6.4$  Hz, 1H), 5.43 (d,  $J = 4.4$  Hz, 1H), 4.40 (d,  $J = 2.4$  Hz, 2H), 4.30 (d,  $J = 1.6$  Hz, 1H), 4.03 (m, 1H), 4.01 (m, 1H), 3.46 (s, 3H), 2.41 (t,  $J = 2.4$  Hz, 1H), 1.08 (m, 3H), 1.09 (s, 18H);  $\text{C}_{25}\text{H}_{38}\text{NaO}_6\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 485.2335; found: 485.2336.

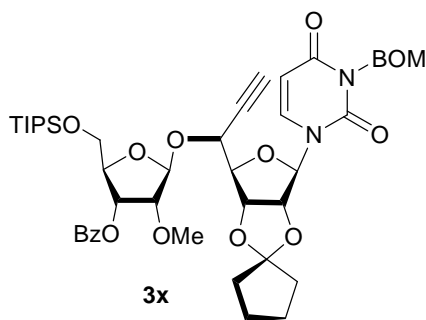
**5-O-(3-O-Acetyl-5-azido-5-deoxyl-2-O-methyl- $\beta$ -D-ribofuranosyl)-1-(3-benzyloxymethyluracil-1-yl)-2,3-O-cyclopentanylidene-5-ethynyl- $\beta$ -ribofuranose (3W).**



**3w** ( $\beta$  isomer):  $[\alpha]_D^{20} = -6.1$  (c 0.2 in  $\text{CHCl}_3$ ); IR (film) 2104, 1669, 1101  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 7.2$  Hz, 2H), 7.31 (t,  $J = 7.2$  Hz, 2H), 7.28 (m, 1H), 5.96 (d,  $J = 3.2$  Hz, 1H), 5.83 (d,  $J = 8.0$  Hz, 1H), 5.48 (d,  $J = 4.0$  Hz, 1H), 5.45 (s, 1H), 5.02 (dd,  $J = 4.8, 7.6$  Hz, 1H), 4.83 (dd,  $J = 3.6, 6.4$  Hz, 1H), 4.80 (dd,  $J = 2.0, 4.0$  Hz, 1H), 4.70 (s, 2H), 4.67 (dd,  $J = 3.2, 6.4$  Hz, 1H), 4.32 (t,  $J = 4.0$  Hz, 1H), 4.29 (m, 1H), 3.98 (d,  $J = 4.8$  Hz, 1H), 3.54 (dd,  $J = 3.2, 13.2$  Hz, 1H), 3.45 (s, 3H), 3.38 (dd,  $J = 5.2, 13.2$  Hz, 1H), 2.61 (d,  $J = 2.0$  Hz, 1H), 2.14 (s, 3H), 2.04 (m, 2H), 1.76 (m, 2H), 1.70 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 169.9, 162.7, 151.0, 139.5, 138.1, 128.5, 127.9, 124.5, 102.7, 102.3, 92.3, 86.0, 84.1, 82.5, 80.3, 79.7, 77.8, 72.8, 72.5, 70.6, 66.1, 59.1, 52.7, 36.9, 36.8, 23.8, 23.4, 20.9; HRMS (ESI) Calcd. for  $\text{C}_{30}\text{H}_{37}\text{N}_5\text{NaO}_{11}$  ( $\text{M}+\text{Na}$ ) $^+$ : 690.2387; found: 690.2381.

**4w** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +2.0$  (c 0.3 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 8.0$  Hz, 1H), 7.38-7.27 (m, 5H), 6.05 (d,  $J = 4.8$  Hz, 1H), 5.71 (d,  $J = 8.4$  Hz, 1H), 5.48 (dd,  $J = 10.0, 18.4$  Hz, 2H), 5.39 (d,  $J = 4.4$  Hz, 1H), 5.10 (dd,  $J = 2.0, 6.8$  Hz, 1H), 4.85 (dd,  $J = 2.0, 6.0$  Hz, 1H), 4.69 (m, 1H), 4.70 (s, 2H), 4.55 (dd,  $J = 2.4, 3.6$  Hz, 1H), 4.43 (dd,  $J = 2.0, 3.6$  Hz, 1H), 4.39 (m, 1H), 3.83 (dd,  $J = 4.4, 6.4$  Hz, 1H), 3.63 (dd,  $J = 3.2, 13.2$  Hz, 1H), 3.52 (dd,  $J = 3.6, 13.2$  Hz, 1H), 2.59 (d,  $J = 2.0$  Hz, 1H), 2.03 (m, 2H), 1.75 (m, 2H), 1.72 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 162.8, 151.4, 140.4, 138.0, 128.5, 127.8, 123.8, 102.5, 101.1, 91.9, 85.9, 83.2, 83.0, 80.9, 80.7, 76.4, 72.4, 70.6, 70.0, 68.5, 59.3, 52.4, 37.2, 23.8, 23.4, 21.1; HRMS (ESI) Calcd. for  $\text{C}_{30}\text{H}_{37}\text{N}_5\text{NaO}_{11}$  ( $\text{M}+\text{Na}$ ) $^+$ : 690.2387; found: 690.2380.

**5-O-(3-O-benzoyl-2-O-methyl-5-triisopropylsilyl- $\beta$ -D-ribofuranosyl)-1-(3-benzoyloxymethyluracil-1-yl)-2,3-O-cyclopentanylidene-5-ethynyl- $\beta$ -ribofuranose (3x).**

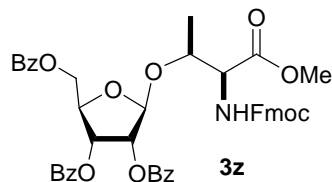


**3x** ( $\beta$  isomer):  $[\alpha]_D^{20} = -28.5$  (c 0.6 in  $\text{CHCl}_3$ ); IR (film) 1720, 768  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.8$  Hz, 2H), 7.70 (d,  $J = 8.4$  Hz, 1H), 7.55 (m, 1H), 7.43 (m, 2H), 7.37-7.24 (m, 5H), 6.11 (d,  $J = 4.4$  Hz, 1H), 5.63 (dd,  $J = 1.2, 6.4$  Hz, 1H), 5.45 (dd,  $J = 9.6, 16.8$  Hz, 1H), 5.29 (d,  $J = 4.4$  Hz, 1H), 4.87 (dd,  $J = 2.0, 6.4$  Hz, 1H), 4.68 (s, 3H), 4.60 (dd,  $J = 4.4, 6.0$  Hz, 1H), 4.50 (t,  $J = 2.0$  Hz, 1H), 4.48 (d,  $J = 1.6$  Hz, 1H), 4.40 (t,  $J = 2.4$  Hz, 1H), 4.04 (dd,  $J = 2.4, 11.2$  Hz, 1H), 3.98 (dd,  $J = 4.0, 6.0$  Hz, 1H), 3.90 (dd,  $J = 2.4, 10.8$  Hz, 1H), 3.44 (s, 2H), 2.54 (d,  $J = 2.4$  Hz, 1H), 2.01 (m, 2H), 1.70 (m, 2H), 1.61 (m, 4H), 1.15 (m, 3H), 1.08 (d,  $J = 4.2$  Hz, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 163.1, 151.8, 140.4, 138.4, 134.1, 133.7, 130.6, 130.2, 129.0, 128.8, 128.2, 128.2, 124.3, 102.9, 102.3, 91.3, 86.2, 85.6, 83.4, 82.2, 80.7, 80.2, 76.0, 72.7, 70.9, 70.5, 68.3, 64.1, 59.6, 37.4, 24.1, 23.7, 18.5, 12.4; HRMS (ESI) Calcd. for  $\text{C}_{46}\text{H}_{60}\text{N}_2\text{NaO}_{12}\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 883.3813; found: 883.3817.

**4x** ( $\alpha$  isomer):  $[\alpha]_D^{20} = -16.0$  (c 0.1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.2$  Hz, 2H), 7.57 (m, 1H), 7.50 (d,  $J = 8.1$  Hz, 1H), 7.44 (d,  $J = 7.5$  Hz, 2H), 7.38-7.70 (m, 5H), 6.03 (d,  $J = 4.4$  Hz, 1H),

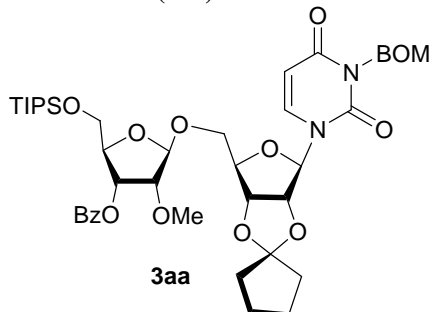
5.89 (d,  $J = 8.1$  Hz, 1H), 5.48 (m, 3H), 5.38 (t,  $J = 6.3$  Hz, 1H), 4.83-4.78 (m, 2H), 4.70 (s, 2H), 4.65 (dd,  $J = 3.3, 6.3$  Hz, 2H), 4.41 (dd,  $J = 8.1, 10.8$  Hz, 1H), 4.33 (t,  $J = 3.6$  Hz, 1H), 4.12 (dd,  $J = 1.5, 4.8$  Hz, 1H), 3.90 (dd,  $J = 5.1, 10.5$  Hz, 1H), 3.80 (dd,  $J = 5.4, 10.5$  Hz, 1H), 3.42 (s, 3H), 2.61 (d,  $J = 2.1$  Hz, 1H), 2.04 (m, 2H), 1.76 (m, 2H), 1.71 (m, 4H), 1.07 (m, 3H), 1.10 (d,  $J = 4.8$  Hz, 18H); HRMS (ESI) Calcd. for  $C_{46}H_{60}N_2NaO_{12}Si$  (M+Na)<sup>+</sup>: 883.3813; found: 883.3821.

**3-(*R*)-(2,3,5-tri-*O*-benzoyl- $\beta$ -D-ribofuranosyloxy)-2-(*S*)-(9H-Fluoren-9-ylmethoxycarbonylamino)-butyric acid methyl ester (3z).**



**3z** ( $\beta$  isomer):  $[\alpha]_D^{20} = +33.6$  (c 0.7 in  $CHCl_3$ ); IR (film) 3422, 1725, 1268  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.04-8.00 (m, 4H), 7.89 (d,  $J = 7.5$  Hz, 2H), 7.87 (d,  $J = 7.2$  Hz, 2H), 7.77 (d,  $J = 7.2$  Hz, 2H), 7.65 (d,  $J = 6.9$  Hz, 2H), 7.61-7.48 (m, 2H), 7.42 (dd,  $J = 7.8, 15.6$  Hz, 4H), 7.35-7.30 (m, 5H), 5.68 (m, 3H), 5.39 (s, 1H), 4.72 (m, 1H), 4.56 (m, 2H), 4.52 (dd,  $J = 1.8, 9.3$  Hz, 1H), 4.39 (m, 2H), 4.27 (m, 1H), 3.83 (s, 3H), 1.33 (d,  $J = 6.6$  Hz, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  171.0, 166.3, 165.5, 165.6, 157.0, 144.1, 144.0, 141.5, 133.8, 133.7, 133.4, 130.0, 130.0, 129.8, 129.2, 129.0, 128.8, 128.6, 127.9, 127.4, 125.5, 120.2, 103.4, 79.1, 76.0, 73.5, 73.0, 67.6, 65.9, 58.8, 53.0, 47.3, 16.4; HRMS (ESI) Calcd. for  $C_{52}H_{45}NNaO_{12}$  (M+Na)<sup>+</sup>: 898.2839; found: 898.2839.

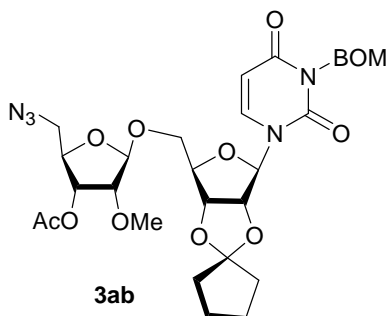
**5-*O*-(3-*O*-benzoyl-2-*O*-methyl-5-triisopropylsilyl- $\beta$ -D-ribofuranosyl)-1-(3-benzyloxymethyluracil-1-yl)-2,3-*O*-cyclopentanylidene- $\beta$ -ribofuranose (3aa).**



**3aa** ( $\beta$  isomer):  $[\alpha]_D^{20} = -14.7$  (c 0.2 in  $CHCl_3$ ); IR (film) 1673, 1273, 1102  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.06 (d,  $J = 7.2$  Hz, 2H), 7.58 (t,  $J = 7.2$  Hz, 1H), 7.44 (m, 3H), 7.38-7.27 (m, 5H), 5.82 (dd,  $J = 3.2, 4.4$  Hz, 2H), 5.47 (dd,  $J = 9.6, 14.8$  Hz, 2H), 5.42 (t,  $J = 4.2$  Hz, 1H), 5.09 (d,  $J = 2.4$  Hz, 1H), 4.71 (s, 1H), 4.70 (s, 2H), 4.33 (m, 2H), 4.06-4.01 (m, 2H), 3.89 (dd,  $J = 4.4, 10.4$  Hz, 1H), 3.81 (dd,  $J = 4.8, 10.4$  Hz, 1H), 3.67 (s, 3H), 2.01 (m, 2H), 1.74 (m, 2H), 1.69 (m, 4H), 1.06 (m, 3H), 1.01 (d,  $J = 6.4$  Hz, 18H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.1, 162.8, 151.0, 140.1, 133.5, 130.0, 129.7, 128.6, 128.5, 127.8, 124.1, 106.0, 102.4, 93.5, 85.4, 84.8, 82.8, 82.2, 80.6, 73.6, 72.5, 70.6, 68.0, 64.7, 59.2, 36.8, 23.8, 23.4, 18.2, 12.1, RMS (ESI) Calcd. for  $C_{44}H_{60}N_2NaO_{12}Si$  (M+Na)<sup>+</sup>: 859.3813; found: 859.3815.

**4aa** ( $\alpha$  isomer):  $[\alpha]_D^{20} = -9.0$  (c 0.1 in  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.95 (d,  $J = 8.4$  Hz, 2H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.47 (m, 1H), 7.38-7.29 (m, 8H), 6.12 (d,  $J = 3.2$  Hz, 1H), 5.61 (d,  $J = 8.0$  Hz, 1H), 5.55 (dd,  $J = 1.6$  Hz, 6.4 Hz, 1H), 5.43 (dd,  $J = 9.6, 14.2$  Hz, 2H), 5.15 (d,  $J = 4.4$  Hz, 1H), 4.69 (m, 2H), 4.68 (s, 2H), 4.45 (dd,  $J = 3.2, 6.0$  Hz, 1H), 4.35 (dd,  $J = 1.6, 21.6$  Hz, 1H), 4.09-3.98 (m, 2H), 3.87 (dd,  $J = 2.0, 10.8$  Hz, 1H), 3.70 (dd,  $J = 2.0, 10.8$  Hz, 1H), 3.47 (s, 3H), 2.03 (m, 2H), 1.69 (m, 2H), 1.55 (m, 4H), 1.10 (m, 3H), 1.09 (d,  $J = 1.2$  Hz, 18H); HRMS (ESI) Calcd. for  $C_{44}H_{60}N_2NaO_{12}Si$  (M+Na)<sup>+</sup>: 859.3813; found: 859.3812.

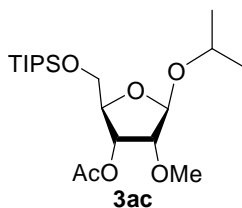
**5-*O*-(3-*O*-Acetyl-5-azido-5-deoxy-2-*O*-methyl- $\beta$ -D-ribofuranosyl)-1-(3-benzyloxymethyluracil-1-yl)-2,3-*O*-cyclopentanylidene- $\beta$ -D-ribofuranose (3ab).**



**3ab** ( $\beta$  isomer):  $[\alpha]_D^{20} = +25.6$  (c 0.3 in  $\text{CHCl}_3$ ); IR (film) 2102, 1714, 1099  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.26 (m, 6H), 5.80 (d,  $J = 8.0$  Hz, 1H), 5.76 (d,  $J = 1.6$  Hz, 1H), 5.47 (dd,  $J = 9.6, 16.0$  Hz, 2H), 5.03 (s, 1H), 5.01 (m, 1H), 4.74 (m, 2H), 4.70 (s, 2H), 4.33 (m, 1H), 4.26 (m, 1H), 3.64 (dd,  $J = 6.4, 11.2$  Hz, 1H), 3.49 (dd,  $J = 3.6, 13.2$  Hz, 1H), 3.40 (s, 3H), 3.45 (dd,  $J = 5.6, 13.2$  Hz, 1H), 2.13 (s, 3H), 2.01 (m, 2H), 1.75 (m, 2H), 1.72 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 162.8, 151.0, 140.3, 138.1, 128.5, 127.9, 124.2, 105.6, 102.4, 94.0, 85.4, 84.8, 82.5, 80.5, 79.8, 73.1, 72.5, 70.5, 68.2, 59.1, 53.2, 36.9, 36.8, 23.7, 23.4, 20.9; HRMS (ESI) Calcd. for  $\text{C}_{30}\text{H}_{37}\text{N}_5\text{NaO}_{11}$  ( $\text{M}+\text{Na}$ ) $^+$ : 666.2387; found: 666.2391.

**4ab** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +12.0$  (c 0.1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.28 (m, 6H), 5.76 (d,  $J = 8.0$  Hz, 1H), 5.69 (d,  $J = 1.6$  Hz, 1H), 5.47 (dd,  $J = 10.0, 19.2$  Hz, 2H), 5.23 (d,  $J = 4.4$  Hz, 1H), 4.97 (s, 1H), 4.78 (dd,  $J = 1.6, 6.4$  Hz, 1H), 4.71 (d,  $J = 4.0$  Hz, 1H), 4.70 (s, 2H), 4.34 (m, 1H), 4.10 (m, 1H), 4.06 (dd,  $J = 3.2, 11.2$  Hz, 1H), 3.91 (dd,  $J = 4.8, 8.4$  Hz, 1H), 3.61 (dd,  $J = 6.0, 10.8$  Hz, 1H), 3.56 (dd,  $J = 3.2, 13.2$  Hz, 1H), 3.37 (m, 1H), 3.35 (s, 3H), 2.12 (s, 3H), 2.02 (m, 2H), 1.74 (m, 2H), 1.70 (m, 4H); HRMS (ESI) Calcd. for  $\text{C}_{30}\text{H}_{37}\text{N}_5\text{NaO}_{11}$  ( $\text{M}+\text{Na}$ ) $^+$ : 666.2387; found: 666.2389.

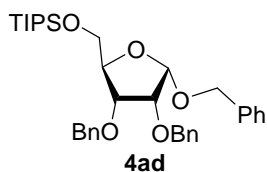
**Isopropyl 3-*O*-acetyl-2-*O*-methyl-5-*O*-triisopropylsilyl- $\beta$ -D-ribofuranoside (3ac).**



**3ac** ( $\beta$  isomer):  $[\alpha]_D^{20} = -38.0$  (c 0.1 in  $\text{CHCl}_3$ ); IR (film) 1645, 1220, 772  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.22 (t,  $J = 4.2$  Hz, 1H), 5.09 (d,  $J = 2.8$  Hz, 1H), 4.11 (dd,  $J = 4.2, 10.4$  Hz, 1H), 3.91 (m, 1H), 3.83 (d,  $J = 4.2$  Hz, 2H), 3.73 (dd,  $J = 6.0, 10.0$  Hz, 1H), 2.11 (s, 3H), 1.17 (d,  $J = 6.4$  Hz, 3H), 1.15 (d,  $J = 6.0$  Hz, 3H), 1.04 (m, 3H), 1.05 (m, 18 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 103.5, 83.3, 81.7, 73.9, 70.1, 65.2, 59.0, 23.6, 21.7, 21.1, 18.2, 12.1; HRMS (ESI) Calcd. for  $\text{C}_{20}\text{H}_{40}\text{NaO}_6\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 427.2492; found: 427.2490.

**4ac** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +58.0$  (c 0.1 in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.27 (dd,  $J = 2.4, 6.8$  Hz, 1H), 5.22 (d,  $J = 4.0$  Hz, 1H), 4.09 (m, 1H), 4.00-3.94 (m, 2H), 3.84-3.80 (m, 2H), 3.42 (s, 3H), 2.10 (s, 3H), 1.25 (d,  $J = 6.4$  Hz, 3H), 1.20 (d,  $J = 6.4$  Hz, 3H), 1.09 (m, 3H), 1.07 (s, 18H); HRMS (ESI) Calcd. for  $\text{C}_{20}\text{H}_{40}\text{NaO}_6\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 427.2492; found: 427.2489.

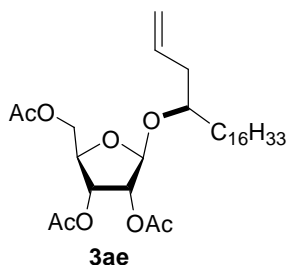
**Benzyl 2,3-di-*O*-benzyl-5-*O*-triisopropylsilyl- $\alpha$ -D-ribofuranoside (4ad).**



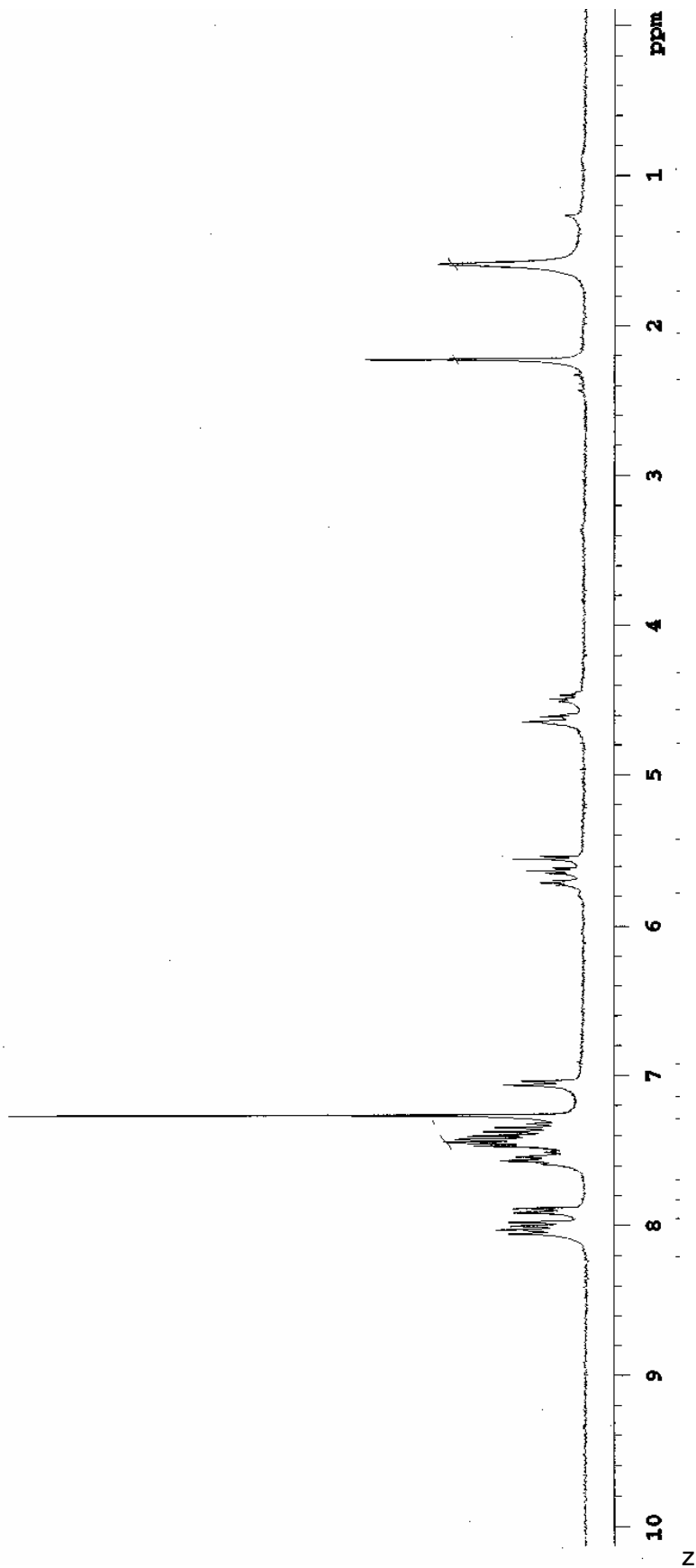
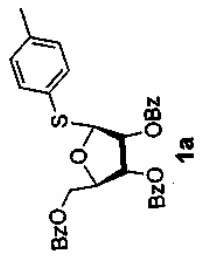
**4ad** ( $\alpha$  isomer):  $[\alpha]_D^{20} = +71.5$  (c 0.4 in  $\text{CHCl}_3$ ); IR (film) 2941, 1651, 1117  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.25 (m, 15H), 5.01 (d,  $J = 4.2$  Hz, 1H), 4.88 (d,  $J = 12.9$  Hz, 1H), 4.78-4.67 (m, 3H), 4.60 (m, 2H), 4.20 (m, 1H), 3.97 (dd,  $J = 2.7, 6.6$  Hz, 1H), 3.77 (dd,  $J = 4.2, 6.6$  Hz, 1H), 3.61 (m, 2H), 0.97 (m, 3H), 0.96 (s, 18H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 138.6, 138.2, 128.5, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 99.7, 84.1, 78.2, 75.5, 72.5, 72.5, 68.9, 64.0, 18.1, 12.1; HRMS (ESI) Calcd. for  $\text{C}_{35}\text{H}_{48}\text{NaO}_5\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 599.3169; found: 599.3179.

**3ad** ( $\beta$  isomer):  $[\alpha]_D^{20} = -3.1$  (c 0.3 in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (m, 15H), 5.22 (s, 1H), 4.73 (d,  $J = 15.9$  Hz, 1H), 4.62 (d,  $J = 6.9$  Hz, 1H), 4.54 (m, 2H), 4.54 (m, 2H), 4.80 (d,  $J = 16.8$  Hz, 1H), 4.24 (t,  $J = 2.4$  Hz, 1H), 4.18 (t,  $J = 5.1$  Hz, 1H), 3.94 (m, 2H), 3.82 (m, 2H), 1.05 (m, 3H), 1.06 (s, 18H); HRMS (ESI) Calcd. for  $\text{C}_{35}\text{H}_{48}\text{NaO}_5\text{Si}$  ( $\text{M}+\text{Na}$ ) $^+$ : 599.3169; found: 599.3170.

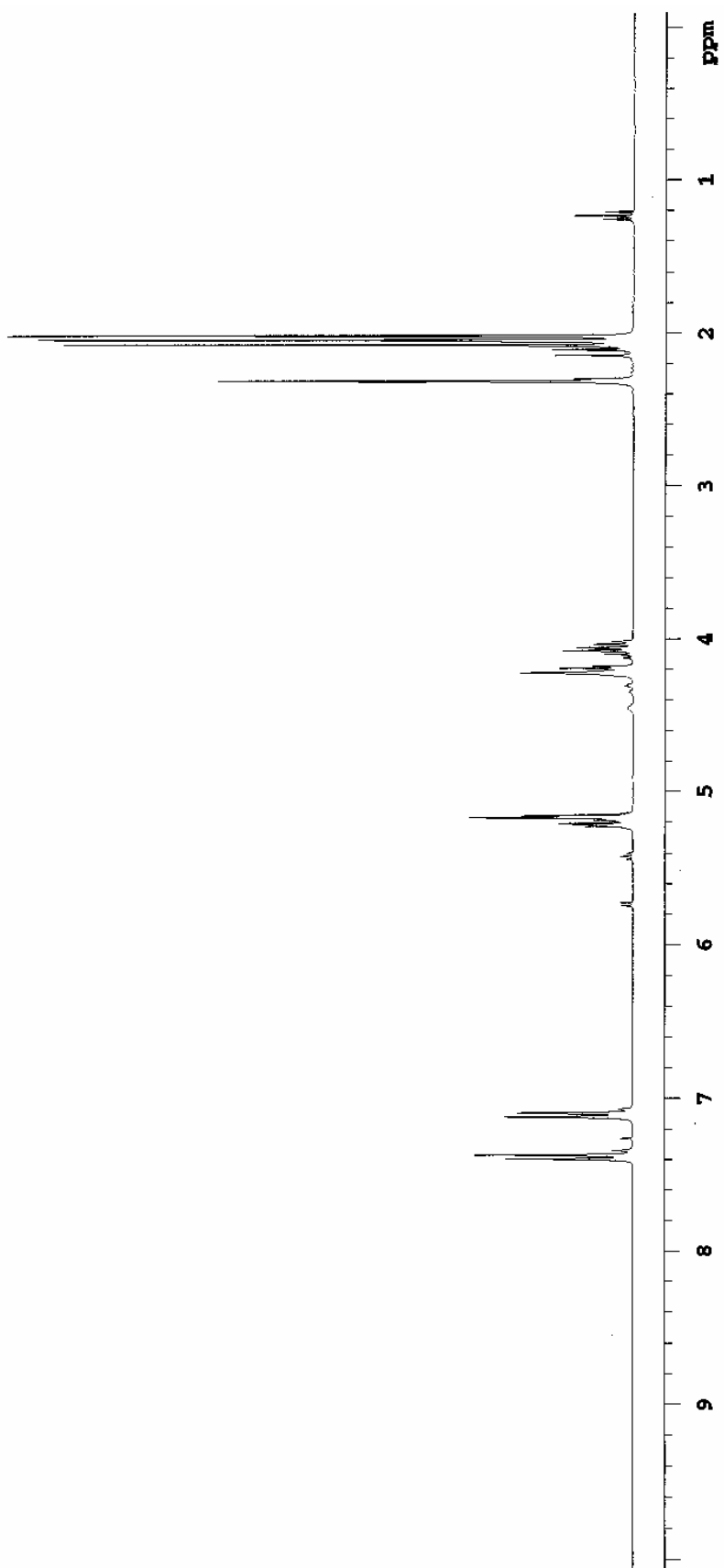
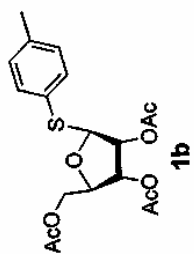
**4-(*R*)-(2,3,5-tri-*O*-acetyl- $\beta$ -D-ribofuranosyl)-icos-1-ene (3ae).**

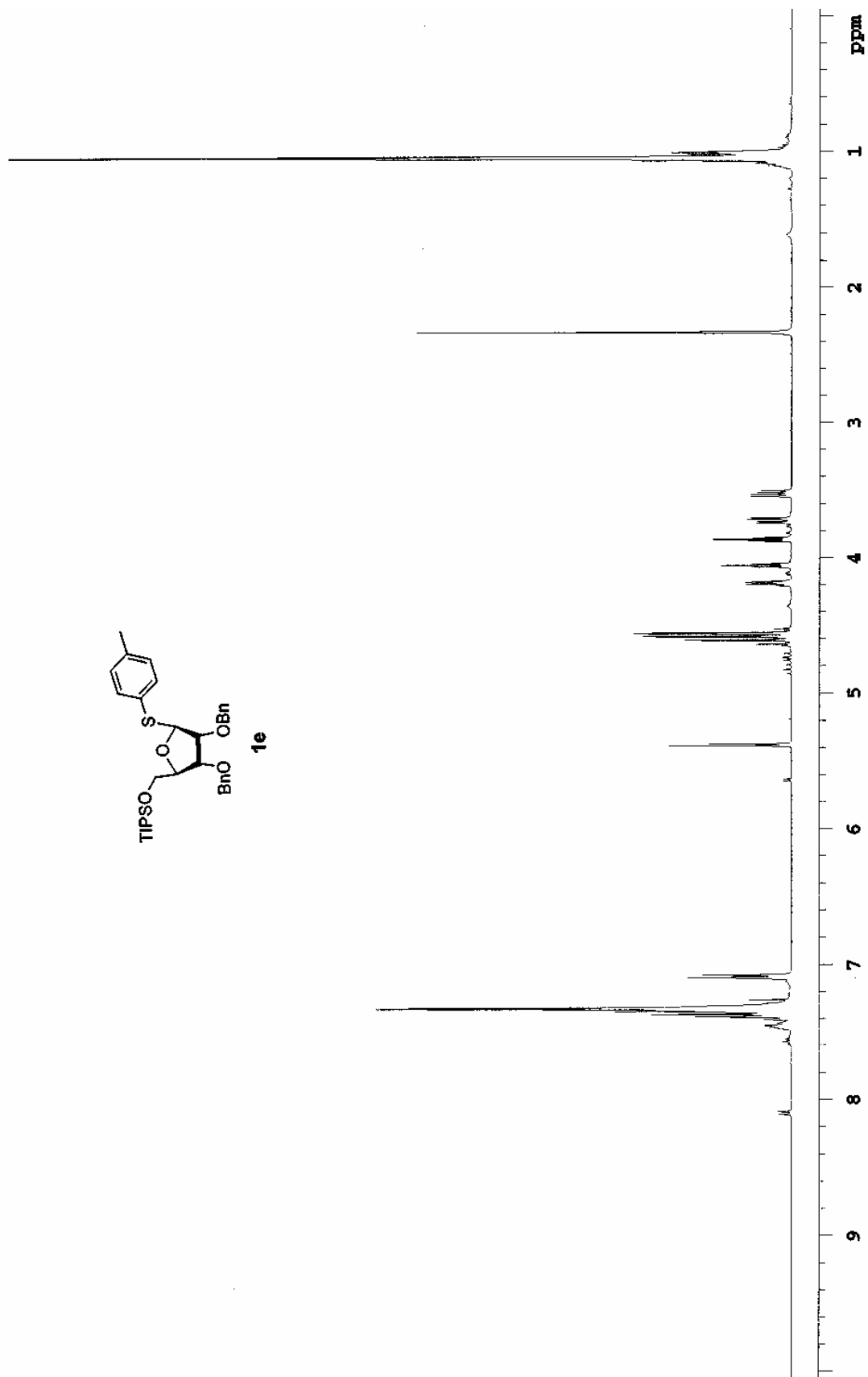
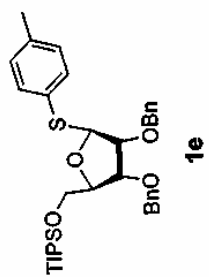


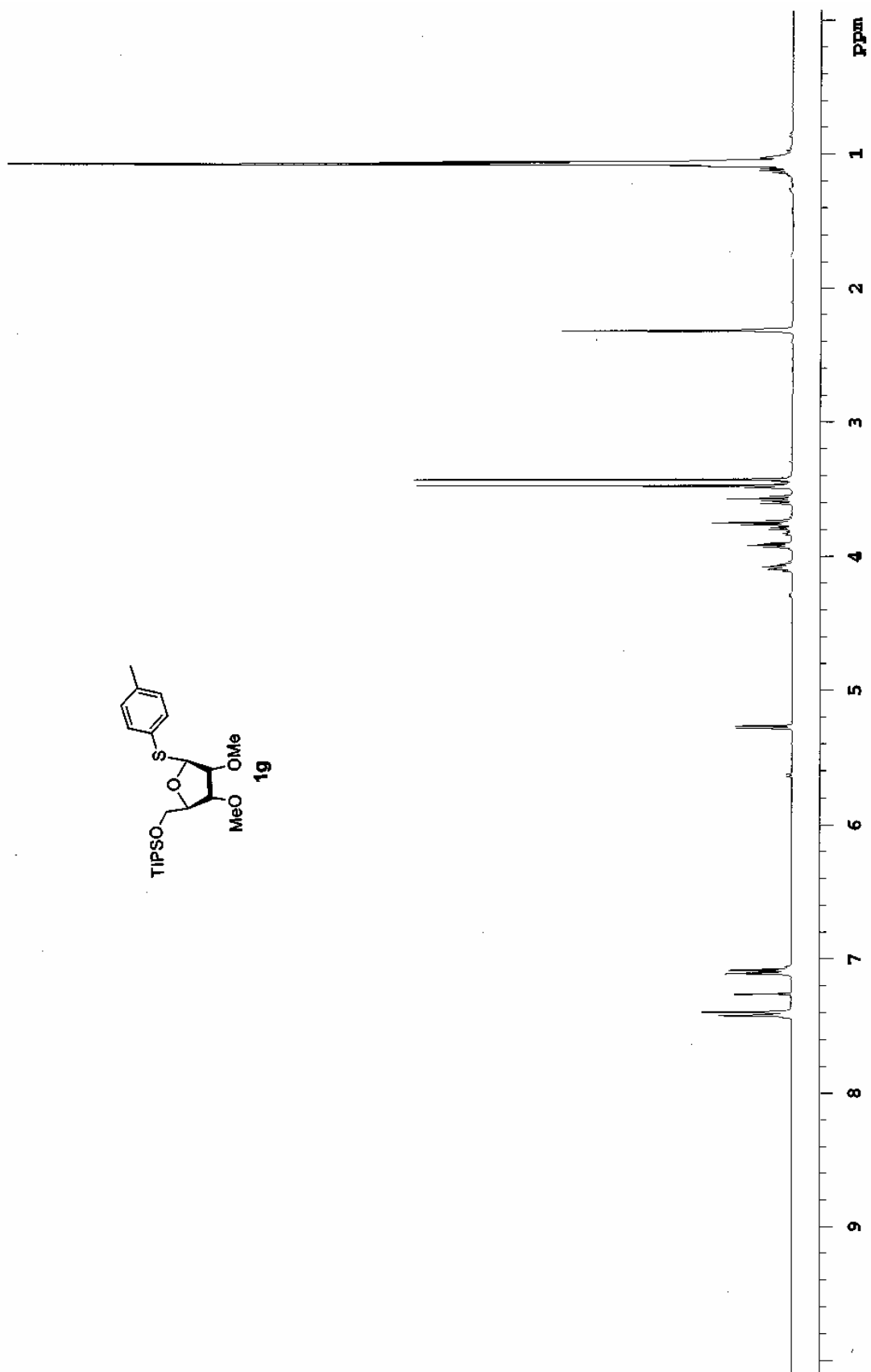
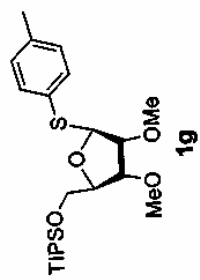
**3ae** ( $\beta$  isomer):  $[\alpha]_D^{20} = -5.0$  (c 0.1 in  $\text{CHCl}_3$ ); IR (film) 2923, 1751, 1231  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.76 (m, 1H), 5.27 (dd,  $J = 4.8, 6.4$  Hz, 1H), 5.16 (d,  $J = 4.4$  Hz, 1H), 5.08 (s, 1H), 5.05-5.01 (m, 2H), 4.31-4.22 (m, 2H), 4.12 (dd,  $J = 6.0, 11.2$  Hz, 1H), 3.61 (t,  $J = 6.0$  Hz, 1H), 2.86 (m, 2H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.42 (m, 2H), 1.23 (s, 28H), 0.86 (t,  $J = 6.8$  Hz, 3H); HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{54}\text{NaO}_8$  ( $\text{M}+\text{Na}$ ) $^+$ : 577.3716; found: 577.3702.

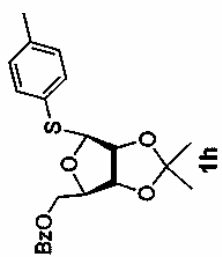


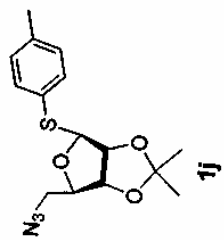












1.510  
1.343  
2.336

