Supporting Information

A novel cobalt (0) alkyne complex assisted “capture and release”
strategy for oligosaccharide rapid assembly

Yan-Bo Liu, Wang Yao, Shuai Meng, Xiang-Bao Meng, Zhong-Jun Li and Qing-Hua Lou
The State Key Laboratory of Natural and Biomimetic Drugs of Peking University school of
pharmaceutical sciences, Beijing 100191, People’s Republic of China
To whom correspondence should be addressed. E-mail: zjli@bjmu.edu.cn

Contents

1. General methods. .......................................................... S2

2. Supplementary experiments ............................................ S3

3. Experimental procedures ................................................ S4

4. NMR Chart. .................................................................. S15

5. References. ................................................................. S32
1. General methods.

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane was distilled over calcium hydride. Analytical TLC was performed on silica gel 60 F254 precoated on glass plates, with detection under UV (254 nm) and/or by staining with 5% concentrated sulfuric acid in EtOH. Column chromatography was performed employing silica gel (200–300 mesh). $^1$H NMR and $^{13}$C NMR spectra were recorded on Advance spectrometers. Chemical shifts (in ppm) were referenced with tetramethylsilane (δ = 0 ppm) for $^1$H NMR and CDCl$_3$ (δ = 77.00 ppm) for $^{13}$C NMR in deuterated chloroform. Mass spectra were measured using an autoflex MALDI-TOF with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix. High resolution mass spectrometry was performed on an FT-ICR mass spectrometer.

**General procedures of glycosylations**

The acceptor, donor and 4 Å molecular sieves (0.25 g per 1.0 mmol acceptor) were dissolved in dry DCM (1.0 mL per 30 mg of donor) under an N$_2$ atmosphere at 0 °C. A catalytic amount of TMSOTf was then added slowly to the solution. The reaction mixture was stirred at ambient temperature for 30 min until TLC showed that the entire acceptor was converted to product. After the glycosylation was complete, the solution was neutralized with triethylamine and the molecular sieves were filtered through Celite.

**General procedure of 2-O-Ac deprotection**

The substrate was dissolved in MeOH (5 mL per 0.15 mmol) and a catalytic amount of MeONa was added. The pH value was adjusted to 9-10 and the mixture was stirred for 30 min at ambient temperature until TLC showed that the reaction was complete. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration and concentration in vacuo, the mixture was dissolved in dry toluene and concentrated in vacuo three times to remove residual water.

**General procedure of cobalt-alkyne complexation**

To a solution of substrate in dry DCM was added Co$_2$(CO)$_8$ under an Ar atmosphere at room temperature. The mixture was stirred for 15 min until TLC showed that the reaction was complete. After 20 min of constant oxygen agitation, the remainder Co$_2$(CO)$_8$ was oxidated and the solution was filtrated through celite and concentrated in vacuo to give crude product of cobalt-alkyne complex.

**General procedure of loading step**

A solution of cobalt-alkyne complex in anhydrous 1,4-dioxane (5 ml per 200 mg resin) was concussed with ultrasonic under constant Argon agitation for 20 min. Polystyrenediphenylphosphine (1.6 mmol/g) was suspended in solution at ambient temperature under an Ar atmosphere for 20 min until the resin was completely swelled. The mixture was heated to 85°C and vibrated in a shaking water bath for 1 h until the liquid phase became colorless. The loaded resin was filtered out and dried in vacuum to give loaded resin as dark purple beads.

**General procedure of releasing step**

The loaded resin was suspended in DMF (5 ml per 300 mg resin) for 20 min at room temperature until the resin was completely swelled. CAN was added and the reaction mixture was heated to
85°C and vibrated in a shaking water bath for 15min until the resin became golden yellow and TLC showed the release of product. After filtration and concentration in vacuo, the remainder was diluted in DCM and washed with 1mol/L HCl and brine then dried over Na₂SO₄. The remainder was then concentrated in vacuo and filtrated through a piece of alkaline aluminum oxide to obtain target product.

2. Supplementary experiments.

Scheme S1 Optimization of complexation in solution phase

<table>
<thead>
<tr>
<th>entry</th>
<th>n</th>
<th>solvent</th>
<th>Co₂(CO)₈/equiv.</th>
<th>T/℃</th>
<th>t/min</th>
<th>yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>DCM</td>
<td>1.1</td>
<td>r.t.</td>
<td></td>
<td>88%</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>DCM</td>
<td>1.1</td>
<td>r.t.</td>
<td></td>
<td>58%</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>DCM</td>
<td>1.5</td>
<td>r.t.</td>
<td>15</td>
<td>76%</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>DCM</td>
<td>2</td>
<td>r.t.</td>
<td></td>
<td>90%</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>MeCN</td>
<td>1.1</td>
<td>r.t.</td>
<td></td>
<td>26%</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>MeCN</td>
<td>1.1</td>
<td>75</td>
<td></td>
<td>25%</td>
</tr>
</tbody>
</table>

Notes: a:isolated yield r.t.=room temperature

Scheme S2 Optimization of deacetylation-glycosylation

<table>
<thead>
<tr>
<th>entry</th>
<th>n</th>
<th>LA</th>
<th>Equiv.</th>
<th>T/℃</th>
<th>yield a</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>TMSOTf</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>19%</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>TMSOTf</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>90%</td>
<td>B</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>TMSOTf</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>80%</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>TMSOTf</td>
<td>0.3</td>
<td>0°C→r.t.</td>
<td>80%</td>
<td>C</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>TMSOTf</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>88%</td>
<td>D</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Sc(OTf)₃</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>97%</td>
<td>B</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>Sc(OTf)₃</td>
<td>0.3</td>
<td>0°C→r.t.</td>
<td>100%</td>
<td>B</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>Sc(OTf)₃</td>
<td>0.1</td>
<td>0°C</td>
<td>77%</td>
<td>B</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>Sc(OTf)₃</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>36%</td>
<td>C</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>Sc(OTf)₃</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>63%</td>
<td>D</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>Sc(OTf)₃</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>-</td>
<td>C</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>In(OTf)₃</td>
<td>0.1</td>
<td>0°C→r.t.</td>
<td>100%</td>
<td>B</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>BF₃·Et₂O</td>
<td>2</td>
<td>0°C→r.t.</td>
<td>63%</td>
<td>C</td>
</tr>
</tbody>
</table>


a:isolated yield r.t.=room temperature
3. Experimental procedures.

1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose (S-1)

To a stirred acetic anhydride (80ml) at 0°C was added perchloric acid (0.8ml) drop wise and the solution became light yellow. α-D-Manose (20g) as dry powder was added in portions during 1h. The reaction was complete after 2h and the solution was poured into 0.3L ice-water in a 1L beaker. The mixture was stirred vigorously for 10min and then 300mL CH₂Cl₂ was added. The organic layer was separated, washed by saturated NaHCO₃ solution three times and brine and then dried over Na₂SO₄. The filtrate was evaporated and 44.6g light yellow syrup was obtained to give 1,2,3,4,6-Penta-O-acetyl-a-D-mannopyranose (44.6g, 114.9 mmol).

To a soln. of 6 or 7 (2.43 g, 6.23 mmol) in dry CH₂Cl₂

The crude product was mixed with Ac₂O (16mL, 157 mmol) and the mixture was cooled to 0 C. HBr (33% in acetic acid, 160 mL) was added to the solution, which was stirred at room temperature for 4 h. The mixture was then diluted with 200ml DCM. The organic phase was washed with brine and saturated NaHCO₃ three times and then dried over Na₂SO₄. After
filtration and concentration, the crude mixture was dried under high vacuum and the crude product (37.1g) was obtained as light yellow oil. [1]

2,3,4,6-Tetra-O-acetyl-a-D-mannopyranosyl bromide (37.1g, 90.1mmol) was dissolved in 120ml dry pyridine and 40ml dry MeOH and the mixture was stirred at room temperature for 12h. The reaction mixture was evaporated in vacuo, diluted with DCM and washed with brine. After dried over Na$_2$SO$_4$, the residual was filtrated and was purified on silica gel with petroleum ether/ethyl acetate 3:1 to give the product 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose S-1 (18.2g, 50.2mmol) in 45% yield for 3 steps as white solid.

$^1$HNMR (400MHz, CDCl$_3$), $\delta$ 5.50(s,1H,H-1), 5.30(t,1H,H-4), 5.15(dd,1H,H-3), 4.62(s,1H,H-2), 4.24(dd,1H,H-6), 4.15(d,1H,H-6), 3.69(dt,1H,H-5), 2.13(s,3H,Ac), 2.08(s,3H,Ac), 2.06(s,3H,Ac), 1.75(s,3H,C-CH$_3$)

$^{13}$CNMR (400MHz, CDCl$_3$), $\delta$ 170.6, 170.3, 169.4, 124.5, 97.4, 76.5, 71.3, 70.6, 65.4, 62.3, 49.9, 24.4, 20.7, 20.7, 20.6

1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose S-1

To a solution of 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose S-1 (4g, 11.0mmol) in MeOH (50ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. A small amount of cation exchange resin was added to neutralize the reaction mixture to pH=8. After filtration and concentration in vacuo, the mixture was dried under vaccum to give 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose.

1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-benzyl-β-D-mannopyranose S-2

To a solution of the crude product (2.6g, 11.0mmol) in DMF (100ml) at 0°C was added NaH (60%, 2.0g, 49.7mmol) in portions, the mixture was stirred in ice bath for 1h. BnBr (4.9ml, 41.4mmol) was added drop wise and the reaction mixture was stirred at 0°C for 2h. The mixture was quenched with MeOH, concentrated in vacuo and washed with 1mol/L HCl, saturated NaHCO$_3$ and brine. After dried over Na$_2$SO$_4$, the mixture was purified on silica gel (petroleum ether/ethyl acetate 4:1) to give 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-benzyl-β-D-mannopyranose S-2 (3.82g, 6.7mmol, 61% for 2 steps) as white solid. [2]

2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose S-3

A solution of 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-benzyl-β-D-mannopyranose S-2 (3.82 g, 6.75 mmol) in acetic acid (54 ml) and water (13.5 ml) was stirred at r.t. for 4h whereupon TLC analysis (petroleum ether/ethyl acetate 2:1) indicated the complete consumption of the starting material and formation of the products. The mixture was diluted with DCM (70ml) and the organic phase was washed with saturated NaHCO3 three times and brine. After dried over
Na₂SO₄, the mixture was purified on silica gel (petroleum ether/ethyl acetate 3:1) to give 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose S-3 (2.38g, 4.83mmol, 62%) as colorless syrup.

**1H NMR** (400MHz, CDCl₃), δ 7.34-7.14(17H,Ar), 5.39(s,1H,H-2), 5.24(s,1H,H-1) 4.86(d,1H,ArCH₂), 4.71(d,1H,ArCH₂), 4.63(d,1H,ArCH₂), 4.55-4.45(m,3H,ArCH₂), 4.05(m,2H), δ 3.80-3.70(m,3H), δ 2.15(s,3H,Ac)

**13C NMR** (400MHz, CDCl₃), δ 170.5, 138.3, 137.9, 137.9, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 92.6, 77.6, 75.2, 74.5, 73.5, 71.8, 71.3, 69.2, 68.9, 21.2

2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate (9)

To a solution of 2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranose S-3 (695mg, 1.41mmol) in dry CH₂Cl₂ (10 mL) at 0 °C was added CNCCl₃ (0.42mL, 4.22mmol) and a catalytic amount of DBU (21μl, 0.14mmol). After 2 h the reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate 1:0→4:1) to obtain 2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate 9 (872mg, 1.36mmol, 97%) as a colorless syrup.

**4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside (3)**

2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate 9 (262mg, 0.41mmol), pent-4-yn-1-ol (41μl, 0.447mmol) and 4 Å molecular sieves (200mg) were dissolved in dry DCM (5ml) under an N₂ atmosphere at 0 °C. The mixture was stirred for 10min. To the solution was added TMSOTf (7μl, 0.04mmol) and the reaction mixture was stirred at room temperature for 30min until TLC showed (petroleum ether/ethyl acetate 6:1x2) that the entire donor was converted to product. The solution was neutralized with triethylamine and the molecular sieves were filtered through Celite. The mixture was purified by chromatography (petroleum ether/ethyl acetate 12:1) to give product 4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside 3 (222mg, 0.39mmol, 98%) as pale yellow syrup.

**1H NMR** (400MHz, CDCl₃), δ 7.36-7.23(m,13H,Ar), 7.18-7.15(m,2H,Ar), 5.36(d,1H,H-1), 4.85(d,1H,ArCH₂), 4.83(s,1H,H-2), 4.70(d,1H,ArCH₂), 4.68(d,1H,ArCH₂), 4.56-4.63(m,3H, ArCH₂), 3.97(dd,1H,H-3), 3.81-3.74(m,3H), 3.71-3.69(d,1H,H-5), 3.51(dt,1H,O-CH₂-C), 2.26(dt,2H,C-CH₂-C), 2.14(s,3H,Ac), 1.92(t,1H,C-C-H), 1.78(m,2H, C-CH₂-C)

**13C NMR** (400MHz, CDCl₃), δ 170.4, 138.3, 138.1, 137.8, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 97.7, 83.3, 78.1, 75.1, 74.2, 73.3, 71.7, 71.3, 68.8, 68.7,68.5, 66.0, 28.1, 21.0, 15.2

To a solution of 4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside 3 (184mg, 0.33mmol) in MeOH (5ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration and concentration in vacuo, the mixture was purified by chromatography (petroleum ether/ethyl acetate 3:1) to give product 4-pentyn-1-yl 3,4,6-tri-O-benzyl-D-mannopyranoside S-4 (150g, 0.29mmol, 88%) as pale yellow syrup.

\[ ^1 \text{HNMR (400MHz, CDCl}_3), \delta \text{7.37-7.26(m,13H,Ar), 7.18-7.16(m,2H,Ar), 4.90(d,1H,H-1),} \]
\[ \text{4.82(d,1H,ArCH}_2, \text{4.72-4.63(m,3H,ArCH}_2, \text{4.54-4.48(m,2H,ArCH}_2,} \]
\[ \text{4.02(d,1H), 3.86-3.73(m,5H), 3.69(d,1H), 3.51(dt,1H,O-CH}_2-C), \text{2.51(s,1H,OH),} \]
\[ \text{2.25(dt,2H,C-CH}_2-C-CH), \text{1.91(t,1H,C-C-H),} \text{1.76(m,2H, C-CH}_2-C) \]

\[ ^{13} \text{CNMR (400MHz, CDCl}_3), \delta \text{138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7,} \]
\[ \text{127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2} \]

HRMS(ESI-FT-ICR): m/z calcd 516.2512, M\(^+\), found 539.2410 [M + Na]\(^+\), 555.2149 [M + K]\(^+\).

\[ ^1 \text{HNMR (400MHz, CDCl}_3), \delta \text{138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7,} \]
\[ \text{127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2} \]

\[ ^{13} \text{CNMR (400MHz, CDCl}_3), \delta \text{138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7,} \]
\[ \text{127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2} \]

HRMS(ESI-FT-ICR): m/z calcd 516.2512, M\(^+\), found 539.2410 [M + Na]\(^+\), 555.2149 [M + K]\(^+\).

\[ ^1 \text{HNMR (400MHz, CDCl}_3), \delta \text{138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7,} \]
\[ \text{127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2} \]

HRMS(ESI-FT-ICR): m/z calcd 516.2512, M\(^+\), found 539.2410 [M + Na]\(^+\), 555.2149 [M + K]\(^+\).

\[ ^{13} \text{CNMR (400MHz, CDCl}_3), \delta \text{138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7,} \]
\[ \text{127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2} \]

HRMS(ESI-FT-ICR): m/z calcd 516.2512, M\(^+\), found 539.2410 [M + Na]\(^+\), 555.2149 [M + K]\(^+\).

To a stirred acetic anhydride (40ml) at 0°C was added perchloric acid (0.4ml) drop wise and the solution became light yellow. α-D-Mannose (10g) as dry powder was added in portions during 1h. The reaction was complete after 2h and the solution was poured into 0.3L ice-water in a 1L beaker. The mixture was stirred vigorously for 10min and then 300mL CH\(_2\)Cl\(_2\) was added. The organic layer was separated, washed by saturated NaHCO\(_3\) solution three times and brine and then dried over Na\(_2\)SO\(_4\). The filtrate was purified by chromatography (petroleum ether/ethyl acetate 2:1) and light yellow syrup was obtained to give 1,2,3,4,6-Penta-O-acetyl-α-D-mannopyranose S-5 (20.3g, 52.0 mmol, 94%).

\[ ^1 \text{HNMR (400MHz, CDCl}_3), \delta \text{138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7,} \]
\[ \text{127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2} \]

HRMS(ESI-FT-ICR): m/z calcd 516.2512, M\(^+\), found 539.2410 [M + Na]\(^+\), 555.2149 [M + K]\(^+\).

β-D-Mannopyranoside, 4-methylphenyl 1-thio-, 2,3,4,6-tetraacetate (S-6)

To a solution of 1,2,3,4,6-Penta-O-acetyl-α-D-mannopyranose S-5 (20.3g, 52.0mmol) and HSTol (7.1g, 57.3mmol) in dry DCM (100ml) at room temperature was added BF\(_3\)•Et\(_2\)O (19.7ml, 156.3mmol). The reaction mixture was stirred for 30min until TLC showed (petroleum
ether/ethyl acetate 3:1) the total conversion of reactant. The mixture was washed with saturated NaHCO₃ three times and brine. After dried over Na₂SO₄, the mixture was purified on silica gel (petroleum ether/ethyl acetate 3:1) to give β-D-Glucopyranoside, 4-methylphenyl 1-thio-, 2,3,4, 6-tetraacetate S-6 (21.3g, 46.9mmol, 90%) as pale yellow syrup after concentration. [3]

α-D-Mannopyranoside, 4-methylphenyl 1-thio (S-7)

To a solution of β-D-Glucopyranoside, 4-methylphenyl 1-thio-, 2,3,4,6-tetraacetate S-6 (21.3g, 46.9mmol) in MeOH (60ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration, the mixture was concentrated in vacuo to give product α-D-Mannopyranoside, 4-methylphenyl 1-thio S-7 (13.4g, 46.9mmol, 100%) as white solid.

1HNMR(400MHz,MeOD), δ 7.38(d,2H, Ar), 7.11(d,2H, Ar), 5.34(d,1H, H-1), 4.06-4.02(m,2H), 3.82-3.68(m,4H), 2.28(s,3H,Ac)

13CNMR(400MHz, MeOD), δ 138.6, 133.2, 131.8, 130.5, 90.5, 75.3, 73.5, 72.9, 68.4, 62.3, 48.8, 20.9

α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-O-[(1,1-dimethylethyl)dimethylsilyl]-1-thio (S-8)

To a solution of α-D-Mannopyranoside, 4-methylphenyl 1-thio S-7 (3.0g, 10.48mmol) in dry pyridine (60ml) was added TBDMSICl (6.32g, 41.94mmol) and catalytic amount of DMAP. The reaction mixture was stirred at 80°C for 10h. The mixture was concentrated in vacuo, diluted with DCM and then washed with 1mol/L HCl, saturated NaHCO₃ and brine. After dried over Na₂SO₄, the mixture was purified on silica gel (petroleum ether/ethyl acetate 10:1) to give α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-O-[(1,1-dimethylethyl)dimethylsilyl]-1-thio S-8 (3.53g, 6.86mmol, 67%) as colorless syrup.

1HNMR(400MHz,CDCl₃), δ 7.43(d,2H, Ar), 7.18(d,2H, Ar), 5.57(d,1H, H-1), 4.19(dt,1H,H-5), 4.10(d,1H,H-2), 3.96-3.89(m,3H,H-4,H-6), 3.86(dd,1H,H-3), 2.95(s,1H,OH), 2.85(s,1H,OH), 2.39(s,3H,PhMe), 1.00(s,9H,tBu), 0.97(s,9H,tBu), 0.25(s,3H,Me), 0.24(s,3H,Me), 0.15(s,6H,Me)

13CNMR(400MHz, CDCl₃), δ 137.5, 131.9, 130.1, 129.7, 87.3, 73.3, 72.5, 71.5, 70.7, 64.8, 25.8, 25.7, 21.0, 18.3, 18.0, -4.4, -4.8, -5.5

β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-1-thio (S-9)
To a solution of the α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-O-[(1,1-dimethylethyl)dimethylsilyl]-1-thio S-8 (3.53g, 6.86mmol) in DMF (100ml) at 0°C was added BnBr (3.3ml, 27.46mmol) drop wise, the mixture was stirred in ice bath for 1h. NaH (60%, 659mg, 16.47mmol) was added in portions, and the reaction mixture was stirred at 0°C for 2h. The mixture was quenched with MeOH, concentrated in vacuo and washed with 1mol/L HCl, saturated NaHCO₃ and brine. After dried over Na₂SO₄, the mixture was concentrated in vacuo and dried under vaccum to give crude product β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-3,6-bis-O-[(1,1-dimethylethyl)dimethylsilyl]-1-thio S-9.

To the solution of crude product (5.31g) in MeOH (50ml) was added catalytic amount of TsOH. The reaction mixture was stirred and refluxed at 75°C for 4h. The mixture was concentrated in vacuo and purified on silica gel (petroleum ether/ethyl acetate 3:1) to give β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-1-thio S-10 (1.43g, 3.06mmol, 45% for 2 steps) as pale yellow syrup.

1HNMR (400MHz, CDCl₃), δ 7.37-7.28(m, 12H, Ar), 7.11(d, 2H, Ar), 5.49(s, 1H, H-1), 4.91(d, 1H, ArCH₂), 4.70(d, 1H, ArCH₂), 4.66(d, 1H, ArCH₂), 4.54(d, 1H, ArCH₂), 4.13(d, 1H, H-5), 4.00(d, 1H, H-6), 3.99(s, 1H, H-2), 3.83(dd, 1H, H-6), 3.81(d, 1H, H-3), 3.75(t, 1H, H-4), 2.32(s, 3H, Ac)

13CNMR (400MHz, CDCl₃), δ 138.1, 138.0, 137.2, 132.5, 129.9, 129.7, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 85.4, 76.4, 74.9, 74.9, 72.4, 72.0, 62.0, 21.0


β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-3,6-bis-O-acetyl-1-thio (S-10)

To the solution of β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-1-thio S-9 (1.25g, 2.68mmol) in pyridine (30ml) at ambient temperature was added acetic anhydride (30ml). The mixture was stirred for 2h until TLC monitored (petroleum ether/ethyl acetate 4:1) the completion of the reaction. The mixture was concentrated in vacuo, washed with 1mol/L HCl, saturated NaHCO₃ and brine then dried over Na₂SO₄. The residual was purified by chromatography (petroleum ether/ethyl acetate 6:1) to obtain β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-3,6-bis-O-acetyl-1-thio S-10 (1.24g, 2.25mmol, 84%) as colorless syrup.

1HNMR (400MHz, CDCl₃), δ 7.37-7.30(m, 12H, Ar), 7.11(d, 2H, Ar), 5.49(d, 1H, H-1), 4.91(d, 1H, ArCH₂), 4.70(d, 1H, ArCH₂), 4.68(d, 1H, ArCH₂), 4.59(d, 1H, ArCH₂), 4.49(d, 1H, ArCH₂), 4.39(m, 1H, H-5), 4.32(d, 2H, H-6), 4.11(dd, 1H, H-2), 3.97(t, 1H, H-4), 2.32(s, 3H, Ac), 2.04(s, 3H, Ac), 1.99(s, 3H, Ac)

13CNMR (400MHz, CDCl₃), δ 170.6, 169.9, 137.8, 137.7, 137.5, 132.3, 129.8, 129.7, 128.4, 128.3, 127.8, 127.8, 127.7, 127.6, 76.4, 74.9, 74.9, 72.4, 72.3, 72.0, 70.5, 63.3, 21.0, 20.9, 20.7


3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose (S-11)
To a solution of β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-3,6-bis-O-acetyl-1-thio S-10 (1.24g, 2.25mmol) in 90% acetone-H2O (30mL) was added NBS (1.6g, 9.01mmol) under dark condition. The reaction mixture was stirred at room temperature for 10h. The mixture was evaporated in vacuo and diluted with DCM (100mL). After washed with saturated Na2SO3, 1mol/L HCl, saturated NaHCO3 and brine, the remainder was dried over Na2SO4 and purified on silica gel (petroleum ether/ethyl acetate 2:1) to give 3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose S-11 (812mg, 1.82mmol, 81%) as colorless syrup.

1HNMR (400MHz, CDCl3), δ 7.36-7.27(m, 10H, Ar), 5.31(dd, 1H, H-3), 5.21(d, 1H, H-1, α/β), 4.70(d, 1H, ArCH2), 4.63(d, 1H, ArCH2), 4.59(d, 1H, ArCH2), 4.55(d, 1H, ArCH2), 4.36(dd, 1H, H-6), 4.23(dd, 1H, H-6), 4.09(m, 1H, H-5), 3.94(t, 1H, H-4), 3.88(dd, 1H, H-2), 2.04(s, 3H, Ac), 1.97(s, 3H, Ac)

13CNMR (400MHz, CDCl3), δ 170.9, 170.1, 137.8, 137.7, 128.3, 128.3, 127.7, 127.7, 127.6, 127.6, 93.6, 92.2, 76.1, 74.6, 73.4, 73.3, 72.8, 69.7, 63.3, 20.9, 20.7


O

\[\text{3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranosyl trichloroacetimidate (S-12)}\]

To a solution of 3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose S-11 (812mg, 1.83mmol) in dry CH2Cl2 (10mL) at 0°C was added CNCCl3 (0.55mL, 5.48mmol) and a catalytic amount of DBU (27μl, 0.18mmol). After 2h the reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate 1:0→4:1) to obtain 2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate S-12 (1.035g, 1.76mmol, 96%) as a colorless syrup.

\[\text{4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside (S-13)}\]

2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate S-12 (1.035g, 1.76mmol), pent-4-yn-1-ol (187μl, 2.01mmol) and 4 Å molecular sieves (400mg) were dissolved in dry DCM (10mL) under an N2 atmosphere at 0°C. The mixture was stirred for 10min. To the solution was added TMSOTf (33μl, 0.18mmol) and the reaction mixture was stirred at room temperature for 30min until TLC showed (petroleum ether/ethyl acetate 3:1) that the entire donor was converted to product. The solution was neutralized with triethylamine and the molecular sieves were filtered through Celite. The mixture was purified by chromatography (petroleum ether/ethyl acetate 10:1) to give product 4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside S-13 (898mg, 1.76mmol, 100%) as colorless syrup.

1HNMR (400MHz, CDCl3), δ 7.35-7.25(m, 10H, Ar), 5.23(dd, 1H, H-3), 4.83(d, 1H, H-1), 4.69(d, 1H, ArCH2), 4.66(d, 1H, ArCH2), 4.57(d, 1H, ArCH2), 4.57(d, 1H, ArCH2), 4.34(dd, 1H, H-6), 4.29(dd, 1H, H-6), 3.93(t, 1H, H-4), 3.89(dt, 1H, H-5), 3.86(dd, 1H, H-6), 3.80(dt, 1H, O-CH2-C), 3.50(dt, 1H, O-CH2-C), 2.27(dt, 2H, C-CH2-C), 2.07(s, 3H, Ac), 1.98(s, 3H, Ac), 1.93(t, 1H, C-C-H), 1.78(m, 2H, C-CH2-C)
To a solution of 4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside S-13 (898mg, 1.76mmol) in MeOH (30ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration and concentration in vacuo, the mixture was purified by chromatography (petroleum ether/ethyl acetate 3:1) to give product 4-pentyn-1-yl 2,4-bis-O-benzyl-D-mannopyranoside 11 (605mg, 1.41mmol, 81%) as colorless syrup.


1H NMR(400MHz, CDCl₃), δ 7.40-7.27(m,10H,Ar), 4.90(d,1H,ArCH₂), 4.85(s,1H,H-1), 4.74-4.59(m,3H,ArCH₂), 3.99(dd,1H,H-6), 3.85(dd,1H,H-6), 3.80(dd,1H,H-6), 3.78(dd,1H,OH), 2.25(dt,2H,CH₂-CH₂), 1.95(t,1H,CH₃), 1.94(d,1H,OH), 1.75(m,2H,CH₂-C)

13CNMR(400MHz, CDCl₃), δ 138.33, 137.7, 128.6, 128.5, 128.1, 128.0, 127.8, 97.2, 83.4, 78.4, 76.4, 74.9, 71.3, 71.3, 68.8, 65.7, 62.2, 28.1, 15.1

144mg of compound 6 (0.145mmol, 81%) was obtained as a colorless syrup by the capture-release separation from the glycosylation between donor 9 (228mg, 0.358mmol) and acceptor 3 (100mg, 0.179mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation, loading step and releasing step.

1H NMR(400MHz, CDCl₃), δ 7.35-7.14(m, 30H,Ar), 5.54(d,1H,H-1), 5.07(d,1H,H-1), 4.87-4.83(m,3H), 4.68-4.64(m,5H), 4.56(d,1H,ArCH₂), 4.51(d,1H,ArCH₂), 4.46(d,1H,ArCH₂), 4.40(d,1H,ArCH₂), 3.99-3.94(m,3H), 3.88(dd,1H), 3.84(t,2H), 3.79-3.68(m,7H), 3.35(dt,1H,OH-CH₂-C), 2.19(dt,2H,CH₂-CH₂), 2.12(s,3H,Ac), 1.89(t,1H,CH₃), 1.70(m,2H,CH₂-C)

13CNMR(400MHz, CDCl₃), δ 170.1, 138.4, 138.4, 138.3, 138.3, 138.1, 137.9, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7 127.7 127.6 127.5 127.5 127.4 127.3, 99.5, 98.6, 83.5, 79.6, 78.1, 77.2, 75.1, 75.0, 74.8, 74.5, 74.3, 73.3, 73.2, 72.0, 71.8, 71.8, 71.7, 69.2, 69.0, 68.7, 65.8, 28.2, 21.1,
15.2


1. MeONa, MeOH, r.t.
2. donor 9, 0.1equiv. TMSOTf,
4AMS, DCM, 0°C⇌r.t.
3. 1.5equiv. Co₂(CO)₉, DCM, r.t.
4. 4equiv. resin-PPPh₃, 1,4-dioxane,
85°C, shaking
5. 8equiv. CAN, DMF, 85°C, shaking

4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (7)

145mg of compound 7 (0.102mmol, 70%) was obtained as a colorless syrup by the capture-release separation from the glycosylation between donor 9 (185mg, 0.290mmol) and acceptor 6 (144mg, 0.145mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation, loading step and releasing step.

1HNMR(400MHz,CDCl₃), δ 7.34-7.13(m,45H,Ar), 5.54(s,1H,Me), 5.18(s,1H,Me), 5.05(s,1H,Me), 4.91(s,1H), 4.85-4.79(m,3H), 4.69-4.65(m,3H), 4.61(s,1H), 4.58(s,1H), 4.56(d,3H), 4.53(s,2H), 4.49(dd,2H), 4.45-4.41(m,2H), 4.31(dd,1H), 4.10(s,1H), 3.99(t,1H), 3.95(s,1H), 3.93(d,1H), 3.90(d,3H), 3.84(dd,1H), 3.80-3.76(m,3H), 3.72(m,3H), 3.70-3.65(m,3H), 3.53(d,1H), 3.31(dt,1H,O-CH₂-C), 2.15(dt,2H,C-CH₂-C), 2.12(s,3H,Ac), 1.87(t,1H,C-CH₂-C), 1.69(m,2H, C-CH₂-C)

13CNMR(400MHz,CDCl₃), δ 170.0, 138.5, 138.5, 138.3, 138.2, 138.1, 137.9, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.3, 100.5, 99.3, 98.6, 83.5, 79.4, 79.2, 78.0, 77.2, 75.0, 75.0, 74.9, 74.7, 74.7, 74.1, 73.2, 73.2, 72.1, 72.0, 71.8, 71.8, 69.5, 69.2, 68.7, 68.6, 65.8, 28.2, 21.1, 15.2


4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (8)

148mg of compound 8 (0.080mmol, 78%) was obtained as a colorless syrup by the capture-release separation from the glycosylation between donor 9 (130mg, 0.204mmol) and acceptor 7 (145mg, 0.102mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation,
loading step and releasing step.

1H NMR (400 MHz, CDCl₃), δ 7.35-7.03 (m, 60H, Ar), 5.55 (s, 1H, H-1), 5.21 (s, 1H, H-1), 5.18 (s, 1H, H-1), 5.04 (s, 1H, H-1), 4.93 (s, 1H), 4.86-4.79 (m, 4H), 4.76 (d, 2H), 4.68-4.65 (m, 2H), 4.64 (d, 2H), 4.59 (d, 2H), 4.56 (s, 2H), 4.55 (s, 2H), 4.52 (d, 2H), 4.50 (d, 1H), 4.45 (d, 1H), 4.43 (d, 2H), 4.38 (d, 2H), 4.32 (d, 2H), 4.16 (d, 1H), 4.09 (s, 2H), 3.99 (m, 1H), 3.94 (s, 2H), 3.92 (s, 1H), 3.89 (d, 2H), 3.85 (d, 1H), 3.80 (d, 1H), 3.74 (m, 4H), 3.72 (s, 1H), 3.69 (d, 2H), 3.65 (d, 2H), 3.60 (d, 2H), 3.46 (d, 1H), 3.29 (dt, 1H, O-CH₂-C), 2.15 (dt, 2H, C-CH₂-C-CH), 2.12 (s, 3H, Ac), 1.87 (t, 1H, C-C-H), 1.67 (m, 2H, C-CH₂-C).

13CNMR (400 MHz, CDCl₃), δ 170.0, 138.6, 138.5, 138.4, 138.4, 138.3, 138.2, 138.1, 138.0, 128.8, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 101.1, 100.7, 99.3, 98.7, 83.6, 79.4, 79.3, 79.2, 79.2, 78.2, 77.2, 75.7, 75.4, 75.1, 75.0, 74.9, 74.8, 74.6, 74.2, 73.3, 73.2, 73.1, 72.3, 72.2, 72.1, 71.9, 71.8, 71.7, 69.6, 69.4, 69.3, 68.6, 65.8, 28.3, 21.1, 15.2


183mg of compound 10 (0.060mmol, 75%) was obtained as a pale yellow syrup by the capture-release separation from the glycosylation between donor 9 (0.102mg, 0.160mmol) and acceptor 8 (0.148mg, 0.080mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation, loading step and releasing step.

1H NMR (400 MHz, CDCl₃), δ 7.36-6.96 (m, 75H, Ar), 5.56 (s, 1H, H-1), 5.25 (s, 2H, H-1), 5.16 (s, 1H, H-1), 5.05 (s, 1H, H-1), 4.96 (s, 1H), 4.88 (d, 1H), 4.83 (d, 2H), 4.76 (t, 2H), 4.68 (d, 1H), 4.65 (s, 1H), 4.62 (s, 2H), 4.59 (s, 3H), 4.55 (s, 4H), 4.51 (s, 3H), 4.49 (s, 1H), 4.46 (s, 1H), 4.43 (s, 2H), 4.40 (s, 2H), 4.38 (s, 2H), 4.35 (s, 1H), 4.22 (d, 1H), 4.17 (s, 1H), 4.14 (s, 1H), 4.11 (s, 2H), 4.08 (s, 1H), 4.00 (s, 1H), 3.96 (s, 5H), 3.89 (s, 3H), 3.84 (s, 1H), 3.82 (s, 2H), 3.79 (d, 1H), 3.73 (s, 5H), 3.69 (s, 2H), 3.64 (s, 2H), 3.61 (s, 2H), 3.53 (d, 1H), 3.45 (d, 1H), 3.29 (dt, 1H, O-CH₂-C), 2.15 (dt, 2H, C-CH₂-C-CH), 2.12 (s, 3H, Ac), 1.86 (t, 1H, C-C-H), 1.79 (m, 2H, C-CH₂-C).

13CNMR (400 MHz, CDCl₃), δ 170.0, 138.6, 138.4, 138.4, 138.3, 138.3, 138.1, 138.0, 132.5, 129.8, 128.8, 128.7, 128.6, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 101.3, 100.7, 99.3, 98.6, 83.6, 79.6, 79.5, 79.2, 79.1, 79.0, 78.1, 77.2, 76.1, 75.8, 75.5, 75.1, 75.0, 74.9, 74.8, 74.7, 74.7, 74.2, 73.2, 73.2, 72.3, 72.2, 72.0, 71.8, 71.8, 71.7, 71.6, 69.6, 69.6, 69.3, 68.6, 65.8, 28.3, 21.1, 15.2

HRMS (ESI-FT-ICR): m/z calcd 2288.0398, M⁺, found 2311.0296 [M + Na]⁺.
4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-[2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl]-α-D-mannopyranoside (12)

123mg of compound 12 (0.094mmol, 80%) was obtained as a pale yellow syrup by the capture-release separation from the glycosylation between donor 11 (499mg, 0.710mmol) and acceptor 8 (50mg, 0.117mmol) after glycosylation, cobalt-alkyne complexation, loading step and releasing step.

$^1$HNMR (400MHz, CDCl₃), δ 7.32-7.10 (m, 40H, Ar), 5.50 (s, 1H, H-1), 5.48 (s, 1H, H-1), 5.19 (s, 1H, H-1), 4.96 (s, 1H), 4.88 (d, 1H, ArCH₂), 4.85 (d, 1H, ArCH₂), 4.77 (s, 1H), 4.74 (d, 1H, ArCH₂), 4.66 (d, 1H), 4.64 (d, 2H), 4.61 (d, 3H), 4.48 (d, 2H), 4.45 (d, 3H), 4.42 (d, 2H), 4.13-4.10 (dd, 1H), 4.04-4.01 (dd, 1H), 3.96-3.93 (dd, 2H), 3.91-3.81 (m, 3H), 3.76-3.67 (m, 2H), 3.64 (d, 2H), 3.58 (d, 1H), 3.38 (dt, 1H, O-CH₂-C), 2.19 (dt, 2H, C-CH₂-C), 2.15 (s, 3H, Ac), 2.09 (s, 3H, Ac), 1.94 (t, 1H, C-C-H), 1.67 (m, 2H, C-CH₂-C)

$^{13}$CNMR (400MHz, CDCl₃), δ 170.2, 170.1, 138.5, 138.4, 138.0, 138.1, 128.0, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 99.7, 98.0, 96.9, 83.5, 78.0, 77.5, 77.5, 77.2, 75.0, 75.0, 74.8, 74.7, 74.2, 74.0, 73.3, 73.3, 72.1, 72.0, 71.7, 71.3, 71.2, 71.1, 68.9, 68.8, 68.7, 68.5, 68.3, 66.4, 65.8, 28.0, 21.1, 21.0, 15.1

HRMS (ESI-FT-ICR): m/z calcd 1374.6127, M⁺, found 1397.6025 [M + Na]⁺.
loading step and releasing step.

\(^1\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\) 7.31-7.13 (m, 70H, Ar), 5.52 (s, 2H, H-1), 5.18 (s, 1H, H-1), 5.07 (s, 1H, H-1), 5.05 (s, 1H, H-1), 4.93 (s, 1H), 4.87 (d, 2H), 4.81 (s, 1H), 4.77 (d, 1H), 4.70 (d, 2H), 4.65 (s, 1H), 4.62 (s, 1H), 4.60 (s, 2H), 4.57 (d, 3H), 4.54 (s, 2H), 4.51 (s, 1H), 4.47 (s, 1H), 4.45 (s, 1H), 4.41 (m, 2H), 4.38 (s, 2H), 4.35 (s, 1H), 4.28 (d, 1H), 4.09 (s, 1H), 4.05 (d, 2H), 3.98 (d, 2H), 3.93 (d, 2H), 3.89 (s, 1H), 3.86 (s, 1H), 3.84 (d, 2H), 3.81 (s, 1H), 3.79 (s, 1H), 3.64 (m, 7H), 3.60 (s, 1H), 3.50-3.46 (m, 2H), 3.36 (d, 2H), 2.15 (dt, 2H, C-CH\(_2\)-C-CH), 2.10 (s, 6H, Ac), 1.90 (t, 1H, C-C-H), 1.64 (m, 2H, C-CH\(_2\)-C)

\(^13\)C NMR (400 MHz, CDCl\(_3\)), \(\delta\) 170.0, 170.0, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 126.9, 101.0, 99.5, 99.2, 99.1, 96.9, 83.5, 79.6, 79.1, 78.1, 78.0, 77.8, 75.0, 74.9, 74.7, 74.7, 74.5, 74.4, 74.2, 74.0, 73.3, 73.2, 73.1, 72.6, 71.9, 71.9, 71.8, 71.3, 71.2, 69.5, 68.9, 68.9, 68.8, 68.6, 68.2, 66.5, 65.9, 28.1, 26.8, 21.1, 15.2


4. NMR Chart.

1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose (S-1)
2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose (S-3)
\( \alpha\)-D-Mannopyranoside, 4-methylphenyl 1-thio (S-7)
α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-O-[(1,1-dimethylethyl)dimethylsilyl]-1-thio (S-8)
β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-1-thio (5-9)
β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-O-(benzyl)-3,6-bis-O-acetyl-1-thio (S-10)
3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose (S-11)
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside (3)
4-pentyn-1-yl 3,4,6-tri-O-benzyl-D-mannopyranoside (S-4)
4-pentyn-1yl 2-O-acetyl-3,4,6-tri-O-benzyl-R-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (6)
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-\( \alpha \)-D-mannopyranosyl-(1\( \rightarrow \)2)-3,4,6-tri-O-benzyl-\( \alpha \)-D-mannopyranoside (7)
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-\(\alpha\)-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-\(\alpha\)-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-\(\alpha\)-D-mannopyranosyl-(1→2)-4,6-tri-O-benzyl-\(\alpha\)-D-mannopyranoside (8)
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (10)
4-pentyl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside (S-13)
4-pentyn-1-yl 2,4-bis-O-benzyl-D-mannopyranoside (11)
4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl)- \( \alpha \)-D-mannopyranoside (12)
4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-[2-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl)-3,4,6-tri-O-benzyl-D-mannopyranosyl]-α-D-mannopyranoside (13)
5. References.

