Supporting Information

Regioselective Alkylation of Carbohydrates and Diols: A Cheaper Iron Catalyst, New Applications and Mechanism

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**General:** All commercially available starting materials and solvents were of reagent grade and used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. $^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker Avance 400 instrument or a Bruker DMX 500 instrument at 298K in CDCl$_3$, using the residual signals from CHCl$_3$ ($^1$H: $\delta = 7.25$ ppm; $^{13}$C: $\delta = 77.2$ ppm) as the internal standard. $^1$H NMR peak assignments were made by first-order analysis of the spectra, supported by standard $^1$H-$^1$H NMR correlation spectroscopy (COSY).

**General method for regioselective alkylation of diols and polyols:**

1. The substrates (50 mg) were allowed to react with RX (alkylation reagents) (1.1 eq.) in dry acetonitrile (1 mL) or a mixed solvent (MeCN/DMF: 10/1) at 40 °C for 2 - 3 h in the presence of Ag$_2$O (0.6 eq.), TBAB (0.1 eq.) and Fe(dipm)$_3$ (0.1 eq.). The reaction mixtures were filtered and directly purified by flash column chromatography (hexanes/EtOAc = 3:1 to 1:1) to afford the pure products.

2. Diol and polyol reactants (50 mg) were allowed to react with RX (alkylation reagents) (1.1 eq.) in 1 mL of dry acetonitrile at 80 °C for 8 h, in the presence of Fe(dipm)$_3$ (0.1 eq.) and K$_2$CO$_3$ (1.5 eq.). After cooling and evaporating the solvent, the reaction mixture was directly purified by flash column chromatography (hexanes–EtOAc 3:1 to 1:1), affording the pure products.

Spectroscopic data of the known products were in accordance with those reported in the literature.

**Methyl 3-O-(4-methoxybenzyl)-4,6-O-benzylidene-\(\alpha\)-D-mannopyranoside (5).** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 – 7.18 (m, 7H, PhCH, MeO-PhCH$_2$), 6.85 (d, $J = 8.6$ Hz, 2H, MeO-PhCH$_2$), 5.60 (s, 1H, PhCH), 4.77 (d, $J = 11.4$ Hz, 1H, MeO-PhCH$_2$), 4.72(s, 1H, H-1), 4.62 (d, $J = 11.4$ Hz, 1H, MeO-PhCH$_2$), 4.27 (dd, $J_1 = 3.9$ Hz, $J_2 = 9.6$ Hz, 1H, H-4), 4.07 (dd, $J_1 = 7.1$ Hz, $J_2 = 14.3$ Hz, 1H, H-6a), 3.96 (s, 1H, H-2), 3.91–3.75 (m, 6H, H-3, H-5, H-6b, MeO-PhCH$_2$), 3.36 (s, 3H, OMe), 2.83 (s,
1H, 2-OH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.5, 137.7, 130.2, 129.7, 129.0, 128.3, 126.2, 113.9, 101.7, 101.2, 78.9, 75.4, 72.8, 69.9, 69.0, 63.3, 55.4, 55.0 ppm.

Methyl 3-O-(4-bromobenzyl)-4,6-O-benzylidene-α-D-mannopyranoside (6). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.55–7.32 (m, 7H, PhCH, Br-PhC$_2$H), 7.21 (d, J = 8.3 Hz, 2H, Br-PhC$_2$H), 5.59 (s, 1H, PhCH), 4.82-4.70 (m, 2H, Br-PhC$_2$H, H-1), 4.66 (d, J = 12.2 Hz, 1H, Br-PhC$_2$H), 4.27 (dd, $J_1$ = 4.1 Hz, $J_2$ = 9.6 Hz, 1H, H-4), 4.08 (dd, $J_1$ = 7.1 Hz, $J_2$ = 14.3 Hz, 1H, H-6a), 4.01 (s, 1H, H-2), 3.94–3.72 (m, 3H, H-3, H-5, H-6b), 3.37 (s, 3H, OMe), 2.73 (s, 1H, 2-OH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.6, 137.1, 131.7, 129.6, 129.1, 128.4, 126.2, 121.9, 101.8, 101.2, 78.9, 75.7, 72.3, 70.0, 69.0, 63.3, 55.1 ppm.

Methyl 3-O-allyl-4,6-O-benzylidene-α-D-mannopyranoside (7). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, J = 7.7 Hz, 2H, PhCH), 7.44-7.30 (m, 3H, PhCH), 5.83-5.61 (m, 1H, CH$_2$C=CH$_2$), 5.59 (s, 1H, PhCH), 5.37-5.25 (m, 2H, CH$_2$C=CH$_2$), 5.19 (d, J = 10.4 Hz, 1H, CH$_2$C=CH$_2$), 4.78 (s, 1H, H-1), 4.39-4.23 (m, 2H, CH$_2$C=CH$_2$), 4.12-4.00 (m, 2H, H-2, H-6a), 3.91-3.75 (m, 3H, H-3, H-5, H-6b), 3.39 (s, 3H, OMe), 2.77 (s, 1H, 2-OH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.6, 137.1, 131.7, 129.6, 129.1, 128.4, 126.2, 121.9, 101.8, 101.2, 78.9, 75.7, 72.3, 70.0, 69.0, 63.3, 55.1 ppm.

Methyl 3-O-(2-cyanobenzyl)-4,6-O-benzylidene-α-D-mannopyranoside (8). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.61 (d, J = 7.6 Hz, 1H, PhCH), 7.56-7.46 (m, 4H, CN-PhCH$_2$), 7.41-7.33 (m, 4H, PhCH), 5.61 (s, 1H, PhCH), 4.98 (d, J = 12.4 Hz, 1H, CN-PhCH$_2$), 4.92 (d, J = 12.4 Hz, 1H, CN-PhCH$_2$), 4.78 (s, 1H, H-1), 4.29 (dd, $J_1$ = 4.3 Hz, $J_2$ = 9.8 Hz, 1H, H-4), 4.23-4.13 (m, 2H, H-2, H-6a), 3.97-3.77 (m, 3H, H-3, H-5, H-6b), 3.39 (s, 3H, OMe), 2.90 (s, 1H, 2-OH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.6, 137.6, 133.1, 132.9, 129.1, 128.3, 126.2, 117.8, 111.7, 101.7, 101.3, 78.8, 76.6, 71.0, 69.8, 69.0, 63.4, 55.1.
Methyl 3-O-allyl-6-O-(tert-butyldimethylsilyloxy)-\(\alpha\)-D-mannopyranoside (10). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.10-5.88 (m, 1H, CH\(_2\)CH=CH\(_2\)), 5.32 (dd, \(J_1 = 17.2, J_2 = 1.5\) Hz, 1H, CH\(_2\)CH=CH\(_2\)), 5.22 (dd, \(J_1 = 10.4, J_2 = 1.1\) Hz, 1H, CH\(_2\)CH=CH\(_2\)), 4.74 (s, 1H, H-1), 4.23–4.11 (m, 2H, CH\(_2\)CH=CH\(_2\)), 3.97 (s, 1H, H-2), 3.93–3.79 (m, 3H, H-4, H-6\(_a\), H-6\(_b\)), 3.67–3.52 (m, 2H, H-3, H-5), 3.37 (s, 3H, OMe), 3.06 (s, 1H, 4-OH), 2.42 (s, 1H, 2-OH), 0.90 (s, 9H, Si(CH\(_3\))\(_3\)), 0.09 (s, 6H, Si(CH\(_3\))\(_2\)) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 134.6, 118.0, 100.5, 79.0, 71.0, 70.8, 69.4, 67.9, 65.0, 55.0, 26.0, 18.4, -5.4 ppm.

Table S1 Comparison the isolation yields of alkylalation methods using catalytic amounts of Fe(dibm)\(_3\) and Fe(dipm)\(_3\).

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<th>Entry</th>
<th>Substrate</th>
<th>Major product</th>
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<th>Yields (Fe(dipm)(_3))</th>
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**Figure S1** Recrystallized Fe(dipm)$_3$. 

![Recrystallized Fe(dipm)$_3$](image21)
Figure S2
$^1$H-NMR of 2,6-dimethyl-4-benzyl-3,5-heptadione (The product of BnBr and dibm)

Methyl 3-O-benzyl-4, 6-O-benzylidene-$\alpha$-D-mannopyranoside (2)$^1$: 
$^1$H-NMR of compound 2 (CDCl$_3$)
Methyl 3-\(O\)-benzyl-6-\((\text{tert}-\text{butyldimethylsilyloxy})\)-\(\alpha\)-D-mannopyranoside (4)\(^2\):
\(^1\)H-NMR of compound 4 (CDCl\(_3\))

Methyl 3-\(O\)-(4-methoxybenzyl)-4, 6-\(O\)-benzylidene-\(\alpha\)-D-mannopyranoside (5)\(^3\):
\(^1\)H-NMR of compound 5 (CDCl\(_3\))
\textsuperscript{13}C-NMR of compound 5 (CDCl\textsubscript{3})

Methyl 3-\textit{O}-(4-bromobenzyl)-4, 6-\textit{O}-benzylidene-\textalpha-\textit{D}-mannopyranoside (6): \textsuperscript{1}H-NMR of compound 6 (CDCl\textsubscript{3})
$^{13}$C-NMR of compound 6 (CDCl$_3$)

Methyl 3-O-allyl-4, 6-O-benzyldene-$\alpha$-D-mannopyranoside (7): $^1$H-NMR of compound 7 (CDCl$_3$)
$^{13}$C-NMR of compound 7 (CDCl$_3$)

Methyl 3-O-(2-cyanobenzyl)-4, 6-O-benzylidene-$\alpha$-D-mannopyranoside (8)$^3$: $^1$H-NMR of compound 8 (CDCl$_3$)
$^{13}$C-NMR of compound 8 (CDCl$_3$)

Methyl 3-\textit{O}-(4-bromobenzyl)-6-\textit{O}-(\textit{tert}-butyldimethylsilyloxy)-\textit{\alpha}-D-mannopyranoside (9)$^4$:

$^1$H-NMR of compound 9 (CDCl$_3$)
Methyl 3-O-allyl-6-O-(tert-butyldimethylsilyloxy)-α-D-mannopyranoside (10)³:
³¹H-NMR of compound 10 (CDCl₃)
Methyl 3-O-benzyl-6-O-(tert-butyldimethylsilyloxy)-β-D-galactopyranoside (12):  
$^1$H-NMR of compound 12 (CDCl$_3$)

Methyl 3-O-benzyl-6-O-(tert-butyldimethylsilyloxy)-α-D-galactopyranoside (14):  
$^1$H-NMR of compound 14 (CDCl$_3$)
Methyl 2, 3, 6-tri-O-benzyl-β-D-galactopyranoside (16)\(^5\):  
\(^1\)H-NMR of compound 16 (CDCl\(_3\))

Methyl 3-O-benzyl-α-D-mannopyranoside (18)\(^1\):  
\(^1\)H-NMR of compound 18 (CDCl\(_3\))
Methyl 3-O-benzyl-β-D-galactopyranoside (20):  
$^1$H-NMR of compound 20 (CDCl₃)

Methyl 3-O-benzyl-α-D-galactopyranoside (22):  
$^1$H-NMR of compound 22 (CDCl₃)
Methyl 2, 3, 6-tri-O-benzyl-α-D-glucopyranoside (26): 
\(^1\)H-NMR of compound 26 (CDCl\(_3\))

2-O-benzyl-1-Phenylethane-1, 2-diol (29): 
\(^1\)H-NMR of compound 29 (CDCl\(_3\))
1-\(O\)-benzyl-1, 2-Propanediol (31):
\(^1\)H-NMR of compound 31 (CDCl\(_3\))

1-\(O\)-benzyl-1, 3-Butanediol (33):
\(^1\)H-NMR of compound 33 (CDCl\(_3\))
1-O-benzyl-1,3-propanediol (35):  
$^1$H-NMR of compound 35 (CDCl$_3$)

Reference