Mild and Selective Deprotection of tert-Butyl(dimethyl)silyl Ethers with Catalytic Amounts of Sodium Tetrachloroauroate(III) Dihydrate

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Abstract A simple and mild method for the removal of tert-butyl(dimethyl)silyl (TBS) protecting groups with catalytic amounts of sodium tetrachloroauroate(III) dihydrate is described. The procedure permits selective deprotection of aliphatic TBS ethers in good to excellent yields in the presence of aromatic TBS ethers, aliphatic triisopropylsilyl ethers, aliphatic tert-butyl(diphenyl)silyl ethers, or sterically hindered aliphatic TBS ethers. Additionally, TBS ethers can also be transformed into 4-methoxybenzyl ethers or methyl ethers in one pot by using larger quantities of the catalyst and a higher reaction temperature.

Key words deprotection, silyl ethers, alcohols, ethers, catalysis, gold

Protection/deprotection strategies play important roles in modern organic synthesis.1,2 The tert-butyl(dimethyl)silyl (TBS) group is one of the most widely used protecting groups for alcohols because of its easy installation, its stability to various reaction conditions, and the selectivity of its cleavage reaction. Numerous methods are available for removal of TBS groups,3–9 including the use of acidic,4 basic,5 reducing,6 oxidizing,7 or fluoride-based reagents8 among others.9 However, new mild and selective protocols for the deprotection of TBS ethers are in great demand for use in syntheses of multifunctional compounds, particularly complex natural products.

Commercially available sodium tetrachloroauroate(III) dihydrate (NaAuCl4·2H2O) is the least expensive gold catalyst and has been used in several types of reaction, including nucleophilic addition to multiple bonds,10–13 nucleophilic substitution of propargylic alcohols,14,15 nonsymmetrical etherization,16 and others.17,18 In the course of an ongoing total-synthesis project, we serendipitously found that the TBS protecting group was cleanly removed in the presence of a small amount of NaAuCl4·2H2O. Inspired by this observation, we explored the possibility of using NaAuCl4·2H2O as an effective catalyst for the deprotection of TBS ethers.

First, we evaluated the effects of the solvent and the catalyst loading on the gold(III)-catalyzed desilylation of the TBS ether of 6-(benzyl oxy)hexan-1-ol (1) (Table 1). In the presence of 0.01 equivalents of sodium tetrachloroauroate(III) in methanol, deprotection of the TBS ether in good to excellent yields after 3.5 hours at room temperature (Table 1, entry 1). The cleavage also proceeded in other polar solvents, but yields were much lower (entries 2–4). Alcohol 1′ was still obtained in excellent yields and in reasonable reaction times when the amount of catalyst was reduced to 0.005, 0.001, or even 0.0005 equivalents, (entries 5–7), but the deprotection became sluggish when 0.0001 equivalents of the catalyst were used (entry 8).

Next, we synthesized several aliphatic and aromatic TBS ethers to examine the substrate scope of our deprotection method. The deprotection reaction of the primary TBS ethers...
ethers was conducted in the presence of 0.001–0.005 equivalents of sodium tetrachloroaurate(III) dihydrate in methanol at room temperature. Primary TBS ethers containing electron-donating or electron-withdrawing groups were readily deprotected to give the corresponding alcohols in high yields (Table 2, entries 1–5). Secondary and tertiary TBS ethers were also desilylated smoothly, although longer reaction times or greater catalyst loadings were required (entries 6 and 7). Although sodium tetrachloroaurate(III) dihydrate catalyzes addition reactions of alkenes or alkynes,10–13 the TBS protecting group of compound 9 was removed successfully under the current condition without any effect on the double bond (entry 8). Aromatic TBS ethers are usually deprotected by treatment with basic reagents or fluoride-based reagents that frequently produce unwanted side reactions, such as silyl migration.19 Gratifyingly, the cleavage of aromatic TBS ethers proceeded well in the presence of 0.05–0.1 equivalents of the catalyst in methanol at room temperature. Aromatic TBS ethers bearing electron-donating groups were much more reactive than those bearing electron-withdrawing groups (entries 9–12).

Next, we examined the selective deprotection of TBS ethers containing various sensitive functional groups under the optimized conditions (Table 3). On treatment with 0.005 equivalents of sodium tetrachloroaurate(III) dihydrate in methanol at room temperature, the TBS group in substrates 14–18 was selectively removed, whereas other

### Table 2: Deprotection of Primary, Secondary, Tertiary and Aryl TBS Ethers Catalyzed by Sodium Tetrachloroaurate(III) in Methanol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst (equiv)</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R = H (2)</td>
<td>0.005</td>
<td>8</td>
<td>R = H (2')</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>R = OMe (3)</td>
<td>0.001</td>
<td>4</td>
<td>R = OMe (3')</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>R = CF₃ (4)</td>
<td>0.005</td>
<td>15</td>
<td>R = CF₃ (4')</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>0.005</td>
<td>8</td>
<td>5'</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.005</td>
<td>2</td>
<td>6'</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>0.01</td>
<td>24</td>
<td>7'</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>0.05</td>
<td>40</td>
<td>8'</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>0.005</td>
<td>12</td>
<td>9'</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>R₁ = All; R₂ = OMe (10)</td>
<td>0.05</td>
<td>7</td>
<td>R₁ = All; R₂ = OMe (10')</td>
<td>87</td>
</tr>
<tr>
<td>10</td>
<td>R₁ = t-Bu; R₂ = OMe (11)</td>
<td>0.05</td>
<td>24</td>
<td>R₁ = t-Bu; R₂ = OMe (11')</td>
<td>92</td>
</tr>
<tr>
<td>11</td>
<td>R₁ = NHAc; R₂ = OMe (12)</td>
<td>0.05</td>
<td>48</td>
<td>R₁ = NHAc; R₂ = OMe (12')</td>
<td>86</td>
</tr>
<tr>
<td>12</td>
<td>R₁ = Ac; R₂ = H (13)</td>
<td>0.1</td>
<td>48</td>
<td>R₁ = Ac; R₂ = H (13')</td>
<td>21 (67%)</td>
</tr>
</tbody>
</table>

*With respect to the substrate.

*Isolated yield of pure product.

### Table 3  Selective Deprotection of Various Silyl Ethers Catalyzed by Sodium Tetrachloroaurate(III) in Methanol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst (equiv(^a))</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R = All (14)</td>
<td>0.005</td>
<td>5</td>
<td>R = All (14)′</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>R = Ac (15)</td>
<td>0.005</td>
<td>2</td>
<td>R = Ac (15)′</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>R = MOM (16)</td>
<td>0.005</td>
<td>4</td>
<td>R = MOM (16)′</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>R = MEM (17)</td>
<td>0.005</td>
<td>4</td>
<td>R = MEM (17)′</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td>0.005</td>
<td>11</td>
<td>18′</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>TBDPSO</td>
<td>0.005</td>
<td>3</td>
<td>TBDPSO (19)′</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>0.005</td>
<td>7</td>
<td>20′</td>
<td>97</td>
</tr>
<tr>
<td>8</td>
<td>TIPSO</td>
<td>0.005</td>
<td>2</td>
<td>TIPSO (21)′</td>
<td>83 (7)(^c)</td>
</tr>
<tr>
<td>9</td>
<td>22</td>
<td>0.005</td>
<td>7</td>
<td>22′</td>
<td>86 (5)(^c)</td>
</tr>
<tr>
<td>10</td>
<td>TESO</td>
<td>0.001</td>
<td>0.5</td>
<td>TESO (23)′</td>
<td>86 (8)(^c)</td>
</tr>
<tr>
<td>11</td>
<td>24</td>
<td>0.001</td>
<td>1</td>
<td>24′</td>
<td>77 (18)(^c)</td>
</tr>
<tr>
<td>12</td>
<td>TBSO</td>
<td>0.005</td>
<td>5</td>
<td>TBSO (25)′</td>
<td>92</td>
</tr>
<tr>
<td>13(^d)</td>
<td></td>
<td>0.005</td>
<td>40</td>
<td>26′</td>
<td>93</td>
</tr>
<tr>
<td>14</td>
<td>TBSO</td>
<td>0.005</td>
<td>7</td>
<td>8′</td>
<td>82 (9)(^c)</td>
</tr>
<tr>
<td>15</td>
<td>28</td>
<td>0.005</td>
<td>5</td>
<td>28′</td>
<td>86 (5)(^c)</td>
</tr>
</tbody>
</table>

\(^a\) With respect to the substrate.

\(^b\) Isolated yield of pure product.

\(^c\) Yield of diol.

\(^d\) EtOAc–MeOH (1:1, v/v) was used as the solvent.
common acid-labile protecting groups such as allyl, acetyl, methoxymethyl, (2-methoxyethoxy)methyl, and isopropyldiene were unaffected (Table 3, entries 1–5). The catalyst also showed good selectivity to various silyl protecting groups. Preferential cleavage of TBS ether groups in the presence of tert-butyl(dimethyl)silyl (TBDS) ether groups gave the monodeprotected products in high yields, and the corresponding diols were not obtained (entries 6 and 7). When a less-bulky triisopropylsilyl group (compared with TBDPS) and a TBS groups were present together, the deprotection was less selective, but the desired monoalcohols were still obtained as the major products (≥83% yield) (entries 8 and 9). Moderate selectivity between triethoxysilylethyl and TBS protecting groups was achieved by using 0.001 equivalents of the catalyst (entries 10 and 11). An aliphatic TBS ether group was selectively removed in the presence of an aromatic TBS ether group in 92% yield (entry 12). We also examined the possibility of selectively deprotecting TBS diethers (entries 13–15). In all cases, the less-hindered TBS ether group was cleaved in preference to the more-hindered one in good to excellent yield; this makes our method very useful in total syntheses of complicated compounds such as natural products or their analogues.

Because nonsymmetrical ethers can be prepared from alcohols by using sodium tetrachloroaurate(III) dihydrate as catalyst, we decided to examine the one-pot transformation of TBS ethers into other frequently used ethers. Under relatively harsh condition [NaAuCl4·2H2O (0.05 equiv), THF, reflux], TBS ether 1 reacted with 4-methoxybenzyl alcohol to give the desired ether 29 directly (Scheme 1). More interestingly, substrate 30, which readily forms the corresponding carbocation, gave either the deprotected product 30′ or the methyl ether 31, depending on the amount of the catalyst used and the reaction temperature (Scheme 1).

In conclusion, we have developed an effective protocol for the deprotection of TBS ethers by using a very small amount of sodium tetrachloroaurate(III) dihydrate as catalyst. Notable features of the protocol include mild conditions, low cost, easy operations, good functional group compatibility, and high selectivity. The method should therefore have widespread applications in syntheses of complex, multifunctional, or sensitive molecules. In addition, by using larger amounts of catalyst and higher reaction temperatures, TBS ethers can also be transformed into 4-methoxybenzyl or methyl ethers in a one-pot process.

1H NMR and 13C NMR spectra were recorded in CDCl3 or CD3OD on a Bruker Avance 300 or Bruker Avance 400 instrument. Chemical shifts (δ) are referenced to internal TMS or CDCl3. High-resolution mass spectra were recorded on a Bruker maXis Impact mass spectrometer.Melting points were determined by using a Stuart Scientific SMP10 instrument and are uncorrected. IR spectra were recorded in the ATR mode on a Nicolet 6700 FT-IR Thermo Scientific spectrometer; only the more significant peaks are reported. All reagents and solvents obtained commercially and were used as received without further purification. Reactions were monitored by TLC on glass-backed plates coated with a 0.2 mm thickness of silica gel 60 F254; chromatograms were visualized by UV radiation (254 nm) or by staining with phosphomolybdic acid and H2SO4. Column chromatography was performed on 300–400 mesh silica gel.

Except for compound 8, 28, and 30, all TBS ethers were prepared according to the procedures reported in the literature.

3-[[tert-Butyl(dimethyl)silyl]oxy]-3-methylbutan-1-ol (8)
Na2O2Cl2·2H2O (4.0 mg, 0.01 mmol, 0.005 equiv) was added to a solution of disilyl ether 27 (665 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 7 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:5)] to give a colorless oil; yield: 358 mg (82%).

IR (KBr): 3355, 2945, 2857, 1468, 1250, 1041 cm–1.
1H NMR (300 MHz, CDCl3): δ = 3.82 (t, J = 5.9 Hz, 2 H), 1.72 (t, J = 5.9 Hz, 2 H), 1.31 (s, 9 H), 0.87 (s, 9 H), 0.13 (s, 6 H).
13C NMR (75 MHz, CDCl3): δ = 75.31, 60.00, 45.70, 29.86, 25.79, 17.90, –2.01.

3-[tert-Butyl]1-[(15′,5′R′)-5-[[tert-Butyl(dimethyl)silyl]oxy]-4-methyloclohexyl-3-en-1-yl]-1-methylethoxy(dimethylsilane) (28)
TBSOT (1.52 mL, 6.6 mmol) was added dropwise to a solution of diol 9 (511 mg, 3 mmol) and 2,6-lutidine (0.76 mL, 6.6 mmol) in dry CH2Cl2 (6 mL) at 0 °C, and the mixture was stirred for 5 h. H2O (5 mL) and CH2Cl2 (20 mL) were added, and the organic layer was separated and washed successively with sat. aq NaHCO3 (5 mL), H2O (2 × 5 mL), and brine (5 mL), then dried (MgSO4) and filtered. The filtrate was concentrated in vacuo and the resulting residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:25)] to give a colorless oil; yield: 1.065 g (89%).
**Synthesis**

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IR (KBr): 2966, 2920, 2861, 1475, 1368, 1256 cm\(^{-1}\).

\(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.52\) (dd, \(J = 3.6, 1.6\) Hz, 1 H), 4.01 (br s, 1 H), 2.11 (dt, \(J = 16.8, 5.6\) Hz, 1 H), 1.88–1.78 (m, 2 H), 1.75–1.67 (m, 4 H), 1.37 (dt, \(J = 3.6, 13.2\) Hz, 1 H), 1.21 (s, 3 H), 1.18 (s, 3 H), 0.91 (s, 9 H), 0.85 (s, 9 H), 0.10 (s, 6 H), 0.07 (s, 6 H).

\(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 134.45, 125.05, 74.73, 69.46, 39.62, 33.58, 28.37, 27.57, 26.86, 25.95, 25.95, 21.25, 18.29, 18.15, -2.02\) (2 C).

MS (ESI, MeOH): \(m/z = 421\) [M + Na\(^+\)].

HRMS-ESI: \(m/z\) [M + Na\(^+\)] calcd for C\(_{22}\)H\(_{46}\)NaO\(_2\)Si\(_2\): 421.2940; found: 421.2940.

**tert-Butyl(dimethyl)[(3,4,5-trimethoxybenzyl)oxy]silane (30)**

A solution of alcohol 30\(^{22}\) (396 mg, 2 mmol), imidazole (300 mg, 4.4 mmol), and TBSOTf (332 mg, 2.2 mmol) in anhyd CH\(_2\)Cl\(_2\) (4 mL) was stirred at overnight at r.t. H\(_2\)O (5 mL) and CH\(_2\)Cl\(_2\) (20 mL) were added to the mixture, and the organic layer was separated, washed successively with sat. aq NaHCO\(_3\) (5 mL), H\(_2\)O (2 × 5 mL), and brine (5 mL), then dried (MgSO\(_4\)) and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:25)] to give a colorless oil; yield: 569 mg (91%).

**3-Butyl(dimethyl)[(3,4,5-trimethoxybenzyl)oxy]silane (30)**

Prepared according to the general procedure from silyl ether 30\(^{21}\) (396 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 4 h. The mixture was then diluted with EtOAc (10 mL) and filtered through activated alumina. The solution was concentrated in vacuo and residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:3)] to give a colorless oil; yield: 277 mg (96%); mp 63–65 °C.

HRMS-ESI: \(m/z\) [M + Na\(^+\)] calcd for C\(_{16}\)H\(_{28}\)NaO\(_4\)Si: 335.1663; found: 335.1663.

**Deprotection of TBS Ethers; General Procedure**

A solution of the TBS ether (2 mmol) in MeOH (4 mL) was treated with NaAuCl\(_4\)·2H\(_2\)O (0.8 mg, 0.002 mmol, 0.001 equiv) was added to a solution of silyl ether 3\(^{25}\) (505 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 4 h. The mixture was then diluted with EtOAc (10 mL) and filtered through activated alumina. The solution was concentrated in vacuo and the resulting residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:3)] to give a colorless oil; yield: 260 mg (94%).

**3-Butyl(dimethyl)[(3,4,5-trimethoxybenzyl)oxy]silane (30)**

Prepared according to the general procedure from silyl ether 3\(^{25}\) (581 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 4 h. The mixture was then diluted with EtOAc (10 mL) and filtered through activated alumina. The solution was concentrated in vacuo and resulting residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:3)] to give a colorless oil; yield: 206 mg (95%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Literature Data</th>
<th>Experimental Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl Alcohol (2)(^{29})</td>
<td>C(<em>{7})H(</em>{11})O</td>
<td>Prepared according to the general procedure from 2(^{29}) (445 mg), and purified by flash column chromatography [silica gel, EtOAc–PE (1:3)] as a colorless oil; yield: 206 mg (95%).</td>
<td></td>
</tr>
<tr>
<td>1H NMR (300 MHz, CDCl(_3)): (\delta = 7.37–7.28) (m, 5 H), 4.69 (s, 2 H), 1.69 (br s, 1 H).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13C NMR (75 MHz, CDCl(_3)): (\delta = 140.83, 128.46, 127.52, 126.91, 65.13.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MS (ESI, MeOH): (m/z = 131) [M + Na(^+)].</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HRMS-ESI: (m/z) [M + Na(^+)] calcd for C(<em>{6})H(</em>{10})NaO: 131.0473; found: 131.0478.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1H NMR (300 MHz, CDCl₃): δ = 7.45 (d, J = 8.7 Hz, 2 H), 7.32 (d, J = 7.0 Hz, 2 H), 6.69–6.67 (m, 2 H), 6.59 (s, 1 H), 6.55 (d, J = 6.6 Hz, 2 H), 6.36 (d, J = 5.9 Hz, 1 H), 5.16–5.06 (m, 2 H), 2.37 (s, 3 H), 3.31 (d, J = 2.7 Hz, 2 H). MS (ESI, MeOH): m/z = 183 [M + Na]+.

**1.**


**2.**

<table>
<thead>
<tr>
<th>R</th>
<th>S*</th>
<th>(R)-(-)-Menthol (7)⁶⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 7⁶⁶ (541 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 24 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (2:1)] to give a pale-yellow oil; yield: 286 mg (92%); mp 42–43 °C.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**3.**

<table>
<thead>
<tr>
<th>R</th>
<th>S*</th>
<th>tert-Butylphenol (11)⁶⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 11⁶⁸ (529 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 24 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:5)] to give a white solid; yield: 277 mg (92%); mp 97–99 °C.</td>
<td></td>
<td></td>
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</tbody>
</table>

**4.**

<table>
<thead>
<tr>
<th>R</th>
<th>S*</th>
<th>tert-Butylphenol (11)⁶⁹</th>
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<tbody>
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<td>NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 11⁶⁸ (529 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 24 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:5)] to give a white solid; yield: 277 mg (92%); mp 97–99 °C.</td>
<td></td>
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</table>

**5.**

<table>
<thead>
<tr>
<th>R</th>
<th>S*</th>
<th>tert-Butylphenol (11)⁶⁹</th>
</tr>
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<tbody>
<tr>
<td>NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 11⁶⁸ (529 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 24 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:5)] to give a white solid; yield: 277 mg (92%); mp 97–99 °C.</td>
<td></td>
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**6.**

<table>
<thead>
<tr>
<th>R</th>
<th>S*</th>
<th>tert-Butylphenol (11)⁶⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 11⁶⁸ (529 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 24 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:5)] to give a white solid; yield: 277 mg (92%); mp 97–99 °C.</td>
<td></td>
<td></td>
</tr>
</tbody>
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**7.**

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<th>R</th>
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<th>tert-Butylphenol (11)⁶⁹</th>
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<tr>
<td>NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 11⁶⁸ (529 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 24 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:5)] to give a white solid; yield: 277 mg (92%); mp 97–99 °C.</td>
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6-(Allyloxy)hexan-1-ol (14)\textsuperscript{15}
Prepared according to the general procedure from 14\textsuperscript{4d} (545 mg), and purified by flash column chromatography [silica gel, EtOAc–PE (3:1)] as a colorless oil; yield: 301 mg (95%).

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 5.98–5.85\) (m, 1 H), 5.27 (dd, \(J = 1.7, 17.3\) Hz, 1 H), 5.17 (dd, \(J = 1.1, 10.4\) Hz, 1 H), 3.97 (d, \(J = 4.2\) Hz, 2 H), 3.65 (t, \(J = 4.1\) Hz, 2 H), 3.44 (t, \(J = 5.0\) Hz, 2 H), 1.62–1.56 (m, 4 H), 1.41–1.38 (m, 5 H).

\(^13\)C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 134.93, 116.64, 71.69, 70.24, 62.64, 32.56, 29.58, 25.89, 25.51.

MS (ESI, MeOH): \(m/z = 181\) [M + Na]\textsuperscript{+}.

HRMS-ESI: \(m/z\) [M + Na]\textsuperscript{+} calcd for C\textsubscript{10}H\textsubscript{14}NaO\textsubscript{2}: 181.1204; found: 181.1198.

6-Hydroxyhexyl Acetate (15)\textsuperscript{16}
Prepared according to the general procedure from 15\textsuperscript{4e} (549 mg), and purified by flash column chromatography [silica gel, EtOAc–PE (1:1)] as a colorless oil; yield: 301 mg (94%).

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 4.06\) (t, \(J = 5.0\) Hz, 2 H), 3.64 (t, \(J = 4.8\) Hz, 2 H), 2.05 (s, 3 H), 1.64–1.58 (m, 4 H), 1.40–1.38 (m, 4 H).

\(^13\)C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 171.20, 64.40, 62.59, 32.49, 28.49, 25.63, 25.31, 20.87.

MS (ESI, MeOH): \(m/z = 183\) [M + Na]\textsuperscript{+}.

HRMS-ESI: \(m/z\) [M + Na]\textsuperscript{+} calcd for C\textsubscript{14}H\textsubscript{16}O\textsubscript{2}: 183.0997; found: 183.0990.

6-(Methoxymethoxy)hexan-1-ol (16)\textsuperscript{17}
Prepared according to the general procedure from 16\textsuperscript{4f} (553 mg), and purified by flash column chromatography [silica gel, EtOAc–PE (1:2)] as a colorless oil; yield: 315 mg (97%).

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 4.62\) (s, 2 H), 3.65 (t, \(J = 6.5\) Hz, 2 H), 3.53 (t, \(J = 6.5\) Hz, 2 H), 3.36 (s, 3 H), 1.75–1.52 (m, 4 H), 1.42–1.39 (m, 4 H).

\(^13\)C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 96.38, 67.72, 62.84, 55.06, 32.67, 29.66, 25.99, 25.53.

MS (ESI, MeOH): \(m/z = 185\) [M + Na]\textsuperscript{+}.

HRMS-ESI: \(m/z\) [M + Na]\textsuperscript{+} calcd for C\textsubscript{14}H\textsubscript{16}O\textsubscript{2}: 185.1145; found: 185.1148.

6-[(2-Methoxyethoxy)methoxy]hexan-1-ol (17)\textsuperscript{17}
Prepared according to the general procedure from 17\textsuperscript{4i} (641 mg), and purified by flash column chromatography [silica gel, EtOAc–PE (1:3)] as a colorless oil; yield: 392 mg (95%).

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 4.71\) (s, 2 H), 3.75–3.62 (m, 4 H), 3.60–3.51 (m, 4 H), 3.40 (s, 3 H), 1.75–1.53 (m, 4 H), 1.46–1.39 (m, 4 H).

\(^13\)C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 95.43, 71.80, 67.77, 66.68, 62.79, 58.95, 32.65, 29.59, 25.95, 25.49.

MS (ESI, MeOH): \(m/z = 229\) [M + Na]\textsuperscript{+}.

HRMS-ESI: \(m/z\) [M + Na]\textsuperscript{+} calcd for C\textsubscript{16}H\textsubscript{18}NaO\textsubscript{2}: 229.1416; found: 229.1413.

1,2,3,4-Bis-(O-(1-Methylhexylidene)-α,O-digalactopyranose (18)\textsuperscript{18}
Prepared according to the general procedure from 18\textsuperscript{4j} (749 mg), and purified by flash column chromatography [silica gel, EtOAc–PE (2:1)] as a colorless oil; yield: 500 mg (96%).
MS (ESI, MeOH): \( m/z = 317 \) \([M + Na]^+\).

HRMS-ESI: \( m/z [M + Na]^+ \) calcld for \( C_{17}H_{30}NaO_2Si: 317.1913 \); found: 317.1912.

\( [4-\{([4-tert-Butyl(dimethyl)silyl)oxy]methyl)phenoxy]methanol (23)^{26} \)

NaAuCl₄·2 H₂O (0.8 mg, 0.002 mmol, 0.001 equiv) was added to a solution of disilyl ether \( 23^{26} \) (733 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was stirred at r.t. for 0.5 h. The mixture was then diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography \([\text{sila gel, EtOAc–PE (1:5)}]\) to give a colorless oil; yield: 435 mg (86%).

\( 1^H \text{NMR (300 MHz, CDCl}_3\): } \delta = 3.46 \text{ (d, } J = 4.8 \text{ Hz, 2 H), 3.41 \text{ (d, } J = 4.5 \text{ Hz, 2 H), 1.82–1.80 \text{ (m, 4 H), 1.44–1.42 \text{ (m, 2 H), 0.96–0.92 \text{ (m, 4 H), 0.89 \text{ (s, 9 H), 0.04 \text{ (s, 6 H).}}}

\( 1^C \text{NMR (75 MHz, CDCl}_3\): } \delta = 67.80, 68.66, 40.73, 40.61, 29.00, 28.89, 25.95, 18.36, –5.37.

MS (ESI, MeOH): \( m/z = 275 [M + Na]^+\).

HRMS-ESI: \( m/z [M + Na]^+ \) calcld for \( C_{14}H_{26}NaO_3Si: 275.1443 \); found: 275.1447.

\( (2)-\text{trans-5-1-([4-tert-Butyl(dimethyl)silyl)oxy]-1-methylthethyl)-2-methylcyclohex-2-en-1-ol (28)^{28} \)

Prepared according to the general procedure from \( 28 \) (798 mg), and purified by flash column chromatography \([\text{sila gel, EtOAc–PE (1:5)}]\) as a colorless oil; yield: 489 mg (86%).

IR (KBr): 3350, 2969, 2922, 2857, 1468, 1379, 1250 cm⁻¹.

\( 1^H \text{NMR (300 MHz, CDCl}_3\): } \delta = 5.57–5.56 \text{ (m, 1 H), 4.01 \text{ (br s, 1 H), 2.13–2.06 \text{ (m, 1 H), 2.02 \text{ (dq, } J = 2.0, 13.6 \text{ Hz, 1 H), 1.86–1.81 \text{ (m, 1 H), 1.78 \text{ (s, 3 H), 1.61 \text{ (ddt, } J = 2.4, 4.8, 12.0 \text{ Hz, 1 H), 1.43 \text{ (dt, } J = 4.0, 13.6 \text{ Hz, 2 H), 1.21 \text{ (s, 3 H), 1.19 \text{ (s, 3 H), 0.85 \text{ (s, 6 H), 0.07 \text{ (s, 6 H).}}}

\( 1^C \text{NMR (75 MHz, CDCl}_3\): } \delta = 134.16, 125.86, 74.70, 69.00, 39.84, 32.88, 37.70, 27.75, 26.93, 25.93, 20.83, 18.28, –2.03.

MS (ESI, MeOH): \( m/z = 307 [M + Na]^+\).

HRMS-ESI: \( m/z [M + Na]^+ \) calcld for \( C_{19}H_{38}NaO_2Si: 307.2069 \); found: 307.2083.

\( 3,4,5\text{-Trimethoxyphenyl}methanol (30)^{22} \)

Prepared according to the general procedure from \( 30 \) (625 mg), and purified by flash column chromatography \([\text{sila gel, EtOAc–PE (1:5)}]\) as a white solid; yield: 361 mg (91%); mp 36–38 °C.

\( 1^H \text{NMR (300 MHz, CDCl}_3\): } \delta = 6.60 \text{ (s, 2 H), 4.63 \text{ (s, 2 H), 3.87 \text{ (s, 6 H), 3.84 \text{ (s, 3 H), 1.81 \text{ (br s, 1 H).}}}

\( 1^C \text{NMR (75 MHz, CDCl}_3\): } \delta = 153.24, 137.16, 136.68, 103.72, 65.32, 60.75, 55.98.

MS (ESI, MeOH): \( m/z = 221 [M + Na]^+\).

HRMS-ESI: \( m/z [M + Na]^+ \) calcld for \( C_{16}H_{28}NaO_3Si: 221.0790 \); found: 221.0792.

\( 1-([6\text{-Benzyloxy}hexyl]oxy)ethyl)-4-methoxybenzene (29)^{28} \)

NaAuCl₄·2 H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether \( 29 \) (737 mg, 2 mmol) in MeOH (4 mL) at r.t., and the mixture was cooled to r.t., diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography \([\text{sila gel, EtOAc–PE (1:1)}]\) to give a colorless oil; yield: 394 mg (60%).

\( 1^H \text{NMR (300 MHz, CDCl}_3\): } \delta = 7.33 \text{ (s, 4 H), 4.74 \text{ (s, 2 H), 4.68 \text{ (s, 2 H), 0.94 \text{ (s, 9 H), 0.10 \text{ (s, 6 H).}}}

\( 1^C \text{NMR (75 MHz, CDCl}_3\): } \delta = 159.06, 138.66, 130.76, 129.13, 128.27, 127.54, 127.39, 113.70, 72.79, 72.45, 70.35, 70.04, 55.19, 29.67, 26.01.

MS (ESI, MeOH): \( m/z = 351 [M + Na]^+\).

HRMS-ESI: \( m/z [M + Na]^+ \) calcld for \( C_{19}H_{30}NaO_2Si: 351.1936 \); found: 351.1939.
1,2,3-Trimethoxy-5-(methoxymethyl)benzene (31)^10
NaAuCl₂·2H₂O (39.8 mg, 0.1 mmol, 0.05 equiv) was added to a solution of silyl ether 30 (624 mg, 2 mmol) in MeOH (4 mL), and the mixture was refluxed for 24 h. The mixture was then cooled down to rt, diluted with EtOAc (10 mL), filtered through activated alumina, and concentrated in vacuo. The residue was purified by flash column chromatography [silica gel, EtOAc–PE (1:10)] to give a colorless oil; yield: 266 mg (63%).

<References>
(3) For a recent review, see: Crouch, R. D. Tetrahedron Lett. 2013, 69, 2383; and references therein.

This article differs from the e-first online version only in its layout; no content has been changed.