Supporting Information

Gold-catalyzed Highly Efficient Benzylation of Alcohols with N-Cbz-N-benzyl-progargylamine

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List of Contents

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>General information</td>
</tr>
<tr>
<td>2.</td>
<td>Preparation of N-Cbz-N-benzyl-progargylamine</td>
</tr>
<tr>
<td>3.</td>
<td>General procedures for the synthesis of benzyl ethers</td>
</tr>
<tr>
<td>4.</td>
<td>General procedures of the IPrAuNTf2-catalyzed Friedel-Crafts reaction of 2-methyfuran</td>
</tr>
<tr>
<td>5.</td>
<td>References</td>
</tr>
<tr>
<td>6.</td>
<td>¹H-NMR and ¹³C-NMR spectra</td>
</tr>
</tbody>
</table>
**General information**

Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 300-400 Mesh silica gels. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light at 254 nm or by dipping the plate into an H₂SO₄-EtOH solution followed by heating.

NMR spectra were obtained on a Bruker AVANCE DMX 400 spectrometer operating at 400 MHz for ¹H-NMR, 100 MHz for ¹³C-NMR. Unless otherwise noted, all the NMR spectra were recorded at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: \( s = \) singlet, \( d = \) doublet, \( t = \) triplet, \( dd = \) doublet of doublets, \( m = \) multiplet. Coupling constants \( J \) were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane (\( \delta = 0 \) ppm) in CDCl₃ as an internal standard. ¹³C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of CDCl₃. Mass spectra were obtained on a HP5989A or a VG Quatro mass spectrometer.

Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Dichloromethane (DCM) was distilled over CaH₂. Analytical and spectral data of all the known compounds are exactly matching with the reported values.
Preparation of benzylation reagent \(N\)-Cbz-\(N\)-benzyl-progargylamine

\[
\begin{array}{c}
\text{苯甲基胺} \quad \text{丙炔烃} \quad \text{CbzCl} \quad \text{Et}_3\text{N} \quad \text{N-苯甲基-N-丙炔基胺}
\end{array}
\]

Scheme 1. Preparation of Cbz-protected \(N\)-Benzyl-progargylamine

\(N\)-Benzyl-\(N\)-prop-2-ynylamine (I)

To a stirred benzylamine (10 mL, 91.6 mmol) was added dropwise propargylic bromide (1.64 mL, 15.3 mmol) over 30 min at room temperature. The solution was stirred overnight. The resulting solution was then quenched with water and extracted with \(\text{Et}_2\text{O}\). The combined organic layer was washed with brine, dried over \(\text{Na}_2\text{SO}_4\), filtered and concentrated under reduced pressure. The resulting residue was purified by gel column chromatography (petroleum ether-ethyl acetate, 2:1) to provide the \(N\)-Benzyl-\(N\)-prop-2-ynylamine as colourless oil (1.34 g, 57%). (The spectral data was in agreement with the reported data. \(^\text{(1)}\))

\(^1\text{H NMR (400 MHz, CDCl}_3\):} \delta 7.29-7.21 (m, 10H), 5.2 (s, 2H), 4.62 (s, 2H), 3.80 (s, \(J\) 2H), 3.43 (s, 2H), 2.23 (s, 1H).

Preparation of \(N\)-Cbz-\(N\)-benzyl-progargylamine (I)

To a stirred mixture of benzyl chloroformate (15 mmol, 2.55 g) and \(\text{Et}_3\text{N}\) (15 mmol, 2 mL) in \(\text{CH}_2\text{Cl}_2\) (20 mL) at room temperature was dropwise added over 0.5 h a solution
of N-benzyl-N-prop-2-ynylamine (10.0 mmol, 1.45g) in CH2Cl2 (10 mL). The mixtures were stirred for 1 h and then diluted with CH2Cl2 (20 mL). The mixture was washed with saturated NaHCO3 (20 mL), brine (20 mL) and dried over Na2SO4. Removal of the solvent, followed by chromatography over silica gel (EtOAc-hexanes, 1:4), afforded the goal product (2.65 g, 95.0%) as a colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.32-7.22 (m, 8H), 5.20 (s, 2H), 4.62 (s, 2H), 4.08 (s, 1H), 3.98 (s, 1H), 2.23 (s, 1H). 13C NMR (100MHz, CDCl3): δ 155.7, 136.7, 136.3, 128.5, 128.4, 128.2, 128.0, 127.9, 127.5, 78.7, 72.1, 67.6, 49.5, 35.6. HRMS (ESI): m/z [M +H+] calcd for C11H12NO2 190.0868, found 190.0869.

General procedure for the synthesis of benzyl ethers compounds

To a stirred mixture of alcohol (0.1 mmol) and N-Cbz- N-benzyl-progargylamine (61 mg, 0.11 mmol) in CH2Cl2 (2.0 mL) at room temperature under Ar atmosphere was added IPrAuNTf2 (8 mg, 0.01 mmol). After stirring at room temperature for 2 h (as monitored by TLC), the mixture was filtered through a Celite® pad and concentrated. The residue was purified by silica gel column chromatography to provide products.

(1R, 2S, 5R)- (–)-O-benzylmenthol (3a) [2]

Yield: 24 mg (94%); colorless oil. [α]D 20 -46.6 (c 0.1, CHCl3). 1H NMR (400 MHz, CDCl3): δ 7.37-7.23 (m, 5 H), 4.65 (d, J = 11.5 Hz, 1H), 4.40 (d, J = 11.5 Hz, 1H), 3.17
O-Benzyl cholesterol (3b) [3]

Yield: 42mg (89%); White solid; m.p 117-119 °C. [α]D20-31.7 (c 0.1, CHCl3). 1HNMR (400 MHz, CDCl3): δ 7.15- 7.40 (m, 5H), 5.30-5.40 (m, 1H), 4.58 (s, 2H), 3.20-3.40 (m, 1H), 0.80-2.50 (m, 43H); 13C NMR (100MHz, CDCl3): δ 140.9, 139.0, 128.0, 127.4, 127.7, 127.5, 127.3, 121.8, 78.5, 69.8, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 39.1, 37.2, 36.8, 36.7, 36.1, 31.8, 29.6, 28.4, 28.2, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. HRMS (ESI): m/z [M +H]+ calcd for C34H53O 477.4096, found 477.4097.

Benzyl adamantyl ether (3c) [4]

Yield: 20 mg (83%); Colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.38-7.20 (m, 5H), 4.51 (s, 2H), 2.18 (s, 3H), 1.88-1.82 (m, 6H), 1.74-1.55 (m, 6H); 13C NMR (100MHz, CDCl3): δ 140.1, 128.2, 127.4, 127.0, 72.7, 62.3, 41.7, 36.4, 30.5. HRMS (ESI): m/z [M +H]+ calcd for C17H23O 243.1749, found 243.1751.

O-Benzyl diosin (3d)
Yield: 44 mg (87%); colorless oil. \([\alpha]_D^{20} = -46.1\) (c 0.2, CHCl\(_3\)). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.56 (s, 2H), 4.40 (dd, \(J = 14.8, 7.6\) Hz, 1H), 3.48 (m, 1H), 3.37 (t, \(J = 11.8\) Hz, 1H), 3.30-3.24 (m, 1H), 2.45-2.41 (m, 1H), 2.28 (t, \(J = 3.2\) Hz, 1H), 1.99-1.95 (m, 3H), 1.88-1.84 (m, 2H), 1.79-1.71 (m, 2H), 1.68-1.61 (m, 10H), 1.32-1.0 (m, 3H), 1.20-1.11 (m, 3H), 1.03 (s, 3H), 0.98 (d, \(J = 3.6\) Hz, 3H), 0.96-0.93 (m, 1H), 0.79 (s, 3H), 0.78 (d, \(J = 3.2\) Hz, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.0, 138.0, 128.5, 127.6, 121.2, 109.2, 80.7, 78.5, 66.7, 62.1, 56.5, 50.0, 41.5, 40.2, 39.7, 39.2, 37.1, 32.0, 31.8, 31.3, 30.2, 28.7, 28.4, 20.8, 19.3, 17.1, 16.2, 14.4. HRMS (ESI): m/z [M +H\(^+\)] calcd for C\(_{34}\)H\(_{49}\)O\(_3\) 505.3682; found 505.3685.

1, 2, 5, 6-Di-O-isopropylidene-3-O-benzyl-\(\alpha\)-D-glucofranose (3e) \([^5]\)

Yield: 30 mg (85%); Colorless oil. \([\alpha]_D^{20} = -23.8\) (c 1.0, EtOH). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.37-7.25 (m, 5H), 5.89 (d, \(J = 3.6\) Hz, 1H), 4.69 (d, \(J = 11.6\) Hz, 1H), 4.63 (d, \(J = 11.6\) Hz, 1H), 4.57 (d, \(J = 2.8\) Hz, 1H), 4.39 (dt, \(J = 6.8, 6.0\) Hz, 1H), 4.15 (dd, \(J = 7.2, 2.4\) Hz, 1H), 4.02-3.98 (m, 2H), 1.48 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H); \(^{13}\text{C}\) NMR (100Hz, CDCl\(_3\)): \(\delta\) 137.5, 128.3, 127.7, 127.5, 117.1, 108.9, 105.2, 82.5, 81.6, 81.2, 72.4, 72.3, 67.3, 26.7, 26.2, 25.4. HRMS (ESI): m/z [M +Na\(^+\)] calcd for C\(_{19}\)H\(_{26}\)NaO\(_6\) 373.1627, found 373.1626.
1, 2:3, 4-Di-O-isopropylidene-6-O-benzyl-α-D-galactopyranose (3f)

Yield: 24 mg (94%); colorless oil. [α]$_D^{20}$ +36.1 (c 0.1, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.35-7.28 (5H, m), 5.53 (d, $J$ = 4.8 Hz, 1H), 4.63 (d, $J$ = 12.0 Hz, 1H), 4.58 (d, $J$ = 2.0 Hz, 1H), 4.53(d, $J$ = 12.0 Hz, 1H), 4.30 (dd, $J$ = 2.0, 4.8 Hz, 1H ), 4.28 (dd, $J$ = 8.0, 6.8 Hz, 1H), 4.0 (t, $J$ = 5.6 Hz, 1H), 3.67 (dd, $J$ = 10.0, 5.6 Hz, 1H), 3.62 (dd, $J$ = 10.0, 6.8 Hz, 1H), 1.53(s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H); $^{13}$C NMR (100Hz, CDCl$_3$): δ 138.2, 128.2, 127.5, 127.4, 109.0, 108.4, 96.2, 73.1, 71.0, 70.5, 68.7, 66.7, 25.9, 25.8, 24.0, 24.3. HRMS (ESI): m/z [M +H$^+$] calcd for C$_{19}$H$_{27}$O$_6$ 351.1806, found 351.1809.

Methyl 4, 6-O-benzylidene-2, 3-Di-O-benzyl-α-D-glucopyranoside (3g)$^6$

Yield: 38 mg (82%); white solid; M.p.95-97 °C. [α]$_D^{20}$ -29.1 (c 0.5, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.48-7.50 (m, 2H), 7.24-7.39 (m, 13H), 5.55 (s, 1H), 4.92 (d, $J$ = 11.2 Hz, 1H), 4.86 (d, $J$ = 12.4 Hz, 1H), 4.84 (d, $J$ = 11.2 Hz, 1H), 4.70 (d, $J$ = 12.4 Hz, 1H), 4.60 (1H, d, $J$ = 3.2 Hz), 4.27 (dd, $J$ = 10.0, 4.0 Hz, 1H), 4.05 (1H, t, $J$ = 9.2 Hz, H-3), 3.83-3.79 (1H, m, H-5), 3.71 (t, $J$ = 9.6 Hz, 1H), 3.60 (d, $J$ = 9.6 Hz, ), 3.56 (1H, dd, $J$ = 9.2, 3.6 Hz) 3.41 (3H, s); $^{13}$C NMR(100 MHz, CDCl$_3$): δ 138.7, 138.1, 137.3, 128.8, 128.3, 128.2, 128.1, 128.0, 127.8, 127.5, 126.0, 101.2, 99.2, 82.0 , 79.1 ,78.5 , 75.3, 73.7 , 69.0 , 62.2, 55.3. HRMS (ESI): m/z [M +H$^+$] calcd for C$_{28}$H$_{31}$O$_6$ 463.2042; found
4-Methoxymethoxy-1-benzyoxy-propane (3h)

Yield: 21 mg (95%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (m, 4H), 7.27 (m, 4H), 4.61 (s, 2H), 4.50 (s, 2H), 3.54 (t, $J = 5.6$ Hz, 2H), 3.51 (t, $J = 5.6$ Hz, 2H), 3.34 (s, 3H), 1.69 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 26.4, 55.0, 67.4, 69.9, 72.8, 96.3, 127.4, 127.5, 128.3, 138.5, 128.3, 127.5, 96.3, 72.8, 69.9, 67.4, 55.0, 26.4. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{13}$H$_{21}$O$_3$ 225.1491, found 225.1493.

O-Benzyl-N-Boc-L-serine methyl ester (3i) $^7$

Yield: 28 mg (93%); Colorless oil. $[\alpha]_D^{20}$-28.2 ($c$ 0.2, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24–7.34 (m, 5H), 5.76 (s, 1H), 5.20 (s, 1H), 4.69 (s, 2H), 3.76 (s, 3H), 1.43 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.2, 154.0, 137.8, 128.1, 127.3, 81.4, 74.6, 71.4, 55.9, 55.3, 29.2.

HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{16}$H$_{24}$NO$_5$ 310.1654, found 310.1653.

1,1,1,12-Tetraphenyl-2,5,8,11-tetraoxadodecane (3j)

Yield: 46 mg (97%); Colorless oil. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 7.47-7.45 (m, 6H), 7.32-7.19 (m, 14H), 3.71-3.66 (m, 8H), 3.63-3.61 (m, 2H), 4.55 (s, 2H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 144.1, 138.2, 128.6, 128.3 127.7, 127.5, 126.8, 86.4, 73.2, 70.7 69.4 63.3. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{32}$H$_{35}$O$_4$ 483.2535, found 483.2537.

2-(2-(2-(Benzyloxy)ethoxy)ethoxy)tetrahydro-2H-pyran (3k)
Yield: 23 mg (95%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.29 (m, 4H), 7.28-7.27 (m, 1H), 4.64 (d, $J$ = 3.6 Hz, 1H), 4.57 (s, 2H), 3.90-3.87 (m, 2H), 3.86-3.84 (m, 4H), 3.70-3.68 (m, 2H), 3.65-3.60 (m, 3H), 3.50-3.47 (m, 1H), 1.86-1.79 (m, 1H), 1.79-1.71(m, 1H), 1.68-1.51(m, 4H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 138.2, 128.2, 127.2, 127.5, 98.8, 73.1, 70.6, 70.5, 69.4, 66.6, 62.1, 30.5, 25.3, 19.4.

9, 9, 10, 10-Tetramethyl-1-phenyl-2, 5, 8-trioxa-9-silaundecane (3l)

Yield: 29 mg (94%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.4-7.27 (m, 5H), 4.57(s, 2H), 3.77 (t, $J$ = 5.6 Hz, 2H), 3.68 (t, $J$ = 4.0 Hz, 2H), 3.62 (t, $J$ = 4.0 Hz, 2H), 3.57 (t, $J$ = 5.6 Hz, 2H), 0.89 (s, 9H), 0.66 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.5, 128.3, 127.7, 127.5, 73.2, 72.6, 70.7, 69.5, 62.7, 25.9, 18.3, -5.26. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{17}$H$_{31}$O$_3$Si 311.2042, found 311.2041.

14, 14-Dimethyl-1, 13, 13-triphenyl-2, 6, 9, 12-tetraoxa-13-silapentadecane (3m)

Yield: 46 mg (96%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.69 (s, 2H), 7.67 (s, 2H), 7.43-7.27 (m, 11H), 4.55 (s, 2H), 3.80 (t, $J$ = 5.2 Hz, 2H), 3.68-3.59 (m, 10H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.2, 136.6, 135.6, 135.3, 133.6, 129.5, 128.4, 127.5, 73.1, 72.3, 70.6, 69.3, 63.3, 26.7, 19.1. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{29}$H$_{39}$O$_4$Si 479.2618, found 479.2617.

2-Benzyloxyethyl $p$-toulenesulfonate (3n)

S8
Yield: 27 mg (94%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80-7.78 (m, 2H), 7.34-7.24 (m, 5H), 4.47 (s, 2H), 4.19 (t, $J$ = 4.4 Hz, 2H), 3.65 (t, $J$ = 4.4 Hz, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.7, 137.5, 132.9, 129.7, 129.5, 128.3, 127.9, 127.7, 73.1, 69.2, 67.2, 21.5. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{16}$H$_{19}$O$_3$S 291.1055, found 291.1057.

2'-Benzyloxyethyl 2, 3, 4, 6-tetra-O-acetyl-$\beta$-D-thioglucopyranoside (3o)

Yield: 43 mg (87%); Colorless oil. $[\alpha]_D^{20}$ -12.1 (c 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36-7.25 (m, 5H), 5.20 (t, $J$ = 9.2 Hz, 1H), 5.07 (t, $J$ = 9.6 Hz, 1H), 5.04 (t, $J$ = 9.6 Hz, 1H), 4.59 (d, $J$ = 10.0 Hz, 1H), 4.54 (s, 2H), 4.21 (dd, $J$ = 12.4, 8.4 Hz, 1H), 4.09 (dd, $J$ = 12.4, 4.0 Hz, 1H), 3.71-3.62 (m, 3H), 2.97 (t, $J$ = 6.8 Hz, 1H), 2.81 (t, $J$ = 6.8 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 170.5, 170.1, 169.3, 128.4, 127.7, 127.6, 83.5, 75.7, 73.7, 72.9, 69.9, 68.1, 62.0, 29.5, 20.6, 20.5. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{23}$H$_{31}$O$_{10}$S 499.1638, found 449.1639.

2'-(Benzyloxy)ethyl 2-chloroacetate (3p)

Yield: 22 mg (96%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 (m, 5H), 4.56 (s, 2H), 4.36 (t, $J$ = 4.4 Hz, 2H), 4.09 (s, 2H), 3.69 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.2, 137.6, 128.4, 127.6, 73.1, 67.4, 65.2, 40.7. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{11}$H$_{14}$ClO$_3$ 229.0631, found 229.0630.

Benzyl 2-bromoethylether (3q) [8]

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S9
Yield: 19 mg (91%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30-7.35 (m, 4H), 7.24-7.29 (m, 1H), 4.58 (s, 2H), 3.77 (t, $J = 6.0$ Hz, 2H), 3.48 (t, $J = 6.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 128.4, 137.6, 128.4, 127.8, 127.6, 73.0, 69.8, 30.4. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_9$H$_{12}$BrO 215.0072, found 215.0071.

**O-Benzyl-N-Fmoc-L-threonine methyl ester (3r)**

Yield: 38 mg (86%); Colorless oil. [a]$_D^{20}$-16.7 ($c$ 0.1, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J = 8.0$ Hz, 2H), 7.62 (t, $J = 7.6$ Hz, 2H), 7.41-7.26 (m, 9H), 5.57 (d, $J = 9.6$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H), 4.41 (m, 4H), 4.25 (t, $J = 7.2$ Hz, 1H), 4.17-4.05 (m, 1H), 3.68 (s, 3H), 1.26 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.2, 156.7, 143.9, 143.7, 141.2, 137.7, 128.8, 128.3, 127.7, 127.6, 127.0, 125.1, 119.9, 74.1, 70.8, 67.2, 58.7, 52.3, 47.1, 16.1. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{27}$H$_{28}$NO$_5$ 446.1967, found 446.1969.

**2-(Benzyl oxy)ethyl 4-oxopentanoate (3s)**

Yield: 25 mg (98%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.27-7.35 (m, 5H), 4.56 (s, 2H), 4.25 (t, $J = 4.8$ Hz, 3H), 3.66 (t, $J = 4.8$ Hz, 2H), 2.74 (t, $J = 4.8$ Hz, 2H), 2.61 (t, $J = 4.8$ Hz, 2H), 2.18 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 206.4, 172.6, 137.8, 128.3, 127.6, 73.0, 67.7, 63.7, 37.8, 29.7, 27.8. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{14}$H$_{19}$O$_4$ 251.1283, found 251.1286.

**1-Benzyl oxy-3- propyne (3t)**

S10
Yield: 15 mg (93%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 - 7.24 (m, 5H), 4.55 (s, 2H), 3.59 (t, 2H, $J$ = 6.9 Hz), 2.48-2.51 (m, 2H), 1.99(s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.9, 128.3, 127.6, 81.2, 69.2, 68.0, 19.8. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{11}$H$_{13}$O 161.0966, found 161.0967.

1-Azido-2-benzyloxyethane (3u)

Yield: 16 mg (89%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 (m, 4H), 7.24 (m, 1H), 4.57(s, 2H), 3.64 (t, $J$ = 4.4 Hz, 2H), 3.40 (t, $J$ = 4.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.6, 128.4, 127.7, 127.5, 76.6, 73.2, 68.8, 50.7. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_9$H$_{12}$N$_3$O 178.0980, found 178.0983.

1-Benzyl-5-methylidene-2-oxazolidinone (D)

Yield: 17 mg (92%); Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.32 (m, 4H), 7.32-7.26 (m, 1H), 5.80 (ddt, $J$ = 16.8, 9.6, 4.0 Hz, 1H), 5.03-4.93 (m, 2H), 4.48 (s, 2H), 3.46 (t, $J$ = 6.4 Hz, 2H), 2.19-2.12 (m, 2H), 1.74-1.67 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.5, 138.2, 128.3, 127.5, 127.4, 114.6, 72.8, 69.6, 30.3, 28.9. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{12}$H$_{15}$O 177.1279, found 177.1279.
It was separated while compound 3a was prepared. Yield: 17 mg (88%); White solid; M.p. 49-51 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.32 (m, 3H), 7.30 (dd, $J = 9.2$, 3.2 Hz, 2H), 4.74 (d, $J = 2.4$ Hz, 1H), 4.46 (s, 2H), 4.24 (d, $J = 2.4$ Hz, 1H), 4.02 (s, $J = 2.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.59, 148.8, 134.9, 128.9, 128.1, 128.1, 86.7, 47.7, 47.1. HRMS (ESI): m/z [M +H]$^+$ calcd for C$_{10}$H$_{12}$NO$_2$ 190.0868, found 190.0869.

**General Procedure of the IPrAuNTf$_2$-catalyzed Friedel-Crafts reaction of 2-methyfuran**

To a stirred mixture of 2-methyfuran (0.5 mmol) and N-Cbz- N-benzyl-progargylamine (61 mg, 0.1 mmol) in CH$_2$Cl$_2$ (2.0 mL) at room temperature under Ar atmosphere was added IPrAuNTf$_2$ (8 mg, 0.01 mmol). After stirring at room temperature for 2 h (as monitored by TLC), the mixture was filtered through a Celite® pad and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether) to provide 2-benzyl-5-methylfuran.

**2-benzyl-5-methylfuran (F2)**

Yield: 12 mg (69%); colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.24 (s, 3H), 3.91 (s, 2H), 5.86 (s, 2H), 7.30-7.22 (m, 5H). The spectral data fully corresponds to the reported data. $^{[12]}$ HRMS (ESI): m/z [M +H$^+$] calcd for C$_{12}$H$_{13}$O 173.0966, found 173.0967.
References


3d
3f
3g
MOMO\textsubscript{3}O\textsubscript{Bn}

3h
$\text{TrO} \sim \text{O} \sim \text{O} \sim \text{OBn}$

3j
TEDMSO\(-O\)\(\cdot\)\(\cdot\)O\(\cdot\)Bn

S38
TBDMSCO

31
$3m$
$\text{Br} - \text{C} - \text{O} - \text{Bn}$

3q
$\text{N}_3 \text{O}^+ \text{Bn}$

$3u$