Supporting Information
for DOI: 10.1055/s-0035-1561498
© Georg Thieme Verlag KG Stuttgart · New York 2016
Oxidative Cleavage of Silyl Ethers by an Oxoammonium Salt

Jacob J. Loman, a,b Vincent A. Pistritto, a,b Christopher B. Kelly, a and Nicholas E. Leadbeater*a,c

a Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, CT 06269, United States.
b These authors contributed equally
c Department of Community Medicine & Health Care, University of Connecticut Health Center, The Exchange, 263 Farmington Ave, Farmington, CT 06030, United States.
* indicates the main/corresponding author.

Supporting Information: Experimental Studies

Key to Abbreviated Terms S2

General Considerations S2
Comments regarding origins of commercial starting materials, purification of solvents, and our spectroscopic techniques.

Synthesis of Substrates S3
Procedures for the preparations of starting materials and spectral characterization information.

Reactions of Substrates with the Oxoammonium Salt S7
Procedures for oxidation of various species with the oxoammonium salt, isolation procedures, and spectral characterization of products.

1H-NMR Spectra of Synthesized Compounds S11

13C-NMR Spectra of Synthesized Compounds S35
Key to Abbreviated Terms:

CDCl₃: deuterated chloroform  
DCM: dichloromethane  
EtOAc: ethyl acetate  
Et₂O: diethyl ether  
Hex: hexanes  
MeCN: acetonitrile  
TBS: tert-butyldimethylsilyl  
TIPS: triisopropylsilyl  
TBDPS: tert-butyldiphenylsilyl

General Considerations:

General:
NMR Spectra (¹H, ¹³C, ¹⁹F) were performed at 298 K on either a Brüker Avance Ultra Shield 300 MHz NMR, Brüker DRX-400 400 MHz NMR, or Brüker Avance 500 MHz NMR. ¹H-NMR Spectra obtained in CDCl₃ were referenced to residual non-deuterated chloroform (7.26 ppm) in the deuterated solvent. ¹³C NMR Spectra obtained in CDCl₃ were referenced to chloroform (77.3 ppm). Spectra were compared to reference compounds when available. High-resolution mass spectra for novel compounds were obtained using a JEOL AccuTOF-DART SVP 100 in positive direct analysis in real time (DART) ionization method, using PEG as the internal standard. Reactions were monitored by an Agilent Technologies 7820A Gas Chromatograph attached to a 5975 Mass Spectrometer, ¹H NMR, and/or by TLC on silica gel plates (60Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/ethyl acetate as the eluent and visualized using permanganate stain, p-anisaldehyde stain, Seebach’s Stain, and/or UV light. Flash chromatography and silica plugs utilized Dynamic Adsorbents Inc. Flash Silica Gel (60Å porosity, 32-63 μm).

Chemicals:
Deuterated NMR solvents (CDCl₃, DMSO-ᵈoriously) were purchased from Cambridge Isotope Laboratories. CDCl₃ stored over 4Å molecular sieves. Na₂SO₄, DCM, MeCN, Et₂O (ACS Grade and reagent grade), and imidazole were purchased from Sigma-Aldrich. Silyl chlorides were purchased from Oakwood Products, Inc. Alcohol starting materials were either prepared via reduction of their corresponding aldehyde or ketone, or purchased from commercial suppliers. The oxoammonium salt 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate was prepared according to established protocol.¹

Synthesis of Substrates

Synthesis of silyl ethers

General Procedure

To a round bottom flask equipped with a stir bar was added the alcohol substrate (1.0 equiv.), TBS-Cl (1.05 equiv.) and DCM (0.164 M in the alcohol). Imidazole (1.1 equiv.) was added and the solution was allowed to stir at room temperature overnight. The reaction was then quenched with pentane (0.819 M in the alcohol). After quenching, the crude mixture was poured atop a medium filter funnel filled with approximately 1 inch of silica gel previously wet with hexanes. The product was then eluted with approximately 300 mL of a 95:5 by volume hexane to ethyl acetate mixture. The eluent was dried with Na$_2$SO$_4$ and the solvent was removed in vacuo by rotary evaporation to give the pure product.

1-Methyl-3-phenylpropyl tert-butyldimethylsilyl ether (2b)

To a 100 mL round bottom flask equipped with a stir bar was added the alcohol substrate (1.64 g, 10.0 mmol, 1.0 equiv.), TBS-Cl (1.58 g, 10.5 mmol, 1.05 equiv.) and DCM (61 mL, 0.164 M in the alcohol). Imidazole (0.75 g, 11 mmol, 1.1 equiv.) was added and the solution was allowed to stir at room temperature overnight. The reaction was then quenched with pentane (12 mL, 0.819 M in the alcohol). After quenching, the crude mixture was poured atop a medium filter funnel filled with approximately 1 inch of silica gel previously wet with hexanes. The product was then eluted with approximately 300 mL of a 95:5 by volume hexane to ethyl acetate mixture. The eluent was dried with Na$_2$SO$_4$ and the solvent was removed in vacuo by rotary evaporation to give the pure product (1.93 g, 73%) as a clear colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.35 - 7.16 (m, 5H), 3.88 (h, $J = 6.1, 5.7$ Hz, 1H), 2.81 - 2.69 (m, 1H), 2.69 - 2.56 (m, 1H), 1.86 - 1.68 (m, 2H), 1.21 (d, $J = 6.2, 0.9$ Hz, 3H), 0.95 (s, 9H), 0.09 (s, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 142.98 (C), 128.63 (CH), 128.58 (CH), 125.90 (CH), 68.50 (O-CH), 41.83 (CH$_2$), 32.47 (CH$_2$), 26.22 ((CH$_3$)$_3$), 24.05 (CH$_3$), 18.46 (C), -4.00 (Si-CH$_3$), -4.38 (Si-CH$_3$)

tert-Butyldimethylsilyl 4-tert-butylbenzyl ether (2c)

The product (2.62 g, 94%) was obtained as a clear colorless liquid via the same protocol as 2b.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.40 - 7.34 (m, 2H) 7.30 - 7.24 (m, 2H) 4.73 (t, $J = 0.8$ Hz, 2H) 1.33 (s, 9H) 0.96 (s, 9H) 0.11 (s, 6H)
**13C NMR** (100 MHz, CDCl₃) δ ppm 150.06 (C), 138.70 (C), 126.11 (CH), 125.38 (CH), 65.07 (O-CH₂), 34.75 (C), 31.71 ((CH₃)₃), 26.29 ((CH₃)₃), 18.75 (C), -4.94 (Si-(CH₃)₂)


**tert-Butyldimethylsilyl 4-methoxybenzyl ether (2d)**

The product (3.79 g, 96%) was obtained as a clear colorless liquid via the same protocol as 2b with the following modification: the reaction was run on a 15.0 mmol scale.

**1H NMR** (300 MHz, CDCl₃) δ ppm 7.24 (m, 2H), 6.93 - 6.82 (m, 2H), 4.68 (s, 2H), 3.80 (s, 3H), 1.41 (d, 3H), 0.93 (s, 9H), 0.09 (s, 6H).

**13C NMR** (CDCl₃, 100 MHz) δ ppm 159.44 (C), 130.73 (C), 129.66 (CH), 114.05 (CH), 71.70 (O-CH₂), 55.52 (O-CH₃), 25.91 ((CH₃)₃), 18.24 (C), -3.32 (Si-(CH₃)₂)

**tert-Butyldimethylsilyl 4-nitrobenzyl ether (2e)**

The product (2.61 g, 98%) was obtained as a pale yellow solid via the same protocol as 2b.

**1H NMR** (400 MHz, CDCl₃) δ ppm 8.26 - 8.18 (m, 2H), 7.51 (m, 2H), 4.85 (s, 2H), 0.98 (s, 9H), 0.15 (s, 6H)

**13C NMR** (100 MHz, CDCl₃) δ ppm 149.34 (C), 147.30 (C), 126.57 (CH), 123.82 (CH), 64.32 (O-CH₂), 26.15 ((CH₃)₃), 18.65 (C), -5.05 (Si-(CH₃)₂)

**1-(4-Methylphenyl)-ethyl-tert-butyldimethylsilyl ether (2f)**

The product (3.38 g, 90%) was obtained as a clear colorless liquid via the same protocol as 2b with the following modification: the reaction was run on a 15.0 mmol scale.

**1H NMR** (300 MHz, CDCl₃) δ ppm 7.24 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 4.86 (m, 1H), 2.35 (s, 3H), 1.41 (d, J = 6.3 Hz, 3H), 0.92 (s, 9H), 0.10 (m, 6H)

**13C NMR** ¹³C NMR (100 MHz, CDCl₃) δ ppm 144.31 (C), 136.39 (C), 129.05 (CH), 125.41 (CH), 71.00 (O-CH₂), 27.64 (CH₃), 26.20 ((CH₃)₃), 21.37 (CH₃), 18.56 (C), -4.46 (Si-(CH₃)₂)

**HRMS** calcd for C₁₅H₂₅OSi [M - H]⁺: 249.1675, found: 249.1699

**1-Naphthylmethyl-tert-butyldimethylsilyl ether (2g)**

The product (3.54 g, 87%) was obtained as a clear yellow liquid via the same protocol as 2b with the following modification: the reaction was run on a 15.0 mmol scale.

**1H NMR** (300 MHz, CDCl₃) δ ppm 8.07 - 7.96 (m, 1H), 7.94 - 7.82 (m, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.67 - 7.41 (m, 4H), 5.24 (s, 2H), 0.99 (s, 9H), 0.16 (s, 6H)

**13C NMR** (100 MHz, CDCl₃) δ ppm 136.93 (C), 133.83 (C), 131.14 (C), 128.86 (CH), 127.87 (CH), 126.06 (CH), 125.78 (CH), 125.69 (CH), 124.10 (CH), 123.57 (CH), 63.72 (O-CH₂), 26.29 ((CH₃)₃), 18.72 (C), -4.90 (Si-(CH₃)₂)
3,4-Methylenedioxybenzyl-\textit{tert}-butyldimethylsilyl ether (2h)

The product (4.63 g, 77\%) was obtained as a clear colorless liquid via the same protocol as 2b with the following modification: the reaction was run on a 17.0 mmol scale.

\textbf{\textit{H NMR}} (300 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 6.86 (s, 1H), 6.78 (d, \(J = 1.0\) Hz, 2H), 5.96 (s, 2H), 4.66 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H).

\textbf{\textit{C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 147.83 (C), 146.70 (C), 135.61 (C), 119.40 (CH), 108.10 (CH), 107.25 (CH), 100.96 (O-CH\textsubscript{2}-O), 65.09 (O-CH\textsubscript{2}), 26.16 ((CH\textsubscript{3})\textsubscript{3}), 18.59 (C), -5.03 (Si-(CH\textsubscript{3})\textsubscript{2})

\textbf{HRMS} calcd for C\textsubscript{14}H\textsubscript{23}O\textsubscript{3}Si [M - H]\textsuperscript{+}: 265.1260, found: 265.1244

2-Methyl-\textit{tert}-butyldimethylsilyl-ether-1-benzofuran (2i)

The product (3.12 g, 79\%) was obtained as a clear colorless liquid via the same protocol as 2b with the following modification: the reaction was run on a 15.0 mmol scale.

\textbf{\textit{H NMR}} (300 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 7.62 - 7.43 (m, 2H), 7.35 - 7.18 (m, 2H), 6.65 (m, 1H), 4.84 (s, 2H), 0.98 (s, 9H), 0.18 (s, 6H).

\textbf{\textit{C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 155.24 (C), 128.62 (C), 124.14 (C), 122.86 (CH), 121.13 (CH), 111.39 (CH), 103.65 (CH), 59.06 (O-CH\textsubscript{2}), 26.14 ((CH\textsubscript{3})\textsubscript{3}), 18.67 (C), -5.00 (Si-(CH\textsubscript{3})\textsubscript{2})

\textbf{HRMS} calcd for C\textsubscript{15}H\textsubscript{22}O\textsubscript{2}Si [M - H]\textsuperscript{+}: 261.1311, found: 261.0952

Cinnamyl \textit{tert}-butyldimethylsilyl ether (2j)

The product (2.20 g, 89\%) was obtained as a clear colorless liquid via the same protocol as 2b.

\textbf{\textit{H NMR}} (300 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 7.45 - 7.18 (m, 5H), 6.62 (dt, \(J = 15.9, 1.8\) Hz, 1H), 6.31 (dt, \(J = 15.8, 5.0\) Hz, 1H), 4.38 (dd, \(J = 5.0, 1.8\) Hz, 2H), 0.97 (s, 9H), 0.14 (s, 6H)

\textbf{\textit{C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 137.38 (C), 129.73 (CH), 129.41 (CH), 128.74 (CH), 127.55 (CH), 126.63 (CH), 64.13 (O-CH\textsubscript{2}), 26.25 ((CH\textsubscript{3})\textsubscript{3}), 18.71 (C), -4.87 (Si-(CH\textsubscript{3})\textsubscript{2})

5-Phenylpenta-2-en-1-\textit{tert}-butyldimethylsilyl ether (2k)

The product (1.28 g, 92\%) was obtained as a clear colorless liquid via the same protocol as 2b with the following modification: the reaction was run on a 5.0 mmol scale.

\textbf{\textit{H NMR}} (300 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 7.36 - 7.14 (m, 5H), 5.80 - 5.52 (m, 2H), 4.19 - 4.10 (m, 2H), 2.72 (m, 2H), 2.38 (m, 2H), 0.93 (s, 9H), 0.09 (s, 6H)

\textbf{\textit{C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 142.15 (C), 130.49 (CH), 130.10 (CH), 128.68 (CH), 128.53 (CH), 126.03 (CH), 64.18 (O-CH\textsubscript{2}), 35.94 (CH\textsubscript{2}), 34.28 (CH\textsubscript{2}), 26.27 ((CH\textsubscript{3})\textsubscript{3}), 18.70 (C), -4.84 (Si-(CH\textsubscript{3})\textsubscript{2})
3-Phenyl-2-methylprop-1-<i>tert-</i>butyldimethylsilyl ether (2l)<sup>6</sup>

The product (4.74 g, 90%) was obtained as a clear colorless liquid via the same protocol as 2b with the following modification: the reaction was run on a 20.0 mmol scale.

**<sup>1</sup>H NMR** (300 MHz, CDCl₃) δ ppm 7.41 - 7.17 (m, 5H), 6.56 (s, 1H), 4.21 (s, 2H), 1.86 (s, 3H), 0.98 (s, 9H), 0.14 (s, 6H)

**<sup>13</sup>C NMR** (100 MHz, CDCl₃) δ ppm 138.28 (C), 137.69 (C), 129.15 (CH), 128.31 (CH), 126.38 (CH), 124.05 (CH), 68.79 (O-CH₂), 26.25 ((CH₃)₃), 18.71 (C), 15.26 (CH₃), -4.96 (Si-(CH₃)₂)

4-Methylphenylpropargyl <i>tert-</i>butyldimethylsilyl ether (2m)

The product (2.77 g, 89%) was obtained as a clear brown liquid via the same protocol as 2b with the following modification: the reaction was run on a 12.0 mmol scale.

**<sup>1</sup>H NMR** (400 MHz, CDCl₃) δ ppm 7.39 - 7.30 (m, 2H), 7.18 - 7.08 (m, 2H), 4.56 (s, 2H), 2.36 (s, 3H), 0.96 (s, 9H), 0.19 (s, 6H)

**<sup>13</sup>C NMR** (100 MHz, CDCl₃) δ ppm 138.56 (C), 131.77 (CH), 129.27 (CH), 120.21 (C), 87.46 (C), 85.21 (C), 52.59 (O-CH₂), 26.16 ((CH₃)₃), 21.72 (CH₃), 18.63 (C), -4.73 (Si-(CH₃)₂)

**HRMS** calcd for C₁₆H₂₄OSi [MH]<sup>+</sup>: 261.1674, found: 261.1665
Reactions of Substrates with the Oxoammonium Salt (1)

Oxidative Deprotection of Silyl Ethers

General Procedure

To a round bottom flask equipped with a stirbar was added the silyl ether (1 equiv.) and the oxoammonium salt 1 (1 equiv.), followed by acetonitrile (0.2 M in the silyl ether). The solution was heated to 40 °C while stirring for 72 hours. After this time, the crude mixture was diluted with Et₂O (200 mL) and deionized water (200 mL). The phases were separated and the aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with deionized water (≈ 100 mL), brine (≈ 100 mL), and dried with Na₂SO₄. The solvent was removed in vacuo by rotary evaporation, and the resulting crude mixture was adhered to silica gel using 1.5 weight equivalents of SiO₂ (relative to the theoretical yield). The dry-packed material was gently added atop a silica gel plug, and the pure product was obtained using an appropriate solvent system as determined via TLC.

4-Phenyl-2-butanone (3b)

To a 100 mL round bottom flask equipped with a stirbar was added the silyl ether (2.64 g, 10.0 mmol, 1 equiv.) and the oxoammonium salt 1 (3.00 g, 10.0 mmol, 1 equiv.), followed by acetonitrile (50 mL, 0.2 M in the silyl ether). The solution was heated to 40 °C while stirring for 72 hours. After this time, the crude mixture was diluted with Et₂O (200 mL) and deionized water (200 mL). The phases were separated and the aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with deionized water (≈ 100 mL), brine (≈ 100 mL), and dried with Na₂SO₄. The solvent was removed in vacuo by rotary evaporation, and the resulting crude mixture was adhered to silica gel using 1.5 weight equivalents of SiO₂ (relative to the theoretical yield). The dry-packed material was gently added atop a silica gel plug. The plug was washed with an excess of hexanes (≈ 5 column volumes). The desired product was eluted off the plug via a 95:5 by volume mixture of hexanes:ethyl acetate (3-4 column volumes). The
solvent was removed in vacuo by rotary evaporation affording the pure aldehyde 3b (0.68 g, 46%) as a clear yellow liquid.

1H NMR (400 MHz, CDCl3) δ ppm 7.34 - 7.19 (m, 5H), 2.97 - 2.88 (m, 2H), 2.80 - 2.75 (m, 2H), 2.15 (s, 3H)

13C NMR (100 MHz, CDCl3) δ ppm 207.96 (C), 141.08 (C), 128.56 (CH), 128.37 (CH), 126.18 (CH), 45.17 (CH2), 30.08 (CH2), 29.81 (CH3)

4-tert-Butylbenzaldehyde (3c)

The product (0.67 g, 59%) was obtained as a clear yellow liquid via the same protocol as 3b with the following modification: the reaction was run on a 7.0 mmol scale.

1H NMR (400 MHz, CDCl3) δ ppm 9.98 (s, 1H), 7.88 - 7.77 (m, 2H), 7.61 - 7.48 (m, 2H), 1.36 (s, 9H)

13C NMR (100 MHz, CDCl3) δ ppm 192.05 (CH), 158.53 (C), 134.30 (C), 129.84 (CH), 126.13 (CH), 35.49 (C), 31.23 (CH3)

4-Methoxybenzaldehyde (3d)

The product (1.02 g, 75%) was obtained as a clear yellow liquid via the same protocol as 3b with the following modification: the reaction was run on a 10.0 mmol scale.

1H NMR (300 MHz, CDCl3) δ ppm 9.90 (s, 1H), 7.91 - 7.79 (m, 2H), 7.08 - 6.96 (m, 2H), 3.91 (s, 3H)

13C NMR (100 MHz, CDCl3) δ ppm 190.77 (CH), 164.65 (C), 131.97 (CH), 129.98 (C), 114.35 (CH), 55.58 (CH3)

4-Nitrobenzaldehyde (3e)

The product (1.22 g, 81%) was obtained as a light orange solid via the same protocol as 3b with the following modifications: the reaction was run on a 10.0 mmol scale. No silica gel plug was utilized. Product was obtained as a solid that was washed with hexanes using a Büchner funnel to remove residual impurities.

1H NMR (400 MHz, CDCl3) δ ppm 10.17 (s, 1H), 8.46 - 8.35 (m, 2H), 8.14 - 8.03 (m, 2H)

13C NMR (100 MHz, CDCl3) δ ppm 190.53 (CH), 151.37 (C), 140.31 (C), 130.72 (CH), 124.54 (CH)
4’-Methylacetophenone (3f)

The product (0.86 g, 64%) was obtained as a light yellow liquid via the same protocol as 3b with the following modification: the reaction was run on a 10.0 mmol scale.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.89 - 7.81 (m, 2H), 7.29 - 7.21 (m, 2H), 2.60 - 2.54 (m, 3H), 2.41 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 198.11 (C), 144.14 (C), 135.02 (C), 129.51 (CH), 128.72 (CH), 26.81 (CH$_3$), 21.91 (CH$_3$)

1-Naphthaldehyde (3g)

The product (1.27 g, 81%) was obtained as a dark orange liquid via the same protocol as 3b with the following modifications: the reaction was run on a 10.0 mmol scale. The desired product was eluted off the plug via a 9:1 by volume mixture of hexanes:ethyl acetate (2-3 column volumes).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 10.44 (s, 1H), 9.33 - 9.24 (m, 1H), 8.17 - 8.11 (m, 1H), 8.06 - 8.00 (m, 1H), 7.97 - 7.93 (m, 1H), 7.76 - 7.60 (m, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 193.61 (CH), 136.75 (CH), 135.35 (CH), 133.79 (C), 131.44 (C), 130.58 (C), 129.13 (CH), 128.58 (CH), 127.04 (CH), 124.95 (CH)

Piperonal (3h)

The product (1.44 g, 96%) was obtained as a light orange crystal via the same protocol as 3b with the following modification: the reaction was run on a 10.0 mmol scale.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 9.84 (s, 1H), 7.44 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.28 (s, 1H), 6.96 (d, $J = 7.9$ Hz, 1H), 6.10 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 189.73 (CH), 152.53 (C), 148.12 (C), 131.29 (C), 128.11 (CH), 107.82 (CH), 106.32 (CH), 101.73 (O-CH$_2$-O)

2-Benzofurancarboxaldehyde (3i)

The product (1.18 g, 81%) was obtained as a clear orange oil via the same protocol as 3b with the following modifications: the reaction was run on a 10.0 mmol scale. The desired product was eluted off the plug via a 95:5 by volume mixture of hexanes:ethyl acetate (5 column volumes).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 9.88 (d, $J = 1.1$ Hz, 1H), 7.78 - 7.73 (m, 1H), 7.64 - 7.49 (m, 3H), 7.38 - 7.31 (m, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 180.02 (CH), 156.57 (C), 153.02 (C), 129.49 (CH), 126.96 (C), 124.50 (CH), 123.94 (CH), 117.95 (CH), 113.02 (CH)
Cinnamaldehyde (3j)

The product (0.41 g, 61%) was obtained as a clear pale yellow liquid via the same protocol as 3b with the following modification: the reaction was run on a 5.0 mmol scale.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 9.73 (d, $J = 7.7$ Hz, 1H), 7.62 - 7.44 (m, 6H), 6.75 (dd, $J = 15.9, 7.7$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 193.67 (CH), 152.77 (CH), 134.04 (C), 131.29 (CH), 129.13 (CH), 128.54 (CH)

5-Phenyl-2-pentenal (3k)

The product (0.35 g, 60%) was obtained as a clear yellow oil via the same protocol as 3b with the following modification: the reaction was run on a 3.6 mmol scale.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 9.50 (d, $J = 7.8$ Hz, 1H), 7.35 - 7.16 (m, 5H), 6.86 (dt, $J = 15.7, 6.6$ Hz, 1H), 6.14 (ddt, $J = 15.7, 7.9, 1.5$ Hz, 1H), 2.89 - 2.80 (m, 2H), 2.67 (dtt, $J = 8.1, 6.6, 1.3$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 194.11 (CH), 157.56 (CH), 140.31 (C), 133.41 (CH), 128.68 (CH), 128.42 (CH), 126.46 (CH), 34.31 (CH$_2$), 34.14 (CH$_2$)

$\alpha$-Methyl cinnamaldehyde (3l)

The product (0.640 g, 44%) was obtained as a clear yellow liquid via the same protocol as 3b with the following modification: the reaction was run on a 10.0 mmol scale.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 9.62 (s, 1H), 7.59 - 7.39 (m, 5H), 7.29 (s, 1H), 2.11 (d, $J = 1.4$ Hz, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 195.51 (CH), 149.83 (CH), 138.41 (C), 135.24 (C), 130.13 (CH), 129.66 (CH), 128.80 (CH), 11.01 (CH$_3$)

(4-Methylphenyl)propargyl aldehyde (3m)

The product (1.17 g, 81%) was obtained as a clear red-orange liquid via the same protocol as 3b with the following modification: the reaction was run on a 10.0 mmol scale.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 9.43 (s, 1H), 7.55 - 7.49 (m, 2H), 7.26 - 7.20 (m, 2H), 2.42 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 176.83 (CH), 142.29 (C), 133.42 (CH), 129.66 (CH), 116.41 (C), 95.97 (C), 88.61 (C), 21.86 (CH$_3$)
$^1$H-NMR Spectra of Synthesized Compounds

1-methyl-3-phenylpropyl tert-butyldimethylsilyl ether (2b)
300 MHz, CDCl$_3$
tert-butyldimethylsilyl 4-tert-butylbenzyl ether (2c)
400 MHz, CDCl₃
*tert*-butyldimethylsilyl 4-methoxybenzyl ether (2d)
300 MHz, CDCl₃
*tert*-butyldimethylsilyl 4-nitrobenzyl ether (2e)

400 MHz, CDCl₃
1-(4-methylphenyl)-ethyl-\textit{tert}-butyldimethylsilyl ether (2f) 
300 MHz, CDCl₃
1-napthylmethyl-tert-butyldimethylsilyl ether (2g)
300 MHz, CDCl₃
3,4-methylenedioxybenzyl-\textit{tert}-butyldimethylsilyl ether (2h)

300 MHz, CDCl₃
2-methyl-tert-butylimethyldimethylsilyl-ether-1-benzofuran (2i)
300 MHz, CDCl₃

![Chemical Structure and NMR Spectra](image)
cinnamyl tert-butyltrimethylsilyl ether (2j)
300 MHz, CDCl₃
5-phenylpenta-2-en-1-tert-butyldimethylsilyl ether (2k)
300 MHz, CDCl₃
3-phenyl-2-methylpropen-1-tert-butyldimethylsilyl ether (2l)
300 MHz, CDCl₃
4-methylphenylpropargyl \textit{tert-}butyldimethylsilyl ether (2m)

300 MHz, CDCl$_3$
4-phenyl-2-butanone (3b)
400 MHz, CDCl₃
4-tert-butylbenzaldehyde (3c)
400 MHz, CDCl₃

3c
4-methoxybenzaldehyde (3d)
300 MHz, CDCl₃
4-nitrobenzaldehyde (3e)
400 MHz, CDCl₃
4’-methylacetophenone (3f)
400 MHz, CDCl₃
1-naphthaldehyde (3g)
400 MHz, CDCl₃

\[
\text{\includegraphics{3g}}
\]
piperonal (3h)
400 MHz, CDCl₃
2-benzofurancarboxaldehyde (3i)

400 MHz, CDCl₃
cinnamaldehyde (3j)
300 MHz, CDCl₃
5-phenyl-2-pentenal (3k)
300 MHz, CDCl₃
α-methyl cinnamaldehyde (3l)
300 MHz, CDCl₃
(4-methylphenyl)propargyl aldehyde (3m)
300 MHz, CDCl₃
$^{13}$C-NMR Spectra of Synthesized Compounds

1-methyl-3-phenylpropyl tert-butyldimethylsilyl ether (2b)
100 MHz, CDCl$_3$
tert-butyldimethylsilyl 4-tert-butylnylbenzyl ether (2c)
100 MHz, CDCl₃
tert-butyldimethylsilyl 4-methoxybenzyl ether (2d)
100 MHz, CDCl₃
*tert*-butyldimethylsilyl 4-nitrobenzyl ether (2e)

100 MHz, CDCl$_3$
1-(4-methylphenyl)-ethyl-tert-butyldimethylsilyl ether (2f)
100 MHz, CDCl₃
1-napthylmethyl-<i>tert</i>-butyldimethylsilyl ether (2g)
100 MHz, CDCl₃
3,4-methylenedioxybenzyl-\textit{ tert-}butyldimethylsilyl ether (2h)
100 MHz, CDCl₃

\begin{figure}
\centering
\includegraphics[width=\textwidth]{s41}
\end{figure}
2-methyl-\textit{tert}-butyldimethylsilyl-ether-1-benzofuran (2i)

100 MHz, CDCl$_3$
cinnamyl tert-butyl(dimethyl)silyl ether (2j)
100 MHz, CDCl₃
5-phenylpenta-2-en-1-tert-butyldimethylsilyl ether (2k)
100 MHz, CDCl₃
3-phenyl-2-methylpropen-1-tert-butyldimethylsilyl ether (2l)
100 MHz, CDCl₃
4-methylphenylpropargyl tert-butyldimethylsilyl ether (2m)
100 MHz, CDCl₃
4-phenyl-2-butanone (3b)
100 MHz, CDCl₃
4-tert-butylbenzaldehyde (3c)
100 MHz, CDCl₃
4-methoxybenzaldehyde (3d)
100 MHz, CDCl₃
4-nitrobenzaldehyde (3e)
100 MHz, CDCl₃
4’-methylacetophenone (3f)
100 MHz, CDCl₃
1-naphthaldehyde (3g)
100 MHz, CDCl₃
piperonal (3h)
100 MHz, CDCl₃
2-benzofurancarboxaldehyde (3i)  
100 MHz, CDCl₃
cinnamaldehyde (3j)
100 MHz, CDCl₃
5-phenyl-2-pentenal (3k)
100 MHz, CDCl₃
\( \alpha \)-methyl cinnamaldehyde (3l)

100 MHz, CDCl\(_3\)
(4-methylphenyl)propargyl aldehyde (3m)
100 MHz, CDCl₃