Supporting Information (ESI)

Chemoselective Activation of Trimethylsilyl Enol Ether Functionalities in the Presence of Silyl-Protected Alcohols by Trimethylsilyl – Nonaflyl Exchange

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This article is dedicated to the memory of our colleague and friend Dr. Ilya Lyapkalo who passed away on September 10, 2010

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Table of contents:
Picture of the apparatus for recondensation S2

1H and 13C NMR data for known compounds S3-S4

1H and 13C NMR spectra of new compounds S5-S17

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Figure 1. Apparatus for recondensation.
**1H and 13C NMR data for known compounds**

**[2-Trimethylsilyloxy-3-methyl-6R-(1'-methyl-1'-trimethylsilyloxy)ethyl]-1,3-cyclohexadiene (1a)**

1H NMR (400 MHz, CDCl$_3$): δ = 0.11 (s, 9H, TMS), 0.21 (s, 9H, TMS), 1.16 (s, 3H, Me-1’), 1.18 (s, 3H, Me-1’), 1.68 (d, $J = 2.0$, 3H, Me-3), 1.93–2.16 (m, 2H, H-5), 2.42 (ddd, $J = 13.8$, 8.8 and 3.4 Hz, 1H, H-6), 4.90 (d, $J = 3.4$ Hz, 1H, H-1), 5.53–5.55 (m, 1H, H-4).

13C NMR (100 MHz, CDCl$_3$): δ = 0.20, 2.60, 17.20; 27.26, 27.52, 27.68, 46.56, 76.46, 104.62, 123.51, 131.82, 149.93.

**1,4-Bis(trimethylsilyloxy)cyclohex-1-ene (1b)**

1H NMR (400 MHz, C$_6$D$_6$): δ = 0.11 (s, 9H, TMS), 0.17 (s, 9H, TMS), 1.73–1.78 (m, 2 H), 2.10–2.31 (m, 4 H), 3.84–3.90 (m, 1H, H-4), 4.79–4.81 (m, 1H, H-2).

13C NMR (100 MHz, C$_6$D$_6$): δ = 0.39, 0.42, 28.71, 32.29, 33.85, 67.63, 100.66, 150.44.

**2,4-Bis(trimethylsilyloxy)-4-methylpent-1-ene (1c)**

1H NMR (400 MHz, CDCl$_3$): δ = 0.11 (s, 9H, TMS), 0.20 (s, 9H, TMS), 1.27 (s, 6H, 2Me-3), 2.20 (s, 2H, H-3), 4.07 (m, 2H, H-1).

13C NMR (100 MHz, CDCl$_3$): δ = –0.79, 1.82, 29.12, 50.96, 72.93, 91.87, 156.12.

**2,3-Bis(trimethylsilyloxy)-3-methylbut-1-ene (1d)**

1H NMR (400 MHz, C$_6$D$_6$): δ = 0.17 (s, 9H, TMS), 0.22 (s, 9H, TMS), 1.43 (s, 6H, 2Me-3), 4.15 (d, $J = 1.0$ Hz, 1H, H-1), 4.69 (d, $J = 1.0$ Hz, 1H, H-1).

13C NMR (100 MHz, C$_6$D$_6$): δ = 0.18, 2.68, 29.17, 75.44, 87.00, 164.57.

**3-(tert-Butyldimethylsilyloxy)-3-methyl-2-butanone (starting material for 1e)**

1H NMR (400 MHz, CDCl$_3$): δ = 0.12 (s, 6H, 2Me-TBS), 0.91 (s, 9H, t-Bu-TBS), 1.33 (s, 6H, 2Me-3), 2.22 (s, 3H, Me-2).

13C NMR (100 MHz, CDCl$_3$): δ = –2.16, 18.23, 24.79, 25.92, 27.08, 80.13, 213.86.
3-tert-Butyldimethylsilyloxy-2-butanone (starting material for 1g)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.08$ (s, 6H, 2Me-TBS), 0.91 (s, 9H, t-Bu-TBS), 1.27 (d, $J = 6.8$ Hz, 3H, Me-3), 2.18 (s, 3H, Me-2), 4.11 (q, $J = 6.8$ Hz, 1H, H-3).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -4.92$, −4.58, 18.21, 20.81, 25.87, 75.19, 212.70.

2-Trimethylsilyloxy-3-tert-butyldimethylsilyloxybut-1-ene (1g)

$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.08$ (s, 3H, Me-TBS), 0.10 (s, 3H, Me-TBS), 0.18 (s, 9H, TMS), 1.00 (s, 9H, t-Bu-TBS), 1.38 (d, $J = 6.3$ Hz, 1H, Me-3), 4.15 (q, $J = 6.3$ Hz, 1H, H-3), 4.22 (br. s, 1H, H-1), 4.65 (br. s, 1H, H-1).
$^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta = -4.80$, −4.66, 0.20, 18.48, 22.87, 26.11, 70.29, 87.99, 162.41.

2-(tert-Butyldimethylsilyloxy)cyclohexanone (starting material for 1h)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.03$ (s, 3H, Me-TBS), 0.10 (s, 3H, Me-TBS), 0.89 (s, 9H, t-Bu-TBS), 1.61–1.81 (m, 3H), 1.89–1.93 (m, 2H), 2.07–2.14 (m, 1H), 2.19–2.26 (m, 1H), 2.51–2.58 (m, 1H), 4.11 (ddd, $J = 1.0$, 5.5, 9.8 Hz, 1H, H-6).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -5.14$, −4.51, 18.54, 23.03, 25.93, 27.61, 37.26, 40.11, 76.98, 209.98.

1,3-Bis(trimethylsilyloxy)-2-methylbut-3-ene (1i)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.10$ (s, 9H, TMS), 0.20 (s, 9H, TMS), 1.01 (d, $J = 6.8$ Hz, 3H, Me-3), 2.20–2.32 (m, 1H, H-3), 3.35 (dd, $J = 9.8$ and 7.5 Hz, 1H, H-4), 3.67 (dd, $J = 9.8$ and 6.0 Hz, 1H, H-4), 4.03–4.06 (m, 2H, H-1).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = -0.52$, −0.11, 14.90, 42.43, 64.34, 87.52, 152.40.

2,3-Bis(trimethylsilyloxy)but-1-ene (1j)

$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.13$ (s, 9H, TMS), 0.18 (s, 9H, TMS), 1.38 (d, $J = 6.5$ Hz, 3H, Me-3), 4.13 (q, $J = 6.5$ Hz, 1H, H-3), 4.21 (brs, 1H, H-1), 4.60 (t, $J = 0.9$ Hz, 1H, H-1).
$^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta = 0.14$, 0.23, 22.79, 70.04, 88.39, 162.21.
$^1$H NMR and $^{13}$C NMR spectra (C$_6$D$_6$) of compound 1e
$^1$H NMR and $^{13}$C NMR spectra (C$_6$D$_6$) of compound 1f
$^1$H NMR and $^{13}$C NMR spectra (C$_6$D$_6$) of compound 1h
$^1$H NMR and $^{13}$C NMR spectra (CDCl$_3$) of compound 2a
$^{1}H$ NMR and $^{13}$C NMR spectra (C$_6$D$_6$) of compound 2b
$^1$H NMR and $^{13}$C NMR spectra (CDCl$_3$) of compound 2e
$^1$H NMR and $^{13}$C NMR spectra (C$_6$D$_6$) of compound 2d
$^1$H NMR and $^{13}$C NMR spectra ($C_6D_6$) of compound 2e
$^{1}$H NMR and $^{13}$C NMR spectra ($C_6D_6$) of compound 2f
$^1$H NMR and $^{13}$C NMR spectra (CDCl$_3$) of compound 2g
$^1$H NMR and $^{13}$C NMR spectra (CDCl$_3$) of compound 2h
$^1$H NMR and $^{13}$C NMR spectra (CDCl$_3$) of compound 2i
$^1$H NMR and $^{13}$C NMR spectra ($\text{C}_6\text{D}_6$) of compound 2j