Supporting Information

R₃Al-R₃'SiOTf-Et₃N: Novel and Powerful Reagent System for Stereospecific Alkylation-Silylation Reactions of Epoxides

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Typical experimental procedure:

To a solution of the epoxide 1 (100 mg, 0.78 mmol) in dry CH₂Cl₂ (2 mL) was added Me₃Al (1 M solution in hexane, 1.2 mL, 1.2 mmol, 1.5 equiv.) and TMSOTf (0.23 mL, 1.2 mmol, 1.5 equiv.) at – 50 °C under an Argon atmosphere. After stirring for 45 min at the same temperature, Et₃N (0.16 mL, 1.2 mmol, 1.5 equiv.) was added and stirring was continued for an additional 15 min at the same temperature. The reaction was quenched with 0.05M HCl and the mixture was diluted with ethyl acetate (50 mL), and successively washed with water (5 X 25 mL) and brine (25 mL), dried (anhydrous MgSO₄) and concentrated in vacuo. The crude product was immediately purified by a silica gel column chromatography to give the pure trimethyl-(2-methyl-1-propylpentyloxy)-silane (159 mg, 93%). It is essential to purify the crude product immediately to obtain the product in high yield. Quenching the reaction with 1M HCl without

adding the Et₃N and followed by the same work-up procedure to afford the pure 5-methyl-oct-4-ol (93 mg, 91%).

Typical experimental procedure for the reaction of epoxides with Gillman reagent

To a slurry of CuI (297.5 mg, 1.56 mmole) in dry ether (2 mL) at 0 °C, methyl lithium (1M solution in ether, 3.1 mL, 3.12 mmol) was added drop wise to form Me₂CuLi. To this, a solution of the epoxide **1** (100mg, 0.78 mmol) in dry ether (1 mL) was added *via* cannula. The mixture was further stirred for 2 h at 0 °C. The reaction was quenched with aqueous CuSO₄ solution (2 mL) and extracted with ether (2 x 25mL). The organic layer was successively washed with aqueous CuSO₄, water, brine and dried over MgSO₄, and concentrated under reduced pressure. Purification of the crude product by a silica gel column (5% hexane: EtOAc) afforded 5-methyl-oct-4-ol in 67% yield.

Table 1. ¹H NMR and ¹³C NMR of the products

Structure of the product	¹ H NMR(270 MHz, CDCl ₃ /TMS): ppm	¹³ C NMR(67.8 MHz, CDCl ₃ /TMS): ppm
By Me₃Al/TMSOTf method: 3.45(m, 1H, CH), 1.7(bris, 1H, OH), 1.7(m, 1H, CH), 1.2-1.5(m, 8H, <i>methylenes</i>), 0.97(t, <i>J</i> =3.51 Hz, 3H, CH ₃), 0.90(t, <i>J</i> =7.02 Hz, 3H, CH ₃), 0.87(d, <i>J</i> =5.4 Hz, 3H, CH ₃).	76.03, 38.87, 35.83, 34.45, 20.75, 19.63, 15.54, 14.73, 14.51.
	By Gillman Reagent method: 3.45(m, 1H, CH), 1.7(bris, 1H, OH), 1.7(m, 1H, CH), 1.2-1.5(m, 8H, <i>methylenes</i>), 0.97(t, <i>J</i> =3.51 Hz, 3H, CH ₃), 0.90(t, <i>J</i> =7.02 Hz, 3H, CH ₃), 0.87(d, <i>J</i> =5.4 Hz, 3H, CH ₃).	75.93, 38.79, 35.75, 34.36, 20.66, 19.64, 15.55, 14.73, 14.52.

<p>By Me₃Al/TMSOTf method: 3.52(m, 1H, CH), 1.67(bris, 1H, OH), 1.1-1.5(m, 9H, CH and <i>methylenes</i>), 0.97(t, <i>J</i>=4.05 Hz, 3H, CH₃), 0.90(t, <i>J</i>=7.02 Hz, 3H, CH₃), 0.85(d, <i>J</i>=6.75 Hz, 3H, CH₃).</p>	<p>75.63, 38.71, 37.43, 36.37, 21.27, 20.24, 15.16, 14.97, 14.36.</p>
	<p>By Gillman Reagent method: 3.52(m, 1H, CH), 1.58(bris, 1H, OH), 1.1-1.5(m, 9H, CH and <i>methylenes</i>), 0.97(t, <i>J</i>=4.05 Hz, 3H, CH₃), 0.90(t, <i>J</i>=7.02 Hz, 3H, CH₃), 0.85(d, <i>J</i>=6.75 Hz, 3H, CH₃).</p>	<p>75.66, 38.71, 37.44, 36.38, 21.27, 20.24, 15.16, 14.97, 14.37.</p>
<p>3.51(m, 1H, CH), 1.2-1.6(m, 9H, CH and <i>methylenes</i>), 0.91(t, <i>J</i>=7.02 Hz, 6H, 2CH₃), 0.87(d, <i>J</i>=6.75 Hz, 3H, CH₃).0.07(s, 9H, CH₃)</p>	<p>77.26, 39.56, 35.98, 35.61, 21.66, 20.30, 15.70, 15.44, 15.30, 1.56(3C).</p>
<p>3.68(m, 1H, CH), 1.2-1.5 (m, 11H, methine and methylenes), 0.86(t, 3H, CH₃), 0.91(t, 9H, 3CH₃), 0.98(t, <i>J</i> =7.8Hz, 6H, CH₃), 0.57(q, <i>J</i> =7.8Hz, 6H, 3CH₂)</p>	<p>74.14, 45.78, 35.22, 32.56, 22.41, 21.41, 19.81, 15.00, 14.68, 12.83, 7.37(3C), 5.63(3C)</p>
<p>3.51 (m, 1H, CH), 1.4-1.1(m, 9H, CH and 4CH₂), 0.98(merged t, 6H, 2CH₃), 0.91(s, 9H, t-Bu), 0.85(d, <i>J</i>=6.75 Hz, 3H, CH₃), 0.6(s, 6H, 2CH₃)</p>	<p>76.56, 38.62, 35.33, 34.58, 26.32(3C), 21.01, 19.52, 14.82, 14.63, 12.61 -4.03, -4.09</p>
<p>3.67(m, 1H, CH), 1.2-1.5 (m, 11H, <i>methine and methylenes</i>), 0.86(merged triplets, 9H, 3CH₃), 0.09(s, 9H, 3CH₃)</p>	<p>74.34, 45.66, 35.33, 32.43, 22.46, 21.25, 19.80, 14.90, 14.54, 12.72, 0.88 (3C)</p>

	3.7(m, 1H, CH), 2.4(m, 1H, CH), 1.7-1.2(m, 8H, <i>methylenes</i>), 0.9(m, 9H, 3CH ₃), 0.02(s, 18H, 6CH ₃)	76.16, 75.02, 67.15, 54.34, 36.71, 35.96, 20.74, 19.42, 14.94, 14.45, 1.33 (3C), 1.26 (3C).
	3.52(m, 1H, CH), 1.3-1.46 (m, 9H, <i>methine and methylenes</i>), 0.96(merged t, 6H, 2CH ₃), 0.91(merged t, 9H, 3CH ₃), 0.85(d, <i>J</i> = 6.75 Hz, 3H, CH ₃), 0.57(q, <i>J</i> = 7.8 Hz, 6H, 3CH ₂)	75.15, 38.16, 36.88, 35.82, 20.74, 19.70, 14.62, 14.44, 13.83, 6.88(3C), 6.08(3C).
	3.52 (m, 1H, CH), 1.42-1.14(m, 9H, CH and CH ₂), 0.98(merged t, 6H, 2CH ₃), 0.91(s, 9H, t-Bu), 0.81(d, <i>J</i> = 6.75 Hz, 3H, CH ₃), 0.06(s, 6H, 2CH ₃)	75.89, 37.81, 36.08, 34.99, 26.30, 26.05(3C), 21.11, 19.50, 14.82, 14.77, 14.33, -3.84(2C)
	3.68(m, 1H, CH), 1.2-1.4 (m, 11H, <i>methine and methylenes</i>), 0.98(t, <i>J</i> = 7.8 Hz, 6H, 2CH ₃), 0.91(t, 9H, 3CH ₃), 0.86(t, 3H, CH ₃), 0.5(q, <i>J</i> = 7.8 Hz, 6H, 3CH ₂)	73.85, 45.57, 35.17, 31.76, 23.07, 21.38, 19.70, 14.90, 14.62, 12.67, 7.31(3C), 5.56(3C)
	3.12(m, 1H, CH), 1.82-1.61(m, 5H, CH and CH ₂), 1.41-1.15.(m, 4H, <i>methylenes</i>), 0.91(t, <i>J</i> = 7.29 Hz, 9H, 3CH ₃) 0.85(d, <i>J</i> = 8.91 Hz, 3H, CH ₃), 0.6(q, <i>J</i> = 7.29 Hz, 6H, 3CH ₂)	76.53, 40.42, 36.15, 33.87, 25.78, 25.41, 19.20, 7.05(3C), 5.25(3C).
	3.1(m, 1H, CH), 1.2-1.7(m, 9H, CH and <i>methylenes</i>), 0.9(d, <i>J</i> = 8.91 Hz, 3H, CH ₃), 0.8(s, 9H, t-Bu), 0.2(s, 6H, 2CH ₃)	76.53, 40.42, 36.03, 33.78, 26.02, 25.77(3C), 25.32, 19.36, -3.92, -4.51

3.2 (m, 1H, CH), 1.7-1.9(m, 7H, CH and CH ₂), 1.2(m, 4H, CH ₂), 0.9(t, $J=7.56$ Hz, 9H, 3CH ₃), 0.8(t, $J=8.91$ Hz, 3H, CH ₃), 0.6(q, $J=7.29$ Hz, 6H, 3CH ₂)	75.33, 46.74, 36.23, 29.59, 25.66, 25.18, 24.85, 11.18, 7.11(3C), 5.35(3C).
7.06(ABq, $J=13.23$ Hz & $J=8.37$ Hz 1H, CH), 5.8 (d, $J=15.62$ Hz, 1H, CH), 4.2(q, $J=7.02$ Hz, 2H, CH ₂), 3.54(m, 1H, CH), 2.4(m, 1H, CH), 1.7(brs, 1H, OH), 1.5-1.4(m, 4H, <i>methylenes</i>), 1.3(t, $J=7.02$ Hz, 3H, CH ₃), 1.1(d, $J=6.75$, 3H, CH ₃), 0.93(t, $J=6.2$ Hz, 3H, CH ₃).	167.09, 150.86, 122.76, 75.22, 61.05, 43.34, 37.51, 19.77, 16.63, 15.06, 14.82.
6.95(dd, $J=8.1$ Hz, 1H, CH), 5.81 (ABq, $J=1.3$ Hz, & $J=1.0$ Hz, 1H, CH), 4.21(q, $J=7.2$ Hz, 2H, CH ₂), 3.60(m, 1H, CH), 2.4(m, 1H, CH), 1.5-1.4(m, 4H, <i>methylenes</i>), 1.3(t, $J=7.2$ Hz, 3H, CH ₃), 1.1(d, $J=7.02$, 3H, CH ₃), 0.93(t, $J=6.75$ Hz, 3H, CH ₃), 0.02(s, 9H, CH ₃).	166.74, 151.43, 121.31, 75.67, 60.39, 42.66, 36.90, 19.28, 15.64, 14.58, 14.45, 0.07(3C).
6.95(dd, $J=7.8$ Hz, 1H, CH), 5.82(ABq, $J=1.5$ Hz, & $J=1.5$ Hz, 1H, CH), 4.21(q, $J=7.2$ Hz, 2H, CH ₂), 3.61(m, 1H, CH), 2.42(m, 1H, CH), 1.5-1.4(m, 4H, <i>methylenes</i>), 1.3(t, $J=7.2$ Hz, 3H, CH ₃), 1.1(d, $J=7.02$, 3H, CH ₃), 0.93(t, $J=6.75$ Hz, 3H, CH ₃), 0.90(t, $J=7.8$ Hz, 9H, 3CH ₃), 0.5(q, $J=7.8$ Hz, 6H, 3CH ₂).	166.37, 151.06, 120.76, 74.98, 59.97, 41.95, 36.24, 18.60, 14.73, 14.15, 14.13, 6.84(3C), 5.00(3C).
6.97(dd, $J=7.8$ Hz, 1H, CH), 5.82(ABq, $J=1.5$ Hz, & $J=1.5$ Hz, 1H, CH), 4.21(q, $J=7.2$ Hz, 2H, CH ₂), 3.59(m, 1H, CH), 2.42(m, 1H, CH), 1.5-1.4(m, 4H,	166.82, 151.56, 121.21, 75.32, 60.40, 42.17, 36.58, 26.18(3C), 18.89,

	methylenes), 1.3(t, $J=7.2\text{Hz}$, 3H, CH_3), 1.0(d, $J=6.75$, 3H, CH_3), 0.93(t, $J=7.02\text{Hz}$, 3H, CH_3), 0.87(s, 9H, $t\text{-Bu}$), 0.02(s, 6H, 2 CH_3).	18.43, 15.24, 14.60, -3.95, -4.18.
6.8 (dd, $J=9.45\text{Hz}$, 1H), 5.8(d, $J=15.93\text{Hz}$, 1H), 4.2(q, $J=7.02\text{ Hz}$, 2H), 3.6(m, 1H, CH), 2.1(m, 1H, CH), 1.2(m, 8H),), 0.9(t, $J=7.56\text{ Hz}$, 9H, 3 CH_3), 0.8(t, $J=8.91\text{Hz}$, 3H, CH_3), 0.5(q, $J=7.29\text{Hz}$, 6H, 3 CH_2)	166.35, 149.93, 122.63, 74.54, 60.15, 50.26, 37.28, 23.25, 18.92, 14.34, 14.29, 12.34, 7.04(3C), 5.30 (3C)
7.06(ABq, $J=13.23\text{Hz}$ & $J=8.37\text{Hz}$ 1H, CH minor isomer peaks merged), 6.07(ABq, $J=1.6\text{Hz}$, & $J=1.6\text{Hz}$, 1H, minor isomer CH), 5.81(d, $J=15.62\text{Hz}$, 1H, CH), 4.21(q, $J=7.02\text{Hz}$, 2H, CH_2), 3.64(m, 1H, CH), 2.43(m, 1H, CH), 1.8(brs, 1H, OH), 1.5-1.4(m, 4H, methylenes), 1.3(t, $J=7.02\text{Hz}$, 3H, CH_3), 1.1(d, $J=6.75$, 3H, CH_3), 0.93(t, $J=6.2\text{Hz}$, 3H, CH_3). All other minor isomer peaks are merged.	167.09, 150.86, 122.76, 75.22, 61.05, 43.34, 37.51, 19.77, 16.63, 15.06, 14.82 and minor merged peaks.
6.99(dd, $J=8.1\text{Hz}$, 1H, CH, minor isomer peaks merged), 5.9(ABq, $J=1.6\text{Hz}$, & $J=1.6\text{Hz}$, 1H, minor isomer CH), 5.7 (ABq, $J=1.3\text{Hz}$, & $J=1.0\text{Hz}$, 1H, major isomer CH), 4.21(q, $J=7.2\text{Hz}$, 2H, CH_2), 3.58(m, 1H, CH), 2.40(m, 1H, CH), 1.5-1.4(m, 4H, methylenes), 1.3(t, $J=7.2\text{Hz}$, 3H, CH_3), 1.03(d, $J=7.02$, 3H, CH_3), 0.93(t, $J=6.75\text{Hz}$, 3H, CH_3), 0.01(s, 9H, CH_3). All other minor peaks are merged.	166.35, 151.47, 149.98(minor), 121.67, 120.28(minor), 75.24, 60.13, 60.11(minor), 44.32, 40.61(minor), 38.44, 36.33(minor), 20.88 (minor), 18.88, 14.43, 14.36, 14.21,

		14.19, 14.14, 14.09, 0.41(3C), 0.08(minor).
<p>7.01(dd, $J=7.8\text{Hz}$, 1H, CH), 6.92(dd, $J=7.8\text{Hz}$, 1H, minor CH), 5.93(ABq, $J=1.5\text{Hz}$, & $J=1.5\text{Hz}$, 1H, CH), 5.72(ABq, $J=1.5\text{Hz}$, & $J=1.5\text{Hz}$, 1H, minor CH), 4.21(q, $J=7.2\text{Hz}$, 2H, merged CH_2), 3.62(m, 1H, CH), 2.41(m, 1H, CH), 1.51-1.42(m, 4H, <i>methylenes</i>), 1.35(t, $J=7.2\text{Hz}$, 3H, CH_3), 1.00(d, $J=7.02$, 3H, CH_3), 0.93(t, $J=6.75\text{Hz}$, 3H, CH_3), 0.90(t, $J=7.8\text{Hz}$, 9H, 3CH_3), 0.56(q, $J=7.8\text{Hz}$, 6H, 3CH_2). All other minor peaks are merged.</p>	<p>166.82, 152.04, 150.14 (minor), 120.91, 120.71 (minor), 75.69 (minor), 75.45, 60.41, 42.27, 39.45(minor), 36.73, 34.68 (minor), 20.84 (minor), 19.02, 14.62, 14.59, 15.50, 7.31, 7.21(minor), 5.47, 5.25 (minor).</p>
<p>7.01(dd, $J=7.2\text{Hz}$, 1H, CH), 6.97(dd, $J=4.5\text{Hz}$, 1H, minor CH), 5.97(ABq, $J=1.5\text{Hz}$, & $J=1.5\text{Hz}$, 1H, minor CH), 5.74(ABq, $J=1.5\text{Hz}$, & $J=1.5\text{Hz}$, 1H, CH), 4.21(q, $J=7.2\text{Hz}$, 2H, CH_2), 3.59(m, 1H, CH), 2.42(m, 1H, CH), 1.5-1.4(m, 4H, <i>methylenes</i>), 1.3(t, $J=7.2\text{Hz}$, 3H, CH_3), 1.0(d, $J=6.75$, 3H, CH_3), 0.93(t, $J=7.02\text{Hz}$, 3H, CH_3), 0.87(s, 9H, <i>t</i>-Bu), 0.02(s, 6H, 2CH_3). All other minor peaks are merged.</p>	<p>166.82, 151.56, 150.98 (minor), 121.87(minor), 121.21, 75.55(minor), 75.32, 60.40, 42.17, 36.58, 36.46(minor), 26.18 (3C), 26.47, 18.89, 18.43, 15.24, 14.60, -3.80 (minor), -3.95, -4.18, -4.01 (minor).</p>

<p>7.2(m, 2H, Ar-H), 6.9(m, 3H, Ar-H), 3.9(m, 2H, CH₂), 3.8(m, 1H, methine), 1.5(m, 2H, CH₂), 1.1(t, <i>J</i>=7.2 Hz, 3H, CH₃), 0.9(t, <i>J</i>=8.1 Hz, 9H, 3CH₃), 0.5(q, <i>J</i>=8.1 Hz, 6H, 3CH₂)</p>	<p>142.14, 130.13 (2C), 120.28 (2C), 114.42, 80.25, 73.31, 28.91, 12.34, 7.04(3C), 5.30 (3C)</p>
<p>5.8 (merged m, 1H, CH), 4.9(m, 2H, <i>terminal methylenes</i>), 3.3 (merged dd, 1H, CH), 2.0 (dd, 1H, CH₂), 1.3-1.5(m, 6H, <i>methylenes</i>), 0.92 (t, <i>J</i>=7.8 Hz, 9H, 3CH₃), 0.87(d, <i>J</i>=7.02Hz, 3H, 3CH₃), 0.56(q, <i>J</i>=7.8Hz, 6H, 3CH₂). All other minor peaks are merged.</p>	<p>139.2(minor), 137.10, 144.29, 106.12(minor), 68.59, 36.13, 34.11, 33.98(minor), 29.56, 26.83, 17.90, 7.19, 4.79.</p>
<p>7.08 and 7.00(dd, <i>J</i>=5.4 Hz,, 1H, CH), 6.08(ABq, <i>J</i>=1.4Hz, 1H, CH), 5.11(t, <i>J</i>=7.02Hz, 1H, CH), 4.2(q, <i>J</i>=7.2Hz, 2H, CH₂), 4.00(t, <i>J</i>=4.5Hz, 1H, methine), 1.9(brs, 1H, OH), 1.77(s, 3H, CH₃), 1.68(s, 3H, CH₃), 1.3 (t, <i>J</i>=3.5Hz, 3H, CH₃), 0.9(s, 6H, 2CH₃)</p>	<p>166.53, 147.86, 131.57, 124.78, 122.04, 76.79, 60.68, 38.99, 38.39, 26.00, 23.18, 23.16, 22.73, 17.92, 14.45.</p>

is epoxyacrylate-H₂/TMS - 100 G