# **Supporting Information**

## Cyclopropenation of Alkylidene Carbenes Derived from a-Silyl Ketones

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I. General information: Reactions were carried out in oven or flame-dried glassware under a nitrogen atmosphere unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether (Et<sub>2</sub>O) were freshly distilled from sodium/benzophenone, and dichloromethane (DCM) was distilled from calcium hydride (CaH<sub>2</sub>) under nitrogen atmosphere. Flash chromatography was performed using silica gel 60 Å (32–63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040–0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-500 spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). <sup>1</sup>H NMR signals that fall within a ca. 0.3 ppm range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, J, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima in the University of Illinois at Urbana-Champaign. Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana-Champaign. IR spectra were recorded using JASCO FT-IR-4100 with  $GLADiATR^{TM}$ Attenuated Total Reflectance (ATR) FT-IR accessory.

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#### II. Preparation of aldehyde 1d, 1f, 1h, 1j, 1l

$$H = R \xrightarrow{1. \text{ mCPBA}} O H = R$$

To a solution of alkene, (10.0 mmol, 1.0 equiv) in 30 mL of dichloromethane was added *meta*-Chloroperoxybenzoic acid (15.0 mmol, 1.5 equiv) slowly at -78 °C. The reaction was slowly warmed up to room temperature and monitored by TLC. Upon reaction completion, sodium thiosulfate aqueous solution was added at 0 °C to quench the reaction. Then the reaction mixture was separated and the aqueous layer was extracted by  $Et_2O$  (25 mL x 3). The extract was combined with the organic layer and then was washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated to obtain the crude product which was purified by column chromatography to afford the pure epoxide.

To finely powered sodium periodate (3.0 mmol, 3 equiv) in a round-bottom flask was added a mixture of CH<sub>3</sub>CN and water (20 mL, 2:1) and stirred for five minutes. The epoxide (1.0 mmol, 1 equiv) was then added and the reaction mixture was stirred at room temperature. Upon reaction completion, as monitored by TLC, the white precipitate was filtered away and washed by  $Et_2O$ . The aqueous layer was extracted by  $Et_2O$  (20 mL x 2) and washed by brine, then combined with the organic layer, dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude aldehyde, which was further purified by column chromatorgraphy on silca gel.



1d (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 3011, 2900, 2822, 2729, 1720, 1408, 1392, 1054, 914, 728, 651; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 9.74 (d, J = 1.6 Hz, 2H), 5.35 (t, J = 4.4 Hz, 2H), 2.48 (t, J = 7.1 Hz, 4H), 2.35 (dd, J = 6.2, 12.0 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 201.84, 128.88, 43.52, 19.95; HRMS (ESI) calcd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>Na, [M+Na]<sup>+</sup> 163.0735, found 163.0730.



The precursor **1f'** was prepared from protection of geraniol using pivaloyl choride. **1f** (colorless oil) IR (ATR diamond crystal, cm<sup>-1</sup>) 2966, 2930, 2874, 2819, 2722, 1724, 1476, 1395, 1284, 1148, 953, 862; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.73 (t, *J* = 1.6 Hz, 1H), 5.30 (ddd, *J* = 1.3, 2.5, 6.8 Hz, 1H), 4.52 (d, *J* = 6.8 Hz, 2H), 2.53 (dt, *J* = 1.4, 7.4, 7.8 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.14 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.74, 178.46, 139.47, 119.72, 60.99, 41.75, 38.69, 31.44, 27.16, 16.58; HRMS (ESI) calcd for C<sub>12</sub>H<sub>20</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 235.1310, found 235.1310.



(The precursor **1h'** was prepared according to the literature<sup>1</sup>.) **1h** (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 3018, 2969, 2952, 2974, 2227, 2104, 1739, 1454, 1421, 1372, 1232, 1009, 722, 524; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.78 (s, 1H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 0.98 (dt, *J* = 0.9, 7.8 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  199.42, 88.89, 82.20, 76.61, 66.56, 41.93, 12.43, 7.38, 4.21.



**1j** (colorless oil) IR (ATR diamond crystal, cm<sup>-1</sup>) 2956, 2921, 2862, 2715, 1720, 1454, 1360, 1092, 1024, 735, 699; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.75 (m, 1H), 7.34 (m, 4H), 7.28 (m, 1H), 4.50 (s, 2H), 3.51 (m, 2H), 2.43 (m, 2H), 1.67 (m, 2H), 1.46 (m, 2H), 0.90 (d, J = 6.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  202.77, 138.56, 128.39, 127.66,

<sup>&</sup>lt;sup>1</sup> Li, J.; Park, S.; Miller, R. L.; Lee, D. Org. Lett. 2009, 11, 571.

127.57, 73.00, 68.29, 41.63, 36.48, 29.55, 28.89, 19.34; HRMS (ESI) calcd for  $C_{14}H_{20}O_2Na [M+Na]^+ 243.1361$ , found 243.1361.



11 (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 2973, 2930, 2865, 2722, 1720, 1454, 1379, 1336, 1099, 1057, 739, 696; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.74 (s, 1H), 7.34 (m, 5H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 3.55 (dq, *J* = 6.1, 11.9 Hz, 1H), 2.53 (m, 2H), 1.84 (m, 2H), 1.22 (d, 3H, *J* = 6.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  202.49, 138.64, 128.40, 127.76, 127.58, 73.81, 70.44, 40.19, 29.18, 19.49; HRMS (EI) calcd for C<sub>12</sub>H<sub>17</sub>O<sub>2</sub> [M+1]<sup>+</sup> 193.12286, found 193.12369.

## III. Preparation of aldehydes 1e and 1g



Aldehyde **1e** was prepared from vinyl Grignard reagent addition of citronella followed by Claisen rearrangement in ethyl vinyl ether in the presence of mercuric acetate.<sup>2</sup> **1e** (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 2963, 2914, 2859, 2715, 1730, 1450, 1386, 1190, 1076, 829; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.75 (t, *J* = 1.8 Hz, 1H), 5.17 (t, *J* = 7.3 Hz, 1H), 5.08 (t, *J* = 7.1 Hz, 1H), 2.51 (dt, *J* = 1.8, 7.5, 7.8 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.03-1.88 (m, 4H), 1.81 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.59 (s, 3H), 1.44 (dt, *J* = 6.7, 13.1 Hz, 1H), 1.35-1.27 (m, 1H), 1.12 (dddd, *J* = 6.0, 7.9, 9.4, 13.6 Hz, 1H), 0.84 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  202.69, 133.47, 131.09, 124.90, 124.56, 42.25, 36.80, 35.15, 33.21, 32.07, 25.75, 25.69, 19.48, 17.65, 16.25 HRMS (CI) calcd for C<sub>15</sub>H<sub>27</sub>O [M+1]<sup>+</sup> 223.20620, found 223.20665.

<sup>&</sup>lt;sup>2</sup> Nagaoka, H.; Iwashima, M.; Abe, H.; Yamada, Y. Tetrahedron Lett. 1989, 30, 5911.



Aldehyde **1g** was prepared using the same strategy as aldehyde **1e**. **1g** (colorless oil): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.72 (d, J = 1.7 Hz, 1H), 4.98 (t, J = 7.2 Hz, 1H), 2.78 (s, 1H), 2.41 (t, J = 7.0 Hz, 2H), 2.34-2.23 (m, 3H), 1.90 (s, 2H), 1.87-1.75 (m, 6H), 1.71-1.64 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  202.74, 149.26, 113.72, 44.48, 40.45, 39.74, 38.85, 37.17, 32.11, 28.54, 19.59; HRMS (CI) calcd for C<sub>14</sub>H<sub>19</sub>O [M-1]<sup>+</sup> 203.14360, found 203.14451.

### IV. Preparation of aldehyde 1k, 1m and 1q



Alcohols 1q'', 1m' and 1k' was prepared according to the reported procedure.<sup>3</sup> To a mixture of benzaldehyde (1.06 g, 10 mmol, 1 equiv) in 20 mL of THF and 40 mL of saturated NH<sub>4</sub>Cl solution was added Zn dust (1.30 g, 20 mmol, 2 equiv) and allyl bromide (2.42 g, 20 mmol, 2 equiv). After the mixture was stirred for 30 min, it was extracted with diethyl ether for 3 times, the combined organic layer was dried over MgSO<sub>4</sub> and diethyl ether and excess amount of allyl bromide was removed under reduced pressure to afford 1-phenyl-3-butenol of colorless oil which was subjected to the next step without further purification.

To a solution of the crude secondary alcohol (296 mg, 2 mmol, 1 equiv) in 10 mL of the corresponding diol, PdCl<sub>2</sub> (36 mg, 0.2 mmol, 0.2 equiv) was added. Thereafter the

<sup>&</sup>lt;sup>3</sup> Tan, J.; Zhang, Z.; Wang, Z. Org. Biomol. Chem. 2008, 6, 1344.

reaction was heated at 40 °C under air overnight, water and diethyl ether were added. The organic layer was separated, and the aqueous portion was extracted with ether for 3 times. The combined organic layers were washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated to obtain the crude product which was purified by column chromatography (Hexane : Ethyl acetate = 6:1) to afford the pure primary alcohol 1q'', 1m', or 1k'.

To a solution of the primary alcohol (1 equiv) in 5 mL of dichloromethane, Dess-Martin periodinane (1.3 equiv) and NaHCO<sub>3</sub> (1.3 equiv) was added. Upon complete consumption of the starting material in 2 hrs, diethyl ether was added and white precipitate was formed. Filtering through a short plug of silica gel and concentrating under reduced pressure afforded the crude product which was purified by column chromatography using Hexane : Ether = 10:1 to give the pure aldehyde **1q'**, **1m**, or **1k**.



**1q'** (colorless oil, 62% over two steps): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.73 (s, 1H), 7.39 (d, *J* = 7.30 Hz, 2H), 7.33 (t, *J* = 7.54 Hz, 2H), 7.27 (t, *J* = 7.22 Hz, 1H), 6.54 (d, *J* = 15.95 Hz, 1H), 6.08 (dd, *J* = 15.95, 8.02 Hz, 1H), 4.11 (m, 3H), 1.43 (d, *J* = 6.30 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.03, 136.11, 132.75, 130.01, 128.69, 128.09, 126.59, 78.01, 73.84, 21.56.



**1q** was obtained quantitatively by hydrogenation of **1q'** using H<sub>2</sub> in the presence of Pd/C in EtOAc. **1q** (colorless oil) IR (ATR diamond crystal, cm<sup>-1</sup>) 2926, 2865, 1730, 1606, 1496, 1454, 1116, 1024, 914, 744, 699; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.74 (s, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.1 Hz, 3H), 4.06 (m, 2H), 3.51 (qt, *J* = 6.0 Hz, 1H), 2.97-2.56 (m, 2H), 2.03-1.87 (m, 1H), 1.80 (m, 1H), 1.23 (d, *J* = 6.1 Hz, 3H); <sup>13</sup>C NMR

(CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.48, 141.96, 128.45, 125.91, 76.14, 74.16, 38.13, 31.72, 19.42; HRMS (ESI) calcd for C<sub>12</sub>H<sub>19</sub>O<sub>2</sub> [M+H]<sup>+</sup> 195.1385, found 195.1381.



**1m** (colorless oil, 56% over two steps): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.80 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 7.7, 15.9 Hz, 1H), 4.03 (qn, *J* = 6.4 Hz, 1H), 3.79 (m, 2H), 2.67 (dt, *J* = 1.8, 6.1 Hz, 2H), 1.33 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.49, 136.49, 131.49, 131.31, 128.63, 128.48, 127.79, 126.51, 77.15, 61.96, 44.06, 21.63.



**1k** (colorless oil, 67% over two steps): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.75 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.09 (ddd, *J* = 1.3, 7.6, 16.0 Hz, 1H), 3.96 (qn, *J* = 6.6 Hz, 1H), 3.59-3.44 (m, 1H), 3.44-3.29 (m, 1H), 2.49 (m, 2H), 1.90 (q, 2H), 1.31 (d, *J* = 6.36 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  202.33, 136.62, 131.75, 131.09, 128.62, 127.70, 126.49, 76.69, 41.10, 22.83, 21.64.

#### V. Preparation of aldehydes 1n, 1o, 1p and 1r



To a solution of alcohol (10.0 mmol, 1.0 equiv) in 30 mL of dimethylformamide was added sodium hydride (60% in oil, 15.0 mmol, 1.5 equiv) and tetrabutylammonium iodide (0.1 mmol, 0.01 equiv.). After the solution was stirred at room temperature for 30 minutes, bromoacetaldehyde diethyl acetal (20.0 mmol, 2.0 equiv) was added into the reaction at 0 °C slowly. Then the reaction was heated to 40 °C and stirred overnight. The reaction was quenched by adding water and diethyl ether. The organic layer was separated, and the aqueous portion was extracted with ether for 3 times. The combined organic layers were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and

concentrated to obtain the crude product which was purified by column chromatography to afford the pure acetal;

To a solution of the corresponding acetal (1.0 mmol, 1.0 equiv) in acetone (3 mL) was added concentrated HCl solution (0.2 mmol, 0.2 equiv). The reaction was monitored by TLC carefully. Upon formation of quite amount of desired aldehyde, the reaction was quenched immediately by adding sodium bicarbonate solution slowly and extracted by Et<sub>2</sub>O. Long reaction time will lead to decomposition of desired aldehyde to starting alcohol. The extract was dried over MgSO<sub>4</sub> and concentrated under reduced pressure to afford a crude oil, which was purified by column chromatography to generate the corresponding  $\alpha$ -alkoxy aldehydes **1n-1p** and **1r**, which were used for cyclopropenation without storage.



**1n** (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 2959, 2917, 2869, 1750, 1720, 1450, 1379, 1252, 1109, 979, 836, 741; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.72 (s, 1H), 5.07 (t, *J* = 7.1 Hz, 1H), 4.04 (s, 2H), 3.55 (dt, *J* = 1.5, 7.0 Hz, 2H), 2.12-1.87 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.42 (m, 1H), 1.38-1.27 (m, 1H), 1.16 (dddd, *J* = 13.5, 9.3, 7.8, 6.2 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.15, 131.27, 124.80, 124.65, 76.34, 70.47, 37.15, 36.45, 29.41, 25.71, 25.43, 19.49, 17.63; LRMS (EI) calcd for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub> [M+1]<sup>+</sup> 198.2, found 198.2.



**10** (colorless oil) IR (ATR diamond crystal, cm<sup>-1</sup>) 3005, 2933, 2859, 1734, 1460, 1376, 1304, 1116, 1076, 962, 709; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.71 (d, *J* = 2.8 Hz, 1H), 5.32 (m, 2H), 4.04 (d, *J* = 2.3 Hz, 2H), 3.51 (dt, *J* = 2.2, 6.6 Hz, 2H), 2.01 (m, 4H), 1.70-1.50 (m, 2H), 1.46-1.17 (m, 4H), 0.93 (dt, *J* = 2.2, 7.5, Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)

δ 201.13, 131.80, 128.90, 76.31, 72.14, 29.50, 29.44, 26.96, 25.59, 20.51, 14.37; LRMS (CI) calcd for C<sub>11</sub>H<sub>21</sub>O<sub>2</sub> [M+1]<sup>+</sup> 185.2, found 185.2.



**1p** (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 2917, 1737, 1464, 1369, 1268, 1090, 1009, 957, 803, 683; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.68 (d, *J* = 4.3 Hz, 1H), 5.50 (s, 1H), 3.97 (d, *J* = 4.3 Hz, 2H), 3.91 (s, 2H), 2.41-2.33 (m, 1H), 2.29 (d, *J* = 18.7 Hz, 1H), 2.21 (d, *J* = 18.7 Hz, 1H), 2.20-2.15 (m, 1H), 2.07 (s, 1H), 1.26 (d, *J* = 3.3 Hz, 3H), 1.24 (s, 2H), 0.79 (d, *J* = 3.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.06, 144.32, 121.69, 74.85, 74.51, 43.21, 40.80, 38.02, 31.49, 31.31, 26.12, 21.07; HRMS (ESI) calcd for C<sub>12</sub>H<sub>19</sub>O<sub>2</sub> [M+1]<sup>+</sup> 195.1385, found 195.1381.



**1r** (colorless oil): IR (ATR diamond crystal, cm<sup>-1</sup>) 2907, 2826, 1739, 1473, 1454, 1372, 1102, 985, 923; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.74 (d, *J* = 1.0 Hz, 1H), 4.08 (d, *J* = 17.7 Hz, 1H), 4.02 (d, *J* = 17.7 Hz, 1H), 3.68 (dt, *J* = 4.7, 9.0 Hz, 1H), 2.46-2.35 (m, 1H), 2.32 (dtd, *J* = 2.1, 6.2, 8.4 Hz, 1H), 2.14-2.00 (m, 1H), 1.99-1.87 (m, 1H), 1.78 (ddd, *J* = 4.0, 6.5, 9.8 Hz, 2H), 1.19 (s, 3H), 1.12 (d, *J* = 7.4 Hz, 3H), 1.04 (d, *J* = 9.8 Hz, 1H), 0.87 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  201.76, 80.31, 74.45, 47.52, 44.37, 41.31, 38.40, 35.30, 33.39, 27.47, 23.77, 21.35; HRMS (ESI) calcd for C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 219.1361, found 219.1357.

### VI. General Procedures for Cyclopropenation and Characterization Data

In a fume hood, a vial equipped with a Teflon-coated stir bar was charged with aldehyde (1 mmol, 1.0 equiv) and 1 mL of anhydrous dichloromethane. Trimethylsilyl diazomethane (2.0 M in diethyl ether, 0.6 mL, 1.2 mmol, 1.2 equiv) was added by syringe at room temperature followed by InCl<sub>3</sub> (4.4 mg, 0.02 mmol, 0.02 equiv) added at once

and vigorous bubbling was observed. The reaction was stirred in the air at room temperature for 10 to 20 min, at which point TLC indicated the consumption of the starting material. Dichloromethane and the excess amount of trimethylsilyldiazomethane was removed under reduced pressure and the crude  $\alpha$ -TMS ketone was subjected to the next step without further purification.

To a cooled (-78 °C) solution of TMS diazomethane (2.0 M in diethyl ether, 0.6 mL, 1.2 mmol, 1.2 equiv) in THF (2 mL) was added *n*-BuLi (2.5 M in hexane, 0.52 mL, 1.3 equiv) dropwise under N<sub>2</sub> atmosphere. After the mixture was stirred at -78 °C for 30 minutes, a solution of the crude  $\alpha$ -TMS ketone in THF (1.0 mL) was added into the mixture dropwise. Then the reaction was stirred at -78 °C for 10 minutes. The reaction mixture was warmed up to room temperature by removing dry ice-acetone bath and quenched by adding several drops of an aqueous saturated NH<sub>4</sub>Cl solution and the mixture was directly dried over MgSO<sub>4</sub>, filtered through a short plug of silica gel and concentrated under reduced pressure to afford the crude oil. Purification by column chromatography gave the desired product **3a-3s** and **4n-4s**.

#### Characterization Data for Table 1



**3a** (colorless oil, 77%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2966, 2922, 2877, 1739, 1717, 1452, 1363, 1245, 1158, 838, 671; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.14-5.08 (m, 1H), 2.55 (dd, *J* = 5.4, 15.8 Hz, 1H), 2.42 (dd, *J* = 7.5, 15.8 Hz, 1H), 2.10-1.94 (m, 1H), 1.82 (dt, *J* = 6.7, 13.4 Hz, 1H), 1.69 (s, 3H), 1.61 (s, 3H), 1.46-1.35 (m, 1H), 1.29-1.17 (m, 1H), 0.94 (dd, *J* = 0.7, 6.7 Hz, 3H), 0.72 (d, *J* = 0.9 Hz, 1H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  134.18, 131.19, 124.72, 105.46, 36.87, 35.63, 31.48, 25.72, 25.62, 19.88, 17.64, 6.32, -1.38; LRMS (CI) calcd for C<sub>15</sub>H<sub>28</sub>Si [M]<sup>+</sup> 236.2, found 236.2.



**3b** (colorless oil, 81%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3008, 2956, 2926, 2871, 1801, 1739, 1457, 1372, 1246, 1223, 992, 839, 758, 634; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.39 (t, J = 4.9 Hz, 2H), 2.59 (t, J = 7.5 Hz, 2H), 2.32 (td, J = 6.4, 12.4 Hz, 2H), 2.04 (dd, J = 6.9, 12.6 Hz, 2H), 1.39-1.24 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H), 0.75 (s, 2H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  134.86, 130.69, 128.72, 105.75, 31.53, 29.38, 28.87, 27.25, 25.20, 22.60, 14.09, 6.47, -1.31; HRMS (CI) calcd for C<sub>15</sub>H<sub>27</sub>Si [M-1]<sup>+</sup> 235.1882, found 235.1879.



**3c** (colorless oil, 78%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2960, 2925, 2871, 2852, 1796, 1460, 1249, 990, 968, 832, 759; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.45 (td, *J* = 3.7, 5.2 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.28 (td, *J* = 12.6, 6.31 Hz, 2H), 2.00-1.94 (m, 2H), 1.41-1.19 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.74 (s, 2H), 0.16 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  134.86, 131.07, 129.17, 105.40, 32.57, 31.41, 30.32, 29.25, 28.87, 22.57, 14.08, 6.36, -1.31; HRMS (CI) calcd for C<sub>15</sub>H<sub>29</sub>Si [M+1]<sup>+</sup> 237.20, found 237.1648.



**3d** (colorless oil, 71%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2959, 2916, 2876, 1796, 1730, 1444, 1376, 1244, 994, 837, 758, 636; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.43 (t, *J* = 4.9 Hz, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.35 (dd, *J* = 7.4, 12.7 Hz, 2H), 0.76 (s, 2H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  134.72, 129.48, 105.89, 28.77, 25.24, 6.46, -1.31; HRMS (CI) calcd for C<sub>18</sub>H<sub>31</sub>Si<sub>2</sub> [M-1]<sup>+</sup> 303.19644, found 303.19618.



**3e** (colorless oil, 69%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.17 (t, *J* = 6.69 Hz, 1H), 5.10 (t, *J* = 7.10 Hz, 1H), 2.68-2.63 (m, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.05-1.90 (m, 3H), 1.88-1.78 (m, 1H), 1.69 (s, 3H), 1.61 (d, *J* = 5.6 Hz, 6H), 1.50-1.40 (m, 1H), 1.39-1.29 (m, 1H), 1.14 (dddd, *J* = 6.0, 7.7, 9.4, 13.5 Hz, 1H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.74 (s, 2H), 0.16 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  135.15, 134.84, 131.02, 125.00, 123.62, 105.25, 37.35, 36.83, 35.16, 35.07, 33.30, 27.49, 25.73, 19.53, 17.65, 16.13, 6.32, -1.29; HRMS (CI) calcd for C<sub>20</sub>H<sub>35</sub>Si [M-1]<sup>+</sup> 303.25081, found 303.25064.



**3f** (colorless oil, 75%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2966, 2906, 2849, 1796, 1448, 1246, 1907, 993, 835, 753; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.34 (ddt, *J* = 1.2, 2.5, 6.8 Hz, 1H), 4.57 (d, *J* = 6.9 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.32 (t, *J* = 7.7 Hz, 2H), 1.72 (s, 3H), 1.19 (s, 9H), 0.73 (s, 2H), 0.15 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 178.61, 140.84, 134.56, 119.00, 105,80, 61.27, 38.75, 36.97, 27.22, 26.96, 16.47, 6.40, -1.31.



**3g** (colorless oil, 81%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2953, 2906, 2849, 1796, 1448, 1246, 1907, 993, 835, 753; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.07 (t, *J* = 7.2 Hz, 1H), 2.81 (s, 1H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 1H), 2.27 (q, *J* = 7.3 Hz, 1H), 1.95 (s, 1H), 1.86, (ddd, *J* = 2.7, 6.3, 11.9 Hz, 6H), 1.82 (s, 1H), 1.76 (d, *J* = 11.7 Hz, 2H), 1.70 (d, *J* = 11.8 Hz, 2H), 0.76 (s, 2H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  148.16, 135.15, 115.36, 105.46, 40.49, 39.85, 38.98, 37.34, 32.14, 29.60, 28.67, 24.49, 6.44, -1.27; HRMS (EI) calcd for C<sub>19</sub>H<sub>30</sub>Si [M]<sup>+</sup> 286.21168, found 286.21278.



**3h** (colorless oil, 54%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3014, 2956, 2914, 2878, 2224, 2107, 1798, 1739, 1460, 1421, 1369, 1229, 1004, 839, 725, 634; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  2.79 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.78 (s, 1H), 0.61 (q, *J* = 7.9 Hz, 6H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  132.69, 107.65, 89.34, 81.45, 78.19, 66.17, 27.85, 17.75, 7.35, 6.68, 4.24, -1.43; HRMS (CI) calcd for C<sub>18</sub>H<sub>29</sub>Si<sub>2</sub> [M-1]<sup>+</sup> 301.18079, found 301.18034.



**3i** (colorless oil, 65%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3028, 2952, 2874, 1798, 1739, 1496, 1454, 1369, 1246, 995, 832, 744, 696, 631; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.32 (t, *J* = 7.7 Hz, 2H), 7.23 (d, J = 7.2 Hz, 3H), 2.93 (m, 4H), 0.83 (s, 2H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  141.71, 134.48, 128.36, 125.97, 106.31, 33.56, 30.48, 6.56, -1.35; HRMS (CI) calcd for C<sub>14</sub>H<sub>19</sub>Si [M-1]<sup>+</sup> 215.1256, found 215.1257.



**3j** (colorless oil, 51%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2956, 2928, 2871, 1796, 1455, 1366, 1246, 1101, 993, 838, 736, 699; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.35 (d, *J* = 4.2 Hz, 4H), 7.32-7.27 (m, 1H), 4.51 (d, *J* = 1.7 Hz, 2H), 3.58-3.48 (m, 2H), 2.64-2.50 (m, 2H), 1.76-1.60 (m, 3H), 1.52-1.41 (m, 2H), 0.93 (d, *J* = 6.3 Hz, 3H), 0.74 (s, 2H), 0.16 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  138.68, 135.30, 128.37, 127.62, 127.50, 105.06, 72.95, 68.64, 36.64, 34.51, 29.61, 26.08, 19.41, 6.31, -1.27; HRMS (ESI) calc. for C<sub>9</sub>H<sub>18</sub>ONaSi [M+Na]<sup>+</sup> 325.1964, found 325.1958.



**3k** (colorless oil, 82%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3031, 2956, 2868, 1791, 1739, 1447, 1369, 1245, 1148, 1096, 966, 832, 748, 692, 637; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.41 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 7.6, 16.0 Hz, 1H), 4.04-3.98 (m, 1H), 3.59 (td, *J* = 6.6, 9.3 Hz, 1H), 3.42 (td, *J* = 6.5, 9.3 Hz, 1H), 2.67 (dt, *J* = 2.0, 7.2 Hz, 2H), 1.91 (qn, *J* = 6.8 Hz, 2H), 1.36 (d, *J* = 6.4 Hz, 3H), 0.76 (s, 2H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  136.73, 134.77, 132.10, 130.89, 128.60, 127.63, 126.48, 105.43, 76.66, 67.73, 27.80, 25.40, 21.75, 6.41, -1.28; HRMS (CI) calcd for C1<sub>9</sub>H<sub>27</sub>OSi [M-1]<sup>+</sup> 299.18313, found 299.18400.



**31** (colorless oil, 71%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3018, 2969, 2950, 2869, 1743, 1447, 1369, 1216, 1090, 1064, 836, 735, 692, 526; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.38-7.33 (m, 4H), 7.30-7.26 (m, 1H), 4.59 (d, J = 11.7 Hz, 1H), 4.45 (d, J = 11.7 Hz, 1H), 3.62-3.53 (m, 1H), 2.66 (t, J = 7.5 Hz, 2H), 1.89 (dt, J = 7.4, 14.3 Hz, 1H), 1.76 (dtd, J = 5.0, 7.7, 13.0 Hz, 1H), 1.24 (d, J = 6.1 Hz, 3H), 0.72 (s, 2H), 0.16 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  138.97, 134.90, 128.35, 127.67, 127.46, 105.21, 74.16, 70.51, 34.37, 24.72, 19.58, 6.33, -1.29; LRMS (CI) calcd for C<sub>17</sub>H<sub>25</sub>OSi [M-1]<sup>+</sup> 273.2, found 273.2.



**3m** (colorless oil, 75%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3028, 2956, 2871, 1795, 1739, 1443, 1366, 1249, 1148, 1092, 972, 836, 748, 692, 637; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.41 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 7.6, 15.9 Hz, 1H), 4.10-4.03 (m, 1H), 3.81-3.74 (m, 1H), 3.65-3.59 (m, 1H), 2.91-2.85 (m, 2H), 1.37 (d, *J* = 6.4 Hz, 3H), 0.78 (s, 2H), 0.18 (s,

9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  136.71, 132.10, 131.88, 131.12, 128.60, 127.67, 126.50, 106.84, 76.78, 66.20, 29.54, 21.75, 6.02, -1.36; HRMS (ESI) calcd for C<sub>18</sub>H<sub>26</sub>ONaSi [M+Na]<sup>+</sup> 309.1651, found 309.1640.

#### **Characterization Data of Table 2**



**3n** (colorless oil, 41%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3014, 2972, 2921, 2852, 1739, 1678, 1454, 1372, 1232, 1216, 1154, 1096, 832, 761, 6926; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.10 (t, *J* = 6.5 Hz, 1H), 4.55 (s, 2H), 3.53 (m, 2H), 2.07-1.90 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.43 (td, *J* = 6.7, 13.4 Hz, 1H), 1.37-1.30 (m, 1H), 1.17 (td, *J* = 8.4, 13.6 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 2H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  131.34, 131.15, 124.81, 108.38, 69.11, 68.02, 37.31, 36.74, 29.64, 25.73, 25.50, 19.60, 17.64, 6.71, -1.50; HRMS (CI) calcd for C<sub>9</sub>H<sub>18</sub>OSi [M-1]<sup>+</sup> 279.2144, found 279.2146.



**4n** (colorless oil, 34%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.21 (d, *J* = 16.0 Hz, 1H), 5.10 (ddd, *J* = 1.3, 5.8, 7.1 Hz, 1H), 4.87 (s, 1H), 4.46 (dm, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 2.08-1.88 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.52 (d, *J* = 4.3 Hz, 2H), 1.48-1.29 (m, 3H), 1.25 (ddd, *J* = 4.3, 8.9, 13.5 Hz, 1H), 1.16 (m, 1H), 0.93 (dd, *J* = 1.9, 6.6 Hz, 3H), 0.04 (s, 9H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  138.02, 124.89, 121.54, 121.24, 85.45, 85.08, 77.61, 44.13, 37.87, 37.31, 29.87, 29.51, 25.75, 25.45, 20.24, 19.54, 17.66, 17.11, -1.43.



**3o** (colorless oil, 60%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3004, 2937, 2852, 1739, 1678, 1450, 1369, 1220, 1076, 1102, 839, 754; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.40-5.28 (m, 2H), 4.55 (s, 2H), 3.49 (t, *J* = 6.71 Hz, 2H), 2.03 (qn, *J* = 7.10 Hz, 4H), 1.66-1.58 (m, 2H), 1.37 (dd, *J* = 3.46, 7.04 Hz, 4H), 0.95 (t, *J* = 7.54 Hz, 3H), 0.88 (s, 2H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  131.71, 131.32, 129.07, 108.34, 70.77, 68.02, 29.71, 27.05, 25.99, 20.52, 14.40, 6.69, -1.50; HRMS (CI) calcd for C<sub>16</sub>H<sub>31</sub>OSi [M+1]<sup>+</sup> 267.21443, found 267.21369.



**4o** (colorless oil, 24%): IR (ATR diamond crystal, cm<sup>-1</sup>) 3004, 2955, 2936, 2860, 1743, 1652, 1454, 1369, 1251, 1064, 968, 844, 695; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  5.39-5.28 (m, 2H), 5.19 (s, 1H), 4.80 (m, 1H), 4.46 (dd, *J* = 5.4, 12.1 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 2.09-1.95 (m, 4H), 1.54-1.46 (m, 4H), 1.36 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.03 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  137.61, 131.65, 129.14, 120.81, 86.90, 77.93, 36.60, 29.94, 27.12, 24.94, 20.52, 17.11, 14.41, -1.42; HRMS (CI) calcd for C<sub>16</sub>H<sub>29</sub>OSi [M-1]<sup>+</sup> 265.19878, found 265.19907.



**3p** (colorless oil, 55%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2982, 2950, 2913, 2836, 1737, 1678, 1464, 1360, 1246, 1083, 843, 758; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.51-5.49 (m, 1H), 4.53 (s, 2H), 3.93-3.89 (m, 2H), 2.40 (td, *J* = 5.6, 8.6 Hz, 1H), 2.32 (d, *J* = 17.8 Hz,

1H), 2.24 (d, J = 17.8 Hz, 1H), 2.20 (dt, J = 1.2, 5.7 Hz, 1H), 2.10 (ddd, J = 2.4, 3.6, 6.9 Hz, 1H), 1.29 (s, 3H), 1.18 (d, J = 8.6 Hz, 1H), 0.88 (s, 3H), 0.84 (s, 3H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  145.15, 131.22, 120.09, 108.35, 73.22, 66.85, 43.35, 40.90, 38.01, 31.58, 31.31, 26.20, 21.08, 6.70, -1.45; HRMS (CI) calcd for C<sub>17</sub>H<sub>28</sub>OSi [M]<sup>+</sup> 276.19095, found 276.19088.



**4p** (colorless oil, 28%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2950, 1743, 1457, 1369, 1249, 1213, 1038, 825, 677; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  1H NMR 5.45 (s, 1H), 5.18 (s, 1H), 4.98 (s, 1H), 4.48 (dd, *J* = 5.7, 11.1 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 2.40 (td, *J* = 5.6, 8.6 Hz, 1H), 2.32 (td, *J* = 2.9, 17.8 Hz, 1H), 2.19 (td, *J* = 2.6, 17.8 Hz, 1H), 2.12 (t, *J* = 5.5 Hz, 1H), 2.06 (s, 1H), 1.62 (d, *J* = 14.0 Hz, 1H), 1.45 (d, *J* = 14.0 Hz, 1H), 1.26 (s, 3H), 1.22 (d, *J* = 8.6 Hz, 1H), 0.79 (s, 3H), 0.05 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$ 148.80, 139.09, 119.21, 118.86, 89.94, 78.73, 41.22, 40.97, 37.83, 31.78, 31.23, 26.14, 21.24, 17.25, -1.34; LRMS (CI) calcd for C<sub>17</sub>H<sub>28</sub>OSi [M-1]<sup>+</sup> 275.2, found 275.2.



**3q** (colorless oil, 57%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2966, 2952, 1739, 1652, 1447, 1366, 1249, 1066, 969, 843, 748, 689; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.28 (m, 2H), 7.19 (m, 3H), 4.62 (d, *J* = 15.7 Hz, 1H), 4.52 (d, *J* = 15.7 Hz, 1H), 3.56 (sext, *J* = 6.1 Hz, 1H), 2.79-2.65 (m, 2H), 1.96-1.85 (m, 1H), 1.80-1.71 (m, 1H), 1.22 (d, *J* = 6.1 Hz, 3H), 0.90 (s, 2H), 0.20 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  142.41, 131.75, 128.44, 128.35, 125.72, 108.62, 74.47, 65.43, 38.44, 31.75, 19.45, 6.89, -1.41; HRMS (CI) calcd for C<sub>17</sub>H<sub>25</sub>OSi [M-1]<sup>+</sup> 273.1675, found 273.1669.



**3r** (colorless oil, 41%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2956, 2904, 1678, 1469, 1447, 1366, 1245, 1076, 836, 758, 703; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  4.60 (d, *J* = 15.6 Hz, 1H), 4.55 (d, *J* = 15.6 Hz, 1H), 3.74 (td, *J* = 9.1, 4.5 Hz, 1H), 2.46-2.36 (m, 1H), 2.36-2.28 (m, 1H), 2.13-2.05 (m, 1H), 1.94 (tt, *J* = 3.1, 5.8 Hz, 1H), 1.88-1.81 (m, 1H), 1.79 (dt, *J* = 2.0, 5.9 Hz, 1H), 1.21 (s, 3H), 1.11 (d, *J* = 7.4 Hz, 3H), 0.92 (s, 2H), 0.90 (s, 3H), 0.19 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  131.92, 109.02, 78.39, 65.46, 47.69, 44.47, 41.42, 38.42, 35.60, 33.28, 27.54, 23.76, 21.52, 6.99, -1.39; HRMS (CI) calcd for C<sub>17</sub>H<sub>29</sub>OSi [M-1]<sup>+</sup> 277.19878, found 277.19812.



**4r** (colorless oil, 28%): IR (ATR diamond crystal, cm<sup>-1</sup>) 2952, 2904, 1739, 1656, 1450, 1369, 1249, 1216, 1154, 1047, 839, 787, 696; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.32 (s, 1H), 4.37 (s, 2H), 2.38 (dq, J = 2.6, 7.9 Hz, 1H), 2.29-2.20 (m, 1H), 2.14 (dd, J = 3.8, 14.9 Hz, 1H), 2.06-2.01 (m, 1H), 1.87-1.81 (m, 1H), 1.58 (d, J = 13.9 Hz, 1H), 1.54-1.47 (m, 2H), 1.20 (s, 3H), 1.01 (d, J = 8.0 Hz, 3H), 0.90 (s, 3H), 0.05 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 136.08, 125.24, 90.95, 75.84, 48.69, 46.92, 41.97, 40.14, 37.98, 29.34, 27.60, 22.90, 18.12, 17.03, -1.36; HRMS (CI) calcd for C<sub>17</sub>H<sub>29</sub>OSi [M-1]<sup>+</sup> 277.1988, found 277.1982.

## VII. <sup>1</sup>H NMR and <sup>13</sup>C NMR









































<sup>&</sup>lt;sup>4</sup>For solvent peaks, see: Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. J. Org. Chem. 1997, 62, 7512.





































