Supporting Information

A Ru-Catalyzed Tandem Alkyne-Enone Coupling/Michael Addition: Synthesis of 4-Methylene-2,6-*cis*-Tetrahydropyrans

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General Procedure for Alkyne Synthesis:

A solution of trimethylsilyl acetylene (1.2 equiv., 0.13 M) in THF was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*-BuLi (1 equiv.) was added slowly. The solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 15 min and then epoxide (1.0 equiv.) in THF (minimal) was added, followed by neat $\text{BF}_3\cdot\text{OEt}_2$ (1.2 equiv.). The reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 45 min before being quenched with saturated aqueous NH_4Cl . After warming to $\sim 0\text{ }^{\circ}\text{C}$, the mixture was extracted with ether (3x). The combined organic extract was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography on silica gel, eluting with ether/petroleum ether.

Reaction of trimethylsilyl acetylene with 2-[2-(4-Methoxy-benzyloxy)-ethyl]-oxirane¹ (3.5 g, 17.0 mmol), product purified by flash chromatography on silica gel with ether in petroleum ether (40%) to give **1b** (4.8 g, 92% yield) as a pale yellow oil.

¹HNMR (500 MHz, CDCl_3) δ 7.25 (d, $J=8.5\text{ Hz}$, 2H), 6.87 (d, $J=8.6\text{ Hz}$, 2H), 4.45 (s, 2H), 3.97-3.92 (m, 1H), 3.81 (s, 3H), 3.73-3.69 (m, 1H), 3.65-3.61 (m, 1H), 2.48-2.38 (m, 2H), 1.93-1.88 (m, 1H), 1.85-1.77 (m, 1H), 0.15 (s, 9H); ¹³CNMR (125 MHz, CDCl_3) δ 159.3, 129.9, 129.3, 113.8, 103.3, 87.0, 72.9, 69.6, 68.3, 55.3, 35.3, 28.5, 0.06; IR (neat film) 3439, 3005, 2165, 1611, 1584, 1510, 1459, 1417, 1362, 1302, 1247, 1173, 1089, 1034, 845, 757 cm^{-1} ; TLC R_f 0.32 (40% ether in petroleum ether); Anal. Calc'd for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Si}$: C, 66.62; H, 8.55. Found: C, 66.80; H, 8.41.

Reaction of trimethylsilyl acetylene with 2-ethyl-oxirane (2.93 g, 40.6 mmol), product purified by flash chromatography on silica gel with ether in petroleum ether (10%, 20%, then 30%) to give **1c** (5.70 g, 84% yield) as an oil.

¹HNMR (500 MHz, CDCl_3) δ 3.68-3.64 (m, 1H), 2.46 (dd, $J=4.7, 117.0\text{ Hz}$, 1H), 2.34 (dd, $J=7.0, 16.7\text{ Hz}$, 1H), 1.92 (br s, 1H), 1.59-1.52 (m, 2H), 0.96 (t, $J=7.5\text{ Hz}$, 3H), 0.16 (s, 9H); ¹³CNMR (125 MHz, CDCl_3) δ 103.2, 87.5, 71.2, 29.1, 24.4, 9.9, 0.1; IR (neat film) 3354, 2178, 1463, 1420, 1400, 1335, 1244, 974, 841, 754, 694, 647 cm^{-1} ; Anal. Calc'd for $\text{C}_9\text{H}_{18}\text{OSi}$: C, 63.47; H, 10.65. Found: C, 63.60; H, 10.63.

(1) Fuerstner, A; Albert, M.; Mlynarski, J.; Matheu, M.; DeClercq, E. *J. Am. Chem. Soc.* **2003**, 125, 13132.

Reaction of trimethylsilyl acetylene with TBDPS-glycidol² (0.654 g, 2.1 mmol), product purified by flash chromatography on silica gel with ether in petroleum ether (10%, then 20%) to give **1d** (0.73 g, 85% yield) as a thick oil.

¹HNMR (500 MHz, CDCl₃) δ 7.68-7.66 (m, 4H), 7.46-7.38 (m, 6H), 3.90-3.86 (m, 1H), 3.76 (dd, J=4.4, 10.3 Hz, 1H), 3.69 (dd, J=5.8, 10.1 Hz, 1H), 2.51 (ddd, J=6.1, 16.9, 18.9 Hz, 2H), 1.08 (s, 9H), 0.11 (s, 9H); ¹³CNMR (125 MHz, CDCl₃) δ 135.5, 133.0, 129.8, 127.8, 102.6, 87.1, 70.2, 69.3, 26.8, 24.6, 19.3, 0.0; IR (neat film) 3571, 3458, 3073, 3045, 2171, 1588, 1470, 1428, 1245, 1109, 841, 700 cm⁻¹; TLC R_f 0.29 (10% ether in petroleum ether); HRMS Calc'd for C₂₀H₂₅O₂Si₂ [M-C₄H₉]⁺: 353.1393. Found: 353.1387.

The procedure of Le Roux³ was followed:

A 100 mL round bottom flask was flame-dried under vacuum and filled with argon. NaI was added (1.125 g, 7.5 mmol), followed by BiCl₃ (0.79 g, 2.5 mmol) in a glove bag. CH₂Cl₂ (50 mL) was then introduced *via* a syringe. The suspension was stirred at room temperature for 5 min, upon which heptanoyl chloride (8.5 mL, 55 mmol) was added. After stirring for another 5 min, allyl trimethyl silane (7.95 mL, 50 mmol) was added all at once. The mixture was stirred for 15 min, briefly cooled with an ice-water bath, and then poured into ice-cold saturated aqueous NaHCO₃. The layers were separated. The aqueous layer was extracted with CH₂Cl₂ (2x). The combined organic layer was dried (Na₂SO₄), filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (5%, then 10%) to give 6.3 g **2b** (82% yield) as a clear oil.

¹HNMR (500 MHz, CDCl₃) δ 5.92 (dddd, J=6.9, 6.9, 10.1, 17.3 Hz, 1H), 5.17 (dq, J=1.2, 10.3 Hz, 1H), 5.13 (dq, J=1.5, 17.1 Hz, 1H), 3.16 (dt, J=7.0, 1.2 Hz, 2H), 2.43 (t, J=7.3 Hz, 2H), 1.59-1.52 (m, 2H), 1.31-1.25 (m, 6H), 0.87 (t, J=6.8 Hz, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 209.1, 130.7, 118.7, 47.7, 42.4, 31.6, 28.8, 23.6, 22.5, 14.0; IR (thin film) 3083, 1714, 1639, 1462, 1407, 1369, 1132, 1057, 993, 914 cm⁻¹; TLC R_f 0.25 (6% Et₂O in petroleum ether); Anal. Calc'd for C₁₀H₁₈O: C, 77.87; H, 11.76. Found: C, 77.64; H, 11.96.

To a 500 mL round-bottom flask were charged 3-(*tert*-butyl-dimethyl-silanyloxy)-2,2-dimethyl-propan-1-ol⁴ (10.92 g, 50 mmol), CH₂Cl₂ (20 mL), KBr (0.66 g, 5.5 mmol) in H₂O (3 mL), and TEMPO (0.1 g, 0.54 mmol). The flask was cooled to -5 °C with a NaCl-ice-H₂O bath. To the vigorously stirred mixture was added sodium chlorite solution

(2) Betancort, J. M.; Martin, T.; Palazon, J. M.; Martin, V. S. *J. Org. Chem.* **2003**, 68, 3216.

(3) Le Roux, C.; Dubac, J. *Organometallics* **1996**, 15, 4646.

(4) Richter, F.; Bauer, M.; Perez, C.; Maichle-Moessmer, C.; Maier, M. E. *J. Org. Chem.* **2002**, 67, 2474.

(10-13% from Aldrich, assuming 1.6 M, 40 mL, 64 mmol) dropwise over 15 min. The color turned from yellow-brown to deep red and then the color dissipated. The content was stirred for another 5 min at -5°C after the addition, poured into H_2O , and extracted with CH_2Cl_2 (3x). The organic layer was washed with H_2O /saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1/1), dried over MgSO_4 , filtered, and concentrated. The residue was redissolved in benzene, and the benzene was removed under reduced pressure to give 10.9 g crude aldehyde as an oil, which is essentially pure by ^1H NMR and used without further purification.

^1H NMR (500 MHz, CDCl_3) δ 9.57 (s, 1H), 3.60 (s, 2H), 1.04 (s, 6H), 0.87 (s, 9H), 0.03 (s, 6H).

To a solution of the above crude aldehyde in ether (150 mL) at -78°C was added allyl magnesium bromide (1.0 M in ether, 60 mL, 60 mmol) dropwise. The reaction was stirred at the same temperature for 30 min, quenched with saturated aqueous NH_4Cl , and warmed to 0°C . The mixture was poured into H_2O , extracted with ether (3x). The combined organic layer was dried (MgSO_4), filtered, and concentrated. Distillation (still head temperature 80°C , 1mm Hg) followed by flash chromatography on silica gel with ether in petroleum ether (5%, 7%, then 10%) gave 8.8 g alcohol **10** as a pale yellow oil (68% yield over two steps).

^1H NMR (500 MHz, CDCl_3) δ 5.98-5.90 (m, 1H), 5.14-5.06 (m, 2H), 3.54 (dd, $J=2.6$, 10.4 Hz, 1H), 3.48 (s, 2H), 2.30-2.24 (m, 1H), 2.13-2.06 (m, 1H), 0.91 (s, 3H), 0.90 (s, 9H), 0.84 (s, 3H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.9, 116.4, 78.3, 73.3, 38.3, 36.4, 25.8, 22.2, 18.8, 18.1, -5.7; IR (thin film) 3499, 3077, 1636, 1487, 1251, 1092, 903, 838, 777, 664 cm^{-1} ; TLC R_f 0.19 (5% Et_2O in petroleum ether); HRMS Calc'd for $\text{C}_{10}\text{H}_{21}\text{O}_2\text{Si}$ [$\text{M}-\text{C}_4\text{H}_9$] $^+$: 201.1311. Found: 201.1300.

To a suspension of allylic alcohol **10** (0.957 g, 3.7 mmol) and NaHCO_3 (3.1 g, 37 mmol) at room temperature was added Dess-Martin periodinane (3.45 g, 8.1 mmol). After stirring at room temperature for 2 h, the reaction was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and saturated aqueous NaHCO_3 (50 mL each), extracted with ether, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (5%) to give 0.93 g **2d** as a clear oil (98% yield).

^1H NMR (500 MHz, CDCl_3) δ 5.94 (ddd, $J=6.8$, 6.8, 10.2, 17.1 Hz, 1H), 5.14 (dq, $J=1.3$, 10.2 Hz, 1H), 5.07 (dq, $J=1.5$, 17.2 Hz, 1H), 3.57 (s, 2H), 3.31 (dq, $J=5.7$, 15.1 Hz, 2H), 1.11 (s, 6H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.8, 131.6, 117.8, 70.2, 49.6, 42.9, 25.7, 21.4, 18.1, -5.7; IR (neat film) 3080, 1706, 1641, 1470, 1388, 1358, 1319, 1255, 1096, 838, 777 cm^{-1} ; TLC R_f 0.44 (5% Et_2O in petroleum ether); Anal. Calc'd for $\text{C}_{14}\text{H}_{28}\text{O}_2\text{Si}$: C, 65.67; H, 11.00. Found: C, 65.80; H, 11.30.

The same procedure for the preparation of **10** was followed. 3-(4-Methoxy-benzyloxy)-2,2-dimethyl-propan-1-ol⁵ (5.6 g, 25 mmol) gave 4.32 g **11** (65% yield).

Characterizations for 3-(4-methoxy-benzyloxy)-2,2-dimethyl-propionaldehyde: ^1H NMR (500 MHz, CDCl_3) δ 9.44 (s, 1H), 7.11 (d, $J=7.8$ Hz, 2H), 6.77 (d, $J=8.8$ Hz, 2H), 4.33 (s, 2H), 3.71 (s, 3H), 3.31 (s, 2H), 0.97 (s, 6H).

Characterizations for **11**: ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, $J=8.8$ Hz, 2H), 6.87 (d, $J=8.7$ Hz, 2H), 5.96-5.88 (m, 1H), 5.12-5.06 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.51 (dd, $J=2.4, 10.4$ Hz, 1H), 3.35 (d, $J=8.9$ Hz, 1H), 3.26 (d, $J=8.8$ Hz, 1H), 2.29-2.24 (m, 1H), 2.08-2.02 (m, 1H), 0.92 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 136.8, 130.0, 129.1, 116.5, 113.8, 79.3, 77.6, 73.2, 55.2, 38.3, 36.5, 22.7, 19.6; IR (thin film) 3492, 3075, 1638, 1612, 1581, 1511, 1464, 1360, 1303, 1247, 1173, 1086, 1034, 908, 821 cm^{-1} ; TLC R_f 0.31 (20% Et_2O in petroleum ether); Anal. Calc'd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C, 72.69; H, 9.15. Found: C, 72.80; H, 8.97.

The oxidation of **10** to **2d** was followed: 2.1 g **1** (7.94 mmol) gave 1.93 g product **2c** (93% yield) after flash chromatography on silica gel with ether petroleum ether (15%, then 20%).

^1H NMR (500 MHz, CDCl_3) δ 7.21 (d, $J=8.7$ Hz, 2H), 6.87 (d, $J=8.8$ Hz, 2H), 5.94 (dddd, $J=6.8, 6.8, 10.3, 17.1$ Hz, 1H), 5.14 (dq, $J=1.5, 10.3$ Hz, 1H), 5.05 (dq, $J=1.5, 17.2$ Hz, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.41 (s, 2H), 3.27 (d, $J=6.7$ Hz, 2H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.2, 159.1, 131.5, 130.1, 129.1, 117.8, 113.7, 76.6, 72.9, 55.2, 48.6, 42.4, 21.9; IR (neat film) 3075, 1703, 1638, 1612, 1581, 1512, 1464, 1247, 1095, 1034, 916, 816 cm^{-1} ; TLC R_f 0.42 (20% Et_2O in petroleum ether); Anal. Calc'd for $\text{C}_{10}\text{H}_{16}\text{O}_3$: C, 73.25; H, 8.45. Found: C, 73.51; H, 8.60.

The same oxidation procedure was followed: 1.4 g 3-hydroxy-2,2-dimethyl-hex-5-enyl acetate⁶ gave 1.25 g **2e** (90% yield) after flash chromatography on silica gel with ether in petroleum ether (20%).

^1H NMR (500 MHz, CDCl_3) δ 5.92 (dddd, $J=6.7, 6.7, 10.3, 17.1$ Hz, 1H), 5.16 (dq, $J=1.3, 10.3$ Hz, 1H), 5.10 (dq, $J=1.5, 17.1$ Hz, 1H), 4.11 (s, 2H), 3.28 (dt, $J=1.5, 16.7$ Hz, 2H), 2.03 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 210.7, 170.8, 130.9, 118.3, 69.8, 47.6, 42.0, 21.7, 20.8; IR (neat film) 3077, 1744, 1710, 1638, 1474, 1372, 1241, 1119, 1038, 992, 924 cm^{-1} ; TLC R_f 0.34 (20% Et_2O in petroleum ether); Anal. Calc'd for $\text{C}_{10}\text{H}_{16}\text{O}_3$: C, 65.19; H, 8.75. Found: C, 65.14; H, 8.84.

A suspension of (S)-3-(4-methoxy-benzyloxy)-2,2-dimethyl-hex-5-en-1-ol⁷ (0.228 g, 0.91 mmol) and IBX (0.766 g, 2.74 mmol) in CH_3CN (4 mL) was heated at 80 $^\circ\text{C}$ for 1 h.

(5) Trieselmann, T.; Hoffmann, R. W.; Menzel, K. *Eur. J. Org. Chem.* **2002**, 7, 1292.

(6) Bode, J. W.; Gauthier, D. R.; Carreira, E. M. *Chem. Commun.* **2001**, 24, 2560.

(7) White, J. D.; Blakemore, P. R.; Browder, C. C.; Hong, J.; Lincoln, C. M.; Nagornyy, P. A.; Robarge, L. A.; Wardrop, D. J. *J. Am. Chem. Soc.* **2001**, 123, 8593.

After cooling to room temperature, the mixture was diluted with ether (5 mL), filtered through celite, and concentrated to give a crude aldehyde (0.23 g).

^1H NMR (500 MHz, CDCl_3) δ 9.52 (s, 1H), 7.21 (d, $J=8.3$ Hz, 2H), 6.88 (d, $J=8.7$ Hz, 2H), 5.76 (ddd, $J=8.3, 10.4, 18.7$ Hz, 1H), 5.43 (ddd, $J=0.7, 1.7, 10.4$ Hz, 1H), 5.31 (ddd, $J=0.8, 1.7, 17.1$ Hz, 1H), 4.55 (d, $J=11.7$ Hz, 1H), 4.26 (d, $J=11.7$ Hz, 1H), 3.84-3.82 (m, 1H), 3.83 (s, 3H), 1.1 (s, 3H), 1.0 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.7, 159.1, 133.7, 130.1, 129.3, 120.6, 113.7, 83.5, 69.8, 55.2, 49.6, 19.5, 16.5.

To a solution of the crude aldehyde in ether (3 mL) at -78°C was added vinylmagnesium bromide (1M in ether, 1.8 mL, 1.8 mmol). The reaction was stirred at the same temperature for 30 min, quenched with saturated aqueous NH_4Cl , and extracted with ether (2x). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated to give an oil.

^1H NMR (500 MHz, CDCl_3) read from the spectrum δ 7.24-7.21 (m, 2.2 H), 6.88-6.84 (m, 2H), 5.97-5.74 (m, 1.9 H), 5.40-5.35 (m, 0.8 H), 5.28-5.21 (m, 1.0H), 5.12-5.04 (m, 2.4 H), 4.55-4.52 (m, 1H), 4.25-4.20 (m, 0.9H), 3.82-3.80 (, 3.8 H), 3.68-3.65 (m, 1.3 H), 3.60-3.55 (m, 1.6 H), 2.28-2.17 (m, 1H), 2.10-1.97 (m, 1H), 0.96 (s, 2H), 0.90 (s, 1.8 H), 0.87 (s, 1.5 H), 0.76 (s, 2.5 H).

A suspension of the above oil and IBX (0.766 g, 2.74 mmol) in CH_3CN was heated at 80°C for 1h. After cooling to room temperature, the mixture was diluted with ether (5 mL), filtered through celite, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (10%, then 20%) to give 0.175 g **2f** (67% yield over 3 steps).

$[\alpha]_{\text{D}}^{23}$ 0.2 (c 1.0, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.17 (d, $J=8.4$ Hz, 2H), 6.85 (d, $J=8.7$ Hz, 2H), 5.92 (dddd, $J=6.9, 6.9, 10.4, 17.1$ Hz, 1H), 5.71 (ddd, $J=8.1, 10.4, 18.5$ Hz, 1H), 5.37 (dd, $J=1.8, 10.4$ Hz, 1H), 5.28 (ddd, $J=0.7, 1.8, 17.2$ Hz, 1H), 5.13 (dq, $J=1.3, 10.2$ Hz, 1H), 5.02 (dq, $J=1.5, 13.7$ Hz, 1H), 4.46 (d, $J=11.3$ Hz, 1H), 4.19 (d, $J=11.3$ Hz, 1H), 3.91 (d, $J=8.1$ Hz, 1H), 3.80 (s, 3H), 3.32-3.18 (m, 2H), 1.16 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.3, 159.0, 134.3, 131.7, 130.3, 129.3, 120.2, 117.8, 113.6, 85.4, 70.1, 55.2, 51.3, 43.2, 22.1, 18.8; IR (neat film): 3078, 1704, 1639, 1611, 1583, 1508, 1461, 1382, 1298, 1247, 1172, 1065, 1032, 990, 930, 818; TLC R_f 0.69 (15% EtOAc in petroleum ether); HRMS Calc'd for $\text{C}_{18}\text{H}_{24}\text{O}_3$: 288.1725. Found: 288.1733.

General Procedure for Carrying out Ru-catalyzed Alkyne- β,γ -enone Coupling Reaction:

A point-shaped vial, equipped with a stir bar and capped with a rubber septum, was flame-dried and cooled under argon atmosphere. The septum was temporarily removed to allow the addition of alkyne (0.25 mmol), enone (0.75 mmol), and acetone (0.5 mL). After stirring at room temperature for 5 min to ensure the formation of a homogeneous solution, the septum was again removed and $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (11 mg, 0.025 mmol) was added quickly. The vial was sealed and the septum was wrapped with a black electric tape. After stirring at room temperature for 40 h, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give the desired product.

Reaction of alkyne **1a** (0.074 g, 0.25 mmol) with β,γ -enone **2d** (0.195 g, 0.76 mmol) gave 0.081 g **12a** (58% yield) and 0.018 g impure **12b** (~13% yield).

Characterizations for **12a**: ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J=8.8$ Hz, 2H), 6.86 (d, $J=8.6$ Hz, 2H), 5.27 (s, 1H), 4.49 (dd, $J=11.8, 15.6$ Hz, 2H), 3.87-3.82 (m, 1H), 3.80 (s, 3H), 3.58 (d, $J=9.8$ Hz, 1H), 3.54 (d, $J=9.7$ Hz, 1H), 3.52-3.42 (m, 3H), 2.93 (dd, $J=5.1, 17.3$ Hz, 1H), 2.59 (dd, $J=7.3, 17.3$ Hz, 1H), 2.39 (d, $J=13.4$ Hz, 1H), 2.28 (d, $J=12.9$, 1H), 2.00-1.94 (m, 2H), 1.08 (s, 3H), 1.06 (s, 3H), 0.86 (s, 9H), 0.08 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.3, 159.1, 152.5, 130.4, 129.2, 123.7, 113.7, 77.4, 74.9, 72.9, 72.8, 69.9, 55.2, 49.6, 45.2, 44.5, 36.5, 25.8, 21.2(2x), 18.2, 0.2, -5.6; IR (neat film) 1708, 1618, 1586, 1510, 1469, 1244, 1172, 1095, 1036, 838, 775 cm^{-1} ; TLC $R_f=0.68$ (15% EtOAc in petroleum ether); Anal. calcd for $\text{C}_{30}\text{H}_{52}\text{O}_5\text{Si}_2$: C, 65.64; H, 9.55. Found C, 65.88; H, 9.25.

Reaction of the racemic alkyne **1e**⁸ (0.093 g, 0.55 mmol) with β,γ -enone **2b** (0.253 g, 1.64 mmol) gave 0.096 g **13** (54% yield) as the only isolated product.

^1H NMR (500 MHz, CDCl_3) δ 5.15 (d, $J=1.7$ Hz, 1H), 4.79-4.74 (m, 1H), 3.52 (ddd, $J=2.5, 6.6, 12.9$ Hz, 1H), 2.69 (dd, $J=7.2, 15.4$, 1H), 2.47-2.41 (m, 3H), 2.35 (dd, $J=2.4, 7.1, 13.9$ Hz, 1H), 2.23 (ddd, $J=1.8, 11.5, 13.3$ Hz, 1H), 1.98 (dd, $J=2.4, 13.2$ Hz, 1H), 1.58-1.53 (m, 2H), 1.32-1.25 (m, 6H), 1.11 (d, $J=6.5$ Hz, 3H), 1.00 (d, $J=7.0$ Hz, 3H), 0.87 (t, $J=6.8$ Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.4, 159.1, 122.3, 76.0, 75.2, 49.2, 43.8, 41.4, 40.6, 31.6, 28.8, 23.5, 22.5, 18.5, 14.0, 12.1, 0.2; IR (neat film): 1711, 1613, 1452, 1426, 1405, 1368, 1244, 1156, 1089, 1016, 860, 840 cm^{-1} ; TLC R_f 0.73 (10% EtOAc in petroleum ether); Anal. calcd for $\text{C}_{19}\text{H}_{36}\text{O}_2\text{Si}$: C, 70.31; H, 11.18. Found: C, 70.47; H, 11.00.

Reaction of alkyne **1a** (0.069 g, 0.24 mmol) with β,γ -enone **2f** (0.205 g, 0.71 mmol) gave 0.054 g **14a** (39% yield) together with 0.010 g of the *trans*-isomer **14b** (7%).

Characterizations for **14a**: $[\alpha]_D^{24.6} +8.7$ (c 3.6, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J=8.4$ Hz, 2H), 7.17 (d, $J=8.6$ Hz, 2H), 6.88-6.82 (m, 4H), 5.70 (ddd, $J=8.0, 10.4, 18.4$ Hz, 1H), 5.34 (dd, $J=7.1, 10.4$ Hz, 1H), 5.28-5.25 (m, 2H), 4.49 (d, $J=3.5$ Hz, 2H),

(8) Trost, B. M., Yang, H.; Probst, G. D. *J. Am. Chem. Soc.*, **2004**, *126*, 48.

4.45 (d, $J=11.3$ Hz, 1H), 4.18 (d, $J=11.3$ Hz, 1H), 3.94 (d, $J=8.0$ Hz, 1H), 3.85-3.80 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.53-2.41 (m, 3H), 2.89 (dd, $J=5.1, 17.5$ Hz, 1H), 2.60 (dd, $J=7.3, 17.4$ Hz, 1H), 2.38 (dt, $J=1.7, 13.3$ Hz, 1H), 2.23 (d, $J=12.9$ Hz, 1H), 1.98-1.90 (m, 2H), 1.16 (s, 3H), 0.99 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 212.4, 159.1, 158.9, 152.6, 134.4, 130.4, 130.3, 129.2 (2x), 123.6, 120.1, 113.7, 113.6, 85.4, 77.2, 74.9, 72.9, 72.8, 70.1, 55.2 (2x), 51.2, 45.2, 45.1, 36.5, 21.8, 18.8, 0.3; IR (neat film) 3076, 1705, 1610, 1580, 1511, 1461, 1361, 1290, 1241, 1092, 1032, 838 cm^{-1} ; TLC R_f 0.29 (10% EtOAc in petroleum ether); MS cal'd for $\text{C}_{34}\text{H}_{48}\text{O}_6\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 603.3. Found: C, 603.3.

Characterizations for **14b**: $[\alpha]_D^{22.3}$ -13.2 (c 0.8, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.26 (d, $J=8.5$ Hz, 2H), 7.17 (d, $J=8.5$ Hz, 2H), 6.88-6.83 (m, 4H), 5.68 (ddd, $J=7.9, 10.4, 18.2$ Hz, 1H), 5.36 (dd, $J=1.8, 10.5$ Hz, 1H), 5.27 (dd, $J=0.8, 17.2$ Hz, 1H), 5.24 (s, 1H), 4.48-4.45 (m, 3H), 4.30-4.26 (m, 1H), 4.20 (d, $J=11.4$ Hz, 1H), 3.90 (d, $J=2.7$ Hz, 1H), 3.81-3.76 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.51 (dd, $J=5.9, 9.6$ Hz, 1H), 3.44 (dd, $J=6.0, 9.7$ Hz, 1H), 2.74 (dd, $J=5.0, 17.5$ Hz, 1H), 2.57 (dd, $J=7.6, 17.4$ Hz, 1H), 2.40-2.34 (m, 2H), 2.23 (dd, $J=6.1, 13.6$ Hz, 1H), 1.98 (dd, $J=6.8, 13.0$ Hz, 1H), 1.11 (s, 3H), 1.01 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 211.8, 159.2, 159.0, 150.5, 134.4, 130.3, 129.4, 129.2, 125.7, 120.2, 113.7, 113.6, 84.7, 73.1, 72.1, 71.0, 69.9, 69.4, 55.2, 51.5, 43.9, 42.2, 35.5, 30.3, 29.7, 21.9, 18.9, 0.2; IR (neat film) 3072, 1705, 1610, 1584, 1512, 1483, 1298, 1249, 1173, 1097, 1034, 837; TLC R_f 0.17 (10% EtOAc in petroleum ether); MS cal'd for $\text{C}_{34}\text{H}_{48}\text{O}_6\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 603.3. Found: 603.3.

Reaction of alkyne **1a** (0.074 g, 0.25 mmol) with β,γ -enone **2e** (0.140 g, 0.76 mmol) gave 0.093 g **15a** and its *trans*-isomer **15b** as an inseparable mixture. The diastereomeric ratio could not be accurately determined due to peaks overlap.

^1H NMR (500 MHz, CDCl_3) δ 7.24 (d, $J=8.7$ Hz, 2H), 6.86 (d, $J=8.8$ Hz, 2H), 5.27 (s, 1H), 4.48 (dd, $J=11.8, 14.7$ Hz, 2H), 4.12 (d, $J=11.1$ Hz, 1H), 4.07 (d, $J=11.2$ Hz, 1H), 3.89-3.84 (m, 1H), 3.80 (s, 3H), 3.52-3.49 (m, 1H), 3.48-3.41 (m, 2H), 2.91 (dd, $J=5.7, 17.0$ Hz, 1H), 2.54 (dd, $J=6.7, 17.0$ Hz, 1H), 2.39 (dt, $J=2.8, 13.3$ Hz, 1H), 2.25 (d, $J=12.9$ Hz, 1H), 2.02 (s, 3H), 2.02-1.94 (m, 2H), 1.15 (s, 3H), 1.14 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 210.5, 170.7, 159.1, 152.2, 130.3, 129.2, 124.0, 113.7, 77.4, 74.8, 72.9, 72.7, 69.7, 55.2, 47.5, 44.9, 43.8, 36.4, 21.4 (2x), 20.8, 0.2; IR (neat film) 1744, 1708, 1613, 1586, 1509, 1465, 1370, 1302, 1244, 1172, 1100, 1032, 838 cm^{-1} ; TLC R_f 0.22 (15% EtOAc in petroleum ether); Anal. calc'd for $\text{C}_{26}\text{H}_{40}\text{O}_6\text{Si}$: C, 65.51; H, 8.46. Found: C, 65.25; H, 8.35.

Reaction of alkyne **1a** (0.074 g, 0.25 mmol) with β,γ -enone **2c** (0.205 g, 0.71 mmol) gave 0.096 g **16** (69% yield).

^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J=9.2$ Hz, 2H), 7.20 (d, $J=8.8$ Hz, 2H), 6.88-6.85 (m, 4H), 5.26 (s, 1H), 4.49 (dd, $J=11.8, 15.9$ Hz, 2H), 4.40 (dd, $J=12.1, 13.7$ Hz, 2H), 3.88-3.83 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.53-3.37 (m, 5H), 2.90 (dd, $J=5.4, 17.2$ Hz, 1H), 2.57 (dd, $J=7.2, 17.2$ Hz, 1H), 2.39 (dt, $J=1.7, 13.1$ Hz, 1H), 2.25 (dt, $J=1.7, 13.0$ Hz, 1H), 1.99-1.94 (m, 2H), 1.11 (s, 3H), 1.10 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 211.8, 159.1, 152.5, 130.4, 130.2, 129.2, 129.1, 123.8, 113.7 (2x), 77.4, 76.5, 74.9, 72.9, 72.8, 55.2, 48.6, 45.0, 44.1, 36.5, 21.7 (2x), 0.3; IR (neat film) 1707, 1609, 1583, 1511, 1460, 1358, 1298, 1249, 1171, 1095, 1031, 835 cm^{-1} ; TLC R_f 0.35 (15% EtOAc in petroleum ether); Anal. Calc'd for $\text{C}_{32}\text{H}_{46}\text{O}_6\text{Si}$: C, 69.28; H, 8.36. Found: C, 69.45; H, 7.14.

Reaction of racemic alkyne **1a** (0.11 g, 0.38 mmol) with 2,2-dimethyl-hex-5-en-3-one **2a** (0.14 g, 1.13 mmol) gave 0.107 g **17a** (68% yield) and 0.023 g **17b** (15% yield).

^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J=8.6$ Hz, 2H), 6.87 (d, $J=8.8$ Hz, 2H), 5.27 (s, 1H), 4.49 (dd, $J=11.8, 15.5$ Hz, 2H), 3.88-3.83 (m, 1H), 3.80 (s, 3H), 3.53-3.49 (m, 1H), 3.49-3.42 (m, 2H), 2.91 (dd, $J=5.7, 16.7$ Hz, 1H), 2.54 (dd, $J=7.0, 17.0$ Hz, 1H), 2.38 (dt, $J=2.0, 13.5$ Hz, 1H), 2.24 (dt, $J=2.0, 13.0$ Hz, 1H), 1.98 (m, 2H), 1.12 (s, 9H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 213.5, 159.1, 152.4, 130.3, 129.2, 123.9, 113.7, 77.4, 75.1, 72.9, 72.8, 55.2, 45.0, 44.2, 43.1, 36.4, 26.1, 0.2; IR (neat film) 1701, 1615, 1585, 1512, 1473, 1460, 1362, 1245, 1099, 1035, 837 cm^{-1} ; TLC R_f 0.38 (6% EtOAc in petroleum ether); HRMS calc'd for $\text{C}_{20}\text{H}_{29}\text{O}_4\text{Si}$ $[\text{M}-\text{C}_4\text{H}_9]^+$: 361.1835. Found: 361.1835.

Reaction of racemic alkyne **1d** (0.102 g, 0.25 mmol) with 2,2-dimethyl-hex-5-en-3-one **2a** (0.095 g, 0.75 mmol) gave 0.074 g **18** (56% yield). The *cis/trans* ratio (5/1) in the crude reaction mixture was determined by integrating peaks at 5.29 PPM for the major and 5.25 PPM for the minor.

^1H NMR (500 MHz, CDCl_3) δ 7.69-7.66 (m, 4H), 7.44-7.36 (m, 6H), 5.29 (s, 1H), 3.85 (dddd, $J=2.2, 6.2, 6.2, 12.8$ Hz, 1H), 3.74 (dd, $J=5.1, 10.1$ Hz, 1H), 3.54 (dd, $J=6.4, 10.0$ Hz, 1H), 3.46 (m, 1H), 2.81 (dd, $J=6.1, 16.7$ Hz, 1H), 2.64 (d, $J=13.3$ Hz, 1H), 2.47 (dd, $J=6.5, 16.7$ Hz, 1H), 2.24 (d, $J=12.8$ Hz, 1H), 1.95 (t, $J=12.0$ Hz, 1H), 1.89 (t, $J=12.0$ Hz, 1H), 1.11 (s, 9H), 1.06 (s, 9H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 213.4, 152.7, 135.6 (2x), 133.5, 129.6, 127.6, 123.7, 78.4, 74.9, 66.9, 45.3, 44.2, 43.0, 36.9, 26.8, 26.0, 19.2, 0.2; IR (neat film) 3076, 3049, 1703, 1619, 1588, 1472, 1424, 1357, 1242, 1109, 1087, 838, 701, 607 cm^{-1} ; TLC R_f 0.52 (10% Et_2O in petroleum ether); HRMS calc'd for $\text{C}_{28}\text{H}_{29}\text{O}_3\text{Si}_2$ $[\text{M}-\text{C}_4\text{H}_9]^+$: 479.2427. Found: 479.2438.

Reaction of racemic alkyne **1c** (0.043 g, 0.25 mmol) with 2,2-dimethyl-hex-5-en-3-one **2a** (0.095 g, 0.75 mmol) gave 0.060 g **19** (80% yield). The *cis/trans* ratio (5/1) in the crude reaction mixture was determined by integrating peaks at 5.24 PPM for the minor and 5.22 PPM for the major.

¹HNMR (500 MHz, CDCl₃) δ 5.23 (s, 1H), 3.84-3.79 (m, 1H), 3.17-3.12 (m, 1H), 2.87 (dd, J=6.5, 16.5 Hz, 1H), 2.46 (dd, J=6.2, 16.5 Hz, 1H), 2.42 (dt, J=2.0, 12.9 Hz, 1H), 2.21 (dt, J=1.9, 12.9 Hz, 1H), 2.0 (t, J=11.4 Hz, 1H), 1.80 (t, J=11.7 Hz, 1H), 1.59-1.50 (m, 1H), 1.48-1.40 (m, 1H), 1.13 (s, 9H), 0.90 (t, J=7.4 Hz, 3H), 0.09 (s, 9H); ¹³CNMR (125 MHz, CDCl₃) δ 213.6, 153.4, 123.1, 79.7, 75.1, 45.3, 44.3, 43.1, 39.5, 29.2, 26.0, 9.9, 0.3; IR (neat film) 1708, 1620, 1478, 1462, 1365, 1242, 1141, 1066, 851, 833 cm⁻¹; TLC R_f 0.69 (10% Et₂O in petroleum ether); Anal. calc'd for C₁₇H₃₂O₂Si: C, 68.86; H, 10.88. Found: C, 69.02; H, 10.92.

Reaction of racemic alkyne **1b** (0.077 g, 0.25 mmol) with 2,2-dimethyl-hex-5-en-3-one **2a** (0.095 g, 0.75 mmol) gave 0.063 g **20** (58% yield). The *cis/trans* ratio (5/1) in the crude reaction mixture was determined by integrating peaks at 5.27 PPM for the minor and 5.24 PPM for the major.

¹HNMR (500 MHz, CDCl₃) δ 7.25 (d, J=8.5 Hz, 2H), 6.86 (d, J=8.5 Hz, 2H), 5.24 (s, 1H), 4.41 (s, 2H), 3.84-3.80 (m, 1H), 3.80 (s, 3H), 3.51 (t, J=6.7 Hz, 2H), 3.43-3.38 (m, 1H), 2.81 (dd, J=6.5, 16.3 Hz, 1H), 2.44 (d, J=6.1 Hz, 1H), 2.41 (d, J=6.0 Hz, 1H), 2.20 (d, J=12.7 Hz, 1H), 1.99 (t, J=12.0 Hz, 1H), 1.86 (t, J=12.3 Hz, 1H), 1.83-1.71 (m, 2H), 1.11 (s, 9H), 0.08 (s, 9H); ¹³CNMR (125 MHz, CDCl₃) δ 213.4, 159.1, 152.9, 130.6, 129.3, 123.5, 113.7, 75.5, 75.0, 72.7, 66.6, 55.2, 45.1, 44.2, 43.0, 40.0, 36.5, 26.0, 0.28; IR (neat film) 1702, 1617, 1583, 1501, 1365, 1246, 1092, 1037, 840; TLC R_f 0.69 (30% Et₂O in petroleum ether); Anal. calc'd for C₂₅H₄₀O₄Si: C, 69.40; H, 9.32. Found: C, 70.22; H, 9.46

Reaction of alkyne **1b** (0.077 g, 0.025 mmol) with β,γ-enone **2b** (0.116 g, 0.075 mmol) gave 0.074 g **21** (64% yield). The *cis/trans* ratio (6/1) in the crude reaction mixture was determined by integrating peaks at 5.28 PPM for the minor and 5.24 PPM for the major.

¹HNMR (500 MHz, CDCl₃) δ 7.24 (d, J=8.5 Hz, 2H), 6.86 (d, J=8.6 Hz, 2H), 5.24 (s, 3H), 4.40 (s, 2H), 3.79 (s, 3H), 3.78-3.73 (m, 1H), 3.52 (t, J=6.7 Hz, 2H), 3.44-3.39 (m, 1H), 2.64 (dd, J=7.8, 15.3 Hz, 1H), 2.44-2.38 (m, 4H), 2.17 (d, J=13.1 Hz, 1H), 2.04 (t,

$J=12.0$ Hz, 1H), 1.87 (t, $J=8.3$ Hz, 1H), 1.83-1.71 (m, 2H), 1.57-1.52 (m, 2H), 1.31-1.24 (m, 6H), 0.87 (t, $J=6.7$ Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.2, 159.1, 152.7, 130.5, 129.2, 123.6, 113.7, 75.4, 75.0, 72.7, 66.5, 55.2, 49.0, 45.3, 43.8, 39.9, 36.4, 31.6, 28.8, 23.5, 22.5, 14.0, 0.2; IR (neat film): 1711, 1617, 1583, 1510, 1463, 1365, 1301, 1246, 1173, 1139, 1096, 1037, 840 cm^{-1} ; TLC R_f 0.41 (20% ether in petroleum ether); Anal. calc'd for $\text{C}_{27}\text{H}_{44}\text{O}_4\text{Si}$: C, 70.39; H, 9.63. Found: 70.52; H, 9.53.

Reaction of alkyne **1c** (0.622 g, 3.65 mmol) with β,γ -enone **2b** (1.69 g, 11.0 mmol) gave 0.733 g **5** (62% yield). The *cis/trans* ratio (8/1) in the crude reaction mixture was determined by integrating peaks at 5.27 PPM for the minor and 5.23 PPM for the major.

^1H NMR (500 MHz, CDCl_3) δ 5.23 (s, 1H), 3.79-3.73 (m, 1H), 3.16-3.11 (m, 1H), 2.69 (dd, $J=7.9, 15.1$ Hz, 1H), 2.49-2.39 (m, 4H), 2.17 (dt, $J=1.8, 12.9$ Hz, 1H), 2.04 (t, $J=12.3$, 1H), 1.81 (t, $J=12.2$, 1H), 1.59-1.52 (m, 2H), 1.49-1.41 (m, 1H), 1.31-1.26 (m, 7H), 0.91 (t, $J=7.4$ Hz, 3H), 0.87 (t, $J=7.1$ Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.5, 153.2, 123.2, 79.8, 75.1, 49.1, 45.4, 43.8, 39.5, 31.6, 29.2, 28.8, 23.4, 22.5, 14.0, 9.9, 0.2; IR (neat film) 1717, 1620, 1462, 1361, 1246, 1141, 1061, 885, 837 cm^{-1} ; Anal. calc'd for $\text{C}_{19}\text{H}_{36}\text{O}_2\text{Si}$: C, 70.31; H, 11.18. Found: C, 70.00; H 11.19.

To a solution of vinylsilane **5** (0.078 g, 0.24 mmol) in toluene (2.4 mL) at 0 $^\circ\text{C}$ was added trifluoroacetic acid (0.071 mL, 0.96 mmol). The ice- H_2O bath was removed after the addition. After stirring at room temperature for 3 h, the mixture was poured into ice-cold saturated aqueous NaHCO_3 , extracted with ether (3x). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (6%, then 8%) to give 0.054 g **6** as an oil (89% yield).

^1H NMR (500 MHz, CDCl_3) δ 4.72 (t, $J=1.8$ Hz, 2H), 3.74-3.69 (m, 1H), 3.19-3.13 (m, 1H), 2.71 (dd, $J=7.9, 15.1$ Hz, 1H), 2.51-2.40 (m, 3H), 2.22 (dddd, $J=2.0, 2.0, 3.9, 17.3$ Hz, 2H), 1.90 (q, $J=13.1$ Hz, 2H), 1.58-1.41 (m, 4H), 1.31-1.24 (m, 6H), 0.90 (t, $J=7.4$ Hz, 3H), 0.87 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.6, 144.2, 108.8, 79.9, 74.9, 49.1, 43.9, 40.7, 40.2, 31.6, 29.1, 28.8, 23.4, 22.5, 14.0, 9.9; IR (neat film): 3078, 1715, 1645, 1461, 1362, 1323, 1147, 1064, 988, 886; TLC R_f 0.33 (8% ether in petroleum ether); HRMS Calc'd for $\text{C}_{16}\text{H}_{28}\text{O}_2$: 252.2089. Found: 252.2096.

To a solution of vinylsilane **5** (0.134 g, 0.41 mmol) in CH₃CN at 0 °C in dark was added *N*-iodosuccinimide (0.149 g, 0.66 mmol). After stirring at 0 °C for 3 h, the mixture was diluted with saturated aqueous Na₂S₂O₃, extracted with ether. The combined organic layer was dried (MgSO₄), filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (5%, then 10%) to give 0.140 g **22** as an oil (90% yield).

¹HNMR (500 MHz, CDCl₃) δ 5.94 (t, J=1.8 Hz, 1H), 3.74-3.69 (m, 1H), 3.19-3.14 (m, 1H), 2.71 (dd, J=7.4, 15.5 Hz, 1H), 2.64 (dt, J=2.1, 13.8 Hz, 1H), 2.50-2.39 (m, 4H), 1.99 (dddd, J=1.7, 1.7, 3.1, 13.3 Hz, 1H), 1.76 (dddd, J=1.3, 1.3, 2.8, 13.9 Hz, 1H), 1.59-1.49 (m, 4H), 1.31-1.24 (m, 6H), 0.94 (t, J=7.4 Hz, 3H), 0.87 (t, J=6.8 Hz, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 209.1, 145.9, 78.7, 74.2, 73.8, 48.3, 43.9, 42.7, 41.0, 31.6, 29.0, 28.8, 23.4, 22.5, 14.0, 9.9; IR (neat film): 3057, 1711, 1618, 1459, 1362, 1136, 1061, 986, 769 cm⁻¹; TLC R_f 0.42 (10% ether in petroleum ether); Anal. Calc'd for C₁₆H₂₇IO₂: C, 50.80; H, 7.19. Found: C, 50.70; H, 6.95.

Vinyl iodide **22** (0.128 g, 0.34 mmol) was dissolved in MeOH (8 mL) under argon. PdCl₂(PhCN)₂ (0.039 g, 0.1 mmol), dppf (0.166 g, 0.3 mmol), and Et₃N (0.095 mL, 0.68 mmol) were added. The argon atmosphere was replaced by an atmosphere of CO (repeated evacuation and venting to a balloon with CO). The reaction mixture was heated at 60 °C for 1 h. The solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (10%, then 20%) to give 0.100 g **7** as an oil (97% yield).

¹HNMR (500 MHz, CDCl₃) δ 5.67 (s, 1H), 3.83-3.78 (m, 2H), 3.68 (s, 3H), 3.24-3.19 (m, 1H), 2.74 (dd, J=7.6, 15.5 Hz, 1H), 2.50-2.39 (m, 3H), 2.24 (d, J=13.3 Hz, 1H), 2.07 (t, J=12.0 Hz, 1H), 1.77 (d, J=13.0 Hz, 1H), 1.59-1.49 (m, 4H), 1.30-1.24 (m, 6H), 0.92 (t, J=7.4 Hz, 3H), 0.86 (t, J=6.8 Hz, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 209.0, 166.8, 157.2, 114.4, 79.1, 74.5, 51.0, 48.9, 43.9, 42.4, 35.3, 31.6, 29.2, 28.8, 23.4, 22.5, 14.0, 9.9; IR (neat film) 2953, 2928, 2873, 2865, 1715, 1648, 1434, 1371, 1238, 1193, 1175, 1149, 1117, 1064, 1019, 921, 863 cm⁻¹; TLC R_f 0.34 (10% ethyl acetate in petroleum ether); HRMS Calcd for C₁₈H₃₀O₄: 310.2144. Found: 310.2139.

To a suspension of vinylsilane **5** (0.068 mg, 0.21 mmol) and Li₂CO₃ (0.008 g, 0.11 mmol) in CH₂Cl₂ (4 mL) at 0 °C was added *m*-CPBA (70% purity, 0.104 g, 0.42 mmol). The mixture was stirred at room temperature for 3 h. Saturated aqueous Na₂S₂O₃ was then added. After stirring at room temperature for additional 30 min, the content was poured into a separatory funnel and extracted with ether (3x). The combined organic layer was dried (Na₂SO₄), filtered, and concentrated. The residue was purified by flash

chromatography on silica gel to give 0.051 g **23** as an oil (72% yield, dr 3/1 by integrating peaks at 4.10 PPM for the major and 3.92-3.87 PPM for the minor).

¹HNMR (500 MHz, CDCl₃) read from the spectrum δ 4.10 (dddd, J=2.3, 4.5, 6.8, 13.8 Hz, 1H), 3.92-3.87 (m, 0.36 H), 3.53-3.47 (m, 1.01 H), 3.42-3.39 (m, 0.37 H), 2.74 (dd, J=7.9, 15.5 Hz, 0.32 H), 2.61 (dd, J=8.3, 14.8 Hz, 0.98 H), 2.46-2.36 (m, 3.74 H), 2.13 (d, J=1.3 Hz, 0.28 H), 2.04 (s, 0.92 H), 1.90-1.76 (m, 1.58 H), 1.70-1.36 (m, 7.22 H), 1.29-1.21 (m, 8.91 H), 1.12 (dt, J=2.2, 13.6 Hz, 1.17 H), 0.90-0.84 (m, 7.4 H), 0.11-0.10 (m, 10.06 H); ¹³CNMR (125 MHz, CDCl₃) read from the spectrum δ 209.4, 209.2, 78.1, 73.3, 73.2, 72.32, 72.25, 61.6, 60.5, 59.8, 59.75, 57.61, 57.57, 49.1, 48.6, 44.1, 43.5, 42.6, 28.96, 28.8, 23.4, 22.4, 14.0, 9.9, -1.8; IR (neat film) 1710, 1461, 1407, 1367, 1327, 1247, 1126, 837, 756 cm⁻¹; TLC R_f 0.4 (10% ether in petroleum ether); MS calc'd for C₁₉H₃₆O₃SiNa [M+Na]⁺: 363.2. Found: 363.2.

To a solution of epoxysilane **23** (0.050 g, 0.15 mmol) in ether (5 mL) at -78 °C was added 48% aqueous HBr (0.1 mL). After stirring at -78 °C for 10 min, the mixture was poured into ice-cold saturated aqueous NaHCO₃, extracted with ether. The organic layer was dried (MgSO₄), filtered, and concentrated. The crude NMR indicated the disappearance of the starting material and formation of two compounds in a 3/1 ratio.

¹HNMR (400 MHz, CDCl₃) of the crude reaction mixture (read from the spectrum) δ 4.16-4.09 (m, 1H), 3.90 (s, 0.36 H), 3.84-3.77 (m, 0.43 H), 3.61-3.54 (m, 0.99 H), 2.73-2.61 (m, 1.43 H), 2.52-2.32 (m, 4.12 H), 2.02 (dt, J=2.7, 13.5 Hz, 1.15H), 1.79-1.74 (m, 2.39 H), 1.56-1.82 (m, 15 H), 0.92-0.85 (m, 6 H), 0.25 (s, 1.92 H), 0.22 (S, 6.40 H).

The residue was dissolved in CH₂Cl₂ (3 mL), and cooled to -78 °C. BF₃•OEt₂ (0.057 mL, 0.45 mmol) was added dropwise. The bath temperature was allowed to warm to 10 °C in 2 h. Then the mixture was poured into ice-cold saturated aqueous NaHCO₃, extracted with ether. The combined organic layer was dried (MgSO₄), filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (8%) to give 0.045 g **8** as an oil (97% yield).

¹HNMR (500 MHz, CDCl₃) δ 5.96 (t, J=2.0 Hz, 1H), 3.77-3.71 (m, 1H), 3.20-3.14 (m, 1H), 2.82 (dt, J=2.0, 13.7 Hz, 1H), 2.73 (dd, J=8.4, 15.2 Hz, 1H), 2.53-2.40 (m, 3H), 2.27 (dt, J=2.0, 13.5 Hz, 1H), 1.88 (ddt, J=1.7, 3.2, 13.3 Hz, 1H), 1.73 (ddt, J=1.5, 3.1, 13.4 Hz, 1H), 1.60-1.39 (m, 4H), 1.29-1.24 (m, 6H), 0.89 (t, J=7.5 Hz, 3H), 0.87 (t, J=7.0 Hz, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 209.5, 139.9, 100.0, 79.2, 73.6, 48.9, 43.3, 40.2, 36.7, 31.6, 28.8, 28.7, 23.4, 22.5, 14.0, 9.8; IR (neat film) 3067, 1713, 1633, 1461, 1363, 1328, 1283, 1150, 1066, 1030, 991, 769, 711 cm⁻¹; TLC R_f 0.39 (8% ether in petroleum ether); HRMS Calc'd for C₁₆H₂₇BrO₂: 330.1194. Found: 330.1204.

To a solution of bromide **8** (0.024 g, 0.076 mmol) in CH₃OH (1 mL) in a 25 mL round-bottom flask was added anhydrous DMF (2 mL) and Et₃N (0.03 mL, 0.21 mmol). The

content was degassed with freeze-pump-thaw (3x) technique and refilled with argon. The septum was quickly removed to allow the introduction of Pd(PPh₃)₄ (0.008 g, 0.007 mmol). The flask was cooled to -78 °C, evacuated, and refilled with CO (2x). The reaction was then heated under 1 atmosphere CO at 85 °C for 14 h. After cooling to room temperature, the content was poured into brine/H₂O (1/1), extracted with Et₂O. The organic layer was dried (MgSO₄), filtered, and concentrated. The residue was purified by flash chromatography on silica gel with ether in petroleum ether (10%, then 15%) to give 0.024 g **9** as an oil (quant. yield).

¹H NMR (500 MHz, CDCl₃) δ 5.68 (t, J=1.7 Hz, 1H), 3.84-3.76 (m, 2H), 3.68 (s, 3H), 3.29-3.24 (m, 1H), 2.72 (dd, J=8.5, 15.1 Hz, 1H), 2.51-2.40 (m, 3H), 2.18 (dt, J=1.7, 13.4 Hz, 1H), 2.04 (t, J=12.2 Hz, 1H), 1.84 (t, J=12.3 Hz, 1H), 1.59-1.52 (m, 3H), 1.51-1.44 (m, 1H), 1.32-1.23 (m, 6H), 0.90 (t, J=7.4 Hz, 3H), 0.87 (t, J=7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 209.0, 166.8, 157.0, 114.5, 79.5, 74.1, 51.0, 49.0, 43.8, 42.0, 35.7, 31.6, 29.1, 28.8, 23.4, 22.5, 14.0, 9.8; IR (neat film) 2953, 2929, 2875, 2849, 1714, 1650, 1434, 1370, 1150, 1073, 1026, 858 cm⁻¹; TLC R_f 0.23 (10% ether in petroleum ether); HRMS Calcd for C₁₈H₃₀O₄: 310.2144. Found: 310.2135.