[1,5]-Brook Rearrangement: An Overlooked but Valuable Silyl Migration to Synthesize Configurationally Defined Vinylsilane. The Unique Steric and Electronic Effects of Geminal Bis(silane)

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Supporting Information

Table of Contents

1. General Methods .......................................................... S2
2. General Procedure and Spectral Data of Products.............................. S2-S19
   2.1. [1,5]-Brook Rearrangement/Addition of Geminal Bis(silyl) Homoallylic Alcohols with Electrophiles ............. S2-S13
   2.2. Control Experiment .......................................................... S13-S14
   2.3. [1,5]-Brook Rearrangement/Addition of Mono-SiMe3-Substituted Homoallylic Alcohol 3 ......................... S14-S16
   2.4. Synthesis and Spectral Data of Z-Vinyliodide 9 and Enynes 10 .................................................. S16-S17
   2.5. Synthesis and Spectral Data of exo-Cyclic Z-Vinyl Bromide 11 and Z-Methyl Enoate 12 .................... S17-S19
3. $^1$H and $^{13}$C NMR Spectral Copies ................................................ S20-S75

Electronic Supplementary Material (ESI) for Chemical Communications

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1. General Methods

TLC was performed on glass-backed silica plates and visualized using UV, KMnO₄ stains, H₃PO₄·12MoO₃/EtOH stains, H₂SO₄(conc.)/anisaldehyde/EtOH stains. Column chromatography was performed using silica gel (300-400 mesh) eluting with EtOAc/petroleum ether. ¹H NMR spectra were recorded at 400 MHz (Varian) and ¹³C NMR spectra were recorded at 100 MHz (Varian) using CDCl₃ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed at State Key Laboratory of Biotherapy, West China Hospital, Sichuan University. HMPA, TMEDA, CH₃CN, DMSO, DMF, CH₂Cl₂ and Et₃N were distilled from CaH₂. Et₂O and THF were distilled from sodium. All spectral data obtained for new compounds are reported here.

2. General Procedure and Spectral Data of Products

2.1. [1,5]-Brook Rearrangement/Addition of Geminal Bis(silyl) Homoallylic Alcohols with Electrophiles

**Preparation of 2a**

![Chemical Structure](image)

2a: To a solution of 1a¹ (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.0 mL) under argon atmosphere was added n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol) at −78 °C. After stirring for 5 min, the resulting solution was warmed to −10 °C. A solution of benzaldehyde (66 µL, 0.6 mmol) and anhyd. HMPA (1.0 mL) in anhyd. Et₂O (0.3 mL) was added. The reaction mixture was stirred for 6 h at −10 °C before quenched with 10% aqueous HCl (1.0 mL). The mixture was extracted with Et₂O (3 × 5 mL). The combined organic layers were then dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded 2a (46 mg, 75% yield) [dr = 55:45]. **major-isomer:** ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9H),

0.93 (t, 3H, J = 6.8 Hz), 1.44-1.49 (m, 4H), 2.19-2.28 (m, 2H), 2.41-2.53 (m, 2H), 3.77 (m, 1H), 4.84 (dd, 1H, J₁ = 3.2 Hz, J₂ = 10.0 Hz), 5.49 (s, 1H), 7.27 (m, 1H), 7.33-7.36 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.4, 14.0, 18.8, 39.7, 44.2, 49.4, 70.5, 73.3, 125.7, 127.3, 128.2, 130.8, 144.1, 152.7; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.14 (s, 9H), 0.94 (t, 3H, J = 6.8 Hz), 1.44-1.49 (m, 4H), 2.30-2.32 (m, 2H), 2.44-2.56 (m, 2H), 3.85 (m, 1H), 4.88 (dd, 1H, J₁ = 5.2 Hz, J₂ = 8.4 Hz), 5.61 (s, 1H), 7.27 (m, 1H), 7.33-7.36 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.5, 14.1, 18.9, 39.5, 43.7, 48.5, 68.6, 73.1, 125.6, 127.4, 128.3, 131.1, 144.2, 152.2. IR (neat) cm⁻¹ 3338brs, 3030w, 2956s, 2873m, 1607s, 1452s, 1345m, 1249s, 1119m, 1054s, 1024s, 839s, 699s; HRMS (MALDI, m/z) calcd for C₁₈H₃₀O₂SiNa (M+Na)⁺: 329.1907, found 329.1904.

**Preparation of 2b**

2b: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 4-methoxybenzaldehyde (73 µL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced 2b (59 mg, 88% yield) [dr = 58:42] as a yellow oil. major-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9H), 0.93 (t, 3H, J = 7.2 Hz), 1.43-1.48 (m, 4H), 1.69 (s, 1H), 2.21-2.34 (m, 2H), 2.36-2.54 (m, 2H), 3.80 (s, 3H), 3.85 (m, 1H), 4.80 (dd, 1H, J₁ = 4.0 Hz, J₂ = 10.0 Hz), 5.49 (s, 1H), 6.86 (d, 2H, J = 8.8 Hz), 7.27 (d, 2H, J = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 0.4, 14.0, 18.8, 39.8, 44.3, 49.4, 55.2, 70.5, 73.0, 113.7, 127.0, 130.8, 136.4, 152.8, 158.8; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.15 (s, 9H), 0.96 (t, 3H, J = 7.2 Hz), 1.43-1.48 (m, 4H), 2.05 (s, 1H), 2.21-2.34 (m, 2H), 2.36-2.54 (m, 2H), 3.80 (s, 3H), 3.85 (m, 1H), 4.84 (t, 1H, J = 6.8 Hz), 5.60 (s, 1H), 6.88 (d, 2H, J = 8.8 Hz), 7.28 (d, 2H, J = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 0.5, 14.1, 18.9, 39.6, 43.8, 48.5, 55.2, 68.6, 72.7, 113.6, 126.9, 131.2, 136.3, 152.3, 158.9. IR (neat) cm⁻¹ 3356 brs, 3067w, 2956s, 2872m, 1610s, 1512s, 1461s, 1248s, 1175s, 1037s, 837s, 769m; HRMS (MALDI, m/z) calcd for C₁₉H₃₂O₃SiNa (M+Na)⁺: 359.2013, found 359.2015.

**Preparation of 2c**
2c: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 4-Chlorobenzaldehyde (84 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at −10 °C for 6 h produced 2c (40 mg, 60% yield) [dr = 52:48] as a yellow oil. major-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9H), 0.93 (t, 3H, J = 7.2 Hz), 1.44-1.49 (m, 4H), 2.20-2.33 (m, 2H), 2.39-2.59 (m, 2H), 3.78 (m, 1H), 4.83 (dd, 1H, J₁ = 3.2 Hz, J₂ = 10.0 Hz), 5.48 (s, 1H), 7.29-7.31 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.4, 14.0, 18.8, 39.9, 44.0, 49.7, 70.8, 72.6, 127.1, 128.3, 128.5, 131.3, 142.7, 152.4; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.15 (s, 9H), 0.94 (t, 3H, J = 7.2 Hz), 1.44-1.49 (m, 4H), 2.20-2.33 (m, 2H), 2.39-2.59 (m, 2H), 3.84 (m, 1H), 4.86 (dd, 1H, J₁ = 4.0 Hz, J₂ = 8.8 Hz), 5.60 (s, 1H), 7.29-7.31 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.5, 14.1, 18.9, 39.7, 43.6, 48.7, 68.8, 72.4, 127.1, 128.1, 128.4, 131.7, 142.6, 151.8. IR (neat) cm⁻¹ 3334brs, 3029w, 2956s, 2873s, 1606s, 1491s, 1458s, 1249s, 1091s, 1063s, 1014s, 840s, 773m, 691m; HRMS (MALDI, m/z) calcd for C₁₈H₂₉ClO₂SiNa (M+Na)⁺: 363.1518, found 363.1521.

Preparation of 2d

2d: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 2-Thenaldehyde (55 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at −10 °C for 6 h produced 2d (48 mg, 78% yield) [dr = 56:44] as a yellow oil. major-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9H), 0.85 (t, 3H, J = 6.8 Hz), 1.44-1.49 (m, 4H), 2.24-2.34 (m, 2H), 2.65-2.71 (m, 2H), 3.79 (m, 1H), 5.11 (dd, 1H, J₁ = 3.6 Hz, J₂ = 10.0 Hz), 5.53 (s, 1H), 6.94-6.97 (m, 2H), 7.22-7.25 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 0.4, 14.0, 18.8, 39.8, 44.0, 49.5, 69.1, 70.4, 123.4, 124.3, 126.5, 131.5, 148.1, 152.0; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.14 (s, 9H), 0.86 (t, 3H, J = 6.8
Hz), 1.44-1.49 (m, 4H), 2.24-2.34 (m, 2H), 2.65-2.71 (m, 2H), 3.85 (m, 1H), 5.14 (dd, 1H, \( J_1 = 4.8 \) Hz, \( J_2 = 8.0 \) Hz), 5.62 (s, 1H), 6.94-6.97 (m, 2H), 7.22-7.25 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl<sub>3</sub>) \( \delta \) 0.5, 14.1, 18.9, 39.7, 43.6, 48.6, 68.7, 69.3, 123.3, 124.4, 126.5, 131.7, 148.0, 151.5. IR (neat) cm\(^{-1}\) 3349 brs, 3074 w, 2956 s, 2931 s, 2872 s, 1609 s, 1438 s, 1248 s, 1123 s, 1034 s, 840 s, 770 m, 749 m, 696 s; HRMS (MALDI, m/z) calcd for C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>SSiNa (M+Na)<sup>+</sup>: 335.1477, found 335.1478.

**Preparation of 2e**

![Image of 2e](image)

2e: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 \( \mu \)L, 0.5 mmol) in anhyd. Et<sub>2</sub>O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), Isobutyraldehyde (55 \( \mu \)L, 0.6 mmol) and anhyd. HMPA (1.0 mL) at -10 °C for 6 h produced 2e (24 mg, 45% yield) \([d.r = 56:44]\) as a yellow oil. **major-isomer:** \(^1\)H NMR (400 MHz, CDCl<sub>3</sub>) \( \delta \) 0.10 (s, 9H), 0.90 (d, 6H, \( J = 7.2 \) Hz), 0.91 (t, 3H, \( J = 7.2 \) Hz), 1.17 (s, 1H), 1.35-1.49 (m, 4H), 1.66 (m, 1H), 2.02 (dd, 1H, \( J_1 = 11.2 \) Hz, \( J_2 = 13.6 \) Hz), 2.18-2.34 (m, 3H), 2.38-2.42 (m, 1H), 3.26 (s, 1H), 3.55 (m, 1H), 3.77 (m, 1H), 5.46 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl<sub>3</sub>) \( \delta \) 0.50, 14.0, 17.4, 18.6, 18.8, 33.6, 39.8, 43.1, 44.4, 70.8, 75.2, 129.9, 154.3; **minor-isomer:** \(^1\)H NMR (400 MHz, CDCl<sub>3</sub>) \( \delta \) 0.11 (s, 9H), 0.91 (d, 6H, \( J = 7.2 \) Hz), 0.92 (t, 3H, \( J = 7.2 \) Hz), 1.16 (s, 1H), 1.35-1.49 (m, 4H), 1.66 (m, 1H), 2.11 (dd, 1H, \( J_1 = 11.2 \) Hz, \( J_2 = 13.6 \) Hz), 2.18-2.34 (m, 3H), 2.38-2.42 (m, 1H), 3.49 (m, 1H), 3.77 (m, 1H), 3.91 (s, 1H), 5.52 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl<sub>3</sub>) \( \delta \) 0.54, 14.1, 17.7, 18.5, 18.9, 33.7, 39.7, 43.3, 44.5, 68.5, 74.5, 131.1, 153.1. IR (neat) cm\(^{-1}\) 3376 brs, 2958 s, 2875 m, 1717 m, 1607 m, 1466 m, 1248 m, 1048 m, 839 s, 690 m; HRMS (MALDI, m/z) calcd for C<sub>15</sub>H<sub>32</sub>O<sub>2</sub>SiNa (M+Na)<sup>+</sup>: 295.2069, found 295.2067.

**Preparation of 2f**

![Image of 2f](image)
2f: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), Pivaldehyde (65 µL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at −10 °C for 6 h produced 2f (25 mg, 44% yield) [dr = 63:37] as a yellow oil. major-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9H), 0.91 (m, 12H), 1.37-1.51 (m, 4H), 1.97 (m, 1H), 2.26-2.38 (m, 2H), 2.45 (m, 1H), 2.35 (d, 1H, J = 10.0 Hz), 3.77 (m, 1H), 5.53 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 0.54, 14.1, 18.9, 25.7, 34.5, 39.6, 40.6, 43.2, 68.4, 77.3, 131.3, 153.5; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9H), 0.91 (m, 12H), 1.37-1.51 (m, 4H), 1.97 (m, 1H), 2.26-2.38 (m, 2H), 2.45 (m, 1H), 2.43 (d, 1H, J = 10.0 Hz), 3.77 (m, 1H), 5.47 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 0.50, 14.0, 18.8, 25.6, 34.7, 39.8, 40.9, 44.5, 71.2, 78.3, 129.5, 155.1. IR (neat) cm⁻¹ 3314brs, 2958s, 2872s, 1605s, 1462s, 1363s, 1251s, 1075s, 1016s, 839s, 690m; HRMS (MALDI, m/z) calcd for C₁₆H₃₄O₂SiNa (M+Na)⁺: 309.2226, found 309.2228.

Preparation of 2g

2g: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 3-(benzyloxy)-2,2-dimethylpropanal (78 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at −10 °C for 6 h produced 2g (45 mg, 58% yield) [dr = 58:42] as a yellow oil. major-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.13 (s, 9H), 0.90 (t, 3H, J = 7.2 Hz), 0.96 (s, 6H), 1.37-1.42 (m, 2H), 1.43-1.49 (m, 2H), 2.04 (dd, 1H, J₁ = 11.2 Hz, J₂ = 13.2 Hz), 2.25 (m, 1H), 2.30-2.43 (m, 2H), 3.32-3.38 (m, 2H), 3.76 (d, 1H, J = 9.6 Hz), 3.80 (m, 1H), 3.80 (m, 1H), 4.18 (d, 1H, J = 12.0 Hz), 4.54 (d, 1H, J = 12.0 Hz), 5.52 (s, 1H), 7.29-7.34 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 0.6, 14.2, 19.0, 19.5, 22.5, 38.2, 39.5, 39.9, 44.4, 67.9, 73.5, 77.6, 79.8, 127.5, 128.4, 129.8, 137.7, 153.7; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9H), 0.91 (t, 3H, J = 7.2 Hz), 0.96 (s, 6H), 1.37-1.42 (m, 2H), 1.43-1.49 (m, 2H), 2.16 (dd, 1H, J₁ = 11.2 Hz, J₂ = 13.2 Hz), 2.25 (m, 1H), 2.30-2.43 (m, 2H), 3.32-3.38 (m, 2H), 3.70 (d, 1H, J = 9.6 Hz), 3.80 (m, 1H), 4.48 (d, 1H, J = 12.0 Hz), 4.54 (d, 1H, J = 12.0 Hz), 5.47 (s, 1H),
Preparation of 2h

2h: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), (E)-5-(benzyloxy)-2,2-dimethylpent-3-enal (130 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced 2h (69 mg, 83% yield) [dr = 51:49] as a yellow oil. **major-isomer:** ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9H), 0.91 (t, 3H, J = 6.8 Hz), 1.06 (s, 6H), 1.34-1.48 (m, 4H), 1.96 (dd, 1H, J₁ = 11.2 Hz, J₂ = 14.0 Hz), 2.20-2.34 (m, 2H), 2.40 (m, 1H), 3.45 (d, 1H, J = 10.8 Hz), 3.75 (m, 1H), 4.01 (d, 1H, J = 5.6 Hz), 4.50 (s, 2H), 5.45 (s, 1H), 5.60 (dt, 1H, J₁ = 5.6 Hz, J₂ = 15.6 Hz), 5.75 (d, 1H, J = 15.6 Hz), 7.26-7.30 (m, 1H), 7.33-7.34 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.5, 14.0, 18.8, 22.8, 23.1, 39.6, 40.4, 43.6, 68.3, 71.0, 72.0, 76.6, 124.9, 127.5, 127.7, 128.3, 129.4, 138.2, 140.5, 154.9; **minor-isomer:** ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9H), 0.92 (t, 3H, J = 6.8 Hz), 1.08 (s, 6H), 1.34-1.48 (m, 4H), 2.04 (dd, 1H, J₁ = 11.2 Hz, J₂ = 14.0 Hz), 2.20-2.34 (m, 2H), 2.40 (m, 1H), 3.51 (d, 1H, J = 10.8 Hz), 3.75 (m, 1H), 4.01 (d, 1H, J = 5.6 Hz), 4.50 (s, 2H), 5.51 (s, 1H), 5.60 (dt, 1H, J₁ = 5.6 Hz, J₂ = 15.6 Hz), 5.75 (d, 1H, J = 15.6 Hz), 7.26-7.30 (m, 1H), 7.33-7.34 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.6, 14.1, 18.9, 22.8, 23.3, 39.8, 41.9, 44.6, 68.3, 71.2, 72.0, 77.5, 125.0, 127.5, 127.7, 128.3, 130.8, 138.2, 140.6, 153.3. IR (neat) cm⁻¹ 3402brs, 3031w, 2957s, 2870s, 1607s, 1456s, 1360s, 1248s, 1103s, 1065s, 1204m, 839s, 740m, 696m; HRMS (MALDI, m/z) calcd for C₂₃H₄₀O₃SiNa (M+Na)⁺: 415.2644, found 415.2640.

Preparation of 2i
2i: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), Cinnamaldehyde (76 µL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced 2i (40 mg, 60% yield) [dr = 55:45] as a yellow oil. major-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.13 (s, 9H), 0.93 (t, 3H, J = 6.8 Hz), 1.37-1.50 (m, 4H), 2.27-2.35 (m, 2H), 2.39-2.51 (m, 2H), 3.84 (m, 1H), 4.49 (m, 1H), 5.55 (s, 1H), 6.20 (dd, 1H, J₁ = 6.4 Hz, J₂ = 15.6 Hz), 6.58 (d, 1H, J = 15.6 Hz), 7.22-7.25 (m, 1H), 7.29-7.33 (m, 2H), 7.36-7.37 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 0.4, 14.0, 18.8, 39.8, 44.1, 47.5, 70.4, 71.6, 126.3, 127.5, 128.5, 129.9, 131.3, 131.8, 136.6, 152.3; minor-isomer: ¹H NMR (400 MHz, CDCl₃) δ 0.15 (s, 9H), 0.94 (t, 3H, J = 6.8 Hz), 1.37-1.50 (m, 4H), 2.27-2.35 (m, 2H), 2.39-2.51 (m, 2H), 3.84 (m, 1H), 4.49 (m, 1H), 5.60 (s, 1H), 6.24 (dd, 1H, J₁ = 6.4 Hz, J₂ = 15.6 Hz), 6.62 (d, 1H, J = 15.6 Hz), 7.22-7.25 (m, 1H), 7.29-7.33 (m, 2H), 7.36-7.37 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 0.5, 14.1, 18.9, 39.6, 43.7, 46.5, 68.7, 71.4, 126.3, 127.6, 128.5, 129.9, 131.5, 131.6, 136.6, 151.8. IR (neat) cm⁻¹ 3353brs, 3027w, 2956s, 2872s, 1607s, 1450s, 1400s, 1307s, 1214s, 1100s, 1023s, 966s, 840s, 748m, 694m; HRMS (MALDI, m/z) calcd for C₂₀H₃₂O₂SiNa (M+Na)⁺: 355.2069, found 355.2071.

Preparation of 2j

2j: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzophenone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 2 h produced 2j (74 mg, 97% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.03 (s, 9H), 0.88 (t, 3H, J = 6.8 Hz), 1.14-1.24 (m, 2H), 1.30-1.35 (m, 2H), 1.80 (dd, 1H, J₁ = 2.8 Hz, J₂ = 13.6 Hz), 1.98 (dd, 1H, J₁ =
9.6 Hz, $J_2 = 13.6$ Hz), 3.13 (d, 1H, $J = 13.2$ Hz), 3.30 (d, 1H, $J = 13.2$ Hz), 3.67 (m, 1H), 5.30 (s, 1H), 7.17-7.22 (m, 2H), 7.26-7.31 (m, 4H), 7.39-7.44 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 0.3, 14.0, 18.6, 39.6, 50.6, 69.6, 76.8, 125.9, 126.0, 126.6, 126.7, 127.9, 128.0, 135.2, 146.8, 147.1, 151.8. IR (neat) cm$^{-1}$ 3381brs, 3028w, 2956s, 2871m, 1602s, 1492s, 1447s, 1247s, 1052s, 859s, 840s, 699s; HRMS (MALDI, m/z) calcd for C$_{24}$H$_{34}$O$_2$SiNa (M+Na)$^+$: 405.2220, found 405.2220.

**Preparation of 2k**

![Image of 2k](image)

2k: Using the same procedure as that used for 2a, 1a (54 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et$_2$O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzyl bromide (72 µL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at $-10$ °C for 8 h produced a mixture of 2k (18 mg, 31% yield) and its $\alpha$-addition isomer (18 mg, 31% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.12 (s, 9H), 0.94 (t, 3H, $J = 6.8$ Hz), 1.42-1.50 (m, 4H), 2.25 (dd, 1H, $J_1 = 4.0$ Hz, $J_2 = 13.2$ Hz), 2.31 (dd, 1H, $J_1 = 9.2$ Hz, $J_2 = 13.2$ Hz), 2.40 (t, 2H, $J = 8.0$ Hz), 2.75 (dt, 2H, $J = 8.0$ Hz, $J_2 = 16.0$ Hz), 3.75 (m, 1H), 5.45 (s, 1H), 7.17-7.23 (m, 3H), 7.26-7.28 (m, 2H); $\alpha$-major: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.08 (s, 9H), 0.80 (t, 3H, $J = 6.8$ Hz), 1.28-1.38 (m, 4H), 1.71 (dd, 1H, $J_1 = 3.6$ Hz, $J_2 = 12.4$ Hz), 1.80-1.87 (m, 2H), 2.63-2.69 (m, 2H), 2.98 (m, 1H), 4.83 (s, 1H), 4.93 (s, 1H), 7.17-7.23 (m, 3H), 7.26-7.28 (m, 2H); $\alpha$-minor: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.06 (s, 9H), 0.83 (t, 3H, $J = 6.8$ Hz), 1.11-1.23 (m, 4H), 1.80-1.87 (m, 2H), 2.05 (dd, 1H, $J_1 = 4.4$ Hz, $J_2 = 13.6$ Hz), 2.80-2.92 (m, 2H), 3.38 (m, 1H), 4.83 (s, 1H), 4.88 (s, 1H), 7.17-7.23 (m, 3H), 7.26-7.28 (m, 2H).

**Preparation of 2l**

![Image of 2l](image)
2l: Using the same procedure as that used for 2a, 1b (38 mg, 0.1 mmol) and TMEDA (37 µL, 0.25 mmol) in anhyd. Et₂O (0.7 mL) with n-BuLi (0.05 mL of 2.5 M solution in hexane, 0.11 mmol), benzophenone (54 mg, 0.3 mmol) and anhyd. HMPA (0.3 mL) at –10 °C for 2 h produced 2l (43 mg, 90% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.03 (s, 9H), 1.40-1.48 (m, 2H), 1.63-1.70 (m, 2H), 1.92 (dd, 1H, J₁ = 2.4 Hz, J₂ = 14.0 Hz), 2.08 (dd, 1H, J₁ = 9.6 Hz, J₂ = 14.0 Hz), 3.20 (d, 1H, J = 13.2 Hz), 3.29 (d, 1H, J = 13.2 Hz), 3.49 (t, 2H, J = 5.6 Hz ), 3.72 (m, 1H), 4.51 (s, 2H), 5.24 (s, 1H), 7.17-7.23 (m, 2H), 7.26-7.32 (m, 4H), 7.32-7.34 (m, 4H), 7.41-7.47 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 0.2, 26.1, 34.9, 43.5, 50.9, 70.1, 70.4, 73.0, 76.9, 126.0, 126.1, 126.5, 126.6, 127.6, 127.7, 127.8, 127.9, 128.3, 134.6, 137.9, 147.0, 147.3, 152.1. IR (neat) cm⁻¹ 3383brs, 3029w, 2951s, 2858m, 1602s, 1448s, 1248s, 1096s, 1057s, 839s, 747s, 698s; HRMS (MALDI, m/z) calcd for C₃₁H₄₀O₃SiNa (M+Na)⁺: 511.2639, found 511.2639.

Preparation of 2m

2m: Using the same procedure as that used for 2a, 1c (57 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzophenone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 2 h produced 2m (60 mg, 76% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.07 (s, 9H), 0.91 (d, 6H, J = 6.8 Hz), 1.03 (ddd, 1H, J₁ = 4.0 Hz, J₂ = 8.8 Hz, J₃ = 13.2 Hz), 1.34 (ddd, 1H, J₁ = 5.6 Hz, J₂ = 8.8 Hz, J₂ = 14.0 Hz), 1.69 (m, 1H), 1.76 (s, 1H), 1.81 (dd, 1H, J₁ = 2.8 Hz, J₂ = 13.6 Hz), 1.99 (dd, 1H, J₁ = 9.2 Hz, J₂ = 13.6 Hz), 3.17 (d, 1H, J = 12.8 Hz), 3.29 (s, 1H), 3.33 (d, 1H, J = 12.8 Hz), 3.77 (m, 1H), 5.34 (s, 1H), 7.21-7.25 (m, 2H), 7.26-7.34 (m, 4H), 7.43-7.47 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.3, 22.0, 23.4, 24.3, 44.1, 46.7, 50.8, 68.0, 76.8, 125.9, 126.0, 126.6, 126.7, 127.9, 135.3, 146.8, 147.0, 151.8. IR (neat) cm⁻¹ 3384brs, 3060w, 3028w, 2955s, 2870m, 1602s, 1429s, 1446s, 1248s, 1055s, 840s, 751s, 699s; HRMS (MALDI, m/z) calcd for C₂₅H₃₆O₂SiNa (M+Na)⁺: 419.2377, found 419.2381.
Preparation of 2n

\[ \text{Ph} \quad \text{Ph} \quad \text{SiMe}_3 \quad \text{OH} \quad \text{2n} \quad \text{Cy} \]

2n: Using the same procedure as that used for 2a, 1d (63 mg, 0.2 mmol) and TMEDA (75 µL, 0.5 mmol) in anhyd. Et\(_2\)O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzophenone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at \(-10^\circ\text{C}\) for 2 h produced 2n (56 mg, 66% yield) as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.05 (s, 9H), 0.85-0.93 (m, 3H), 1.11-1.20 (m, 4H), 1.48 (d, 1H, \(J = 12.8\) Hz), 1.63-1.72 (m, 4H), 1.77 (dd, 1H, \(J_1 = 2.4\) Hz, \(J_2 = 13.6\) Hz), 2.04 (dd, 1H, \(J_1 = 10.8\) Hz, \(J_2 = 13.6\) Hz), 3.10 (d, 1H, \(J = 13.2\) Hz), 3.24 (s, 1H), 3.34 (d, 1H, \(J = 13.2\) Hz), 3.44 (m, 1H), 5.34 (s, 1H), 7.20-7.22 (m, 2H), 7.27-7.34 (m, 4H), 7.38-7.45 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 0.3, 26.1, 26.2, 26.4, 28.1, 28.7, 40.3, 43.9, 50.4, 73.5, 76.7, 125.9, 126.0, 126.6, 126.7, 127.9, 135.5, 146.8, 147.1, 152.3. IR (neat) cm\(^{-1}\) 3389brs, 3028w, 2926s, 2853m, 1601s, 1492s, 1447s, 1248s, 1053s, 1033s, 862s, 839s, 752s, 699s; HRMS (MALDI, m/z) calcd for C\(_{27}\)H\(_{38}\)O\(_2\)SiNa (M+Na\(^+\)): 445.2533, found 445.2531.

Preparation of 2o

\[ \text{Ph} \quad \text{Ph} \quad \text{SiMe}_3 \quad \text{OH} \quad \text{2o} \quad \text{Me} \]

2o: Using the same procedure as that used for 2a, 1e (54 mg, 0.2 mmol) in Et\(_2\)O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), TMEDA (75 µL, 0.5 mmol), diphenylmethanone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at \(-10^\circ\text{C}\) for 2h produced 2o (70 mg, 93% yield) as a yellow oil; after flash column chromatography on silica gel using EtOAc: petroleum ether (1:20). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.03 (s, 9H), 1.67 (d, 3H, \(J = 6.0\) Hz), 1.90 (s, 1H), 1.96 (dd, 1H, \(J_1 = 4.0\) Hz, \(J_2 = 14.0\) Hz), 2.12 (dd, 1H, \(J_1 = 8.8\) Hz, \(J_2 = 14.0\) Hz), 3.21 (d, 1H, \(J = 13.6\) Hz), 3.30 (d, 1H, \(J = 13.6\) Hz), 3.44 (s, 1H), 4.14 (m, 1H), 5.26 (s, 1H), 5.35 (dd, 2H, \(J_1 = 3.0\) Hz, \(J_2 = 13.6\) Hz), 6.90 (d, 2H, \(J = 8.8\) Hz), \(J_1 = 8.8\) Hz, \(J_2 = 14.0\) Hz), 7.20-7.30 (m, 4H), 7.40-7.50 (m, 4H), 7.60-7.70 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 0.3, 26.1, 26.2, 26.4, 28.1, 28.7, 40.3, 43.9, 50.4, 73.5, 76.7, 125.9, 126.0, 126.6, 126.7, 127.9, 135.5, 146.8, 147.1, 152.3. IR (neat) cm\(^{-1}\) 3389brs, 3028w, 2926s, 2853m, 1601s, 1492s, 1447s, 1248s, 1053s, 1033s, 862s, 839s, 752s, 699s; HRMS (MALDI, m/z) calcd for C\(_{27}\)H\(_{38}\)O\(_2\)Si (M): 429.2533, found 429.2531.
6.0 Hz, J₂ = 15.6 Hz), 5.60 (dq, 1H, J₁ = 6.4 Hz, J₂ = 15.6 Hz), 7.20-7.22 (m, 2H), 7.27-7.32 (m, 4H), 7.41-7.45 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.2, 17.6, 43.6, 50.9, 71.6, 77.0, 126.0, 126.1, 126.5, 126.6, 126.7, 127.8, 127.9, 133.4, 135.0, 146.9, 147.1, 151.3; IR (neat) cm⁻¹ 3379brs, 3059w, 3028w, 2856s, 1602s, 1492s, 1445s, 1247s, 1052s, 966s, 863s, 840s, 751s, 699s; HRMS (MALDI, m/z) calcd for C₂₄H₃₂O₂SiNa (M+Na)⁺: 403.2064, found 403.2066.

**Preparation of 2p**

2p: Using the same procedure as that used for 2a, 1f (50 mg, 0.14 mmol) in Et₂O (1.0 mL) with n-BuLi (0.06 mL of 2.5 M solution in hexane, 0.15 mmol), TMEDA (52 µL, 0.35 mmol), diphenylmethanone (76 mg, 0.42 mmol) and anhyd. HMPA (0.7 mL) at −10 °C for 2h produced 2p (35 mg, 56% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.07 (s, 9H), 1.74 (s, 3H), 1.98 (dd, 1H, J₁ = 2.8 Hz, J₂ = 13.6 Hz), 2.05 (s, 1H), 2.26 (dd, 1H, J₁ = 10.4 Hz, J₂ = 13.6 Hz), 3.25 (d, 1H, J = 13.2 Hz), 3.30 (s, 1H), 3.39 (d, 1H, J = 13.2 Hz), 4.24 (dd, 1H, J₁ = 2.8 Hz, J₂ = 10.4 Hz), 5.37 (s, 1H), 6.47 (s, 1H), 7.21-7.24 (m, 4H), 7.28-7.33 (m, 7H), 7.44-7.47 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 0.3, 13.7, 42.2, 50.7, 75.9, 76.9, 124.9, 126.0, 126.1, 126.3, 126.7, 126.8, 128.0, 128.9, 135.8, 137.4, 139.9, 146.8, 147.2, 151.6; IR (neat) cm⁻¹ 3381brs, 3026w, 2926s, 2858s, 1601s, 1492s, 1445s, 1248s, 1054s, 910s, 838s, 750s, 698s; HRMS (MALDI, m/z) calcd for C₃₀H₂₆O₂SiNa (M+Na)⁺: 479.2377, found 479.2374.

**Preparation of 2q**

2q: Using the same procedure as that used for 2a, 1g (61 mg, 0.2 mmol) in Et₂O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), TMEDA (75 µL, 0.5 mmol),
diphenylmethanone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 4h produced 2q (72 mg, 87% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.04 (s, 9H), 2.01 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 13.6$ Hz), 2.14 (s, 1H), 2.30 (dd, 1H, $J_1 = 10.0$ Hz, $J_2 = 13.6$ Hz), 3.14 (s, 1H), 3.19 (d, 1H, $J = 13.2$ Hz), 3.37 (d, 1H, $J = 13.2$ Hz), 4.74 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 10.0$ Hz), 5.39 (s, 1H), 7.19-7.24 (m, 5H), 7.28-7.32 (m, 6H), 7.43-7.44 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 0.2, 46.0, 50.6, 72.5, 76.6, 125.4, 126.0, 126.1, 126.7, 126.8, 127.3, 128.0, 128.1, 128.3, 136.1, 144.2, 146.8, 147.1, 151.2; IR (neat) cm$^{-1}$ 3388brs, 3029w, 2953s, 2897s, 1602s, 1492s, 1447s, 1248s, 1053s, 862s, 839s, 753s, 699s; HRMS (MALDI, m/z) calcd for C$_{27}$H$_{32}$O$_2$SiNa (M+Na)$^+$: 439.2064, found 439.2066.

2.2. Control Experiment

**Preparation of 1a-Piv**

![1a-Piv](image)

1a-Piv: To a solution of 1a (54 mg, 0.2 mmol) and DMAP (0.5 mg, 0.2% mmol) in pyridine (0.5 mL) under argon atmosphere was added Pivaloyl chloride (50 µL, 0.4 mmol) at 25°C. After stirring for 2 h, the reaction mixture was quenched with water and extracted with Et$_2$O (3 × 5 mL). Combined organic extracts were washed with water (2 × 2 mL) and brine (2 × 2 mL), then dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-0.5% of EtOAc/petroleum ether) afforded 1g (60 mg, 85% yield) as a colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.04 (s, 9H), 0.06 (s, 9H), 0.83 (s, 1H), 0.89 (t, 3H, $J = 7.2$), 1.16 (s, 9H), 1.26-1.35 (m, 2H), 1.50-1.57 (m, 2H), 2.08 (dd, 1H, $J_1 = 5.6$, $J_2 = 15.6$), 2.18 (dd, 1H, $J_1 = 6.8$, $J_2 = 15.6$), 4.50 (s, 1H), 4.66 (s, 1H), 4.95 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 0.1, 0.3, 14.0, 18.5, 27.1, 27.9, 36.3, 38.7, 46.0, 71.5, 108.5, 145.5, 178.0; IR (neat) cm$^{-1}$ 3081w, 2959s, 1726s, 1480m, 1250s, 1162s, 1031m, 879s, 840s; HRMS (MALDI, m/z) calcd for C$_{19}$H$_{40}$O$_2$Si$_2$Na (M+Na)$^+$: 379.2459, found 379.2464.
To a solution of 1a (19 mg, 0.07 mmol), 1a-Piv (25 mg, 0.07 mmol) and TMEDA (26 µL, 0.18 mmol) in anhyd. Et₂O (0.35 mL) under argon atmosphere was added n-BuLi (0.03 mL of 2.5 M solution in hexane, 0.08 mmol) at −78 ºC. After stirring for 5 min, the resulting solution was warmed to −10 ºC. A solution of benzophenone (38 mg, 0.21 mmol) and anhyd. HMPA (0.35 mL) in anhyd. Et₂O (0.1 mL) was added. The reaction mixture was stirred for 2 h at −10 ºC before quenched with H₂O (1.0 mL). The mixture was extracted with Et₂O (3 × 5 mL). The combined organic layers were then dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-0.5% of EtOAc/petroleum ether) afforded 2a (15 mg, 58% yield), 2a-SiMe₃ (10 mg, 33% yield), and 1a-Piv (25 mg, 98% yield) in recovered.

2.3. [1,5]-Brook Rearrangement/Addition of Mono-SiMe₃-Substituted Homoallylic Alcohol 3

To a solution of 3 (60 mg, 0.3 mmol) and TMEDA (0.11 mL, 0.75 mmol) in anhyd. Et₂O (1.5 mL) under argon atmosphere was added n-BuLi (0.13 mL of 2.5 M solution in hexane, 0.33 mmol) at −78 ºC. After stirring for 5 min, the resulting solution was warmed to −10 ºC. A solution of benzophenone (164 mg, 0.9 mmol) and anhyd. HMPA (1.5 mL) in anhyd. Et₂O (0.5 mL) was added. The reaction mixture was stirred for 2 h at −10 ºC before quenched with aqueous HCl (10%, 1.0 mL). The mixture was extracted with Et₂O (3 × 5 mL). The combined organic layers were then dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography afforded 4 (66 mg, 70% yield) as a yellow oil, and 5 (8 mg,

20% yield) as a colorless oil.

4: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, 3H, $J = 6.8$ Hz), 1.22-1.27 (m, 2H), 1.31-1.35 (m, 2H), 1.82-1.86 (m, 2H), 1.89 (s, 1H), 3.12 (d, 1H, $J = 13.6$ Hz), 3.21 (d, 1H, $J = 13.6$ Hz), 3.40 (s, 1H), 3.65 (m, 1H), 4.86 (s, 1H), 4.98 (s, 1H), 7.21-7.23 (m, 2H), 7.26-7.33 (m, 4H), 7.44-7.48 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 18.7, 39.2, 44.7, 47.4, 69.4, 76.7, 118.5, 125.8, 125.9, 126.6, 126.7, 128.0, 142.9, 146.8, 146.9. IR (neat) cm$^{-1}$ 3388brs, 3061w, 2957s, 2929m, 1640s, 1446s, 1280s, 1055s, 901s, 751s, 700s; HRMS (MALDI, m/z) calcd for C$_{21}$H$_{26}$O$_2$Na (M+Na)$^+$: 333.1825, found 333.1828.

5: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.92 (t, 3H, $J = 6.8$ Hz), 1.35-1.47 (m, 4H), 1.74 (s, 3H), 1.77 (s, 1H), 2.06 (dd, 1H, $J_1 = 9.6$ Hz, $J_2 = 13.2$ Hz), 2.18 (dd, 1H, $J_1 = 2.4$ Hz, $J_2 = 13.2$ Hz), 3.71 (m, 1H), 4.77 (s, 1H), 4.85 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 18.8, 22.3, 39.2, 46.1, 68.3, 113.3, 142.8. IR (neat) cm$^{-1}$ 3436brm, 2959s, 2926s, 1731m, 1461m, 1260m, 1036m, 800m; HRMS (MALDI, m/z) calcd for C$_8$H$_{16}$ONa (M+Na)$^+$: 151.1099, found 151.1098.

2.4. Synthesis and Spectral Data of Z-Vinyliodide 9 and Enynes 10

**Synthesis of 9**

$N$-Iodosuccinimide (70 mg, 0.3 mmol) was added to a solution of 2j (60 mg, 0.15 mmol) in CH$_3$CN
(2.0 mL) in a flask protected from light. After stirring for 1 h at room temperature, sat aq NaS₂O₃ (2.0 mL) solution was added and the mixture was stirred vigorously for 5 min until colorless. The mixture was extracted with Et₂O (2 × 10 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. To the crude residue dissolved in anhyd. THF (0.5 mL) was added tetrabutylammonium fluoride (0.3 mL of 1.0 M solution in THF, 0.3 mmol). The reaction mixture was stirred for 30 min at 25 °C before quenched with H₂O (1.0 mL). The mixture was extracted with Et₂O (3 × 5 mL). The combined organic layers were then dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded 9 (64 mg, 93% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, 3H, J = 6.8 Hz), 1.31-1.44 (m, 4H), 1.85 (s, 1H), 2.19 (dd, 1H, J₁ = 3.2 Hz, J₂ = 14.0 Hz), 2.28 (dd, 1H, J₁ = 6.4 Hz, J₂ = 14.0 Hz), 3.30 (d, 1H, J = 14.0 Hz), 3.38 (d, 1H, J = 14.0 Hz), 3.69 (s, 1H), 3.84 (m, 1H), 5.91 (s, 1H), 7.21-7.23 (m, 2H), 7.28-7.32 (m, 4H), 7.38-7.42 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 18.7, 39.9, 44.9, 49.5, 70.6, 77.5, 82.1, 125.9, 126.0, 126.9, 127.0, 128.1, 128.2, 144.8, 146.5, 146.6; IR (neat) cm⁻¹ 3285brs, 3059w, 2955s, 2923s, 1601m, 1447s, 1326m, 1230s, 1046s, 756m, 722m, 697s; HRMS (MALDI, m/z) calcd for C₂₁H₂₅IO₂Na (M+Na)+: 459.0791, found 459.0796.

**Synthesis of 10**

A solution of 9 (60 mg, 0.14 mmol) in NEt₃ (1.0 mL) and DMSO (1.0 mL) was degassed with Ar three times. To the mixture were added CuI (0.5 mg, 2 mol %), Pd(PPh₃)₂Cl₂ (2.0 mg, 2 mol %) and 1-decyne (50 μL, 0.28 mmol). The resulting mixture was then heated at 45 °C. After complete conversion of the starting material as monitored by TLC, the reaction was quenched with sat aq NH₄Cl (2.0 mL) and extracted with Et₂O (3 × 5 mL). The combined organic layer was washed sequentially with 5% HCl, sat aq NaHCO₃, and sat aq NaCl and then dried over Na₂SO₄. Concentrated under reduced pressure and purification of the crude residue via silica gel flash
column chromatography (gradient eluent: 0-1% of EtOAc/petroleum ether) afforded pure 10 (54 mg, 87% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, 3H, $J = 6.8$ Hz), 0.88 (t, 3H, $J = 6.8$ Hz), 1.26-1.32 (m, 12H), 1.34-1.37 (m, 2H), 1.46-1.50 (m, 2H), 1.81 (s, 1H), 2.18 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 14.0$ Hz), 2.28 (dd, 1H, $J_1 = 9.2$ Hz, $J_2 = 14.0$ Hz), 2.26-2.29 (m, 2H), 3.21 (s, 2H), 3.71 (s, 1H), 3.82 (m, 1H), 5.35 (s, 1H), 7.19-7.22 (m, 2H), 7.28 (q, 4H, $J = 7.6$ Hz), 7.43 (t, 4H, $J = 7.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 18.6, 19.5, 22.6, 28.7, 28.9, 29.0, 29.1, 31.8, 39.9, 41.0, 48.6, 70.9, 77.4, 77.8, 95.1, 113.0, 125.8, 125.9, 126.6, 126.7, 128.0, 128.05, 146.7, 146.9, 147.0; IR (neat) cm$^{-1}$ 3237brs, 3031w, 2953s, 2925s, 1604m, 1448s, 1057s, 894m, 758m, 699s; HRMS (MALDI, m/z) calcd for C$_{31}$H$_{42}$O$_2$Na (M+Na)$^+$: 469.3077, found 469.3075.

2.5. Synthesis and Spectral Data of exo-Cyclic Z-Vinyl Bromide 11 and Z-Methyl Enoate 12

**Synthesis of 11**

![Diagram of the synthesis of 11]

To a solution of $2j$ (190 mg, 0.5 mmol) and NEt$_3$ (0.2 mL, 1.5 mmol) in CH$_2$Cl$_2$ (4.0 mL) was added chlorotriethylsilane (0.13 mL, 0.75 mmol) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C before quenched with sat aq NH$_4$Cl (3.0 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic layers were then dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-0.5% of EtOAc/petroleum ether) afforded $2j$-SiEt$_3$ (200 mg, 81% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.05 (s, 9H), 0.58 (q, 6H, $J = 8.0$ Hz), 0.85 (t, 3H, $J = 7.2$ Hz), 0.95 (t, 9H, $J = 8.0$ Hz), 1.15-1.20 (m, 2H), 1.27-1.33 (m, 2H), 1.77 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 13.6$ Hz), 1.99 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 13.6$ Hz), 3.23 (s, 2H), 3.52 (s, 1H), 3.78 (m, 1H), 5.29 (s, 1H), 7.19-7.22 (m, 2H), 7.26-7.31 (m, 4H), 7.43-7.45 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 0.3, 5.1, 6.9, 14.3, 18.0, 40.4, 42.6, 51.6, 72.2, 76.1, 125.05, 125.06, 126.4, 126.5, 127.8, 127.9, 133.7, 147.1, 147.5, 153.2. IR (neat) cm$^{-1}$ 3520brm, 2956s, 2877m, 1601m, 1448m, 1246s, 1099m, 1009s, 839s, 745s, 699s; HRMS (MALDI, m/z) calcd for C$_{30}$H$_{48}$O$_2$Si$_2$Na (M+Na)$^+$: 519.3085, found 519.3090.
To a solution of 2j-SiEt₃ (50 mg, 0.1 mmol) in CH₂Cl₂ (0.5 mL) under argon atmosphere was added Br₂ (6 µL, 0.11 mmol) at -78 °C. The reaction mixture was stirred for 15 min at -78 °C before quenched with sat aq Na₂S₂O₃ (0.5 mL). The mixture was extracted with Et₂O (3 × 5 mL). The combined organic layers were then dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (petroleum ether) afforded 11 (18 mg, 50% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, 3H, J = 7.2 Hz), 1.43-1.53 (m, 2H), 1.62-1.74 (m, 2H), 1.87 (dd, 1H, J₁ = 12 Hz, J₂ = 13.2 Hz), 2.48 (d, 1H, J = 14.4 Hz), 2.68 (d, 1H, J = 14.0 Hz), 3.37 (m, 1H), 3.39 (d, 1H, J = 14.4 Hz), 6.11 (s, 1H), 7.14-7.19 (m, 1H), 7.21-7.29 (m, 4H), 7.31-7.37 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 18.7, 36.5, 38.6, 44.0, 70.1, 79.9, 101.1, 124.9, 126.4, 126.9, 127.8, 128.0, 128.3, 138.8, 142.8, 148.3. IR (neat) cm⁻¹ 3448w, 2956s, 2925s, 1634m, 1443m, 1276m, 1050m, 760s, 700s; HRMS (MALDI, m/z) calcd for C₂₁H₂₃BrONa (M+Na)⁺: 393.0824, found 393.0821.

**Synthesis of 12**

![Synthesis of 12](image)

To a mixture of 11 (67 mg, 0.18 mmol), PdCl₂(CH₃CN)₂ (4 mg, 0.014 mmol) and dppf (22 mg, 0.040 mmol) under CO was added a mixed solution of DMF/MeOH/NEt₃ (4:2:0.06, 6 mL), which was degassed via freeze-pump-thaw technique. The resulting solution was stirred vigorously under CO (1 atm) at 80 °C for 20 h, before it was poured into sat aq NaCl/H₂O (1:1) solution (10 mL). The mixture was and extracted with Et₂O (3 × 10 mL) and the combined organic extracts were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-2%, EtOAc/petroleum ether) afforded 12 (45 mg, 72%) as a colorless solid. ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, 3H, J = 7.2 Hz), 1.49-1.73 (m, 4H), 2.00 (t, 1H, J = 12.8 Hz), 2.64 (d, 1H, J = 14.4 Hz), 3.33 (d, 1H, J = 14.4 Hz), 3.42 (m, 1H), 3.67 (s, 3H), 3.73 (d, 1H, J = 14.4 Hz), 5.86 (s, 3H), 7.16-7.23 (m, 2H), 7.24-7.33 (m, 4H), 7.36 (t, 4H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 18.7, 35.6, 38.7, 46.0, 50.9, 70.7,
80.8, 116.0, 124.8, 126.5, 127.0, 127.7, 128.0, 128.3, 143.0, 148.3, 156.5, 166.6; IR (neat) cm⁻¹

3057w, 2957s, 2872m, 1714s, 1650s, 1441s, 1258s, 1151s, 1027s, 910m, 870m, 750s, 700s; HRMS (MALDI, m/z) calcd for C_{23}H_{26}O_{3}Na (M+Na)⁺: 373.1774, found 373.1776.
Gao 8-8 H1 CDCl3 400 M Hz
Gao 8-21 C13 CDCl3 100 MHz

13C NMR Spectra of Compound 2j

Ph | Pi
\[\text{SiMe}_3\]
Oh | Oh

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 (ppm)
Gao 8-82 C13 CDCl3 100 MHz
Gao 8-77-1 H1  CDCl3 400 M Hz

[Chemical structure and spectroscopic data image]

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Gao 8-81 C13 CDCl3 100 M Hz
Gao 8-95 H1  CDCl3 400 MHz

4

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Pulse Sequence: gCOSY
Gao 8-75-a NOEDS 6.11 CDCl3 400 MHz

\[ \text{Diagram of chemical structure} \]

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