

Alkylidenesilacyclopropanes Derived from Allenes: Applications to the Selective Synthesis of Triols and Homoallylic Alcohols

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Supporting Information

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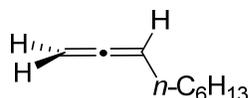
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Experimental Section

General Procedures. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker DRX 400 (400 and 100 MHz, respectively) or DRX 500 (500 and 125 MHz, respectively) spectrometers, as indicated. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (appar = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet), coupling constants (Hz), and integration. Due to difficulties with purification for certain products, only distinctive peaks are listed in tabulated ^1H NMR spectral data as indicated, and the structures were assigned using a combination of COSY, HMQC, HMBC, NOESY, and NOE experiments. ^{29}Si NMR spectra were recorded at ambient temperature using a Bruker DRX 500 (99.3 MHz) spectrometer relative to an external tetramethylsilane standard on the δ scale. NMR yields were determined relative to a known concentration of internal standard (PhSiMe_3). Melting points were obtained using a Büchi 510 melting point apparatus and were reported uncorrected. Infrared (IR) spectra were obtained using Perkin Elmer Paragon 1000PC FT-IR or Mattson Galaxy FT-IR 5000 spectrometers. Optical rotations were measured using a Jasco DIP-370 Digital Polarimeter. Gas chromatography–mass spectrometry (GC-MS) was performed with

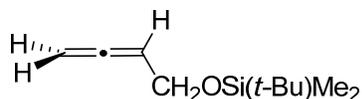
a Thermo-Finnigan Trace Mass Spectrometer Plus quadrupole system with a fused silica capillary column (30 m \times 0.32 mm \times 0.25 μ m) wall-coated with DB-5 (J & W Scientific) using electron ionization (70 eV). High and low resolution mass spectra (HRMS/LRMS) were acquired on a Waters LCT Premier quadrupole time-of-flight spectrometer and were obtained by peak matching. HPLC determination of enantiopurity was performed with Mettler Toledo supercritical CO₂ fluid chromatography (SFC) using a Daicel Chiralpak AD column calibrated with a sample of the racemate. Air-sensitive microanalyses were performed by Columbia Analytical Services Inc., Tucson, AZ. All other microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Analytical thin layer chromatography was performed on EM reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Sorbent Technologies silica gel (SiO₂) 60 (230–400 mesh). Metal salts and silacyclopropanes were stored and manipulated in an Innovative Technologies nitrogen-atmosphere dry box. All reactions were performed under an atmosphere of nitrogen in glassware that had been flame-dried under vacuum. Solvents were distilled or filtered before use. Unless otherwise noted, all reagents and substrates were commercially available.

I. Syntheses of Allenes



1a

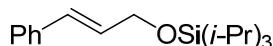
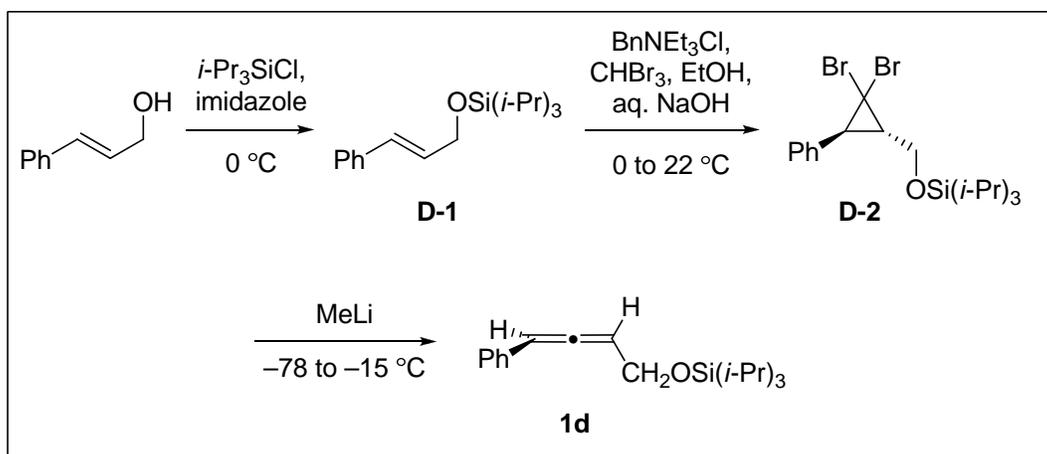
Allene 1a. A procedure reported by Jamison¹ was used to prepare allene **1a**. To a cooled (–15 °C) solution of PPh₃ (11.8 g, 45.1 mmol) in 63 mL of anhydrous THF was added diethyl azodicarboxylate (7.1 mL, 45 mmol). The resulting reaction mixture was stirred for 10 min, and then a solution of 2-nonyn-1-ol (4.19 g, 29.9 mmol) in 63 mL of anhydrous THF was added. After 10 min, a solution of *o*-nitrobenzylsulfonylhydrazine² (4.58 g, 21.1 mmol) in 40 mL of anhydrous THF was added. The reaction mixture was stirred at –15 °C for 2 h then slowly warmed to 22 °C over 18 h. The reaction mixture was cooled to 0 °C and diluted with 400 mL of pentane. The organic layer was washed with ice-cold H₂O (10 \times 200 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography (pentane) gave allene **1a** as a colorless oil (1.32 g, 35%). The spectral data are consistent with the data reported.³ ¹H NMR (500 MHz, C₆D₆) δ 5.08 (quint, *J* = 6.8, 1H), 4.64 (dtd, *J* = 6.7, 3.2, 0.5, 2H), 1.93 (qt, *J* = 7.2, 3.4, 2H), 1.35 (quint, *J* = 7.3, 2H), 1.23 (m, 6H), 0.87 (t, *J* = 7.0, 3H); ¹³C NMR (125 MHz, C₆D₆) δ 209.4, 90.8, 75.2, 32.4, 29.8, 29.5, 29.0, 23.4, 14.6.



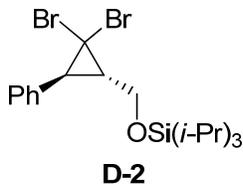
1b

Allene 1b. A procedure reported by Price⁴ was adapted to prepare **1b**. CuI (9.52 g, 50.0 mmol) was added in small portions to a solution of paraformaldehyde (7.5 g, 250 mmol), propargyl alcohol (5.82 mL, 100 mmol), and *i*-Pr₂NH (30 mL, 200 mmol) in THF (192 mL). The reaction mixture was heated at reflux for 15 h, then cooled off and vacuum-filtered through Celite, and

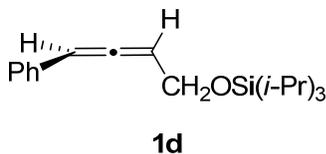
concentrated *in vacuo*. The resulting brown oil was diluted with H₂O (50 mL) and Et₂O (70 mL) and the aqueous layer was acidified using 3 M HCl (50 mL). The mixture was vacuum-filtered to remove solids and the layers were separated. The aqueous layer was extracted with Et₂O (4 × 25 mL). The combined organic layers were washed with H₂O (3 × 30 mL) and brine (70 mL), dried over MgSO₄, and concentrated *in vacuo* to give an orange-red oil. The oil was dissolved in DMF (10 mL), and imidazole (2.87 g, 42.1 mmol) was added. The reaction mixture was cooled to 0 °C and *t*-BuMe₂SiCl (6.35 g, 42.1 mmol) was added. After 1.5 h at 0 °C, the reaction mixture was warmed to 22 °C and stirred for an additional 16 h. The mixture was diluted with pentane (60 mL), washed with H₂O (3 × 30 mL), dried over MgSO₄, and concentrated *in vacuo*. Purification by column chromatography (pentane) gave allene **1b** (1.105 g, 6%) as a colorless oil. The spectral data are consistent with the data reported:⁵ ¹H NMR (500 MHz, CDCl₃) δ 5.15 (quint, *J* = 6.5, 1H), 4.69 (dt, *J* = 6.6, 2.8, 2H), 4.11 (dt, *J* = 6.4, 2.8, 2H), 0.83 (s, 9H), 0.01 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 208.3, 91.1, 76.3, 61.6, 26.1, 18.6, -4.9.

**D-1**

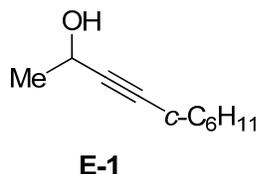
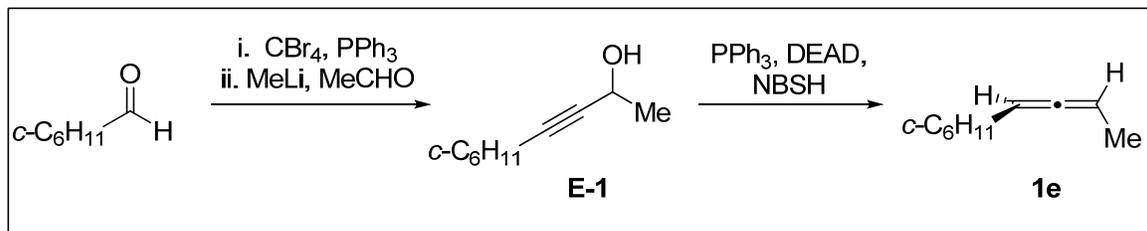
Alkene D-1. To a cooled (0 °C) solution of cinnamyl alcohol (5.33 g, 39.7 mmol) and imidazole (5.45 g, 80.0 mmol) in DMF (13 mL) was added *i*-Pr₃SiCl (8.99 mL, 42.0 mmol). After 3 h at 0 °C, the reaction mixture was warmed to 22 °C and stirred for an additional 20 h. The reaction mixture was diluted with H₂O (50 mL) and extracted with Et₂O (3 × 40 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. Purification by column chromatography (15:85 CH₂Cl₂/hexanes) gave alkene **D-1** (9.95 g, 82%) as a colorless oil. The spectral data are consistent with the data reported:⁶ ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, *J* = 7.5, 2H), 7.31 (t, *J* = 7.4, 2H), 7.21 (t, *J* = 7.3, 1H), 6.64 (d, *J* = 15.9, 1H), 6.30 (dt, *J* = 15.8, 4.8, 1H), 4.43 (dd, *J* = 4.8, 1.7, 2H), 1.16 (m, 3H), 1.10 (d, *J* = 6.4, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 137.5, 129.6, 129.3, 128.7, 127.4, 126.6, 64.1, 18.3, 12.3; IR (thin film) 3026, 2942, 2865, 1460, 1131 cm⁻¹; LRMS (APCI) calcd for C₉H₉O (M - C₉H₂₁Si)⁺ 133, found 133; *m/z* calcd for C₉H₉ (M - C₉H₂₁OSi)⁺ 117, found 117.



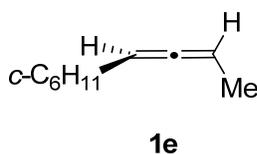
Dibromocyclopropane D-2. A procedure reported by Tanino⁷ was adapted to prepare **D-2**. To a cooled (0 °C) solution of alkene **D-1**⁶ (3.46 g, 11.3 mmol), BnNEt_3Cl (0.257 g, 1.13 mmol), CHBr_3 (4.93 mL, 56.5 mmol), and ethanol (0.050 mL) in 11.3 mL of CH_2Cl_2 was added a 50% aqueous NaOH solution (11.3 mL). The reaction mixture was stirred vigorously and allowed to slowly warm to 22 °C. After 16 h, the reaction mixture was cooled to 0 °C, and ethanol (0.50 mL) and 50% aqueous NaOH (3.0 mL) were added. After 5 h, the reaction mixture was diluted with H_2O (200 mL) and extracted with Et_2O (3 \times 75 mL). The combined organic layers were washed with saturated aqueous sodium potassium tartrate (100 mL) and brine (150 mL), dried over MgSO_4 and concentrated *in vacuo* to give a brown oil. Purification by column chromatography (10:90 CH_2Cl_2 /hexanes) gave dibromocyclopropane **D-2** as a yellow oil (4.34 g, 83%): ^1H NMR (500 MHz, CDCl_3) δ 7.39–7.26 (m, 5H), 4.08 (dd, J = 10.9, 6.9, 1H), 3.98 (dd, J = 10.9, 5.8, 1H), 2.69 (d, J = 8.4, 1H), 2.20 (ddd, J = 8.4, 6.8, 6.0, 1H), 1.17–1.07 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.3, 129.1, 128.5, 127.8, 65.4, 39.7, 37.3, 34.8, 18.3, 12.2; IR (thin film) 3026, 2942, 2865, 1459, 1103 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{Br}_2\text{NaOSi}$ ($\text{M} + \text{Na}$)⁺ 483.0331, found 483.0330. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{Br}_2\text{OSi}$: C, 49.36; H, 6.54. Found: C, 49.16; H, 6.41.



Allene 1d. To a cooled (–78 °C) solution of dibromocyclopropane **D-2** (2.28 g, 4.93 mmol) in 16 mL of Et_2O was added MeLi (4.93 mL, 7.89 mmol, 1.60 M solution in Et_2O) over 5 min. The reaction mixture was allowed to stir at –78 °C for 20 min, then was transferred to an ice-MeOH bath (–15 °C) and stirred for 20 min. The reaction mixture was diluted with phosphate buffer (30 mL, pH 7) and extracted with Et_2O (3 \times 20 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO_4 , and concentrated *in vacuo* to give a yellow-orange oil. Purification by column chromatography (10:90 CH_2Cl_2 /hexanes) gave **1d** as a light yellow oil (0.810 g, 62%): ^1H NMR (500 MHz, CDCl_3) δ 7.29 (m, 4H), 7.19 (m, 1H), 6.23 (dt, J = 6.1, 2.6, 1H), 5.71 (q, J = 6.2, 1H), 4.38 (m, 2H), 1.17–1.03 (sept, J = 5.7, 3H and d, J = 6.2, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 204.7, 134.5, 128.7, 127.12, 127.05, 96.2, 96.1, 61.8, 18.2, 12.2; IR (neat) 3032, 2942, 1951, 1599, 1496 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{31}\text{OSi}$ ($\text{M} + \text{H}$)⁺ 303.2144, found 303.2143.

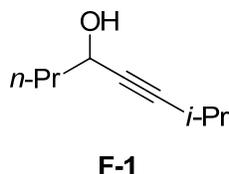
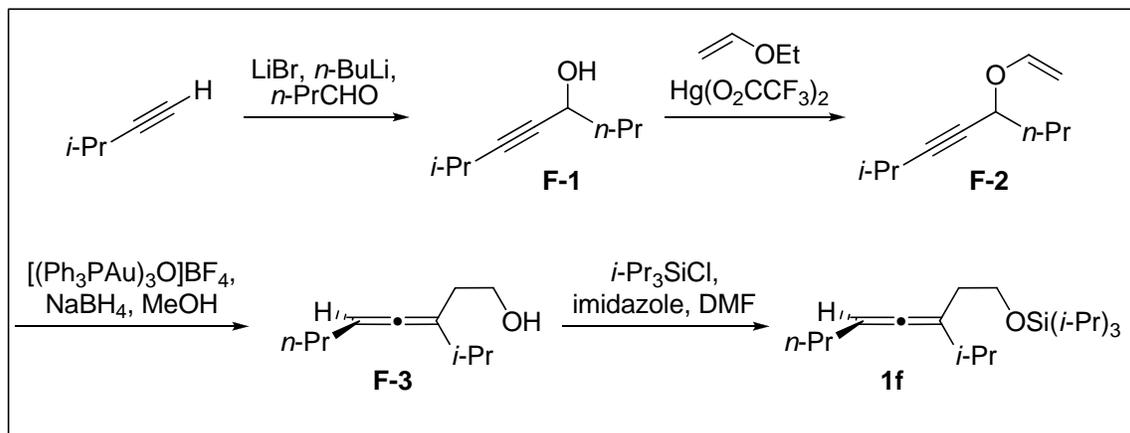


Propargylic alcohol E-1. A procedure reported by Jamison¹ was adapted to prepare **E-1**. To a cooled (0 °C) solution of CBr₄ (30 g, 100 mmol) in CH₂Cl₂ (70 mL) was added PPh₃ (50 g, 200 mmol). The reaction mixture was stirred at 0 °C for 30 min, and then cyclohexanecarboxaldehyde (6 mL, 50 mmol) was added dropwise. The reaction mixture was warmed to 22 °C and stirred for an additional 22 h. The mixture was vacuum-filtered through SiO₂ with hexanes and concentrated *in vacuo*. The resulting oil was dissolved in THF (50 mL) and cooled to -78 °C. MeLi (52 mL, 1.6 M in Et₂O, 84 mmol) was slowly added and the reaction mixture was stirred at -78 °C for 2.5 h. Acetaldehyde (6 mL, 100 mmol) was added and after 15 h at -78 °C the mixture was gradually warmed to 22 °C. The reaction mixture was diluted with H₂O (40 mL) and the layers separated. The aqueous layer was extracted with Et₂O (100 mL). The combined organic layers were washed with H₂O (4 × 50 mL) and brine (50 mL), dried over MgSO₄, and concentrated *in vacuo*. Purification by column chromatography (10:90 EtOAc/hexanes) gave propargylic alcohol **E-1** as a yellow oil (5.42 g, 71%). The spectral data are consistent with the data reported:¹ ¹H NMR (400 MHz, CDCl₃) δ 4.52 (qdd, *J* = 6.6, 5.2, 1.7, 1H), 2.37 (m, 1H), 1.89 (d, *J* = 5.2, 1H), 1.76 (m, 2H), 1.69 (m, 2H), 1.52 (m, 1H), 1.41 (m, 2H), 1.42 (d, *J* = 6.6, 3H), 1.29 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 88.8, 82.2, 58.7, 32.7, 29.0, 25.9, 24.93, 24.89; HRMS (ESI) *m/z* calcd for C₁₀H₁₆ONa (M + Na)⁺ 175.1099, found 175.1098.

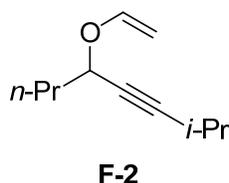


Allene (1e). A procedure reported by Myers⁸ and adapted by Jamison¹ was used to prepare allene **1e**. To a cooled (-15 °C) solution of PPh₃ (2.61 g, 9.95 mmol) in 14 mL of anhydrous THF was added diethyl azodicarboxylate (1.6 mL, 9.9 mmol). The resulting reaction mixture was stirred for 10 min, and then a solution of alcohol **E-1** (1.00 g, 6.57 mmol) in 14 mL of anhydrous THF was added. After 10 min, a solution of *o*-nitrobenzylsulfonylhydrazine² (2.16 g, 9.94 mmol) in 9 mL of anhydrous THF was added. The reaction mixture was stirred at -15 °C for 2 h then slowly warmed to 22 °C over 17 h. The reaction mixture was cooled to 0 °C and diluted with 100 mL of pentane. The organic layer was washed with ice-cold H₂O (10 × 60 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography

(pentane) gave allene **1e** as a colorless oil (0.471 g, 52%). The spectral data are consistent with the data reported:^{1,9} ¹H NMR (500 MHz, C₆D₆) δ 5.11 (m, 2H), 1.95 (m, 1H), 1.75 (m, 2H), 1.65 (m, 2H), 1.59 (dd, *J* = 6.8, 3.4, 3H), 1.54 (m, 1H), 1.15 (m, 5H); ¹³C NMR (125 MHz, C₆D₆) δ 203.9, 96.5, 86.3, 37.2, 33.1, 26.02, 26.00, 14.6.

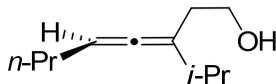


Propargylic alcohol F-1.¹⁰ To a cooled (−78 °C) solution of LiBr (1.27 g, 14.7 mmol) and 3-methyl-1-butyne (3.00 mL, 29.3 mmol) in 15 mL of THF was slowly added *n*-BuLi (12.6 mL, 2.44 M in hexanes, 30.8 mmol). After 10 min, butyraldehyde (2.64 mL, 29.3 mmol) was added. The reaction mixture was slowly warmed to 22 °C and stirred for 18 h. The reaction mixture was diluted with saturated aqueous NH₄Cl (50 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography (10:90 EtOAc/hexanes) gave **F-1** as an oil (2.26 g, 55%): ¹H NMR (400 MHz, CDCl₃) δ 4.35 (ddd, *J* = 11.7, 6.7, 1.7, 1H), 2.57 (septd, *J* = 6.9, 1.8, 1H), 1.72–1.57 (m, 3H), 1.46 (appar sext, *J* = 7.4, 2H), 1.16 (d, *J* = 6.9, 6H), 0.95 (t, *J* = 7.4, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 91.2, 80.7, 62.7, 40.6, 23.2, 20.7, 18.7, 14.0; IR (thin film) 3355, 2961, 2873, 2242, 1466, 1023 cm^{−1}; HRMS (ESI) *m/z* calcd for C₉H₁₆NaO (M + Na)⁺ 163.1099, found 163.1098.

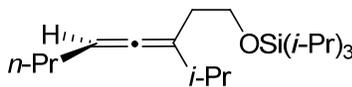


Vinyl ether F-2. A procedure reported by Yamamoto¹¹ was adapted to prepare **F-2**. To a solution of propargylic alcohol **F-1** (1.00 g, 7.13 mmol) in 19 mL of ethyl vinyl ether was added Hg(O₂CCF₃)₂ (0.304 g, 0.713 mmol). The reaction mixture was allowed to stir for 18 h and was then diluted with 5% aqueous KOH (9 mL) and extracted with hexanes (3 × 15 mL). The

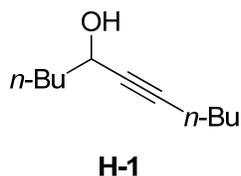
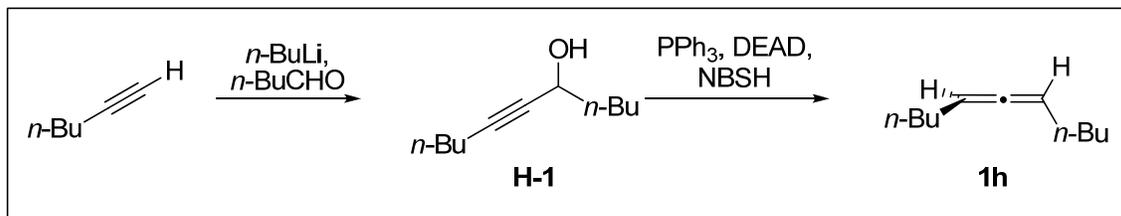
combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (hexanes) gave **F-2** as a colorless oil (0.606 g, 51%): ^1H NMR (400 MHz, CDCl_3) δ 6.43 (dd, $J = 14.1, 6.6$, 1H), 4.39 (td, $J = 5.9, 1.5$, 1H and dd, $J = 14.1, 1.6$, 1H), 4.07 (dd, $J = 6.6, 1.6$, 1H), 2.58 (septd, $J = 6.9, 1.7$, 1H), 1.74 (m, 2H), 1.48 (sext, $J = 7.5$, 2H), 1.16 (d, $J = 6.9$, 6H), 0.93 (t, $J = 7.4$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 92.9, 89.5, 89.5, 69.4, 38.0, 23.2, 20.7, 18.6, 13.9; IR (thin film) 2966, 2874, 2244, 1636, 1615, 1190 cm^{-1} .

**F-3**

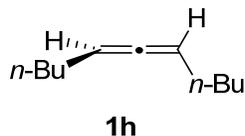
Homoallenic alcohol F-3. A procedure reported by Toste¹² was adapted to prepare **F-3**. A solution of vinyl ether **F-2** (0.600 g, 3.61 mmol) and $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$ ¹³ (0.063 g, 0.036 mmol) in 10 mL of CH_2Cl_2 was stirred at 22 °C. After 18 h, MeOH (20 mL) and NaBH_4 (0.136 g, 3.61 mmol) were added to the reaction mixture. After 1 h, the reaction mixture was diluted with H_2O (30 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were dried over MgSO_4 and concentrated *in vacuo*. Purification by column chromatography (70:30 CH_2Cl_2 /hexanes) gave **F-3** as an oil (0.515 g, 85%): ^1H NMR (500 MHz, CDCl_3) δ 5.24 (m, 1H), 3.73 (q, $J = 6.1$, 2H), 2.23 (td, $J = 6.1, 3.1$, 2H), 2.09 (septd, $J = 6.7, 2.3$, 1H), 1.97 (q, $J = 7.1$, 2H), 1.68 (t, $J = 6.2$, 1H), 1.43 (sext, $J = 7.3$, 2H), 1.03 (d, $J = 6.7$, 3H and d, $J = 6.7$, 3H), 0.93 (t, $J = 7.3$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.5, 107.8, 94.2, 61.5, 34.2, 31.9, 31.5, 22.8, 22.0, 21.8, 14.0; IR (thin film) 3338, 2960, 2930, 1957, 1045 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{20}\text{ONa}$ ($\text{M} + \text{Na}$)⁺ 191.1412, found 191.1409.

**1f**

Allene 1f. To a cooled (0 °C) solution of homoallenic alcohol **F-3** (0.380 g, 2.26 mmol) and imidazole (0.307 g, 4.52 mmol) in 0.8 mL of DMF was slowly added $\text{ClSi}(i\text{-Pr})_3$ (0.51 mL, 2.4 mmol). The reaction mixture was slowly warmed to 22 °C and stirred for 18 h. The reaction mixture was diluted with H_2O (10 mL) and extracted with Et_2O (3×20 mL). The combined organic layers were washed with 1 M aqueous HCl (50 mL) and brine (50 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. Purification by column chromatography (hexanes) gave **1f** as a colorless oil (0.644 g, 88%): ^1H NMR (500 MHz, CDCl_3) δ 5.11 (m, 1H), 3.73 (t, $J = 7.7$, 2H), 2.22 (td, $J = 7.7, 2.8$, 2H), 2.09 (septd, $J = 6.8, 2.2$, 1H), 1.91 (q, $J = 7.2$, 2H), 1.40 (sext, $J = 7.3$, 2H), 1.12–1.03 (sept, $J = 4.2$, 3H and d, $J = 4.8$, 18H), 1.00 (d, $J = 6.7$, 3H and d, $J = 6.7$, 3H), 0.92 (t, $J = 7.4$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.1, 107.3, 93.1, 63.1, 34.4, 31.9, 31.6, 22.8, 22.1, 21.9, 18.2, 14.0, 12.3; IR (thin film) 2960, 2867, 1958, 1464, 1100, 882 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{41}\text{OSi}$ ($\text{M} + \text{H}$)⁺ 325.2927, found 325.2924. Anal. Calcd for $\text{C}_{20}\text{H}_{40}\text{OSi}$: C, 74.00; H, 12.42. Found: C, 73.83; H, 12.58.



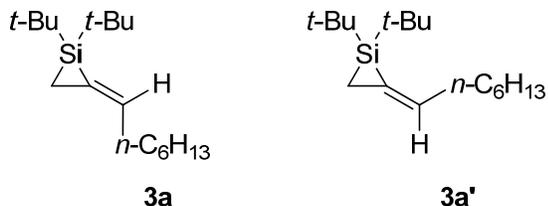
Propargylic alcohol H-1. A procedure reported by Hailes¹⁴ was adapted to prepare **H-1**. To a cooled ($-78\text{ }^\circ\text{C}$) solution of 1-hexyne (9.20 mL, 80.0 mmol) in THF (40 mL) was slowly added *n*-BuLi (31 mL, 2.9 M in hexanes, 90 mmol). After 10 min, valeraldehyde (8.50 mL, 80.0 mmol) was added. The reaction mixture remained at $-78\text{ }^\circ\text{C}$ for 15 min, then was slowly warmed to $22\text{ }^\circ\text{C}$ and stirred for an additional 1 h. The reaction mixture was quenched with saturated NH_4Cl (50 mL), diluted with EtOAc, and the layers were separated. The organic layer was washed with brine (100 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. Purification by column chromatography (20:80 Et_2O /hexanes) gave alcohol **H-1** as a light yellow oil (11.76 g, 87%). The spectral data are consistent with the data reported:¹⁴ ^1H NMR (500 MHz, CDCl_3) δ 4.36 (m, 1H), 2.22 (td, $J = 7.0, 2.0$, 2H), 1.74–1.62 (m, 2H), 1.69 (d, $J = 5.3$, 1H), 1.53–1.32 (m, 8H), 0.924 (t, $J = 7.2$, 3H), 0.918 (t, $J = 7.3$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 85.5, 81.4, 62.8, 38.0, 30.8, 27.4, 22.4, 22.0, 18.4, 14.1, 13.6; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{20}\text{ONa}$ ($\text{M} + \text{Na}$)⁺ 191.1412, found 191.1411.



Allene 1h. A procedure reported by Myers¹⁷ and adapted by Jamison¹⁸ was used to prepare **1h**. To a cooled ($-10\text{ }^\circ\text{C}$) solution of PPh_3 (7.11 g, 27.1 mmol) in 36 mL of THF was added diethyl azodicarboxylate (4.3 mL, 27 mmol). The resulting reaction mixture was allowed to stir for 10 min, then a solution of alcohol **H-1** (3.04 g, 18.1 mmol) in 27 mL of THF was added. After 10 min, *o*-nitrobenzylsulfonylhydrazine² (5.89 g, 27.1 mmol) in 36 mL of THF was added. The resulting reaction mixture was kept below $0\text{ }^\circ\text{C}$ for 1.5 h and was slowly warmed to $22\text{ }^\circ\text{C}$ over 15 h. The reaction mixture was cooled to $0\text{ }^\circ\text{C}$ and diluted with pentane (400 mL) and the layers were separated. The organic layer was washed with ice-cold H_2O ($10 \times 100\text{ mL}$), dried with Na_2SO_4 , and concentrated *in vacuo* at $0\text{ }^\circ\text{C}$ to give an orange liquid. Purification by column chromatography (pentane) gave **1h** as a colorless liquid (1.88 g, 68%). The spectral data are consistent with the data reported:¹⁴ ^1H NMR (500 MHz, CDCl_3) δ 5.06 (m, 2H), 1.98 (m, 4H), 1.36 (m, 8H), 0.90 (t, $J = 7.0$, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 204.0, 91.1, 31.6, 28.9, 22.4, 14.2.

II. Silver-Catalyzed Synthesis of Alkylidenesilacyclopropanes

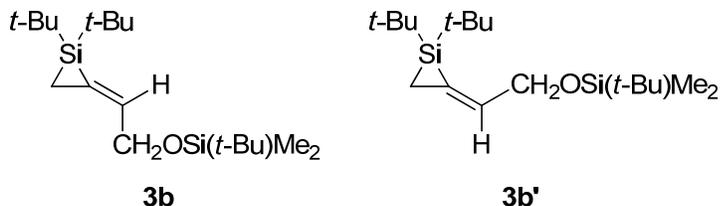
Representative Procedure for the silver-catalyzed silacyclopropanation of allenes:



Alkylidenesilacyclopropanes 3a and 3a'. To a flask containing allene **1a** (0.300 mL, 0.048 mmol, 0.160 M of the allene and 0.0386 M solution of PhSiMe₃ in C₆D₆) and cyclohexenesilacyclopropane **2** (0.200 mL, 0.100 mmol, 0.500 M solution of **2** and 0.0386 M solution of PhSiMe₃ in C₆D₆) was added AgO₂CCF₃ (0.005 mL, 0.0005 mmol, 0.096 M in C₆D₆). The progress of the reaction was monitored using ¹H NMR spectroscopy. After 1 h, alkylidenesilacyclopropanes **3a** and **3a'** were formed in 77% combined yield (71% and 6%, respectively) with ≥95:5 regioselectivity and 93:7 diastereoselectivity, as determined by ¹H NMR spectroscopy (compared to the PhSiMe₃ internal standard) using a single scan. Full characterization is provided for an isolated sample of **3a** (see below).

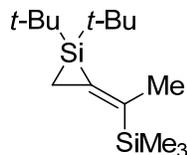
Procedure for the isolation of alkylidenesilacyclopropane 3a:

Cyclohexenesilacyclopropane **2**^{15,16} (0.816 g, 3.64 mmol) was added to a solution of allene **1a** (0.373 g, 3.00 mmol) in anhydrous toluene (13 mL). The mixture was cooled to -19 °C followed by the addition of Ag₃PO₄ (0.087 g, 0.21 mmol). The resulting reaction mixture remained at -19 °C for 30 min, then was slowly warmed to 22 °C. After 20 h, the reaction mixture was filtered through Celite and concentrated *in vacuo*. Kugelrohr distillation under vacuum (0.3 mm Hg) at 95 °C yielded alkylidenesilacyclopropane **3a** as a colorless oil (0.51 g, 63%): ¹H NMR (500 MHz, C₆D₆) δ 6.50 (tt, *J* = 6.9, 3.2, 1H), 2.43 (qt, *J* = 6.6, 1.6, 2H), 1.52 (quint, *J* = 7.4, 2H), 1.40–1.34 (m, 2H), 1.33–1.25 (m, 4H), 1.16 (dt, *J* = 3.1, 1.7, 2H), 1.11 (s, 18H), 0.90 (t, *J* = 7.0, 3H); ¹³C NMR (125 MHz, C₆D₆) δ 138.5, 133.2, 32.8, 31.9, 29.4, 29.1, 29.0, 22.8, 18.3, 14.0, 4.5; ²⁹Si NMR (99.3 MHz, C₆D₆) δ -45.4; IR (thin film) 2956, 2931, 2858, 1471, 1363, 823 cm⁻¹; HRMS (APCI) *m/z* calcd for C₁₃H₂₅Si (M - C₄H₉)⁺ 209.1726, found 209.1722.



Alkylidenesilacyclopropanes 3b and 3b'. The representative procedure for silver-catalyzed silacyclopropanation was followed using **1b** (0.250 mL, 0.125 mmol, 0.500 M of the allene and 0.0465 M solution of PhSiMe₃ in C₆D₆), cyclohexenesilacyclopropane **2** (0.300 mL, 0.150 mmol, 0.500 M solution of **2** and 0.0465 M solution of PhSiMe₃ in C₆D₆) and Ag₃PO₄ (0.003 g, 0.006 mmol). After 34 h, alkylidenesilacyclopropanes **3b** and **3b'** were formed in 74% combined yield (61% and 13%, respectively) with ≥95:5 regioselectivity and 83:17 diastereoselectivity, as determined by ¹H NMR spectroscopy (compared to the PhSiMe₃ internal standard) using a single

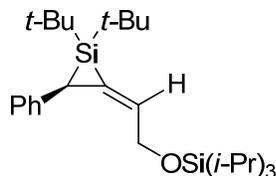
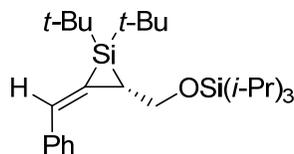
scan. Major isomer **3b**: ^1H NMR (400 MHz, C_6D_6) δ 6.68 (tt, $J = 5.8, 3.1$, 1H), 4.52 (dt, $J = 5.8, 1.9$, 2H), 1.10 (m, 2H), 1.05 (s, 18H), 1.02 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 138.5, 135.0, 64.5, 29.6, 26.6, 18.98, 18.95, 5.2, -4.4 ; ^{29}Si NMR (99.3 MHz, C_6D_6) δ -47.0 , 19.5.

**3c**

Alkylidenesilacyclopropane 3c. The representative procedure for silver-catalyzed silacyclopropanation was followed using 3-(trimethylsilyl)-1,2-butadiene **1c** (0.250 mL, 0.125 mmol, 0.500 M of the allene and 0.0465 M solution of PhSiMe_3 in C_6D_6), cyclohexenesilacyclopropane **2**^{15,16} (0.300 mL, 0.150 mmol, 0.500 M solution of **2** and 0.0465 M solution of PhSiMe_3 in C_6D_6) and Ag_3PO_4 (0.003 g, 0.006 mmol). After 2.5 h, alkylidenesilacyclopropane **3c** was formed in 87% yield with $\geq 95:5$ regioselectivity and $\geq 95:5$ diastereoselectivity, as determined by ^1H NMR spectroscopy. Full characterization is provided for an isolated sample of **3c** (see below).

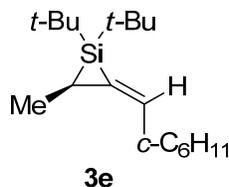
Procedure for the isolation of alkylidenesilacyclopropane **3c**:

To a vessel fitted with an air-free seal containing a cooled ($-26\text{ }^\circ\text{C}$) solution of 3-(trimethylsilyl)-1,2-butadiene **1c** (0.500 mL, 3.00 mmol) and cyclohexenesilacyclopropane **2**^{15,16} (0.808 g, 3.60 mmol) in 13 mL of toluene was added Ag_3PO_4 (0.063 g, 0.15 mmol). The reaction mixture was kept at $-26\text{ }^\circ\text{C}$ for 30 min and then was allowed to warm to $22\text{ }^\circ\text{C}$. After 3.5 h, the reaction mixture was filtered through a pad of Celite with hexanes under N_2 in the dry box and concentrated *in vacuo* to give a light brown oil. Kugelrohr distillation under vacuum (0.3 mm Hg) at $40\text{ }^\circ\text{C}$ gave **3c** as a colorless oil (0.360 g, 45%): ^1H NMR (400 MHz, C_6D_6) δ 2.06 (t, $J = 2.6$, 3H), 1.27 (q, $J = 2.6$, 2H), 1.08 (s, 18H), 0.27 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 149.0, 146.8, 30.0, 28.1, 18.9, 8.5, -0.3 ; ^{29}Si NMR (99.3 MHz, C_6D_6) δ -51.4 , -6.4 ; IR (neat) 2959, 2857, 1646, 1471, 1246, 834 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{Si}_2$: C, 67.08; H, 12.01. Found: C, 66.82; H, 11.97.

**3d****3d'**

Alkylidenesilacyclopropanes 3d and 3d'. The representative procedure for silver-catalyzed silacyclopropanation was followed using 1-(triisopropylsilyloxy)-4-phenyl-2,3-butadiene **1d** (0.250 mL, 0.125 mmol, 0.500 M of the allene and 0.0581 M solution of PhSiMe_3 in C_6D_6), cyclohexenesilacyclopropane **2**^{15,16} (0.300 mL, 0.150 mmol, 0.500 M solution of **2** and 0.0465 M solution of PhSiMe_3 in C_6D_6) and Ag_3PO_4 (0.003 g, 0.006 mmol). After 1.5 h, a mixture of alkylidenesilacyclopropane **3d** and regioisomer alkylidenesilacyclopropane **3d'** was formed in 82% yield with 79:21 regioselectivity, as determined by ^1H NMR spectroscopy. Both **3d** and

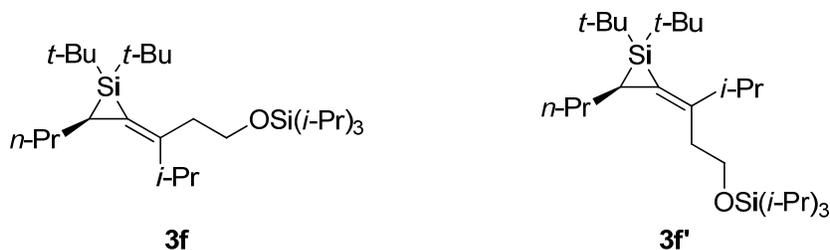
3d' were each formed with $\geq 95:5$ diastereoselectivity, as determined by ^1H NMR spectroscopy: ^1H NMR (500 MHz, C_6D_6) δ 7.63 (dd, $J = 8.3, 0.6, 0.6\text{H}$), 7.44 (m, 0.6H), 7.27–7.18 (m, 4H), 7.06 (m, 0.3H), 6.97 (m, 1H), 6.93 (ddd, $J = 6.5, 5.5, 3.2, 1\text{H}$), 4.70–4.62 (dd, $J = 10.4, 7.8, 0.3\text{H}$ and ddd, $J = 12.8, 5.5, 2.4, 1\text{H}$), 4.48 (ddd, $J = 12.9, 6.3, 1.7, 1\text{H}$), 3.75 (dd, $J = 10.7, 9.8, 0.3\text{H}$), 3.14 (m, 1H), 2.55 (ddd, $J = 9.7, 7.8, 3.4, 0.3\text{H}$), 1.27 (s, 3H), 1.16 (s, 3H), 1.15–1.07 (s, 9H; d, $J = 2.7, 18\text{H}$; m, 3H; d, $J = 2.7, 5.4\text{H}$; m, 0.9H), 0.92 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.6, 141.6, 141.5, 139.9, 136.2, 135.5, 129.0, 128.9, 128.5, 124.3, 30.6, 30.5, 30.2, 29.8, 29.4, 28.6, 21.6, 20.7, 20.1, 19.9, 18.78, 18.75, 18.67, 12.8; ^{29}Si NMR (99.3 MHz, C_6D_6) δ –54.2 (minor), –47.6 (major), 12.4 (minor), 13.5 (major).



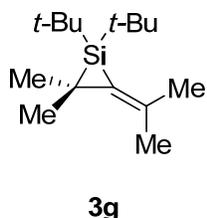
Alkylidenesilacyclopropane 3e.¹⁷ The representative procedure for silver-catalyzed silacyclopropanation was followed using allene **1e** (0.250 mL, 0.125 mmol, 0.500 M solution of the allene and 0.0465 M solution of PhSiMe_3 in C_6D_6), cyclohexenesilacyclopropane **2**^{15,16} (0.300 mL, 0.150 mmol, 0.500 M solution of **2** and 0.465 M solution of PhSiMe_3 in C_6D_6) and AgO_2CCF_3 (0.050 mL, 0.0013 mmol, 0.026 M solution in C_6D_6). After 2.5 h, alkylidenesilacyclopropane **3e** was formed in 70% yield with 95:5 regioselectivity and 95:5 diastereoselectivity. Full characterization is provided for an isolated sample of **3e** (see below).

Procedure for the isolation of alkylidenesilacyclopropane 3e:

Cyclohexenesilacyclopropane **2**^{15,16} (0.514 g, 2.29 mmol) was added to a solution of allene **1e** (0.217 g, 1.59 mmol) in anhydrous toluene (8 mL). The mixture was cooled to $-18\text{ }^\circ\text{C}$ followed by the addition of Ag_3PO_4 (0.037 g, 0.090 mmol). The resulting reaction mixture remained at $-18\text{ }^\circ\text{C}$ for 30 min, then was slowly warmed to $22\text{ }^\circ\text{C}$. After 19 h, the reaction mixture was filtered through Celite and concentrated *in vacuo*. Kugelrohr distillation under vacuum (0.3 mm Hg) at $95\text{ }^\circ\text{C}$ yielded alkylidenesilacyclopropane **3e** as a colorless oil (0.31 g, 69%): ^1H NMR (400 MHz, C_6D_6) δ 6.27 (dd, $J = 8.7, 3.3, 1\text{H}$), 2.53 (m, 1H), 1.88 (m, 2H), 1.71 (m, 3H), 1.63 (m, 1H), 1.58 (d, $J = 7.0, 3\text{H}$), 1.30 (m, 5H), 1.18 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 143.3, 137.6, 42.2, 33.9, 33.0, 30.2, 29.3, 26.2, 20.1, 18.9, 16.2, 15.2; ^{29}Si NMR (99.3 MHz, C_6D_6) δ –47.0; IR (thin film) 2929, 2856, 1676, 1473, 1363, 843 cm^{-1} ; LRMS (APCI) m/z calcd for $\text{C}_{18}\text{H}_{35}\text{Si}$ ($\text{M} + \text{H}$)⁺ 279, found 279; m/z calcd for $\text{C}_{18}\text{H}_{35}\text{OSi}$ ($\text{M} + \text{OH}$)⁺ 295; found 295; m/z calcd for $\text{C}_{18}\text{H}_{37}\text{OSi}$ ($\text{M} + \text{H}_3\text{O}$)⁺ 297, found 297. Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{Si}$: C, 77.61; H, 12.30. Found: C, 76.54; H, 12.17 (Anal. passed for H, not for C).



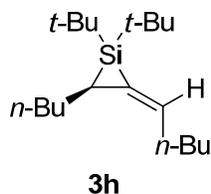
Alkylidenesilacyclopropanes 3f and 3f'. The representative procedure for silver-catalyzed silacyclopropanation was followed using allene **1f** (0.250 mL, 0.0635 mmol, 0.254 M solution of the allene and 0.465 M solution of PhSiMe_3 in C_6D_6), cyclohexenesilacyclopropane **2**^{15,16} (0.152 mL, 0.0762 mmol, 0.500 M solution of **2** and 0.465 M solution of PhSiMe_3 in C_6D_6), and AgO_2CCF_3 (0.0300 mL, 0.000678 mol, 0.0226 M solution in C_6D_6). The reaction mixture was diluted with additional C_6D_6 (0.150 mL) before addition of AgO_2CCF_3 . After 25 h, alkylidenesilacyclopropanes **3f** and **3f'** were formed in quantitative yield with $\geq 95:5$ regioselectivity and with 78:22 diastereoselectivity, as determined by ^1H NMR spectroscopy: ^1H NMR (500 MHz, C_6D_6) δ 4.12–4.00 (dt, $J = 16.7, 9.2$, 1H and dt, $J = 16.4, 9.2$, 1H), 3.91 (td, $J = 9.5, 6.1, 0.3$ H), 3.06 (sept, $J = 7.0$, 1H), 2.85 (m, 0.3H), 2.73 (ddd, $J = 12.4, 9.4, 6.2$, 0.3H), 2.63 (appar t, $J = 9.2$, 2H), 2.53 (sept, $J = 6.8$, 0.3H), 2.26 (m, 0.3 H), 2.14 (m, 1H), 1.51 (m, 5H), 1.26–1.02 (m, 60H), 1.00 (t, $J = 7.3$, 3H), 0.28 (s, 0.3H); ^{13}C NMR (125 MHz, C_6D_6) δ 150.8, 150.6, 133.3, 132.9, 65.5, 63.8, 38.1, 37.9, 37.8, 35.7, 33.1, 32.4, 31.0, 30.9, 30.4, 30.3, 27.5, 27.4, 23.3, 23.0, 22.8, 22.6, 22.4, 21.8, 20.6, 20.5, 19.7, 19.5, 18.8, 18.7, 14.71, 14.68, 12.9, 12.8; ^{29}Si NMR (99.3 MHz, C_6D_6) δ –47.7 (minor), –47.4 (major), 12.1 (major), 12.2 (minor).



Alkylidenesilacyclopropane 3g. The representative procedure for silver-catalyzed silacyclopropanation was followed using tetramethylallene **1g** (0.250 mL, 0.125 mmol, 0.500 M solution of the allene and 0.0465 M solution of PhSiMe_3 in C_6D_6), cyclohexenesilacyclopropane **2**^{15,16} (0.300 mL, 0.150 mmol, 0.500 M solution of **2** and 0.0465 M solution of PhSiMe_3 in C_6D_6), and AgO_2CCF_3 (0.003 g, 0.01 mmol). After 34 h, alkylidenesilacyclopropane **3g** was formed in 79% yield, as determined by ^1H NMR spectroscopy. Full characterization is provided for an isolated sample of **3g** (see below).

Procedure for the isolation of **3g**:

Cyclohexenesilacyclopropane **2**^{15,16} was added to a solution of tetramethylallene **1g** (0.061 g, 0.64 mmol) in toluene (6 mL) followed by the addition of AgO_2CCF_3 (0.72 mL, 0.014 M in toluene, 0.010 mmol). The reaction had gone to completion after 14 h, and the mixture was filtered through Celite and concentrated *in vacuo*. Kugelrohr distillation under vacuum (0.3 mm Hg) at 60 °C yielded alkylidenesilacyclopropane **3g** as a colorless oil (0.050 g, 32%): ^1H NMR (400 MHz, C_6D_6) δ 1.88 (s, 3H), 1.86 (s, 3H), 1.61 (s, 6H), 1.20 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 139.3, 139.1, 31.3, 28.0, 25.5, 21.8, 21.8, 21.0; ^{29}Si NMR (99.3 MHz, C_6D_6) –54.8.



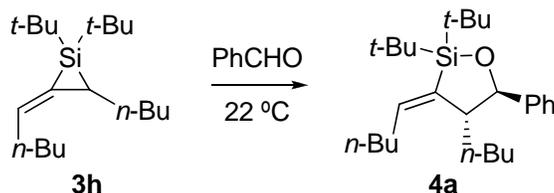
Alkylidenesilacyclopropane 3h. The representative procedure for silver-catalyzed silacyclopropanation was followed using allene **3h** (0.250 mL, 0.125 mmol, 0.500 M solution of the allene and 0.0465 M solution of PhSiMe₃, the internal standard in C₆D₆), cyclohexenesilacyclopropane **2**^{15,16} (0.300 mL, 0.150 mmol, 0.500 M solution of **2** and 0.0465 M solution of PhSiMe₃ in C₆D₆), and Ag₃PO₄ (0.003 g, 0.006 mmol). After 2.5 h at 22 °C, alkylidenesilacyclopropane **3h** was formed in 86% yield with 94:6 diastereoselectivity, as determined by ¹H NMR spectroscopy. Full characterization is provided for an isolated sample of **3h** (see below).

Procedure for the isolation of 3h:

Cyclohexenesilacyclopropane **2**^{15,16} (1.1 g, 4.8 mmol) was added to a solution of allene **1h** (0.61 g, 4.0 mmol) in anhydrous toluene (17 mL). The mixture was cooled to -20 °C followed by the addition of Ag₃PO₄ (0.08 g, 0.2 mmol). The resulting reaction mixture remained at -20 °C for 30 min, then slowly warmed to 22 °C. After 5 h, the reaction mixture was filtered through Celite and concentrated *in vacuo*. Kugelrohr distillation under vacuum (0.3 mm Hg) at 95 °C yielded alkylidenesilacyclopropane **3h** as a colorless oil (0.88 g, 74%): ¹H NMR (400 MHz, C₆D₆) δ 6.38 (td, *J* = 7.0, 3.4, 1H), 2.41 (m, 2H), 2.27 (m, 1H), 1.76 (m, 1H), 1.65 (m, 1H), 1.45 (m, 8H), 1.19 (s, 9H), 1.12 (s, 9H), 0.97 (t, *J* = 7.2, 3H), 0.93 (t, *J* = 7.1, 3H); ¹³C NMR (125 MHz, C₆D₆) δ 139.6, 137.8, 36.6, 33.6, 32.9, 30.9, 30.4, 30.2, 25.5, 23.34, 23.27, 20.8, 19.6, 14.9, 14.7; ²⁹Si NMR (99.3 MHz, C₆D₆) δ -46.2; IR (thin film) 2854, 1673, 1471, 1363, 823 cm⁻¹; HRMS (APCI) *m/z* calcd for C₁₉H₃₉OSi (M + OH)⁺ 311.2770, found 311.2782; Anal. Calcd for C₁₉H₃₈Si: C, 77.46; H, 13.00. Found: C, 77.51; H, 13.09.

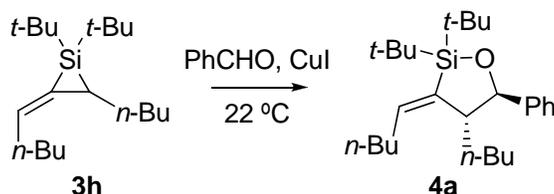
III. Thermal vs. Copper-Catalyzed Carbonyl Insertion Reactions

Representative procedure for the synthesis of oxasilacyclopentanes using a pure sample of alkylidenesilacyclopropane:

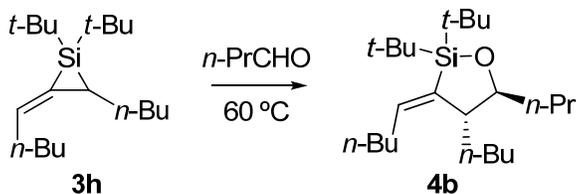


Oxasilacyclopentane 4a (thermolysis). To a J. Young NMR tube containing alkylidenesilacyclopropane **3h** (0.550 mL, 0.127 mmol, 0.231 M solution of the alkylidenesilacyclopropane and 0.0465 M solution of PhSiMe₃, the internal standard, in C₆D₆) was added benzaldehyde (0.039 mL, 0.38 mmol). The reaction mixture was left at 22 °C and the progress of the reaction was monitored using ¹H NMR spectroscopy. After 1.5 h,

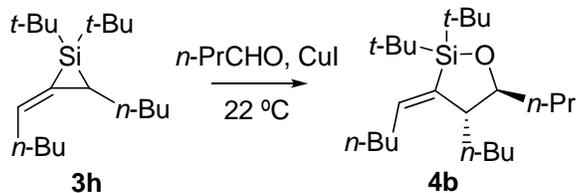
oxasilacyclopentane **4a** was formed in 82% yield, as determined by ^1H NMR spectroscopy (compared to the PhSiMe_3 internal standard) using a single scan. The reaction mixture was concentrated *in vacuo* and a GC–MS spectrum of the unpurified reaction mixture showed that oxasilacyclopentane **4a** was formed with 93:7 diastereoselectivity: ^1H NMR (400 MHz, C_6D_6 , distinctive peaks) δ 5.94 (td, $J = 6.7, 3.0$, 1H), 4.98 (d, $J = 7.9$, 1H), 2.87 (m, 1H), 2.14 (m, 2H), 1.22 (s, 9H), 1.18 (s, 9H). Full characterization is provided for an isolated sample using the two-step, one-flask reaction (see Section IV).



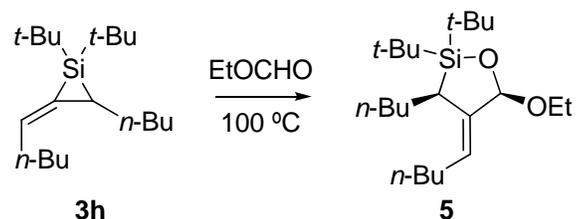
Oxasilacyclopentane 4a (copper-catalysis). The representative procedure for carbonyl insertion was followed using alkyldenesilacyclopropane **3h** (0.550 mL, 0.127 mmol, 0.231 M solution of the alkyldenesilacyclopropane and 0.0465 M solution of PhSiMe_3 , the internal standard, in C_6D_6), benzaldehyde (0.039 mL, 0.38 mmol), and CuI (0.002 g, 0.01 mmol). The reaction mixture was left at 22 °C and after 30 min, oxasilacyclopentane **4a** was formed in 90% yield, as determined by ^1H NMR spectroscopy. The reaction mixture was concentrated *in vacuo* and a GC–MS spectrum of the unpurified reaction mixture showed that oxasilacyclopentane **4a** was formed with 90:10 diastereoselectivity. Distinctive peaks were consistent with those reported for the thermolysis-derived product (see above) and full characterization is provided for an isolated sample using the two-step, one-flask reaction (see Section IV).



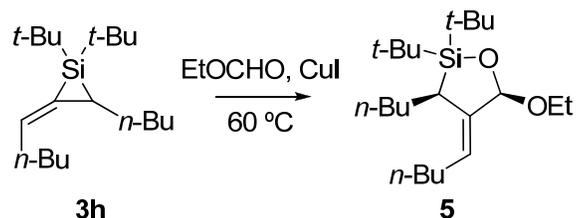
Oxasilacyclopentane 4b (thermolysis). The representative procedure for thermal carbonyl insertion was followed using alkyldenesilacyclopropane **3h** (0.550 mL, 0.127 mmol, 0.231 M solution of the alkyldenesilacyclopropane and 0.0465 M solution of PhSiMe_3 , the internal standard, in C_6D_6) and *n*-butyraldehyde (0.034 mL, 0.38 mmol). The reaction mixture was left at 22 °C for 2 h and was then heated at 60 °C. After 15 h at 60 °C, oxasilacyclopentane **4b** was formed in 82% yield, as determined by ^1H NMR spectroscopy. The reaction mixture was concentrated *in vacuo* and a GC–MS spectrum of the unpurified reaction mixture showed that oxasilacyclopentane **4b** was formed with >99:1 diastereoselectivity: ^1H NMR (400 MHz, C_6D_6 , distinctive peaks) δ 5.88 (td, $J = 6.6, 2.8$, 1H), 4.04 (m, 1H), 2.37 (m, 1H), 2.14 (m, 2H), 1.17 (s, 9H), 1.15 (s, 9H). Full characterization is provided for an isolated sample using the two-step, one-flask reaction (see Section IV).



Oxasilacyclopentane 4b (copper-catalysis). The representative procedure for carbonyl insertion was followed using alkylidenesilacyclopropane **3h** (0.550 mL, 0.127 mmol, 0.231 M solution of the alkylidenesilacyclopropane and 0.0465 M solution of PhSiMe₃, the internal standard, in C₆D₆), *n*-butyraldehyde (0.034 mL, 0.38 mmol), and CuI (0.002 g, 0.01 mmol). The reaction mixture was left at 22 °C and after 30 min oxasilacyclopentane **4b** was formed in 89% yield, as determined by ¹H NMR spectroscopy. The reaction mixture was concentrated *in vacuo* and a GC–MS spectrum of the unpurified reaction mixture showed that oxasilacyclopentane **4b** was formed with >99:1 diastereoselectivity. Distinctive peaks were consistent with those reported for the thermolysis-derived product (see above) and full characterization is provided for an isolated sample using the two-step, one-flask reaction (see Section IV).



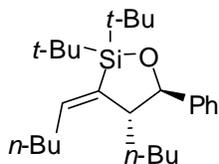
Oxasilacyclopentane 5 (thermolysis). The representative procedure for thermal carbonyl insertion was followed using alkylidenesilacyclopropane **3h** (0.550 mL, 0.127 mmol, 0.231 M solution of the alkylidenesilacyclopropane and 0.0465 M solution of PhSiMe₃, the internal standard, in C₆D₆) and ethyl formate (0.031 mL, 0.38 mmol). The reaction mixture was left at 22 °C for 2 h and was then heated at 60 °C for 15 h, but no reaction was observed. After the reaction mixture was heated at 100 °C for 7 d, oxasilacyclopentane **5** was formed in 82% yield, as determined by ¹H NMR spectroscopy. The reaction mixture was concentrated *in vacuo* and a GC–MS spectrum of the unpurified reaction mixture showed that oxasilacyclopentane **5** was formed with >95:5 diastereoselectivity: ¹H NMR (400 MHz, C₆D₆, distinctive peaks) δ 5.87 (td, *J* = 6.9, 2.4, 1H), 5.12 (d, *J* = 0.9, 1H), 3.96 (dq, *J* = 9.5, 7.1, 1H), 3.43 (dq, *J* = 9.5, 7.1, 1H), 2.82 (m, 1H), 2.08 (m, 2H), 1.22 (s, 9H), 1.17 (s, 9H). Full characterization is provided for an isolated sample using the two-step, one-flask reaction (see Section IV).



Oxasilacyclopentane 5 (copper-catalysis). The representative procedure for thermal carbonyl insertion was followed using alkylidenesilacyclopropane **3h** (0.550 mL, 0.127 mmol, 0.231 M solution of the alkylidenesilacyclopropane and 0.0465 M solution of PhSiMe₃, the internal standard, in C₆D₆), ethyl formate (0.031 mL, 0.38 mmol), and CuI (0.002 g, 0.01 mmol). The

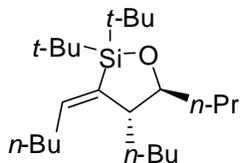
reaction mixture was left at 22 °C for 2 h and was then heated at 60 °C for 21 h, forming oxasilacyclopentane **5** in 82% yield, as determined by ¹H NMR spectroscopy. The reaction mixture was concentrated *in vacuo* and a GC–MS spectrum of the unpurified reaction mixture showed that oxasilacyclopentane **5** was formed with 95:5 diastereoselectivity. Distinctive peaks were consistent with those reported for the thermolysis-derived product (see above) and full characterization is provided for an isolated sample using the two-step, one-flask reaction (see Section IV).

IV. Two-Step, One-Flask Reactions to Form Oxasilacyclopentanes



4a

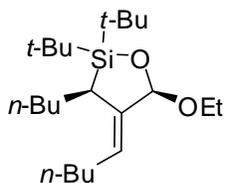
Oxasilacyclopentane 4a. To a cooled solution (–26 °C) of undeca-5,6-diene **1h** (0.152 g, 1.00 mmol) and **2** (0.269 g, 1.20 mmol) in 4 mL of toluene was added Ag₃PO₄ (0.021 g, 0.050 mmol). The reaction flask was kept at –26 °C for 30 min and was then allowed to warm to 22 °C. After 3 h, the reaction mixture was cooled to –26 °C. Benzaldehyde (0.30 mL, 3.0 mmol) was added, followed by ZnBr₂ (0.023 g, 0.10 mmol). The reaction mixture was kept at –26 °C for 1 h and was then allowed to warm to 22 °C. After 1 h, the reaction mixture was filtered through Celite with CH₂Cl₂ and concentrated *in vacuo* to give a colorless oil (87:13 mixture of diastereomers by GC-MS). Purification by column chromatography (0:100 – 20:80 CH₂Cl₂/hexanes) gave **4a** as a colorless oil (0.263 g, 66%): ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 7.2, 2H), 7.33 (t, *J* = 7.3, 2H), 7.25 (tt, *J* = 7.2, 1.2, 1H), 5.88 (td, *J* = 6.8, 3.2, 1H), 4.78 (d, *J* = 8.4, 1H), 2.68 (m, 1H), 2.17 (m, 2H), 1.72 (m, 1H), 1.50 (m, 1H), 1.33 (m, 8H), 1.10 (s, 9H), 1.08 (s, 9H), 0.91 (t, *J* = 7.3, 3H), 0.85 (t, *J* = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 145.2, 140.7, 140.4, 128.4, 127.6, 127.2, 85.2, 51.6, 31.9, 31.3, 30.9, 28.5, 28.2, 28.1, 23.4, 22.8, 21.9, 20.8, 14.2; IR (thin film) 3029, 2958, 2360, 1625, 1472, 1024 cm⁻¹; HRMS (ESI) *m/z* calcd for C₂₆H₄₄NaOSi (M + Na)⁺ 423.3059, found 423.3068. Anal. Calcd for C₂₆H₄₄OSi: C, 77.93; H, 11.07. Found: C, 77.75; H, 11.10.



4b

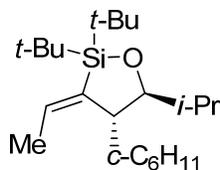
Oxasilacyclopentane 4b. To a solution of undeca-5,6-diene **1h** (0.152 g, 1.00 mmol) and **2** (0.269 g, 1.20 mmol) in 4 mL of toluene was added AgO₂CCF₃ (0.002 g, 0.01 mmol). After 15 min, butyraldehyde (0.27 mL, 3.0 mmol) was added, followed by CuI (0.019 g, 0.10 mmol). After 25 min, the reaction mixture was filtered through Celite with CH₂Cl₂ and concentrated *in vacuo* to give a colorless oil (93:7 mixture of diastereomers by GC-MS). Purification by column chromatography (0:100 – 5:95 CH₂Cl₂/hexanes) gave **4b** as a colorless oil (0.297 g, 81%): ¹H NMR (500 MHz, CDCl₃) δ 5.78 (td, *J* = 7.1, 2.7, 1H), 3.87 (dt, *J* = 7.9, 4.5, 1H), 2.28 (m, 1H),

2.12 (q, $J = 6.8$, 2H), 1.57–1.20 (m, 14H), 1.02 (s, 9H), 0.99 (s, 9H), 0.95–0.87 (t, $J = 5.5$, 3H; t, $J = 5.7$, 3H; t, $J = 7.2$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.0, 140.6, 84.2, 49.1, 42.3, 35.6, 31.9, 30.9, 30.5, 28.5, 28.3, 23.2, 22.8, 21.0, 20.3, 19.7, 14.4, 14.3, 14.2; IR (thin film) 2958, 1627, 1471, 1362, 1093, 822 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{47}\text{OSi}$ ($\text{M} + \text{H}$) $^+$ 367.3396, found 367.3400. Anal. Calcd for $\text{C}_{23}\text{H}_{46}\text{OSi}$: C, 75.33; H, 12.64. Found: C, 75.46; H, 12.80.



5

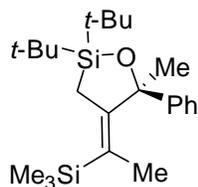
Oxasilacyclopentane 5. A solution of undeca-5,6-diene **1h** (0.457 g, 3.00 mmol) and **2** (0.808 g, 3.60 mmol) in 13 mL of toluene was prepared in a vessel fitted with an air-free seal. The reaction mixture was cooled to -26 $^{\circ}\text{C}$ and AgO_2CCF_3 (0.60 mL, 0.015 mmol, 0.025 M) was added. The reaction flask was kept at -26 $^{\circ}\text{C}$ for 45 min. Ethyl formate (0.73 mL, 9.0 mmol) was added, followed by CuI (0.057 g, 0.30 mmol). The reaction mixture was heated at 60 $^{\circ}\text{C}$ for 19 h. After the reaction mixture was cooled to 22 $^{\circ}\text{C}$, it was vacuum-filtered through a pad of Celite with CH_2Cl_2 and concentrated *in vacuo* to give a colorless oil (97:3 mixture of diastereomers by GC-MS). Purification by column chromatography (0:100 – 10:90 CH_2Cl_2 /hexanes) gave **5** as a colorless oil (0.996 g, 90%): ^1H NMR (500 MHz, CDCl_3) δ 5.79 (td, $J = 6.9$, 2.4, 1H), 4.94 (d, $J = 0.8$, 1H), 3.82 (dq, $J = 9.6$, 7.1, 1H), 3.46 (dq, $J = 9.6$, 7.1, 1H), 2.53 (m, 1H), 2.11 (q, $J = 6.9$, 2H), 1.37 (m, 10H), 1.19 (t, $J = 7.1$, 3H), 1.03 (s, 9H), 1.02 (s, 9H), 0.90 (t, $J = 7.3$, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.0, 140.0, 108.0, 62.6, 50.5, 34.3, 31.9, 31.2, 30.9, 28.3, 28.2, 22.9, 22.8, 20.41, 20.36, 15.3, 14.32, 14.28; IR (thin film) 2959, 1631, 1473, 1363, 1114 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{44}\text{NaO}_2\text{Si}$ ($\text{M} + \text{Na}$) $^+$ 391.3008, found 391.2998. Anal. Calcd for $\text{C}_{22}\text{H}_{44}\text{O}_2\text{Si}$: C, 71.67; H, 12.03. Found: C, 71.85; H, 12.09.



6

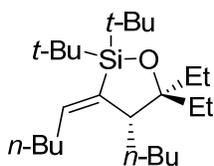
Oxasilacyclopentane 6. To a cooled (-18 $^{\circ}\text{C}$) solution of allene **1e** (0.14 g, 1.0 mmol) and **2** (0.28 g, 1.3 mmol) in 4.5 mL of toluene was added AgO_2CCF_3 (0.010 g, 0.05 mmol). The reaction mixture was kept at -18 $^{\circ}\text{C}$ for 30 min and was then slowly warmed to 22 $^{\circ}\text{C}$. After 2 h, the reaction mixture was cooled to -18 $^{\circ}\text{C}$. Isobutyraldehyde (0.27 mL, 3.0 mmol) was added, followed by CuI (0.030 g, 0.16 mmol). The reaction mixture was kept at -18 $^{\circ}\text{C}$ for 30 min and then slowly warmed to 22 $^{\circ}\text{C}$ over 15 h. The reaction mixture was filtered through Celite with Et_2O and concentrated *in vacuo* to give a colorless oil (96:3:1 mixture of diastereomers by GC-MS). Purification by column chromatography (10:90 CH_2Cl_2 /hexanes) gave **6** as a colorless oil (0.256 g, 70%) that solidified upon storage (-20 $^{\circ}\text{C}$): mp 54 – 55 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 6.12 (qd, $J = 6.7$, 1.8, 1H), 3.60 (dd, $J = 9.5$, 1.2, 1H), 2.38 (m, 1H), 1.90 (m, 1H), 1.74 (m, 3H and d, $J = 6.7$, 3H), 1.64 (m, 1H), 1.45 (m, 2H), 1.15 (m, 3H), 1.04 (s, 9H), 1.02 (s, 9H), 0.99 (d,

$J = 6.6$, 3H), 0.94 (m, 1H), 0.89 (d, $J = 6.6$, 3H and m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.1, 137.6, 88.9, 51.1, 43.0, 34.7, 33.9, 31.3, 29.0, 28.8, 27.4, 27.3, 27.0, 20.8, 20.6, 19.6, 18.7; IR (thin film) 2930, 2855, 1629, 1474, 1039, 821 cm^{-1} ; HRMS (APCI) m/z calcd for $\text{C}_{22}\text{H}_{43}\text{OSi}$ ($\text{M} + \text{H}$) $^+$ 351.3083, found 351.3073. Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{OSi}$: C, 75.36; H, 12.07. Found: C, 75.15; H, 12.09.



7

Oxasilacyclopentane 7.¹⁸ To a cooled (-26 °C) solution of 3-(trimethylsilyl)-1,2-butadiene **1c** (0.17 mL, 1.0 mmol) and **2** (0.269 g, 1.20 mmol) in 4 mL of toluene was added Ag_3PO_4 (0.021 g, 0.050 mmol). The reaction mixture was kept at -26 °C for 30 min and was then allowed to warm to 22 °C. After 2 h, the reaction mixture was cooled to -26 °C. Acetophenone (0.35 mL, 3.0 mmol) was added, followed by $\text{Cu}(\text{OTf})_2$ (0.036 g, 0.10 mmol). After 5 d, the reaction mixture was filtered through silica gel with Et_2O and concentrated *in vacuo* to give a yellow oil (95:5 mixture of diastereomers by GC-MS). Purification by column chromatography (20:80 CH_2Cl_2 /hexanes) gave **7** as a light yellow oil (0.281 g, 72%) that solidified upon storage (-20 °C). Crystallization by slow evaporation of pentane afforded crystals suitable for X-ray crystallographic analysis: mp 73–75 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (m, 2H), 7.27 (m, 2H), 7.20 (m, 1H), 1.98 (dq, $J = 17.6$, 1.2, 1H), 1.88 (s, 3H), 1.71 (dq, $J = 17.6$, 2.7, 1H), 1.60 (dd, $J = 2.7$, 1.2, 3H), 1.05 (s, 9H), 0.72 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.5, 146.2, 130.1, 128.0, 126.9, 126.7, 87.5, 31.8, 28.2, 28.0, 21.1, 20.7, 19.9, 17.6, 0.4; IR (thin film) 3060, 2932, 2360, 1472, 1249, 1028 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{40}\text{NaOSi}_2$ ($\text{M} + \text{Na}$) $^+$ 411.2516, found 411.2522. Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{OSi}_2$: C, 71.06; H, 10.37. Found: C, 71.35; H, 10.48. Details of the X-ray crystallographic study are described in Section IX.

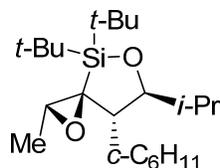


8

Oxasilacyclopentane 8. A solution of undeca-5,6-diene **1h** (0.152 g, 1.00 mmol) and **2** (0.269 g, 1.20 mmol) in 4 mL of toluene was prepared in a vessel fitted with an air-free seal. The reaction mixture was cooled to -26 °C and Ag_3PO_4 (0.021 g, 0.050 mmol) was added. The reaction flask was kept at -26 °C for 1 h and was then allowed to warm to 22 °C. After 2 h, 3-pentanone (0.32 mL, 3.0 mmol) was added, followed by ZnBr_2 (0.023 g, 0.10 mmol). The reaction mixture was heated at 50 °C for 18 h. After the reaction mixture was cooled to 22 °C, it was vacuum-filtered through a pad of Celite with CH_2Cl_2 and concentrated *in vacuo* to give a colorless oil (99:1 mixture of regioisomers by GC-MS). Purification by column chromatography (hexanes) gave **8** as a colorless oil (0.204 g, 54%): ^1H NMR (500 MHz, CDCl_3) δ 5.82 (ddd, $J = 8.0$, 5.2, 2.1, 1H), 2.46 (m, 1H), 2.11 (m, 2H), 1.66 (m, 2H), 1.54 (m, 2H), 1.34 (m, 10H), 1.03 (s, 9H), 1.02 (s, 9H), 0.94–0.87 (t, $J = 7.0$, 3H; t, $J = 7.4$, 3H; t, $J = 7.0$, 3H), 0.79 (t, $J = 7.5$,

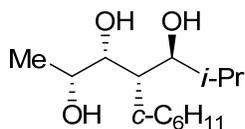
3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.1, 141.2, 85.9, 50.5, 33.6, 32.6, 32.3, 31.9, 31.2, 29.2, 29.0, 27.0, 23.6, 22.8, 20.7, 20.5, 14.4, 14.2, 9.5, 8.8; IR (thin film) 2961, 1627, 1470, 1378, 970, 821 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{49}\text{OSi}$ ($\text{M} + \text{H}$) $^+$ 381.3553, found 381.3553. Anal. Calcd for $\text{C}_{24}\text{H}_{48}\text{OSi}$: C, 75.71; H, 12.71. Found: C, 75.73; H, 12.89.

V. Functionalization of Oxasilacyclopentanes



9

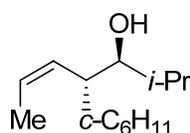
Epoxide 9. To a cooled (0 °C) solution of *m*-chloroperoxybenzoic acid (2.42 g, 9.82 mmol) in 7 mL of CH_2Cl_2 was added a solution of oxasilacyclopentane **6** (1.15 g, 3.27 mmol) in 13 mL of CH_2Cl_2 . The reaction mixture was stirred for 3 hours at 0 °C, then allowed to warm to 22 °C and stirred for 3 days. The reaction mixture was diluted with saturated aqueous NaHCO_3 (60 mL) and extracted with CH_2Cl_2 (3 \times 50 mL). The combined organic layers were washed with brine (2 \times 90 mL), dried over Na_2SO_4 , and concentrated *in vacuo* to give an oil with white solids, as a 98:2 mixture of diastereomers (as determined by GC-MS). Purification by column chromatography (4:96 CH_2Cl_2 /hexanes – 6:94 CH_2Cl_2 /hexanes) afforded **9** as a colorless oil (0.862 g, 72%): ^1H NMR (500 MHz, CDCl_3) δ 4.05 (dd, $J = 10.4, 1.6$, 1H), 3.07 (q, $J = 5.6$, 1H), 1.86 (septd, $J = 6.7, 1.5$, 1H), 1.70 (m, 3H), 1.62 (m, 2H), 1.45 (m, 2H), 1.34 (d, $J = 5.6$, 3H), 1.32–1.12 (m, 4H), 1.08 (d, $J = 6.8$, 3H and m, 1H), 1.03 (s, 9H), 0.99 (s, 9H), 0.87 (d, $J = 6.7$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 82.6, 59.7, 54.4, 46.5, 36.2, 33.7, 32.1, 29.8, 28.2, 28.0, 27.42, 27.37, 26.8, 22.2, 21.4, 20.3, 14.1, 12.9; IR (thin film) 2931, 2855, 1473, 1024, 848, 824 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{43}\text{O}_2\text{Si}$ ($\text{M} + \text{H}$) $^+$ 367.3032, found 367.3023. Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{O}_2\text{Si}$: C, 72.07; H, 11.55. Found: C, 72.06; H, 11.67.



10

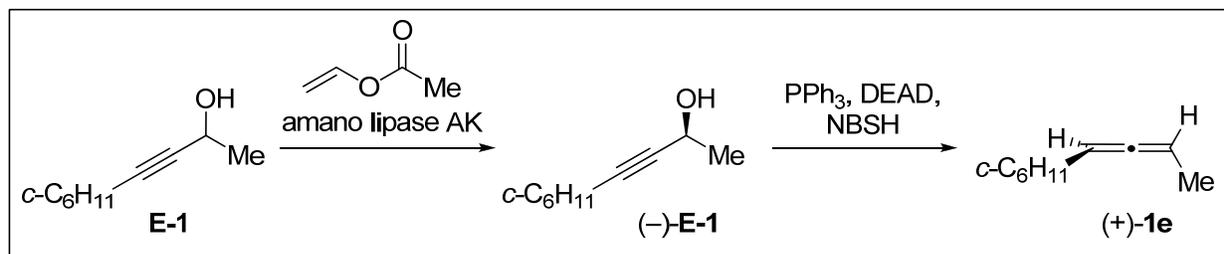
1,2,4-Triol 10. To a solution of $\text{KO}t\text{-Bu}$ (0.444 g, 3.96 mmol) in 1-methyl-2-pyrrolidinone (9.4 mL) was added a solution of epoxide **9** (0.484 g, 1.32 mmol) in toluene (6.3 mL) and THF (6.3 mL), followed by a 1.0 M solution of *n*- Bu_4NF in THF (7.90 mL, 7.8 mmol). The reaction mixture was heated to 70 °C for 6 h. After the reaction mixture was cooled to 22 °C, it was diluted with H_2O (100 mL) and extracted with MTBE (4 \times 40 mL). The combined organic layers were washed with H_2O (3 \times 40 mL), dried with Na_2SO_4 , and concentrated *in vacuo* to give a pink liquid. Purification by column chromatography (40:60 EtOAc/hexanes) did not completely remove excess *n*- Bu_4NF , so a second aqueous extraction was undertaken. The mixture was dissolved in H_2O (100 mL) and extracted with EtOAc (3 \times 30 mL). The combined

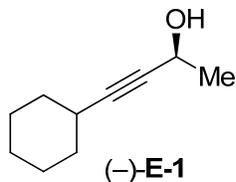
organic layers were washed with brine (150 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography (2:30:70 Et₃N/EtOAc/hexanes) gave triol **10** as a white solid (0.271 g, 84%). Crystallization by slow evaporation of hexanes and CH₂Cl₂ afforded crystals suitable for X-ray crystallographic analysis: mp 72–73 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.96 (dq, *J* = 7.6, 6.3, 1H), 3.75 (dd, *J* = 7.7, 1.7, 1H), 3.56 (dd, *J* = 8.6, 2.0, 1H and br s, 1H), 2.81 (br s, 1H), 2.62 (d, *J* = 4.4, 1H), 2.08 (d, *J* = 9.1, 1H), 1.85 (septd, *J* = 6.7, 1.8, 1H), 1.74 (m, 2H), 1.65 (m, 2H), 1.48 (m, 2H), 1.36–1.09 (m, 5H and d, *J* = 6.3, 3H), 1.01 (d, *J* = 6.7, 3H), 0.85 (d, *J* = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 78.3, 77.4, 68.8, 45.4, 37.3, 33.6, 32.1, 31.5, 27.4, 27.2, 26.7, 19.8, 19.6, 19.2; IR (thin film) 3356, 2923, 1448, 1365, 1060 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₄H₂₈NaO₃ (M + Na)⁺ 267.1936, found 267.1933. Anal. Calcd for C₁₄H₂₈O₃: C, 68.81; H, 11.55. Found: C, 68.43; H, 11.42. Details of the X-ray crystallographic study are described in Section IX.

**11**

Homoallylic alcohol 11. To a solution of KO*t*-Bu (0.303 g, 2.70 mmol) in 1-methyl-2-pyrrolidinone (6.4 mL) was added a solution of oxasilacyclopentane **6** (0.316 g, 0.901 mmol) in toluene (4.3 mL) and THF (4.3 mL), followed by a 1.0 M solution of *n*-Bu₄NF in THF (5.40 mL, 5.4 mmol). The reaction mixture was heated to 70 °C for 22 h. After the reaction mixture was cooled to 22 °C, it was diluted with H₂O (50 mL) and extracted with MTBE (4 × 30 mL). The combined organic layers were washed with H₂O (3 × 30 mL), dried over Na₂SO₄, and concentrated *in vacuo* to give a pink liquid. Purification by column chromatography (8:92 Et₂O/hexanes) gave **11** as a yellow oil (0.168 g, 89%): ¹H NMR (500 MHz, CDCl₃) δ 5.71 (dq, *J* = 11.5, 6.8, 1H), 5.35 (tq, *J* = 11.0, 1.7, 1H), 3.37 (dd, *J* = 10.4, 5.5, 1H), 2.32 (dt, *J* = 11.4, 6.1, 1H), 1.70 (m, 6H), 1.62 (dd, *J* = 6.8, 1.8, 3H), 1.43 (m, 1H), 1.30 (d, *J* = 4.3, 1H), 1.12 (m, 5H), 0.94 (d, *J* = 6.7, 3H), 0.91 (d, *J* = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 129.0, 127.5, 76.3, 45.5, 38.9, 31.9, 30.9, 29.7, 26.9, 26.8, 20.0, 17.5, 14.0; IR (thin film) 3465, 3012, 2923, 2360, 1448 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₄H₂₆NaO (M + Na)⁺ 233.1881, found 233.1879. Anal. Calcd for C₁₄H₂₆O: C, 79.94; H, 12.46. Found: C, 79.66; H, 12.35.

VI. Synthesis of an Enantiopure Homoallylic Alcohol Using the Two-Step, One-Flask Silacyclopropanation/Carbonyl Insertion Reaction:

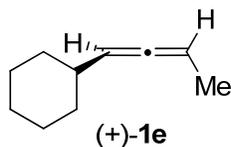
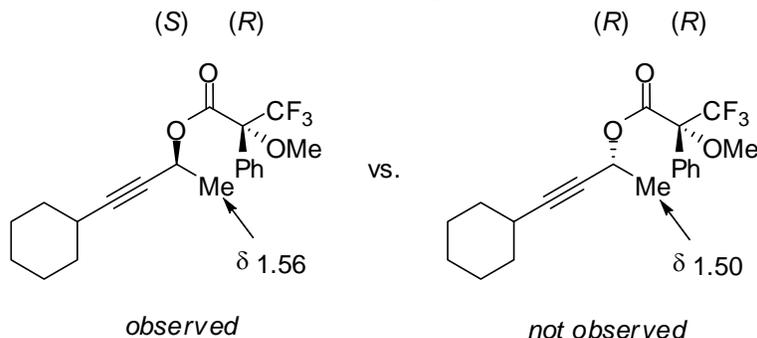




(S)-(-)-Propargylic alcohol (-)-E-1. To a flask containing 4Å molecular sieves (~50 mL) was added propargylic alcohol **E-1** (4.36 g, 28.7 mmol) dissolved in anhydrous pentane (96 mL). Amano lipase AK from *pseudomonas fluorescens* (2.42 g) was added followed by vinyl acetate (7.1 mL, 77 mmol). The slurry was stirred at 22 °C for 6 h. The reaction mixture was filtered through Celite, washed with pentane, and concentrated *in vacuo*. Purification by column chromatography (10:90 EtOAc/hexanes) afforded alcohol (-)-**E-1** as a colorless oil with ~98% ee (1.41 g, 64% yield based on 50% conversion). Both the % ee and the absolute configuration were assigned according to Mosher's ester analysis.^{19,20} The spectral data are consistent with the data reported,¹ and were reported for racemic **E-1** (see Section I): $[\alpha]_D^{23} -24.1$ (*c* 1.00, CHCl₃).

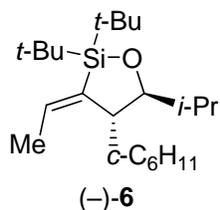
Mosher's ester analysis of alcohol (-)-E-1: To a solution of alcohol (-)-**E-1** (0.040 g, 0.3 mmol) in CH₂Cl₂ (2 mL) was added (*R*)-(+)- α -methoxy- α -trifluoromethylphenylacetic acid (0.084 g, 0.36 mmol), *N,N'*-dicyclohexylcarbodiimide (0.068 g, 0.34 mmol), and *N,N'*-dimethylaminopyridine (0.004 g, 0.03 mmol). After stirring for 3 d at rt, the reaction mixture was filtered through SiO₂, washed with EtOAc, and concentrated *in vacuo*. ¹H NMR spectroscopy (400 MHz, CDCl₃) of the unpurified mixture revealed a single methyl doublet at δ 1.56 ppm (Figure S1). Therefore, the 4-cyclohexyl-but-3-yn-2-ol prepared from lipase resolution was determined to have >98% ee and an absolute configuration of (*S*).^{1,19-21}

Figure S1. Possible (*R*)-Mosher's esters resulting from lipase resolution of alcohol **E-1**.

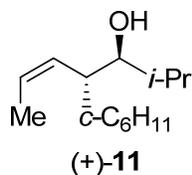


(a*S*)-(+)-Allene (+)-1e. A procedure reported Myers⁸ and adapted by Jamison¹ was used to prepare (+)-**1e**. To a cooled (-15 °C) solution of PPh₃ (3.58 g, 13.6 mmol) in 19 mL of anhydrous THF was added diethyl azodicarboxylate (2.1 mL, 13 mmol). The reaction mixture was stirred for 10 min, then a solution of alcohol (-)-**E-1** (1.37 g, 9.00 mmol) in 19 mL of anhydrous THF was added. After 10 min, a solution of *o*-nitrobenzylsulfonylhydrazine² (2.92 g, 13.5 mmol) in 12 mL of anhydrous THF was added. The reaction mixture was stirred at -15 °C

for 2 h then slowly warmed to rt over 17 h. The reaction mixture was cooled to 0 °C and diluted with pentane (150 mL). The organic layer was washed with ice-cold H₂O (10 × 60 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography (pentane) gave allene (+)-**1e** as a colorless oil (0.794 g, 64%). The absolute configuration was determined⁸ based on the absolute configuration of alcohol (–)-**E-1** and is consistent with the Lowe–Brewster rule.²² The spectral data are consistent with the data reported,^{1,9} and were reported for racemic **1e** (see Section I): $[\alpha]_D^{22} +70.1$ (*c* 1.00, CHCl₃).

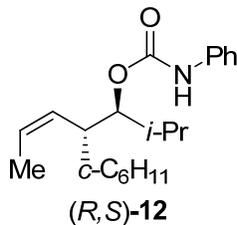


(R,S)-(–)-Oxasilacyclopentane (–)-6. Cyclohexenesilacyclopropane **2**^{15,16} (1.44 g, 6.42 mmol) was added to a solution of allene (+)-**1e** (0.73 g, 5.4 mmol) in anhydrous toluene (20 mL). The mixture was cooled to –18 °C, then AgO₂CCF₃ (0.015 g, 0.068 mmol) was added. The reaction mixture remained at –18 °C for 30 min, then was slowly warmed to 22 °C. After 2 h, the mixture was cooled to –18 °C, then isobutyraldehyde (1.5 mL, 16 mmol) and CuI (0.100 g, 0.525 mmol) were added. The reaction mixture remained at –18 °C for 30 min, then was slowly warmed to 22 °C. After 15 h, the reaction mixture was filtered through Celite, washed with Et₂O, and concentrated *in vacuo*. Purification by column chromatography (10:90 CH₂Cl₂/hexanes) gave oxasilacyclopentane (–)-**6** as a white solid in 96% ee (1.2 g, 65%). The % ee was determined based on the % ee of alcohol (+)-**11** and assumes retention of stereochemistry upon protodesilylation.²³ The absolute configuration was assigned by X-ray crystallographic analysis after conversion to carbamate (+)-**13**. Full characterization data was reported for racemic **6** (see Section IV): $[\alpha]_D^{23} -29.6$ (*c* 1.00, CHCl₃).

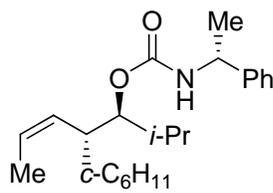


(R,S)-(+)–Homoallylic alcohol (+)-11. To a solution of KO*t*-Bu (0.471 g, 4.20 mmol) in 23 mL of anhydrous DMSO²⁴ was added *n*-Bu₄NF (8.5 mL, 1.0 M in THF, 8.5 mmol) followed by a solution of oxasilacyclopentane (–)-**6** (0.496 g, 1.41 mmol) in 5 mL of anhydrous THF. The reaction mixture was heated to 120 °C for 17 h. The reaction mixture was cooled to 22 °C, diluted with H₂O (100 mL), and extracted with MTBE (2 × 100 mL). The combined organic layers were washed with H₂O (2 × 100 mL). NEt₃ (20 mL) was added, and the solution was stirred for 1 min. The organic layer was washed with 1 M HCl (5 × 100 mL), H₂O (5 × 100 mL), and brine (100 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by column chromatography (4:96 Et₂O/hexanes) gave homoallylic alcohol (+)-**11** as a yellow oil with 96% ee (0.236 g, 79%). The % ee was assigned after conversion²⁵ to carbamate **12** using SFC analysis (Daicel Chiralpak AD, 10:90 *i*-PrOH/CO₂, λ = 220 nm, 1.0 mL/min): *t*_R 13.4 min (major), 14.2 min (minor). The absolute configuration was assigned by X-ray crystallographic

analysis after conversion to carbamate (+)-**13**. Full characterization data was reported for racemic **11** (see Section V): $[\alpha]_D^{22} +23.2$ (*c* 1.00, CHCl₃).



Conversion of alcohol (+)-11** to carbamate (R,S)-**12** for SFC analysis:** A procedure reported by Kanai²⁵ was adapted to prepare (R,S)-**12**. Anhydrous CuCl (0.010 g, 0.10 mmol) and DMF (0.01 mL, 0.1 mmol) were added to a solution of homoallylic alcohol (+)-**11** (0.020 g, 0.10 mmol) in phenyl isocyanate (0.22 mL, 2.0 mmol). After 3 h, the solid reaction mixture was diluted with 3 mL of hexanes, filtered through Celite, and concentrated *in vacuo* to give carbamate (R,S)-**12** as a white solid (0.016 g, 56%). The structure was assigned using HMQC and HMBC experiments, and the compound was subjected to SFC analysis without further purification: mp 94–95 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 6.5, 2H), 7.32 (t, *J* = 8.0, 2H), 7.06 (t, *J* = 7.4, 1H), 6.58 (br s, 1H), 5.65 (dq, *J* = 11.1, 6.8, 1H), 5.37 (td, *J* = 10.9, 1.6, 1H), 4.90 (dd, *J* = 6.9, 4.4, 1H), 2.48 (ddd, *J* = 10.7, 7.2, 4.4, 1H), 1.89 (m, 2H), 1.71 (td, *J* = 12.3, 2.2, 3H), 1.62 (m, 4H), 1.36–1.06 (m, 4H), 1.00 (qd, *J* = 11.7, 3.4, 1H), 0.97–0.89 (m, 1H), 0.94 (d, *J* = 6.8, 3H), 0.93 (d, *J* = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 153.8, 138.3, 129.1, 128.9, 126.1, 123.2, 118.6, 79.5, 44.1, 38.8, 31.6, 30.4, 30.0, 26.7, 26.61, 26.58, 19.5, 18.0, 13.7; IR (thin film) 3442, 2924, 1641, 1523, 1442, 1223 cm⁻¹; HRMS (ESI) *m/z* calcd for C₂₁H₃₁NO₂Na (M + Na)⁺ 352.2253, found 352.2257.



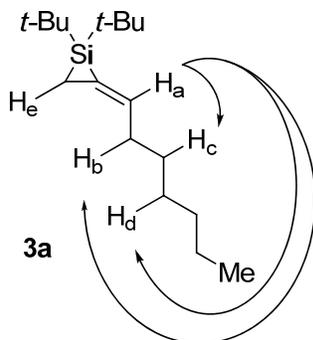
(+)-13

Conversion of alcohol (+)-11** to carbamate (+)-**13** for X-ray crystallographic analysis:** A procedure reported by Woerpel²⁶ was modified to prepare (+)-**13**. (*R*)-(+)-Methylbenzyl isocyanate (0.16 mL, 1.2 mmol) was added to a solution of alcohol (+)-**11** (0.222 g, 1.06 mmol) in anhydrous toluene (2 mL) and 4 Å molecular sieves. The reaction flask was sealed under vacuum and heated to 100 °C. After 3 d, the reaction mixture was cooled to 22 °C and concentrated *in vacuo*. Purification by column chromatography (2:98 EtOAc/hexanes) gave carbamate (+)-**13** as a white solid (0.207 g, 54%). X-ray crystallographic analysis was performed after recrystallization from EtOAc/hexanes: mp 135–136 °C; ¹H NMR (400 MHz, CDCl₃, 50 °C)²⁷ δ 7.35–7.28 (m, 4H), 7.26–7.22 (m, 1H), 5.58 (dq, *J* = 11.1, 6.8, 1H), 5.32 (tq, *J* = 10.9, 1.8, 1H)²⁸, 4.80–4.75 (m, 3H), 2.41 (ddd, *J* = 10.7, 6.8, 4.2, 1H), 1.84–1.76 (m, 2H), 1.69–1.66 (m, 3H), 1.60 (dd, *J* = 6.8, 1.7, 4H), 1.48 (d, *J* = 6.6, 3H), 1.28–1.21 (m, 1H), 1.18–1.03 (m, 3H), 1.01–0.86 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 156.1, 144.0, 129.1, 128.5, 127.1, 125.9, 125.7, 78.9, 50.4, 44.2, 39.0, 30.4, 30.1, 26.68, 26.65, 26.57, 22.4, 19.4, 18.2, 13.7; IR (thin film) 3263, 2924, 1680, 1537, 1448, 1255 cm⁻¹; HRMS (ESI) *m/z* calcd for

$C_{23}H_{35}NO_2Na$ ($M + Na$)⁺ 380.2566, found 380.2562. Anal. Calcd for $C_{23}H_{35}NO_2$: C, 77.27; H, 9.87. Found: C, 77.33; H, 10.12. $[\alpha]_D^{22} +5.34$ (c 1.00, $CHCl_3$).

VII. Regiochemistry of Alkylidenesilacyclopropanes

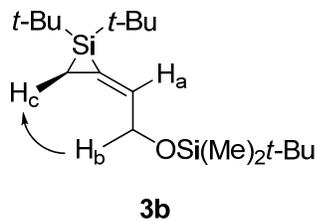
A. NOE experiments for alkylidenesilacyclopropane 3a.



H_a irradiated: **H_b** (1.2%), **H_c** (1.1%), **H_d** (0.3%)

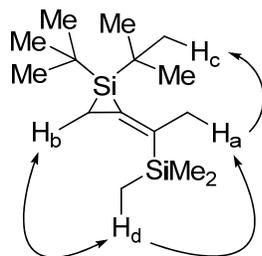
Note: The observation of an NOE between **H_a** and **H_b**, **H_c**, and **H_d** and the absence of an NOE between **H_a** and **H_e** suggests an (*E*)-alkene geometry.

B. NOE experiments for alkylidenesilacyclopropane 3b.



H_b irradiated: **H_a** (4.1%), **H_c** (1.8%)

Note: The observation of an NOE between **H_b** and **H_c** suggests an (*E*)-alkene geometry.

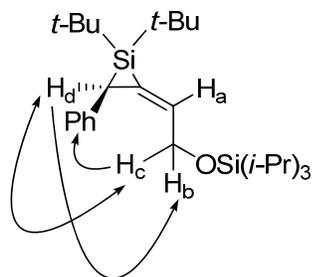
C. NOE experiments for alkylidenesilacyclopropane 3c.**3c**

H_a irradiated: **H_b** (0.2%), **H_c** (0.2%)

H_b irradiated: **H_d** (0.6%)

H_d irradiated: **H_a** (1.2%), **H_b** (1.9%)

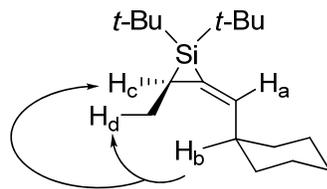
Note: The observation of an NOE between **H_b** and **H_d** and the small NOE between **H_a** and **H_b**, suggests an (*E*)-alkene geometry.

D. NOE experiments for alkylidenesilacyclopropane 3d.**3d**

H_c irradiated: **H_d** (2.5%), **Ph** (NOE is present, but it cannot be quantified because the enhanced resonance overlaps with other aryl resonances).

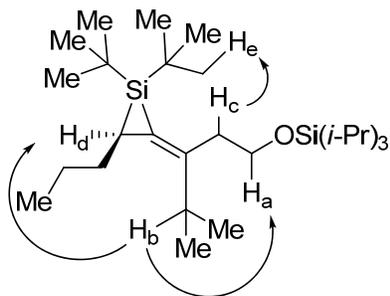
H_d irradiated: **H_c** (1.4%), **H_b** (NOE is present, but it cannot be quantified because the resonance of **H_b** overlaps with a resonance from the minor diastereomer).

Note: The observation of a large NOE between **H_c** and **H_d** suggests an (*E*)-alkene geometry.

E. NOE experiments for alkylidenesilacyclopropane 3e.**3e**

H_b irradiated: **H_c** (NOE is present, but it cannot be quantified because the resonance of **H_c** overlaps with cyclohexene that was formed in reaction mixture), **H_d** (1.4%)

Note: The observation of an NOE between **H_b** and **H_d** suggests an (*E*)-alkene geometry.

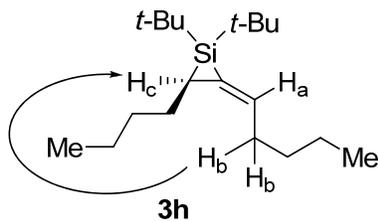
F. NOE experiments for alkylidenesilacyclopropane 3f.**3f**

H_b irradiated: **H_a** (0.6%), **H_c** (0.6%), **H_d** (8.4%)

H_c irradiated: **H_b** (2.2%), **H_e** (NOE is present, but it cannot be quantified because the resonance of H_e overlaps with other resonances)

H_d irradiated: **H_b** (17.4%)

Note: The observation of a large NOE between **H_b** and **H_d** and the absence of NOE between **H_c** and **H_d**, suggests an (*E*)-alkene geometry.

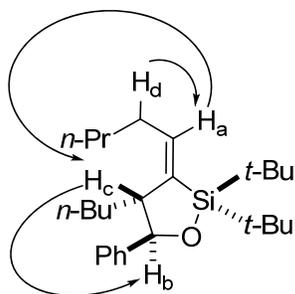
G. NOESY experiment for alkylidenesilacyclopropane 3h.**3h**

NOESY cross peaks were observed between **H_b** and **H_c**. This correlation suggests an (*E*)-alkene geometry.

VIII. Regiochemistry of Oxasilacyclopentanes

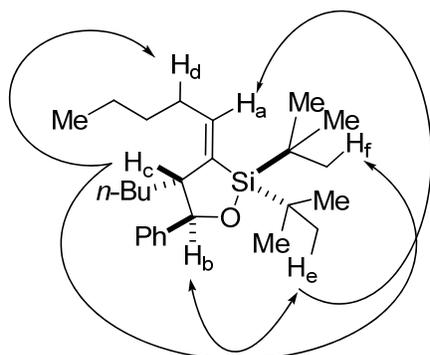
The regiochemistry of the oxasilacyclopentanes that were derived from insertion of aldehydes or formates into alkylidenesilacyclopropanes could be determined by $^1\text{H}/^1\text{H}$ COSY experiments. For oxasilacyclopentanes derived from insertions of ketones (oxasilacyclopentanes **6** and **7**), the regiochemistry of insertion can be determined by NOE or NOESY experiments. Unless otherwise noted, the NOE or NOESY experiments were conducted in CDCl_3 .

A. COSY and NOE experiments for oxasilacyclopentane **4a** (conducted in CD_3CN).



COSY cross peaks

4a



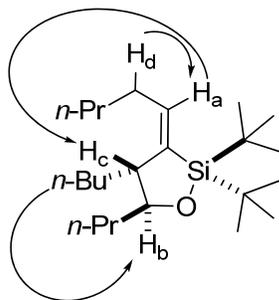
4a

H_b irradiated: **H_e** (0.9%)

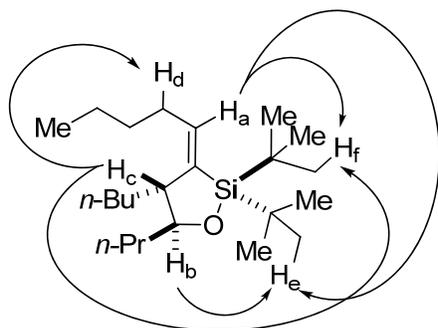
H_c irradiated: **H_b** (1.1%), **H_d** (1.6%), **H_f** (0.2%)

H_e irradiated: **H_a** (13.8%), **H_b** (14.4%)

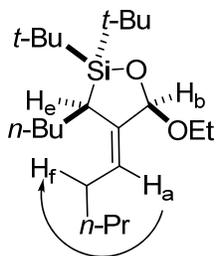
Note: The observation of an NOE between **H_b** and **H_e** and the absence of an NOE between **H_c** and **H_e** suggests a 1,2-trans configuration. The observation of an NOE between **H_c** and **H_d** suggests an (*E*)-alkene geometry.

B. COSY and NOESY experiments for oxasilacyclopentane 4b.

COSY cross peaks

4b**4b**

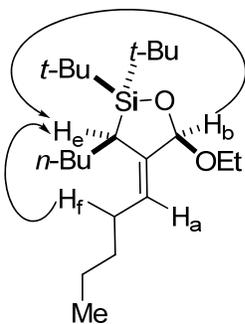
Note: The presence of NOESY cross peaks between **H_b** and **H_e** and between **H_c** and **H_f** suggests a 1,2-*trans* configuration. The presence of a NOESY cross peak between **H_c** and **H_a** suggests an (*E*)-alkene geometry.

C. COSY and NOE experiments for oxasilacyclopentane 5.

COSY cross peak

5

Note: For oxasilacyclopentane **5**, COSY cross peaks were not observed between **H_b** and **H_e**, **H_a** and **H_b**, or **H_a** and **H_e**, which suggests that ethyl formate insertion occurred adjacent to the double bond (through Si-*C_{sp}²* bond cleavage).

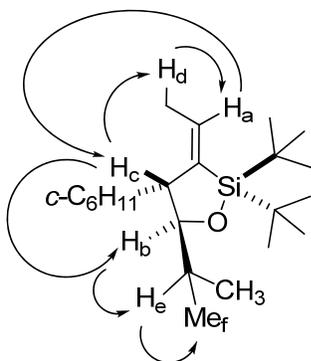


5

 $\mathbf{H_b}$ irradiated: $\mathbf{H_e}$ (3.8%) $\mathbf{H_e}$ irradiated: $\mathbf{H_b}$ (4.0%), $\mathbf{H_f}$ (4.0%) $\mathbf{H_f}$ irradiated: $\mathbf{H_e}$ (17.4%)

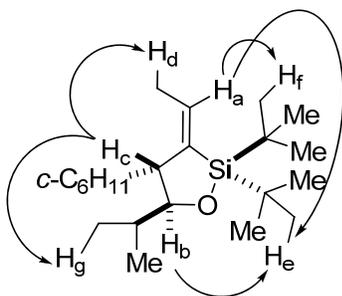
Note: The observation of an NOE between $\mathbf{H_b}$ and $\mathbf{H_e}$ suggests a 1,3-cis configuration. The observation of an NOE between $\mathbf{H_e}$ and $\mathbf{H_f}$ suggests an (*E*)-alkene geometry.

D. COSY and NOESY experiments for oxasilacyclopentane 6.



COSY cross peaks

6



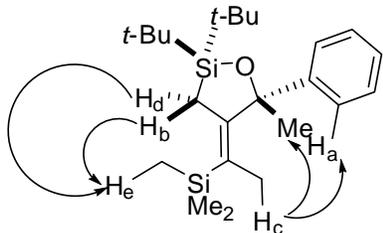
NOESY cross peaks

6

Note: No NOESY cross peak was observed between $\mathbf{H_c}$ and either $\mathbf{H_e}$ or $\mathbf{H_f}$, so the 1,2-stereochemistry could not be determined by this method. The large coupling constant value ($J_{bc} = 9.5$ Hz) suggests a 1,2-trans stereochemistry, and it is consistent with reported values for other

1,2-trans oxasilacyclopentanes.^{29,30} Furthermore, the 1,2-trans stereochemistry of **6** is confirmed by X-ray crystallographic data of its derivatives, triol **10** and carbamate (+)-**13** (see Section IX). The presence of a NOESY cross peak between **H_c** and **H_d** suggests an (*E*)-alkene geometry.

E. NOE experiments for oxasilacyclopentane **7**.



7

H_b irradiated: **H_e** (1.1%)

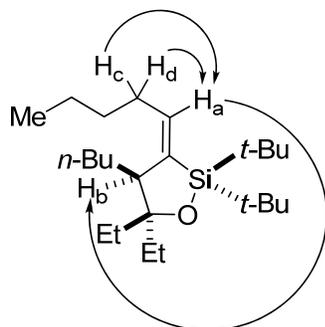
H_c irradiated: **H_a** (3.9%), **Me** (3.8%)

H_e irradiated: **H_b** (6.3%), **H_d** (3.5%), **Me** (0.4%)

Me irradiated: **H_c** (6.0%), **H_e** (0.1%)

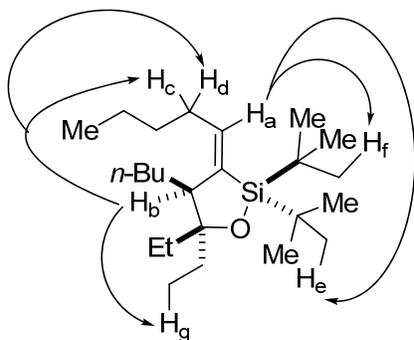
Note: The observation of NOE between **H_b** and **H_e**, **H_d** and **H_e**, and **H_c** and **Me** suggests a (*Z*)-alkene geometry. The data obtained from NOE experiments of **7** were verified with an X-ray crystal structure (see Section IX).

F. COSY and NOE experiments for oxasilacyclopentane **8** (conducted in C₆D₆).



COSY cross peaks

8



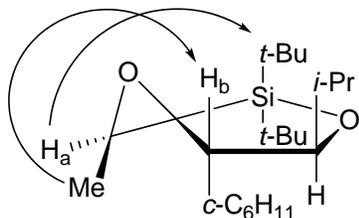
8

H_a irradiated: **H_e** (0.6%), **H_f** (0.2%)

H_b irradiated: **H_c** (7.1%), **H_d** (2.9%), **H_g** (2.2%)

Note: The observation of an NOE between **H_b** and **H_g** suggests that 3-pentanone insertion occurred adjacent to **H_b** (through formal Si–C sp^3 bond cleavage). The observation of an NOE between **H_b** and **H_c** and between **H_b** and **H_d** suggests an (*E*)-alkene geometry.

G. NOE experiments for oxasilacyclopentane 9.



9

H_a irradiated: ***t*-Bu** (0.7%)

Me irradiated: **H_b** (NOE is present, but it cannot be quantified because the resonance of H_b overlaps with another proton).

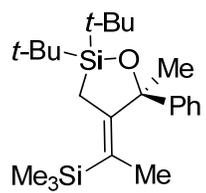
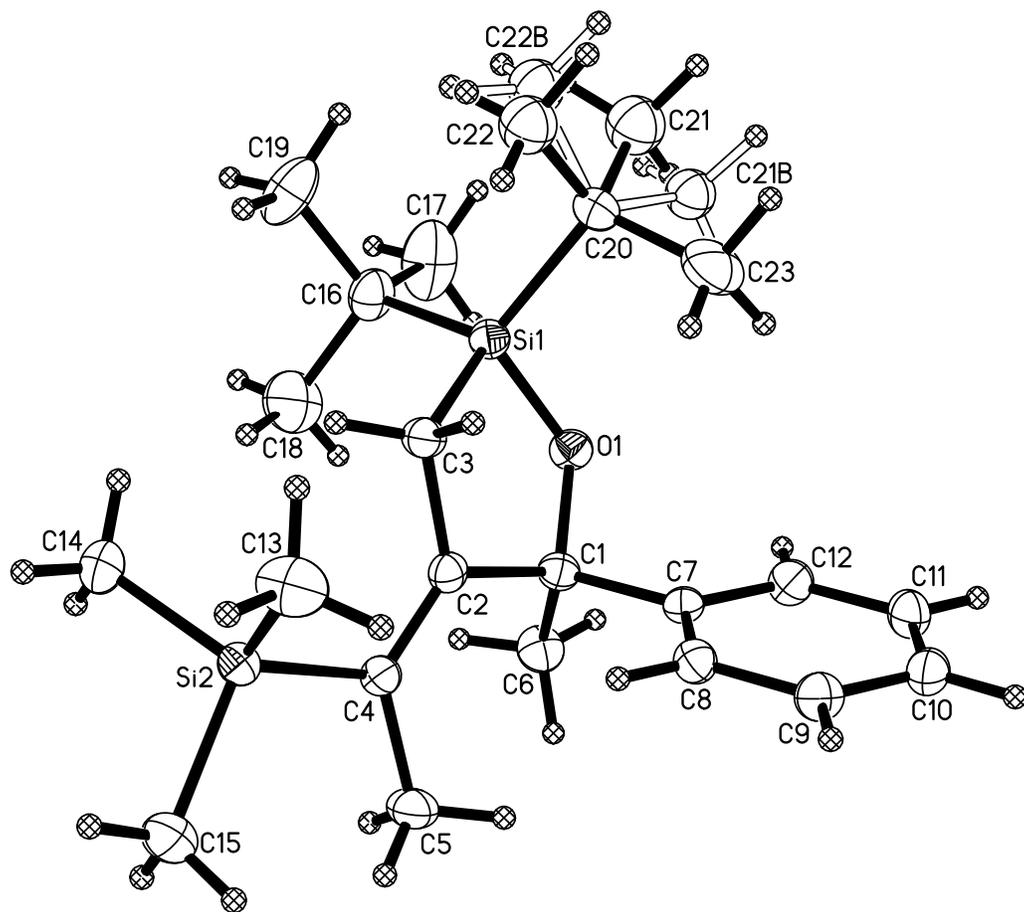
Note: The stereochemistry of oxasilacyclopentane **9** is not conclusive, but, it is believed that epoxidation occurs opposite the large cyclohexyl group. Oxasilacyclopentane **9** was converted to triol **10**, whose stereochemistry was determined by X-ray crystallography (see Section IX).

IX. X-ray Crystallographic Data (Oxasilacyclopentane 7, Triol 10, and Carbamate (+)-13)

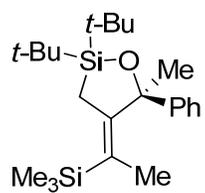
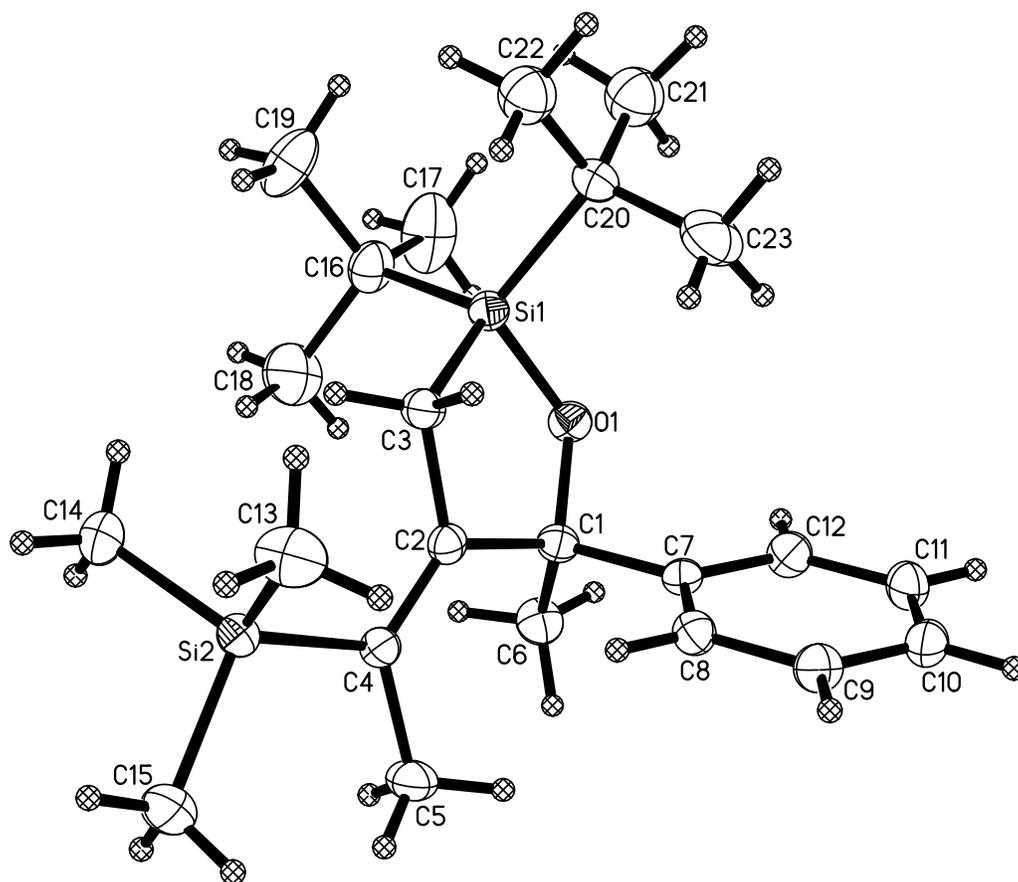
A. X-ray Data Collection, Structure Solution and Refinement for Oxasilacyclopentane 7.

A colorless crystal of approximate dimensions 0.26 x 0.27 x 0.29 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Carbon atoms C(21) and C(22) were disordered and included using multiple components, partial site-occupancy-factors and isotropic temperature parameters. Hydrogen atoms associated with the disordered carbon atoms were included using a riding model. The remaining hydrogen atoms were located from a difference-Fourier map and refined (x, y, z and U_{iso}). At convergence, $wR2 = 0.1124$ and $Goof = 1.070$ for 373 variables refined against 5380 data (0.78\AA), $R1 = 0.0417$ for those 4363 data with $I > 2.0\sigma(I)$.



7



7

References.

1. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
3. Sheldrick, G. M. SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2002.
4. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

Table 1. Crystal data and structure refinement for **7**.

Identification code	kaw112 (Janice Loy)	
Empirical formula	C ₂₃ H ₄₀ O Si ₂	
Formula weight	388.73	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 11.2644(12) Å	α = 90°.
	b = 18.238(2) Å	β = 111.178(2)°.
	c = 12.7049(14) Å	γ = 90°.
Volume	2433.8(5) Å ³	
Z	4	
Density (calculated)	1.061 Mg/m ³	
Absorption coefficient	0.155 mm ⁻¹	
F(000)	856	
Crystal color	colorless	
Crystal size	0.29 x 0.27 x 0.26 mm ³	
Theta range for data collection	1.94 to 27.10°	
Index ranges	-14 ≤ h ≤ 14, -23 ≤ k ≤ 23, -16 ≤ l ≤ 16	
Reflections collected	24656	
Independent reflections	5380 [R(int) = 0.0321]	
Completeness to theta = 27.10°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9609 and 0.9565	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5380 / 0 / 373	
Goodness-of-fit on F ²	1.070	
Final R indices [I > 2σ(I) = 4363 data]	R1 = 0.0417, wR2 = 0.1013	
R indices (all data; 0.78Å)	R1 = 0.0563, wR2 = 0.1124	
Largest diff. peak and hole	0.618 and -0.556 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	7829(1)	460(1)	2416(1)	20(1)
Si(2)	11809(1)	1514(1)	2279(1)	23(1)
O(1)	6987(1)	979(1)	1335(1)	22(1)
C(1)	7685(2)	1547(1)	995(1)	20(1)
C(2)	9130(2)	1419(1)	1638(1)	19(1)
C(3)	9345(2)	985(1)	2721(1)	22(1)
C(4)	10091(2)	1682(1)	1352(1)	20(1)
C(5)	9881(2)	2170(1)	330(2)	29(1)
C(6)	7238(2)	1470(1)	-295(1)	27(1)
C(7)	7257(2)	2289(1)	1307(1)	19(1)
C(8)	8113(2)	2835(1)	1873(1)	22(1)
C(9)	7683(2)	3507(1)	2114(1)	25(1)
C(10)	6393(2)	3640(1)	1803(2)	27(1)
C(11)	5531(2)	3097(1)	1252(2)	28(1)
C(12)	5955(2)	2427(1)	1003(2)	25(1)
C(13)	12162(2)	1857(1)	3756(2)	38(1)
C(14)	12248(2)	523(1)	2322(2)	41(1)
C(15)	12889(2)	2025(1)	1707(2)	36(1)
C(16)	7904(2)	-505(1)	1875(2)	31(1)
C(17)	6572(2)	-825(2)	1276(3)	54(1)
C(18)	8607(3)	-456(1)	1047(3)	54(1)
C(19)	8666(3)	-1026(1)	2826(2)	49(1)
C(20)	7185(2)	549(1)	3603(2)	28(1)
C(21)	6046(3)	71(2)	3477(2)	44(1)
C(22)	8268(2)	350(1)	4755(2)	38(1)
C(21B)	5597(11)	461(6)	2933(10)	32(2)
C(22B)	7560(12)	-34(7)	4432(10)	37(3)
C(23)	6887(3)	1352(1)	3718(2)	47(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **7**.

Si(1)-O(1)	1.6561(12)
Si(1)-C(3)	1.8722(17)
Si(1)-C(16)	1.9011(18)
Si(1)-C(20)	1.9019(18)
Si(2)-C(14)	1.869(2)
Si(2)-C(15)	1.875(2)
Si(2)-C(13)	1.879(2)
Si(2)-C(4)	1.8916(17)
O(1)-C(1)	1.4571(19)
C(1)-C(7)	1.536(2)
C(1)-C(6)	1.538(2)
C(1)-C(2)	1.553(2)
C(2)-C(4)	1.348(2)
C(2)-C(3)	1.529(2)
C(4)-C(5)	1.522(2)
C(7)-C(8)	1.393(2)
C(7)-C(12)	1.397(2)
C(8)-C(9)	1.391(2)
C(9)-C(10)	1.383(3)
C(10)-C(11)	1.386(3)
C(11)-C(12)	1.389(3)
C(16)-C(18)	1.530(3)
C(16)-C(17)	1.532(3)
C(16)-C(19)	1.533(3)
C(20)-C(22B)	1.448(12)
C(20)-C(21)	1.510(3)
C(20)-C(23)	1.522(3)
C(20)-C(22)	1.572(3)
C(20)-C(21B)	1.687(11)
O(1)-Si(1)-C(3)	94.90(7)
O(1)-Si(1)-C(16)	108.43(8)
C(3)-Si(1)-C(16)	113.04(8)
O(1)-Si(1)-C(20)	109.87(7)

C(3)-Si(1)-C(20)	111.94(8)
C(16)-Si(1)-C(20)	116.44(8)
C(14)-Si(2)-C(15)	106.88(10)
C(14)-Si(2)-C(13)	109.52(12)
C(15)-Si(2)-C(13)	106.75(11)
C(14)-Si(2)-C(4)	112.07(10)
C(15)-Si(2)-C(4)	109.81(9)
C(13)-Si(2)-C(4)	111.56(9)
C(1)-O(1)-Si(1)	116.33(9)
O(1)-C(1)-C(7)	107.27(12)
O(1)-C(1)-C(6)	104.33(13)
C(7)-C(1)-C(6)	110.04(14)
O(1)-C(1)-C(2)	108.23(12)
C(7)-C(1)-C(2)	111.34(13)
C(6)-C(1)-C(2)	115.10(14)
C(4)-C(2)-C(3)	123.02(15)
C(4)-C(2)-C(1)	126.61(14)
C(3)-C(2)-C(1)	110.25(13)
C(2)-C(3)-Si(1)	104.07(11)
C(2)-C(4)-C(5)	123.07(15)
C(2)-C(4)-Si(2)	120.99(12)
C(5)-C(4)-Si(2)	115.80(12)
C(8)-C(7)-C(12)	118.40(15)
C(8)-C(7)-C(1)	122.70(14)
C(12)-C(7)-C(1)	118.90(15)
C(9)-C(8)-C(7)	120.82(16)
C(10)-C(9)-C(8)	120.34(16)
C(9)-C(10)-C(11)	119.36(17)
C(10)-C(11)-C(12)	120.53(17)
C(11)-C(12)-C(7)	120.55(16)
C(18)-C(16)-C(17)	109.8(2)
C(18)-C(16)-C(19)	107.3(2)
C(17)-C(16)-C(19)	108.9(2)
C(18)-C(16)-Si(1)	107.25(14)
C(17)-C(16)-Si(1)	111.62(15)
C(19)-C(16)-Si(1)	111.94(14)

C(22B)-C(20)-C(21)	70.6(5)
C(22B)-C(20)-C(23)	130.8(5)
C(21)-C(20)-C(23)	110.94(19)
C(22B)-C(20)-C(22)	39.6(5)
C(21)-C(20)-C(22)	108.04(18)
C(23)-C(20)-C(22)	104.83(18)
C(22B)-C(20)-C(21B)	106.0(6)
C(21)-C(20)-C(21B)	35.7(4)
C(23)-C(20)-C(21B)	84.8(4)
C(22)-C(20)-C(21B)	140.5(4)
C(22B)-C(20)-Si(1)	114.8(5)
C(21)-C(20)-Si(1)	114.81(15)
C(23)-C(20)-Si(1)	108.59(13)
C(22)-C(20)-Si(1)	109.16(14)
C(21B)-C(20)-Si(1)	103.4(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Si(1)	20(1)	18(1)	24(1)	0(1)	9(1)	-2(1)
Si(2)	20(1)	23(1)	29(1)	4(1)	11(1)	1(1)
O(1)	19(1)	21(1)	24(1)	0(1)	7(1)	-4(1)
C(1)	20(1)	20(1)	20(1)	-1(1)	7(1)	-2(1)
C(2)	22(1)	17(1)	19(1)	-1(1)	8(1)	2(1)
C(3)	20(1)	25(1)	21(1)	4(1)	7(1)	0(1)
C(4)	22(1)	19(1)	20(1)	1(1)	9(1)	1(1)
C(5)	27(1)	35(1)	27(1)	10(1)	12(1)	0(1)
C(6)	29(1)	32(1)	19(1)	-2(1)	7(1)	0(1)
C(7)	22(1)	20(1)	17(1)	3(1)	8(1)	2(1)
C(8)	21(1)	24(1)	21(1)	0(1)	7(1)	1(1)
C(9)	29(1)	23(1)	24(1)	-3(1)	10(1)	-2(1)
C(10)	32(1)	24(1)	26(1)	2(1)	14(1)	6(1)
C(11)	22(1)	32(1)	30(1)	4(1)	10(1)	6(1)
C(12)	22(1)	25(1)	28(1)	0(1)	7(1)	-1(1)
C(13)	33(1)	50(1)	28(1)	0(1)	5(1)	-10(1)
C(14)	40(1)	30(1)	62(2)	13(1)	30(1)	13(1)
C(15)	27(1)	38(1)	46(1)	10(1)	17(1)	-2(1)
C(16)	32(1)	21(1)	39(1)	-4(1)	12(1)	-1(1)
C(17)	42(1)	38(1)	73(2)	-28(1)	8(1)	-6(1)
C(18)	83(2)	33(1)	63(2)	-11(1)	47(2)	6(1)
C(19)	56(2)	23(1)	59(2)	1(1)	10(1)	9(1)
C(20)	28(1)	28(1)	33(1)	4(1)	18(1)	0(1)
C(23)	71(2)	39(1)	47(1)	-6(1)	41(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **7**.

	x	y	z	U(eq)
H(21A)	5726	185	4080	67
H(21B)	6298	-446	3527	67
H(21C)	5377	164	2742	67
H(22A)	7951	416	5373	57
H(22B)	9001	672	4874	57
H(22C)	8526	-161	4735	57
H(21D)	5400	-38	2637	49
H(21E)	5303	813	2309	49
H(21F)	5167	559	3466	49
H(22D)	7206	60	5020	56
H(22E)	8491	-54	4774	56
H(22F)	7237	-503	4065	56
H(3A)	10100(20)	698(12)	2941(17)	29(5)
H(3B)	9460(20)	1329(13)	3340(20)	40(6)
H(5A)	9120(20)	2482(12)	175(18)	35(6)
H(5B)	10590(20)	2477(14)	430(20)	50(7)
H(5C)	9800(20)	1884(15)	-310(20)	54(7)
H(6A)	6320(20)	1390(12)	-570(18)	34(6)
H(6B)	7440(20)	1896(12)	-654(18)	33(5)
H(6C)	7650(20)	1039(13)	-493(19)	40(6)
H(8A)	9004(18)	2751(10)	2095(15)	17(4)
H(9A)	8300(20)	3884(12)	2531(18)	35(6)
H(10A)	6090(20)	4101(12)	1957(17)	32(5)
H(11A)	4660(20)	3179(11)	1046(17)	28(5)
H(12A)	5380(20)	2064(12)	638(18)	36(6)
H(13A)	11910(30)	1523(15)	4210(20)	60(8)
H(13B)	13010(30)	1936(17)	4060(30)	76(9)
H(13C)	11790(30)	2340(20)	3740(30)	95(11)
H(14A)	11880(30)	220(16)	2690(20)	68(9)
H(14B)	13140(30)	473(18)	2710(30)	90(11)
H(14C)	12150(30)	357(17)	1640(30)	78(10)

H(15A)	12790(20)	2556(14)	1709(19)	42(6)
H(15B)	13740(30)	1903(14)	2210(20)	51(7)
H(15C)	12780(30)	1876(15)	960(20)	60(8)
H(17A)	6630(20)	-1291(15)	970(20)	51(7)
H(17B)	6140(30)	-500(17)	690(30)	69(9)
H(17C)	6110(30)	-881(16)	1810(30)	69(9)
H(18A)	8610(30)	-957(16)	730(20)	65(8)
H(18B)	8080(30)	-213(16)	420(20)	57(8)
H(18C)	9530(30)	-232(19)	1410(30)	90(11)
H(19A)	8720(30)	-1518(15)	2480(20)	60(8)
H(19B)	9550(30)	-850(15)	3230(20)	59(8)
H(19C)	8180(30)	-1110(19)	3350(30)	94(11)
H(23A)	7600(30)	1663(14)	3790(20)	52(7)
H(23B)	6630(20)	1420(13)	4370(20)	48(7)
H(23C)	6110(40)	1540(20)	2940(40)	111(13)

Table 6. Torsion angles [°] for **7**.

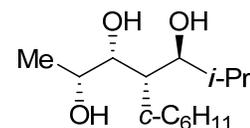
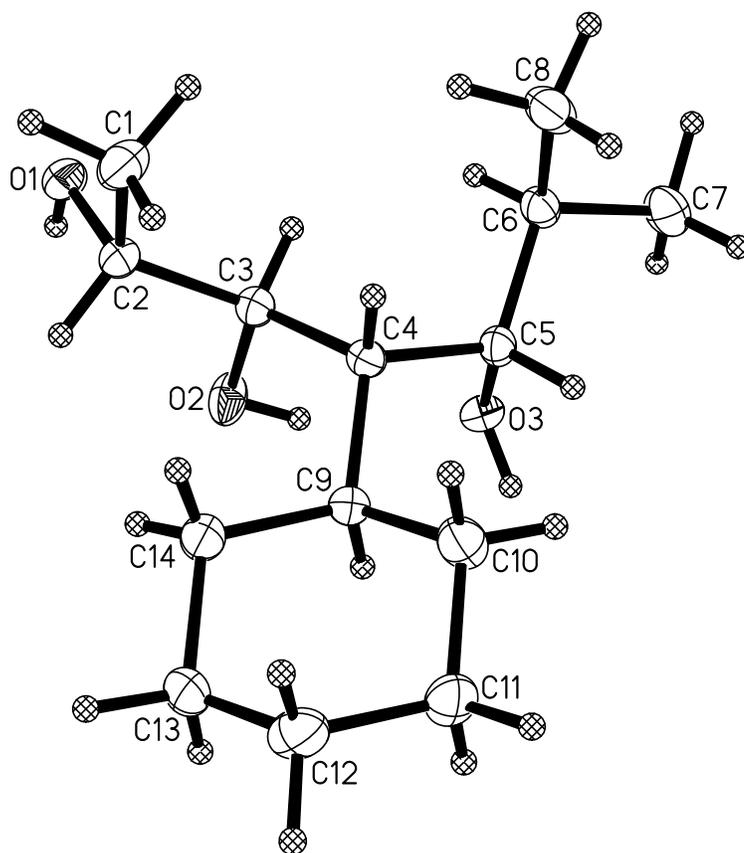
C(3)-Si(1)-O(1)-C(1)	4.82(12)
C(16)-Si(1)-O(1)-C(1)	-111.46(11)
C(20)-Si(1)-O(1)-C(1)	120.27(11)
Si(1)-O(1)-C(1)-C(7)	-110.37(12)
Si(1)-O(1)-C(1)-C(6)	132.89(12)
Si(1)-O(1)-C(1)-C(2)	9.87(15)
O(1)-C(1)-C(2)-C(4)	160.27(15)
C(7)-C(1)-C(2)-C(4)	-82.07(19)
C(6)-C(1)-C(2)-C(4)	44.0(2)
O(1)-C(1)-C(2)-C(3)	-23.62(17)
C(7)-C(1)-C(2)-C(3)	94.05(15)
C(6)-C(1)-C(2)-C(3)	-139.85(15)
C(4)-C(2)-C(3)-Si(1)	-158.14(14)
C(1)-C(2)-C(3)-Si(1)	25.58(15)
O(1)-Si(1)-C(3)-C(2)	-17.76(11)
C(16)-Si(1)-C(3)-C(2)	94.66(12)
C(20)-Si(1)-C(3)-C(2)	-131.48(11)
C(3)-C(2)-C(4)-C(5)	-174.51(16)
C(1)-C(2)-C(4)-C(5)	1.1(3)
C(3)-C(2)-C(4)-Si(2)	1.0(2)
C(1)-C(2)-C(4)-Si(2)	176.69(12)
C(14)-Si(2)-C(4)-C(2)	66.63(16)
C(15)-Si(2)-C(4)-C(2)	-174.74(14)
C(13)-Si(2)-C(4)-C(2)	-56.59(16)
C(14)-Si(2)-C(4)-C(5)	-117.51(15)
C(15)-Si(2)-C(4)-C(5)	1.12(16)
C(13)-Si(2)-C(4)-C(5)	119.27(15)
O(1)-C(1)-C(7)-C(8)	132.48(15)
C(6)-C(1)-C(7)-C(8)	-114.61(17)
C(2)-C(1)-C(7)-C(8)	14.2(2)
O(1)-C(1)-C(7)-C(12)	-48.10(18)
C(6)-C(1)-C(7)-C(12)	64.81(19)
C(2)-C(1)-C(7)-C(12)	-166.34(14)
C(12)-C(7)-C(8)-C(9)	-1.0(2)

C(1)-C(7)-C(8)-C(9)	178.42(15)
C(7)-C(8)-C(9)-C(10)	0.6(3)
C(8)-C(9)-C(10)-C(11)	0.2(3)
C(9)-C(10)-C(11)-C(12)	-0.6(3)
C(10)-C(11)-C(12)-C(7)	0.1(3)
C(8)-C(7)-C(12)-C(11)	0.7(2)
C(1)-C(7)-C(12)-C(11)	-178.80(15)
O(1)-Si(1)-C(16)-C(18)	62.87(18)
C(3)-Si(1)-C(16)-C(18)	-41.00(19)
C(20)-Si(1)-C(16)-C(18)	-172.67(17)
O(1)-Si(1)-C(16)-C(17)	-57.38(19)
C(3)-Si(1)-C(16)-C(17)	-161.24(18)
C(20)-Si(1)-C(16)-C(17)	67.1(2)
O(1)-Si(1)-C(16)-C(19)	-179.75(16)
C(3)-Si(1)-C(16)-C(19)	76.39(18)
C(20)-Si(1)-C(16)-C(19)	-55.28(19)
O(1)-Si(1)-C(20)-C(22B)	161.6(6)
C(3)-Si(1)-C(20)-C(22B)	-94.3(6)
C(16)-Si(1)-C(20)-C(22B)	37.9(6)
O(1)-Si(1)-C(20)-C(21)	82.53(17)
C(3)-Si(1)-C(20)-C(21)	-173.37(16)
C(16)-Si(1)-C(20)-C(21)	-41.19(19)
O(1)-Si(1)-C(20)-C(23)	-42.28(17)
C(3)-Si(1)-C(20)-C(23)	61.82(17)
C(16)-Si(1)-C(20)-C(23)	-166.00(15)
O(1)-Si(1)-C(20)-C(22)	-156.02(13)
C(3)-Si(1)-C(20)-C(22)	-51.93(16)
C(16)-Si(1)-C(20)-C(22)	80.26(16)
O(1)-Si(1)-C(20)-C(21B)	46.6(4)
C(3)-Si(1)-C(20)-C(21B)	150.7(4)
C(16)-Si(1)-C(20)-C(21B)	-77.1(4)

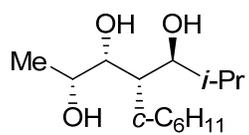
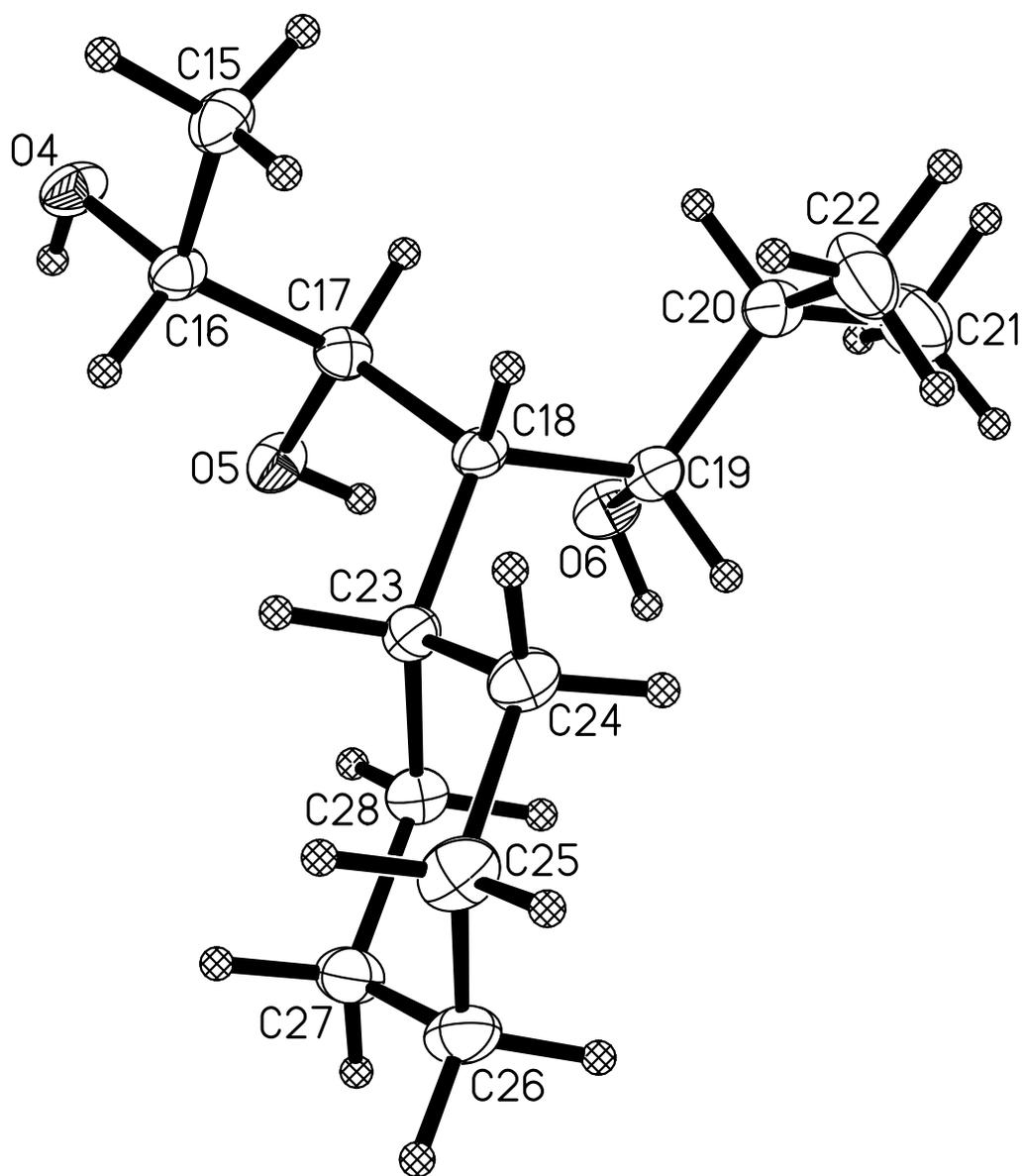
B. X-ray Data Collection, Structure Solution and Refinement for Triol 10.

A colorless crystal of approximate dimensions 0.21 x 0.26 x 0.38 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x, y, z and U_{iso}). There were two molecules of the formula unit present ($Z = 8$). At convergence, $wR2 = 0.1033$ and $Goof = 1.030$ for 531 variables refined against 6341 data (0.78\AA), $R1 = 0.0389$ for those 4540 data with $I > 2.0\sigma(I)$.



10



References.

6. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
 7. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
 8. Sheldrick, G. M. SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2002.
 9. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
 10. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
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Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

Table 1. Crystal data and structure refinement for **10**.

Identification code	kaw111 (Janice Loy)	
Empirical formula	C ₁₄ H ₂₈ O ₃	
Formula weight	244.36	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 11.9103(11) Å	α = 90°.
	b = 19.0369(17) Å	β = 91.289(2)°.
	c = 12.6994(11) Å	γ = 90°.
Volume	2878.7(4) Å ³	
Z	8	
Density (calculated)	1.128 Mg/m ³	
Absorption coefficient	0.077 mm ⁻¹	
F(000)	1088	
Crystal color	colorless	
Crystal size	0.38 x 0.26 x 0.21 mm ³	
Theta range for data collection	1.93 to 27.10°	
Index ranges	-15 ≤ h ≤ 15, -24 ≤ k ≤ 24, -16 ≤ l ≤ 16	
Reflections collected	29465	
Independent reflections	6341 [R(int) = 0.0448]	
Completeness to theta = 27.10°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9841 and 0.9714	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6341 / 0 / 531	
Goodness-of-fit on F ²	1.030	
Final R indices [I > 2σ(I) = 4540 data]	R1 = 0.0389, wR2 = 0.0867	
R indices (all data; 0.78 Å)	R1 = 0.0674, wR2 = 0.1033	
Largest diff. peak and hole	0.270 and -0.204 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6740(1)	382(1)	6560(1)	23(1)
O(2)	5715(1)	-77(1)	8475(1)	25(1)
O(3)	5891(1)	-1330(1)	9453(1)	20(1)
C(1)	8537(1)	341(1)	7376(1)	27(1)
C(2)	7293(1)	375(1)	7581(1)	20(1)
C(3)	6844(1)	-253(1)	8201(1)	19(1)
C(4)	7502(1)	-554(1)	9159(1)	16(1)
C(5)	7092(1)	-1323(1)	9329(1)	17(1)
C(6)	7357(1)	-1843(1)	8446(1)	20(1)
C(7)	7007(2)	-2587(1)	8749(2)	29(1)
C(8)	8594(1)	-1831(1)	8167(2)	28(1)
C(9)	7460(1)	-131(1)	10200(1)	18(1)
C(10)	8314(1)	-419(1)	11017(1)	26(1)
C(11)	8306(2)	-18(1)	12058(1)	26(1)
C(12)	8524(2)	759(1)	11892(1)	29(1)
C(13)	7674(2)	1056(1)	11107(1)	31(1)
C(14)	7666(2)	657(1)	10062(1)	27(1)
O(4)	4617(1)	1205(1)	8475(1)	23(1)
O(5)	4408(1)	554(1)	6589(1)	21(1)
O(6)	2751(1)	450(1)	5171(1)	24(1)
C(15)	3925(1)	2295(1)	7857(1)	23(1)
C(16)	4494(1)	1618(1)	7537(1)	18(1)
C(17)	3818(1)	1206(1)	6713(1)	18(1)
C(18)	3594(1)	1578(1)	5653(1)	16(1)
C(19)	2633(1)	1197(1)	5032(1)	19(1)
C(20)	1461(1)	1438(1)	5372(1)	26(1)
C(21)	536(2)	974(1)	4897(2)	39(1)
C(22)	1248(2)	2200(1)	5057(2)	37(1)
C(23)	4646(1)	1731(1)	4993(1)	18(1)
C(24)	4436(1)	2381(1)	4297(1)	22(1)
C(25)	5444(1)	2574(1)	3633(1)	27(1)

C(26)	5838(1)	1951(1)	2981(1)	26(1)
C(27)	6081(1)	1319(1)	3679(1)	25(1)
C(28)	5056(1)	1116(1)	4317(1)	21(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **10**.

O(1)-C(2)	1.4412(17)
O(2)-C(3)	1.4356(17)
O(3)-C(5)	1.4426(17)
C(1)-C(2)	1.511(2)
C(2)-C(3)	1.534(2)
C(3)-C(4)	1.5439(19)
C(4)-C(9)	1.5488(19)
C(4)-C(5)	1.5592(19)
C(5)-C(6)	1.5344(19)
C(6)-C(8)	1.524(2)
C(6)-C(7)	1.528(2)
C(9)-C(14)	1.532(2)
C(9)-C(10)	1.537(2)
C(10)-C(11)	1.527(2)
C(11)-C(12)	1.518(2)
C(12)-C(13)	1.514(2)
C(13)-C(14)	1.529(2)
O(4)-C(16)	1.4314(17)
O(5)-C(17)	1.4364(17)
O(6)-C(19)	1.4382(17)
C(15)-C(16)	1.516(2)
C(16)-C(17)	1.524(2)
C(17)-C(18)	1.5395(19)
C(18)-C(23)	1.5497(19)
C(18)-C(19)	1.5559(19)
C(19)-C(20)	1.541(2)
C(20)-C(22)	1.524(3)
C(20)-C(21)	1.526(2)
C(23)-C(28)	1.537(2)
C(23)-C(24)	1.538(2)
C(24)-C(25)	1.527(2)
C(25)-C(26)	1.526(2)
C(26)-C(27)	1.518(2)
C(27)-C(28)	1.530(2)

O(1)-C(2)-C(1)	106.04(12)
O(1)-C(2)-C(3)	108.12(12)
C(1)-C(2)-C(3)	114.21(13)
O(2)-C(3)-C(2)	106.41(11)
O(2)-C(3)-C(4)	110.93(11)
C(2)-C(3)-C(4)	121.15(12)
C(3)-C(4)-C(9)	116.97(12)
C(3)-C(4)-C(5)	107.63(11)
C(9)-C(4)-C(5)	110.69(11)
O(3)-C(5)-C(6)	107.12(11)
O(3)-C(5)-C(4)	109.82(11)
C(6)-C(5)-C(4)	115.73(12)
C(8)-C(6)-C(7)	110.07(13)
C(8)-C(6)-C(5)	112.15(12)
C(7)-C(6)-C(5)	110.62(13)
C(14)-C(9)-C(10)	108.69(13)
C(14)-C(9)-C(4)	113.79(12)
C(10)-C(9)-C(4)	110.92(12)
C(11)-C(10)-C(9)	112.92(13)
C(12)-C(11)-C(10)	111.28(14)
C(13)-C(12)-C(11)	109.93(14)
C(12)-C(13)-C(14)	112.19(15)
C(13)-C(14)-C(9)	112.63(13)
O(4)-C(16)-C(15)	106.37(12)
O(4)-C(16)-C(17)	109.34(12)
C(15)-C(16)-C(17)	112.87(12)
O(5)-C(17)-C(16)	105.50(11)
O(5)-C(17)-C(18)	112.23(11)
C(16)-C(17)-C(18)	116.21(12)
C(17)-C(18)-C(23)	115.65(11)
C(17)-C(18)-C(19)	109.80(11)
C(23)-C(18)-C(19)	114.05(11)
O(6)-C(19)-C(20)	110.27(12)
O(6)-C(19)-C(18)	109.29(11)
C(20)-C(19)-C(18)	112.26(12)

C(22)-C(20)-C(21)	109.43(15)
C(22)-C(20)-C(19)	110.91(14)
C(21)-C(20)-C(19)	111.50(14)
C(28)-C(23)-C(24)	109.95(12)
C(28)-C(23)-C(18)	115.51(12)
C(24)-C(23)-C(18)	109.79(12)
C(25)-C(24)-C(23)	113.04(13)
C(26)-C(25)-C(24)	111.60(13)
C(27)-C(26)-C(25)	110.80(13)
C(26)-C(27)-C(28)	111.43(13)
C(27)-C(28)-C(23)	111.78(13)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	29(1)	25(1)	16(1)	2(1)	0(1)	3(1)
O(2)	20(1)	25(1)	30(1)	11(1)	1(1)	3(1)
O(3)	21(1)	24(1)	16(1)	0(1)	3(1)	-1(1)
C(1)	30(1)	31(1)	21(1)	5(1)	4(1)	-1(1)
C(2)	27(1)	19(1)	15(1)	1(1)	1(1)	1(1)
C(3)	22(1)	18(1)	17(1)	0(1)	0(1)	2(1)
C(4)	17(1)	16(1)	16(1)	-1(1)	1(1)	2(1)
C(5)	19(1)	16(1)	17(1)	1(1)	-1(1)	1(1)
C(6)	24(1)	17(1)	19(1)	-2(1)	-1(1)	2(1)
C(7)	37(1)	18(1)	33(1)	-3(1)	3(1)	-1(1)
C(8)	30(1)	22(1)	33(1)	-4(1)	7(1)	5(1)
C(9)	20(1)	17(1)	16(1)	-1(1)	1(1)	1(1)
C(10)	30(1)	23(1)	24(1)	-4(1)	-7(1)	4(1)
C(11)	32(1)	25(1)	19(1)	-1(1)	-6(1)	-3(1)
C(12)	38(1)	27(1)	21(1)	-5(1)	2(1)	-13(1)
C(13)	55(1)	16(1)	21(1)	-3(1)	0(1)	-1(1)
C(14)	43(1)	19(1)	19(1)	-1(1)	2(1)	-2(1)
O(4)	32(1)	21(1)	14(1)	2(1)	1(1)	7(1)
O(5)	30(1)	15(1)	19(1)	-2(1)	-3(1)	4(1)
O(6)	32(1)	18(1)	21(1)	-3(1)	2(1)	-4(1)
C(15)	28(1)	21(1)	20(1)	-4(1)	-3(1)	3(1)
C(16)	21(1)	19(1)	14(1)	2(1)	1(1)	1(1)
C(17)	20(1)	15(1)	19(1)	1(1)	2(1)	2(1)
C(18)	20(1)	15(1)	15(1)	-2(1)	1(1)	2(1)
C(19)	21(1)	20(1)	17(1)	0(1)	1(1)	-2(1)
C(20)	21(1)	35(1)	21(1)	-4(1)	2(1)	0(1)
C(21)	21(1)	44(1)	51(1)	-6(1)	3(1)	-6(1)
C(22)	25(1)	36(1)	49(1)	-6(1)	-5(1)	8(1)
C(23)	19(1)	19(1)	16(1)	0(1)	0(1)	-1(1)
C(24)	28(1)	19(1)	19(1)	0(1)	2(1)	-1(1)
C(25)	33(1)	24(1)	24(1)	2(1)	3(1)	-8(1)

C(26)	26(1)	31(1)	20(1)	-3(1)	6(1)	-9(1)
C(27)	22(1)	30(1)	23(1)	-5(1)	5(1)	-1(1)
C(28)	23(1)	20(1)	20(1)	0(1)	2(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **10**.

	x	y	z	U(eq)
H(1)	6046(17)	436(10)	6630(15)	34(5)
H(2)	5472(17)	-435(11)	8784(17)	48(6)
H(3)	5761(14)	-1313(9)	10092(15)	28(5)
H(1A)	8994(15)	396(9)	8036(14)	31(5)
H(1B)	8750(15)	-103(10)	7045(14)	34(5)
H(1C)	8743(15)	706(10)	6889(15)	36(5)
H(2A)	7087(13)	806(8)	7939(12)	17(4)
H(3A)	6803(12)	-637(8)	7664(12)	17(4)
H(4A)	8291(13)	-578(7)	8974(11)	11(3)
H(5A)	7454(12)	-1509(8)	9980(12)	14(4)
H(6A)	6912(13)	-1699(8)	7825(13)	22(4)
H(7A)	6221(18)	-2599(10)	8885(15)	44(6)
H(7B)	7412(16)	-2741(10)	9385(16)	41(5)
H(7C)	7149(16)	-2932(11)	8149(16)	44(5)
H(8A)	8836(16)	-1385(11)	7824(15)	42(5)
H(8B)	8751(16)	-2207(11)	7668(15)	41(5)
H(8C)	9079(15)	-1893(9)	8790(15)	35(5)
H(9A)	6713(14)	-181(8)	10492(12)	23(4)
H(10A)	9050(16)	-374(9)	10700(14)	33(5)
H(10B)	8184(15)	-913(10)	11138(14)	36(5)
H(11A)	7551(15)	-70(9)	12372(13)	26(4)
H(11B)	8858(16)	-217(10)	12566(15)	35(5)
H(12A)	8512(15)	999(10)	12570(15)	35(5)
H(12B)	9287(16)	822(10)	11623(14)	38(5)
H(13A)	6903(15)	1028(9)	11389(13)	29(5)
H(13B)	7836(15)	1557(11)	10975(15)	40(5)
H(14A)	8391(16)	731(9)	9727(14)	34(5)
H(14B)	7098(15)	857(9)	9606(14)	30(5)
H(4)	4907(17)	841(11)	8339(15)	37(6)
H(5)	4036(18)	339(11)	6157(17)	44(6)

H(6)	2843(17)	239(11)	4570(17)	48(6)
H(15A)	3914(14)	2641(9)	7278(14)	31(5)
H(15B)	4337(15)	2505(9)	8464(14)	31(5)
H(15C)	3160(16)	2194(9)	8069(13)	31(5)
H(16A)	5245(13)	1723(8)	7264(12)	16(4)
H(17A)	3074(12)	1101(7)	7035(11)	11(4)
H(18A)	3299(12)	2024(8)	5847(11)	13(4)
H(19A)	2689(12)	1308(7)	4264(12)	12(4)
H(20A)	1436(14)	1393(9)	6160(14)	29(4)
H(21A)	669(17)	501(11)	5109(16)	46(6)
H(21B)	524(16)	1011(10)	4097(17)	41(5)
H(21C)	-195(18)	1146(11)	5128(16)	47(6)
H(22A)	498(18)	2348(10)	5262(15)	46(6)
H(22B)	1315(18)	2236(11)	4282(19)	57(7)
H(22C)	1780(20)	2532(12)	5366(18)	65(7)
H(23A)	5274(13)	1861(8)	5511(12)	16(4)
H(24B)	3779(15)	2289(9)	3819(14)	31(5)
H(24A)	4247(14)	2781(9)	4749(13)	27(4)
H(25A)	6062(15)	2737(9)	4113(13)	28(4)
H(25B)	5248(15)	2990(10)	3173(14)	35(5)
H(26A)	5240(14)	1841(9)	2440(14)	28(4)
H(26B)	6491(15)	2084(9)	2581(14)	31(5)
H(27A)	6329(14)	920(9)	3246(13)	29(4)
H(27B)	6715(14)	1425(8)	4169(13)	22(4)
H(28A)	4447(15)	964(9)	3815(14)	30(5)
H(28B)	5189(14)	712(10)	4766(14)	30(5)

Table 6. Torsion angles [°] for **10**.

O(1)-C(2)-C(3)-O(2)	-71.89(14)
C(1)-C(2)-C(3)-O(2)	170.35(12)
O(1)-C(2)-C(3)-C(4)	160.29(12)
C(1)-C(2)-C(3)-C(4)	42.52(19)
O(2)-C(3)-C(4)-C(9)	-49.65(16)
C(2)-C(3)-C(4)-C(9)	76.14(17)
O(2)-C(3)-C(4)-C(5)	75.64(14)
C(2)-C(3)-C(4)-C(5)	-158.58(12)
C(3)-C(4)-C(5)-O(3)	-56.06(14)
C(9)-C(4)-C(5)-O(3)	72.90(14)
C(3)-C(4)-C(5)-C(6)	65.34(15)
C(9)-C(4)-C(5)-C(6)	-165.71(12)
O(3)-C(5)-C(6)-C(8)	174.51(12)
C(4)-C(5)-C(6)-C(8)	51.67(17)
O(3)-C(5)-C(6)-C(7)	-62.18(15)
C(4)-C(5)-C(6)-C(7)	174.98(13)
C(3)-C(4)-C(9)-C(14)	-46.87(18)
C(5)-C(4)-C(9)-C(14)	-170.61(13)
C(3)-C(4)-C(9)-C(10)	-169.79(13)
C(5)-C(4)-C(9)-C(10)	66.47(15)
C(14)-C(9)-C(10)-C(11)	54.09(18)
C(4)-C(9)-C(10)-C(11)	179.92(13)
C(9)-C(10)-C(11)-C(12)	-56.85(19)
C(10)-C(11)-C(12)-C(13)	55.96(19)
C(11)-C(12)-C(13)-C(14)	-55.8(2)
C(12)-C(13)-C(14)-C(9)	55.9(2)
C(10)-C(9)-C(14)-C(13)	-53.20(19)
C(4)-C(9)-C(14)-C(13)	-177.34(14)
O(4)-C(16)-C(17)-O(5)	-55.66(14)
C(15)-C(16)-C(17)-O(5)	-173.84(12)
O(4)-C(16)-C(17)-C(18)	179.30(11)
C(15)-C(16)-C(17)-C(18)	61.12(17)
O(5)-C(17)-C(18)-C(23)	-56.17(16)
C(16)-C(17)-C(18)-C(23)	65.36(16)

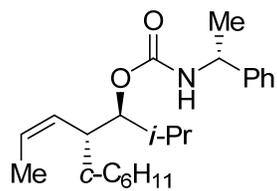
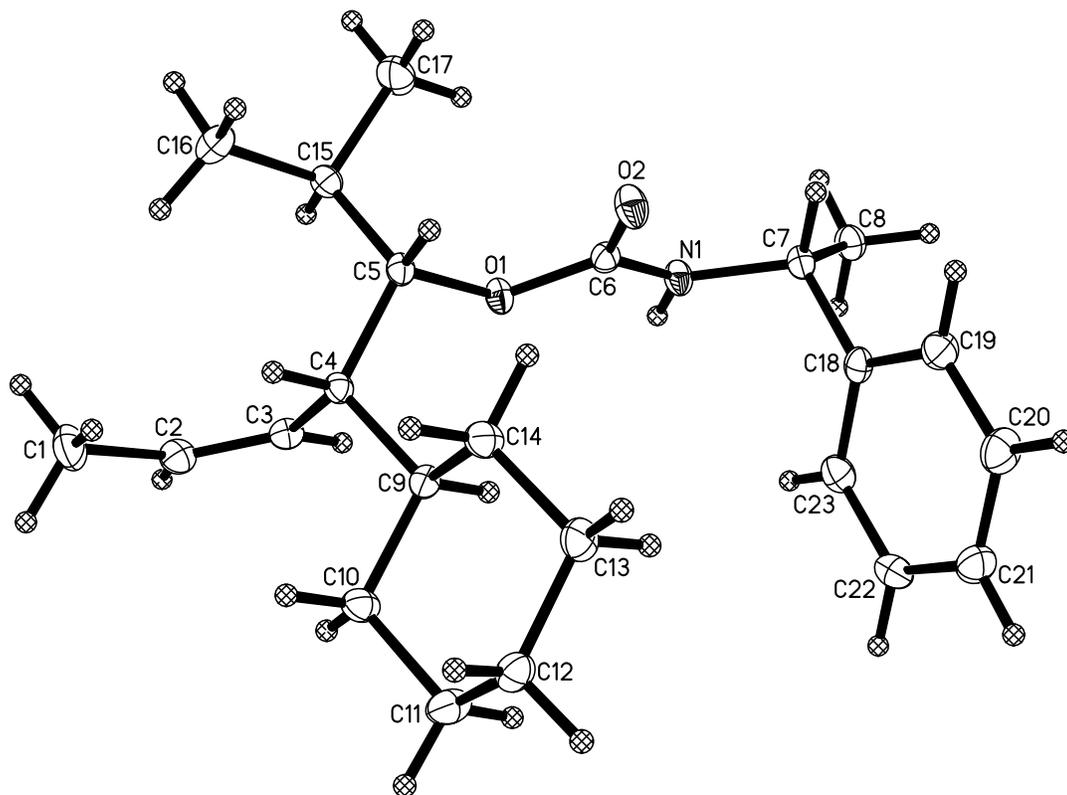
O(5)-C(17)-C(18)-C(19)	74.62(14)
C(16)-C(17)-C(18)-C(19)	-163.84(12)
C(17)-C(18)-C(19)-O(6)	-39.03(15)
C(23)-C(18)-C(19)-O(6)	92.61(14)
C(17)-C(18)-C(19)-C(20)	83.65(15)
C(23)-C(18)-C(19)-C(20)	-144.71(13)
O(6)-C(19)-C(20)-C(22)	-170.34(13)
C(18)-C(19)-C(20)-C(22)	67.54(17)
O(6)-C(19)-C(20)-C(21)	-48.11(18)
C(18)-C(19)-C(20)-C(21)	-170.23(14)
C(17)-C(18)-C(23)-C(28)	82.93(15)
C(19)-C(18)-C(23)-C(28)	-45.81(17)
C(17)-C(18)-C(23)-C(24)	-152.08(12)
C(19)-C(18)-C(23)-C(24)	79.18(15)
C(28)-C(23)-C(24)-C(25)	-52.80(17)
C(18)-C(23)-C(24)-C(25)	179.07(12)
C(23)-C(24)-C(25)-C(26)	53.80(18)
C(24)-C(25)-C(26)-C(27)	-54.77(18)
C(25)-C(26)-C(27)-C(28)	56.56(18)
C(26)-C(27)-C(28)-C(23)	-56.99(17)
C(24)-C(23)-C(28)-C(27)	53.98(17)
C(18)-C(23)-C(28)-C(27)	178.89(12)

C. X-ray Data Collection, Structure Solution and Refinement for Carbamate (+)-13.

A colorless crystal of approximate dimensions 0.12 x 0.16 x 0.33 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2¹ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups $P2_1$ and $P2_1/m$. It was later determined that the noncentrosymmetric space group $P2_1$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined (x, y, z and U_{iso}) or were included using a riding model (mixed hydrogen atom treatment).

At convergence, $wR2 = 0.0798$ and $Goof = 1.045$ for 360 variables refined against 4982 data (0.75\AA), $R1 = 0.0303$ for those 4780 data with $I > 2.0\sigma(I)$. The absolute structure could not be assigned by inversion of the model or by refinement of the Flack parameter⁶.



(+)-13

References.

11. APEX2 Version 2008.3-0, or (Version 2.2-0) Bruker AXS, Inc.; Madison, WI 2008.
 12. SAINT Version 7.53a, Bruker AXS, Inc.; Madison, WI 2007.
 13. Sheldrick, G. M. SADABS, Version 2007/4, Bruker AXS, Inc.; Madison, WI 2007.
 14. Sheldrick, G. M. SHELXTL, Version 6.12, Bruker AXS, Inc.; Madison, WI 2001.
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 16. Flack, H. D. Acta. Cryst., A39, 876-881, 1983.
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Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

Table 1. Crystal data and structure refinement for (+)-**13**.

Identification code	kaw132 (Kay Buchner)	
Empirical formula	C ₂₃ H ₃₅ N O ₂	
Formula weight	357.52	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁	
Unit cell dimensions	a = 5.2823(2) Å	α = 90°.
	b = 15.4651(6) Å	β = 100.7230(4)°.
	c = 13.0625(5) Å	γ = 90°.
Volume	1048.46(7) Å ³	
Z	2	
Density (calculated)	1.132 Mg/m ³	
Absorption coefficient	0.071 mm ⁻¹	
F(000)	392	
Crystal color	colorless	
Crystal size	0.33 x 0.16 x 0.12 mm ³	
Theta range for data collection	1.59 to 28.30°	
Index ranges	-6 ≤ h ≤ 7, -20 ≤ k ≤ 20, -17 ≤ l ≤ 17	
Reflections collected	12542	
Independent reflections	4982 [R(int) = 0.0171]	
Completeness to theta = 28.30°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9914 and 0.9772	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4982 / 1 / 360	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I) = 4780 data]	R1 = 0.0303, wR2 = 0.0786	
R indices (all data, 0.75 Å)	R1 = 0.0319, wR2 = 0.0798	
Largest diff. peak and hole	0.227 and -0.184 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-**13**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5909(1)	8222(1)	2377(1)	15(1)
O(2)	9393(1)	8125(1)	3698(1)	19(1)
N(1)	5298(2)	8004(1)	3998(1)	15(1)
C(1)	5308(2)	9270(1)	-1485(1)	25(1)
C(2)	3584(2)	9114(1)	-713(1)	18(1)
C(3)	4255(2)	9056(1)	319(1)	14(1)
C(4)	6930(2)	9110(1)	978(1)	12(1)
C(5)	7577(2)	8264(1)	1599(1)	13(1)
C(6)	7068(2)	8121(1)	3386(1)	14(1)
C(7)	6085(2)	8038(1)	5134(1)	14(1)
C(8)	4161(2)	7536(1)	5645(1)	18(1)
C(9)	7237(2)	9919(1)	1692(1)	14(1)
C(10)	6532(2)	10749(1)	1061(1)	18(1)
C(11)	6766(2)	11553(1)	1761(1)	21(1)
C(12)	9446(2)	11632(1)	2435(1)	18(1)
C(13)	10204(2)	10806(1)	3050(1)	20(1)
C(14)	9967(2)	10015(1)	2332(1)	18(1)
C(15)	7170(2)	7431(1)	960(1)	15(1)
C(16)	8860(2)	7418(1)	130(1)	20(1)
C(17)	7762(3)	6639(1)	1659(1)	26(1)
C(18)	6364(2)	8965(1)	5532(1)	15(1)
C(19)	8588(2)	9222(1)	6211(1)	20(1)
C(20)	8830(2)	10064(1)	6596(1)	23(1)
C(21)	6847(2)	10654(1)	6311(1)	22(1)
C(22)	4601(2)	10397(1)	5640(1)	21(1)
C(23)	4372(2)	9558(1)	5255(1)	19(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for (+)-**13**.

O(1)-C(6)	1.3554(13)
O(1)-C(5)	1.4645(12)
O(2)-C(6)	1.2201(13)
N(1)-C(6)	1.3505(13)
N(1)-C(7)	1.4661(13)
C(1)-C(2)	1.4983(16)
C(2)-C(3)	1.3319(15)
C(3)-C(4)	1.5142(14)
C(4)-C(5)	1.5440(14)
C(4)-C(9)	1.5505(14)
C(5)-C(15)	1.5284(15)
C(7)-C(18)	1.5225(15)
C(7)-C(8)	1.5273(14)
C(9)-C(14)	1.5339(15)
C(9)-C(10)	1.5345(15)
C(10)-C(11)	1.5343(16)
C(11)-C(12)	1.5267(16)
C(12)-C(13)	1.5237(16)
C(13)-C(14)	1.5318(16)
C(15)-C(17)	1.5253(16)
C(15)-C(16)	1.5270(15)
C(18)-C(19)	1.3917(15)
C(18)-C(23)	1.3920(16)
C(19)-C(20)	1.3929(17)
C(20)-C(21)	1.3868(18)
C(21)-C(22)	1.3946(18)
C(22)-C(23)	1.3887(17)
<hr/>	
C(6)-O(1)-C(5)	117.30(8)
C(6)-N(1)-C(7)	119.84(9)
C(3)-C(2)-C(1)	127.68(10)
C(2)-C(3)-C(4)	128.03(10)
C(3)-C(4)-C(5)	110.10(8)
C(3)-C(4)-C(9)	111.64(8)

C(5)-C(4)-C(9)	112.26(8)
O(1)-C(5)-C(15)	107.44(8)
O(1)-C(5)-C(4)	107.39(8)
C(15)-C(5)-C(4)	115.62(8)
O(2)-C(6)-N(1)	124.60(10)
O(2)-C(6)-O(1)	124.63(9)
N(1)-C(6)-O(1)	110.77(9)
N(1)-C(7)-C(18)	111.75(8)
N(1)-C(7)-C(8)	109.74(9)
C(18)-C(7)-C(8)	111.07(9)
C(14)-C(9)-C(10)	108.74(9)
C(14)-C(9)-C(4)	112.86(8)
C(10)-C(9)-C(4)	111.33(9)
C(11)-C(10)-C(9)	111.93(9)
C(12)-C(11)-C(10)	111.85(9)
C(13)-C(12)-C(11)	111.17(10)
C(12)-C(13)-C(14)	111.36(9)
C(13)-C(14)-C(9)	111.85(9)
C(17)-C(15)-C(16)	109.39(10)
C(17)-C(15)-C(5)	111.00(9)
C(16)-C(15)-C(5)	110.95(9)
C(19)-C(18)-C(23)	118.99(10)
C(19)-C(18)-C(7)	120.22(10)
C(23)-C(18)-C(7)	120.75(10)
C(18)-C(19)-C(20)	120.49(11)
C(21)-C(20)-C(19)	120.24(12)
C(20)-C(21)-C(22)	119.53(11)
C(23)-C(22)-C(21)	120.04(11)
C(22)-C(23)-C(18)	120.70(11)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-**13**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	13(1)	20(1)	11(1)	2(1)	3(1)	-1(1)
O(2)	14(1)	28(1)	14(1)	2(1)	2(1)	-1(1)
N(1)	12(1)	20(1)	12(1)	0(1)	1(1)	-1(1)
C(1)	24(1)	35(1)	15(1)	4(1)	2(1)	5(1)
C(2)	14(1)	20(1)	18(1)	-1(1)	-1(1)	2(1)
C(3)	12(1)	14(1)	17(1)	-1(1)	2(1)	0(1)
C(4)	12(1)	14(1)	11(1)	1(1)	1(1)	1(1)
C(5)	12(1)	16(1)	11(1)	0(1)	2(1)	0(1)
C(6)	17(1)	12(1)	12(1)	-1(1)	3(1)	-1(1)
C(7)	15(1)	17(1)	11(1)	1(1)	2(1)	0(1)
C(8)	19(1)	19(1)	15(1)	2(1)	5(1)	-1(1)
C(9)	13(1)	15(1)	13(1)	-1(1)	3(1)	0(1)
C(10)	19(1)	15(1)	17(1)	0(1)	-2(1)	1(1)
C(11)	20(1)	16(1)	25(1)	-4(1)	0(1)	3(1)
C(12)	20(1)	16(1)	18(1)	-3(1)	3(1)	-2(1)
C(13)	22(1)	19(1)	16(1)	-2(1)	-2(1)	-3(1)
C(14)	17(1)	16(1)	17(1)	-1(1)	-3(1)	1(1)
C(15)	14(1)	15(1)	14(1)	1(1)	1(1)	0(1)
C(16)	21(1)	18(1)	23(1)	-5(1)	9(1)	-1(1)
C(17)	42(1)	15(1)	21(1)	2(1)	4(1)	0(1)
C(18)	17(1)	17(1)	11(1)	0(1)	5(1)	-2(1)
C(19)	17(1)	22(1)	19(1)	-2(1)	1(1)	2(1)
C(20)	20(1)	26(1)	23(1)	-6(1)	0(1)	-3(1)
C(21)	27(1)	16(1)	22(1)	-1(1)	5(1)	-2(1)
C(22)	23(1)	18(1)	20(1)	4(1)	2(1)	3(1)
C(23)	19(1)	21(1)	17(1)	2(1)	0(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (+)-**13**.

	x	y	z	U(eq)
H(1A)	4651	9760	-1932	37
H(1B)	5348	8752	-1914	37
H(1C)	7054	9401	-1113	37
H(7A)	7802	7749	5326	17
H(1)	3800(30)	8075(10)	3749(11)	16(3)
H(2)	1800(30)	9038(11)	-1025(12)	27(4)
H(3)	2930(30)	8946(9)	721(10)	14(3)
H(4)	8180(30)	9166(9)	516(11)	14(3)
H(5)	9310(30)	8259(9)	1957(10)	12(3)
H(8A)	4680(30)	7563(9)	6395(11)	14(3)
H(8B)	2420(30)	7812(10)	5478(12)	26(4)
H(8C)	4070(30)	6936(11)	5428(12)	22(4)
H(9)	6020(30)	9842(10)	2167(12)	17(3)
H(10A)	4830(30)	10718(11)	651(12)	24(4)
H(10B)	7720(30)	10804(11)	534(12)	28(4)
H(11A)	5500(30)	11509(11)	2222(13)	29(4)
H(11B)	6370(30)	12063(11)	1345(13)	27(4)
H(12A)	9490(30)	12135(10)	2919(12)	17(3)
H(12B)	10720(30)	11750(11)	2027(14)	29(4)
H(13A)	9120(30)	10721(11)	3581(12)	24(4)
H(13B)	11960(30)	10847(12)	3444(14)	34(4)
H(14A)	11150(30)	10090(10)	1808(13)	28(4)
H(14B)	10470(30)	9467(11)	2751(13)	26(4)
H(15)	5460(30)	7389(10)	648(11)	15(3)
H(16A)	8770(30)	6864(10)	-225(12)	21(4)
H(16B)	10660(40)	7486(13)	454(15)	42(5)
H(16C)	8390(30)	7860(11)	-394(13)	29(4)
H(17A)	7560(30)	6098(13)	1274(14)	38(5)
H(17B)	6570(30)	6600(12)	2177(14)	33(4)
H(17C)	9640(40)	6646(14)	2021(16)	47(5)

H(19)	9990(30)	8827(11)	6396(12)	24(4)
H(20)	10460(30)	10244(11)	7062(14)	31(4)
H(21)	6990(30)	11217(11)	6538(12)	22(4)
H(22)	3140(30)	10802(10)	5438(11)	21(4)
H(23)	2830(30)	9383(9)	4812(11)	17(3)

Table 6. Torsion angles [°] for (+)-**13**.

C(1)-C(2)-C(3)-C(4)	-1.62(19)
C(2)-C(3)-C(4)-C(5)	-119.92(12)
C(2)-C(3)-C(4)-C(9)	114.69(12)
C(6)-O(1)-C(5)-C(15)	109.91(10)
C(6)-O(1)-C(5)-C(4)	-125.11(9)
C(3)-C(4)-C(5)-O(1)	-68.43(10)
C(9)-C(4)-C(5)-O(1)	56.61(10)
C(3)-C(4)-C(5)-C(15)	51.47(11)
C(9)-C(4)-C(5)-C(15)	176.51(8)
C(7)-N(1)-C(6)-O(2)	11.90(16)
C(7)-N(1)-C(6)-O(1)	-168.93(9)
C(5)-O(1)-C(6)-O(2)	5.54(15)
C(5)-O(1)-C(6)-N(1)	-173.63(9)
C(6)-N(1)-C(7)-C(18)	79.78(12)
C(6)-N(1)-C(7)-C(8)	-156.55(10)
C(3)-C(4)-C(9)-C(14)	-177.30(9)
C(5)-C(4)-C(9)-C(14)	58.51(11)
C(3)-C(4)-C(9)-C(10)	-54.68(11)
C(5)-C(4)-C(9)-C(10)	-178.87(9)
C(14)-C(9)-C(10)-C(11)	-56.38(12)
C(4)-C(9)-C(10)-C(11)	178.66(9)
C(9)-C(10)-C(11)-C(12)	55.50(13)
C(10)-C(11)-C(12)-C(13)	-53.39(14)
C(11)-C(12)-C(13)-C(14)	54.03(13)
C(12)-C(13)-C(14)-C(9)	-57.07(13)
C(10)-C(9)-C(14)-C(13)	57.28(12)
C(4)-C(9)-C(14)-C(13)	-178.67(9)
O(1)-C(5)-C(15)-C(17)	-57.79(11)
C(4)-C(5)-C(15)-C(17)	-177.66(10)
O(1)-C(5)-C(15)-C(16)	-179.64(9)
C(4)-C(5)-C(15)-C(16)	60.49(12)
N(1)-C(7)-C(18)-C(19)	-129.94(10)
C(8)-C(7)-C(18)-C(19)	107.15(11)
N(1)-C(7)-C(18)-C(23)	52.42(13)

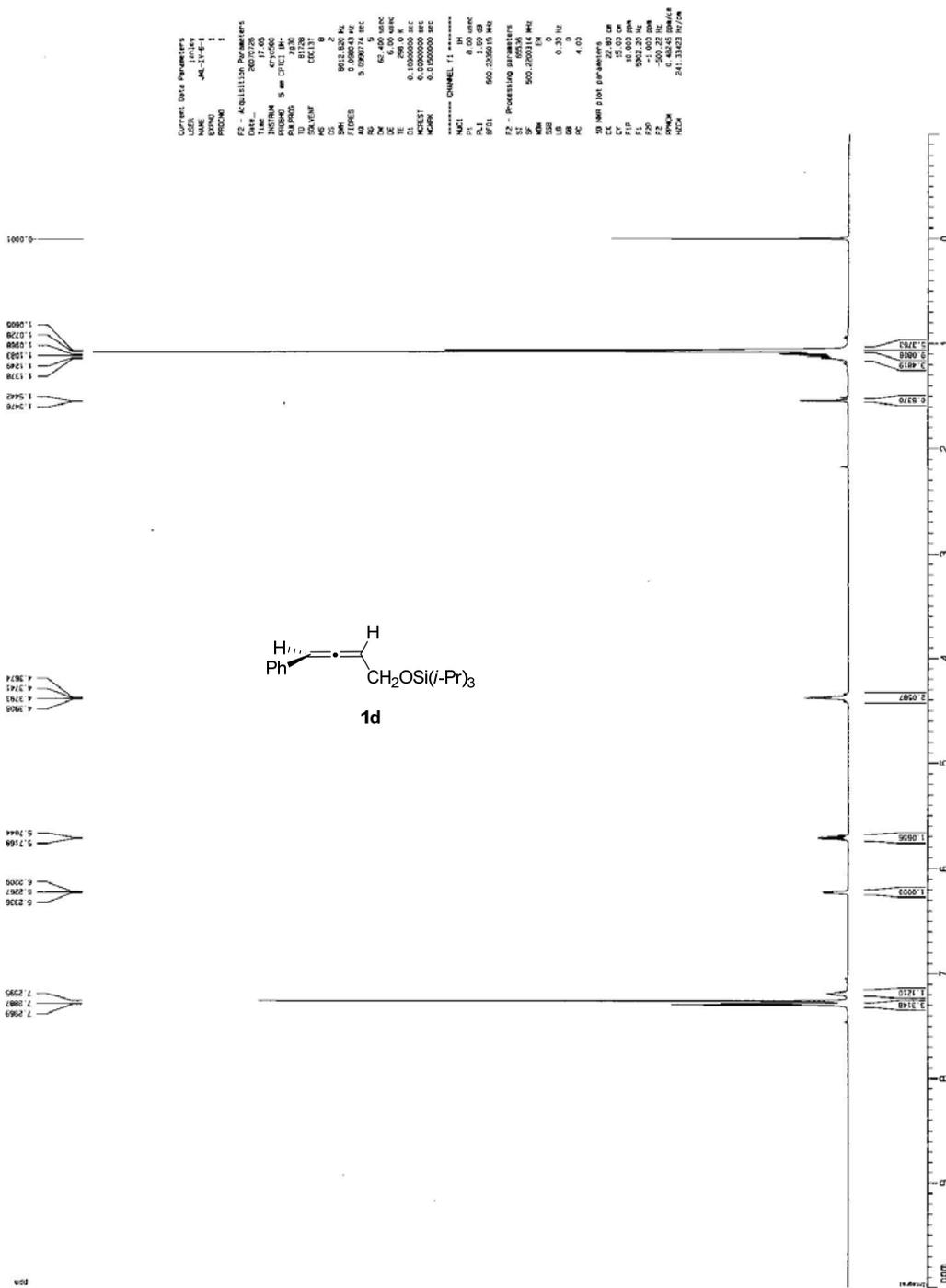
C(8)-C(7)-C(18)-C(23)	-70.49(12)
C(23)-C(18)-C(19)-C(20)	-0.85(16)
C(7)-C(18)-C(19)-C(20)	-178.53(10)
C(18)-C(19)-C(20)-C(21)	0.37(18)
C(19)-C(20)-C(21)-C(22)	0.35(19)
C(20)-C(21)-C(22)-C(23)	-0.57(18)
C(21)-C(22)-C(23)-C(18)	0.08(18)
C(19)-C(18)-C(23)-C(22)	0.63(16)
C(7)-C(18)-C(23)-C(22)	178.30(10)

References and Notes

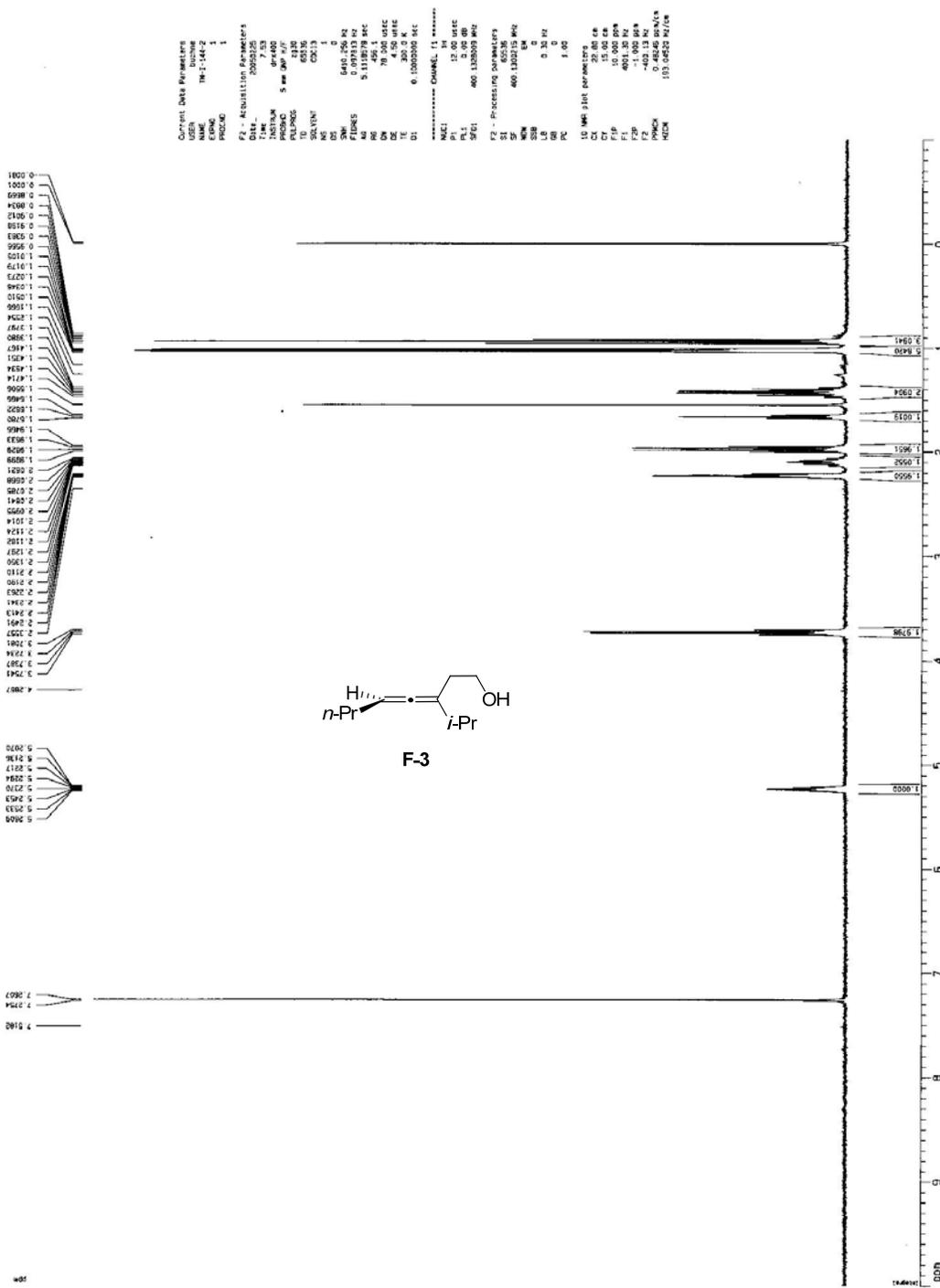
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- (17) The yields of each regioisomer were monitored closely by ¹H NMR spectroscopy vs. an internal standard. The yield of the major isomer remained constant while that of the minor isomer decreased, indicating decomposition and not isomerization of the minor isomer.
- (18) Carbonyl insertion with ketones and aldehydes tended to favor allylic transposition except in the case of silacyclopropane **3b**. Presumably, the exocyclic vinyl silane stabilizes the double bond which inhibits allylic transposition in favor of Si–C(sp²) bond cleavage.
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- (28) An apodization function was applied to the spectrum to resolve the splitting of this peak (MestRe-C 4.9.9.6; Gaussian 0.70 Hz, SineBell 0.00 Deg).
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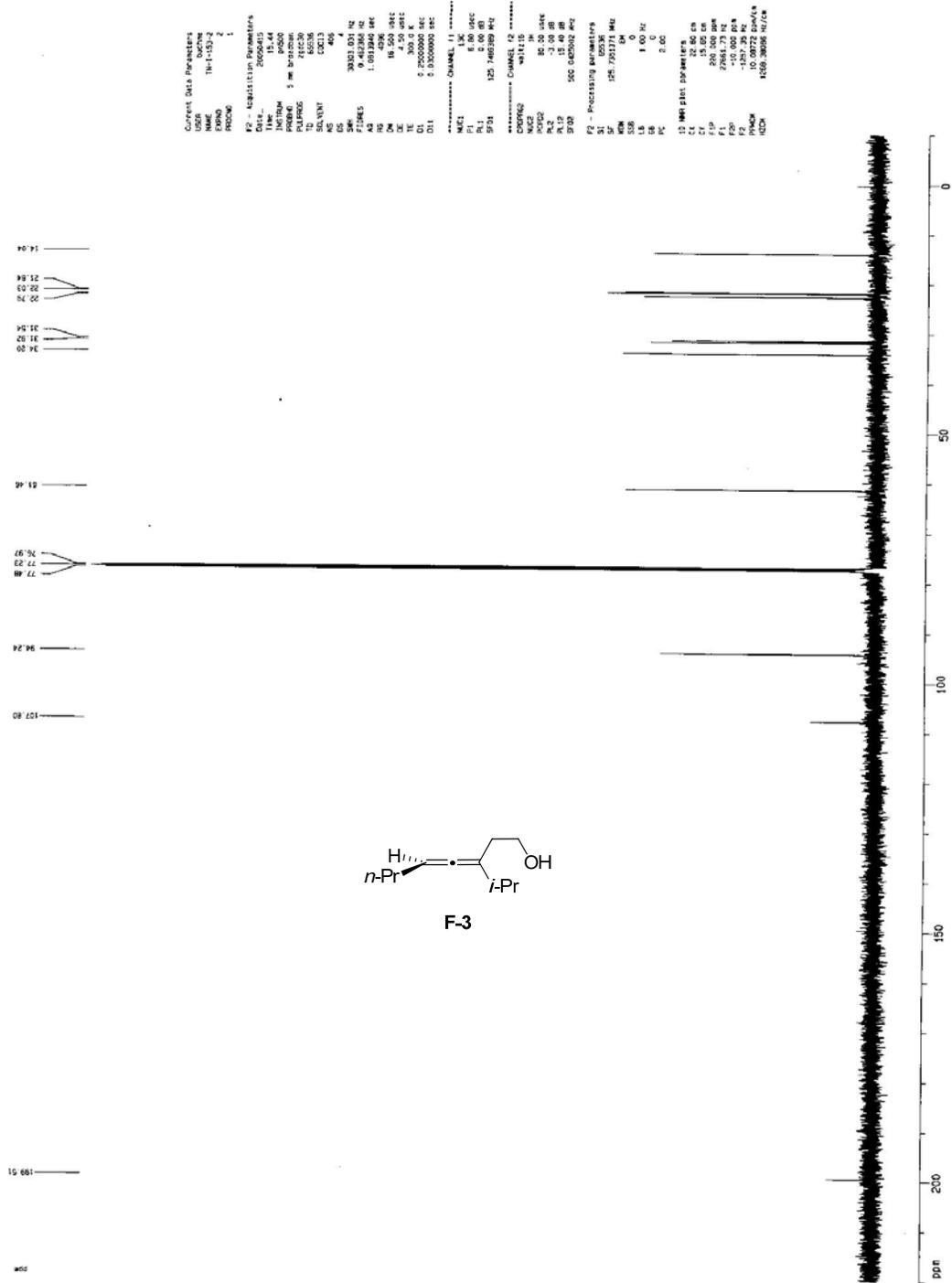
1d
1H spectrum



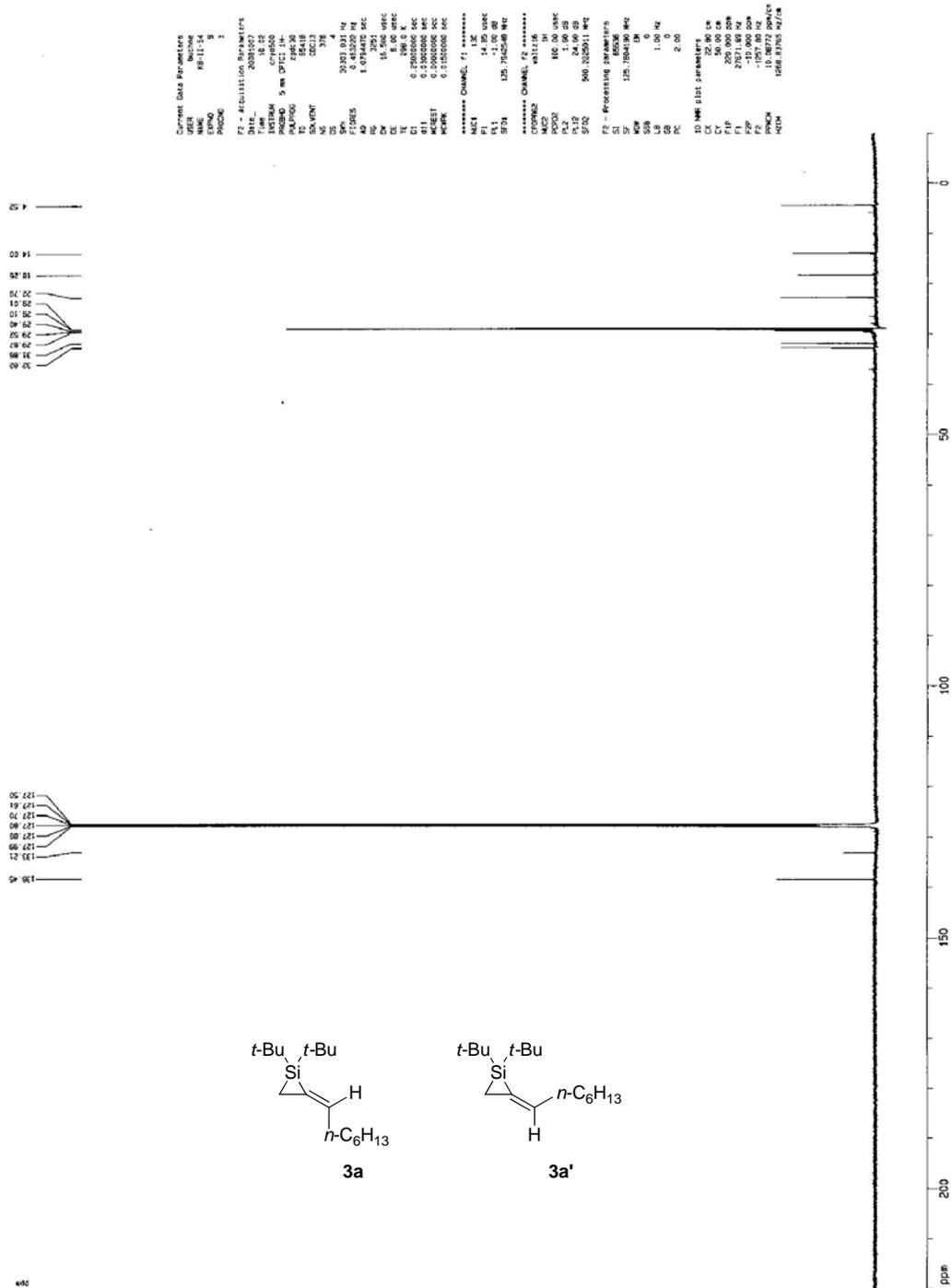
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¹H spectrum

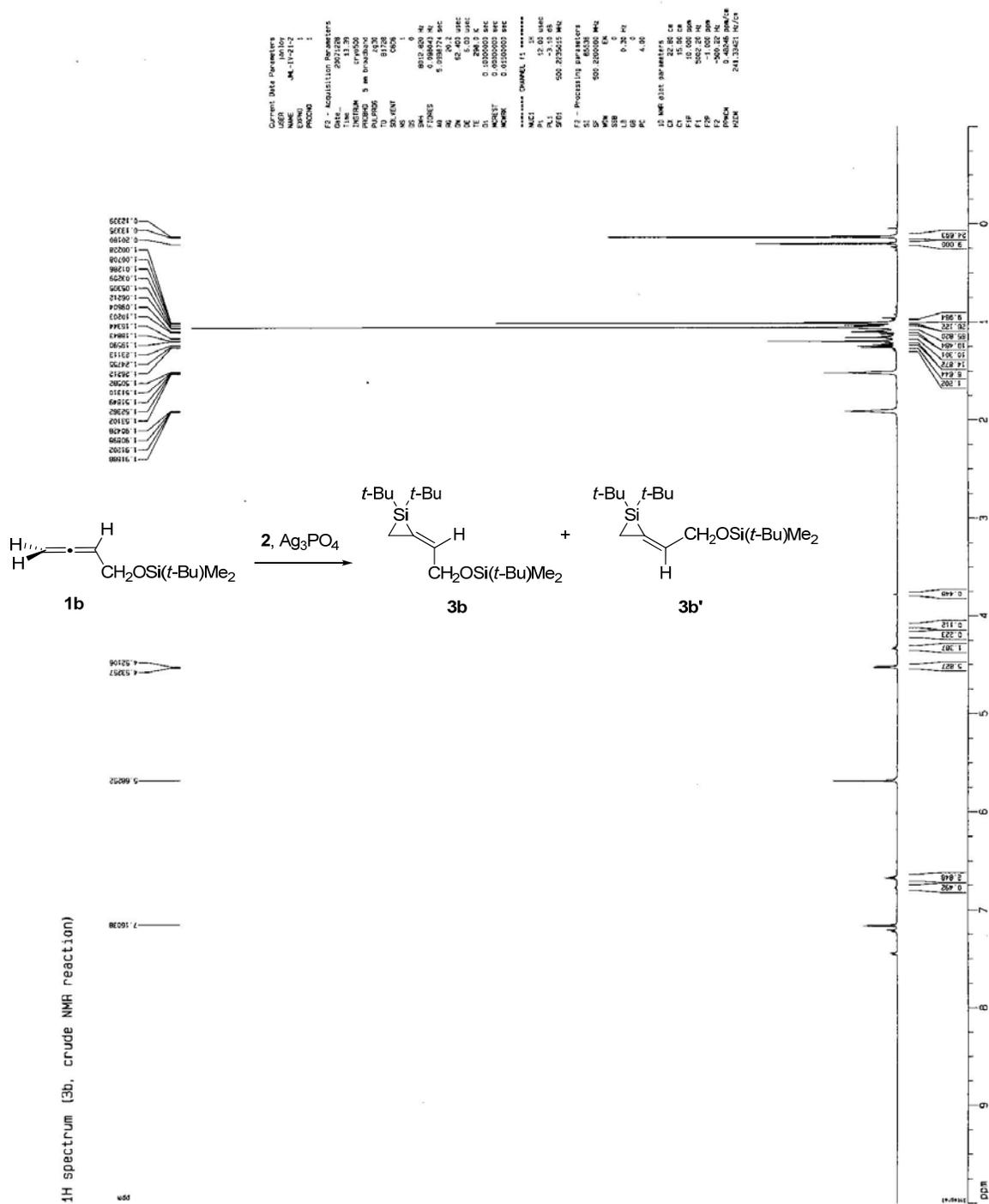


F-3
¹³C spectrum with ¹H decoupling

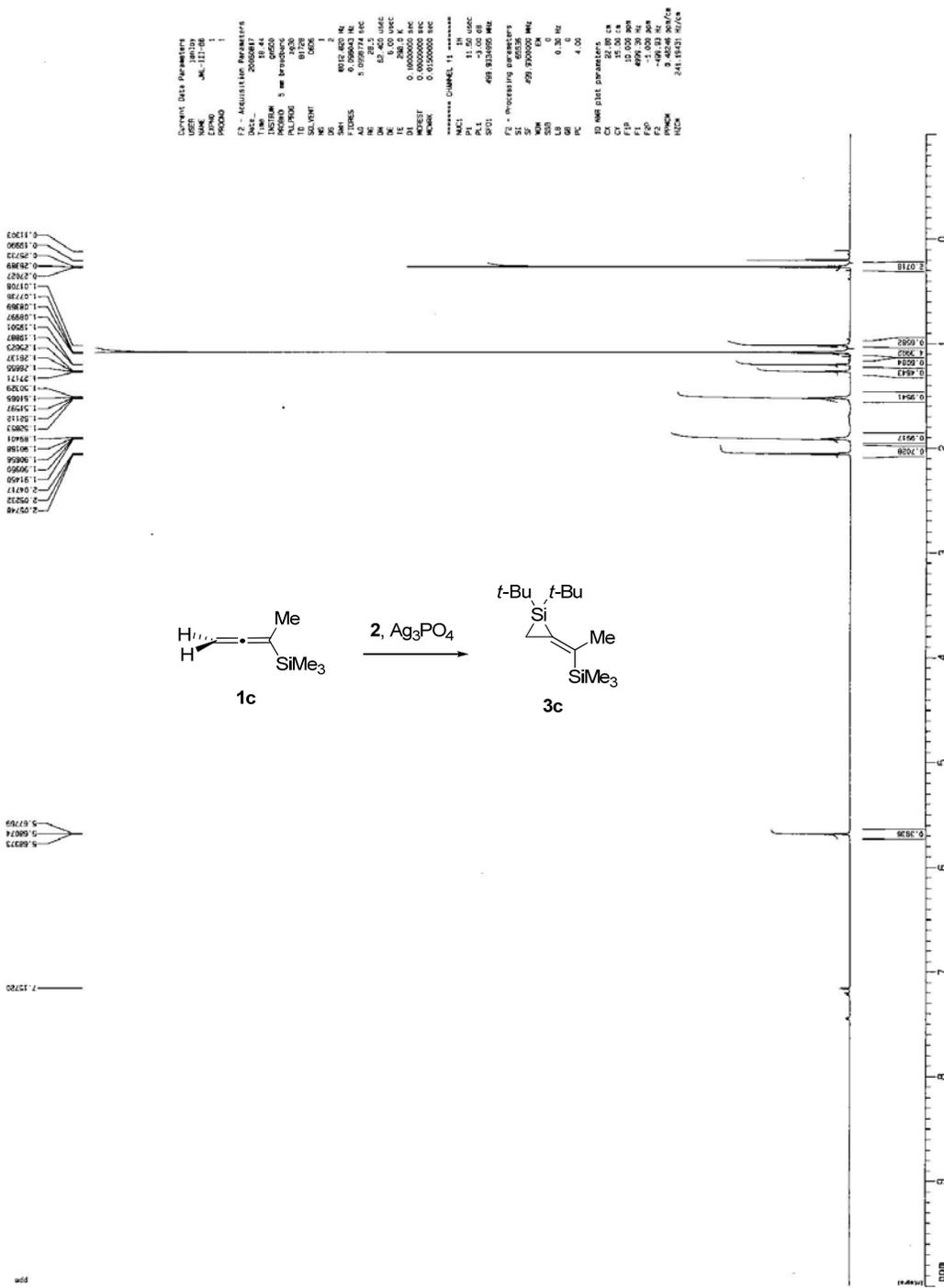


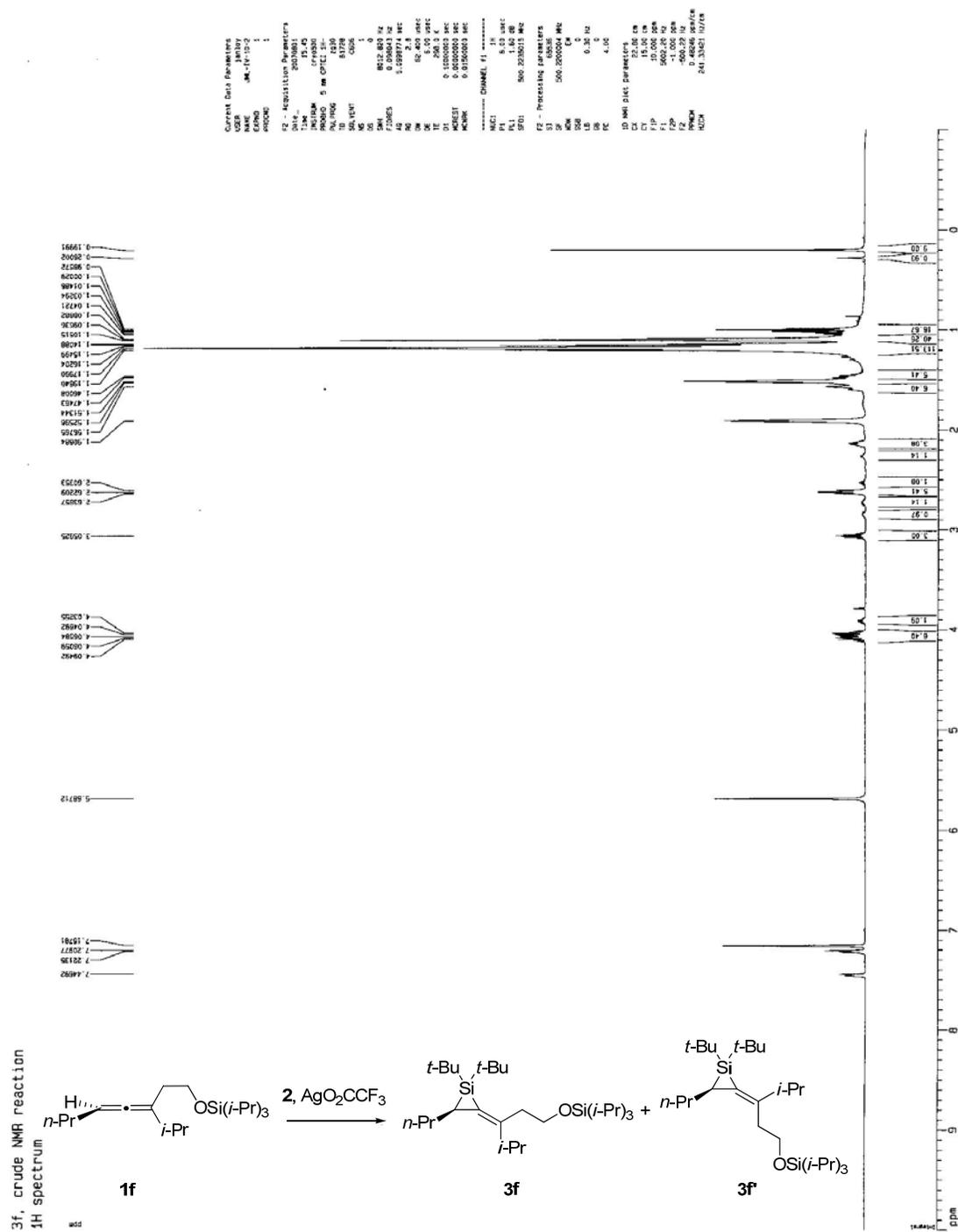
¹³C spectrum with ¹H decoupling (3a)



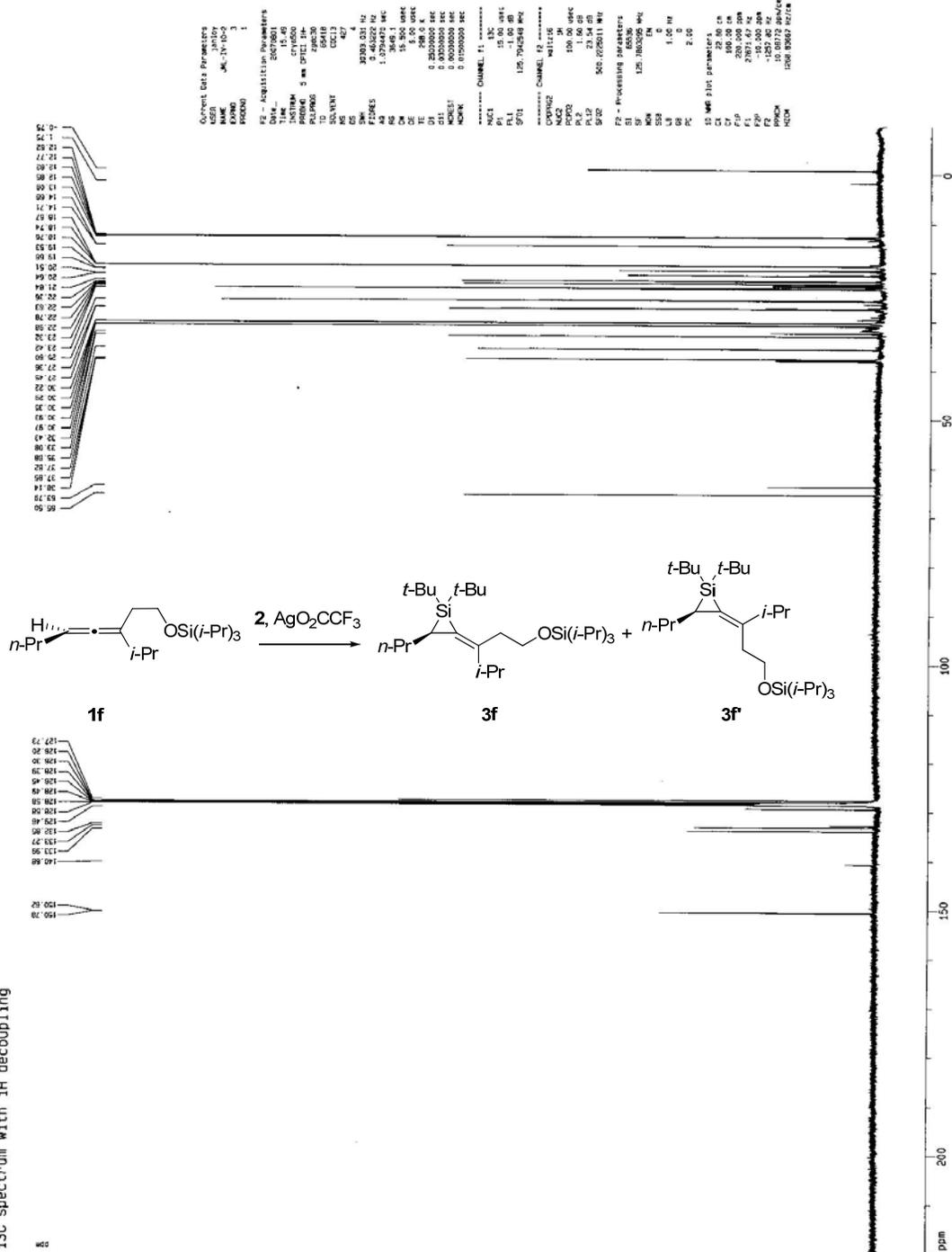


3c, crude NMR reaction
1H spectrum

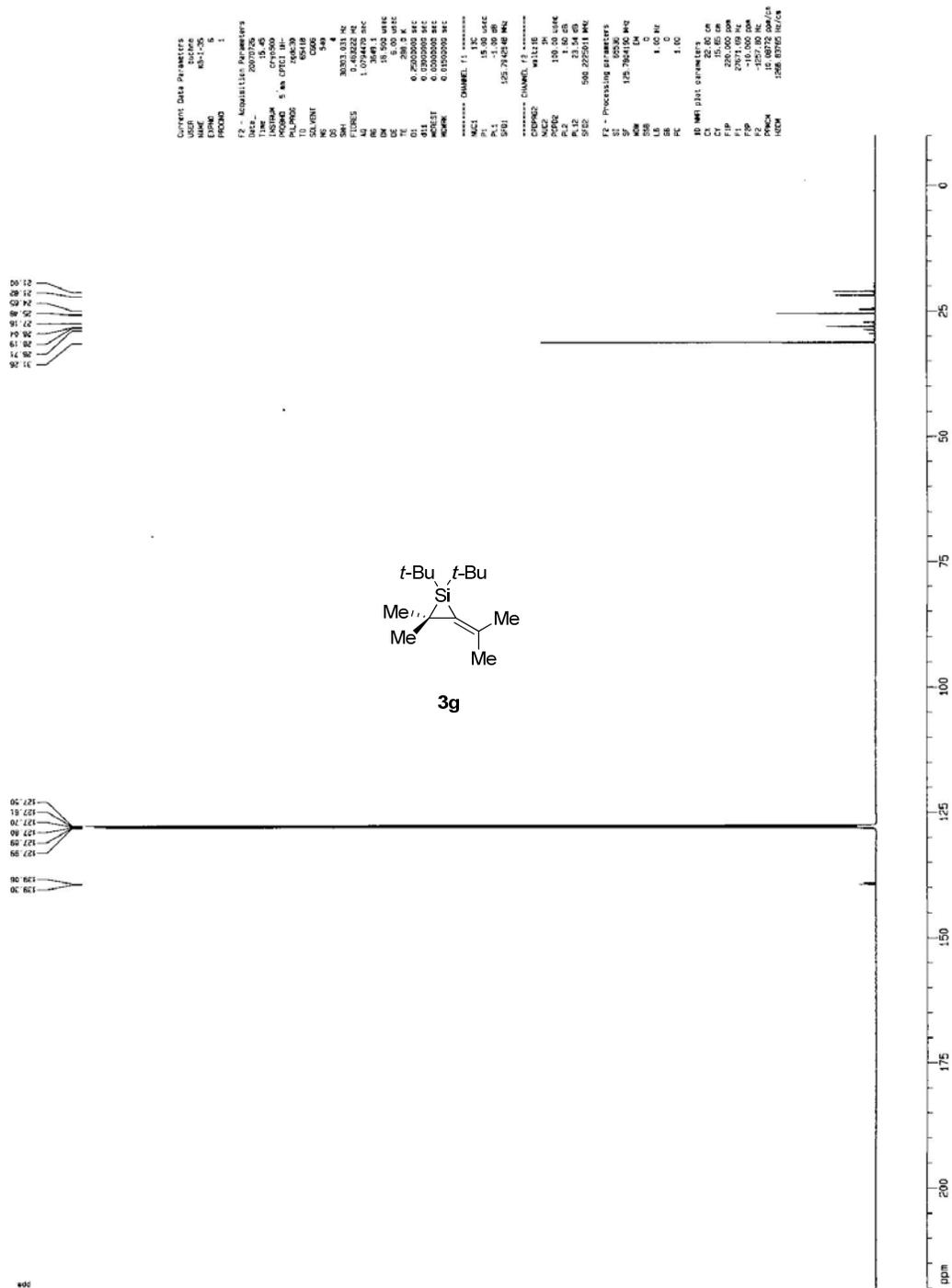




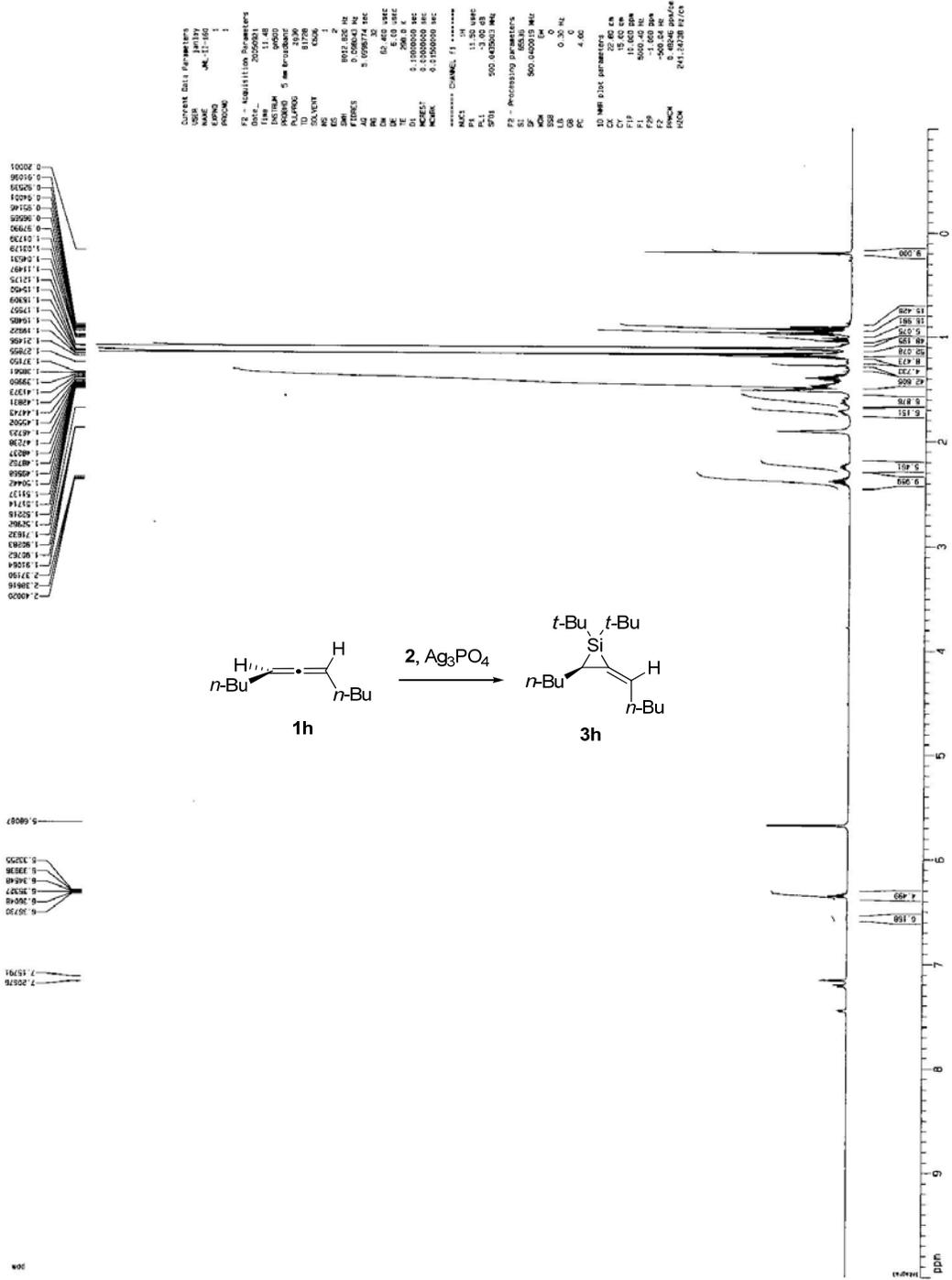
3f, crude NMR reaction
¹³C spectrum with ¹H decoupling

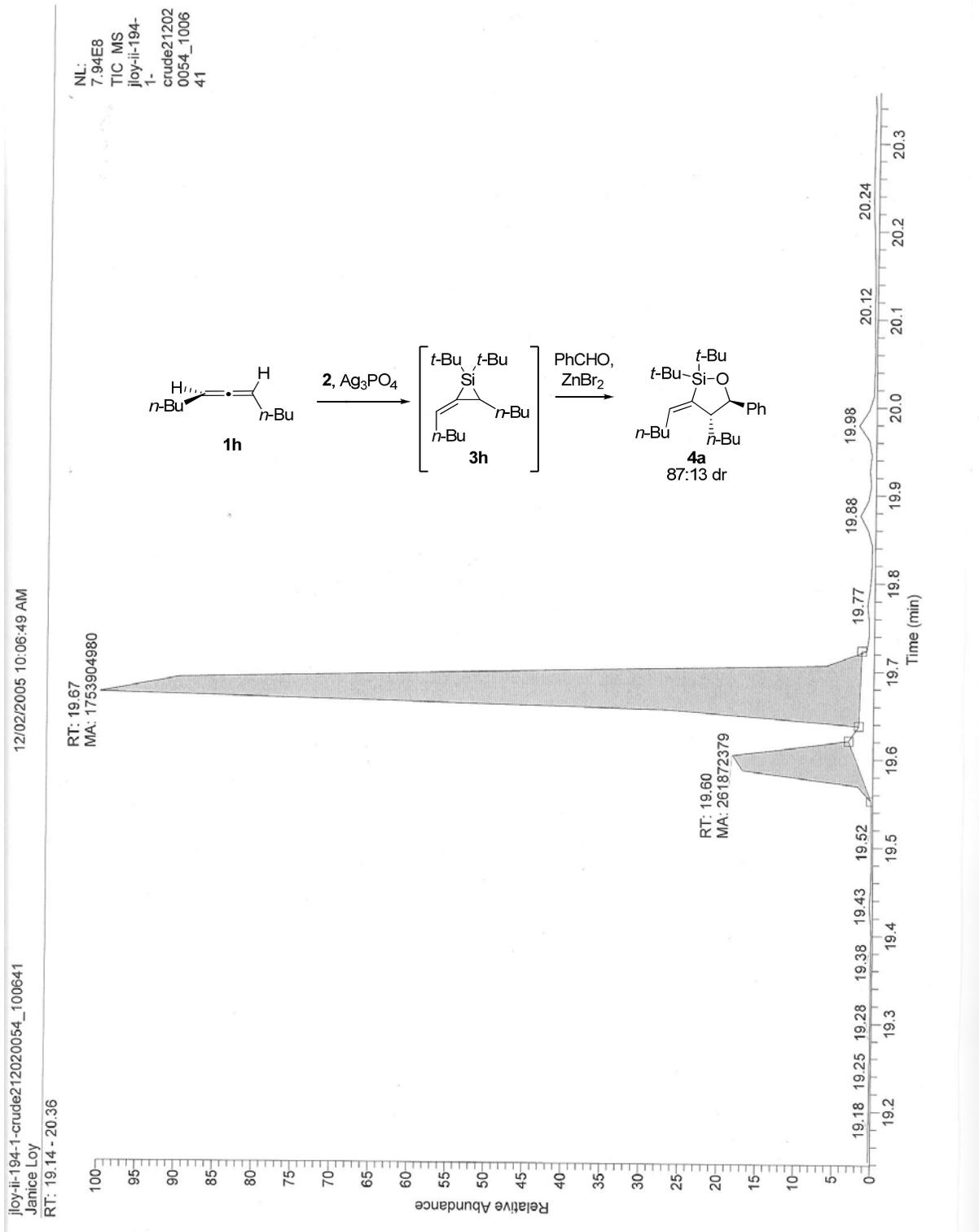


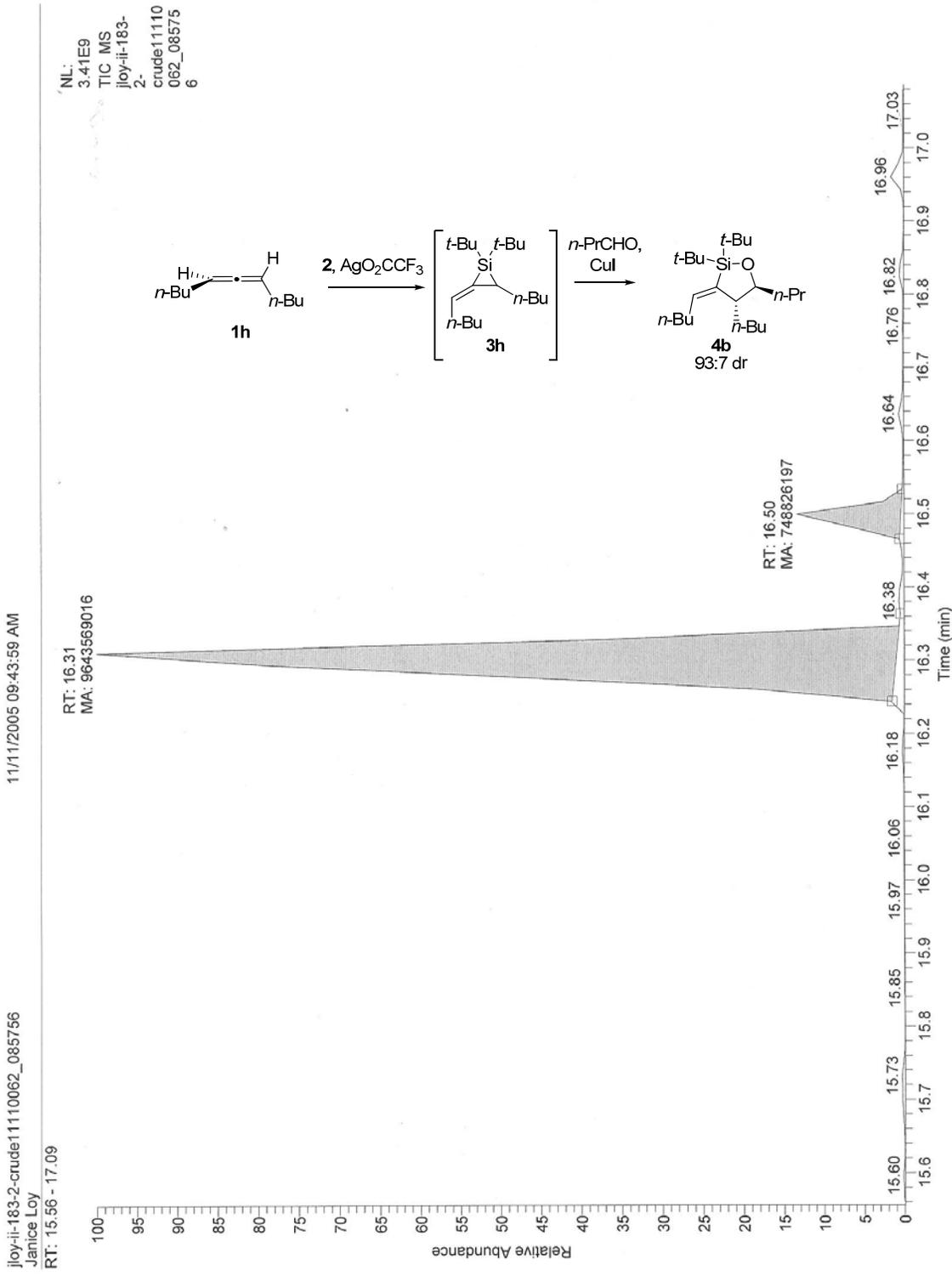
3g
¹³C spectrum with ¹H decoupling

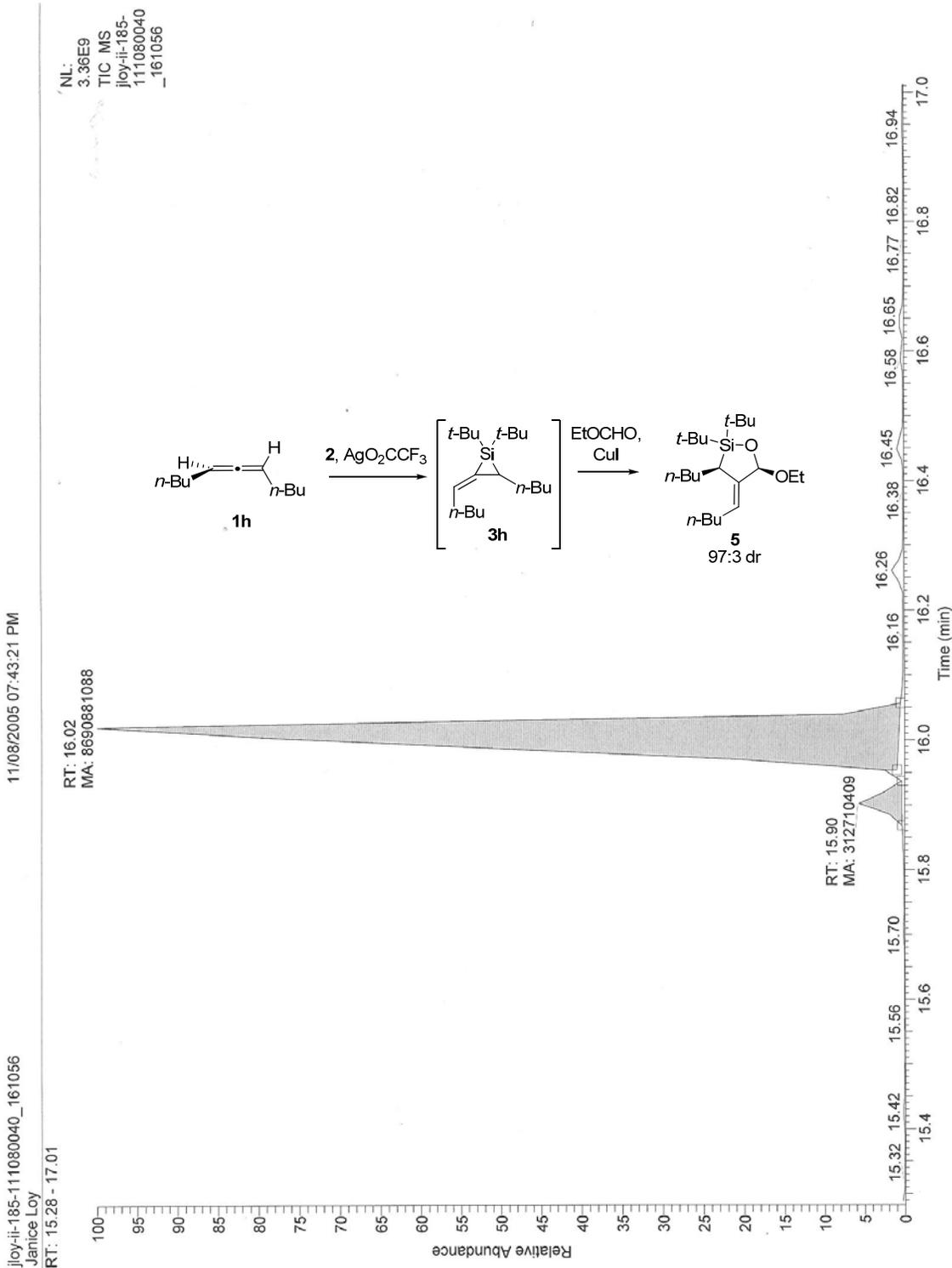


3h, crude NMR reaction
1H spectrum









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Janice Loy
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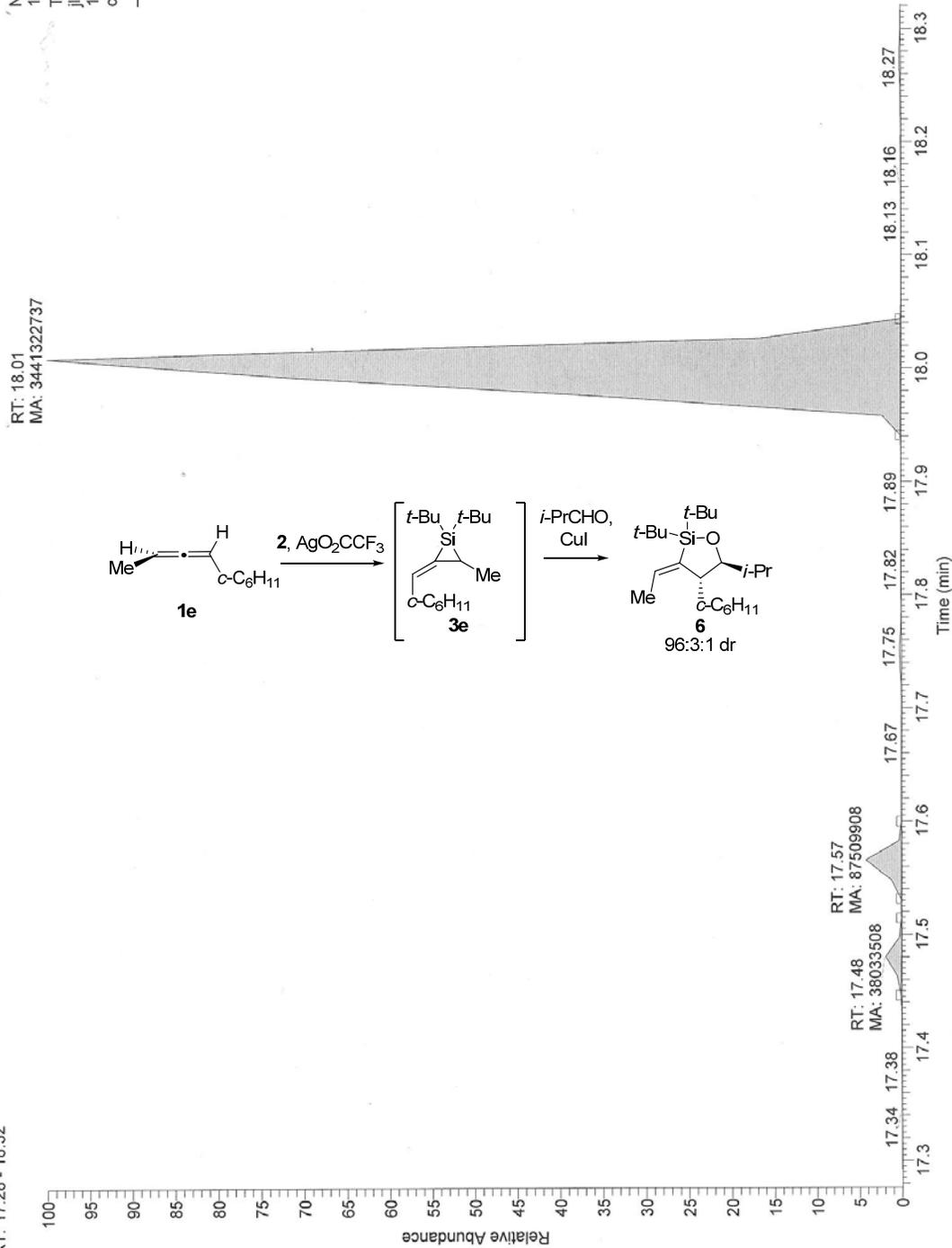
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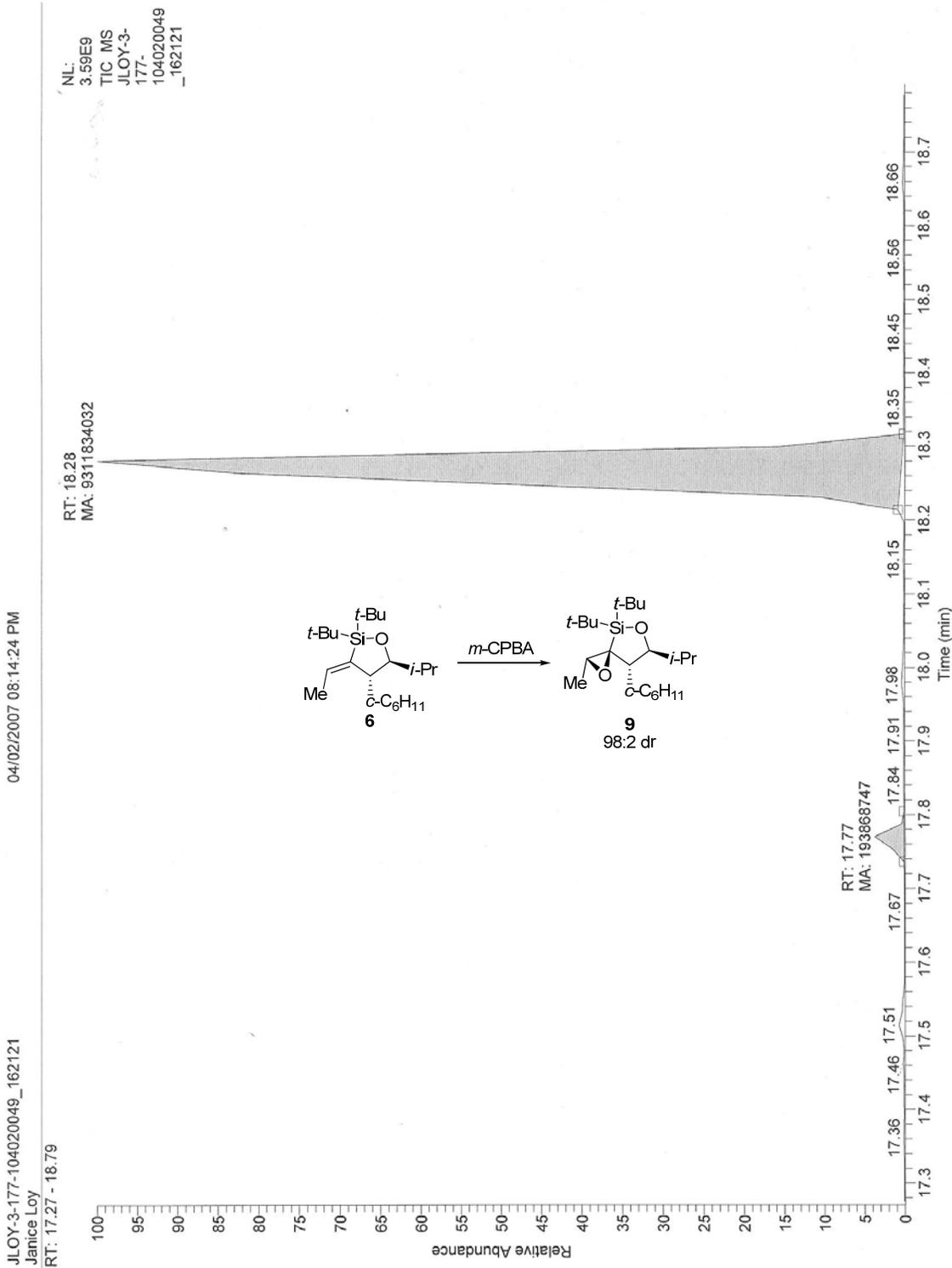
Janice Loy

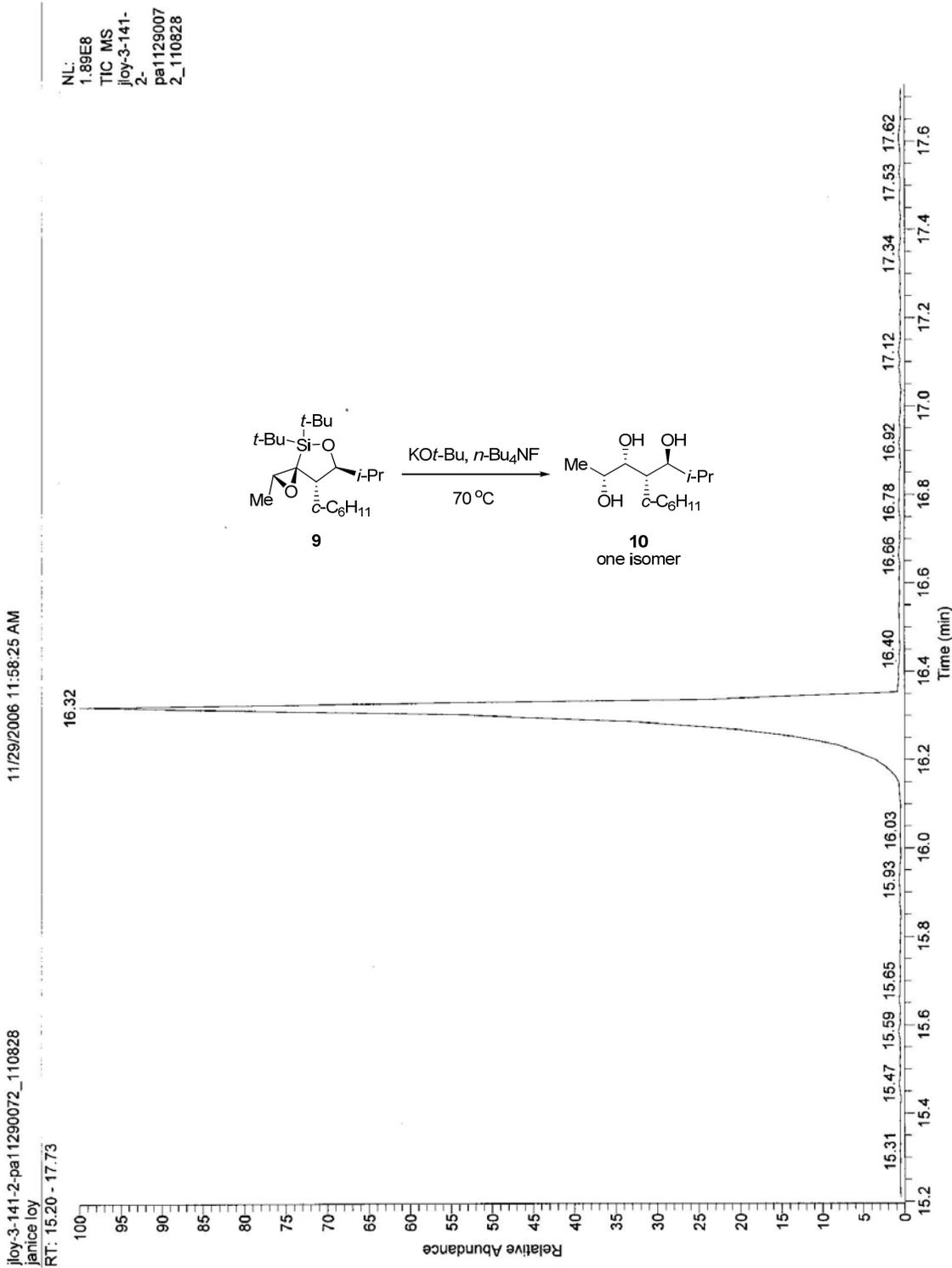
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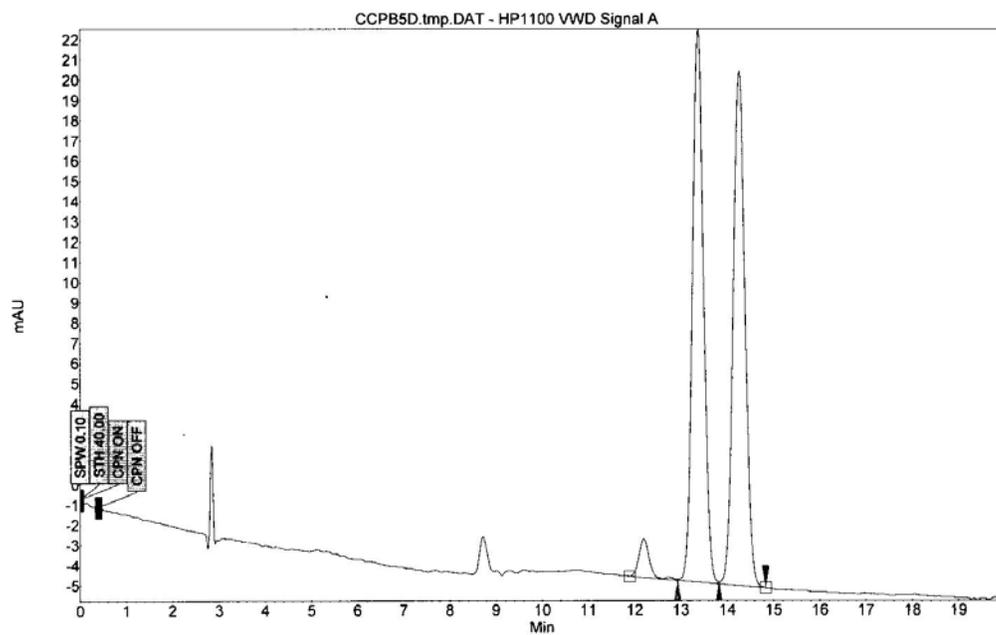
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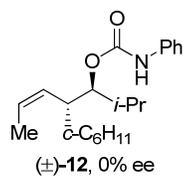




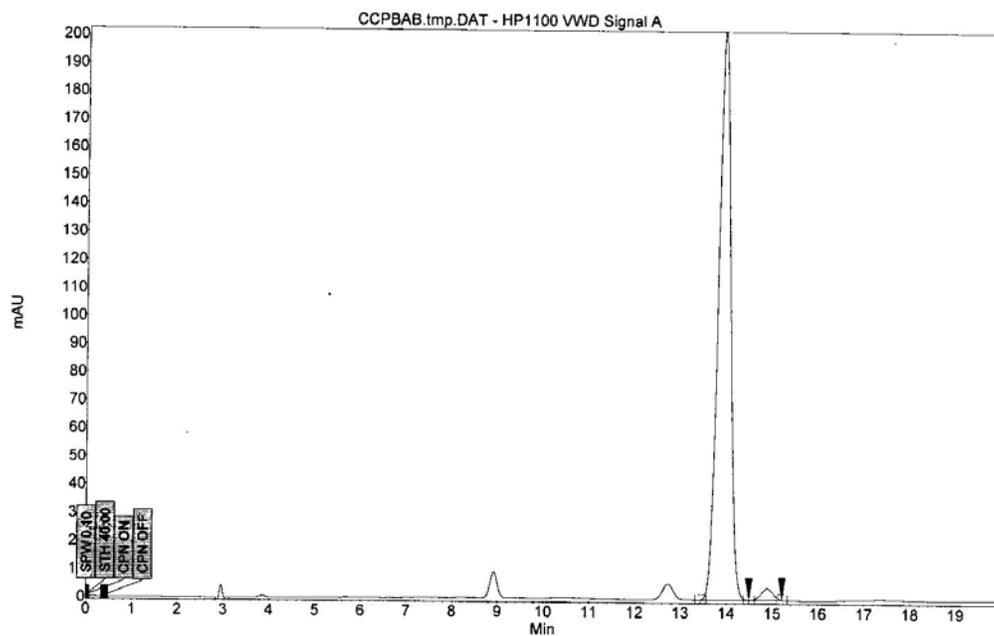
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Index	Name	Time	Area	Height	Width	Area
		[Min]	[mAU*min]	[mAU]	[Min]	[%]
1	UNKNOWN	13.3721	7.5994	27.40	0.26	50.161
2	UNKNOWN	14.2636	7.5505	25.50	0.28	49.839
Total			15.1500			100.000



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Run Name: KB-II-38-5
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Index	Name	Time [Min]	Area [mAU*min]	Height [mAU]	Width [Min]	Area [%]
1	UNKNOWN	13.9050	62.4472	202.01	0.29	98.059
2	UNKNOWN	14.8837	1.2358	4.24	0.28	1.941
Total			63.6831			100.000

