SUPPORTING INFORMATION

FOR

CYCLOPROPANE STRUCTURAL UNITS FROM HOMOALDOL ADDUCTS

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Experimental

General. Unless otherwise noted, all materials were used as received from a commercial supplier without further purification. All anhydrous reactions were performed using oven-dried or flame-dried glassware under argon. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and toluene were filtered through activated alumina under nitrogen. Barium(II) iodide was prepared via dehydration of $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) under high vacuum (0.5-1.0 Torr) at 160 °C–190 °C for 2 hours.

All reactions were monitored by either E. Merck analytical thin layer chromatography (TLC) plates (silica gel 60 GF, glass back) or Whatman UV active aluminum backed TLC plates (silica gel 250 μm) and analyzed with 254 nm UV light and/or anisaldehyde/sulfuric acid treatment. Silica gel for column chromatography was purchased from E. Merck (Silica Gel 60, 230-400 mesh). Preparative thin layer chromatography (PTLC) plates were purchased from Whatman (LK6F Silica Gel 60 Å). Biotage chromatography was performed using Flash 12+M, 25+S, and 25+M KP-Sil™ Silica (32-63 μm , 60 Å, nominally 500 m^2/g silica) Cartridges.

Unless specified otherwise all ^1H and ^{13}C NMR spectra were obtained in CDCl_3 or $(\text{CD}_3)_2\text{CO}$ on Varian Unity Plus 300 spectrometer (operating at 299.701 MHz for ^1H and 75.367 MHz for ^{13}C). Chemical shifts (δ) were reported in ppm relative to residual CHCl_3 as internal reference (^1H : 7.26 ppm, ^{13}C : 77.00 ppm) or to residual acetone (^1H : 2.05 ppm, ^{13}C : 29.22), and coupling constants (J) were reported in hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), b (broad), and v (virtual). (Note: All NMR spectra for the ene carbamate products (**8a,b** and **10a-e**) were recorded in $(\text{CD}_3)_2\text{CO}$ to avoid isomerization of the Z-olefin. Additionally, when collecting the ^{13}C NMR spectra for these compounds, it was determined that long relaxation times (d_1 = 8s–30s) were necessary to effectively observe all substituted aromatic carbons and the carbonyl of the carbamate). FTIR spectra were obtained on PE Paragon 1000 spectrometer. Mass spectra (CI/FAB/EI) were obtained at the Department of Chemistry and Biochemistry, University of Notre Dame.

Silyl Enol Ethers (**5a-5e**):

Representative Lithiation/Transmetalation/Substitution of Allyloxy-triethyl-silane (4**): Preparation of (Z)-2-Methyl-1-phenyl-6-(triethyl-silanyloxy)-hexa-1,5-dien-3-ol (**5e**).**

A 100 mL round bottom flask (**Flask A**) with stir bar was flame dried and charged with $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ (1.656 g, 3.88 mmol) under argon atmosphere. The flask with the dihydrate was placed in an oil bath and heated to 160 °C–190 °C for 2 hours under high vacuum (0.5–1.0 Torr). In the meantime, another 100 mL round bottom flask (**Flask B**) containing a magnetic stir bar was flame dried under vacuum and flushed with argon. The sealed flask was cooled to room temperature and then filled with 5 mL of THF. The solvent and flask are cooled to –78 °C while under a head pressure of argon. Then, a solution of *s*-BuLi in cyclohexane (1.3M) was added (872 μL , 1.134 mmol) to the THF solution at –78 °C. This mixture was a bright yellow and was allowed to cool at –78 °C for 15 minutes. Then a clean 10 mL round bottom flask was charged with the allyl triethylsilyl ether (215 mg, 1.25 mmol). The flask was sealed with a rubber septum, flushed with argon, and THF (3–5 mL) was added. The resulting solution was added via syringe pump to the *s*-BuLi solution in THF slowly over a 15 minutes. The yellowish color of the *s*-BuLi in THF disappeared over the course of an hour to provide a colorless solution at –78 °C. The solution was then warmed to –40 °C and the deprotonation was allowed to occur for 60–90 minutes with the temperature carefully kept at –40 °C. After 2 hours, the BaI_2 is dry and **Flask A** was removed from the oil bath, flushed with argon, and cooled to room temperature. The BaI_2 was a white solid after dehydration and was soluble in THF, albeit slowly. So, to the flask containing the BaI_2 , THF (19.40 mL) was added to provide a 0.2M solution of BaI_2 in THF. Upon swirling and much agitation, all of the BaI_2 was solvated providing a transparent (colorless, sometimes pale yellow) 0.2M solution. After the described deprotonation of allyl triethylsilyl ether in **Flask B**, the BaI_2 solution in THF (0.2M, 5.67 mL, 1.134 mmol) from **Flask A** was added at –78 °C via syringe pump over 15 minutes. Transmetalation was allowed to proceed for 30 minutes at –78 °C. Then α -*trans*-methyl-cinnamaldehyde (83 mg, 0.567 mmol) was added in 1 mL of THF to **Flask B**. The resulting solution was colorless and reacted at –78 °C for 10 minutes. Then the reaction mixture was removed from the dry ice bath and allowed to react for another 10–15 minutes. At this point, the reaction was quenched with a saturated solution of NH_4Cl (5 mL) via syringe and lots of white precipitate was observed in the colorless reaction mixture. Then 10 mL of water was added to dissolve the inorganic salts and the mixture was extracted with diethyl ether (3×20 mL). The ethereal extracts were then combined and washed with saturated sodium thiosulfate (15 mL). The ether was then dried with MgSO_4 . Rotary evaporation concentrated the residue and the product was purified using flash column chromatography with 1:5 (EtOAc:hexanes) as eluent ($R_f = 0.15$), providing silyl enol ether **5e** (180 mg, 80%).

(Z)-1-(Triethyl-silanyloxy)-non-1-en-4-ol (5a). See the Representative Lithiation/Transmetalation/Substitution of Allyloxy-triethyl-silane **4** for the preparation of **5e** above. Enol ether **5a** (471 mg, 76%) was obtained as a colorless oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 6.35 (d, $J = 6.0$, 1H), 4.51 (td, $J = 7.4$, 5.8, 1H), 3.66-3.62 (m, 1H), 2.28-2.23 (m, 2H), 1.89 (d, $J = 4.2$, 2H), 1.48-1.25 (m, 8H), 0.98 (t, $J = 8.1$, 9H), 0.95-0.86 (m, 3H), 0.66 (q, $J = 8.1$, 6H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 140.7, 105.7, 71.9, 36.9, 31.9, 31.8, 25.4, 22.6, 14.0, 6.5, 4.4. FTIR (cm^{-1}) 3369, 2957, 2932, 2877, 1656, 1460, 1413, 1378, 1241, 1100, 1048, 1016, 810, 745. HRMS calculated for $\text{C}_{15}\text{H}_{32}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$ m/z 273.2250, found 273.2242.

(Z)-1-Phenyl-6-(triethyl-silanyloxy)-hex-5-en-3-ol (5b). See the Representative Lithiation/Transmetalation/Substitution of Allyloxy-triethyl-silane **4** for the preparation of **5e** above. Enol ether **5b** (187 mg, 71%) was obtained as a colorless oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 7.30-7.17 (m, 5H), 6.36 (dt, $J = 5.8$, 1.4, 1H), 4.51, (td, $J = 7.5$, 5.8, 1H), 3.72-3.62 (m, 1H), 2.86-2.63 (m, 2H), 2.29 (td, $J = 7.4$, 1.4 2H), 1.98 (d, $J = 4.2$, 1H), 1.82-1.75 (m, 2H), 0.97 (t, $J = 8.1$, 9H), 0.66 (q, $J = 8.1$, 6H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 142.4, 140.9, 128.4, 128.3, 125.7, 105.4, 71.2, 38.6, 32.1, 31.9, 6.5, 4.4. FTIR (cm^{-1}) 3401, 3028, 2956, 2877, 1655, 1496, 1456, 1241, 1118, 1057, 1016, 811, 745, 698. HRMS calculated for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$ m/z 307.2093, found 307.2119.

(Z)-1-Cyclohexyl-4-(triethyl-silanyloxy)-but-3-en-1-ol (5c). See the Representative Lithiation/ Transmetalation/Substitution of Allyloxy-triethyl-silane **4** for the preparation of **5e** above. Enol ether **5c** (331 mg, 63%) was obtained as a colorless oil. ^1H NMR (300MHz,

CDCl₃) δ (ppm) 6.36 (dt, J = 5.8, 1.2, 1H), 4.52 (td, J = 7.5, 6.0, 1H), 3.37 (ddd, J = 10.2, 5.9, 5.9, 1H), 2.27 (td, J = 6.6, 1.2, 1H), 1.90-1.86 (m, 1H), 1.79-1.67 (m, 5H), 1.41-1.02 (m, 6H), 0.98 (t, J = 7.9, 9H), 0.66 (q, J = 7.9, 6H), 0.90-0.84 (m, 1H). ¹³C NMR (75MHz, CDCl₃) δ (ppm) 140.6, 106.1, 76.1, 43.1, 29.1, 28.7, 28.2, 26.6, 26.4, 26.2, 6.5, 4.4. FTIR (cm⁻¹) 3392, 2956, 2923, 2878, 2853, 1656, 1450, 1402, 1241, 1116, 1081, 1058, 1044, 1007, 892, 811, 745. HRMS calculated for C₁₆H₃₂O₂Si (M+H)⁺ m/z 285.2250, found 285.2244.

(Z)-1-Phenyl-4-(triethyl-silanyloxy)-but-3-en-1-ol (5d). See the Representative Lithiation/ Transmetalation/Substitution of Allyloxy-triethyl-silane **4** for the preparation of **5e** above. Enol ether **5d** (206 mg, 67%) was obtained as a colorless oil. ¹H NMR (300MHz, CDCl₃) δ (ppm) 7.40-7.25 (m, 5H), 6.37 (dt, J = 6.0, 1.3, 1H), 4.74 (ddd, J = 8.0, 5.1, 3.0, 1H), 4.50 (td, J = 7.4, 6.0, 1H), 2.65-2.46 (m, 3H), 0.98 (t, J = 7.9, 9H), 0.67 (q, J = 8.1, 6H). ¹³C NMR (75MHz, CDCl₃) δ (ppm) 141.1, 128.23, 128.17, 127.2, 125.8, 105.3, 74.1, 34.0, 6.5, 4.4. FTIR (cm⁻¹) 3369, 2957, 1657, 1454, 1115, 1050, 743, 699. HRMS calculated for C₁₆H₂₆O₂Si (M-1)⁺ m/z 277.1624, found 277.1626.

(Z)-2-Methyl-1-phenyl-6-(triethyl-silanyloxy)-hexa-1,5-dien-3-ol (5e). See the Representative Lithiation/ Transmetalation/Substitution of Allyloxy-triethyl-silane **4** for the preparation of **5e** above. ¹H NMR (300MHz, CDCl₃) δ (ppm) 7.35-7.18 (m, 5H), 6.53 (bs, 1H), 6.38 (dt, J = 5.8, 1.4, 1H), 4.53 (td, J = 7.4, 5.8, 1H), 4.23-4.18 (m, 1H), 2.50-2.44 (m, 2H), 2.19 (d, J = 3.7, 1H), 1.88 (d, J = 1.4, 3H), 0.99 (t, J = 8.1, 9H), 0.68 (q, J = 8.1, 6H). ¹³C NMR (75MHz, CDCl₃) δ (ppm) 140.9, 140.1, 137.9, 129.0, 128.0, 126.2, 125.2, 105.3, 77.5, 30.3, 13.7, 6.5, 4.4. FTIR (cm⁻¹) 3369, 2956, 1656, 1458, 1240, 1114, 1050, 744, 698. HRMS calculated for C₁₉H₃₀O₂Si (M-1)⁺ m/z 317.1937, found 317.1922.

Cyclopropyl Aldehydes (6a-e):

Representative Activation of Silyl Enol Ethers (5a-e) and the Ene Carbamates (8a,b and 10a-e): Preparation of *trans*-2-Pentyl-cyclopropanecarbaldehyde (6a) from silyl enol ether (5a). A flame dried flask was charged with silyl enol ether **5a** (33.6 mg, 0.123 mmol) and CH₂Cl₂ (2 mL). The flask was flushed with argon and 2,6-lutidine (58 µL, 0.493 mmol) was added via syringe. The resulting mixture was cooled to -78 °C and then triflic anhydride (63 µL, 0.370 mmol) was added neat. The mixture was stirred for 5-15 min. and then removed from dry ice bath. The solution was quenched with water and allowed to warm to room temperature. The mixture was then diluted with 25 mL of CH₂Cl₂ and washed with NaHCO₃ (1 × 10 mL) and dried over MgSO₄ and concentrated. The yellow residue (R_f = 0.50) was purified via pipette column using 1:15 (EtOAc:hexanes) as eluent to provide aldehyde **6a** (15 mg, 89%) as a volatile oil! Spectral data for cyclopropyl aldehyde **6a** below:

Preparation of *trans*-2-Phenyl-cyclopropanecarbaldehyde (6d) from ene carbamate (10d). A flame dried flask was charged with ene carbamate **10d** (34.6 mg, 0.094 mmol) and CH₂Cl₂ (3 mL). The flask was flushed with argon and diisopropylethylamine (50 µL, 0.281 mmol) was added via syringe. The resulting mixture was cooled to -20 °C and then mesyl anhydride (65 mg, 0.375 mmol) was added in a single solid portion. The mixture was allowed to warm to 0 °C and then to room temperature over the course of 1-4 hours. The reaction mixture slowly changes from having a colorless appearance to a pale yellow and finally an intense yellow by the end of the reaction. The solution was quenched with water and diluted with 25 mL of CH₂Cl₂ and washed with NaHCO₃ (1 × 10 mL) and then dried over MgSO₄ and concentrated. The concentrated material was a solid. The solid was re-dissolved in 1:2 (CH₂Cl₂:hexanes) and allowed to sit overnight during which the Boc-protected anisidine auxiliary crystallized out of solution. The remaining mother liquor was removed, concentrated and purified via pipette column using 1:15 (EtOAc:hexanes) as eluent to provide aldehyde **6d** (10 mg, 72%) as a colorless oil. (Note: The crystallized Boc-protected anisidine can be recovered (> 80%) and collected for reuse.) Spectral data for cyclopropyl aldehyde **6d** below:

trans-2-Pentyl-cyclopropanecarbaldehyde (6a). See the Representative Activation of Silyl Enol Ethers (**5a-e**) and Ene Carbamates (**8a,b** and **10a-e**). Aldehyde **6a** was obtained from **10a** (5 mg, 88%) as a colorless volatile oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 8.98 (d, J = 5.6, 1H), 1.64-1.57 (m, 1H), 1.50-1.19 (m, 10H), 0.95-0.86 (m, 4H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 201.0, 32.6, 31.4, 30.5, 28.7, 22.7, 22.5, 14.9, 14.0. FTIR (cm^{-1}) 2929, 2858, 1709, 1512, 1425, 1210, 1144, 1031. HRMS calculated for $\text{C}_9\text{H}_{16}\text{O}$ M^+ m/z 140.1202, found 140.1215.

trans-2-Phenethyl-cyclopropanecarbaldehyde (6b). See the Representative Activation of Silyl Enol Ethers (**5a-e**) and Ene Carbamates (**8a,b** and **10a-e**). Aldehyde **6b** was obtained from **5b** (11 mg, 89%), from **8a** (17 mg, 97%), and from **10b** (22 mg, 90%) as a colorless oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 8.98 (d, J = 5.3, 1H), 7.32-7.15 (m, 5H), 2.73 (t, J = 7.5, 2H), 1.78-1.58 (m, 2H), 1.53-1.42 (m, 2H), 1.33-1.21 (m, 1H), 0.95-0.88 (m, 1H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 200.9, 141.3, 128.4 (2Cs), 126.0, 35.4, 34.5, 30.4, 22.2, 14.8. FTIR (cm^{-1}) 3027, 2924, 2856, 2727, 1706, 1603, 1496, 1454, 1168, 1037, 867, 751, 700. HRMS calculated for $\text{C}_{12}\text{H}_{14}\text{O}$ ($\text{M}+\text{H}$) $^+$ m/z 175.1123, found 175.1134.

trans-2-Cyclohexyl-cyclopropanecarbaldehyde (6c). See the Representative Activation of Silyl Enol Ethers (**5a-e**) and Ene Carbamates (**8a,b** and **10a-e**). Aldehyde **6c** was obtained from **5c** (13 mg, 84%), from **8b** (8 mg, 97%), and from **10c** (21 mg, 86%) as a colorless volatile oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 8.96 (d, J = 5.8, 1H), 1.76-1.68 (m, 3H), 1.68-1.61 (m, 2H), 1.36-1.28 (m, 1H), 1.27-1.21 (m, 1H), 1.21-1.00 (m, 6H), 0.98-0.92 (m, 1H), 0.82-0.71 (m, 1H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 201.0, 41.2, 32.6, 32.5, 29.2, 29.0, 26.2, 26.0, 25.9, 13.4. FTIR (cm^{-1}) 2925, 2852, 2723, 1710, 1512, 1449, 1231, 1198, 1166, 1034, 940, 896. HRMS calculated for $\text{C}_{10}\text{H}_{16}\text{O}$ M^+ m/z 152.1202, found 152.1228.

trans-2-Phenyl-cyclopropanecarbaldehyde (6d). See the Representative Activation of Silyl Enol Ethers (**5a-e**) and Ene Carbamates (**8a,b** and **10a-e**). Aldehyde **6d** was obtained from **5d** (9 mg, 89%) and from **10d** (10 mg, 72%) as a colorless oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 9.33 (d, $J = 4.6$, 1H), 7.33-7.20 (m, 3H), 7.13-7.09 (m, 2H), 2.63 (ddd, $J = 9.3$, 6.7, 3.9, 1H), 2.22-2.14 (m, 1H), 1.74 (ddd, $J = 9.3$, 5.1, 5.1, 1H), 1.54 (ddd, $J = 8.1$, 6.7, 4.9, 1H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 199.6, 139.0, 128.6, 126.8, 126.3, 33.7, 26.6, 16.4. FTIR (cm^{-1}) 3031, 1704, 1605, 1499, 1162, 1029, 965, 758, 697. HRMS calculated for $\text{C}_{10}\text{H}_{10}\text{O}$ ($\text{M}+\text{H}$) $^+$ m/z 147.0810, found 147.0825.

trans-2-(1-Methyl-2-phenyl-vinyl)-cyclopropanecarbaldehyde (6e). See the Representative Activation of Silyl Enol Ethers (**5a-e**) and Ene Carbamates (**8a,b** and **10a-e**). Aldehyde **6e** was obtained from **5e** (20 mg, 86%) and from **10e** (26 mg, 90%) as a colorless oil. ^1H NMR (300MHz, CDCl_3) δ (ppm) 9.24 (d, $J = 4.6$, 1H), 7.35-7.20 (m, 5H), 6.42 (bs, 1H), 2.32-2.26 (m, 1H), 2.11-2.03 (m, 1H), 1.77 (d, $J = 1.4$, 3H), 1.54-1.42 (m, 2H). ^{13}C NMR (75MHz, CDCl_3) δ (ppm) 200.2, 137.5, 134.7, 128.8, 128.1, 126.6, 126.4, 31.0, 30.2, 15.5, 13.5. FTIR (cm^{-1}) 3022, 2829, 2729, 1705, 1598, 1492, 1442, 1400, 1162, 1103, 1070, 1000, 959, 918, 858, 741, 699. HRMS calculated for $\text{C}_{13}\text{H}_{14}\text{O}$ ($\text{M}+\text{H}$) $^+$ m/z 187.1123, found 187.1115.

O-Ene Carbamates (8a,b):

Representative Lithiation/Substitution of Diisopropyl-carbamic acid allyl ester (7): Preparation of Diisopropyl-carbamic acid 4-hydroxy-6-phenyl-hex-1-enyl ester (8a).

To carbamate **7** (1.00 g, 5.41 mmol) in a flame dried 100 mL round bottom flask flushed with argon was added toluene (49 mL) followed by (-)-sparteine (1.49 mL, 6.49 mmol). The reaction flask was cooled to $-78\text{ }^\circ\text{C}$ and a 2.5M solution of *n*-BuLi in hexanes (2.6 mL, 6.49 mmol) was added dropwise via syringe. After 2 hours, a solution of $\text{Ti}(\text{OiPr})_4$ (4.86 mL, 16.2

mmol) in toluene (10 mL) cooled to $-30\text{ }^{\circ}\text{C}$ was added via cannula. The reaction mixture was allowed to stir at $-78\text{ }^{\circ}\text{C}$ for an additional 30 min. before hydrocinnamaldehyde (1.45 mL, 10.8 mmol) in toluene (1 mL) was added dropwise. Allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 1hr followed by another hour $-40\text{ }^{\circ}\text{C}$. The reaction was quenched with a saturated solution of NH_4Cl and extracted with CH_2Cl_2 . The organic layer was dried with MgSO_4 and concentrated in vacuo. The residue was purified via a Biotage using a Flash 25+M Cartridge (16% EtOAc in hexanes) to afford ene carbamate **8a** (1.46 g, 84%) as a clear oil. Spectral data for **8a** below:

Diisopropyl-carbamic acid 4-hydroxy-6-phenyl-hex-1-enyl ester (8a). ^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.30-7.11 (m, 5H), 7.06 (dt, $J = 6.5, 1.5$, 1H), 4.86 (ddd, $J = 7.5, 7.5, 6.5$, 1H), 3.99 (m, 2H), 3.74 (m, OH), 3.71-3.60 (m, 1H), 2.82 (ddd, $J = 13.8, 10.0, 6.7$, 1H), 2.67 (ddd, $J = 13.8, 10.0, 6.7$, 1H), 2.47-2.32 (m, 2H), 1.87-1.64 (m, 2H), 1.23 (d, $J = 6.7$, 12H). ^{13}C NMR (75MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 152.5, 143.0, 136.5, 128.6, 128.5, 125.8, 107.1, 70.2, 46.5, 39.2, 33.6, 32.2, 20.7. FTIR (cm^{-1}) 3445, 2972, 2933, 1704, 1472, 1440, 1371, 1309, 1248, 1211, 1189, 1157, 1134, 1103, 1061, 762, 748, 700. HRMS calculated for $\text{C}_{19}\text{H}_{29}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ m/z 320.2226, found 320.2209.

Diisopropyl-carbamic acid 4-cyclohexyl-4-hydroxy-but-1-enyl ester (8b). See the Representative Lithiation/Substitution of Diisopropyl-carbamic Acid Allyl Ester **7** for the Preparation of *O*-Ene Carbamate **8a**. *O*-Ene carbamate **8b** (1.43 g, 89%) was obtained as a clear oil. ^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.03 (dt, $J = 6.5, 1.5$, 1H), 4.88 (vq, $J = 6.7$, 1H), 4.00 (m, 2H), 3.46 (m, OH), 3.38 (dt, $J = 9.8, 5.0$, 1H), 2.25 (dddd, $J = 14.8, 7.5, 7.5, 1.5$, 1H), 2.43 (dddd, $J = 14.8, 7.5, 7.5, 1.5$, 1H), 1.95-1.58 (m, 5H), 1.42-0.94 (m, 18H). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 152.5, 136.2, 107.9, 75.0, 46.5, 43.6, 30.4, 30.0, 28.1, 26.8, 26.6, 26.5, 20.7. FTIR (cm^{-1}) 3468, 2925, 2852, 1692, 1439, 1370, 1290, 1209, 1210, 1133, 1078, 1057, 761. HRMS calculated for $\text{C}_{17}\text{H}_{31}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ m/z 298.2382, found 298.2381.

***N*-Ene Carbamates (10a-e):**

Representative Lithiation/Substitution of Allyl-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (9): Preparation of (Z)-(4-Hydroxy-non-1-enyl)-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (10a). To a pre-cooled ($-78\text{ }^\circ\text{C}$) solution of (-)-sparteine (0.093 mL, 0.406 mmol) and *n*-BuLi (2.2M) (0.170 mL, 0.372 mmol) in toluene (5 mL) under argon was added allylamine **9** (89 mg, 0.338 mmol) in toluene (1 mL) and the reaction turned bright yellow. After stirring for 2 hours at $-78\text{ }^\circ\text{C}$ hexanal (31 mg, 0.304 mmol) in toluene (1 mL) was added dropwise. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 2 hours and then quenched with MeOH (1 mL). Reaction was diluted with diethyl ether and 2M HCl was added. The aqueous layer was extracted with Et_2O ($3 \times 20\text{ mL}$), the ethereal extracts were pooled and then washed with NaHCO_3 to neutralize residual acid. (Note: It is important to neutralize the ether layer as residual acid will decompose the product ene carbamates). Then the organic layer was dried over MgSO_4 and concentrated by rotary evaporation. Flash column chromatography with 1:5 (EtOAc:hexanes) as eluent provided ene carbamate ($R_f = 0.15$) **10a** (85 mg, 77%). (Note: The ene carbamates **10a-e** are extremely polar and viscous compounds and readily hold onto the ethyl acetate they are exposed to during chromatography. Treatment of the oils for several hours under high vacuum (0.1-0.5 Torr) is necessary to remove any traces of the ethyl acetate before further reaction to give the

corresponding cyclopropyl aldehydes **6a-e**. Failure to properly dry these compounds will result in low yields for the cyclopropyl aldehyde reactions due to residual ethyl acetate in the ene carbamate starting material resulting in a “wet” weight.)

(Z)-(4-Hydroxy-non-1-enyl)-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (10a).

^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.17 (d, $J = 9.2$, 2H), 6.90 (d, $J = 9.0$, 2H), 6.48 (dt, $J = 8.8$, 1.5, 1H), 5.04 (vq, $J = 7.7$, 1H), 3.80 (s, 3H), 3.39-3.35 (m, 2H), 1.78-1.60 (m, 2H), 1.42 (s, 9H), 1.31-1.17 (m, 8H), 0.87 (t, $J = 7.0$, 3H). ^{13}C NMR (75MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 158.0, 153.5, 135.5, 128.8, 128.4 (2 Cs), 113.9, 80.3, 70.4, 55.1, 37.5, 34.8, 32.1, 27.8, 25.4, 22.7, 13.7. FTIR (cm^{-1}) 3440, 2956, 2931, 2859, 1708, 1657, 1610, 1587, 1512, 1457, 1423, 1393, 1368, 1325, 1297, 1247, 1166, 1037, 1005, 858, 835, 794, 758, 738, 690. HRMS calculated for $\text{C}_{21}\text{H}_{33}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ m/z 363.2410, found 363.2411.

(Z)-(4-Hydroxy-6-phenyl-hex-1-enyl)-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (10b). See the Representative Lithiation/Substitution of Allyl-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester **9** for the preparation of **10a**. Ene carbamate **10b** (1.218 g, 57%) was obtained as a viscous colorless oil. ^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.28-7.12 (m, 7H), 6.89 (d, $J = 9.0$, 2H), 6.51 (dt, $J = 9.0$, 1.7, 1H), 5.04 (vq, $J = 7.3$, 1H), 3.78 (s, 3H), 3.56 (d, $J = 5.4$, 1H), 3.47-3.37 (m, 1H), 2.70-2.60 (m, 1H), 2.55-2.45 (m, 1H), 1.81-1.67 (m, 2H), 1.56-1.46 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (75MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 157.9, 153.4, 142.9, 135.3, 128.9, 128.6, 128.5 (2 Cs), 128.4, 125.8, 113.9, 80.4, 69.7, 55.1, 39.4, 34.8, 32.0, 27.7. FTIR (cm^{-1}) 3436, 2931, 1706, 1656, 1607, 1511, 1455, 1393, 1368, 1324, 1297, 1247, 1162, 1035, 1006, 837, 749, 700. HRMS calculated for $\text{C}_{24}\text{H}_{31}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ m/z 398.2331, found 398.2339.

(Z)-(4-Cyclohexyl-4-hydroxy-but-1-enyl)-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (10c). See the Representative Lithiation/Substitution of Allyl-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester **9** for the preparation of **10a**. Ene carbamate **10c** (173 mg, 61%) was obtained as a viscous colorless oil. ^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.17 (d, $J = 8.8$, 2H), 6.91 (d, $J = 8.8$, 2H), 6.46 (dt, $J = 8.8$, 1.6, 1H), 5.07 (vq, $J = 7.6$, 1H), 3.80 (s, 3H), 3.30 (d, $J = 5.4$, 1H), 3.17-3.09 (m, 1H), 1.81-1.59 (m, 7H), 1.42 (s, 9H), 1.22-1.08 (m, 4H), 0.99-0.84 (m, 2H). ^{13}C NMR (75MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 158.0, 153.5, 135.5, 128.7, 128.3, 114.0, 80.3, 74.5, 55.1, 43.9, 31.7, 29.3, 28.0, 27.8, 26.5, 26.4. FTIR (cm^{-1}) 3437, 2926, 2852, 1707, 1655, 1610, 1512, 1451, 1393, 1368, 1324, 1297, 1247, 1165, 1106, 1037, 1004, 857, 835, 794, 758, 691. HRMS calculated for $\text{C}_{22}\text{H}_{33}\text{NO}_4$ M^{+} m/z 375.2410, found 375.2389.

(Z)-(4-Hydroxy-4-phenyl-but-1-enyl)-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (10d). See the Representative Lithiation/Substitution of Allyl-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester **9** for the preparation of **10a**. Ene carbamate **10d** (344 mg, 94%) was obtained as a viscous colorless oil. ^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.29-7.16 (m, 5H), 7.10 (d, $J = 8.8$, 2H), 6.88 (d, $J = 8.8$, 2H), 6.45 (dt, $J = 9.0$, 1.5, 1H), 5.01 (dt, $J = 9.0$, 7.3, 1H), 4.48 (dt, $J = 6.4$, 4.5, 1H), 4.17 (d, $J = 4.3$, 1H), 3.79 (s, 3H), 1.99 (t, $J = 7.0$, 2H), 1.41 (s, 9H). ^{13}C NMR (75MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 158.0, 153.4, 145.9, 135.2, 129.0, 128.4, 128.1, 127.0, 126.0, 114.0, 80.4, 72.7, 55.1, 36.8, 27.7. FTIR (cm^{-1}) 3436, 2977, 1705, 1511, 1454, 1368, 1325, 1297, 1247, 1163, 1036, 831, 701. HRMS calculated for $\text{C}_{22}\text{H}_{27}\text{NO}_4$ M^{+} m/z 369.1942, found 369.1930.

(Z)-(4-Hydroxy-5-methyl-6-phenyl-hexa-1,5-dienyl)-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester (10e). See the Representative Lithiation/Substitution of Allyl-(4-methoxy-phenyl)-carbamic acid *tert*-butyl ester **9** for the preparation of **10a**. Ene carbamate **10e** (348 mg, 86%) was obtained as a viscous colorless oil. ^1H NMR (300MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 7.35-7.17 (m, 7H), 6.90 (d, $J = 8.8$, 2H), 6.50 (dt, $J = 8.8$, 1.7 1H), 6.38 (bs, 1H), 5.02 (dt, $J = 9.0$, 7.3, 1H), 3.99-3.93 (m, 1H), 3.90 (d, $J = 4.1$, 1H), 3.77 (s, 3H), 1.94-1.87 (m, 2H), 1.68 (d, $J = 1.3$, 3H), 1.42 (s, 9H). ^{13}C NMR (75MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 158.0, 153.4, 141.1, 138.3, 135.4, 129.1, 128.9, 128.4, 128.3 (2 Cs), 126.4, 124.9, 114.0, 80.4, 76.3, 55.1, 33.0, 27.7, 13.0. FTIR (cm^{-1}) 3438, 3053, 2977, 2933, 2837, 1705, 1656, 1609, 1587, 1511, 1456, 1423, 1393, 1368, 1327, 1297, 1247, 1163, 1106, 1036, 1006, 919, 858, 835, 794, 751, 700. HRMS calculated for $\text{C}_{25}\text{H}_{31}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ m/z 410.2331, found 410.2311.

Allyltributyltin Trapping of Cyclopropyl Carbinyl Oxonium Ion Intermediate and Carbamate Deprotection: Preparation of 1-(2-Phenethyl-cyclopropyl)-but-3-en-1-ol (11). To a solution of **8a** (27 mg, 0.085 mmol) in a flame dried 10 mL round bottom flask flushed with argon was added CH_2Cl_2 (0.94 mL), 2,6-lutidine (15 μL , 0.13 mmol) and allyltributylstannane (0.13 mL, 0.43 mmol). The reaction flask was cooled to -78°C and freshly distilled Tf_2O (14 μL , 0.10 mmol) was added. The reaction mixture was allowed to slowly warm to -10°C . The reaction was quenched with a saturated solution of NH_4Cl and extracted with CH_2Cl_2 . The organic layer was dried with MgSO_4 and concentrated in vacuo. The residue was purified via Biotage using a Flash 12+M Cartridge (10% EtOAc in hexanes) to afford the carbamate protected cyclopropyl alcohol (28 mg, 96%). A flame dried round bottom flask (10 mL) equipped with a condenser was flushed with argon and charged with the carbamate protected cyclopropyl alcohol prepared above (10 mg, 0.029 mmol) in THF (1 mL). Then LiAlH_4 (6 mg, 0.15 mmol) was added and the solution was allowed to reflux overnight. Following consumption of starting material (TLC), the reaction mixture was quenched with H_2O , dried with MgSO_4 , filtered through a pad of Celite with EtOAc and concentrated in vacuo. The residue was purified via Biotage using a Flash 12+M Cartridge (16% EtOAc in hexanes) to afford the more polar diastereomer **11** (3 mg, 48%) and the less

polar diastereomer **11** (3 mg, 48%) in a 1:1 diastereomeric ratio. Spectral data for the less polar diastereomer **11** and the more polar diastereomer **11** are included below:

1-(2-Phenethyl-cyclopropyl)-but-3-en-1-ol (11) less polar diastereomer. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.32-7.15 (m, 5H), 5.86 (dddd, $J = 16.9, 10.2, 7.7, 6.5$, 1H), 5.17-5.07 (m, 2H), 2.94 (td, $J = 7.7, 4.6$, 1H), 2.73 (t, $J = 7.9$, 2H), 2.42-2.20 (m, 2H), 1.70-1.43 (m, 2H), 0.78-0.63 (m, 2H), 0.38 (ddd, $J = 8.1, 5.0, 5.0$, 1H), 0.33 (ddd, $J = 8.6, 5.0, 5.0$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 142.3, 135.0, 128.5, 128.4, 125.8, 117.3, 75.1, 41.6, 35.9, 35.4, 25.3, 16.7, 9.7. FTIR (cm^{-1}) 3401, 3063, 3026, 2996, 2920, 2854, 1640, 1603, 1496, 1454, 1030, 996, 912, 745, 698. HRMS calculated for $\text{C}_{15}\text{H}_{20}\text{O}$ ($\text{M}-\text{OH}$) $^+$ m/z 199.1487, found 199.1498.

1-(2-Phenethyl-cyclopropyl)-but-3-en-1-ol (11) more polar diastereomer. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.32-7.14 (m, 5H), 5.87 (dddd, $J = 16.9, 10.4, 7.7, 6.5$, 1H), 5.19-5.09 (m, 2H), 2.98 (td, $J = 7.9, 4.8$, 1H), 2.70 (t, $J = 7.7$, 2H), 2.45-2.24 (m, 2H), 1.62-1.52 (m, 2H), 0.77-0.63 (m, 2H), 0.52 (ddd, $J = 9.2, 4.8, 4.8$, 1H), 0.35 (ddd, $J = 9.8, 4.8, 4.8$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 142.3, 134.9, 128.4, 128.3, 125.8, 117.5, 74.8, 41.8, 35.8, 35.5, 25.4, 16.5, 10.0. FTIR (cm^{-1}) 3392, 3064, 3026, 2996, 2921, 2854, 1640, 1604, 1496, 1454, 1432, 1062, 1030, 995, 912, 745, 698. HRMS calculated for $\text{C}_{15}\text{H}_{20}\text{O}$ ($\text{M}-\text{OH}$) $^+$ m/z 199.1487, found 199.1465.

Triethylsilane Trapping of Cyclopropyl Carbinyl Iminium Ion Intermediate: Preparation of (4-Methoxy-phenyl)-(2-phenethyl-cyclopropylmethyl)-carbamic acid *tert*-butyl ester (12). **Method A:** A flame dried flask was charged with ene carbamate **10b** (21.3 mg, 0.054 mmol) and CH_2Cl_2 (3 mL). The flask was flushed with argon and 2,6-lutidine (16 μL , 0.135 mmol) and triethylsilane (44 μL , 0.270 mmol) were added via syringe. The resulting mixture was cooled to -78°C and then freshly distilled triflic anhydride (18 μL , 0.108 mmol) was added in a single addition via syringe. The mixture was removed from the dry ice bath and

monitored by TLC. The reaction was complete within 5-15 minutes. The solution was quenched with saturated sodium bicarbonate, diluted with 25 mL of CH₂Cl₂, washed with NaHCO₃ (1 × 10 mL) and then dried over MgSO₄ and concentrated. The residue was purified via pipette column using 1:15 (EtOAc:hexanes) as eluent to provide cyclopropane **12** (19.8 mg, 93%) as a colorless oil. **Method B:** A flame dried flask was charged with ene carbamate **10b** (21.3 mg, 0.054 mmol) and CH₂Cl₂ (3 mL). The flask was flushed with argon and 2,6-lutidine (16 µL, 0.135 mmol) was added via syringe. The resulting mixture was cooled to -78 °C and then freshly distilled triflic anhydride (18 µL, 0.108 mmol) was added in a single addition via syringe. The mixture was monitored by TLC and complete consumption of starting material was observed within minutes, confirmed by the presence of the corresponding cyclopropyl aldehyde on the TLC plate. At this point triethylsilane (44 µL, 0.270 mmol) was added via syringe and the mixture was removed from the dry ice bath. After 10 minutes the reaction was quenched with sodium bicarbonate solution. The reaction mixture was diluted with 25 mL of CH₂Cl₂, washed with NaHCO₃ (1 × 10 mL) and then dried over MgSO₄ and concentrated. The concentrated residue was purified via pipette column using 1:15 (EtOAc:hexanes) as eluent to provide cyclopropane **12** (20.4 mg, 96%) as a colorless oil. (Note: For these trapping reactions it is essential that the triflic anhydride was *freshly distilled* over P₂O₅. The trace amount of water and triflic acid contaminants in commercially available triflic anhydride react with the cyclopropyl oxonium or iminium ions and result in only the isolation of the corresponding cyclopropyl aldehydes.)

(4-Methoxy-phenyl)-(2-phenethyl-cyclopropylmethyl)-carbamic acid *tert*-butyl ester (12**).**

¹H NMR (500MHz, CDCl₃) δ (ppm) 7.27-7.24 (m, 2H), 7.17-7.09 (m, 5H), 6.84 (d, *J* = 8.8, 2H), 3.80 (s, 3H), 3.46 (dd, *J* = 14.6, 6.8, 1H), 3.43 (dd, *J* = 13.7, 6.8, 1H), 2.65-2.61 (m, 2H), 1.58-1.40 (m, 11H), 0.80-0.73 (m, 1H), 0.61-0.55 (m, 1H), 0.30 (ddd, *J* = 4.9, 4.4, 3.9, 1H), 0.22 (ddd, *J* = 4.9, 4.4, 3.4 1H). ¹³C NMR (125MHz, CDCl₃) δ (ppm) 157.6, 155.1, 142.4, 135.7, 128.7, 128.3, 128.2, 125.6, 113.8, 79.7, 55.4, 54.1, 35.8, 35.7, 28.4, 18.0, 17.7, 10.6. FTIR (cm⁻¹) 2976, 2928, 2854, 1694, 1604, 1585, 1512, 1454, 1390, 1366, 1293, 1246, 1179, 1153, 1106, 1035, 1005, 859, 834, 743, 699. HRMS calculated for C₂₄H₃₁NO₃ M⁺ *m/z* 381.2304, found 381.2283.