Supporting Information

Ketyl-Allene Cyclizations Promoted By Samarium(II) Iodide

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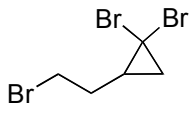
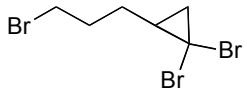
Contents:

Experimental Section

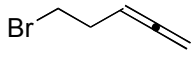
General Procedures (Reagents). Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone under a nitrogen atmosphere. Samarium metal (99.9%, ~40 mesh) was purchased from a commercial supplier and stored in an inert atmosphere. Diiodomethane was distilled under nitrogen, stored over copper beads, and protected from light. HMPA was distilled under nitrogen and stored over 4Å molecular sieves in a Schlenk flask. HMPA is a cancer suspect agent and should be handled with discretion. Standard flash chromatography procedures were followed using 32-63 mm silica gel.[1] The residual $CHCl_3$ was applied as an internal standard (δ = 7.27 ppm) for ^1H spectra while the $CDCl_3$ signal served as internal standard (δ = 77.00) for ^{13}C spectra. Standard benchtop techniques were employed for handling air-sensitive reagents.[2]



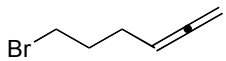
1,1-Dibromo-2-(2-bromo-ethyl)-cyclopropane (**1**).[3] Bromoform (41.90 mL, 480 mmol), 1-bromobutene (6.10 mL, 60 mmol), and benzyltriethylammonium chloride (0.68 g, 3 mmol) were combined in a two-necked round bottomed flask equipped with an addition funnel and reflux condenser. To this solution was added a 50% w/v solution of NaOH in H_2O (72 mL) over 1.5 h at 60 °C. The color of the reaction mixture changed from colorless to yellow to brown after stirring overnight. The reaction was then filtered through a pad of Celite. The reaction mixture was subjected to an aqueous workup, washed with 1 M HCl, then brine and concentrated. The crude material was distilled to provide 13.6 g (74%) of **1** as a clear colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 3.57-3.54 (m, 2H), 2.25-2.18 (m, 1H), 2.08-2.01 (m, 1H), 1.87-1.76 (m, 2H), 1.32 (app t, J = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.7, 30.7, 30.0, 28.3, 27.2; HRMS calcd for $(M-H)^+$ $C_5H_6Br_3$ 302.8029, found 302.8034.



1,1-Dibromo-2-(3-bromo-propyl)-cyclopropane (**2**).[29] Prepared from 1-bromopentene (17.85 g, 120 mmol) according to the procedure of **1** to afford **2** in 81% yield (31.27 g, 97.0 mmol) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.51-3.43 (m, 2H), 2.17-2.01 (m, 2H), 1.80-1.64 (m, 3H), 1.60-1.54 (m, 1H), 1.26 (app t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.8, 31.3, 31.1, 30.4, 28.5, 28.4; IR (neat) 2959, 2943, 1432, 1250, 1206, 1116 cm^{-1}; HRMS triple Br pattern calcd for $C_6H_9Br_3$ (M^+) 317.8254, found 317.8240, calcd for $C_6H_9Br_2{}^{81}Br$ (M^+) 319.8234, found 319.8225, calcd for $C_6H_9Br^{81}Br_2$ (M^+) 321.8213, found 321.8207.

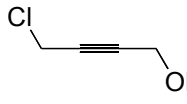


5-Bromo-penta-1,2-diene (**3**).[4,5] To a solution of **1** (13.20 g, 43.0 mmol) in Et_2O (17 mL) was added MeLi (29.5 mL as a 1.6 M solution in Et_2O, 47.3 mmol) via a syringe pump over 45 min at – 40 °C. The reaction mixture was warmed to 0 °C, then was carefully quenched with water followed by an aqueous workup. The crude mixture was purified by a bulb to bulb distillation to provide 4.50 g (72%) of **3** as a clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 (dddd, J = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.76 (ddd, J = 6.7, 3.0, 3.0 Hz, 2H), 3.44 (t, J = 7.1 Hz, 2H), 2.60-2.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 87.6, 75.9, 31.8, 31.7.

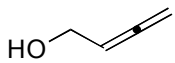


6-Bromo-hexa-1,2-diene (**4**).[4] Prepared from **2** (4.00 g, 12.47 mmol) according to the procedure for **2** to provide 1.66 g (83%) of **4** as a clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (dddd, J = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.70 (ddd, J = 6.6, 3.3, 3.3 Hz, 2H), 3.46 (appt t, J = 6.7 Hz, 2H), 2.18-2.13 (m, 2H), 2.01-1.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.6, 88.3, 75.3, 32.8,

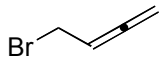
31.8, 26.5; IR (neat) 2940, 1956, 1704, 1436, 846 cm^{-1}; HRMS calcd for $C_6H_{10}Br$ ($M+H^+$) 160.9966, found 160.9974.



4-Chloro-but-2-yn-1-ol (**46**).[6] To a solution of but-2-yne-1,4-diol (64.59 g, 0.75 mol) in a mixture of benzene (75 mL) and pyridine (67.1 mL, 0.825 mol) was added thionyl chloride (60.17 mL, 0.825 mmol) dropwise over 5 h at 0 °C. The reaction mixture was stirred overnight and allowed to warm to rt. The reaction mixture was then poured into ice water (200 mL) and then extracted with Et_2O, washed with an aqueous solution of sodium bicarbonate and water, then dried with $MgSO_4$. The crude mixture was distilled to provide 30.0 g (40%) of 4-chloro-but-2-yn-1-ol as well as 15.2 g (17%) of 1,4-dichloro-but-2-yne. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 (t, J = 2.0 Hz, 2H), 4.16 (t, J = 2.0 Hz, 2H), 3.05 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 84.6, 80.5, 50.9, 30.3.

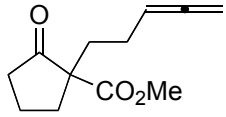


Buta-2,3-dien-1-ol (**5**).[7] To a solution of **46** (20.91 g, 200 mmol) in Et_2O (400 mL) in a three-necked round bottom flask equipped with a stirrer, solid addition funnel, and reflux condenser was added $LiAlH_4$ (8.40 g of 95% solid, 210 mmol) slowly to maintain a gentle reflux. After the addition of the solid was complete, the addition funnel was rinsed with Et_2O (20 mL). The suspension was stirred for an additional 30 min and then cooled to 0 °C. The reaction mixture was then quenched with water (8.4 mL), and a 15% aqueous solution of NaOH (8.4 mL), followed by an additional 25.2 mL of ice/water. The gray slurry was stirred overnight, filtered, dried, and then distilled to provide 12.18 g (87%) of **5** as a clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (dddd, J = 6.2, 6.2, 6.2, 6.2 Hz, 1H), 4.86 (ddd, J = 6.6, 3.0, 3.0 Hz, 2H), 4.15 (ddd, J = 6.1, 3.0, 3.0 Hz, 2H), 1.65 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 90.6, 77.2, 60.2.

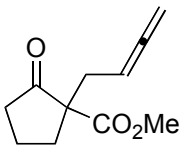


4-Bromo-buta-1,2-diene (**6**). Prepared according to a literature procedure[8] from **5**, then purified via a bulb to bulb distillation to afford 8.04 g (60%) of **6**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (dddd, *J* = 8.2, 8.2, 6.5, 6.5 Hz, 1H), 4.91 (ddd, *J* = 6.6, 2.0, 2.0 Hz, 2H), 3.93 (ddd, *J* = 8.2, 2.0, 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 89.3, 77.1, 29.8.

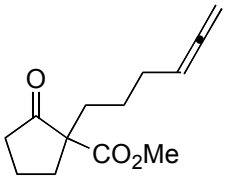
General Procedure for Alkylation of β-Keto Esters.[11]



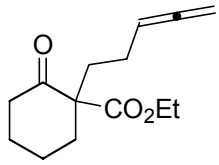
2-Oxo-1-penta-3,4-dienyl-cyclopentanecarboxylic Acid, Methyl Ester (**8**). To a suspension of NaH (0.295 g of a 60% dispersion in mineral oil, 7.4 mmol) in DMF (6 mL) was added 2-oxo-cyclopentanecarboxylic acid, methyl ester (952 mg, 6.70 mol) at 0 °C. The reaction mixture was stirred for 1 h and allowed to warm to rt. After 3 h at rt, the reaction mixture was cooled to 0 °C and to it was added 5-bromo-penta-1,2-diene **3** (1.0 g, 7.4 mmol). The reaction was stirred for 24 h and then quenched with a saturated aqueous solution of NH_4Cl and subjected to an aqueous workup. Purification by column chromatography (15% Et_2O in petroleum ether) provided the desired β-keto ester in 55% yield (770 mg, 3.70 mmol) as a colorless oil. R_f = 0.52 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (dddd, *J* = 6.5, 6.5, 6.5, 6.5 Hz, 1H), 4.67 (ddd, *J* = 6.5, 3.2, 3.2 Hz, 2H), 3.71 (s, 3H), 2.55-2.51 (m, 1H), 2.40-2.36 (m, 1H), 2.29-2.22 (m, 1H), 2.07-1.88 (m, 6H), 1.71-1.65 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.4, 208.7, 171.3, 89.3, 75.5, 60.1, 52.4, 37.8, 33.1, 32.8, 23.7, 19.5; IR (neat) 2954, 1955, 1750, 1724, 848 cm^{-1}; HRMS calcd for $C_{12}H_{17}O_3$ ($M+H^+$) 209.1178, found 209.1188; LRMS (CI) *m/z* 209, 191, 177, 149, 131.



1-Buta-2,3-dienyl-2-oxo-cyclopentanecarboxylic Acid, Methyl Ester (**7**).[12] Prepared with slight modification of the general procedure for alkylations of β-keto esters using bromoallene **6** (3.99 g, 30 mmol, 1.5 equiv) and heating the reaction mixture for 12 h to 50 °C to afford 3.66 g (94%) of **7** as a colorless oil. R_f = 0.15 (15% Et_2O in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.99 (dddd, *J* = 7.6, 7.6, 6.7, 6.7 Hz, 1H), 4.65 (ddd, *J* = 6.7, 2.6, 2.6 Hz, 2H), 3.65 (s, 3H), 2.62-2.57 (m, 1H), 2.45-2.36 (m, 2H), 2.31-2.20 (m, 2H), 2.08-1.89 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.0, 210.0, 171.0, 84.9, 74.7, 60.1, 52.2, 37.9, 32.7, 32.1, 19.3; IR (neat) 2955, 1955, 1751, 1726, 849 cm^{-1}; HRMS calcd for $C_{11}H_{14}O_3Na$ ($M+Na^+$) 217.0841, found 217.0851. LRMS (CI) *m/z* 195, 177, 163, 135, 117.

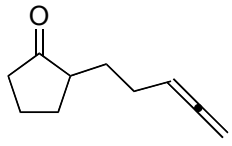


1-Hexa-4,5-dienyl-2-oxo-cyclopentanecarboxylic Acid, Methyl Ester (**9**). Prepared according to the general procedure for alkylations of β-keto esters using bromoallene **4** (848 mg, 5.27 mmol) to afford 706 mg (61%) of **9** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (dddd, *J* = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.63 (ddd, *J* = 6.6, 3.2, 3.2 Hz, 2H), 3.68 (s, 3H), 2.53-2.50 (m, 1H), 2.40-2.35 (m, 1H), 2.28-2.20 (m, 1H), 2.00-1.86 (m, 6H), 1.61-1.55 (m, 1H), 1.47-1.39 (m, 1H), 1.36-1.29 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.5, 208.5, 171.4, 89.3, 74.9, 60.4, 52.4, 37.8, 33.3, 32.7, 28.3, 24.3, 19.5; IR (neat) 2953, 1955, 1752, 1724, 847 cm^{-1}; HRMS calcd for $C_{13}H_{18}O_3Na$ ($M+Na^+$) 245.1155, found 245.1142.



2-Oxo-1-penta-3,4-dienyl-cyclohexanecarboxylic Acid, Ethyl Ester (**10**). Prepared from 2-oxo-1-penta-3,4-dienyl-cyclohexanecarboxylic acid, ethyl ester (2.50 g, 18.50 mmol) according to the general procedure for alkylations of β-keto esters to afford **10** in 57% yield (2.37 g, 10.5 mmol) as a pale yellow, clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (dddd, J = 6.6, 6.6, 6.6, 6.6 Hz, 1H), 4.62 (ddd, J = 6.6, 3.3, 3.3 Hz, 2H), 4.20-4.11 (m, 2H), 2.48-2.36 (m, 3H), 1.98-1.93 (m, 3H), 1.87-1.81 (m, 1H), 1.70-1.59 (m, 4H), 1.44-1.39 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 207.5, 171.8, 89.5, 75.3, 61.1, 60.4, 41.0, 36.1, 33.9, 27.5, 23.0, 22.5, 14.0; IR (neat) 2940, 1956, 1716, 850 cm^{-1}; HRMS calcd for $C_{14}H_{21}O_3$ ($M+H^+$) 237.1491, found 237.1687; LRMS (CI) *m*/*z* 265, 191, 171.

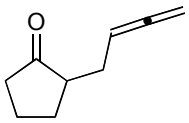
General Procedure for Synthesis of Carbonyl Substrates via Alkylation of Hydrazones.[13,14]



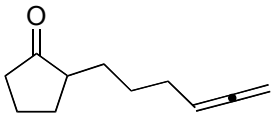
2-Penta-3,4-dienyl-cyclopentanone (**12**).[15] To a solution of LDA (13.2 mmol) in THF (22 mL) was added *N*'-cyclopentylidene-*N*,*N*-dimethyl-hydrazine (1.51 g, 12 mmol) at -78 °C. The resulting suspension was stirred for 2 h, warming to rt. The reaction mixture was then cooled to –78 °C, followed by addition of 5-bromo-penta-1,2-diene **3** (1.78 g, 13.2 mmol). The reaction was then stirred overnight, warming to rt.

Aqueous workup afforded the crude alkylated hydrazone, which could be used without further purification in the next step. To a solution of the crude alkylated hydrazone in acetone (50 mL) was added wet Amberlyst ion-exchange resin (6 g). The reaction was stirred for 4 h at rt. The reaction was filtered then concentrated. The residue was diluted with Et_2O. This was followed by an aqueous

workup and purification by via column chromatography (15% Et_2O in petroleum ether) to afford 1.53 g (85%) of **12** as a colorless, clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (dddd, *J* = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.65 (ddd, *J* = 6.7, 3.2, 3.2 Hz, 2H), 2.28-2.20 (m, 2H), 2.13-1.98 (m, 5H), 1.88-1.86 (m, 1H), 1.78-1.75 (m, 1H), 1.54-1.49 (m, 1H), 1.40-1.34 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 221.2, 208.5, 89.3, 75.0, 48.5, 38.1, 29.5, 28.9, 26.1, 20.7; IR (neat) 2940, 1955, 1736, 1452, 844 cm^{-1}; HRMS calcd for $C_{10}H_{14}O$ (M+) 150.1045; found 150.1050.

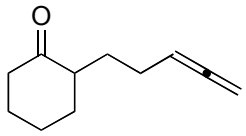


2-Buta-2,3-dienyl-cyclopentanone (**11**).[15] Prepared with slight modification of the general procedure for carbonyl substrates by alkylation with bromoallene **6** (500 mg, 3.76 mmol, 1 equiv) to afford 358 mg (70%) of **11** as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (dddd, *J* = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.70-4.67 (m, 2H), 2.47-2.42 (m, 1H), 2.30-2.15 (m, 3H), 2.13-2.08 (m, 1H), 2.04-1.98 (m, 2H), 1.82-1.78 (m, 1H), 1.64-1.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.3, 208.9, 87.6, 75.2, 48.7, 38.1, 29.1, 28.4, 20.6; IR (neat) 2963, 1956, 1739 cm^{-1}; HRMS calcd for $C_9H_{12}O$ (M^+) 136.0888, found 136.0893.

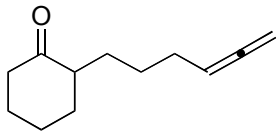


2-Hexa-4,5-dienyl-cyclopentanone (**13**). Prepared according to the general procedure for carbonyl substrates by alkylation with bromoallene **4** (665 mg, 4.12 mmol) to afford 636 mg (94% yield, 90% pure) of **13** as a pale yellow, clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (dddd, *J* = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.64 (ddd, *J* = 6.7, 3.3, 3.3 Hz, 2H), 2.31-2.18 (m, 2H), 2.14-1.98 (m, 5H), 1.82-1.71 (m, 2H), 1.56-1.42 (m, 3H), 1.32-124 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 221.4, 208.5,

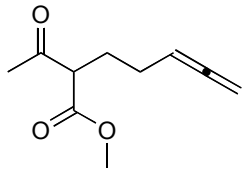
89.6, 74.8, 49.0, 38.1, 29.6, 29.1, 28.1, 27.0, 20.7; IR (neat) 2936, 1955, 1732, 1455, 843 cm^{-1}; HRMS calcd for $C_{10}H_{16}O$ (M^+) 164.1201, found 164.1196; calcd for ($M+H^+$) 165.1279, found 165.1282.



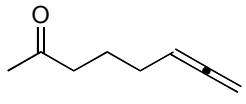
2-Penta-3,4-dienyl-cyclohexanone (**14**).[16] Prepared from the hydrazone of cyclohexanone (694 mg, 4.95 mmol) according to the general procedure for carbonyl substrates to afford 2.98 g (60%) of **14** as a clear, colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.08 (dddd, J = 6.5, 6.5, 6.5, 6.5 Hz, 1H), 4.66 (ddd, J = 6.5, 3.2, 3.2 Hz, 2H), 2.42-2.27 (m, 3H), 2.14-2.10 (m, 1H), 2.07-1.99 (m, 3H), 1.97-1.91 (m, 1H), 1.89-1.84 (m, 1H), 1.74-1.61 (m, 2H), 1.42-1.37 (m, 1H), 1.36-1.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.1, 208.5, 89.7, 74.9, 49.9, 42.1, 33.9, 28.6, 28.0, 25.7, 25.0; IR (neat) 2933, 1954, 1750, 1709, 1448, 843 cm^{-1}; HRMS calcd for $C_{11}H_{16}O$ (M^+) 164.1201, found 164.1205, calcd for $C_{11}H_{15}$ ($M\text{-}OH^+$) 147.1177, found 147.1178.



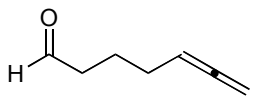
2-Hexa-4,5-dienyl-cyclohexanone (**15**).[16] Prepared from the hydrazone of cyclohexanone (695 mg, 4.95 mmol) according to the general procedure for carbonyl substrates by alkylation with bromoallene **4** (806 mg, 5.0 mmol) to afford 573 mg (65%) of **15** as a clear, colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.09 (dddd, J = 6.6, 6.6, 6.6, 6.6 Hz, 1H), 4.65 (ddd, J = 6.5, 3.2, 3.2 Hz, 2H), 2.42-2.36 (m, 1H), 2.33-2.25 (m, 2H), 2.15-2.08 (m, 1H), 2.07-1.95 (m, 3H), 1.89-1.78 (m, 2H), 1.74-1.59 (m, 2H), 1.44-1.35 (m, 3H), 1.28-1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 208.4, 89.7, 74.7, 50.5, 41.9, 33.8, 28.8, 28.2, 28.0, 26.6, 24.8; IR (neat) 2933, 1956, 1711, 842 cm^{-1}; HRMS calcd for $C_{12}H_{19}O$ ($M+H^+$) 179.1436, found 179.1830.



2-Acetyl-hepta-5,6-dienoic Acid, Methyl Ester (**16**). Prepared from 3-oxo-butyric acid, methyl ester (1.28 g, 11.0 mmol) according to the general procedure for alkylation of β-keto esters to afford 6.59 g (60% yield, 88% pure by GC/MS) of **16**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (dddd, *J* = 6.4, 6.4, 6.4, 6.4 Hz, 1H), 4.73-4.69 (m, 2H), 3.75 (s, 3H), 3.54 (dd, *J* = 7.0, 6.3 Hz, 1H), 2.25 (s, 3H), 2.05-1.97 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 202.8, 170.1, 88.6, 75.5, 58.6, 52.4, 29.0, 27.2, 25.1; IR (neat) 2954, 1955, 1744, 1716, 849 cm^{-1}; HRMS calcd for $C_{10}H_{15}O_3$ ($M+H^+$) 183.1021, found 183.1029.

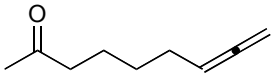


Octa-6,7-dien-2-one (**17**).[17] Prepared from the hydrazone of acetone (400 mg, 4.00 mmol) according to the general procedure for carbonyl substrates to afford 1.49 g (31%) of **17** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (dddd, *J* = 6.6, 6.6, 6.6, 6.6 Hz, 1H), 4.68 (ddd, *J* = 6.6, 3.2, 3.2 Hz, 2H), 2.48 (t, *J* = 7.4 Hz, 2H), 2.14 (s, 3H), 2.05-1.99 (m, 2H), 1.72 (dddd, *J* = 7.4, 7.4, 7.4, 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 208.6, 89.2, 76.0, 42.8, 29.9, 27.5, 23.0; IR (neat) 2941, 1956, 1716, 1439, 846 cm^{-1}; HRMS calcd for $C_8H_{13}O$ ($M+H^+$) 125.0966, found 125.09697.

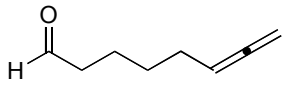


Hepta-5,6-dienal (**18**).[26] Prepared from the hydrazone of acetaldehyde (379 mg, 4.40 mmol) according to the general procedure for carbonyl substrates to afford 107 mg (24%) of **18** as

an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.7 Hz, 1H), 5.07 (dddd, *J* = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.67 (ddd, *J* = 6.6, 3.2 Hz, 2H), 2.48 (td, *J* = 7.3, 1.7 Hz, 2H), 2.05-1.99 (m, 2H), 1.76 (dddd, *J* = 7.2, 7.2, 7.2, 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 202.2, 89.0, 75.2, 43.1, 27.3, 21.2; IR (neat) 2936, 2362, 1956, 1742 cm^{-1}; HRMS calcd for C_7H_9 ($M\text{-}OH^+$) 93.0704, found 93.0704.

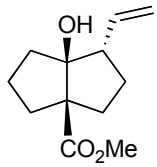


Nona-7,8-dien-2-one (**19**). Prepared from the hydrazone of acetone (440 mg, 4.40 mmol) with modification to the general procedure for carbonyl substrates by alkylation with bromoallene **4** (644 mg, 4.00 mmol) to afford 182 mg (30%) of **19**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (dddd, *J* = 6.8, 6.8, 6.8, 6.8 Hz, 1H), 4.65 (ddd, *J* = 7.3, 3.2, 3.2 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 2.03-1.98 (m, 2H), 1.64-1.59 (m, 2H), 1.45-1.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 208.5, 89.5, 74.8, 43.5, 29.8, 29.3, 27.9, 23.2; IR (neat) 2923, 2360, 1713 cm^{-1}; HRMS calcd for C_9H_{13} ($M\text{-}OH^+$) 121.1017, found 121.1014.

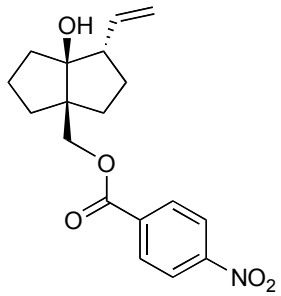


Octa-6,7-dienal (**20**).[27] Prepared from the hydrazone of acetaldehyde (379 mg, 4.40 mmol) with modification to the general procedure for carbonyl substrates by alkylation with bromoallene **4** (600 mg, 3.7 mmol) to afford 238 mg (27% yield, 80% pure by GC/MS) of **20** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.8 Hz, 1H), 5.09 (dddd, *J* = 6.7, 6.7, 6.7, 6.7 Hz, 1H), 4.66 (ddd, *J* = 6.6, 3.2, 3.2 Hz, 2H), 2.44 (td, *J* = 7.3, 1.8 Hz, 2H), 2.06-2.00 (m, 2H), 1.71-1.65 (m, 2H), 1.50-1.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.6, 202.5, 89.4, 74.9, 43.6, 28.4, 27.8, 21.5; IR (neat) 2929, 1954, 1724, 844 cm^{-1}; HRMS calcd for $C_8H_{12}O$ (M^+) 124.0888, found 124.0883.

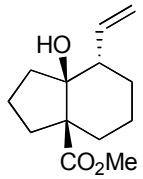
General Procedure for the Ketyl-Allene Cyclization Reactions Using Samarium(II) Iodide.



(1*R, 3a*S**, 6a*R**) 6a-Hydroxy-1-vinyl-hexahydro-pentalene-3a-carboxylic Acid, Methyl Ester** (**21**). To a vigorously stirred suspension of Sm metal (211 mg, 1.4 mmol) in dry THF (13 mL) under N_2 was added diiodomethane (100.4 μL, 1.25 mmol). The resultant mixture was stirred for a minimum of 2 h at ambient temperature and protected from light to afford a deep blue solution To this solution was added HMPA (1.74 mL, 10 mmol), changing the reagent color to purple, followed by dropwise addition of a 0.1 M solution of **8** (104 mg, 0.5 mmol) via cannula in THF (5 mL). The reaction mixture was stirred for 0.5 - 4 h until completion (determined by TLC or GC) and quenched with an aqueous solution of Rochelle's salt[19] (potassium sodium tartrate) and extracted with Et_2O or EtOAc (4 x 6 mL). The combined organic layers were then washed with H_2O (5 x 3 mL) and with brine, then dried over $MgSO_4$. The product was purified by flash chromatography (30% Et_2O in petroleum ether) to afford 72 mg (68%, >95:5 ds) of **21** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93-5.87 (m, 1H), 5.12-5.08 (m, 2H), 3.73 (s, 3H), 2.67 (bs, 1H), 2.65-2.60 (m, 1H), 2.50-2.45 (m, 1H), 2.32 (ddd, *J* = 13.1, 11.8, 7.5 Hz, 1H), 1.83-1.74 (m, 2H), 1.72-1.65 (m, 1H), 1.64-1.54 (m, 3H), 1.51-1.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 137.0, 116.0, 93.5, 61.9, 54.5, 51.0, 37.7, 36.8, 35.0, 27.9, 25.2; IR (neat) 3500, 3078, 2952, 1713, 1435, 1640 cm^{-1}; HRMS calcd for $C_{12}H_{19}O_3$ ($M+H^+$) 211.1334, found 211.1338.

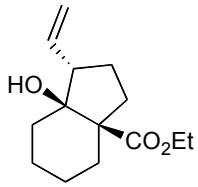


(1*R, 3a*R**, 4*R**) 4-Nitro-benzoic Acid, 6a-Hydroxy-1-vinyl-hexahydro-pentalen-3a-yl Methyl Ester** (**22**). To a solution of 6a-hydroxymethyl-3-vinyl-hexahydro-pentalen-3a-ol, **53**, (24 mg, 0.132 mmol) in CH_2Cl_2 (2.0 mL) was added pyridine (21 μL, 0.26 mmol), DMAP (1 mg, catalytic), and 4-nitrobenzoyl chloride (31 mg, 0.17 mmol). The reaction was stirred overnight at room temperature, then subjected to an aqueous workup. The crude material was then purified via column chromatography (25% EtOAc in hexanes) to provided 31 mg (71%) of **22** as a white powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 5.95-5.88 (m, 1H), 5.16-5.12 (m, 2H), 4.41-4.36 (m, 2H), 2.54-2.45 (m, 1H), 2.00-1.22 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 150.6, 137.3, 135.9, 130.6, 123.6, 116.3, 91.6, 70.3, 55.4, 53.7, 38.6, 38.4, 34.5, 27.1, 24.1; IR (neat) 3520, 3078, 1723, 1640, 1608, 1529, 1276 cm^{-1}; HRMS calcd for $C_{18}H_{22}NO_5$ ($M+H^+$) 332.14980, found 332.1496, calcd for $C_{18}H_{20}NO_4$ ($M-OH^+$) 314.1392, found 314.1391; mp 79 – 80 °C; X-ray structure see page S147.

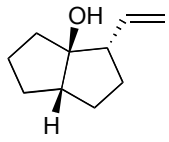


(3a*R, 7*R**, 7a*R**) 7a-Hydroxy-7-vinyl-octahydro-indene-3a-carboxylic Acid, Methyl Ester (23)**. Prepared from **9** (114 mg, 0.5 mmol) according to the general procedure for cyclization using SmI_2 to afford 30 mg (27%) of **23**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (ddd, *J* = 17.4, 10.6, 6.9 Hz, 1H), 5.08 (ddd, *J* =17.4, 1.7, 1.7 Hz, 1H), 5.06 (ddd, *J* =10.5, 1.8, 1.8 Hz, 1H), 3.73 (s, 3H), 3.50 (bs, 1H), 2.65-2.60 (m, 1H), 2.29-2.24 (m, 1H), 2.02-1.98 (m, 1H), 1.91-1.83 (m, 2H), 1.76-1.51 (m, 5H), 1.41-1.25 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 139.7, 114.8, 83.5, 56.9, 51.8, 47.4,

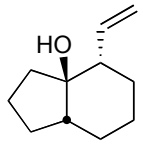
34.6, 33.5, 30.6, 29.1, 22.5, 18.7; IR (neat) 3524, 2947, 2864, 1709, 1452 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_3$ (M^+) 224.1412, found 224.1415.



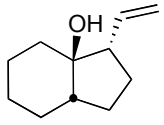
(1*R, 3a*S**, 7a*R**) 7a-Hydroxy-1-vinyl-octahydro-indene-3a-carboxylic Acid, Ethyl Ester** (**24**).[20] Prepared from **10** (112 mg, 0.50 mmol) according to the general procedure for cyclization using SmI_2 to afford 29 mg (24% yield, 84% pure) of **24**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 17.2, 10.6, 7.2 Hz, 1H), 5.08-5.03 (m, 2H), 4.34 (bd, *J* = 2.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.63 (br q, *J* = 9.6 Hz, 1H), 2.15-2.10 (m, 1H), 1.95-1.78 (m, 3H), 1.74-1.67 (m, 1H), 1.64-1.47 (m, 6H), 1.45-1.37 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 137.7, 115.9, 79.7, 60.9, 52.4, 54.4, 29.8 (29.4), 28.8 (28.2), 26.8 (26.5), 23.7 (24.0), 20.8, 20.5, 14.1; IR (neat) 3482, 2935, 1955, 1693, 1649 cm^{-1}; HRMS calcd for $C_{14}H_{22}O_3Na$ ($M+Na^+$) 216.1467, found 261.1470.



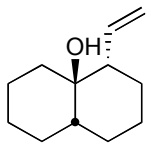
(3*R, 3a*R**, 6*R**) 3-Vinyl-hexahydro-pentalen-3a-ol** (**25**).[15] Prepared from **12** (75 mg, 0.5 mmol) according to the general procedure for cyclization using SmI_2 to afford 51 mg (68%, >95:5 ds) of **25** as a clear, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.5, 10.3, 7.3 Hz, 1H), 5.11-5.04 (m, 2H), 2.48-2.43 (m, 1H), 2.19 (appt q, *J* = 8.5 Hz, 1H), 2.13-2.07 (m, 1H), 1.93-1.85, (m, 1H), 1.78-1.71 (m, 2H), 1.67-1.60 (m, 2H), 1.51-1.41 (m, 3H), 1.31-1.25 (m, 1H), 1.12-1.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 115.5, 92.6, 55.5, 50.5, 37.5, 34.8, 29.9, 29.6, 25.8; IR (neat) 3372, 2949, 2867, 1638 cm^{-1}; HRMS calcd for $C_{10}H_{17}O$ ($M+H^+$) 151.1123, found 151.1124; LRMS (CI) 135.11658.



(3a*R, 4*R**) 4-Vinyl-octahydro-inden-3a-ol** (**26**).[20] Prepared from **13** (82 mg, 0.5 mmol) according to the general procedure for cyclization using SmI_2 to afford 60 mg (72%, >95:5 ds) of **26** as an oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddd, *J* = 17.2, 10.2, 8.6 Hz, 1H), 5.15-5.07 (m, 2H), 2.31-2.26 (m, 1H), 2.14-2.07 (m, 1H), 1.89-1.59 (m, 8H), 1.36-1.23 (m, 4H), 1.03-0.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 116.1, 83.2, 50.8, 47.1, 31.2, 30.8, 29.6, 29.5, 25.0, 20.0; IR (neat) 3395, 3076, 2926, 2855, 2356, 1637 cm^{-1}; HRMS calcd for $C_{11}H_{18}O$ (M^+) 166.1358, found 166.1357.

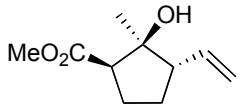


(3*R, 3a*R**) 3-Vinyl-octahydro-inden-3a-ol** (**27**). Prepared from **14** (82 mg, 0.5 mmol) according to the general procedure for cyclization using SmI_2 to afford 73 mg (87%, >95:5 ds) of **27**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H), 5.10-5.04 (m, 2H), 2.42 (ddd, *J* = 9.4, 9.4, 9.4 Hz, 1H), 2.00-1.95 (m, 1H), 1.96-1.83 (m, 1H), 1.71-1.46 (m, 9H), 1.38-1.31 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 117.2, 79.9, 57.0, 44.9, 30.1, 26.6, 25.1, 24.6, 22.0, 21.2; IR (neat) 3395, 2930, 1639 cm^{-1}; HRMS calcd for $C_{11}H_{18}O$ (M^+) 166.1358, found 166.1359.

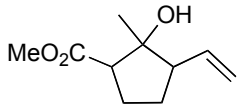


(4*R, 4a*R**) 4-Vinyl-octahydro-naphthalen-4a-ol** (**28**).[20] Prepared from **15** (89 mg, 0.5 mmol) according to the general procedure for cyclization using SmI_2 to afford 41 mg (15%, 88:12 ds) of **28**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02 (ddd, *J* = 16.9, 10.0, 10.0 Hz, 1H), 5.09-5.00 (m, 2H), 2.15-2.11 (m, 1H), 2.09-2.00 (m, 1H), 1.67-1.17 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.95, (138.89), 115.9 (116.4), 72.0, (54.1), 51.4, (42.7), 39.2, 37.4, 28.8, 28.7, 28.0, 26.0, 21.7, 21.0; IR (neat) 3460,

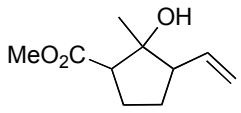
2928, 1715 cm^{-1}; HRMS calcd for $C_{12}H_{20}O$ (M+) 180.1514, found 180.1509; LRMS (CI) *m/z* $(M\text{-}OH)^+$ 163.1492.



(1*R, 2*S**, 3*S**) 2-Hydroxy-2-methyl-3-vinyl-cyclopentanecarboxylic Acid, Methyl Ester** (**29**). According to the general procedure for cyclization using SmI_2, **16** (103 mg with 88% purity, 0.50 mmol) cyclized to provide 52 mg (56%) of a mixture of diastereomers of **29** : **29b** : **29c** in a ratio of 73:20:7. **29**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.5, 10.5, 7.3 Hz, 1H), 5.13-5.08 (m, 2H), 3.73 (s, 3H), 2.88 (app t, *J* = 9.8 Hz, 1H), 2.63-2.58 (m, 1H), 2.47 (bs, 1H), 2.03-1.84 (m, 3H), 1.61-1.52 (m, 1H), 1.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 136.9, 116.7, 80.6, 55.1, 54.0, 51.6, 25.3, 22.2, 18.6; IR (neat) 3484, 2952, 1733, 1640, 1213 cm^{-1}; HRMS calcd for $C_{10}H_{17}O_3$ $(M+H^+)$ 185.1178, found 185.1178, calcd for $(M\text{-}H^+)$ 183.1021, found 183.1022.

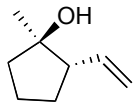


2-Hydroxy-2-methyl-3-vinyl-cyclopentanecarboxylic Acid, Methyl Ester (**29b**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (ddd, *J* = 17.1, 10.2, 8.3 Hz, 1H), 5.09-5.04 (m, 2H), 3.73 (s, 3H), 3.11 (bs, 1H), 2.67-2.59 (m, 2H), 2.16-1.98 (m, 3H), 1.57-1.50 (m, 1H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 115.7, 81.4, 54.5, 52.5, 51.7, 28.2, 26.4, 24.3; IR (neat) 3484, 2954, 1718, 1638, 1211 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$ $(M\text{-}H_2O^+)$ 166.0994, found 166.0987.

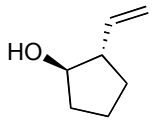


2-Hydroxy-2-methyl-3-vinyl-cyclopentanecarboxylic Acid, Methyl Ester (29c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 17.4, 10.3, 8.1 Hz, 1H), 5.15 (ddd, *J* = 10.3, 2.0, 0.6 Hz,

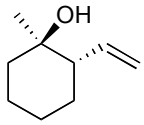
1H), 5.09 (ddd, J = 17.2, 2.0, 1.0 Hz, 1H), 3.74 (s, 3H), 2.67 (appt t, J= 9.74 Hz, 1H), 2.28-2.21 (m, 1H), 2.14-1.85 (m, 5H), 1.32 (s, 3H); IR (neat) 3506, 2955, 1714, 1602 cm^{-1}.



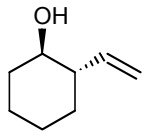
(1*R*, 2S) 1-Methyl-2-vinyl-cyclopentanol** (**30**). Prepared from **17** (125 mg, 1.00 mmol) according to the general procedure for cyclization using SmI_2 to afford 109 mg (87% 94:6 ds) of **30**. ^1H NMR (500 MHz, $CDCl_3$) δ 5.76-5.68 (m, 1H), 5.08-5.02 (m, 2H), 2.40 (app dt, J = 8.3 Hz 1H), 2.00-1.96 (m, 1H), 1.78-1.66 (m, 4H), 1.65 (s, 1H), 1.53-1.47 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 115.5, 80.9, 55.4, 40.2, 29.3, 23.8, 20.7; IR (neat) 3358, 2961, 2874, 1638, 1456, 1375, 911 cm^{-1}; HRMS calcd for $C_8H_{14}O$ (M^+) 126.1045, found 126.1041, calcd for C_8H_{12} ($M\text{-}H_2O^+$) 108.0939, found 108.934.



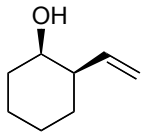
***trans*-2-Vinyl-cyclopentanol** (**31**).[21] Prepared from **18** (81 mg, 0.74 mmol) according to the general procedure for cyclization using SmI_2 to afford 58 mg (70%, >95:5 ds) of **31**. ^1H NMR (500 MHz, $CDCl_3$) δ 5.80-5.72 (m, 1H), 5.80-5.72 (m, 2H), 3.88 (app dq J = 6.7, 0 Hz, 1H), 2.39-2.27 (m, 1H), 2.02-1.89 (m, 2H), 1.80-1.71 (m, 2H), 1.68-1.54 (m, 2H), 1.48-1.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 114.9, 78.3, 52.9, 33.6, 29.5, 21.2; IR (neat) 3336, 2958, 1649, 910 cm^{-1}; HRMS calcd for C_7H_{11} ($M\text{-}OH^+$) 95.0861, found 95.0854.



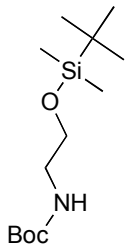
(1*R*, 2S) 1-Methyl-2-vinyl-cyclohexanol** (**32**).[22] Prepared from **19** (138 mg, 1.0 mmol) according to the general procedure for cyclization using SmI_2 to afford 71 mg (51% >95:5 ds) of **32**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85-5.78 (m, 1H), 5.12-5.08 (m, 2H), 2.08-2.04 (m, 1H), 1.26-1.67 (m, 5H), 1.45-1.26 (m, 4H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 116.5, 71.9, 52.8, 40.3, 29.2, 25.1, 23.7, 22.0; IR (neat) 3402, 2930, 1636, 1447, 910 cm^{-1}; HRMS calcd for C_9H_{14} (M-H_2O^+) 122.1096, found 122.1090.



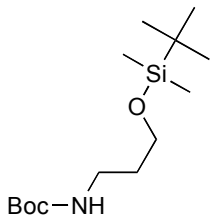
***trans*-2-Vinyl-cyclohexanol** (**33**).[23] According to the general procedure for cyclization using SmI_2, **20** (124 mg, 1.0 mmol) provided 38 mg (30% yield, 89:11 ds) of **33** and 11 mg (9%) of **33B**. **33**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (ddd, *J* = 17.3, 10.3, 8.8 Hz, 1H), 5.19-5.12 (m, 2H), 3.29-3.24 (m, 1H), 2.05-1.16 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 116.7, 72.8, 51.2, 33.8, 31.1, 25.2, 24.8; IR (neat) 3388, 2928, 1640, 1450, 1057 cm^{-1}.



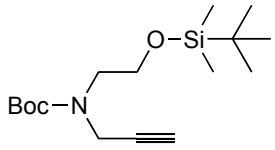
***cis*-2-Vinyl-cyclohexanol** (**33b**).[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (ddd, *J* = 17.3, 10.6, 6.6 Hz, 1H), 5.18-5.11 (m, 2H), 3.87 (bs, 1H), 3.21-2.27 (m, 1H), 1.80-1.26 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 116.9, 69.3, 45.3, 32.2, 25.5, 24.2, 20.9; IR (neat) 3423, 2923, 1728, 1649, 1459 cm^{-1}.



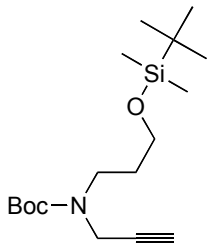
[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-carbamic Acid, *tert*-Butyl Ester (**34**). To a solution of (2-hydroxy-ethyl)-carbamic acid *tert*-butyl ester (65.7 mmol, 10.6 g) in CH_2Cl_2 (150 mL) was added TBSCl (72.27 mmol, 10.9 g), imidazole (98.55 mmol, 6.7 g) and DMAP (9.86 mmol, 1.23 g). The reaction was stirred at rt overnight then quenched with water. The mixture was extracted with CH_2Cl_2, then the combined organic layers were washed with water, a saturated aqueous solution of ammonium chloride, and then brine. The solution was dried with $MgSO_4$ and concentrated. The crude material was purified via column chromatography (30% EtOAC in hexanes) to provide 18.5 g (100%) of **34** as a clear colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (bs, 1H), 3.25-3.22 (m, 2H), 3.66 (t, *J* = 5.0 Hz, 2H), 1.45 (bs, 9H), 0.90 (bs, 9H), 0.07 (bs, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 79.6, 62.7, 43.3, 28.8, 26.3, 18.7, -5.0; IR (neat) 3360, 2931, 2859, 1707, 1508 cm^{-1}; HRMS calcd for $C_{13}H_{29}NO_3Si$ ($M+H^+$) 276.1995, found 276.1989.



[3-(*tert*-Butyl-dimethyl-silanyloxy)-propyl]-carbamic Acid, *tert*-Butyl Ester (**35**).[10] Prepared from (3-hydroxy-propyl)-carbamic acid, *tert*-butyl ester (13.0 g, 74.23 mmol) according to the procedure for **34** to afford 20.0 g (100%) of **35**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (bs, 1H), 3.67 (t, *J* = 5.7 Hz, 2H), 3.24-3.21 (m, 2H), 1.69 (app q, *J* = 6.0 Hz, 2H), 1.39 (m, 9H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 78.6, 62.0, 39.0, 32.0, 28.3, 25.8, 18.1, -5.6; IR (neat) 3358, 2930, 1700, 1506 cm $^{-1}$; HRMS calcd for $C_{14}H_{31}NO_3NaSi$ ($M+Na^+$) 312.1971, found 312.1972.

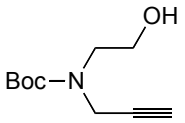


[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-prop-2-ynyl-carbamic Acid, *tert*-Butyl Ester (**36**). To a solution of **34** (18.20 g, 66.1 mmol) in THF (100 mL) was added NaH (3.95 g of a 60% dispersion in mineral oil, 98.55 mmol) in three portions at 0 °C. The suspension was then stirred for 1.5 h at rt and then cooled to 0 °C. To the reaction mixture was added propargyl bromide (24.2 mL of a 80% wt solution in toluene, 164.25 mmol) at 0 °C. The reaction mixture was stirred overnight warming to rt, and then quenched with MeOH. Water was then added to the dark brown reaction mixture, followed by an aqueous workup. The crude material was then purified by column chromatography (5% Et_2O in hexanes) to afford 12.70 g (62%) of **36**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16-4.11 (m, 2H), 3.77-3.75 (m, 2H), 3.43 (t, J = 5.8 Hz, 2H), 2.18 (s, 1H), 1.48 (s, 9H), 0.90 (s, 9H), 0.06 (s, 6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 80.1, 71.3, 61.7, 48.5, 38.1 (37.1), 31.6, 28.4, 25.9, 22.6, 18.2, -5.4; IR (neat) 3313, 2931, 1702, 1249 cm^{-1}; HRMS calcd for $C_{16}H_{31}NO_3Si$ ($M+H^+$) 314.2151, found 314.2167.

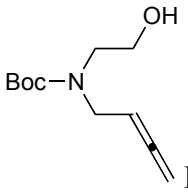


[3-(*tert*-Butyl-dimethyl-silanyloxy)-propyl]-prop-2-ynyl-carbamic acid, *tert*-Butyl Ester (**37**). Prepared from **35** (14.70 g, 50.82 mmol) according to the procedure of **36** to afford 6.54 g (40%) of **37**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.04 (bs, 2H), 2.64 (t, J = 6.3 Hz, 2H), 3.39 (t, J = 7.2 Hz, 2H), 2.17 (app t, J = 2.4 Hz, 1H), 1.81-1.75 (m, 2H), 1.47 (s, 9H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 80.0, 71.1, 60.7, 43.9, 36.6, 31.6, 28.8, 25.9, 22.6, 18.6, -5.4; IR

(neat) 3317, 2955, 2119, 1694, 1410 cm^{-1}; HRMS calcd for $C_{17}H_{34}NO_3Si$ ($M+H^+$) 328.238, found 328.2300.

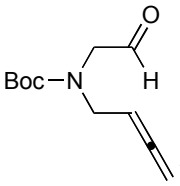


(2-Hydroxy-ethyl)-prop-2-ynyl-carbamic Acid, *tert*-Butyl Ester (**47**). To a solution of **36** (12.90 g, 41.15 mmol) in CH_2Cl_2 (200 mL) was added TBAF (50 mL of a 1.0 M solution in THF, 49.37 mmol) at rt. The reaction mixture was stirred overnight followed then quenched with an aqueous solution of NH_4Cl. Aqueous work up followed by column chromatography (40% EtOAc in hexanes) provided 8.00 g (98%) of (2-hydroxy-ethyl)-prop-2-ynyl-carbamic acid, *tert*-butyl ester as carbamate rotamers. ^1H NMR (500 MHz, $CDCl_3$) δ 4.08 bs, 2H), 3.77 (t, J = 5.1 Hz, 2H), 3.48 (t, J = 5.3 Hz, 2H), 2.82 (bs, 1H) 2.23 (t, J = 2.5 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0 (155.1), 80.8 (79.7), 71.6, 61.6 (60.3), 49.4, 37.8, 29.0, 28.4; IR (neat) 3428, 3296, 2977, 1682, 1411 cm^{-1}; HRMS calcd for $C_{10}H_{18}NO_3$ ($M+H^+$) 200.1287, found 200.1278.

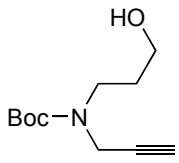


Buta-2,3-dienyl-(2-hydroxy-ethyl)-carbamic Acid, *tert*-Butyl Ester (**48**).[9] A two-necked 500 mL round bottomed flask equipped with a thermometer and reflux condenser with a drying tube was charged with **47** (7.35 g, 36.88 mmol), Cu(I)Br (2.65 g, 18.44 mmol), paraformaldehyde (2.90 g, 92.20 mmol), and diisopropylamine (10.34 mL, 73.76 mmol) in dioxane (100 mL). The reaction mixture was heated to a gentle reflux for 3 h and allowed to stir overnight cooling to rt. The orange-brown solution was then filtered through a plug of Celite, concentrated, then diluted with H_2O (25 mL) and Et_2O (50 mL). The reaction mixture was acidified with 6 M HCl to a pH of 2. The ether layer was

decanted and the organic layer was then extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with water until a pH of 6.5 was obtained, followed by a wash with brine. The solution was dried with $MgSO_4$ and concentrated. The crude material was purified via column chromatography (40% EtOAc in hexanes) to provide 5.25 g (67%) of buta-2,3-dienyl-(2-hydroxy-ethyl)-carbamic acid, *tert*-butyl ester. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17-5.11 (m, 1H), 4.78 (ddd, J = 6.6, 2.8, 2.8 Hz, 2H), 3.86 (bs, 2H), 3.74-3.72 (m, 2H), 3.40 (bt, J = 5.2 Hz, 2H), 2.98 (bs, 1H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 157.0 (155.5), 87.3, 80.3, 76.5, 62.2, 50.0, 47.4, 28.4; IR (neat) 3433, 2977, 1957, 1674, 851 cm^{-1}; HRMS calcd for $C_{11}H_{20}NO_3$ ($M+H^+$) 214.1443, found 214.1447.

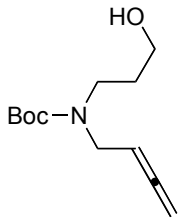


Buta-2,3-dienyl-(2-oxo-ethyl)-carbamic Acid, *tert*-Butyl Ester (**38**).[28] Prepared from **48** (4.00 g, 18.7 mmol) following a literature procedure for a Swern oxidation[18] to provide **38** (3.80 g, 97% yield) as carbamate rotamers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (bs, 1H), 5.09 (bs, 1H), 4.78-4.75 (m, 2H), 3.93-3.83 (m, 4H), 1.44-1.41 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4 (209.0), 199.0, 154.7 (155.5), 86.6, 80.9 (80.7), 76.7, 56.6, (47.3) 47.0, 28.1; IR (neat) 2977, 2818, 1956, 1736, 1698, 854 cm^{-1}; HRMS calcd for $C_{11}H_{18}NO_3$ ($M+H^+$) 212.1287, found 212.1289.

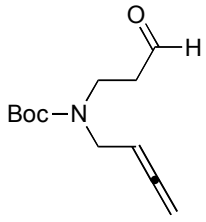


(3-Hydroxy-propyl)-prop-2-ynyl-carbamic Acid, *tert*-Butyl Ester (**49**). Prepared from **37** (10.20 g, 31.10 mmol) according to the procedure of to provide 5.35 g (81%) of (3-hydroxy-propyl)-prop-2-ynyl-carbamic acid, *tert*-butyl ester as carbamate rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (bs, 2H), 3.57 (bs, 2H), 3.50-3.47 (m, 3H), 2.20 (app t, J = 2.5 Hz, 1H), 1.77 (bs, 2H), 1.49 (s,

9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 80.9, 79.5, 71.3, 58.3 (59.7), 42.8, 36.8 (36.0), 30.2 (30.9), 28.2; IR (neat) 3440, 3299, 2976, 1693, 1414, 1367, 1251, 1167 cm^{-1}; HRMS calcd for $C_{11}H_{20}NO_3$ ($M+H^+$) 214.1443, found 214.1443.

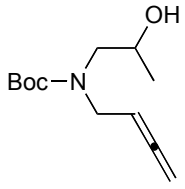


Buta-2,3-dienyl-(3-hydroxy-propyl)-carbamic Acid, *tert*-Butyl Ester (**50**). Prepared from **49** (3.90 g, 18.29 mmol) according to the procedure for **48** to yield 2.80 g (67%) of buta-2,3-dienyl-(3-hydroxy-propyl)-carbamic acid, *tert*-butyl ester as carbamate rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (dddd, J = 6.5, 6.5, 6.5, 6.5 Hz, 1H), 4.74 (ddd, J = 6.6, 2.8, 2.8 Hz, 2H), 3.80-3.67 (m, 3H), 3.54 (bs, 2H), 3.36 (bs, 2H), 1.66 (bs, 2H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 156.6, 87.1, 80.1, 76.1, 58.4 (59.7), 46.2, 42.7, 30.6, 28.4; IR (neat) 3445, 2976, 1957, 1694, 1417 cm^{-1}; HRMS calcd for $C_{12}H_{21}NO_3Na$ ($M+Na^+$) 250.1419, found 250.1428.

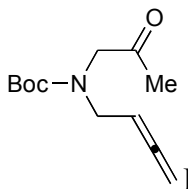


Buta-2,3-dienyl-(3-oxo-propyl)-carbamic Acid, *tert*-Butyl Ester (**39**).[28] Prepared from **50** (2.80 g, 12.3 mmol) following a literature procedure for a Swern oxidation[18] to provide **39** (1.75 g, 63% yield) as carbamate rotamers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, J = 1.7 Hz, 1H), 5.10-5.06 (m, 1H), 4.75 (ddd, J = 5.7, 2.8, 2.8 Hz, 2H), 3.81 (bs, 2H), 3.52 (bs, 2H), 2.69 (bs, 2H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 200.8, 155.0, 87.2, 80.0, 76.4, 46.6 (46.2), 43.3, 40.9,

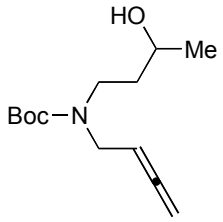
28.3; IR (neat) 2977, 1957, 1731, 1694, 854 cm^{-1}; HRMS calcd for $C_{12}H_{20}NO_3$ ($M+H^+$) 226.1443, found 226.1438.



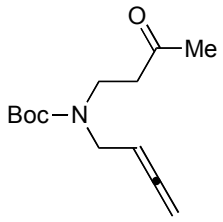
Buta-2,3-dienyl-(2-hydroxy-propyl)-carbamic Acid, *tert*-Butyl Ester (**51**). To a solution of **38** (1.00 g, 4.74 mmol) in THF (10 mL) was added methylmagnesium bromide (1.74 mL of a 3.0 M solution. in Et_2O, 5.21 mmol) at 0 °C. The reaction was stirred for 2 h. The reaction mixture was quenched with water followed by an aqueous workup. Crude material was purified via column chromatography (30% EtOAc in hexanes) to provide 1.05 g (98%) of buta-2,3-dienyl-(2-hydroxy-propyl)-carbamic acid, *tert*-butyl ester. ^1H NMR (500 MHz, $CDCl_3$) δ 5.16-5.13 (m, 1H), 4.81-4.78 (m, 2H), 4.02-3.97 (m, 1H), 3.87 (bs, 2H), 3.32-3.18 (m, 3H), 1.47 (s, 9H), 1.17-1.16 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 157.2, 87.3, 80.3, 76.5, 67.5, 55.2, 47.9, 28.4, 20.9; IR (neat) 3430. 2975, 1957, 1693, 848 cm^{-1}; HRMS calcd for $C_{12}H_{22}NO_3$ ($M+H^+$) 228.1600, found 228.1599.



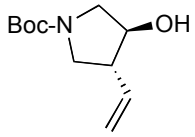
Buta-2,3-dienyl-(2-oxo-propyl)-carbamic Acid, *tert*-Butyl Ester (**40**). Prepared from **51** (1.00 g, 4.40 mmol) following a literature procedure for a Swern oxidation[18] to provide **40** (880 mg, 89% yield) as carbamate rotamers: ^1H NMR (500 MHz, $CDCl_3$) δ 5.02 (bs, 1H), 4.69-4.66 (m, 2H), 3.99 (bs, 1H), 3.92 (bs, 1H), 3.88-3.85 (m, 2H), 2.15 (s, 3H), 1.46 (s, 4.5H), 1.41 (s, 4.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.1, (208.7), 204.1 (204.0), 155.1 (154.7), (86.7) 86.6, 80.4, 76.1 (76.0), 56.0 (56.2), 46.9 (46.6), (28.1) 28.0, 26.7 (26.5); IR (neat) 2977, 1957, 1736, 1698, 1456, 852 cm^{-1}; HRMS calcd for $C_{12}H_{20}NO_3$ ($M+H^+$) 226.1443, found 226.1453.



Buta-2,3-dienyl-(3-hydroxy-butyl)-carbamic Acid, *tert*-Butyl Ester (**52**). Prepared from **39** (1.20 g, 5.30 mmol) according to the procedure for **51** to provide 1.12 g (88%) of buta-2,3-dienyl-(3-hydroxy-butyl)-carbamic acid, *tert*-butyl ester as carbamate rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12, (bs, 1H), 4.79-4.78 (m, 2H), 4.01 (bs, 1H), 3.90-3.61 (m, 4H), 3.41 (bs, 0.5H), 3.21 (bs, 0.5H), 3.00-2.98 (m, 1H), 1.70-1.67 (m, 1H), 1.47 (s, 9H), 1.20-1.19 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 87.2, 80.2, 76.2, (65.17) 63.6, 46.2, (39.5) 43.2, 37.6, 28.4, 22.7; IR (neat) 3440, 2973, 1957, 1674, 1170 cm^{-1}; HRMS calcd for $C_{13}H_{24}NO_3$ ($M+H^+$) 242.1756, found 242.1760.

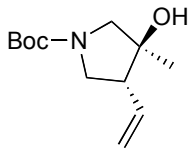


Buta-2,3-dienyl-(3-oxo-butyl)-carbamic Acid, *tert*-Butyl Ester (**41**). Prepared from **52** (1.06 g, 4.39 mmol) following a literature procedure for a Swern oxidation[18] to provide **41** (580 mg, 90% yield) as carbamate rotamers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (bs, 1H), 4.78-4.76 (m, 2H), 3.81 (bs, 2H), 3.44 (bt, J = 6.4 Hz, 2H), 2.71 (bs, 2H), 2.14 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.6, 207.3, 155.1, 87.4, 79.6, 76.3, 46.8 (46.1), 42.5, 42.2 (41.9), 30.1, 28.4; IR (neat) 2976, 1956, 1694, cm^{-1}; HRMS calcd for $C_{13}H_{22}NO_3$ ($M+H^+$) 240.1600, found 240.1603.

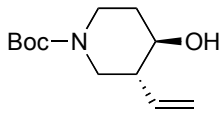


(3*R, 4*S**) 3-Hydroxy-4-vinyl-pyrrolidine-1-carboxylic Acid, *tert*-Butyl Ester** (**42**).[24] Prepared according to the general procedure for cyclization using SmI_2 from **38** (106 mg, 0.5

mmol) to afford 82 mg (77%, 92:8 ds) of **42** as carbamate rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddd, *J* = 17.5, 10.4, 7.7 Hz, 1H), 5.21-5.14 (m, 2H), 4.10 (app q, *J* = 5.7 Hz, 1 H), 3.65 (bs, 2H), 3.23 (bs, 2H), 2.68 (bs, 1H), 2.03 (bs, 1H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 136.4, 117.1, 79.5, 74.8 (74.1), 52.2 (52.0), 50.3 (49.7), 48.8 (48.2), 28.4; IR (neat) 3401, 2977, 1687, 1647, 1478, 1416 cm^{-1}; HRMS calcd for $C_{11}H_{19}NO_3$ ($M+Na^+$) 236.1263, found 236.1260.

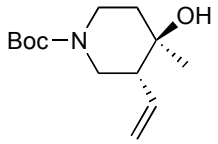


(3*R, 4*S**) 3-Hydroxy-3-methyl-4-vinyl-pyrrolidine-1-carboxylic Acid, *tert*-Butyl Ester** (**43**). Prepared according to the general procedure for cyclization using SmI_2 from **40** (112 mg, 0.5 mmol) to afford 112 mg (98% 95:5 ds) of **43** as carbamate rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73-5.65 (m, 1H), 5.15-5.12 (m, 2H), 3.72-3.64 (m, 1H), 3.40-3.21 (m, 3H), 2.69-2.63 (m, 1H), 2.11 (s, 0.85H), 1.85 (s, 0.15H), 1.46 (s, 9H), 1.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 135.3 (135.2), 117.6 (117.5), 79.5, 78.2 (77.6), 57.9 (57.4), 53.5 (52.9), 49.7 (49.1) 28.5, 22.3; IR (neat) 3408, 2977, 2933, 1682, 1478, 1367 cm^{-1}; HRMS calcd for $C_{12}H_{22}NO_3$ ($M+H^+$) 228.1600, found 228.1591.

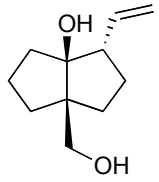


***trans*-4-Hydroxy-3-vinyl-piperidine-1-carboxylic Acid, *tert*-Butyl Ester** (**44**).[25] Prepared from **39** (225 mg, 1.0 mmol) according to the general procedure for cyclization using SmI_2 to afford a 130 mg mixture of **44** and reduced starting material in 57% yield as a 4:1 mixture (with carbamate rotamers). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (ddd, *J* = 17.4, 10.4, 8.4 Hz, 1H), 5.30-5.24 (m, 2H), 4.12-3.74 (m, 2H), 3.48-3.42 (m, 1H), 2.82-2.78 (m, 1H), 2.63-2.58 (m, 1H), 2.11-2.05 (m, 1H), 1.99-1.69 (m, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 136.4, 118.8, 79.7, 71.6,

49.3, 46.5, 42.5, 32.7, 28.4 (29.6); IR (neat) 3434, 2927, 1957, 1694, 1573, 1422 cm^{-1}; HRMS calcd for $C_{12}H_{21}NO_3$ (M^+) 227.1521, found 227.1527.

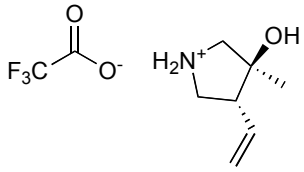


(3*R, 4*R**) 4-Hydroxy-4-methyl-3-vinyl-piperidine-1-carboxylic Acid, *tert*-Butyl Ester** (**45**). Prepared according to the general procedure for cyclization using SmI_2 from **41** (120 mg, 0.5 mmol) to afford 105 mg of a mixture **45** : reduced starting material in 87% yield as a 3.5:1 mixture (with carbamate rotamers). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddd, *J* = 17.1, 10.4, 8.8 Hz, 1H), 5.20-5.12 (m, 2H), 3.86-3.65 (m, 2H), 3.31-2.99 (m, 2H), 2.17 (bs, 1H), 1.90-1.66 (m, 2H), 1.56-1.51 (m, 1H), 1.45 (s, 9H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 136.2, 118.5, 76.1 (72.3), 68.7 (68.6), 51.4, 45.3 (44.5), 42.4 (42.3), 41.5 (40.6), 38.24 (37.4), 20.2, 28.3 (28.4), 26.1 (26.3); IR (neat) 3430, 2976, 1958, 1694, 1672 cm^{-1}; HRMS calcd for $C_{13}H_{23}NO_3Na$ ($M+Na^+$) 264.1576, found 264.1581.

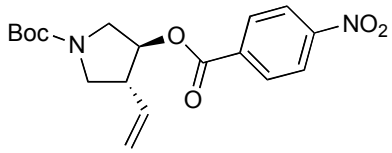


(3*R, 4*S**) 6a-Hydroxymethyl-3-vinyl-hexahydro-pentalen-3a-ol** (**53**). To **21** (0.36 mmol, 75.0 mg) in Et_2O (2 mL) at 0 °C was added a solution of $LiAlH_4$ (0.75 mL of a 1 M solution in Et_2O, 0.75 mmol). The reaction was allowed to warm to rt followed by quenching with 20 μL H_2O, 20 μL of a 15% solution of NaOH, and then 600 μL of water. The crude material was purified via column chromatography to provide 45 mg of 6a-hydroxymethyl-3-vinyl-hexahydro-pentalen-3a-ol in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 17.4, 10.3, 7.4 Hz, 1H), 5.13-5.08, (m, 2H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.55 (d, *J* = 10.7 Hz, 1H), 2.75 (bs, 1H), 2.48-2.42 (m, 1H), 2.36 (s, 1H), 1.88-1.29 (m,

10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 116.0, 92.7, 67.7, 55.8, 54.8, 38.7, 38.4, 33.5, 27.3, 24.5; IR (neat) 3328, 2847, 1640, 1415 cm^{-1}; HRMS calcd for $C_{11}H_{19}O_2$ ($M+H^+$) 183.1385, found 183.1392, calcd for $C_{11}H_{17}O$ ($M-OH^+$) 165.1279, found 165.1281, calcd for $C_{11}H_{16}O$ ($M-H_2O^+$) 164.1201, found 164.1196.



(3*R, 4*S**) 3-Methyl-4-vinyl-pyrrolidin-3-ol, Trifluoro-Acetic Acid Salt** (**54**). To a solution of **43** in CH_2Cl_2 (2.5 mL) was added TFA (0.5 mL). The reaction mixture was stirred for 1 h and then concentrated to a purple oil. The oil was further dried under high-vacuum, then taken up into ether to provide crystals of **43B**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76-8.60 (m, 2H), 5.64 (ddd, *J* = 17.0, 10.4, 8.8 Hz, 1H), 5.27-5.21 (m, 2H), 3.87-3.81 (m, 1H), 3.41-3.30 (m, 2H), 3.18-3.13 (m, 1H), 2.91-2.87 (m, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4 (161.1), 133.6, 119.3, 79.4, 55.4, 52.7, 49.5, 21.0; X-ray structure see page S147.



***trans*-3-(4-Nitro-benzoyloxy)-4-vinyl-pyrrolidine-1-carboxylic Acid, *tert*-Butyl Ester** (**55**). Prepared from **42** (80 mg, 0.22 mmol) according to the procedure for **22** to provide 92 mg (100%) of **55**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 2H), 5.79 (ddd, *J* = 17.5, 10.3, 7.3 Hz, 1H), 5.29 (m, 3H), 3.85-3.81 (m, 1H), 3.69 (bs, 1H), 3.55-3.41 (m, 2H), 3.05 (bs, 1H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 154.3, 150.7, 135.0, 130.8, 123.6, 117.8, 79.9, 78.4, 77.7, 50.1 (49.7), 48.1 (48.7), 46.4 (47.4), 28.4; IR (neat) 2977, 1728, 1698, 1604, 1530 cm^{-1}; HRMS calcd for $C_{18}H_{23}N_2O_6$ ($M+H^+$) 363.1556, found 363.1546, calcd for

$C_{17}H_{19}N_2O_6$ ($M\text{-}CH_3^+$) 347.1243, calcd for $C_{18}H_{21}N_2O_6$ found 347.1245, calcd for ($M\text{-}H^+$) 361.1340, found 361.1395.

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