

Oxidative Carbon–Carbon Bond Formation via Allyldimethylsilyl Enol Ethers

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Part 1: General Methods

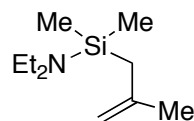
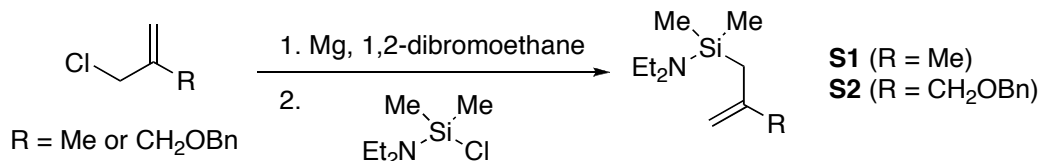
All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. Acetonitrile, THF and CH₂Cl₂ were purified by passage through a bed of activated alumina.¹ 1,2-Dimethoxyethane was distilled from sodium/benzophenone under argon immediately prior to use. Commercially available enones were distilled prior to use. Reagents were purified² prior to use unless otherwise stated. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde, ceric ammonium nitrate stain or potassium permanganate followed by heating. Film infrared spectra were recorded using a BioRad Excalibur and a BioRad FTS-60. Diamond infrared spectra were recorded using a Thermo Mattson ATR. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Inova 500 (500 MHz), Inova 400 (400 MHz) or Bruker Advance III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm) or tetramethylsilane (0.00 ppm). Data are reported as (app = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, sep = septet, o = octet, m = multiplet, b = broad; integration; coupling constant(s) in Hz. Proton-decoupled ¹³C-NMR spectra were recorded on a Varian Inova 500 (125 MHz), Inova 400 (100 MHz) or Bruker Advance III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.00 ppm). Mass spectra data were obtained on an Agilent 6210 Time-of-Flight LC/MS and a Thermo Finnegan Mat 900 XL High Resolution Magnetic Sector.

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

2. Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford. 19388

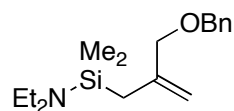
Part 2: Experimental Procedures.

A: Synthesis of Aminosilanes.



***N,N*-Diethyl-1,1-dimethyl-1-(2-methylallyl)silanamine (S1):** 1,2-dibromoethane (0.5 mL) and magnesium turnings (2.0 g, 82 mmol) were dissolved in THF (98 mL) and chilled to 0 °C. Freshly distilled 2-methylallylchloride (8.0 mL, 82 mmol) was added and the reaction was left warming

to room temperature overnight. The reaction mixture was titrated using 2-hydroxybenzaldehyde phenylhydrazone as an indicator to determine a 39% yield (32 mmol). The reaction was then chilled to -78 °C before cannulation of (diethylamino)chlorodimethylsilane (6.3 mL, 32 mmol) in THF (20 mL). After stirring for 15 mins at -78 °C the reaction was left to warm to room temperature overnight. Trituration with pentanes (500 mL) and filtration over celite followed by removal of solvent gave a crude mixture which was purified by vacuum distillation (59 torr, 98–104 °C) to give the desired aminosilane in 72% yield (4.3 g, 23 mmol) as a translucent oil. IR (film) 2963, 1372, 1279, 1248, 1203, 1174, 1027; ¹H NMR (500 MHz, CDCl₃) 4.57 (s, H); 4.48 (s, 1H); 2.79 (dt, 4H, *J*_S = 7.08 Hz, *J*_L = 13.92 Hz); 1.72 (s, 3H); 1.56 (s, 2H); 0.97 (t, 6H, *J* = 7.08 Hz); 0.08 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) 144.4, 108.1, 40.2, 29.2, 25.4, 16.1, -1.6; HRMS (ESI): Exact mass calcd for [M-C₄H₅]⁺, 130.1047. Found 130.1052.

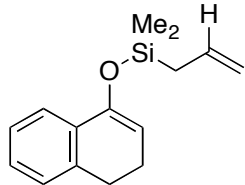


***N,N*-Diethyl-1,1-dimethyl-1-(2-(benzyloxymethyl)allyl)silanamine (S2):**

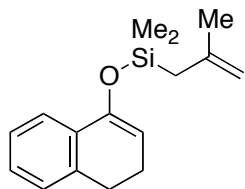
1,2-dibromoethane (69 μL, 0.8 mmol) and magnesium turnings (972 mg, 40 mmol) were dissolved in THF (50 mL) and chilled to 0° C. Freshly prepared benzyloxy-2-chloromethyl-1-propene³ (7.87g, 40.0 mmol) was added and the reaction was left warming to room temperature overnight. The reaction mixture was titrated using 2-hydroxybenzaldehyde phenylhydrazone as an indicator to determine a 45% yield (18 mmol). The reaction was then chilled to -78° C before cannulation of (diethylamino)chlorodimethylsilane (3.6 mL, 18 mmol) in THF (10 mL). After stirring for 15 mins at -78° C the reaction was left to warm to room temperature overnight. Trituration with pentanes (500 mL) and filtration over celite followed by removal of solvent gave a crude mixture which was purified by vacuum distillation (60 millitorr, 100° C) to give the desired aminosilane in 23% yield (1.23g) as a translucent oil. IR (film) 2961, 2856, 1453, 1372, 1248, 1173, 1027; ¹H NMR (500 MHz, CDCl₃) 7.36–7.30 (m, 5H); 4.92 (s, 1H); 4.79 (s, 1H); 4.53 (s, 2H); 3.95 (s, 2H); 2.66 (q, 4H, *J* = 7.1 Hz); 1.12 (t, 6H, *J* = 7.1 Hz); 0.14 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) 143.0, 137.9, 128.9, 128.0, 112.5, 73.0, 71.9, 44.4, 26.6, 15.7, 0.0; HRMS (APPI): Exact mass calcd for C₁₇H₃₀NOSi [M+H]⁺, 292.2091. Found 292.2097.

³Aho, J. E.; Salomaki, E.; Rissanen, K.; Pihko; P. M. *Org. Lett.* **2008**, 10, 4179–4182.

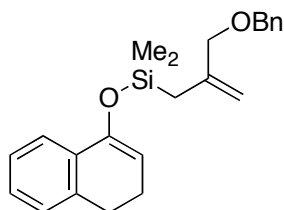
B: Synthesis of the Allylethers.



Allyl(3,4-dihydronaphthalen-1-yloxy)dimethylsilane (5a): A solution of tetralone (0.584 g, 4 mmol) in THF (2 mL) was added dropwise to a stirred solution of LDA at $-78\text{ }^{\circ}\text{C}$ (4.4 mmol, prepared by adding *n*-BuLi [4.4 mmol] to a stirred solution of diisopropylamine [4.8 mmol] in 10 mL THF at $0\text{ }^{\circ}\text{C}$) and was allowed to stir for 30 min. To this mixture, allyl(chloro)dimethyl silane (643 μL , 4.4 mmol) was added dropwise. The reaction was monitored by TLC and upon completion (30 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (873 mg, 89%). IR (film) 3073, 2959, 2883, 1651, 1440, 1426; ^1H NMR (500 MHz, CDCl_3) 7.41 (d, 1H, $J = 7.3$ Hz); 7.21–7.14 (m, 2H); 7.11 (d, 1H, $J = 7.2$ Hz); 5.87–5.79 (m, 1H); 5.20 (t, 1H, $J = 4.6$ Hz); 4.96–4.90 (m, 2H); 2.76 (t, 2H, $J = 7.8$ Hz); 2.32 (ddd, 2H, $J = 4.6, 8.0, 8.2$ Hz); 1.77 (d, 2H, $J = 8.1$ Hz); 0.26 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 148.1, 137.3, 133.8, 133.6, 127.6, 127.2, 126.4, 122.0, 114.4, 105.8, 28.3, 24.8, 22.4, -1.62 ; HRMS (APPI): Exact mass calcd for $\text{C}_{16}\text{H}_{27}\text{OSi}$ [$\text{M}+\text{H}$] $^+$, 244.1278. Found 244.1293.

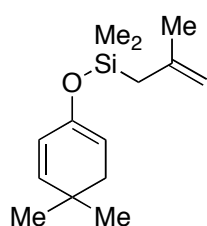


(3,4-Dihydronaphthalen-1-yloxy)dimethyl(2-methylallyl)silane (5b): A solution of tetralone (293 mg, 2 mmol) in THF (4 mL) was added dropwise to a stirred solution of LDA at $-78\text{ }^{\circ}\text{C}$ (2.2 mmol, prepared by adding *n*-BuLi [2.2 mmol] to a stirred solution of diisopropylamine [2.4 mmol] in 15 mL THF at $0\text{ }^{\circ}\text{C}$). In a separate round-bottom flask, acetyl chloride (156 μL , 2.2 mmol) was added dropwise to a stirred solution of aminosilane **S1** (488 mg, 2.2 mmol) in THF (5 mL) at $0\text{ }^{\circ}\text{C}$ and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (473 mg, 92%). IR (film) 3072, 2963, 2887, 1638, 1359; ^1H NMR (500 MHz, CDCl_3) 7.42 (d, 1H, $J = 7.1$ Hz); 7.21–7.10 (m, 3H); 5.20 (t, 1H, $J = 4.4$ Hz); 4.67 (s, 1H); 4.58 (s, 1H); 2.78–2.75 (m, 2H); 2.34–2.30 (m, 2H); 1.79–1.78 (m, 5H); 0.28 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 148.2, 142.5, 137.3, 133.6, 127.5, 126.4, 122.0, 109.7, 105.5, 28.7, 28.4, 25.7, 22.4, -1.17 ; HRMS (APPI): Exact mass calcd for $\text{C}_{16}\text{H}_{23}\text{OSi}$ [$\text{M}+\text{H}$] $^+$, 259.1513. Found 259.1507.



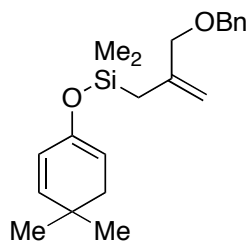
(2-(Benzyloxymethyl)allyl)(3,4-dihydronaphthalen-1-yloxy)dimethylsilane (5c): A solution of tetralone (585 mg, 4.0 mmol) in THF (4 mL) was added dropwise to a stirred solution of LDA at $-78\text{ }^{\circ}\text{C}$ (4.4 mmol, prepared by adding *n*-BuLi [4.4 mmol] to a stirred solution of diisopropylamine [4.8 mmol] in 15 mL THF at $0\text{ }^{\circ}\text{C}$). In a separate round-bottom flask, acetyl chloride (341 μL , 4.8 mmol) was added dropwise to a stirred solution of aminosilane **S2** (1.4 g, 4.8 mmol) in THF (10 mL) at $0\text{ }^{\circ}\text{C}$ and was allowed to stir for 10 min after which time the solution was

transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (30 mL). The mixture was extracted with pentanes (3 x 30 mL), washed with brine (60 mL), and dried (Na₂SO₄). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (1.45 g, 99%). IR (film) 3065, 3031, 2856, 1639, 1496, 1384, 1254; ¹H NMR (500 MHz, CDCl₃) 7.41 (d, 1H, *J* = 6.8 Hz); 7.33 (m, 5H); 7.28 (m, 1H); 7.17 (dt, 1H, *J* = 7.1, 12.7 Hz); 7.11 (m, 1H); 5.19 (t, 1H, *J* = 4.6 Hz); 5.02 (s, 1H); 4.85 (s, 1H); 4.48 (s, 2H); 3.95 (s, 2H); 2.75 (t, 2H, *J* = 7.9 Hz); 2.31 (m, 2H); 1.84 (s, 2H); 0.27 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 148.1, 142.6, 138.6, 137.3, 133.6, 128.6, 127.9, 127.7, 127.6, 127.2, 126.4, 122.0, 110.8, 105.6, 74.4, 72.2, 28.3, 23.5, 22.4, -1.1; HRMS (APPI): Exact mass calcd for C₂₃H₂₉O₂Si [M+H]⁺, 365.1931. Found 365.1903



(4,4-Dimethylcyclohexa-1,5-dienyloxy)dimethyl(2-methylallyl)silane (7a):

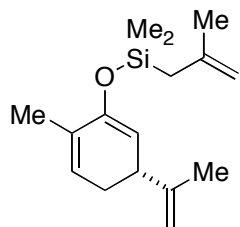
A solution of 4,4-Dimethyl-2-cyclohexen-1-one (186 mg, 1.5 mmol) in THF (2 mL) was added dropwise to a stirred solution of LDA at -78 °C (1.65 mmol, prepared by adding *n*-BuLi [1.65 mmol] to a stirred solution of diisopropylamine [1.8 mmol] in 8 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (117 μL, 1.65 mmol) was added dropwise to a stirred solution of aminosilane **S1** (366 mg, 1.65 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na₂SO₄). Removal of solvent under reduced pressure followed by flash column chromatography on reverse phase 18C column with 20% EtOAc in acetonitrile afforded the desired silyl allyl ether (243 mg, 68%). IR (film) 3075, 2957, 2817, 1652, 1204; ¹H NMR (500 MHz, CDCl₃) 5.55 (s, 2H); 4.79 (s, 1H); 4.64 (s, 1H); 4.55 (s, 1H); 2.11 (d, 2H, *J* = 4.6); 1.76 (s, 3H); 1.70 (s, 2H); 1.00 (s, 6H); 0.21 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 147.3, 142.6, 140.4, 123.9, 109.5, 101.7, 37.2, 31.4, 28.6, 27.9, 25.4, -1.2; HRMS (APPI): Exact mass calcd for C₁₄H₂₅OSi [M+H]⁺, 237.1669. Found 237.1682.



(2-(Benzyloxymethyl)allyl)(4,4-dimethylcyclohexa-1,5-dienyloxy)dimethylsilane (7b):

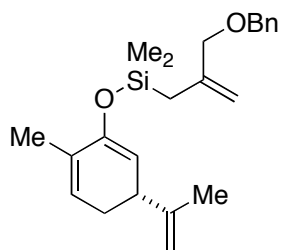
A solution of 4,4-Dimethyl-2-cyclohexen-1-one (100 mg, 0.8 mmol) in THF (1 mL) was added dropwise to a stirred solution of LDA at -78 °C (0.88 mmol, prepared by adding *n*-BuLi [0.88 mmol] to a stirred solution of diisopropylamine [0.96 mmol] in 5 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (68 μL, 0.96 mmol) was added dropwise to a stirred solution of aminosilane **S2** (280 mg, 0.96 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (10 mL). The mixture was extracted with pentanes (3 x 10 mL), washed with brine (20 mL), and dried (Na₂SO₄). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (151 mg, 55%). IR (film) 3031, 2961, 2868.7, 1694, 1469, 1177; ¹H

NMR (500 MHz, CDCl₃) 7.35–7.27 (m, 5H); 5.53 (s, 2H); 5.00 (s, 1H); 4.81 (s, 1H); 4.77 (bs, 1H); 4.50 (s, 2H); 3.93 (s, 2H); 2.10 (d, 2H, *J* = 4.6 Hz); 1.74 (s, 2H); 1.00 (s, 6H); 0.20 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 147.2, 142.6, 140.5, 138.6, 128.6, 127.9, 127.8, 127.7, 123.8, 110.6, 101.7, 74.4, 72.2, 60.7, 37.2, 31.4, 27.9, 23.4, 21.3, 14.4, –1.2; HRMS (APPI): Exact mass calcd for C₂₁H₃₁O₂Si [M+H]⁺, 343.2088. Found 343.2093.



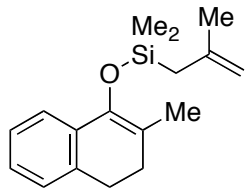
(R)-Dimethyl(6-methyl-3-(prop-1-en-2-yl)cyclohexa-1,5-dienyloxy) (2-methylallyl)silane (7c):

A solution of (–)-Carvone (150 mg, 1.0 mmol) in THF (1 mL) was added dropwise to a stirred solution of LDA at –78 °C (1.1 mmol, prepared by adding *n*-BuLi [1.1 mmol] to a stirred solution of diisopropylamine [1.2 mmol] in 5 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (78 μL, 1.1 mmol) was added dropwise to a stirred solution of aminosilane **S1** (283mg, 1.1 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na₂SO₄). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (240 mg, 92%). [α]_D +51.9 (*c* 1.4, DCM), IR (film) 3075, 2967, 1660, 1641, 1450, 1253; ¹H NMR (500 MHz, CDCl₃) 5.56 (s, 1H); 4.78 (s, 2H); 4.72 (s, 1H); 4.64 (s, 1H); 4.55 (s, 1H); 3.04–2.99 (m, 1H); 2.20–2.09 (m, 2H); 1.76–1.71 (m, 11H); 0.24 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 150.0, 148.7, 142.6, 132.1, 123.5, 110.3, 109.6, 105.9, 42.1, 28.8, 28.7, 25.4, 20.8, 17.7, –1.2; HRMS (APPI): Exact mass calcd for C₁₆H₂₇OSi [M+H]⁺, 263.1826. Found 263.1824.



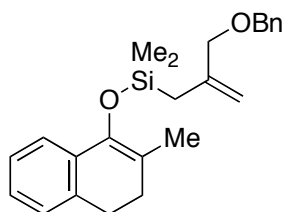
(R)-(2-(Benzyloxymethyl)allyl)dimethyl(6-methyl-3-(prop-1-en-2-yl)cyclohexa-1,5-dienyloxy)silane (7d):

A solution of (–)-Carvone (225 mg, 1.5 mmol) in THF (1 mL) was added dropwise to a stirred solution of LDA at –78 °C (1.65 mmol, prepared by adding *n*-BuLi [1.65 mmol] to a stirred solution of diisopropylamine [1.8 mmol] in 8 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (128 μL, 1.8 mmol) was added dropwise to a stirred solution of aminosilane **S2** (525 mg, 1.8 mmol) in THF (8 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na₂SO₄). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (563 mg, 99%). [α]_D +4.9 (*c* 0.3, DCM), IR (film) 3086, 3030, 2957, 2860, 1640, 1567, 1290; ¹H NMR (500 MHz, CDCl₃) 7.35–7.34 (m, 4H); 7.32–7.28 (m, 1H); 5.56 (s, 1H); 5.01 (s, 1H); 4.82 (s, 1H); 4.77 (s, 2H); 4.71 (s, 1H); 4.50 (s, 2H); 3.93 (s, 2H); 2.19–2.04 (m, 2H); 1.77–1.69 (m, 8H); 0.23 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 149.9, 148.6, 142.6, 138.6, 132.0, 128.6, 127.9, 127.7, 123.5, 110.7, 110.3, 105.9, 74.4, 72.2, 42.1, 28.8, 23.4, 20.8, 17.7, –1.18; HRMS (APPI): Exact mass calcd for C₂₃H₃₃O₂Si [M+H]⁺, 369.2213. Found 369.2227.



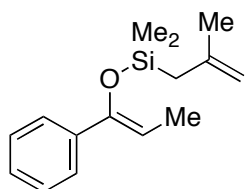
Dimethyl(2-methyl-3,4-dihydronaphthalen-1-yloxy)(2-methylallyl)silane (7e): A solution of alpha methyl tetralone (80 mg, 0.5 mmol) in THF (1 mL) was added dropwise to a stirred solution of LDA at $-78\text{ }^{\circ}\text{C}$ (0.55 mmol, prepared by adding *n*-BuLi [0.55 mmol] to a stirred solution of diisopropylamine [0.6 mmol] in 5 mL THF at $0\text{ }^{\circ}\text{C}$). The reaction was warmed to $0\text{ }^{\circ}\text{C}$ for 30 min to aid in enolization and was then cooled back

down to $-78\text{ }^{\circ}\text{C}$. In a separate round-bottom flask, acetyl chloride (39 μL , 0.55 mmol) was added dropwise to a stirred solution of aminosilane **S1** (102 mg, 0.55 mmol) in THF (3 mL) at $0\text{ }^{\circ}\text{C}$ and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (98 mg, 72%). IR (film) 3073, 2919, 2829, 1651, 1211, 1087, 1043, 841; ^1H NMR (500 MHz, CDCl_3) 7.32 (d, 1H, $J = 7.6$); 7.18–7.16 (m, 1H); 7.15–7.08 (m, 2H); 4.66 (s, 1H); 4.57 (s, 1H); 2.73 (t, 2H, $J = 7.8$); 2.25 (t, 2H, $J = 7.8$); 1.82 (s, 3H); 1.77 (s, 6H); 0.21 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 142.5, 142.4, 136.1, 134.4, 126.9, 126.4, 126.2, 121.6, 117.3, 109.7, 29.3, 28.9, 28.4, 25.5, 17.6, -0.8 ; HRMS (APPI): Exact mass calcd for $\text{C}_{17}\text{H}_{25}\text{OSi}$ $[\text{M}+\text{H}]^+$, 273.1669. Found 273.1681.



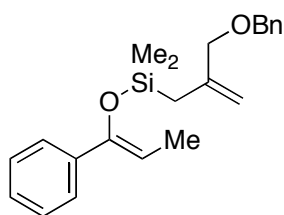
(2-(Benzyloxymethyl)allyl)dimethyl(2-methyl-3,4-dihydronaphthalen-1-yloxy)silane (7f): A solution of alpha methyl tetralone (160 mg, 1.0 mmol) in THF (1 mL) was added dropwise to a stirred solution of LDA at $-78\text{ }^{\circ}\text{C}$ (1.1 mmol, prepared by adding *n*-BuLi [1.1 mmol] to a stirred solution of diisopropylamine [1.2 mmol] in 5 mL THF at $0\text{ }^{\circ}\text{C}$). The reaction was warmed to $0\text{ }^{\circ}\text{C}$ for 30 min to aid in

enolization and was then cooled back down to $-78\text{ }^{\circ}\text{C}$. In a separate round-bottom flask, acetyl chloride (85 μL , 1.2 mmol) was added dropwise to a stirred solution of aminosilane **S2** (350 mg, 1.2 mmol) in THF (5 mL) at $0\text{ }^{\circ}\text{C}$ and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (368 mg, 97%). IR (film) 3089, 2926, 2854, 1689, 1087, 946; ^1H NMR (500 MHz, CDCl_3) 7.36–7.27 (m, 6H); 7.17–7.13 (m, 1H); 7.11–7.07 (m, 2H); 5.02 (s, 1H); 4.83 (s, 1H); 4.50 (s, 2H); 3.93 (s, 2H); 2.73 (t, 2H, $J = 7.7\text{ Hz}$); 2.24 (t, 2H, $J = 7.7\text{ Hz}$); 1.81 (obs, 5H); 0.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 142.6, 142.4, 138.6, 136.1, 134.4, 128.6, 127.9, 127.7, 126.9, 126.4, 126.3, 121.6, 117.3, 110.8, 74.4, 72.2, 29.3, 28.4, 23.7, 17.6, -0.8 ; HRMS (APPI): Exact mass calcd for $\text{C}_{24}\text{H}_{31}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$, 379.2115. Found 379.2102.



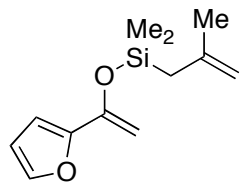
(Z)-Dimethyl(2-methylallyl)1-phenylprop-1-enyloxy)silane (7g): A solution of propiophenone (201 mg, 1.5 mmol) in THF (2 mL) was added dropwise to a stirred solution of LDA at $-78\text{ }^{\circ}\text{C}$ (1.65 mmol, prepared by adding *n*-BuLi [1.65 mmol] to a stirred solution of diisopropylamine [1.8

mmol] in 10 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (117 μ L, 1.65 mmol) was added dropwise to a stirred solution of aminosilane **S1** (366mg, 1.65 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (370 mg, 84%). IR (film) 2917, 1652, 1264, 1117; ^1H NMR (500 MHz, CDCl_3) 7.47 (d, 2H, $J = 7.4$ Hz); 7.32–7.24 (obs, 3H); 5.30 (q, 1H, $J = 6.8$ Hz); 4.66 (s, 1H); 4.56 (s, 1H); 1.77–1.56 (m, 5H); 0.16 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 150.0, 142.4, 139.4, 128.3, 128.2, 127.6, 125.5, 109.8, 105.8, 30.0, 29.0, 25.5, 12.0, -0.75 ; HRMS (APPI): Exact mass calcd for $\text{C}_{15}\text{H}_{23}\text{OSi}$ $[\text{M}+\text{H}]^+$, 247.1513. Found 247.1506.



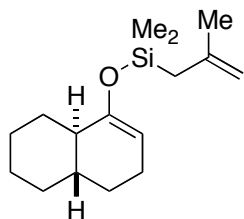
(Z)-(2-(Benzyloxymethyl)allyl)dimethyl(1-phenylprop-1-enyloxy)silane (7h): A solution of propiophenone (110 mg, 0.82 mmol) in THF (1 mL) was added dropwise to a stirred solution of LDA at -78 °C (0.9 mmol, prepared by adding *n*-BuLi [0.9 mmol] to a stirred solution of diisopropylamine [0.98 mmol] in 5 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (64 μ L, 0.9 mmol) was

added dropwise to a stirred solution of aminosilane **S2** (262 mg, 0.9 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (10 mL). The mixture was extracted with pentanes (3 x 10 mL), washed with brine (20 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (300 mg, 62%). IR (film) 3063, 3031, 2957, 2922, 2857, 1651, 1453, 1322; ^1H NMR (500 MHz, CDCl_3) 7.46 (d, 2H, $J = 7.4$ Hz); 7.36 (d, 5H, $J = 4.2$ Hz); 7.31–7.24 (m, 3H); 5.32 (q, 1H, $J = 6.9$ Hz); 5.02 (s, 1H); 4.83 (s, 1H); 4.51 (s, 2H); 3.93 (s, 2H); 1.76 – 1.74 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) 149.9, 142.5, 139.3, 138.6, 128.6, 128.3, 127.9, 127.8, 127.7, 127.6, 125.5, 110.9, 105.9, 74.4, 72.2, 23.7, 12.0, -0.7 ; HRMS (APPI): Exact mass calcd for $\text{C}_{22}\text{H}_{29}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$, 353.1931. Found 353.1939.



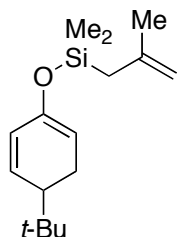
(1-(Furan-2-yl)vinyl)oxydimethyl(2-methylallyl)silane (7i): A solution of 2-furyl methyl ketone (165 mg, 1.5 mmol) in THF (3 mL) was added dropwise to a stirred solution of LDA at -78 °C (1.65 mmol, prepared by adding *n*-BuLi [1.65 mmol] to a stirred solution of diisopropylamine [1.8 mmol] in 10 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (128 μ L, 1.8 mmol) was added dropwise to a stirred solution of aminosilane **S1** (400 mg, 1.8 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the

desired silyl allyl ether (336 mg, 59%). IR (film) 3075, 2965, 1635, 1491, 1315, 1173; ^1H NMR (500 MHz, CDCl_3) 7.34 (s, 1H); 6.38 (d, 2H, $J = 11.0$ Hz); 4.89 (s, 1H); 4.67 (s, 1H); 4.58 (s, 1H); 4.37 (s, 1H); 1.78 (obs, 5H); 0.28 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 152.3, 147.7, 142.6, 142.3, 111.3, 109.9, 107.3, 90.5, 28.5, 25.4, -1.4; HRMS (APPI): Exact mass calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$, 223.1149. Found 223.1141.



Dimethyl(2-methylallyl)(3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yloxy) silane (7j):

A solution of trans decalone (305 mg, 2.0 mmol) in THF (3 mL) was added dropwise to a stirred solution of LDA at -78 °C (2.2 mmol, prepared by adding *n*-BuLi [2.2 mmol] to a stirred solution of diisopropylamine [2.4 mmol] in 10 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (156 μL , 2.2 mmol) was added dropwise to a stirred solution of aminosilane **S1** (488 mg, 2.2 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (419 mg, 78%). IR (film) 2919, 2853, 1658, 1448, 1123; ^1H NMR (500 MHz, CDCl_3) 4.77 (t, 1H, $J = 2.8$ Hz); 4.63 (s, 1H); 4.54 (s, 1H); 2.09–2.05 (m, 2H); 2.01–1.97 (m, 1H); 1.81–1.63 (m, 9H); 1.55–1.51 (m, 1H); 1.27–1.17 (m, 4H); 1.08–1.02 (m, 1H); 0.93–0.85 (m, 1H); 0.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 152.6, 142.8, 109.4, 103.5, 45.8, 41.8, 33.8, 30.3, 28.9, 28.8, 27.1, 25.4, 24.1, -1.2; HRMS (APPI): Exact mass calcd for $\text{C}_{16}\text{H}_{29}\text{OSi}$ $[\text{M}+\text{H}]^+$, 265.1982. Found 265.1958.

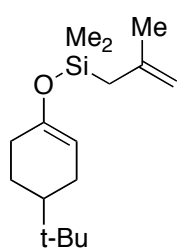


(4-*tert*-Butylcyclohexa-1,5dienyloxy)dimethyl(2-methylallyl)silane (7k):

A solution of 4-*tert*-butylcyclohex-2-enone⁴ (304 mg, 2.0 mmol) in THF (3 mL) was added dropwise to a stirred solution of LDA at -78 °C (2.2 mmol, prepared by adding *n*-BuLi [2.2 mmol] to a stirred solution of diisopropylamine [2.4 mmol] in 12 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (171 μL , 0.96 mmol) was added dropwise to a stirred solution of aminosilane **S1** (280 mg, 2.4 mmol) in THF (3 mL) at 0 °C and was allowed to stir for 10 min after which time the solution was transferred by cannula to the previously prepared enolate (1 mL rinse). The reaction was monitored by TLC and upon completion (60 minutes) was warmed to room temperature and quenched with pH 7.0 buffer (15 mL). The mixture was extracted with pentanes (3 x 15 mL), washed with brine (30 mL), and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 5% EtOAc in hexanes afforded the desired silyl allyl ether (467 mg, 88%). IR (film) 2961, 2871, 1651, 1333, 1210; ^1H NMR (500 MHz, CDCl_3) 5.81 (dd, 1H, $J = 2.5, 10.2$ Hz); 5.70 (dt, 1H, $J = 2.3, 10.2$ Hz); 4.86–4.84 (m, 1H); 4.64 (s, 1H); 4.54 (s, 1H); 2.18–2.05 (m, 3H); 1.75 (s, 3H); 1.70 (s, 2H); 0.90 (s, 9H); 0.20 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 147.9, 142.6, 131.3, 126.5, 109.5, 102.6,

⁴ Prepared from the corresponding saturated ketone using IBX, see: Nicolaou, K. C.; Montagnon, T.; Baran, P. S.; Zhong, Y.-L. *J. Am. Chem. Soc.*, **2002**, 124, 2245–2258.

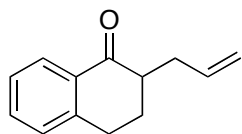
44.2, 33.0, 28.6, 27.7, 25.4, 23.5, -1.17; HRMS (APPI): Exact mass calcd for C₁₆H₂₉OSi [M+H]⁺, 265.1982. Found 265.1981.



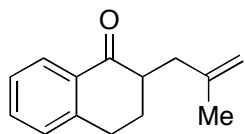
(4-*tert*-Butyl-1-yloxy)dimethyl(2-methylallyl)silane (71): A solution of 4-*tert*-butylcyclohexanone (0.31g, 2.0 mmol) in THF (5 mL) was added dropwise to a stirred solution of LDA at -78 °C (2.2 mmol, prepared by adding *n*-BuLi [2.2 mmol] to a stirred solution of diisopropylamine [2.4 mmol] in 20 mL THF at 0 °C). In a separate round-bottom flask, acetyl chloride (0.17 mL, 2.4 mmol) was added dropwise to a stirred solution of aminosilane (**S1**) (0.45 g, 2.4 mmol) in THF (5 mL) at 0 °C and was allowed to stir for 10 min after which time the solution warmed to room temperature and transferred by cannula to the previously prepared enolate at -78 °C. The reaction was monitored by TLC while slowly warming from -78 °C for 3 hrs. Then the reaction was maintained at 0 °C and upon completion (2 hrs) was diluted with pentanes (10 mL) then quenched with pH 7 buffer (20 mL). The mixture was extracted with pentanes (3 x 10 mL), washed with brine (20 mL), and dried with Na₂SO₄. Removal of solvent under reduced pressure followed by flash column chromatography on silica gel with 3% EtOAc in hexanes afforded the desired silyl allyl ether in 89% yield (0.47 g, 1.8 mmol). IR (film) 2962, 1673, 1374, 1279, 1253, 908; ¹H NMR (500 MHz, CDCl₃) 4.84 (m, 1H); 4.63 (s, 1H); 4.54 (s, 1H); 2.12–1.95 (m, 3H); 1.84–1.76 (m, 2H); 1.75 (s, 3H); 1.68 (s, 2H); 1.30–1.16 (m, 2H); 0.86 (s, 9H); 0.20 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) 151.5, 144.0, 110.5, 105.4, 45.2, 33.4, 32.2, 29.8, 28.6, 26.5, 26.3, 25.6, 0.00; HRMS (APPI): Exact mass calcd for [M+H]⁺, 267.2139. Found 267.2146.

C: Oxidative Allylations.

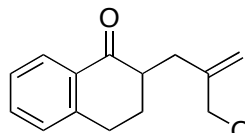
General Procedure for Oxidative Coupling: A solution of the silyl bis-enol ether (1 mmol) in acetonitrile (4 mL) was pre-cooled to -25 °C and transferred by cannula (1 mL acetonitrile rinse) to a stirred suspension of cerium(IV) ammonium nitrate (1.21 g, 2.2 mmol), 2,6 di-*tert*-butyl pyridine (988 μL, 4.4 mmol) in acetonitrile (30 mL) at -25 °C. When the reaction was judged to be complete by TLC (times ranging between 5 minutes and 24 hours) the solution was diluted with 1 M HCl (35 mL) and extracted with EtOAc (3 x 35 mL). The combined organic layers were washed with brine (100 mL) and dried (Na₂SO₄). Removal of the solvent under reduced pressure, followed by flash column chromatography on silica gel afforded the desired allylated product. *Note:* All reactions were carried out at -25 °C unless otherwise stated. Compounds that were deemed to be volatile (low molecular weight) were extracted with Et₂O instead of EtOAc.



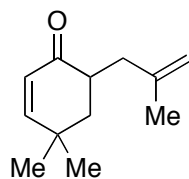
2-Allyl-3,4-dihydronaphthalen-1(2H)-one (6a) Prepared from **5a** (1.0 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **6a** (81 mg, 44%). IR (neat) cm⁻¹ 3073, 2978, 2932, 2863, 1682, 1454, 1294; ¹H NMR (500 MHz, CDCl₃); 8.03 (d, 1H, *J* = 7.6 Hz); 7.46 (t, 1H, *J* = 7.4 Hz); 7.30 (t, 1H, *J* = 7.4 Hz); 7.25 (d, 1H, *J* = 7.6); 5.89–5.81 (m, 1H); 5.13–5.06 (m, 2H); 3.01–2.99 (m, 2H); 2.79–2.74 (m, 1H); 2.58–2.52 (m, 1H); 2.29–2.04 (m, 2H); 1.91–1.83 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) 144.3, 136.4, 133.4, 132.7, 128.9, 127.7, 126.8, 117.1, 47.4, 34.3, 28.8, 28.2; HRMS (ESI): Exact mass calcd for C₁₃H₁₄O [M+H]⁺, 187.1117. Found 187.1112.



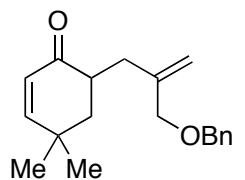
2-(2-Methylallyl)-3,4-dihydronaphthalen-1(2H)-one (6b): Prepared from **5b** (0.5 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **6b** (83 mg, 83%). IR (neat) cm^{-1} 3072, 2932, 2861, 1683, 1599, 1357; ^1H NMR (500 MHz, CDCl_3) 8.03 (d, 1H, $J = 7.6$ Hz); 8.47 (t, 1H, $J = 7.3$ Hz); 7.31 (t, 1H, $J = 7.3$ Hz); 7.25 (obs, 1H); 4.84 (s, 1H); 4.75 (s, 1H); 3.00–2.96 (m, 2H); 2.81 (dd, 1H, $J = 3.5, 14.1$ Hz); 2.67–2.62 (m, 1H); 2.26–2.20 (m, 1H); 2.12 (dd, 1H, $J = 10.0, 14.1$ Hz); 1.76 (obs, 4H); ^{13}C NMR (100 MHz, CDCl_3) 200.2, 144.3, 143.5, 133.4, 132.7, 128.9, 127.7, 126.8, 112.8, 45.42, 38.0, 28.5, 27.8, 22.2; HRMS (ESI): Exact mass calcd for $\text{C}_{14}\text{H}_{16}\text{O}$ $[\text{M}+\text{H}]^+$, 201.1274. Found 201.1274.



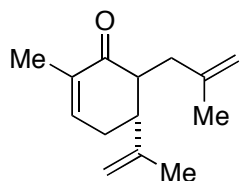
2-(2-(Benzyloxymethyl)allyl)-3,4-dihydronaphthalen-1(2H)-one (6c): Prepared from **5c** (0.5 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **6c** (100 mg, 65%). IR (neat) cm^{-1} 3064, 3029, 2843, 1671, 1495, 1143; ^1H NMR (500 MHz, CDCl_3) 7.94 (1H, $J = 7.8$ Hz); 7.39–7.36 (m, 1H); 7.27–7.14 (m, 7H); 5.11 (s, 1H); 4.91 (s, 1H); 4.43 (s, 1H); 3.92 (s, 2H); 2.94–2.83 (m, 3H); 2.64–2.58 (m, 1H); 2.17 (ddd, 1H, $J = 4.5, 9.1, 17.9$ Hz); 2.08 (dd, 1H, $J = 4.7, 9.3$ Hz); 1.76–1.68 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) 199.9, 144.2, 143.8, 138.4, 133.4, 132.7, 128.9, 128.6, 127.9, 127.8, 127.7, 126.8, 114.2, 73.0, 72.3, 45.8, 33.8, 28.7, 28.3; HRMS (ESI): Exact mass calcd for $\text{C}_{21}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$, 307.1693. Found 307.1697.



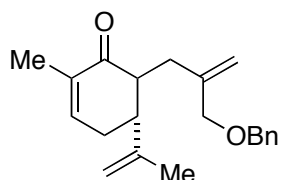
4,4-Dimethyl-6-(2-methylallyl)cyclohex-2-enone (8a): Prepared from **7a** (0.5 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8a** (64 mg, 72%). IR (neat) cm^{-1} 3076, 2961, 2931, 2869, 1681, 1648, 1393; ^1H NMR (500 MHz, CDCl_3) 6.60 (dd, 1H, $J = 2.0, 10.0$ Hz); 5.84 (d, 1H, $J = 10.0$ Hz); 4.79 (s, 1H); 4.69 (s, 1H); 2.84 (d, 1H, $J = 13.4$ Hz); 2.61–2.54 (m, 1H); 1.91–1.82 (m, 2H); 1.70 (s, 3H); 1.49 (t, 1H, $J = 13.7$ Hz); 1.18 (s, 3H); 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 201.3, 159.1, 143.4, 126.8, 112.5, 41.6, 40.5, 37.5, 33.8, 30.8, 25.4, 22.2; HRMS (ESI): Exact mass calcd for $\text{C}_{12}\text{H}_{18}\text{O}$ $[\text{M}+\text{H}]^+$, 179.1430. Found 179.1422.



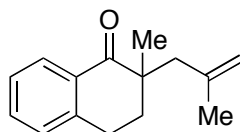
6-(2-(Benzyloxymethyl)allyl)-4,4-dimethylcyclohex-2-enone (8b): Prepared from **7b** (0.3 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8b** (44 mg, 51%). IR (neat) cm^{-1} 2960, 2916, 2866, 1677, 1469, 1392, 1186; ^1H NMR (500 MHz, CDCl_3) 7.34–7.32 (m, 4H); 7.29–7.27 (m, 1H); 6.57 (dd, 1H, $J = 2.2, 10.0$ Hz); 5.82 (d, 1H, $J = 10.0$ Hz); 5.16 (s, 1H); 4.94 (s, 1H); 4.50 (dd, 2H, $J = 11.9, 30.5$ Hz); 3.94 (dd, 2H, $J = 12.6, 17.8$ Hz); 2.95 (dd, 1H, $J = 3.5, 14.7$ Hz); 2.63 (dddd, 1H, $J = 4.2, 5.4, 8.6, 9.5$ Hz); 1.90 (dd, 1H, $J = 9.7, 14.7$ Hz); 1.85 (dddd, 1H, $J = 2.2, 4.6, 6.7, 8.8$ Hz); 1.56 (d, 1H, $J = 31.0$ Hz); 1.53 (d, 1H, $J = 27.0$ Hz); 1.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 200.9, 158.9, 143.7, 138.4, 128.6, 128.0, 127.8, 126.7, 113.9, 73.0, 72.3, 41.9, 40.8, 33.8, 33.3, 30.8, 25.3; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$, 285.1849. Found 285.1847.



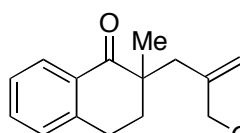
(5R,6S)-2-Methyl-6-(2-methylallyl)-5-(prop-1-en-2-yl)cyclohex-2-enone (8c): Prepared from **7c** (0.53 mmol) according to the general procedure. ¹H-NMR spectroscopic analysis of the unpurified reaction mixture revealed formation of a 1:1 mixture of diastereomers. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8c** (58 mg, 54%). [α]_D + 0.72 (*c* 0.5, DCM), IR (neat) cm^{-1} : 3075, 2970, 2921, 1672, 1449, 1375, 890; ¹H NMR (500 MHz, CDCl₃) 6.64–6.62 (m, 2H); 4.94 (s, 1H); 4.80 (d, 2H, *J* = 13.7 Hz); 4.74 (s, 3H); 4.69 (s, 1H); 4.58 (s, 1H); 2.81–2.74 (m, 2H); 2.61 (bs, 2H); 2.58–2.18 (m, 8H); 1.77–1.71 (m, 18H); ¹³C NMR (100 MHz, CDCl₃); 202.3, 201.5, 146.1, 144.0, 143.3, 142.8, 142.7, 135.0, 134.1, 47.9, 47.2, 46.0, 44.6, 37.1, 34.0, 29.2, 22.8, 22.4, 22.2, 20.4, 16.4, 16.2; HRMS (ESI): Exact mass calcd for C₁₄H₂₁O [M+H]⁺, 205.1587. Found 205.1582.



6-(2-(Benzyloxymethyl)allyl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone (8d): Prepared from **7d** (0.5 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8d** (104 mg, 67%). [α]_D + 2.9 (*c* 2.0, DCM), IR (neat) cm^{-1} : 3068, 3029, 2919, 1670, 1496, 1366, 1159, 897; ¹H NMR (500 MHz, CDCl₃) 7.35–7.32 (m, 9H); 7.29–7.27 (m, 2H); 6.66–6.61 (m, 2H); 5.13 (s, 1H); 5.04 (s, 1H); 4.94–4.93 (m, 2H); 4.85 (s, 1H); 4.81 (s, 1H); 4.75–4.74 (m, 2H); 4.49 (s, 2H); 4.46 (d, 2H, *J* = 3.0 Hz); 4.10 (d, 1H, *J* = 12.1 Hz); 4.02–3.91 (m, 2H); 2.83–2.79 (m, 2H); 2.68–2.63 (m, 2H); 2.52–2.45 (m, 1H); 2.41–2.40 (m, 2H); 2.37 (bs, 1H); 2.34–2.31 (m, 2H); 2.29–2.05 (m, 2H); 1.76 (s, 6H); 1.69 (d, 6H, *J* = 4.4 Hz); ¹³C NMR (100 MHz, CDCl₃) 202.3, 201.4, 146.0, 144.9, 144.5, 143.8, 143.0, 142.8, 138.6, 135.0, 134.0, 128.5, 128.0, 127.7, 114.7, 113.5, 113.2, 112.5, 73.5, 72.9, 72.1, 48.2, 47.2, 47.1, 44.7, 32.3, 30.4, 30.1, 29.4, 22.3, 19.8, 16.4, 16.2; HRMS (ESI): Exact mass calcd for C₂₁H₂₇O₂ [M+H]⁺, 311.2006. Found 311.1999.

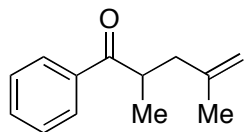


2-Methyl-2-(2-methylallyl)-3,4-dihydronaphthalen-1(2H)-one (8e): Prepared from **7e** (0.91 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8e** (143 mg, 73%). IR (neat) cm^{-1} : 3072, 2965, 2930, 1681, 1375, 1156; ¹H NMR (500 MHz, CDCl₃) 8.04 (d, 1H, *J* = 7.9 Hz); 7.46 (adt, 1H, *J* = 1.3, 7.4 Hz); 7.31 (t, 1H, *J* = 7.46 Hz); 4.83 (s, 1H); 4.67 (s, 1H); 2.99 (t, 2H, *J* = 6.49 Hz); 2.66 (d, 1H, *J* = 13.5 Hz); 2.23 (d, 1H, *J* = 13.5 Hz); 2.13–2.07 (m, 1H); 1.90–1.85 (m, 1H); 1.64 (s, 3H); 1.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 202.5, 143.4, 142.7, 133.3, 132.0, 128.9, 128.3, 126.9, 115.2, 45.2, 44.9, 33.7, 25.7, 24.8, 23.5; HRMS (ESI): Exact mass calcd for C₁₅H₁₈O [M+H]⁺, 214.1352. Found 214.1353.

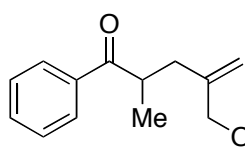


2-(2-(Benzyloxymethyl)allyl)-2-methyl-3,4-dihydronaphthalen-1(2H)-one (8f): Prepared from **7f** (0.5 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8f** (99 mg, 61%). IR (neat) cm^{-1} : 3065, 3029, 2928, 1680, 1495, 1298, 1156; ¹H NMR (500 MHz, CDCl₃) 8.05 (d, 1H, *J* = 7.8 Hz); 7.47 (t, 1H, *J* = 7.3 Hz); 7.32–7.23 (m, 7H); 5.23 (s, 1H); 4.96 (s, 1H); 4.46 (s, 2H); 3.9 (dd, 2H, *J* = 12.9, 29.5 Hz); 3.02 (bs, 2H); 2.67 (d, 1H, *J* = 13.9 Hz); 2.37 (d, 1H, *J* = 13.9 Hz); 2.19–2.14 (m, 1H); 1.94–1.92 (m, 1H); 1.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 202.2, 143.3, 142.5, 138.5,

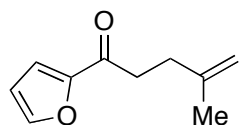
133.3, 131.9, 128.9, 128.5, 128.2, 127.8, 126.9, 116.4, 74.0, 72.3, 45.1, 40.3, 34.0, 30.3, 25.6, 23.3; HRMS (ESI): Exact mass calcd for C₂₂H₂₅O₂ [M+H]⁺, 321.1849. Found 321.1848



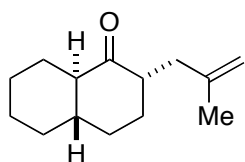
2,4-Dimethyl-1-phenylpent-4-en-1-one (8g): Prepared from **7g** (1.26 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8g** (192 mg, 81%). IR (neat) cm⁻¹ 3076, 2970, 2934, 1683, 1448, 1229; ¹H NMR (500 MHz, CDCl₃) 7.97 (ad, 2H); 7.58–7.55 (m, 1H); 7.49–7.46 (at, 2H); 4.77 (s, 1H); 4.69 (s, 1H); 3.68 (ddq, 1H, *J* = 6.8, 13.7, 21.0 Hz); 2.55 (dd, 1H, *J* = 6.2, 14.4); 2.12 (dd, 1H, *J* = 0.35, 7.8 Hz); 1.75 (s, 3H); 1.18 (d, 3H, *J* = 6.84); ¹³C NMR (100 MHz, CDCl₃) 204.1, 143.3, 136.6, 133.1, 128.9, 128.5, 112.4, 41.6, 38.8, 22.8, 17.4; HRMS (ESI): Exact mass calcd for C₁₃H₁₇O [M+H]⁺, 189.1274. Found 189.1278.



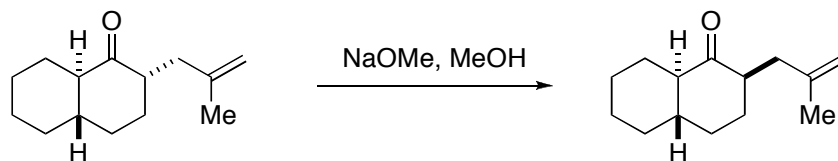
4-(Benzyloxymethyl)-2-methyl-1-phenylpent-4-en-1-one (8h): Prepared from **7h** (0.23 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8h** (40 mg, 59%). IR (neat) cm⁻¹ 3064, 3030, 2872, 1682, 1448, 1196, 1001; ¹H NMR (500 MHz, CDCl₃) 7.95 (d, 2H, *J* = 7.2 Hz); 7.55–7.51 (m, 1H); 7.42–7.28 (m, 7H); 5.09 (s, 1H); 4.96 (s, 1H); 4.48 (s, 2H); 4.0 (dd, 2H, *J* = 12.4, 35.8 Hz); 3.74 (dd, 1H, *J* = 6.9, 14.2 Hz); 2.70 (dd, 1H, *J* = 6.3, 14.5 Hz); 2.17 (dd, 1H, *J* = 7.8, 14.5 Hz); 1.19 (d, 3H, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) 203.9, 143.7, 138.4, 136.5, 133.1, 128.8, 128.6, 128.0, 127.8, 114.7, 73.4, 72.2, 38.8, 37.4, 17.4; HRMS (ESI): Exact mass calcd for C₂₀H₂₃O₂ [M+H]⁺, 295.1693. Found 295.1699.



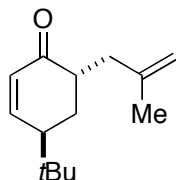
1-(Furan-2-yl)-4-methylpent-4-en-1-one (8i): Prepared from **7i** (0.35 mmol) according to the general procedure. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8i** (42 mg, 73%). IR (neat) cm⁻¹ 3133, 2973, 2362, 1671, 1568, 1468; ¹H NMR (500 MHz, CDCl₃) 7.57 (s, 1H); 7.19 (d, 1H, *J* = 3.4 Hz); 6.53 (s, 1H); 4.74 (d, 2H, *J* = 19.5 Hz); 2.90 (t, 2H, *J* = 7.5 Hz); 2.36 (t, 2H, *J* = 7.8 Hz); 1.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 189.3, 152.9, 146.5, 144.7, 117.2, 112.4, 110.6, 36.9, 32.0, 22.9; HRMS (ESI): Exact mass calcd for C₁₀H₁₂O [M+H]⁺, 164.0832. Found 164.0827.



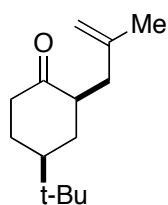
2-(2-Methylallyl)octahydronaphthalen-1(2H)-one (8j) : Prepared from **7j** (0.5 mmol) according to the general procedure. ¹H-NMR spectroscopic analysis of the unpurified reaction mixture revealed a 3:1 mixture of diastereomers favoring the isomer shown. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8j** (44 mg, 43%). IR (neat) cm⁻¹ 2924, 2854, 1699, 1447, 1372, 1254; ¹H NMR (500 MHz, CDCl₃) 4.74 (s, 1H); 4.68 (s, 1H); 2.60–2.58 (m, 1H); 2.36–2.32 (m, 1H); 2.27–2.23 (m, 1H); 2.09–2.04 (m, 1H); 1.81–1.76 (m, 5H); 1.67 (s, 3H); 1.55–1.51 (m, 3H); 1.40–1.35 (m, 1H); 1.18–1.15 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) 215.9, 142.8, 113.0, 51.4, 48.2, 45.1, 40.0, 34.6, 29.5, 28.1, 26.0, 25.8, 25.4, 21.9; HRMS (ESI): Exact mass calcd for C₁₄H₂₂O [M+H]⁺, 207.1743. Found 207.1745. Confirmation of the stereochemistry was achieved by exposure of **8j** to NaOMe in methanol, which resulted in epimerization to the thermodynamically favored equatorial isomer:



Allylation product (**8j**) (7 mg, 0.034 mmol) was stirred in a solution of NaOMe (2. mg, 0.036 mmol) and MeOH (1 mL) at room temperature for 48 hours. The reaction was then quenched with water (1 mL), extracted in ether (2x2 mL), washed with brine (2 mL), and dried with Na₂SO₄. The crude mixture gave a 9:1 mixture of diastereomers favoring the shown isomer.

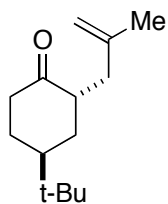


4-tert-Butyl-6-(2-methylallyl)cyclohex-2-enone (8k): Prepared from **7k** (1.0 mmol) according to the general procedure. ¹H-NMR spectroscopic analysis of the unpurified reaction mixture revealed a single diastereomer favoring the isomer shown. Purification on silica gel using 5% EtOAc in hexanes afforded the title compound **8k** (135 mg, 67%). IR(neat) cm⁻¹ 3038, 2869, 1677, 1469, 1368, 889; ¹H NMR (500 MHz, CDCl₃) 6.96 (d, 1H, *J* = 10.4 Hz); 5.97 (dd, 1H, *J* = 2.7, 10.3 Hz); 4.84 (s, 1H); 4.74 (s, 1H); 2.1–2.58 (m, 1H); 2.29–2.19 (m, 3H); 1.94–1.91 (m, 1H); 1.86–1.79 (m, 1H); 1.74 (s, 3H); 0.97 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 202.7, 152.2, 143.1, 129.0, 113.4, 43.3, 42.1, 38.6, 33.3, 27.7, 26.9, 21.8; HRMS (ESI): Exact mass calcd for C₁₄H₂₃O [M+H]⁺, 207.1743. Found 207.1747.



4-tert-Butyl-2-(2-methylallyl)cyclohexane (8l): A solution of silyl bis-enol ether (**7l**) (0.53 g, 2 mmol) in acetonitrile (12 mL) was pre-cooled to -40 °C and transferred by cannula to a stirred suspension of cerium(IV) ammonium nitrate (2.4 g, 4.4 mmol), and 2,6-di-*tert*-butyl pyridine (2.0 mL, 8.8 mmol) in acetonitrile (45 mL) at -40 °C. The reaction was then left stirring for 24 hrs at 0 °C monitoring by TLC. The reaction was quenched with 1 M HCl (60 mL) and extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine (60 mL) and dried with Na₂SO₄. Removal of the solvent under reduced pressure gave a mixture of diastereomers in 5:1 ratio favoring the shown isomer. Flash column chromatography on silica gel with 100 mL of hexanes followed by 400 mL of 3% EtOAc in hexanes afforded the desired allylated product in 52% yield (220 mg, 1.0 mmol). IR (film) 2959, 1713, 1444, 1366, 1070, 888; ¹H NMR (500 MHz, CDCl₃) 4.76 (s, 1H); 4.64 (s, 1H); 2.53 (dd, 1H, *J*_S=3.99 Hz, *J*_L = 14.98 Hz); 2.49–2.31 (m, 3H); 2.17–2.07 (m, 2H); 1.86 (dd, 1H, *J*_S = 8.8 Hz, *J*_L = 14.8 Hz); 1.68 (s, 3H); 1.57 (m, 1H); 1.44 (ddd, 1H, *J*_S = 4.6 Hz, *J*_M = 12.9 Hz, *J*_L = 25.7 Hz); 1.04 (q, 1H, *J* = 12.8 Hz); 0.90 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) 213.2, 143.8, 111.7, 47.4, 47.1, 41.8, 37.2, 34.6, 32.6, 28.8, 27.7, 22.5; HRMS (ESI): Exact mass calcd for [M+H]⁺, 209.1900. Found 209.1900.

Preparation of the 1,3-anti isomer by hydrazone alkylation:



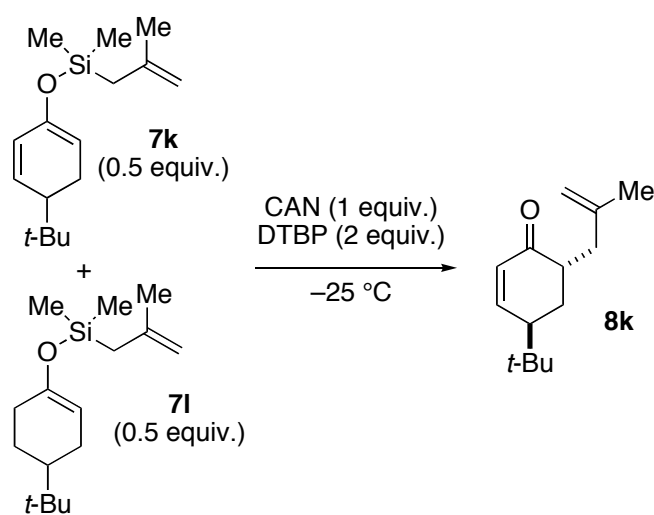
4-tert-Butyl-2-(2-methylallyl)cyclohexane (epi-8l): A solution of the dimethylhydrazone derivative of 4-*tert*-butylcyclohexanone⁵ (0.39 g, 2.0 mmol) in THF (2 mL) was chilled to 0 °C and added dropwise to a stirred solution of LDA at 0 °C (2.2 mmol, prepared by adding *n*-BuLi [2.2 mmol] to a stirred

⁵ Prepared by a modification of the procedure for axial alkylation reported by Lightner, D. A.; Bouman, T. D.; Vincent Crist, B.; Rodgers, S. L.; Knobloch, M. A.; Jones, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 6248–6259.

solution of diisopropylamine [2.4 mmol] in 4 mL THF at 0 °C). This was stirred at -10 °C for 30 hrs before being chilled to -78 °C. A solution of 2-bromo-2-methylpropene⁶ (0.54 g, 4.0 mmol) in THF (2 mL) was added and the reaction was stirred at -78 °C for 1 hour before warming to room temperature. The mixture was diluted with 8 mL of a 3:1 H₂O:DCM solution. The aqueous layer was washed with DCM (3x5 mL), rinsed with brine (10 mL), dried with Na₂SO₄, and condensed. The resultant crude mixture was then stirred for a 24 hours in a solution of MeOH and pH7 buffer (13:8 mL) with NaIO₄ (0.94 g, 4.4 mmol) in 3 mL H₂O. Extraction in DCM (3x10 mL), washing with brine (10 mL), and drying with MgSO₄ gave a mixture of diastereomers in 9:1 ratio favoring the shown isomer. Flash column chromatography on silica gel with 500 mL 4% EtOAc in hexanes gave a 9% yield of the desired product (0.04 g, 0.18 mmol). IR (film) 2959, 1713, 1395, 1326, 1258, 1092; ¹H NMR (500 MHz, CDCl₃) 4.80 (s, 1H); 4.72 (s, 1H); 2.62–2.55 (m, 1H); 2.46–2.23 (m, 3H); 2.05–1.98 (m, 1H); 1.87–1.79 (m, 1H); 1.70 (s, 3H); 1.64–1.53 (m, 3H); 1.51–1.41 (m, 1H); 0.89 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) 215.9, 142.6, 113.2, 46.81, 40.8, 39.6, 38.5, 32.4, 30.2, 27.5, 27.1, 21.7; HRMS (ESI): Exact mass calcd for [M+H]⁺, 209.1900. Found 209.1900.

D: Additional Experiments.

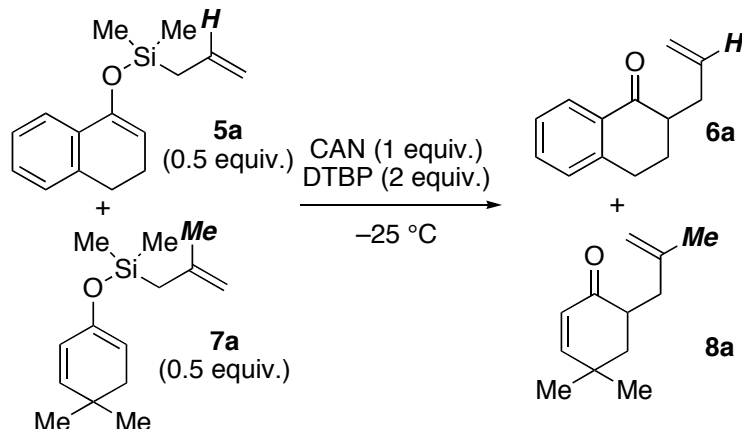
Oxidation Competition Experiment:



A solution of silyl allyl ether **7k** (0.04 g, 0.14 mmol) and silyl allyl ether **7l** (0.04 g, 0.14 mmol) in acetonitrile (3 mL) was chilled to -40 °C before being transferred by cannula to a stirred suspension of cerium(IV) ammonium nitrate (0.17 g, 0.31 mmol), and 2,6-di-*tert*-butyl pyridine (0.14 mL, 0.62 mmol) in acetonitrile (5 mL) at -40 °C. The reaction was warmed to -25 °C and monitored by TLC for 36 hrs. The reaction was then quenched with 1M HCl (10 mL), extracted in EtOAc (3x5 mL), washed with brine (10 mL), and dried with Na₂SO₄. After removal of solvent ¹H NMR in CDCl₃ of the crude material showed only formation of ketone **8k**.

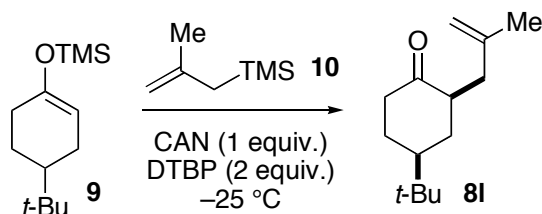
⁶ Prepared according to procedure: Teuscher, P. *J. Am. Chem. Soc.* **1950**, 72, 4316-4318.

Cross-over Experiment:



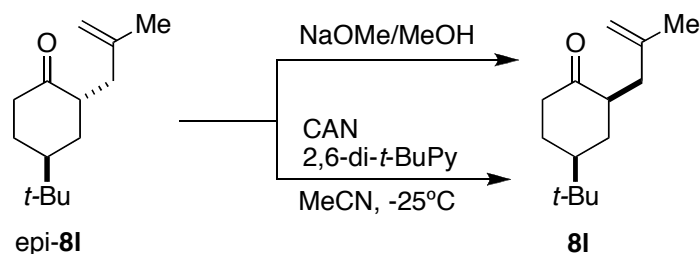
A solution of silyl allyl ether **5a** (0.08 g, 0.35 mmol) and silyl allyl ether **7a** (0.09 g, 0.35 mmol) in acetonitrile (2 mL) and chilled to $-40\text{ }^{\circ}\text{C}$ before being transferred by cannula to a stirred suspension of cerium(IV) ammonium nitrate (0.42 g, 0.77 mmol), and 2,6-di-*tert*-butyl pyridine (0.35 mL, 1.5 mmol) in acetonitrile (10 mL) at $-40\text{ }^{\circ}\text{C}$. The reaction was warmed to $-25\text{ }^{\circ}\text{C}$ and monitored by TLC for 12 hrs. The reaction was then quenched with 1M HCl (20 mL), extracted in EtOAc (3x10 mL), washed with brine (20 mL), and dried with Na_2SO_4 . The resulting products were separated by flash column chromatography using 100 mL of hexanes followed by 500 mL of 2% EtOAc in hexanes. Only products **6a** and **8a** were isolated along with return of the respective unallylated ketones.

Intermolecular Allylation using Allyltrimethylsilane:



A solution of silyl allyl ether **9** (0.14 g, 0.63 mmol) and allyl silane **10** (1.1 mL, 6.3 mmol) were dissolved in acetonitrile (5 mL) and chilled to $-40\text{ }^{\circ}\text{C}$ before being transferred by cannula to a stirred suspension of cerium(IV) ammonium nitrate (0.73 g, 1.39 mmol), and 2,6-di-*tert*-butyl pyridine (0.62 mL, 2.8 mmol) in acetonitrile (10 mL) at $-40\text{ }^{\circ}\text{C}$. The reaction was warmed to $-25\text{ }^{\circ}\text{C}$ and monitored by TLC for 24 hours. The reaction was then quenched with 1M HCl (20 mL), extracted in EtOAc (3x10 mL), washed with brine (20 mL), and dried with Na_2SO_4 . This gave a mixture of diastereomers in 1.5:1 ratio favoring the shown isomer. Flash column chromatography on silica gel with 100 mL of hexanes followed by 300 mL of 3% EtOAc in hexanes afforded the desired allylated product in 57% yield (80 mg, 0.36 mmol).

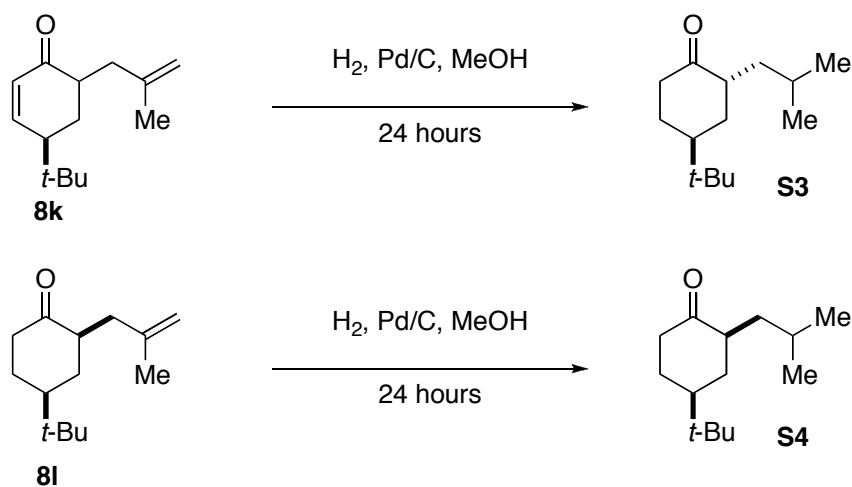
Epimerization Experiments of the 1,3-anti isomer epi-**8l**:



Procedure for Epimerization 1: Allylation product epi-**8l** (prepared by alkylation as described above, 9 mg, 0.04 mmol) was stirred in a solution of NaOMe (2.5 mg, 0.05 mmol) in MeOH (1 mL) at room temperature for 24 hours. The reaction was then quenched with water (1 mL), extracted in ether (2x2 mL), washed with brine (2 mL), and dried with MgSO₄. The crude mixture gave a 9:1 mixture of diastereomers favoring the shown isomer.

Procedure for Epimerization 2: Allylation product epi-**8l** (prepared by alkylation as described above, 7 mg, 0.03 mmol) was stirred in a solution of cerium(IV) ammonium nitrate (0.04 g, 0.07 mmol) and 2,6-di-*tert*-butyl pyridine (0.03 mL, 0.14 mmol) in acetonitrile (1 mL) at -25 °C for 24 hours. The reaction was then quenched with 1M HCl (1 mL), extracted in EtOAc (3x2 mL), washed with brine (2 mL), and dried with Na₂SO₄. The crude mixture gave a 5:1 mixture of diastereomers favoring the shown isomer.

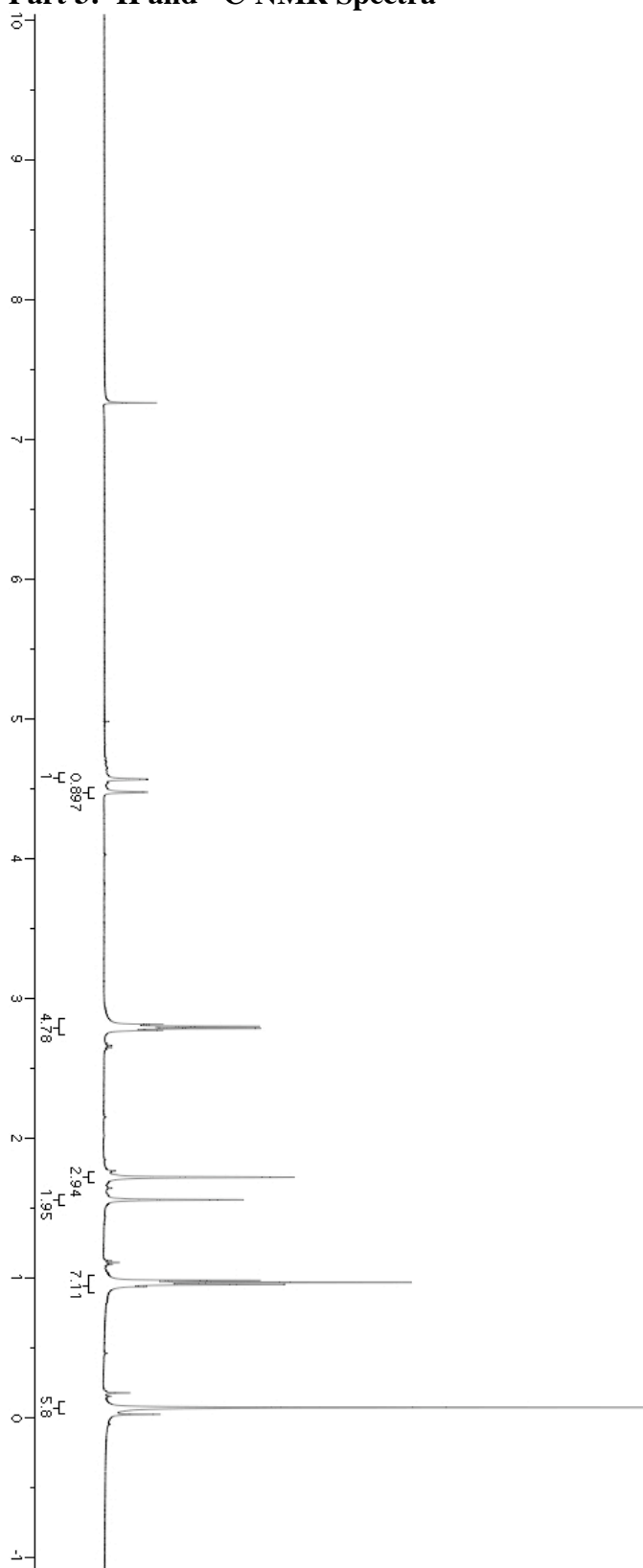
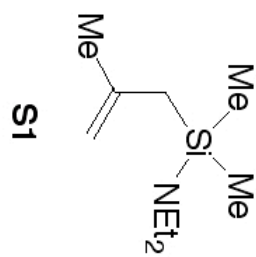
Stereochemical Proof for formation of **8k**:

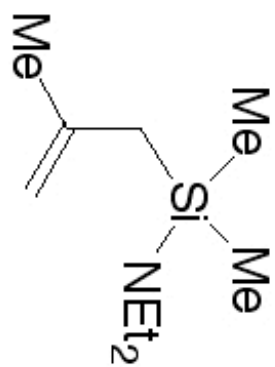


8k (35 mg, 0.17 mmol) and Pd/C (10 mol%) in MeOH (2 mL) were maintained under a balloon of hydrogen at room temperature for 24 hours. The reaction mixture was filtered through a bed of SiO₂ and rinsed with DCM. Removal of the solvent afforded **S3**.

In a separate experiment, **8l** (obtained as a 5:1 mixture of 1,3-syn to 1,3-anti isomers) was subjected to hydrogenation to afford **S4** using the procedure described for the synthesis of **S3**. Comparison of **S3** with the 5:1 mixture obtained from **8l** revealed that **S3** was identical to the minor isomer of **S4** and therefore has 1,3-anti stereochemistry.

Part 3: ^1H and ^{13}C -NMR Spectra





S1

