Supporting Information:

Annulations of Enantioenriched Allenylsilanes with *In Situ* Generated Iminium Ions: Stereoselective Synthesis of Diverse Heterocycles

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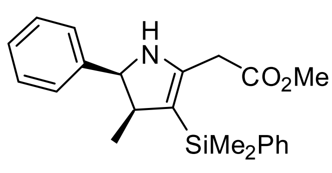
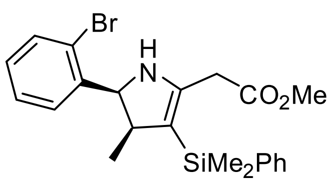
General Information:

All reactions were carried out in oven or flame dried glassware under an atmosphere of argon or nitrogen and using standard techniques for handling air sensitive materials. All solvents were reagent grade. Boron triflouride diethyl etherate was freshly distilled from calcium hydride before use. Trimethylsilyltriflouromethanesulfonate was freshly distilled before use. All other reagents were purchased from Aldrich of Alfa Aesar and used as supplied. All reactions were magnetically stirred and monitored by thin layer chromatography using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash chromatography was performed with silica gel 60 (particle size 0.032-0.063mm) provided by Sorbent Technologies. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. ^{1}H NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Varian 400MHz spectrometer. An internal reference of 7.24 was used for δ_H $CDCl_3$. Data are presented as follows: chemical shift (on a δ scale relative to $\delta_{TMS} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant (*J*/Hz), and integration. Carbon-13 NMR spectra were recorded on a Varian 75 MHz spectrometer. An internal reference of δ_C 77.00 was used for $CDCl_3$. All 2D spectra (Apt, HMBC, HSQC) were recorded on a Varian 400MHz spectrometer. Infrared spectra were recorded on a Nexus 670 FT-IR spectrophotometer. Optical rotations were recorded on an Autopol III digital polarimeter at 589 nm and reported as follows: $[\alpha]_D^{20}$, concentration (*c* in g/100mL) and solvent. High resolution mass spectra were obtained on a Waters Q-TOF mass spectrometer in the Boston University Mass Spectrometry Laboratory.

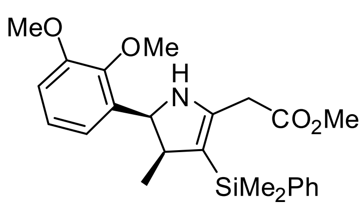
Experimental Procedures:



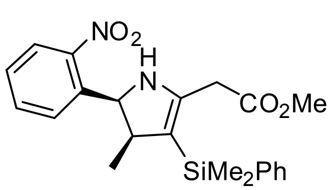
Methyl 2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl-4-methyl-5-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2a): A solution of benzaldehyde (0.064 g., 0.6 mmol) and *tert*-butyl carbamate (0.070 g., 0.6 mmol) in propionitrile (3 mL) was chilled to -78 °C. Boron triflouride diethyl etherate (0.15 mL, 1.2 mmol) was added slowly, followed by a solution of *S*-methyl 3-(dimethyl(phenyl)silyl)hexa-3,4-dienoate (***S**$_a$***-1**) (0.130 g., 0.5 mmol) in propionitrile (2 mL) and the reaction was immediately warmed to -40 °C. The reaction was stirred for 3 days at -40 °C. The reaction was quenched with saturated sodium bicarbonate, and extracted with diethyl ether (2 X 5mL). The combined organic layers were washed with water, dried with magnesium sulfate, filtered and evaporated. Purification over silica gel (gradient elution 10:1 to 10:3 hexanes: ethyl acetate) yields **2a** (0.122 g., 0.334 mmol, 67 % yield) as a clear viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (m, 2H), 7.42 (m, 3H), 7.22 (m, 3H), 6.61 (m, 2H), 6.13 (s, 1H), 4.30 (d, J=4.0, 1H), 3.67 (s, 3H), 3.43 (dd, J=17.2, 46.3, 2H), 2.60 (m, 1H), 0.69 (d, J=7.2, 3H), 0.44 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 157.4, 151.3, 138.8, 136.8, 133.9, 129.4, 128.6, 128.2, 128.0, 125.8, 106.6, 56.0, 51.8, 35.8, 32.4, 11.0, -1.5, -2.4; IR (film) υ_{max} 3253, 2952, 1724, 1634, 1454 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{27}O_2NSi$ $[M+H]^+$ 366.1889, found: 366.1910; $[\alpha]^{20}_D$ +64.8 (c 3.7, CH_2Cl_2).



Methyl 2-((4*S*,5*S*)-5-(2-bromophenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2b): Same procedure as **2a** using 2-bromobenzaldehyde (0.111 g., 0.6 mmol) yields **2b** (0.183 g., 0.412 mmol, 82 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.46 (m, 1H), 7.33 (m, 5H), 7.13 (m, 1H), 6.50 (s, 1H), 4.97 (d, J=4.4, 1H), 3.61 (s, 3H), 3.36 (dd, J=17.2, 22.0, 2H), 3.03 (m, 1H), 0.56 (d, J=7.2, 3H), 0.45 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 156.8, 151.4, 137.8, 136.0, 134.1, 133.3, 129.6, 129.3, 128.2, 128.0, 127.5, 122.3, 107.8, 55.8, 51.7, 32.9, 32.3, 12.2, -1.3, -1.6; IR (film) υ_{max} 3244, 2953, 1722, 1632, 1428 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{26}O_2NBrSi$ $[M+H]^+$ 444.0994, found: 444.0974; $[\alpha]^{20}_D$ +64.8 (c 3.0, CH_2Cl_2).

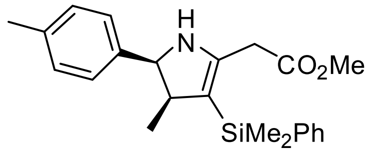


Methyl 2-((4*S*,5*S*)-5-(2,3-dimethoxyphenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2c): Same procedure as **2a** using 2,3-dimethoxybenzaldehyde (0.100 g., 0.6 mmol) yields **2c** (0.128 g., 0.301 mmol, 60 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.29 (m, 3H), 7.33 (m, 5H), 7.06 (t, J=8.0, 1H), 6.85 (m, 2H), 5.97 (s, 1H), 4.97 (d, J=4.0, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 3.59 (s, 3H) 3.23 (dd, J=17.2, 42.0, 2H), 3.02 (m, 1H), 0.54 (d, J=6.8, 3H), 0.51 (s, 3H), 0.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 157.4, 152.5, 151.4, 146.1, 137.7, 134.0, 130.6, 129.2, 127.8, 124.0, 118.0, 112.1, 107.2, 60.3, 55.7, 51.8, 51.7, 33.9, 32.8, 11.4, -1.6, -2.1; IR (film) υ_{max} 3248, 2951, 2838, 1722, 1633, 1480, 1430 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{32}O_4NSi$ $[M+H]^+$ 426.2101, found: 426.2074; $[\alpha]^{20}_D$ +17.2 (c 5.9, CH_2Cl_2).

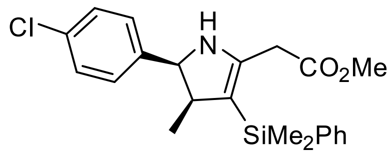


Methyl 2-((4*S*,5*S*)-5-(2-nitrophenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2d): Same procedure as **2a** using 2-nitrobenzaldehyde (0.091 g., 0.6 mmol) yields **2d** (0.102 g., 0.248 mmol, 50 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (m, 1H), 7.56 (m, 5H), 7.28 (m, 3H), 5.29 (d, J=4.4, 1H), 4.97 (s, 1H), 3.63 (s, 3H), 3.34 (dd, J=17.2, 26.4, 2H), 3.21 (m, 1H), 0.59 (s, 3H), 0.53 (d, J=7.2, 3H), 0.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 156.0, 151.4, 148.5, 137.5, 134.0, 133.3, 132.3, 129.3, 129.2, 128.9, 127.8, 125.3, 109.0, 52.6, 51.8, 33.6, 32.9, 12.0, -1.7, -2.5; IR (film)

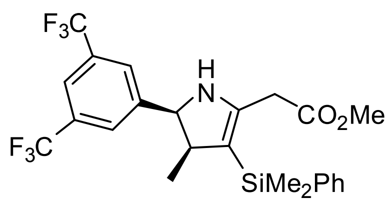
υ_{max} 3245, 2952, 2250, 1721, 1632, 1525, 1348, 1160 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{26}O_4N_2Si$ $[M+H]^+$ 411.1740, found: 411.1750; $[\alpha]^{20}_D$ +66.6 (c 5.1, CH_2Cl_2).



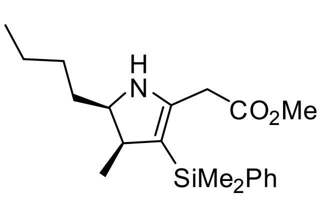
Methyl 2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl)-4-methyl-5-*p*-tolyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2e): Same procedure as **2a** using *p*-tolylaldehyde (0.072 g., 0.6 mmol) yields **2e** (0.127 g., 0.335 mmol, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (m, 2H), 7.42 (m, 3H), 7.02 (d, J=8.0, 2H), 6.50 (d, J=8.0, 2H), 5.74 (s, 1H), 4.27 (d, J=3.2, 1H), 3.68 (s, 3H), 3.46 (dd, J=17.2, 46.4, 2H), 2.57 (m, 1H), 2.27 (s, 3H), 0.70 (d, J=6.8, 3H), 0.43 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 157.6, 151.1, 138.9, 137.9, 133.9, 133.8, 129.4, 129.3, 128.2, 125.8, 106.6, 55.9, 51.8, 35.9, 32.4, 21.0, 11.0, -1.6, -2.4; IR (film) υ_{max} 3247, 2952, 1726, 1635, 1319, 1165 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{23}H_{29}O_2NSi$ $[M+H]^+$ 380.2046, found: 380.2078; $[\alpha]^{20}_D$ +71.4 (c 2.5, CH_2Cl_2).



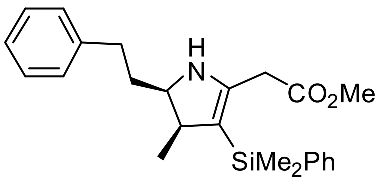
Methyl 2-((4*S*,5*S*)-5-(4-chlorophenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2f): Same procedure as **2a** using 4-chlorobenzaldehyde (0.084 g., 0.6 mmol) yields **2f** (0.137 g., 0.343 mmol, 69 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (m, 2H), 7.42 (m, 3H), 7.19 (d, J=8.4, 2H), 6.50 (d, J=8.4, 2H), 5.15 (s, 1H), 4.25 (d, J=3.2, 1H), 3.70 (s, 3H), 3.45 (dd, J=17.2, 59.2, 2H), 2.57 (m, 1H), 0.70 (d, J=7.2, 3H), 0.45 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 157.1, 151.6, 138.9, 135.3, 133.8, 133.7, 129.4, 128.7, 128.2, 127.2, 106.8, 55.5, 51.8, 35.7, 32.3, 10.9, -1.6, -2.5; IR (film) υ_{max} 3249, 2953, 1722, 1636, 1319, 1163 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{26}O_2NClSi$ $[M+H]^+$ 400.1500, found: 400.1500; $[\alpha]^{20}_D$ +83.3 (c 3.0, CH_2Cl_2).



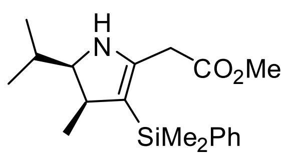
Methyl 2-((4*S*,5*S*)-5-(3,5-bis(triflouromethyl)phenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2g): Same procedure as **2a** using 3,5-bis(triflouromethyl)benzaldehyde (0.145 g., 0.6 mmol) yields **2g** (0.145 g., 0.289 mmol, 58 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.68 (m, 2H), 7.45 (m, 3H), 6.95 (s, 2H), 5.34 (s, 1H), 4.26 (d, J=3.6, 1H), 3.73 (s, 3H), 3.48 (dd, J=17.2, 59.6, 2H), 2.60 (m, 1H), 0.75 (d, J=7.2, 3H), 0.46 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 156.1, 151.6, 139.7, 138.9, 133.8, 132.1, 131.8, 129.9, 128.5, 126.4, 124.3, 122.1, 121.6, 108.4, 55.4, 51.9, 35.1, 32.3, 11.0, -1.7, -2.8; IR (film) υ_{max} 3249, 2956, 1732, 1637, 1380, 1277, 1171, 1132 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{25}O_2NF_6Si$ $[M+H]^+$ 502.1637, found: 502.1634; $[\alpha]^{20}_D$ +69.3 (c 2.2, CH_2Cl_2).



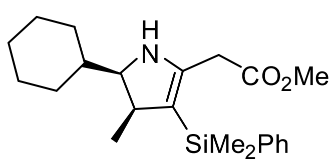
Methyl 2-((4*S*,5*R*)-5-butyl-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2h): Same procedure as **2a** using valeraldehyde (0.052 g., 0.6 mmol) yields **2h** (0.099 g., 0.211 mmol, 57 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 2H), 7.33 (m, 3H), 4.82 (s, 1H), 3.66 (s, 3H), 3.37 (dd, J=17.2, 48.8, 2H), 3.08 (m, 1H), 2.47 (m, 1H), 1.15 (m, 4H), 0.80 (d, J=7.2, 3H), 0.70 (m, 5H), 0.44 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 158.3, 151.3, 138.5, 133.7, 129.3, 128.0, 105.5, 51.8, 51.7, 32.4, 31.9, 30.5, 26.5, 22.2, 13.9, 9.9, -1.7, -2.1; IR (film) υ_{max} 3255, 2954, 2872, 1725, 1633, 1163 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{20}H_{31}O_2NSi$ $[M+H]^+$ 346.2202, found: 346.2220; $[\alpha]_D^{20}$ +71.2 (c 3.3, CH_2Cl_2).



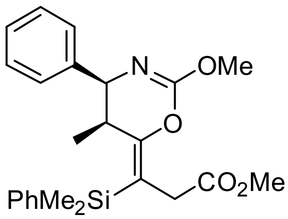
Methyl 2-((4*S*,5*R*)-3-(dimethyl(phenyl)silyl)-4-methyl-5-phenethyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2i): Same procedure as **2a** using hydrocinnamaldehyde (0.081 g., 0.6 mmol) yields **2i** (0.094 g., 0.239 mmol, 49 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.35 (m, 3H), 7.27 (m, 3H), 7.00 (m, 2H), 4.87 (s, 1H), 3.66 (s, 3H), 3.30 (dd, J=17.2, 43.2, 2H), 3.17 (m, 1H), 2.52 (m, 1H), 2.10 (m, 2H), 1.46 (m, 1H), 0.84 (d, J=7.2, 3H), 0.44 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 158.0, 151.2, 140.3, 138.5, 133.7, 129.4, 128.5, 128.2, 128.1, 126.2, 105.8, 51.8, 51.8, 32.6, 32.4, 32.2, 30.8, 10.0, -1.7, -2.1; IR (film) υ_{max} 3253, 2950, 1724, 1633, 1161 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{31}O_2NSi$ $[M+H]^+$ 394.2202, found: 394.2231; $[\alpha]_D^{20}$ +53.1 (c 1.9, CH_2Cl_2).



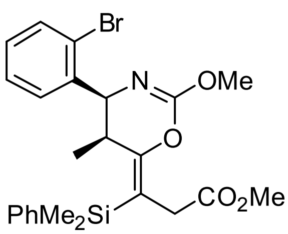
Methyl 2-((4*S*,5*R*)-3-(dimethyl(phenyl)silyl)-4-methyl-5-isopropyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2j): Same procedure as **2a** using isobutyraldehyde (0.043 g., 0.6 mmol) yields **2j** (0.054 g., 0.163 mmol, 33 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 2H), 7.33 (m, 3H), 5.73 (s, 1H), 3.65 (s, 3H), 3.37 (dd, 2H), 3.64 (dd, J=17.2, 52.4 1H), 2.55 (m, 1H), 1.34 (m, 1H), 0.82 (d, J=6.4, 3H), 0.75 (d, J=6.8, 3H), 0.42 (s, 3H), 0.33 (s, 3H), 0.32 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 158.2, 151.3, 138.5, 133.7, 129.3, 128.0, 105.4, 58.5, 51.8, 51.7, 32.4, 31.7, 28.3, 19.1, 17.5, 10.0, -1.7, -2.1; IR (film) υ_{max} 3269, 2967, 2901, 1723, 1633, 1165 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{19}H_{29}O_2NSi$ $[M+H]^+$ 332.2046, found: 332.2020; $[\alpha]_D^{20}$ +62.1 (c 2.3, CH_2Cl_2).



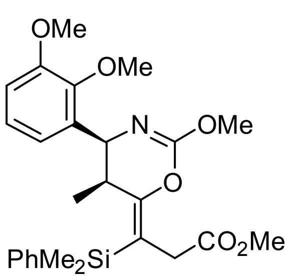
Methyl 2-((4*S*,5*R*)-5-cyclohexyl-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (2k): Same procedure as **2a** using cyclohexanecarboxaldehyde (0.067 g., 0.6 mmol) yields **2k** (0.068 g., 0.183 mmol, 37 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 2H), 7.33 (m, 3H), 5.10 (s, 1H), 3.66 (s, 3H), 3.37 (dd, J=17.2, 57.2, 2H), 2.72 (dd, 1H), 2.57 (m, 1H), 1.60 (m, 4H), 1.00 (m, 6H), 0.75 (d, J=6.8, 3H), 0.70 (m, 5H), 0.42 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 158.3, 151.0, 138.5, 133.8, 129.3, 128.0, 105.5, 57.1, 51.8, 37.1, 32.3, 31.1, 29.3, 27.3, 25.9, 25.3, 25.2, 10.1, -1.7, -2.0; IR (film) υ_{max} 2925, 2851, 1725, 1633, 1157 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{33}O_2NSi$ $[M+H]^+$ 372.2359, found: 372.2361; $[\alpha]_D^{20}$ +43.7 (c 2.4, CH_2Cl_2).



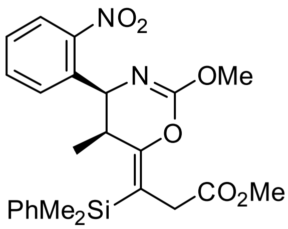
(*E*)-Methyl 3-(dimethyl(phenyl)silyl)-3-((4*S*,5*S*)-2-methoxy-5-methyl-4-phenyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)propanoate (3a): A solution of benzaldehyde (0.064 g., 0.6 mmol), methyl carbamate (0.045 g., 0.6 mmol) and *S*-methyl 3-(dimethyl(phenyl)silyl)hexa-3,4-dienoate (***S**$_a$***-1**) (0.130 g., 0.5 mmol) in dichloromethane (1.0 mL) was chilled to -60 °C. Trimethylsilyltriflouromethanesulfonate (0.116 mL, 0.6 mmol) was added slowly, and the reaction was stirred 48 hours at -60 °C. The reaction was quenched with saturated sodium bicarbonate, and extracted with dichloromethane (2 X 5 mL). The combined organic layers were washed with water, dried with magnesium sulfate, filtered and evaporated. Purification over silica gel (97:3 hexanes: ethyl acetate) yields **3a** (0.133 g., 0.314 mmol, 63 % yield) as a clear viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (m, 2H), 7.41 (m, 3H), 7.15 (m, 3H), 6.76 (m, 2H), 4.34 (d, J=4.0, 1H), 3.85 (s, 3H), 3.68 (s, 3H), 3.39 (d, J=2.4, 2H), 2.61 (m, 1H), 0.49 (d, J=7.2, 3H), 0.45 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 159.2, 150.5, 140.8, 138.7, 133.7, 129.2, 128.1, 127.9, 126.5, 126.4, 103.9, 57.0, 55.0, 51.7, 35.3, 32.1, 11.0, -1.5, -2.0; IR (film) υ_{max} 3023, 2951, 1738, 1686, 1643, 1438, 1284, 1166 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{29}O_4NSi$ $[M+H]^+$ 424.1944, found: 424.1940; $[\alpha]_D^{20}$ +115.2 (c 2.3, CH_2Cl_2).



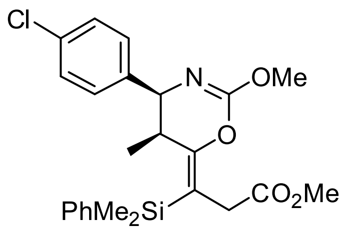
(*E*)-Methyl 3-((4*S*,5*S*)-4-(2-bromophenyl)-2-methoxy-5-methyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)-3-(dimethyl(phenyl)silyl)propanoate (3b): Same procedure as **3a** using 2-bromobenzaldehyde (0.111 g., 0.6 mmol) yields **3b** (0.204 g., 0.406 mmol, 81 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 2H), 7.43 (m, 1H), 7.43 (d, J=8.4, 1H), 7.30 (m, 4H), 7.07 (m, 1H), 4.88 (d, J=4.0, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 3.32 (s, 2H), 3.06 (m, 1H), 0.46 (s, 3H), 0.45 (s, 3H), 0.42 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 158.4, 150.7, 139.8, 138.0, 134.0, 132.3, 130.3, 129.1, 128.3, 127.8, 126.8, 122.2, 105.1, 57.5, 54.8, 51.6, 32.6, 31.9, 12.1, -1.3, -1.4; IR (film) υ_{max} 3067, 2950, 1738, 1686, 1638, 1439, 1294, 1164 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{28}O_4NBrSi$ $[M+H]^+$ 502.1049, found: 502.1066; $[\alpha]_D^{20}$ +115.2 (c 2.3, CH_2Cl_2).



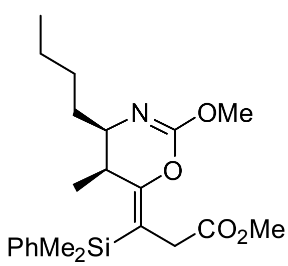
(*E*)-Methyl 3-((4*S*,5*S*)-4-(2,3-dimethoxyphenyl)-2-methoxy-5-methyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)-3-(dimethyl(phenyl)silyl)propanoate (3c): Same procedure as **3a** using 2,3-dimethoxybenzaldehyde (0.100 g., 0.6 mmol) yields **3c** (0.130 g., 0.269 mmol, 54 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.29 (m, 2H), 7.08 (m, 1H), 7.01 (t, J=8.0 1H), 6.81 (m, 1H), 4.89 (d, J=4.0, 1H), 3.85, (s, 3H), 3.85 (s, 3H), 3.68 (s, 3H), 3.60 (s, 3H), 3.27 (s, 2H), 3.09 (m, 1H), 0.51 (s, 3H), 0.45 (s, 3H), 0.39 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 159.1, 152.1, 150.6, 146.0, 138.0, 134.6, 134.0, 129.0, 127.7, 123.3, 120.7, 110.9, 104.7, 60.0, 55.6, 54.8, 53.7, 51.6, 33.5, 32.6, 11.6, -1.6, -2.0; IR (film) υ_{max} 2951, 2837, 1738, 1691, 1478, 1438, 1286, 1166 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{26}H_{33}O_6NSi$ $[M+H]^+$ 484.2155, found: 484.2137; $[\alpha]^{20}_{D}$ +40.0 (c 1.0, CH_2Cl_2).



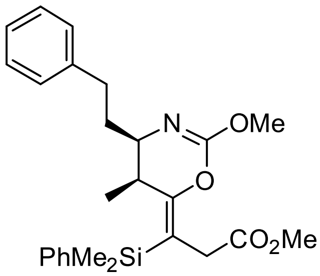
(*E*)-Methyl 3-(dimethyl(phenyl)silyl)-3-((4*S*,5*S*)-2-methoxy-5-methyl-4-(2-nitrophenyl)-4*H*-1,3-oxazin-6(5*H*)-ylidene)propanoate (3d): Same procedure as **3a** using 2-nitrobenzaldehyde (0.091 g., 0.6 mmol) yields **2d** (0.135 g., 0.288 mmol, 58 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (m, 1H), 7.68 (m, 1H), 7.54 (m, 3H), 7.38 (m, 1H), 7.28 (m, 3H), 5.31 (d, J=4.0, 1H), 3.82, (s, 3H), 3.63 (s, 3H), 3.27 (dd, J=16.8, 10.0, 2H), 2.97 (m, 1H), 0.55 (s, 3H), 0.42 (s, 3H), 0.31 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 157.7, 150.9, 148.2, 137.9, 136.0, 134.0, 132.5, 130.9, 129.1, 127.8, 127.8, 124.5, 106.0, 54.9, 54.4, 51.7, 33.4, 32.6, 11.8, -1.7, -2.5; IR (film) υ_{max} 3070, 2951, 1738, 1691, 1525, 1441, 1295, 1165 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{28}O_6N_2Si$ $[M+H]^+$ 469.1795, found: 469.1804; $[\alpha]^{20}_{D}$ -50.0 (c 1.1, CH_2Cl_2).



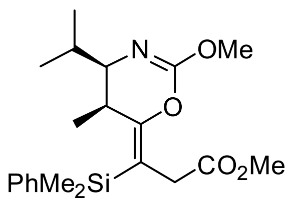
(*E*)-Methyl 3-((4*S*,5*S*)-4-(4-chlorophenyl)-2-methoxy-5-methyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)-3-(dimethyl(phenyl)silyl)propanoate (3e): Same procedure as **3a** using 4-chlorobenzaldehyde (0.084 g., 0.6 mmol) yields **3e** (0.136 g., 0.297 mmol, 59 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (m, 2H), 7.40 (m, 3H), 7.13 (m, 2H), 6.63 (d, J=8.4, 2H), 4.27 (d, J=3.6, 1H), 3.84, (s, 3H), 3.69 (s, 3H), 3.39 (d, J=6.4, 2H), 2.56 (m, 1H), 0.47 (d, J=6.8, 3H) 0.44 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 158.8, 150.7, 139.4, 138.8, 133.7, 132.1, 129.3, 128.1, 128.0, 127.9, 104.2, 56.6, 55.0, 51.8, 35.1, 32.1, 10.9, -1.6, -2.1; IR (film) υ_{max} 2951, 1738, 1686, 1644, 1490, 1439, 1290, 1166 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{28}O_4NSiCl$ $[M+H]^+$ 458.1554, found: 458.1547; $[\alpha]^{20}_{D}$ +92.5 (c 2.2, CH_2Cl_2).



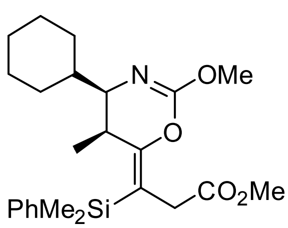
(*E*)-Methyl 3-((4*R*,5*S*)-4-butyl-2-methoxy-5-methyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)-3-(dimethyl(phenyl)silyl)propanoate (3f): Same procedure as **3a** using valeraldehyde (0.052 g., 0.6 mmol) yields **3f** (0.123 g., 0.305 mmol, 61 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 2H), 7.32 (m, 3H), 3.70, (s, 3H), 3.64 (s, 3H), 3.20 (d, J=3.2, 2H), 3.00 (m, 1H), 2.38 (m, 1H), 1.35 (m, 1H), 1.14 (m, 3H), 0.83 (m, 5H), 0.68 (d, J=6.8, 3H) 0.43 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 160.1, 149.3, 138.6, 133.7, 129.1, 127.9, 102.8, 54.7, 54.1, 51.7, 33.1, 32.3, 32.2, 27.7, 22.5, 14.0, 10.3, -1.7, -1.8; IR (film) υ_{max} 2953, 2860, 1740, 1687, 1437, 1283, 1166 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{33}O_4NSi$ $[M+H]^+$ 404.2257, found: 404.2224; $[\alpha]^{20}_{D}$ +59.1 (c 1.1, CH_2Cl_2).



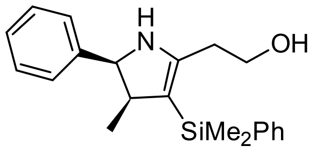
(*E*)-Methyl 3-(dimethyl(phenyl)silyl)-3-((4*R*,5*S*)-2-methoxy-5-methyl-4-phenethyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)propanoate (3g): Same procedure as **3a** using hydrocinnamaldehyde (0.081 g., 0.6 mmol) yields **3g** (0.086 g., 0.190 mmol, 38 % yield).). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 2H), 7.32 (m, 3H), 7.19 (m, 3H), 7.07 (m, 2H), 3.72, (s, 3H), 3.64 (s, 3H), 3.30 (s, 2H), 3.08 (m, 1H), 2.38 (m, 2H), 2.26 (m, 1H), 1.35 (m, 1H), 0.72 (d, J=7.2, 3H) 0.42 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 159.8, 149.5, 142.1, 138.6, 133.7, 129.2, 128.3, 128.2, 127.9, 125.6, 103.1, 54.8, 53.8, 51.7, 35.0, 32.7, 32.2, 31.9, 10.6, -1.7, -1.8; IR (film) υ_{max} 3025, 2950, 1738, 1686, 1438, 1285, 1164 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{26}H_{33}O_4NSi$ $[M+H]^+$ 452.2257, found: 452.2233; $[\alpha]_D^{20}$ +94.3 (c 1.1, CH_2Cl_2).



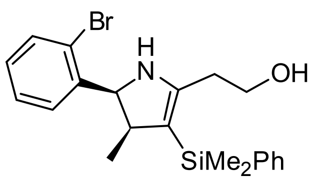
(*E*)-Methyl 3-(dimethyl(phenyl)silyl)-3-((4*R*,5*S*)-4-isopropyl-2-methoxy-5-methyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)propanoate (3h): Same procedure as **3a** using isobutyraldehyde (0.043 g., 0.6 mmol) yields **3h** (0.091 g., 0.234 mmol, 48 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 2H), 7.32 (m, 3H), 3.71, (s, 3H), 3.65 (s, 3H), 3.30 (dd, J=17.2, 12.0, 2H), 3.50 (m, 2H), 2.38 (m, 1H), 1.30 (m, 1H), 0.93 (d, J=6.4, 3H), 0.84 (d, J=6.8, 3H), 0.42 (s, 3H), 0.35 (d, J=6.8, 3H), 0.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 160.3, 149.2, 138.6, 133.7, 129.1, 127.9, 102.7, 60.7, 54.7, 51.7, 32.1, 31.3, 30.2, 20.0, 18.1, 10.4, -1.7, -1.8; IR (film) υ_{max} 2956, 2872, 1740, 1691, 1438, 1287, 1200, 1167 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{21}H_{31}O_4NSi$ $[M+H]^+$ 390.2101, found: 390.2092; $[\alpha]_D^{20}$ +93.7 (c 1.6, CH_2Cl_2).



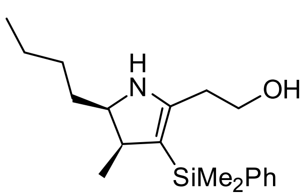
(*E*)-Methyl 3-(dimethyl(phenyl)silyl)-3-((4*R*,5*S*)-4-cyclohexyl-2-methoxy-5-methyl-4*H*-1,3-oxazin-6(5*H*)-ylidene)propanoate (3i): Same procedure as **3a** using cyclohexanecarboxaldehyde (0.067 g., 0.6 mmol) yields **3i** (0.104 g., 0.242 mmol, 48 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.32 (m, 3H), 3.70, (s, 3H), 3.64 (s, 3H), 3.29 (dd, J=17.2, 10.8, 2H), 2.58 (m, 1H), 2.50 (m, 1H), 2.25 (d, J=13.2, 1H), 1.65 (m, 2H), 1.05 (m, 6H) 0.66 (m, 1H), 0.64 (d, J=6.8, 3H), 0.41 (s, 3H), 0.33 (s, 3H), 0.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 160.3, 149.2, 138.6, 133.7, 129.1, 127.9, 102.6, 59.3, 54.6, 51.7, 39.3, 32.1, 30.8, 30.2, 28.5, 26.6, 25.9, 25.9, 10.4, -1.7, -1.8; IR (film) υ_{max} 2925, 2850, 1740, 1689, 1641, 1438, 1286, 1200, 1166 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{35}O_4NSi$ $[M+H]^+$ 430.2414, found: 430.2440; $[\alpha]_D^{20}$ +94.5 (c 2.3, CH_2Cl_2).



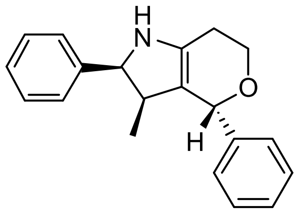
2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl)-4-methyl-5-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (4a): A solution of Methyl 2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl-4-methyl-5-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (**2a**) (0.92 g., 2.52 mmol) in DCM (15 mL) was chilled to -78 °C. DIBAL-H (1.0M in DCM, 10.08 mL, 10.08 mmol) was added dropwise, and the solution was slowly warmed to 0 °C and stirred 12 hours. The reaction was quenched by pouring onto a rapidly stirring mixture of sat. aqueous Rochelle's salt and DCM. The organics are extracted with DCM (3 X 5 mL), washed with sat. $NaHCO_3$, then water, dried with $MgSO_4$, filtered and concentrated under vacuum. Purification over silica gel (98:2 DCM:MeOH) yields **4a** (0.64 g., 1.90 mmol, 75 % yield) as a viscous clear oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 2H), 7.41 (m, 3H), 7.22 (m, 3H), 6.62 (m, 2H), 5.89 (s, 1H), 4.27 (d, J=3.6, 1H), 3.69 (m, 2H), 3.62 (m, 2H), 2.57 (m, 1H), 2.00 (s, 1H), 0.67 (d, J=6.8, 3H), 0.42 (s, 3H), 0.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.8, 151.7, 139.2, 137.0, 133.7, 129.4, 128.6, 128.2, 128.0, 125.8, 110.4, 62.5, 56.3, 35.9, 31.1, 11.3, -1.0, -1.9; IR (film) υ_{max} 3400, 3259, 2954, 2878, 1723, 1632, 1455, 1172 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{21}H_{27}ONSi$ $[M+H]^+$ 338.1940, found: 338.1970; $[\alpha]^{20}_D$ +50.0 (c 3.4, CH_2Cl_2).



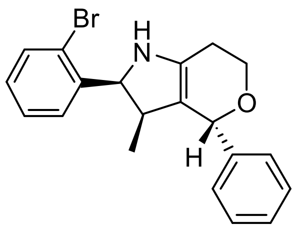
2-((4*S*,5*S*)-5-(2-bromophenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (4b): The same procedure as **4a** using Methyl 2-((4*S*,5*S*)-5-(2-bromophenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (**2b**) (1.20 g., 2.70 mmol), yields **4b** (0.75 g. 1.80 mmol, 67 % yield) as a clear viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (m, 3H), 7.32 (m, 5H), 7.16 (m, 1H), 5.28 (s, 1H), 4.96 (d, J=4.0, 1H), 3.66 (m, 2H), 3.02 (m, 1H), 2.61 (m, 2H), 1.59 (s, 1H), 0.59 (d, J=7.2, 3H), 0.48 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 151.9, 138.2, 136.1, 133.9, 133.3, 129.6, 129.3, 128.2, 128.0, 127.5, 122.3, 111.2, 62.2, 56.0, 32.3, 31.6, 12.4, -0.9, -1.1; IR (film) υ_{max} 3400, 3253, 2953, 1721, 1628, 1387, 1171 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{21}H_{26}ONSiBr$ $[M+H]^+$ 416.1045, found: 416.1078; $[\alpha]^{20}_D$ +4.1 (c 1.2, CH_2Cl_2).



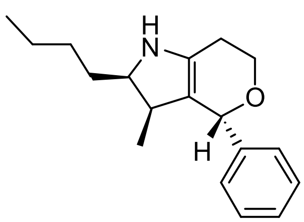
2-((4*S*,5*R*)-5-butyl-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (4c): The same procedure as **5a** using Methyl 2-((4*S*,5*R*)-5-butyl-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (**2h**) (0.51 g., 1.48 mmol), yields **4c** (0.37 g., 1.17 mmol, 79 % yield) as a clear viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H), 7.33 (m, 3H), 5.11 (s, 1H), 3.65 (m, 2H), 3.06 (m, 1H), 2.56 (m, 2H), 2.44 (m, 1H), 1.50 (s, 1H), 1.14 (m, 4H), 0.71 (m, 8H), 0.44 (s, 3H), 0.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 151.8, 138.8, 133.5, 129.2, 128.0, 109.0, 62.5, 52.0, 31.9, 31.1, 30.5, 26.5, 22.2, 13.9, 10.1, -1.3, -1.7; IR (film) υ_{max} 3400, 3259, 2955, 2872, 1725, 1631, 1391, 1177 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{19}H_{31}ONSi$ $[M+H]^+$ 318.2253, found: 318.2265; $[\alpha]^{20}_D$ +62.5 (c 1.2, CH_2Cl_2).



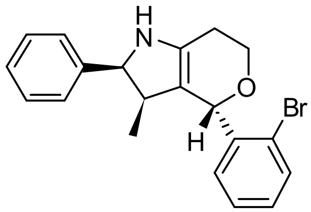
(2*S*, 3*R*, 4*R*)-3-methyl-2,4-diphenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5a): A solution of 2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl)-4-methyl-5-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (**4a**) (0.048 g., 0.142 mmol) and benzaldehyde (0.030 g., 0.284 mmol) in DCM (1 mL) was chilled to -20 °C. Trimethylsilyltriflouromethanesulfonate (33 μL, 0.171 mmol) was added slowly, and the resulting solution was stirred for 12 hours at -20 °C. The reaction was quenched with saturated sodium bicarbonate, and extracted with dichloromethane (2 X 5 mL). The combined organic layers were washed with water, dried with magnesium sulfate, filtered and evaporated. Purification over silica gel (90:10 DCM: ethyl acetate) yields **5a** (0.037 g., 0.127 mmol, 89 % yield) as a clear viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 5H), 7.37 (m, 3H), 6.70 (m, 2H), 5.30 (s, 1H), 5.22 (s, 1H), 4.19 (m, 1H), 4.15 (d, J=4.0, 1H), 3.87 (m, 1H), 2.94 (m, 2H), 2.31 (m, 1H), 0.76 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 143.5, 141.0, 136.8, 128.8, 128.7, 128.6, 128.1, 128.1, 125.8, 121.9, 80.6, 67.7, 56.2, 32.9, 30.1, 10.4; IR (film) υ_{max} 3274, 2980, 2892, 1747, 1706, 1455, 1235 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{20}H_{21}ON$ $[M+H]^+$ 292.1701, found: 292.1729; $[\alpha]_D^{20}$ +97.0 (c 3.0, CH_2Cl_2).



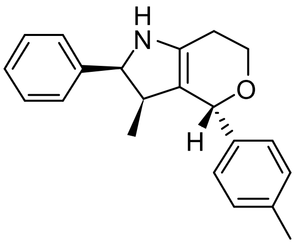
(2*S*, 3*R*, 4*R*)-2-(2-bromophenyl)-3-methyl-4-phenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5b): Same procedue as **5a** using 2-((4*S*,5*S*)-5-(2-bromophenyl)-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (**4b**)(0.044 g., 0.106 mmol) and benzaldehyde (0.022 g., 0.212 mmol) yields **5b** (0.037 g., 0.100 mmol, 94 % yield) as a viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 5H), 7.30 (m, 3H), 7.12 (m, 1H), 5.37 (s, 1H), 5.10 (s, 1H), 4.73 (d, J=4.0, 1H), 4.10 (m, 1H), 3.89 (m, 1H), 3.05 (m, 1H), 2.86 (m, 2H), 0.82 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 143.5, 140.6, 135.8, 133.4, 129.7, 129.2, 128.6, 128.3, 127.6, 127.5, 122.5, 122.1, 80.5, 67.2, 55.6, 30.3, 29.6, 11.7; IR (film) υ_{max} 3265, 2980, 1751, 1708, 1457, 1226 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{20}H_{20}ONBr$ $[M+H]^+$ 370.0807, found: 370.0822; $[\alpha]_D^{20}$ +119.2 (c 1.3, CH_2Cl_2).



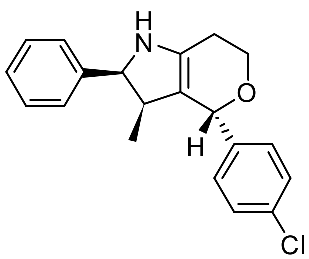
(2*R*, 3*R*, 4*R*)-2-butyl-3-methyl-4-phenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5c): Same procedure as **5a** using 2-((4*S*,5*R*)-5-butyl-3-(dimethyl(phenyl)silyl)-4-methyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (**4c**)(0.065 g., 0.205 mmol) and benzaldehyde (0.041 g., 0.410 mmol) yields **5c** (0.052 g., 0.192 mmol, 93 % yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 5H), 5.29 (s, 1H), 4.85 (s, 1H), 4.11 (m, 1H), 3.85 (q, 1H), 2.94 (m, 2H), 2.81 (m, 1H), 1.14 (m, 2H), 1.00 (m, 2H), 0.94 (d, J=7.2, 3H) 0.73, (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 144.4, 140.7, 128.7, 128.5, 127.8, 120.5, 80.5, 67.5, 51.5, 30.2, 29.9, 28.8, 26.5, 21.9, 13.9, 9.4; IR (film) υ_{max} 3256, 3133, 2933, 2870, 1741, 1705, 1456, 1387, 1053 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{18}H_{25}ON$ $[M+H]^+$ 272.2014, found: 272.2054; $[\alpha]_D^{20}$ +44.2 (c 0.7, CH_2Cl_2).



(2*S*, 3*R*, 4*S*)-4-(2-bromophenyl)-3-methyl-2-phenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5d): Same procedure as **5a** using **4a** (0.055 g., 0.163 mmol) and 2-bromobenzaldehyde (0.060 g., 0.326 mmol) yields **5e** (0.047 g., 0.127 mmol, 78 % yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J=8.0, 1H), 7.40 (d, J=4.4, 2H), 7.27 (m, 4H), 6.71 (m, 2H), 5.77 (s, 1H), 5.23 (s, 1H), 4.20 (m, 1H), 4.14 (d, J=3.6, 1H), 3.90 (m, 1H), 2.98 (m, 2H), 2.24 (m, 1H), 0.81 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.6, 143.6, 139.8, 136.7, 133.2, 130.1, 129.9, 128.8, 128.2, 128.0, 125.7, 124.7, 121.6, 79.2, 67.8, 56.3, 33.2, 30.3, 10.6; IR (film) υ_{max} 3254, 2925, 1739, 1701, 1455, 1378 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{20}H_{20}ONBr$ $[M+CO_2H^1]^+$ 414.0705, found: 414.0688; $[\alpha]^{20}_{D}$ +19.1 (c 1.2, CH_2Cl_2).

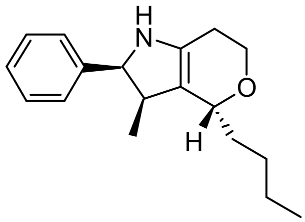


(2*S*, 3*R*, 4*R*)-3-methyl-2-phenyl-4-*p*-tolyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5e): Same procedure as **5a** using **4a** (0.047 g., 0.139 mmol) and *p*-tolualdehyde (0.033 g., 0.278 mmol) yields **5e** (0.028 g., 0.092 mmol, 66 % yield) white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (m, 7H), 6.71 (m, 2H), 5.26 (s, 1H), 5.11 (s, 1H), 4.17 (d, J=4.0, 1H), 4.14 (m, 1H), 3.86 (m, 1H), 2.92 (m, 2H), 2.41 (s, 3H), 2.30 (m, 1H), 0.75 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5, 143.4, 138.5, 138.0, 137.0, 129.5, 128.8, 128.2, 128.1, 125.8, 122.2, 80.5, 67.6, 56.4, 32.8, 30.1, 10.4; IR (film) υ_{max} 3261, 2923, 1739, 1702, 1455, 1377 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{21}H_{23}ON$ $[M+CO_2H^1]^+$ 370.1756, found: 370.1770; $[\alpha]^{20}_{D}$ +28.0 (c 1.5, CH_2Cl_2).

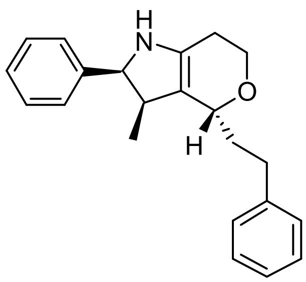


(2*S*, 3*R*, 4*R*)-4-(4-chlorophenyl)-3-methyl-2-phenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5f): Same procedure as **5a** using **4a** (0.040 g., 0.119 mmol) and *p*-chlorobenzaldehyde (0.033 g., 0.238 mmol) yields **5f** (0.037 g., 0.114 mmol, 95 % yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 2H), 7.32 (m, 5H), 6.77 (m, 2H), 5.27 (s, 1H), 5.15 (s, 1H), 4.19 (d, J=4.0, 1H), 4.14 (m, 1H), 3.87 (m, 1H), 2.98 (m, 1H), 2.87 (m, 1H), 2.26 (m, 1H), 0.78 (d, J=6.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5, 143.8, 139.5, 136.6, 134.5, 129.5, 129.0, 128.9, 128.3, 125.8, 121.5, 79.8, 67.7, 56.4, 33.1, 30.0, 10.5; IR (film) υ_{max} 3264, 2933, 1739, 1702, 1455, 1378 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{20}H_{20}ONCl$ $[M+H]^+$ 326.1312, found: 306.1348; $[\alpha]^{20}_{D}$ +35.5 (c 1.4, CH_2Cl_2).

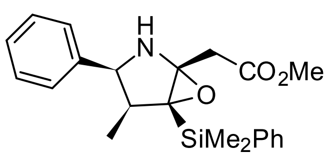
[1] The pyranopyrrole products were reactive with the formic acid used in the mass spec procedure, giving a spectra with a mixture of the pyranopyrrole product and the product plus formate in all cases. In a few of the cases the formate product was the major product, and it is the reported mass in the data.



(2*S*, 3*R*, 4*R*)-4-butyl-3-methyl-2-phenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5g): A solution of 2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl)-4-methyl-5-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)ethanol (**4a**) (0.048 g., 0.142 mmol) and valeraldehyde (0.030 g., 0.284 mmol) in MeCN (1 mL) was chilled to -20 °C. Boron triflouride diethyl etherate (21 μL, 0.171 mmol) was added slowly, and the resulting solution was stirred for 12 hours at -20 °C. The reaction was quenched with saturated sodium bicarbonate, and extracted with dichloromethane (2 X 5mL). The combined organic layers were washed with water, dried with magnesium sulfate, filtered and evaporated. Purification over silica gel (90:10 DCM: ethyl acetate) yields **5g** (0.024 g., 0.088 mmol, 62 % yield) as a clear viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.23 (m, 2H), 5.42 (s, 1H), 4.74 (d, J=4.0, 1H), 4.46 (m, 1H), 3.98 (m, 1H), 2.82 (m, 1H), 2.86 (m, 1H), 2.74 (m, 1H), 2.59 (m, 1H), 1.44 (m, 6H), 0.94 (m, 3H), 0.89 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5, 141.5, 137.2, 129.1, 128.6, 126.2, 121.8, 77.6, 66.6, 57.5, 34.7, 34.0, 29.7, 28.4, 27.7, 22.7, 14.1, 11.2; IR (film) υ_{max} 3254, 2931, 2871, 1736, 1705, 1456, 1379, 1073 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{18}H_{25}ON$ $[M+H]^+$ 272.2014, found: 272.2072; $[\alpha]_D^{20}$ +14.0 (c 1.0, CH_2Cl_2).



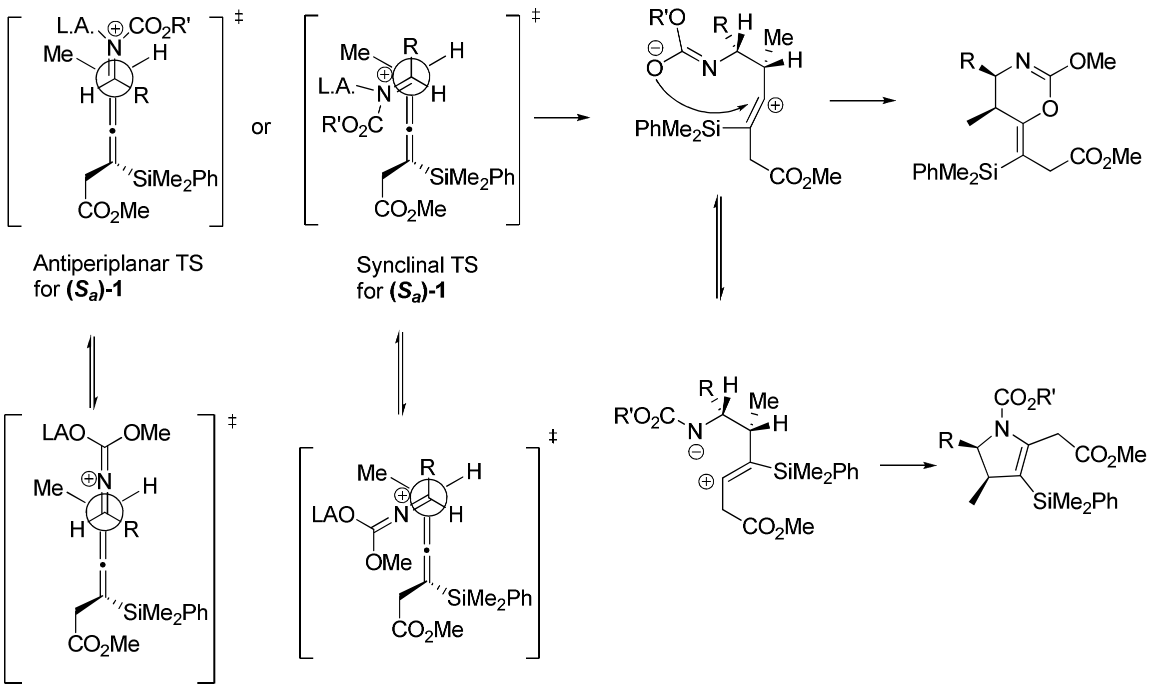
(2*S*, 3*R*, 4*R*)-3-methyl-4-phenethyl-2-phenyl-1,2,3,4,6,7-hexahydropyrano[4,3-*b*]pyrrole (5h): Same procedure as **5g** using **4a** (0.040 g., 0.119 mmol) and hydrocinnamaldehyde (0.032 g., 0.237 mmol) yields **5h** (0.022 g., 0.069 mmol, 58 % yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 5H), 7.20 (m, 5H), 5.45 (s, 1H), 4.67 (d, J=3.6, 1H), 4.49 (m, 1H), 4.02 (m, 1H), 3.87 (q, 1H), 2.86 (m, 1H), 2.83 (m, 1H), 2.64 (m, 2H), 1.96 (m, 1H), 1.79 (m, 1H), 0.82 (d, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5, 141.7, 137.1, 129.0, 128.6, 128.5, 128.4, 126.1, 126.0, 121.5, 76.7, 66.8, 57.4, 36.8, 33.9, 31.8, 28.5, 11.1; IR (film) υ_{max} 3254, 2924, 1738, 1703, 1455, 1379, 1032 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{20}H_{25}ON$ $[M+H]^+$ 320.2014, found: 320.1995; $[\alpha]_D^{20}$ +13.0 (c 1.0, CH_2Cl_2).



6

Methyl 2-((1*R*, 3*S*, 4*S*, 5*S*)-5-(dimethyl(phenyl)silyl)-4-methyl-3-phenyl-6-oxa-2-azabicyclo[3.1.0]hexan-1-yl)acetate (6): A solution of mCPBA (0.390 g. of a 75% solution, 1.30 mmol) in DCM (5 mL) was chilled to 0 °C. A solution of Methyl 2-((4*S*,5*S*)-3-(dimethyl(phenyl)silyl-4-methyl-5-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)acetate (**2a**) (0.318 g., 0.870 mmol) in DCM (5 mL) was added dropwise and the resulting solution was stirred 12 hours warming slowly from 0 °C to room temperature. The reaction was quenched with sat. $Na_2S_2O_3$ (10 mL), and extracted with DCM (3 X 10 mL). The combined organic layers were washed with water, dried with $MgSO_4$, filtered and concentrated under vacuum. Purification over silica gel (70:30 hexanes: ethyl acetate) yields **6** (0.262 g., 0.687 mmol, 79 % yield) as a clear viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 2H), 7.39 (m, 6H), 7.00 (m, 2H), 5.25 (s, 1H), 4.79 (d, J=3.6, 1H), 3.62 (s, 3H), 3.93 (dd, J=17.2, 10.0, 2H), 2.56 (m, 1H), 0.74 (d, J=6.8, 3H), 0.49 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 152.8, 136.9, 134.7, 134.3, 130.0, 128.6, 128.0, 127.9, 125.8, 91.2, 61.8, 54.8, 51.6, 36.4, 35.7, 9.1, -3.7, -3.8; IR (film) υ_{max} 3256, 3138, 3070, 2953, 2248, 1731, 1455, 1325, 1168 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{27}O_3NSi$ $[M+H]^+$ 382.1892, found: 382.1838; $[\alpha]_D^{20}$ +24.0 (c 1.0, CH_2Cl_2).

Expanded Transition State Analysis:

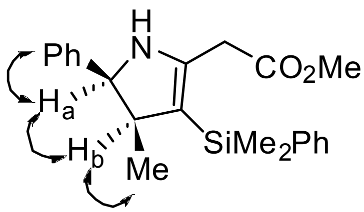


The antiperiplanar and synclinal transition states proposed in Figure 1 of the manuscript may be in equilibrium with an ester enolate/iminium ion that is stabilized by coordination of the Lewis acid to the oxygen anion. After attack of the allenylsilane on the *si* face of the iminium ion two different pathways can occur, leading to each of the observed products. If the oxygen from the carbamate carbonyl closes on the initial vinyl cation, the dihydrooxazine product is obtained. If a 1,2-silyl shift occurs, followed by attack of the nitrogen anion, the dihydropyrrole product is obtained. The pyrrole formation may occur by either by a concerted mechanism,[2] or by a two step mechanism where the silyl shift precedes the attack of the nitrogen nucleophile.[3]

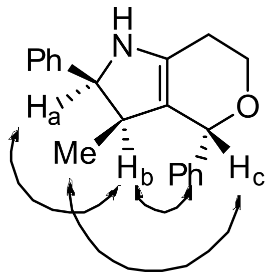
[2] Fuchibe, K.; Hatemata, R.; Akiyama, T. *Tetrahedron Lett.* **2005**, *46*, 8563-8566.

[3] Danheiser, R. L.; Stoner, E. J. ; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111,* 4407-4413.

Assignment of stereochemistry as illustrated by 2a (see table 1) and 5a (see scheme 1) using NOE measurements:



2a

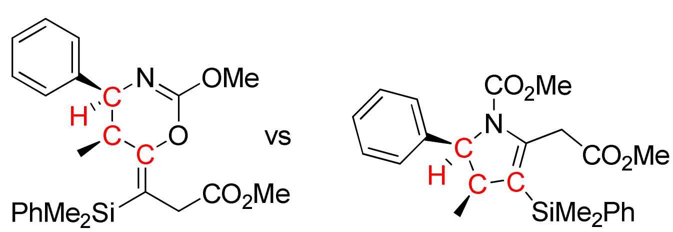


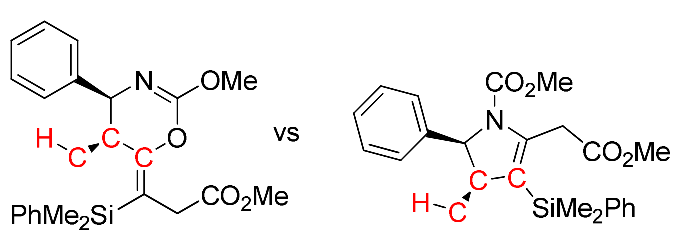
5a

Annulation product **2a** shows a strong NOE between the methyl group and the phenyl group, and between the protons C5-H_a and C4-H_b of the dihydropyrrole ring. This relationship confirms the proposed 4,5-*cis* confirmation. Pyranopyrrole **5a** shows strong NOE between the benzylic H_c proton and the methyl group on the dihydropyrrole ring. Strong NOE between H_b and the protons on the phenyl ring substituent of the pyran is also evident. No NOE is observed between H_c and H_b, further confirming the relative configuration of the pryanopyrrole products.

Confirmation of dihydrooxazine formation (instead of protected dihydropyrrole formation):

A series of experiments were run to confirm that the dihydrooxazine products in table 3 were not methyl carbamate protected dihydropyrroles.[4] After assigning the positions of all of the proton and carbon signals in the ^{1}H and ^{13}C spectra using APT (Attached proton test) and HSQC (Heteronuclear single quantum coherence), we looked for differences that could be distinguished by HMBC (Heteronuclear multiple bond coorelation) 3-bond coupling.

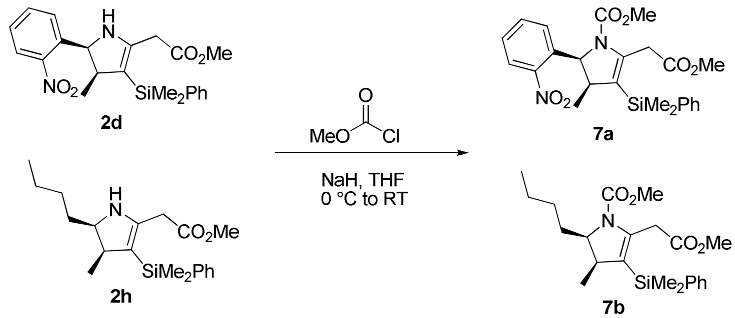




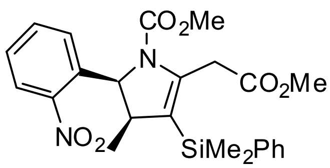
[4] Danheiser sees both dihydrooxazine and dihydropyrrole products from reactions with acyclic iminium ion precursors: Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985**, *107,* 7233-7235.

The main difference between the two possible products was the 3-bond coupling to the two distinct olefin carbons. Since the benzylic proton (δ 4.24 ppm) and the protons on the methyl group (δ 0.49 ppm) both demonstrated strong 3-bond coupling to the olefin carbon at δ 161 ppm, but did not show any 3-bond coupling to the silylated olefin carbon at δ 106 ppm, we determined that the oxazine was the correct structure. In the case of the dihydropyrrole, we would expect to see 3-bond coupling from these two protons to the silylated olefin carbon, but no coupling to the carbon at δ 161 ppm.

This assignment was further confirmed by the acylation of the enamine nitrogen in dihydropyrroles **2d** and **2h**, affording the N-protected dihydropyrrole products.

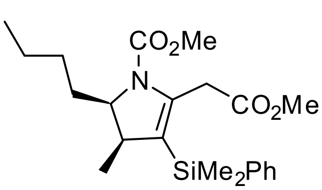


These new protected dihydropyrroles (**7a** and **7b**) are distinctly different from the dihydrooxazines in the proton and carbon NMR (provided in the second section of supporting information). These protected pyrroles were also used in HPLC to show that the axial chirality of the allenylsilane is fully transferred to central chirality in the product.



7a

(2*S*, 3*S*)-methyl 4-(dimethyl(phenyl)silyl)-5-(2-methoxy-2-oxoethyl)-3-methyl-2-(2-nitrophenyl)-2,3-dihydro-1*H*-pyrrole-1-carboxylate (7a): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J=8.0, 1H), 7.58 (m, 3H), 7.33 (m, 5H), 5.63 (d, J=7.6, 1H), 3,67 (s, 3H), 3.64 (s, 3H), 3.58 (m, 1H), 3.34 (dd, J=17.2, 26.4, 2H), 0.61 (s, 3H), 0.45 (d, J=5.6, 3H), 0.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 154.0, 152.9, 148.2, 148.0, 136.9, 134.7, 133.9, 133.4, 129.5, 128.6, 127.9, 127.4, 125.1, 112.3, 58.3, 54.4, 52.0, 35.3, 33.2, 14.8, -1.9, -2.3; IR (film) υ_{max} 2970, 1779, 1732, 1651, 1526, 1437, 1350, 1297 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{24}H_{28}O_6N_2Si$ $[M+H]^+$ 469.1795, found: 469.1795; $[\alpha]_D^{20}$ +110.7 (c 1.4, CH_2Cl_2).



7b

(2*R*, 3*S*)-methyl 2-butyl-4-(dimethyl(phenyl)silyl)-5-(2-methoxy-2-oxoethyl)-3-methyl-2,3-dihydro-1*H*-pyrrole-1-carboxylate (7b): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 2H), 7.32 (m, 3H), 3.83 (s, 3H), 3.65 (s, 3H), 3.45 (m, 1H), 3.32 (dd, J=6.0, 32.0, 2H), 2.71 (m, 1H), 1.67 (m, 1H), 1.15 (m, 3H), 0.86 (d, J=6.8, 3H) 0.78 (m, 3H), 0.59 (m, 2H), 0.43 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 156.1, 153.7, 147.5, 137.9, 133.7, 129.6, 128.2, 107.7, 57.3, 54.3, 51.9, 33.0, 32.6, 28.8, 26.9, 22.3, 13.9, 11.5, -1.8, -2.3; IR (film) υ_{max} 2957, 2873, 1770, 1736, 1644, 1437, 1263, 1171 cm^{-1}; HRMS(CI, NH_3) m/z calc'd for $C_{22}H_{33}O_4NSi$ $[M+H]^+$ 404.2257, found: 404.2271; $[\alpha]_D^{20}$ +17.0 (c 1.0, CH_2Cl_2).