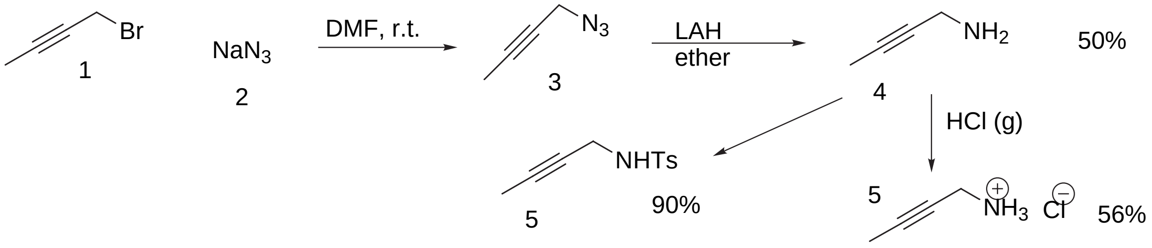
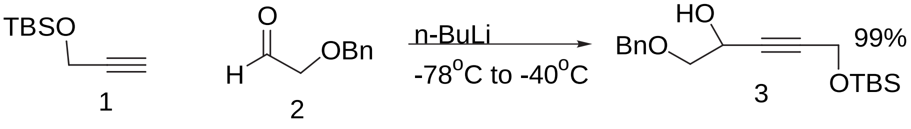


To a cooled, dry flask was added 2 (48.9 g, 0.75 mol), DMF (150 mL), and 1 (13.17 mL, 0.15 mol). The mixture was then stirred for 24 hr and 500 mL ether was added to precipitate excess sodium azide. The heterogeneous mixture was then filtered through a pad of celite which was washed with an additional 400 mL ether. The organic layer was then extracted with water (6 x 150 mL), dried over $MgSO_4$, and concentrated to approx. 200 mL (in order to avoid excessive loss of 3) *en vacuo*. The solution of 3 in ether (in a 1 L flask) was then cooled to 0^{o}C and excess LAH (8.5 g, 0.225 mol) was added **slowly** over 1.5 hr. The mixture was then stirred an additional 1.5 hr and quenched by **slow** addition of water saturated ether and small portions of water until all foaming has ceased (do not add excess water as 4 is quite water soluble). The solid was then filtered off and washed with additional ether. The organic layer was then dried over $MgSO_4$, filtered, and the ether was distilled off at atmospheric pressure (alternatively a rotovap can be used to remove the majority of the ether if done carefully). After distillation of all the ether, 4 was distilled over (bp = 110-115^{o}C) to yield 5.2 g (50%).

If the HCl salt is desired, bubble HCl gas through the dry (*after* filtration of $MgSO_4$) ether solution until no more precipitate forms, and collect the solid.

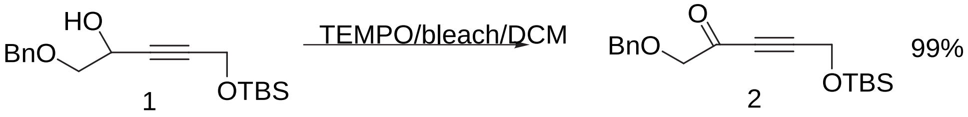
To a cooled, dry flask containing 4 (4.03 g, 58 mmol) and 250 mL DCM was added triethylamine (15.3 mL, 111 mmol), and tosylchloride (10.5 g, 55 mmol) at 0^{o}C. The mixture was then warmed to room temperature, and stirred for 24 hrs. Water was then added and the mixture was extracted with additional DCM. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *en vacuo* to yield a light yellow solid which was further purified by recrystalization (ether/pet. ether) to yield 5 (11.1 g, 90%).

Data for 4: ^{1}**H NMR** (200 MHz, Benzene-d_6): 3.1 (q, J = 2.4 Hz, 2 H), 1.50 (t, J = 2.4 Hz, 3H), 0.69 (very broad s, 2H).
Data for 5: ^{1}**H NMR** (300 MHz, $CDCl_3$): 7.76 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.49 (bs, 1H), 3.76 (m, 2H), 2.42 (s, 3H), 1.60 (t, J = 2.4 Hz, 2H).



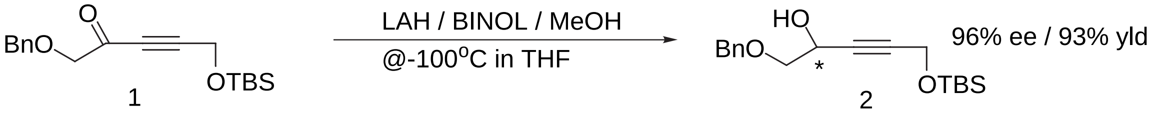
To a cooled, dry flask was added TBS protected propargyl alcohol 1 (1.37 g, 8.05 mmol) and THF (70 mL). The mixture was then cooled to —78^{o}C, and 1.6 M n-butyl lithium (4.81 ml, 7.7 mmol) was added slowly. After stirring for 1 hr, benzyloxyacetaldehyde 2 (1.05 g, 7.0 mmol) was added dropwise. The mixture was stirred at —78^{o}C for 1.5 hr, and then warmed to —40°C (dry ice/CH_3CN bath) for 2 additional hours. The reaction was then quenched with saturated aqueous NH_4Cl and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *en vacuo* to yield a light yellow oil which was further purified on silica (40% ether/pet. ether) to yield 2.23g (99%) of 3 as a clear liquid.

Data for 3: Rf (30% ether/pet. ether): 0.4. **IR** (neat): 3417, 3031, 2954, 2929, 2885, 2858, 1471, 1454, 1362, 1316, 1255, 1089, 1006, 837, 779, 736, 698 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.1 (m, 5H), 4.43 (m, 1H), 4.16 (d, J = 3.6 Hz, 2H), 4.13 (s, 2H), 3.37 (d, J = 5.2 Hz, 2H), 2.38 (d, J = 5.6 Hz, 1H), 0.90 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (75.4 MHz, C_6D_6): 138.1, 128.2, 127.6, 127.5, 83.9, 83.5, 73.7, 72.9, 61.6, 51.5, 25.6, 21.9, -5.4. **HRMS** (EI, $[M\text{-}t\text{-}Bu]^+$) Cal c for $C_{14}H_{19}O_3Si$: 263.1103. Found: 263.1086 (0.1), 91.0575 (100).



To a flask containing 1 (2.23 g, 6.95 mmol) and DCM (30 mL) was added 5% $NaHCO_3$ solution (15 mL). To this biphasic mixture was added TEMPO (11 mg, 0.069 mmol), KBr (83 mg, 0.69 mmol), and bleach (15.5 mL of a 5% solution of NaOCl, 10.4 mmol). The mixture was stirred for 1.5 hr, quenched with saturated aqueous $NaHSO_4$, and extracted with DCM. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *en vacuo* to yield 2 as a light yellow oil (2.2 g, 99%) which was pure by NMR.

Data for 2: Rf (30% ether/pet. ether): 0.6. **IR** (neat): 3065, 2965, 2930, 2886, 2858, 2212, 1697, 1681, 1605, 1497, 1474, 1390, 1363, 1257, 1216, 1171, 1111, 1006, 939, 837, 780, 737, 698 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.2 — 7.0 (m, 5H), 4.27 (s, 2H), 3.95 (s, 2H), 3.80 (s, 2H), 0.84 (s, 9H), -0.05 (s, 6H). **^{13}C NMR** (75.4 MHz, $CDCl_3$): 184.4, 160.8, 136.9, 128.5, 128.0, 93.2, 81.6, 75.6, 73.4, 65.7, 51.5, 25.7, 18.2, -5.3. **LRMS** (CI, $[M+1]^+$) Cal c for $C_{18}H_{27}O_3Si$: 319.1. Found: 319.1

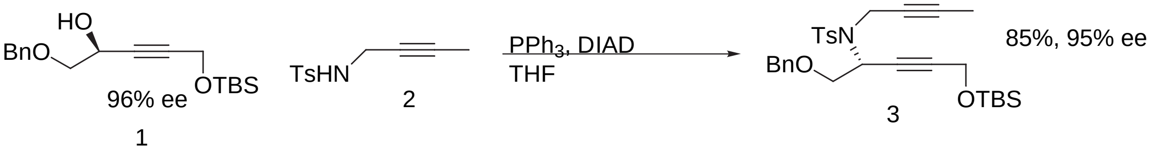


Standardized lithium aluminum hydride solution: To a cooled, dry flask was added LAH (~3.8 g , 100 mmol) and THF (~100 mL). The heterogeneous solution was then filtered through dry celite using a Schlenk type column under argon to yield a clear solution of LAH in THF. The concentration was measured by quenching a known amount of the solution with water and measuring the gas output with a gas buret. The concentration was approximately 1M.

To a cooled, dry flask containing LAH (10.57 mL of a 0.98 M soln. in THF, 10.36 mmol) was added a freshly prepared 1M solution of dry methanol in THF (10.36 mL, 10.36 mmol) dropwise at room temperature. R-BINOL (>99% ee) (2.97 g, 10.36 mmol) in

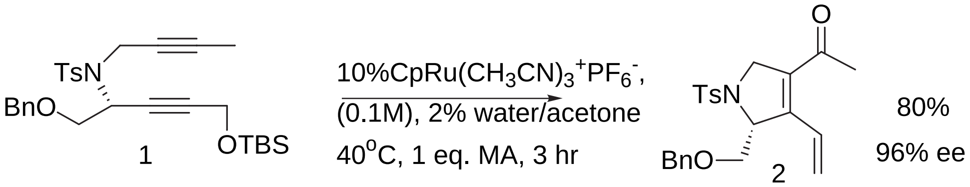
THF (25 mL, washed with 4 mL) was then added slowly. During the addition the solution became a milky white dispersion (if the solution does not go to milky white, then yield (~50%) and ee (~80%) are adversely affected). After the dispersion is allowed to stir for 30 min, the flask is cooled to —100°C (ether, liquid N_2), and 1 (1.1 g, 3.45 mmol) in THF (5 mL, washed with 2mL) is added over 15 min down the side of the flask. Following 1 hr at this temperature, the reaction is warmed to —78°C and stirred a further 2 hrs. Methanol is added to quench the reaction, and it is then worked up with ether and dilute aqueous HCl. The organic layer is washed with $NaHCO_3$, dried over $MgSO_4$, filtered, and the solvent was removed *en vacuo* to yield a light yellow oil. 50/50 ether/pet. ether was then added to the oil in order to precipitate most of the BINOL. The solid is filtered off and washed with 50/50 ether/pet. ether. The solvent was removed *en vacuo* and the residue was then further purified on silica (20% ether/pet. ether) to yield 1.0g (93%) of 2 as a clear liquid with 96% ee. BINOL is also recovered in 80-90% yield and can be reused.

Data for 2: Rf (30% ether/pet. ether): see above. $[\alpha]_D^{25}$ = -3.6 (c = 0.7, MeOH). The ee was evaluated using a chiral HPLC: OD column, flow rate = 1 mL/min, solvent = 90/10 IPA/heptane, retention times = 7.43, 11.19 min.



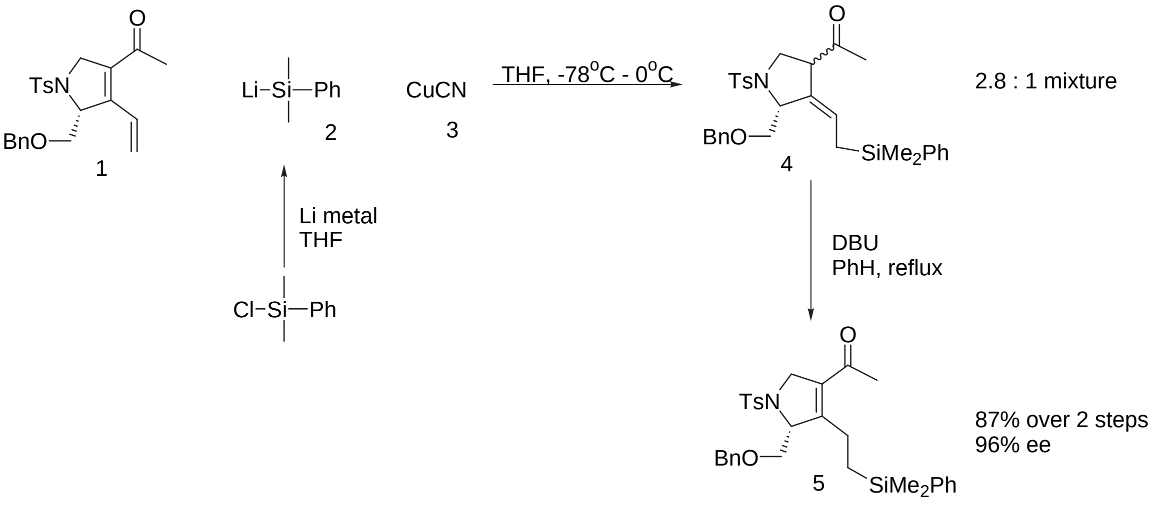
To a cooled, dry flask was added 2 (0.76 g, 3.43 mmol), triphenylphosphine (0.85 g, 3.27 mmol), and THF (10 mL). The flask was cooled to 0°C, and 1 (1 g, 3.12 mmol) in THF (10 mL, washed with 10 mL) was added. DIAD (0.64 mL, 3.25 mmol) was then added and the reaction was warmed to room temperature. The mixture was stirred for 48 hrs and silica gel was added directly to the flask, and the heterogeneous mixture was filtered through silica gel, and the solvent was removed *en vacuo* to yield an oil which was then further purified on silica (15-30% ether/pet. ether) to yield 1.41g (86%) of 3 as a clear oil with 96% ee.

Data for 3: Rf (40% ether/pet. ether): 0.6. **IR** (neat): 3030, 2927, 2856, 2234, 1596, 1492, 1455, 1351, 1254, 1163, 1092, 1030, 898, 836, 779, 740 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.78 (d, J = 8 Hz, 2H), 7.2 (m, 2H), 7.1 (m, 3H), 6.9 (d, J = 8 Hz, 2H), 5.32 (tt, J1 = 5.2 Hz, J2 = 1.6 Hz, 1H), 4.37 (dq, J1 = 17.8 Hz, J2 = 2.4 Hz, 1H), 4.30 (d, J = 11.6 Hz, 1H), 4.25 (d, J = 11.6 Hz, 1H), 4.15 (dq, J1 = 17.8 Hz, J2 = 2.4 Hz, 1H), 3.94 (d, J = 1.6 Hz, 2H), 3.77 (m, 2H), 1.83 (s, 3H), 1.28 (t, J = 2.4 Hz, 3H), 0.87 (s, 9H), -0.027 (s, 3H), -0.032 (s, 3H). **^{13}C NMR** (125 MHz, C_6D_6): 142.8, 138.4, 137.9, 129.3, 128.5, 128.4, 128.0, 127.685.5, 80.3, 79.6, 75.3, 72.9, 72.0, 51.5, 50.7, 35.2, 25.8, 21.1, 18.2, 3.1, -5.2. **LRMS** (CI, $[M+1]^+$) Cal'c for $C_{29}H_{40}NO_4SSi$: 526.1. Found: 526.1 **HRMS** (EI, $[M-CH_3]^+$) Cal c for $C_{28}H_{36}NO_4SSi$: 510.2134. Found: 510.2141 (0.1), 468.1621 (5.3), 404.1577 (15.5), 91.0558 (100). $[\alpha]_D^{25}$ = -24.96 (c = 0.1, MeOH). The ee was evaluated using a chiral HPLC: OD column, flow rate = 1 mL/min, solvent = 98/2 IPA/heptane, retention times = 13.85, 15.29 min.



To a flask containing 1 (1.4 g, 2.66 mmol), 27 mL acetone, and 0.54 mL water, was added $CpRu(CH_3CN)_3^+PF_6^-$ (116 mg, 0.266 mmol) and malonic acid (280 mg, 2.66 mmol) under argon. The resulting yellow solution was sealed and stirred at 40°C for 3 hours and filtered through a pad of silica with ether as the eluent. The solvent was then removed *en vacuo* to yield a yellow oil which was further purified on silica (60% ether/pet. ether) to yield 870 mg (80%) of 2.

Data for 2: Rf (60% ether/pet. ether): 0.35. **IR** (neat): 3089, 3031, 2922, 2867, 1732, 1681, 1652, 1622, 1597, 1580, 1495, 1454, 1343, 1262, 1163, 1099, 1049, 1017, 925, 816, 740, 698, 665 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): 7.74 (d, J = 8.1 Hz, 2H), 7.3-7.2 (m, 7H), 7.15 (dd, J1 = 17.8 Hz, J2 = 11.4 Hz, 1H), 5.53 (d, J = 11.4 Hz, 1H), 5.47 (d, J = 17.8 Hz, 1H), 5.12 (bs, 1H), 4.56 (d, J = 12.3 Hz, 1H), 4.45 (s, 2H), 4.48 (d, J = 12.3 Hz, 1H), 3.38 (m, 2H), 2.44 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (75.4 MHz, $CDCl_3$): 194.6, 144.8, 143.9, 138.0, 135.2, 132.8, 129.9, 128.6, 128.3, 127.6, 127.4, 127.1, 123.3, 73.5, 71.7, 67.9, 55.9, 30.6, 21.6. **HRMS** (EI, $[M]^+$) Cal c for $C_{23}H_{25}NO_4S$: 411.1504. Found: 411.1509 (0.9), 290.0851 (45.3, $-CH_2OBn$), 248.0738 (59.4), 155.0170 (25.4). $[\alpha]_D^{25}$ = 69.64 (c = 0.1, MeOH). The ee was evaluated using a chiral HPLC: OD column, flow rate = 1 mL/min, solvent = 90/10 IPA/heptane, retention times = 17.30, 20.66 min.



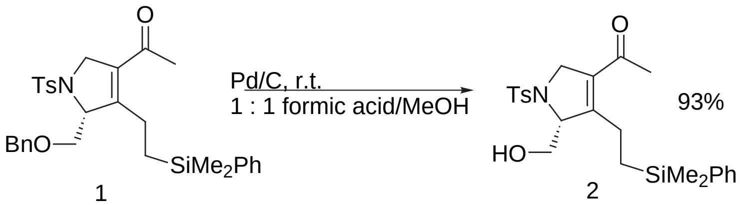
To a cooled, dry flask with a Schlenk fitting on top was added Li granules (0.208 g, 30 mmol). The flask was then cooled to 0°C, and THF (15 mL) and phenyldimethylsilylchloride (1.66 mL, 10 mmol) were added under argon. After 30 minutes the solution was a dark red color and the reaction was stirred a further 4 hrs at 0^{o}C. The flask was then placed in a —15^{o}C freezer overnight. The concentration was then measured by the Gillman double titration method. A 0.5 mL aliquot was quenched with 2 mL of water, and titrated with standardized 0.1 M HCl using phenolphthalein to give the total base. A second 0.5 mL aliquot was then quenched with 2 mL of 1,2-dibromoethane in a dry test tube. After mixing for 30 seconds, 2 mL of water was added and titrated with standardized 0.1 M HCl using phenolphthalein to give the amount of alkoxide base. The amount of alkoxide is subtracted from the total base to give the concentration of silyl lithium. The concentration was generally ~0.5 M.

To a cooled, dry flask containing CuCN (0.142 g, 1.58 mmol) was added THF (5.5 mL) at 0^{o}C. The 0.52 M solution of 2 (8.0 mL, 4.1 mmol) is then added and stirred 25 minutes and cooled to —78^{o}C. 1 (0.62 g, 1.51 mmol) in THF (5.5 mL, washed with 2 mL) was then added slowly. After 1 hr, the reaction was warmed to 0^{o}C and stirred an additional 4 hr. Saturated aqueous NH_4Cl was then added to quench the reaction, which was then filtered through celite to remove most of the copper residues. The biphasic mixture was then extracted with ether and more NH_4Cl. The solvent was then removed *en vacuo* to yield a yellow oil which was further purified on silica (50% ether/pet. ether) to yield 0.82 g of a 2.8 : 1mixture of diastereomers 4. The diastereomers can be separated on silica (40% ether/pet. ether), but were generally carried on as a mixture.

Data for major diastereomer of 4: Rf (50% ether/pet. ether): 0.2. **IR** (neat): 3067, 3029, 2955, 2922, 2856, 1715, 1598, 1495, 1454, 1427, 1403, 1347, 1249, 1161, 1113, 1093, 1027, 835, 734, 700, 666 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.78 (d, J = 8 Hz, 2H), 7.31 (m, 2H), 7.17-7.0 (m, 8H), 6.74 (d, J = 8 Hz, 2H), 5.13 (t, J = 7.6 Hz, 1H), 4.56 (bs, 1H), 4.21 (dd, J1 = 10 Hz, J2 = 2.8 Hz, 1H), 4.18 (d, J = 12 Hz, 1H), 4.13 (d, J = 12 Hz, 1H), 3.57 (m, 2H), 3.17 (dd, J1 = 10 Hz, J2 = 8 Hz, 1 H), 2.54 (d, J = 4.8 Hz, 1H), 1.83 (s, 3H), 1.67 (s, 3H), 1.50 (t, J = 7.6 Hz, 2H), 0.058 (s, 3H), 0.051 (s, 3H). **^{13}C NMR** (125 MHz, C_6D_6): 202.9, 142.9,138.3, 138.0, 136.5, 134.4, 133.7, 129.6, 129.5, 128.4, 128.2, 127.8, 127.6, 73.5, 73.0, 60.6, 57.2, 47.8, 30.1, 26.6, 21.0, 19.5, -3.2. **HRMS** (EI, $[M]^+$) Calc for $C_{31}H_{37}NO_4SSi$: 547.2213. Found: 547.2233 (0.1), 504.2039 (0.5), 426.1570 (38.0), 135.0623 (100).

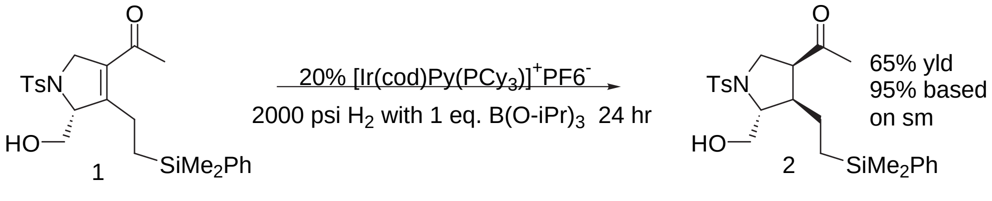
To a cooled, dry flask containing 4 (0.82 g, 1.5 mmol) was added benzene (55 mL) and DBU (45 μL, 0.3 mmol). The solution was then refluxed for 7 hrs, and worked up with ether and dilute HCl. The solvent was then removed *en vacuo* to yield a yellow oil which was further purified on silica (30% ether/pet. ether) to yield 5 (0.72 g, 87% over 2 steps).

Data for 5: Rf (50% ether/pet. ether): 0.25. **IR** (neat): 3058, 3030, 2958, 2923, 2854, 1687, 1658, 1626, 1598, 1495, 1454, 1427, 1347, 1259, 1163, 1112, 1093, 816, 734, 700, 665 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.69 (d, J = 8 Hz, 2H), 7.34 (m, 2H), 7.2-7.0 (m, 8H), 6.68 (d, J = 8 Hz, 2H), 4.69 (m, 1H), 4.43 (d, J = 14 Hz, 1H), 4.34 (ddd, J1 = 13.6 Hz, J2 = 4.4 Hz, J3 = 2 Hz, 1H), 4.30 (d, J = 12 Hz, 1H), 4.18 (d, J = 12 Hz, 1H), 3.76 (dd, J1 = 10 Hz, J2 = 4.8 Hz, 1H), 3.66 (dd, J1 = 10 Hz, J2 = 2.4 Hz, 1H), 2.69 (td, J1 = 13.2, J2 = 4.4 Hz, 1H), 2.0 (td, J1 = 13.2, J2 = 4 Hz, 1H), 1.76 (s, 3H), 1.45 (s, 3H), 0.69 (td, J1 = 14.2 Hz, J2 = 4.4 Hz, 1H), 0.45 (td, J1 = 14.2 Hz, J2 = 4.4 Hz, 1H), 0.14 (s, 3H), 0.13 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6): 193.2, 154.2, 143.2, 138.4, 138.3, 135.8, 133.7, 130.2, 129.7, 129.2, 128.5, 128.0, 127.8, 127.6, 73.5, 71.7, 69.4, 56.2, 29.4, 21.3, 20.9, 14.2, -3.5, -3.6. **HRMS** (EI, $[M]^+$) Cal c for $C_{31}H_{37}NO_4SSi$: 547.2213. Found: 547.2224 (0.2), 426.1501 (16.5), 398.1307 (26.2), 348.1115 (16.2), 306.1022 (21.9), 135.0621 (100). $[\alpha]_D^{25}$ = 109.35 (c = 0.24, MeOH).The ee was evaluated using a chiral HPLC: OD column, flow rate = 1 mL/min, solvent = 90/10 IPA/heptane, retention times = 15.14, 18.66 min.



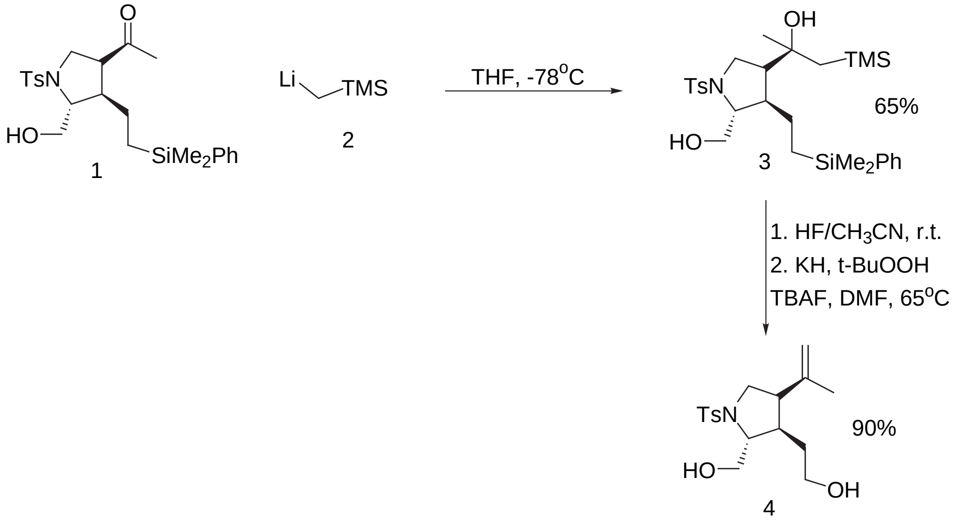
To a flask containing 1 (460 mg, 0.84 mmol) was added methanol (25 mL) and the solution was cooled to 0°C. 5% Pd/C (200 mg) was added, followed by slow addition of formic acid (25 mL). When addition was complete, the reaction was warmed to room temperature and stirred for 4 hrs with a nitrogen line attached to allow pressure to be released. The mixture was then filtered through silica using ether as the eluent, and extracted with water, $NaHCO_3$(aq), and NaCl(aq). The solvent was then removed *en vacuo* to yield a yellow oil which was further purified on silica (80% ether/pet. ether) to yield 2 (356 mg, 93%).

Data for 2: Rf (40% ether/pet. ether): 0.10. **IR** (neat): 3518, 3068, 2954, 2924, 1714, 1687, 1657, 1626, 1598, 1493, 1427, 1343, 1258, 1163, 1113, 1094, 1064, 960, 838, 816, 733, 702, 663 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.65 (d, J = 8.4 Hz, 2H), 7.34 (m, 2H), 7.16 (m, 3H), 6.71 (d, J = 8.4 Hz, 2H), 4.47 (bs, 1H), 4.38 (m, 2H), 4.02 (dd, J1 = 12 Hz, J2 = 3.2 Hz, 1H), 3.61 (dd, J1 = 12 Hz, J2 = 3.2 Hz, 1H), 2.48 (td, J1 = 13.2 Hz, J2 = 4.4 Hz, 1H), 1.90 (td, J1 = 14.8 Hz, J2 = 4.4 Hz, 1H), 1.76 (s, 3H), 1.53 (s, 3H), 0.64 (td, J1 = 14.8 Hz, J2 = 4.4 Hz, 1H), 0.41 (td, J1 = 13.2 Hz, J2 = 4.4 Hz, 1H), 0.13 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6): 193.5, 153.2, 143.6, 138.2, 134.8, 133.7, 130.6, 129.8, 129.3, 128.0, 127.7, 71.9, 63.6, 56.5, 29.4, 21.4, 20.9, 14.2, -3.6, -3.7. **LRMS** (CI, $[M+1]^+$) Cal'c for $C_{24}H_{34}NO_4SSi$: 458.1. Found: 458.1. **HRMS** (EI, $[M-CH_2OH]^+$) Cal c for $C_{23}H_{31}NO_3SSi$: 426.1559. Found: 426.1557 (4.1), 336.1122 (31.4), 307.1049 (17.0), 306.0982 (75.7). $[\alpha]_D^{25}$ = 82.31 (c = 1.48, MeOH).



To a cooled, dry flask under hydrogen containing 1 (121 mg, 0.265 mmol) was added degassed (freeze-pump-thaw 3x) and hydrogen purged (15 min H_2 bubble through) DCM (13.2 mL) and $B(O\text{-}iPr)_3$ (61 μL, 0.265 mmol). Crabtree s catalyst (43 mg, 0.053 mmol) was then added quickly under hydrogen. The flask was then added to a Parr apparatus, sealed quickly under hydrogen, purged 2 times with 1000 psi hydrogen and then sealed under 2000 psi hydrogen. The reaction was stirred for 24 hrs, the pressure was released, and pet. ether was added to precipitate most of the iridium, and filtered through silica using ether as the eluent. The solvent was then removed *en vacuo* to yield a yellow oil which was further purified on silica (80% ether/pet. ether) to yield 2 (79 mg, 65%) and recovered 1 (40 mg).

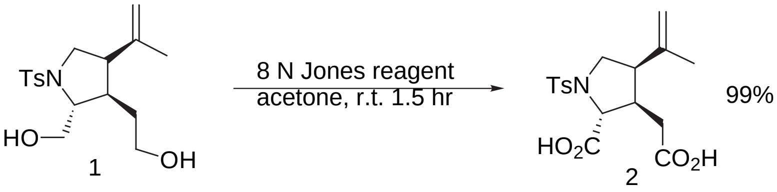
Data for 2: Rf (50% ether/pet. ether): 0.10. **IR** (neat): 3516, 3058, 2958, 2922, 2849, 1710, 1596, 1426, 1343, 1248, 1162, 1113, 1091, 1055, 835, 816, 731, 702, 667 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6): 7.70 (d, J = 8.4 Hz, 2H), 7.28 (m, 2H), 7.13 (m, 3H), 6.72 (d, J = 8.4 Hz, 2H), 3.82 (m, 2H), 3.6 (m, 3H), 3.05 (m, 1H), 2.99 (bs, 1H), 2.10 (m, 1H), 1.87 (s, 3H), 1.49 (s, 3H), 0.64 (m, 1H), 0.41 (m, 1H), 0.17 (m, 2H), -0.06 (s, 3H), -0.11 (s, 3H). **^{13}C NMR** (100 MHz, C_6D_6): 204.5, 143.3, 138.6, 133.8, 133.6, 129.8, 129.2, 128.0, 127.9, 66.1, 65.6, 53.2, 48.2, 46.6, 28.6, 22.4, 21.1, 13.2, -3.06, -3.90. **LRMS** (CI, $[M+1]^{+}$) Cal'c for $C_{24}H_{33}NO_4SSi$: 460.1. Found: 460.1. **HRMS** (EI, $[M-CH_2OH]^{+}$) Cal c for $C_{23}H_{30}NO_3SSi$: 428.1716. Found: 428.1730 (34.4). 306.1008 (6.4), 135.0627 (100). $[\alpha]_D^{25}$ = -15.83 (c = 0.75, MeOH).



To a cooled, dry flask was containing THF (0.75 mL) at —78^{o}C was added a 1M solution of 2 in pentane (0.39 mL, 0.39 mmol). To this was added 1 (36 mg, 0.078 mmol) in THF (0.75 mL, washed with 0.5 mL), and the mixture was stirred 5 hrs at —78^{o}C. The reaction was then quenched with saturated aqueous NH_4Cl, and extracted with ether. The solvent was then removed *en vacuo* to yield a yellow oil which was filtered through silica (60% ether/pet. ether) to yield 3 (28 mg, 65%) which was used directly in the next reaction. To a flask containing 3 (25 mg, 0.045 mmol) was added acetonitrile (4.7 mL) and 50% aqueous HF (~15 µL). After 1 hr, the reaction was quenched with $NaHCO_3$, and extracted with ether. The solvent was then removed *en vacuo* to yield a yellow oil which was used directly in the next reaction.

To a flask under argon was added KH (washed with hexanes) (40 mg, 0.99 mmol) and DMF (1.2 mL). After cooling to 0^{o}C, ~4M (in decane) t-butyl hydroperoxide (78 µL, 0.31 mmol) was added, and the reaction was warmed to room temperature. The residue from the previous step was then added in DMF (0.75 mL, washed with 0.75 mL) and stirred for 10 minutes. 1M (in THF) TBAF (0.27 mL, 0.27 mmol) was then added, and the reaction was stirred at 65^{o}C for 4 hrs. The mixture was then worked up with ethyl acetate and sodium sulfite (aq). The solvent was then removed *en vacuo* to yield an oil which was further purified on silica (50% ether/EtOAc) to yield 4 as a white solid (14 mg, 90%).

Data for 4: mp = 93-95^{o}C. Rf (50% ether/EtOAc): 0.25. **IR** (neat): 3383, 2922, 2871, 2844, 1597, 1336, 1162, 1092, 1051, 885, 816 cm^{-1}. **^{1}H NMR** (400 MHz, CD$_2$Cl$_2$): 7.76 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 4.84 (q, J = 1.2 Hz, 1H), 4.52 (s, 1H), 3.80 (dd, J1 = 10.6 Hz, J2 = 6.0 Hz, 1H), 3.60 (dd, J1 = 10.6 Hz, J2 = 6.4 Hz, 1H), 3.53 (dd, J1 = 8.4 Hz, J2 = 6.4 Hz, 1H), 3.49 (t, J = 6.0 Hz, 1H), 3.33 (m, 2H), 3.05 (dd, J1 = 11.8 Hz, J2 = 8.4 Hz, 1H), 2.95 (m, 1H), 2.44 (s, 3H), 2.24 (ddd, J1 = 12.0 Hz, J2 = 6.2 Hz, J3 = 2.8 Hz, 1H), 1.66 (d, J = 1.2 Hz, 3H), 1.31 (m, 1H), 1.03 (m, 1H). **^{13}C NMR** (125 MHz, CD$_2$Cl$_2$): 144.6, 141.7, 132.9, 130.0, 127.9, 111.7, 66.0, 65.7, 60.2, 50.0, 46.1, 39.2, 29.3, 22.7, 21.6, 14.3. **HRMS** (EI, [M-CH$_2$OH]$^+$) Cal c for C$_{16}$H$_{22}$NO$_3$S (-CH$_2$OH): 308.1320. Found: 308.1330 (100), 155.0158 (29.8). $[\alpha]_D^{25}$ = 5.0 (c = 0.42, MeOH).

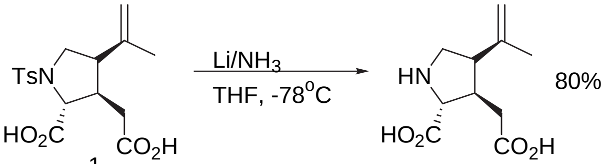


Jones reagent preparation: To a flask containing CrO$_3$ (2.67 g, 26.7 mmol) was added water (4 mL) at 0^{o}C. Concentrated sulfuric acid (2.3 mL, 43.1 mmol) was then added slowly causing an orange precipitate to form. Water was then added to bring the total volume to 10 mL. The orange precipitate dissolved to give a deep red solution that is 8N in oxygen.

To a flask containing 1 (8.5 mg, 0.025 mmol) and acetone (0.4 mL) at 0^{o}C was added 8N Jones reagent (31µL, 0.25 mmol). The mixture was stirred for 5 minutes and then warmed to room temperature for an additional 10 minutes. Water (~15µL) was then added and the reaction was stirred for 1.5 hrs more. Isopropanol (0.3 mL) was then added to quench the remaining oxidant, EtOAc and water were added and the 2 phase mixture was then made basic with NaOH. The organic layer was taken off and the aqueous layer was acidified with HCl and extracted thoroughly with EtOAc. The solvent was then removed *en vacuo* to yield a white solid which was pure by NMR.

Data for 2: mp = 190-195^{o}C . **IR** (neat): 3300, 2920, 2850, 1715, 1647, 1597, 1443, 1407, 1339, 1164, 1121, 1090, 816, 666 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$): 7.80 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 4.92 (s, 1H), 4.58 (s, 1H), 4.35 (s, 1H), 3.64 (t, J = 6.4 Hz, 1H), 3.15 (t, J = 10.8 Hz, 1H), 3.08 (m, 1H), 2.93 (m, 1H), 2.46 (s, 3H), 2.05 (m, 1H), 1.69 (s, 3H), 1.30 (m, 1H). **^{13}C NMR** (125 MHz, CDCl$_3$): 177.3, 176.6, 144.9, 139.9, 133.8, 130.3, 127.7, 113.7, 48.8, 46.3, 41.1, 31.6, 29.9, 22.8, 21.9. **HRMS** (EI,

$[M-CO_2H]^+$) Cal c for $C_{16}H_{20}NO_4S$ ($-CO_2H$): 322.1113. Found: 322.1112 (74.0), 280.0630 (6.2), 212.0916 (11.2), 168.1024 (11.7), 155.0156 (34.5), 91.0545 (100). $[\alpha]_D^{25}$ = -36.4 (c = 0.70, $CHCl_3$).



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Kainic acid

To a cooled, dry flask containing 1 (10 mg, 0.025 mmol) was added THF (0.3 mL). The flask was cooled to —78°C, and liquid ammonia (~1.5 mL) was added. Li granules (~1 mg, 0.16 mmol) was then dropped into the flask. A blue color immediately developed. The reaction was stirred 30 minutes and quenched with isoprene (~1 mL) or until the blue color disappeared. The mixture was warmed to room temperature and all the volatile were blown off under argon. Water (0.2 mL) was then added and the pH was adjusted to ~7. The solution was then passed through an ion exchange column (Amberlight CG-50) eluting with water and then 3% ammonium hydroxide. The fractions containing kainic acid were then collected and water was removed on a lyophilizer to yield kainic acid, which was recrystallized with ethanol/water. (4.2 mg, 80%).

Data for kainic acid: mp = 240-245°C (lit.: 243-244) . **^{1}H NMR** (500 MHz, D_2O): 5.0 (s, 1H), 4.71 (s, 1H), 4.03 (d, J = 3.0 Hz, 1H), 3.60 (dd, J1 = 12.5 Hz, J2 = 7.0 Hz, 1H), 3.41 (t, J = 11.0 Hz, 1H), 2.91 (m, 2H), 2.23 (dd, J1 = 15.5 Hz, J2 = 6.5 Hz, 1H), 2.12 (dd, J1 = 15.5 Hz, J2 = 8.0 Hz, 1H), 1.76 (s, 3H). $[\alpha]_D^{25}$ = +13.7 (c = 0.13, H_2O). (lit: $[\alpha]_D^{25}$ = —14.2 (c=0.18, H_2O).