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Supporting Information

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An Efficient One-pot Enantio and Diastereoselective Synthesis of Heterocycles

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Supporting Information

All reactions were preformed under a positive atmosphere of dry argon unless otherwise indicated. Acetone was distilled from calcium sulfate before use. Methylene chloride (CH_2Cl_2) was purified on an alumina column solvent purification system. All solvents were degassed for 15 minutes with dry argon immediately prior to use. Anhydrous solvents and reaction mixtures were transferred by oven-dried syringe or cannula. Tris(dibenzylidideneacetone) monochloroform complex, $Pd_2dba_3 \bullet CHCl_3$, was prepared according to the literature[1]. Cyclopentadienyl ruthenium trisacetonitrile hexafluorophosphate complex, $CpRu(CH_3CN)_3^+PF_6^-$, was prepared according to the literature[2]. Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation.

Flash chromatography was performed with ICN silica gel (Kiesselgel 60, 230-400 mesh). Analytical thin layer chromatogrpahy was preformed with 0.2mm coated commerical silica gel plates (E. Merck, DC Plastifolien, kieselgel 60 F_{254}). Proton and broad band decoupled ^{13}C nuclear magnetic resonance (NMR) data were aquired on a Varian GEM-300 or Inova Unity-500 spectrophotomer as indicated. Chemical shifts are reported in ppm relative to $CDCl_3$ as internal standard. Infrared (IR) data were recorded on sodium chloride plates on a PerkinElmer Paragon 500 FT-IR spectrophotometer. Melting ponts were determined on a Thomas-Hoover oil bath apparatus and were not corrected. Mass spectral analyses were performed by the NIH Mass Spectral Facility at the School of Pharmacy, University of California on a Kratos MS-90 instrument with an ionizing current of 98 mA and an ionizing voltage of 70 eV. Microanalyses were performed by M-H-W Laboratories, Phoenix, AZ.

Representative procedure for Condition A:

To a test tube containing $CpRu(CH_3CN)_3^+PF_6^-$ (0.004mmol) is added a solution of sulfonamide (0.20mmol) and 1-butenyl-4-*p*-nitrophenyl ether (0.35mmol), in acetone (0.4mL). Stir at room temperature for 3-4 hours. Dilute with 2.6ml CH_2Cl_2. Add 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.21mmol) followed by a solution of $(Pd(\pi\text{-allyl})Cl)_2$ (0.004mmol) and chiral ligand **5** (0.012mmol) in 1.0mL CH_2Cl_2. Stir one hour at room temperature. The mixture is then concentrated in vacuo and purified directly via flash chromatography (SiO_2, ether/petroleum ether) to yield a white solid.

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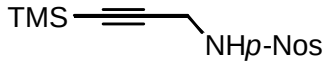
[1] Ukai, T.; Kawazura, H.; Iishii, Y.; Bonnett, J.J.; Ibers, J.A. *J. Organomet. Chem.* **1974**, *65*, 263.

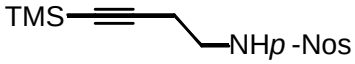
[2] T. P. Gill, K. R. Mann, *Organometallics* **1982**, *1*, 485. For improved procedure, see B. M. Trost, C. M. Older, *Organometallics*, **2002**, *8*, 2455-2546.

Representative procedure for Condition B:
To a degassed test tube containing $CpRu(CH_3CN)_3^+PF_6^-$ (0.01mmol) is added a solution of sulfonamide (0.20mmol) and 1-butenyl-4-*p*-nitrophenyl ether (0.35mmol), in acetone (1.0mL). Stir at room temperature for 3-4 hours. Dilute with 2.0ml CH_2Cl_2 and add DBU (0.21mmol) followed by a solution of $(Pd(\pi\text{-allyl})Cl)_2$ (0.004mmol) and chiral ligand **5** (0.012mmol) in 1.0mL CH_2Cl_2. Stir one hour at room temperature. The mixture is then concentrated in vacuo and purified directly via flash chromatography (SiO_2, ether/petroleum ether) to yield a white solid.

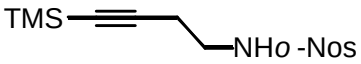
Representative procedure for Condition C:
To a degassed test tube containing $CpRu(CH_3CN)_3^+PF_6^-$ (0.0086g, 0.02mmol) is added a solution of alcohol (0.20mmol) and 1-butenyl-4-*p*-nitrophenyl ether (1.2mmol), in acetone (1.0mL). Stir at room temperature for 3 hours. Remove acetone in vacuo. Dissolve residue in 3.0ml CH_2Cl_2. Cool to 0°C and add triethylamine (NEt_3) (0.21mmol) followed by a solution of $Pd_2(dba)_3 \bullet CHCl_3$ (0.0041g, 0.004mmol) and chiral ligand **5** (0.012mmol) in 1.0mL CH_2Cl_2. Stir two hours at 0°C. The mixture is then concentrated in vacuo and purified directly via flash chromatography (SiO_2, ether/petroleum ether) to yield a colorless oil.



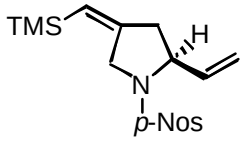
Compound **1a(n=0)**
white solid. melting point=147-148°C. IR(film from Et_2O): 3318, 1066, 1530, 1401, 1340, 1312, 1288, 1242, 1172, 1111, 1099, 1081, 997, 847, 818, 761, 734, 704, 684 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.37(d, J=9.0Hz, 2H), 8.10(d, J=9.0Hz, 2H), 4.82(m, 1H), 3.97(d, J=6.0Hz, 2H), -0.01(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 145.42, 141.03, 123.98, 119.48, 93.76, 85.96, 29.12, -5.31. Anal calcd for $C_{12}H_{16}N_2O_4SSi$: C, 46.13%; H, 5.16%; N, 8.97%. Found: C, 46.40%; H, 5.25%; N, 8.99%.



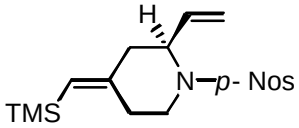
Compound **1a(n=1)**
white solid. melting point=114-115°C. IR(film from $CDCl_3$): 3300, 2959, 2171, 1531, 1350, 1250, 1165, 1094, 844, 735 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.38(d, J=8.7Hz, 2H), 8.07(d, J=8.7Hz, 2H), 4.89(m, 1H), 3.17(q, J=6.3Hz, 2H), 2.42(t, J=6.3Hz, 2H), 0.14(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 150.10, 145.95, 128.25, 124.46, 101.69, 88.26, 41.73, 21.15, -0.06. Anal calcd for $C_{13}H_{18}N_2O_4SSi$: C, 47.83%; H, 5.56%; N, 8.58%. Found: C, 47.67%; H, 5.47%; N, 8.56%.



Compound **1b(n=1)**
white solid. melting point = 71-73°C. IR(film from $CDCl_3$): 3345, 2960, 2177, 1542, 1415, 1347, 1250, 1169, 1126, 1081, 844, 783, 761, 741 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.14(m, 1H), 7.90(m, 1H), 7.76(m, 2H), 5.77(t, J=6.0Hz, 1H), 3.25(q, J=6.3Hz, 2H), 2.46(t, J=6.3Hz, 2H), 0.12(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 148.03, 133.85, 133.64, 132.92, 130.89, 125.54, 101.67, 88.05, 42.41, 20.92, -0.16. Anal calcd for $C_{13}H_{18}N_2O_4SSi$: C, 47.83%; H, 5.56%; N, 8.58%. Found: C, 48.08%; H, 5.61%; N, 8.73%.

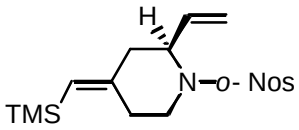


Compound **7a(n=0)**
White solid. melting point = 90-91°C. $[\alpha]_D$ +86.14 (c=0.94, CH_2Cl_2) for 92% ee. Enantiomeric excess determined by chiral high performance liquid chromatography (HPLC) analysis. (Chiralcel OD column, 98:2 heptane:iPrOH, flow rate = 1.0 mL/min, 254nm, t_r: xxxx (major), xxxx (minor)).IR(film from CH_2Cl_2): 2956, 1638, 1606, 1401, 1351, 1306, 1249, 1168, 1091, 1053, 926, 840, 736, 688 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 8.39(d, J=9.0Hz, 2H), 8.03(d, J=9.5Hz, 2H), 5.68(ddd, J=17.0, 10.0, 7.0Hz, 1H), 5.50(s, 1H), 5.24(d, J=15.0Hz, 1H), 5.13(d, J=9.5Hz, 1H), 4.30(m, 1H), 3.99(t, J=1.0Hz, 2H), 2.68(dd, J=18.0, 8.0Hz, 1H), 2.40(d, J=16.0Hz, 1H), 0.10(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 150.02, 149.66, 144.14, 136.52, 128.63, 124.22, 123.67, 116.57, 61.57, 50.98, 42.72, -0.68. Anal calcd for $C_{16}H_{22}N_2O_4SSi$: C, 52.43%, H, 6.05%, N, 7.64%. Found: C, 52.31%; H, 6.24%; N, 7.64%.



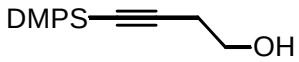
Compound **7a(n=1)**
white solid. melting point = 83-85°C. $[\alpha]_D$ –26.31 (c=1.51, CH_2Cl_2) for 89%ee. Enantiomeric excess determined by HPLC analysis. (Chiralcel OD column, 98:2 heptane:iPrOH, flow rate = 1.0 mL/min, 254nm, t_r: 20.93 (major), 24.73 (minor)). IR(neat): 3104, 2953, 2899, 1625, 1606, 1530, 1350, 1310, 1248, 1166, 1093, 952, 855, 839, 762, 738, 687, 639 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.32(d, J=9.0Hz, 2H), 7.97(d, J=9.0Hz, 2H), 5.59(ddd, J=17.4, 10.2, 6.9Hz, 1H), 5.28(s, 1H), 5.09(m, 2H), 4.69(m, 1H), 3.87(dd, J=12.6, 4.5Hz, 1H), 295(dt, J=3.3, 12.6Hz, 1H), 2.59(dd, J=13.2, 5.7Hz, 1H), 2.44(d, J=13.2Hz, 1H), 2.20(m, 2H), 0.06(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 149.80, 148.35, 146.20, 133.55, 128.46, 127.85, 124.19, 118.51, 57.08, 43.76, 42.45,

32.85, 0.16. Anal calcd for $C_{17}H_{24}N_2O_4SSi$: C, 53.66%; H, 6.36%; N, 7.36%. Found: C, 53.69%; H, 6.46%; N, 7.18%.



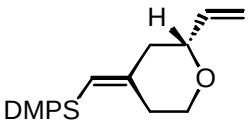
Compound **7b(n=1)**

oily solid. $[\alpha]_D$ –53.35 (c=1.03, CH_2Cl_2) for 88%ee. Enantiomeric excess determined by HPLC analysis. (Chiralcel OD column, 98:2 heptane:iPrOH, flow rate = 0.6 mL/min, 254nm, t_r: 28.17 (minor), 30.21 (major)). IR(film from $CDCl_3$): 2954, 2360, 1625, 1545, 1439, 1372, 1248, 1164, 1126, 1082, 978, 929, 864, 838, 775, 743 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 8.10(m, 1H), 7.70(m, 3H), 5.75(ddd, J=16.0, 10.5, 6.0Hz, 1H), 5.32(s, 1H), 5.19(dd, J=16.0, 1.5Hz, 1H), 5.16(dd, J=10.5, 1.5Hz, 1H), 4.71(m, 1H), 3.83(ddd, J=13.0, 3.5, 1.5Hz, 1H), 3.17(dt, J=3.4, 13.0Hz, 1H), 2.71(dd, J=13.0, 6.0Hz, 1H), 2.46(dd, J=13.0, 1.5Hz, 1H), 2.32(dd, J=13.0, 2.0Hz, 1H), 2.21(dt, J=5.5, 13.0Hz, 1H), 0.10(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 149.11, 147.74, 134.50, 133.90, 133.42, 131.72, 130.94, 127.39, 124.25, 118.28, 56.54, 42.58, 33.15, 0.17. Anal calcd for $C_{17}H_{24}N_2O_4SSi$: C, 53.66%; H, 6.36%; N, 7.36%. Found: 53.54%; H, 6.08%, N, 7.34%.



Compound **8a**

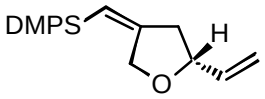
colorless oil. IR(neat): 3356, 3070, 2959, 2176, 1428, 1250, 1115, 1031, 892, 838, 816, 781, 732, 701, 662 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 7.63(m, 2H), 7.37(m, 3H), 3.75(t, J=6.3Hz, 2H), 2.56(t, J=6.6Hz, 2H), 1.69(s, 1H), 0.41(s, 6H). ^{13}CNMR(125MHz, $CDCl_3$) δ 137.10, 133.59, 129.40, 127.88, 105.19, 85.03, 60.89, 24.37, -0.78. Anal calcd for $C_{12}H_{16}OSi$: C, 70.53%; H, 7.89%. Found: C, 70.59%; H, 7.66%.



Compound **11a**

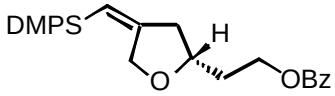
colorless oil. $[\alpha]_D$ -37.948 (c=1.00, CH_2Cl_2) for 92%ee. Enantiomeric excess determined via HPLC analysis (Chiralcel OD column, 100% heptane, flow rate = 1.0mL/min, 254nm, t_r: 10.05 (major), 11.01 (minor)). IR(neat): 3069, 2956, 2896, 2847, 1621, 1428, 1374, 1254, 1138, 1113, 1090, 1037, 991, 924, 883, 868, 834, 776, 729, 700, 665 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$): δ 7.46(m, 2H), 7.26(m, 3H), 5.79(ddd, J=5.7, 10.5, 17.4Hz, 1H), 5.34(s, 1H), 5.18(d, J=17.4Hz, 1H), 5.05(d, J=10.5Hz, 1H), 3.92(m, 1H), 3.75(m, 1H), 3.23(dt, J=3.3, 10.8Hz, 1H), 2.15(m, 4H), 0.28(s, 3H), 0.27(s, 3H).

^{13}CNMR(75MHz, $CDCl_3$): δ 154.89, 139.68, 138.54, 133.66, 128.84, 127.78, 121.08, 115.33, 79.34, 68.04, 45.66, 34.61, -0.67, -0.86. Anal calcd for $C_{16}H_{22}OSi$: C, 74.36%; H, 8.58%. Found: C, 74.23%; H, 8.62%.

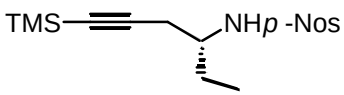


Compound **11b**

colorless oil. $[\alpha]_D$ +31.46 (c=1.32, CH_2Cl_2) for 73% ee. Enantiomeric excess determined via HPLC analysis of the derivative shown below (hydroboration/ benzoate protection). IR(neat): 3069, 2956, 2841, 2362, 1634, 1428, 1331, 1248, 1117, 1053, 988, 924, 863, 831, 730, 700 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 7.54(m, 2H), 7.38(m, 3H), 5.89(ddd, J=17.0, 10.5, 6.5 Hz, 1H), 5.64(dt, J=17.0, 1.5Hz, 1H), 5.18(dt, J=10.5, 1.5Hz, 1H), 4.36(m, 1H), 4.29(d, J=13.5Hz, 1H), 4.13(dh, J=13.5, 1.0Hz, 1H), 2.79(dd, J=16.0, 6.5Hz, 1H), 2.50(dd, J=16.0, 8.5Hz, 1H), 0.39(s, 3H), 0.37(s, 3H). ^{13}CNMR(125MHz, $CDCl_3$) δ 158.36, 138.59, 137.76, 133.65, 129.07, 127.87, 116.67, 116.31, 79.43, 70.26, 42.64, -1.73, -1.75. Anal calcd for $C_{15}H_{20}OSi$: C, 73.71%; H, 8.25%. Found: C, 73.95%; H, 8.46%.



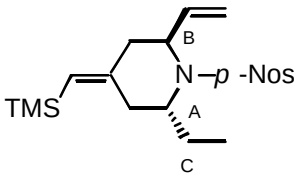
colorless oil. Enantiomeric excess determined by HPLC analysis. (Chiralcel OD column, 99:1 heptane:iPrOH, flow rate = 1.0 mL/min, 254nm, t_r: 13.41 (minor), 14.82 (major)). For ee=30%, $[\alpha]_D$ +16.25 (c=0.24, $CDCl_3$). IR(film from $CDCl_3$): 2957, 1721, 1633, 1452, 1428, 1315, 1274, 1176, 1113, 1069, 831, 712 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.03(d, J=8.1Hz, 2H), 7.50(m, 3H), 7.44(m, 2H), 7.35(m, 3H), 5.65(m, 1H), 4.43(q, J=6.3Hz, 2H), 4.24(d, J=14.1 Hz, 1H), 4.06(d, J=14.1Hz, 1H), 2.77(dd, J=16.5, 6.0Hz, 1H), 2.41(dd, J=16.5, 8.7Hz, 1H), 2.20(p, J=6.3Hz, 2H), 0.35(s, 6H). ^{13}CNMR(75MHz, $CDCl_3$) δ 166.55, 158.39, 138.60, 133.65, 132.90, 130.95, 129.55, 129.08, 128.08, 127.89, 116.92, 75.77, 70.17, 62.13, 42.60, 34.03, -1.75. Anal calcd for $C_{22}H_{26}O_3Si$: C, 72.09%; H, 7.15%. Found: C, 71.99%; H, 7.03%.



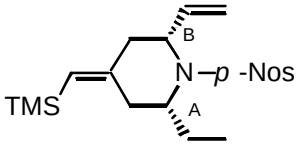
Compound **12**

white solid. melting point=109-113^{o}C. Recrystallized from hot ether/pet ether to obtain analytically pure crystals. Note: it is *very* important to obtain crystalline material from recrystallization. 3rd crop recrystallization gives 93% ee. $[\alpha]_D$ +105.77 (c=1.66, CH_2Cl_2) Enantiomeric excess determined by HPLC (Chiralcel OD column. 90:10

heptane:isopropanol, flow rate =1.0mL/min, 254 nm, τ_R= 13.03(major), 14.20(minor)). IR(film from CH_2Cl_2): 3290, 2966, 2177, 1608, 1532, 1426, 1350, 1310, 1250, 1167, 1094, 1012, 844, 761, 747, 736, 686, 614 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.36(d, J=9.0Hz, 2H), 8.08(d, J=9.0Hz, 2H), 4.89(d, J=9.0Hz, 1H), 3.34(m, 1H), 2.38(dd, J=17.1, 3.9Hz, 1H), 2.29(dd, J=17.1, 5.7Hz, 1H), 1.58(hept, J=7.2Hz, 2H), 0.82(t, J=7.2Hz, 3H), 0.14(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 149.95, 146.97, 128.16, 124.36, 100.75, 88.92, 29.67, 27.15, 25.94, 10.20, -0.04. Anal calcd for $C_{15}H_{22}N_2O_4SSi$: C, 50.82%; H, 6.26%; N, 7.90%. Found: C, 50.58%; H, 6.38%; N, 8.03%.

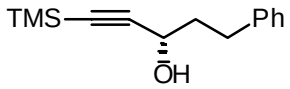


Compound **13**
Note: starting sulfonamide **12** was of 92% optical purity.
oily solid. For *trans* diastereomer with 92%ee at center A, $[\alpha]_D$ +32.60 (c=0.18, CH_2Cl_2) Enantio and diastereomeric excess determined via HPLC analysis. Chiralcel OD column. Flow rate =1.0mL/min. 99:1 heptane:isopropanol, 254 nm, τ_r= 16.61(major mismatched isomer), 18.15(minor mismatched isomer), 23.11(major matched isomer), 24.20(minor matched isomer). IR(film from CD_3CN): 2956, 1618, 1350, 1349, 1248, 1164, 1090, 855, 741 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.20(d, J=9.0Hz, 2H), 7.90(d, J=9.0Hz, 2H), 5.74(ddd, J=17.1, 9.9, 7.5Hz, 1H), 5.29(s, 1H), 5.04(d, J=17.1Hz, 1H), 4.97(d, J=9.9Hz, 1H), 4.01(m, 2H), 2.41(m, 4H), 1.62(m 1H), 1.45(m, 1H), 0.79(t, J=7.5Hz, 3H), 0.00(s, 9H). There is a 3.7% NOE between H_B and H_C, as is most clearly seen in CD_3CN as solvent. ^{13}CNMR(75MHz, $CDCl_3$) δ 149.60, 148.66, 148.11, 136.81, 128.57, 128.07, 123.94, 118.29, 57.62(2C), 43.17, 35.69, 26.00, 11.34, 0.09. . Anal calcd for $C_{19}H_{28}N_2O_4SSi$: C, 55.85%; H, 6.91%. Found: C, 55.63%; H, 6.84%.



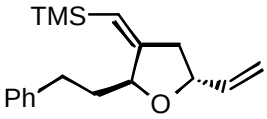
Compound **14**
Note: starting sulfonamide **12** was of 88% optical purity.
White solid. melting point=83-85°C. For *cis* diastereomer with 88%ee at center A, $[\alpha]_D$ +18.92 (c=0.78, CH_2Cl_2) %excess of stereoisomers determined via HPLC analysis. (Chiralcel OD column, Flow rate =1.0mL/min, 99:1 heptane:isopropanol, 254 nm, τ_r= 16.61(minor – mismatched isomer), 18.15(major mismatched isomer), 23.11(minor – matched isomer), 24.20(major – matched isomer)). IR(film from Et_2O): 3282, 2964, 2922, 2176, 1608, 1533, 1425, 1350, 1309, 1250, 1166, 1093, 1008, 843, 736 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 8.35(d, J=9.0Hz, 2H), 8.05(d, J=9.0Hz, 2H), 5.90(ddd,

J=17.1, 10.5, 6.0Hz, 1H), 5.38(s, 1H), 5.27(d, J17.1Hz, 1H), 5.14(d, J=10.2Hz, 1H), 4.67(m, 1H), 4.07(q, J=6.9Hz, 1H), 2.30(m, 2H), 2.16(dd, J=13.5, 6.3Hz, 1H), 2.00(dd, J=13.5, 6.3Hz, 1H), 1.59(m, 1H), 1.42(m, 1H), 0.91(t, J=7.5Hz, 3H), 0.06(s, 9H). Weak NOE between H_A and H_B. ^{13}CNMR(125MHz, CDCl3) δ 149.75, 147.45, 145.98, 137.77, 129.31, 127.99, 124.41, 117.44, 56.92, 55.39, 40.90, 35.69, 27.73, 11.56, 0.19. Anal calcd for C19H28N2O4SSi: C, 55.85%; H, 6.91%, N, 6.86%. Found: C, 56.02; H, 7.06; N, 6.64%.



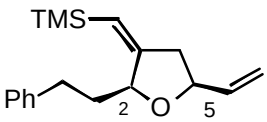
Compound **15**

For ee= 98.7%, $[\alpha]_D$ +32.91 (c=2.37, CH_2Cl_2). Enatiomeric excess determined by HPLC analysis (Chiralcel OD column, 90:10 heptane/iPrOH, flow rate = 1.0 mL/min, 254nm, t_r: 7.87 (minor), 5.51 (major)). IR(film from $CDCl_3$): 3356, 3028, 2958, 2172, 1604, 1496, 1455, 1251, 1047, 1011, 844, 760, 699 cm-1. 1HNMR(500MHz, CDCl3): δ 7.33(m, 2H), 7.24(m, 3H), 4.40(t, J=6.5Hz, 1H), 2.83(t, J=8.0Hz, 2H), 2.04(m, 2H), 0.23(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$): δ 141.25, 128.47, 128.39, 125.95, 106.45, 89.83, 62.08, 39.14, 31.36, -0.16. Anal calcd for $C_{14}H_{20}OSi$: C, 72.36%; H, 8.67%. Found: C, 72.13%; H, 8.48%.



Compound **16**

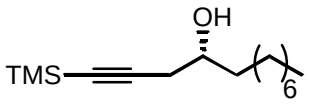
colorless oil. Isolated as a 3.5:1 ratio of inseparable trans/cis isomers. Characterized as mixture of diastereomers. IR(film from $CDCl_3$): 3027, 2953, 1635, 1496, 1455, 1430, 1248, 1044, 988, 923, 836, 747, 699 cm^{-1}. In ^{1}H and ^{13}C spectra, peaks for major isomer were identifiable: ^{1}HNMR(500MHz, $CDCl_3$) δ 7.28(m, 2H), 7.24(m, 3H), 5.90(ddd, J=6.5, 10.5, 17.0Hz, 1H), 5.47(s, 1H), 5.30(d, J=17Hz, 1H), 5.17(d, J=10.5Hz, 1H), 4.57(m, 2H), 2.91(m, 2H), 1.79(m, 1H), 2.40(ddd, J=16.0, 6.0, 2.0Hz, 1H), 1.90(m, 1H), 1.80(m, 1H), 0.07(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 159.40, 142.05, 138.63, 128.56, 128.35, 125.76, 119.70, 115.63, 79.05(2C), 42.22, 37.84, 32.19, -0.13. Anal calcd for $C_{18}H_{26}OSi$: C, 75.48%; H, 9.15%. Found: C, 75.62%; H, 9.25%.



Compound **17**

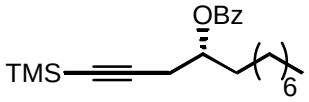
Colorless oil. For 10:1 cis:trans mixture, $[\alpha]_D$ –126.00 (c=0.455, CH_2Cl_2). 4.2% NOE between H_2 and H_5 in $CDCl_3$ for the major isomer. IR(film from $CDCl_3$): 2954, 1737, 1636, 1497, 1451, 1429, 1249, 1044, 925, 839, 745, 699 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$)

δ 7.29(m, 2H), 7.22(m, 3H), 5.96(ddd, J=7.0, 10.5, 10.0Hz, 1H), 5.51(s, 1H), 5.37(d, J=17.0Hz, 1H), 5.18(d, J=10.5Hz, 1H), 4.54(d, J=7.5Hz, 1H), 4.36(m, 1H), 2.78(m, 2H), 2.58(d, J=8.0Hz, 1H), 1.95(m, 1H), 1.86(m, 1H), 0.09(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 159.93, 142.19, 139.75, 128.53, 128.33, 125.71, 119.73, 116.32, 79.24, 79.17, 44.01, 39.36, 31.51, -0.10. Anal calcd for $C_{18}H_{26}OSi$: C, 75.48%; H, 9.15%. Found: C, 75.45%; H, 8.97%.

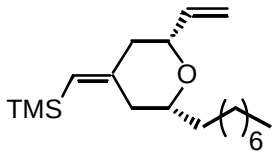


Compound **18**

colorless oil. For 99% ee, $[\alpha]_D$ –3.82 (c=1.66, CH_2Cl_2). Enantiomeric excess determined via HPLC analysis of benzoate derivative (see following compound). IR(neat): 3374, 2958, 2927, 2858, 2176, 1466, 1250, 1033, 843, 760, 698, 648 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 3.76(m, 1H), 2.48(dd, J=16.5, 4.5 Hz, 1H), 2.37(dd, J=16.5, 7.0 Hz, 1H), 1.53(m, 2H), 1.45(m,1H), 1.30(m, 12H), 0.90(t, J=7.)Hz, 3H), 0.18(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 103.31, 87.51, 69.84, 36.18, 31.84, 29.50, 29.48, 29.23, 28.84, 25.54, 22.64, 14.08, 0.04. Anal calcd for $C_{15}H_{30}OSi$: C, 70.79%; H, 11.88%. Found: C, 70.86%; H, 11.68%.



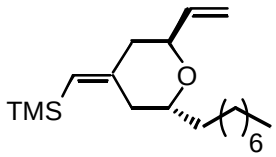
Colorless oil. For 99% ee, $[\alpha]_D$ +24.32 (c=1.71, CH_2Cl_2). Enantiomeric excess determined by HPLC analysis. (Chiralcel OD column, 99.9:0.1 heptane:iPrOH, flow rate = 1.0 mL/min, 254nm, t_r: 6.69 (minor), 8.13 (major)). IR(neat): 2926, 2856, 2179, 1722, 1451, 1314, 1271, 1250, 1176, 1110, 1069, 1027, 842, 756, 710 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 7.90(d, J=8.4Hz, 2H), 7.40(t, J=7.5Hz, 1H), 7.28(t, J=7.5Hz, 2H), 5.03(p, J=6.3Hz, 1H), 2.46(d, J=6.3Hz, 2H), 1.66(m, 2H), 1.10(m, 10H), 0.71(t, J=6.9Hz, 3H), -0.04(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 166.01, 132.84, 130.46, 129.62, 128.24, 102.29, 87.05, 72.42, 33.12, 31.81, 29.33, 29.17, 25.47, 25.13, 22.62, 14.06, -0.12. Anal calcd for $C_{22}H_{34}O_2Si$: C, 73.69%; H, 9.56%. Found: C, 73.53%; H, 9.29%.



Compound **19**

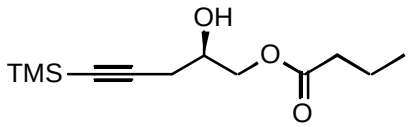
colorless oil. $[\alpha]_D$ –13.35 (c=2.34, CH_2Cl_2). IR(film from $CDCl_3$): 2927, 2856, 1623, 1466, 1420, 1314, 1248, 1142, 1066, 987, 922, 892, 840, 748, 690 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 5.90(ddd, J=5.5, 10.5, 16.5 Hz, 1H), 5.27(m, 2H), 5.14(d, J=10.5Hz, 1H), 3.84(m, 1H), 3.28(m, 1H), 2.47(dt, J=13.5, 2 Hz, 1H), 2.22(m, 2H),

1.89(t, J=12.5Hz, 1H), 1.66(m, 1H), 1.47(m, 1H), 1.35(m, 12H), 0.90(t, J=6.5Hz, 3H), 0.13(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 153.73, 138.85, 122.89, 115.04, 79.22, 78.35, 45.34, 39.88, 36.39, 31.86, 29.67, 29.52, 29.28, 25.50, 22.66, 14.11, 0.32. Anal calcd for $C_{19}H_{36}OSi$: C, 73.95%; H, 11.76%. Found: C, 74.17%; H, 11.60%.



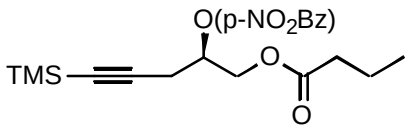
Compound **20**

colorless oil. $[\alpha]_D$ +42.16 (c=2.04, CH_2Cl_2). IR(film from $CDCl_3$): 2928, 2856, 1623, 1468, 1420, 1358,, 1248, 1144, 1112, 1053, 989, 922, 869, 841, 765, 690 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 5.90(ddd, J=5.5, 10.5, 16.5 Hz, 1H), 5.28(d, J=16.5Hz, 1H), 5.23(s, 1H), 5.18(d, J=10.5Hz, 1H), 5.29(q, J=5.5Hz, 1H), 3.82(m, 1H), 2.45(dd, J=13.5, 4.0Hz, 2H), 2.24(dd, J=13.5, 6.5Hz, 1H), 2.12(dd, J=13.5, 6.5Hz, 1H), 1.66(m, 1H), 1.35(m, 1H), 1.29(s, 12H), 0.90(st, J=7.0Hz, 3H), 0.12(s, 9H). ^{13}CNMR(125MHz, $CDCl_3$) δ 151.26, 138.25, 124.66, 116.32, 72.91, 72.44, 43.85, 38.81, 33.73, 31.84, 29.57, 29.55, 29.26, 25.55, 22.65, 14.10, 0.30. Anal calcd for $C_{19}H_{36}OSi$: C, 73.95%; H, 11.76%. Found: C, 73.82%; H, 11.61%.



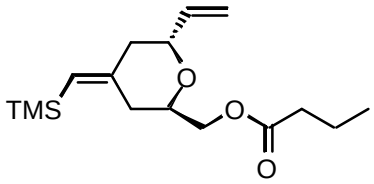
Compound **21**

colorless oil. $[\alpha]_D$ –10.57 (c=2.23, CH_2Cl_2) for 98.5% ee as determined from p-nitrobenzoate derivative (see following compound). IR(neat): 3462, 2963, 2177, 1741, 1459, 1420, 1385, 1250, 1179, 1100, 1034, 937, 844, 760, 799, 647 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 4.05(dd, J=11.4, 3.9Hz, 1H), 3.96(dd, J=11.4, 6.3Hz, 2H), 3.83(m,1H), 2.34(d, J=6.3Hz, 2H), 2.24(d, J=4.8Hz, 1H), 2.18(t, J=7.5Hz, 2H), 1.51(qt, J=7.5, 7.5Hz, 2H), 0.79(t, J=7.5Hz, 3H), -0.01(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 173.77, 101.48, 88.08, 68.15, 66.77, 35.97, 25.21, 18.35, 13.61, -0.07. Anal calcd for $C_{12}H_{22}O_3Si$: C, 59.46%; H, 9.15%. Found: C, 59.60%; H, 9.26%.



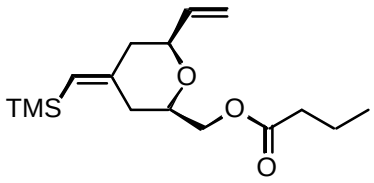
colorless oil. $[\alpha]_D$ –11.76 (c=1.40, CH_2Cl_2) for 98.5% ee as determined via HPLC analysis. (Chiralcel OD column, 98:2 heptane:iPrOH, flow rate = 1.0 mL/min, 254nm, t_r: 11.76 (major), 13.26 (minor)). IR(neat): 2924, 2181, 1734, 1609, 1531, 1350, 1273, 1171, 1102, 1016, 844, 761, 720 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 8.14(d, J=9.0Hz, 2H),

8.05(d, J=9.0Hz, 2H), 5.26(m, 1H), 4.32(dd, J=12.0, 3.6Hz, 1H), 4.23(dd, J=12.0, 6.6Hz, 1H), 2.57(d, J=6.3Hz, 2H), 2.15(t, J=7.5Hz, 2H), 2.47(qt, J=7.5, 7.5Hz, 2H), 0.76(t, J=7.5Hz, 3H), -0.48(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 173.13, 163.79, 150.64, 135.15, 130.85, 123.53, 100.02, 88.29, 71.06, 63.39, 35.89, 22.34, 18.32, 13.57, -0.20. Anal calcd for $C_{19}H_{28}NO_6Si$: C, 58.29%; H, 6.44%; N, 3.58%. Found: C, 58.48%; H, 6.65%; N, 3.56%.



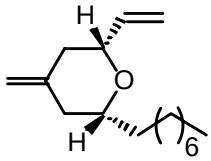
Compound **22**

colorless oil. $[\alpha]_D$ –42.23 (c=1.40, CH_2Cl_2). IR(film from $CDCl_3$): 2956, 2895, 1741, 1624, 1421, 1249, 1177, 1146, 1107, 1052, 924, 869, 840, 765 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 5.77(ddd, J=5.4, 10.5, 15.9Hz, 1H), 5.24(s, 1H), 5.12(m, 2H), 4.28(m, 1H), 4.15(m, 1H), 3.94(m, 2H), 2.37(m, 2H), 2.31(t, J=7.5Hz, 2H), 2.14(m, 2H), 1.55(qt, J=7.5, 7.5Hz, 2H), 0.86(t, J=7.5Hz, 3H), 0.01(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 173.44, 149.47, 137.44, 125.88, 116.95, 73.65, 70.12, 64.83, 43.31, 36.03, 35.32, 18.38, 13.62, 0.18. Anal calcd for $C_{16}H_{28}O_3Si$: C, 64.82%; H, 9.52%. Found: C, 64.64%; H, 9.50%.



Compound **23**

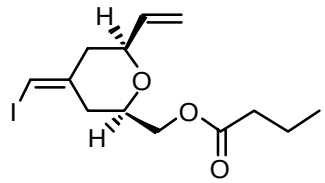
colorless oil. $[\alpha]_D$ +5.85 (c=1.10, CH_2Cl_2). IR(film from $CDCl_3$): 2956, 1742, 1624, 1420, 1249, 1178, 1143, 1102, 1064, 1016, 924, 879, 841 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 5.90(ddd, J=10.2, 6.3, 3.3Hz, 1H), 5.34(s, 1H), 5.29(d, J=10.2Hz, 1H), 5.16(d, J=6.3Hz, 1H), 4.20(dd, J=6.9, 3.9Hz, 1H), 4.14(dd, J=6.9, 2.7Hz, 1H), 3.88(m, 1H), 3.56(m, 1H), 2.46(d, J=8.1Hz, 1H), 2.35(t, J=4.5Hz, 2H), 2.33(m, 2H), 2.00(t, J=7.5Hz, 1H), 1.69(dt, J=4.5, 4.5Hz, 2H), 0.98(t, J=4.5Hz, 3H), 0.13(s, 9H). ^{13}CNMR(75MHz, $CDCl_3$) δ 173.47, 151.88, 138.29, 124.26, 115.43, 79.33, 75.75, 66.55, 45.08, 36.27, 36.06, 18.39, 13.64, 0.22. Anal calcd for $C_{16}H_{28}O_3Si$: C, 64.82%; H, 9.52%. Found: C, 64.60%; H, 9.26%.



Compound **24**

To a solution of vinyl silane **19** (0.024g, 0.079mmol) in toluene (1.5mL) is added trifluoroacetic acid (0.025g, 0.325mmol). Stir at room temperature for 8 hours. Concentrate in vacuo and purify directly via flash chromatography (silica, ether/petroleum ether) to yield 0.017g (92%) of **24** as a colorless oil.

IR(film from $CDCl_3$): 3075, 2929, 2856, 1781, 1654, 1466, 1315, 1221, 1169, 1125, 1065, 987, 922, 889, 665 cm^{-1}. ^{1}HNMR(500MHz, $CDCl_3$) δ 5.93(ddd, J=5.3, 10.5, 17.0Hz, 1H), 5.30(d, J=17.0Hz, 1H), 5.15(d, J=10.5Hz, 1H), 4.77(s, 2H), 3.80(m, 1H), 3.32(m, 1H), 2.29(d, J=13.5Hz, 1H), 2.25(d, J=13.0Hz, 1H), 2.07(t, J=12.5Hz, 1H), 1.95(t, J=12.5Hz, 1H), 1.62(m, 2H), 1.46(m, 2H), 1.30(m, 10H), 0.91(t, J=7.0Hz, 3H). ^{13}CNMR(125MHz, $CDCl_3$) δ 144. 65, 138.87, 115.04, 108.50, 78.81, 78.45, 40.61, 40.61, 40.57, 36.33, 31.87, 29.68, 29.53, 29.26, 25.48, 22.66, 14.10. Anal calcd for $C_{16}H_{28}O$: C, 81.29%; H, 11.94%. Found: C; 81.08%; H, 12.16%.



Compound **25**

To a cooled (0^{o}C) solution of vinyl silane **23** (0.1195g, 0.4mmol) in 10mL MeCN is added N-iodosuccinimide (0.16g, 0.69mmol). Stir at 0^{o}C, wrapped in tin foil, for 3 hours. Dilute with ether and water. Extract aqueous layer once with ether. Combined organics are washed with 20% sodium sulfite, and brine, dried over $MgSO_4$, and concentrated in vacuo. Purify via flash chromatography (silica, ether/petroleum ether) to yield 0.136g (96%) of vinyl iodide **25** as a colorless oil. Rf=0.50 in 10% ether/petroleum ether, $KMnO_4$ stain.

$[\alpha]_D$ +50.58 (c=0.22, CH_2Cl_2). IR(film from $CDCl_3$): 2963, 2875, 1738,1455,1418, 1358, 1253, 1178, 1141, 1101, 1062, 1016, 928, 775 cm^{-1}. ^{1}HNMR(300MHz, $CDCl_3$) δ 5.93(s, 1H), 5.76(ddd, J=5.4, 10.5, 17.1Hz, 1H), 5.18(d, J=17.1Hz, 1H), 5.06(d, J=10.5Hz, 1H), 4.09(d, J=4.8Hz, 2H), 3.72(m, 1H), 3.48(m, 1H), 2.57(d, J=13.5Hz, 1H), 2.37(d, J=13.8Hz, 1H), 2.24(t, J=7.5Hz, 2H), 2.03(t, J=12.0Hz, 1H), 1.83(t, J=12.3Hz, 1H), 1.57(tq, J=7.5, 7.5Hz, 2H), 0.85(t, J=7.5Hz, 3H). ^{13}CNMR(75MHz, $CDCl_3$) δ 173.44, 144.82, 137.18, 116.04, 78.33, 74.72, 74.52, 66.14, 42.36, 37.62, 36.00, 18.38, 13.62. . Anal calcd for $C_{13}H_{19}IO_3$: C, 44.59%; H, 5.47%. Found: C; 44.30%; H, 5.33%.