Supporting Information for

# Asymmetric Copper Hydride-Catalyzed Markovnikov Hydrosilylation of Vinylarenes and Vinyl Heterocycles

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## 1. General Information

### 1.1 General Reagent Information

Unless noted otherwise, reagents and starting materials were purchased from commercial vendors and used as supplied. Diphenylsilane (Aldrich) and phenylsilane (TCI America) were degassed by a freeze-pump-thaw sequence using a dual manifold (this process was repeated three times) and stored under nitrogen in dry Schlenk tubes sealed with screw-in Teflon plugs. The (+)-(2*S*,5*S*) and (-)-(2*R*,5*R*) isomers of 1,2-bis(2,5-

diphenylphospholano)ethane (i.e., Ph-BPE) were obtained through Strem, Aldrich, or Namëna Chemicals. $Cu(OAc)_2$ was either obtained through Strem (amorphous powder, 97% min.) and used directly or obtained though Aldrich (microcrystalline powder, 99.99% metals basis) and crushed inside a dry glass vial with a stainless steel spatula to give a fine powder prior to use. The latter material was used exclusively for examples **11**-**21** (Procedure C and D).[1] THF and toluene were obtained from J.T. Baker in CYCLE-TAINER® delivery kegs and purified by successive filtrations though packed columns of neutral alumina and copper(II) oxide under argon pressure; dichloromethane used as a reaction solvent was purified in the same manner. MTBE, 2-Me-THF and dioxane were obtained from Aldrich in SureSeal® bottles and vigorously sparged with argon prior to use. EtOAc used in chromatography eluents for hydrosilylation products and their derivatives was HPLC grade (Aldrich HPLC plus, 99.9%, Aldrich catalog number 650528); EtOAc used in all other applications was ACS reagent grade (Aldrich, 99.5%). Flash chromatography was performed on wet-loaded, manually eluted silica columns using SiliCycle SiliaFlash® F60 silica gel (40-63 µm, 230-400 mesh, 60 Å pore diameter). Analtech Uniplate™ preparative thin-layer chromatography (TLC) plates (silica gel GF, 1000 micron, UV254 indicator, 20x20 cm) were employed in preparative TLC purifications. Hydrosilylation reactions were performed in glass culture tubes with threaded ends (oven dried at 140 °C for at least 16 h prior to use) that were sealed with screw-thread caps fitted with PTFE/silicone septa (see general procedures for sizes and part numbers). An illustration of the reaction apparatus used in the hydrosilylation of vinylarenes is provided in figure SI-1.

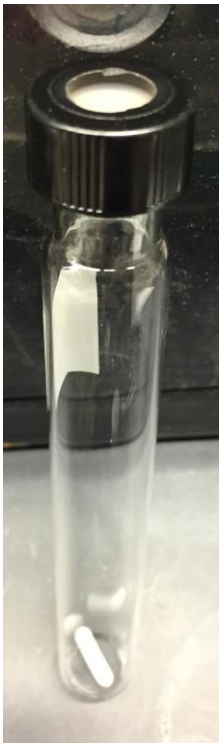


**Figure SI-1**. Reaction apparatus for hydrosilylation reactions: glass culture tube with threaded end (Fisher scientific part # 14-959-35A), phenolic screw-thread open-top cap (Kimble-Chase part # 73804-15425), PTFE-lined silicone septum (Thermo Fisher scientific part # B7995-15), and a small Teflon-coated stir bar.

**General Analytical Information**

Proton and Carbon NMR spectra were recorded using Bruker 400 MHz, Bruker 600 MHz, and Varian 500 MHz instruments. Fluorine NMR spectra were recorded using a Varian 300 MHz spectrometer. Chemical shifts of $^{1}H$ NMR signals are referenced to the indicated residual solvent peak ($CDCl_3$, $\delta = 7.26$; $CD_2Cl_2$, $\delta = 5.32$; benzene-*d6*, $\delta = 7.16$; acetone-*d6*, $\delta = 2.05$) and reported in ppm relative to tetramethylsilane. All $^{13}C$ spectra are proton-decoupled, and $^{13}C$ shifts are reported in ppm with reference to the indicated solvent shifts at $\delta = 77.16$ ($CDCl_3$), 53.84 ppm ($CD_2Cl_2$), or 206.26 (acetone-*d6*). Fluorine NMR shifts were indirectly referenced to $CFCl_3$ by way of external hexafluorobenzene ($\delta = -164.9$). Acetone-*d6*, benzene-*d6*, $CDCl_3$, and $CD_2Cl_2$ were obtained from Cambridge Isotope Laboratories; the latter three were stored over activated 3Å molecular sieves for 48 h prior to use. IR spectra were acquired from neat samples using a Thermo Scientific Nicolet iS5 spectrometer equipped with an iD5 diamond laminate ATR accessory, and representative peaks are reported as wavenumbers in units of $cm^{-1}$. Specific optical rotations were recorded for chloroform solutions at a standard concentration of 5 mg/mL using a Jasco 1010 polarimeter operating at 589 nm. High-resolution mass spectrometry was performed using a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were performed for carbon and hydrogen by Atlantic Microlabs Inc., Norcross, GA. Enantiomeric excesses (ee's) were determined either by chiral HPLC analysis using Agilent 1200 Series chromatographs or by chiral SFC analysis using a Waters Acquity UPC$^2$ instrument; specific columns and analytic methods are provided in the experimental details for individual compounds; the wavelengths of light used for chiral analyses are provided with the associated chromatograms (see pp 75-96). Gas Chromatography (GC) was performed using an Agilent 7890A gas chromatograph equipped with an FID detector and a J&W DB-1 column (10 mm, 0.1 mm I.D.). Analytical TLC was performed using Silicycle SiliaPlate® glass-backed extra-hard-layer TLC plates (60 Å, 250 µm thickness, 20x20 cm, UV-254 indicator) and visualization with 254 nm light. Melting ranges of crystalline solids were determined using a Mel-Temp capillary melting point apparatus and are uncorrected.

## 2. Experimental Details and Characterization

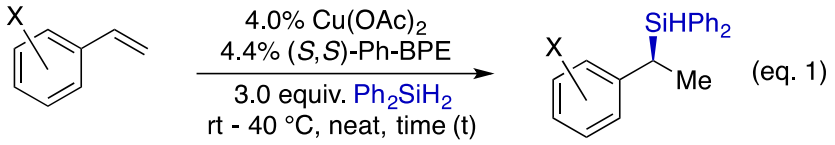
### 2.1. Reaction Optimization

*Table One, Entries 1-7 and 9-10:* Inside a nitrogen-atmosphere glovebox, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 0.04 equiv.) and (*S*,*S*)-Ph-BPE (11 mg, 0.022 mmol, 0.044 equiv.) were weighed into an oven-dried glass culture tube with a threaded end (Fisher Scientific part # 14-959-35C). The tube was sealed with a phenolic screw-thread cap with a Teflon/silicone septum (Thermo Scientific part number C4015-66A) and brought outside the glovebox. Solvent (if used, 0.5 M) and silane (1.50 mmol, 3.0 equiv.) were then added via syringe while the reaction vessel was maintained under positive argon pressure using an argon inlet needle. The reaction mixture was stirred for approximately 15 min. In some cases, a color change to orange or red was observed (**Caution!** *Gas evolution can occur at this stage*). Styrene (57 µL, 0.50 mmol, 1.0 equiv.) was subsequently added,

the argon inlet needle was removed, and the reaction mixture was stirred in a 40 °C oil bath for the specified amount of time. Upon cooling to rt, the mixture was diluted with EtOAc and the resulting solution was used for yield-determination by GC with dodecane as an internal standard. In entries 1-7, the solution of the crude product was concentrated and purified by preparative TLC (3:97 EtOAc:hexanes), and the enantiomeric excess of the purified product was determined by chiral HPLC (refer to characterization data for compound **1** for method details).

*Table One, Entry 8:* The reaction mixture was prepared in a manner similar to those described above using $Cu(OAc)_2$ (1.45 mg, 0.008 mmol, 0.04 equiv.), (*S*,*S*)-Ph-BPE (4.5 mg, 0.0088 mmol, 0.044 equiv.), styrene (23 µL, 0.20 mmol, 1.0 equiv.), THF (0.4 mL), and phenylsilane (74 µL, 0.6 mmol, 3.0 equiv.). After 48 h, the reaction mixture was partitioned between EtOAc and saturated $NaHCO_3$, and the organic phase was dried over $Na_2SO_4$, filtered, and concentrated *in vacuo* to give a residue that was purified by flash column chromatography (1:9 $CH_2Cl_2$:hexanes) to provide (*S*)-phenyl(1-phenylethyl)silane as an oil (38 mg, 90% yield). The $^1$H NMR data were identical to those in an earlier report[2] [**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 2H), 7.36 – 7.19 (m, 4H), 7.18 – 7.05 (m, 3H), 4.34 (d, *J* = 3.2 Hz, 2H), 2.63 (qt, *J* = 7.2, 3.2 Hz, 1H), 1.47 (d, *J* = 7.5 Hz, 3H)]. The enantiomeric excess was determined as *96%* by chiral HPLC analysis (OJ-H column, isocratic hexanes, 30 min, 1 mL/min flow rate; $t_M$ = 11.71 min, $t_m$ = 12.85 min).

## 2.2. General Hydrosilylation Procedures



(eq. 1)

*Procedure A: Hydrosilylation of Styrene Derivatives:*

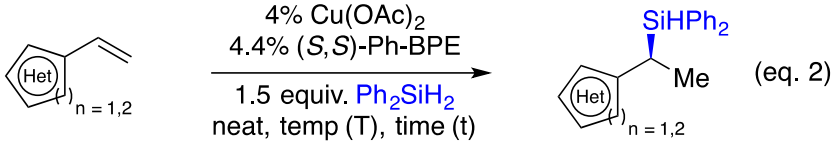
**Caution:** *According to the National Institutes of Health National Toxicology Program,*[3] *Styrene is "'reasonably anticipated to be a human carcinogen' based on sufficient animal evidence and limited evidence in humans." As the toxicological properties of most of the vinylarenes and vinyl heterocycles used in this paper are either unknown or poorly characterized, we recommend handling all of them with the presumption of carcinogenicity.*

Inside a nitrogen-atmosphere glovebox, a borosilicate glass culture tube with a threaded end (Fisher Scientific part # 14-959-35A; oven-dried at 140 °C for 16 h prior to use) was charged with $Cu(OAc)_2$ (7.2 mg, 0.040 mmol) and (*S*,*S*)-Ph-BPE (22.2 mg, 0.044 mmol) and equipped with a small Teflon-coated stir bar. The reaction tube was charged with diphenylsilane (0.560 mL, 556 mg, 3.02 mmol) and then securely sealed with a phenolic screw-thread open-top cap (Kimble-Chase part # 73804-15425) fitted with a PTFE-lined silicone septum (Thermo Fisher scientific part # B799515; See Figure SI-1 for a picture

of the apparatus). The reaction mixture was removed from the glovebox and stirred at rt, taking care to ensure that all particulate solids remained suspended in the bulk mixture. After 80 min, a homogeneous orange-red or orange-brown solution was obtained, and at this juncture the septum was penetrated with an inlet needle connected to a glass manifold pressurized with nitrogen at ca. 2 psi via a well-purged length of Tygon tubing. The vinylarene (1.0 mmol; weighed by difference) was added to the tube using a tared disposable plastic 1 mL syringe from which all air had been excluded, and the resulting reaction mixture was stirred at the indicated temperature under a nitrogen atmosphere. After the specified amount of time, the mixture was allowed to cool to rt (if applicable) and was loaded onto a plug of silica gel (ca. 15 g) that had been wetted with hexanes. The plug was flushed under vacuum with EtOAc (ca. 200 mL), and the filtrate was concentrated to give a residue that was purified by column chromatography. The fractions containing the pure product were combined, concentrated *in vacuo*, and finally dried under high vacuum for at least 16 h to provide the desired diphenylsilane adduct.

*Procedure B: Hydrosilylation of Styrene Derivatives, Alternative Method:*

Inside a nitrogen-atmosphere glovebox, a borosilicate glass culture tube with a threaded end (Fisher Scientific part # 14-959-35A; oven-dried at 140 °C for 16 h prior to use) was charged with $Cu(OAc)_2$ (3.6 mg, 0.020 mmol) and (*S*,*S*)-Ph-BPE (11.1 mg, 0.022 mmol) and equipped with a small Teflon-coated stir bar. The reaction vessel was charged with diphenylsilane (0.560 mL, 556 mg, 3.02 mmol) and then securely sealed with a phenolic screw-thread open-top cap (Kimble-Chase part # 73804-15425) fitted with a PTFE-lined silicone septum (Thermo Fisher scientific part # B7995-15). The reaction mixture was removed from the glovebox and stirred in an oil bath at 40 °C until it became deep orange in color. The reaction vessel was then charged with the vinylarene (1.0 mmol) via syringe. The mixture was stirred in a 40 °C oil bath for the indicated amount of time, allowed to cool to rt, and subjected to the filtration and chromatography protocols described in procedure A.[4]

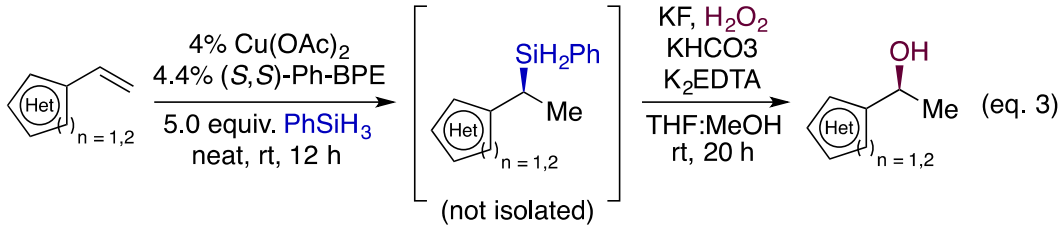


(eq. 2)

*Procedure C: Hydrosilylation of Vinyl Heterocycles with Diphenylsilane:*

Inside a nitrogen-atmosphere glovebox, a borosilicate glass culture tube with a threaded end (Fisher Scientific part # 14-959-35C; oven-dried at 140 °C for 16 h prior to use) was charged with $Cu(OAc)_2$ (3.6 mg, 0.020 mmol), (*S*,*S*)-Ph-BPE (11.1 mg, 0.022 mmol), and the heterocycle (0.50 mmol) and was equipped with a small Teflon-coated stir bar. The reaction vessel was charged with diphenylsilane (0.140 mL, 139 mg, 0.75 mmol) and then securely sealed with a phenolic screw-thread cap with a Teflon/silicone septum (Thermo Scientific part number C4015-66A). The reaction mixture was removed from the glovebox and stirred at the indicated temperature under a nitrogen atmosphere. After

the specified amount of time, the mixture was allowed to cool to rt (if applicable) and subjected to the filtration and chromatography protocols described in procedure A.




*Procedure D: Hydrosilylation/Tamao Oxidation Sequence:*

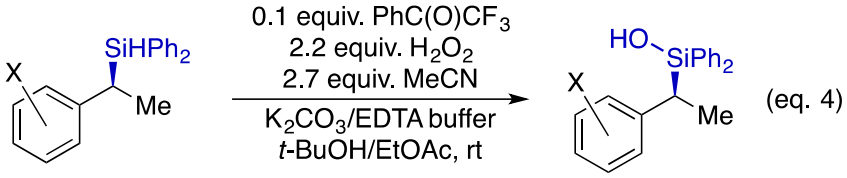
Inside a nitrogen-atmosphere glovebox, $Cu(OAc)_2$, (7.2 mg, 0.040 mmol), (*S*,*S*)-Ph-BPE (22.2 mg, 0.044 mmol), and the indicated heterocycle (1.0 mmol) were weighed into an oven-dried glass culture tube with a threaded end (Fisher Scientific part # 14-959-37A). An oven dried stir bar and phenylsilane (0.620 mL, 5.02 mmol) were added to the vial, and it was sealed with a phenolic screw-thread open-top cap (Kimble-Chase part # 73804-18400) fitted with a PTFE-lined silicone septum (Thermo Fisher scientific part # B7995-18). Stirring of the reaction mixture at rt was begun immediately. Once all of the solid reactants had dissolved, the orange-brown reaction mixture was removed from the glovebox and stirred at rt under a nitrogen atmosphere. After a total reaction time of 12 h, excess phenylsilane was removed using a dual-manifold with a liquid nitrogen-cooled solvent trap by outfitting the reaction vessel with a 24/40 gas adapter with a greased ground-glass stopcock by way of a connecting adapter (Chemglass part numbers CG-1318-10 and CG-1318-23) whose threads were wound with Teflon tape (see Figure SI-2 for a picture of the apparatus). Further drying under high vacuum yielded the crude hydrosilylation product as a viscous brown oil.

The crude product was transferred as a solution in THF (6 mL) to a flask containing KF (232 mg, 3.99 mmol), $K_2EDTA•(H_2O)_2$ (404 mg, 1.00 mmol) and $KHCO_3$ (400 mg, 4.00 mmol). The resulting suspension was stirred at rt while MeOH (6 mL) was gradually added to it via syringe (**caution!** *vigorous gas evolution occurs during this manipulation*). After 40 min, the pale blue-green suspension was treated dropwise with $H_2O_2$ (50% w/w, 0.51 mL, 8.7 mmol) and then stirred at rt for 20 h. Excess oxidant was quenched by addition of sodium thiosulfate (anhydrous, 4.0 g, 25.3 mmol) and MeOH (6 mL) followed by vigorous stirring until starch-iodine testing indicated total destruction of peroxides. (**Caution!** *Potentially explosive organic peroxides are generated during the Tamao oxidation, and the reaction mixture must be thoroughly quenched prior to any attempt to isolate the crude product. It is mandatory to use an analytical test for confirming the destruction of peroxides at this stage, since inefficient stirring of the mixture can result in incomplete reduction even when superstoichiometric quantities of sodium thiosulfate are present for extended times. Note, however, that the copper-containing solids present in the fully quenched mixture give a false positive for peroxides using starch-iodine strips; it is therefore important to sample only the liquid phase during peroxide analysis.*) The quenched mixture was taken up into EtOAc, dried over $Na_2SO_4$, filtered, and concentrated to give a residue that was purified by flash column

chromatography on silica gel. The fractions containing the pure product were combined and the solvent was removed *in vacuo* to provide the desired alcohol.

**Figure SI-2**: apparatus for solvent removal from the hydrosilylation mixture Procedure D.

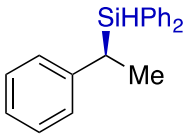
### 2.3. General Procedure for the Synthesis of Silanol Derivatives (Procedure E)



(eq. 4)

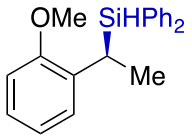
Direct chiral analysis of several diphenylsilane adducts by HPLC or SFC was challenging due to a lack of enantiomer separation. To permit the determination of enantiomeric excesses for these compounds, we converted them to the corresponding silanols, the enantiomers of which were generally much more easily resolved, using a slightly modified version of the procedure described by Kokotos, et al.[5] Thus, the indicated diphenylsilane adduct (0.20 mmol) was weighed into a 10 mL pear-shaped flask equipped with a small Teflon stir bar. The flask was sequentially charged with 2,2,2-trifluoroacetophenone (3.0 µL, 0.02 mmol), *tert*-butyl alcohol (0.38 mL), EtOAc (0.12 mL), MeCN (0.030 mL, 0.57 mmol, 2.7 equiv.), and 0.40 mL of aqueous buffer (0.6 M in potassium carbonate, $4x10^{-5}$ M in tetrasodium EDTA). $H_2O_2$ (50% w/w in water, 25 µL, 0.43 mmol, 2.15 equiv.) was added dropwise and the resulting cloudy biphasic reaction mixture was vigorously stirred at ambient temperature for the reaction period specified and then partitioned between EtOAc and water. The organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a crude residue that was purified by preparative TLC with the specified eluent. Extraction of silica containing the product band with EtOAc, filtration, and concentration *in vacuo* provided the desired silanol.

### 2.4. Synthesis and Characterization of Hydrosilylation Products and Their Derivatives



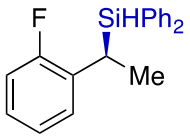
**(*S*)-diphenyl(1-phenylethyl)silane (1):** Prepared according to procedure A using styrene (105.1 mg, 1.009 mmol) and a reduced loading of $Cu(OAc)_2$ (3.6 mg, 0.020 mol) and (*S*,*S*)-Ph-BPE (11.1 mg, 0.022 mmol). The reaction mixture was stirred in a 40 °C oil bath for 24 h. The crude residue was purified by flash column chromatography (20 g silica gel, 55 mm outer-circumference column, gradient of 100% hexanes [150 mL] → 1:99 $CH_2Cl_2$:hexanes [150 mL] → 2:98 $CH_2Cl_2$:hexanes [400 mL] → 4:96 $CH_2Cl_2$:hexanes [150 mL]) to provide the title compound as clear oil (260 mg, 89% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.45 – 7.39 (m, 1H), 7.39 – 7.32 (m, 5H), 7.30 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 7.14 – 7.07 (m, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 4.85 (dd, *J* = 3.4, 1.2 Hz, 1H), 2.84 (qd, *J* = 7.5, 3.3 Hz, 1H), 1.48 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.46, 135.83, 135.68, 133.15, 129.84, 129.70, 128.29, 128.04, 127.85, 127.83, 125.03, 27.09, 16.63. Note that two signals overlap. **IR** (neat) 3067, 3022, 2952, 2868, 2118, 1598, 1489, 1427, 1111, 798, 729, 694 $cm^{-1}$. **EA** Calcd. for $C_{20}H_{20}Si$: C, 83.28; H, 6.99. Found: C, 83.58; H, 7.00. **Specific Rotation** $[\alpha]_D^{26}$ – 45.4 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OJ-H column, isocratic hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 14.90 min, $t_m$ = 11.24 min) indicated *94% ee*. **Duplicate Experiment** 80% yield, *94% ee*.

**Large-scale synthesis of (*S*)-diphenyl(1-phenylethyl)silane (1):** This example was conducted according to procedure A, albeit on tenfold scale and with a reduced catalyst loading. Thus, inside a nitrogen-atmosphere glovebox, $Cu(OAc)_2$ (36.0 mg, 0.200 mmol) and 111.0 mg of (*S*,*S*)-Ph-BPE (0.220 mmol) were weighed into an oven-dried borosilicate glass culture tube with a threaded end (Fisher Scientific part # 14-959-37C) that contained an oven-dried Teflon-coated stir bar. Diphenylsilane (5.60 mL, 30.2 mmol) was added to the tube via syringe. The vessel was sealed with a phenolic screw-thread open-top cap (Kimble-Chase part # 73804-18400) fitted with a PTFE-lined silicone septum (Thermo Fisher scientific part # B7995-18) and removed from the glovebox. The reaction mixture was stirred at rt for 80 minutes. The septum was then punctured with a nitrogen inlet needle, and the mixture was charged with styrene (1.046 g, 10.0 mmol), stirred in a 40 °C oil bath for 24 h, allowed to cool to rt, and then filtered through a pad of silica gel (ca. 50 g). The filtrate was concentrated to give a residue that was purified by flash column chromatography (125 g silica gel, gradient of 100% hexanes (400 mL) → 2:98 $CH_2Cl_2$:hexanes (1200 mL) → 3:97 $CH_2Cl_2$:hexanes (400 mL) → 4:96 $CH_2Cl_2$:hexanes (800 mL) to provide the title compound as a slightly turbid, colorless oil (2.191 g, 76% yield). The $^1$H NMR spectrum of this compound matched that of a sample prepared on 1 mmol scale. **Chiral HPLC analysis** (25 cm OD-H column, isocratic hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 23.72 min [very broad], $t_m$ = 12.65 min) indicated *93% ee*.

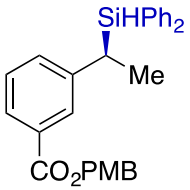



**(*S*)-(1-(2-methoxyphenyl)ethyl)diphenylsilane (2):** Prepared according to procedure A using 2-vinylanisole (136.4 mg, 1.017 mmol). The reaction mixture was stirred at ambient temperature for 48 h. The crude residue was purified by flash column

chromatography (110 g silica gel, 1:7.5:91.5 EtOAc:$CH_2Cl_2$:hexanes) to give the title compound as a colorless oil (237.1 mg, 74% yield). **$^1$H NMR** (500 MHz, Benzene-*d6*) δ 7.63 – 7.57 (m, 2H), 7.47 – 7.40 (m, 2H), 7.19 – 7.14 (m, 3H), 7.12 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.10 – 7.03 (m, 3H), 7.01 (td, *J* = 7.8, 1.7 Hz, 1H), 6.88 (t, *J* = 7.5, 1H), 6.45 (d, *J* = 8.1 Hz, 1H), 5.06 (d, *J* = 3.4 Hz, 1H), 3.52 (qd, *J* = 7.6, 3.4 Hz, 1H), 3.11 (s, 3H), 1.47 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 156.23, 135.79, 135.39, 134.15, 134.04, 133.32, 129.60, 129.29, 127.93, 127.54, 127.36, 125.75, 120.59, 109.98, 54.86, 18.97, 15.83. **IR** (neat) 3067, 2953, 2115, 1488, 1427, 1239, 1113, 793, 729, 696 cm$^{-1}$. **EA** Calcd. for $C_{21}H_{22}OSi$: C, 79.20; H, 6.96. Found: C, 79.09; H, 7.05. **Specific Rotation** $[\alpha]_D^{25}$ – 13.5 (c 0.50, $CHCl_3$). **Chiral SFC analysis** (25 cm OJ-H column, 5:95 IPA:$scCO_2$ to 10:90 IPA:$scCO_2$ linear gradient over 6 min with 1 min hold time, 210-400 nm detection, 2.5 mL/min flow rate, 40 °C, $t_M$ = 5.19 min, $t_m$ = 4.82 min) indicated *99%* ee. **Duplicate experiment** 77% yield, *98% ee*.

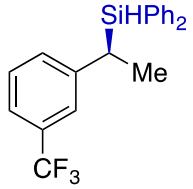



**(*S*)-(1-(2-fluorophenyl)ethyl)diphenylsilane (3):** Prepared according to procedure B using 2-fluorostyrene (120 µL, 1.01 mmol) and an increased loading of $Cu(OAc)_2$ (7.2 mg, 0.040 mmol) and (*S*,*S*)-Ph-BPE (22.2 mg, 0.044 mmol). The reaction mixture was stirred in a 40 °C oil bath for 48 h. The crude product was purified by flash chromatography (18 g silica, 350 mL hexanes) to give the title compound as colorless oil (262.4 mg, 85% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.43 – 7.29 (m, 6H), 7.27 – 7.22 (m, 2H), 7.07 – 6.95 (m, 3H), 6.88 (ddd, *J* = 9.5, 8.0, 1.3 Hz, 1H), 4.81 (t, *J* = 3.2 Hz, 1H), 3.16 (qd, *J* = 7.5, 3.5 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.34, 158.92, 135.80, 135.44, 132.99, 132.85, 131.90, 131.75, 129.95, 129.75, 128.73, 128.69, 128.08, 127.88, 126.33, 126.25, 124.08, 124.04, 115.22, 114.99, 18.67, 18.66, 15.95, 15.94. Note that eight signals are doubled due to $^{19}$F,$^{13}$C-coupling. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -120.08. **IR** (neat) 3068, 2958, 2870, 2122, 1487, 1428, 1225, 1107, 797 cm$^{-1}$. **EA** Calcd. for $C_{20}H_{19}FSi$: C, 78.39; H, 6.25. Found: C, 78.66; H, 6.28. **Specific Rotation** $[\alpha]_D^{25}$ – 44.4 (c 0.50, $CHCl_3$). The enantiomeric excess of this compound was determined as *97%* by chiral HPLC analysis of silanol derivative **22** (see page S21). **Duplicate experiment** 77% yield of silane **3**, analysis of silanol **22** indicated *97% ee*.

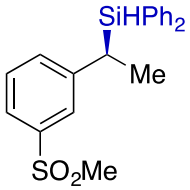



**4-methoxybenzyl (*S*)-3-(1-(diphenylsilyl)ethyl)benzoate (4):** Prepared according to procedure A, with one modification: the substrate, 4-methoxybenzyl 3-vinylbenzoate (**27**, 264.6 mg, 0.986 mmol), was weighed into the reaction tube inside the glovebox along with the catalyst precursors. The reaction mixture obtained upon addition of the silane

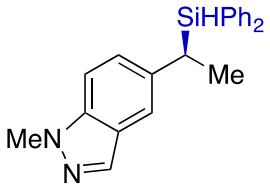
was removed from the glovebox and stirred at ambient temperature for 48 h. The crude residue was purified by flash chromatography (60 g silica, gradient of 1:19 to 1:7 EtOAc:hexanes) to provide the title compound as a very viscous colorless oil (331.0 mg, 74% yield). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.73 (t, *J* = 1.8 Hz, 1H), 7.52 (dt, *J* = 6.6, 1.4 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.39 – 7.32 (m, 7H), 7.29 – 7.24 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.15 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.97 – 6.88 (m, 2H), 5.30 – 5.24 (m, 2H), 4.84 (d, *J* = 3.4 Hz, 1H), 3.84 (s, 3H), 2.90 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.49 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 166.81, 159.74, 144.95, 135.77, 135.61, 132.67, 132.64, 132.41, 130.21, 130.13, 129.97, 129.84, 128.95, 128.48, 128.24, 128.12, 127.94, 126.49, 114.07, 66.50, 55.44, 27.14, 16.47. **IR** (neat) 3068, 2955, 2870, 2120, 1714, 1612, 1514, 1428, 1277, 1245, 1172, 1106, 1083, 1034, 799, 757, 696 $cm^{-1}$. **EA** Calcd. for $C_{29}H_{28}O_3Si$: C, 76.96; H, 6.24. Found: C, 77.16; H, 6.24. **Specific Rotation** $[\alpha]_D^{26}$ – 29.3 (c 0.50, $CHCl_3$). The enantiomeric excess of this compound was determined as *93%* by chiral HPLC analysis of silanol derivative **23** (see page S21). **Duplicate experiment** 80% yield of silane **4**, analysis of silanol **23** indicated *92% ee*.




**(*S*)-diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silane (5):** Prepared according to procedure A using 3-(trifluoromethyl)styrene (171.4 mg, 0.996 mmol). The reaction mixture was stirred in a 40 °C oil bath for 72 h. The crude product was purified by flash chromatography (75 g silica gel, 700 mL of 1:39 $CH_2Cl_2$:hexanes followed by sufficient 1:19 $CH_2Cl_2$:hexanes to elute all product) to provide the title compound as a colorless oil (284.1 mg, 80% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.32 (m, 6H), 7.32 – 7.26 (m, 3H), 7.18 – 7.14 (m, 2H), 4.83 (d, *J* = 3.2 Hz, 1H), 2.91 (qd, *J* = 7.5, 3.2 Hz, 1H), 1.50 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 145.50, 135.96, 135.75, 135.60, 132.34, 131.02, 131.01, 131.01, 131.00, 130.78, 130.57, 130.36, 130.15, 130.12, 130.00, 128.57, 128.19, 128.02, 127.09, 125.29, 124.53, 124.50, 124.48, 124.45, 123.48, 121.84, 121.81, 121.79, 121.76, 121.68, 27.42, 16.21. Note that five signals are perceptibly split as quartets due to $^{19}$F,$^{13}$C-coupling. These quartets occur at δ = 131 ($^4J$ = 1.1 Hz), 130.7 ($^2J$ = 31.9 Hz), 124.5 ($^3J$ = 3.8 Hz), 124.4 ($^1J$ = 272.3 Hz), 121.8 ($^3J$ = 3.8 Hz). **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -65.81. **IR** (neat) 3070, 2958, 2872, 2122, 1429, 1328, 1162, 1117, 801, 696 $cm^{-1}$. **EA** Calcd. for $C_{21}H_{19}F_3Si$: C, 70.76; H, 5.37. Found: C, 70.71; H, 5.33. **Specific Rotation** $[\alpha]_D^{25}$ – 35.3 (c 0.50, $CHCl_3$). The enantiomeric excess of this compound was determined as *87%* by chiral HPLC analysis of silanol derivative **24** (see page S22). **Duplicate experiment** 67% yield of **5**, analysis of silanol derivative **24** indicated *88% ee*. The product of this reaction possesses a very weak chromophore and elutes in a broad band which has some overlap with another broad band associated with a diphenylsilane-derived byproduct. The analytically challenging nature of this purification resulted in slightly greater variability in the isolated yield than typically observed for CuH-catalyzed hydrosilylation reactions.

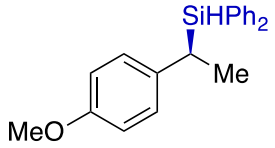



**(*S*)-(1-(3-(methylsulfonyl)phenyl)ethyl)diphenylsilane (6):** Prepared according to procedure A, with the following modification: the mixture of catalyst precursors in diphenylsilane was stirred at ambient temperature in a sealed reaction tube inside the glovebox rather than in a fumehood. After 80 min, the reaction tube was uncapped, and the substrate, 1-(methylsulfonyl)-3-vinylbenzene (**28**, 182.1 mg, 0.999 mmol), was weighed into it as the solid. The vial was resealed, and the reaction mixture was removed from the glovebox and stirred at ambient temperature for 48 h. The crude residue was purified by flash chromatography (80 g silica gel, gradient of 3:17 [50 mL] to 1:4 [300 mL] EtOAc:hexanes followed by sufficient 1:3 EtOAc:hexanes to elute all product) to provide the title compound as a clear oil (313.5 mg, 86% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.46 – 7.40 (m, 2H), 7.40 – 7.32 (m, 6H), 7.32 – 7.25 (m, 3H), 4.81 (d, *J* = 3.4 Hz, 1H), 2.97 (qd, *J* = 7.5, 3.5 Hz, 1H), 2.80 (s, 3H), 1.52 (d, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 146.52, 140.31, 135.66, 135.55, 132.67, 132.22, 132.06, 130.22, 130.05, 129.15, 128.28, 128.09, 126.37, 123.79, 44.46, 27.66, 15.95. **IR** (neat) 3068, 3017, 2955, 2869, 2120, 1594, 1454, 1299, 1142, 1108, 956, 802, 732, 668 $cm^{-1}$. **EA** Calcd. for $C_{21}H_{22}O_2SSi$: C, 68.81; H, 6.05. Found: C, 69.04; H, 6.05. **Specific Rotation** $[\alpha]_D^{26}$ – 39.4 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm AD-H column, isocratic 5:95 IPA:hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 11.61 min, $t_m$ = 13.89 min) indicated *85% ee*. **Duplicate experiment** 86% yield, *87% ee*.

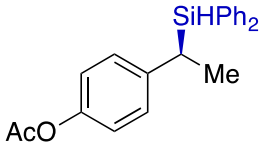



**(*S*)-5-(1-(diphenylsilyl)ethyl)-1-methyl-1*H*-indazole (7):** Prepared according to the modification of procedure A described in the synthesis of sulfone **6**, using 1-methyl-5-vinyl-1*H*-indazole (**29**, 158.3 mg, 1.001 mmol). The reaction mixture was stirred at ambient temperature for 48 h. The crude product was purified by flash silica chromatography (gradient of 1:9 to 1:4 acetone:hexanes) to provide the title compound as a pale yellow-beige oil (314.6 mg, 92% yield). **$^{1}$H NMR** (500 MHz, Benzene-*d6*) δ 7.84 (s, 1H), 7.58 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.28 (s, 1H), 7.21 – 7.14 (m, 3H), 7.13 – 7.04 (m, 3H), 7.03 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 5.14 (d, *J* = 3.3 Hz, 1H), 3.41 (s, 3H), 2.87 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.52 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.64, 136.68, 135.83, 135.68, 133.26, 133.22, 132.27, 129.85, 129.71, 128.07, 127.89, 127.63, 124.56, 118.67, 108.59, 35.63, 26.74, 17.29. **IR** (neat) 3067, 2950, 2867, 2117, 1505, 1427, 1224, 1107, 987, 803, 731, 697 $cm^{-1}$. **EA** Calcd. for $C_{22}H_{22}N_2Si$: C, 77.15; H, 6.47. Found: C, 77.15; H, 6.51. **Specific Rotation** $[\alpha]_D^{26}$ – 49.1

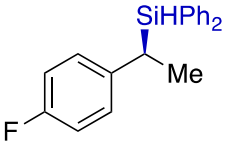
(c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OD-H column, isocratic 1:99 IPA:hexanes over 15 min, 1.0 mL/min flow rate, $t_M$ = 9.96 min, $t_m$ = 9.33 min) indicated *92% ee*. **Duplicate experiment** 85%, *93% ee*.



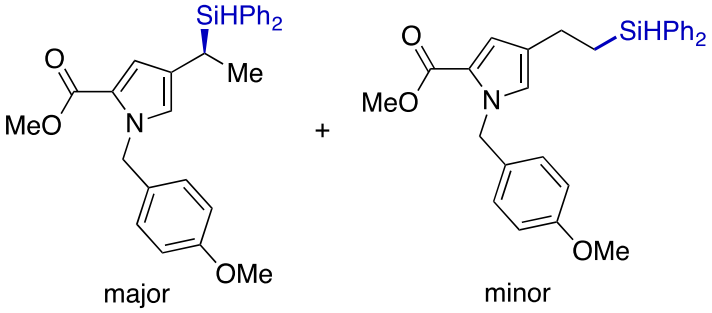

**(*S*)-(1-(4-methoxyphenyl)ethyl)diphenylsilane (8):** prepared according to procedure A using 4-methoxystyrene (136.6 mg, 1.018 mmol) and a reduced silane loading (280 µL, 1.51 mmol). The reaction mixture was stirred in a 40 °C oil bath for 24 h. The crude product was purified by flash column chromatography (20 g silica gel, 55 mm outer circumference column, 1:39 $CH_2Cl_2$:hexanes [200 mL] → 1:19 $CH_2Cl_2$:hexanes [400 mL] → 1:4 $CH_2Cl_2$: hexanes [400 mL]) to provide the title compound as a clear oil (270.7 mg, 83% yield). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 6.7, 1.4 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.40 – 7.33 (m, 5H), 7.32 – 7.26 (m, 2H), 6.97 – 6.90 (m, 2H), 6.79 – 6.74 (m, 2H), 4.84 (d, *J* = 3.4 Hz, 1H), 3.78 (s, 3H), 2.78 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.45 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.23, 136.42, 135.83, 135.71, 133.34, 133.30, 129.78, 129.65, 128.67, 128.03, 127.85, 113.77, 55.37, 25.94, 16.99. **IR** (neat) 3067, 2952, 2867, 2832, 2115, 1609, 1508, 1428, 1243, 1177, 1113, 1037, 830, 797, 731, 696 $cm^{-1}$. **EA** Calcd. for $C_{21}H_{22}OSi$: C, 79.20; H, 6.96. Found: C, 79.37; H, 7.03. **Specific Rotation** $[\alpha]_D^{26}$ – 39.9 (c 0.50, $CHCl_3$). The enantiomeric excess of this compound was determined as *96%* by chiral HPLC analysis of the silanol derivative **25** (see pp. S22-S23). **Duplicate experiment** 83% yield of **8**, analysis of silanol **25** indicated *95%* ee.




**(*S*)-4-(1-(diphenylsilyl)ethyl)phenyl acetate (9):** Prepared according to procedure B using 4-acetoxystyrene (155µL, 1.013 mmol). The reaction mixture was heated in a 40 °C oil bath for 12 h. The crude product was purified by flash column chromatography (12 g silica gel, 55 m outer circumference column, 1:19 to 1:1 $CH_2Cl_2$:hexanes gradient) to provide the title compound as a colorless oil (326.3 mg, 94% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.44 – 7.39 (m, 1H), 7.39 – 7.32 (m, 5H), 7.32 – 7.30 (m, 2H), 7.01 – 6.94 (m, 2H), 6.94 – 6.86 (m, 2H), 4.82 (d, *J* = 3.3 Hz, 1H), 2.83 (qd, *J* = 7.5, 3.4 Hz, 1H), 2.27 (s, 3H), 1.45 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.70, 148.16, 141.98, 135.80, 135.66, 132.86, 129.90, 129.77, 128.54, 128.09, 127.91, 121.22, 26.59, 21.28, 16.59 (one signal missing due to overlap). **IR** (neat) 3068, 2954, 2869, 2118, 1764, 1504, 1187, 1009, 731, 697 $cm^{-1}$. **EA** Calcd. for $C_{22}H_{22}O_2Si$: C, 76.26; H, 6.40. Found: C, 76.28; H, 6.32. **Specific Rotation** $[\alpha]_D^{25}$ – 38.7 (c 0.50, $CHCl_3$). The enantiomeric excess of this compound was determined as *97%* by chiral HPLC analysis of silanol derivative **26** (see page S23). **Duplicate experiment** 84% yield of silane **9**, analysis of silanol **26** indicated *95% ee*.

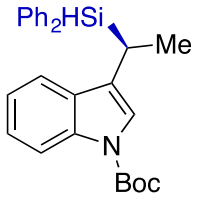



**(*S*)-(1-(4-fluorophenyl)ethyl)diphenylsilane (10):** Prepared according to procedure A using 4-fluorostyrene (123.0 mg, 1.007 mmol) and a reduced catalyst loading of 3.6 mg $Cu(OAc)_2$ (0.02 mmol) and 11.1 mg (*S*,*S*)-Ph-BPE. The reaction mixture was stirred in a 40 °C oil bath for 12 h. The crude product was purified by flash chromatography (20 g silica column, 55 mm outer-circumference, 200 mL 1:39 $CH_2Cl_2$:hexanes followed by sufficient 1:19 $CH_2Cl_2$:hexanes to elute all product) to provide the tile compound as a colorless oil (255.4 mg, 83% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.34 (m, 5H), 7.32 – 7.27 (m, 2H), 6.97 – 6.92 (m, 2H), 6.92 – 6.85 (m, 2H), 4.83 (d, *J* = 3.4 Hz, 1H), 2.82 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.46 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 161.60, 159.99, 140.04, 140.02, 135.79, 135.65, 132.91, 132.90, 129.94, 129.81, 128.99, 128.94, 128.11, 127.93, 115.07, 114.93, 77.16, 26.35, 16.83. Note that four aryl resonances are doubled due to $^{19}$F,$^{13}$C-coupling. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -121.97. **IR** (neat) 3068, 2956, 2868, 2119, 1505, 1428, 1221, 1158, 1107, 1008, 834, 797, 730, 696 cm$^{-1}$. **EA** Calcd. for $C_{20}H_{19}FSi$: C, 78.39; H, 6.25. Found: C, 78.43; H, 6.40. **Specific Rotation** $[\alpha]_D^{26}$ – 42.2 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OD-H column, isocratic hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 13.27 min, $t_m$ = 9.32 min) indicated *97% ee*. **Duplicate experiment** 83% yield, *97% ee*.



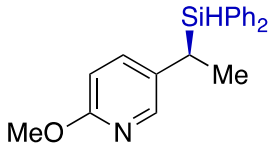

**Methyl (*S*)-4-(1-(diphenylsilyl)ethyl)-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate and methyl 4-(2-(diphenylsilyl)ethyl)-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate, 41:1 regioisomer mixture (11):** Prepared according procedure C using Methyl 1-(4-methoxybenzyl)-4-vinyl-1*H*-pyrrole-2-carboxylate (**31**, 138.8 mg, 0.512 mmol). The reaction mixture was stirred in a 40 °C oil bath for 48 h. The filtration step was omitted in this experiment. Instead, the crude product was distributed evenly over two preparative TLC plates, using small aliquots of dichloromethane to complete the transfer. The plates were jointly eluted in a solvent chamber containing 400 mL 1:9 acetone:hexanes. When elution was complete, the plates were removed and air dried. A second elution was performed after 200 mL of 1:4 acetone:hexanes were added the solvent chamber. Drying and re-elution were performed a third time after adding a second 200 mL portion of 1:4 acetone hexanes to the chamber. The plates were visualized with 254 nm light, and the intensely fluorescent blue-purple band immediately

below the black product band was stripped away from the plate with an industrial flat-edged razor blade and discarded. The silica containing the product band was similarly stripped from the plate, pulverized, and stirred in the presence of ca. 10 mL EtOAc for 1 h. The mixture was filtered, copiously rinsing the filter cake with EtOAc. The filtrate was concentrated *in vacuo* to give an extremely viscous colorless oil that crystallized as a white solid over the course of several days (163.7 mg, 70% yield, 41:1 regioisomer ratio). **$^1$H NMR** (500 MHz, $CD_2Cl_2$) *Major regioisomer*: δ 7.57 – 7.51 (m, 2H), 7.47 – 7.43 (m, 2H), 7.43 – 7.33 (m, 4H), 7.31 (t, *J* = 7.3 Hz, 2H), 6.97 – 6.88 (m, 2H), 6.82 – 6.77 (m, 2H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 5.34 (s, 2H), 4.81 (d, *J* = 3.5 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.72 (qd, *J* = 7.5, 3.5 Hz, 1H), 1.37 (d, *J* = 7.5 Hz, 3H); *Unobscured minor regioisomer signals*: 6.85 – 6.82 (m, 2H), 6.67 – 6.64 (m, = 1H), 5.39 (s, 2H, $R_2NCH_2PMP$), 4.85 (t, *J* = 3.8 Hz, 1H, Si-*H*), 3.77 (s, 3H, $OCH_3$), 3.74 (s, 3H, $OCH_3$), 2.63 – 2.56 (m, 2H, $ArCH_2CH_2SiHPh_2$), 1.49 – 1.44 (m, 2H, $ArCH_2$-$CH_2SiHPh_2$). A ratio of 41:1 for the major and minor regioisomers was determined from the integrals of the diagnostic signals at 2.72 and ca. 2.59 ppm of the major and minor regioisomers, respectively. **$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ *Major regioisomer*: 161.66, 159.33, 135.94, 135.92, 133.96, 133.82, 131.15, 130.03, 129.97, 128.54, 128.30, 128.19, 126.75, 126.38, 121.52, 117.37, 114.19, 55.62, 51.60, 51.14, 18.07, 16.87. *Visible minor regioisomer signals*: 135.49, 128.77, 128.38, 114.24, 51.55, 21.75, 13.97. **IR** (neat) 3071, 2948, 2836, 2126, 1703, 1514, 1445, 1426, 1185, 1105, 1301, 1093, 797, 723, 639 $cm^{-1}$. **EA** Calcd. for $C_{28}H_{29}NO_3Si$: C, 73.81; H, 6.42. Found: C, 73.55; H, 6.38. **m.p.** 56-58 °C. **Specific Rotation** $[\alpha]_D^{26}$ – 10.8 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OD-H column, isocratic 1:99 IPA:hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 15.23 min, $t_m$ = 14.09 min) indicated *97% ee*.[6] **Duplicate experiment** 66% yield, *97% ee*, 41:1 regioisomer ratio. The innate regioselectivity of the reaction was determined as follows: a reaction mixture containing 136.0 mg of the pyrrole substrate was prepared according to the procedure above and aged at 40 °C for 78 h. Afterward, the mixture was diluted with EtOAc and filtered through a plug of silica gel. The filtrate was concentrated to give a crude residue that was redissolved in $CD_2Cl_2$ in the presence of the internal standard 1,2-bis(trimethylsilyl)benzene (12.5 mg, 0.0562 mmol), and the resulting mixture was analyzed by $^1$H NMR. Integration of the diagnostic signals at δ = ca. 2.71 and 2.60 ppm for the major and minor regioisomers, respectively, indicated a ratio of 96.5:3.5 = ca. *28:1*. Integration of the diagnostic signal of the major diastereomer to the ArSi($CH_3$) signal of the internal standard indicated an *81%* yield of the major diastereomer. A duplicate experiment gave a regioisomer ratio of 95:5 = *19:1* and a 78% yield for the major regioisomer.

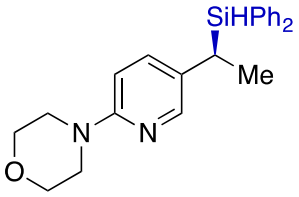



***Tert*-butyl (*S*)-3-(1-(diphenylsilyl)ethyl)-1*H*-indole-1-carboxylate (12):** Prepared according to procedure C using *tert*-butyl 3-vinyl-1*H*-indole-1-carboxylate (**32**, 122.1 mg, 0.502 mmol). The reaction mixture was heated in a 40 °C oil bath for 36 h. The

crude product was purified by flash silica chromatography (3:7 $CH_2Cl_2$:hexanes) to provide the title compound as an extremely viscous colorless oil (130.1 mg, 61% yield). **$^1$H NMR** (500 MHz, Benzene-*d6*) δ 8.52 (br. s, 1H), 7.55 – 7.47 (m, 4H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.38, (br. s, 1H) 7.28 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.13 – 7.08 (m, 4H), 7.06 (dd, *J* = 7.9, 6.4 Hz, 2H), 5.18 (d, *J* = 2.6 Hz, 1H), 2.95 (qd, *J* = 7.5, 2.5 Hz, 1H), 1.44 (d, *J* = 7.5 Hz, 3H), 1.34 (s, 9H). **$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ 150.05, 136.11, 135.**81**, 133.68, 133.38, 130.71, 130.20, 130.10, 128.31, 128.25, 124.44, 124.05, 122.27, 122.22, 119.80, 115.41, 83.59, 28.35, 16.79, 16.53. **IR** (neat) 3068, 2975, 2868, 2122, 1727, 1450 1367, 1249, 1154, 1084, 780, 731, 697 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{27}H_{29}NO_2Si + H]^+$: 428.2040. Found: 428.2031. **Specific Rotation** $[\alpha]_D^{26}$ – 23.3 (c 0.50, $CHCl_3$). The enantiomeric excess of this compound was determined as *90%* by analysis of the alcohol derivative **19**. **Duplicate Experiment** 62% yield of silane **12**, analysis of **19** indicated *90% ee.*




**(*S*)-5-(1-(diphenylsilyl)ethyl)-2-methoxypyridine (13):** Prepared according to procedure C, with the following modification: inside a nitrogen-atmosphere glovebox, $Cu(OAc)_2$ (3.6 mg, 0.020 mmol) and (*S*,*S*)-Ph-BPE (11.1 mg, 0.022 mmol) were weighed into a dry reaction tube, which was then equipped with a stir bar, sealed with a septum cap, and finally removed from the glovebox. The septum was penetrated with a nitrogen inlet needle, and diphenylsilane (0.140 mL, 556 mg, 0.75 mmol) was added via syringe followed immediately by the substrate, 2-methoxy-5-vinylpyridine (**33**, 69.9 mg, 0.517 mmol). The resulting mixture was stirred at ambient temperature for 36 h. The filtration step was omitted. Instead, the crude reaction mixture was distributed over two preparative TLC plates, which were then jointly eluted four times in a solvent chamber (once with 3:97 acetone:hexanes, 3X with 4:96 acetone:hexanes). The product bands were stripped from the plate and extracted as described in the synthesis of pyrrole **11** to provide the title compound as a colorless oil (132.8 mg, 80% yield). **$^1$H NMR** (500 MHz, Benzene-*d6*) δ 8.02 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.20 – 7.10 (m, 4H), 7.10 – 7.03 (m, 2H), 6.94 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 4.97 (d, *J* = 3.4 Hz, 1H), 3.82 (s, 3H), 2.50 (qd, *J* = 7.6, 3.4 Hz, 1H), 1.28 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.21, 145.44, 138.21, 135.76, 135.62, 132.72, 132.68, 132.53, 130.03, 129.93, 128.20, 128.07, 110.29, 53.40, 23.24, 16.77. **IR** (neat) 3068, 3010, 2945 2118, 1602, 1488, 1461, 1387, 1295, 1274, 1114, 1029, 798, 730, 696 cm$^{-1}$. **EA** Calcd. for $C_{20}H_{21}NOSi$: C, 75.19; H, 6.63. Found: C, 75.36; H, 6.74. **Specific Rotation** $[\alpha]_D^{26}$ – 18.8 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm AD-H column, isocratic 1:99 IPA:hexanes over 15 min, 1.0 mL/min flow rate, $t_M$ = 6.46 min, $t_m$ = 5.87 min) indicated *71% ee*. **Duplicate experiment** 75% yield, *69% ee*.




**(*S*)-4-(5-(1-(diphenylsilyl)ethyl)pyridin-2-yl)morpholine (14):** Prepared according to procedure C using 4-(5-vinylpyridin-2-yl)morpholine (**34**, 95.9 mg, 0.504 mmol) and an increased diphenylsilane loading (190 µL, 1.02 mmol, 2.03 equiv.). The reaction mixture was stirred at ambient temperature for 16 h. The crude product was purified by flash column chromatography (40 g silica gel, 15:85 acetone:hexanes) to provide the product as a viscous oil that became an off-white solid upon drying under high vacuum (151 mg, 80% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.33 (m, 3H), 7.38 – 7.32 (m, 2H), 7.12 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 1H), 4.84 (d, *J* = 3.4 Hz, 1H), 3.91 – 3.72 (m, 4H), 3.45 – 3.38 (m, 4H), 2.72 (qd, *J* = 7.6, 3.4 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.94, 147.01, 137.07, 135.79, 135.66, 133.00, 132.95, 129.94, 129.89, 129.84, 128.16, 128.04, 106.94, 66.96, 46.27, 23.05, 16.87. **IR** (neat) 2954, 2855, 2126, 1602, 1492, 1301, 1191, 1185, 1114, 945, 825, 801, 743, 704 $cm^{-1}$. **EA** Calcd. for $C_{23}H_{26}N_2OSi$: C, 73.75; H, 7.00. Found: C, 73.65; H, 6.94. **Specific Rotation** $[\alpha]_D^{26}$ – 15.2 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm AD-H column, isocratic 10:90 IPA:hexanes over 15 min, 0.8 mL/min flow rate, $t_M$ = 6.60 min, $t_m$ = 7.23 min) indicated *89% ee*. **Duplicate experiment** 86% yield, *88% ee*.

Highly compounded block-like white crystals of **14** suitable for X-Ray diffraction were grown by vapor diffusion of hexanes into a solution of ca. 70 mg **14** in 0.5 mL THF. The

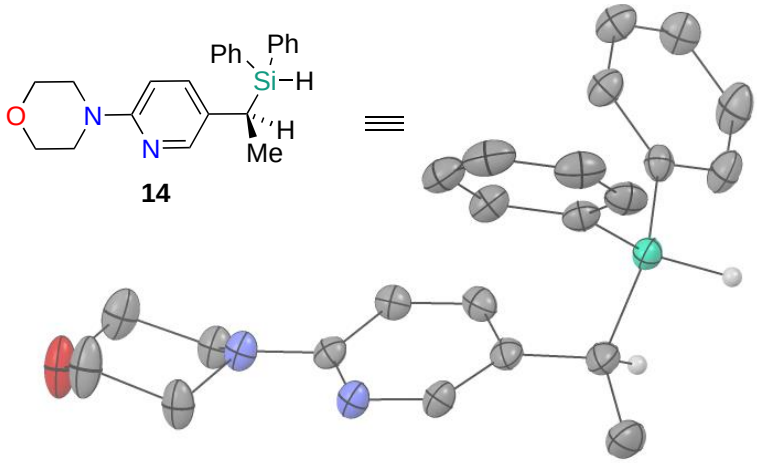
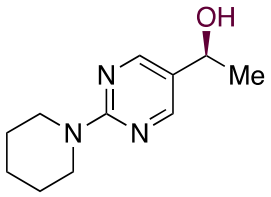


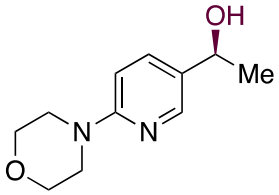

**Figure SI-3**: ORTEP diagram of **14**

crystals were submitted to diffraction analysis without further manipulation. The crystal used in the diffraction experiments was recovered, re-purified away from the mounting oil by preparative TLC on an analytical TLC plate using the chromatography eluent above, and analyzed by chiral HPLC. Its enantiomeric composition (88% ee) was

identical to that of the bulk sample. The Flack and Parsons parameter for the crystal structure indicated zero probability that the enantiomer in the asymmetric unit [which was (*S*)] was the minor enantiomer in the crystal, transitively confirming (*S*) absolute configuration for the major enantiomer produced by the reaction. A second crystal grown in this manner and submitted to X-ray analysis also resulted in an X-ray structure of the (*S*) enantiomer. The absolute configurations for all other compounds obtained by hydrosilylation with diphenylsilane were assigned by analogy to **14** (Figure SI-3). See the supplementary CIF file for crystal data.

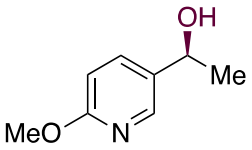



**(*S*)-1-(2-(piperidin-1-yl)pyrimidin-5-yl)ethan-1-ol (15):** Prepared according to procedure D using 2-(piperidin-1-yl)-5-vinylpyrimidine (**35**, 190.0 mg, 1.004 mmol). The reaction mixture was stirred at ambient temperature for 12 h. The crude product was purified by flash column chromatography (80 g silica gel, isocratic 1:1 EtOAc:hexanes) to provide the title compound as a pale yellow oil (178 mg, 86% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 2H), 4.77 (apparent q, *J* = 6.3 Hz, 1H), 3.85 – 3.71 (m, 4H), 1.72 (br. s, 1H), 1.70 – 1.64 (m, 2H), 1.63 – 1.56 (m, 4H), 1.49 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.72, 156.03, 125.46, 66.63, 45.11, 25.87, 25.00, 24.54. **IR** (neat) 3345, 2930, 2851, 1601, 1500, 1442, 1399, 1324, 1226, 945, 798, 657 $cm^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{11}H_{17}N_3O + H]^+$: 208.1444. Found: 208.1435. **Specific Rotation** $[\alpha]_D^{26}$ – 41.9 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm AD-H column, isocratic 10:90 IPA:hexanes over 15 min, 1.0 mL/min flow rate, $t_M$ = 9.09 min, $t_m$ = 8.20 min) indicated *98% ee*. **Duplicate experiment** 84% yield, *98% ee*.

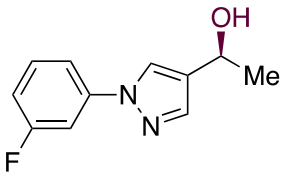



**(*S*)-1-(6-morpholinopyridin-3-yl)ethan-1-ol (16):** Prepared according to procedure D using 4-(5-vinylpyridin-2-yl)morpholine (**34**, 189.2 mg, 0.995 mmol). The reaction mixture was stirred at ambient temperature for 12 h. The crude product was purified by flash column chromatography (80 g silica gel, 3:1 EtOAc:hexanes) to provide the title compound as a faintly discolored oil that crystallized as a white solid upon storage in a -30 °C freezer (129.0 mg, 62% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 4.84 (q, *J* = 6.5 Hz, 1H), 3.88 – 3.75 (m, 4H), 3.57 – 3.42 (m, 4H), 1.81 (br. s, 1H), 1.48 (d, *J* = 6.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.47, 145.72, 135.39, 130.85, 107.02, 68.07, 66.88, 45.93, 24.82. **IR** (neat) 3366, 3309, 2968, 2854, 1604, 1498, 1407, 1239, 939, 812, 623 $cm^{-1}$. **EA** Calcd. for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74. Found: C, 63.55; H, 7.84. **m.p.** 64-66 °C. **Specific Rotation** $[\alpha]_D^{26}$ – 41.3 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OJ-H

column, isocratic 25:75 IPA:hexanes over 30 min, 0.88 mL/min flow rate, $t_M$ = 14.51 min, $t_m$ = 16.55 min) indicated *96% ee*. **Duplicate experiment** 65.0% yield, *97% ee*.

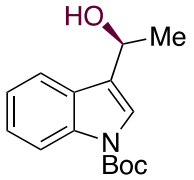



**(*S*)-1-(6-methoxypyridin-3-yl)ethan-1-ol (17):** Prepared according to procedure D with the following modification: the $Cu(OAc)_2$ (7.2 mg, 0.040 mmol) and (*S*,*S*)-Ph-BPE (22.2 mg, 0.044 mmol) were weighed into a dry reaction tube inside a nitrogen-atmosphere glovebox, and the reaction tube was equipped with a stir bar, sealed with a septum-cap, removed from the glovebox, and maintained under a nitrogen atmosphere using a nitrogen-inlet needle. The substrate, 2-methoxy-5-vinylpyridine (**33**, 134.7 mg, 0.997 mmol) was added to the mixture via syringe, immediately followed by phenylsilane (0.62 mL, 5.0 equiv.). The reaction mixture was stirred at ambient temperature for 12 h. The crude product was purified by flash column chromatography (3:7 to 2:3 gradient of EtOAc in hexanes) to provide the title compound as a semi-volatile colorless oil (122.7 mg, 80% yield). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.64 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 4.89 (qd, *J* = 6.4, 3.4 Hz, 1H), 3.93 (s, 3H), 1.76 (d, *J* = 3.6 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.94, 144.31, 136.47, 133.85, 111.02, 68.00, 53.60, 25.03. **IR** (neat) 3338, 2972, 1607, 1574, 1492, 1389, 1281, 1251, 1073, 1025, 896, 830, 761 $cm^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_8H_{11}NO_2 + H]^+$: 154.0863. Found: 154.0866. **Specific Rotation** $[\alpha]_D^{26}$ – 41.6 (c 0.50, $CHCl_3$); Literature value for (*R*) enantiomer (98.0% ee): $[\alpha]_D^{23}$ + 33.7 (c 2.7, $CHCl_3$).[7] The sign of the optical rotation indicated that the hydrosilylation with $PhSiH_3$ also occurs to give the (*S*) enantiomer of the silane. This is consistent with both reactions sharing a common stereodetermining hydrosilylation step. See also the optical rotation data for **20** and **21**. **Chiral HPLC analysis** (25 cm OJ-H column, isocratic 10:90 IPA:hexanes over 20 min, 1.0 mL/min flow rate, $t_M$ = 7.98 min, $t_m$ = 8.48 min) indicated 96% ee. **Duplicate experiment** 80% yield, *96% ee*.




**(*S*)-1-(1-(3-fluorophenyl)-1*H*-pyrazol-4-yl)ethan-1-ol (18):** Prepared according to procedure D using 1-(3-fluorophenyl)-4-vinyl-1*H*-pyrazole (**36**, 186.8 mg, 0.993 mmol) and implementing the following modification: $Cu(OAc)_2$ (7.2 mg, 0.040 mmol), (*S*,*S*)-Ph-BPE (22.2 mg, 0.044 mmol), and the vinyl heterocycle were weighed into a dry reaction tube containing a dry stir bar inside the glovebox, and MTBE (0.620 mL) was added to the tube via syringe, followed by phenylsilane (0.620 mL, 5.0 mmol). The tube was sealed, and the reaction mixture was stirred at rt until an orange brown solution containing no particulates was obtained. The mixture was removed from the glovebox at that juncture and stirred at ambient temperature for 36 h, after which it was cooled in an ice-water bath so as to prevent flash-boiling and the solvent was removed as described in

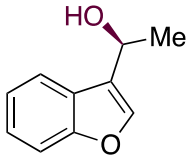
procedure D. The residue was subjected to the Tamao oxidation protocol in procedure D, and the crude product was purified by flash column chromatography (80 g silica gel, 3:7 EtOAc:hexanes [225 mL] → 4:6 EtOAc:hexanes [500 mL] → 9:11 EtOAc: hexanes [300 mL]) to provide the title compound as a colorless oil (153.5 mg, 75% yield). **$^{1}$H NMR** (500 MHz, Benzene-*d6*) δ 7.54 (s, 1H), 7.36 (dt, *J* = 10.2, 2.3 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.79 (td, *J* = 8.2, 6.2 Hz, 1H), 6.58 (td, *J* = 8.3, 2.5 Hz, 1H), 4.57 – 4.46 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 4.6 Hz, 1H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 162.57, 141.59, 141.52, 139.42, 130.89, 130.83, 129.51, 124.27, 114.26, 114.24, 113.36, 113.22, 106.88, 106.71, 62.80, 24.83. Notes that five signals are doubled due to $^{19}$F,$^{13}$C-coupling. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -111.65. **IR** (neat) 3341, 2972, 1612, 1601, 1498, 1394, 1257, 1181, 1151, 1074, 1030, 968, 862, 774, 677 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{11}H_{11}FN_2O + H]^+$: 207.0928. Found: 207.0927. **Specific Rotation** $[\alpha]_D^{26}$ – 2.1 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm AD-H column, isocratic 5:95 IPA:hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 24.55 min, $t_m$ = 22.15 min) indicated *96% ee*. **Duplicate experiment** 75% yield, *97% ee*.



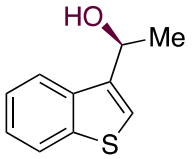

***Tert*-butyl (S)-3-(1-hydroxyethyl)-1H-indole-1-carboxylate (19):** This compound was synthesized according to procedure B implementing the modification described for the synthesis of pyrazole **18** and using *tert*-butyl 3-vinyl-1*H*-indole-1-carboxylate (**32**, 243.8 mg, 1.002) as the substrate. The crude product was purified by flash column chromatography (85 g silica gel, isocratic 1:4 EtOAc:hexanes) to provide the product as an extremely viscous colorless oil (176 mg, 67% yield). **$^{1}$H NMR** (500 MHz, $CD_2Cl_2$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 7.8, 1H), 7.54 (s, 1H), 7.32 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 5.14 (q, *J* = 6.5 Hz, 1H), 2.18 (s, 1H), 1.67 (s, 9H), 1.63 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ 150.15, 136.36, 129.12, 125.79, 124.75, 122.80, 122.25, 120.24, 115.67, 84.07, 64.15, 28.35, 23.83. **IR** (neat) 3390, 2975, 1729, 1450, 1368, 1252, 1154, 1131, 855, 744 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{15}H_{19}NO_3]^+$: 261.1359. Found: 261.1353. **Specific Rotation** $[\alpha]_D^{26}$ – 16.7 (c 0.50, $CHCl_3$). **Chiral SFC analysis** (25 cm AD-H column, 5:95 MeOH:$scCO_2$ to 40:60 MeOH:$scCO_2$ linear gradient over 6 min with 1 min hold time, 210-400 nm detection, 2.5 mL/min flow rate, 40 °C, $t_M$ = 3.47 min, $t_m$ = 3.34 min) indicated *91% ee*. **Duplicate experiment** 68% yield, *90% ee*.

**Synthesis of *tert*-butyl (S)-3-(1-hydroxyethyl)-1H-indole-1-carboxylate (19) from diphenylsilane adduct 12:** A solution of **12** (117.1, 0.274 mmol) in THF (1.6 mL) was transferred to a round-bottom flask containing KF (64.0 mg, 1.09 mmol, 4.0 equiv.) and potassium bicarbonate (110 mg, 1.09 mmol, 4.0 equiv.) and a Teflon stir bar. MeOH (1.6 mL) was used to complete the transfer. $H_2O_2$ (50% w/w in water, 0.14 mL, 2.46 mmol, 9.0 equiv.) was added dropwise to the mixture while it was stirred at ambient temperature. The stirred mixture was aged at rt for 28 h, after which the excess oxidant was quenched by addition of anhydrous sodium thiosulfate (2.0 g) and MeOH (3.0 mL)

followed by vigorous stirring until starch-iodine testing showed that all peroxides had been destroyed. The mixture was diluted with EtOAc, dried over $Na_2SO_4$, filtered and concentrated in vacuo to give a crude residue that was purified by flash column chromatography (10 g silica column, isocratic 1:4 EtOAc:hexanes) to give the title compound (57.7 mg, 81% yield). The proton NMR spectrum was identical to that obtained from material generated according to procedure D. **Chiral HPLC analysis** (25 cm OD-H column, isocratic 10:90 IPA:hexanes over 20 min, 1.0 mL/min flow rate, $t_M$ = 10.37 min, $t_m$ = 7.89 min) indicated *90% ee*. A second experiment with the duplicate lot of **12** also furnished the alcohol **19** with *90% ee*.

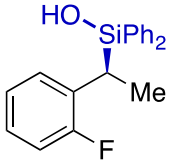



**(*S*)-1-(benzofuran-3-yl)ethan-1-ol (20):** Prepared according to the procedure D using 3-vinylbenzofuran (**37**, 144.9 mg, 1.005 mmol). The product was purified by flash chromatography (80 g silica gel, gradient of 3:17 to 1:4 EtOAc:hexanes) to provide the product as a semi-volatile pale yellow oil (126.4 mg, 78% yield). **$^1$H NMR** (500 MHz, Benzene-*d6*) δ 7.64 – 7.57 (m, 1H), 7.40 – 7.33 (m, 1H), 7.12 (s, 1H), 7.11 – 7.05 (m, 2H), 4.64 (q, *J* = 6.5 Hz, 1H), 1.30 (d, *J* = 6.5 Hz, 3H), 1.00 (br. s, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.90, 140.90, 126.24, 125.31, 124.63, 122.74, 120.61, 111.76, 63.35, 23.57. **IR** (neat) 3341, 2975, 1579, 1451, 1278, 1187, 1071, 857, 742 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{10}H_{10}O - H]^+$: 161.0597. Found: 161.0591. **Specific Rotation** $[\alpha]_D^{26}$ – 14.2 (c 0.50, $CHCl_3$); literature value for (*R*) enantiomer (> 99% ee): $[\alpha]_D^{20}$ + 18.9 (c 1.00, $CHCl_3$).[8] **Chiral SFC analysis** (25 cm OJ-H column, 5:95 MeOH:$scCO_2$ to 40:60 MeOH:$scCO_2$ linear gradient over 12 min with 2 min hold time, 210-400 nm detection, 2.5 mL/min flow rate, 40 °C, $t_M$ = 3.96 min, $t_m$ = 4.11 min) indicated *97% ee*. **Duplicate experiment** 71% yield, *98% ee*.

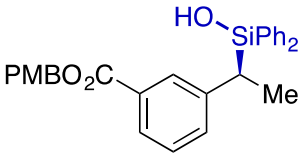



**(*S*)-1-(benzo[*b*]thiophen-3-yl)ethan-1-ol (21):** prepared according to procedure D using 3-vinylbenzo[*b*]thiophene (**38**, 161.2 mg, 1.006 mmol). The crude product was purified by flash column chromatography (80 g silica gel, 1:9 EtOAc:hexanes [100 mL] → 3:17 EtOAc:hexanes [700 mL] → 1:4 EtOAc:hexanes [200 mL]) to provide the title compound as a colorless oil (116.4 mg, 65.0% yield). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.42 – 7.33 (m, 3H), 5.29 (qd, *J* = 6.4, 4.3 Hz, 1H), 1.88 (t, *J* = 4.4 Hz, 1H), 1.68 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 141.16, 140.89, 137.43, 124.59, 124.21, 123.09, 122.46, 121.63, 65.96, 23.61. **IR** (neat) 3320, 2971, 1427, 1368, 1254, 1118, 1069, 889, 839, 759, 731 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{10}H_1OS]^+$: 178.0447. Found: 178.0452. **Specific Rotation** $[\alpha]_D^{26}$ – 23.9 (c 0.50, $CHCl_3$); literature value for (*R*) enantiomer (>

99% ee): $[\alpha]_D^{20}$ + 27.1 (c 1.00, $CHCl_3$).[8] **Chiral HPLC analysis** (25 cm OB-H column, isocratic 1:19 IPA:hexanes over 30 min, 0.95 mL/min flow rate, $t_M$ = 21.50 min, $t_m$ = 17.40 min) indicated 67% yield, *66% ee*. **Duplicate Experiment** *57% ee*. The duplicate experiment was performed after the starting material had been stored in a -8 °C refrigerator for ca. 24 h, and the purity of the starting material had degraded slightly during that time, as assessed by TLC. We believe the accumulation of low-level impurities in the starting material was responsible for the lower ee observed in the duplicate run. It would appear that this substrate is intrinsically problematic for the reproducibility of the hydrosilylation reaction.

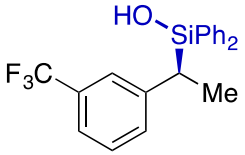



**(*S*)-(1-(2-fluorophenyl)ethyl)diphenylsilanol (22):** Prepared according to procedure E using (*S*)-(1-(2-fluorophenyl)ethyl)diphenylsilane (**3**, 62.7 mg, 0.205 mmol) and a reaction time of 25 h. The crude product was purified by preparative TLC (1:9 EtOAc:hexanes eluent) to provide the title compound as an extremely viscous oil (51.1 mg, 77% yield). **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.64 – 7.59 (m, 2H), 7.51 – 7.44 (m, 3H), 7.43 – 7.36 (m, 3H), 7.34 – 7.29 (m, 2H), 7.13 – 7.06 (m, 2H), 7.05 – 7.00 (m, 1H), 6.97 – 6. 90 (m, 1H), 3.20 (q, *J* = 7.6 Hz, 1H), 2.54 (s, 1H), 1.45 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ 161.47, 159.87, 135.32, 134.98, 134.80, 134.74, 131.51, 131.41, 130.40, 130.36, 129.60, 129.57, 128.24, 128.12, 126.70, 126.65, 124.46, 124.44, 115.34, 115.19, 21.29, 21.29, 15.12. Note that as in the $^{13}$C spectrum of the parent compound **M**, seven signals are doubled due to $^{19}$F,$^{13}$C-coupling. **IR** (neat) 3618, 3417, 3070, 2961, 2872, 1488, 1451, 1428, 1226, 1116, 997, 819, 735, 698 $cm^{-1}$. **EA** Calcd. for $C_{20}H_{19}FOSi$: C, 74.50; H, 5.94. Found: C, 74.39; H, 5.90. **Specific Rotation** $[\alpha]_D^{23}$ – 42.4 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OJ-H column, isocratic 5:95 IPA:hexanes over 30 min, 1.0 mL/min flow rate, $t_M$ = 17.10 min, $t_m$ = 14.62 min) indicated *97% ee*. A second experiment performed using the duplicate lot of **3** also gave silanol **23** with *97% ee*.

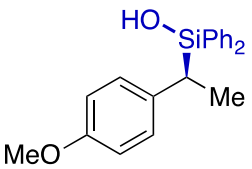



**4-methoxybenzyl (*S*)-3-(1-(hydroxydiphenylsilyl)ethyl)benzoate (23):** Prepared according to procedure E using 4-methoxybenzyl (*S*)-3-(1-(diphenylsilyl)ethyl)benzoate (**4**, 91.0 mg, 0.20 mmol) and a reaction time of 12 h. The crude product was purified by preparative TLC (1:4 EtOAc:hexanes eluent) to provide the title compound as a colorless glass upon evaporation as a thin film from $Et_2O$ (73.1 mg, 78% yield). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.79 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.46 – 7.43 (m, 2H), 7.43 – 7.41 (m, 1H), 7.40 – 7.32 (m, 5H), 7.31 – 7.27 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.18 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.98 – 6.87 (m, 2H), 5.34 – 5.09

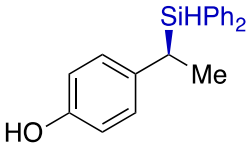
(m, 2H), 3.83 (s, 3H), 2.90 (q, *J* = 7.5 Hz, 1H), 2.83 (br. s, 1H), 1.48 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 166.94, 159.68, 144.24, 134.78, 134.75, 134.48, 134.20, 132.74, 130.11, 130.09, 130.08, 130.04, 129.21, 128.38, 128.17, 127.93, 127.84, 126.48, 114.04, 66.52, 55.41, 29.28, 15.44. **IR** (neat) 3455, 3069, 2956, 2871, 1713, 1695, 1612, 1514, 1428, 1279, 1245, 1173, 1109, 1087, 1033, 822, 739, 694 $cm^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{29}H_{28}O_4Si + NH4]^+$: 486.2095. Found: 486.2092. **Specific Rotation** $[\alpha]_D^{24}$ – 30.1 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OD-H column, isocratic 10:90 IPA:hexanes over 20 min, 1.0 mL/min flow rate, $t_M$ = 11.36 min, $t_m$ = 9.53 min) indicated *93% ee*. A second experiment conducted using the duplicate lot of **4** gave silanol **24** with *92% ee*.




**(*S*)-diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silanol (24):** Prepared according to procedure E using (*S*)-diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silane (**5**, 89.0 mg, 0.25 mmol) with the following modifications: the EtOAc was omitted in this example. Instead 0.40 mL *tert*-butanol was used. The quantities of reagents were 2,2,2-trifluoroacetophenone (4.0 µL, 0.27 mmol, 1.1 equiv.), MeCN (0.040 mL, 0.77 mmol, 3.1 equiv.), and 0.030 mL $H_2O_2$ (0.51 mmol, 2.0 equiv.). The reaction mixture was stirred at rt for 12 h. The crude product was purified by preparative TLC using 1:9 EtOAc:hexanes eluent to give the title compound as an extremely viscous oil (75.8 mg, 81% yield). **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.61 – 7.56 (m, 2H), 7.50 – 7.39 (m, 6H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 2.93 (q, *J* = 7.5 Hz, 1H), 2.49 (s, 1H), 1.49 (d, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ 145.37, 135.03, 134.99, 134.61, 134.41, 131.84, 131.84, 131.83, 131.82 130.74, 130.57, 130.54, 130.32, 130.11, 128.85, 128.35, 128.24, 127.56, 125.76, 125.13, 125.11, 125.08, 125.05, 123.96, 122.15, 122.06, 122.03, 122.00, 121.98, 29.77, 15.36. The coupling patterns observed here are essentially the same as those in the NMR spectrum for the parent silane **5**; i.e., there are quartets arising from $^{19}$F-coupling at 131.83 ($^4J$ = 1.2 Hz), 130.43 ($^2J$ = 31.7 Hz), 125.09 ($^3J$ = 3.8 Hz), 124.86 ($^1J$ = 272.2 Hz), 122.01 ppm ($^3$J = 3.9 Hz). One inner line of the quartet signal of aryl C3 is obscured by a larger peak at 130.54 ppm. **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -64.96. **IR** (neat) 3385, 3070, 2959, 2872, 1428, 1328, 1161, 1117, 1075, 854, 800, 739, 698 $cm^{-1}$. **EA** Calcd. for $C_{21}H_{19}F_3OSi$: C, 67.72; H, 5.14. Found: C, 67.56; H, 5.15. **Specific Rotation** $[\alpha]_D^{23}$ – 35.2 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OD-H column, isocratic 5:95 IPA:hexanes over 15 min, 1.0 mL/min flow rate, $t_M$ = 7.49 min, $t_m$ = 6.34 min) indicated *87% ee*. A second experiment performed using the duplicate lot of **5** gave silanol **25** having *88% ee*.

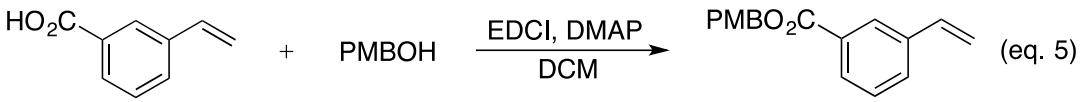


**(*S*)-(1-(4-methoxyphenyl)ethyl)diphenylsilanol (25):** Prepared according to procedure E using (*S*)-(1-(4-methoxyphenyl)ethyl)diphenylsilane (**8**, 65.2 mg, 0.205) and a reaction time of 18 h. The crude product was purified by preparative TLC (1:9 EtOAc:hexanes eluent) to provide the title compound as a colorless glass (45.7 mg, 67% yield). **$^1$H NMR** (500 MHz, $CD_2Cl_2$) δ 7.62 – 7.55 (m, 2H), 7.51 – 7.43 (m, 3H), 7.43 – 7.37 (m, 3H), 7.36 – 7.30 (m, 2H), 7.00 – 6.92 (m, 2H), 6.78 – 6.71 (m, 2H), 3.74 (s, 3H), 2.79 (q, *J* = 7.6 Hz, 1H), 2.46 (s, 1H), 1.42 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CD_2Cl_2$) δ 157.61, 135.83, 135.48, 135.20, 134.98, 134.97, 130.20, 129.11, 128.13, 128.08, 128.06, 113.92, 55.48, 28.13, 16.00. **IR** (neat) 3417, 2954, 2868, 2834, 1608, 1508, 1427, 1242, 1178, 1114, 1035, 997, 828, 738, 698 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{21}H_{22}O_2Si + NH4]^+$: 352.1727. Found: 352.1740. **Specific Rotation** $[\alpha]_D^{24}$ – 25.5 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OD-H column, isocratic 5:95 IPA:hexanes over 20 min, 1.0 mL/min flow rate, $t_M$ = 9.79 min, $t_m$ = 8.52 min) indicated *96% ee*. A second experiment preformed using the duplicate lot of **8** provided silanol **26** with *95% ee*.



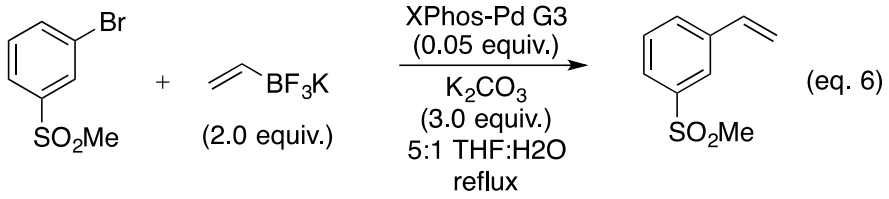

**(*S*)-4-(1-(diphenylsilyl)ethyl)phenol (26):** Prepared according to procedure E using (*S*)-4-(1-(diphenylsilyl)ethyl)phenyl acetate (**9**, 70.3 mg, 0.203 mmol) and a reaction time of 27 h. Saponification of the acetate ester occurred concomitantly with oxidation under these conditions. The crude product was purified by preparative TLC (1:3 EtOAc:hexanes eluent) to provide the title compound as a colorless glass (45.7 mg, 74% yield). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.48 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.35 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 2H), 6.90 – 6.83 (m, 2H), 6.66 – 6.59 (m, 2H), 4.85 (s, 1H), 2.77 (q, *J* = 7.6 Hz, 1H), 2.35 (s, 1H), 1.42 (d, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 153.12, 135.60, 134.87, 134.85, 134.52, 130.07, 130.03, 129.03, 127.91, 127.87, 115.31, 28.07, 15.78. Note that two signals overlap. **IR** (neat) 3308, 3069, 2958, 2869, 1610, 1589, 1509, 1427, 1261, 1223, 1191, 1110, 997, 830, 748, 727, 698 cm$^{-1}$. **HRMS** (m/z, DART-TOF, +'ve) Calcd. For $[C_{20}H_{20}O_2Si + NH_4]^+$: 338.1571. Found: 338.1575. **Specific Rotation** $[\alpha]_D^{24}$ – 29.3 (c 0.50, $CHCl_3$). **Chiral HPLC analysis** (25 cm OJ-H column, isocratic 15:85 IPA:hexanes over 40 min, 1.0 mL/min flow rate, $t_M$ = 25.76 min, $t_m$ = 21.86 min) indicated *97% ee*. A second experiment using the duplicate lot of **9** gave silanol **27** with *95% ee*.

### 2.5. Synthesis and Characterization of Hydrosilylation Substrates




**4-methoxybenzyl 3-vinylbenzoate (27):** Solid *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDCI, 3.30, 17.2 mmol, 1.50 equiv.) was added

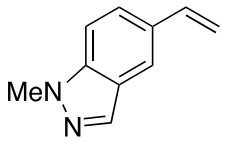
portionwise to a stirred rt solution of 3-vinylbenzoic acid (1.70 g, 11.5 mmol) and 4-methoxybenzyl alcohol (1.80 mL, 14.4 mmol, 1.26 equiv.) in anhydrous $CH_2Cl_2$ (58 mL). *N*,*N*-dimethylpyridin-4-amine (4.21 g, 34.4 mmol, 3.00 equiv.) was added to the resulting solution, and it was stirred at ambient temperature for 15 h under an argon atmosphere. The mixture was then partitioned between $CH_2Cl_2$ and 1 M aqueous HCl (ca. 100 mL). The organic layer was sequentially washed with 1 M HCl (2X), water, saturated $NaHCO_3$, and brine. The organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a crude residue that was further purified by flash chromatography (125 g silica, 1:19 to 1:9 gradient of EtOAc in hexanes). The fractions containing the pure product were combined in the presence of the radical inhibitor 4-*tert*-butylcatechol (TBC, 9.1 mg, 0.055 mmol) and concentrated to give the title compound as a clear viscous oil that weighed (2.106 g, 68% yield corrected for 0.70 mol% TBC present). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.7 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.59 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.44 – 7.36 (m, 3H), 6.97 – 6.89 (m, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.37 – 5.29 (m, 3H), 3.82 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 166.54, 159.81, 137.97, 136.05, 130.73, 130.59, 130.23, 129.03, 128.67, 128.27, 127.61, 115.24, 114.12, 66.75, 55.41. **IR** (neat) 3004, 2956, 2836, 1714, 1612, 1514, 1441, 1276, 1190, 1174, 1105, 1083, 1033, 911, 817, 761, 706 cm$^{-1}$. **EA** Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.85; H, 5.96.



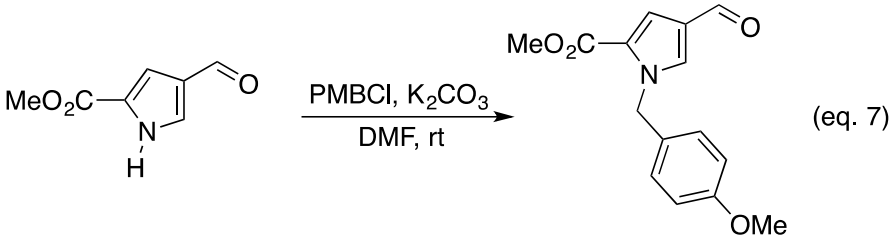
(eq. 6)

**1-(methylsulfonyl)-3-vinylbenzene (28). Representative procedure[9] for the synthesis of vinylarene and vinyl heterocycles by Suzuki coupling:** A mixture of 1-bromo-3-(methylsulfonyl)benzene (2.50 g, 10.63 mmol), potassium vinyltrifluoroborate (2.88 g, 21.50 mol, 2.0 equiv.) and potassium carbonate (4.41 g, 31.9 mmol, 3.0 equiv.) in 5:1 THF:water (36 mL) was vigorously sparged with argon for 30 min. XPhos-Pd G3 precatalyst (455 mg, 0.538 mmol, 5.1 mol%) was added, and the reaction mixture was heated at reflux under an argon atmosphere for 12 h in an oil bath. Upon cooling the rt, the mixture was diluted with EtOAc, and the resulting mixture was dried with a copious amount of $MgSO_4$ and filtered through a pad of celite. The filtrate was concentrated, redissolved in $CH_2Cl_2$, stirred in the presence of Quadrapure® TU polystyrene beads, and then filtered and concentrated again to give a crude residue that was purified by flash silica chromatography (15 to 30% gradient of EtOAc in hexanes). The fractions containing the pure product were combined and concentrated *in vacuo* in the presence of TBC (8.2 mg, 0.049 mmol) to give a viscous oil that crystallized as a beige solid upon standing in a -30 °C freezer overnight (1.45 g, 74% yield corrected for 0.62 mol% TBC present). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94 (apparent t, *J* = 1.9 Hz, 1H), 7.80 (ddd, *J* = 7.8, 1.9, 1.1 Hz, 1H), 7.65 (apparent dt, *J* = 7.7, 1.4 Hz, 1H), 7.51 (apparent t, *J* = 7.8 Hz, 1H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.9 Hz, 1H), 3.05 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 141.07, 139.12, 135.07, 131.29, 129.69, 126.35, 124.90, 116.87, 44.55. **IR** (neat) 3064, 3014, 2919, 1475, 1413, 1317,

1293, 1211, 1138, 1088, 1000, 963, 917, 855, 810, 758, 711, 656 $cm^{-1}$. **EA** Calcd. for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.55; H, 5.57. **m.p.** 51-53 °C.



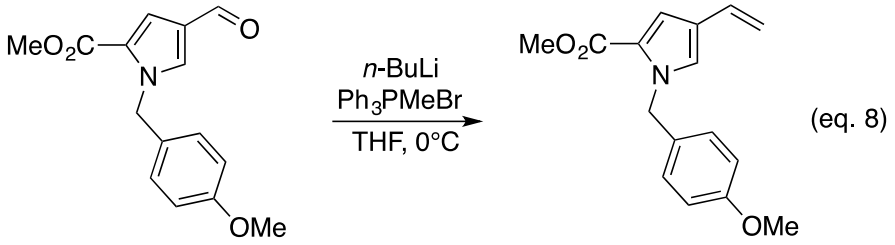

**1-methyl-5-vinyl-1*H*-indazole (29):** This compound was prepared according to the general procedure described for the preparation of sulfone **28**, using 5-bromo-1-methyl-1H-indazole (2.5 g, 11.84 mmol), XPhos-Pd G3 precatalyst (447 mg, 0.528 mmol, 4.5 mol%), potassium vinyltrifluoroborate (3.17 g, 23.69 mmol, 2.00 equiv.), potassium carbonate (4.91 g, 35.5 mmol, 3.00 equiv.), and 5:1 THF:$H_2O$ (48 mL). The reaction mixture was heated at reflux for 28 h and allowed to cool to rt. A $CH_2Cl_2$ solution of the crude product was stirred in the presence of 2.00 g Quadrapure® IMDAZ metal-scavenger beads, filtered, and concentrated in the presence of TBC (6.67 mg, 0.040 mmol) to give a crude residue that was partially purified by flash column chromatography (20 to 30% gradient of EtOAc in hexanes). The fractions containing the pure product were concentrated in the presence of TBC (7.1 mg, 0.043 mmol) to give a solid residue that was triturated with 1.5 mL pentane, filtered, and rinsed with two small aliquots of pentane that had been cooled to -78 °C in a dry ice/acetone slurry. The filter cake was dried under high vacuum to give the title compound as a very pale yellow solid (631 mg, 34% yield; by $^1$H NMR, the solids appeared to retain TBC at the level of ca. 0.2 mol%). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.0 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.54 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.22 (dd, *J* = 10.9, 0.7 Hz, 1H), 4.06 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 139.79, 137.07, 133.18, 130.63, 124.44, 124.39, 119.37, 112.39, 109.14, 35.70. **IR** (neat) 3086, 3000, 1626, 1616, 1500, 1352, 1308, 1224, 1148, 986, 906, 890, 817, 756, 663 $cm^{-1}$. **EA** Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37. Found: C, 75.82; H, 6.34.




(eq. 7)

**Methyl 4-formyl-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate (30):** *Para*-methoxybenzyl chloride (2.10 mL, 15.5 mmol, 1.16 equiv.) was added dropwise to a mixture of methyl 4-formyl-1H-pyrrole-2-carboxylate (2.04 g, 13.32 mmol) and potassium carbonate (3.61 g, 26.1 mmol, 1.96 equiv.) in anhydrous DMF (24 mL) that was being stirred at ambient temperature under an atmosphere of argon. After 48 h, the reaction mixture was partitioned between $Et_2O$ and water, and the $Et_2O$ layer was extracted with three additional portions of water to remove DMF. The organics were then washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a crude residue that was further purified by silica gel chromatography (1:4 to 2:3 gradient of

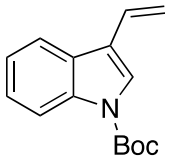
EtOAc in hexanes) to yield the product as a viscous oil that was dried under high vacuum overnight and gradually crystallized as a yellow-orange solid (3.40 g, 93% yield) upon storage in a -30 °C freezer. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 1.9 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.89 – 6.82 (m, 2H), 5.48 (s, 2H), 3.80 (s, 3H), 3.76 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 185.19, 161.12, 159.56, 132.88, 129.24, 128.21, 124.98, 124.26, 117.90, 114.34, 55.30, 52.49, 51.61. **IR** (neat) 3113, 2945, 2838, 2793, 1714, 1668, 1544, 1510, 1444, 1269, 1243, 1176, 1122, 1097, 1028, 811, 768, 754, 726, 667 $cm^{-1}$. **EA** Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53. Found: C, 66.04; H, 5.43. **m.p.** 62-64 °C.



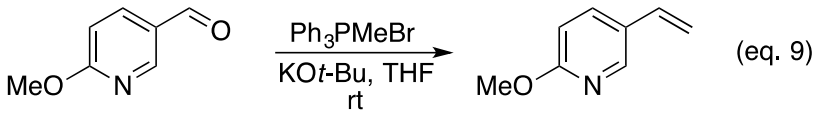
(eq. 8)

**Methyl 1-(4-methoxybenzyl)-4-vinyl-1*H*-pyrrole-2-carboxylate (31). Representative procedure for synthesis of vinyl heterocycles by Wittig methylenation:** Methyltriphenylphosphonium bromide (5.23 g, 14.6 mmol, 2.00 equiv.) was suspended in anhydrous, degassed THF (25 mL) under an argon atmosphere in an oven-dried flask containing a dry stir bar. The resulting mixture was stirred under an argon atmosphere in an ice-water bath for ca. 30 min, and then *n*-butyllithium (4.40 mL, nominally 2.5 M solution in hexanes) was added to it dropwise over the course of five min via syringe, causing the appearance of a dark red-orange color. The mixture was stirred for five more minutes in the ice bath and then allowed to gradually warm at rt over 20 min, during which time the mixture became a much lighter and more nearly pure orange in color. Stirring was terminated and reaction solids were allowed to settle to the bottom of the flask. A 24 mL portion of the resulting orange supernatant was withdrawn with a large syringe and gradually transferred to an ice-cooled solution of methyl 4-formyl-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate (**30**, 2.00 g, 7.32 mmol) in anhydrous, degassed THF (20 mL) that was being stirred under an argon atmosphere in a dry flask. Consumption of the ylide was evident from disappearance of the orange color. After 20 mL of the ylide solution had been added, a persistent light orange color developed in the reaction mixture, and the addition was terminated. The reaction mixture was allowed to warm to rt over the course of 15 min and was subsequently quenched by addition of saturated aqueous $NH_4Cl$ (30 mL). The crude product was extracted into EtOAc, and the organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in the presence of TBC (7.1 mg, 0.043 mmol; note: *the product of this reaction polymerizes very rapidly in the absence of a free-radical inhibitor*) to yield a crude residue that was further purified by silica gel chromatography (5 to 20% gradient of EtOAc in hexanes). The fractions containing the pure product were combined in the presence of TBC (10.5 mg, 0.063 mmol) and concentrated in vacuo to give the product as a viscous pale-beige oil that crystallized as a white solid upon drying under high vacuum (1.632 g, 82% yield corrected for 1.0 mol% TBC present). Once stabilized, this compound could be stored

for extended periods in a -30°C freezer in a nitrogen glovebox without apparent degradation. **$^1$H NMR** (600 MHz, Acetone-*d6*) δ 7.22 (d, *J* = 2.0 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.54 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.49 (s, 2H), 5.47 (dd, *J* = 17.6, 1.6 Hz, 1H), 4.95 (dd, *J* = 10.9, 1.6 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H). **$^{13}$C NMR** (151 MHz, Acetone-*d6*) δ 162.07, 160.28, 131.63, 130.39, 129.63, 128.63, 123.77, 123.20, 115.69, 114.86, 111.05, 55.66, 51.92, 51.44. **IR** (neat) 3111, 2954, 2837, 1698, 1511, 1449, 1367, 1268, 1222, 1176, 1099, 1040, 995, 896, 823, 805, 759 cm$^{-1}$. **EA** Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 71.03; H, 6.26. **m.p.** 66-68 °C.



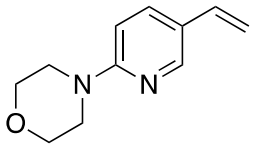

***Tert*-butyl 3-vinyl-1*H*-indole-1-carboxylate (32):** Prepared according to the general procedure described for the synthesis or pyrrole **31**. The phosphonium slurry was prepared from methyltriphenylphosphonium bromide (5.83 g, 16.3 mmol, 1.60 equiv.) and THF (20 mL) and treated with *n*-butyllithium (9.6 mL, nominally 1.6 M in hexanes, 15.4 mmol, 1.51 equiv.) to furnish the ylide mixture, which was aged at rt for 30 min. A portion of the orange supernatant (26 mL) was transferred to an ice-cooled solution of *tert*-butyl 3-formyl-1H-indole-1-carboxylate (2.50 g, 10.2 mmol) in 20 mL THF. After being stirred for 2 h in an ice-water bath, the reaction mixture was quenched and allowed to warm to rt. The crude residue was purified by flash column chromatography (125 g silica, 5% EtOAc in hexanes; the crude product was loaded onto the column as a slurry in minimal toluene), and the fractions containing the pure product were combined in the presence of TBC (10.2 mg, 0.061 mmol) to provide the title compound as a viscous pale-yellow oil (1.92 g, 77% yield corrected for TBC present at 0.77 mol%). **$^1$H NMR** (400 MHz, Acetone-*d6*) δ 8.19 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.88 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 1H), 7.77 (s, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.30 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 6.90 (ddd, *J* = 17.9, 11.4, 0.7 Hz, 1H), 5.87 (ddd, *J* = 17.9, 1.3, 0.5 Hz, 1H), 5.31 (dd, *J* = 11.4, 1.3 Hz, 1H), 1.68 (s, 9H). The $^1$H NMR spectrum was consistent with literature data for this compound.[10]



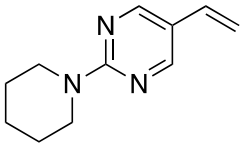
(eq. 9)

**2-methoxy-5-vinylpyridine (33). Alternative procedure for synthesis of vinyl heterocycles by Wittig methylenation:** Potassium *tert*-butoxide (3.41 g, 30.4 mmol, 1.52 equiv.) was added portionwise to a mixture of 6-methoxynicotinaldehyde (2.75 g, 20.0 mmol) and methyltriphenylphosphonium bromide (14.0 g, 39.2 mmol, 1.95 equiv.) in dry THF (54 mL) that was being stirred at ambient temperature in a dry flask under argon, giving a dark orange reaction mixture (**caution**: *this step results in a significant exotherm*). After 4.5 h, saturated $NH_4Cl$ (30 mL) was added to the flask, and the mixture was partitioned between saturated $NH_4Cl$ and $Et_2O$. The organics were washed with

brine, dried over $MgSO_4$, filtered, and carefully concentrated in the presence of TBC (6.2 mg, 0.037 mmol) to give a crude residue that was purified by flash column chromatography (200 g silica, 1:39 to 1:9% gradient of $Et_2O$ in pentane). The fractions containing the pure product were combined and concentrated on a rotary evaporator in the presence of TBC (6.0 mg, 0.036 mmol) to give the product as clear oil, volatile oil (1.507 g, 55% yield corrected for 0.32 mol% TBC present). **$^1$H NMR** (500 MHz, Benzene-*d6*) δ 8.13 (d, *J* = 2.3 Hz, 1H), 7.20 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.56 (d, *J* = 8.6 Hz, 1H), 6.34 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.36 (d, *J* = 17.6 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 3.81 (s, 3H). The $^1$H NMR spectrum was consistent with literature data reported for this compound.[11]

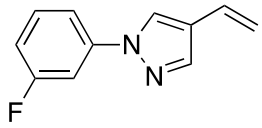



**4-(5-vinylpyridin-2-yl)morpholine (34):** Prepared according to the general procedure described for the synthesis of sulfone **28**, using 4-(5-bromopyridin-2-yl)morpholine (3.67 g, 15.10 mmol), potassium vinyltrifluoroborate (4.04 g, 30.2 mmol, 2.00 equiv.), potassium carbonate (6.24 g, 45.2 mmol, 2.99 equiv.), XPhos-Pd G2 precatalyst (597 mg, 0.759 mmol, 0.50 mol%) and 5:1 THF:$H_2O$ (27 mL). The reaction mixture was heated at reflux for 14.5 h and then allowed to cool to rt. Treatment of the crude product with a metal scavenger was omitted in this procedure. The crude product was purified by flash silica chromatography (10 to 20% gradient of EtOAc in hexanes) to give the product as a pale-yellow powder (1.04 g, 36%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.4 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.72 – 6.53 (m, 2H), 5.58 (d, *J* = 17.7 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 3.94 – 3.67 (m, 4H), 3.63 – 3.40 (m, 4H). The $^1$H NMR spectrum was consistent with literature data for the desired product.[12] This compound was stabilized with 0.4 mol% TBC prior to use in hydrosilylation experiments.

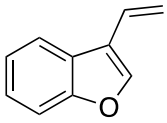



**2-(piperidin-1-yl)-5-vinylpyrimidine (35):** This compound was prepared according to the general procedure described for the synthesis of sulfone **28**, using 5-bromo-2-(piperidin-1-yl)pyrimidine (2.50 g, 10.33 mmol), potassium vinyltrifluoroborate (2.84 g, 21.20 mmol, 2.05 equiv.), potassium carbonate (4.30 g, 31.1 mmol, 3.01 equiv.), XPhos-Pd G2 precatalyst (423 mg, 0.537 mmol, 5.2 mol%), and 5:1 THF:$H_2O$ (36 mL). The reaction mixture was heated at reflux for 16 h and then allowed to cool to rt. Treatment of the crude product with metal-scavenging beads was omitted in this experiment. Instead, upon completion of the reaction, the mixture was filtered through celite, and the filtrate was washed with 100 mL aqueous $Na_2EDTA•(H_2O)_2$ (0.2 g/L) followed by brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give a residue that was further purified by flash column chromatography (5% EtOAc in hexanes) to give the compound as a yellow oil (1.26 g, 65% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s,

2H), 6.48 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.57 (dd, *J* = 17.7, 0.8 Hz, 1H), 5.10 (dd, *J* = 11.1, 0.8 Hz, 1H), 3.82 – 3.77 (m, 4H), 1.72 – 1.64 (m, 2H), 1.64 – 1.52 (m, 4H). The $^1$H NMR spectrum is consistent with literature data for the desired product.[9] This compound was stabilized with ca. 0.7 mol% TBC prior to use in hydrosilylation experiments.

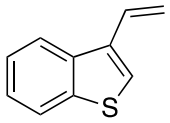



**1-(3-fluorophenyl)-4-vinyl-1*H*-pyrazole (36):** This compound was prepared according to the general procedure described for the synthesis of pyrrole **31**. The phosphonium slurry was prepared from methyltriphenylphosphonium bromide (7.90 g, 22.1 mmol, 2.19 equiv.) and THF (25 mL) and treated with *n*-butyllithium (12.0 mL, nominally 1.6 M in hexanes, 19.2 mmol, 1.90 equiv.) to furnish the ylide mixture, which was aged at 0 °C and warmed to rt for 10 min prior to use. A portion of the orange supernatant (24 mL) was transferred to an ice-cooled solution of 1-(3-fluorophenyl)-1H-pyrazole-4-carbaldehyde (1.924 g, 10.11 mmol) in THF (20 mL). The reaction mixture was quenched after being stirred for 3.5 h in an ice-water bath and then allowed to warm to rt. The crude residue was purified by flash column chromatography (100 g silica, 15% EtOAc in hexanes; the crude product was loaded onto the column as a slurry in minimal toluene), and the fractions containing the pure product were combined in the presence of TBC (4.2 mg, 0.025 mmol) to provide the title compound as a viscous pale beige oil (1.46 g, 77% yield corrected for 0.32 mol% TBC present) that froze as a white solid upon storage in a -8 °C refrigerator. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.81 (s, 1H), 7.49 – 7.35 (m, 3H), 6.98 (tdd, *J* = 8.2, 2.4, 1.3 Hz, 1H), 6.59 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.58 (dd, *J* = 17.7, 1.1 Hz, 1H), 5.19 (dd, *J* = 11.0, 1.1 Hz, 1H). The $^1$H NMR spectrum was consistent with literature data.[13] *Caution*: this compound has an unusually persistent, sickening odor and should not be manipulated outside a well-ventilated fumehood or inert-atmosphere glovebox.




**3-vinylbenzofuran (37):** *N*-butyllithium (7.00 ml, nominally 1.6 M in hexanes, 11.2 mmol, 1.52 equiv.) was added dropwise to a stirred, ice-cooled slurry of methyltriphenylphosphonium bromide (5.27 g, 14.74 mmol, 2.00 equiv.) in dry THF (32 mL) under an atmosphere or argon. The resulting red-orange mixture was allowed to warm to ambient temperature over ca. 15 min and was then re-cooled in the ice-water bath. To the resulting orange ylide-containing mixture was added a solution of benzofuran-3-carbaldehyde[14] (1.077 g, 7.37 mmol) in dry THF (6 mL) over the course of ten min. The mixture was gradually warmed to rt over the course of an hour, quenched with saturated $NH_4Cl$, and partitioned between $Et_2O$ and saturated $NH_4Cl$. The organics were washed with brine, dried over $MgSO_4$, filtered and carefully concentrated in vacuo in the presence of TBC (12.7 mg, 0.076 mmol). The resulting residue was suspended in hexanes and filtered to remove some triphenylphosphine. The filtrate was concentrated a second time to give a crude residue that was further purified by flash column

chromatography (100 g silica, isocratic pentane; crude loaded onto column as a slurry in hexanes). The fractions containing the pure product were combined and concentrated on a rotary evaporator in the presence of TBC (4.2 mg, 0.025 mmol) to give the title compound as a colorless, volatile oil (610.4 mg, 57% yield corrected for 0.59 mol% TBC present). **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.95 – 7.84 (m, 1H), 7.60 – 7.48 (m, 1H), 7.46 – 7.30 (m, 2H), 6.86 (ddd, *J* = 17.8, 11.3, 0.6 Hz, 1H), 5.90 (ddd, *J* = 17.8, 1.2, 0.6 Hz, 1H), 5.42 (dd, *J* = 11.3, 1.2 Hz, 1H), 5.39 – 5.32 (m, 1H). The $^1$H NMR spectrum was consistent with literature data reported for this compound.[15]




**3-vinylbenzo[*b*]thiophene (38):** This compound was prepared according to the general procedure described for the synthesis of methoxypyridine substrate **33**, using benzo[b]thiophene-3-carbaldehyde (2.00 g, 12.33 mmol), methyltriphenylphosphonium bromide (8.81 g, 24.66 mmol, 2.00 equiv.) and potassium tert-butoxide (2.00 g, 17.8 mmol, 1.45 equiv.). The mixture was quenched after being stirred at ambient temperature for 2 h. The crude residue was purified by flash column chromatography (110 g silica, isocratic pentane). The fractions containing the pure product were combined and concentrated on a rotary evaporator in the presence of TBC (9.0 mg, 0.054 mmol) to provide the title compound as a colorless, volatile oil (1.05 g, 53% yield corrected for 0.82 mol% TBC present). This compound rapidly decomposed with concomitant formation of unidentified polar impurities even when stored at low temperature. **$^1$H NMR** (400 MHz, Acetone-*d6*) δ 8.15 – 7.91 (m, 2H), 7.77 (s, 1H), 7.48 – 7.34 (m, 2H), 7.08 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.89 (dt, *J* = 17.6, 1.4 Hz, 1H), 5.38 (dt, *J* = 11.2, 1.3 Hz, 1H). The $^1$H NMR spectrum was consistent with literature data for this compound.[16]

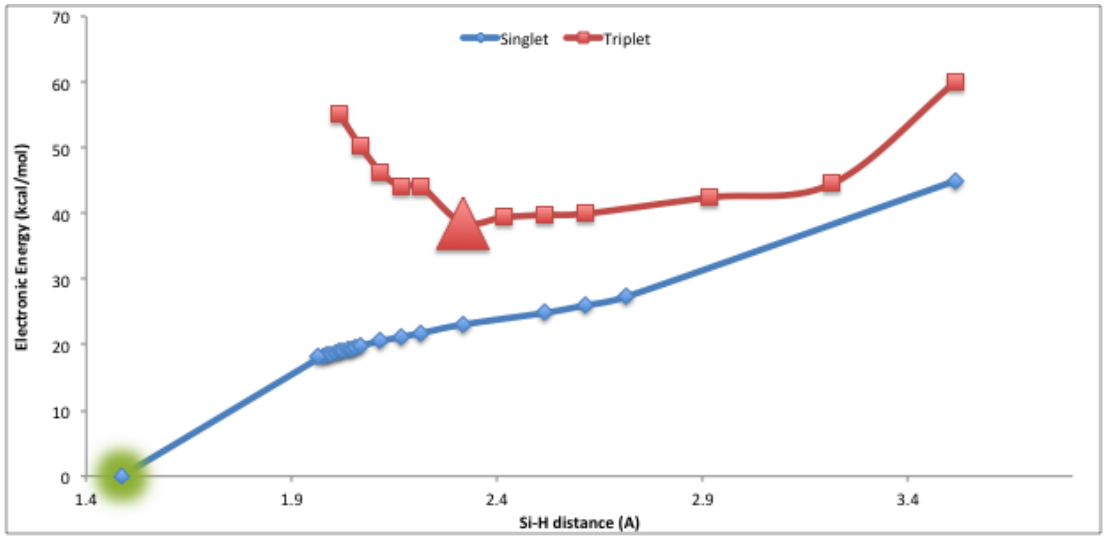
## 3. Computational Details

All reported calculations were performed using the ORCA software[17] or GAUSSIAN 03.[18] Images of the 3D structures were rendered using CYLView.[19] The geometry of all reactants and transition states were optimized using the B3LYP[20,21] functional in the gas phase. In these geometry optimizations, a mixed basis set of SDD for Cu and 6-31G(d) for all other atoms was used. Ground and transition state geometries were validated by vibrational analysis at the same level, showing zero and one imaginary frequencies respectively. Single point energies were calculated using the M06[22] or PBE0[23] functional on a mixed basis set of SDD for Cu and 6-311+G(d,p) for all other atoms. In these energy calculations, the SMD solvation model[24] with THF as solvent was applied. The reported Gibbs free energies and enthalpies include zero-point and thermal corrections calculated at 298 K using B3LYP/SDD-6-31G(d).

*Investigation of Carbon–Silicon Bond Formation*

As a model system, the hydrosilylation reaction of styrene with phenylsilane was modeled using DCyPE (1,2-bis(dicyclohexylphosphino)ethane) as the supporting ligand

on copper. This ligand is known to be competent experimentally, although less efficient than Ph-BPE, but was selected as an achiral bis(trialkylphosphine) analogue of Ph-BPE to simplify calculation and interpretation. Two possible types of pathways for formation of the carbon–silicon bond from (DCyPE)Cu-CH($CH_3$)$C_6H_5$ were studied. A direct sigma-bond metathesis transition state structure was located which leads directly to the organosilane product and DCyPECuH (Figure 2, main text). Alternatively, one might consider oxidative addition into the Si–H bond, followed by C–Si reductive elimination. A scan of the insertion of DCyPECu-benzyl into the Si–H bond of phenylsilane using B3LYP/6-31G(d)-SDD did not reveal any transition state or minimum corresponding to an oxidative addition complex (Figure SI-4). While a scan of the triplet surface revealed a minimum corresponding to oxidative addition into the Si–H bond (triangle point, Figure SI-4), the oxidative addition event was accompanied by dissociation of benzyl radical from the complex. Furthermore, the energy of these points on the triplet surface is prohibitively high compared to the sigma-bond metathesis transition state (+28.0 kcal/mol electronic energy on the same scale). Based on these observations, we consider the oxidative addition mechanism to be unlikely.



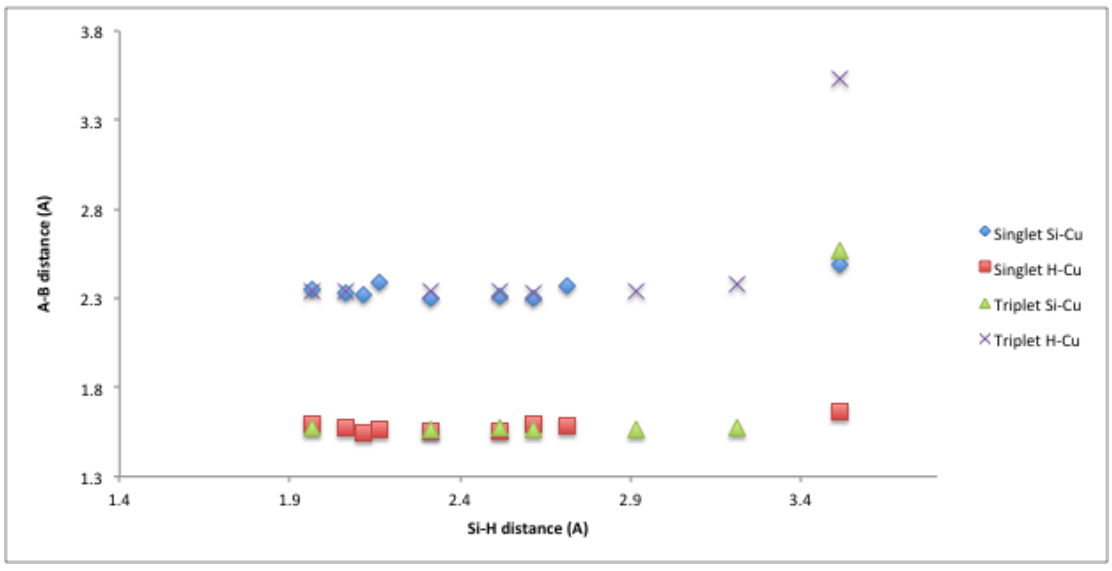



**Figure SI-4.** Scan of the singlet and triplet surfaces of DCyPECuH oxidative insertion into the Si–H bond of phenylsilane. The point highlighted in green corresponds to the sigma-complex **C**, which has been referenced to zero energy. Geometries and electronic energies are reported for optimized structures at B3LYP/SDD-6-31G(d) with frozen Si– H bond distance.

## *Cartesian Coordinates and Calculated Thermodynamic Properties of Selected Structures*

Styrene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -309.648259
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.102245
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -309.477223
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -309.351819
Total Free Energy (M06): -309.374978
Total Free Energy (PBE0): -309.249574

| | | | |
|---|---|---|---|
| C | -0.40645500 | -1.28139000 | 0.00000100 |
| C | 0.51524000 | -0.22036300 | 0.00001700 |
| C | 0.00876000 | 1.09236200 | 0.00005800 |
| C | -1.36241800 | 1.32954200 | 0.00001500 |
| C | -2.26536300 | 0.26182300 | -0.00003900 |
| C | -1.78074400 | -1.04623400 | -0.00002600 |
| H | -0.03485700 | -2.30383900 | 0.00001000 |
| H | 0.69376200 | 1.93534700 | 0.00014000 |
| H | -1.73047700 | 2.35232700 | 0.00003000 |
| H | -3.33551900 | 0.45040100 | -0.00006500 |
| H | -2.47184000 | -1.88509800 | -0.00005100 |
| C | 1.95480100 | -0.52917800 | 0.00005000 |
| H | 2.18619100 | -1.59464000 | 0.00019900 |
| C | 2.97747100 | 0.33501400 | -0.00007600 |
| H | 2.84052100 | 1.41305500 | -0.00023500 |
| H | 4.00447700 | -0.01701200 | -0.00002600 |

DCyPECuH
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -1900.375094
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.645239
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -1899.898139
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -1899.133543
Total Free Energy (M06): -1899.252900
Total Free Energy (PBE0): -1898.488304

| | | | |
|---|---|---|---|
| Cu | -0.00120500 | -0.00008000 | -1.82999500 |
| C | 0.70322400 | -0.31765300 | 1.45948800 |
| H | 1.25264800 | -0.01941000 | 2.35908900 |
| H | 0.61264100 | -1.41162100 | 1.49462800 |
| C | -0.70300400 | 0.31813800 | 1.45961800 |
| H | 0.00094600 | -0.00078100 | -3.38408200 |
| H | -1.25232700 | 0.01980700 | 2.35925000 |
| H | -0.61246200 | 1.41210700 | 1.49480500 |
| P | 1.64600700 | 0.06476400 | -0.12420200 |
| P | -1.64591400 | -0.06440500 | -0.12391600 |
| C | 2.99247500 | -1.24672300 | -0.12392200 |
| C | 3.80195700 | -1.19308700 | -1.43857000 |
| C | 3.93578200 | -1.30101700 | 1.09466500 |
| H | 2.41013300 | -2.18256800 | -0.14119000 |
| C | 4.78731300 | -2.36986400 | -1.53892400 |
| H | 4.36862200 | -0.25062900 | -1.48108700 |
| H | 3.12072800 | -1.18801000 | -2.29688700 |
| C | 4.91312900 | -2.48638900 | 0.99084000 |
| H | 4.51587100 | -0.36908500 | 1.14784500 |
| H | 3.36341000 | -1.37131700 | 2.02815100 |
| C | 5.71595000 | -2.44286500 | -0.31767200 |
| H | 5.37523800 | -2.28289800 | -2.46128800 |

| | | | |
|---|---|---|---|
| H | 4.21828200 | -3.30792300 | -1.61935400 |
| H | 5.58962600 | -2.48736100 | 1.85543700 |
| H | 4.34404400 | -3.42675800 | 1.03775200 |
| H | 6.37313800 | -3.31889200 | -0.38892700 |
| H | 6.37229000 | -1.55970200 | -0.30822400 |
| C | 2.52242300 | 1.71526000 | 0.17437800 |
| C | 1.77477700 | 2.85640400 | -0.55393100 |
| C | 2.79714100 | 2.10878200 | 1.64063200 |
| H | 3.49305900 | 1.58888800 | -0.32952100 |
| C | 2.54125200 | 4.18586000 | -0.46124900 |
| H | 0.77944500 | 2.98351900 | -0.10076000 |
| C | 2.54125200 | 4.18586000 | -0.46124900 |
| H | 0.77944500 | 2.98351900 | -0.10076000 |
| H | 1.60365800 | 2.58393700 | -1.60160200 |
| C | 3.57149400 | 3.43681800 | 1.72943100 |
| H | 1.84154600 | 2.22332500 | 2.17282400 |
| H | 3.35267800 | 1.32125700 | 2.16195300 |
| C | 2.84122200 | 4.57028000 | 0.99482500 |
| H | 1.96865200 | 4.98019300 | -0.95656400 |
| H | 3.48762800 | 4.09302100 | -1.01467100 |
| H | 3.73031400 | 3.70298500 | 2.78258500 |
| H | 4.56988500 | 3.30139400 | 1.28759800 |
| H | 3.43568500 | 5.49199000 | 1.03249500 |
| H | 1.89582500 | 4.78709800 | 1.51477500 |
| C | -2.99266200 | 1.24673000 | -0.12378200 |
| C | -3.80238500 | 1.19251700 | -1.43824300 |
| C | -3.93569600 | 1.30125500 | 1.09499300 |
| H | -2.41048600 | 2.18267300 | -0.14150100 |
| C | -4.78779700 | 2.36921500 | -1.53883800 |
| H | -4.36903800 | 0.25003100 | -1.48027100 |
| H | -3.12122200 | 1.18703000 | -2.29661200 |
| C | -4.91319900 | 2.48647800 | 0.99096400 |
| H | -4.51564800 | 0.36926000 | 1.14858200 |
| H | -3.36313800 | 1.37192800 | 2.02833300 |
| C | -5.71621200 | 2.44250600 | -0.31742700 |
| H | -5.37589600 | 2.28190900 | -2.46105700 |
| H | -4.21883800 | 3.30728200 | -1.61967200 |
| H | -5.58959300 | 2.48763000 | 1.85564000 |
| H | -4.34421300 | 3.42692400 | 1.03753600 |
| H | -6.37348100 | 3.31846100 | -0.38881600 |
| H | -6.37248100 | 1.55929500 | -0.30761500 |
| C | -2.52176100 | -1.71518600 | 0.17458700 |
| C | -1.77361900 | -2.85622400 | -0.55338100 |
| C | -2.79681200 | -2.10861200 | 1.64081000 |
| H | -3.49229300 | -1.58918300 | -0.32961700 |
| C | -2.53982800 | -4.18584300 | -0.46078600 |
| H | -0.77839600 | -2.98307600 | -0.09990900 |
| H | -1.60225600 | -2.58381700 | -1.60103200 |
| C | -3.57089800 | -3.43681100 | 1.72950600 |
| H | -1.84134800 | -2.22290600 | 2.17328700 |
| H | -3.35267100 | -1.32117400 | 2.16191900 |
| H | -1.84134800 | -2.22290600 | 2.17328700 |
| H | -3.35267100 | -1.32117400 | 2.16191900 |
| C | -2.84015100 | -4.57017900 | 0.99523400 |
| H | -1.96689300 | -4.98009400 | -0.95584500 |
| H | -3.48604900 | -4.09326800 | -1.01451700 |
| H | -3.72998000 | -3.70291100 | 2.78263500 |
| H | -4.56918200 | -3.30164300 | 1.28735400 |
| H | -3.43441400 | -5.49202100 | 1.03282900 |
| H | -1.89485800 | -4.78673100 | 1.51548800 |

DCyPECu-benzyl
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2210.05244
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.778386
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -2209.420725
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -2208.521343
Total Free Energy (M06): -2208.642339
Total Free Energy (PBE0): -2207.742957

| | | | |
|---|---|---|---|
| C | -1.07528100 | 1.13504800 | -1.90147000 |
| H | -1.59104400 | 0.94126800 | -2.85059000 |
| H | -1.27007700 | 2.18527300 | -1.65168300 |
| C | 0.44426100 | 0.92302600 | -2.07714500 |
| H | 0.84114500 | 1.65483600 | -2.78905500 |
| H | 0.63257600 | -0.06971200 | -2.50550900 |
| P | -1.81566100 | 0.09898800 | -0.50428200 |
| P | 1.38399400 | 0.92244500 | -0.45025400 |
| C | -3.16030800 | 1.27108300 | 0.11779500 |
| C | -4.33720300 | 1.52883800 | -0.84447000 |
| C | -3.66381100 | 0.90408400 | 1.53063200 |
| H | -2.60611200 | 2.21828100 | 0.22199700 |
| C | -5.28756900 | 2.60475400 | -0.28782600 |
| H | -4.90196500 | 0.59799200 | -0.99124700 |
| H | -3.96859700 | 1.83144600 | -1.83319300 |
| C | -4.61376200 | 1.98285000 | 2.07765400 |
| H | -4.19274900 | -0.05740500 | 1.50280600 |
| H | -2.81050700 | 0.76695800 | 2.20512800 |
| C | -5.78613800 | 2.24647700 | 1.12025700 |
| H | -6.13588800 | 2.74059100 | -0.97102000 |
| H | -4.75831500 | 3.56857900 | -0.25126900 |
| H | -4.98709400 | 1.68309000 | 3.06492900 |
| H | -4.05119100 | 2.91674200 | 2.22689000 |
| H | -6.42522700 | 3.04835100 | 1.51111800 |
| H | -6.41530400 | 1.34575000 | 1.06213000 |
| C | -2.69033900 | -1.28214300 | -1.44375500 |
| C | -1.66029800 | -2.13540000 | -2.21795400 |
| C | -3.52162000 | -2.17386600 | -0.49751600 |
| H | -3.36906900 | -0.81737400 | -2.17507200 |
| C | -2.32995700 | -3.30304400 | -2.96350200 |
| H | -0.91664700 | -2.53385100 | -1.51297700 |
| H | -1.11376600 | -1.51275600 | -2.93718400 |
| C | -4.18259200 | -3.34526000 | -1.24452300 |
| H | -1.11376600 | -1.51275600 | -2.93718400 |
| C | -4.18259200 | -3.34526000 | -1.24452300 |
| H | -2.86591400 | -2.56578400 | 0.29248300 |
| H | -4.29534800 | -1.58260500 | 0.00472700 |
| C | -3.15218000 | -4.18346000 | -2.01241600 |
| H | -1.56322900 | -3.90071100 | -3.47247000 |
| H | -2.98872500 | -2.90280100 | -3.74890300 |
| H | -4.73120500 | -3.97236300 | -0.53039900 |
| H | -4.92842300 | -2.95045000 | -1.95087000 |
| H | -3.65189700 | -4.98493300 | -2.57105300 |
| H | -2.47559800 | -4.67243500 | -1.29672200 |
| C | 3.04491600 | 0.20016500 | -0.95561600 |
| C | 3.80836500 | 0.91269200 | -2.09131200 |
| C | 3.95324500 | 0.00671000 | 0.27753700 |
| H | 2.76656700 | -0.80483100 | -1.31080600 |
| C | 5.09584800 | 0.15285100 | -2.45908600 |
| H | 4.07761800 | 1.92905600 | -1.77001500 |
| H | 3.17615600 | 1.01881100 | -2.98158800 |
| C | 5.24632300 | -0.73981000 | -0.09027700 |
| H | 4.21370800 | 0.98866400 | 0.70154800 |
| H | 3.41194500 | -0.54628700 | 1.05197500 |
| C | 6.00156100 | -0.04967100 | -1.23557100 |
| H | 5.63328800 | 0.69418400 | -3.24868600 |
| H | 4.82708100 | -0.82756000 | -2.87911700 |
| H | 5.88952500 | -0.82086800 | 0.79515100 |
| H | 4.98956400 | -1.76772600 | -0.38322600 |
| H | 6.88893300 | -0.63257900 | -1.51353000 |
| H | 6.36656800 | 0.92994000 | -0.89160600 |
| C | 1.72195000 | 2.73376600 | -0.01634000 |
| C | 1.65877200 | 3.74982200 | -1.17552300 |
| C | 0.80960100 | 3.18846400 | 1.14565500 |
| H | 2.75367500 | 2.72406200 | 0.36669700 |
| C | 2.01430500 | 5.16990600 | -0.69766600 |
| H | 0.64226800 | 3.76270800 | -1.59550100 |
| H | 2.32893800 | 3.45463900 | -1.99043100 |
| C | 1.15981600 | 4.60787300 | 1.62064600 |
| H | -0.23931400 | 3.16891700 | 0.81226700 |

| | | | |
|---|---|---|---|
| H | 0.88084200 | 2.47844600 | 1.97780000 |
| C | 1.11855800 | 5.61910500 | 0.46584900 |
| H | 1.93453700 | 5.87375700 | -1.53621400 |
| C | 1.11855800 | 5.61910500 | 0.46584900 |
| H | 1.93453700 | 5.87375700 | -1.53621400 |
| H | 3.06555500 | 5.18726800 | -0.37414000 |
| H | 0.47403200 | 4.91283800 | 2.42129400 |
| H | 2.16823400 | 4.59988800 | 2.06037600 |
| H | 1.42254200 | 6.61315900 | 0.81736400 |
| H | 0.08277200 | 5.71764900 | 0.10731700 |
| Cu | -0.00731700 | -0.34970400 | 0.97271300 |
| C | 0.22031700 | -1.56642000 | 2.56828800 |
| H | -0.79301300 | -1.91930000 | 2.80635400 |
| C | 0.80965300 | -0.88398000 | 3.80954900 |
| H | 1.02828300 | -1.59304000 | 4.62881300 |
| H | 1.74564700 | -0.34908100 | 3.59955800 |
| H | 0.10827700 | -0.13804900 | 4.20429100 |
| C | 1.00233000 | -2.71163800 | 2.03026600 |
| C | 0.37612100 | -3.71047100 | 1.24188900 |
| C | 2.39058200 | -2.87668000 | 2.24662300 |
| C | 1.08518200 | -4.76931700 | 0.68323200 |
| H | -0.69926200 | -3.64239600 | 1.08147000 |
| C | 3.10398900 | -3.93793700 | 1.68391400 |
| H | 2.91726600 | -2.16672200 | 2.87830100 |
| C | 2.46484000 | -4.89182500 | 0.89019300 |
| H | 0.55702700 | -5.51500600 | 0.09119400 |
| H | 4.17081300 | -4.02584200 | 1.88268700 |
| H | 3.02045800 | -5.72031400 | 0.45873400 |

phenylsilane
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -522.936273
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.083652
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -522.807641
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -522.597855
Total Free Energy (M06): -522.723989
Total Free Energy (PBE0): -522.514203

| | | | |
|---|---|---|---|
| C | -0.25667700 | -1.20535900 | -0.00941800 |
| C | 0.46879600 | 0.00000700 | -0.01143200 |
| C | -0.25660700 | 1.20528600 | -0.00944000 |
| C | -1.65249600 | 1.20793600 | 0.00325000 |
| C | -2.35277900 | 0.00002400 | 0.01029700 |
| C | -1.65244900 | -1.20799500 | 0.00325500 |
| H | 0.27181300 | -2.15634000 | -0.02275500 |
| H | 0.27199700 | 2.15616000 | -0.02273000 |
| H | -2.19286700 | 2.15105000 | 0.00320400 |
| H | -3.43966300 | -0.00001400 | 0.01687900 |
| H | -2.19289800 | -2.15106500 | 0.00322200 |
| Si | 2.34805300 | 0.00000600 | 0.00579100 |
| H | 2.89514100 | -0.01925600 | 1.39220000 |
| H | 2.86463000 | -1.20357600 | -0.70183700 |
| H | 2.86237000 | 1.22356300 | -0.66832200 |

sigma-bond metathesis TS (TS-C)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2732.944829
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.88778
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -2732.204831
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -2731.087462
Total Free Energy (M06): -2731.317051
Total Free Energy (PBE0): -2730.199682

| | | | |
|---|---|---|---|
| C | -0.25598900 | -2.50847400 | 1.52044900 |
| H | 0.07590300 | -3.54287400 | 1.67453800 |
| H | -0.42797800 | -2.08748700 | 2.51644000 |
| C | -1.57807700 | -2.51147200 | 0.72607700 |

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|---|---|---|---|
| H | -2.35589400 | -3.02469100 | 1.30415400 |
| H | -1.44756800 | -3.08535400 | -0.19877100 |
| P | 1.14148200 | -1.50275800 | 0.74192200 |
| P | -2.13812300 | -0.80999200 | 0.17803400 |
| C | 2.02670000 | -0.91249200 | 2.29876900 |
| C | 2.61963700 | -2.01570500 | 3.19897700 |
| C | 3.05887700 | 0.20296800 | 2.02746600 |
| H | 1.19817500 | -0.44041000 | 2.85066600 |
| C | 3.16714600 | -1.42723700 | 4.51262800 |
| H | 3.43763400 | -2.52431600 | 2.67071900 |
| H | 1.86750200 | -2.78264800 | 3.42455500 |
| C | 3.59962700 | 0.78154100 | 3.34641100 |
| H | 3.89743900 | -0.19100300 | 1.43963900 |
| H | 2.59778300 | 0.99240300 | 1.42472400 |
| C | 4.18904400 | -0.31140100 | 4.25014600 |
| H | 3.61674700 | -2.22548400 | 5.11734100 |
| H | 2.33062300 | -1.02200300 | 5.10128100 |
| H | 4.35571400 | 1.54726700 | 3.13166700 |
| H | 2.78219400 | 1.29088700 | 3.87867300 |
| H | 4.53036900 | 0.12018700 | 5.19966000 |
| H | 5.07766400 | -0.74260100 | 3.76523000 |
| C | 2.19392400 | -2.88742300 | 0.00312800 |
| C | 1.46376000 | -3.51150800 | -1.20734900 |
| C | 3.61548800 | -2.44293200 | -0.39374700 |
| H | 2.27852900 | -3.65824900 | 0.78465500 |
| C | 2.26987300 | -4.66333400 | -1.83215800 |
| H | 1.29680000 | -2.73134300 | -1.96285600 |
| H | 0.47552400 | -3.88463800 | -0.91079500 |
| C | 4.41473100 | -3.59555200 | -1.02928900 |
| H | 0.47552400 | -3.88463800 | -0.91079500 |
| C | 4.41473100 | -3.59555200 | -1.02928900 |
| H | 3.55726700 | -1.60746300 | -1.10072300 |
| H | 4.15835400 | -2.07684600 | 0.48387100 |
| C | 3.68150000 | -4.21179300 | -2.22796300 |
| H | 1.73269300 | -5.05727900 | -2.70452600 |
| H | 2.34141400 | -5.48946000 | -1.10880400 |
| H | 5.40207800 | -3.22671800 | -1.33479800 |
| H | 4.59301400 | -4.37592100 | -0.27378200 |
| H | 4.25300200 | -5.05738100 | -2.63143200 |
| H | 3.61084100 | -3.46527100 | -3.03163200 |
| C | -3.32606200 | -1.17748800 | -1.24168500 |
| C | -4.19301200 | -2.45392900 | -1.16938300 |
| C | -4.19684200 | 0.05461500 | -1.57577100 |
| H | -2.63081000 | -1.31304300 | -2.08409200 |
| C | -4.96528800 | -2.66128500 | -2.48592700 |
| H | -4.91305600 | -2.37994800 | -0.34510000 |
| H | -3.57437200 | -3.33573300 | -0.96626600 |
| C | -4.97642600 | -0.15690200 | -2.88510200 |
| H | -4.91391400 | 0.22925600 | -0.76106000 |
| H | -3.57709600 | 0.95567900 | -1.64896100 |
| C | -5.82266800 | -1.43758100 | -2.84018400 |
| H | -5.59236600 | -3.55889200 | -2.40873500 |
| H | -4.24777600 | -2.84994600 | -3.29821800 |
| H | -5.61301900 | 0.71511400 | -3.08027800 |
| H | -4.26453100 | -0.21783800 | -3.72097500 |
| H | -6.32818500 | -1.59438000 | -3.80143900 |
| H | -6.61526000 | -1.32158700 | -2.08574700 |
| C | -3.15013600 | -0.08792600 | 1.59275800 |
| C | -4.33985500 | -0.91583000 | 2.12103700 |
| C | -2.22894500 | 0.33561600 | 2.76021900 |
| H | -3.54258600 | 0.84017600 | 1.15368400 |
| C | -5.11091100 | -0.15490800 | 3.21729000 |
| H | -3.97585800 | -1.86876300 | 2.53229600 |
| H | -5.03026000 | -1.16753000 | 1.30996100 |
| C | -3.00795600 | 1.10833800 | 3.83659800 |
| H | -1.79006500 | -0.55994100 | 3.22425200 |
| H | -1.40241100 | 0.94545300 | 2.38068200 |
| C | -4.19578700 | 0.29186700 | 4.36515700 |
| H | -5.92476000 | -0.78544700 | 3.59828100 |
| C | -4.19578700 | 0.29186700 | 4.36515700 |
| H | -5.92476000 | -0.78544700 | 3.59828100 |

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|---|---|---|---|
| H | -5.58568500 | 0.73002600 | 2.76898000 |
| H | -2.33312800 | 1.37862100 | 4.65891700 |
| H | -3.37039900 | 2.05245400 | 3.40600300 |
| H | -4.76640700 | 0.87475000 | 5.09920600 |
| H | -3.81839300 | -0.59580000 | 4.89543400 |
| C | 0.17929700 | 1.56585100 | -2.35643900 |
| H | 0.19154800 | 2.62888000 | -2.63263000 |
| C | -0.78191900 | 0.87356700 | -3.32528300 |
| H | -0.48822800 | 1.01636300 | -4.37699700 |
| H | -0.84482800 | -0.20835900 | -3.15496600 |
| H | -1.78991700 | 1.28659300 | -3.21314100 |
| C | 1.61537100 | 1.12859100 | -2.45252700 |
| C | 2.62571100 | 1.86779500 | -1.79648200 |
| C | 2.03839600 | 0.06061100 | -3.27117200 |
| C | 3.97520800 | 1.56246000 | -1.95632800 |
| H | 2.34054600 | 2.71333200 | -1.17766700 |
| C | 3.39274700 | -0.23729200 | -3.44140700 |
| H | 1.30335400 | -0.52453600 | -3.81522100 |
| C | 4.37354300 | 0.50811900 | -2.78461300 |
| H | 4.72322900 | 2.16531200 | -1.44603300 |
| H | 3.68115900 | -1.04764800 | -4.10804600 |
| H | 5.42744400 | 0.28277300 | -2.92603200 |
| Cu | -0.07278700 | 0.26915500 | -0.22539000 |
| H | 0.24630500 | 1.73326500 | 0.48532900 |
| Si | -0.82813300 | 2.55757300 | -0.58593600 |
| H | -1.83914500 | 2.91173800 | -1.67214200 |
| H | -1.86020100 | 2.52615600 | 0.53238900 |
| C | 0.10982800 | 4.20367100 | -0.38190500 |
| C | -0.14347700 | 5.26854300 | -1.26546200 |
| C | 1.02105000 | 4.43732500 | 0.66395700 |
| C | 0.48385000 | 6.50816200 | -1.11654300 |
| H | -0.84784800 | 5.12693900 | -2.08281200 |
| C | 1.64965100 | 5.67403100 | 0.82367800 |
| H | 1.24226300 | 3.63469800 | 1.36472400 |
| C | 1.38360200 | 6.71455900 | -0.06959000 |
| H | 0.26966200 | 7.31195100 | -1.81730900 |
| H | 2.34796400 | 5.82608800 | 1.64383100 |
| H | 1.87422800 | 7.67763500 | 0.04966100 |
| H | 2.34796400 | 5.82608800 | 1.64383100 |
| H | 1.87422800 | 7.67763500 | 0.04966100 |

DCyPECu-benzyl/PhSiH3 sigma complex (C)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2732.98956
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.875572
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -2732.228567
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -2731.114169
Total Free Energy (M06): -2731.352995
Total Free Energy (PBE0): -2730.238597

| | | | |
|---|---|---|---|
| C | -1.57004800 | -2.40295300 | -0.06265100 |
| H | -1.44067300 | -3.40889900 | -0.47763900 |
| H | -2.24690000 | -2.50985200 | 0.79355600 |
| C | -2.19010000 | -1.48484000 | -1.13532500 |
| H | -3.04514400 | -1.99355900 | -1.59470100 |
| H | -1.45506100 | -1.31726800 | -1.93248200 |
| P | 0.10491300 | -1.83107800 | 0.57565200 |
| P | -2.64472200 | 0.22425000 | -0.48846900 |
| C | -0.28329900 | -1.37365700 | 2.35988900 |
| C | -0.61757300 | -2.56096800 | 3.28658100 |
| C | 0.78118300 | -0.45135000 | 2.99201300 |
| H | -1.19419800 | -0.76809900 | 2.24034700 |
| C | -1.05223300 | -2.07302900 | 4.68056300 |
| H | 0.26523300 | -3.20548600 | 3.39459000 |
| H | -1.40781300 | -3.18573800 | 2.84997500 |
| C | 0.34126200 | 0.02441600 | 4.38718900 |
| H | 1.73817500 | -0.98210600 | 3.07871900 |
| H | 0.95876200 | 0.40987000 | 2.33787300 |
| C | 0.00504100 | -1.15511800 | 5.31179000 |

| | | | |
|---|---|---|---|
| H | -1.24911900 | -2.93546200 | 5.33024400 |
| H | -2.00144300 | -1.52465600 | 4.59010400 |
| H | 1.12934600 | 0.64507200 | 4.83161600 |
| H | -0.54415200 | 0.66872900 | 4.28413000 |
| H | -0.34455400 | -0.78848700 | 6.28515600 |
| H | 0.91886000 | -1.73619100 | 5.50620300 |
| C | 1.10896800 | -3.42410900 | 0.58605200 |
| C | 1.33355900 | -3.92029400 | -0.86237500 |
| C | 2.47092500 | -3.24225200 | 1.29154000 |
| H | 0.52788200 | -4.18336400 | 1.13132400 |
| C | 2.16818400 | -5.21220500 | -0.89762900 |
| H | 1.85609900 | -3.13981600 | -1.43266500 |
| H | 0.37630400 | -4.09197200 | -1.37035100 |
| C | 3.31185700 | -4.53045300 | 1.24908200 |
| H | 0.37630400 | -4.09197200 | -1.37035100 |
| C | 3.31185700 | -4.53045300 | 1.24908200 |
| H | 3.02543900 | -2.43286500 | 0.79571800 |
| H | 2.32894600 | -2.93755600 | 2.33406000 |
| C | 3.51632500 | -5.02865000 | -0.18764800 |
| H | 2.32347600 | -5.51607900 | -1.94023700 |
| H | 1.60543000 | -6.02428300 | -0.41271800 |
| H | 4.27973100 | -4.34893100 | 1.73334300 |
| H | 2.80810300 | -5.31124200 | 1.83886300 |
| H | 4.07794600 | -5.97151600 | -0.18695000 |
| H | 4.11976100 | -4.29816500 | -0.74450200 |
| C | -2.83803500 | 1.16999200 | -2.11171600 |
| C | -3.85535400 | 0.63191000 | -3.13773900 |
| C | -3.08911800 | 2.66850900 | -1.83386800 |
| H | -1.83304400 | 1.08911100 | -2.55602400 |
| C | -3.84198100 | 1.46027300 | -4.43571600 |
| H | -4.86532000 | 0.67006100 | -2.70503400 |
| H | -3.65077500 | -0.42048400 | -3.37037800 |
| C | -3.08608800 | 3.49611500 | -3.13088000 |
| H | -4.06224900 | 2.79246200 | -1.33434600 |
| H | -2.33033600 | 3.05318800 | -1.14167400 |
| C | -4.08958200 | 2.94974800 | -4.15656100 |
| H | -4.59488400 | 1.07157700 | -5.13395700 |
| H | -2.86609100 | 1.34074700 | -4.92881400 |
| H | -3.30636900 | 4.54685000 | -2.90255600 |
| H | -2.07586100 | 3.47542300 | -3.56486400 |
| H | -4.03350000 | 3.52606000 | -5.08885300 |
| H | -5.11153000 | 3.07982500 | -3.76940200 |
| C | -4.43018700 | 0.04086100 | 0.15392600 |
| C | -5.23673400 | -1.19134100 | -0.30257200 |
| C | -4.43953100 | 0.14048900 | 1.69651500 |
| H | -4.94312100 | 0.93650800 | -0.22944500 |
| C | -6.66937800 | -1.17563500 | 0.26226000 |
| H | -4.73367500 | -2.10643900 | 0.04297900 |
| H | -5.27301100 | -1.24996800 | -1.39607700 |
| C | -5.86779700 | 0.14884100 | 2.26612800 |
| H | -3.88917000 | -0.71568300 | 2.11750400 |
| H | -3.89862600 | 1.03933900 | 2.01593500 |
| C | -6.67362600 | -1.06965800 | 1.79379900 |
| H | -7.20589700 | -2.07766300 | -0.05998800 |
| C | -6.67362600 | -1.06965800 | 1.79379900 |
| H | -7.20589700 | -2.07766300 | -0.05998800 |
| H | -7.21464700 | -0.31970600 | -0.16233300 |
| H | -5.83417800 | 0.18373900 | 3.36282800 |
| H | -6.37716700 | 1.06810500 | 1.94047700 |
| H | -7.70328600 | -1.01633100 | 2.16974800 |
| H | -6.23193800 | -1.98307700 | 2.21986500 |
| C | 2.27500100 | 0.82161800 | -1.86198600 |
| H | 2.77409400 | 1.54332300 | -1.19886400 |
| C | 1.51627500 | 1.59356100 | -2.95191300 |
| H | 2.19372800 | 2.10427200 | -3.65821900 |
| H | 0.86133000 | 0.95139600 | -3.55483400 |
| H | 0.87288400 | 2.35887900 | -2.50084200 |
| C | 3.30136400 | -0.15076300 | -2.34898000 |
| C | 4.44420000 | -0.44217300 | -1.56729500 |
| C | 3.18465500 | -0.84722700 | -3.57225000 |
| C | 5.39198400 | -1.38156600 | -1.96599700 |

| | | | |
|---|---|---|---|
| H | 4.58007700 | 0.08968500 | -0.62627800 |
| C | 4.13388900 | -1.78969100 | -3.97329900 |
| H | 2.33596100 | -0.64658900 | -4.22094100 |
| C | 5.24410500 | -2.07182100 | -3.17479900 |
| H | 6.25957200 | -1.56821800 | -1.33599400 |
| H | 4.00642600 | -2.30214500 | -4.92500100 |
| H | 5.98559900 | -2.80032100 | -3.49200700 |
| Cu | 1.14149500 | -0.26049100 | -0.66857500 |
| H | 0.59960300 | 2.41337400 | 0.74899600 |
| Si | 0.49606600 | 3.83538500 | 1.16833600 |
| H | -0.21386200 | 4.57678500 | 0.08714700 |
| H | -0.32971300 | 3.92728600 | 2.40529500 |
| C | 2.19246400 | 4.56775600 | 1.51658300 |
| C | 3.25144000 | 4.41682300 | 0.60109000 |
| C | 2.44065200 | 5.28811200 | 2.69844400 |
| C | 4.50770700 | 4.96828300 | 0.85517300 |
| H | 3.09795200 | 3.85976200 | -0.32104500 |
| C | 3.69669000 | 5.84209600 | 2.95664600 |
| H | 1.64563300 | 5.41766600 | 3.42964500 |
| C | 4.73210600 | 5.68299300 | 2.03454200 |
| H | 5.31142800 | 4.83796900 | 0.13504900 |
| H | 3.86636300 | 6.39503500 | 3.87717800 |
| H | 5.71097000 | 6.11153000 | 2.23417300 |
| H | 3.86636300 | 6.39503500 | 3.87717800 |
| H | 5.71097000 | 6.11153000 | 2.23417300 |

PhSiH2-benzyl
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -832.629376
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.211596
Single-Point Energy (M06-2X/SDD-6-311G+(2d,p)/SMD(THF)): -832.329567
Single-Point Energy (PBE0/SDD-6-311G+(2d,p)/SMD(THF)): -831.996203
Total Free Energy (M06): -832.117971
Total Free Energy (PBE0): -831.784607

| | | | |
|---|---|---|---|
| C | 2.85107100 | 1.32068700 | -0.16491700 |
| C | 2.21953700 | 0.09366400 | -0.44132700 |
| C | 3.00285700 | -1.07375000 | -0.37858400 |
| C | 4.35773200 | -1.02043200 | -0.04707500 |
| C | 4.96094200 | 0.20806000 | 0.22772600 |
| C | 4.20502500 | 1.38047700 | 0.16721100 |
| H | 2.28120400 | 2.24664100 | -0.21709800 |
| H | 2.55243000 | -2.03946100 | -0.59895500 |
| H | 4.94306600 | -1.93567300 | -0.00797700 |
| H | 6.01648200 | 0.25236200 | 0.48349600 |
| H | 4.67132100 | 2.34051400 | 0.37385600 |
| Si | 0.38191400 | 0.02112900 | -0.84702000 |
| H | 0.00647900 | 1.24868000 | -1.60150900 |
| H | 0.12628900 | -1.17799500 | -1.69494900 |
| C | -0.71034700 | -0.09327600 | 0.72339500 |
| H | -0.45338300 | 0.79100300 | 1.32400900 |
| C | -0.37911300 | -1.34394300 | 1.56533700 |
| H | 0.67250700 | -1.34060100 | 1.87284400 |
| H | -0.99748600 | -1.38048800 | 2.47038100 |
| H | -0.55518100 | -2.27208800 | 1.00996200 |
| C | -2.17616400 | 0.01893000 | 0.34415800 |
| C | -2.88031500 | 1.21223600 | 0.56837900 |
| C | -2.86718900 | -1.04655800 | -0.25675000 |
| C | -4.22330800 | 1.33860300 | 0.21289800 |
| H | -2.36762600 | 2.05141500 | 1.03408400 |
| C | -4.21103900 | -0.92463000 | -0.61142400 |
| H | -2.35148600 | -1.98376700 | -0.44912100 |
| C | -4.89647300 | 0.26870900 | -0.37855300 |
| H | -4.74456000 | 2.27351700 | 0.40290100 |
| H | -4.72275300 | -1.76572900 | -1.07245300 |
| H | -5.94338900 | 0.36319700 | -0.65404200 |

## 4. References and Notes

1. The microcrystalline powder exhibits much higher kinetic solubility in silane-based reaction media, and this was important for procedures C and D. In particular, the amorphous powder was very poorly soluble in $PhSiH_3$ and consequently sluggish in forming the active catalyst in that medium, whereas the microcrystalline material generally underwent reaction in < 30 min. However, we noted that one commercial lot of microcrystalline powder exhibited degraded enantioselectivity in the hydrosilylation of styrene (procedure A), although the effect was much attenuated or altogether absent for various heterocycles (morpholinopyridine **14**, pyrrole **11**) or styrenes bearing various polar functional groups (e.g., fluoroarene **10**). We thus recommend employing the amorphous powder if such a situation is encountered in the hydrosilylation of any nonpolar styrene derivative. The extended catalyst pre-formation step of Procedure A and the better solvating power of diphenylsilane make the kinetic solubility of the copper source relatively unimportant in this variant of the reaction.
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3. NTP (National Toxicology Program). 2016. Report on Carcinogens, Fourteenth Edition.; Research Triangle Park, NC: U.S. Department of Health and Human Services, Public Health Service. http://ntp.niehs.nih.gov/go/roc14.
4. For certain substrates (e.g., styrene and 4-methoxystyrene), we found that conducting the reaction according to procedure B resulted in undesirable levels of variability in the enantiomeric excess, whereas reactions conducted according to procedure A were generally free from this problem. An experiment performed by heating a mixture of styrene and the two catalyst precursors at 40 °C without prior catalyst formation resulted in significantly reduced enantioselectivity; thus, it seems probable that premature use of the catalyst mixture and an attendant poorly selective background reaction were responsible for the erosion of selectivity observed in certain reactions employing procedure B. The alternative catalyst generation step described in procedure A reliably gave complete formation of the desired catalyst within 80 min.
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6. In the chiral HPLC analysis of **11**, We were not able to confirm directly that the minor regioisomer peak was completely resolved from the peaks associated with the Markovnikov product. However, we found that a sample of racemic **1** and a sample of racemic **11** prepared using the same lot of racemic catalyst had the same apparent ee; thus, the signal from the minor regioisomer was not making a noticeable contribution to the area of either Markovnikov enantiomer peak. In the case of coelution with the minor Markovnikov enantiomer (*R*), the true ee would be somewhat greater than 97%. Conversely, if one assumes that the minor regioisomer (which is present at the level of ca. 2.5%) coelutes with the major Markovnikov enantiomer (*S*), and that the two species possess very similar extinction coefficients, once can calculate a corrected ee that excludes the area contribution from the anti-Markovnikov product. According to that analysis, an apparent ee of 97% would have to be revised as 96.9%. This discrepancy is within the expected error of the measurement.
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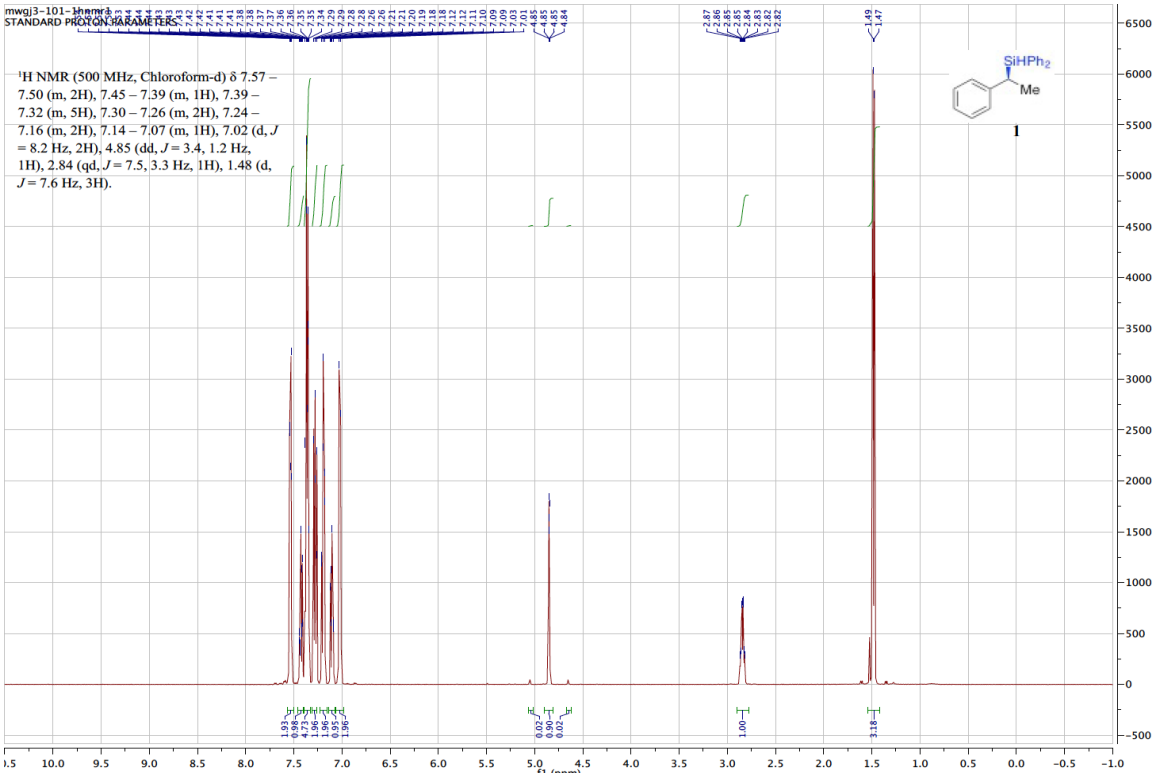
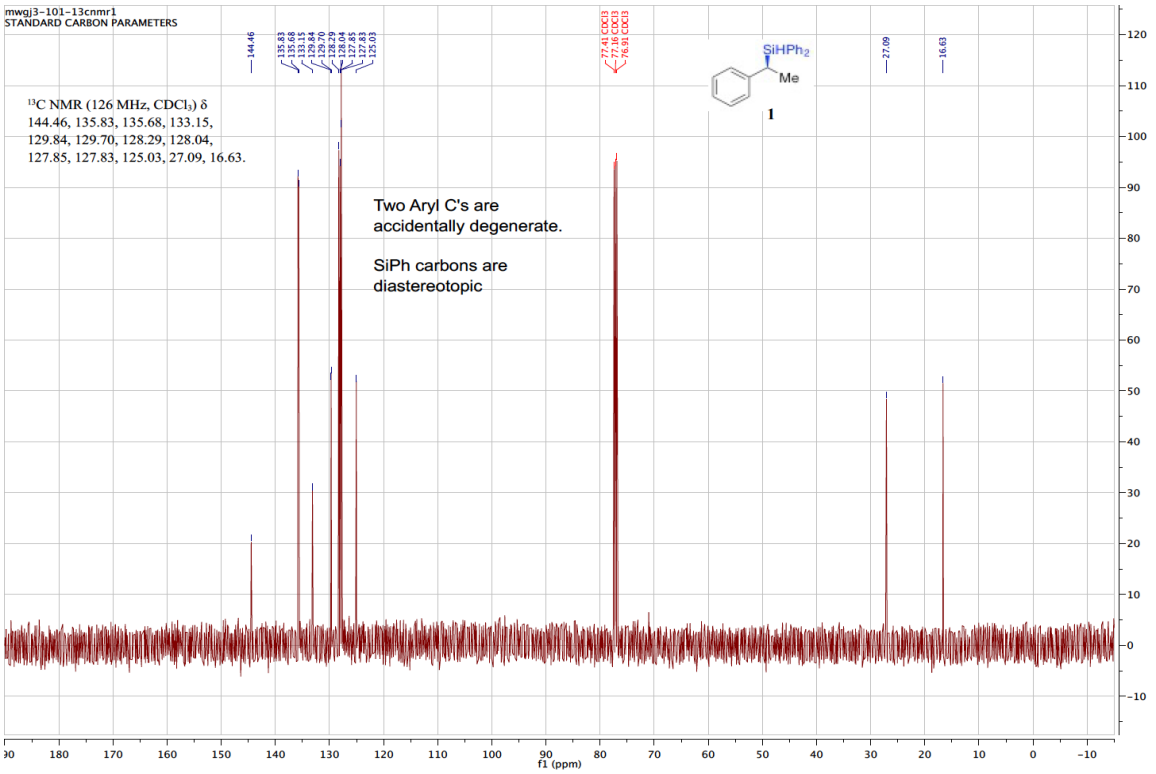
## 5.1 $^{1}$H and $^{13}$C NMR Spectra for Hydrosilylation Products and Substrates

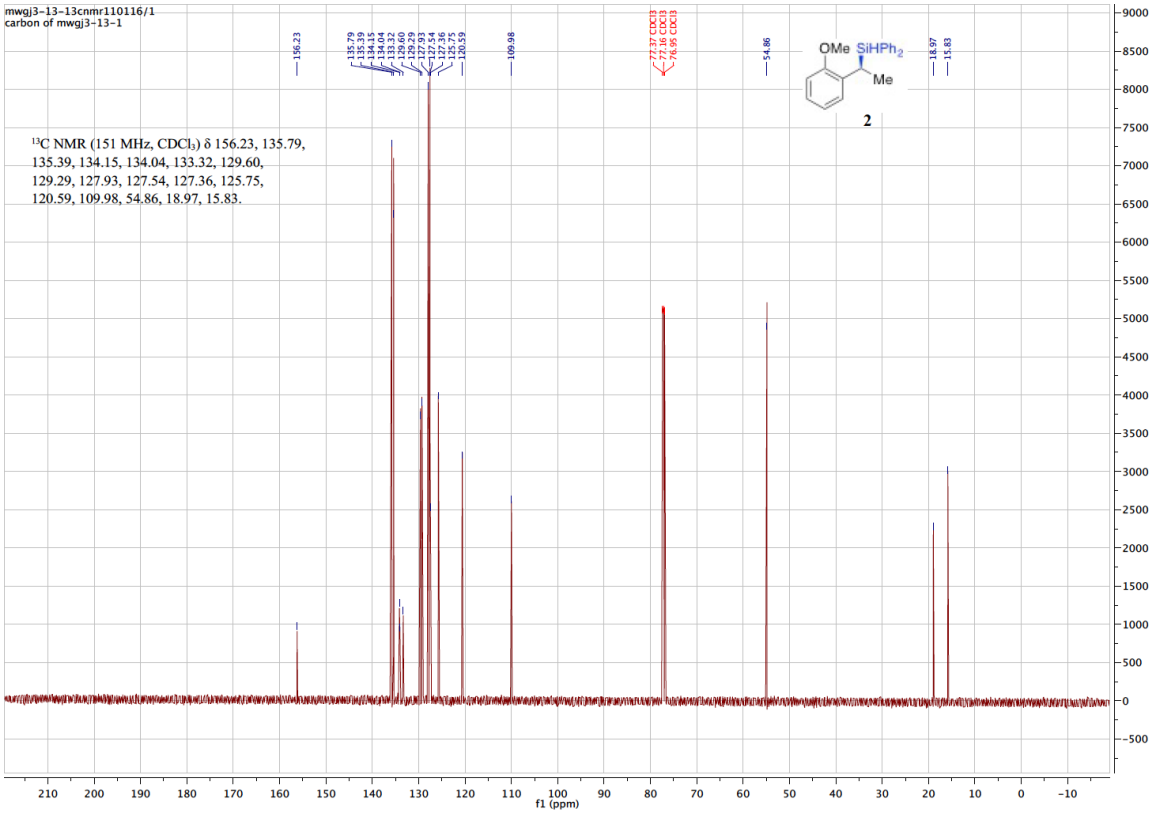
(*S*)-diphenyl(1-phenylethyl)silane (**1**)



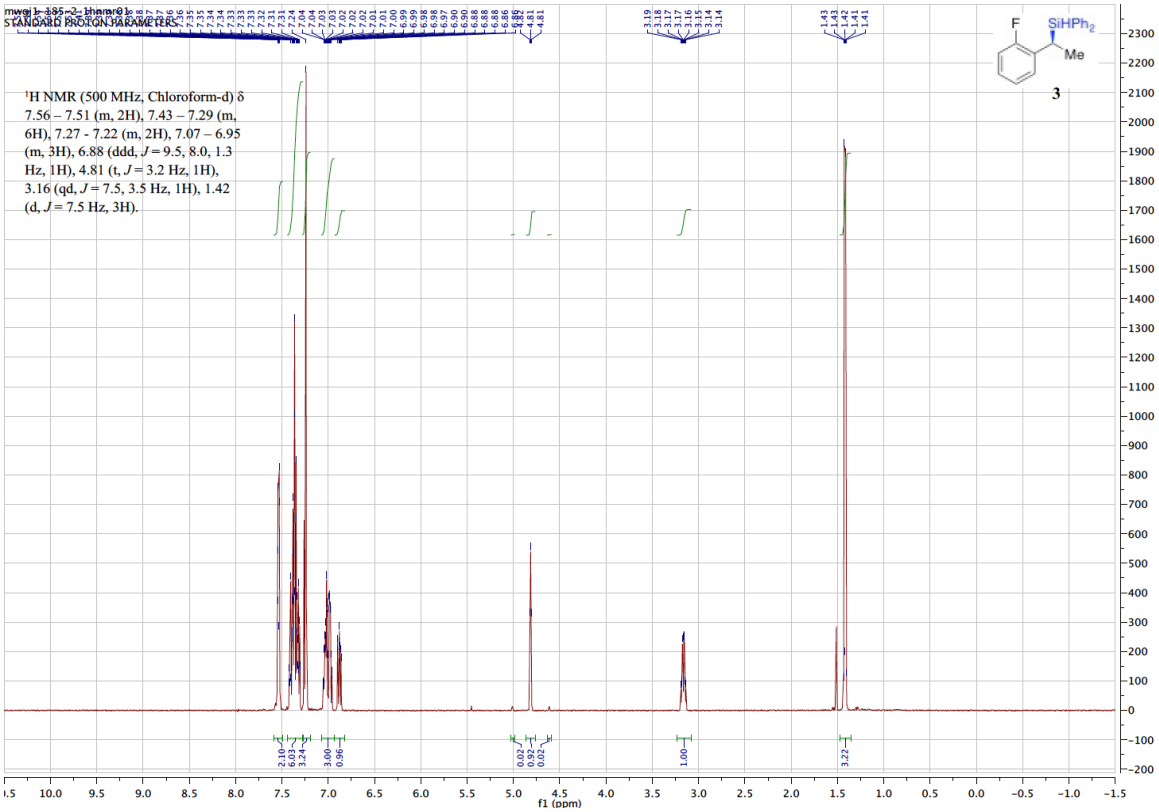



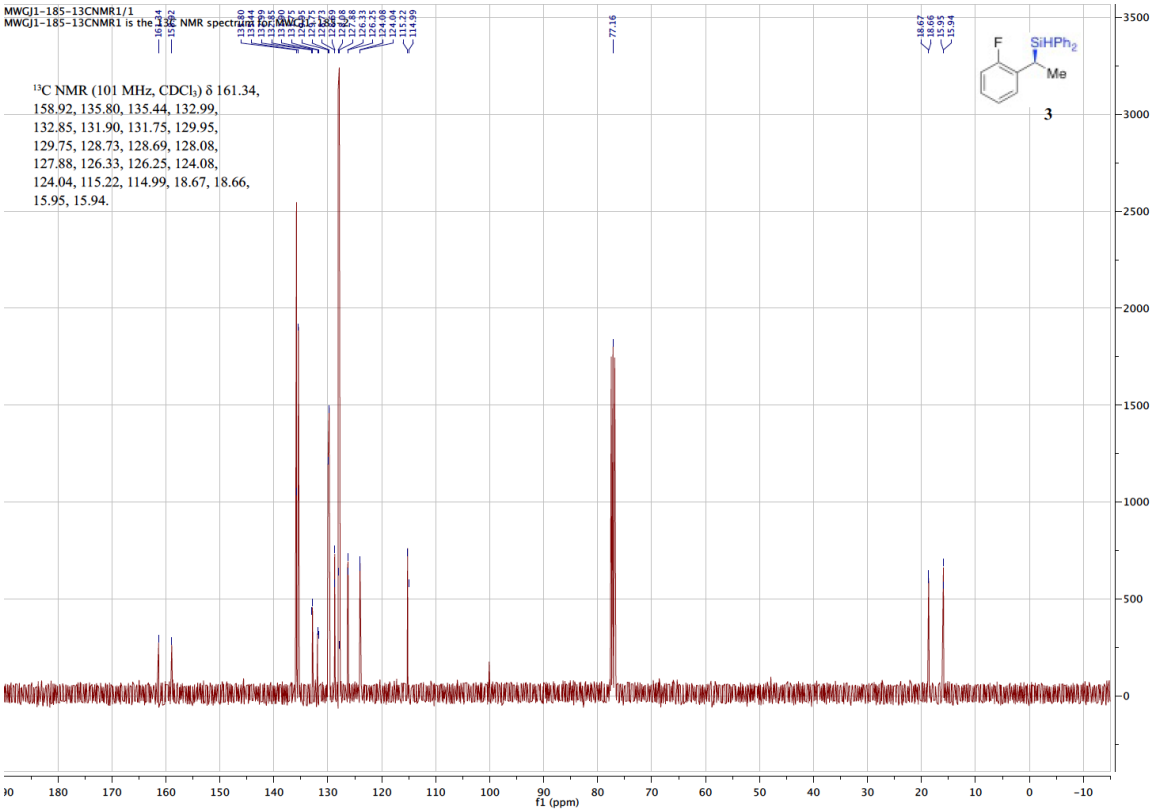

mwgj3-113--1hnmrel
STANDARD PROTON PARAMETERS
$^1$H NMR (500 MHz, Chloroform-d) δ 7.59 – 7.53 (m, 2H), 7.49 – 7.41 (m, 1H), 7.42 – 7.34 (m, 5H), 7.33 – 7.27 (m, 2H), 7.22 (t, J = 7.5 Hz, 2H), 7.16 – 7.09 (m, 1H), 7.08 – 7.00 (m, 2H), 4.87 (d, J = 3.3 Hz, 1H), 2.86 (qd, J = 7.5, 3.4 Hz, 1H), 1.50 (d, J = 7.5 Hz, 3H).
SiHPh2
Me
1
(scale-up lot)
f1 (ppm)

(*S*)-(1-(2-methoxyphenyl)ethyl)diphenylsilane **(2)**

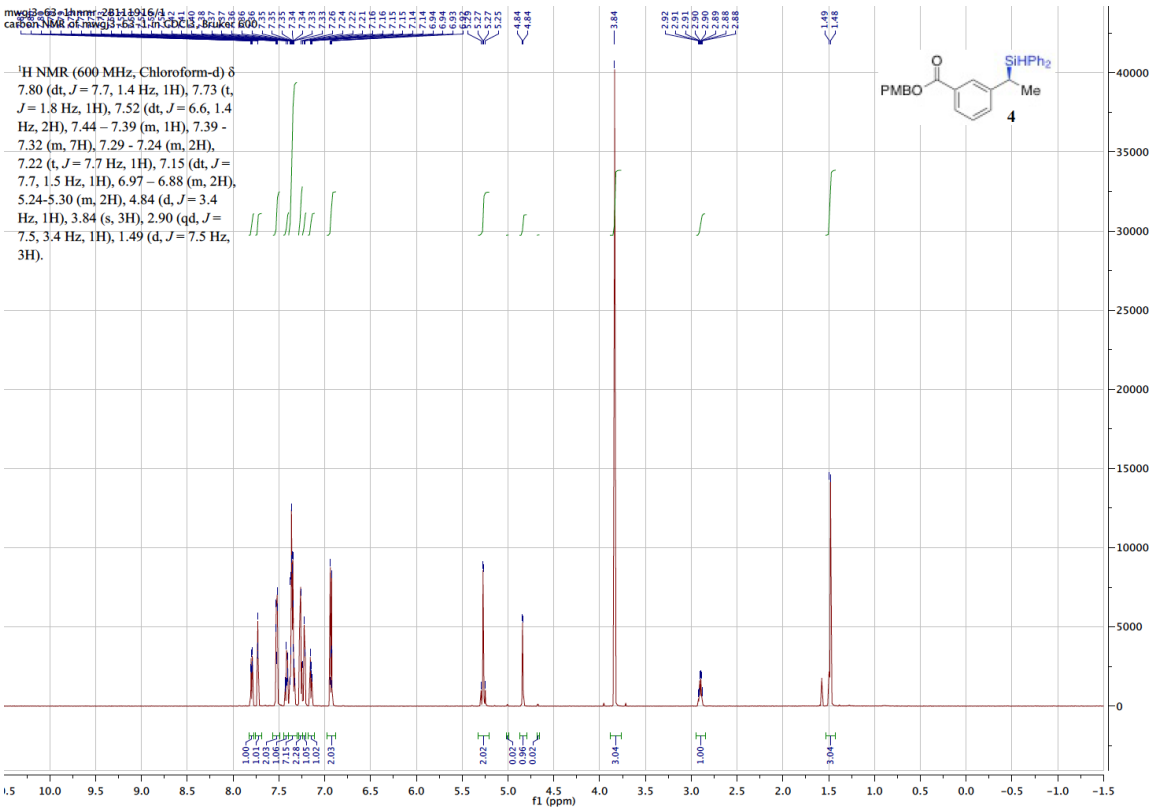



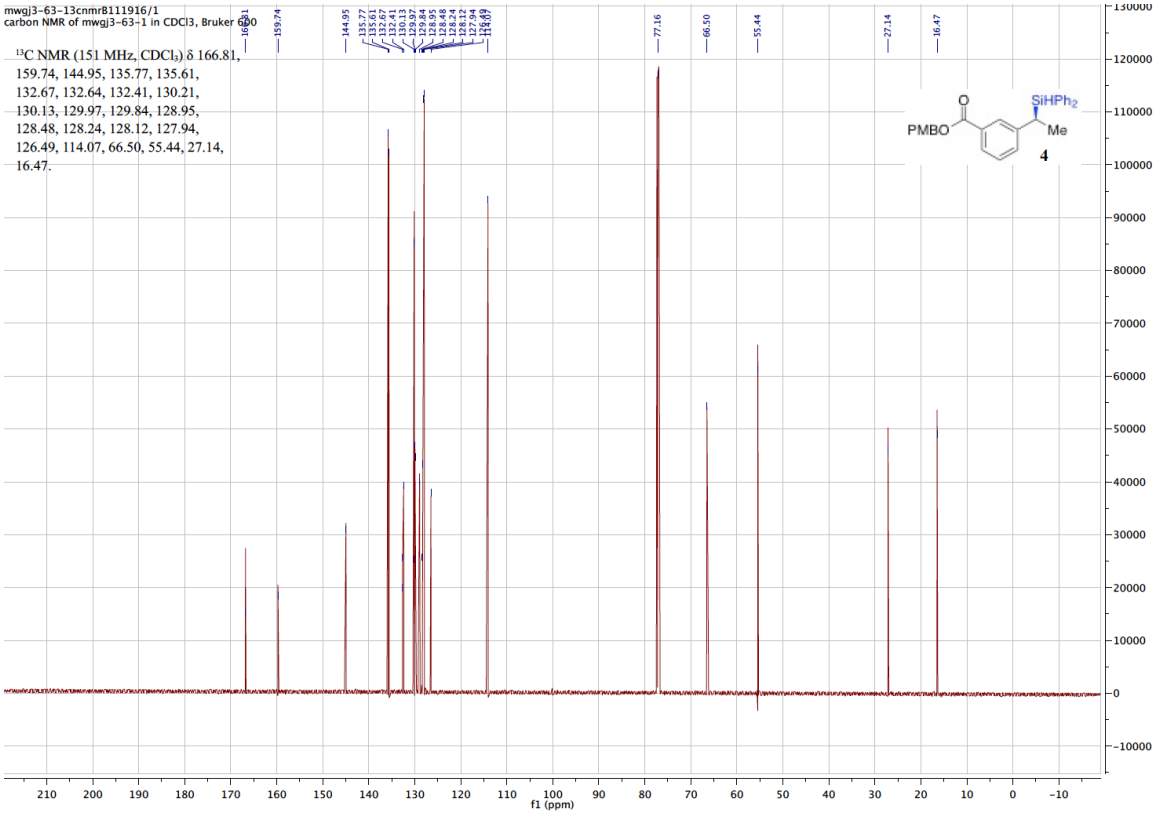
(*S*)-(1-(2-fluorophenyl)ethyl)diphenylsilane **(3)**



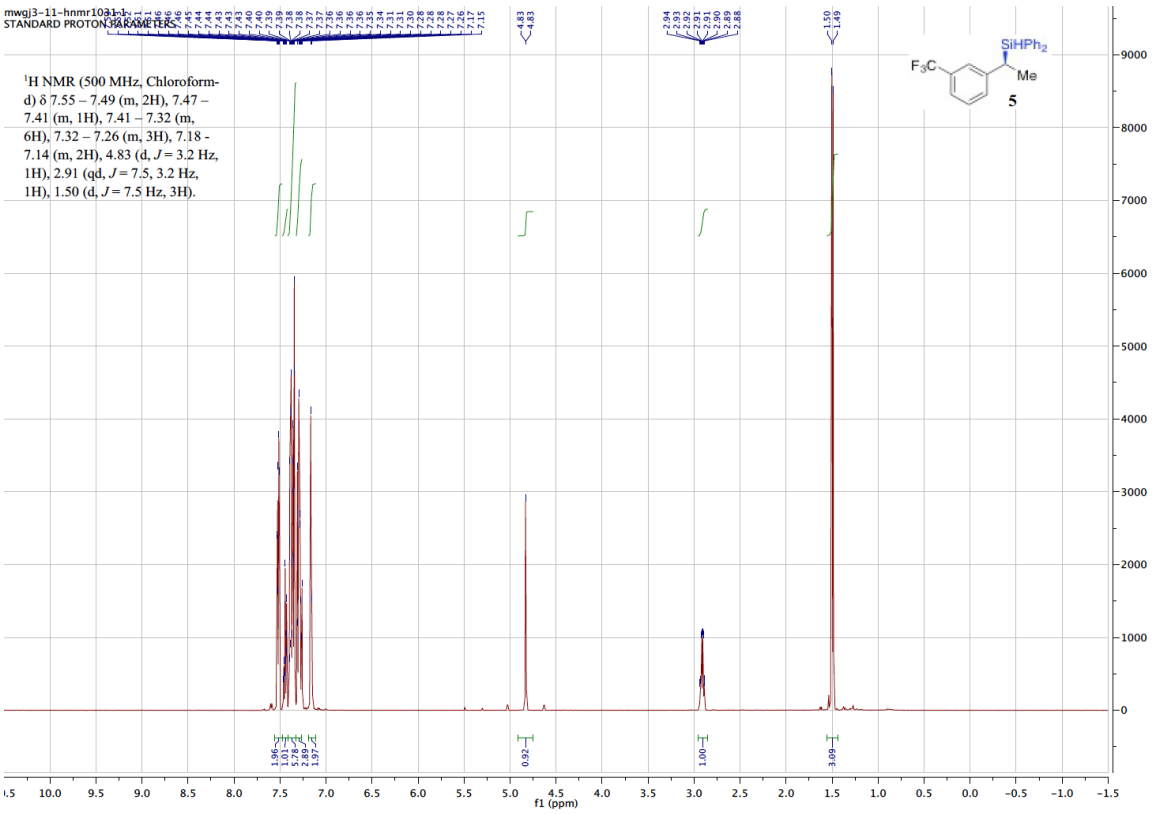



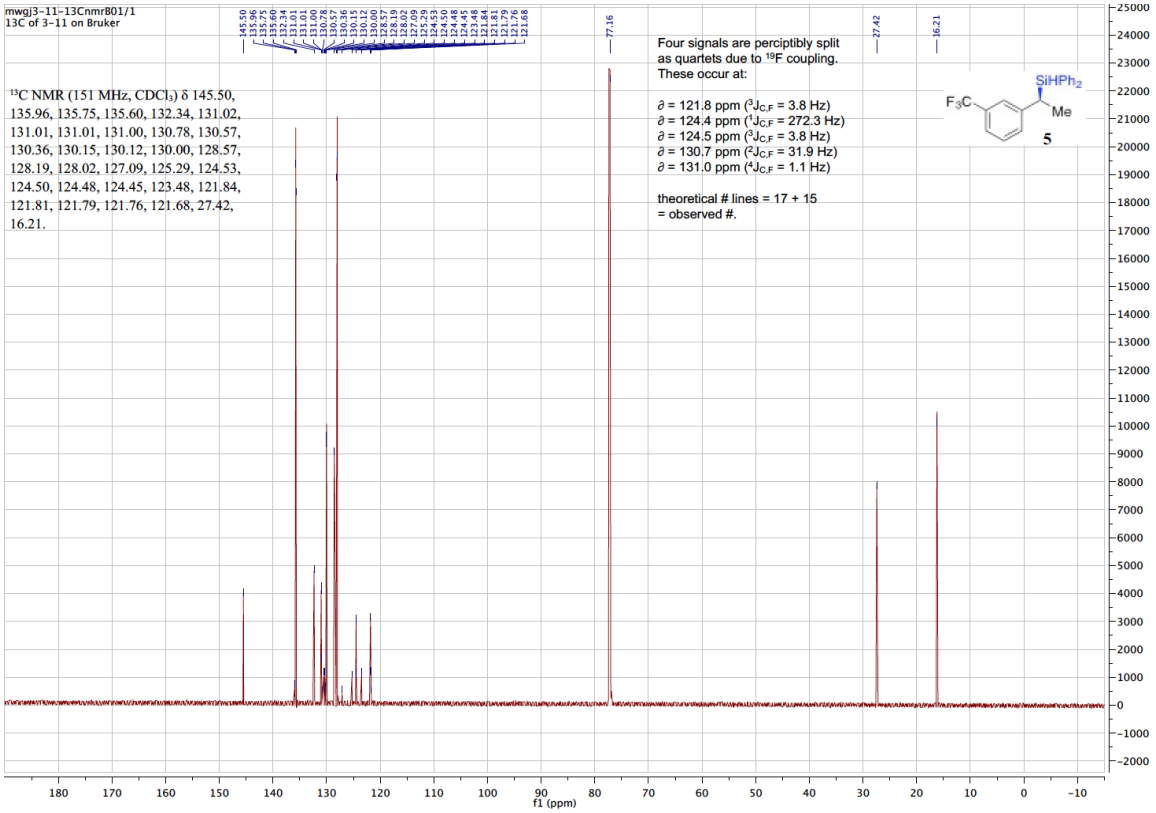
4-methoxybenzyl (*S*)-3-(1-(diphenylsilyl)ethyl)benzoate (**4**):



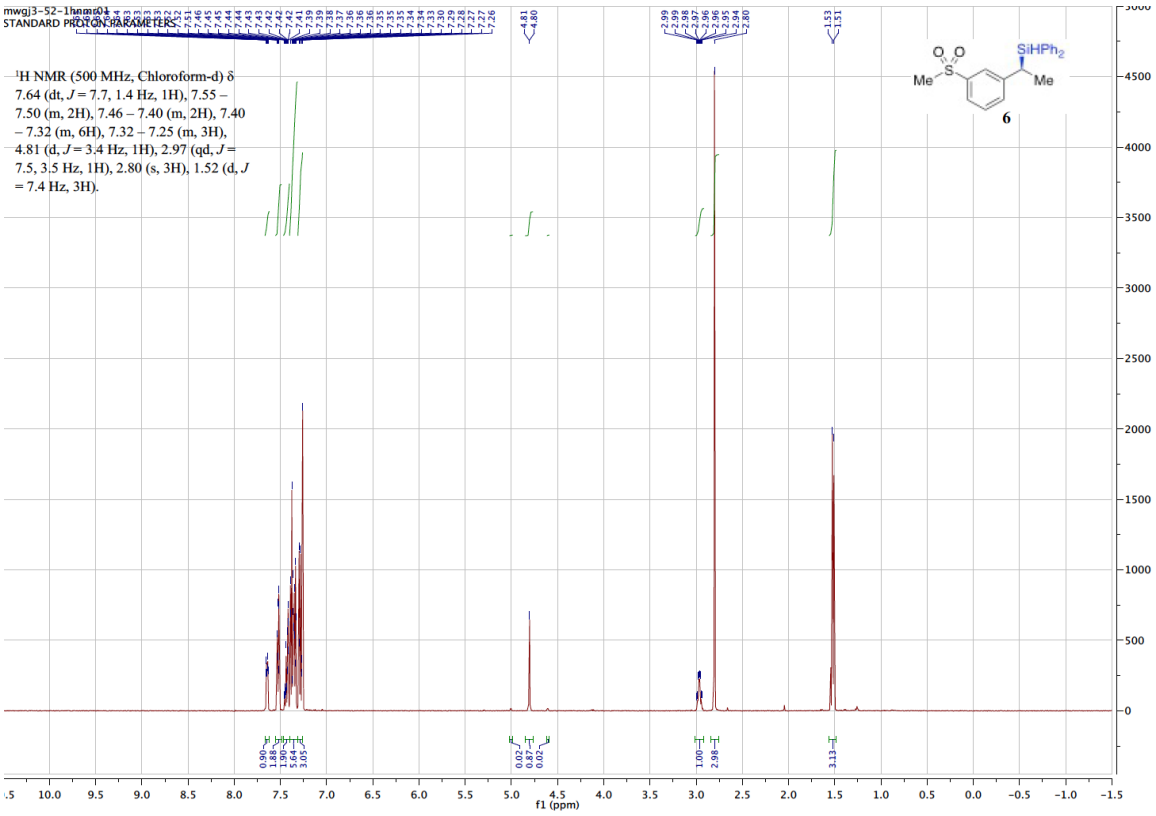



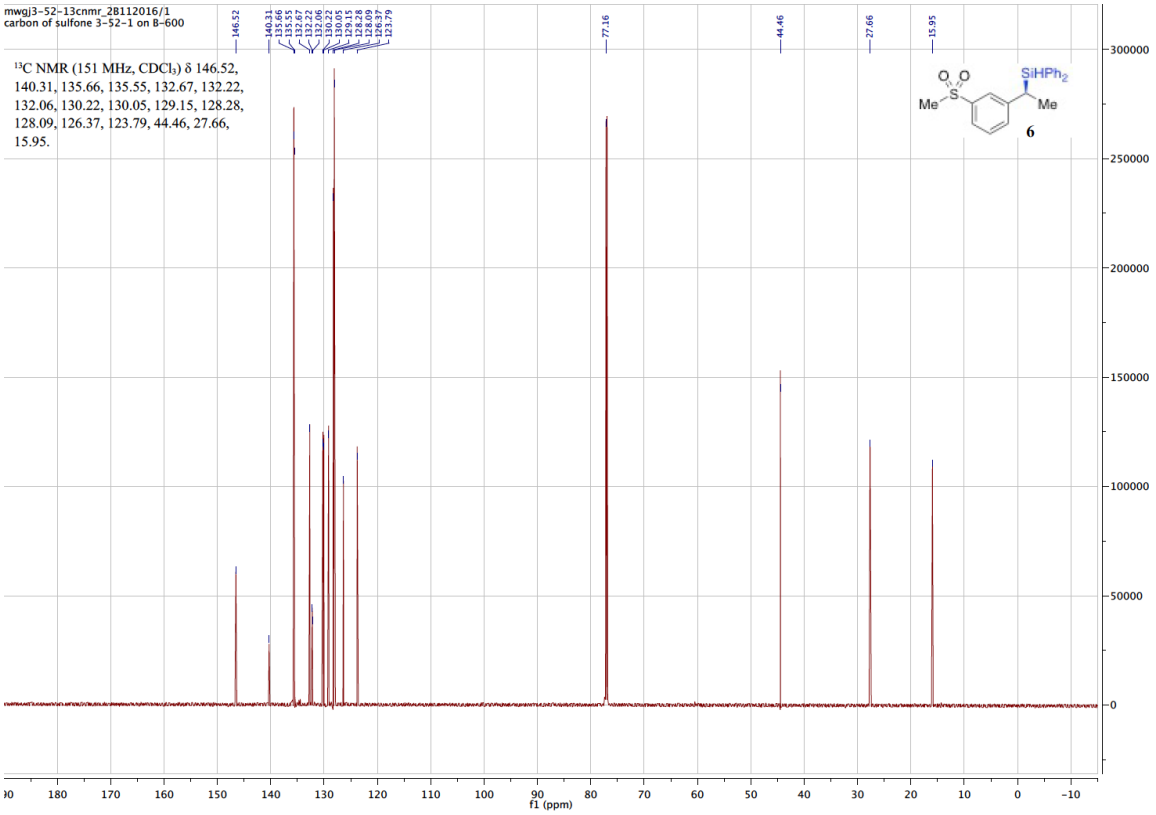
(*S*)-diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silane (**5**)



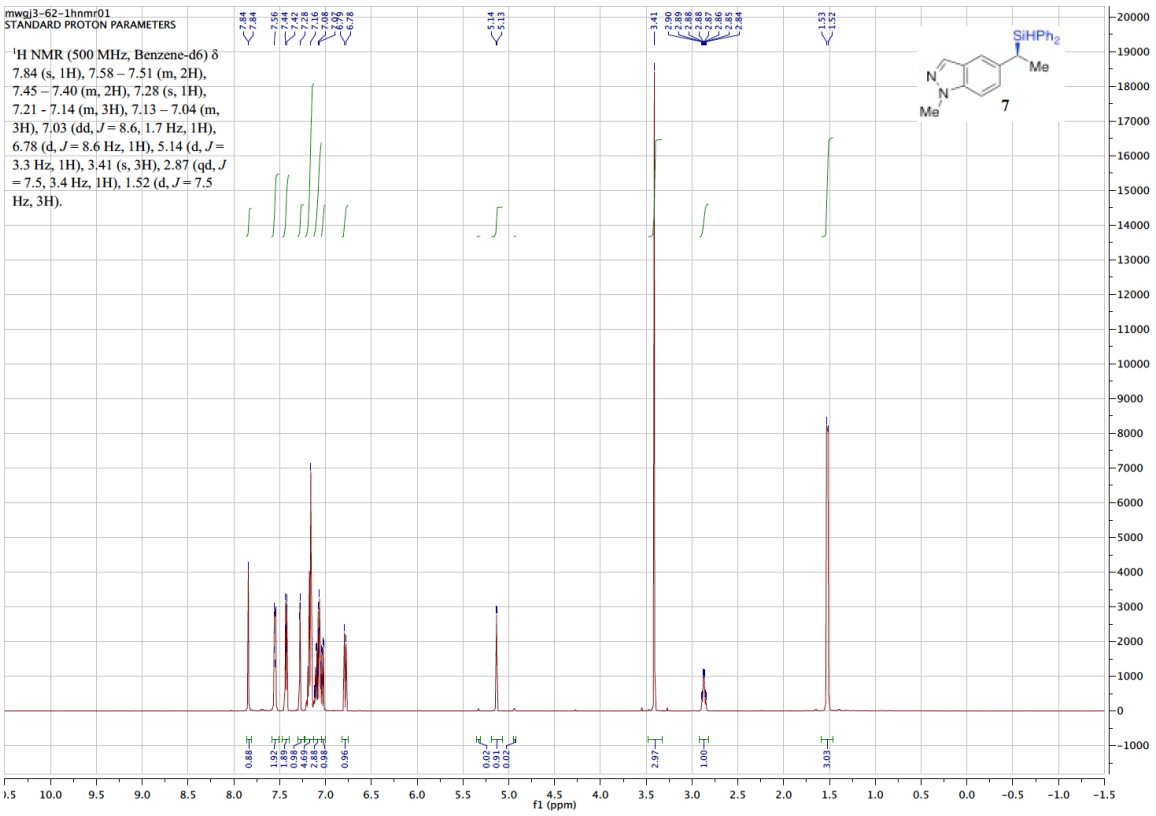



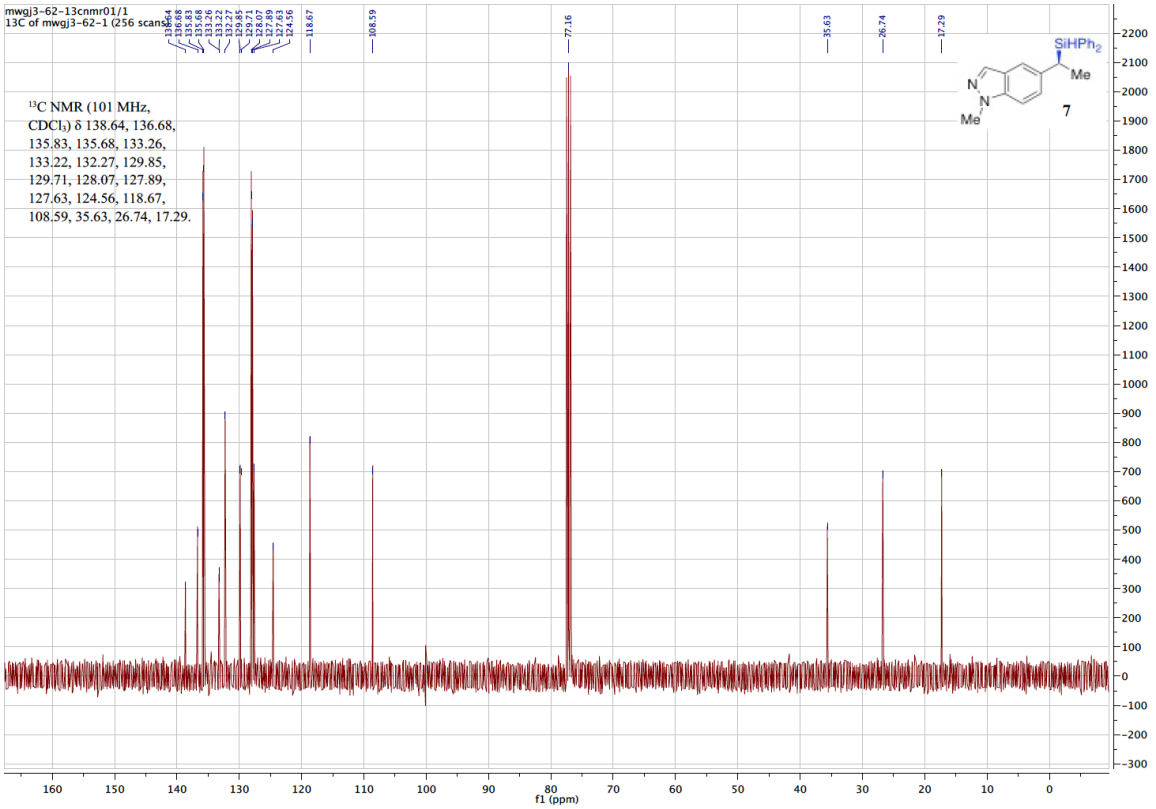
(*S*)-(1-(3-(methylsulfonyl)phenyl)ethyl)diphenylsilane (**6**)



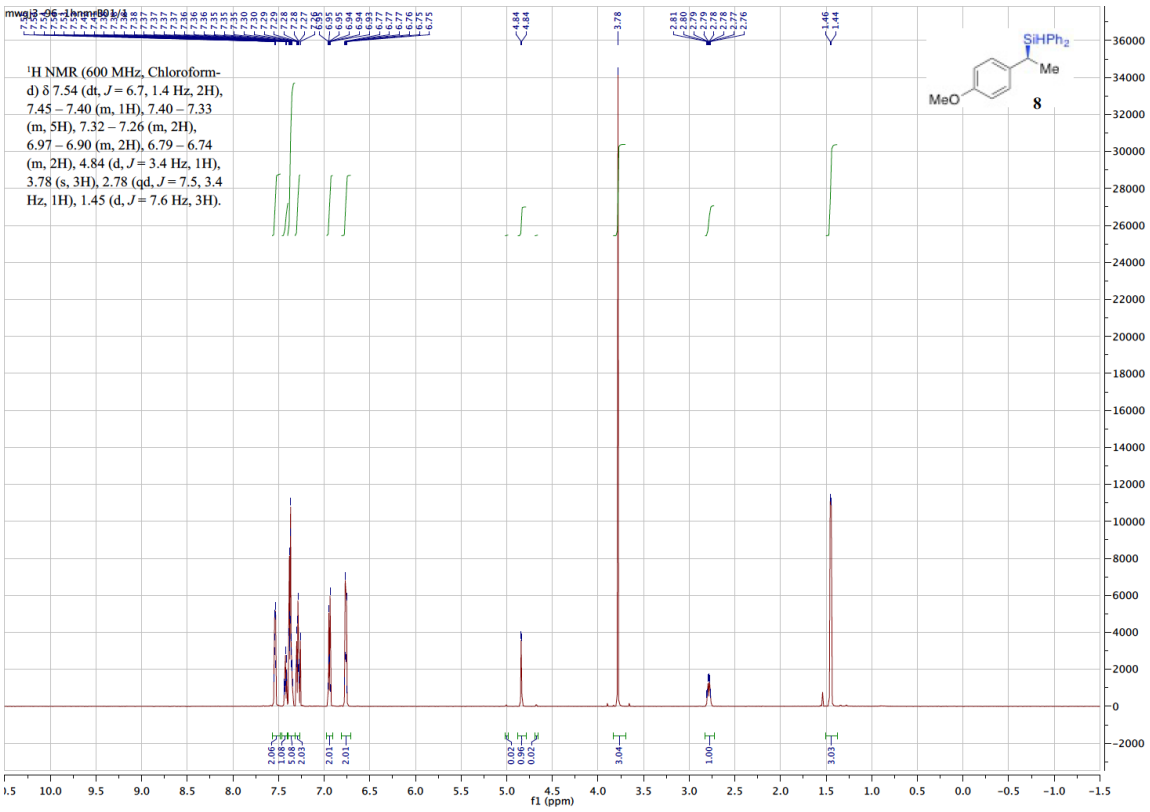



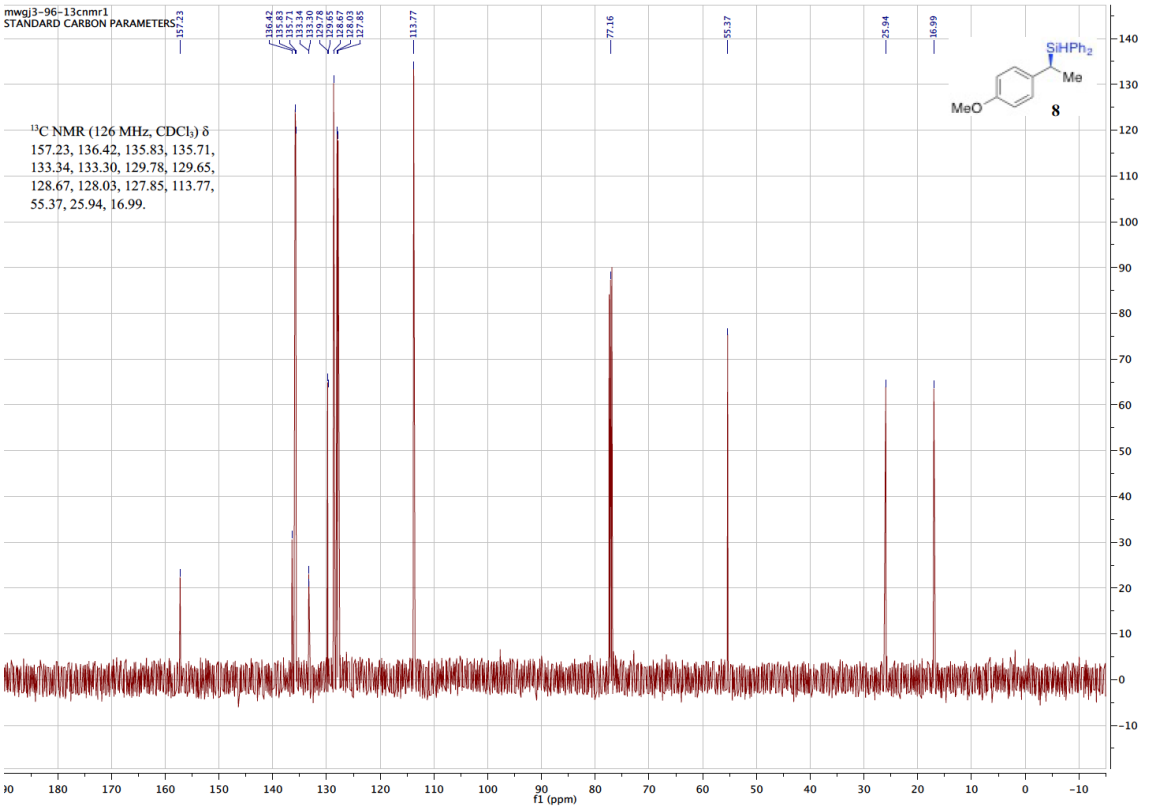
(*S*)-5-(1-(diphenylsilyl)ethyl)-1-methyl-1*H*-indazole (**7**)



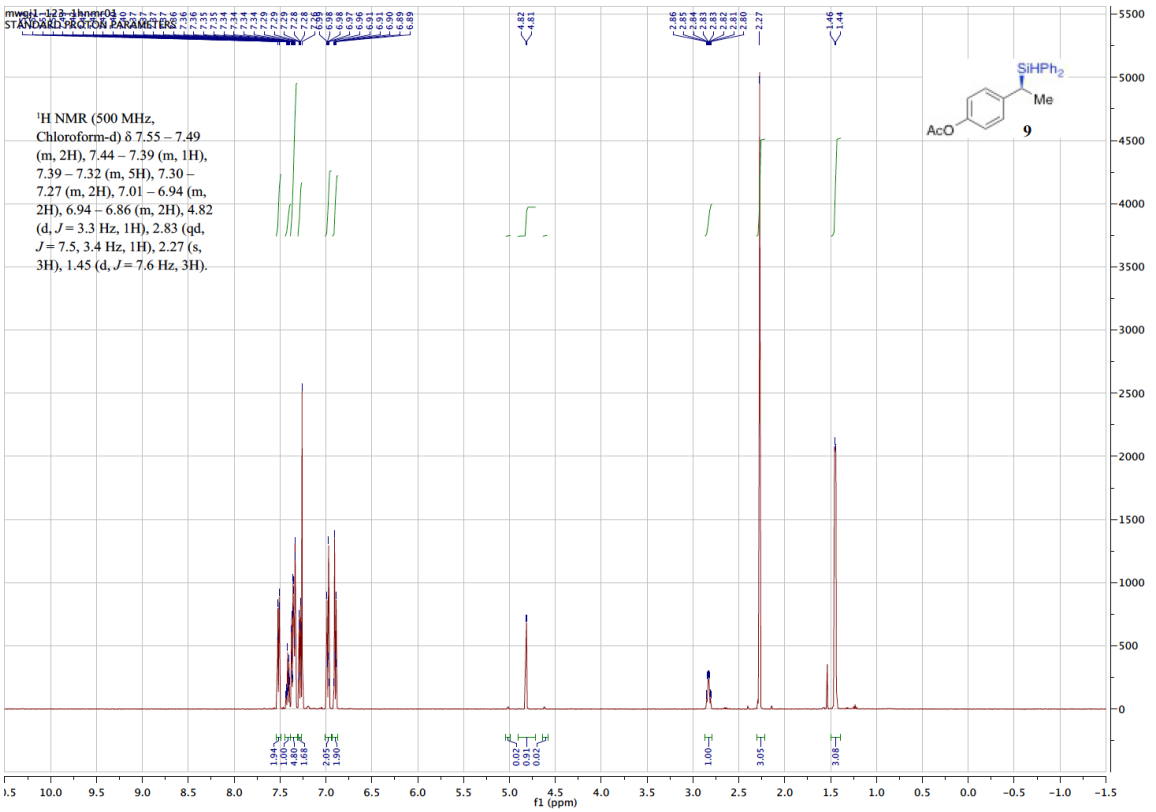



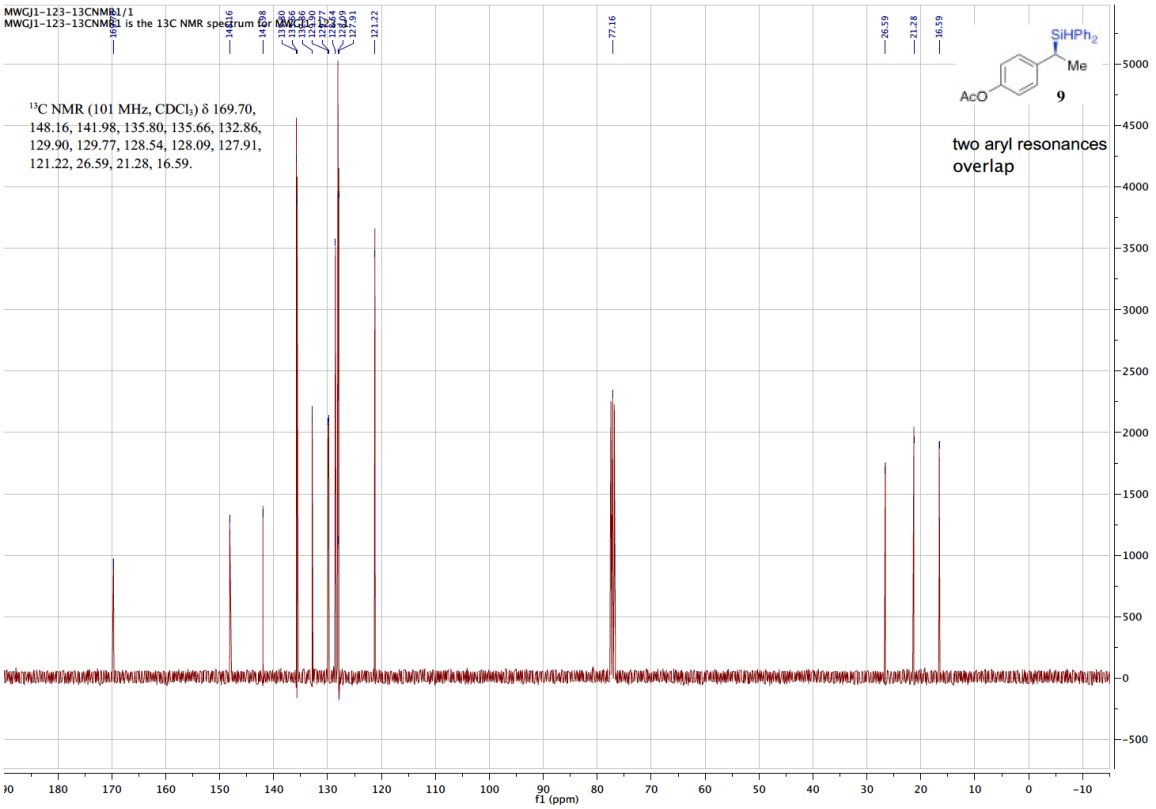
(*S*)-(1-(4-methoxyphenyl)ethyl)diphenylsilane (**8**)



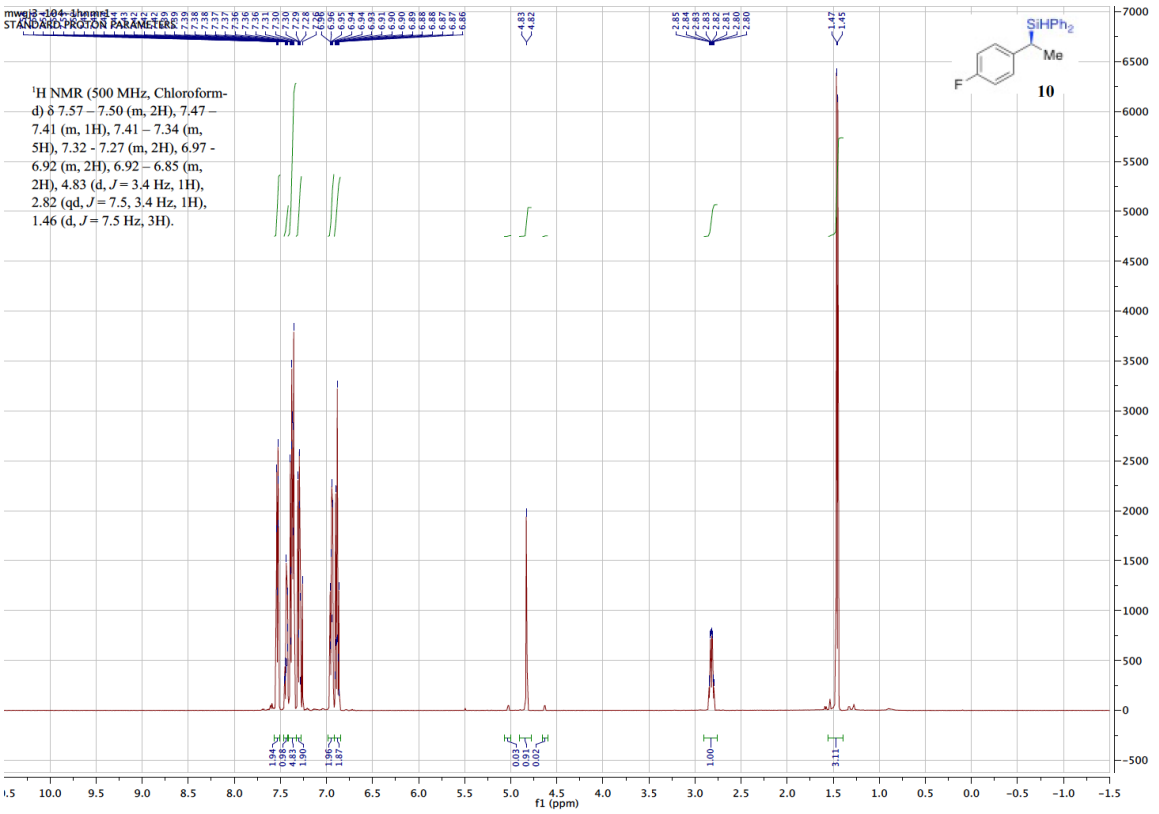



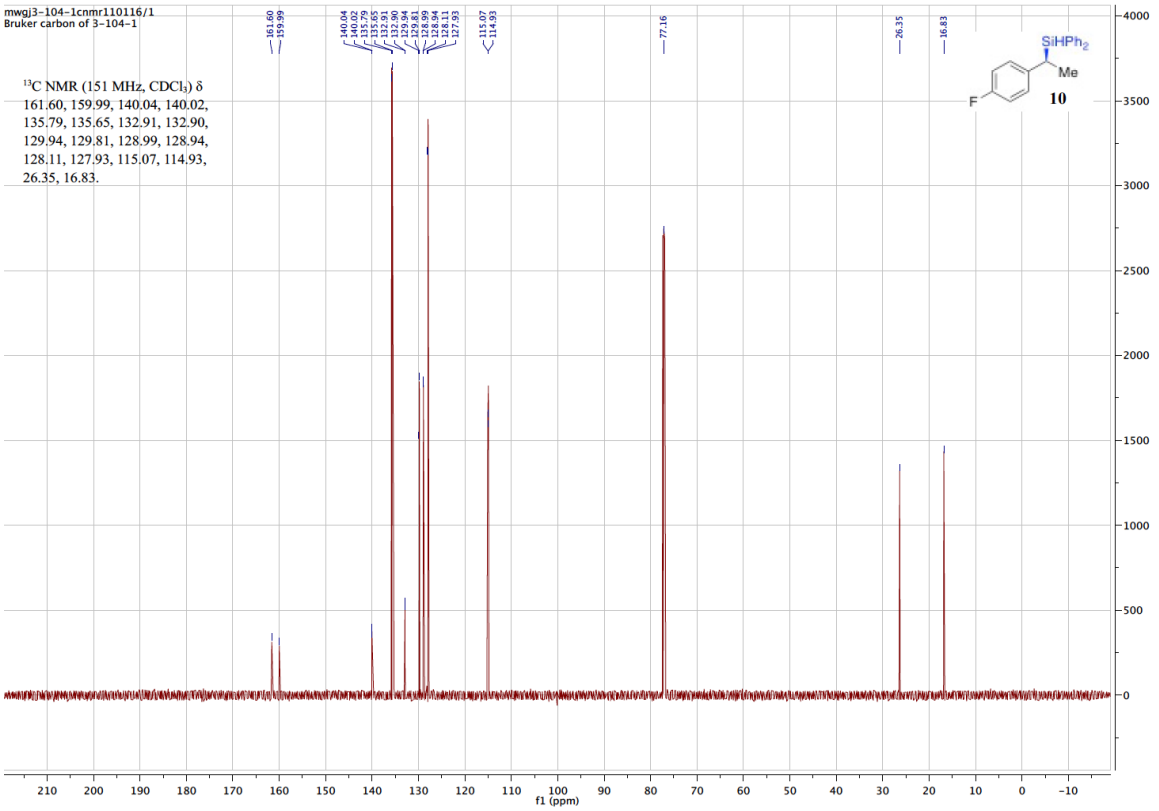
(*S*)-4-(1-(diphenylsilyl)ethyl)phenyl acetate (**9**)



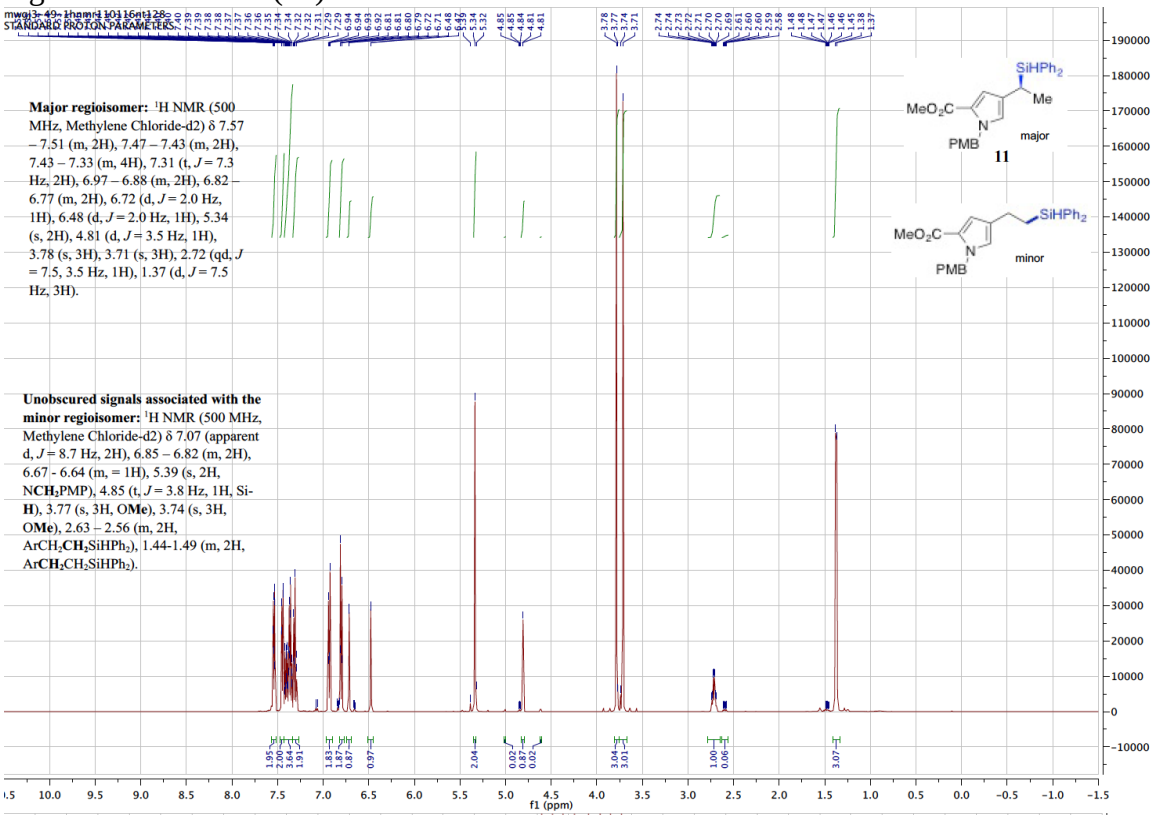



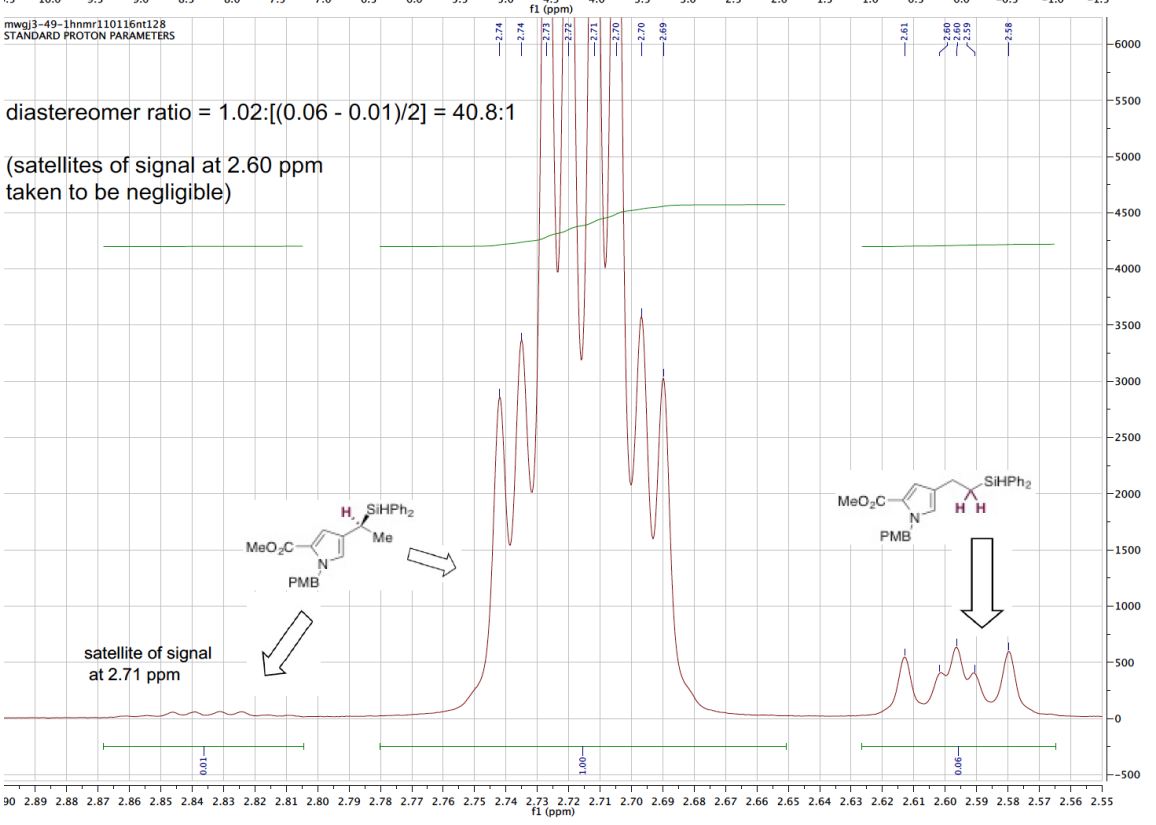
(*S*)-(1-(4-fluorophenyl)ethyl)diphenylsilane **(10)**

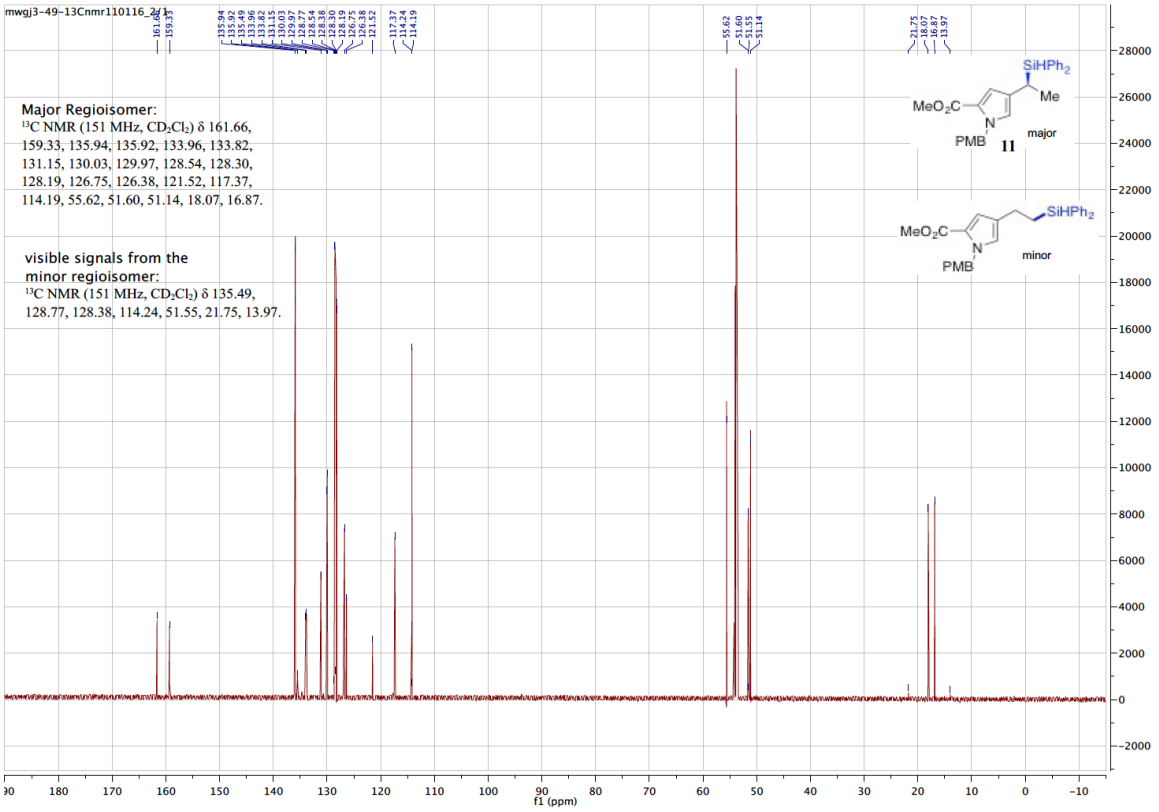


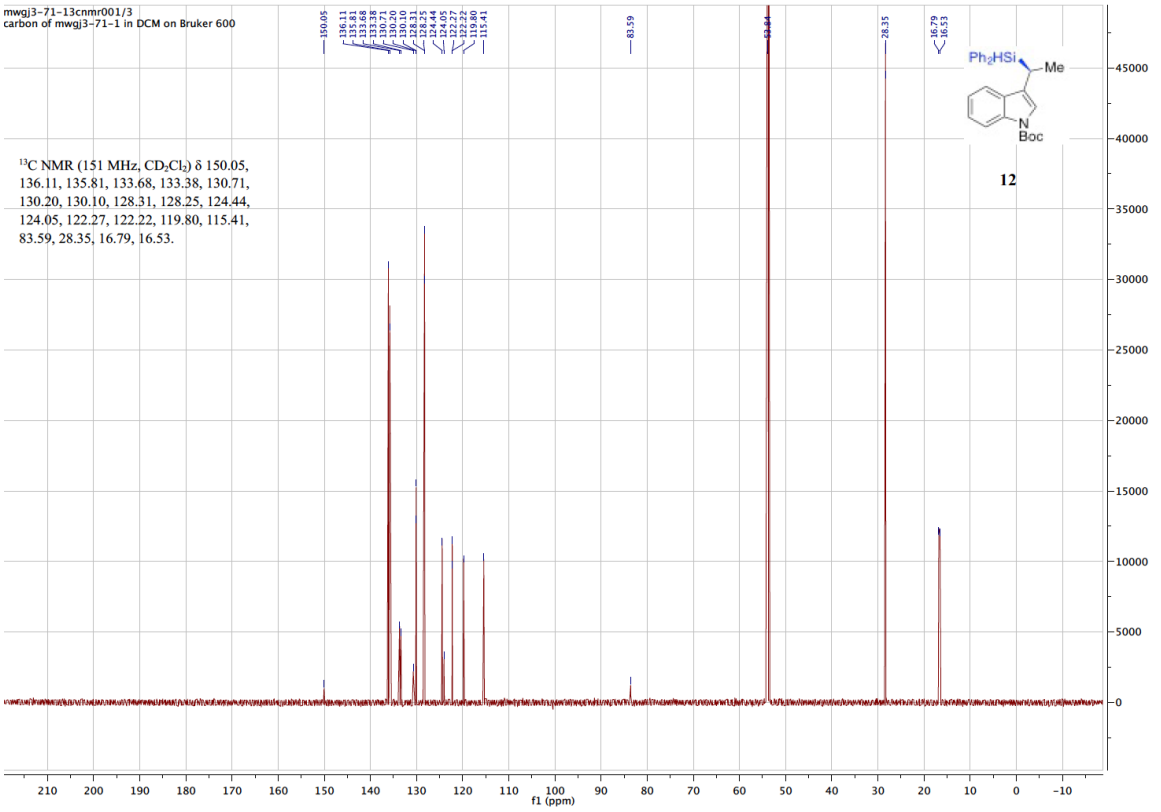
Methyl (*S*)-4-(1-(diphenylsilyl)ethyl)-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate and methyl 4-(2-(diphenylsilyl)ethyl)-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate, 41:1 regioisomer mixture (**11**)



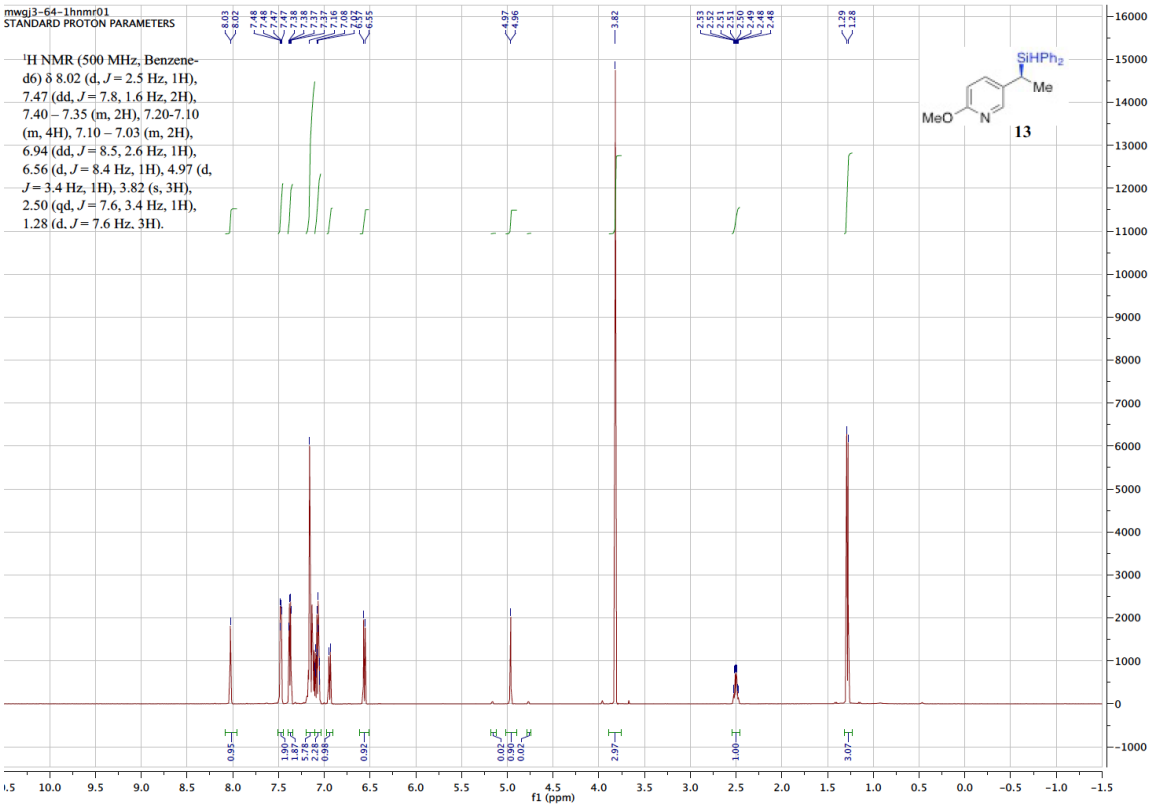



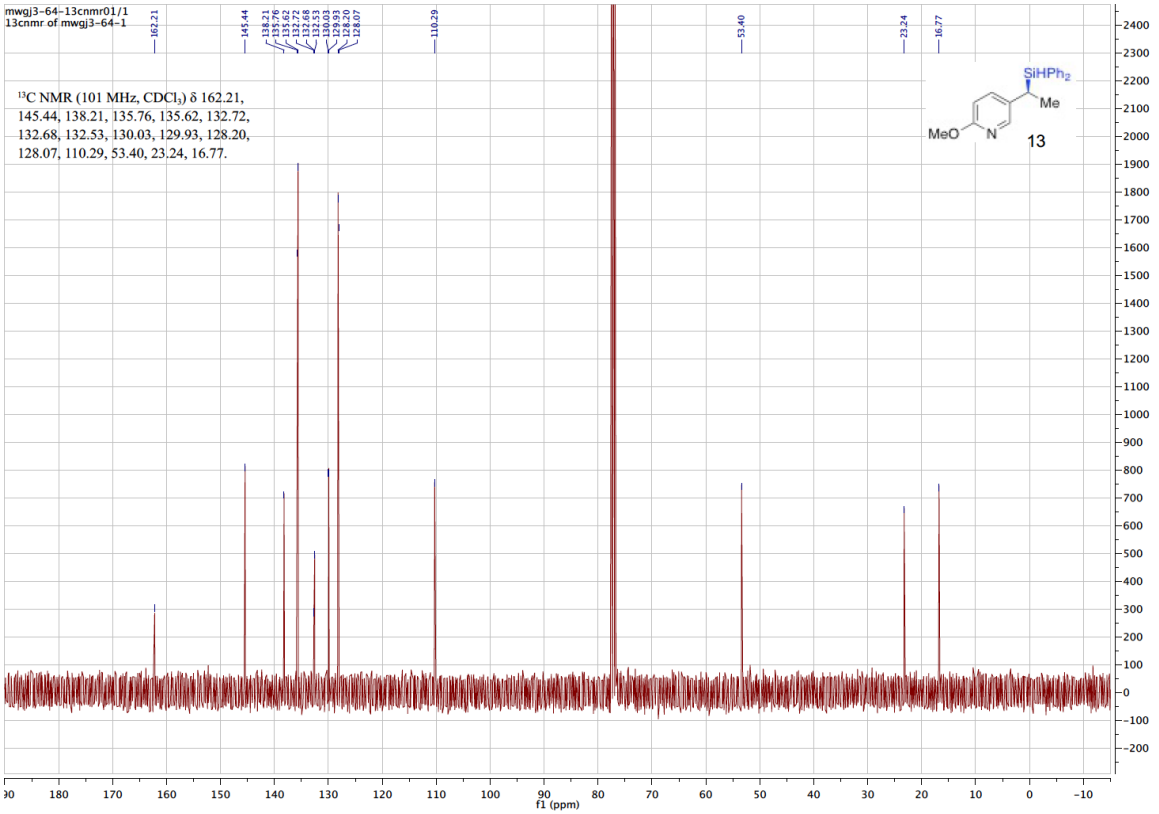

mwgj3-49-13Cnmr110116_2/1
Major Regioisomer:
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 161.66, 159.33, 135.94, 135.92, 133.96, 133.82, 131.15, 130.03, 129.97, 128.54, 128.30, 128.19, 126.75, 126.38, 121.52, 117.37, 114.19, 55.62, 51.60, 51.14, 18.07, 16.87.
visible signals from the minor regioisomer:
$^{13}$C NMR (151 MHz, $CD_2Cl_2$) δ 135.49, 128.77, 128.38, 114.24, 51.55, 21.75, 13.97.
SiHPh2
Me
MeO2C
N
PMB
major
11
SiHPh2
MeO2C
N
PMB
minor
f1 (ppm)

*Tert*-butyl (*S*)-3-(1-(diphenylsilyl)ethyl)-1*H*-indole-1-carboxylate (**12**):

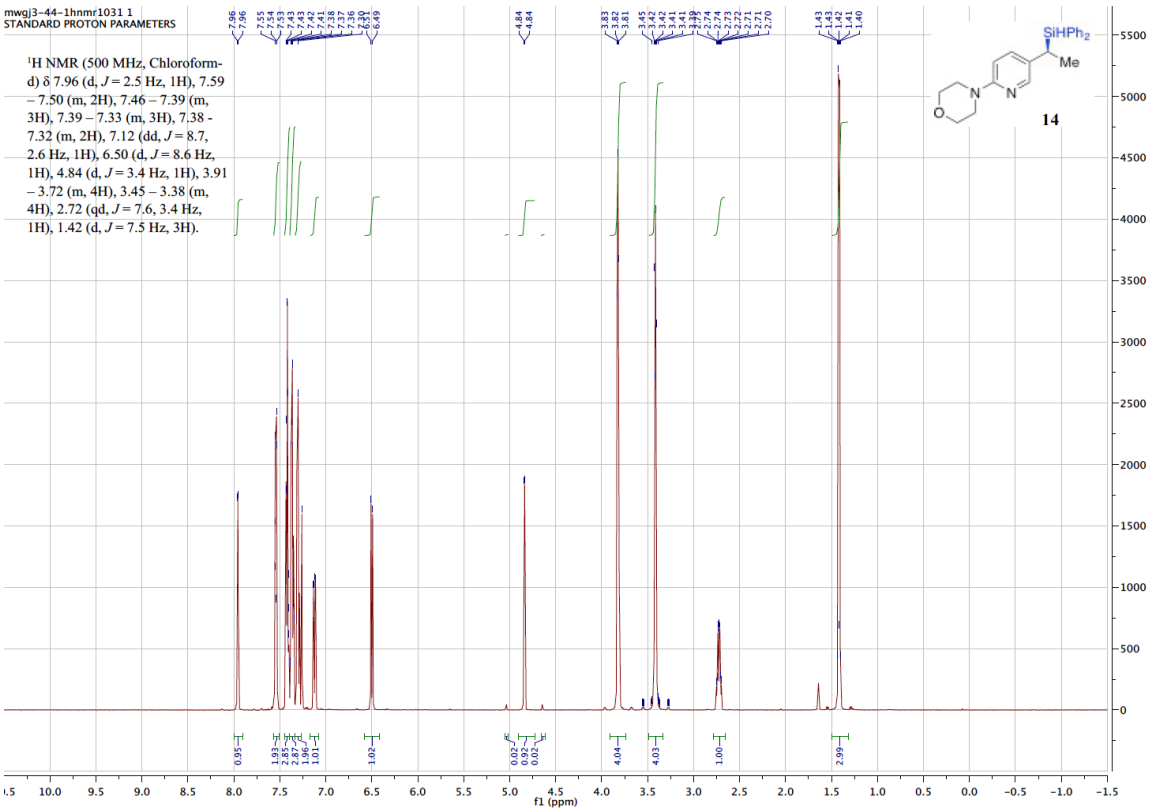



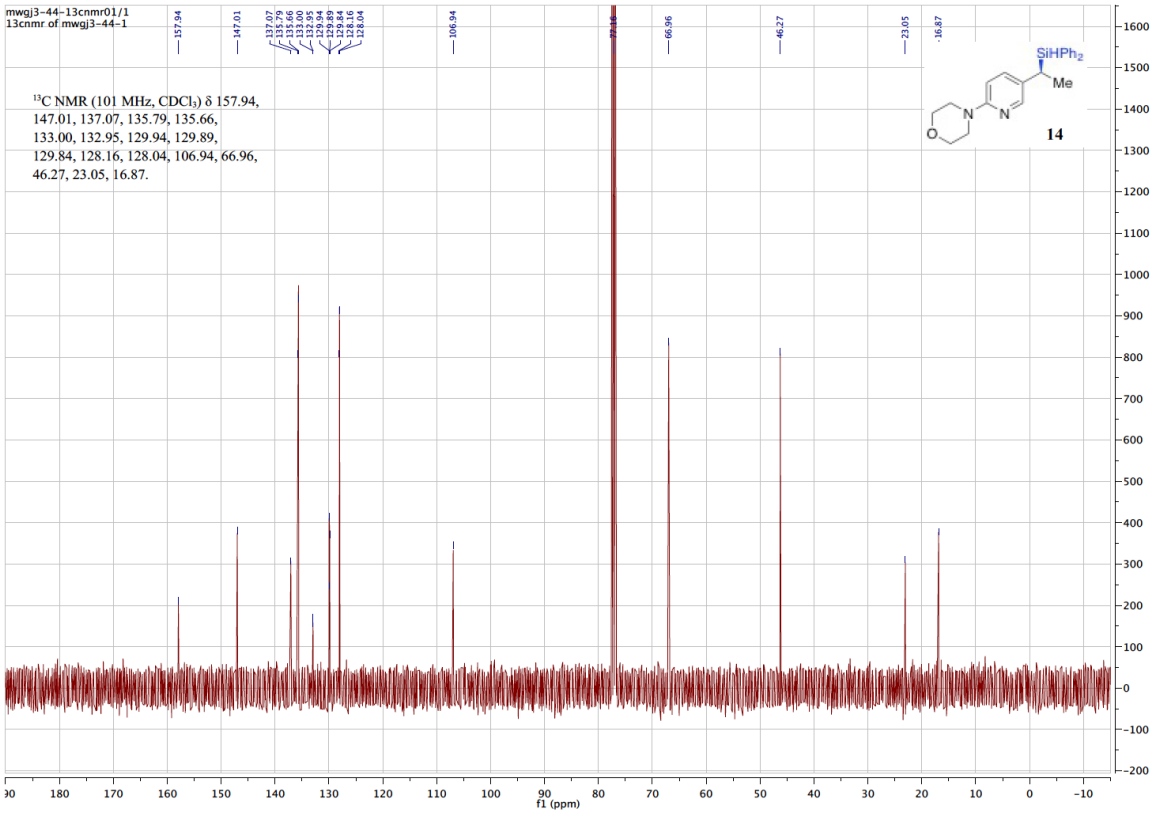
(*S*)-5-(1-(diphenylsilyl)ethyl)-2-methoxypyridine (**13**)



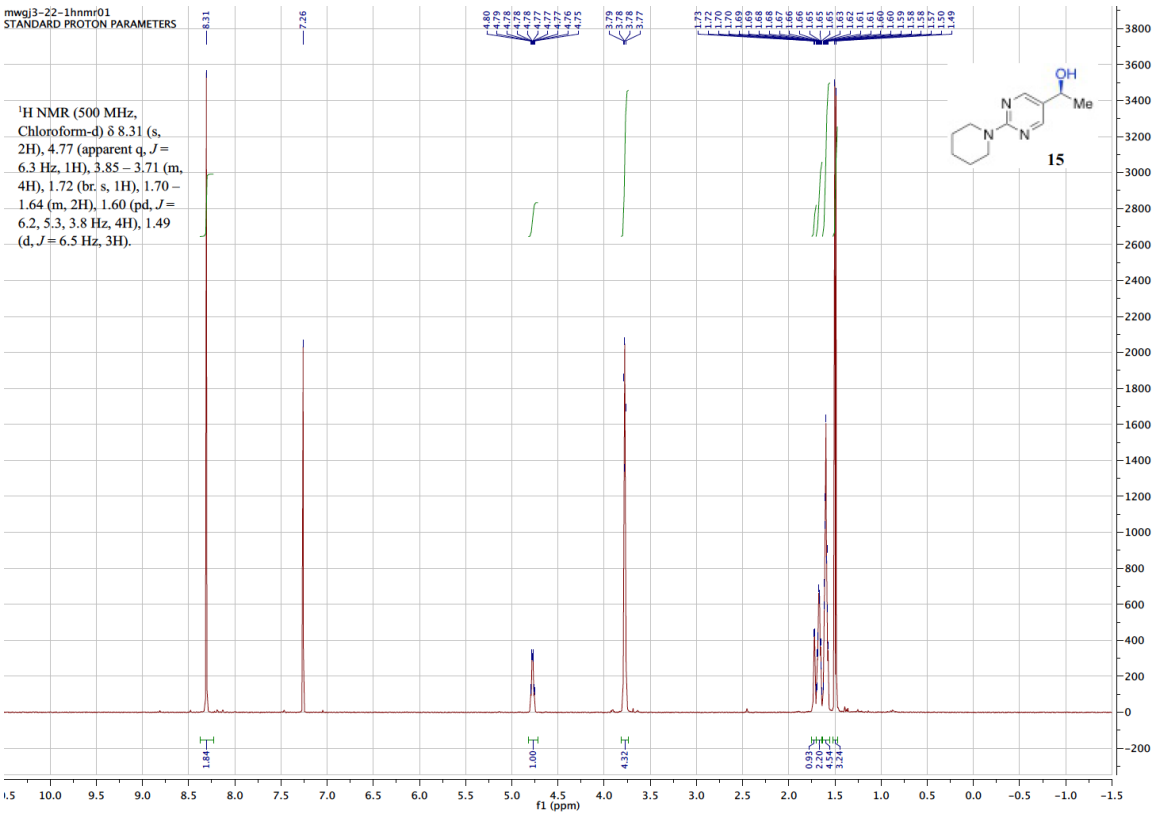



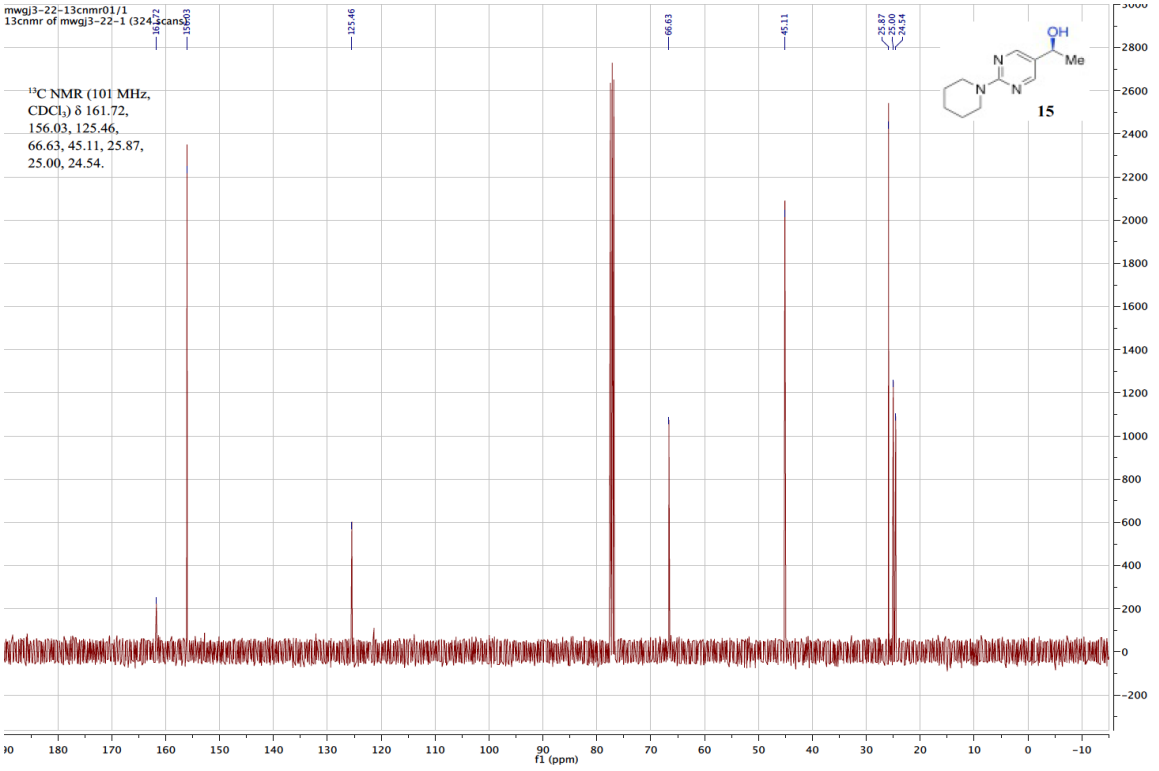
(*S*)-4-(5-(1-(diphenylsilyl)ethyl)pyridin-2-yl)morpholine (**14**)



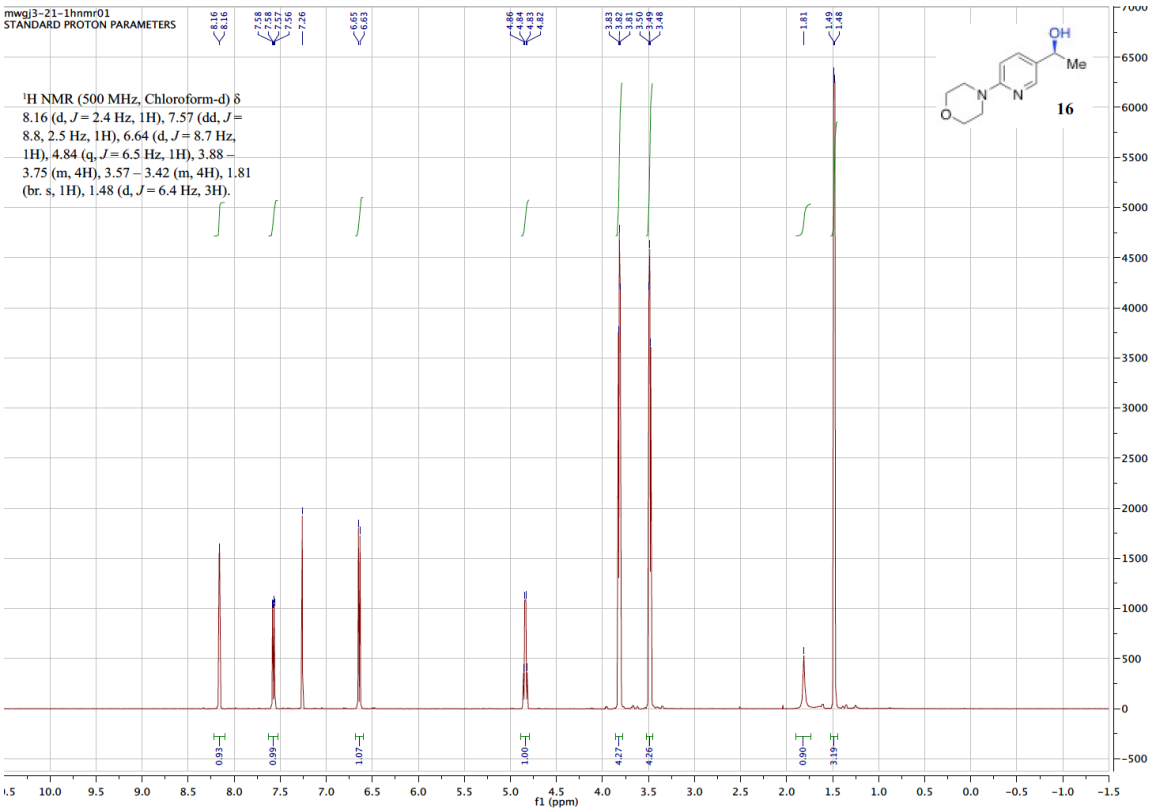



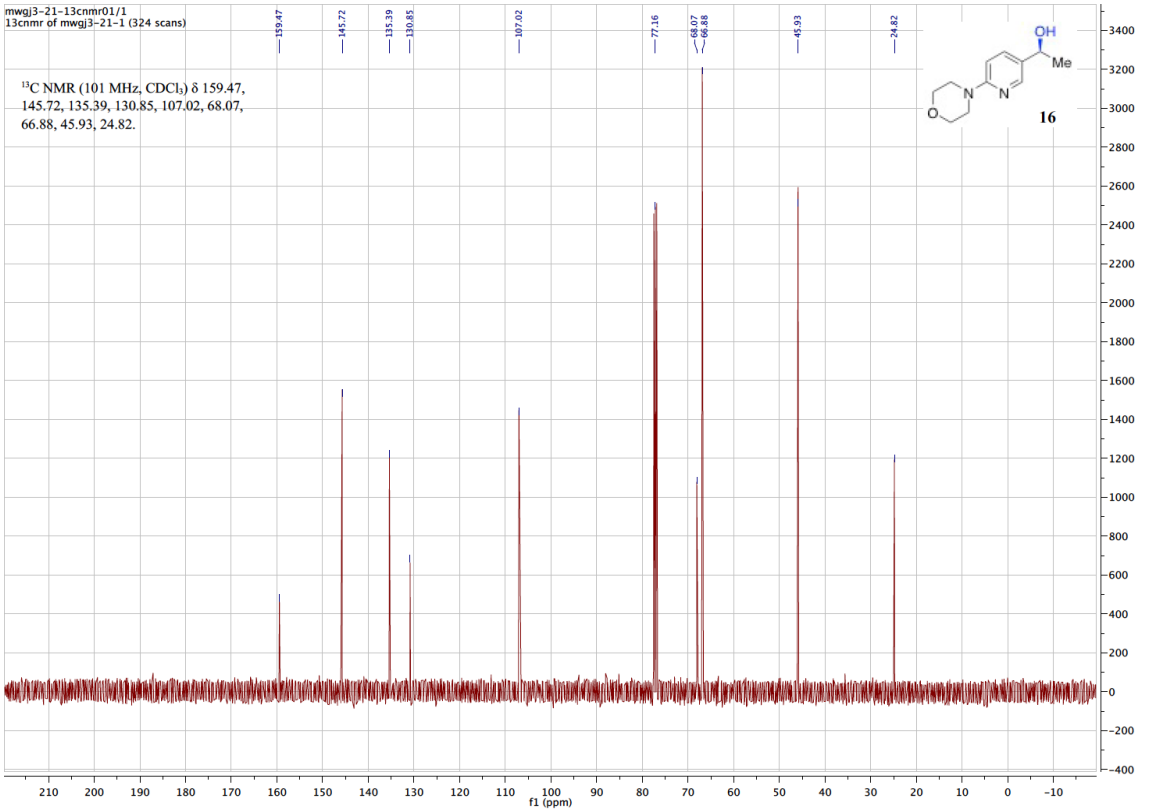
(*S*)-1-(2-(piperidin-1-yl)pyrimidin-5-yl)ethan-1-ol (**15**)



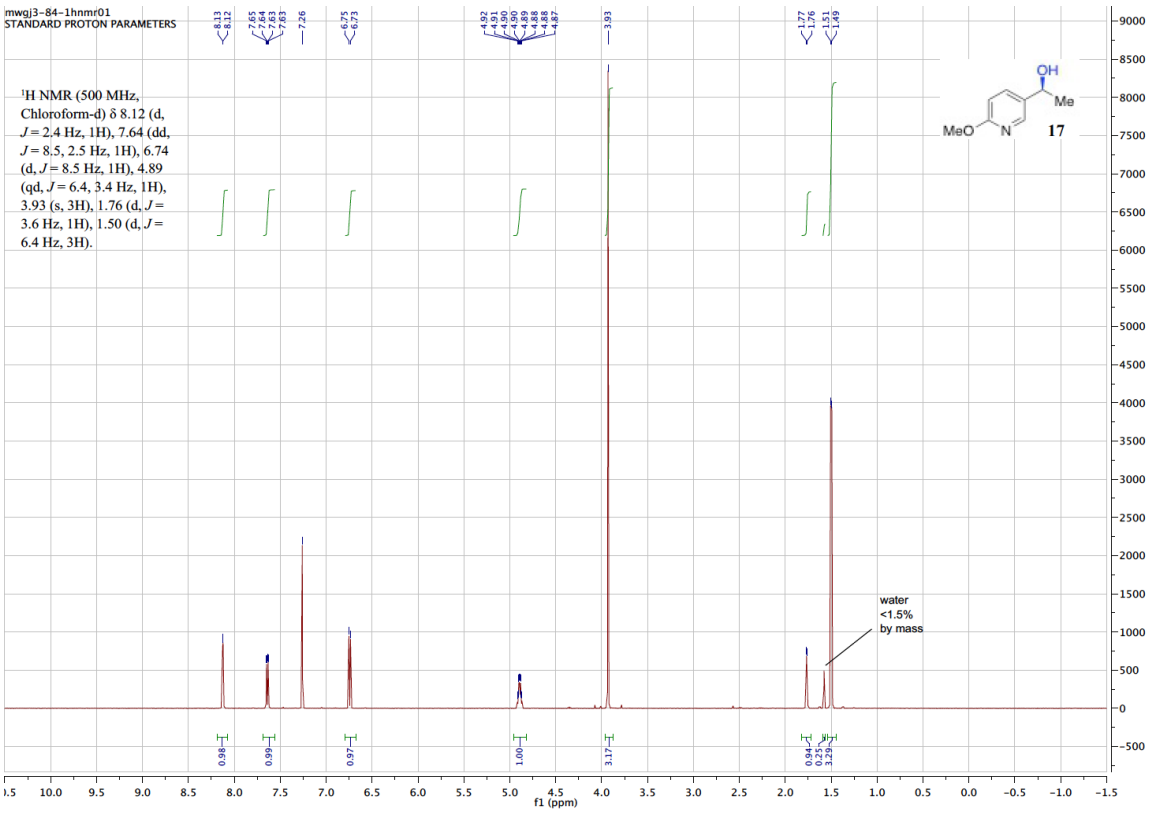



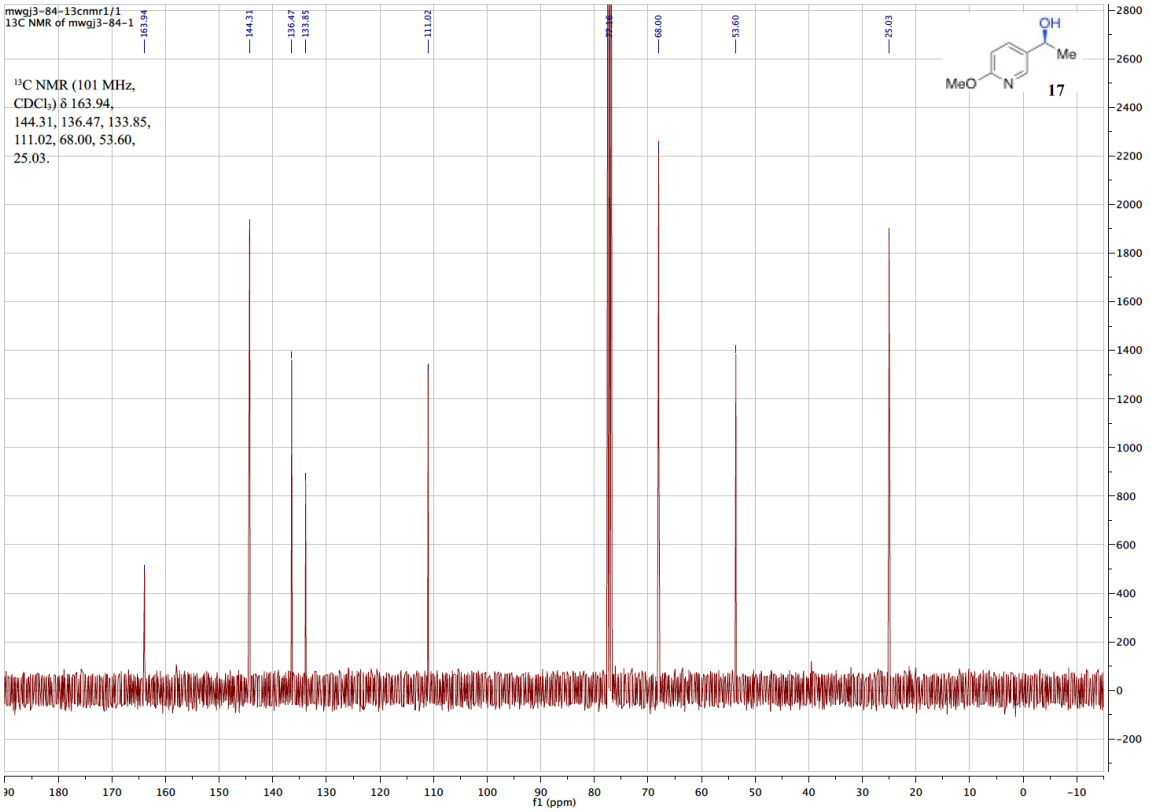
(*S*)-1-(6-morpholinopyridin-3-yl)ethan-1-ol (**16**)



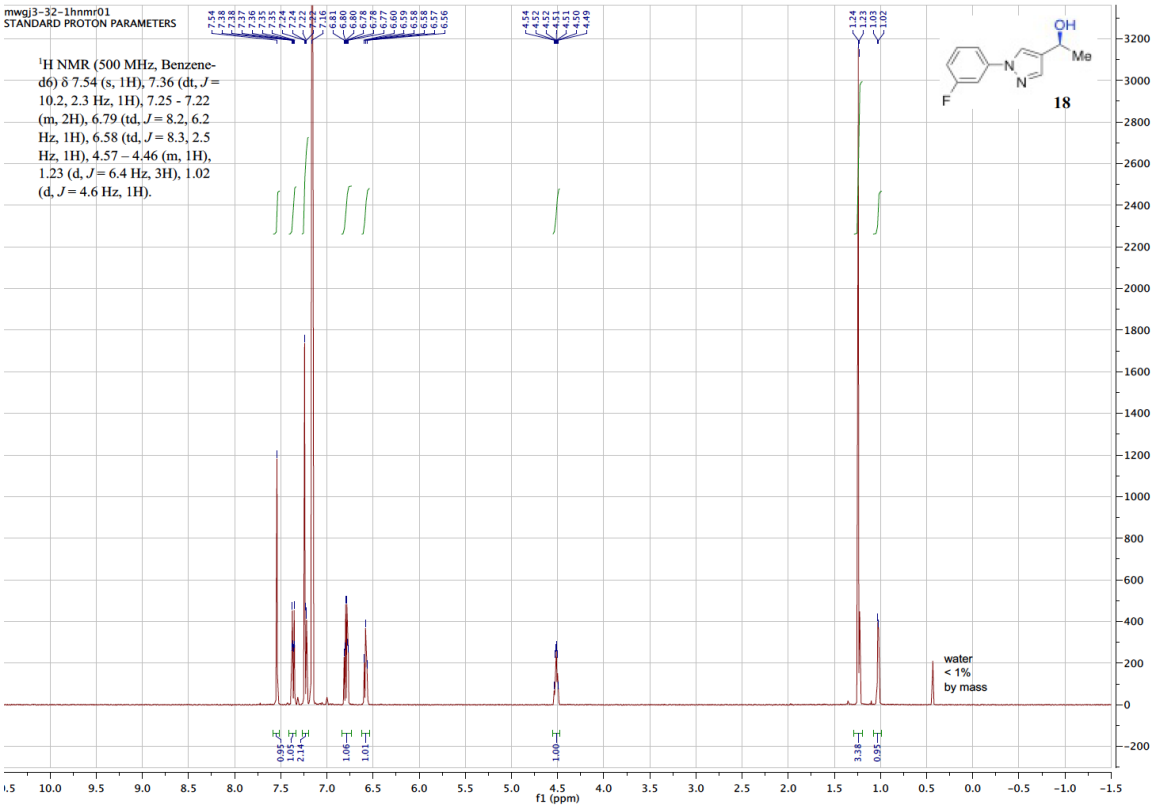



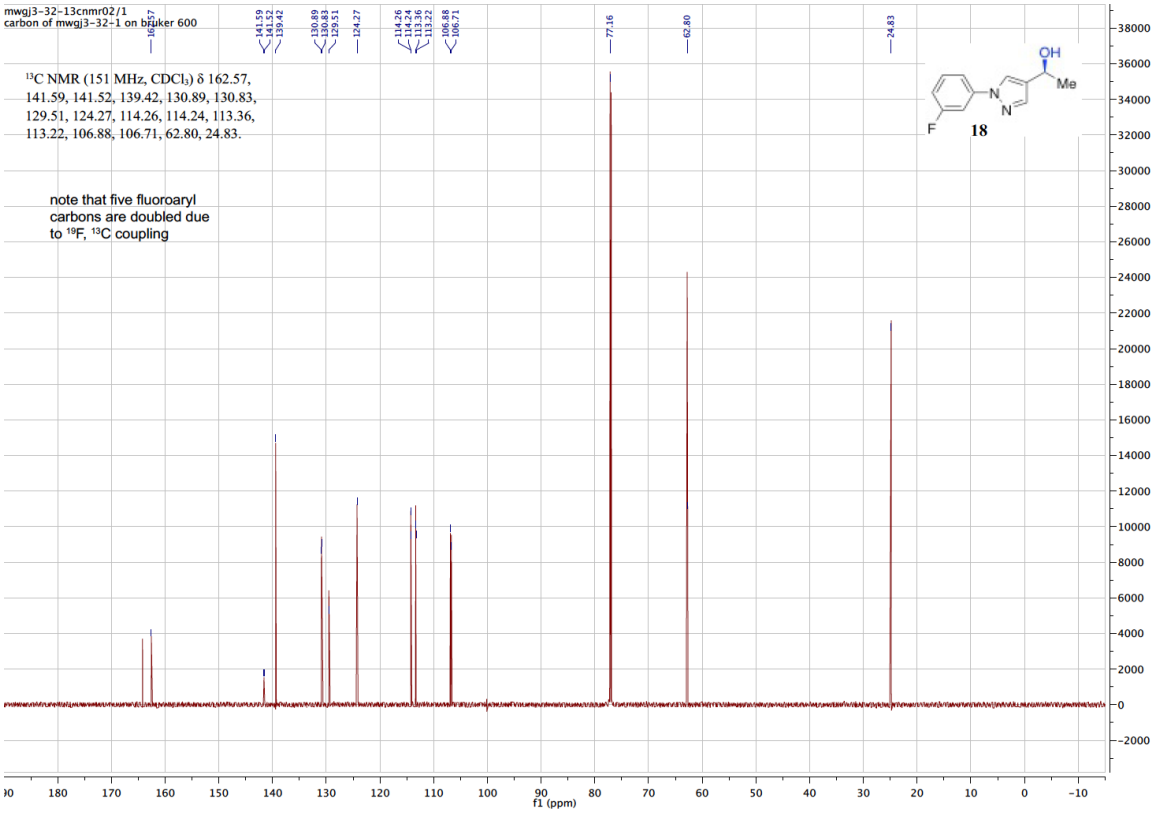
(*S*)-1-(6-methoxypyridin-3-yl)ethan-1-ol (**17**)



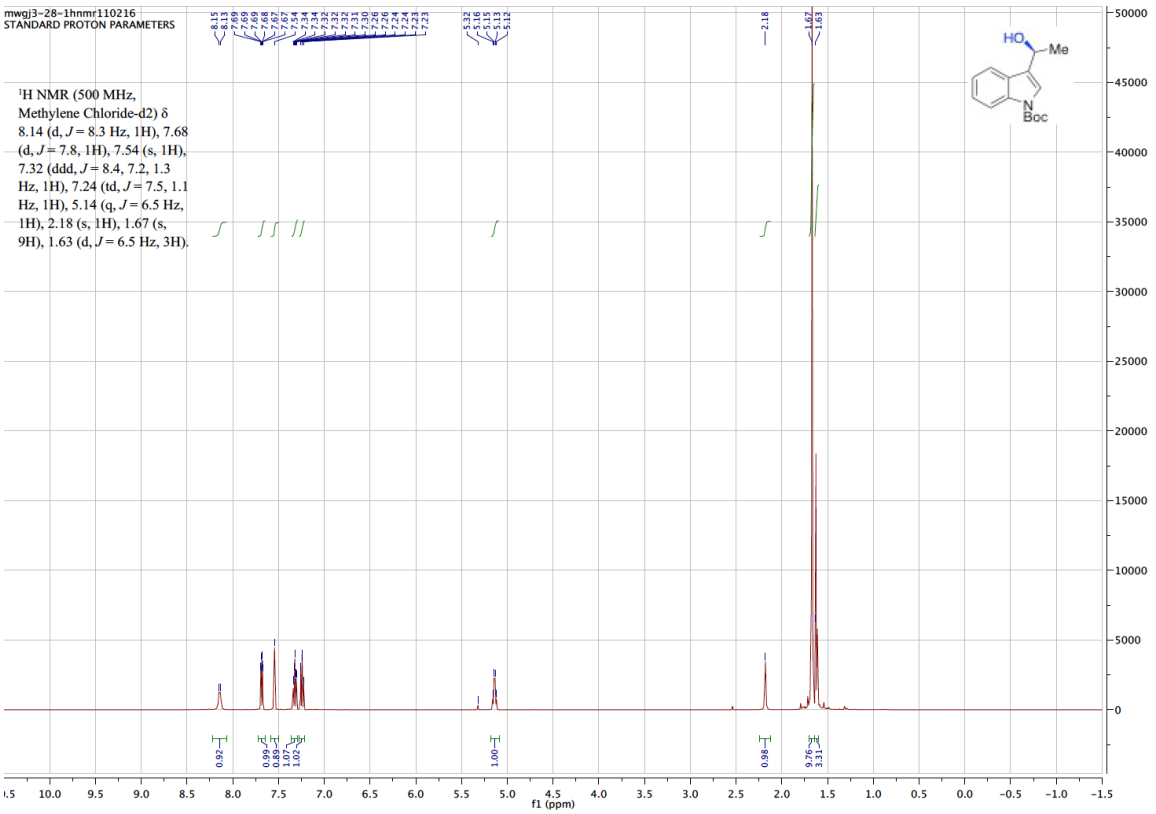



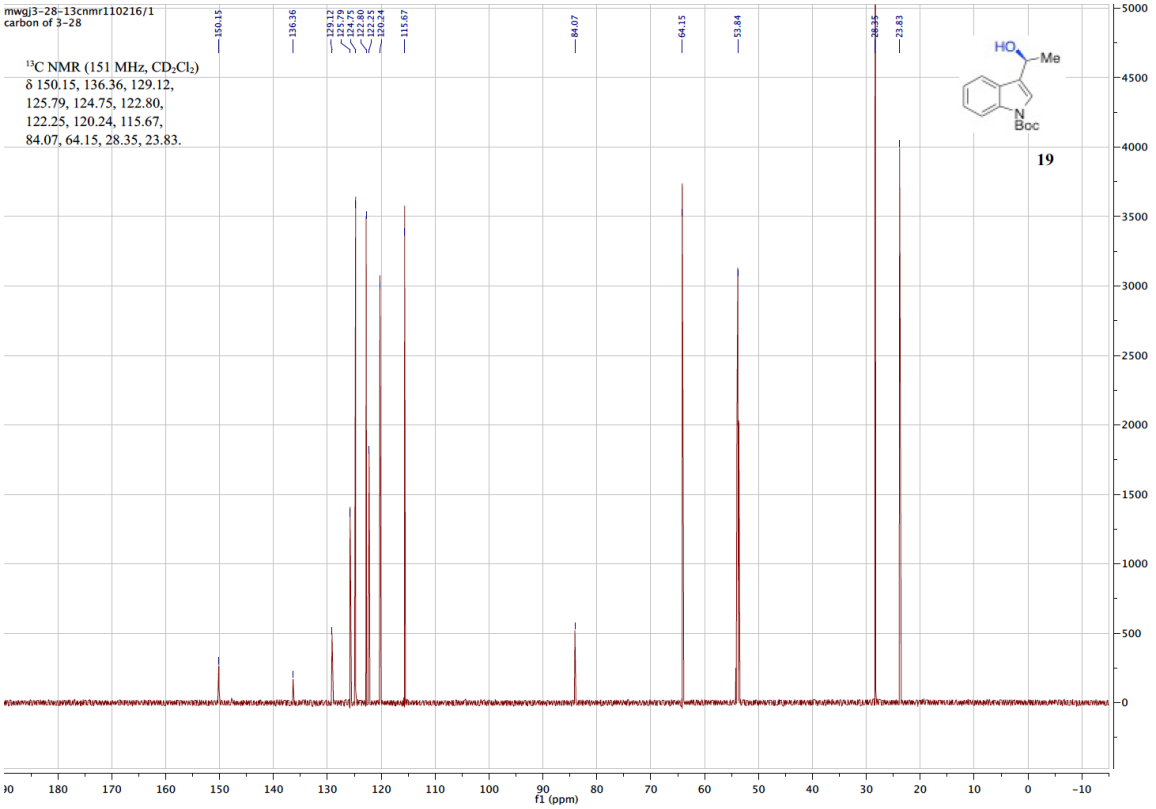
(*S*)-1-(1-(3-fluorophenyl)-1*H*-pyrazol-4-yl)ethan-1-ol (**18**)



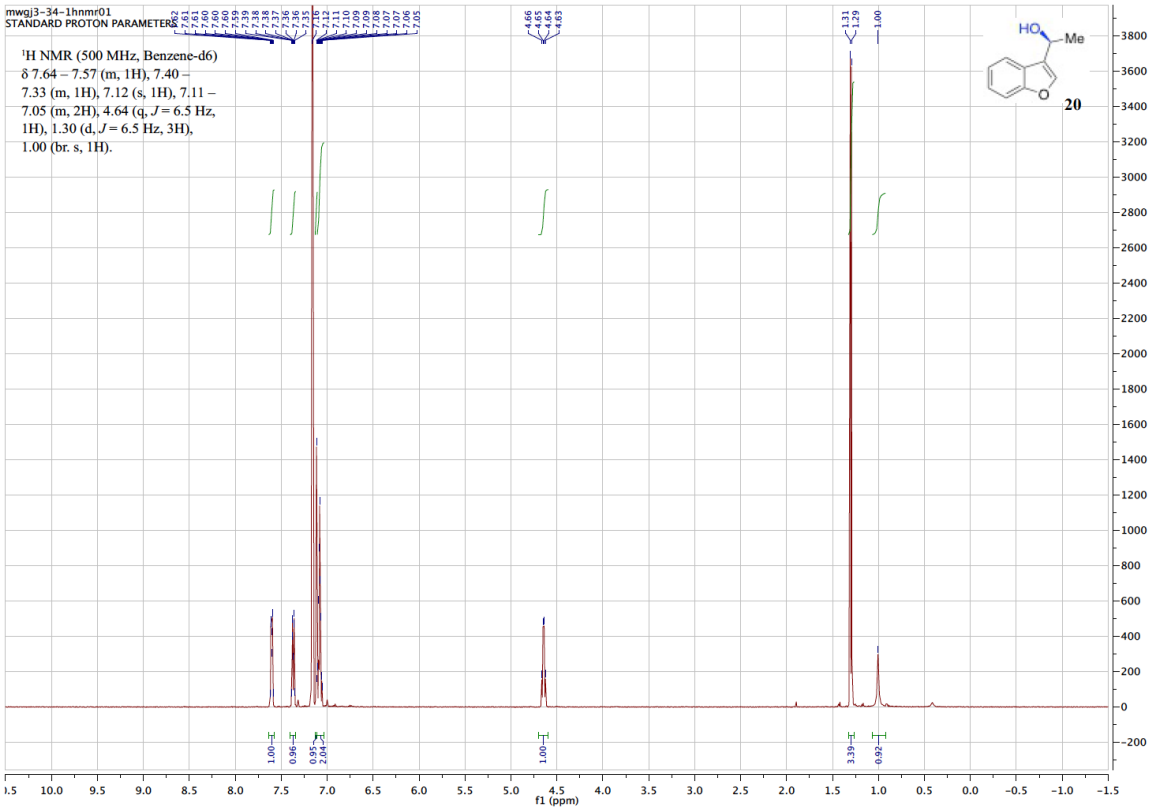



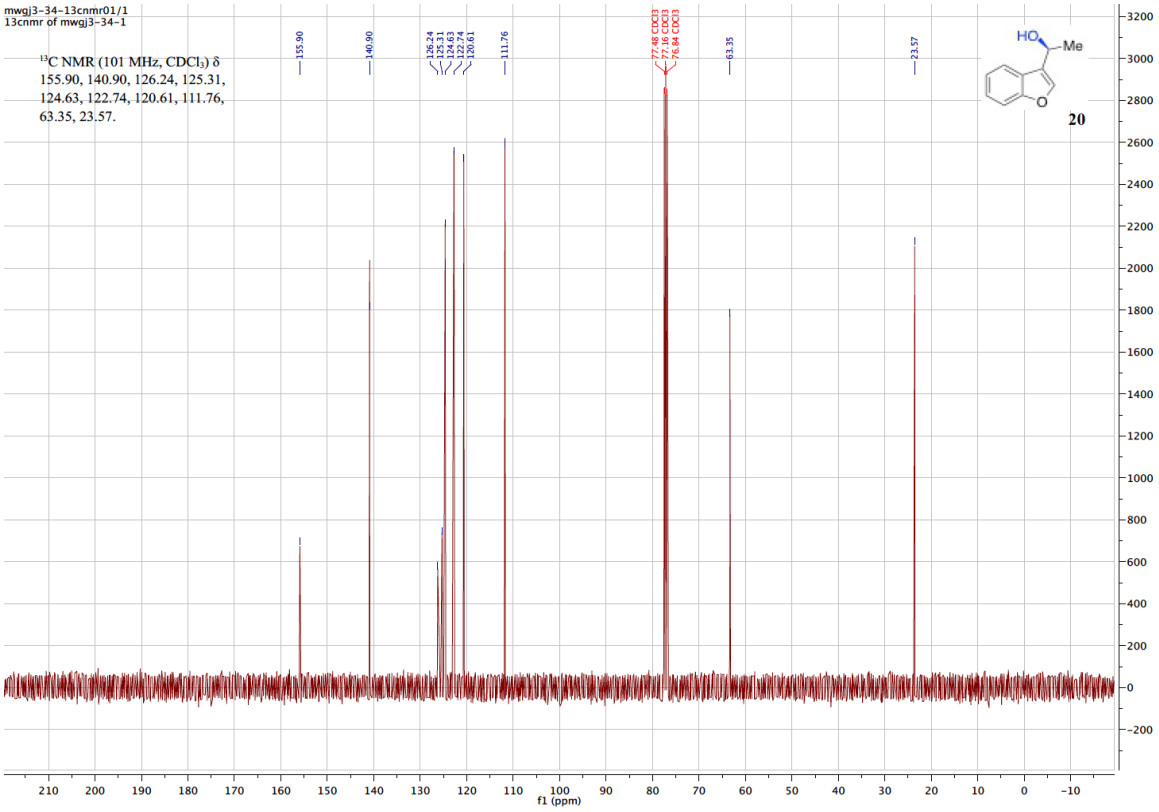
*Tert*-butyl (S)-3-(1-hydroxyethyl)-1H-indole-1-carboxylate (**19**)



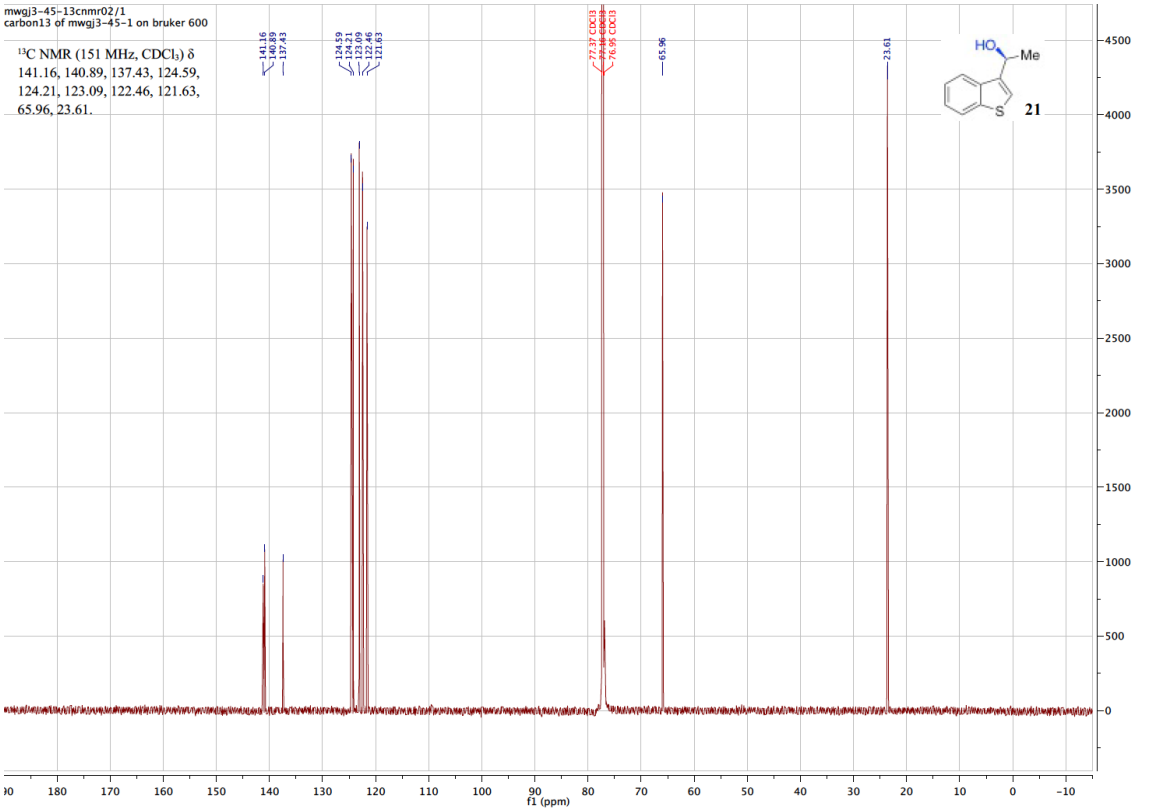



(*S*)-1-(benzofuran-3-yl)ethan-1-ol (**20**)

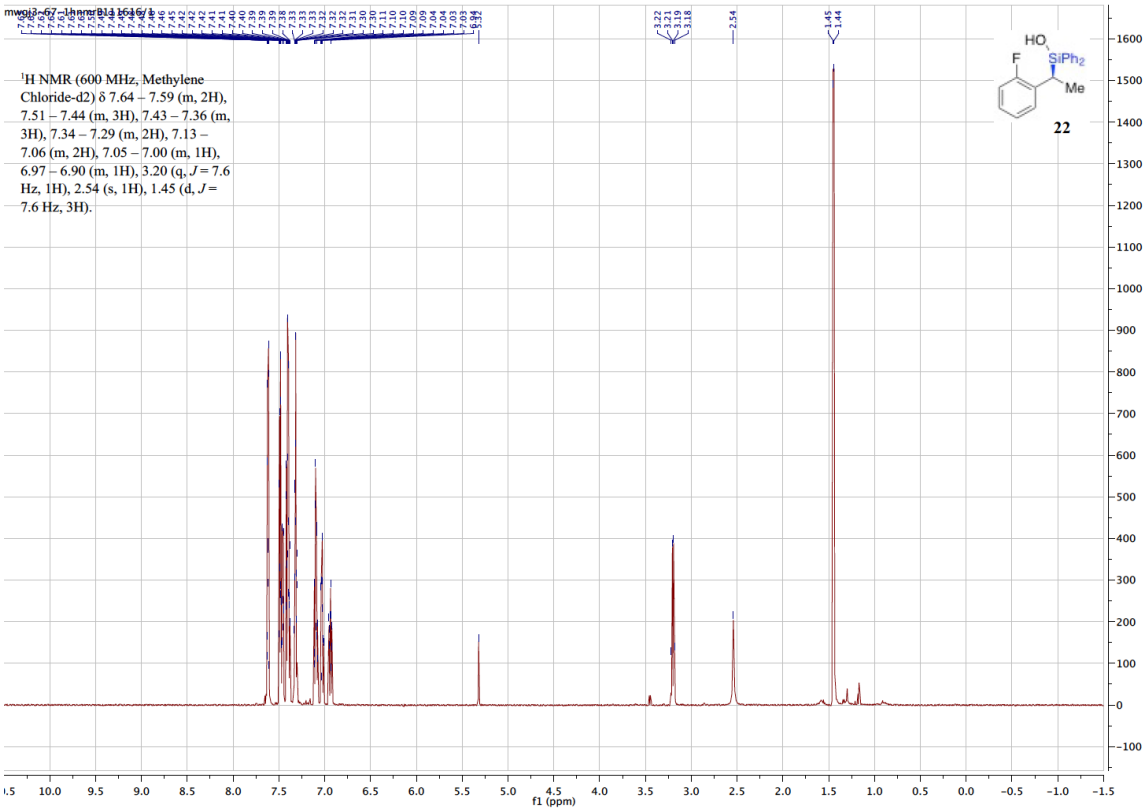


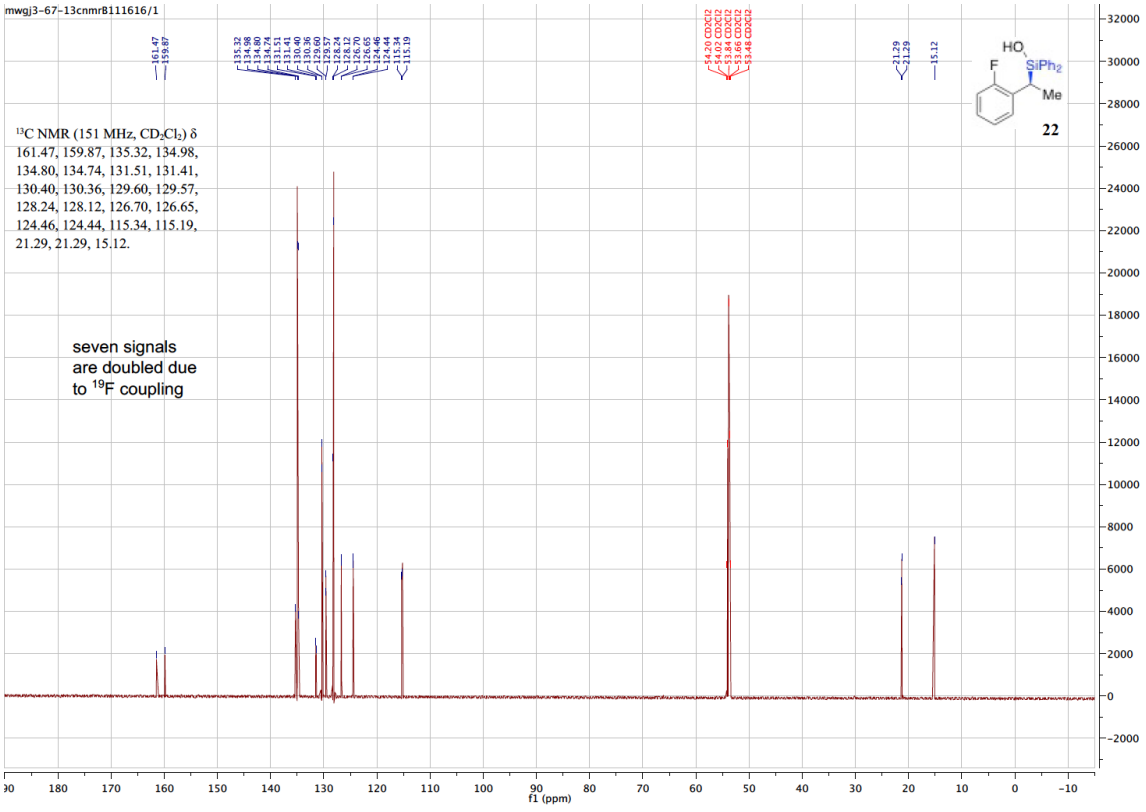



(*S*)-1-(benzo[*b*]thiophen-3-yl)ethan-1-ol (**21**)

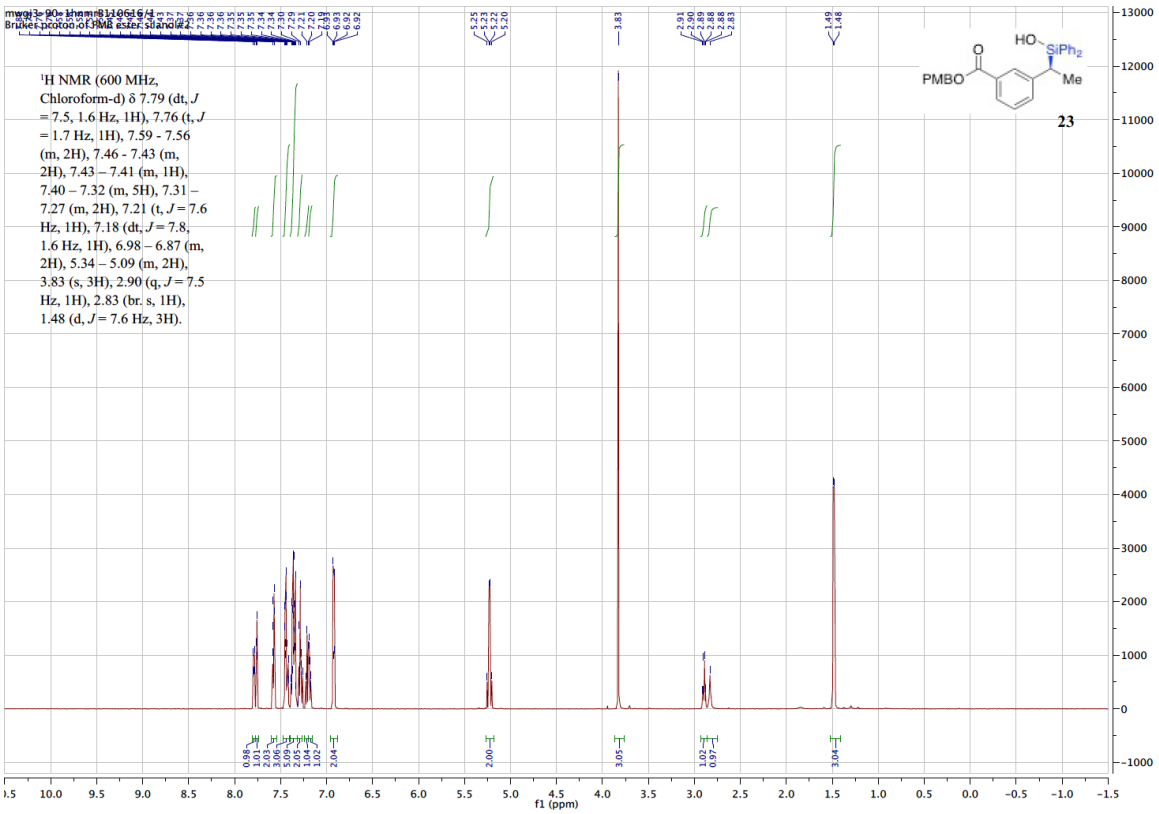



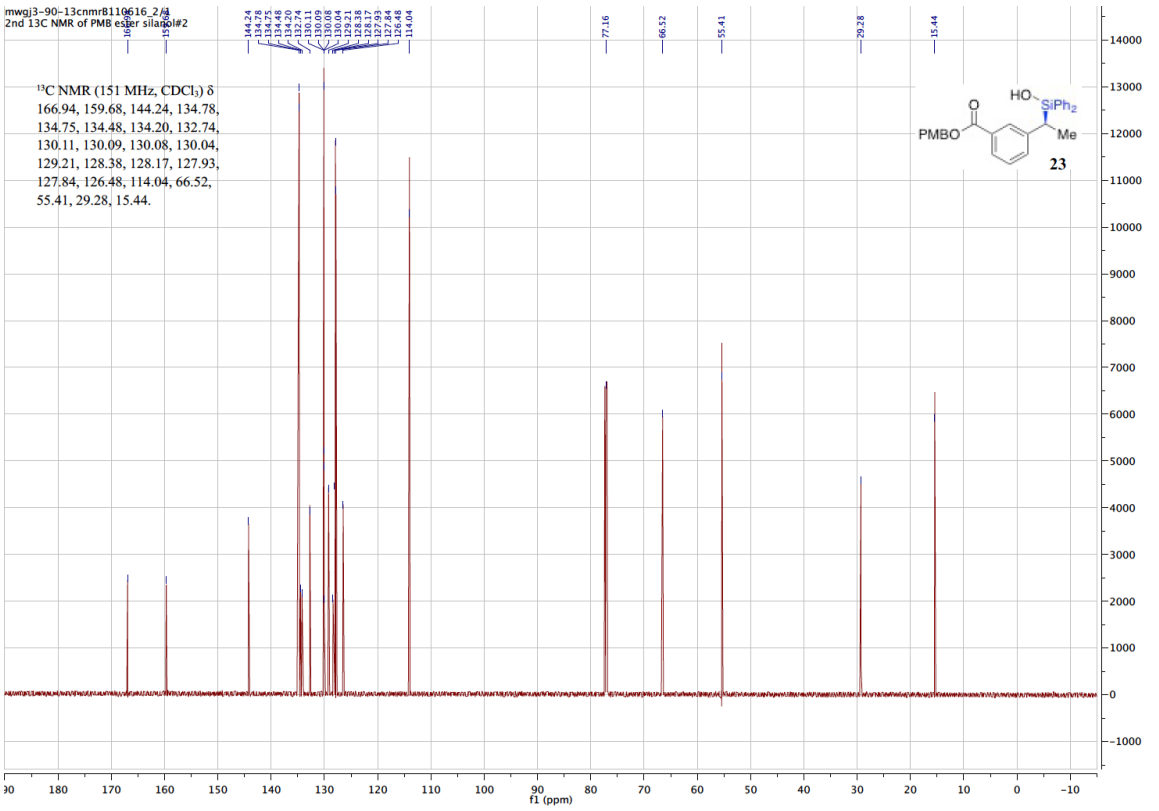
(*S*)-(1-(2-fluorophenyl)ethyl)diphenylsilanol (**22**)



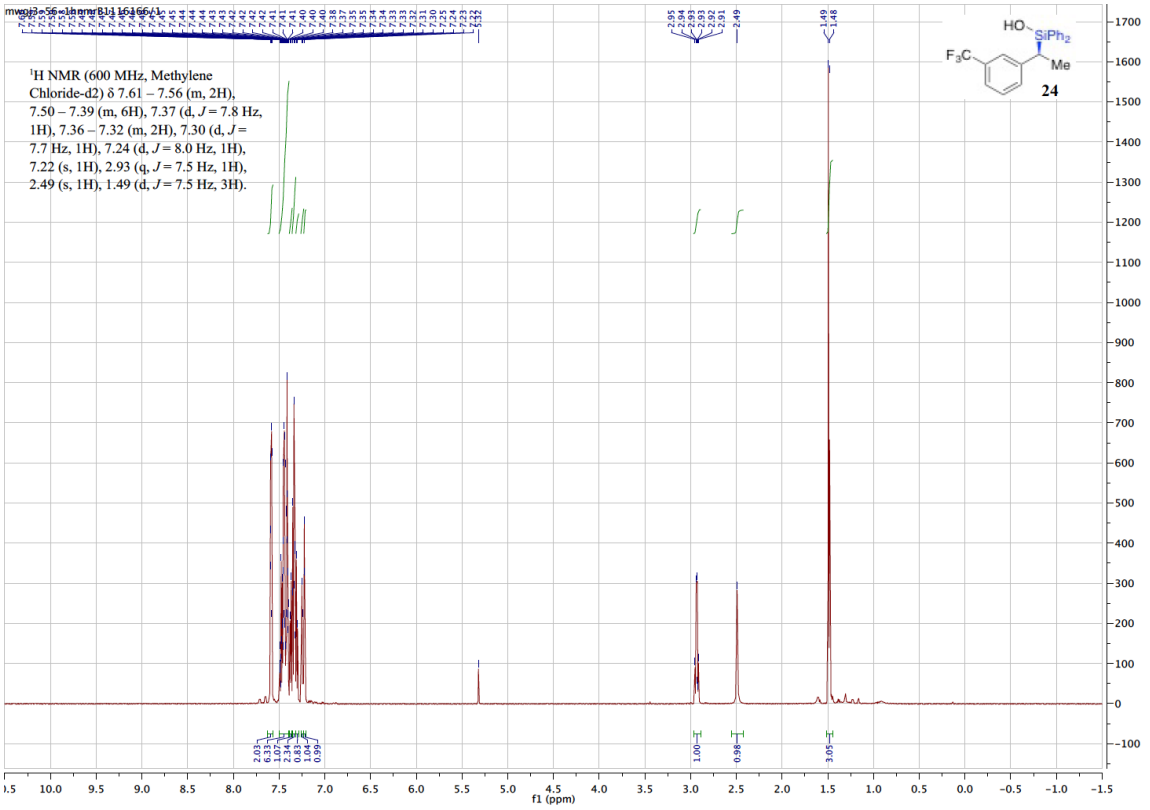



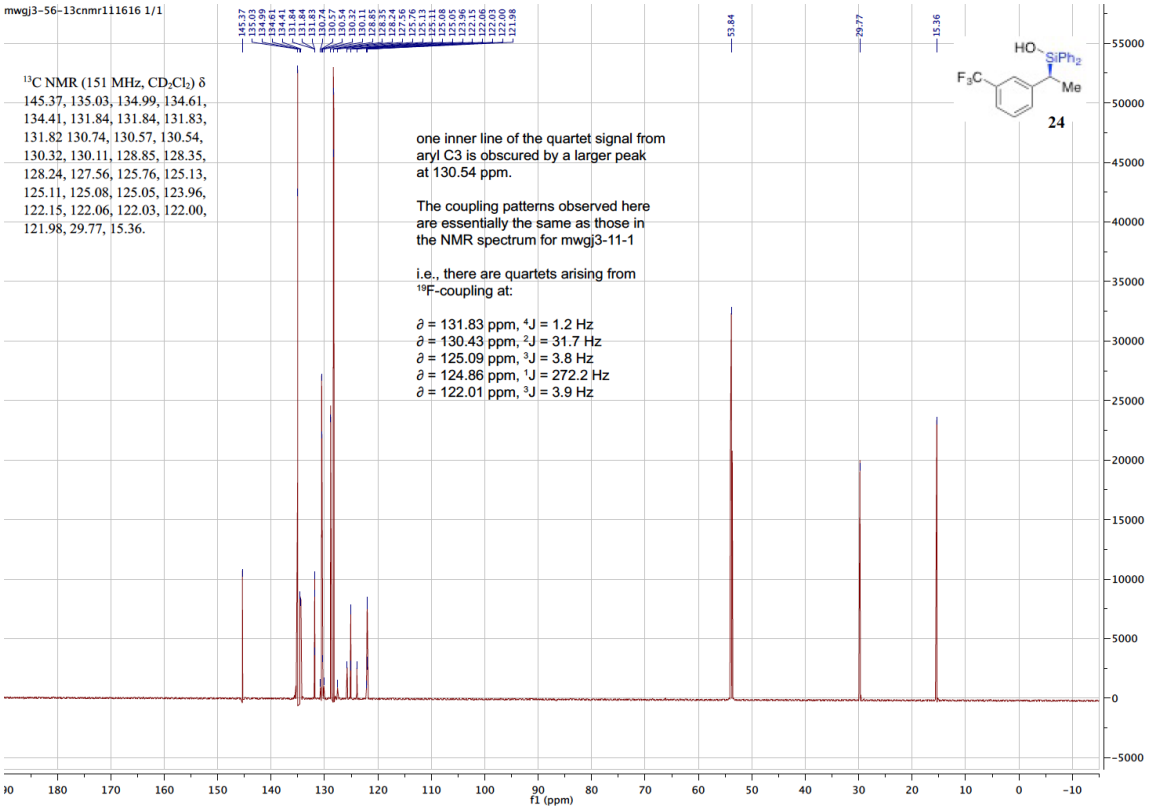
4-methoxybenzyl (*S*)-3-(1-(hydroxydiphenylsilyl)ethyl)benzoate (**23**)



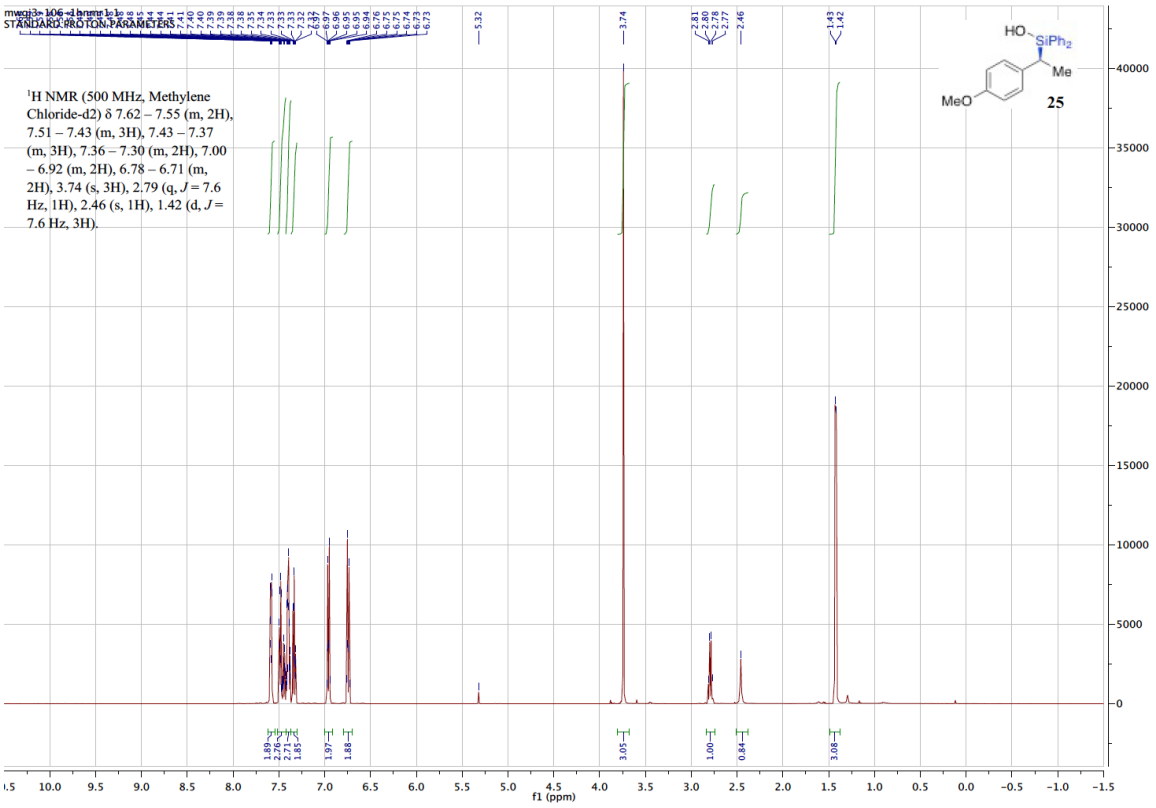



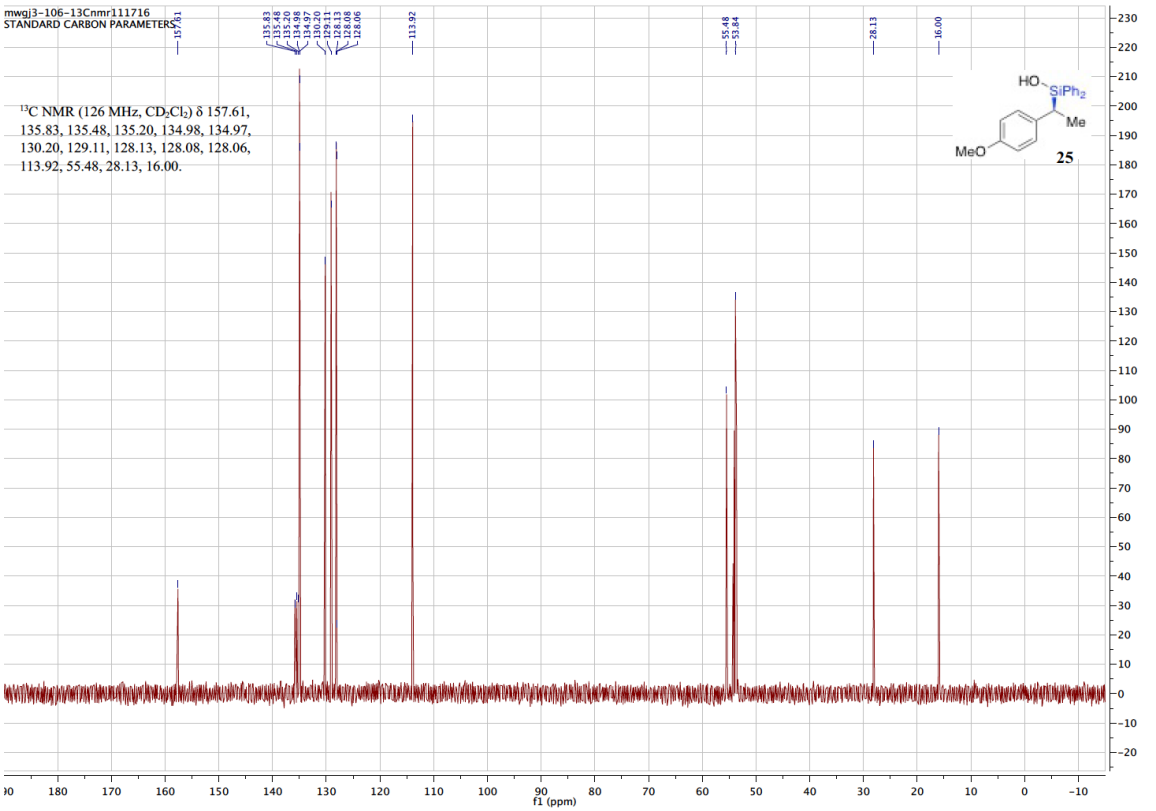
(*S*)-diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silanol (**24**)



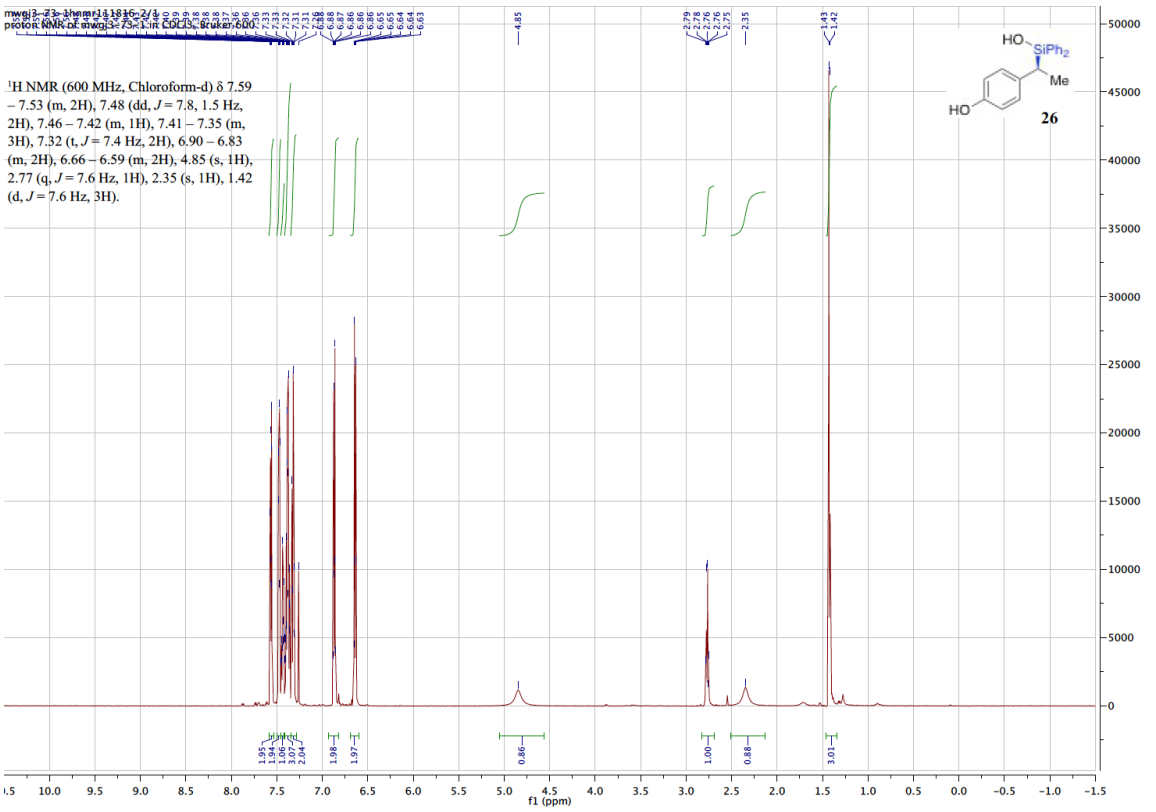



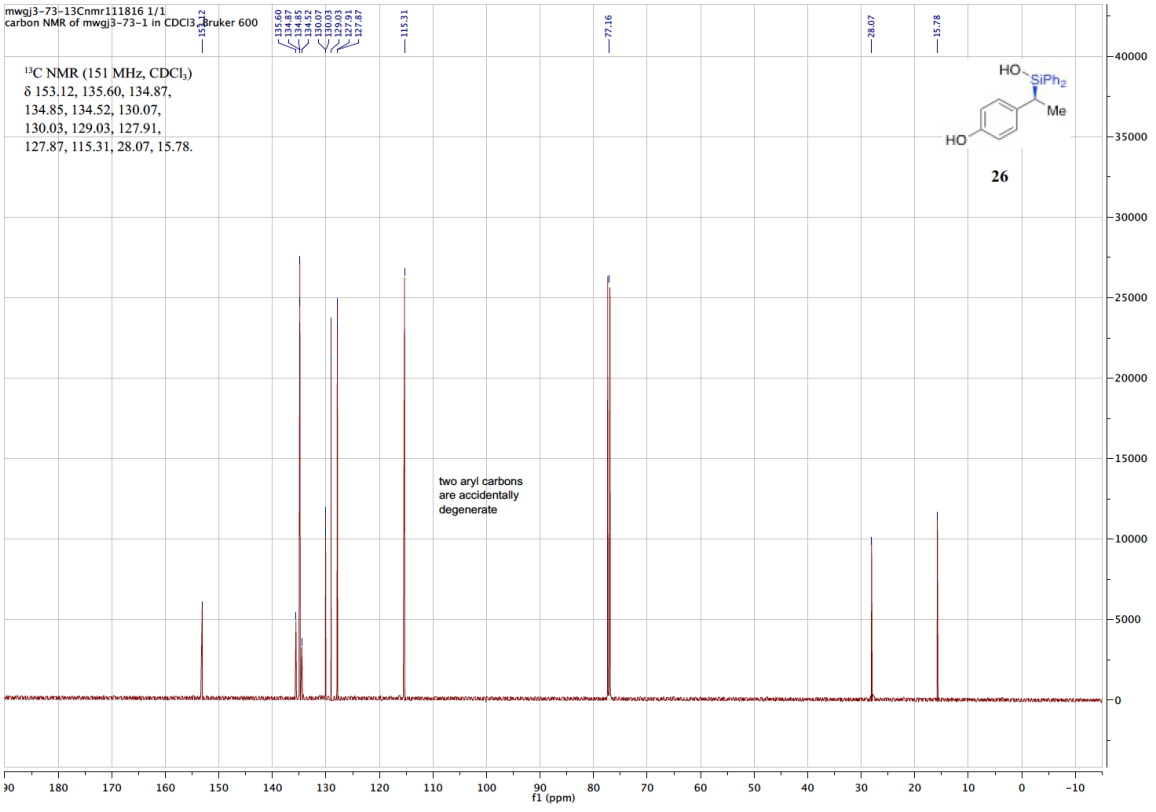
(*S*)-(1-(4-methoxyphenyl)ethyl)diphenylsilanol (**25**)



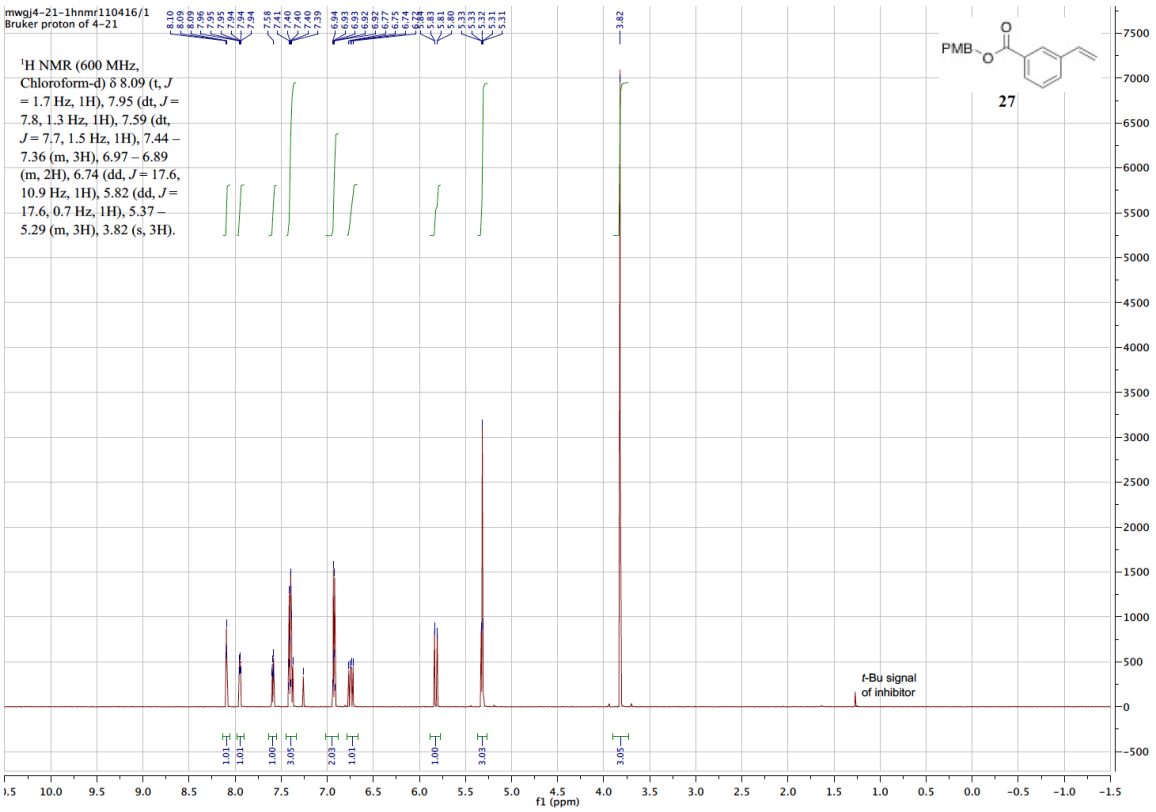



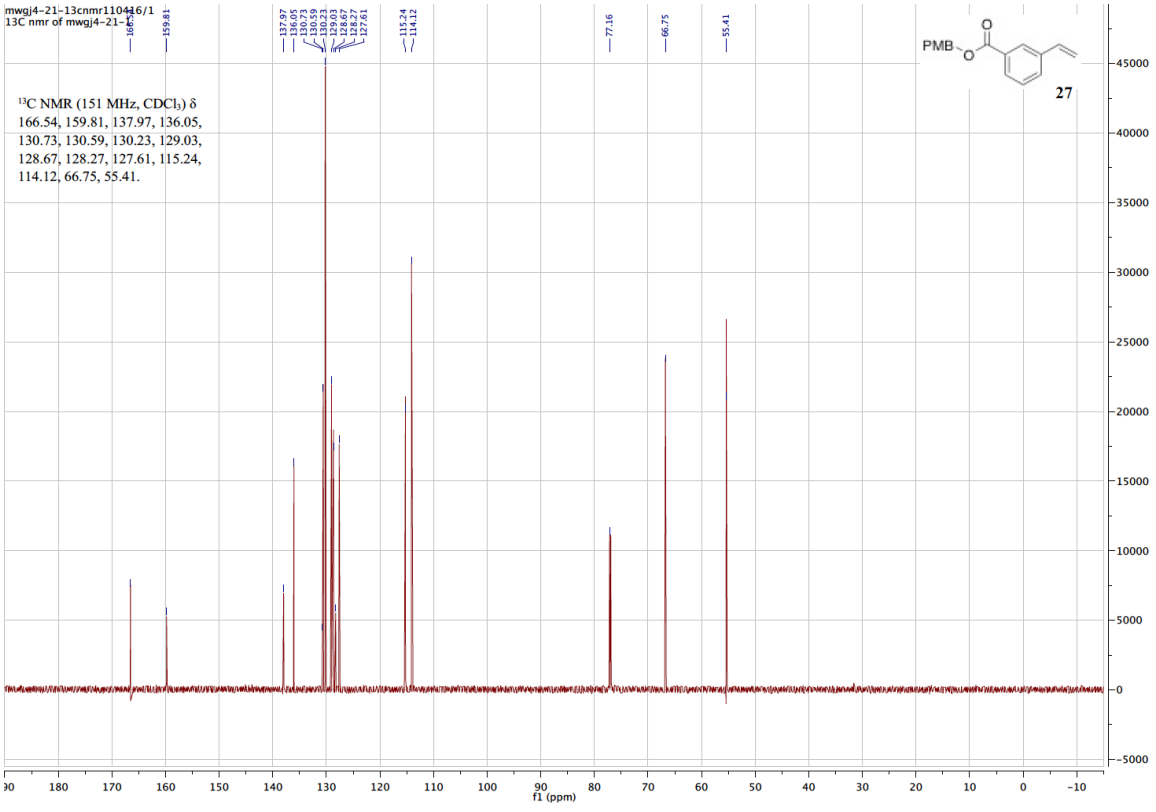
(*S*)-4-(1-(diphenylsilyl)ethyl)phenol (**26**)



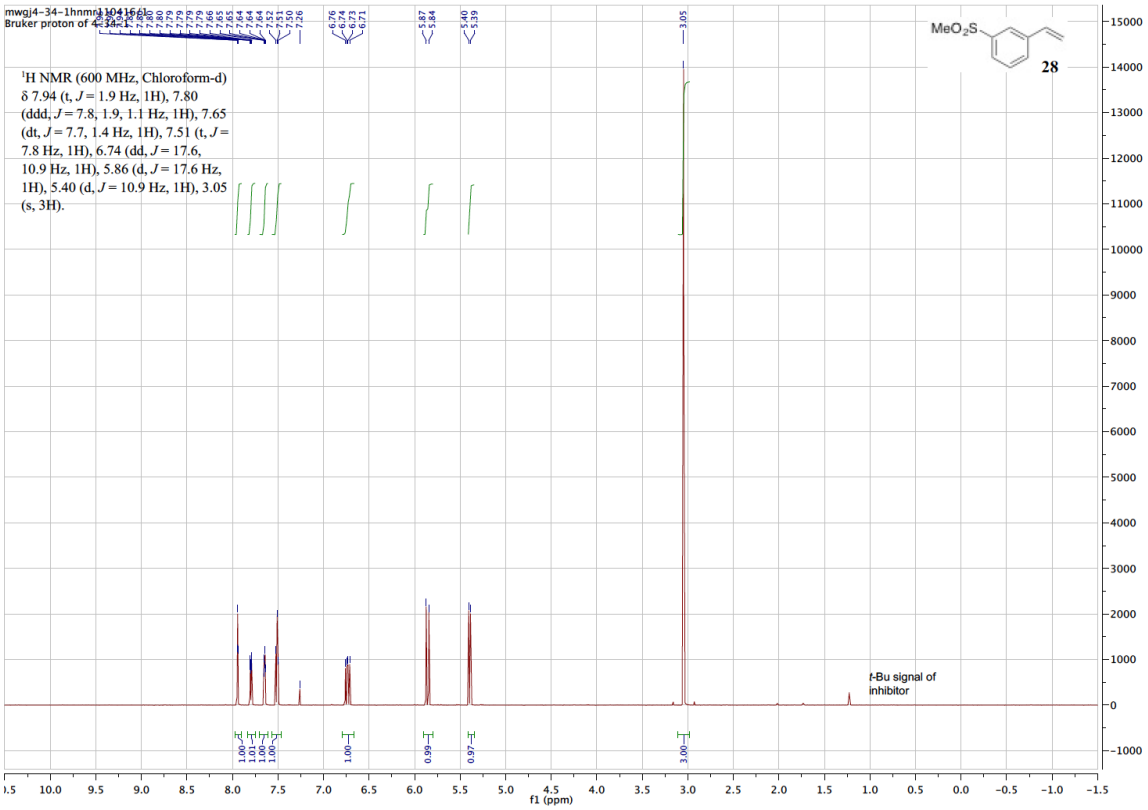



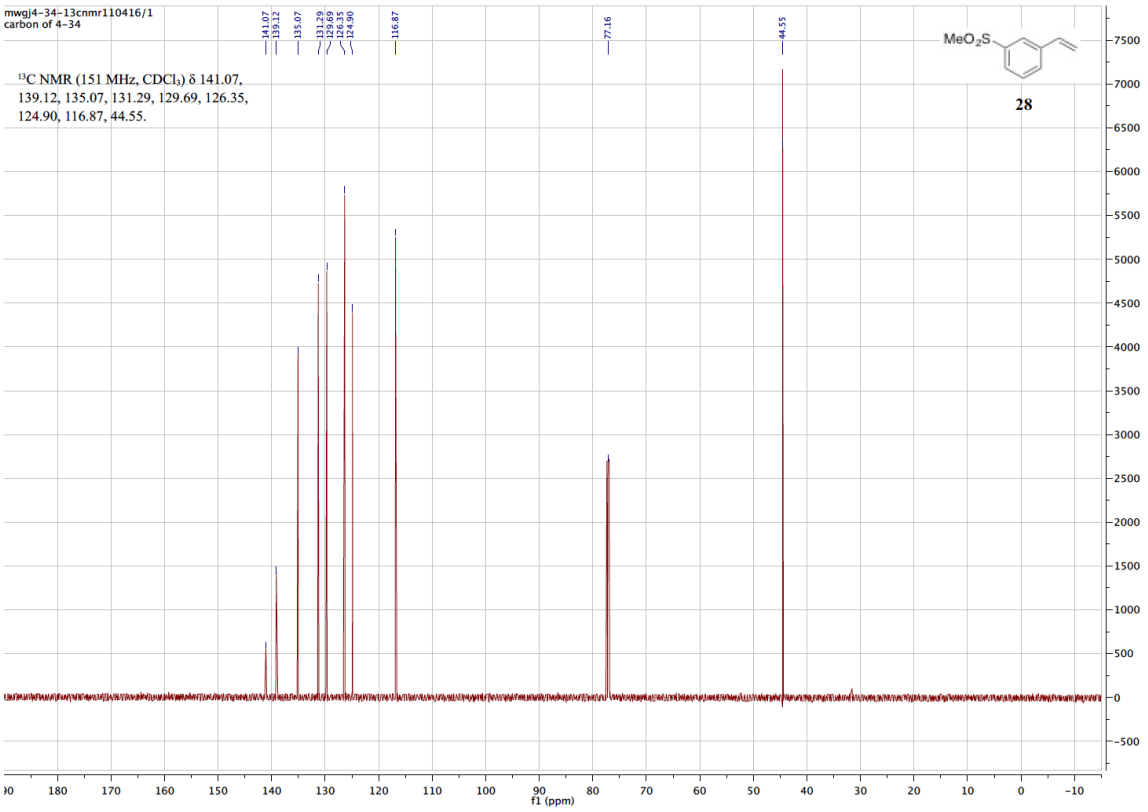
4-methoxybenzyl 3-vinylbenzoate (**27**)



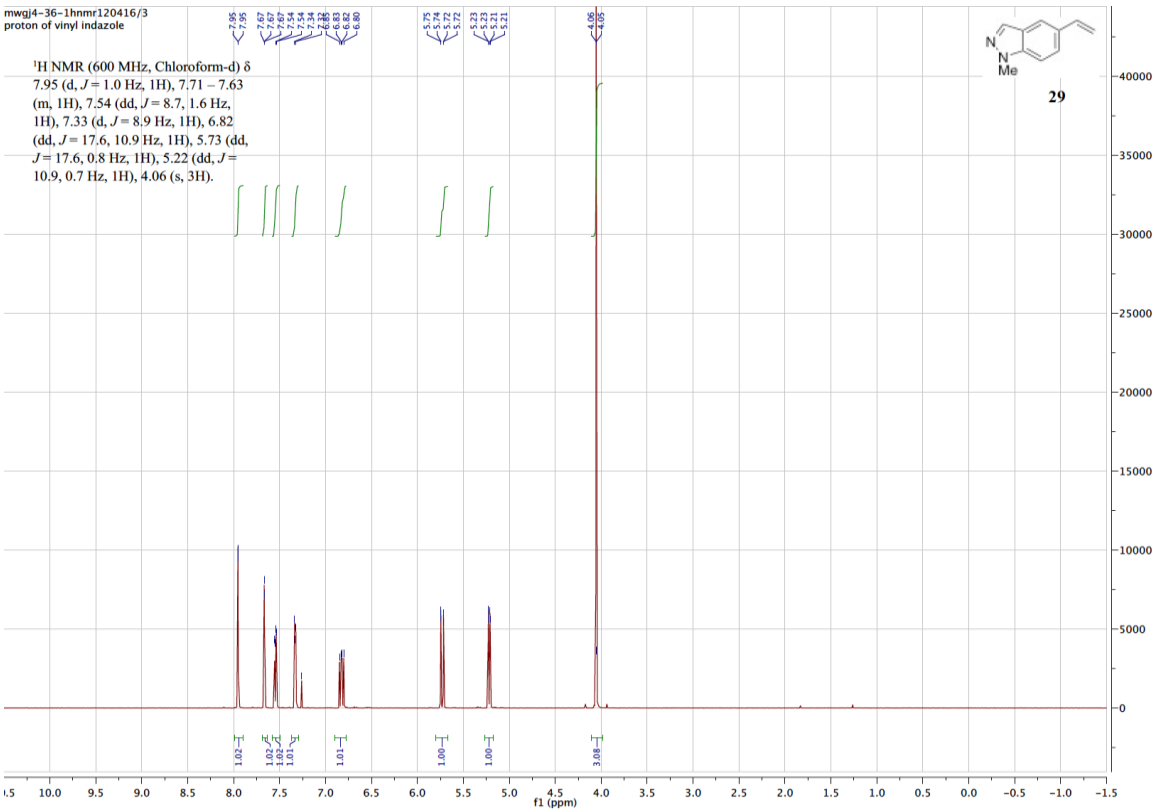



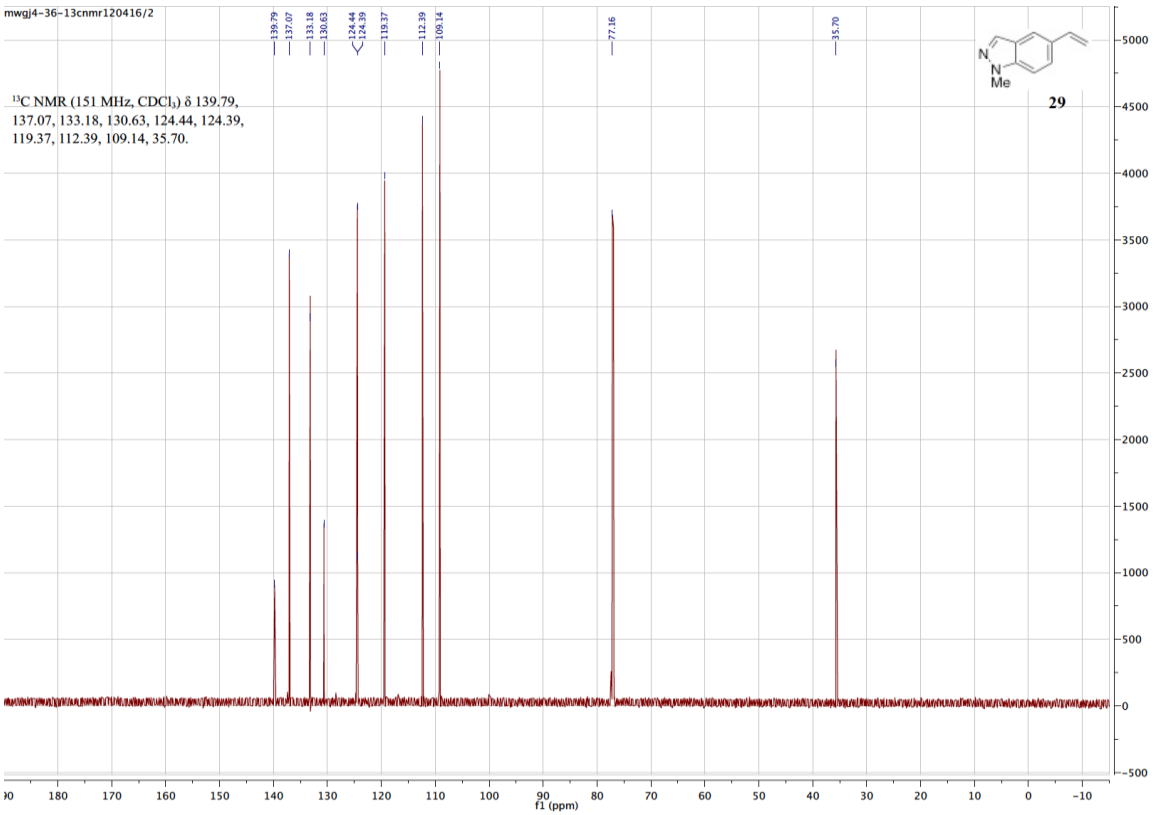
1-(methylsulfonyl)-3-vinylbenzene (**28**)



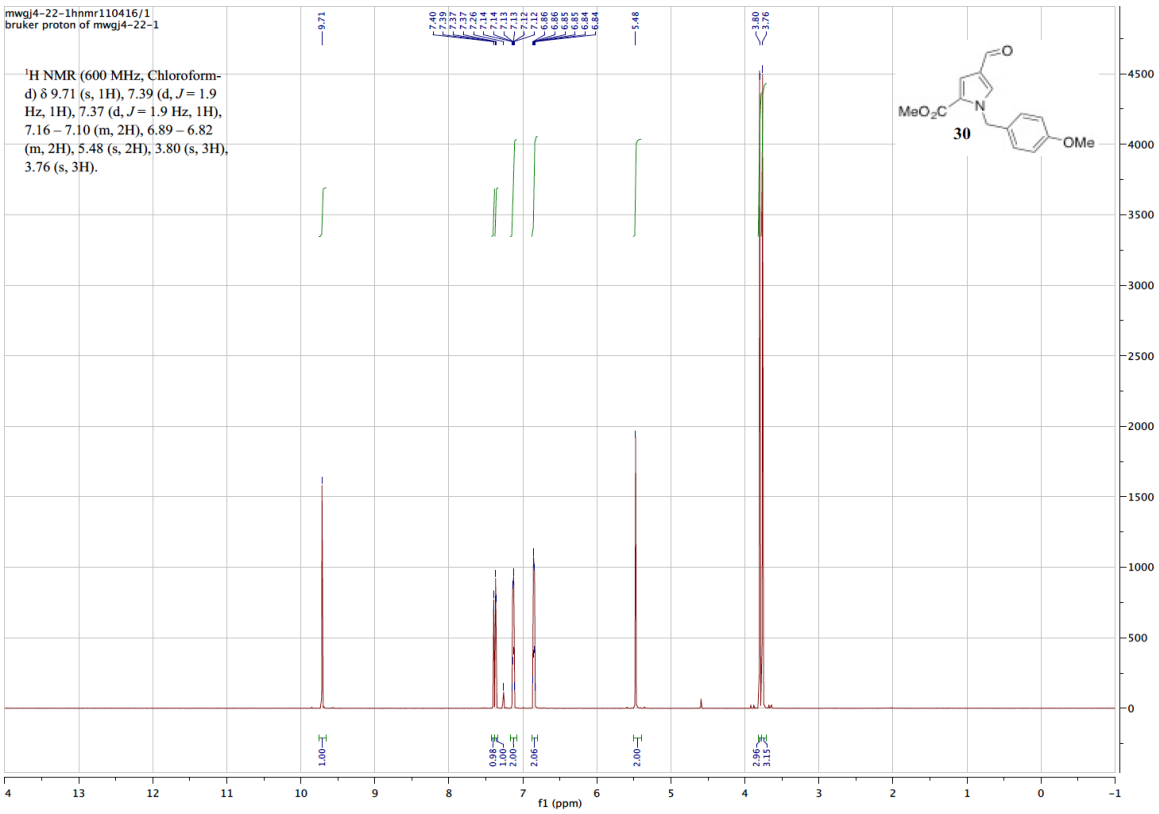



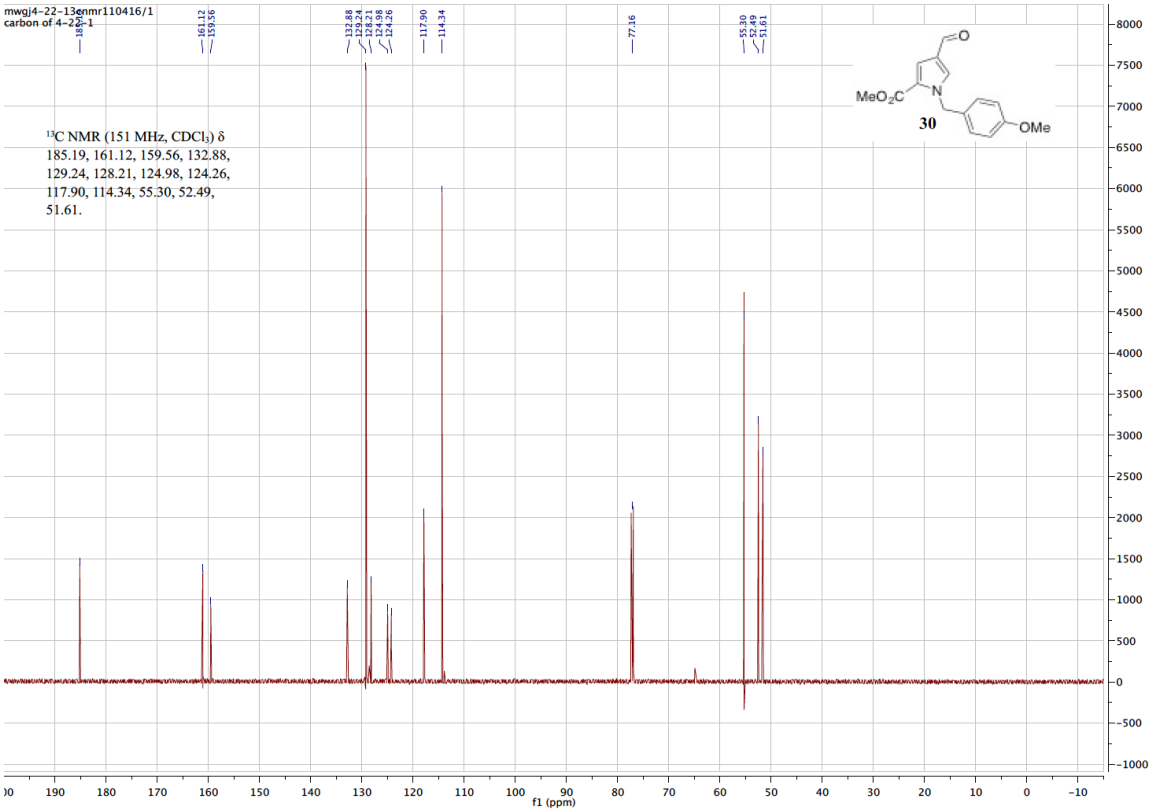
1-methyl-5-vinyl-1*H*-indazole (**29**)



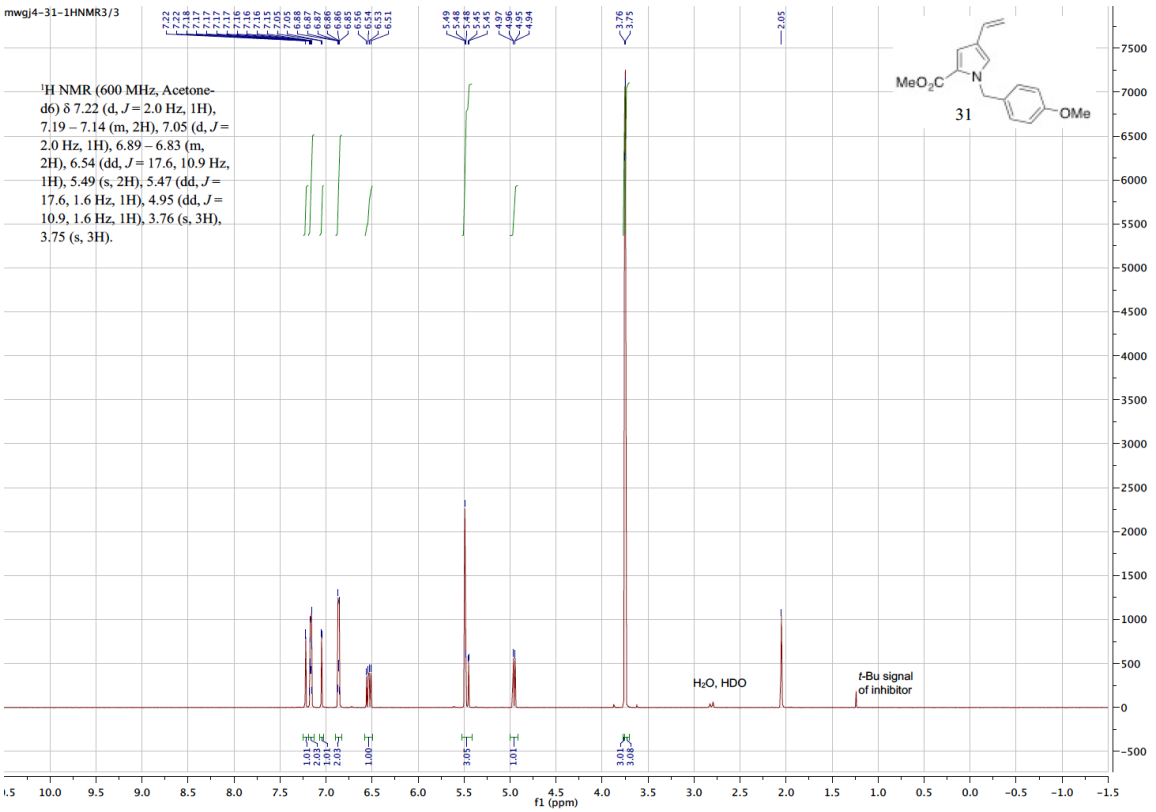



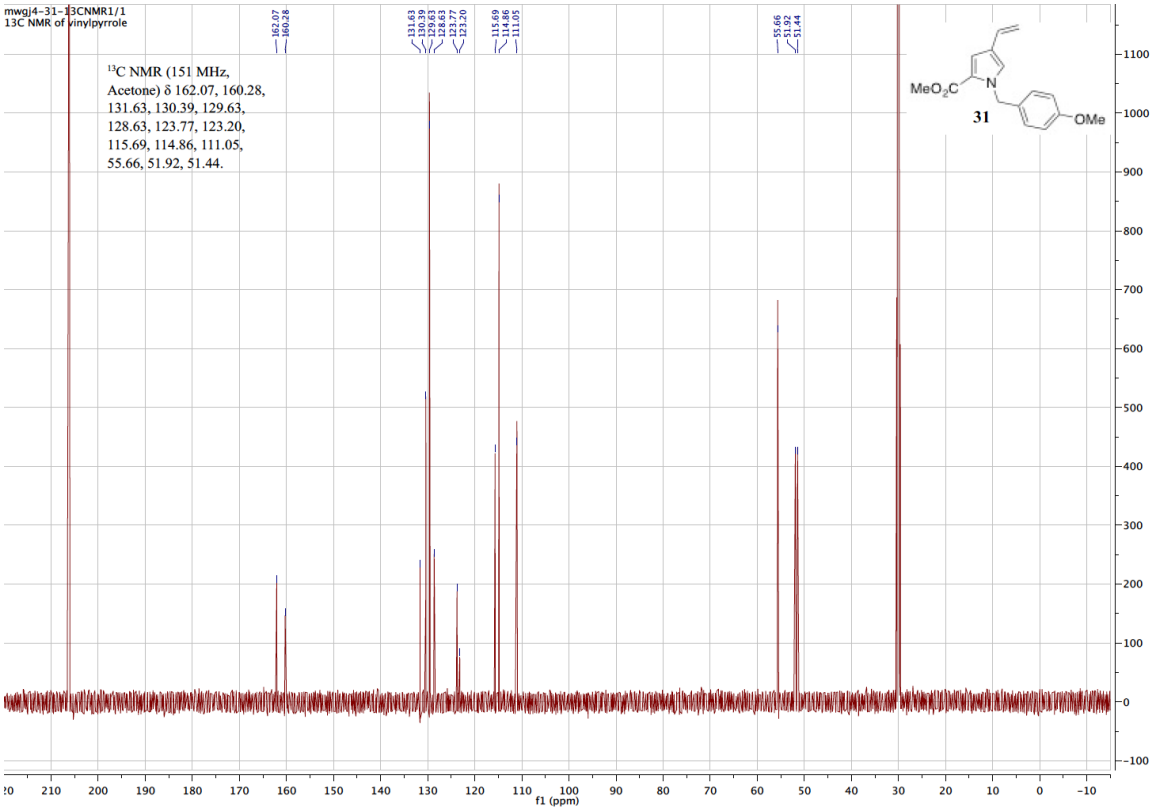
Methyl 4-formyl-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate (**30**)



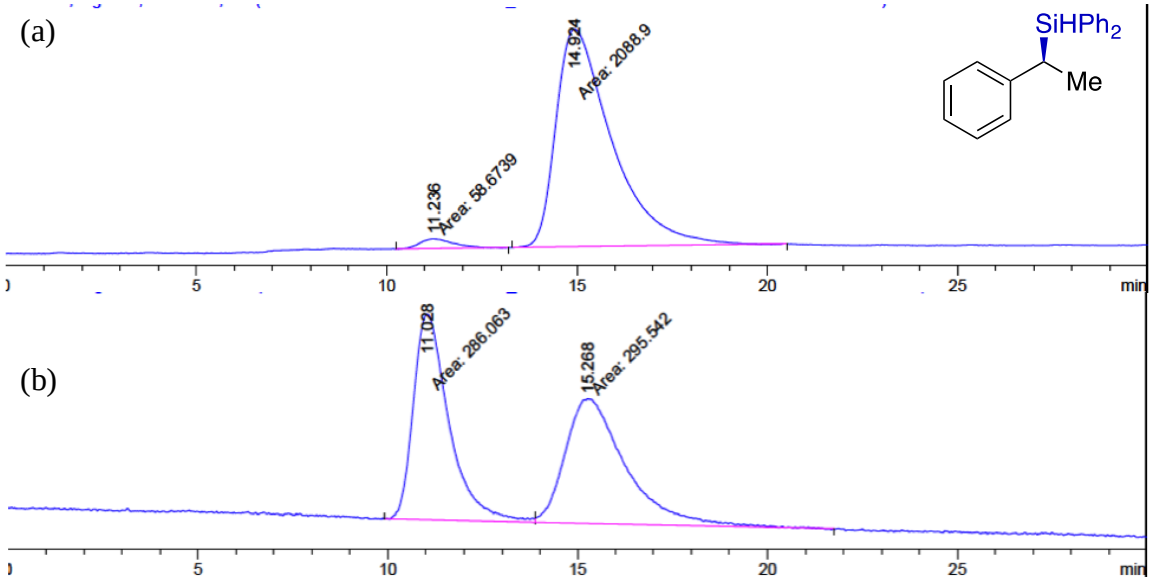
Methyl 1-(4-methoxybenzyl)-4-vinyl-1*H*-pyrrole-2-carboxylate (**31**)



## 5.2. Chiral HPLC and SFC Traces for Hydrosilylation Products and Their Derivatives

(*S*)-diphenyl(1-phenylethyl)silane (**1**). 1 mmol lot:




(a)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

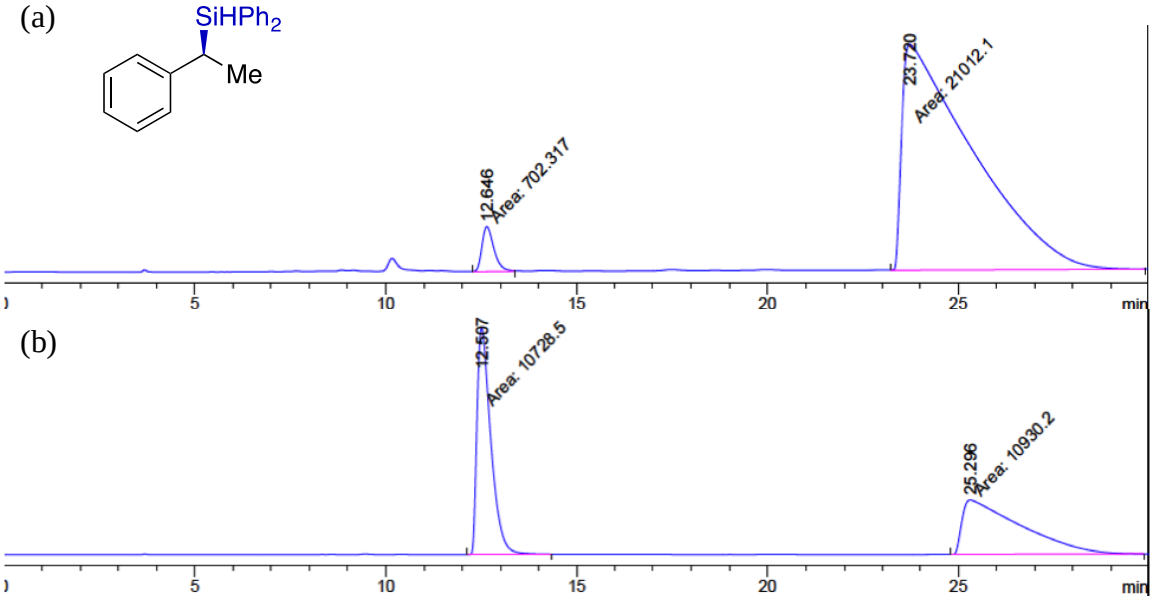
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.236 | MM | 1.0634 | 58.67394 | 9.19599e-1 | 2.7321 |
| 2 | 14.924 | MM | 1.7090 | 2088.89941 | 20.37190 | 97.2679 |
| Totals : | | | | 2147.57336 | 21.29150 | |

(b)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.028 | MF | 1.0864 | 286.06311 | 4.38872 | 49.1851 |
| 2 | 15.268 | FM | 1.8496 | 295.54172 | 2.66314 | 50.8149 |
| Totals : | | | | 581.60483 | 7.05186 | |

(*S*)-diphenyl(1-phenylethyl)silane (**1**). 10 mmol lot:




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

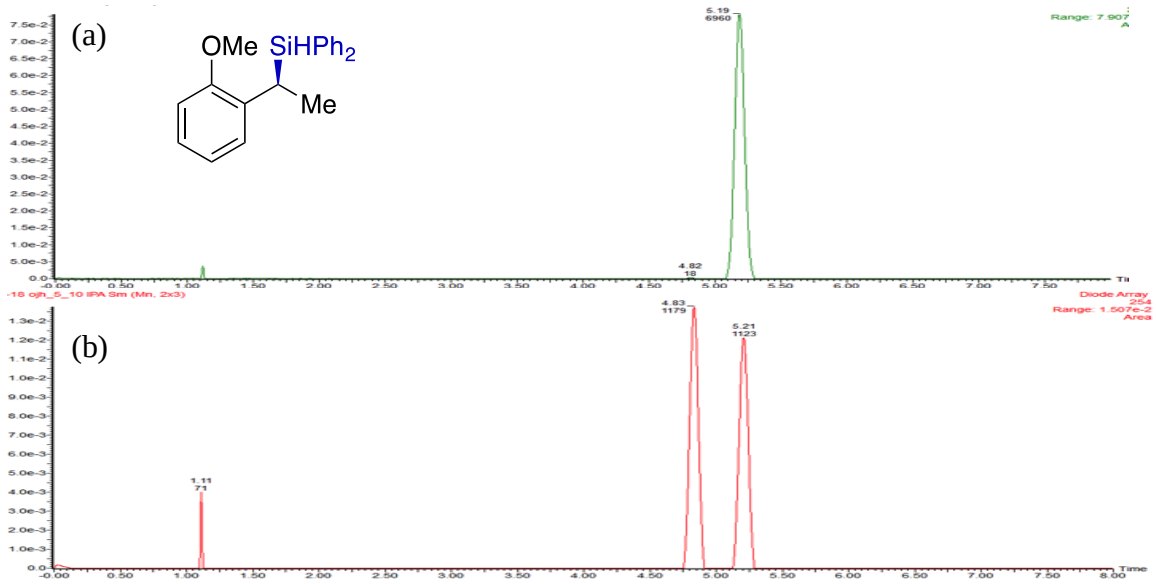
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.646 | MM | 0.3634 | 702.31708 | 32.20910 | 3.2343 |
| 2 | 23.720 | MM | 2.1619 | 2.10121e4 | 161.98946 | 96.7657 |
| Totals : | | | | 2.17144e4 | 194.19855 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.507 | MM | 0.4185 | 1.07285e4 | 427.27054 | 49.5344 |
| 2 | 25.296 | MM | 1.7808 | 1.09302e4 | 102.29418 | 50.4656 |
| Totals : | | | | 2.16588e4 | 529.56472 | |

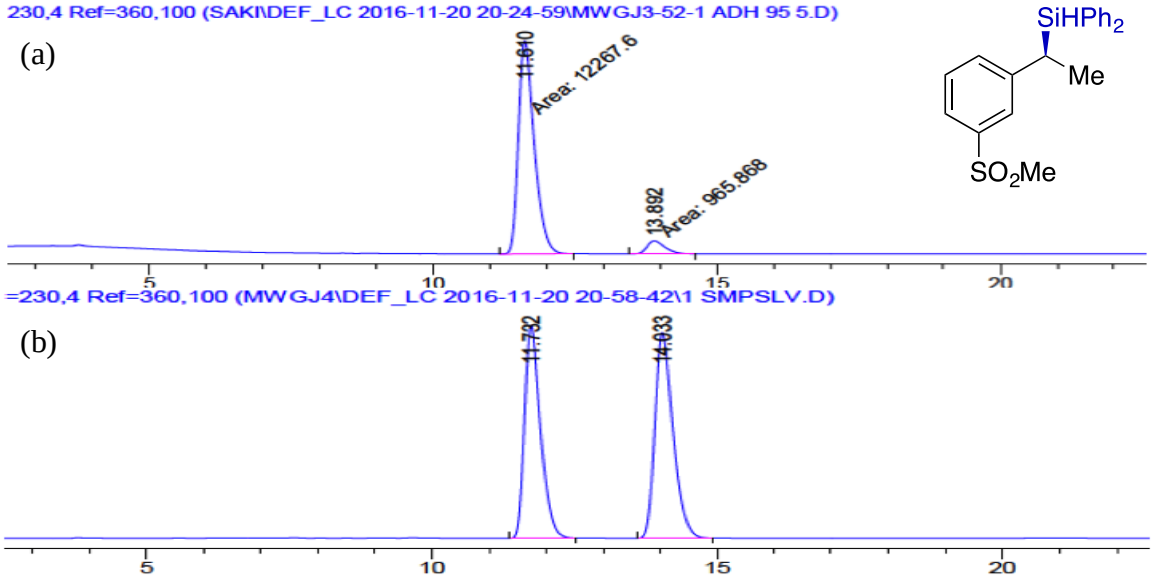
(*S*)-(1-(2-methoxyphenyl)ethyl)diphenylsilane (**2**)




(a)
$t_M$ = 5.19 min, area (254 nm) = 6960, area% (254 nm) = 99.74
$t_m$ = 4.82 min, area (254 nm) = 18, area% (254 nm) = 0.26

(b)
$t_S$ = 5.21 min, area (254 nm) = 1123, area% (254 nm) = 48.78
$t_R$ = 4.83 min, area (254 nm) = 1179, area% (254 nm) = 51.22

(*S*)-(1-(3-(methylsulfonyl)phenyl)ethyl)diphenylsilane (**6**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

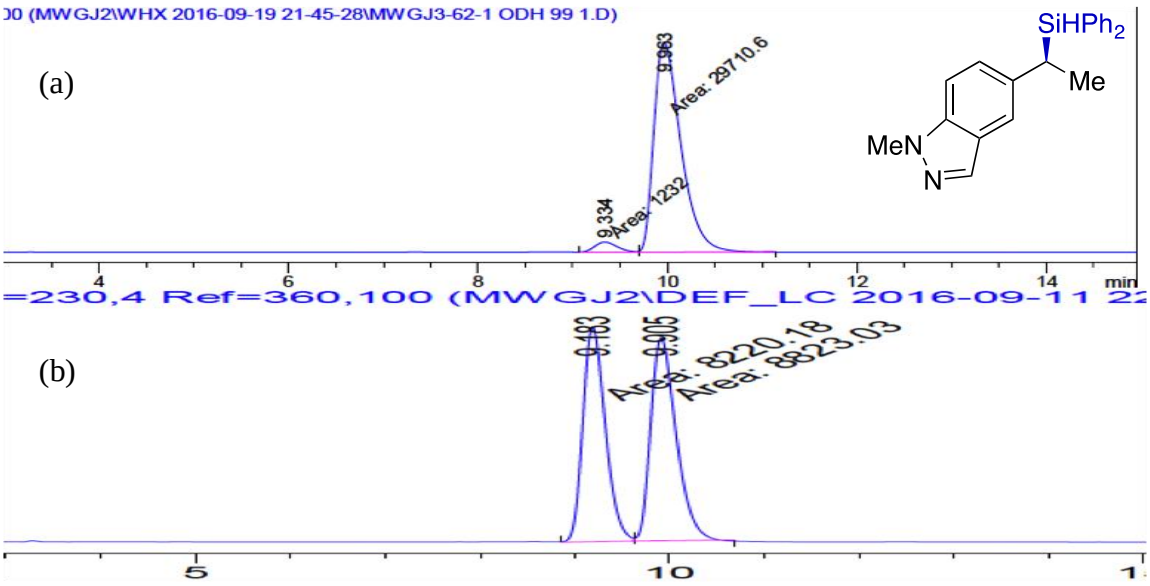
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.610 | MM | 0.3232 | 1.22676e4 | 632.70569 | 92.7013 |
| 2 | 13.892 | MM | 0.3996 | 965.86798 | 40.28540 | 7.2987 |
| Totals : | | | | 1.32334e4 | 672.99109 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.732 | BB | 0.2918 | 1.19450e4 | 617.12366 | 47.6506 |
| 2 | 14.033 | BB | 0.3328 | 1.31228e4 | 596.21179 | 52.3494 |
| Totals : | | | | 2.50678e4 | 1213.33545 | |

(*S*)-5-(1-(diphenylsilyl)ethyl)-1-methyl-1*H*-indazole (**7**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

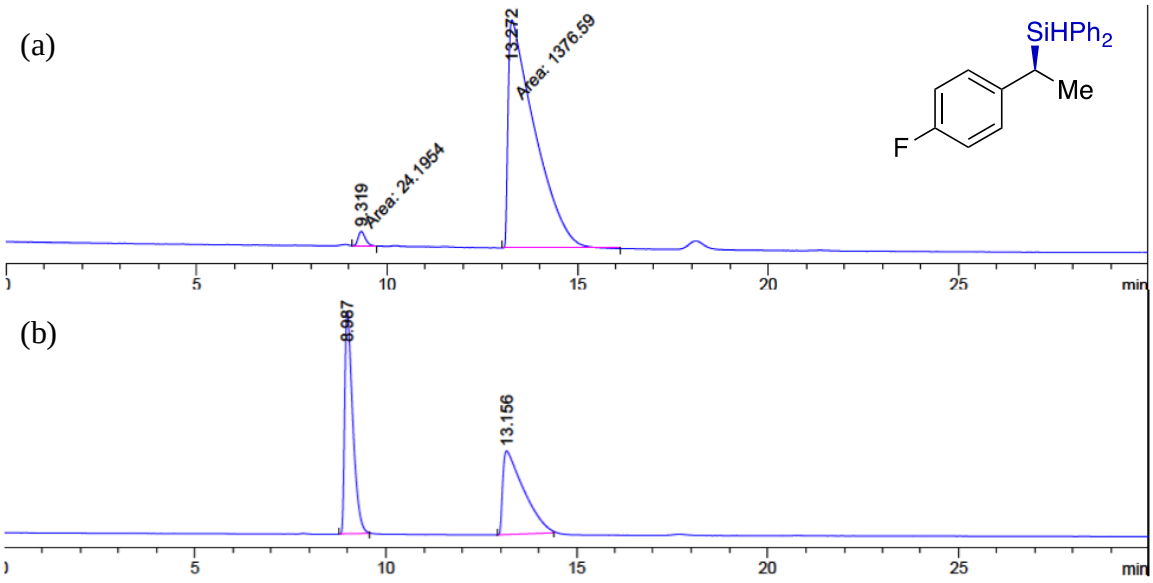
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.334 | MF | 0.2833 | 1231.99951 | 72.47260 | 3.9816 |
| 2 | 9.963 | FM | 0.3334 | 2.97106e4 | 1485.01416 | 96.0184 |
| Totals : | | | | 3.09426e4 | 1557.48676 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.183 | MF | 0.2746 | 8220.17871 | 498.99936 | 48.2314 |
| 2 | 9.905 | FM | 0.3122 | 8823.02832 | 470.98190 | 51.7686 |
| Totals : | | | | 1.70432e4 | 969.98126 | |

**(*S*)-(1-(4-fluorophenyl)ethyl)diphenylsilane (10)**




(a)

Signal 3: DAD1 E, Sig=280,16 Ref=360,100

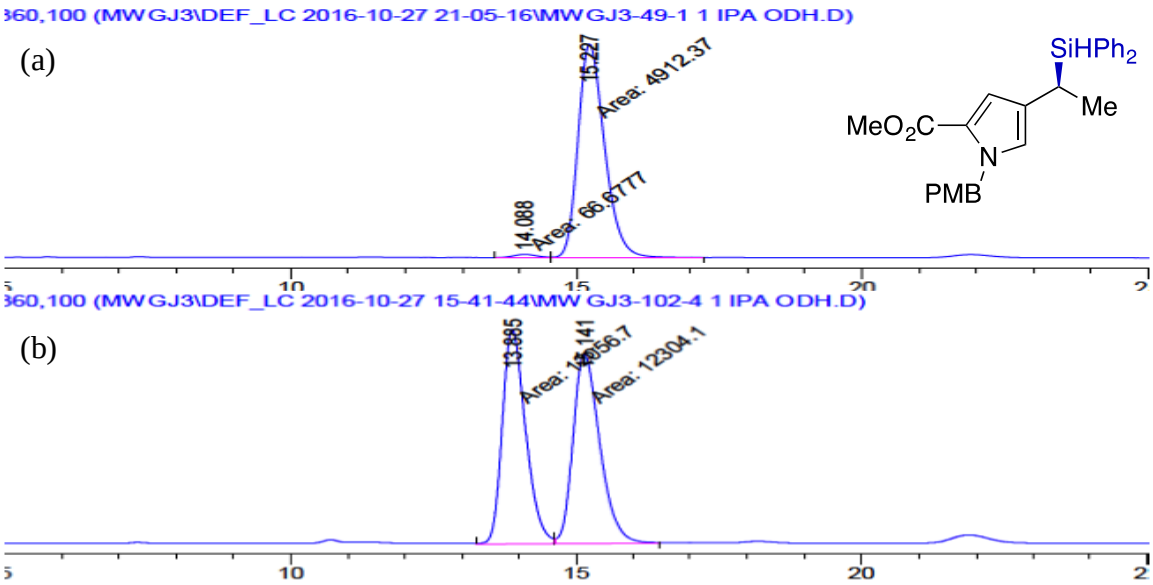
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.319 | MM | 0.2228 | 24.19545 | 1.80960 | 1.7273 |
| 2 | 13.272 | MM | 0.8134 | 1376.58643 | 28.20583 | 98.2727 |
| Totals : | | | | 1400.78187 | 30.01543 | |

(b)

Signal 3: DAD1 E, Sig=280,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.987 | BB | 0.2234 | 771.77747 | 52.54768 | 50.6360 |
| 2 | 13.156 | BB | 0.5146 | 752.38965 | 19.74485 | 49.3640 |
| Totals : | | | | 1524.16711 | 72.29252 | |

Methyl (*S*)-4-(1-(diphenylsilyl)ethyl)-1-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxylate (**11**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

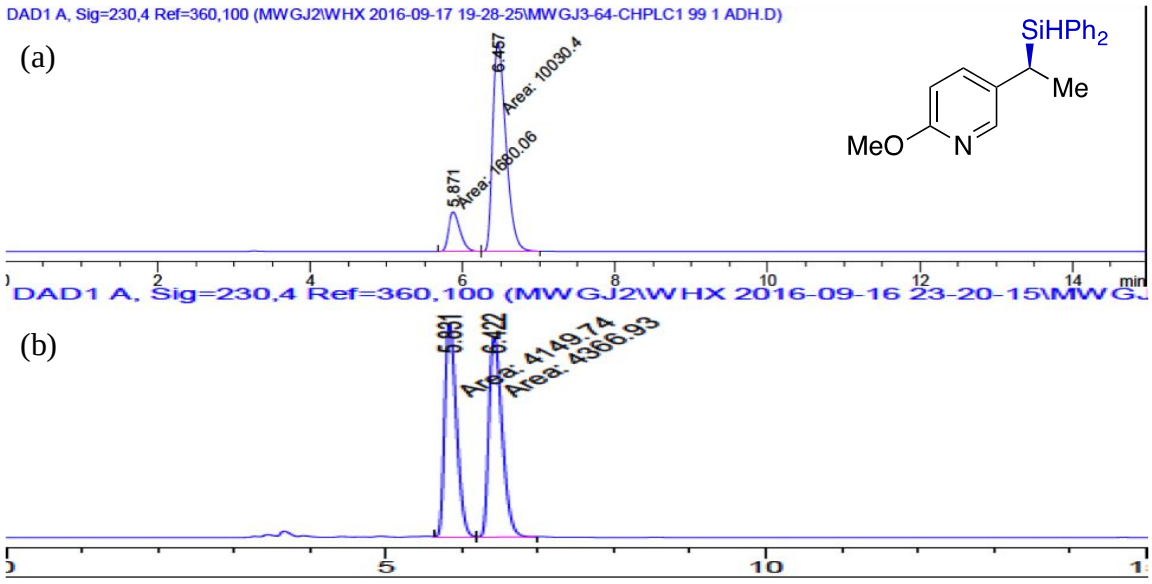
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.088 | MF | 0.4775 | 66.67770 | 2.32745 | 1.3392 |
| 2 | 15.227 | FM | 0.5368 | 4912.37305 | 152.50717 | 98.6608 |
| Totals : | | | | 4979.05074 | 154.83462 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.885 | MF | 0.4727 | 1.20567e4 | 425.06979 | 49.4921 |
| 2 | 15.141 | FM | 0.5446 | 1.23041e4 | 376.51929 | 50.5079 |
| Totals : | | | | 2.43608e4 | 801.58908 | |

(*S*)-5-(1-(diphenylsilyl)ethyl)-2-methoxypyridine (**13**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

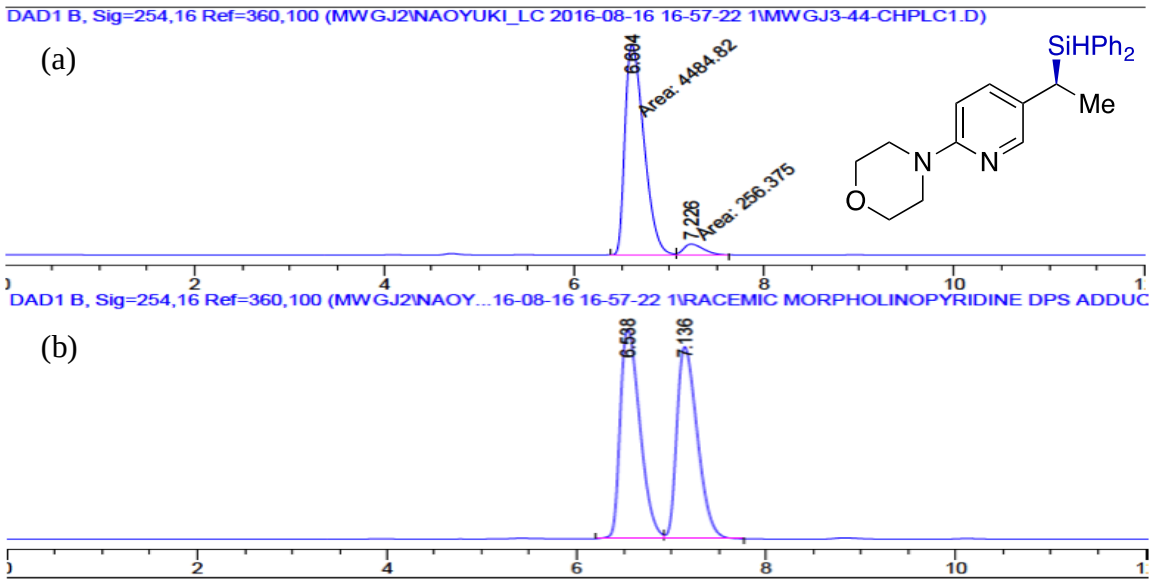
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.871 | MM | 0.1763 | 1680.05603 | 158.81860 | 14.3466 |
| 2 | 6.457 | MM | 0.1996 | 1.00304e4 | 837.63513 | 85.6534 |
| Totals : | | | | 1.17105e4 | 996.45374 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.831 | MM | 0.1793 | 4149.74414 | 385.68689 | 48.7249 |
| 2 | 6.422 | MM | 0.2018 | 4366.92822 | 360.63968 | 51.2751 |
| Totals : | | | | 8516.67236 | 746.32657 | |

(*S*)-4-(5-(1-(diphenylsilyl)ethyl)pyridin-2-yl)morpholine (**14**)




(a)

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

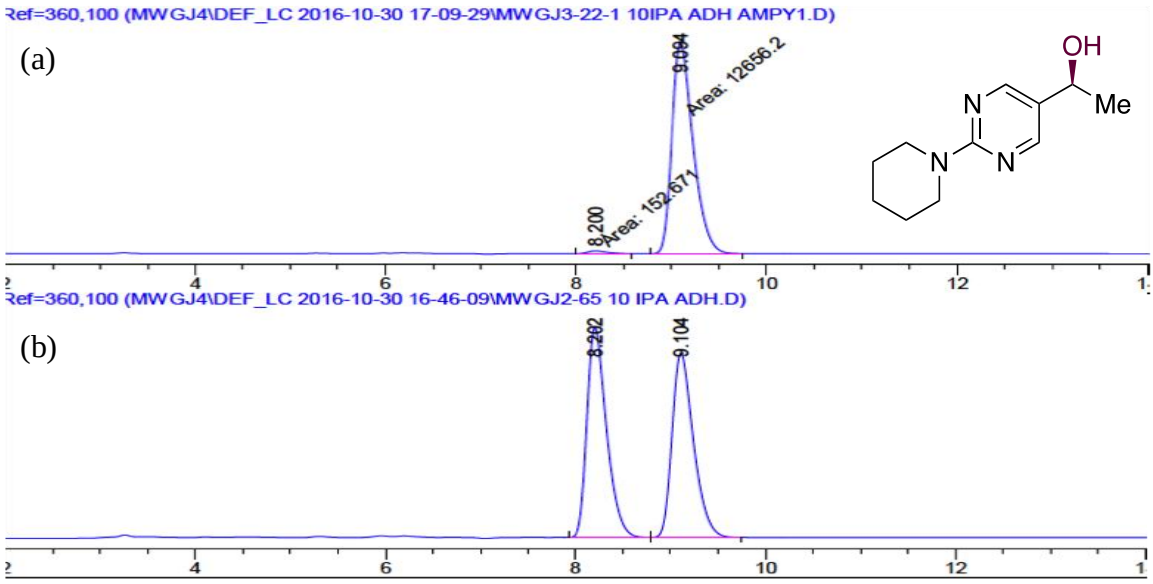
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.604 | MF | 0.2317 | 4484.81592 | 322.54694 | 94.5926 |
| 2 | 7.226 | FM | 0.2491 | 256.37534 | 17.15194 | 5.4074 |
| Totals : | | | | 4741.19125 | 339.69888 | |

(b)

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.538 | BV | 0.2256 | 6614.92188 | 460.50409 | 51.1459 |
| 2 | 7.136 | VB | 0.2370 | 6318.52295 | 421.30811 | 48.8541 |
| Totals : | | | | 1.29334e4 | 881.81219 | |

(*S*)-1-(2-(piperidin-1-yl)pyrimidin-5-yl)ethan-1-ol (**15**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

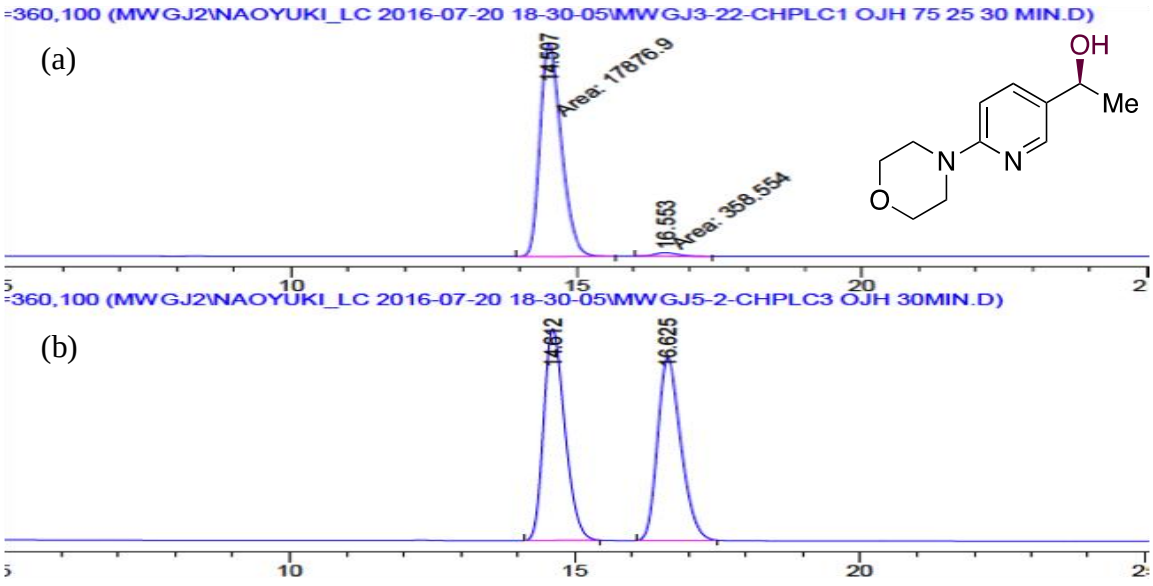
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.200 | MM | 0.2395 | 152.67105 | 10.62328 | 1.1919 |
| 2 | 9.094 | MM | 0.2591 | 1.26562e4 | 814.02203 | 98.8081 |
| Totals : | | | | 1.28089e4 | 824.64532 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.202 | BV | 0.2190 | 6157.60498 | 430.19339 | 51.0505 |
| 2 | 9.104 | VB | 0.2366 | 5904.19727 | 377.23392 | 48.9495 |
| Totals : | | | | 1.20618e4 | 807.42731 | |

(*S*)-1-(6-morpholinopyridin-3-yl)ethan-1-ol (**16**)




(a)

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

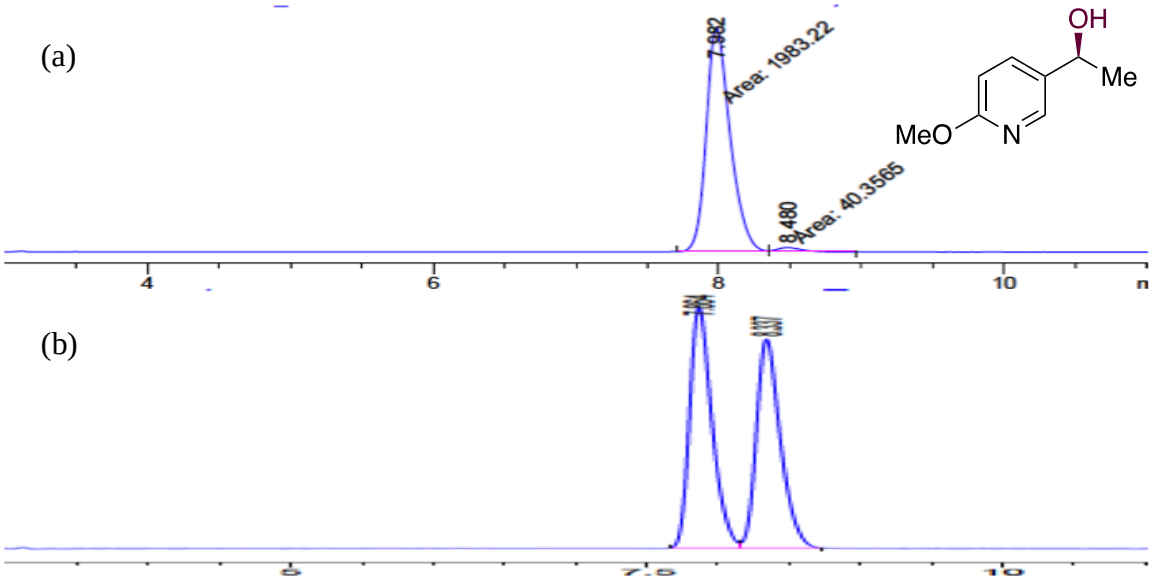
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.507 | MM | 0.4332 | 1.78769e4 | 687.71796 | 98.0338 |
| 2 | 16.553 | MM | 0.5375 | 358.55399 | 11.11861 | 1.9662 |
| Totals : | | | | 1.82355e4 | 698.83657 | |

(b)

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.612 | BB | 0.3958 | 4881.77686 | 189.95599 | 50.8386 |
| 2 | 16.625 | BB | 0.4441 | 4720.72607 | 163.87592 | 49.1614 |
| Totals : | | | | 9602.50293 | 353.83191 | |

**(*S*)-1-(6-methoxypyridin-3-yl)ethan-1-ol (17)**




(a)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

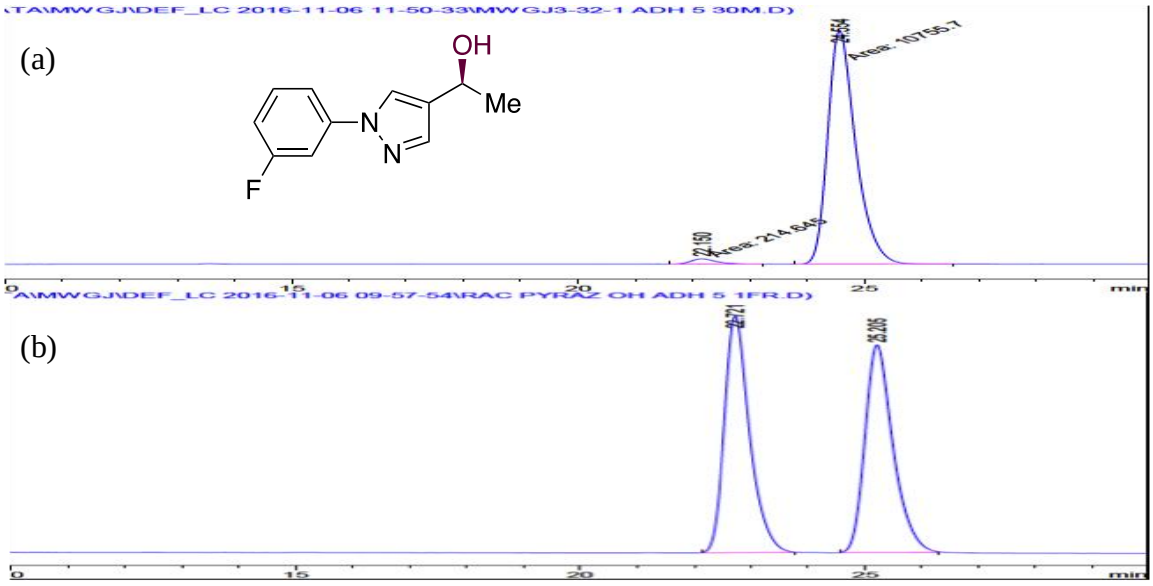
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.982 | MF | 0.1945 | 1983.22034 | 169.90463 | 98.0057 |
| 2 | 8.480 | FM | 0.2037 | 40.35651 | 3.30255 | 1.9943 |
| Totals : | | | | 2023.57685 | 173.20718 | |

(b)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.864 | BV | 0.1660 | 744.07367 | 67.83721 | 51.8086 |
| 2 | 8.337 | VB | 0.1791 | 692.12268 | 58.91120 | 48.1914 |
| Totals : | | | | 1436.19635 | 126.74841 | |

(*S*)-1-(1-(3-fluorophenyl)-1*H*-pyrazol-4-yl)ethan-1-ol (**18**)




(a)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.150 | MM | 0.5011 | 214.64462 | 7.13869 | 1.9566 |
| 2 | 24.554 | MM | 0.5646 | 1.07557e4 | 317.52478 | 98.0434 |
| Totals : | | | | 1.09703e4 | 324.66347 | |

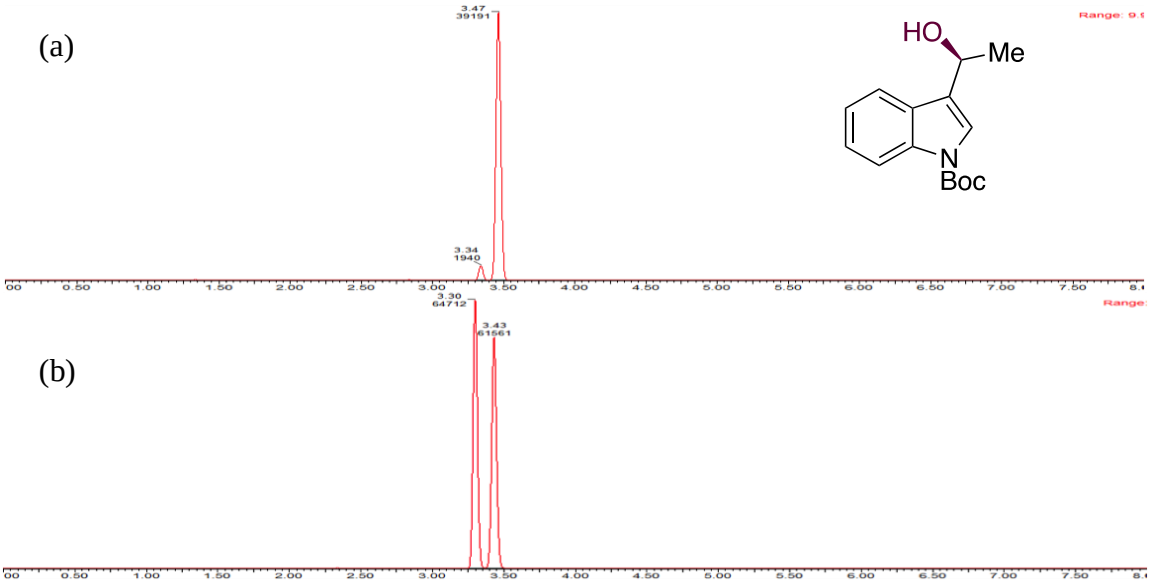
(b)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.721 | BB | 0.4663 | 4255.09229 | 137.77196 | 50.5058 |
| 2 | 25.205 | BB | 0.5221 | 4169.85742 | 120.98190 | 49.4942 |
| Totals : | | | | 8424.94971 | 258.75386 | |

*Tert*-butyl (S)-3-(1-hydroxyethyl)-1H-indole-1-carboxylate (**19**).

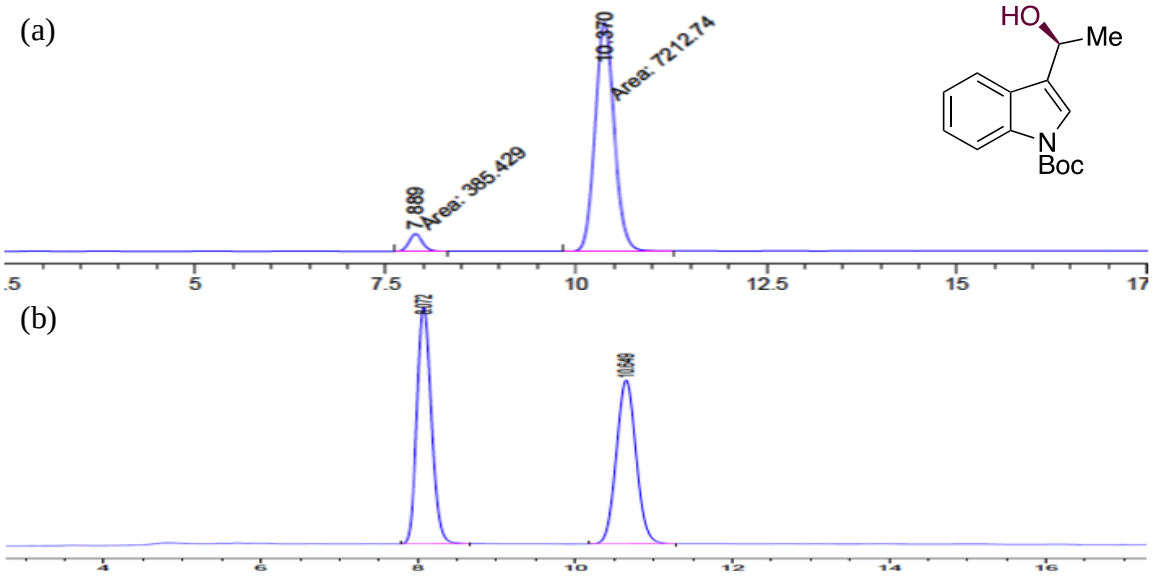
Lot from Hydrosilylation with $PhSiH_3$ followed by Tamao Oxidation:




(a)
$t_M$ = 3. 47 min, area (254 nm) = 39191, area% (254 nm) = 95.28
$t_m$ = 3.34 min, area (254 nm) = 1940, area% (254 nm) = 4.72

(b)
$t_S$ = 3.43 min, area (254 nm) = 64712, area% (254 nm) = 51.25
$t_R$ = 3.30 min, area (254 nm) = 61561, area% (254 nm) = 48.75

lot from Tamao oxidation of diphenylsilane adduct **12**:




(a)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

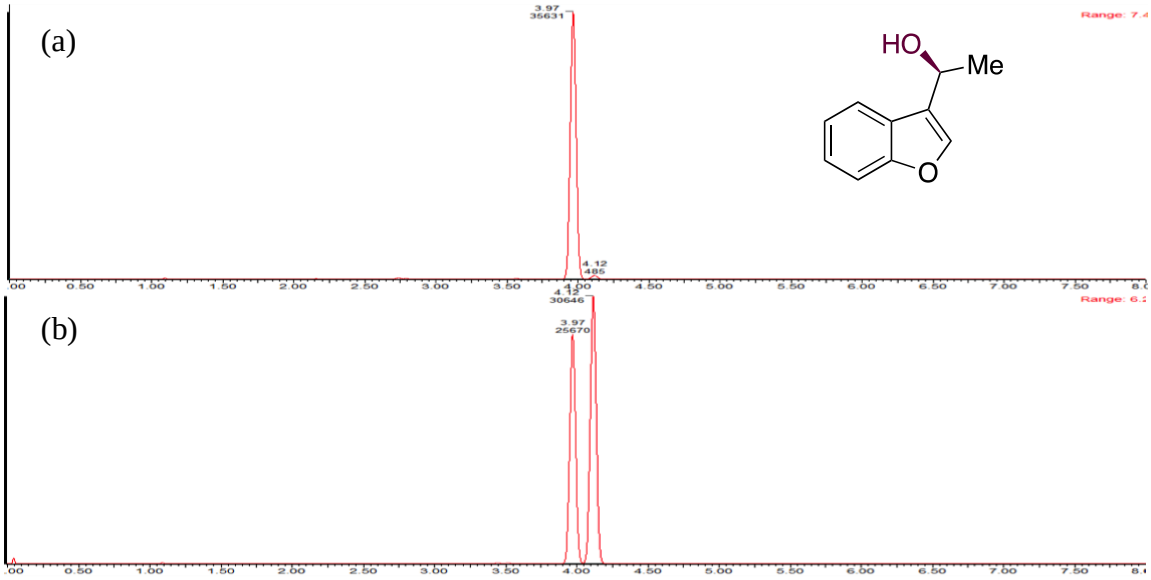
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.889 | MM | 0.2057 | 385.42886 | 31.23144 | 5.0727 |
| 2 | 10.370 | MM | 0.2903 | 7212.73779 | 414.09732 | 94.9273 |
| Totals : | | | | 7598.16666 | 445.32876 | |

(b)

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.072 | BB | 0.2023 | 1.08943e4 | 845.81244 | 51.6995 |
| 2 | 10.649 | BB | 0.2712 | 1.01781e4 | 584.33954 | 48.3005 |
| Totals : | | | | 2.10724e4 | 1430.15198 | |

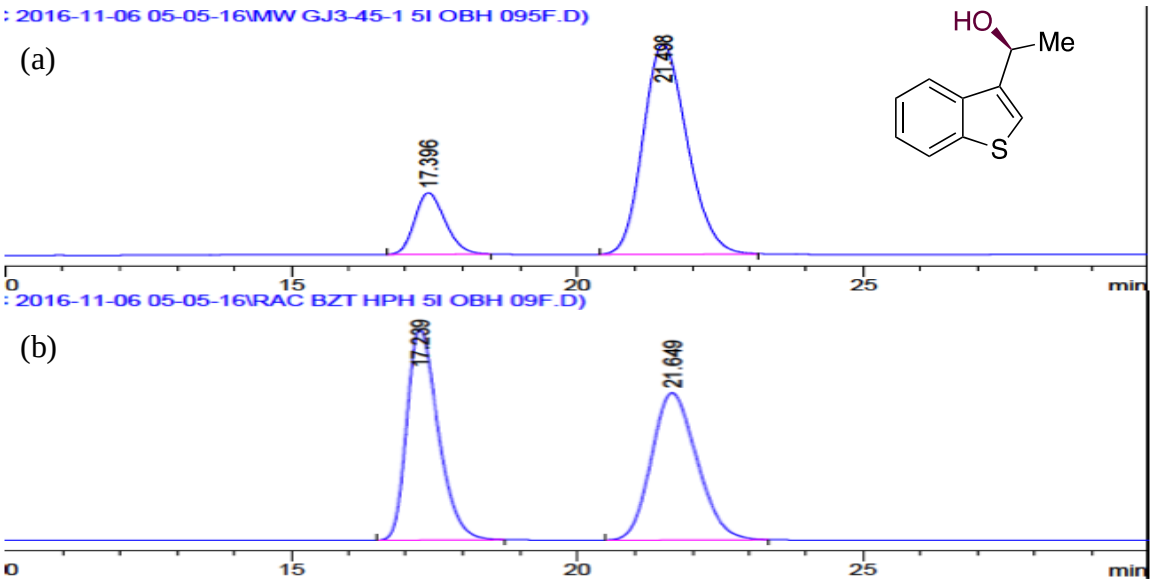
(*S*)-1-(benzofuran-3-yl)ethan-1-ol (**20**)




(a)
$t_M$ = 3. 97 min, area (254 nm) = 35631, area% (254 nm) = 98.66
$t_m$ = 4.12 min, area (254 nm) = 1940, area% (254 nm) = 1.34

(b)
$t_S$ = 3.97 min, area (254 nm) = 25670, area% (254 nm) = 45.58
$t_R$ = 4.12 min, area (254 nm) = 30646, area% (254 nm) = 54.42

(*S*)-1-(benzo[*b*]thiophen-3-yl)ethan-1-ol (**21**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

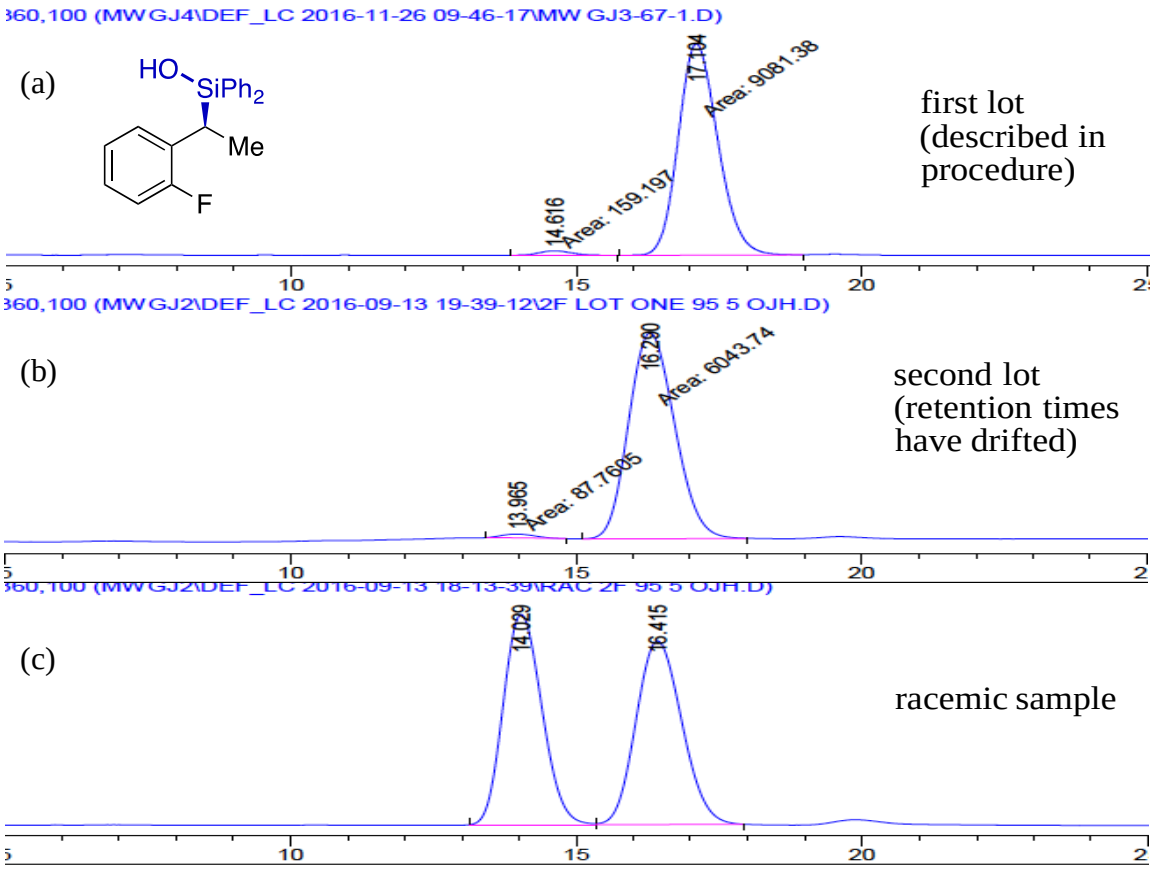
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.396 | BB | 0.5739 | 4338.12207 | 116.65466 | 16.9551 |
| 2 | 21.498 | BB | 0.8306 | 2.12479e4 | 396.88239 | 83.0449 |
| Totals : | | | | 2.55860e4 | 513.53704 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.239 | BB | 0.5867 | 2.10201e4 | 551.51892 | 49.7168 |
| 2 | 21.649 | BB | 0.8632 | 2.12596e4 | 384.43103 | 50.2832 |
| Totals : | | | | 4.22797e4 | 935.94995 | |

(*S*)-(1-(2-fluorophenyl)ethyl)diphenylsilanol (**22**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

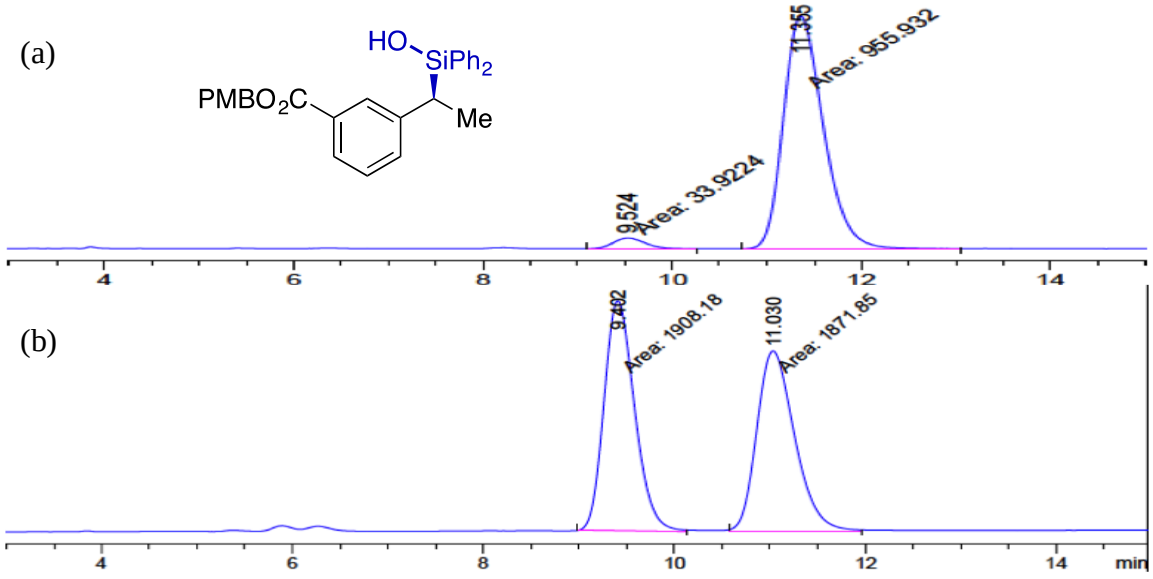
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.616 | MM | 0.6592 | 159.19685 | 4.02494 | 1.7228 |
| 2 | 17.104 | MM | 0.8032 | 9081.38086 | 188.43982 | 98.2772 |

(c)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.029 | BB | 0.7458 | 5416.82080 | 114.94668 | 49.1554 |
| 2 | 16.415 | BB | 0.8809 | 5602.95947 | 100.43362 | 50.8446 |

4-methoxybenzyl (*S*)-3-(1-(hydroxydiphenylsilyl)ethyl)benzoate (**23**)




(a)

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

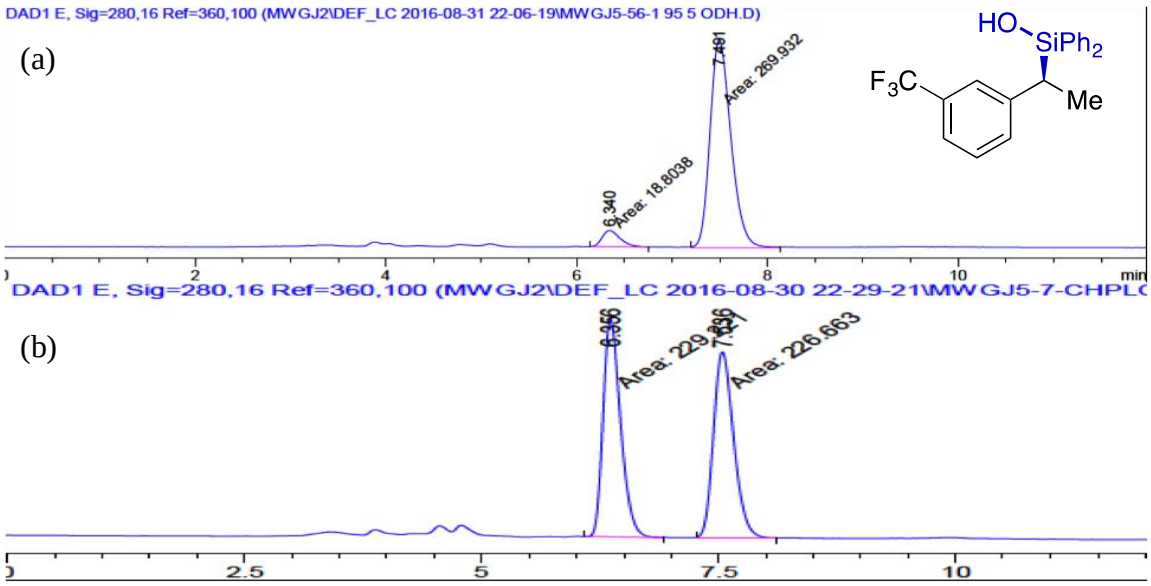
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.524 | MM | 0.3855 | 33.92236 | 1.46644 | 3.4270 |
| 2 | 11.355 | MM | 0.4876 | 955.93170 | 32.67552 | 96.5730 |
| Totals : | | | | 989.85406 | 34.14196 | |

(b)

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.402 | MM | 0.3702 | 1908.17615 | 85.91026 | 50.4804 |
| 2 | 11.030 | MM | 0.4616 | 1871.85425 | 67.58727 | 49.5196 |
| Totals : | | | | 3780.03040 | 153.49753 | |

(*S*)-diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silanol (**24**)




(a)

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

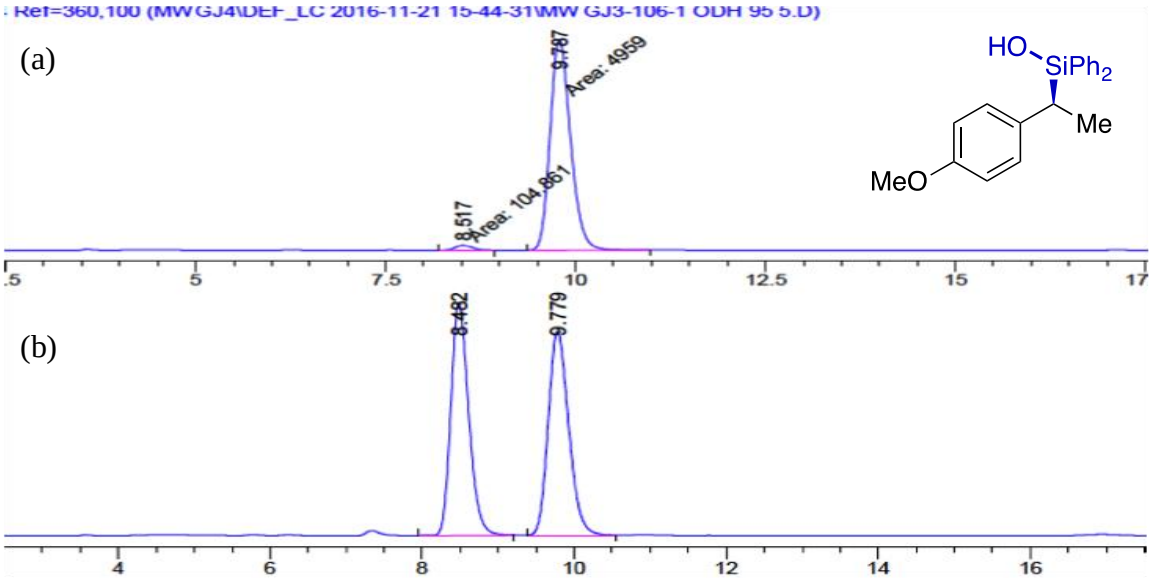
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.340 | MM | 0.2235 | 18.80378 | 1.40245 | 6.5125 |
| 2 | 7.491 | MM | 0.2528 | 269.93161 | 17.79787 | 93.4875 |
| Totals : | | | | 288.73539 | 19.20032 | |

(b)

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.356 | MM | 0.2134 | 229.22101 | 17.90295 | 50.2805 |
| 2 | 7.536 | MM | 0.2475 | 226.66315 | 15.26456 | 49.7195 |
| Totals : | | | | 455.88416 | 33.16751 | |

(*S*)-(1-(4-methoxyphenyl)ethyl)diphenylsilanol (**25**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

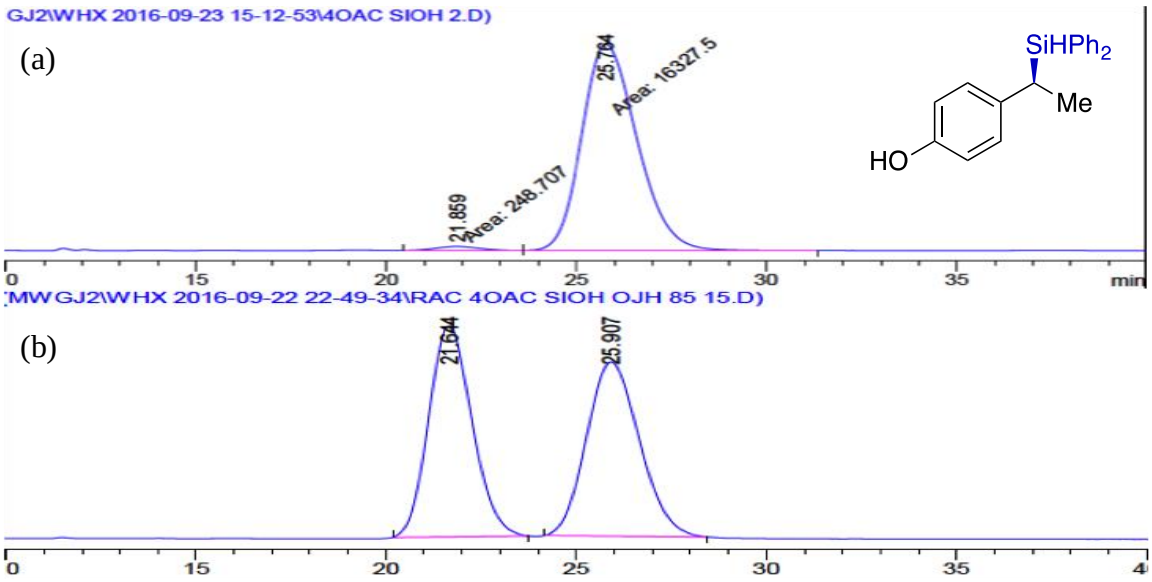
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.517 | MM | 0.2715 | 104.86123 | 6.43742 | 2.0708 |
| 2 | 9.787 | MM | 0.3121 | 4959.00293 | 264.79623 | 97.9292 |
| Totals : | | | | 5063.86416 | 271.23366 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.651 | MM | 0.2424 | 7091.31348 | 487.60974 | 48.9530 |
| 2 | 8.810 | MM | 0.2859 | 7394.64941 | 431.02771 | 51.0470 |
| Totals : | | | | 1.44860e4 | 918.63745 | |

(*S*)-4-(1-(diphenylsilyl)ethyl)phenol (**26**)




(a)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.859 | MF | 1.3345 | 248.70749 | 3.10602 | 1.5004 |
| 2 | 25.764 | FM | 1.6829 | 1.63275e4 | 161.70064 | 98.4996 |
| Totals : | | | | 1.65762e4 | 164.80666 | |

(b)

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.644 | BB | 1.1848 | 6230.08984 | 78.26025 | 49.8119 |
| 2 | 25.907 | BB | 1.4189 | 6277.13232 | 64.64204 | 50.1881 |
| Totals : | | | | 1.25072e4 | 142.90229 | |