Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Regiodivergent and Stereoselective Hydrosilylation of 1,3-Disubstituted Allenes**

*Zachary D. Miller, Ruth Dorel, and John Montgomery**

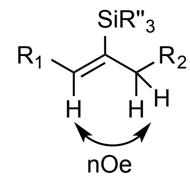
anie_201503521_sm_miscellaneous_information.pdf

All reagents were used as received unless otherwise noted. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, Inc. Model # SPS-400-3 and PS-400-3). *Tris*(dibenzylideneacetone)-dipalladium (Pd_2dba_3) was purchased from Sigma Aldrich and was stored in a glovebox and on the benchtop. All reactions were conducted under an atmosphere of nitrogen with magnetic stirring in flame-dried or oven-dried (120 ˚C) glassware. All acyclic allenes were made according to literature precedent from the terminal alkyne and aldehyde.[1] Cyclic allenes were made according to literature precedent from the respective ketone.[2] Ligand **6** (IPr*^{OMe}) was purchased from Strem and was stored in a glovebox. NHC Ligands **4** (IMes·HCl) and **5** (IPr·HCl) were purchased from Sigma-Aldrich and stored and weighed in a glovebox. Ligand DP-IPr was prepared according to literature procedure.[3] Dimethylphenylsilane and dimethylbenzylsilane (purchased from Sigma-Aldrich) were used as received. A solution of tetra-*n*-butylammonium (TBAF, 1.0 M in THF) was purchased from Sigma-Aldrich and used as received. Cyclohexylallene, propylsilane, and *d*-triethylsilane (97% *d*-purity) were purchased from Sigma-Aldrich and were used as received. 4'-Iodoacetophenone and *N*-iodosuccinimide were purchased from Sigma-Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ at rt (25 ˚C), unless otherwise noted, on a Varian Mercury 400 MHz instrument, Varian Unity 500 MHz instrument, or Varian Unity 700 MHz instrument. Chemical shifts of ^{1}H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.24 ppm). Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High-resolution mass spectra (HRMS) were obtained on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory. Regioisomeric ratios were determined on crude reaction mixtures using NMR or GC. GC analyses were carried out on an HP 6980 Series GC System with HP-5MS column (30 m x 0.252 mm x 0.25 μm). When noted, a Biotage purification system (model # SP1) was utilized with SNAP (10 g) silica columns. Reported regioselectivities were determined by GCMS analysis and confirmed by ^{1}H NMR analysis by comparing the ratios of detectable alkenyl protons of the major and minor regioisomers in the crude reaction mixture. In cases where >98:2 regio- or stereoselectivity is reported, minor isomers were not detected by either GCMS or NMR based methods.

General Procedure I for the $Ni(COD)_2$/IPr*^{OMe} – promoted hydrosilylation of 1,3-disubstituted allenes:

THF (1.0 mL) was added to a solid mixture of IPr*OMe **6** (0.05 mmol) and $Ni(COD)_2$ (0.05 mmol) at rt. After stirring for 10 min at rt the silane (0.5 mmol) was added. The reaction mixture was stirred for 10 min at rt followed by the addition of allene (0.5 mmol) in THF (3.0 mL) over 1 h by syringe pump. The reaction mixture was stirred at rt until TLC analysis indicated disappearance of the allene. The reaction mixture was filtered through silica gel eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash column chromatography on silica gel to afford the desired product.

The alkene configuration of representative alkenylsilanes was determined by 1D NOE, where alkenyl protons for major isomers were determined to have the following observable correlation (confirming *Z* stereochemistry):



General Procedure II for the Pd_2dba_3/ IPr·HCl – promoted hydrosilylation of 1,3-disubstituted allenes

THF (1.0 mL) was added to a solid mixture of IPr·HCl **5** (0.025 mmol), *t*-BuOK (0.025 mmol), and Pd_2dba_3 (0.0125 mmol) at rt. After stirring for 10 min at rt, the reaction mixture turned dark red and the silane (0.5 mmol) was added. The reaction mixture was stirred for 10 min at rt followed by addition of the allene (0.5 mmol) neat by syringe. The reaction mixture was stirred at rt for 2 h. The reaction mixture was filtered through silica gel eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash column chromatography on silica gel to afford the desired product. Product stereochemistry is confirmed via determination of ^3J(H-H) coupling across the alkene.

General procedure III for the $Ni(COD)_2$/DP-IPr-promoted hydrosilylation of monosubstituted allenes affording alkenylsilane authentic standards:

THF (1.0 mL) was added to a solid mixture of DP-IPr·HBF_4 (0.03 mmol), *t*-BuOK (0.03 mmol), and $Ni(COD)_2$ (0.03 mmol) at rt. After stirring for 10 min at rt, the silane (0.3 mmol) was added. The reaction mixture was stirred for 10 min at rt followed by the addition of allene (0.3 mmol) in THF (4.0 mL) over 2 h by syringe pump. The reaction mixture was stirred at rt until TLC analysis indicated disappearance of the allene. The reaction mixture was filtered through silica gel eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash column chromatography on silica gel to afford the desired product.

General procedure IV for the Pd_2dba_3/ IMes –promoted hydrosilylation of monosubstituted allenes affording allylsilane authentic standards:

THF (1.0 mL) was added to a solid mixture of IMes·HCl **4** (0.03 mmol), KO-*t*-Bu (0.03 mmol), and Pd_2dba_3 (0.015 mmol) at rt. After stirring for 10 min at rt, the reaction mixture turned bright red and triethylsilane (0.3 mmol) was added. The reaction mixture was stirred for 10 min at rt followed by dilution with THF (4.0 mL) and addition of the allene (0.3 mmol) neat by syringe. The reaction mixture was stirred at rt for 2 h. The reaction mixture was filtered through silica gel eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash column chromatography on silica gel to afford the desired product.

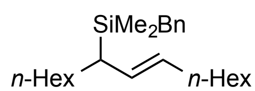
General procedure V for the $Ni(COD)_2$/DP-IPr-promoted hydrosilylation crossover experiment:

THF (1.0 mL) was added to a solid mixture of DP-IPr·HBF_4 (0.03 mmol), KO-t-Bu (0.03 mmol) and $Ni(COD)_2$ (0.03 mmol) at rt. After stirring for 10 min at rt, the Et_3SiD (0.3 mmol) and *n*-Pr_3SiH (0.3 mmol) and cyclohexylallene (0.3 mmol) were added in THF (4.0 mL) over 2 h by syringe pump. The reaction mixture was filtered through silica gel eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was directly analyzed by GCMS and GCFID.

General procedure VI for the Pd_2dba_3/ IMes –promoted hydrosilylation crossover experiment:

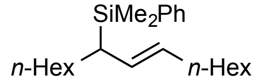
THF (1.0 mL) was added to a solid mixture of IMes·HCl **4** (0.03 mmol), and Pd_2dba_3 (0.015 mmol) at rt. Then n-BuLi (0.0.3 mmol) was slowly added to the stirring solution. After stirring for 10 min at rt, the Et_3SiD (0.3 mmol) and *n*-Pr_3SiH (0.3 mmol) addition of cyclohexylallene (0.3 mmol) in THF (4.0 mL) over 2 h by syringe pump. The reaction mixture was filtered through silica gel eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was directly analyzed by GCMS and GCFID.

(*E*)-Benzyldimethyl(pentadec-8-en-7-yl)silane (2a) (Table 2, Entry 1)



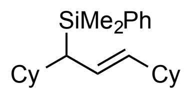
General procedure II was followed with Pd_2dba_3 (11.4 mg, 0.0125 mmol), IPr·HCl salt **5** (10.6 mg, 0.025 mmol), *t*-BuOK (2.8 mg, 0.025 mmol), benzyldimethylsilane (79 μL, 0.5 mmol), and pentadeca-1,7-diene (104 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (135 mg, 75 % yield) (in >98:2 regiosel, >98:2 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$): 7.19 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 6.8 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2H), 5.22 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.14 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.07 (s, 2H), 1.98 (q, J = 7.0 Hz, 2H), 1.36 – 1.48 (m, 3H), 1.14 – 1.34 (m, 17H), 0.87 (t, *J* = 6.6 Hz, 6H), -0.10 (s, 3H), -0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 131.0, 129.0, 128.2, 128.1, 123.8, 32.9, 31.9, 31.8, 31.7, 30.0, 29.2, 29.2, 28.9, 28.7, 23.9, 22.7, 14.1, -5.10, -5.15; IR (thin film): ν 2954.8, 2924.4, 2856.0, 1703.5, 1600.0, 1493, 1452, 1057, 827.8, 697.7 cm^{-1}; HRMS (EI^+) (m/z): $[M]^+$ calc for $C_{24}H_{42}Si$, 358.3056; found, 358.3068.

(*E*)-Dimethyl(pentadec-8-en-7-yl)(phenyl)silane (2b) (Table 2, Entry 2)



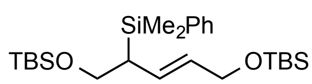
General procedure II was followed with Pd_2dba_3 (11.4 mg, 0.0125 mmol), IPr·HCl salt **5** (10.6 mg, 0.025 mmol), *t*-BuOK (2.8 mg, 0.025 mmol), dimethylphenylsilane (77 μL, 0.5 mmol), and pentadeca-1,7-diene (104 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (151 mg, 84 % yield) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (m, 2H), 7.32 (m, 3H), 5.17 (dt, *J* = 15.9, 6.2 Hz, 1H), 5.11 (dd, *J* = 15.9, 6.2 Hz, 1H), 1.95 (q, *J* = 6.5 Hz, 2H), 1.60 (t, *J* = 11.7 Hz, 1H), 1.10 – 1.39 (m, 21H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 6.8 Hz, 3H), 0.22 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4, 134.1, 130.9, 129.0, 128.7, 127.5, 32.9, 32.4, 31.83, 31.80, 30.0, 29.2, 29.0, 28.9, 28.8, 22.70, 22.68, 14.12, 14.10, -4.25, -5.10; IR (thin film): ν 2954.0, 2925.1, 2857, 1709.7, 1465.4, 1427.5, 1249.4, 1117.7, 829.3, 698.2 cm^{-1}; HRMS (EI$^+$) (m/z): [M]$^+$ calc for $C_{23}H_{40}Si$, 344.2899; found, 344.2907.

(*E*)-(1,3-Dicyclohexylallyl)dimethyl(phenyl)silane. (2c) (Table 2, Entry 3)



General procedure II was followed with Pd_2dba_3 (13.7 mg, 0.015 mmol), IPr·HCl salt **5** (12.8 mg, 0.03 mmol), *t*-BuOK (3.6 mg, 0.03 mmol), dimethylphenylsilane (46 μL, 0.3 mmol), and 1,3-dicyclohexylpropa-1,2-diene (61 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (98.7 mg, 58 % yield) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.46 (m, 2H), 7.37 – 7.29 (m, 3H), 5.31 – 5.21 (m, 1H), 5.13 (dd, *J* = 15.2, 6.7 Hz, 1H), 1.93 (m, *J* = 10.6, 7.0 Hz, 1H), 1.76 – 1.56 (m, 11H), 1.50 – 1.38 (m, 2H), 1.33 – 0.90 (m, 11H), 0.30 (d, *J* = 2.0 Hz, 3H), 0.27 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.43, 136.25, 133.96, 128.50, 127.43, 125.88, 41.11, 40.14, 38.69, 34.08, 33.64, 33.48, 31.48, 26.77, 26.74, 26.32, 26.26, 26.14, -2.64, -3.37; IR (thin film): ν 2917.9, 2847.5, 1446.9, 1426.0, 1245.3, 1109.7, 997.9, 966.1, 891.9, 851.1, 811.4, 767.3, 732.3, 697.5, 641.7 cm^{-1}; HRMS (EI$^+$) (m/z): [M$^+$] calc for $C_{23}H_{36}Si$, 340.2586; found, 340.2589.

(*E*)-8-(dimethyl(phenyl)silyl)-2,2,3,3,11,11,12,12-octamethyl-4,10-dioxa-3,11-disilatridec-6-ene (2d) (Table 2, Entry 4)



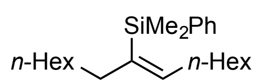
General procedure II was followed with Pd_2dba_3 (4.8 mg, 0.0052 mmol), IPr·HCl salt **5** (4.5 mg, 0.0105 mmol), *t*-BuOK (1.2 mg, 0.0105 mmol), dimethylphenylsilane (32 μL, 0.21 mmol), and 2,2,3,3,11,11,12,12-octamethyl-4,10-dioxa-3,11-disilatrideca-6,7-diene

(70 mg, 0.21 mmol). The crude residue was purified by flash chromatography (10% EtOAc:hexanes) affording a clear oil (60 mg, 64 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (m, 2H), 7.35 (m, 3H), 5.63 (dd, J = 15.0, 9.0 Hz, 1H), 5.40 (dt, J = 15.0, 6.1 Hz, 1H), 4.12 (d, J = 5.8 Hz, 2H), 3.73 (m, 2H), 2.00 (m, 1H), 0.912 (s, 9H), 0.872 (s, 9H), 0.322 (s, 3H), 0.309 (s, 3H),0.063 (s, 6H), -0.0047 (s, 3H), -0.014 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.0, 133.0, 130.0, 128.8, 128.4, 127.5, 64.2, 63.9, 36.6, 26.0, 18.3, -3.7, -4.0, -5.11, -5.14, -5.40, -5.43; IR (thin film): ν 2953.5, 2926.2, 1704.1, 1462.4, 1250.7, 1089.8, 831.8 cm^{-1}; HRMS (ESI$^+$) (m/z): [M+Na]$^+$ calc for $C_{25}H_{48}O_2Si_3$, 487.2854; found, 487, 2851.

(*Z*)-Benzyldimethyl(tetradec-7-en-7-yl)silane (3a) (Table 2, Entry 5)

General procedure I was followed with $Ni(COD)_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), benzyldimethylsilane (79 µL, 0.5 mmol), and pentadeca-1,7-diene (104 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (159 mg, 89% yield) (in >98:2 regiosel.; >98:2 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, J = 7.8 Hz, 2H), 7.05 (m, 1H), 7.00 (m, 2H), 5.97 (t, J = 7.2 Hz, 1H), 2.20 (s, 2H), 2.01 – 2.08 (m, 2H), 1.93 – 1.99 (m, 3H), 1.15 – 1.36 (m, 18H), 0.88 (m, 6H), 0.080 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.3, 137.4, 128.32, 128.27, 128.0, 123.9, 38.4, 32.3, 31.9, 31.8, 30.0, 29.4, 29.2, 29.1, 28.5, 26.7, 22.7, 22.6, 14.1, -1.7; IR (thin film): ν 2953.5, 2923.7, 2853.6, 1716.2, 1600.8, 1493.2, 1452.2, 1377.5, 1248.7, 1056.5, 826.3 cm^{-1}; HRMS (EI$^+$) (m/z): [M$^+$] calc for $C_{24}H_{42}Si$, 358.3056; found, 358.3066.

(*Z*)-Dimethyl(phenyl)(tetradec-7-en-7-yl)silane (3b) (Table 2, Entry 6)

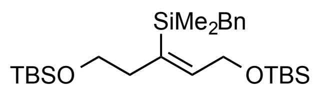


General procedure I was followed with $Ni(COD)_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), dimethylphenylsilane (77 µL, 0.5 mmol), and pentadeca-1,7-diene (104 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (147 mg, 85 % yield) (in >98:2 regosel, >98:2 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 2H), 7.33 (m, 3H), 6.04 (t, J = 7.2 Hz, 2H), 1.08-1.36 (m, 18H), 0.87 (t, J = 8.0 Hz, 3H), 0.83 (t, J = 8.0 Hz, 3H), 0.369 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 140.2, 136.9, 133.8, 128.6, 127.6, 38.6, 32.5, 31.9, 31.7, 31.0, 29.8, 29.4, 29.2, 28.9, 22.7, 22.6, 14.12, 14.06, -0.83; IR (thin film): 2954.0, 2923.6, 2855.0, 1708.5, 1610.1, 1465.0, 1427.5, 1248.5, 1110.7, 831.2 cm-1; HRMS (EI+) (m/z): [M-CH_3]+ calc for $C_{22}H_{37}Si$, 329.2665; found, 329.2669.

(*Z*)-(1,3-Dicyclohexylprop-1-en-2-yl)dimethyl(phenyl)silane (3c) (Table 2, Entry 7)

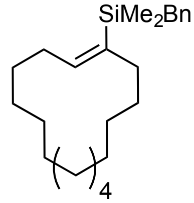
General procedure I was followed with Ni(COD)$_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), dimethylphenylsilane (77 μL, 0.5 mmol), and 1,3-dicyclohexylpropa-1,2-diene (102 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (110.7 mg, 65%) (in >98:2 regiosel., 96:4 d.r.). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.50 - 7.57 (m, 2H), 7.30 – 7.36 (m, 3H), 5.75 (d, *J* = 10.4 Hz, 1H), 5.70 (d, J = 10.4 Hz, 0.06H, minor *E*-isomer), 1.99 - 2.05 (m, 1H), 1.97 (dd, *J* = 6.8, 0.6 Hz, 2H), 1.63 – 1.71 (m, 5H), 1.50 – 1.60 (m, 4H), 1.41 – 1.36 (m, 2H), 1.11 – 1.22 (m, 4H), 0.91 – 1.01 (m, 4H), 0.74 – 0.84 (m, 2H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 151.72, 140.51, 133.70, 132.89, 128.48, 127.50, 46.62, 41.24, 37.65, 33.11, 32.95, 26.77, 26.49, 25.92, 25.65, -0.81; IR (thin film): ν 2918.4, 2846.8, 1609.5, 1446.8, 1426.3, 1245.8, 1108.6, 903.4, 830.3, 812.1, 768.4, 727.2, 698.0, 675.0 cm^{-1}; HRMS (EI$^+$) (m/z): [M$^+$] calc for $C_{23}H_{36}Si$, 340.2586; found, 340.2585.

(*Z*)-7-(benzyldimethylsilyl)-2,2,3,3,11,11,12,12-octamethyl-4,10-dioxa-3,11-disilatridec-6-ene (3d) (Table 2, Entry 8)



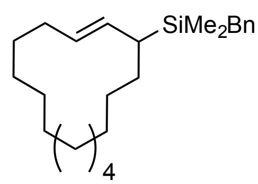
General procedure I was followed with Ni(COD)$_2$ (2.9 mg, 0.00105 mmol), IPr*OMe **6** (9.8 mg, 0.00105 mmol), benzyldimethylsilane (33 μL, 0.21 mmol), and 2,2,3,3,11,11,12,12-octamethyl-4,10-dioxa-3,11-disilatrideca-6,7-diene (70 mg, 0.21 mmol). The crude residue was purified by flash column chromatography (10% EtOAc: hexanes) affording a clear oil (75 mg, 75 % yield) (in >98:2 regiosel., 85:15 d.r.). ^{1}H NMR (500 MHz): δ 7.18 (t, *J* = 9.0 Hz, 2H), 7.05 (t, *J* = 9.0 Hz, 1H), 6.97 (d, J = 9.0 Hz, 2H), 6.13 (t, *J* = 7.4, 1 H, major isomer), 5.90 (t, *J* = 7.4 Hz, 0.1H, minor *E*-isomer), 4.04 (d, *J* = 9.4 Hz, 2H), 3.42 (t, *J* = 8.5 Hz, 2H), 2.23 (t, *J* = 7.4 Hz, 2H), 2.16 (s, 2H), 0.88 (s, 10H), 0.86 (s, 10H), 0.098 (s, 6H), 0.035 (s, 6H), 0.0093 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 145.4, 143.9 (minor), 139.6, 139.4 (minor),135.3, 128.3, 128.1, 124.2, 124.0 (minor),63.9, 62.7, 40.9, 26.5, 26.02, 26.00, 18.4, -0.09, -1.9, -5.1, -5.2; IR (thin film): ν 2953.5, 2926.2, 2856.6, 1704.1, 1601.0, 1462.4, 1250.7, 1089.8, 831.8, 697.8 cm^{-1}; HRMS (ESI$^+$) (m/z): [M+Na]$^+$ calc for $C_{26}H_{50}S_3O_2$, 501.3011; found, 501.3009.

(*Z*)-Benzyl(cyclopentadec-1-en-1-yl)dimethylsilane (8) (Scheme 1)



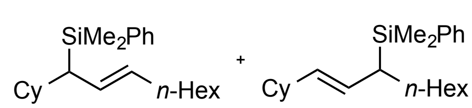
General procedure I was followed with $Ni(COD)_2$ (6.6 mg, 0.024 mmol), IPr*OMe **6** (22.7 mg, 0.024 mmol), benzyldimethylsilane (37.9 μL, 0.24 mmol), and cyclopentadeca-1,2-diene (50 mg, 0.24 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (61 mg, 71% yield) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (t, *J* = 9.9 Hz, 2H), 7.04 (t, *J* = 9.9 Hz, 1H), 7.00 (d, *J* = 9.9 Hz, 2H), 5.94 (t, *J* = 8.6 Hz, 1H), 2.21 (s, 2H), 2.17 (m, 2H), 2.07 (m, 2H), 1.39 – 1.47 (m, 2H), 1.16 – 1.38 (m, 20H), 0.069 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): 145.2, 140.3, 137.3, 128.3, 128.0, 123.9, 37.6, 31.2, 29.4, 29.0, 27.7, 27.6, 27.25, 27.20, 27.1, 26.9, 26.8, 26.7, 26.5, 26.0, -1.7; IR (thin film): ν 2925.9, 2855.4, 1493.2, 1451.4, 1248.6, 1151.4, 828.7 cm^{-1}; HRMS (EI^+) (m/z): $[M]^+$ calc for $C_{24}H_{40}Si$, 356.2899; found, 356.2901.

(*E*)-Benzyl(cyclopentadec-2-en-1-yl)dimethylsilane (9) (Scheme 1)



General procedure II was followed with Pd_2dba_3 (5.5 mg, 0.006 mmol), IPr·HCl salt **5** (5.1 mg, 0.012 mmol), *t*-BuOK (1.3 mg, 0.012 mmol), benzyldimethylsilane (37.9 μL, 0.24 mmol), and cyclopentadeca-1,2-diene (50 mg, 0.24 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (57 mg, 66 % yield) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.5 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5, 2H), 5.15 (m, 2H), 2.15 (m, 1H), 2.07 (s, 2H), 1.96 (m, 1H), 1.09 – 1.5 (m, 26H), -0.103 (s, 3H), -0.118 (s, 3H). ^{1}H NMR (700 MHz, C_6D_6): 7.21 (m, 2H (overlapping signals)), 7.03-7.10 (m, 3H), 5.20 (dd, *J* = 15.8, 10.2 Hz, 1H), 5.15 (ddd, J = 15.8, 10.2, 4.0 Hz, 1H), 2.21 (m, 1H), 2.10 (s, 2H), 2.04 (m, 1H), 1.25 – 1.52 (m, 26H), -0.0039 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 140.5, 131.7, 129.1, 128.2, 128.1, 123.8, 31.9, 31.5, 29.0, 28.7, 28.2, 27.2, 27.1, 26.9, 26.8, 26.7, 25.4, 23.8, -5.2, -5.3; IR (thin film): ν 2926.0, 2856.4, 1599.8, 1451.8, 1257.8, 1152.4, 826.8 cm^{-1}; HRMS (EI^+) (m/z): $[M]^+$ calc for $C_{24}H_{40}Si$, 356.2899; found, 356.2902.

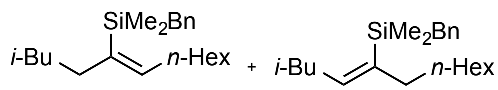
(*E*)-(1-Cyclohexylnon-2-en-1-yl)dimethyl(phenyl)silane and (*E*)-(1-cyclohexylnon-1-en-3-yl)dimethyl(phenyl)silane (10a & 11a) (Scheme 2)



General procedure II was followed with Pd_2dba_3 (22.9 mg, 0.025 mmol), IPr·HCl salt **5** (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), dimethylphenylsilane (77 μL, 0.5 mmol), and nona-1,2-dien-1-ylcyclohexane (103.2 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (137 mg, 80 %

yield) (in 60:40 regiosel. **10a** & **11a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (m, 4 H), 7.37 (m, 6H), 5.33 (dd, *J* = 15.7, 10.8 Hz, 1H), 5.21 (dt, *J* = 16, 11 Hz, 1H), 5.19 (dd, *J* = 16, 11 Hz, 0.7 Hz), 5.14 (dd, *J* = 16, 9.2 Hz, 0.7H), 2.02 (m, 2H), 1.94 (m, 1H), 1.57 – 1.76 (m, 11H), 1.10 – 1.38 (m, 26H), 0.936 (t, *J* = 10 Hz, 3H), 0.90 (t, *J* = 10 Hz, 3H), 0.33 (s, 3H), 0.30 (s, 3H), 0.29 (2H), 0.278 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.5, 138.4, 135.1, 134.2, 134.0, 130.3, 128.7, 128.60, 128.55, 128.2, 127.5, 41.1, 40.3, 38.8, 34.2, 33.7, 33.6, 32.9, 32.4, 31.9, 31.8, 31.5, 30.0, 29.10, 29.06, 28.9, 28.8, 26.82, 26.80, 26.4, 26.2, 22.74, 22.71, 14.2, 14.1, -2.6, -3.3, -4.3, -5.1; IR (thin film); ν 2925.4, 2852.1, 1725.7, 1448.5, 1427.5, 1249.4, 1117.9, 1061.8, 971.7, 828.9, 698.7, 418.6 cm^{-1}; HRMS (EI^{+}) (m/z): [M]$^{+}$ calc for $C_{23}H_{38}Si$, 342.2743; found, 342.2749.

(*Z*)-Benzyldimethyl(2-methyldodec-5-en-5-yl)silane and (*Z*)-benzyldimethyl(2-methyldodec-4-en-5-yl)silane (12a & 13a) (Table 3, Entry 1)

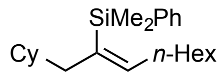


General procedure I was followed with Ni(COD)$_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), benzyldimethylsilane (79 μL, 0.5 mmol), and 2-methyldodeca-14,5-diene (90.2 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (114 mg, 69% yield) (in 50:50 rr, of **12a**:**13a**, 91:9 allyl:vinyl regiosel). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 8.0 Hz, 4H), 7.07 (t, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.1 Hz, 4H), 6.02 (t, *J* = 8.0 Hz, 1H), 5.99 (t, *J* = 8.0 Hz, 1H), 5.09 (m, 0.19H (minor allyl isomer)), 2.22 (s, 4H), 2.13 (m, 1H), 1.94 -2.09 (m, 9H), 1.61 (m, 1H), 1.48 (m, 2H), 1.20 – 1.39 (m, 25H), 1.05 – 1.12 (m, 2H), 0.88 – 0.94 (m, 15H), 0.87 (s, 4H), 0.85 (s, 3H), 0.10 (s, 4H), 0.097 (s, 4H), 0.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, major signals from the 3 isomers are listed): δ 146.2, 143.9, 142.9 140.4, 140.29, 140.27, 139.7, 134.9, 128.3, 128.0, 125.1, 123.9, 123.8, 45.3, 41.1, 40.5, 38.6, 37.2, 36.3, 32.3, 31.9, 31.8, 31.02, 30.1, 29.6, 29.4, 29.2, 29.1, 29.0, 28.3, 27.9, 26.8, 26.7, 26.5, 22.64, 22.60, 22.46, 14.1, -1.64, -1.7, -1.9; IR (thin film): ν 2952.9, 2924.8, 1600.8, 1493.1, 1465.3, 1248.1, 1205.2, 1153.5, 1055.9 826.1 cm^{-1}; HRMS (EI^{+}) (m/z): [M]$^{+}$ calc for $C_{22}H_{38}Si$, 330.2743; found, 330.2739.

(*Z*)-Benzyldimethyl(2-methylundec-4-en-4-yl)silane (12b) (Table 3, Entry 2).

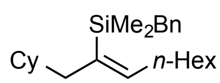
General procedure I was followed with Ni(COD)$_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), benzyldimethylsilane (79 μL, 0.5 mmol), and 2-methylundeca-3,4-diene (83.2 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (101.3 mg, 64%) (in 98:2 regiosel., >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.08 – 7.05 (m, 2H), 5.99 (t, *J* = 7.5 Hz, 1H), 2.27 (s, 2H), 2.15 (q, *J* = 7.3 Hz, 2H), 1.94 (d, *J* = 6.9 Hz, 2H), 1.55 – 1.45 (m, 1H), 1.43 – 1.30 (m, 8H), 0.95 (t, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.14 (s, *J* = 12.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.62, 140.29, 136.17, 128.29, 128.07, 123.96, 48.37, 32.48, 31.88, 30.17, 29.21, 28.18, 26.77, 22.69, 22.34, 14.12, -1.70. IR (cm^{-1}): ν 2951.5, 2921.7, 2851.0, 1601.2, 1492.6, 1461.3, 1451.2, 1363.5, 1247.3, 1204.7, 1153.3, 1055.9, 901.0, 825.2, 789.5, 759.3, 696.5 cm^{-1}; HRMS (EI^+) (m/z): [M^+] calc for $C_{21}H_{36}Si$, 316.2586; found, 316.2590.

(*Z*)-(1-Cyclohexylnon-2-en-2-yl)dimethyl(phenyl)silane (12c) (Table 3, Entry 3)



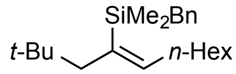
General procedure I was followed with $Ni(COD)_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), dimethylphenylsilane (77 μL, 0.5 mmol), and nona-1,2-dien-1-ylcyclohexane (103 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (87.3 mg, 51%) (in >98:2 regiosel, >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 – 7.52 (m, 2H), 7.37 – 7.32 (m, 3H), 6.00 (t, *J* = 7.5 Hz, 1H), 2.01 (d, *J* = 6.8 Hz, 2H), 1.96 (q, *J* = 7.4 Hz, 2H), 1.74 – 1.67 (m, 4H), 1.67 – 1.62 (m, 1H), 1.28 – 1.11 (m, 12H), 0.93 – 0.77 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.12, 140.23, 134.89, 133.73, 128.52, 127.58, 46.90, 37.72, 33.19, 32.54, 31.70, 29.81, 28.96, 26.75, 26.47, 22.58, 14.05, -0.84; IR (thin film): ν 2918.3, 2848.9, 1609.0, 1447.8, 1426.7, 1246.4, 1109.0, 831.0, 812.4, 769.2, 726.6, 698.3, 669.5 cm^{-1}; HRMS (EI^+) (m/z): [M^+] calc for $C_{23}H_{38}Si$, 342.2743; found 342.2740.

(*Z*)-Benzyl(1-cyclohexylnon-2-en-2-yl)dimethylsilane (12d) (Table 3, Entry 4)



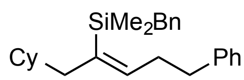
General procedure I was followed with $Ni(COD)_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), benzyldimethylsilane (79 μL, 0.5 mmol), and nona-1,2-dien-1ylcyclohexane (103 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (125 mg, 70 %) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.05 – 7.01 (m, 2H), 5.93 (t, *J* = 7.5 Hz, 1H), 2.23 (s, 2H), 2.11 (q, *J* = 7.4 Hz, 2H), 1.90 (d, *J* = 6.8 Hz, 2H), 1.73 – 1.63 (m, 5H), 1.41 – 1.27 (m, 8H), 1.21 – 1.12 (m, 3H), 1.11 – 1.04 (m, 1H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.86 – 0.74 (m, 2H), 0.10 (s, *J* = 2.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.51, 140.29, 135.36, 128.24, 128.05, 123.92, 46.79, 37.67, 33.21, 32.43, 31.82, 30.14, 29.18, 26.76, 26.74, 26.47, 22.66, 14.09, -1.70; IR (thin film): ν 2918.5, 2849.2, 1600.9, 1492.4, 1448.8, 1246.7, 1205.0, 1153.4, 1055.7, 900.8, 826.8, 789.5, 759.1, 696.3 cm^{-1}; HRMS (EI^+) (m/z): [M^+] calc for $C_{24}H_{40}Si$, 356.2899; found, 356.2894.

(*Z*)-Benzyl(2,2-dimethylundec-4-en-4-yl)dimethylsilane (12e) (Table 3, Entry 5)



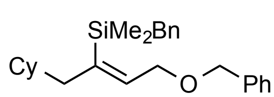
General procedure I was followed with Ni(COD)$_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), benzyldimethylsilane (79 μL, 0.5 mmol), and 2,2-dimethylundeca-3,4-diene (90.2 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (86.0 mg, 52%) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.22 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.05 (t, *J* = 7.6 Hz, 1H), 2.26 (s, 2H), 2.17 (d, *J* = 7.6 Hz, 2H), 1.97 (s, 2H), 1.45 – 1.38 (m, 2H), 1.37 – 1.28 (m, 6H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.87 (s, 9H), 0.10 (s, *J* = 4.4 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 148.74, 140.56, 134.38, 128.32, 128.05, 123.90, 49.36, 32.99, 32.04, 31.85, 30.14, 29.87, 29.25, 26.90, 22.66, 14.11, -1.18. IR (cm^{-1}): ν 2949.6, 2853.0, 1600.2, 1492.4, 1451.1, 1361.0, 1247.7, 1203.8, 1153.8, 1056.5, 826.5, 790.3, 759.8, 696.5; HRMS (EI$^+$) (m/z): [M$^+$] calc for $C_{22}H_{38}Si$ [M-H]$^+$ 315.2508, found 315.2508.

(*Z*)-Benzyl(1-cyclohexyl-5-phenylpent-2-en-2-yl)dimethylsilane (12f) (Table 3, Entry 6)



General procedure I was followed with Ni(COD)$_2$ (13.8 mg, mmol), IPr*OMe **6** (16.3 mg, 0.03 mmol), benzyldimethylsilanesilane (79 μL, 0.5 mmol), and (5-cyclohexylpenta-3,4-dien-1-yl)benzene (113 mg, 0.5 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (141 mg, 71 % yield) (in 95:5 d.r., >98:2 regiosel.). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.27 (m, 2H), 7.16 (m, 4H), 7.04 (m, 1H), 6.95 (m, 3H), 5.93 (t, *J* = 7.3 Hz, 1H), 5.80 (t, *J* = 7.3 Hz, 0.05H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.40 (q, *J* = 8.0 Hz, 2H), 2.15 (s, 2H), 2.04 (s, 2H), 1.86 (d, *J* = 7.1 Hz, 2H), 1.56 – 1.70 (m, 9H), 1.04 – 1.23 (m, 6H), 0.732 (m, 3H), 0.043 (s, 6H); ^{13}C NMR (175 MHz, CDCl$_3$): δ 144.0, 141.9, 140.1, 136.5, 128.5, 128.3, 128.2, 128.1, 125.8, 124.0, 46.7, 37.6, 36.4, 34.3, 33.2, 26.7, 26.6, 26.4, -1.74; IR (thin film): ν 2361.1, 2339.1, 2177.6, 1134.0, 667.9, 437.8 cm^{-1}; HRMS (EI$^+$) (m/z): [M-Me]$^+$ calc for $C_{25}H_{33}Si$, 261.2352; found, 361.2359.

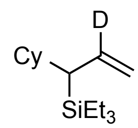
(*Z*)-Benzyl(4-(benzyloxy)-1-cyclohexylbut-2-en-2-yl)dimethylsilane (12g) (Table 3, Entry 7)



General procedure I was followed with Ni(COD)$_2$ (13.8 mg, 0.05 mmol), IPr*OMe **6** (47.2 mg, 0.05 mmol), benzyldimethylsilane (79 mL, 0.5 mmol), and (((4-cyclohexylbuta-2,3-dien-1-yl)oxy)methyl)benzene (121 mg, 0.5 mmol). The crude residue was purified by flash chromatography (5 % EtOAc: hexanes) affording a clear oil

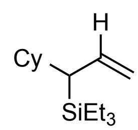
(130 mg, 66 % yield) (in >98:2 regosel., 90:10 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$): 7.32 (d, J = 4.5 Hz, 4H), 7.27 (m, 1H), 7.17 (t, J = 7.4 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 7.4 Hz, 2H), 6.09 (t, J = 6.9 Hz, 1H), 4.46 (s, 2H), 3.93 (d, J = 6.9 Hz, 2H), 2.12 (s, 2H), 1.93 (d, J = 6.5 Hz, 2H), 1.56 – 1.70 (m, 6H), 1.11 (m, 4H), 0.796 (m, 2H), 0.030 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.5, 139.7, 138.2, 128.4, 128.3, 128.1, 128.0, 127.7, 124.1, 72.5, 69.4, 46.6, 37.3, 33.2, 26.6, 26.4, -1.8; IR (thin film): 2920.1, 2849.3, 1599.7, 1493.4, 1449.7, 1248.7, 1096.0, 1027.8 cm^{-1}; HRMS (APCI) (m/z): $[M+H]^+$ calc for $C_{23}H_{36}OSi$, 393.2608; found, 393.2627.

(1-Cyclohexylallyl-2-d)triethylsilane (14) (Scheme 3)



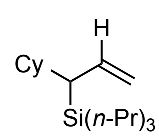
General procedure IV was followed with Pd_2dba_3 (13.7 mg, 0.015 mmol), IMes·HCl salt **4** (10.2 mg, 0.03 mmol), *n*-BuLi (12 mL, 0.03 mmol, 2.5 M in hexanes), triethylsilane (47.7 µL, 0.3 mmol), and cyclohexylallene (36.6 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (50 mg, 70 % yield) (in >98:2 regiosel.). ^{1}H NMR (700 MHz, $CDCl_3$): δ 4.83 (s, 1H), 4.77 (s, 1H), 1.65 – 1.74 (m, 3H), 1.44 – 1.63 (m, 2H), 0.986 – 1.27 (m, 6H), 0.93 (t, J = 8.9 Hz, 9H), 0.561 (q, J = 8.9 Hz, 6H); ^{13}C NMR (174 MHz, $CDCl_3$): d 112.6, 39.8, 38.3, 34.3, 31.6, 26.90, 26.89, 26.3, 7.7, 3.3; IR (thin film): n 2922.1, 1259.9, 1088.6, 799.9 cm^{-1}; HRMS (EI^+) (m/z): [M]+ calc for $C_{15}H_{29}DSi$, 239.2180; found, 239.2185.

[3-(Triethylsilyl)-2-propen-1-yl]-cyclohexane (15) (Scheme 3)



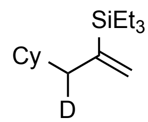
General procedure IV was followed with Pd_2dba_3 (13.7 mg, 0.015 mmol), IMes·HCl salt **4** (10.2 mg, 0.03 mmol), *t*-BuOK (3.4 mg, 0.03 mmol), triethylsilane (48 µL, 0.3 mmol), and cyclohexylallene (36.6 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (57 mg, 80% yield) (in >98:2 regiosel.). Spectral data matched that previously reported.[4]

(1-Cyclohexylallyl)tripropylsilane (16) (Scheme 3)



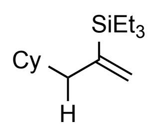
General procedure IV was followed with Pd_2dba_3 (13.7 mg, 0.015 mmol), IMes·HCl salt **4** (10.2 mg, 0.03 mmol), *t*-BuOK (3.4 mg, 0.03 mmol), triethylsilane (48 µL, 0.3 mmol), and cyclohexylallene (36.6 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (49 mg, 58 56 % yield) (in >98:2 regiosel.). ^{1}H NMR (700 MHz, $CDCl_3$): 5.69 (dt, J = 17.2, 9.5 Hz, 1H), 4.83 (dd, J =10.5, 2.7 Hz, 1H), 4.77 (dd, J = 17.2, 2.3 Hz, 1H), 1.66 (m, 3H), 1.58 - 1.60 (m, 1H), 1.50 – 1.57 (m, 3H), 1.41 – 1.48 (m, 1H), 1.27 – 1.37 (m, 6 H), 1.00 – 1.22 (m, 1H), 0.935 (t, J = 8.0 Hz, 9H), 0.513 – 0.569 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): 138.6, 112.8, 40.5, 38.4, 34.3, 31.6, 26.9, 26.3, 18.8, 17.7 ,15.3; IR (thin film): n 3073.1, 2954.5, 2924.1, 2867.7, 2661.8, 1623.3, 1450.1, 1331.9, 1203.2, 1067.5, 998.8, 894.7, 740.4 cm^{-1}; HRMS (EI$^+$) (m/z): [M]$^+$ calc for $C_{18}H_{36}Si$, 280.2586; found, 280.2588.

(3-Cyclohexylprop-1-en-2-yl-3-*d*)triethylsilane (18) (Scheme 3)



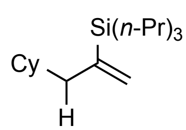
General procedure III was followed with $Ni(COD)_2$ (8.25 mg, 0.03 mmol), DP-IPr·HBF_4 (18.9 mg, 0.03 mmol), *n*-BuLi (12 mL, 0.03 mmol, 2.5 M in hexanes), *d*-triethylsilane (47.7 µL, 0.3 mmol), and cyclohexylallene (36.6 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (60 mg, 83 % yield) (in >98:2 regiosel.). ^{1}H NMR (700 MHz, $CDCl_3$): d 5.56 (dd, J = 3.3, 1.1 Hz, 1H), 5.31 (d, J = 3.3 Hz, 1H), 1.94 (d, J = 7 Hz, 1H), 1.64 – 1.72 (m, 5H), 1.11-1.20 (m, 4H), 0.91 (t, J = 8.0 Hz, 9H), 0.77 – 0.83 (m, 2H), 0.58 (q, J = 8.0 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): d 147.3, 126.5, 36.3, 33.43, 33.41, 26.7, 26.4, 7.3, 3.0; IR (thin film): n 2922.3, 2874.8, 2850.5, 1447.7, 1415.9, 1348.1, 1261.0 1236.3, 1012.0, 923.5, 892.9 cm^{-1}; HRMS (EI) (m/z): [M]$^+$ calc for $C_{13}H_{24}DSi$, 210.1788; found, 210.1789.

[2-(Triethylsilyl)-2-propen-1-yl]-cyclohexane (19) (Scheme 3)



General procedure III was followed with $Ni(COD)_2$ (8.25 mg, 0.03 mmol), DP-IPr·HBF_4 (18.9 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), triethylsilane (48 µL, 0.3 mmol), and cyclohexylallene (36.6 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (60 mg, 84 % yield) (in >98:2 regiosel.). Spectral data matched that previously reported.[4]

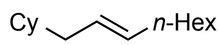
(3-Cyclohexylprop-1-en-2-yl)tripropylsilane (20) (Scheme 3)



General procedure III was followed with $Ni(COD)_2$ (8.25 mg, 0.03 mmol), DP-IPr·HBF_4 (18.9 mg, 0.03 mmol), *t*-BuOK (3.4 mg, 0.03 mmol), tripropysilane (µL, 0.3 mmol), and cyclohexylallene (36.6 mg, 0.3 mmol). The crude residue was purified by flash chromatography (100% hexanes) affording a clear oil (47 mg, 56 % yield) (in >98:2 regiosel.). ^{1}H NMR (700 MHz, $CDCl_3$): d 5.54 (m, 1H), 5.30 (d, *J* = 3.4 Hz, 1H), 1.96 (d, *J* = 5.9 Hz, 2H), 1.60-1.71 (m, 6H), 1.25-1.32 (m, 6H), 1.10-1.22 (m, 3H), 0.943 (t, *J* = 8.0 Hz, 9 H), 0.77 – 0.84 (m, 2H), 0.55 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): d 148.0, 126.2, 45.1, 36.4, 33.5, 26.7, 26.4, 18.6, 17.4, 15.0; IR (thin film): n 2922.4, 2954.2, 2867.7, 1449.6, 10654, 923, 806.5 cm^{-1}; HRMS (EI$^+$) (m/z): [M-propyl]$^+$ calc for $C_{15}H_{29}Si$, 237.2039; found, 237.2041.

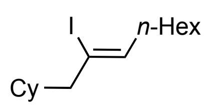
Synthetic Manipulations of Alkenylsilane 12d:

(*E*)-Non-2-en-1-ylcyclohexane (28) (Scheme 4)



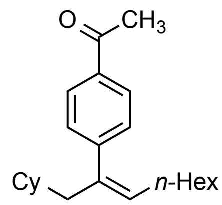
Alkenylsilane **12d** (70 mg, 0.196 mmol) in DMSO (50 µL) was added to a 6 mL dram vial with sir bar. TBAF (1.96 mL, 1.96 mmol, 1.0 M in THF) was then slowly added and the vessel was subsequently heated at 50 °C for 6 h when the reaction was judged complete by TLC analysis. The solvent was removed *in vacuo* and the crude material was purified by flash column chromatography (100 % hexanes) affording a clear oil (35.2 mg, 86 %) (in >98:2 regiosel, >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.38 (m, 2H), 1.98 (m, 2 H), 1.88 (m, 2H), 1.614-1.78 (m, 6H), 1.14 – 1.42 (m, 15H), 0.894 (t, *J* = 8.7 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 131.4, 128.7, 40.7, 38.1, 33.1, 32.6, 31.7, 29.6, 28.8, 26.6, 26.3, 22.6, 14.1; IR (thin film): ν 2920.3, 2851.3, 1707.9, 1448.0, 1259.5, 966.2 cm^{-1}; HRMS (EI$^+$) (m/z): [M]$^+$ calc for $C_{15}H_{29}$, 208.2191; found, 208.2189.

(*Z*)-(2-Iodonon-2-en-1-yl)cyclohexane (29) (Scheme 4)



Alkenylsilane **12d** (70 mg, 0.196 mmol) in CH_3CN (1 mL) was added to a 6 mL dram vial equipped with a stir bar. The reaction vessel was cooled in an ice bath to 0 °C and then NIS (110 mg, 0.491 mmol) was added. The reaction was then removed from the ice bath and warmed to RT. After 12 h the reaction was judged complete by TLC analysis and sodium thiosulfate was added (2 mL) to quench the reaction. The solution was then extracted with EtOAc (3 X 2 mL) and washed with water (3 X 3 mL) and subsequently dried over anhydrous $MgSO_4$. The solvent was then removed in vacuo and the crude material was purified by flash column chromatography (100 % hexanes) affording a clear oil (50 mg, 77 %) (in >98:2 regiosel., 98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.23 (t, *J* = 8.0 Hz , 0.2H, minor *E*-isomer), 5.43 (t, *J* = 7.2 Hz, 1H), 2.32 (d, *J* = 7.5 Hz, 2H), 2.26 (d, *J* = 7.0 Hz , 0.14H, minor *E*-isomer), 2.09 – 2.16 (m, 2H), 2.04 (q, *J* = 7.0 Hz, 0.18H), 1.60 – 1.75 (m, 8H), 1.22 – 1.46 (m, 12H), 1.10-1.19 (m, 1H), 0.90 (t, J = 7.2 Hz, 3H), 0.84 – 0.88 (m, 2H); ^{13}C NMR ((175 MHz, $CDCl_3$): δ 135.8, 108.2, 52.6, 36.4, 36.3, 32.6, 31.7, 28.8, 28.4, 26.5, 26.2, 26.1, 22.6, 14.0; IR (thin film): ν 2925.6, 2852.2, 1972.0, 1718.2, 1449.4, 1249.4, 1118.1, 827.3, 698.5 cm^{-1}; HRMS (EI^+) (m/z): $[M]^+$ calc for $C_{15}H_{27}I$, 334.1158; found, 334.1161.

(*Z*)-1-(4-(1-Cyclohexylnon-2-en-2-yl)phenyl)ethan-1-one (30) (Scheme 4)



Alkenylsilane **12d** (125 mg, 0.7 mmol) in THF (1 mL) was added to a flame-dried 6 mL dram vial with a stir bar. TBAF (2.1 mL, 2.1 mmol, 1.0 M in THF) was then slowly added followed by addition of 4'-iodoacetophenone (172 mg, 0.7 mmol) and Pd_2dba_3 (16 mg, 0.0175 mmol). The reaction vessel was then heated at 50 °C for 30 min when the reaction was judged complete by TLC analysis. DCM (1 mL) was added to the vial and the solution was filtered with 50 % EtOAc:hexanes and the solvent was removed *in vacuo*. The crude material was purified by flash column chromatography (5 – 15% EtOAc:hexanes) affording a clear oil (180 mg, 79 %) (in >98:2 regiosel., >98:2 d.r.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 8.2, 2H), 7.21 (d, J = 8.2 2H), 5.43 (t, J = 7.2 Hz, 1H), 2.59 (s, 3H), 2.31 (d, J = 7.5 Hz, 2H), 1.89 (q, J = 7.0 Hz, 2H), 1.54 – 1.67 (m, 6H), 1.14 – 1.34 (m, 10H), 1.00 – 1.11 (m, 5H), 0.824 (t, J = 7.5 Hz, 5H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 197.9, 147.0, 138.3, 135.2, 130.0, 128.6, 128.1, 47.2, 35.4, 33.1, 31.6, 30.0, 28.9, 28.9, 26.6, 26.1, 22.6, 14.0; IR (thin film): ν 2925.3, 1682.0, 1604.1, 1358.0, 1263.3, 1120.1, 833.1 cm^{-1}; HRMS (ESI^+) (m/z): $[M+H]^+$ calc for $C_{23}H_{34}O$, 327.2682; found, 327.2682.

Analysis of the crossover experiment:

For detailed experimental crossover studies including an excel spreadsheet for calculating ratios of isotopic products, please see Montgomery *et. al.* 2014 (reference 5). Pure samples of products derived from Et_3SiH (MW 238), Et_3SiD (MW 239), and Pr_3SiH (MW 280) were independently prepared and GCMS analysis was performed. Based on the similarity of the molecular ion minus ethyl regions (M-Et = 209) of the Et_3SiH and Et_3SiD derived product, the molecular ion region of the Pr_3SiD derived product was assumed to appear as the molecular ion (M = 280) region of the Pr_3SiH-derived product, shifted by one mass unit. Relative peak heights in the molecular ion minus ethyl region of the spectra of each pure compound were normalized, with a value of 1 assigned to the base peak. In the crude product of an experiment that employed 0.5 equiv each of Et_3SiD and Pr_3SiH, the ratio of Et_3Si products to Pr_3Si products was determined by GC. From the crude GCMS, the relative intensity of the products were normalized, with the value of 1 assigned to the base peak. The ratio of the Et_3Si-(H) product to Et_3Si-(D) product was determined as follows:

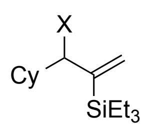
$$\frac{\text{intensity of 209 peak in crossover experiment}}{\text{intensity of 210 peak in crossover experiment}} = \frac{[X][\text{ rel. height of 209 peak for } Et_3Si\text{-(H) product}] + [Y]\ [\text{rel. height of 209 peak for } Et_3Si\text{-(D) product}]}{[X][\text{ rel. height of 210 peak for } Et_3Si\text{-(H) product}] + [Y]\ [\text{rel. height of 210 peak for } Et_3Si\text{-(D) product}]}$$

$$X = 1/100 \times \text{relative \% of } Et_3Si\text{-(H) product}$$
$$Y = 1/100 \times \text{relative \% of } Et_3Si\text{-(D) product} = 1\text{-}X$$

In the above equation, after substitution of [1-X] for [Y], the experimental values were inserted and the equation was solved for [X]. The ratio of Pr_3Si-(H) product to the intensity of 280 peak in crossover experiment and Pr_3Si-(D) products was determined in a similar fashion. Merging the GCFID ratios of Et_3Si products to Pr_3Si products with the data calculated from the above equation, an overall ratio of the products were obtained.

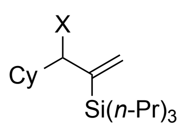
Triethylsilyl : tripropylsilyl product ratios were determined by GC-FID detection and are corrected for molecular weight to provide molar ratios. GCMS chromatograms and MS spectra for authentic samples and crossover experiments are included as pages S17-S26.

Ratio of Ethyl:Propyl products (nickel crossover): [72:28]
Ratio of Ethyl:Propyl products (palladium crossover): [38:62]



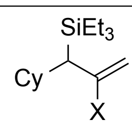
Ni crossover experiment

Authentic H Sample		**Authentic D Sample**		**Crossover Experiment**		**Calculation Results**	
Ion 209	Ion 210	Ion 209	Ion 210	Ion 209	Ion 210	% H:	% D:
1654272	378496	117712	2918912	72912	1783296	0 %	100 %



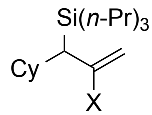
Ni crossover experiment

Authentic H Sample		**Authentic D Sample**		**Crossover Experiment**		**Calculation Results**	
Ion 280	Ion 281	Ion 280	Ion 281	Ion 280	Ion 281	% H:	% D:
2186	710	0	2186	276	100	96 %	4 %



Pd crossover experiment

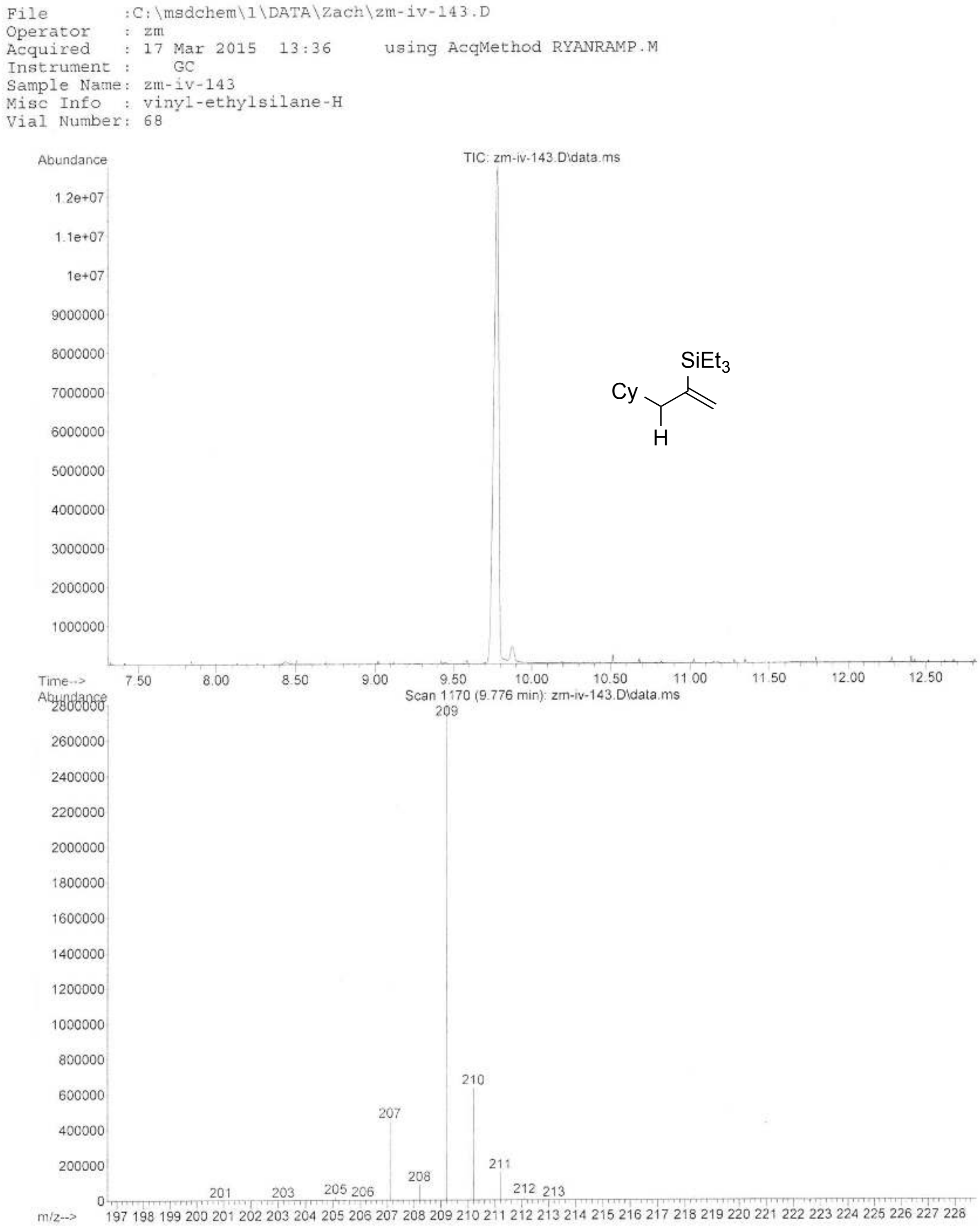
Authentic H Sample		**Authentic D Sample**		**Crossover Experiment**		**Calculation Results**	
Ion 209	Ion 210	Ion 209	Ion 210	Ion 209	Ion 210	% H:	% D:
285888	56432	17680	1077760	587	21952	1 %	99 %



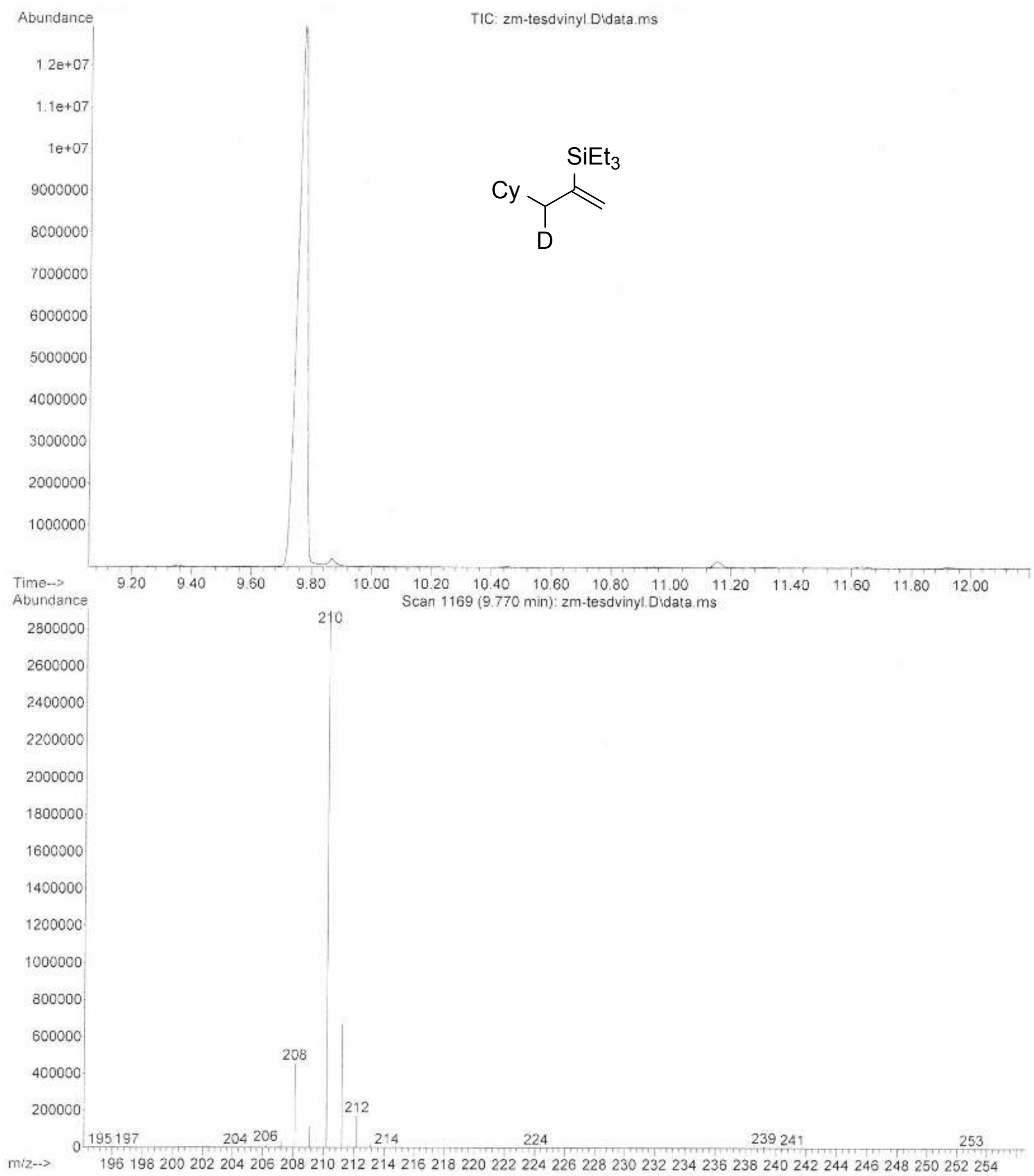
Pd crossover experiment

Authentic H Sample		Authentic D Sample		Crossover Experiment		Calculation Results	
Ion 280	Ion 281	Ion 280	Ion 281	Ion 280	Ion 281	% H:	% D:
53264	12224	154	53264	7333	1956	96 %	4 %

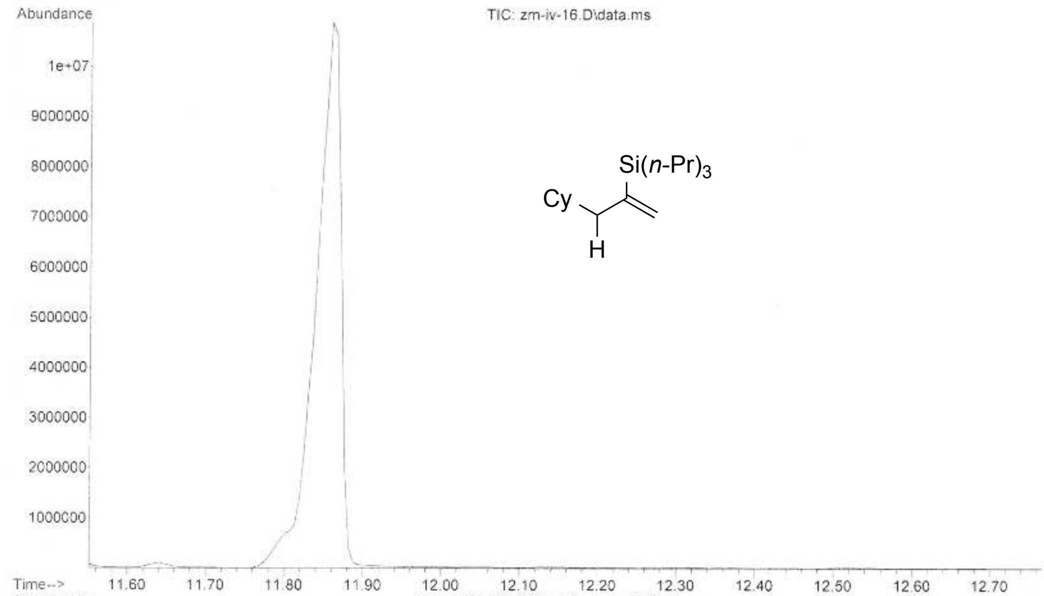
Authentic Standards Chromatograms:

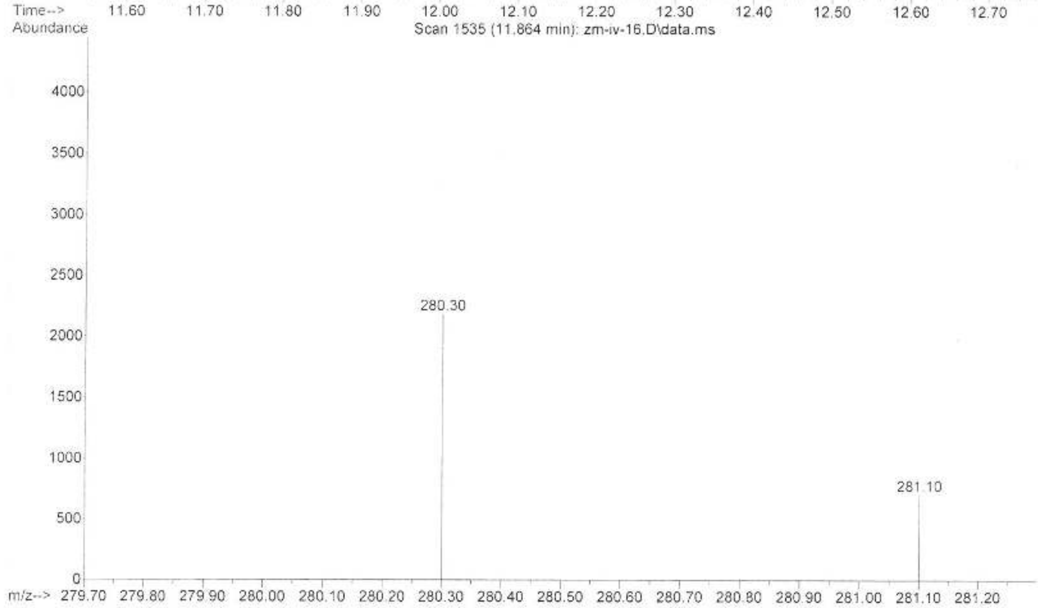


```
File        :C:\msdchem\1\DATA\Zach\zm-tesdvinyl.D
Operator    : zm
Acquired    : 18 Mar 2015  15:41      using AcqMethod RYANRAMP.M
Instrument  :    GC
Sample Name: zm-tesdvinyl
Misc Info   :
Vial Number: 97
```

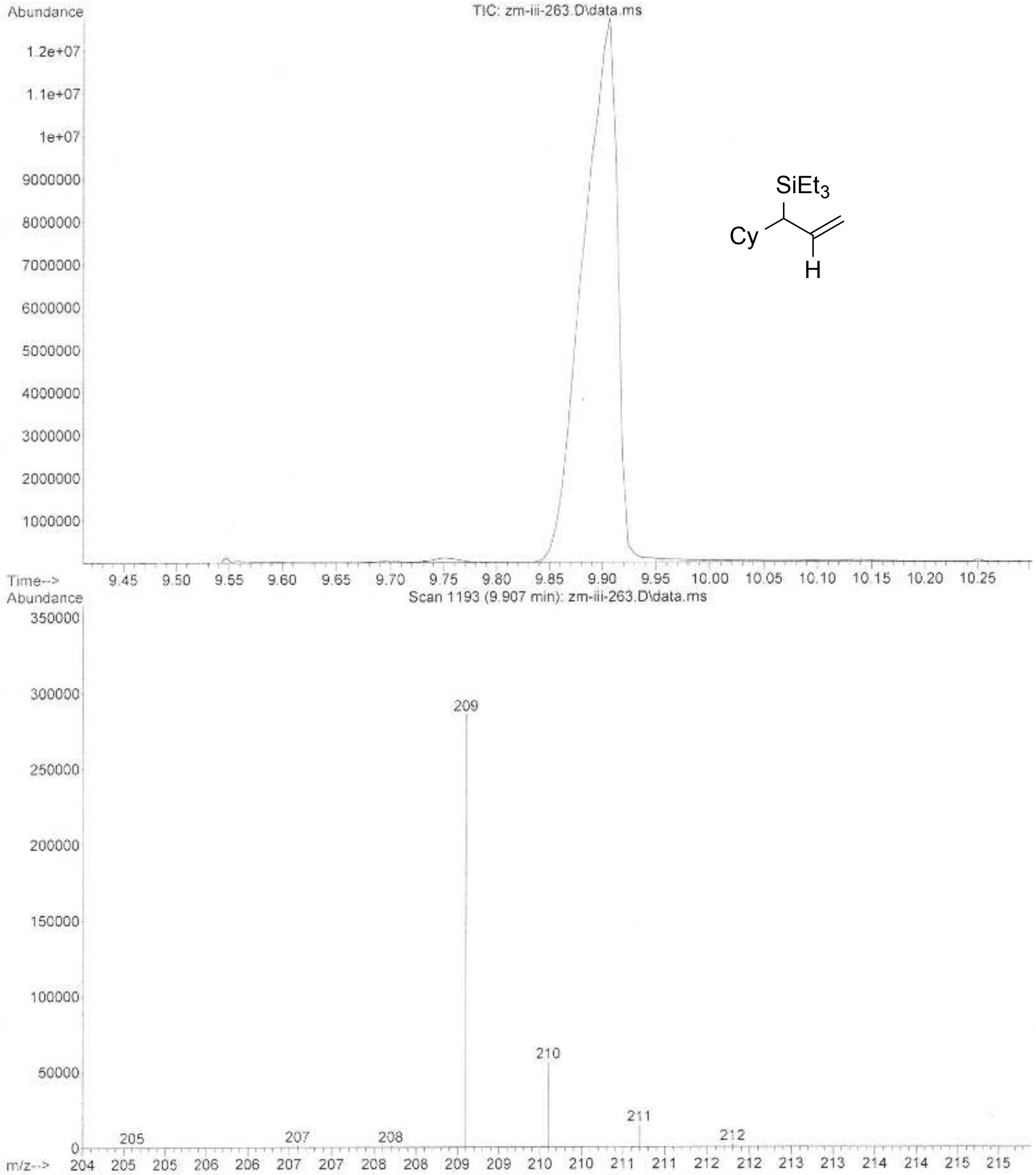


```
File        :C:\msdchem\1\DATA\Zach\zm-iv-16.D
Operator    : zm
Acquired    : 17 Mar 2015   12:36      using AcqMethod RYANRAMP.M
Instrument  :     GC
Sample Name: zm-iv-16
Misc Info   : vinyl-propylsilane-H
Vial Number: 70
```

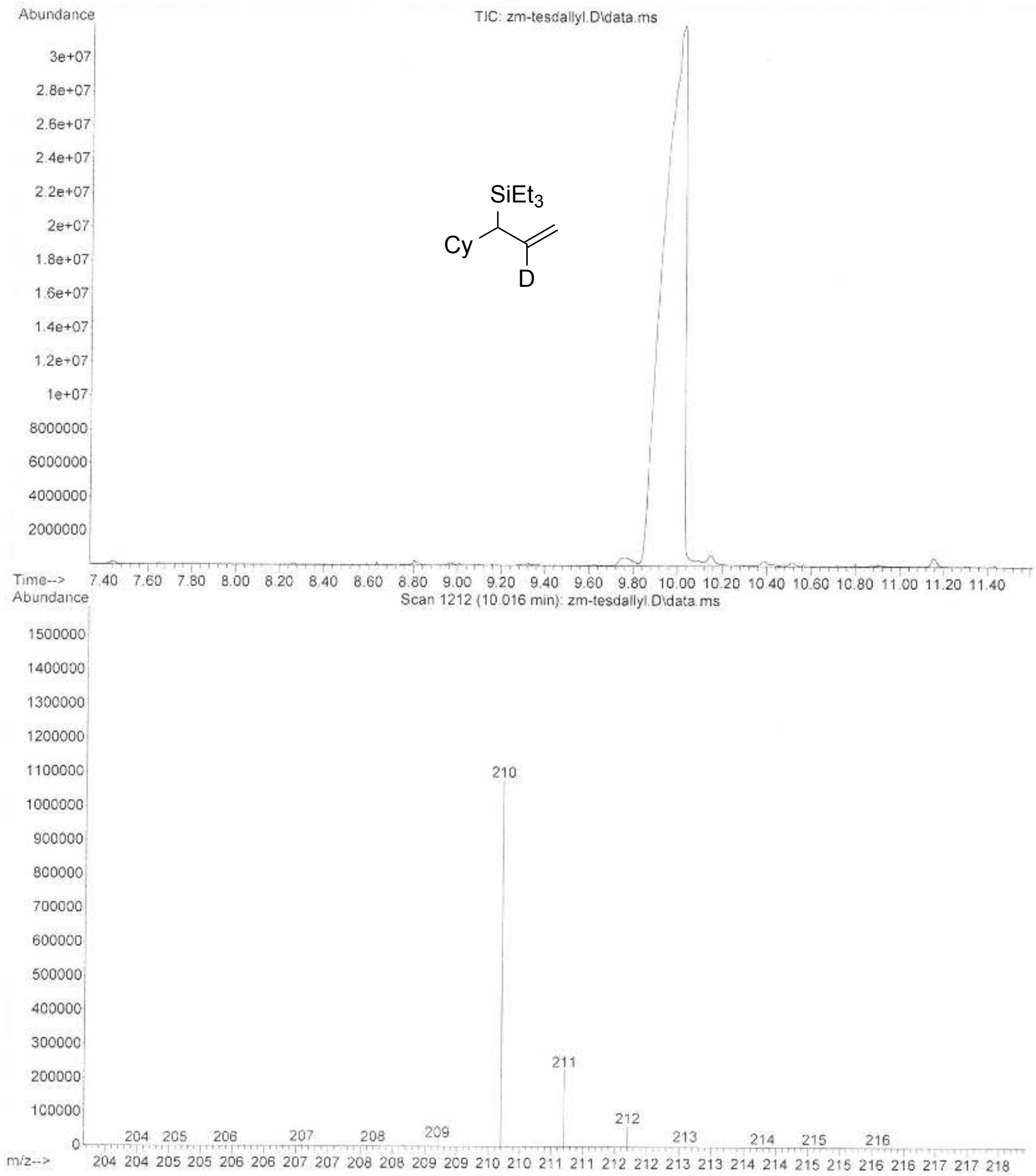




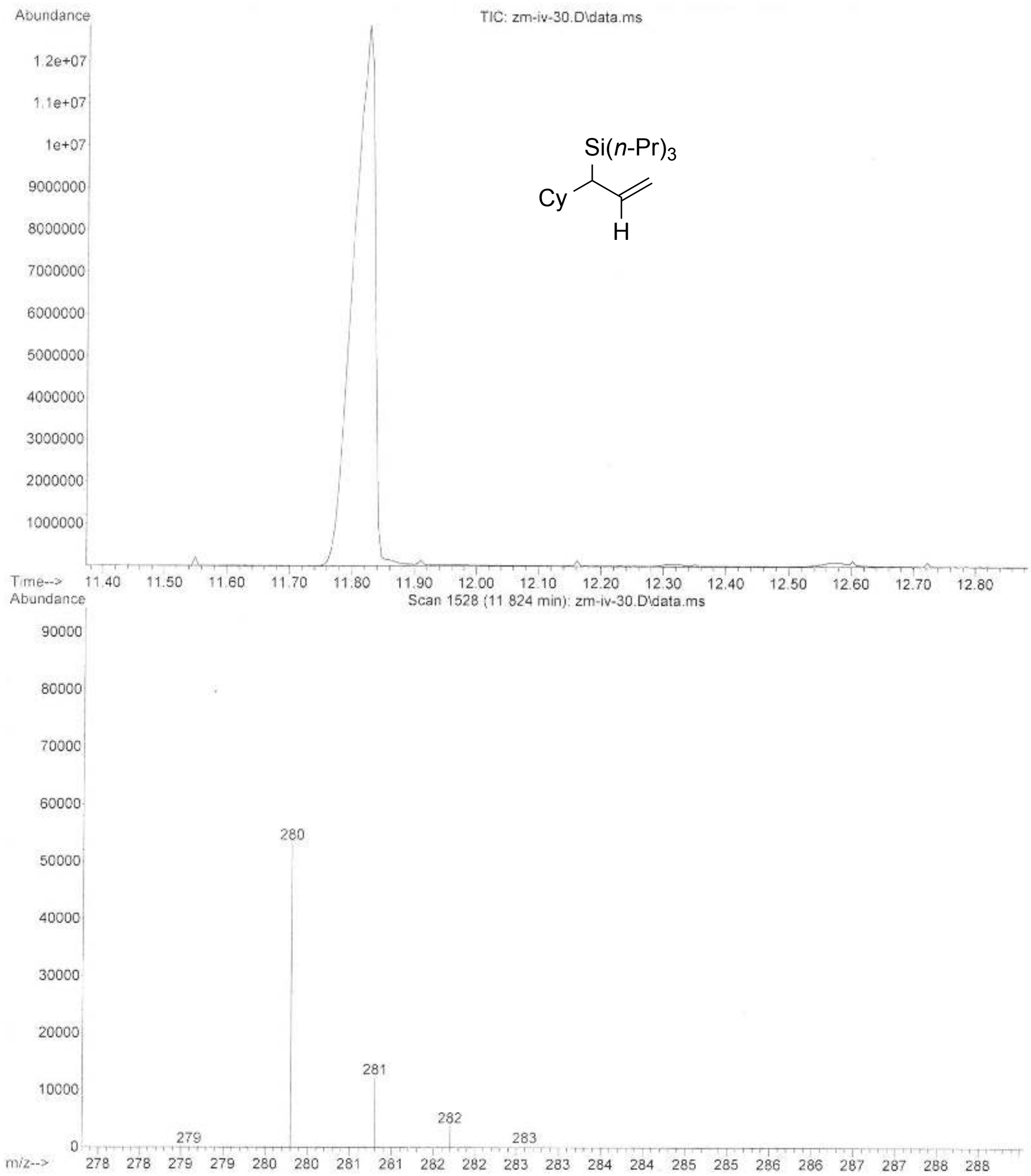
```
File        :C:\msdchem\1\DATA\Zach\zm-iii-263.D
Operator    : zm
Acquired    : 17 Mar 2015  14:07      using AcqMethod RYANRAMP.M
Instrument  :    GC
Sample Name: zm-iii-263
Misc Info   : allyl-ethylsilane-H
Vial Number: 67
```



File   :C:\msdchem\1\DATA\Zach\zm-tesdallyl.D
Operator   : zm
Acquired   : 18 Mar 2015 16:11   using AcqMethod RYANRAMP.M
Instrument :   GC
Sample Name: zm-tesdallyl
Misc Info :
Vial Number: 96

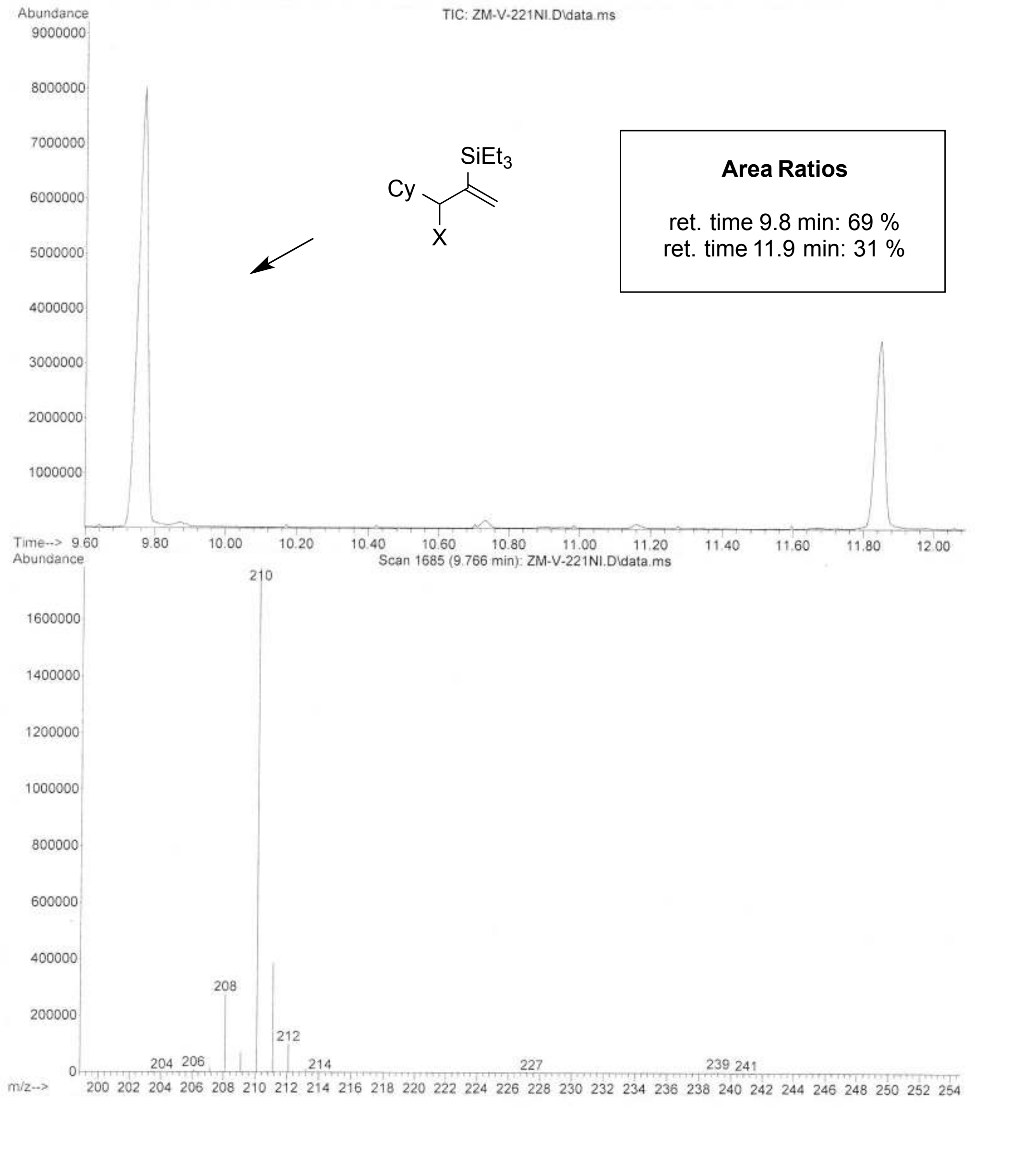


File :C:\msdchem\1\DATA\Zach\zm-iv-30.D
Operator : zm
Acquired : 17 Mar 2015 15:07 using AcqMethod RYANRAMP.M
Instrument : GC
Sample Name: zm-iv-30
Misc Info : allyl-ethylsilane-D
Vial Number: 75



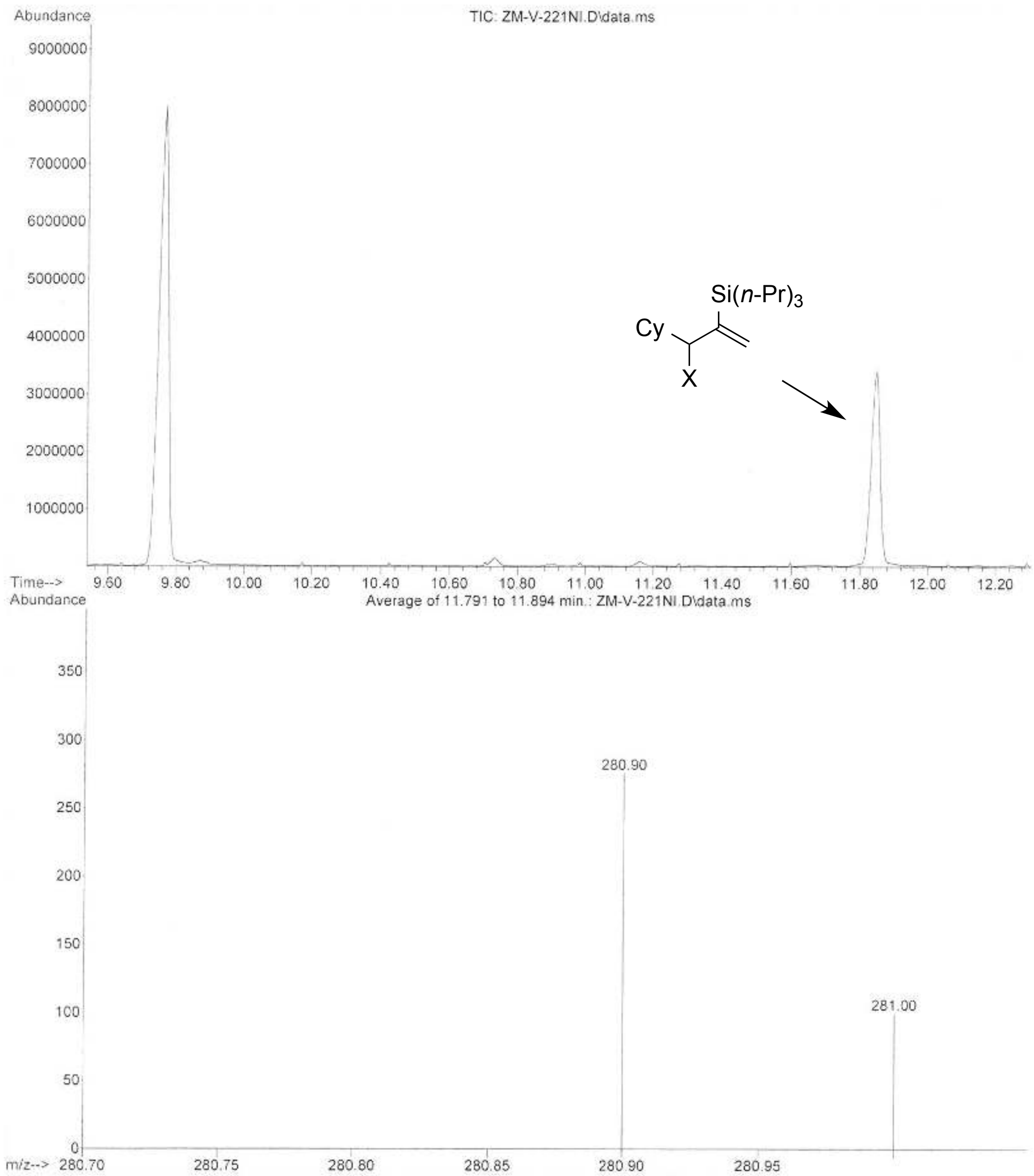
Nickel Crossover Experiment:

```
File        :C:\msdchem\1\DATA\Zach\ZM-V-221NI.D
Operator    : zm
Acquired    : 20 Mar 2015  15:42     using AcqMethod RYANRAMP.M
Instrument  :    GC
Sample Name: ZM-V-221NI
Misc Info   :
Vial Number: 75
```

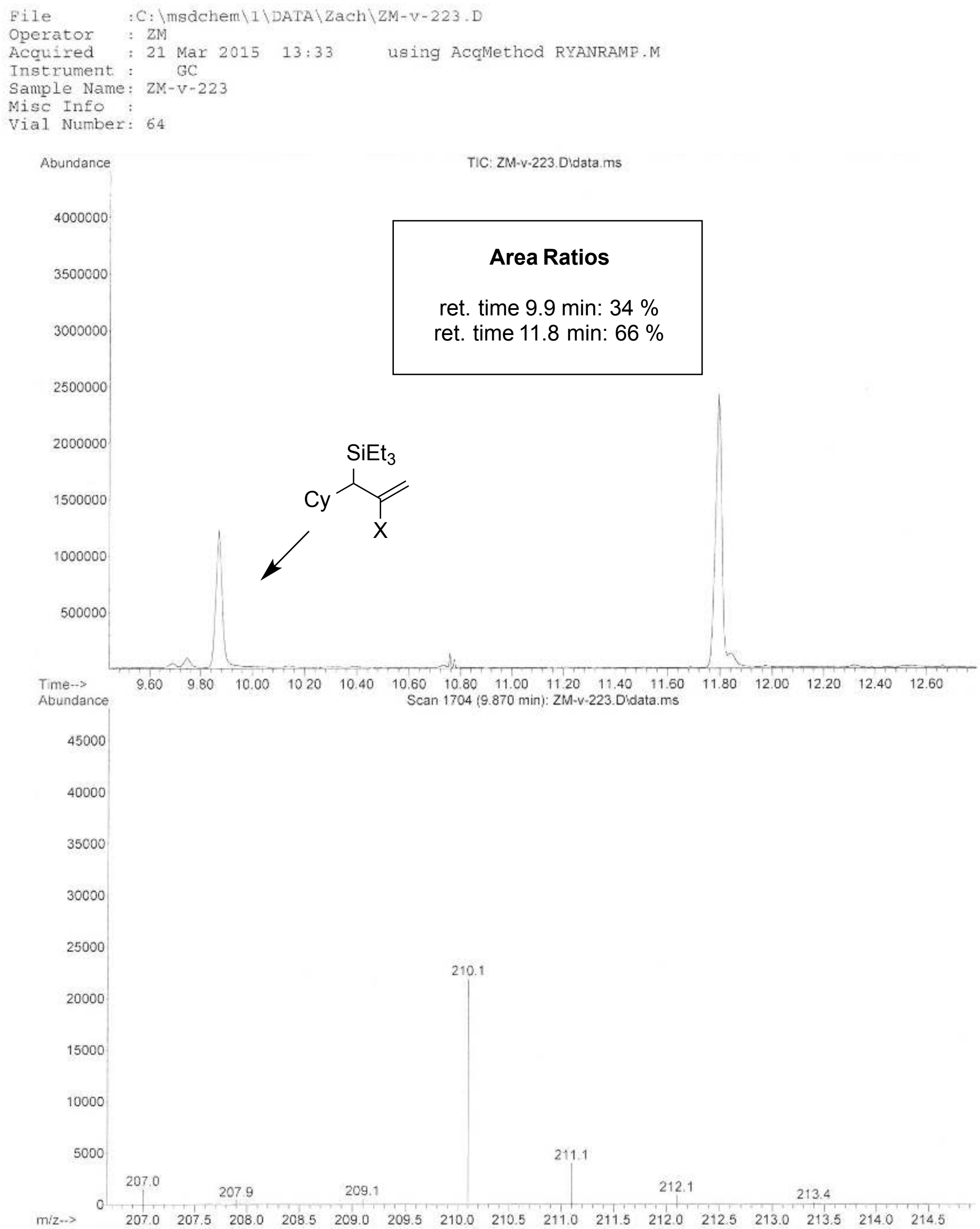


Nickel Crossover Experiment:

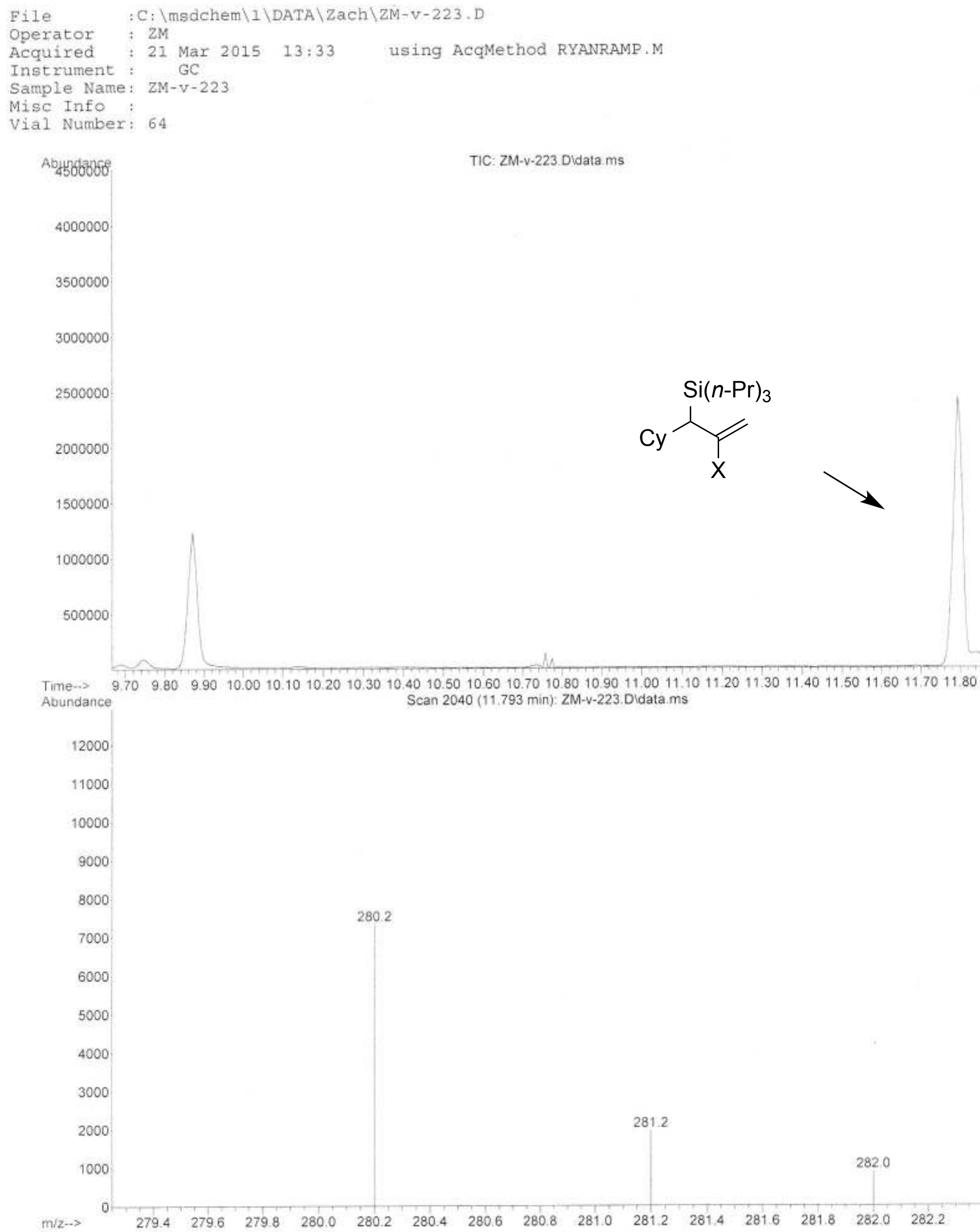
```
File        :C:\msdchem\1\DATA\Zach\ZM-V-221NI.D
Operator    : zm
Acquired    : 20 Mar 2015  15:42     using AcqMethod RYANRAMP.M
Instrument  :    GC
Sample Name: ZM-V-221NI
Misc Info   :
Vial Number: 75
```



Palladium Crossover Experiment:



Palladium Crossover Experiment:



References:

1. M. L. Hossain; F. Ye; Y. Zhang; J. Wang, *J. Org. Chem*. **2013**, *78*, 1236.

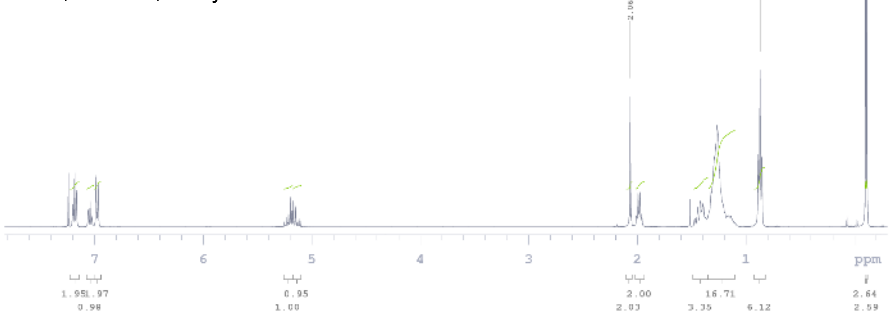
2. K. M. Brummond; E. A. Dingess; J. L. Kent, *J. Org. Chem*. **1996**, *61*, 6096.

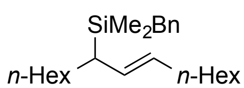
3. H. A. Malik; G. J. Sormunen; J. Montgomery, *J. Am. Chem. Soc*. **2010**, *132*, 6304.

4. Z. D. Miller; W. Li; T. R. Belderrain; J. Montgomery, *J. Am. Chem. Soc*. **2013**, *135*, 15282.

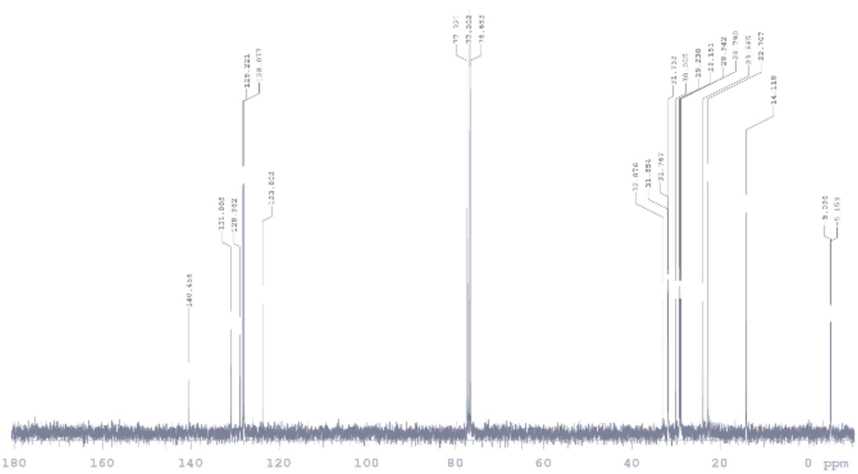
5. M. T. Haynes; P. Liu; R. D. Baxter; A. J. Nett; K. N. Houk; J. Montgomery, *J. Am. Chem. Soc.* **2014**, *136*, 17495-17504.

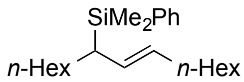
2a, Table 2, Entry 1



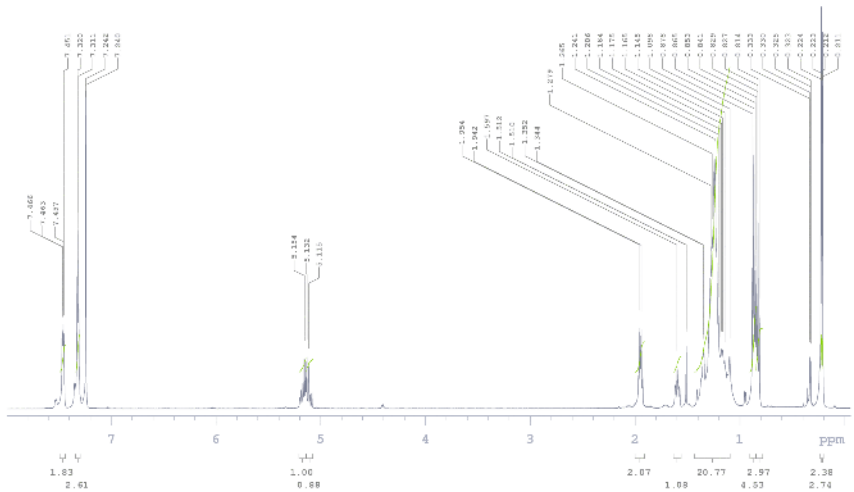


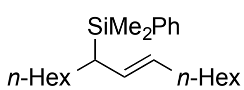
2a, Table 2, Entry 1



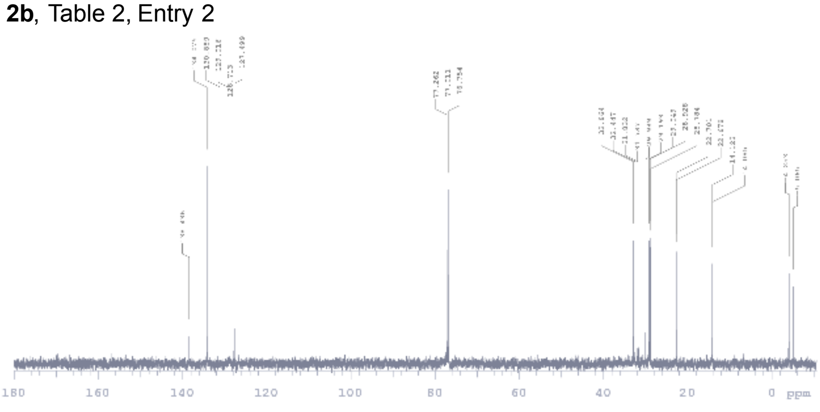


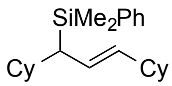
2b, Table 2, Entry 2



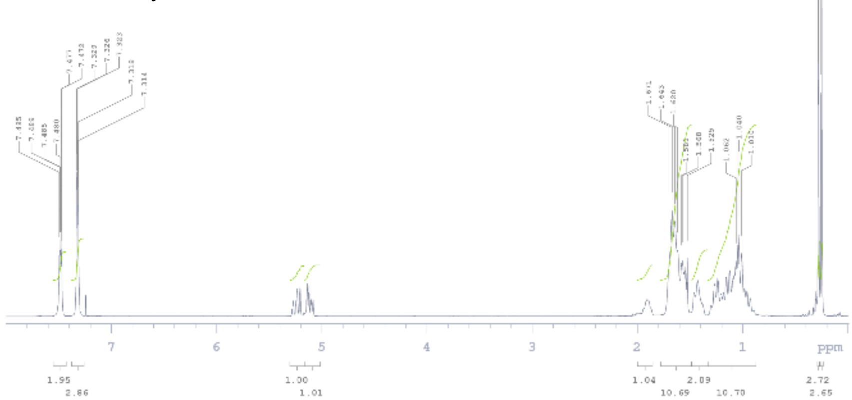


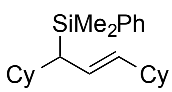
2b, Table 2, Entry 2



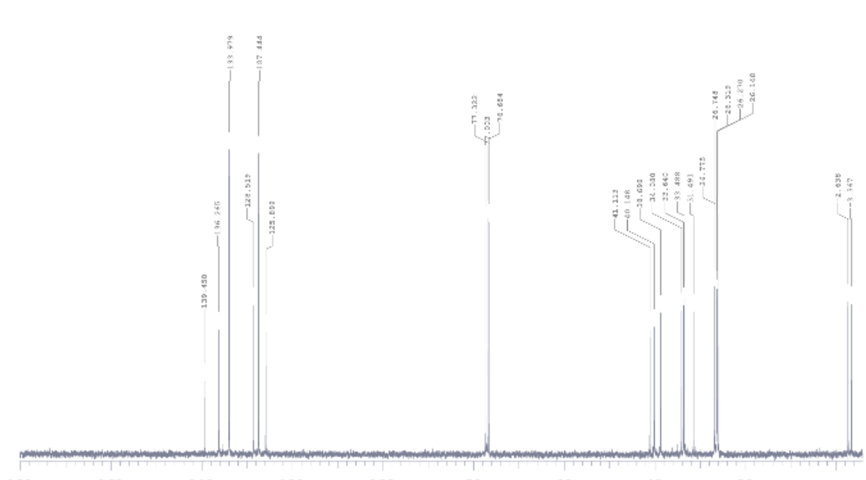


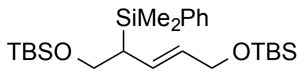
2c, Table 2, Entry 3



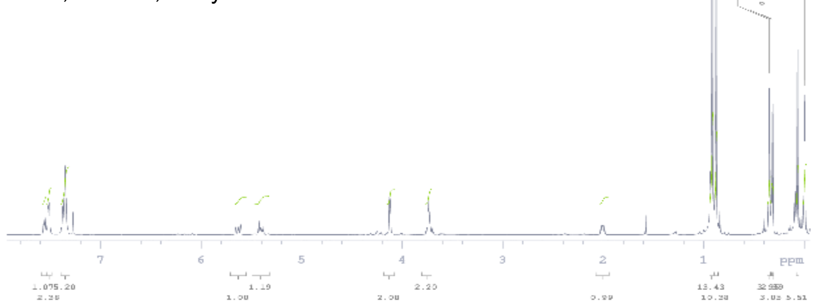


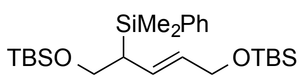
2c, Table 2, Entry 3



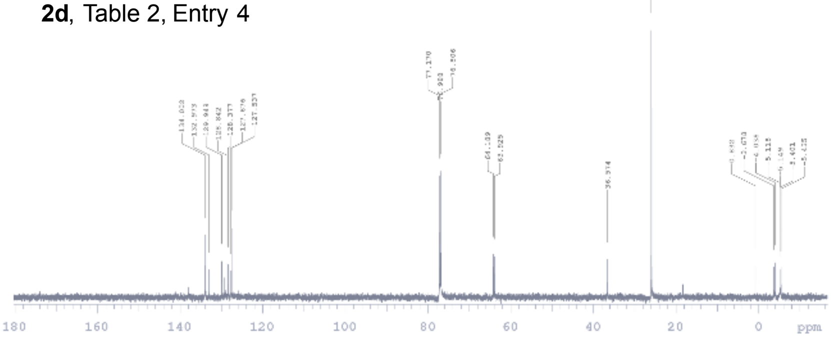


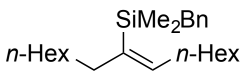
2d, Table 2, Entry 4



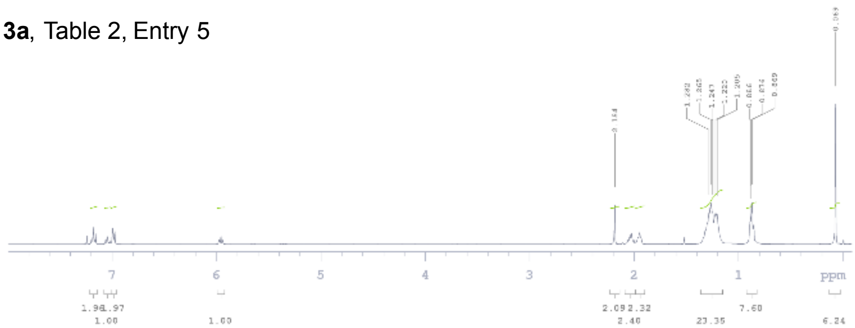


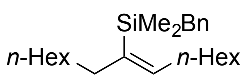
2d, Table 2, Entry 4



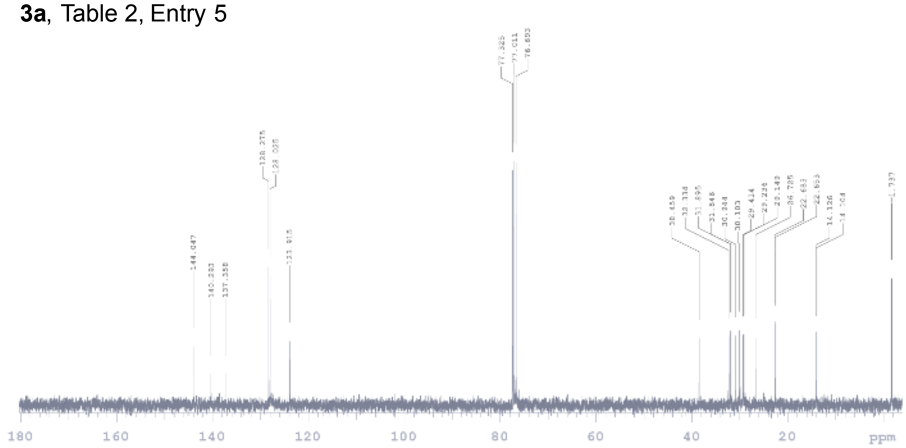


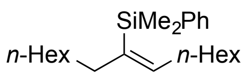
3a, Table 2, Entry 5



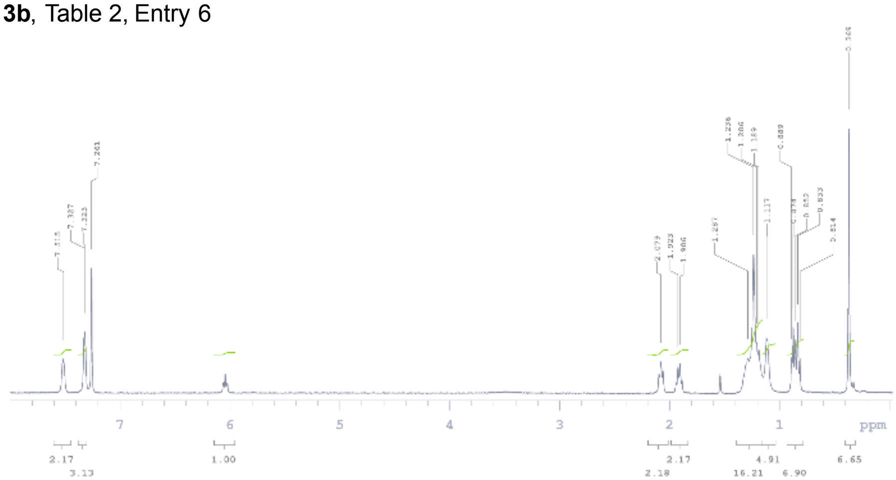


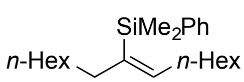
3a, Table 2, Entry 5



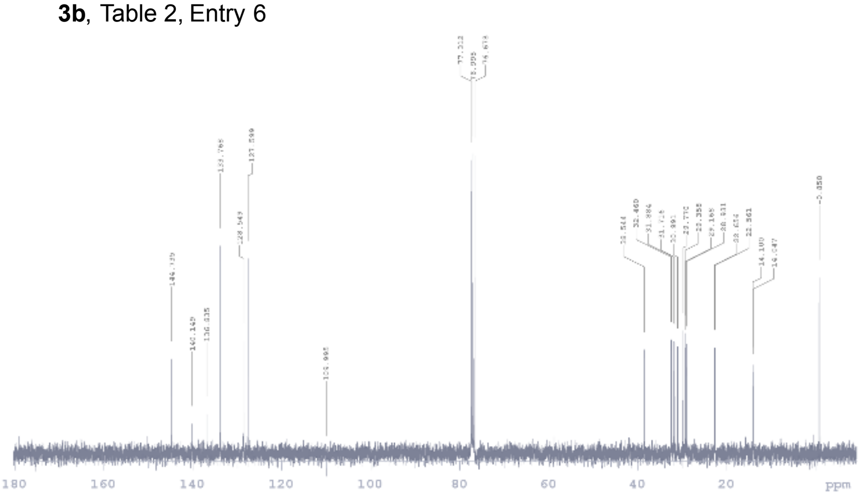


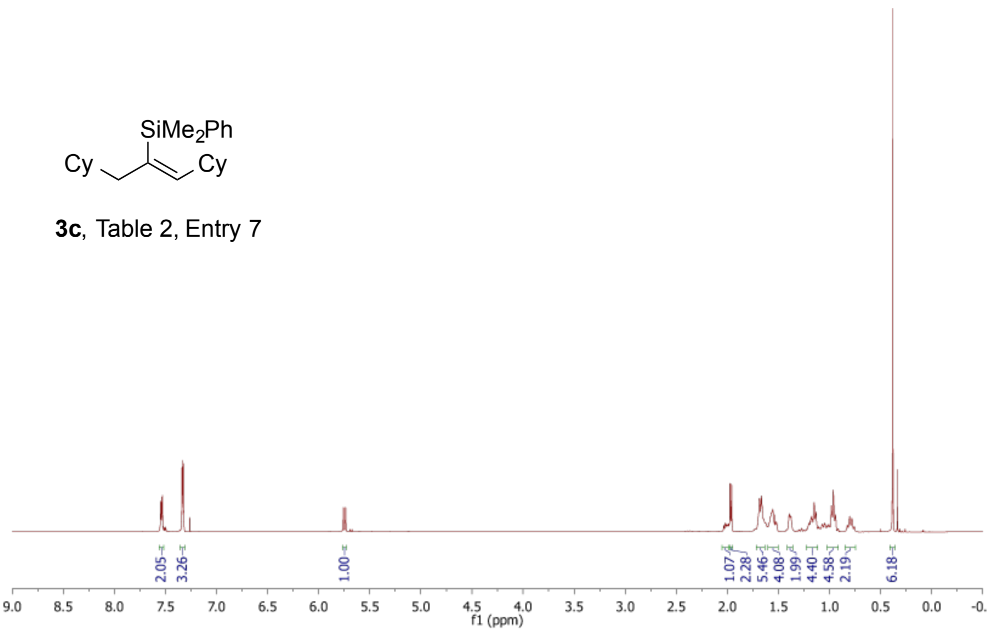
3b, Table 2, Entry 6



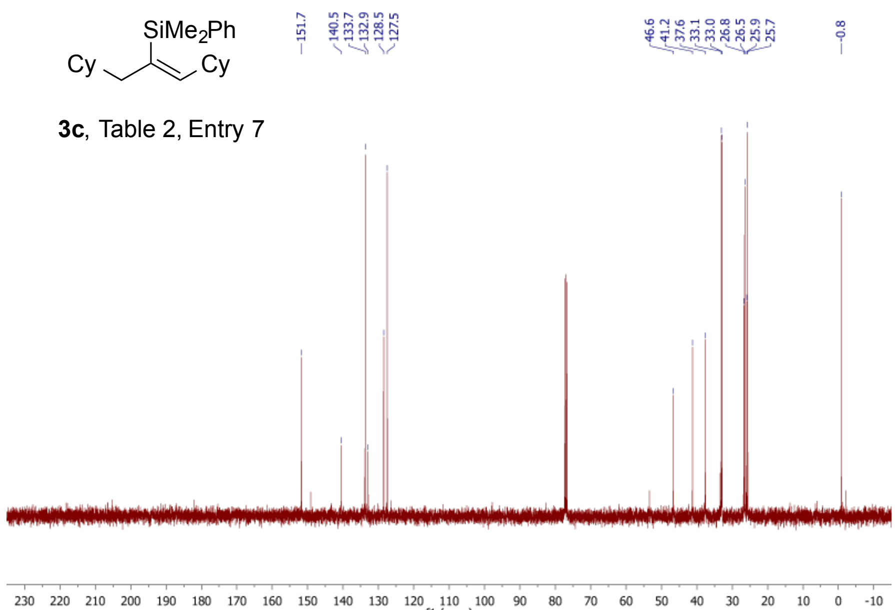


3b, Table 2, Entry 6

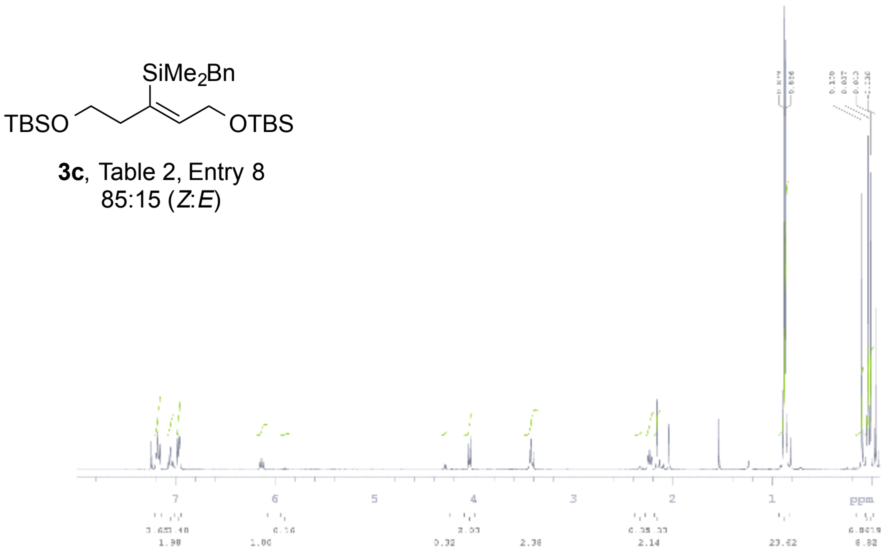




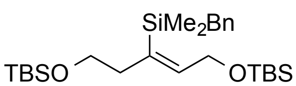
3c, Table 2, Entry 7



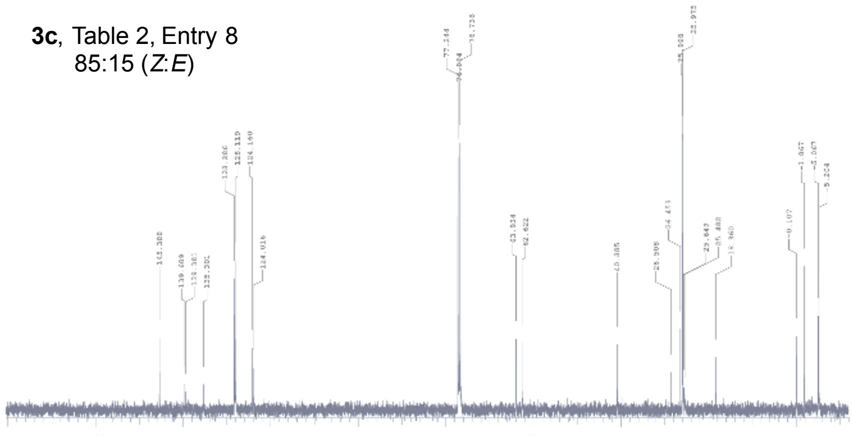
3c, Table 2, Entry 7

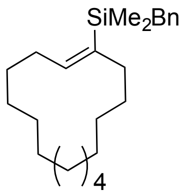


3c, Table 2, Entry 8
85:15 (*Z*:*E*)

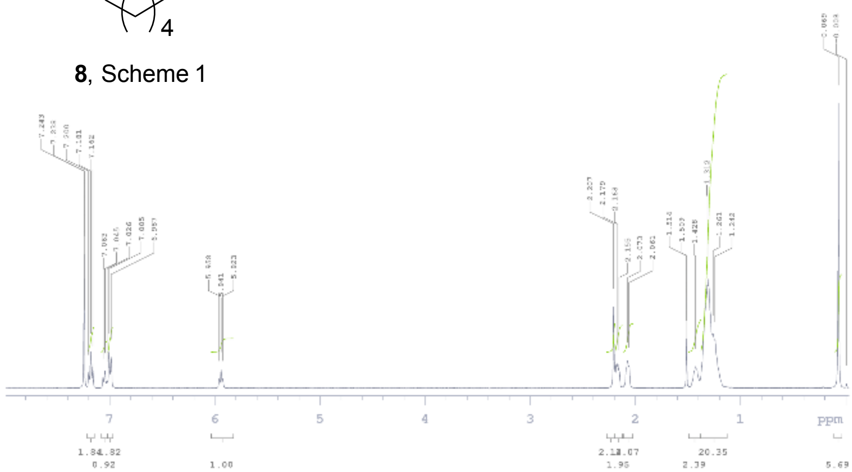


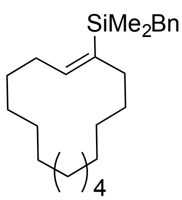
3c, Table 2, Entry 8
85:15 (*Z*:*E*)



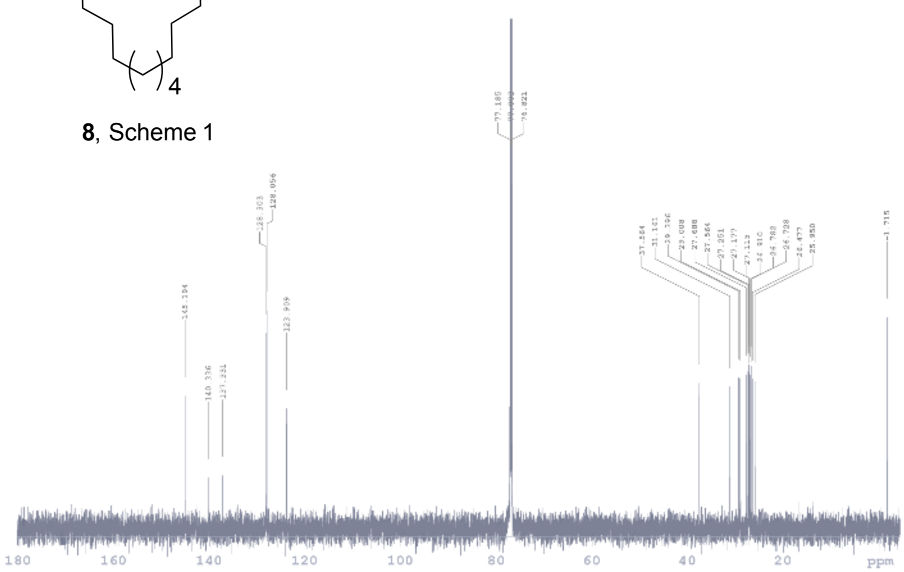


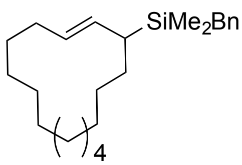
8, Scheme 1



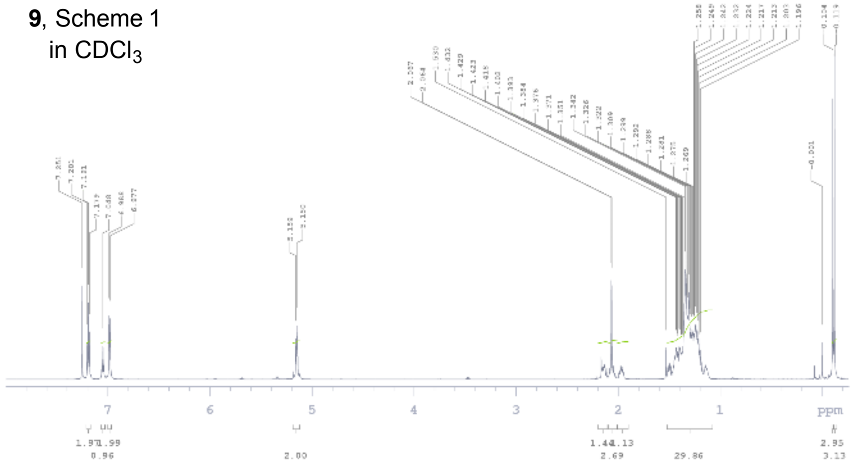


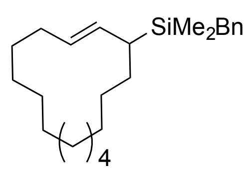
8, Scheme 1



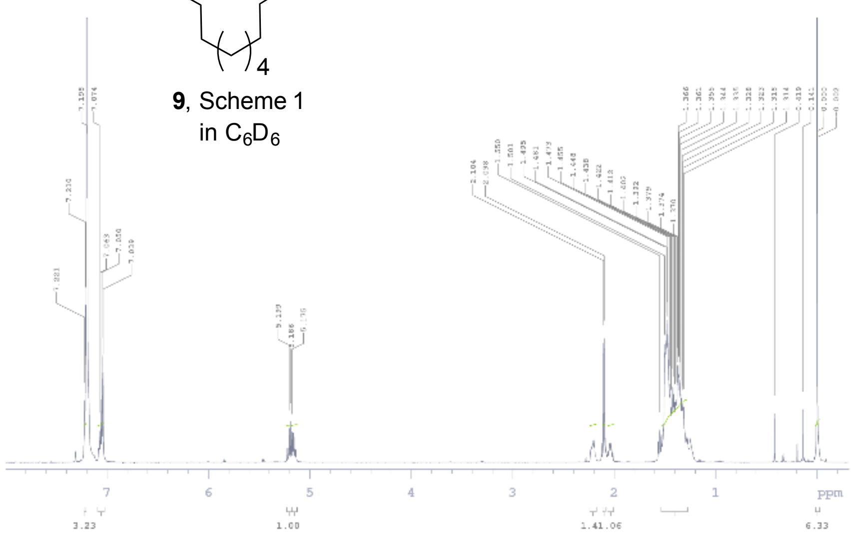


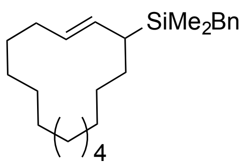
9, Scheme 1
in $CDCl_3$



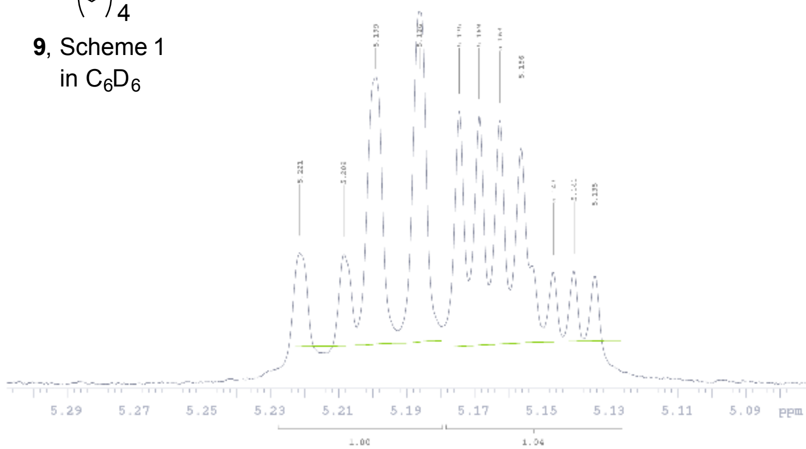


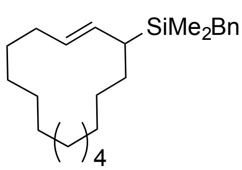
9, Scheme 1
in C_6D_6



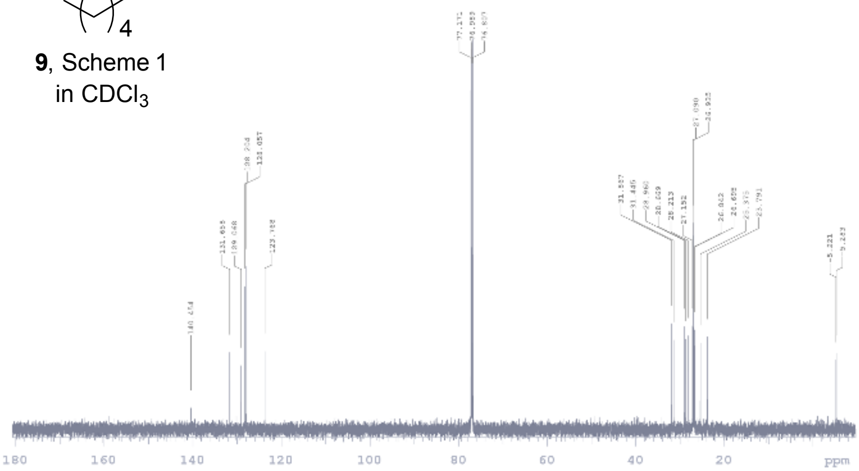


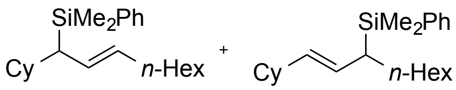
9, Scheme 1
in C_6D_6



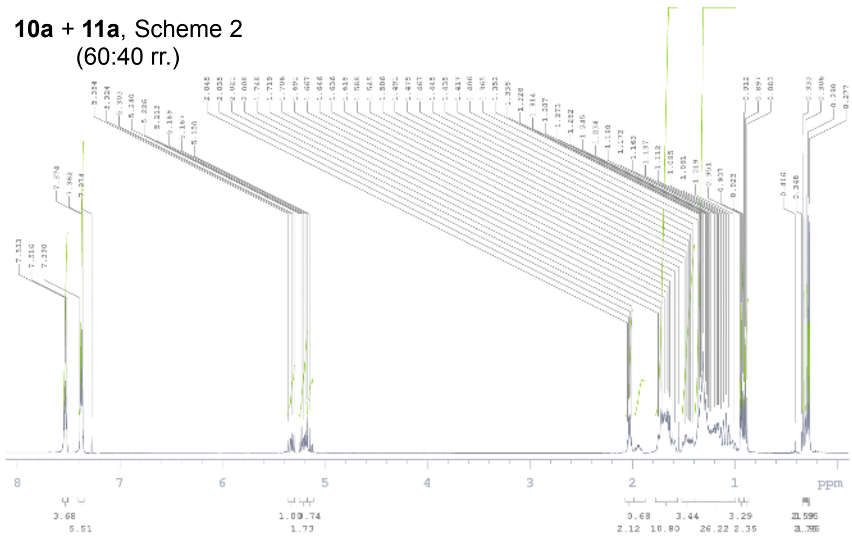


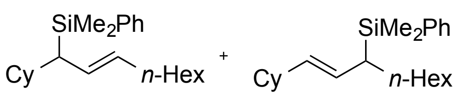
9, Scheme 1
in $CDCl_3$



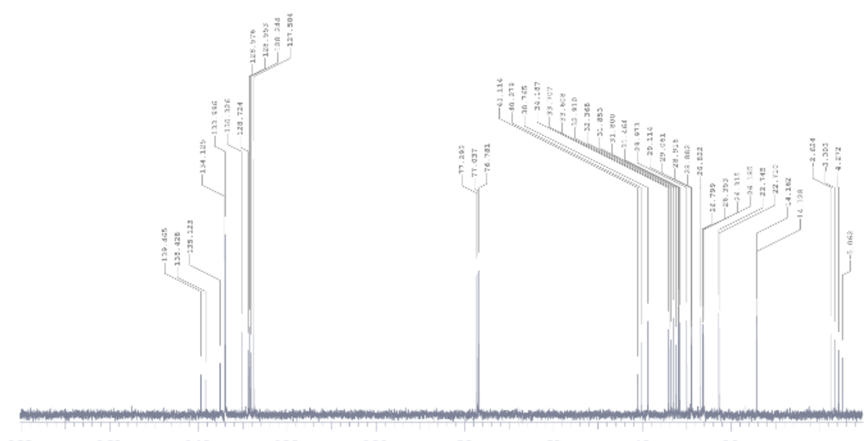


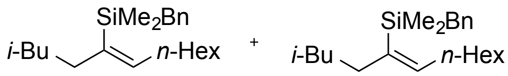
10a + **11a**, Scheme 2
(60:40 rr.)



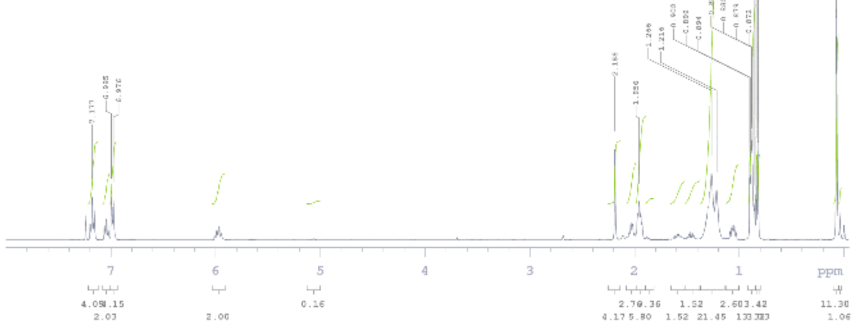


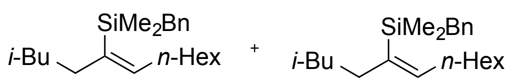
10a + **11a**, Scheme 2
(60:40 rr.)



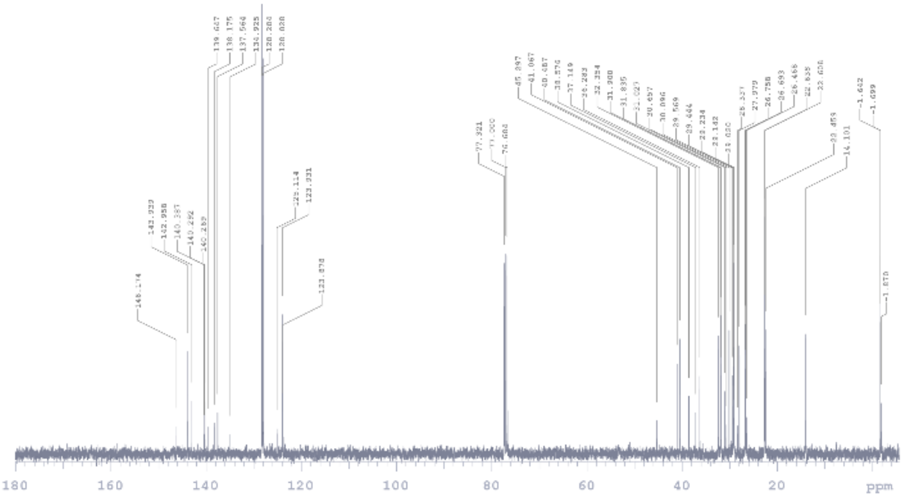


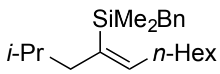
12a + **13a**, Table 3, Entry 1
(50:50) mixture + 9% allylsilane



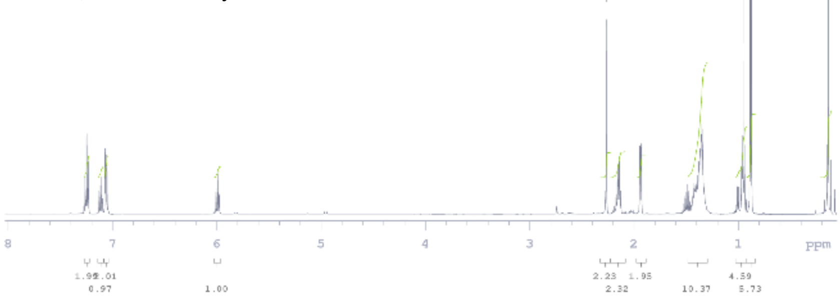


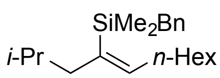
12a + **13a**, Table 3, Entry 1
(50:50) mixture + 9% allylsilane



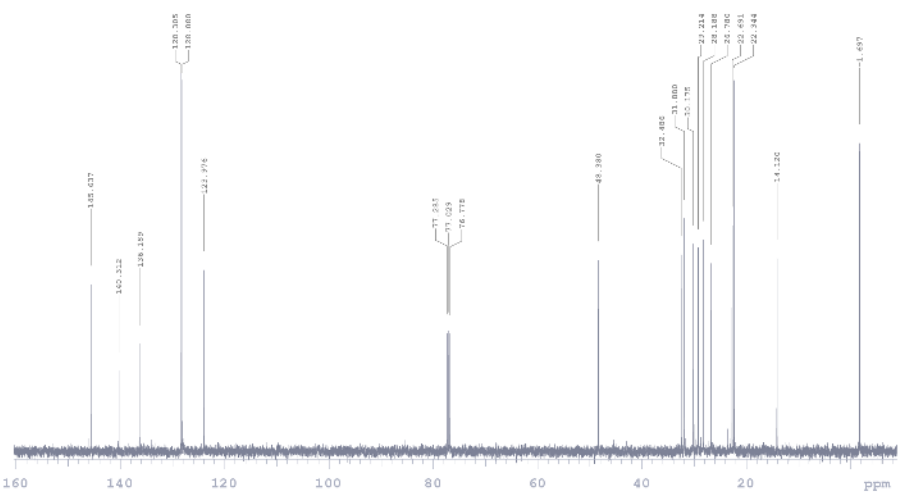


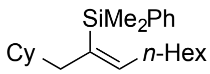
12b, Table 3, Entry 2



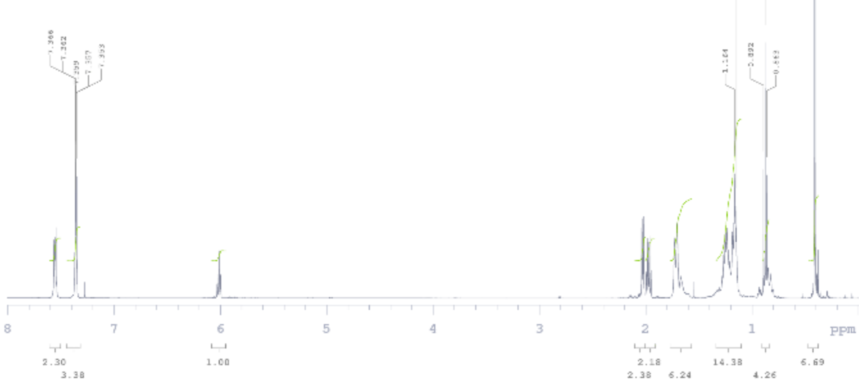


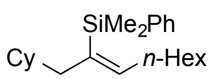
12b, Table 3, Entry 2



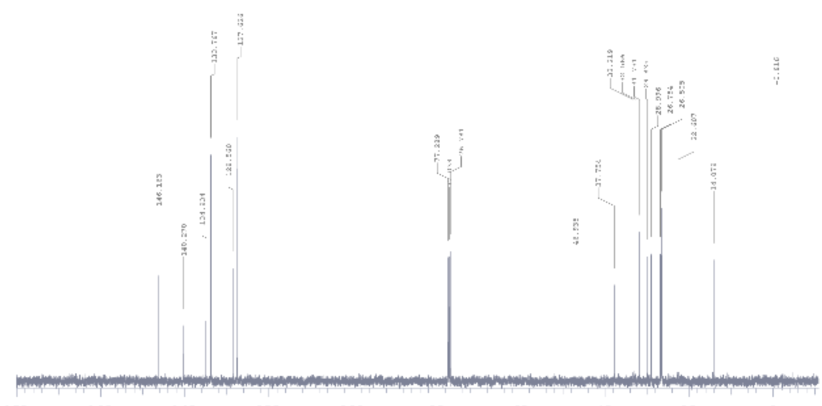


12c, Table 3, Entry 3

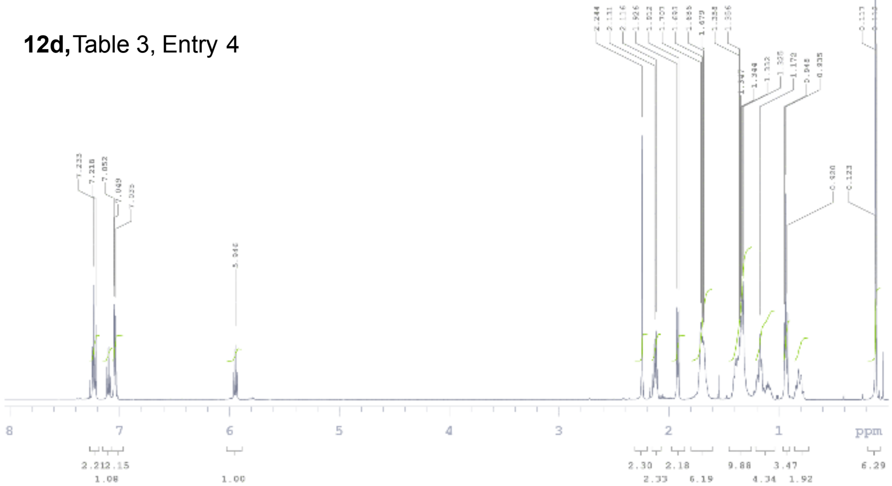


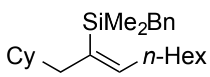


12c, Table 3, Entry 3

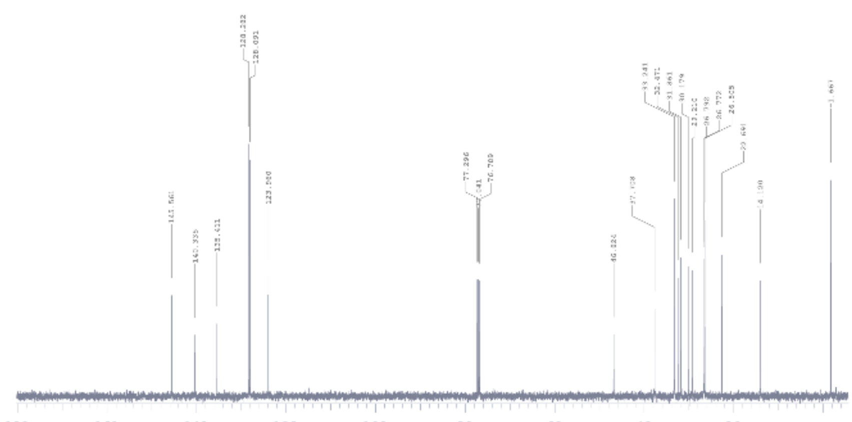


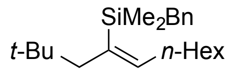
12d, Table 3, Entry 4



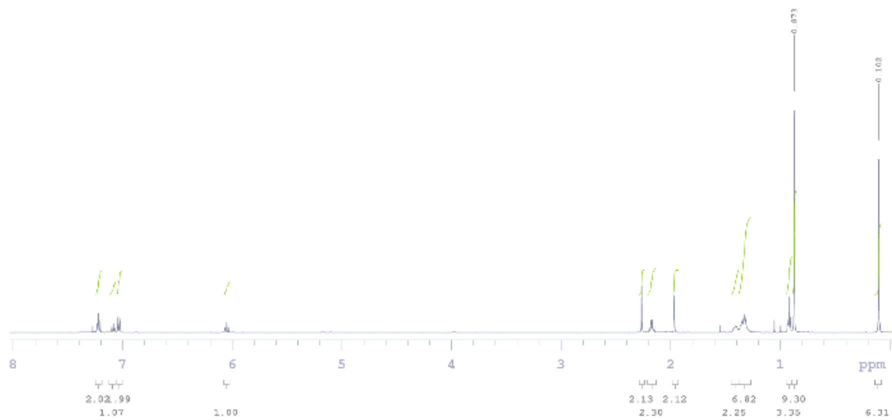


12d, Table 3, Entry 4

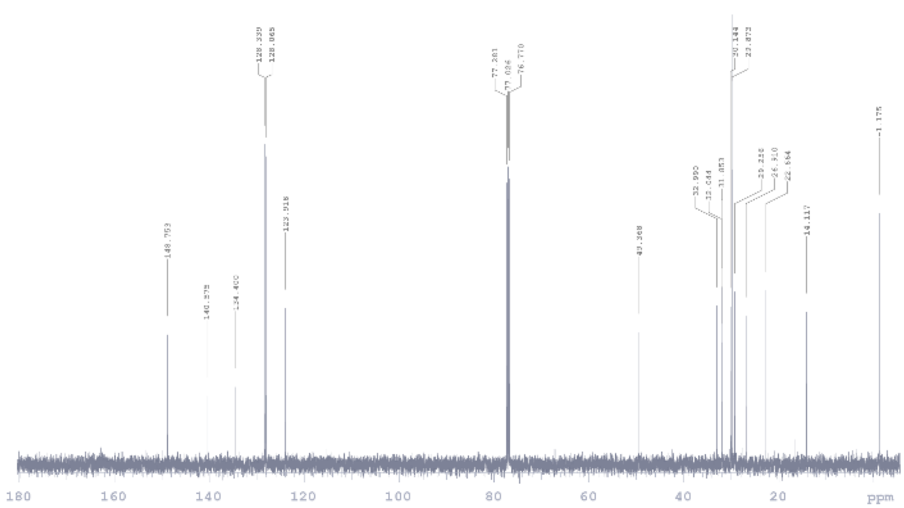


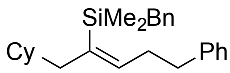


12e, Table 3, Entry 5

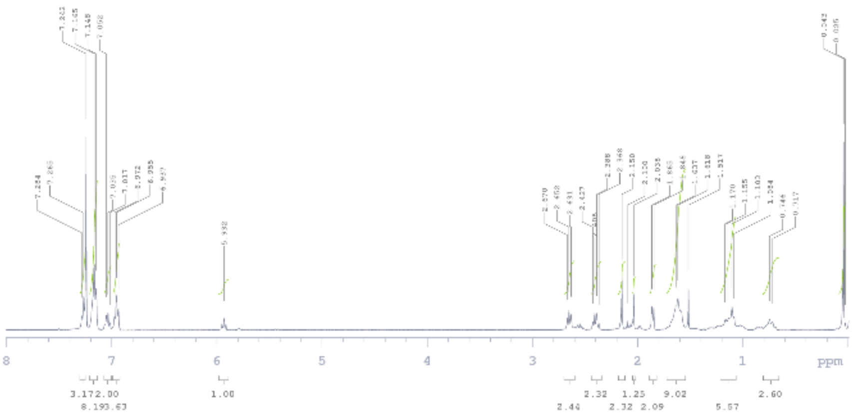


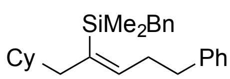
12e, Table 3, Entry 5



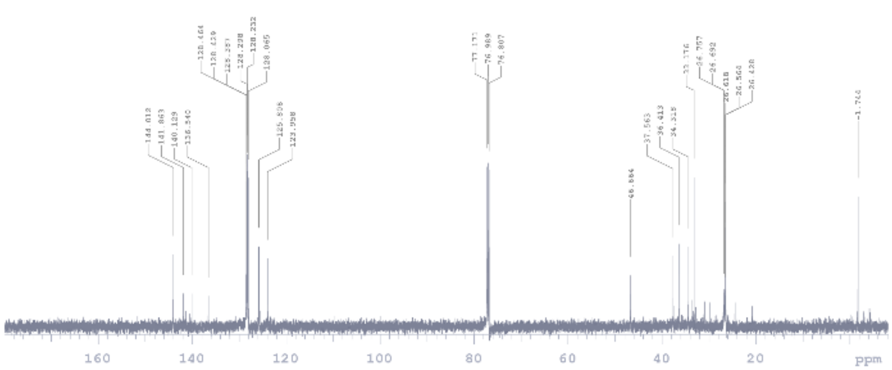


12f, Table 3, Entry 6

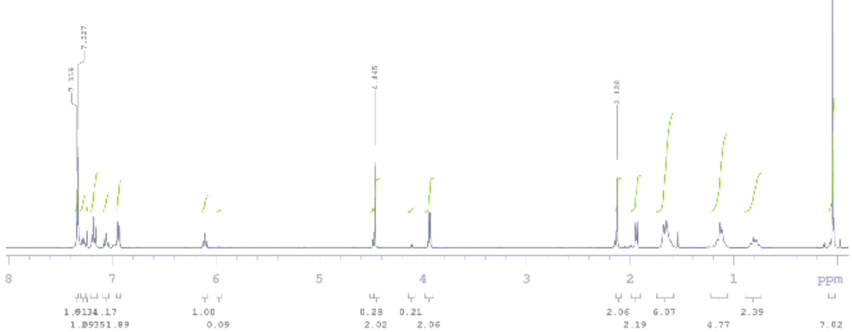


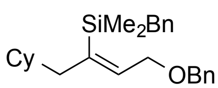


12f, Table 3, Entry 6

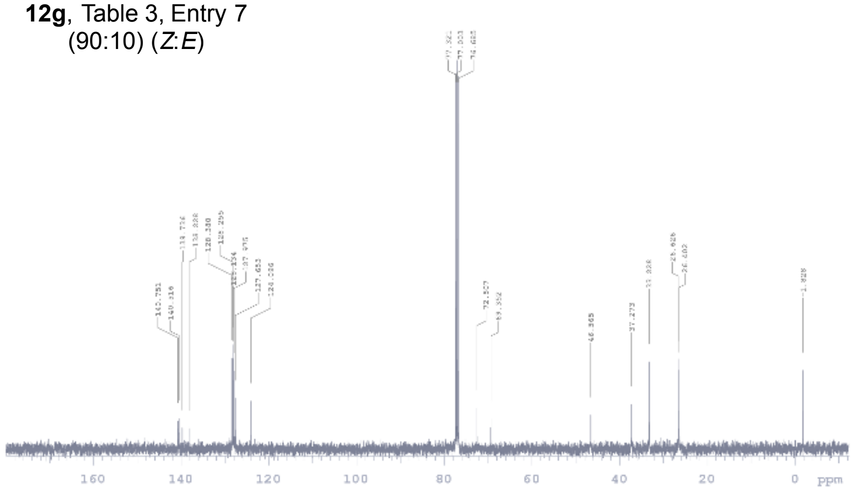


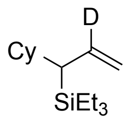
12g, Table 3, Entry 7
(90:10) (*Z*:*E*)



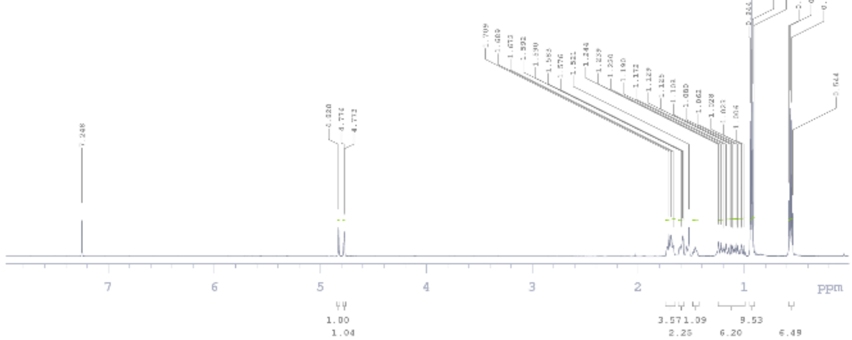


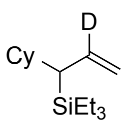
12g, Table 3, Entry 7
(90:10) (*Z*:*E*)



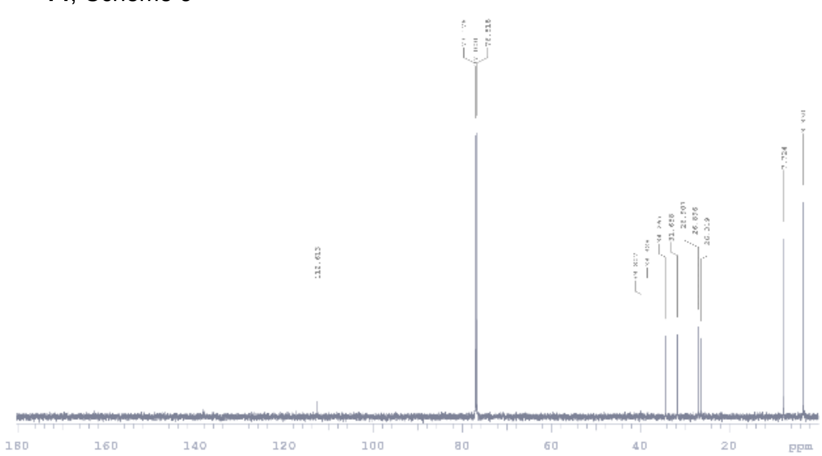


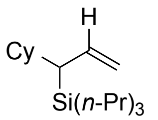
14, Scheme 3



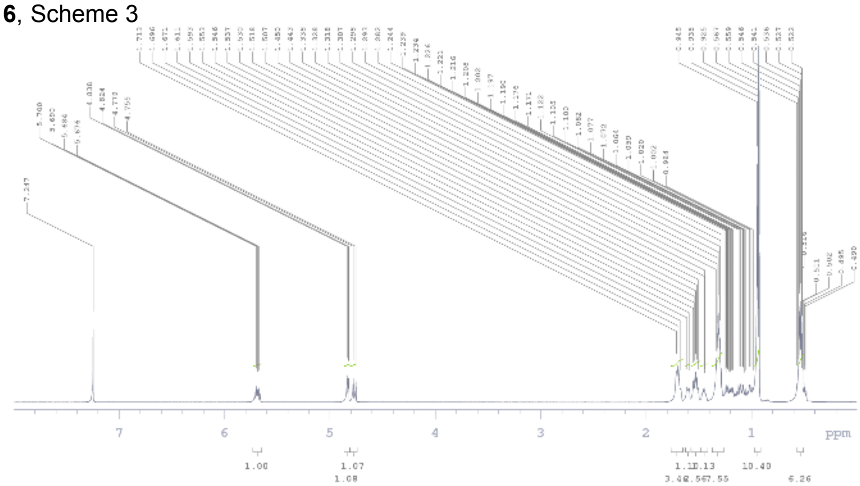


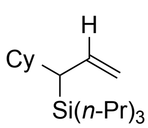
14, Scheme 3



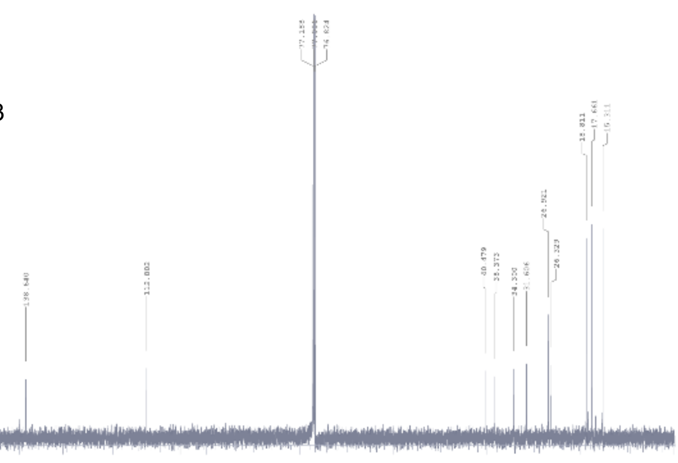


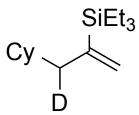
16, Scheme 3



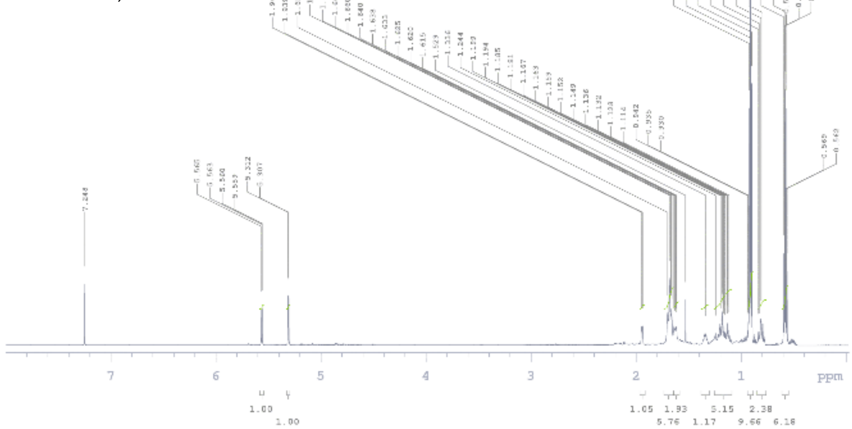


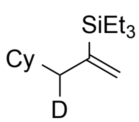
16, Scheme 3



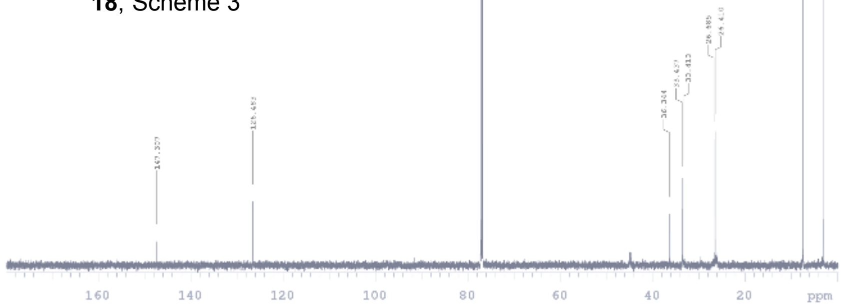


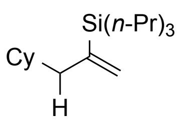
18, Scheme 3



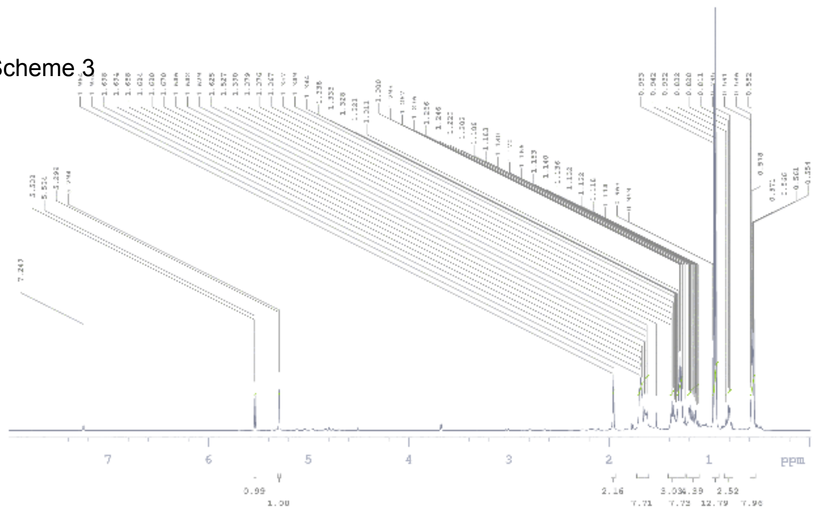


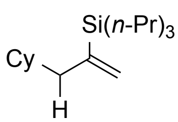
18, Scheme 3



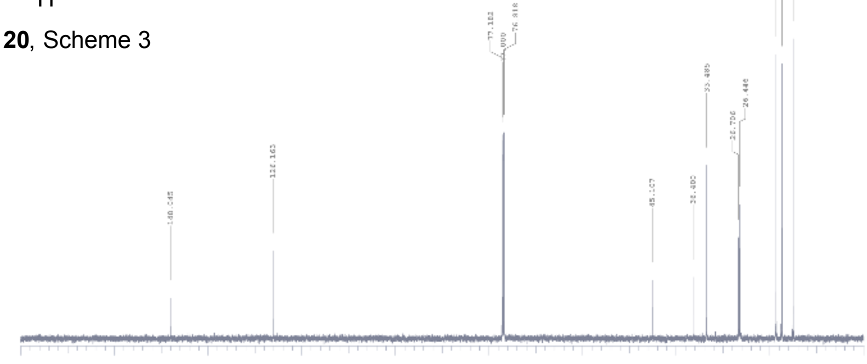


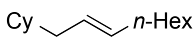
20, Scheme 3



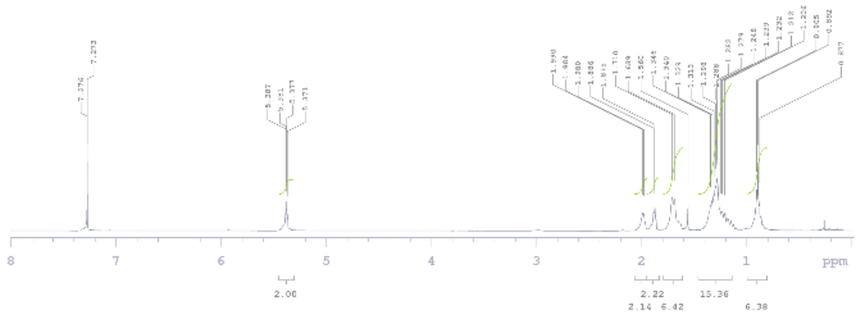


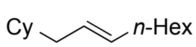
20, Scheme 3



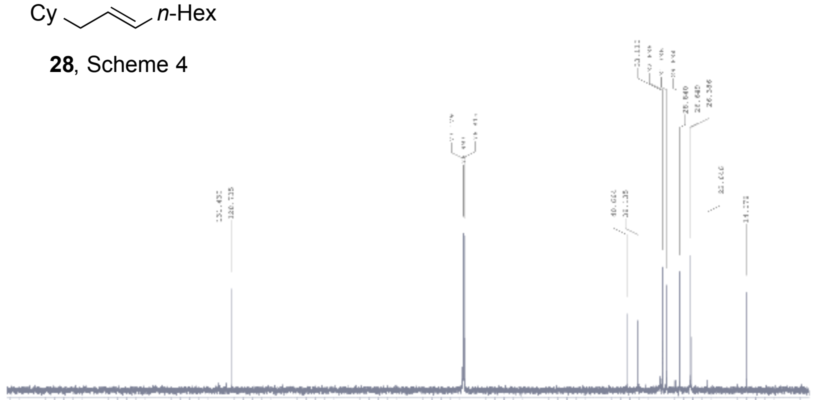


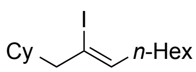
28, Scheme 4



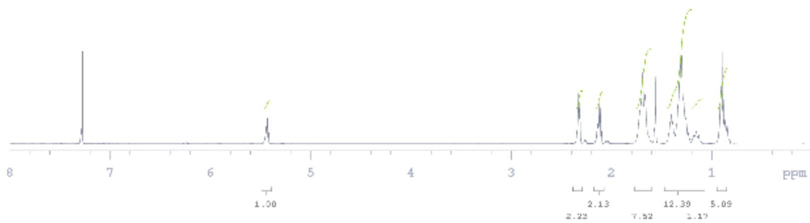


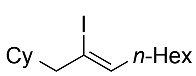
28, Scheme 4



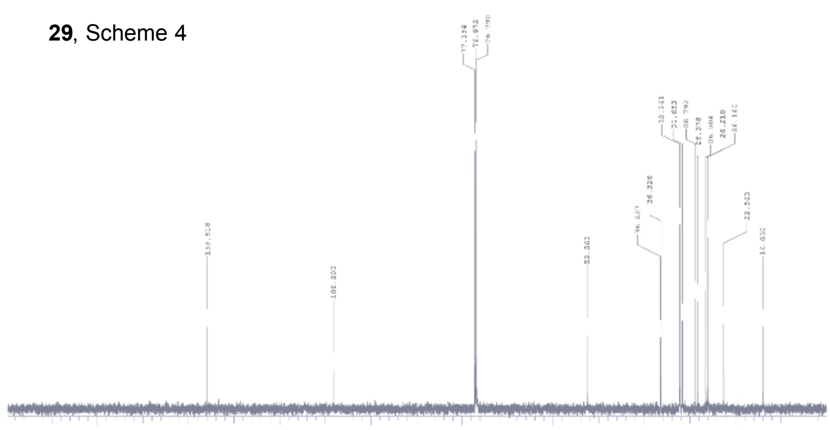


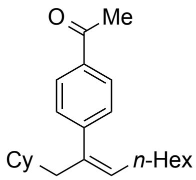
29, Scheme 4



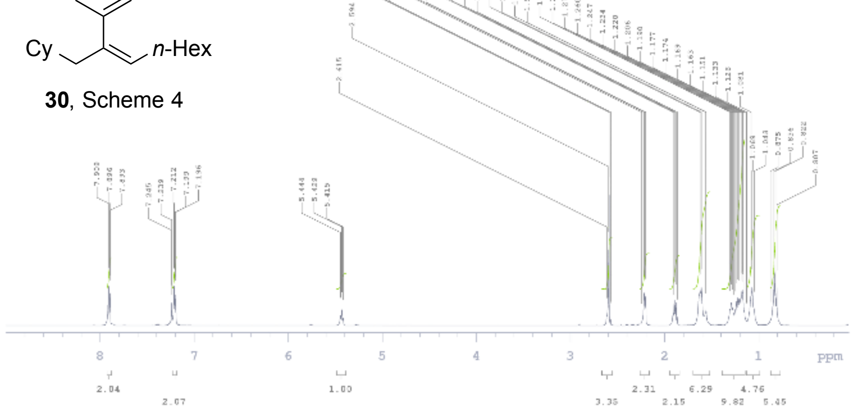


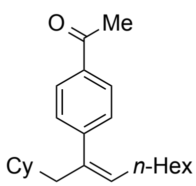
29, Scheme 4





30, Scheme 4





30, Scheme 4