

Supporting Information

Regiocontrol in Catalytic Reductive Couplings through Alterations of Silane Rate Dependence

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All reactions were conducted in flame-dried or oven dried (120 °C) glassware with magnetic stirring under an atmosphere of dry nitrogen. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, Inc. Model # SPS-400-3 and PS-400-3). Unless otherwise noted, alkynes were used as received. Aldehydes were distilled prior to use. Et₃SiH, *i*-Pr₃SiH (Aldrich) and *t*-Bu₂MeSiH (\$82/10 g, Gelest & Chem-Impex) were passed through basic alumina before use and stored under nitrogen. Ni(COD)₂ (Strem Chemicals, Inc), *N*-heterocyclic carbene salts (Sigma Aldrich, Strem), and *t*-BuOK (Strem) were stored and weighed in an inert atmosphere glovebox.

¹H and ¹³C were obtained in CDCl₃ at rt on a Varian Unity 500 MHz or Varian Unity 700 MHz instrument. Chemical shifts of ¹H 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 ¹³C NMR spectra were recorded in ppm from the central peak of CDCl₃ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained at the University of Michigan Mass Spectrometry Laboratory on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK). Regioisomeric ratios were determined on crude reaction mixtures using either ¹H NMR or GC. GCMS analysis was carried out on a HP 6980 Series GC system with HP-5MS column (30 m x 0.250 mm x 0.25 μm). GCFID analysis was carried out on a HP 6980N Series GC system with a HP-5 column (30 m x 0.32 mm x 0.25 μm).

General Procedure A for Ni(COD)₂/SIPr Promoted Reductive Coupling of Internal Alkynes, Aldehydes and Triisopropylsilane:

2 mL of THF was added to a solid mixture of Ni(COD)₂ (0.06 mmol), SIPr•HCl salt (0.05 mmol), and *t*-BuOK (0.05 mmol). The resulting solution was stirred for 5 min at rt until the solution turned dark brown. The alkyne (0.5 mmol), aldehyde (0.5 mmol), and triisopropylsilane (1.0 mmol) were combined together with 2 mL of THF. The catalyst was immersed in a 50 °C oil bath and the mixture of aldehyde, alkyne, and silane was added over the course of 60 minutes using a syringe pump. The reaction mixture was allowed to stir until starting materials were consumed. 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 chromatography on silica gel to afford the desired product.

General Procedure B for Ni(COD)₂/SIPr Promoted Reductive Coupling of Terminal Alkynes, Aldehydes and Di-*tert*-butyl(methyl)silane:

38 mL of THF was added to a solid mixture of Ni(COD)₂ (0.11mmol), SIPr•HCl salt (0.1 mmol), and *t*-BuOK (0.1 mmol). The resulting solution was stirred for 10 min at rt until the solution turned light brown. The alkyne (1.2 equiv, 0.6 mmol), aldehyde (1.0 equiv, 0.5 mmol), and di-*tert*-butyl(methyl)silane (2.0 equiv, 1 mmol) were combined together with 2 mL of THF and the mixture was added over the course of 60 minutes using a syringe pump at rt. The reaction mixture was allowed to stir until starting materials were consumed. 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 chromatography on silica gel to afford the desired product.

In cases where duplicate products were reported in more than one table, the compound characterization is provided for the optimized Table 4 procedure.

(E)-((1,2-diphenylbut-2-en-1-yl)oxy)triisopropylsilane

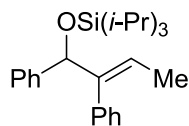


Table 4, Entry 1: Following a modified procedure B, Ni(COD)₂ (16.5 mg, 0.06 mmol), SiPr·HCl salt (21.3 mg, 0.05 mmol), and *t*-BuOK (5.6 mg, 0.05 mmol) were dissolved in 38 mL THF. Triisopropylsilane (158 mg, 1 mmol), prop-1-yn-1-ylbenzene (58 mg, 0.5 mmol), benzaldehyde (53 mg, 0.5 mmol) were combined with 2 mL THF and added to the reaction over 1 hour. This gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (>98:2 crude regioselectivity) (157 mg, 0.41 mmol, 82 % yield).

Spectra data as previously reported¹

(E)-((1-(4-fluorophenyl)-2-phenylbut-2-en-1-yl)oxy)triisopropylsilane.

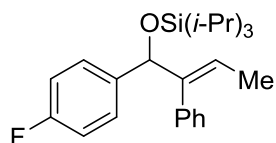


Table 4, Entry 2: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SiPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), prop-1-yn-1-ylbenzene (58 mg, 0.5 mmol), 4-fluorobenzaldehyde (62 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (93:7 crude regioselectivity) (169 mg, 0.43 mmol, 85 % yield).

¹H NMR (700 MHz, CDCl₃) δ 7.18-7.14 (m, 3H), 7.04-7.00 (m, 2H), 6.84-6.80 (m, 2H), 6.79-6.76 (m, 2H), 6.03 (qd, *J* = 7.0 Hz, 0.7 Hz, 1H), 5.36 (s, 1H), 1.49 (dd, *J* = 7.0 Hz, 0.7 Hz, 3H), 1.13-1.07 (m, 3H), 1.02 (d, *J* = 7.0 Hz, 9H), 0.97 (d, *J* = 7.7 Hz, 9H)

¹³C NMR (175 MHz, CDCl₃): δ 161.6 (d, *J* = 242.6 Hz), 144.7, 139.5 (d, *J* = 2.8 Hz), 138.0, 129.6, 128.0 (d, *J* = 8.1 Hz), 127.5, 126.5, 121.2, 114.3 (d, *J* = 21.0 Hz), 78.7, 18.02, 17.95, 14.1, 12.3

IR (film, cm⁻¹): 2943, 2865, 1602, 1506, 1463

HRMS (EI) (*m/z*): [M-ⁱPr]⁺ calcd for C₂₂H₂₈FOSi 355.1893; found 355.1888

(E)-triisopropyl((3-phenylundec-2-en-4-yl)oxy)silane. Major Regioisomer

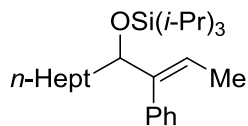


Table 3, Entry 3: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SiPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), prop-1-yn-1-ylbenzene (58 mg, 0.5 mmol), octanal (64 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (>98:2 crude regioselectivity) (156 mg, 0.39 mmol, 77 % yield).

¹H NMR (500 MHz, CDCl₃) δ 7.32-7.28 (m, 2H), 7.24-7.20 (m, 1H), 7.18-7.12 (m, 2H), 5.76 (q, *J* = 7.0 Hz, 1H), 4.45 (t, *J* = 5.0 Hz, 1H), 1.54 (d, *J* = 7.0 Hz, 3H), 1.43-1.04 (m, 33H), 0.84 (t, *J* = 7.0 Hz, 3 H)

¹³C NMR (125 MHz, CDCl₃): δ 143.2, 138.9, 129.3, 127.8, 126.4, 122.6, 77.3 35.7, 31.8, 29.6, 29.2, 23.9, 22.6, 18.20, 18.18, 14.13, 14.08, 12.5

IR (film, cm⁻¹): 2925, 2864, 1493, 1463, 1382

HRMS (EI) (*m/z*): [M-ⁱPr]⁺ calcd for C₂₃H₃₉OSi 359.2770; found 359.2772

(E)-((1-cyclohexyl-2-phenylbut-2-en-1-yl)oxy)triisopropylsilane.

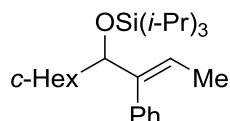


Table 4, Entry 4: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SiPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), prop-1-yn-1-ylbenzene (58 mg, 0.5 mmol), cyclohexanecarbaldehyde (56 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (>98:2 crude regioselectivity) (174 mg, 0.45 mmol, 90 % yield).

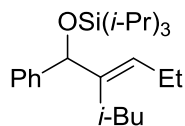
¹H NMR (500 MHz, CDCl₃) δ 7.32-7.28 (m, 2H), 7.24-7.18 (m, 3H), 5.74 (q, *J* = 7.0 Hz, 1H), 4.30 (d, *J* = 4.5 Hz, 1H), 1.70-1.47 (m, 8H), 1.25-0.86 (m, 27 H)

¹³C NMR (175 MHz, CDCl₃): δ 142.2, 139.5, 129.3, 127.8, 126.4, 123.1, 81.6, 42.5, 30.0, 27.2, 26.7, 26.5, 26.4, 18.4, 18.3, 14.2, 12.9

IR (film, cm⁻¹): 2924, 2864, 1492, 1449, 1387

HRMS (EI) (*m/z*): [M]⁺ calcd for C₂₅H₄₂OSi 386.3005; found 386.2996

(E)-((2-isobutyl-1-phenylpent-2-en-1-yl)oxy)triisopropylsilane Major Regioisomer



(E)-((2-ethyl-5-methyl-1-phenylhex-2-en-1-yl)oxy)triisopropylsilane Minor regioisomer

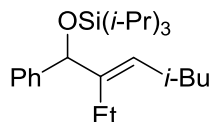


Table 4, Entry 5: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SIPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), 6-methylhept-3-yne (55 mg, 0.5 mmol), benzaldehyde (53 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a mixture of regioisomers in a 95:5 regioselectivity (94:6 crude regioselectivity) (161 mg, 0.43 mmol, 86 % yield).

¹H NMR (700 MHz, CDCl₃) δ 7.33-7.30 (m, 2 H), 7.26-7.22 (m, 2 H), 7.19-7.15 (m, 1 H), 5.79 (t, *J* = 7 Hz, 1 H), 5.14 (s, 1 H), 2.09-1.99 (m, 2 H), 1.78 (dd, *J* = 14, 8.4 Hz, 1 H), 1.66 (dd, *J* = 14 Hz, 6.3 Hz, 1 H), 1.57-1.51 (m, 1 H), 1.1-1.03 (m, 3 H), 1.02-0.94 (m, 21 H), 0.75 (d, *J* = 6.3 Hz, 3 H), 0.72 (d, *J* = 6.3 Hz, 3 H)

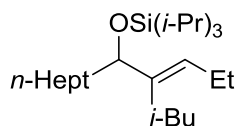
¹³C NMR (175 MHz, CDCl₃): δ 144.8, 139.6, 128.3, 127.6, 126.6, 126.5, 78.9, 36.1, 27.4, 23.2, 22.3, 21.2, 18.04, 17.97, 14.3, 12.3

IR (film, cm⁻¹): 2945, 2866, 1463

HRMS (EI) (*m/z*): [M]⁺ calcd for C₂₄H₄₂OSi 374.3005; found 374.2991

Characteristic ¹H NMR of minor isomer: 5.64 (t, *J* = 7.7 Hz, 1 H), 5.17 (s, 1 H)

(E)-((4-isobutyldodec-3-en-5-yl)oxy)triisopropylsilane Major regioisomer



(E)-((5-ethyl-2-methyltridec-4-en-6-yl)oxy)triisopropylsilane Minor regioisomer

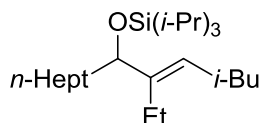


Table 4, Entry 6: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SIPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), 6-methylhept-3-yne (55 mg, 0.5 mmol), octanal (64 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography

(100 % hexanes) to afford a mixture of regioisomers in 94:6 regioselectivity (96:4 crude regioselectivity) (132 mg, 0.33 mmol, 66 % yield).

¹H NMR (700 MHz, CDCl₃) δ 5.40 (t, *J* = 7.0 Hz, 1 H), 4.13 (t, *J* = 4.0 Hz, 1 H), 2.07-1.97 (m, 2 H), 1.89 (dd, *J* = 14.0, 8.4 Hz, 1 H), 1.84 (dd, *J* = 14.0, 6.3 Hz, 1 H), 1.80-1.74 (m, 1 H), 1.62-1.46 (m, 2 H), 1.31-1.10 (m, 10 H), 1.08-1.00 (m, 21 H), 0.91 (t, *J* = 7 Hz, 3 H), 0.87 (d, *J* = 6.3 Hz, 3 H), 0.85 (t, *J* = 7.0 Hz, 3 H), 0.84 (d, *J* = 7 Hz, 3 H)

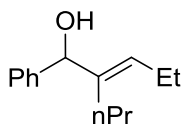
¹³C NMR (125 MHz, CDCl₃): δ 138.3, 129.3, 76.96, 36.6, 36.5, 31.8, 29.7, 29.3, 27.8, 24.5, 23.3, 22.7, 22.6, 21.2, 18.17, 18.15, 14.3, 14.1, 12.5

IR (film, cm⁻¹): 2926, 2865, 1463

HRMS (EI) (*m/z*): [M-iPr]⁺ calcd for C₂₂H₄₅OSi 353.3240; found 353.3233

Characteristic ¹H NMR of minor isomer: 5.24 (t, *J* = 7.7 Hz, 1 H), 4.09 (t, *J* = 6.3 Hz, 1 H)

(E)-1-phenyl-2-propylpent-2-en-1-ol Major regioisomer



(E)-2-ethyl-1-phenylhex-2-en-1-ol Minor regioisomer

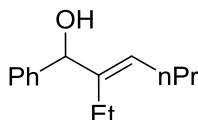


Table 4, Entry 7: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SiPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), hept-3-yne (48 mg, 0.5 mmol), benzaldehyde (53 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a mixture of regioisomers in a 68:32 regioselectivity (68:32 crude regioselectivity). The product was subjected to tetra-*n*-butylammonium fluoride deprotection for characterization purposes. (57 mg, 0.28 mmol, 56 % yield). Spectral data is provided for the mixture of regioisomers.

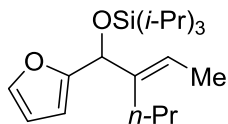
¹H NMR (700 MHz, CDCl₃): 7.36-7.33 (m, 2.8 H), 7.32-7.29 (m, 2.9 H), 7.25-7.24 (m, 0.6 H), 7.23-7.22 (m, 0.3 H), 5.59 (t, *J* = 7 Hz, 1 H), 5.58 (t, *J* = 7 Hz, 0.44 H), 5.15 (d, *J* = 2.1 Hz, 0.47 H), 5.13 (d, *J* = 2.1 Hz, 1 H), 2.11-2.03 (m, 3 H), 2.00 (dd, *J* = 14, 7.7 Hz, 0.5 H), 1.98-1.93 (m, 1.16 H), 1.91-1.85 (m, 0.56 H), 1.84-1.79 (m 1.1 H), 1.75 (br s, 1.35 H), 1.42 (sex, 7.7 Hz, 1 H), 1.30-1.23 (m, 1.32 H), 1.22-1.15 (m, 1.15 H), 0.995 (t = 7.7 Hz, 3 H), 0.92 (t, *J* = 7.7 Hz, 1.65 H), 0.82 (t, *J* = 7.7 Hz, 1.65 H), 0.80 (t, *J* = 7 Hz, 3 H)

¹³C NMR (175 MHz, CDCl₃): 142.79, 142.78, 142.75, 140.6, 129.1, 128.2, 127.3, 127.3, 126.8, 126.54, 126.53, 78.2, 78.1, 29.9, 29.5, 22.9, 22.8, 21.0, 20.6, 14.41, 14.36, 14.15, 13.95

IR (film, cm⁻¹): 3362, 2958, 2930, 2869, 1492, 1451

HRMS (EI) (m/z): calcd for $C_{14}H_{20}O$ 204.1514; found 204.1516

(E)-((2-ethylidene-1-(furan-2-yl)pentyl)oxy)triisopropylsilane Major regioisomer



(E)-((1-(furan-2-yl)-2-methylhex-2-en-1-yl)oxy)triisopropylsilane Minor regioisomer

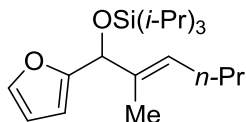


Table 4, Entry 8: Following Procedure A, $Ni(COD)_2$ (16.5 mg, 0.06 mmol), $SiPr \cdot HCl$ salt (21.3 mg, 0.05 mmol), $tBuOK$ (5.6 mg, 0.1 mmol), triisopropylsilane (158 mg, 1 mmol), 2-hexyne (41 mg, 0.5 mmol), 2-furancarboxaldehyde (48 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a mixture of regioisomers in 92:8 regioselectivity (93:7 crude regioselectivity) (128 mg, 0.38 mmol, 76 % yield).

1H NMR (700 MHz, $CDCl_3$) δ 7.28 (dd, $J = 1.4, 0.7$ Hz, 1 H), 6.27 (dd, $J = 3.5, 1.4$ Hz, 1 H), 6.19-6.18 (m, 1 H), 5.73 (q, $J = 7.0$ Hz, 1 H), 5.14 (s, 1H), 1.97 (ddd, $J = 13.3, 10.5, 6.3$ Hz, 1 H), 1.87 (ddd, $J = 13.7, 10.5, 5.6$, 1 H) (m, 1 H), 1.64 (d, $J = 7.0$ Hz, 3H), 1.22-1.16 (m, 1 H), 1.13-1.03 (m, 4H), 1.01 (d, $J = 7.7$ Hz, 9H), 0.99 (d, $J = 7.0$ Hz, 9 H), 0.80 (t, $J = 7.0$ Hz, 3 Hz)

^{13}C NMR (175 MHz, $CDCl_3$): δ 156.9, 141.0, 140.4, 121.2, 110.0, 105.9, 73.3, 29.1, 21.9, 18.0, 17.9, 14.5, 13.1, 12.3

IR (film, cm^{-1}): 2943, 2866, 1464

HRMS (ESI+) (m/z): $[M+H]^+$ calcd for $C_{20}H_{40}O_2Si$ 337.2557; found 337.2549

Characteristic 1H NMR of minor isomer: 5.58 (t, $J = 7$ Hz, 1 H), 5.13 (s, 1 H), 0.89 (t, $J = 7.0$ Hz, 3 H)

(E)-triisopropyl((2-isopropyl-1-phenylbut-2-en-1-yl)oxy)silane

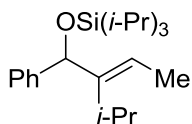


Table 4, Entry 9: Following Procedure A, $Ni(COD)_2$ (16.5 mg, 0.06 mmol), $SiPr \cdot HCl$ salt (21.3 mg, 0.05 mmol), $t-BuOK$ (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), 4-methylpent-2-yne (41 mg, 0.5 mmol), benzaldehyde (53 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (>98:2 crude regioselectivity) (135 mg, 0.39 mmol, 78 % yield).

Spectral data as previously reported¹

(E)-((1-cyclohexyl-2-isopropylbut-2-en-1-yl)oxy)triisopropylsilane

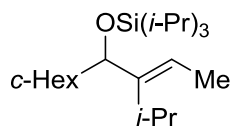


Table 4, Entry 10: Following Procedure A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SiPr·HCl salt (21.3 mg, 0.05 mmol), *t*-BuOK (5.6 mg, 0.05 mmol), triisopropylsilane (158 mg, 1 mmol), 4-methylpent-2-yne (41 mg, 0.5 mmol), cyclohexanecarbaldehyde (56 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (>98:2 crude regioselectivity) (133 mg, 0.38 mmol, 75 % yield).

¹H NMR (500 MHz, CDCl₃) δ 5.31 (q, *J* = 7 Hz, 1H), 3.93 (d, *J* = 5 Hz, 1 H), 2.46 (sept, *J* = 7 Hz, 1H), 1.75-1.68 (m, 3H), 1.66 (d, *J* = 7.0 Hz), 1.64-1.57 (m, 2H), 1.34-0.88 (m, 33H)

¹³C NMR (125 MHz, CDCl₃): δ 144.8, 120.3, 81.3, 42.9, 31.0, 28.0, 26.81, 26.78, 26.6, 21.4, 21.2, 18.4, 18.3, 13.5, 13.0

IR (film, cm⁻¹): 2925, 2865, 1464

HRMS (EI) (*m/z*): [M]⁺ calcd for C₂₂H₄₄OSi 352.3161; found 352.3151

Di-*tert*-butyl(methyl)(3-methyl-2-methylene-1-phenylbutoxy)silane

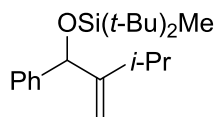


Table 4, Entry 11: Following Procedure B, Ni(COD)₂ (30.2 mg, 0.11 mmol), SiPr·HCl salt (42.6 mg, 0.1 mmol), *t*-BuOK (11.2 mg, 0.1 mmol), Di-*t*-butylmethylsilane (158 mg, 1 mmol), 3-methylbut-1-yne (41 mg, 0.6 mmol), benzaldehyde (53 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to afford a single regioisomer in a >98:2 isolated regioselectivity (>98:2 crude regioselectivity) (101 mg, 0.30 mmol, 61 % yield).

¹H NMR (700 MHz, CDCl₃) δ 7.32-7.30 (m, 2H), 7.27-7.24 (m, 2H), 7.20-7.17 (m, 1 H), 5.38 (s, 1 H), 5.16 (s, 1 H), 4.9 (s, 1 H), 2.04 (sept, *J* = 7.0 Hz, 1 H), 0.99 (s, 9 H), 0.89 (d, *J* = 7.0 Hz, 3 H), 0.84 (s, 9 H), 0.83 (d, *J* = 7 Hz, 3 H), -0.04 (s, 3 H)

¹³C NMR (175 MHz, CDCl₃): δ 158.2, 143.6, 127.8, 126.98, 126.97, 106.6, 78.4, 28.8, 27.8, 27.6, 23.7, 22.3, 21.1, 20.5, -8.6

IR (film, cm⁻¹): 2960, 2857, 1471

HRMS (EI) (*m/z*): [M-^tBu]⁺ calcd for C₁₇H₂₇OSi 275.1813; found 275.1833

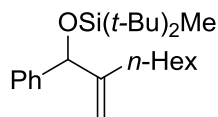
Di-tert-butyl(methyl)((2-methylene-1-phenyloctyl)oxy)silane

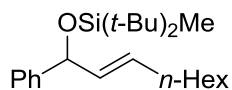
Table 4, Entry 12: Following Procedure B, Ni(COD)₂ (30.2 mg, 0.11 mmol), SIPr·HCl salt (42.6 mg, 0.1 mmol), *t*-BuOK (11.2 mg, 0.1 mmol), Di-*t*-butylmethylsilane (158 mg, 1 mmol), 1-octyne (66 mg, 0.6 mmol), benzaldehyde (53 mg, 0.5 mmol) gave a crude residue which was purified via flash chromatography (100 % hexanes) to give a mixture of regioisomers in 95:5 isolated regioselectivity (95:5 crude regioselectivity) (121 mg, 0.32 mmol, 65 % yield) Major (115 mg, 0.31 mmol), Minor (6 mg, 0.016 mmol)

¹H NMR (700 MHz, CDCl₃) δ 7.33-7.31 (m, 2 H), 7.28 (t, *J* = 7.7 Hz, 2 H), 7.21-7.18 (m, 1 H), 5.29 (s, 1 H), 5.15 (s, 1 H), 4.82 (d, *J* = 1.4 Hz, 1 H), 1.91 (dt, *J* = 16.1, 7.7 Hz, 1 H), 1.70 (dt, *J* = 16.1, 7.7 Hz, 1 H), 1.32-1.26 (m, 2 H), 1.26-1.13 (m, 6 H), 1.00 (s, 9 H), 0.87 (s, 9 H), 0.82 (t, *J* = 7 Hz, 3 H), -0.01 (s, 3 H)

¹³C NMR (175 MHz, CDCl₃): δ 151.9, 143.6, 127.8, 126.8, 126.5, 108.8, 79.3, 31.7, 30.3, 29.1, 27.8, 27.7, 27.5, 22.5, 20.9, 20.7, 14.0, -8.7

IR (film, cm⁻¹): 2930, 2856, 1471

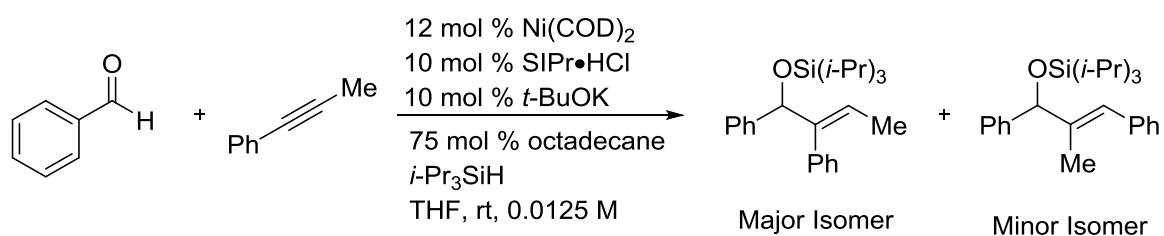
HRMS (EI) (*m/z*): [M-^tBu]⁺ calcd for C₂₀H₃₃OSi 317.2301; found 317.2305

(E)-di-tert-butyl(methyl)((1-phenylnon-2-en-1-yl)oxy)silane

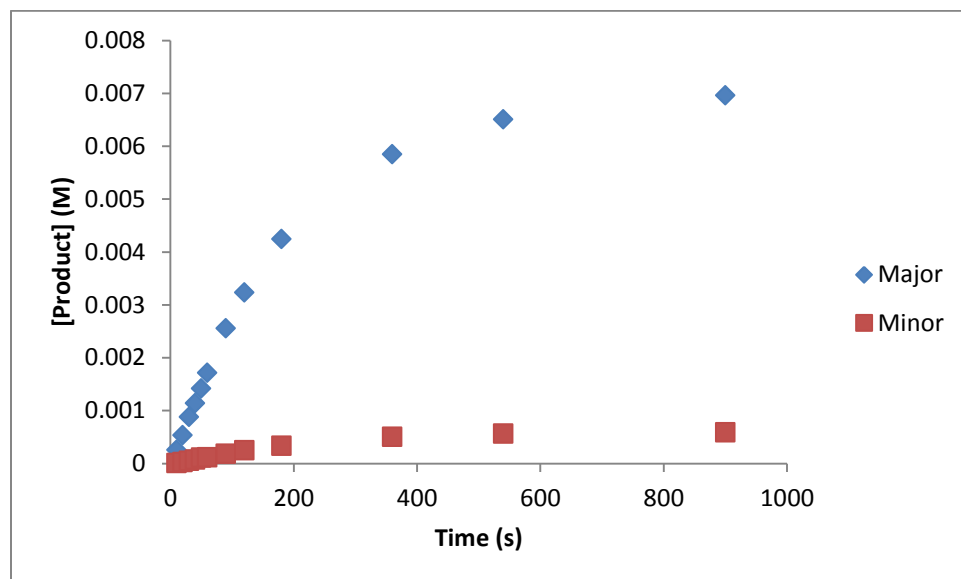
Spectral data as previously reported¹

Kinetics experiments

Following a modified method A, Ni(COD)₂ (16.5 mg, 0.06 mmol), SIPr·HCl salt (21.3 mg, 0.05 mmol), and *t*-BuOK (5.6 mg, 0.05 mmol) were dissolved in 38 mL THF. The mixture was stirred for approximately 15 min until the solution turned light brown. Triisopropylsilane (2, 3, 4, 6 equiv), prop-1-yn-1-ylbenzene (58 mg, 0.5 mmol), benzaldehyde (53 mg, 0.5 mmol), and octadecane (95 mg, 0.0375 mmol) were combined with THF to a total volume of 2 mL. This mixture was injected into the reaction as quickly as possible. Reaction aliquots (1.0 mL) were taken every 10 seconds, diluted in CH₂Cl₂ (0.8 mL), and shaken. Aliquots were then filtered through a pipette of silica gel. Samples were analyzed by GCFID and product concentration was determined using a calibration curve. The first 6 data points were used for initial rates.



Example plot of reaction progression for both regioisomers using 2 equiv *i*-Pr₃SiH



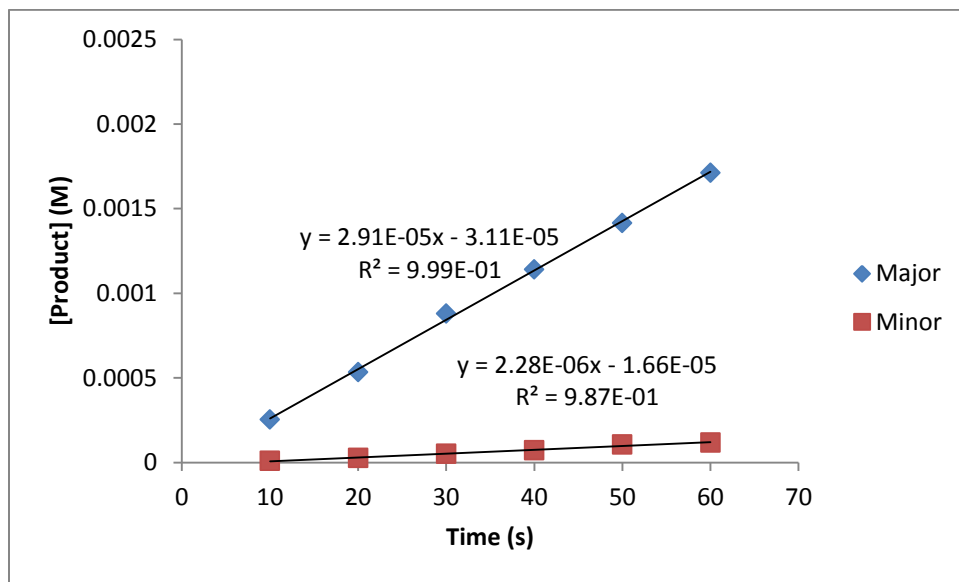
Initial rates of Major regioisomer

Equip Silane	$\Delta[\text{Major}]/\Delta t$ (M/Sec)* 10^{-5}	Avg. $\Delta[\text{Major}]/\Delta t$	Std. Dev.
2	2.87	2.71	0.22
	2.48		
	2.91		
	2.56		
3	2.60	3.21	0.46
	3.11		
	3.61		
	3.51		
4	3.44	3.03	0.56
	2.47		
	2.64		
	3.57		
6	3.51	3.21	0.90
	4.33		
	2.67		
	2.32		

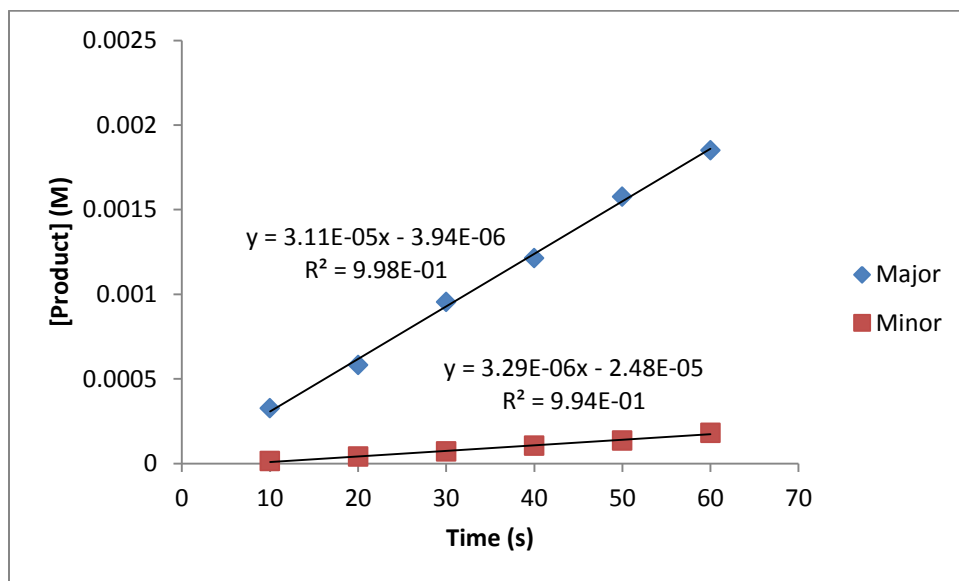
Initial rates of Minor regioisomer

Equip Silane	$\Delta[\text{Minor}]/\Delta t$ (M/Sec)* 10^{-5}	Avg. $\Delta[\text{Minor}]/\Delta t$	Std. Dev.
2	0.206	0.207	0.016
	0.202		
	0.228		
	0.190		
3	0.251	0.332	0.058
	0.329		
	0.373		
	0.374		
4	0.457	0.405	0.058
	0.352		
	0.359		
	0.453		
6	0.638	0.582	0.156
	0.777		
	0.473		
	0.441		

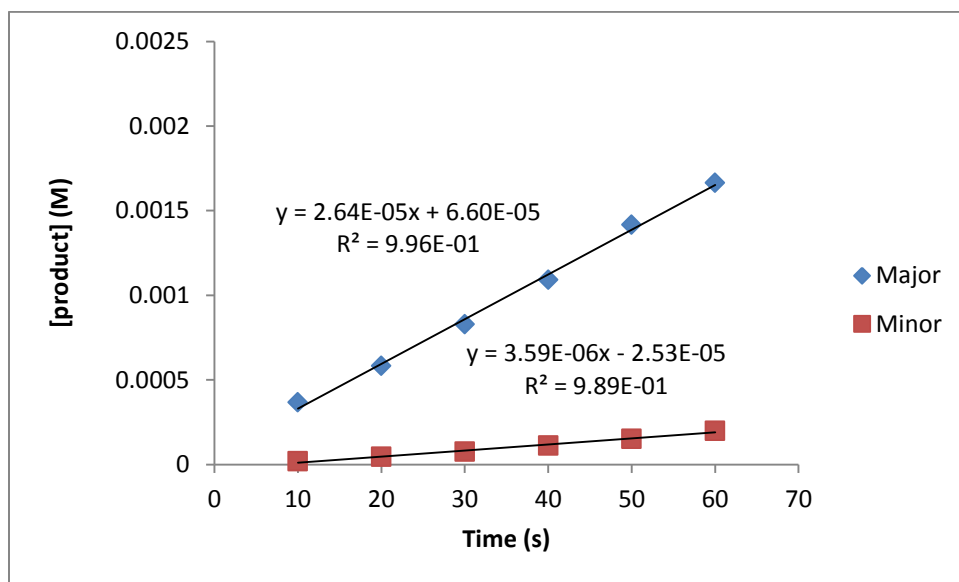
2 equiv *i*-Pr₃SiH



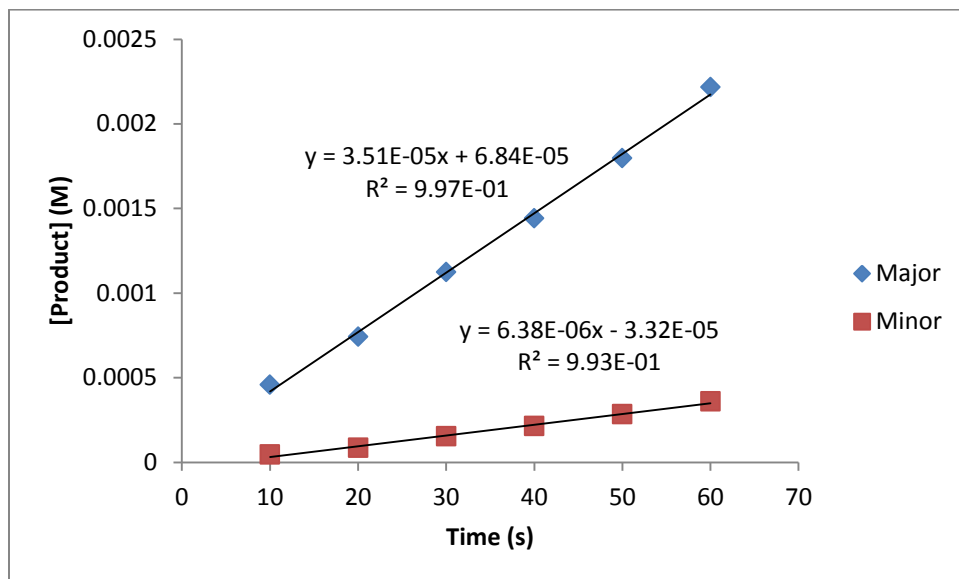
3 equiv *i*-Pr₃SiH



4 equiv *i*-Pr₃SiH



6 equiv *i*-Pr₃SiH



1. H. A. Malik, G. J. Sormunen, J. Montgomery, *J. Am. Chem. Soc.* **2010**, *132*, 6304–6305

Table 4, Entry 2 (E)-((1-(4-fluorophenyl)-2-phenylbut-2-en-1-yl)oxy)triisopropylsilane

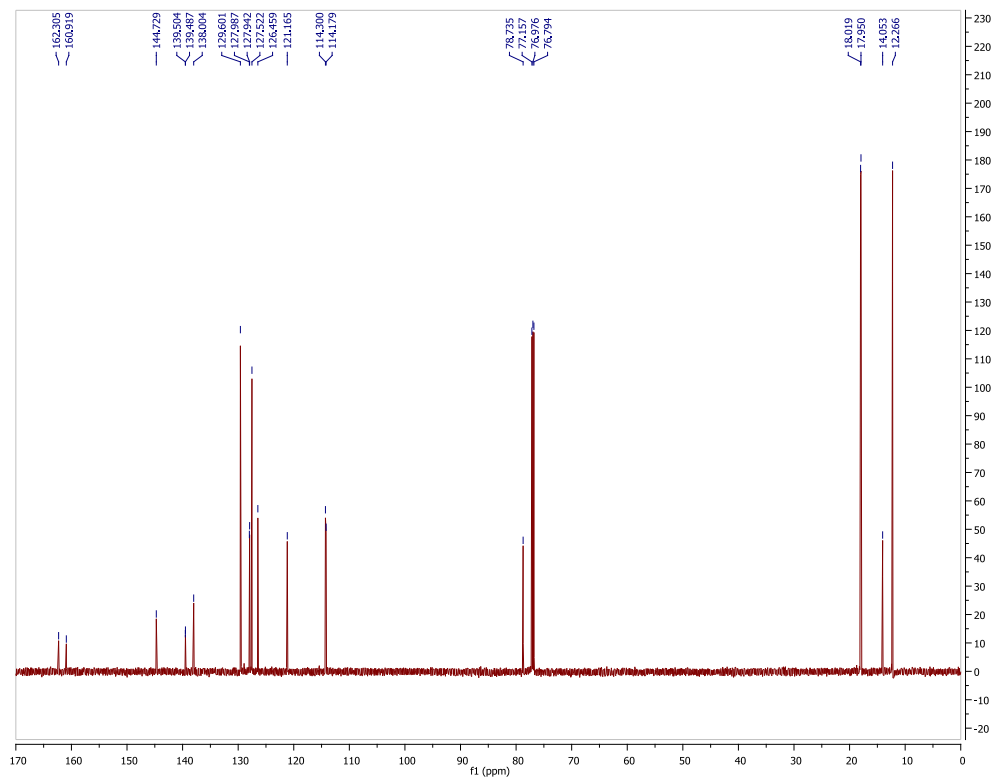
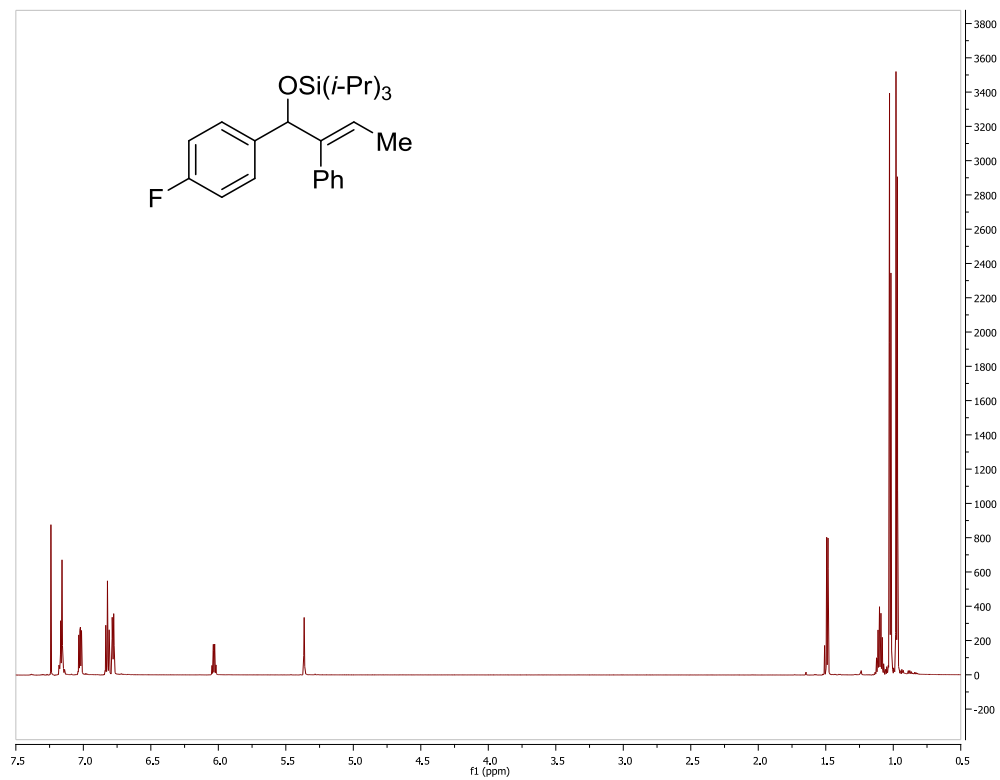


Table 4, Entry 3 (E)-triisopropyl((3-phenylundec-2-en-4-yl)oxy)silane

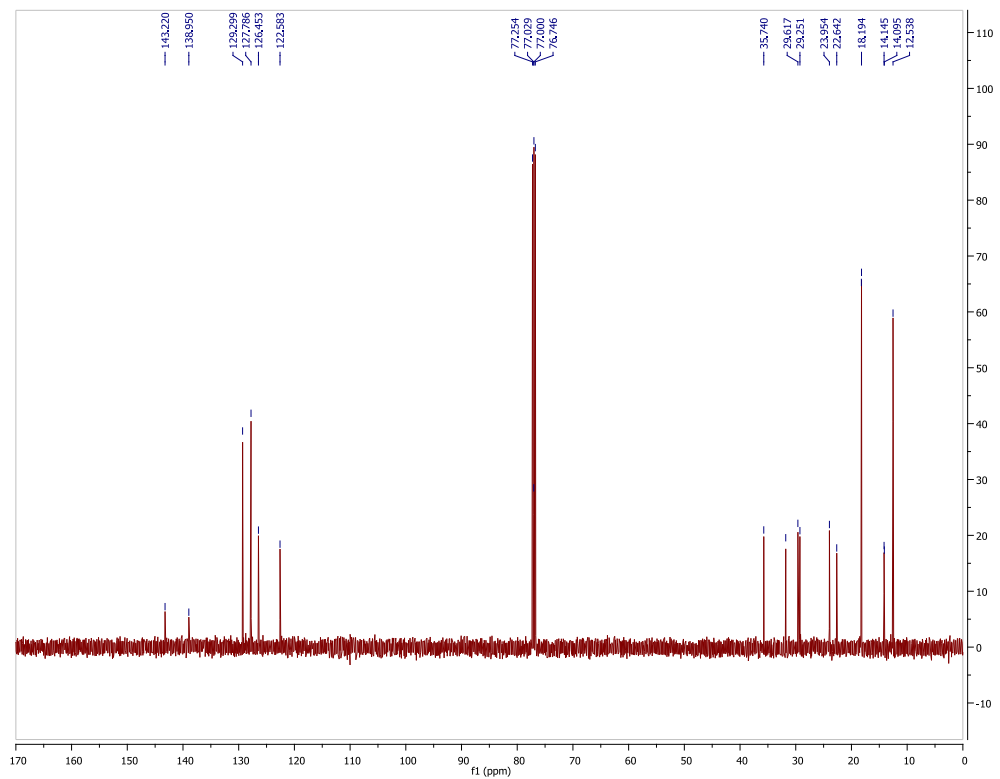
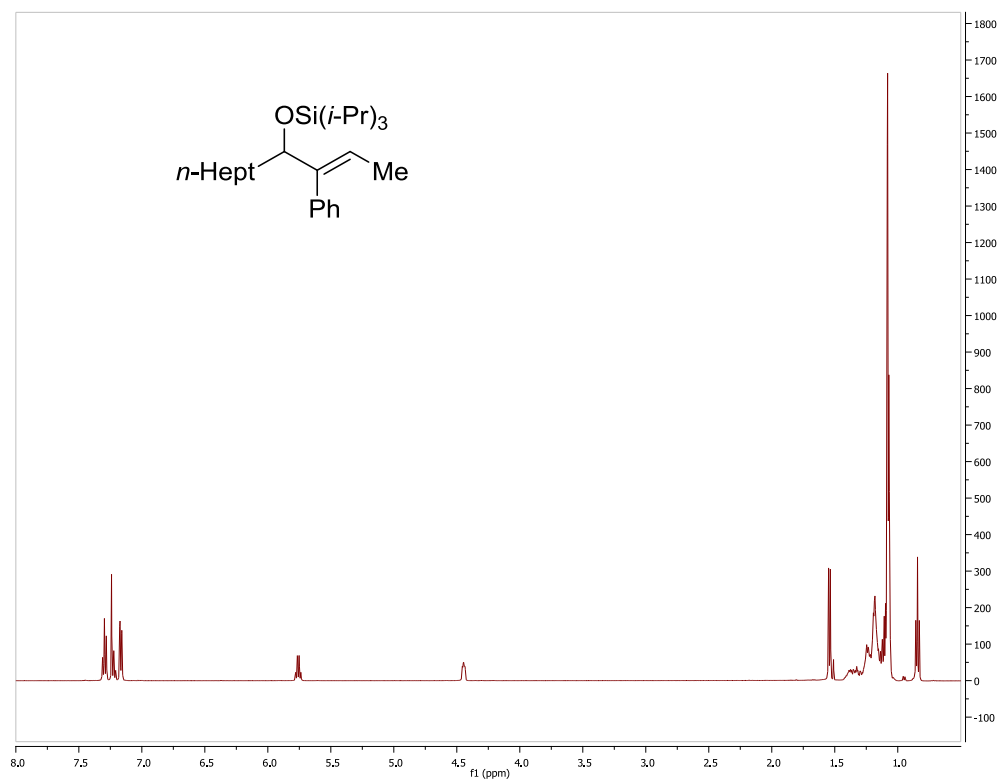


Table 4, Entry 4 (E)-((1-cyclohexyl-2-phenylbut-2-en-1-yl)oxy)triisopropylsilane

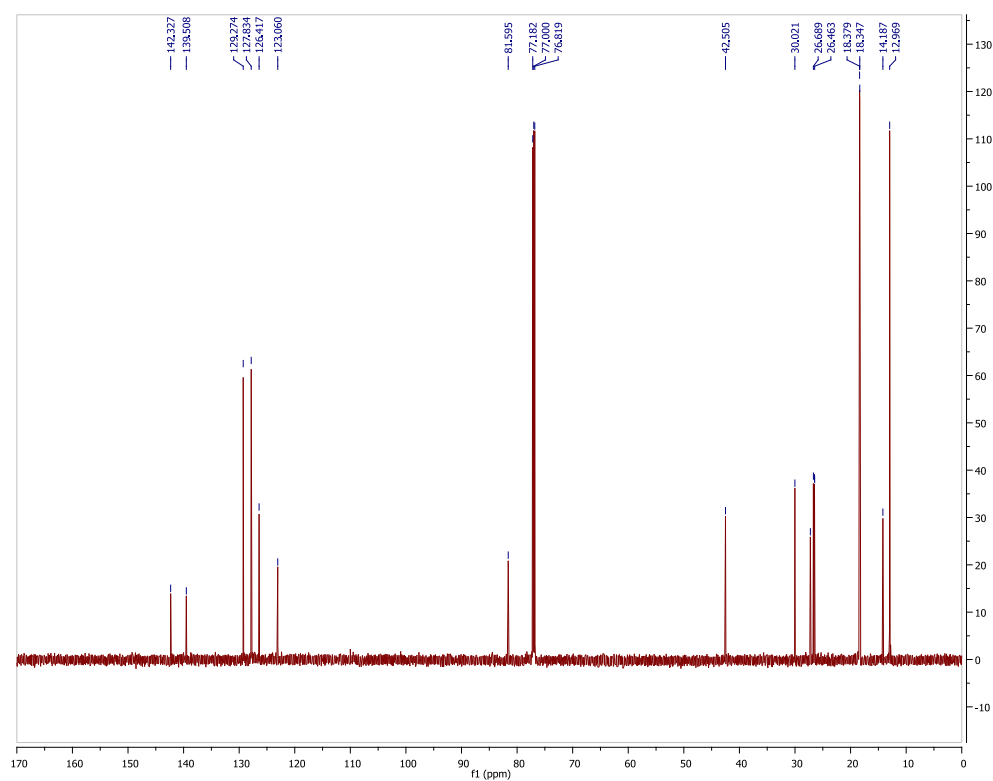
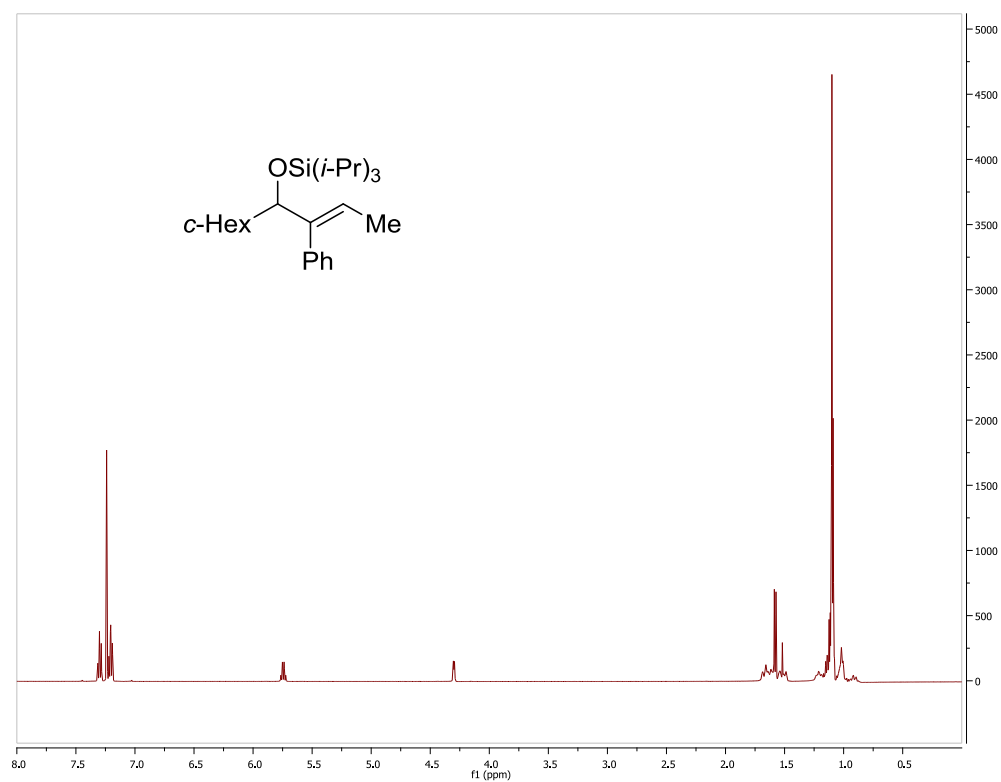


Table 4, Entry 5

Major isomer (E)-((2-isobutyl-1-phenylpent-2-en-1-yl)oxy)triisopropylsilane

Minor isomer (E)-((2-ethyl-5-methyl-1-phenylhex-2-en-1-yl)oxy)triisopropylsilane

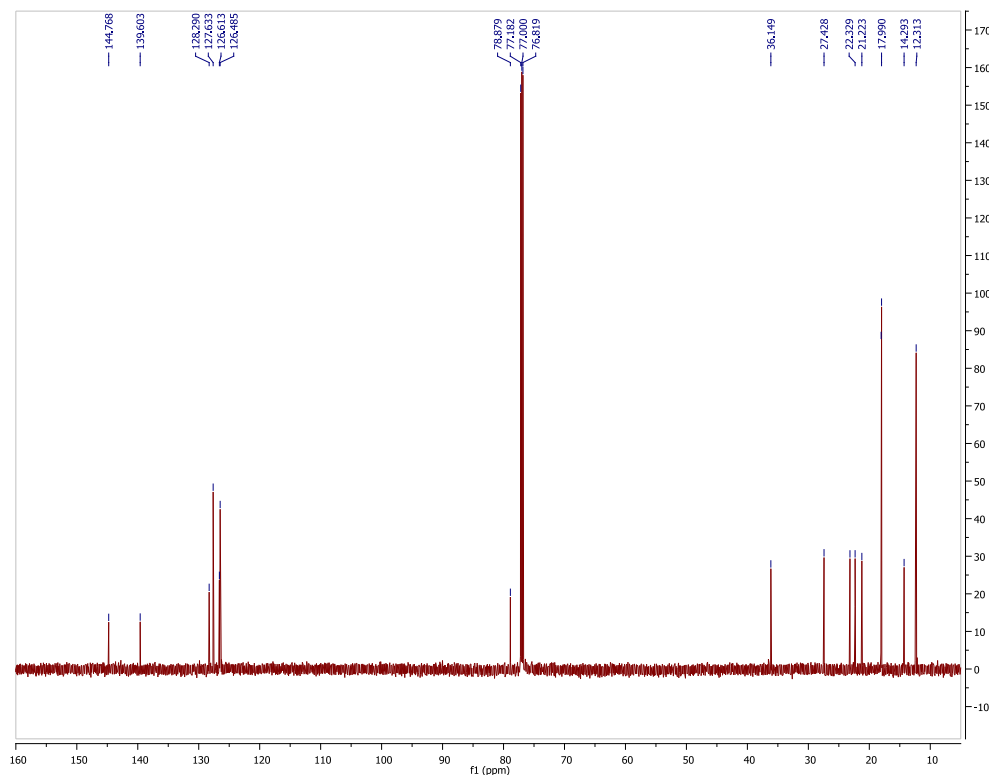
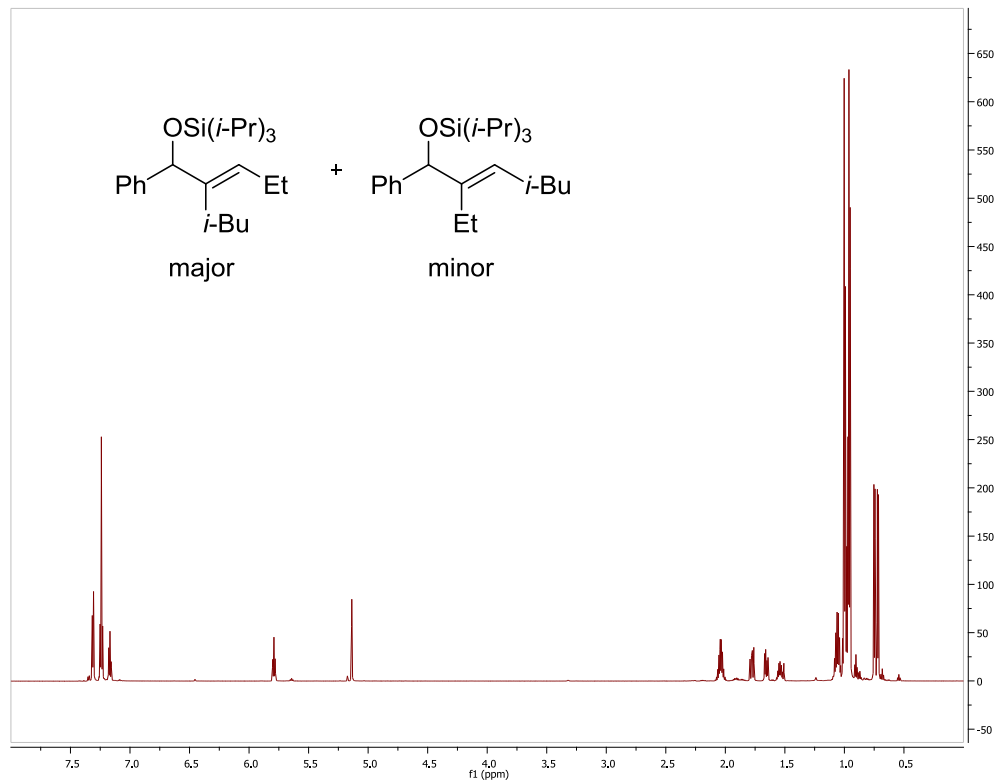


Table 4, Entry 6

Major regioisomer (E)-((4-isobutyldodec-3-en-5-yl)oxy)triisopropylsilane

Minor regioisomer (E)-((5-ethyl-2-methyltridec-4-en-6-yl)oxy)triisopropylsilane

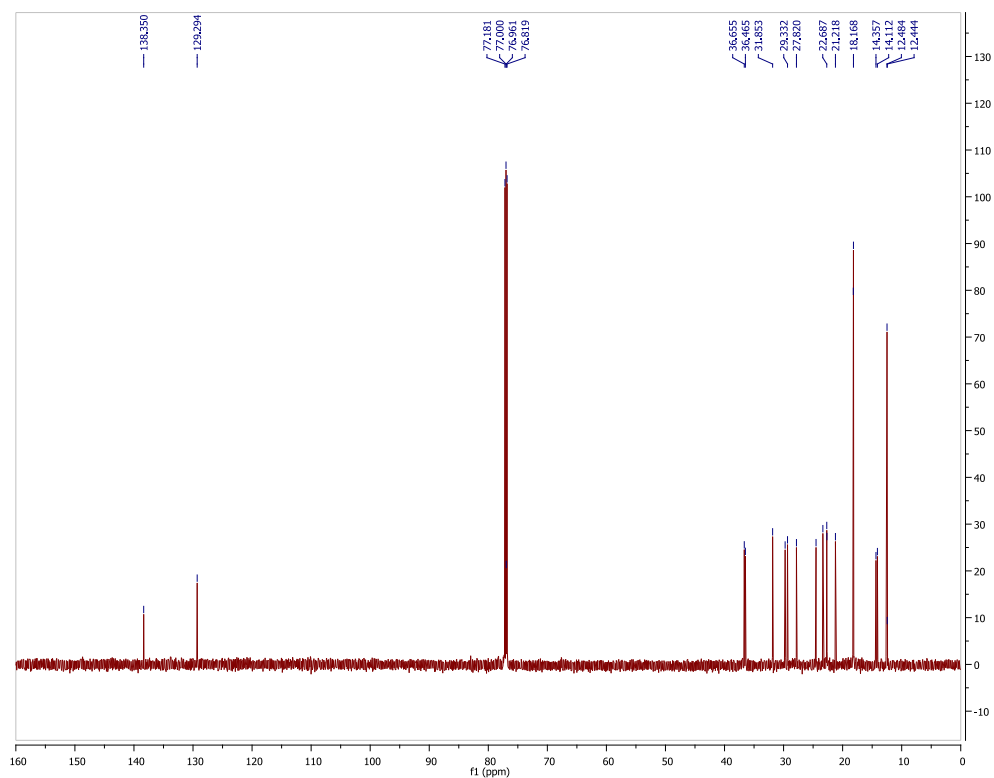
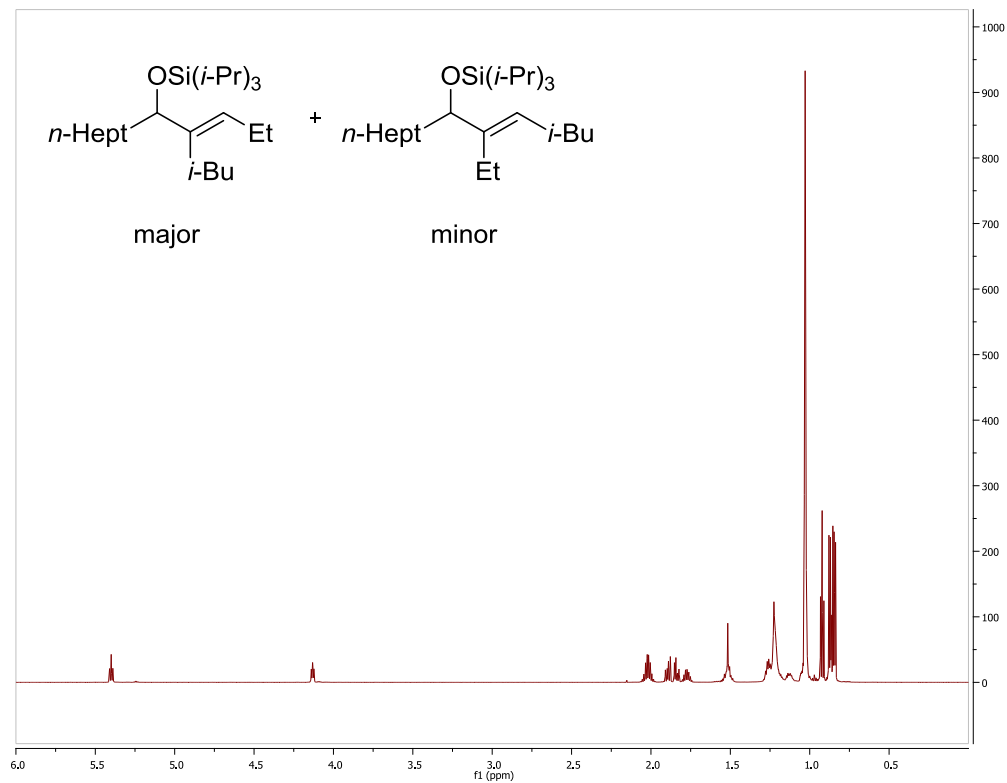


Table 4, Entry 7

Major regioisomer (E)-1-phenyl-2-propylpent-2-en-1-ol

Minor regioisomer (E)-2-ethyl-1-phenylhex-2-en-1-ol

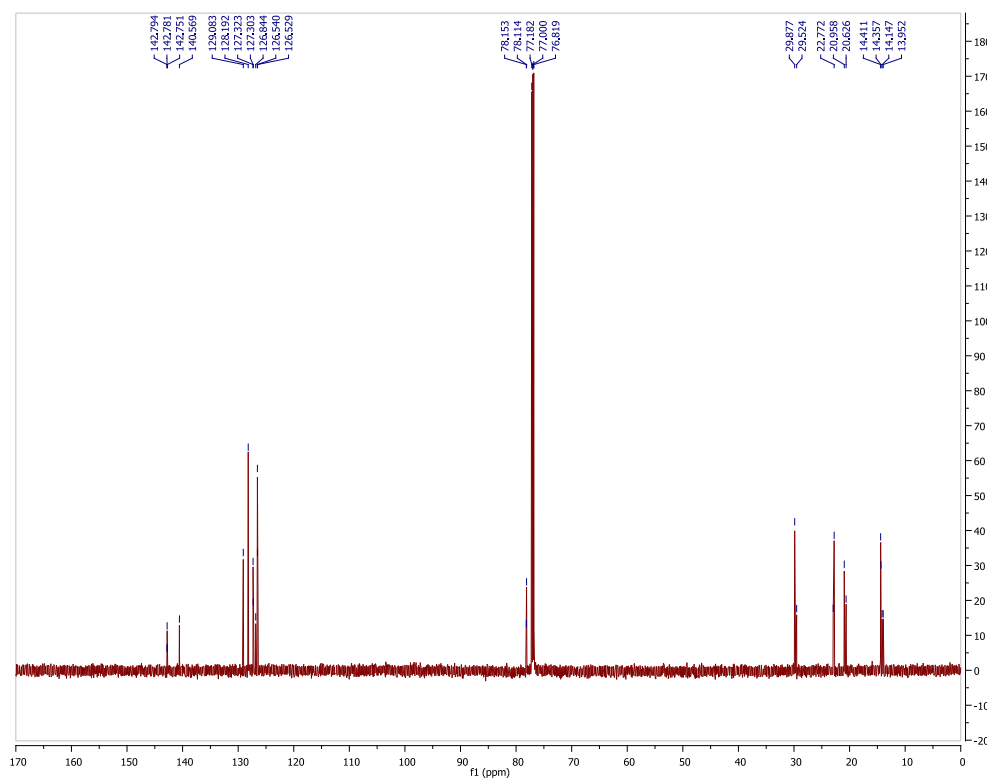
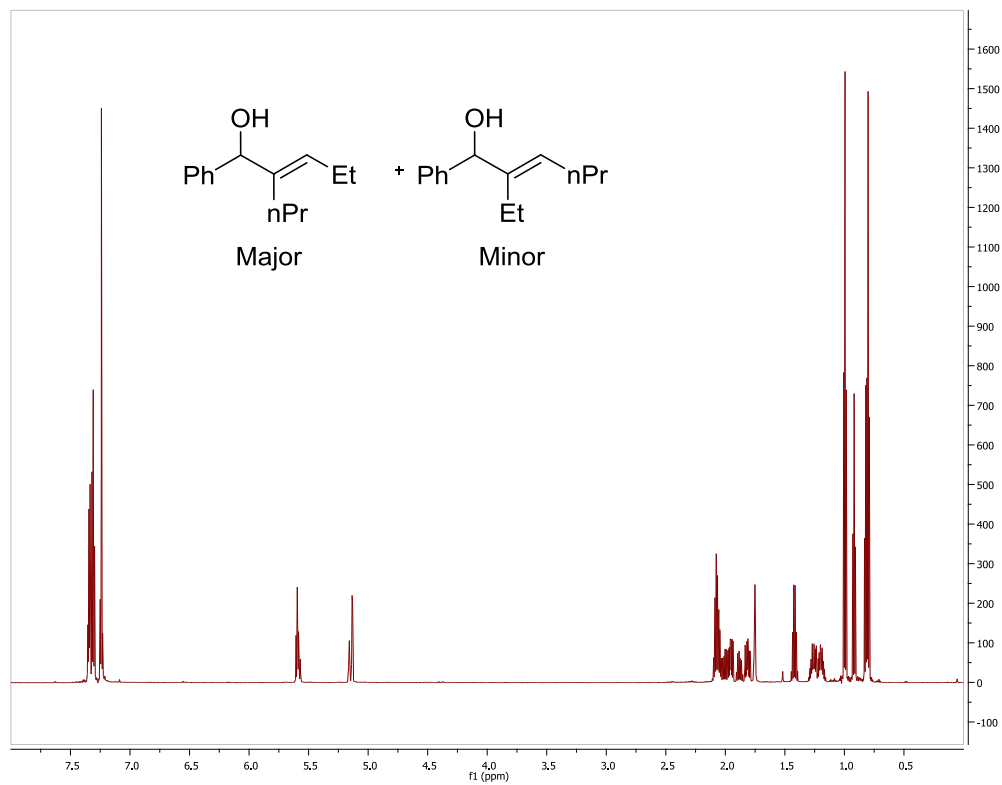


Table 4, Entry 8

Major regioisomer (E)-((2-ethylidene-1-(furan-2-yl)pentyl)oxy)triisopropylsilane

Minor regioisomer (E)-((1-(furan-2-yl)-2-methylhex-2-en-1-yl)oxy)triisopropylsilane

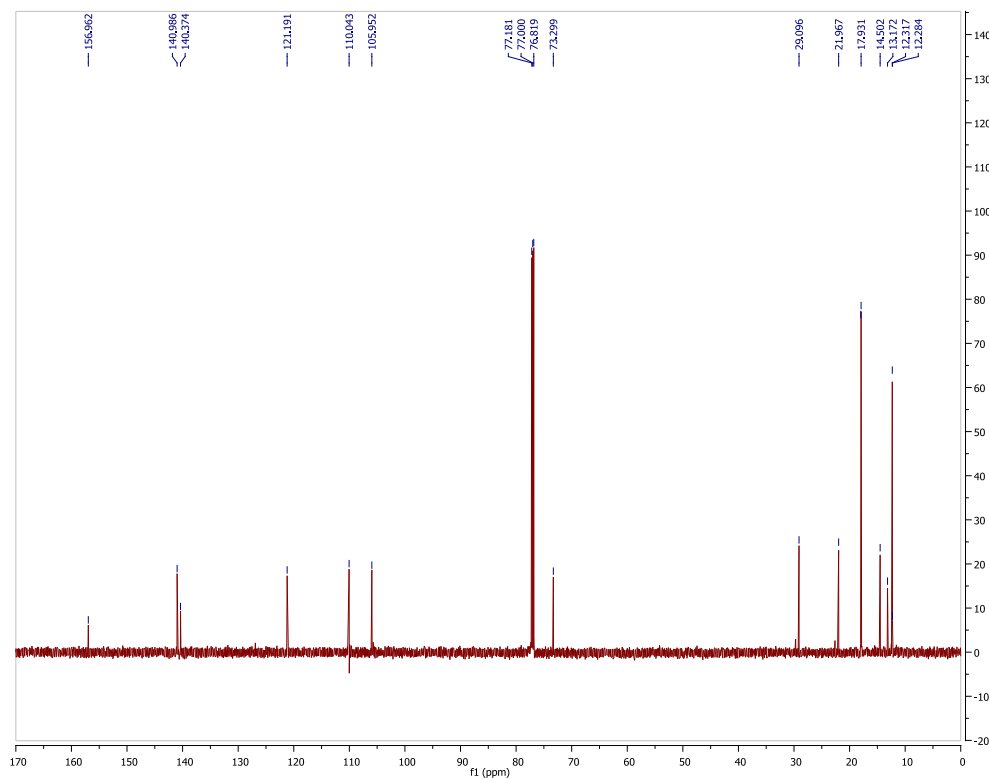
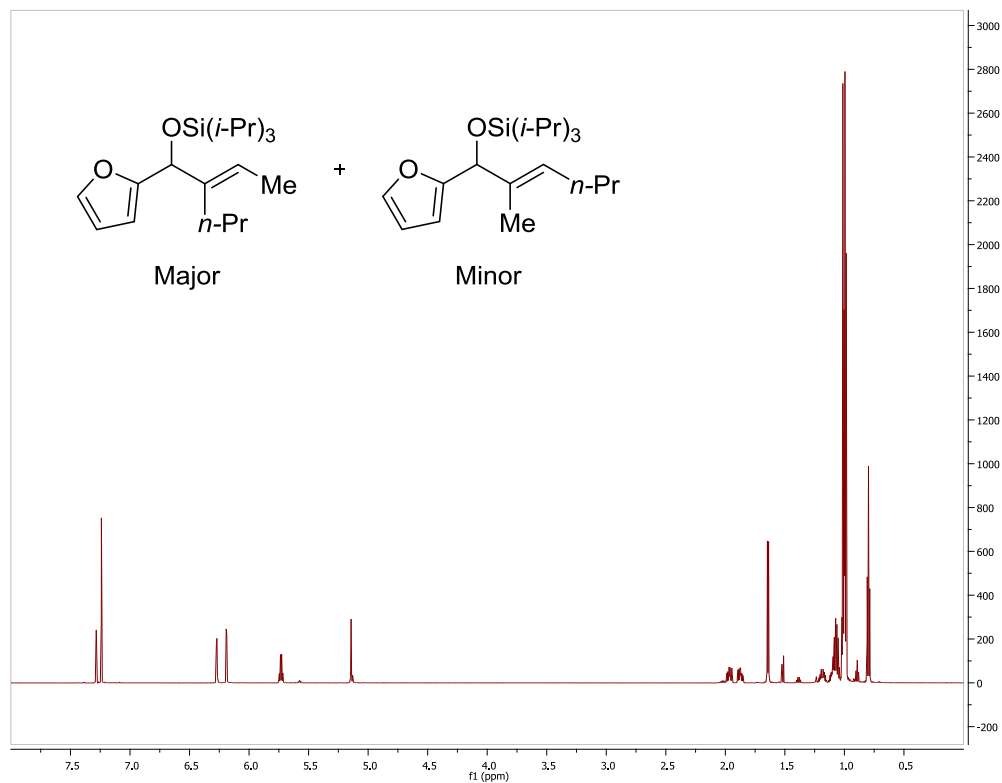


Table 4, Entry 10 (E)-((1-cyclohexyl-2-isopropylbut-2-en-1-yl)oxy)triisopropylsilane

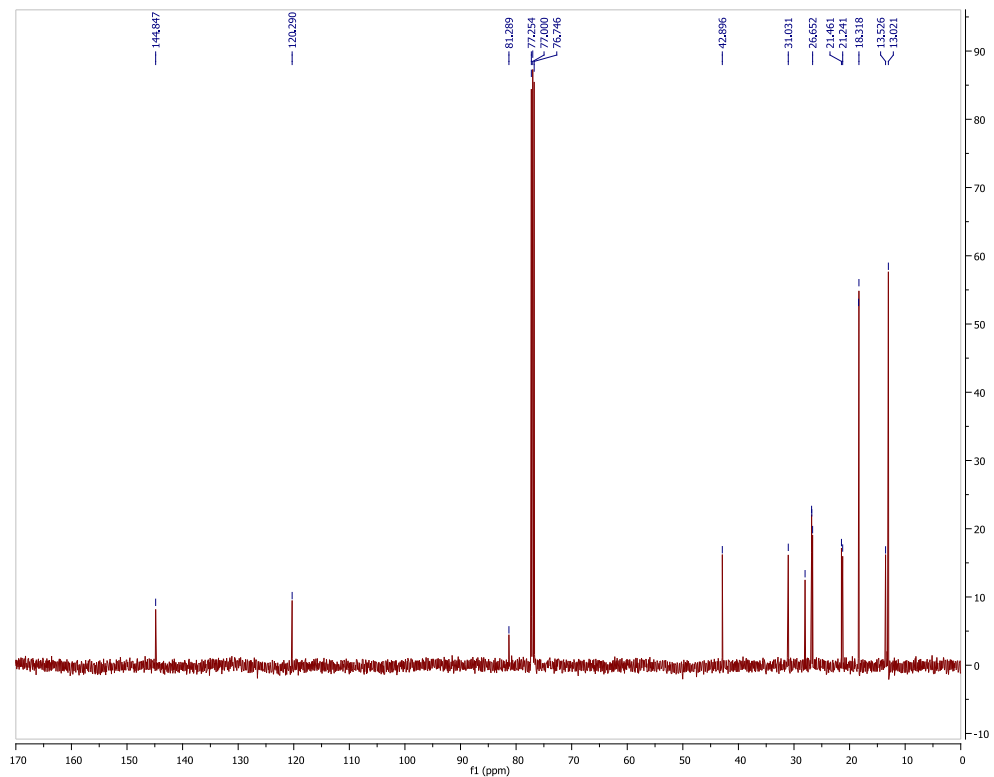
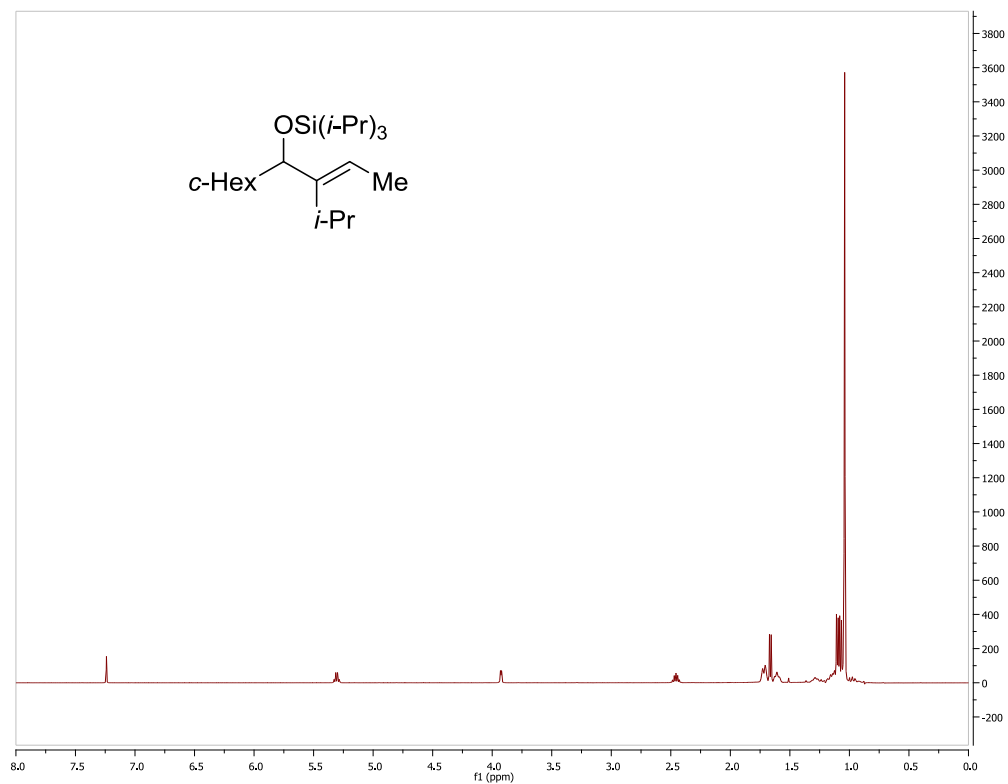


Table 4, Entry 11 Di-tert-butyl(methyl)(3-methyl-2-methylene-1-phenylbutoxy)silane

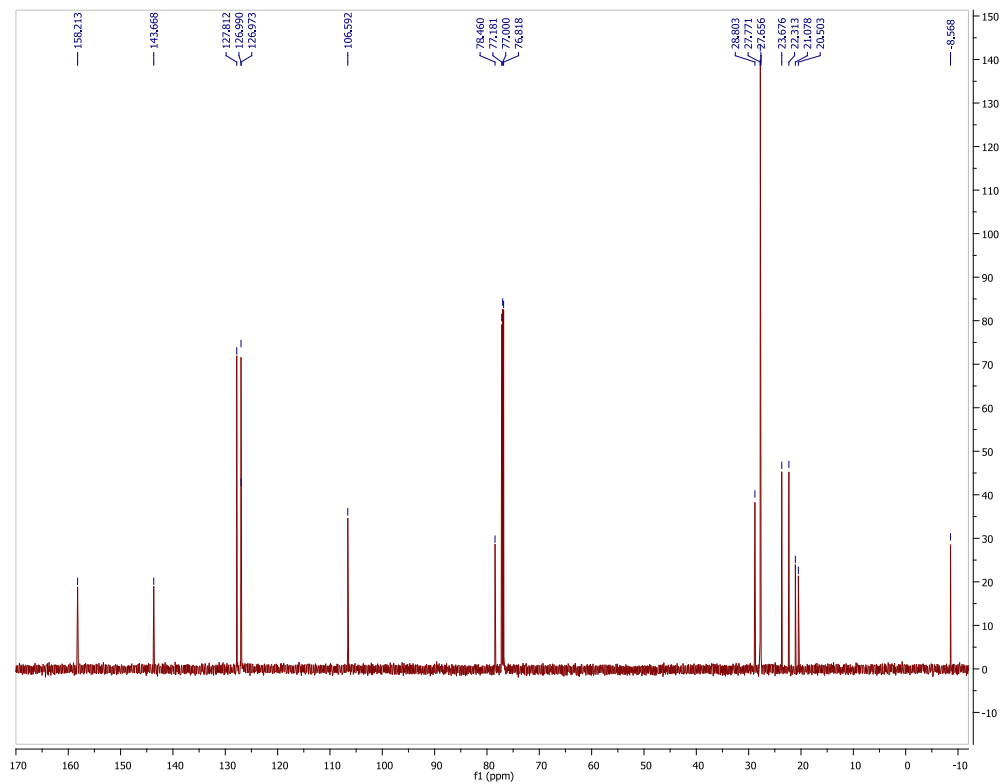
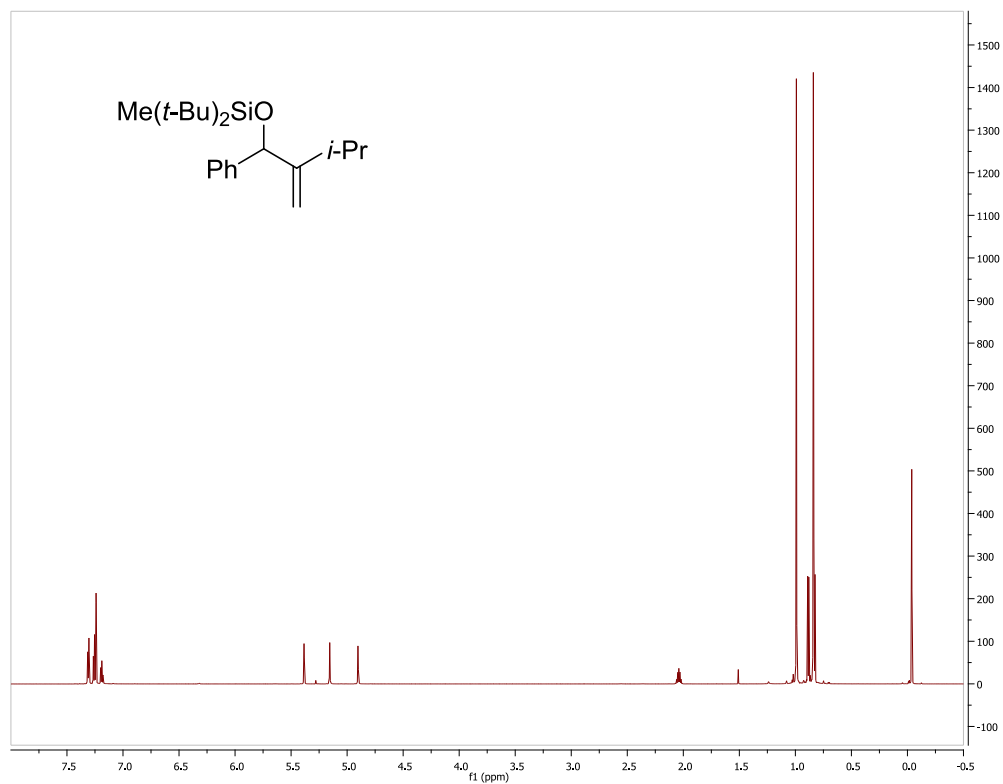


Table 4, Entry 12 Di-tert-butyl(methyl)((2-methylene-1-phenyloctyl)oxy)silane Major regioisomer

