Supplementary Information

Inverse regioselectivity in the silylstannylation of alkynes and allenes: Copper-catalyzed three-component coupling with a silylborane and a tin alkoxide

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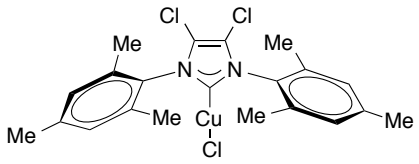
General remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{119}Sn, 186 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard, and tetramethyltin (^{119}Sn, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merk Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. MeCN was distilled from P_2O_5. Toluene and THF were distilled from sodium/benzophenone ketyl. DMF was distilled from CaH_2.

Materials.

IMesCuCl[1] and allenes (**3**)[2] were prepared according to literature procedures. ^{Cl}IMesCuCl was synthesized according to a method for preparing ^{Cl}IPrCuCl.[3]

^{Cl}IMesCuCl



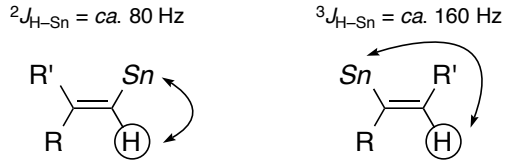
^{1}H NMR ($CDCl_3$) δ 7.03 (s, 4H), 2,36 (s, 6H), 2.10 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 178.68, 140.65, 135.08, 132.09, 129.71, 118.00, 21.14, 17.74

HRMS Calcd for $C_{21}H_{22}N_2Cl_3CuNa$: $[M+Na]^+$, 493.00368. Found: m/z 493.00363

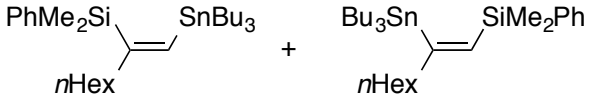
Cu-catalyzed silylstannylation of alkynes: a general procedure.

To an MeCN solution (1 mL) of CuCl (6.0 μmol) and P(*t*Bu)$_3$ (6.0 μmol) were added a

silylborane (0.36 mmol), an alkyne (0.30 mmol) and tributyltin *tert*-butoxide (0.36 mmol), and the resulting mixture was stirred at room temperature for the period as described in Table 2. The mixture was diluted with ethyl acetate and filtered through a Celite plug. Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. Stereochemistry of the product was determined by H–Sn coupling constants.[4]



A mixture of (*Z*)-dimethyl(phenyl)(1-(tributylstannyl)non-1-en-2-yl)silane (2a) and (*Z*)-dimethyl(phenyl)(2-(tributylstannyl)non-1-en-1-yl)silane (2'a)



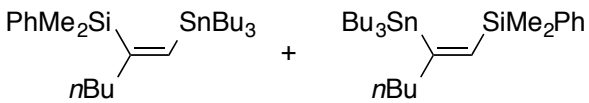
2a **2'a**

Isolated in 86% (**2a**:**2'a** = 93:7) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.56 (m), 7.32-7.37 (m), 6.78 (s, $J_{^{119}Sn-H}$ = 66.5 Hz, $J_{^{117}Sn-H}$ = 64.0 Hz, 1H, major), 6.53 (s, 1H, minor), 2.36 (t, *J* = 7.0 Hz, 2H, minor), 2.26 (t, *J*= 7.5 Hz, 2H, major), 1.21-1.68 (m), 0.89 (t, *J*= 7.5 Hz, 9H, major), 0.70-0.84 (m), 0.39 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 168.83, 161.11 (J_{Sn-C} = 22.4 Hz), 144.31 ($J_{^{119}Sn-C}$ = 409.8 Hz, $J_{^{117}Sn-C}$ = 391.7 Hz), 140.69, 139.43, 134.20, 133.99, 128.78, 128.72, 127.64, 47.78, 43.54 (J_{Sn-C} = 75.4 Hz), 31.81, 31.74, 30.13, 29.95, 29.22, 29.13, 29.06, 28.92, 27.86, 27.47, 27.33 (J_{Sn-C} = 57.7 Hz), 26.87, 22.66, 17.50, 14.10, 13.70, 13.65, 13.62, 11.19 ($J_{^{119}Sn-C}$ = 335.8 Hz, $J_{^{117}Sn-C}$ = 321.0 Hz), 11.08, -0.67, -0.86; ^{119}Sn NMR ($CDCl_3$) δ -57.16, -69.48

HRMS Calcd for $C_{24}H_{43}SiSn$: $[M-Bu]^+$, 479.21505. Found: m/z 479.21524

A mixture of (*Z*)-dimethyl(phenyl)(1-(tributylstannyl)hex-1-en-2-yl)silane (2b) and (*Z*)-dimethyl(phenyl)(2-(tributylstannyl)hex-1-en-1-yl)silane (2'b)



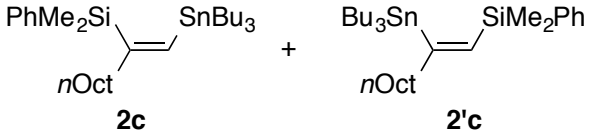
2b **2'b**

Isolated in 76% (**2b**:**2'b** = 95:5) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.53-7.56 (m), 7.32-7.35 (m), 6.79 (s, J_{Sn-H} = 65.0 Hz, 1H, major), 6.54 (s, 1H, minor), 2.27 (t, *J* = 7.5 Hz, 2H, major), 1.24-1.46 (m), 0.89 (t, *J* = 7.5 Hz, 9H, major), 0.87 (t, *J* = 7.0 Hz, 3H, major), 0.70-0.80 (m), 0.39 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 168.82, 161.06 (J_{Sn-C}= 22.0 Hz), 144.32 ($J_{^{119}Sn-C}$= 409.8 Hz, $J_{^{117}Sn-C}$= 391.7 Hz), 139.42, 134.19, 133.99, 128.78, 128.71, 127.63, 47.46, 43.24 (J_{Sn-C}= 77.3 Hz), 32.43, 32.17, 29.13 (J_{Sn-C}= 20.0 Hz), 27.47, 27.33 (J_{Sn-C}= 58.6 Hz), 24.57, 22.46, 22.35, 14.04, 13.98, 13.70, 11.19 ($J_{^{119}Sn-C}$= 336.3 Hz, $J_{^{117}Sn-C}$= 321.5 Hz), 11.07, -0.66, -0.85; ^{119}Sn NMR ($CDCl_3$) δ -60.27, -69.49

HRMS Calcd for $C_{22}H_{39}SiSn$: $[M-Bu]^+$, 451.18375. Found: m/z 451.18356

A mixture of (*Z*)-dimethyl(phenyl)(1-(tributylstannyl)dec-1-en-2-yl)silane (2c) and (*Z*)-dimethyl(phenyl)(2-(tributylstannyl)dec-1-en-1-yl)silane (2'c)



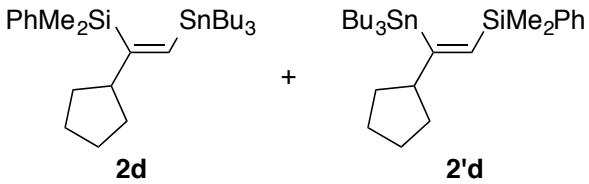
2c **2'c**

Isolated in 68% (**2c**:**2'c** = 94:6) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.57 (m), 7.32-7.37 (m), 6.78 (s, J_{Sn-H} = 66.0, 1H, major), 6.53 (s, 1H, minor), 2.26 (t, *J* = 8.0 Hz, 2H, major), 1.22-1.61 (m), 0.91 (t, *J* = 7.0 Hz, 3H, major), 0.89 (t, *J* = 7.5 Hz, 9H, major), 0.70-0.84 (m), 0.39 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 168.84 (minor), 161.10 (J_{Sn-C} = 22.4 Hz), 144.30 ($J_{^{119}Sn-C}$ = 409.8 Hz, $J_{^{117}Sn-C}$ = 392.2 Hz), 140.68, 139.43, 134.19, 134.00, 128.78, 128.71, 127.63, 47.79, 43.55 (J_{Sn-C} = 76.7 Hz), 31.91, 30.17, 29.99, 29.55, 29.48, 29.38, 29.33, 29.22, 29.14, 29.06, 27.47, 27.33 ($J_{^{119}Sn-C}$ = 57.3 Hz, $J_{^{117}Sn-C}$ = 57.2 Hz), 22.69, 14.13, 13.71, 13.64, 11.20 ($J_{^{119}Sn-C}$ = 336.3 Hz, $J_{^{117}Sn-C}$ = 321.5 Hz), 11.09, -0.67, -0.86; ^{119}Sn NMR ($CDCl_3$) δ -57.16, -69.48

HRMS Calcd for $C_{26}H_{47}SiSn$: $[M-Bu]^+$, 507.24635. Found: m/z 507.24670

A mixture of (*Z*)-(1-cyclopentyl-2-(tributylstannyl)vinyl)dimethyl(phenyl)silane (2d) and (*Z*)-(2-cyclopentyl-2-(tributylstannyl)vinyl)dimethyl(phenyl)silane (2'd)



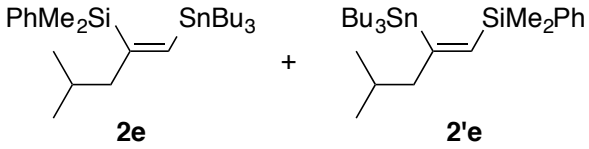
2d **2'd**

Isolated in 65% (**2d**:**2'd** = 93:7) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.53-7.54 (m), 7.32-7.35 (m), 6.93 (t, J_{Sn-H} = 60.5 Hz, 1H, major), 6.61 (s, J_{Sn-H} = 183.0 Hz, 1H, minor), 2.69 (quint, J = 8.0 Hz, 1H, major), 1.65-1.72 (m), 1.39-1.54 (m), 1.28 (sext, J = 7.5 Hz, 6H, major), 0.71-0.95 (m), 0.40 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 172.32, 164.55 (J_{Sn-C} = 22.9 Hz), 140.28, 140.07 ($J_{^{119}Sn-C}$ = 417.8 Hz, $J_{^{117}Sn-C}$ = 399.2 Hz), 139.66, 135.88, 134.22, 133.97, 128.71, 128.66, 127.64, 127.60, 54.55, 49.23 (J_{Sn-C} = 73.9 Hz), 33.60, 32.50 (J_{Sn-C} = 14.5 Hz), 29.21, 29.13 (J_{Sn-C} = 21.0 Hz), 27.48, 27.29 (J_{Sn-C} = 57.3 Hz), 25.23, 24.86, 13.71, 13.65, 11.42 ($J_{^{119}Sn-C}$ = 335.8 Hz, $J_{^{117}Sn-C}$ = 321.0 Hz), -0.42, -0.72; ^{119}Sn NMR ($CDCl_3$) δ -57.93, -65.71

HRMS Calcd for $C_{23}H_{39}SiSn$: $[M-Bu]^+$, 463.18375. Found: m/z 463.18362

A mixture of (*Z*)-dimethyl(4-methyl-1-(tributylstannyl)pent-1-en-2-yl)(phenyl)silane (2e) and (*Z*)-dimethyl(4-methyl-2-(tributylstannyl)pent-1-en-1-yl)(phenyl)silane (2'e)



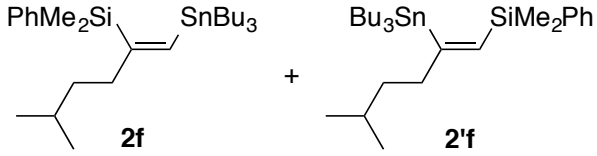
2e **2'e**

Isolated in 64% (**2e**:**2'e** = 97:3) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.51-7.57 (m), 7.32-7.37 (m), 6.72 (s, $J_{^{119}Sn-H}$ = 67.0 Hz, $J_{^{117}Sn-H}$ = 64.0 Hz, 1H, major), 6.48 (s, J_{Sn-H} = 175.3 Hz, 1H, minor), 2.25 (d, J= 7.0 Hz, 2H, minor), 2.17 (dd, J = 7.0, 0.5 Hz, 2H, major), 1.67 (sept, J = 7.0 Hz, 1H, major), 1.34-1.50 (m), 1.27 (sext, J = 7.0 Hz, 6H, major), 0.88 (t, J = 7.0 Hz, 9H, major), 0.85 (d, J = 6.5 Hz, 6H, major), 0.68-0.82 (m), 0.38 (s, 6H, major); ^{13}C NMR ($CDCl_3$) δ 159.80 (J_{Sn-C} = 21.4 Hz), 146.11 ($J_{^{119}Sn-C}$ = 396.4 Hz, $J_{^{117}Sn-C}$ = 387.1 Hz), 142.36, 139.43, 134.22, 133.99, 128.79, 127.64, 57.87, 53.96 (J_{Sn-C} = 77.2 Hz), 29.20, 29.14 (J_{Sn-C} = 20.0 Hz), 27.38, 27.33 (J_{Sn-C} = 58.2 Hz), 22.25, 13.70, 11.15 ($J_{^{119}Sn-C}$ = 335.9 Hz, $J_{^{117}Sn-C}$ = 321.0 Hz), -0.70; ^{119}Sn NMR ($CDCl_3$) δ -56.88, -70.05

HRMS Calcd for $C_{22}H_{39}SiSn$: $[M-Bu]^+$, 451.18375. Found: m/z 451.18365

A mixture of (*Z*)-dimethyl(5-methyl-1-(tributylstannyl)hex-1-en-2-yl)(phenyl)silane (2f) and (*Z*)-dimethyl(5-methyl-2-(tributylstannyl)hex-1-en-1-yl)(phenyl)silane (2'f)

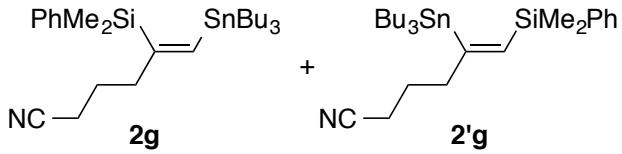


Isolated in 61% (**2f**:**2'f** = 90:10) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.53-7.56 (m), 7.32-7.36 (m), 6.79 (s, $J_{^{119}Sn\text{-}H}$ = 66.0 Hz, $J_{^{117}Sn\text{-}H}$ = 64.0 Hz, 1H, major), 6.55 (s, $J_{Sn\text{-}H}$ = 176.6 Hz, 1H, minor), 2.34-2.38 (m, 2H, minor), 2.24-2.27 (m, 2H, major), 1.34-1.62 (m), 1.21-1.32 (m), 0.93 (d, *J* = 7.0 Hz, 6H, minor), 0.89 (t, *J* = 7.5 Hz, 9H, major), 0.85 (d, *J* = 6.5 Hz, 6H, major), 0.70-0.83 (m), 0.40 (s, 6H, major), 0.37 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 169.04, 161.38 ($J_{Sn\text{-}C}$ = 24.3 Hz), 144.32 ($J_{^{119}Sn\text{-}C}$ = 409.8 Hz, $J_{^{117}Sn\text{-}C}$ = 391.7 Hz), 140.52, 140.05, 139.41, 134.22, 134.00, 128.79, 128.72, 127.64, 45.66, 41.48 ($J_{Sn\text{-}C}$ = 77.6 Hz), 39.75, 39.41, 29.22, 29.13 ($J_{Sn\text{-}C}$ = 19.5 Hz), 27.91, 27.47, 27.33 ($J_{Sn\text{-}C}$ = 58.2 Hz), 22.66, 22.55, 13.70, 13.65, 11.19 ($J_{^{119}Sn\text{-}C}$ = 336.3 Hz, $J_{^{117}Sn\text{-}C}$ = 321.0 Hz), 11.10, -0.66, -0.81; ^{119}Sn NMR ($CDCl_3$) δ -56.76, -69.58

HRMS Calcd for $C_{23}H_{41}SiSn$: $[M\text{-}Bu]^+$, 465.19940. Found: m/z 465.19955

A mixture of (*Z*)-5-(dimethyl(phenyl)silyl)-6-(tributylstannyl)hex-5-enenitrile (2g) and (*Z*)-6-(dimethyl(phenyl)silyl)-5-(tributylstannyl)hex-5-enenitrile (2'g)



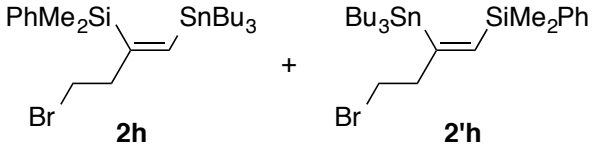
Isolated in 56% (**2g**:**2'g** = 94:6) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.48-7.53 (m), 7.32-7.38 (m), 6.82 (s, $J_{^{119}Sn\text{-}H}$ = 61.0 Hz, $J_{^{117}Sn\text{-}H}$ = 58.0 Hz, 1H, major), 6.59 (s, $J_{Sn\text{-}H}$ = 166.5 Hz, 1H, minor), 2.48 (td, *J* = 7.0, 0.5 Hz, 2H, minor), 2.36 (td, *J* = 7.5, 1.5 Hz, 2H, major), 2.32 (t, *J* = 7.0 Hz, 2H, minor), 2.22 (t, *J* = 7.0 Hz, 2H, major), 1.74 (quint, *J* = 7.5 Hz, 2H, minor), 1.66 (quint, *J* = 7.5 Hz, 2H, major), 1.35-1.51 (m), 1.27 (sext, *J* =7.5 Hz, 6H, major), 0.88 (t, *J* = 7.5 Hz, 9H, major), 0.73-0.86 (m), 0.40 (s, 6H, major), 0.37 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 165.38, 158.40 ($J_{Sn\text{-}C}$ = 23.8 Hz), 147.09 ($J_{^{119}Sn\text{-}C}$ = 389.9 Hz, $J_{^{117}Sn\text{-}C}$ = 373.0 Hz), 143.74, 138.50, 133.99, 133.85, 129.08, 128.91, 127.82, 127.74, 119.64, 119.56, 45.79, 41.78 ($J_{Sn\text{-}C}$ = 77.7 Hz), 29.12, 29.07 ($J_{Sn\text{-}C}$ = 20.0 Hz), 27.36, 27.26 ($J_{Sn\text{-}C}$ = 59.1 Hz), 25.42

(J_{Sn-C} = 7.9 Hz), 25.11, 16.43, 16.28, 13.65, 13.59, 11.28 ($J_{^{119}Sn-C}$ = 339.1 Hz, $J_{^{117}Sn-C}$ = 324.3 Hz), 11.02, -0.86, -1.12; ^{119}Sn NMR ($CDCl_3$) δ -54.98, -69.03

HRMS Calcd for $C_{26}H_{45}NNaSiSn$: $[M+Na]^+$, 542.22355. Found: m/z 542.22369

A mixture of (*Z*)-(4-bromo-1-(tributylstannyl)but-1-en-2-yl)dimethyl(phenyl)silane (2h) and (*Z*)-(4-bromo-2-(tributylstannyl)but-1-en-1-yl)dimethyl(phenyl)silane (2'h)

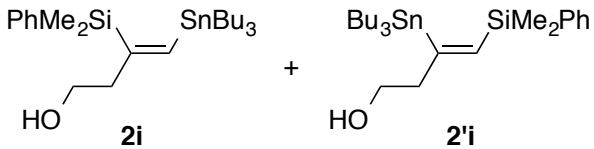


Isolated in 47% (**2h**:**2'h** = 91:9) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.54 (m, 2H), 7.33-7.35 (m, 3H), 6.91 (s, $J_{^{119}Sn-H}$ = 59.0 Hz, $J_{^{117}Sn-H}$ = 57.0 Hz, 1H, major), 6.45 (s, J_{Sn-H} = 164.9 Hz, 1H, minor), 3.36 (t, *J* =8.0 Hz, 2H, minor), 3.29 (t, *J* = 8.0 Hz, 2H, major), 2.86 (t, *J* = 8.0 Hz, 2H, minor), 2.76 (t, *J* = 7.7 Hz, 2H, major), 1.47-1.37 (m), 1.27 (sext, *J* = 7.5 Hz, 6H, major), 0.88 (t, *J* = 7.5 Hz, 9H, major), 0.84-0.74 (m), 0.41 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 163.89, 157.19 (J_{Sn-C} = 24.8 Hz), 149.62 ($J_{^{119}Sn-C}$ = 384.3 Hz, $J_{^{117}Sn-C}$ = 379.0 Hz), 145.57, 139.20, 138.36, 134.05, 133.97, 129.16, 128.94, 127.86, 127.75, 49.65, 45.94 (J_{Sn-C} = 75.4 Hz), 32.63 (J_{Sn-C} = 11.2 Hz), 31.92, 29.11, 29.07 (J_{Sn-C} = 20.0 Hz), 27.39, 27.29 ($J_{^{119}Sn-C}$ = 58.7 Hz, $J_{^{117}Sn-C}$ = 56.7 Hz), 24.58, 13.68, 13.61, 11.32 ($J_{^{119}Sn-C}$ = 340.1 Hz, $J_{^{117}Sn-C}$ = 324.8 Hz), 11.07 ($J_{^{119}Sn-C}$ = 327.1 Hz, $J_{^{117}Sn-C}$ = 312.6 Hz), -0.86, -1.17; ^{119}Sn NMR ($CDCl_3$) δ -53.74, -67.17

HRMS Calcd for $C_{20}H_{34}BrSiSn$: $[M-Bu]^+$, 501.06296. Found: m/z 501.06216

A mixture of (*Z*)-3-(dimethyl(phenyl)silyl)-4-(tributylstannyl)but-3-en-1-ol (2i) and (*Z*)-4-(dimethyl(phenyl)silyl)-3-(tributylstannyl)but-3-en-1-ol (2'i)



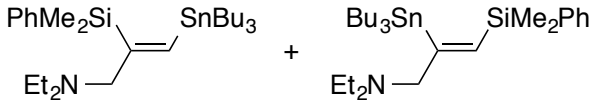
Isolated in 43% (**2i**:**2'i** = 97:3) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.50 (m, 2H), 7.36-7.32 (m, 3H), 6.86 (s, $J_{^{119}Sn-H}$ = 62 Hz, $J_{^{117}Sn-H}$ = 61 Hz, 1H, major), 6.65 (s, J_{Sn-H} = 166.6 Hz, 1H, minor), 3.62 (q, *J* = 6.0 Hz, 2H,

minor), 3.54 (q, J = 6.5 Hz 2H, major), 2.63 (t, J = 6.0 Hz, 2H, minor), 2.55 (t, J = 6.5 Hz, 2H, major), 1.47-1.36 (m), 1.26 (sext, J = 7.0 Hz, 6H, major), 0.87 (t, J = 7.0 Hz, 9H, major), 0.84-0.73 (m), 0.40 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 157.07 ($J_{Sn\text{-}C}$ = 23.3 Hz), 149.07 ($J_{^{119}Sn\text{-}C}$ = 385.6 Hz, $J_{^{117}Sn\text{-}C}$ = 368.0 Hz), 145.78, 138.59, 134.04, 133.88, 129.07, 128.93, 127.83, 61.63 ($J_{Sn\text{-}C}$ = 9.7 Hz), 61.04, 50.17, 46.40 ($J_{Sn\text{-}C}$ = 74.5 Hz), 29.08 ($J_{Sn\text{-}C}$ = 20.0 Hz), 27.39, 27.29 ($J_{Sn\text{-}C}$ = 59.6 Hz), 13.65, 13.60, 11.28 ($J_{^{119}Sn\text{-}C}$ = 339.6 Hz, $J_{^{117}Sn\text{-}C}$ = 323.8 Hz), 11.10, -0.81, -1.02; ^{119}Sn NMR ($CDCl_3$) δ -55.20, -69.08

HRMS Calcd for $C_{24}H_{44}ONaSiSn$: $[M+Na]^+$, 519.20756. Found: m/z 519.20764

A mixture of (*Z*)-2-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-3-(tributylstannyl)prop-2-en-1-amine (2j) and (*Z*)-3-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-2-(tributylstannyl)prop-2-en-1-amine (2'j)



2j **2'j**

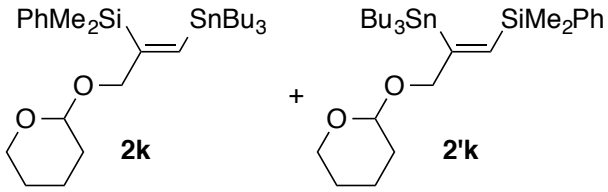
Isolated in 39% (**2j**:**2'j** = 90:10) as a yellow oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.57 (m), 7.30-7.35 (m), 6.86 (s, $J_{^{119}Sn\text{-}H}$ = 67.0 Hz, $J_{^{117}Sn\text{-}H}$ = 64.0 Hz, 1H, major), 6.69 (s, $J_{Sn\text{-}H}$ = 170.5 Hz, 1H, minor), 3.24 (d, J = 1.5 Hz, $J_{Sn\text{-}H}$ = 42.0 Hz, 2H, minor), 3.13 (d, J = 1.5 Hz, 2H, major), 2.52 (q, J = 7.5 Hz, 4H, minor), 2.40 (q, J = 7.0 Hz, 4H, major), 1.36-1.45 (m, 8H, major), 1.27 (sext, J = 7.5 Hz, 6H, major), 0.97 (t, J = 7.0 Hz, 6H, minor), 0.69-0.92 (m), 0.40 (s, 6H, major), 0.37 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 168.96, 159.31 ($J_{Sn\text{-}C}$ = 24.6 Hz), 146.19 ($J_{^{119}Sn\text{-}C}$ = 402.4 Hz, $J_{^{117}Sn\text{-}C}$ = 384.7 Hz), 141.15, 139.98, 139.80, 134.35, 133.96, 128.71, 128.54, 127.65, 127.45, 70.87, 68.13 ($J_{Sn\text{-}C}$ = 82.8 Hz), 45.17, 44.97, 29.23, 29.14 ($J_{Sn\text{-}C}$ = 21.0 Hz), 27.55, 27.32 ($J_{Sn\text{-}C}$ = 56.3 Hz), 24.72, 16.11, 13.72, 13.68, 11.12 ($J_{^{119}Sn\text{-}C}$ = 337.2 Hz, $J_{^{117}Sn\text{-}C}$ = 322.4 Hz), 11.08, 10.74, 10.26, -0.62, -0.89; ^{119}Sn NMR ($CDCl_3$) δ -61.94, -68.81

HRMS Calcd for $C_{27}H_{52}NSiSn$: $[M+H]^+$, 538.28855. Found: m/z 538.28864

A mixture of (*Z*)-dimethyl(phenyl)(3-((tetrahydro-2*H*-pyran-2-yl)oxy)-1-(tributylstannyl)prop-1-

en-2-yl)silane (2k) and (*Z*)-dimethyl(phenyl)(3-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(tributylstannyl)prop-1-en-1-yl)silane (2'k)

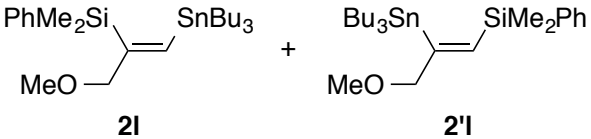


Isolated in 75% (**2k**:**2'k** = 10:90) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.53-7.57 (m), 7.31-7.37 (m), 7.10 (t, J = 1.0 Hz, $J_{^{119}Sn-H}$ = 63.5 Hz, $J_{^{117}Sn-H}$ = 61.0 Hz, 1H, minor), 6.84 (t, J = 1.5 Hz, $J_{^{119}Sn-H}$ = 170.4 Hz, $J_{^{117}Sn-H}$ = 156.4 Hz, 1H, major), 4.65 (t, J = 3.5 Hz, 1H, major), 4.51 (t, J = 3.5 Hz, 1H, minor), 4.40 (dd, J = 13.1, 1.6 Hz, 1H, major), 4.16 (dd, J = 13.1, 1.6 Hz, 1H, major), 3.86-3.95 (m, 1H, major), 3.49-3.56 (m, 1H, major), 1.50-1.94 (m) 1.36-1.45 (m), 1.27 (sext, J = 7.5 Hz, 6H, major), 0.75-0.92 (m), 0.42 (s, 3H, minor), 0.41 (s, 3H, minor), 0.39 (s, 6H, major); ^{13}C NMR ($CDCl_3$) δ 164.20 ($J_{^{119}Sn-C}$ = 377.3 Hz, $J_{^{117}Sn-C}$ = 360.6 Hz), 156.37, 146.07, 140.25 (J_{Sn-C} = 49.4 Hz), 139.52, 138.85, 134.15, 133.99, 128.79, 127.65, 97.87, 97.68, 78.46 (J_{Sn-C} = 55.3 Hz), 76.23, 62
.08, 61.99, 30.59, 30.51, 29.11 (J_{Sn-C} = 19.1 Hz), 27.39 ($J_{^{119}Sn-C}$ = 63.2 Hz, $J_{^{117}Sn-C}$ = 61.0 Hz), 27.30, 25.49, 19.47, 19.41, 13.63, 11.14 ($J_{^{119}Sn-C}$ = 339.6 Hz, $J_{^{117}Sn-C}$ = 324.3 Hz), 10.91 ($J_{^{119}Sn-C}$ = 332.2 Hz, $J_{^{117}Sn-C}$ = 317.2 Hz), -0.70, -1.10, -1.25; ^{119}Sn NMR ($CDCl_3$) δ -57.58, -67.31

HRMS Calcd for $C_{28}H_{50}O_2NaSiSn$: $[M+Na]^+$, 589.24943. Found: m/z 589.25067

A mixture of (*Z*)-(3-methoxy-1-(tributylstannyl)prop-1-en-2-yl)dimethyl(phenyl)silane (2l) and (*Z*)-(3-methoxy-2-(tributylstannyl)prop-1-en-1-yl)dimethyl(phenyl)silane (2'l)

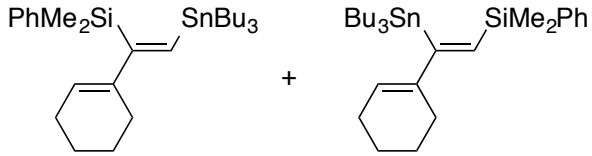


Isolated in 59% (**2l**:**2'l** = 1:99) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.57 (m), 7.31-7.39 (m), 7.04 (s, 1H, minor), 6.80 (s, J_{Sn-H} = 163.9 Hz, 1H, major), 4.07 (d, J = 1.5 Hz $J_{^{119}Sn-H}$ = 32 Hz, $J_{^{117}Sn-H}$ = 30 Hz, 2H, major), 3.33 (s, 3H, major), 3.26 (s, 3H, minor), 1.36-1.45 (m, 6H, major), 1.27 (sext, J = 7.5

Hz, 6H, major), 0.87 (t, J = 7.5 Hz, 9H, major), 0.75-0.89 (m), 0.42 (s, 6H, minor), 0.39 (s, 6H, major); ^{13}C NMR ($CDCl_3$) δ 164.62 ($J_{^{119}Sn\text{-}C}$ = 373.5 Hz, $J_{^{117}Sn\text{-}C}$ = 365.1 Hz), 141.01 ($J_{Sn\text{-}C}$ = 50.3 Hz), 139.36, 134.00, 128.85, 127.69, 84.40 ($J_{Sn\text{-}C}$ = 53.5 Hz), 57.68, 29.11 ($J_{Sn\text{-}C}$ = 18.6 Hz), 27.39 ($J_{^{119}Sn\text{-}C}$ = 63.2 Hz, $J_{^{117}Sn\text{-}C}$ = 61.0 Hz), 24.71, 16.08, 13.65, 10.89 ($J_{^{119}Sn\text{-}C}$ = 332.2 Hz, $J_{^{117}Sn\text{-}C}$ = 317.7 Hz), -0.79, -1.28; ^{119}Sn NMR ($CDCl_3$) δ -57.58
HRMS Calcd for $C_{20}H_{35}OSiSn$: $[M\text{-}Bu]^+$, 439.14737. Found: m/z 439.14752

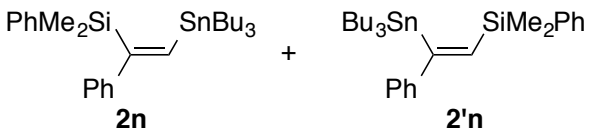
A mixture of (*Z*)-(1-(cyclohex-1-en-1-yl)-2-(tributylstannyl)vinyl)dimethyl(phenyl)silane (2m) and (*Z*)-(2-(cyclohex-1-en-1-yl)-2-(tributylstannyl)vinyl)dimethyl(phenyl)silane (2'm)



2m **2'm**

Isolated in 61% (**2m**:**2'm** = 61:39) as a colorless oil
^{1}H NMR ($CDCl_3$) δ 7.53-7.58 (m), 7.31-7.36 (m), 6.78 (s, $J_{^{119}Sn\text{-}H}$ = 68.0 Hz, $J_{^{117}Sn\text{-}H}$ = 65.0 Hz, 1H, major), 6.57 (s, $J_{^{119}Sn\text{-}H}$ = 175.0 Hz, $J_{^{117}Sn\text{-}H}$ = 155.0 Hz, 1H, minor), 5.33-5.37 (m, 1H, minor), 5.26-5.30 (m, 1H, major), 2.06-2.14 (m), 1.93-2.04 (m), 1.36-1.62 (m), 1.22-1.32 (m), 0.71-0.93 (m), 0.40 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 171.30, 165.29 ($J_{Sn\text{-}C}$ = 23.3 Hz), 147.69, 146.63, 144.83 ($J_{^{119}Sn\text{-}C}$ = 391.2 Hz, $J_{^{117}Sn\text{-}C}$ = 373.5 Hz), 139.95, 139.61, 139.39, 139.15, 134.24, 134.02, 128.72, 128.69, 127.65, 127.51, 120.91 ($J_{Sn\text{-}C}$ = 23.3 Hz), 120.72, 29.85, 29.16, 29.10 ($J_{Sn\text{-}C}$ = 20.0 Hz), 28.70, 27.42 ($J_{Sn\text{-}C}$ = 62.8 Hz), 27.32 ($J_{Sn\text{-}C}$ = 59.1 Hz), 25.42, 25.34, 23.04, 22.36, 22.20, 13.69, 13.65, 11.87 ($J_{^{119}Sn\text{-}C}$ = 324.3 Hz, $J_{^{117}Sn\text{-}C}$ = 309.3 Hz), 11.26 ($J_{^{119}Sn\text{-}C}$ = 336.3 Hz, $J_{^{117}Sn\text{-}C}$ = 321.5 Hz), -0.43, -0.55; ^{119}Sn NMR ($CDCl_3$) δ -57.22, -67.27
HRMS Calcd for $C_{24}H_{39}SiSn$: $[M\text{-}Bu]^+$, 475.18375. Found: m/z 475.18436

A mixture of (*Z*)-dimethyl(phenyl)(1-phenyl-2-(tributylstannyl)vinyl)silane (2n) and (*Z*)-dimethyl(phenyl)(2-phenyl-2-(tributylstannyl)vinyl)silane (2'n)



2n **2'n**

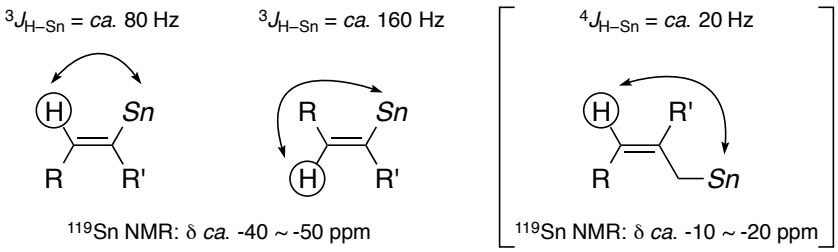
Isolated in 64% (**2n**:**2'n** = 14:86) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.60-7.64 (m), 7.37-7.41 (m), 7.31 (t, *J* = 8.5 Hz, 2H, major), 7.26 (t, *J* = 7.5 Hz, 2H, minor), 7.19 (tt, *J* = 7.5, 1.5 Hz, 1H, major), 7.06-7.10 (m), 6.79 ($J_{^{119}Sn\text{-}H}$ = 162.9 Hz, $J_{^{117}Sn\text{-}H}$ = 155.4 Hz, 1H, major), 1.26-1.51 (m), 1.22 (sext, *J* = 7.5 Hz, 6H, major), 0.91 (t, *J* = 7.0 Hz, 9H, minor), 0.85 (t, *J* = 7.5 Hz, 9H, major), 0.74-0.88 (m), 0.48 (s, 6H, major), 0.38 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 168.87 ($J_{^{119}Sn\text{-}C}$ = 360.1 Hz, $J_{^{117}Sn\text{-}C}$ = 344.2 Hz), 162.56, 151.82 ($J_{Sn\text{-}C}$ = 42.9 Hz), 151.36, 150.17, 145.85 ($J_{^{119}Sn\text{-}C}$ = 70.8 Hz, $J_{^{117}Sn\text{-}C}$ = 54.4 Hz), 139.47, 139.03, 134.34, 134.05, 128.96, 128.91, 127.90, 127.76, 126.76, 125.83 ($J_{Sn\text{-}C}$ = 14.5 Hz), 125.60, 29.10, 28.98 ($J_{Sn\text{-}C}$ = 19.5 Hz), 27.29 ($J_{^{119}Sn\text{-}C}$ = 63.2 Hz, $J_{^{117}Sn\text{-}C}$ = 60.5 Hz), 13.68, 13.59, 11.83 ($J_{^{119}Sn\text{-}C}$ = 321.5 Hz, $J_{^{117}Sn\text{-}C}$ = 314.6 Hz), 11.34 ($J_{^{119}Sn\text{-}C}$ = 339.2 Hz, $J_{^{117}Sn\text{-}C}$ = 323.8 Hz, -0.29, -0.69; ^{119}Sn NMR ($CDCl_3$) δ -54.83, -66.60

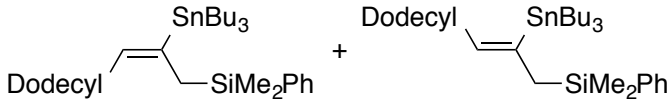
HRMS Calcd for $C_{24}H_{35}SiSn$: $[M\text{-}Bu]^+$, 471.15245. Found: m/z 471.15265

Cu-catalyzed silylstannylation of allenes: a general procedure.

To an MeCN solution (1 mL) of ^{Cl}IMesCuCl (6.0 μmol) were added a silylborane (0.36 mmol), an allene (0.30 mmol) and tributyltin methoxide (0.36 mmol), and the resulting mixture was stirred at room temperature for the period as described in Table 3. The mixture was diluted with ethyl acetate and filtered through a Celite plug. Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. Stereochemistry of the product was determined by H–Sn coupling constants.[4]



A mixture of (*E*)-dimethyl(phenyl)(2-(tributylstannyl)pentadec-2-en-1-yl)silane ((*E*)-4a) and (*Z*)-dimethyl(phenyl)(2-(tributylstannyl)pentadec-2-en-1-yl)silane ((*Z*)-4a)



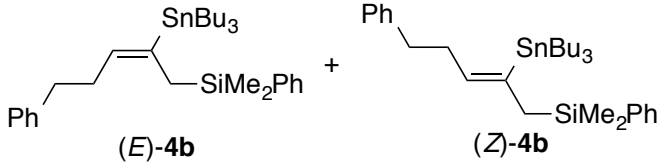
(*E*)-**4a** (*Z*)-**4a**

Isolated in 87% (*E*:*Z* = 78:22) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.47-7.54 (m), 7.31-7.37 (m), 5.81 (t, *J* = 6.7 Hz, 1H, minor), 5.34 (t, *J* = 6.5 Hz, J_{Sn-H} = 70.4 Hz, 1H, major), 2.02 (s, J_{Sn-H} = 64.3 Hz, 2H, major), 1.86-1.96 (m), 1.18-1.51 (m), 0.82-0.96 (m), 0.65-0.81 (m), 0.28 (s, 6H, major), 0.26 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 140.16, 139.57, 137.87, 133.81, 133.66, 129.03, 128.86, 128.21, 127.69, 127.63, 31.98, 29.72, 29.43, 29.25, 29.14, 29.02, 27.48 (J_{Sn-C} = 56.3 Hz), 24.01 (J_{Sn-C} = 46.8 Hz), 22.74, 14.15, 13.74, 10.46, 9.89 ($J_{^{119}Sn-C}$ = 324.6 Hz, $J_{^{117}Sn-C}$ = 310.3 Hz), -2.40, -2.88; ^{119}Sn NMR ($CDCl_3$) δ -45.96, -54.49

HRMS Calcd for $C_{31}H_{57}SiSn$: $[M-Bu]^+$, 577.32460. Found: m/z 577.32507

A mixture of (*E*)-dimethyl(phenyl)(5-phenyl-2-(tributylstannyl)pent-2-en-1-yl)silane ((*E*)-4b) and (*Z*)-dimethyl(phenyl)(5-phenyl-2-(tributylstannyl)pent-2-en-1-yl)silane ((*Z*)-4b)



(*E*)-**4b** (*Z*)-**4b**

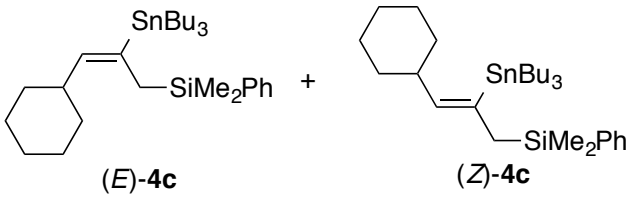
Isolated in 86% (*E*:*Z* = 77:23) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.49-7.59 (m), 7.34-7.42 (m), 7.24-7.33 (m), 7.14-7.23 (m), 5.90 (t, *J* = 7.1 Hz, J_{Sn-H} = 135.6 Hz, 1H, minor), 5.44 (t, *J* = 5.9 Hz, J_{Sn-H} = 70.7 Hz, 1H, major), 2.63 (t, *J* = 7.6 Hz, 2H, major), 2.29 (q, *J* = 7.6 Hz, 2H, major), 2.05 (s, J_{Sn-H} = 63.8 Hz, 2H, major), 1.24-1.58 (m), 0.69-1.00 (m), 0.31 (s, 6H, major), 0.30 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 142.32, 142.09, 139.37, 139.18 (J_{Sn-C} = 20.2 Hz), 138.53 (J_{Sn-C} = 27.4 Hz), 133.81, 133.65, 128.92, 128.83, 128.39, 128.29, 128.17, 127.71, 127.63, 125.71, 125.62, 37.56, 36.96, 35.88, 30.80 (J_{Sn-C} = 55.8 Hz), 29.23, 29.08 (J_{Sn-C} = 19.0 Hz), 27.45 (J_{Sn-C} = 56.1 Hz), 24.11 (J_{Sn-C} = 45.8 Hz), 13.74, 10.41, 9.86 ($J_{^{119}Sn-C}$ = 325.8 Hz, $J_{^{117}Sn-C}$ = 311.5 Hz), -2.40, -2.91; ^{119}Sn NMR ($CDCl_3$) δ -45.30, -54.17

HRMS Calcd for $C_{27}H_{41}SiSn$: $[M-Bu]^+$, 513.19940. Found: m/z 513.19952

A mixture of (*E*)-(3-cyclohexyl-2-(tributylstannyl)allyl)dimethyl(phenyl)silane

((*E*)-4c) and (*Z*)-(3-cyclohexyl-2-(tributylstannyl)allyl)dimethyl(phenyl)silane ((*Z*)-4c)



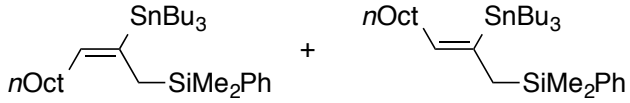
(*E*)-**4c** (*Z*)-**4c**

Isolated in 77% (*E*:*Z* = 87:13) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.52-7.61 (m), 7.34-7.43 (m), 5.69 (d, J = 9.8 Hz, J_{Sn-H} = 138.7 Hz, 1H, minor), 5.21 (d, J = 9.5 Hz, J_{Sn-H} = 70.8 Hz, 1H, major), 2.07 (s, J_{Sn-H} = 65.2 Hz, 2H, major), 1.41-1.74 (m), 1.34 (sext, J = 7.4 Hz, 6H, major), 0.73-1.24 (m), 0.34 (s, 6H, major), 0.31 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 146.21 (J_{Sn-C} = 22.1 Hz), 139.53, 134.81, 133.83, 133.67, 128.84, 127.69, 37.59 (J_{Sn-C} = 54.7 Hz), 33.98, 32.98, 29.27, 29.08 (J_{Sn-C} = 19.4 Hz), 27.56, 27.41 (J_{Sn-C} = 54.9 Hz), 26.17, 26.08, 23.64 (J_{Sn-C} = 47.9 Hz), 13.75, 10.51, 9.89 ($J_{^{119}Sn-C}$ = 323.6 Hz, $J_{^{117}Sn-C}$ = 309.8 Hz), -2.54, -2.98; ^{119}Sn NMR ($CDCl_3$) δ -41.71, -45.35

HRMS Calcd for $C_{25}H_{43}SiSn$: $[M-Bu]^+$, 491.21505. Found: m/z 491.21524

A mixture of (*E*)-dimethyl(phenyl)(2-(tributylstannyl)undec-2-en-1-yl)silane ((*E*)-4d) and (*Z*)-dimethyl(phenyl)(2-(tributylstannyl)undec-2-en-1-yl)silane ((*Z*)-4d)



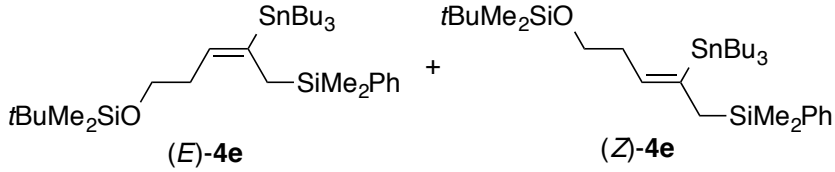
(*E*)-**4d** (*Z*)-**4d**

Isolated in 71% (*E*:*Z* = 91:9) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.50-7.61 (m), 7.35-7.43 (m), 5.87 (t, J = 7.3 Hz, J_{Sn-H} = 138.9 Hz, 1H, minor), 5.40 (t, J = 6.6 Hz, J_{Sn-H} = 70.9 Hz, 1H, major), 2.08 (s, J_{Sn-H} = 63.7 Hz, 2H, major), 1.92-2.03 (m), 1.23-1.58 (m), 0.90-1.00 (m), 0.73-0.89 (m), 0.33 (s, 6H, major), 0.31 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 140.13 (J_{Sn-C} = 24.8 Hz), 139.58, 137.82, 133.63, 128.85, 127.67, 31.90, 29.66, 29.59, 29.40, 29.34, 29.11, 28.97, 27.44 (J_{Sn-C} = 56.3 Hz), 23.95, 22.69, 14.13, 13.73, 9.84, -2.43, -2.92; ^{119}Sn NMR ($CDCl_3$) δ -54.43, -55.87

HRMS Calcd for $C_{27}H_{49}SiSn$: $[M-Bu]^+$, 521.26200. Found: m/z 521.26208

A mixture of (*E*)-*tert*-butyl((5-(dimethyl(phenyl)silyl)-4-(tributylstannyl)pent-3-en-1-yl)oxy)dimethylsilane ((*E*)-4e) and (*Z*)-*tert*-butyl((5-(dimethyl(phenyl)silyl)-4-(tributylstannyl)pent-3-en-1-yl)oxy)dimethylsilane ((*Z*)-4e)



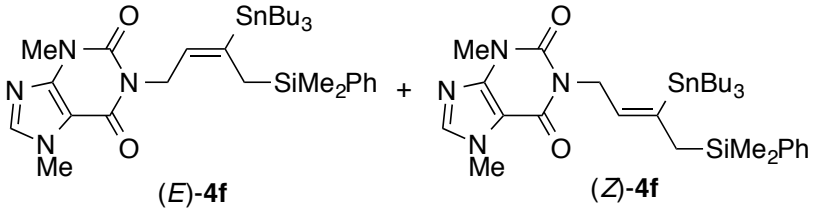
(*E*)-**4e** (*Z*)-**4e**

Isolated in 93% (*E*:*Z* = 75:25) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.46-7.54 (m), 7.31-7.37 (m), 5.78 (t, *J* = 7.7 Hz, J_{Sn-H} = 134.3 Hz, 1H, minor), 5.38 (t, *J* = 6.6 Hz, J_{Sn-H} = 70.2 Hz, 1H, major), 3.66 (t, *J* = 7.0 Hz, 2H, minor), 3.54 (t, *J* = 7.0 Hz, 2H, major), 2.18 (q, *J* = 6.8 Hz, 2H, major), 2.04 (s, J_{Sn-H} = 63.8 Hz, 2H, major), 1.34-1.50 (m), 1.27 (sext, *J* = 7.4 Hz, 6H, major), 0.84-0.92 (m), 0.67-0.83 (m), 0.28 (s, 6H, major), 0.25 (s, 6H, minor), 0.05 (s, 6H, minor), 0.04 (s, 6H, major); ^{13}C NMR ($CDCl_3$) δ 140.38, 139.33, 135.25 (J_{Sn-C} = 27.3 Hz), 133.77, 133.64, 133.53, 133.02, 128.89, 127.69, 127.61, 126.58, 123.87, 62.95, 62.88, 32.62 (J_{Sn-C} = 55.6 Hz), 29.08 (J_{Sn-C} = 19.6 Hz), 27.43 (J_{Sn-C} = 56.3 Hz), 25.96, 25.82, 24.24 (J_{Sn-C} = 47.2 Hz), 18.32, 13.69, 9.83 ($J_{^{119}Sn-C}$ = 326.1 Hz, $J_{^{117}Sn-C}$ = 312.0 Hz), -2.44, -2.95, -3.32, -5.26; ^{119}Sn NMR ($CDCl_3$) δ -45.44, -54.65

HRMS Calcd for $C_{27}H_{51}OSi_2Sn$: $[M-Bu]^+$, 567.24949. Found: m/z 567.24976

A mixture of (*E*)-1-(4-(dimethyl(phenyl)silyl)-3-(tributylstannyl)but-2-en-1-yl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione ((*E*)-4f) and (*Z*)-1-(4-(dimethyl(phenyl)silyl)-3-(tributylstannyl)but-2-en-1-yl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione ((*Z*)-4f)



(*E*)-**4f** (*Z*)-**4f**

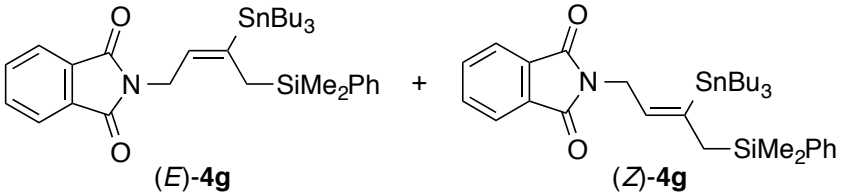
Isolated in 76% (*E*:*Z* = 83:17) as a colorless oil

7.49-7.57 (m), 7.43-7.48 (m), 7.27-7.38 (m), 5.67 (t, *J* = 6.0 Hz, J_{Sn-H} = 131.9 Hz, 1H,

minor), 5.34 (t, J = 6.2 Hz, J_{Sn-H} = 67.0 Hz, 1H, major), 4.35 (d, J = 6.3 Hz, 2H, major), 3.66 (t, J = 7.0 Hz, 2H, minor), 3.96 (s, 3H, minor), 3.93 (s, 3H, major), 3.56 (s, 3H, minor), 3.53 (s, 3H, major), 2.34 (s, J_{Sn-H} = 61.5 Hz, 2H, major), 1.13-1.48 (m), 0.61-0.91 (m), 0.33 (s, 6H, major), 0.30 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 154.76, 151.12, 148.53, 144.34, 141.14, 138.68, 134.04, 133.68, 131.88 (J_{Sn-C} = 30.8 Hz), 128.87, 127.62, 127.52, 107.50, 38.91 (J_{Sn-C} = 66.0 Hz), 33.43, 29.52, 28.86 (J_{Sn-C} = 18.8 Hz), 27.21 (J_{Sn-C} = 56.4 Hz), 24.45 (J_{Sn-C} = 39.9 Hz), 13.59, 13.52, 9.85, 9.74 ($J_{^{119}Sn-C}$ = 327.6 Hz, $J_{^{117}Sn-C}$ = 313.9 Hz), -2.65, -3.09; ^{119}Sn NMR ($CDCl_3$) δ -43.19, -51.73

HRMS Calcd for $C_{31}H_{50}N_4O_2NaSiSn$: $[M+Na]^+$, 681.26172. Found: m/z 681.26233

A mixture of (*E*)-2-(4-(dimethyl(phenyl)silyl)-3-(tributylstannyl)but-2-en-1-yl)isoindoline-1,3-dione ((*E*)-4g) and (*Z*)-2-(4-(dimethyl(phenyl)silyl)-3-(tributylstannyl)but-2-en-1-yl)isoindoline-1,3-dione ((*Z*)-4g)



(*E*)-**4g** (*Z*)-**4g**

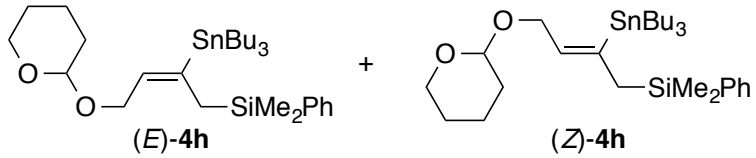
Isolated in 63% (*E*:*Z* = 79:21) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.77-7.89 (m), 7.64-7.74 (m), 7.46-7.62 (m), 7.29-7.45 (m), 5.69 (t, J = 6.4 Hz, J_{Sn-H} = 122.8 Hz, 1H, minor), 5.39 (t, J = 6.4 Hz, J_{Sn-H} = 64.6 Hz, 1H, major), 4.20 (d, J = 6.1 Hz, 2H, minor), 4.02 (d, J = 6.1 Hz, 2H, major), 2.32 (s, J_{Sn-H} = 61.3 Hz, 2H, major), 1.15-1.57 (m), 0.64-1.04 (m), 0.37 (s, 6H, major), 0.33 (s, 6H, minor); ^{13}C NMR ($CDCl_3$) δ 167.97, 167.87, 145.13, 138.55, 137.84, 134.04, 133.71, 133.67, 132.22, 130.95 (J_{Sn-C} = 30.1 Hz), 129.06, 127.78, 127.67, 127.45, 123.09, 122.99, 35.47 (J_{Sn-C} = 63.3 Hz), 29.16, 28.90 (J_{Sn-C} = 19.3 Hz), 27.40, 27.27 (J_{Sn-C} = 57.2 Hz), 24.51 (J_{Sn-C} = 36.9 Hz), 13.66, 13.57, 9.99, 9.82 ($J_{^{119}Sn-C}$ = 329.4 Hz, $J_{^{117}Sn-C}$ = 315.6 Hz), -2.61, -3.16; ^{119}Sn NMR ($CDCl_3$) δ -41.71, -45.35

HRMS Calcd for $C_{32}H_{47}NO_2NaSiSn$: $[M+Na]^+$, 648.22902. Found: m/z 648.22955

A mixture of (*E*)-dimethyl(phenyl)(4-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(tributylstannyl)but-2-e

n-1-yl)silane ((*E*)-4h) and (*Z*)-dimethyl(phenyl)(4-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-(tributylstannyl)but-2-en-1-yl)silane ((*Z*)-4h)



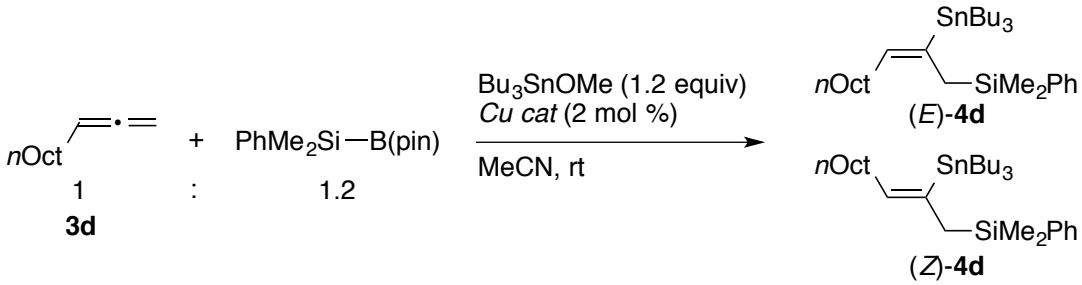
(*E*)-**4h** (*Z*)-**4h**

Isolated in 56% (*E*:*Z* = 75:25) as a colorless oil

^{1}H NMR ($CDCl_3$) δ 7.47-7.56 (m), 7.30-7.41 (m), 6.03 (t, J = 6.6 Hz, J_{Sn-H} = 131.9 Hz, 1H, minor), 5.55 (t, J = 5.9 Hz, J_{Sn-H} = 68.6 Hz, 1H, major), 4.52-4.66 (m), 4.15-4.32 (m), 3.93-4.09 (m), 3.78-3.92 (m), 3.43-3.56 (m), 1.93-2.29 (m), 1.18-1.91 (m), 0.67-0.98 (m), 0.36 (s, 6H, minor), 0.302 (s), 0.296 (s); ^{13}C NMR ($CDCl_3$) δ 143.63, 138.83, 135.09 (J_{Sn-C} = 27.5 Hz), 134.06, 133,74, 133.64, 128.98, 128.88, 127.72, 127.64, 97.72, 97.48, 63.22 (J_{Sn-C} = 62.0 Hz), 62.29, 62.19, 30.72, 29.03, 27.40 (J_{Sn-C} = 57.1 Hz), 25.48, 24.71, 19.63, 13.68, 10.47, 9.84 ($J_{^{119}Sn-C}$ = 328.3 Hz, $J_{^{117}Sn-C}$ = 314.4 Hz), -2.62, -2.66, -2.88, -2.96; ^{119}Sn NMR ($CDCl_3$) δ -43.35, -52.87

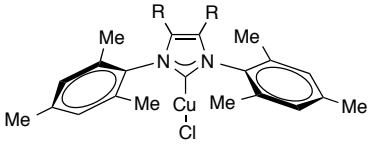
HRMS Calcd for $C_{29}H_{52}O_2NaSiSn$: $[M+Na]^+$, 603.26508. Found: m/z 603.26563

Table S1 Ligand effect on silylstannylation of undeca-1,2-diene

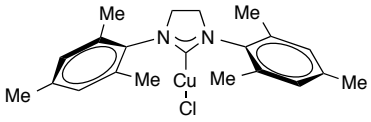


Cu cat	Time (h)	Isolated yield (%)	*E*:*Z*
^{Cl}IMesCuCl	0.25	71	91:9
SIMesCuCl	4	75	80:20
SIMesCuCl[a]	6	46	82:18
IMesCuCl	1	45	81:19
IPrCuCl	10	47	77:23
CuCl–PCy_3	0.25	71	79:21
CuCl–BINAP	1	54	78:22
$(Ph_3P)_3CuOAc$	10	38	79:21

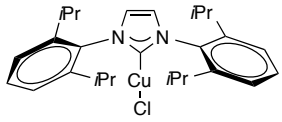
[a] $Bu_3SnOtBu$ was used instead of Bu_3SnOMe.



^{Cl}IMesCuCl: R = Cl
IMesCuCl: R = H



SIMesCuCl



IPrCuCl

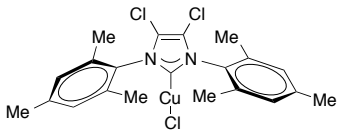
References

(1) C. A. Citadelle, E. Le Nouy, F. Bisaro, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans*., 2010, **39**, 4489.

(2) K. Jinqiang and M. Shengming, *J. Org. Chem*., 2009, **74**, 1763.

(3) T. Fujihara, T. Xu, K. Semba, J. Terao and Y. Tsuji, *Angew. Chem. Int. Ed*., 2011, **50**, 523.

(4) (*a*) A. J. Leusink, H. A. Budding and J. W. Marsman, *J. Organomet. Chem*., 1967, **9**, 285; (*b*) Y. Takemoto, H. Yoshida and K. Takaki, *Chem. Eur. J.*, 2012, **18**, 14841; (*c*) Y. Takemoto, H. Yoshida and K. Takaki, *Synthesis*, 2014, **46**, 3024.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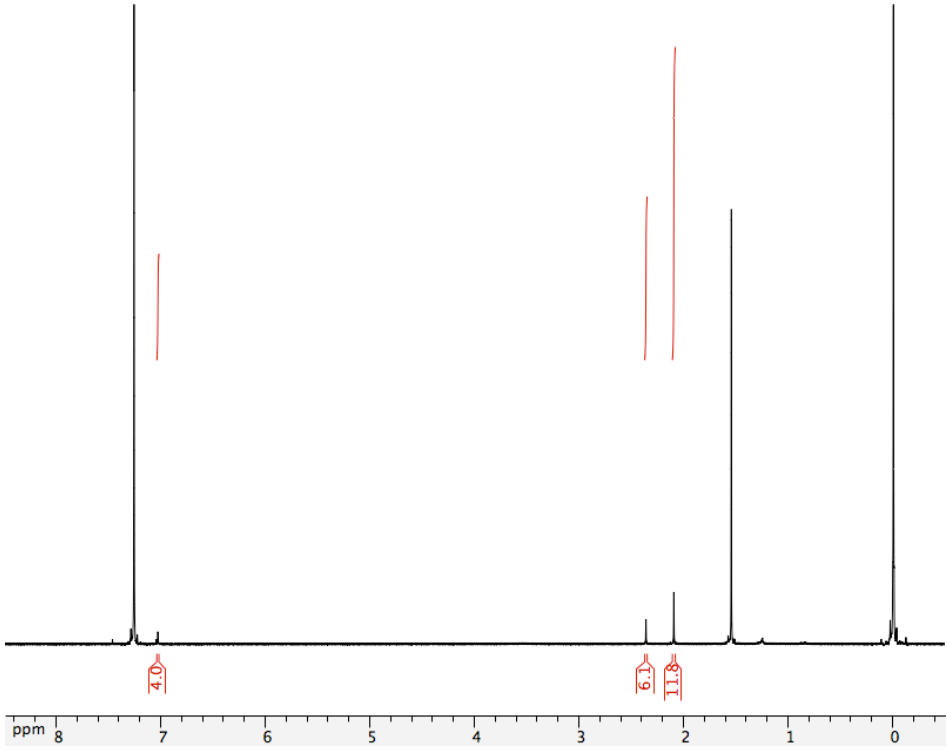
Me
N
N
Me
Me
Cu
Me
Me
Me
Cl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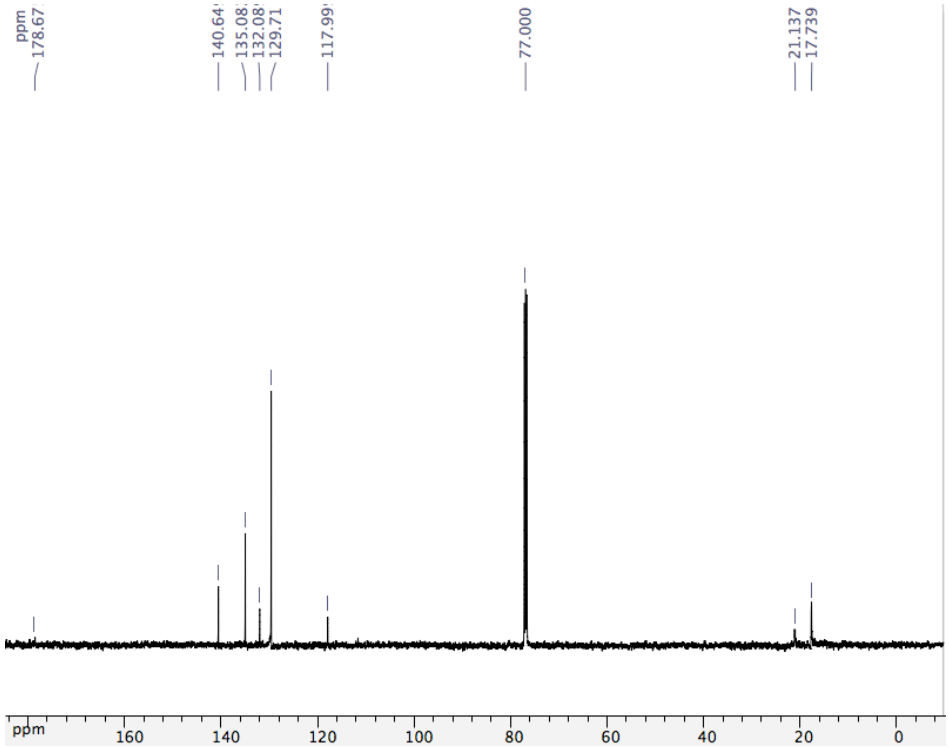
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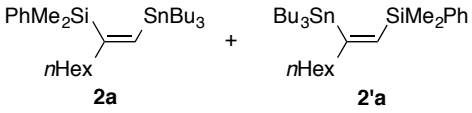
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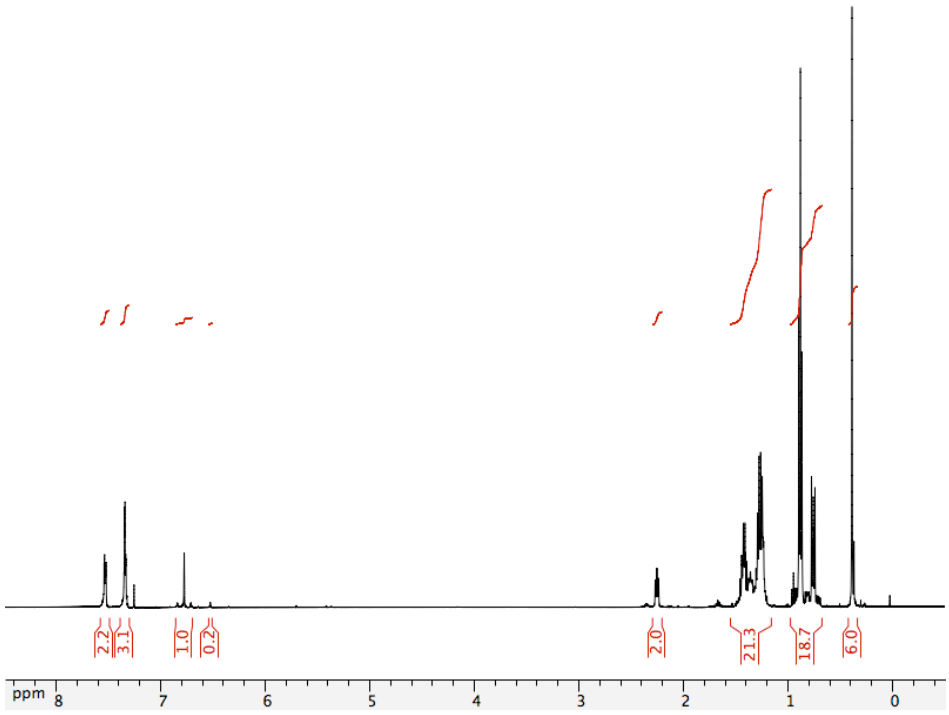
SiMe2Ph
nHex

2a **2'a**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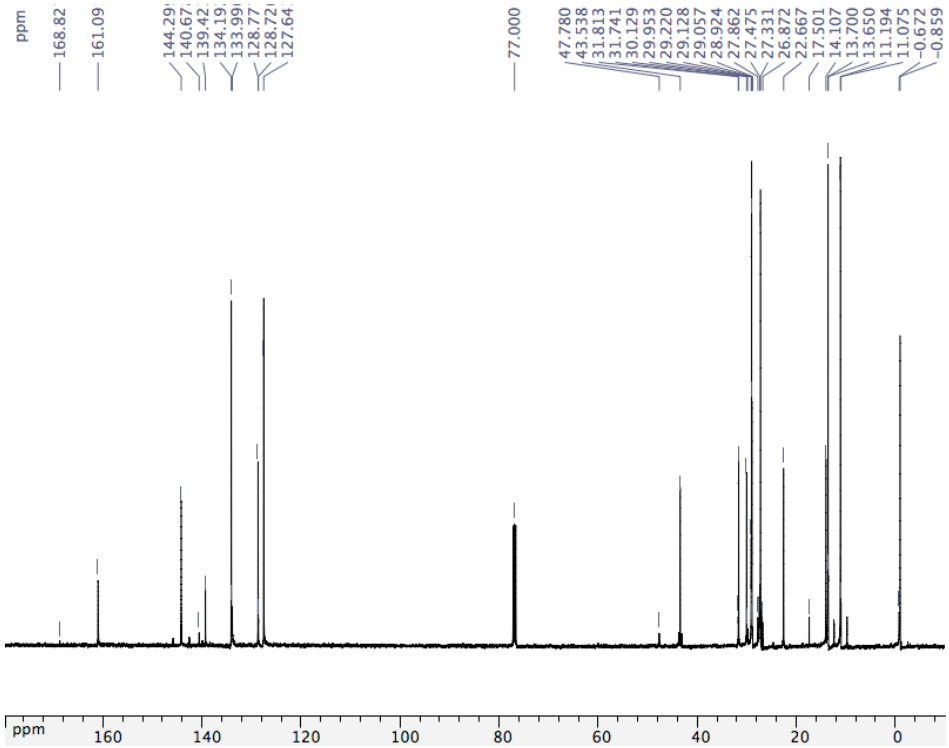
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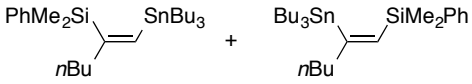
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2b

+

Bu3Sn
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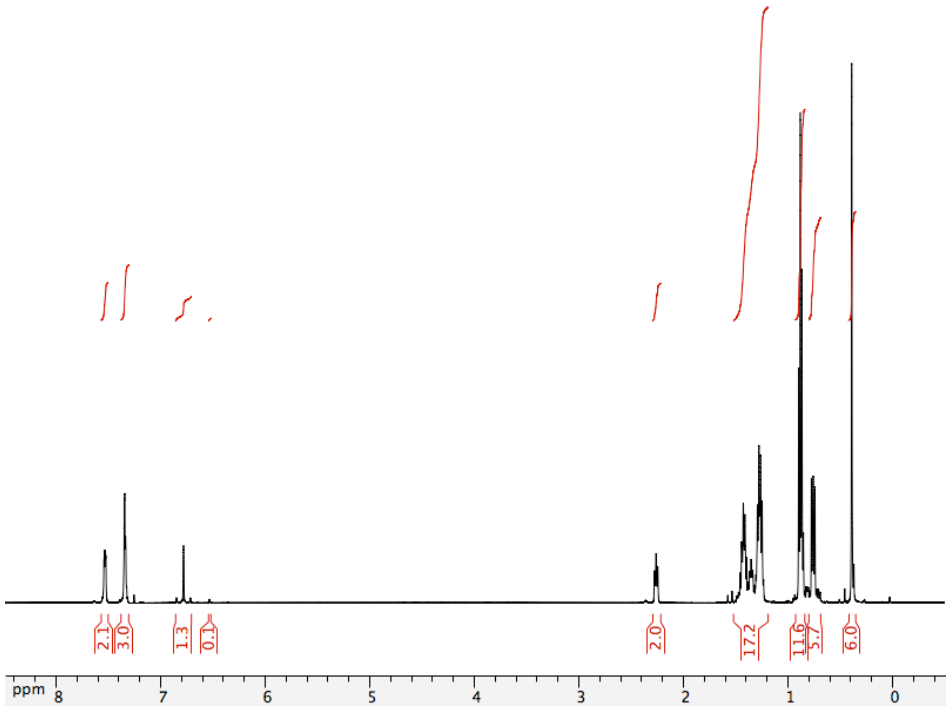
2'b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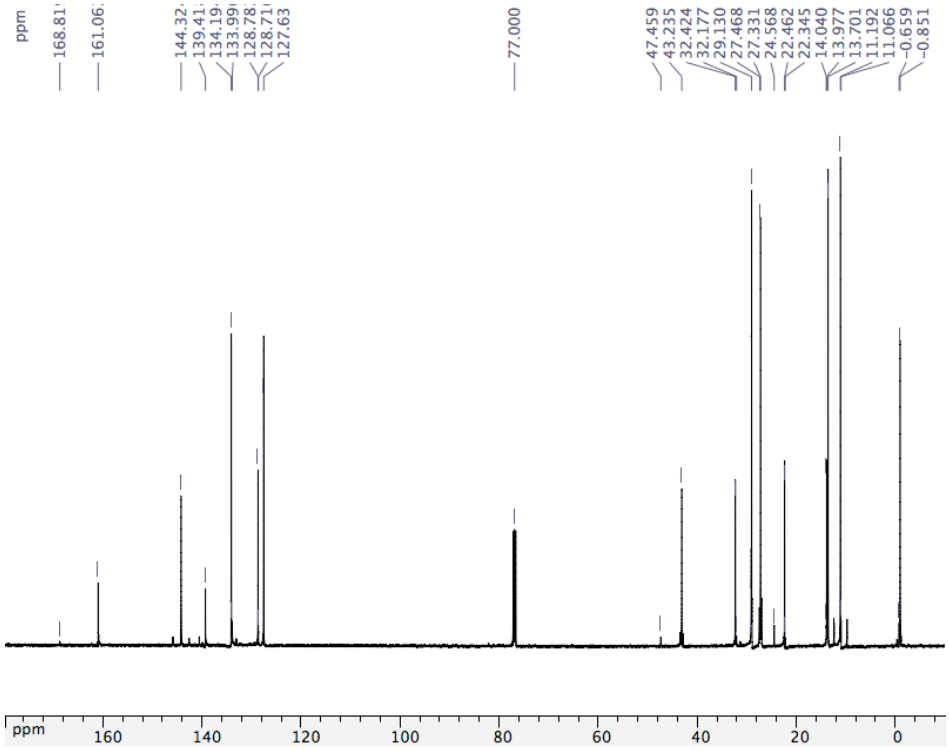
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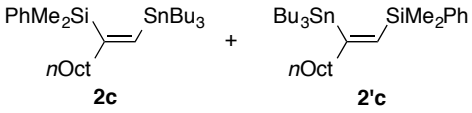
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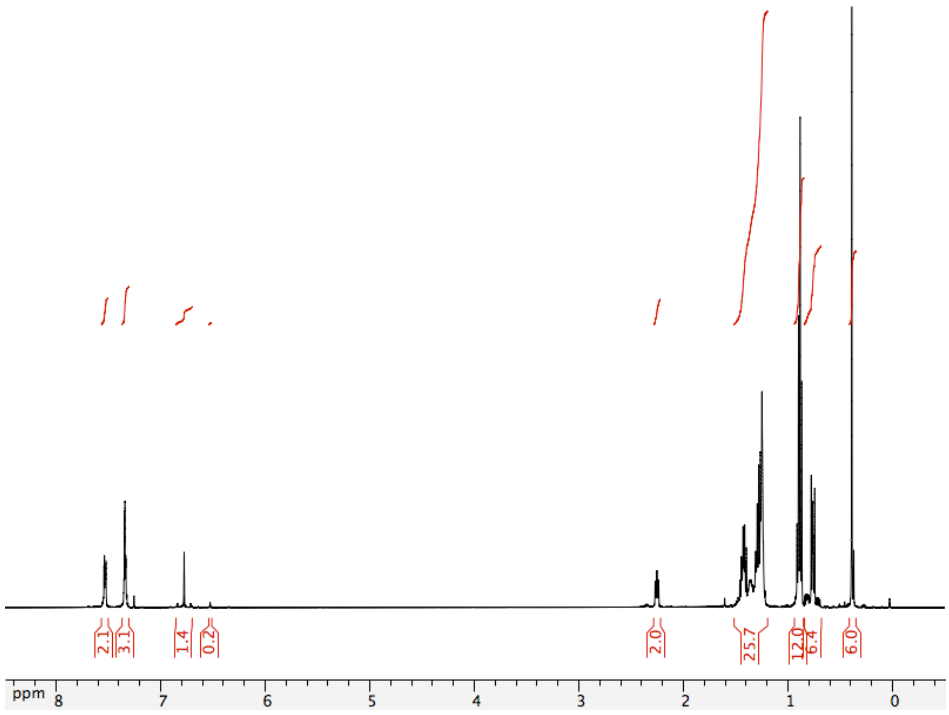
2c **2'c**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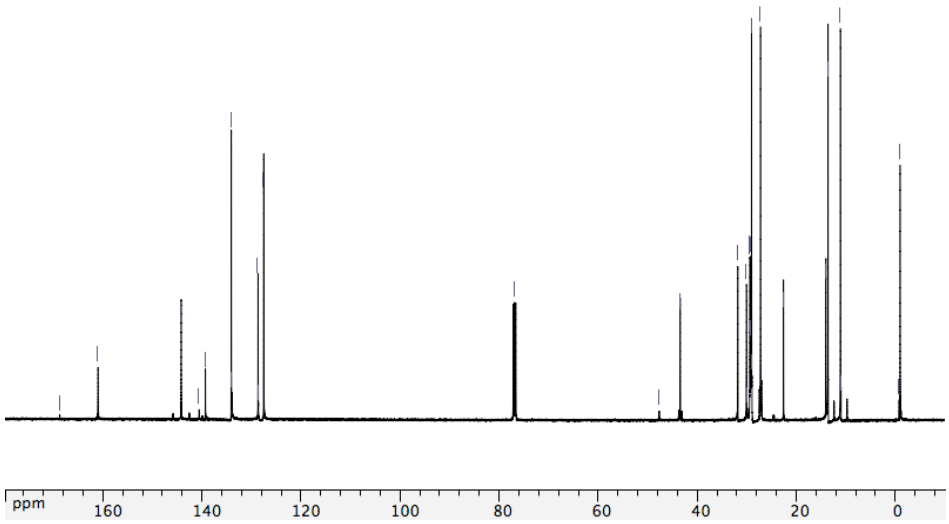
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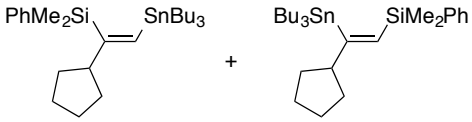
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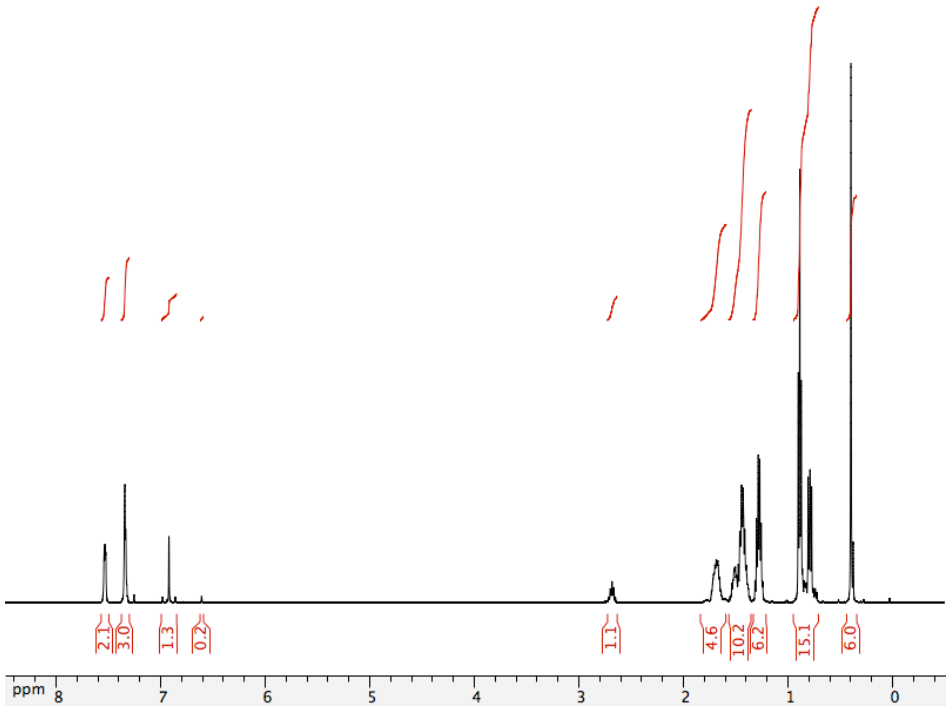
2d **2'd**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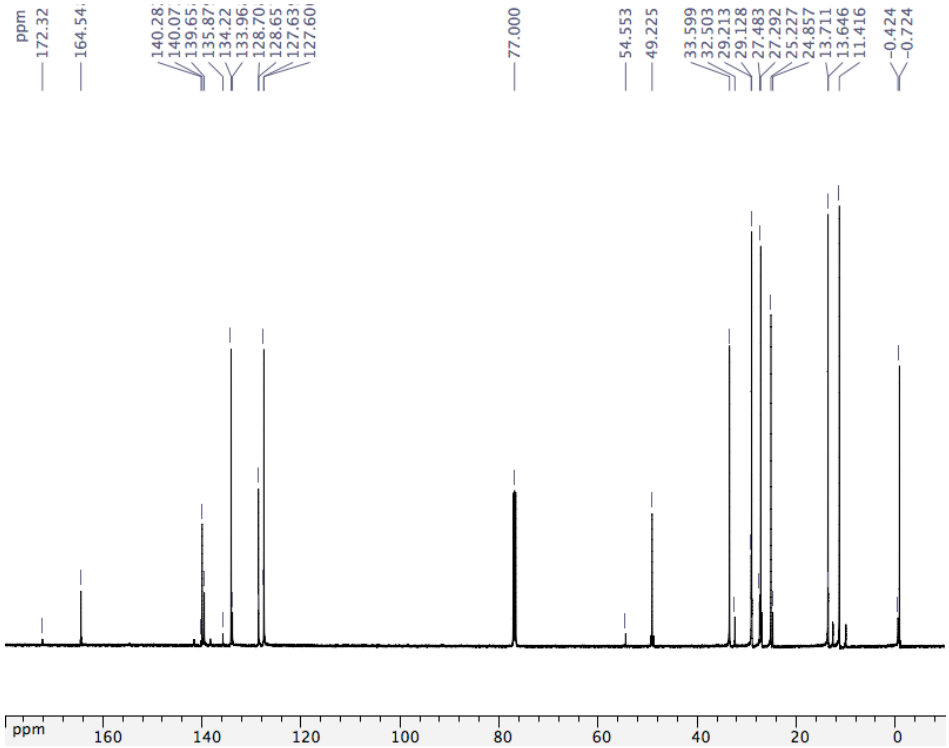
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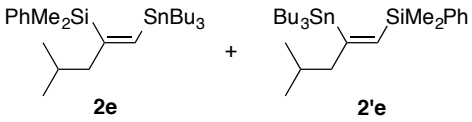
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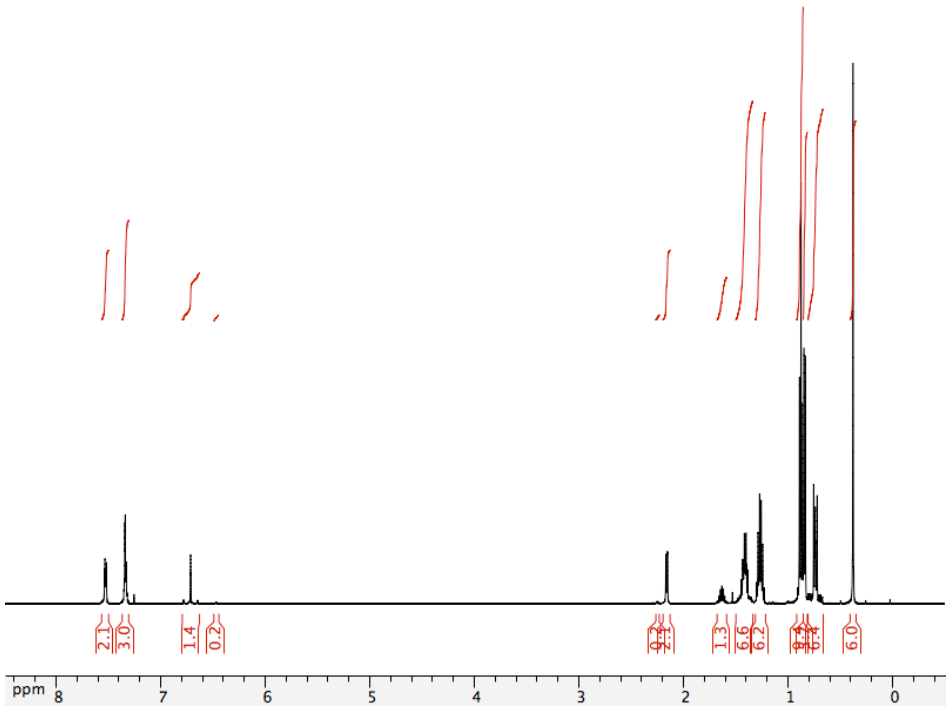
2e **2'e**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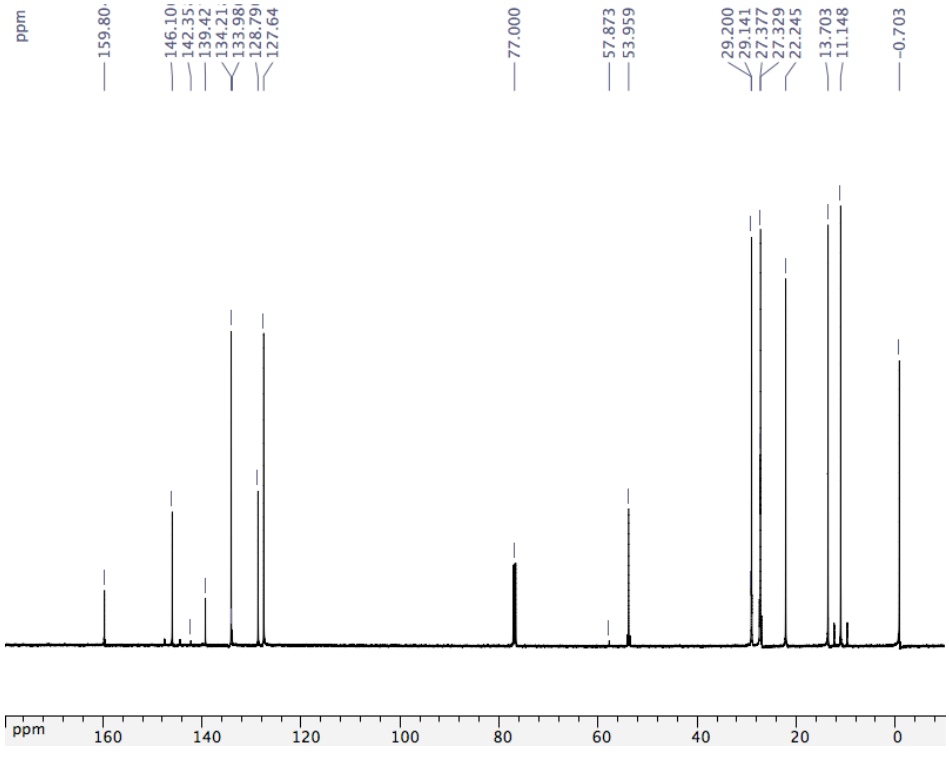
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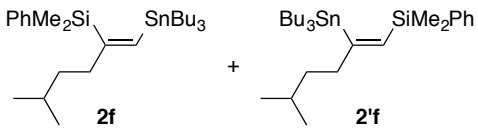
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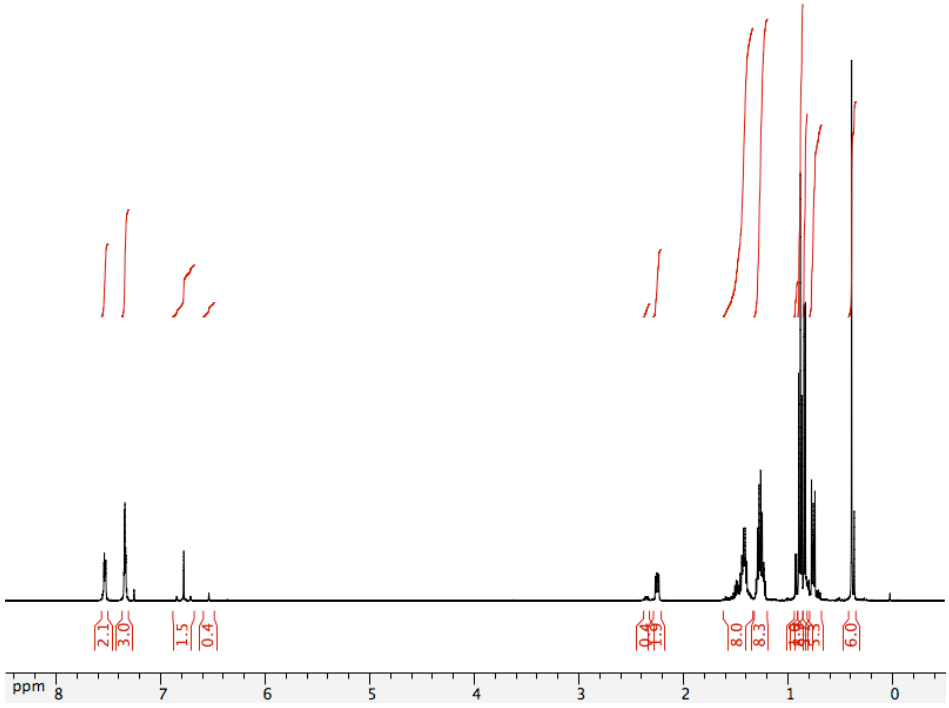
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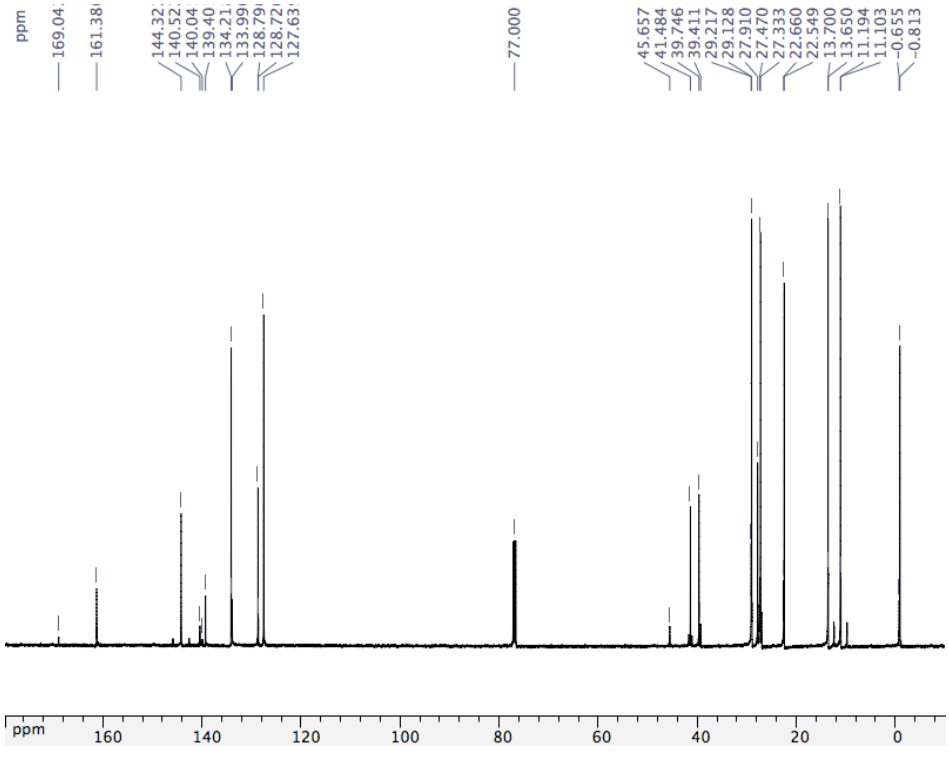
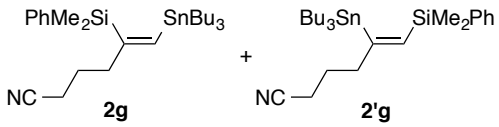
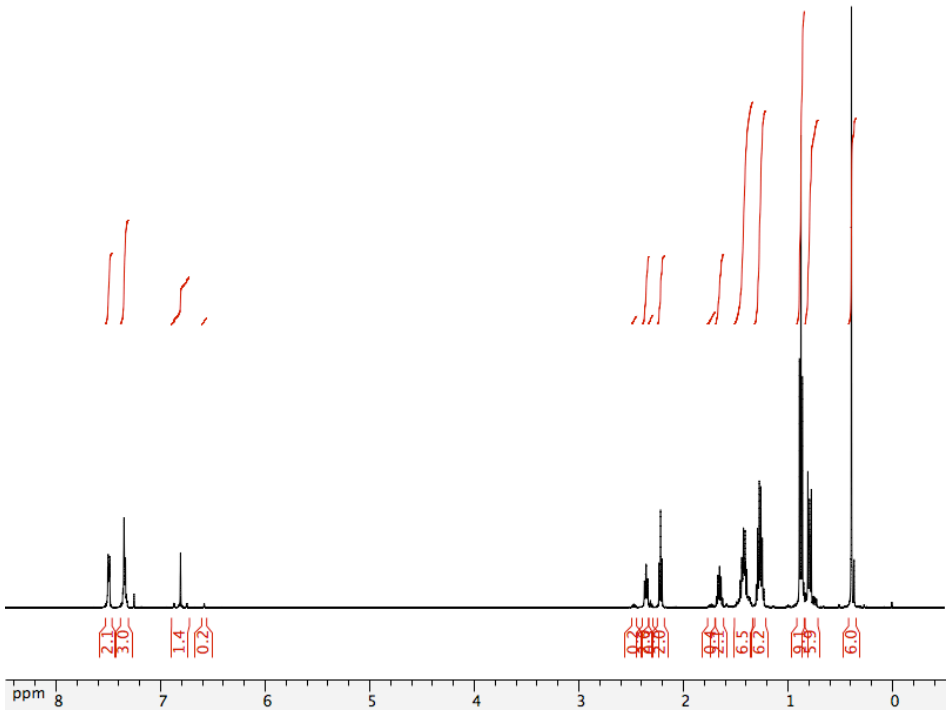
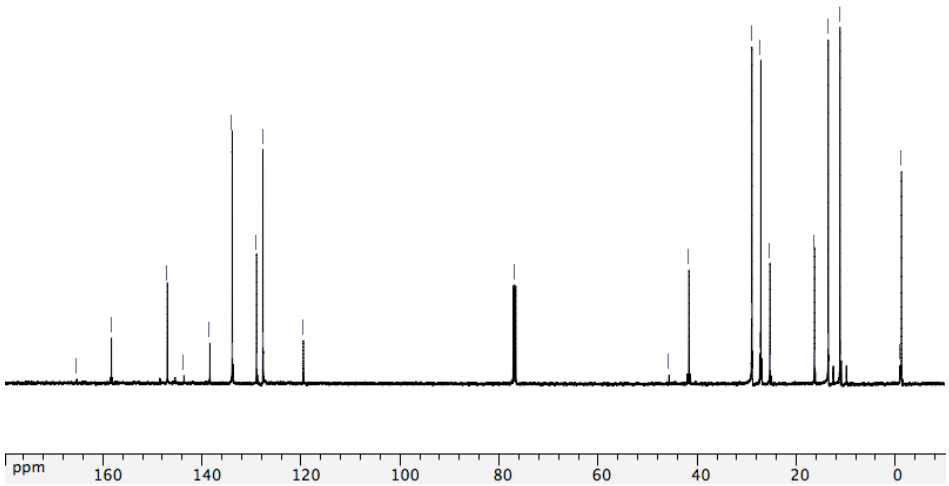
8.0
8.3
3.3
6.0
ppm
8
7
6
5
4
3
2
1
0

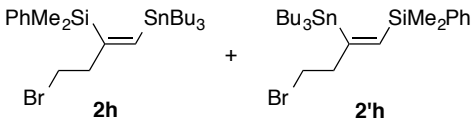

ppm
169.04
161.38
144.32
140.52
140.04
139.40
134.21
133.99
128.79
128.72
127.63
77.000
45.657
41.484
39.746
39.411
29.217
29.128
27.910
27.470
27.333
22.660
22.549
13.700
13.650
11.194
11.103
-0.655
-0.813
ppm
160
140
120
100
80
60
40
20
0

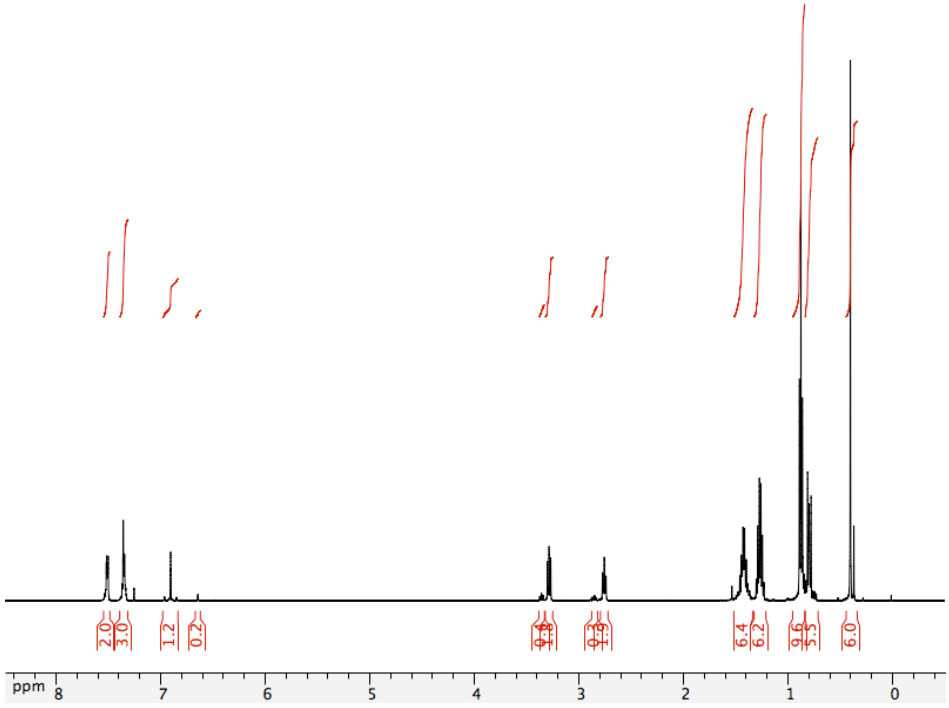

PhMe2Si
SnBu3
NC
2g
+
Bu3Sn
SiMe2Ph
NC
2'g


2.1
3.0
1.4
0.2
9.4
2.1
6.5
6.2
9.1
3.9
6.0
ppm
8
7
6
5
4
3
2
1
0

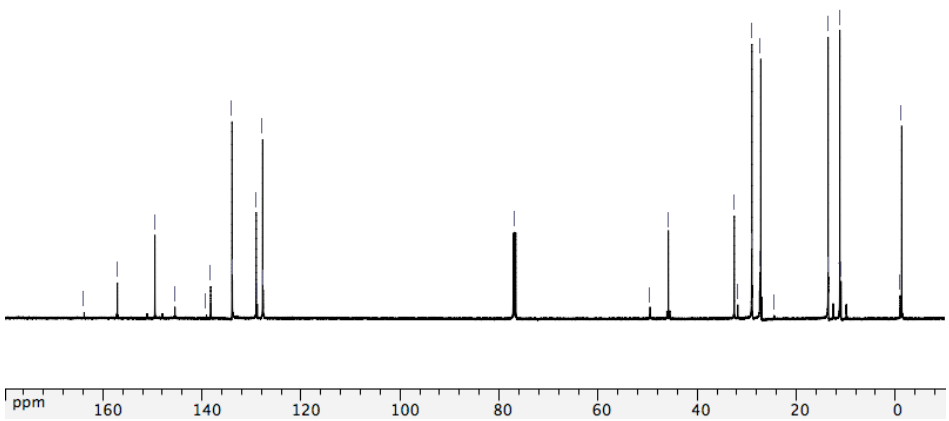

ppm
165.37
158.39
147.09
143.73
138.50
133.99
133.85
129.08
128.91
127.81
127.74
119.64
77.000
45.792
41.780
29.124
29.069
27.362
27.261
25.423
25.114
16.427
16.276
13.651
13.587
11.277
11.024
-0.855
-1.123

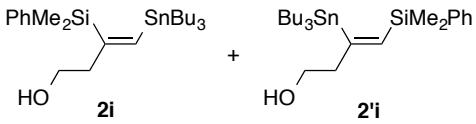

ppm
160
140
120
100
80
60
40
20
0

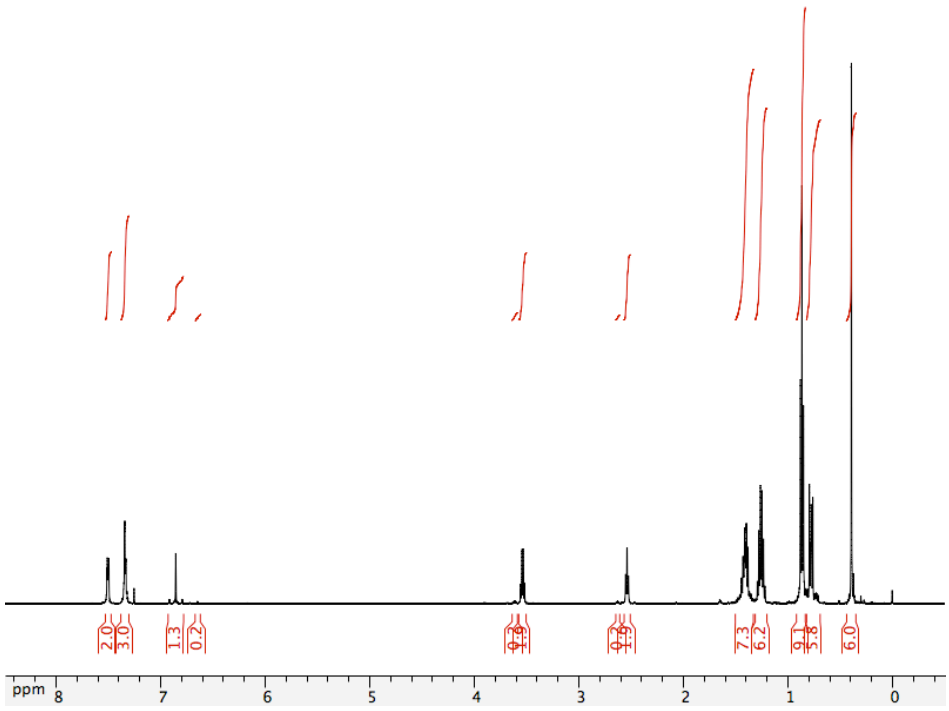

PhMe2Si
SnBu3
Br
2h
+
Bu3Sn
SiMe2Ph
Br
2'h

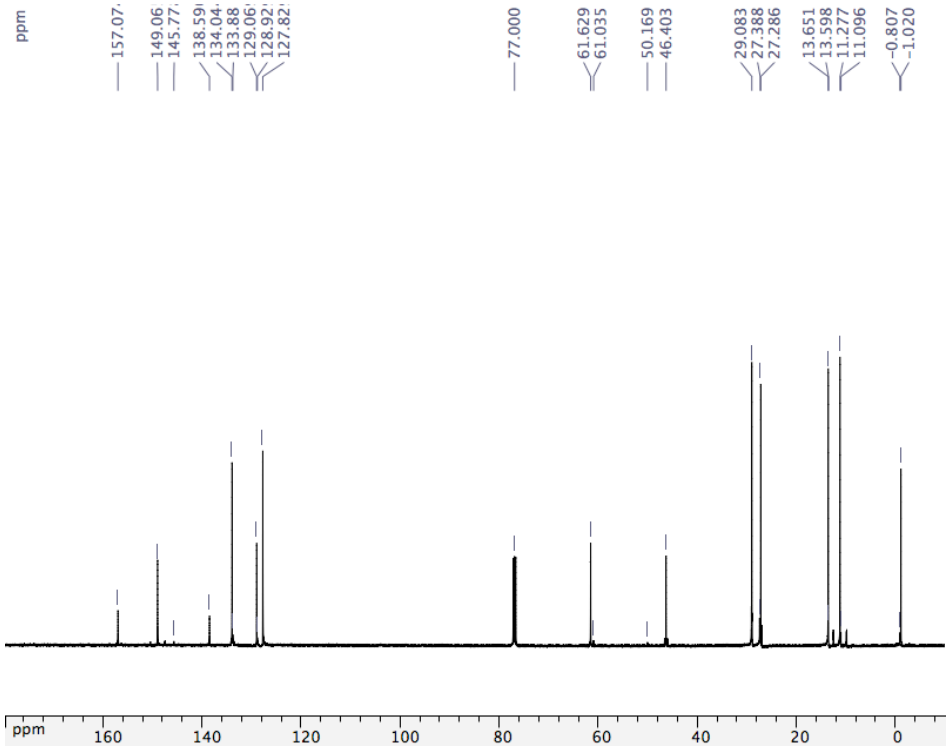

2.0
3.0
1.2
0.2
9.8
9.9
6.4
6.2
9.6
5.5
6.0
ppm
8
7
6
5
4
3
2
1
0

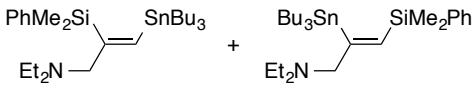

ppm
163.89
157.18
149.61
145.56
139.20
138.35
134.05
133.97
129.15
128.94
127.86
127.75
77.000
49.647
45.944
32.629
31.922
29.113
29.065
27.385
27.285
24.575
13.681
13.613
11.320
11.066
-0.859
-1.172


ppm
160
140
120
100
80
60
40
20
0

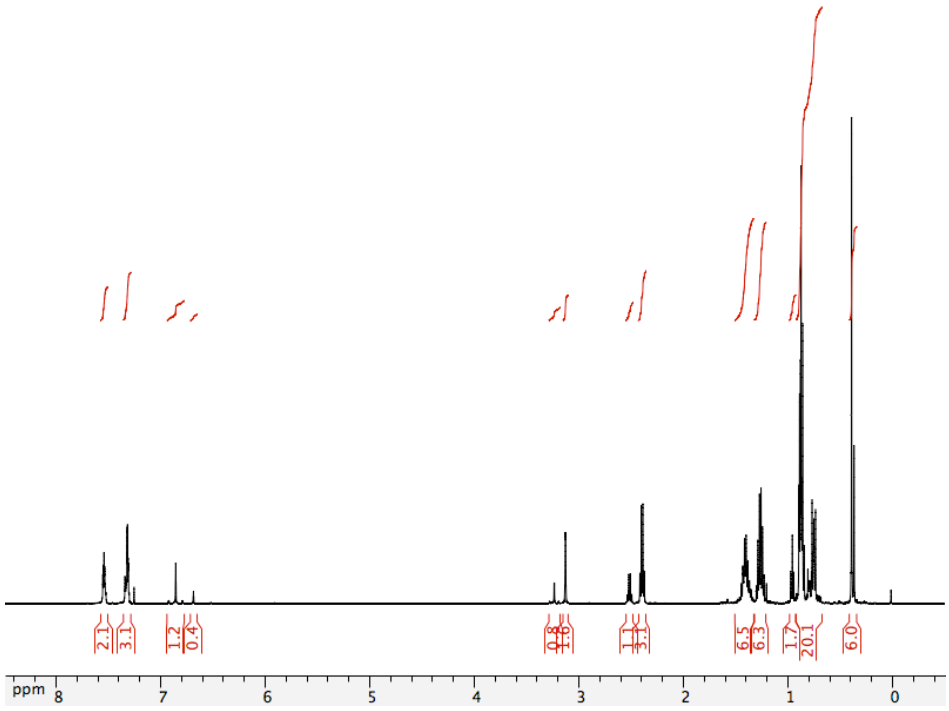

PhMe2Si
SnBu3
HO
2i
+
Bu3Sn
SiMe2Ph
HO
2'i


2.0
3.0
1.3
0.2
0.9
1.9
0.3
1.9
7.3
6.2
9.1
5.8
6.0
ppm
8
7
6
5
4
3
2
1
0

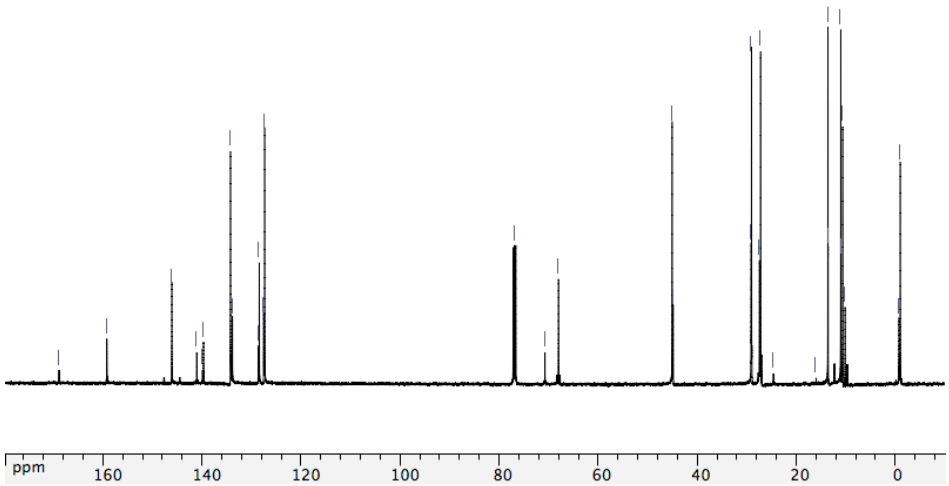

ppm
157.07
149.06
145.77
138.59
134.04
133.88
129.06
128.92
127.82
77.000
61.629
61.035
50.169
46.403
29.083
27.388
27.286
13.651
13.598
11.277
11.096
-0.807
-1.020
ppm
160
140
120
100
80
60
40
20
0

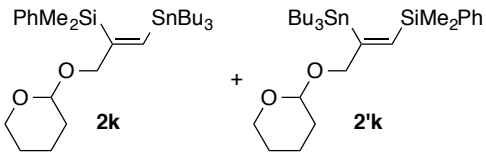

PhMe2Si
SnBu3
Et2N
+
Bu3Sn
SiMe2Ph
Et2N

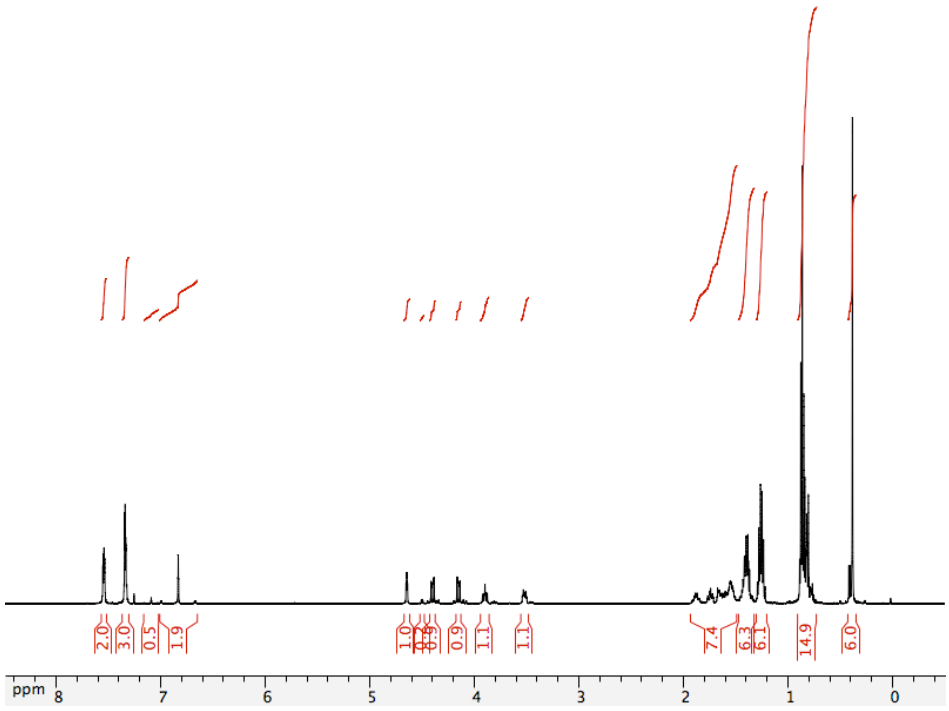
2j **2'j**

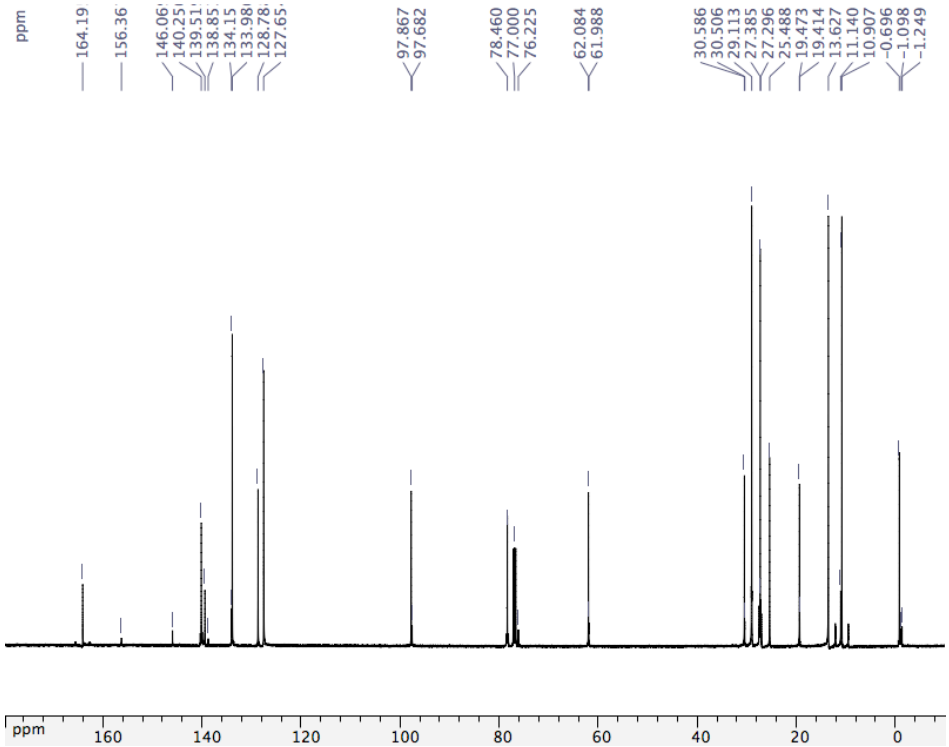

2.1
3.1
1.2
0.4
0.8
1.0
1.1
3.1
6.5
6.3
1.7
20.1
6.0
ppm
8
7
6
5
4
3
2
1
0

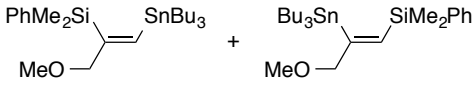

ppm
168.96
159.30
146.18
141.15
139.98
139.79
134.34
133.95
128.70
128.53
127.64
127.44
77.000
70.865
68.125
45.174
44.969
29.230
29.143
27.546
27.322
24.718
16.105
13.720
13.679
11.124
11.079
10.737
10.256
-0.618
-0.885


ppm
160
140
120
100
80
60
40
20
0

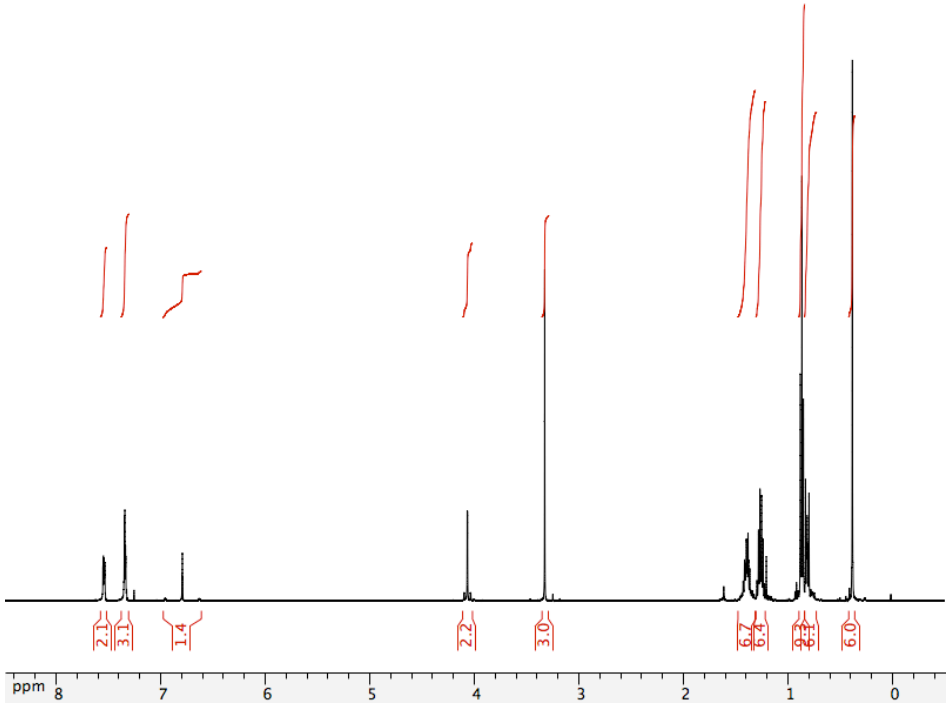

PhMe2Si
SnBu3
O
O
2k
+
Bu3Sn
SiMe2Ph
O
O
2'k

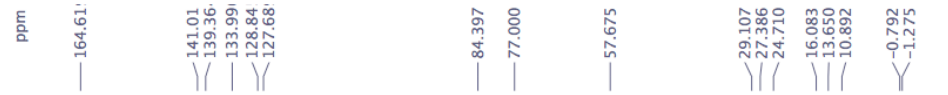

2.0
3.0
0.5
1.9
1.0
0.9
1.1
1.1
7.4
6.3
6.1
14.9
6.0
ppm
8
7
6
5
4
3
2
1
0

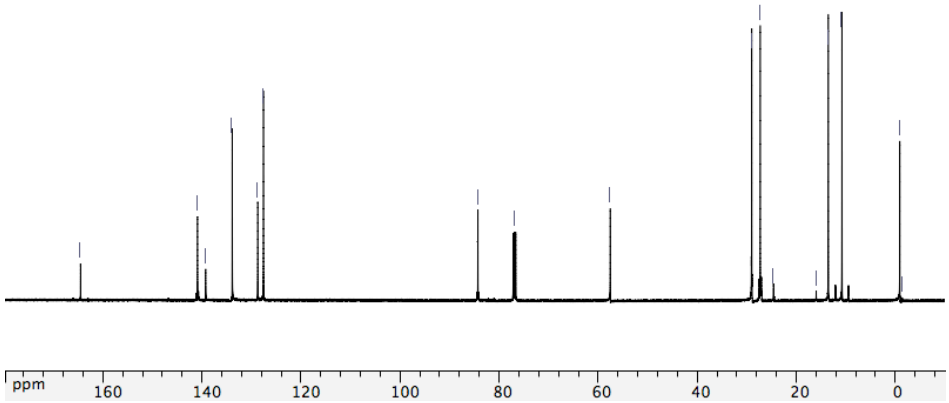

ppm
164.19
156.36
146.06
140.25
139.51
138.85
134.15
133.98
128.78
127.65
97.867
97.682
78.460
77.000
76.225
62.084
61.988
30.586
30.506
29.113
27.385
27.296
25.488
19.473
19.414
13.627
11.140
10.907
-0.696
-1.098
-1.249
ppm
160
140
120
100
80
60
40
20
0

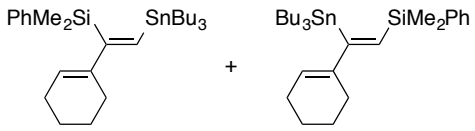

PhMe2Si
SnBu3
MeO
+
Bu3Sn
SiMe2Ph
MeO

2l **2'l**

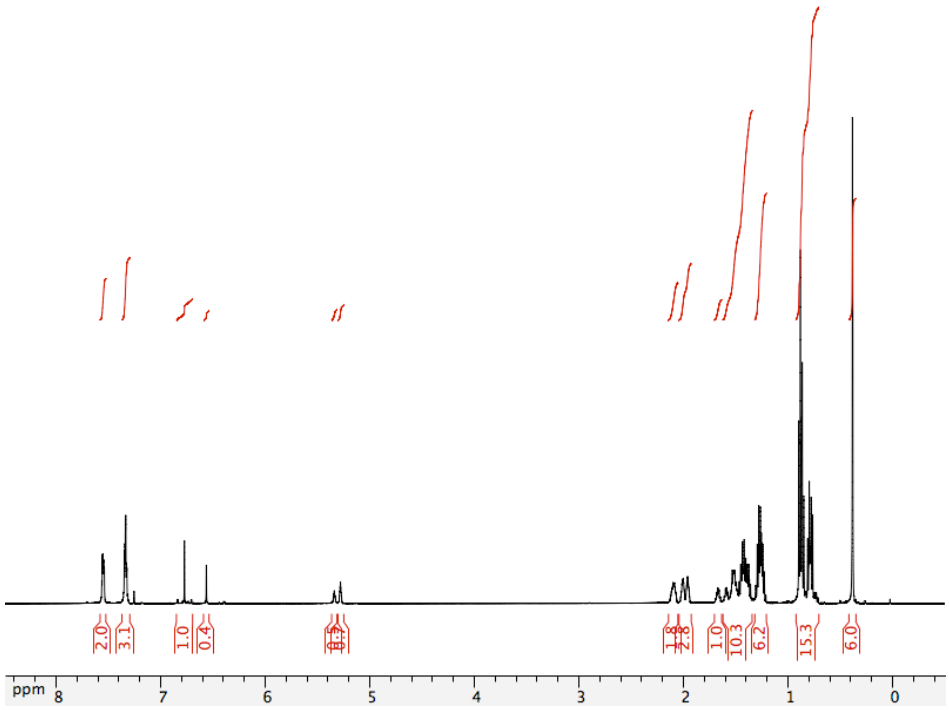

2.1
3.1
1.4
2.2
3.0
6.7
6.4
6.0
ppm
8
7
6
5
4
3
2
1
0


ppm
164.61
141.01
139.36
133.99
128.84
127.68
84.397
77.000
57.675
29.107
27.386
24.710
16.083
13.650
10.892
-0.792
-1.275

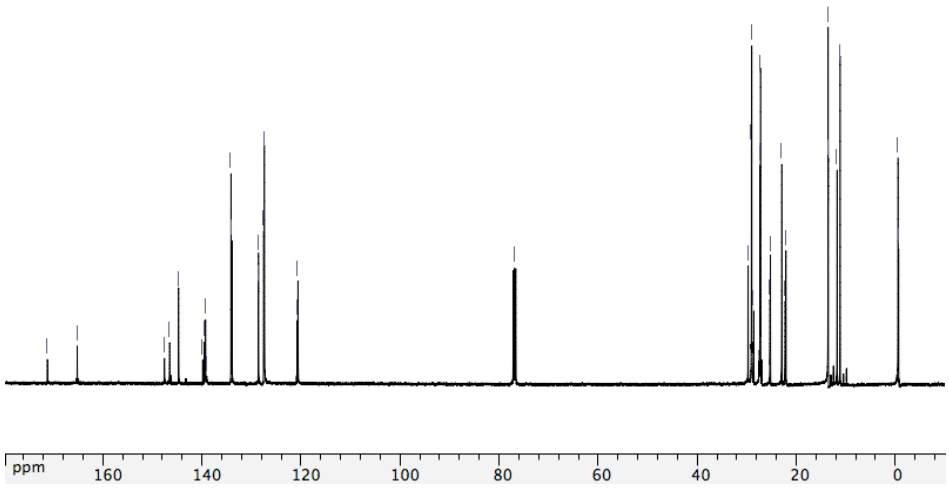

ppm
160
140
120
100
80
60
40
20
0

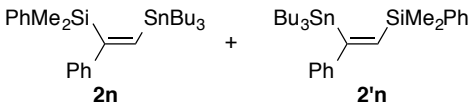

PhMe2Si
SnBu3
+
Bu3Sn
SiMe2Ph

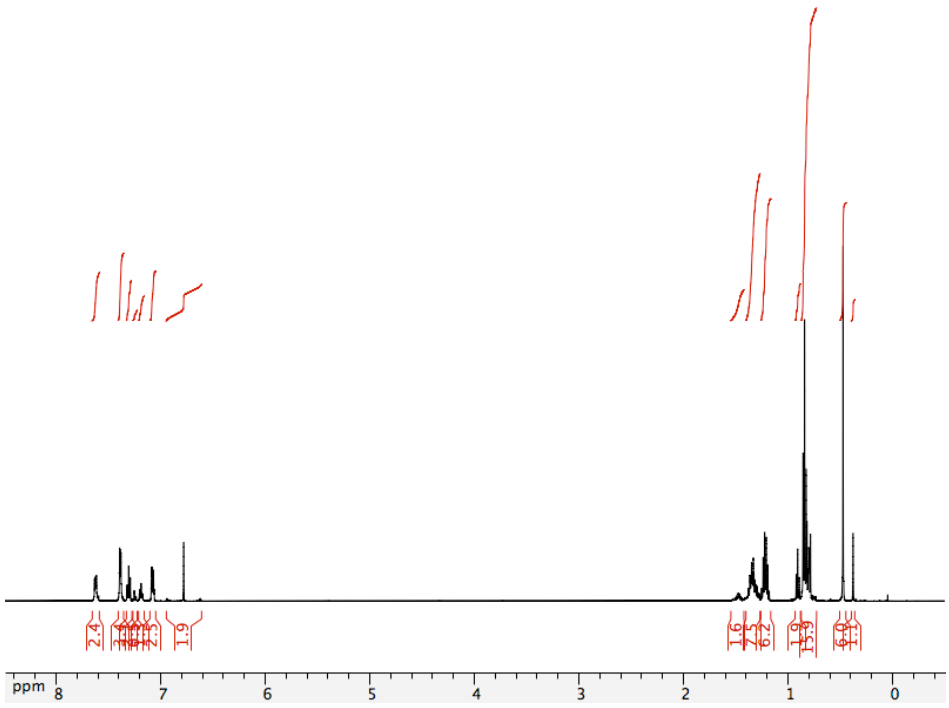
2m **2'm**

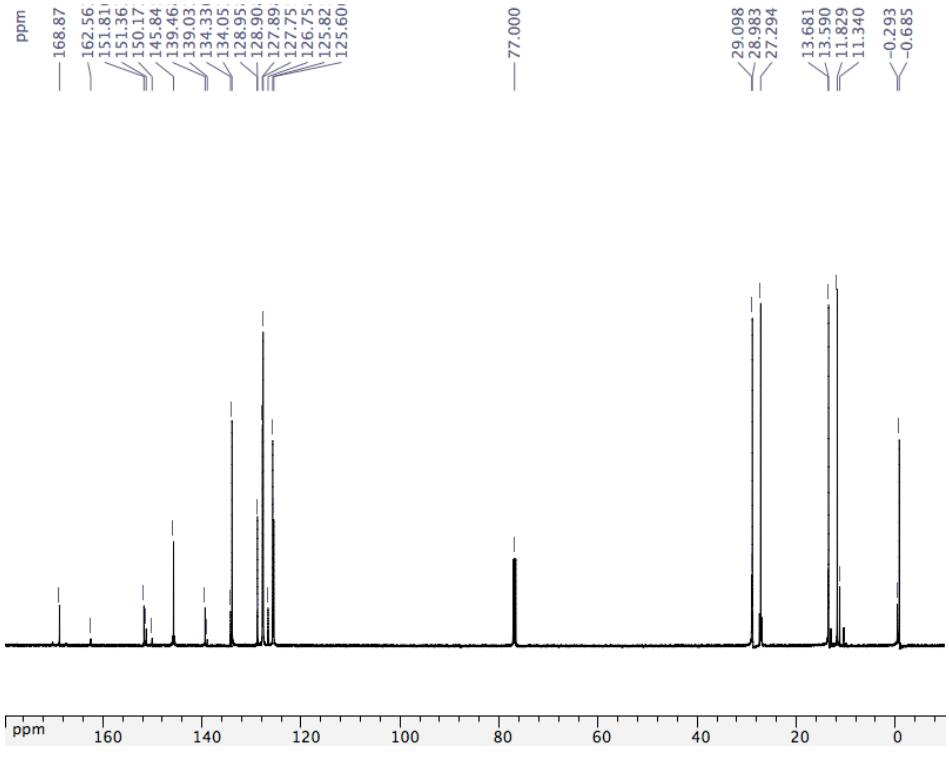

2.0
3.1
1.0
0.4
1.8
2.8
1.0
10.3
6.2
15.3
6.0
ppm
8
7
6
5
4
3
2
1
0

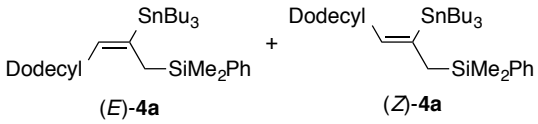

ppm
171.30
165.29
147.69
146.63
144.82
139.95
139.61
139.38
139.15
134.24
134.02
128.72
128.69
127.64
127.50
120.90
120.71
77.000
29.848
29.156
29.104
28.697
27.423
27.323
25.423
25.336
23.041
22.364
22.201
13.685
13.653
11.868
11.259
-0.433
-0.548


ppm
160
140
120
100
80
60
40
20
0

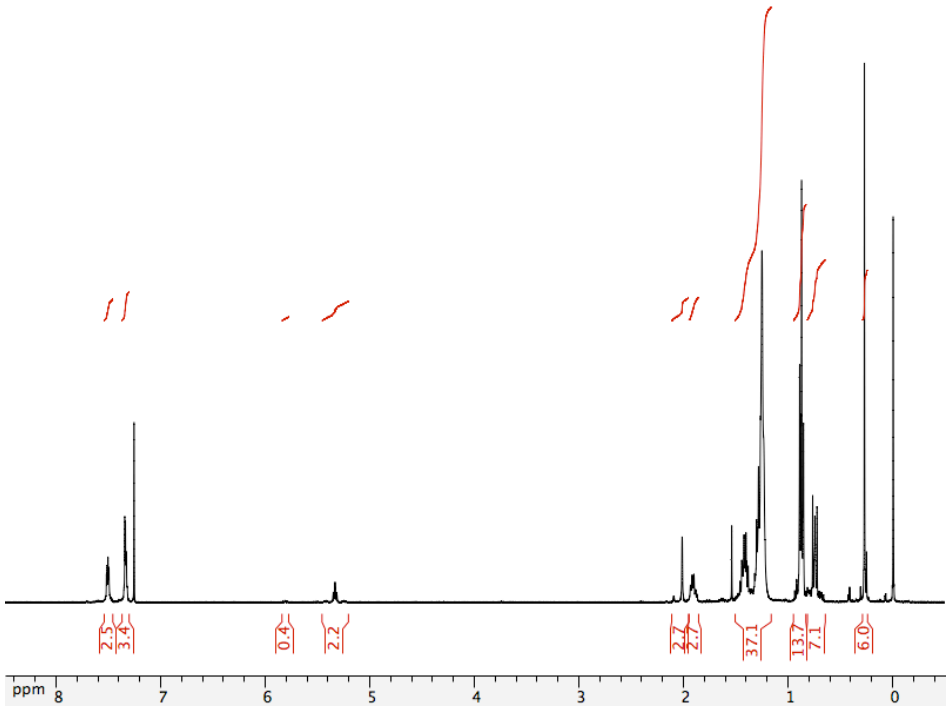

PhMe2Si
SnBu3
Ph
2n
+
Bu3Sn
SiMe2Ph
Ph
2'n


2.4
1.9
1.6
7.5
6.2
1.9
15.9
6.0
4.1
ppm
8
7
6
5
4
3
2
1
0

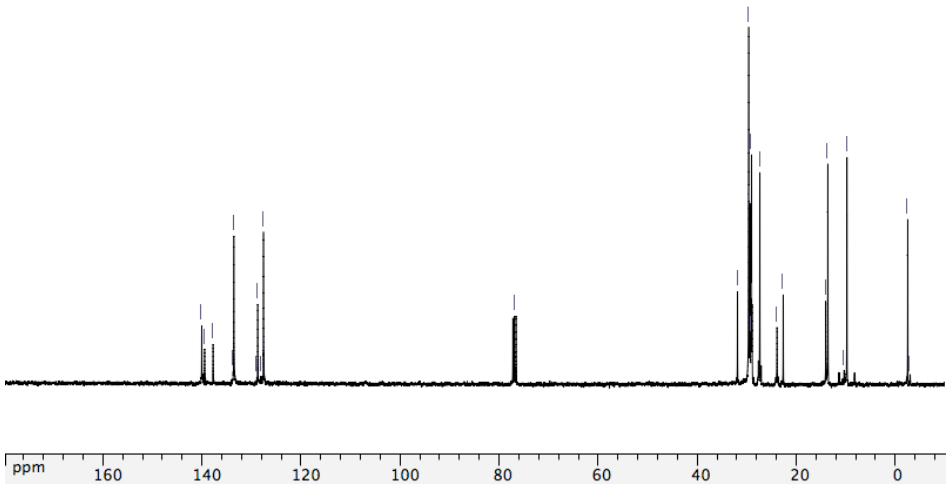

ppm
168.87
162.56
151.81
151.36
150.17
145.84
139.46
139.03
134.33
134.05
128.95
128.90
127.89
127.75
126.75
125.82
125.60
77.000
29.098
28.983
27.294
13.681
13.590
11.829
11.340
-0.293
-0.685
ppm
160
140
120
100
80
60
40
20
0

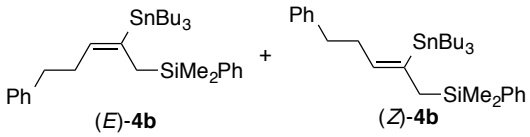

SnBu3
Dodecyl
SiMe2Ph
+
Dodecyl
SnBu3
SiMe2Ph

(*E*)-**4a** (*Z*)-**4a**

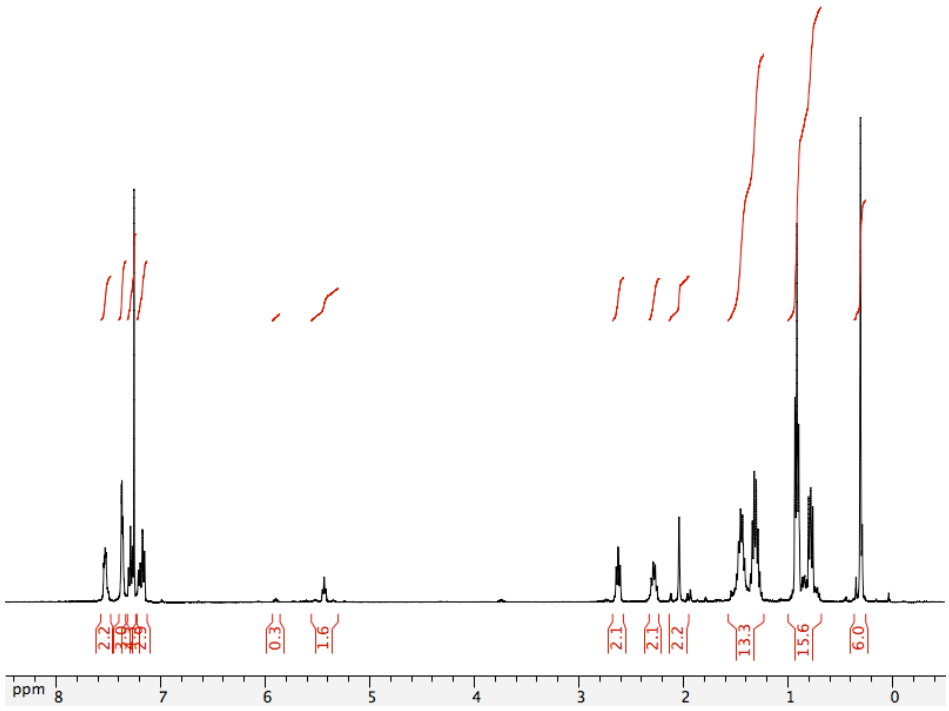

2.5
3.4
0.4
2.2
2.7
2.7
37.1
13.7
7.1
6.0
ppm
8
7
6
5
4
3
2
1
0


ppm
140.15
139.57
137.87
133.80
133.66
129.02
128.86
128.21
127.69
127.62
77.000
31.982
29.717
29.429
29.251
29.144
29.015
27.475
24.008
22.741
14.150
13.736
10.459
9.886
-2.396
-2.882

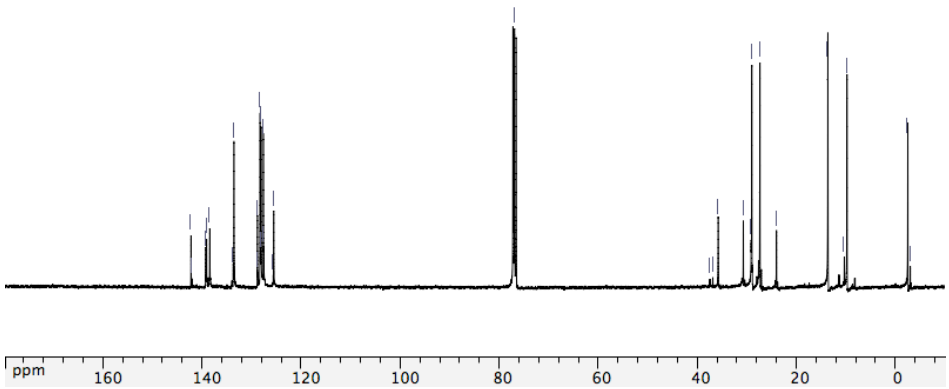

ppm
160
140
120
100
80
60
40
20
0

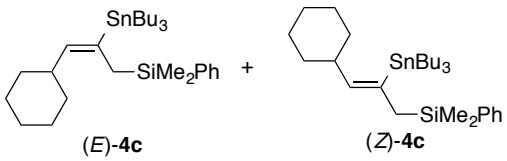

SnBu3
SiMe2Ph
Ph
+
Ph
SnBu3
SiMe2Ph

(*E*)-**4b** (*Z*)-**4b**

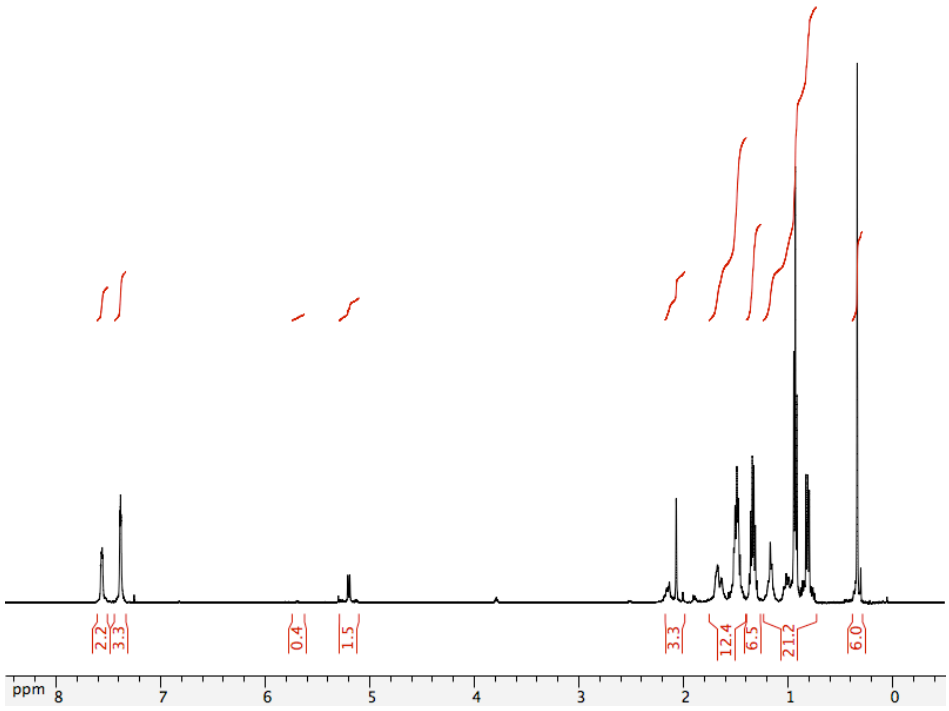

2.2
0.3
1.6
2.1
2.1
2.2
13.3
15.6
6.0
ppm
8
7
6
5
4
3
2
1
0


ppm
142.32
142.09
139.36
139.17
138.53
133.80
133.64
128.91
128.82
128.39
128.29
128.16
127.70
127.63
125.70
125.61
77.000
37.557
36.962
35.880
30.799
29.229
29.084
27.447
24.111
13.741
10.412
9.861
-2.402
-2.908

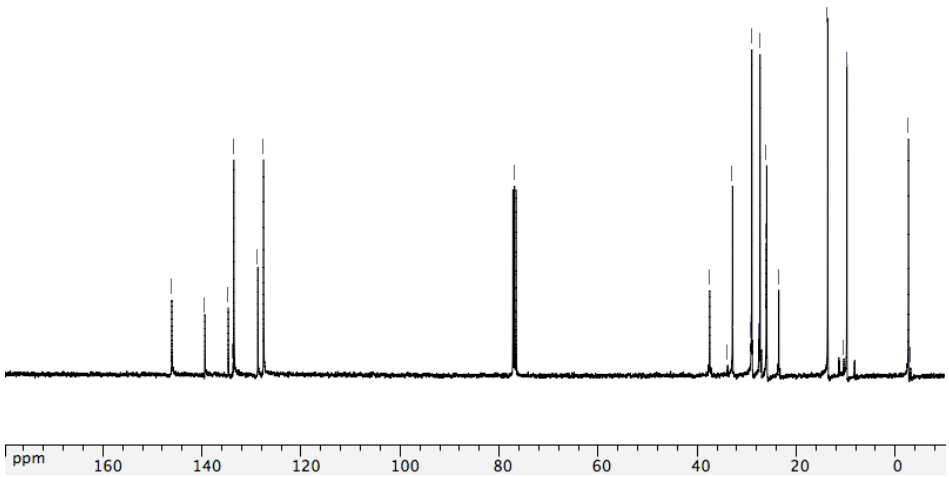

ppm
160
140
120
100
80
60
40
20
0

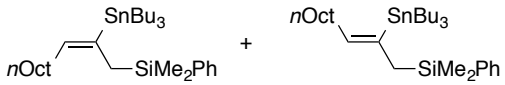

SnBu3
SiMe2Ph
+
SnBu3
SiMe2Ph

(*E*)-**4c** (*Z*)-**4c**

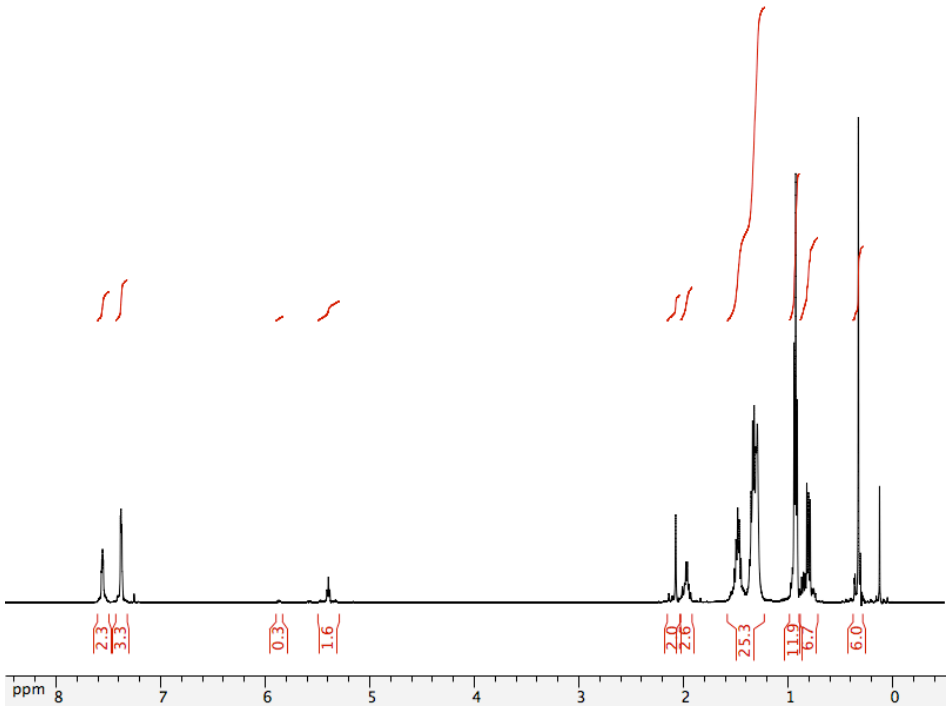

2.2
3.3
0.4
1.5
3.3
12.4
6.5
21.2
6.0
ppm
8
7
6
5
4
3
2
1
0


ppm
146.20
139.53
134.80
133.83
133.66
128.83
127.68
77.000
37.591
33.979
32.975
29.274
29.084
27.563
27.414
26.172
26.082
23.639
13.752
10.505
9.887
-2.540
-2.979

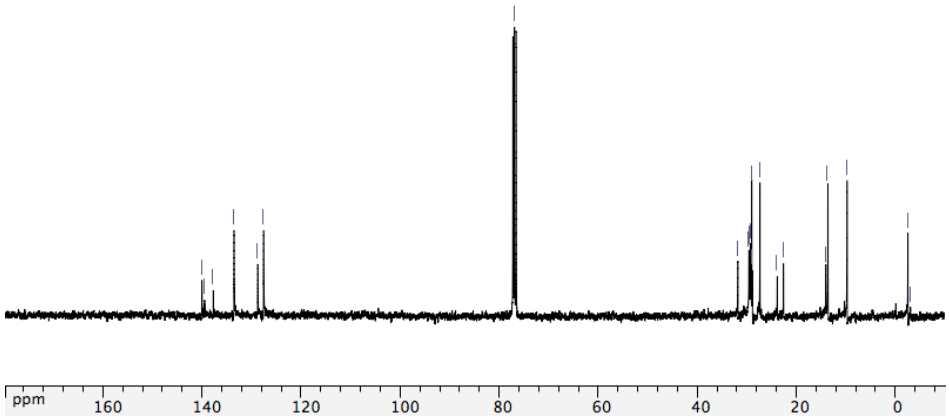

ppm
160
140
120
100
80
60
40
20
0

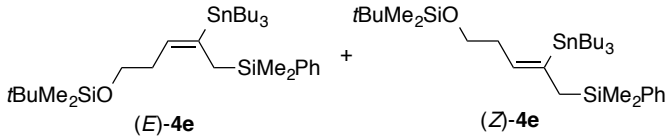

SnBu3
nOct
SiMe2Ph
+
nOct
SnBu3
SiMe2Ph

(*E*)-**4d** (*Z*)-**4d**

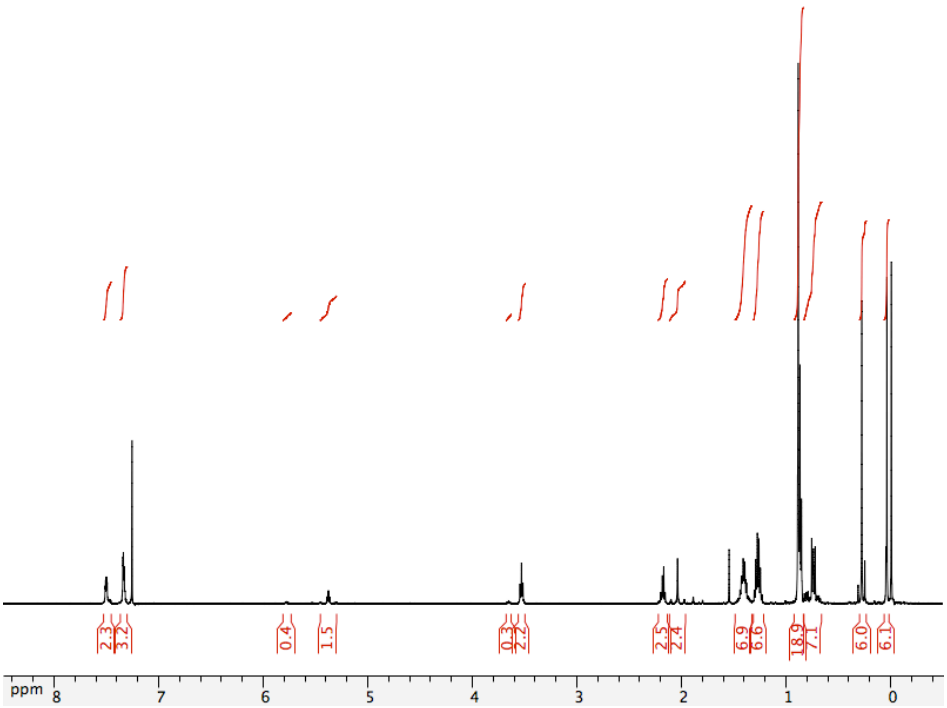

2.3
3.3
0.3
1.6
2.0
2.6
25.3
11.9
6.7
6.0
ppm
8
7
6
5
4
3
2
1
0

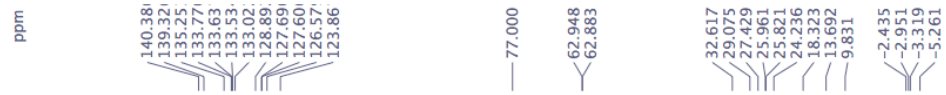

ppm
140.12
139.57
137.81
133.63
128.84
127.66
77.000
31.904
29.657
29.586
29.396
29.337
29.106
28.972
27.444
23.951
22.694
14.128
13.730
9.843
-2.425
-2.916

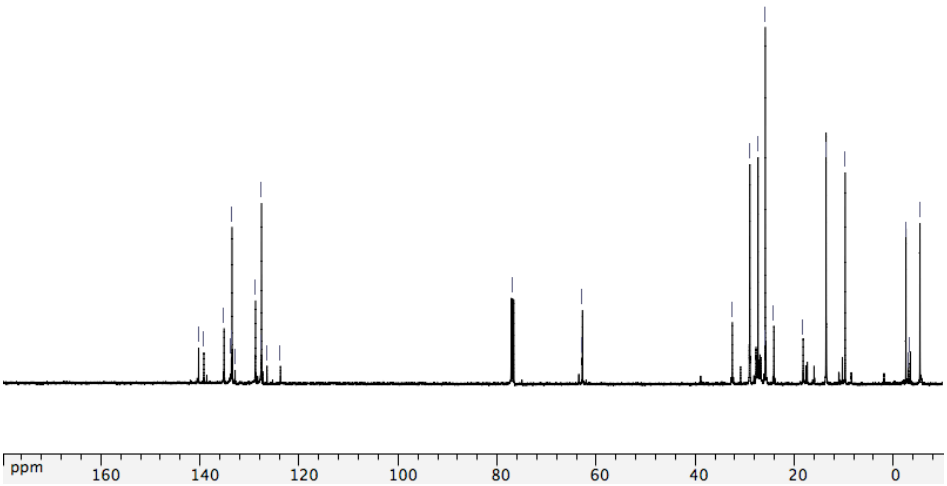

ppm
160
140
120
100
80
60
40
20
0

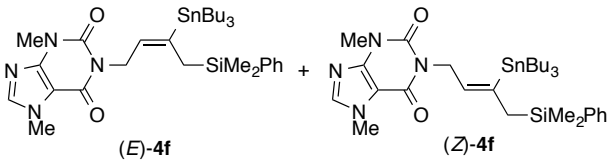

SnBu3
tBuMe2SiO
SiMe2Ph
+
tBuMe2SiO
SnBu3
SiMe2Ph

(*E*)-**4e** (*Z*)-**4e**

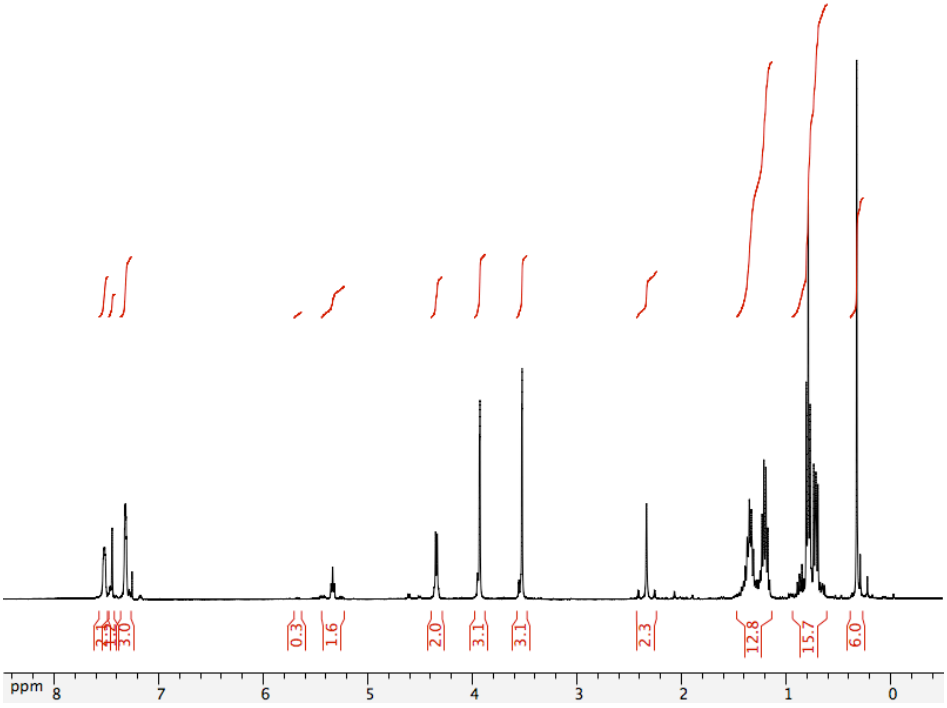

2.3
3.2
0.4
1.5
0.3
2.2
2.5
2.4
6.9
6.6
18.9
7.1
6.0
6.1
ppm
8
7
6
5
4
3
2
1
0

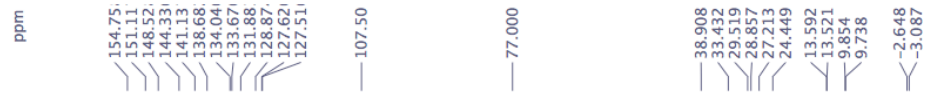

ppm
140.38
139.32
135.25
133.77
133.63
133.53
133.02
128.89
127.69
127.60
126.57
123.86
77.000
62.948
62.883
32.617
29.075
27.429
25.961
25.821
24.236
18.323
13.692
9.831
-2.435
-2.951
-3.319
-5.261

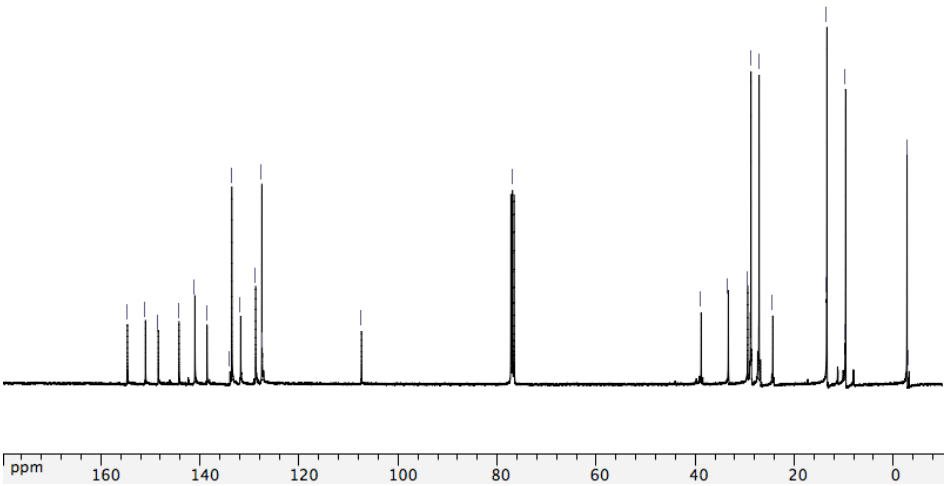

ppm
160
140
120
100
80
60
40
20
0

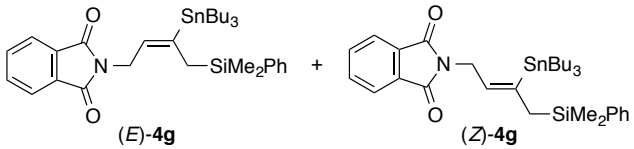

MeN
O
N
N
Me
O
SnBu3
SiMe2Ph
+
MeN
O
N
N
Me
O
SnBu3
SiMe2Ph

(*E*)-**4f** (*Z*)-**4f**

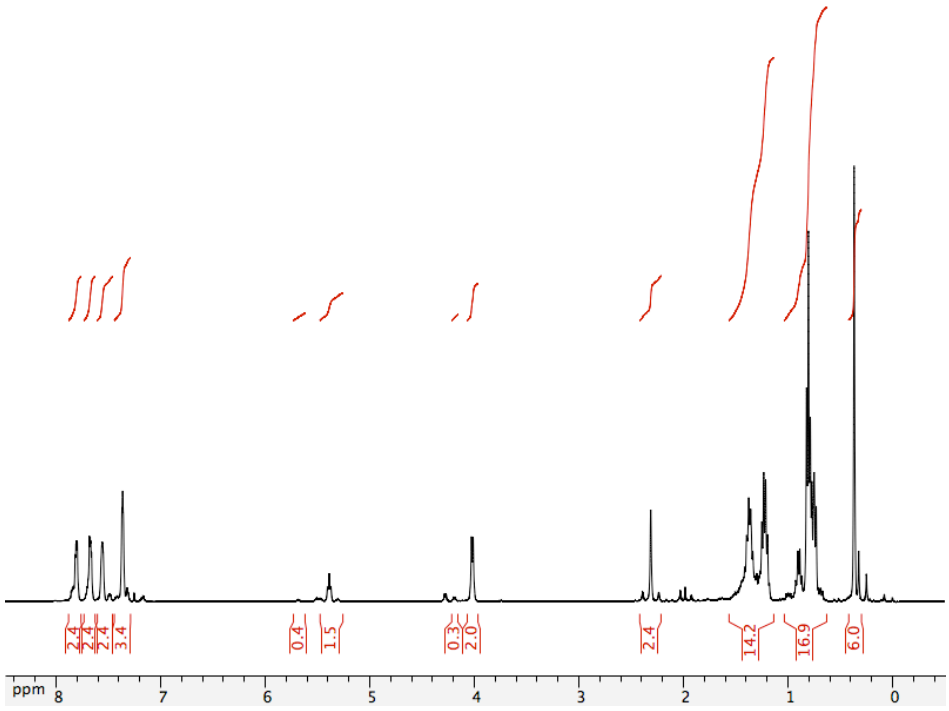

2.1
1.3
3.0
0.3
1.6
2.0
3.1
3.1
2.3
12.8
15.7
6.0
ppm
8
7
6
5
4
3
2
1
0


ppm
154.75
151.11
148.52
144.33
141.13
138.68
134.04
133.67
131.88
128.87
127.62
127.51
107.50
77.000
38.908
33.432
29.519
28.857
27.213
24.449
13.592
13.521
9.854
9.738
-2.648
-3.087

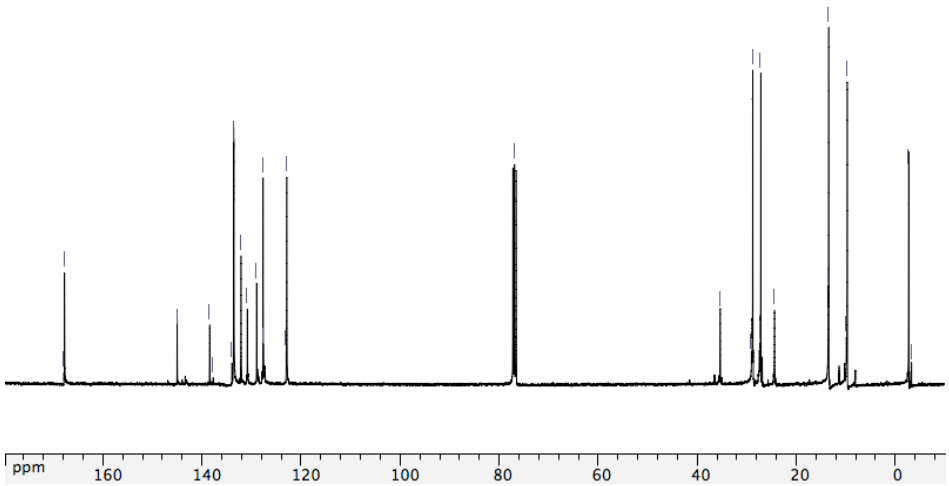

ppm
160
140
120
100
80
60
40
20
0

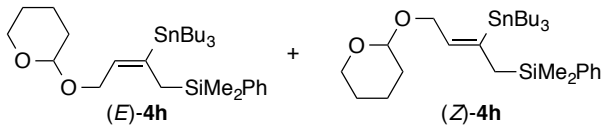

O
N
O
SnBu3
SiMe2Ph
+
O
N
O
SnBu3
SiMe2Ph

(*E*)-**4g** (*Z*)-**4g**

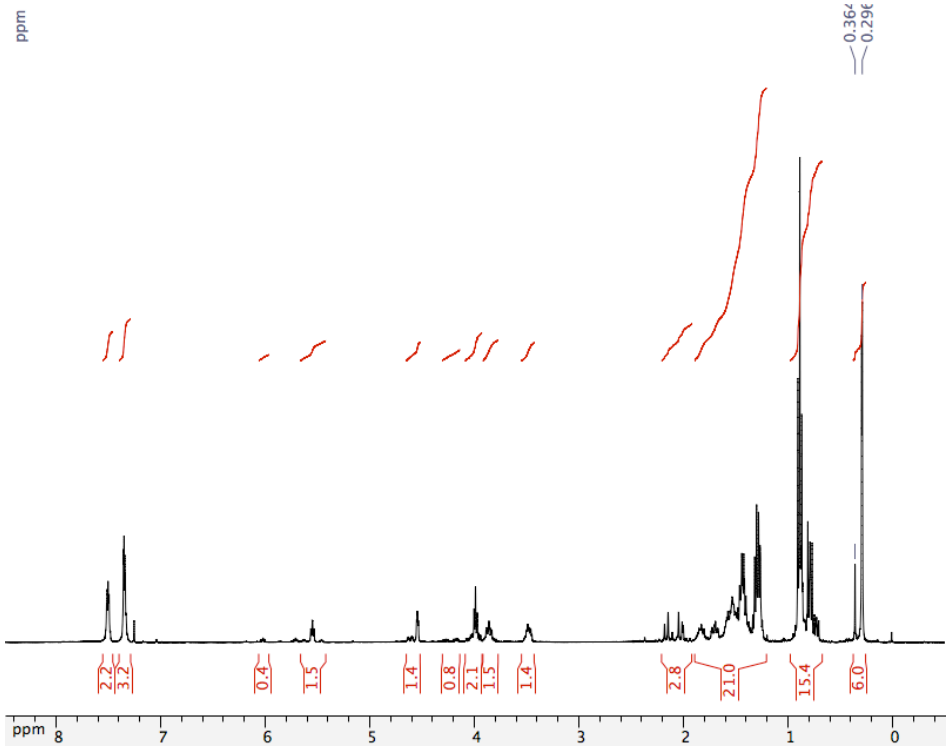

2.4
2.4
2.4
3.4
0.4
1.5
0.3
2.0
2.4
14.2
16.9
6.0
ppm
8
7
6
5
4
3
2
1
0

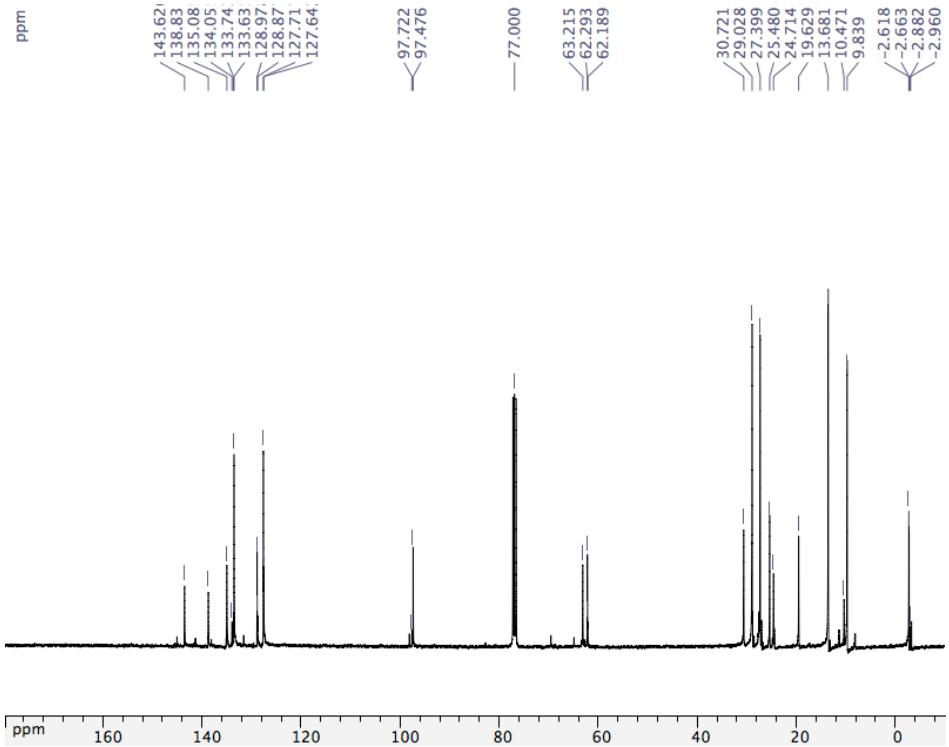

ppm
167.97
167.86
145.12
138.55
137.83
134.04
133.71
133.66
132.22
130.94
129.06
127.77
127.66
127.44
123.09
122.98
77.000
35.467
29.158
28.898
27.403
27.273
24.505
13.659
13.570
9.988
9.820
-2.607
-3.157


ppm
160
140
120
100
80
60
40
20
0


SnBu3
SiMe2Ph
+
SnBu3
SiMe2Ph

(*E*)-**4h** (*Z*)-**4h**


ppm
0.364
0.298
2.2
3.2
0.4
1.5
1.4
0.8
2.1
1.5
1.4
2.8
21.0
15.4
6.0
ppm
8
7
6
5
4
3
2
1
0


ppm
143.62
138.83
135.08
134.05
133.74
133.63
128.97
128.87
127.71
127.64
97.722
97.476
77.000
63.215
62.293
62.189
30.721
29.028
27.399
25.480
24.714
19.629
13.681
10.471
9.839
-2.618
-2.663
-2.882
-2.960
ppm
160
140
120
100
80
60
40
20
0