# SUPPORTING INFORMATION

**Interligand Interactions Dictate the Regioselectivity of *trans*-Hydrometallations and Related Reactions Catalyzed by [Cp*RuCl]. Hydrogen Bonding to a Chloride Ligand as a Steering Principle in Catalysis**

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## Crystallographic Information

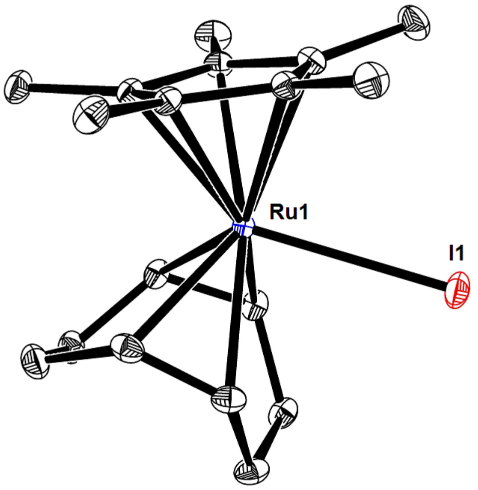



**Figure S-1**. Structure of [Cp*RuI(cod)] in the solid state[1]

**X-ray Crystal Structure Analysis of [Cp*RuI(cod)]**: $C_{18}$ $H_{27}$ I Ru, $M_r$ = 471.36 g · mol$^{-1}$, orange plate, crystal size 0.28 x 0.22 x 0.08 mm, triclinic, space group *P1*, *a* = 8.9058(14) Å, *b* = 9.1793(15) Å, *c* = 12.254(2) Å, $\alpha$ = 71.447(3)°, $\beta$ = 84.938(2)°, $\gamma$ = 63.920(2)°, *V* = 851.5(2) Å$^3$, *T* = 100 K, *Z* = 2, $D_{calc}$ = 1.839 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 2.723 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.55, $T_{max}$ = 0.82), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 1.756° < $\theta$ < 34.971°, 29615 measured reflections, 7464 independent reflections, 6815 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.016 [$I > 2\sigma(I)$], $wR_2$ = 0.041, 289 parameters, H atoms riding, *S* = 1.113, residual electron density +0.8 / -1.2 Å$^{-3}$.

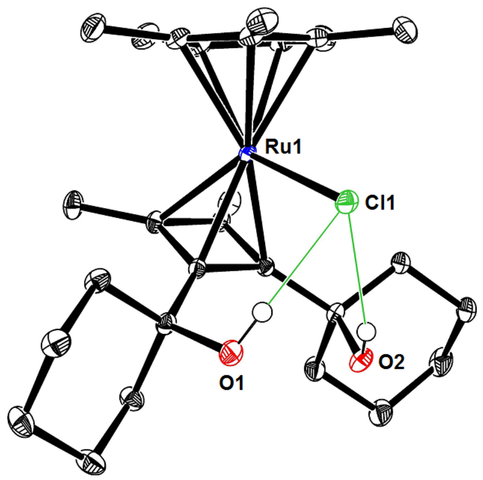



**Figure S-2**. Structure of complex **10a** in the solid state; co-crystallized $CH_2Cl_2$ is not shown for clarity. The position of the H-atoms in the hydrogen bonding array were localized on a difference Fourier map; all other hydrogen atoms are omitted for clarity.

**X-ray Crystal Structure Analysis of Complex 10a**: $C_{29} H_{45} Cl_3 O_2 Ru$, $M_r$ = 633.07 g · mol$^{-1}$, orange block, crystal size 0.18 x 0.10 x 0.03 mm, monoclinic, space group *P2₁/c, a* = 16.545(3) Å, *b* = 8.6384(14) Å, *c* = 20.662(3) Å, $\beta$ = 97.279(3)°, *V* = 2929.3(8) Å$^3$, *T* = 100 K, *Z* = 4, $D_{calc}$ = 1.435 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.833 mm$^{-1}$, Semi-empirical absorption correction ($T_{min}$ = 0.63, $T_{max}$ = 0.93), Bruker-AXS Smart APEX-II diffractometer, 2.473° < θ < 30.032°, 63753 measured reflections, 8545 independent reflections, 7053 reflections with *I* > 2σ(*I*). Structure solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.034 [*I* > 2σ(*I*)], $wR_2$ = 0.080, 325 parameters, H atoms riding, *S* = 1.054, residual electron density +1.6 / -1.2 e Å$^{-3}$.

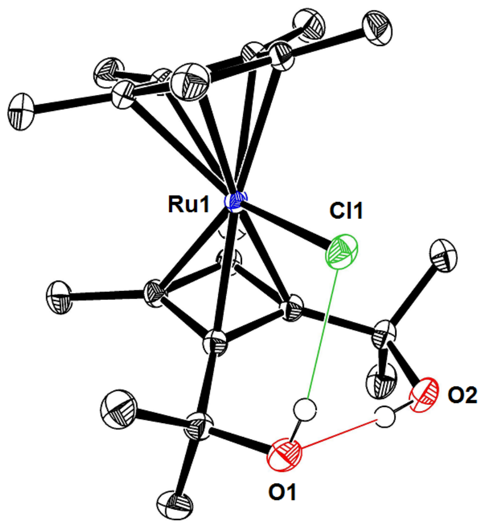



**Figure S-3**. Structure of complex **10b** in the solid state; the position of the H-atoms in the hydrogen bonding array were localized on a difference Fourier map; all other hydrogen atoms are omitted for clarity.

**X-ray Crystal Structure Analysis of Complex 10b**: $C_{22} H_{35} Cl O_2 Ru$, $M_r$ = 468.02 g · mol$^{-1}$, red block, crystal size 0.11 x 0.09 x 0.06 mm, monoclinic, space group *P2₁/n*, *a* = 8.4479(4) Å, *b* = 16.3891(4) Å, *c* = 15.7906(11) Å, $\beta$ = 97.620(5)°, *V* = 2166.96(19) Å$^3$, *T* = 100 K, *Z* = 4, $D_{calc}$ = 1.435 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.860 mm$^{-1}$, Semi-empirical absorption correction ($T_{min}$ = 0.91, $T_{max}$ = 0.95), Nonius KappaCCD diffractometer, 2.732 < θ < 38.074°, 64195 measured reflections, 11848 independent reflections, 10480 reflections with *I* > 2σ (*I*). Structure solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.037 [*I* > 2σ(*I*)], $wR_2$ = 0.102, 251parameters, H atoms riding, *S* = 1.051, residual electron density +4.3 / -2.5 e Å$^{-3}$.

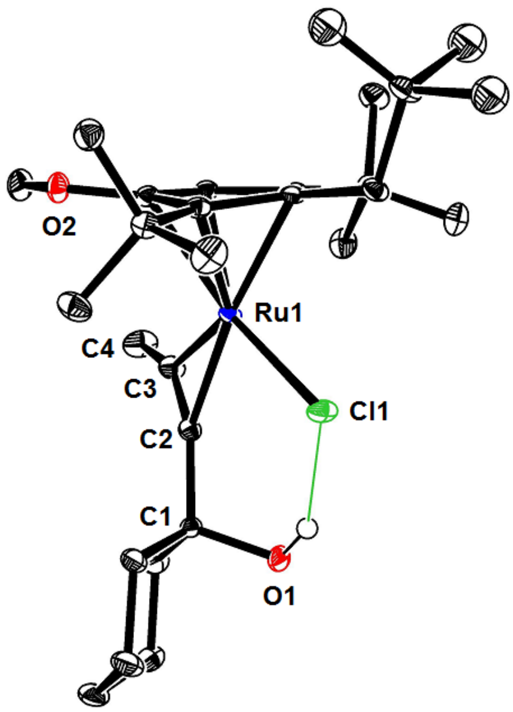



**Figure S-4**. Structure of complex **11** in the solid state; the disorder of the CH2CMe3 substituent on the cyclopentadienyl ring is not shown for clarity

**X-ray Crystal Structure Analysis of Complex 11**: $C_{28}$ $H_{47}$ Cl $O_2$ Ru, $M_r$ = 552.17 g · mol$^{-1}$, orange block, crystal size 0.10 x 0.07 x 0.02 mm, monoclinic, space group $P2_1/c$, $a$ = 13.386(3) Å, $b$ = 13.440(3) Å, $c$ = 15.706(3) Å, $\beta$ = 108.401(4)°, $V$ = 2681.2(9) Å$^3$, $T$ = 100 K, $Z$ = 4, $D_{calc}$ = 1.368 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.706 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.93, $T_{max}$ = 0.99), Bruker-AXS Smart APEX-II diffractometer, 2.313° < θ < 31.059°, 61963 measured reflections, 8501 independent reflections, 6739 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.031 [$I > 2\sigma(I)$], $wR_2$ = 0.069, 301 parameters, H atoms riding, $S$ = 1.026, residual electron density +0.8 / -1.2 e Å$^{-3}$.

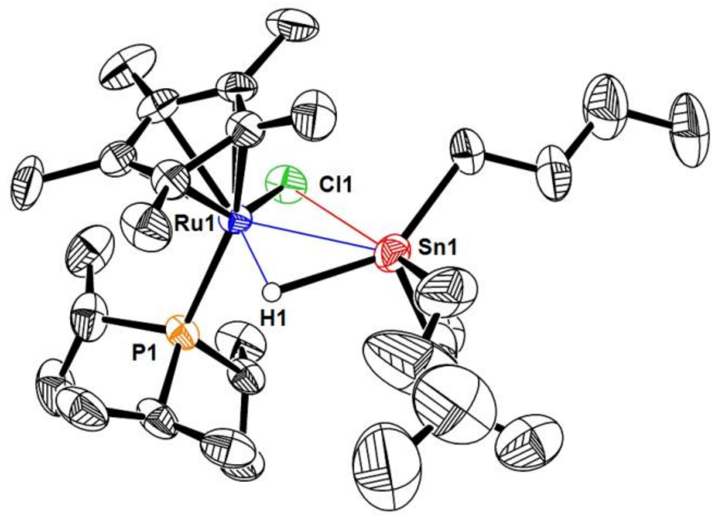



**Figure S-5**. Structure of complex **12a** in the solid state.

**X-ray Crystal Structure Analysis of Complex 12a**: $C_{31}H_{64}ClPRuSn$, $M_r$ = 732.00 g · mol$^{-1}$, orange plate, crystal size 0.40 x 0.04 x 0.01 mm, monoclinic, space group $P2_1/n$, $a$ = 12.986(3) Å, $b$ = 18.957(4) Å, $c$ = 15.039(3) Å, $\beta$ = 108.169(4)°, $V$ = 3517.5(12) Å$^3$, $T$ = 200 K, $Z$ = 4, $D_{calc}$ = 1.365 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu$($Mo$-$K_\alpha$) = 1.278 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.78, $T_{max}$ = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.495° < $\theta$ < 26.372°, 72405 measured reflections, 7181 independent reflections, 4959 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.054 [$I > 2\sigma(I)$], $wR_2$ = 0.176, 325 parameters, H atoms riding, $S$ = 1.099, residual electron density +1.0 / -1.7 Å$^{-3}$.

**General**. Unless stated otherwise, all reactions were carried out under Argon in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents and were transferred under Argon: THF, $Et_2O$ (Mg/anthracene), $CH_2Cl_2$, $CH_3CN$ ($CaH_2$), hexane, toluene (Na/K), EtOH, MeOH (Mg). Flash chromatography: Merck silica gel 60 (40-63 µm).

MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). Accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

NMR spectra were recorded on Bruker DPX 300, AV VIII 300, 400, 500 or 600 spectrometers in the solvents indicated; chemical shifts ($\delta$) are given in ppm relative to TMS, coupling constants ($J$) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C$ = 77.00 ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H$ = 7.26 ppm; $CD_2Cl_2$: $\delta_C$ = 53.8 ppm; residual $CHDCl_2$ in $CD_2Cl_2$: $\delta_H$ = 5.32 ppm); proton and carbon assignments were established using NOESY, HSQC, and HMBC experiments.

For clarity, Sn–H couplings of the vinylic protons were omitted in the multiplet analysis, but are given in brackets (averaged over $^{117/119}Sn$); in the stannane complexes, they are taken from the $^{119}Sn$ satelites.

$^{119}Sn$ NMR spectra were recorded on a Bruker AV VIII 300, 400 or 500 spectrometer using $Me_4Sn$ as external standard.

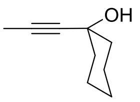
$\alpha$:$\beta$ is used to denote the ratio of the regioisomers formed by proximal:distal delivery of the $R_3M$-residue (M = Si, Ge, Sn)

Unless stated otherwise, all commercially available compounds were used as received. [Cp*Ru($CH_3CN$)$_3$]$PF_6$,[2] [(Cp*Ru$Cl_2$)$_n$],[3] [(Cp*RuCl)$_4$],[4] and [Cp*Ru(*i*Pr$_3$P)Cl][5] were prepared according to literature procedures and were stored under Argon. [Cp*Ru(cod)Cl] was purchased from Strem and stored under Ar.

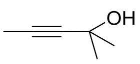
Commercial $Bu_3SnH$ is stabilized with 0.05% of 3,5-di-*tert*-butyl-4-hydroxytoluene, which was not removed in any of the reactions described herein. $Me_3SnH$ was prepared according to a literature procedure.[6]

## Reference data for the alkyne substrates

**1-(Propynyl)cyclohexanol (8a).** $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ = 1.88 (s, 1H, O*H*), 1.83 (s, 3H, *H$_3$*C-C≡C), 1.81 – 1.09 (m, 11H, $CH_2$ cyclohexyl); $^{13}C\{^1H\}$ NMR (75 MHz, $CD_2Cl_2$, RT) δ = 83.6 ($H_3$C-C≡*C*-), 80.0 ($H_3$C-*C*≡C-) , 68.8 (cyclohexyl ipso *C*-OH), 40.7 ($CH_2$-cyclohexyl), 25.7 ($CH_2$-cyclohexyl), 23.7 ($CH_2$-cyclohexyl), 3.5 (C—*C*$H_3$).



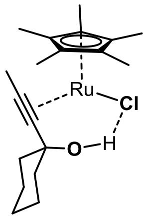
**2-Methylpent-3-yn-2-ol (8b).** $^1H$ NMR (300 MHz $CD_2Cl_2$) δ = 2.44 (s, 1H), 1.79 (s, 3H), 1.43 (s, 7H); $^{13}C$ NMR (126 MHz, $CD_2Cl_2$, RT) δ = 84.8 (oct., *J* = 5 Hz, $H_3$C-C≡*C*- ), 78.0 (q, *J* = 10.2 Hz, $H_3$C-*C*≡C-), 65.4 (dq, *J* = 4.3, 1 Hz, $Me_2$*C*-OH,), 31.9 (qd, *J* = 127.6, 4.2 Hz, *Me$_2$*C-OH), 3.5 (q, *J* = 131.4 Hz).



## Ruthenium Complexes

**[Cp*Ru(cod)I]**. 1,5-Cyclooctadiene (0.19 mL, 1.6 mmol) was added to a solution of [{Cp*RuI}$_4$][7] (428 mg, 0.29 mmol) in THF (6.5 mL) and the resulting mixture was stirred for 1 h. The mixture was filtered, the filtrate was evaporated and the solid residue triturated with pentane (5 mL). The resulting orange solid was washed with pentane (2 x 3 mL) and dried to yield [Cp*Ru(cod)I] as an orange solid (87 %, 486 mg, 1.03 mmol). Single crystals suitable for X-ray diffraction were grown by cooling a solution of [Cp*Ru(cod)I] (40 mg) in $Et_2O$ (2 mL) from 10 → –70 °C over the course of 38 h. $^1H$ NMR (400 MHz, $CD_2Cl_2$): δ = 4.02 – 3.88 (m, 2H), 3.82 – 3.71 (m, 2H), 2.76 – 2.63 (m, 2H), 2.24 – 2.07 (m, 4H), 2.00 – 1.89 (m, 2H), 1.75 ppm (s, 15H); $^{13}C$ NMR (101 MHz, $CD_2Cl_2$): δ = 95.2, 81.7, 78.4, 32.0, 30.1, 11.3 ppm.

**[Cp*Ru{$H_3C$–C≡C–(cyclohexyl)OH}Cl] (9b)**. 1-(Propynyl)cyclohexanol **8a** (17.3 mg, 0.125 mmol) was added to a solution of $[Cp*RuCl]_4$ **4** (34 mg, 0.0312 mmol) in $CD_2Cl_2$ (0.6 mL), causing an instant color change from brown to cherry-red. Full conversion to the title compound was noted by NMR spectroscopy. $^1H$ NMR (400 MHz, $CD_2Cl_2$, RT) δ = 5.07 (s, 1H), 2.77 (s, 3H), 1.72 (s, 15H), 1.71 – 1.11 (m, 11H; $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$, RT) δ = 154.7 ($H_3C$-C≡C), 130.1 ($H_3C$-C≡C), 89.5 (Cp*), 74.2 (cyclohexyl ipso *C*-OH), 39.3 (*C*$H_2$-cyclohexyl), 26.1 (*C*$H_2$-cyclohexyl), 22.77 (*C*$H_2$-cyclohexyl), 14.85 (C—*C*$H_3$), 10.42 (*C*$H_3$ of Cp*).



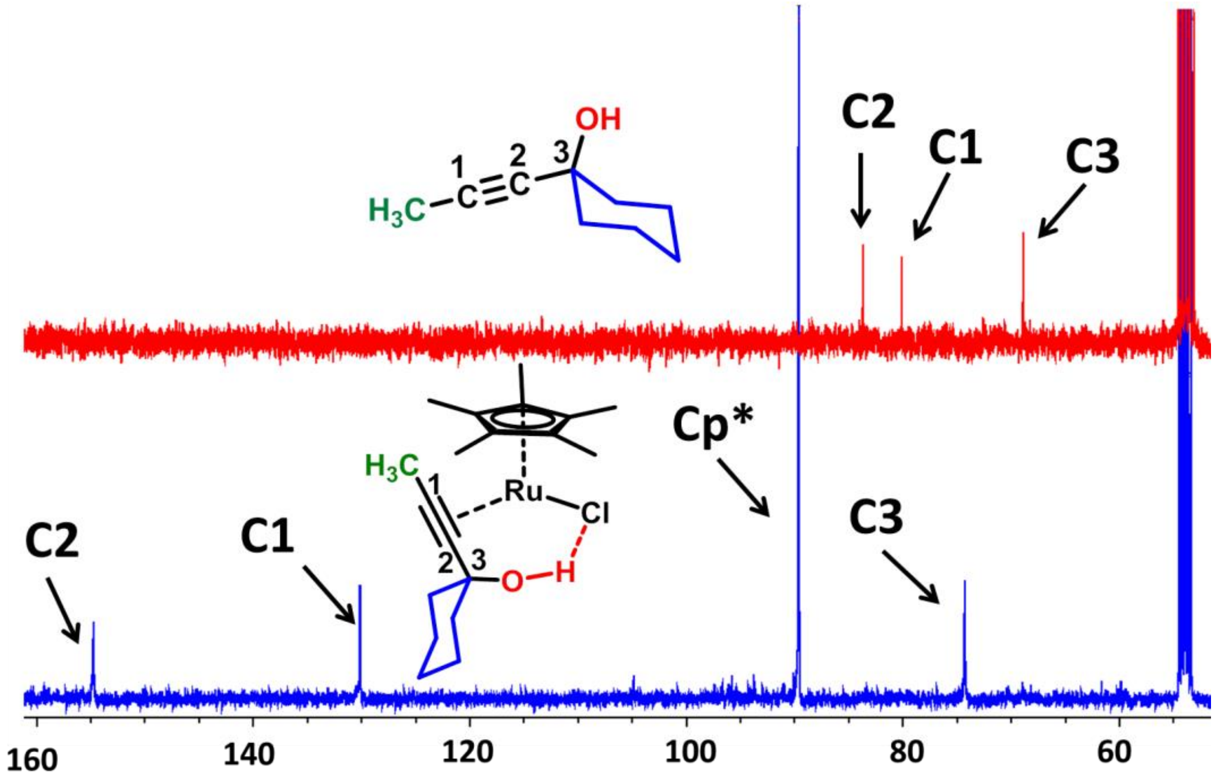
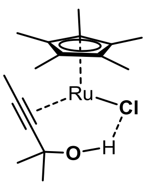



**Figure S-6**. Low-field region of the $^{13}C$ NMR spectrum ($CD_2Cl_2$) of the propargyl alcohol **8a** (top) and the putative complex **9a** (bottom), which shows the massive deshielding of the alkyne C-atoms upon complex formation; arbitrary numbering scheme as shown.

**[Cp*Ru{$H_3C$–C≡C–$(CH_3)_2$OH}Cl]** (**9a**). Prepared analogously. $^1H$ NMR (400 MHz, $CD_2Cl_2$) δ = 5.31 (s, 1H, O*H*), 2.71 (s, 3H, C≡C-C*$H_3$*), 1.73 (s, 15H, Cp*), 1.38 (s, 6H, (C*$H_3$*)$_2$OH ); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$) δ = 155.8 ($H_3C$-C≡C)), 130.5 ($H_3C$-C≡C), 89.8 (Cp*), 72.3 (Me$_2$*C*-OH), 68.1 (residual THF), 30.9 (*Me*$_2$C-OH), 26.0 (residual THF), 14.2 (C≡C-C*$H_3$*), 10.4 (*C*$H_3$ of Cp*).



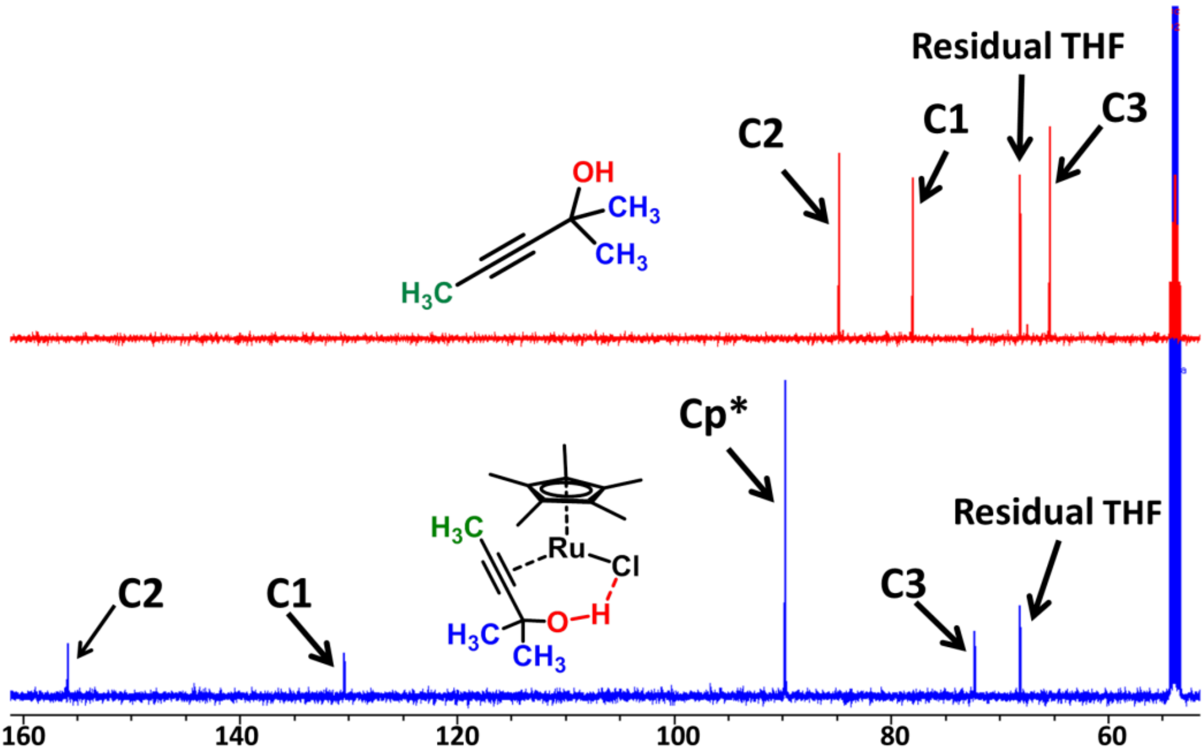
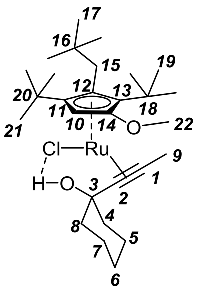
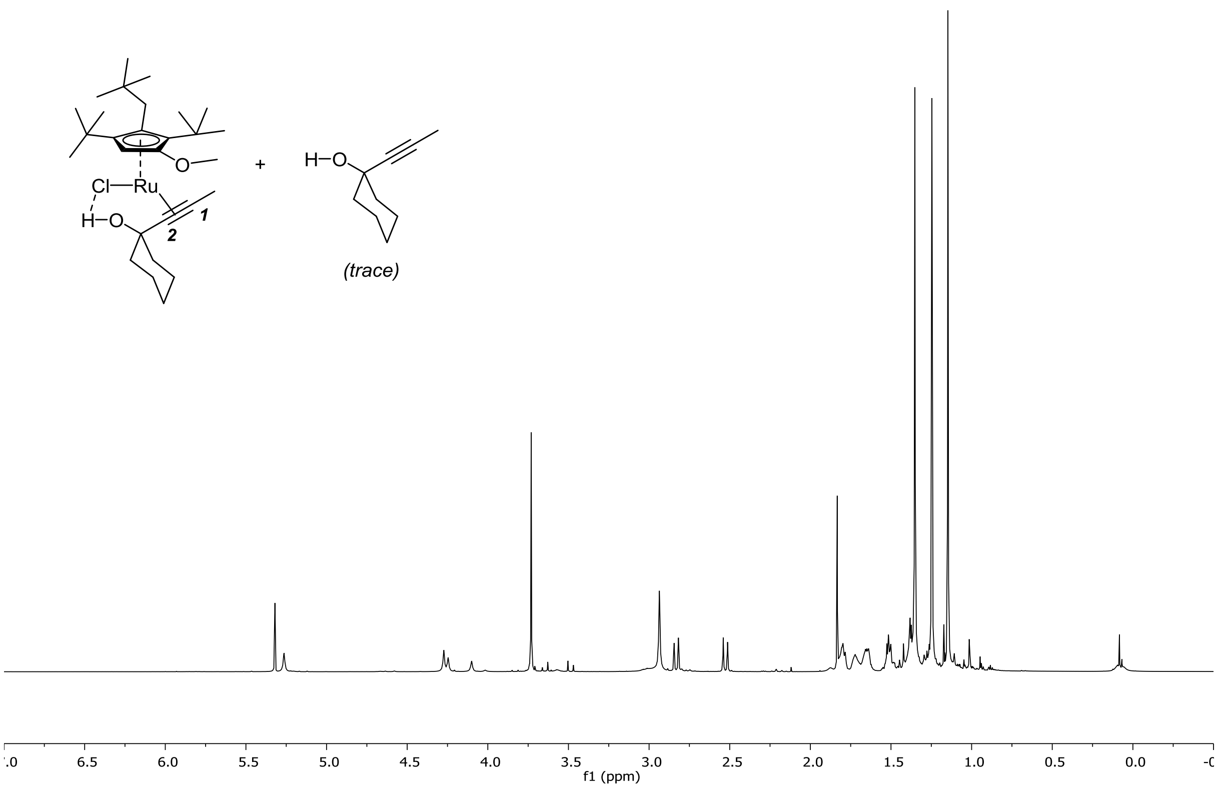



**Figure S-7**. Low-field region of the $^{13}C$ NMR spectrum ($CD_2Cl_2$) of the propargyl alcohol **8b** (top) and the putative complex **9b** (bottom), which shows the massive deshielding of the alkyne C-atoms upon complex formation; arbitrary numbering scheme as shown.



**Complex 11.** A mixture of [{Cp^RuCl}$_2$] (20.8 mg, 0.025 mmol, 1.0 equiv) and 1-(1-propynyl)cyclohexanol (7.0 mg, 0.51 mmol, 2.0 equiv) was dissolved in dry and degassed $CD_2Cl_2$ (0.7 mL) and the resulting violet mixture was analyzed by NMR. $^1H$ NMR (600 MHz, $CD_2Cl_2$): δ = 5.26 (s, 1H, O–H), 4.27 (s, 1H, H10), 3.73 (s, 3H, H22), 2.94 (s, 3H, H9), 2.83 (d, *J* = 16.1 Hz, 1H, H15a), 2.53 (d, *J* = 16.1 Hz, 1H, H15b), 1.83–1.37 (m, 10H), 1.35 (s, 9H, H19), 1.25 (s, 9H, H21), 1.15 (s, 9H, H17); $^{13}C$ NMR (151 MHz, $CD_2Cl_2$): δ = 150.3 (C2), 129.1 (C14), 123.0 (C1), 102.3 (C12), 93.7 (C11), 86.8 (C13), 74.5 (C3), 64.7 (C10), 60.3 (C22), 39.92 (C4/C8), 39.86 (C4/C8), 36.5 (C15), 33.6 (C18), 32.61 (C20), 32.55 (C17), 32.12 (C16), 32.08 (C21), 31.3 (C19), 23.9 (C6), 23.32 (C5/C7), 23.28 (C5/C7), 17.5 (C9). Single crystals suitable for X-ray diffraction were obtained by slowly cooling such a mixture to –78°C.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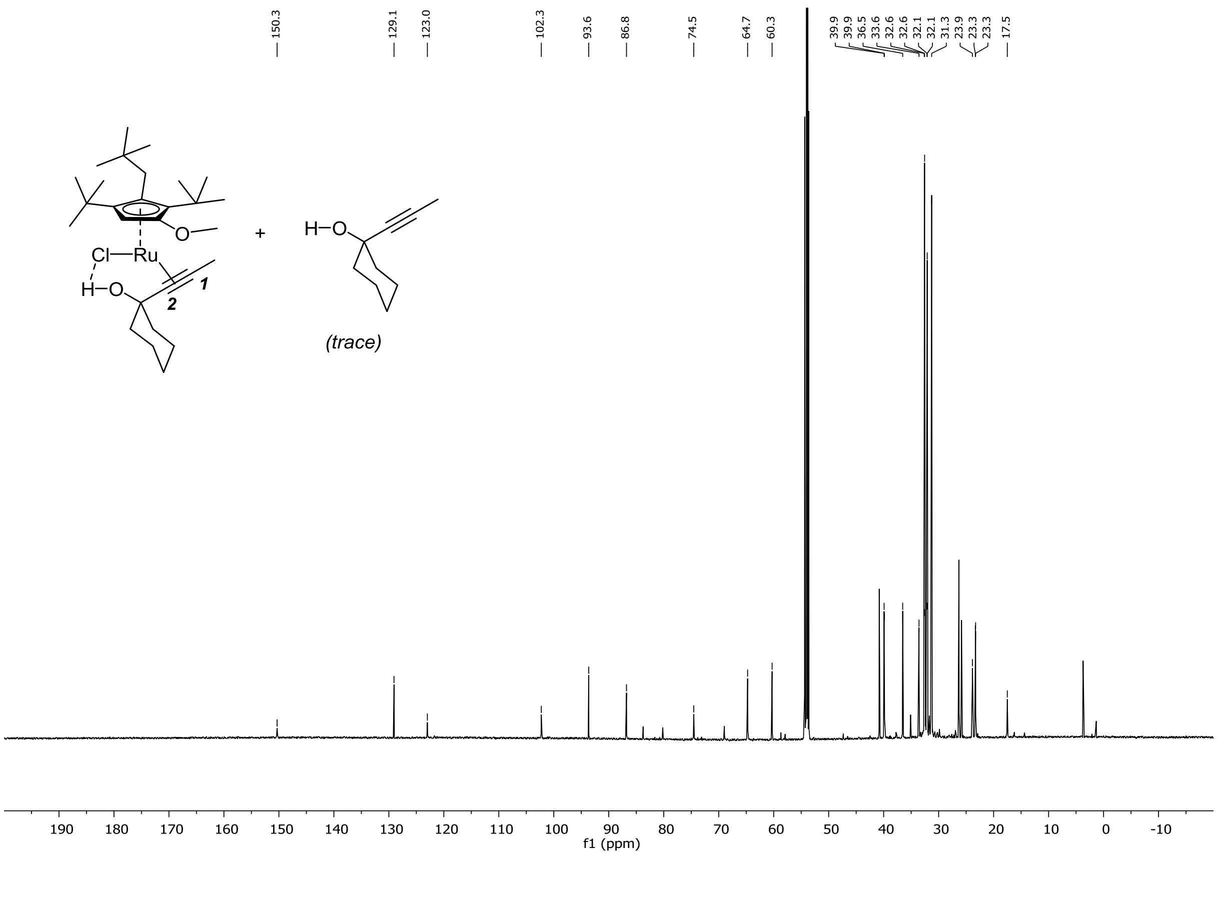
2
H—O
(trace)
f1 (ppm)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93.6
86.8
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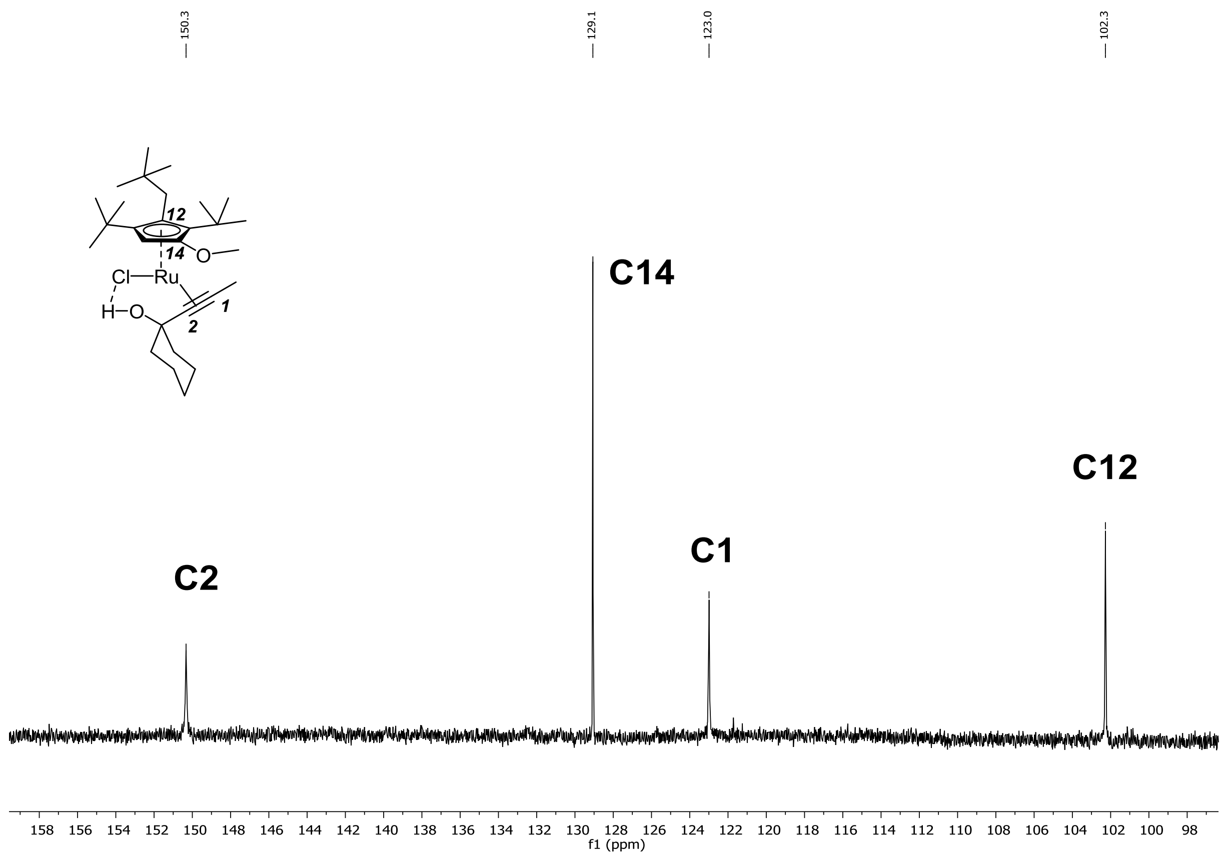
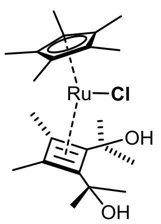
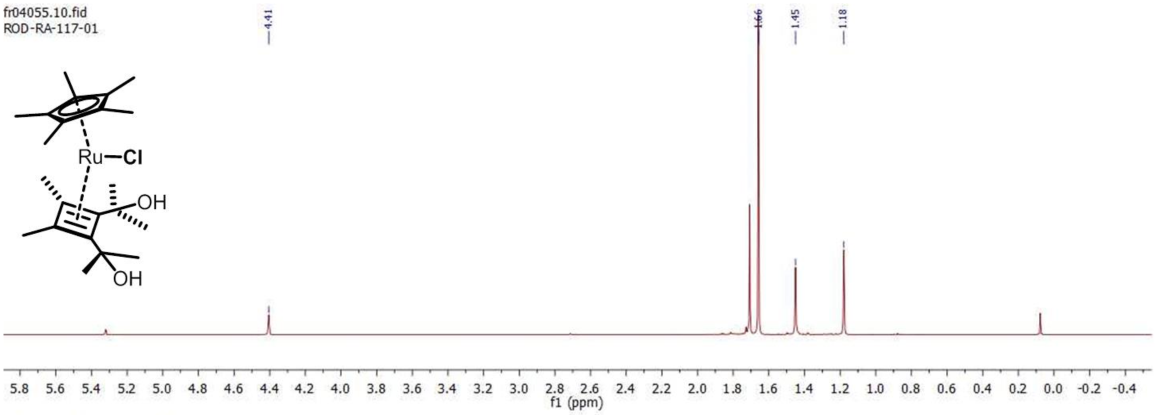
f1 (ppm)

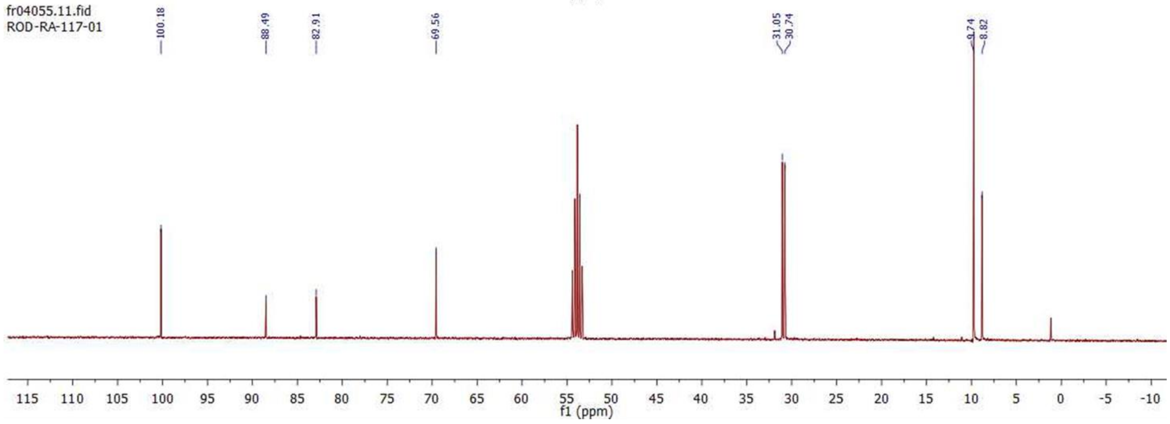



**Complex 10b**. A sample of [Cp*Ru{$H_3C$−C≡C−$(CH_3)_2OH$}Cl] was prepared as described above in the presence of excess alkyne. The resulting mixture was stored at –20 °C for 24 h to give the [2+2] cycloadduct as red crystals suitable for single crystal X-ray diffraction. $^1H$ NMR (400 MHz, $CD_2Cl_2$, RT) δ = 4.41 (s, 1H, O*H*), 4.40 (s, 1H, O*H*) 1.71 (s, 6H, $CH_3$), 1.66 (s, 15H, Me of Cp*), 1.45 (s, 6H, $CH_3$), 1.18 (s, 6H, $CH_3$); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$, RT) δ = 99.0 (Cp*), 87.3 (cyclobutadiene ring), 81.8 (cyclobutadiene ring), 68.4 (*C*$Me_2$OH) , 29.9 (Me of cyclobutadiene, couples with proton 1.18), 29.6 (Me of cyclobutadiene, couples with proton 1.45), 8.6 (Me of Cp*) , 7.7 (Me of cyclobutadiene, couples with proton at 1.71).

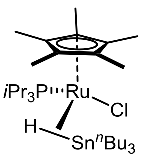



**Complex 10a**. Prepared analogously from [{Cp*RuCl}$_4$] (53 mg, 0.049 mmol) and 1-(1-propynyl)cyclohexanol (81 mg, 0.585 mmol) in $CH_2Cl_2$ (0.25 mL) and pentane (0.25 mL). Slow evaporation of the solvent at RT over the course of 2 d yielded single crystals suitable for X-ray crystallography.

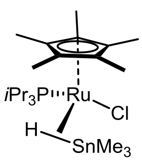


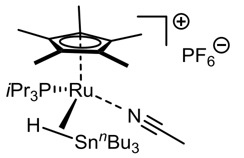

**[Cp*Ru(*i*Pr$_3$P)(σ-HSn$^n$Bu$_3$)Cl] (12a)**. [Cp*Ru(*i*Pr$_3$P)Cl] **16** was generated in an NMR tube by mixing [Cp*RuCl]$_4$ **4** (13.0 mg, 0.0112 mmol) with *i*Pr$_3$P (9.1 µL, 0.0478 mmol) in $CD_2Cl_2$ (0.6 mL). The mixture was then cooled to –50 °C and *n*Bu$_3$SnH (12.9 µL, 0.0478 mmol) was added, promoting a color change from deep blue to orange. The tube was then placed in the probe of an NMR spectrometer pre-cooled to –30 °C. The resulting product **12a** showed the following spectroscopic data:[8] $^1$H NMR (400 MHz, $CD_2Cl_2$, –30 °C) δ = 2.20 (sept, *J* = 7.5 Hz, 3H, *H*C(CH$_3$)$_2$ ), 1.61 (s, 15H, Me of Cp*), 1.54 – 0.74 (m, 45H, $^n$Bu and HC(CH$_3$)$_2$, overlapping), –10.29 (d, $^2J_{PH}$ = 32.3 Hz, $^1J_{SnH}$ = 192 Hz, 1H, Ru (σ-*H*Sn$^n$Bu$_3$); $^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$, –30 °C) δ = 93.3 (Cp*), 30.6 ($^n$Bu), 28.3 ($^n$Bu), 21.1 (d, $J_{CP}$ = 16 Hz) 20.5 ($J_{CP}$ = 13 Hz), 19.9 (br s), 13.8 ($^n$Bu), 12.3 ($^n$Bu), 10.8 (Me of Cp*); $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$, –30 °C) δ = +58.19 (s, $^2J_{SnP}$ = 85 Hz); $^{119}$Sn{$^1$H} NMR (149 MHz, $CD_2Cl_2$, –30 °C) δ = +57.0 (d, $^2J_{SnP}$ = 85 Hz).



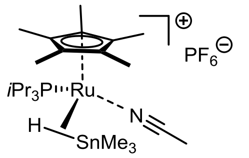

**[Cp*Ru(*i*Pr$_3$P)(σ-HSnMe$_3$)Cl] (12b).** Prepared analogously, using Me$_3$SnH as the reagent.[9] $^1$H NMR (400 MHz, $CD_2Cl_2$, –30 °C) δ = 2.15 (hept, *J* = 7.3 Hz, 3H, *H*CMe$_2$), 1.60 (s, 15H, Cp*), 1.15 (dq, *J* = 16.5, 7.1, 6.5 Hz, 18H), 0.12 (s, 9H, SnMe$_3$), –10.59 (d, $^2J_{PH}$ = 32.8 Hz, 1H, $^1J_{SnH}$ 178 Hz, Ru(σ-*H*SnMe$_3$)); $^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$, –30 °C) δ = 94.6 (d, $^3J_{PC}$ = 2.1 Hz, Cp*), 23.7 (d, $J_{CP}$ = 19.33), 20.7 (br s), 10.7 (Me of Cp*), –3.8 (Sn*Me$_3$* $^1J_{SnC}$ = 249 Hz); $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$, –30 °C) δ = +58.26 ($^1J_{SnP}$ = 78 Hz); $^{119}$Sn{$^1$H} NMR (149 MHz, $CD_2Cl_2$, –30 °C) δ = 23.2 (d, $^2J_{SnP}$ 78 Hz) .



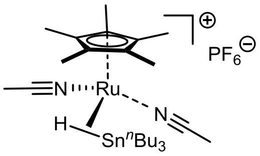
**[Cp*Ru(*i*Pr$_3$P)(σ-HSn$^n$Bu$_3$)(MeCN)]PF$_6$ (13a).** [Cp*Ru(*i*Pr$_3$P)(MeCN)$_2$]PF$_6$ was first generated in an NMR tube by mixing [Cp*Ru(MeCN)$_3$]PF$_6$ (**1**) (9 mg, 0.0178 mmol) with *i*Pr$_3$P (3.4 µL, 0.0178 mmol) in CD$_2$Cl$_2$ (0.6 mL). The mixture was then cooled to –50 °C and *n*Bu$_3$SnH (4.8 µL, 0.0178 mmol) was added, promoting a color change from green-orange to orange. The tube was then placed in the probe of an NMR spectrometer pre-cooled to –40 °C. 80% conversion to **13a** was noted (mixture ca. 7:2:1 between **13a** [Cp*Ru(*i*Pr$_3$P)(MeCN)$_2$]PF$_6$ and free $^n$BuSnH). Characteristic NMR data for **13a**: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, –40 °C) δ = 2.36 (br s, 3H, co-ordinated MeCN), 2.24 – 2.00 (br m, 3H, *H*CMe$_2$), 1.93 (s, 6H, free MeCN), 1.65 (s, 15H, Me of Cp*), 1.45 – 0.70 (m, 45H, HC*Me$_2$* and $^n$Bu overlapping); $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, –40 °C) δ = 130.1 (co-ordinated MeCN) , 117.3 (free MeCN), 94.9 (d, $^3J_{CP}$ = 1.2 Hz, Cp*), 30.1 ($^n$Bu), 27.7 ($^n$Bu) 19.3 (br s), 13.7 (d, $J_{CP}$ = 2.7 Hz, HC*Me$_2$*), 13.6 ($^n$Bu), 13.5 ($^n$Bu) 10.8 (Me of Cp*), 5.1 (free MeCN), 2.2 (co-ordinated MeCN); $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, –40 °C) δ = 60.96 (s, $^2J_{SnH}$ = 97 Hz); $^{119}$Sn{$^1$H} NMR (149 MHz, CD$_2$Cl$_2$, –40 °C) δ = +61.4 (d, $^2J_{SnP}$ = 93 Hz)



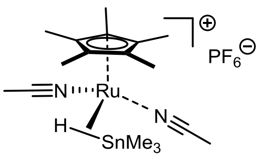

**[Cp*Ru(*i*Pr$_3$P)(σ-HSnMe$_3$)(MeCN)]PF$_6$ (13b).** Prepared analogously to **13a**, using Me$_3$SnH as the reagent. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, –30 °C) δ = 2.47 (d, $^4J_{PH}$ = 1 Hz, 3H, co-ordinated MeCN), 2.13 (br s, 3H, *H*C(CH$_3$)$_2$), 1.98 (s, 6H, free MeCN), 1.72 (s, 15 H), 1.18 (ddd, *J* = 46.0, 13.7, 7.1 Hz, 18H), 0.34 (s, 9H, Sn*Me$_3$*), –9.70 (d, *J* = 29.6 Hz, $^1J_{SnH}$ 284 Hz, 1H, Ru(σ-*H*SnMe$_3$)); $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, –30 °C) δ = 123.0 (co-ordinated MeCN), 117.2 (free MeCN), 95.4 (d, $^3J_{PC}$ = 1.4 Hz, Cp*), 26.9 (d, $J_{CP}$ = 21 Hz) 19.4 (d, $^1J_{PC}$ = 50.6 Hz), 10.7 (Me of Cp*), 5.0 (free MeCN), 2.1 (co-ordinated MeCN) , –4.2 (SnMe$_3$); $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, –30 °C) δ = +61.36 (s, $^2J_{SnP}$ = 98 Hz).

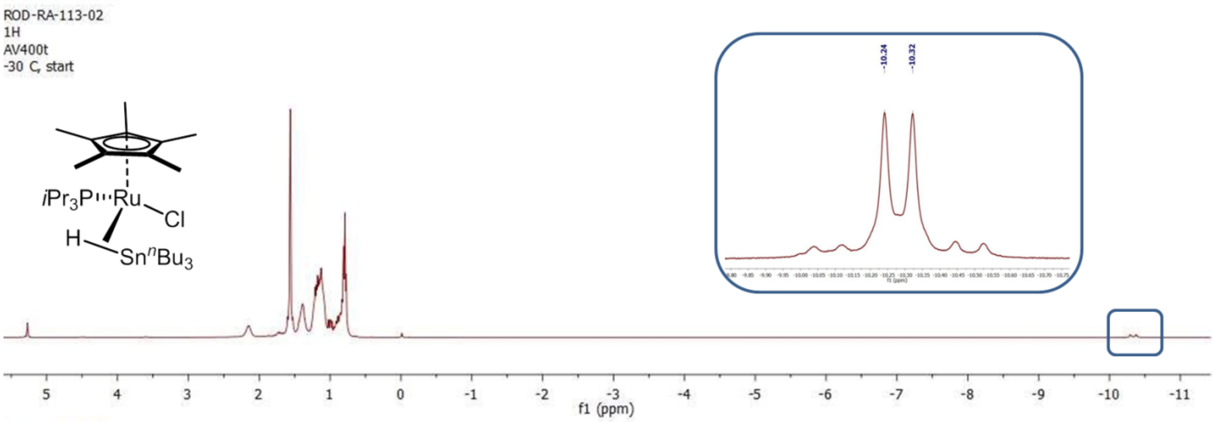



**[Cp*Ru(σ-HSn$^n$Bu$_3$)(MeCN)$_2$]PF$_6$ (14a).** In an NMR tube, *n*Bu$_3$SnH (6.6 µL, 0.0244 mmol) was added to a solution of [Cp*Ru(MeCN)$_3$]PF$_6$ **1** (12.3 mg, 0.0244 mmol) in CD$_2$Cl$_2$ (0.6 mL) at –50 °C. The tube was then placed in the probe of an NMR spectrometer pre-cooled to –30 °C. $^1$H NMR (500 MHz CD$_2$Cl$_2$, –30 °C) δ = 2.42 (s, 6H, co-ordinated MeCN), 1.98 (s, 3H, free MeCN), 1.65 (s, 15H, Cp*), 1.48 – 0.82 (m, 27H, $^n$Bu), -6.47 (s, 1H, $^1J_{SnH}$ 383 Hz, Ru(σ-*H*Sn$^n$Bu$_3$)); $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$, –30 °C) δ = 128.4 (co-ordinated MeCN), 117.3 (free MeCN) 90.9 (Cp*), 30.1 ($^n$Bu $^2J_{SnC}$ = 19.1 Hz), 27.5 ($^n$Bu, $^1J_{SnC}$ = 70.1 Hz), 13.7 ($^n$Bu), 12.3 ($^n$Bu), 9.9 (Me of Cp*), 7.9 (co-ordinated MeCN), 4.3 (free MeCN);$^{119}$Sn{$^1$H} (186 MHz, CD$_2$Cl$_2$, –30 °C) δ = +27.3; $^{31}$P{$^1$H} (202 MHz, CD$_2$Cl$_2$, –30 °C) δ = –144.7 (sept, PF$_6$); $^{19}$F (470 MHz, CD$_2$Cl$_2$, –30 °C) δ = –73.0 (d, $^1J_{PF}$ = 711 Hz).




**[Cp*Ru(σ-HSnMe$_3$)(MeCN)$_2$]PF$_6$ (14a).** Prepared analogously, using Me$_3$SnH as the reagent. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, –30 °C) δ = 2.43 (s, 6H, co-ordinated MeCN), 1.98 (s, 3H, free MeCN), 1.67 (s, 15H, Me of Cp*), 0.32 (s, 9H, SnMe$_3$), –6.38 (s, 1H, $^1J_{SnH}$ = 441 Hz, Ru(σ-*H*Sn$^n$Bu$_3$); $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, –30 °C) δ = 128.3 (co-ordinated MeCN), 91.4 (Cp*) , 9.9 (Me of Cp*) , 4.2 (free MeCN) , 2.1 (co-ordinated MeCN) , –6.5 (SnMe$_3$); $^{119}$Sn{$^1$H} NMR (149 MHz, CD$_2$Cl$_2$, –30 °C) δ = +15.9 ppm.

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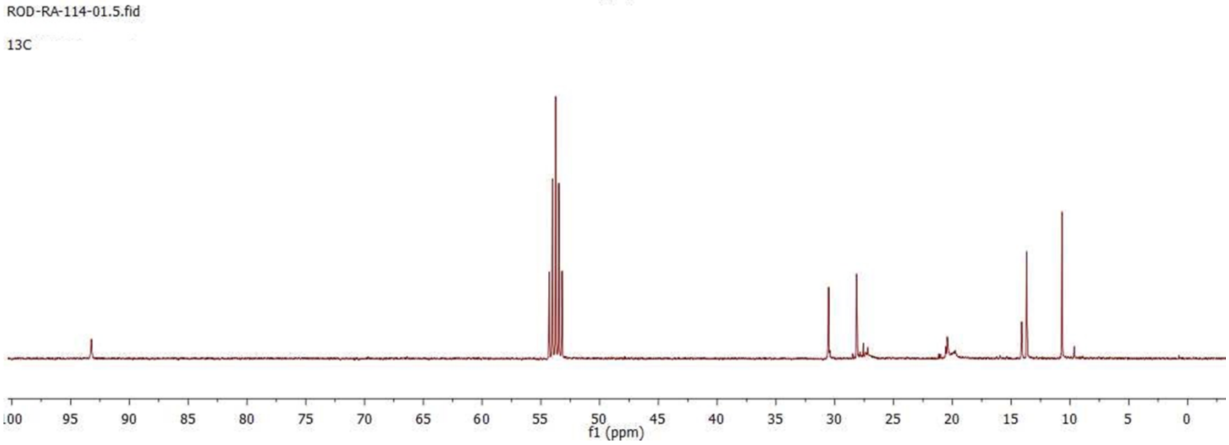
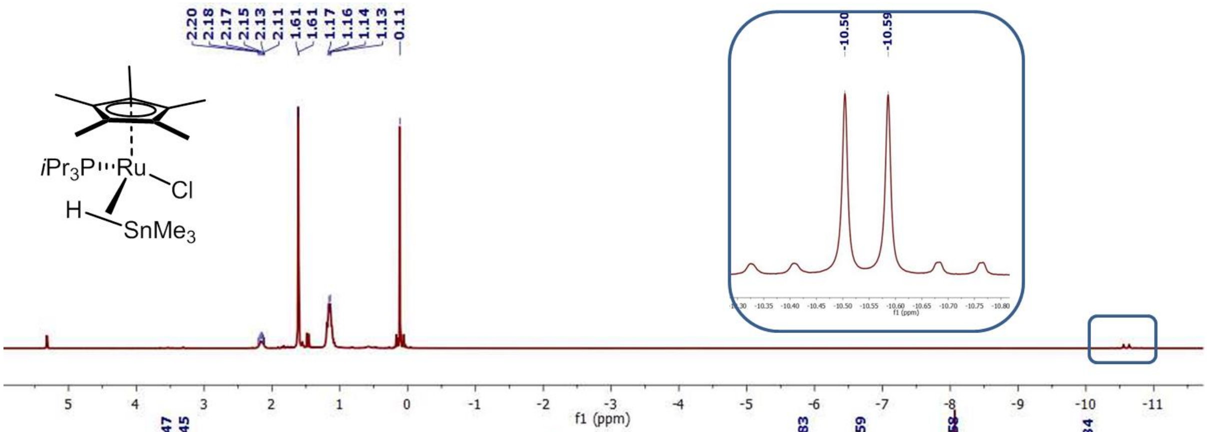
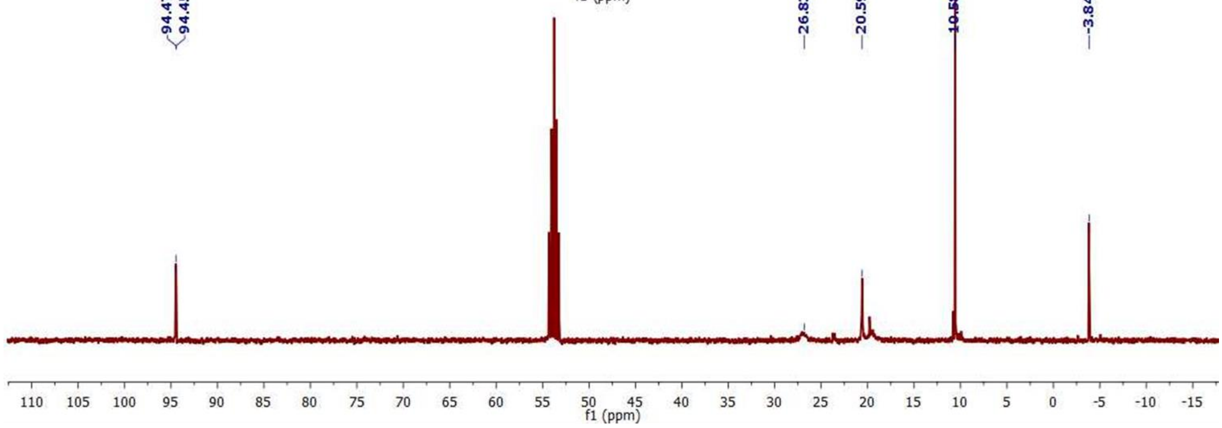
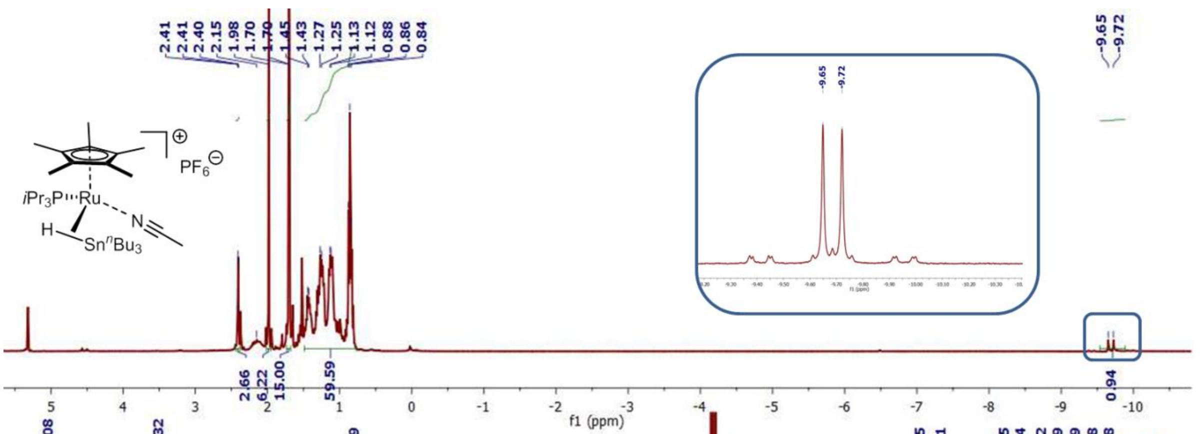
AV400t
-30 C, start
iPr3P Ru Cl
H SnnBu3
-10.24
-10.32
f1 (ppm)


ROD-RA-114-01.5.fid
13C
f1 (ppm)


2.20
2.18
2.17
2.15
2.13
2.11
1.61
1.61
1.17
1.16
1.14
1.13
0.11
iPr3P Ru Cl
H SnMe3
-10.50
-10.59
f1 (ppm)


94.47
94.45
26.83
20.59
10.58
-3.84
f1 (ppm)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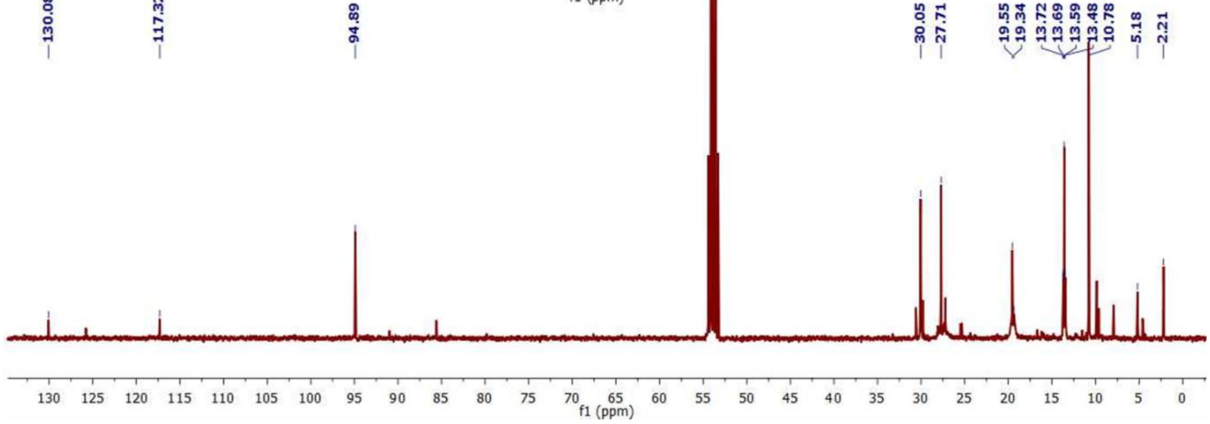
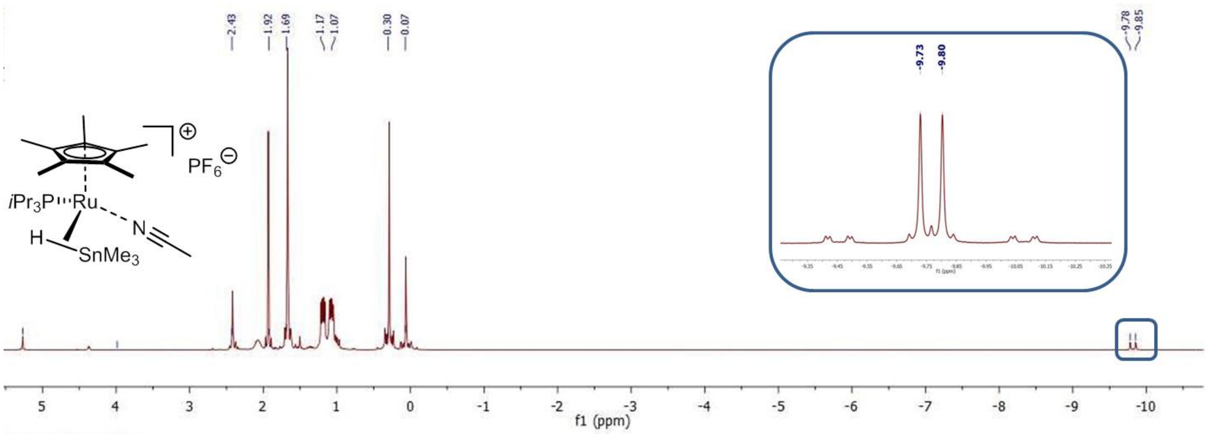
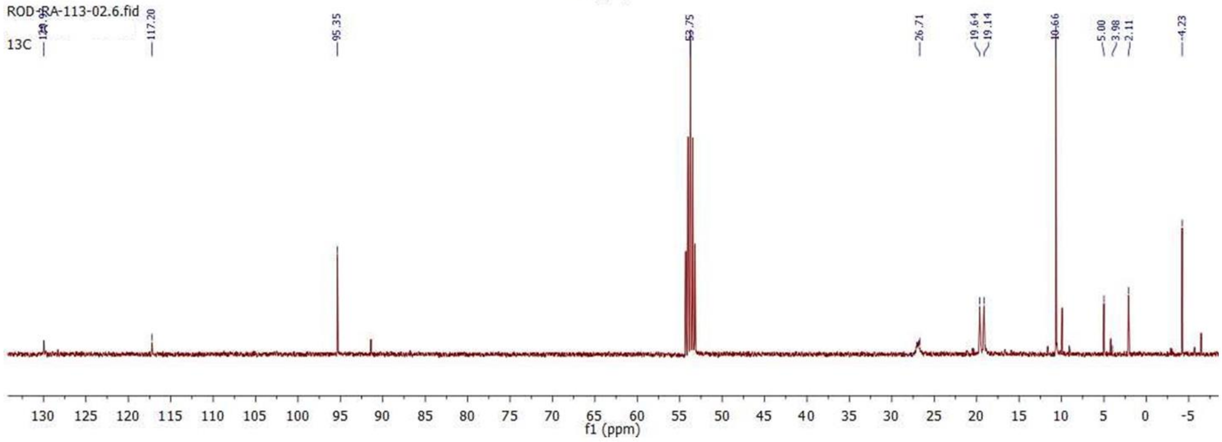
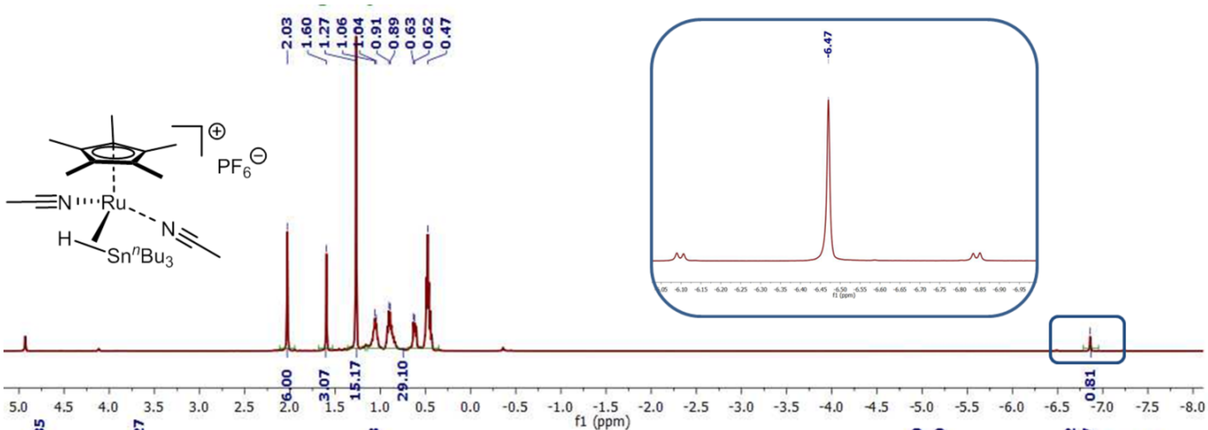
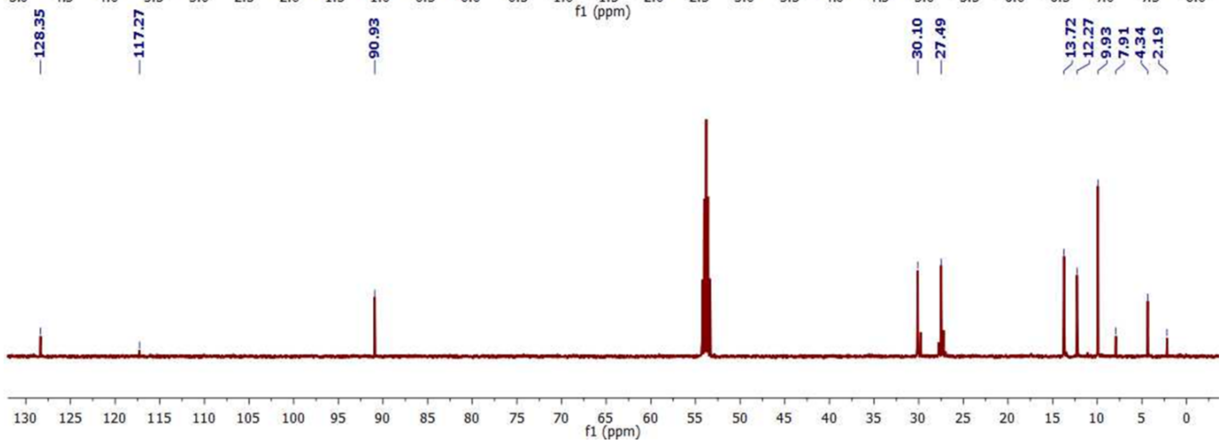
-9.65 -9.72
PF6
iPr3P
Ru
N
H
SnnBu3
-9.65 -9.72
2.66 6.22 15.00 59.59
0.94
f1 (ppm)

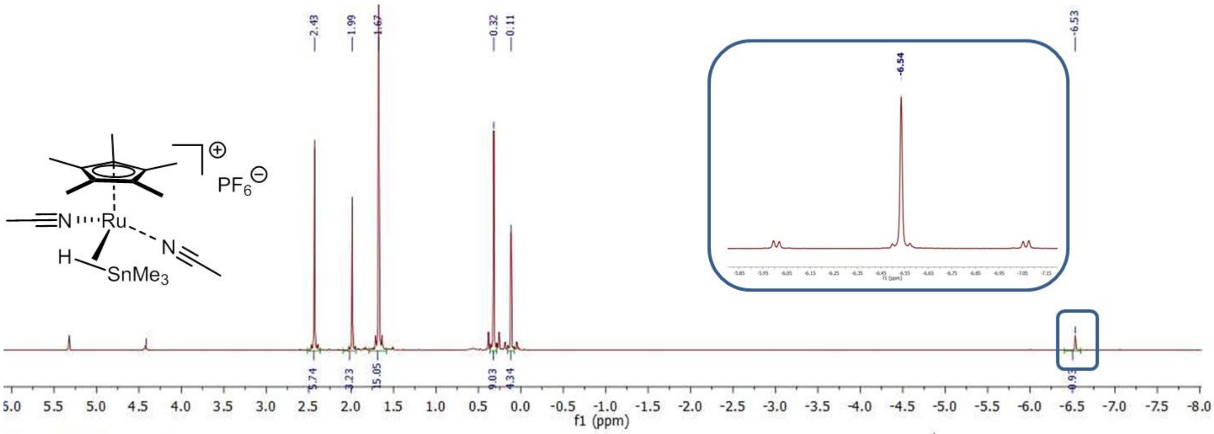

130.08
117.32
94.89
30.05 27.71
19.55 19.34 13.72 13.69 13.59 13.48 10.78
5.18 2.21
f1 (ppm)


2.43 1.92 1.69 1.17 1.07 0.30 0.07
-9.78 -9.85
PF6
iPr3P
Ru
N
H
SnMe3
-9.73 -9.80
f1 (ppm)


ROD-RA-113-02.6.fid
13C
117.20
95.35
53.75
26.71
19.64 19.14
10.66
5.00 3.98 2.11
-4.23
f1 (ppm)


PF6
N
Ru
N
H
SnⁿBu3
2.03 1.60 1.27 1.06 1.04 0.91 0.89 0.63 0.62 0.47
-6.47
6.00 3.07 15.17 29.10 0.81
f1 (ppm)


128.35 117.27 90.93 30.10 27.49 13.72 12.27 9.93 7.91 4.34 2.19
f1 (ppm)


PF6
N
Ru
N
H
SnMe3
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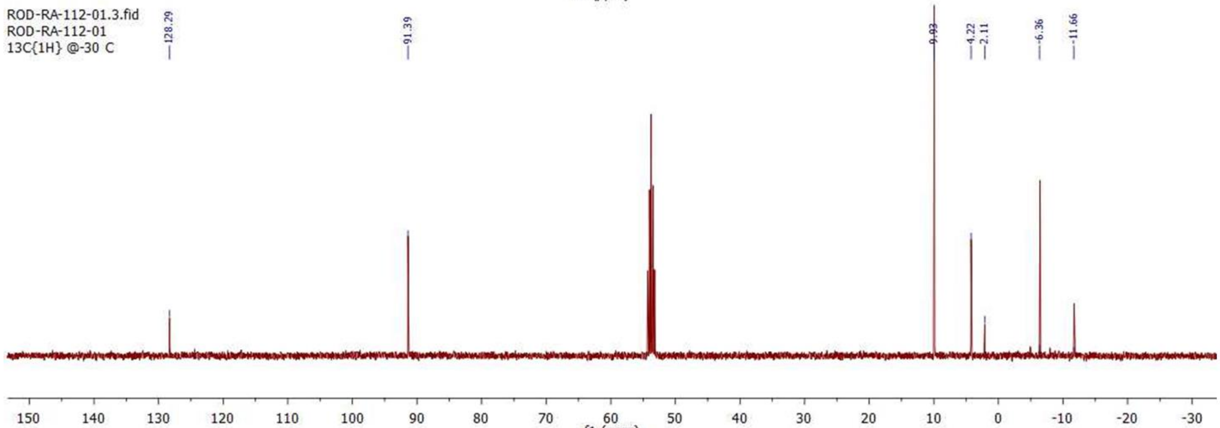
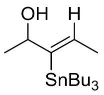
-6.54
5.74 3.23 15.05 9.03 4.34 0.93
f1 (ppm)


ROD-RA-112-01.3.fid
ROD-RA-112-01
13C{1H} @-30 C
128.29 91.39 9.93 4.22 2.11 -6.36 -11.66
f1 (ppm)

## Directed *trans*-Hydrostannation

**Representative Procedure. (*Z*)-3-(Tributylstannyl)pent-3-en-2-ol.** Tributyltin hydride (1.1 mmol, 0.30 mL, 1.1 equiv) was added dropwise over 5 min to a stirred solution of $[Cp^*RuCl_2]_n$ (15.4 mg, 0.025 mmol, 0.025 equiv) and 3-pentyn-2-ol (93 µL, 1.0 mmol) in $CH_2Cl_2$ (5.0 mL, 0.2 M) under argon. The resulting mixture was stirred for 15 min before all volatile materials were evaporated. The residue was loaded on top of a flash column packed with $SiO_2$ and the product was eluted with hexane/EtOAc (50/1→30/1) to give the title compound as a pale yellow oil (329 mg, 88%, α/β = 98/2). The *Z/E* ratio was found to be >99/1 for the α-isomer. $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.27 (qd, *J* = 6.7, 1.2, $J_{Sn-H}$ = 125.5 Hz, 1H), 4.35 (qd, *J* = 6.3, 3.1 Hz, 1H), 1.76 – 1.69 (m, 3H), 1.60 – 1.40 (m, 6H), 1.39 – 1.28 (m, 7H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.07 – 0.92 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 150.5, 133.6, 75.8, 29.4, 27.5, 24.4, 19.3, 13.8, 11.0; $^{119}$Sn NMR (186 MHz, $CDCl_3$): δ = –54.6 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3345, 2955, 2922, 2871, 2853, 1621, 1456, 1375, 1289, 1248, 1069; ESI-MS calcd for $C_{17}H_{35}OSn$ (M-H$^+$) 375.17147; found 375.17160.



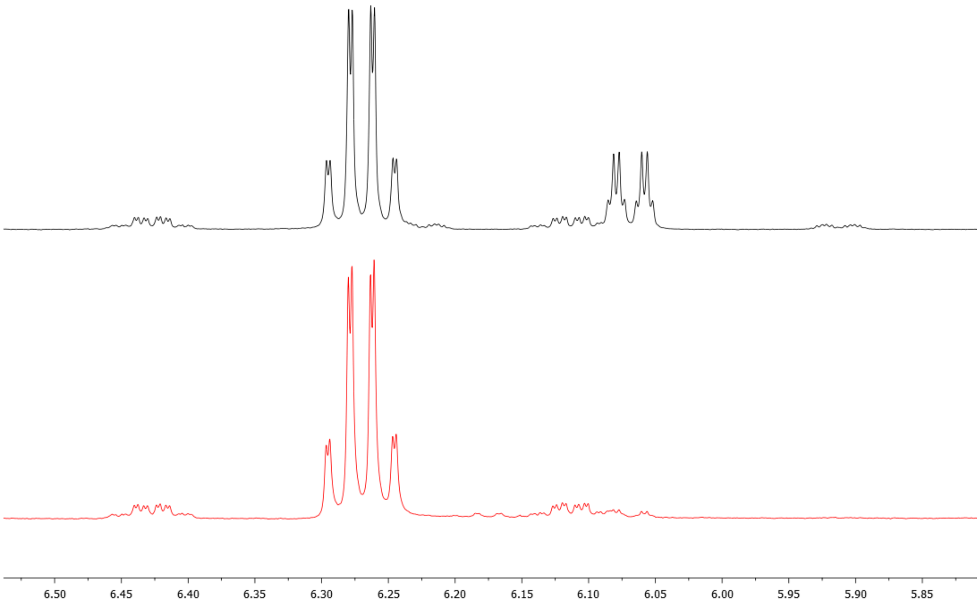
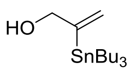




**Figure S-8.** Olefinic region of the $^1$H NMR spectrum of the crude product formed by hydrostannation of 3-pentyn-2-ol in the presence of $[Cp^*Ru(MeCN)_3]PF_6$ (**1**) (top, black) or $[Cp^*RuCl]_4$ (**4**) (bottom, red), respectively; although the reaction catalyzed by **1** is regio-unselective, both isomers obviously originate from a *trans*-addition process as evident from the characteristic $^3J_{Sn,H}$ coupling constants (expressed in the satellites) which are of the same magnitude.

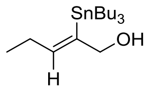
The following compounds were prepared analogously:

**2-(Tributylstannyl)prop-2-en-1-ol**. Pale yellow oil (33 mg, 40%, α:β > 99:1). $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.88 (s, 1H), 5.24 (s, 1H), 5.28 (d, *J* = 5.9 Hz, 2H), 1.54 – 1.45 (m, 7H), 1.36 – 1.26 (m, 6H), 0.96 – 0.86 (m, 15H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 154.7, 122.9, 69.6,

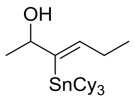


29.1, 27.4, 13.7, 9.5; $^{119}$Sn (112 MHz, $CDCl_3$): δ = –45.7 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3300, 2955, 2922, 2871, 2852, 1462, 1417, 1376, 1340, 1292, 1249, 1180, 1150, 1073, 1020, 961, 918, 874, 688, 665; ESI-MS calcd for $C_{15}H_{31}OSn$ (M-H) 347.14017; found 347.14031.

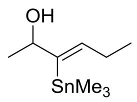
**(*Z*)-2-(Tributylstannyl)pent-2-en-1-ol**. Colorless oil (670 mg, 83%) (α:β = 95:5, *Z/E* > 99:1 for the major isomer (NMR)); $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.21 (tt, *J* = 7.1, 1.4, $J_{Sn-H}$ = 122.9 Hz, 1H), 4.25 – 4.08 (m, 2H), 2.10 – 1.98 (m, 2H), 1.59 – 1.39 (m, 6H), 1.38 – 1.25 (m, 6H), 1.20 (t, *J* = 5.9 Hz, 1H), 1.06 – 0.92 (m, 9H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 143.6, 142.6, 70.6, 29.4, 27.9, 27.5, 14.6, 13.8, 10.4; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –52.3 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3316, 2956, 2923, 2871, 2851, 1622, 1459, 1418, 1376, 1291, 1148, 1080, 1000; ESI-MS calcd for $C_{17}H_{35}OSn$ (M-$H^+$) 375.17147; found 375.17155.



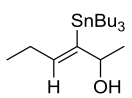

**(*Z*)-3-(Tricyclohexylstannyl)hex-3-en-2-ol**. White wax (84 mg, 87%, α:β > 99:1, *Z/E* > 99:1 (NMR)). $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.26 (td, *J* = 7.2, 1.0 Hz, 1H), 4.34 (m, 1H), 2.06 – 1.97 (m, 2H), 1.89 (m, 6H), 1.69 (m, 9H), 1.63 – 1.46 (m, 9H), 1.40 (d, *J* = 3.6 Hz, OH), 1.36 – 1.16 (m, 12H), 1.00 (t, *J* = 7.2, 1.0 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 147.3, 140.9, 74.6, 32.45, 32.40, 29.6, 28.5, 27.9, 27.2, 24.2, 14.3; $^{119}$Sn (112 MHz, $CDCl_3$): δ = – 95.2 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3452, 2964, 2912, 2843, 1613, 1444, 1373, 1350, 1293, 1256, 1168, 1113, 1071, 1042, 991, 944, 907, 879, 840, 733, 653; ESI-MS calcd for $C_{24}H_{44}OSnNa$ (M+$Na^+$) 491.23056; found 491.23115.



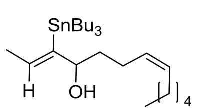

**(Z)-3-(Trimethylstannyl)hex-3-en-2-ol.** White solid (79 mg, 79 %, α:β > 99:1, *Z:E* > 99:1 (NMR)). $^{1}$H NMR (400 MHz, $CD_2Cl_2$): δ = 6.10 (td, *J* = 7.3, 1.1 Hz, 1H), 4.38 – 4.27 (m, 1H), 2.04 (dq, 2H), 1.57 (s, 1H), 1.51 (d, *J* = 3.3 Hz, 1H), 1.19 (d, *J* = 6.4 Hz, 4H), 0.20 (s, 9H, $^{2}J_{SnH}$ = 55 Hz). $^{13}$C NMR (101 MHz, $CD_2Cl_2$): δ = 149.2, 141.2 ($J_{SnC}$ = 28.0 Hz), 75.9 ($J_{SnC}$ = 39.3 Hz), 27.3 ($J_{SnC}$ = 41.1 Hz), 24.4 ($J_{SnC}$ = 11.3 Hz), 14.7, –7.1 ($SnMe_3$, $^{1}J_{SnC}$ = 341.0 Hz).$^{119}$Sn NMR (149 MHz, $CD_2Cl_2$): δ = –52.9 ppm ; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3359, 2964, 2930, 2871, 1717, 1621, 1454, 1366, 1283, 1187, 1117, 1055, 948, 869, 766, 712, 521; ESI-MS calcd for $C_9H_{20}OSnNa$ (M+$Na^+$): 287.04276; found 287.04279.




**(*Z*)-3-(Tributylstannyl)hex-3-en-2-ol**. Colorless oil (65.5 mg, 84%) (α:β = 98:2, *Z/E* > 99:1 (NMR)); $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.15 (td, *J* = 7.2, 1.1, $J_{Sn-H}$ = 125.7 Hz, 1H), 4.34 (qdd, *J* = 6.4, 3.4, 1.0 Hz, 1H), 2.09 – 1.94 (m, 2H), 1.59 – 1.39 (m, 6H), 1.38 – 1.26 (m, 7H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.09 – 0.92 (m, 9H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 148.4, 141.2, 75.7, 29.4, 27.6, 27.5, 24.4, 14.6, 13.8, 11.2; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –53.8 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3354, 2957, 2923, 2871, 2853, 1619, 1458, 1376, 1287, 1247, 1149, 1115, 1070, 1005; ESI-MS calcd for $C_{18}H_{37}OSn$ (M-$H^+$) 389.18712; found 389.18728.

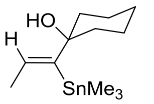



**(2*Z*,7*Z*)-3-(Tributylstannyl)trideca-2,7-dien-4-ol**. Colorless oil (69.5 mg, 72%) (α:β = 98:2, *Z/E* > 99:1 for the major isomer (NMR)); $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.25 (qd, *J* = 6.6, 1.1, $J_{Sn-H}$ = 125.5 Hz, 1H), 5.44 – 5.30 (m, 2H), 4.13 (td, *J* = 6.7, 3.1 Hz, 1H), 2.16 – 1.95 (m, 4H), 1.74 (d, *J* = 6.5 Hz, 3H), 1.60 – 1.42 (m, 8H), 1.41 (d, *J* = 3.2 Hz, 1H), 1.39 – 1.23 (m, 12H), 1.08 – 0.93 (m, 6H), 0.92 – 0.84 (m, 12H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 149.3, 134.9,

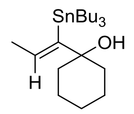


130.7, 129.2, 80.0, 37.8, 31.7, 29.6, 29.4, 27.6, 27.4, 24.0, 22.8, 19.4, 14.2, 13.8, 11.1; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –55.6 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3466, 3004, 2955, 2922, 2871, 2854, 1620, 1457, 1376, 1290, 1070, 1003; ESI-MS calcd for $C_{25}H_{49}OSn$ (M-H$^+$) 485.28102; found 485.28128.

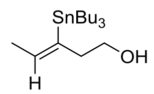
**(*Z*)-1-(1-(Trimethylstannyl)prop-1-en-1-yl)cyclohexan-1-ol.** Prepared analogously using $Me_3SnH$ as the reagent; white solid. (76 mg, 89 %, α:β >99:1, *Z:E* > 99:1 (NMR)). $^1$H NMR (400 MHz, $CD_2Cl_2$): δ = 6.18 (q, $^3J$ = 6.7 Hz, $^3J_{SnH}$ = 152 Hz, 1H), 1.74 (d, $^3J$ = 6.7 Hz, 3H), 1.68 – 1.40 (m, 11H, $CH_2$ Cy), 0.20 (s, 9H, $^2J_{SnH}$ = 54 Hz). $^{13}$C NMR (101 MHz, $CD_2Cl_2$): δ = 155.8, 130.7 ($^1J_{SnC}$ = 25.9 Hz), 76.1 ($^2J_{SnC}$ = 29.6 Hz), 38.3 ($J_{SnC}$ = 12.0 Hz), 25.9, 22.6, 19.1 ($J_{SnC}$ = 49.7 Hz), –5.6 ($^1J_{SnC}$ = 340.6 Hz). $^{119}$Sn NMR (149 MHz, $CDCl_3$): δ = –57.2 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3464, 2929, 2854, 1718, 1620, 1448, 1375, 1309, 1255, 1185, 1148, 956, 907, 831, 766, 518; ESI-MS calcd for $C_{12}H_{24}OSnNa$ (M+Na$^+$): 327.07406; found 327.07432.



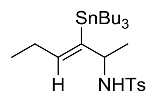

**(*Z*)-1-(1-(Tributylstannyl)prop-1-en-1-yl)cyclohexan-1-ol**. Colorless oil (82.9 mg, 97%) (α:β > 99:1, *Z/E* > 99:1 (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.24 (q, *J* = 6.7, $J_{Sn–H}$ = 137.8 Hz, 1H), 1.74 (d, *J* = 6.6 Hz, 3H), 1.69 – 1.53 (m, 6H), 1.53 – 1.38 (m, 9H), 1.38 – 1.27 (m, 6H), 1.26 (s, 1H), 1.22 – 1.07 (m, 1H), 1.06 – 0.86 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 155.3, 130.3, 75.7, 38.2, 29.4, 27.6, 25.7, 22.4, 19.3, 13.9, 12.4; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –55.7 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3449, 2953, 2923, 2870, 2852, 1448, 1375, 1340, 1293, 1253, 1149, 1071; ESI-MS calcd for $C_{21}H_{42}OSnNa$ (M+Na$^+$) 453.21492; found 453.21520.



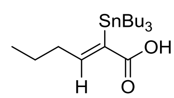

**(*Z*)-3-(Tributylstannyl)pent-3-en-1-ol**. Colorless oil (61.0 mg, 81%) (α:β = 81:19, *Z/E* = 95:5 for the major isomer (NMR)); Data of the major isomer: $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.20 (qt, *J* = 6.6, 1.3, $J_{Sn–H}$ = 129.6 Hz, 1H), 3.53 (q, *J* = 6.1 Hz, 2H), 2.53 – 2.34 (m, 2H), 1.74 (dt, *J* = 6.6, 0.9 Hz, 3H), 1.60 – 1.37 (m, 7H), 1.37 – 1.25 (m, 6H), 1.03 – 0.84 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 140.7, 138.6, 61.8, 43.6, 29.3, 27.5, 20.2, 13.8, 10.3; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –52.6 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3319, 2955, 2922, 2871, 2852, 1620, 1462, 1418, 1376, 1291, 1181, 1040; ESI-MS calcd for $C_{17}H_{35}OSn$ (M-H$^+$) 375.17147; found 375.17149.




**(*Z*)-4-Methyl-*N*-(3-(tributylstannyl)hex-3-en-2-yl)benzenesulfonamide**. Colorless oil (48.7 mg, 90%) (α:β > 99:1, *Z/E* > 99:1 (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.74 – 7.66 (m, 2H), 7.30 – 7.22 (m, 2H), 5.93 (td, *J* = 7.2, 1.0, $J_{Sn–H}$ = 120.7 Hz, 1H), 4.30 (d, *J* = 6.3 Hz, 1H), 4.04 – 3.81 (m, 1H), 2.41 (s, 3H), 1.94 – 1.79 (m, 2H), 1.53 – 1.32 (m, 6H), 1.37 – 1.22 (m, 6H), 1.14 (d, *J* = 6.7 Hz, 3H), 0.95 – 0.72 (m, 18H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 144.4, 143.2, 142.6, 138.2, 129.6, 127.5, 58.5, 29.3, 27.7, 27.5, 23.9, 21.6, 14.3, 13.8, 11.0; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –52.9 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3268, 2956, 2924, 2871, 2853, 1456, 1417, 1374, 1325, 1160, 1094, 1071; ESI-MS calcd for $C_{25}H_{45}NO_2SSnNa$ (M+Na$^+$) 566.20845; found 566.20883.

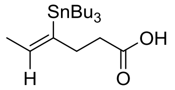



**(*Z*)-2-(Tributylstannyl)hex-2-enoic acid**. Prepared analogously using [(Cp*RuCl)$_4$] (1.25 mol%) as the catalyst and limiting the amount of $Bu_3SnH$ to exactly 1 equivalent relative to the substrate; colorless oil (389 mg, 87%) (α:β = 90:10, *Z/E* = 96:4 for the major isomer

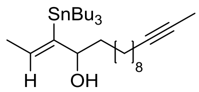


(NMR)); $^{1}$H NMR (500 MHz, $CDCl_3$): δ =7.50 (t, *J* = 7.3, $J_{Sn-H}$ = 103 Hz, 1H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.56 – 1.41 (m, 8H), 1.37 – 1.27 (m, 6H), 1.09 – 0.85 (m, 18H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ = 177.5, 160.2, 135.8, 36.3, 29.2, 27.4, 22.5, 14.0, 13.8, 11.5; $^{119}$Sn NMR (186 MHz, $CDCl_3$): δ = –45.7 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3042, 2956, 2922, 2871, 2853, 2621, 1662, 1600, 1462, 1404, 1377, 1272, 1073; ESI-MS calcd for $C_{18}H_{35}O_2Sn$ (M-H$^+$) 403.16638; found 403.16671.

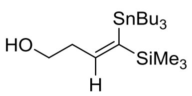
**(*Z*)-4-(Tributylstannyl)hex-4-enoic acid**. Prepared analogously using [(Cp*RuCl)$_4$] (1.25 mol%) as the catalyst and limiting the amount of $Bu_3SnH$ to exactly 1 equivalent relative to the substrate; colorless oil (211 mg, 87%) (α:β = 93:7, *Z/E* > 99:1 for the major isomer (NMR)). Data of the major isomer: $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 6.14 (qt, *J* = 6.6, 1.4, $J_{Sn-H}$ = 129.8 Hz, 1H), 2.56 – 2.40 (m, 2H), 2.40 – 2.28 (m, 2H), 1.69 (dt, *J* = 6.5, 1.0 Hz, 3H), 1.57 – 1.40 (m, 6H), 1.38 – 1.26 (m, 6H), 1.01 – 0.86 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ = 179.3, 142.3, 135.8, 35.3, 35.2, 29.4, 27.5, 20.1, 13.8, 10.2; $^{119}$Sn NMR (186 MHz, $CDCl_3$): δ = –51.5 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3025, 2956, 2921, 2872, 2853, 1708, 1455, 1416, 1376, 1291, 1210, 1071, 1021; ESI-MS calcd for $C_{18}H_{35}O_2Sn$ (M-H$^+$) 403.16639; found 403.16678. *Note: this product is prone to slow proto-destannation (ca. 10% after 24h, NMR)*



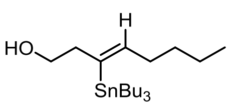

**(*Z*)-3-(Tributylstannyl)hexadec-2-en-14-yn-4-ol**. Prepared analogously with [(Cp*RuCl)$_4$] (1.25 mol%) as the catalyst and 1.05 equiv. of $Bu_3SnH$; purification by flash chromatography (hexane/EtOAc, 100/1 → 20/1) allowed minor by-products to be removed and gave the title compound as a colorless oil (57.7 mg, 55%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.23 (qd, *J* = 6.6, 1.0, $J_{Sn-H}$ = 126.0 Hz, 1H), 4.20 – 3.98 (m, 1H), 2.11 (tq, *J* = 7.3, 2.5 Hz, 2H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.73 (d, *J* = 6.5 Hz, 3H), 1.57 – 1.40 (m, 9H), 1.40 – 1.18 (m, 20H), 1.06 – 0.87 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 149.6, 134.8, 80.5, 79.6, 75.4, 37.9, 29.8, 29.7, 29.4, 29.34, 29.27, 29.1, 27.6, 26.1, 19.4, 18.9, 13.8, 11.1, 3.6; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –55.2 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3468, 2954, 2922, 2853, 1462, 1375, 1290, 1148, 1070, 1046, 1004; ESI-MS calcd for $C_{28}H_{54}OSnNa$ (M+Na$^+$) 549.30881; found 549.30917.




**(*Z*)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-1-ol.** Colorless oil (35.5 mg, 82%, *Z/E* > 99/1 (NMR)). $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.72 (t, *J* = 6.6, $J_{Sn-H}$ = 170.6 Hz, 1H), 3.73 (t, *J* = 6.6 Hz, 2H), 2.42 (q, *J* = 6.6 Hz, 2H), 1.59 – 1.38 (m, 6H), 1.38 – 1.25 (m, 7H), 1.04 – 0.92 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H), 0.05 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 150.8, 148.0, 62.3, 42.5, 29.4, 27.6, 13.8, 11.5, –0.1; $^{119}$Sn NMR (112 MHz, $CDCl_3$): δ = –53.7 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3310, 2954, 2923, 2871, 2854, 1571, 1463, 1376, 1245, 1046; ESI-MS calcd for $C_{19}H_{43}OSiSn$ (M+H$^+$) 435.21045; found 435.21003.

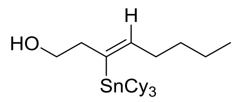



**(*Z*)-3-(Tributylstannyl)oct-3-en-1-ol**. Pale yellow oil (66 mg, 79%, α:β = 80:20, *Z/E* = 92:8 for the major isomer (NMR)). $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 6.13 (t, *J* = 7 Hz, 1H), 3.52 (q, *J* = 6.2 Hz, 2H), 2.43 (t, *J* = 6.2 Hz, 2H), 2.02 (m, 2H), 1.53 – 1.38 (m, 6H), 1.41 (t, *J* = 7 Hz, OH), 1.37 – 1.26 (m, 10H), 0.96 – 0.85 (m, 18H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.0, 138.9, 61.5, 43.4, 34.9, 32.5, 29.2, 27.4, 22.6, 14.1, 13.7, 10.2; $^{119}$Sn (112 MHz, $CDCl_3$): δ = –52.2 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3308, 2955, 2922, 2871, 2854, 1617, 1463, 1418, 1376,



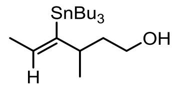
1339, 1339, 1291, 1180, 1070, 1043, 960, 863, 769, 688, 664; ESI-MS calcd for $C_{20}H_{41}OSn$ (M–H) 417.21842; found 417.21872.

**(*Z*)-3-(Tricyclohexylstannyl)oct-3-en-1-ol**. Pale yellow wax (90 mg, 89%, α:β = 82:18, *Z/E* > 97:3 for



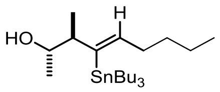

the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.17 (t, *J* = 7.2, Hz), 3.54 (q, *J* = 6 Hz, 2H), 2.42 (t, *J* = 6 Hz, 2H), 2.01 (m, 2H), 1.86 (m), 1.69 (m), 1.63 – 1.43 (m), 1.41 – 1.17 (m), 0.96 – 0.81 (m); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.4, 138.0, 61.4, 43.4, 32.5, 35.4, 32.4, 29.5, 28.0, 27.2, 22.7, 14.1; $^{119}$Sn (112 MHz, $CDCl_3$): δ = –97.8 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3313, 2915, 2845, 1612, 1444, 1377, 1349, 1293, 1258, 1168, 1072, 1039, 1019, 879, 840, 656; ESI-MS calcd for $C_{26}H_{48}OSnNa$ (M+Na$^+$) 519.26186; found 519.26226.

**(*Z*)-3-Methyl-4-(tributylstannyl)hex-4-en-1-ol.** Colorless oil (66.6 mg, 83%) (α:β = 96:4, *Z/E* > 99:1 for



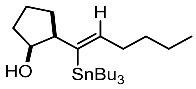

the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.13 (qd, *J* = 6.6, 0.9, $J_{Sn-H}$ = 134.1 Hz, 1H), 3.60 (tdd, *J* = 6.6, 5.4, 1.5 Hz, 2H), 2.54 – 2.26 (m, 1H), 1.70 (d, *J* = 6.5 Hz, 3H), 1.63 – 1.38 (m, 8H), 1.39 – 1.26 (m, 7H), 1.03 – 0.84 (m, 6H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 151.2, 133.1, 62.0, 41.8, 39.9, 29.4, 27.6, 22.1, 19.7, 13.8, 11.1; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –55.1 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3314, 2955, 2923, 2871, 2853, 1456, 1376, 1290, 1150, 1068, 1051, 1011; ESI-MS calcd for $C_{19}H_{39}OSn$ (M-H$^+$) 403.20277; found 403.20295.

**(*Z*)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol.** Colorless oil (74.3 mg, 83%) (α:β = 94:6, *Z/E* = 98:2 for

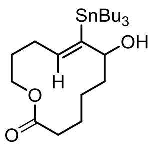



the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.07 (td, *J* = 7.1, 1.1 Hz, $J_{Sn-H}$ = 138.1 Hz, 1H), 3.67 – 3.54 (m, 1H), 2.38 – 2.19 (m, 1H), 2.02 (qd, *J* = 7.2, 2.5 Hz, 2H), 1.55 – 1.40 (m, 7H), 1.39 – 1.24 (m, 10H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.98 – 0.81 (m, 9H), 0.89 (t, *J* = 7.2 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 147.0, 141.1, 69.7, 49.6, 35.1, 32.7, 29.4, 27.6, 22.8, 21.2, 14.4, 14.3, 13.8, 11.0; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –52.2 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3350, 2956, 2923, 2871, 2854, 1458, 1376, 1249, 1075, 1019; ESI-MS calcd for $C_{22}H_{45}OSn$ (M-H$^+$) 445.24972; found 445.25022.

**2-((*Z*)-1-(Tributylstannyl)hex-1-en-1-yl)cyclopentan-1-ol**. Colorless oil (80.5 mg, 88%) (α:β = 96:4, *Z/E*



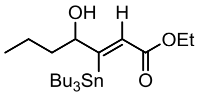

> 99:1 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.08 (td, *J* = 7.1, 1.1, $J_{Sn-H}$ = 133.4 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 1H), 2.51 – 2.26 (m, 1H), 2.09 – 1.93 (m, 3H), 1.86 (dtd, *J* = 12.5, 8.3, 4.0 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.58 (dddd, *J* = 16.9, 12.3, 6.3, 3.3 Hz, 3H), 1.52 – 1.41 (m, 6H), 1.40 – 1.23 (m, 11H), 1.01 – 0.79 (m, 9H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.0, 141.5, 77.7, 34.7, 33.2, 32.7, 31.0, 29.4, 27.6, 22.8, 21.0, 14.2, 13.8, 11.1; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –53.5 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3343, 2955, 2923, 2871, 2854, 1463, 1376, 1339, 1292, 1150, 1071, 1001; ESI-MS calcd for $C_{23}H_{45}OSn$ (M-H$^+$) 457.24972; found 457.24996.



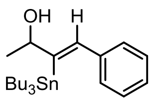

**(*Z*)-7-Hydroxy-8-(tributylstannyl)oxacyclododec-8-en-2-one.** Colorless oil (44.8 mg, 86%) (α:β = 95:5, *Z/E* = 96:4 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.29 (ddd, *J* = 10.3, 3.6, 0.9 Hz, 1H), 4.54 – 4.27 (m, 1H), 4.26 – 3.98 (m, 2H), 2.51 –

2.38 (m, 2H), 2.21 – 2.05 (m, 2H), 1.99 – 1.87 (m, 1H), 1.87 – 1.76 (m, 2H), 1.70 (tdd, *J* = 12.7, 5.0, 2.7 Hz, 1H), 1.56 – 1.39 (m, 8H), 1.37 – 1.26 (m, 8H), 1.15 – 1.03 (m, 1H), 1.02 – 0.86 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 173.2, 144.9, 143.3, 80.1, 66.0, 35.5, 34.4, 33.3, 29.4, 28.3, 27.6, 24.8, 22.1, 13.8, 11.3; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –59.8 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3486, 2953, 2921, 2870, 2852, 1733, 1455, 1376, 1293, 1248, 1156, 1072, 1016; ESI-MS calcd for $C_{23}H_{44}O_3SnNa$ (M+Na$^+$) 511.22039; found 511.22072.

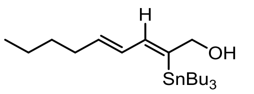
**Ethyl (*Z*)-4-hydroxy-3-(tributylstannyl)hept-2-enoate.** Prepared analogously but the $HSnBu_3$ was added more slowly over ca. 20 min; pale yellow oil (61.0 mg, 66%) (α:β = 97:3, *Z/E* > 99:1 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.61 (d, *J* = 1.5, $J_{Sn-H}$ = 102.0 Hz, 1H), 4.44 (dtd, *J* = 7.7, 4.1, 1.7 Hz, 1H), 4.18 (qd, *J* = 7.1, 2.9 Hz, 2H), 1.60 (d, *J* = 4.0 Hz, 1H), 1.58 – 1.35 (m, 10H), 1.35 – 1.23 (m, 9H), 1.10 – 0.80 (m, 9H), 0.88 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 176.7, 168.1, 126.0, 77.0, 60.5, 39.0, 29.4, 27.6, 19.2, 14.5, 14.1, 13.8, 11.8; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –52.2 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3382, 2956, 2921, 2871, 2853, 1702, 1463, 1368, 1304, 1188, 1132, 1044; ESI-MS calcd for $C_{21}H_{42}O_3SnNa$ (M+Na$^+$) 485.20474; found 485.20519.



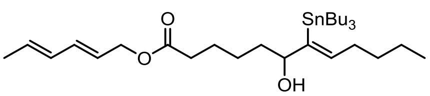

**(*Z*)-4-Phenyl-3-(tributylstannyl)but-3-en-2-ol.** Colorless oil (73.1 mg, 84%) (α:β > 99:1, *Z/E* > 99:1 (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, $J_{Sn-H}$ = 122.6 Hz, 1H), 7.36 – 7.24 (m, 3H), 7.24 – 7.18 (m, 2H), 4.69 – 4.50 (m, 1H), 1.63 (d, *J* = 4.1 Hz, 1H), 1.49 – 1.32 (m, 9H), 1.31 – 1.19 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 9H), 0.84 – 0.68 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 154.3, 140.8, 138.5, 128.2, 128.0, 127.1, 75.1, 29.2, 27.5, 24.4, 13.8, 11.6; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –51.1 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3350, 2955, 2921, 2870, 2852, 1491, 1457, 1419, 1376, 1289, 1124, 1071; ESI-MS calcd for $C_{22}H_{37}OSn$ (M-H$^+$) 437.18712; found 437.18732.




**(2*Z*,4*E*)-2-(Tributylstannyl)nona-2,4-dien-1-ol.** Prepared analogously except that the $HSnBu_3$ was added as a solution in 0.5 mL $CH_2Cl_2$ over 2 h and the product was purified by column chromatography ($Al_2O_3$); pale yellow oil (54.4 mg, 60%) (α:β = 99:1, *Z/E* = 87:13 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.78 (dq, *J* = 10.4, 1.2, $J_{Sn-H}$ = 116.6 Hz, 1H), 6.00 (ddt, *J* = 15.0, 10.5, 1.5 Hz, 1H), 5.73 (dt, *J* = 14.5, 6.9 Hz, 1H), 4.34 – 4.18 (m, 2H), 2.15 – 2.07 (m, 2H), 1.60 – 1.41 (m, 6H), 1.41 – 1.20 (m, 11H), 1.09 – 0.91 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 146.2, 140.3, 136.9, 131.1, 70.5, 32.5, 31.3, 29.3, 27.5, 22.3, 14.1, 13.8, 10.5; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –50.2 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3323, 2955, 2922, 2871, 2853, 1463, 1376, 1291, 1071, 1001, 958; ESI-MS calcd for $C_{21}H_{41}OSn$ (M-H$^+$) 429.21842; found 429.21862.

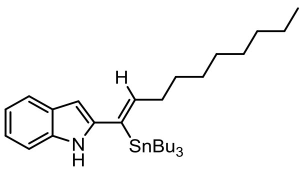



**(2*E*,4*E*)-Hexa-2,4-dien-1-yl (*Z*)-6-hydroxy-7-(tributylstannyl)dodec-7-enoate.** Prepared analogously except that the $HSnBu_3$ was added as a solution in 0.5 mL $CH_2Cl_2$ over 2 h; pale yellow oil (43.5 mg, 37%) (α:β = 96:4, *Z/E* > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.24 (dd, *J* = 15.2, 10.4 Hz, 1H), 6.13 (td, *J* = 7.2, 1.0, $J_{Sn-H}$ = 128.7 Hz, 1H), 6.05 (ddd, *J* = 15.0, 10.4, 1.7 Hz, 1H), 5.81 – 5.68 (m, 1H), 5.61 (dt, *J* = 14.5, 6.6 Hz, 1H), 4.56 (d, *J* = 6.6 Hz, 2H), 4.19 – 3.98 (m, 1H),

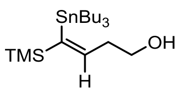


2.38 – 2.26 (m, 2H), 2.08 – 1.95 (m, 2H), 1.79 – 1.73 (m, 3H), 1.68 – 1.59 (m, 2H), 1.56 – 1.41 (m, 6H), 1.42 – 1.22 (m, 15H), 1.04 – 0.80 (m, 9H), 0.89 (t, *J* = 7.2 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 173.6, 147.7, 141.2, 134.9, 131.4, 130.6, 123.9, 80.2, 63.0, 37.4, 34.5, 34.1, 32.4, 29.4, 27.6, 25.7, 25.0, 22.7, 18.3, 14.2, 13.9, 11.2; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –55.2 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3502, 2954, 2923, 2871, 2854, 1736, 1458, 1377, 1230, 1157, 1071, 987; ESI-MS calcd for $C_{30}H_{56}O_3SnNa$ $(M+Na^+)$ 607.31429; found 607.31469.

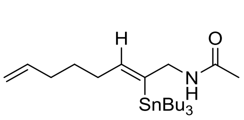
**(*Z*)-2-(1-(Tributylstannyl)dec-1-en-1-yl)-1*H*-indole.** Prepared analogously using [$(Cp^*RuCl)_4$] (1.25 mol%); the compound was purified by column chromatography over $Al_2O_3$; orange oil (88.3 mg, 81%) (α:β = 95:5, *Z/E* > 99:1 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.88 (bs, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.29 (dq, *J* = 8.0, 1.0 Hz, 1H), 7.11 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.05 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 6.57 (t, *J* = 7.3, $J_{Sn-H}$ = 117.4 Hz, 1H), 6.20 (dd, *J* = 2.2, 0.9 Hz, 1H), 2.21 (q, *J* = 7.4 Hz, 2H), 1.62 – 1.41 (m, 8H), 1.41 – 1.23 (m, 16H), 1.15 – 0.95 (m, 6H), 0.94 – 0.85 (m, 12H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 144.1, 143.4, 136.0, 134.3, 129.4, 121.5, 120.1, 119.7, 110.4, 100.7, 35.2, 32.0, 30.3, 29.8, 29.7, 29.5, 29.2, 27.5, 22.8, 14.3, 13.8, 11.6; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –47.8 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3417, 2955, 2922, 2870, 2852, 1454, 1376, 1342, 1290, 1072, 1014; ESI-MS calcd for $C_{30}H_{50}NSn$ $(M-H^+)$ 544.29700; found 544.29749.



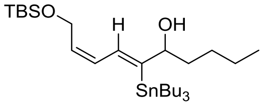

**(*Z*)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-1-ol**. Prepared analogously except that a solution of $Bu_3SnH$ in $CH_2Cl_2$ (0.5 mL) was added over 1 h; colorless oil (55.8 mg, 64%) (C1/C2 = 93:7, *Z/E* > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.71 (t, *J* = 6.6, $J_{Sn-H}$ = 170.4 Hz, 1H), 3.72 (td, *J* = 6.6, 5.6 Hz, 2H), 2.41 (q, *J* = 6.5 Hz, 2H), 1.56 – 1.37 (m, 7H), 1.36 – 1.21 (m, 6H), 1.05 – 0.82 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H), 0.05 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 150.7, 147.9, 62.3, 42.5, 29.4, 27.6, 13.8, 11.4, –0.1; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –53.7 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3313, 2954, 2923, 2871, 2854, 1571, 1463, 1376, 1245, 1046; ESI-MS calcd for $C_{19}H_{41}O_4SiSn$ $(M-H^+)$ 433.19535; found 433.19576.




**(*Z*)-*N*-(2-(Tributylstannyl)octa-2,7-dien-1-yl)acetamide**. Colorless oil (28.8 mg, 93%) (α:β = 91:9, *Z/E* > 95:5 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$) δ = 6.17 (t, J = 7.1 Hz, 1H), 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.23 (br s, NH), 5.07 – 4.89 (m, 2H), 3.91 (d, J = 5.3 Hz, 2H), 2.03 (td, J = 15.3, 7.3 Hz, 4H), 1.96 (s, 3H), 1.51 – 1.41 (m, 8H), 1.34 – 1.26 (m, 6H), 0.95 – 0.84 (m, 15H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 169.4, 143.5, 139.1, 138.6, 114.9, 48.6, 34.3, 33.7, 29.4, 29.3, 27.5, 23.5, 13.8, 10.2; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –50.0 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3276, 3077, 2955, 2922, 2871, 2852, 1644, 1548, 1457, 1374, 1282, 1071, 991.

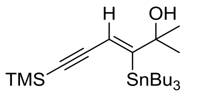



**(6*Z*,8*Z*)-10-((*tert*-Butyldimethylsilyl)oxy)-6-(tributylstannyl)deca-6,8-dien-5-ol**. Prepared accoriding to the representative procedure except that the $HSnBu_3$ was added as a solution in $CH_2Cl_2$ over 1 h; colorless oil (71 mg, 64%) (α:β = 98:2, *Z/E* > 99:1 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.95 (dt, *J* = 11.3, 1.1 Hz, $J_{Sn-H}$ = 115.2 Hz, 1H), 5.98 (ddt, *J* = 13.0, 11.2, 1.7 Hz, 1H), 5.57 (dtd, *J* = 11.0, 6.3, 1.1 Hz, 1H), 4.39 (ddd, *J* = 6.3,

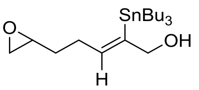


3.1, 1.6 Hz, 2H), 4.30 – 4.12 (m, 1H), 1.59 – 1.38 (m, 9H), 1.37 – 1.18 (m, 10H), 1.08 – 0.90 (m, 6H), 0.92 – 0.85 (m, 21H), 0.08 (s, 6H).; $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 156.4, 133.3, 131.9, 129.2, 80.1, 59.8, 37.5, 29.3, 28.2, 27.5, 26.1, 22.8, 18.5, 14.2, 13.8, 11.4, –4.9; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –52.8 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3379, 2958, 2928, 2857, 1643, 1462, 1376, 1294, 1257, 1089, 939; ESI-MS calcd for $C_{28}H_{58}O_2SiSnNa$ ($M+Na^+$) 597.31196; found 597.31256.

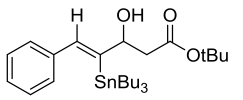
**(*Z*)-2-Methyl-3-(tributylstannyl)-6-(trimethylsilyl)hex-3-en-5-yn-2-ol**. Prepared accoriding to the representative procedure except that the $HSnBu_3$ was added as a solution in $CH_2Cl_2$ over 1.5 h; pale yellow oil (52 mg, 55%) (α:β = 99:1, *Z/E* > 99:1 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.31 (s, $J_{Sn-H}$ = 113.6 Hz, 1H), 1.58 – 1.42 (m, 6H), 1.40 (s, 1H), 1.38 – 1.30 (m, 6H), 1.30 (s, 6H), 1.17 – 0.97 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H), 0.18 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 172.6, 115.7, 105.4, 96.5, 75.6, 30.2, 29.4, 27.6, 13.9, 11.9, 0.0; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –46.5 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3398, 2956, 2922, 2871, 2854, 1459, 1376, 1249, 1068, 840; ESI-MS calcd for $C_{22}H_{43}OSiSn$ ($M-H^+$) 471.21100; found 471.21152.



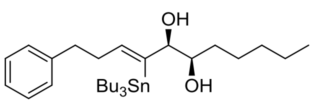

**(*Z*)-5-(Oxiran-2-yl)-2-(tributylstannyl)pent-2-en-1-ol**. Colorless oil (26 mg, 66%) (α:β = 90:10, *Z/E* > 99:1 for the major isomer (NMR)); the product contained ca. 10 % of an unidentified impurity. $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.25 (tt, *J* = 7.3, 1.5 Hz, $J_{Sn-H}$ = 120.3 Hz, 1H), 4.19 (dd, *J* = 6.1, 1.3 Hz, 2H), 2.92 (dtdd, *J* = 6.8, 5.5, 3.9, 2.7 Hz, 1H), 2.76 (ddd, *J* = 5.9, 3.9, 2.0 Hz, 1H), 2.48 (dt, *J* = 5.5, 2.8 Hz, 1H), 2.28 – 2.16 (m, 2H), 1.71 – 1.58 (m, 2H), 1.54 – 1.41 (m, 6H), 1.40 – 1.25 (m, 6H), 1.21 (t, *J* = 5.9 Hz, 1H), 1.08 – 0.89 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 144.4, 139.9, 70.3, 51.9, 47.1, 32.9, 29.2, 27.4, 13.7, 10.2; $^{119}$Sn NMR (112 MHz, $CD_2Cl_2$) δ = –52.3 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3429, 2955, 2921, 2871, 2852, 1462, 1376, 1072, 1000; ESI-MS calcd for $C_{19}H_{37}O_2Sn$ ($M-H^+$) 417.18204; found 417.18234.




***tert*-Butyl (*Z*)-3-hydroxy-5-phenyl-4-(tributylstannyl)pent-4-enoate**. Colorless oil (122 mg, 85%) (α:β = 99:1, *Z/E* > 99:1 (NMR)). $^1$H NMR (400 MHz, $CD_2Cl_2$): δ = 7.44 (d, *J* = 1.3 Hz, $J_{Sn-H}$ = 120.2 Hz, 1H), 7.35 – 7.21 (m, 3H), 7.21 – 7.16 (m, 2H), 4.78 – 4.62 (m, 1H), 3.16 (d, *J* = 3.8 Hz, 1H), 2.54 (dd, *J* = 15.8, 3.8 Hz, 1H), 2.44 (dd, *J* = 15.8, 8.7 Hz, 1H), 1.46 (s, 9H), 1.42 – 1.28 (m, 6H), 1.28 – 1.11 (m, 6H), 0.83 (t, *J* = 7.3 Hz, 9H), 0.80 – 0.64 (m, 6H); $^{13}$C NMR (101 MHz, $CD_2Cl_2$): δ = 172.4, 151.8, 141.2, 139.8, 128.6, 128.4, 127.6, 81.7, 75.2, 43.6, 29.6, 28.5, 27.9, 14.0, 12.0; $^{119}$Sn NMR (112 MHz, $CD_2Cl_2$) δ = –50.2 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3499, 2955, 2921, 2871, 2853, 1711, 1457, 1368, 1255, 1143, 1070, 1030; ESI-MS calcd for $C_{27}H_{46}O_3SnNa$ ($M+Na^+$) 561.23604; found 561.23626.

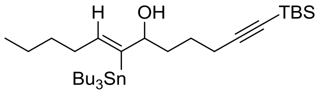



**(5*S*,6*R*,*Z*)-1-Phenyl-4-(tributylstannyl)dec-3-ene-5,6-diol**. Colorless oil (2.23 g, 93%) (α:β = 98:2, *Z/E* = > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.27 (m, 2H), 7.21 – 7.16 (m, 3H), 6.26 (t, *J* = 7.2, $J_{Sn-H}$ = 121.1 Hz, 1H), 3.92 (dd, *J* = 7.0, 3.2, 1H), 3.36 (s br, 1H), 2.70 (t, *J* = 7.3, 2H), 2.43 – 2.35 (m, 2H), 2.24 – 2.16 (m, 2H), 1.61 – 1.26 (m, 20H), 0.95 – 0.81 (m, 16H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 144.6, 142.0, 140.7, 127.7, 127.7, 125.3, 82.6, 73.4, 35.52, 35.5, 31.9, 28.5, 28.4, 27.3, 26.7, 22.1, 13.4, 13.0, 10.4; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –53.9 ppm; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3402, 2954, 2929,



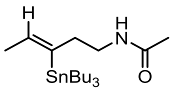
2871, 2855, 1455, 1376, 1073, 1032, 865, 746, 697, 594; ESI-MS calcd for $C_{28}H_{50}O_2SnNa$ ($M+Na^+$) 561.27251; found 561.27243.

**(*Z*)-1-(*tert*-Butyldimethylsilyl)-7-(tributylstannyl)dodec-7-en-1-yn-6-ol**. Colorless oil (57 mg, 87%)



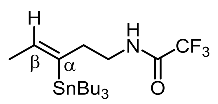

(α:β = 99:1, *Z/E* = > 99:1 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.14 (td, *J* = 7.2, 1.1, $J_{Sn-H}$ = 125.2 Hz, 1H), 4.19 – 4.05 (m, 1H), 2.26 – 2.23 (m, 2H), 2.04 – 1.99 (m, 2H), 1.63 – 1.28 (m, 22H), 0.97 – 0.85 (m, 25H), 0.07 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 147.7, 141.2, 107.9, 82.75, 79.9, 36.9, 34.1, 32.4, 29.4, 27.6, 26.3, 25.4, 22.7, 19.9, 16.7, 14.2, 13.9, 11.2, –4.3; $^{119}$Sn NMR (149 MHz, $CDCl_3$) δ = –54.9 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3464, 2954, 2926, 2871, 2855, 1462, 1361, 1249, 1048, 1006, 837, 825, 810, 774, 679, 594; ESI-MS calcd for $C_{30}H_{60}OSiSnNa$ ($M+Na^+$) 607.33289; found 607.33269.

**(*Z*)-*N*-(3-(Tributylstannyl)pent-3-en-1-yl)acetamide.** Colorless oil (81.8 mg, 98%) (α:β = 87:13, *Z/E* =



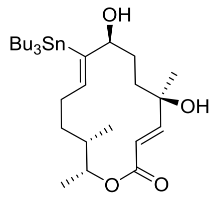

94:6 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.16 (dt, *J* = 6.5, 1.3, $J_{Sn-H}$ = 126.9 Hz, 1H), 5.42 – 5.28 (bs, 1H), 3.21 (td, *J* = 6.8, 5.4 Hz, 2H), 2.44 – 2.25 (m, 2H), 1.95 (s, 3H), 1.73 (dt, *J* = 6.5, 1.0 Hz, 3H), 1.56 – 1.39 (m, 6H), 1.37 – 1.24 (m, 6H), 1.02 – 0.84 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 169.9, 141.7, 137.4, 40.1, 39.2, 29.4, 27.5, 23.5, 20.1, 13.8, 10.2; $^{119}$Sn NMR (112 MHz, $CDCl_3$) δ = –52.5 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3281, 3084, 2955, 2922, 2871, 2852, 1649, 1556, 1456, 1375, 1293, 1206, 1071; ESI-MS calcd for $C_{19}H_{39}NOSnNa$ ($M+Na^+$) 440.19451; found 440.19479.

**(*Z*)-2,2,2-Trifluoro-N-(3-(tributylstannyl)pent-3-en-1-yl)acetamide.** Colorless oil (87 mg, 90%, α:β =



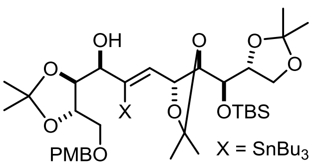

95:5, *Z/E* = 95:5 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.20 (q, *J* = 6.5 Hz, 1H + NH), 3.32 (q, *J* = 6.2 Hz, 2H), 2.43 (t, *J* = 6.6 Hz, 2H) 1.75 (d, *J* = 6.5 Hz, 3H), 1.51 – 1.42 (m, 6H), 1. 36 – 1.27 (m, 6H), 0.98 – 0.92 (m, 6H), 0.90 (t, *J* = 7 Hz, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 156.8 (q, *J* = 36 Hz), 140.4, 138.6, 115.9 (q, *J* = 288 Hz), 39.3, 39.1, 29.2, 27.3, 19.9, 13.6, 10.0; $^{119}$Sn (112 MHz, $CDCl_3$): δ = – 51.4 ppm; IR (film/cm$^{-1}$) $\tilde{\nu}$ = 3303, 3102, 2957, 2924, 2873, 2853, 1701, 1620, 1558, 1457, 1376, 1340, 1293, 1204, 1161, 1072, 1022, 960, 875, 864, 831, 769, 724, 688, 665; ESI-MS calcd for $C_{19}H_{36}F_3NOSnNa$ ($M+Na^+$) 494.16625; found 494.16661.

**(3*E*,5*R*,8*S*,9*Z*,13*S*,14*R*)-5,8-Dihydroxy-5,13,14-trimethyl-9-(tributylstannyl)oxacyclo-tetra-deca-3,9-**



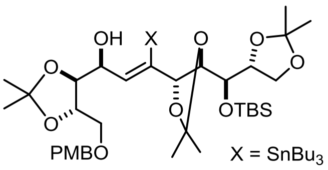

**dien-2-one.** Yellow oil that solidified upon standing. $[\alpha]_D^{20}$ -41.2 (c = 1, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.91 (d, *J* = 15.6 Hz, 1H), 6.36 (dd, *J* = 9.2, 5.2, $J_{Sn-H}$ = 121.7 Hz, 1H), 5.99 (d, *J* = 15.6 Hz, 1H), 4.58 (dq, *J* = 10.2, 6.3 Hz, 1H), 4.28 – 4.04 (m, 1H), 2.09 – 1.93 (m, 2H), 1.89 – 1.80 (m, 1H), 1.80 – 1.66 (m, 3H), 1.56 – 1.39 (m, 8H), 1.36 (s, 3H), 1.36 – 1.16 (m, 12H), 1.02 – 0.82 (m, 18H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 166.0, 153.5, 146.4, 143.0, 119.7, 83.2, 76.4, 73.9, 39.8, 38.4, 34.4, 32.6, 31.5, 29.4, 28.1, 27.5, 19.0, 17.7, 13.9, 11.2; $^{119}$Sn NMR (186 MHz, $CDCl_3$) δ = –54.9 ppm; IR (film/cm$^{-1}$) $\tilde{\nu}$ = 3450, 2954, 2924, 2871, 2853, 1698, 1640, 1455, 1377, 1281, 1267, 1153, 1133, 1104, 1044; ESI-MS calcd for $C_{28}H_{52}O_4SnNa$ ($MNa^+$) 595.277909; found 595.277500.

**Compound *prox*-19**. $^{1}$H NMR (500 MHz, CDCl$_3$): δ = 7.24 (m, 2H), 6.85 (m, 2H), 6.24 (dd, *J* = 9.8, 1.1




Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.34 (dd, *J* = 9.8, 1.1 Hz, 1H), 4.22 (ddd, *J* = 7.8, 2, 1.4 Hz, 1H), 4.02 (m, 1H), 4.01 (m, 1H), 3.97 (m, 1H), 3.95 (m, 1H), 3.86 (dd, *J* = 6.8, 5.8 Hz, 1H), 3.82 (dd, *J* = 7.6, 5.9 Hz, 1H), 3.78 (s, 3H), 3.65 (dd, *J* = 5.6, 4.9 Hz, 1H), 3.56 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.55 (dd, *J* = 9.6, 6.2Hz, 1H), 3.10 (d, *J* = 2 Hz, OH), 1.47 (m, 6H), 1.43 (s, 3H), 1.36 (s, 3H), 1.36 (s, 3H), 1.30 (m, 3H), 1.29 (m, 9H), 1.26 (m, 3H), 0.95 (m, 6H), 0.89 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 9H), 0.13 (s, 3H), 0.10 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ = 159.4, 153.6, 135.6, 129.5, 129.3, 113.8, 109.0, 108.5, 108.1, 82.7, 79.6, 78.8, 78.3, 78.0, 75.9, 73.5, 70.7, 70.6, 64.5, 55.2, 29.1, 27.8, 27.5, 27.0, 26.8, 26.4, 26.1, 25.53, 25.50, 18.6, 13.6, 11.7, –4.0, –4.1; $^{119}$Sn (112 MHz, CDCl$_3$): δ = – 56.7 ppm; IR (film/cm$^{-1}$) $\tilde{\nu}$ = 3440, 2985, 2955, 2928, 2856, 1613, 1587, 1514, 1462, 1418, 1378, 1370, 1302, 1248, 1215, 1148, 1075, 1057, 1035, 906, 859, 835, 779, 734, 667; $C_{46}H_{82}O_{10}SiSnNa$ (M+Na$^+$) 965.45908; found 965.45949.

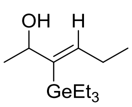
**Compound *dist*-19**. $^{1}$H NMR (500 MHz, CDCl$_3$): δ = 7.23 (m, 2H), 6.85 (m, 2H), 6.44 (d, *J* = 7.3 Hz, 1H),




4.63 (d, *J* = 7.1 Hz, 1H), 4.50 (m, 2H), 4.09 (m, 1H), 4.07 (m, 1H), 4.02 (m, 2H), 3.94 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.80 (s, 1H), 3.78 (m, 3H), 3.76 (m, 1H), 3.71 (dd, *J* = 7.7, 7.0 Hz, 1H), 3.65 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.55 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.02 (d, *J* = 2 Hz, OH), 1.48 (s, 3H), 1.47 (m, 6H), 1.38 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.30 (m, 6H), 1.29 (s, 3H), 1.24 (s, 3H), 0.97 (m, 6H), 0.88 (s, 9H), 0.87 (m, 9H), 0.10 (s, 3H), 0.06 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ = 159.4, 146.2, 143.3, 129.5, 129.3, 113.8, 109.3, 108.3, 107.5, 81.8, 81.5, 80.4, 78.2, 75.2, 73.41, 73.36, 70.9, 70.5, 63.6, 55.2, 29.1, 27.5, 26.9, 26.7, 26.4, 26.13, 26.06, 25.3, 24.1, 18.5, 13.7, 12.0, –3.9, –4.0; $^{119}$Sn (112 MHz, CDCl$_3$): δ = –55.3 ppm; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3421, 2985, 2954, 2928, 2871, 2855, 1613, 1587, 1514, 1462, 1379, 1371, 1248, 1209, 1162, 1144, 1077, 1032, 908, 859, 835, 778, 733, 689.

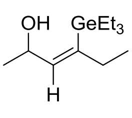
## Directed *trans*-Hydrogermylation

**(*Z*)-3-(Triethylgermyl)hex-3-en-2-ol**. Colorless oil (37 mg, 78%, α:β = 86:14, *Z/E* > 99:1 for the major



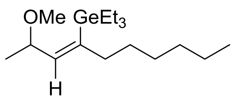

isomer (NMR)). $^{1}$H NMR (400 MHz, CDCl$_3$): δ = 6.19 (td, *J* = 7.4, 1 Hz, 1H), 4.31 (m, 1H), 2.09 (quint., *J* = 7.4 Hz, 2H), 1.32 (m, OH), 1.23 (d, *J* = 6.6 Hz, 3H), 1.06 – 0.96 (m, 12H), 0.94 – 0.84 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 143.0, 140.1, 72.9, 25.1, 24.0, 14.3, 9.1, 5.7; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3384, 2957, 2931, 2907, 2871, 1673, 1621, 1458, 1427, 1376, 1362, 1238, 1172, 1116, 1068, 1051, 1010, 957, 912, 874, 863, 700; ESI-MS calcd for $C_{12}H_{26}OGeNa$ (M+Na$^+$) 283.10877; found 283.10875.

**(*Z*)-4-(Triethylgermyl)hex-3-en-2-ol**. Colorless oil (37 mg, 83%, α:β = 24:76, *Z/E* > 99:1 for the major

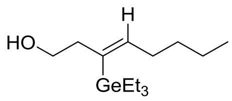



isomer (NMR)). $^{1}$H NMR (400 MHz, CDCl$_3$): δ = 5.94 (dt, *J* = 9.4, 1.4 Hz, 1H), 4.33 (m, 1H), 2.10 (m, 2H), 1.26 (m, OH), 1.24 (d, *J* = 6.4 Hz, 3H), 1.06 – 0.84 (m, 18H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 144.3, 141.8, 68.1, 31.1, 23.5, 14.4, 9.0, 5.5; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3346, 2958, 2930, 2907, 2871, 1673, 1622, 1458, 1427, 1370, 1362, 1268, 1172, 1244, 1155, 1114, 1072, 1049, 1011, 971, 942, 874, 862, 701, 673; ESI-MS calcd for $C_{12}H_{26}OGeNa$ (M+$Na^+$) 283.10877; found 283.10892.

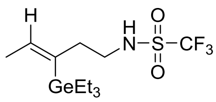
**(Z)-Triethyl(2-methoxydec-3-en-4-yl)germane**. Pale yellow oil (65 mg, 88%, α:β = 20:80, *Z/E* = 95:1 for the major isomer (NMR)). Data of the major regioisomer: $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.79 (dt, *J* = 9.3, 1.2 Hz, 1H), 3.84 (m, 1H), 3.26 (s, 3H), 2.07 (m., 2H), 1.39 – 1.23 (m, 8H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.06 – 0.99 (m, 9H), 0.91 – 0.83 (m, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 143.1, 142.0, 76.2, 55.6, 38.6, 31.7, 30.1, 29.0, 22.7, 21.7, 14.1, 9.0, 5.4; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 2954, 2926, 2871, 2857, 2816, 2732, 1692, 1617, 1577, 1459, 1428, 1377, 1368, 1342, 1320, 1201, 1156, 1106, 1087, 1047, 1011, 971, 919, 887, 868, 846, 700, 665, 640; ESI-MS calcd for $C_{17}H_{36}OGeNa$ (M+$Na^+$) 353.18702; found 353.18697.



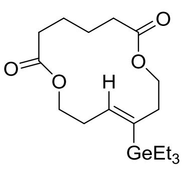

**(*Z*)-3-(Triethylgermyl)oct-3-en-1-ol**. Colorless oil (37 mg, 96%, α:β = 86:14, *Z/E* > 98:2 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.04 (t, *J* = 7.3 Hz, 1H), 3.53 (t, *J* = 6.3 Hz, 2H), 2.34 (t, *J* = 6.3 Hz, 2H), 2.07 (m, 2H), 1.43 (m, OH), 1.38 – 1.31 (m, 4H), 1.02 (m, 9H), 0.93– 0.82 (m, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 144.5, 134.7, 61.5, 41.6, 32.3, 32.2, 22.5, 14.0, 9.0, 5.3; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3319, 2952, 2927, 2871, 1618, 1458, 1427, 1377, 1235, 1182, 1040, 1012, 971, 855, 700; ESI-MS calcd for $C_{14}H_{31}OGe$ (M+H) 289.15867; found 289.15839.




**(*Z*)-1,1,1-Trifluoro-N-(3-(triethylgermyl)pent-3-en-1-yl)methanesulfonamide**. Pale yellow oil (37 mg, 78%, α:β = 92:8, *Z/E* > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.15 (qt, *J* = 6.8, 1.0 Hz, 1H), 4.69 (s (br), NH), 3.25 (q, *J* = 6.4 Hz, 2H), 2.37 (t, *J* = 6.4 Hz, 2H), 1.76 (d, *J* = 6.8 Hz, 3H), 1.03 (t, *J* = 8 Hz, 9H), 0.92– 0.84 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 139.0, 135.6, 119.6 (q, $J_{CF}$ = 320 Hz), 43.6, 38.9, 17.8, 9.0, 5.0; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3311, 2952, 2909, 2873, 1622, 1426, 1371, 1230, 1186, 1145, 1063, 1012, 970, 847, 801, 755, 701, 607; ESI-MS calcd for $C_{12}H_{23}NOFGeS$ (M-H) 376.06189; found 376.06206.

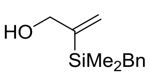



**(*Z*)-11-(Triethylgermyl)-1,8-dioxacyclotetradec-11-ene-2,7-dione**. Colorless oil (65 mg, 96%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.98 (t, *J* = 6.5 Hz, 1H), 4.16 (t, *J* = 5.4 Hz, 2H), 4.08 (m, 2H), 2.49 – 2.41 (m, 4H), 2.38 – 2.32 (m, 4H), 1.63 (m, 4H), 1.03 (m, 9H), 0.92– 0.85 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 173.3, 173.1, 139.5, 137.8, 64.1, 63.1, 37.7, 35.1, 35.0, 30.9, 24.6, 24.3, 9.0, 5.2; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 2949, 2932, 2905, 2871, 2837, 1728, 1626, 1459, 1428, 1383, 1337, 1317, 1266, 1240, 1141, 1067, 1048, 1013, 972, 945, 913, 887, 860, 828, 798, 701, 672; ESI-MS calcd for $C_{18}H_{32}O_4GeNa$ (M+$Na^+$) 409.14046; found 409.14050.




## Directed *trans*-Hydrosilylation

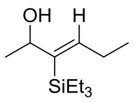
**Large Scale Synthesis of 2-(Benzyldimethylsilyl)prop-2-en-1-ol.** ***Method A***: $(Cp^*RuCl)_4$ (138 mg, 0.127 mmol, 3 mol%) was added under Ar to a vigorously stirred solution of $BnMe_2SiH$ (3.07 g, 20.4 mmol) and propargyl alcohol (954 mg, 17.02 mmol) in pentane (85 mL) at



ambient temperature. The mixture was stirred overnight before the residue was purified by filtration through a short pad of silica, eluting with pentane/*tert*-butyl methyl ether (9:1 → 5:1) as the eluent. Evaporation of the product-containing fractions afforded the title compound as a colorless oil (2.73 g, 78 %, α:β ≥ 99:1 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.18 (m, 2H), 7.11 – 7.05 (m, 1H), 7.02 – 6.98 (m, 2H), 5.84 (s, 1H), 5.41 (s, 1H), 4.19 (s, 2H), 2.20 (s, 2H), 1.24 (s (br), OH), 0.10 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 150.0, 139.6, 128.2, 124.2, 124.1, 66.6, , 25.5. –3.7; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3312, 3081, 3060, 3024, 2955, 2894, 1600, 1493, 1451, 1408, 1248, 1206, 1177, 1154, 1028, 930, 826, 792, 760, 697; ESI-MS calcd for $C_{12}H_{18}OSiNa$ (M+Na$^+$) 229.10191; found 229.10190.

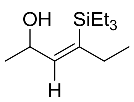
***Method B***: $(Cp^*RuCl)_4$ (142 mg, 0.1306 mmol, 3 mol%) was added under Ar to a stirred solution of $BnMe_2SiH$ (3.098 g, 20.61 mmol) and propargyl alcohol (967 mg, 17.25 mmol) in $CH_2Cl_2$ (90 mL) and the resulting mixture was stirred overnight at ambient temperature. For work up, a solution of tris(hydroxymethyl)phosphine (325 mg, 2.62 mmol) in $H_2O$ (10 mL) was added and stirring continued for 4 h. More water (30 mL) was then added, the phases were separated and the organic phase was extracted with water (3x30 mL) before it was passed through a short pad of silica (1 cm). After evaporation of the solvent, the residue was purified by distillation (bp = 70-80°C, 1 x $10^{-3}$ mbar) to afford the title compound as a colorless oil (2.2 g, 62%).[10]

**Representative Procedure. (*Z*)-3-(Triethylsilyl)hex-3-en-2-ol.** Triethylsilane (27 mg, 0.232 mmol) was added under Argon to a stirred solution of 3-hexyn-2-ol (19.0 mg, 0.194 mmol) and $(Cp^*RuCl)_4$ (2.65 mg, 0.002438 mmol, 5 mol%) in $CH_2Cl_2$ (1 mL) at ambient temperature. Once the reaction was complete (ca. 30 min), the mixture was purified by filtration through a short pad of silica, eluting with hexanes/ethyl acetate (20:1). Evaporation of the product-containing fractions afforded the title compound as a colorless oil (40 mg, 96 %, α:β = 88:12, *Z/E* > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.33 (td, *J* = 7.5, 1.0 Hz, 1H), 4.32 (q, *J* = 6.3 Hz, 1H), 2.14 (quint, *J* = 7.5 Hz, 2H), 1.34 (s (br), OH), 1.24 (d, *J* = 6.3 Hz, 3H), 1.01 - 0.91 (m, 12H), 0.73 - 0.65 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 143.4, 140.7, 71.4, 24.9, 24.4, 14.2, 7.6, 4.3; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3346, 2955, 2912, 2874, 1612, 1459, 1417, 1365, 1238, 1155, 1114, 1050, 1003, 882, 862, 716, 675; ESI-MS calcd for $C_{12}H_{26}OSiNa$ (M+Na$^+$) 237.16451; found 237.16458.

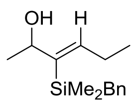



The following compounds were prepared analogously; in cases, in which mixtures were formed that did not allow for a full assignment of the NMR spectra, the characteristic data are contained in Table S-1.

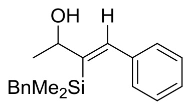
**(*Z*)-4-(Triethylsilyl)hex-3-en-2-ol**. Formed as the major product using $[Cp^*Ru(MeCN)_3]PF_6$ as the catalyst (72%, α:β = 12:88, *Z/E* = 98:2 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.97 (dt, *J* = 9.6, 1.4 Hz, 1H), 4.46 (m, 1H), 2.06 (qd, *J* = 7.4, 1.4 Hz, 2H), 1.33 (s (br), OH), 1.23 (d, *J* = 6.2 Hz, 3H), 1.01 - 0.91 (m, 12H), 0.72 - 0.63 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.0, 141.2, 67.3, 30.2, 23.4, 14.8, 7.6, 4.4; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3335, 2955, 2912, 2874, 1614, 1457, 1417, 1368, 1237, 1157, 1112, 1050, 1002, 943, 881, 862, 716, 675 ; ESI-MS calcd for $C_{12}H_{26}OSiNa$ (M+Na$^+$) 237.16451; found 237.16433.



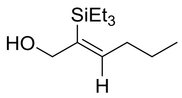
**(*Z*)-3-(Benzyldimethylsilyl)hex-3-en-2-ol.** Pale yellow oil (51 mg, 90%, α:β = 86:14, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): ṽ = 3358, 3081, 3060, 3024, 2965, 2930, 2895, 2873, 1600, 1493, 1452, 1407, 1366, 1249, 1206, 1154, 1114, 1055, 960, 824, 790, 760, 697; ESI-MS calcd for $C_{15}H_{24}OSiNa$ ($M+Na^+$) 271.14886; found 271.14887.



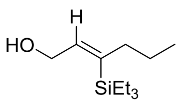
**(*Z*)-3-(Benzyldimethylsilyl)-4-phenylbut-3-en-2-ol**. Pale yellow oil (41 mg, 97%, α:β = 84:16, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): ṽ = 3339, 3079, 3058, 3023, 2968, 2897, 1597, 1492, 1451, 1407, 1366, 1249, 1205, 1154, 1127, 1057, 1029, 978, 904, 876, 823, 792, 752, 696; ESI-MS calcd for $C_{19}H_{24}OSiNa$ ($M+Na^+$) 319.14886; found 319.14887



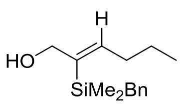
**(*Z*)-2-(Triethylsilyl)hex-2-en-1-ol**. Pale yellow oil (33 mg, 84%, α:β = 91:9, *Z/E* > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.25 (tt, *J* = 7.4, 1.3 Hz, 1H), 4.09 (s (br), 2H), 2.11 (q, *J* = 7.4, Hz, 2H), 1.40 (hex, *J* = 7.4 Hz, 2H), 1.18 (s (br), OH), 0.97 - 0.90 (m, 12H), 0.73 - 0.65 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 145.5, 136.3, 69.3, 33.8, 23.0, 13.9, 7.5, 3.9; IR (film, $cm^{-1}$): ṽ = 3312, 2954, 2934, 2911, 2873, 1614, 1458, 1417, 1378, 1236, 1148, 1073, 1001, 902, 836, 717, 675; ESI-MS calcd for $C_{12}H_{26}OSiNa$ ($M+Na^+$) 237.16451; found 237.16456.

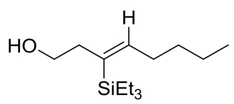


**(*Z*)-3-(Triethylsilyl)hex-2-en-1-ol)**. Formed as the major product using $[Cp^*Ru(MeCN)_3]PF_6$ as the catalyst (28 mg, 70%, α:β = 7:93, *Z/E* > 99:1 for the major isomer (NMR)); $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.19 (tt, *J* = 7.0, 1.3 Hz, 1H), 4.17 (d, *J* = 7.0 Hz, 2H), 2.04 (m, 2H), 1.37 (m, 2H), 1.19 (s (br) OH), 0.97 - 0.87 (m, 12H), 0.70 - 0.62 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 141.3, 141.1, 62.3, 40.2, 23.5, 13.9, 7.5, 4.3; IR (film, $cm^{-1}$): ṽ = 3314, 2954, 2933, 2912, 2873, 1612, 1457, 1416, 1377, 1235, 1073, 1001, 713; ESI-MS calcd for $C_{12}H_{26}OSiNa$ ($M+Na^+$) 237.16451; found 237.16463.



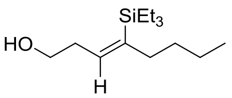
**(*Z*)-2-(Benzyldimethylsilyl)hex-2-en-1-ol**. Colorless oil (40 mg, 84%, α:β = 91:9, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): ṽ = 3317, 3081, 3060, 3024, 2957, 2929, 2897, 2871, 1615, 1600, 1493, 1452, 1408, 1378, 1248, 1206, 1074, 1056, 989, 903, 826, 791, 760, 697; ESI-MS calcd for $C_{15}H_{24}OSiNa$ ($M+Na^+$) 271.14886; found 271.14884.



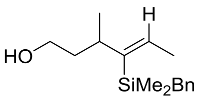


**(*Z*)-3-(Triethylsilyl)oct-3-en-1-ol**. Colorless oil (26 mg, 83%, α:β = 87:13, *Z/E* > 99:1 for the major isomer (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.09 (t, *J* = 7.4 Hz, 1H), 3.54 (m, 2H), 2.30 (t, *J* = 6.5 Hz, 2H), 2.12 (m, 2H), 1.50 (s(br), OH), 1.38 – 1.30 (m, 4H), 0.97 – 0.87 (m, 12H), 0.69 – 0.61 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 147.8, 132.0, 62.1, 41.2, 32.3, 31.9, 22.5, 14.00, 7.5, 4.1; IR (film, $cm^{-1}$): ṽ = 3436, 3401, 2954, 2934, 2912, 2874, 1608, 1459, 1416, 1378, 1238, 1176, 1043, 1005, 967, 860, 716, 673; ESI-MS calcd for $C_{14}H_{30}OSiNa$ ($M+Na^+$) 265.19581; found 265.19594.

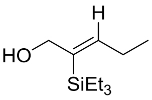
**(*Z*)-4-(Triethylsilyl)oct-3-en-1-ol**. Formed as the major product using [Cp*Ru(MeCN)$_3$]PF$_6$ as the catalyst (35 mg, 99%, α:β = 45:55, *Z/E* > 99:1 for the major isomer (NMR)); characteristic data: $^{1}$H NMR (400 MHz, CDCl$_3$): δ = 5.98 (t, *J* = 7.5 Hz, 1H), 3.66 (m, 2H), 2.39 (q, *J* = 6.9 Hz, 2H), 2.02 (m, 2H), 1.48 (br. s, OH), 1.38-1.24 (m, 4H), 0.97 – 0.87 (m, 12H), 0.71 – 0.63 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 140.7, 138.4, 62.7, 38.2, 35.3, 33.2, 22.6, 14.02, 7.6, 4.2; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3317, 2953, 2924, 2873, 1609, 1458, 1416, 1377, 1237, 1044, 1002, 972, 859, 713, 673; ESI-MS calcd for $C_{14}H_{30}OSiNa$ (M+Na$^+$) 265.19581; found 265.19591.



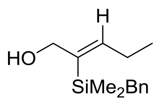

**(*Z*)-4-(Benzyldimethylsilyl)-3-methylhex-4-en-1-ol.** Colorless oil (33 mg, 78%, α:β = 66:34, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3329, 3081, 3060, 3024, 2955, 2928, 1615, 1600, 1493, 1451, 1408, 1372, 1248, 1205, 1154, 1053, 1010, 977, 963, 903, 872, 824, 790, 759, 679; ESI-MS calcd for $C_{16}H_{26}OSiNa$ (M+Na$^+$) 285.16451; found 285.16450.



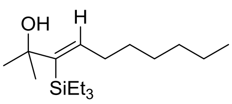

**(*Z*)-2-(Triethylsilyl)pent-2-en-1-ol**. Pale yellow oil (43 mg, 78%, α:β = 91:9, *Z/E* > 99:1 for the major isomer (NMR)). $^{1}$H NMR (400 MHz, CDCl$_3$): δ = 6.23 (t, *J* = 7.5 Hz, 1H), 4.09 (d, *J* = 6.3 Hz, 2H), 2.15 (quint., *J* = 7.5 Hz, 2H), 1.10 (m, OH), 1.00 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.73 – 0.66 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 147.0, 135.6, 69.2, 25.0, 14.2, 7.5, 3.9; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3316, 2953, 2911, 2874, 1614, 1459, 1417, 1376, 1236, 1149, 1079, 1064, 1001, 971, 900, 871, 711, 674, 628; ESI-MS calcd for $C_{11}H_{24}OSiNa$ (M+Na$^+$) 223.14886; found 223.14893.



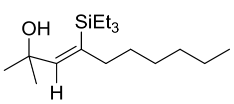

**(*Z*)-2-(Benzyldimethylsilyl)pent-2-en-1-ol**. Pale yellow oil (48 mg, 92%, α:β = 90:10, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3318, 3081, 3060, 3024, 2932, 2894, 2872, 1615, 1600, 1493, 1493, 1452, 1408, 1374, 1249, 1206, 1153, 1080, 1058, 1030, 1000, 903, 872, 825, 791, 760, 697; ESI-MS calcd for $C_{14}H_{22}OSiNa$ (M+Na$^+$) 257.13321; found 257.13319.




**(*Z*)-2-Methyl-3-(triethylsilyl) dec-3-en-2-ol**. Colorless oil (32 mg, 99%, α:β ≥ 99:1, *Z/E* > 99:1 (NMR)). $^{1}$H NMR (400 MHz, CDCl$_3$): δ = 6.19 (t, *J* = 7.5 Hz, 1H), 2.14 (m, 2H), 1.40-1.27 (m, 8H), 1.33 (s, 6H), 1.25 (s, OH), 0.97 - 0.86 (m, 12H), 0.79 - 0.72 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 144.3, 140.3, 75.2, 31.8, 31.3, 31.2, 30.0, 29.2, 22.6, 14.1, 7.9, 5.6; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3436, 2955, 2924, 2873, 1744, 1600, 1460, 1418, 1378, 1236, 1132, 1002, 971, 724, 695; ESI-MS calcd for $C_{17}H_{36}OSiNa$ (M+Na$^+$) 307.24276; found 307.24283.

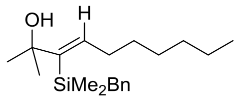



**(*Z*)-2-Methyl-4-(triethylsilyl) dec-3-en-2-ol**. Formed as the major product using [Cp*Ru(MeCN)$_3$]PF$_6$ as the catalyst (29 mg, 86%, α:β = 43:57, *Z/E* > 99:1 for the major isomer (NMR)); $^{1}$H NMR (400 MHz, CDCl$_3$): δ = 5.72 (s, 1H), 2.34 (m, 2H), 1.39 (s, 6H), 1.37-1.25 (m, 9H), 0.97-0.86 (m, 12H), 0.61-0.54 (m, 6H); $^{13}$C NMR (101 MHz,



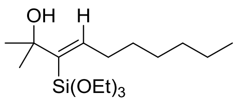
$CDCl_3$): δ = 146.8, 139.3, 73.0, 31.7, 31.3, 31.0, 30.5, 30.1, 22.7, 14.0, 7.4, 3.3; IR (film, $cm^{-1}$): ṽ = 3439, 2954, 2925, 2873, 1600, 1460, 1417, 1377, 1361, 1235, 1118, 1002, 957, 717, 675; ESI-MS calcd for $C_{17}H_{36}OSiNa$ ($M+Na^+$) 307.24276; found 307.24290.

**(*Z*)-3-(Benzyldimethylsilyl)-2-methyldec-3-en-2-ol**. Pale yellow oil (33 mg, 92%, α:β ≥ 99:1, *Z/E* > 99:1 (NMR)).



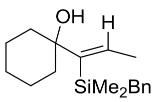

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.18 (m, 2H), 7.09 – 7.04 (m, 1H), 7.02 – 6.99 (m, 2H), 6.16 (t, *J* = 7.5 Hz, 1H), 2.26 (s, 2H), 2.17 (m, 2H), 1.44 – 1.26 (m, 8H), 1.22 (s, 6H), 0.90 (m, 4H), 0.24 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 145.3, 140.6, 140.5, 128.3, 128.1, 124.1, 75.1, 31.8, 31.7, 30.8, 30.0, 29.2, 27.8, 22.6, 14.1, 1.1; IR (film, $cm^{-1}$): ṽ = 3454, 3080, 3060, 3024, 2957, 2924, 2855, 1710, 1600, 1493, 1453, 1409, 1378, 1363, 1317, 1250, 1205, 1152, 1056, 1030, 829, 812, 789, 761, 697; ESI-MS calcd for $C_{20}H_{34}OSiNa$ ($M+Na^+$) 341.22711; found 341.22721.

**(*Z*)-2-Methyl-3-(triethoxysilyl)dec-3-en-2-ol**. Colorless oil (35 mg, 86%, α:β > 99:1, *Z/E* > 99:1 (NMR)).



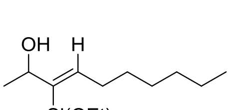

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 6.25 (t, *J* = 7.5 Hz, 1H), 4.06 (s, OH), 3.84 (q, *J* = 7 Hz, 6H), 2.24 (m, 2H), 1.35 (s, 6H), 1.25 (t, *J* = 7 Hz, 9H), 1.40 – 1.20 (m, 8H), 0.88 (m, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 144.2, 139.8, 73.3, 58.3, 31.8, 31.7, 30.1, 29.7, 29.1, 22.6, 18.0, 14.0; IR (film, $cm^{-1}$): ṽ = 3515, 2973, 2925, 2896, 2857, 1608, 1482, 1458, 1444, 1390, 1366, 1296, 1166, 1160, 1072, 954, 900, 821, 777, 708; ESI-MS calcd for $C_{17}H_{36}O_4SiNa$ ($M+Na^+$) 355.22751; found 355.22768.

**(*Z*)-1-(1-(Benzyldimethylsilyl)prop-1-en-1-yl) cyclohexan-1-ol.** Colorless oil (44 mg, quant., α:β ≥ 99:1, *Z/E* > 99:1 (NMR)).



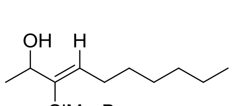

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.22 – 7.17 (m, 2H), 7.08 – 7.03 (m, 1H), 7.02 – 6.98 (m, 2H), 6.30 (q, *J* = 7.3 Hz, 1H), 2.28 (s, 2H), 1.82 (d, *J* = 7.3 Hz, 3H), 1.64 –1.38 (m, 10H), 0.78 (s, OH) 0.24 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 147.5, 140.6, 134.3, 128.3, 128.0, 124.0, 75.6, 37.7, 27.7, 25.5, 22.0, 17.7, 1.3; IR (film, $cm^{-1}$): ṽ = 3597, 3562, 3481, 3081, 3060, 3023, 2926, 2855, 1600, 1493, 1450, 1408, 1375, 1248, 1206, 1152, 1078, 1030, 961, 903, 828, 760, 697; ESI-MS calcd for $C_{18}H_{28}OSiNa$ ($M+Na^+$) 311.18016; found 311.17999.

**(*Z*)-3-(Triethoxysilyl)dec-3-en-2-ol**. Pale yellow oil (27 mg, 76%, α:β > 99:1, *Z/E* > 99:1 (NMR)).



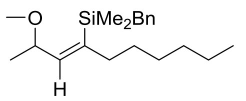

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 6.23 (t, *J* = 7.6 Hz, 1H), 4.19 (m, 1H), 3.84 (q, *J* = 7 Hz, 6H), 3.22 (d, *J* = 9.5 Hz, OH), 2.22 (m, 2H), 1.32 (d, *J* = 6.5 Hz, 3H), 1.24 (t, *J* = 7 Hz, 9H), 1.41 – 1.20 (m, 8H), 0.88 (m, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 147.1, 136.4, 74.6, 58.3, 31.8, 31.7, 29.5, 29.1, 24.8, 22.6, 18.1, 14.0; ESI-MS calcd for $C_{16}H_{34}O_4SiNa$ ($M+Na^+$) 341.21186; found 341.21179.

**(*Z*)-3-(Benzyldimethylsilyl)dec-3-en-2-ol**. Pale yellow oil (32 mg, 95%, α:β = 88:12, *Z/E* > 99:1 for the major isomer (NMR));

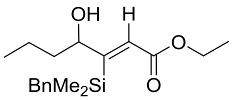



for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): ṽ = 3348, 3081, 3060, 3024, 2956, 2924, 2855, 1601, 1493, 1452, 1407, 1365, 1249, 1206, 1154, 1116, 1057, 958, 902, 824, 791, 760, 697; ESI-MS calcd for $C_{19}H_{32}OSiNa$ ($M+Na^+$) 327.21146; found 327.21147.

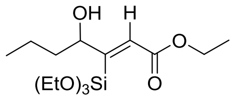
**(*Z*)-Benzyl(2-methoxydec-3-en-4-yl)dimethylsilane**. Pale yellow oil (35 mg, 93%, α:β = 24:76, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3082, 3061, 3024, 2956, 2856, 2817, 1723, 1601, 1493, 1452, 1249, 1204, 1155, 1105, 1087, 1056, 826, 791, 761, 698; ESI-MS calcd for $C_{20}H_{34}OSiNa$ ($M+Na^+$) 341.22711; found 341.22714.



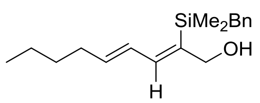

**Ethyl (*Z*)-3-(benzyldimethylsilyl)-4-hydroxyhept-2-enoate**. Orange oil (32 mg, 77%, α:β ≥ 99:1, *Z/E* > 99:1 (NMR)). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.22 – 7.16 (m, 2H), 7.08 – 7.03 (m, 1H), 7.02 – 6.99 (m, 2H), 6.67 (s, 1H), 4.28 – 4.19 (m, 3H), 2.43 (m, 2H), 1.51 – 1.37 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.27 (m, OH), 1.30 – 1.20 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 3H), 0.16 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 167.2, 166.0, 140.0, 128.5, 128.4, 128.1, 124.1, 74.3, 60.3, 39.1, 25.0, 19.3, 14.3, 13.8, –2.20, –2.23; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3196, 3083, 3062, 3026, 2957, 2872, 1713, 1600, 1493, 1453, 1368, 1246, 1151, 1135, 1096, 1070, 1042, 988, 974, 855, 832, 807, 793, 753, 721, 697; ESI-MS calcd for $C_{18}H_{28}O_3SiNa$ ($M+Na^+$) 343.16999; found 343.16991.



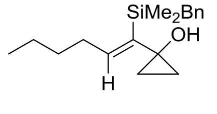

**Ethyl (*Z*)-4-hydroxy-3-(triethoxysilyl)hept-2-enoate**. Orange oil (28 mg, 59%, α:β > 99:1, *Z/E* > 99:1 (NMR)). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 6.42 (s, 1H), 4.21 (q, *J* = 7 Hz, 2H), 4.19 – 4.12 (m, 1H), 3.88 (q, *J* = 7 Hz, 6H), 3.45 (d, *J* = 9.5 Hz, OH), 1.68 – 1.32 (m, 4H), 1.30 (t, *J* = 7 Hz, 3H), 1.22 (t, *J* = 7 Hz, 9H), 0.93 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 166.3, 156.4, 132.9, 77.7, 60.6, 59.0, 39.7, 19.2, 18.0, 14.2, 13.9; ESI-MS calcd for $C_{15}H_{30}O_6SiNa$ ($M+Na^+$) 357.17039; found 357.17064.



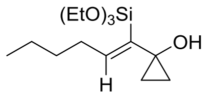

**(2*Z*,4*E*)-2-(Benzyldimethylsilyl)-3-methylnona-2,4-dien-1-ol.** Pale yellow oil (22 mg, 53%, α:β = 90:10, *Z/E* > 99:1 for the major isomer (NMR)). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.17 (m, 2H), 7.11 – 7.04 (m, 1H), 7.02 –6.97 (m, 2H), 6.73 (d, *J* = 11 Hz, 1H), 6.24 (dd, *J* = 16, 11 Hz, 1H), 5.79 (dt, *J* = 16, 8 Hz, 1H), 4.06 (s (br), 2H), 2.28 (s, 2H), 2.12 (q, *J* = 7 Hz, 2H), 1.44 – 1.28 (m, 4H), 0.92 (t, *J* = 8 Hz, 3H), 0.84 (s (br), OH), 0.20 (s, 6H); $^{13}C$ NMR (126 MHz, $CDCl_3$): δ = 143.4, 139.8, 138.8, 137.8, 128.8, 128.2, 128.1, 124.1, 69.1, 32.5, 31.1, 26.6, 22.2, 13.8, -2.3; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3405, 3082, 3060, 3025, 2957, 2931, 2873, 1723, 1600, 1493, 1452, 1407, 1252, 1207, 1156, 1053, 904, 835, 808, 794, 760, 697; ESI-MS calcd for $C_{18}H_{28}OSiNa$ ($M+Na^+$) 311.18016; found 311.18023.



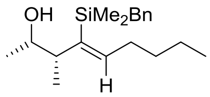

**(*Z*)-1-(1-(Benzyldimethylsilyl)hex-1-en-1-yl) cyclopropan-1-ol.** Yellow oil (34 mg, 66%, α:β ≥ 99:1, *Z/E* > 99:1 (NMR)). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.22 – 7.17 (m, 2H), 7.09 – 7.03 (m, 1H), 7.01 – 6.97 (m, 2H), 6.27 (t, *J* = 7.6 Hz, 1H), 2.28 (s, 2H), 2.13 (m, 2H), 1.39 (s, OH), 1.41 – 1.29 (m, 4H), 0.92 (m, 3H), 0.71 (m, 2H), 0.49 (m, 2H), 0.21 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 146.0, 140.2, 138.1, 128.2, 128.1, 124.1, 61.4, 31.8, 31.4, 26.9. 22.6, 14.1, 12.9, –1.6; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3445, 3081, 3060, 3024, 2957, 2928, 2873, 2859, 1722, 1665, 1599, 1493, 1452, 1409, 1377, 1249, 1206, 1154, 1119, 1056, 904, 825, 792, 760, 698; ESI-MS calcd for $C_{18}H_{28}OSiNa$ ($M+Na^+$) 311.18016; found 311.18012.



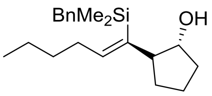
**(*Z*)-1-(1-(Triethoxysilyl)hex-1-en-1-yl)cyclopropan-1-ol**. Pale yellow oil (32 mg, 61%, α:β > 99:1, *Z/E* > 99:1 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 6.23 (t, *J* = 7.5 Hz, 1H), 3.97 (s, OH), 3.85 (q, *J* = 7 Hz, 6H), 2.22 (m, 2H), 1.36 – 1.29 (m, 4H), 1.24 (t, *J* = 7 Hz, 9H), 0.90 – 0.82 (m, 5H), 0.71 – 0.67 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 146.0, 132.5, 59.2, 58.4, 31.6, 31.2, 22.5, 18.1, 14.0, 13.6; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3370, 2957, 2928, 2872, 1659, 1604, 1458, 1377, 1220, 1047, 914, 807; ESI-MS calcd for $C_{15}H_{30}O_4SiNa$ (M+Na$^+$) 325.18056; found 325.18047.



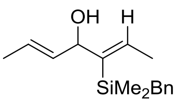

**(2*S*,3*R*,*Z*)-4-(Benzyldimethylsilyl)-3-methylnon-4-en-2-ol.** Colorless oil (35 mg, 72%, α:β = 66:34, *Z/E* = 95:1 for the major isomer (NMR)). $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.23 – 7.18 (m, 2H), 7.10 – 7.04 (m, 1H), 7.03 – 6.97 (m, 2H), 6.06 (t, *J* = 8 Hz, 1H), 3.52 (quint, *J* = 6 Hz, 1H), 2.22 (s, 3H), 2.16 (m, 2H), 1.58 (s(br), OH), 1.34 (m, 4H), 1.10 (d, *J* = 6 Hz, 3H), 0.95 (d, *J* = 8 Hz, 3H), 0.92 (t, *J* = 7 Hz, 3H), 0.12 (s, 3H), 0.09 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ = 143.8, 140.7, 140.0, 128.2, 128.1, 124.1 69.4, 44.1, 32.4, 32.4, 26.8, 22.4, 20.7, 14.1, 13.9, −1.5, −1.3; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3369, 3081, 3061, 3025, 2958, 2926, 2872, 1601, 1493, 1452, 1407, 1371, 1249, 1205, 1154, 1088, 1056, 1030, 901, 825, 790, 759, 697; ESI-MS calcd for $C_{19}H_{32}OSiNa$ (M+Na$^+$) 327.21146; found 327.21151.



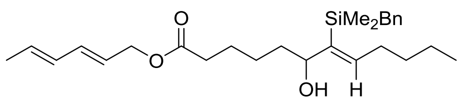

**(1R,2S)-2-((*Z*)-1-(Benzyldimethylsilyl) hex-1-en-1-yl) cyclopentan-1-ol.** Pale yellow oil (42 mg, 93%, α:β = 82:18, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3378, 3081, 3060, 3024, 2954, 2926, 2872, 1600, 1493, 1452, 1407, 1378, 1248, 1205, 1154, 1086, 1057, 1029, 978, 902, 826, 790, 760, 697; ESI-MS calcd for $C_{20}H_{32}OSiNa$ (M+Na$^+$) 339.21146; found 339.21142.



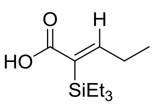

**(2*Z*,5*E*)-3-(Benzyldimethylsilyl)hepta-2,5-dien-4-ol.** Pale yellow oil (37 mg, 86%, α:β = 60:40, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3415, 3081, 3060, 3024, 2958, 2892, 1720, 1600, 1493, 1451, 1374, 1250, 1206, 1154, 1056, 1030, 969, 905, 823, 792, 760, 698; ESI-MS calcd for $C_{16}H_{24}OSiNa$ (M+Na$^+$) 283.14886; found 283.14883.




**(2*E*,4*E*)-Hexa-2,4-dien-1-yl (*Z*)-7-(benzyldimethylsilyl)-6-hydroxydodec-7-enoate.** Colorless oil (25 mg, 59%, α:β = 83:17, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3468, 3080, 3059, 3024, 2954, 2929, 2858, 1733, 1662, 1600, 1493, 1452, 1414, 1378, 1352, 1249, 1206, 1155, 1097, 1057, 1029, 988, 905, 871, 827, 792, 761, 733, 698; ESI-MS calcd for $C_{27}H_{42}O_3SiNa$ (M+Na$^+$) 465.27954; found 465.27957.

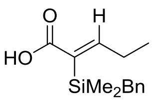



**(*Z*)-2-(Triethylsilyl)pent-2-enoic acid.** Colorless oil (70 mg, 82%, α:β = 83:17, *Z/E* = 95:1 for the major isomer (NMR)). $^1$H NMR (500 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7 Hz, 1H), 2.29 (quint., *J* = 7 Hz, 2H), 1.07 (t, *J* = 7 Hz, 3H), 0.95 (t, *J* = 8 Hz, 9H), 0.77 (q, *J* = 6 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ = 177.6, 161.5, 130.5, 25.3, 13.5, 7.5, 4.3; IR (film, cm$^{-1}$): $\tilde{\nu}$ = 3043,

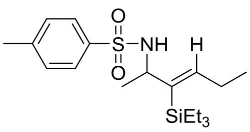


2955, 2937, 2875, 2635, 1670, 1596, 1458, 1405, 1271, 1144, 1072, 1002, 961, 721, 690; ESI-MS calcd for $C_{11}H_{21}O_2Si$ $(M{-}H)^-$ 213.13163; found 213.13149.

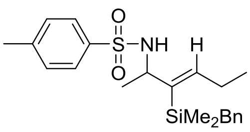
**(*Z*)-2-(Benzyldimethylsilyl) pent-2-enoic acid.** Pale yellow oil (61 mg, 83%, α:β = 71:29, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3024, 2965, 2935, 2896, 2876, 1672, 1597, 1493, 1452, 1407, 1248, 1205, 1153, 1056, 1029, 826, 792, 761, 697; ESI-MS calcd for $C_{14}H_{20}O_2SiNa$ $(M+Na^+)$ 271.11248; found 271.11259.



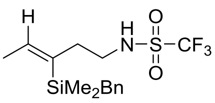

**(*Z*)-4-Methyl-N-(3-(triethylsilyl)hex-3-en-2-yl)benzenesulfonamide**. Colorless oil (21 mg, 78%, α:β = 86:14, *Z/E* 97:3 for the major isomer (NMR)). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.72 (m, 2H), 7.27 (m, 2H), 6.10 (t, *J* = 7.5 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 3.82 (quint., *J* = 6.8 Hz, 1H), 2.40 (s, 3H), 2.01 (m, 2H), 1.15 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.82 (t, *J* = 7.8 Hz, 9H), 0.53 (t, *J* = 7.8 Hz, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 145.2, 143.0, 138.0, 137.7, 129.4, 127.2, 52.8, 25.0, 24.2, 21.4, 13.9, 7.5, 4.0; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3276, 2956, 2874, 1599, 1496, 1457, 1417, 1376, 1321, 1238, 1152, 1125, 1094, 1003, 978, 906, 857, 813, 728, 709, 666; ESI-MS calcd for $C_{19}H_{33}NO_2SSiNa$ $(M+Na^+)$ 390.18935; found 390.18950.



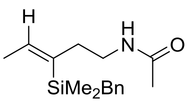

**(*Z*)-N-(3-(Benzyldimethylsilyl) hex-3-en-2-yl)-4-methylbenzenesulfonamide.** Colorless oil (30 mg, 82%, α:β = 79:21, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3277, 3080, 3060, 3025, 2966, 2930, 2897, 2873, 1599, 1493, 1452, 1409, 1374, 1322, 1305, 1289, 1250, 1206, 1154, 1094, 1058, 1020, 979, 948, 905, 826, 813, 792, 762, 699, 661; ESI-MS calcd for $C_{22}H_{31}NO_2SSiNa$ $(M+Na^+)$ 424.17370; found 424.17397.



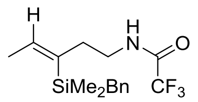

**(*Z*)-N-(3-(Benzyldimethylsilyl) pent-3-en-1-yl)-1,1,1-trifluoromethanesulfonamide.** Colorless oil (38 mg, 86%, α:β = 92:8, *Z/E* > 99:1 for the major isomer (NMR)). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.26 – 7.21 (m, 2H), 7.13 – 7.08 (m, 1H), 7.01 – 6.97 (m, 2H), 6.19 (qt, *J* = 7.1, 1 Hz, 1H), 4.12 (s (br), NH), 2.86 (q, *J* = 6.3 Hz, 2H), 2.25 (s, 2H), 2.18 (t, *J* = 6.3 Hz, 2H), 1.87 (d, *J* = 7.1 Hz, 3H), 0.19 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ = 142.8, 139.9, 133.2, 128.4, 127.9, 124.7, 119.6 (q, *J* = 320 Hz, $CF_3$), 43.9, 38.9, 26.3, 18.4, –1.9; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3318, 3083, 3061, 3025, 2953, 2916, 1614, 1601, 1493, 1424, 1370, 1252, 1229, 1186, 1142, 1058, 967, 905, 825, 791, 759, 699; ESI-MS calcd for $C_{15}H_{21}F_3NO_2SSi$ (M-H) 364.10199; found 364.10212.



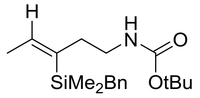

**(*Z*)-N-(3-(Benzyldimethylsilyl) pent-3-en-1-yl) acetamide**. Colorless oil (55 mg, 86%, α:β = 52:48, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3286, 3081, 3024, 2930, 1740, 1647, 1600, 1553, 1493, 1438, 1372, 1294, 1249, 1206, 1154, 1100, 1057, 992, 903, 825, 791, 759, 697; ESI-MS calcd for $C_{16}H_{25}ONSiNa$ $(M+Na^+)$ 298.15976; found 298.15962.



**(*Z*)-N-(3-(Benzyldimethylsilyl) pent-3-en-1-yl)-2,2,2-trifluoroacetamide.** Colorless oil (54 mg, 98%, α:β = 74:26, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3310, 3102, 3082, 3061, 3025, 2952, 2900, 2862, 1701, 1614, 1600, 1555, 1493, 1451, 1409, 1367, 1338, 1251, 1204, 1153, 1057, 1030, 904, 825, 792, 760, 723, 697; ESI-MS calcd for $C_{16}H_{21}F_3NOSi$ (M-H) 328.13500; found 328.13509.




***tert*-Butyl (*Z*)-(3-(benzyldimethylsilyl) pent-3-en-1-yl) carbamate.** Colorless oil (49 mg, 94%, α:β = 58:42, *Z/E* > 99:1 for the major isomer (NMR)); for characteristic NMR shifts, see Table S-1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3428, 3352, 3081, 3060, 3024, 2975, 2930, 1697, 1615, 1600, 1506, 1493, 1452, 1391, 1365, 1248, 1206, 1166, 1057, 1030, 982, 904, 826, 791, 760, 698; ESI-MS calcd for $C_{19}H_{31}NO_2SiNa$ ($M+Na^+$) 356.20163; found 356.20163.




**(*Z*)-2-(1-(Benzyldimethylsilyl) dec-1-en-1-yl)-1*H*-indole.** Pale yellow oil (27 mg, 81%, α:β ≥ 99:1, *Z/E* > 99:1 (NMR)). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 7.10 – 6.98 (m, 5H), 6.68 (s (br), NH), 6.49 (t, *J* = 7.5 Hz, 1H), 6.06 (s, 1H), 2.33 (s, 2H), 2.30 (q, *J* = 7.5 Hz, 2H), 1.51 – 1.42 (m, 2H), 1.42 – 1.25 (m, 9H), 0.93 – 0.83 (m, 4H), 0.18 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ = 150.3, 143.1, 140.0, 135.6, 131.5, 128.7, 128.5, 124.5, 120.8, 119.7, 119.4, 110.3, 99.1, 32.5, 31.9, 29.7, 29.5, 29.3, 26.7, 22.7, 14.1, –1.1; IR (film, $cm^{-1}$): $\tilde{\nu}$ = 3415, 3079, 3057, 3024, 2954, 2923, 2853, 1666, 1599, 1527, 1492, 1454, 1400, 1343, 1318, 1289, 1251, 1206, 1151, 1056, 1029, 905, 860, 826, 794, 763, 745, 699, 680; ESI-MS calcd for $C_{27}H_{37}NSiNa$ ($M+Na^+$) 426.25875; found 426.25874.

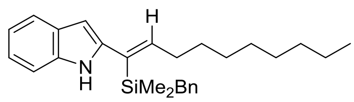
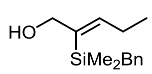
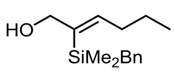
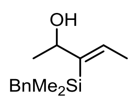
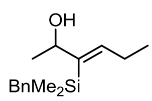
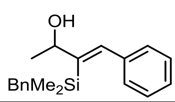
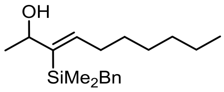
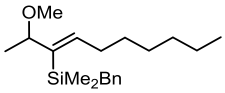
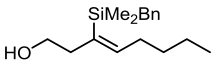
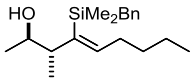
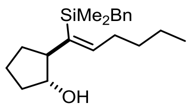
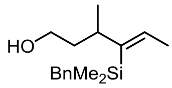
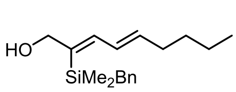
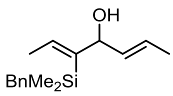
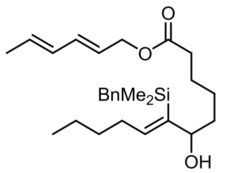
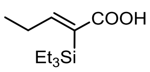
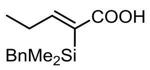
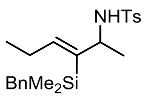
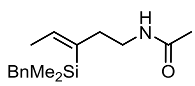
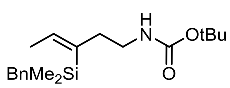
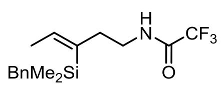
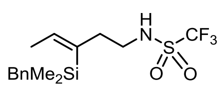
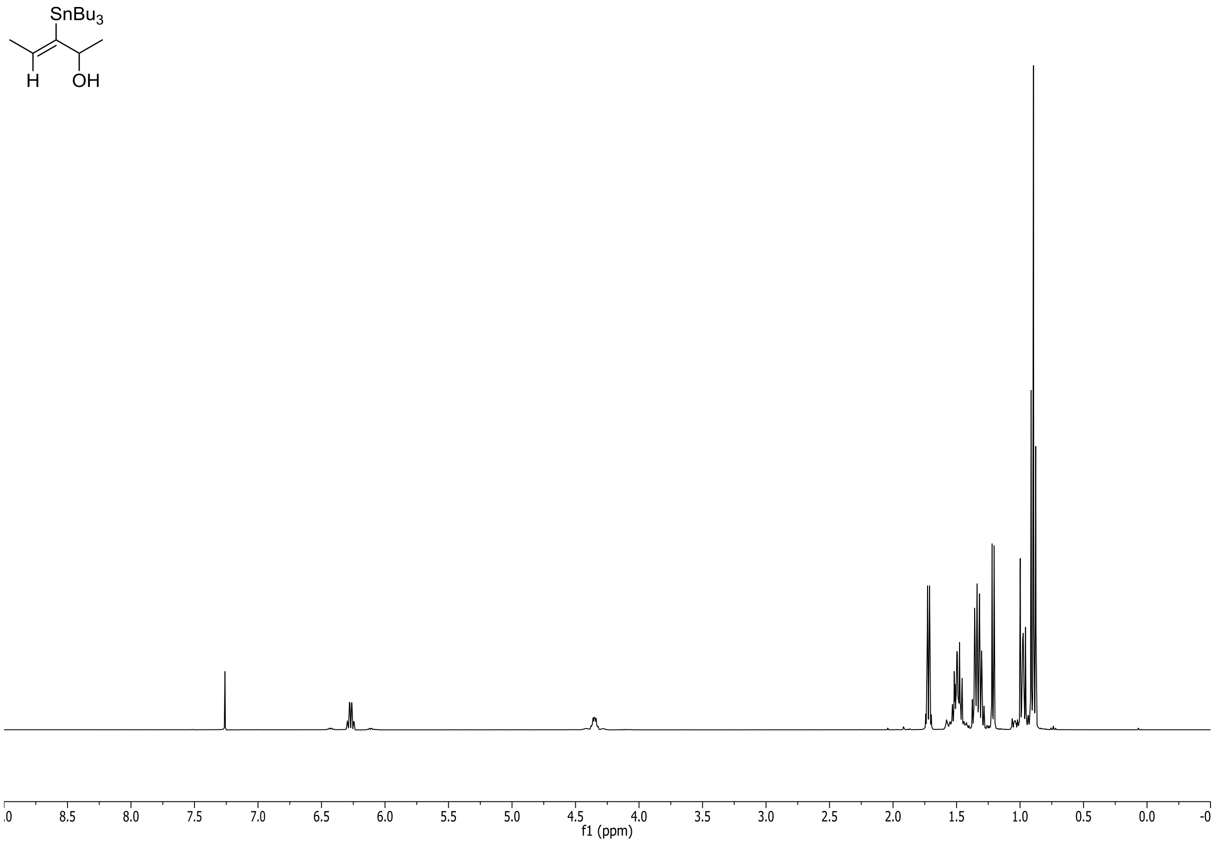


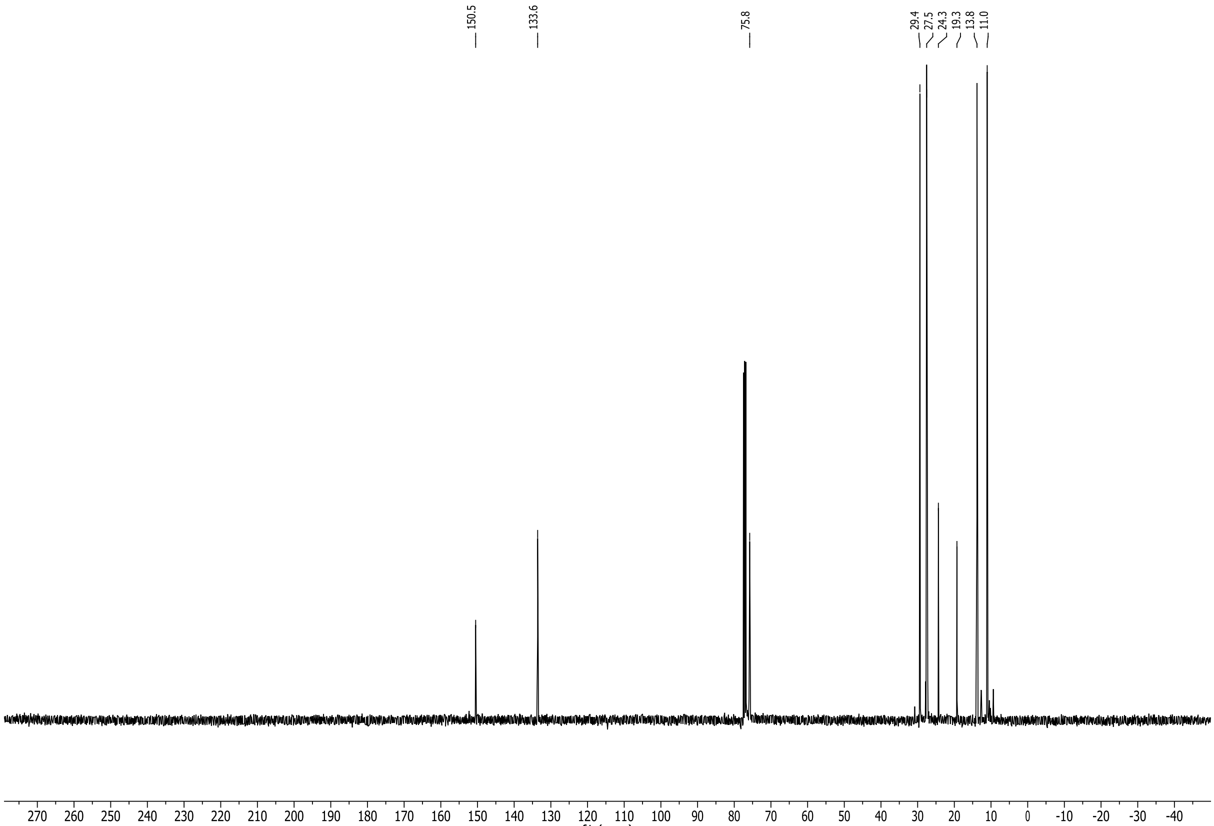

**Table S-1**. Directed *trans*-Hydrosilylation: the spectral data show a consistent trend, which facilitates the assignment in cases, in which detectable amounts of the second isomer were formed.

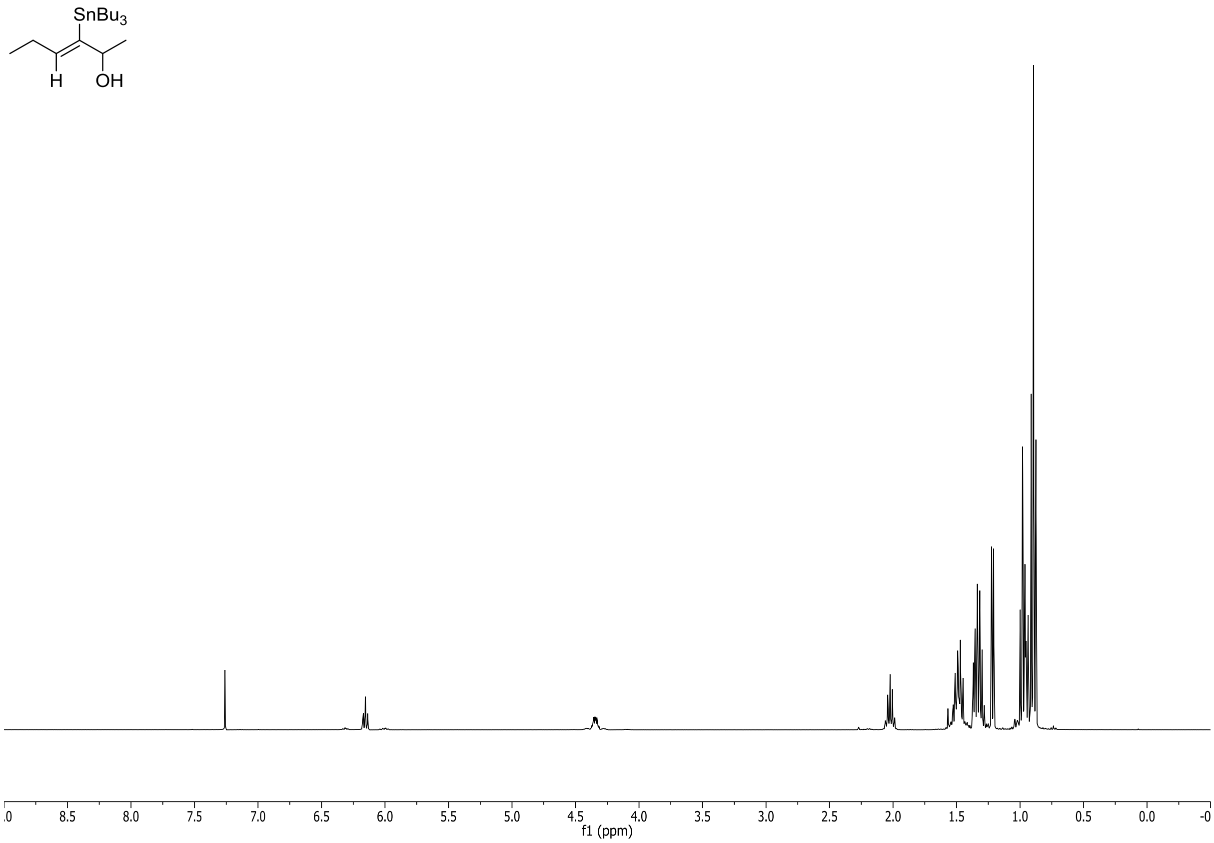
| **Product** | **Characteristic Olefinic Signal [$\delta_H$ (ppm, $CDCl_3$), *J* (Hz)]** | |
|---|---|---|
| **Proximal Isomer** | **Proximal Isomer** | **Distal Isomer** |
|  | 6.21 (tt, *J* = 7.5, 1 Hz) | 6.14 (tt, *J* = 7, 1.5 Hz) |
|  | 6.24 (tt, *J* = 7.5, 1 Hz) | 6.14 (tt, *J* = 7, 0.9 Hz) |
|  | 6.40 (qd, *J* = 7.1, 1.2 Hz) | 5.96 (dq, *J* = 9.4, 1.6 Hz) |
|  | 6.26 (td, *J* = 7.5, 1.1 Hz) | 5.92 (dt, *J* = 9.5, 1.1 Hz) |
|  | 7.55 (s (br)) | 6.05 (d, *J* = 9.5 Hz) |

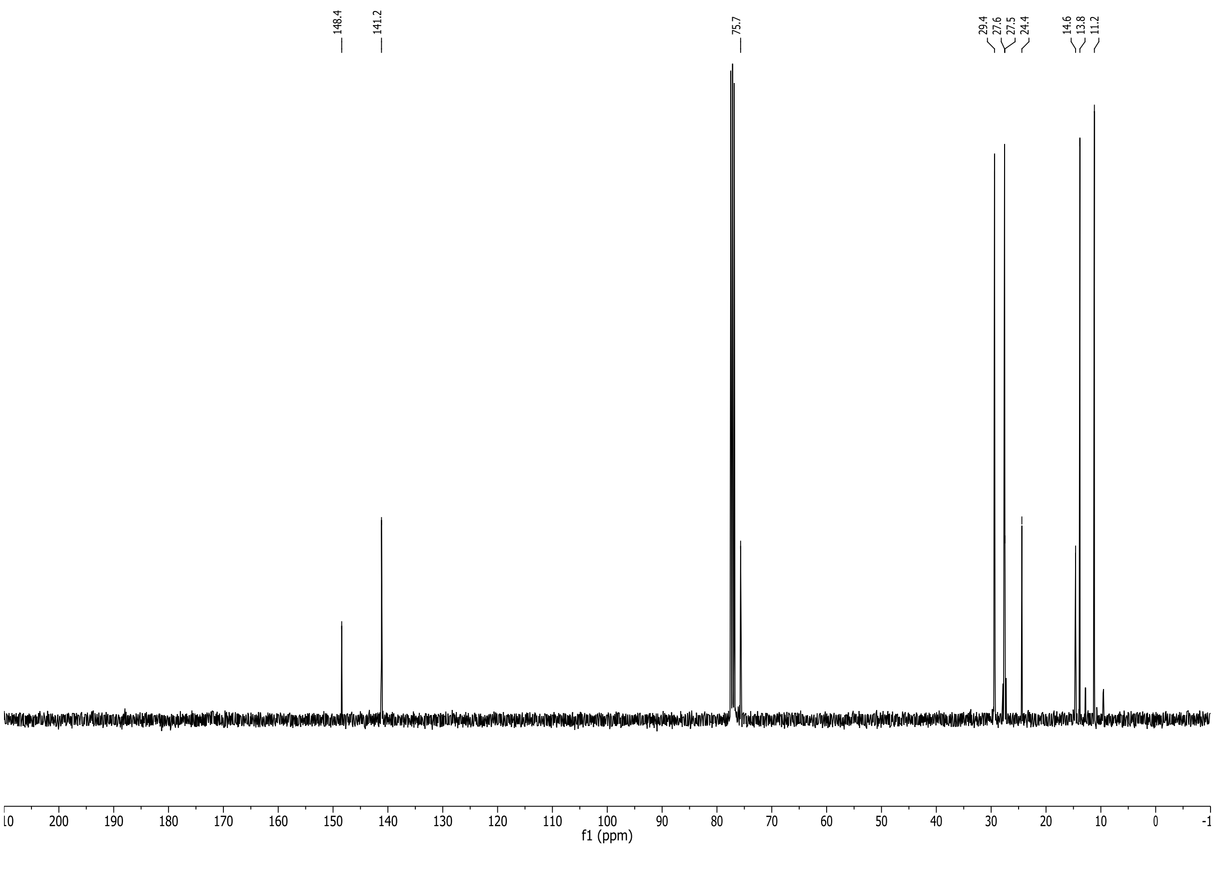
| | | |
|---|---|---|
|  | 6.29 (td, *J* = 7.5, 1.1 Hz) | 5.92 (dt, *J* = 9.5, 1.1 Hz) |
|  | 6.20 (td, *J* = 7.5, 1 Hz) | 5.84 (dt, *J* = 9.5, 1.1 Hz) |
|  | 6.09 (t, *J* = 7.5 Hz) | 5.96 (t, *J* = 7.5 Hz) |
|  | 6.06 (t, *J* = 7.5 Hz) | 5.84 (d, *J* = 10.6 Hz) |
|  | 6.05 (t, *J* = 7.5 Hz) | 5.78 (d, *J* = 10.6 Hz) |
|  | 6.16 (qd, *J* = 7, 0.8 Hz) | 5.80 (dq, *J* = 10.3, 1.6 Hz) |
|  | 6.73 (d, *J* = 11 Hz) | 6.24[a] |
|  | 6.39 (qd, *J* = 7.1, 1 Hz) | 5.96 (dq, *J* = 9.6, 1.5 Hz) |
|  | 6.24 (td, *J* = 7.1, 1 Hz) | 5.90 (d, *J* = 9.7 Hz) |
|  | 7.31 (t, *J* = 7 Hz) | 6.35 (t, *J* = 2 Hz) |
|  | 7.36 (t, *J* = 7.7 Hz) | 6.36 (br s) |
|  | 6.02 (t, *J* = 7.6 Hz) | 5.60 (dt, *J* = 9.7, 1.4 Hz) |
|  | 6.11 (q, *J* = 7 Hz) | 5.93 (t, *J* = 7 Hz) |
|  | 6.13 (qt, *J* = 7.1, 1.1 Hz) | 5.93 (tq, *J* = 7.4, 1.6 Hz) |
|  | 6.09 (qt, *J* = 7.0, 1.1 Hz) | 5.89 (tq, *J* = 7.5, 1.6 Hz) |
|  | 6.19 (qt, *J* = 7.1, 1 Hz) | 5.85 (tq, *J* = 7.3, 1.6 Hz) |

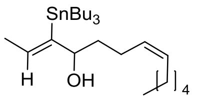
[a] overlapping signals

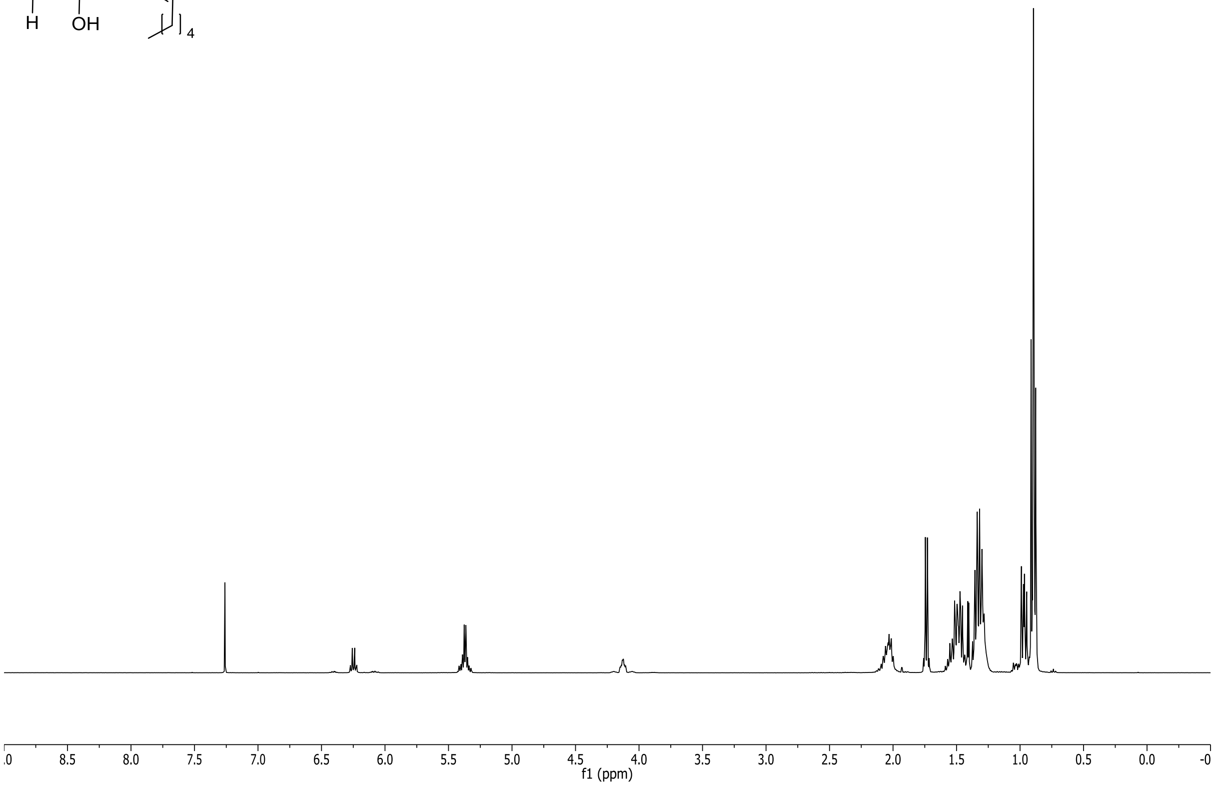

SnBu3
H
OH
f1 (ppm)

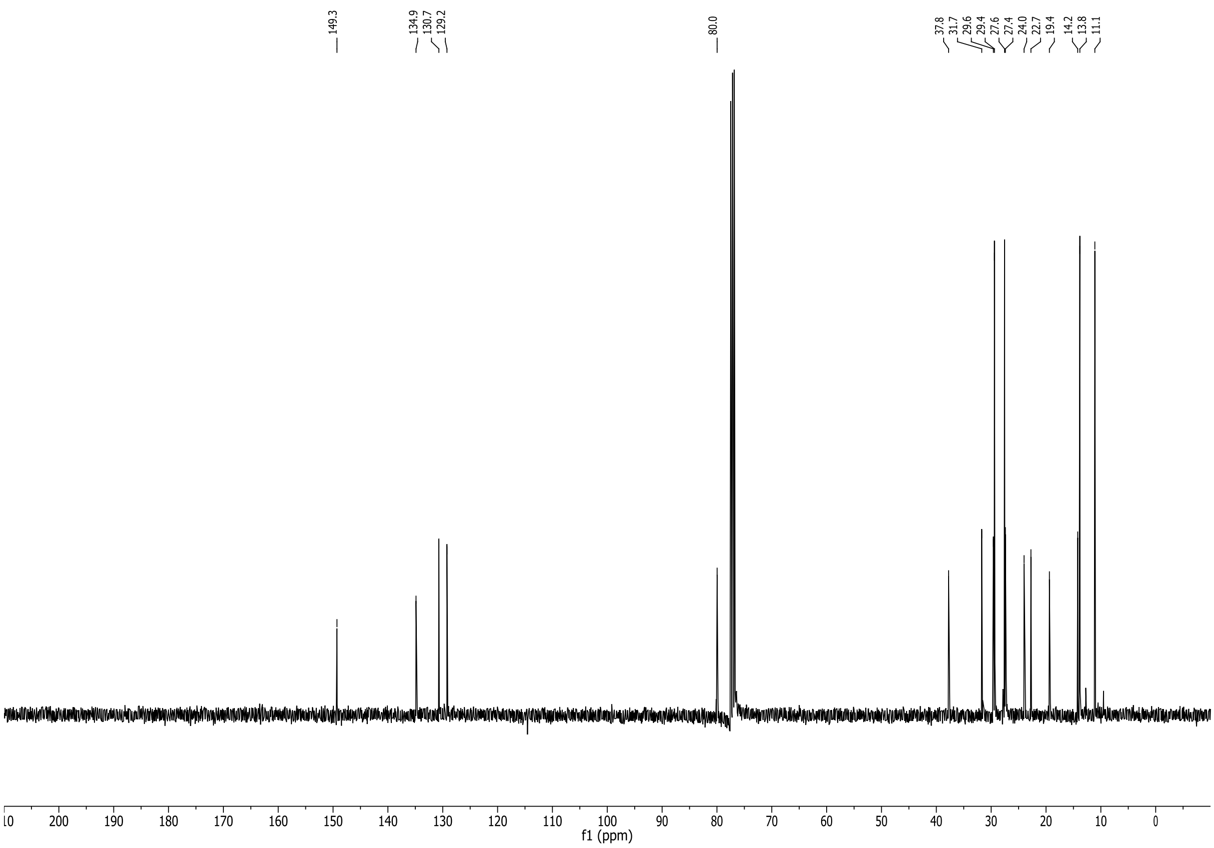

150.5
133.6
75.8
29.4
27.5
24.3
19.3
13.8
11.0
f1 (ppm)

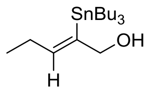

SnBu3
H
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

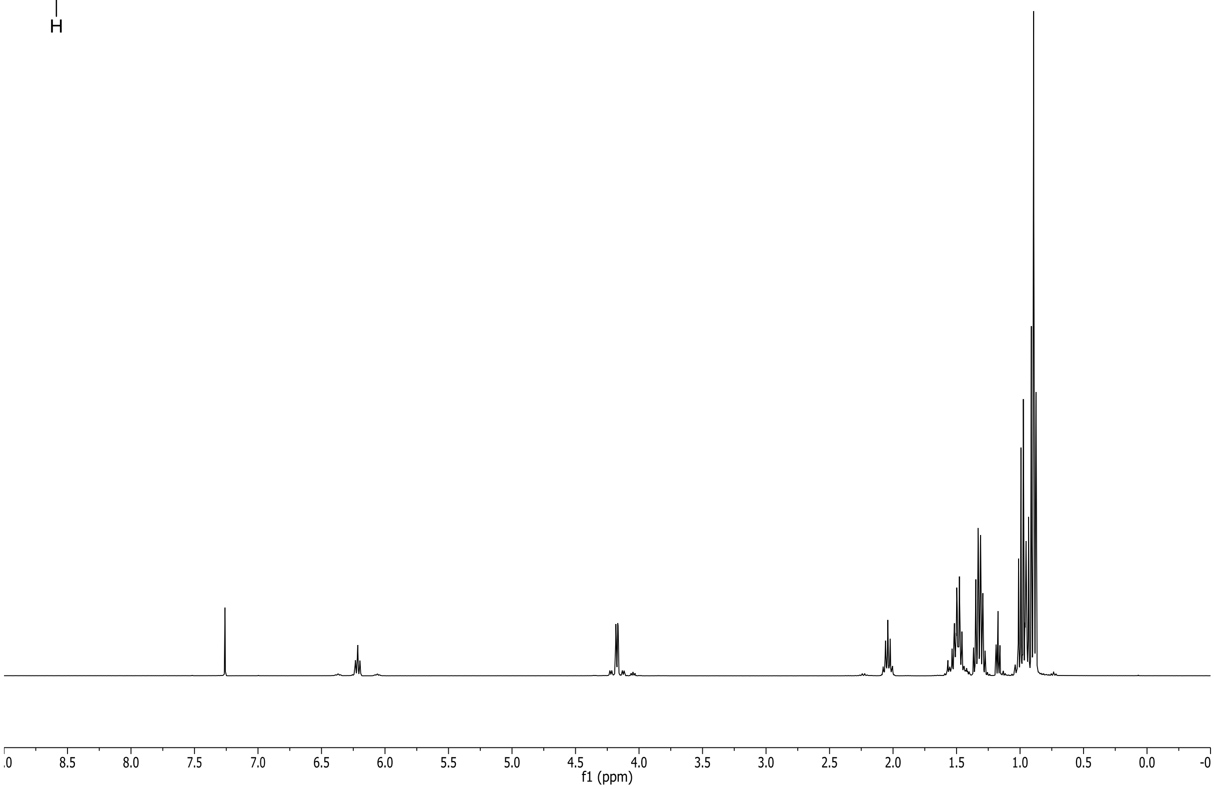

148.4
141.2
75.7
29.4
27.6
27.5
24.4
14.6
13.8
11.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

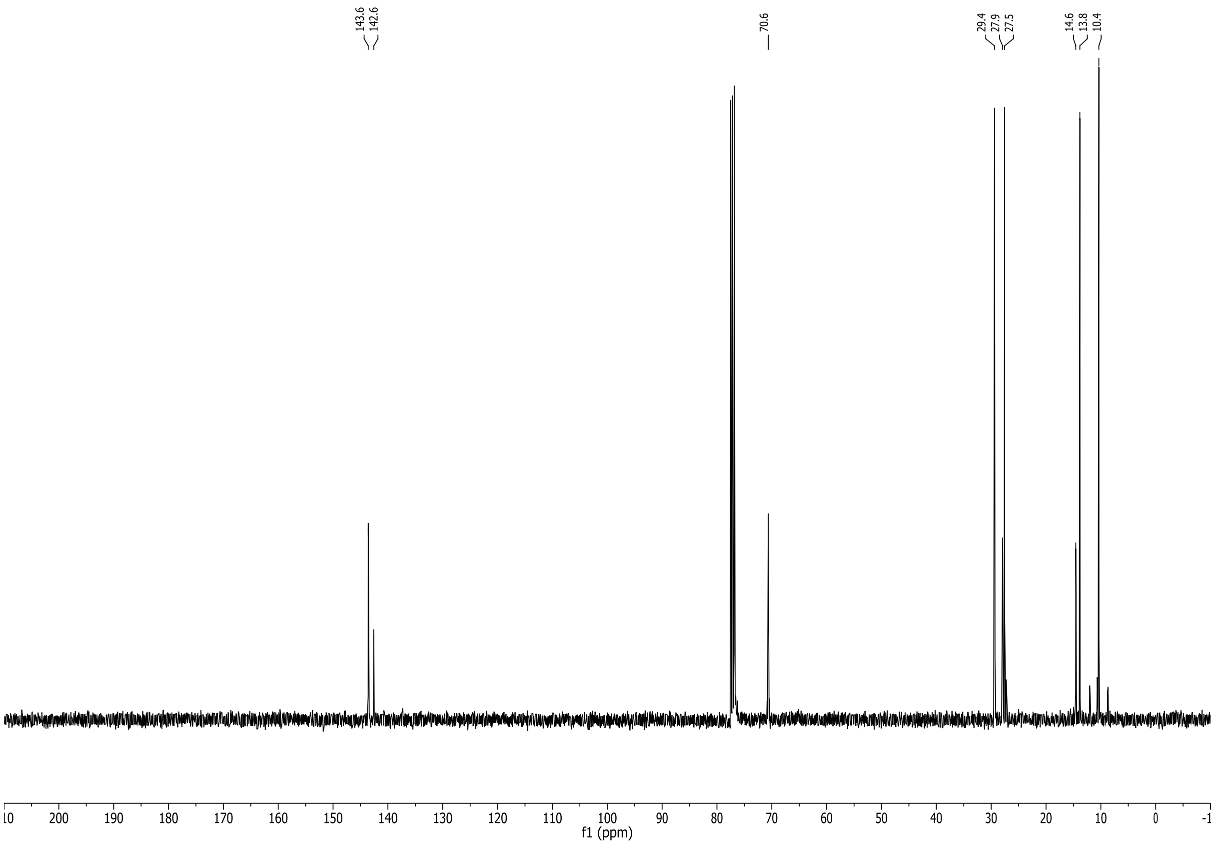

SnBu3
H
OH
4

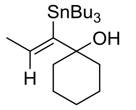

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

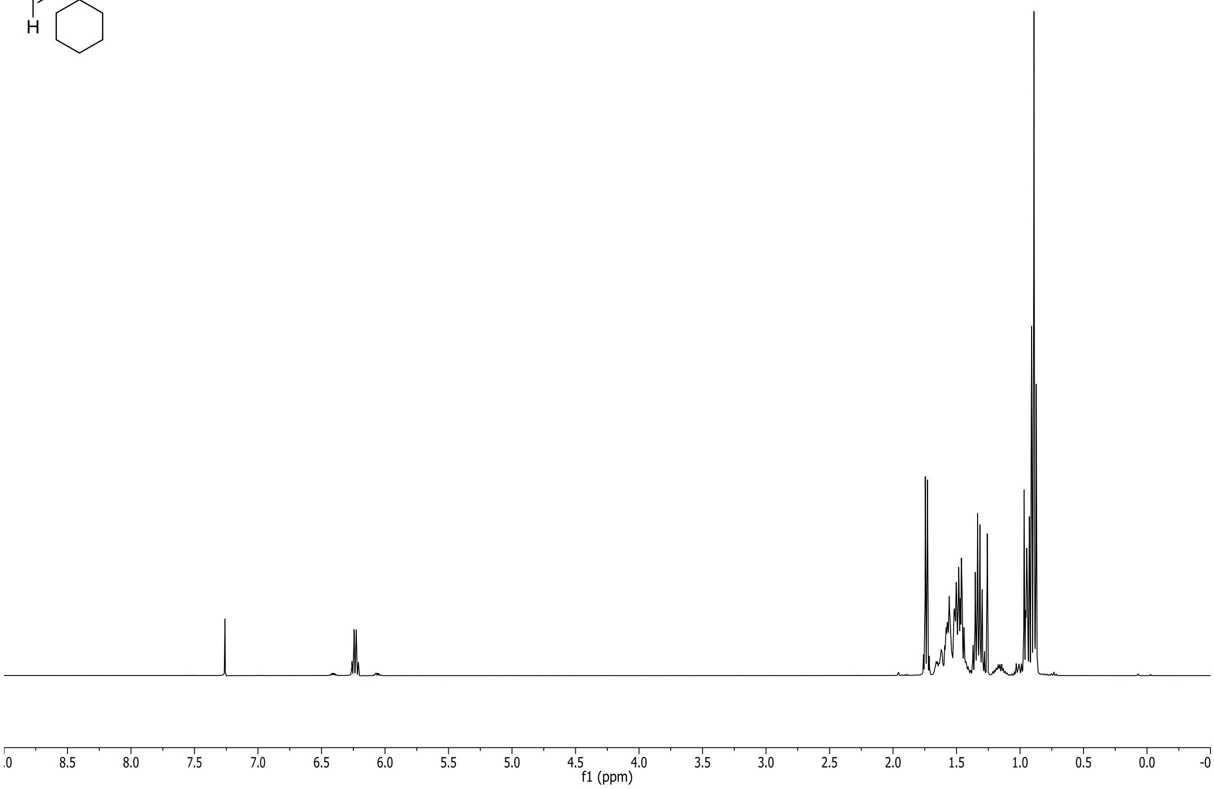

149.3
134.9
130.7
129.2
80.0
37.8
31.7
29.6
29.4
27.6
27.4
24.0
22.7
19.4
14.2
13.8
11.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

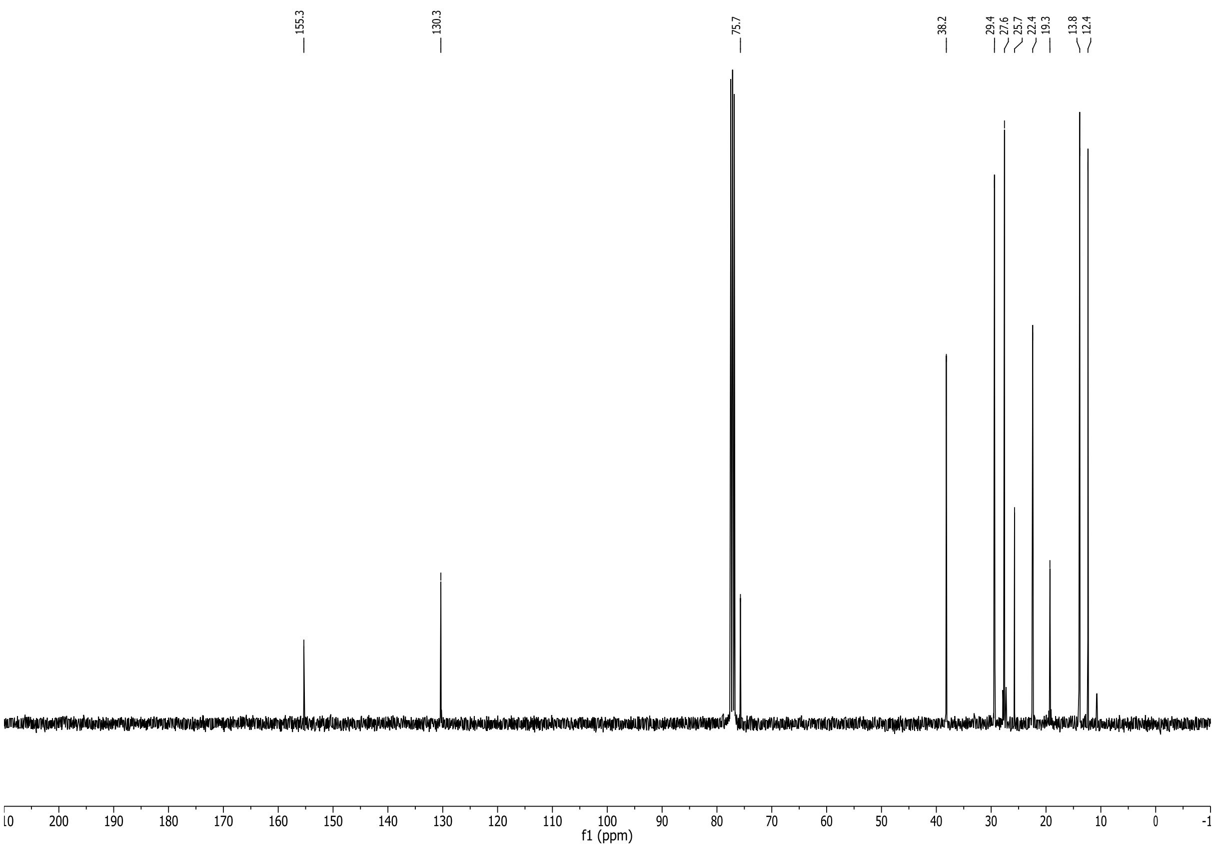

SnBu3
OH
H

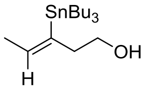

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.6
142.6
70.6
29.4
27.9
27.5
14.6
13.8
10.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

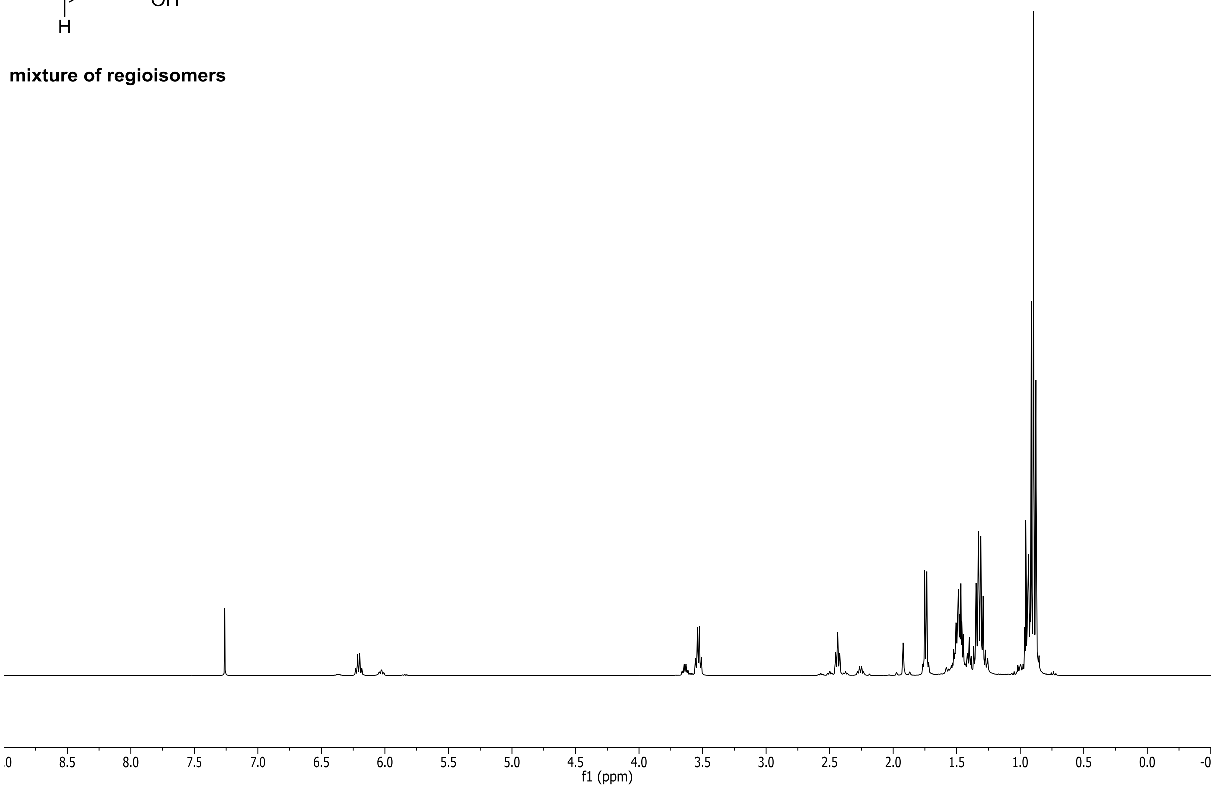

SnBu3
OH
H

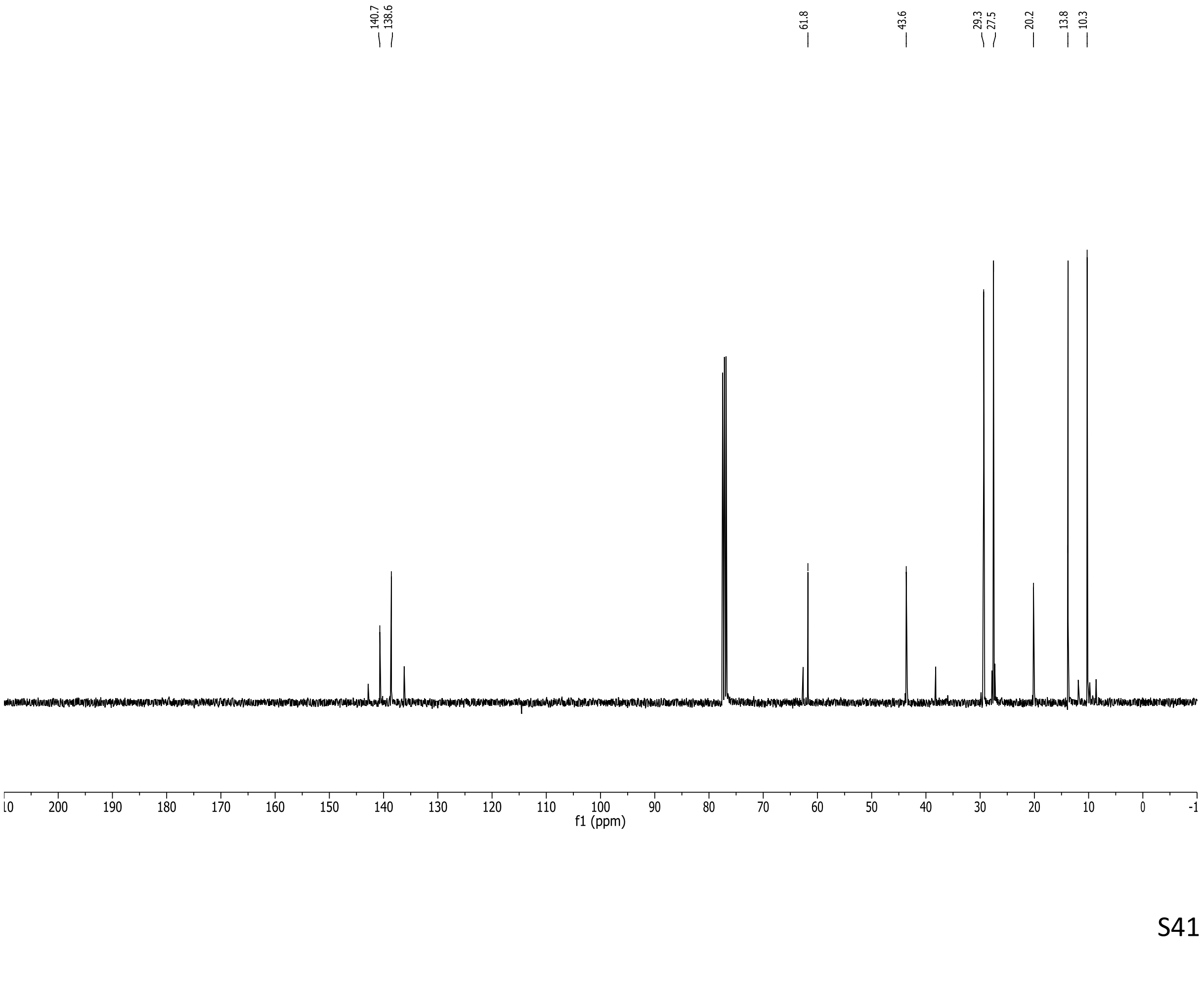

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

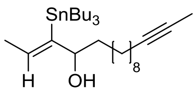

155.3
130.3
75.7
38.2
29.4
27.6
25.7
22.4
19.3
13.8
12.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

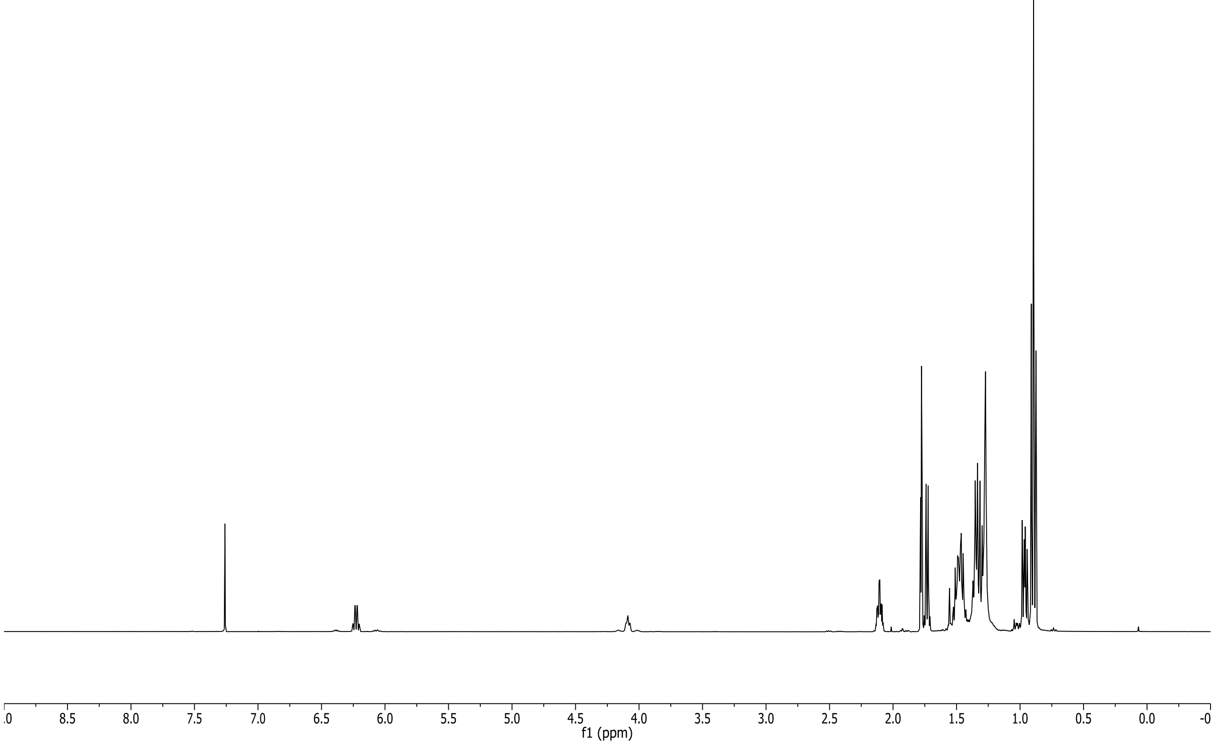


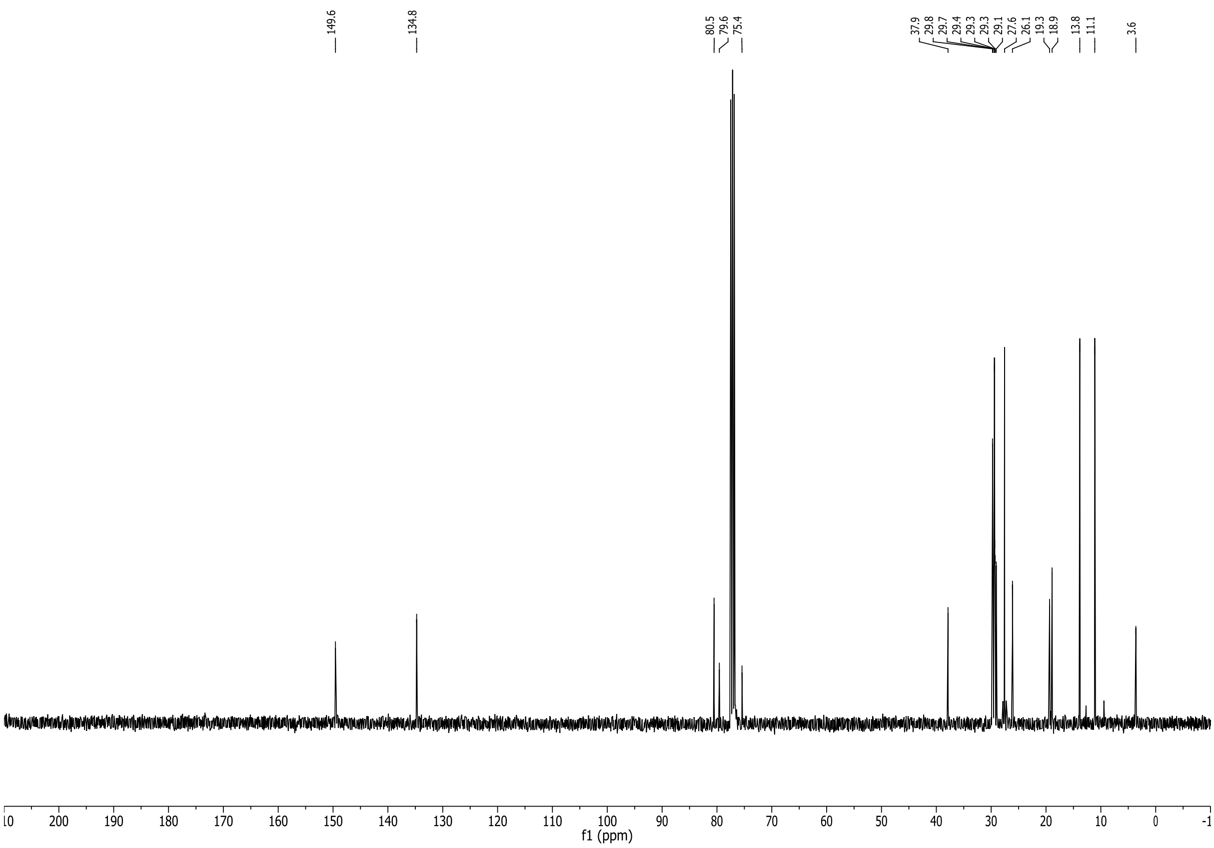

**mixture of regioisomers**

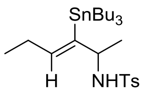


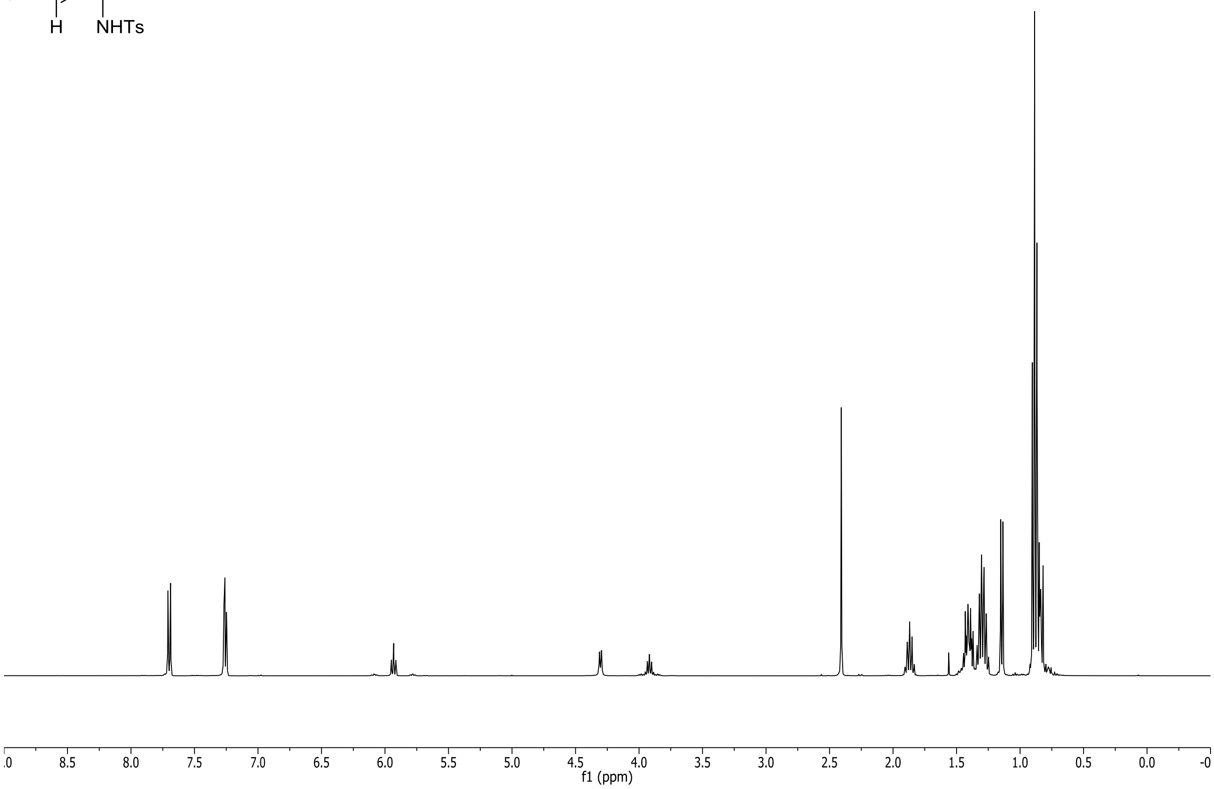



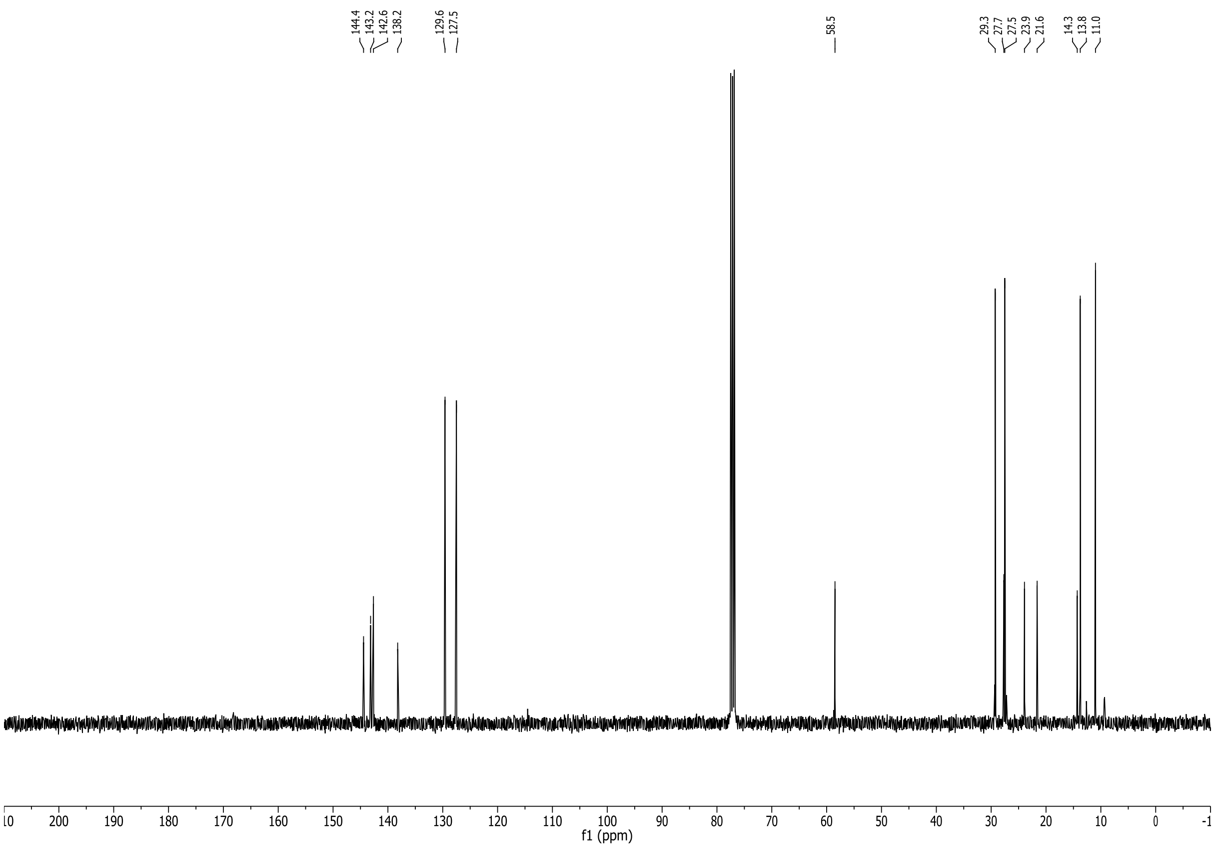

SnBu3
H
OH
8

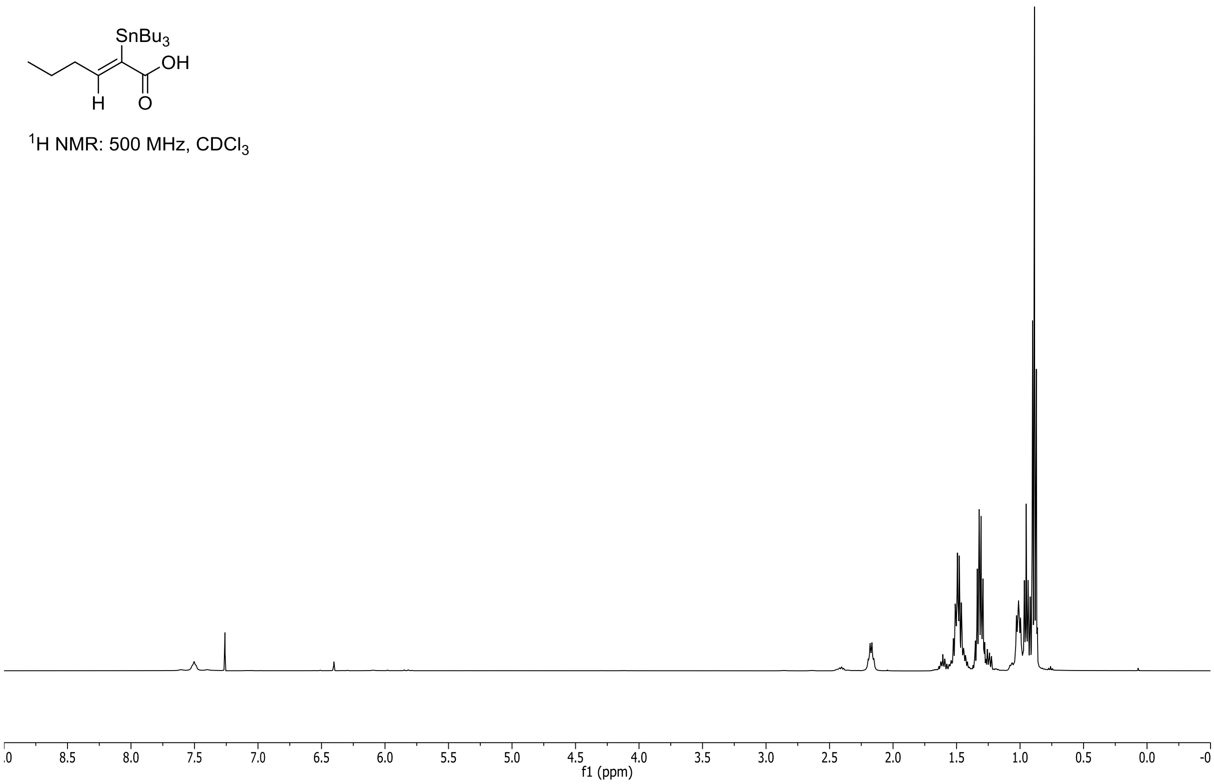

.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


149.6
134.8
80.5
79.6
75.4
37.9
29.8
29.7
29.4
29.3
29.3
29.1
27.6
26.1
19.3
18.9
13.8
11.1
3.6
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

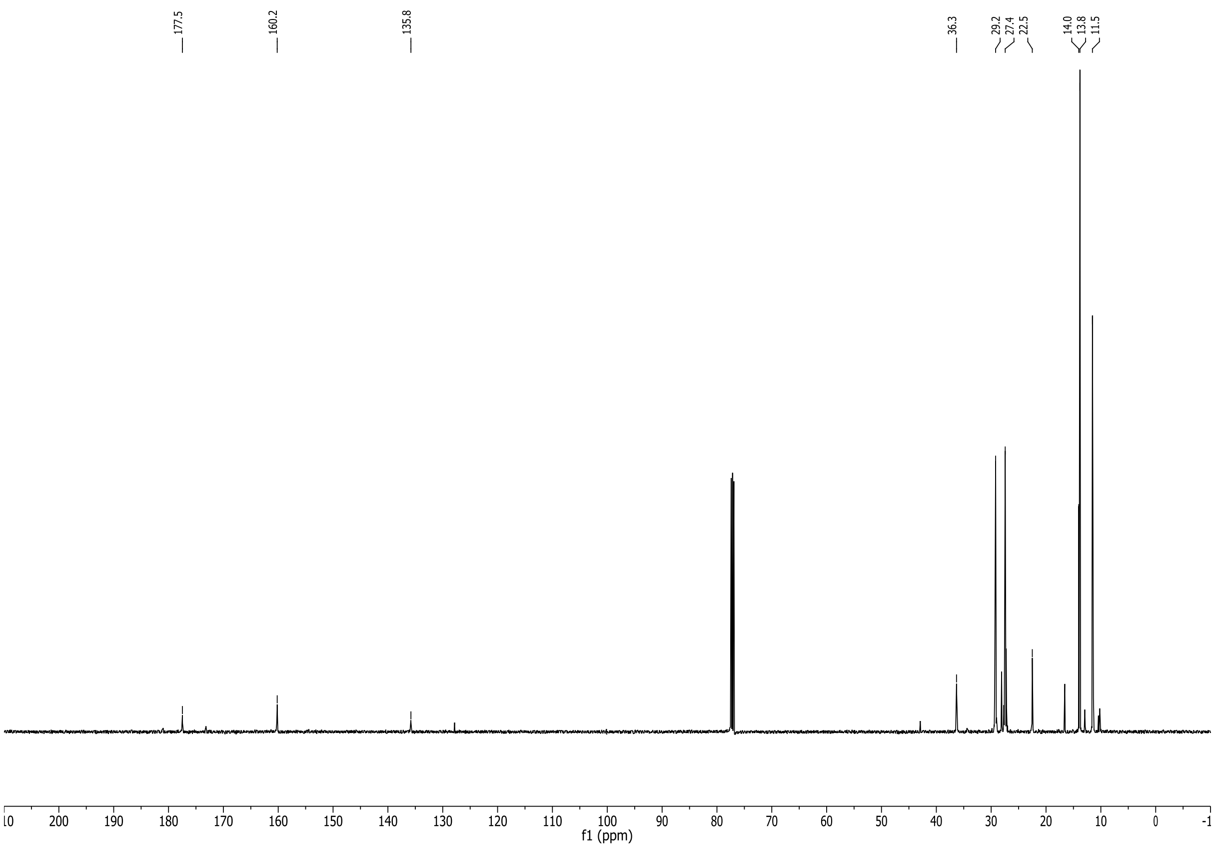

SnBu3
H
NHTs

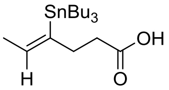

f1 (ppm)


144.4
143.2
142.6
138.2
129.6
127.5
58.5
29.3
27.7
27.5
23.9
21.6
14.3
13.8
11.0
f1 (ppm)

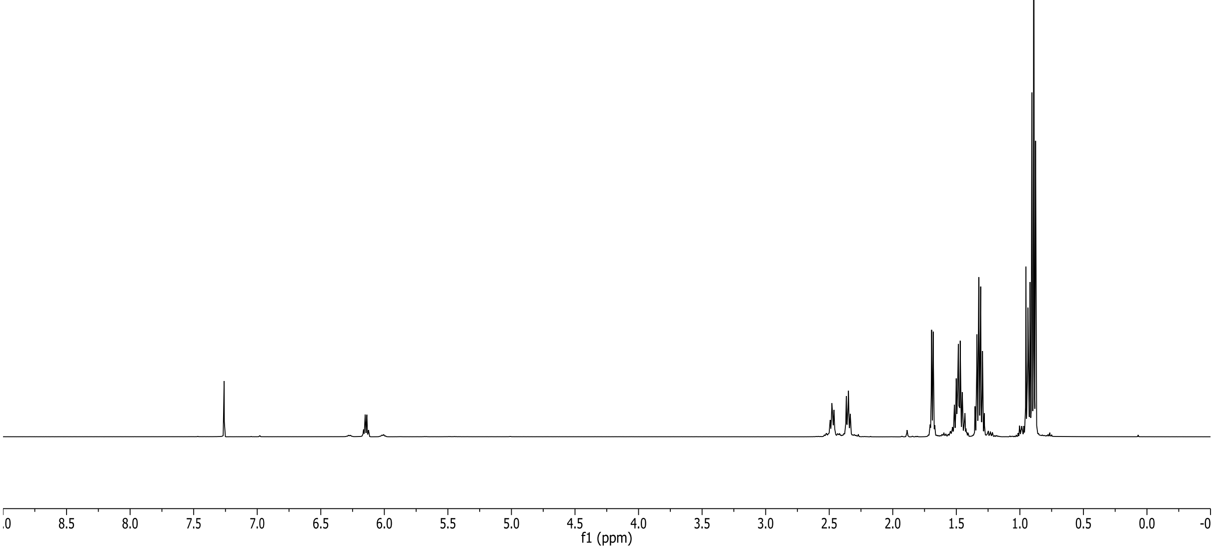


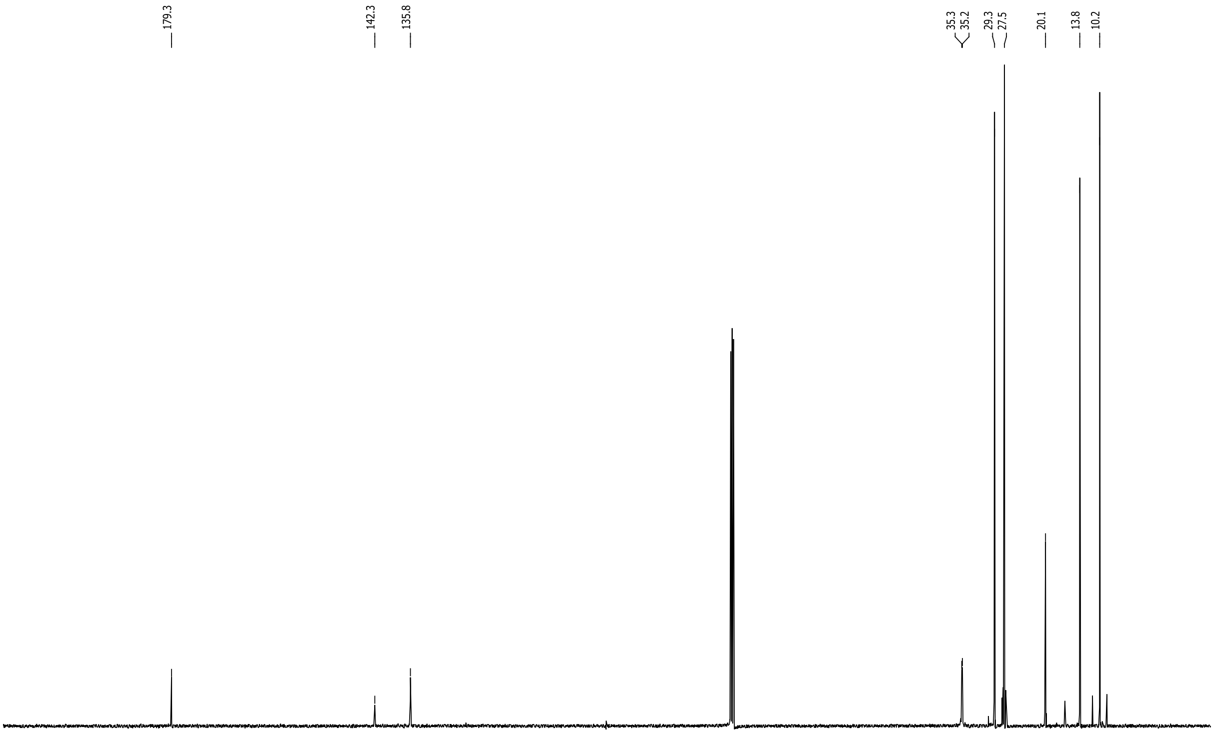

$^1$H NMR: 500 MHz, $CDCl_3$

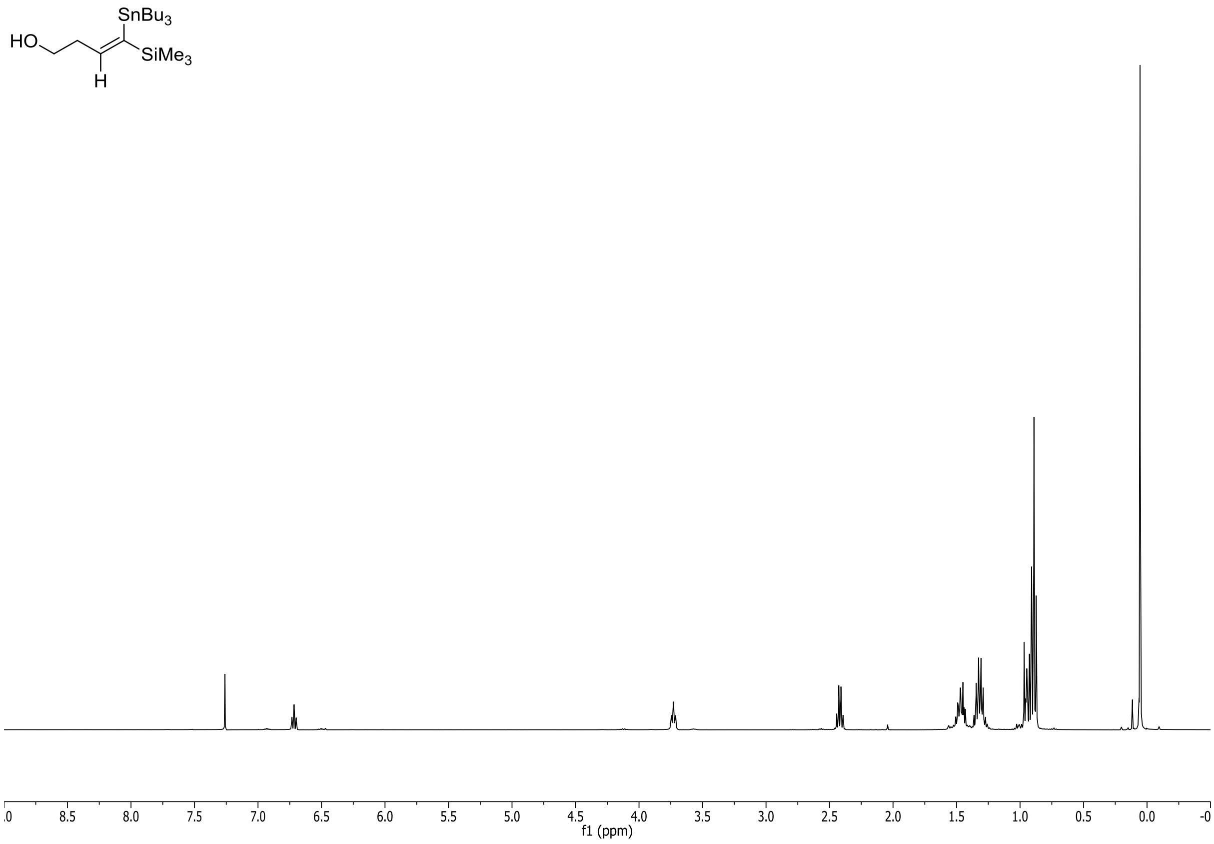


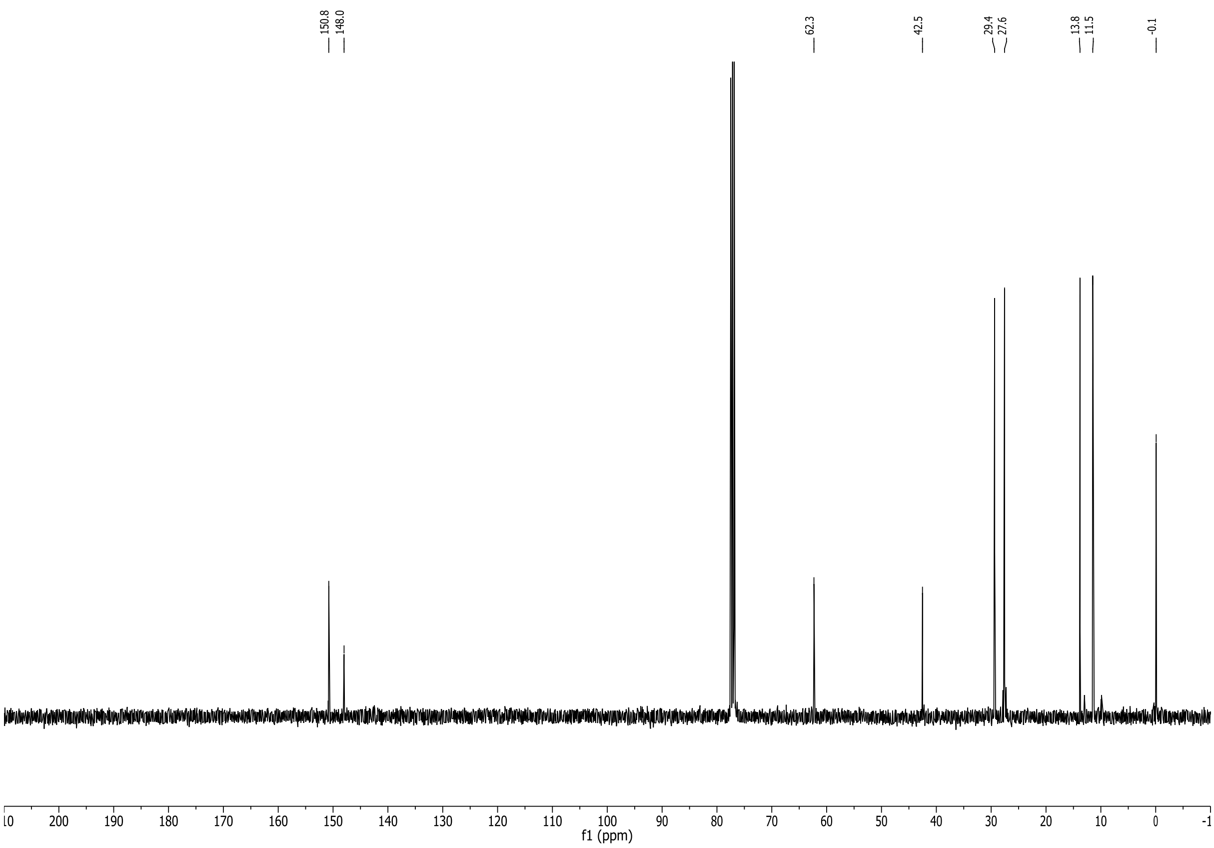



500 MHz, $CDCl_3$




SnBu3
HO
SiMe3
H
f1 (ppm)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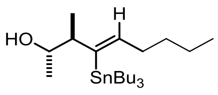
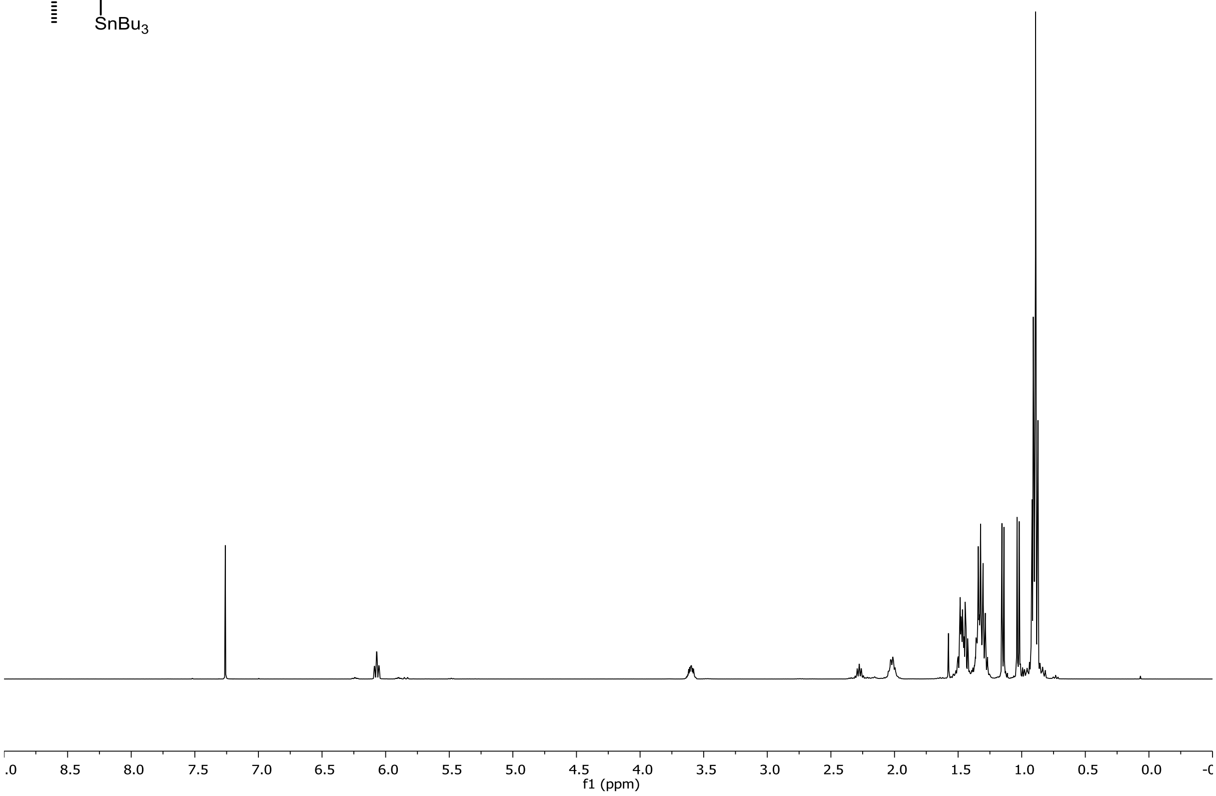
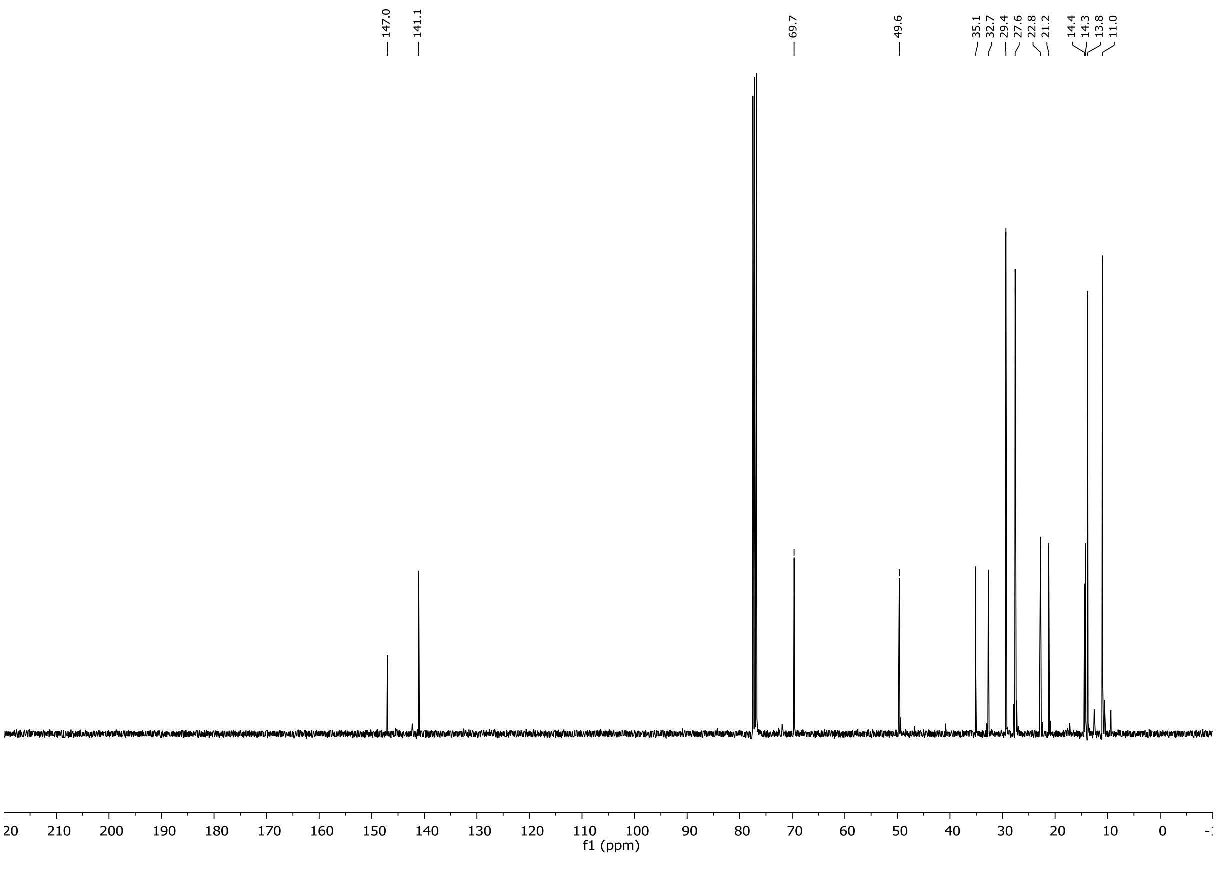
62.3
42.5
29.4
27.6
13.8
11.5
-0.1
f1 (ppm)


HO
H
SnBu3


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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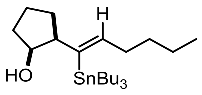
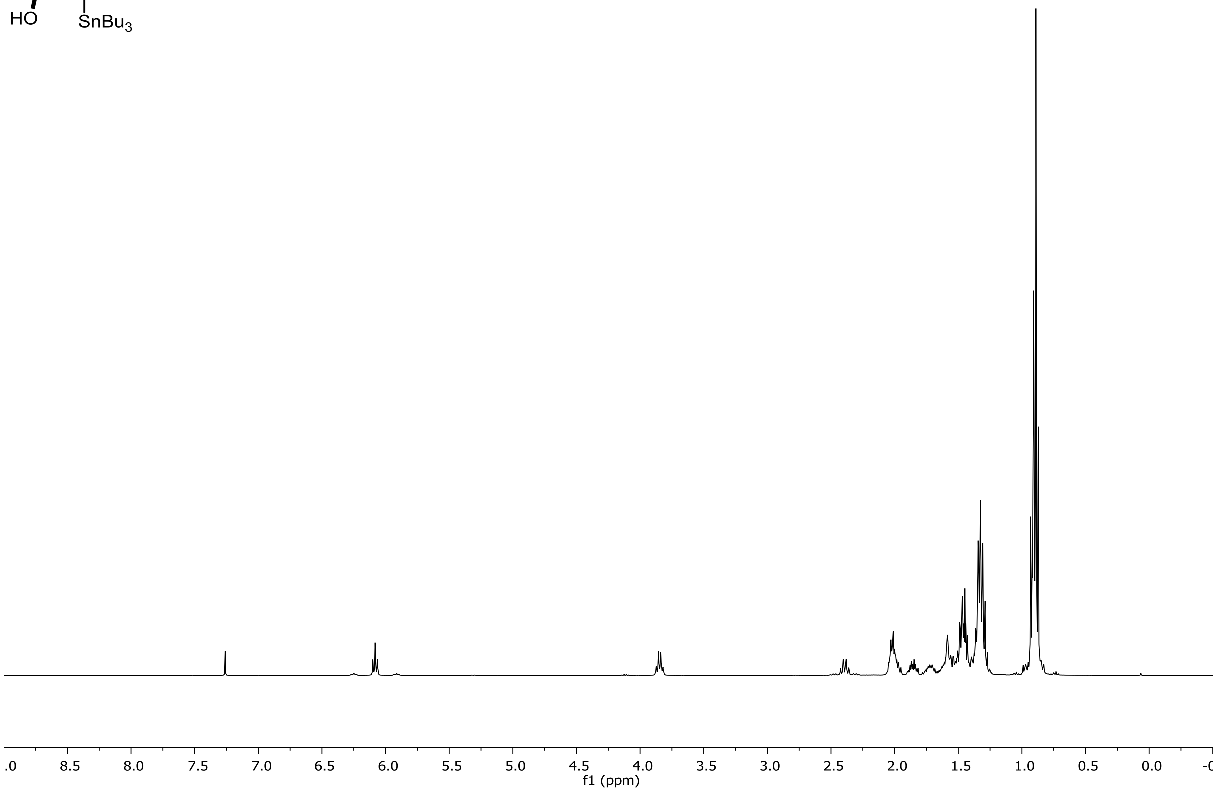
141.1
69.7
49.6
35.1
32.7
29.4
27.6
22.8
21.2
14.4
14.3
13.8
11.0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H
HO
SnBu3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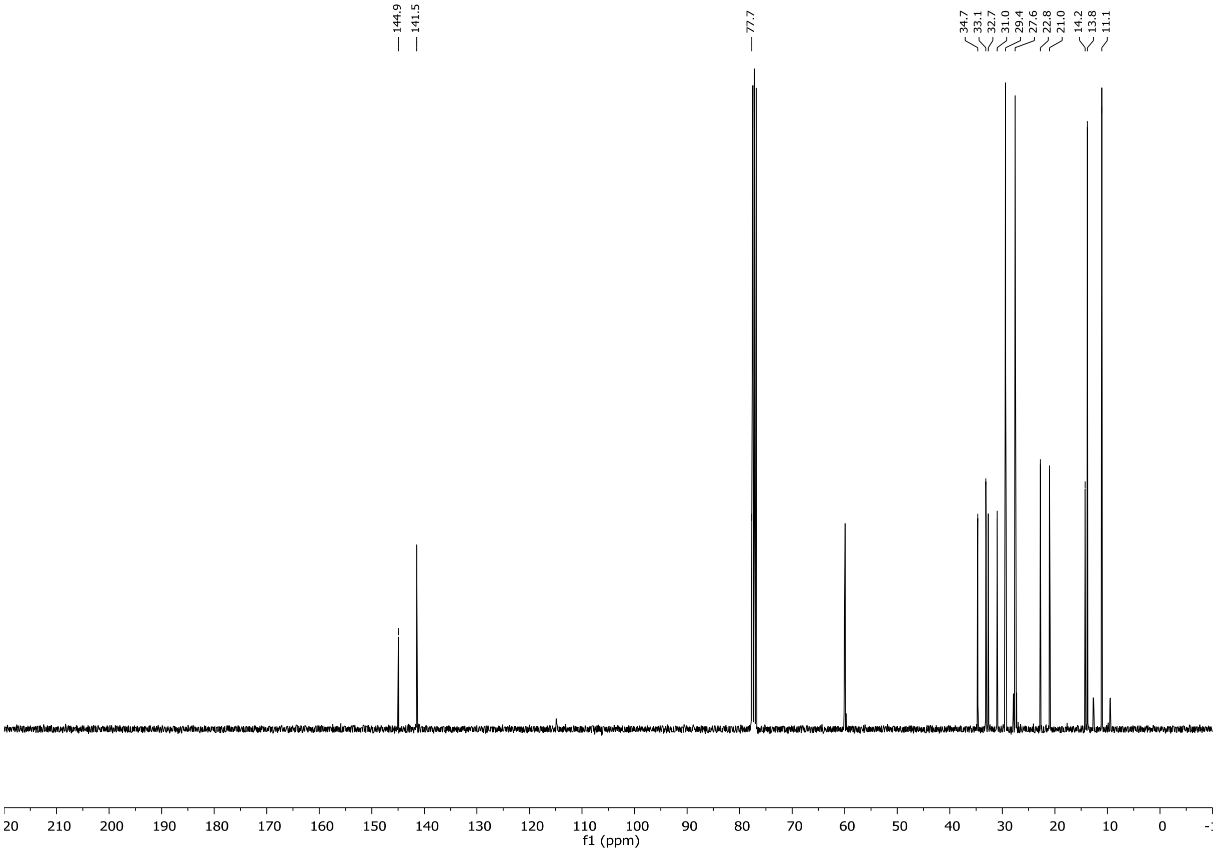
f1 (ppm)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141.5
77.7
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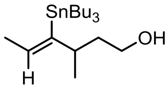
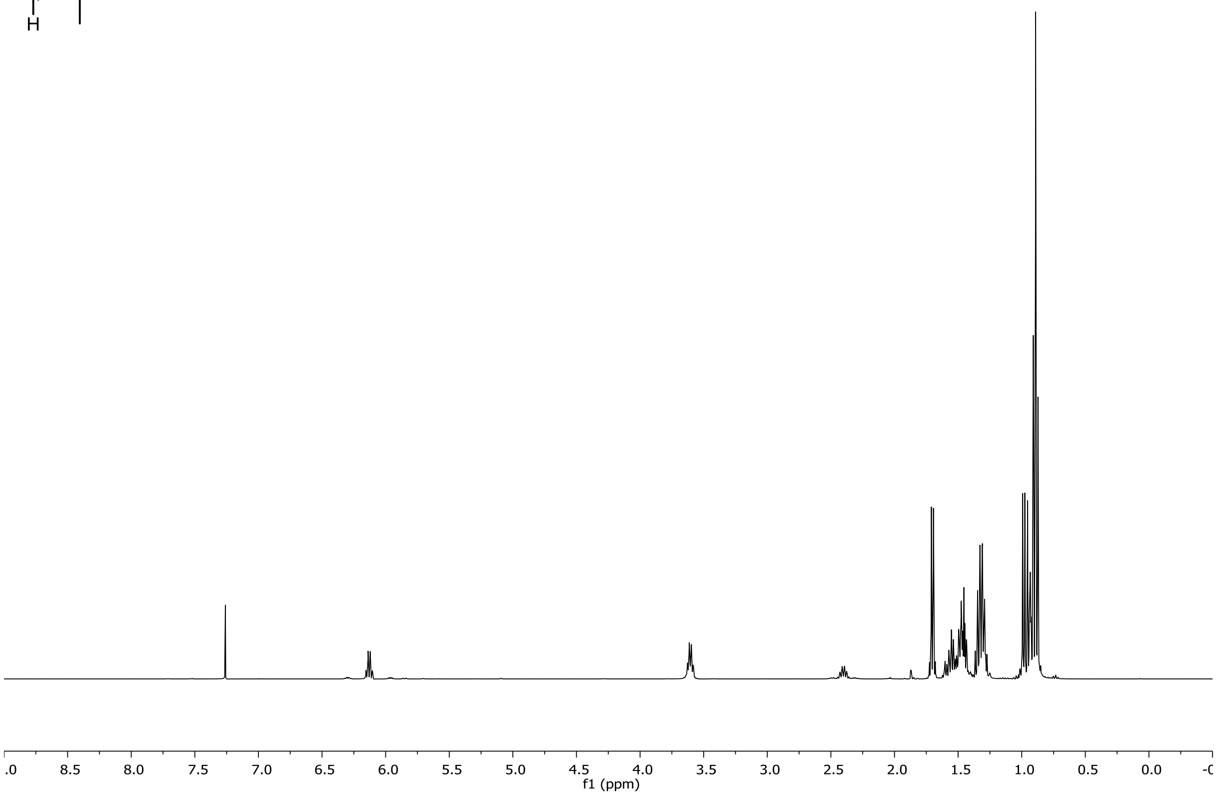
33.1
32.7
31.0
29.4
27.6
22.8
21.0
14.2
13.8
11.1
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -:
f1 (ppm)


SnBu$_3$
OH
H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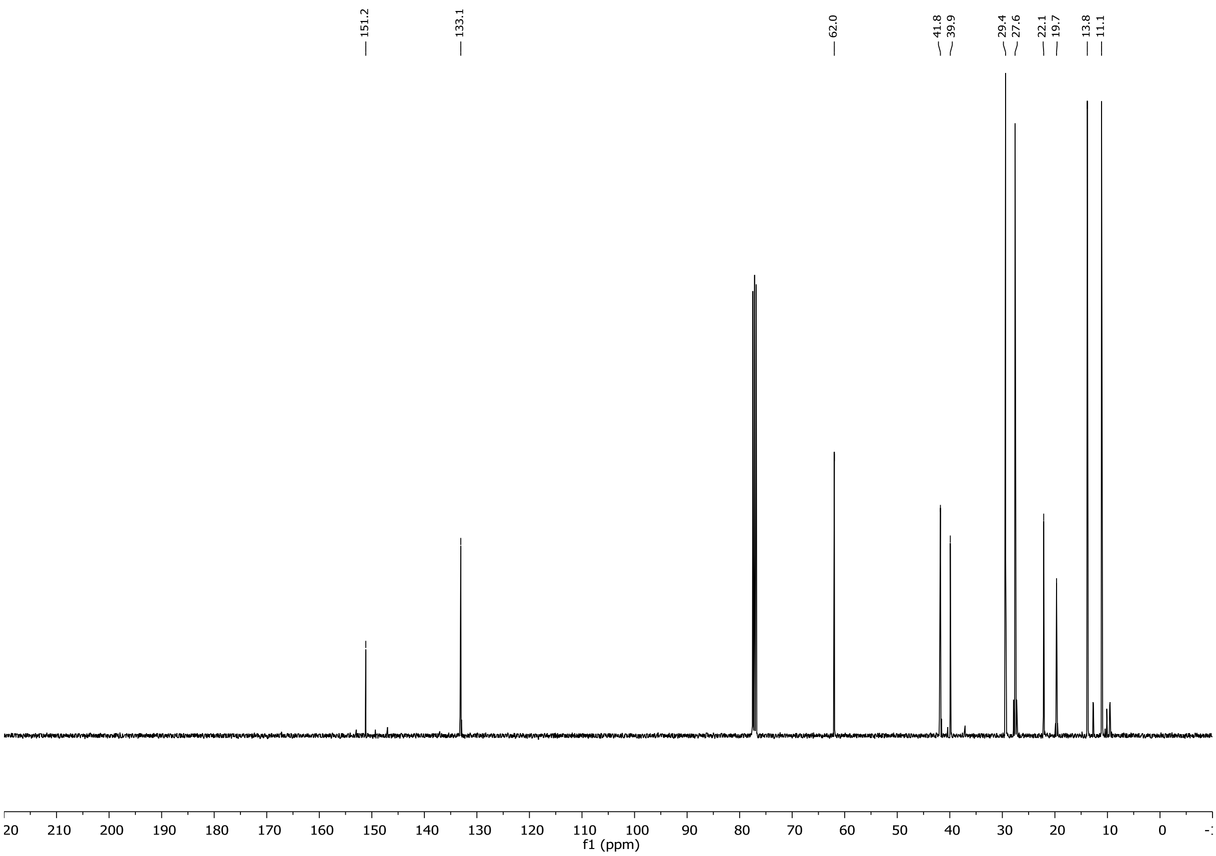
f1 (ppm)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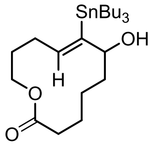
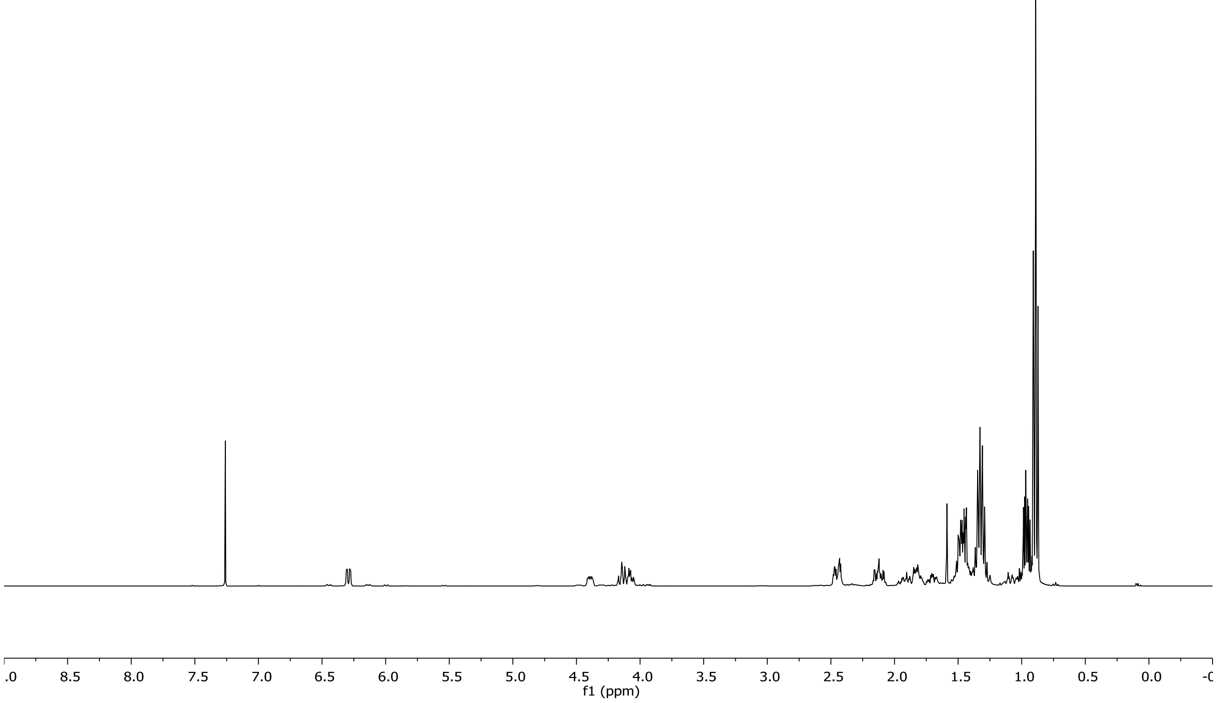
133.1
62.0
41.8
39.9
29.4
27.6
22.1
19.7
13.8
11.1
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SnBu3
OH
H
O
O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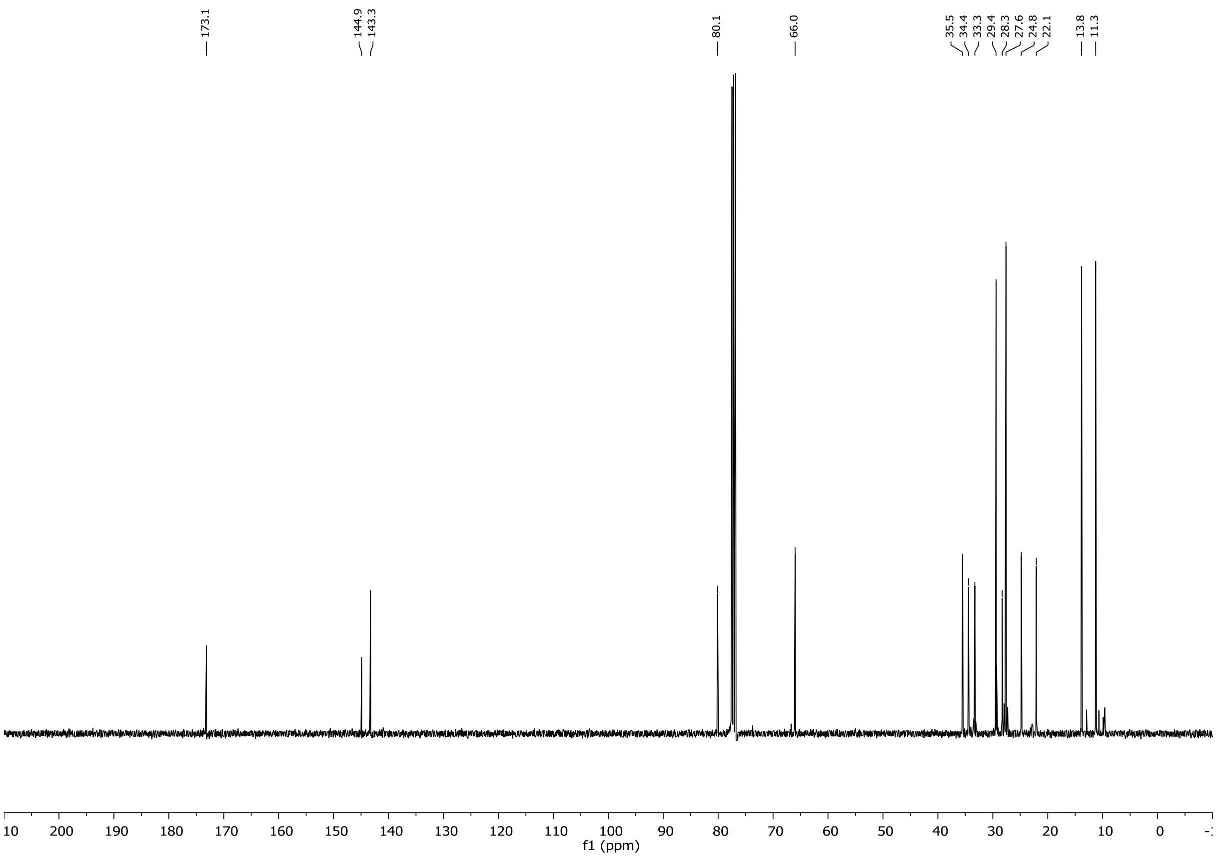
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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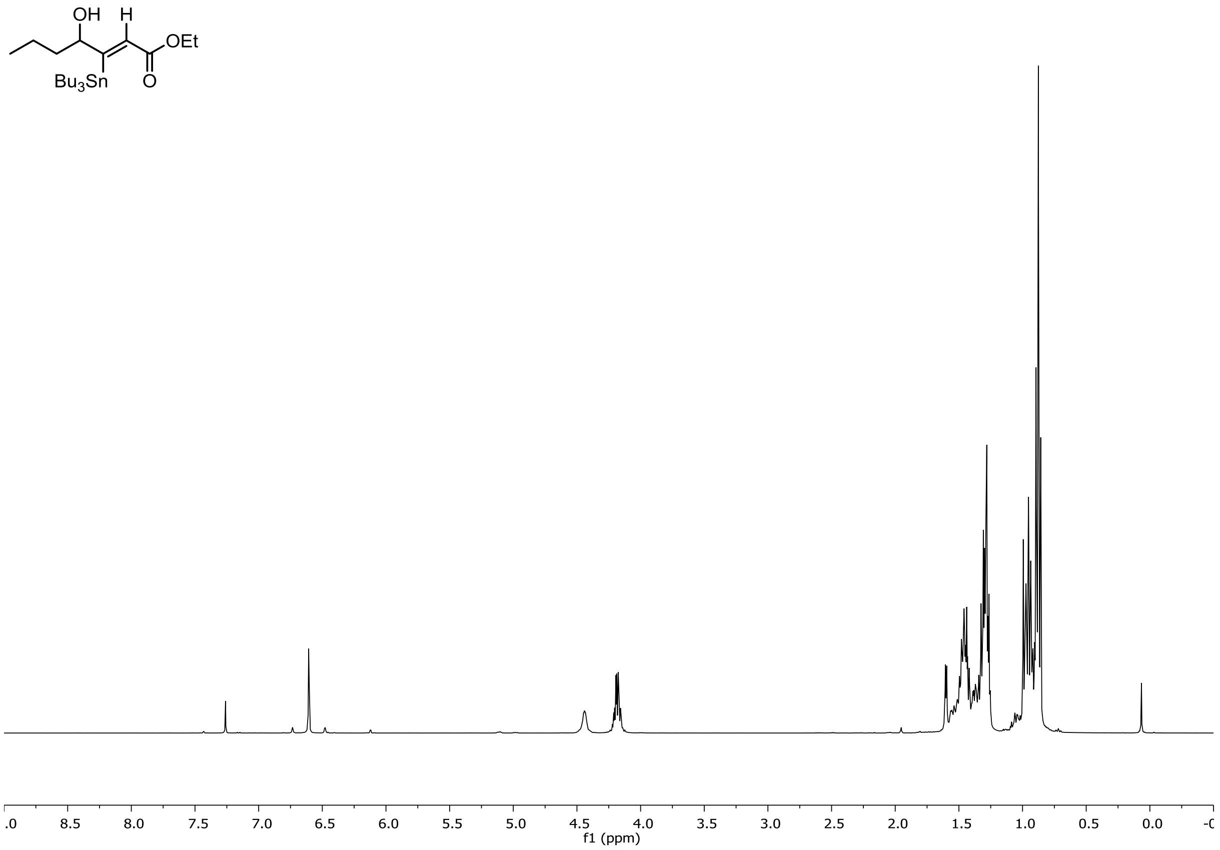
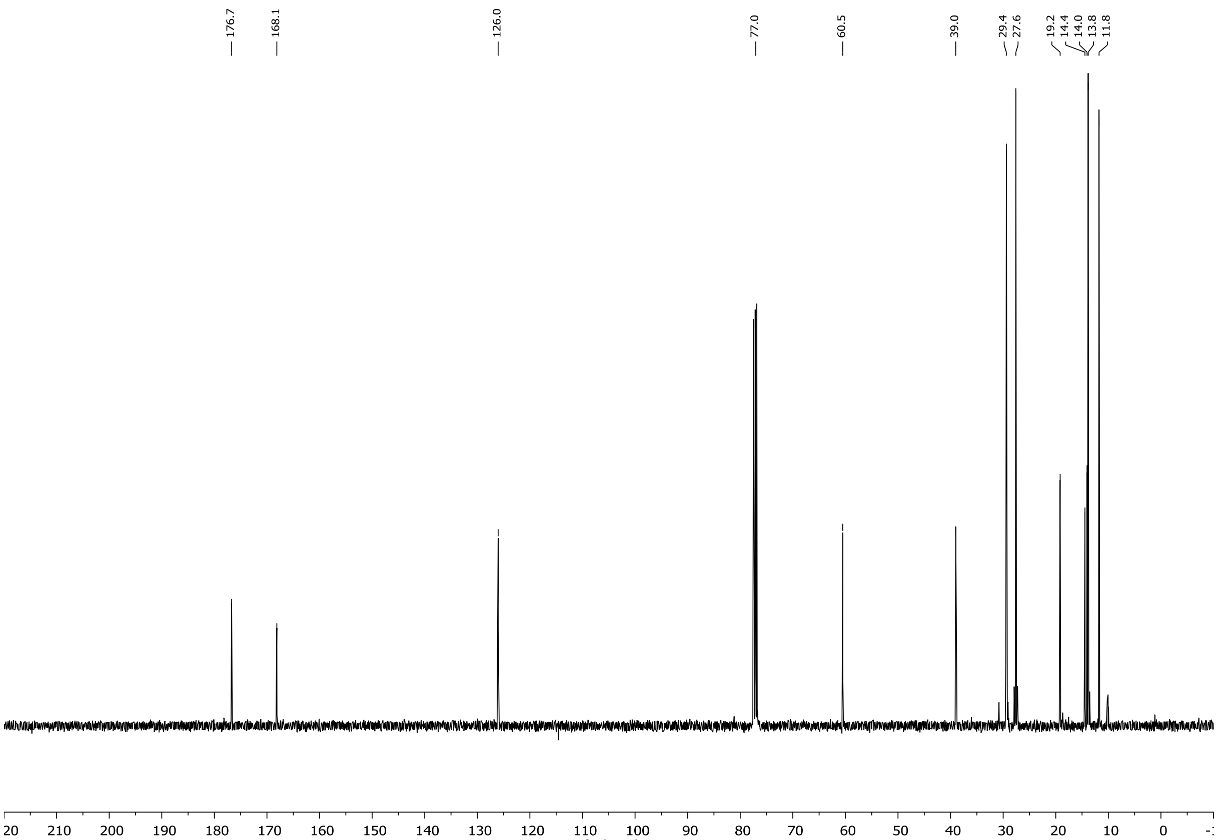
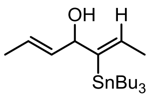
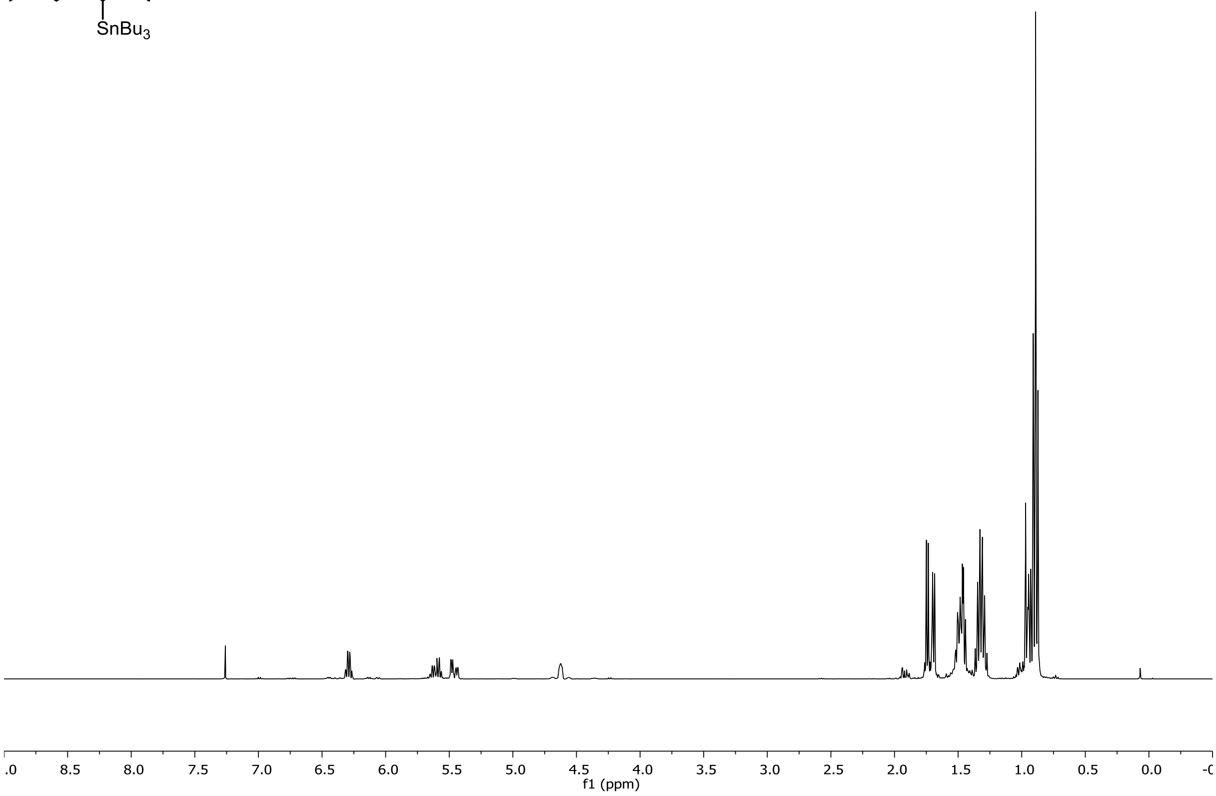
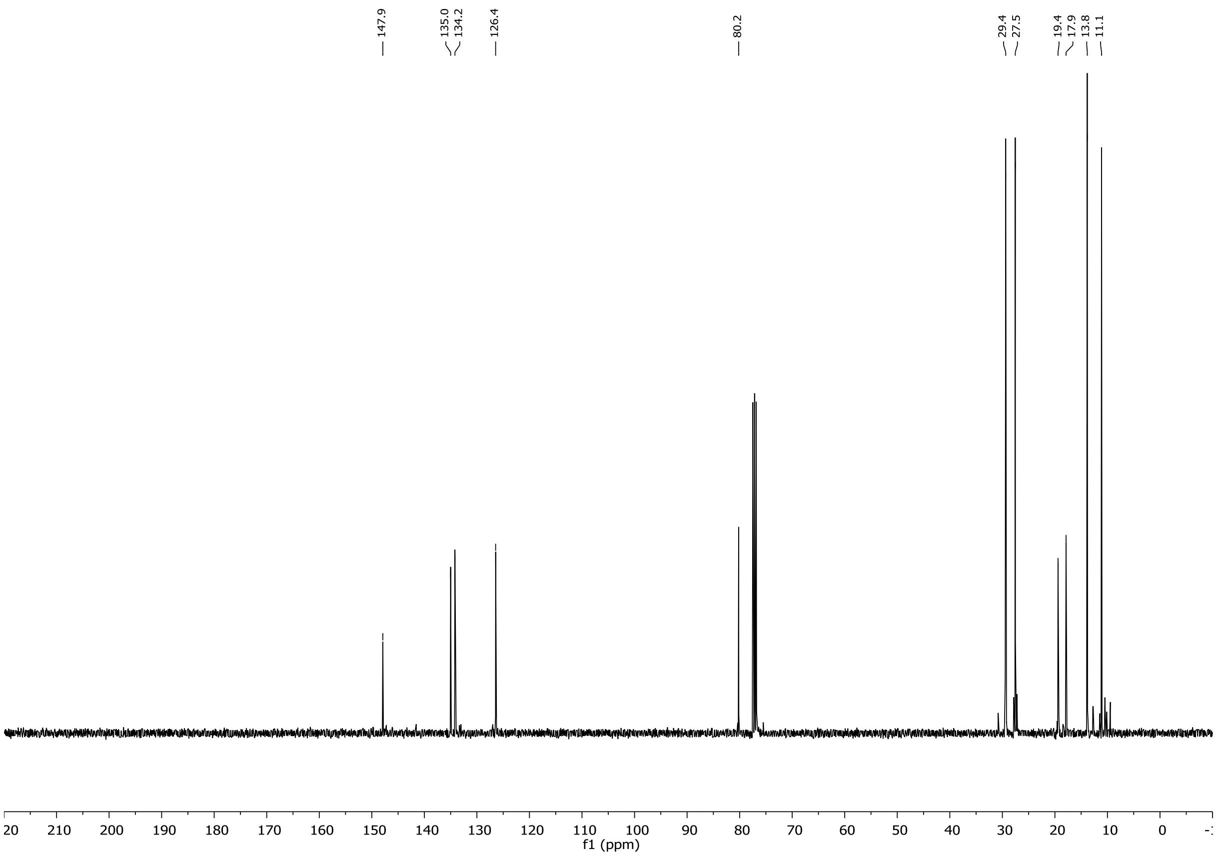
144.9
143.3
80.1
66.0
35.5
34.4
33.3
29.4
28.3
27.6
24.8
22.1
13.8
11.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
H
OEt
Bu3Sn
O
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.7
168.1
126.0
77.0
60.5
39.0
29.4
27.6
19.2
14.4
14.0
13.8
11.8
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
H
SnBu3


f1 (ppm)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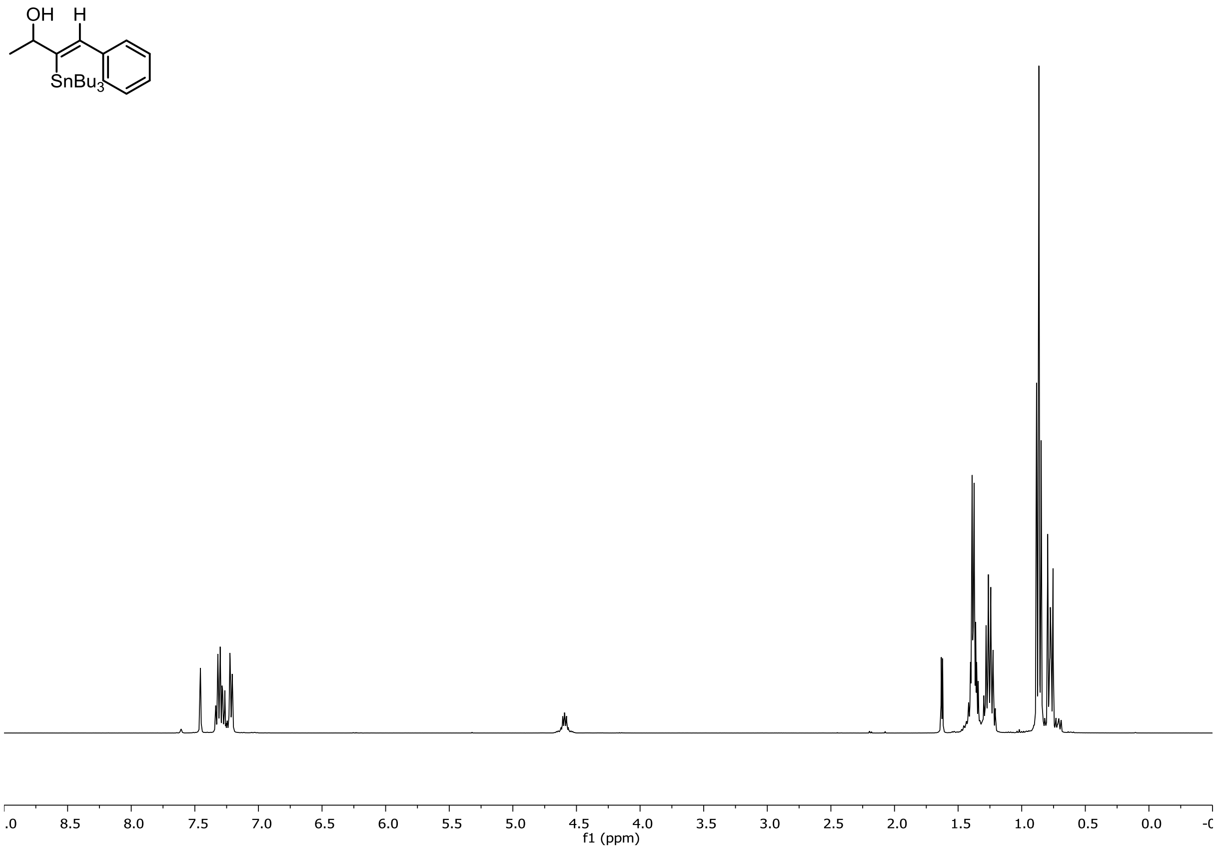
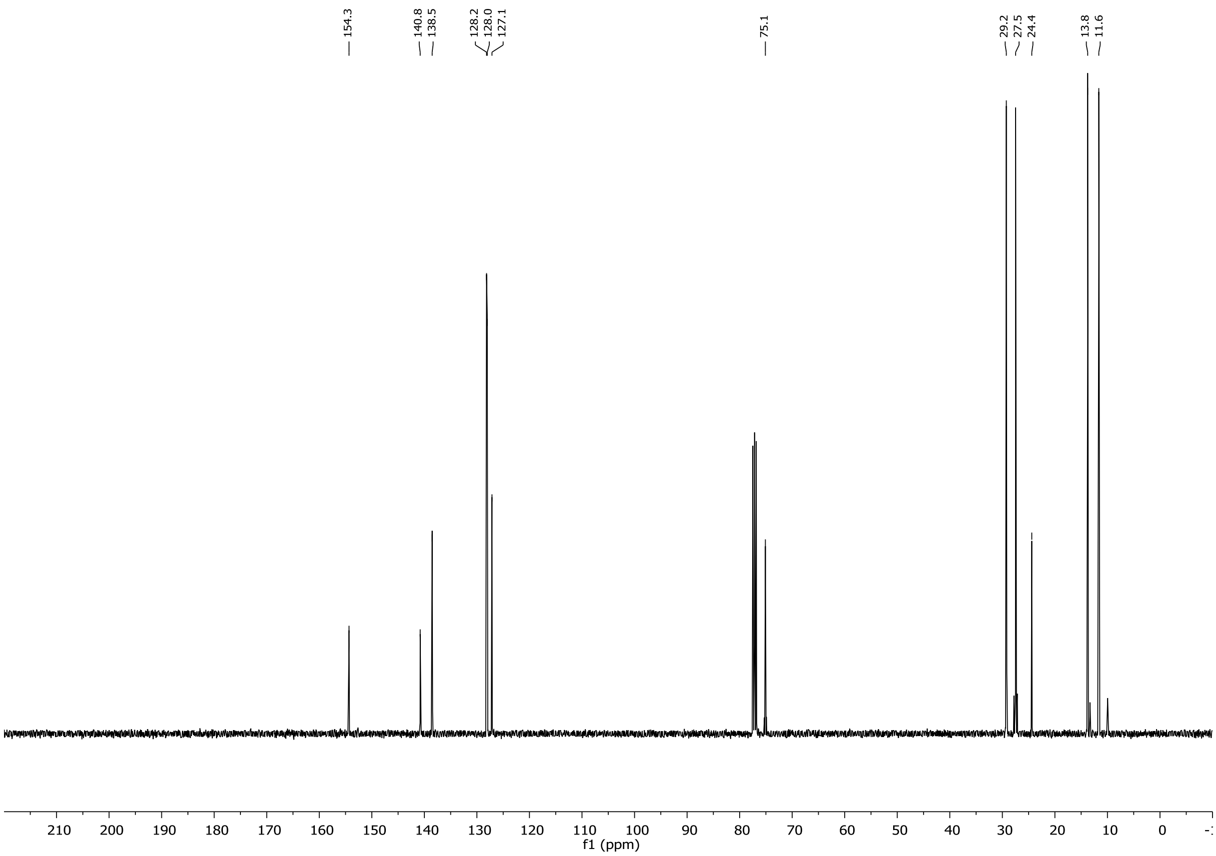
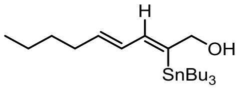
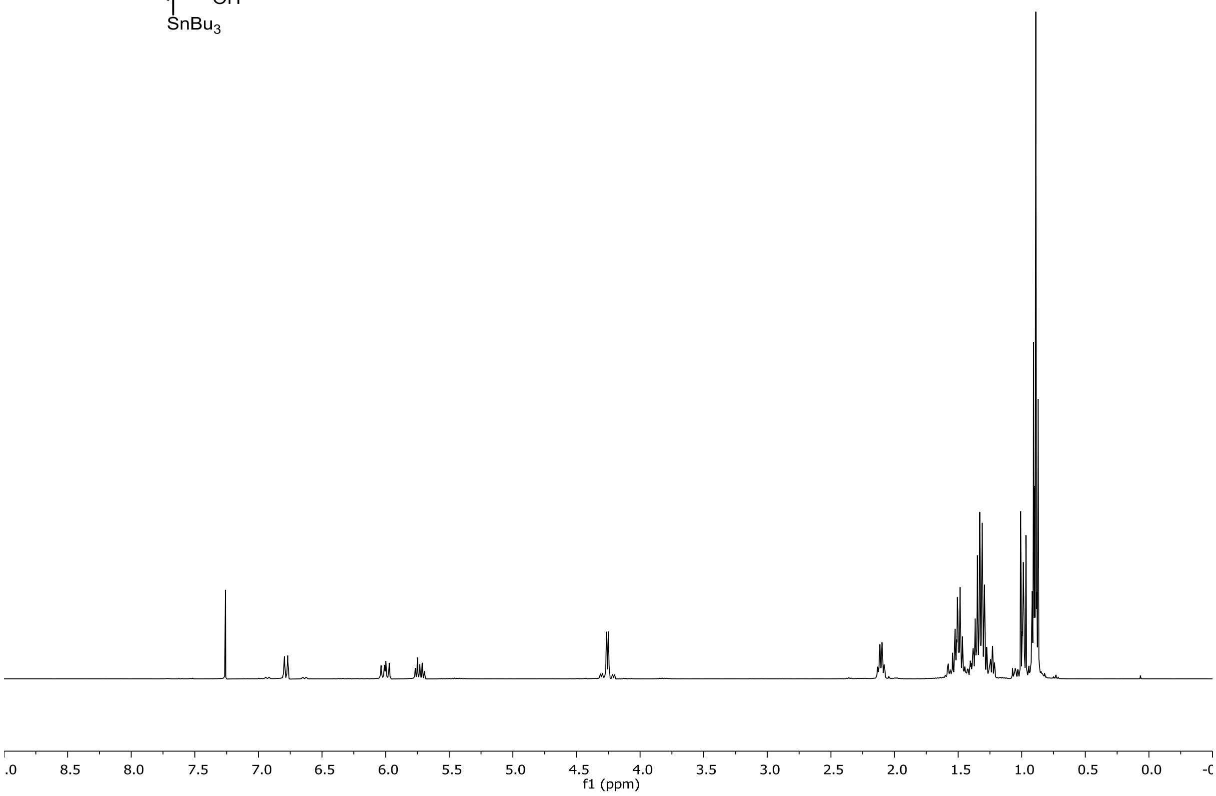
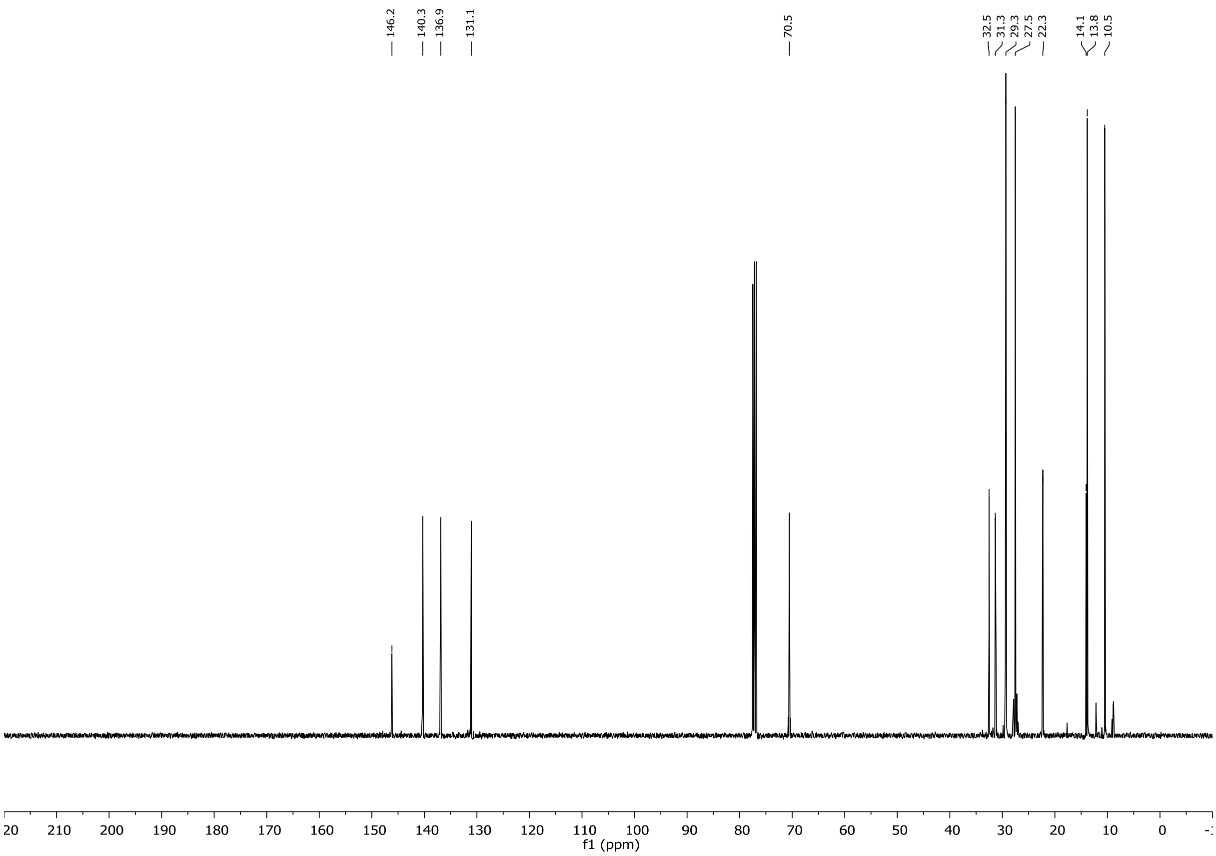
135.0
134.2
126.4
80.2
29.4
27.5
19.4
17.9
13.8
11.1
f1 (ppm)

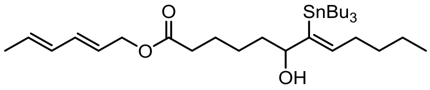

OH
H
SnBu3
f1 (ppm)

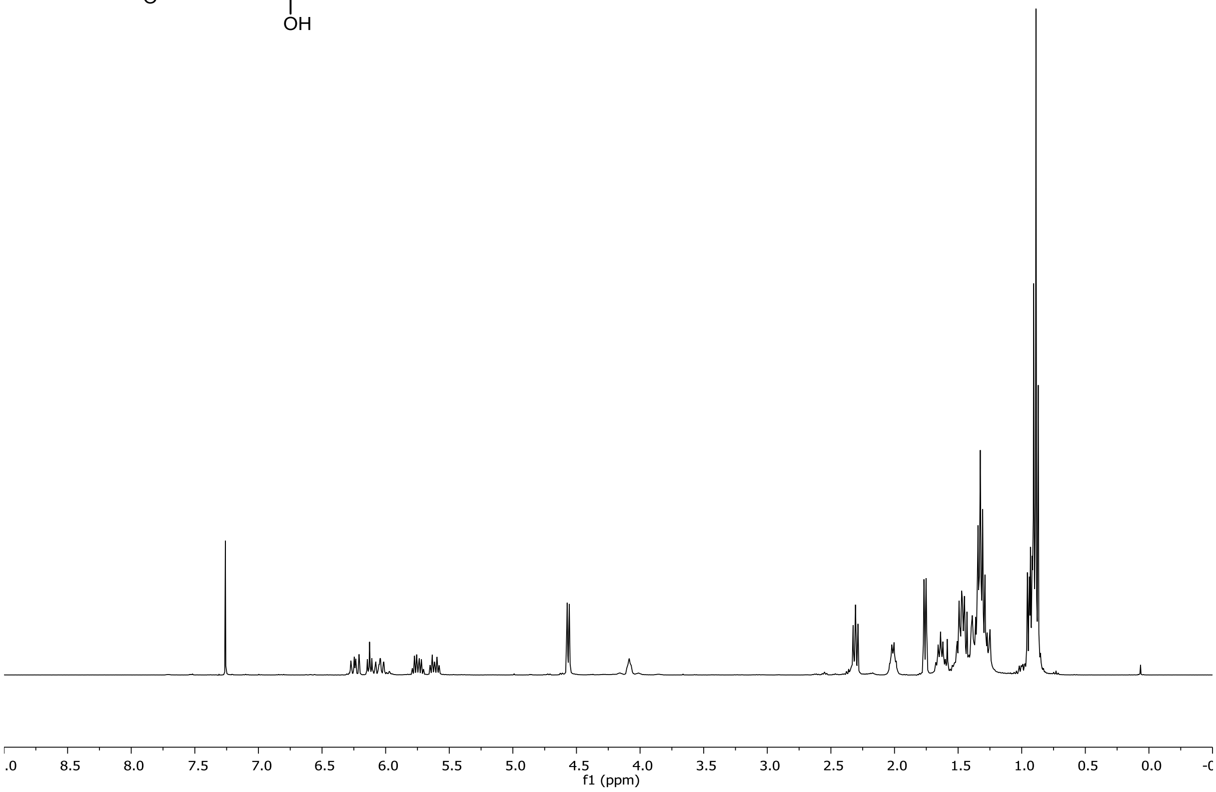

154.3
140.8
138.5
128.2
128.0
127.1
75.1
29.2
27.5
24.4
13.8
11.6
f1 (ppm)


H
OH
SnBu3


.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.2
140.3
136.9
131.1
70.5
32.5
31.3
29.3
27.5
22.3
14.1
13.8
10.5
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


SnBu3
O
O
OH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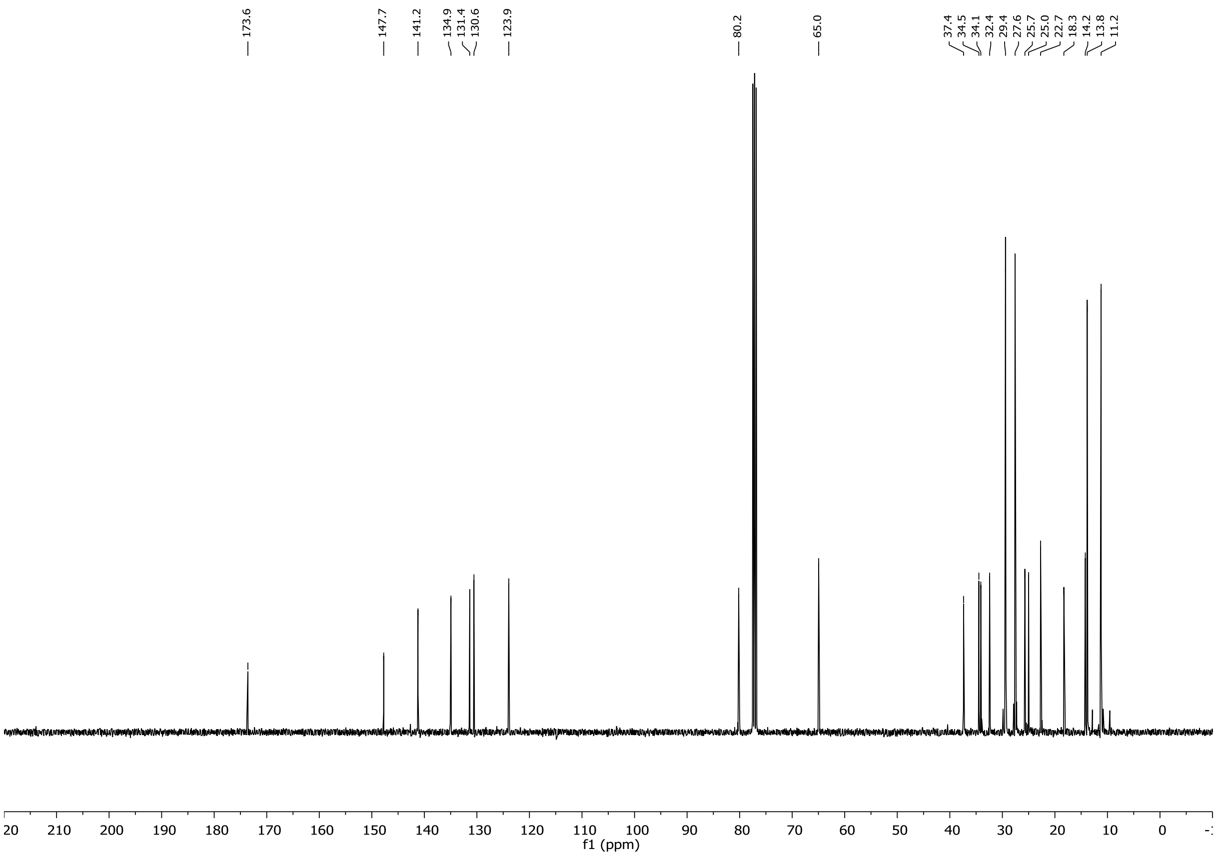
f1 (ppm)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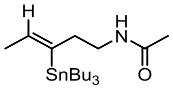
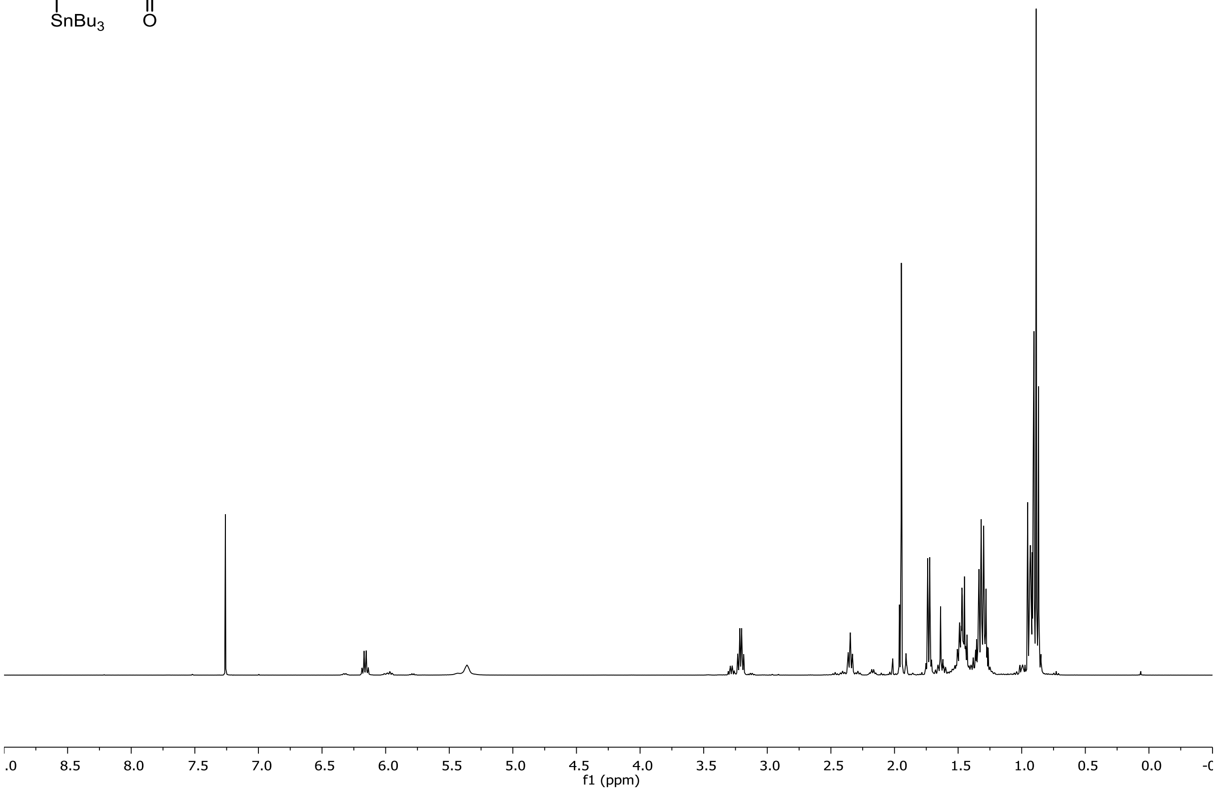
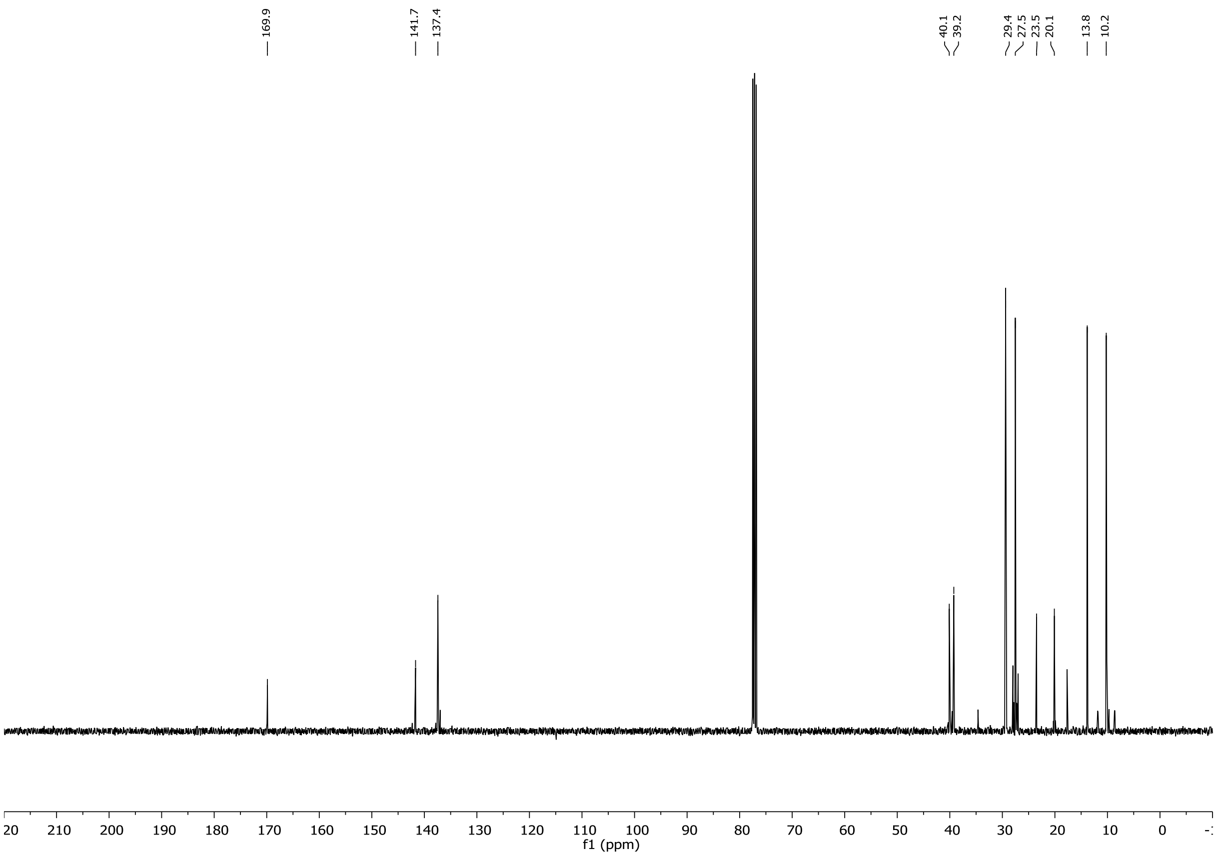
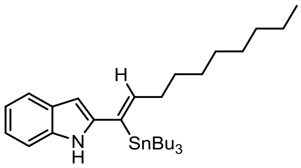
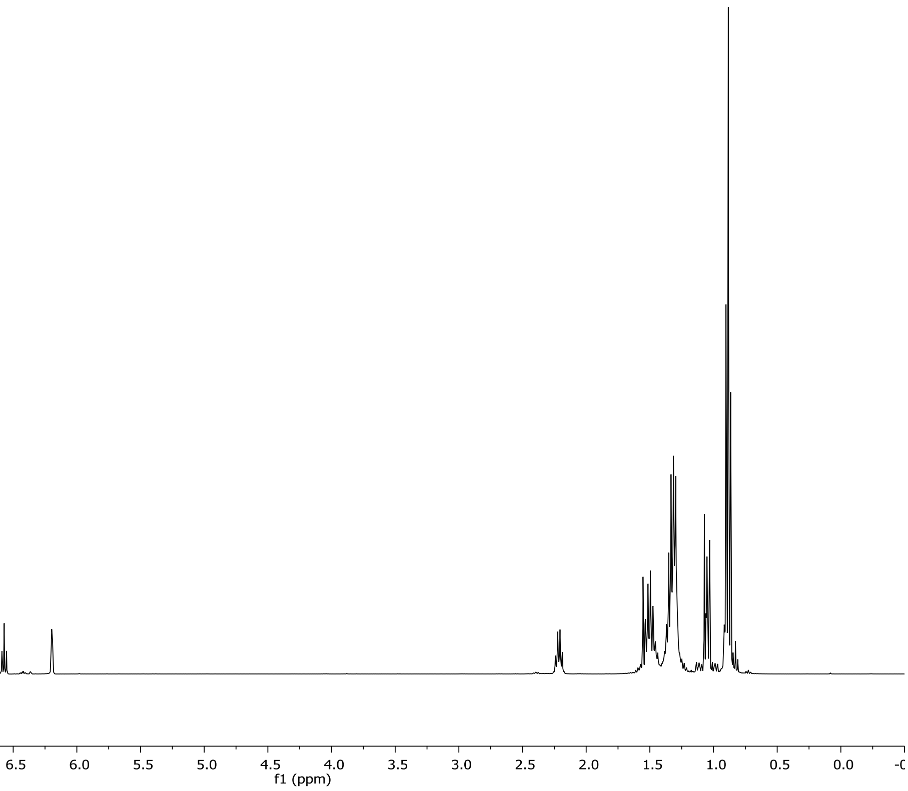
141.2
134.9
131.4
130.6
123.9
80.2
65.0
37.4
34.5
34.1
32.4
29.4
27.6
25.7
25.0
22.7
18.3
14.2
13.8
11.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

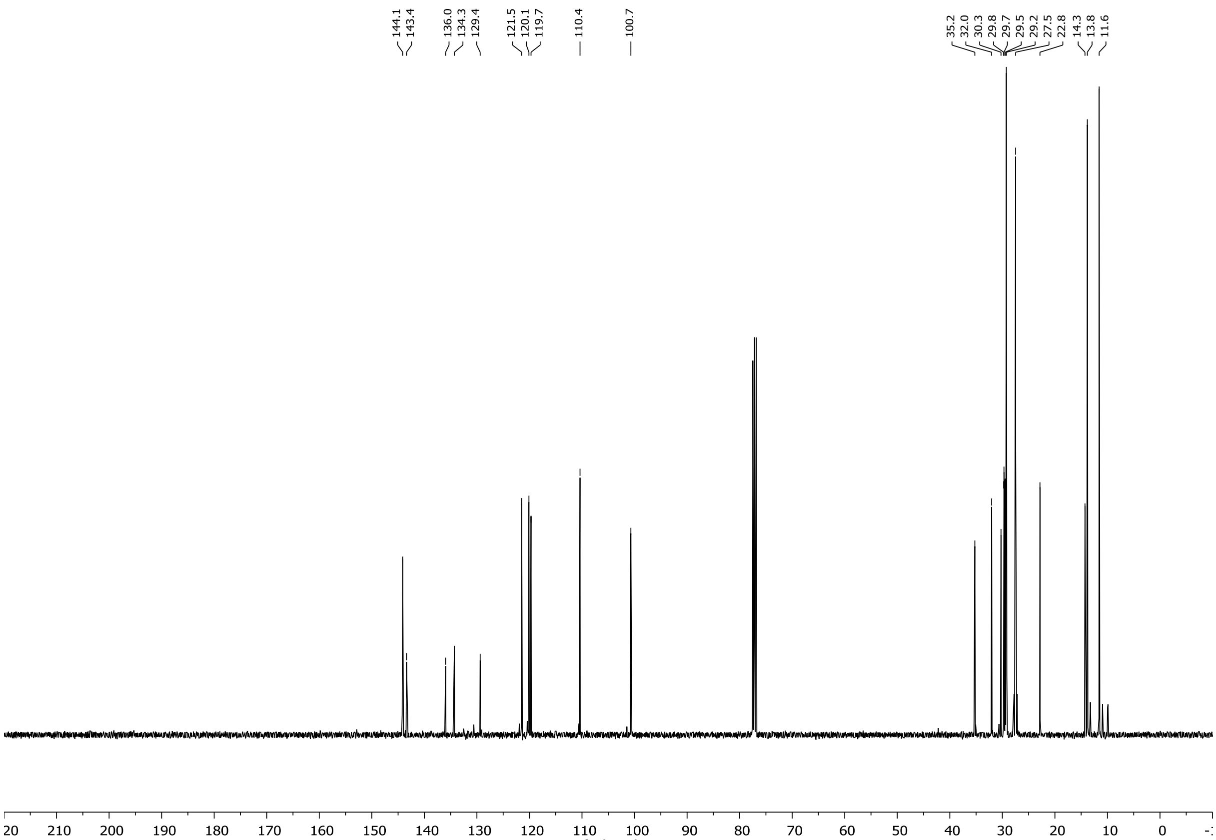

H
H
N
SnBu3
O


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)


169.9
141.7
137.4
40.1
39.2
29.4
27.5
23.5
20.1
13.8
10.2
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -:
f1 (ppm)


H
SnBu3
N
H


f1 (ppm)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143.4
136.0
134.3
129.4
121.5
120.1
119.7
110.4
100.7
35.2
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30.3
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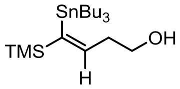
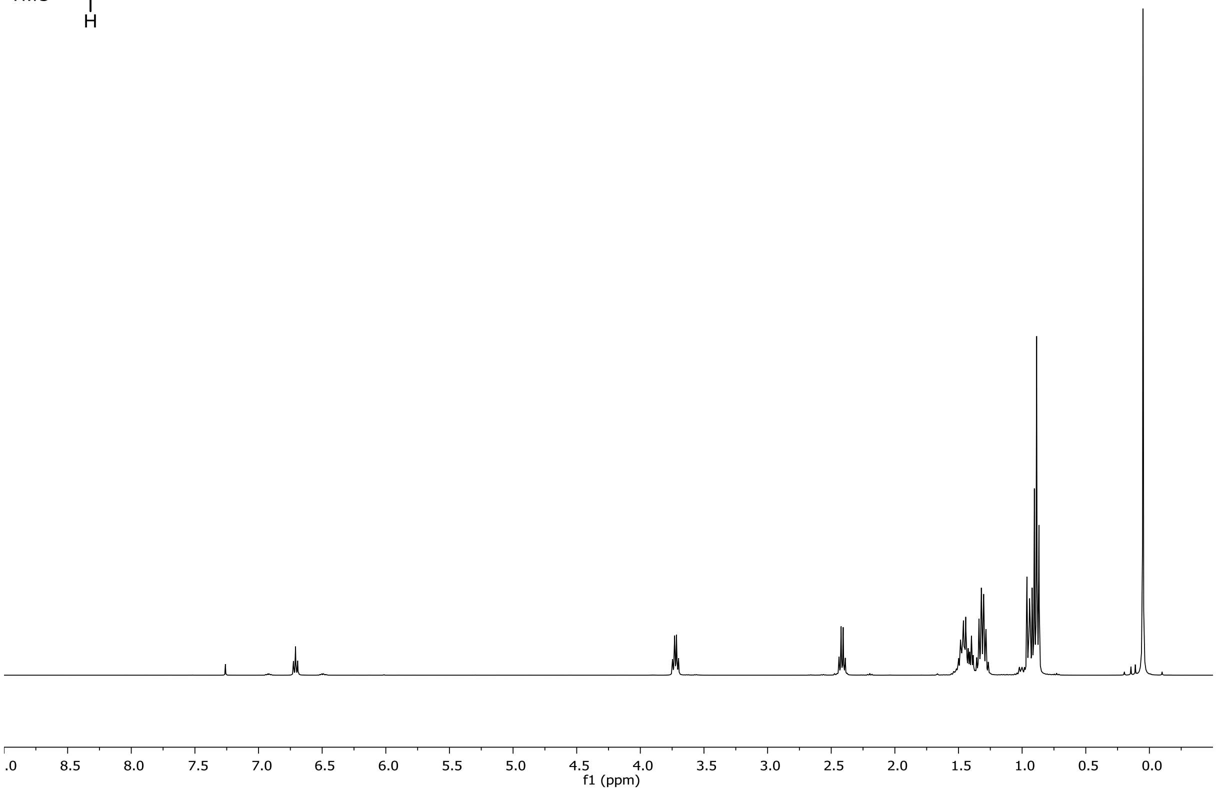
29.7
29.5
29.2
27.5
22.8
14.3
13.8
11.6
f1 (ppm)


SnBu3
TMS
OH
H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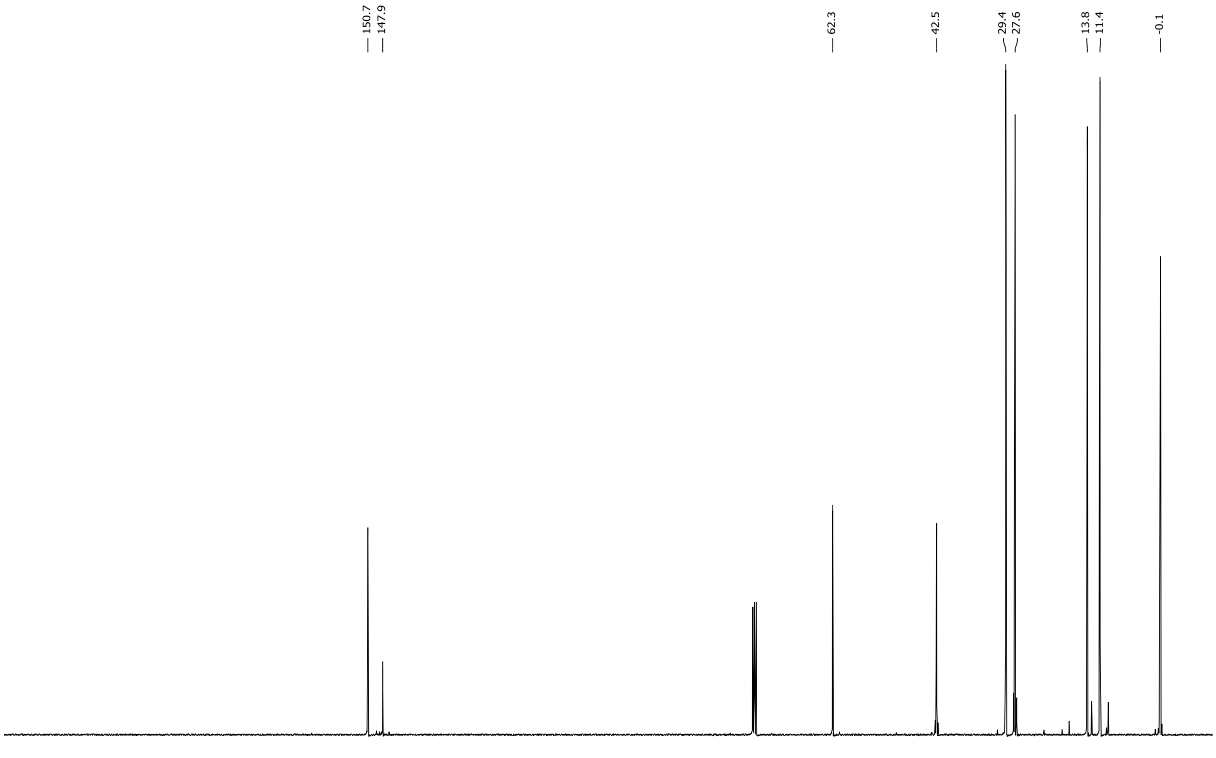
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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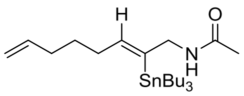
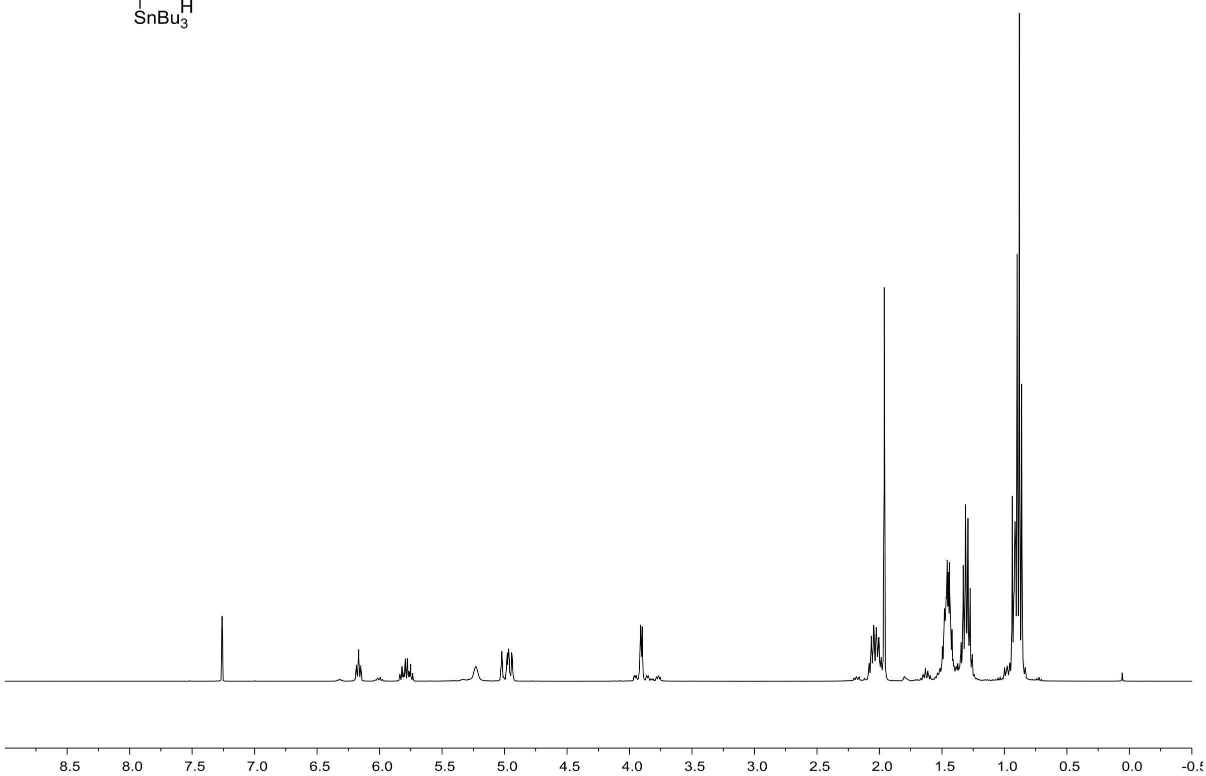
147.9
62.3
42.5
29.4
27.6
13.8
11.4
-0.1
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
O
N
H
SnBu3


8.5
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7.5
7.0
6.5
6.0
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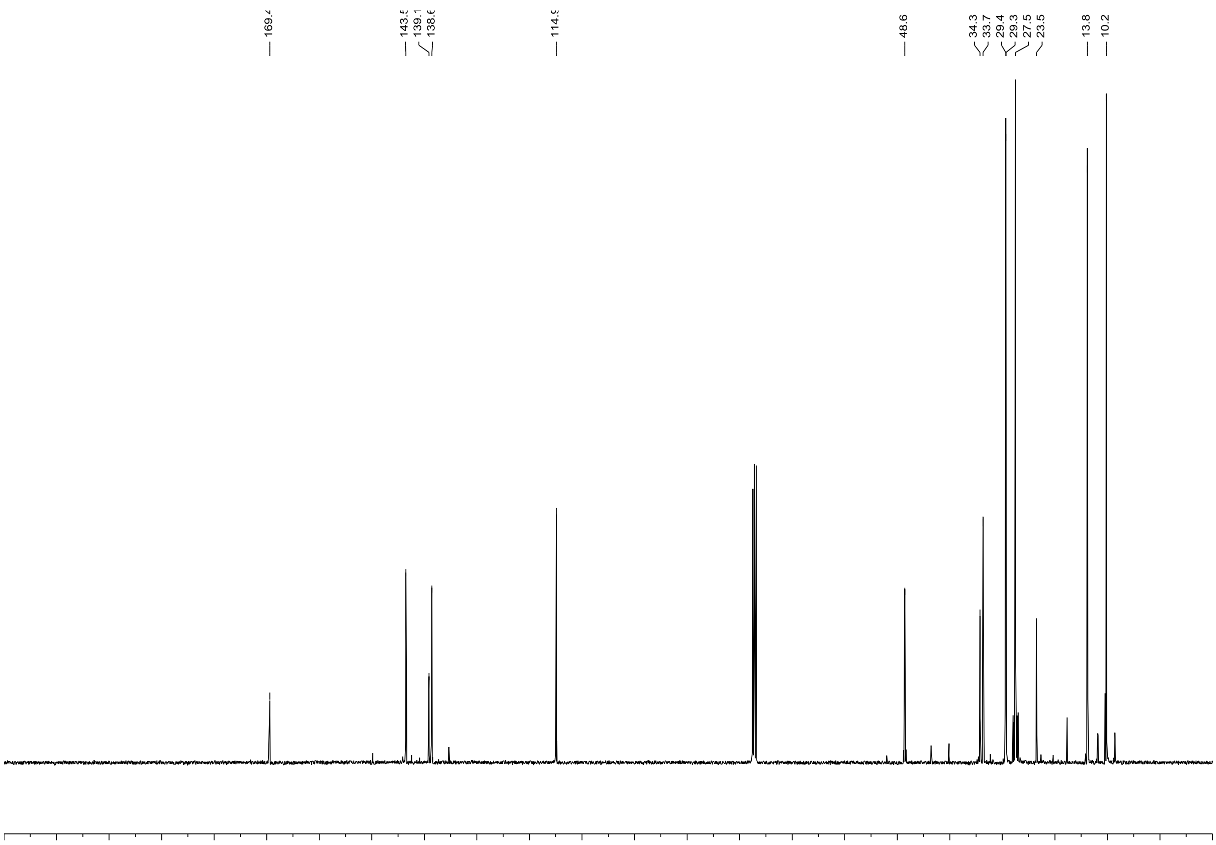
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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34.3
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29.3
27.5
23.5
13.8
10.2
210
200
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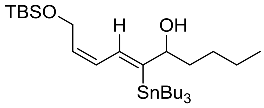
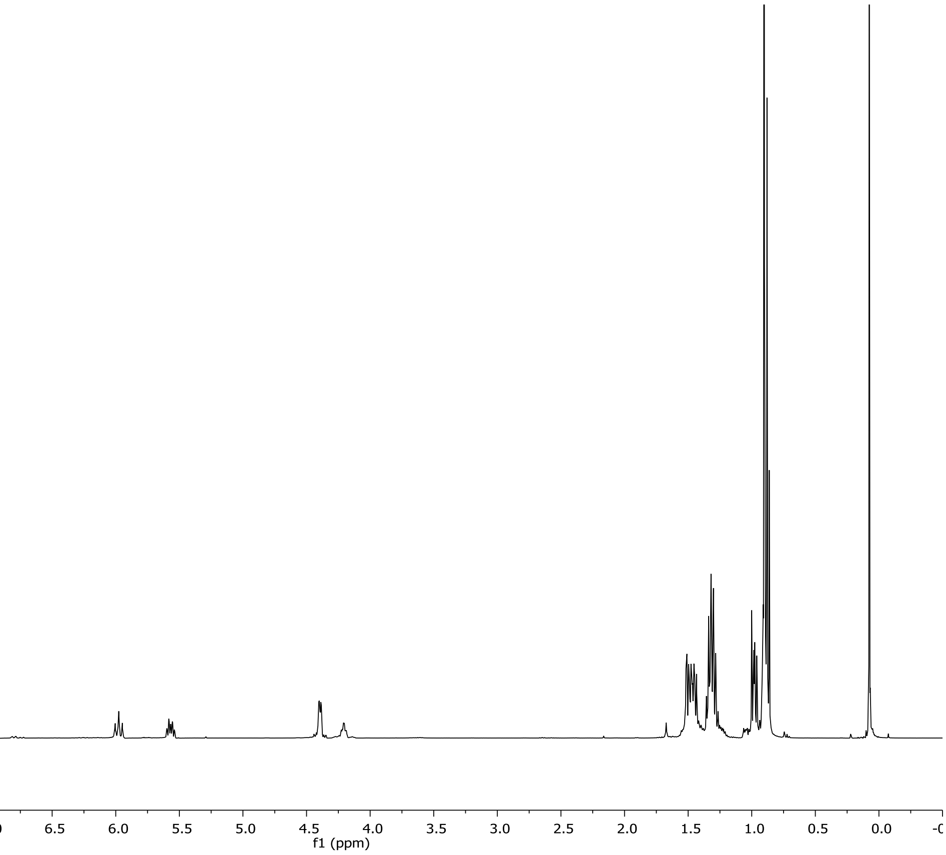
40
30
20
10
0


TBSO
H
OH
SnBu3


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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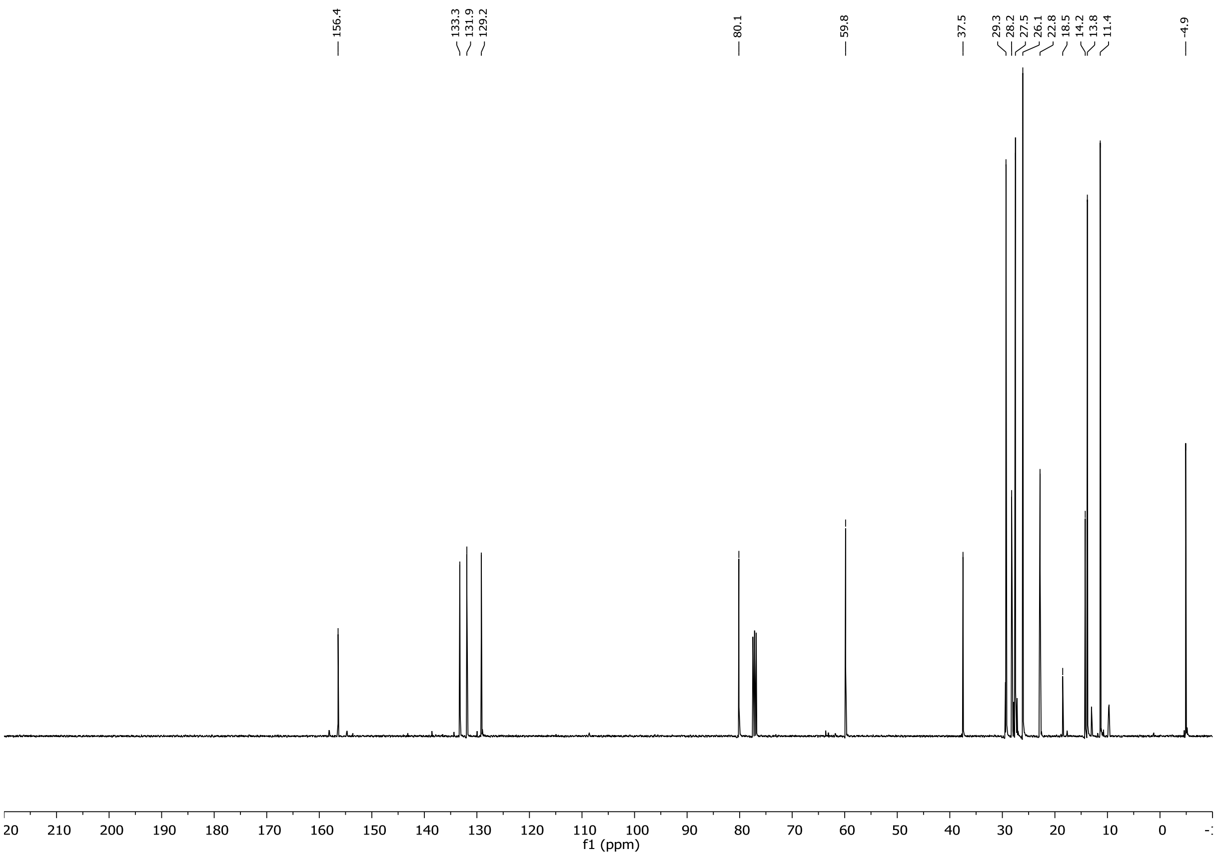
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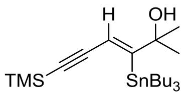
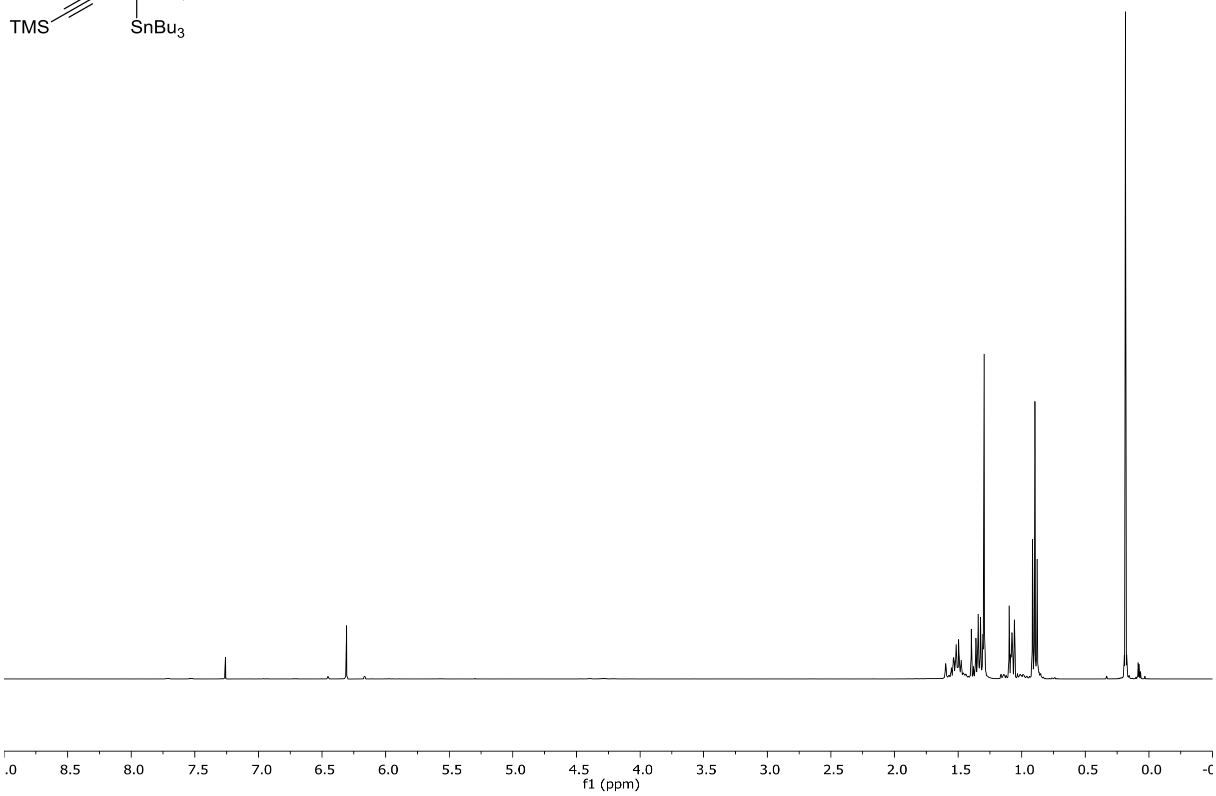
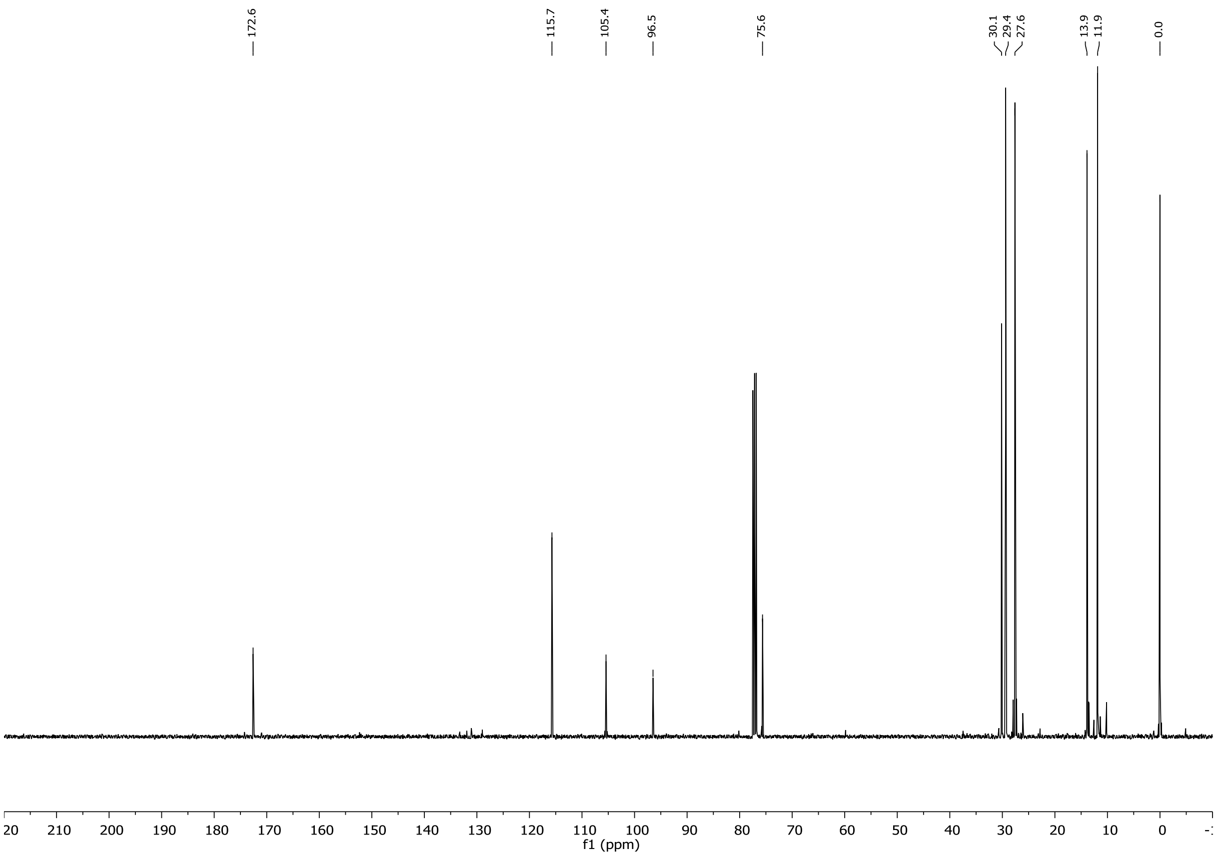
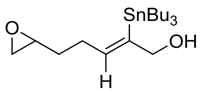
129.2
80.1
59.8
37.5
29.3
28.2
27.5
26.1
22.8
18.5
14.2
13.8
11.4
-4.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

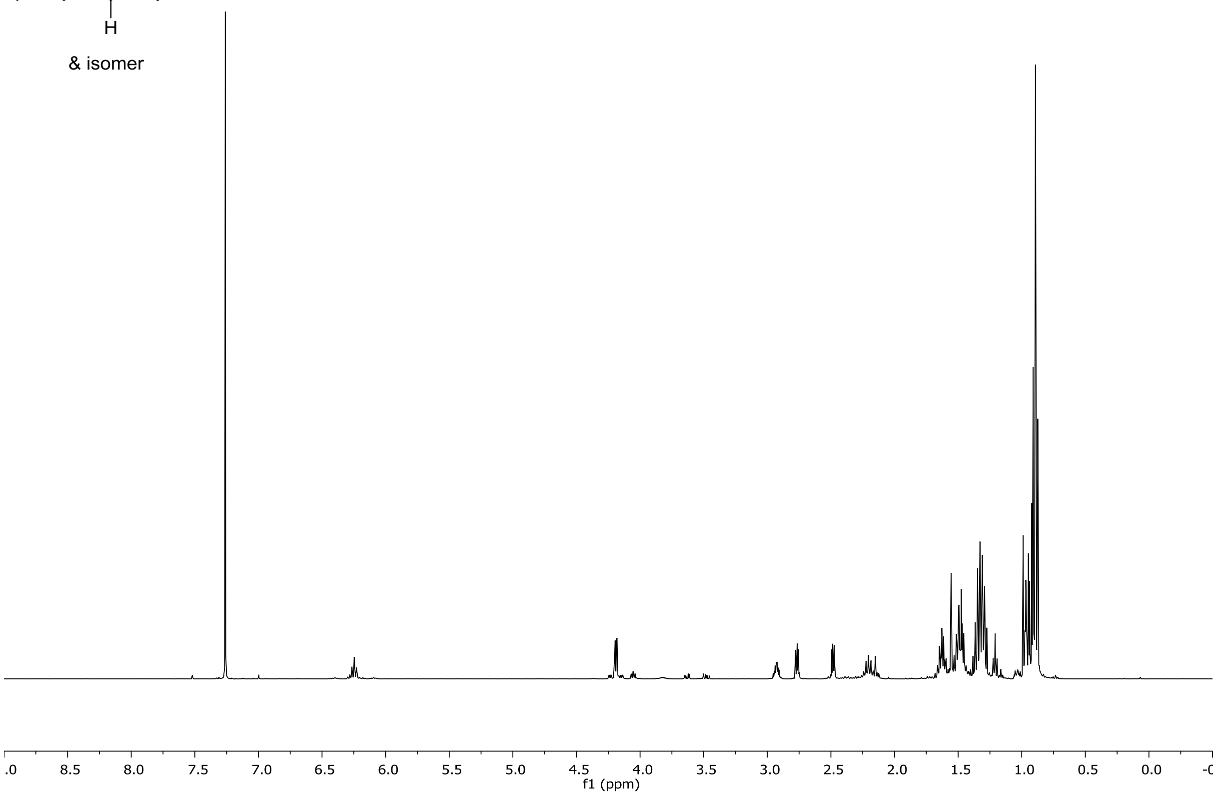

H
OH
TMS
$SnBu_3$

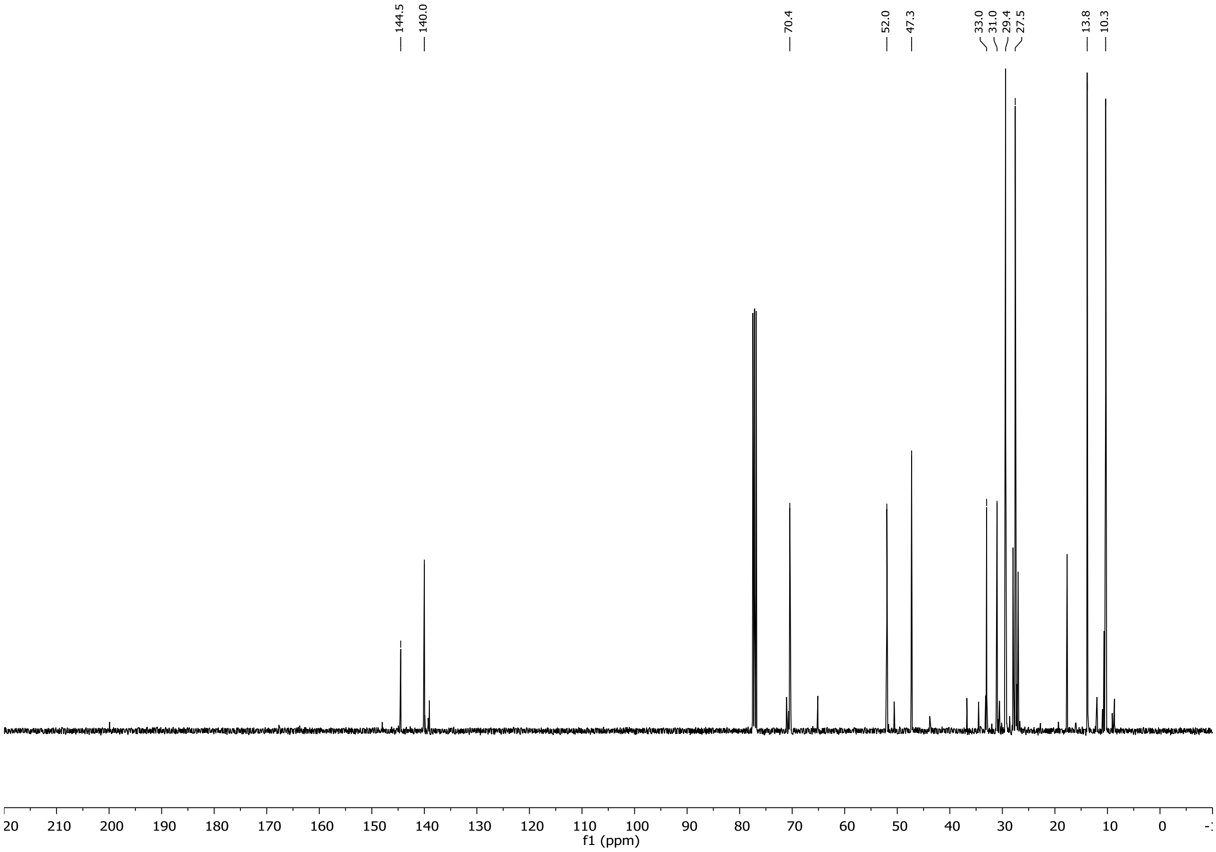

.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

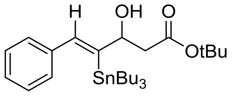

172.6
115.7
105.4
96.5
75.6
30.1
29.4
27.6
13.9
11.9
0.0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SnBu3
OH
O
H

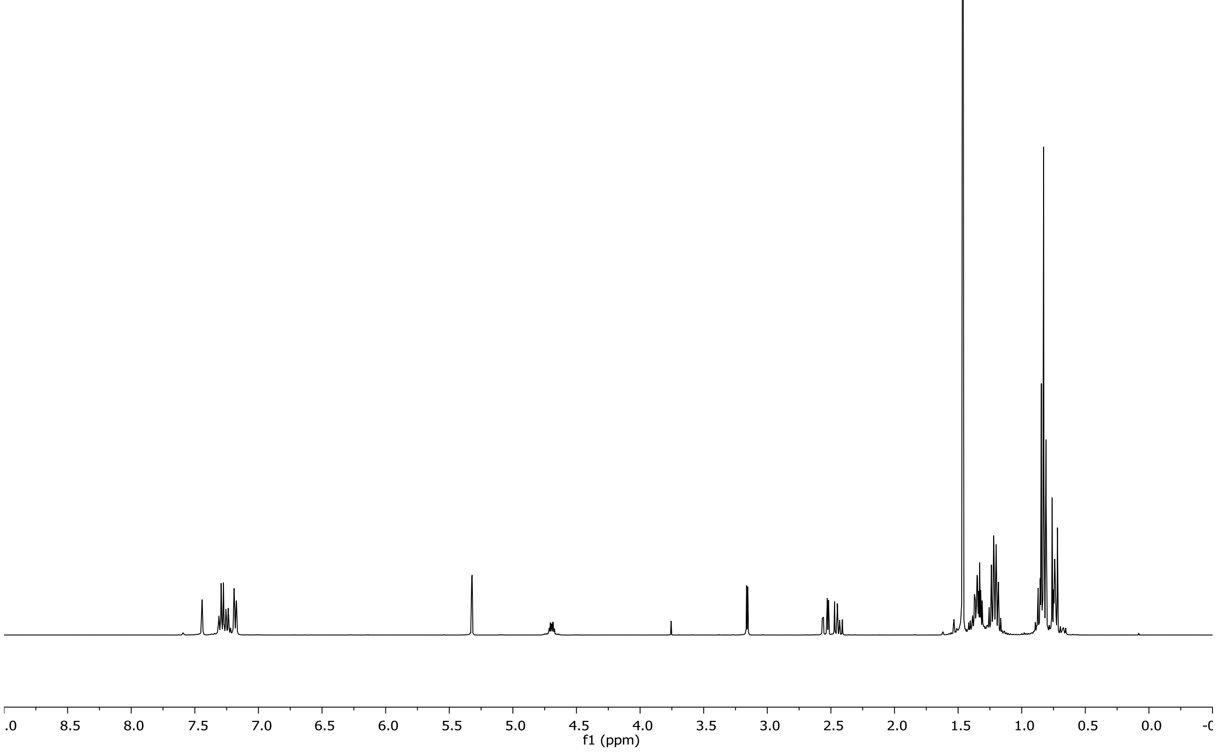
& isomer


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

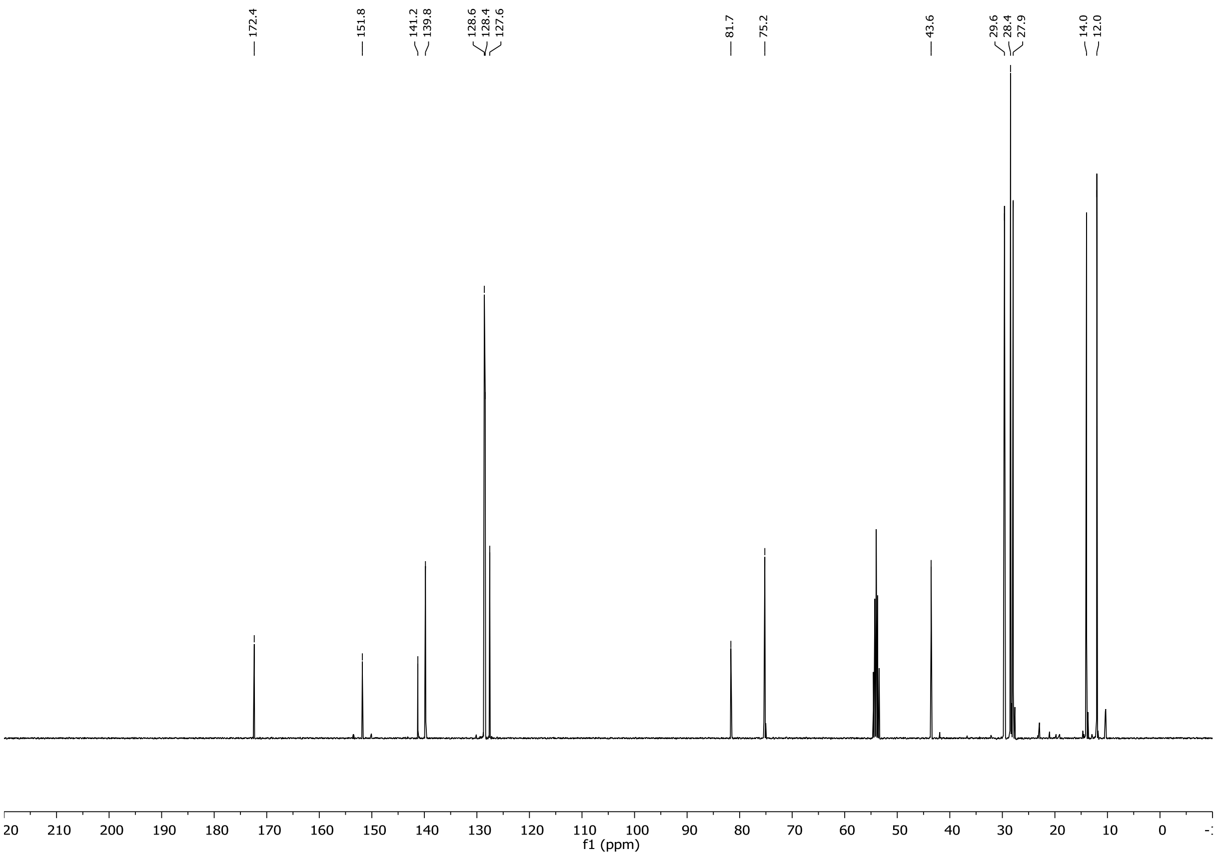

144.5
140.0
70.4
52.0
47.3
33.0
31.0
29.4
27.5
13.8
10.3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



H
OH
O
OtBu
SnBu3

.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

172.4
151.8
141.2
139.8
128.6
128.4
127.6
81.7
75.2
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29.6
28.4
27.9
14.0
12.0
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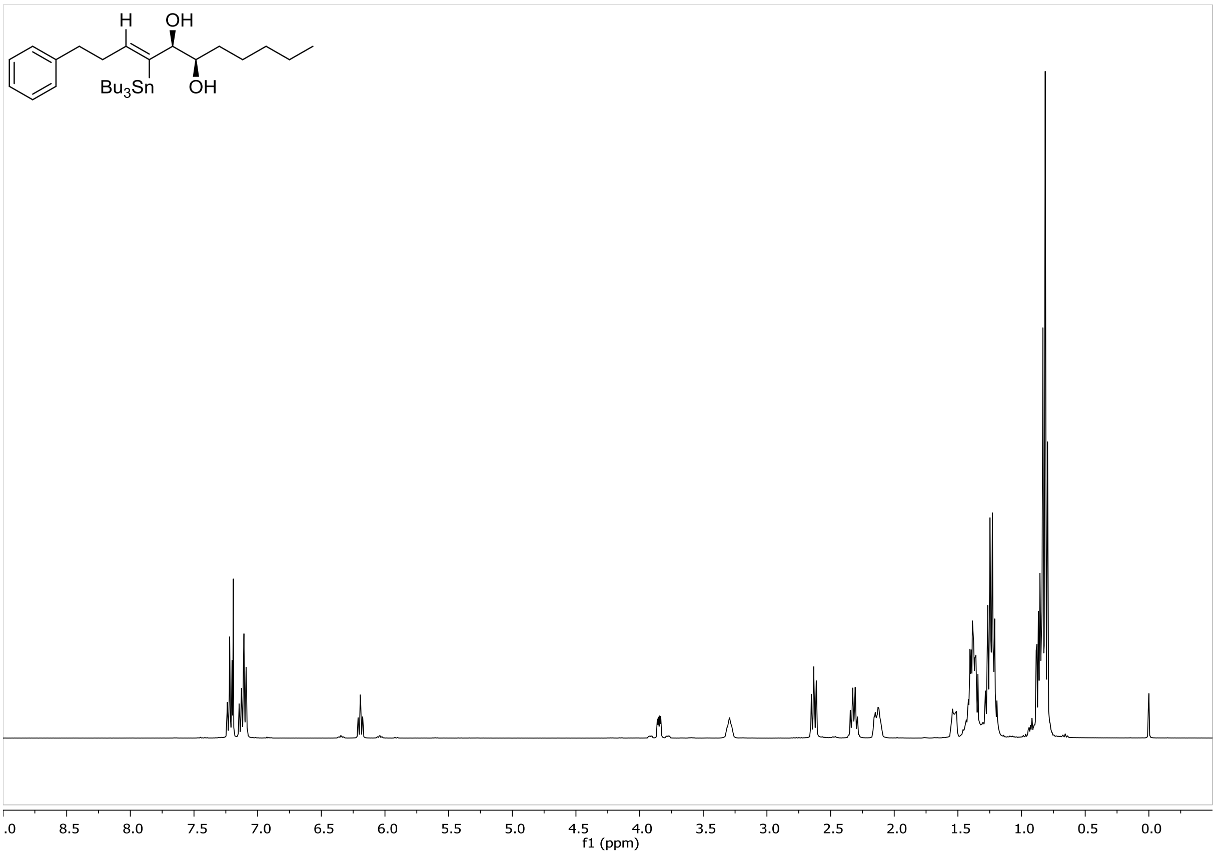
f1 (ppm)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H
Bu3Sn
OH
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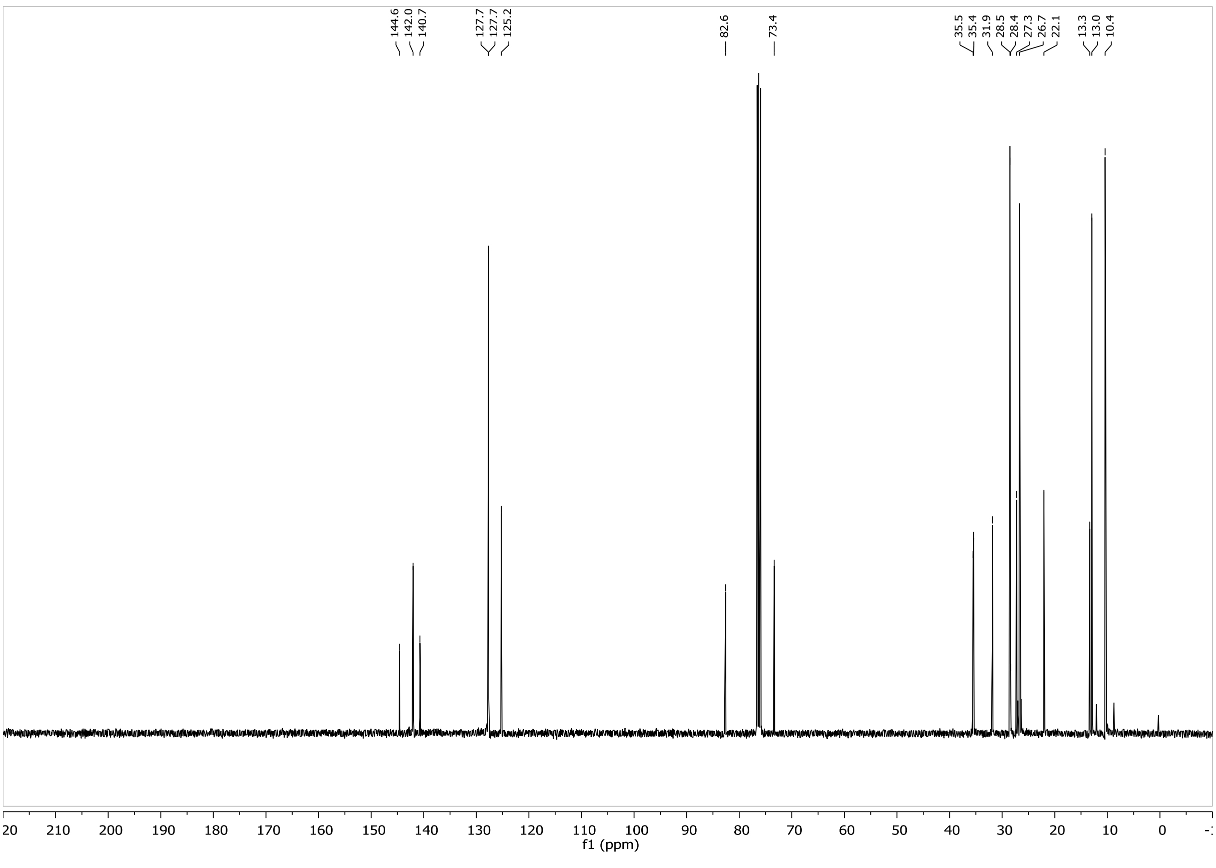
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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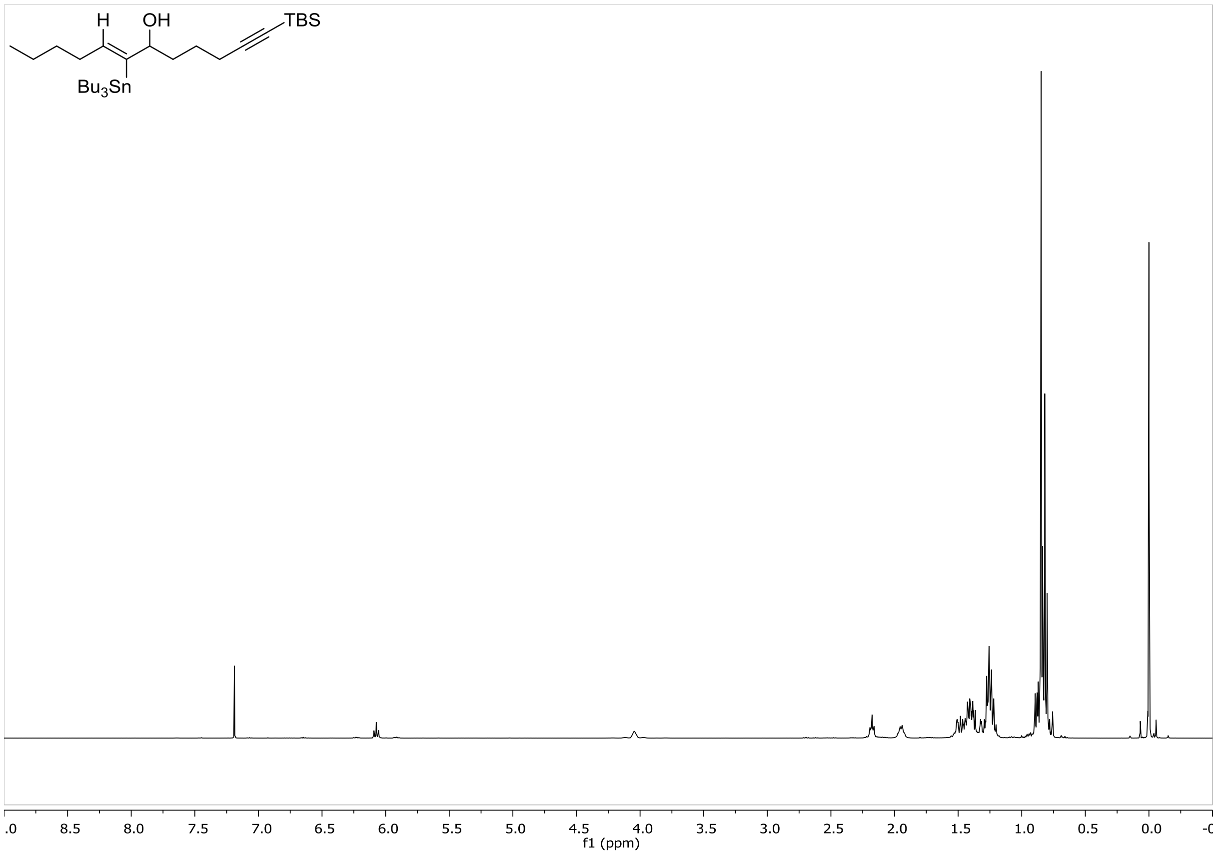
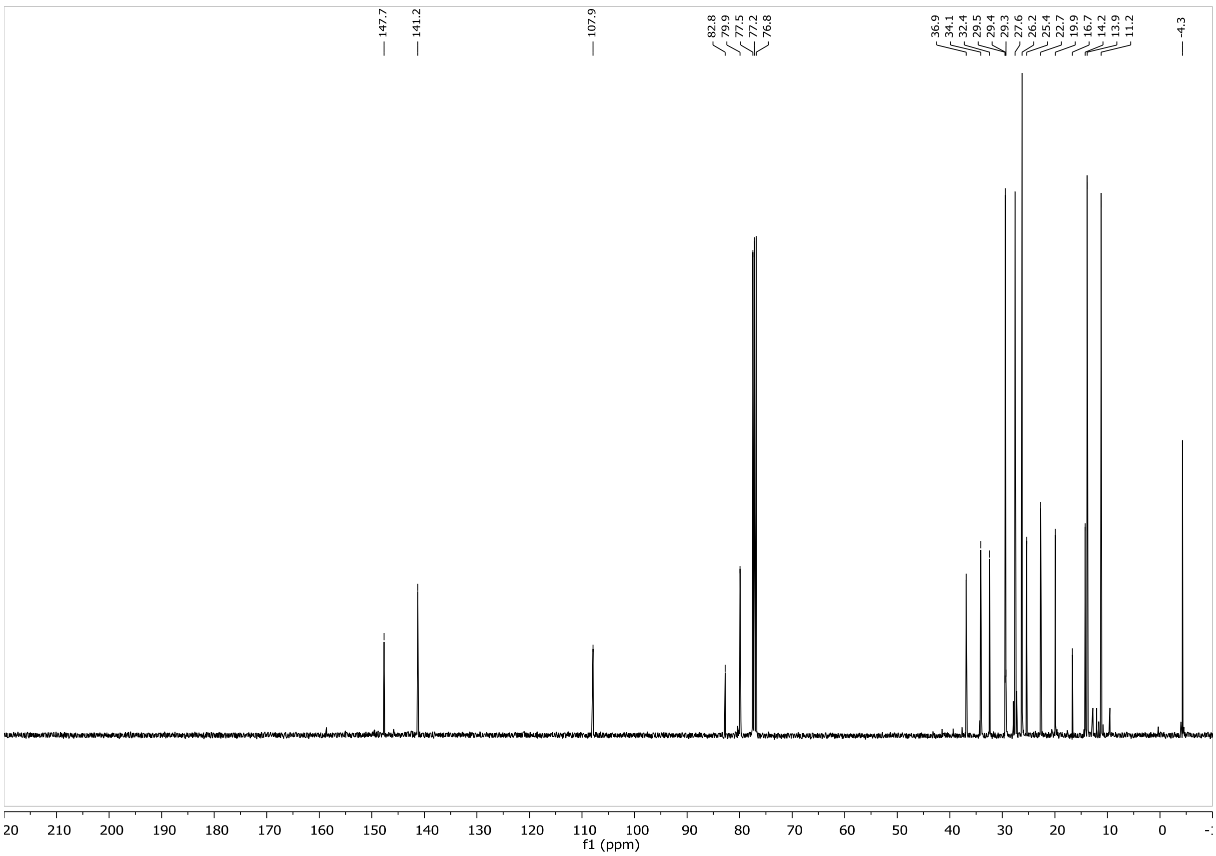
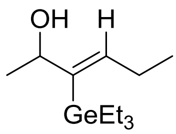
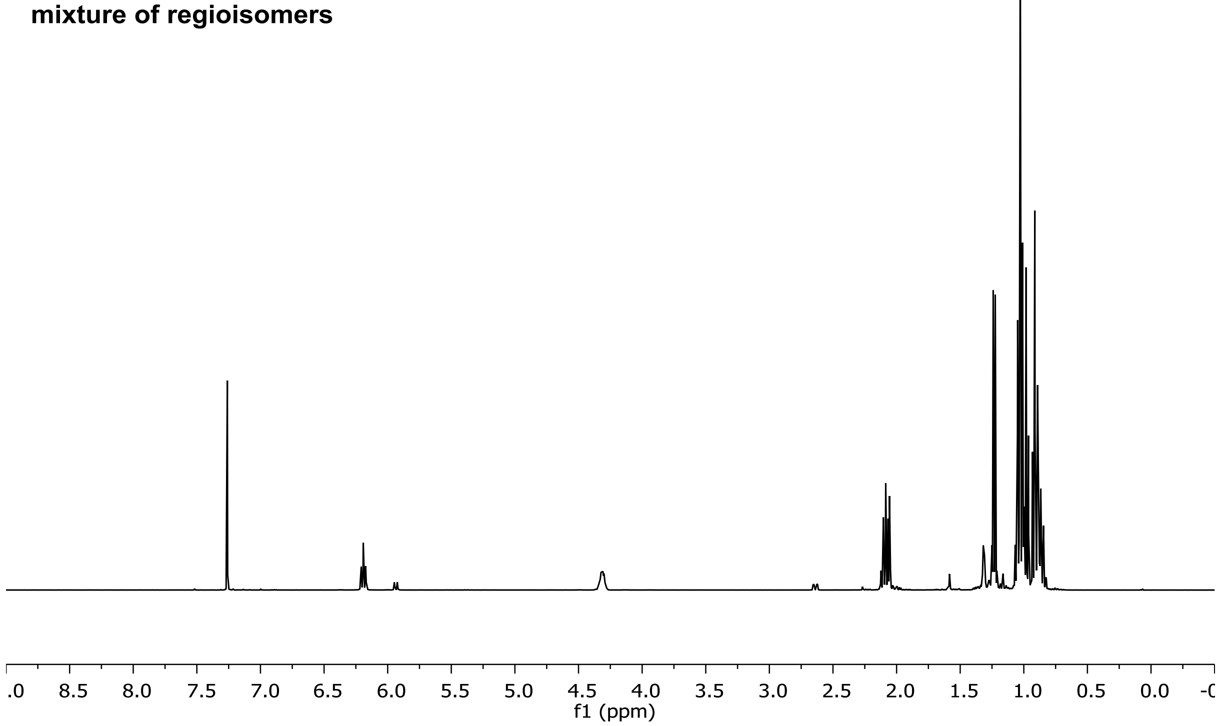
142.0
140.7
127.7
127.7
125.2
82.6
73.4
35.5
35.4
31.9
28.5
28.4
27.3
26.7
22.1
13.3
13.0
10.4
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

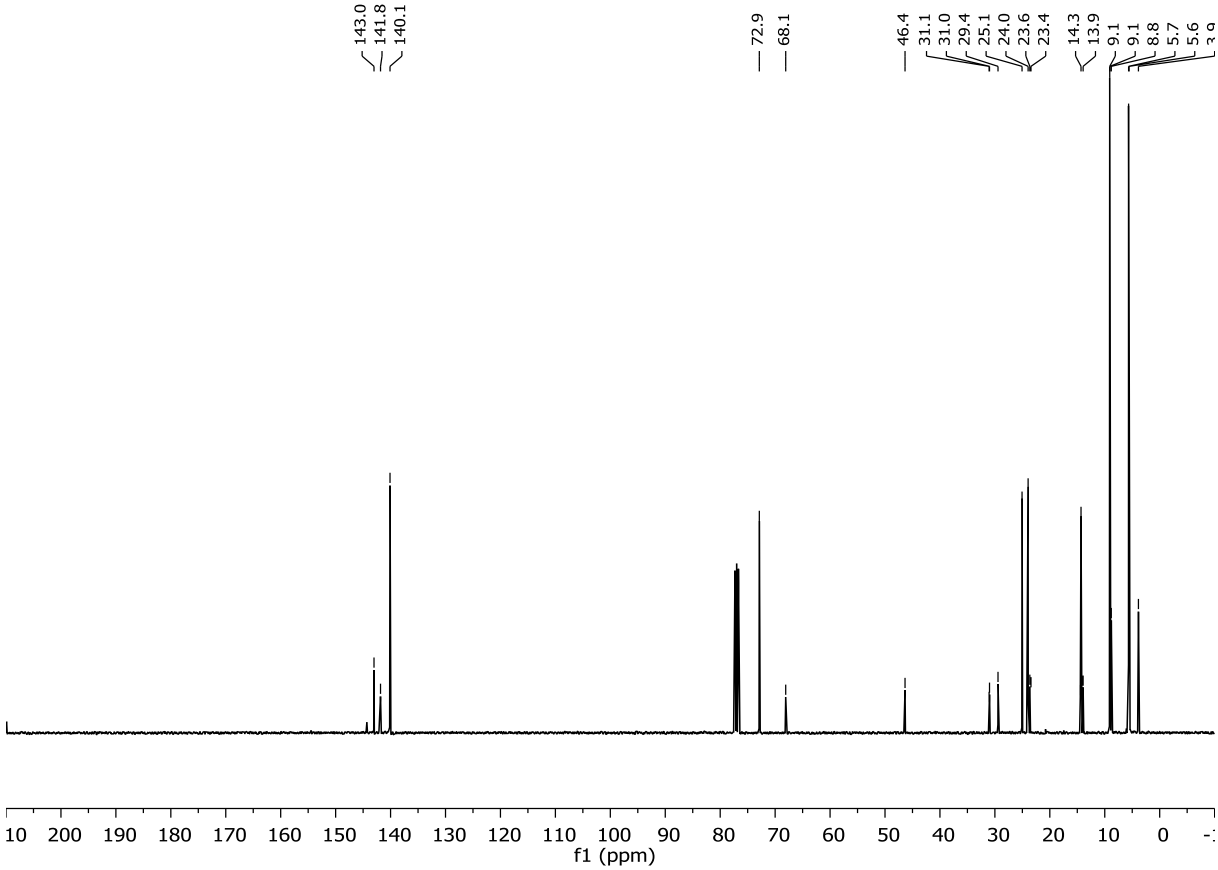

H
OH
TBS
Bu3Sn
f1 (ppm)

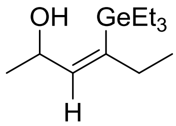

147.7
141.2
107.9
82.8
79.9
77.5
77.2
76.8
36.9
34.1
32.4
29.5
29.4
29.3
27.6
26.2
25.4
22.7
19.9
16.7
14.2
13.9
11.2
-4.3
f1 (ppm)



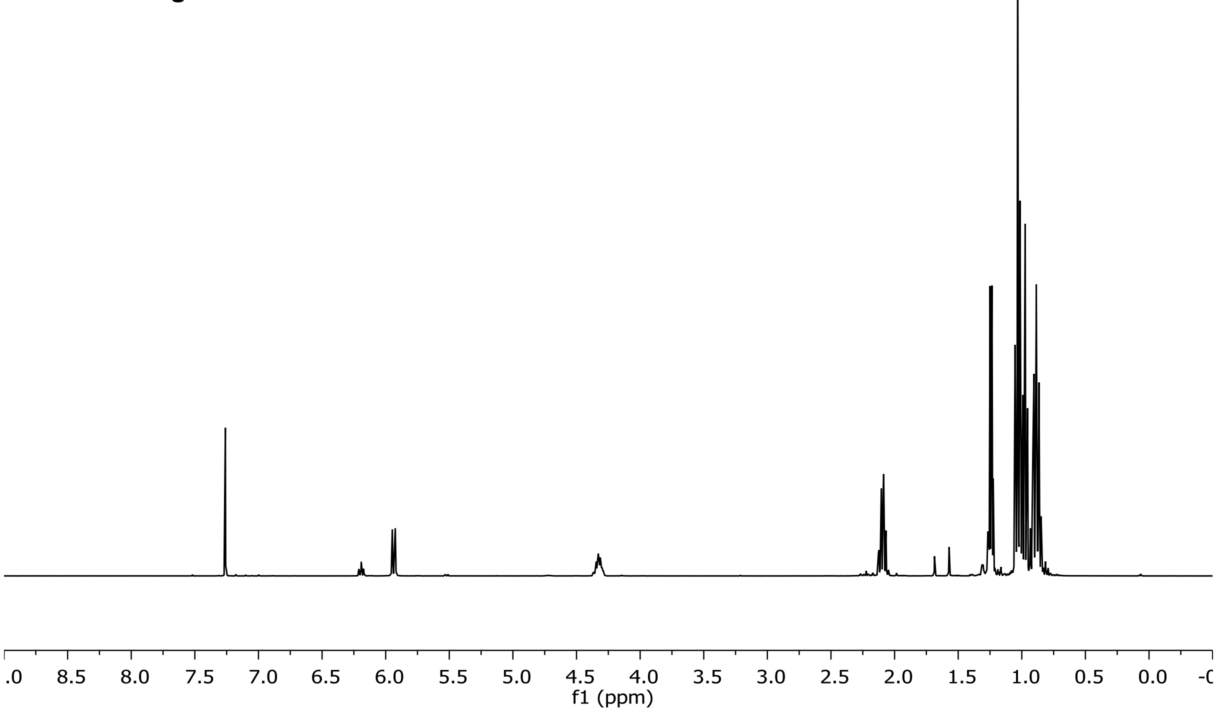

**mixture of regioisomers**

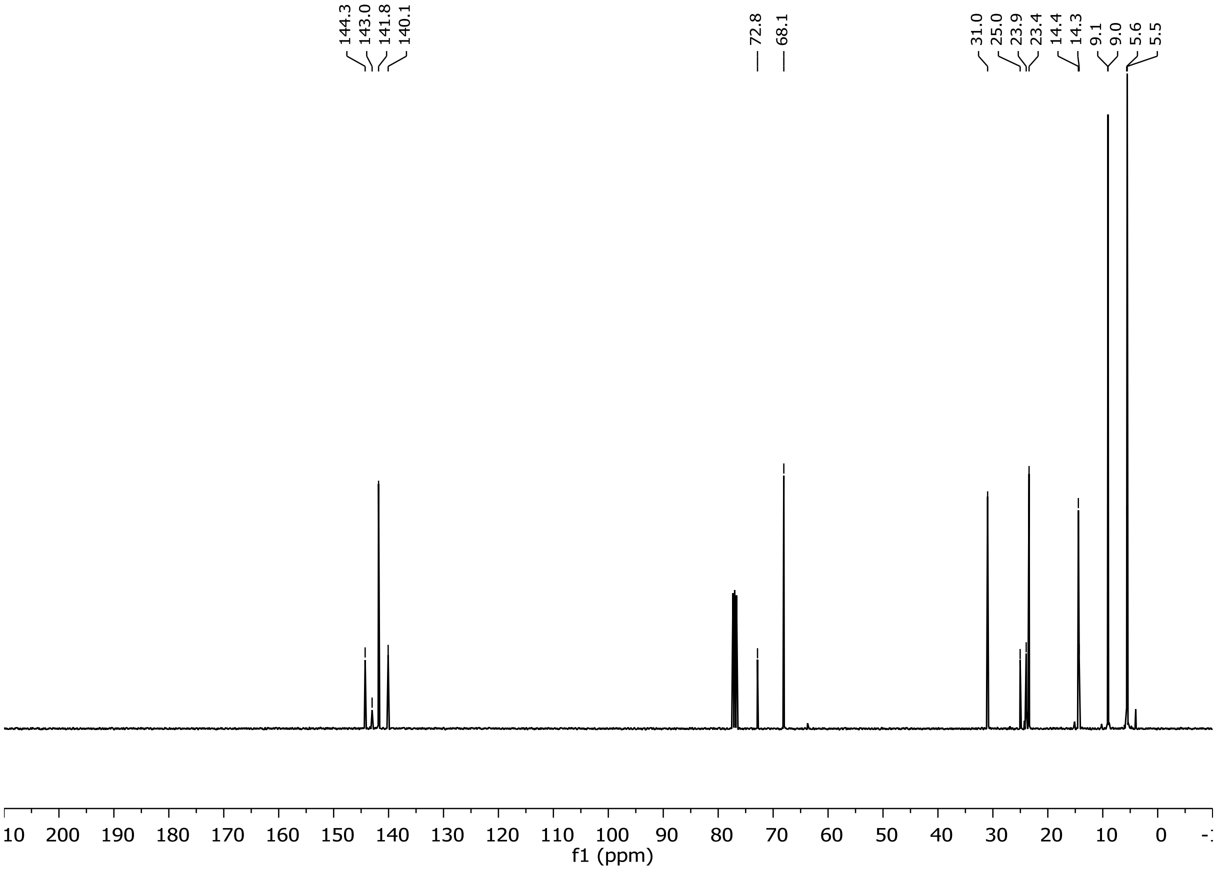


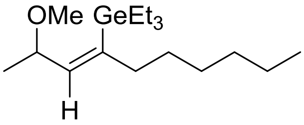





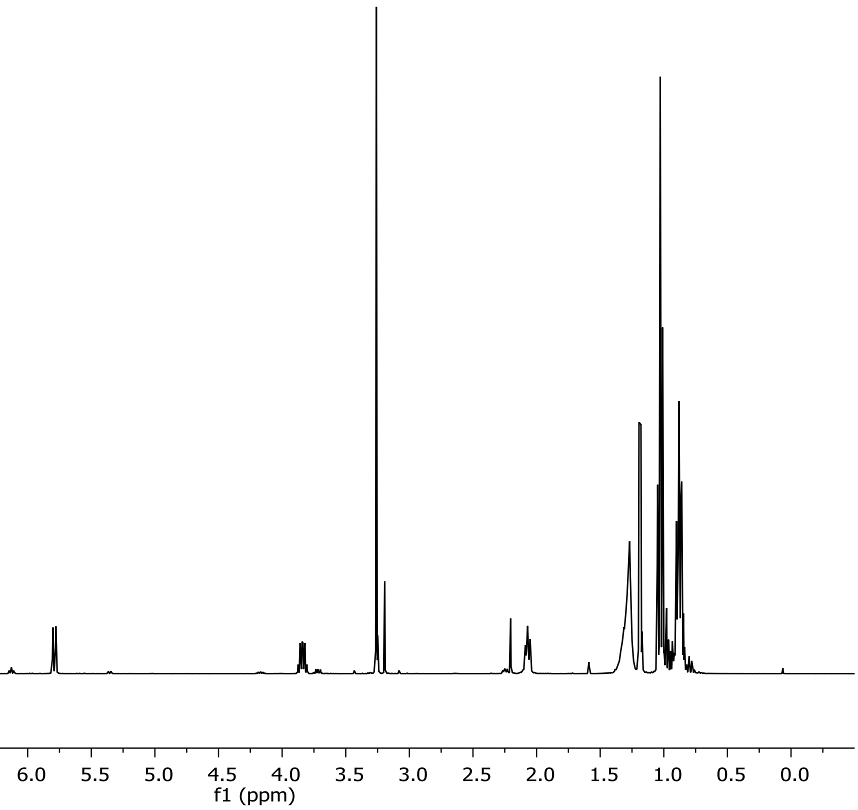

**mixture of regioisomers**

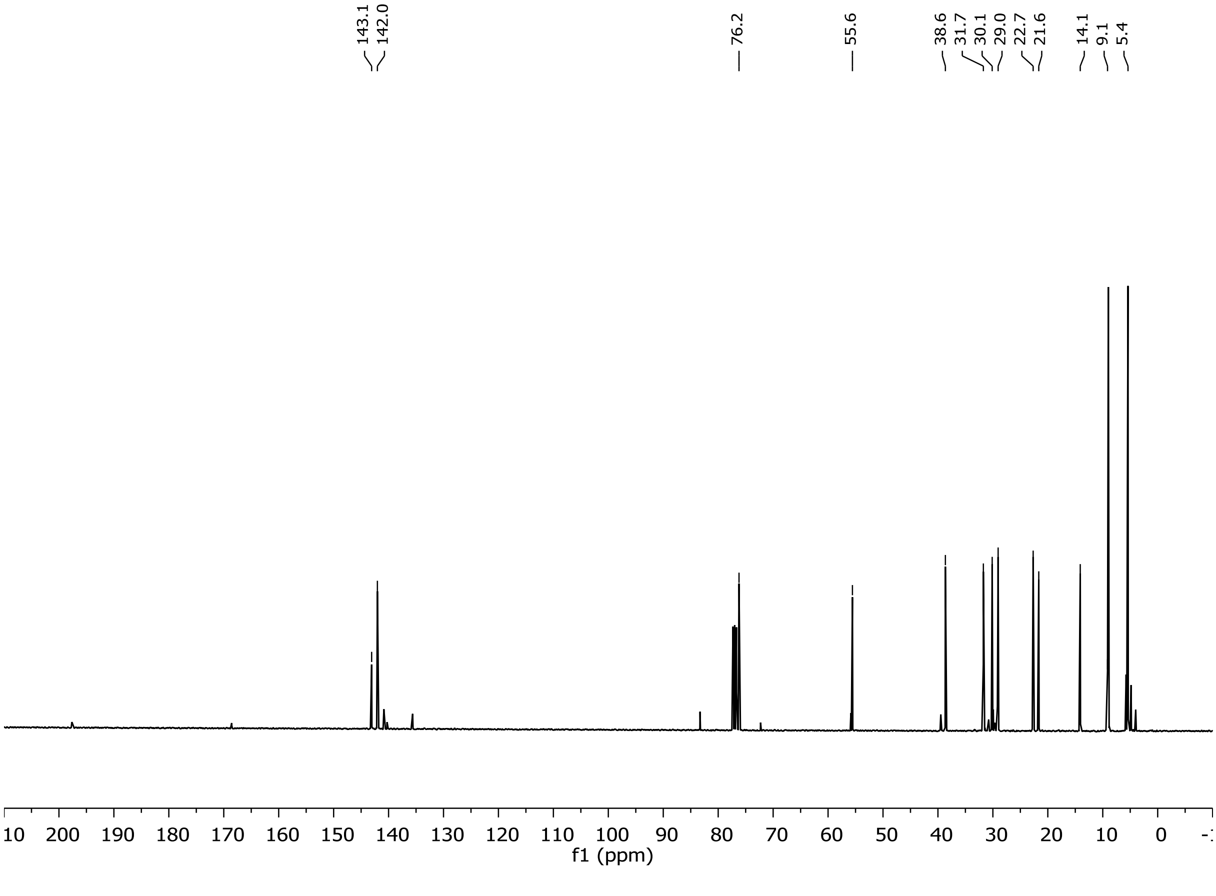


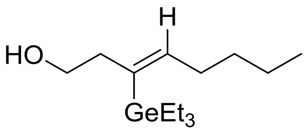





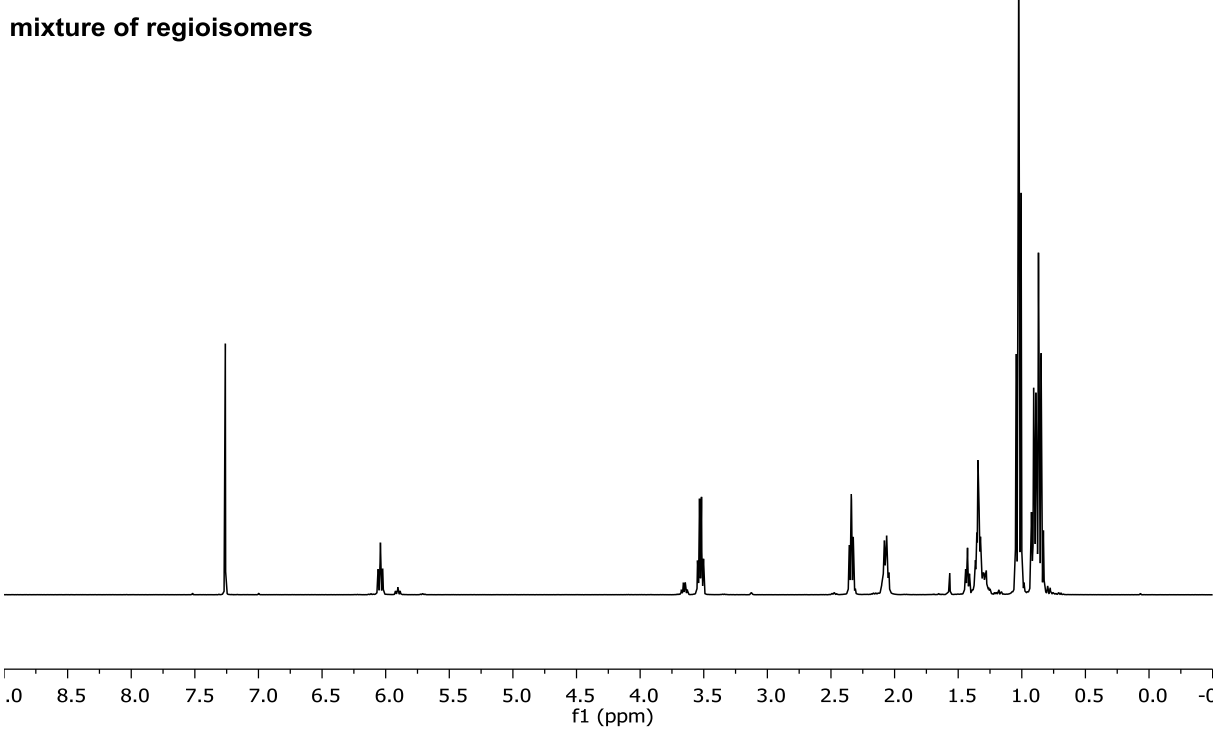

mixture of regioisomers

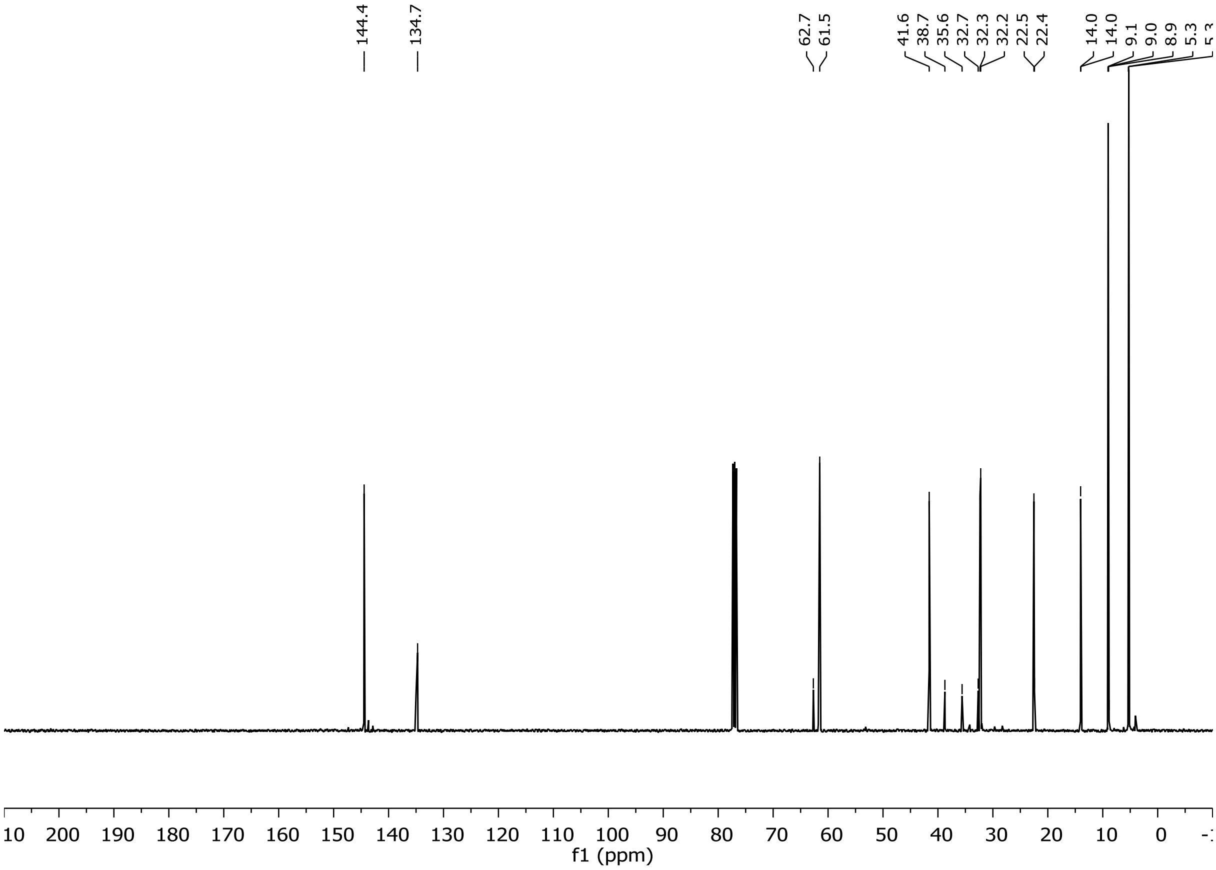


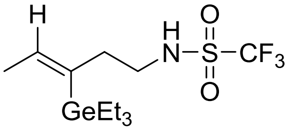





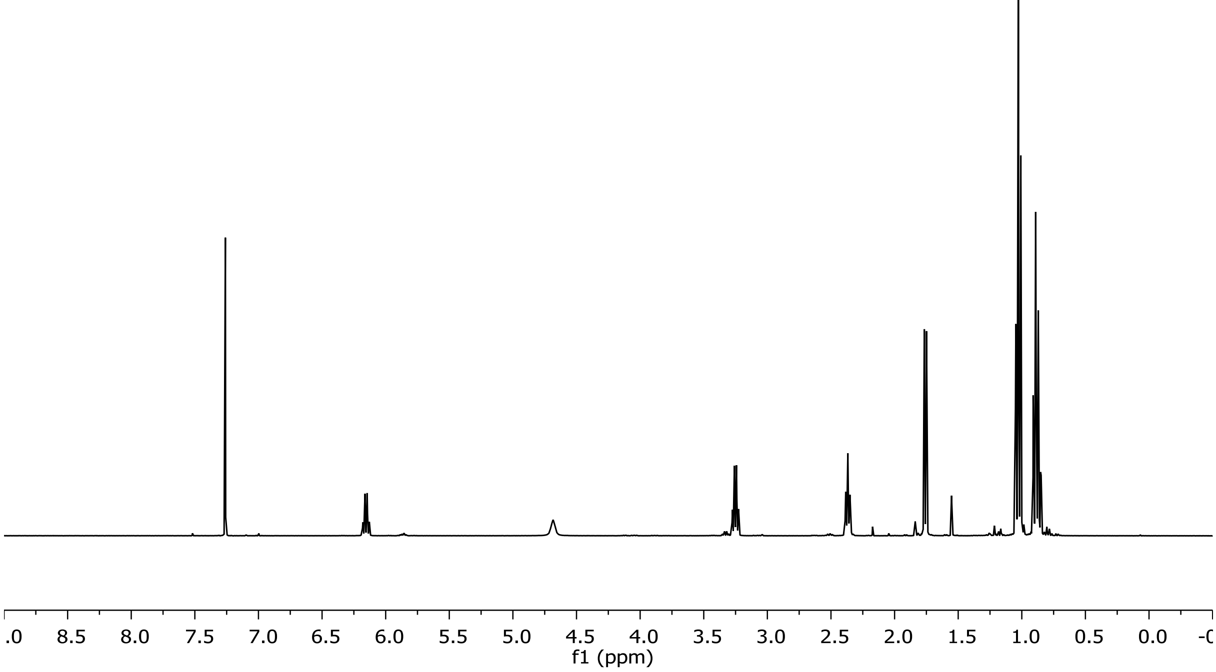

**mixture of regioisomers**

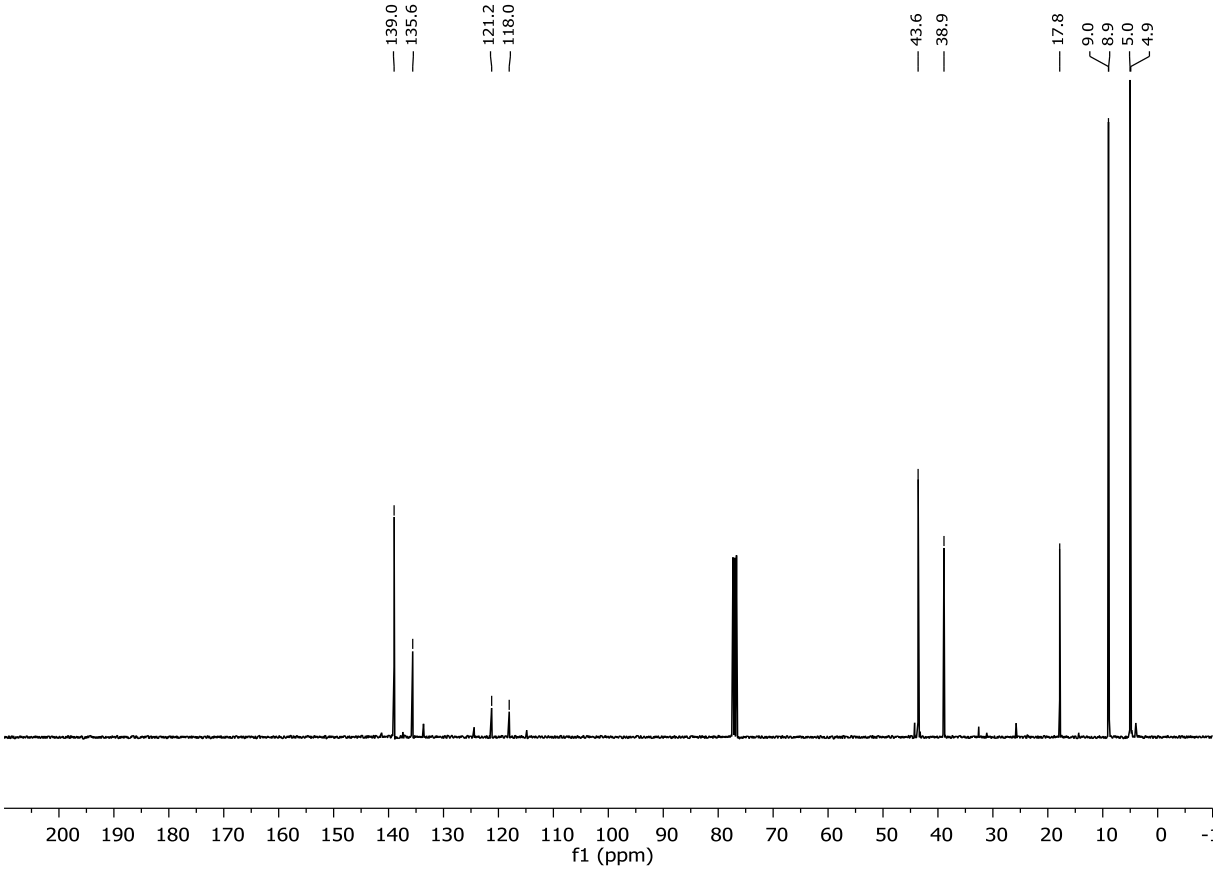


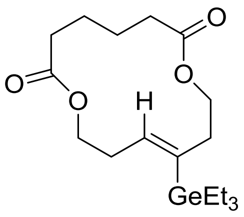



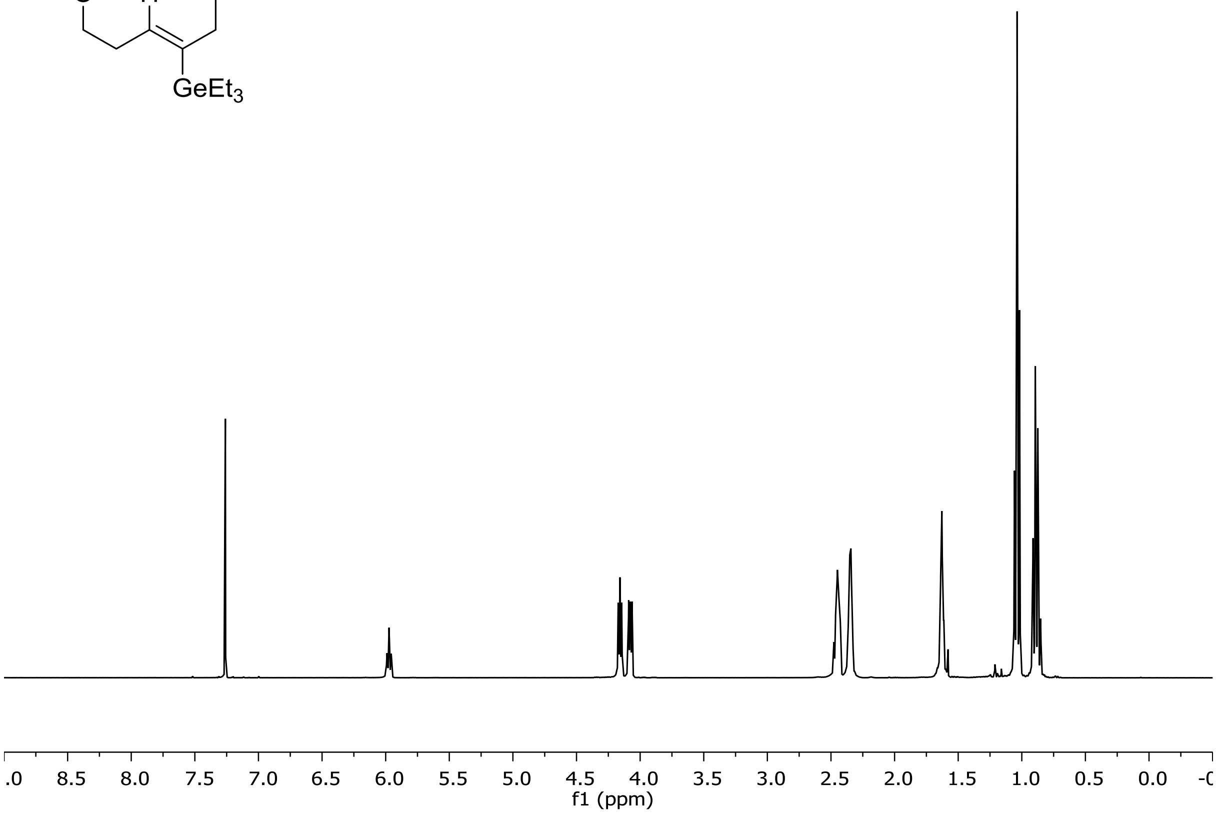


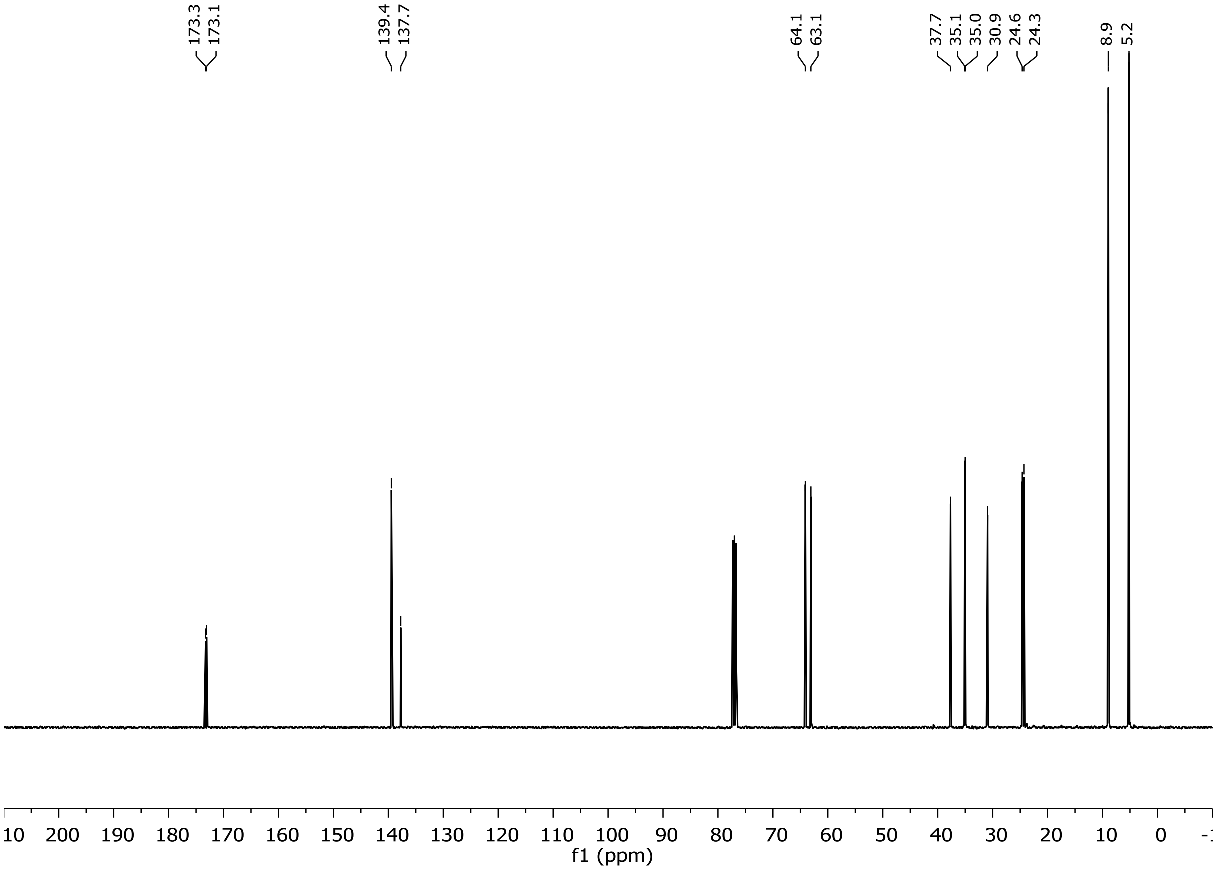

**mixture of regioisomers**

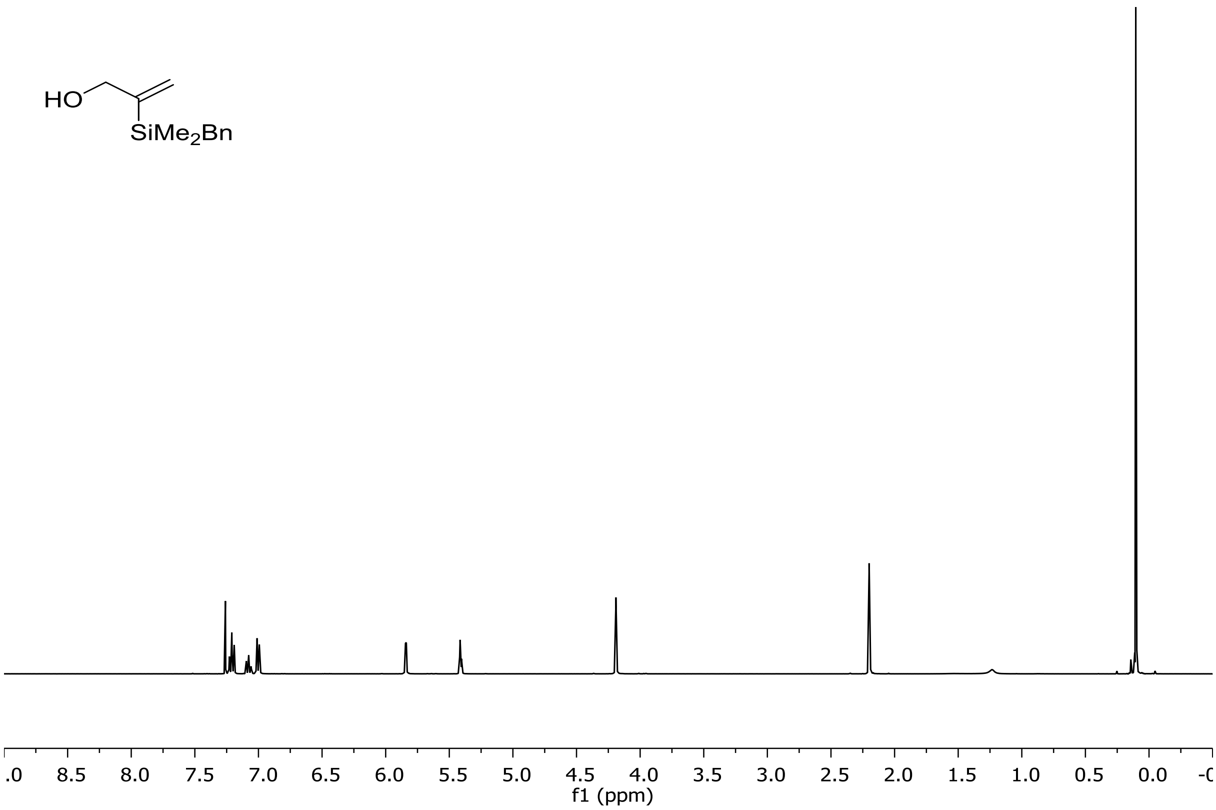


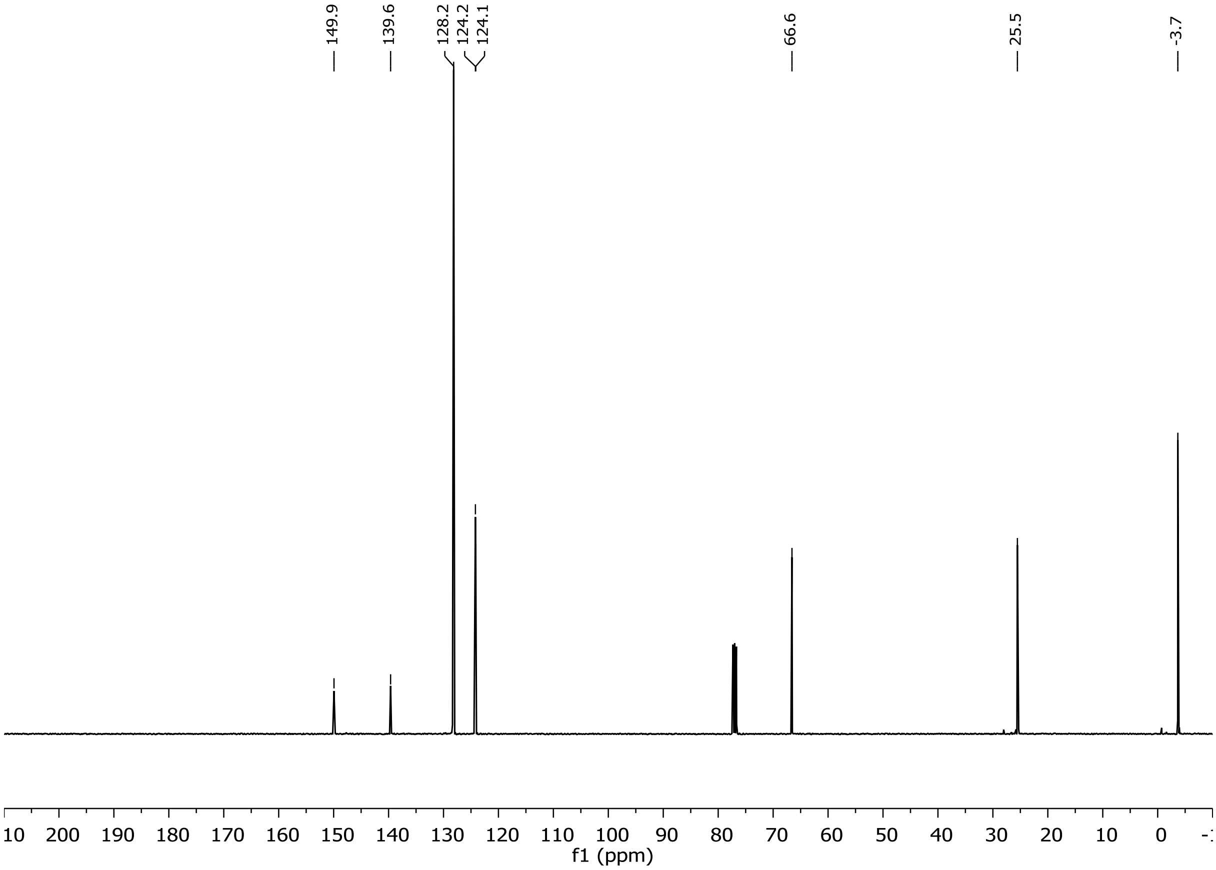



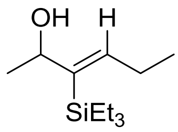

O
O
O
H
O
GeEt3


f1 (ppm)

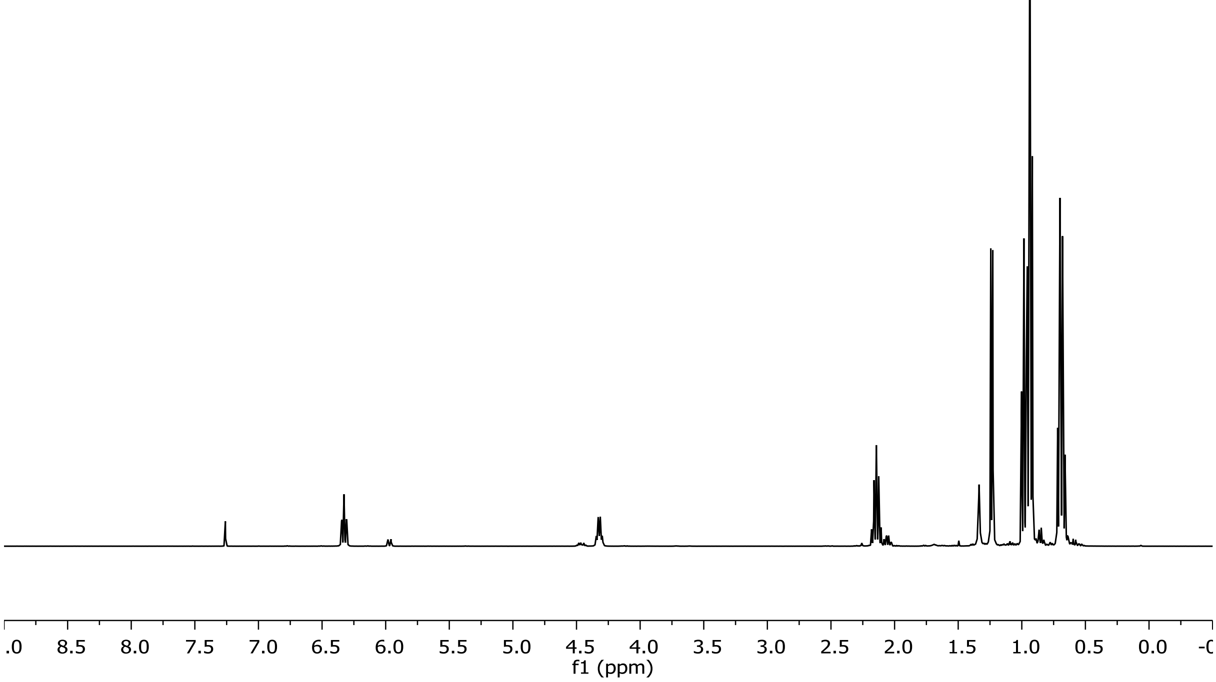

173.3
173.1
139.4
137.7
64.1
63.1
37.7
35.1
35.0
30.9
24.6
24.3
8.9
5.2
f1 (ppm)

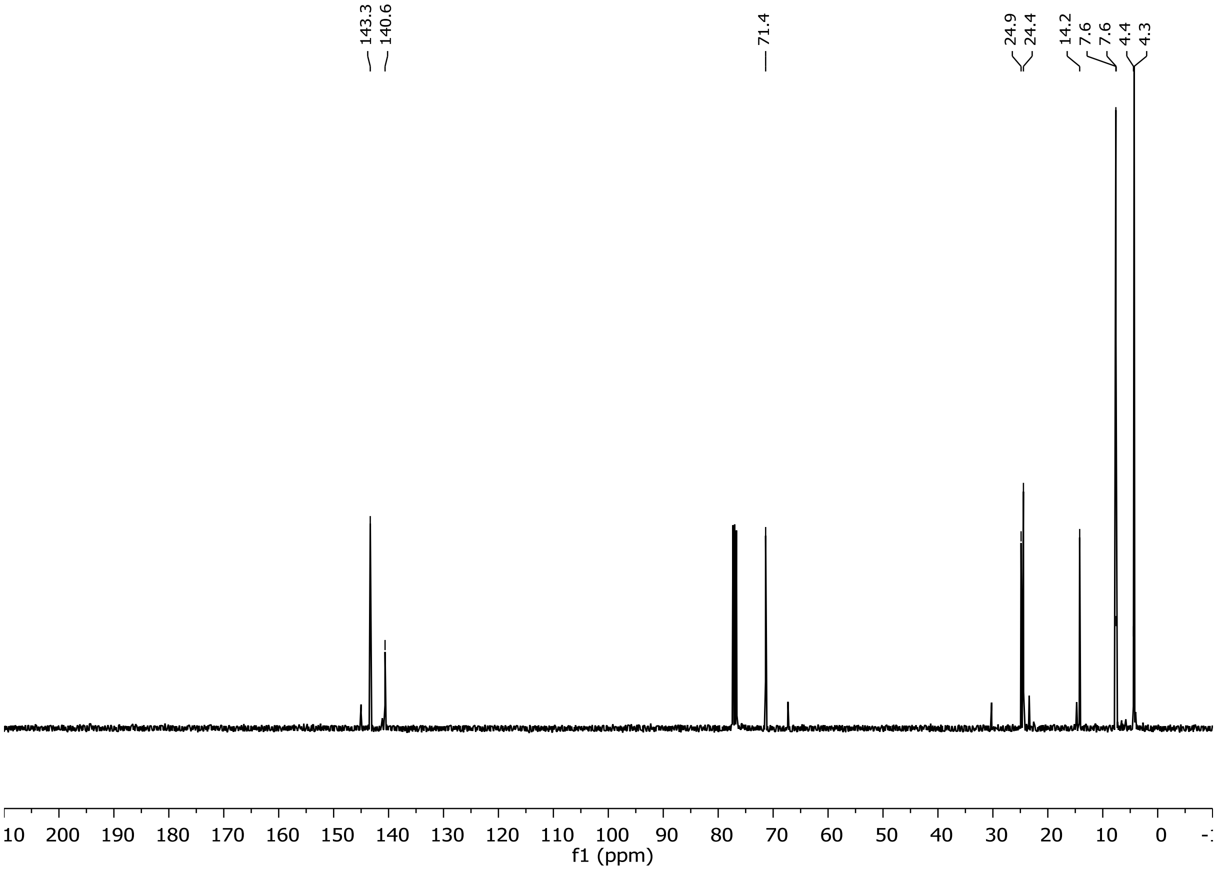

HO
SiMe2Bn
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

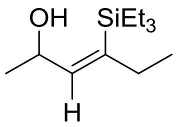

149.9
139.6
128.2
124.2
124.1
66.6
25.5
-3.7
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



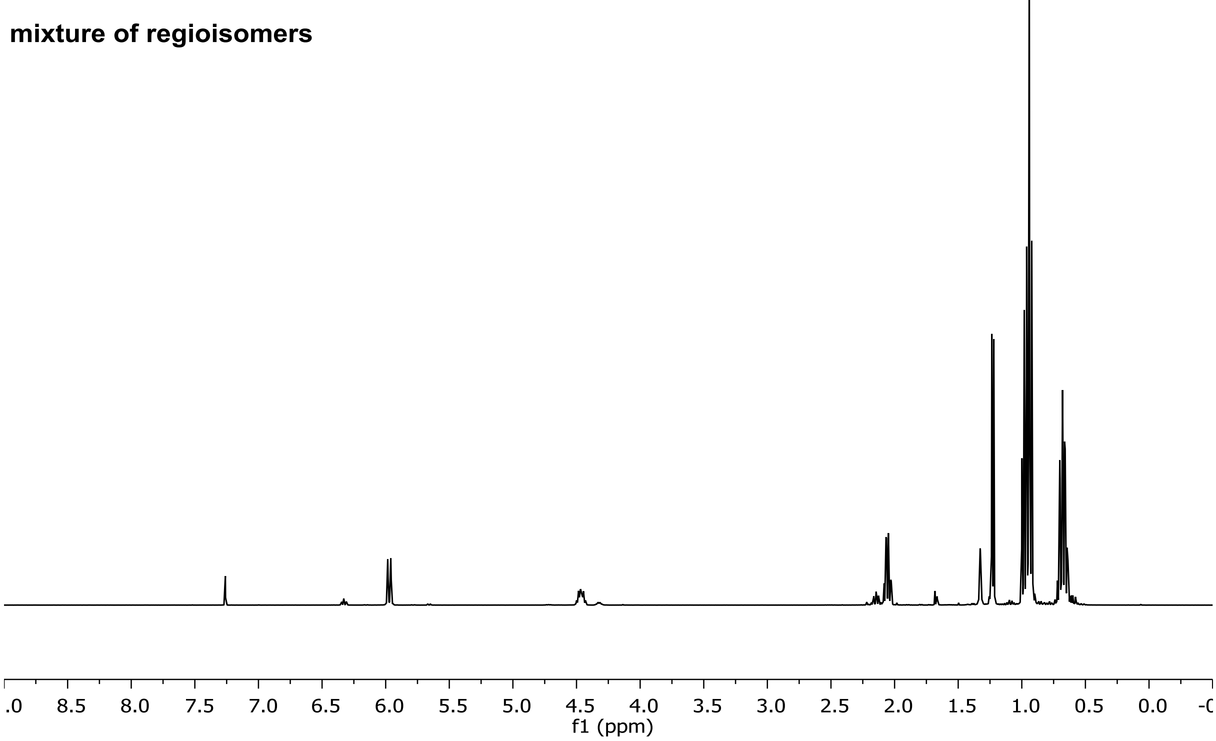

**mixture of regioisomers**

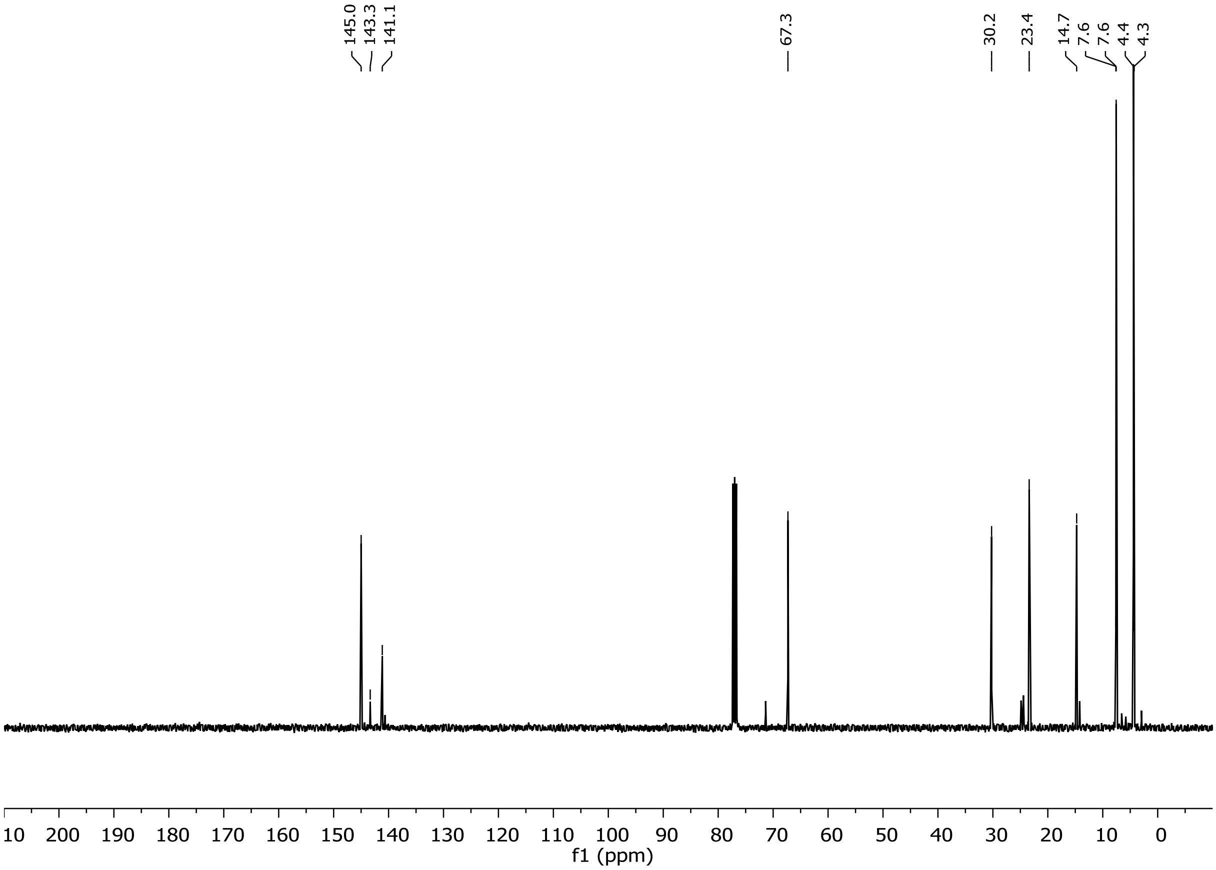


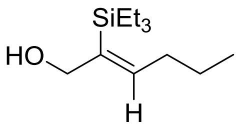





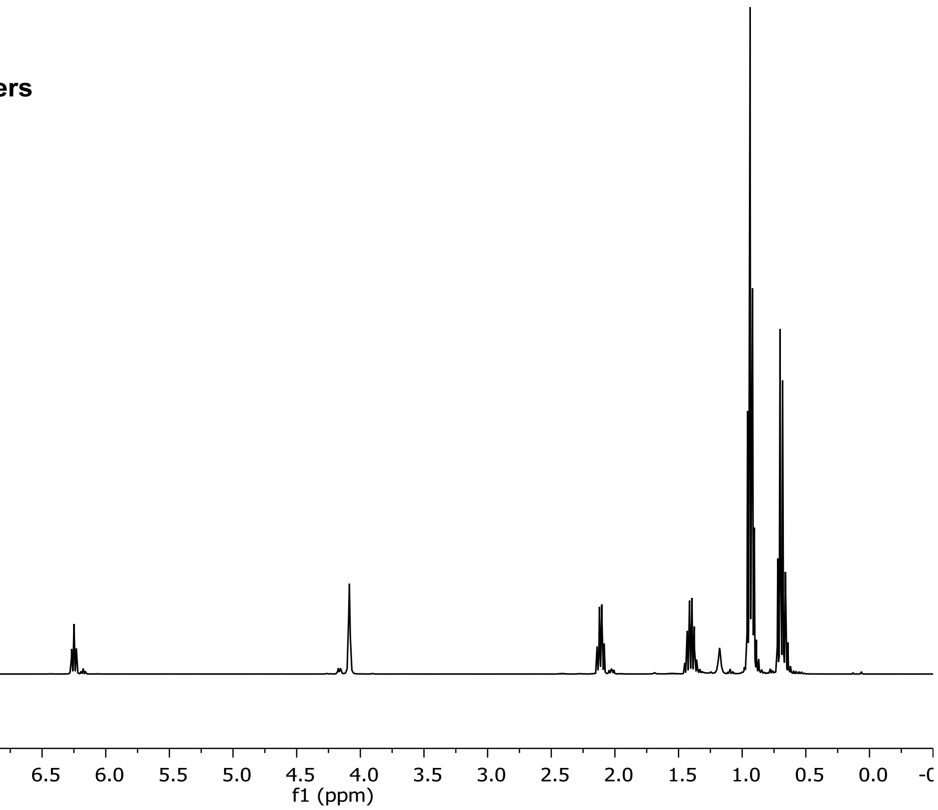

**mixture of regioisomers**

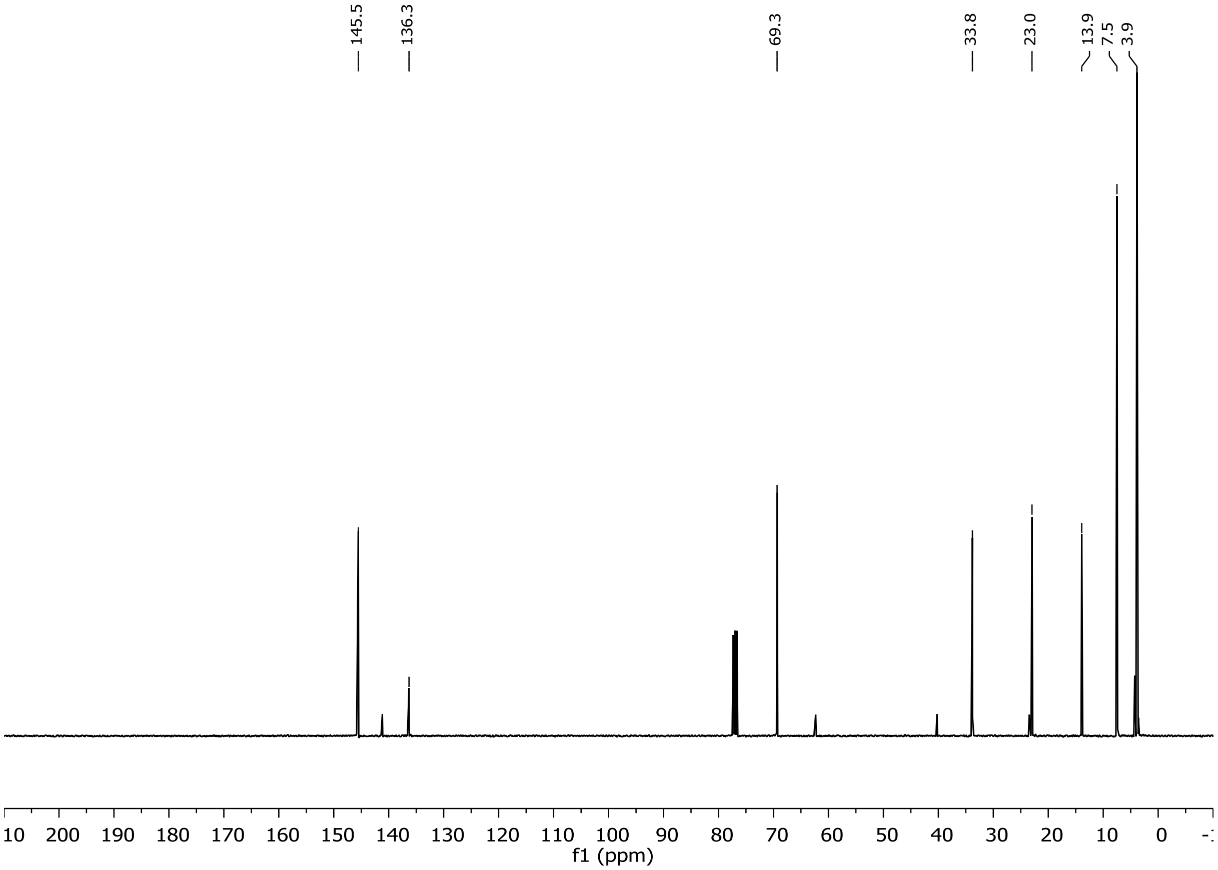


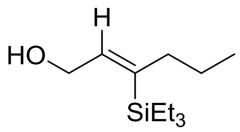






**mixture of regioisomers**



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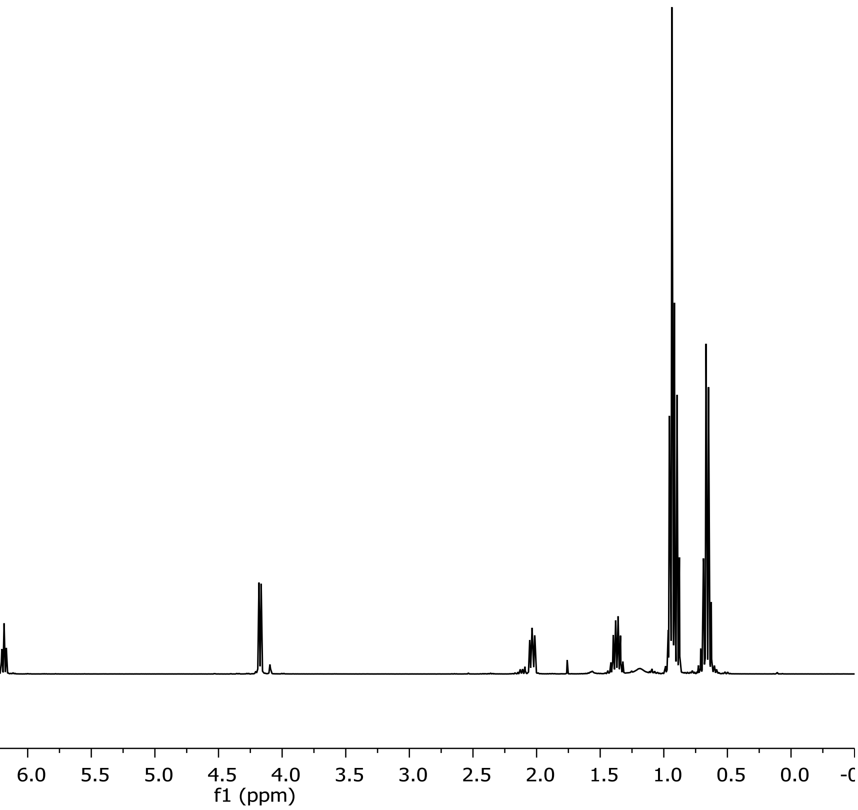
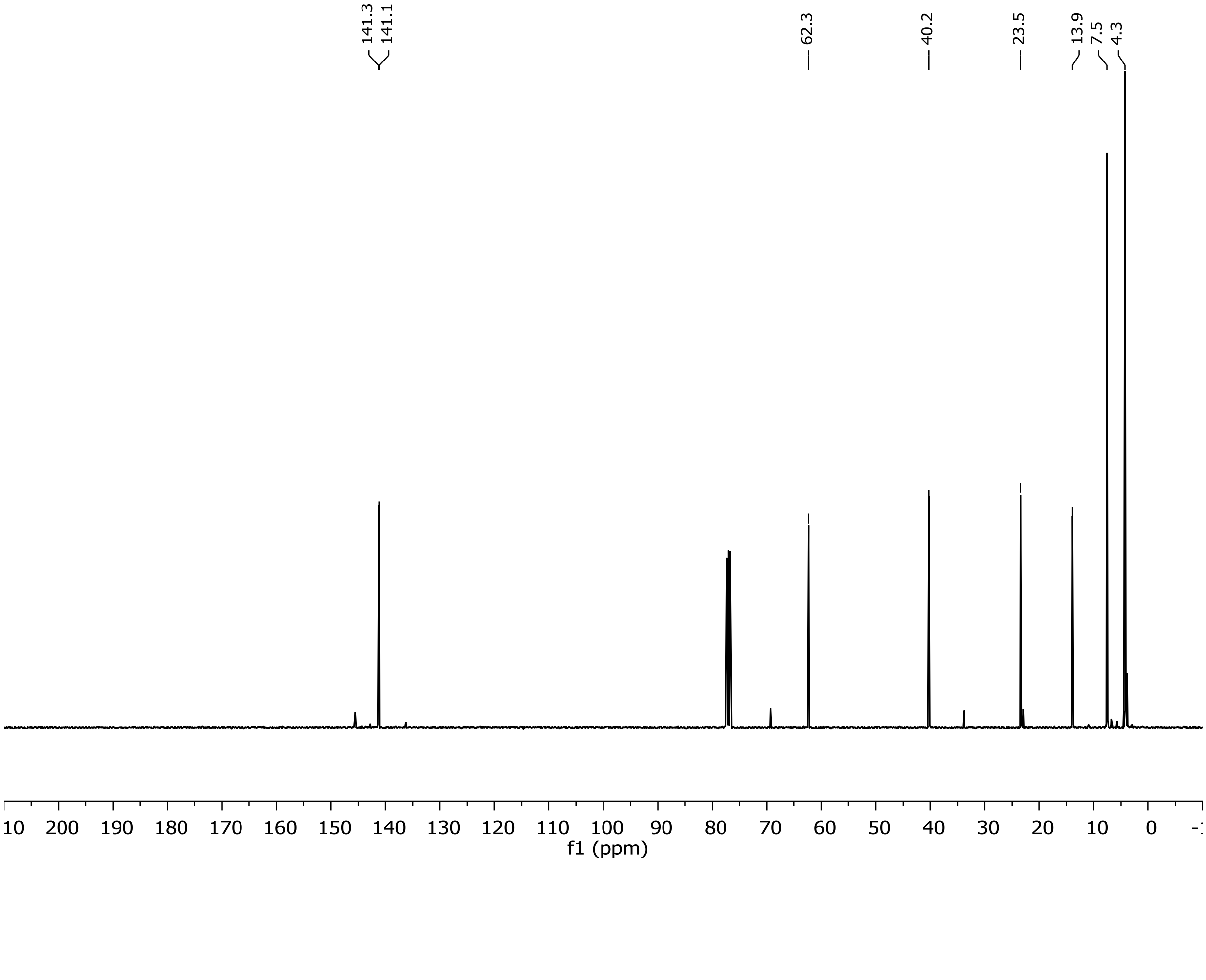
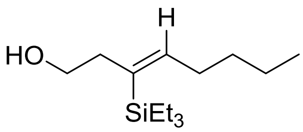
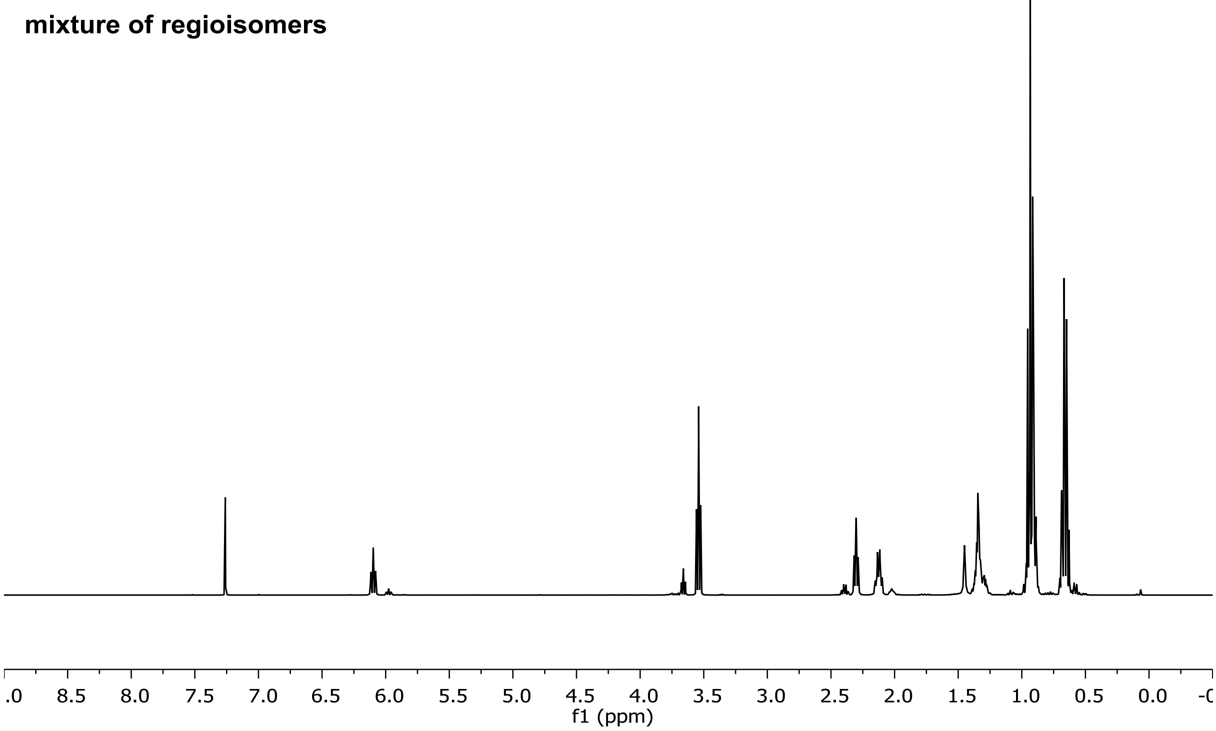
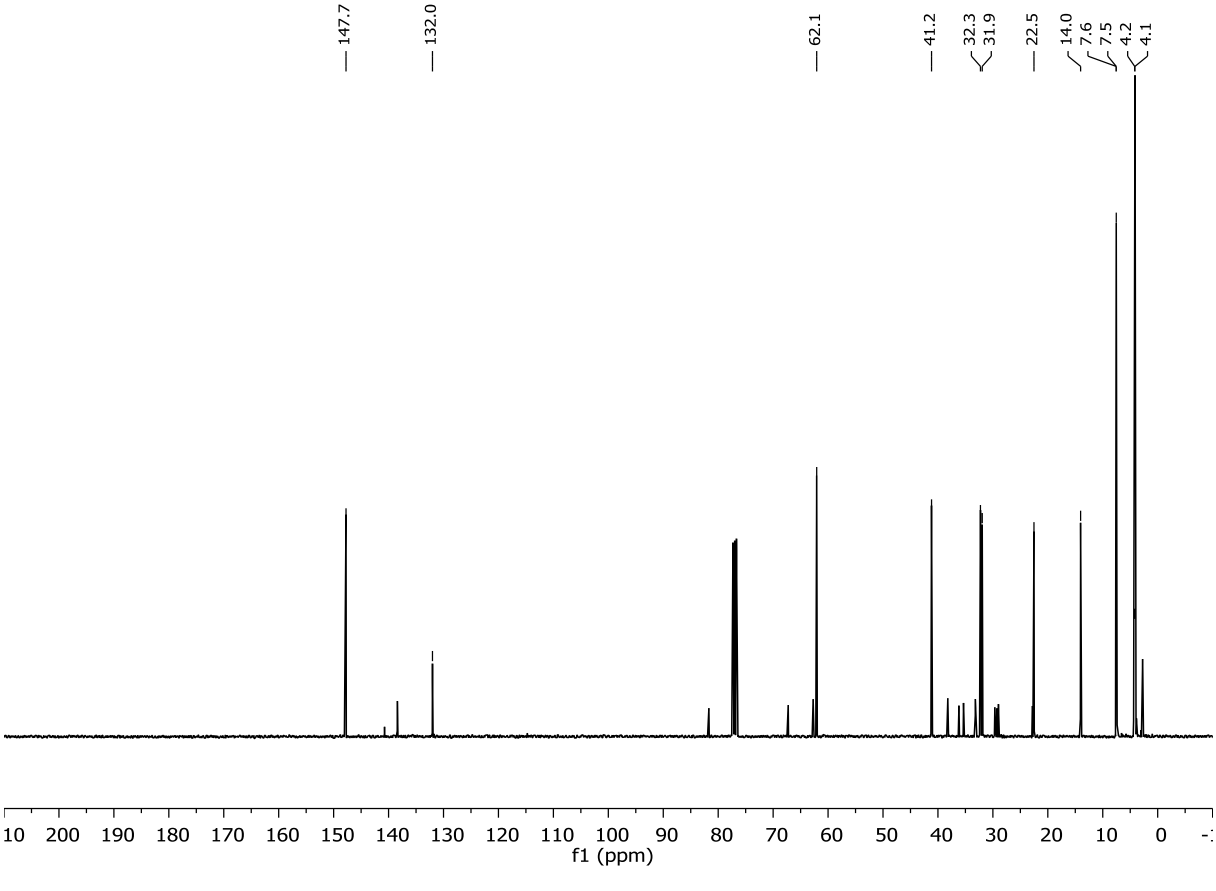


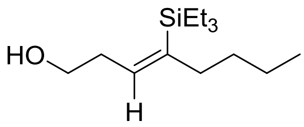





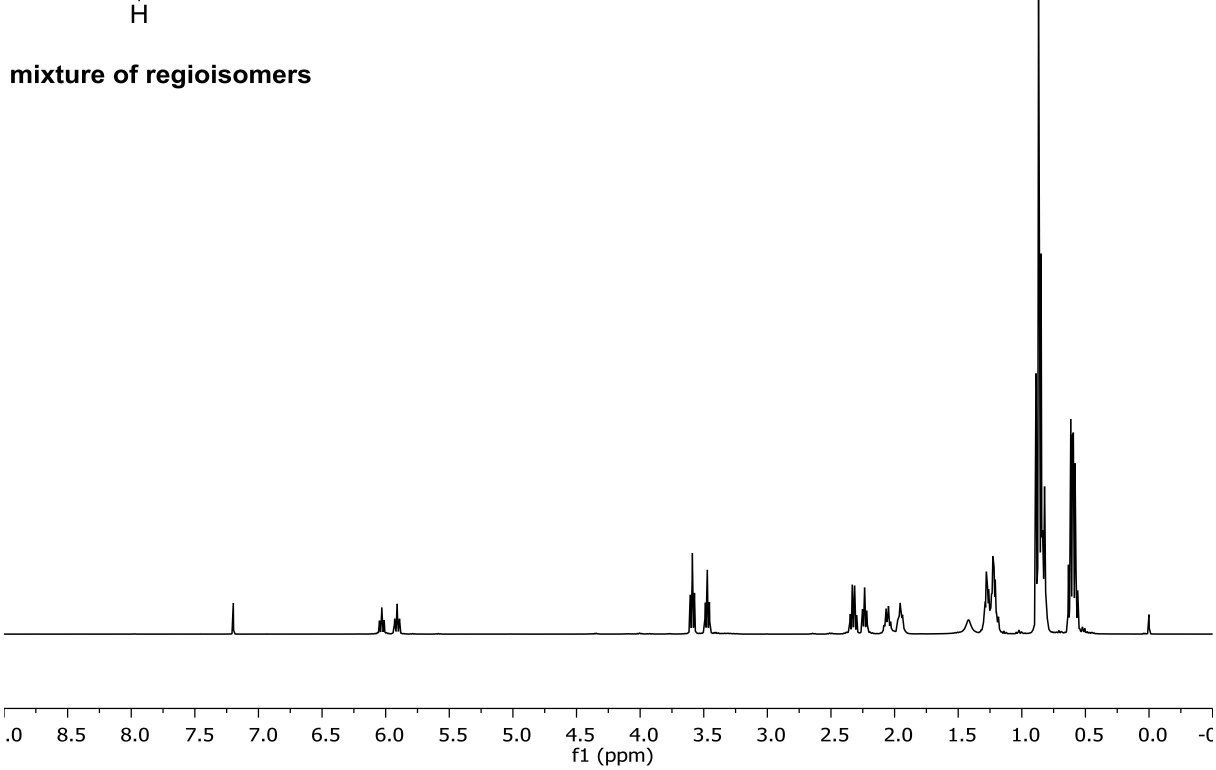

**mixture of regioisomers**

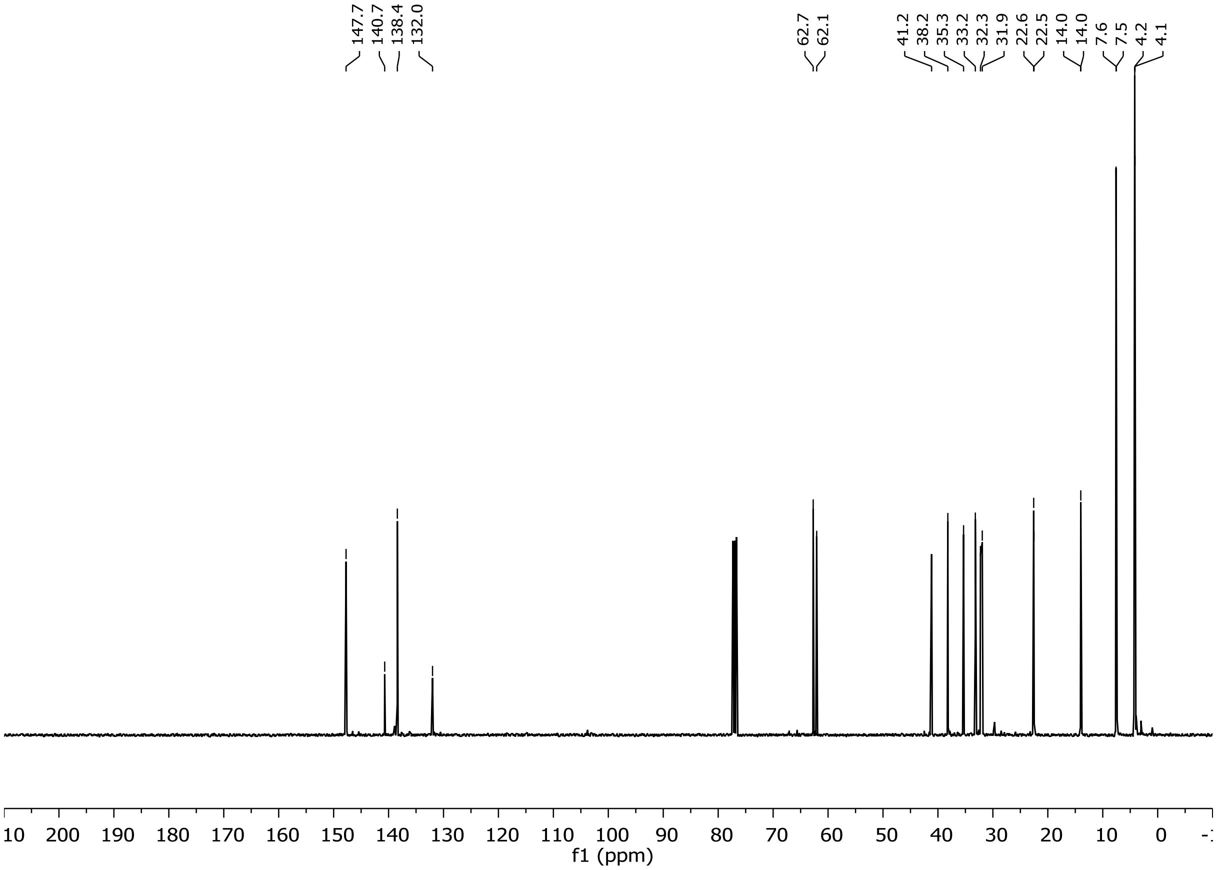


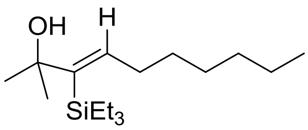



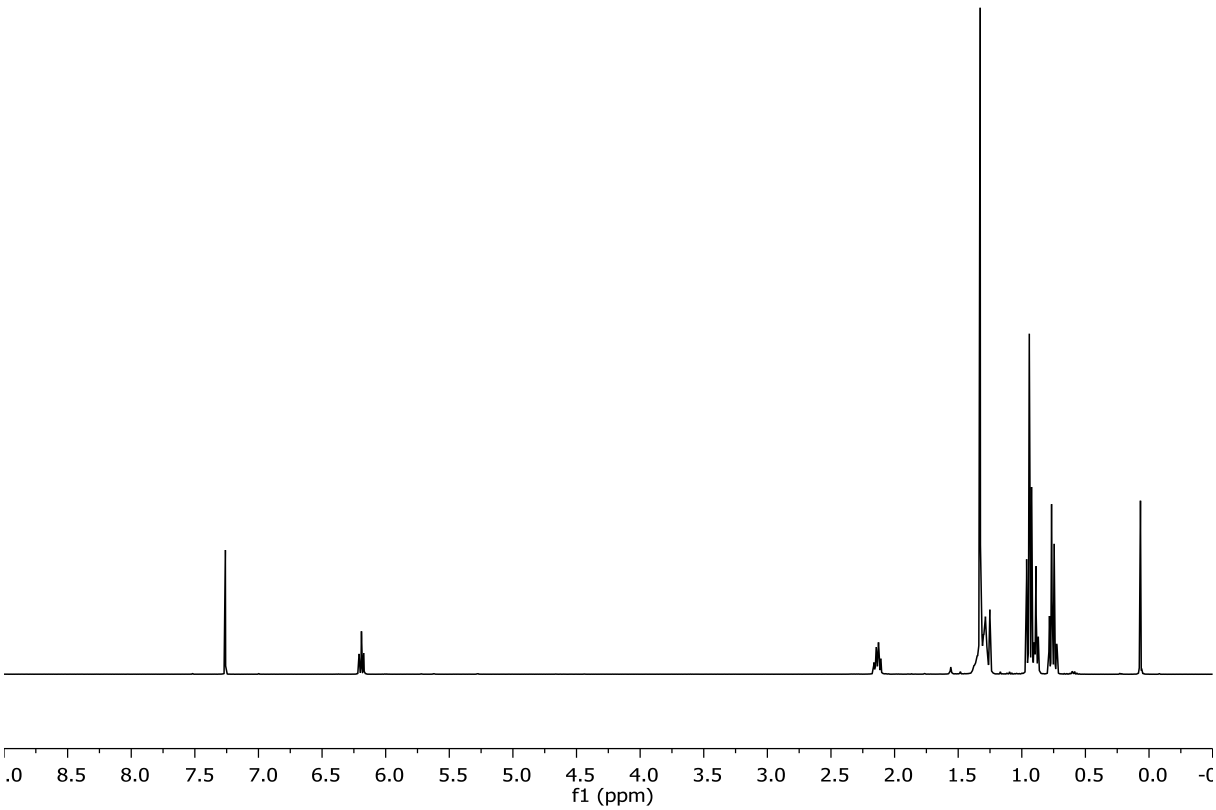


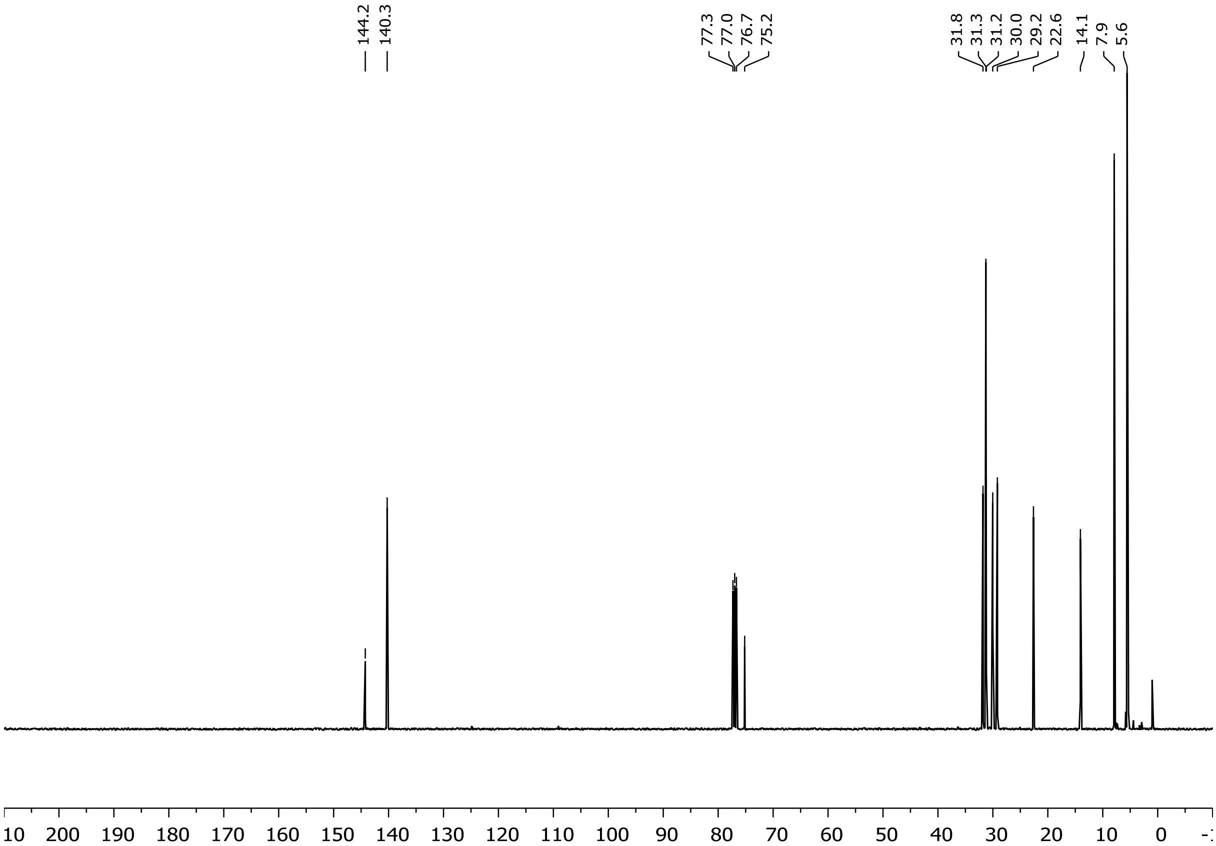

**mixture of regioisomers**

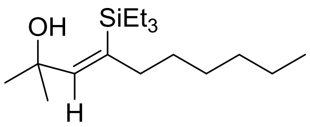


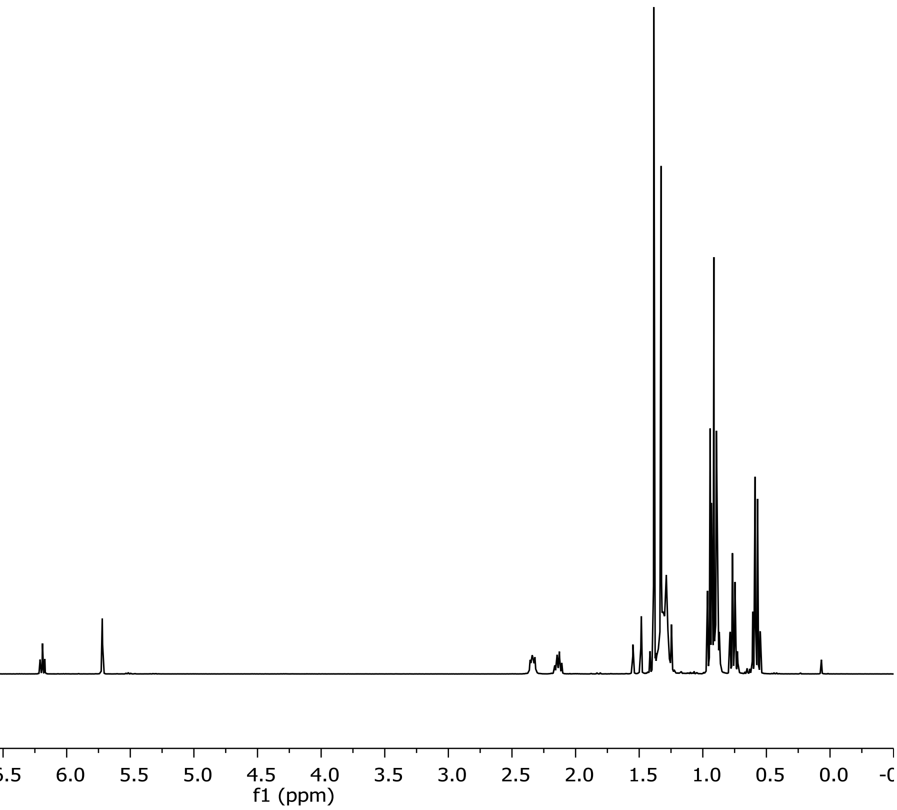

OH
H
SiEt3

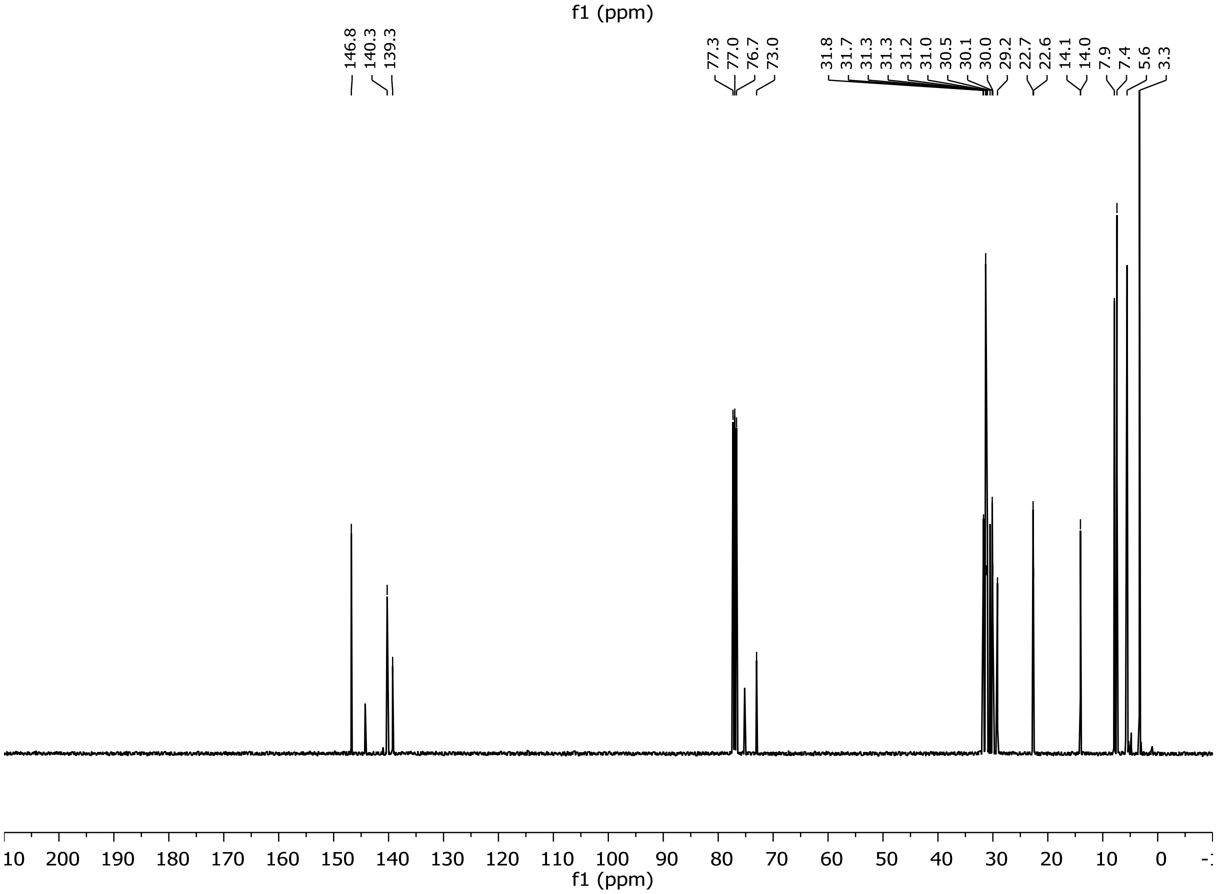

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

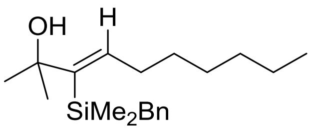

144.2
140.3
77.3
77.0
76.7
75.2
31.8
31.3
31.2
30.0
29.2
22.6
14.1
7.9
5.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

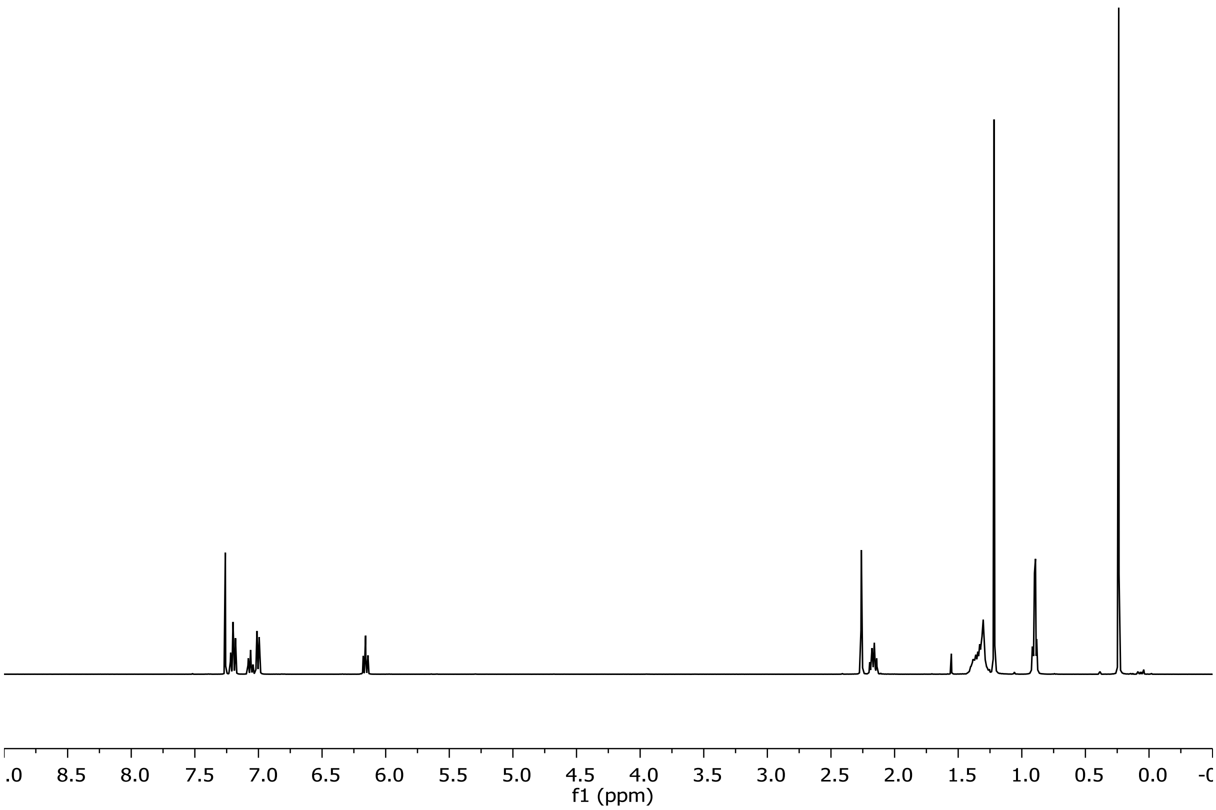


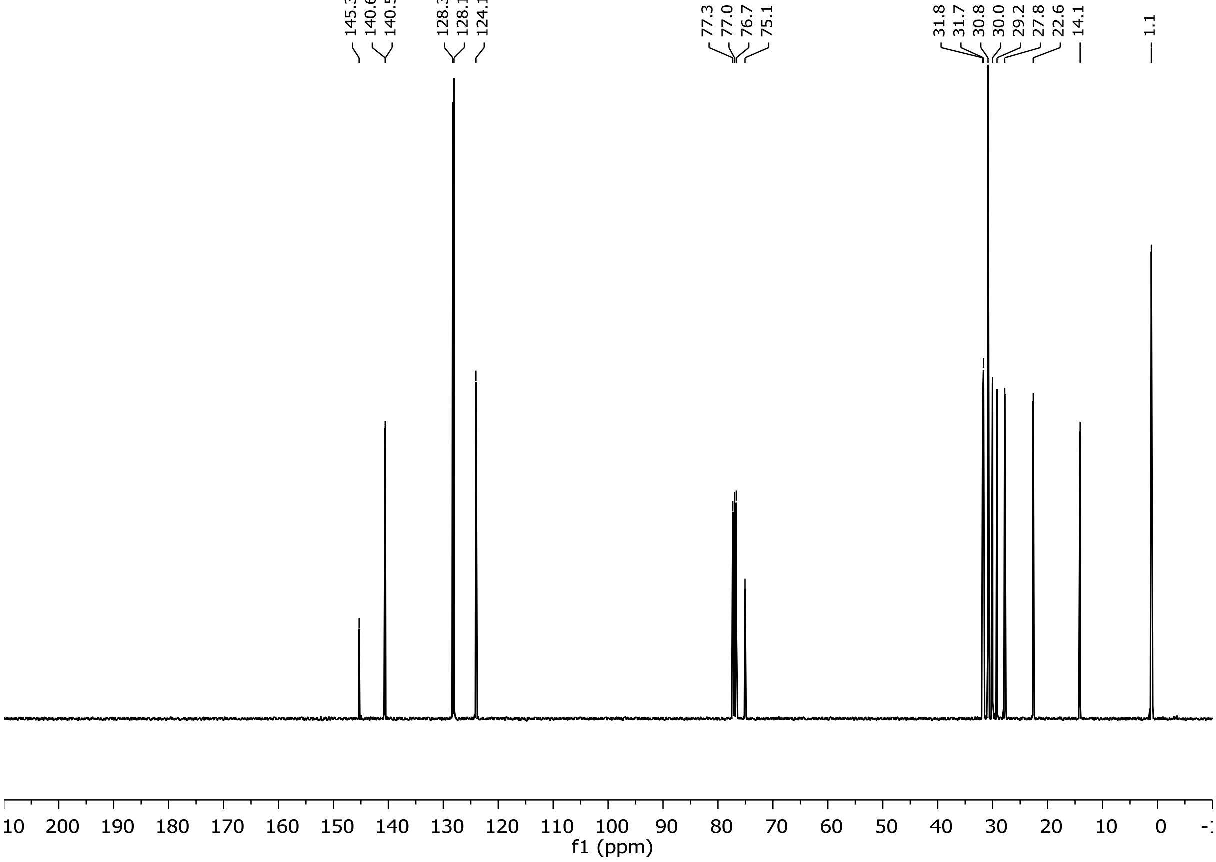

**mixture of regioisomers**




OH
H
SiMe2Bn


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.5
128.3
128.1
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77.3
77.0
76.7
75.1
31.8
31.7
30.8
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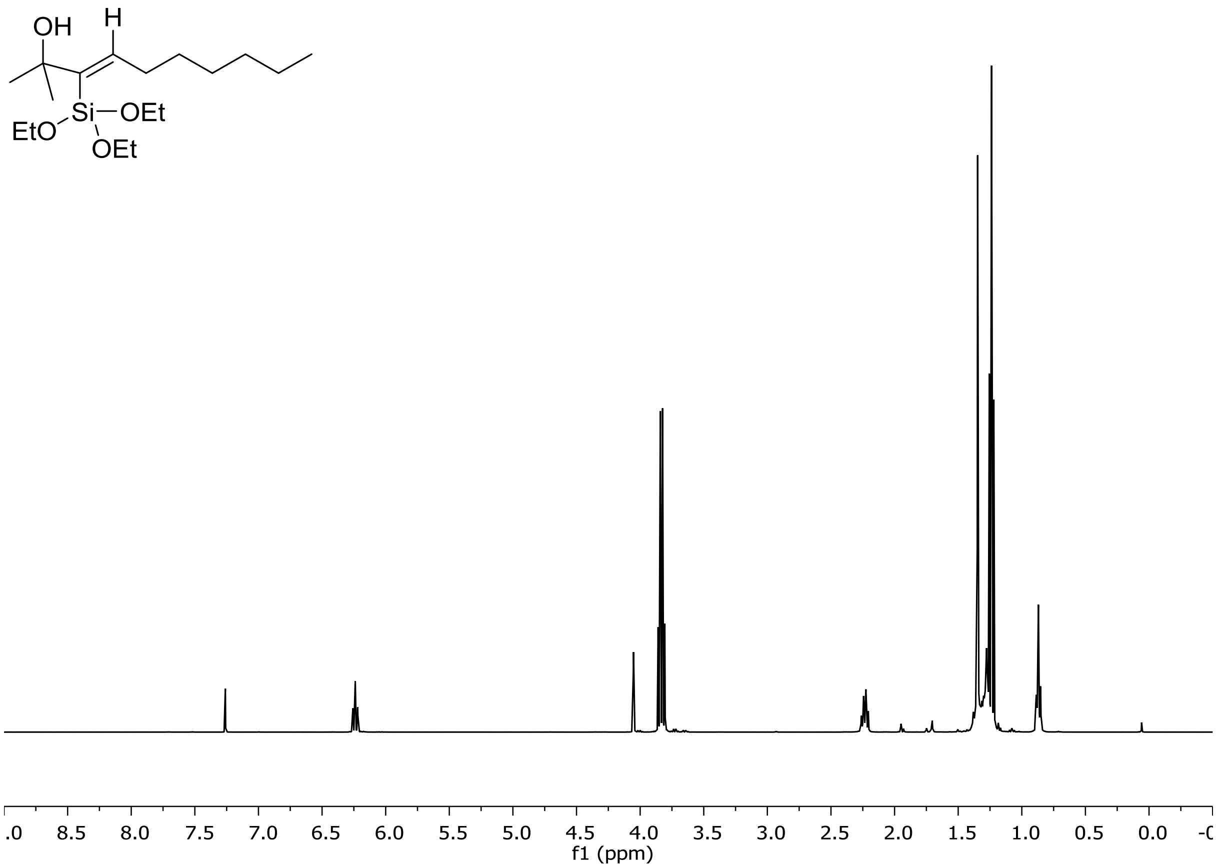
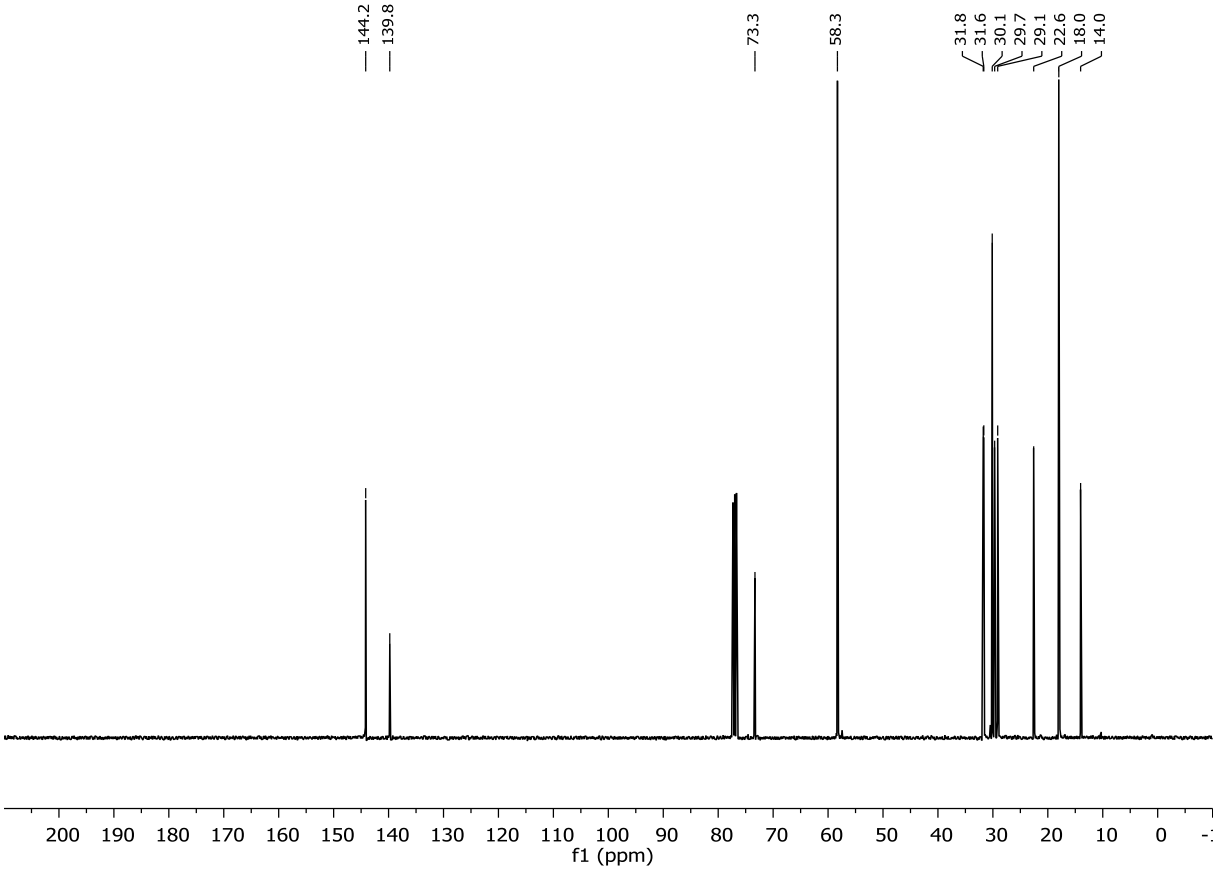
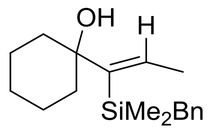
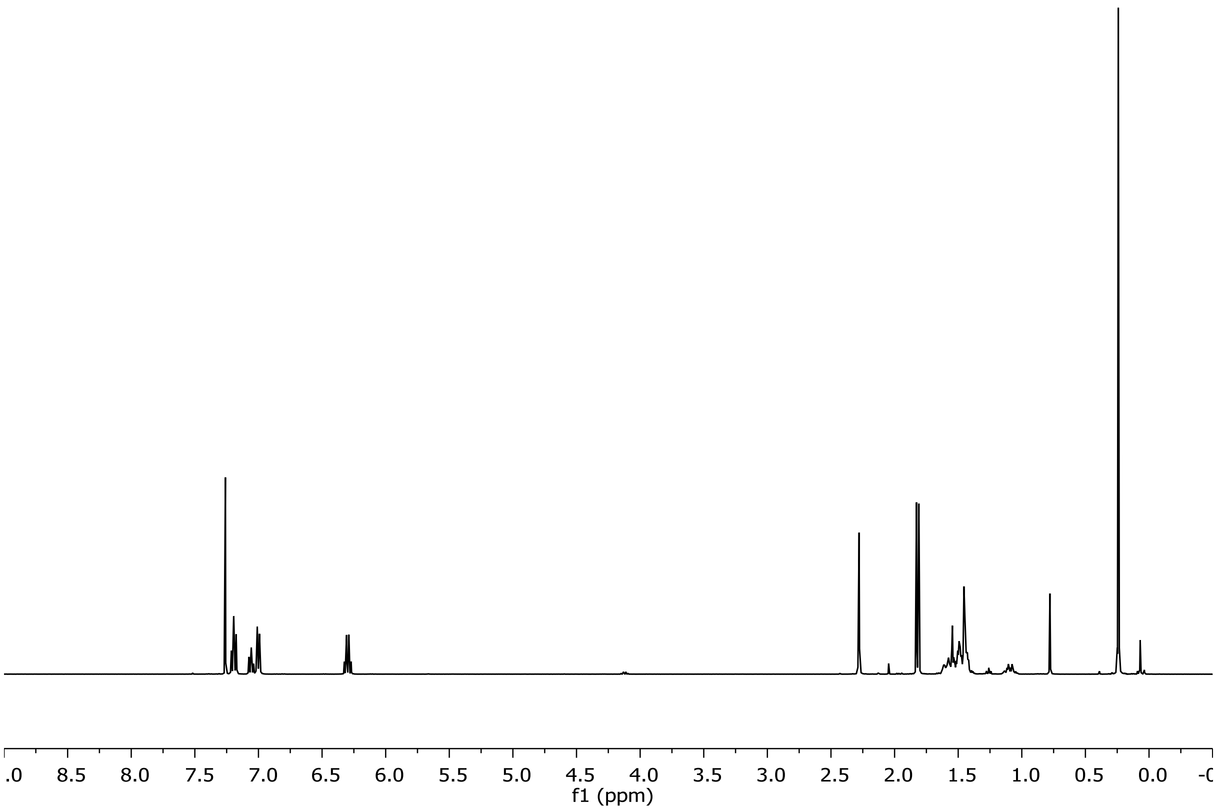
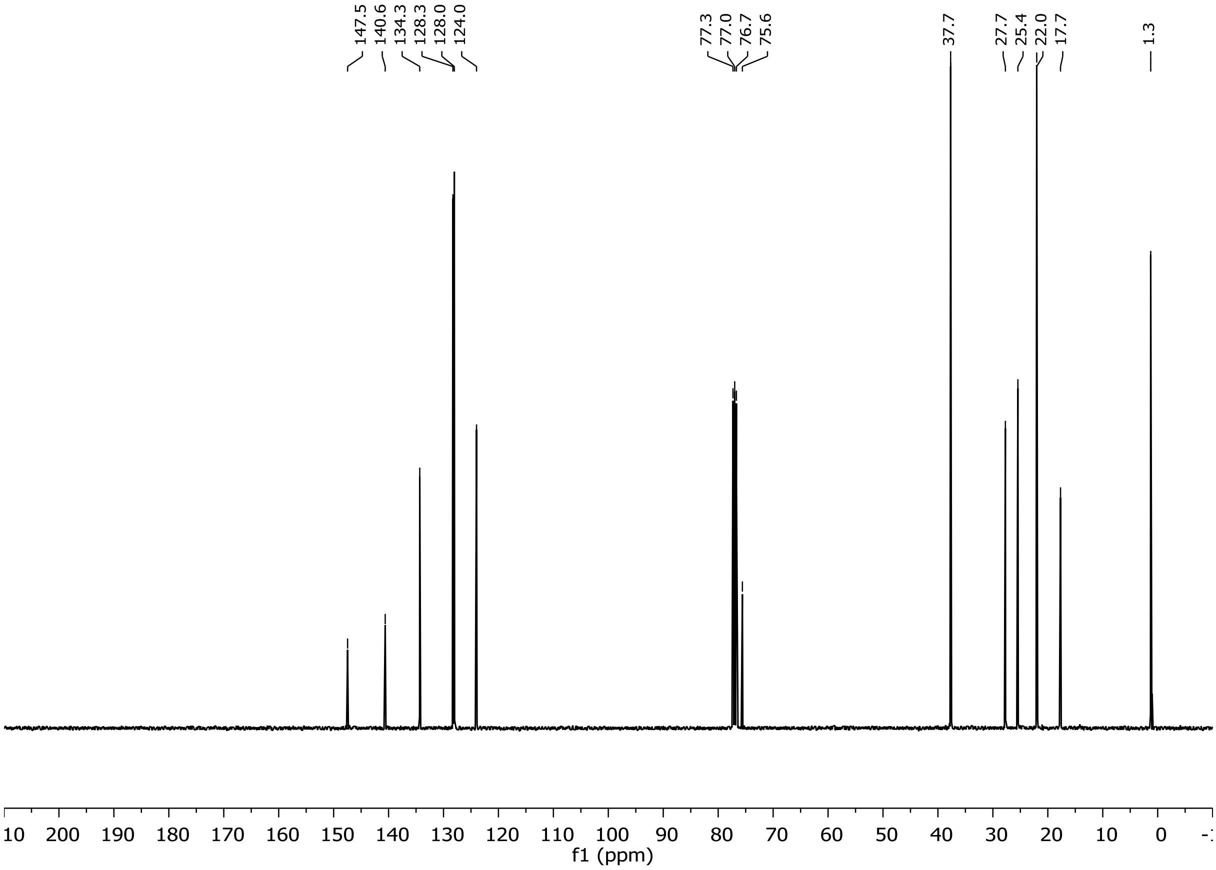
27.8
22.6
14.1
1.1
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

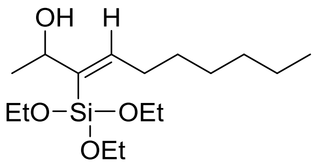

OH
H
Si
OEt
EtO
OEt
f1 (ppm)

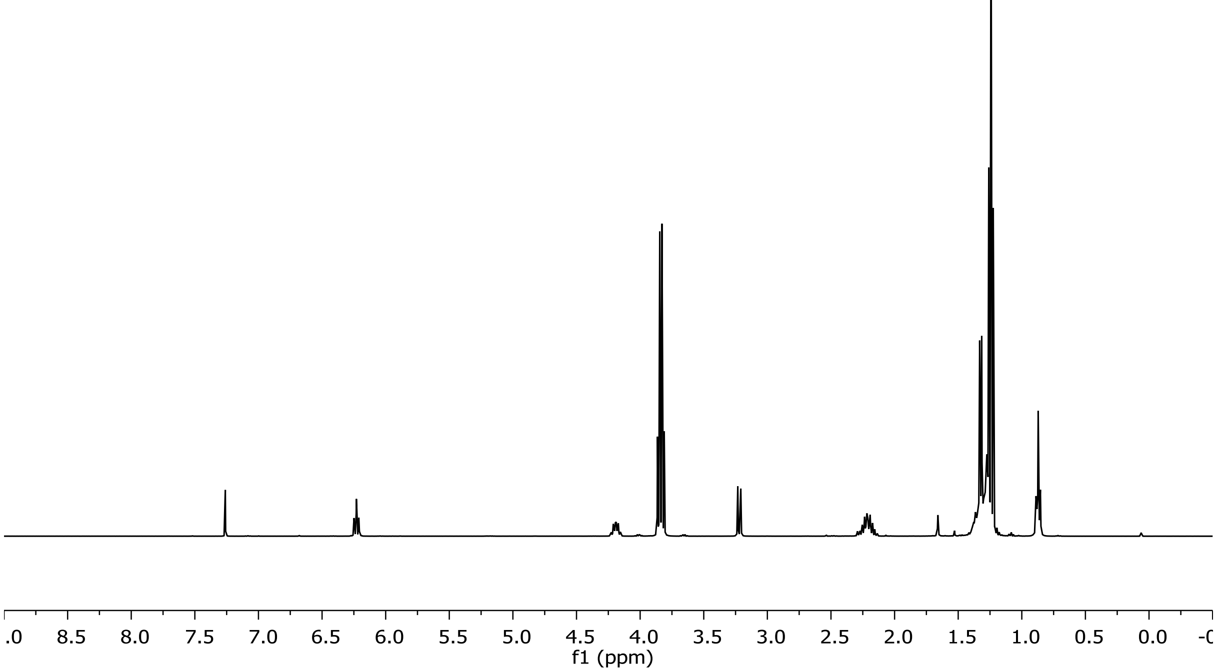

144.2
139.8
73.3
58.3
31.8
31.6
30.1
29.7
29.1
22.6
18.0
14.0
f1 (ppm)

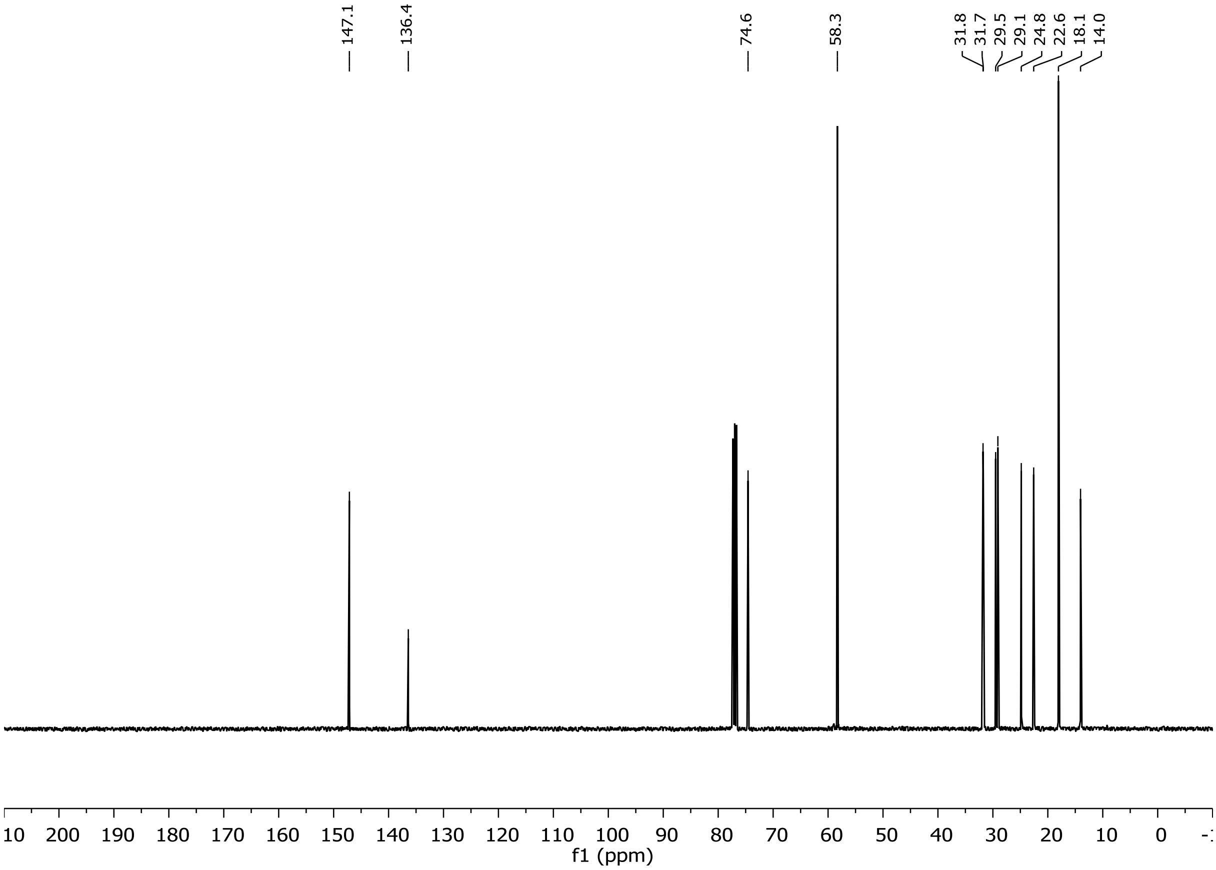

OH
H
SiMe$_2$Bn


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.5
140.6
134.3
128.3
128.0
124.0
77.3
77.0
76.7
75.6
37.7
27.7
25.4
22.0
17.7
1.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
H
EtO
Si
OEt
OEt


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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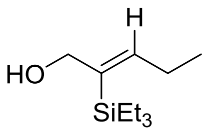
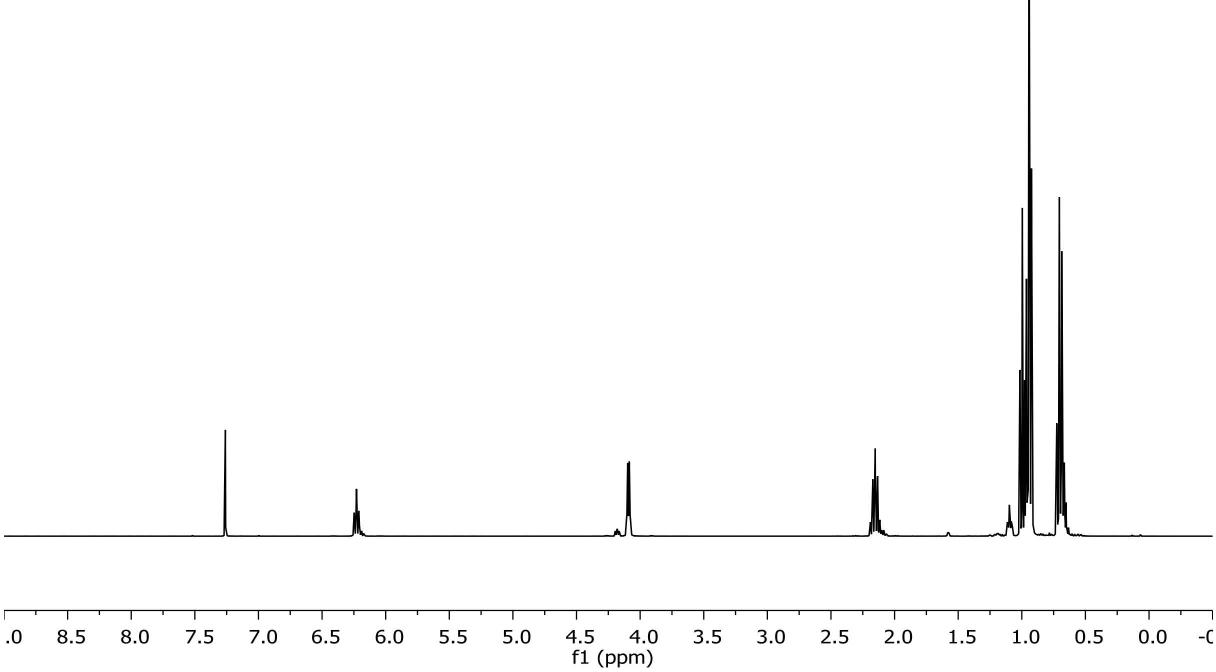
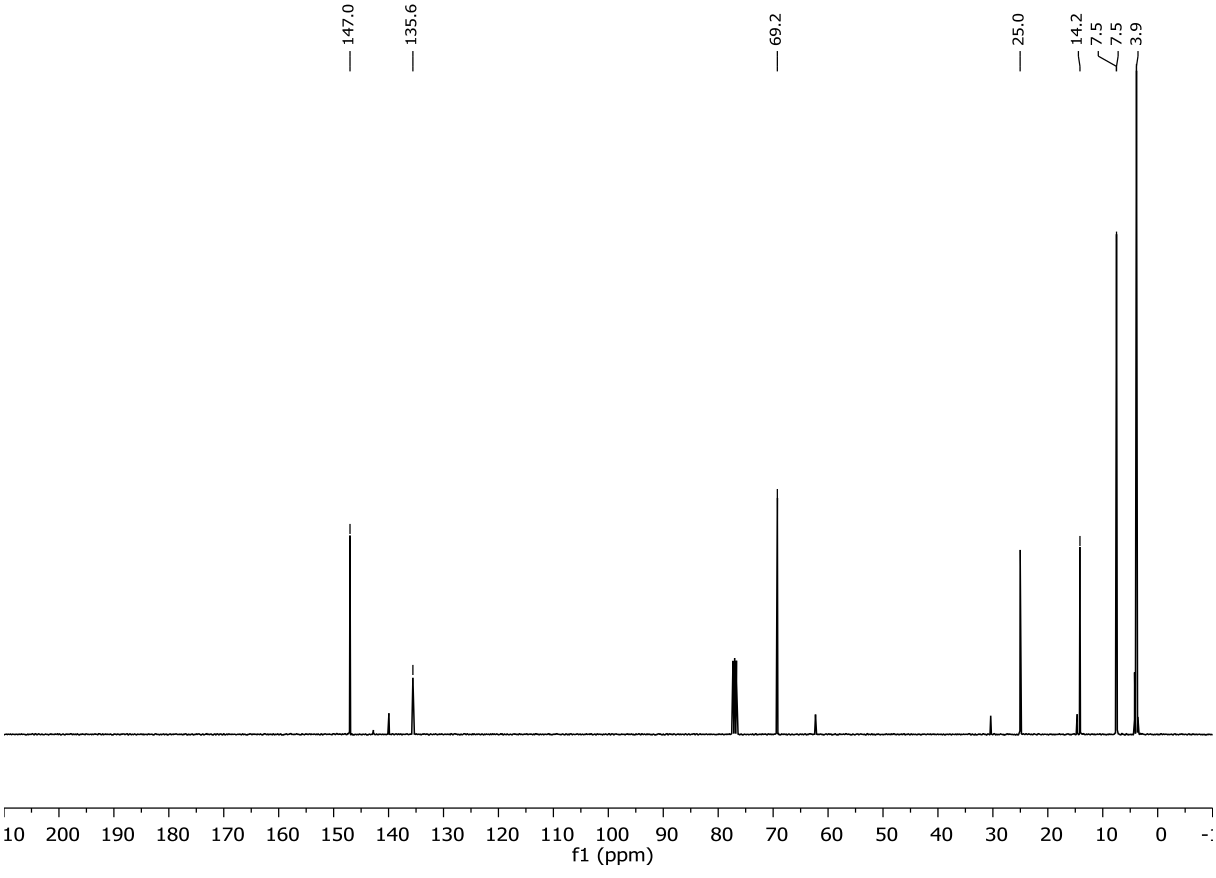
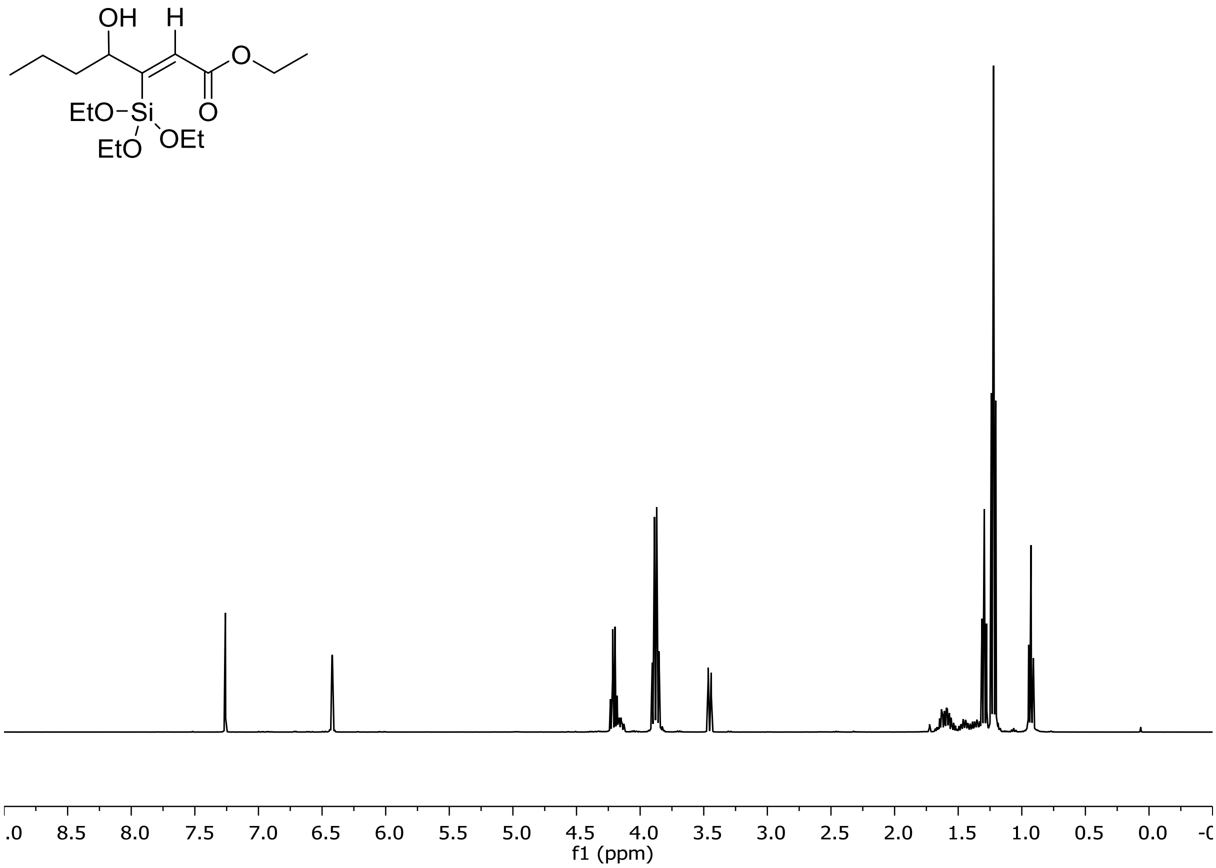
136.4
74.6
58.3
31.8
31.7
29.5
29.1
24.8
22.6
18.1
14.0
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

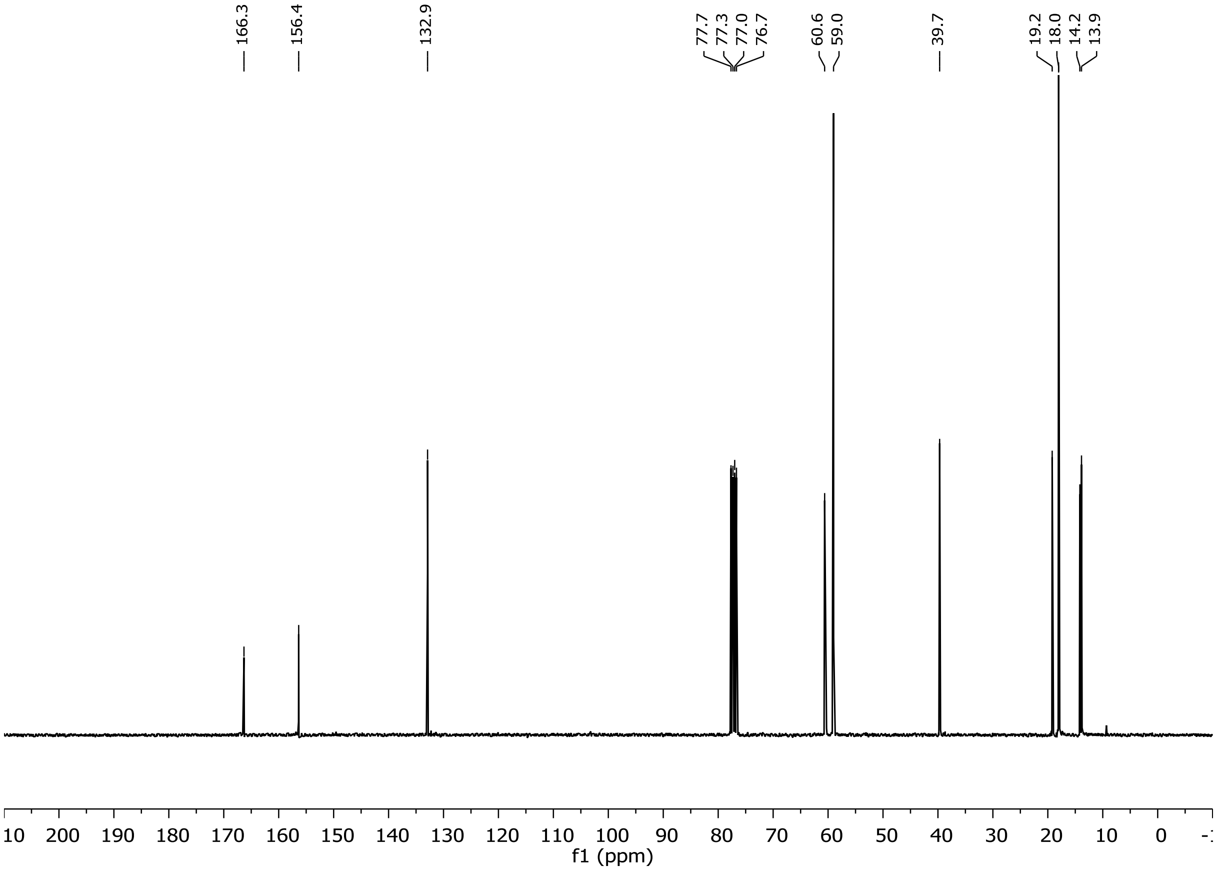


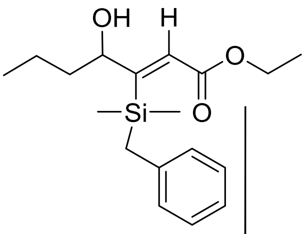

**mixture of regioisomers**

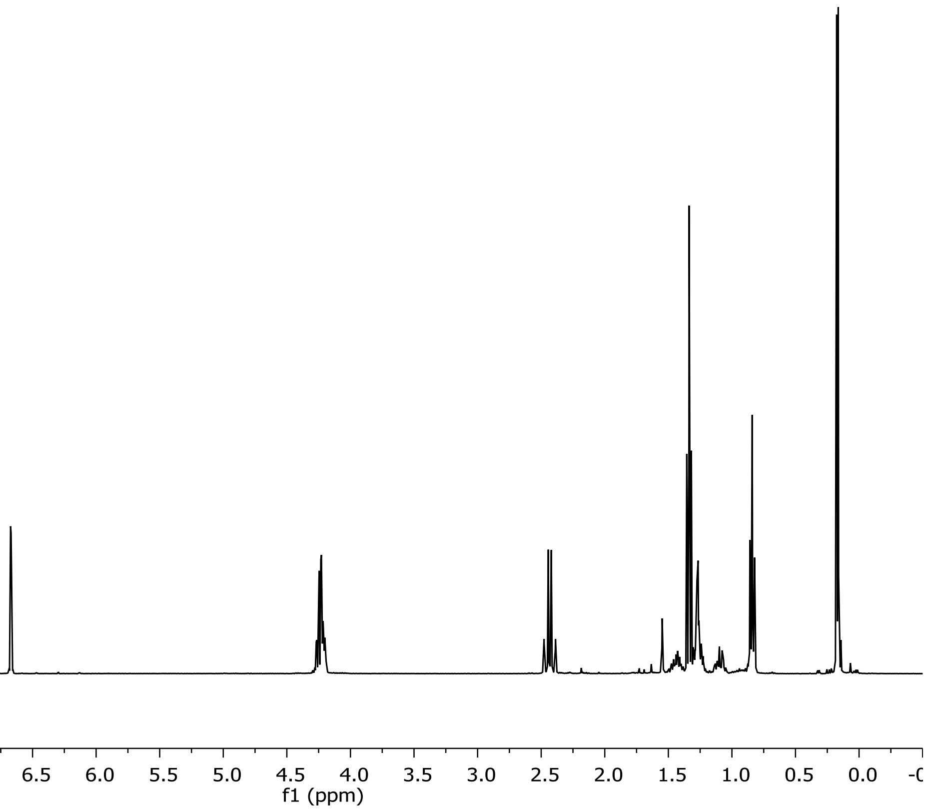


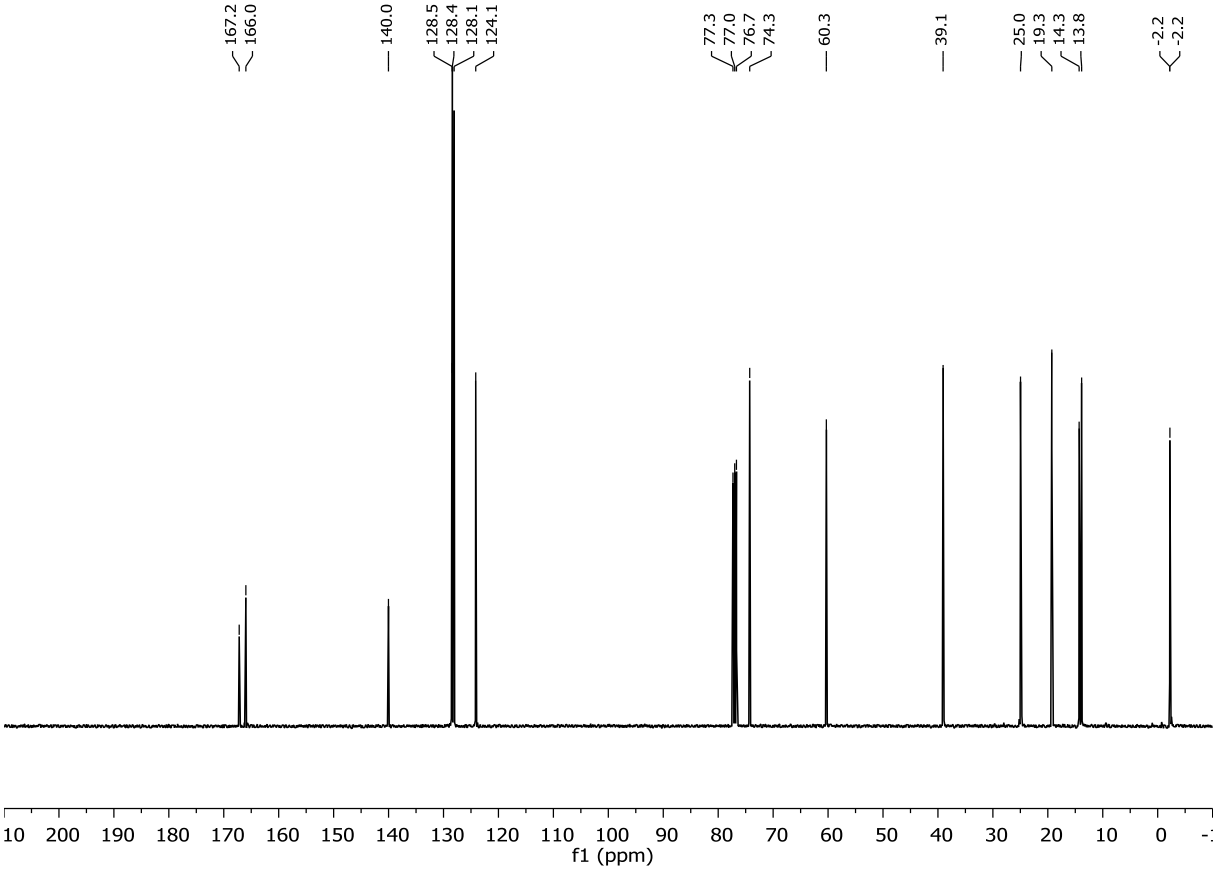



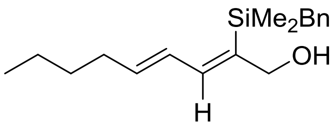

OH
H
O
O
EtO−Si
OEt
EtO
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)


166.3
156.4
132.9
77.7
77.3
77.0
76.7
60.6
59.0
39.7
19.2
18.0
14.2
13.9
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -:
f1 (ppm)

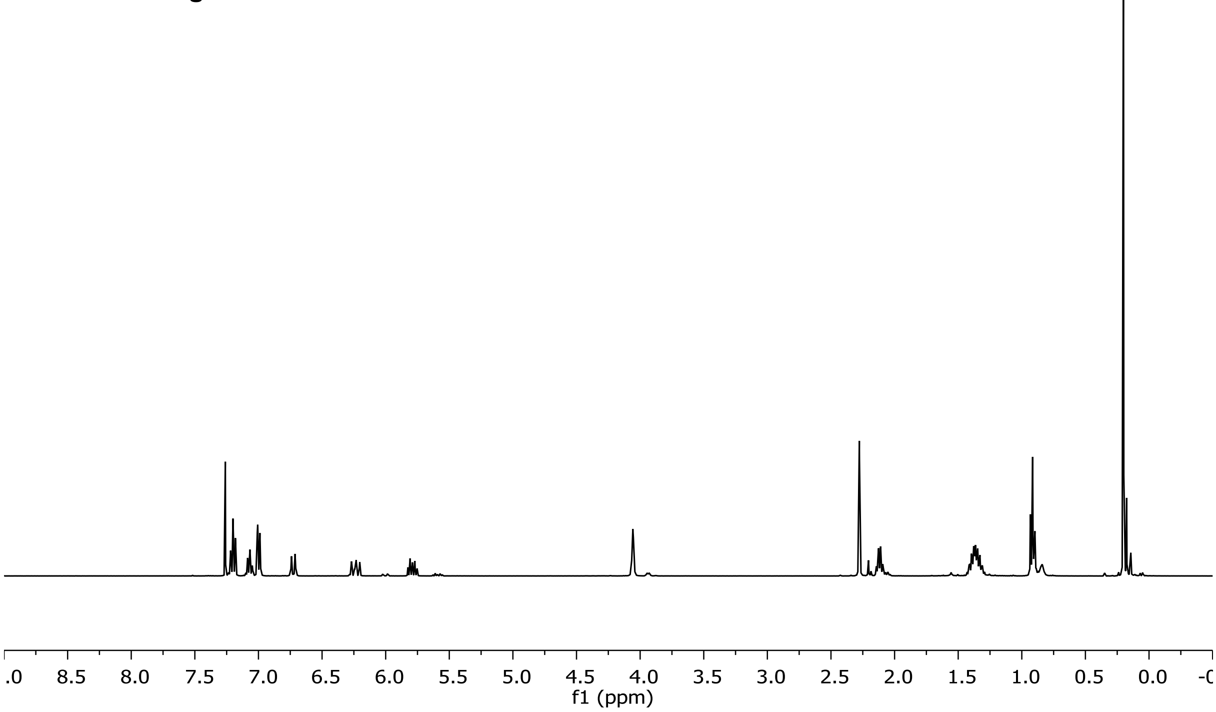

OH
H
O
Si
O

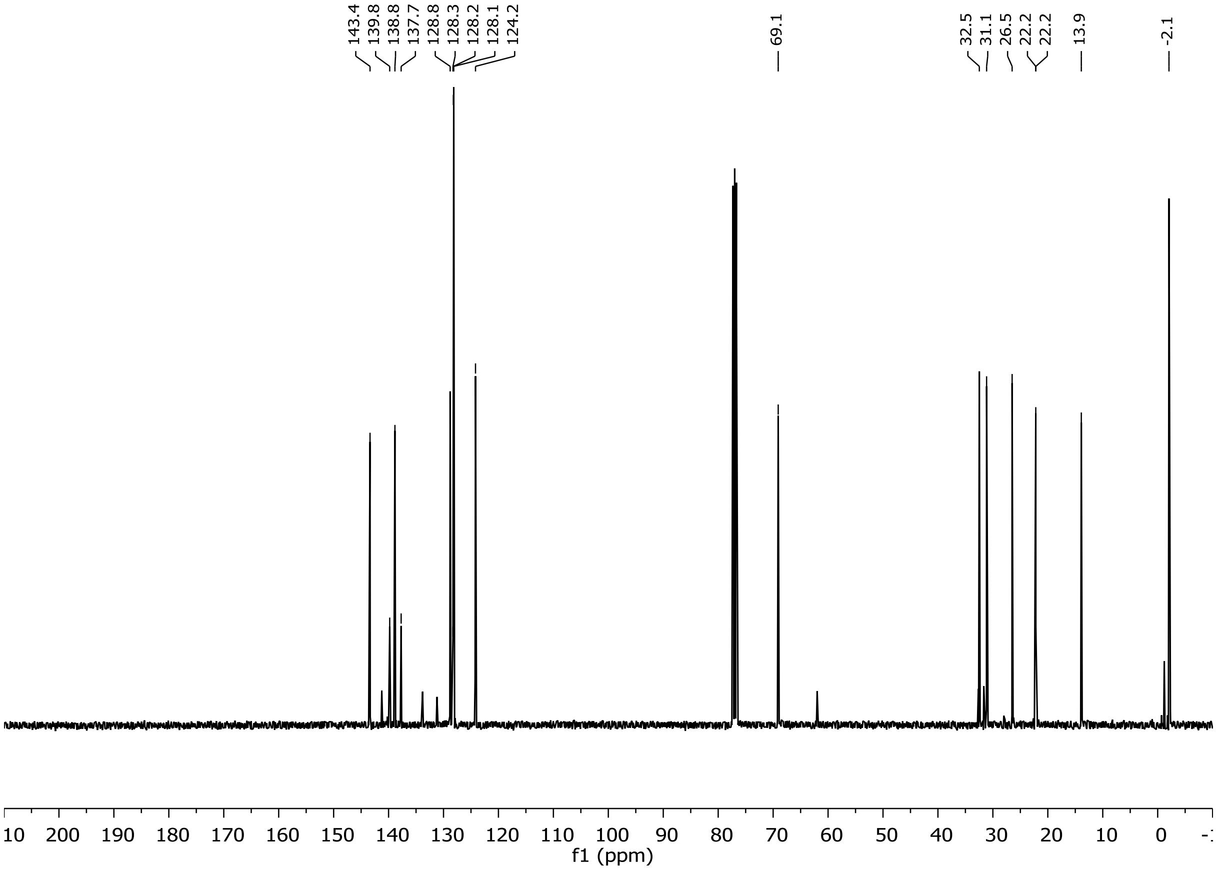

.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

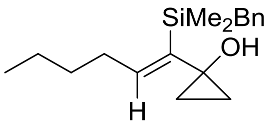

167.2
166.0
140.0
128.5
128.4
128.1
124.1
77.3
77.0
76.7
74.3
60.3
39.1
25.0
19.3
14.3
13.8
-2.2
-2.2
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

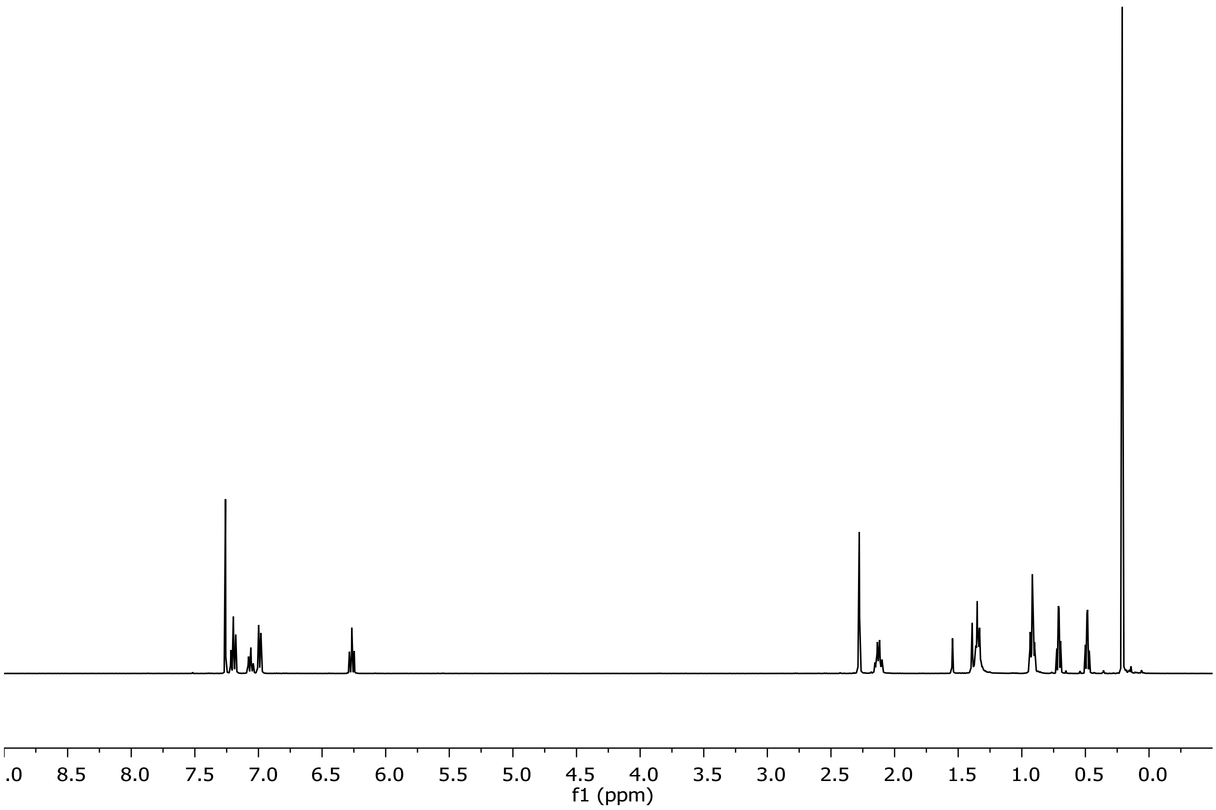


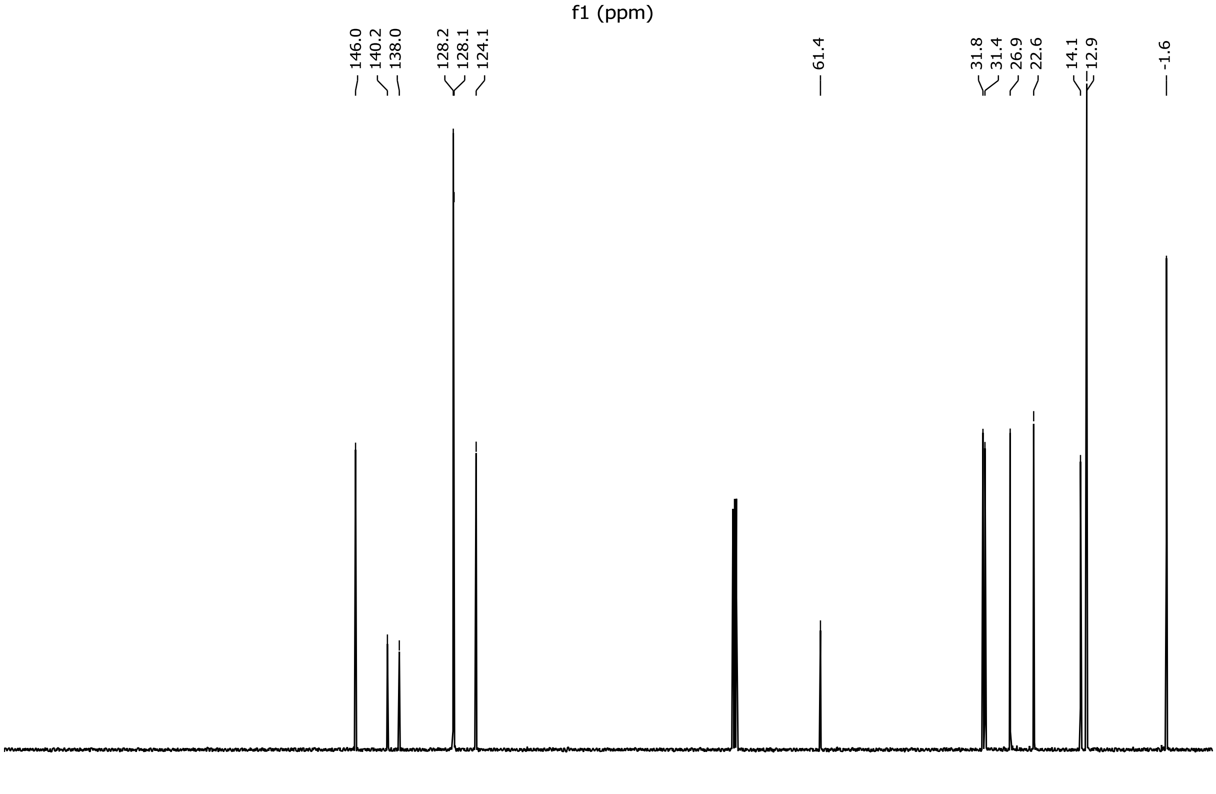

**mixture of regioisomers**

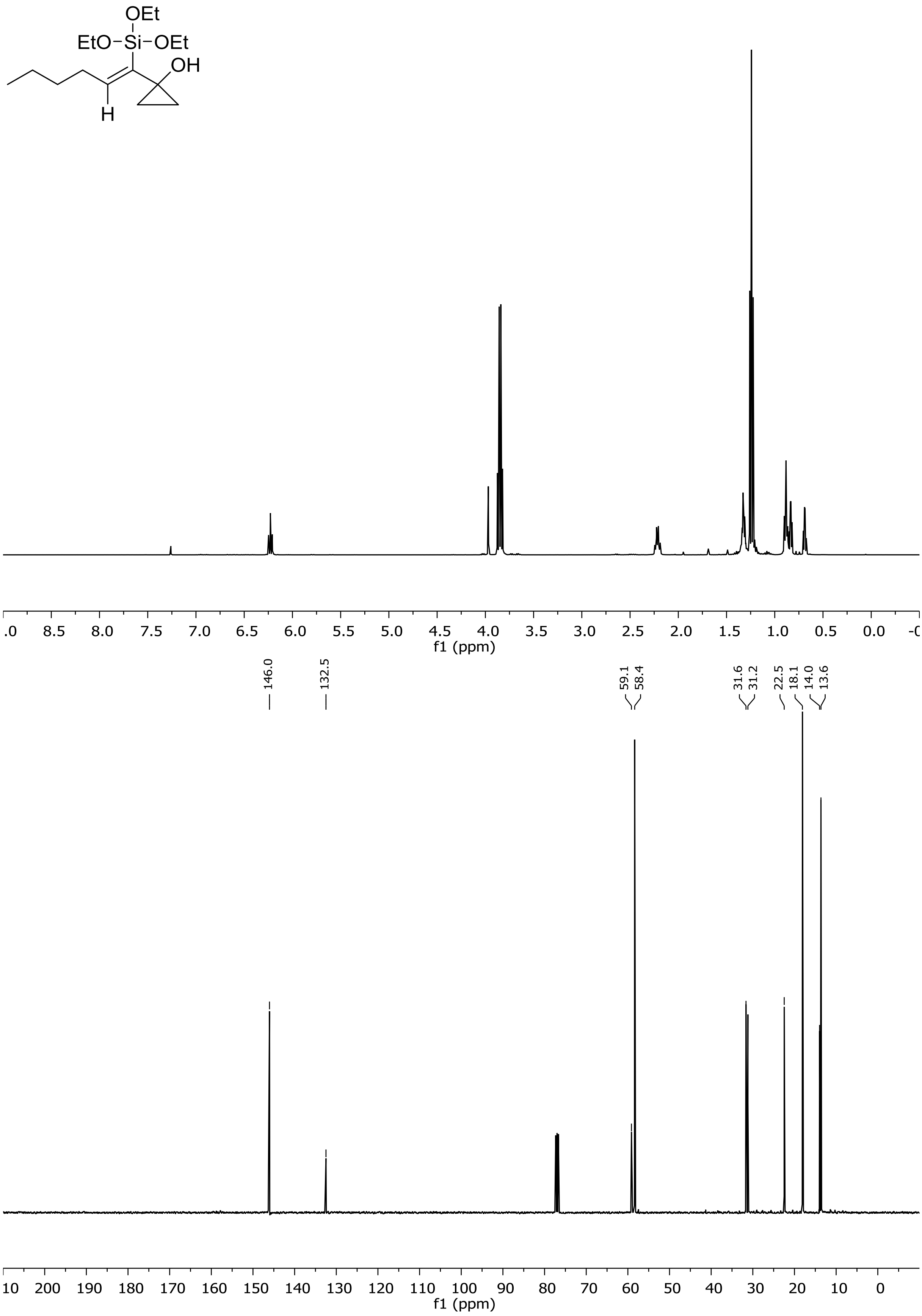


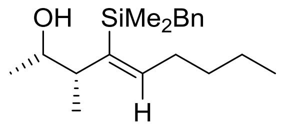

SiMe2Bn
OH
H


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

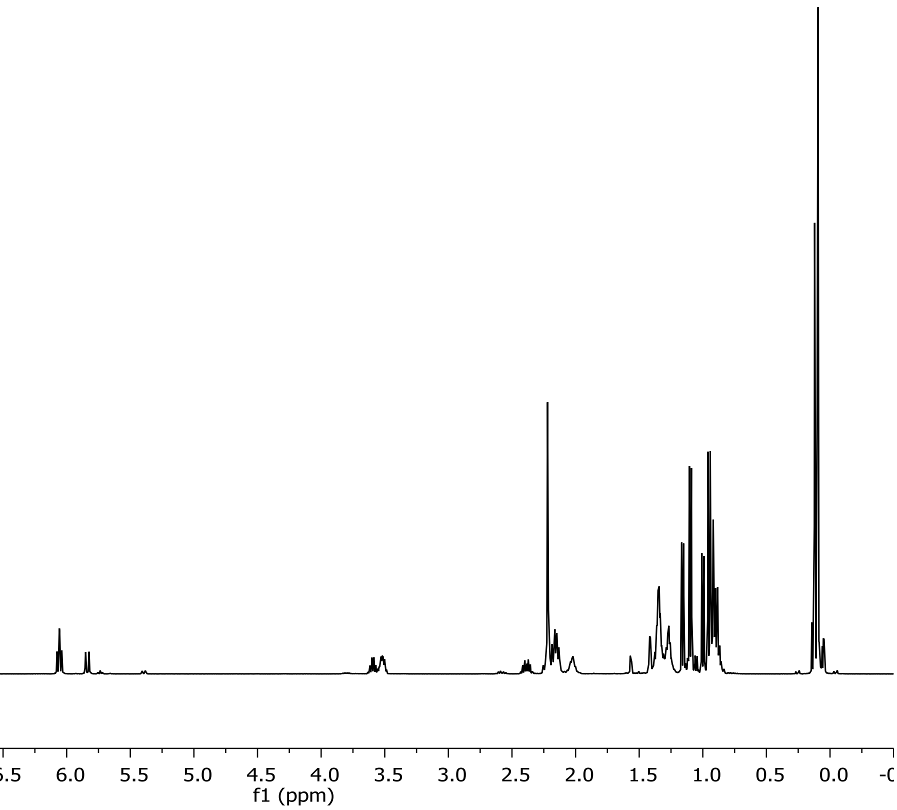

146.0
140.2
138.0
128.2
128.1
124.1
61.4
31.8
31.4
26.9
22.6
14.1
12.9
-1.6
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

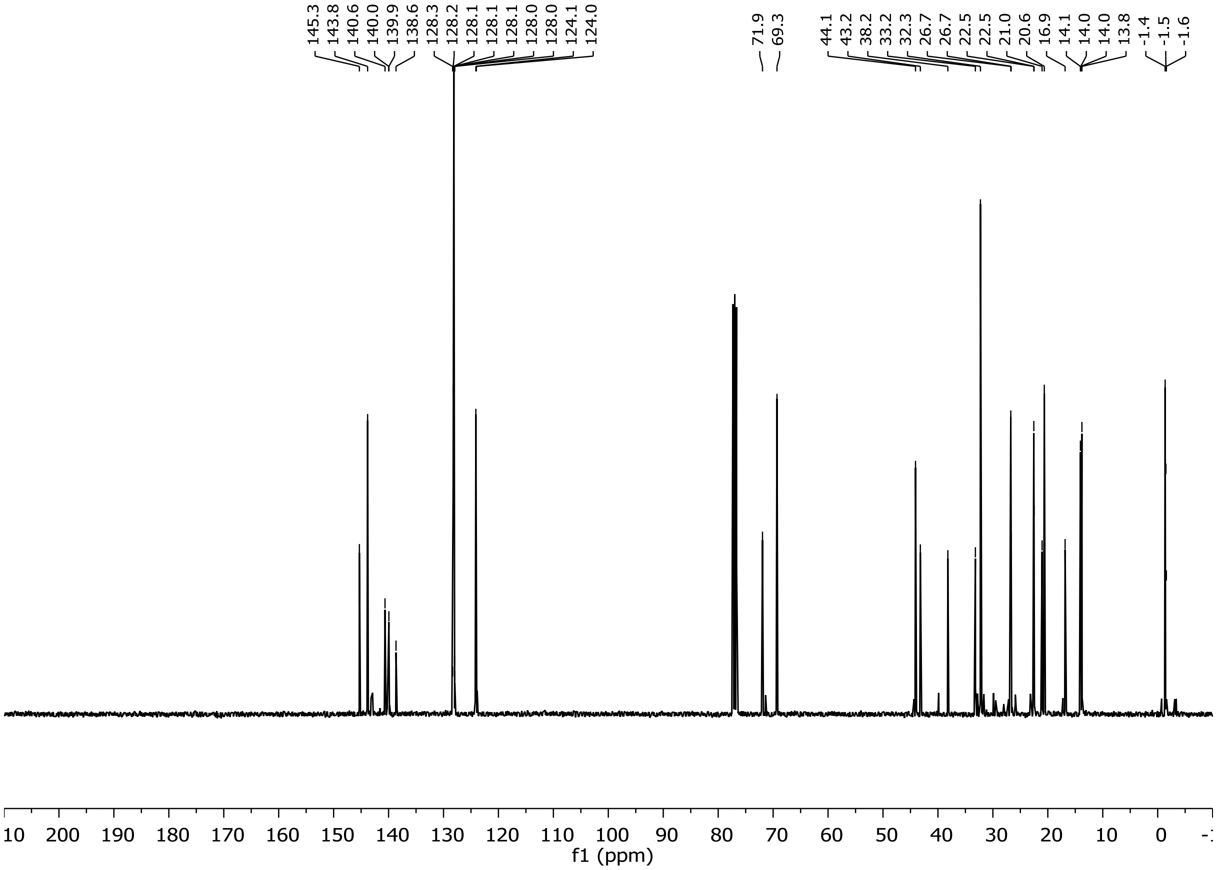


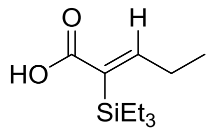
OEt
EtO–Si–OEt
OH
H
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)
146.0
132.5
59.1
58.4
31.6
31.2
22.5
18.1
14.0
13.6
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



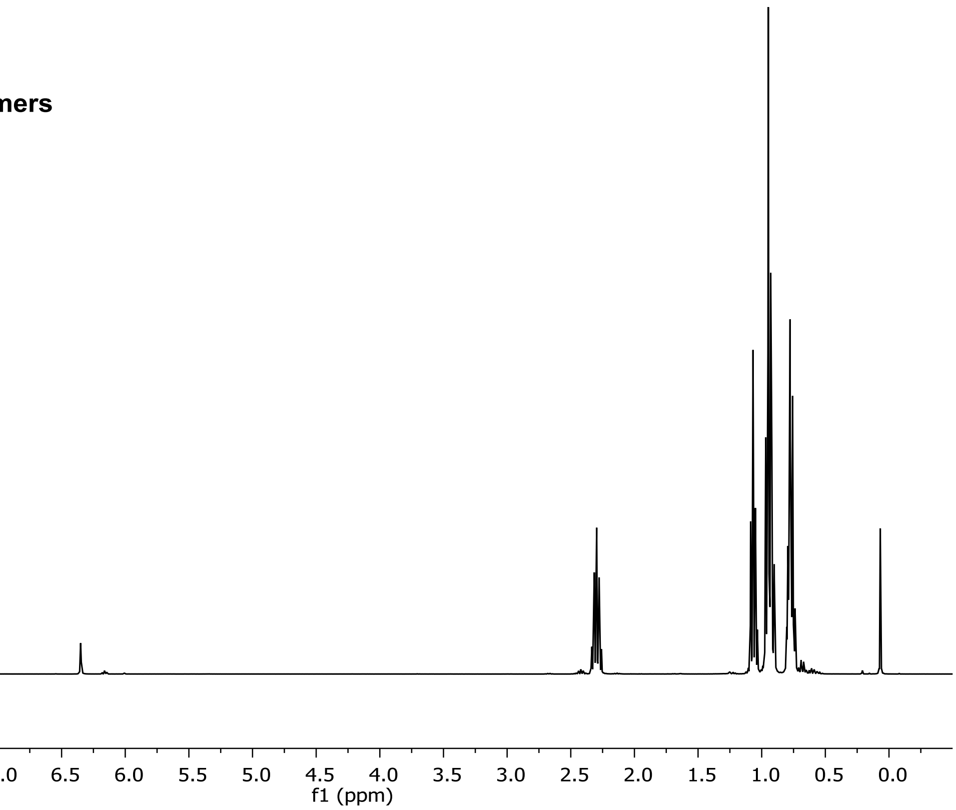

**mixture of regioisomers**

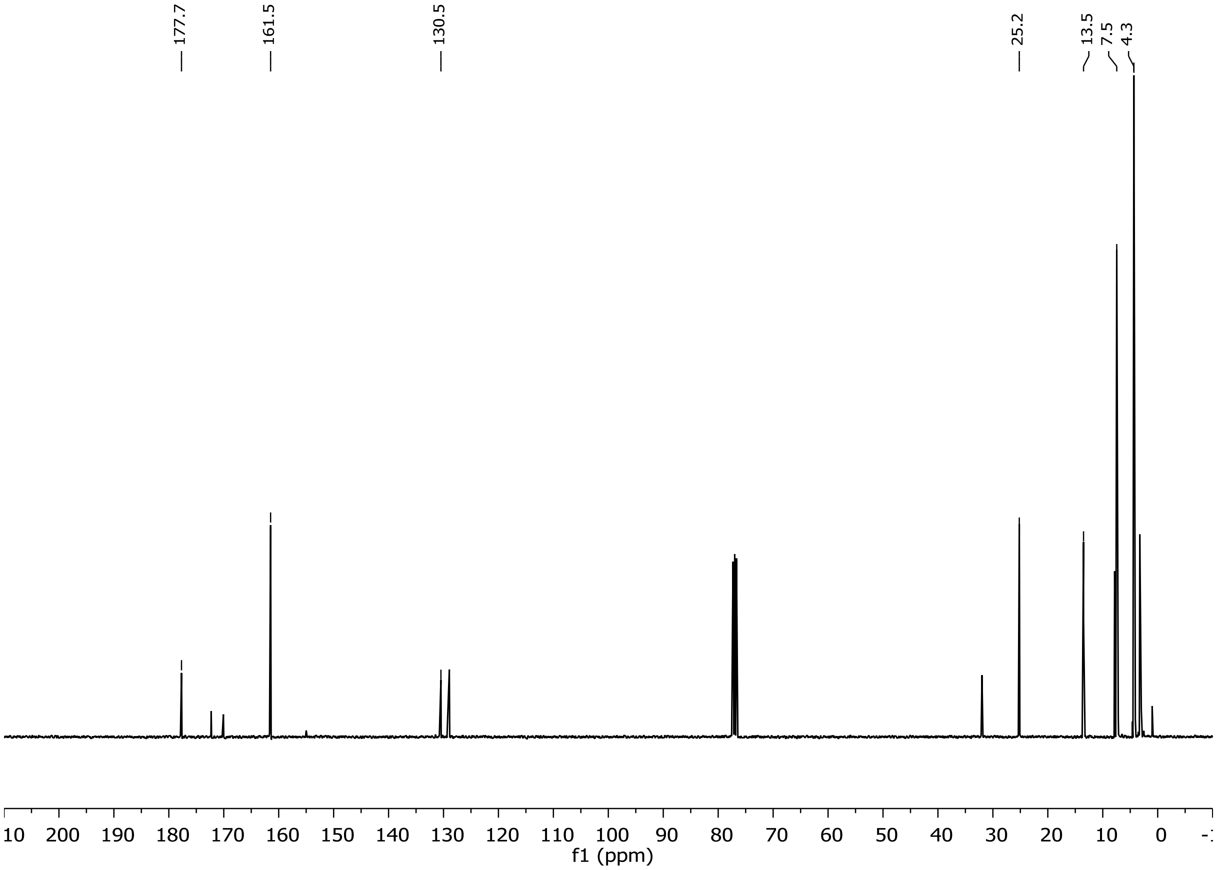


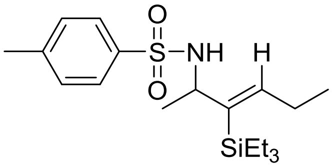





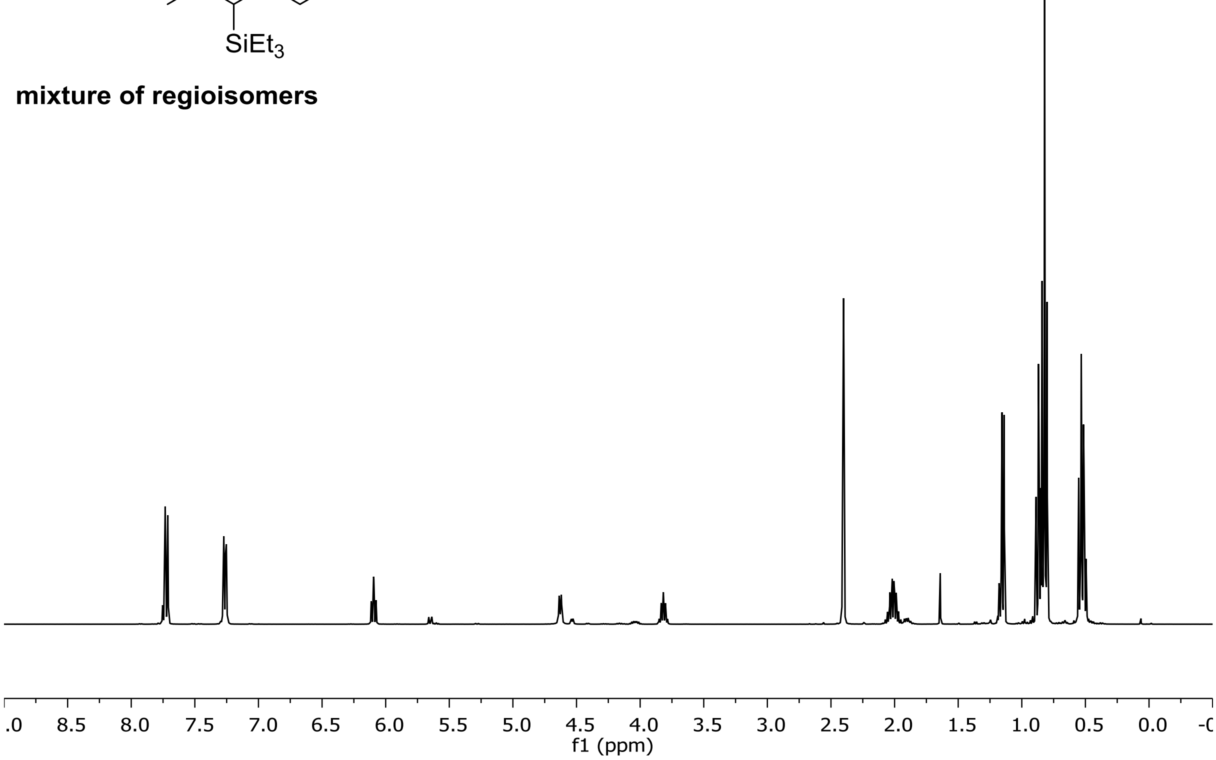

**mixture of regioisomers**

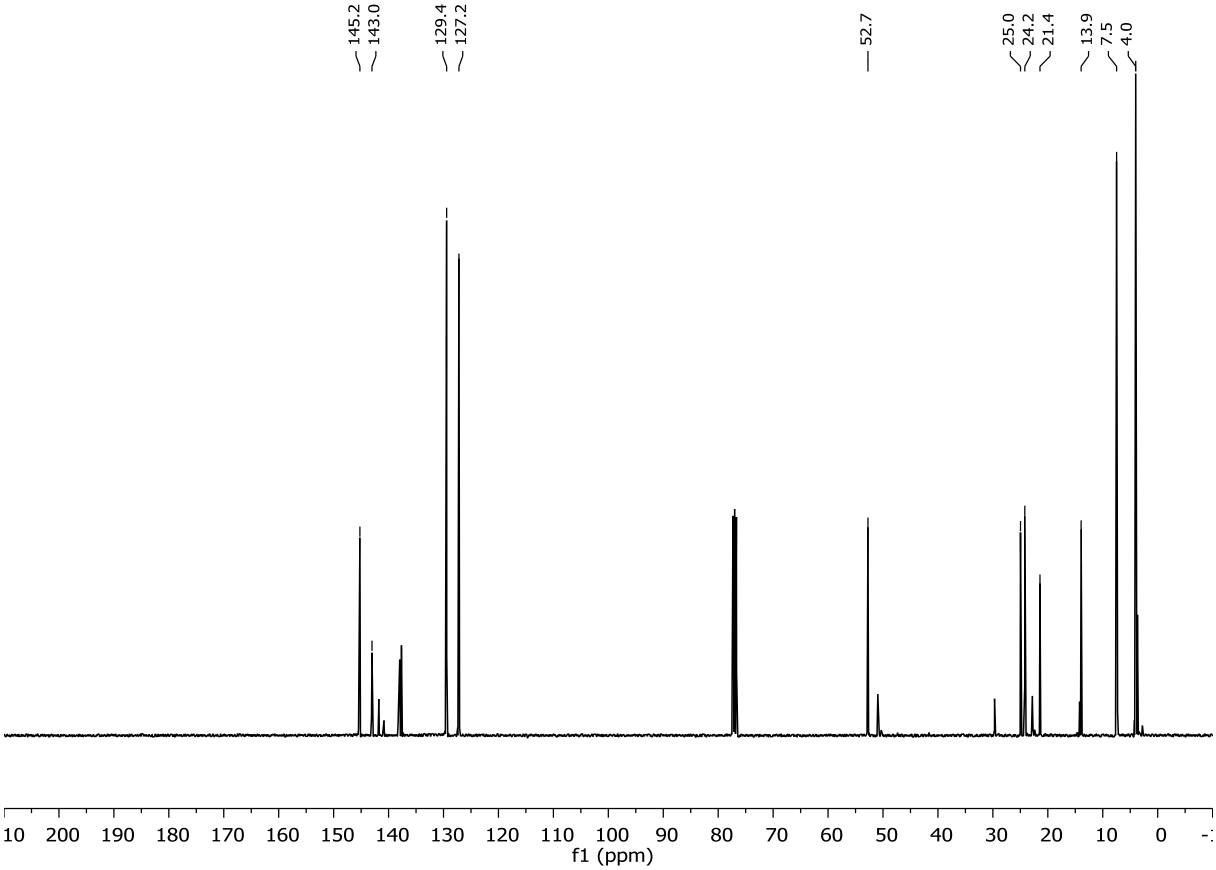


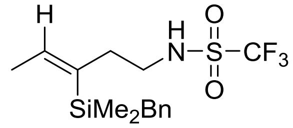





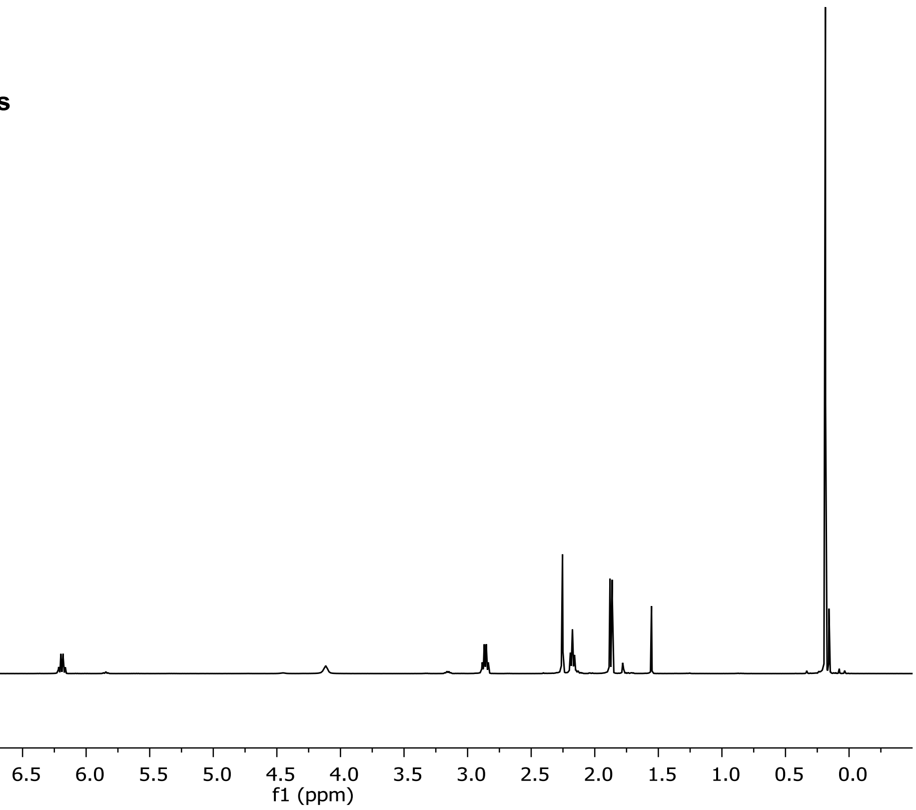

**mixture of regioisomers**

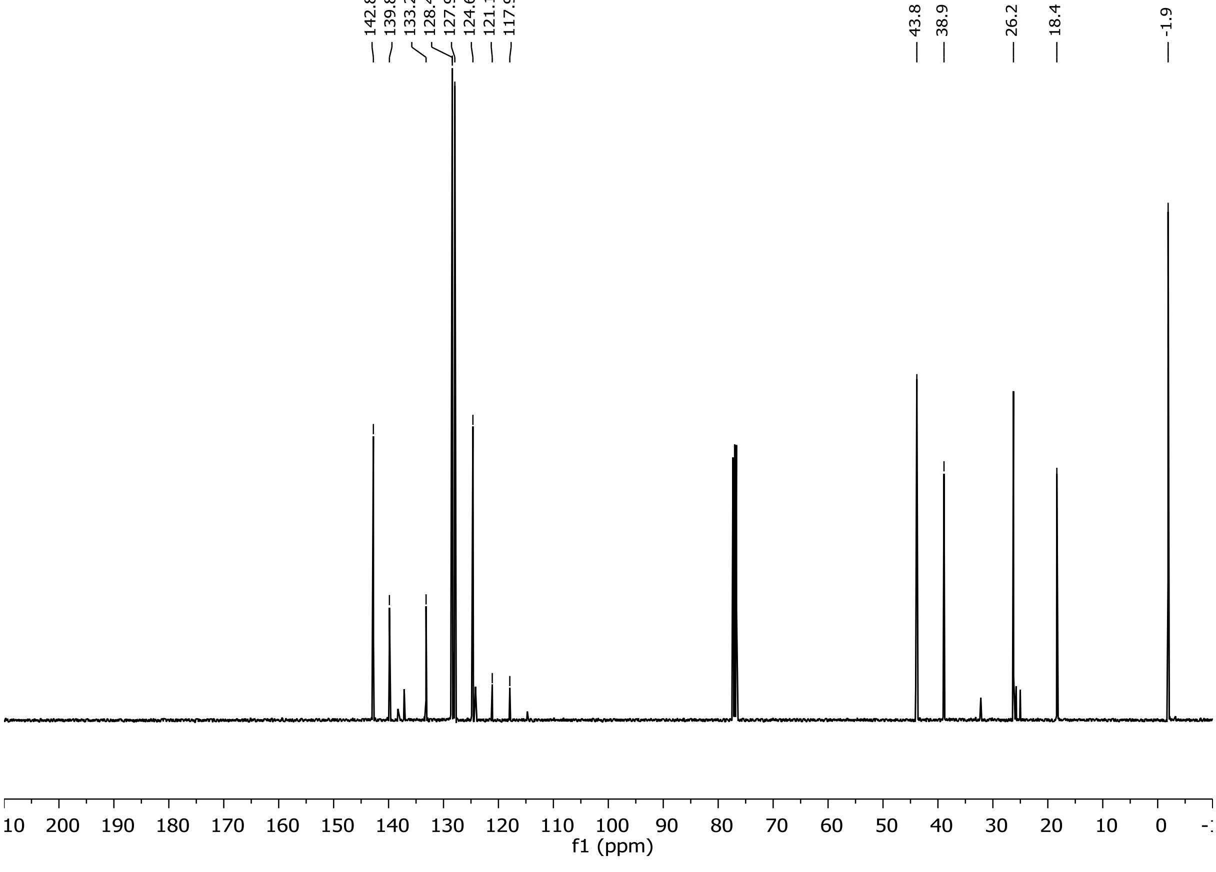


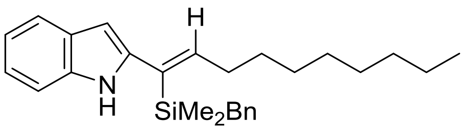



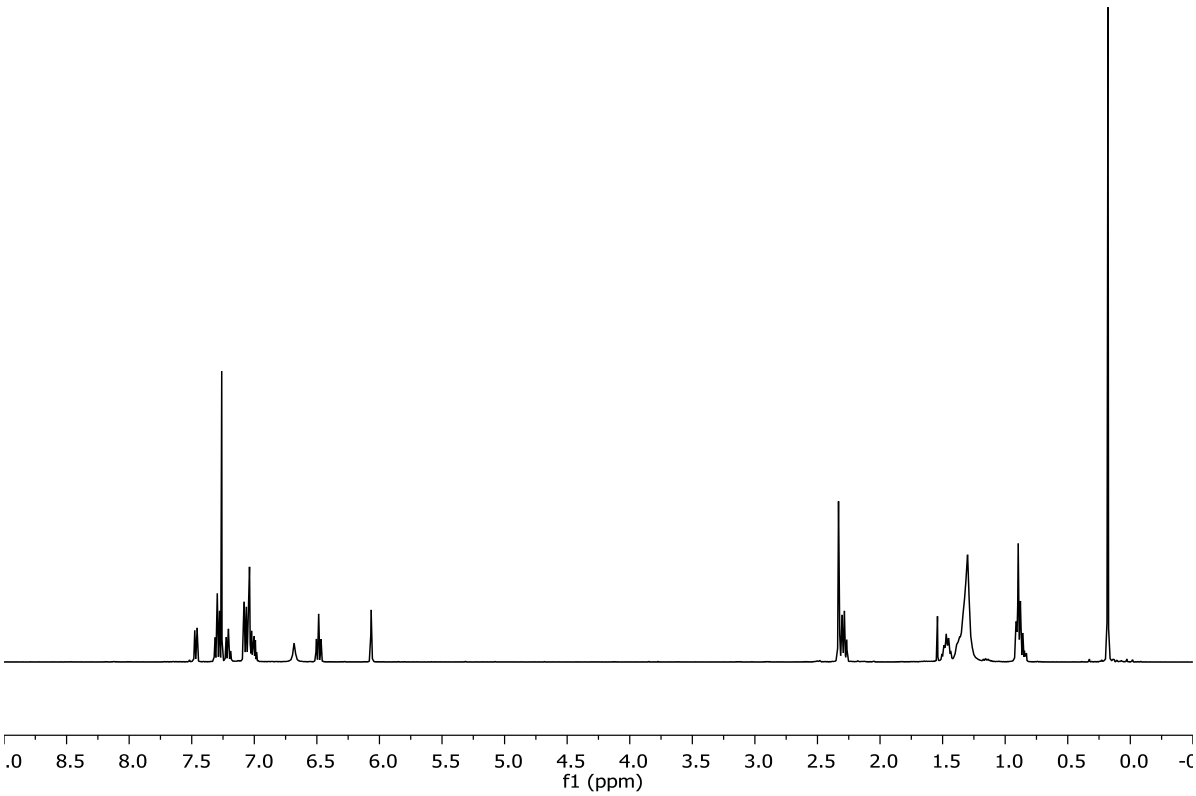


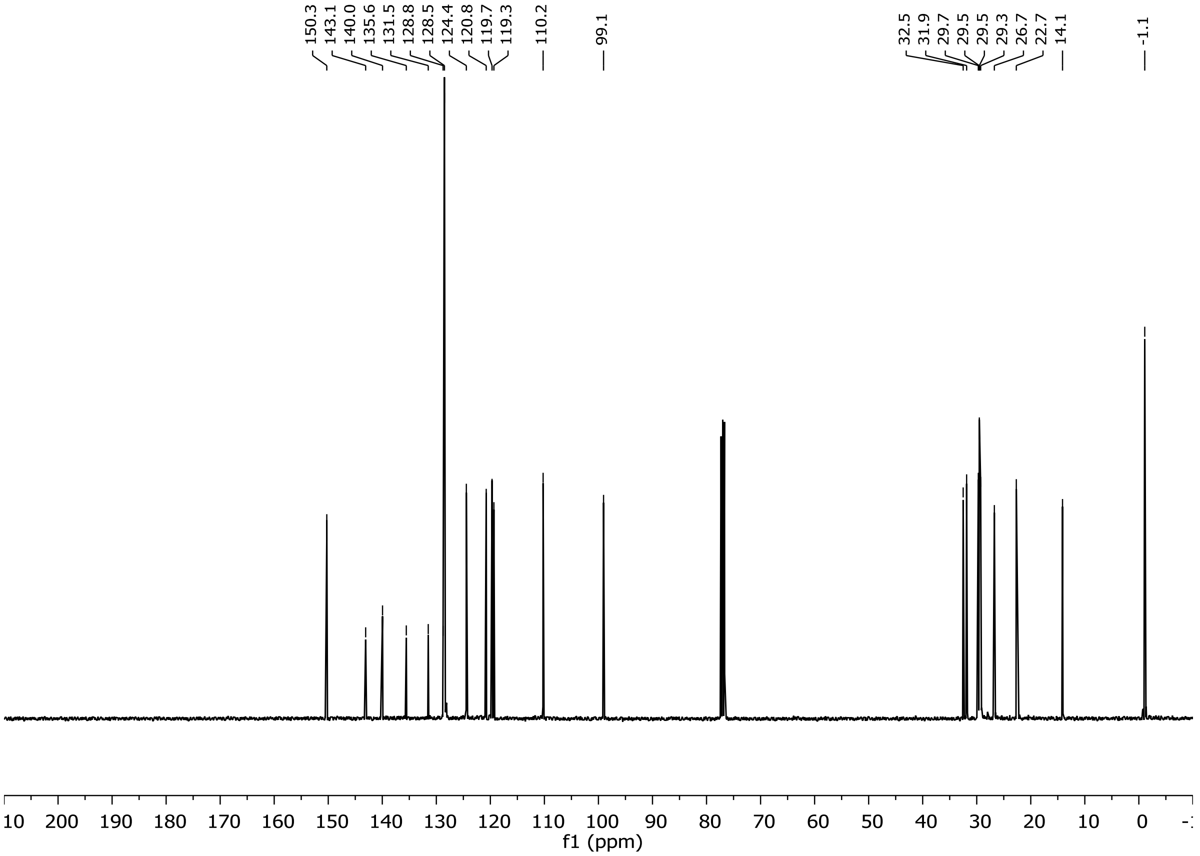

**mixture of regioisomers**




H
N
H
SiMe2Bn


.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.3
143.1
140.0
135.6
131.5
128.8
128.5
124.4
120.8
119.7
119.3
110.2
99.1
32.5
31.9
29.7
29.5
29.5
29.3
26.7
22.7
14.1
-1.1
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

## REFERENCES


1 For the related complex [CpRuI(cod)], see: Perekalin, D. S.; Karslyan, E. E.; Trifanova, E. A.; Konovalov, A. I.; Loskutova, N. L.; Nelyubina, Y. V.; Kudinov, A. R. *Eur. J. Inorg. Chem*. **2013**, 481-493.

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3 Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274–278.

4 Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111,* 1698–1719.

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6 Lipshutz, B. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 4617-4620.

7 Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843-1852.

8 The solution contained ca. 7% of free $P^iPr_3$.

9 The solution contained ca. 4% of free $P^iPr_3$.

10 The remainder still contained some product, admixed with O-silylated by-products.