

Supporting Information

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Ruthenium-Catalyzed *trans*-Selective Hydrostannation of Alkynes**

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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, Et₂O (Mg/anthracene), CH₂Cl₂, CH₃CN (CaH₂), 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 (δ) 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 (CDCl₃: δ_C = 77.16 ppm; residual CHCl₃ in CDCl₃: δ_H = 7.26 ppm; CD₂Cl₂: δ_C = 54.0 ppm; residual CHDCl₂ in CD₂Cl₂: δ_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).

¹¹⁹Sn NMR spectra were recorded on a Bruker AV VIII 300 or Bruker AV VIII 500 spectrometer using Me₄Sn as external standard.

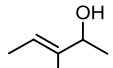
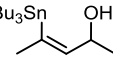
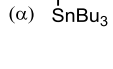
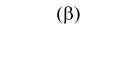
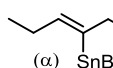
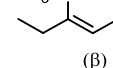
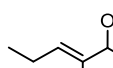
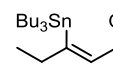
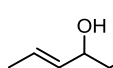
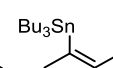
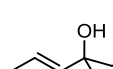
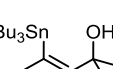
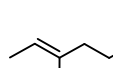
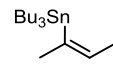
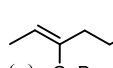
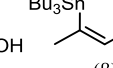
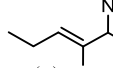
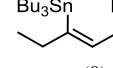
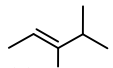
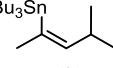
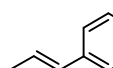
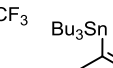
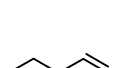
Unless stated otherwise, all commercially available compounds were used as received. [Cp*Ru(CH₃CN)₃]PF₆,¹ [(Cp*RuCl₂)_n],² and [(Cp*RuCl)₄]³ were prepared according to literature procedures and were stored under Argon. [Cp*Ru(cod)Cl] was purchased from Strem and stored under Ar. Commercial Bu₃SnH is stabilized with 0.05% of 3,5-di-*tert*-butyl-4-hydroxytoluene, which was not removed in any of the reactions described herein.

¹ M. D. Mbaye, B. Demerseman, J.-L. Renaud, L. Toupet, C. Bruneau, *Adv. Synth. Catal.* **2004**, *346*, 835-841.

² T. D. Tilley, R. H. Grubbs, J. E. Bercaw, *Organometallics* **1984**, *3*, 274-278.

³ P. J. Fagan, M. D. Ward, J. C. Calabrese, *J. Am. Chem. Soc.* **1989**, *111*, 1698-1719.

Table S1. *trans*-Hydrostannation of Unsymmetrical Alkynes (complete list)^[a]

Entry	Products	Catalyst ^[b]	$\alpha:\beta$ ^[c]	Z:E ^[c]	Yield [%]
1		3	74:26	99:1 (α)	91
2		5	97:3	99:1 (α)	73
3		6	97:3	99:1 (α)	88 ^[d]
4		7	98:2	99:1 (α)	81
5		3	60:40	99:1 (α)	quant. ^[e]
6		7	95:5	99:1 (α)	83 ^[f]
7		7	98:2	99:1 (α)	84 (R = H) ^[g]
8		7	75:25	94:6 (α)	86 (R = Ac)
9		7	97:3	99:1 (α)	77 (R = H)
10		7	98:2	99:1 (α)	72 (R = butyl)
11		7	99:1	99:1 (α)	97
12		7	81:19	95:5 (α)	81
13		7	83:17	99:1 (α)	86
14		7	99:1	99:1 (α)	90
15		3	79:21	99:1 (α)	90
16		7	84:16	99:1 (α)	68
17		3	65:35	99:1 (α)	93
18		7	55:45	99:1 (α)	78 ^[e]
19		3	50:50	91:9 (β)	77
20		7	90:10	96:4 (α)	87 ^[d,h]
21		3	40:60	99:1 (β)	90
22		7 ^[i]	6:94	95:5 (β)	71 ^[i,j]
23		7	93:7	99:1 (α)	87 ^[h,k]

^[a] unless stated otherwise, all reactions were performed on 0.1-0.2 mmol scale by adding Bu₃SnH (1.1 equiv.) over \approx 5 min to a solution of the substrate and the respective catalyst in CH₂Cl₂ (0.2 M) under Ar; ^[b] using either 5 mol% of **3** or **5**, or 1.25 mol% of **7**; ^[c] ratio is the crude product, as determined by ¹H NMR; ^[d] \geq 1 mmol scale; ^[e] conversion (¹H NMR); ^[f] 2.1 mmol scale; ^[g] small amounts of the corresponding ketone were also found; ^[h] using 1.0 eq. of Bu₃SnH; ^[i] the substrate was added over 1.5 h; ^[j] the yield refers to the pure Z-configured β -stannylated isomer obtained by flash chromatography; ^[k] 0.6 mmol scale

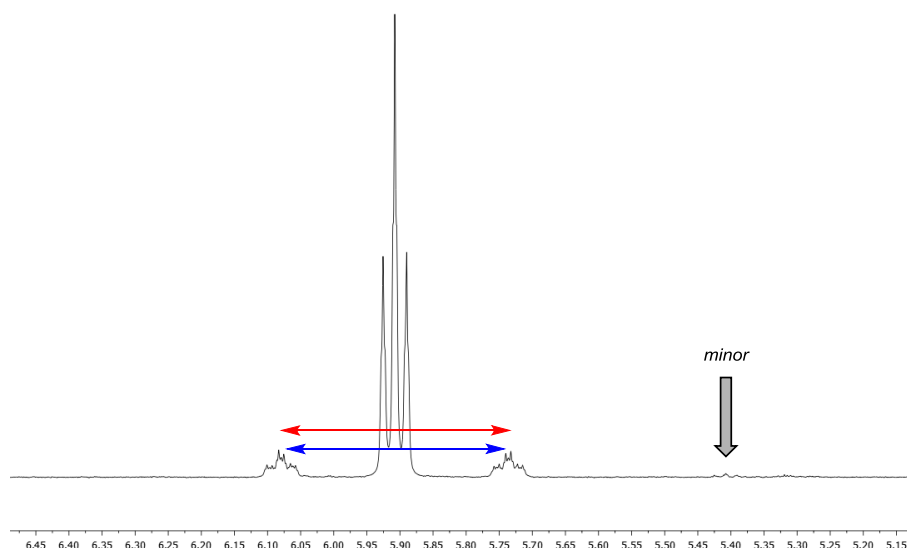
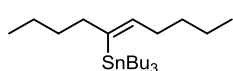


Figure S-1. Olefinic region of the ^1H NMR spectrum of (*Z*)-tributyl(dec-5-en-5-yl)stannane prepared by *trans*-hydrostannation showing the characteristic satellites caused by coupling with the $^{117}\text{Sn}/^{119}\text{Sn}$ nuclei; the (*E*)-configured isomer is marked “minor”; the *Z*:*E* ratio is ≥ 99 :1

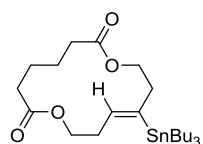
(*Z*)-Tributyl(dec-5-en-5-yl)stannane. Tributyltin hydride (0.99 mL, 3.68 mmol, 1.05 equiv) was added



dropwise under Argon over 6 min to a stirred solution of 5-decyne (0.63 mL, 3.5 mmol) and $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (88.2 mg, 0.175 mmol, 0.05 equiv) in CH_2Cl_2 (17.5 mL, 0.2 M) at ambient temperature. Once the addition was complete, stirring was

continued for 15 min before the solvent was evaporated. The residue was purified by filtration through a short pad of silica using hexane as the eluent. Evaporation of the product-containing fractions afforded (*Z*)-tributyl(dec-5-en-5-yl)stannane as a colorless oil (1.42 g, 94%) (*Z*/*E* > 99:1 (NMR)). ^1H NMR (400 MHz, CDCl_3): δ = 5.98 (tt, J = 7.1, 1.2, $J_{\text{Sn-H}}$ = 137.4 Hz, 1H), 2.25 – 2.05 (m, 2H), 2.03 – 1.91 (m, 2H), 1.59 – 1.39 (m, 6H), 1.39 – 1.22 (m, 14H), 1.00 – 0.80 (m, 21H); ^{13}C NMR (101 MHz, CDCl_3): δ = 143.4, 140.8, 40.6, 34.9, 33.1, 32.8, 29.4, 27.6, 22.7, 22.4, 14.3, 14.2, 13.8, 10.4; ^{119}Sn NMR (186 MHz, CDCl_3): δ = –53.3 ppm; IR (film, cm^{-1}): $\tilde{\nu}$ = 2955, 2922, 2872, 2854, 1463, 1377, 1071.

(*Z*)-11-(Tributylstannyl)-1,8-dioxacyclotetradec-11-ene-2,7-dione. Prepared analogously (using 1.1 equiv.



of Bu_3SnH) as a colorless oil (50.1 mg, 97%) (*Z*/*E* = 85:15 (NMR)). ^1H NMR (400 MHz, CDCl_3): δ = 6.01 (tt, J = 6.6, 1.3, $J_{\text{Sn-H}}$ = 124.5 Hz, 1H), 4.20 – 4.04 (m, 4H), 2.61 – 2.44 (m, 2H), 2.43 – 2.36 (m, 2H), 2.36 – 2.27 (m, 4H), 1.71 – 1.56 (m, 4H), 1.56 – 1.38 (m, 6H), 1.39 – 1.24 (m, 6H), 1.07 – 0.78 (m, 6H), 0.89 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz,

CDCl_3): δ = 173.4, 173.2, 142.5, 140.0, 63.9, 63.4, 39.8, 35.2, 33.8, 29.3, 27.6, 24.9, 24.5, 13.8, 10.3; ^{119}Sn NMR (112 MHz, CDCl_3): δ = –53.1 ppm; IR (film, cm^{-1}): $\tilde{\nu}$ = 2954, 2923, 2871, 2853, 1731, 1458, 1378, 1338, 1266, 1144, 1068, 1047; ESI-MS calcd for $\text{C}_{24}\text{H}_{44}\text{O}_4\text{SnNa}$ ($\text{M}+\text{Na}^+$) 539.21531; found 539.21566.

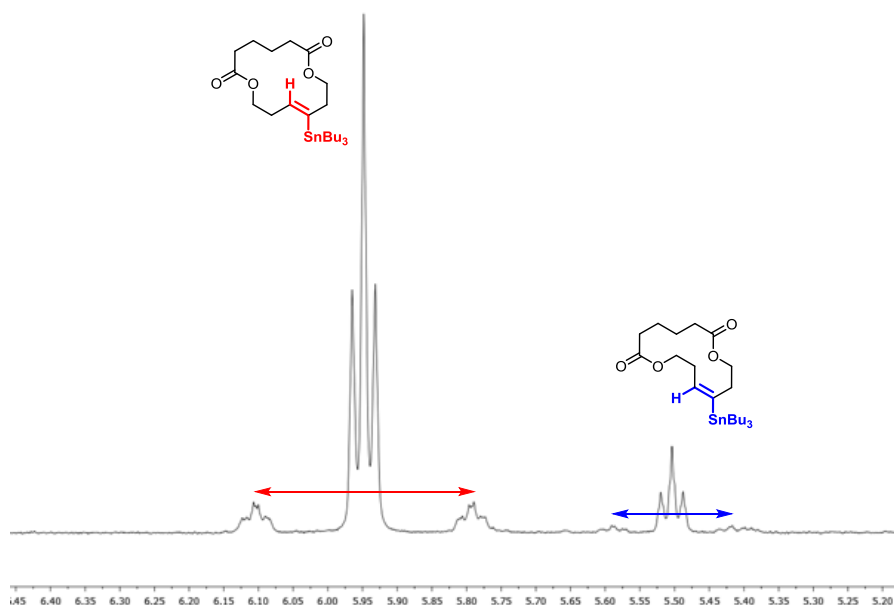
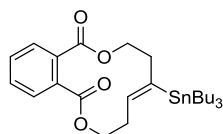


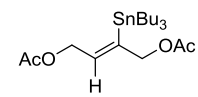
Figure S-2. Olefinic region of the ^1H NMR spectrum of crude (Z)-11-(tributylstannyl)-1,8-dioxacyclotetradec-11-ene-2,7-dione formed by hydrostannation in the presence of $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$. The fact that the $^3J_{\text{Sn,H}}$ of the major isomer is about twice as large as that of the minor isomer shows that the former derives from a *trans*-addition pathway, whereas the latter derives from *cis*-addition of Bu_3SnH across the triple bond.^{4,5}

(Z)-5-(Tributylstannyl)-3,4,7,8-tetrahydrobenzo[c][1,6]dioxacyclododecine-1,10-dione. Prepared analogously as a colorless oil (52.1 mg, 97%) (*Z/E* = 95:5 (NMR)).



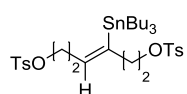
^1H NMR (400 MHz, CDCl_3): δ = 7.84 – 7.73 (m, 1H), 7.60 – 7.51 (m, 1H), 7.55 – 7.44 (m, 2H), 6.16 (t, J = 7.3, $J_{\text{Sn-H}}$ = 127.1 Hz, 1H), 4.47 (t, J = 5.8 Hz, 2H), 4.34 (t, J = 5.9 Hz, 2H), 2.74 – 2.52 (m, 2H), 2.43 (dt, J = 7.1, 5.6 Hz, 2H), 1.52 – 1.32 (m, 6H), 1.26 – 1.16 (m, 6H), 0.99 – 0.81 (m, 6H), 0.80 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ = 168.4, 167.5, 141.4, 139.8, 133.8, 131.9, 131.1, 130.5, 129.5, 128.3, 64.2, 64.1, 38.5, 34.6, 29.2, 27.5, 13.7, 10.4; ^{119}Sn NMR (112 MHz, CDCl_3): δ = –52.6 ppm; IR (film, cm^{-1}): $\tilde{\nu}$ = 2954, 2922, 2870, 2851, 1730, 1462, 1376, 1282, 1128, 1072, 1039, 1017; ESI-MS calcd for $\text{C}_{26}\text{H}_{40}\text{O}_4\text{SnNa}$ ($\text{M}+\text{Na}^+$) 559.18401; found 559.18418.

(Z)-2-(Tributylstannyl)but-2-ene-1,4-diyl diacetate. Prepared analogously as a colorless oil (73.8 mg, 80%)



(*Z/E* = 99:1 (NMR)); ^1H NMR (400 MHz, CDCl_3): δ = 6.39 (tt, J = 6.9, 1.6, $J_{\text{Sn-H}}$ = 106.9 Hz, 1H), 4.74 – 4.63 (m, 2H), 4.56 – 4.47 (m, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 1.57 – 1.39 (m, 6H), 1.38 – 1.25 (m, 6H), 1.03 – 0.93 (m, 6H), 0.89 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ = 170.8, 170.6, 145.6, 135.6, 71.1, 65.7, 29.1, 27.4, 21.10, 21.08, 13.8, 10.6; ^{119}Sn NMR (112 MHz, CDCl_3): δ = –48.5 ppm; IR (film, cm^{-1}): $\tilde{\nu}$ = 2956, 2925, 2872, 2853, 1740, 1459, 1376, 1217, 1077, 1021; ESI-MS calcd for $\text{C}_{20}\text{H}_{38}\text{O}_4\text{SnNa}$ ($\text{M}+\text{Na}^+$) 485.16836; found 485.16855.

(Z)-3-(Tributylstannyl)hex-3-ene-1,6-diyl bis(4-methylbenzene-sulfonate). Prepared analogously as a



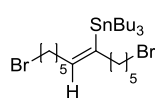
colorless oil (69.6 mg, 98%) (*Z/E* = 99:1 (NMR)); ^1H NMR (400 MHz, CDCl_3): δ = 7.77 (dq, J = 8.5, 2.1 Hz, 4H), 7.39 – 7.31 (m, 4H), 5.85 (tt, J = 7.1, 1.3, $J_{\text{Sn-H}}$ = 118.0 Hz, 1H), 3.95 (t, J =

⁴ A. J. Leusink, H. A. Budding, J. W. Marsman, *J. Organomet. Chem.* **1967**, *9*, 285-294.

⁵ B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73-186.

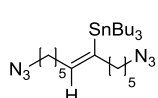
6.9 Hz, 2H), 3.88 (t, $J = 7.4$ Hz, 2H), 2.52 – 2.38 (m, 8H), 2.32 (q, $J = 7.0$ Hz, 2H), 1.45 – 1.31 (m, 6H), 1.32 – 1.19 (m, 6H), 0.86 (t, $J = 7.3$ Hz, 9H), 0.84 – 0.79 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 145.0, 144.9, 142.2, 137.8, 133.3, 133.2, 130.01, 129.99, 128.1, 128.0, 69.9, 69.6, 39.3, 34.5, 29.2, 27.4, 21.8, 13.8, 10.3$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -49.5$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2924, 2871, 2853, 1598, 1463, 1360, 1188, 1174, 1097$; ESI-MS calcd for $\text{C}_{32}\text{H}_{50}\text{O}_6\text{S}_2\text{SnNa}$ ($\text{M}+\text{Na}^+$) 737.19623; found 737.19663.

(Z)-Tributyl(1,12-dibromododec-6-en-6-yl)stannane. Prepared analogously as a colorless oil (49.1 mg,



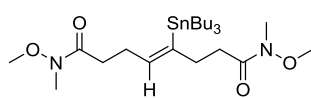
80%). ($Z/E = 97:3$ (NMR)); ^1H NMR (400 MHz, CDCl_3): $\delta = 5.97$ (tt, $J = 7.2, 1.2, J_{\text{Sn-H}} = 134.3$ Hz, 1H), 3.40 (td, $J = 6.8, 3.3$ Hz, 4H), 2.26 – 2.06 (m, 2H), 2.04 – 1.93 (m, 2H), 1.93 – 1.78 (m, 4H), 1.57 – 1.37 (m, 12H), 1.37 – 1.25 (m, 8H), 0.99 – 0.80 (m, 15H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 143.6, 140.6, 40.6, 34.9, 34.1, 33.9, 33.0, 32.9, 29.9, 29.6, 29.4, 28.2, 27.9, 27.6, 13.7, 10.5$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.2$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2924, 2870, 2853, 1459, 1264, 1071$.

(Z)-Tributyl(1,12-diazidododec-6-en-6-yl)stannane. Prepared analogously as a yellow oil (30.2 mg, 56%)



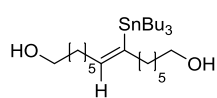
($Z/E = 98:2$ (NMR)); ^1H NMR (400 MHz, CDCl_3) $\delta = 5.97$ (tt, $J = 7.1, 1.3, J_{\text{Sn-H}} = 134.3$ Hz, 1H), 3.31 – 3.22 (m, 4H), 2.27 – 2.05 (m, 2H), 2.05 – 1.91 (m, 2H), 1.67 – 1.54 (m, 4H), 1.53 – 1.42 (m, 6H), 1.42 – 1.36 (m, 4H), 1.36 – 1.25 (m, 10H), 0.99 – 0.80 (m, 15H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 143.6, 140.6, 51.64, 51.57, 40.6, 34.9, 30.2, 30.0, 29.4, 29.0, 28.9, 27.6, 26.7, 26.4, 13.8, 10.4$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.1$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2954, 2925, 2870, 2854, 2090, 1457, 1347, 1256, 1072$.

(Z)- N^1, N^8 -Dimethoxy- N^1, N^8 -dimethyl-4-(tributylstannyl)oct-4-enediamide. Prepared analogously as a



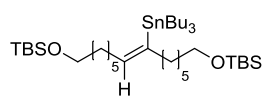
yellow oil (48.2 mg, 88%) ($Z/E = 99:1$ (NMR)); ^1H NMR (500 MHz, CDCl_3): $\delta = 6.07$ (t, $J = 7.1, J_{\text{Sn-H}} = 128.4$ Hz, 1H), 3.67 (s, 6H), 3.17 (s, 3H), 3.16 (s, 3H), 2.54 – 2.36 (m, 6H), 2.30 (dt, $J = 9.4, 7.2$ Hz, 2H), 1.57 – 1.39 (m, 6H), 1.37 – 1.25 (m, 6H), 1.01 – 0.86 (m, 6H), 0.87 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (126 MHz, CDCl_3): $\delta = 174.2, 173.9, 143.5, 139.7, 61.3, 61.3, 33.1, 32.5, 32.3, 29.9, 29.4, 27.5, 13.8, 10.3$; ^{119}Sn NMR (186 MHz, CDCl_3): $\delta = -51.0$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2924, 2871, 2853, 1665, 1462, 1413, 1380, 1176, 1115, 1073, 992$; ESI-MS calcd for $\text{C}_{24}\text{H}_{48}\text{N}_2\text{O}_4\text{SnNa}$ ($\text{M}+\text{Na}^+$) 571.25276; found 571.25288.

(Z)-7-(Tributylstannyl)tetradec-7-ene-1,14-diol. Prepared analogously as a yellow oil (39.4 mg, 76%) ($Z/E =$



99:1 (NMR)); ^1H NMR (400 MHz, CDCl_3): $\delta = 5.96$ (tt, $J = 7.0, 1.2, J_{\text{Sn-H}} = 136.3$ Hz, 1H), 3.63 (tdd, $J = 6.6, 4.6, 1.8$ Hz, 4H), 2.24 – 2.05 (m, 2H), 2.03 – 1.90 (m, 2H), 1.63 – 1.53 (m, 4H), 1.53 – 1.40 (m, 6H), 1.40 – 1.23 (m, 20H), 0.97 – 0.79 (m, 6H), 0.89 (t, $J = 7.2$ Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 143.5, 140.8, 63.22, 63.16, 40.7, 35.1, 33.0, 32.9, 30.7, 30.5, 29.43, 29.39, 29.1, 27.6, 25.9, 25.8, 13.8, 10.4$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.5$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3318, 2953, 2923, 2870, 2852, 1461, 1376, 1071, 1055$; ESI-MS calcd for $\text{C}_{26}\text{H}_{53}\text{OSn}$ ($\text{M}-\text{H}^-$) 517.30724; found 517.30758.

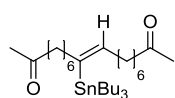
(Z)-2,2,3,3,20,20,21,21-Octamethyl-11-(tributylstannyl)-4,19-dioxa-3,20-disiladocos-11-ene. Prepared



analogously as a yellow oil (66.3 mg, 89%) ($Z/E = 99:1$ (NMR)); ^1H NMR (400 MHz, CDCl_3): $\delta = 5.97$ (tt, $J = 7.1, 1.2, J_{\text{Sn-H}} = 137.0$ Hz, 1H), 3.60 (td, $J = 6.6, 1.3$ Hz, 4H), 2.26 – 2.03 (m, 2H), 1.96 (q, $J = 6.9$ Hz, 2H), 1.61 – 1.40 (m, 10H), 1.40 – 1.21 (m, 18H), 1.03 – 0.77 (m, 33H), 0.05 (s, 12H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 143.5, 140.7, 63.5, 63.4, 40.9, 35.2,$

33.11, 33.06, 30.9, 30.6, 29.5, 29.4, 29.2, 27.6, 26.2, 26.0, 25.9, 18.5, 13.9, 10.4, -5.1; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.4$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2954, 2926, 2855, 1462, 1387, 1361, 1253, 1099, 1005$; ESI-MS calcd for $\text{C}_{38}\text{H}_{82}\text{O}_2\text{Si}_2\text{SnNa}$ ($\text{M}+\text{Na}^+$) 769.47669; found 769.47757.

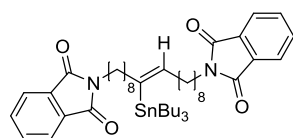
(Z)-9-(Tributylstannyl)octadec-9-ene-2,17-dione. Prepared analogously as a colorless oil (53.3 mg, 94%)



($Z/E = 99:1$ (NMR)); ^1H NMR (400 MHz, CDCl_3) $\delta = 5.94$ (tt, $J = 7.1, 1.3$, $J_{\text{Sn-H}} = 136.3$ Hz, 1H), 2.40 (td, $J = 7.5, 1.8$ Hz, 4H), 2.18 – 2.03 (m, 2H), 2.12 (s, 6H), 1.99 – 1.91 (m, 2H), 1.61 – 1.51 (m, 4H), 1.50 – 1.41 (m, 6H), 1.37 – 1.21 (m, 18H), 0.95 – 0.79 (m, 15H); ^{13}C NMR (101

MHz, CDCl_3) $\delta = 209.4, 209.3, 143.5, 140.7, 44.0, 43.9, 40.8, 35.1, 30.7, 30.3, 29.97, 29.95, 29.41, 29.39, 29.36, 29.25, 29.1, 27.6, 24.1, 24.0, 13.8, 10.4$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.9$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2953, 2923, 2870, 2852, 1717, 1458, 1417, 1357, 1161, 1071$; ESI-MS calcd for $\text{C}_{30}\text{H}_{59}\text{O}_2\text{Sn}$ ($\text{M}+\text{H}^+$) 571.35364; found 571.35409.

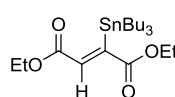
(Z)-2,2'-(9-(Zributylstannyl)octadec-9-ene-1,18-diyl)bis(isoindoline-1,3-dione). Prepared analogously as a



colorless oil (81.2 mg, 98%) ($Z/E = 99:1$ (NMR)); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.88 - 7.78$ (m, 4H), 7.75 – 7.65 (m, 4H), 5.95 (tt, $J = 7.1, 1.2$, $J_{\text{Sn-H}} = 137.1$ Hz, 1H), 3.67 (dd, $J = 8.0, 6.7$ Hz, 4H), 2.20 – 2.00 (m, 2H), 1.98 – 1.88 (m, 2H), 1.72 – 1.60 (m, 4H), 1.54 – 1.38 (m, 6H), 1.37 – 1.18 (m, 26H), 0.96 – 0.78 (m, 6H), 0.87 (t, $J =$

7.3 Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 168.6, 143.5, 140.7, 133.9, 132.4, 123.3, 40.8, 38.3, 38.2, 35.2, 30.8, 30.5, 29.7, 29.59, 29.58, 29.42, 29.36, 29.3, 28.8, 27.6, 27.07, 27.05, 13.8, 10.4$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.5$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2922, 2852, 1773, 1709, 1465, 1436, 1394, 1367, 1188, 1060$; ESI-MS calcd for $\text{C}_{46}\text{H}_{68}\text{N}_2\text{O}_4\text{SnNa}$ ($\text{M}+\text{Na}^+$) 855.40926; found 855.40912.

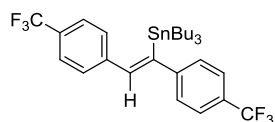
Diethyl 2-(tributylstannyl)fumarate.⁶ Prepared analogously as a colorless oil (63.8 mg, 69%) ($Z/E = 94:6$



(NMR)); ^1H NMR (400 MHz, CDCl_3): $\delta = 6.82$ (s, $J_{\text{Sn-H}} = 81.8$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.20 (q, $J = 7.2$ Hz, 2H), 1.58 – 1.37 (m, 6H), 1.37 – 1.24 (m, 12H), 1.14 – 0.94 (m, 6H), 0.88 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 172.5, 167.4, 161.7, 134.8, 61.19, 61.15,$

29.1, 27.4, 14.43, 14.36, 13.8, 12.1; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -37.0$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2956, 2921, 2872, 2853, 1709, 1463, 1367, 1313, 1193, 1036$; ESI-MS calcd for $\text{C}_{20}\text{H}_{38}\text{O}_4\text{Sn}+\text{Na}$ (MNa^+) 485.16836; found 485.16858.

(Z)-(1,2-Bis(4-(trifluoromethyl)phenyl)vinyl)tributylstannane. Prepared analogously as a colorless oil (120



mg, 98%) ($Z/E = 98:2$ (NMR)); ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.65$ (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.43 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 1.40 – 1.22 (m, 6H), 1.21 – 1.10 (m, 6H), 0.78 (t, $J = 7.3$ Hz, 9H), 0.82 – 0.63

(m, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 152.9, 152.4, 145.0, 143.5, 128.8, 127.6, 125.83, 125.79, 125.76, 125.72, 125.69, 125.65, 29.4, 27.8, 13.8, 12.3$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -43.5$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2957, 2925, 2873, 2854, 1612, 1319, 1163, 1123, 1105, 1065, 1016$.

⁶ In this particular case, the $^3J_{\text{Sn,H}} = 81.8$ Hz is significantly smaller than for most other products described herein; yet, it is in good agreement with the literature, which reports a $^3J_{\text{Sn,H}} = 83.5$ Hz for the *Z*-isomer and 50.0 Hz for the *E*-isomer, cf. ref. 4.

(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 CH₂Cl₂ (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 SiO₂ and the product eluted with hexane/EtOAc (50/1→30/1) to give the title compound as a pale yellow oil (329 mg, 88%, α/β isomer = 98/2). The *Z/E* ratio was found to be >99/1 for the α-isomer. ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (101 MHz, CDCl₃): δ = 150.5, 133.6, 75.8, 29.4, 27.5, 24.4, 19.3, 13.8, 11.0; ¹¹⁹Sn NMR (186 MHz, CDCl₃): 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 C₁₇H₃₅OSn (M-H⁻) 375.17147; found 375.17160.

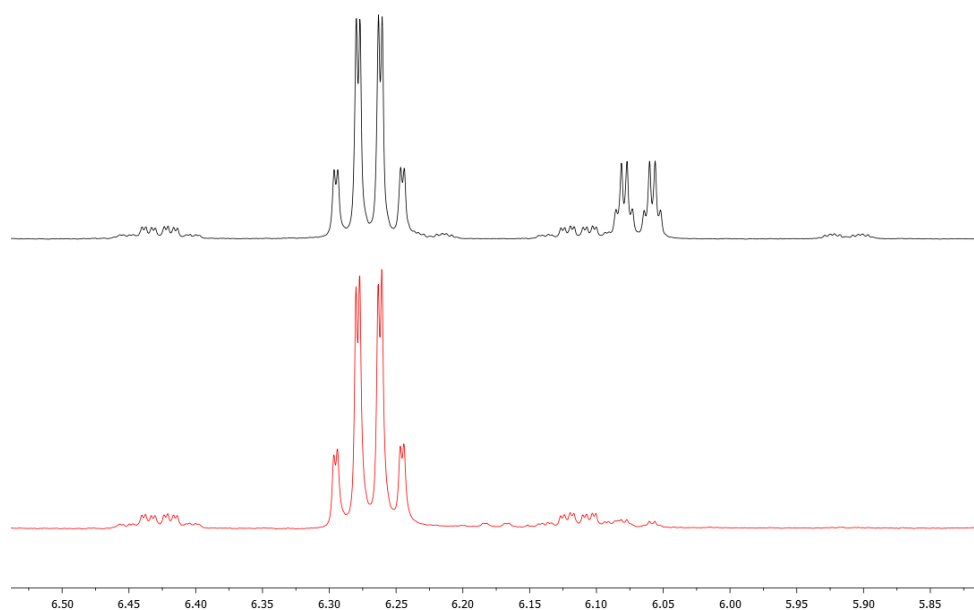
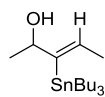
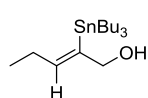
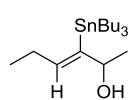


Figure S-3. Olefinic region of the ¹H NMR spectrum of the crude product formed by hydrostannylation of 3-pentyn-2-ol in the presence of [Cp**Ru*(MeCN)₃]*PF*₆ (**3**) (top, black) or [Cp**RuCl*]₄ (**7**) (bottom, red), respectively; although the reaction catalyzed by **3** is regio-unselective, both isomers obviously originate from a *trans*-addition process as evident from the characteristic ³*J*_{Sn,H} coupling constants (expressed in the satellites) which are of the same magnitude.

(Z)-2-(Tributylstannyl)pent-2-en-1-ol. Prepared analogously using [(Cp**RuCl*)₄] (1.25 mol%) as the catalyst; colorless oil (670 mg, 83%) (α/β = 95/5) (*Z/E* = 99:1 for the major isomer (NMR)); ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (101 MHz, CDCl₃): δ = 143.6, 142.6, 70.6, 29.4, 27.9, 27.5, 14.6, 13.8, 10.4; ¹¹⁹Sn NMR (112 MHz, CDCl₃): 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 C₁₇H₃₅OSn (M-H⁻) 375.17147; found 375.17155.



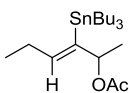
(Z)-3-(Tributylstannyl)hex-3-en-2-ol. Prepared analogously using [(Cp**RuCl*)₄] (1.25 mol%) as the catalyst;



colorless oil (65.5 mg, 84%) ($\alpha/\beta = 98/2$) ($Z/E = 99:1$ for the major isomer (NMR)); ¹H NMR (400 MHz, CDCl₃): $\delta = 6.15$ (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); ¹³C NMR (101 MHz, CDCl₃): $\delta = 148.4, 141.2, 75.7, 29.4, 27.6, 27.5, 24.4, 14.6, 13.8, 11.2$; ¹¹⁹Sn NMR (112 MHz, CDCl₃): $\delta = -53.8$ 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 C₁₈H₃₇OSn (M-H⁻) 389.18712; found 389.18728.

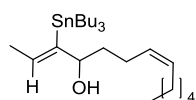
(Z)-3-(Tributylstannyl)hex-3-en-2-yl acetate. Prepared analogously using [(Cp**RuCl*)₄] (1.25 mol%) as the catalyst; colorless oil (73.8 mg, 86%) ($\alpha/\beta = 75:25$) ($Z/E = 94:6$ for the major isomer (NMR)); ¹H



NMR (400 MHz, CDCl₃): $\delta = 6.18$ (td, $J = 7.2, 1.0, J_{Sn-H} = 122.3$ Hz, 1H), 5.49 – 5.28 (m, 1H), 2.08 – 1.94 (m, 2H), 2.00 (s, 3H), 1.59 – 1.38 (m, 6H), 1.38 – 1.27 (m, 6H), 1.25 (d, $J = 6.4$ Hz, 3H),

1.05 – 0.85 (m, 18H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 170.2, 151.1, 143.5, 78.6, 29.3, 27.54, 27.50, 22.1, 21.7, 14.4, 13.8, 11.1$; ¹¹⁹Sn NMR (112 MHz, CDCl₃): $\delta = -52.4$ ppm; IR (film, cm⁻¹): $\tilde{\nu} = 2957, 2926, 2871, 2854, 1737, 1457, 1368, 1235, 1126, 1070, 1041, 1012$; ESI-MS calcd for C₂₀H₄₀O₂SnNa (M+Na⁺) 455.19418; found 455.19459.

(2Z,7Z)-3-(Tributylstannyl)trideca-2,7-dien-4-ol. Prepared analogously using [(Cp**RuCl*)₄] (1.25 mol%) as

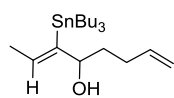


the catalyst; colorless oil (69.5 mg, 72%) ($\alpha/\beta = 98:2$) ($Z/E = 99:1$ for the major isomer

(NMR)); ¹H NMR (400 MHz, CDCl₃): $\delta = 6.25$ (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); ¹³C NMR (101 MHz, CDCl₃): $\delta = 149.3, 134.9, 130.7, 129.2, 80.0, 37.8, 31.7, 29.6, 29.4, 27.6, 27.4, 24.0, 22.8, 19.4, 14.2, 13.8, 11.1$; ¹¹⁹Sn NMR (112 MHz, CDCl₃): $\delta = -55.6$ ppm; IR (film, cm⁻¹): $\tilde{\nu} = 3466, 3004, 2955, 2922, 2871, 2854, 1620, 1457, 1376, 1290, 1070, 1003$; ESI-MS calcd for C₂₅H₄₉OSn (M-H⁻) 485.28102; found 485.28128.

(Z)-3-(Tributylstannyl)octa-2,7-dien-4-ol. Prepared analogously using [(Cp**RuCl*)₄] (1.25 mol%) as the

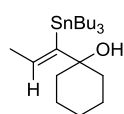


catalyst; colorless oil (31.9 mg, 77%) ($\alpha/\beta = 97:3$) ($Z/E = 99:1$ for the major isomer (NMR));

¹H NMR (400 MHz, CDCl₃): $\delta = 6.25$ (qd, $J = 6.7, 1.1, J_{Sn-H} = 125.0$ Hz, 1H), 5.83 (ddt, $J = 16.9, 10.2, 6.6$ Hz, 1H), 5.02 (dq, $J = 17.1, 1.7$ Hz, 1H), 4.96 (ddt, $J = 10.2, 2.3, 1.3$ Hz, 1H), 4.24 –

4.02 (m, 1H), 2.19 – 1.96 (m, 2H), 1.74 (d, $J = 6.6$ Hz, 3H), 1.66 – 1.42 (m, 8H), 1.41 (d, $J = 3.1$ Hz, 1H), 1.39 – 1.22 (m, 6H), 1.09 – 0.69 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 149.3, 138.7, 135.0, 114.8, 79.9, 36.9, 30.4, 29.4, 27.6, 19.4, 13.8, 11.1$; IR (film, cm⁻¹): $\tilde{\nu} = 3429, 2956, 2922, 2871, 2853, 1641, 1620, 1456, 1376, 1260, 1071, 1046, 1016$; ESI-MS calcd for C₂₀H₄₀OSnNa (M+Na⁺) 439.19926; found 439.19957.

(Z)-1-(1-(Tributylstannyl)prop-1-en-1-yl)cyclohexan-1-ol. Prepared analogously using [(Cp**RuCl*)₄] (1.25

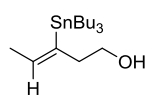


mol%) as the catalyst; colorless oil (82.9 mg, 97%) ($\alpha/\beta = 99:1$) ($Z/E = 99:1$ for the major isomer (NMR)); ¹H NMR (400 MHz, CDCl₃): $\delta = 6.24$ (q, $J = 6.7, J_{Sn-H} = 137.8$ Hz, 1H), 1.74 (d, $J = 6.6$ Hz, 3H), 1.69 – 1.53 (m, 6H), 1.53 – 1.38 (m, 9H), 1.38 – 1.27 (m, 6H), 1.26 (s, 1H), 1.22 – 1.07 (m,

1H), 1.06 – 0.86 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 155.3, 130.3, 75.7, 38.2,$

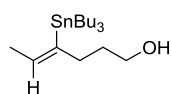
29.4, 27.6, 25.7, 22.4, 19.3, 13.9, 12.4; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -55.7$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3449$, 2953, 2923, 2870, 2852, 1448, 1375, 1340, 1293, 1253, 1149, 1071; ESI-MS calcd for $\text{C}_{21}\text{H}_{42}\text{OSnNa}$ ($\text{M}+\text{Na}^+$) 453.21492; found 453.21520.

(Z)-3-(Tributylstannyl)pent-3-en-1-ol. Prepared analogously using $[(\text{Cp}^*\text{RuCl})_4]$ (1.25 mol%) as the catalyst;



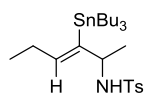
colorless oil (61.0 mg, 81%) ($\alpha/\beta = 81:19$) ($Z/E = 95:5$ for the major isomer (NMR)); Data of the major isomer: ^1H NMR (400 MHz, CDCl_3): $\delta = 6.20$ (qt, $J = 6.6, 1.3$, $J_{\text{Sn-H}} = 129.6$ Hz, 1H), 3.53 (q, $J = 6.1$ Hz, 2H), 2.53 – 2.34 (m, 2H), 1.74 (dt, $J = 6.6, 0.9$ Hz, 3H), 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): $\delta = 140.7, 138.6, 61.8, 43.6, 29.3, 27.5, 20.2, 13.8, 10.3$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -52.6$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3319$, 2955, 2922, 2871, 2852, 1620, 1462, 1418, 1376, 1291, 1181, 1040; ESI-MS calcd for $\text{C}_{17}\text{H}_{35}\text{OSn}$ ($\text{M}-\text{H}^-$) 375.17147; found 375.17149.

(Z)-4-(Tributylstannyl)hex-4-en-1-ol. Prepared analogously using $[(\text{Cp}^*\text{RuCl})_4]$ (1.25 mol%) as the catalyst;



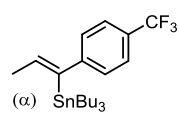
colorless oil (66.7 mg, 86%) ($\alpha/\beta = 83:17$) ($Z/E = 99:1$ for the major isomer (NMR)); Data of the major isomer: ^1H NMR (400 MHz, CDCl_3): $\delta = 6.12$ (qt, $J = 6.6, 1.3$, $J_{\text{Sn-H}} = 132.7$ Hz, 1H), 3.68 – 3.58 (m, 2H), 2.24 (ddt, $J = 8.7, 6.3, 1.2$ Hz, 2H), 1.70 (dt, $J = 6.6, 1.0$ Hz, 3H), 1.66 – 1.38 (m, 8H), 1.38 – 1.23 (m, 7H), 1.02 – 0.83 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 144.3, 135.0, 62.8, 37.1, 33.6, 29.4, 27.6, 20.0, 13.8, 10.3$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.0$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3318, 2955, 2923, 2871, 2852, 1456, 1376, 1291, 1180, 1071, 1052, 1002$; ESI-MS calcd for $\text{C}_{18}\text{H}_{37}\text{OSn}$ ($\text{M}-\text{H}^-$) 389.18712; found 389.18720.

(Z)-4-Methyl-N-(3-(tributylstannyl)hex-3-en-2-yl)benzenesulfonamide. Prepared analogously using



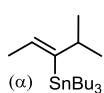
$[(\text{Cp}^*\text{RuCl})_4]$ (1.25 mol%) as the catalyst; colorless oil (48.7 mg, 90%) ($\alpha/\beta = 99:1$) ($Z/E = 99:1$ (NMR)); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.74 - 7.66$ (m, 2H), 7.30 – 7.22 (m, 2H), 5.93 (td, $J = 7.2, 1.0$, $J_{\text{Sn-H}} = 120.7$ Hz, 1H), 4.30 (d, $J = 6.3$ Hz, 1H), 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): $\delta = 144.4, 143.2, 142.6, 138.2, 129.6, 127.5, 58.5, 29.3, 27.7, 27.5, 23.9, 21.6, 14.3, 13.8, 11.0$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -52.9$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3268, 2956, 2924, 2871, 2853, 1456, 1417, 1374, 1325, 1160, 1094, 1071$; ESI-MS calcd for $\text{C}_{25}\text{H}_{45}\text{NO}_2\text{SSnNa}$ ($\text{M}+\text{Na}^+$) 566.20845; found 566.20883.

(Z)-Tributyl(1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)stannane. Prepared analogously using



$[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ as the catalyst; colorless oil (88.4 mg, 93%) ($\alpha/\beta = 65:35$) ($Z/E = 99:1$, α -isomer (NMR)); Data of major α -isomer: ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 7.53 - 7.48$ (m, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 6.32 (q, $J = 6.7$ Hz, 1H), 1.91 (d, $J = 6.7$ Hz, 3H), 1.51 – 1.40 (m, 6H), 1.32 – 1.24 (m, 6H), 1.05 – 0.89 (m, 6H), 0.86 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2 , resolved signals): $\delta = 152.7, 146.2, 140.3, 127.7, 127.3, 125.4, 125.4, 125.4, 125.3, 29.6, 27.9, 20.8, 14.0, 11.4$; ^{119}Sn NMR (186 MHz, CD_2Cl_2): $\delta = -48.1$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2957, 2925, 2872, 2853, 1614, 1463, 1377, 1322, 1162, 1123, 1105, 1067, 1016$.

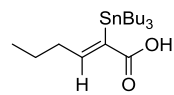
(Z)-Tributyl(4-methylpent-2-en-3-yl)stannane. Prepared analogously using $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ as the



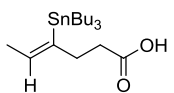
catalyst; colorless oil (67.1 mg, 90%) ($\alpha/\beta = 79:21$) ($Z/E = 99:1$, α -isomer; $Z/E = 57:43$, β -isomer (NMR)); α -isomer: ^1H NMR (400 MHz, CDCl_3): $\delta = 6.10$ (qd, $J = 6.6, 1.2$, $J_{\text{Sn-H}} = 139.8$ Hz, 1H), 2.51

– 2.29 (m, 1H), 1.74 – 1.66 (m, 3H), 1.60 – 1.38 (m, 6H), 1.39 – 1.24 (m, 6H), 0.97 (d, $J = 6.8$ Hz, 6H), 0.90 (t, $J = 7.3$ Hz, 9H), 1.00 – 0.86 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 152.3, 130.5, 38.0, 29.4, 27.6, 23.4, 19.8, 13.8, 10.9$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -53.6$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2923, 2871, 2855, 1462, 1376, 1359, 1339, 1288, 1181, 1071, 1002$.

(Z)-2-(Tributylstannyl)hex-2-enoic acid. Prepared analogously using $[(\text{Cp}^*\text{RuCl})_4]$ (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%) ($\alpha/\beta = 90:10$) ($Z/E = 96:4$ (NMR)); ^1H NMR (500 MHz, CDCl_3): $\delta = 7.50$ (t, $J = 7.3$, $J_{\text{Sn-H}} = 103$ 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): $\delta = 177.5, 160.2, 135.8, 36.3, 29.2, 27.4, 22.5, 14.0, 13.8, 11.5$; ^{119}Sn NMR (186 MHz, CDCl_3): $\delta = -45.7$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3042, 2956, 2922, 2871, 2853, 2621, 1662, 1600, 1462, 1404, 1377, 1272, 1073$; ESI-MS calcd for $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Sn}$ (M-H^-) 403.16638; found 403.16671.

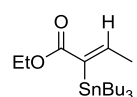


(Z)-4-(Tributylstannyl)hex-4-enoic acid. Prepared analogously using $[(\text{Cp}^*\text{RuCl})_4]$ (1.25 mol%) as the catalyst and limiting the amount of Bu_3SnH to exactly 1 equivalent relative to the substrate; colorless oil (211 mg, 87%) ($\alpha/\beta = 93:7$) ($Z/E = 99:1$ (NMR)). Data of the major isomer: ^1H NMR (500 MHz, CDCl_3): $\delta = 6.14$ (qt, $J = 6.6, 1.4$, $J_{\text{Sn-H}} = 129.8$ 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): $\delta = 179.3, 142.3, 135.8, 35.3, 35.2, 29.4, 27.5, 20.1, 13.8, 10.2$; ^{119}Sn NMR (186 MHz, CDCl_3): $\delta = -51.5$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 3025, 2956, 2921, 2872, 2853, 1708, 1455, 1416, 1376, 1291, 1210, 1071, 1021$; ESI-MS calcd for $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Sn}$ (M-H^-) 403.16639; found 403.16678.

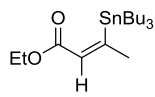


Note: this product is prone to proto-destannylation (ca. 10% after 24h, NMR)

Ethyl (Z)-2-(tributylstannyl)but-2-enoate and Ethyl (Z)-3-(tributylstannyl)but-2-enoate. Method A:



alpha-isomer



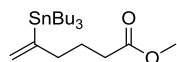
beta-isomer

Prepared according to the standard procedure as a mixture of regioisomers ($\alpha/\beta = 1/1.5$) using $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (5 mol%) as the catalyst; colorless oil (72.8 mg, 90%). The Z/E ratio (NMR) was found to be 99/1 for the β -isomer and $>99/1$ for the α -isomer. The regioisomers can be separated by flash chromatography (SiO_2) using hexanes/ EtOAc (1/0 \rightarrow 50/1 \rightarrow 5/1) as the eluent. β -Isomer: ^1H NMR (400 MHz, CDCl_3): $\delta = 6.41$ (q, $J = 1.7$, $J_{\text{Sn-H}} = 106.1$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 2.13 (d, $J = 1.7$ Hz, 3H), 1.54 – 1.37 (m, 6H), 1.36 – 1.23 (m, 9H), 1.07 – 0.91 (m, 6H), 0.88 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 171.7, 167.9, 129.4, 60.2, 29.4, 27.6, 27.5, 14.5, 13.9, 11.1$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -50.6$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2920, 2871, 2852, 1701, 1600, 1463, 1368, 1315, 1191, 1099, 1043$; ESI-MS calcd for $\text{C}_{18}\text{H}_{36}\text{O}_2\text{SnNa}$ ($\text{M}+\text{Na}^+$) 427.16288; found 427.16337; Characteristic data of the α -isomer: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.46$ (q, $J = 6.9$ Hz, $J_{\text{Sn-H}} = 106.1$ Hz 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 1.91 – 1.85 (m, 3H), 1.56 – 1.42 (m, 6H), 1.37 – 1.24 (m, 9H), 1.09 – 0.92 (m, 6H), 0.88 (t, $J = 7.3$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 171.7, 152.3, 137.4, 60.5, 29.2, 27.4, 19.7, 14.5, 13.8, 11.5$.

Method B: A solution of Bu_3SnH (0.22 mmol, 59 μL , 1.1 equiv) in CH_2Cl_2 (0.5 mL) was added via syringe pump over 1.5 h to a solution of ethyl 2-butynoate (23 μL , 0.20 mmol) and $[(\text{Cp}^*\text{RuCl})_4]$ (2.7 mg, 2.5 μmol , 0.0125 equiv) in CH_2Cl_2 (1.0 mL) under Ar. Stirring was continued for 15 min once the addition was

complete. For work up, all volatile materials were evaporated; the resulting crude product consisted of a mixture of regioisomers ($\alpha/\beta = 6/94$), with a *Z/E* ratio of 95/5 for the β -isomer (NMR). Purification by flash chromatography (hexane/EtOAc, 50/1) furnished pure ethyl (*Z*)-3-(tributylstannyl)but-2-enoate (β -isomer) as a colorless oil (57.1 mg, 71%).

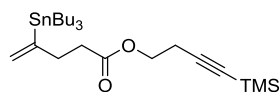
Representative Procedure for the *trans*-Hydrostannylation of Terminal Alkynes: Methyl 5-(tributylstannyl)hex-5-enoate. A solution of methyl hex-5-ynoate (26 μ L, 0.20 mmol) and



tributyltin hydride (0.22 mmol, 59 μ L, 1.1 equiv) in CH_2Cl_2 (0.5 mL) was added dropwise

over 12 min to a stirred solution of $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (5.0 mg, 10 μ mol, 0.05 equiv) in CH_2Cl_2 (0.5 mL) under argon. Once the addition was complete, the mixture was stirred for another 15 min before all volatile materials were evaporated. The residue was passed through a short plug of silica, eluting with hexanes/EtOAc (20:1) to give the title compound as a mixture of regioisomers (terminal:internal = 3:97) as a colorless oil (60.5 mg, 73%). Data of the major isomer: ^1H NMR (400 MHz, CDCl_3) $\delta = 5.67$ (dt, $J = 2.8, 1.5$, $J_{\text{Sn-H}} = 137.6$ Hz, 1H), 5.14 (dt, $J = 2.3, 1.0$, $J_{\text{Sn-H}} = 62.9$ Hz, 1H), 3.66 (s, 3H), 2.37 – 2.20 (m, 4H), 1.77 – 1.66 (m, 2H), 1.58 – 1.38 (m, 6H), 1.36 – 1.25 (m, 6H), 1.00 – 0.78 (m, 15H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 174.1, 154.4, 125.9, 51.6, 40.6, 33.6, 29.3, 27.5, 24.7, 13.8, 9.7$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -45.2$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2925, 2872, 2852, 1742, 1457, 1436, 1376, 1245, 1222, 1193, 1170, 1072$; ESI-MS calcd for $\text{C}_{19}\text{H}_{39}\text{O}_2\text{Sn}$ ($\text{M}+\text{H}^+$) 419.19713; found 419.19730

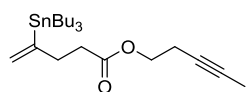
4-(Trimethylsilyl)but-3-yn-1-yl 4-(tributylstannyl)pent-4-enoate. Prepared analogously (using only 1.0 equiv. of Bu_3SnH) as a colorless oil (isomer ratio for stannylation at the terminal



versus the silylated triple bond = 93:7) (98.2 mg, 96%); ^1H NMR (400 MHz, CDCl_3): $\delta = 5.70$ (dt, $J = 2.3, 1.6$, $J_{\text{Sn-H}} = 133.2$ Hz, 1H), 5.15 (dt, $J = 2.3, 1.2$, $J_{\text{Sn-H}} = 62.4$ Hz,

1H), 4.16 (t, $J = 7.1$ Hz, 2H), 2.64 – 2.46 (m, 4H), 2.46 – 2.34 (m, 2H), 1.59 – 1.40 (m, 6H), 1.38 – 1.25 (m, 6H), 1.00 – 0.82 (m, 15H), 0.15 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 173.0, 153.1, 125.6, 102.4, 86.6, 62.3, 35.8, 34.1, 29.2, 27.5, 20.5, 13.8, 9.7, 0.2$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -44.0$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2956, 2925, 2872, 2853, 2181, 1741, 1457, 1419, 1377, 1337, 1248, 1162, 1071, 1026$; ESI-MS calcd for $\text{C}_{24}\text{H}_{46}\text{O}_2\text{SiSnNa}$ ($\text{M}+\text{Na}^+$) 537.21806; found 537.21852.

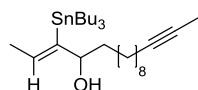
Pent-3-yn-1-yl 4-(tributylstannyl)pent-4-enoate. Prepared analogously (using only 1.0 equiv. of Bu_3SnH) as



a colorless oil (isomer ratio for stannylation at the terminal versus the internal triple bond = 76:24) (80.6 mg, 89%); ^1H NMR (400 MHz, CDCl_3): $\delta = 5.70$ (dq, $J = 3.5, 1.7$,

$J_{\text{Sn-H}} = 135.0$ Hz, 1H), 5.15 (dq, $J = 2.0, 1.0$, $J_{\text{Sn-H}} = 62.6$ Hz, 1H), 4.13 (t, $J = 7.0$ Hz, 2H), 2.65 – 2.50 (m, 2H), 2.50 – 2.34 (m, 4H), 1.77 (t, $J = 2.5$ Hz, 3H), 1.63 – 1.38 (m, 6H), 1.37 – 1.23 (m, 6H), 1.01 – 0.82 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 173.1, 153.2, 125.5, 77.4, 74.9, 62.9, 35.8, 34.0, 29.2, 27.5, 19.4, 13.8, 9.7, 3.6$; ^{119}Sn NMR (112 MHz, CDCl_3): $\delta = -44.0$ ppm; IR (film, cm^{-1}): $\tilde{\nu} = 2955, 2922, 2871, 2852, 1739, 1457, 1419, 1377, 1340, 1245, 1165, 1072, 1002$; ESI-MS calcd for $\text{C}_{22}\text{H}_{40}\text{O}_2\text{SnNa}$ ($\text{M}+\text{Na}^+$) 479.19418; found 479.19459.

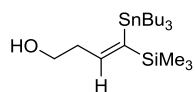
(*Z*)-3-(Tributylstannyl)hexadec-2-en-14-yn-4-ol. Prepared according to the standard procedure but using



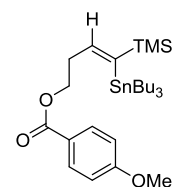
$[(\text{Cp}^*\text{RuCl})_4]$ (1.25 mol%) as the catalyst and 1.05 equiv. of Bu_3SnH ; purification by flash chromatography (hexane/EtOAc, 100/1 \rightarrow 20/1) allowed minor by-products to be removed and gave the title compound as a colorless oil (57.7 mg, 55%). ^1H NMR (400

MHz, CDCl₃): 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); ¹³C NMR (101 MHz, CDCl₃): 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; ¹¹⁹Sn NMR (112 MHz, CDCl₃): 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 C₂₈H₅₄OSnNa (M+Na⁺) 549.30881; found 549.30917.

(Z)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-1-ol. Prepared according to the standard procedure as a

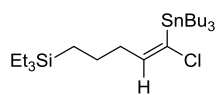


mixture of regioisomers (α/β = 96/4); colorless oil (35.5 mg, 82%). The *Z/E* ratio (NMR) was found to be >99/1 for the α -isomer. ¹H NMR (400 MHz, CDCl₃): δ = 6.72 (t, J = 6.6, J_{Sn-H} = 170.6 Hz, 1H), 3.73 (t, J = 6.6 Hz, 2H), 2.42 (q, J = 6.6 Hz, 2H), 1.59 – 1.38 (m, 6H), 1.38 – 1.25 (m, 7H), 1.04 – 0.92 (m, 6H), 0.89 (t, J = 7.3 Hz, 9H), 0.05 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ = 150.8, 148.0, 62.3, 42.5, 29.4, 27.6, 13.8, 11.5, –0.1; ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ = –53.7 ppm; IR (film, cm⁻¹): $\tilde{\nu}$ = 3310, 2954, 2923, 2871, 2854, 1571, 1463, 1376, 1245, 1046; ESI-MS calcd for C₁₉H₄₃OSiSn (M+H⁺) 435.21045; found 435.21003.

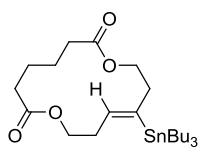


(Z)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-1-yl 4-methoxybenzoate. Prepared according to the standard procedure as a mixture of regioisomers (α/β = 98/2); colorless oil (111.7 mg, 98%); The *Z/E* ratio (NMR) was found to be >99/1 for the α -isomer. ¹H NMR (400 MHz, CDCl₃) δ = 8.05 – 7.95 (m, 2H), 6.95 – 6.88 (m, 2H), 6.78 (t, J = 6.4, J_{Sn-H} = 169.6 Hz, 1H), 4.37 (t, J = 6.7 Hz, 2H), 3.86 (s, 3H), 2.65 – 2.52 (m, 2H), 1.57 – 1.38 (m, 6H), 1.38 – 1.25 (m, 6H), 1.06 – 0.92 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H), 0.06 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ = 166.4, 163.5, 150.3, 147.4, 131.7, 123.0, 113.7, 63.9, 55.6, 38.5, 29.4, 27.5, 13.8, 11.4, –0.1; ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ = –53.1 ppm; IR (film, cm⁻¹): $\tilde{\nu}$ = 2954, 2926, 2871, 2853, 1715, 1607, 1511, 1459, 1273, 1254, 1166, 1099, 1033; ESI-MS calcd for C₂₇H₄₉O₃SiSn (M+H⁺) 569.24723; found 569.24702.

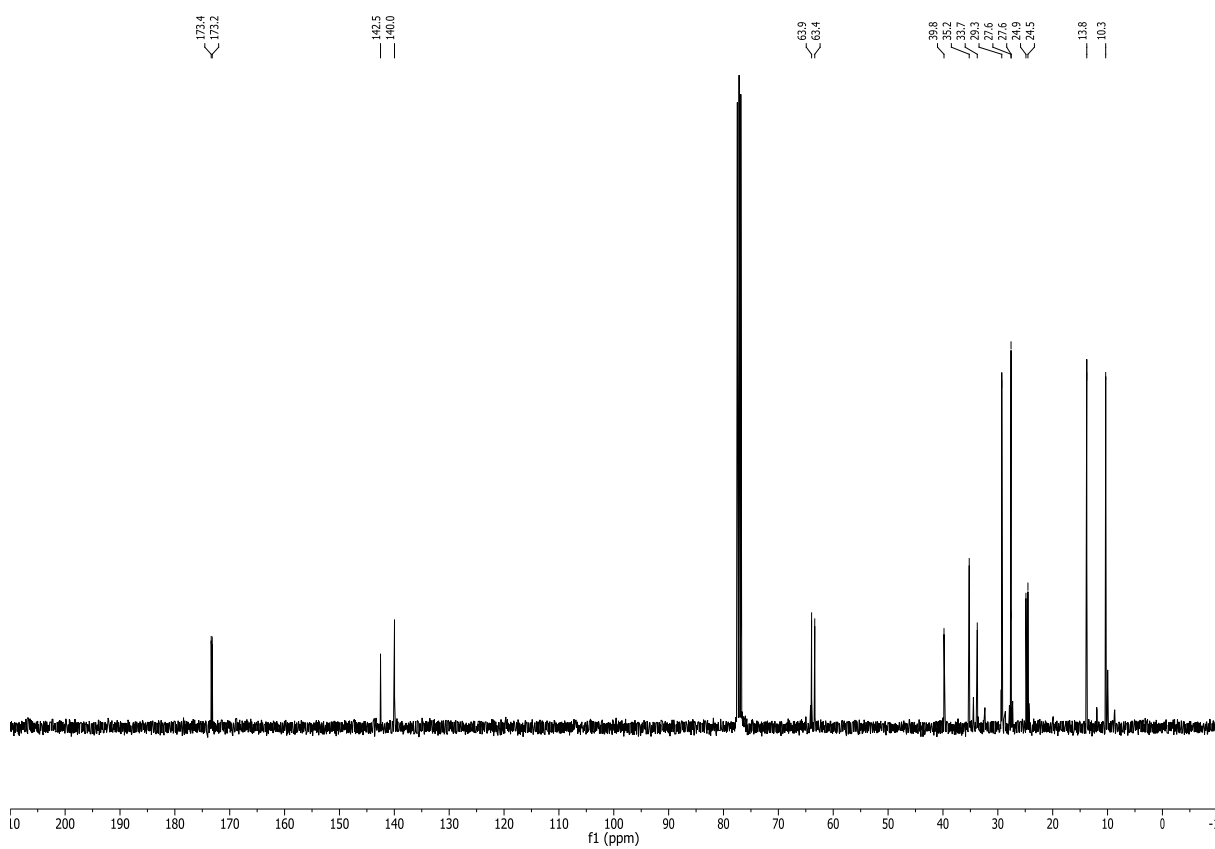
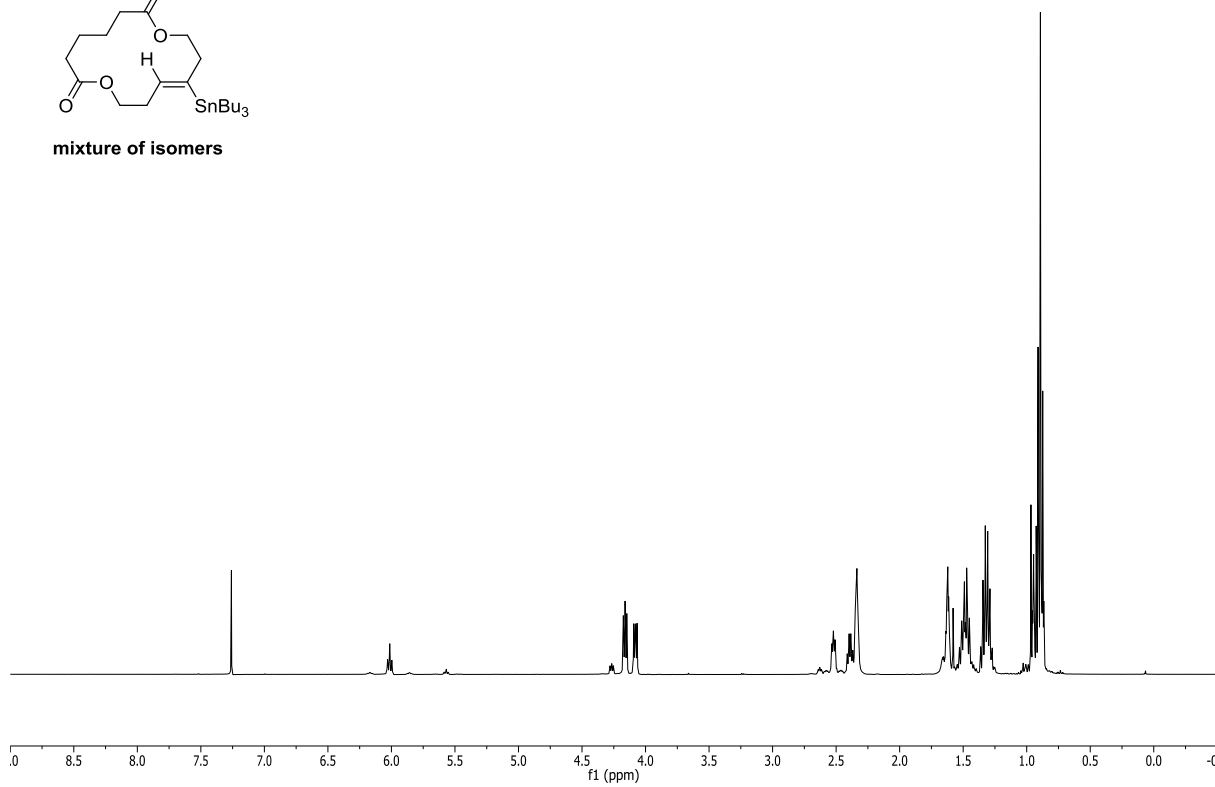
(Z)-5-Chloro-5-(tributylstannyl)pent-4-en-1-yltriethylsilane. Prepared according to the standard

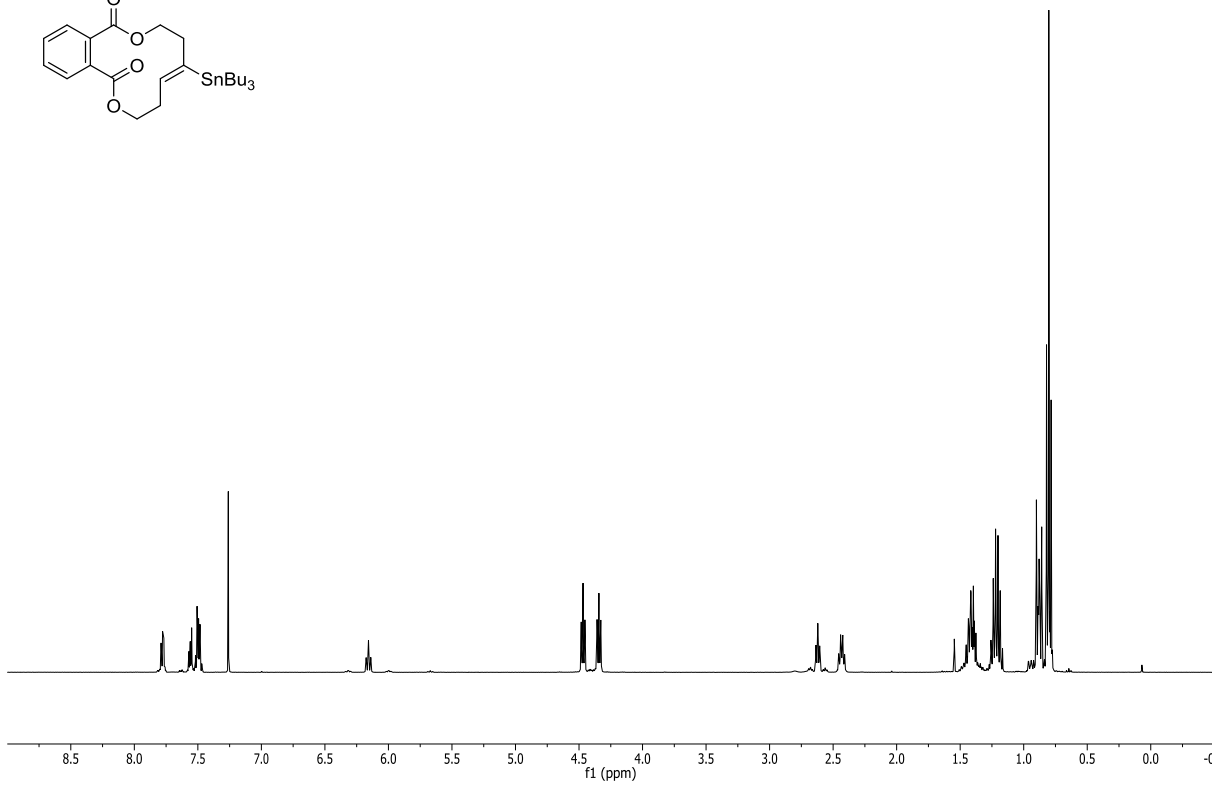
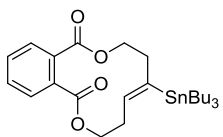


procedure; colorless oil (47.6 mg, 94%) (α/β = 99:1) (*Z/E* = 99:1 (NMR)); ¹H NMR (400 MHz, CDCl₃) δ = 6.65 (t, J = 6.6, J_{Sn-H} = 174.8 Hz, 1H), 3.55 (t, J = 6.7 Hz, 2H), 2.36 – 2.23 (m, 2H), 1.96 – 1.85 (m, 2H), 1.57 – 1.39 (m, 6H), 1.39 – 1.25 (m, 6H), 1.02 – 0.79 (m, 24H), 0.56 (q, J = 7.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ = 155.3, 141.6, 44.7, 36.9, 32.8, 29.4, 27.6, 13.8, 11.6, 7.7, 3.9; ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ = –54.7 ppm; IR (film, cm⁻¹): $\tilde{\nu}$ = 2953, 2927, 2872, 2854, 1570, 1458, 1376, 1235, 1071, 1003.



mixture of isomers





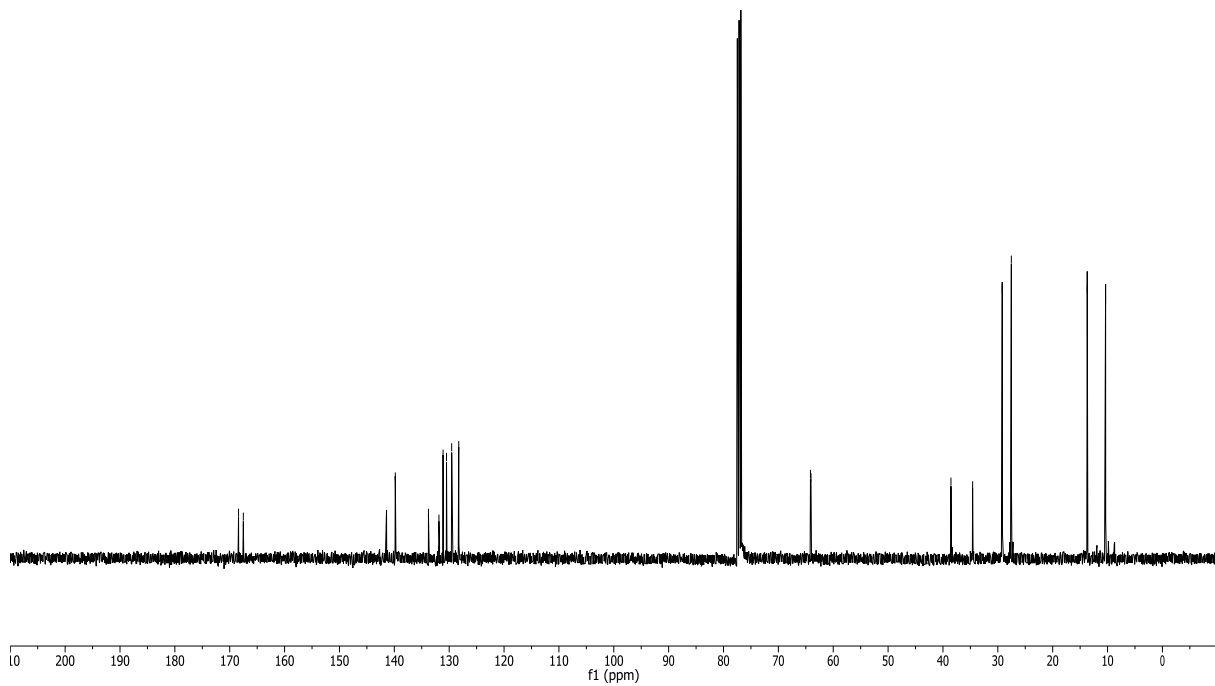
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167.5

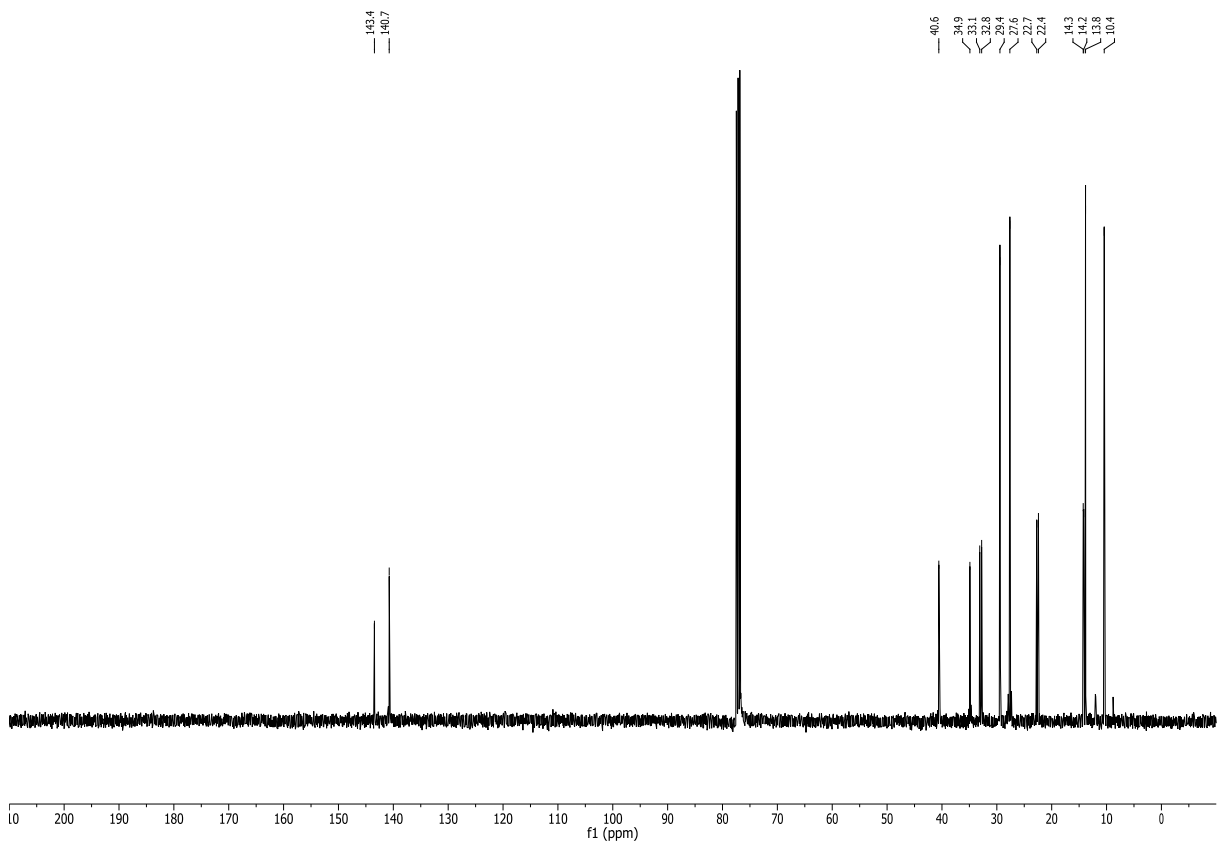
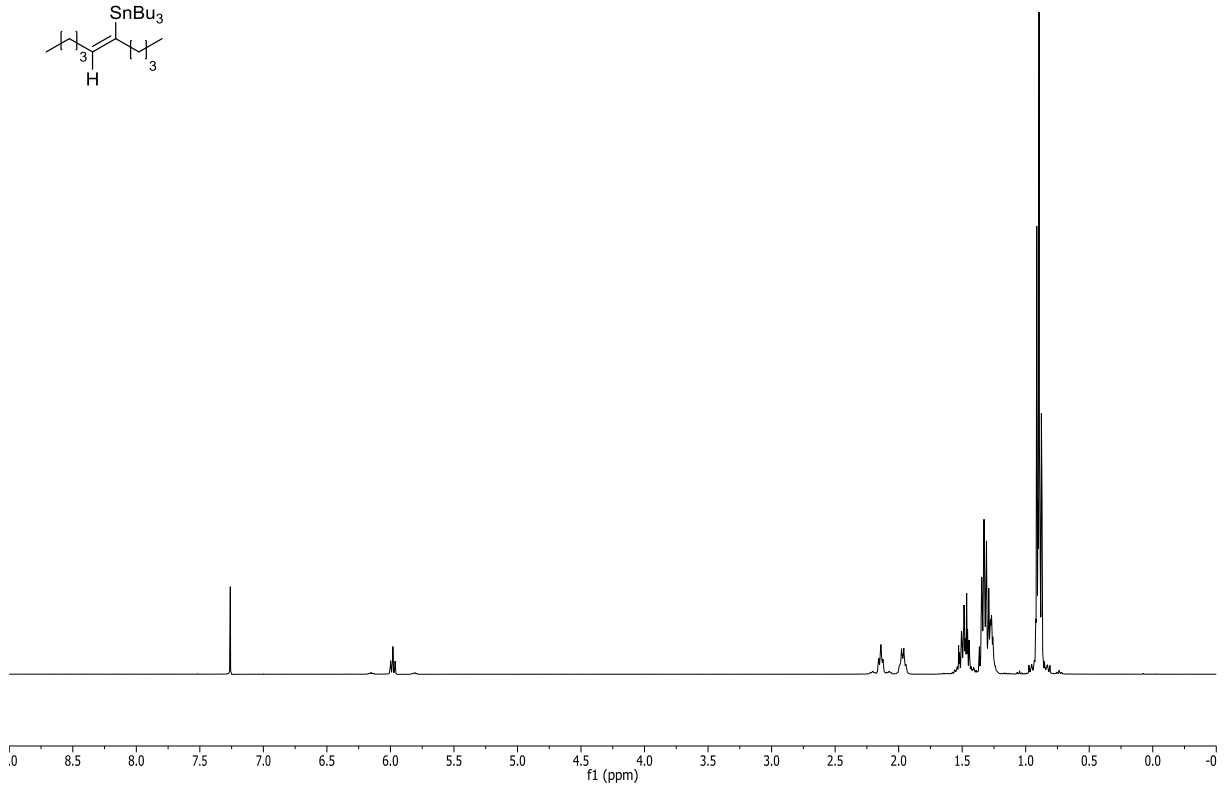
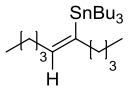
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139.8
133.8
131.9
131.1
130.5
128.5

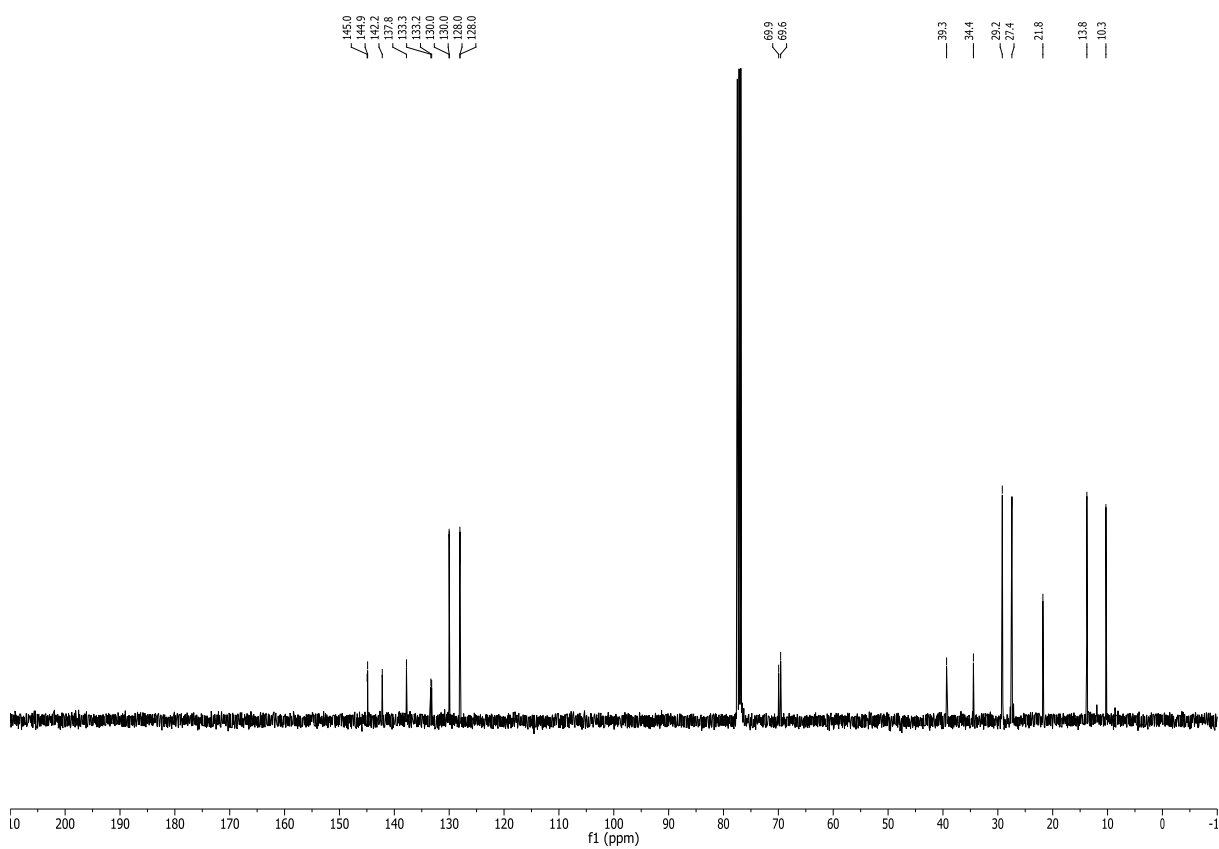
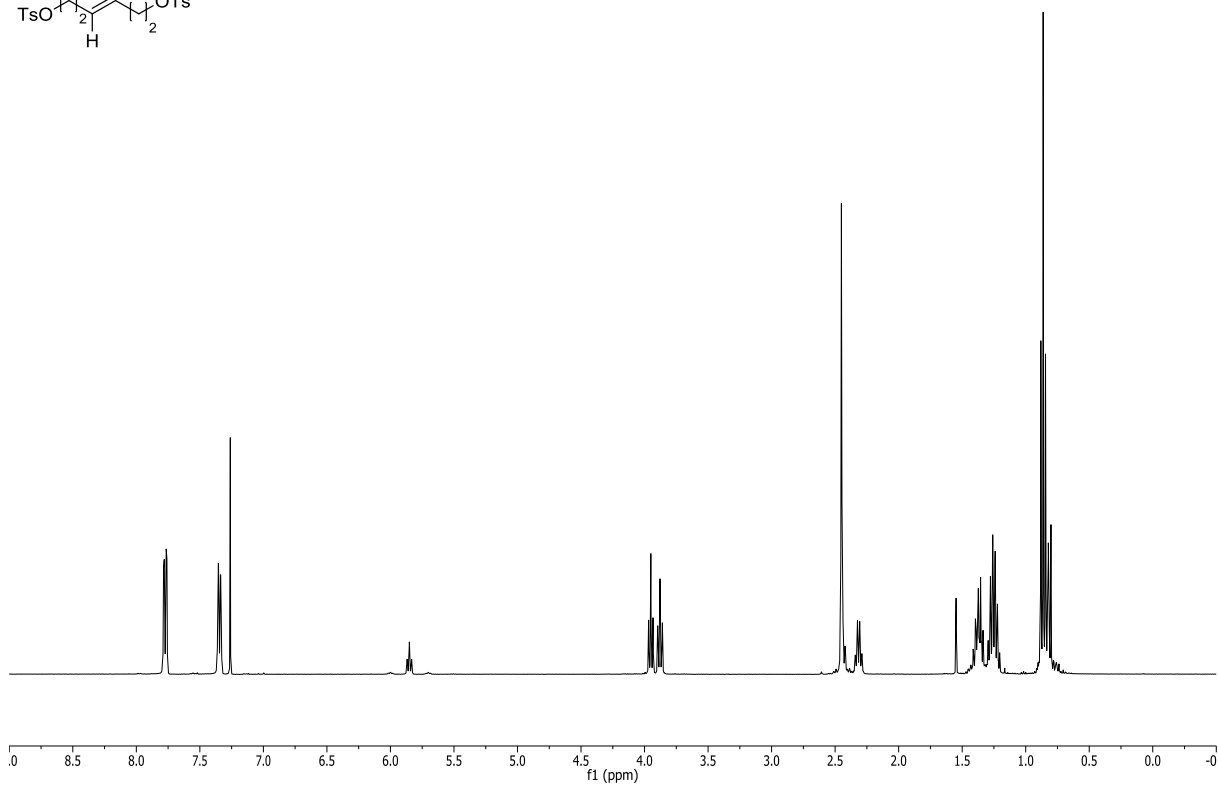
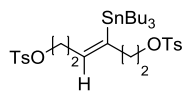
64.2
64.0

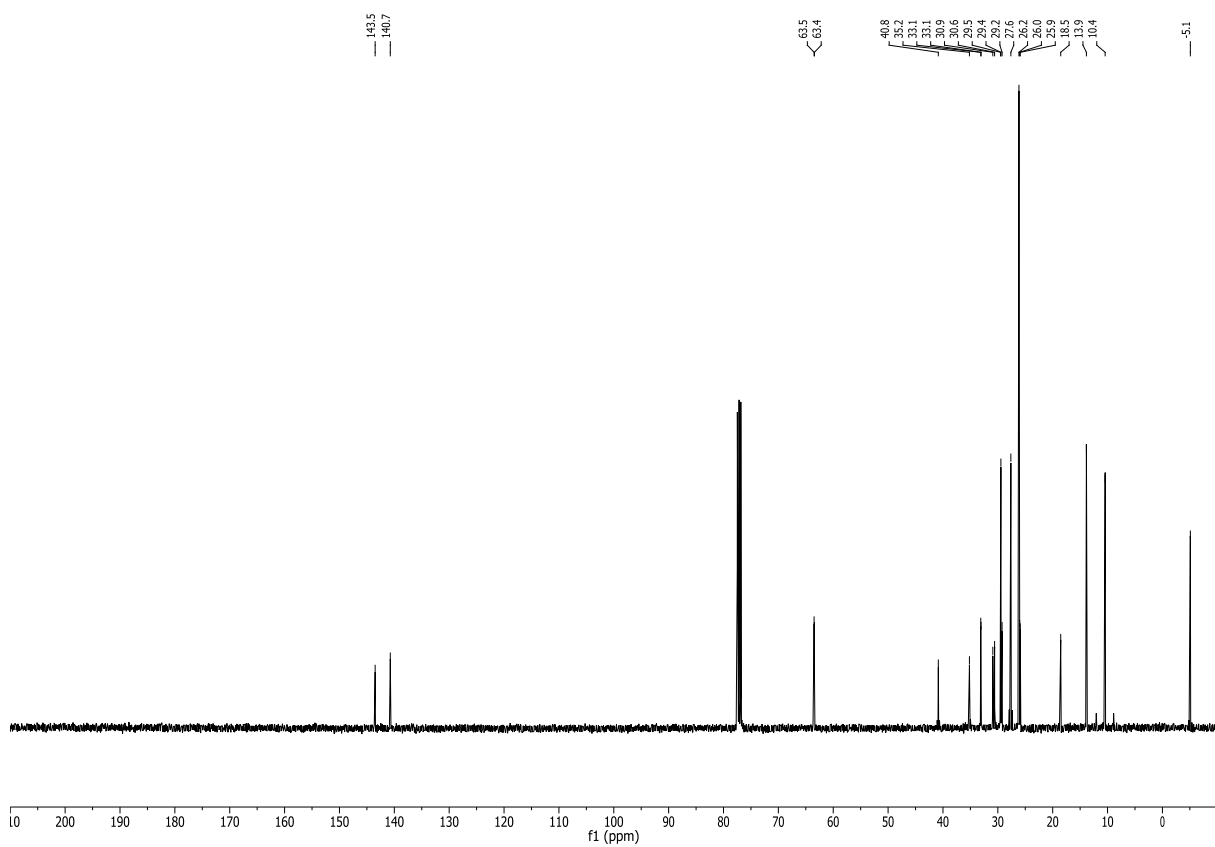
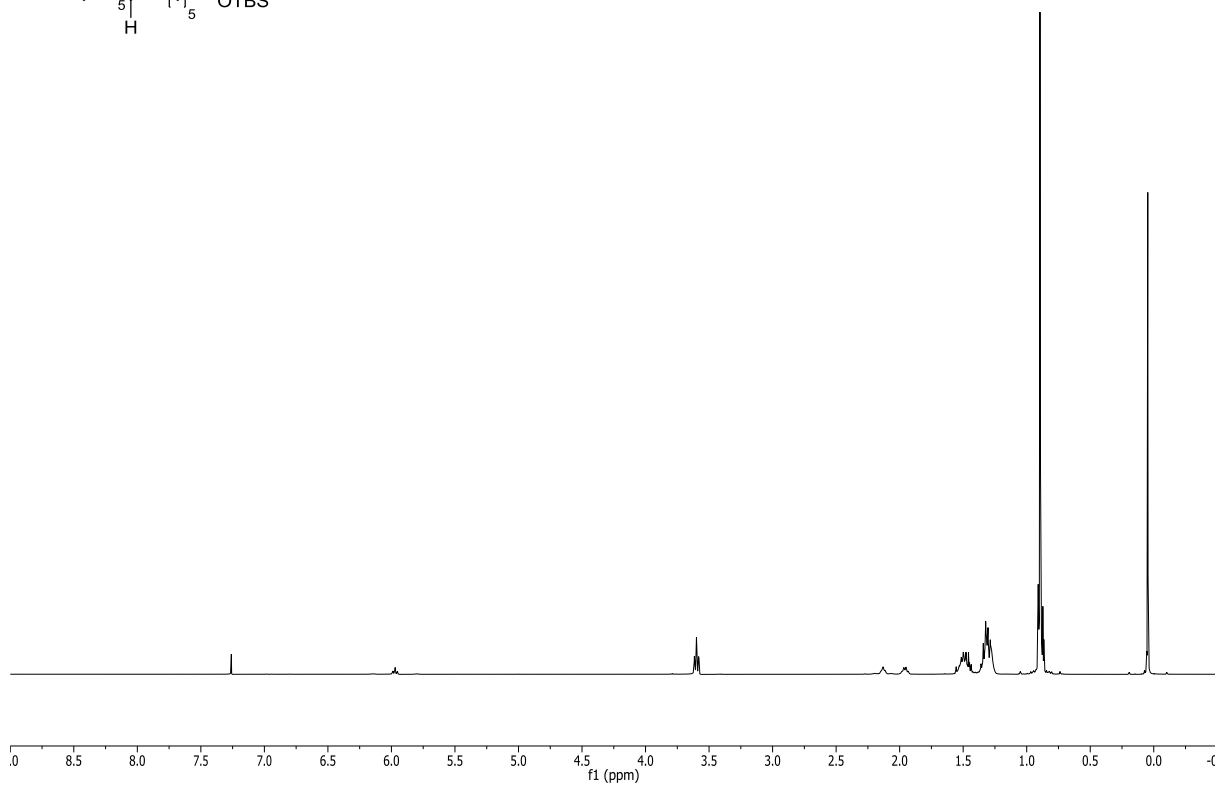
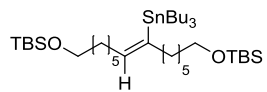
38.5
31.6
29.2
27.5

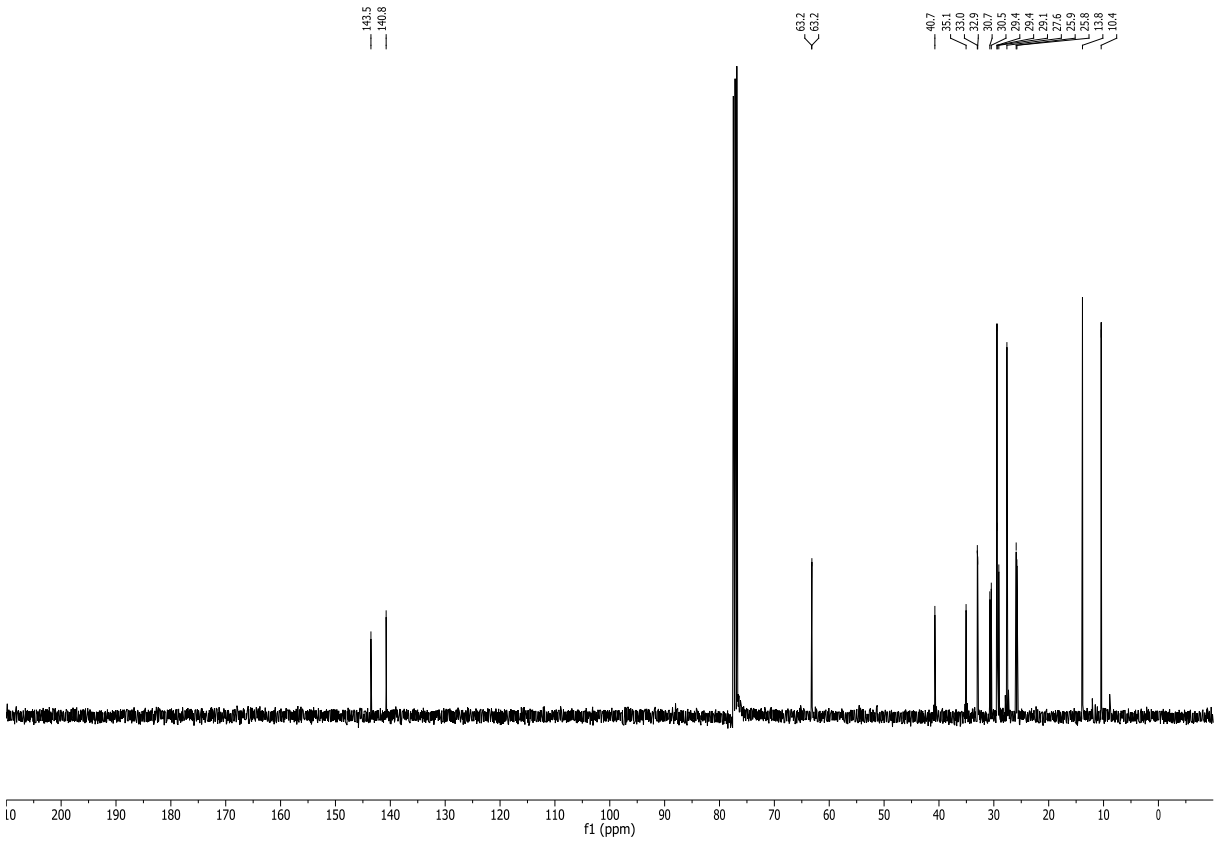
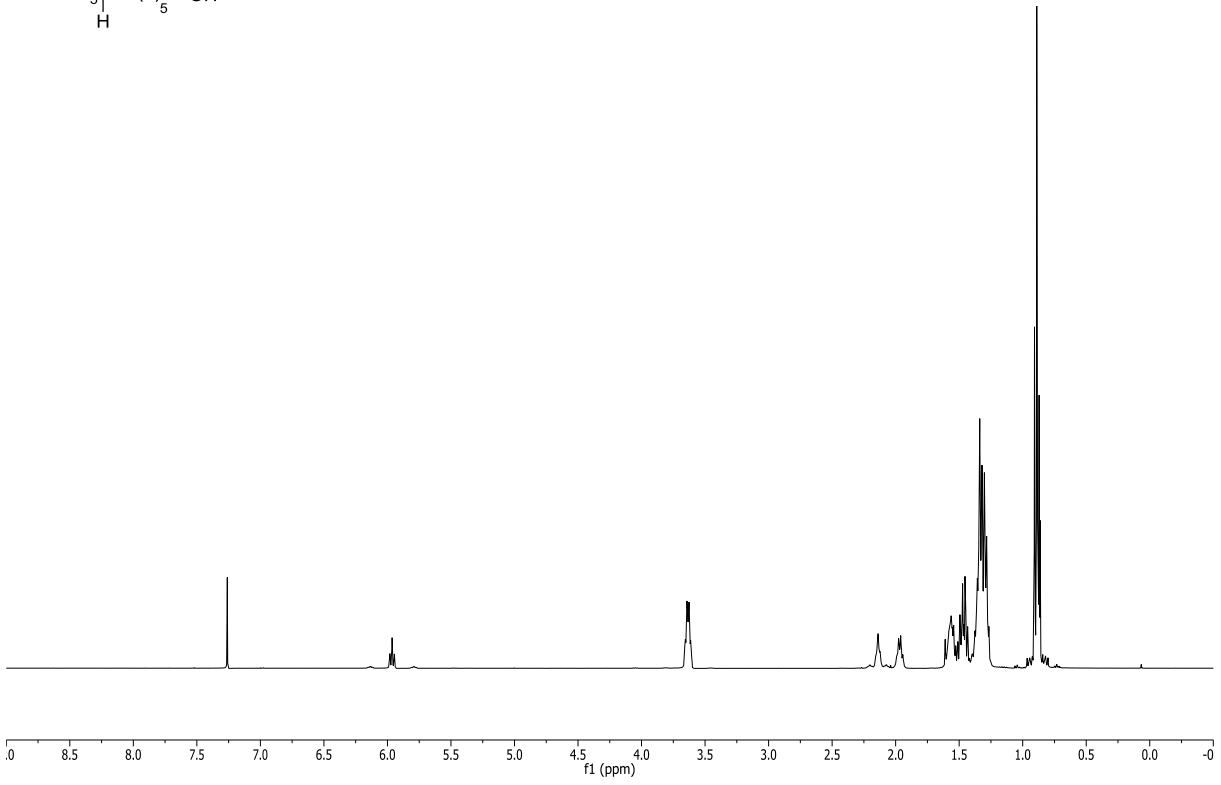
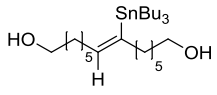
13.7
10.4

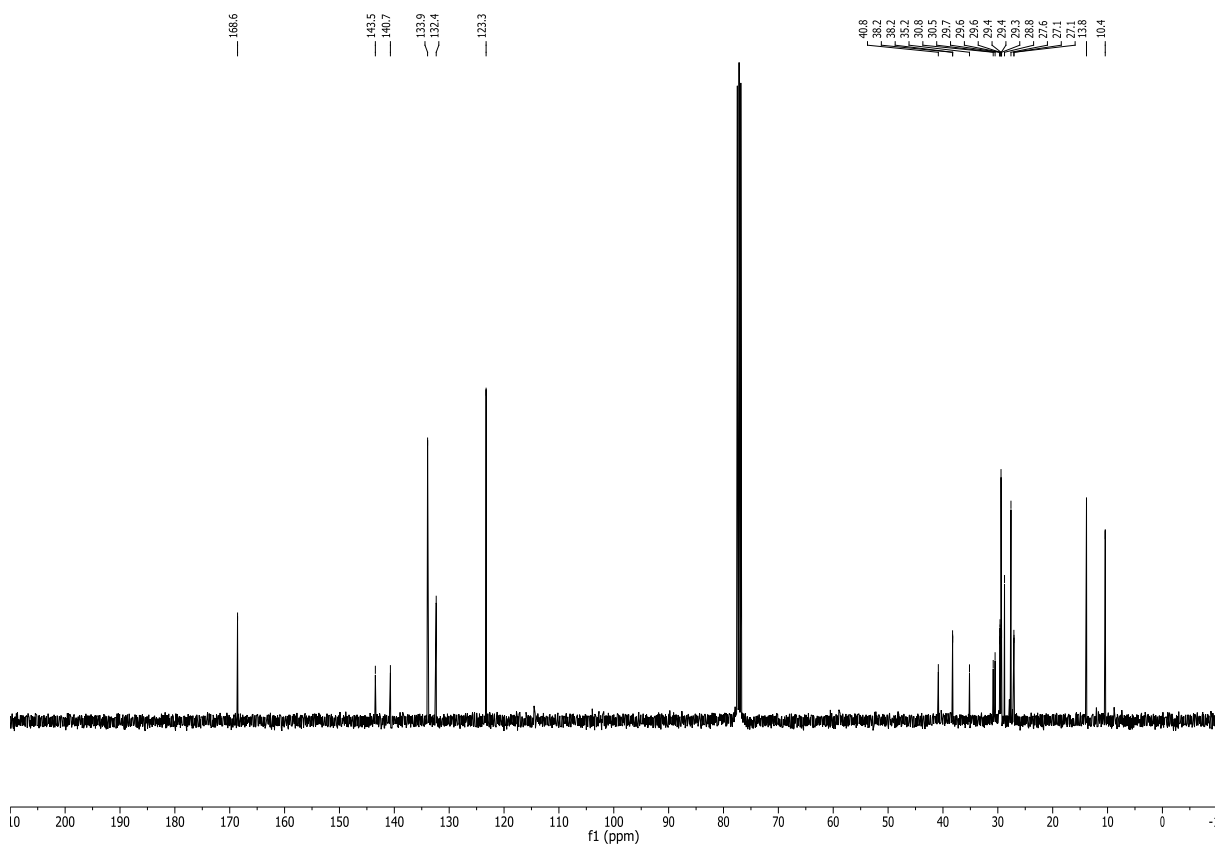
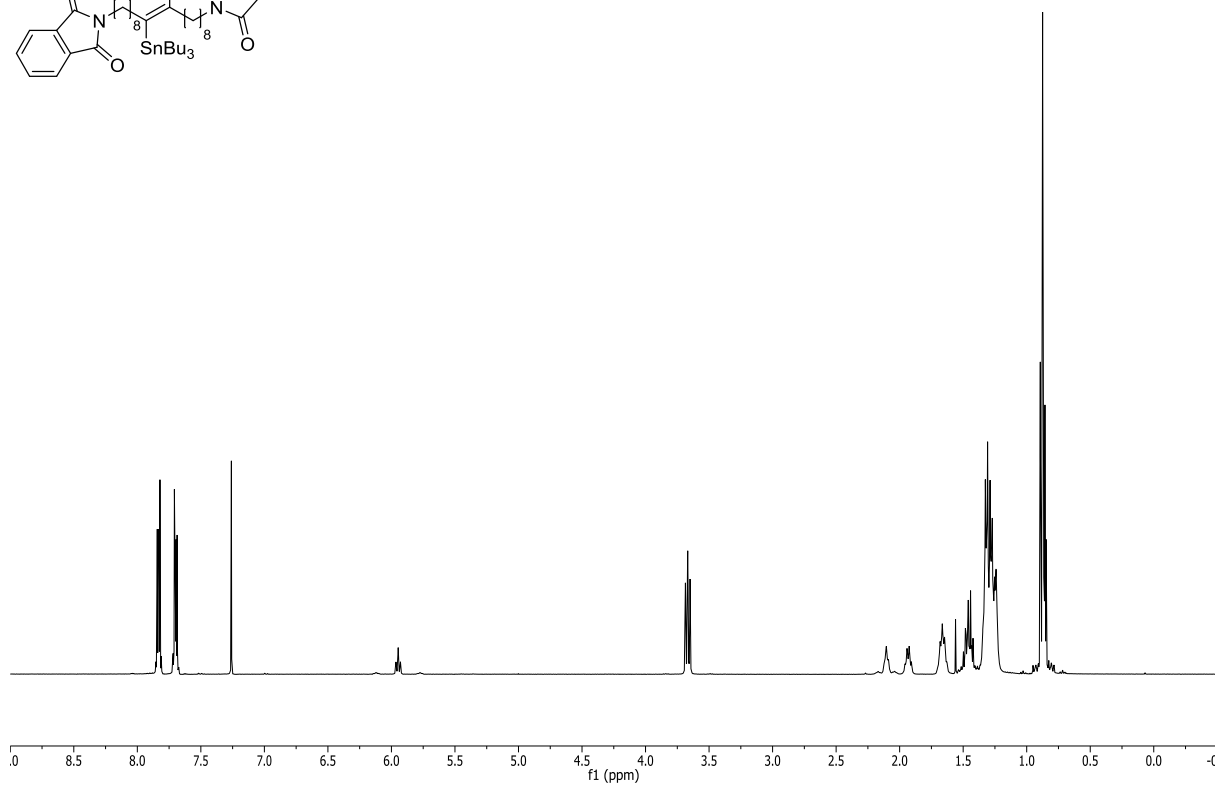
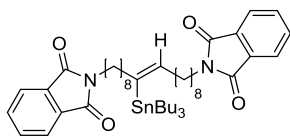


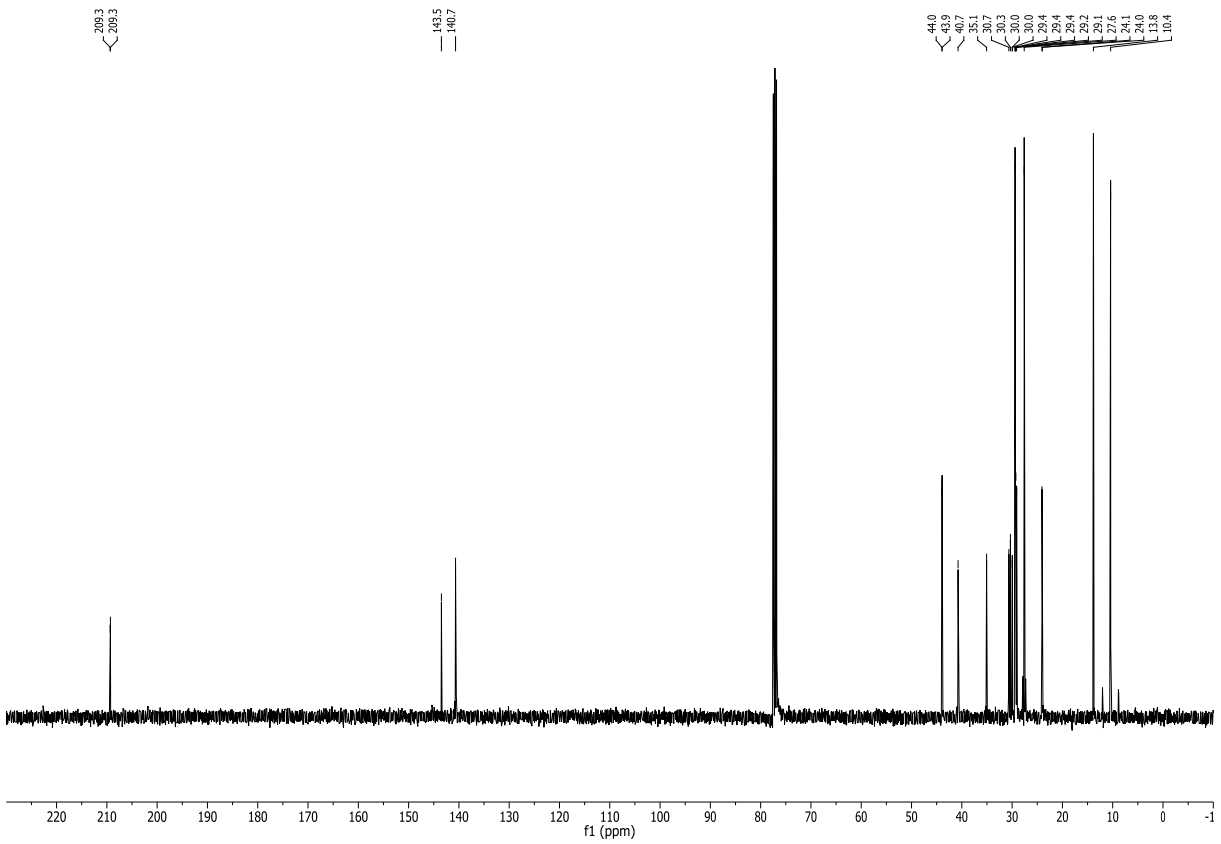
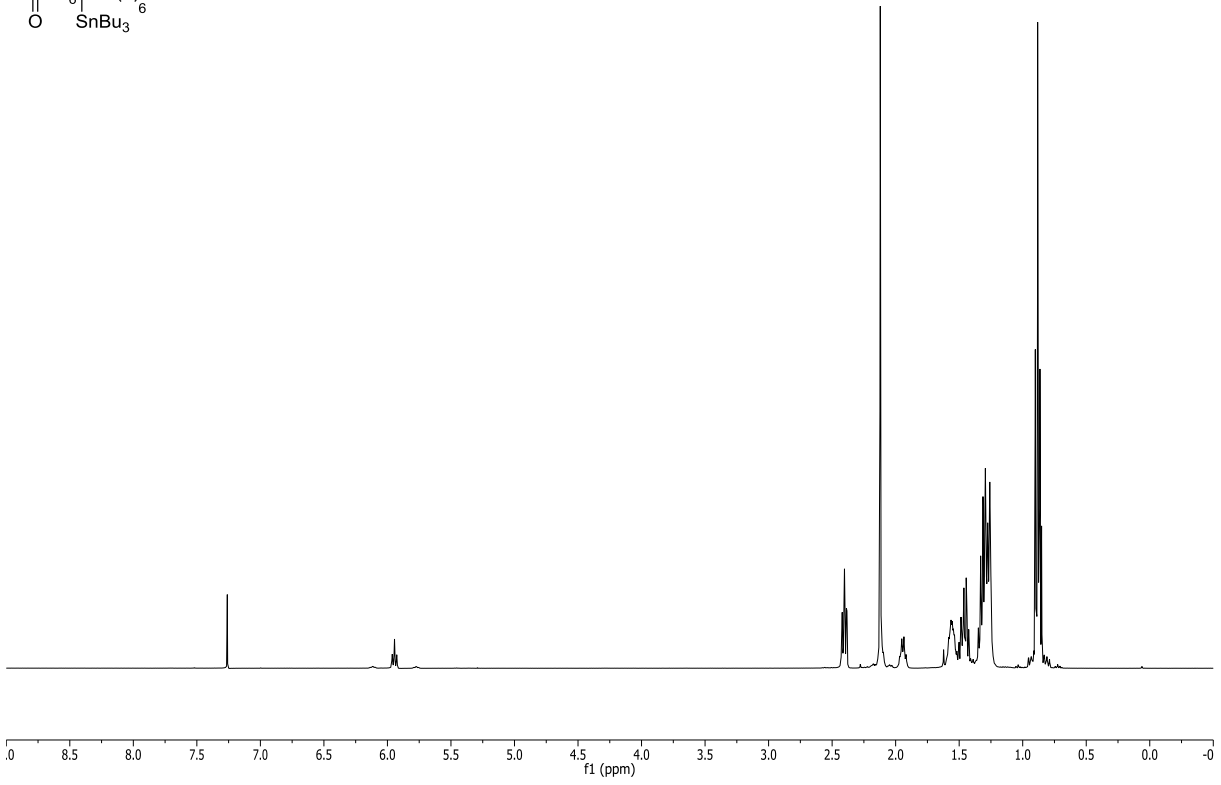
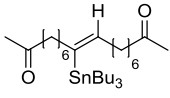


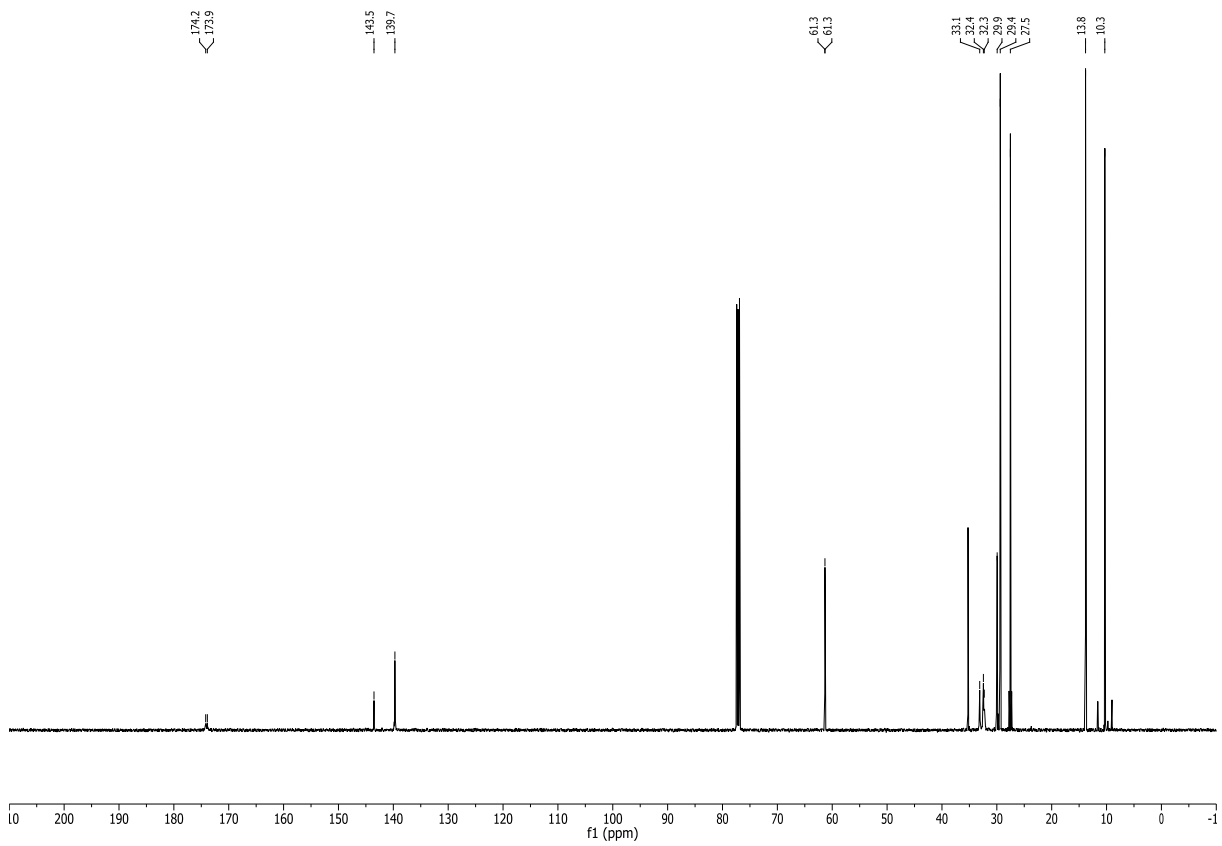
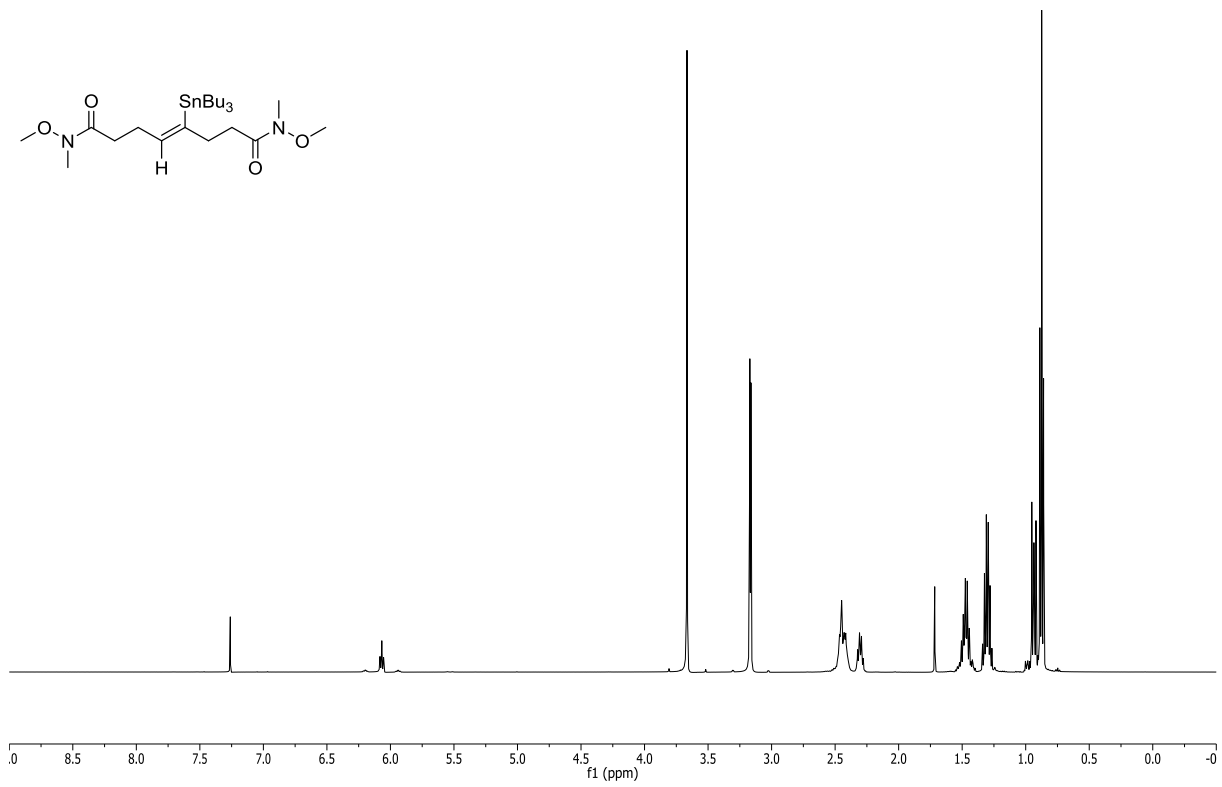
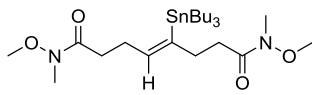


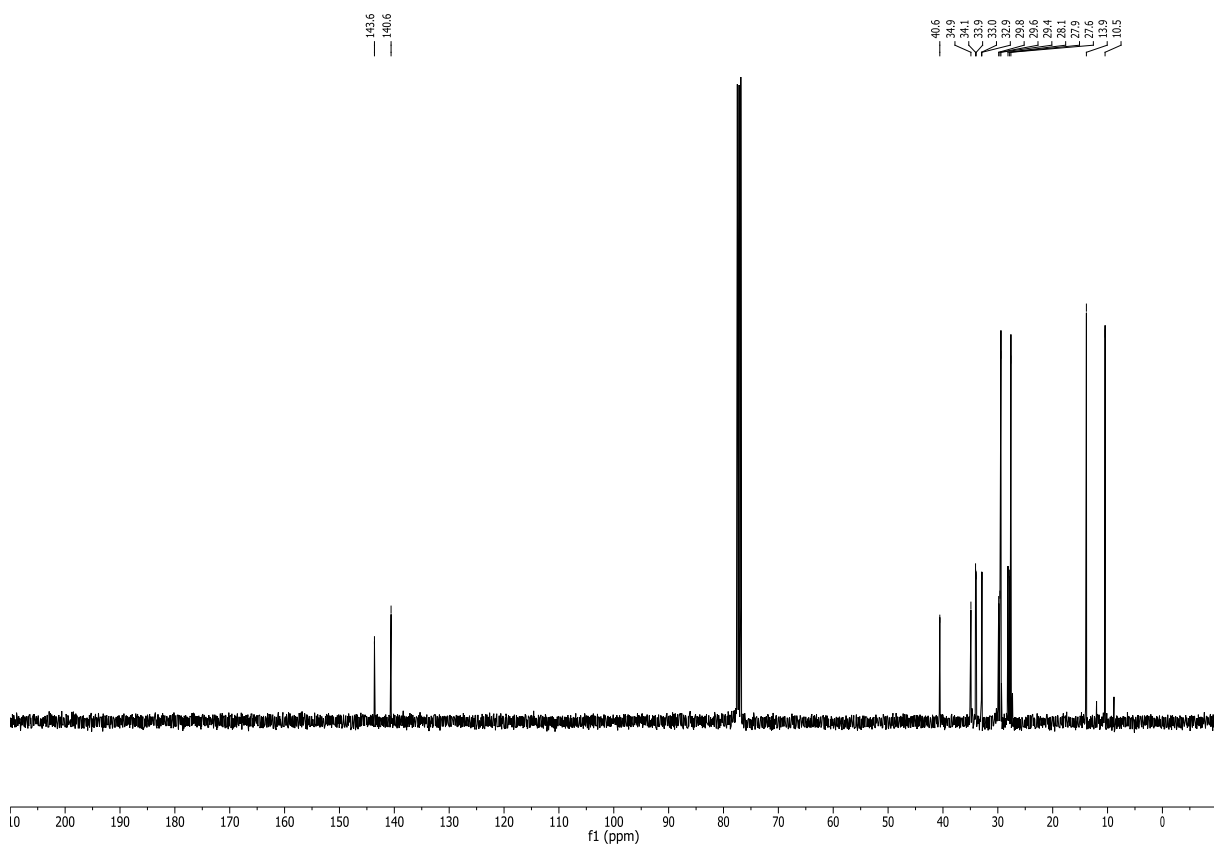
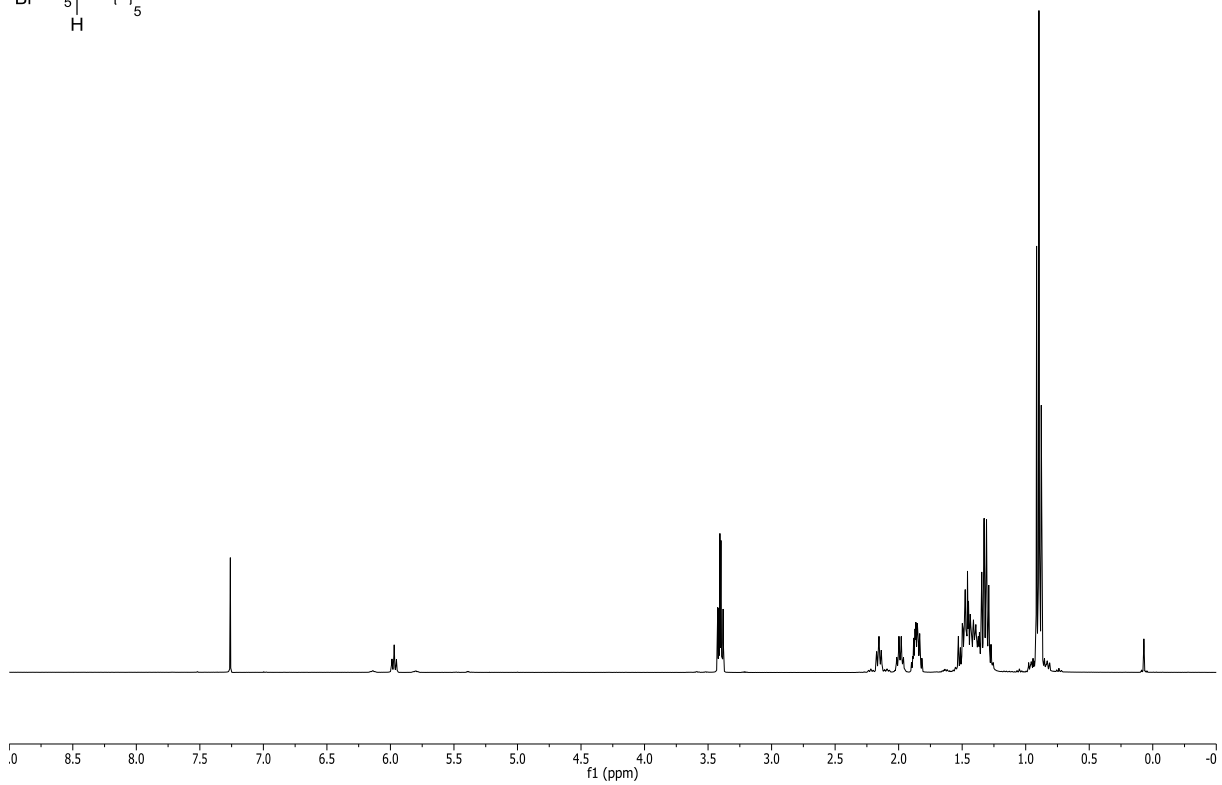
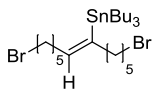


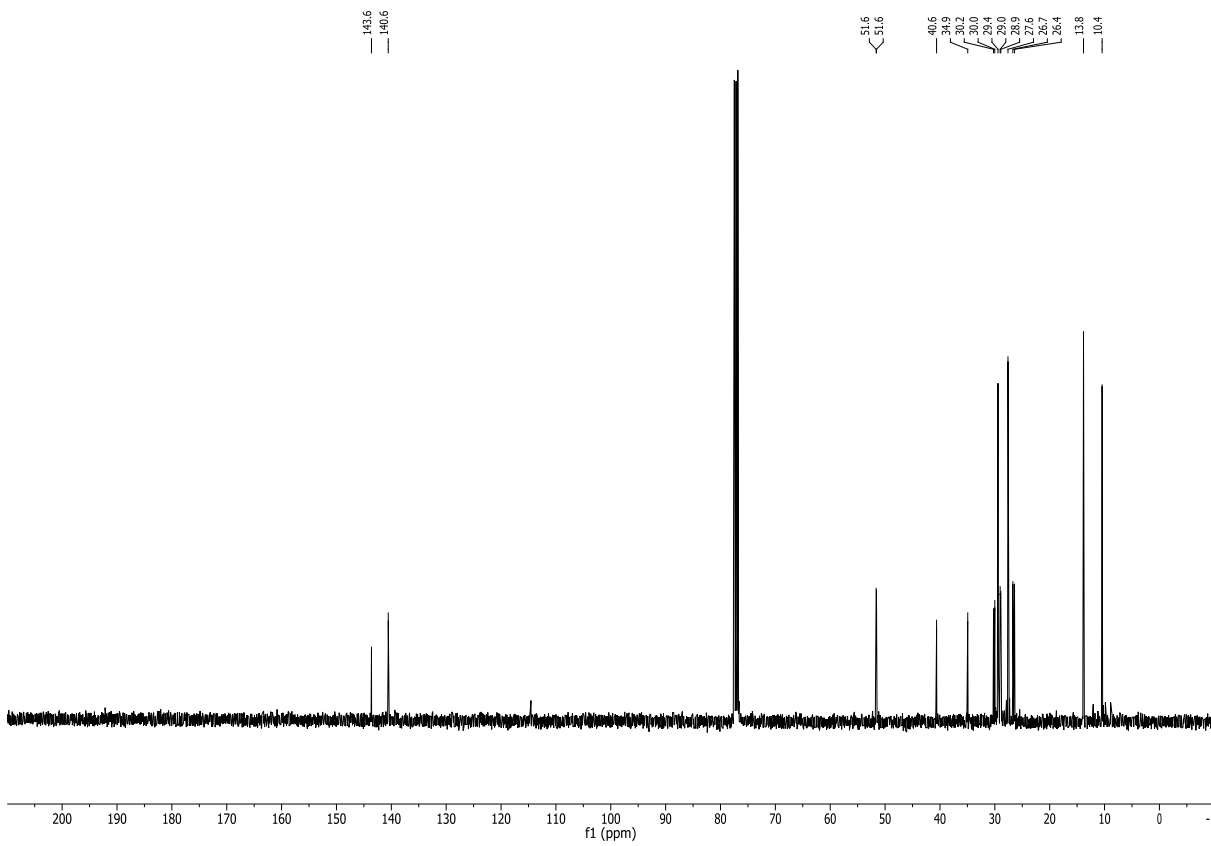
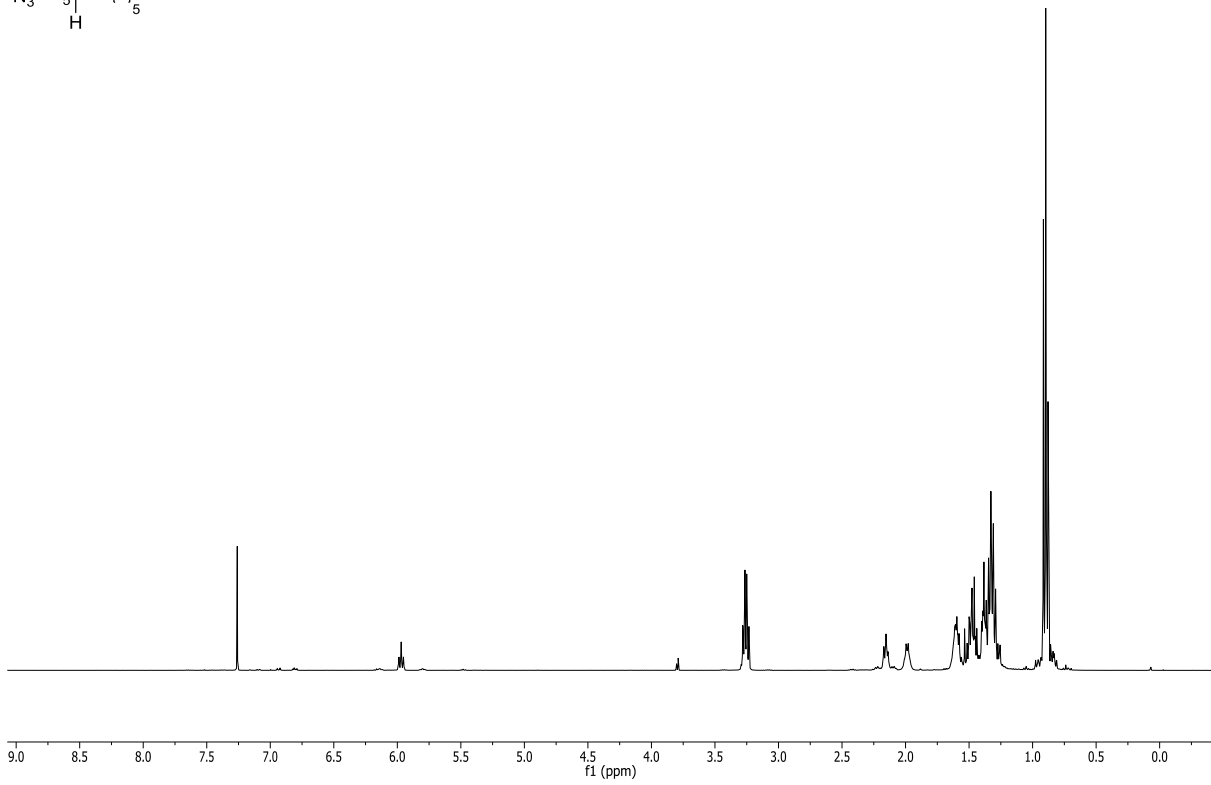
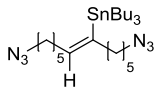


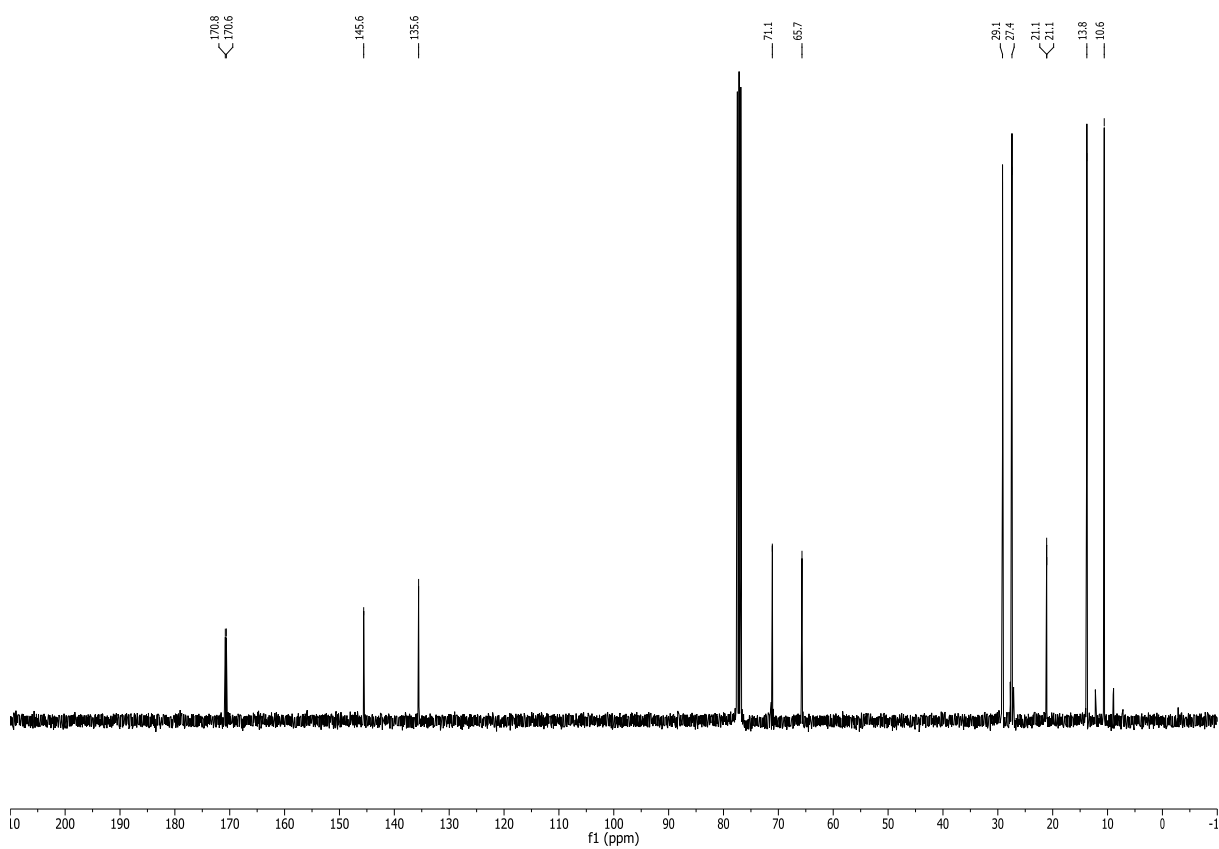
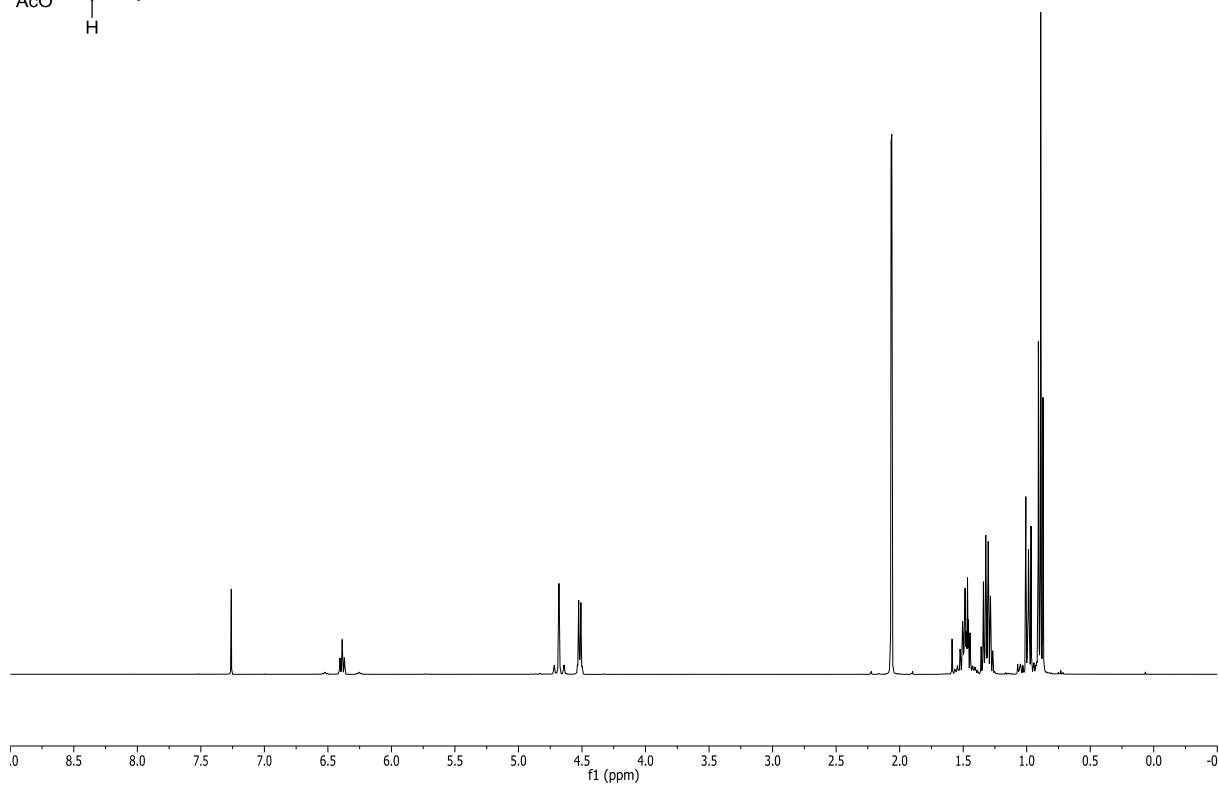
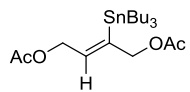


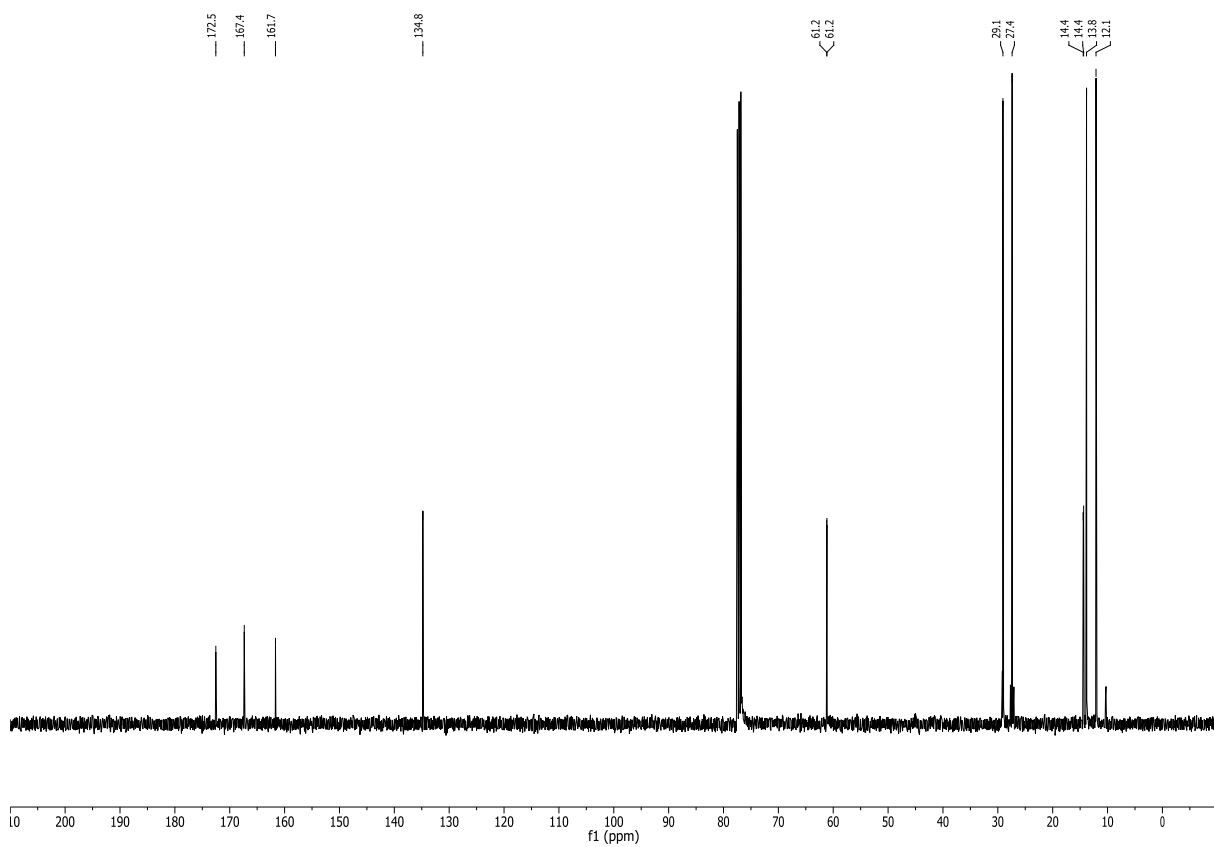
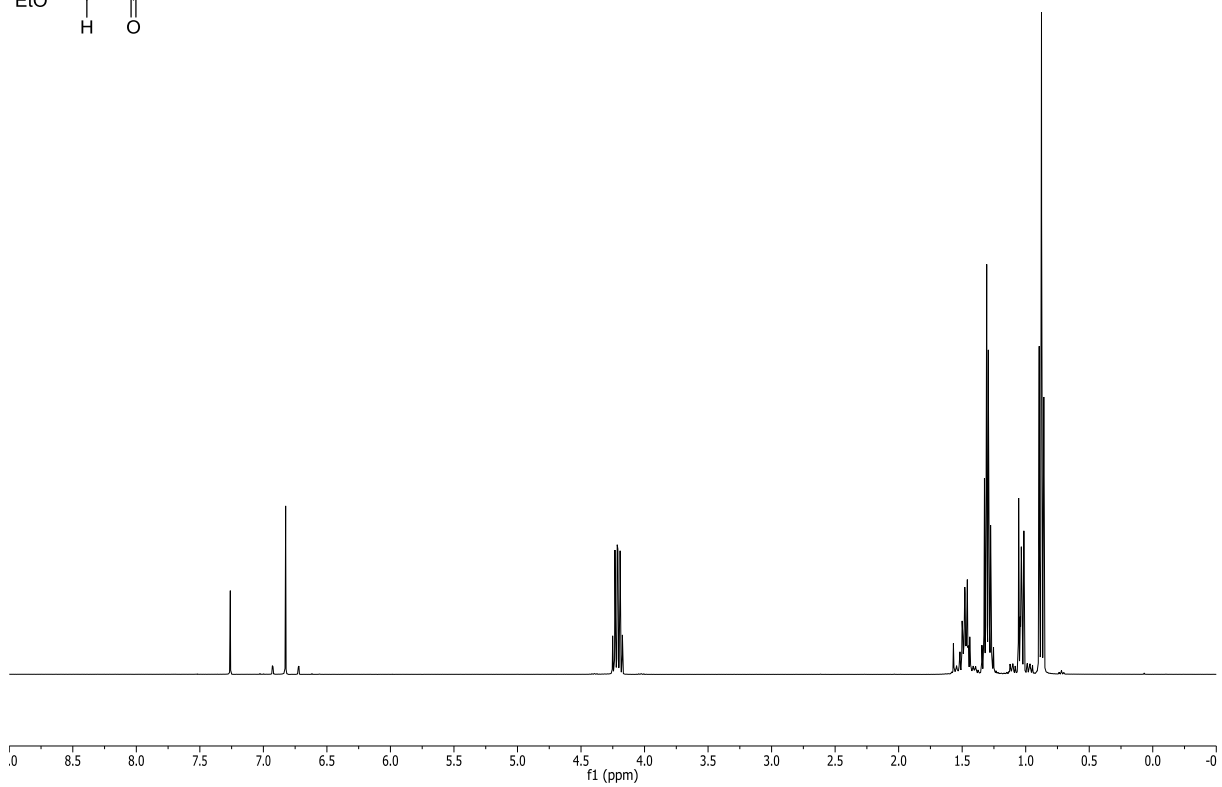
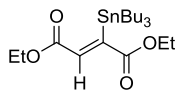


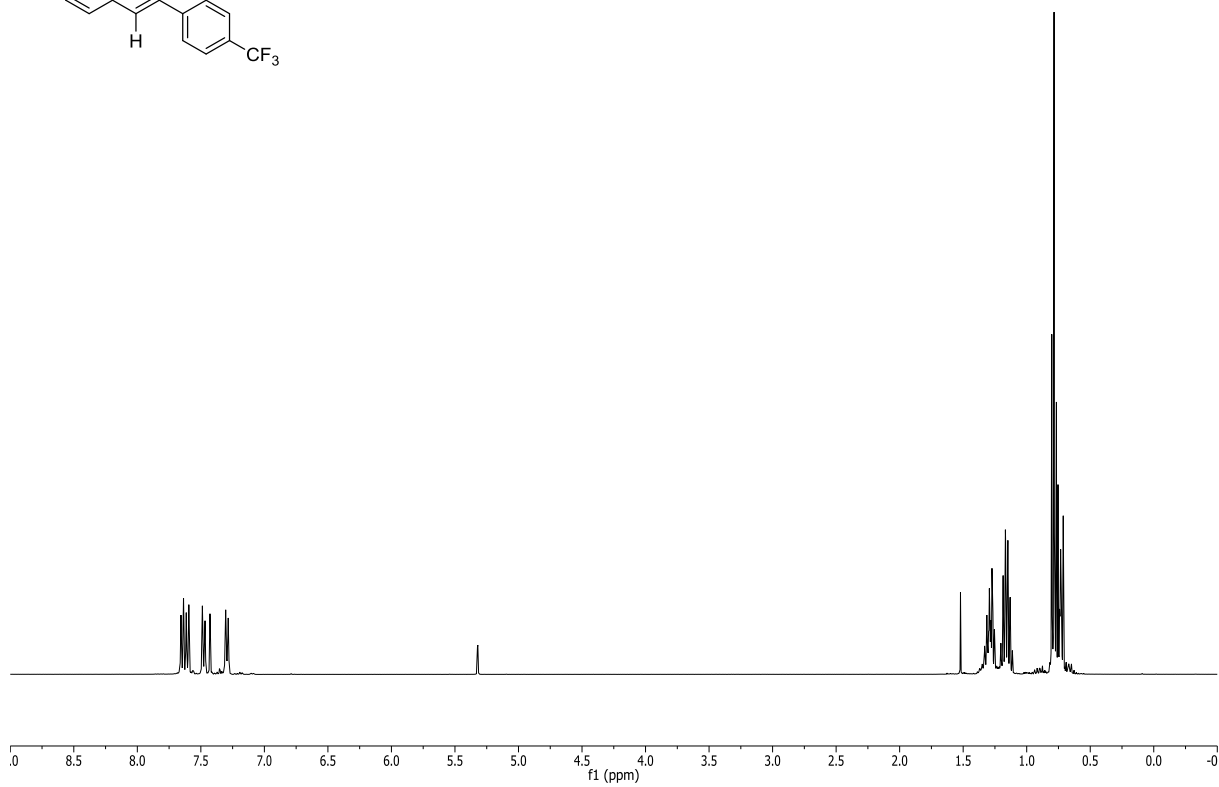
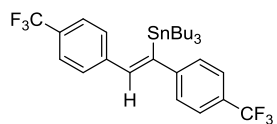




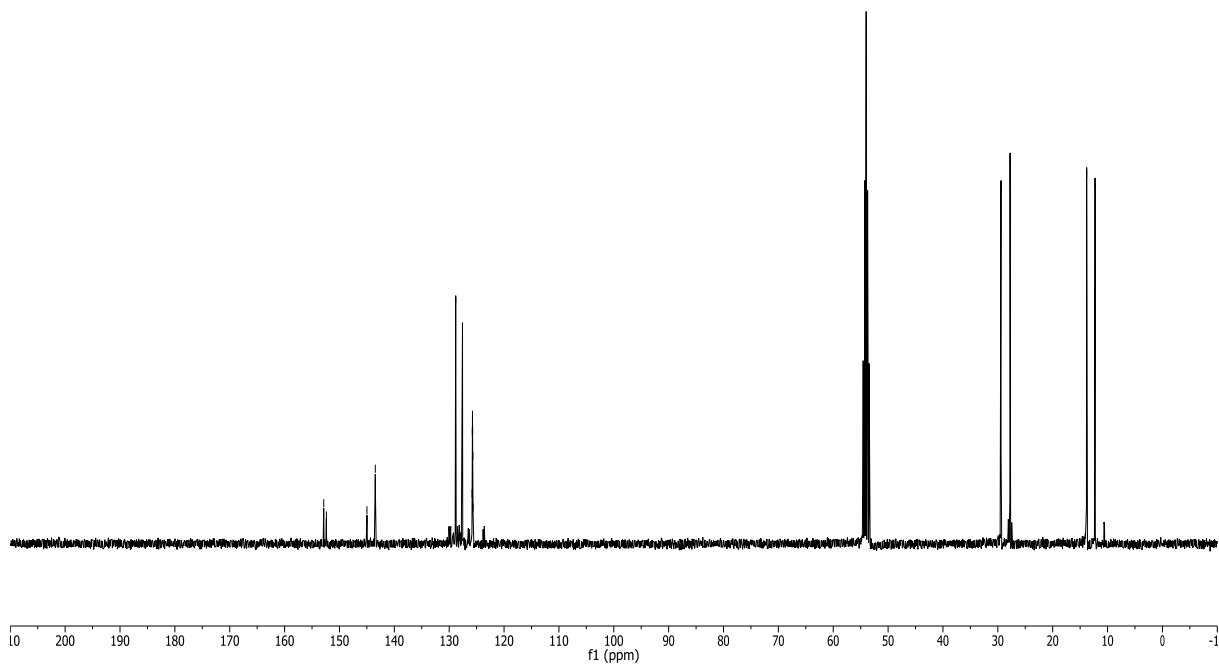


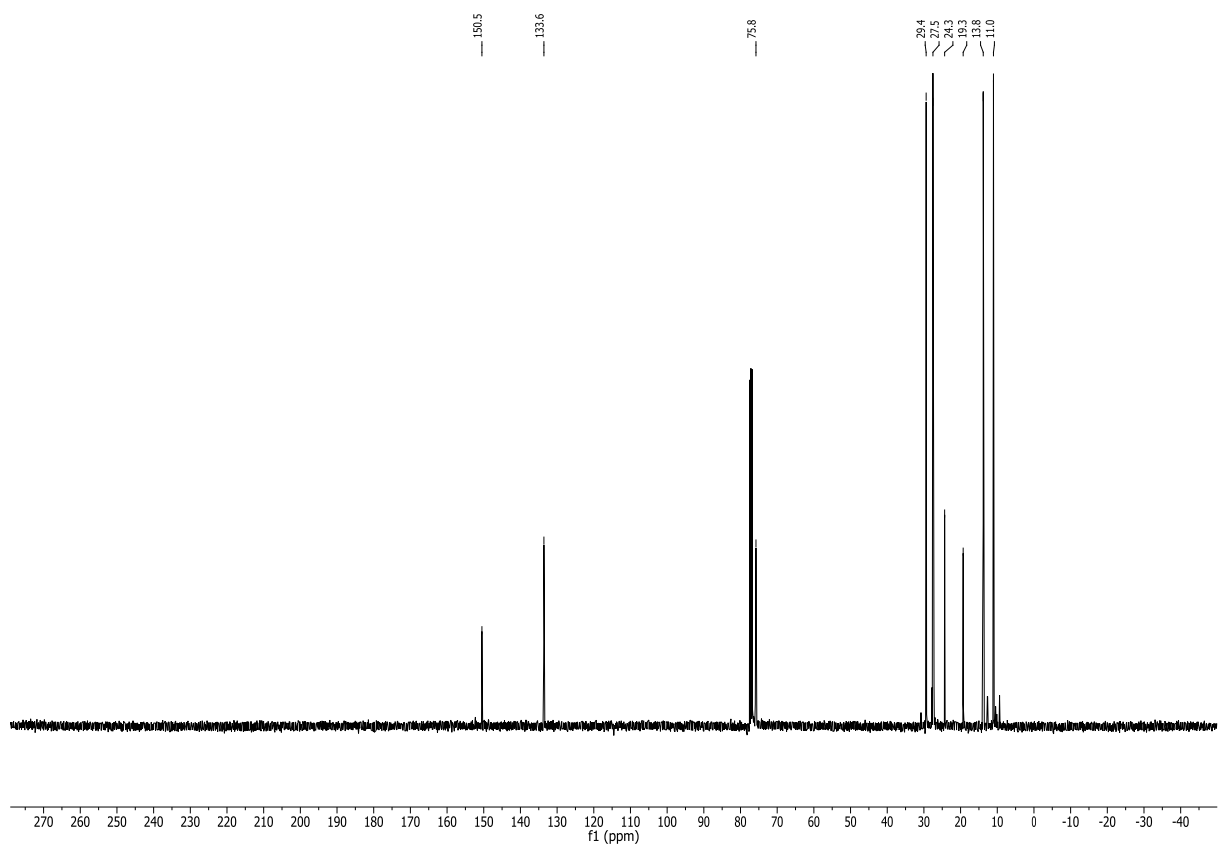
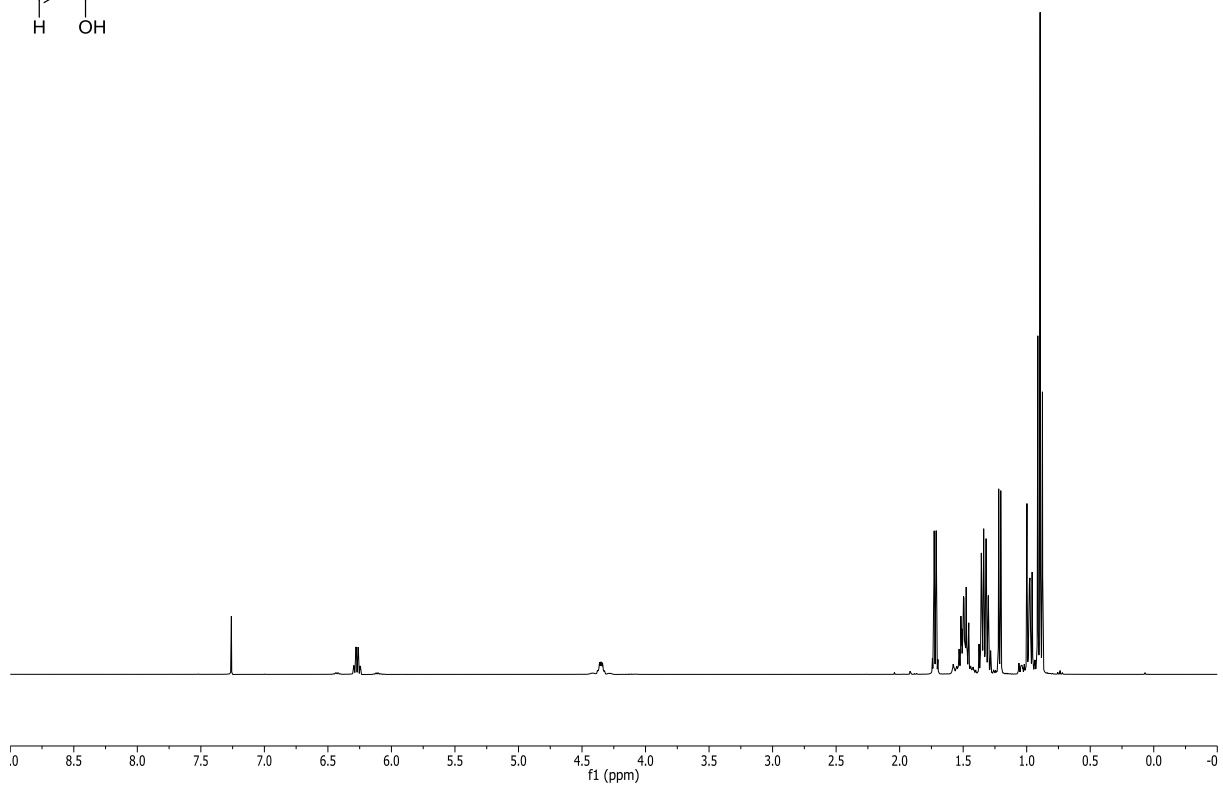
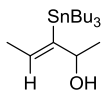


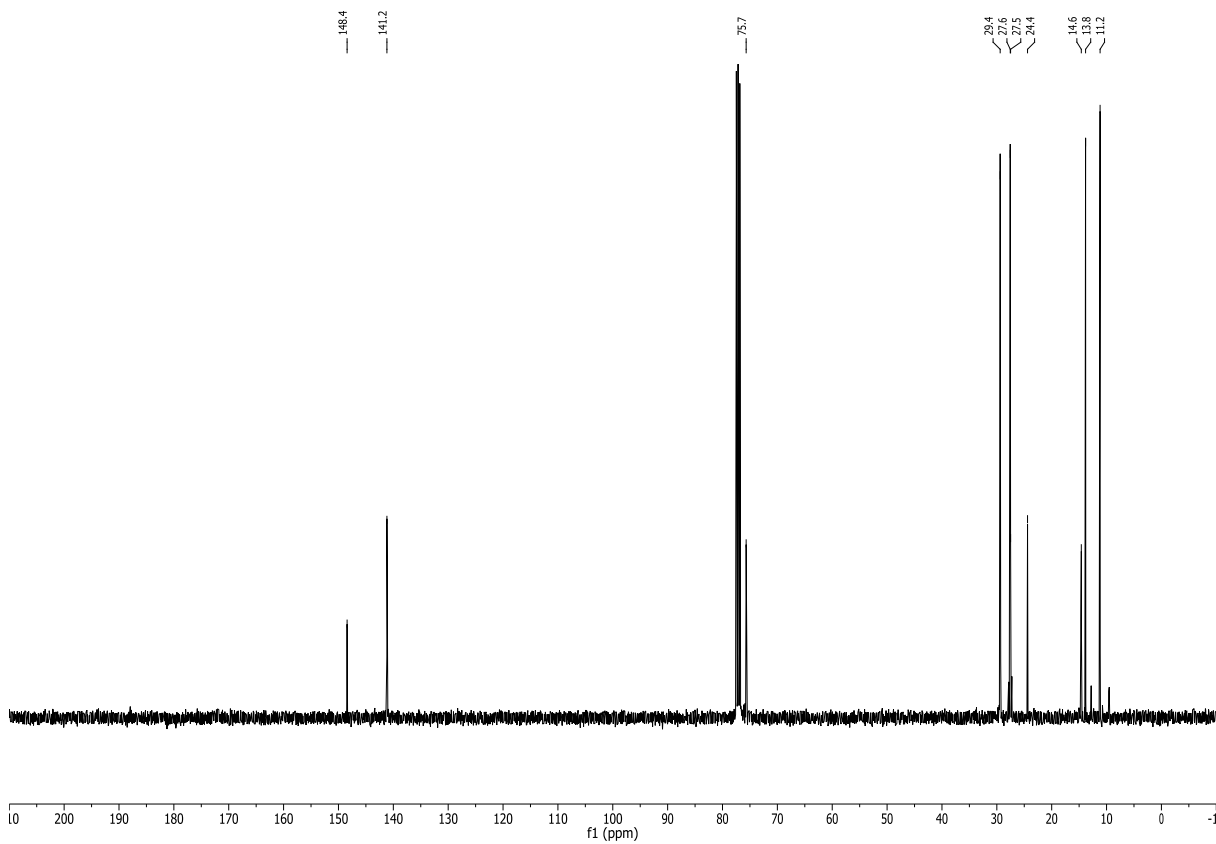
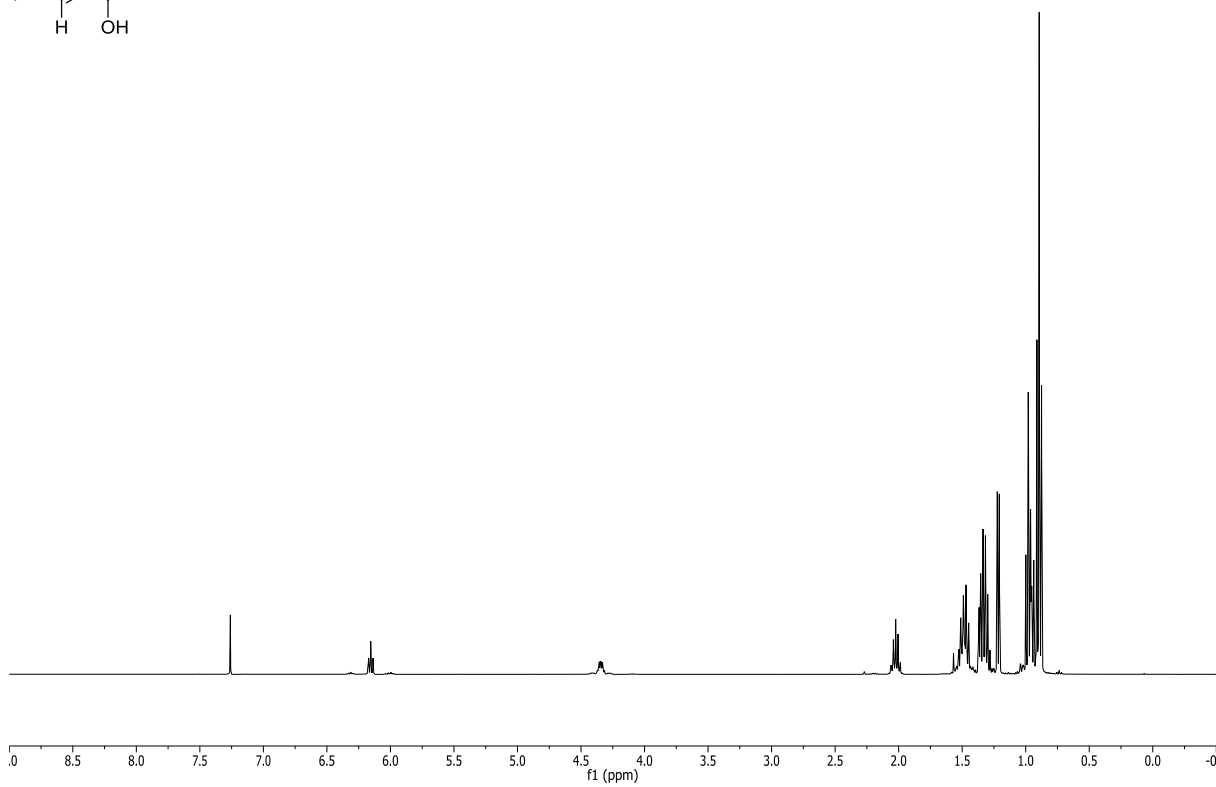
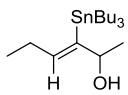


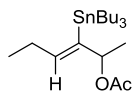


152.9
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13.3

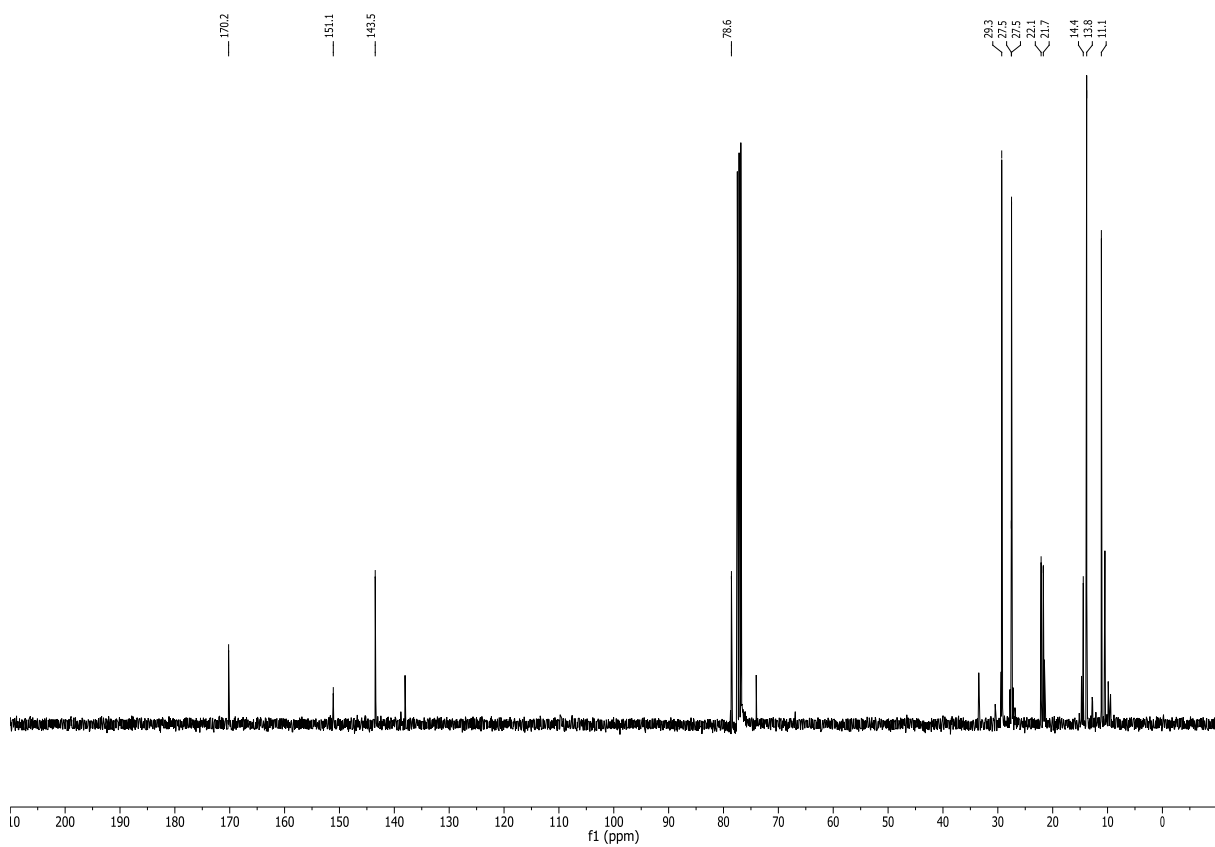
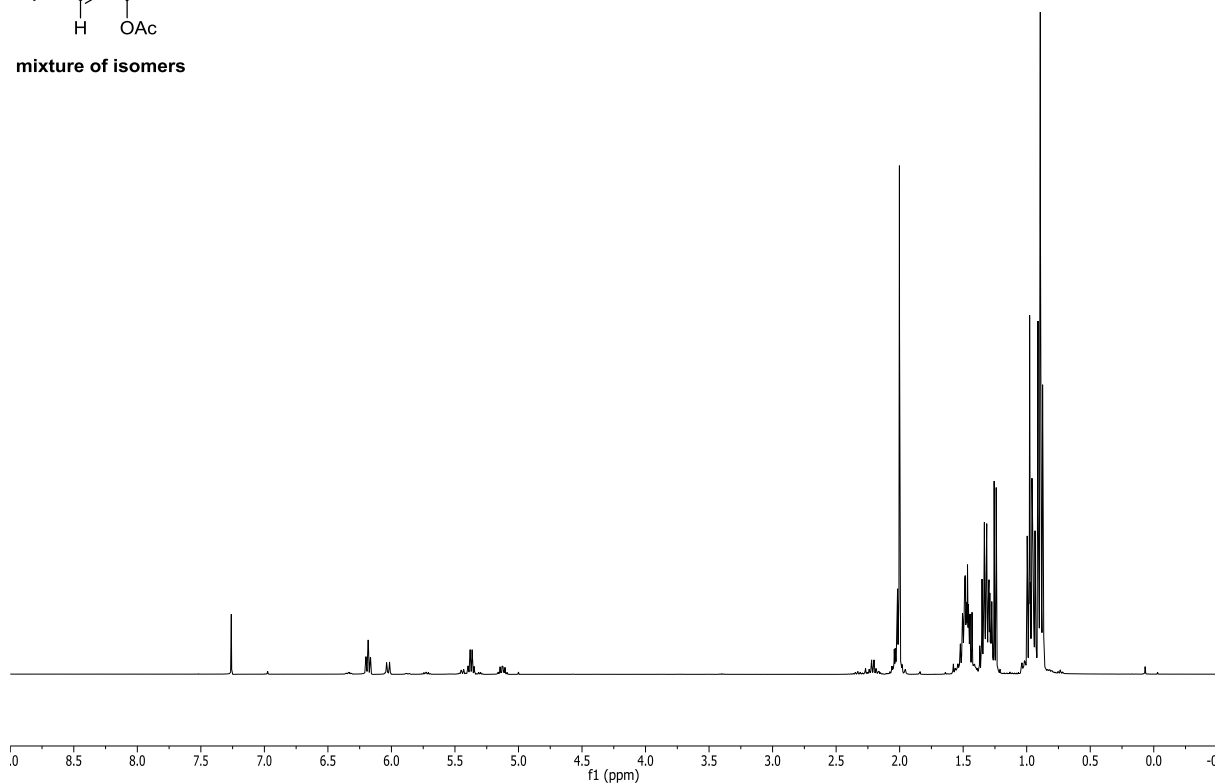


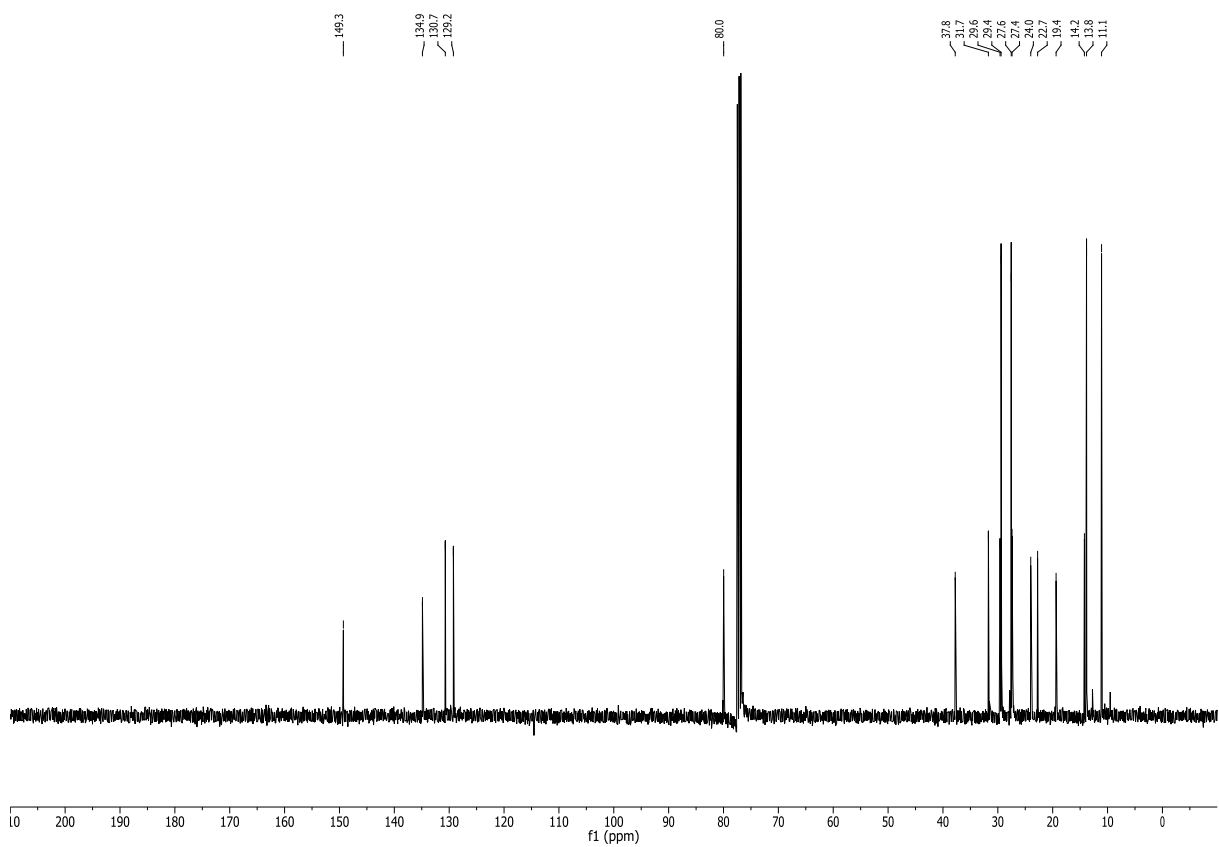
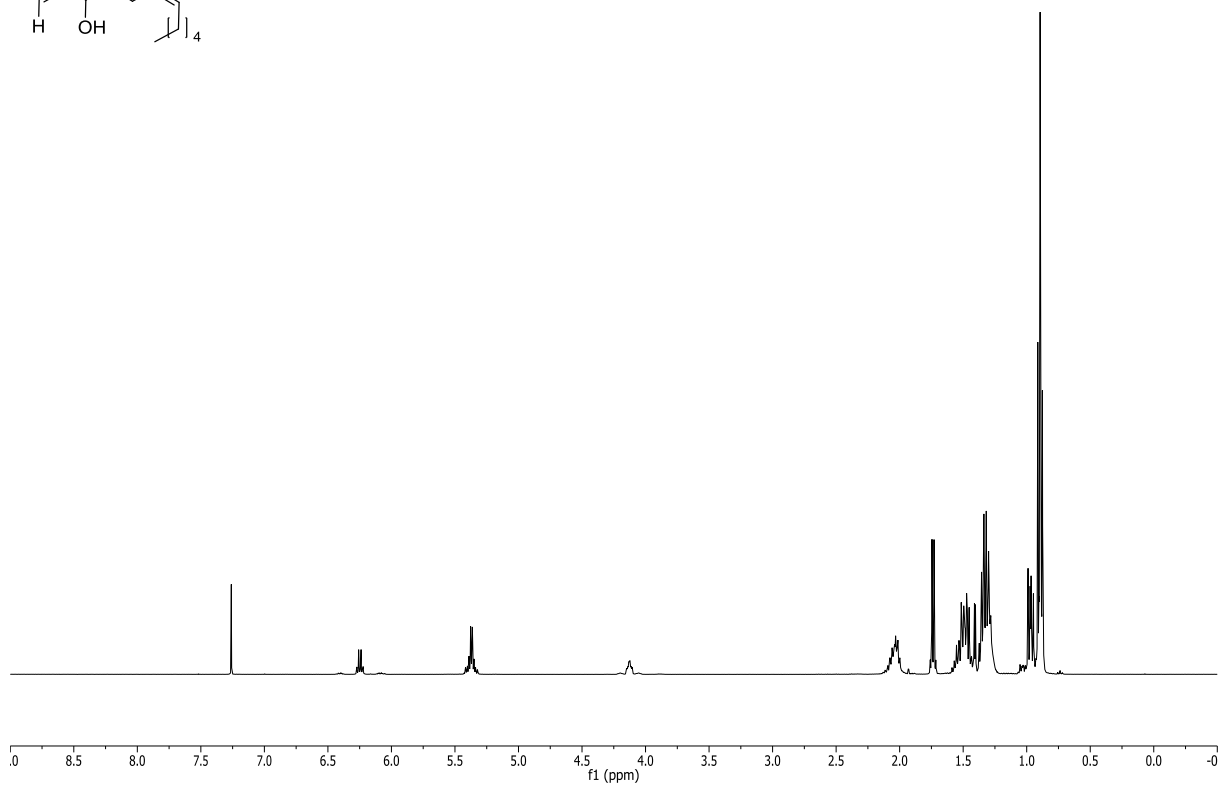
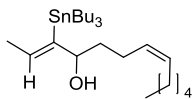


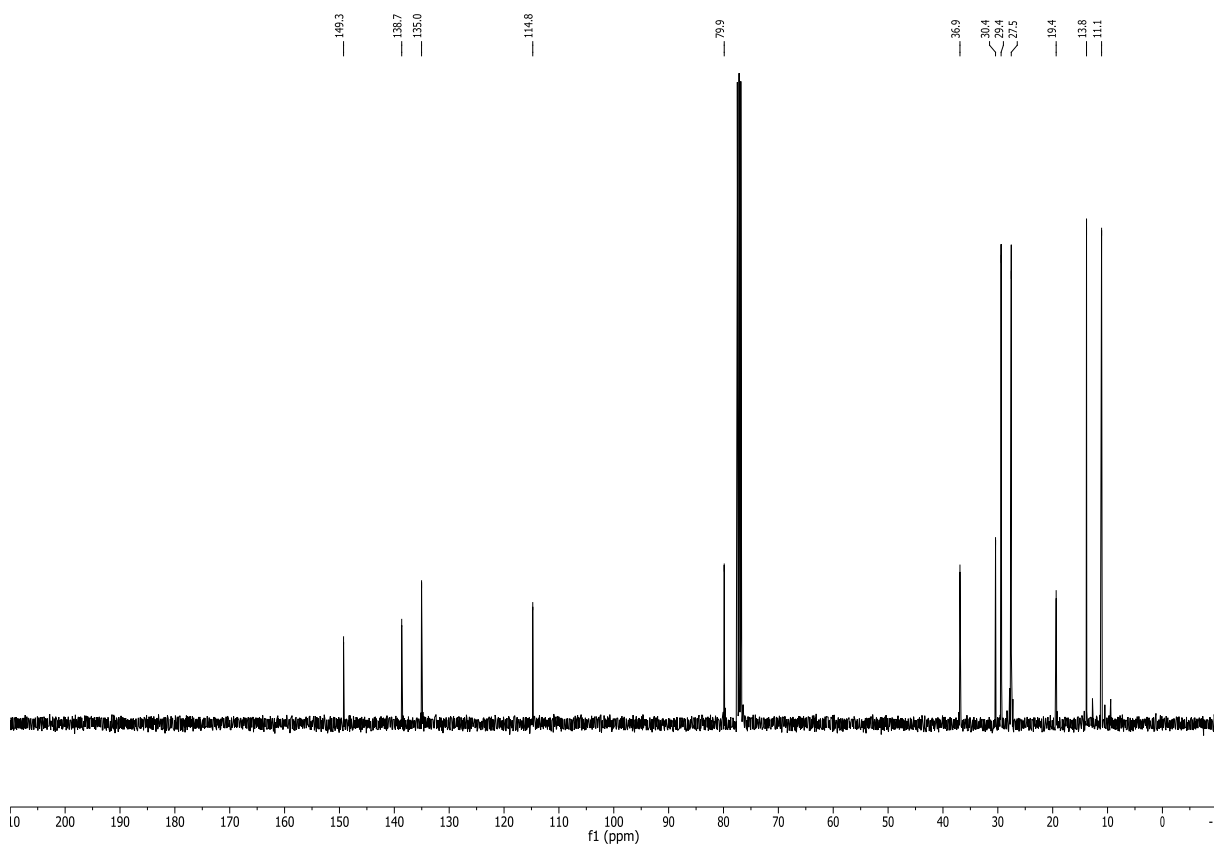
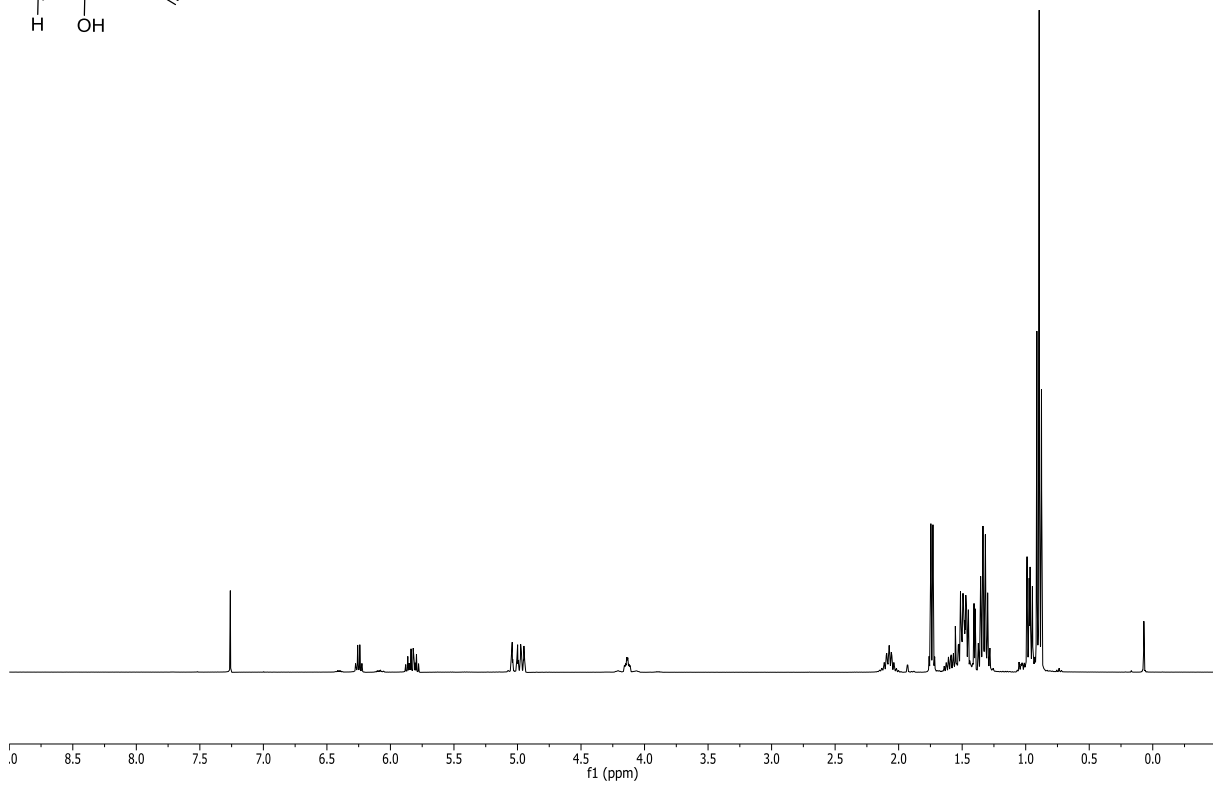
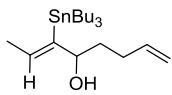


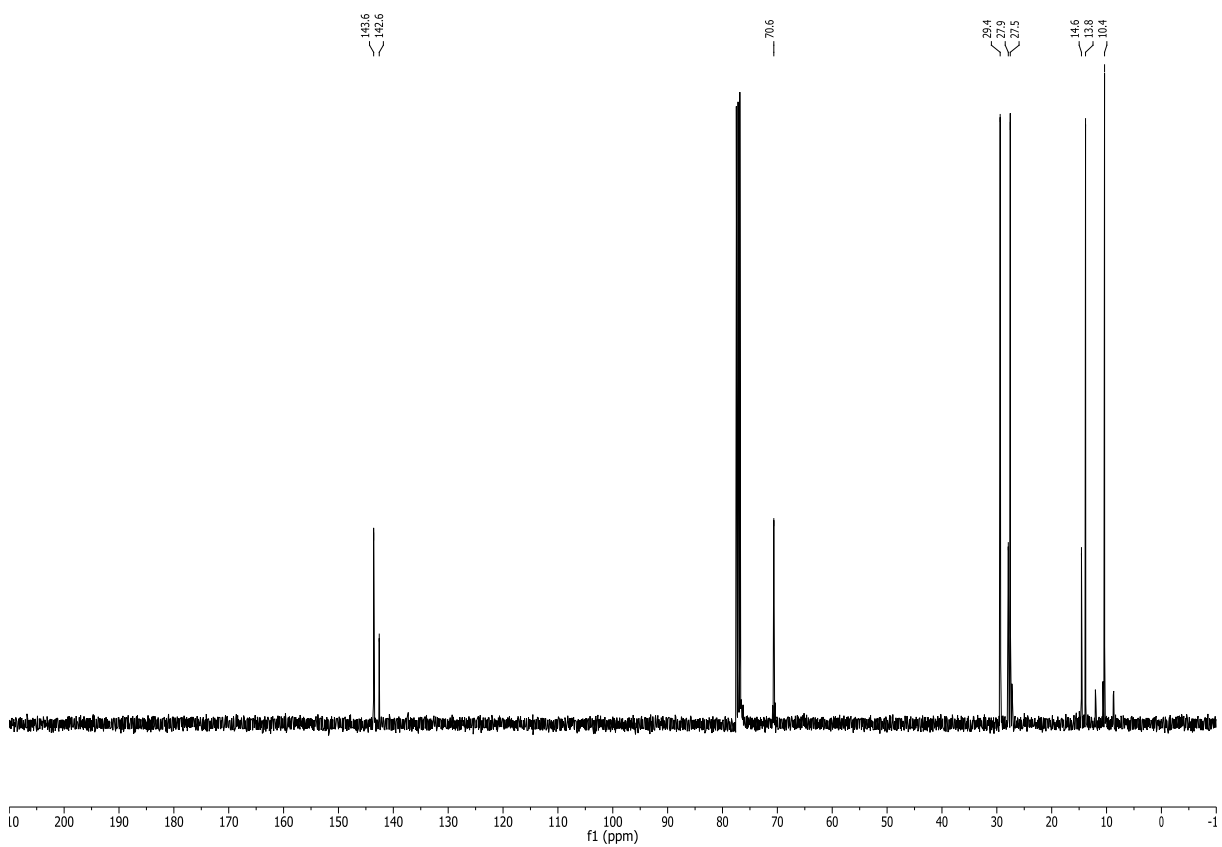
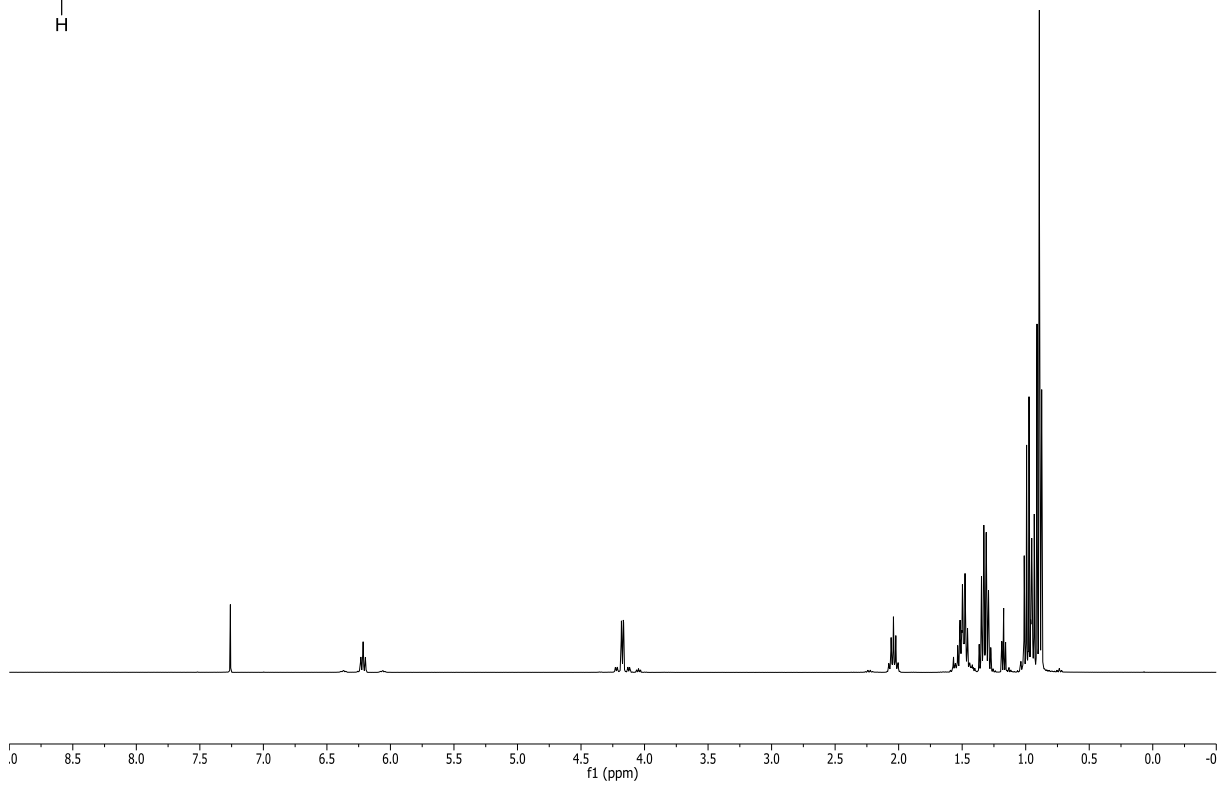
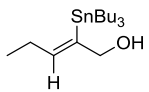


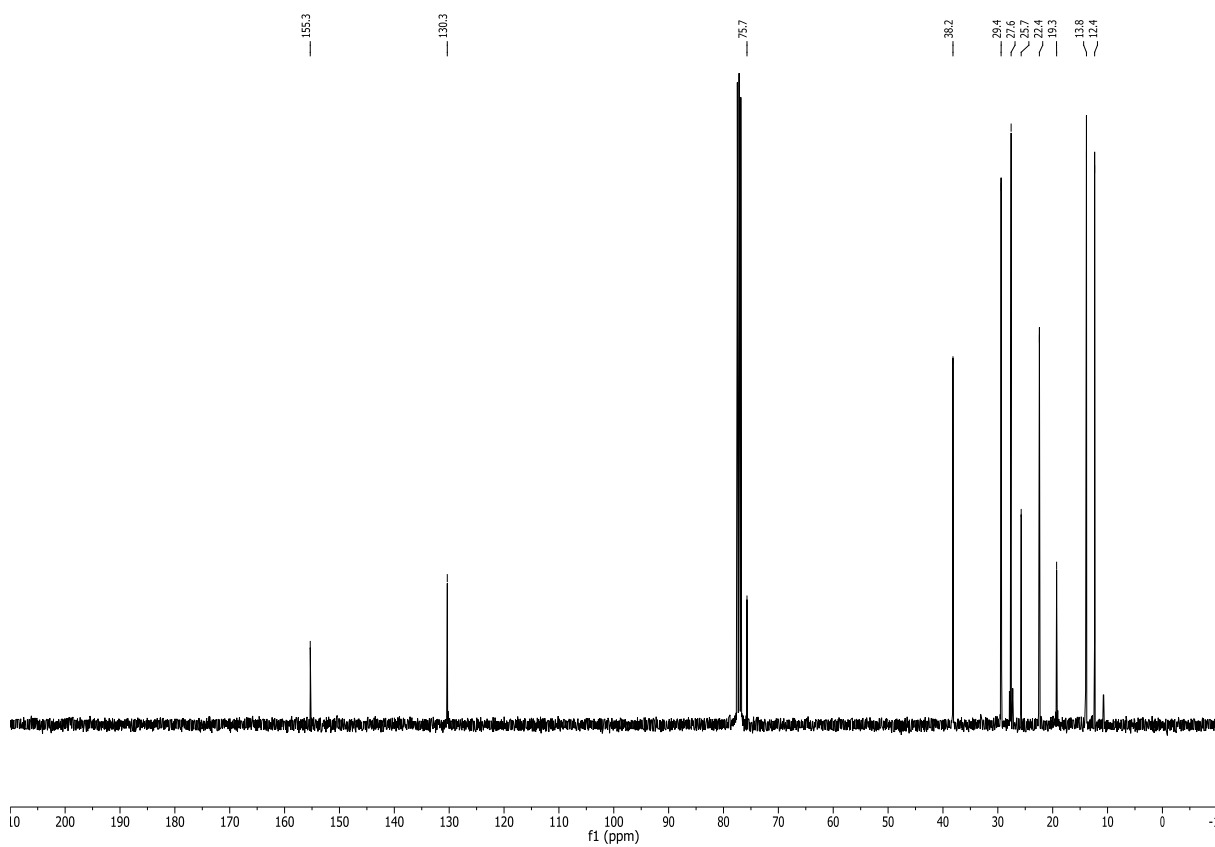
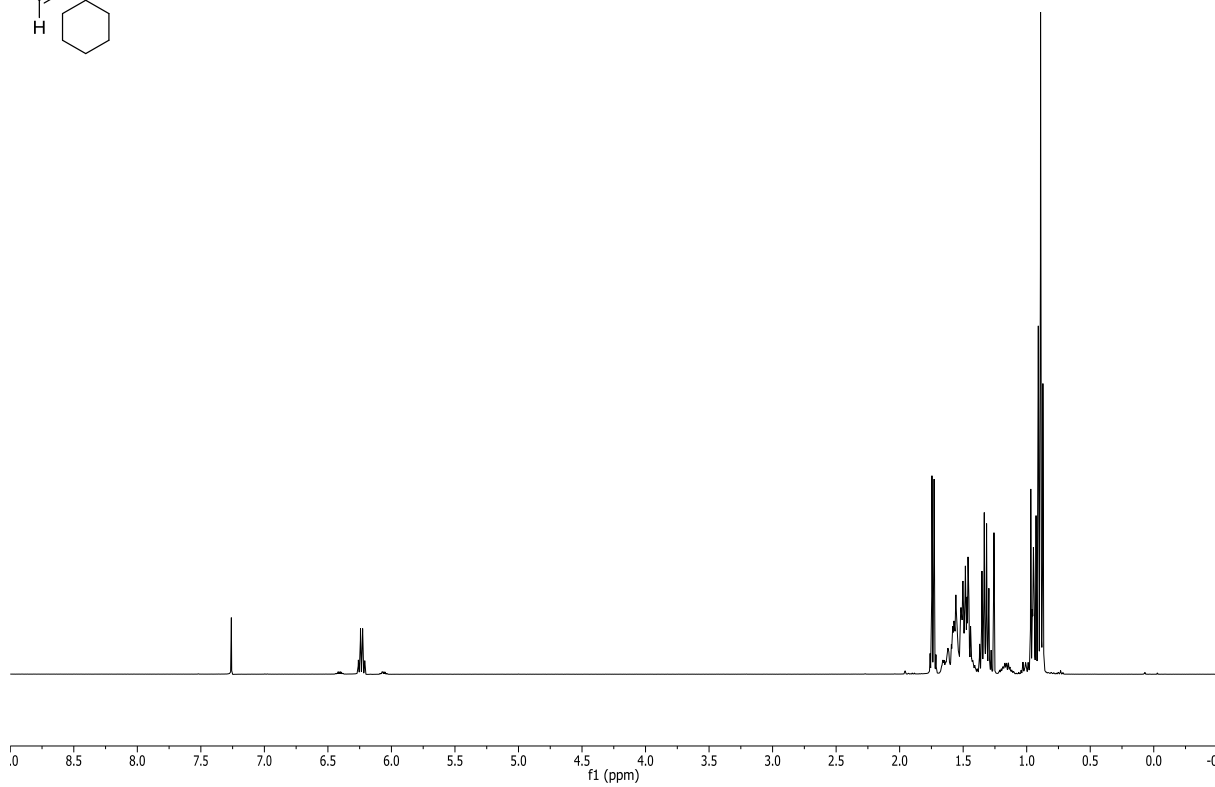
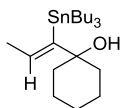
mixture of isomers

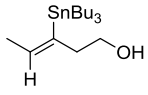




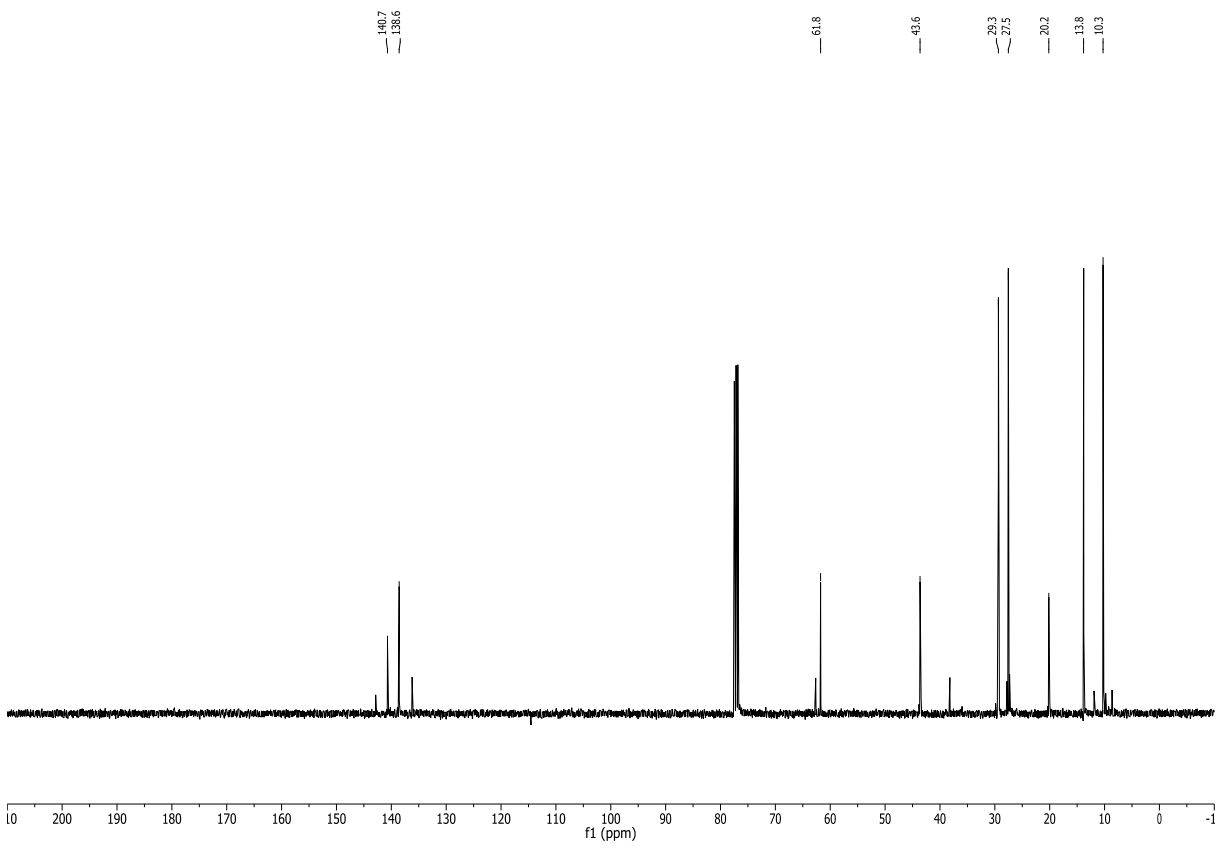
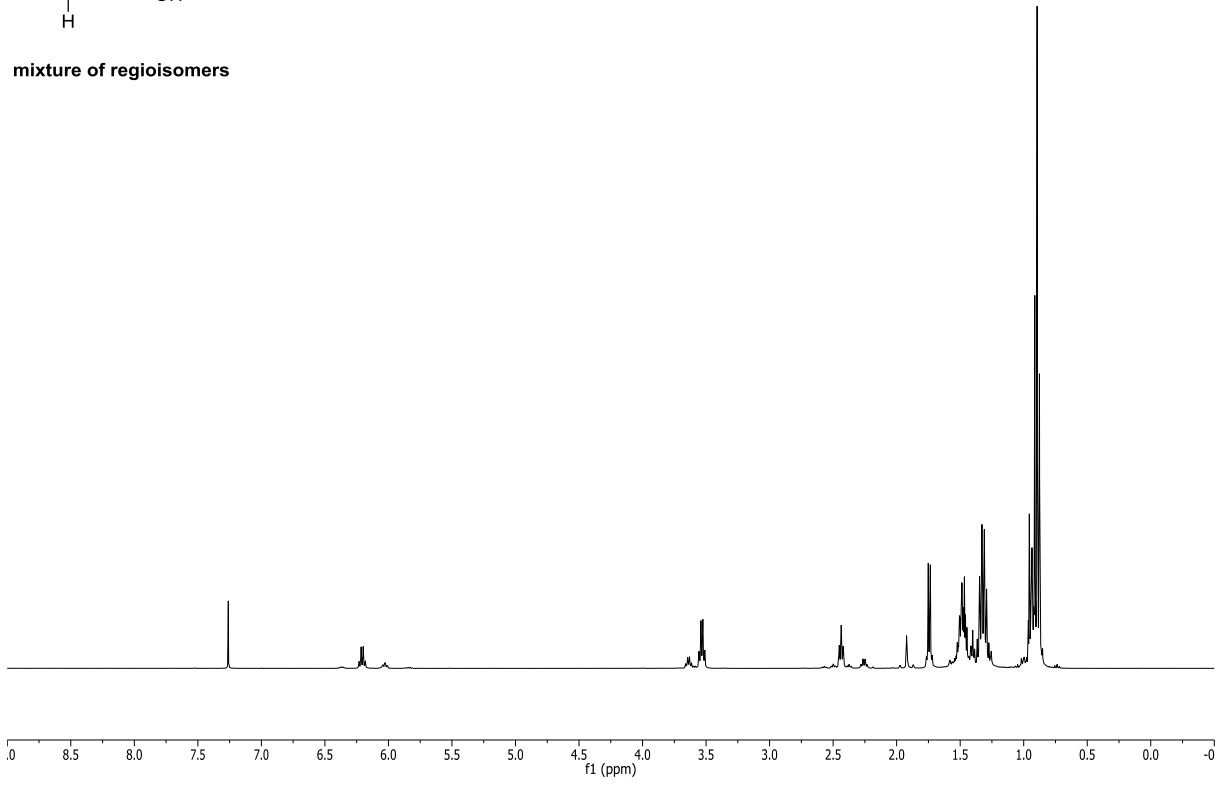


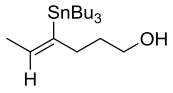




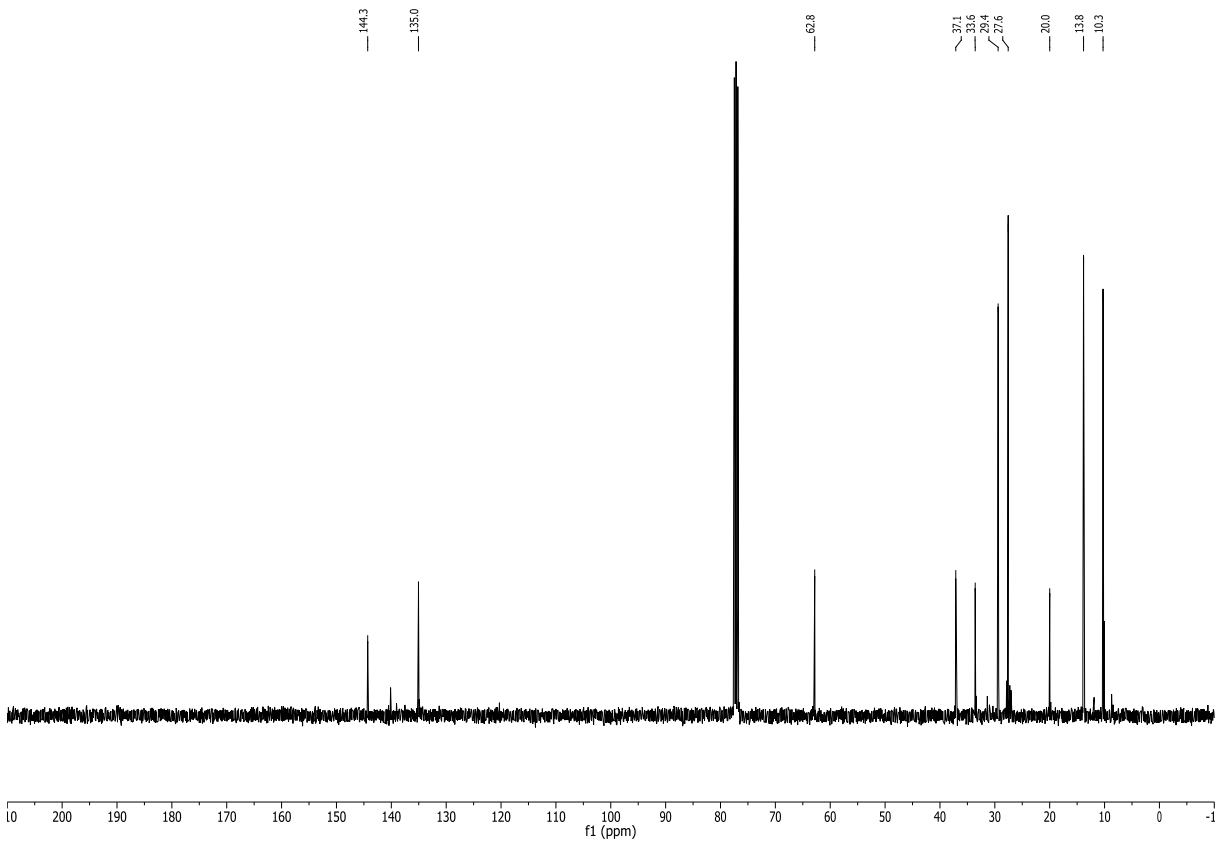
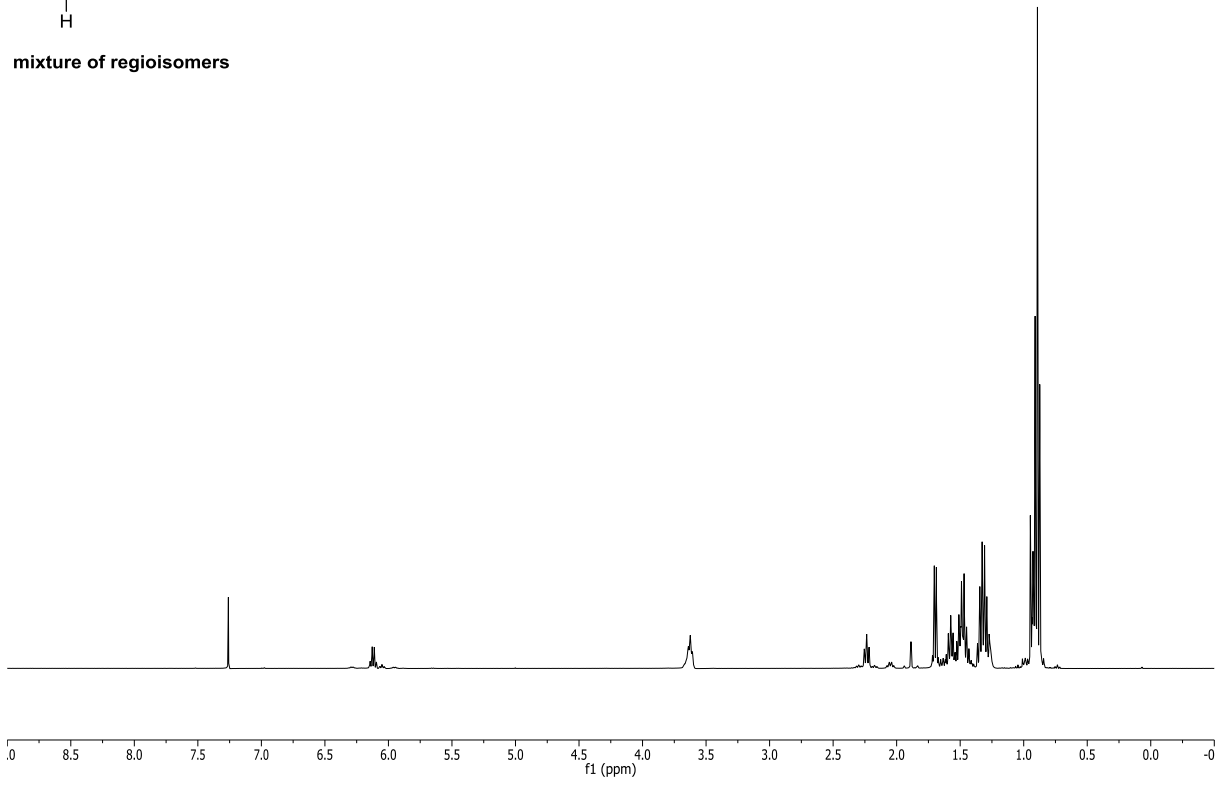


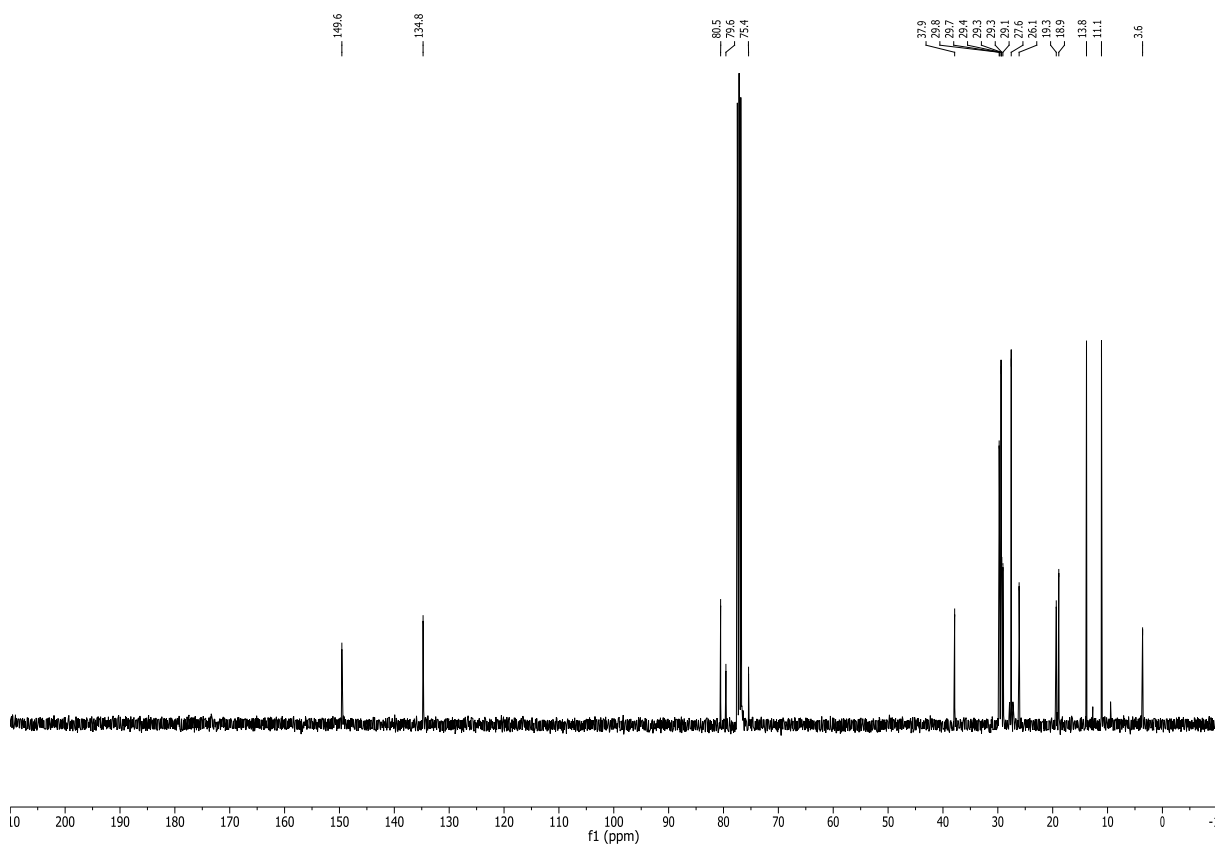
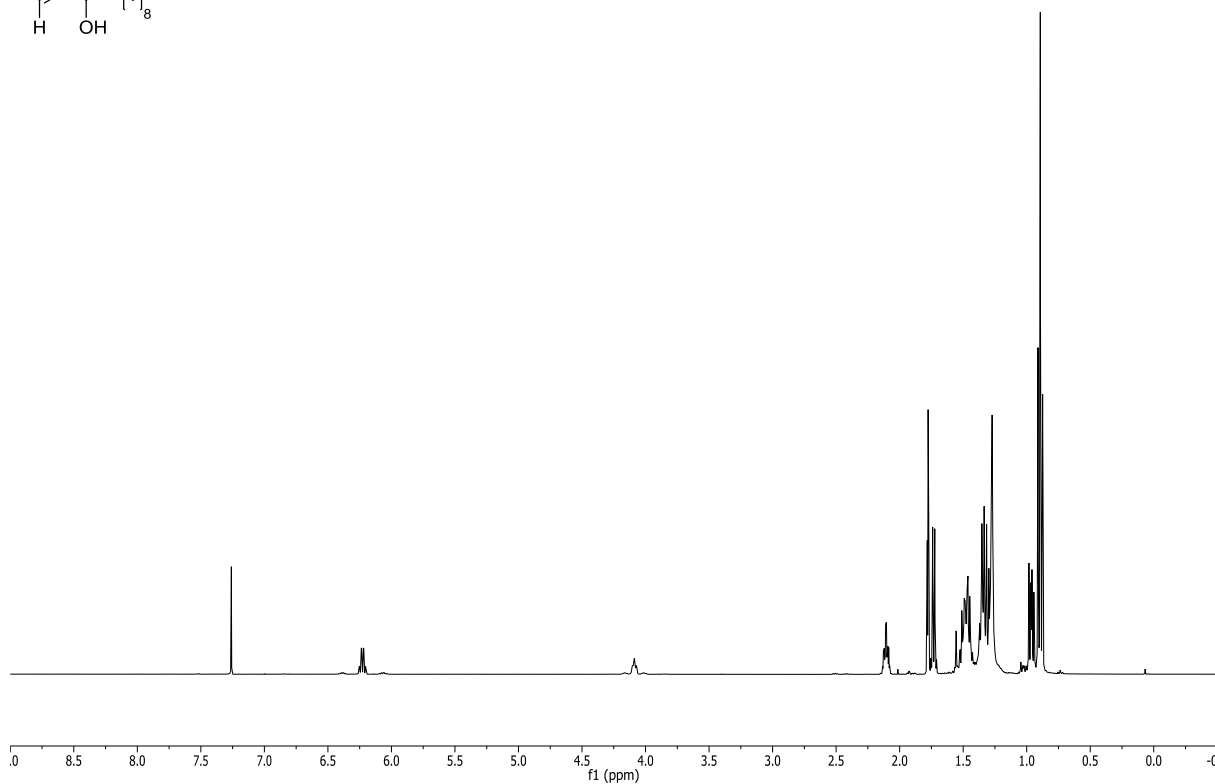
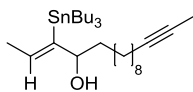
mixture of regioisomers

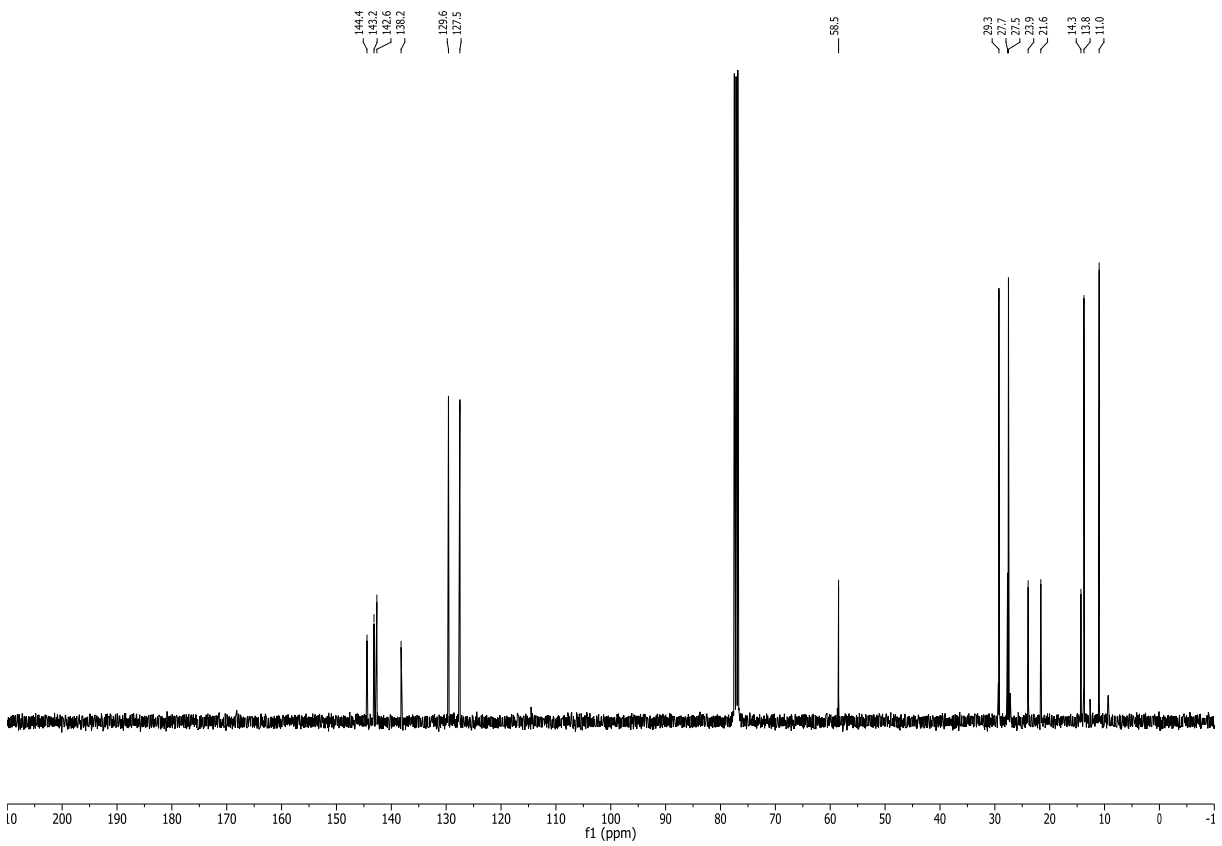
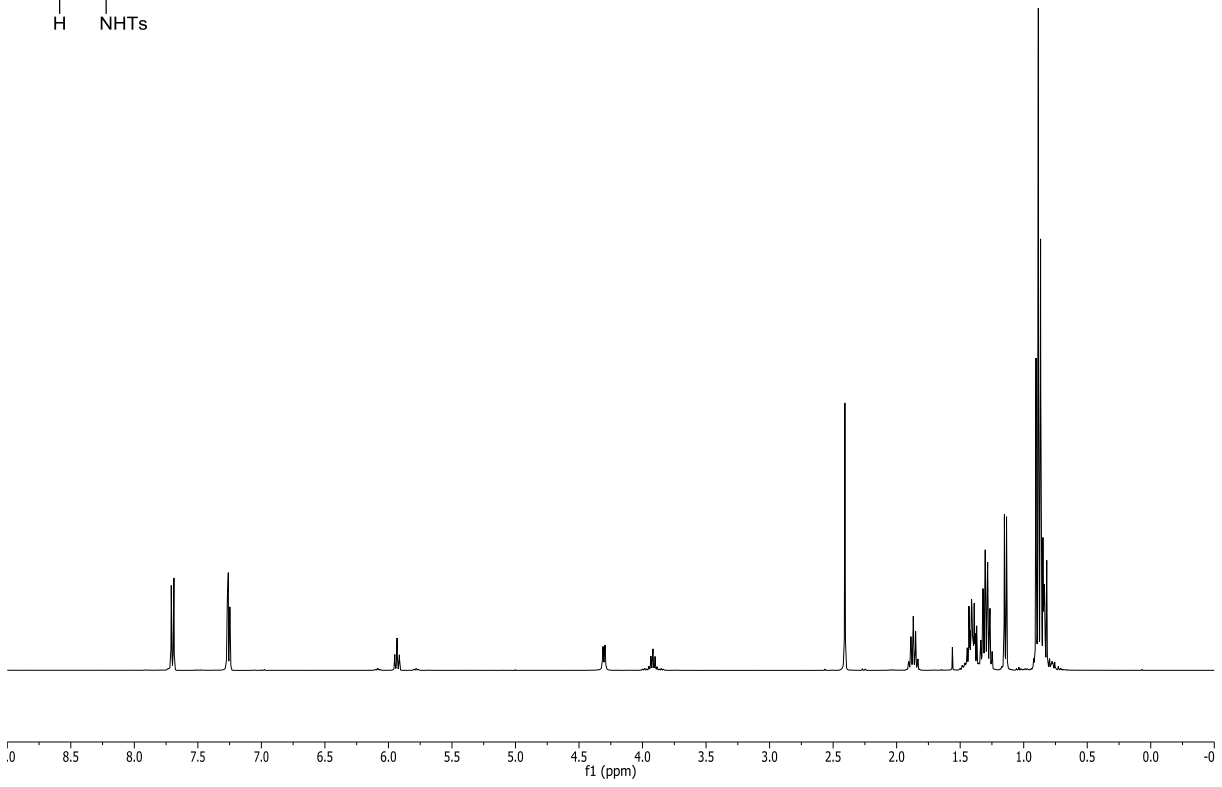
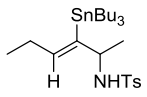


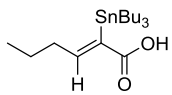


mixture of regioisomers

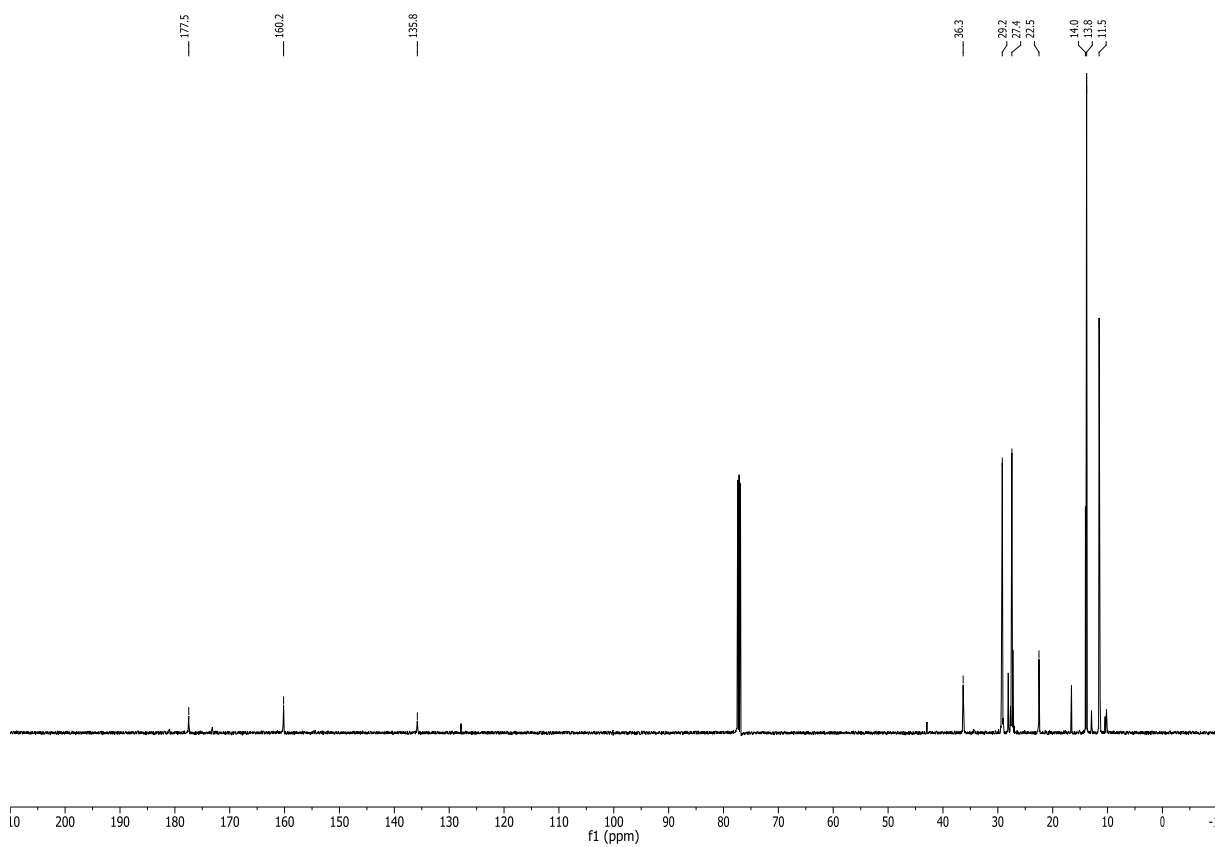
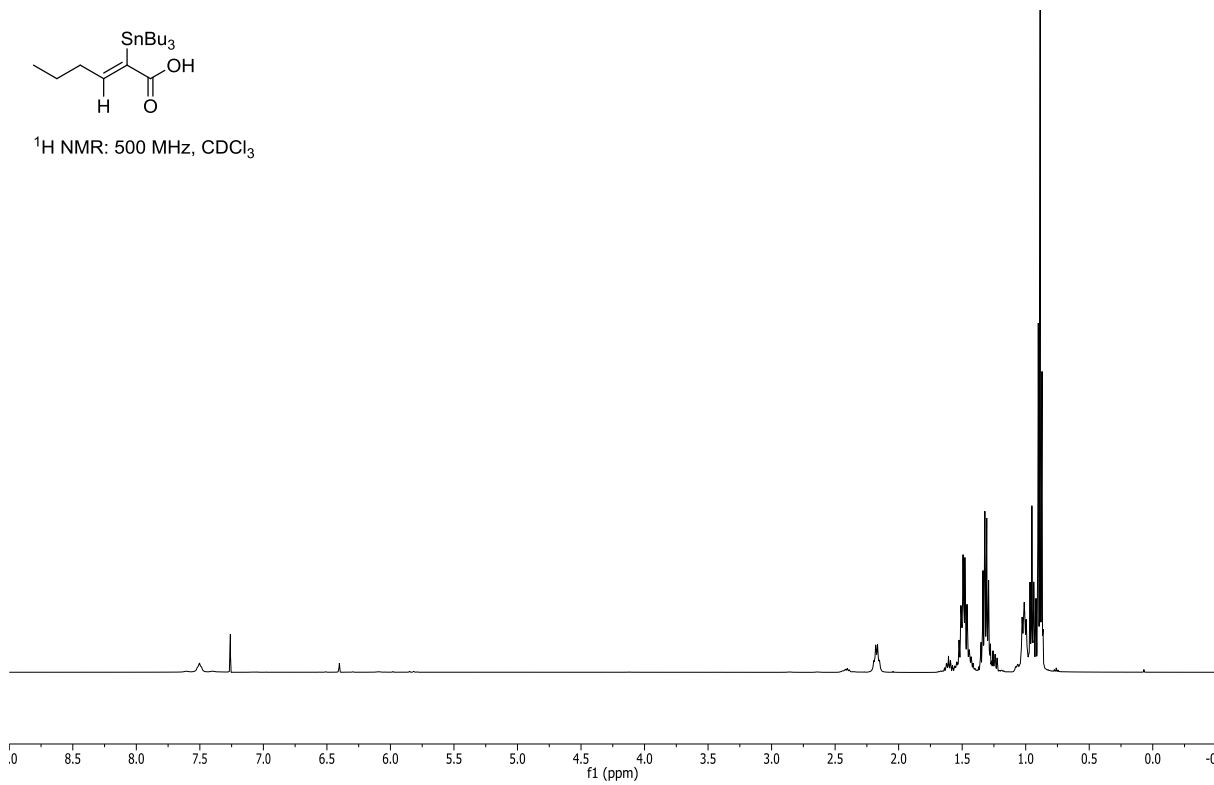


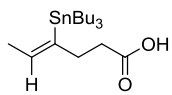




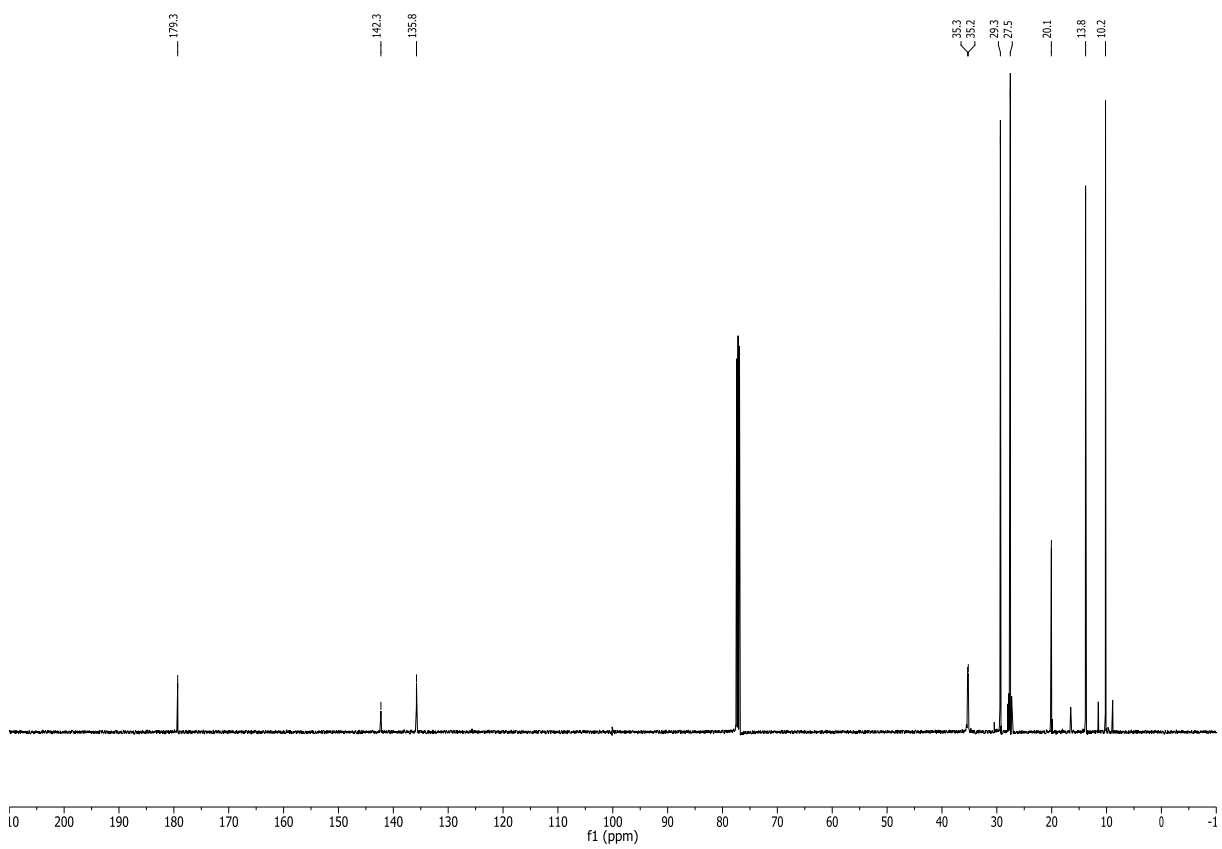
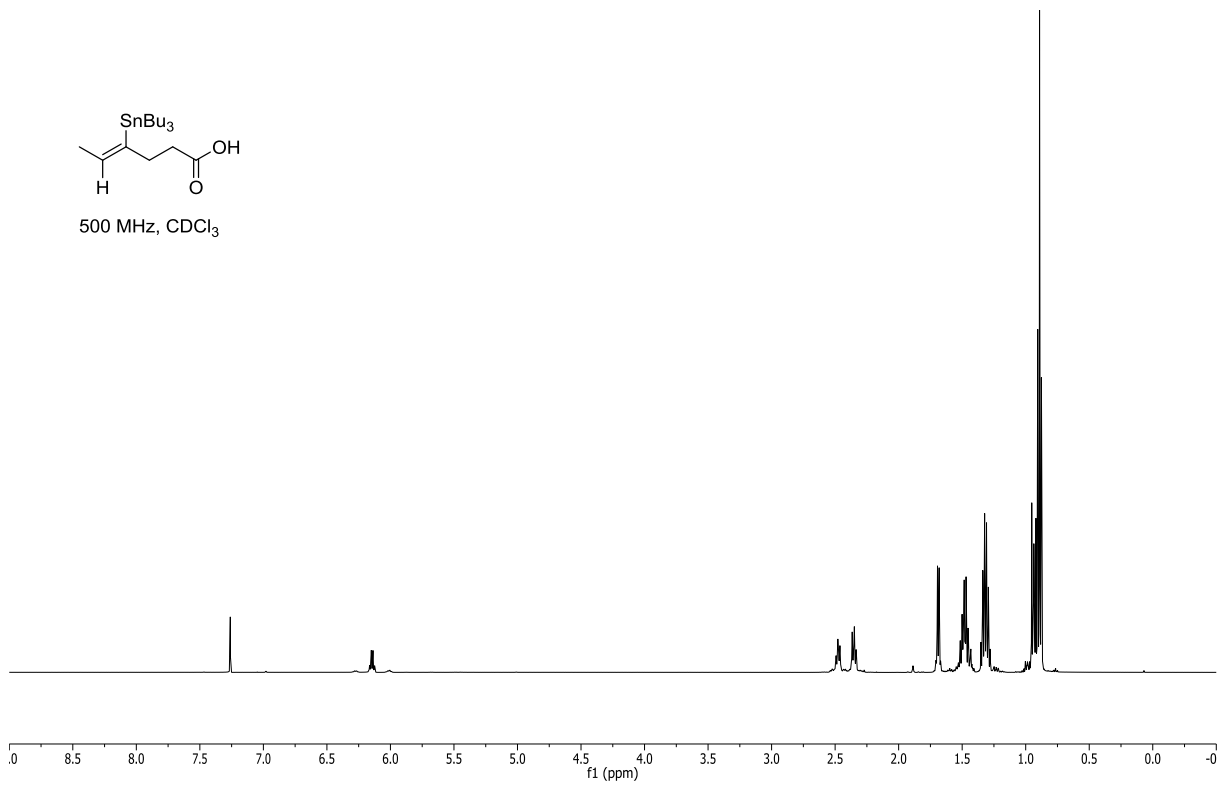


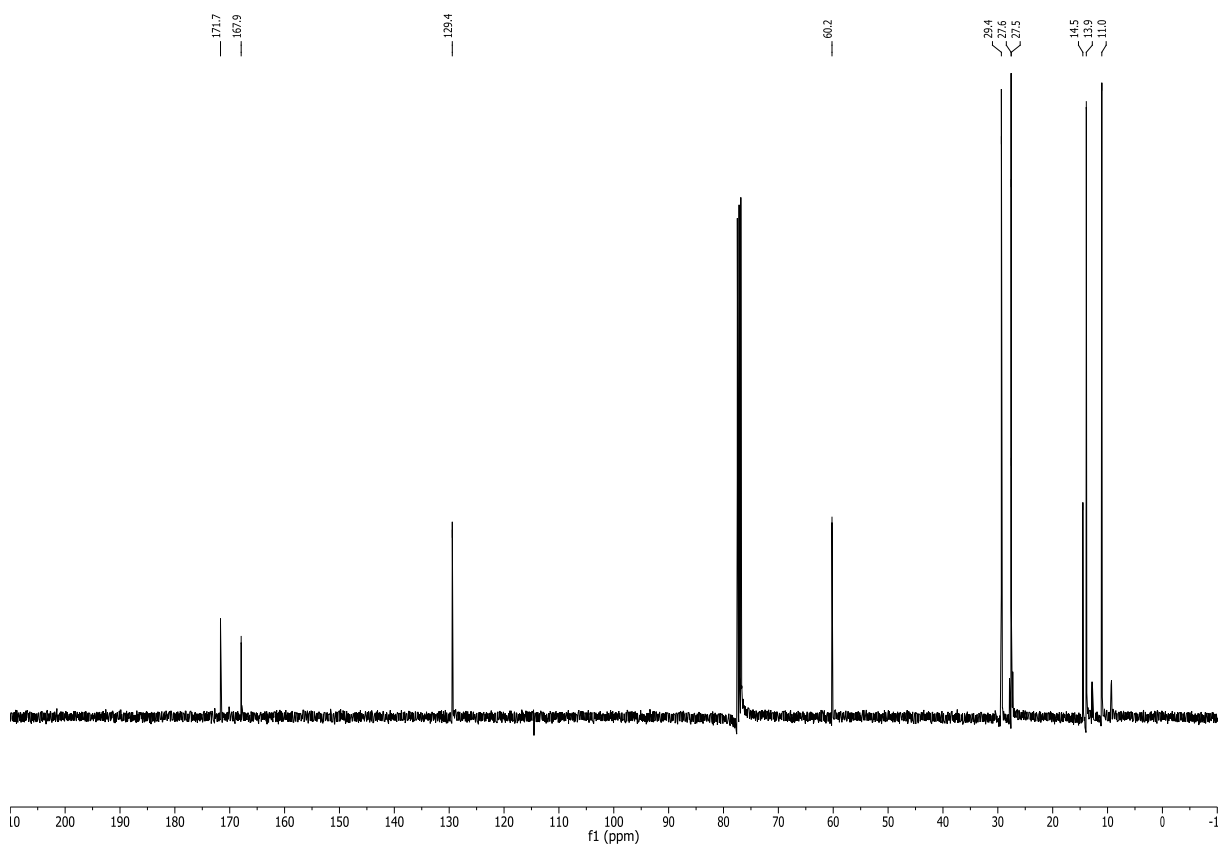
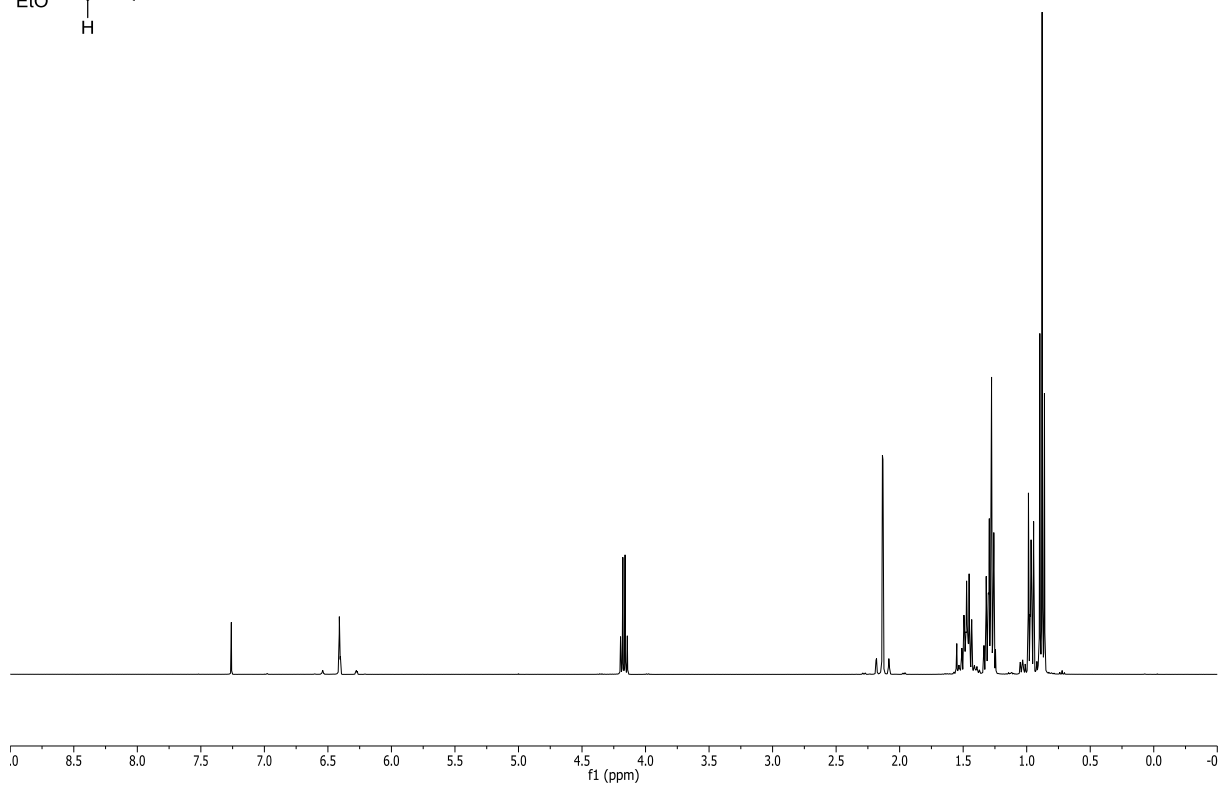
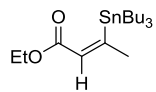
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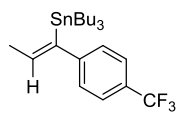




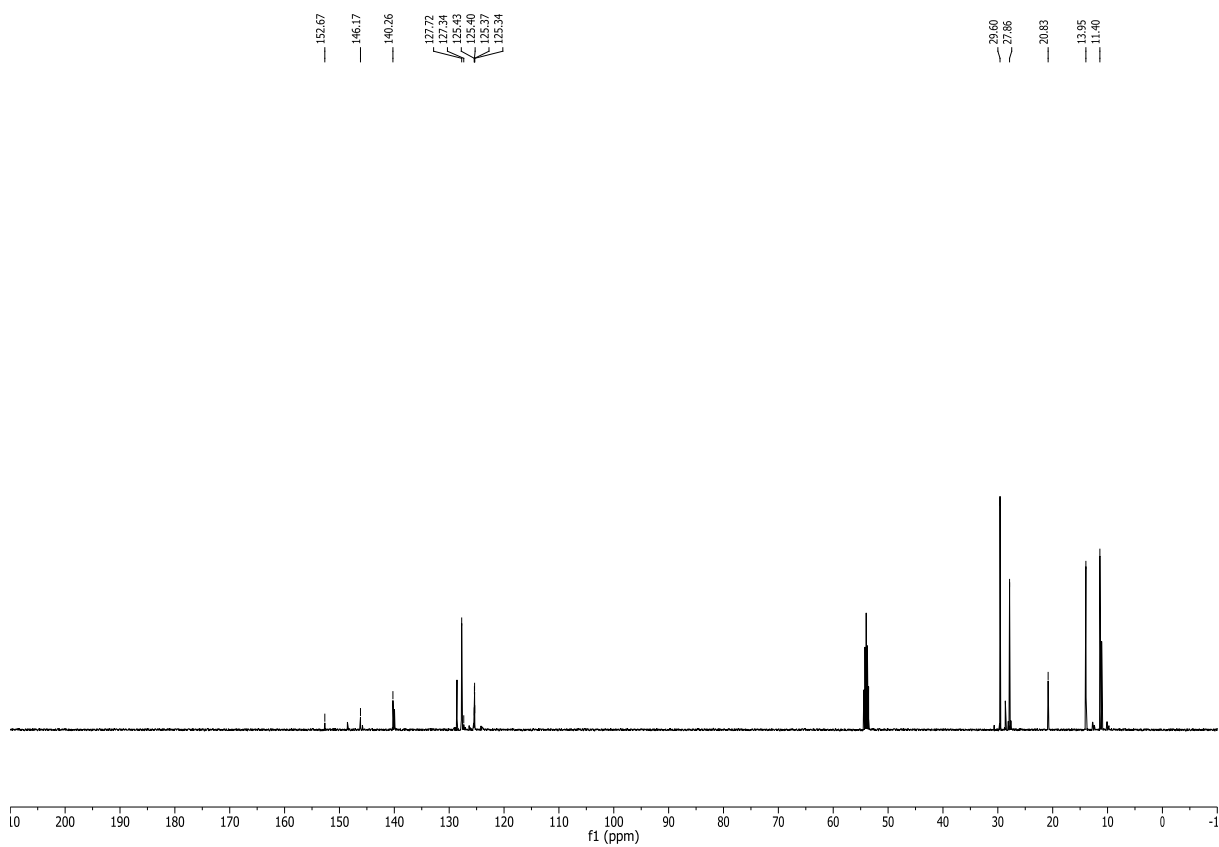
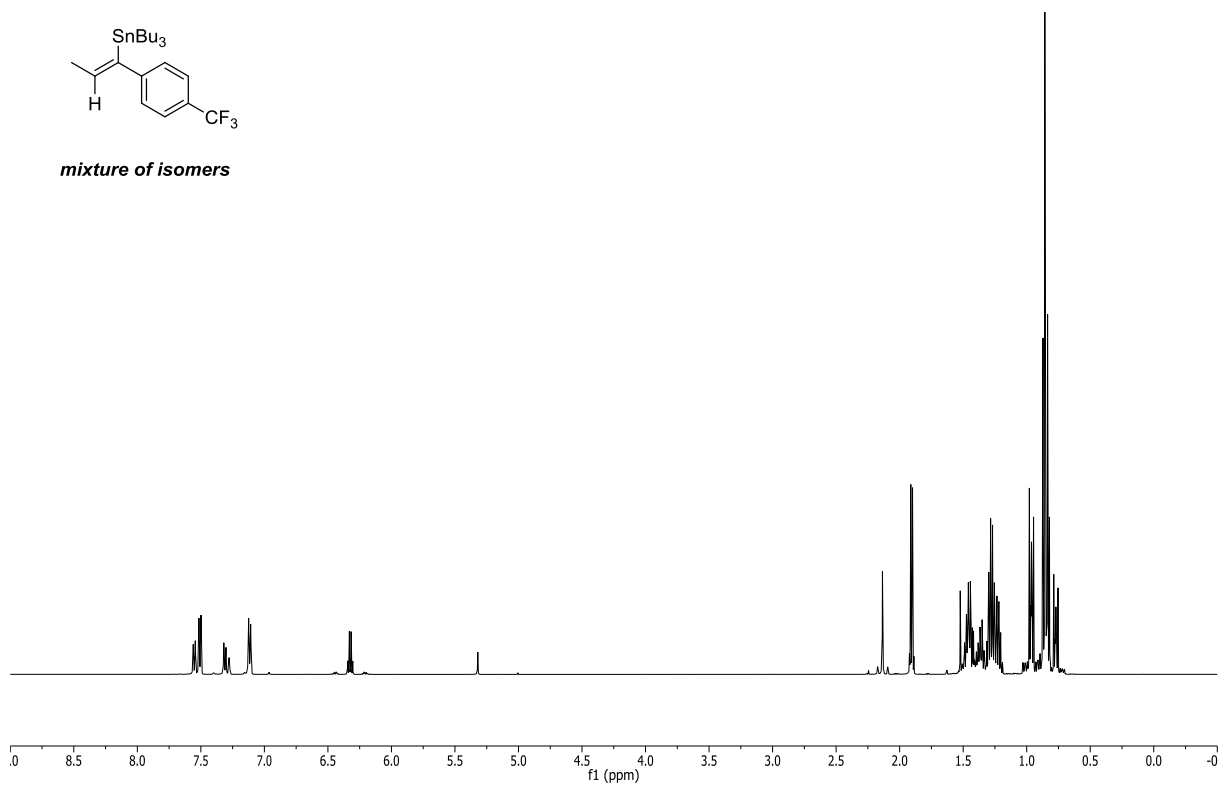
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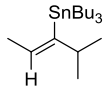




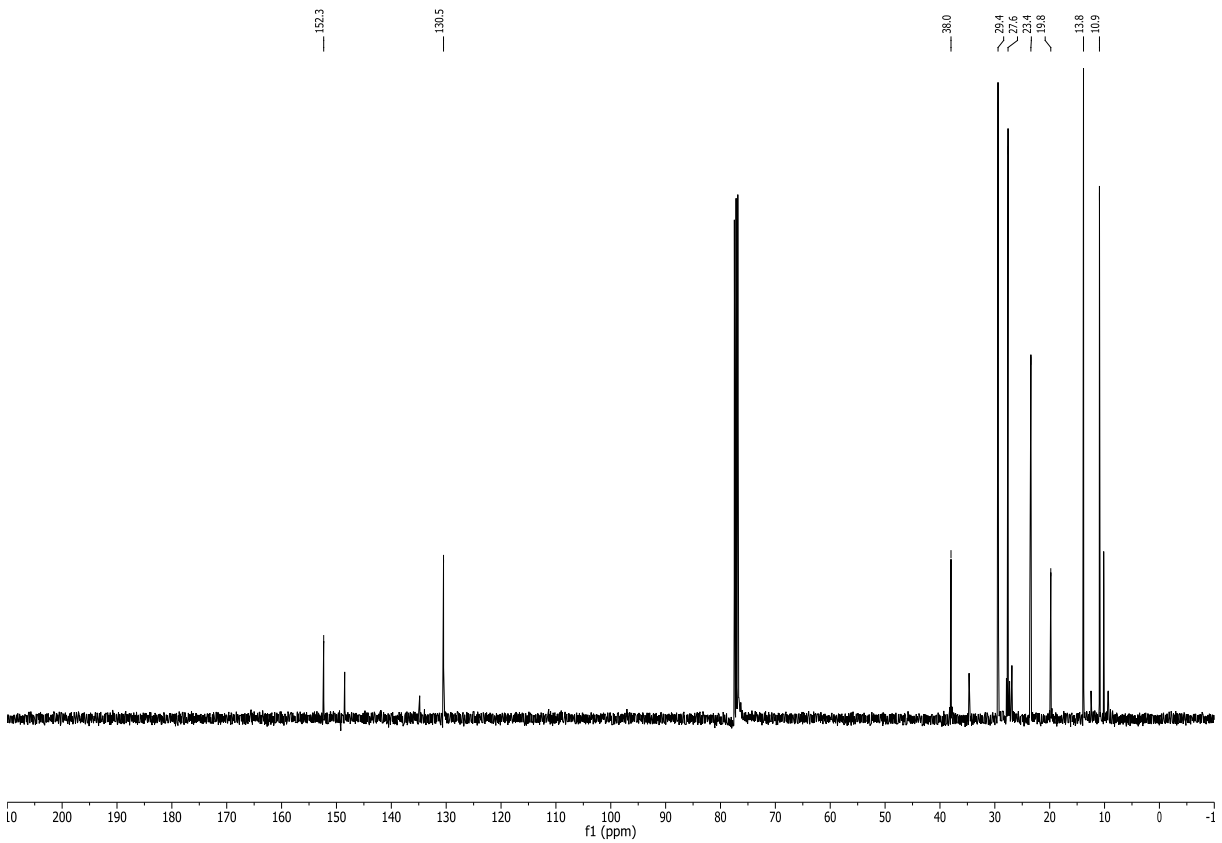
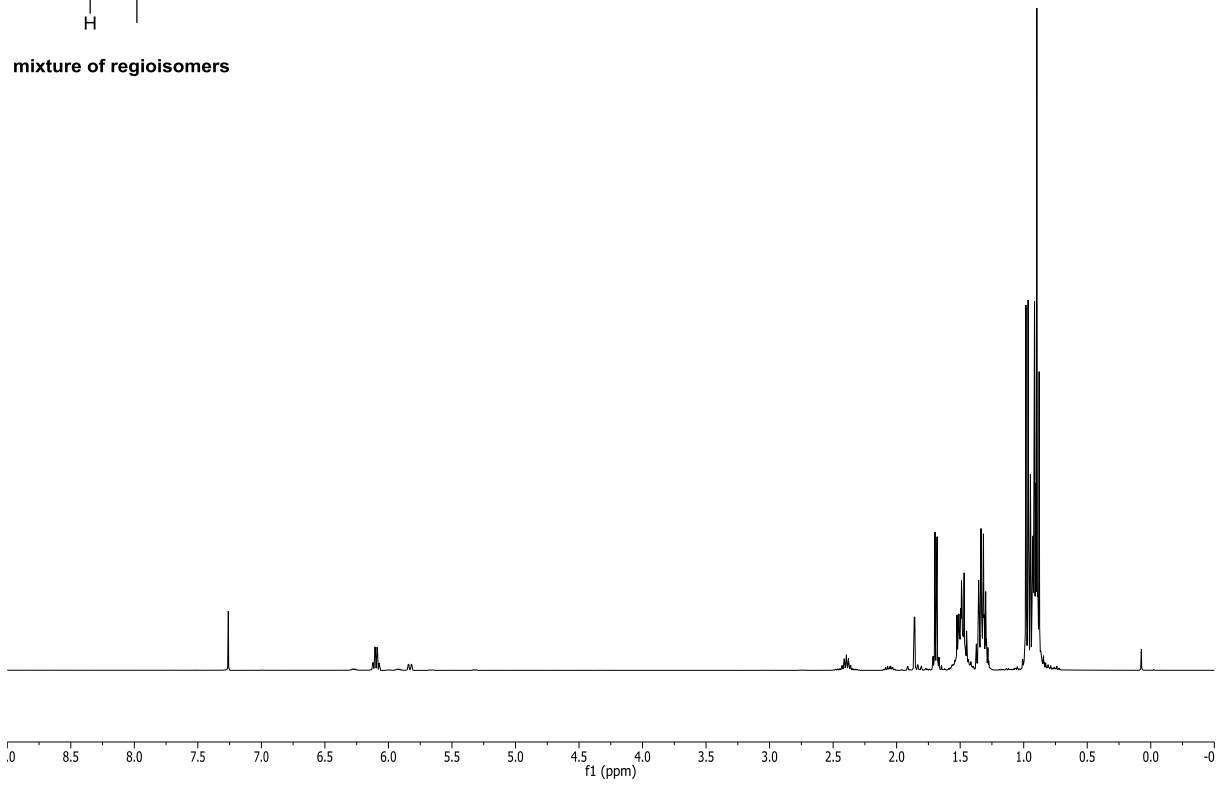


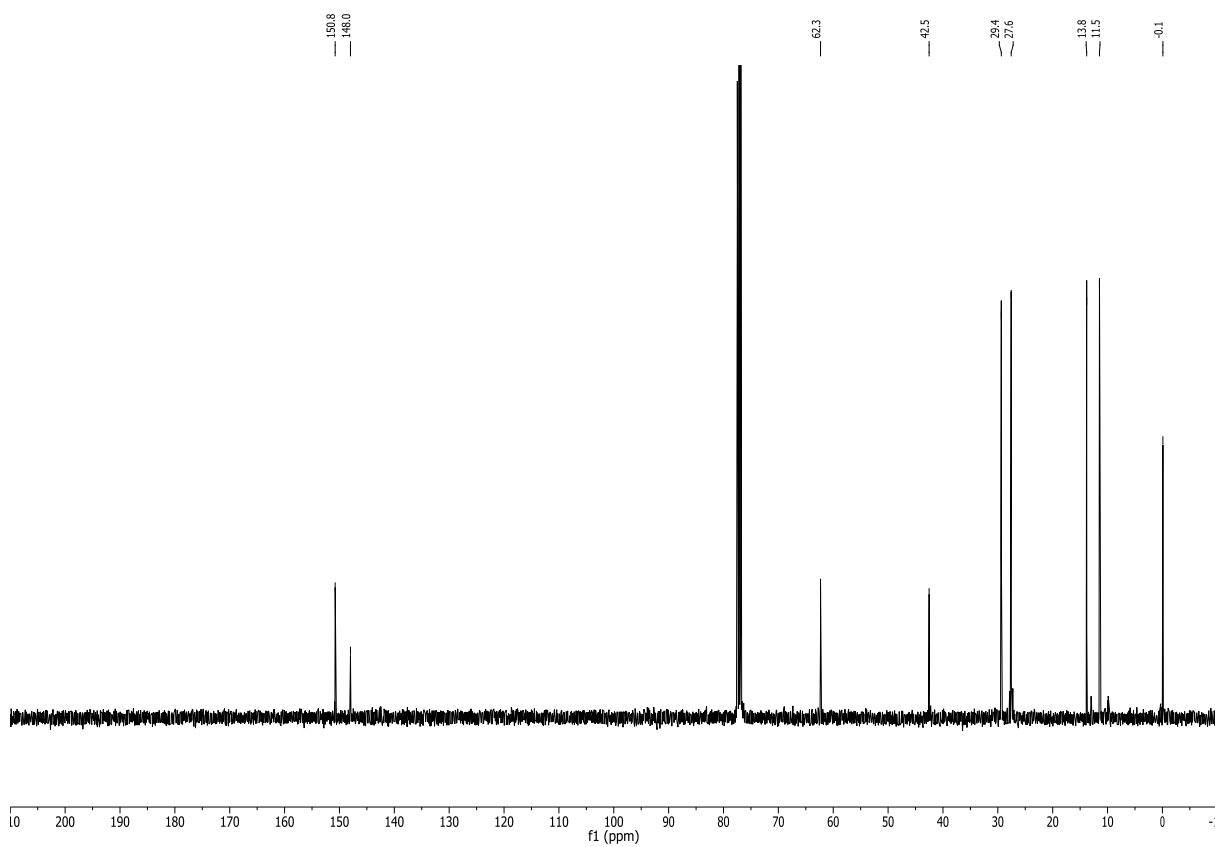
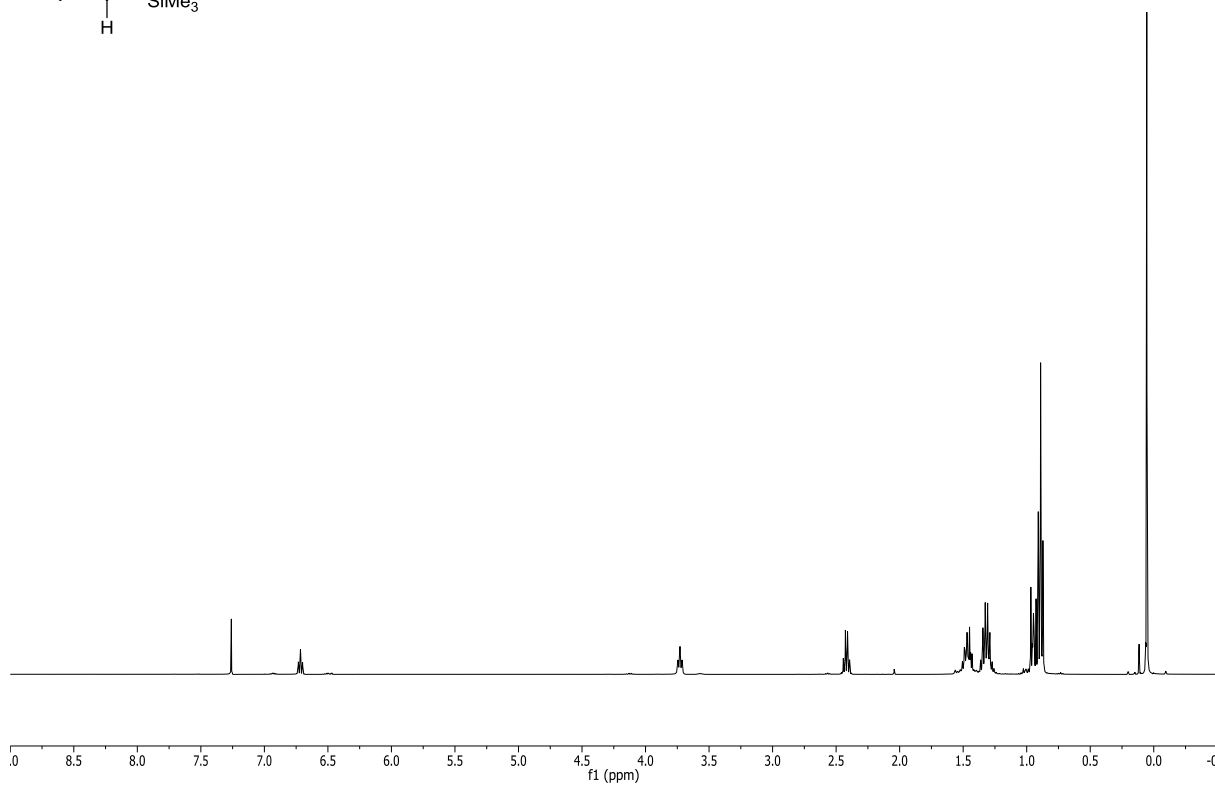
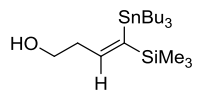
mixture of isomers

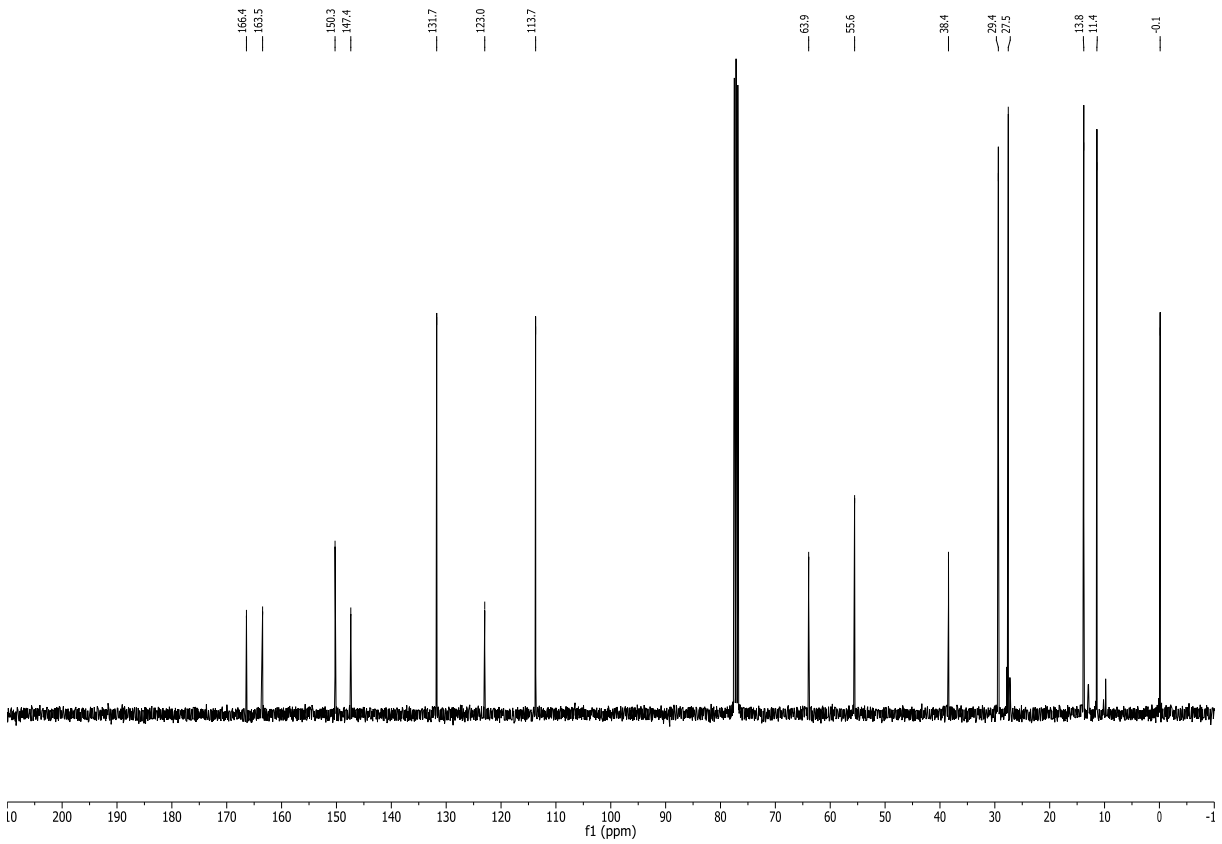
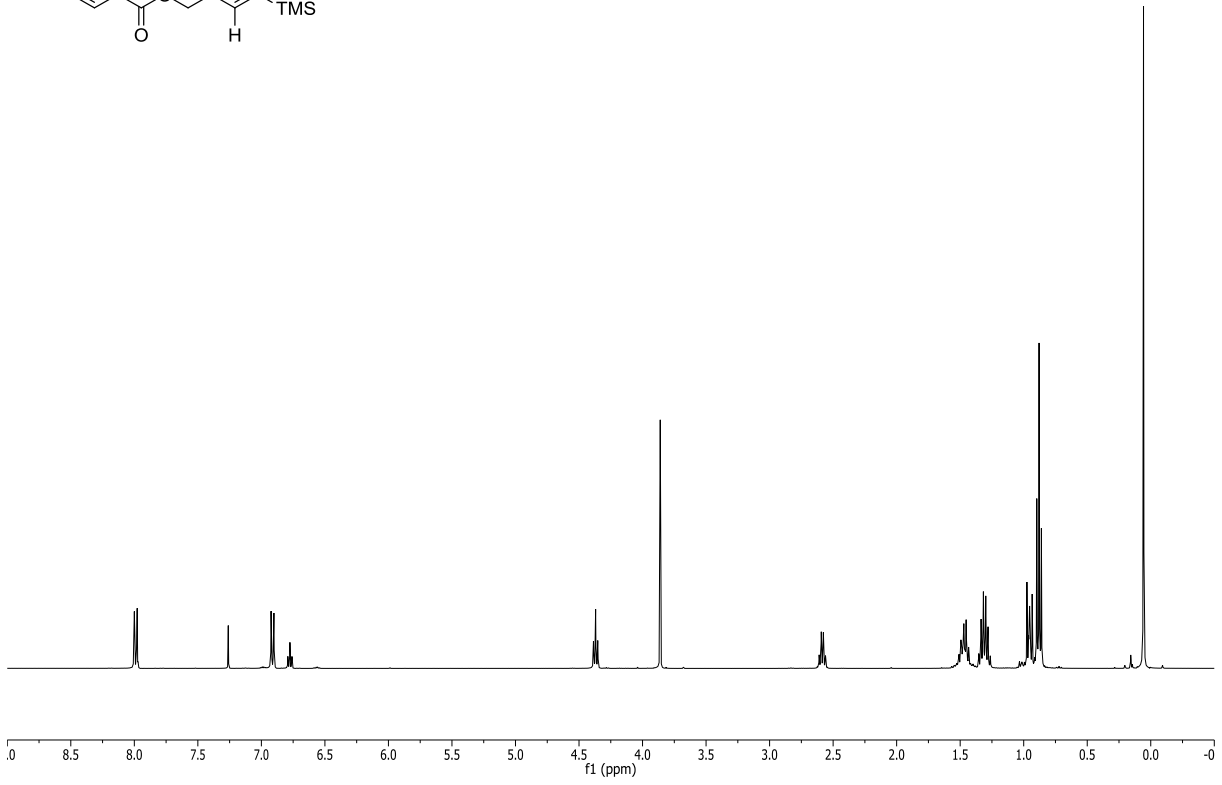
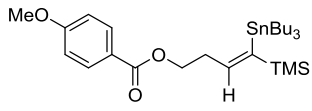


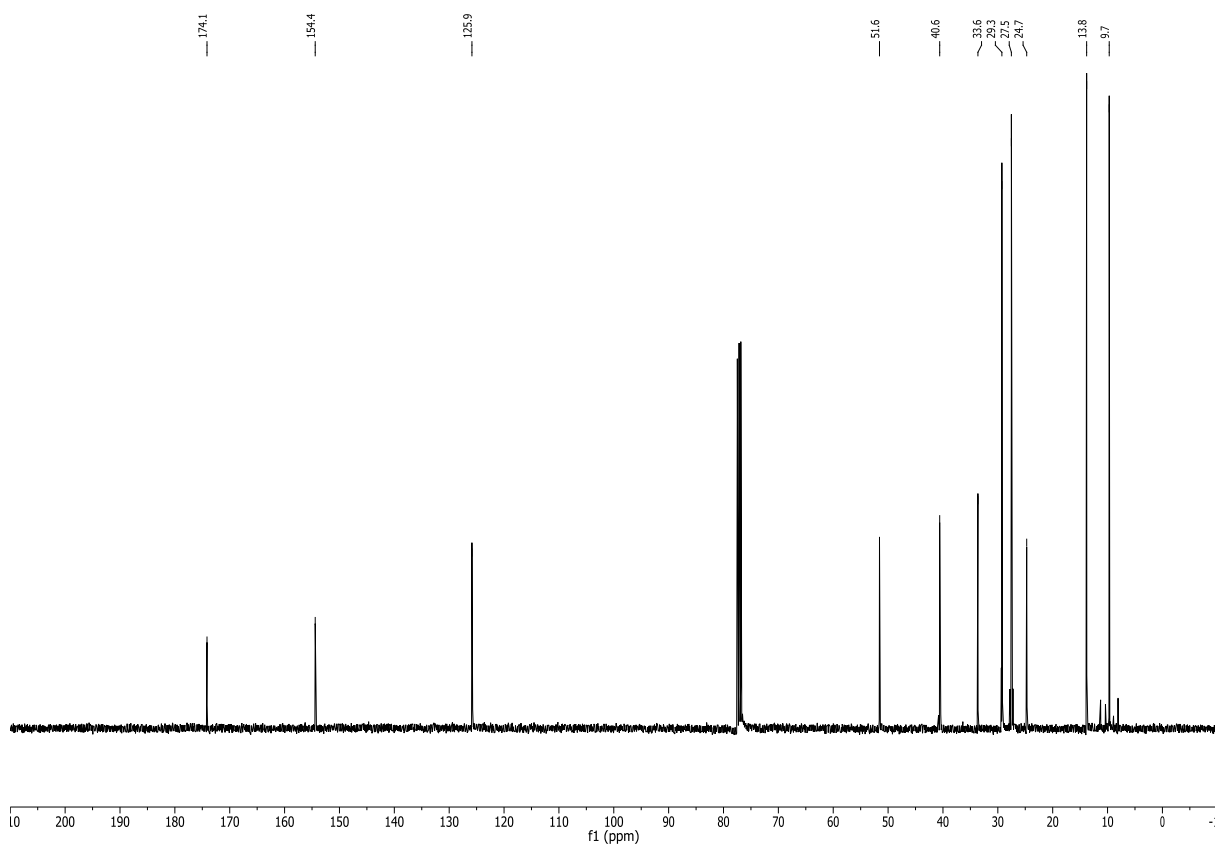
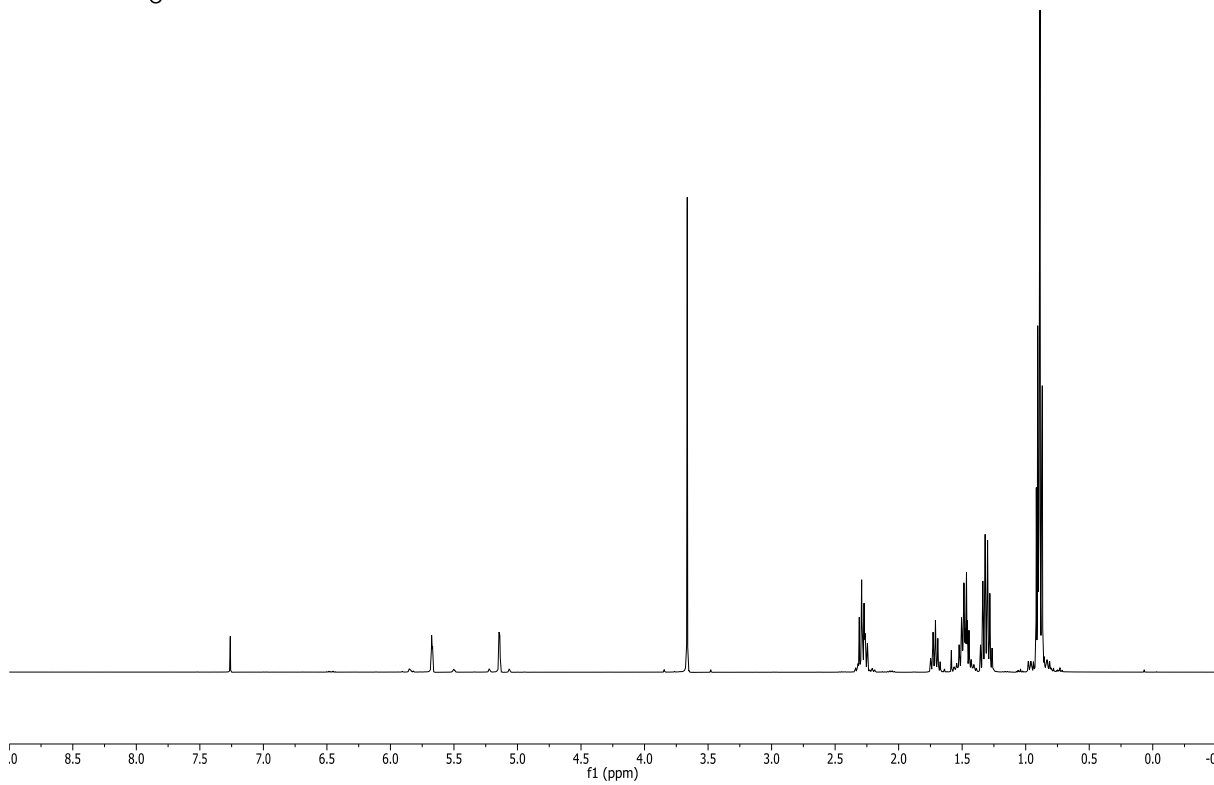
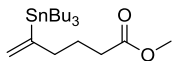


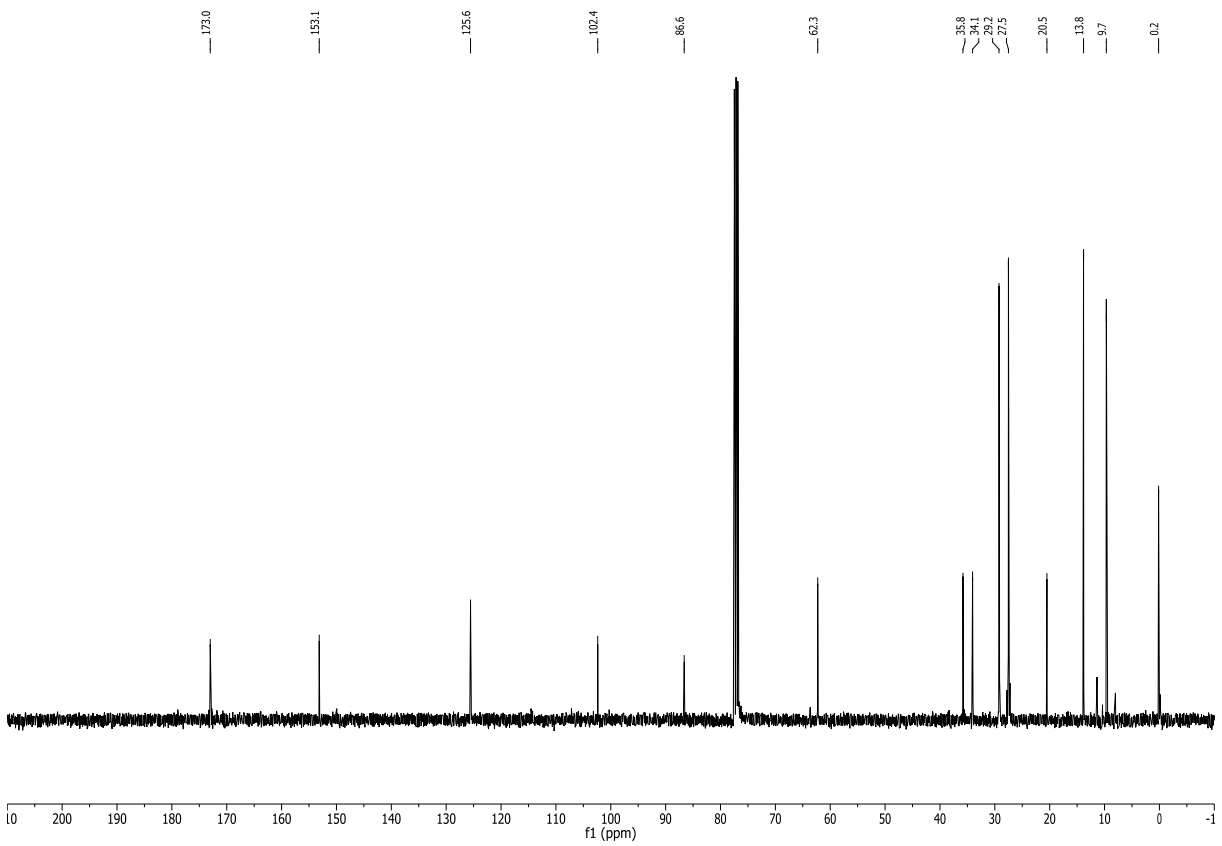
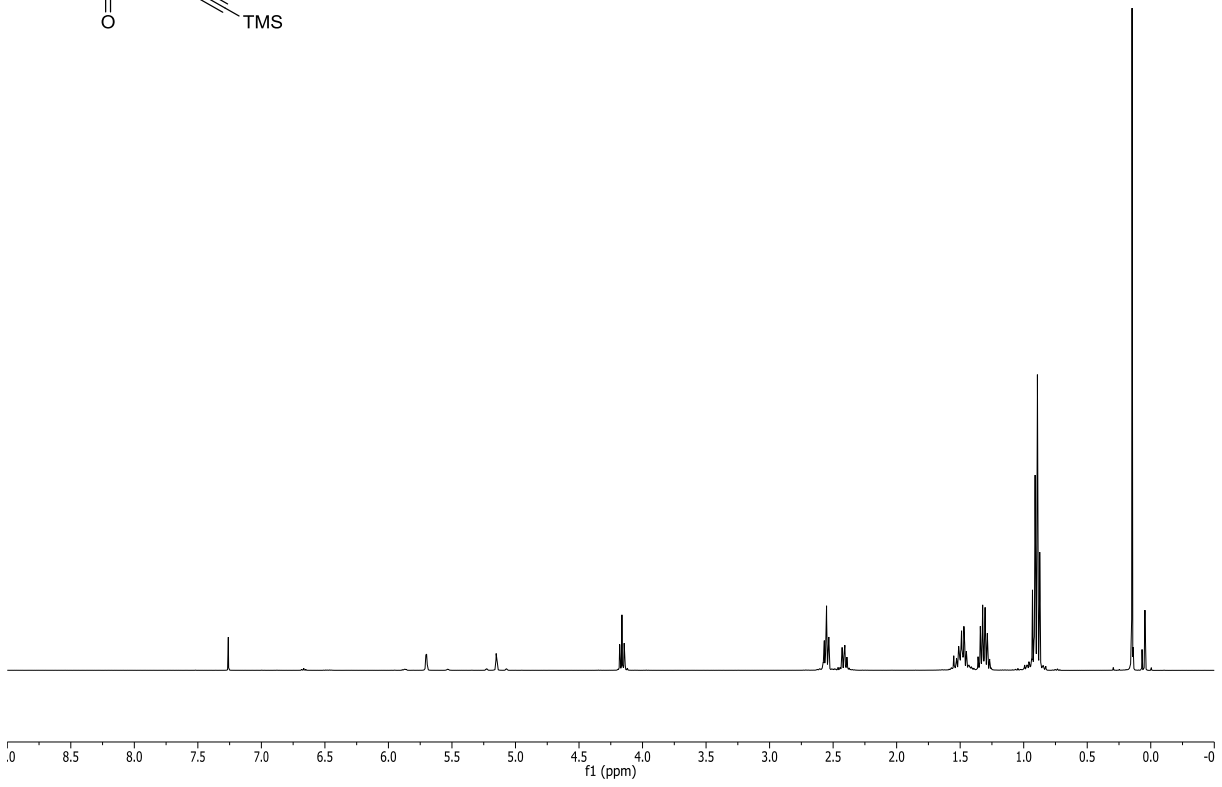
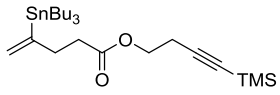
mixture of regioisomers

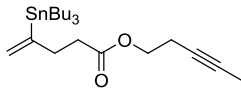












mixture of regioisomers

