SUPPORTING INFORMATION

for

Homologation of Halostannanes with Carbenoids: a Convenient and Straightforward One-step Access to α-Functionalized Organotin Reagents

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1. Instrumentation and General Analytical Methods

Melting Points were determined on a Reichert-Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H, ^{119}Sn and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 149 MHz for ^{119}Sn) at 297 K using a directly detecting broadband observe (BBFO) probe. The centre of the (residual) solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 77.00 ppm (^{13}C in $CDCl_3$). ^{119}Sn NMR spectra were referenced against external Me_4Sn (0.0 ppm). Spin-spin coupling constants (*J*) are given in Hz.

In nearly all cases, full and unambiguous assignment of all resonances could be performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, COSY and NOESY experiments.

All the reactions were carried out under inert atmosphere of Argon. THF was distilled over Na/benzophenone. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Fluorochem, Acros, and TCI Europe. Solutions were evaporated under reduced pressure with a rotary evaporator.

TLC was carried out on aluminium sheets precoated with silica gel $60F^{254}$ (Merchery-Nagel, Merk); the spots were visualised under UV light (λ=254 nm) and/or $KMnO_4$ (aq.) was used as revealing system.

Synthetic Methodology and Characterization of the Compounds

General procedure for homologation of R_nSnX_n and R_nGeX_n (General Procedure 1, GP1)

The electrophile (R_nSnX_n/R_nGeX_n, 1.0 equiv) was dissolved in dry THF under Argon and cooled down to -78 °C. The appropriate dihalomethane (3.0 equiv) was added and the whole was allowed to mix for 5 min. MeLi-LiBr (2.2 M solution in Et_2O, 2.8 equiv) was added dropwise during 15 min and, then the mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with aqueous saturated NH_4Cl solution and then was allowed to warm to rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude compounds were purified as reported below through column chromatography.

General Procedure for the preparation of lithium dihalocarbenoids and its subsequent addition to different electrophiles (General Procedure 2, GP2)

Preparation of LDA. A solution of dry diisopropylamine (DIPA, 2.8 equiv) in anhydrous THF was added to a flask under Argon. MeLi-LiBr (2.2 M, 2.8 equiv) was added dropwise at 0 °C and allowed to react for 30 minutes to generate lithium diisopropylamide (LDA).

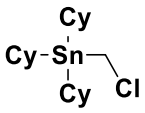
The appropriate dihalomethane (3.0 equiv) was dissolved in anhydrous THF under Argon and, the above prepared LDA (2.8 equiv) was added dropwise at -78 °C and, the mixture was stirred for 10 min. Then, the electrophile (1.0 equiv) dissolved in dry THF (1.0 M final concentration) was slowly added to the flask and stirred for 60 min. and quenched with aqueous NH_4Cl. The reaction mixture was quenched with aqueous saturated NH_4Cl solution and then was allowed to warm to rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude compounds were purified as reported below through column chromatography.

General Procedure for the preparation of lithiated allyl fragment and its subsequent addition to electrophiles (General Procedure 3, GP3)

Preparation of LDA. A solution of dry diisopropylamine (DIPA, 2.8 equiv) in anhydrous THF was added to a flask under Argon. MeLi-LiBr (2.2 M, 2.8 equiv) was added dropwise at 0 °C and allowed to react for 30 minutes to generate lithium diisopropylamide (LDA).

A solution of allyl chloride (3.0 equiv) in dry THF was prepared under Argon and to this LDA (2.8 equiv) was added dropwise at -78 °C and the mixture stirred for 10 min. Then the electrophile (1.0 equiv) solution prepared in dry THF was added slowly to the flask and stirred for 60 min and then quenched with aqueous NH_4Cl. The quenched reaction mixture was allowed to stay at -78 °C for 10 minutes and subsequently allowed to warm at r.t. The resulting organic phase was exhaustively extracted 3 times with Et_2O, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude compounds were purified as reported below through column chromatography.

(chloromethyl)(tricyclohexyl)stannane (2)



By following general procedure 1, starting from tricyclohexylchlorostannane (0.404 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 ml, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **2** was obtained in 93% yield (0.376 g) as a colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

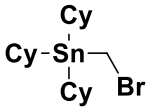
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.10 (s, 2H, CH_2Cl), 1.89 (m, 6H, Cy H-2,6), 1.66 (m, 6H, Cy H-3,5), 1.64 (m, 9H, Cy H-1, Cy H-4), 1.62 (m, 6H, Cy H-2`,6`), 1.30 (m, 6H, Cy H-3`,5`).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.1 (Cy C-2,6), 29.1 (Cy C-3,5), 27.3 (Cy C-1), 27.1 (Cy C-4), 23.9 (CH_2Cl).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -79.1 ($SnCH_2Cl$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{35}ClSnNa$ 441.1338 $[M+Na]^+$; found 441.1341.

(bromomethyl)(tricyclohexyl)stannane (3)



By following general procedure 1, starting from tricyclohexylchlorostannane (0.404 g, 1.0 mmol, 1.0 equiv), $BrCH_2I$ (0.663 ml, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **3** was obtained in 90% yield (0.416 g) as a colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

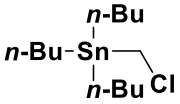
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.67 (s, 2H, CH_2Br), 1.89 (m, 6H, Cy H-2,6), 1.66 (m, 6H, Cy H-3,5), 1.65 (m, 6H, Cy H-4), 1.64 (m, 3H, Cy H-1), 1.62 (m, 6H, Cy H-2`,6`), 1.30 (m, 6H, Cy H-3`,5`),.

^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.1 (Cy C-2,6), 29.1 (Cy C-3,5), 27.6 (Cy C-1), 27.1 (Cy C-4), 8.4 (1C, $CHCl_2$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -78.9 ($SnCH_2Br$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{35}BrSnNa$ 485.0836 $[M+Na]^+$; found 485.0829.

Tri-n-butyl(iodomethyl)stannane (4)



By following general procedure 1, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.87 ml, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **4** was obtained in 89% yield (0.303 g) as colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

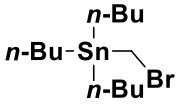
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.06 (s, 2H, $SnCH_2Cl$), 1.53 (m, 6H, $SnCH_2\underline{CH_2}CH_2CH_3$), 1.32 (m, 6H, $SnCH_2CH_2\underline{CH_2}CH_3$), 0.99 (m, 6H, $Sn\underline{CH_2}CH_2CH_2CH_3$), 0.90 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.9 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.2 ($SnCH_2CH_2\underline{C}H_2CH_3$), 24.4 ($SnCH_2Cl$), 13.7 ($SnCH_2CH_2CH_2\underline{C}H_3$), 9.5 ($Sn\underline{C}H_2CH_2CH_2CH_3$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -13.0 ($SnCH_2Cl$).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{29}ClSnNa$ 363.0872 $[M+Na]^+$; found 363.0888.

(bromomethyl)(tributyl)stannane (5)



By following general procedure 1, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), $BrCH_2I$ (0.663 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.87 ml, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **5** was obtained in 83% yield (0.319 g) as colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

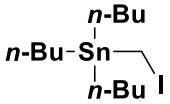
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.65 (s, 2H, $SnCH_2Br$), 1.53 (m, 6H, $SnCH_2\underline{CH_2}CH_2CH_3$), 1.32 (m, 6H, $SnCH_2CH_2\underline{CH_2}CH_3$), 0.99 (m, 6H, $Sn\underline{CH_2}CH_2CH_2CH_3$), 0.90 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.8 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.2 ($SnCH_2CH_2\underline{C}H_2CH_3$), 13.7 ($SnCH_2CH_2CH_2\underline{C}H_3$), 9.9 ($Sn\underline{C}H_2CH_2CH_2CH_3$), 9.2 ($SnCH_2Br$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -11.1 ($SnCH_2Br$).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{29}BrSnNa$ 407.0367 $[M+Na]^+$; found 407.0358.

tributyl(iodomethyl)stannane (6)



By following general procedure 1, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), ICH_2I (0.804 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.87 ml, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **6** was obtained in 85% yield (0.367 g) as colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

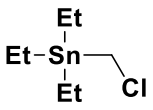
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94 (s, 2H, $SnCH_2I$), 1.53 (m, 6H, $SnCH_2C\underline{H_2}CH_2CH_3$), 1.32 (m, 6H, $SnCH_2CH_2C\underline{H_2}CH_3$), 0.98 (m, 6H, $SnC\underline{H_2}CH_2CH_2CH_3$), 0.90 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2C\underline{H_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.8 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.2 ($SnCH_2CH_2\underline{C}H_2CH_3$), 13.7 ($SnCH_2CH_2CH_2\underline{C}H_3$), 10.7 ($Sn\underline{C}H_2CH_2CH_2CH_3$), -26.9 ($SnCH_2I$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -3.0 ($SnCH_2I$).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{29}ISnNa$ 455.0228 $[M+Na]^+$; found 455.0230.

(chloromethyl)(triethyl)stannane (7)



By following general procedure 1, starting from triethylchlorostannane (0.242 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **7** was obtained in 86% yield (0.220 g) as a colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

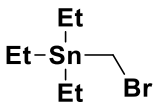
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.10 (s, 2H, $SnCH_2Cl$), 1.22 (t, *J* = 7.9 Hz, 9H, $SnCH_2C\underline{H}_3$), 0.97 (q, *J* = 7.9 Hz, 6H, $SnC\underline{H}_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.6 ($SnCH_2I$), 10.8 ($SnCH_2\underline{C}H_3$), 0.8 ($Sn\underline{C}H_2CH_3$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -4.8 ($SnCH_2Cl$).

HRMS (ESI), *m/z*: calcd. for $C_7H_{17}ClSnNa$ 278.9933 $[M+Na]^+$; found 278.9927.

(bromomethyl)(triethyl)stannane (8)



By following general procedure 1, starting from triethylchlorostannane (0.242 g, 1.0 mmol, 1.0 equiv), $BrCH_2I$ (0.663 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **8** was obtained in 81% yield (0.243 g) as a colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

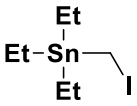
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.68 (s, 2H, $SnCH_2Br$), 1.22 (t, *J* = 8.0 Hz, 9H, $SnCH_2C\underline{H}_3$), 0.97 (q, *J* = 8.0 Hz, 6H, $SnC\underline{H}_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.8 ($SnCH_2\underline{C}H_3$), 8.2 ($SnCH_2Br$), 1.2 ($Sn\underline{C}H_2CH_3$)

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -2.9 ($SnCH_2Br$)

HRMS (ESI), *m/z*: calcd. for $C_7H_{17}BrSnNa$ 322.9428 $[M+Na]^+$; found 322.9418.

triethyl(iodomethyl)stannane (9)



By following general procedure 1, starting from triethylchlorostannane (0.242 g, 1.0 mmol, 1.0 equiv), ICH_2I (0.804 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **9** was obtained in 89% yield (0.310 g) as a pale oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

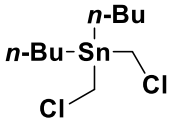
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.95 (s, 2H, $SnCH_2I$), 1.22 (t, *J* = 8.0 Hz, 9H, $SnCH_2C\underline{H_3}$), 0.96 (q, *J* = 8.0 Hz, 6H, $SnC\underline{H_2}CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.7 ($SnCH_2\underline{C}H_3$), 2.0 ($Sn\underline{C}H_2CH_3$), -28.5 ($SnCH_2I$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: 5.2 ($SnCH_2I$).

HRMS (ESI), *m/z*: calcd. for $C_7H_{17}ISnNa$ 370.9289 $[M+Na]^+$; found 370.9290.

dibutyl[bis(chloromethyl)]stannane (10)



By following general procedure 1, starting from dibutyldichlorostannane (0.304 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.437 ml, 6.0 mmol, 6.0 equiv), MeLi-LiBr complex (2.55 ml, 5.6 mmol, 5.6 equiv) in dry THF (3 mL), **10** was obtained in 82% yield (0.272 g) as a colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

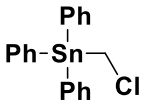
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.18 (s, 4H, $SnCH_2Cl$), 1.58 (m, 4H, $SnCH_2\underline{CH_2}CH_2CH_3$), 1.34 (m, 4H, $SnCH_2CH_2\underline{CH_2}CH_3$), 1.18 (m, 4H, $Sn\underline{CH_2}CH_2CH_2CH_3$), 0.91 (t, *J* = 7.3 Hz, 6H, $SnCH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.5 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.1 ($SnCH_2CH_2\underline{C}H_2CH_3$), 24.2 ($SnCH_2Cl$), 13.6 ($SnCH_2CH_2CH_2\underline{C}H_3$), 10.1 ($Sn\underline{C}H_2CH_2CH_2CH_3$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -24.6 ($SnCH_2Cl$).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{22}Cl_2SnNa$ 355.0013 $[M+Na]^+$; found 355.0001.

(chloromethyl)(triphenyl)stannane (11)



By following general procedure 1, starting from triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (15 mL), **11** was obtained in 92% yield (0.368 g) as a white solid (mp 78-80 °C) after column chromatography on silica using *n*-hexane as mobile phase.

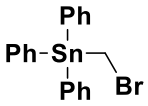
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (m, 6H, Ph H-2,6), 7.41 (m, 9H, Ph H-3,4,5), 3.62 (s, 2H, CH_2Cl).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1 (Ph C-2,6), 136.8 (Ph C-1), 129.5 (Ph C-4), 128.7 (Ph C-3,5), 25.1 (CH_2Cl).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -130.5 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}ClSnNa$ 422.9933 $[M+Na]^+$; found 422.9929.

(bromomethyl)(triphenyl)stannane (12)



By following general procedure 1, starting from triphenylchlorostannane (0.340 g, 1.0 mmol, 1.0 equiv), $BrCH_2I$ (0.663 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **12** was obtained in 79% yield (0.351 g) as a white solid (mp 68-70 °C) after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

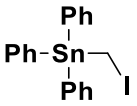
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (m, 6H, Ph H-2,6), 7.41 (m, 9H, Ph H-3,4,5), 3.17 (s, 2H, CH_2Br).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0 (Ph C-2,6), 136.9 (Ph C-1), 129.5 (Ph C-4), 128.7 (Ph C-3,5), 8.2 (CH_2Br).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -129.3 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}BrSnNa$ 466.9428 $[M+Na]^+$; found 466.9420.

(iodomethyl)(triphenyl)stannane (13)



By following general procedure 1, starting from triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv), ICH_2I (0.804 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **13** was obtained in 85% yield (0.418 g) as a yellow solid (mp 72-74 °C) after column chromatography on silica using *n*-hexane as mobile phase.

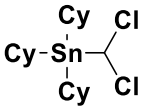
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (m, 6H, Ph H-2,6), 7.41 (m, 9H, Ph H-3,4,5), 2.47 (s, 2H, CH_2I).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4 (Ph C-1), 137.0(Ph C-2,6), 129.5 (Ph C-4), 128.7 (Ph C-3,5), -29.7 (1C, CH_2I).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -120.4 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}ISnNa$ 514.9289 $[M+Na]^+$; found 514.9292.

(tricyclohexyl)(dichloromethyl)stannane (14)



By following general procedure 2, starting from tricyclohexylchlorostannane (0.404 g, 1.0 mmol, 1.0 equiv), dichloromethane (0.192 g, 3.0 mmol, 3.0 equiv), lithium diisopropylamide (0.347 g, 2.8 mmol, 2.8 equiv), diisopropylamide (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M, 2.8 mmol, 2.8 equiv). Dry THF (10.0 ml each for generation of LDA and the main reaction). The electrophile was dissolved in 3.0 ml dry THF before adding to the reaction flask. The reaction provided 0.407 g (90% yield) of **14** as a colorless oil after column chromatography on Florisil with *n*-hexane as the eluent.

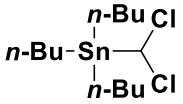
^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.62 (s, 1H, $CHCl_2$), 1.96 (m, 6H, Cy H-2,6), 1.70 (m, 6H, Cy H-2`,6`), 1.69 (m, 6H, Cy H-3,5), 1.67 (m, 6H, Cy H-4), 1.31 (m, 6H, Cy H-3`,5`).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 60.3 ($CHCl_2$), 32.0 (Cy C-2,6), 29.5 (Cy C-1), 29.1 (Cy C-3,5), 27.0 (Cy C-4).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -80.1 (SnCH).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{34}Cl_2SnNa$ 475.0952 $[M+Na]^+$; found 475.0990.

tributyl(dichloromethyl)stannane (15)



By following general procedure 2, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), dichloromethane (0.192g, 3.0 mmol, 3.0 equiv), lithium diisopropylamide (0.347 g, 2.8 mmol, 2.8 equiv), diisopropylamide (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27ml of 2.2M, 2.8 mmol, 2.8 equiv). Dry THF (10.0 ml each for generation of LDA and the main reaction). The electrophile was dissolved in 3.0 ml dry THF before adding to the reaction flask. The reaction provided 0.363 g (97% yield) of **15** as an orange yellow oil after column chromatography on Florisil with *n*-hexane as the eluent.

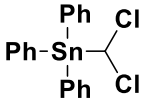
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.56 (s, 1H, $SnCHCl_2$), 1.58 (m, 6H, $SnCH_2C\underline{H_2}CH_2CH_3$), 1.34 (m, 6H, $SnCH_2CH_2C\underline{H_2}CH_3$), 1.13 (m, 6H, $Sn\underline{CH_2}CH_2CH_2CH_3$), 0.91 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2C\underline{H_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 59.4 ($SnCHCl_2$), 28.6 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.3 ($SnCH_2CH_2\underline{C}H_2CH_3$), 13.6 ($SnCH_2CH_2CH_2\underline{C}H_3$), 10.8 ($Sn\underline{C}H_2CH_2CH_2CH_3$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: 9.0 ($SnCHCl_2$).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{28}Cl_2SnNa$ 397.0482 $[M+Na]^+$; found 397.0491.

(dichloromethyl)(triphenyl)stannane (16)



By following general procedure 2, starting from triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv), dichloromethane (0.192 g, 3.0 mmol, 3.0 equiv), lithium diisopropylamide (0.347 g, 2.8 mmol, 2.8 equiv), diisopropylamide (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M, 2.8 mmol, 2.8 equiv). The electrophile was dissolved in 3.0 ml dry THF before adding to the reaction flask. The reaction provided 0.365 g (84% yield) of **16** as orange brown solid (mp 103-105 °C) after column chromatography on Florisil with *n*-hexane as the eluent.

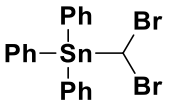
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (m, 6H, Ph H-2,6), 7.45 (m, 9H, Ph H-3,4,5), 6.00 (s, 1H, $CHCl_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (Ph C-2,6), 135.6 (Ph C-1), 129.9 (Ph C-4), 128.9 (Ph C-3,5), 59.4 (1C, $CHCl_2$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -139.1 (SnCH).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{16}Cl_2SnNa$ 456.9543 $[M+Na]^+$; found 456.9533.

(dibromomethyl)(triphenyl)stannane (17)



By following general procedure 2, starting from triphenylchlorostannane (0.385 g, 1.0 mmol, 1.0 equiv), dibromomethane (0.197 g, 3.0 mmol, 3.0 equiv), lithium diisopropylamide (0.347 g, 2.8 mmol, 2.8 equiv), diisopropylamide (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M in Et_2O, 2.8 mmol, 2.8 equiv). The electrophile was dissolved in 3.0 ml dry THF before adding to the reaction flask. The reaction provided 0.339 g (88% yield) of **17** as white amorphous solid (mp 104-106 °C) after column chromatography on Florisil with *n*-hexane as the eluent.

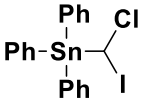
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (m, 6H, Ph H-2,6), 7.47 (m, 9H, Ph H-3,4,5), 5.71 (s, 1H, $SnCHBr_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (Ph C-2,6), 136.1 (Ph C-1), 129.9 (Ph C-4), 128.9 (Ph C-3,5), 25.6 ($CHBr_2$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -136.6 ($SnCHBr_2$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{16}Br_2SnNa$ 544.8533 $[M+Na]^+$; found 544.8495.

[chloro(iodo)methyl](triphenyl)stannane (18)



By following general procedure 2, starting from triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.204 g, 3.0 mmol, 3.0 equiv), diisopropylamine (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M, 2.8 mmol, 2.8 equiv). The electrophile was dissolved in 3.0 ml dry THF before adding to the reaction flask. The reaction provided 421 mg (80% yield) of **18** as a colorless oil after column chromatography on silica and *n*-hexane.

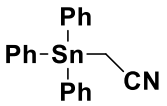
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (m, 6H, Ph H-2,6), 7.45 (m, 9H, Ph H-3,4,5), 5.74 (s, 1H, ICHCl).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (Ph C-2,6), 136.3 (Ph C-1), 129.9 (Ph C-4), 128.9 (Ph C-3,5), 6.2 (ICHCl).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -131.5 (SnCHClI)

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{16}ClISnNa$ 548.8899 $[M+Na]^+$; found 548.8896.

(triphenylstannyl)acetonitrile (19)



Dry acetonitrile (0.123 g, 3.0 mmol, 3.0 equiv) was dissolved in 9 ml of anhydrous THF under argon. To this solution MeLi-LiBr (0.45 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) was added dropwise at -78 °C and the mixture stirred for 30 min for the generation of lithium acetonitrile. Triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv) dissolved in 3 ml of dry THF was added dropwise to the prepared lithium acetonitrile solution at the same temperature and allowed to react for 1 h. The reaction was quenched with aqueous NH_4Cl solution and allowed to stand at -78 °C for 10 min before warming at rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude was washed with *n*-heptane giving **19** (97% yield, 0.378 g) as a light brown solid (mp: 107-110 °C).

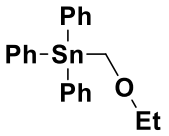
^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.60 (m, 6H, Ph H-2,6), 7.45 (m, 9H, Ph H-3,4,5), 2.10 (s, 2H, CH_2CN).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 136.7 (Ph C-2,6), 135.4 (Ph C-1), 130.0 (Ph C-4), 129.1 (Ph C-3,5), 120.4 (CN), -4.9 ($SnCH_2$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -122.0 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{20}H_{17}NSnNa$ 414.0275 $[M+Na]^+$; found 414.0314.

(ethoxymethyl)(triphenyl)stannane (20)



Lithium metal (7.0 mmol, 7.0 equiv, 25% dispersion in mineral oil) was placed under Argon in a Schlenk tube, washed with dry THF for three times and suspended in the same solvent (1.4 M concentration). DTBB (4,4'-di-tert-butylbiphenyl, 5% mol) was added and the mixture was stirred until the appearance of the dark green colour. To this suspension, cooled down to -78°C, chloromethylethylether (0.260 g, 2.8 mmol, 2.8 equiv) was added dropwise and stirred for 10 min. Triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv) in THF (1.0 M) was added dropwise and the mixture was stirred at -78 °C for 60 min and quenched with aqueous NH_4Cl solution and allowed to stand at the same temperature for 10 min. Subsequently, the reaction mixture was allowed to warm at r.t and the resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Compound **20** was obtained in 90% yield (0.369 g) as white solid (mp 28-30 °C) after column chromatography on silica using *n*-hexane:EtoAc (9:1, *v*/*v*) as the mobile phase.

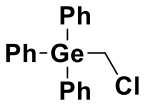
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (m, 6H, Ph H-2,6), 7.37 (m, 9H, Ph H-3,4,5), 4.38 (s, 2H, $SnC\underline{H_2}$), 3.50 (q, *J* = 7.0 Hz, 2H, $SnCH_2OC\underline{H_2}CH_3$), 1.16 (t, *J* = 7.0 Hz, 3H, $SnCH_2OCH_2C\underline{H_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.5 (Ph C-1), 137.1 (Ph C-2,6), 128.9 (Ph C-4), 128.5 (Ph C-3,5), 70.8 ($SnCH_2O\underline{C}H_2CH_3$), 63.2 ($Sn\underline{C}H_2OCH_2CH_3$), 15.0 ($SnCH_2OCH_2\underline{C}H_3$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -145.5 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{21}H_{22}OSnNa$ 433.0585 $[M+Na]^+$; found 433.0599.

(chloromethyl)(triphenyl)germane (21)



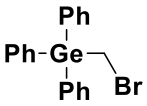
By following general procedure 1, starting from triphenylchlorogermane (0.340 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **21** was obtained in 93% yield (0.329 g) as a white solid (mp 115-118 °C) after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane as mobile phase.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (m, 6H, Ph H-2,6), 7.42 (m, 3H, Ph H-4), 7.40 (m, 6H, Ph H-3,5), 3.66 (s, 2H, $GeCH_2Cl$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.0 (Ph C-2,6), 134.5 (Ph C-1), 129.6 (Ph C-4), 128.4 (Ph C-3,5), 28.4 ($GeCH_2Cl$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}ClGeNa^+$ 377.0123 $[M+Na]^+$; found 377.0122.

(bromomethyl)(triphenyl)germane (22)



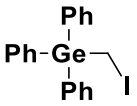
By following general procedure 1, starting from triphenylchlorogermane (0.340 g, 1.0 mmol, 1.0 equiv), $BrCH_2I$ (0.662 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **22** was obtained in 86% yield (0.342 g) as a light pink solid (mp 117-118 °C) after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (m, 6H, Ph H-2,6), 7.42 (m, 3H, Ph H-4), 7.40 (m, 6H, Ph H-3,5), 3.29 (s, 2H, $GeCH_2Br$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.0 (Ph C-2,6), 134.7 (Ph C-1), 129.6 (Ph C-4), 128.4 (Ph C-3,5), 13.1 ($GeCH_2Br$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}BrGeNa$ 420.9649 $[M+Na]^+$; found 420.9649.

(iodomethyl)(triphenyl)germane (23)



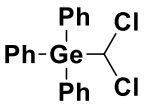
By following general procedure 1, starting from triphenylchlorogermane (0.340 g, 1.0 mmol, 1.0 equiv), ICH_2I (0.803 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (3 mL), **23** was obtained in 80% yield (0.356 g) as a white solid (mp 108-109 °C) after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (m, 6H, Ph H-2,6), 7.42 (m, 3H, Ph H-4), 7.40 (m, 6H, Ph H-3,5), 2.78 (s, 2H, $GeCH_2I$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.2 (Ph C-1), 134.9 (Ph C-2,6), 129.5 (Ph C-4), 128.3 (Ph C-3,5), -20.7 ($GeCH_2I$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}IGeNa$ 468.9479 $[M+Na]^+$; found 468.9482.

(dichloromethyl)(triphenyl)germane (24)



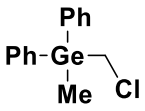
By following general procedure 2, starting from triphenylchlorogermane (0.340 g, 1.0 mmol, 1.0 equiv), dichloromethane (0.192 g, 3.0 mmol, 3.0 equiv), diisopropylamine (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M, 2.8 mmol, 2.8 equiv). Dry THF (10.0 ml each for generation of LDA and the main reaction). The electrophile was dissolved in 3.0 ml dry THF before adding to the reaction flask. The reaction provided 0.353 g (91% yield) of **24** as a white solid (mp 143-145 °C) after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.61 (m, 6H, Ph H-2,6), 7.45 (m, 3H, Ph H-4), 7.42 (m, 6H, Ph H-3,5), 6.03 (s, 1H, $CHCl_2$).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 135.4 (Ph C-2,6), 132.7 (Ph C-1), 130.0 (Ph C-4), 128.5 (Ph C-3,5), 61.4 ($CHCl_2$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{16}Cl_2GeNa^+$ 410.9728 $[M+Na]^+$; found 410.9699.

(chloromethyl)(methyl)diphenylgermane (25)



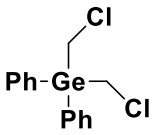
Diphenyldichlorogermane (0.298 g, 1.0 mmol, 1.0 equiv) was dissolved in 3 mL of dry THF under Argon and cooled down to -78 °C and, to this $ClCH_2I$ (0.109 g, 1.5 mmol, 1.5 equiv) was added and allowed to mix for 5 min. MeLi-LiBr complex (0.59 ml of 2.2 M in Et_2O, 1.3 mmol, 1.3 equiv) was added dropwise and allowed to stir for 2 h and then, finally MeLi (1.00 ml of 1.6 M in Et_2O, 1.6 mmol, 1.6 equiv) was added dropwise at -78 °C and allowed to reach 0 °C. After 4 h the reaction mixture was quenched with aqueous saturated NH_4Cl solution. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Compound **25** was obtained in 75% yield (0.223 g) as a pale yellow oil after column chromatography on Silica using *n*-hexane as mobile phase.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (m, 4H, Ph H-2,6), 7.40 (m, 6H, Ph H-3,4,5), 3.39 (s, 2H, CH_2), 0.81 (s, 3H, $GeCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.5 (Ph C-1), 134.0 (Ph C-2,6), 129.3 (Ph C-4), 128.3 (Ph C-3,5), 29.3 (CH_2), -6.0 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{15}ClGeNa$ 314.9966 $[M+Na]^+$; found 314.9989.

bis(chloromethyl)(diphenyl)germane (26)



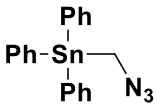
By following general procedure 1, starting from diphenyldichlorogermane (0.298 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.741 g, 4.2 mmol, 4.2 equiv), MeLi-LiBr complex (1.82 mL of 2.2 M in Et_2O, 4.0 mmol, 4.0 equiv) in dry THF (3 mL), **26** was obtained in 88% yield (0.287 g) as a colourless oil after column chromatography on neutral Alumina (Brockmann grade II) using *n*-hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (m, 4H, Ph H-2,6), 7.44 (m, 2H, Ph H-4), 7.43 (m, 4H, Ph H-3,5), 3.58 (s, 4H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.5 (Ph C-2,6), 133.0 (Ph C-1), 130.0 (Ph C-4), 128.5 (Ph C-3,5), 26.9 ($GeCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{14}Cl_2GeNa$ 348.9577 $[M+Na]^+$; found 348.9571.

(azidomethyl)(triphenyl)stannane (27)



By following general procedure 1, starting from triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (15 mL), the mixture was quenched with NH_4Cl (after 1 h) and, after removing the cooling bath, the temperature was increased up to 0 °C. Sodium azide (0.85 g, 1.3 mmol, 1.3 equiv) and sodium iodide (cat.) were solubilized in 3 ml of DMF and added to the mixture, leaving to reach gradually rt during 6 h. The organic phase was extracted 3 times whit *n*-pentane, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude was washed with *n*-heptane giving **27** (0.382 g, 94% yield) as a white solid (mp 37-40 °C).

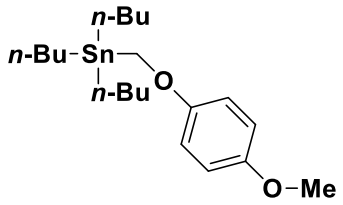
^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.59 (m, 6H, Ph H-2,6), 7.41 (m, 9H, Ph H-3,4,5), 3.69 (s, 2H, CH_2N_3).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.0 (Ph C-2,6), 136.6 (Ph C-1)**,** 129.5 (Ph C-4), 128.8 (Ph C-3,5), 37.4 (1C, CH_2N_3).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -130 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{17}N_3SnNa$ 430.0337 $[M+Na]^+$; found 430.0290.

tributyl[(4-methoxyphenoxy)methyl]stannane (28)



By following general procedure 1, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (15 mL), the mixture was quenched with saturated aqueous NH_4Cl solution (after 1 h) and, after removing the cooling bath, the temperature was increased up to 0 °C. 4-Methoxyphenol (0.104 g, 1.3 mmol, 1.3 equiv) and sodium iodide (cat.) were solubilized in 3 ml of DMF and added to the mixture, leaving to reach gradually rt during 12 h. The organic phase was extracted 3 times whit Et_2O, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude was purified with column chromatography on silica using *n*-hexane:EtOAc (9:1, *v*/*v*) as the mobile phase, giving **28** in 91% yield (0.390 g) as a colourless oil.

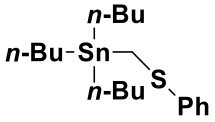
^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.87 (m, 2H, Ph H-2,6), 6.82 (m, 2H, Ph H-3,5), 4.13 (s, 2H, $SnC\underline{H_2}OPhOCH_3$), 3.77 (s, 3H, $PhOC\underline{H_3}$), 1.51 (m, 6H, $SnCH_2C\underline{H_2}CH_2CH_3$), 1.31 (m, 6H, $SnCH_2CH_2C\underline{H_2}CH_3$), 0.94 (m, 6H, $SnC\underline{H_2}CH_2CH_2CH_3$), 0.89 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2C\underline{H_3}$)

^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.9 (Ph C-1), 153.4 (Ph C-4), 114.8 (Ph C-2,6), 114.5 (Ph C-3,5), 59.1 ($SnC\underline{H_2}OPhOCH_3$), 55.8 ($OC\underline{H_3}$), 29.0 ($SnCH_2C\underline{H_2}CH_2CH_3$), 27.3 ($SnCH_2CH_2C\underline{H_2}CH_3$), 13.7 ($SnCH_2CH_2CH_2C\underline{H_3}$), 9.2 ($SnC\underline{H_2}CH_2CH_2CH_3$)

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -33.1 ($SnCH_2OPh$)

HRMS (ESI), *m/z*: calcd. for $C_{20}H_{36}O_2SnNa$ 451.1630 $[M+Na]^+$; found 451.1586.

tributyl[(phenylsulfanyl)methyl]stannane (29)



By following general procedure 1, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), $ClCH_2I$ (0.529 g, 3.0 mmol, 3.0 equiv), MeLi-LiBr complex (1.27 ml of 2.2 M in Et_2O, 2.8 mmol, 2.8 equiv) in dry THF (15 mL), the mixture was quenched with saturated aqueous NH_4Cl solution (after 1 h) and, after removing the cooling bath, the temperature was increased up to 0 °C. Thiophenol (0.133 g, 1.3 mmol, 1.3 equiv), was solubilized in 5 ml of DMF and added to the mixture, leaving to reach gradually rt during 3 h. The organic phase was extracted 3 times whit Et_2O, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude was purified with column chromatography on silica using *n*-hexane:EtOAc (9:1, *v*/*v*) as the mobile phase, giving **29** in 96% yield (0.397 g) as a colourless oil.

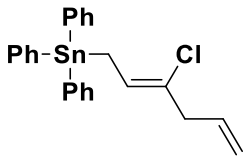
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (m, 2H, Ph H-2,6), 7.28 (m, 2H, Ph H-3,5), 7.09 (m, 1H, Ph H-4), 2.25 (s, 2H, $SnCH_2S$), 1.55 (m, 6H, $SnCH_2\underline{CH_2}CH_2CH_3$), 1.34 (m, 6H, $SnCH_2CH_2\underline{CH_2}CH_3$), 1.01 (m, 6H, $Sn\underline{CH_2}CH_2CH_2CH_3$), 0.91 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2\underline{CH_3}$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5 (Ph C-1), 128.5 (Ph C-3,5), 125.3 (Ph C-2,6), 124.3 (Ph C-4), 29.0 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.3 ($SnCH_2CH_2\underline{C}H_2CH_3$), 13.7 ($SnCH_2CH_2CH_2\underline{C}H_3$), 9.7 ($Sn\underline{C}H_2CH_2CH_2CH_3$), 8.0 ($SnCH_2S$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -11.5 ($SnCH_2S$).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{34}SSnNa$ 437.1295 $[M+Na]^+$; found 437.1296.

[(2*Z*)-3-chloro-2,5-hexadien-1-yl](triphenyl)stannane (30)



By following general procedure 3, starting from triphenylchlorostannane (0.386 g, 1.0 mmol, 1.0 equiv), allyl chloride (0.244 g, 3.0 mmol, 3.0 equiv), diisopropylamine (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M, 2.8 mmol, 2.8 equiv) in dry THF (10 mL), **30** was obtained in 79% yield (0.368 g) as a yellow oil after column chromatography on Florisil with *n*-hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (m, 6H, Ph H-2,6), 7.38 (m, 9H, Ph H-3,4,5), 5.80 (tt, *J* = 8.7 Hz, *J* = 1.0 Hz, 1H, $SnCH_2C\underline{H}$), 5.60 (m, 1H, $SnCH_2CHCClCH_2C\underline{H}CH_2$), 5.01 (m, 1H, $SnCH_2CHCClCH_2CHC\underline{H_2}$), 5.00 (m, 1H, $SnCH_2CHCClCH_2CHC\underline{H_2}$), 2.94 (m, 2H, $SnCH_2CHCClC\underline{H_2}CHCH_2$), 2.50 (td, J^d = 8.7 Hz, J^t = 0.9 Hz, 2H, $SnC\underline{H_2}$).

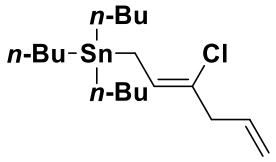
^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4 (Ph C-1), 137.0 (Ph C-2,6), 134.3 ($SnCH_2CHCClCH_2\underline{C}HCH_2$), 129.4 ($SnCH_2CH\underline{C}ClCH_2CHCH_2$), 129.0 (Ph C-4), 128.5 (Ph C-3,5), 123.6 ($SnCH_2\underline{C}HCClCH_2CHCH_2$), 117.1 ($SnCH_2CHCClCH_2CH\underline{C}H_2$), 43.3 ($SnCH_2CHCl\underline{C}H_2CH\ CH_2$), 13.6 ($Sn\underline{C}H_2CHCClCH_2CHCH_2$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -113.1 ($SnCH_2$).

HRMS (ESI), *m/z*: calcd. for $C_{24}H_{23}ClSnNa$ 489.0402 $[M+Na]^+$; found 489.0413.

ST065

tributyl[(2Z)-3-chloro-2,5-hexadien-1-yl]stannane (31)



By following general procedure 3, starting from tributylchlorostannane (0.326 g, 1.0 mmol, 1.0 equiv), allyl chloride (0.244 g, 3.0 mmol, 3.0 equiv), diisopropylamine (0.392 g, 2.8 mmol, 2.8 equiv) and MeLi-LiBr complex (1.27 ml of 2.2M, 2.8 mmol, 2.8 equiv) in dry THF (10 mL), **31** was obtained as a yellow oil in 73% yield (0.296 g) after column chromatography on Florisil with *n*-hexane.

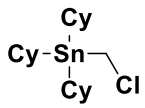
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.81 (m, 1H, $SnCH_2CHCClCH_2C\underline{H}CH_2$), 5.69 (tt, *J* = 8.9 Hz, *J* = 1.0 Hz, 1H, $SnCH_2C\underline{H}CClCH_2CHCH_2$), 5.11 (m, 1H, $SnCH_2CHCClCH_2CHC\underline{H}_2$), 5.08 (m, 1H, $SnCH_2CHCClCH_2CHC\underline{H}_2$), 3.03 (m, 2H, $SnCH_2CHCClC\underline{H}_2CHCH_2$), 1.80 (d, *J* = 8.9 Hz, 2H, $SnC\underline{H}_2CHCClCH_2CHCH_2$), 1.49 (m, 6H, $SnCH_2C\underline{H}_2CH_2CH_3$), 1.30 (m, 6H, $SnCH_2CH_2C\underline{H}_2CH_3$), 0.89 (t, *J* = 7.3 Hz, 9H, $SnCH_2CH_2CH_2C\underline{H}_3$), 0.88 (m, 6H, $SnC\underline{H}_2CH_2CH_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.9 ($SnCH_2CHCClCH_2\underline{C}HCH_2$), 126.5 ($SnCH_2CH\underline{C}ClCH_2CHCH_2$), 125.7 ($SnCH_2\underline{C}HCClCH_2CHCH_2$), 116.8 ($SnCH_2CHCClCH_2CH\underline{C}H_2$), 43.5 ($SnCH_2CHCCl\underline{C}H_2CHCH_2$), 29.1 ($SnCH_2\underline{C}H_2CH_2CH_3$), 27.3 ($SnCH_2CH_2\underline{C}HCH_3$), 13.7 ($SnCH_2CH_2CH_2\underline{C}H_3$), 11.6 ($Sn\underline{C}H_2CHCClCH_2CHCH_2$), 9.8 ($Sn\underline{C}H_2CH_2CH_2CH_3$).

^{119}Sn NMR (149 MHz, $CDCl_3$) δ: -7.6 ($SnCH_2$).

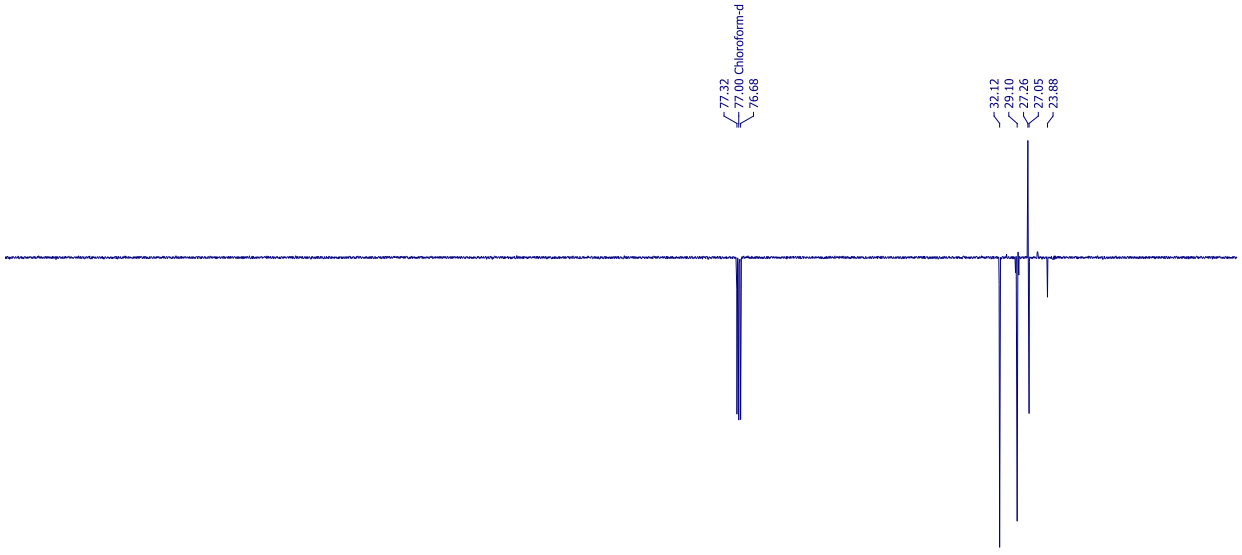
HRMS (ESI), *m/z*: calcd. for $C_{18}H_{35}ClSnNa$ 429.1341 $[M+Na]^+$; found 429.1296.

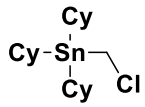
Copies of ^{1}H- and ^{13}C-NMR spectra



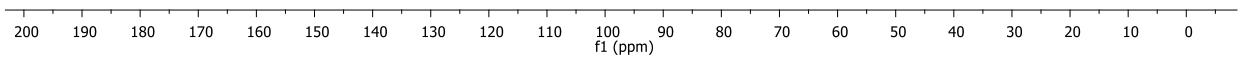
ST007

(2) (^{1}H-NMR, 400 MHz, $CDCl_3$)

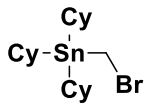




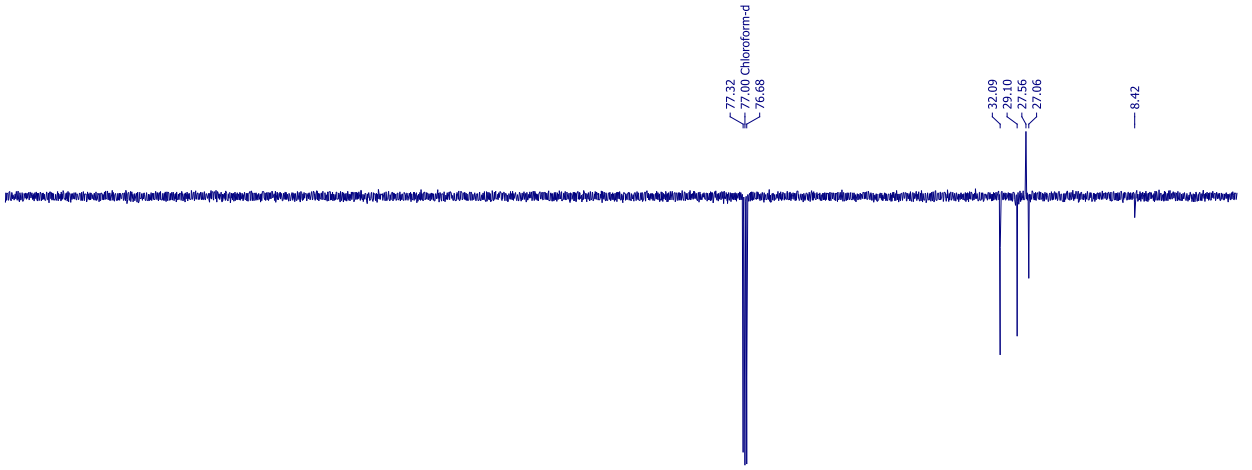
(2) (^{13}C-NMR, 100 MHz, $CDCl_3$)

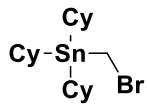


ST009

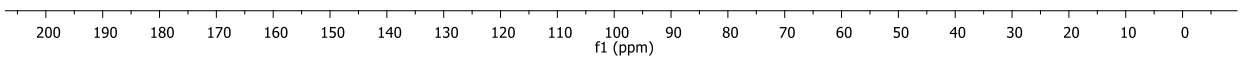


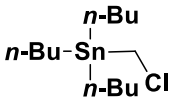
(3) (^{1}H-NMR, 400 MHz, $CDCl_3$)





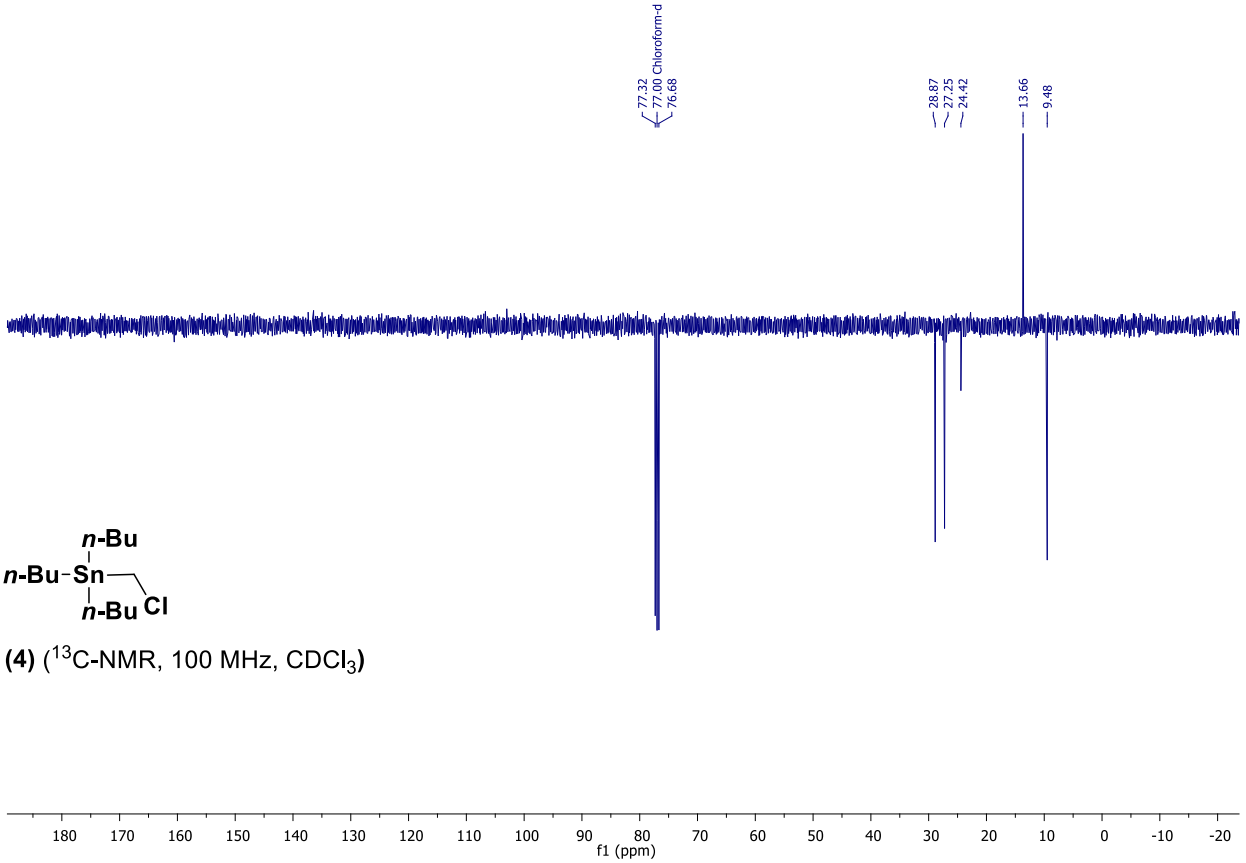
(3) (^{13}C-NMR, 100 MHz, $CDCl_3$)



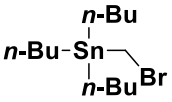


SNVC2

(4) (^{1}H-NMR, 400 MHz, $CDCl_3$)

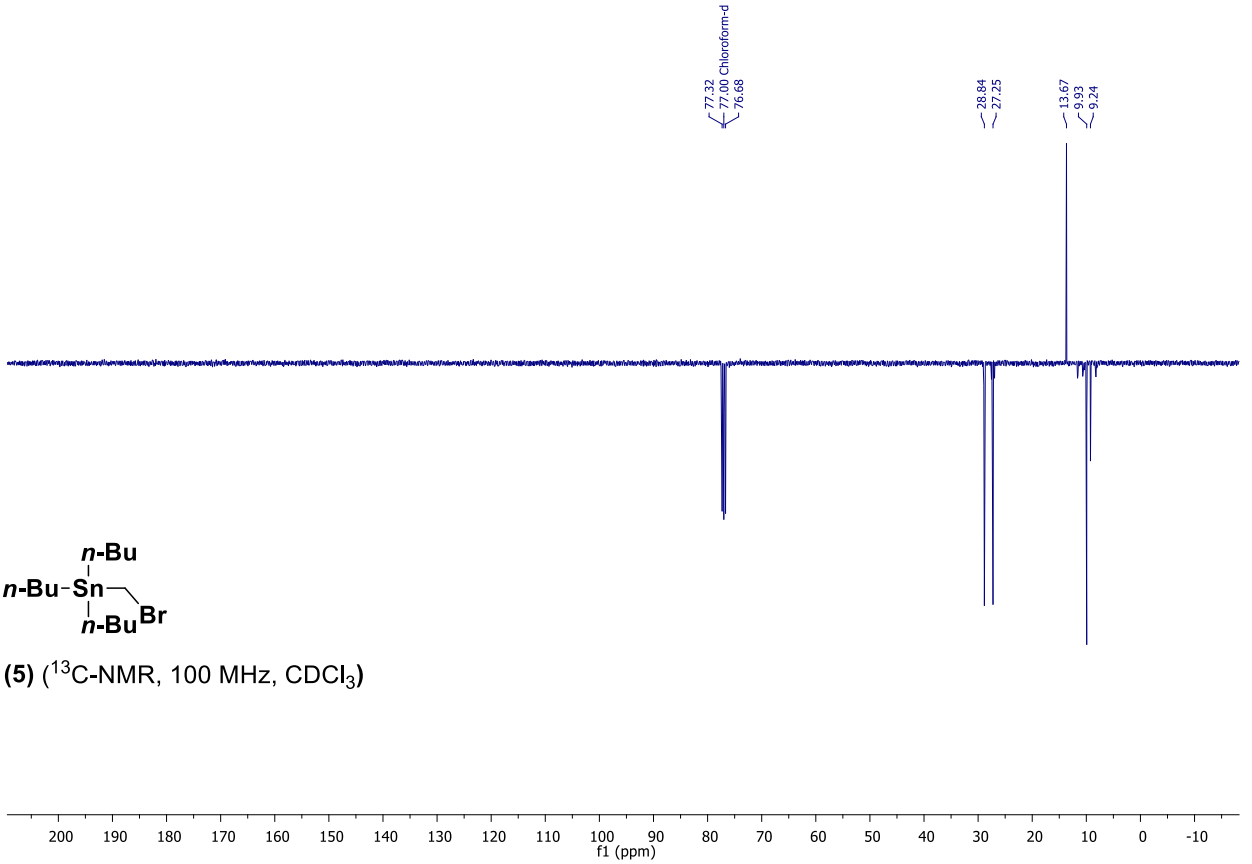


(4) (^{13}C-NMR, 100 MHz, $CDCl_3$)

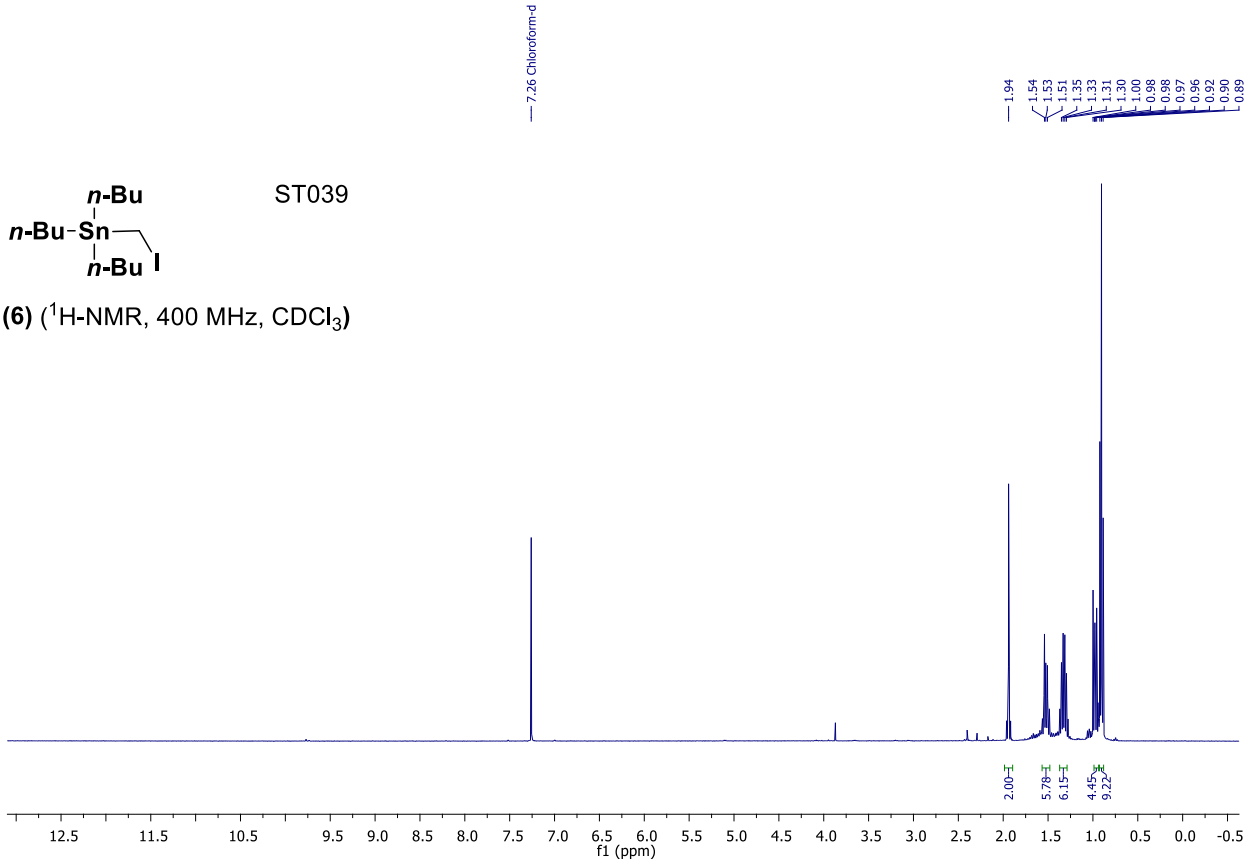


ST030

(5) (^{1}H-NMR, 400 MHz, $CDCl_3$)

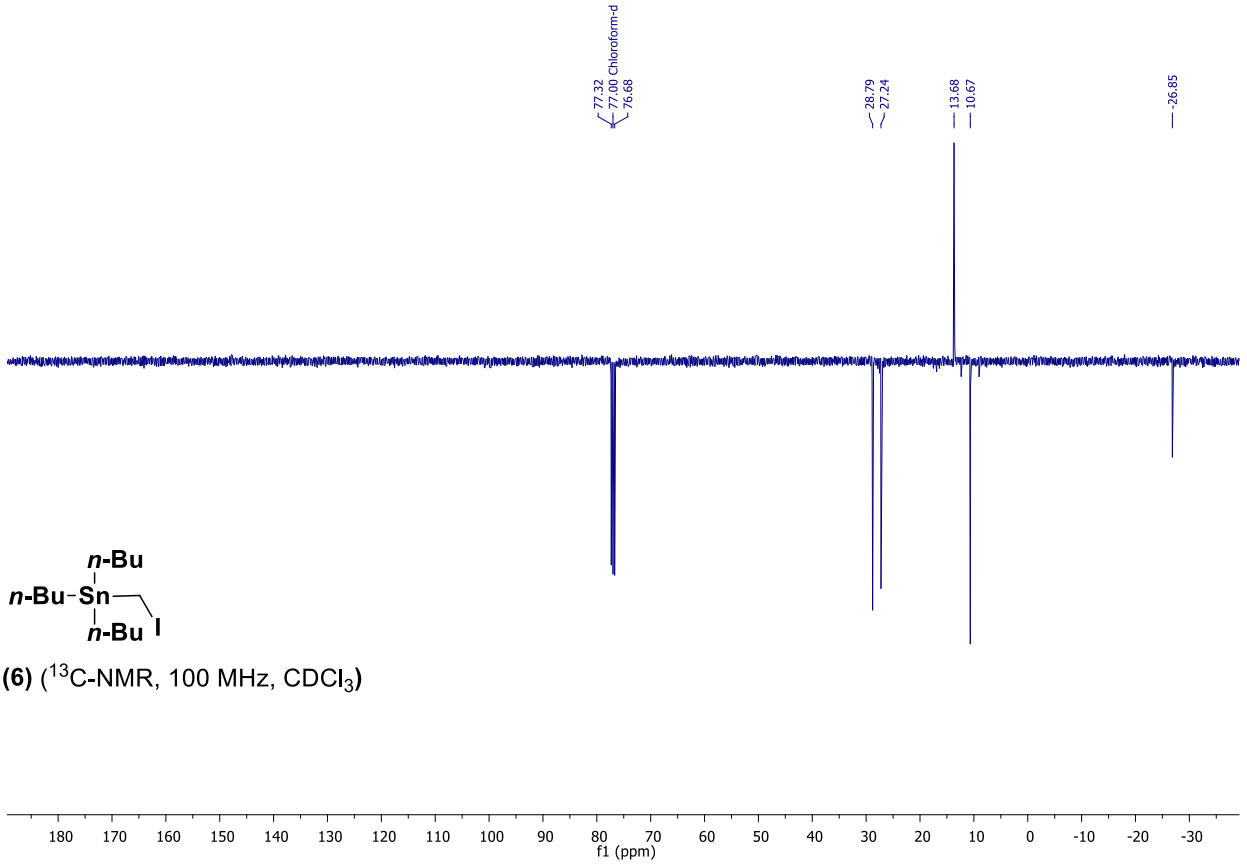


(5) (^{13}C-NMR, 100 MHz, $CDCl_3$)

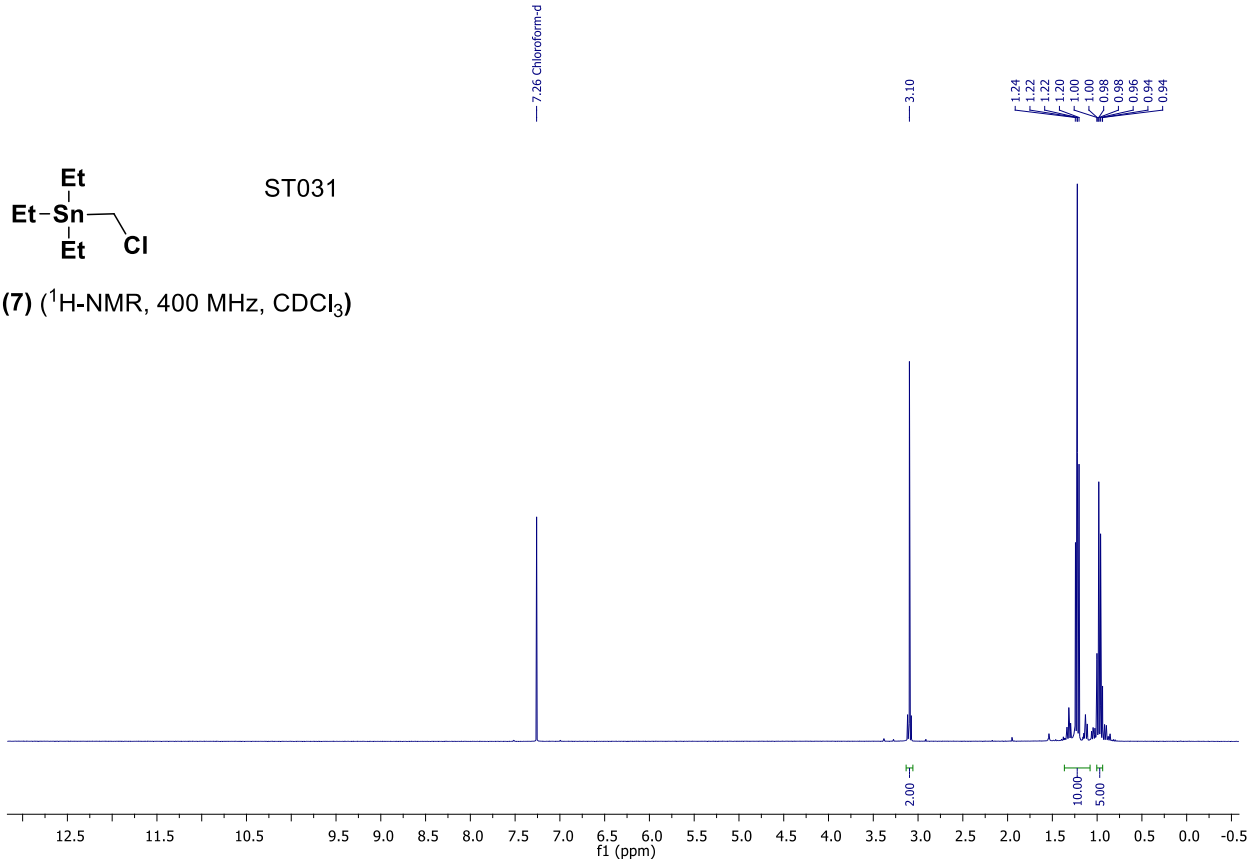


ST039

(6) (^{1}H-NMR, 400 MHz, $CDCl_3$)

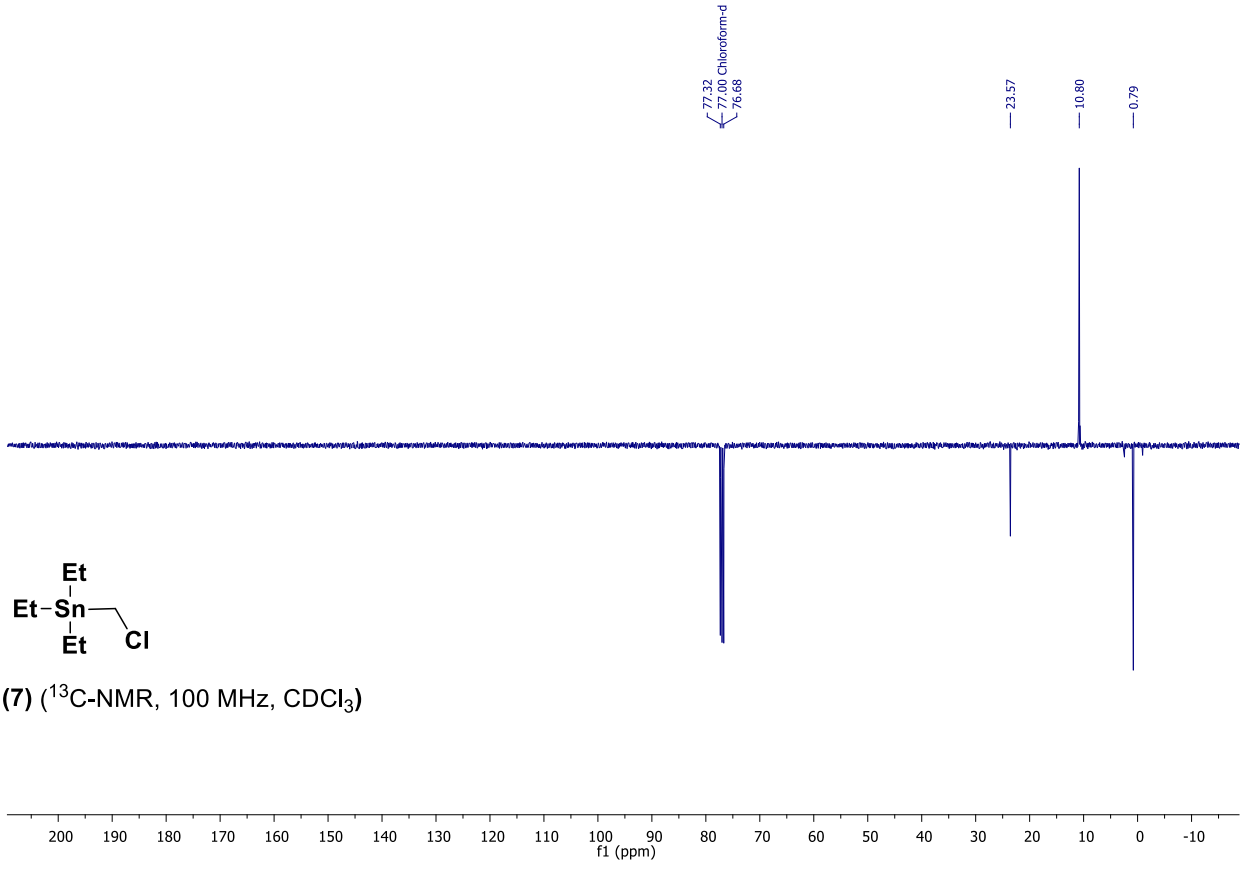


(6) (^{13}C-NMR, 100 MHz, $CDCl_3$)

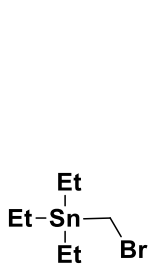


ST031

(7) (^{1}H-NMR, 400 MHz, $CDCl_3$)

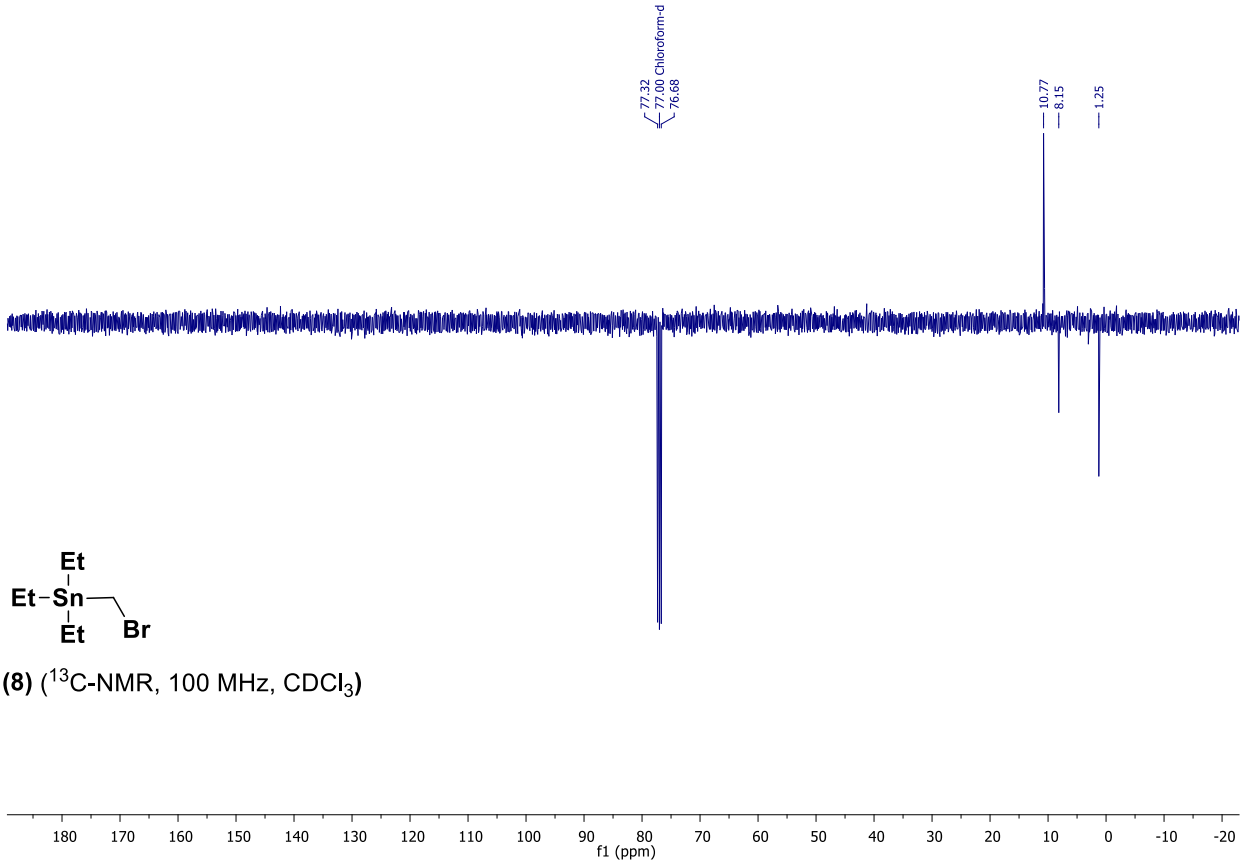


(7) (^{13}C-NMR, 100 MHz, $CDCl_3$)

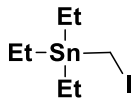


ST058

(8) (^{1}H-NMR, 400 MHz, $CDCl_3$)

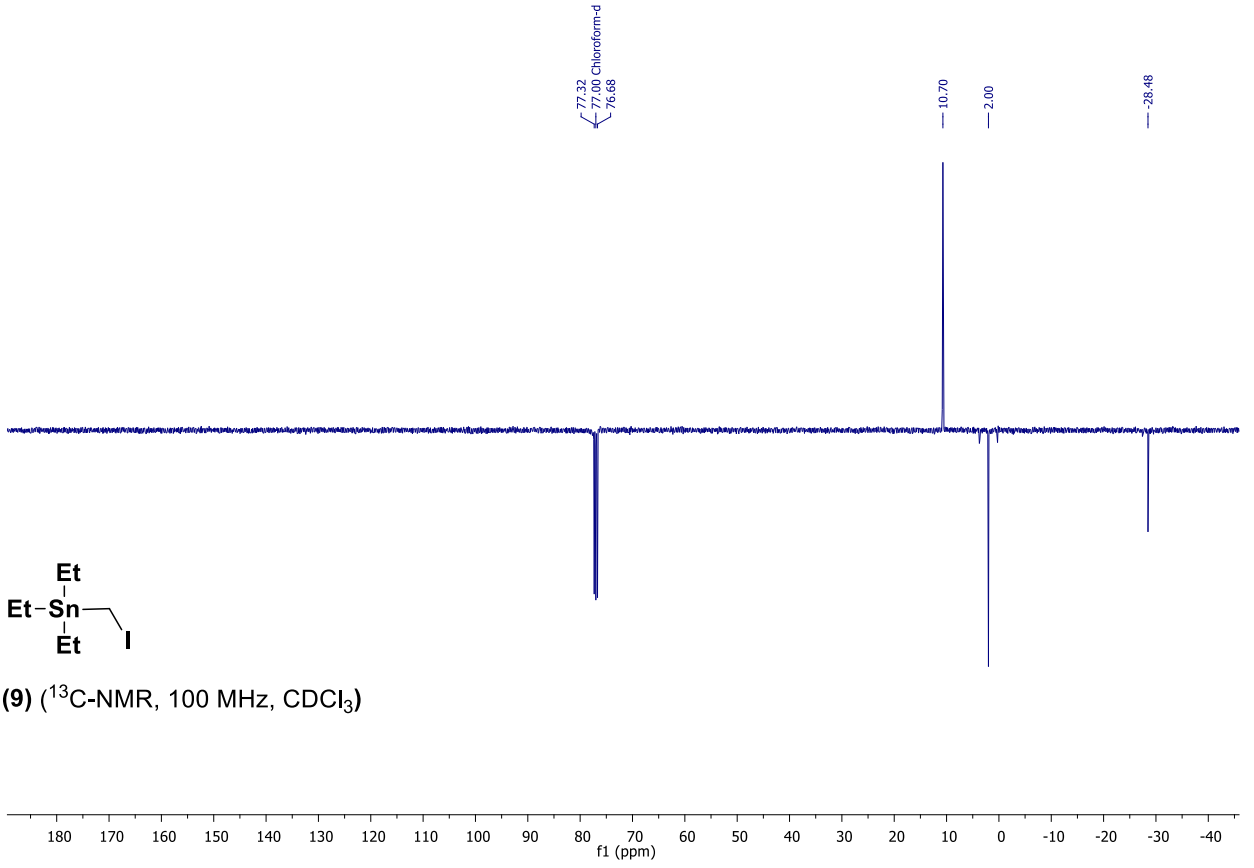


(8) (^{13}C-NMR, 100 MHz, $CDCl_3$)

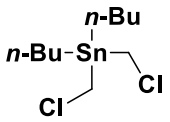


ST032

(9) (^{1}H-NMR, 400 MHz, $CDCl_3$)

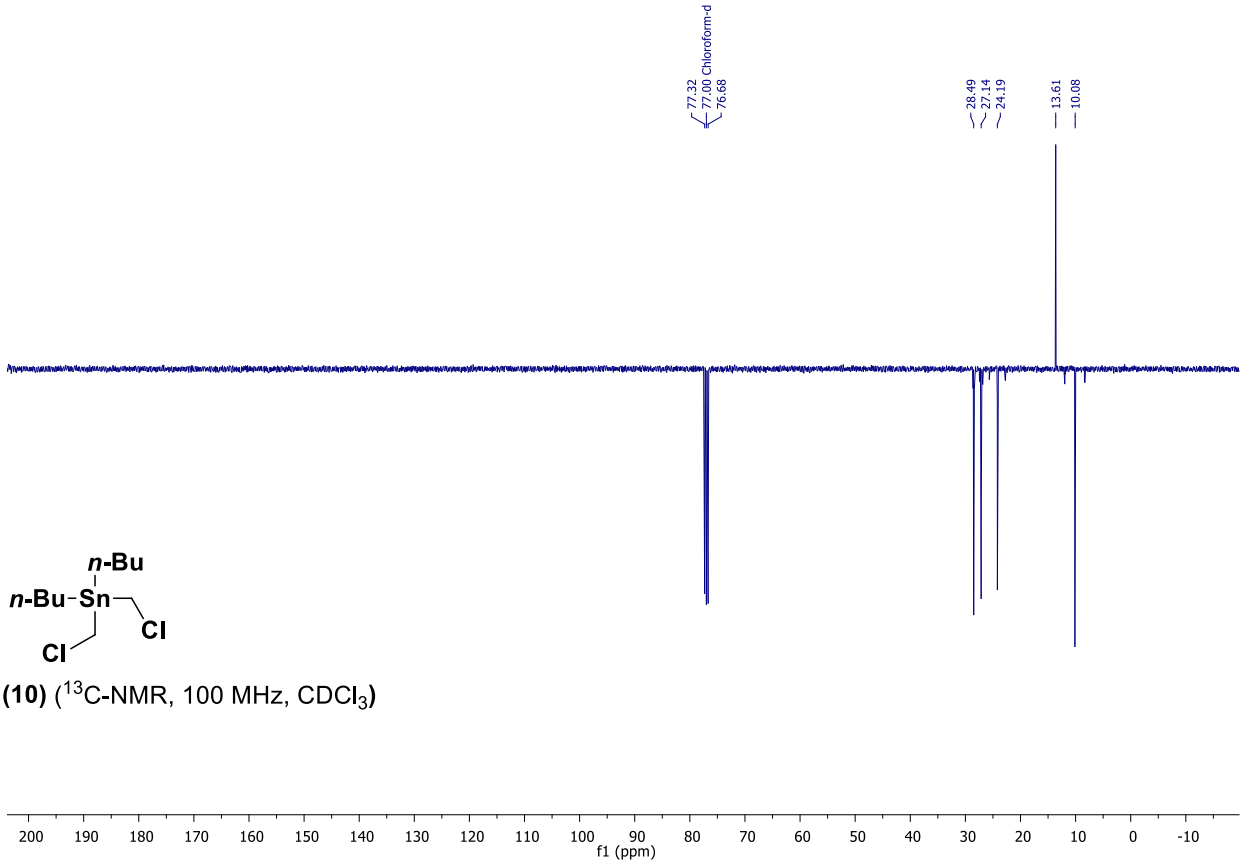


(9) (^{13}C-NMR, 100 MHz, $CDCl_3$)

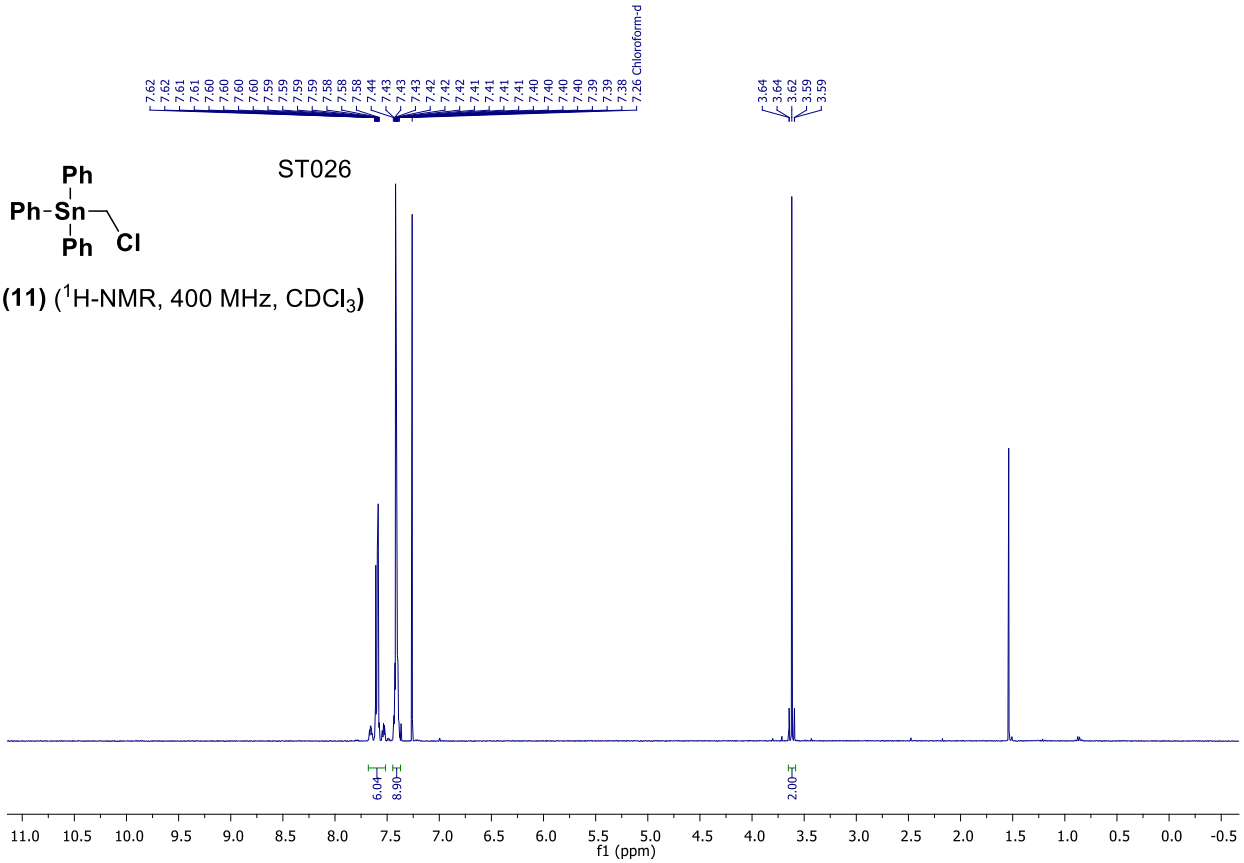


ST025

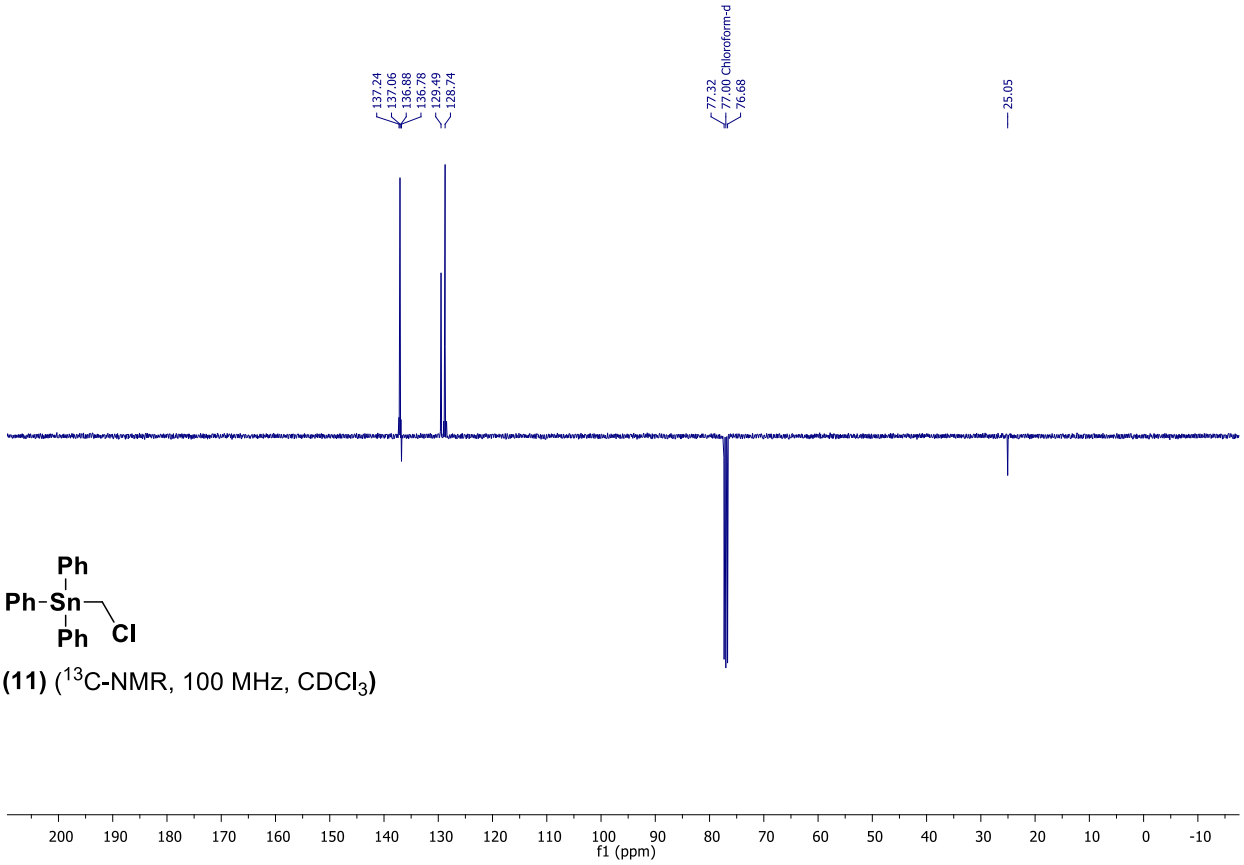
(10) (^{1}H-NMR, 400 MHz, $CDCl_3$)



(10) (^{13}C-NMR, 100 MHz, $CDCl_3$)

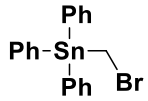


(11) (^{1}H-NMR, 400 MHz, $CDCl_3$)

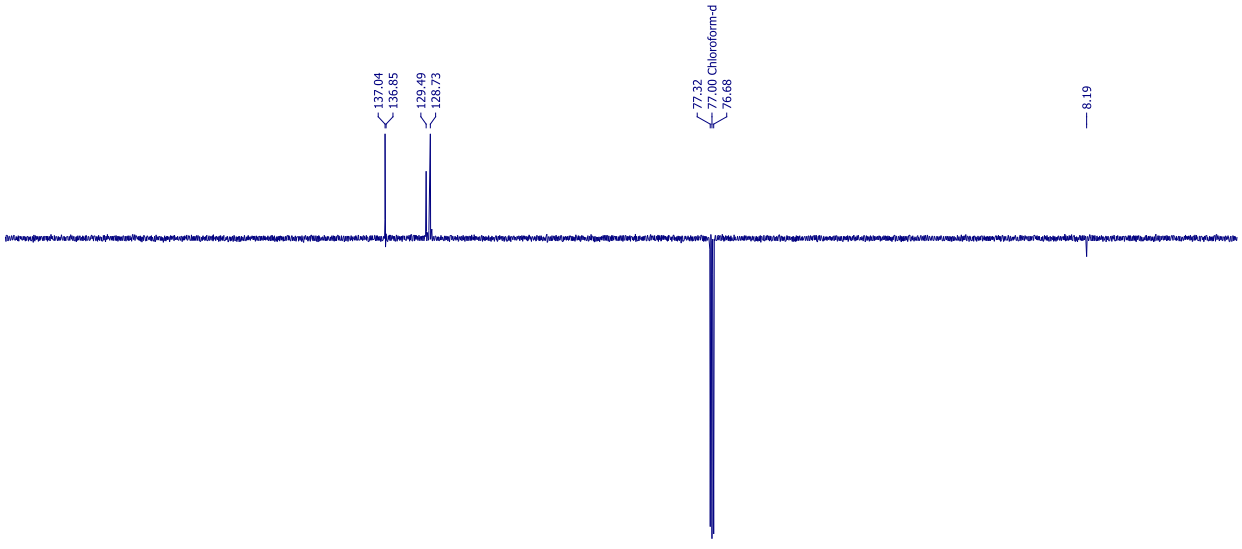


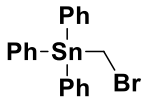
(11) (^{13}C-NMR, 100 MHz, $CDCl_3$)

ST038

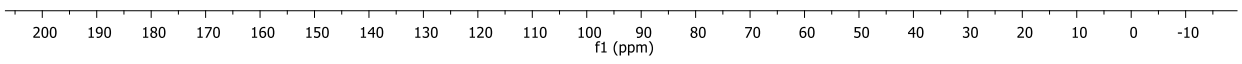


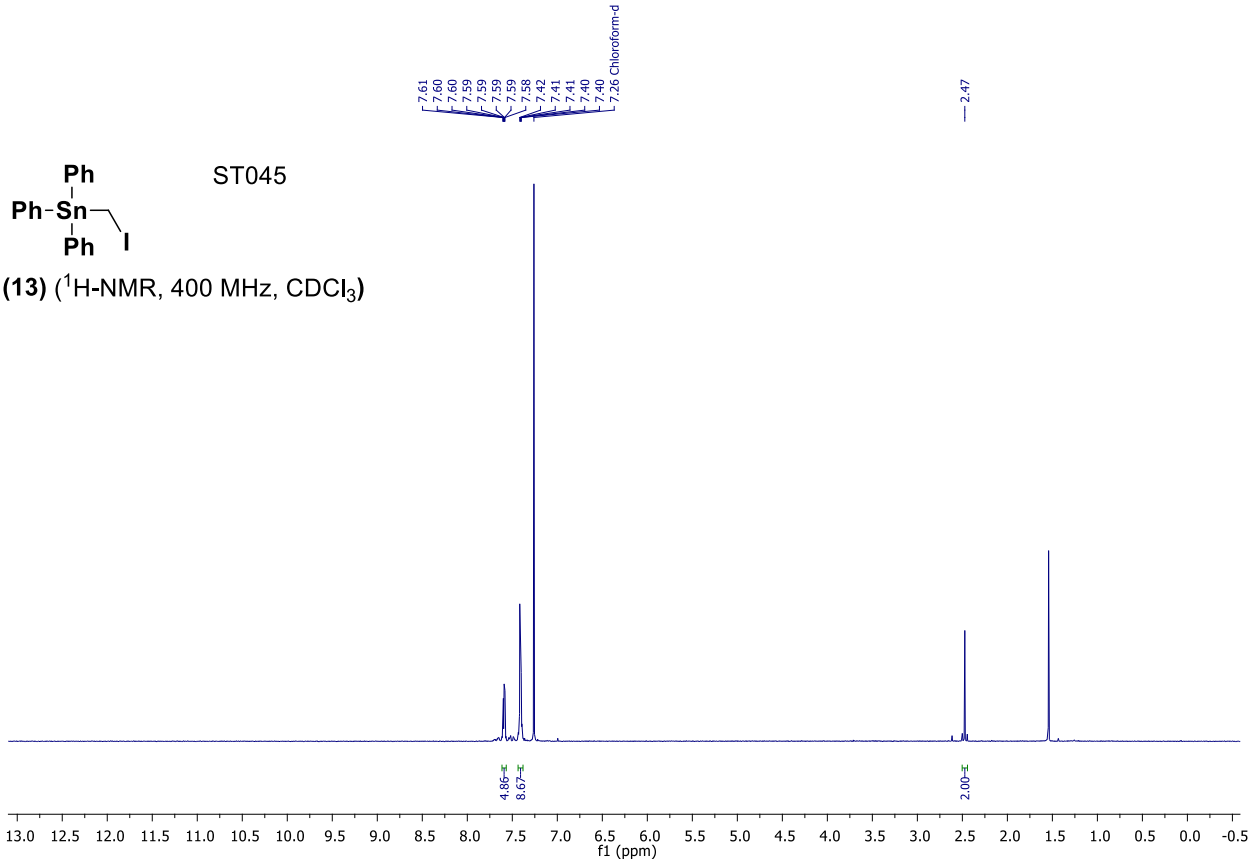
(12) (^{1}H-NMR, 400 MHz, $CDCl_3$)



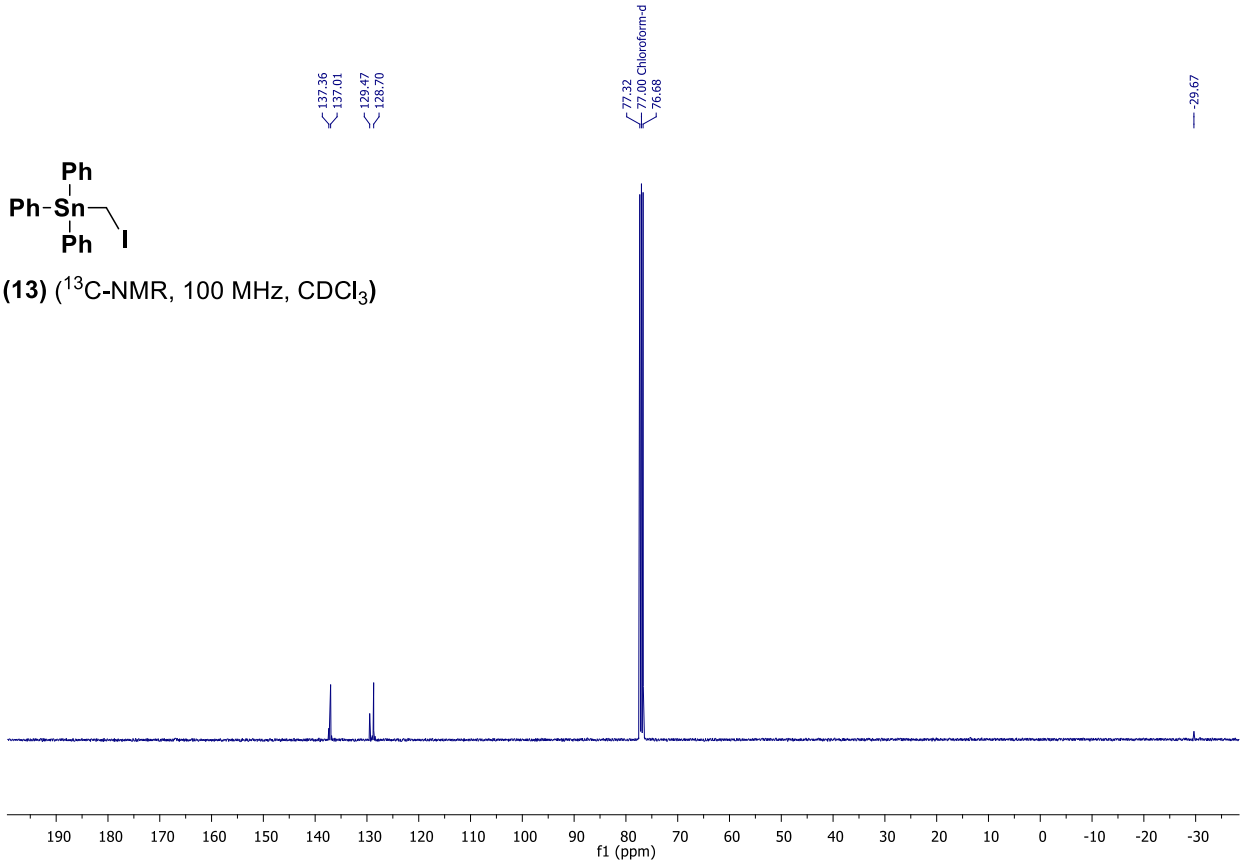


(12) (^{13}C-NMR, 100 MHz, $CDCl_3$)

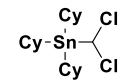




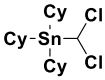
(13) (^{1}H-NMR, 400 MHz, $CDCl_3$)



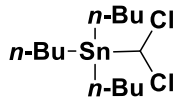
(13) (^{13}C-NMR, 100 MHz, $CDCl_3$)



(14) (^{1}H-NMR, 200 MHz, $CDCl_3$)

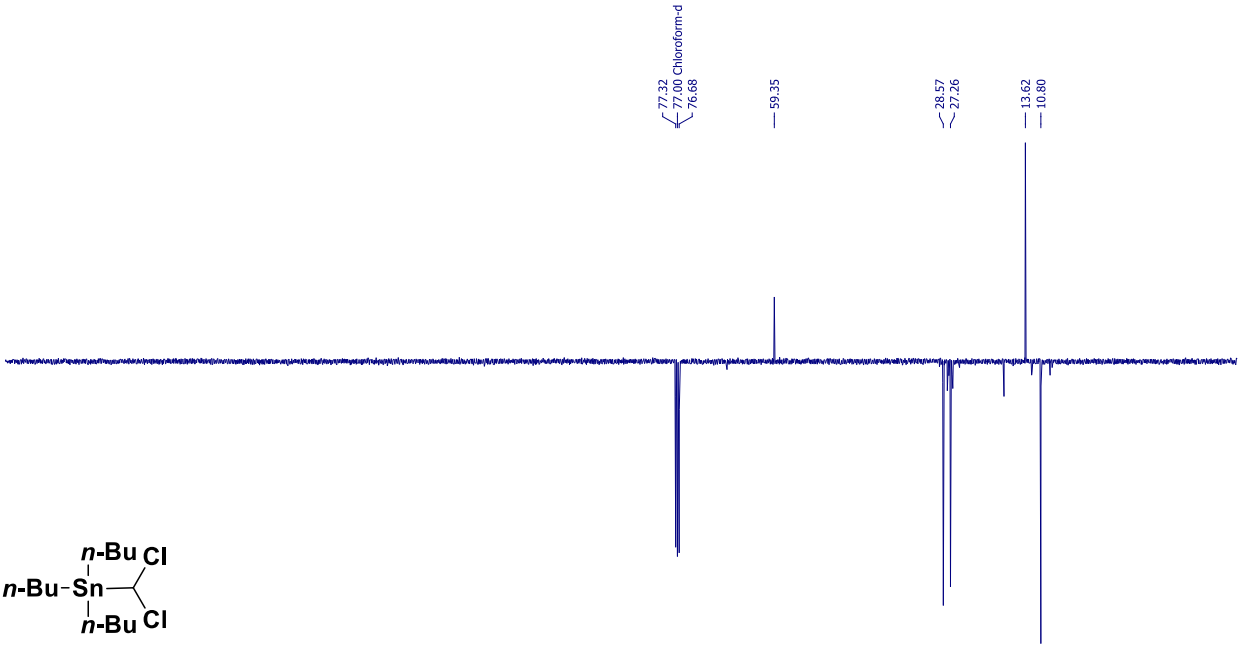


(14) (^{13}C-NMR, 50 MHz, $CDCl_3$)

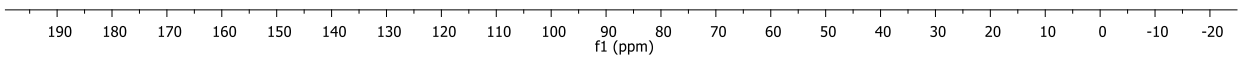


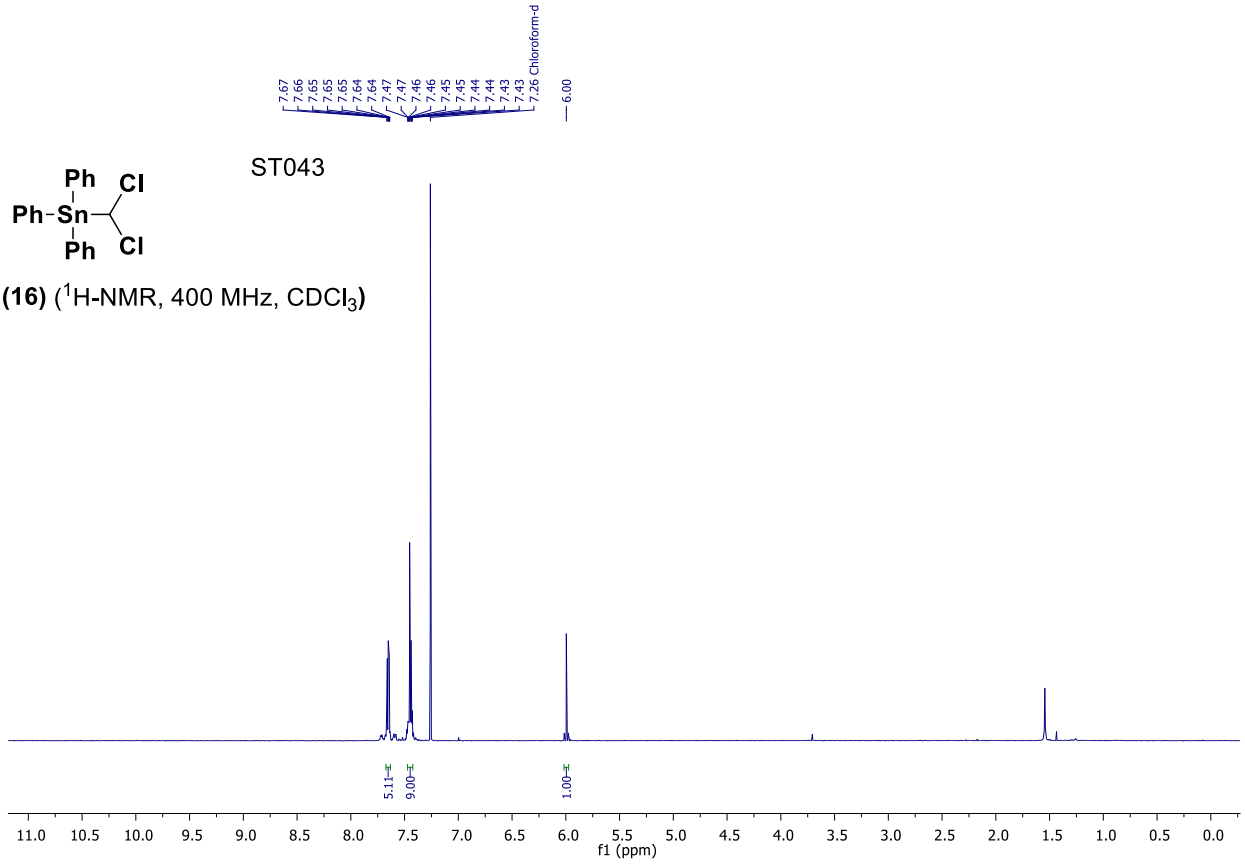
ST048

(15) (^{1}H-NMR, 400 MHz, $CDCl_3$)

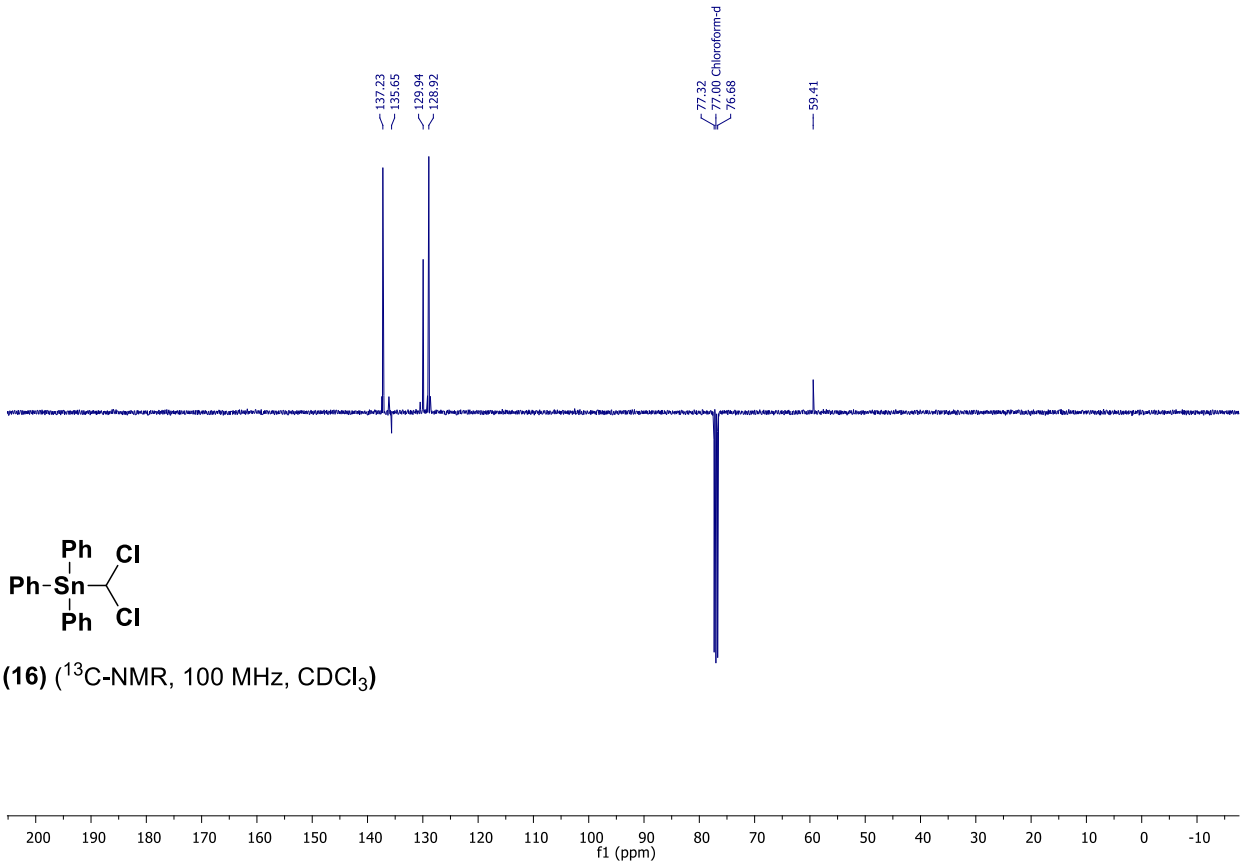


(15) (^{13}C-NMR, 100 MHz, $CDCl_3$)

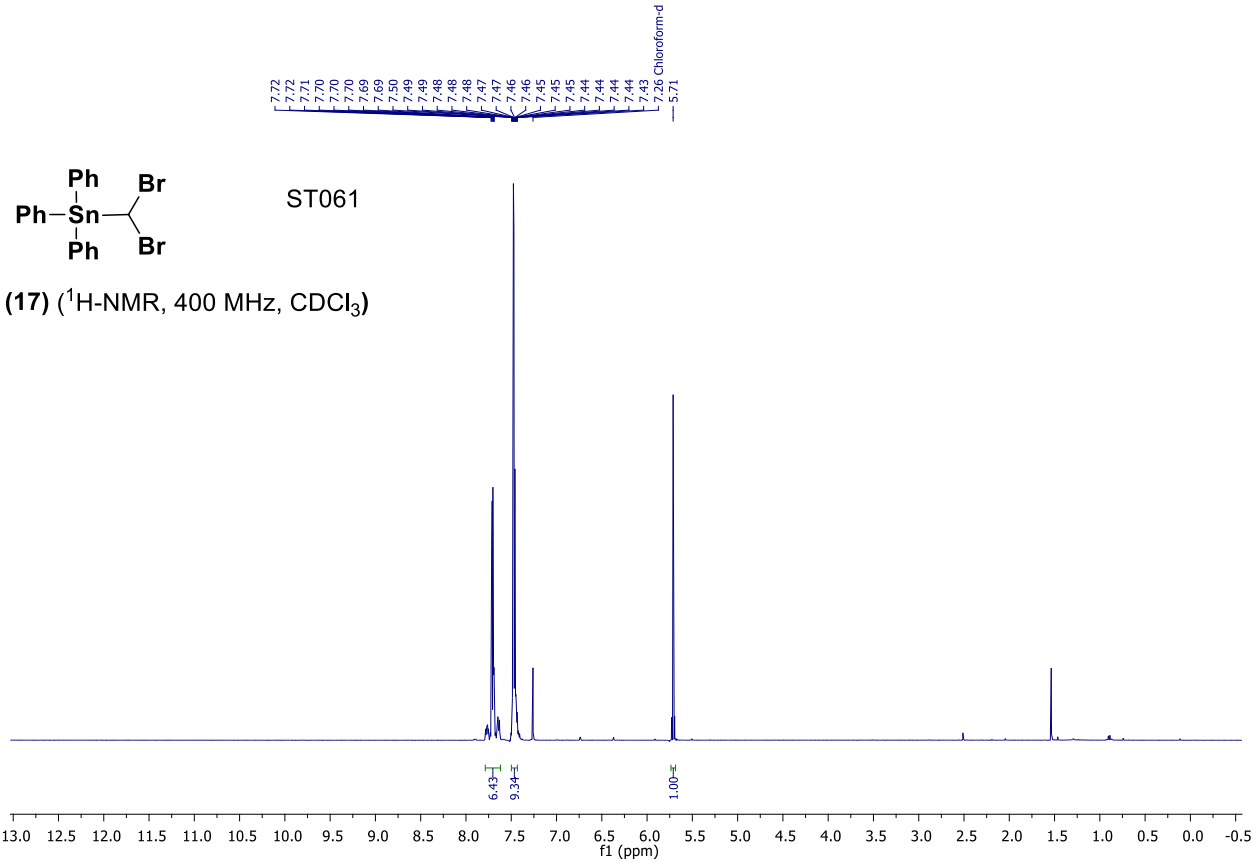




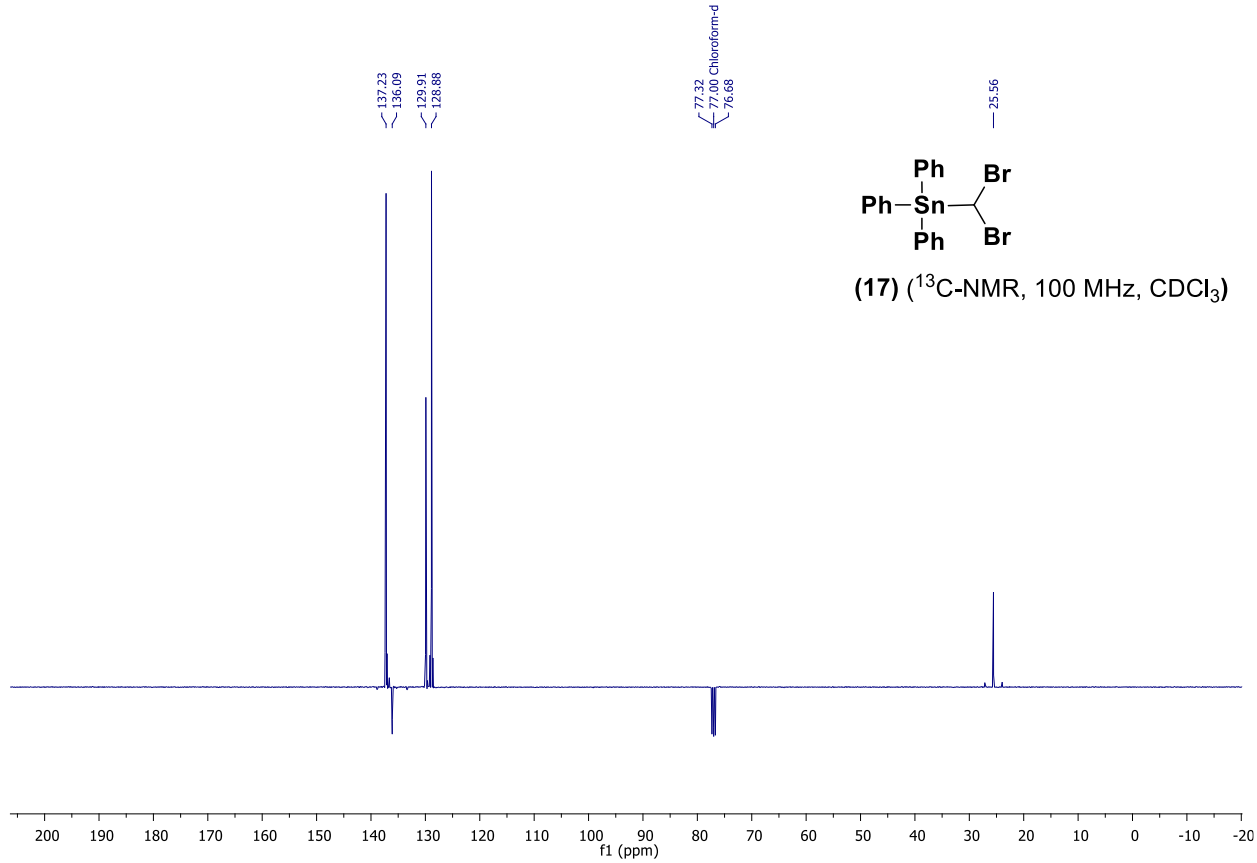
(16) (^{1}H-NMR, 400 MHz, $CDCl_3$)



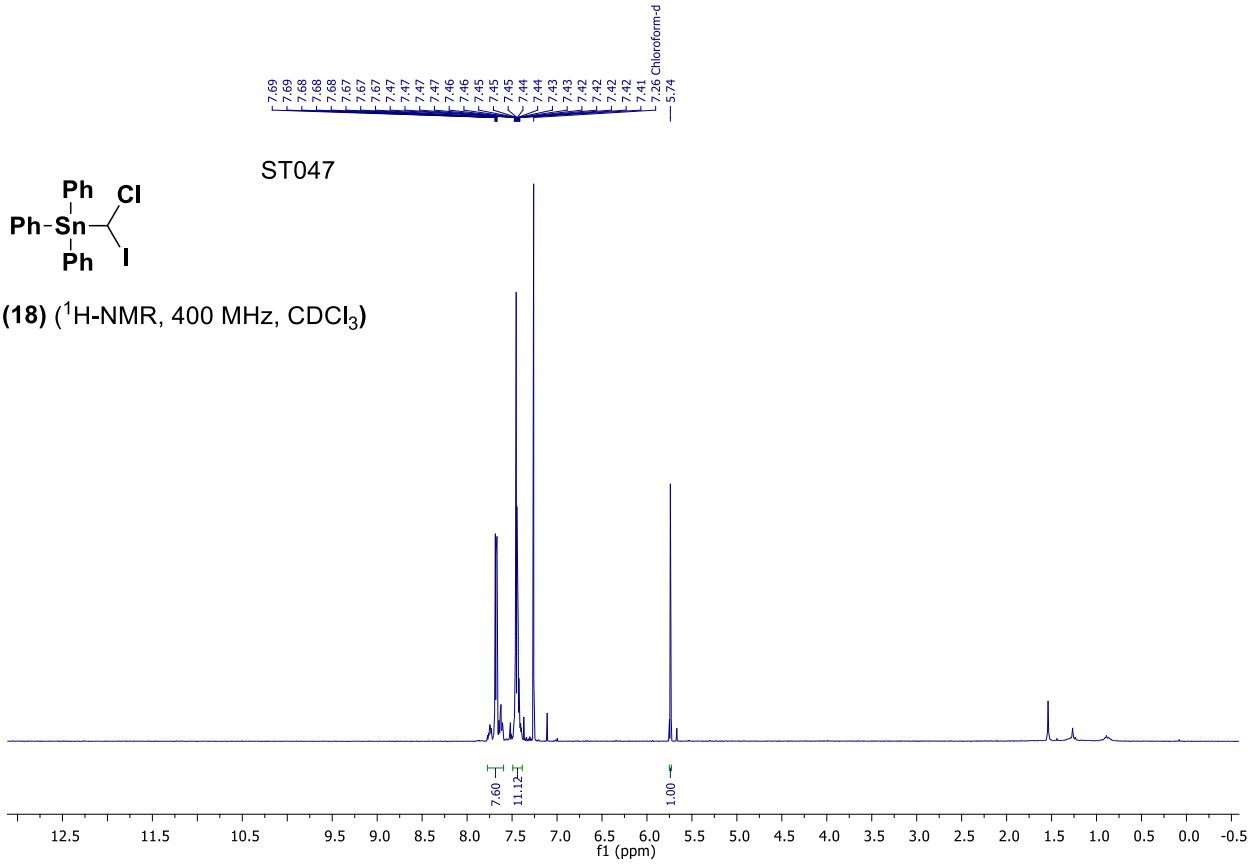
(16) (^{13}C-NMR, 100 MHz, $CDCl_3$)



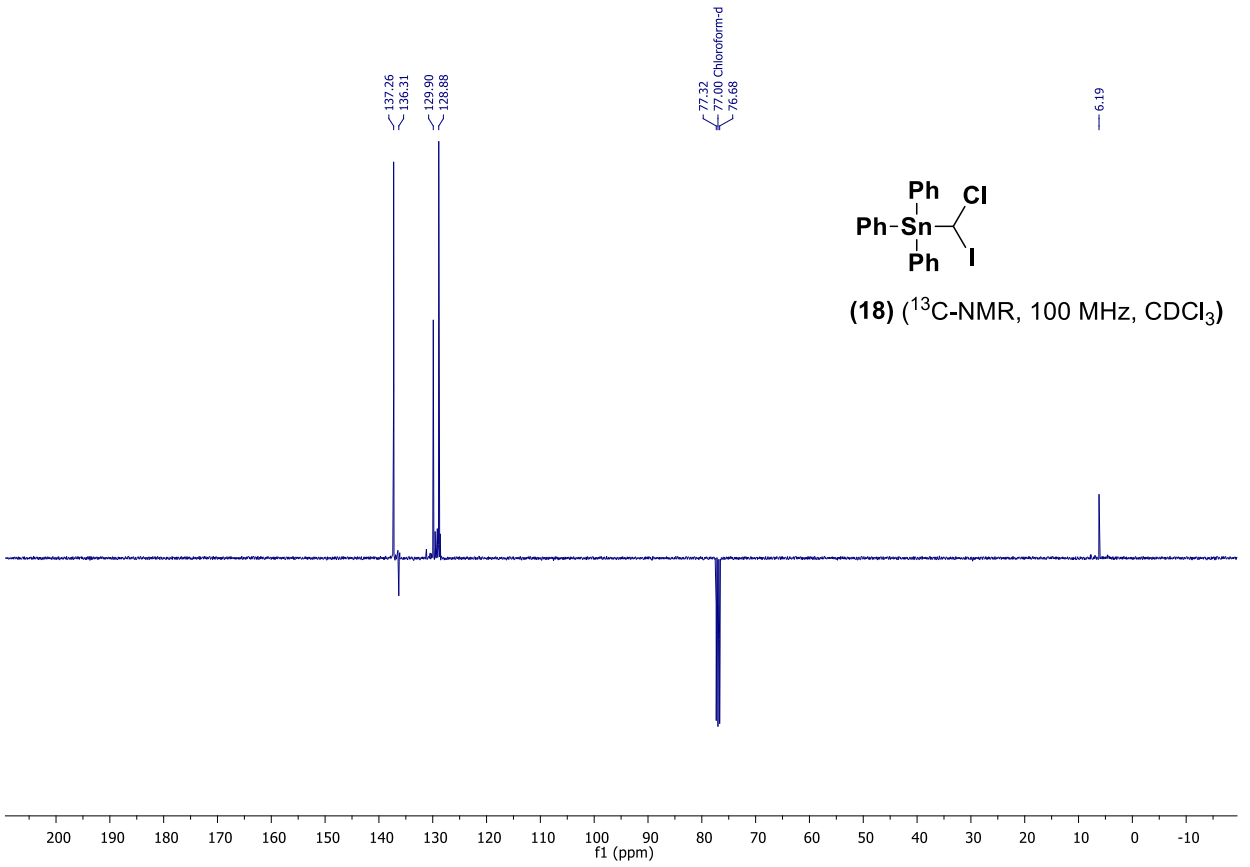
(17) (^{1}H-NMR, 400 MHz, $CDCl_3$)



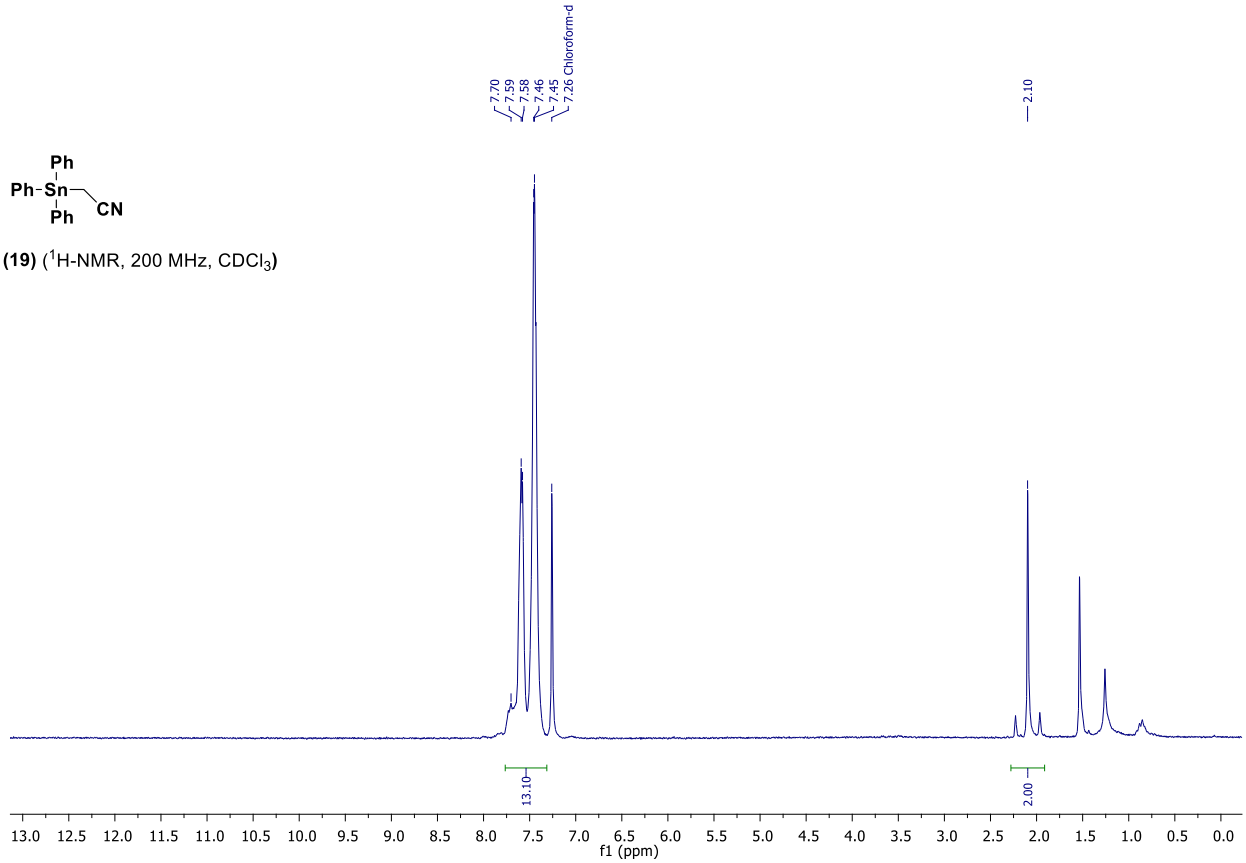
(17) (^{13}C-NMR, 100 MHz, $CDCl_3$)



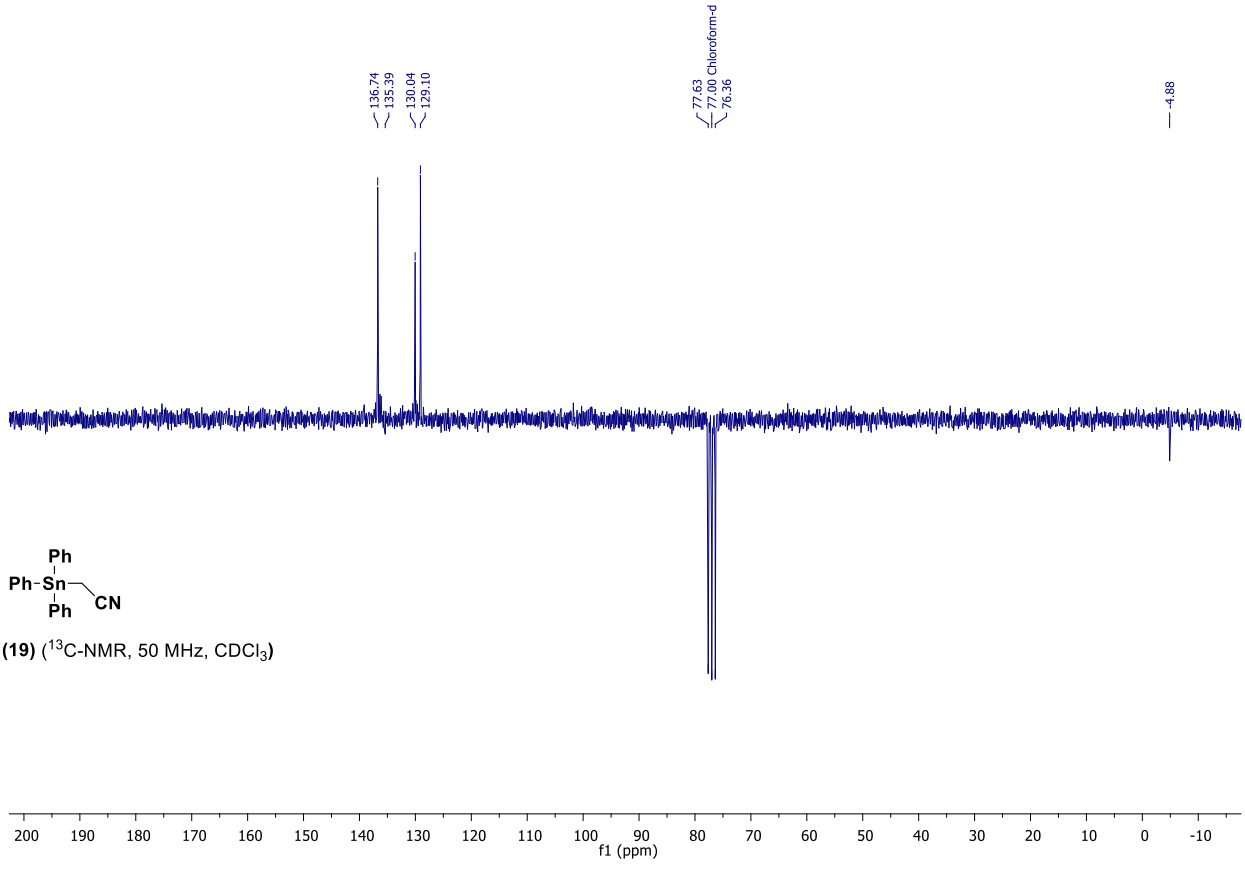
(18) (^{1}H-NMR, 400 MHz, $CDCl_3$)



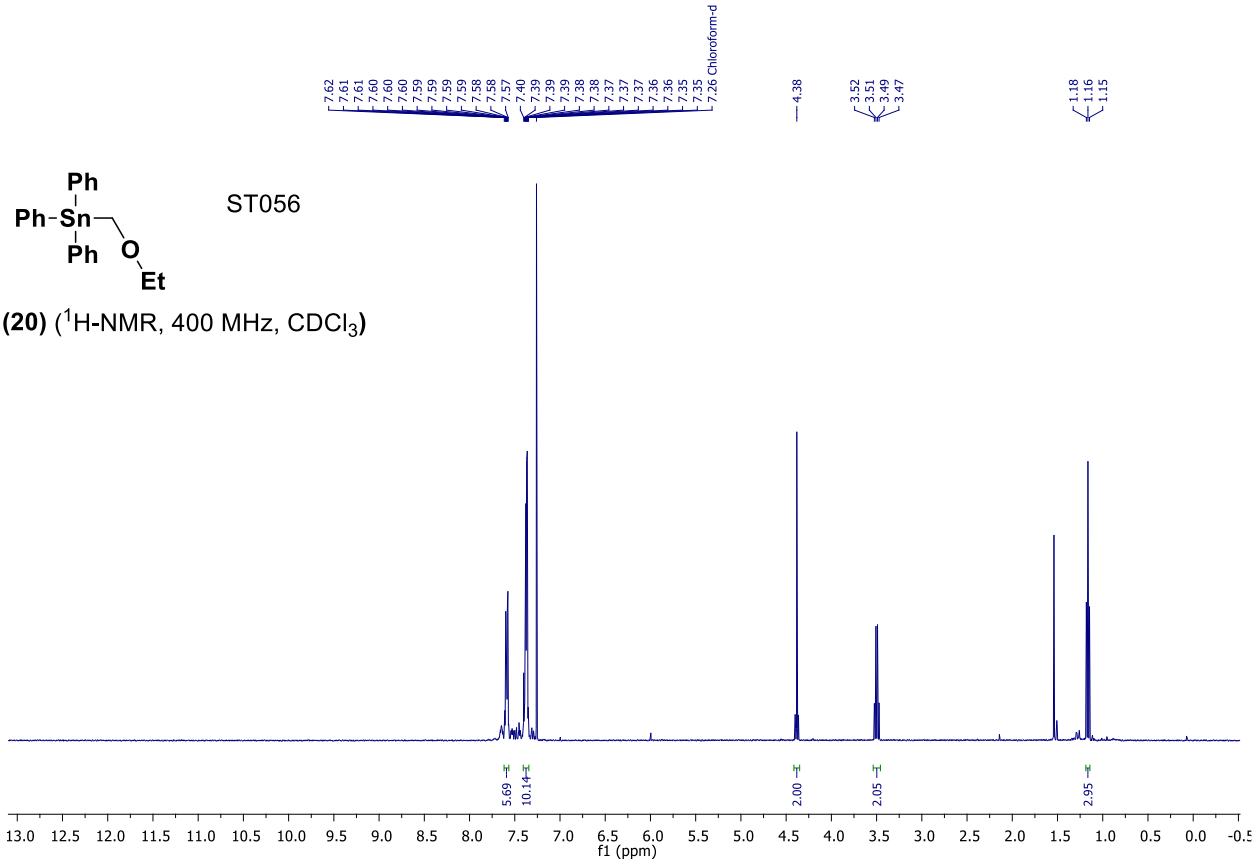
(18) (^{13}C-NMR, 100 MHz, $CDCl_3$)



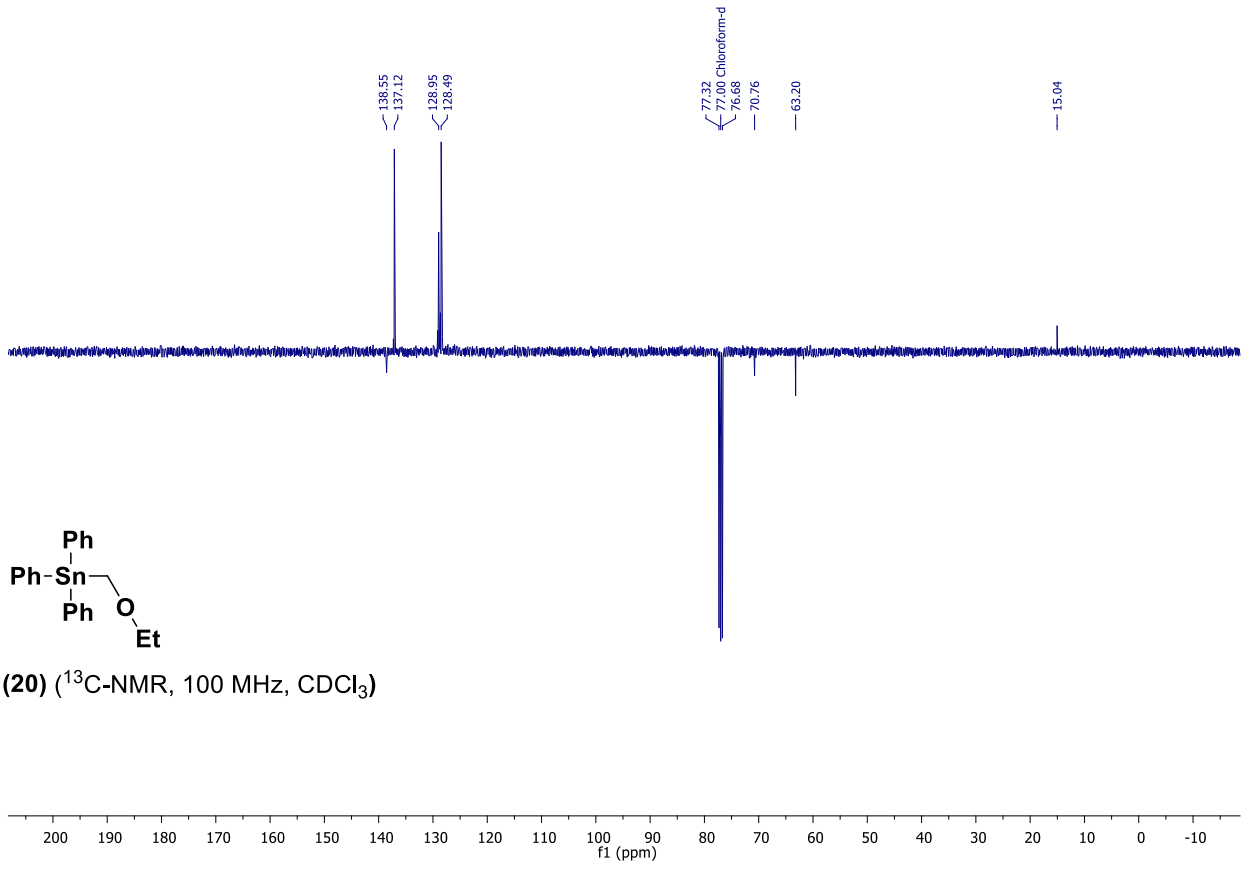
(19) (^{1}H-NMR, 200 MHz, $CDCl_3$)



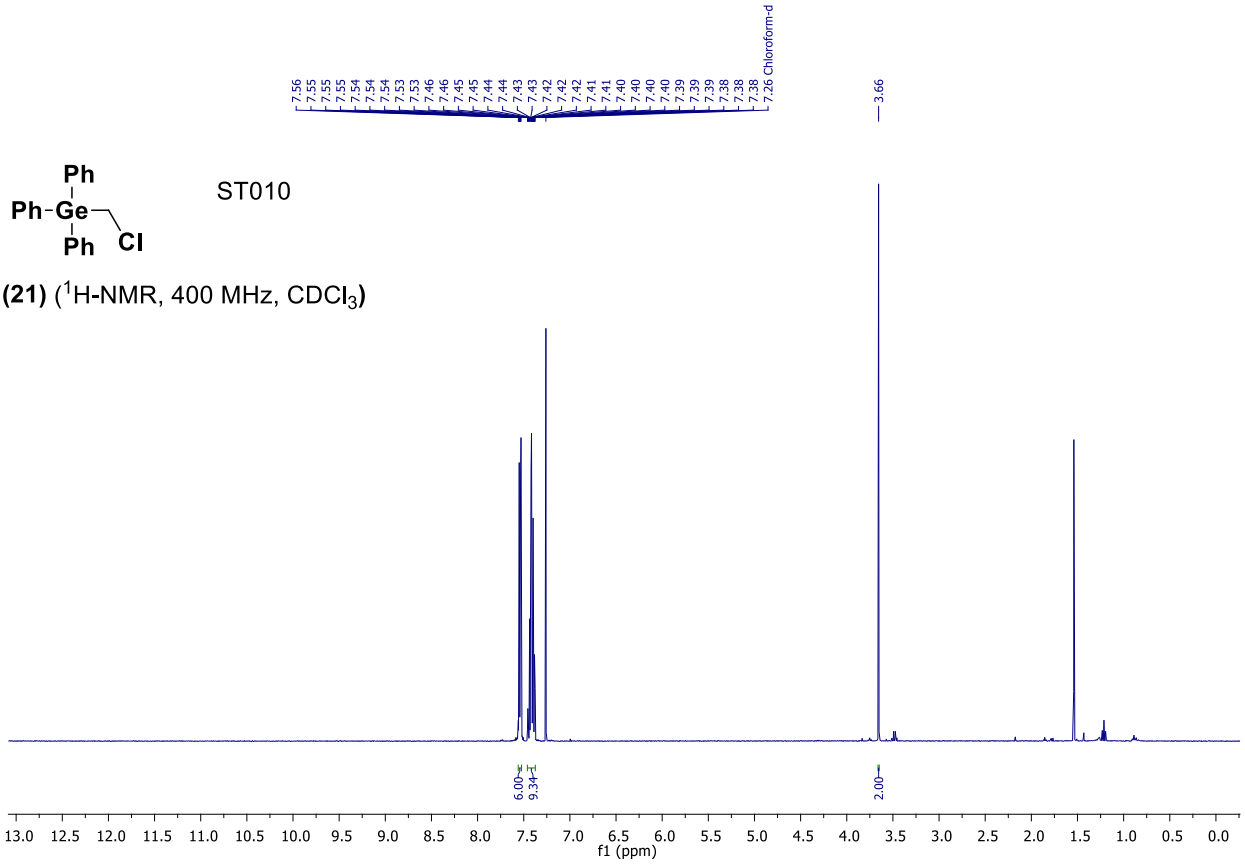
(19) (^{13}C-NMR, 50 MHz, $CDCl_3$)



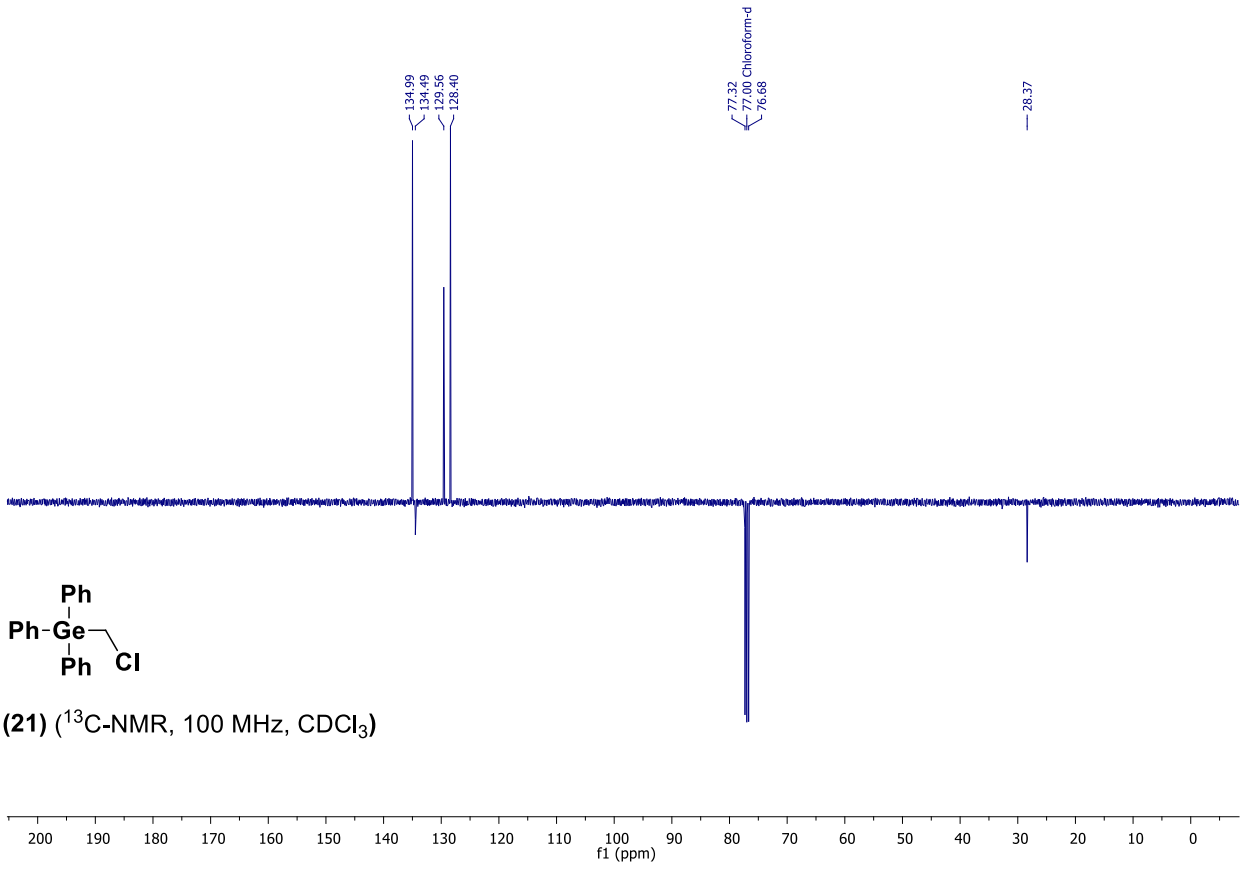
(20) (^{1}H-NMR, 400 MHz, $CDCl_3$)



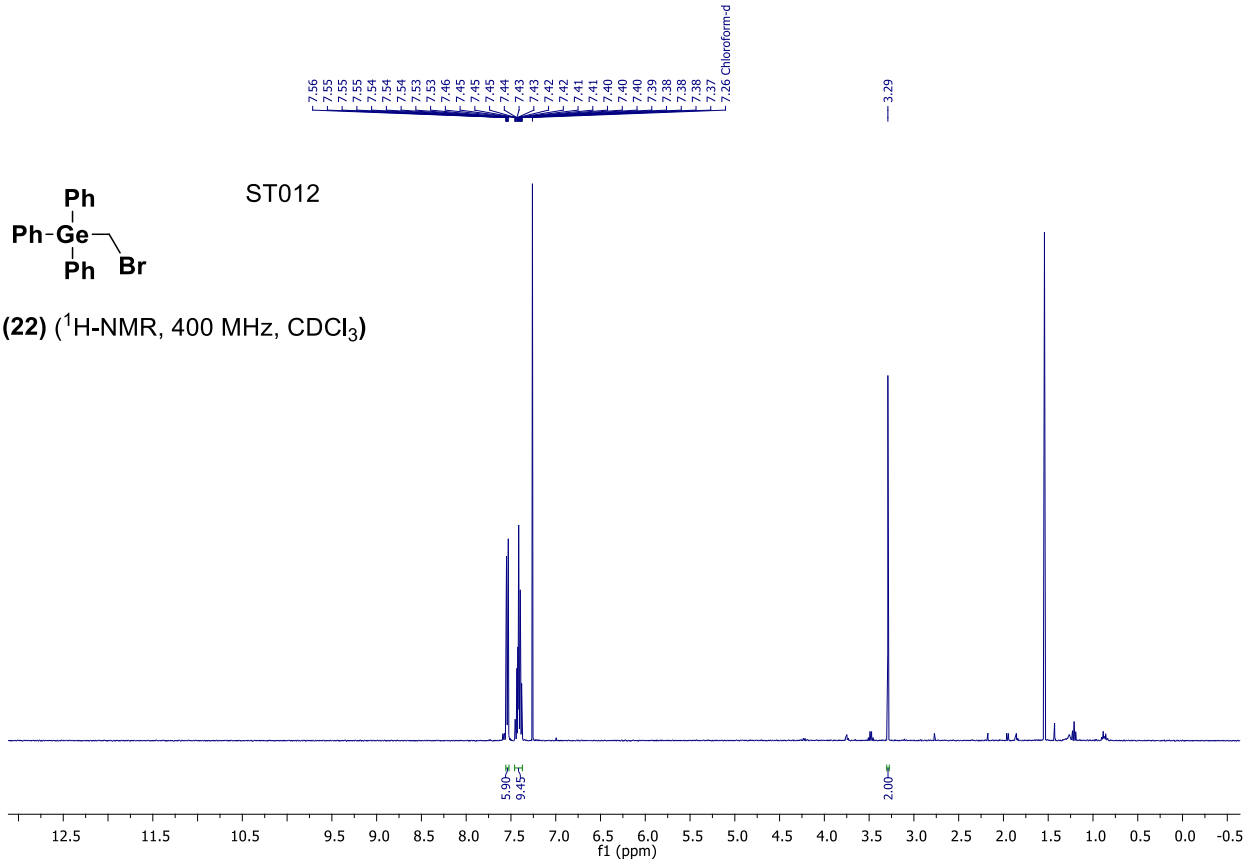
(20) (^{13}C-NMR, 100 MHz, $CDCl_3$)



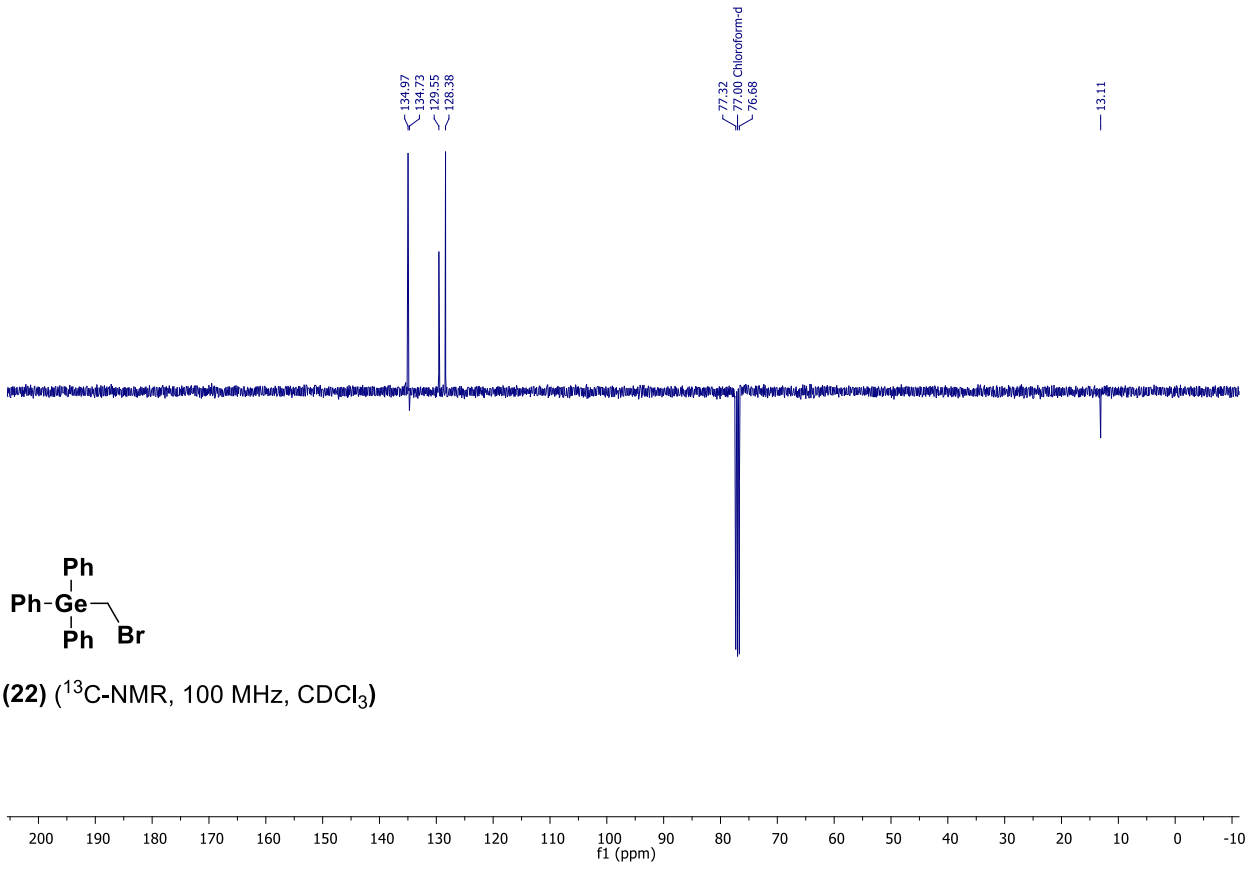
(21) (^{1}H-NMR, 400 MHz, $CDCl_3$)



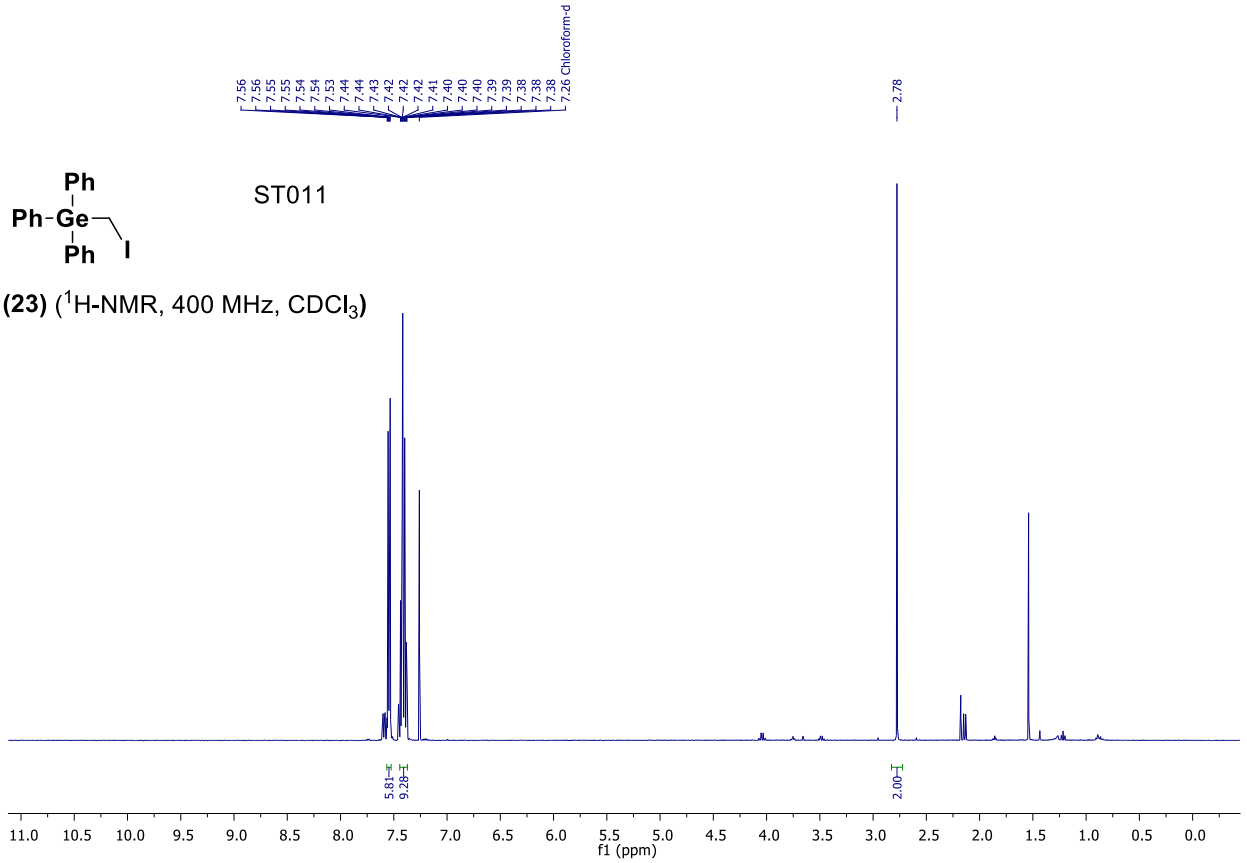
(21) (^{13}C-NMR, 100 MHz, $CDCl_3$)



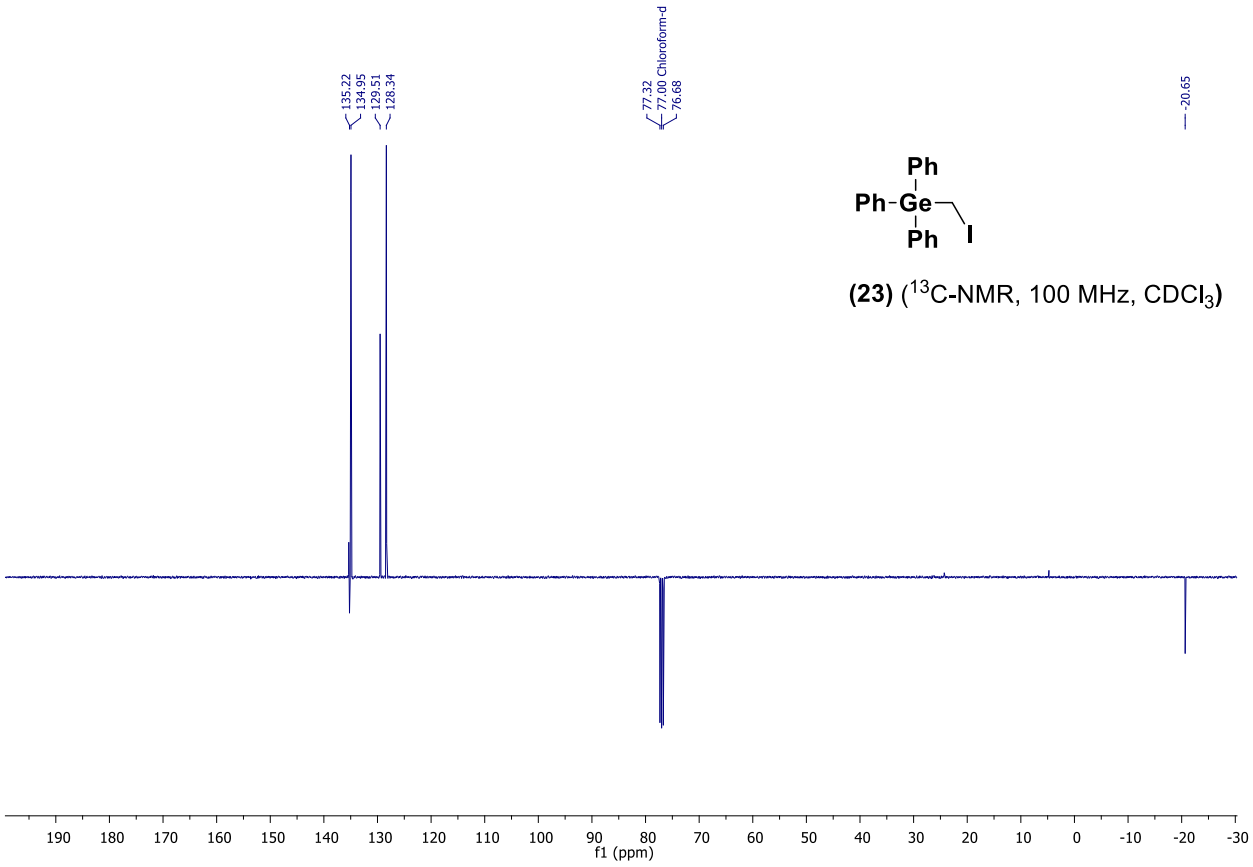
(22) (^{1}H-NMR, 400 MHz, $CDCl_3$)



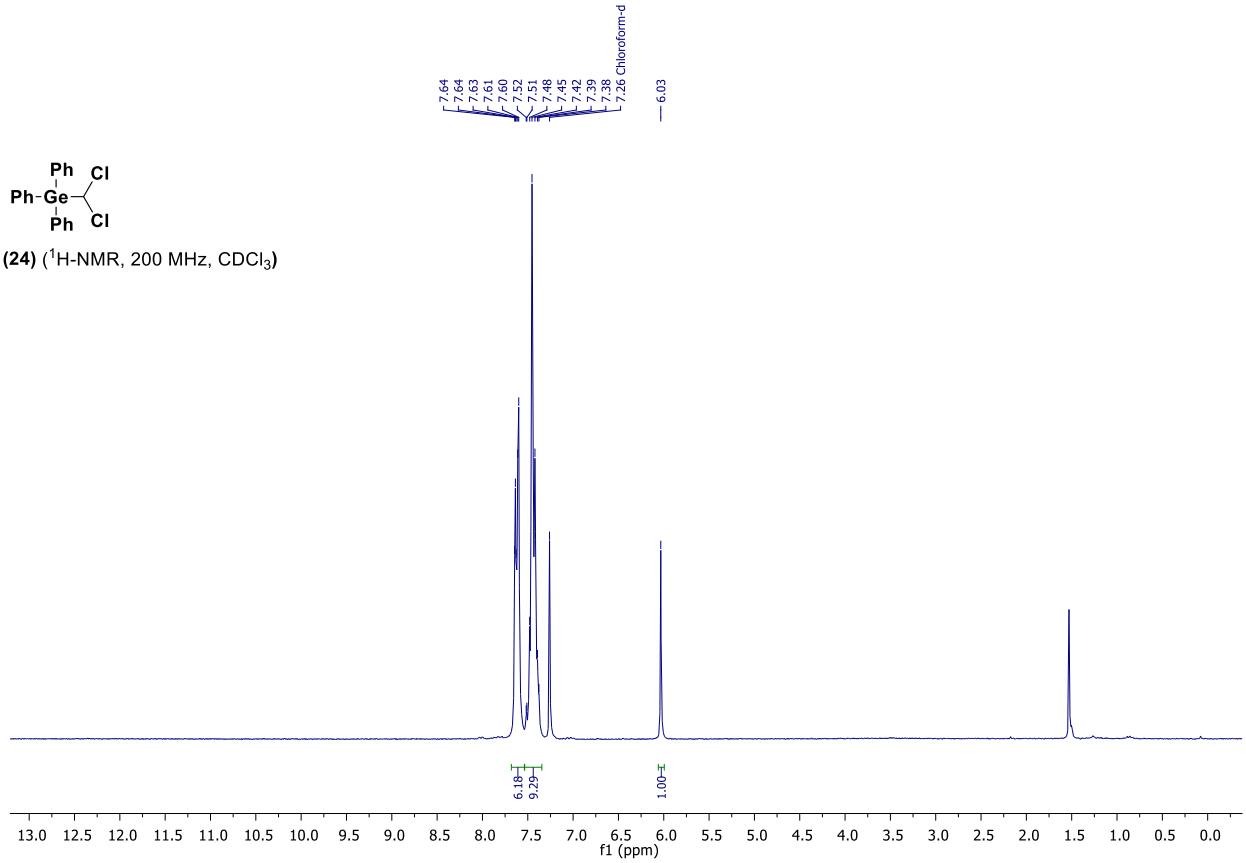
(22) (^{13}C-NMR, 100 MHz, $CDCl_3$)



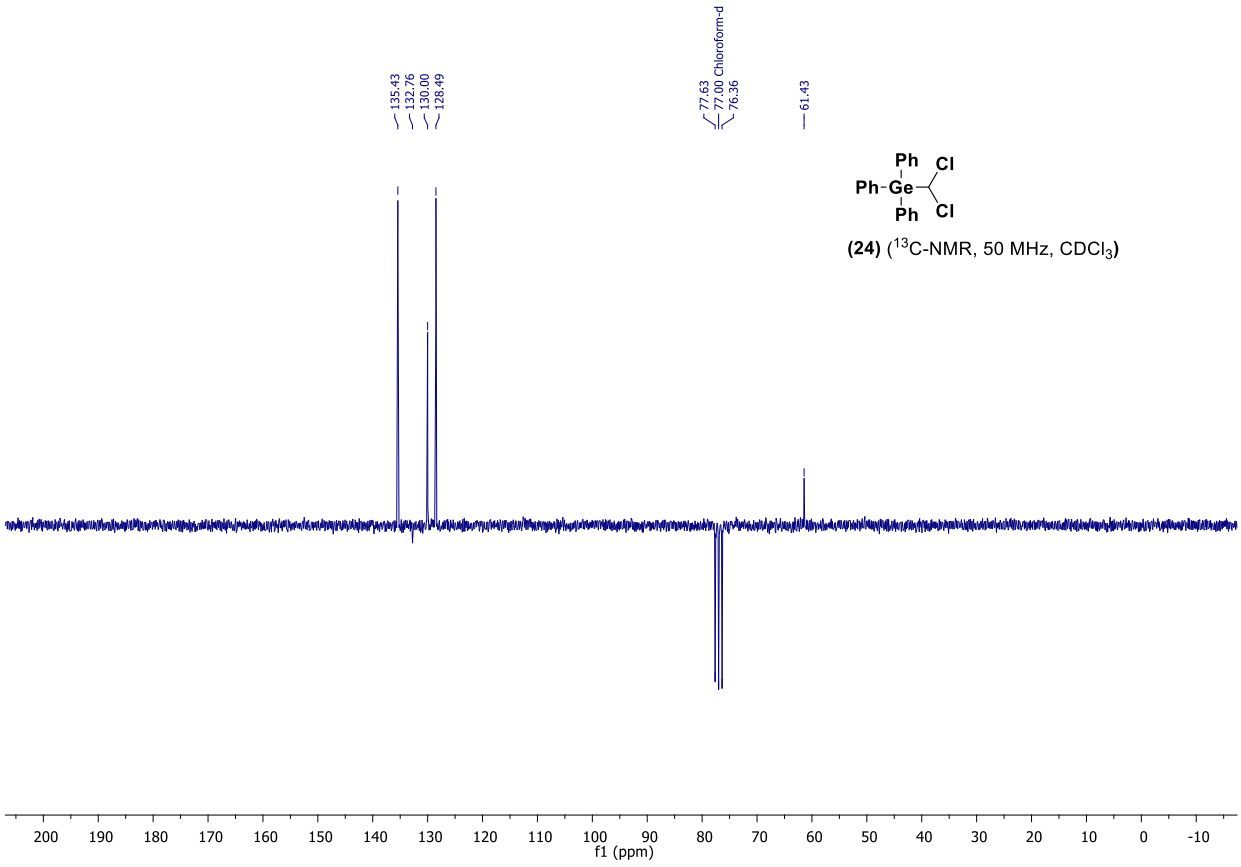
(23) (^{1}H-NMR, 400 MHz, $CDCl_3$)



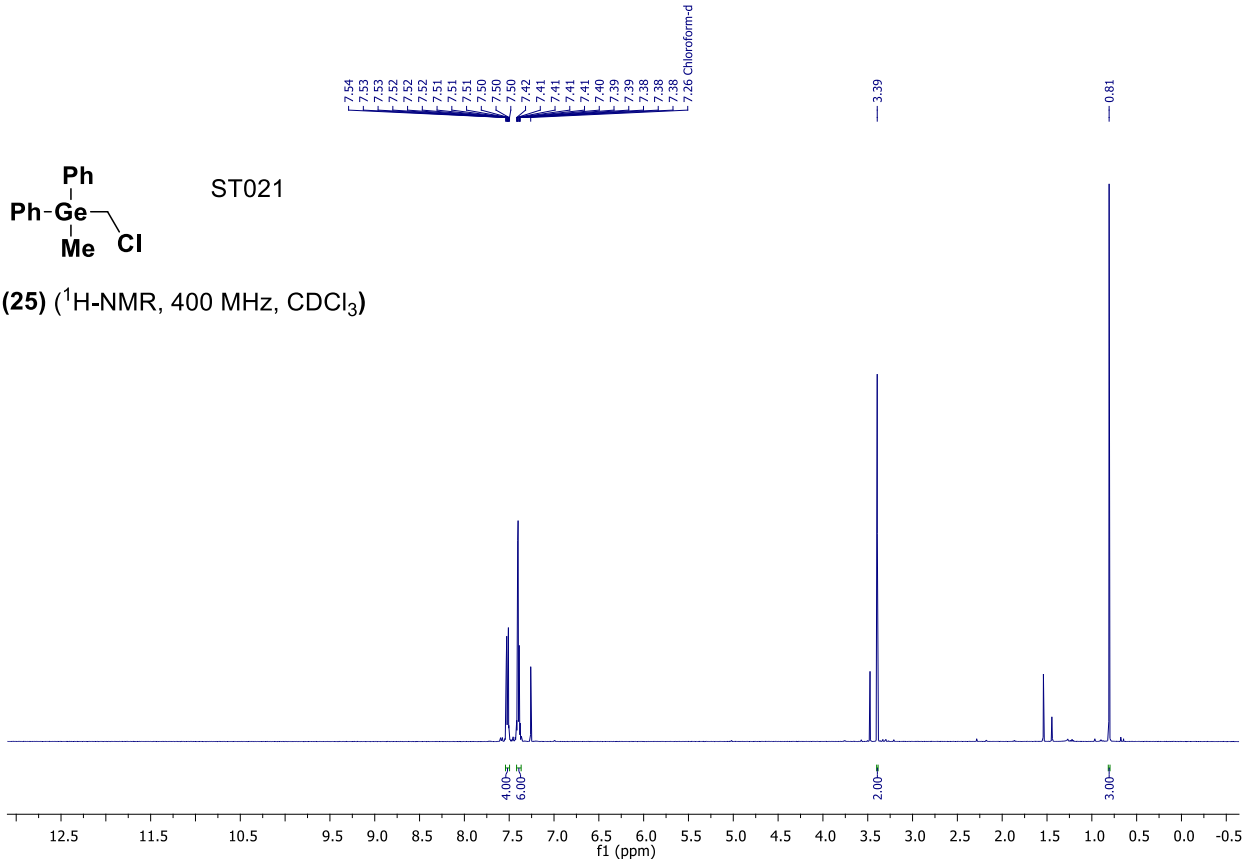
(23) (^{13}C-NMR, 100 MHz, $CDCl_3$)



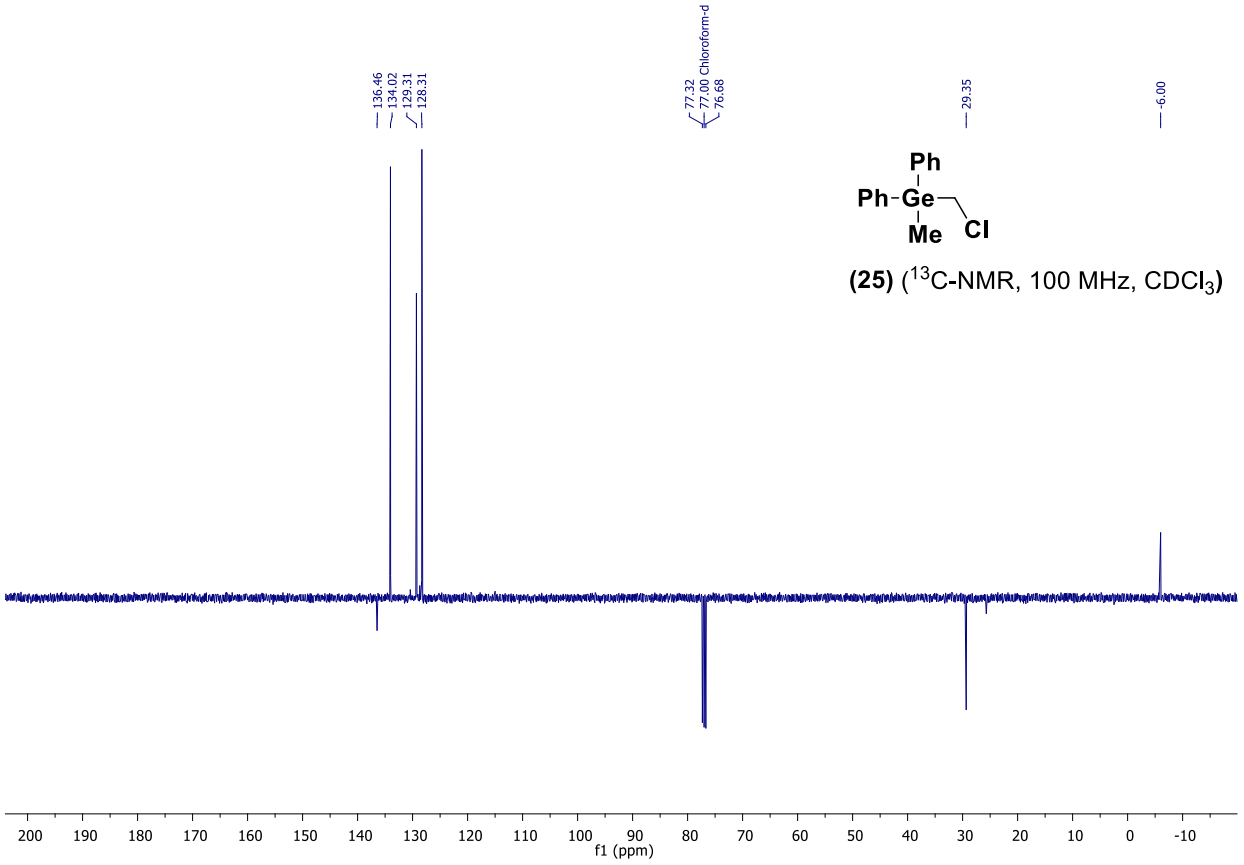
(24) (^{1}H-NMR, 200 MHz, $CDCl_3$)



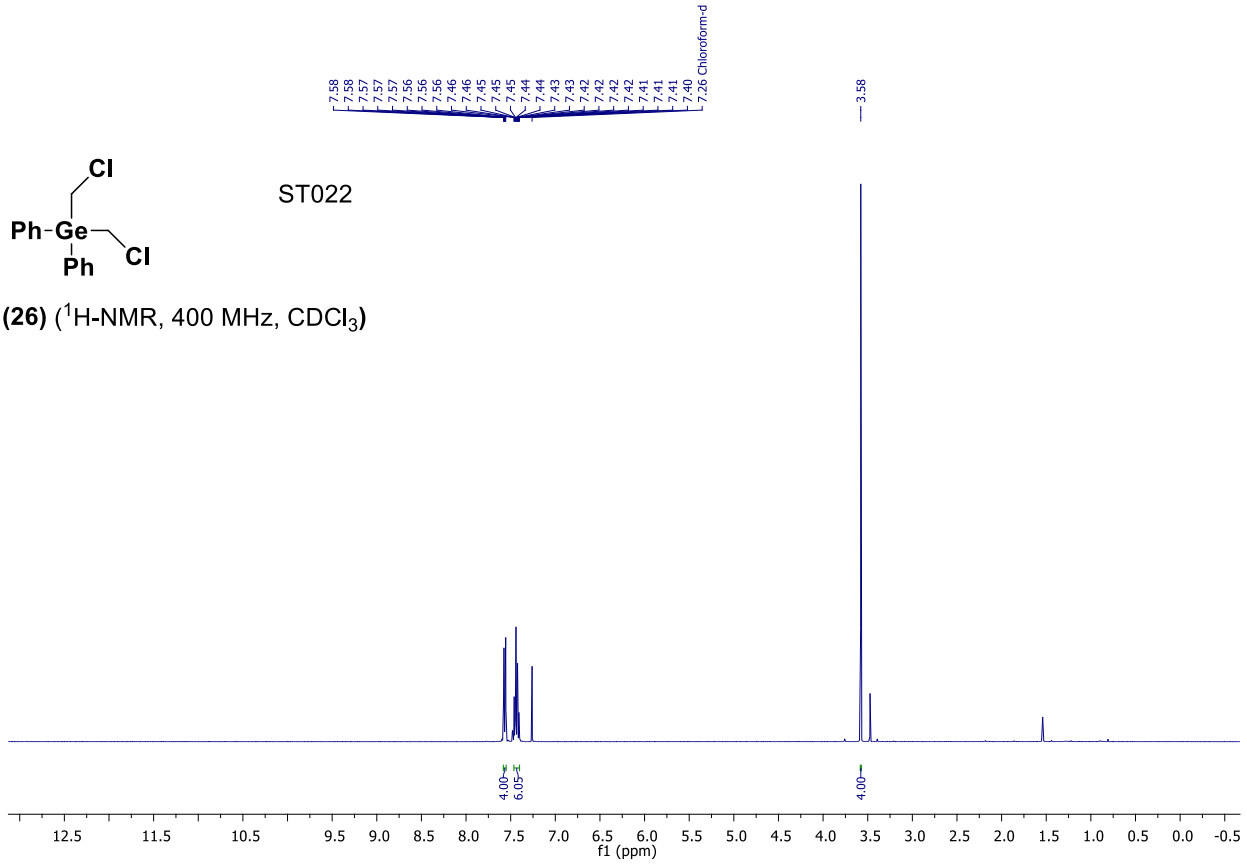
(24) (^{13}C-NMR, 50 MHz, $CDCl_3$)



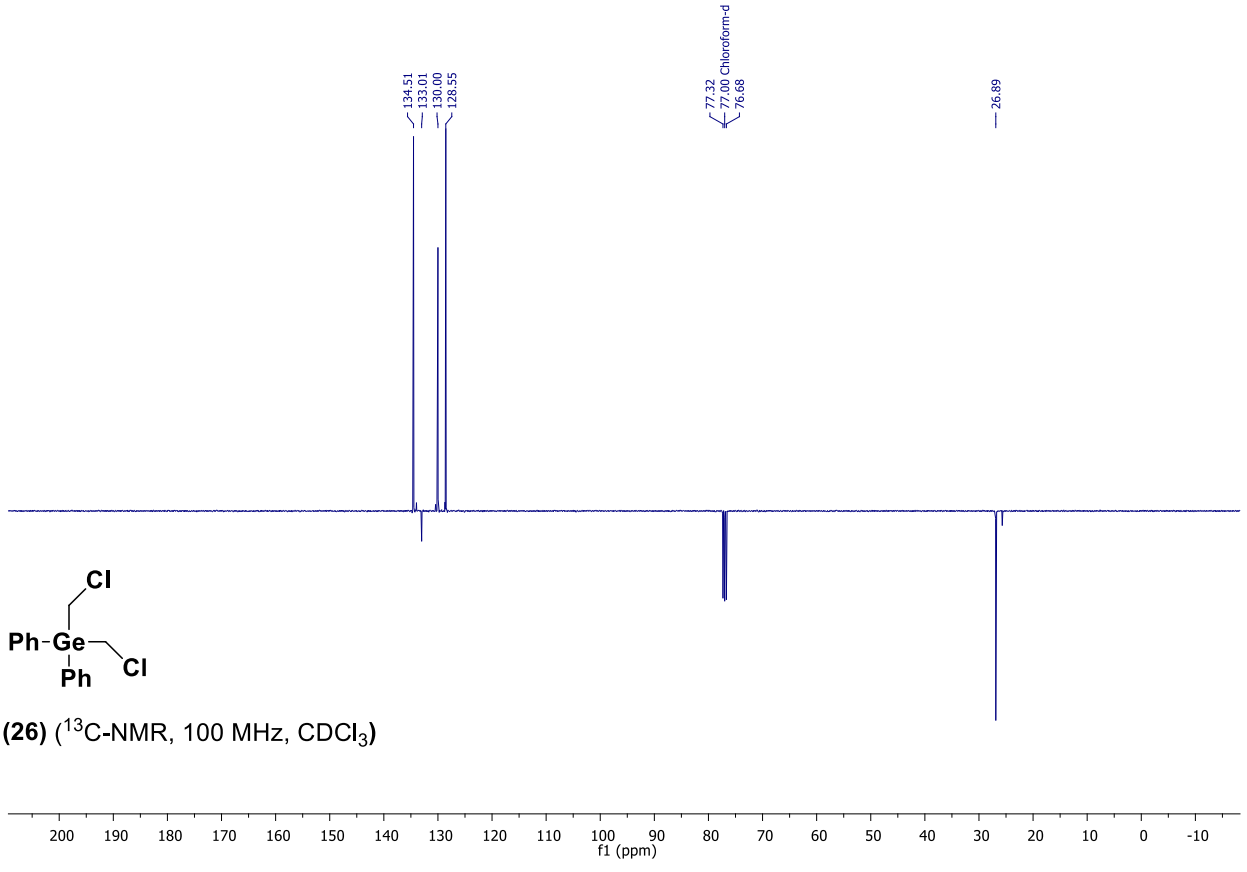
(25) (^{1}H-NMR, 400 MHz, $CDCl_3$)



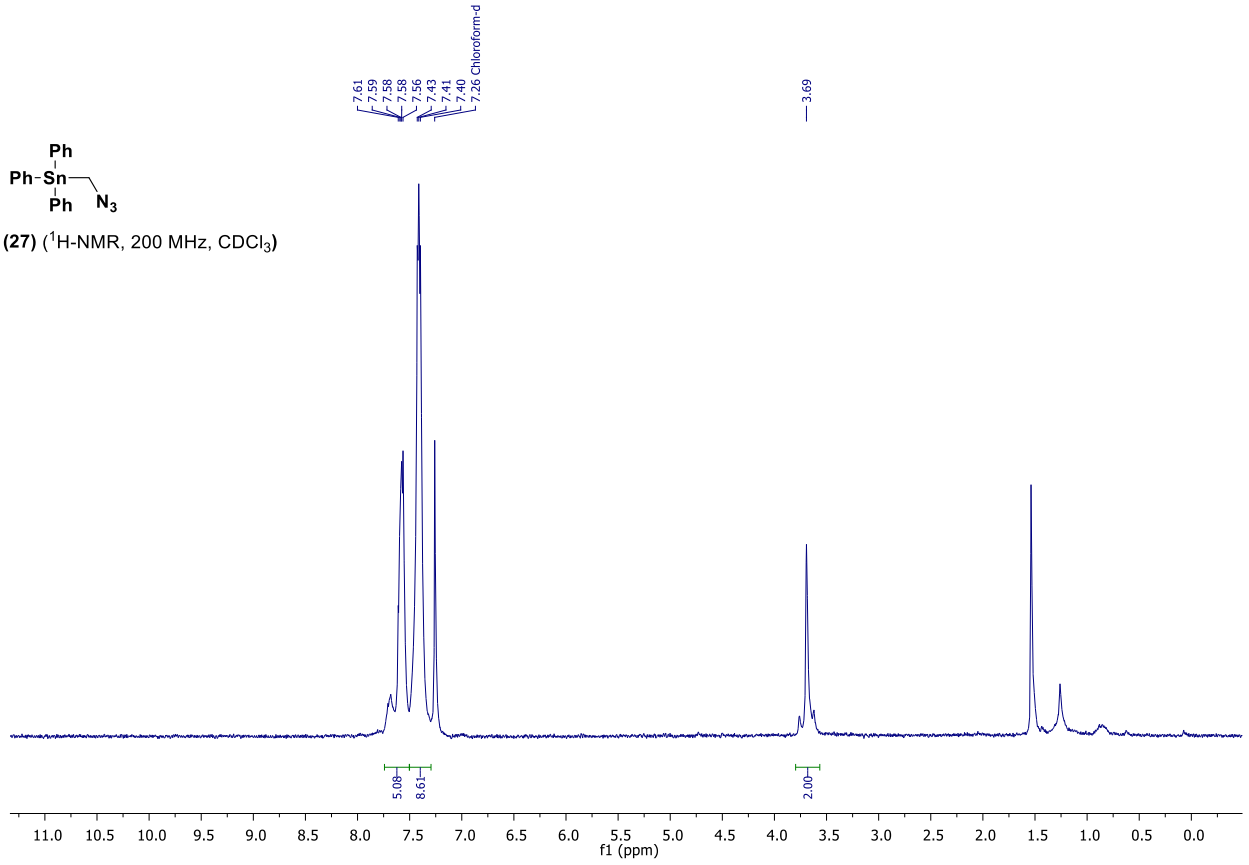
(25) (^{13}C-NMR, 100 MHz, $CDCl_3$)



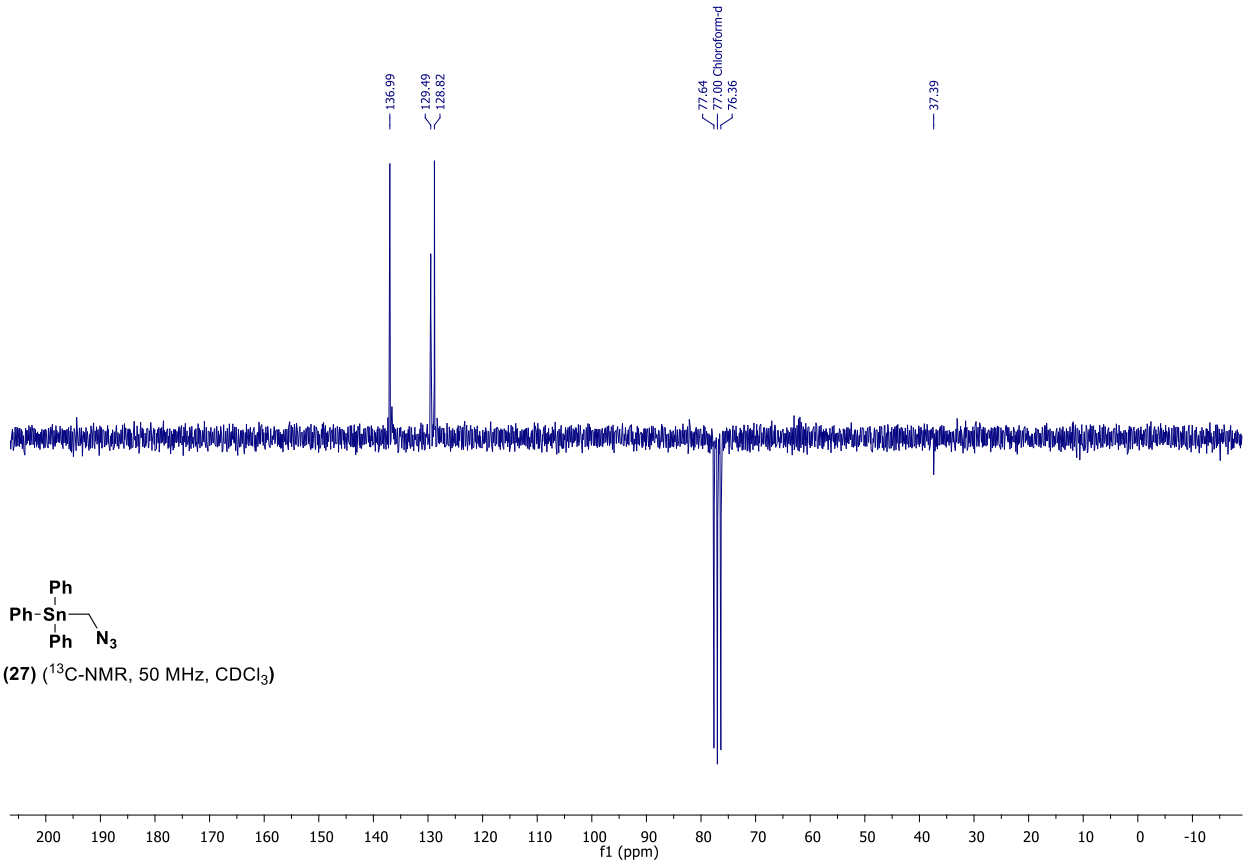
(26) (^{1}H-NMR, 400 MHz, $CDCl_3$)



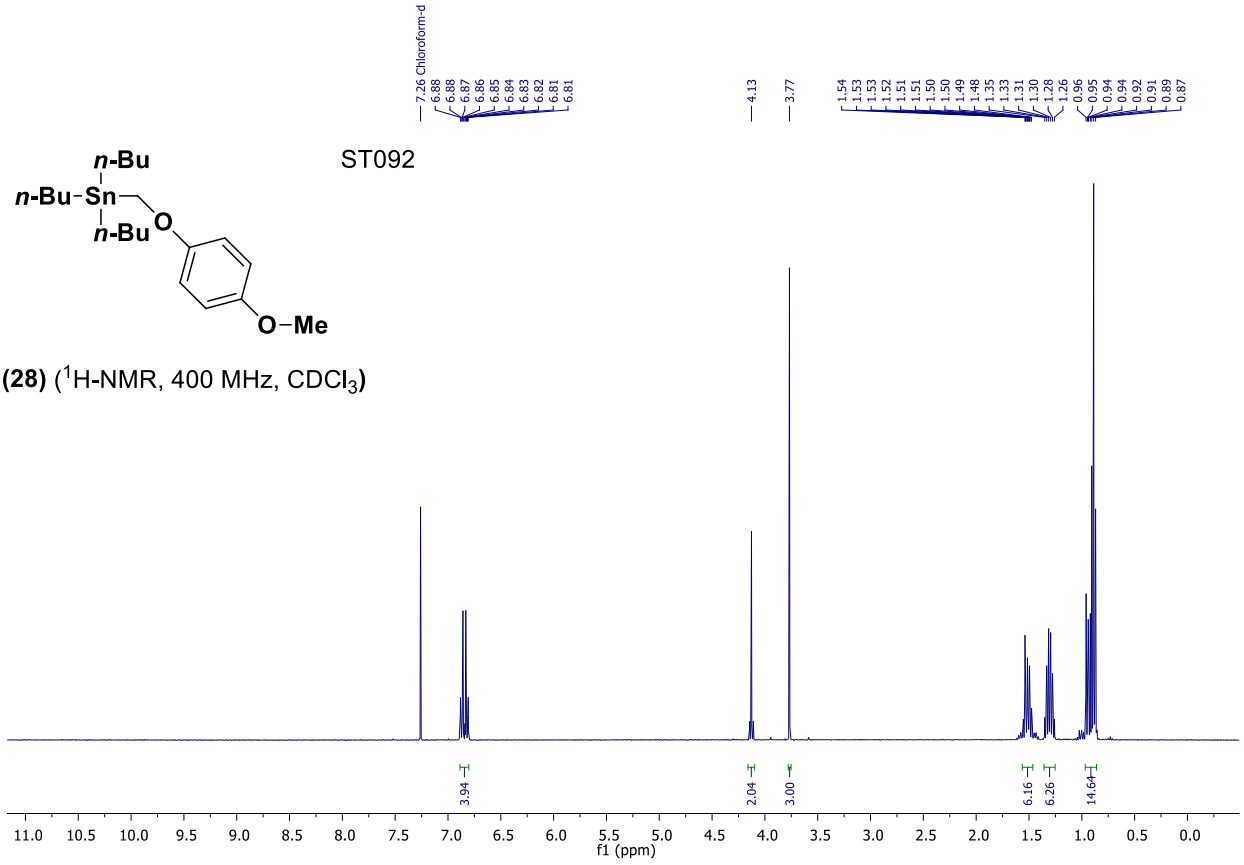
(26) (^{13}C-NMR, 100 MHz, $CDCl_3$)



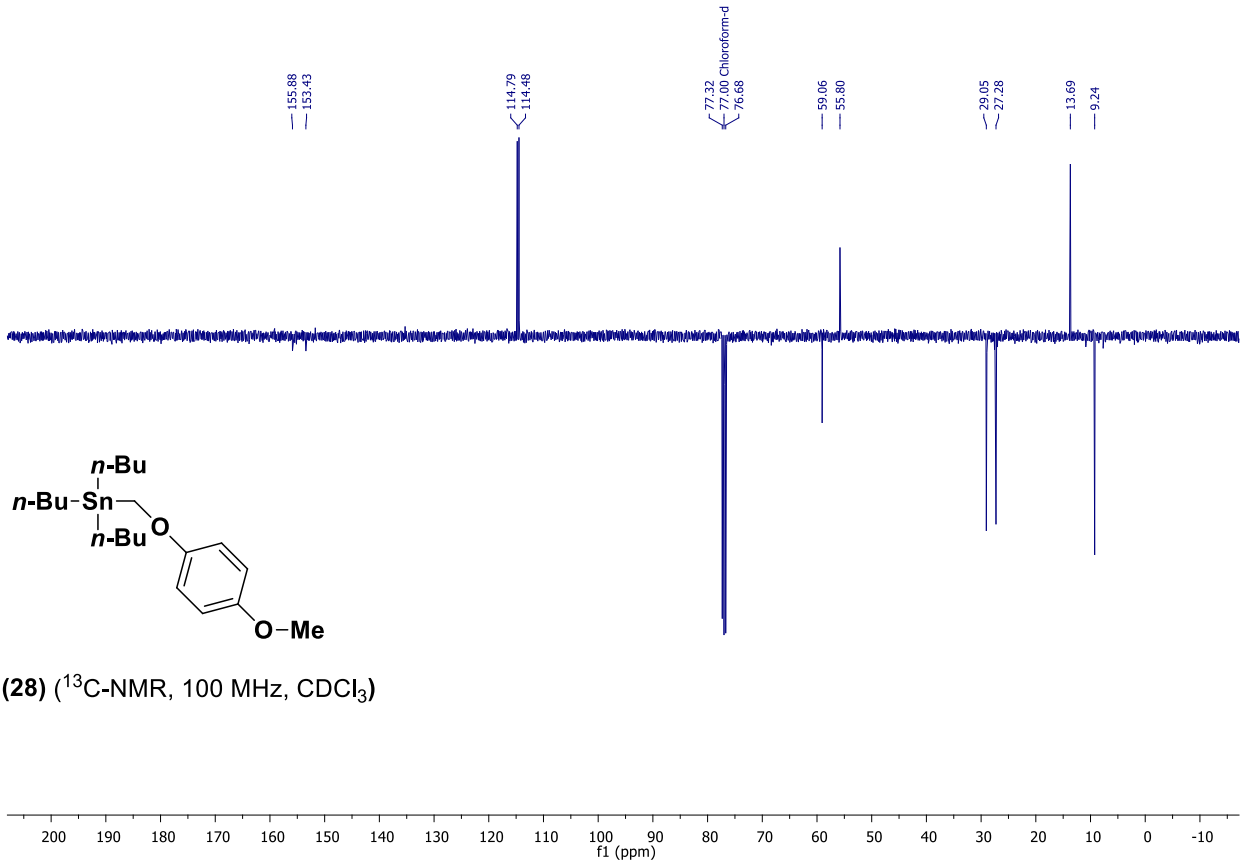
(27) (^{1}H-NMR, 200 MHz, $CDCl_3$)



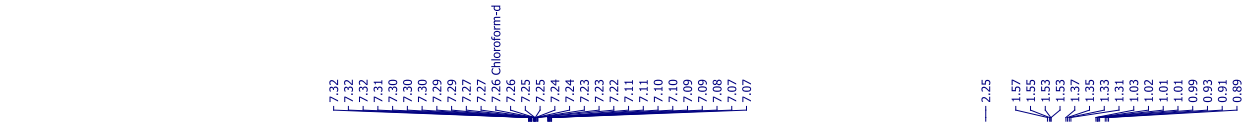
(27) (^{13}C-NMR, 50 MHz, $CDCl_3$)



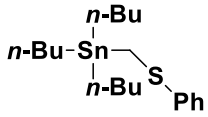
(28) (^{1}H-NMR, 400 MHz, $CDCl_3$)



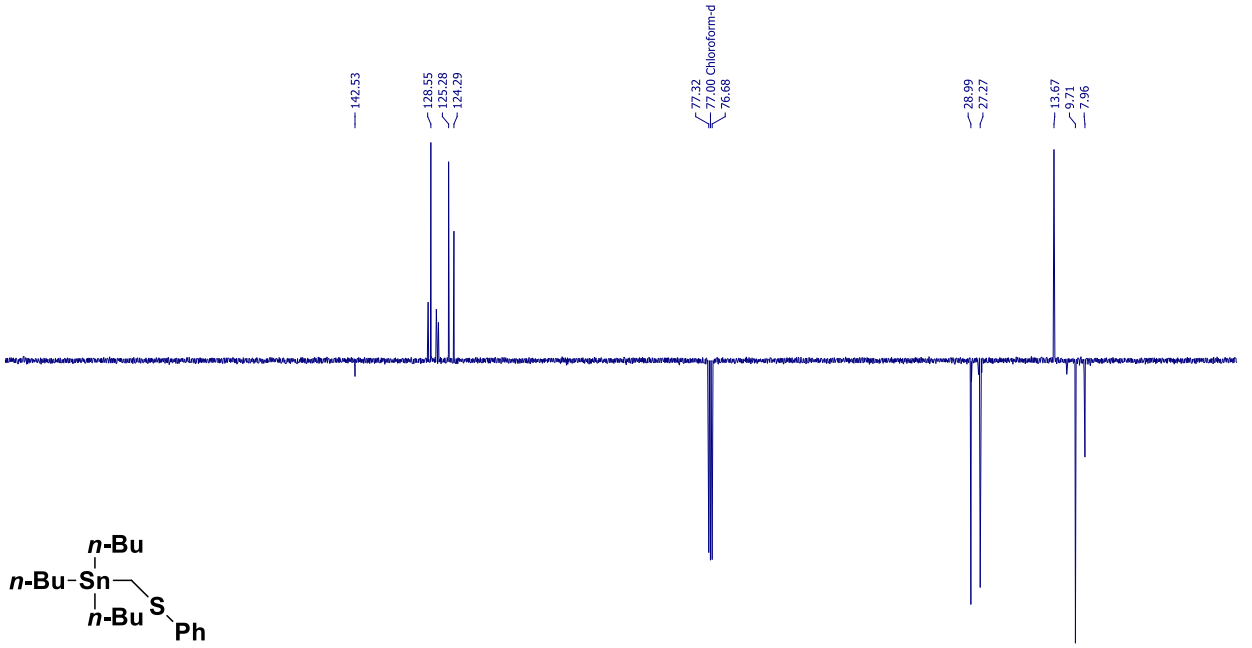
(28) (^{13}C-NMR, 100 MHz, $CDCl_3$)



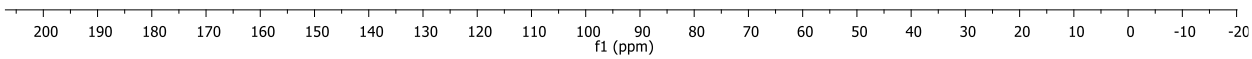
ST091

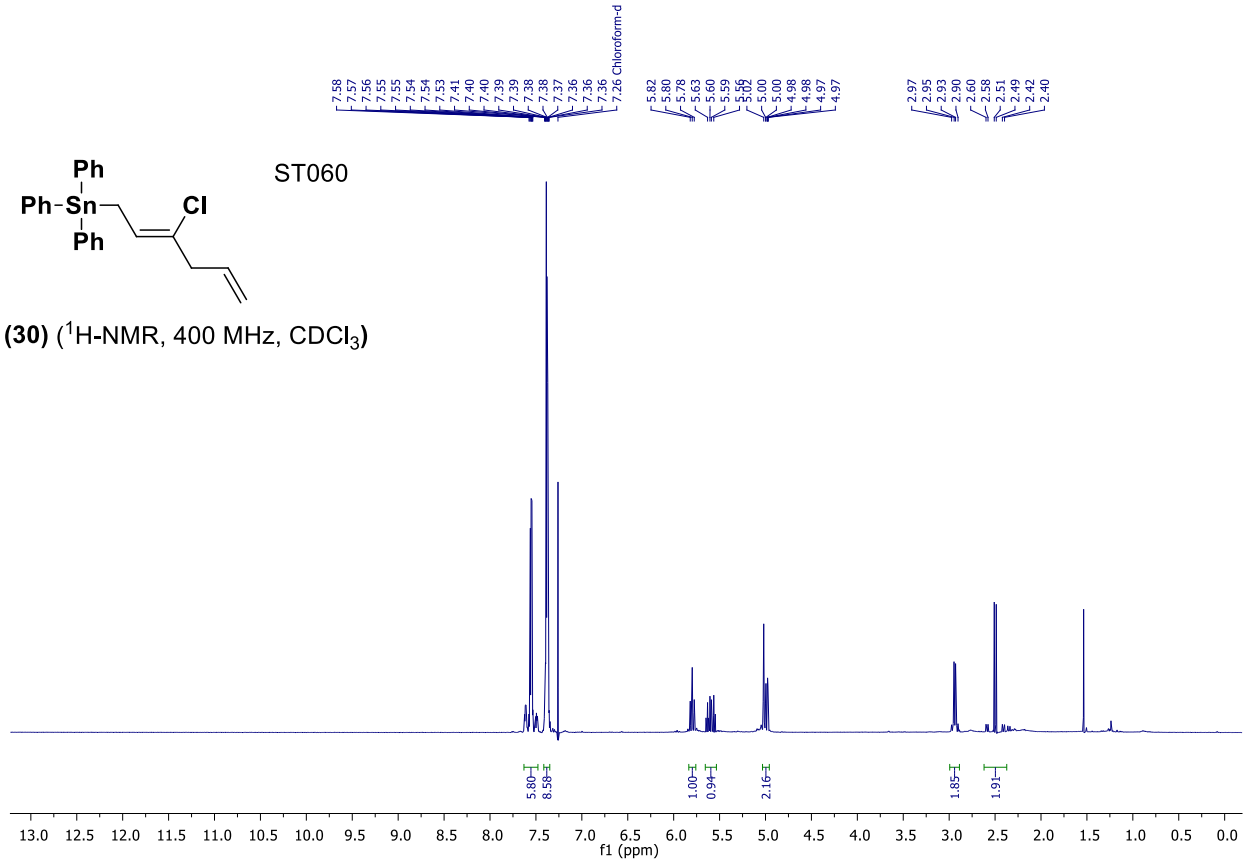


(29) (^{1}H-NMR, 400 MHz, $CDCl_3$)

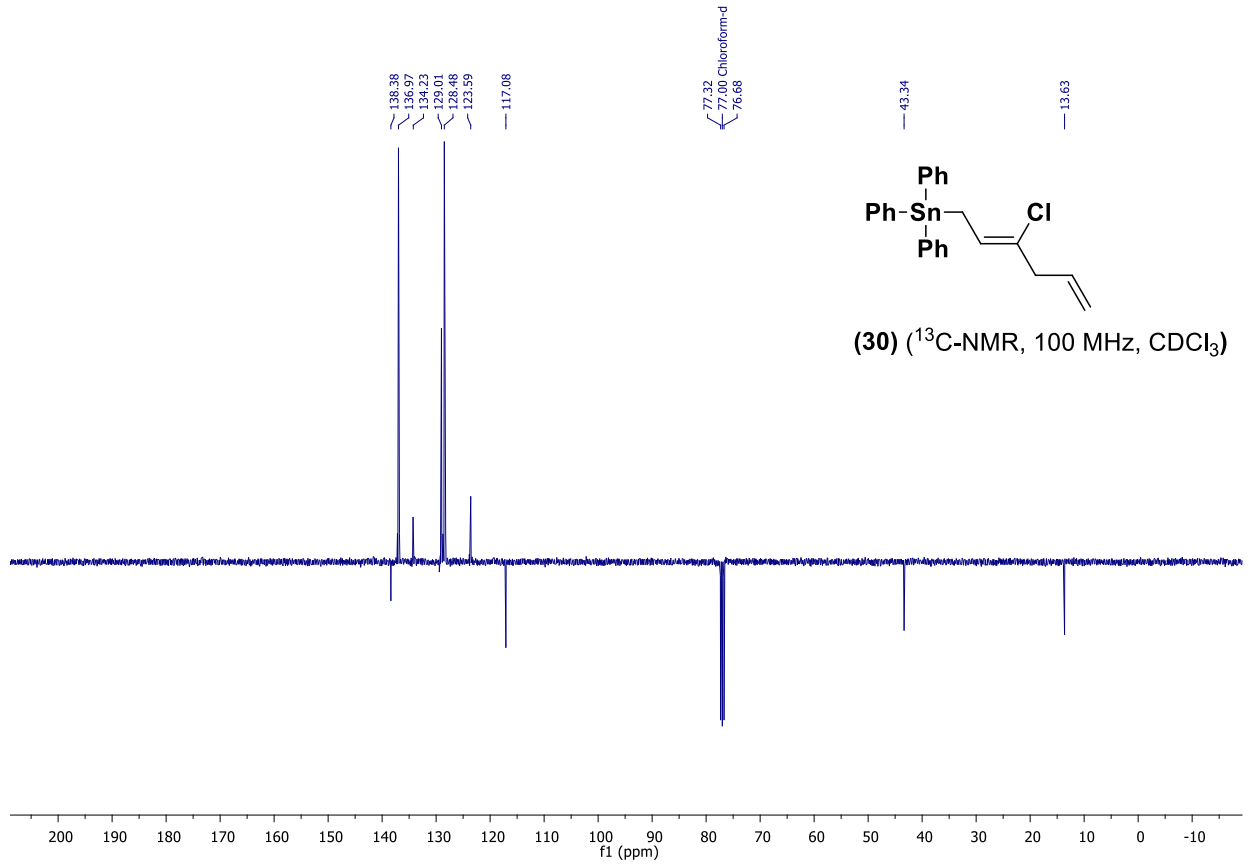


(29) (^{13}C-NMR, 100 MHz, $CDCl_3$)

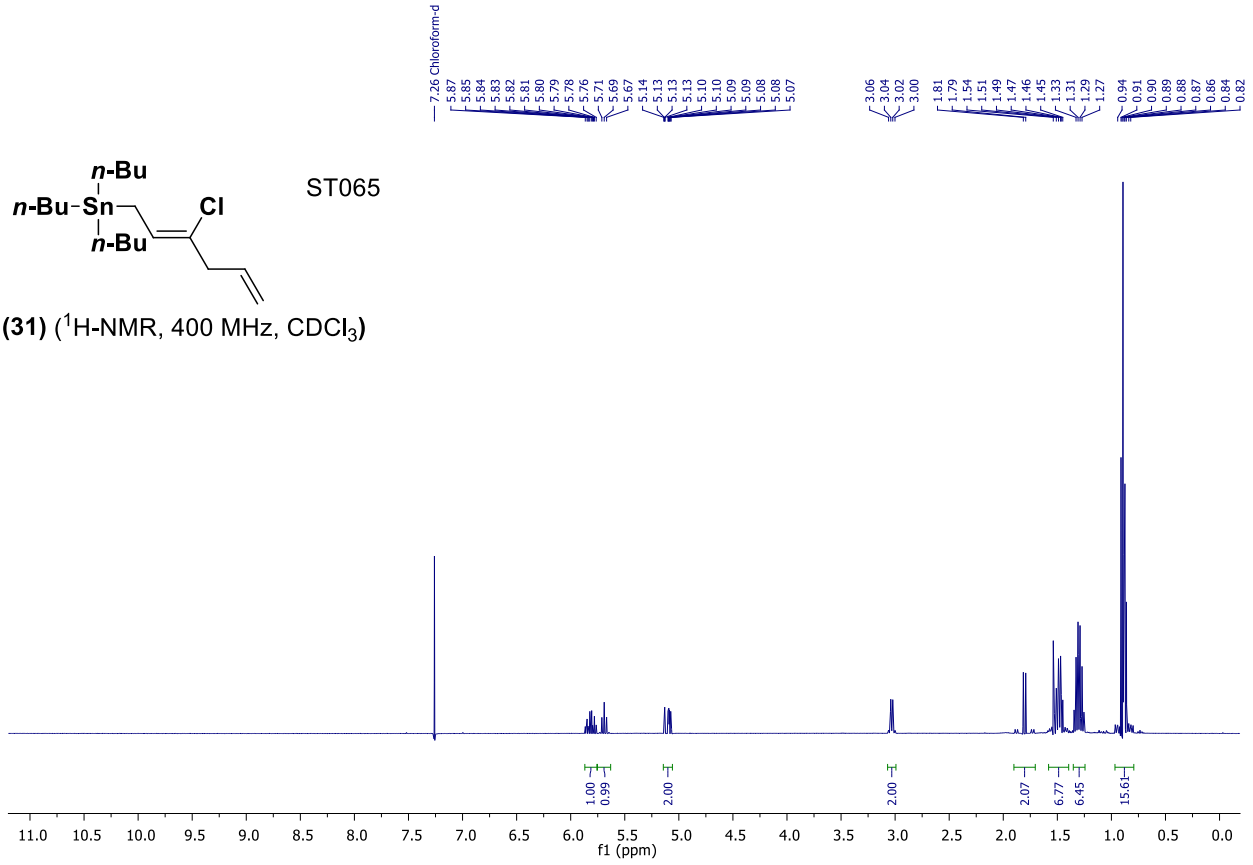




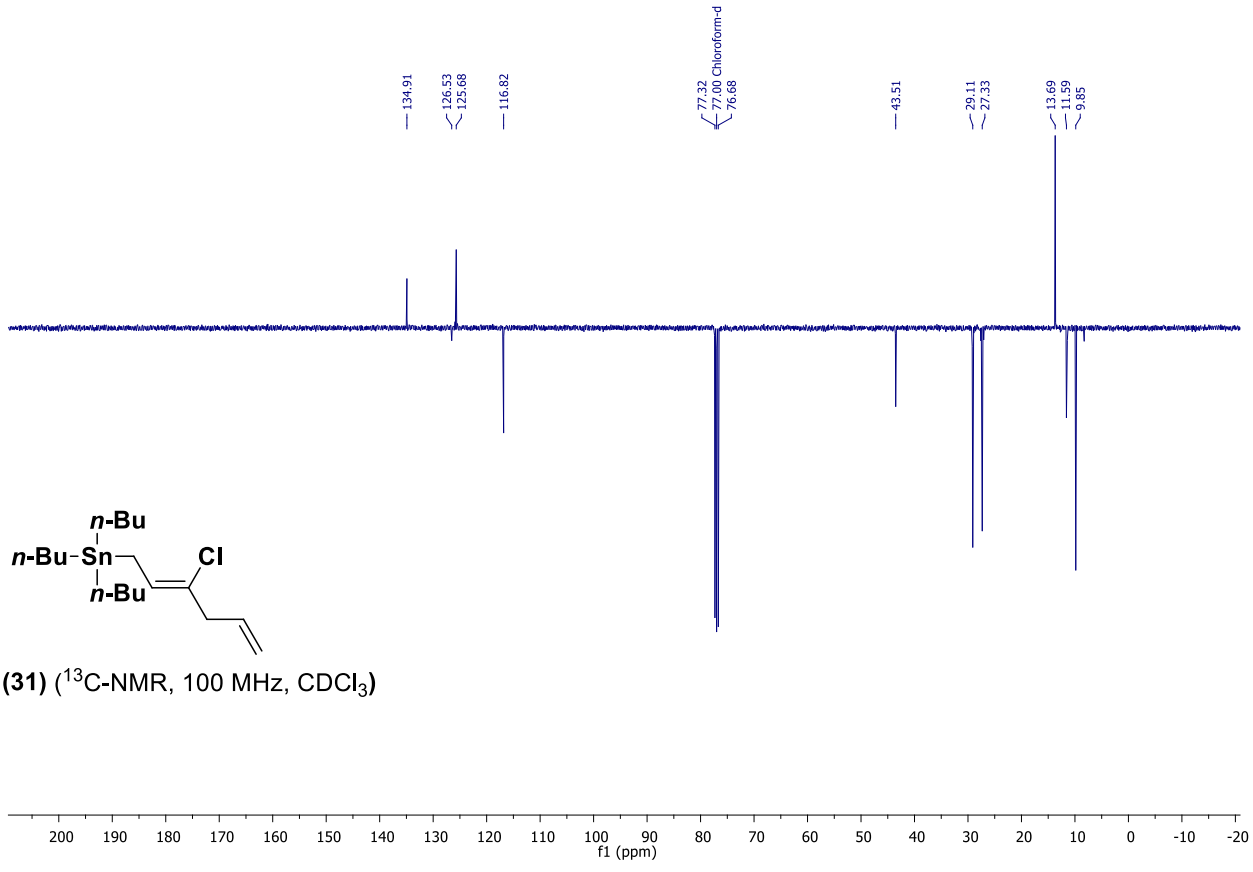
(30) (^{1}H-NMR, 400 MHz, $CDCl_3$)



(30) (^{13}C-NMR, 100 MHz, $CDCl_3$)

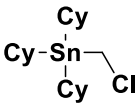


(31) (^{1}H-NMR, 400 MHz, $CDCl_3$)



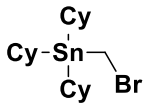
(31) (^{13}C-NMR, 100 MHz, $CDCl_3$)

Copies of ^{119}Sn-NMR spectra



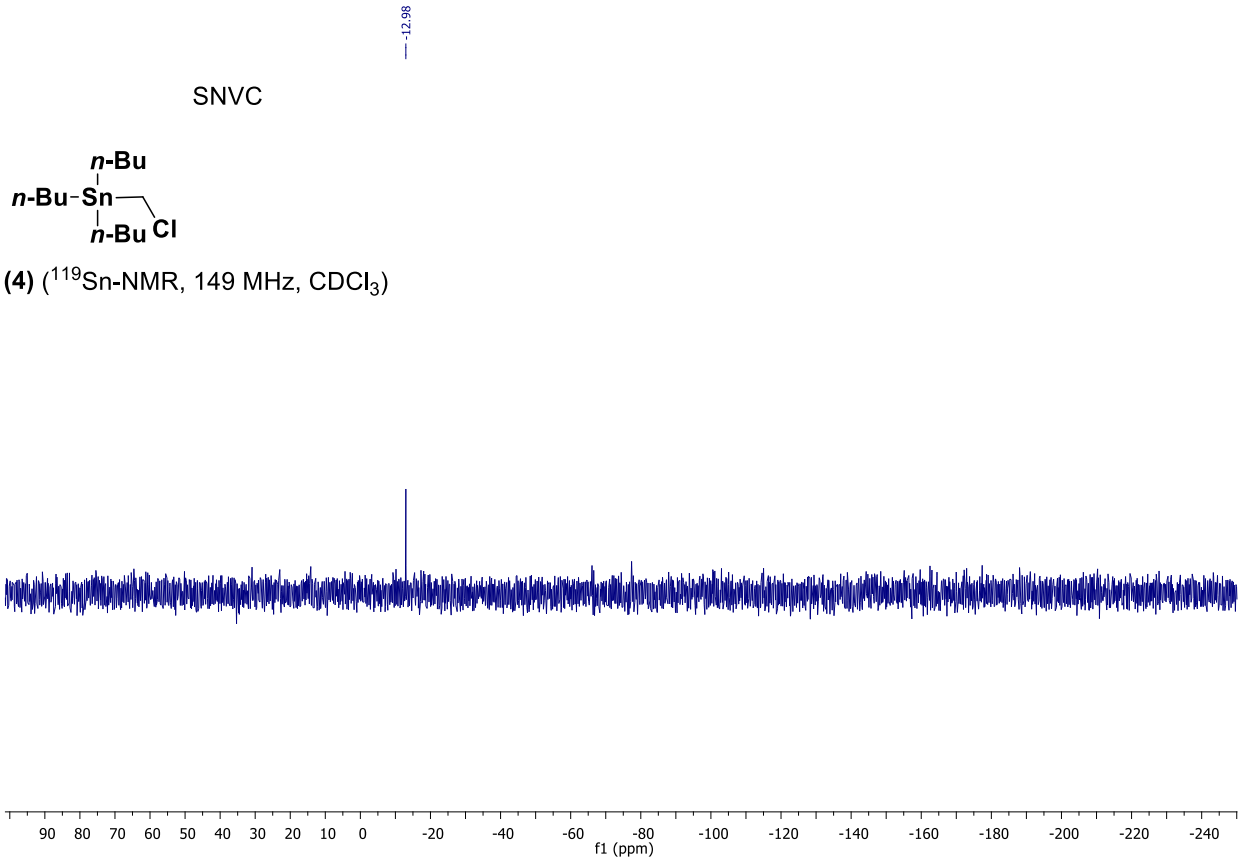
(2) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST007



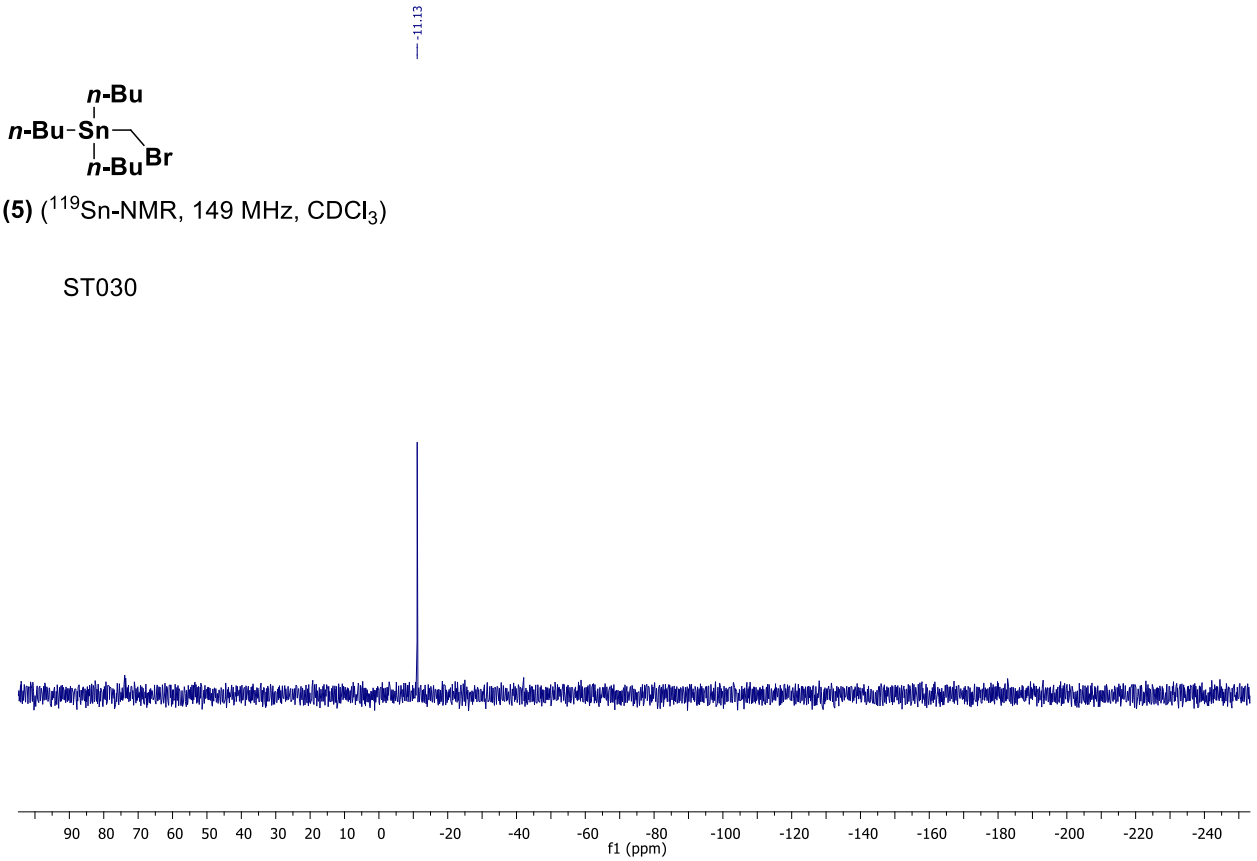
(3) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST009



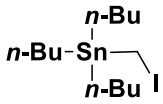
SNVC

(4) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)



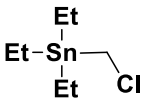
(5) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST030



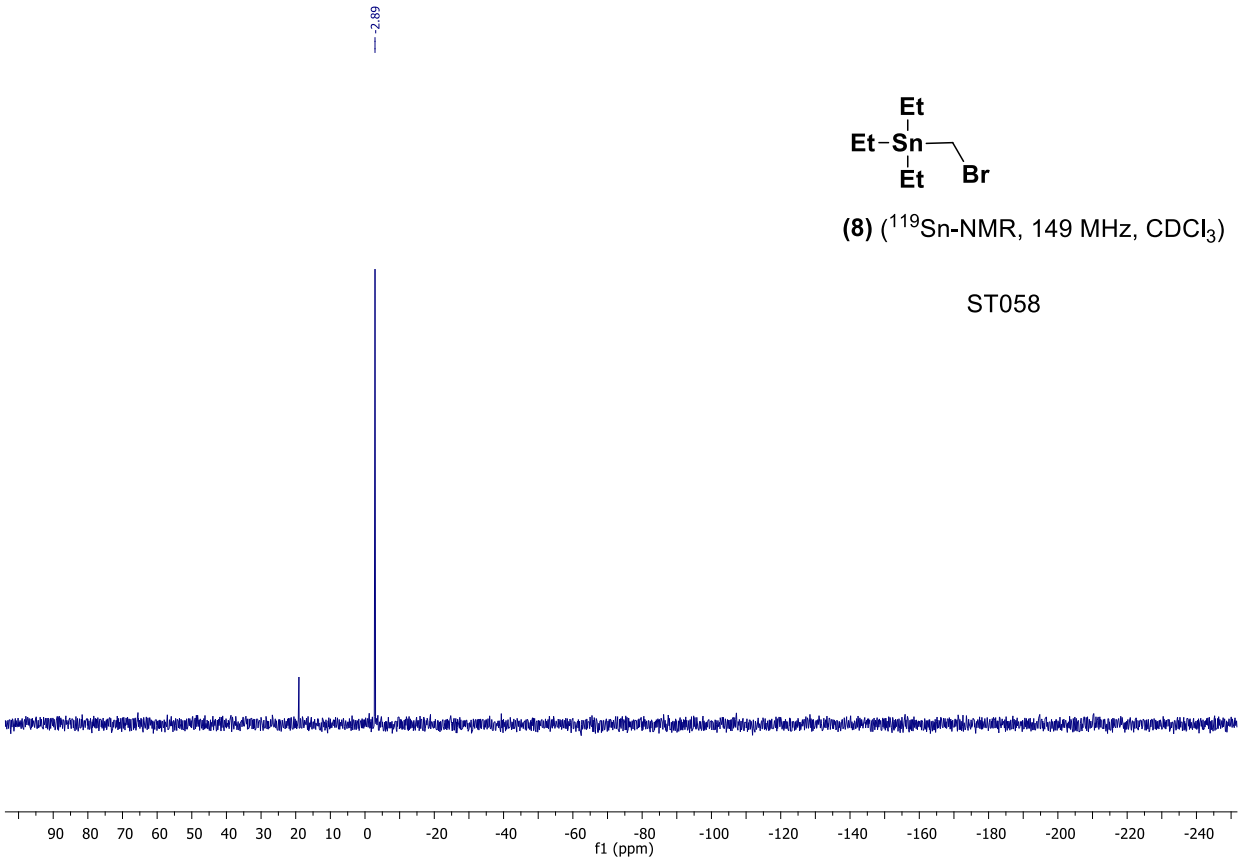
(6) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST039



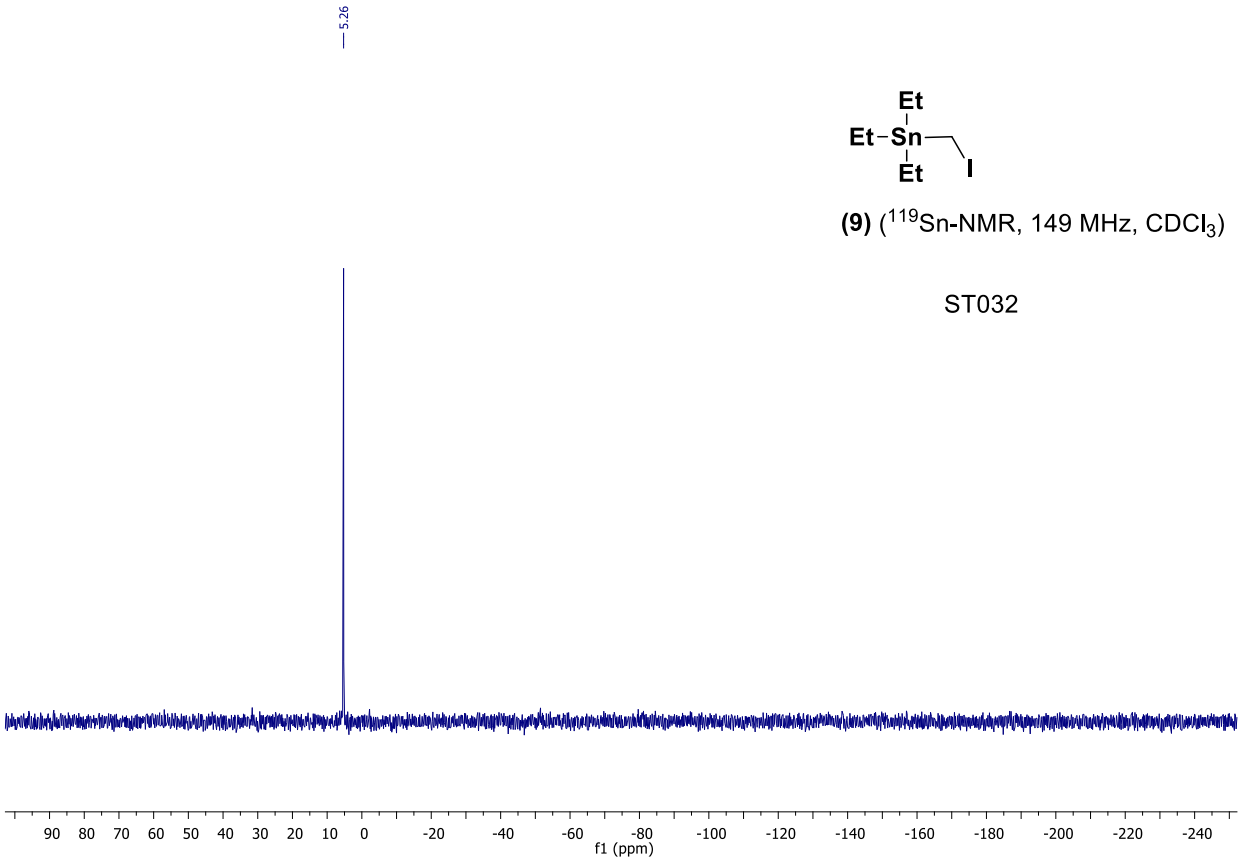
(7) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST031



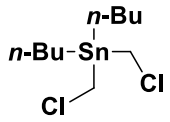
(8) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST058



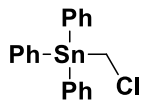
(9) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST032



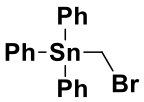
(10) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST025



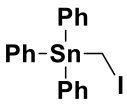
(11) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST026



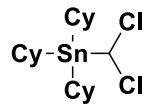
(12) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST038



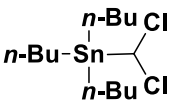
(13) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST045



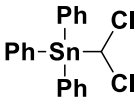
(14) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST049



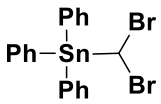
(15) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST048



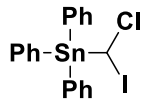
(16) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST043



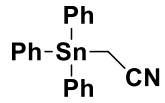
(17) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST061



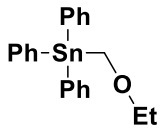
(18) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST047



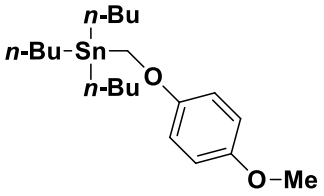
(19) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST051



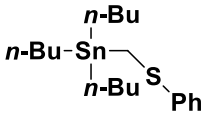
(20) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST056



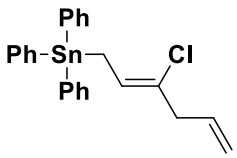
(28) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST092



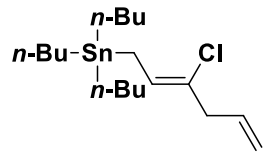
(29) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST091



(30) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST060



(31) (^{119}Sn-NMR, 149 MHz, $CDCl_3$)

ST065