

Supporting Information

Alternating Polystannanes: Synthesis and Properties

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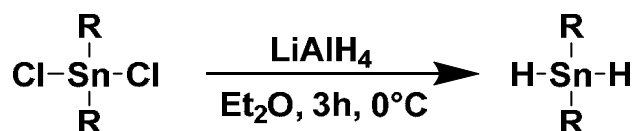
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1.0 Experimental

1.1 Materials and Methods

All reagents were purchased from Sigma Aldrich. Solvents were dried using an MBraun solvent drying system. All glassware was first dried in an oven then flame dried to remove surface moisture. ^1H NMR (400 MHz), ^{13}C NMR (100.6 MHz) and ^{119}Sn NMR (149.2 MHz) spectra were recorded on a Bruker Advance 400 MHz NMR spectrometer with a BBFO 5-mm direct probe. A ^1H pulse width of 30° was used, acquiring a spectral window of 8223 Hz (20 ppm) using a relaxation delay of 1s, acquisition time 3.98s, 32k points (16 scans). The ^1H 90° pulse width was 10.4 μs . A ^{13}C pulse width of 30° was used, acquiring a spectral window of 24038 Hz (239 ppm) using a relaxation delay of 2s, acquisition time 1.36s, 32k points (4096 scans). The ^{13}C 90° pulse width was 8.7 μs . A ^{119}Sn pulse width of 30° was used, 8.75 μs , acquiring a spectral window of 100000 Hz (670 ppm) using a relaxation delay of 1s, acquisition time 0.33s, 32k points (15360 scans) with inverse gated proton decoupling. All results were analysed on MestReNova LITE 5.2.5 software. Chemical shifts were calculated using the chemical deuterated standards as a reference for ^1H and ^{13}C . The ^{119}Sn was referenced to SnMe_4 as an internal standard. All J coupling values are reported as absolute values. UV-Vis evaluations were carried out using a Perkin Elmer Lambda 20 UV-Vis spectrometer. Elemental Analysis was performed by Atlantic Microlab, Inc. of Norcross Georgia. Time-of-flight mass spectrometry analyses were performed at the AIMS Mass Spectrometry Laboratory, University of Toronto using a JMS-T1000LC mass spectrometer (JEOL Inc., Peabody, MA) equipped with a Direct Analysis in Real Time (DART) ionization source (DART-SVP, Ionsense Inc., Saugus, MA). The DART source was operated with He gas and the temperature was adjusted in the range 100-400°C. Isotopic distributions for the observed ionic species were calculated using the Mass Center utility (JEOL) and were in good agreement with the measured mass spectra. The DSC of

polymers from this study were analyzed using a Perkin Elmer Pyris Diamond differential scanning calorimeter. Triplicate DSC scans were carried out at 5°C/min and take over temperature range of -45 to 200-225°C. Molecular weight determinations of polymer samples were made by GPC using a Viscotek TDAmix with THF as the elution solvent attached to a triple detector array (TDA 302). All reactions took place under nitrogen (N₂) atmosphere or in a sealed Schlenk flask placed under reduced pressure (closed) or finally in a Schlenk flask exposed to dynamic reduced pressure (open). Pressures measured in mmHg using a mercury manometer attached to the Schlenk line.



Scheme S1: General reaction scheme for dihydrides.

1.2 Preparation of di(*n*-butyl)stannane (**1**)

Dry Et₂O (30 mL) was used to dissolve (*n*-Bu)₂SnCl₂ (1.53 mmol, 4.65 g) in a 250 mL Schlenk flask. An equimolar solution of LiAlH₄ in Et₂O was added drop wise with constant stirring over a 30 min period at 0°C. The resultant solution was allowed to react for 3 h at constant temperature. The reaction was quenched with 30 mL chilled degassed water. The organic layer was separated and the aqueous layer extracted with 20 mL Et₂O. The combined organic layers were dried over CaCl₂ for 2 h. After filtration, the solution containing **1** was removed *in vacuo* to yield a cloudy coloured liquid. The sample was stored at -20 °C to avoid decomposition. Yield: 3.63 g (78%).

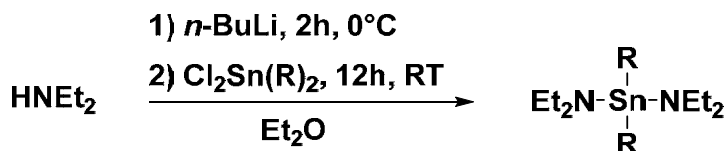
¹H NMR (C₆D₆): δ 0.86 (t, 6H, -SnCH₂CH₂CH₂CH₃); 0.96 (sex, 4H, -SnCH₂CH₂CH₂CH₃); 1.27 (m, 4H, -SnCH₂CH₂CH₂CH₃); 1.49 (m, 4H, -SnCH₂CH₂CH₂CH₃); 4.77 (q, 2H, -SnH₂) ppm; ¹¹⁹Sn {¹H} NMR (C₆D₆): δ -203.7 ppm. This data is in good agreement with reported literature values.¹⁰

1.3 Preparation of diphenylstannane (**2**)

Dry Et₂O (30 mL) was used to dissolve Ph₂SnCl₂ (1.53 mmol, 4.65 g) in a 250 mL Schlenk flask. An equimolar solution of LiAlH₄ in Et₂O was added drop wise with constant stirring over a 30 min at 0 °C. The resultant solution was allowed to react for further 3 h at this temperature. Then the reaction was quenched with 30 mL chilled degassed water. The organic layer was separated and aqueous layer extracted using a 20 mL of Et₂O. The combined organic layers were dried

over CaCl₂ for 2 h. After filtration, the solvent was removed *in vacuo* yielding a cloudy white coloured liquid. The sample was stored at -20 °C to avoid decomposition. Yield: 3.81 g (82%).

¹H NMR (C₆D₆) δ 6.07 (s, 2H, -SnH₂), 7.10 (dd, ³J_{119Sn-1H} = 4.8 Hz, ³J_{117Sn-1H} = 1.8 Hz, 4H, *o*-C₆H₅), 7.41 (dd, ⁴J_{119Sn-1H} = 6.3 Hz, ⁵J_{119Sn-1H} = 3.1 Hz, 6H, *m,p*-C₆H₅) ppm; ¹¹⁹Sn {¹H} NMR (C₆D₆): δ -234.3 ppm. This data is in good agreement with reported literature values.¹³



Scheme S2 General reaction scheme for tin diamides.

1.4 Preparation of bis(diethylamino)di(*n*-butyl)stannane (**3**)

Dry Et₂O (30 mL) was used to dissolve (*n*-Bu)₂SnCl₂ chloride (1.53 mmol, 4.65 g) in a 250 mL Schlenk flask. In a second 250 mL Schlenk flask, 20 mL of Et₂O was added along with (3.06 mmol, 2.23 g) of HNEt₂, cooled to 0 °C, and an equimolar amount of *n*-BuLi (3.06 mmol) added dropwise over 15 min. The mixture was allowed to warm to room temperature with stirring for 2 h. The flask containing the lithiated amine was then cooled again to 0 °C and the solution containing the tin halide added dropwise. A salt formed upon addition and the solution was stirred for 12 h. The solution was filtered and the solvent removed *in vacuo* to yield an orange coloured liquid. Yield: 4.80 g (83%).

¹H NMR (C₆D₆) δ 0.93-0.81 (m, 6H, -SnCH₂CH₂CH₂CH₃), 1.08-0.99 (m, 4H, -SnCH₂CH₂CH₂CH₃), 1.17-1.08 (m, 6H, -SnN(CH₂CH₃)₂), 1.39-1.26 (m, 4H, -SnCH₂CH₂CH₂CH₃), 1.64-1.52 (m, 4H, -SnCH₂CH₂CH₂CH₃), 3.15-2.99 (m, 4H, -SnN(CH₂CH₃)₂) ppm; ¹¹⁹Sn {¹H} NMR (C₆D₆): δ 19.63 ppm. This data is in good agreement with reported literature values.³⁷

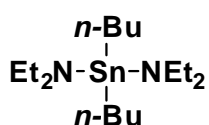


Figure S1 Bis(diethylamino)di(*n*-butyl)stannane.

1.5 Preparation of bis(diethylamino)dimethylstannane (**4**)

Dry Et₂O (30 mL) was used to dissolve Me₂SnCl₂ (1.53 mmol, 3.36 g) in a 250 mL Schlenk flask. In a second 250 mL Schlenk flask, 20 mL of Et₂O was added along with (3.06 mmol 2.23 g) of HNEt₂, cooled to 0 °C, and an equimolar amount of *n*-BuLi (3.06 mmol) added dropwise over 15 min. The mixture was allowed to warm to room temperature with stirring for 2 h. The flask containing the lithiated amine was then cooled to again to 0 °C and the solution containing the tin halide added dropwise. A salt formed upon addition and the solution was stirred for 12 h. After filtration, the solvent was removed *in vacuo* to yield an orange coloured liquid. Yield: 5.03 g (87 %).

¹H NMR (C₆D₆) δ 0.19 (s, ²J_{119Sn-1H} = 224 Hz, 6H, -Sn(CH₃)₂), 1.07 (t, 6H, -SnN(CH₂CH₃)₂), 3.02 (q, ³J_{119Sn-1H} = 7.0 Hz, 4H, -SnN(CH₂CH₃)₂) ppm; ¹¹⁹Sn {¹H} NMR (C₆D₆): δ 43.41 ppm.

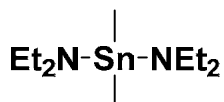


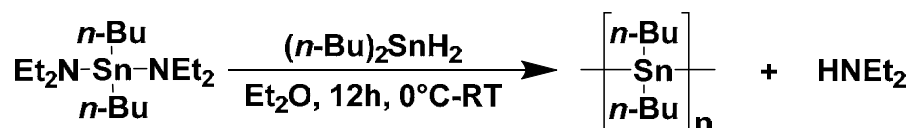
Figure S2 Bis(diethylamino)dimethylstannane.

1.6 Preparation of poly(di(*n*-butyl)stannane (**5**)

To a dry 250 mL Schlenk flask wrapped in tin foil was added 30 mL of dry Et₂O and **2** (1.50 mmol, 0.567 g). This solution cooled to 0 °C, and a solution of **1** (1.50 mmol, 0.354 g) in dry Et₂O (15 mL) was added dropwise over 15 min without notable colour change. The polymerization was allowed to proceed for 12 h, where after the remaining solvent and by-products removed *in vacuo*. Yield 3.49 g (75 %).

¹H NMR (C₆D₆) δ 0.89 (t, ⁵J_{119Sn-1H} = 4.7 Hz, 6H, -SnCH₂CH₂CH₂CH₃), 0.95 (m, ²J_{119Sn-1H} = 17.3 Hz, 4H, -SnCH₂CH₂CH₂CH₃), 1.36 (dd, ³J_{119Sn-1H} = 14.3 Hz, 4H, -SnCH₂CH₂CH₂CH₃),

1.80 (dd, $^4J_{119\text{Sn}-1\text{H}} = 13.9$ Hz, 4H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm; ^{119}Sn { ^1H } NMR (C_6D_6): δ -190.6 ppm. UV-VIS λ_{max} (THF) = 379 nm ($\epsilon = 5.184$ L \cdot mol $^{-1}\cdot$ cm $^{-1}$). This data is in good agreement with reported literature values.³ EA $C_{\text{calc}/\text{found}}$: 41.07/39.81, $H_{\text{calc}/\text{found}}$: 7.79/7.61.

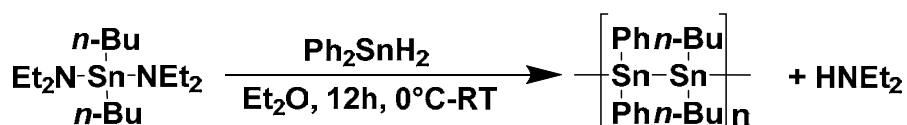


Scheme S3 Synthesis of poly(di(*n*-butyl)) stannane **5**.

1.7 Preparation of poly(diphenyl-alt-di(*n*-butyl)) stannane (**6**)

To a 250 mL Schlenk flask wrapped in tin foil was added 30 mL of dry Et₂O and **2** (1.50 mmol, 0.567 g). The flask was then cooled to 0°C, after which a solution of **4** (1.50 mmol, 0.413 g) in dry Et₂O (15 mL) was added dropwise over 15 minutes. The polymerization was allowed to proceed for 12 h. The remaining solution and by-products were removed *in vacuo*. Yield: 4.00 g (86%).

^1H NMR (C_6D_6) δ 0.74 (t, $^5J_{119\text{Sn}-1\text{H}} = 7.3$ Hz, 6H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.98-0.75 (m, 4H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.27 (ddd, $^3J_{119\text{Sn}-1\text{H}} = 21.4$ Hz, 4H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85-1.42 (m, 4H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.10-6.79 (m, 4H, *o*-C₆H₅), 7.34 (t, $^4J_{119\text{Sn}-1\text{H}} = 10.4$ Hz, 6H, *m,p*-C₆H₅) ppm; ^{13}C { ^1H } NMR (C_6D_6): δ 13.75 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 25.82 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 30.22 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 67.83 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 128.91 (*p*-C₆H₅), 129.06 (*m*-C₆H₅), 137.70 (*o*-C₆H₅), 138.67 (*i*-C₆H₅) ppm; ^{119}Sn { ^1H } NMR (C_6D_6): δ -187.4 ($-\text{Sn}(n\text{Bu}_2)$) and -208.0 ($-\text{SnPh}_2$) ppm. UV-VIS λ_{max} (THF) = 390 nm ($\epsilon = 2.554$ L \cdot mol $^{-1}\cdot$ cm $^{-1}$). EA $C_{\text{calc}/\text{found}}$: 47.30/46.56, $H_{\text{calc}/\text{found}}$: 5.95/5.39.

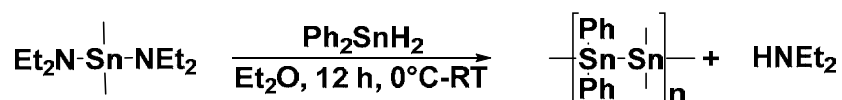


Scheme S4 Synthesis of poly(diphenyl-*alt*-di(*n*-butyl)) stannane 6.

1.8 Preparation of poly(diphenyl-*alt*-dimethyl) stannane (7)

To a 250 mL Schlenk flask wrapped in tin foil was added 30 mL of dry Et₂O and **3** (1.50 mmol, 0.441 g). The flask was then cooled to 0°C, after which a solution of **4** (1.50 mmol, 0.413 g) in dry Et₂O (15 mL) was added dropwise over 15 min. The polymerization was allowed to react for 12 h. Then the remaining solution and by-products were removed *in vacuo*. Yield: 3.82 g (82 %).

¹H NMR (C₆D₆): δ 1.35 (t, 6H, (-SnCH₃)₂); 7.10 – 6.65 (m, 6H, (*m,p*-C₆H₅)₂), 7.42 (t, 6H, *o*-C₆H₅)₂) ppm, ¹³C {¹H} NMR (C₆D₆): δ 1.03 (-SnCH₃), 128.81 (*p*-C₆H₅), 129.03 (*m*-C₆H₅), 136.14 (*o*-C₆H₅), 136.26 (*i*-C₆H₅) ppm; ¹¹⁹Sn {¹H} NMR (C₆D₆): δ -59.8 (*J*_{119Sn-117Sn} = 4421 Hz, (-SnMe₂)), -200.5 (-SnPh₂) ppm. UV-VIS λ_{max} (THF) = 395 nm (ε = 7.745 L·mol⁻¹·cm⁻¹). EA C_{calc}/found: 34.81/33.72, H_{calc}/found: 5.50/5.63.

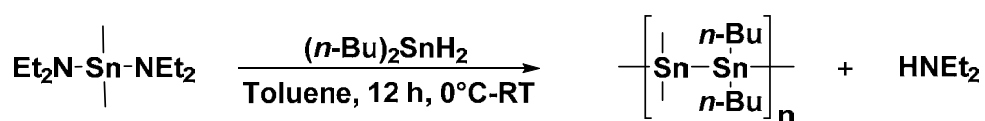


Scheme S5 Synthesis of poly(diphenyl-*alt*-dimethyl) stannane 7.

1.9 Preparation of poly(dimethyl-*alt*-di(*n*-butyl)) stannane (8)

To a 250 mL Schlenk flask wrapped in tin foil was added 30 mL of dry toluene and **3** (1.50 mmol, 0.441 g). The flask was then cooled to 0 °C, after which a solution of **1** (1.50 mmol, 0.354 g) in dry Et₂O (15 mL) was added dropwise over 15 min. The polymerization was allowed to react for a total of 12 h. The remaining solution and by-products were then removed under reduced pressure. Yield: 2.93 g (63 %).

^1H NMR (C_6D_6): δ 0.31 (s, 6H, $(-\text{SnCH}_3)_2$); 0.64 (t, 6H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 0.86 (t, 4H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.10(m, 4H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.34 (m, 4H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6): δ 10.11 ($J_{119\text{Sn}-13\text{C}} = 120$ Hz, $J_{117\text{Sn}-13\text{C}} = 115$ Hz, $-\text{SnCH}_3$), 10.47 ($J_{119\text{Sn}-13\text{C}} = 120$ Hz, $J_{117\text{Sn}-13\text{C}} = 115$ Hz, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.61 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 27.59 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 30.82 ($-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm ; ^{119}Sn $\{^1\text{H}\}$ NMR (C_6D_6): δ -185 ($-\text{SnMe}_2$), -235 ($-\text{Sn}(n\text{-Bu})_2$) ppm. UV-VIS λ_{max} (THF) = 311 nm ($\epsilon = 2.420 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). EA $\text{C}_{\text{calc}/\text{found}}$: 31.30/29.24, $\text{H}_{\text{calc}/\text{found}}$: 6.83/6.37.



Scheme S6: Synthesis of poly(dimethyl-*alt*-di(*n*-butyl)) stannane **8**.

2.0 Elemental Analysis

The elemental analysis was conducted by Atlantic Microlabs and examined for C and H. These elements account for less than half of the molecular weight of one unit within the polymer chain. As a result the uncertainty of these polymers is relatively high. The process itself has an uncertainty of $\pm 0.3\%$ which can skew values significantly when coupled with a relative weight of tin used for calculations. Lastly the PDI of these polymers is slightly > 2 , which is the value for an ideal condensation polymerization. With all of these factors in mind we used GPC to support an estimate of the EA values. Since the PDI is not perfectly symmetrical, the idealized monomer repeat unit is not fully representative of the equally distributed polymeric chain. Considering all of these factors, we determined the approximate number of repeat units for the polystannanes prepared by condensation as follows: **5** = 77 units, **6** = 74 units, **7** = 1150 units and **8** = 180 units. As observed by the repeat unit sizes for these polymers, end group affects are negligible. The calculated mass for the degree of polymerization of these polymers was then used to calculate the weight fractions (Sn, C and H) and to determine their total mass contribution to the polymer. The collective elemental data is presented and used for the calculated values of polymers **6-8**. Importantly, a 10% deviation of the starting material ratios from 1.0 causes a pronounced decrease in molar mass and is expected for a polycondensation type reaction of the *in situ* formed stannides, according to Carother's equation.³⁸ The deviation takes into account a non-idealized situation, whereas the calculations are assumed under an ideal working situation.

3.0 DSC

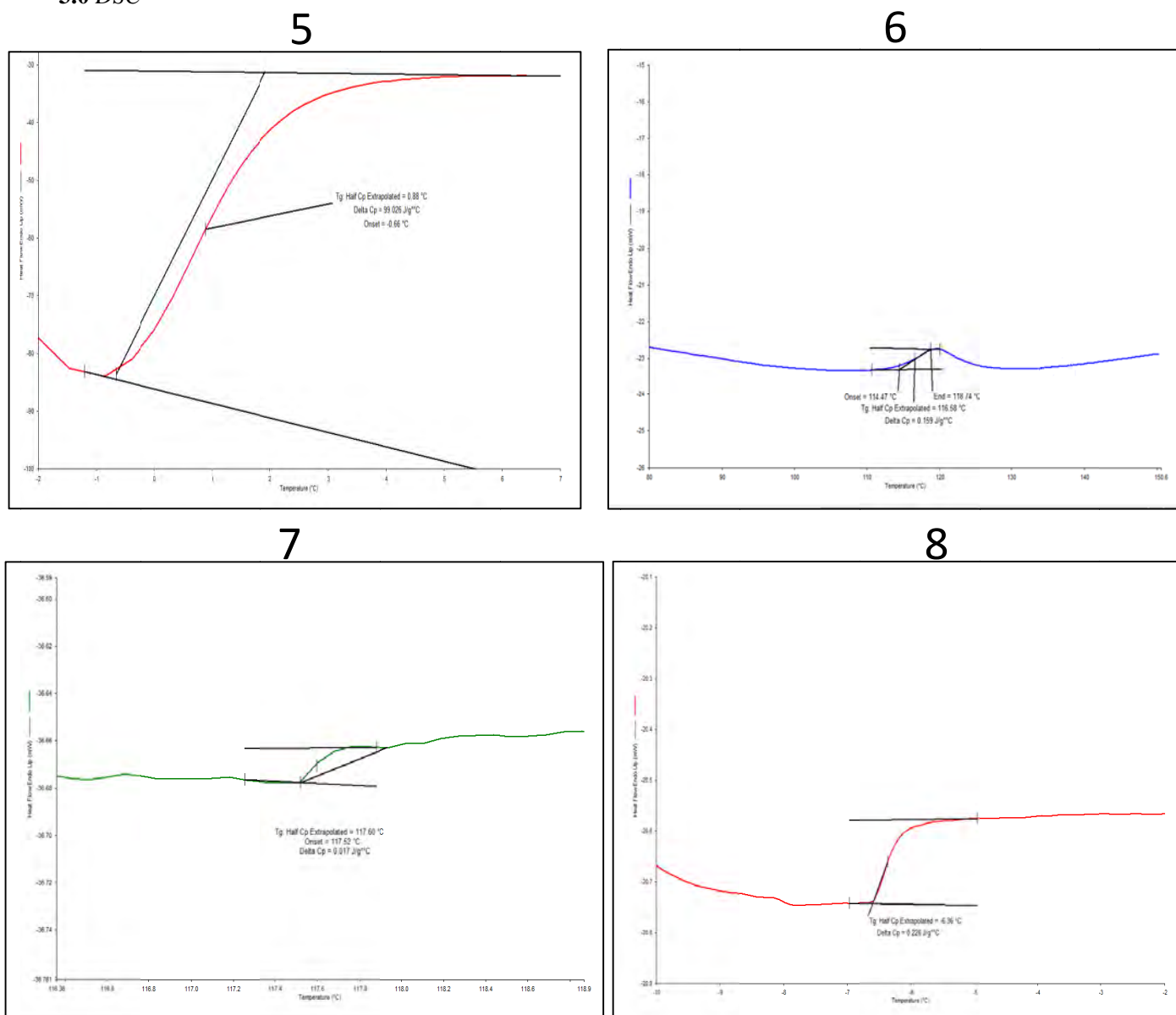


Figure S3: DSC of synthesized polymers **5-8**.

Note on DSC acquisition: All of these samples were run between -45°C-200°C then cooled to complete the cycle at 5-10°C a minute in triplicate with a 20 mL/min flow of N₂(g)

4.0 Polymer Images

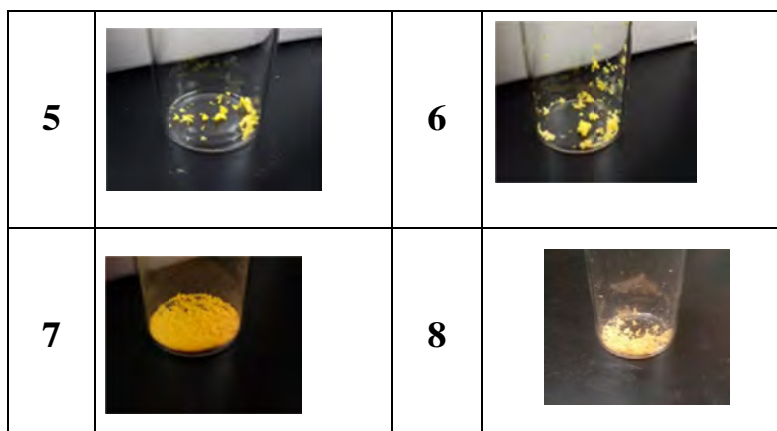


Figure S4: Images of all the synthesized polymers 5-8.

5.0 GPC

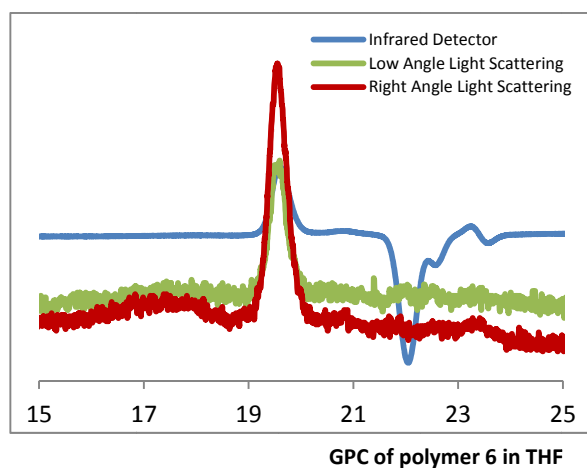
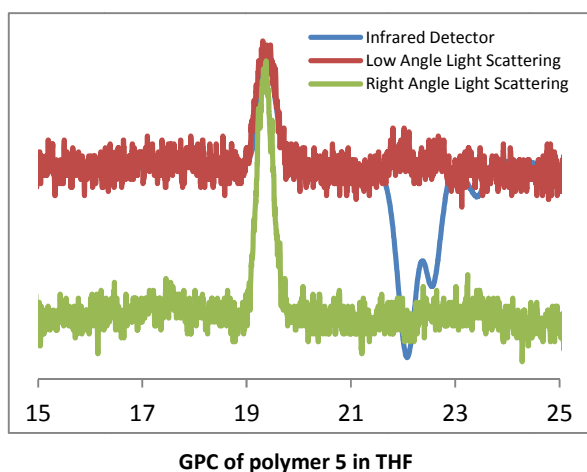
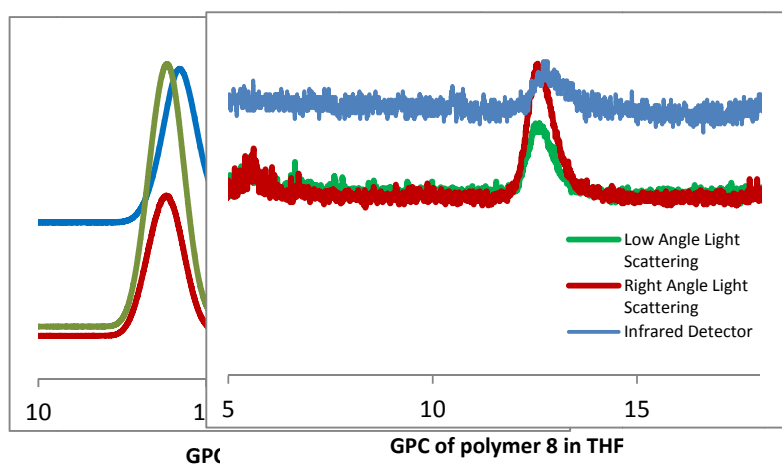


Figure S5: GPC chromatograms of polymers 5-8.

Note on Molecular weight determinations:

The GPC analysis of these polymers was done in triplicate to ensure accuracy. We estimated the molecular weights of alternating polymers by using the calculated dn/dc for homopolymer 5. This estimation allowed for a calculation of



polymer PDI for polymers **6-8**. While the dn/dc for each alternating polymers is unique, an estimation using the dn/dc for the more similar polystannane **5** is reasonable compared to conventional systems calibrated with polystyrene standards. These issues have been previously reported in the literature. Caseri *et al.* had also previously reported that as the phenyl substituents ratio increased for a random copolymer, the polymer moved to a more insoluble state until no useful M_w information was obtainable.²⁵

The solutions were made at 10 mg/mL for **5**, **6** and **8** while **7** was made at 2 mg/mL due to solubility restraints. All solutions were run in THF.

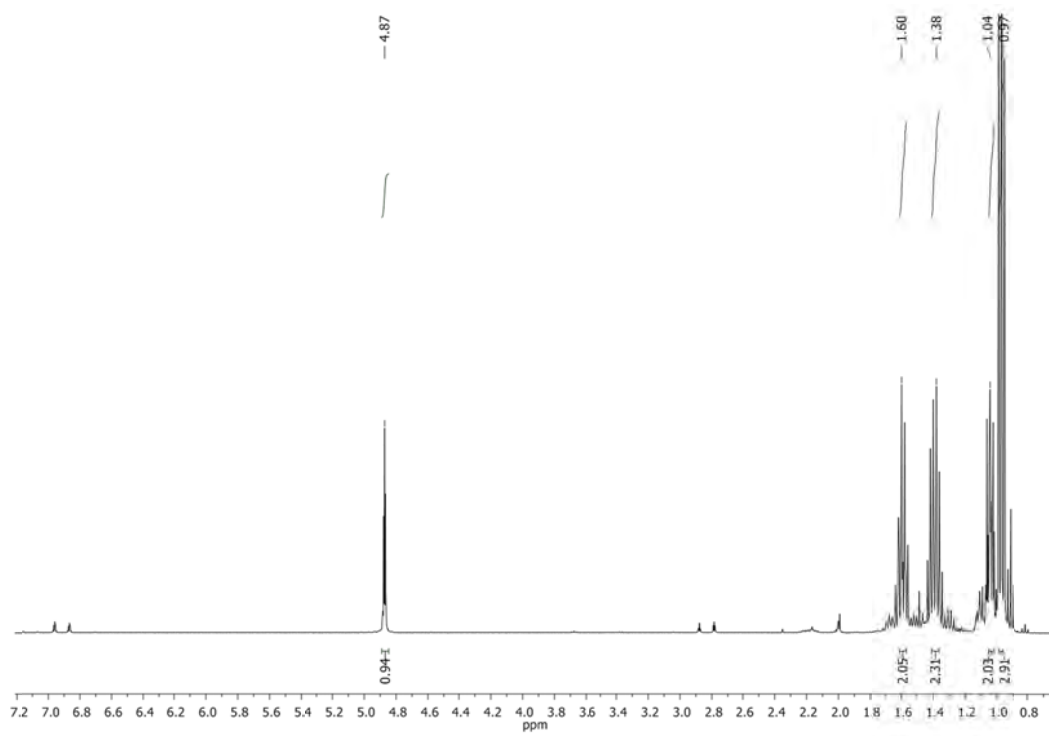


Figure S6 ^1H NMR (C_6D_6) spectrum of **1**.

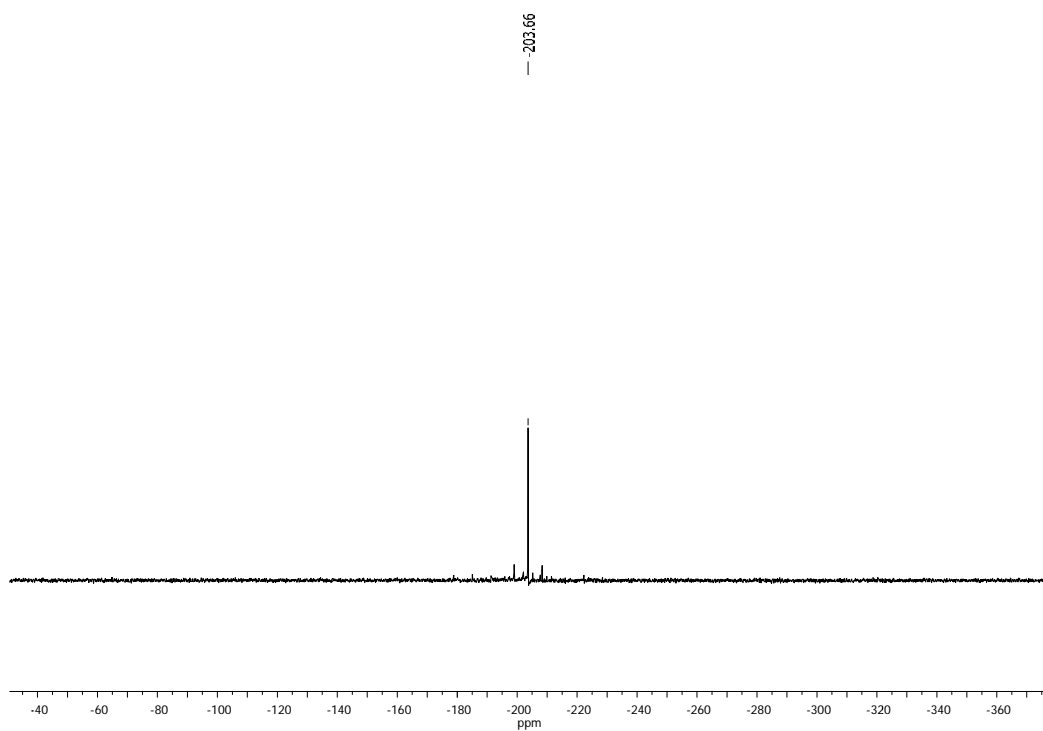


Figure S7 ^{119}Sn NMR (C_6D_6) spectrum of **1**.

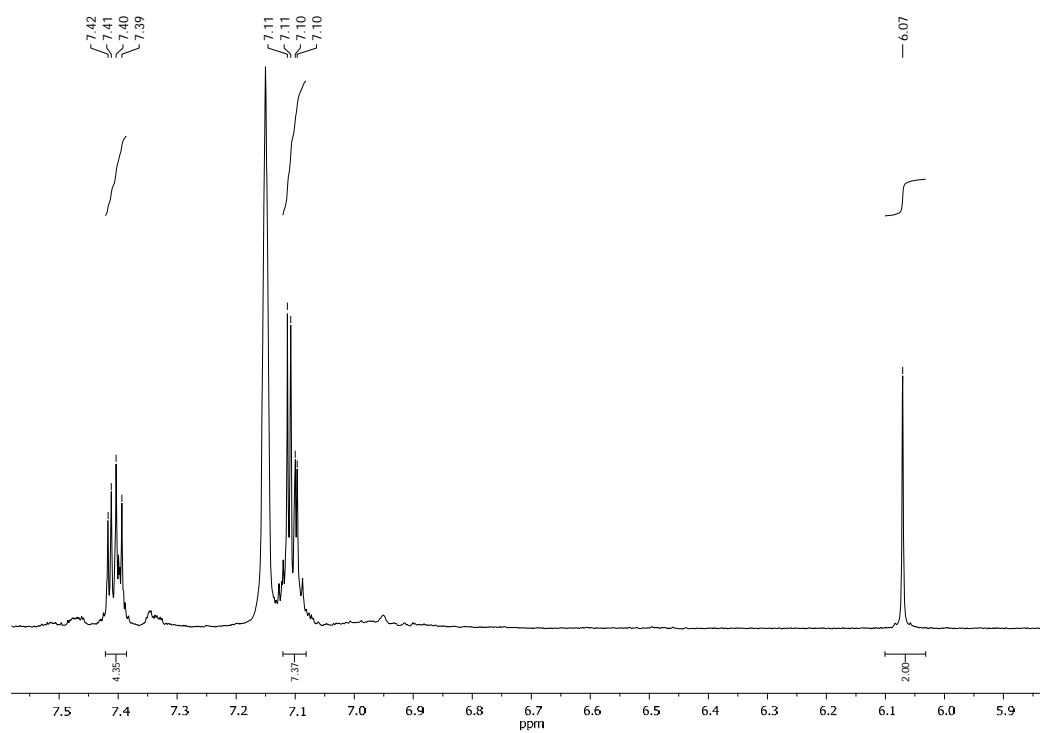


Figure S8 ^1H NMR (C_6D_6) spectrum of **2**.

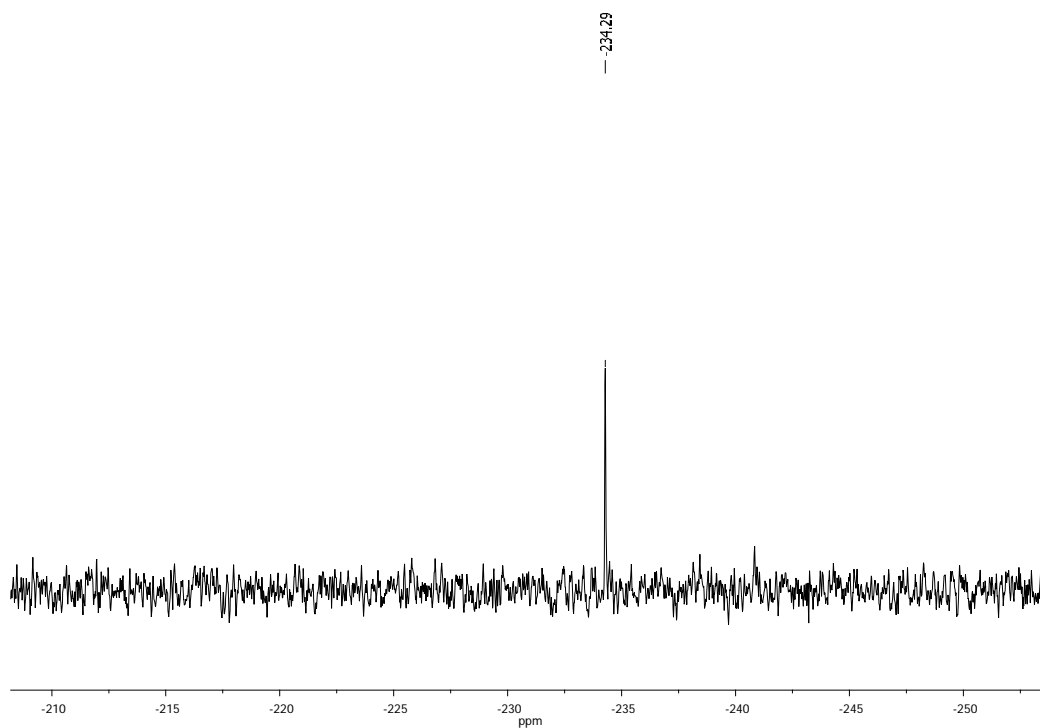


Figure S9 ^{119}Sn NMR (C_6D_6) spectrum of **2**.

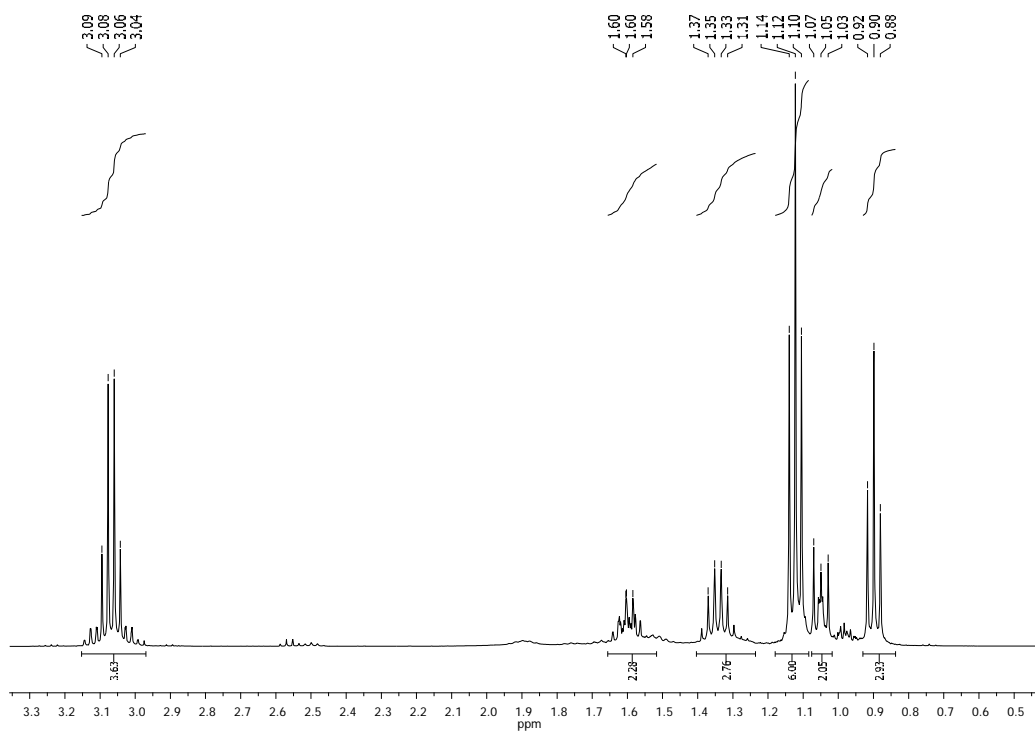


Figure S10 ^1H NMR (C_6D_6) spectrum of **3**.

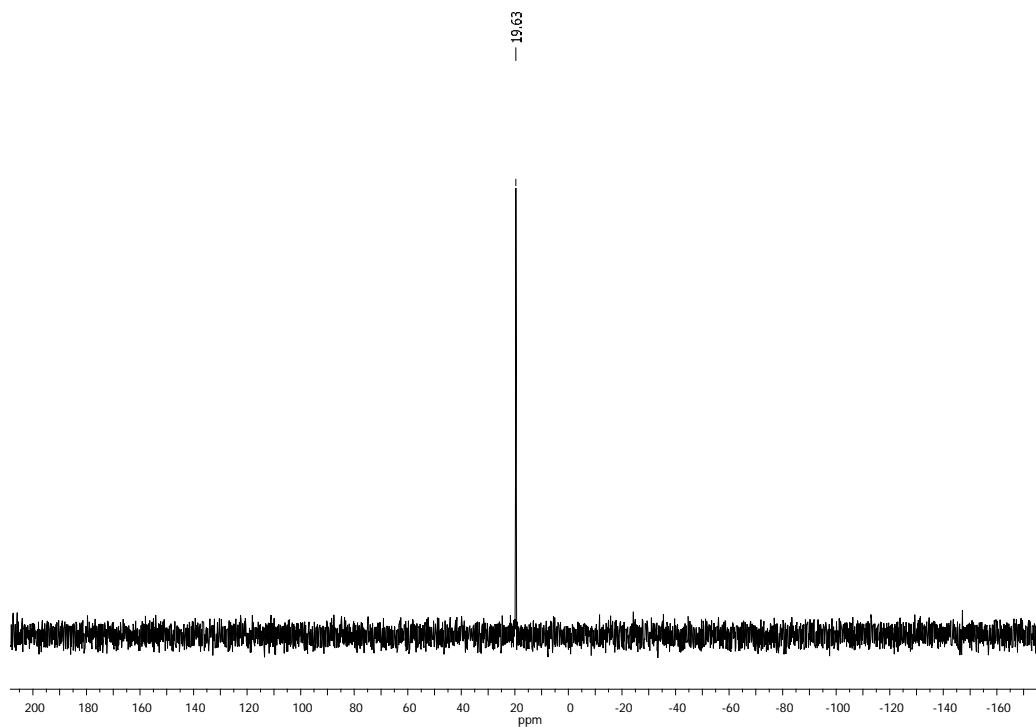


Figure S11 ^{119}Sn NMR (C_6D_6) spectrum of **3**.

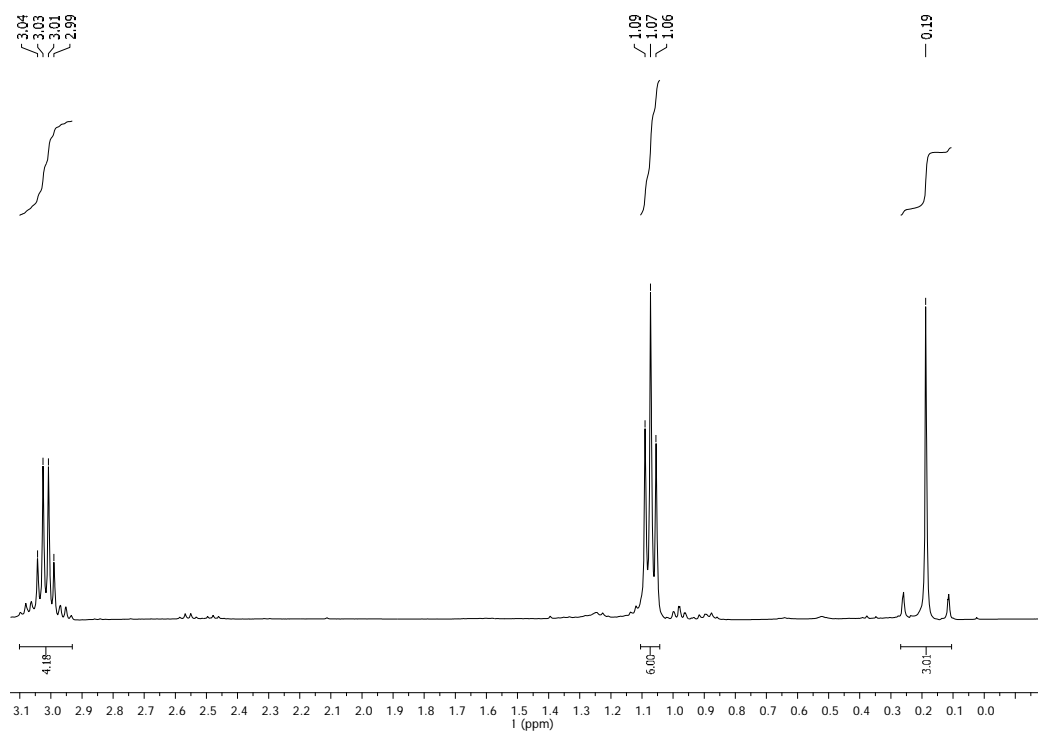


Figure S12 ^1H NMR (C_6D_6) spectrum of **4**.

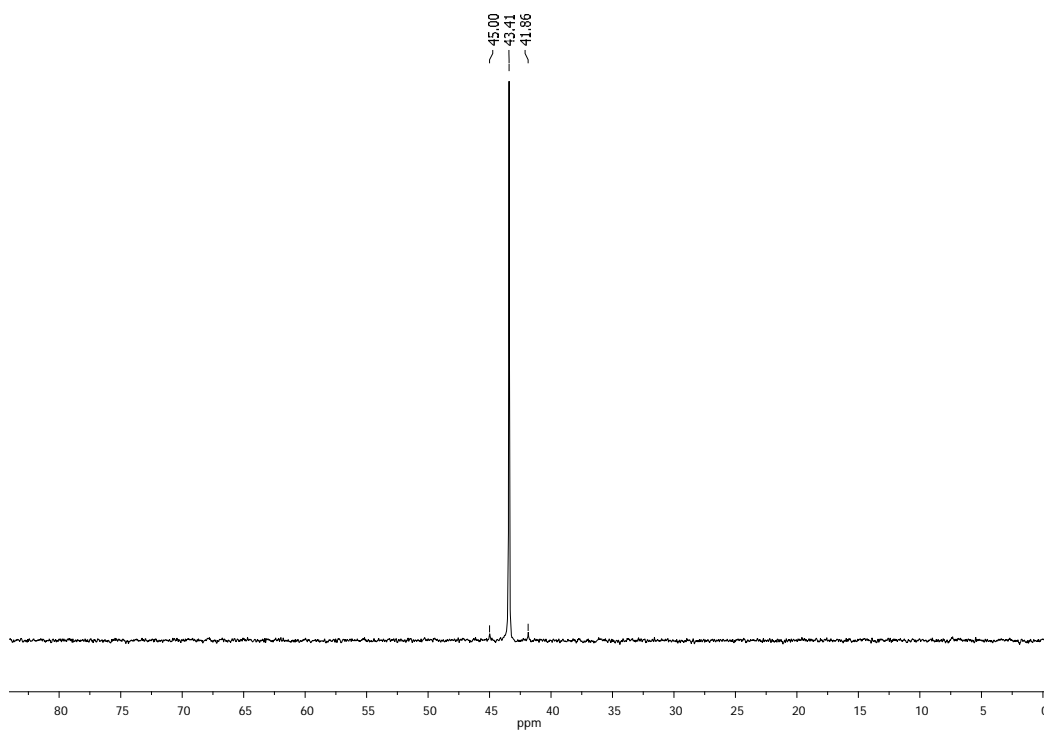


Figure S13 ^{119}Sn NMR (C_6D_6) spectrum of **4**.

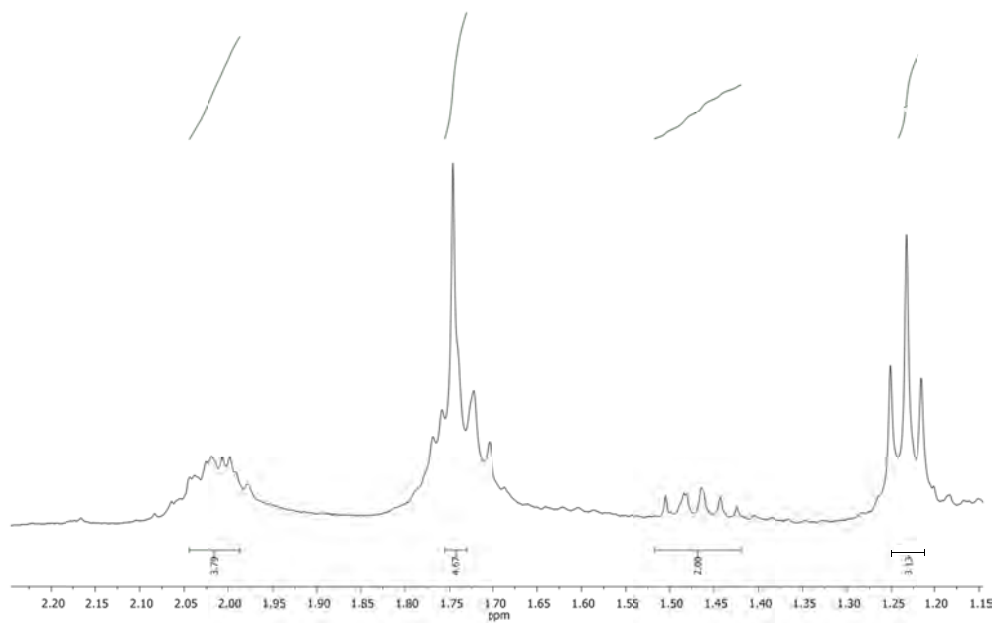


Figure S14: ^1H (C_6D_6) spectrum of **5**.

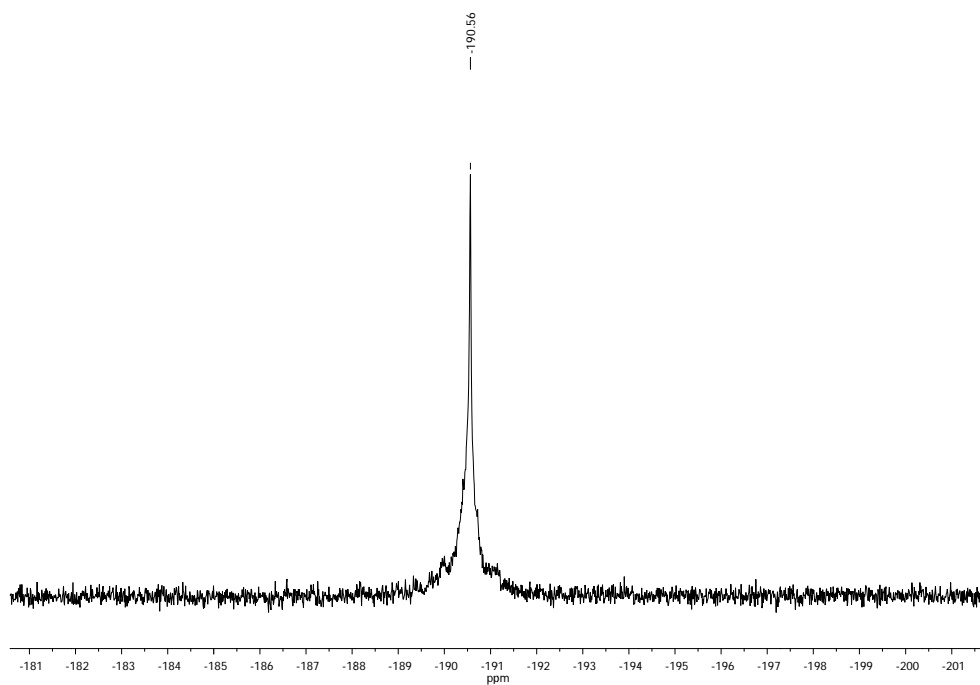


Figure S15 ^{119}Sn NMR (C_6D_6) spectrum of **5**.

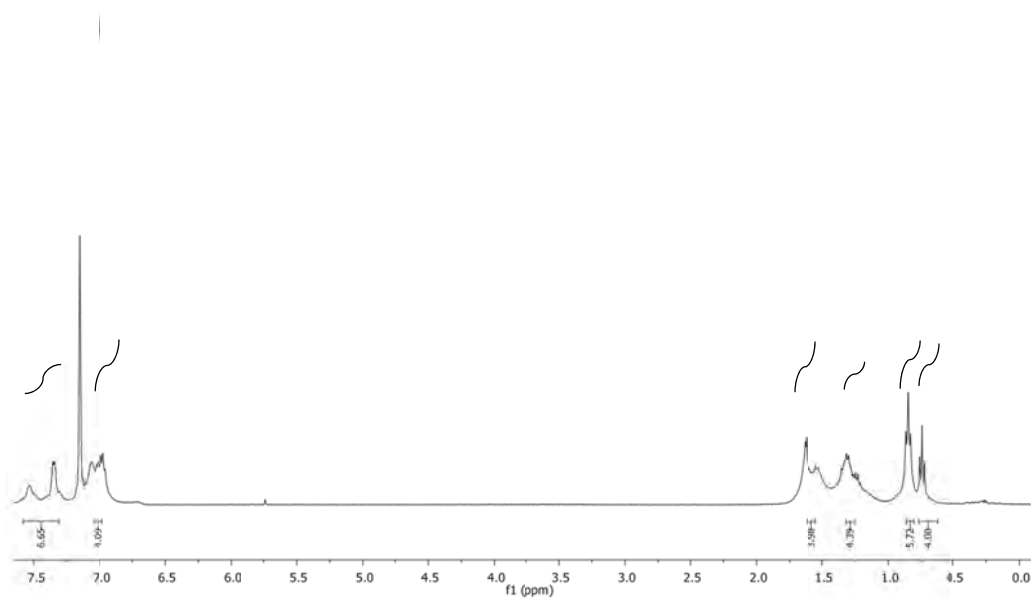


Figure S16: ^1H (C_6D_6) spectrum of **6**.

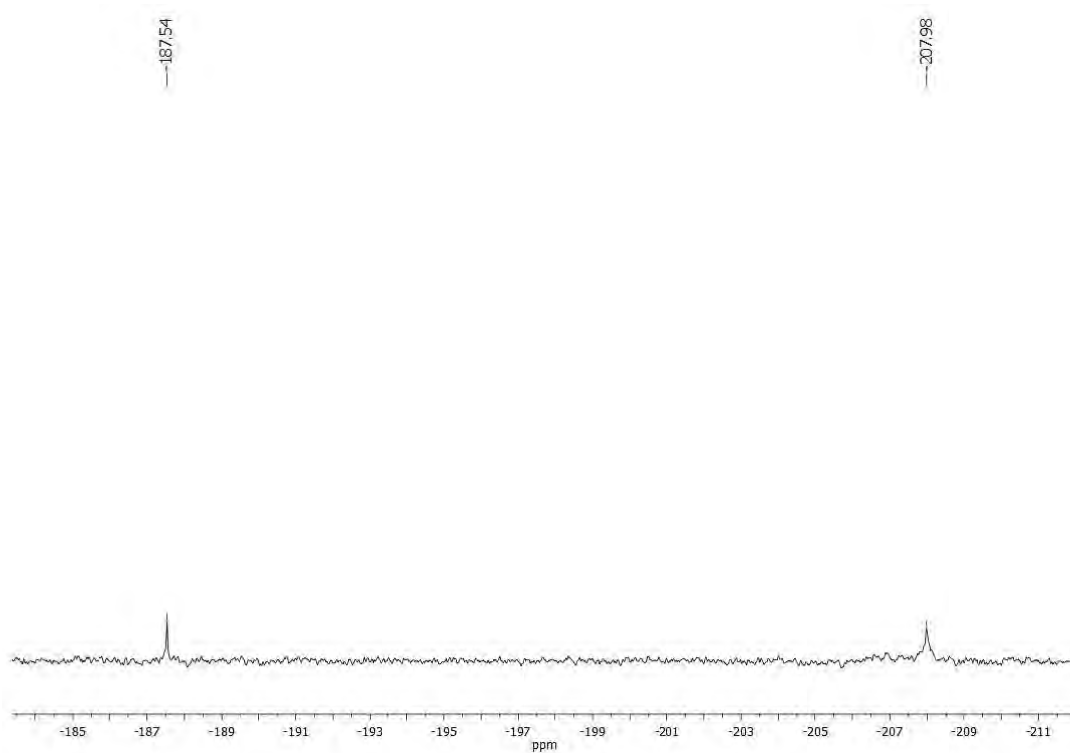


Figure S17 ^{119}Sn NMR (C_6D_6) spectrum of **6**.

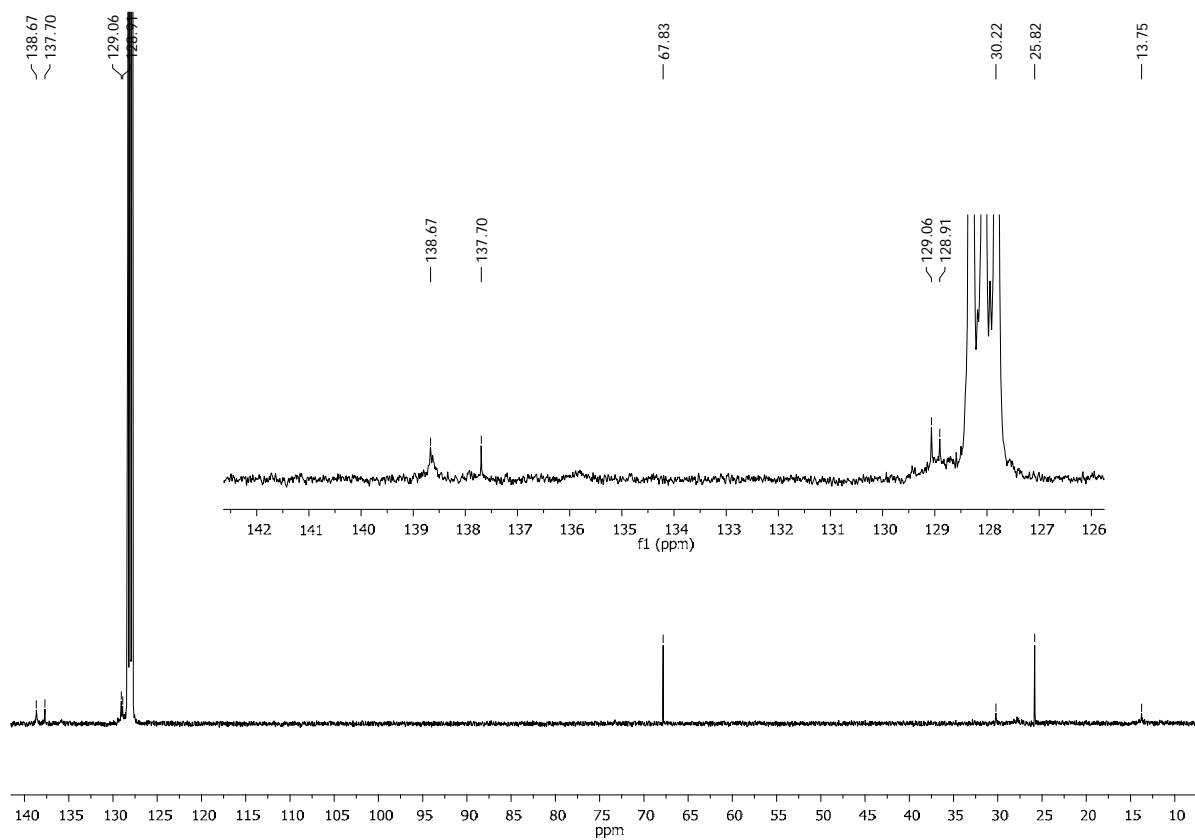


Figure S18 ^{13}C NMR (C_6D_6) spectrum of **6**.

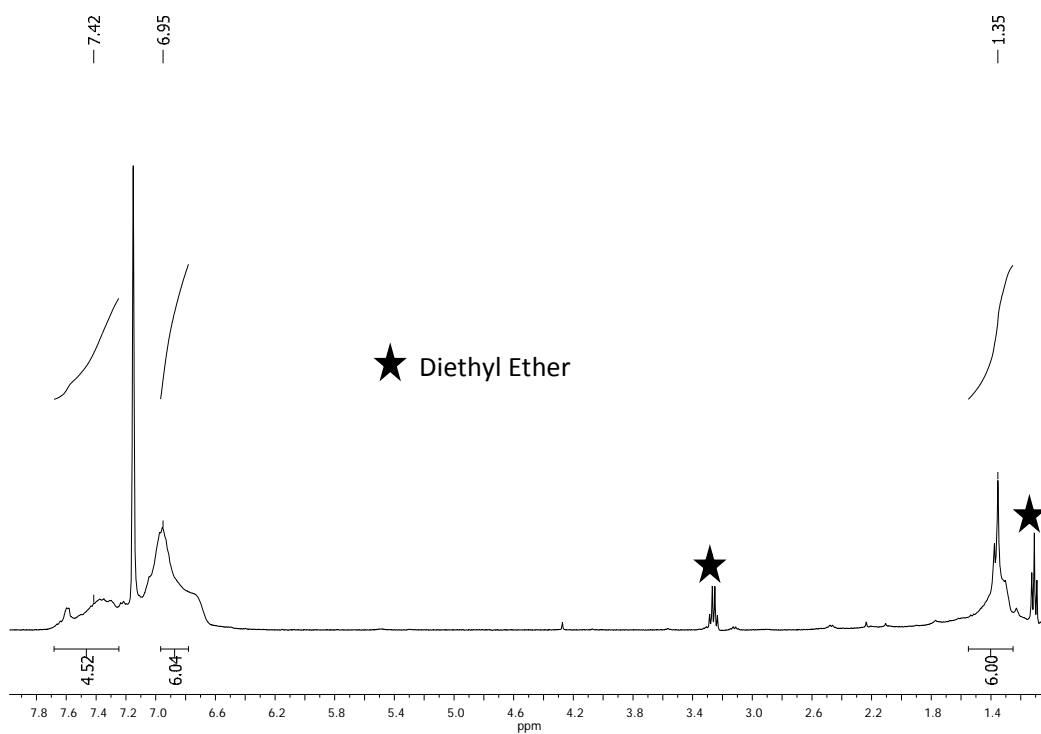


Figure S19 ^1H NMR (C_6D_6) spectrum of **7**.

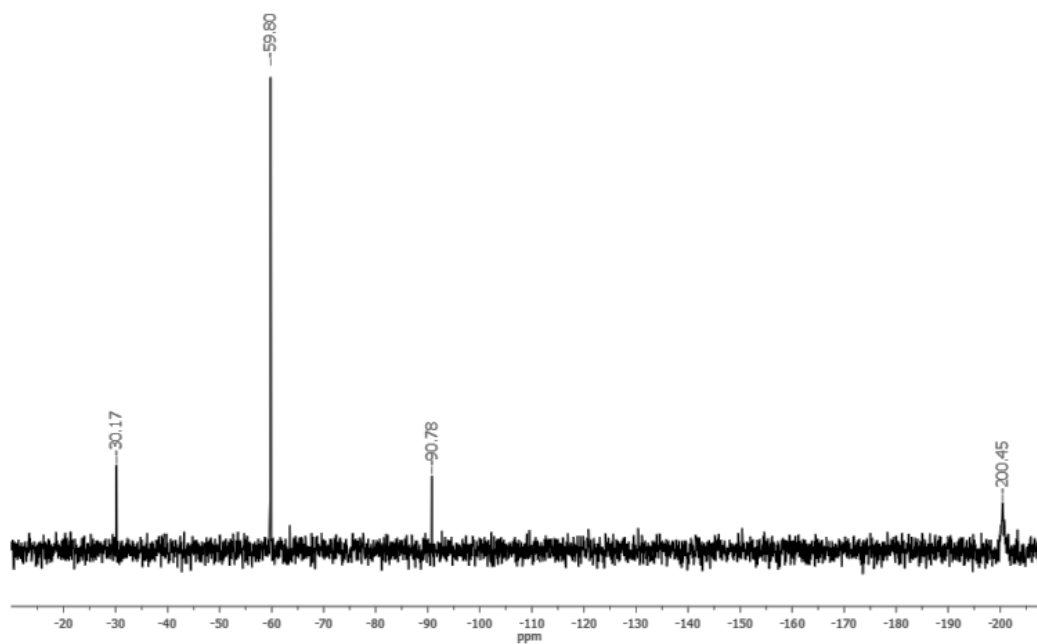


Figure S20 ^{119}Sn NMR (C_6D_6) spectrum of **7**.

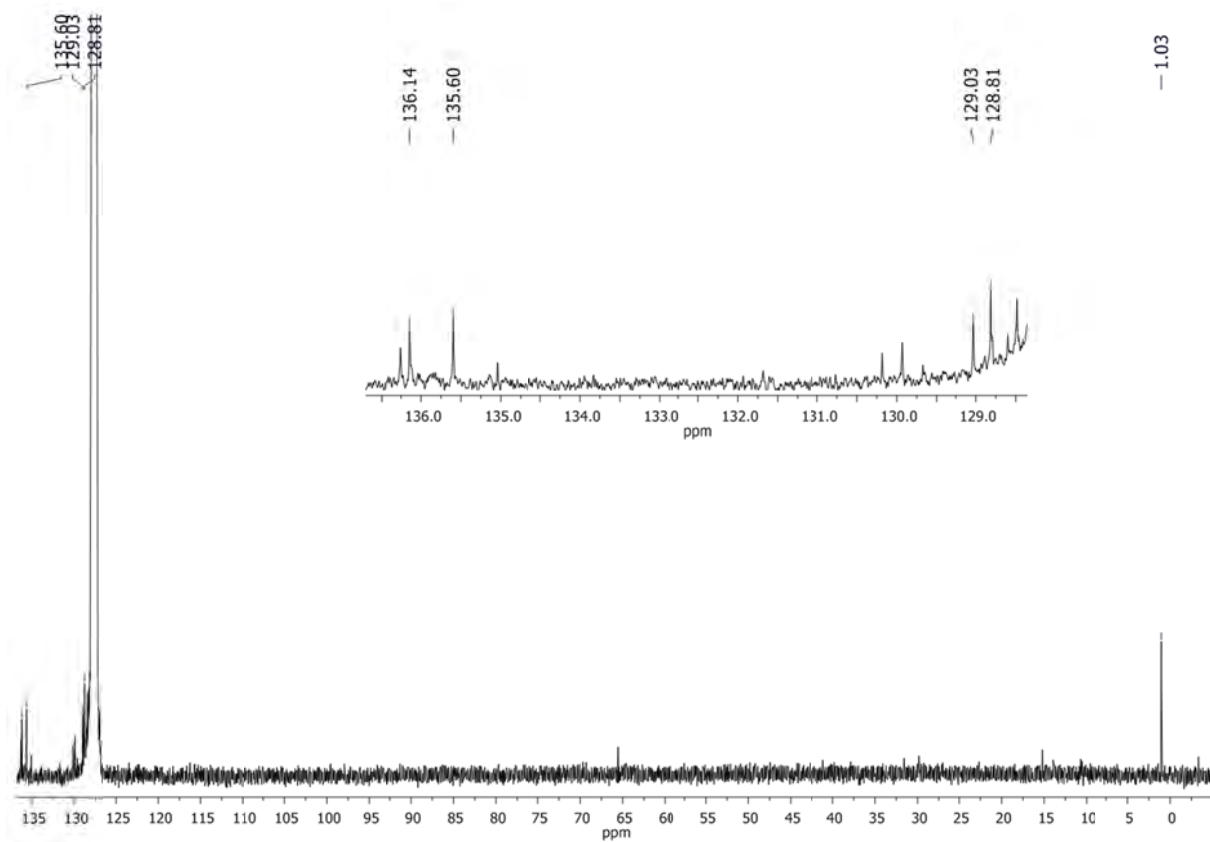


Figure S21 ^{13}C NMR (C_6D_6) spectrum of **7**.

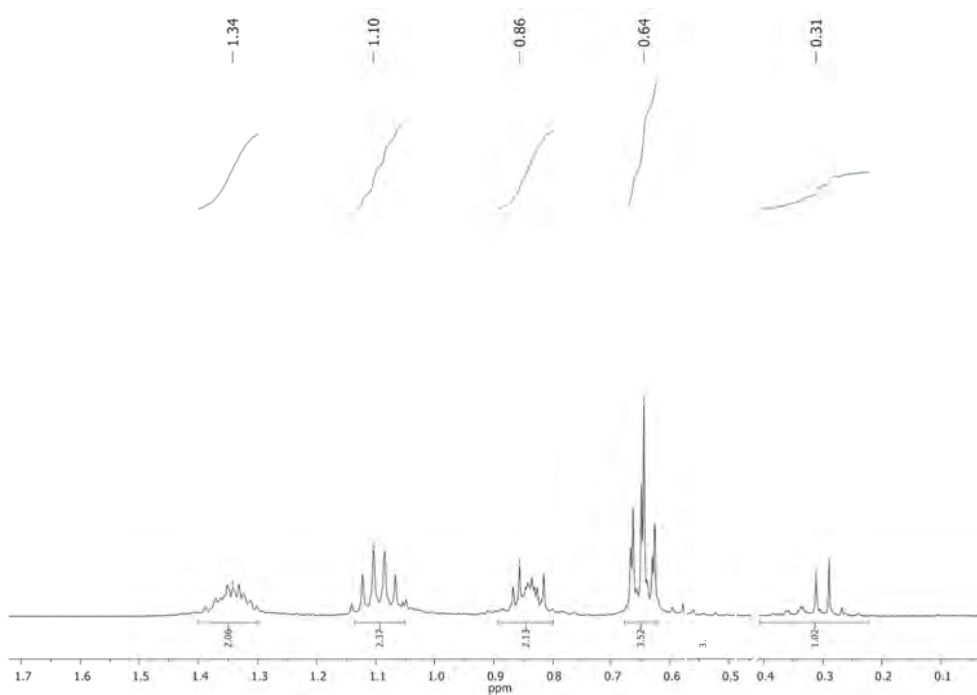


Figure S22 ^1H NMR (C_6D_6) spectrum of **8**.

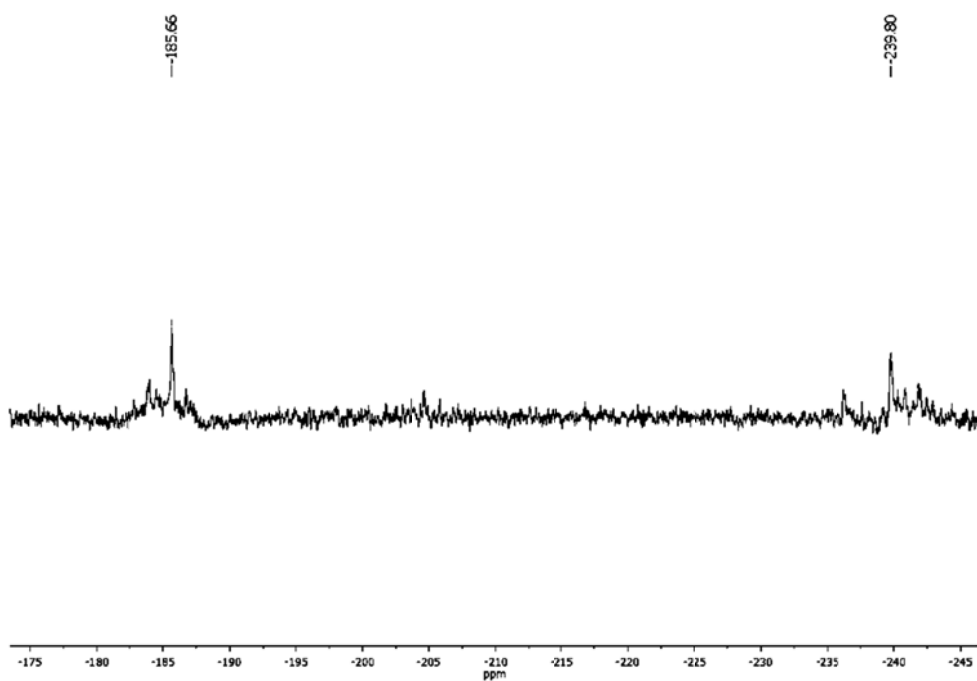


Figure S23 ^{119}Sn NMR (C_6D_6) spectrum of **8**.

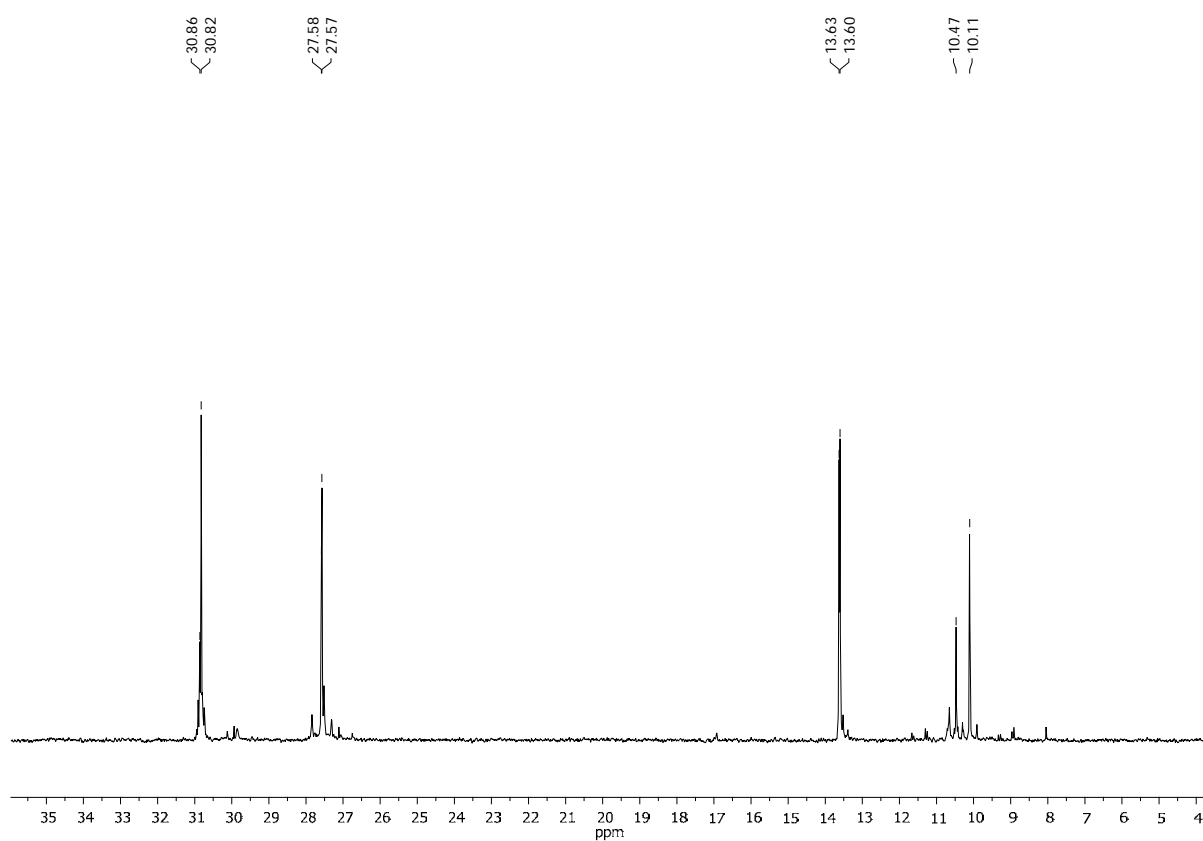


Figure S24 ^{13}C NMR (C_6D_6) spectrum of **8**.

7.0 References

37. J. Lorberth, *J. Organomet. Chem.* 1969, **19**, 435-438.
38. W. H. Carothers, *Trans. Faraday Soc.*, 1936, **32**, 39-49.