

Supporting Information for

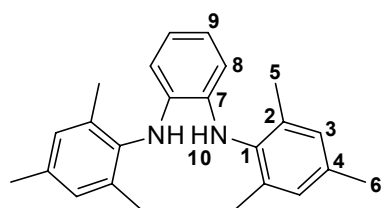
**Sterically demanding and chiral N,N'-disubstituted N-heterocyclic
germylenes and stannylenes**

Julia V. Dickschat, Slawomir Urban, Tania Pape, Frank Glorius and F.
Ekkehardt Hahn

General remarks

If not described differently, all manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. Solvents were dried over sodium/benzophenone under argon and were freshly distilled prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $\text{Sn}\{^1\text{H}\}$ spectra were recorded on Bruker AVANCE II 200 (QNP-probehead), Bruker AVANCE I 400 (BBO-probehead) or Bruker AVANCE III 400 (BBFO-probehead) spectrometers. The chemical shifts are reported as parts per million relative to the used solvent or tetramethylsilane. Optical rotations were measured on a Perkin Elmer 341 polarimeter, using a quartz cell ($l = 100$ mm) with a Na high-pressure lamp ($\lambda = 589$ nm). ESI-spectra were recorded on a Bruker-Daltonics MicroTof.

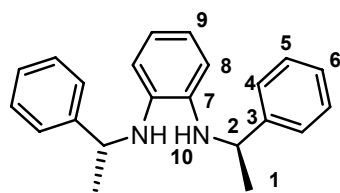
Synthesis



Diamine 1: According to a literature known procedure,¹ an oven-dried Schlenk tube was cooled under Argon and charged with $\text{Pd}(\text{OAc})_2$ (157 mg, 0.70 mmol), $[\text{t-Bu}_3\text{PH}]\text{BF}_4$ (203 mg, 0.70 mmol), NaOt-Bu (2.02 g, 21.00 mmol) and toluene (16.0 mL). The mixture was degassed, backfilled with Argon three times and heated to 60 °C for 15 min. Subsequently, 1,2-dibromobenzene (0.85 mL, 7.00 mmol) and 2,4,6-trimethylaniline (2.1 mL, 14.70 mmol) were added under argon. The reaction mixture was then heated at 135 °C until all 1,2-dibromobenzene had been consumed as judged by TLC. The reaction mixture was allowed to cool to ambient temperature and a saturated aqueous NH_4Cl solution (40 mL) was added under argon. The resulting mixture was extracted with Et_2O (3×20 mL) and the organic layer was washed twice with a saturated NH_4Cl solution. The organic phase was dried over MgSO_4 and filtered. After removal of the solvent a green/black

solid was obtained which was purified by column chromatography (SiO₂, CH₂Cl₂/*n*-pentane, 1:20). Yield: 2.10 g, 87% of a colorless solid.

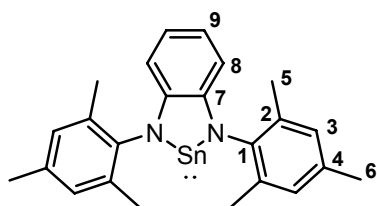
¹H NMR (600 MHz, CDCl₃): δ = 6.96 (s, 4H, H-3), 6.67-6.65 (m, 2H, H-9), 6.31-6.29 (m, 2H, H-8), 5.12 (s, 2H, H-10) 2.32 (s, 6H, H-6), 2.19 (s, 12H, H-5). ¹³C NMR (150 MHz, CDCl₃): δ = 137.1 (C-1), 135.4 (C-7), 134.2 (C-4), 133.6 (C-2), 129.5 (C-3), 120.2 (C-9), 114.4 (C-8), 21.0 (C-6), 18.3 (C-5). EM (ESI): *m/z* [M + H⁺] *calcd* for C₂₄H₂₉N₂: 345.2325; *found*: 345.2315. R_f = 0.33 (CH₂Cl₂/*n*-pentane, 1:4)



Diamine *R,R*-3: According to a literature known procedure,² an oven-dried Schlenk tube was cooled under Argon and charged with Pd₂dba₃ (458 mg, 0.50 mmol), *rac*-BINAP (623 mg, 1.00 mmol), and toluene (60 mL). The mixture was degassed,

backfilled with Argon three times and heated to 135 °C in an oil bath for 15 min. After cooling to ambient temperature NaOt-Bu (4.87 g, 50.60 mmol), (*R*)- α -methylbenzylamine (8.1 mL, 62.50 mmol), 1,2-dibromobenzene (1.52 mL, 12.50 mmol), and toluene (25.0 mL) were added. The reaction mixture was again degassed and the flask was refilled with argon. The mixture was then heated to 135 °C with stirring until the initially formed monoaminated compound had been completely consumed as judged by GC-MS analysis. The reaction mixture was allowed to cool to ambient temperature, diluted with diethyl ether, filtered through a pad of celite and concentrated *in vacuo* (rotary evaporator). The crude reaction product was purified by column chromatography (SiO₂, CH₂Cl₂/*n*-pentane, 1:10). Yield: 1.20 g, 30% of a slightly yellow oil.

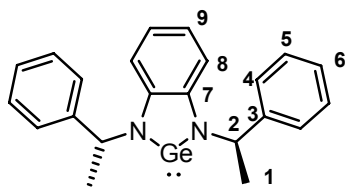
¹H NMR (300 MHz, CDCl₃): δ = 7.42-7.40 (m, 4H, H-4), 7.35-7.32 (m, 4H, H-5), 7.26-7.21 (m, 2H, H-6), 6.59-6.57, 6.46-6.44 (m, H-8, H-9), 4.51 (q, ³J_{HH} = 6.6 Hz, 2H, H-2), 3.73 (s, br, 2H, H-10), 1.60 (d, ³J_{HH} = 6.6 Hz, 6H, H-1). ¹³C NMR (75 MHz, CDCl₃): δ = 145.3, 136.3, 128.7, 127.0, 126.1, 119.3, 113.8, 54.0 (C-2), 25.4 (C-1). EM (ESI): *m/z* [M + H⁺] *calcd* for C₂₂H₂₅N₂: 317.2012; *found*: 317.2019). R_f = 0.3 (CH₂Cl₂/*n*-pentane, 4:6). [α]_D²⁰ -278.3 (*c* = 2.01, CH₂Cl₂).



Stannylene 2: A oven-dried Schlenk flask was cooled under argon and charged with diamine **1** (100 mg, 0.29 mmol) and tetrahydrofuran (20.0 mL). To this was added Sn[N(SiMe₃)₂]₂ (128 mg, 0.29 mmol). The reaction mixture was heated for 24

h at 70 °C in an oil bath. After cooling to ambient temperature the solvent was removed *in vacuo*, the resulting solid residue was taken up in *n*-hexane and the slurry was filtered. Removal of the solvent gave compound **2**. Yield 100 mg, 75% of an orange solid. Crystals of **2** were obtained by cooling of a THF solution of the compound under argon to 0 °C for 2 weeks.

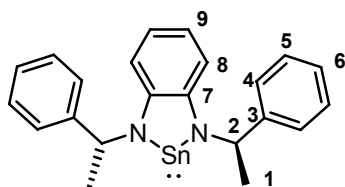
^1H NMR (200 MHz, THF- d_8): δ = 7.02 (s, 4H, H-3), 6.47 (m, 2H, H-8), 6.12 (m, br, 2H, H-9), 2.33 (s, 6H, H-6), 2.13 (s, 12H, H-5). ^{13}C NMR (50.3 MHz, THF- d_8): δ = 145.2, 142.8, 135.6, 135.0, 129.8, 117.9, 111.1, 21.0 (C-6), 18.4 (C-5). ^{119}Sn NMR (149.2 MHz, THF- d_8): δ = 172.0. ^{119}Sn NMR (149.2 MHz, C_6D_6): δ = 236.2 Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{Sn}$ (461.17): C, 62.51; H, 5.68; N, 6.07. Found: C, 61.89; H, 5.94, N, 5.37. MS (EI, 70 eV): m/z = 462 (100%, $[\text{M}]^+$).



Germylene *R,R*-4: A tetrahydrofuran solution of diamine *R,R*-**3** (100 mg, 0.32 mmol) was treated with $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ (124 mg, 0.32 mmol) as described for the preparation of **2**. The reaction mixture was heated for 24 h at 60 °C in an oil bath. After

cooling to ambient temperature the solvent was removed *in vacuo* and the solid residue was taken up in *n*-hexane. The suspension was filtered and the solvent was removed to give *R,R*-**4** as an orange solid. Yield: 115 mg, 93%.

^1H NMR (200 MHz, THF- d_8): δ = 7.15 (d, $^3J_{\text{HH}} = 7.5$ Hz, 4H, H-4), 7.08 (dd, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, 4H, H-5), 7.01 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H, H-6), 6.90 (m, 2H, H-8), 6.82 (m, 2H, H-9), 5.25 (q, $^3J_{\text{HH}} = 7.8$ Hz, 2H, H-2), 1.85 (d, $^3J_{\text{HH}} = 7.8$ Hz, 6H, H-1). ^{13}C NMR (50.3 MHz, THF- d_8): δ = 145.6 (C-3), 143.0 (C-7), 128.9 (C-5), 127.3 (C-6), 126.2 (C-4), 119.0 (C-9), 111.4 (C-8), 57.7 (C-2), 27.6 (C-1). MS (EI, 70 eV): m/z = 388 (100%, $[\text{M}]^+$).



Stannylene *R,R*-5: A tetrahydrofuran solution (10 mL) of diamine *R,R*-**3** (50 mg, 0.16 mmol) was treated with $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (70 mg, 0.16 mmol) as described for the preparation of **2**. The reaction mixture was heated for 24 h at 70

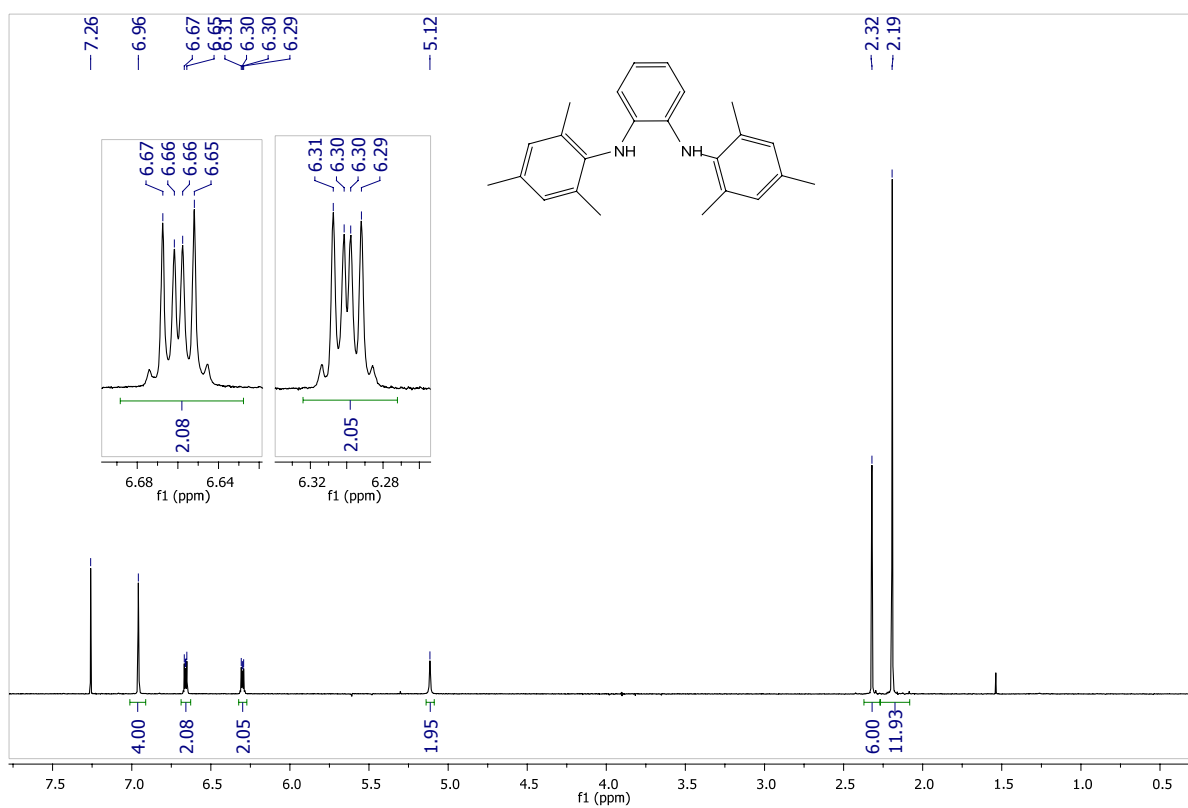
°C in an oil bath. After cooling to ambient temperature the solvent was removed *in vacuo* and the solid residue was taken up in *n*-hexane. Filtration of the suspension gave *R,R*-**5** as yellow solid. Yield: 51 mg, 73%. Yellow crystals of *R,R*-**5** were obtained by cooling of a THF solution of the compound under argon to 0 °C for 2 weeks. ^1H NMR (200 MHz, THF- d_8): δ = 7.38-7.35 (m, 4H, H-4), 7.35-7.13 (m, 4H, H-5), 7.15 (d, $^3J_{\text{HH}} = 6.9$ Hz, 2H, H-6), 6.41 (m,

2H, H-8), 6.36 (m, 2H, H-9), 5.40 (m, 2H, H-2), 1.91 (d, $^3J_{\text{HH}} = 5.9$ Hz, 6H, H-1). ^{13}C NMR (50.3 MHz, THF- d_8): $\delta = 147.0$ (C-3), 146.2 (C-7), 138.6 (C-5), 137.0 (C-6), 119.0 (C-4), 117.3 (C-9), 113.9 (C-8), 58.3 (C-2), 26.2 (C-1). ^{119}Sn NMR (149.2 MHz, THF- d_8): $\delta = 167.8$ (br). ^{119}Sn NMR (149.2 MHz, C_6D_6): $\delta = 250.4$. MS (EI, 70 eV): $m/z = 434$ (40%, $[\text{M}]^+$).

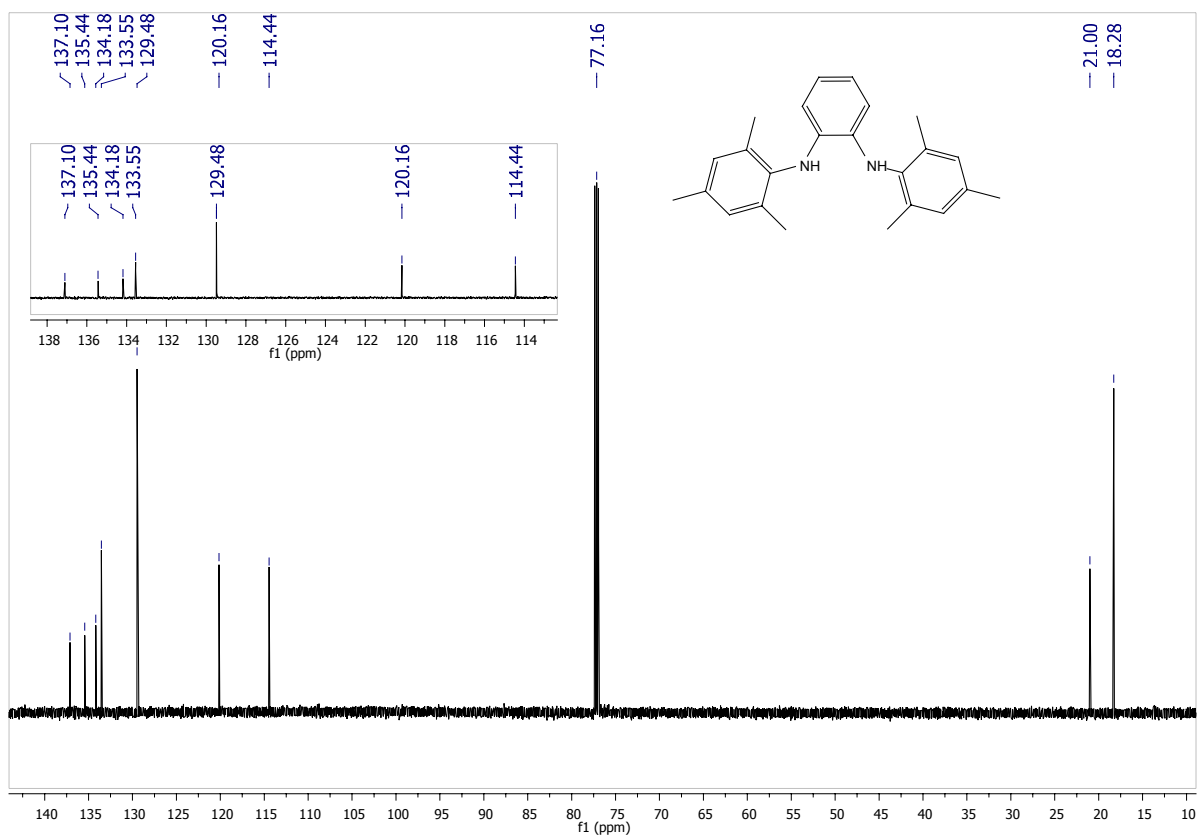
X-Ray diffraction studies: All diffraction data were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART program package.³ Structure solutions were found with the SHELXS-97⁴ package using the heavy-atom method and were refined with SHELXL-97⁵ against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

References:

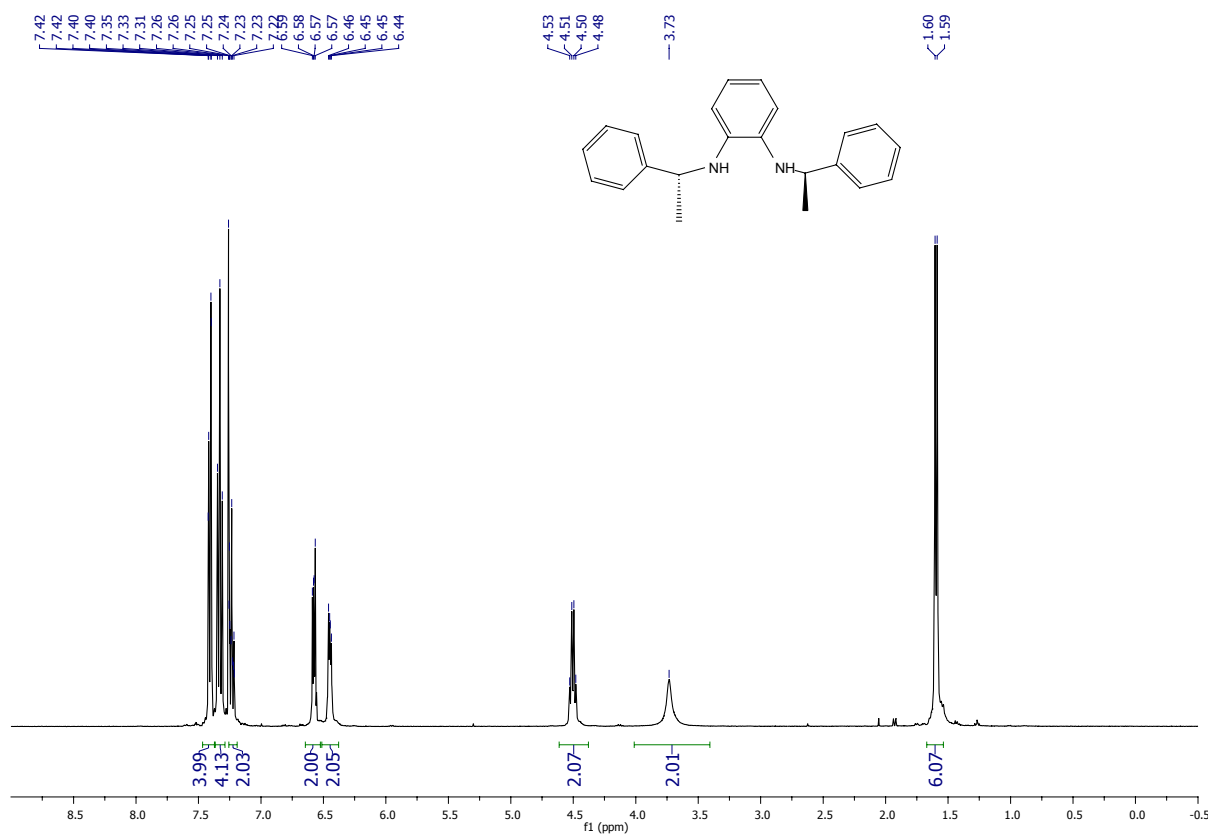
- 1 (a) J. M. Berlin, K. Campbell, T. Ritter, T. W. Funk, A. Chlenov and R. H. Grubbs, *Org. Lett.*, 2007, **9**, 1339–1342; (b) H. Sakurai, K. Sugitani, T. Moriuchi and T. Hirao, *J. Organomet. Chem.*, 2005, **690**, 1750–1755.
- 2 F. M. Rivas, U. Riaz and S. T. Diver, *Tetrahedron Asymmetry*, 2000, **11**, 1703–1707.
- 3 *SMART*, Bruker AXS, 2000.
- 4 *SHELXS-97*, G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467–473.
- 5 *SHELXL-97*, G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.



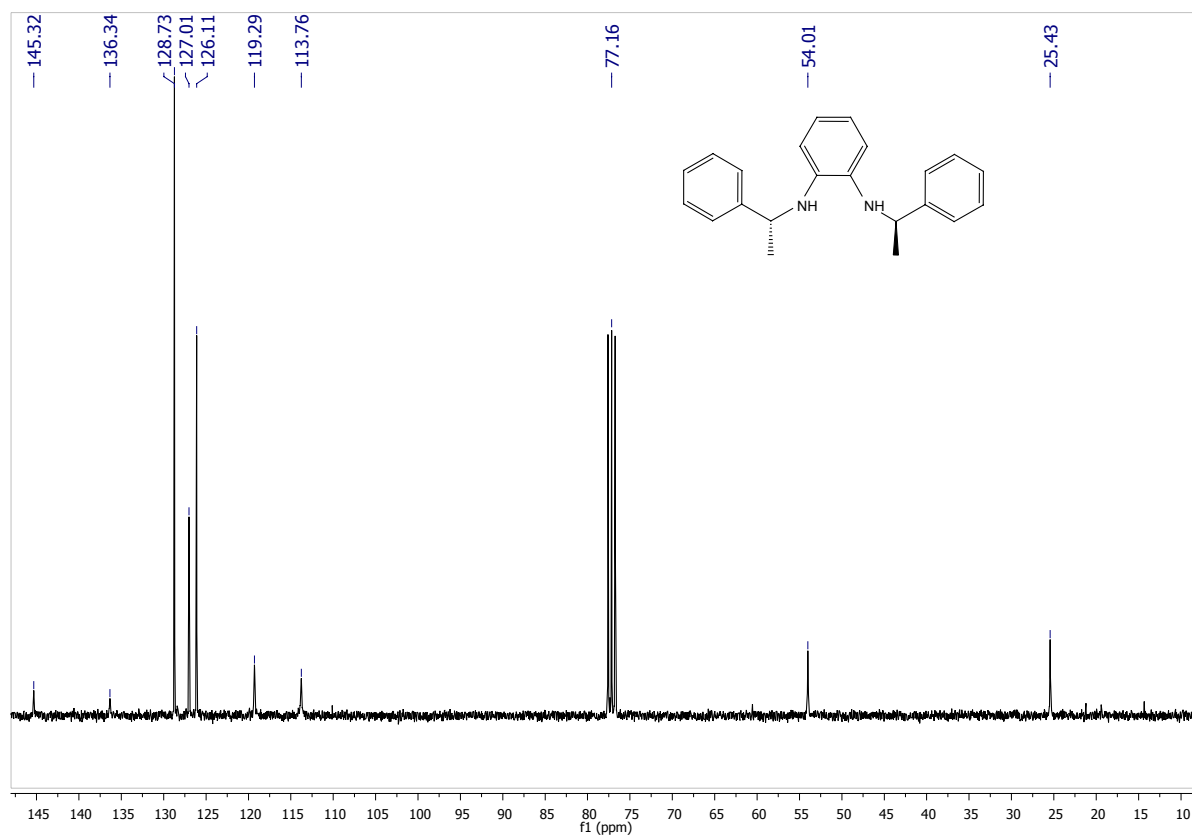
¹H NMR of Diamine 1



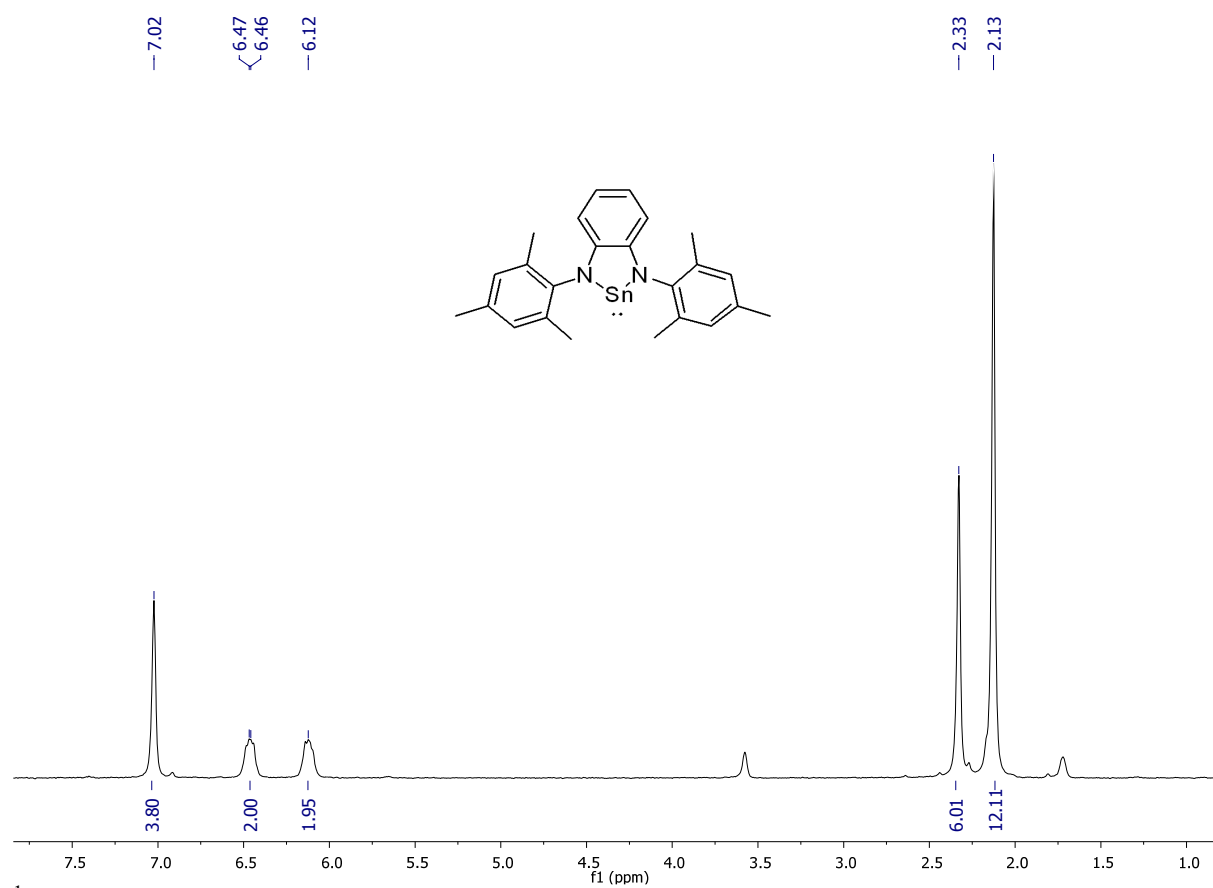
¹³C NMR of Diamine 1



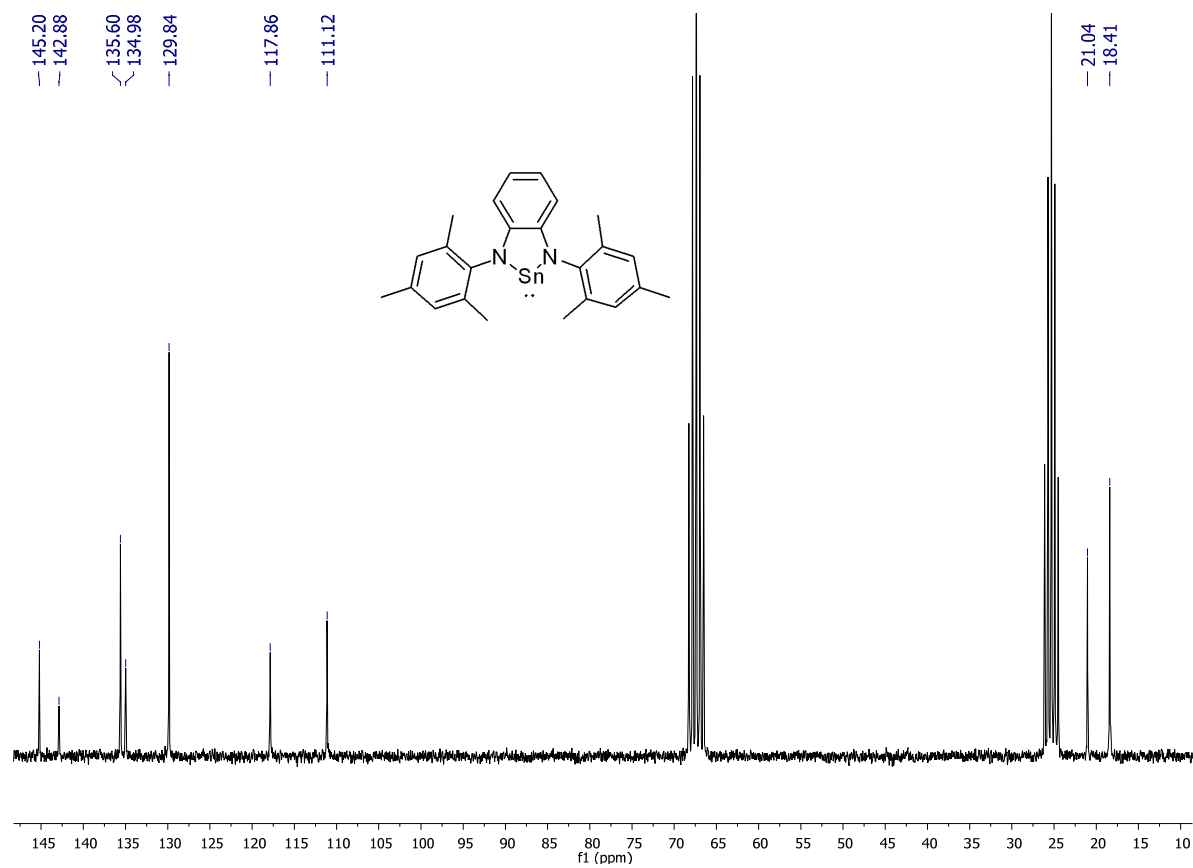
$^1\text{H NMR}$ of Diamine *R,R*-3



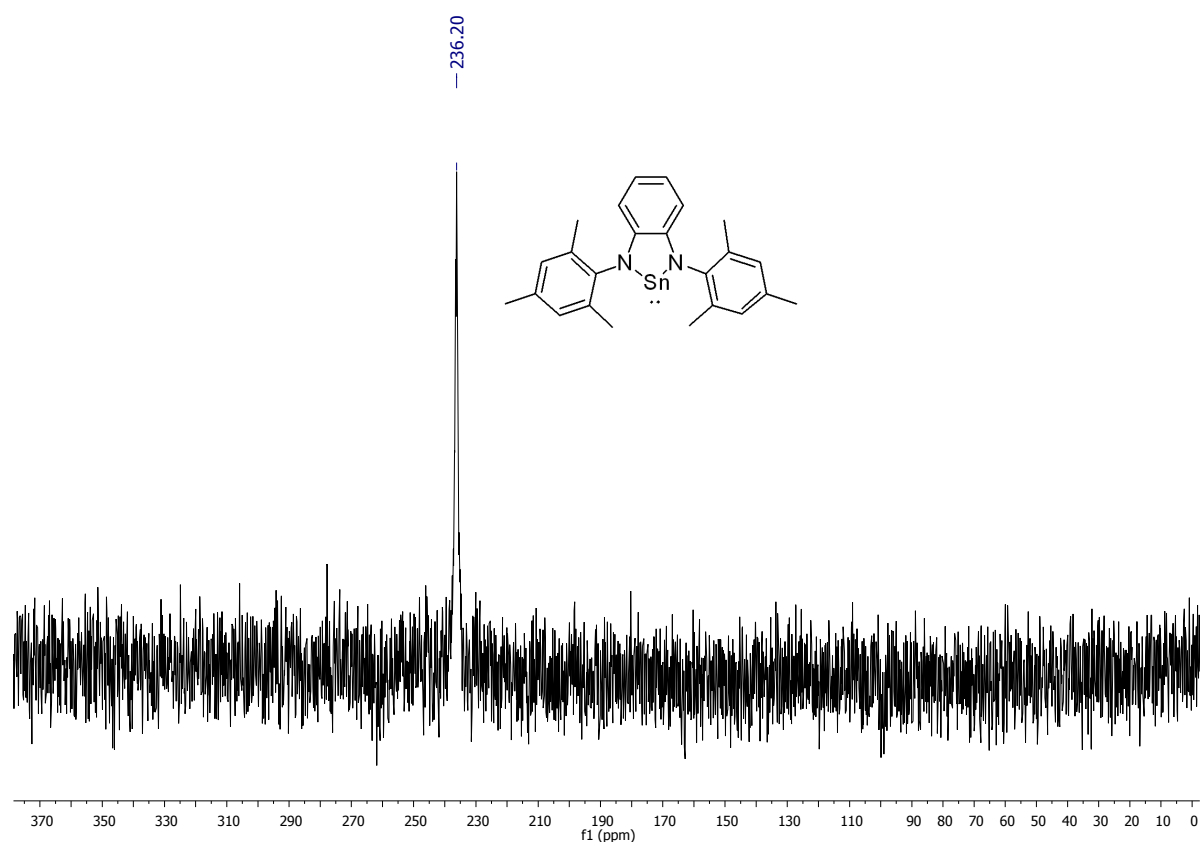
¹³C NMR of Diamine *R,R*-3



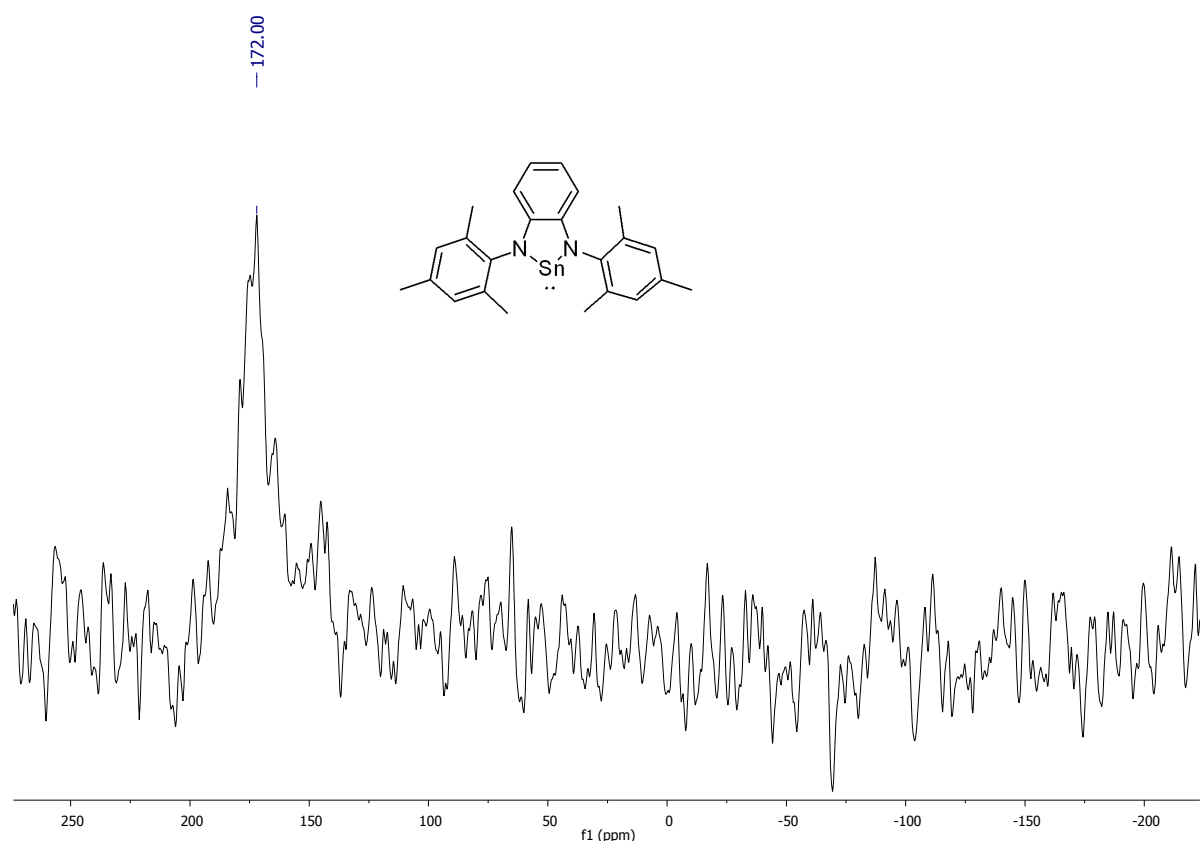
¹H NMR of Stannylene 2



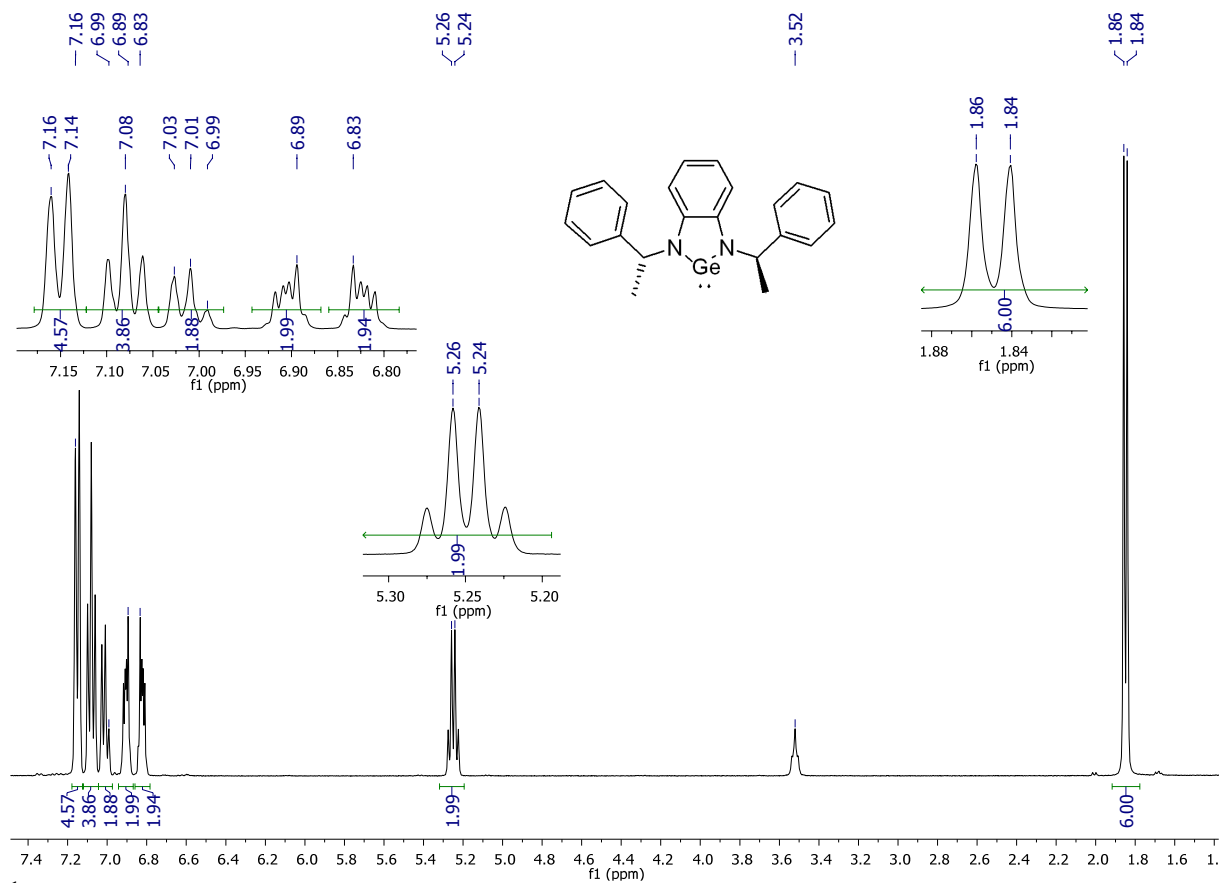
^{13}C NMR of Stannylene 2



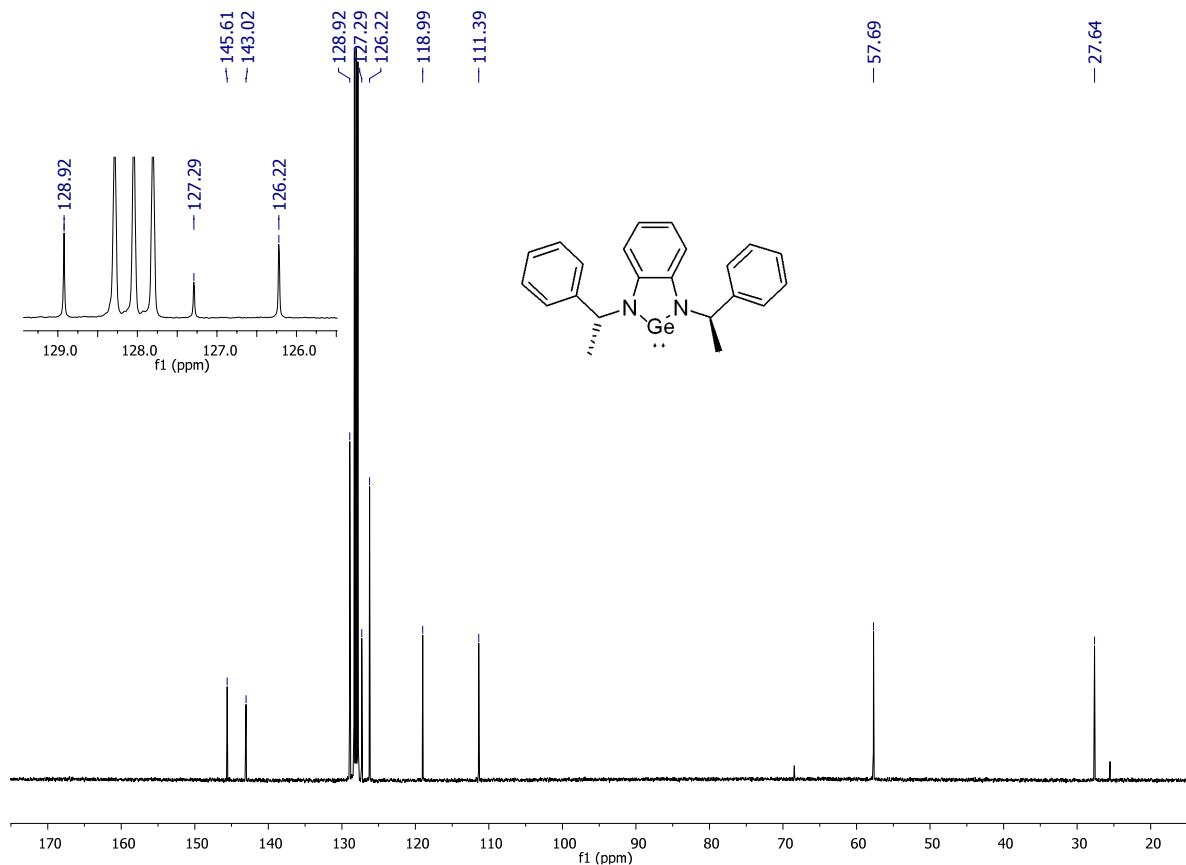
^{119}Sn NMR of Stannylene2 in C_6D_6 .



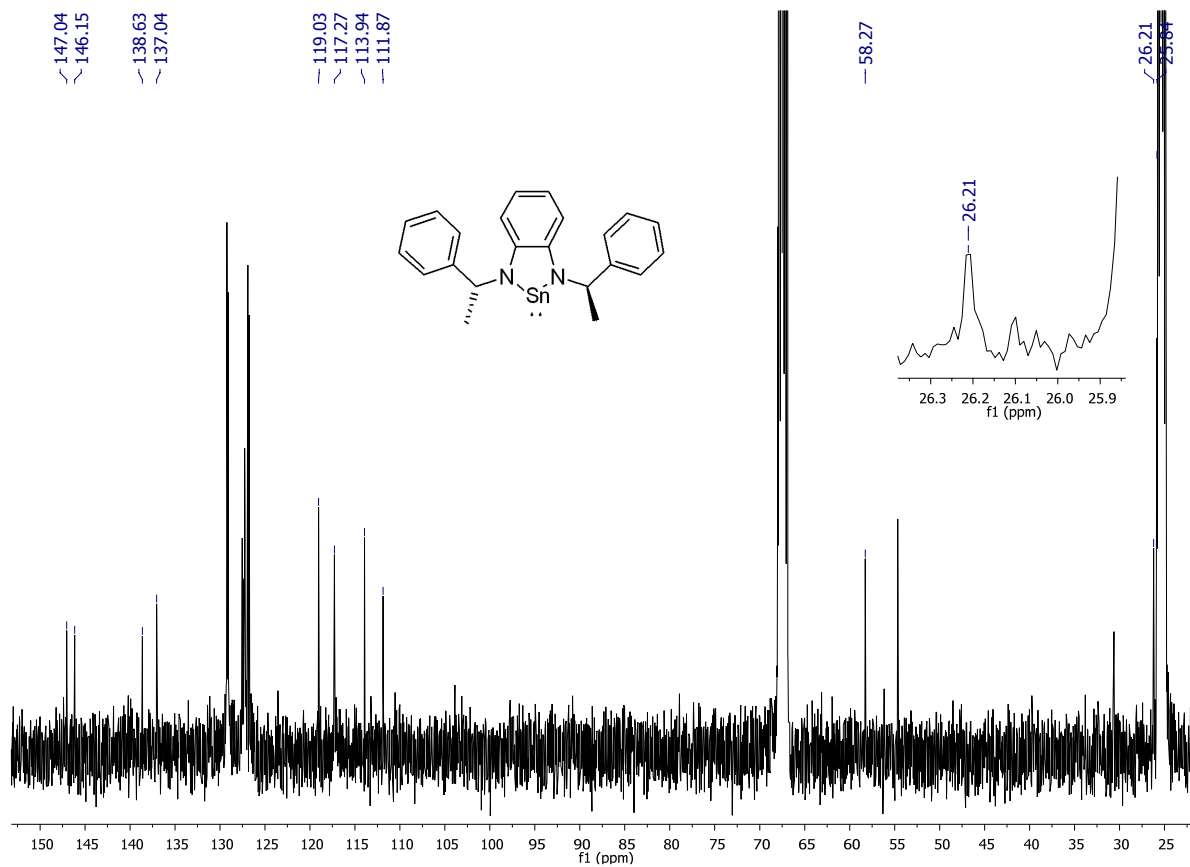
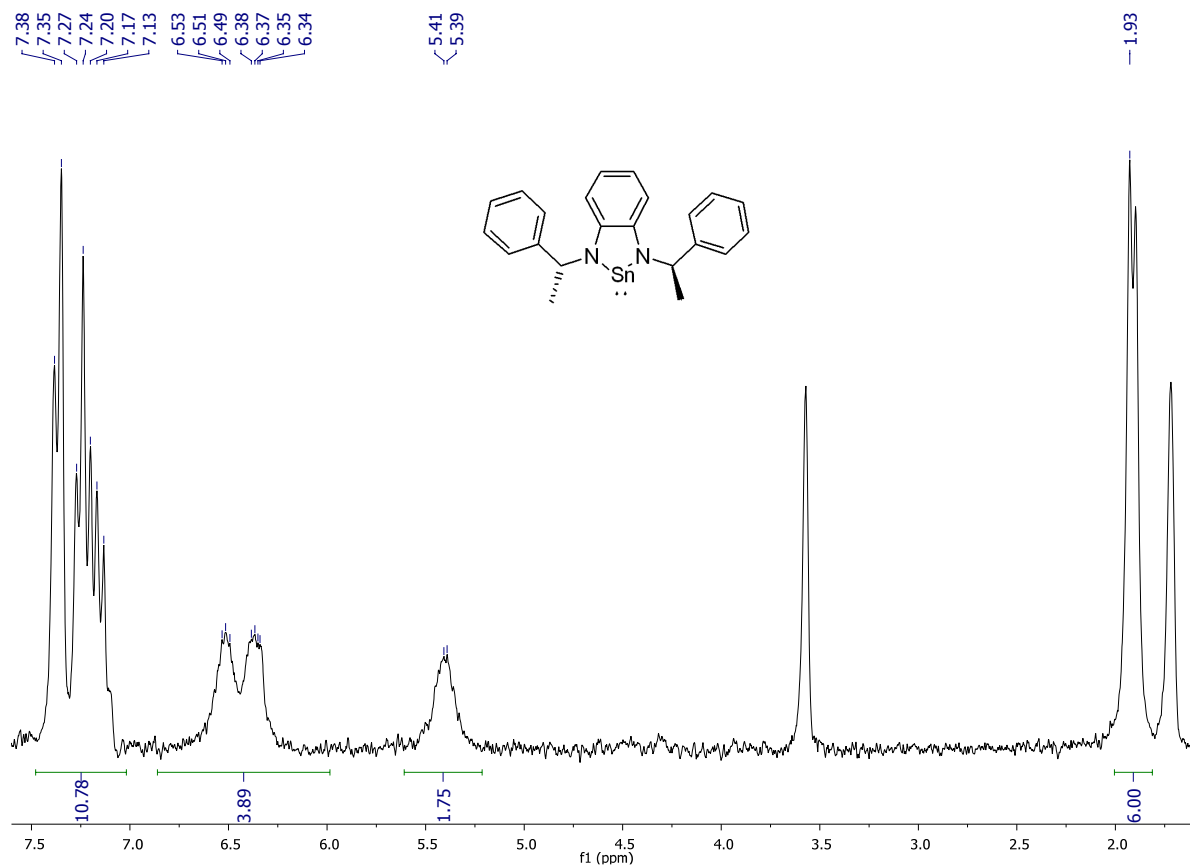
^{119}Sn NMR of Stannylene2 in $\text{THF-}d_8$.

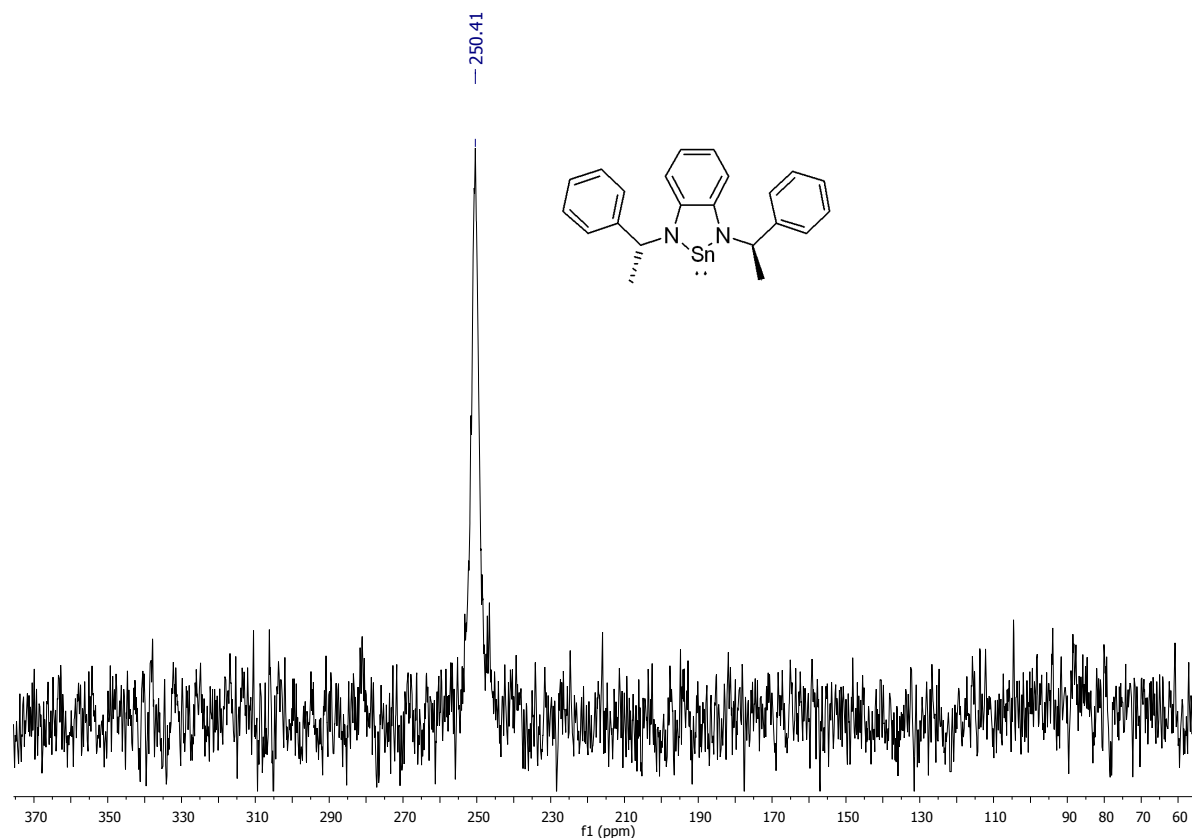


¹H NMR of Germylene *R,R*-4.

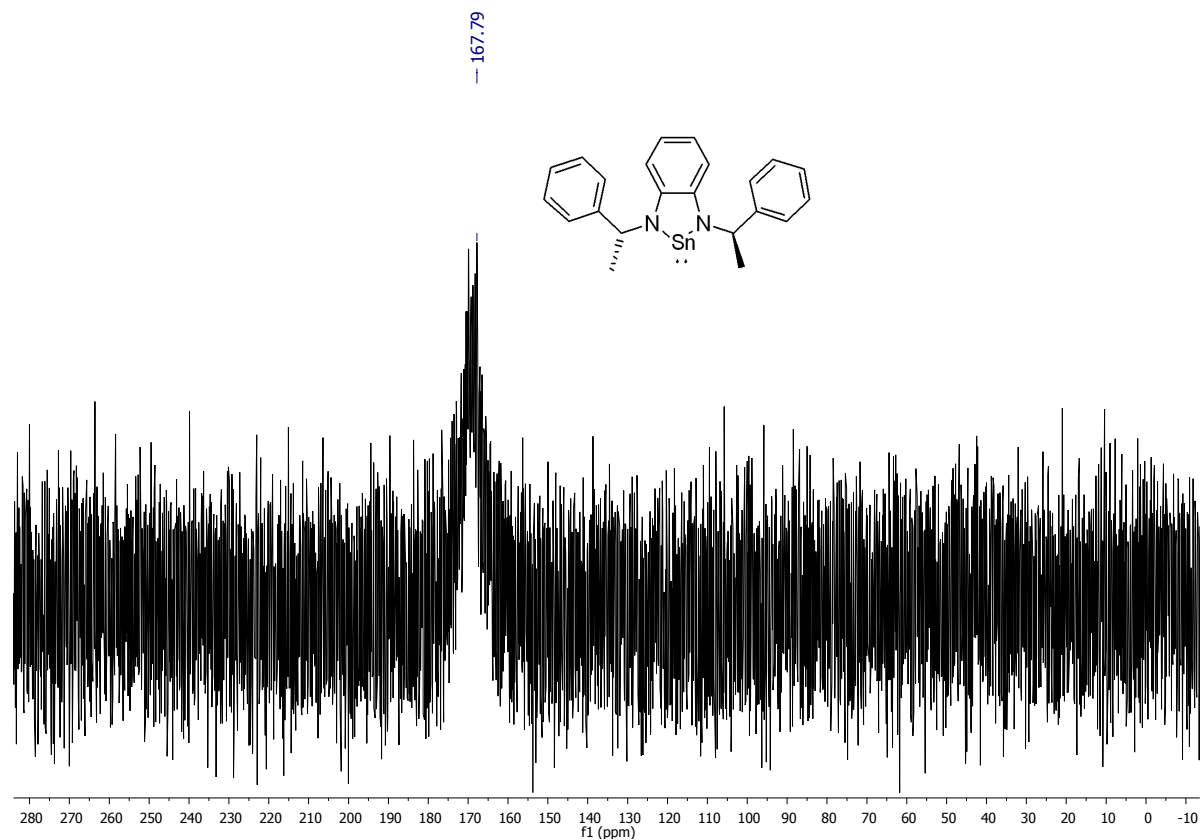


¹³C NMR of Germylene *R,R*-4.





^{119}Sn NMR of Stannylene *R,R*-5 in C_6D_6 .



^{119}Sn NMR of Stannylene *R,R*-5 in $\text{THF-}d_8$.