Hypercoordinating Stannanes with *C,N*-Donor Ligands: a Structural, DFT and Polymerization Study

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Supplementary Information

Appendix S:

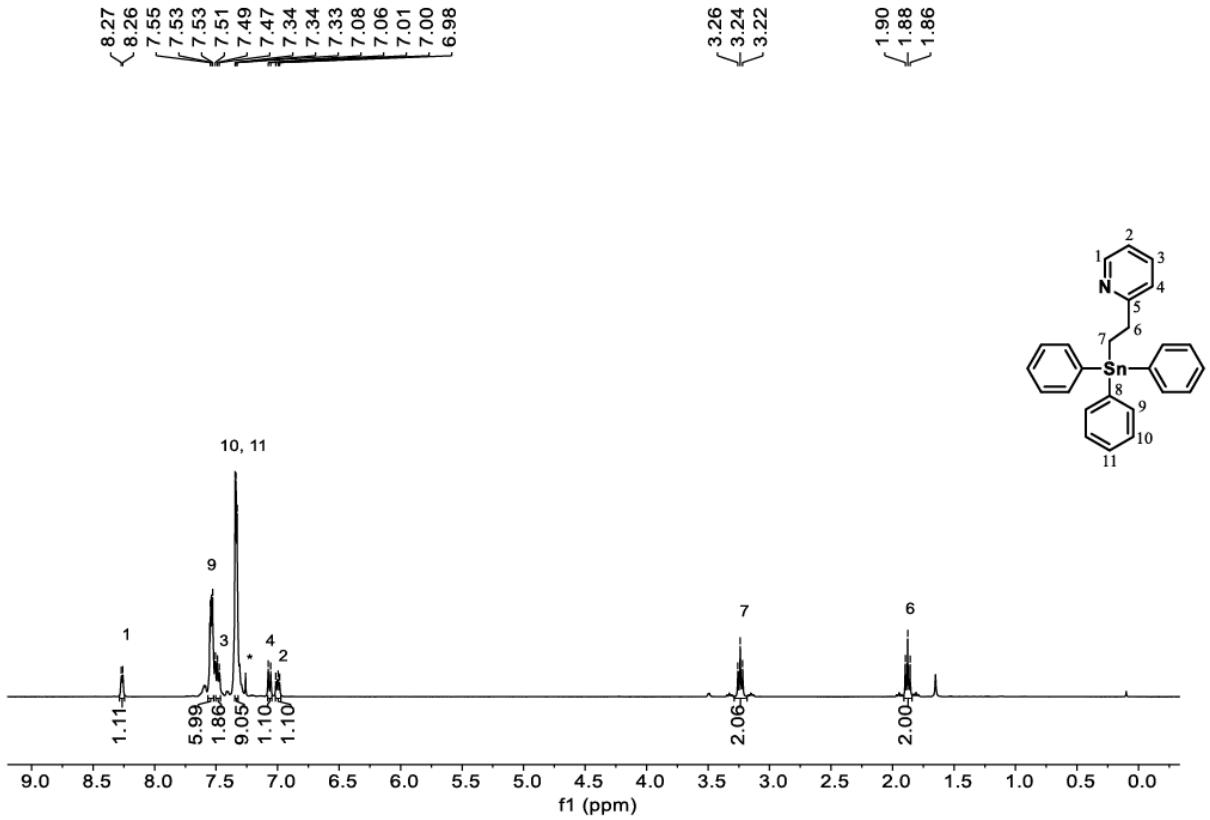


Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

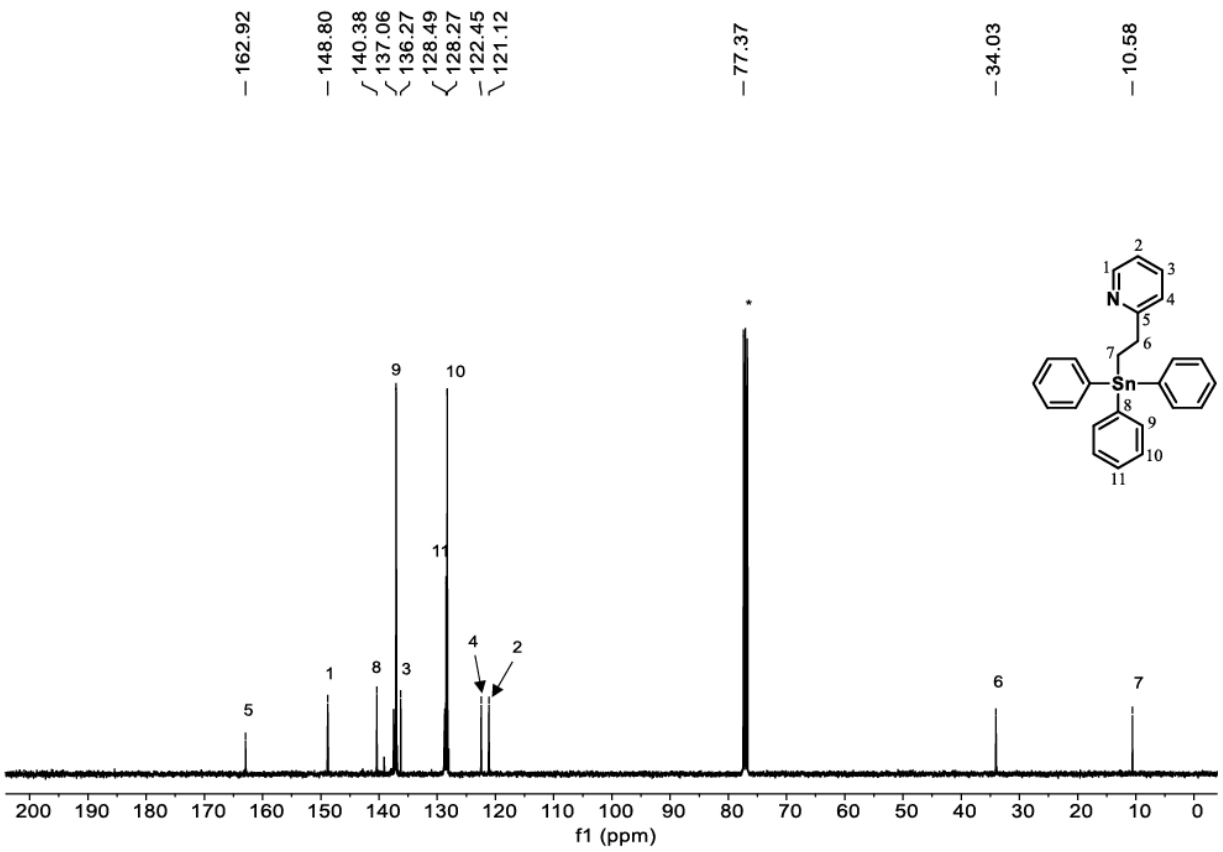


Figure S2. ^{13}C NMR spectrum of **2** in $CDCl_3$.

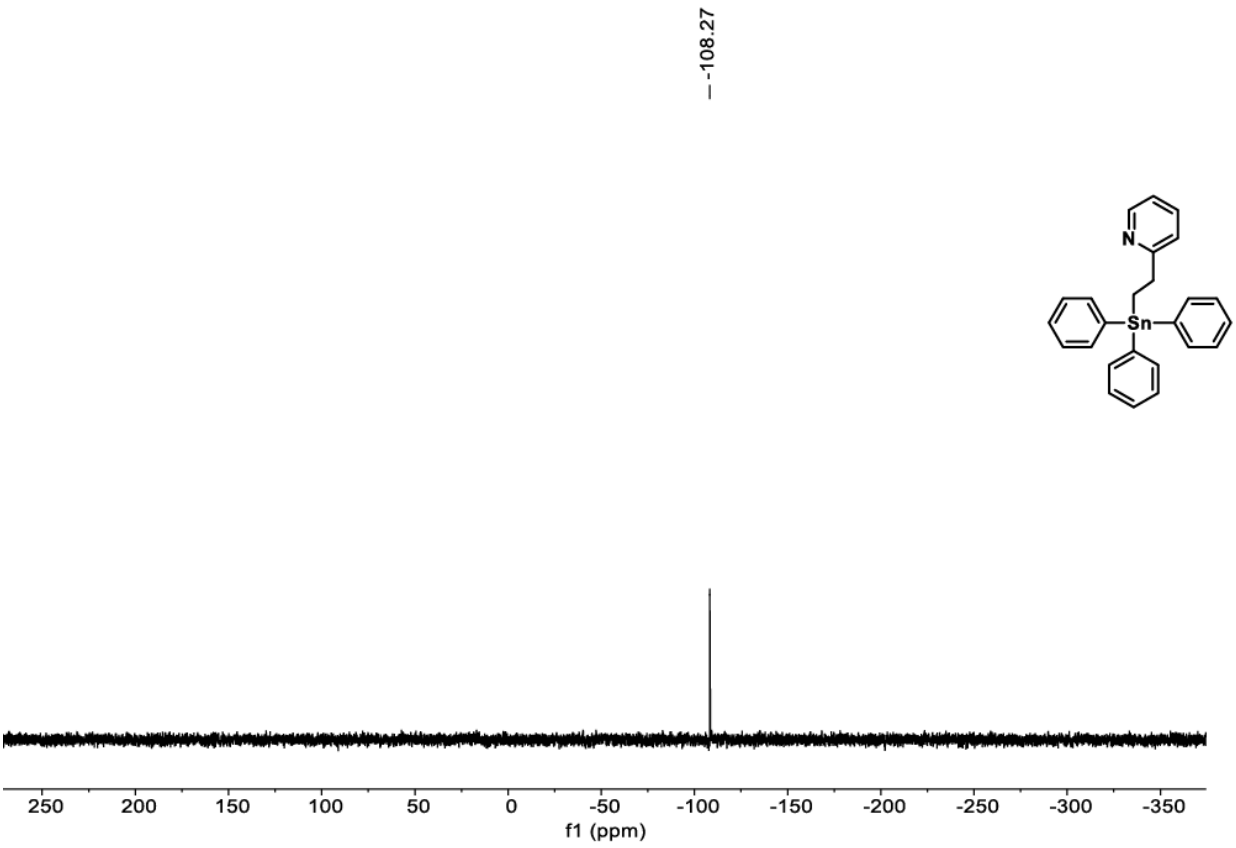


Figure S3. ^{119}Sn NMR spectrum of **2** in $CDCl_3$.

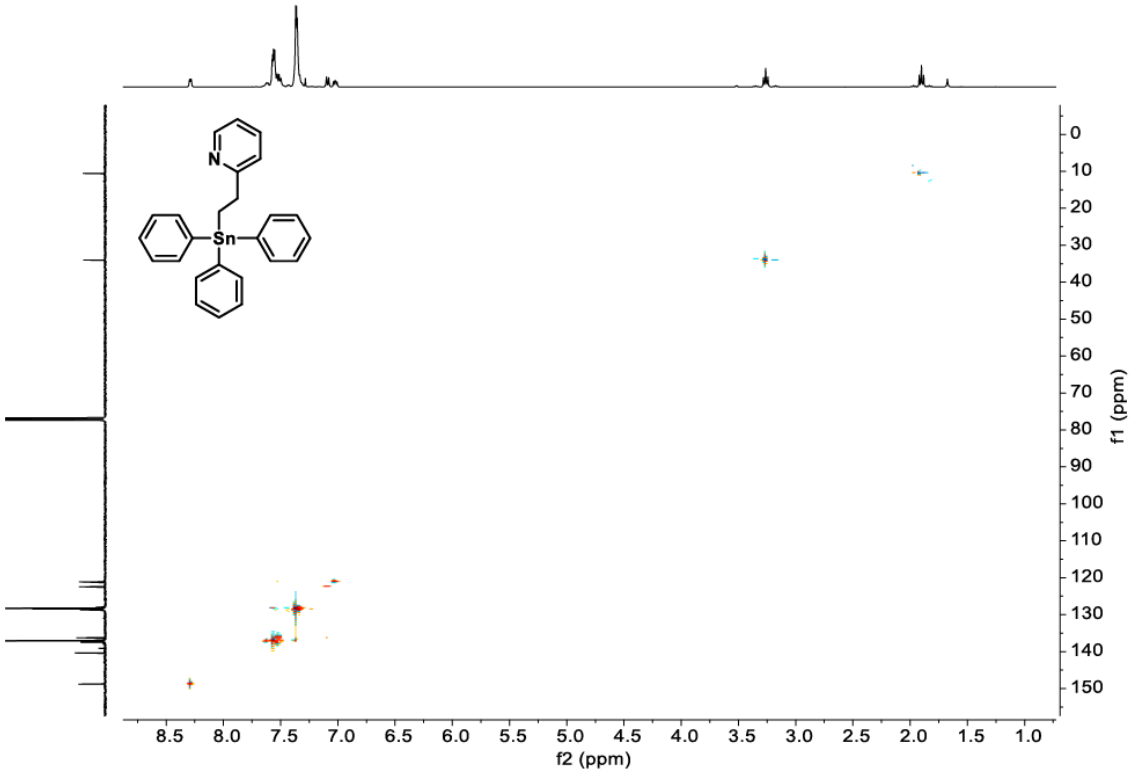


Figure S4. HSQC NMR spectrum of **2** in $CDCl_3$.

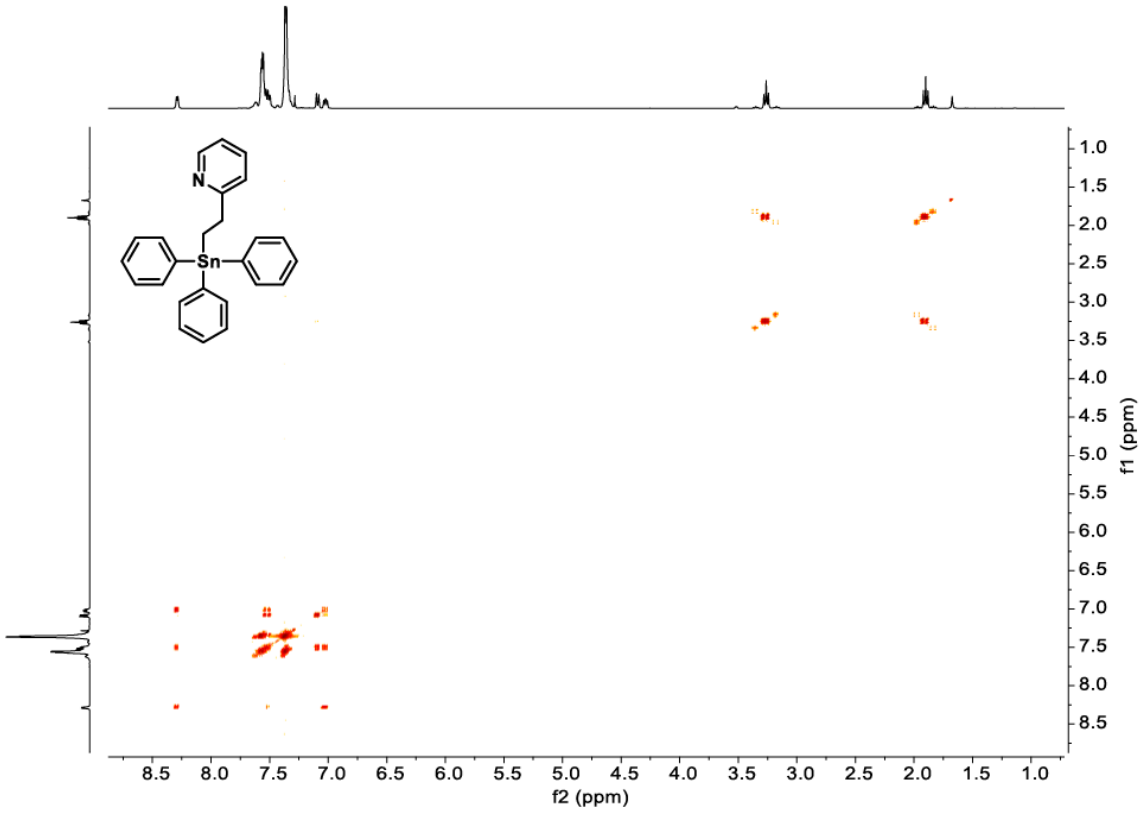


Figure S5. COSY NMR spectrum of **2** in $CDCl_3$.

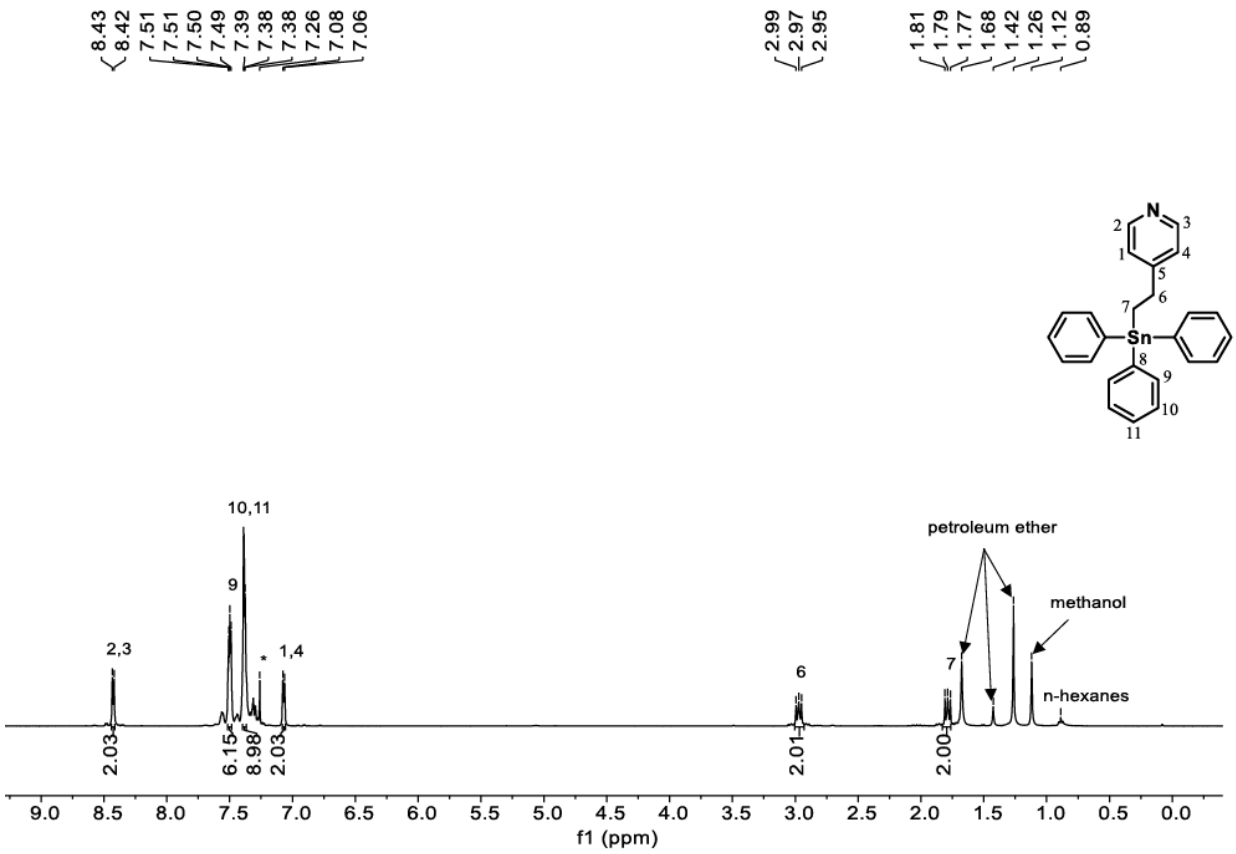


Figure S6. ^{1}H NMR spectrum of **3** in $CDCl_3$.

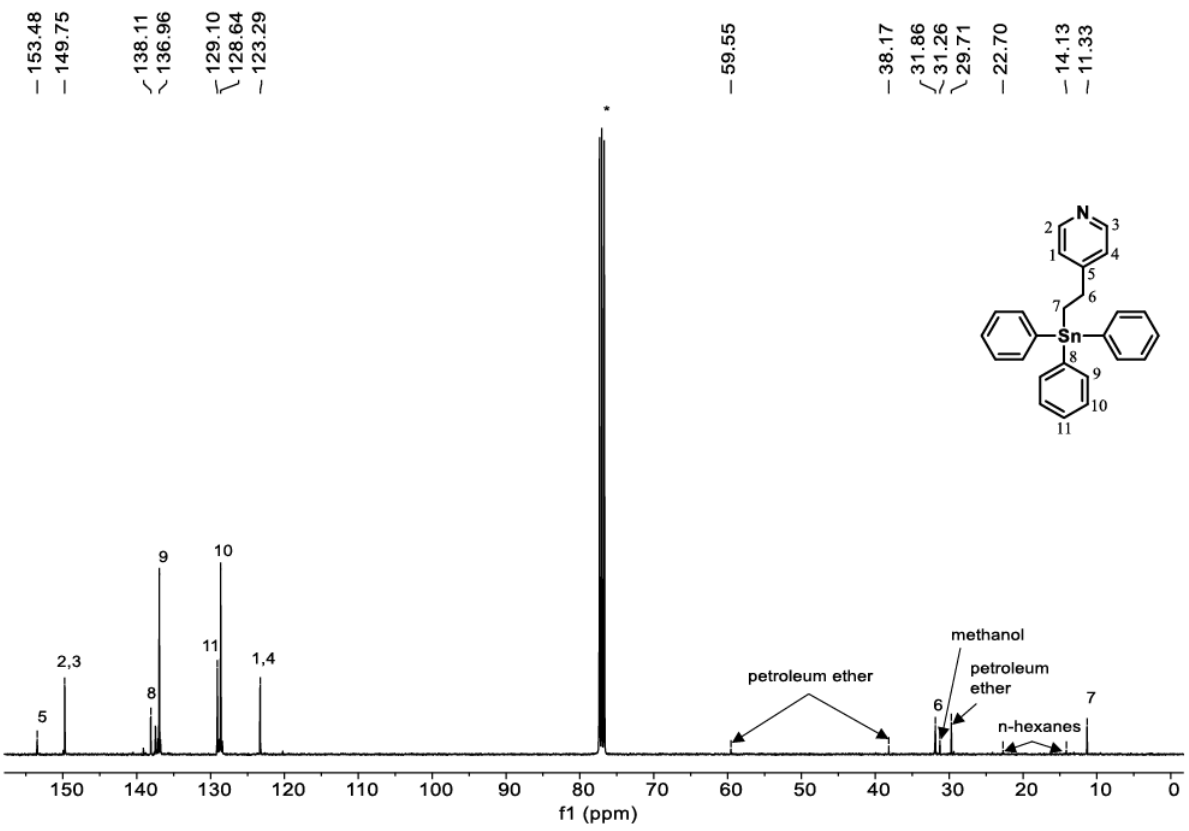


Figure S7. ^{13}C NMR spectrum of **3** in $CDCl_3$.

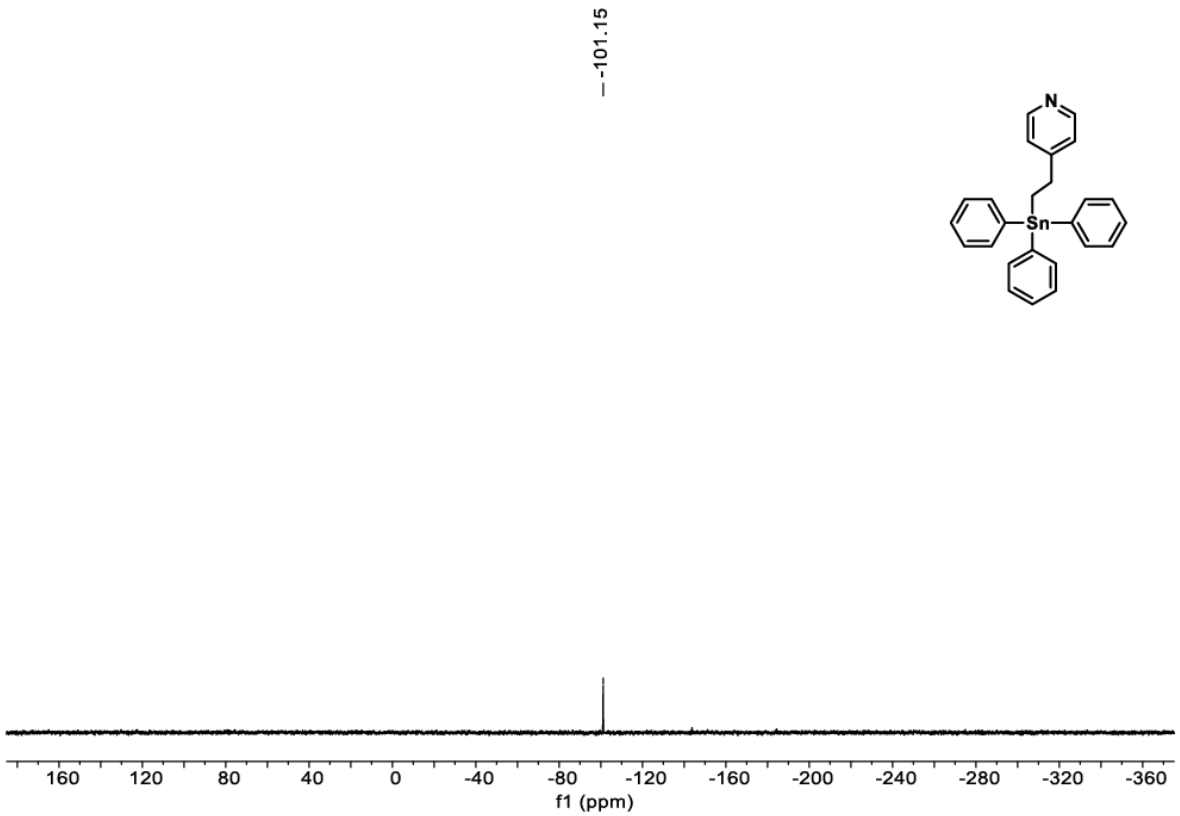


Figure S8. ^{119}Sn NMR spectrum of **3** in $CDCl_3$.

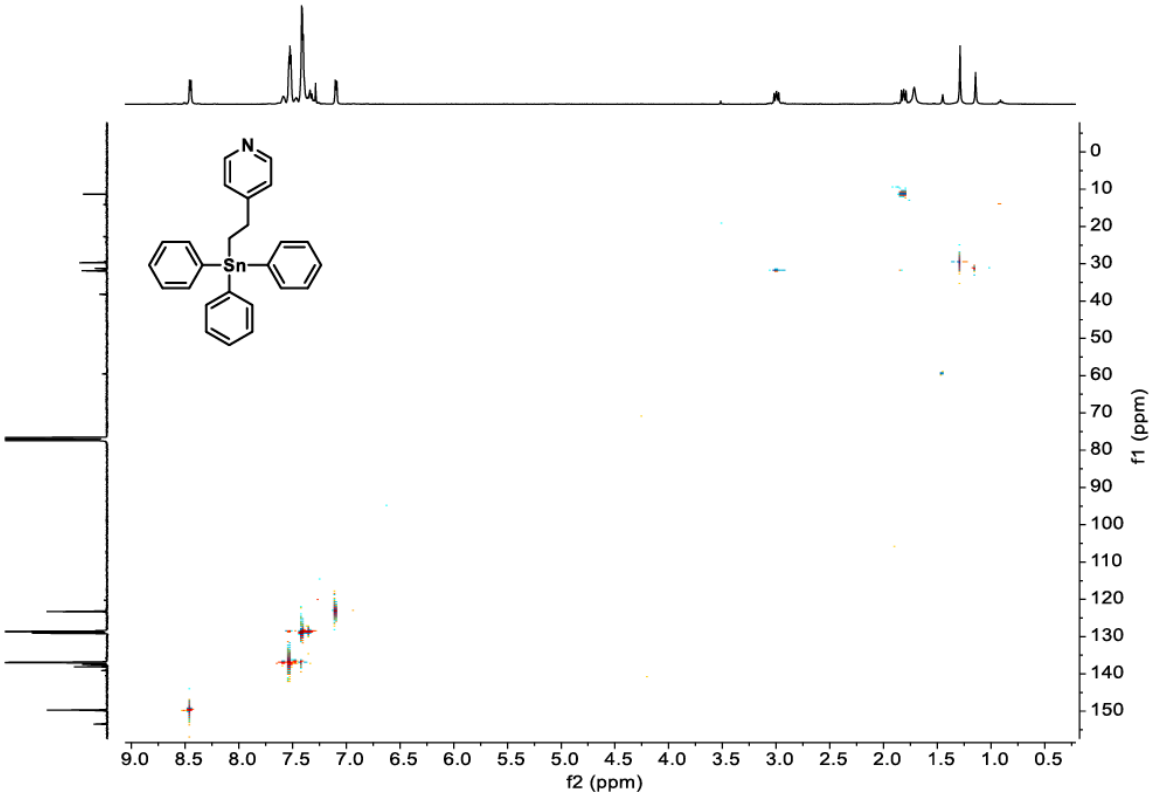


Figure S9. HSQC NMR spectrum of **3** in $CDCl_3$

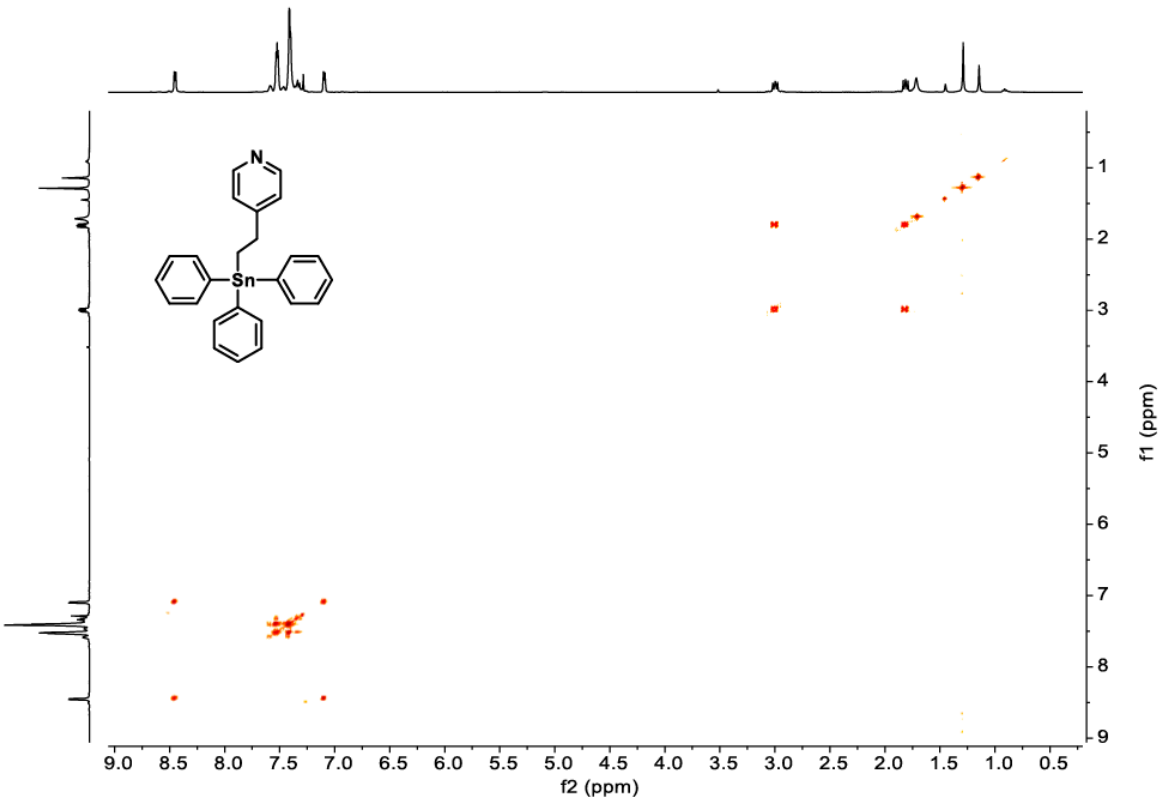


Figure S10. COSY NMR spectrum of **3** in $CDCl_3$.

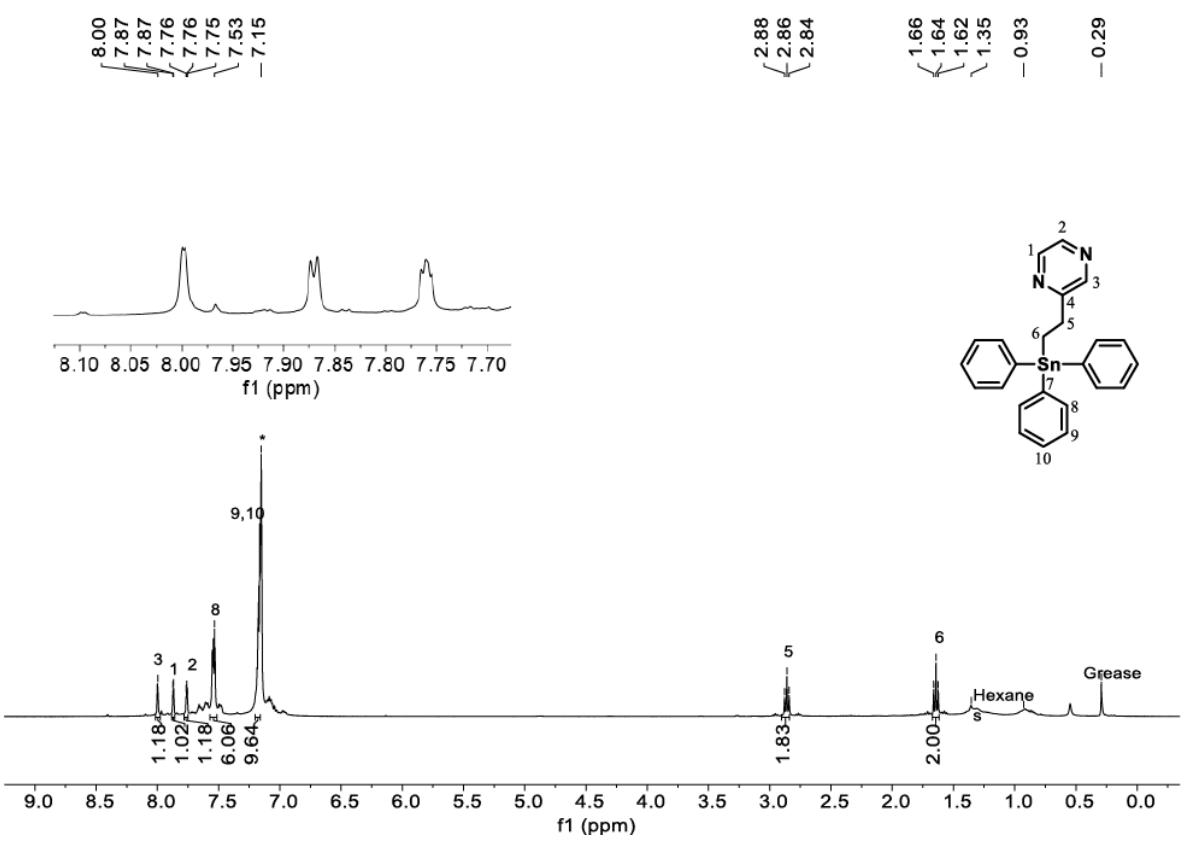


Figure S11. ^{1}H NMR spectrum of **4** in C_6D_6.

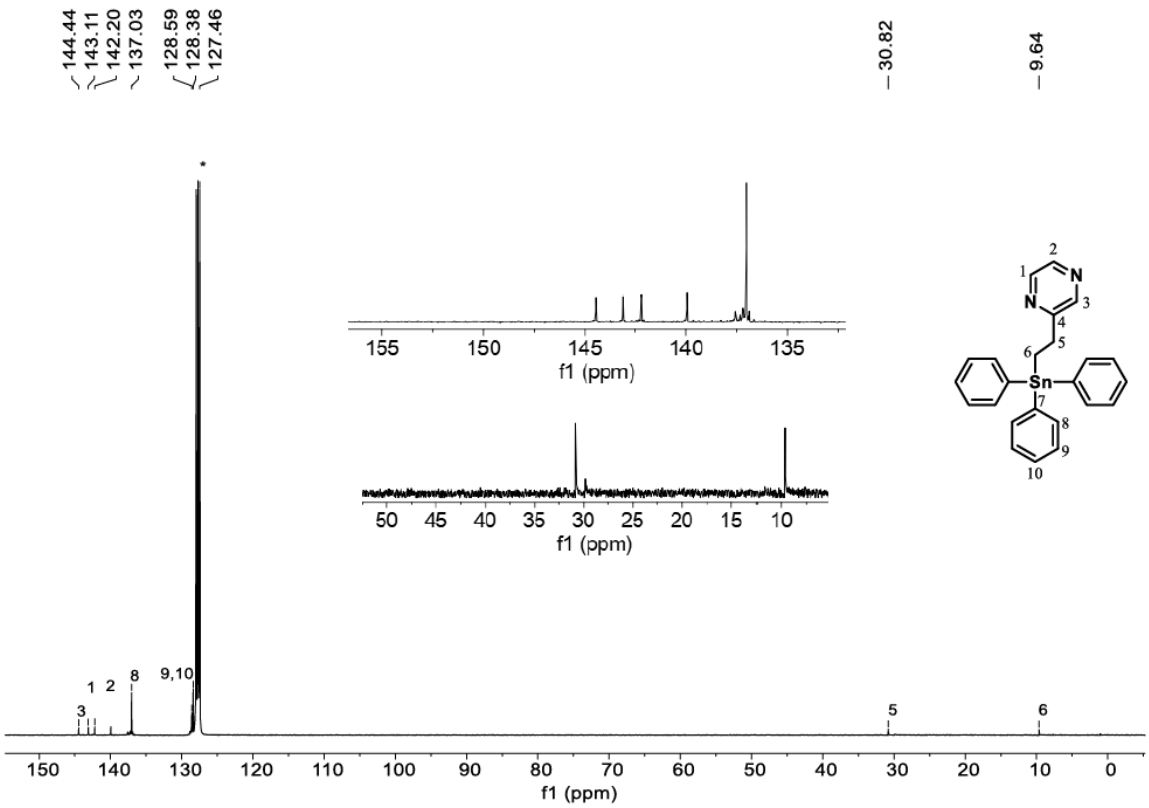


Figure S12. ^{13}C NMR spectrum of **4** in C_6D_6.

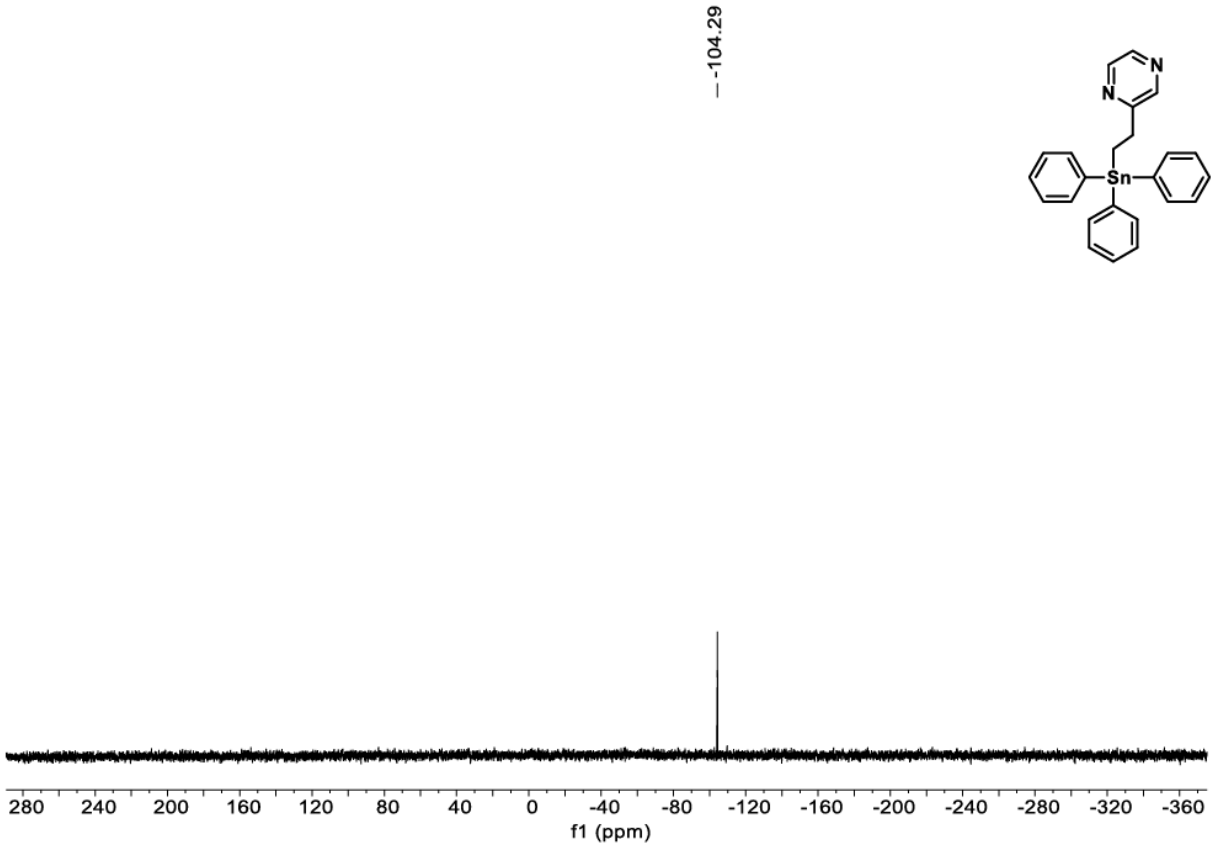


Figure S13. ^{119}Sn NMR spectrum of **4** in C_6D_6.

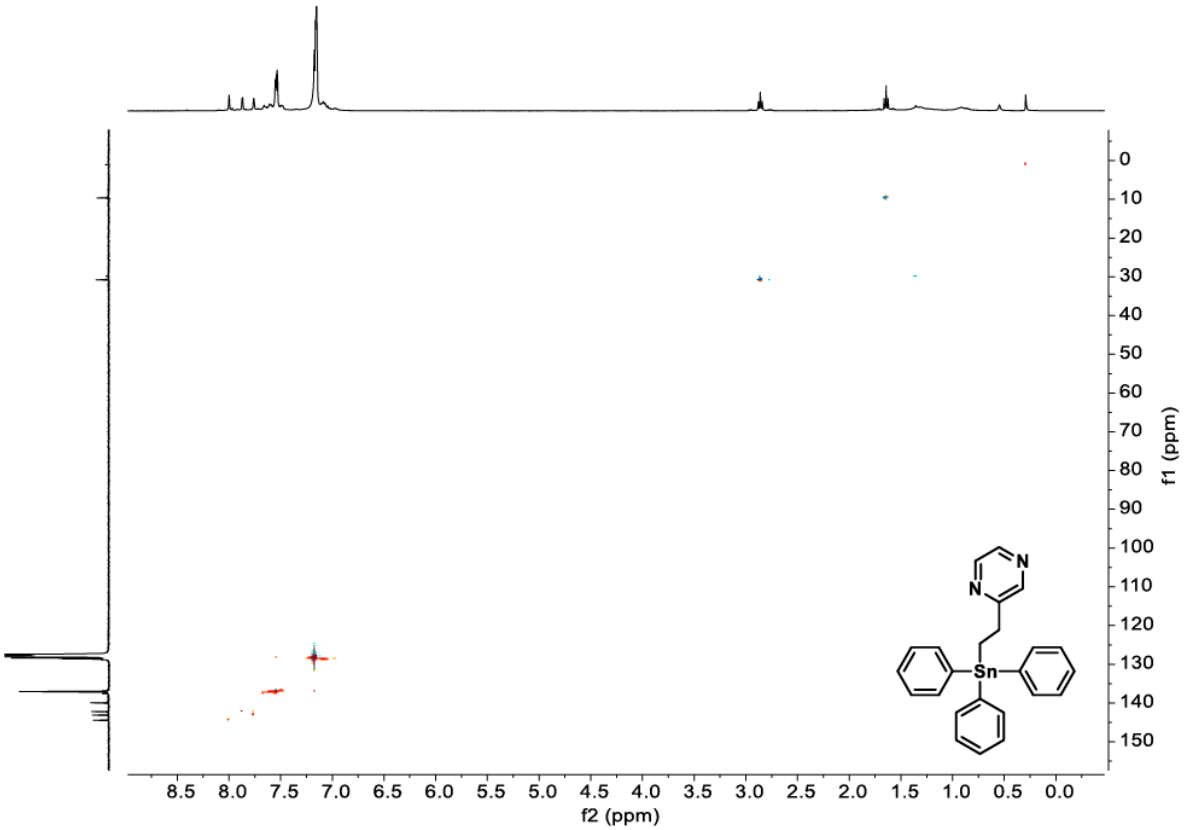


Figure S14. HSQC NMR spectrum of **4** in C_6D_6.

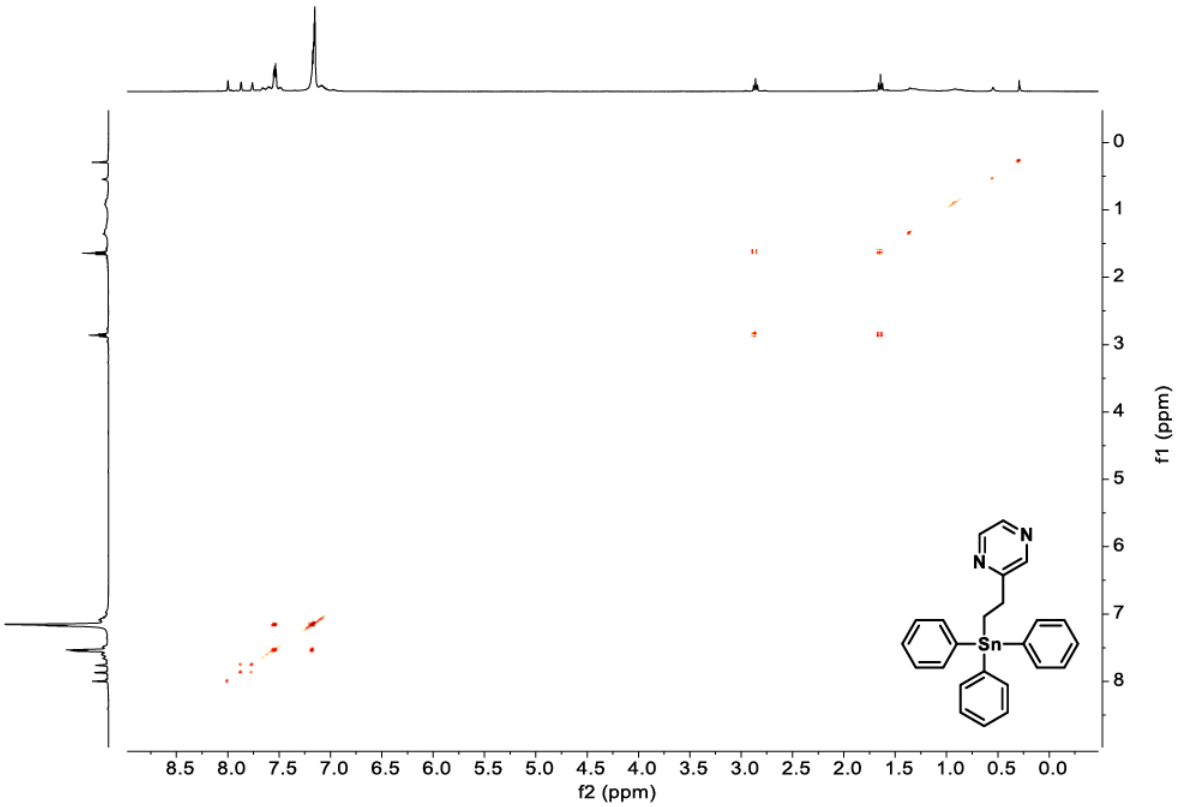


Figure S15. COSY NMR spectrum of **4** in C_6D_6.

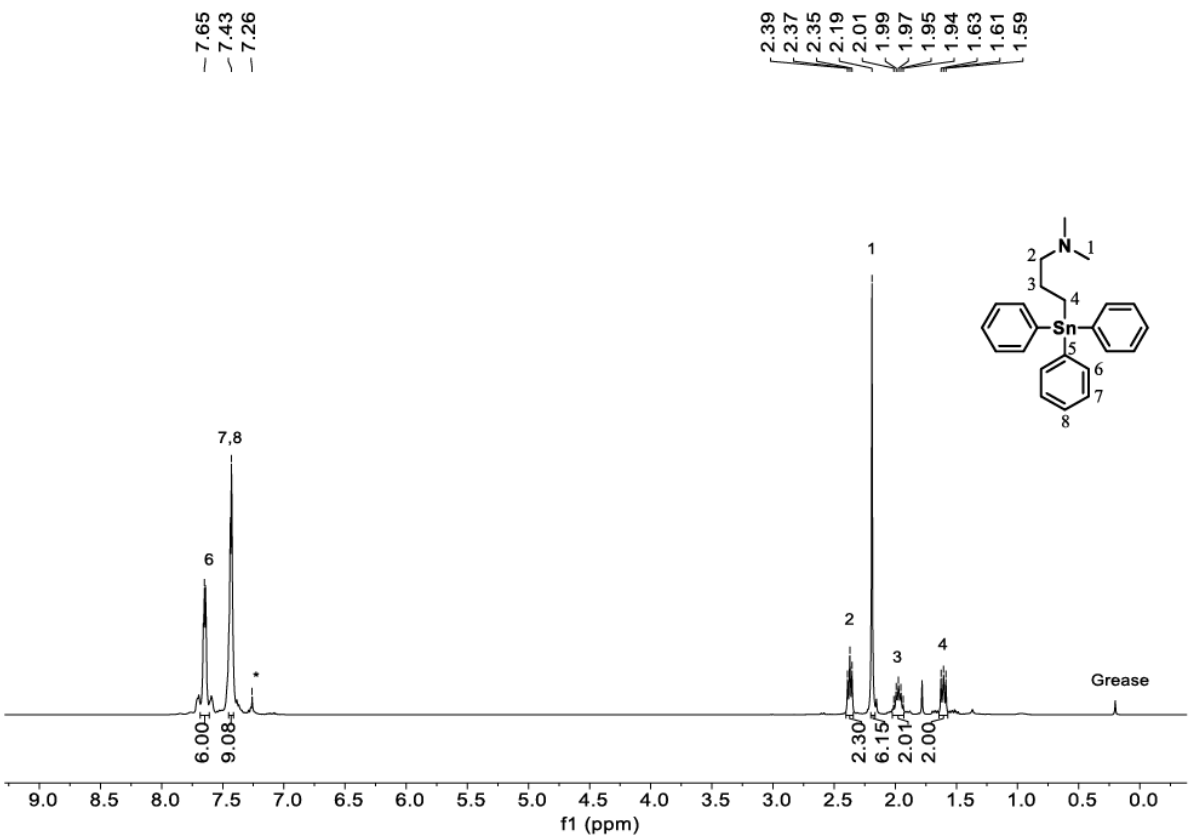


Figure S16. ^{1}H NMR spectrum of **6** in $CDCl_3$.

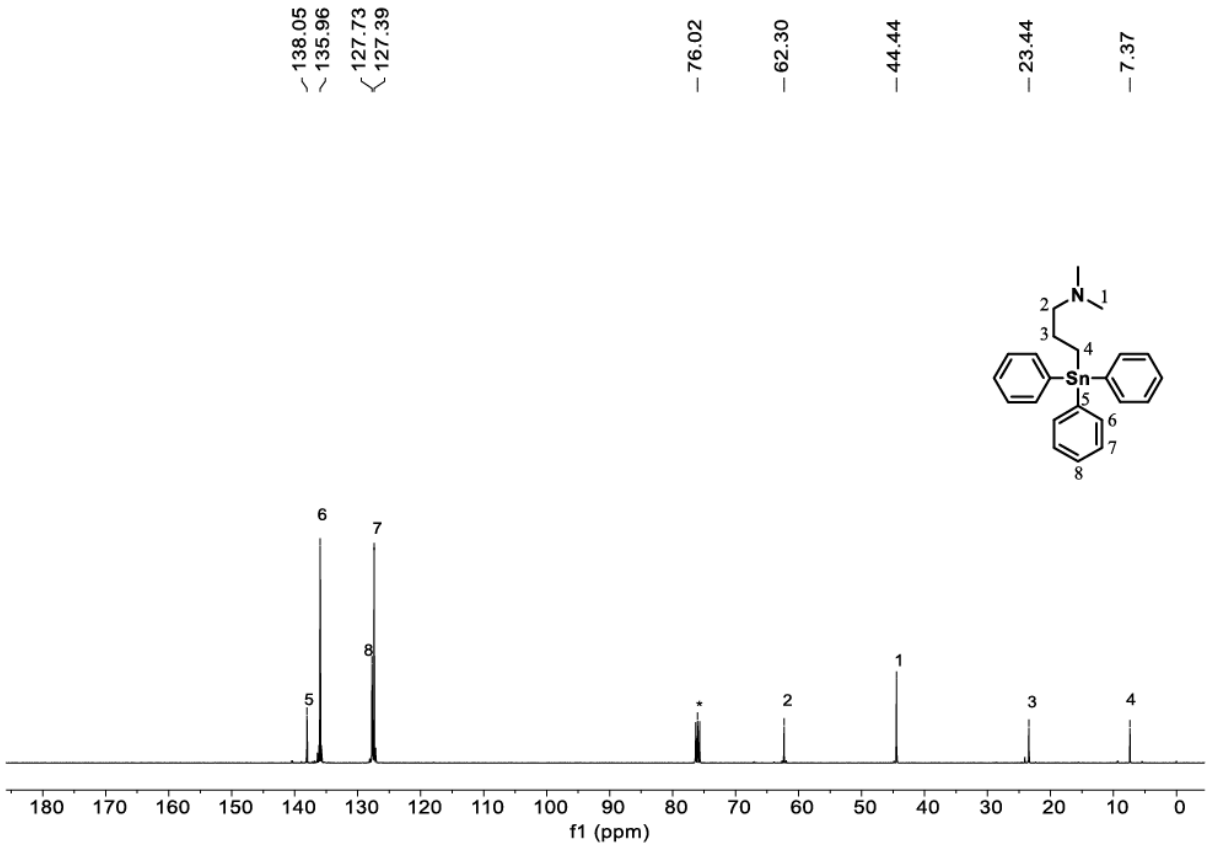


Figure S17. ^{13}C NMR spectrum of **6** in $CDCl_3$.

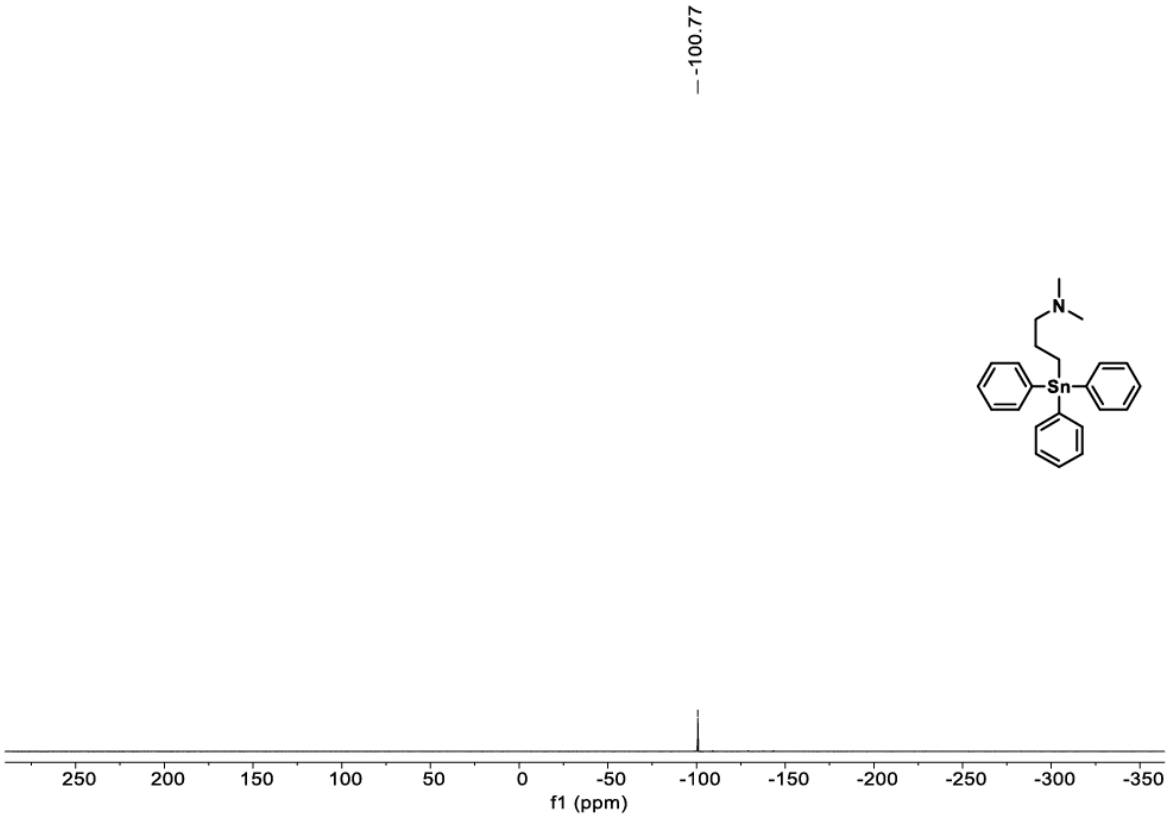


Figure S18. ^{119}Sn NMR spectrum of **6** in $CDCl_3$.

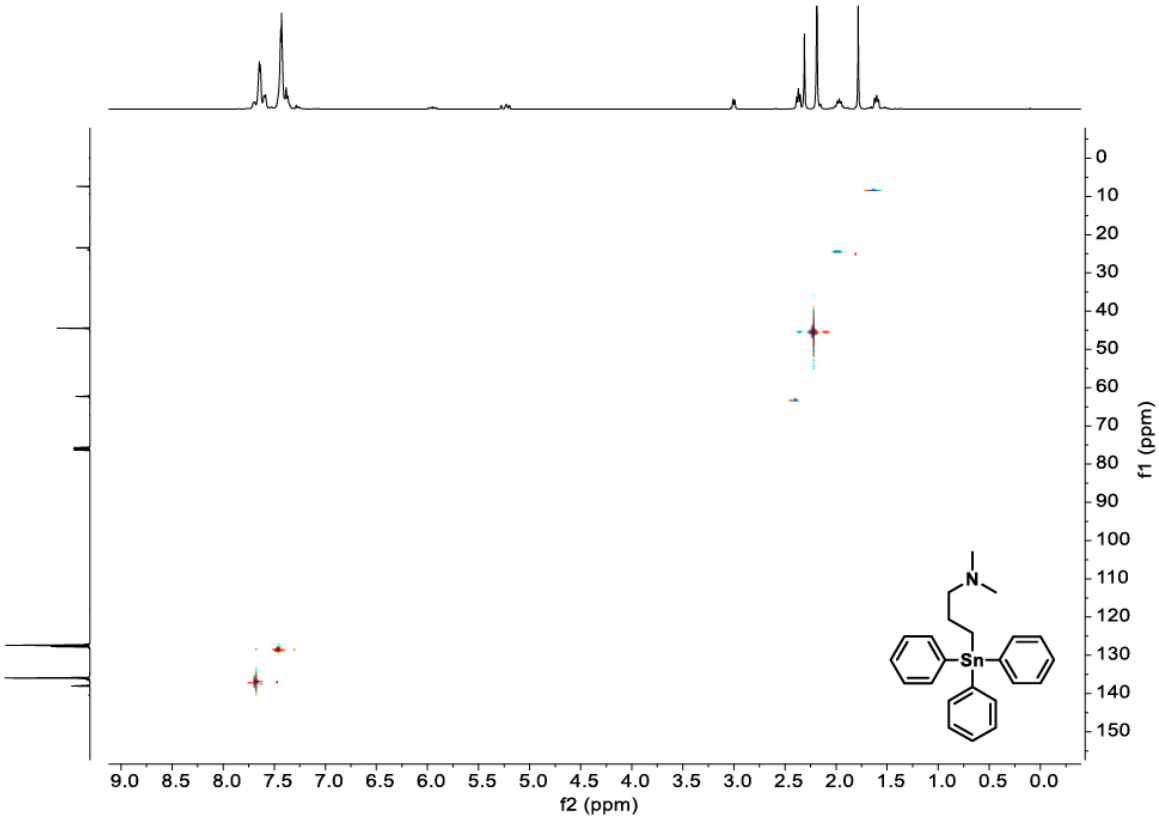


Figure S19. HSQC NMR spectrum of **6** in $CDCl_3$.

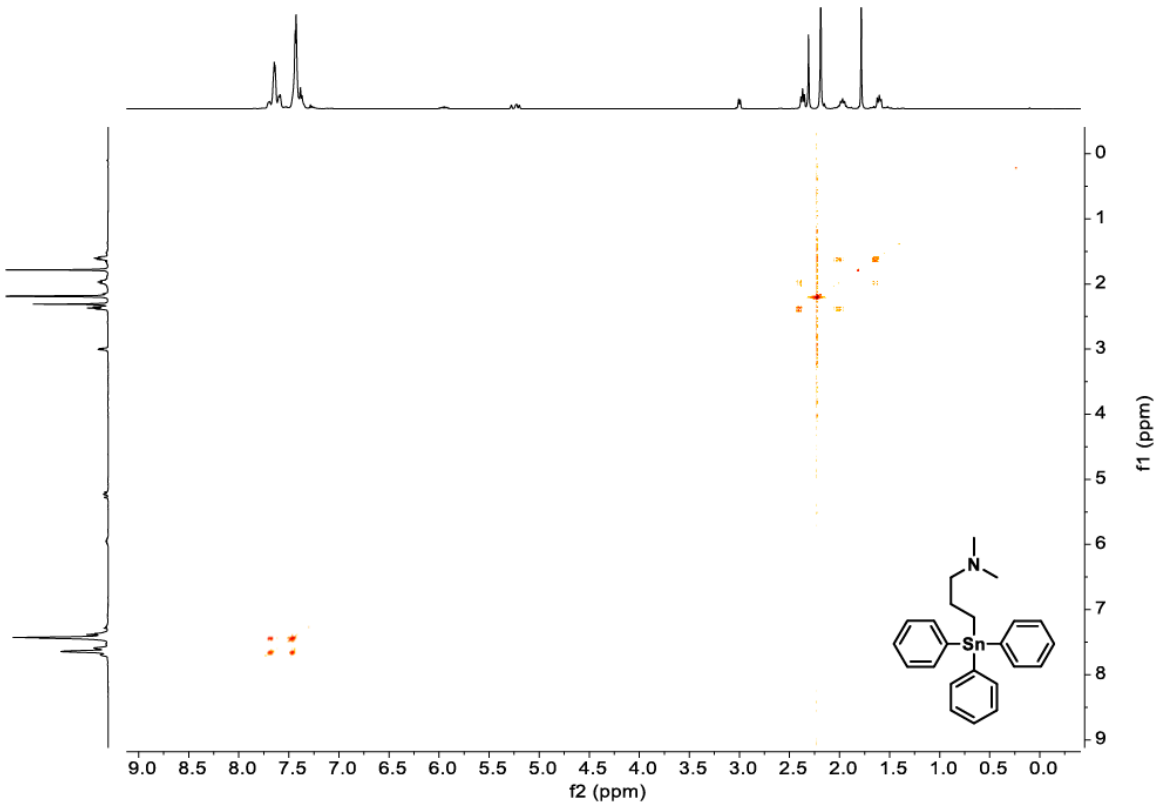


Figure S20. COSY NMR spectrum of **6** in $CDCl_3$.

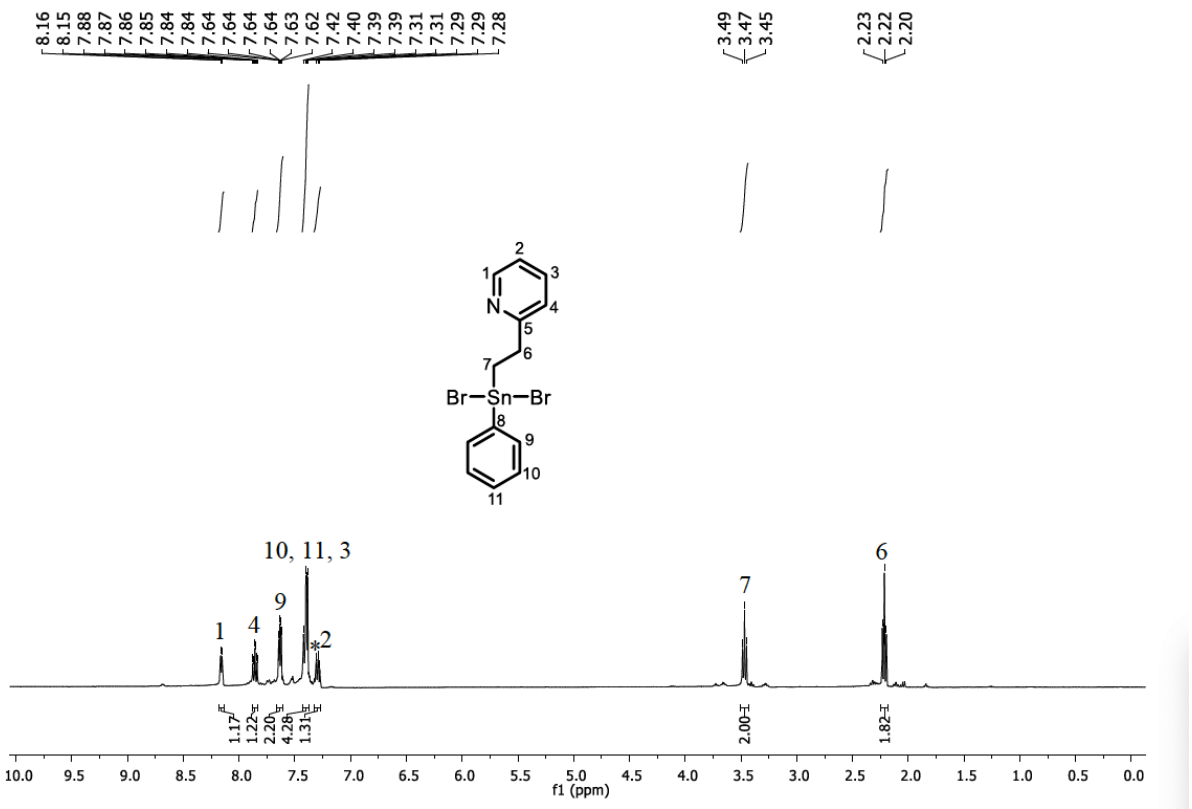


Figure S21. ^{1}H NMR spectrum of **8** in $CDCl_3$.

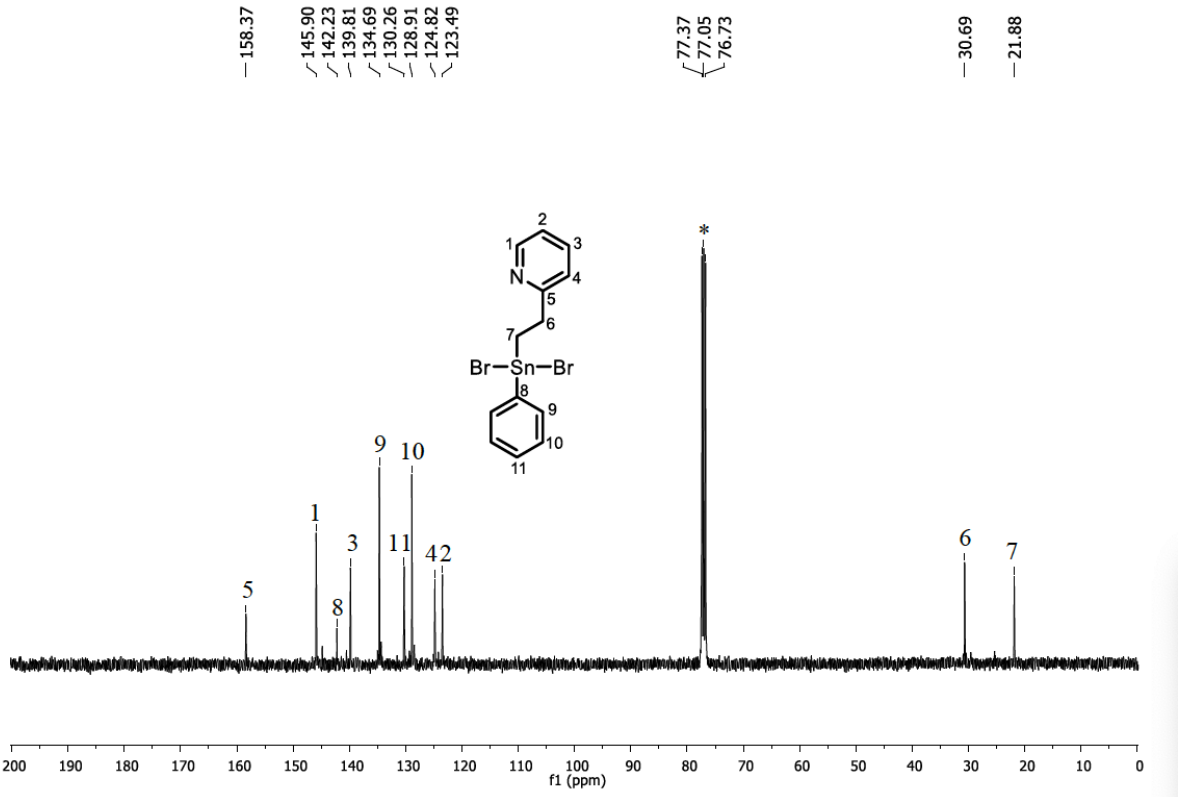


Figure S22. ^{13}C NMR spectrum of **8** in $CDCl_3$.

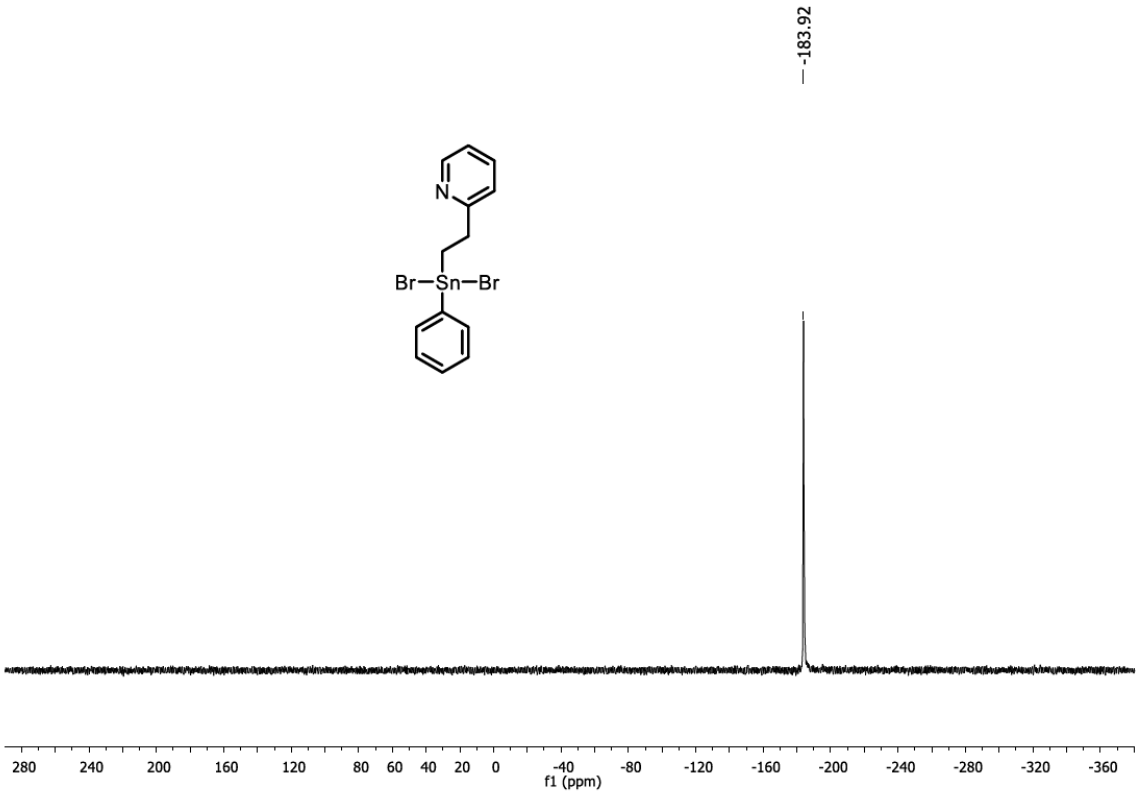


Figure S23. ^{119}Sn NMR spectrum of **8** in $CDCl_3$.

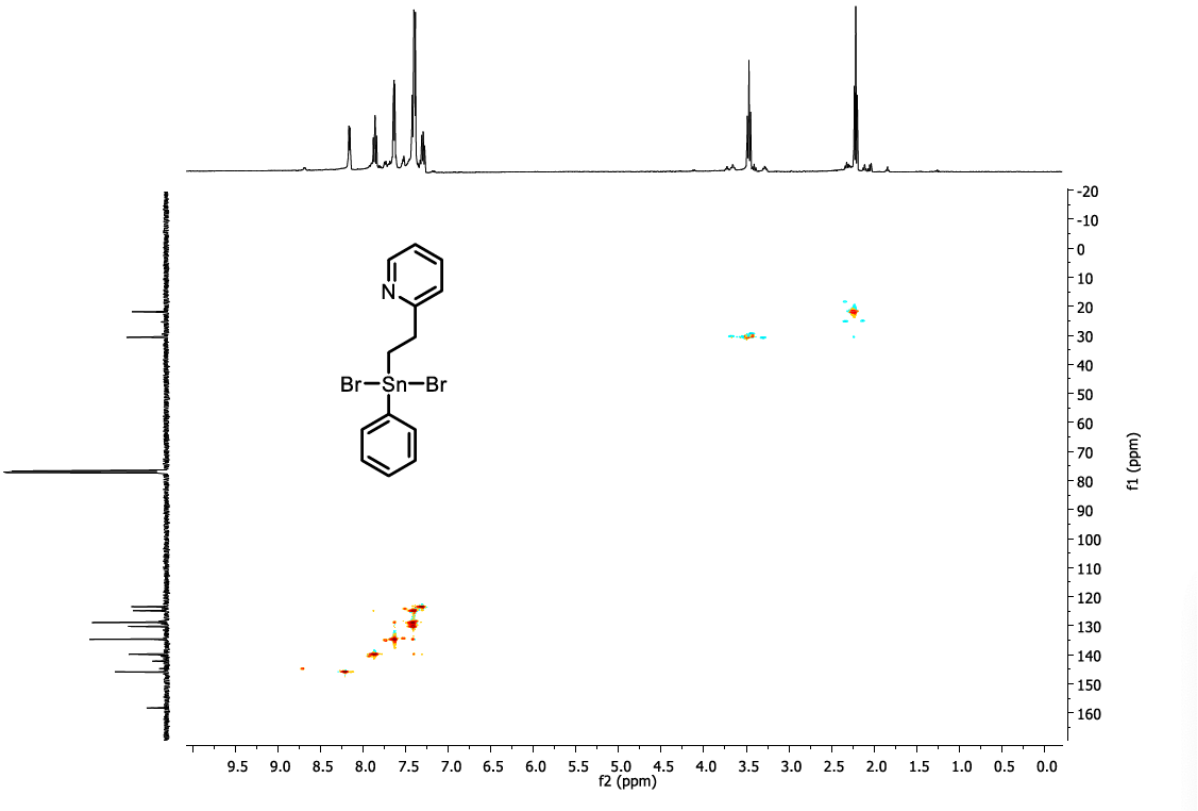


Figure S24. HSQC NMR spectrum of **8** in $CDCl_3$.

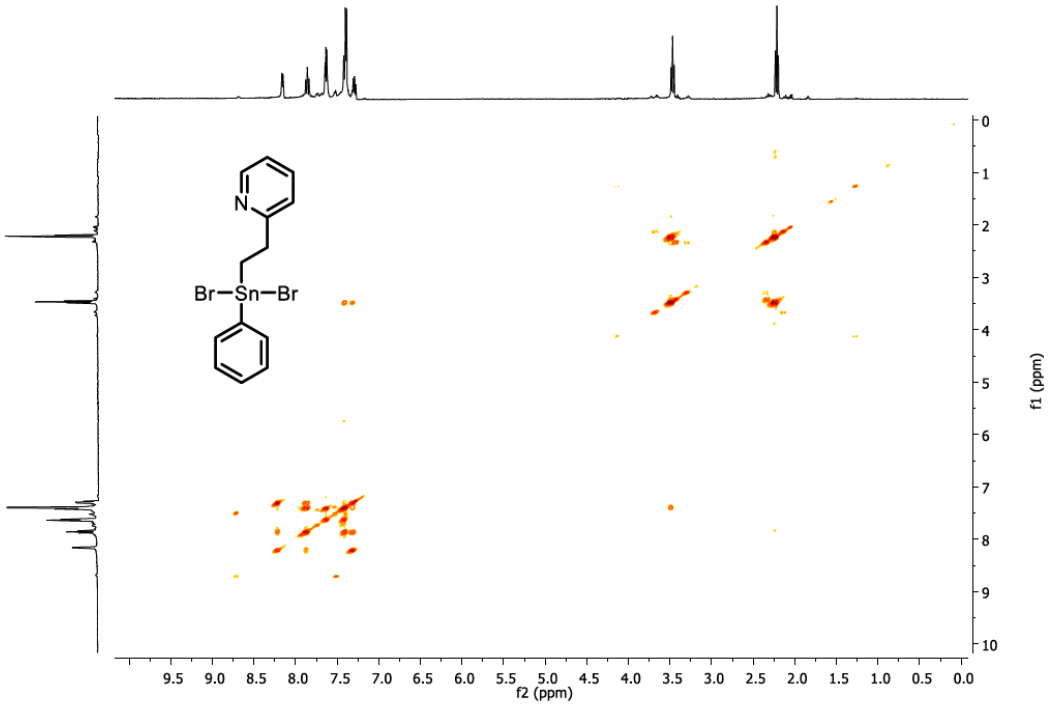


Figure S25. COSY NMR spectrum of **8** in $CDCl_3$.

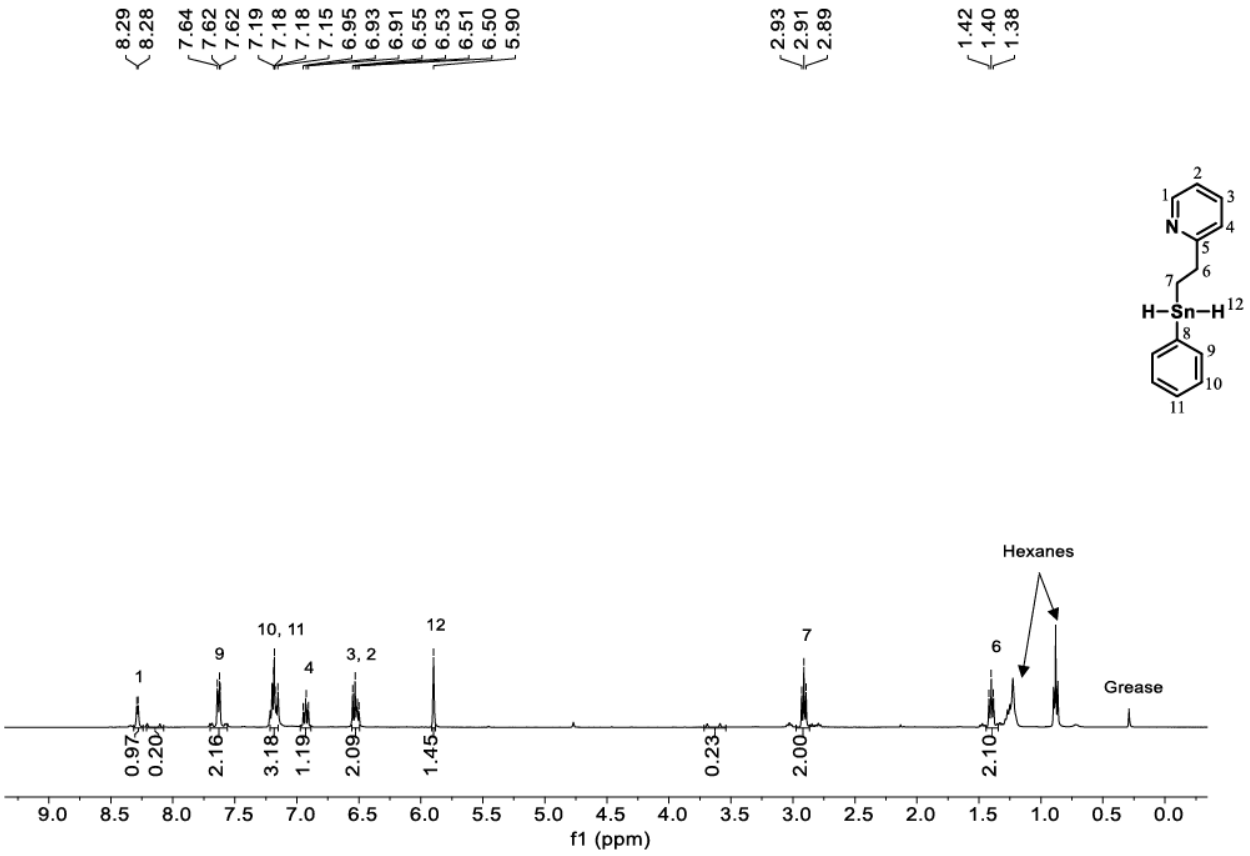


Figure S26. ^{1}H NMR spectrum of **9** in C_6D_6.

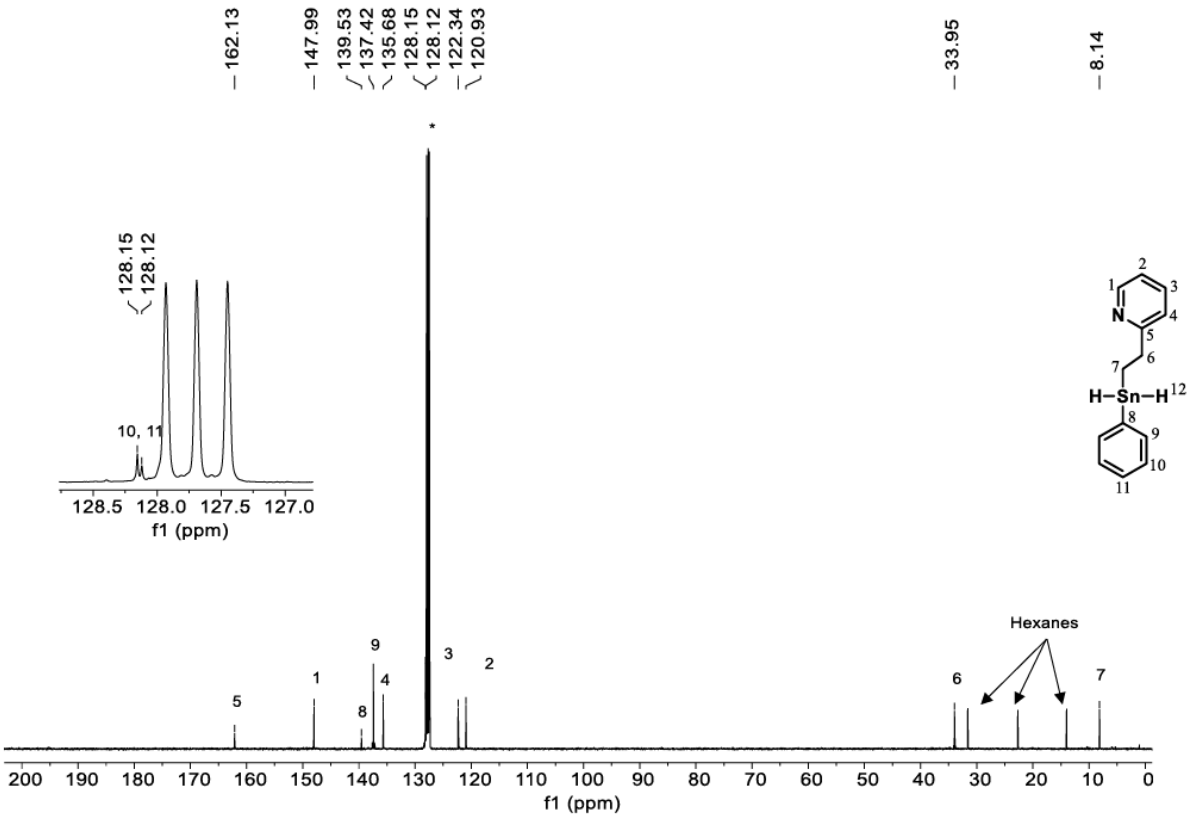


Figure S27. ^{13}C NMR spectrum of **9** in C_6D_6.

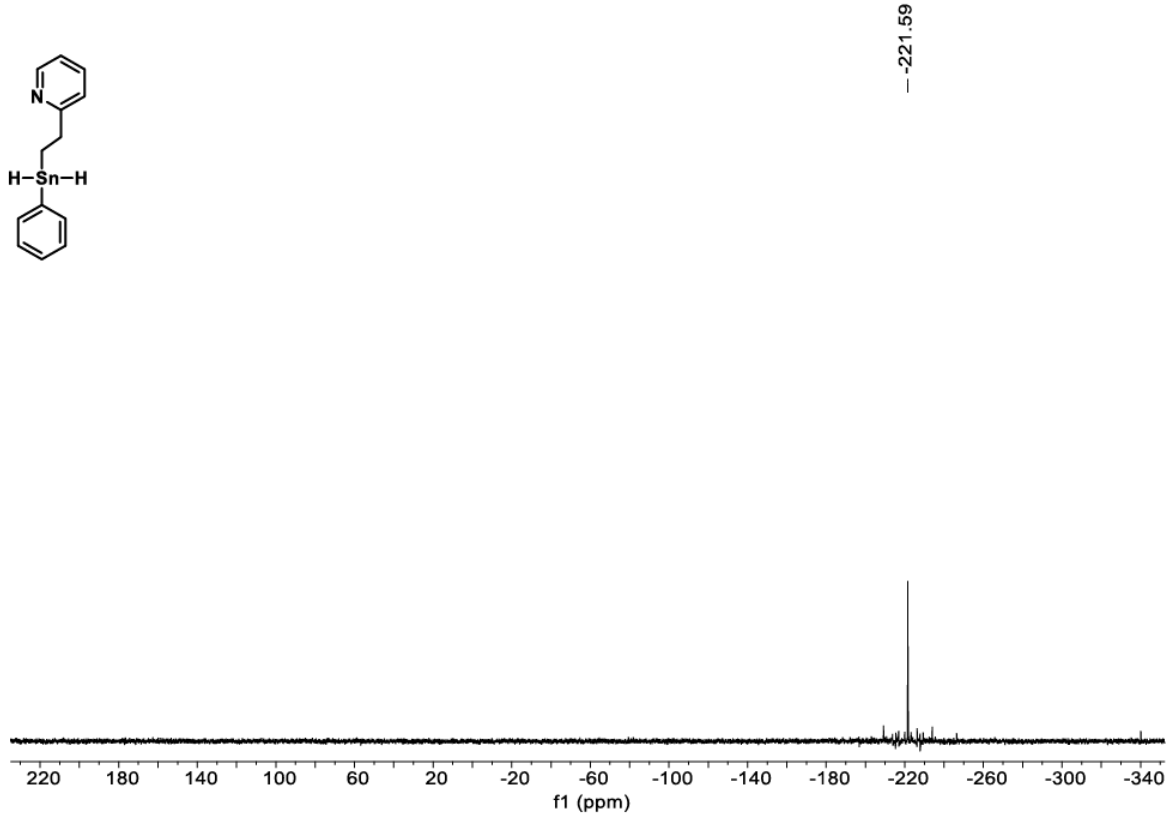


Figure S28. ^{119}Sn NMR spectrum of **9** in C_6D_6.

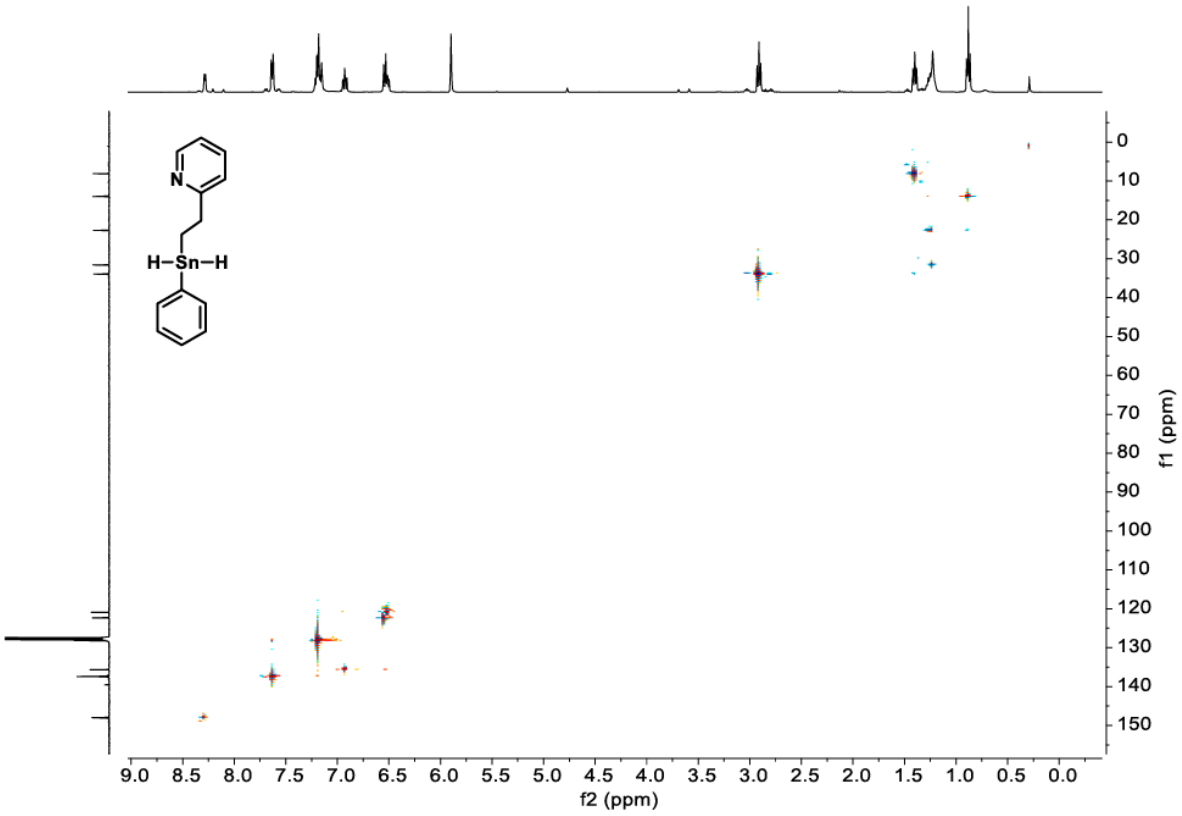


Figure S29. HSQC NMR spectrum of **9** in C_6D_6.

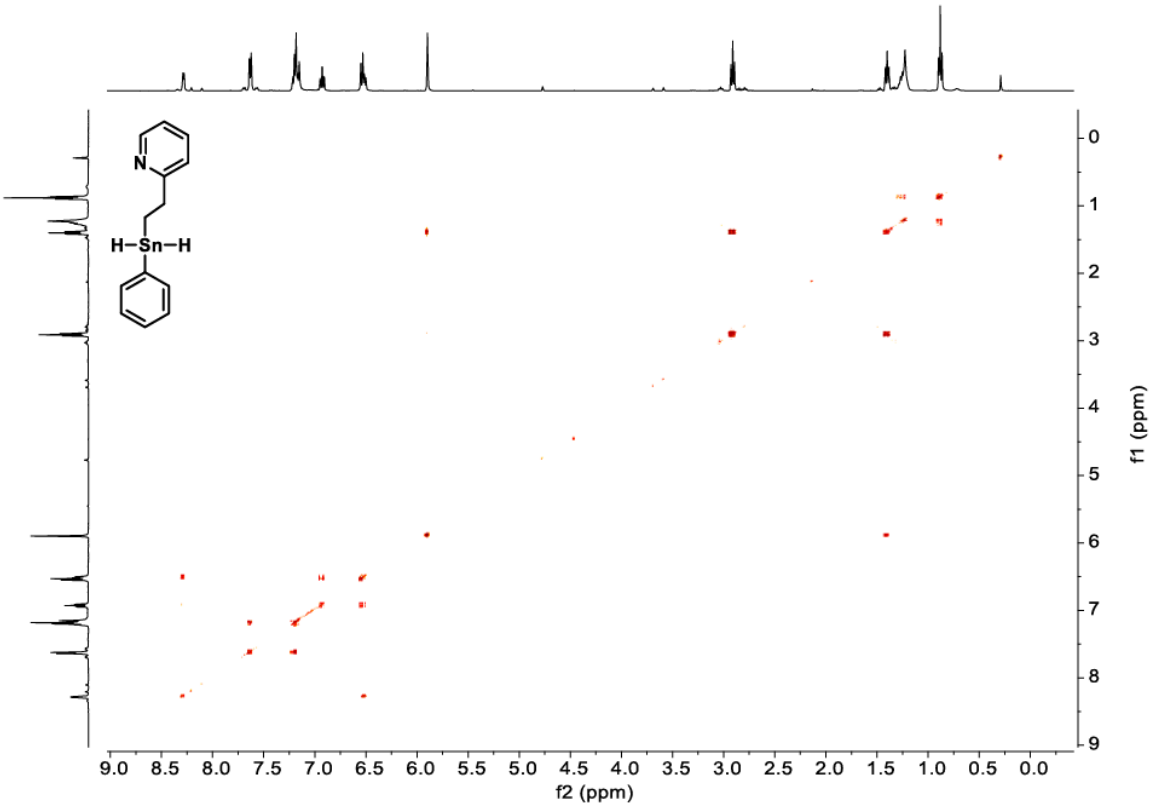


Figure S30. COSY NMR spectrum of **9** in C_6D_6.

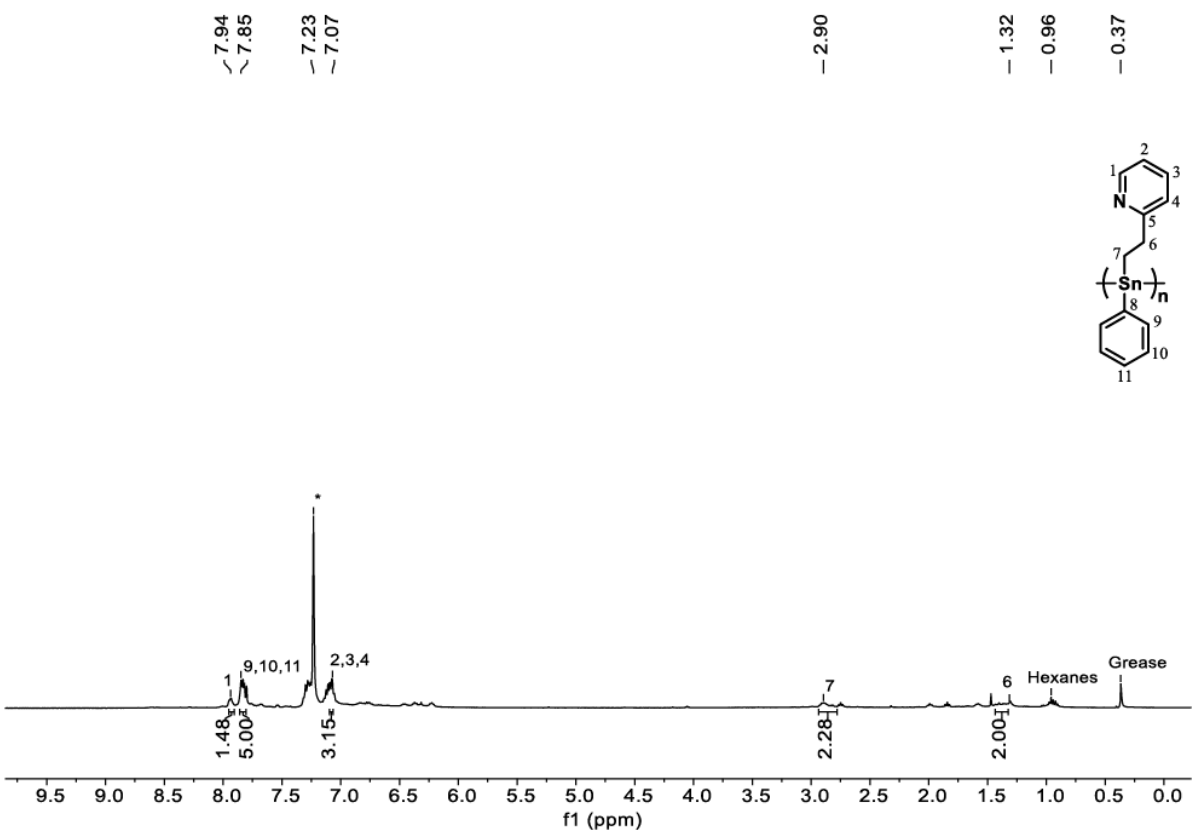


Figure S31. ^{1}H NMR spectrum of **15** prepared with 2 mol % Wilkinson Catalyst in C_6D_6.

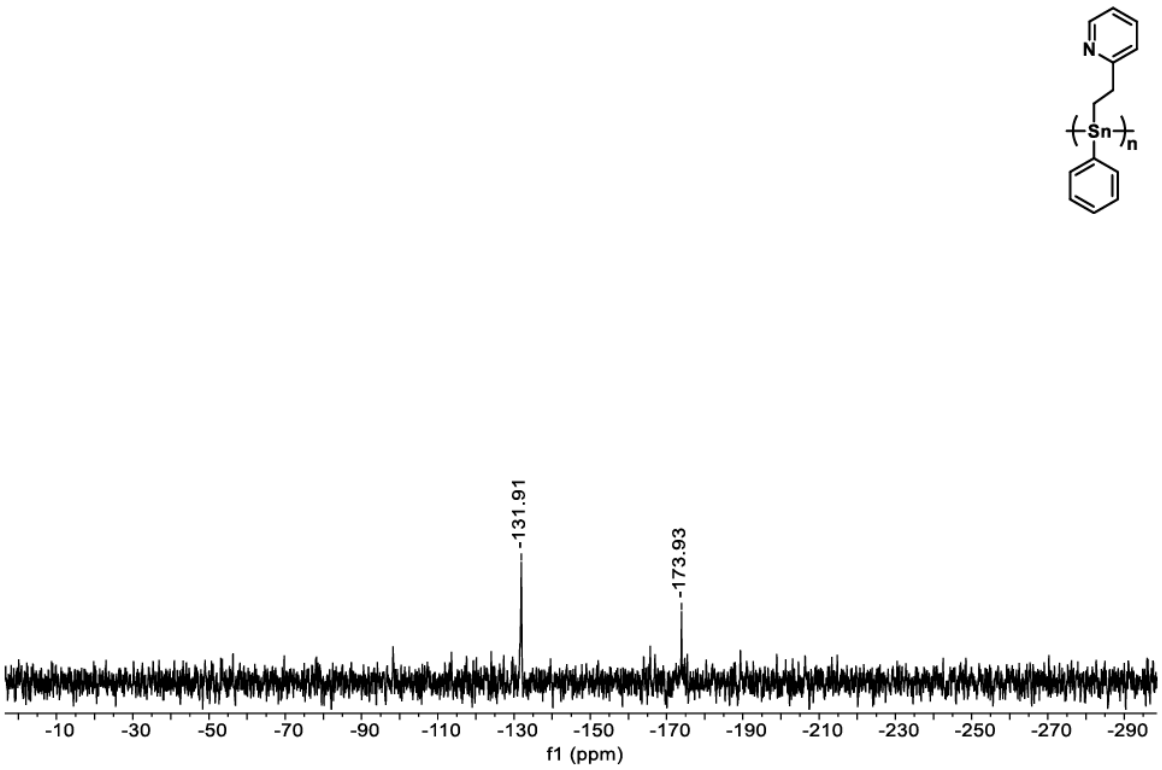


Figure S32. ^{119}Sn NMR spectrum of **15** prepared with 2 mol % Wilkinson Catalyst in C_6D_6.

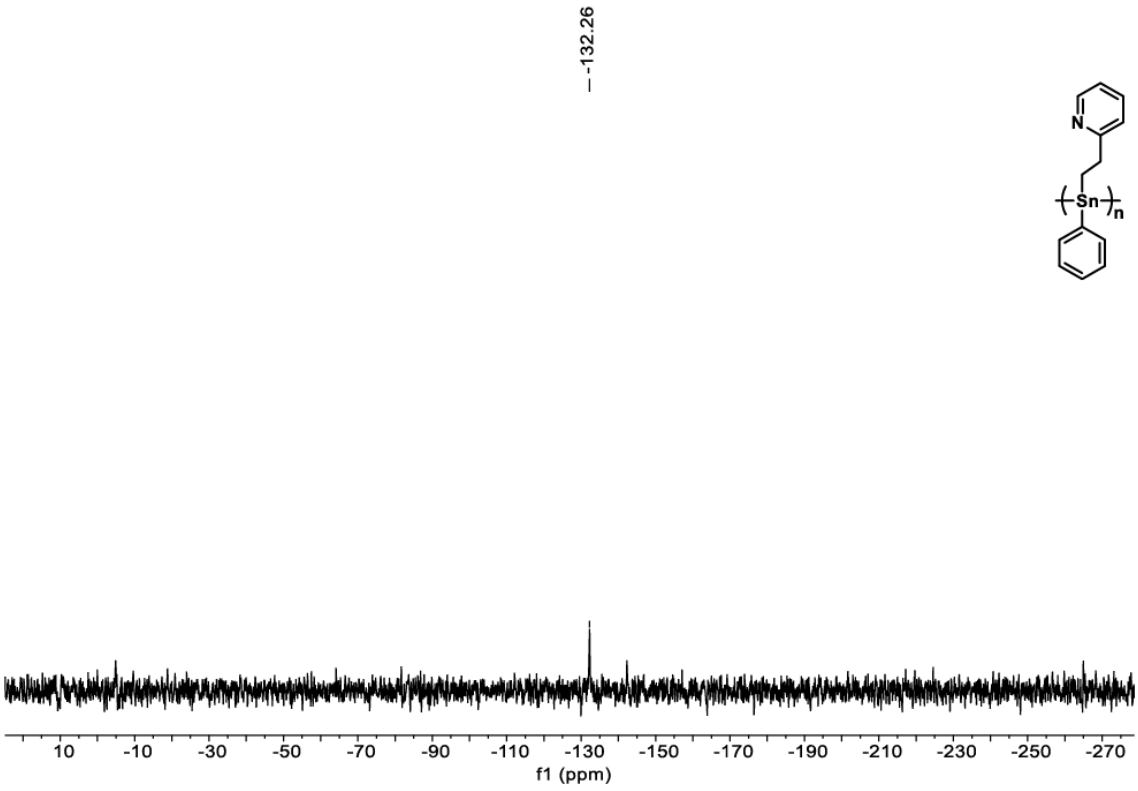


Figure S33. ^{119}Sn NMR spectrum of **15** prepared with 4 mol % Wilkinson Catalyst in C_6D_6.

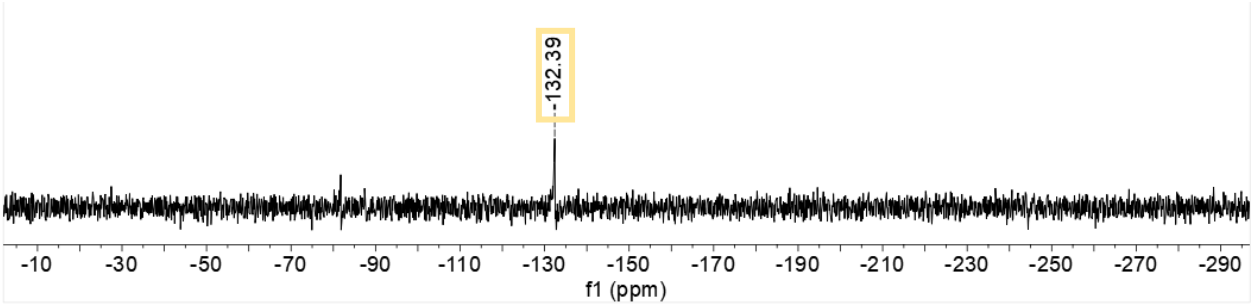


Figure S34. ^{119}Sn NMR spectrum (C_6D_6) of polymer **15** with a few drops of d^8-THF.

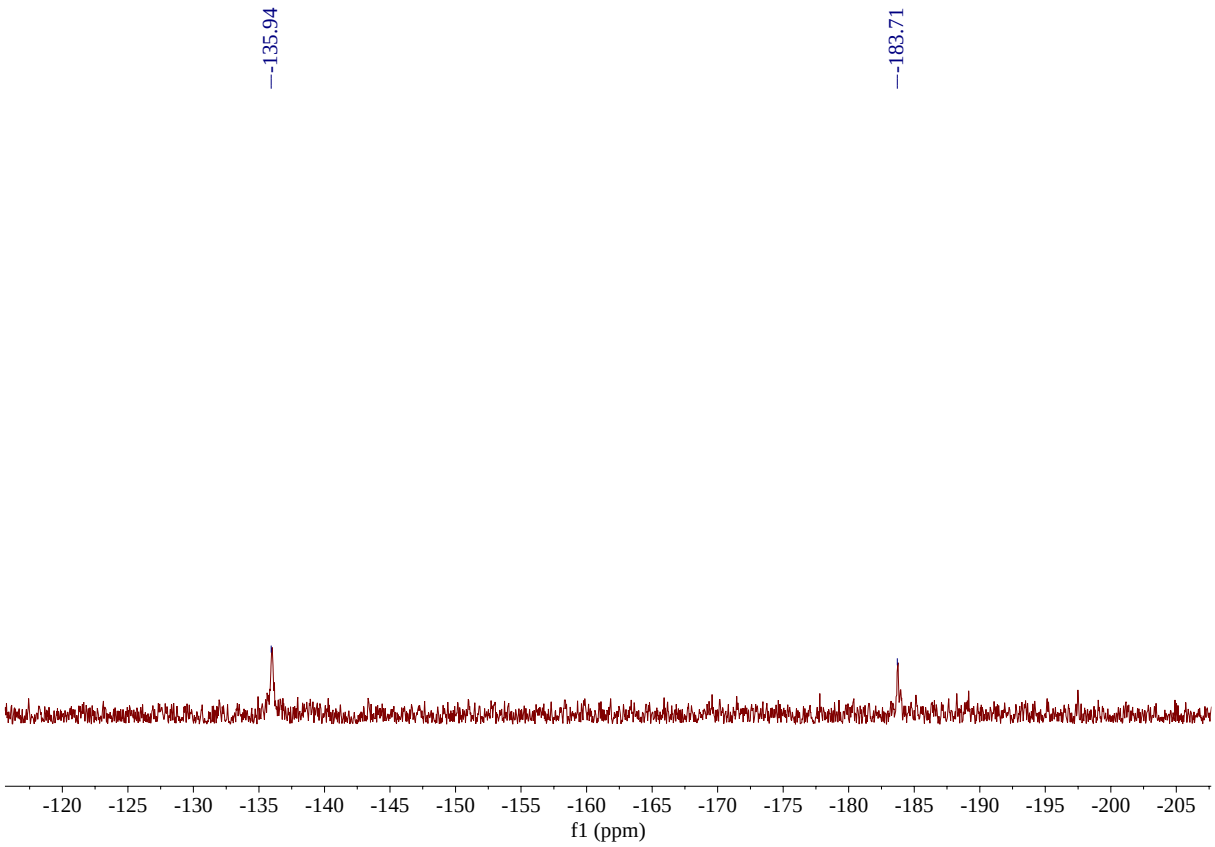


Figure S35. ^{119}Sn NMR spectrum (C_6D_6) of open conformer of **15** (δ = -135 ppm) and new distannoxane tin species **16** (δ = -184 ppm).

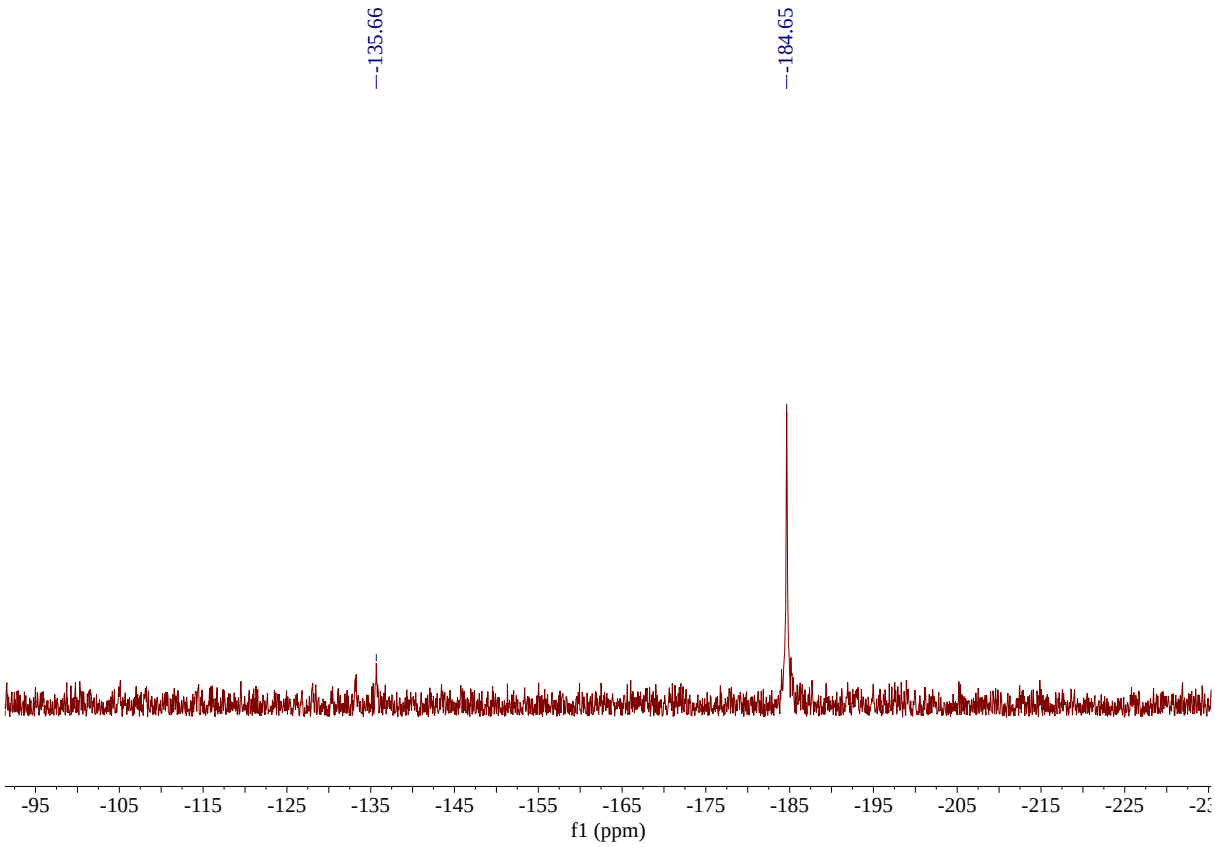


Figure S36.[119]Sn NMR spectrum (C_6D_6) of purified polymer **15** with a few drops of d^8-THF.

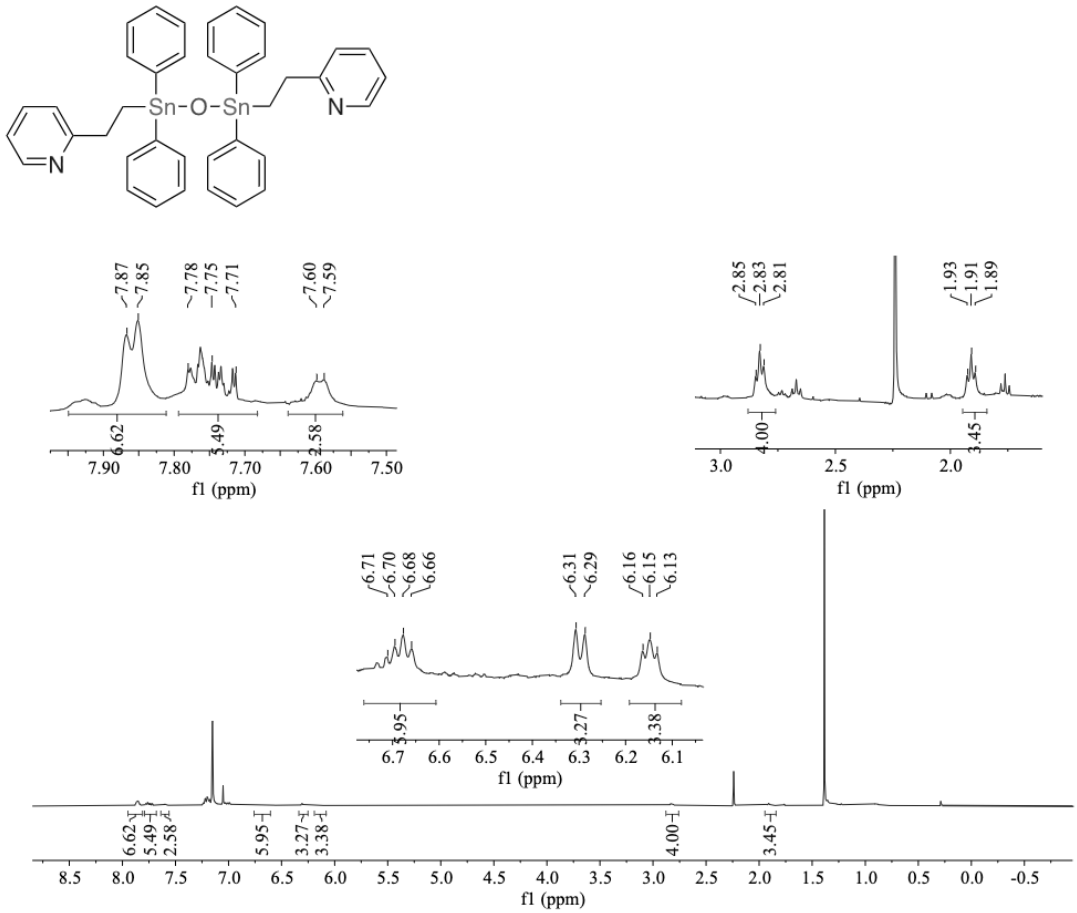


Figure S37. ^{1}H NMR (C_6D_6) spectrum of **16**.

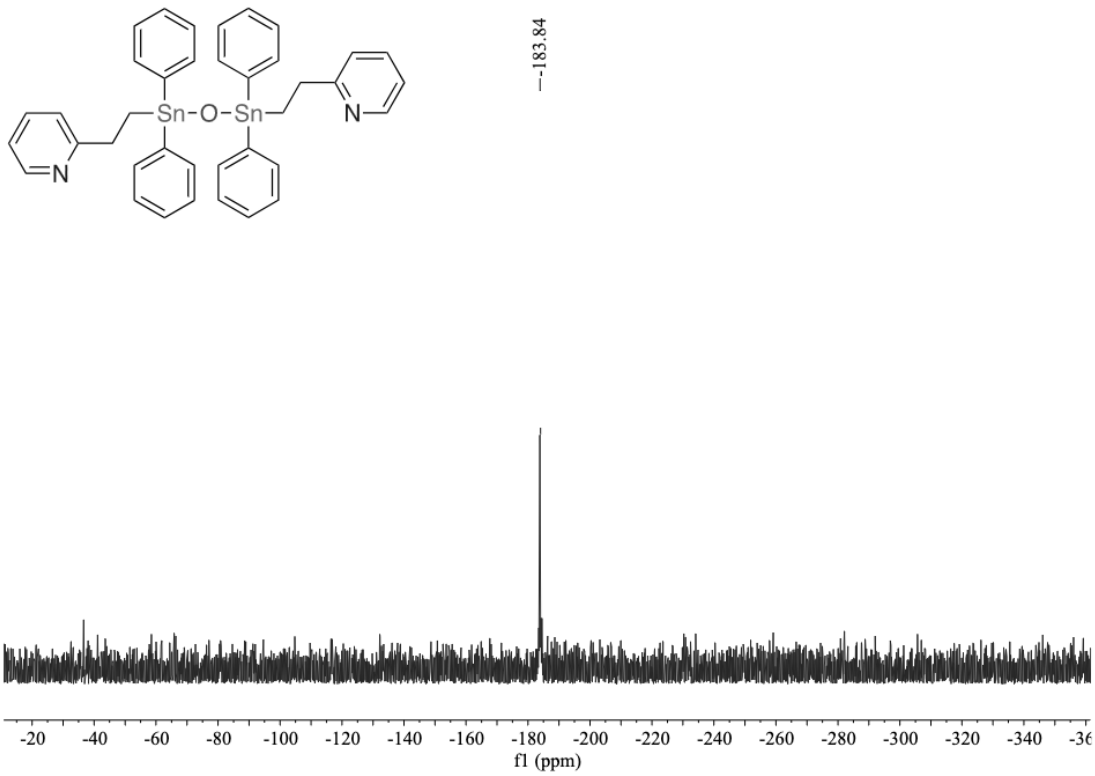


Figure S38. ^{119}Sn NMR (C_6D_6) spectrum of **16.**

Table S1. Minimized mean sum of squared distances (MSSDs) between equivalent heavy (nonH) atoms in calculated and experimental structures, with DFT method rank ()

Compound	PBE0-GD3BJ	B3PW91-GD3BK	M052X-GD3
2[a]	0.0190 (3)	0.0163 (2)	0.00923 (1)
8-*A*[b]	0.0633 (3)	0.0629 (2)	0.0569 (1)
8-*B*[b]	0.0230 (3)	0.0222 (2)	0.0191 (1)

[a]Fitting 11 of 26 non-H atoms. [b]Fitting 11 of 16 non-H atoms.

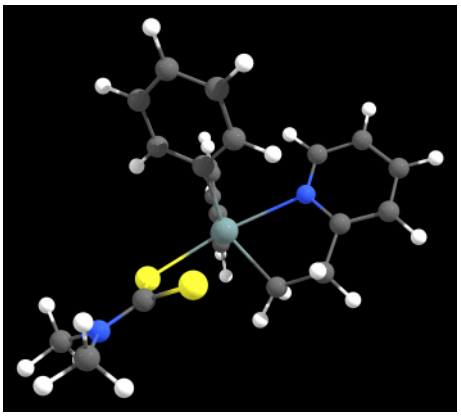
Table S2. Influence of DFT functional and CPCM parameters of selected bond distances in conformer **8**-A[a]

Method	*d* Sn-N1 /Å	*d* Sn-Br(*trans*) /Å	*d* Sn-Br(*cis*) /Å	*d* Sn-C(Ph) /Å	*d* Sn-C(CH_2-) /Å
M05-2X-GD3	2.427	2.585	2.534	2.118	2.135
PBE0-GD3BJ	2.438	2.580	2.533	2.129	2.145
B3LYP-GD3BJ	2.448	2.592	2.542	2.125	2.145
B97D3	2.467	2.605	2.554	2.137	2.158
wB97XD	2.480	2.580	2.532	2.132	2.145
M06-GD3	2.489	2.584	2.542	2.124	2.142
r^2SCAN-3c	2.500	2.583	2.533	2.142	2.164
M06-GD3 CPCM Bondi radii 1.2	2.383	2.654	2.562	2.121	2.133
PBE0-GD3BJ CPCM Bondi radii1.2	2.347	2.651	2.551	2.126	2.138

[a]See Table S-3, p. 50.

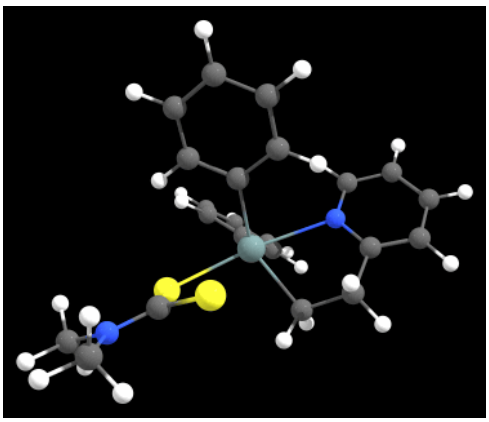
Table S3 Major conformers, Gibbs energies, and Boltzmann-weighted contributions for Compounds **1-9**

Conformer 1-A



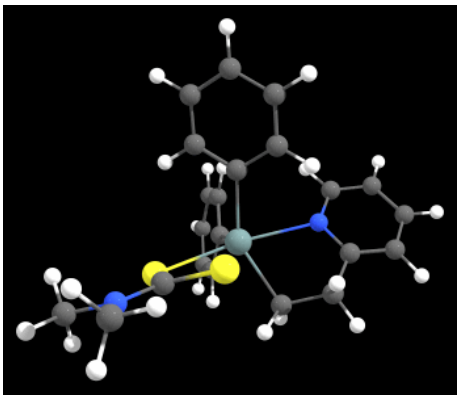
G=-1972.469071 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.49
Sn-N=2.559 Å, Sn-S=2.560 Å, Sn-S'=3.181 Å

Conformer 1-B



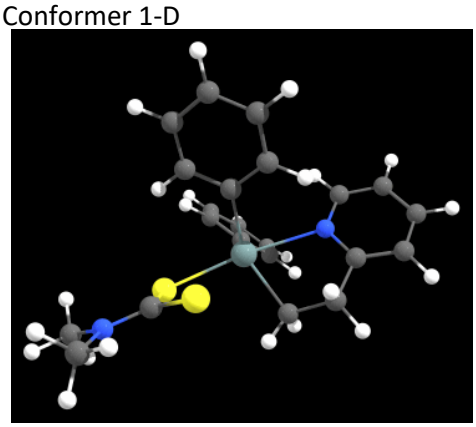
G_{rel} = 1.76 kJ mol^{-1}
Est. fract. abundance = 0.24
Sn-N=2.547 Å, Sn-S=2.554 Å, Sn-S'=3.272 Å

Conformer 1-C



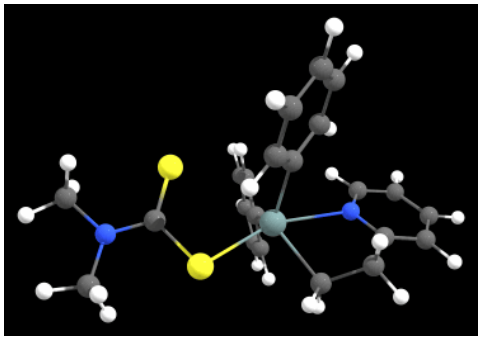
G_{rel} = 2.57 kJ mol^{-1}
Est. fract. abundance = 0.17
Sn-N=2.560 Å, Sn-S=2.560 Å, Sn-S'=3.170 Å

Conformer 1-D



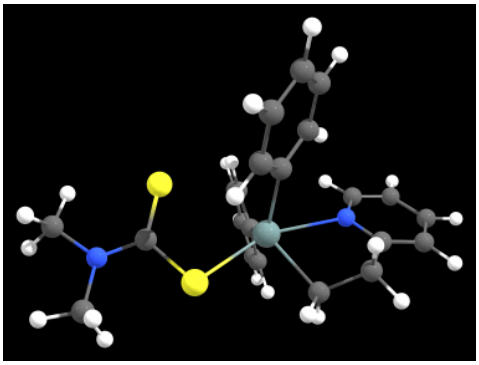
G_{rel} = 4.31 kJ mol^{-1}
Est. fract. abundance = 0.08
Sn-N=2.548 Å, Sn-S=2.554 Å, Sn-S'=3.264 Å

Conformer 1-E



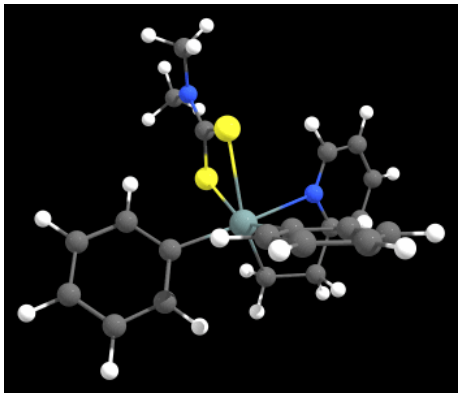
G_{rel} = 9.30 kJ mol^{-1}
Est. fract. abundance = 0.01
Sn-N=2.664 Å, Sn-S=2.542 Å, Sn-S'=3.325 Å

Conformer 1-F



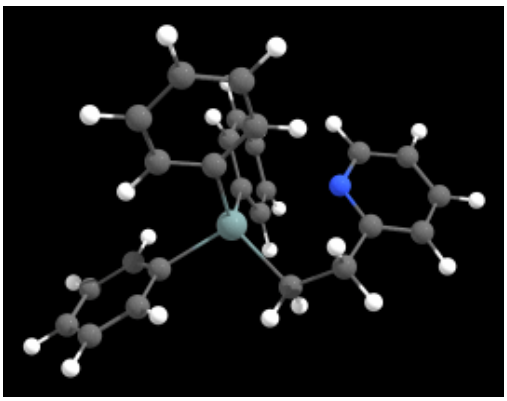
G_{rel} = 12.1 kJ mol^{-1}
Est. fract. abundance = 0.004
Sn-N=2.666 Å, Sn-S=2.543 Å, Sn-S'=3.312 Å

Conformer 1-G



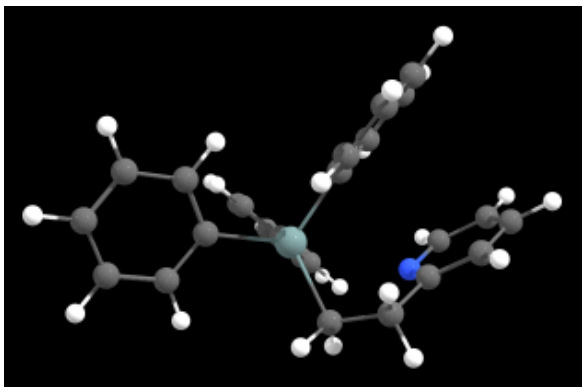
G_{rel} = 18.6 kJ mol^{-1}
Est. fract. abundance = 0.0003
Sn-N=2.573 Å, Sn-S=2.651 Å, Sn-S'=2.822 Å

Conformer 2-A



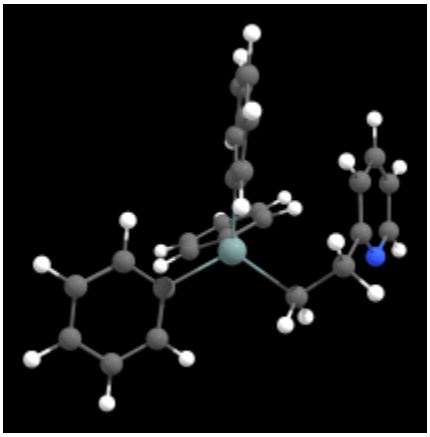
G= -1235.033378 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.57
Sn-N=2.935 Å, Sn-C(Ph)=2.173 Å, Sn-C(Ph')
=2.152 Å, 2.159 Å

Conformer 2-B



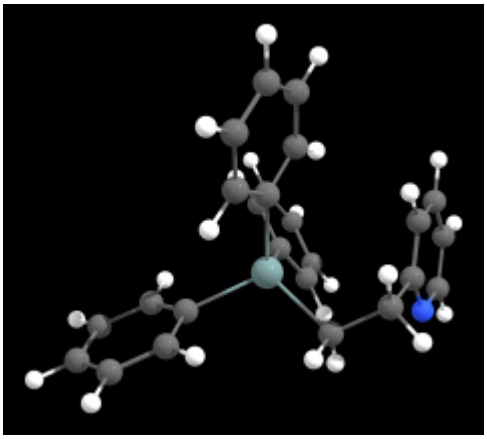
G_{rel} = 0.96 kJ mol^{-1}
Est. fract. abundance = 0.38
Sn-N=3.134 Å, Sn-C(Ph)=2.163 Å, Sn-C(Ph')
=2.156 Å, 2.151 Å

Conformer 2-C



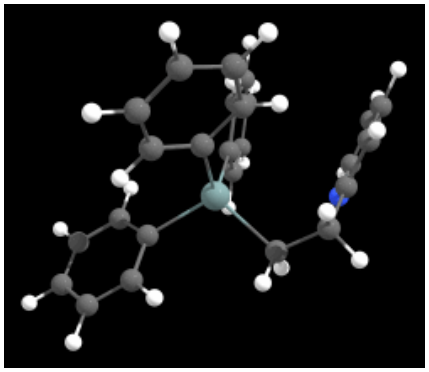
G_{rel} = 6.92 kJ mol^{-1}
Est. fract. abundance = 0.035
Sn-N=4.187 Å, Sn-C(Ph)=2.152 Å, Sn-C(Ph')
=2.155 Å, 2.150 Å

Conformer 2-D



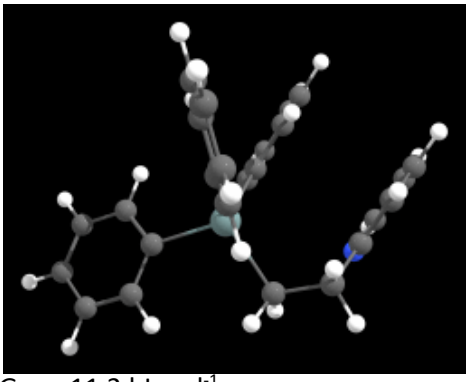
G_{rel} = 9.56 kJ mol^{-1}
Est. fract. abundance = 0.012
Sn-N=4.145 Å, Sn-C(Ph)=2.154 Å, Sn-C(Ph')
=2.160 Å, 2.149 Å

Conformer 2-E



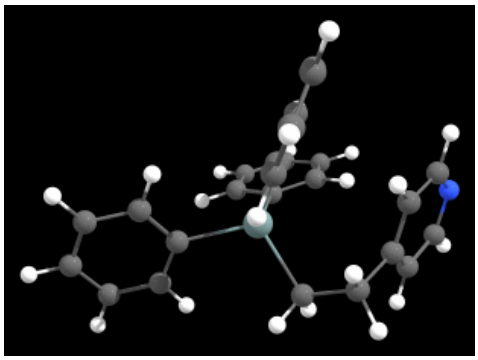
G_{rel} = 9.98 kJ mol^{-1}
Est. fract. abundance = 0.010
Sn-N=3.679 Å, Sn-C(Ph)=2.153 Å, Sn-C(Ph')
=2.157 Å, 2.152 Å

Conformer 2-F



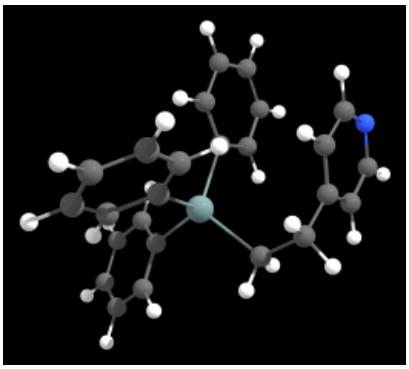
G_{rel} = 11.2 kJ mol^{-1}
Est. fract. abundance = 0.006
Sn-N=3.710 Å, Sn-C(Ph)=2.155 Å, Sn-C(Ph')
=2.157 Å, 2.153 Å

Conformer 3-A



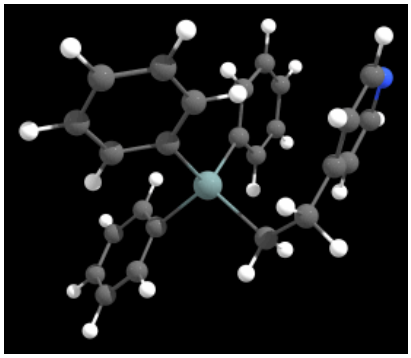
G= -1235.028108 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.8
Sn-N=5.391 Å, Sn-C(Ph)=2.152 Å, Sn-C(Ph')
=2.151 Å, 2.149 Å

Conformer 3-B



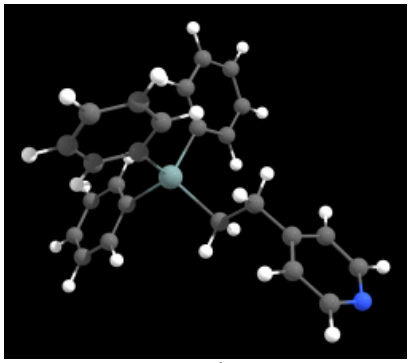
G_{rel} = 5.74 kJ mol^{-1}
Est. fract. abundance = 0.08
Sn-N=5.510 Å, Sn-C(Ph)=2.151 Å, Sn-C(Ph')
=2.155 Å, 2.147 Å

Conformer 3-C



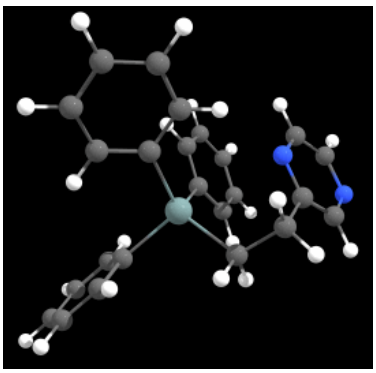
G_{rel} = 6.23 kJ mol^{-1}
Est. fract. abundance = 0.06
Sn-N=5.407 Å, Sn-C(Ph)=2.152 Å, Sn-C(Ph')
=2.152 Å, 2.149 Å

Conformer 3-ref



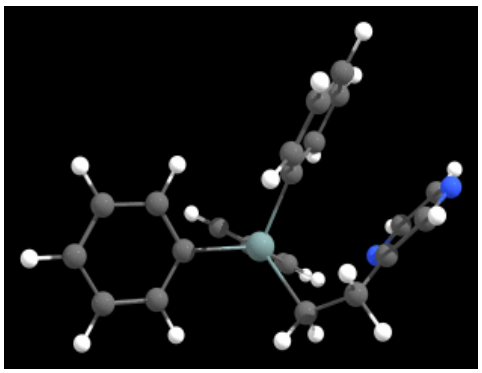
G_{rel} = 7.03 kJ mol^{-1}
Est. fract. abundance = 0.05
Sn-N=7.178 Å, Sn-C(Ph)=2.151 Å, Sn-C(Ph')
=2.150 Å, 2.148 Å

Conformer 4-A



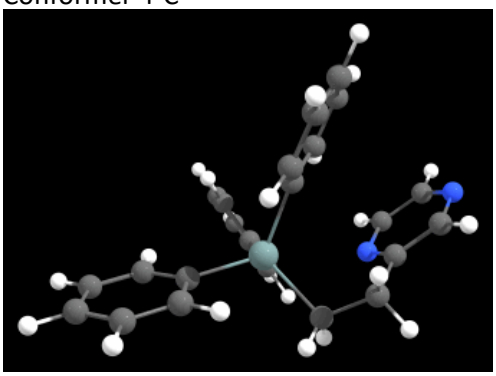
G= -1251.076886 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.36
Sn-N=3.341 Å, Sn-C(Ph)=2.157 Å, Sn-C(Ph')
=2.150 Å, 2.152 Å

Conformer 4-B



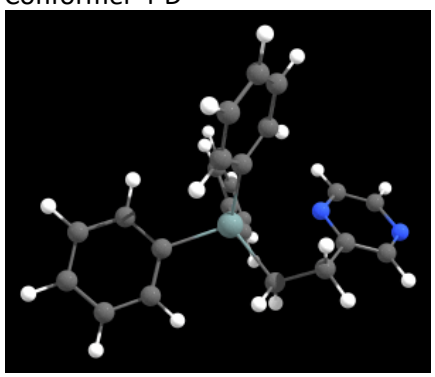
G_{rel} = 0.25 kJ mol^{-1}
Est. fract. abundance = 0.33
Sn-N=3.302 Å, Sn-C(Ph)=2.157 Å, Sn-C(Ph')
=2.154 Å, 2.150 Å

Conformer 4-C



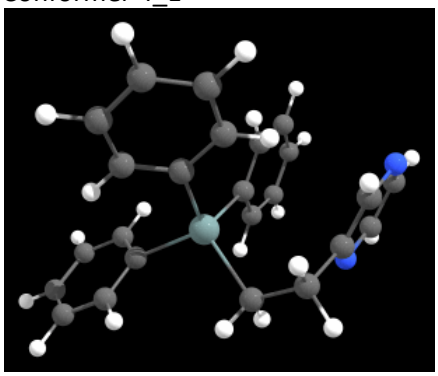
G_{rel} = 2.21 kJ mol^{-1}
Est. fract. abundance = 0.15
Sn-N=3.130 Å, Sn-C(Ph)=2.158 Å, Sn-C(Ph')
=2.149 Å, 2.160 Å

Conformer 4-D



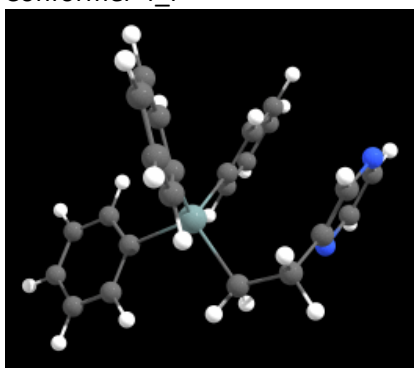
G_{rel} = 2.82 kJ mol^{-1}
Est. fract. abundance = 0.12
Sn-N=2.951 Å, Sn-C(Ph)=2.170 Å, Sn-C(Ph')
=2.154 Å, 2.152 Å

Conformer 4_E



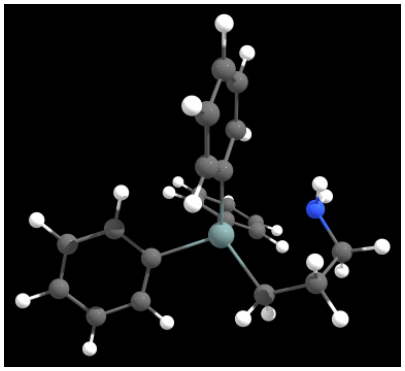
G_{rel} = 6.59 kJ mol^{-1}
Est. fract. abundance = 0.02
Sn-N=3.752 Å, Sn-C(Ph)=2.151 Å, Sn-C(Ph')
=2.152 Å, 2.155 Å

Conformer 4_F



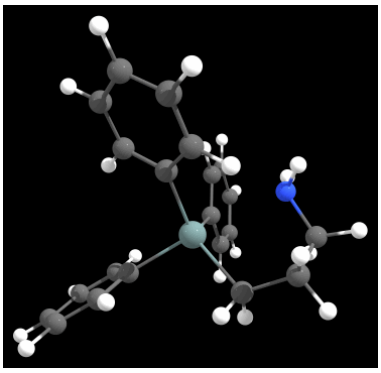
G_{rel} = 7.18 kJ mol^{-1}
Est. fract. abundance = 0.02
Sn-N=3.763 Å, Sn-C(Ph)=2.153 Å, Sn-C(Ph')
=2.155 Å, 2.152 Å

Conformer 5-A



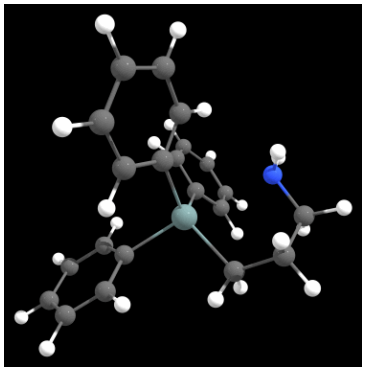
G= -1082.65347 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.46
Sn-N=2.883 Å, Sn-C(Ph)=2.179 Å, Sn-C(Ph')
=2.159 Å, 2.156 Å

Conformer 5-B



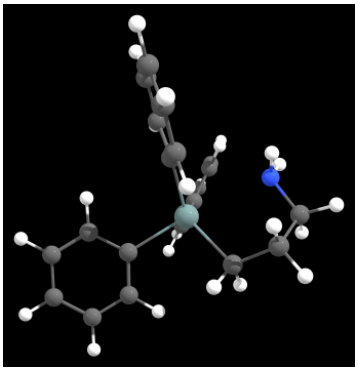
G_{rel} = 1.86 kJ mol^{-1}
Est. fract. abundance = 0.22
Sn-N=2.838 Å, Sn-C(Ph)=2.181 Å, Sn-C(Ph')
=2.160 Å, 2.156 Å

Conformer 5-C



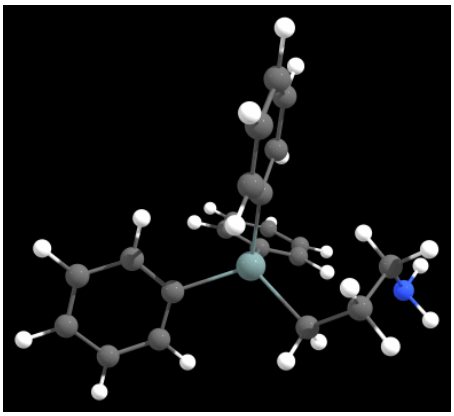
G_{rel} = 2.67 kJ mol^{-1}
Est. fract. abundance = 0.16
Sn-N=2.867 Å, Sn-C(Ph)=2.181 Å, Sn-C(Ph')
=2.162 Å, 2.155 Å

Conformer 5-D



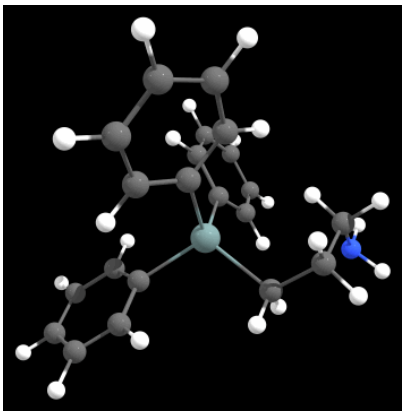
G_{rel} = 3.71 kJ mol^{-1}
Est. fract. abundance = 0.10
Sn-N=2.886 Å, Sn-C(Ph)=2.179 Å, Sn-C(Ph')
=2.161 Å, 2.155 Å

Conformer 5-E



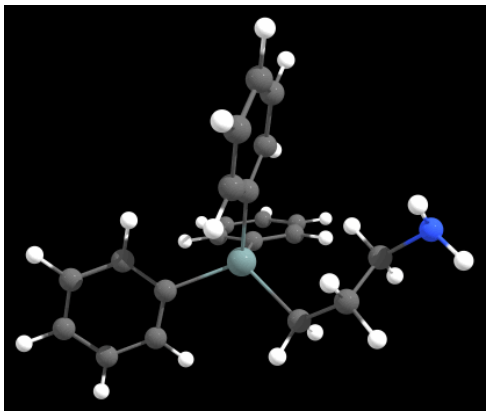
G_{rel} = 8.52 kJ mol^{-1}
Est. fract. abundance = 0.02
Sn-N=4.178 Å, Sn-C(Ph)=2.154 Å, Sn-C(Ph')
=2.157 Å, 2.150 Å

Conformer 5-F



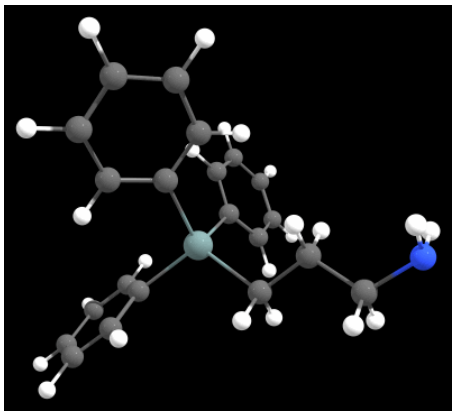
G_{rel} = 9.00 kJ mol^{-1}
Est. fract. abundance = 0.01
Sn-N=4.179 Å, Sn-C(Ph)=2.153 Å, Sn-C(Ph')
=2.158 Å, 2.152 Å

Conformer 5-G



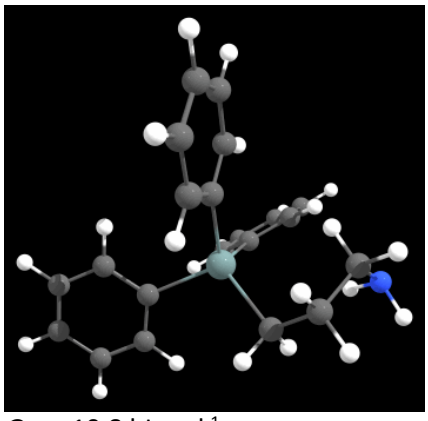
Grel = 10.1 kJ mol^{-1}
Est. fract. abundance = 0.008
Sn-N=4.832 Å, Sn-C(Ph)=2.152 Å, Sn-C(Ph')
=2.155 Å, 2.152 Å

Conformer 5-ref



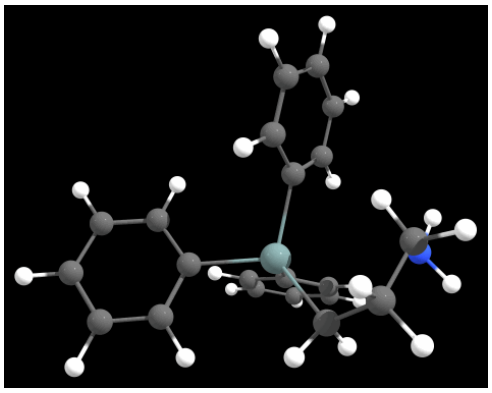
G_{rel} = 10.3 kJ mol^{-1}
Est. fract. abundance = 0.007
Sn-N=5.629 Å, Sn-C(Ph)=2.151 Å, Sn-C(Ph')
=2.153 Å, 2.152 Å

Conformer 5-H



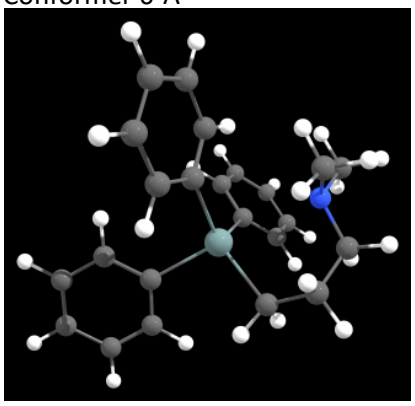
G_{rel} = 10.8 kJ mol^{-1}
Est. fract. abundance = 0.006
Sn-N=4.061 Å, Sn-C(Ph)=2.152 Å, Sn-C(Ph')
=2.156 Å, 2.152 Å

Conformer 5-I



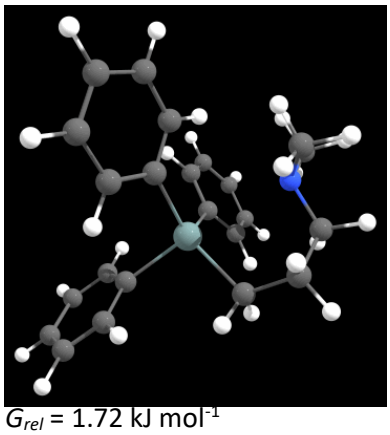
G_{rel} = 12.0 kJ mol^{-1}
Est. fract. abundance = 0.004
Sn-N=3.419 Å, Sn-C(Ph)=2.161 Å, Sn-C(Ph')
=2.157 Å, 2.153 Å

Conformer 6-A



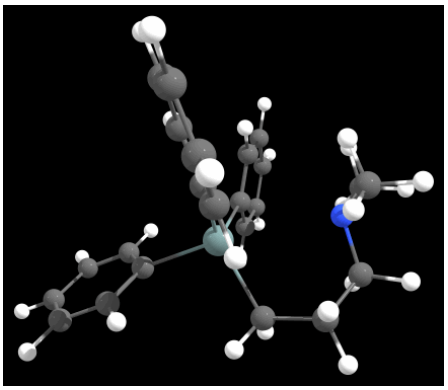
G= -1161.180498 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.43
Sn-N=3.036 Å, Sn-C(Ph)=2.177 Å, Sn-C(Ph')
=2.155 Å, 2.153 Å

Conformer 6-B



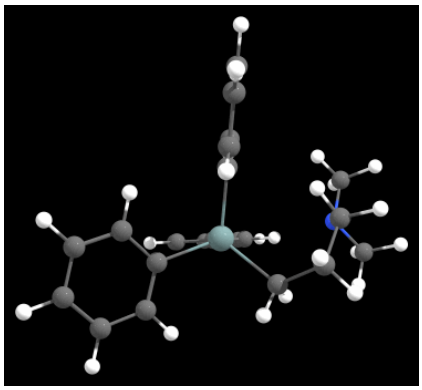
G_{rel} = 1.72 kJ mol^{-1}
Est. fract. abundance = 0.21
Sn-N=3.074 Å, Sn-C(Ph)=2.176 Å, Sn-C(Ph')
=2.156 Å, 2.153 Å

Conformer 6-C



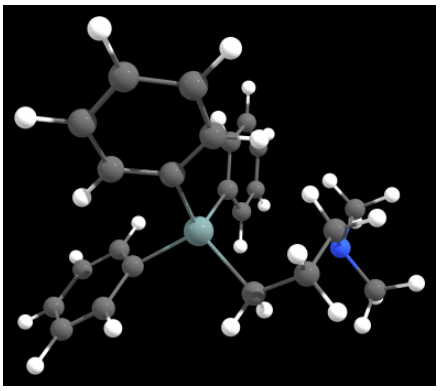
G_{rel} = 3.03 kJ mol^{-1}
Est. fract. abundance = 0.13
Sn-N=3.078 Å, Sn-C(Ph)=2.176 Å, Sn-C(Ph')
=2.154 Å, 2.153 Å

Conformer 6-D



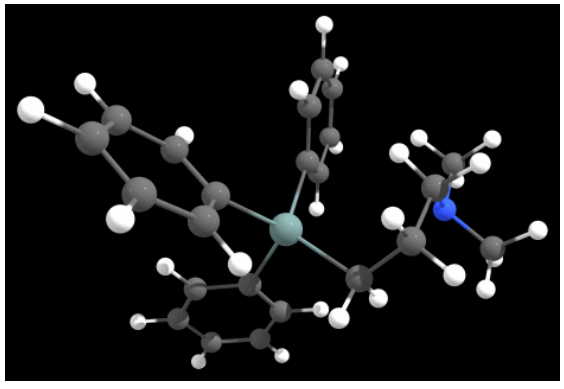
G_{rel} = 3.55 kJ mol^{-1}
Est. fract. abundance = 0.10
Sn-N=3.598 Å, Sn-C(Ph)=2.159 Å, Sn-C(Ph')
=2.155 Å, 2.152 Å

Conformer 6-E



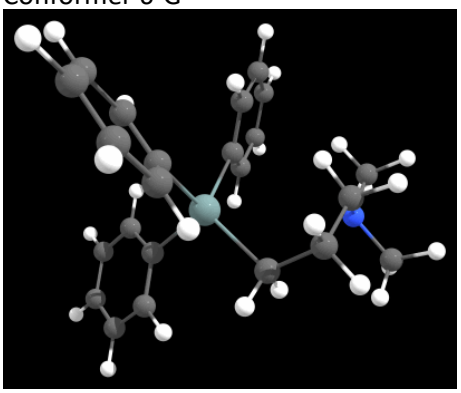
G_{rel} = 4.63 kJ mol^{-1}
Est. fract. abundance = 0.066
Sn-N=3.915 Å, Sn-C(Ph)=2.153 Å, Sn-C(Ph')
=2.158 Å, 2.152 Å

Conformer 6-F



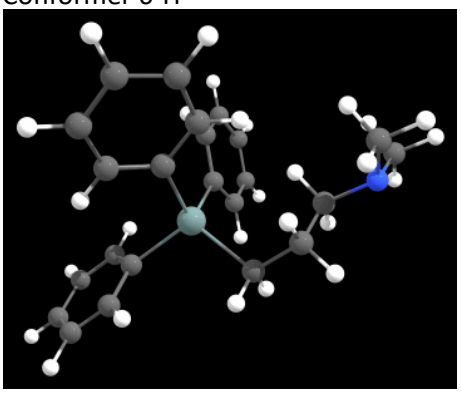
G_{rel} = 7.39 kJ mol^{-1}
Est. fract. abundance = 0.022
Sn-N=3.822 Å, Sn-C(Ph)=2.154 Å, Sn-C(Ph')
=2.154 Å, 2.156 Å

Conformer 6-G



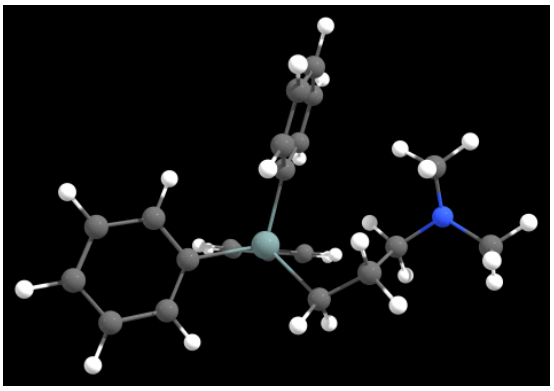
G_{rel} = 8.24 kJ mol^{-1}
Est. fract. abundance = 0.015
Sn-N=3.821 Å, Sn-C(Ph)=2.157 Å, Sn-C(Ph')
=2.156 Å, 2.154 Å

Conformer 6-H



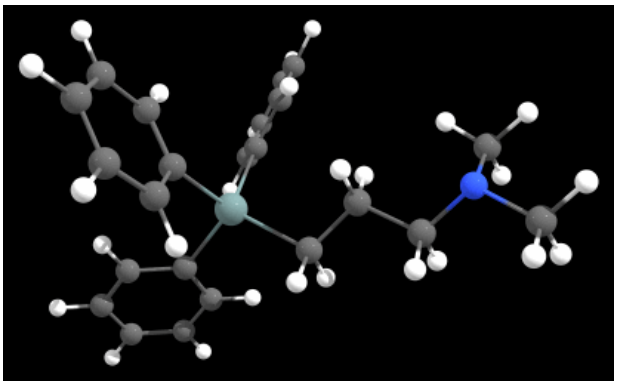
G_{rel} = 8.76 kJ mol^{-1}
Est. fract. abundance = 0.012
Sn-N=4.909 Å, Sn-C(Ph)=2.152 Å, Sn-C(Ph')
=2.154 Å, 2.152 Å

Conformer 6-I



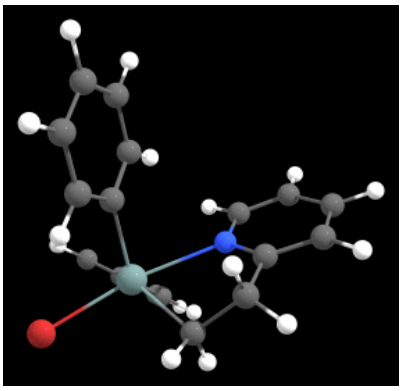
G_{rel} = 10.6 kJ mol^{-1}
Est. fract. abundance = 0.006
Sn-N=3.821 Å, Sn-C(Ph)=2.157 Å, Sn-C(Ph')
=2.156 Å, 2.154 Å

Conformer 6-ref



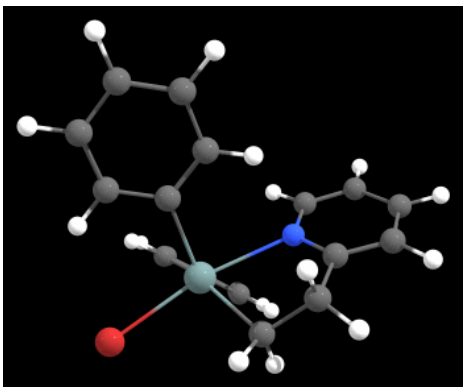
G_{rel} = 10.9 kJ mol^{-1}
Est. fract. abundance = 0.005
Sn-N=5.581 Å, Sn-C(Ph)=2.151 Å, Sn-C(Ph')
=2.153 Å, 2.151 Å

Conformer 7-A



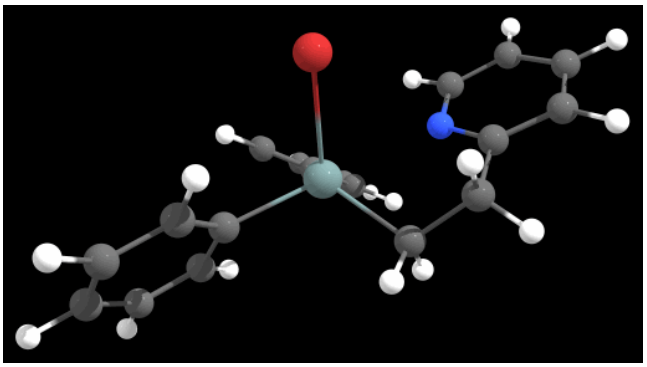
G= -3577.736696 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.61
Sn-N=2.567 Å, Sn-Br=2.606 Å, Sn-C(Ph)
=2.153 Å, 2.146 Å

Conformer 7-B



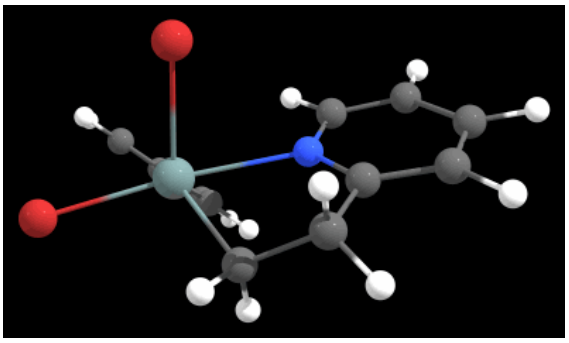
G_{rel} = 1.11 kJ mol^{-1}
Est. fract. abundance = 0.39
Sn-N=2.527 Å, Sn-Br=2.615 Å, Sn-C(Ph)
=2.163 Å, 2.151 Å

Conformer 7-C



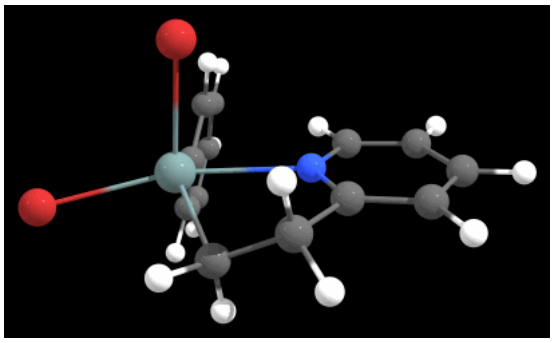
G_{rel} = 19.7 kJ mol^{-1}
Est. fract. abundance = 0.0002
Sn-N=2.726 Å, Sn-C(Ph)=2.172 Å, Sn-Br =2.552 Å, Sn-C(Ph')=2.150 Å

Conformer 8-A



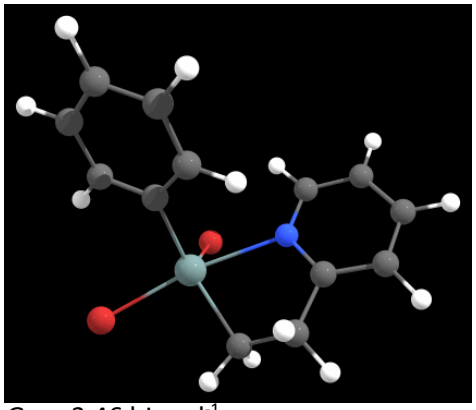
G= -5920.428216 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.48
Sn-N=2.500 Å, Sn-Br=2.583 Å, Sn-Br'=2.533 Å, Sn-C(Ph)=2.142 Å

Conformer 8-B



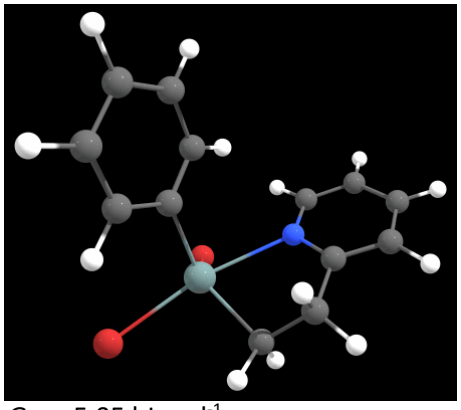
G_{rel} = 1.26 kJ mol^{-1}
Est. fract. abundance = 0.29
Sn-N=2.551 Å, Sn-Br=2.583 Å, Sn-Br'=2.528 Å, Sn-C(Ph)=2.141 Å

Conformer 8-C



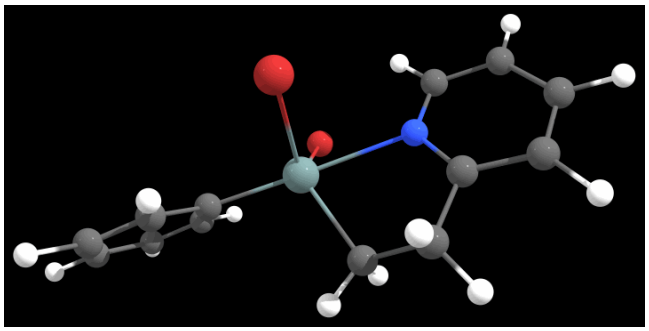
G_{rel} = 2.46 kJ mol^{-1}
Est. fract. abundance = 0.18
Sn-N=2.480 Å, Sn-Br=2.588 Å, Sn-Br'=2.537 Å, Sn-C(Ph)=2.149 Å

Conformer 8-D



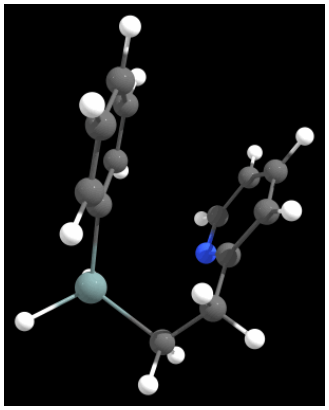
G_{rel} = 5.05 kJ mol^{-1}
Est. fract. abundance = 0.06
Sn-N=2.538 Å, Sn-Br=2.584 Å, Sn-Br'=2.529 Å, Sn-C(Ph)=2.149 Å

Conformer 8-E



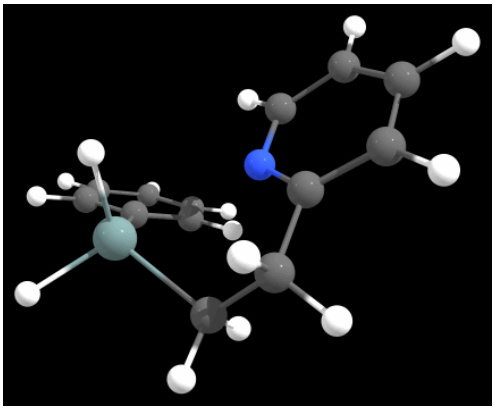
G_{rel} = 19.4 kJ mol^{-1}
Est. fract. abundance = 0.0002
Sn-N=2.517 Å, Sn-C(Ph)=2.171 Å, Sn-Br =2.557 Å, 2.555 Å

Conformer 9-A



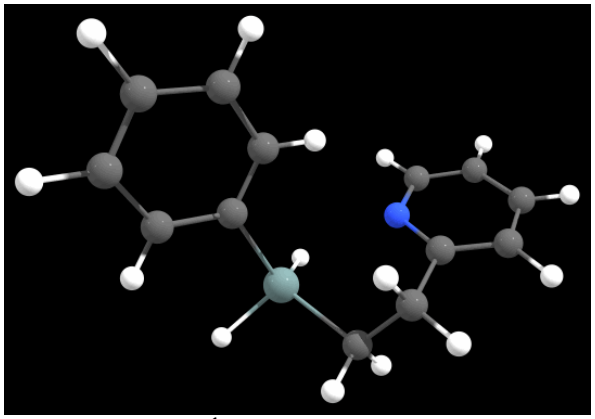
G= -773.182769 Ha, G_{rel} = 0.0 kJ mol^{-1}
Est. fract. abundance = 0.33
Sn-N=3.154 Å, Sn-H=1.723 Å, Sn-H'=1.708 Å, Sn-C(Ph)=2.153 Å

Conformer 9-B



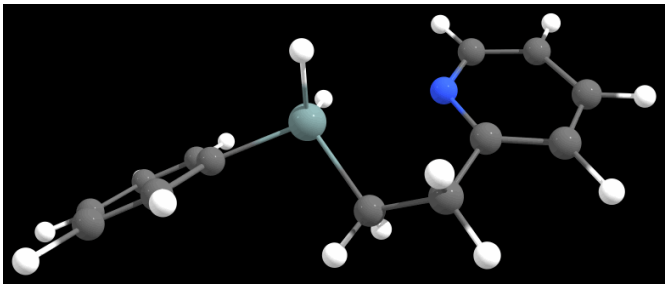
G_{rel} = 0.44 kJ mol^{-1}
Est. fract. abundance = 0.28
Sn-N=2.873 Å, Sn-H=1.736 Å, Sn-H'=1.715 Å, Sn-C(Ph)=2.155 Å

Conformer 9-C



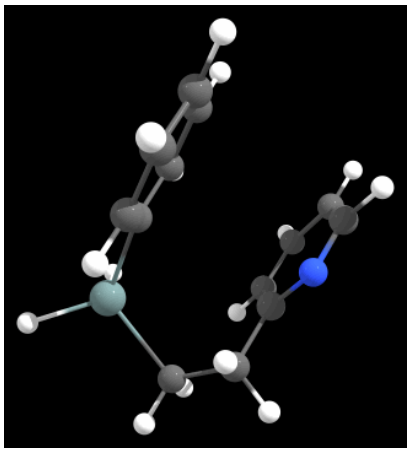
G_{rel} = 0.54 kJ mol^{-1}
Est. fract. abundance = 0.27
Sn-N=2.930 Å, Sn-H=1.736 Å, Sn-H'=1.710 Å, Sn-C(Ph)=2.157 Å

Conformer 9-D



G_{rel} = 2.48 kJ mol^{-1}
Est. fract. abundance = 0.12
Sn-N=2.849 Å, Sn-C(Ph)=2.173 Å, Sn-H=1.712 Å, 1.713 Å

Conformer 9-E



G_{rel} = 10.3 kJ mol^{-1}
Est. fract. abundance = 0.005
Sn-N=4.381 Å, Sn-H=1.715 Å, Sn-H'=1.714 Å,
Sn-C(Ph)=2.146 Å

References

(1) Mahon, M. F.; Molloy, K. C.; Waterfield, P. C. Synthesis, Characterization, and Reaction Chemistry of [2-(2-Pyridyl)Ethyl]-, [2-(4-Pyridyl)Ethyl]-, and [2-(2-Oxo-IV-Pyrrolidinyl)Ethyl]Triphenyltin(IV). *Organometallics* **1993**, *12*, 769–774.

(2) Zickgraf, A.; Beuter, M.; Kolb, U.; Dräger, M.; Tozer, R.; Dakternieks, D.; Jurkschat, K. Nucleophilic Attack within Ge, Sn and Pb Complexes Containing $Me_2N(CH_2)_3$ - As a Potential Intramolecular Donor Ligand. *Inorganica Chim Acta* **1998**, *275–276*, 203–214. https://doi.org/10.1016/s0020-1693(98)00071-1.