Electronic Supplementary Information

Generation of Stannabenzenes and Their Monomer-Dimer Equilibration

Yoshiyuki Mizuhata,*[a,b] Shiori Fujimori,[a] Naoya Noda,[a] Shuhei Kanesato,[a] and Norihiro Tokitoh *[a,b]

[a]*Institute for Chemical Research, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan*

[b]*Integrated Research Consortium on Chemical Sciences, Gokasho, Uji, Kyoto 611-0011, Japan*

tokitoh@boc.kuicr.kyoto-u.ac.jp (NT)

mizu@boc.kuicr.kyoto-u.ac.jp (YM)

Tel: +81-774-38-3200

Fax: +81-774-38-3209

Table of Contents

1. NMR Spectra of All New Compounds

Figure S1. ^{1}H NMR spectrum (300 MHz, 298 K, C_6D_6) of **8a**.

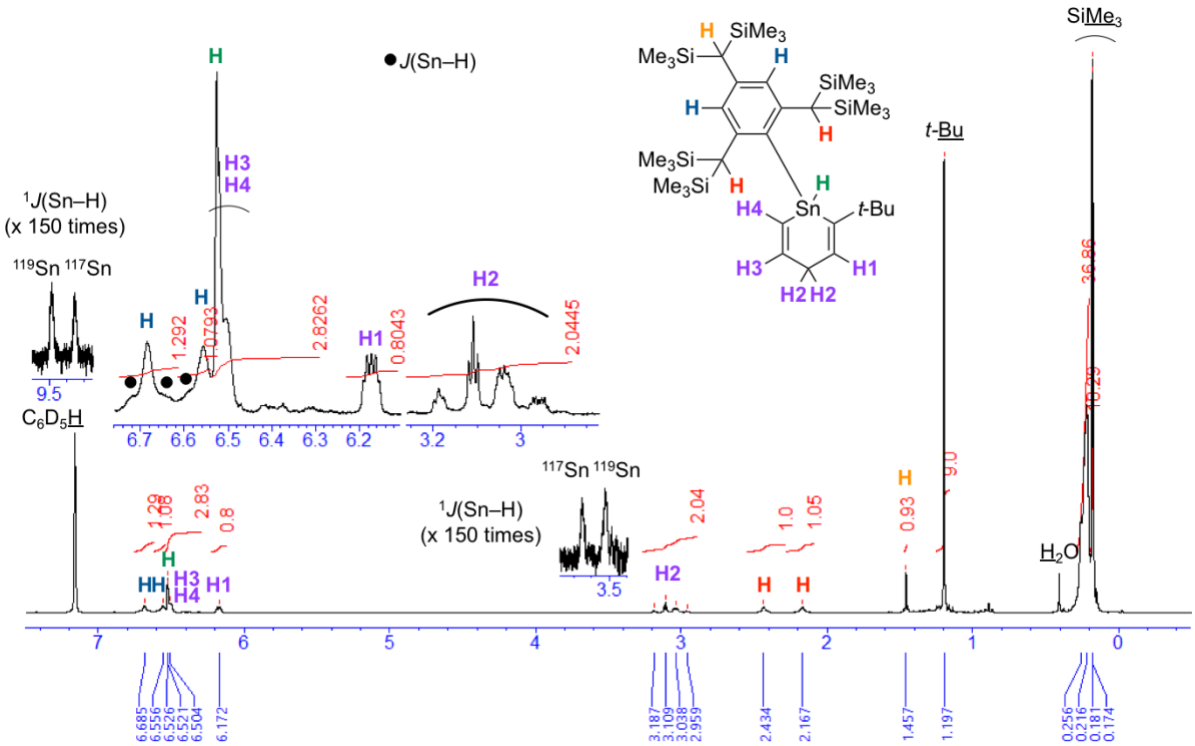


Figure S2. ^{1}H NMR spectrum (300 MHz, 298 K, C_6D_6) of **8b**.

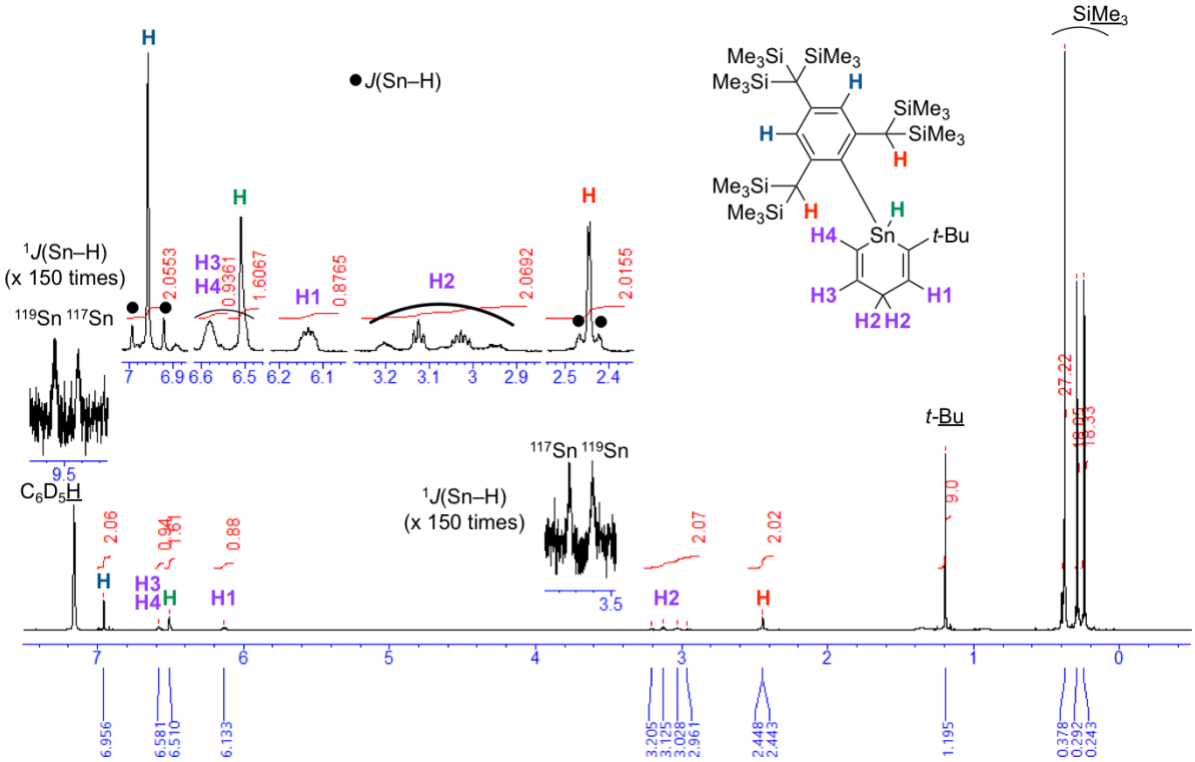


Figure S3. ^{1}H NMR spectrum (300 MHz, 298 K, C_6D_6) of **5a**.

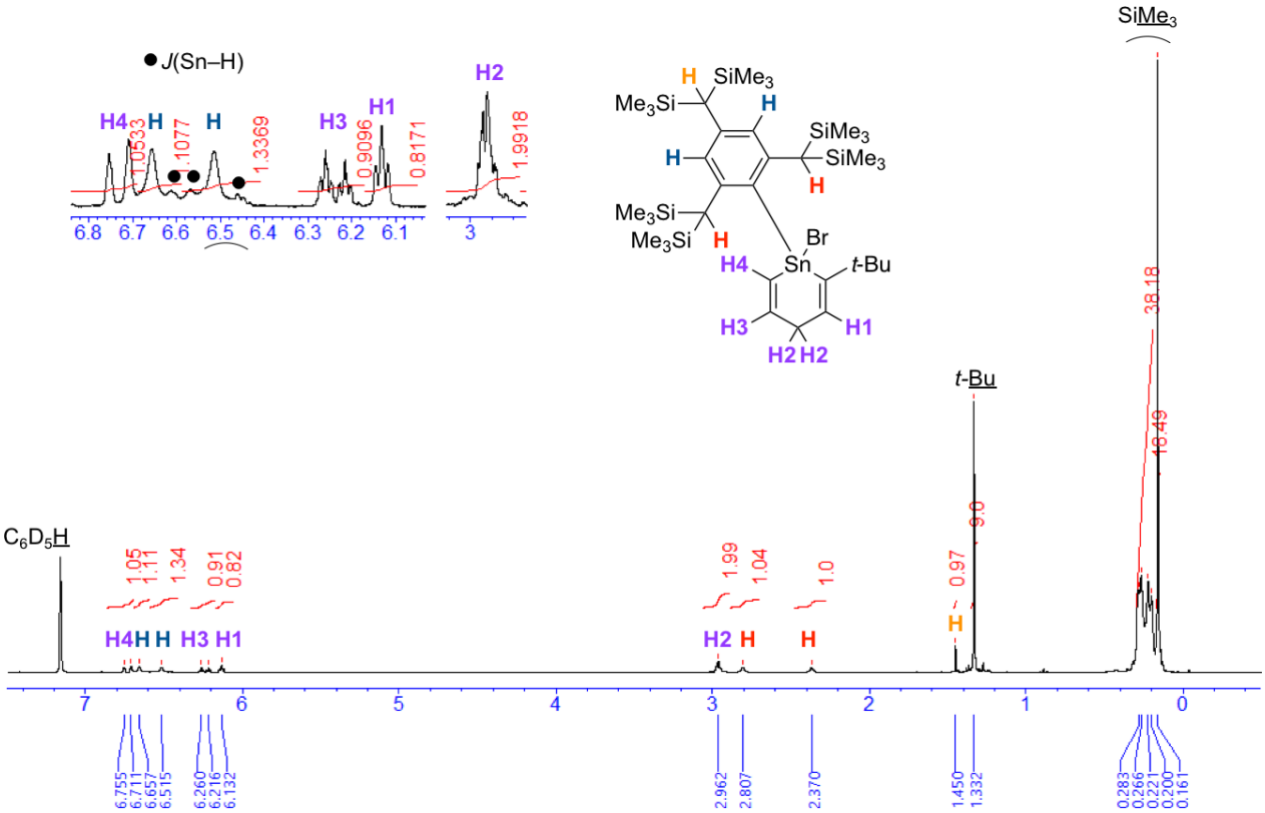


Figure S4. ^{1}H NMR spectrum (300 MHz, 298 K, C_6D_6) of **5b**.

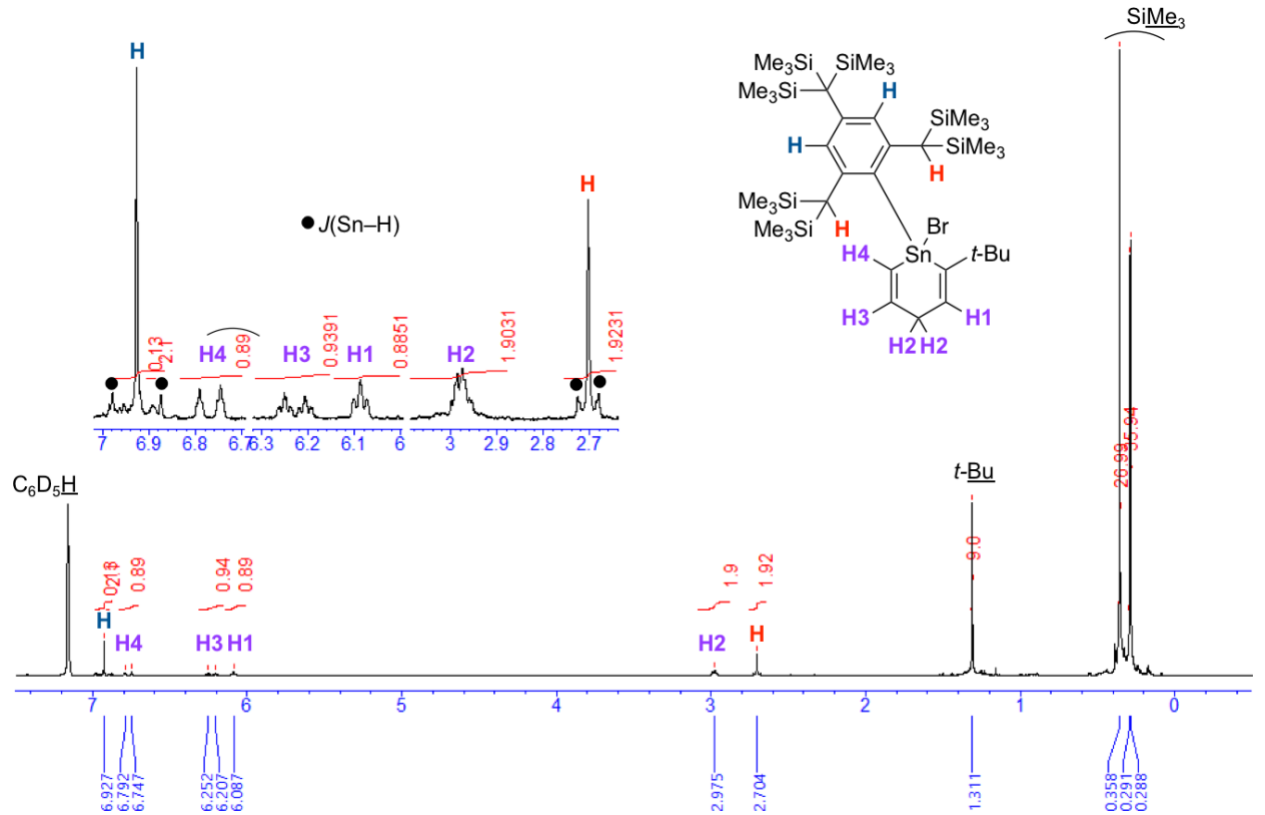


Figure S5. ^{1}H NMR spectrum of the mixture of **3a** and **4a** at various temperature (300 MHz, benzene-d_6).

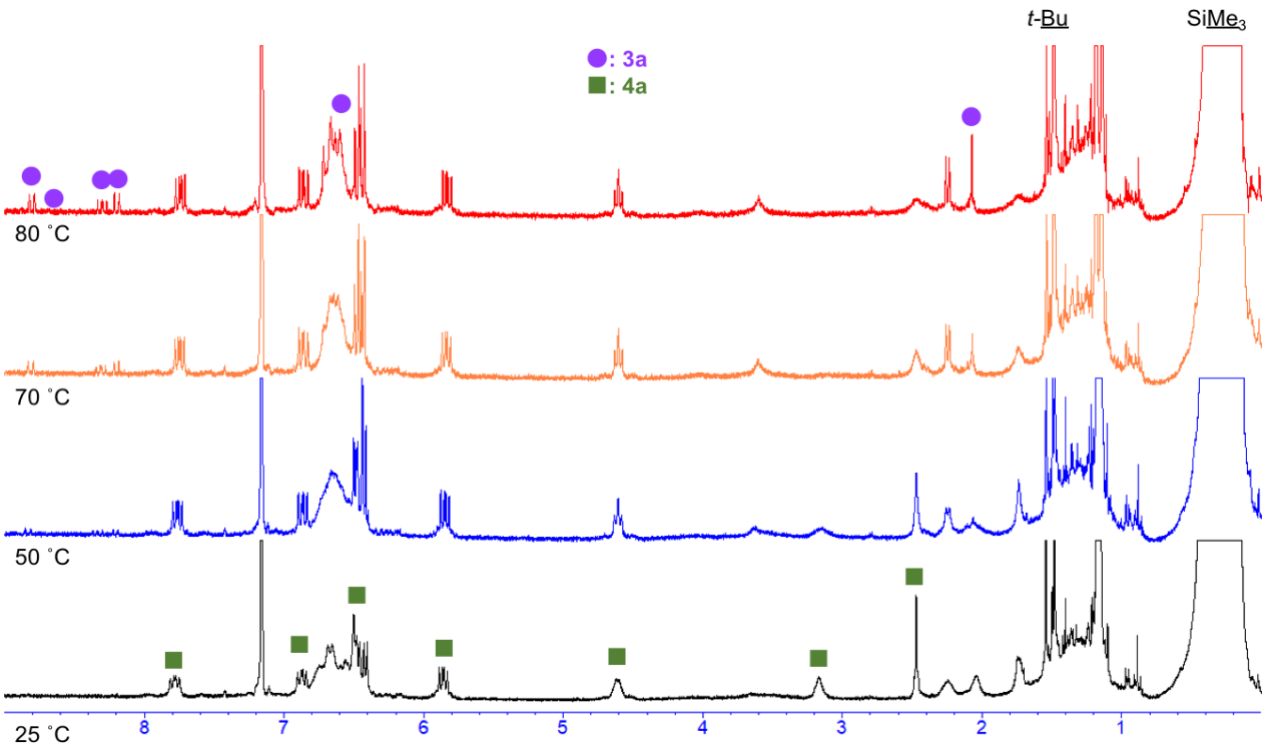


Figure S6. ^{1}H NMR spectrum of the mixture of **3b** and **4b** at various temperature (300 MHz, benzene-d_6).

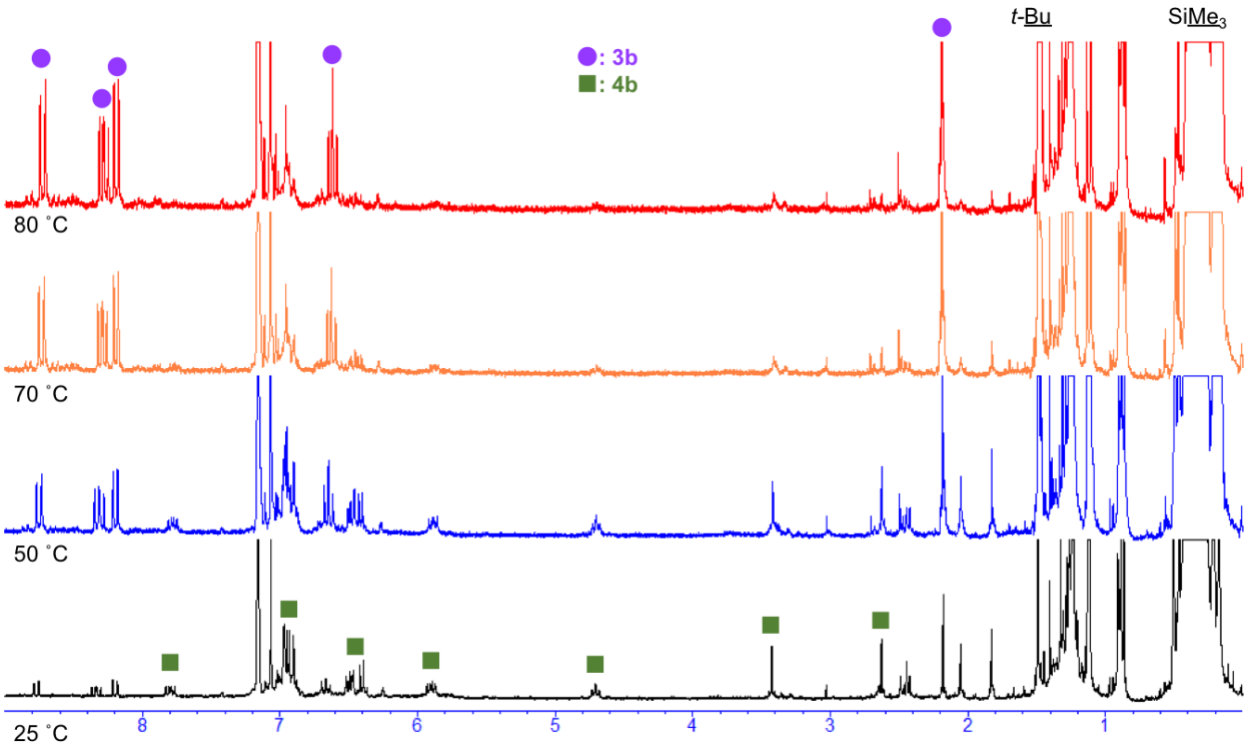


Figure S7. ^{1}H NMR spectrum (300 MHz, 353 K, C_6D_6) of **3b**.

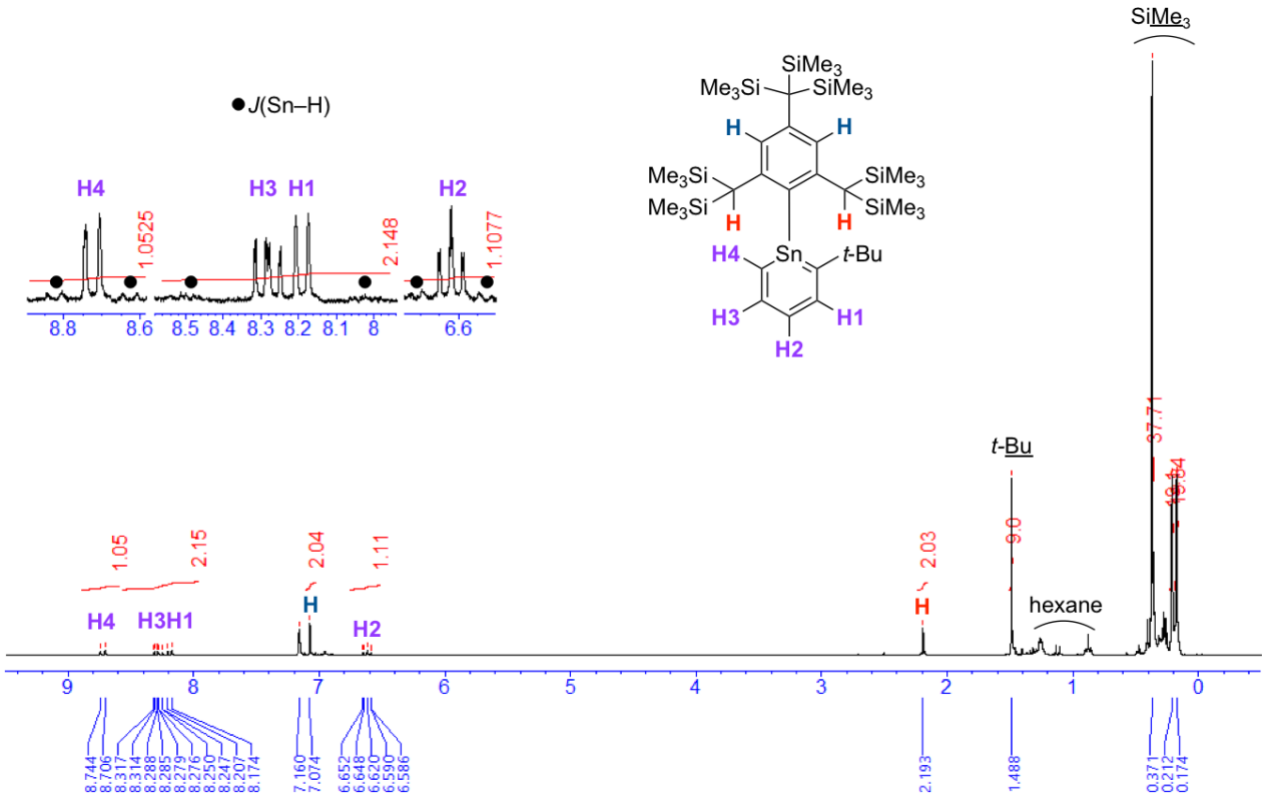


Figure S8. ^{13}C NMR spectrum (201 MHz, 343 K, C_6D_6) of **3b**.

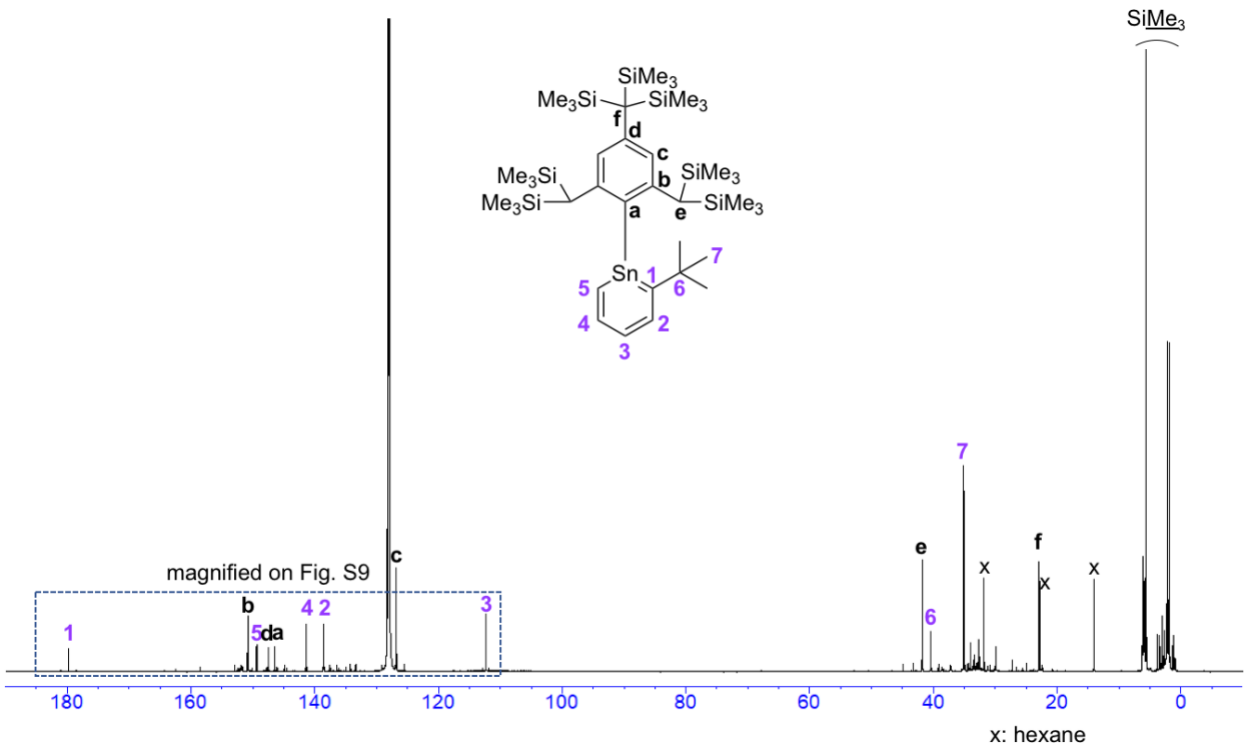


Figure S9. ^{13}C NMR spectrum (201 MHz, 343 K, C_6D_6) of **3b**.

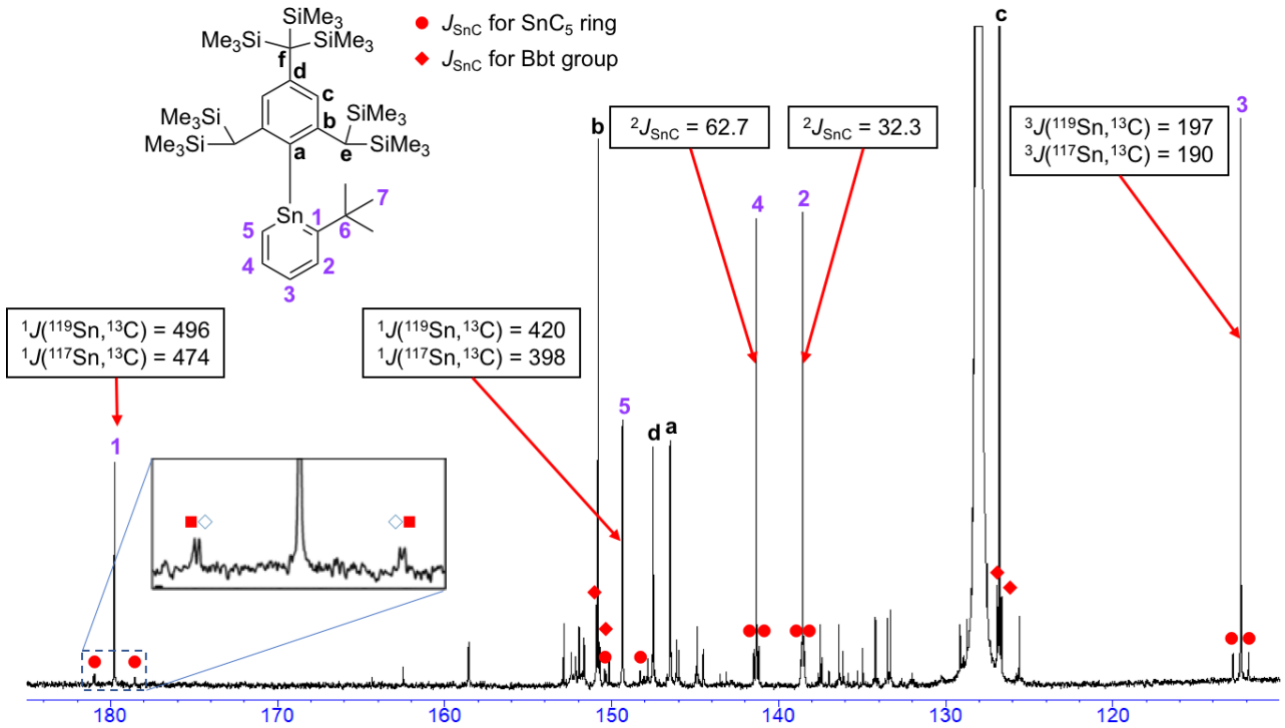
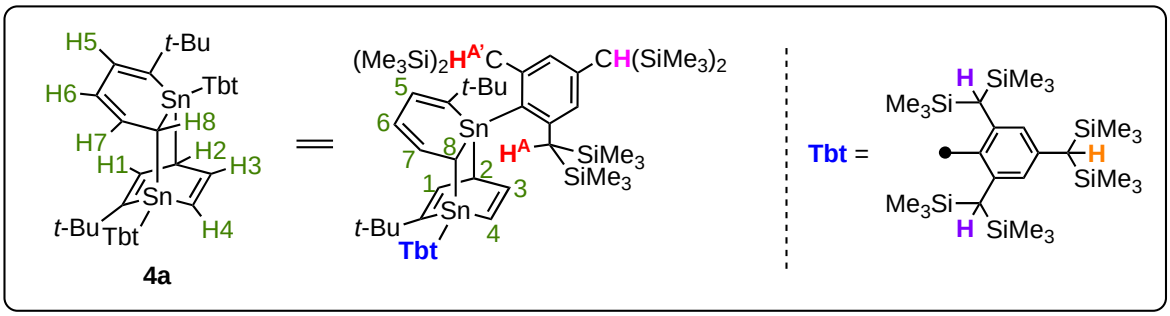


Figure S10. (a)–(h) Differential NOE measurement of **4a** (600 MHz, 298 K, C_6D_6). (i) ^1H NMR spectrum of **4a** (600 MHz, 298 K, C_6D_6).



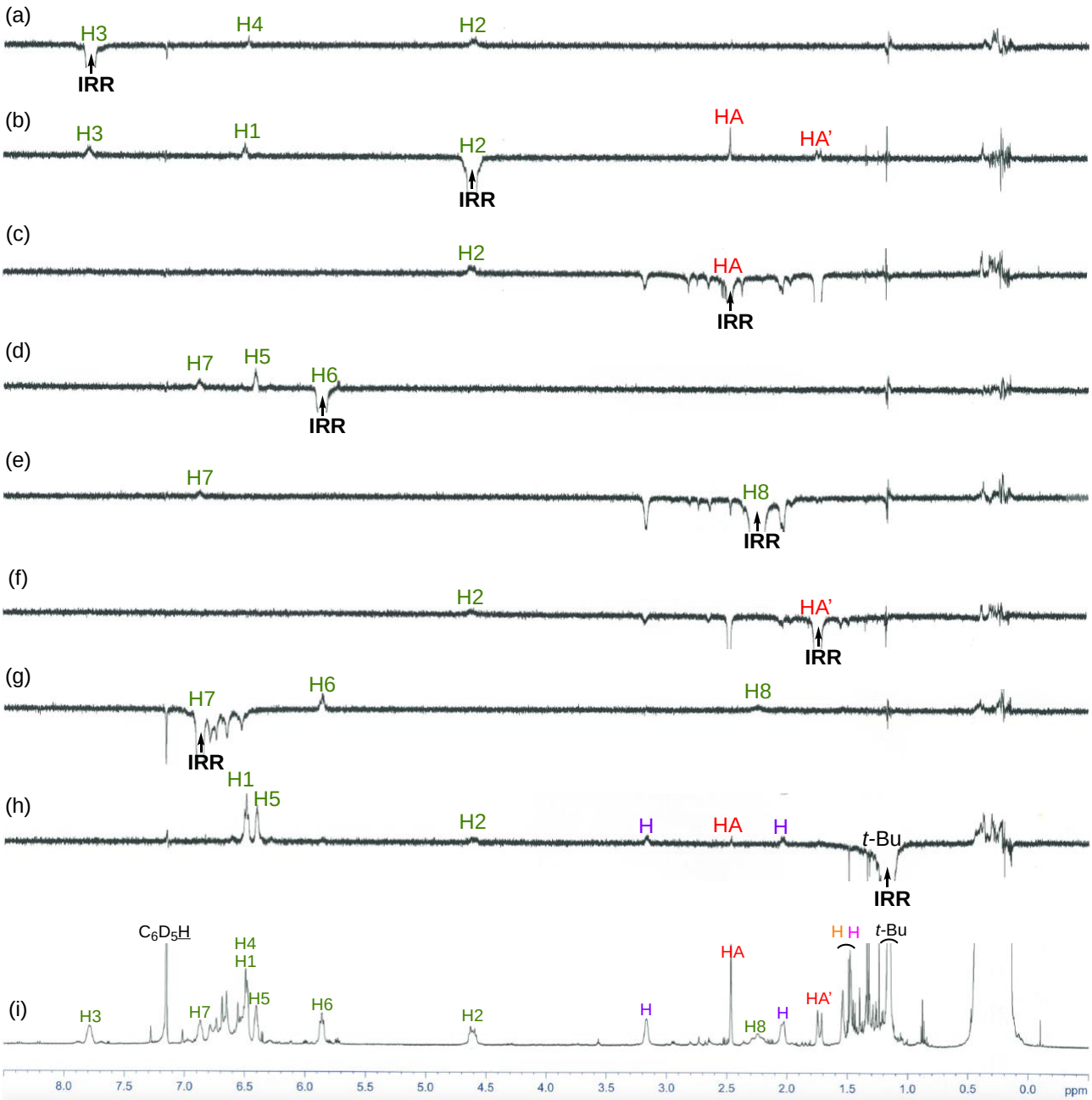


Figure S11. ^{1}H–^{1}H COSY NMR spectrum (600 MHz, 343 K, C_6D_6) of **4a**.

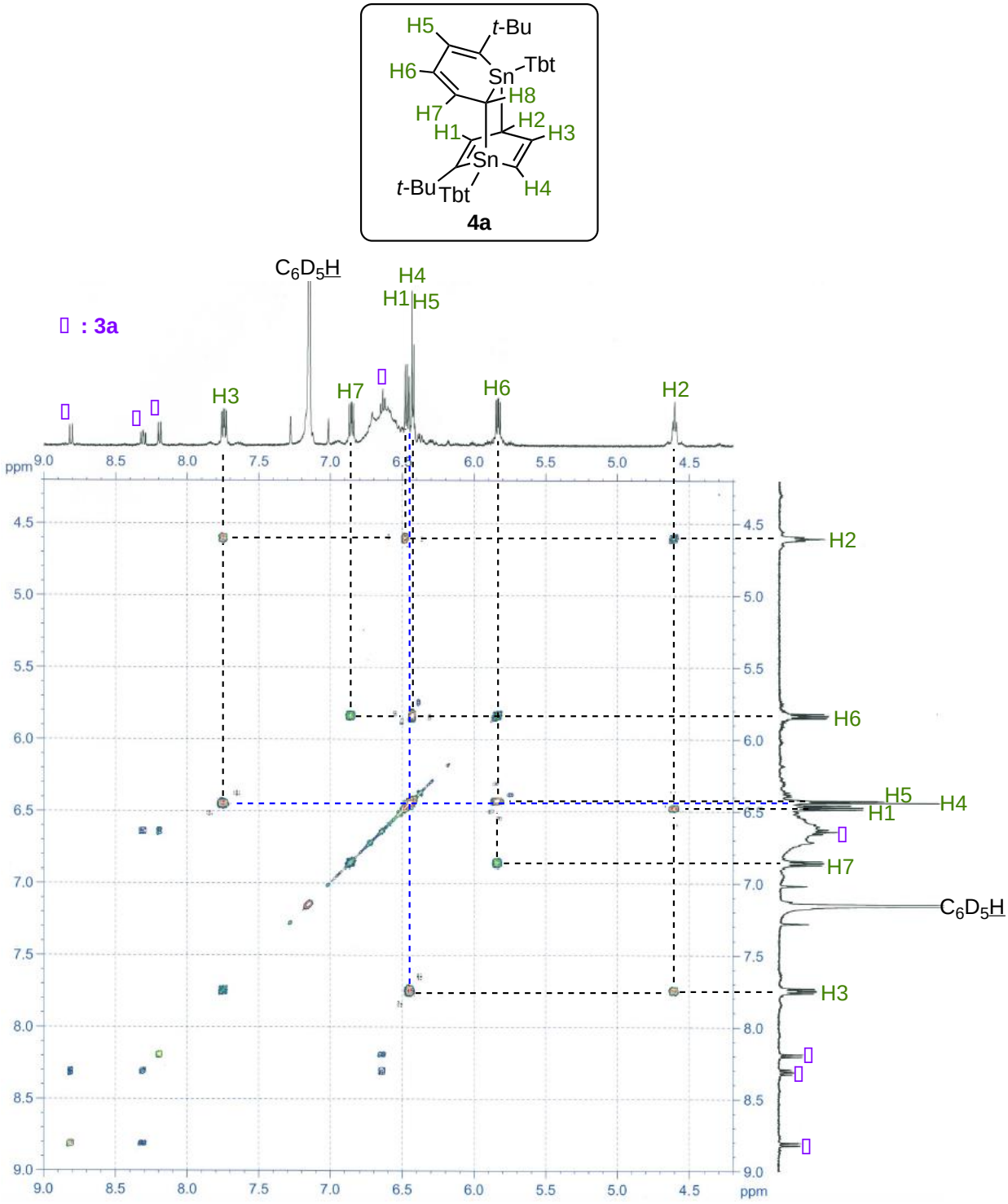


Figure S12. ^{1}H–^{1}H COSY NMR spectrum (600 MHz, 343 K, C_6D_6) of **4a**.

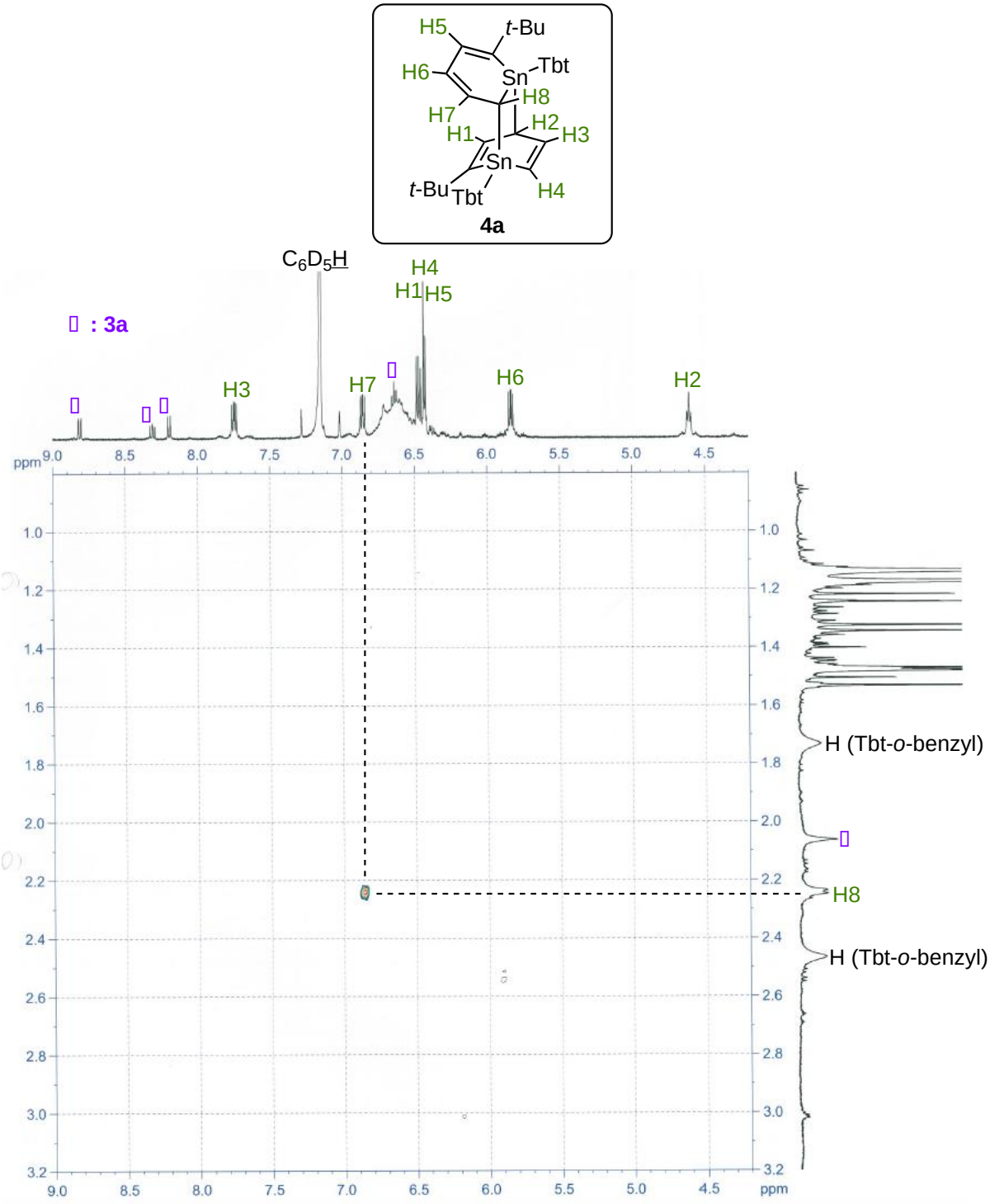


Figure S13. ^{1}H–^{13}C HSQC NMR spectrum (600 MHz, 343 K, C_6D_6) of **4a**.

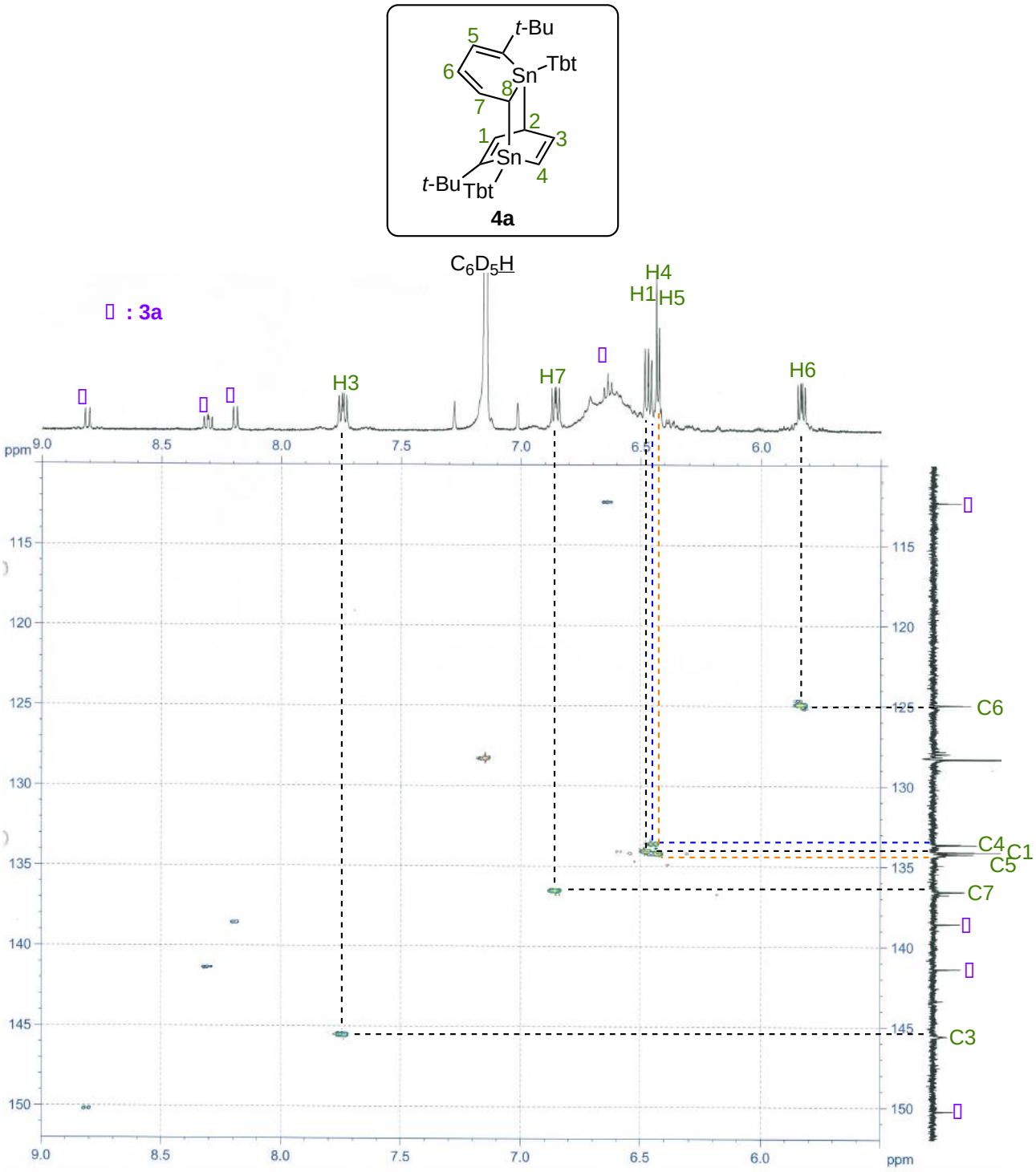
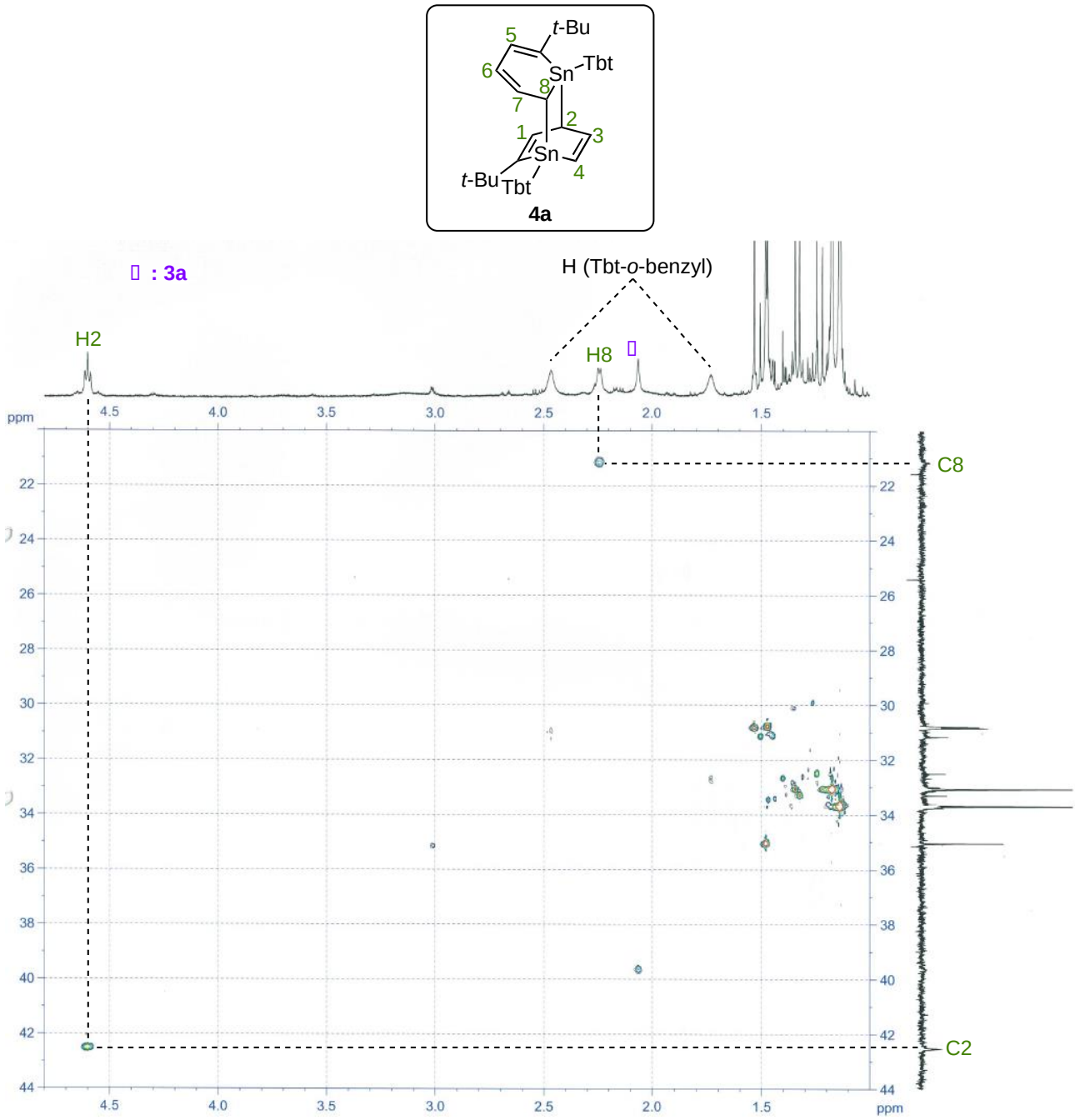


Figure S14. ^{1}H–^{13}C HSQC NMR spectrum (600 MHz, 343 K, C_6D_6) of **4a**.



2. Equilibrium between Stannabenzene Monomer and Dimer

Table S1. Equilibrium constants K_{eq} between **3a** and **4a** in benzene-d_6 at various temperatures[a]

Temp/°C	[**3a**]/M^{-1}	[**4a**]/M^{-1}	K_{eq}/M^{-1}
50	0.000708	0.00249	4960
55	0.000909	0.00239	2890
60	0.00112	0.00228	1810
65	0.00141	0.00213	1070
70	0.00171	0.00199	679

[a] Equilibrium constants (K_{eq} = [**4a**]/[**3a**]^2) were calculated by integral ratio of ^{1}H NMR signals.

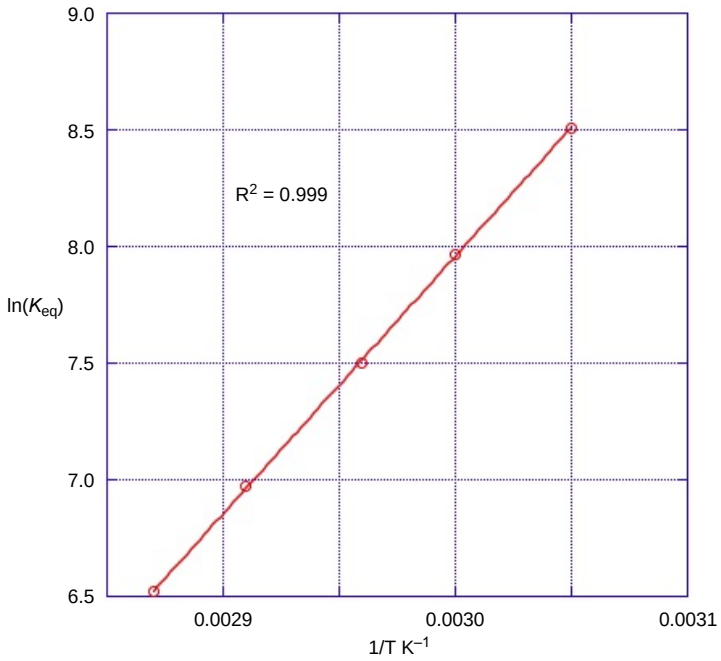


Figure S15. A plot of ln(K_{eq}) vs 1/T.

Table S2. Equilibrium constants K_{eq} between **3a** and **4a** in THF-d_8 at various temperatures[a]

Temp/°C	[**3a**]/M^{-1}	[**4a**]/M^{-1}	K_{eq}/M^{-1}
40	0.000530	0.00699	24900
45	0.000723	0.00690	13200
50	0.000944	0.00679	7620
55	0.00120	0.00666	4590
60	0.00150	0.00651	2910

[a] Equilibrium constants (K_{eq} = [**4a**]/[**3a**]^2) were calculated by integral ratio of ^{1}H NMR signals.

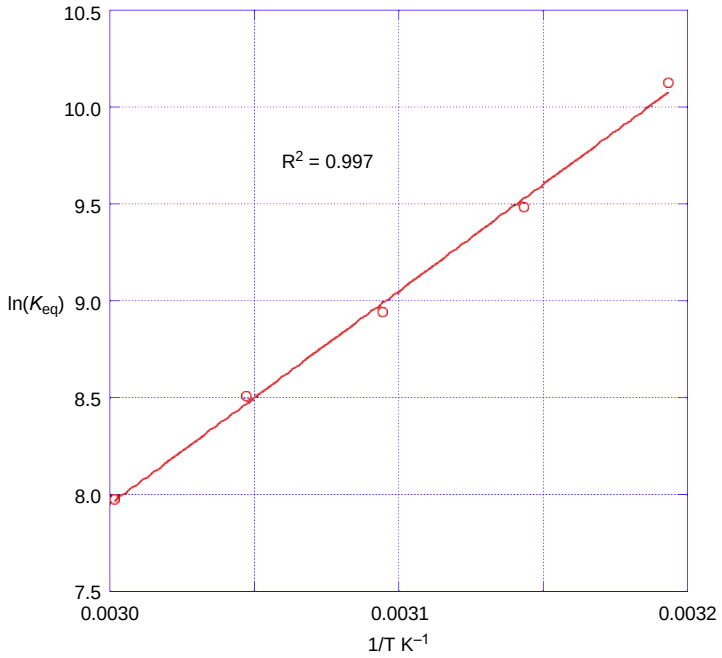


Figure S16. A plot of ln(K_{eq}) vs 1/T.

Table S3. Equilibrium constants K_{eq} between **3b** and **4b** in benzene-d_6 at various temperatures[a]

Temp/°C	[**3b**]/M^{-1}	[**4b**]/M^{-1}	K_{eq}/M^{-1}
30	0.0147	0.0541	250
40	0.0239	0.0494	86.3
50	0.0383	0.0423	28.9
60	0.0539	0.0345	11.9
70	0.0743	0.0243	4.39
80	0.0891	0.0168	2.12

[a] Equilibrium constants (K_{eq} = [**4b**]/[**3b**]^2) were calculated by integral ratio of ^{1}H NMR signals.

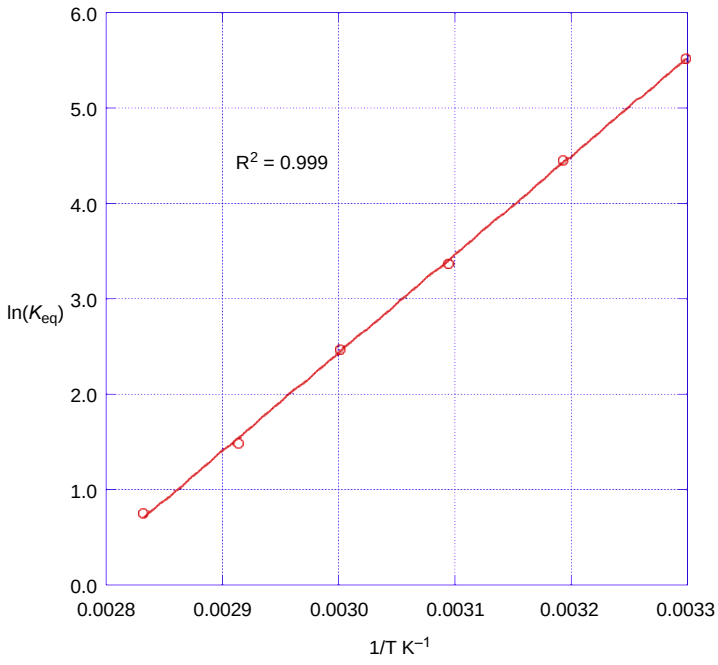


Figure S17. A plot of ln(K_{eq}) vs 1/T.

Table S4. Equilibrium constants K_{eq} between **3b** and **4b** in THF-d_8 at various temperatures[a]

Temp/°C	[**3a**]/M^{-1}	[**4a**]/M^{-1}	K_{eq}/M^{-1}
30	0.0168	0.0530	188
40	0.0288	0.0470	56.6
50	0.0429	0.0400	21.7
60	0.0531	0.0348	12.3
70	0.0632	0.0298	7.46
80	0.0741	0.0244	4.45

[a] Equilibrium constants (K_{eq} = [**4b**]/[**3b**]^2) were calculated by integral ratio of ^{1}H NMR signals.

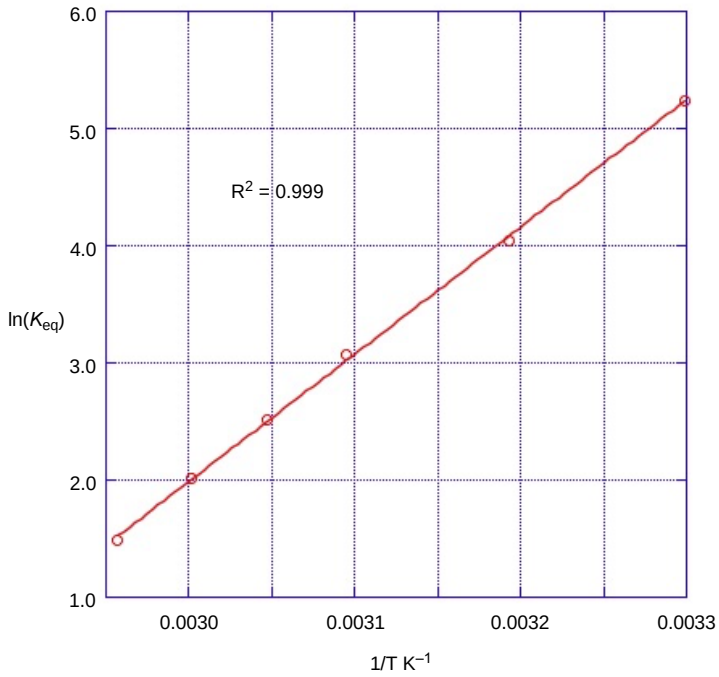


Figure S18. A plot of ln(K_{eq}) vs 1/T.

3. X-Ray Diffraction Studies

Figure S19. Crystal structure of [**4a**•benzene]. Independent part 0 (bold and black lines, occupancy is 1), part –1 (red lines, occupancy is essentially 0.5), and symmetrically expanded part (thin and black lines, except for a benzene molecule).

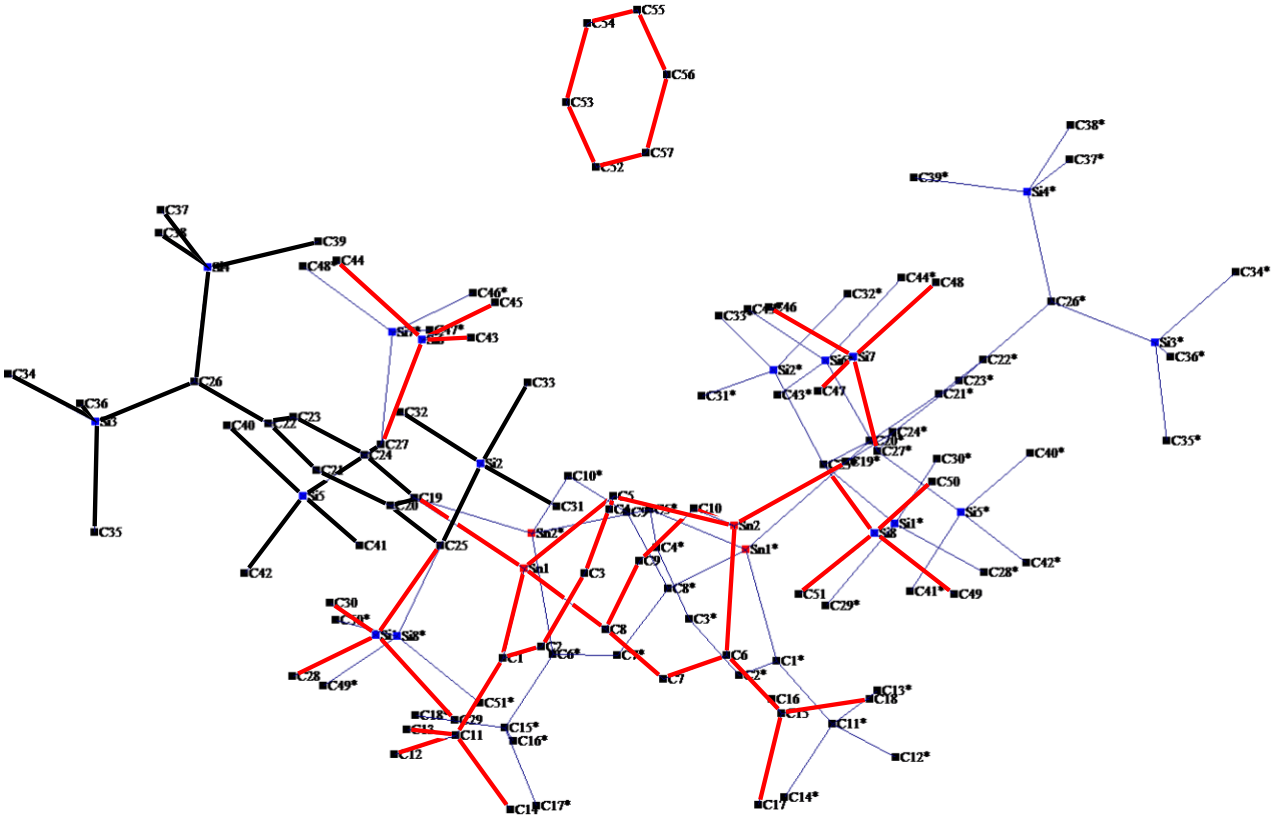
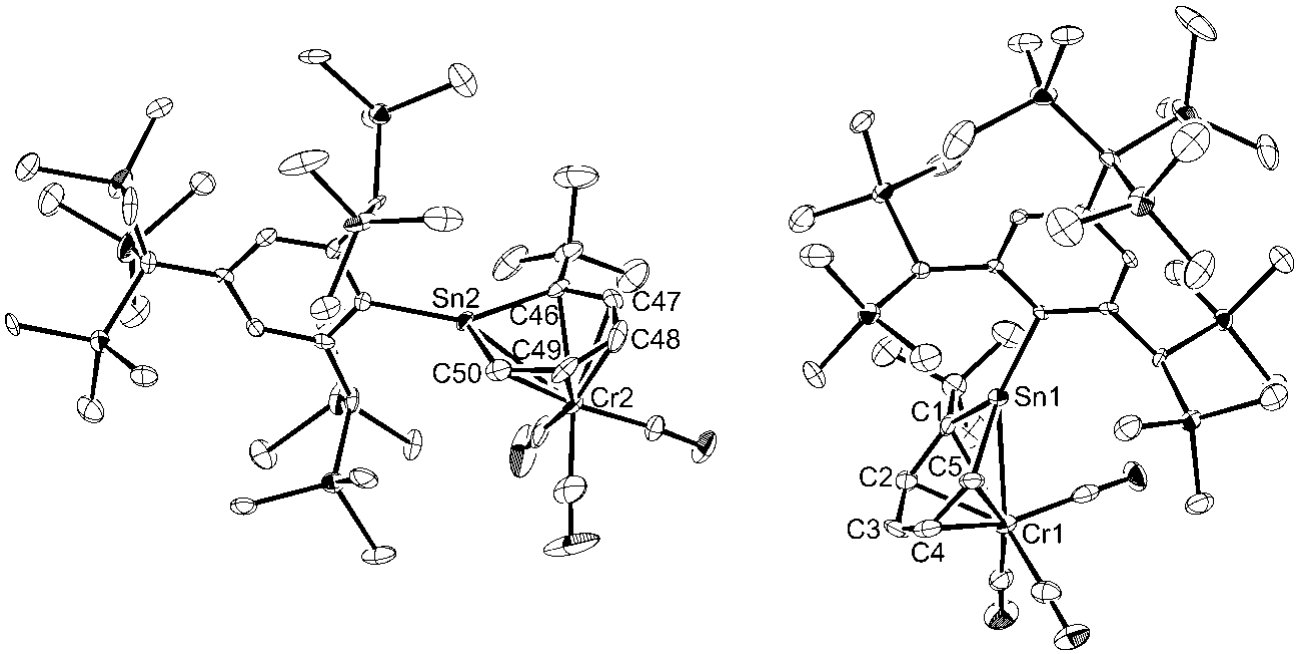


Figure S20. Crystal structure of **6b** (ORTEP drawing; thermal ellipsoids set 50% probability). Hydrogen atoms and disordered part were omitted for clarity.



4. Coordinates (xyz) for the calculated structures

[Sn] head-to-head

C	-1.11632700	1.00845400	1.72752500
C	-0.17083300	2.12596500	-0.37463200
C	-0.45002100	2.00350300	1.12190200
C	-2.21701100	0.82368900	-1.19038100
C	-1.36309100	1.85546200	-1.28675400
C	2.42066300	-1.33472000	0.70830200
C	2.33618500	1.73890200	-0.13765800
C	3.24864700	-0.32956900	1.06255000
C	3.21806200	1.07932400	0.64165600
H	2.59887700	-2.32068300	1.13255800
H	4.07073900	-0.55762600	1.74613100
H	4.04866800	1.66970200	1.02709100
H	2.54475600	2.80181400	-0.29725500
H	-1.47432900	2.57420500	-2.10285200
H	-3.00814900	0.71240700	-1.92858800
H	0.12945000	3.16866800	-0.55023800
H	-1.21773500	1.01210100	2.81029700
H	-0.02337900	2.80944300	1.72305100
Sn	-1.78190800	-0.51556900	0.40684500
H	-2.98296900	-1.61753900	0.92408500
C	1.08551800	1.25042500	-0.81992000
H	1.20111200	1.44236900	-1.89594900
Sn	0.80633300	-0.91017200	-0.59098100
H	0.94099000	-1.73644600	-2.09710000

[Sb] head-to-head

C	-0.92649800	1.14634700	1.60771100
C	0.08548800	2.13794400	-0.48691800
C	-0.19452500	2.08515500	0.99824700
C	-2.01634200	0.92761200	-1.20825000
C	-1.11706700	1.90572000	-1.37410900
C	1.91774100	-1.25371100	1.07513600
C	2.54195400	1.52458900	-0.19149100
C	2.82916500	-0.34992400	1.48291600
C	3.17626600	0.91255700	0.82725400
H	1.78351300	-2.16385300	1.65696100
H	3.40563700	-0.56642900	2.38488600
H	4.05979100	1.40913800	1.22595200
H	2.95922500	2.47742000	-0.52756300
H	-1.20114200	2.57621400	-2.23250900
H	-2.82778400	0.80042600	-1.92129900
H	0.48302900	3.13556900	-0.71584900
H	-1.03319600	1.14880700	2.68993600
H	0.29525500	2.85747100	1.59322800
C	1.26920400	1.13033300	-0.89009400
H	1.40848200	1.28115600	-1.96687800
Sb	-1.86277700	-0.41649500	0.47177300
Sb	0.78973500	-1.03361500	-0.73117100

[Sn] head-to-tail

C	1.19893800	0.19278200	1.89673800
C	0.28824400	-1.90176100	0.78049900
C	0.56579900	-0.99621900	1.94983600
C	2.21480500	-1.21009000	-0.73059300
C	1.39345900	-2.14844700	-0.21239200
C	-0.25069300	0.93777700	-1.04491000
C	-0.93684500	2.19362700	-0.64787500
C	-2.82125300	0.02335700	0.70738700
C	-1.98924600	2.37227100	0.18991100
C	-2.84687700	1.37311900	0.82727100
H	-0.00292100	0.94806400	-2.11223800
H	-0.52024800	3.10638600	-1.08236200
H	-2.28737500	3.40246700	0.37691400
H	-3.63992800	1.81127300	1.43945000
H	-3.59394800	-0.55029200	1.21489400
H	1.48123800	-3.18793100	-0.53906900
H	2.98209800	-1.50366900	-1.44204300
H	-0.12653500	-2.85118200	1.12557900
H	1.34246000	0.76785300	2.80698200
H	0.16396400	-1.35552200	2.90051400
Sn	1.73191000	0.73392300	-0.06752700
H	2.79852000	2.04587900	-0.34872000
Sn	-1.28606800	-0.84818700	-0.43181300
H	-1.78742900	-1.93863600	-1.66813100

[Sb] head-to-tail

C	1.16314200	0.26363500	1.79651900
C	-0.05382400	-1.79742400	1.03672300
C	0.31733100	-0.76091100	2.01853100
C	1.92022100	-1.57159500	-0.49930100
C	0.97183900	-2.31595400	0.10399000
C	-0.16894200	0.79916100	-1.06044100
C	-0.56552200	2.18992200	-0.75991400
C	-2.61085700	0.49815600	0.84874600
C	-1.48316300	2.63344700	0.13302400
C	-2.40310700	1.83145400	0.92658800
H	0.08282600	0.68215600	-2.11814500
H	0.00204000	2.95682000	-1.29192700
H	-1.57707700	3.71069300	0.25498300
H	-3.01860700	2.40399600	1.62454100
H	-3.38179500	0.05351400	1.47583800
H	0.88887000	-3.37952300	-0.13238600
H	2.62210700	-2.03659000	-1.18726600
H	-0.64862100	-2.59644900	1.48011200
H	1.36310800	0.98651700	2.58256700
H	-0.19487700	-0.83454700	2.98020900
Sb	-1.56080000	-0.77421100	-0.49960400
Sb	1.97921800	0.52782000	-0.14618700

2-t-Bu-stannabenzene [$HSnC_5(t\text{-}Bu)H_4$]

C	-1.07338700	2.33715700	0.00003700
C	0.21450400	1.77353800	0.00000900
C	0.62199400	0.43279700	-0.00005200
C	-2.55961900	0.31310200	-0.00013000
C	-2.31860700	1.68576600	-0.00002000
H	-1.10649000	3.42420800	0.00006900
H	1.01804900	2.51393600	0.00000100
H	-3.58872600	-0.03348500	-0.00014500
H	-3.18994600	2.34395100	0.00001000
Sn	-0.93555900	-0.88315900	0.00001700
H	-0.93220900	-2.58087900	-0.00005200
C	2.11753600	0.08321800	-0.00000900
C	2.79593700	0.66790000	-1.26289500
H	3.86643800	0.42709700	-1.26980400
H	2.34636800	0.25583800	-2.17340900
H	2.69857800	1.75757900	-1.30721900
C	2.33404600	-1.44103200	-0.00085500
H	3.40337200	-1.68232400	-0.00051800
H	1.89246200	-1.90897700	0.88840400
H	1.89323900	-1.90790400	-0.89106000
C	2.79547500	0.66650400	1.26379100
H	3.86592900	0.42551700	1.27088300
H	2.69819100	1.75614900	1.30906200
H	2.34543300	0.25356600	2.17366100

5 Author Contributions

Y.M. conceived and designed the work, carried out the X-ray diffraction analyses, performed the DFT calculations, and analyzed the computational data. S.F., N.N., and S.K. performed the experiments and analyzed the experimental data. Y.M., S.F., and N.T. co-wrote the paper.