# Reversible Addition of Tin(II) Amides to Nitriles

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## TABLE OF CONTENTS

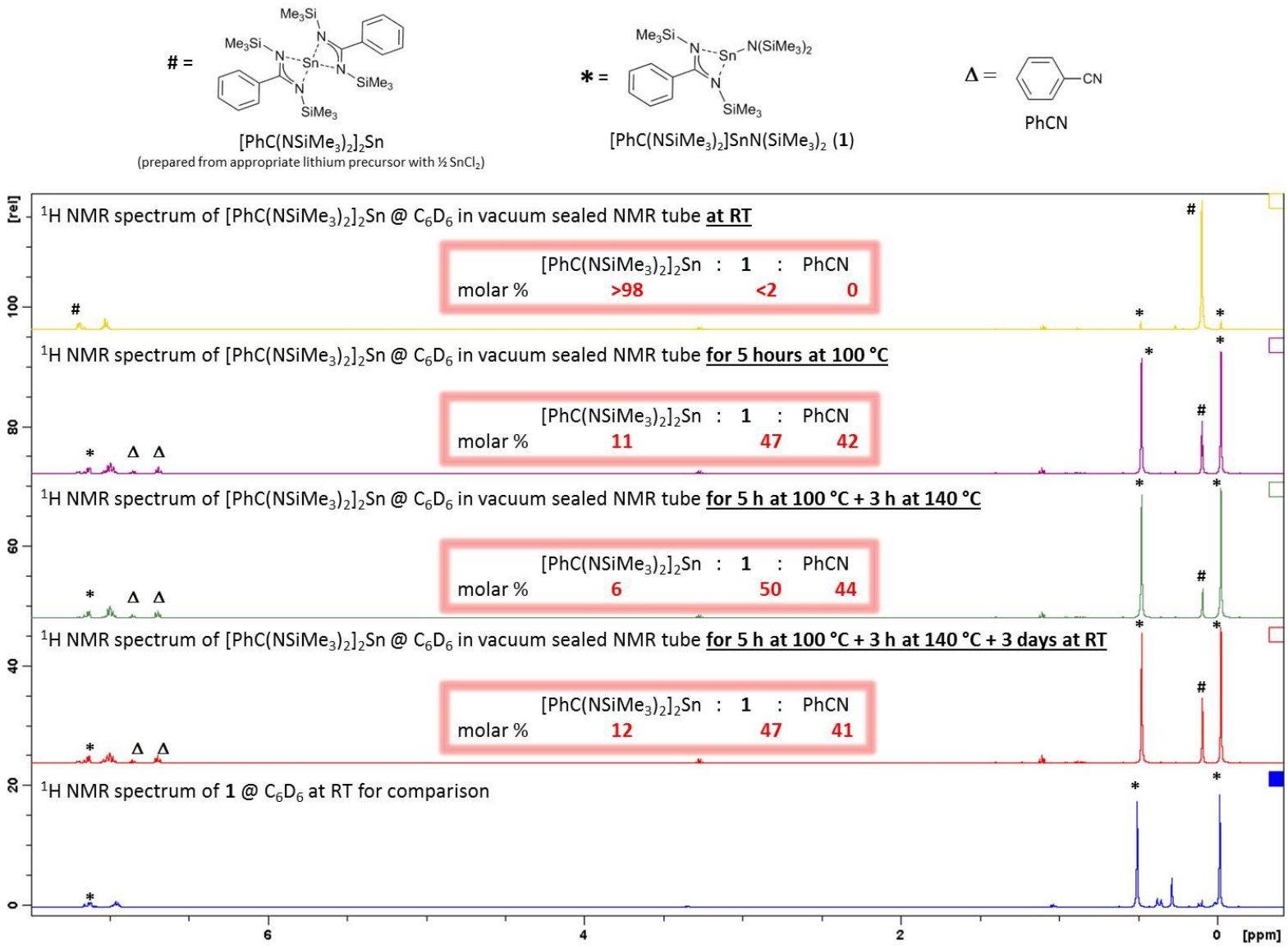


**Fig. S1A** $^1$H NMR spectral study of elimination of $[PhC(NSiMe_3)_2]SnN(SiMe_3)_2$ (**1**) and PhCN from heated $[PhC(NSiMe_3)_2]_2Sn$ (prepared from appropriate lithium precursor with ½ $SnCl_2$) @ $C_6D_6$ in vacuum sealed NMR tube and their reverse addition. $^1$H NMR spectrum of pure **1** @ $C_6D_6$ at RT is attached for comparison.

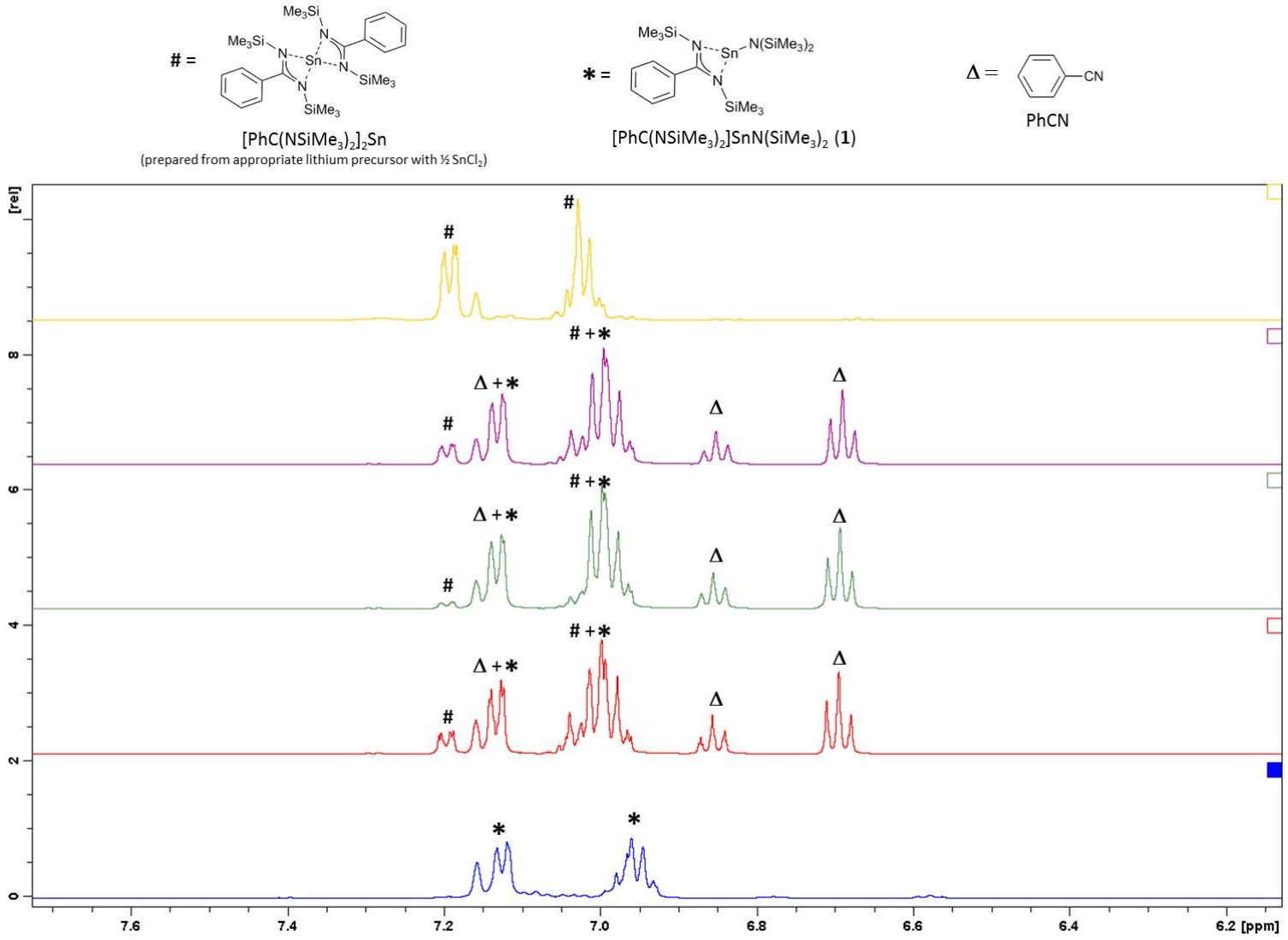


**Fig. S1B** Detail of aromatic part of $^{1}H$ NMR spectral study of elimination of $[PhC(NSiMe_3)_2]SnN(SiMe_3)_2$ (**1**) and PhCN from heated $[PhC(NSiMe_3)_2]_2Sn$ (prepared from appropriate lithium precursor with ½ $SnCl_2$) @ $C_6D_6$ in vacuum sealed NMR tube and their reverse addition. $^{1}H$ NMR spectrum of pure **1** @ $C_6D_6$ at RT is attached for comparison.

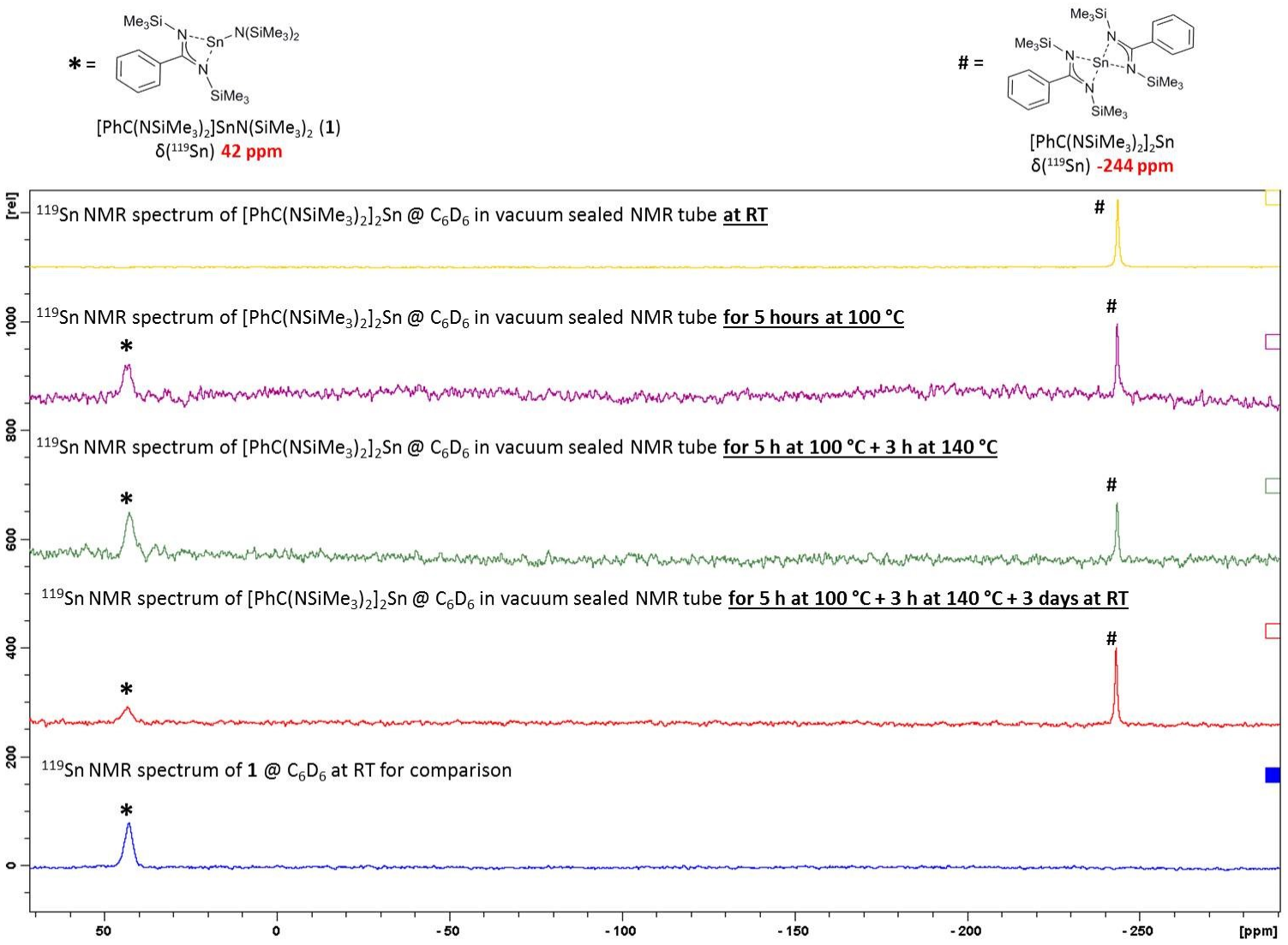


**Fig. S1C** $^{119}$Sn NMR spectral study of elimination of $[PhC(NSiMe_3)_2]SnN(SiMe_3)_2$ (**1**) and PhCN from heated $[PhC(NSiMe_3)_2]_2Sn$ (prepared from appropriate lithium precursor with ½ $SnCl_2$) @ $C_6D_6$ in vacuum sealed NMR tube and their reverse addition. $^{119}$Sn NMR spectrum of pure **1** @ $C_6D_6$ at RT is attached for comparison.

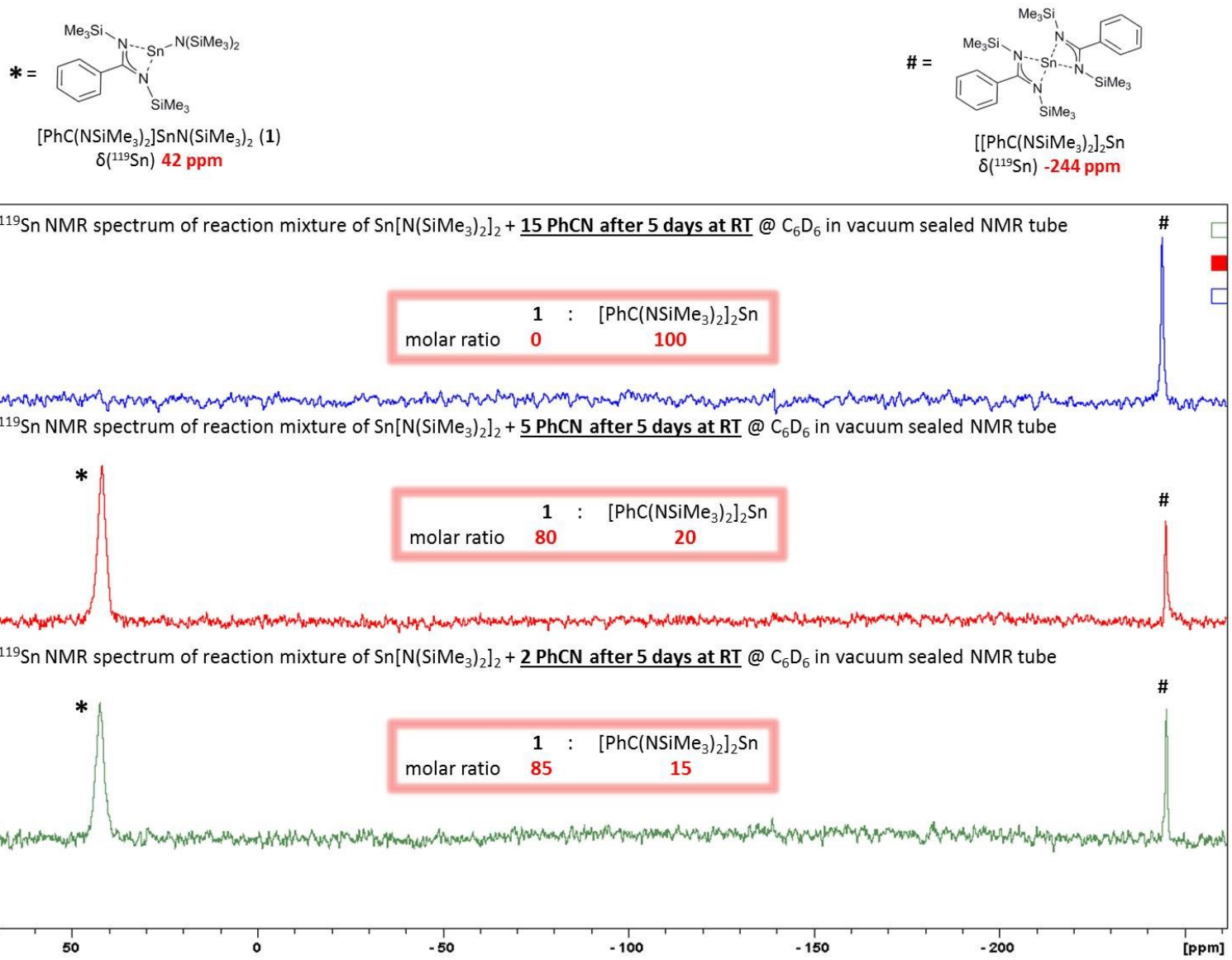


**Fig. S2** Molar fraction (in %; benzonitrile in the mixture is not taken into account) of **1** and ($[PhC(NSiMe_3)_2]_2Sn$) from the reaction mixtures of $Sn[N(SiMe_3)_2]_2$ with various amount of benzonitrile after 5 days at room temperature in the $^{119}Sn$ NMR spectra at $C_6D_6$ in vacuum sealed NMR tube.

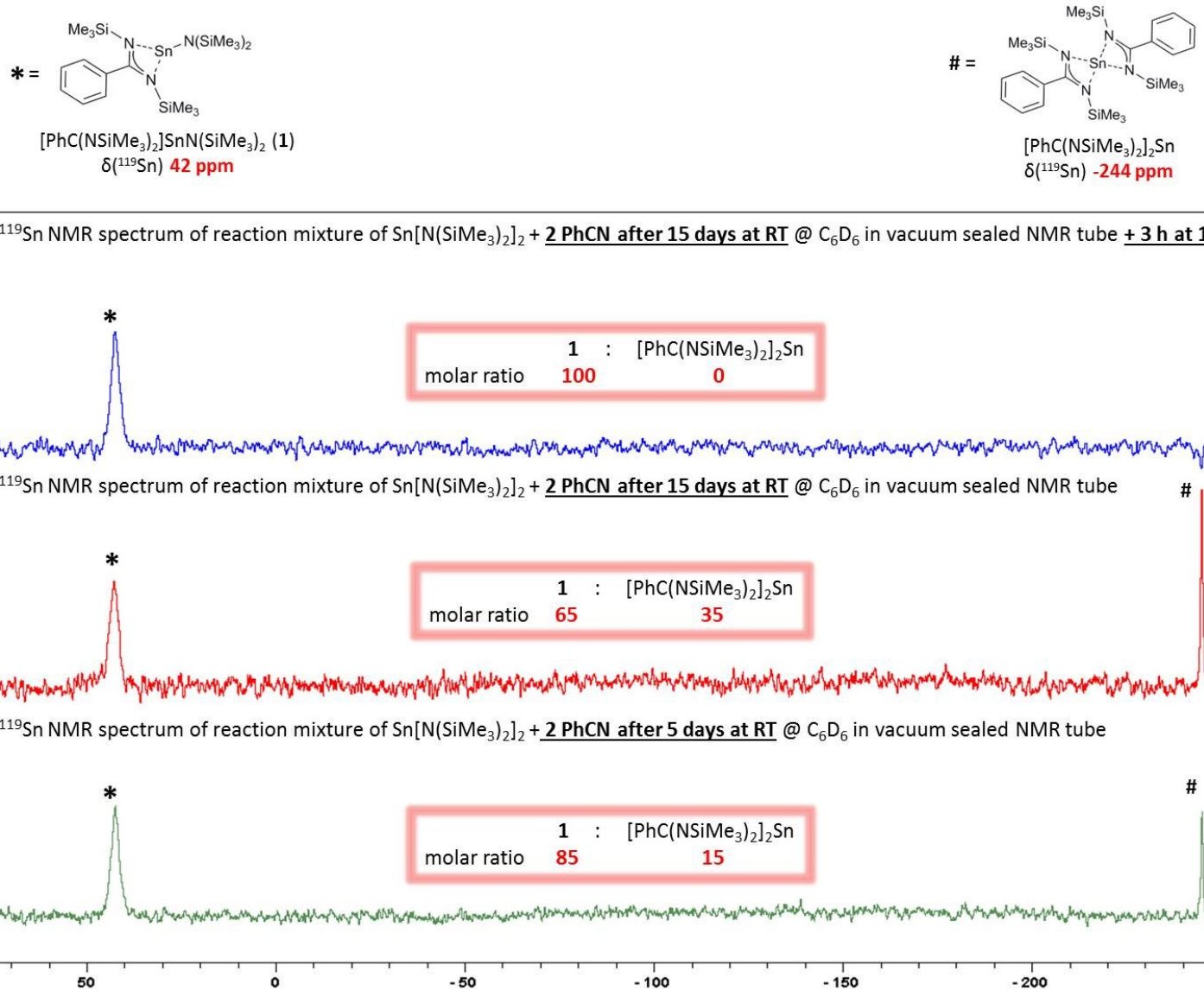


**Fig. S3** Molar fraction (in %; benzonitrile in the mixture is not taken into account) of **1** and ($[PhC(NSiMe_3)_2]_2Sn$) from the reaction mixtures of $Sn[N(SiMe_3)_2]_2$ with 2 equivalents of benzonitrile in time in the $^{119}Sn$ NMR spectra at $C_6D_6$ in vacuum sealed NMR tube.

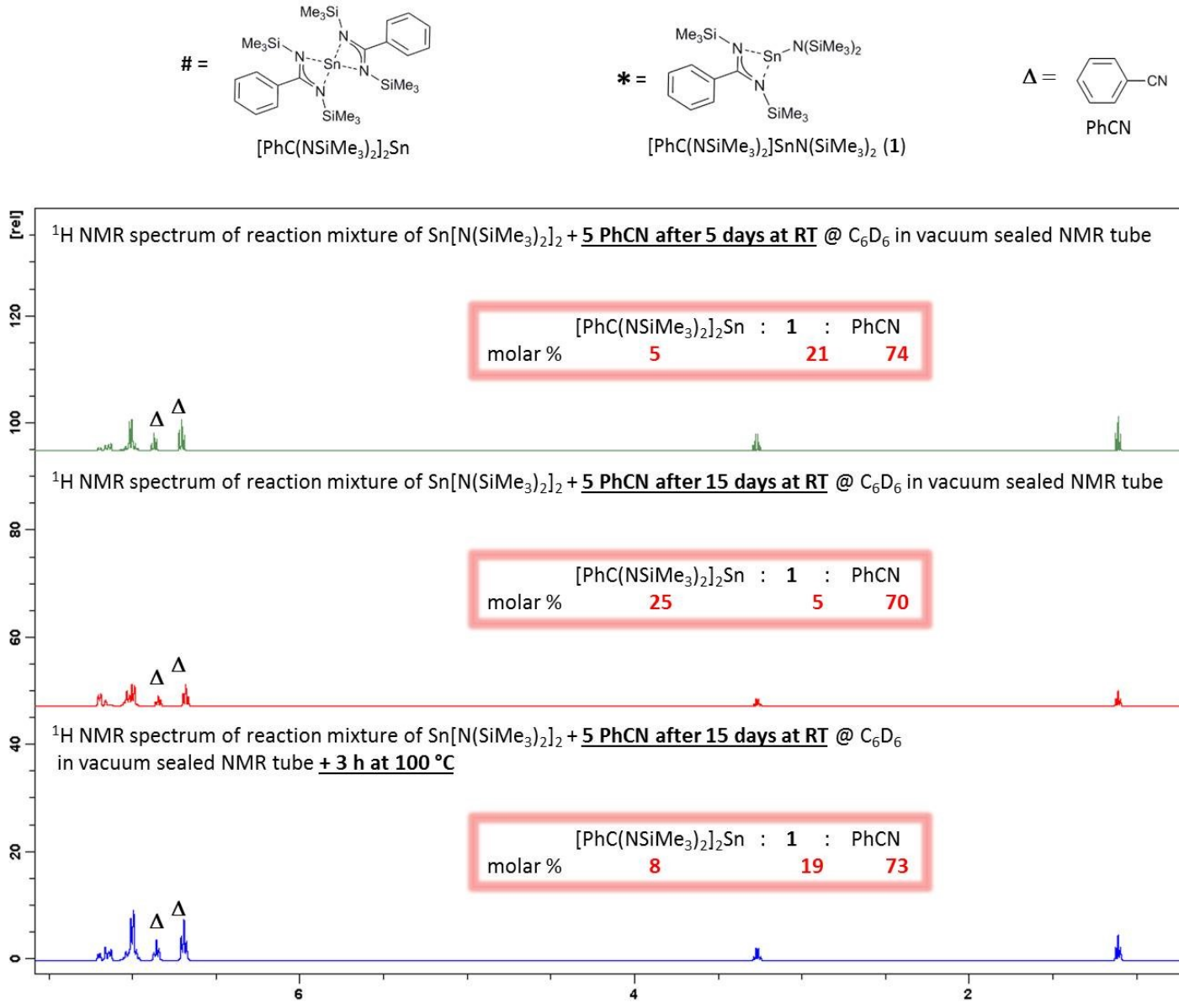


**Fig. S4A** $^{1}H$ NMR spectral study of reversible addition of $Sn[N(SiMe_3)_2]_2$ with 5 equivalents of PhCN in the timeline in vacuum sealed NMR tube @ $C_6D_6$.

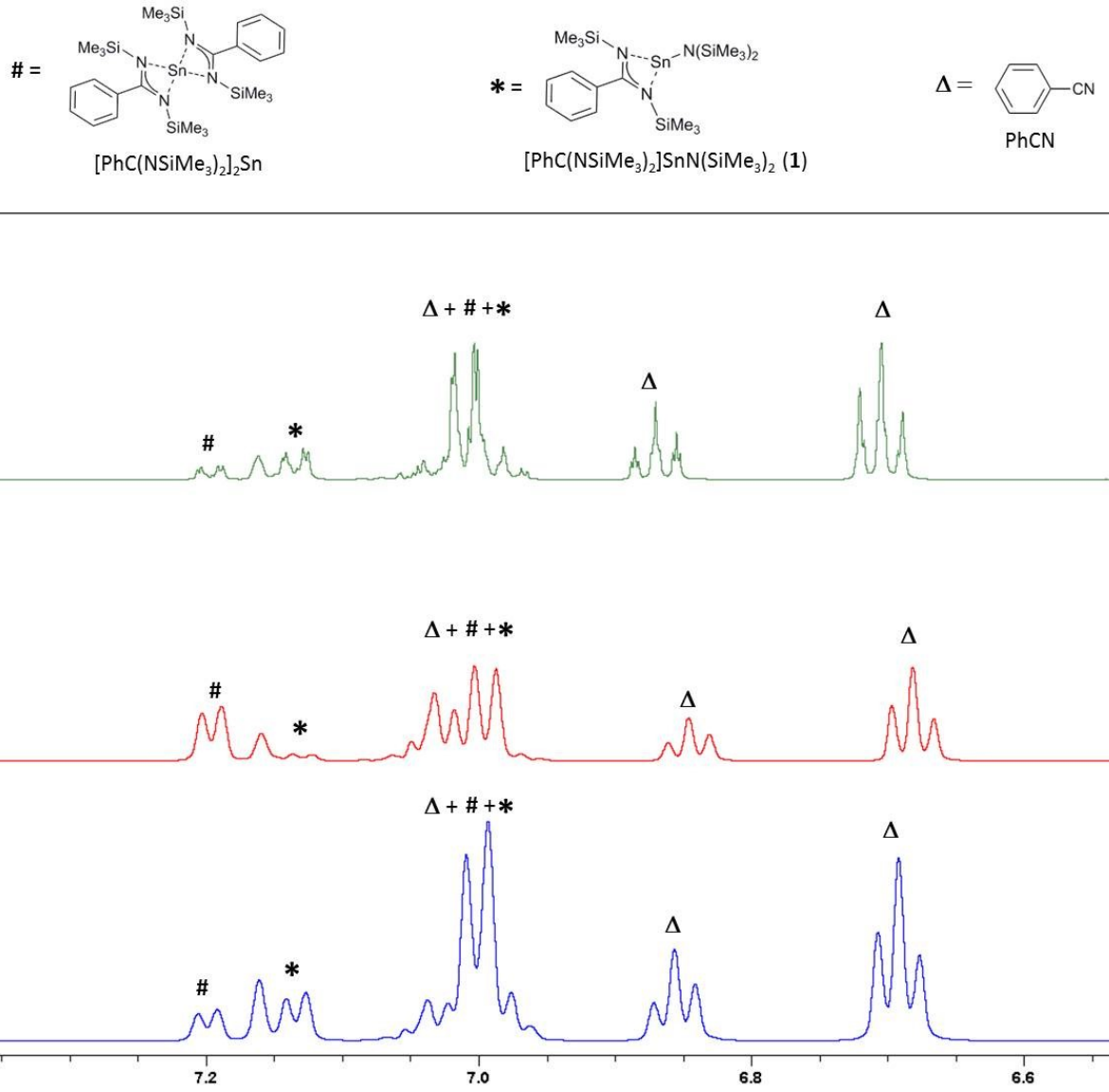


**Fig. S4B** Detail of aromatic part of $^{1}H$ NMR spectral study of reversible addition of $Sn[N(SiMe_3)_2]_2$ with 5 equivalents of PhCN in the timeline in vacuum sealed NMR tube @ $C_6D_6$.

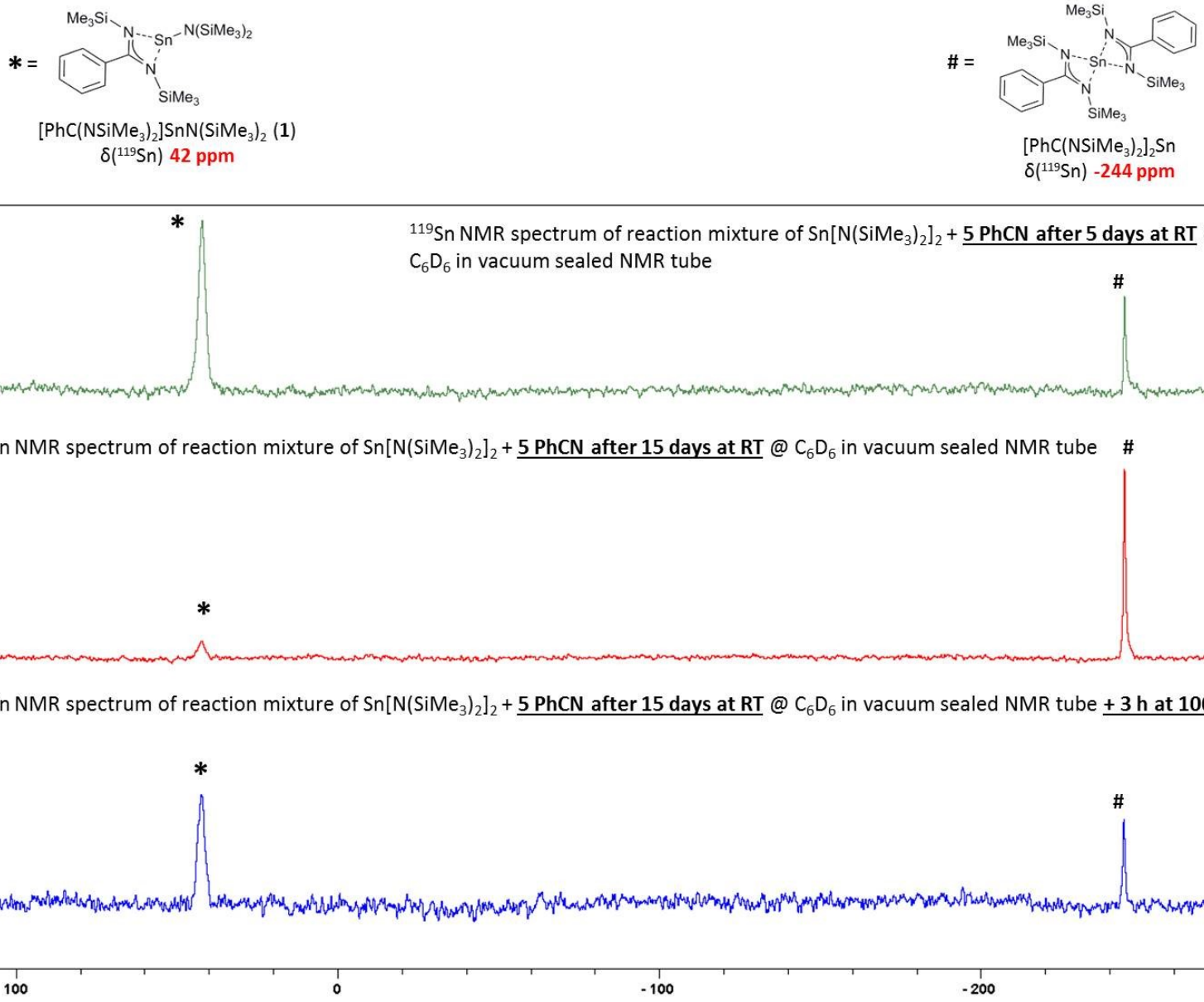


**Fig. S4C** $^{119}$Sn NMR spectral study of reversible addition of $Sn[N(SiMe_3)_2]_2$ with 5 equivalents of PhCN in the timeline in vacuum sealed NMR tube @ $C_6D_6$.

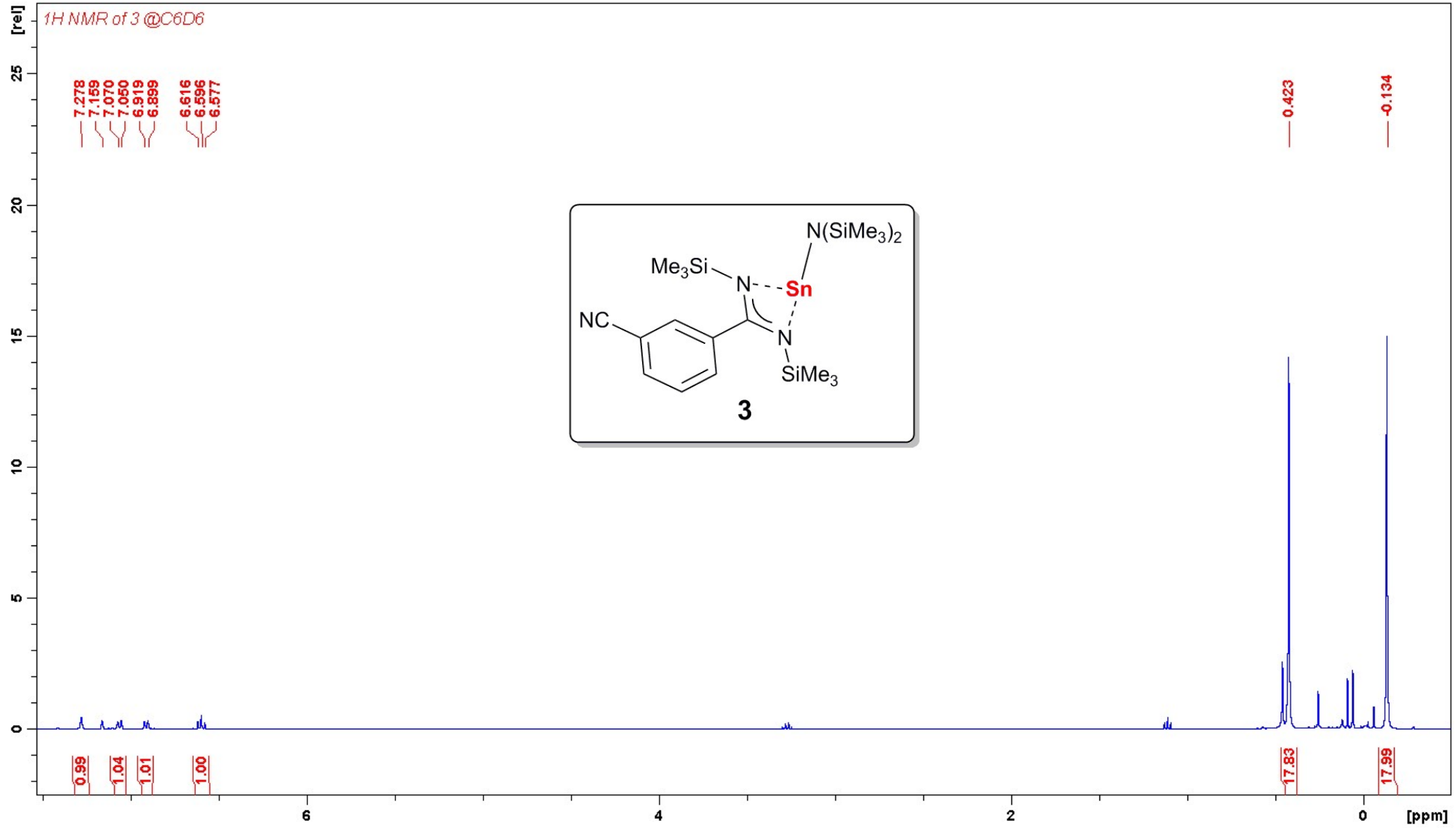


**Fig. S5A** $^{1}$H NMR spectrum of **3** @ $C_6D_6$.

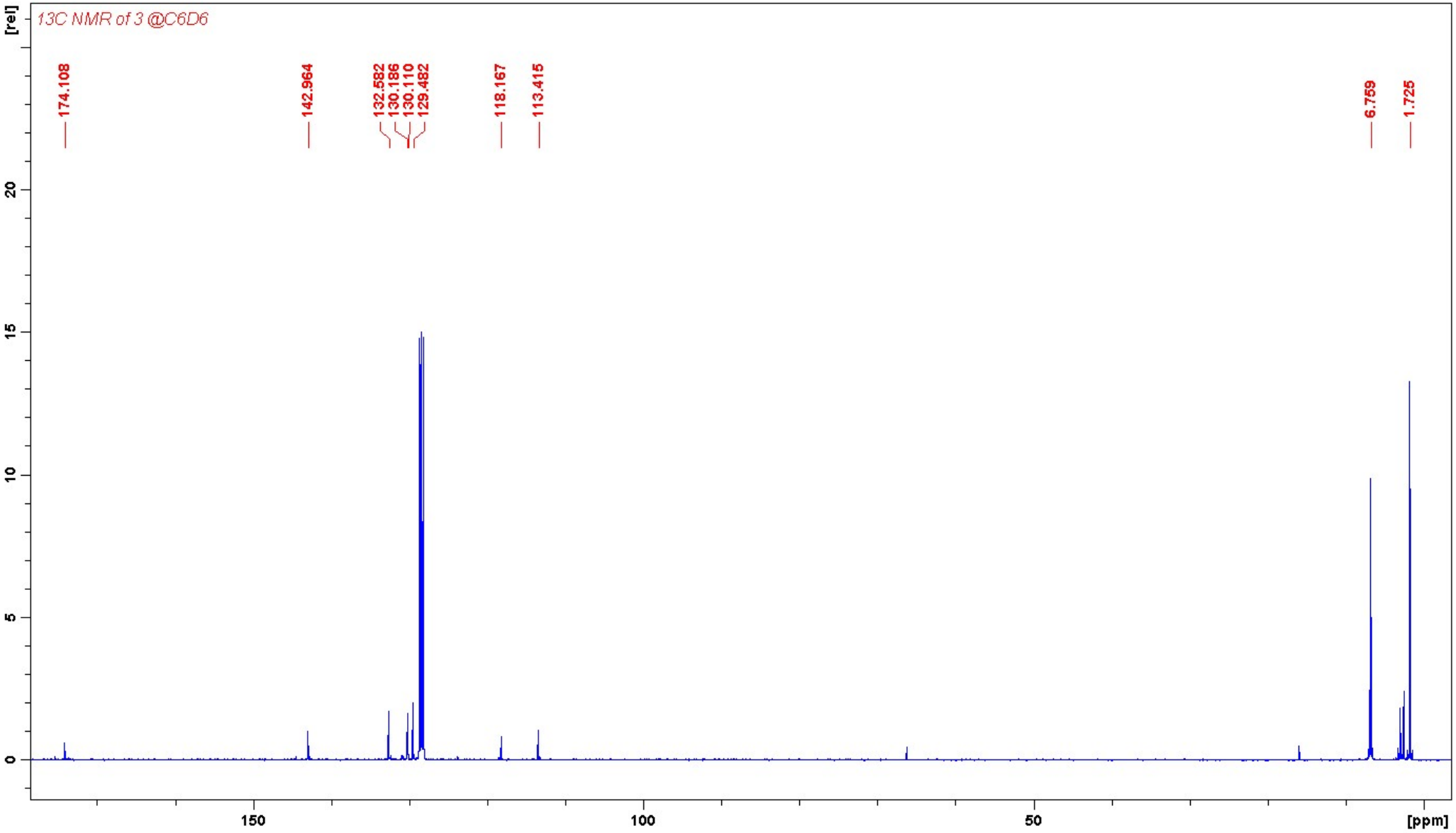


**Fig. S5B** $^{13}C$ NMR spectrum of **3** @ $C_6D_6$.

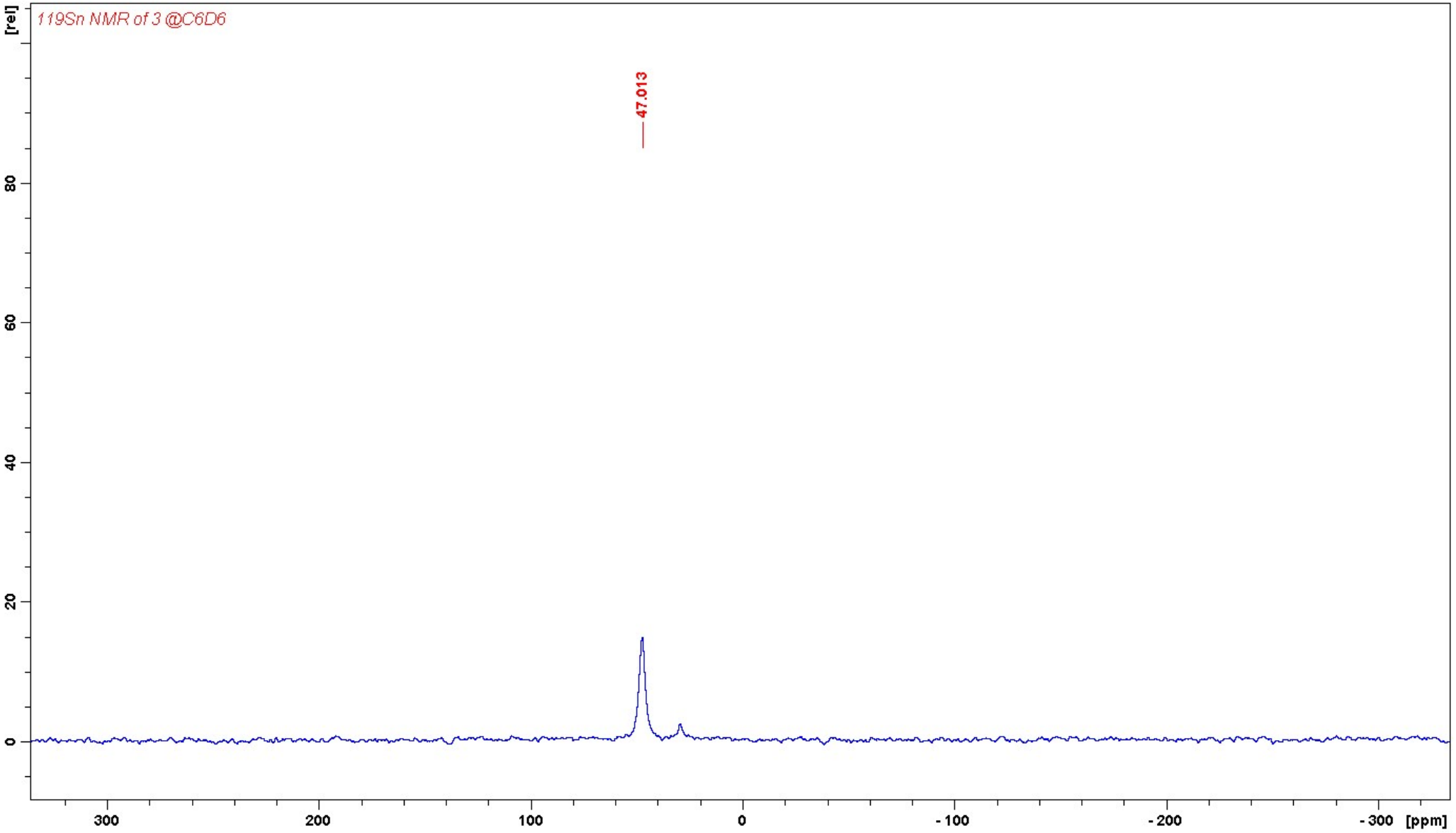


**Fig. S5C** $^{119}$Sn NMR spectrum of **3** @ $C_6D_6$.

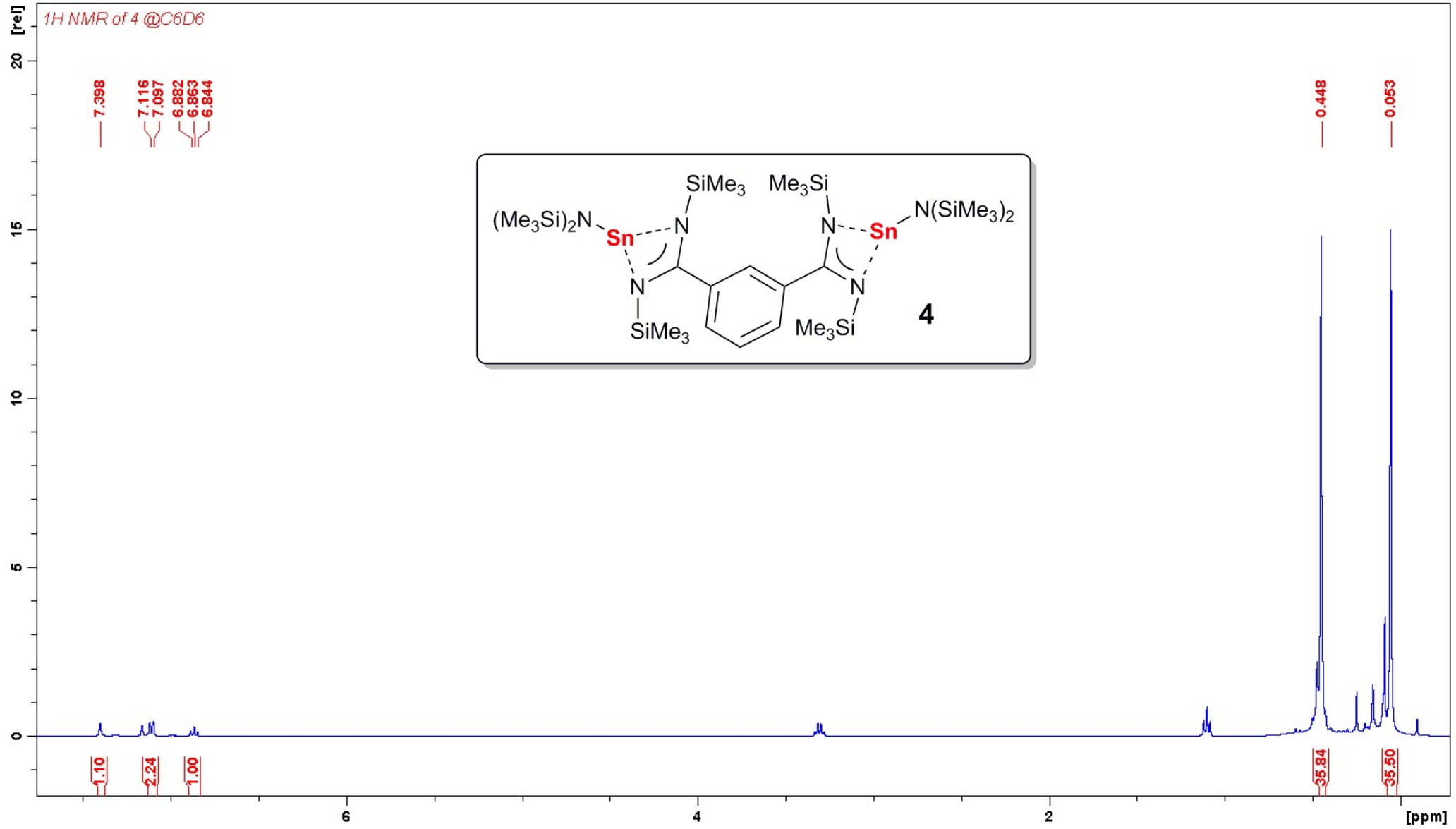


**Fig. S6A** $^{1}$H NMR spectrum of **4** @ $C_6D_6$.

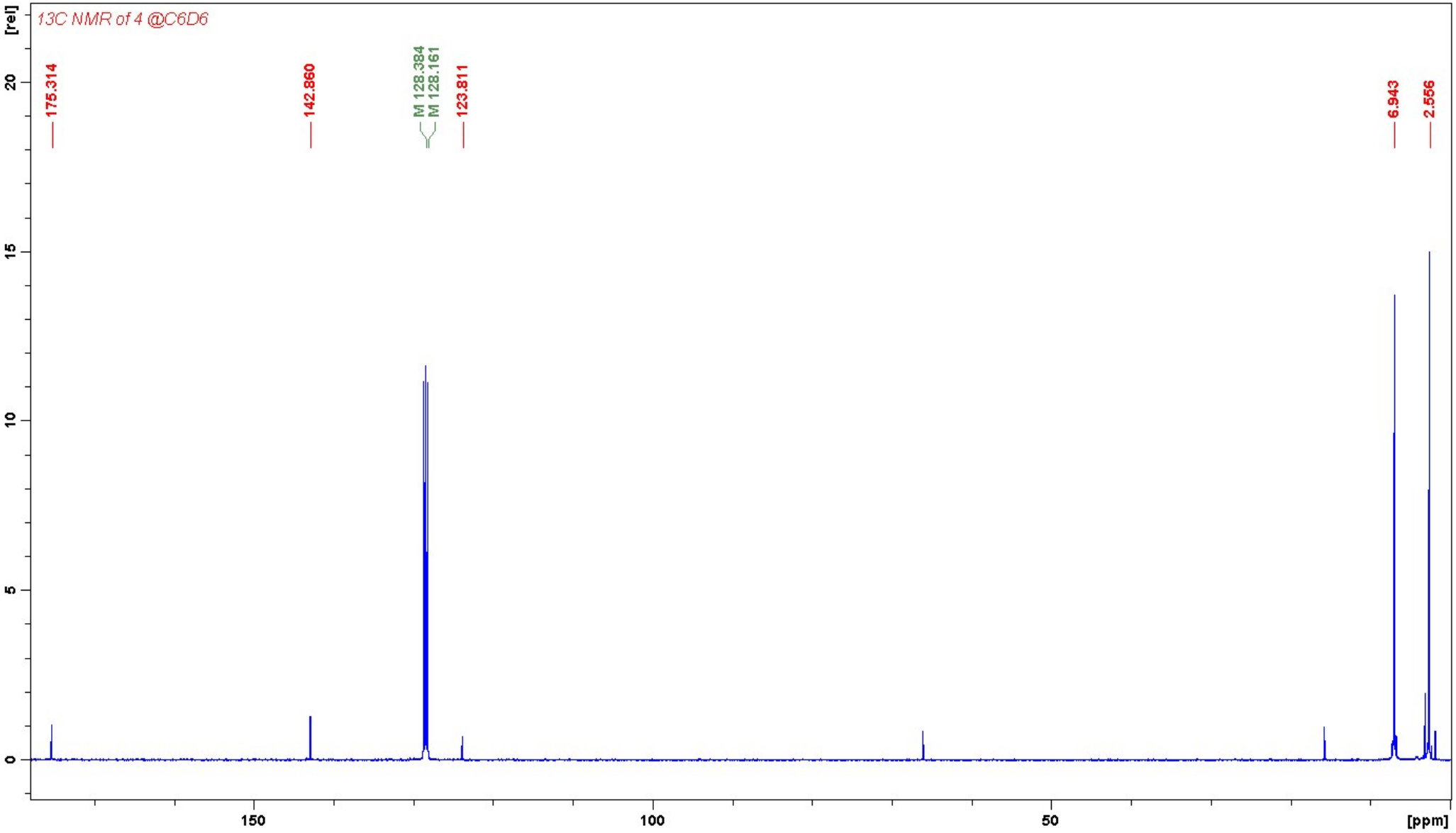


**Fig. S6B** $^{13}C$ NMR spectrum of **4** @ $C_6D_6$.

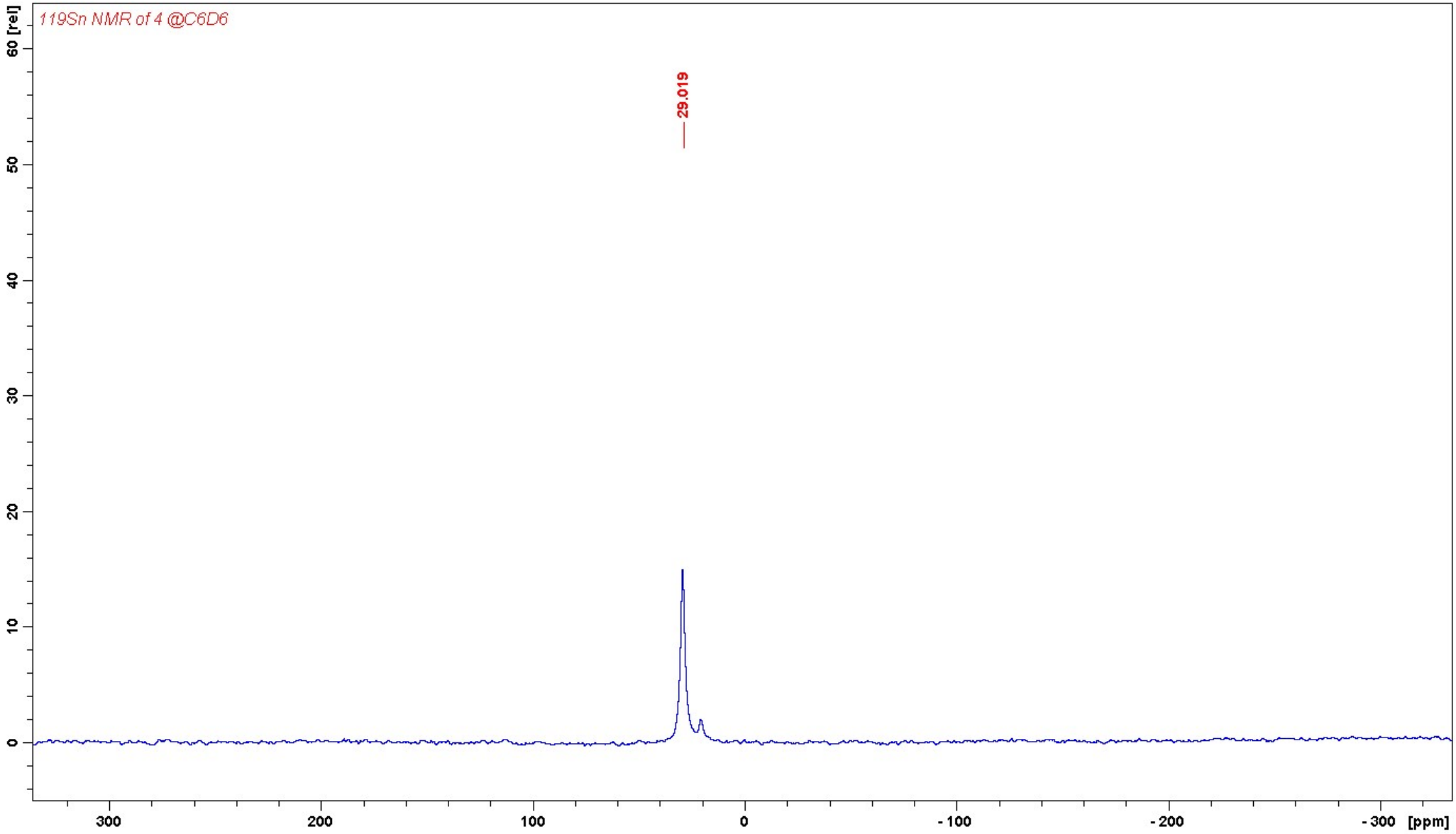


**Fig. S6C** $^{119}$Sn NMR spectrum of **4** @ $C_6D_6$.

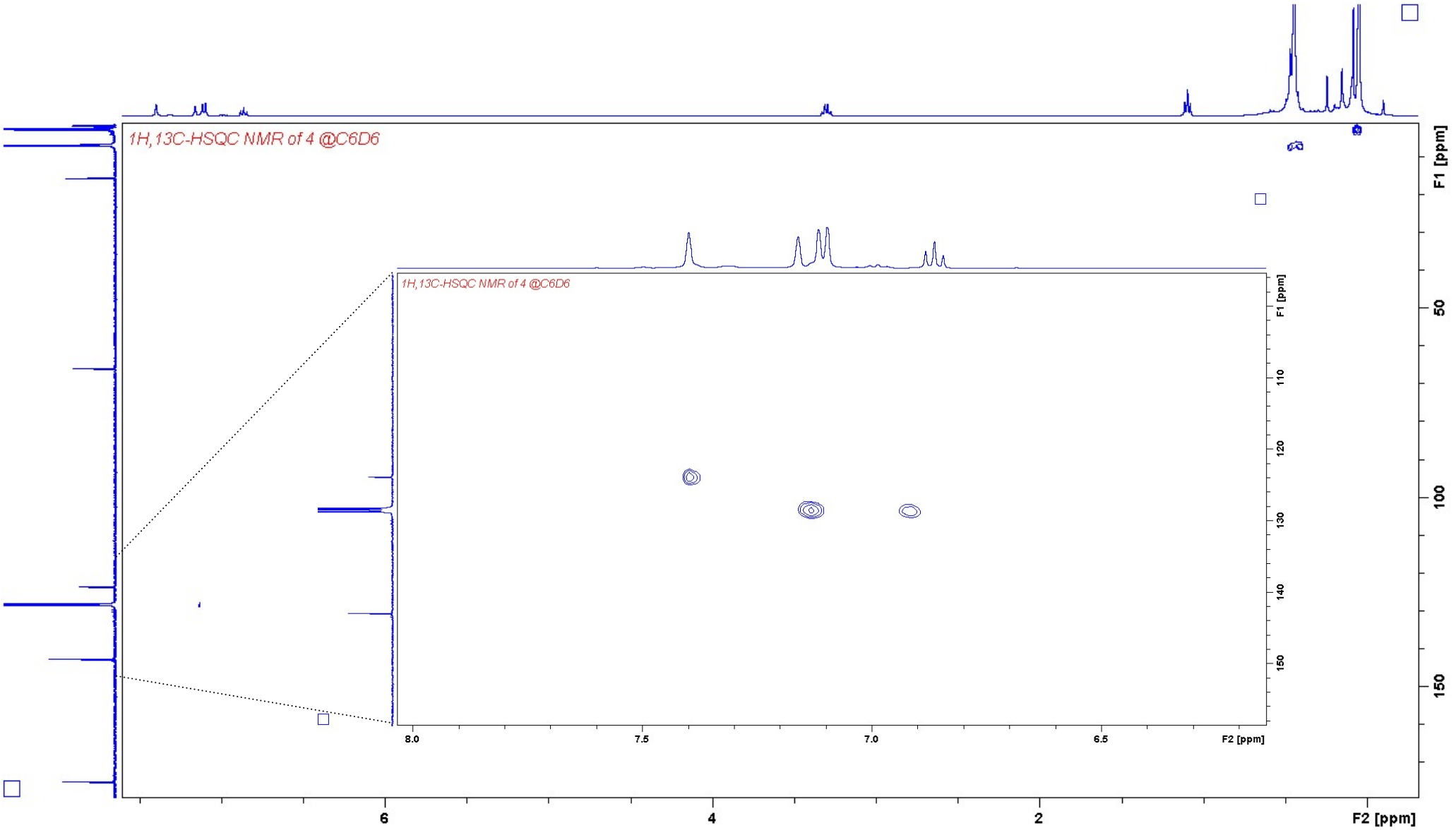


**Fig. S6D** $^{1}H,^{13}C$-HSQC NMR spectrum of **4** @ $C_6D_6$.

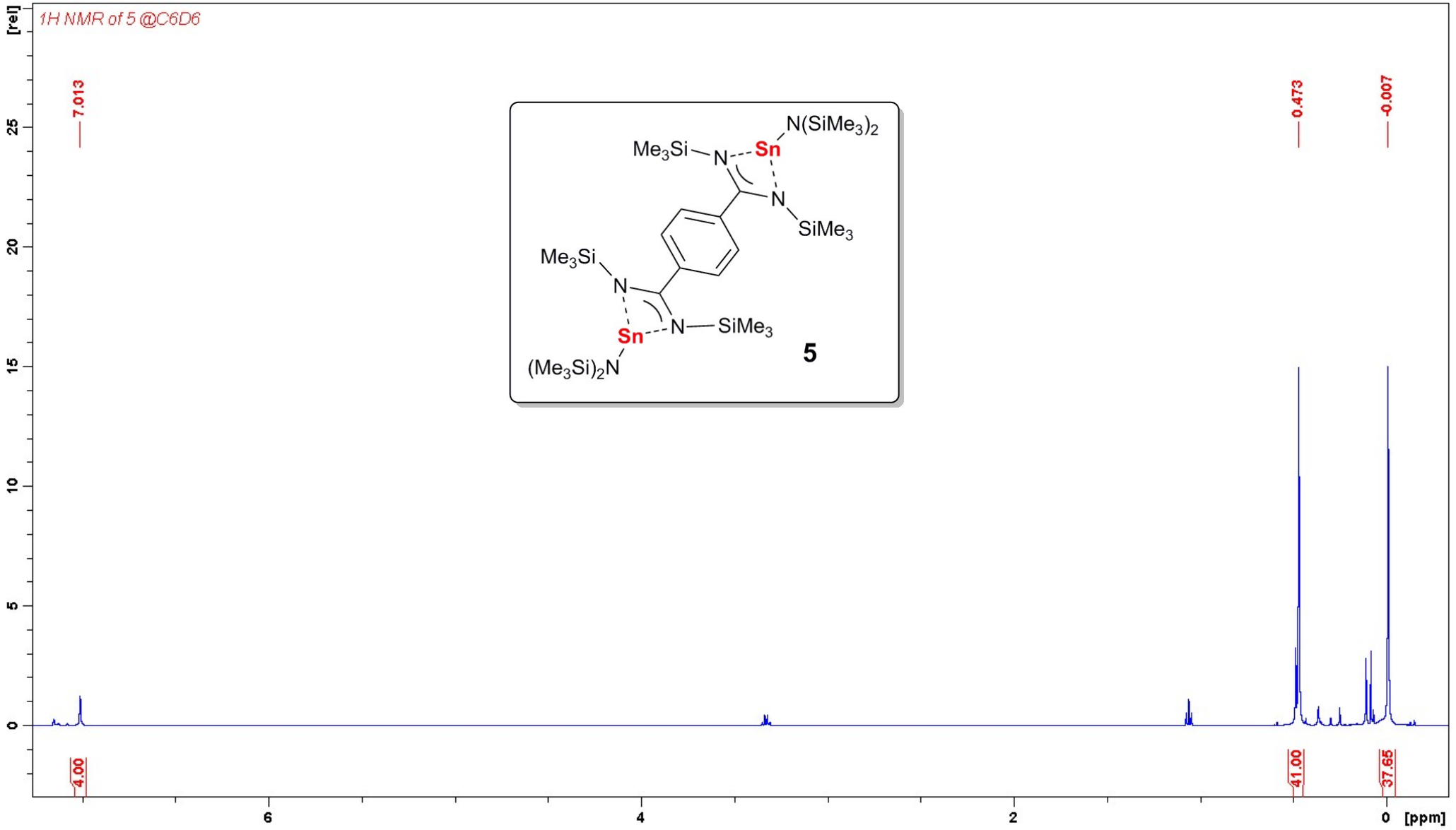


**Fig. S7A** $^{1}$H NMR spectrum of **5** @ $C_6D_6$.

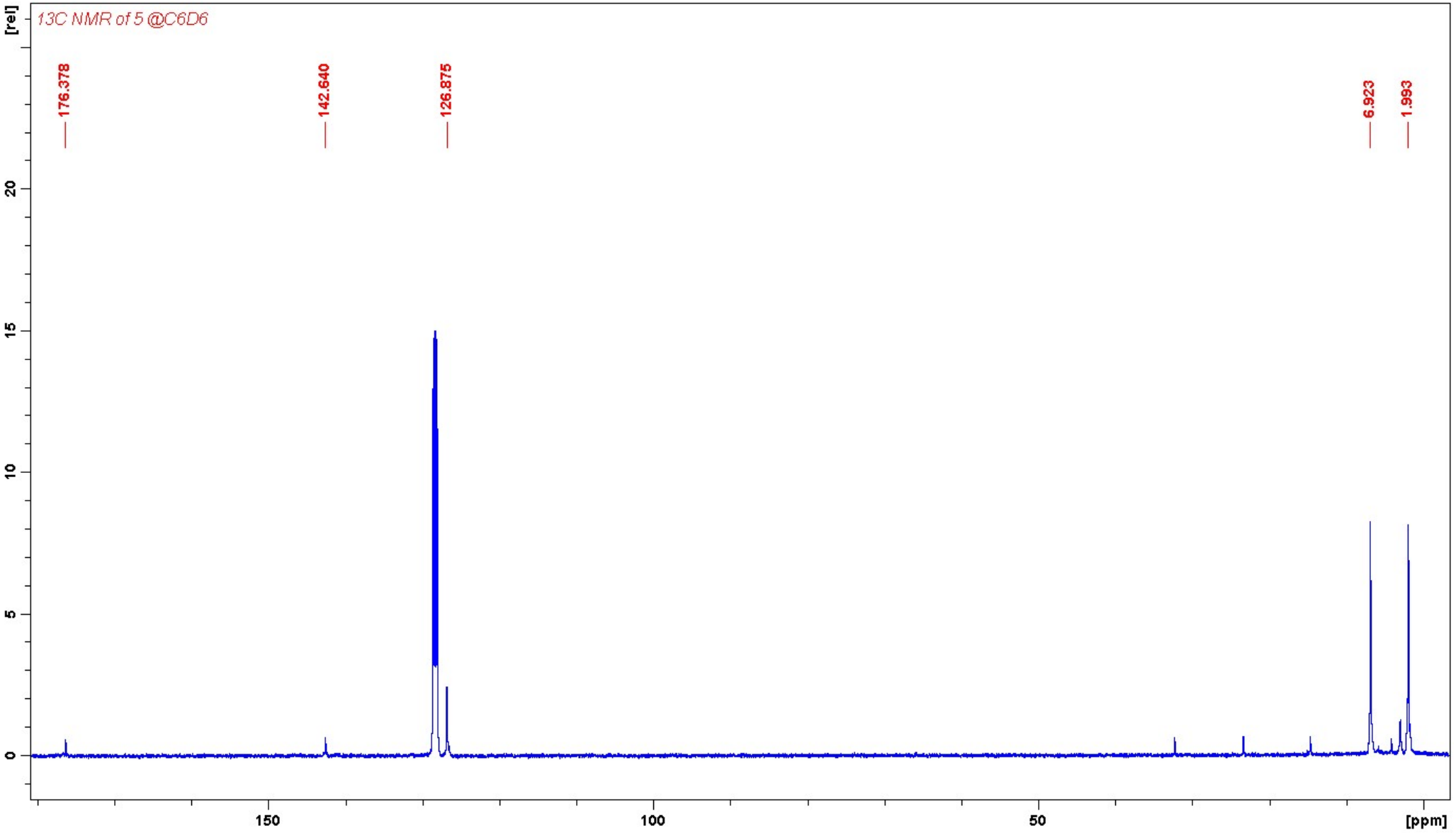


**Fig. S7B** $^{13}C$ NMR spectrum of **5** @ $C_6D_6$.

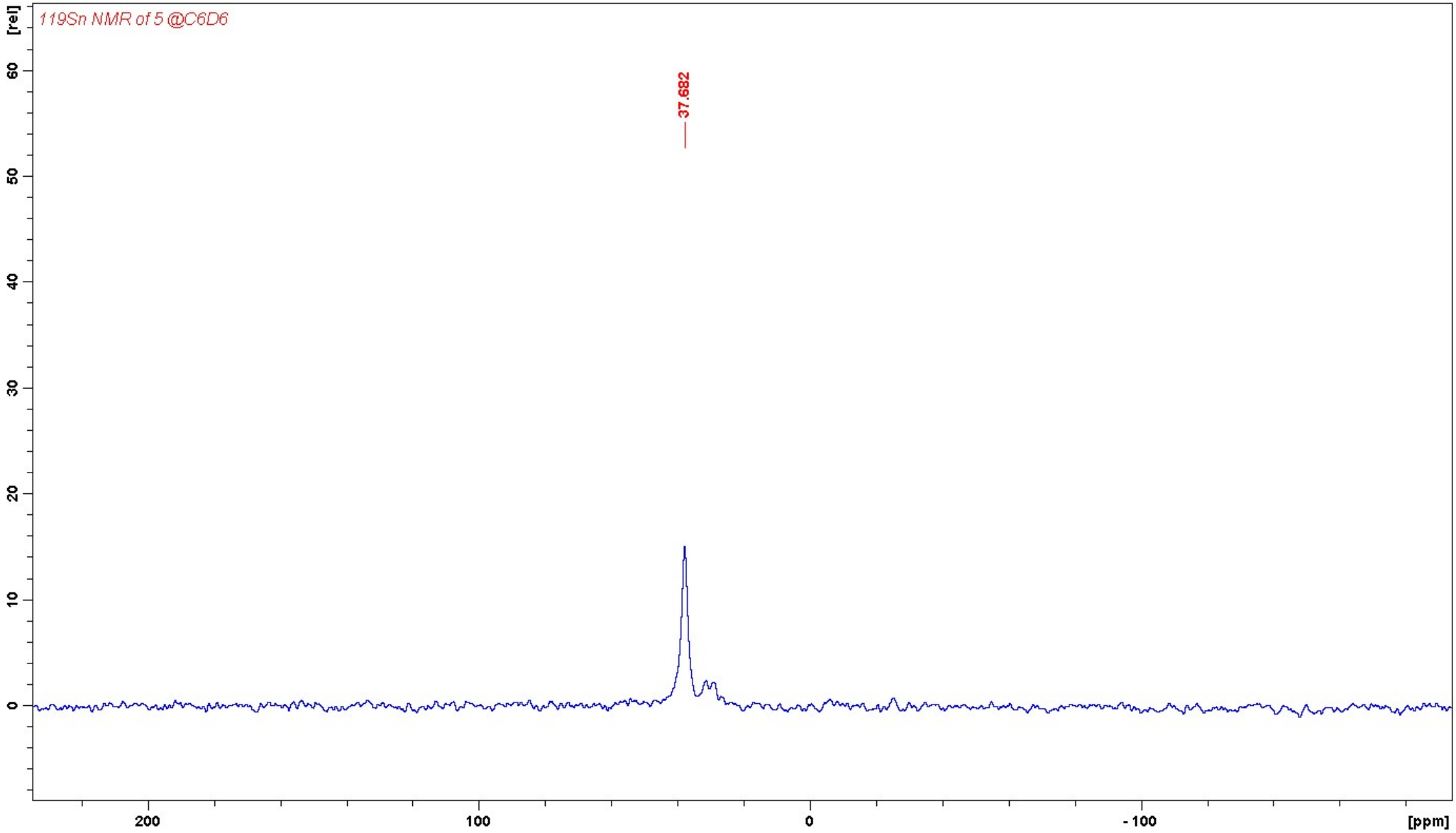


**Fig. S7C** $^{119}$Sn NMR spectrum of **5** @ $C_6D_6$.

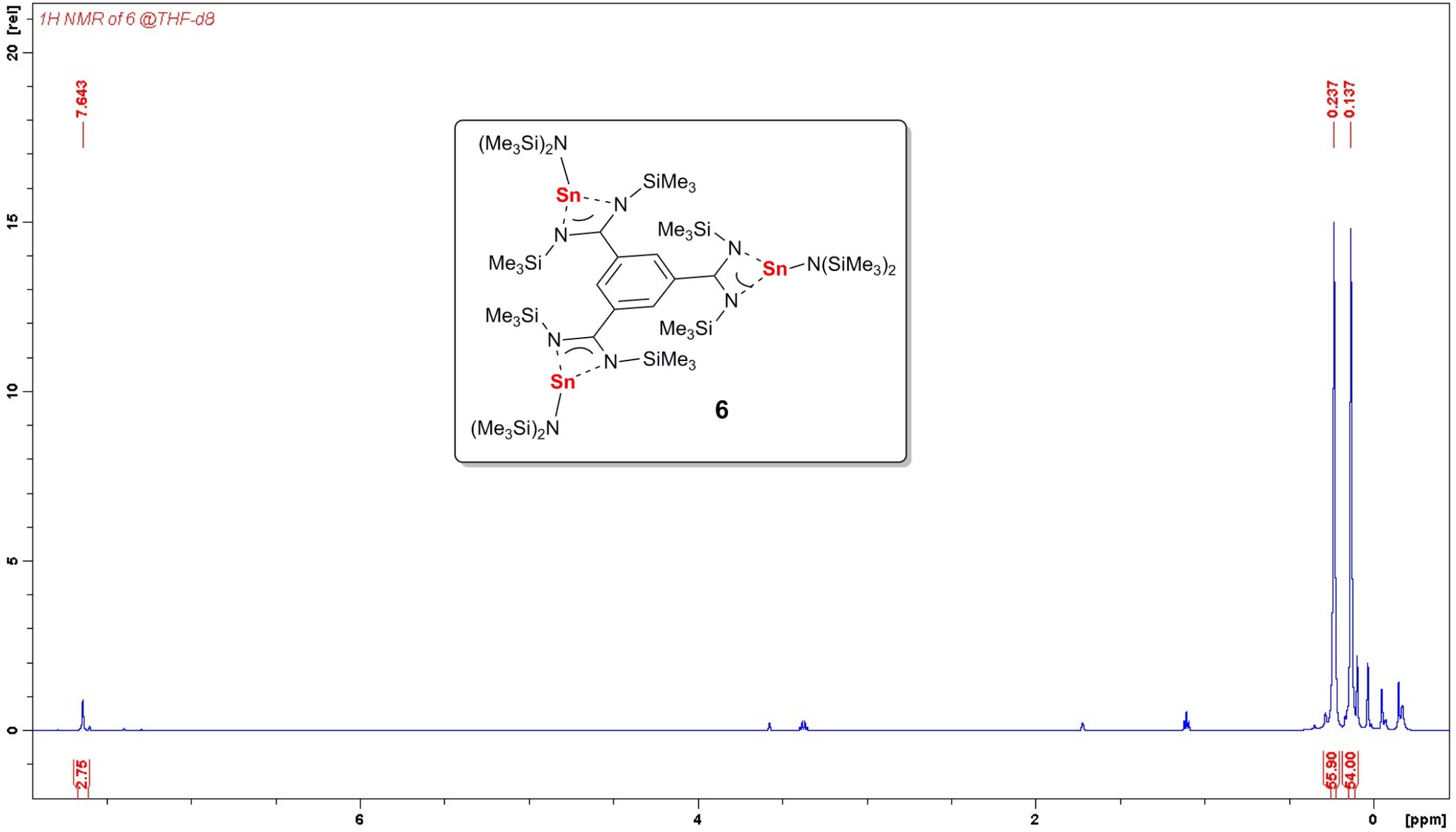


**Fig. S8A** $^{1}$H NMR spectrum of **6** @ THF-$d_8$.

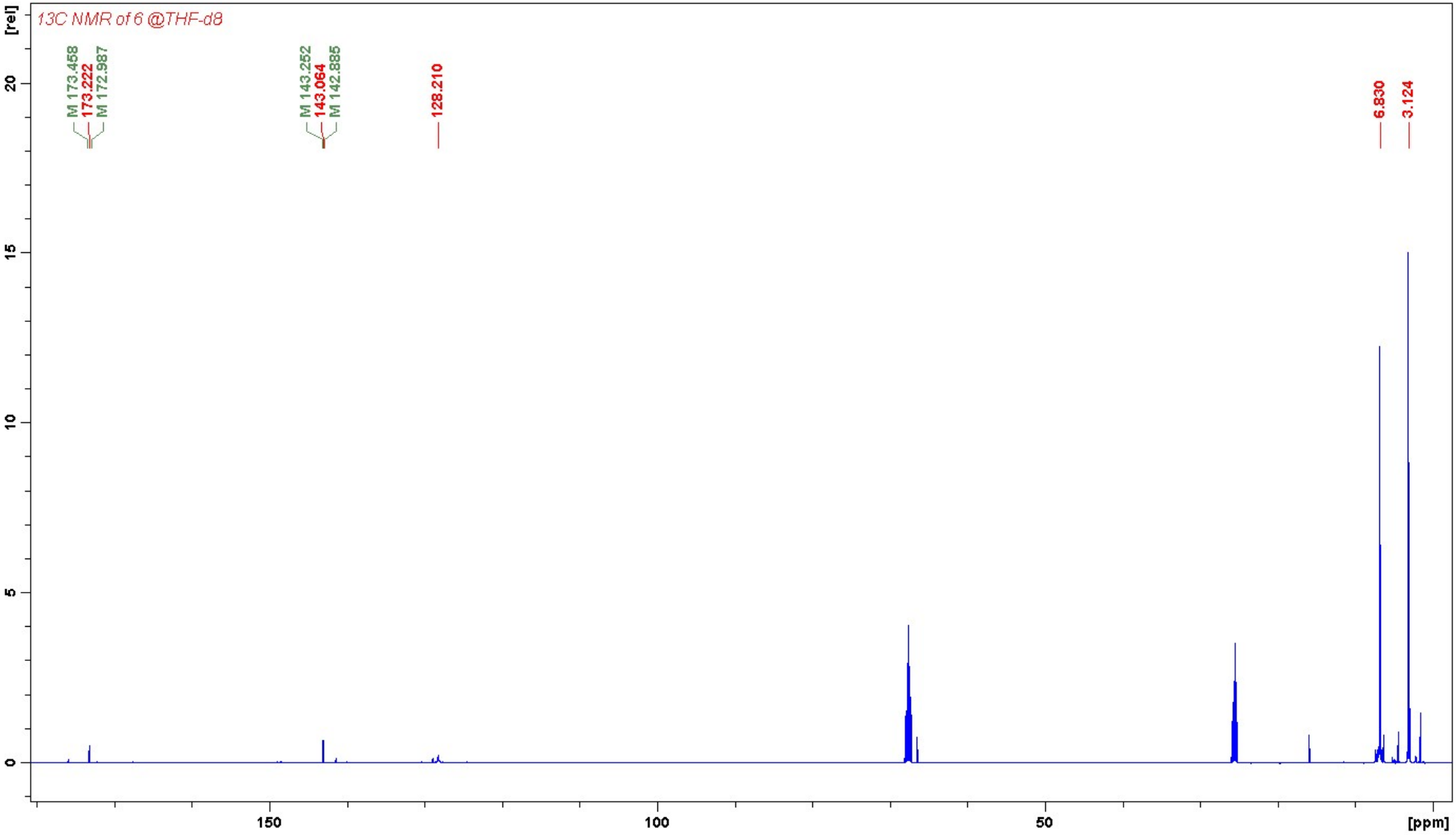


**Fig. S8B** $^{13}C$ NMR spectrum of **6** @ THF-$d_8$.

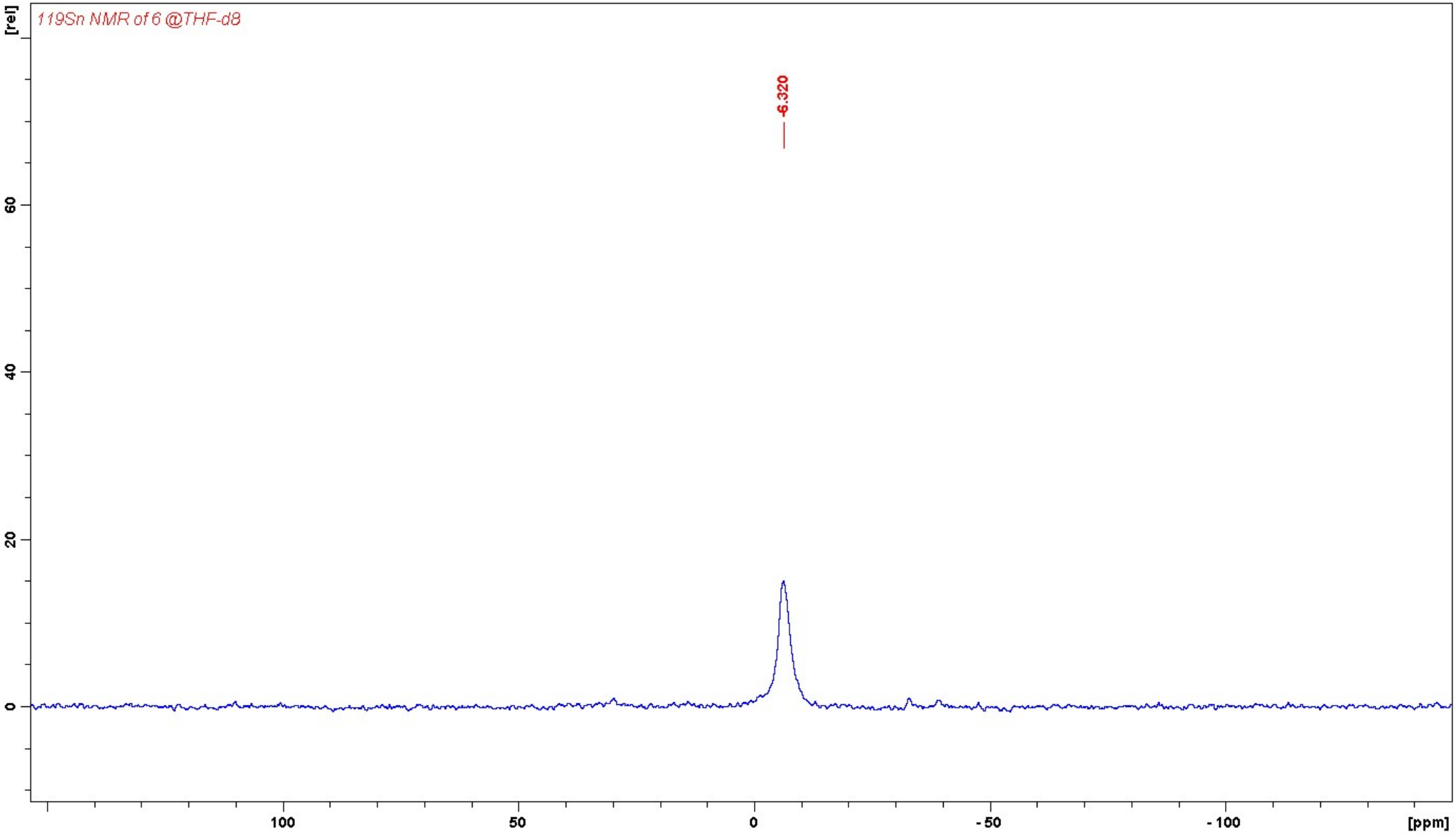


**Fig. S8C** $^{119}$Sn NMR spectrum of **6** @ THF-$d_8$.

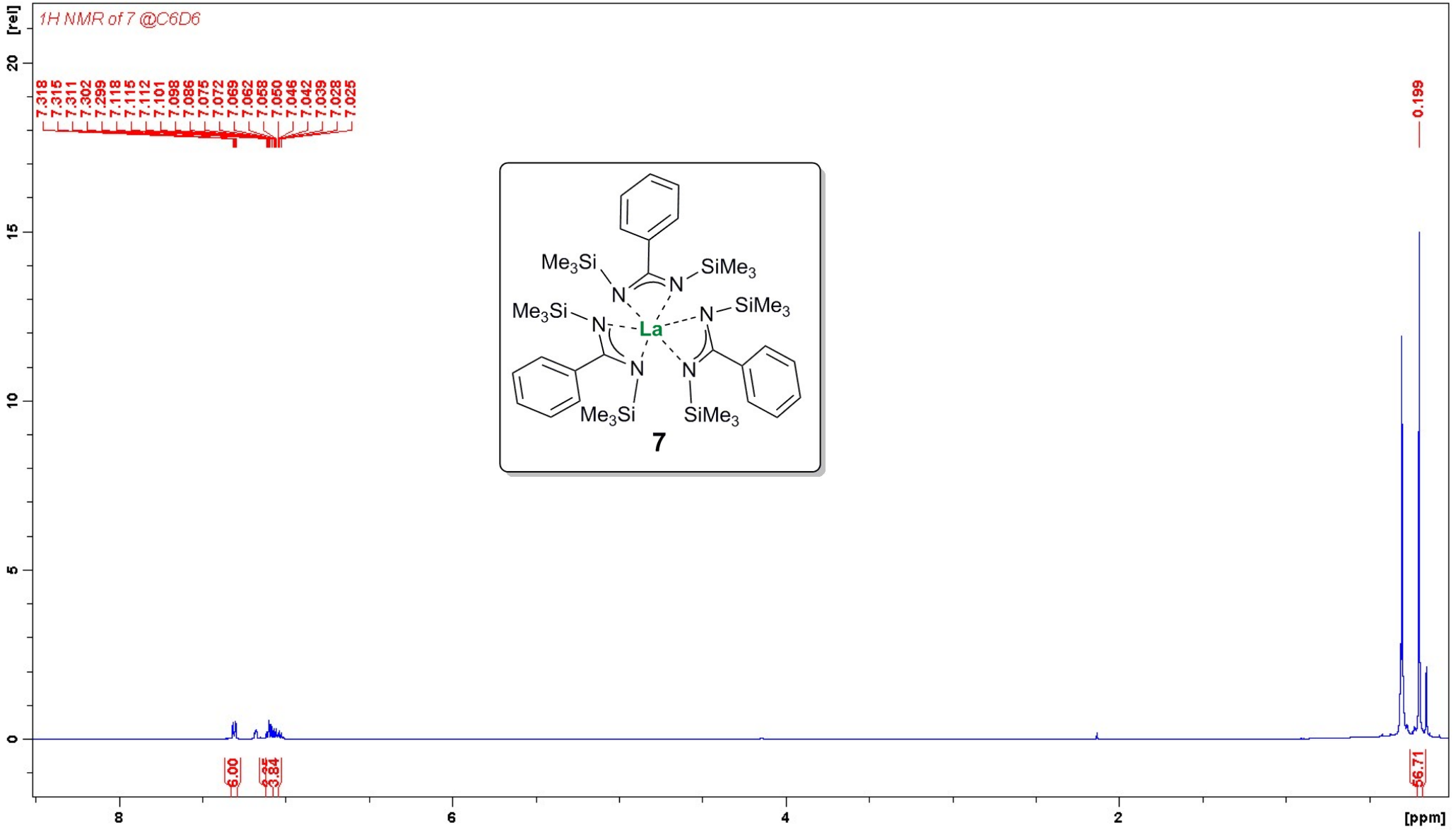


**Fig. S9A** $^{1}$H NMR spectrum of **7** @ $C_6D_6$.

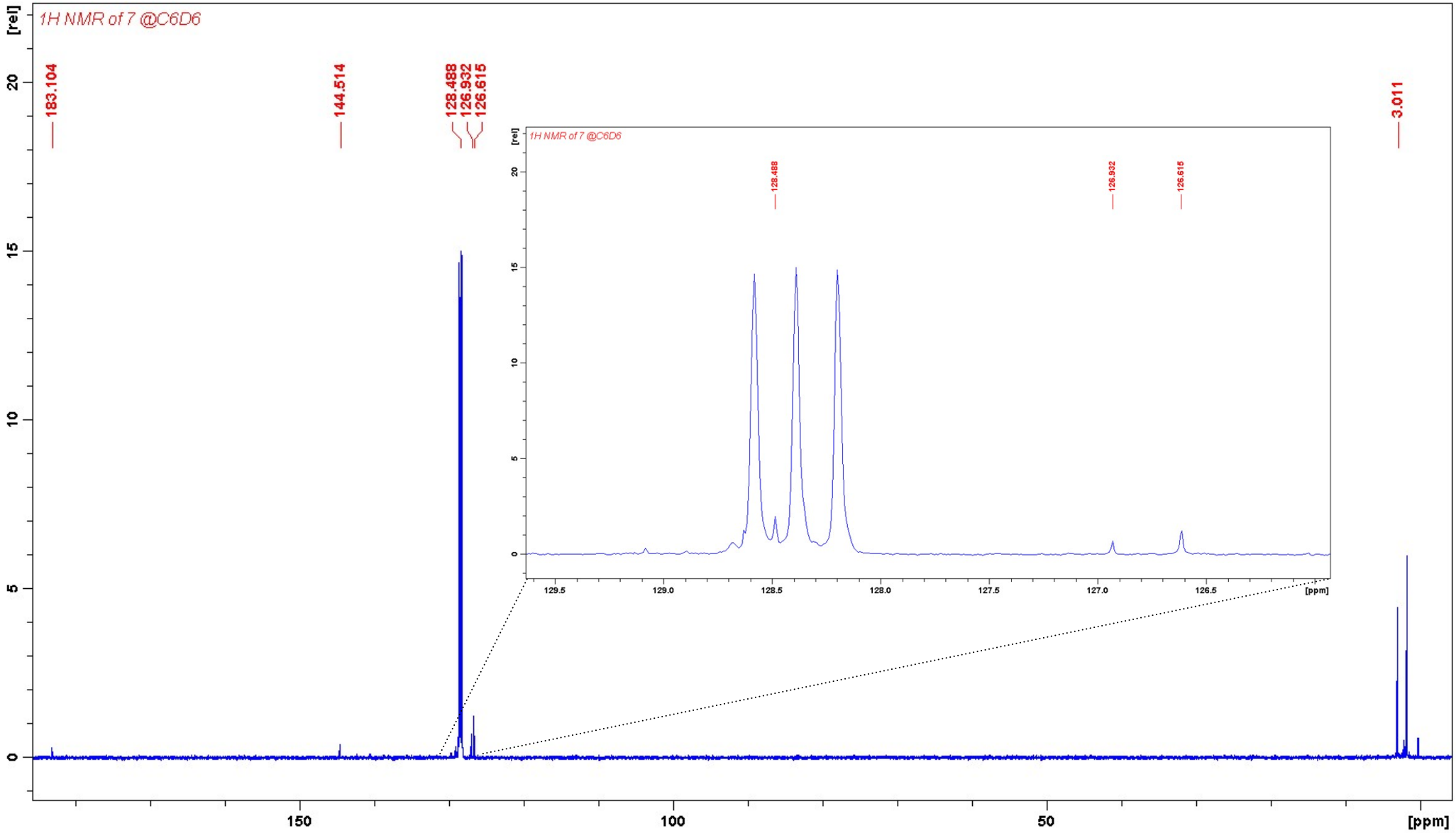


**Fig. S9B** $^{13}C$ NMR spectrum of **7** @ $C_6D_6$.

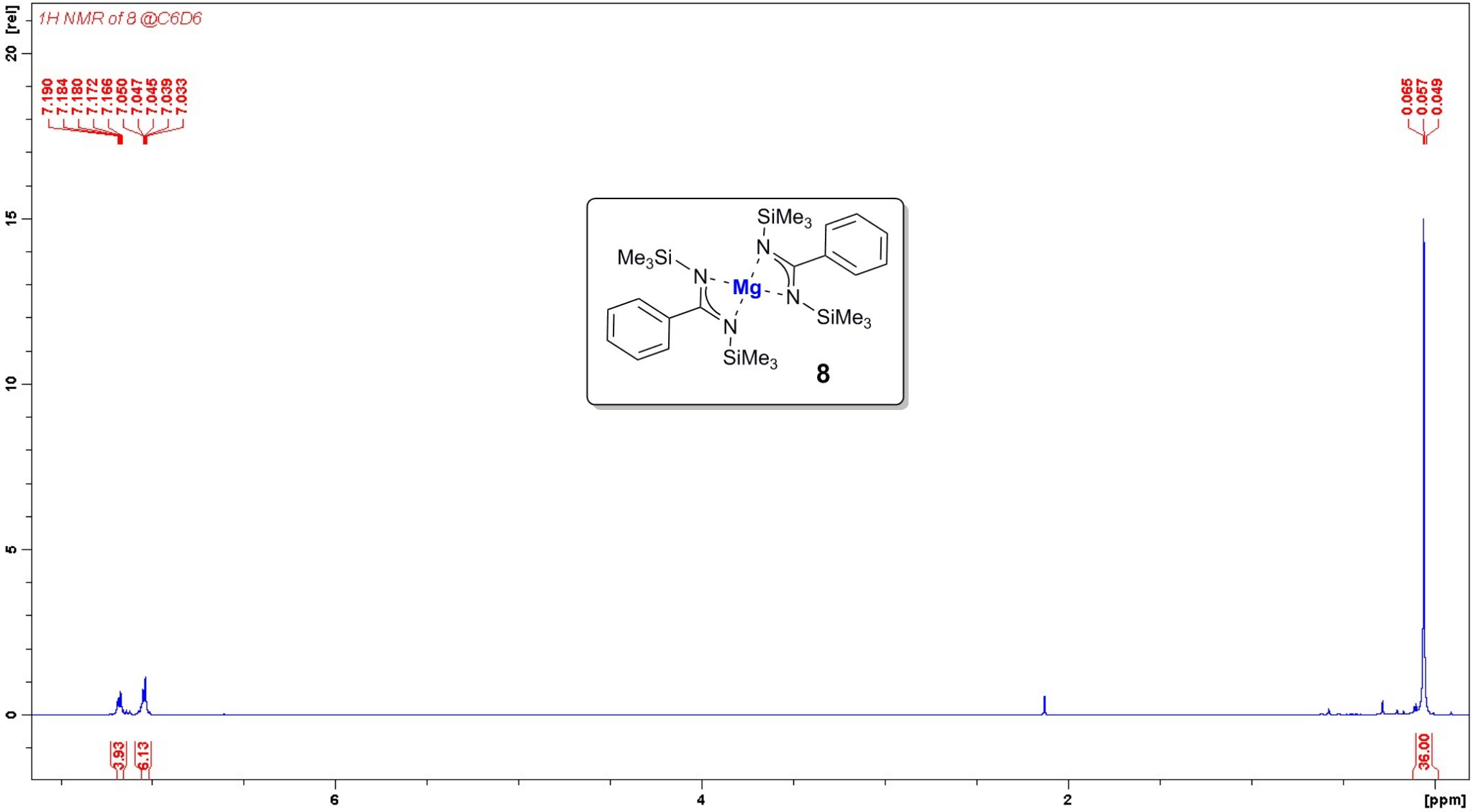


**Fig. S10A** $^{1}H$ NMR spectrum of **8** @ $C_6D_6$.

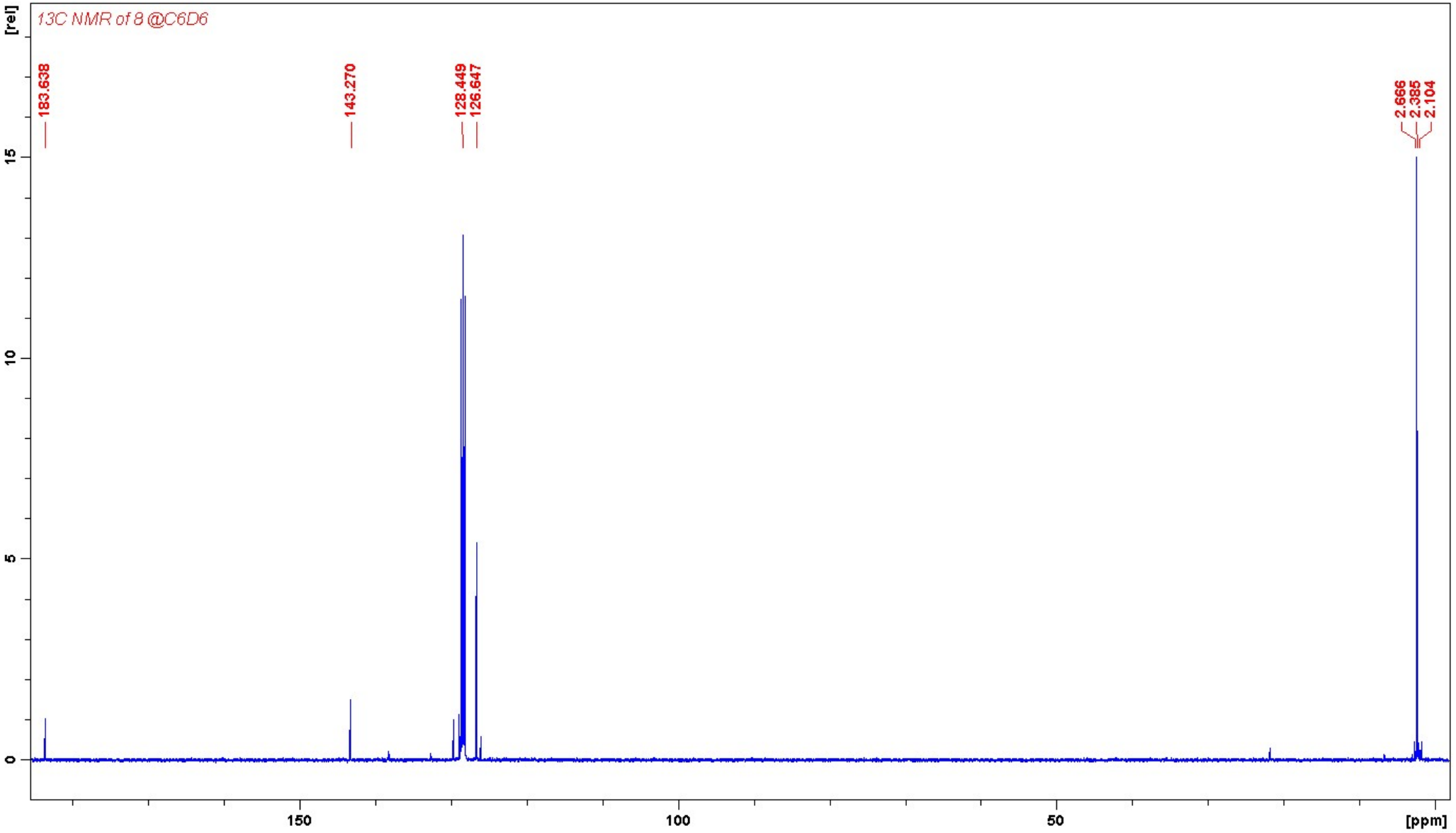


**Fig. S10B** $^{13}C$ NMR spectrum of **8** @ $C_6D_6$.

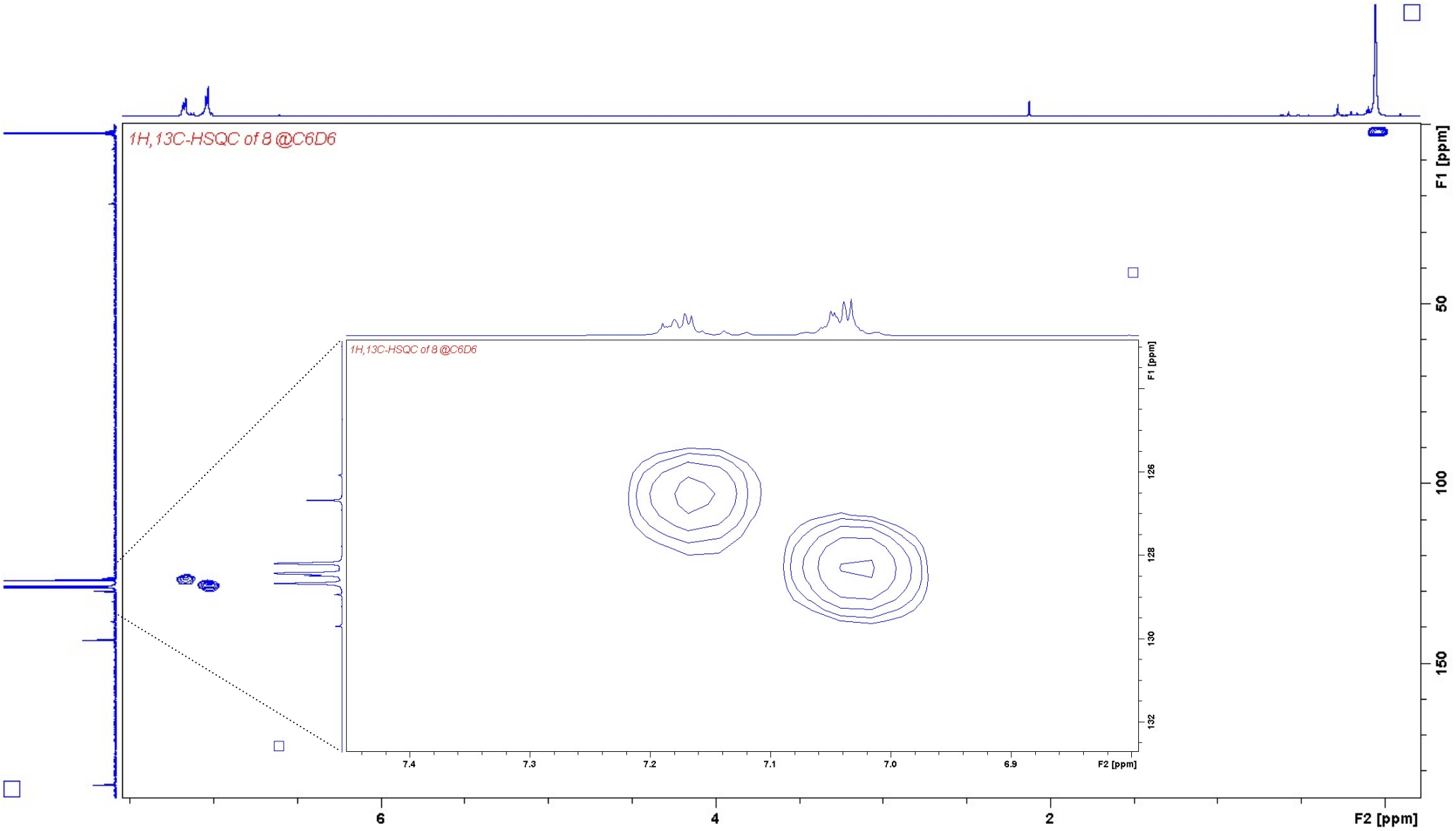


**Fig. S10C** $^{1}H,^{13}C$-HSQC NMR spectrum of **8** @ $C_6D_6$.

**Table S1:** Crystallographic data for **3** and **5**.

| Crystal data | **3** | **5** |
|---|---|---|
| Chemical formula | $C_{20}H_{40}N_4Si_4Sn$ | $C_{32}H_{76}N_6Si_8Sn_2$ |
| $M_r$ | 567.61 | 1007.08 |
| Crystal system, space group | Triclinic, *P*-1 | Monoclinic, *C*2/*c* |
| Temperature (K) | 150 | 150 |
| *a*, *b*, *c* (Å) | 10.1620(4), 11.2190(6), 14.3991(10) | 15.7127(5), 13.8541(3), 24.4276(4) |
| α, β, γ (°) | 68.279(5), 73.507(4), 80.199(4) | 90, 101.591(5), 90 |
| *V* (Å$^3$) | 1458.38(15) | 5208.9(4) |
| *Z* | 2 | 4 |
| Radiation type | Mo*K*α | Mo*K*α |
| μ (mm$^{-1}$) | 1.05 | 1.17 |
| Crystal size (mm) | 0.27 × 0.15 × 0.14 | 0.59 × 0.28 × 0.22 |
| Data collection | | |
| $T_{min}$, $T_{max}$ | 0.841, 0.935 | 0.629, 0.824 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 29840, 6672, 5889 | 27817, 5967, 4989 |
| $R_{int}$ | 0.047 | 0.056 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.649 | 0.650 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.042, 0.099, 1.23 | 0.034, 0.083, 1.04 |
| No. of reflections | 6672 | 5967 |
| No. of parameters | 262 | 227 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.51, −0.72 | 0.50, −0.66 |

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL97* (Sheldrick, 1997), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008). $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$. $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffr.} - N_{param.})]^{½}$. Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{½}$; $w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 15.9517P]$, where $P = (F_o^2 + 2F_c^2)/3$

***DFT calculations***

All the calculations were performed with the Gaussian 16 program.[1] The geometries of complexes were fully optimised at the M06-2X/def2-TZVP level of theory.[2,3] The structures of the related complexes obtained by X-ray diffraction analysis were used as the initial data. The polarisable continuum model (PCM)[4] was employed for solvation effects (diethyl ether). We additionally took into account the dispersion corrections (D3 version of Grimme's dispersion).[5] All the computed structures are minima on the potential energy surface, as confirmed by the frequency calculations at the same level of theory and transition states with only one imaginary frequency. Geometries of optimized structures are presented in xyz-file.

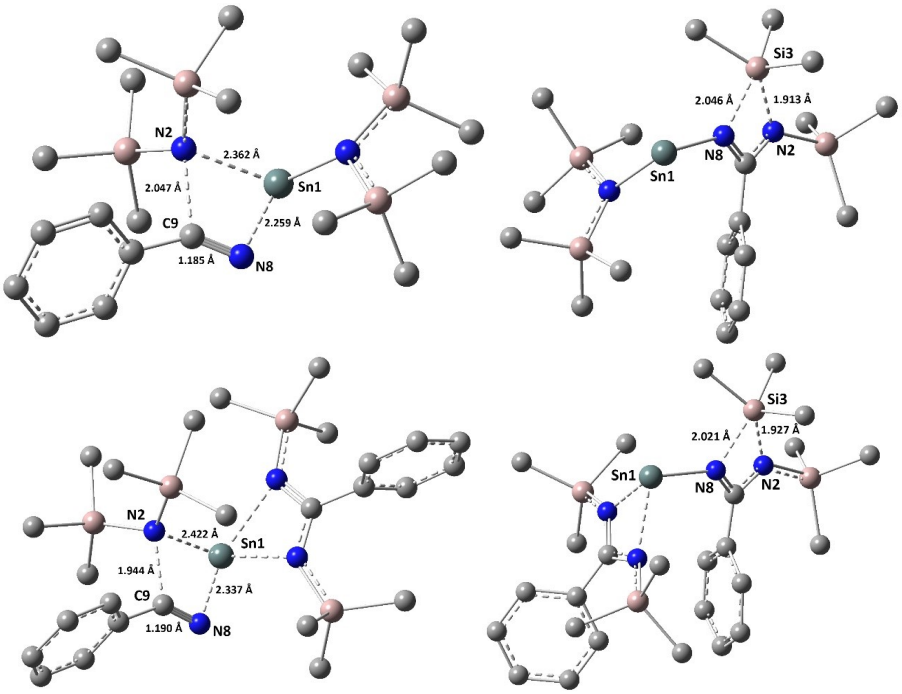


**Fig. S11** Geometries of transition states TS-1A, TS-2A (top), TS-1B, TS-2B (bottom).

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[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16*, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

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[5] V. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.