

Complete Disassembly of Carbon Disulfide by a Ditantalum Complex

Joachim Ballmann, Alyssa Yeo, Bruce A. MacKay, Sabine van Rijt, Brian O. Patrick, and Michael D. Fryzuk*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1 CANADA.

Experimental Procedures

All manipulations were performed under an atmosphere of dry and oxygen-free dinitrogen by means of standard Schlenk or Glovebox techniques. Anhydrous Et₂O, hexanes and toluene were purchased from Aldrich, sparged with dinitrogen and dried further by passage through towers containing activated alumina and molecular sieves. Benzene was purchased from Aldrich, dried over sodium benzophenone ketyl and distilled under positive pressure. Toluene-d₈ and benzene-d₆ were refluxed over sodium, vacuum transferred and freeze-pump-thaw degassed. ¹H, ³¹P and ¹³C NMR spectra were recorded on a Bruker AV-400 MHz spectrometer. Unless noted otherwise, all spectra were recorded at room temperature. ¹H NMR spectra were referenced to residual proton signals in C₆D₆ (7.16 ppm) or C₇D₈ (2.09); ³¹P NMR spectra were referenced to external P(OMe)₃ (141.0 ppm with respect to 85% H₃PO₄ at 0.0 ppm); ¹³C NMR spectra were referenced to the solvent resonances of C₆D₆ (128.0 ppm) or C₇H₈ (20.4 ppm). Microanalyses (C, H, N) and mass spectroscopy (low and high resolution EI) were performed at the Department of Chemistry at the University of British Columbia. Carbon disulfide and ¹³CS₂ were purchased from Aldrich, distilled, degassed and stored over molecular sieves prior to use. Compounds [PhP(CH₂SiMe₂NPh)₂]TaMe₃, [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ-H)₂(μ-η²:η¹-N₂), [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ-D)₂(μ-η²:η¹-N₂) and [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ-H)₂(μ-η²:η¹⁻¹⁵N₂) were prepared according to literature methods.^[1] Hydrogen gas, ¹⁵N₂ gas (isotopic purity 98%+) and D₂ gas (HD 0.4%) were purchased from Praxair or from Cambridge Isotopes Ltd. and passed through activated molecular sieves prior to use.

[PhP(CH₂SiMe₂NPh)₂Ta(μ-S)]₂(μ-CH₂) (2).

Starting from [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ-H)₂(μ-η²:η¹-N₂): A stirred solution of [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ-H)₂(μ-η²:η¹-N₂) (**1**) (315 mg, 0.25 mmol) in a mixture of toluene (10 ml) and Et₂O (30 ml) was heated in an oil bath to 40°C. A 0.2 M solution of carbon disulfide in Et₂O (1.25 ml, 0.25 mmol) was then added dropwise over a period of 15 minutes. Stirring at 40°C was continued for 10 min, before the reaction mixture was allowed to cool to room temperature. After stirring for 1.5 h at room temperature, all volatiles were removed in vacuum and the brown residue triturated with a mixture of hexanes (10 ml) and benzene (1 ml). The orange product was filtered off, washed with hexanes (5 ml) and dried in vacuum. Yield: 290 mg, 0.22 mmol, 88%. ¹H NMR (C₆D₆): δ 0.09 and 0.15 (s, 24H total, SiCH₃), 0.86 - 1.45 (m, 8H total, SiCH₂P), 4.95 (t, 2H, ³J_{H,P} = 6 Hz, TaCH₂Ta), 6.7 - 7.8 (overlapping signals, approx. 30H, phenyl protons and residual protons in C₆D₆). ¹H{³¹P} NMR (C₆D₆), selected peaks only: δ 4.95 (s, 2H, TaCH₂Ta), 7.56 (d, 2H, ²J_{H,H} = 7.2 Hz, *o*-PPh). ³¹P{¹H} NMR (C₆D₆): δ -5.2 (s). ¹H NMR (C₇D₈, -30°C): δ 0.05, 0.13, 0.14 and 0.20 (s, 24H total, SiCH₃), 0.85 - 0.95 and 1.30 - 1.50 (m, 8H total, SiCH₂P), 4.89 (m/unresolved dd, 2H, TaCH₂Ta), 6.80 - 7.15 (t and m overlapping with solvent signals, approx. 10H, phenyl protons), 7.21 (t, 2H, ²J_{H,H} = 7.3 Hz, *p*-Ph protons), 7.31 (t, 4H, ²J_{H,H} = 7.3 Hz, phenyl protons), 7.41 (t, 4H, ²J_{H,H} = 7.7 Hz, phenyl protons), 7.52 (m, 4H, *o*-PPh), 7.76 (d, 4H, ²J_{H,H} = 7.4 Hz, *o*-NPh). ¹H{³¹P} NMR (C₇D₈, -

30°C), selected peaks only: δ 0.90 (d, 2H, $^2J_{\text{H,H}} = 14.5$ Hz, SiCH₂P), 1.32 (dd, 4H, $^2J_{\text{H,H}} = 14.5$ Hz, SiCH₂P), 1.45 (d, 2H, $^2J_{\text{H,H}} = 14.5$ Hz, SiCH₂P), 4.87 (s, 2H, TaCH₂Ta), (7.51 (d, 4H, $^2J_{\text{H,H}} = 7.4$ Hz, *o*-PPh). ¹³C APT NMR (C₇D₈, -30°C): δ 1.16, 1.39, 2.79 and 2.92 (s, SiCH₃), 12.99 and 17.18 (s, SiCH₂P), 122.76, 124.53, 128.33, 129.35, 131.49 and 131.90 (s, *o*-, *m*- and *p*-Ph carbons), 141.47 (broad s, TaCH₂Ta), 153.79 (d, $^1J_{\text{C,P}} = 6.0$ Hz, *i*-PPh), 155.30 (s, *i*-NPh). MS (EI) *m/z* (%): 1308 (50) [M]⁺, 661 (40) [M - PhP(CH₂SiMe₂NPh)₂TaS]⁺, 661 (40) [M - PhP(CH₂SiMe₂NPh)₂TaS(CH₂)]⁺. Anal. Calcd for C₄₉H₆₄N₄P₂S₂Si₄Ta₂: C 44.95, H 4.93, N 4.28. Found: C 44.57, H 5.31, N 4.59.

Starting from [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ -H)₄ (prepared in situ): A yellow solution of [PhP(CH₂SiMe₂NPh)₂]TaMe₃ (850 mg, 1.28 mmol) in Et₂O (50 ml) was transferred into a thick-wall glass vessel equipped with a Teflon valve and thoroughly degassed via three freeze-pump-thaw cycles. The vessel was cooled in liquid nitrogen, filled with H₂ gas and sealed under atmospheric pressure. The reaction mixture was allowed to warm to room temperature, while the pressure inside the vessel slowly rose to approximately four atmospheres. After stirring at room temperature over night, a purple solution of [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ -H)₄ was obtained. The vessel was cooled in liquid nitrogen, the headspace evaporated and a thoroughly degassed solution of carbon disulfide (3.5 ml, 0.2M in Et₂O, 0.70 mmol, 1.1 eq) condensed into the vessel. Note that exposure to dinitrogen has to be avoided during this procedure, due to the N₂-sensitivity of [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ -H)₄. The vessel was then sealed and warmed to room temperature under static vacuum while stirring. Shortly after the reaction mixture had reached room temperature, the purple solution turned brown-orange within a few minutes. Stirring was continued for 1 h and all volatiles removed in vacuum subsequently. Hexanes (10 ml) and a few drops of benzene were added to the residue to precipitate the product as an orange powder, which was filtered off, rinsed with hexanes (2 × 5 ml) and dried in vacuum. Yield: 480 mg, 0.37 mmol, 58%. A second crop (80 mg, 0.06 mmol, 9%) was obtained from the filtrate after 2 d at -40°C. Analytical data were found to be identical with that above.

[PhP(CH₂SiMe₂NPh)₂Ta(μ -S)]₂ (3).

Starting from [PhP(CH₂SiMe₂NPh)₂Ta(μ -S)]₂(μ -CH₂): A solution of [PhP(CH₂SiMe₂NPh)₂Ta(μ -S)]₂(μ -CH₂) (2) (250 mg, 0.20 mmol) dissolved in Et₂O (60 ml) was transferred into a thick-wall glass vessel equipped with a Teflon valve and degassed via two freeze-pump-thaw cycles. Dihydrogen gas was added to the vessel at -196°C before it was sealed and warmed to room temperature. After stirring for 4 d under H₂-pressure (approximately four atmospheres), excess dihydrogen was released and the solvent evaporated to dryness. The residual brown powder was triturated with hexanes (10 ml) and the brownish-ocher product filtered off, washed with hexanes (2 × 5 ml) and dried in vacuum. Yield: 180 mg, 0.14 mmol, 69%. ¹H NMR (C₆D₆): δ -0.21 (s, 12H, SiCH₃), 0.32 (s, 12H, SiCH₃), 1.62 (ABX, 4H, SiCH₂P), 1.84 (ABX, 4H, SiCH₂P), 7.00, 7.18, 7.40 and 7.68 (m, 30H total, phenyl protons). ¹H{³¹P} NMR (C₆D₆), selected peaks only: 1.62 (d, 4H, $^2J_{\text{H,H}} = 13.7$ Hz, SiCH₂P), 1.84 (d, 4H, $^2J_{\text{H,H}} = 13.7$ Hz, SiCH₂P). ³¹P{¹H} NMR (C₆D₆): δ 13.0 (s). ¹³C APT NMR (C₆D₆): δ 2.13 (s, SiCH₃), 2.58 (s, SiCH₃), 16.16 (s, SiCH₂P), 122.54, 128.47, 128.56, 130.13, 134.13 and 134.25 (*o*-, *m*- and *p*-Ph carbons), 155.25 and 155.28 (overlapping s and d, *i*-Ph carbons). MS (EI) *m/z* (%): 1294 (100) [M]⁺. MS (EI, high resolution) Calcd for C₄₈H₆₂N₄P₂S₂Si₄Ta₂: 1294.19286. Found: 1294.19364. Anal. Calcd for C₄₈H₆₂N₄P₂S₂Si₄Ta₂: C 44.51, H 4.82, N 4.33. Found: C 44.58, H 4.87, N 4.10.

Starting from [PhP(CH₂SiMe₂NPh)₂Ta]₂(μ -H)₄ (prepared in situ): A solution of [PhP(CH₂SiMe₂NPh)₂]TaMe₃ (410 mg, 0.62 mmol) as described in the preparation of 2. The purple solution was frozen in liquid nitrogen and the headspace of the vessel evaporated. Subsequently, a thoroughly degassed solution of carbon disulfide (1.7 ml, 0.2M in Et₂O, 0.34 mmol, 1.1 eq) was condensed in and the vessel filled with dihydrogen, sealed and warmed to room temperature. The pressurized reaction mixture (approximately four atmospheres) was stirred for 4 d at room temperature. The over-pressure was then released and the brown solution evaporated to dryness. Hexanes (5 ml) was added to the tacky residue, resulting in the

precipitation of the product as a brownish-ocher powder, which was filtered off, rinsed with hexanes (2×2 ml) and dried in vacuum. Yield: 260 mg, 0.20 mmol, 64%. Analytical data were found to be identical with that above.

X-ray Crystallographic Analyses

Suitable single crystals were selected in a Glovebox, coated in Fomblin oil and mounted on a glass fiber. X-ray data were collected on a Rigaku/ADSC CCD (compound **2**) or on a Bruker X8 Apex II diffractometer (compound **3**) with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at a temperature of $-100 \pm 1^{\circ}\text{C}$. Data were collected and integrated using the Bruker SAINT software package.^[2] Absorption corrections were performed using the using the multiscan technique (SADABS).^[3] The structures were solved by direct methods and refined using all reflections with the SHELX-97 program package.^[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter. Structures were solved and refined using the WinGX (version 1.80.05) software package.^[5]

Solvent accessible voids with virtually no residual electron density are found in the crystal packing of **2**. The highest peak ($1.38 \text{ e}^{-}/\text{\AA}^3$) and the deepest hole ($-0.96 \text{ e}^{-}/\text{\AA}^3$) in the residual electron density map indicate the absence of co-crystallized solvents. However, co-crystallized solvent molecules might have been present before the crystals were immersed and selected under Fomblin oil. During the time of crystal selection, the latter solvents might have diffused out of the cavities into the surrounding oil.

In the unit cell of compound **3**, two independent molecules are present, which differ slightly in the positions of the ligand's methylene linkers. One molecule is perfectly symmetric (inversion center; half of the molecule is generated by symmetry operation), while the second one deviates marginally from ideal C_i symmetry (a complete molecule is present in the asymmetric unit). However, the molecules' bond lengths and angles between the heavy atoms are only insignificantly different. Therefore, only the crystallographically asymmetric molecule is shown in Figure S1 below (hydrogen atoms, phenyl and silylmethyl groups omitted for sake of clarity).

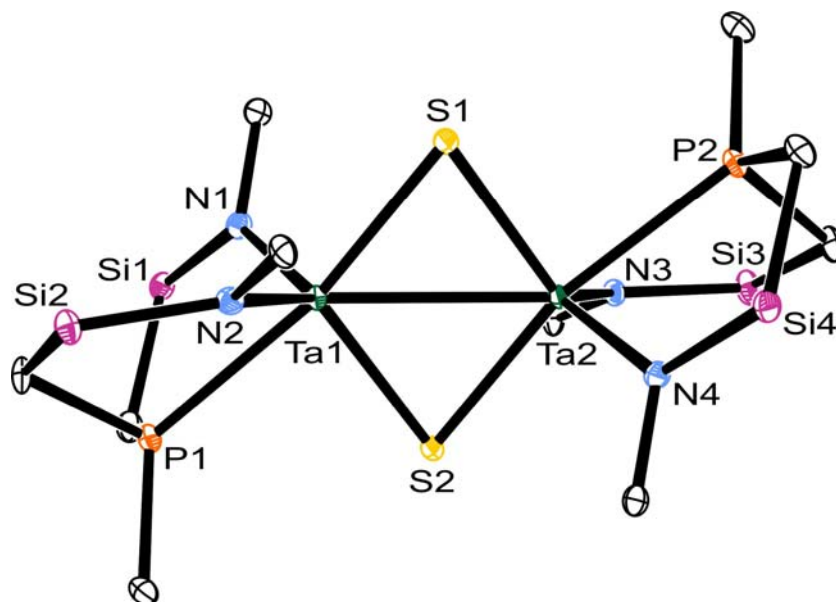


Figure S1: Molecular structure of **3**. Selected bond lengths (\AA) and angles (deg): Ta1-Ta2, 2.8612(2); Ta1-S1, 2.3760(8); Ta1-S2, 2.3641(8); Ta2-S1, 2.3641(8), Ta2-S2, 2.3689(7); S1...S2, 3.7745(2); S1-Ta1-S2, 105.55(3); S1-Ta2-S2, 105.78(3); Ta1-S1-Ta2, 74.26(2); Ta1-S2-Ta2, 74.39(2); P2-Ta2-Ta1-P1, 179.83(4).

Table S1: Crystal data and refinement details for **2** and **3**.

compound	2	3
empirical formula	C ₄₉ H ₆₂ N ₄ P ₂ S ₂ Si ₄ Ta ₂	C ₄₈ H ₆₂ N ₄ P ₂ S ₂ Si ₄ Ta ₂
formula weight	1307.35	1295.34
crystal size [mm]	0.30 × 0.25 × 0.05	0.20 × 0.16 × 0.12
crystal system	orthorhombic	monoclinic
space group	<i>Pbcn</i> (No. 60)	<i>P2₁/n</i> (No. 14)
<i>a</i> [Å]	21.9524(8)	13.9856(8)
<i>b</i> [Å]	21.7688(9)	16.6498(10)
<i>c</i> [Å]	24.6370(10)	35.4061(18)
β [°]	90.0	100.996(3)
<i>V</i> [Å ³]	11773.5(8)	8093.2(8)
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.475	1.595
<i>Z</i>	8	6
<i>F</i> (000)	5184	3852
μ [mm ⁻¹]	3.955 (Mo-K α)	4.214 (Mo-K α)
<i>T</i> _{max} / <i>T</i> _{min}	0.631 / 0.821	0.441 / 0.596
<i>hkl</i> range	0 - 28, 0 - 26, \pm 31	-15 - 16, -18 - 19, \pm 42
θ range [°]	2.49 - 28.08	1.49 - 25.07
measured reflections	22431	55572
unique reflections	13086	14312
observed reflections <i>I</i> > 2 σ (<i>I</i>)	7696	12540
refined parameters	576	850
goodness-of-fit	1.015	1.048
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0368, 0.0857	0.0215, 0.0435
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0922, 0.1010	0.0288, 0.0450
residual electron dens. [e Å ⁻³]	1.368 / -0.964	0.800 / -0.693

References

- [1] a) M. D. Fryzuk, S. A. Johnson, B. O. Patrick, A. Albinati, S. A. Mason, T. F. Koetzle, *J. Am. Chem. Soc.* **2001**, *123*, 3960-3973; b) M. D. Fryzuk, S. A. Johnson, S. J. Rettig, *J. Am. Chem. Soc.* **1998**, *120*, 11024-11025.
- [2] SAINT. Version 7.03A. Bruker AXS Inc., Madison, Wisconsin, USA (1997-2003).
- [3] SADABS. Bruker Nonius area detector scaling and absorption correction - V2.10, Bruker AXS Inc., Madison, Wisconsin, USA (2003).
- [4] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
- [5] L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837-838.

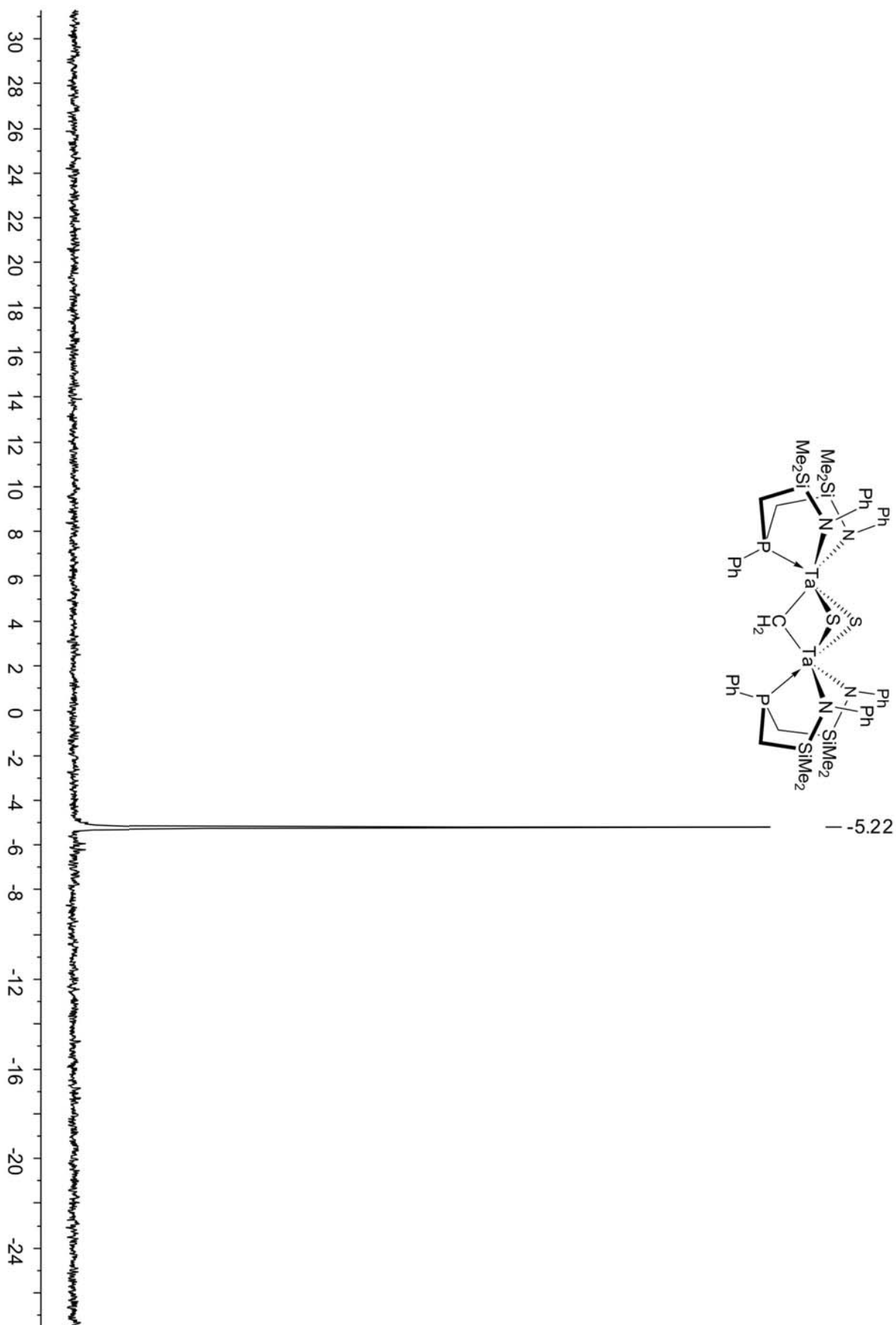


Figure S2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (161.9 MHz, RT) of **2** in C_6D_6 .

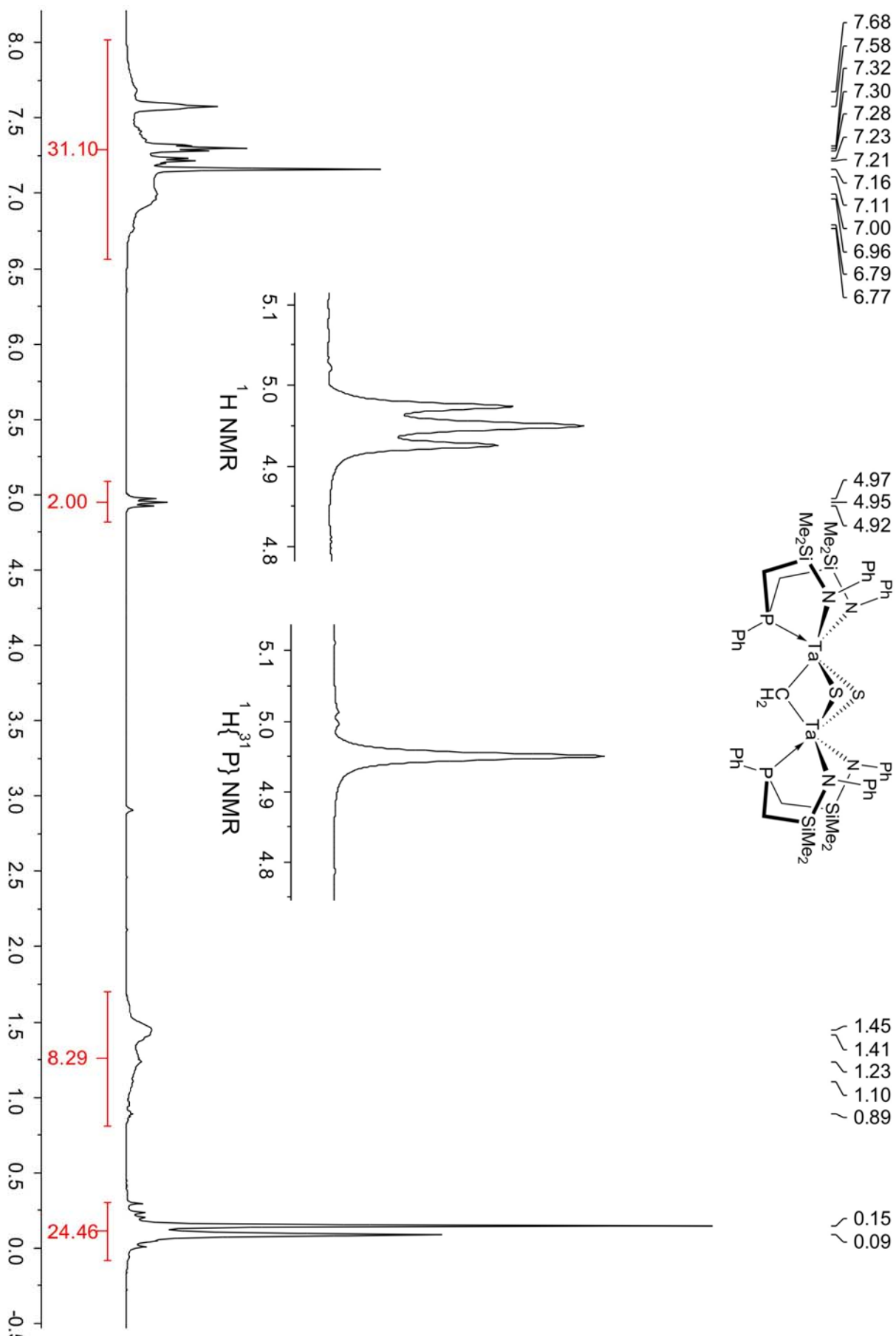


Figure S3: ^1H NMR spectrum (400MHz, RT) of **2** in C_6D_6 .

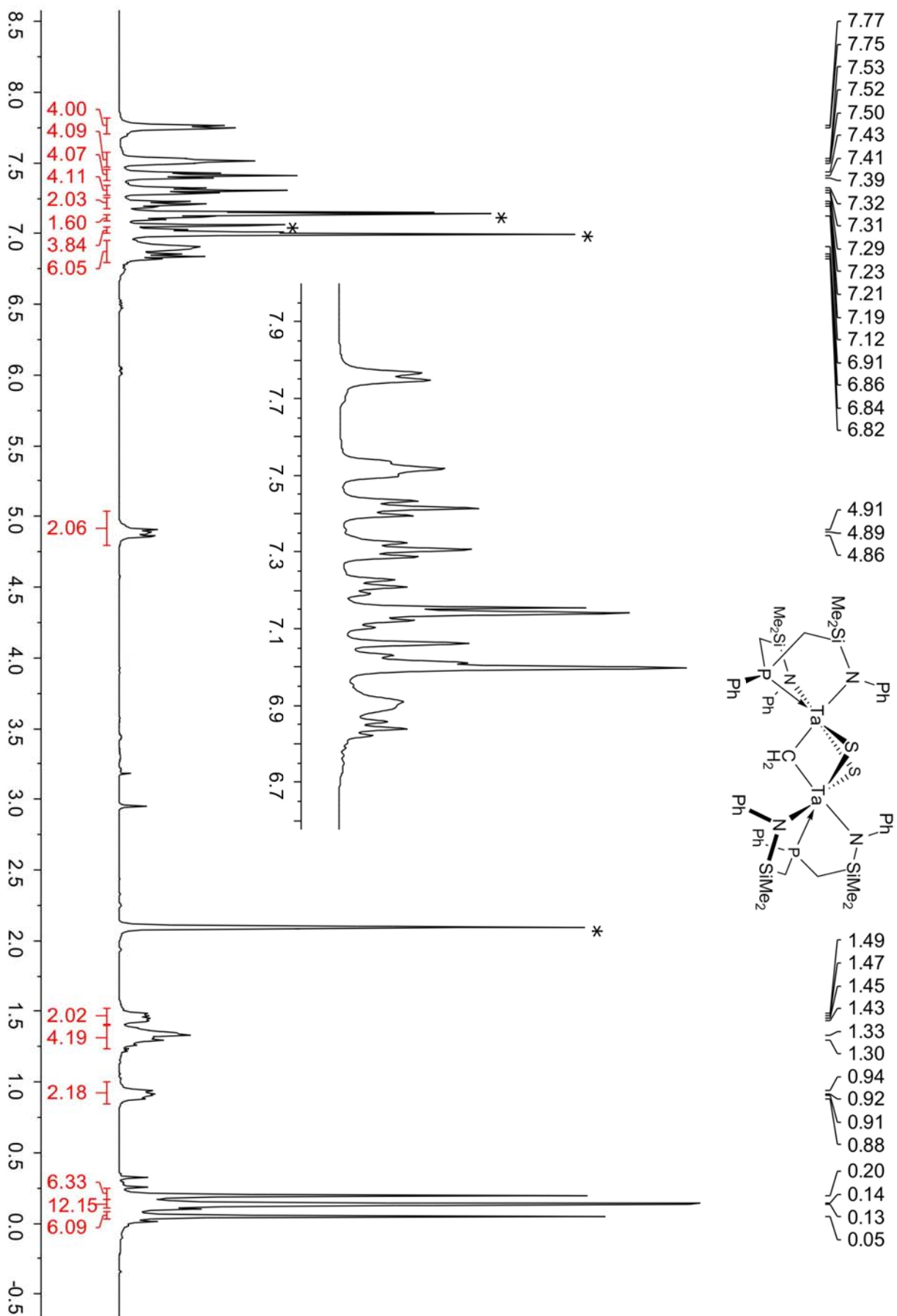


Figure S4: ¹H NMR spectrum (400 MHz, -30°C) of **2** in C₇D₈. Residual proton signals of C₇D₈ are marked by an asterisk.

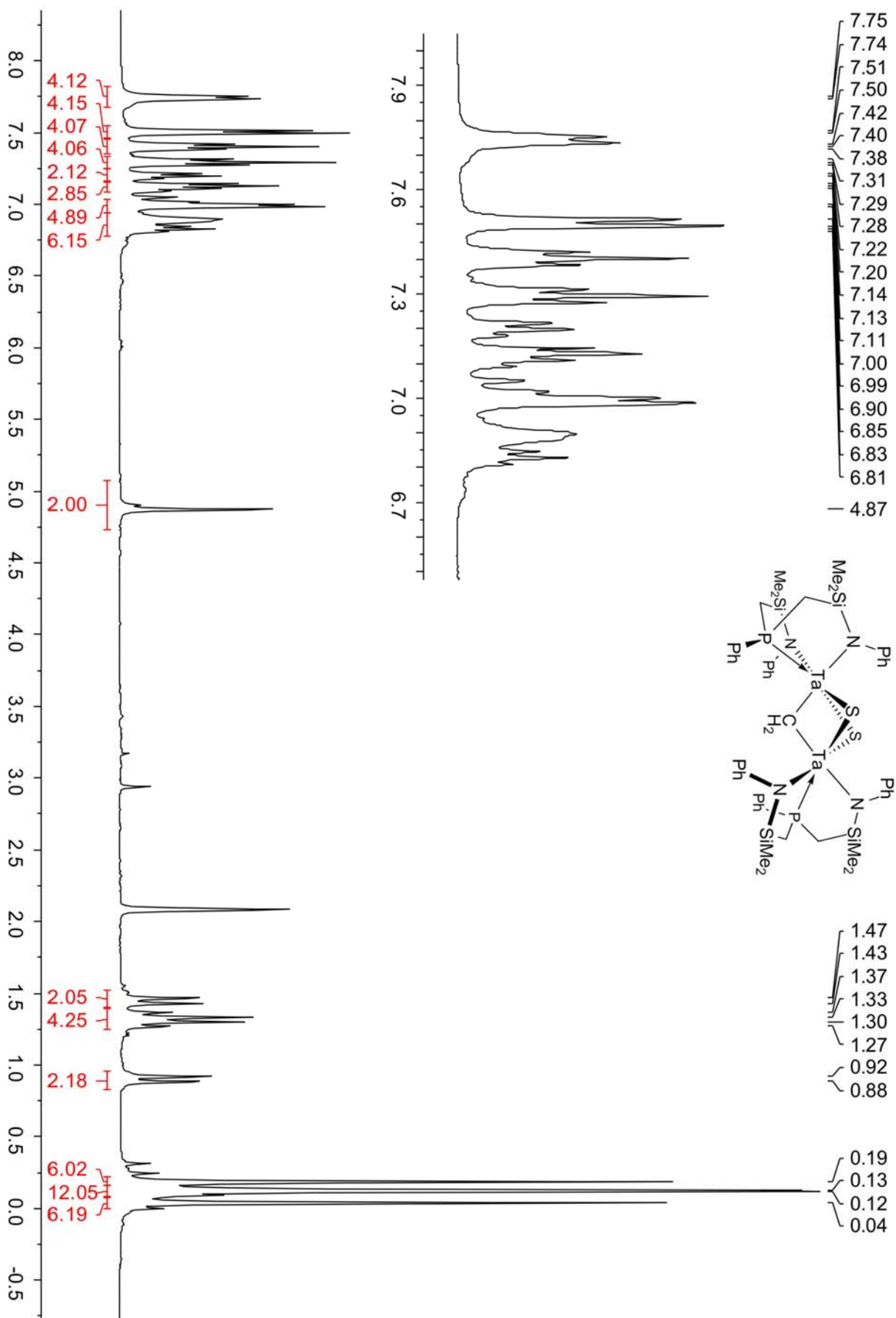


Figure S5: $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (400MHz, -30°C) of **2** in C_7D_8 .

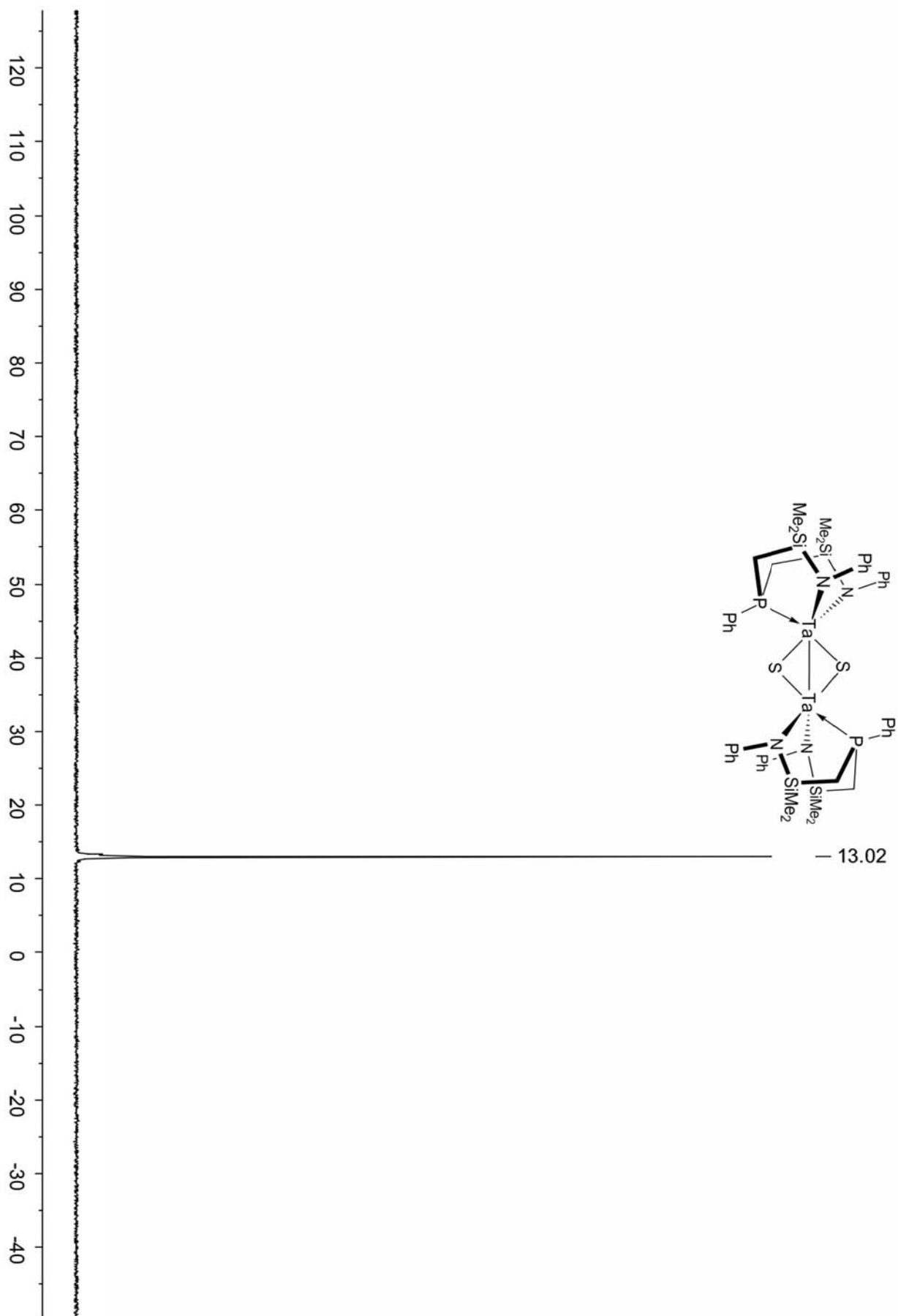


Figure S6: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (161.9 MHz, RT) of **3** in C_6D_6 .

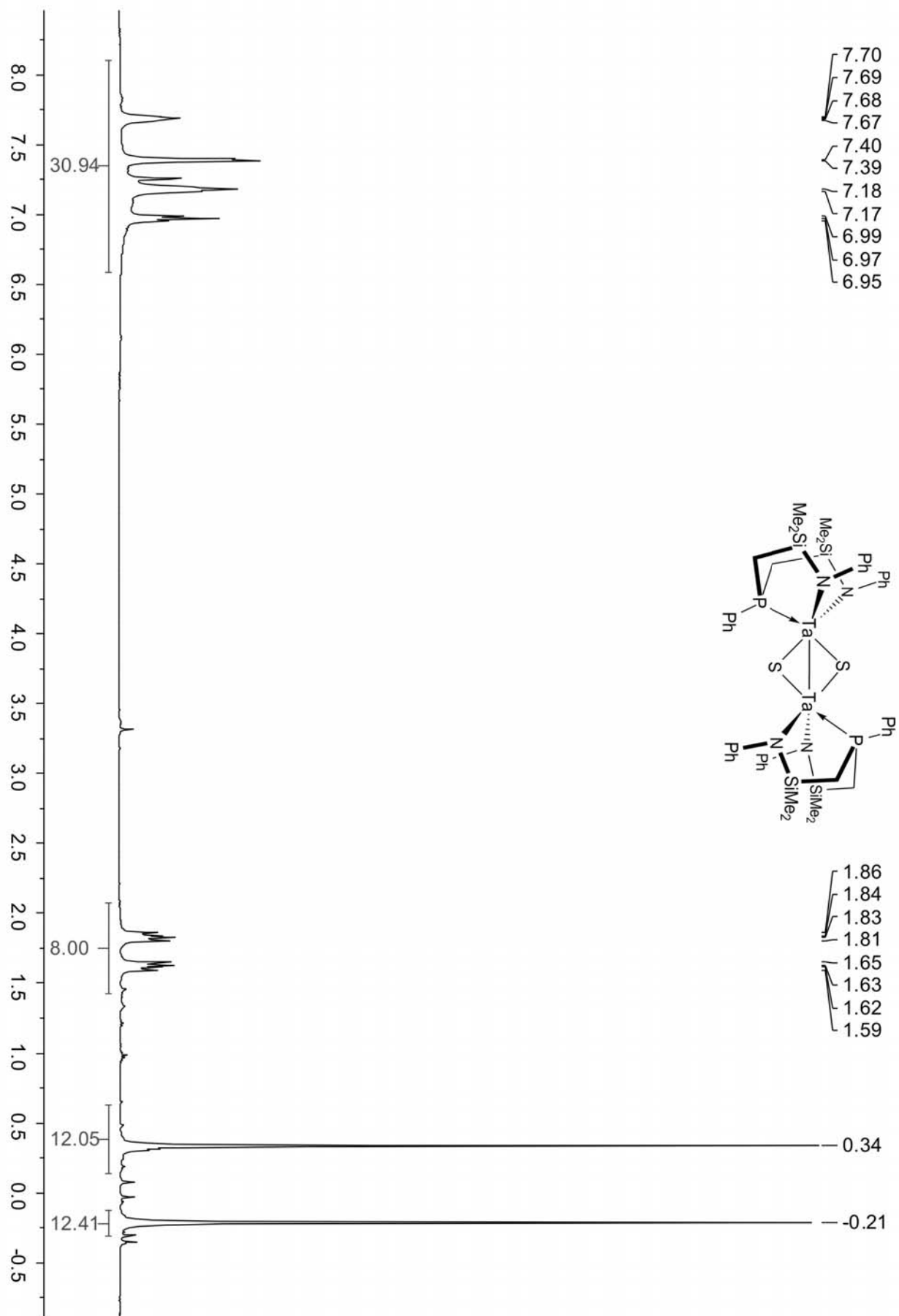


Figure S7: ¹H NMR spectrum (400MHz, RT) of **3** in C₆D₆.

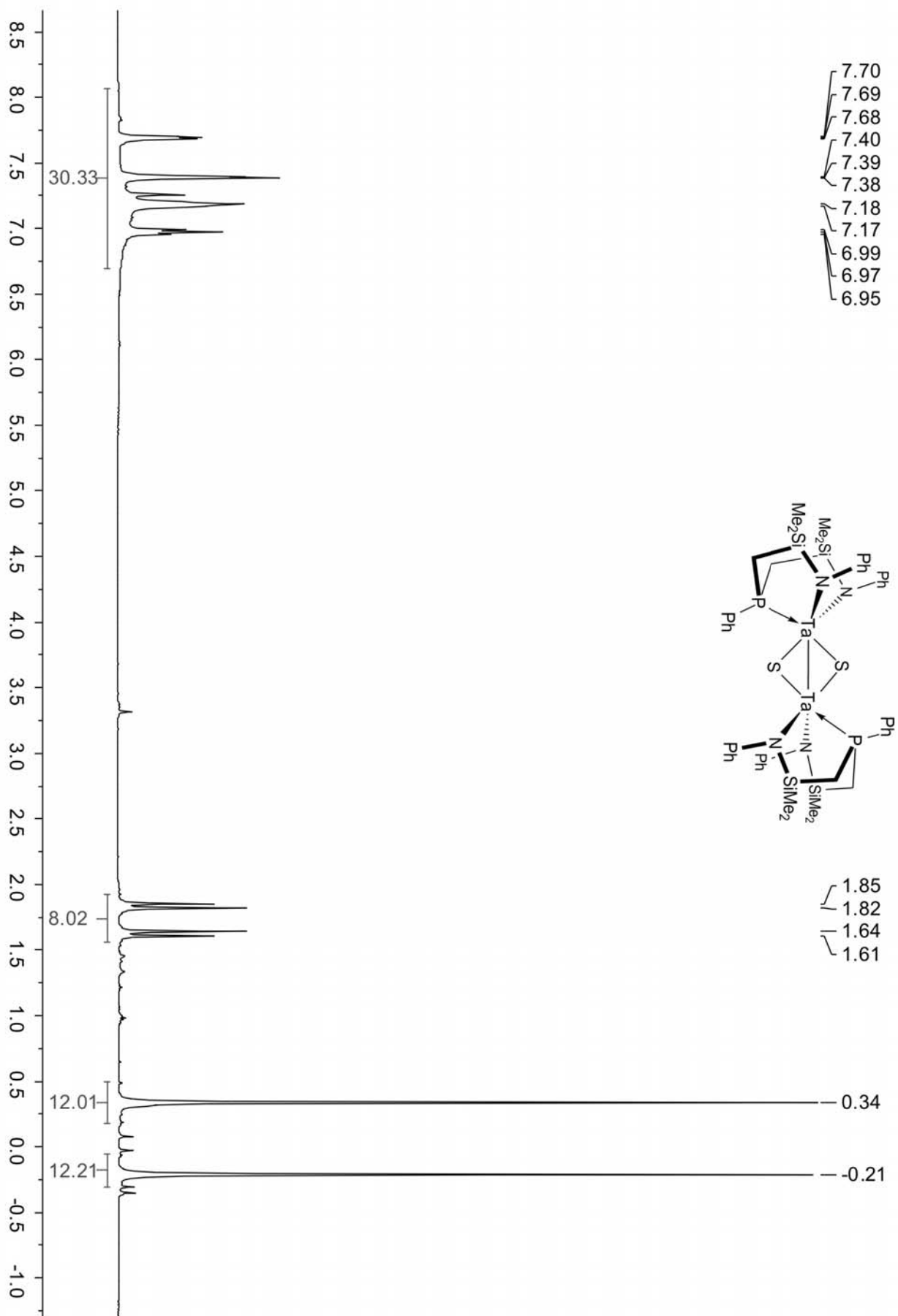


Figure S8: $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (400MHz, RT) of **3** in C_6D_6 .