

## Supporting Information for

# A Twist on a Classic Scaffold: Rational Design of a New Bimetallic Platform

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### Table of Contents

I. General Considerations	S2
II. Syntheses	S3
III. NMR spectra	S11
IV. UV/Vis spectrophotometry	S25
V. X-ray Crystallography	S27
V. References	S30

**I. General Considerations:** Unless stated otherwise, all reactions were performed in a N<sub>2</sub>-filled glovebox or on a Schlenk line under an atmosphere of pure N<sub>2</sub> using standard Schlenk techniques. Solvents were stored over molecular sieves (4 Å) after collection from a JC Meyers Phoenix solvent purification system. C<sub>6</sub>D<sub>6</sub> was purchased from Cambridge Isotope Laboratories and dried over sodium/benzophenone before being distilled and degassed by three freeze-pump-thaw cycles. TiCl<sub>4</sub>(THF)<sub>2</sub>,<sup>1</sup> TiCl<sub>3</sub>(THF)<sub>3</sub>,<sup>2</sup> (tmeda)Ti(N<sup>t</sup>Bu)Cl<sub>2</sub>,<sup>3</sup> VCl<sub>3</sub>(THF)<sub>3</sub>,<sup>4</sup> and compound **1**<sup>5</sup> were prepared according to literature procedures. All other reagents were purchased from commercial suppliers and used as received.

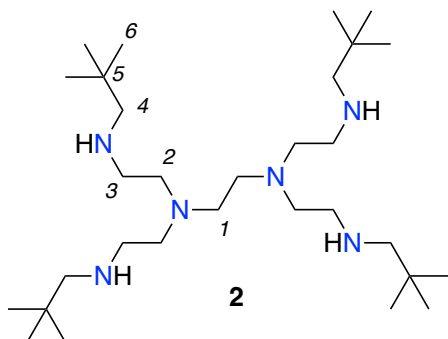
NMR spectra were recorded on Bruker Avance 400, 500 and 700 MHz spectrometers and are referenced to residual protio solvent for <sup>1</sup>H NMR spectroscopy. THF was used as solvent for Non-deuterium (No-D) NMR experiments.<sup>6</sup> Quantitative <sup>1</sup>H NMR data were acquired with a minimum of eight scans, with the delay time set to 5x the longest T<sub>1</sub> value present. 1,3,5-Trimethoxybenzene (TMB) was used as an internal standard for quantitative <sup>1</sup>H NMR spectroscopy. NMR spectra were taken at 25°C unless otherwise noted. Structural assignments were performed using HSQC and HMBC NMR spectroscopic experiments when necessary. All ESI-MS spectra were obtained at the Oregon State University Mass Spectrometry Center. Elemental analyses were performed by Midwest Microlab in Indianapolis, IN, USA. Buried volumes were calculated using SambVca 2.1 by uploading .xyz files generated from the .cif files. A standard sphere radius of 3.5 Å was used, and all atoms from non-tada ligands (i.e. N<sup>t</sup>Bu, THF or Cl) were deleted prior to the calculation.

### Statement on Elemental Analysis

Despite repeated attempts, the compounds reported herein all fall outside the typical 0.4% error range required to satisfy elemental analysis. Nevertheless, we have included representative examples of typical results for each compound. This is in part due to the extreme air sensitivity of these compounds. For instance, upon air exposure, compounds **4**, **5**, and **6** all rapidly hydrolyze, with **4** and **5** immediately re-forming compound **1**. Similarly, compounds **7**, **8**, and **9** all change colour immediately upon air exposure. For the diamagnetic compounds reported here, we point toward their NMR spectra to support purity of these compounds. Difficulties obtaining satisfactory elemental analyses of early transition metal complexes has been noted by others,<sup>7,8</sup> and the challenges and limitations of elemental analysis are an ongoing topic of discussion in the literature.<sup>9,10</sup>

## II. Syntheses

### Synthesis of 2



A 50 mL round bottom flask was charged with a solution of compound **1** (262.0 mg, 1.13 mmol, 1.00 equiv.) dissolved in 10 mL of MeOH. To this clear and colourless solution was added a solution of pivaldehyde (432.6 mg, 5.02 mmol, 4.44 equiv.) dissolved in 5 mL of MeOH. The flask was fitted with a reflux condenser and was heated to reflux for 3 hours.

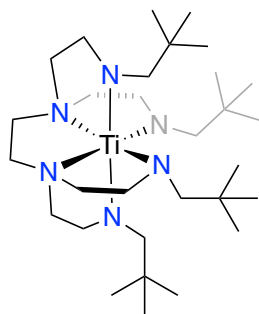
After cooling to room temperature, NaBH<sub>4</sub> (201.1 mg, 5.32 mmol, 4.70 equiv.) was added portionwise over 5 minutes, resulting in effervescence. The resulting cloudy, colourless solution was stirred at room temperature for 18 hours before the volatiles were removed *in vacuo*. The resulting white residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL), washed with DI water (30 mL) and brine (30 mL) before being dried over MgSO<sub>4</sub>. After filtration, the organic phase was concentrated *in vacuo* to give compound **2** as a thick, off-white oil (310.2 mg, 53% yield).

<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 2.66 (br. t, *J* = 5.7 Hz, 8H, **H3**), 2.61 (br. t, *J* = 5.6 Hz, 8H, **H2**), 2.55 (s, 4H, **H1**), 2.36 (s, 8H, **H4**), 0.92 (s, 36H, **H6**).

<sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 62.83 (**C4**), 54.92 (**C2**), 53.14 (**C1**), 49.05 (**C3**), 32.65 (**C5**), 28.06 (**C6**).

HRMS (ESI) Calcd for [M+H, C<sub>30</sub>H<sub>69</sub>N<sub>6</sub>]<sup>+</sup>: 513.5584. Found: 513.5594.

### Synthesis of **3**



**3**

In a glovebox, a scintillation vial was charged with compound **2** (97.2 mg, 0.190 mmol, 1.0 equiv.) and THF (5 mL) and stirred. To this cloudy, white solution was added dropwise <sup>n</sup>BuLi (1.6 M in hexane, 0.52 mL, 0.83 mmol, 4.4 equiv.), resulting in a rapid colour change to pale yellow. The reaction mixture was stirred at room temperature for 2 hours before a bright yellow THF solution (5 mL) of TiCl<sub>4</sub>(THF)<sub>2</sub> (74.2 mg, 0.224 mmol, 1.2 equiv.) was added dropwise, resulting in a rapid colour change to dark red. The solution was stirred for another hour at room temperature before the volatiles were removed *in vacuo* to yield a brown residue. The solid was extracted with hexane and filtered through glass fiber to yield a dark red-brown solution, which upon further drying *in vacuo* yielded compound **3** (92.1 mg, 87% yield) as a red-orange powder. Blocky red X-ray quality crystals of **3** were grown by cooling a concentrated hexane solution to -35 °C overnight.

<sup>1</sup>H NMR (700 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.45 (d, *J* = 12.7 Hz, 2H), 4.03 (d, *J* = 13.7 Hz, 2H), 3.92 (dd, *J* = 13.2 Hz, 6.6 Hz, 2H), 3.60-3.54 (m, 2H), 3.39 (dt, *J* = 11.3 Hz, 6.8 Hz, 2H), 3.31 (d, *J* = 12.8 Hz, 2H), 3.03-2.97 (m, 4H), 2.94 (dt, *J* = 12.4 Hz, 6.3 Hz, 2H), 2.82-2.76 (m, 2H), 2.70 (d, *J* = 13.8 Hz, 2H), 2.39 (dd, *J* = 10.9 Hz, 6.2 Hz, 2H), 2.20-2.14 (m, 2H), 2.02-1.95 (m, 2H), 1.25 (s, 18H), 1.18 (s, 18H).

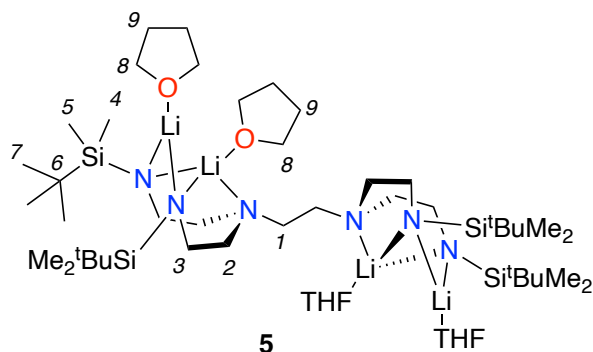
<sup>13</sup>C {<sup>1</sup>H} NMR (176 MHz, C<sub>6</sub>D<sub>6</sub>) δ 73.45, 73.39, 62.62, 62.33, 60.25, 59.63, 58.35, 36.48, 33.81, 31.51, 30.04.

Attempts to analyze **3** by HRMS (ESI) in NCMe resulted only in the detection of hydrolyzed ligand **2**.

Anal. Calcd for: [C<sub>30</sub>H<sub>64</sub>N<sub>6</sub>Ti]: C, 64.72; H, 11.59; N, 15.10. Found: C, 54.45; H, 10.10; N, 11.89.



## Synthesis of 5



In a glovebox, a colourless solution of compound **1** (103 mg, 0.430 mmol, 1.0 equiv.) in 4 mL of THF was stirred at room temperature. Subsequently, a solution of <sup>n</sup>BuLi (1.6 M, 1.10 mL, 1.7 mmol, 4.0 equiv.) was added dropwise. The solution was then stirred rapidly for 2 hours, leading to a color change from colorless to pale

yellow. A THF (1 mL) solution of <sup>t</sup>BuMe<sub>2</sub>SiCl (266 mg, 1.77 mmol, 4.0 equiv.) was then added dropwise, and the mixture was stirred for an additional 2 hours. The volatiles were removed *in vacuo*, and the residue was extracted with hexane and concentrated to yield a yellow oil, which was redissolved in THF (5 mL) and stirred for 20 minutes. A further dropwise addition of <sup>n</sup>BuLi (1.6 M, 0.48 mL, 0.76 mmol, 5.0 equiv.) was then carried out, followed by stirring for 1.5 hours. After removal of the solvent *in vacuo*, the resulting white residue was recrystallized from hexane to afford **5** (94 mg, 83% yield) as white crystals. Crystals suitable for X-ray diffraction were grown by cooling a concentrated THF solution layered with hexane to -35 °C overnight. High quality crystals could also be grown by cooling a concentrated Et<sub>2</sub>O solution to -35 °C overnight.

<sup>1</sup>H NMR (700 MHz, C<sub>6</sub>D<sub>6</sub>) δ 3.57 (m, 16H, **H8**), 3.55-3.51 (m, 4H, **H3**), 3.32-3.28 (m, 4H, **H3**), 2.85 (s, 4H, **H1**), 2.58-2.49 (m, 8H, **H2**), 1.36 (m, 16H, **H9**), 1.19 (s, 36H, **H7**), 0.28 (s, 12H, **H4**), 0.20 (s, 12H, **H5**).

<sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, C<sub>6</sub>D<sub>6</sub>) δ 68.40 (**C8**), 59.16 (**C2**), 53.63 (**C1**), 46.71 (**C3**), 28.30 (**C7**), 25.54 (**C9**), 20.78 (**C6**), -2.18 (**C5**), -3.37 (**C4**).

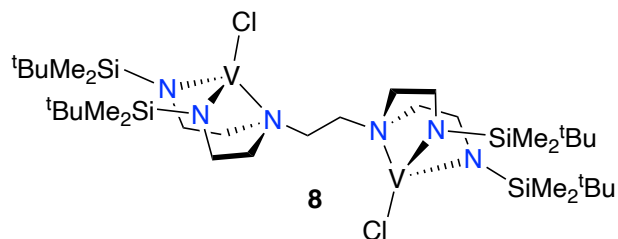
Anal. Calcd for: C<sub>50</sub>H<sub>110</sub>Li<sub>4</sub>N<sub>6</sub>O<sub>4</sub>Si<sub>4</sub>: C, 60.08; H, 11.09; N, 8.41. Found: C, 52.57; H, 10.57; N, 6.57.







## Synthesis of **8**



To a colourless solution of compound **5** (30 mg, 0.042 mmol, 1.0 equiv.) in 5 mL of THF, a red solution of  $\text{VCl}_3(\text{THF})_3$  (31 mg, 0.084 mmol, 2.0 equiv.) in 1 mL of THF was added dropwise. This addition resulted in a rapid color change to

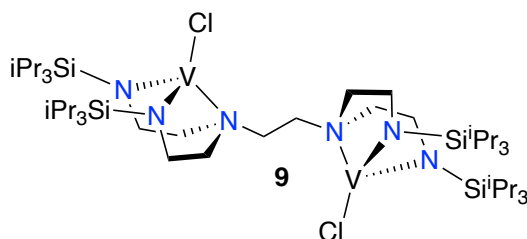
red-brown. The solution was then stirred at room temperature for 16 hours. The volatiles were then removed *in vacuo*, yielding a red-brown residue that was extracted with hexane, filtered through glass fiber, and dried *in vacuo* to yield compound **8** as a red powder (31 mg, 86% yield). X-ray quality crystals of compound **8** were grown by cooling a concentrated solution in hexane at  $-35^\circ\text{C}$  overnight.

Red solutions of compound **8** in  $\text{C}_6\text{D}_6$  are  $^1\text{H}$  NMR silent, showing no observable resonances between  $-50$  and  $+100$  ppm.

Effective magnetic moment, (Evans' method, THF)  $\mu_{\text{eff}} = 3.4 \mu_{\text{B}}$ . The observed value may indicate a degree of antiferromagnetic coupling between the two ( $d^2$ ) V(III) centers. Similar coupling has recently been observed with dititanium.<sup>11</sup>

Despite repeated attempts, we were unable to obtain satisfactory elemental analysis of **8**, likely due to its extreme air sensitivity.

## Synthesis of **9**



To a colorless solution of compound **6** (30 mg, 0.031 mmol, 1.0 equiv.) in 5 mL of THF, a red solution of  $\text{VCl}_3(\text{THF})_3$  complex (23 mg, 0.062 mmol, 2.0 equiv.) in 1 mL of THF was added dropwise. This addition resulted in a rapid color change to purple. The solution

was then stirred at room temperature for 16 hours. The volatiles were removed *in vacuo*, yielding a purple residue that was extracted with hexane, filtered through glass fiber, and dried *in vacuo* to yield compound **9** as a purple powder (25 mg, 82% yield). X-ray quality crystals of compound **9** were grown by cooling a concentrated solution in hexane at  $-35\text{ }^\circ\text{C}$  overnight.

Purple solutions of compound **9** in  $\text{C}_6\text{D}_6$  are  $^1\text{H}$  NMR silent, showing no observable resonances between  $-50$  and  $+100$  ppm.

Effective magnetic moment, (Evans' method, THF)  $\mu_{\text{eff}} = 3.6\ \mu_{\text{B}}$ . The observed value may indicate a degree of antiferromagnetic coupling between the two ( $d^2$ ) V(III) centers. Similar coupling has recently been observed with dititanium.<sup>11</sup>

Anal. Calcd for  $[\text{C}_{46}\text{H}_{104}\text{Cl}_2\text{N}_6\text{Si}_4\text{V}_2]$ : C, 53.82; H, 10.21; N, 8.19; Found: C, 48.48; H, 10.54; N, 8.79.

### III. NMR Spectra

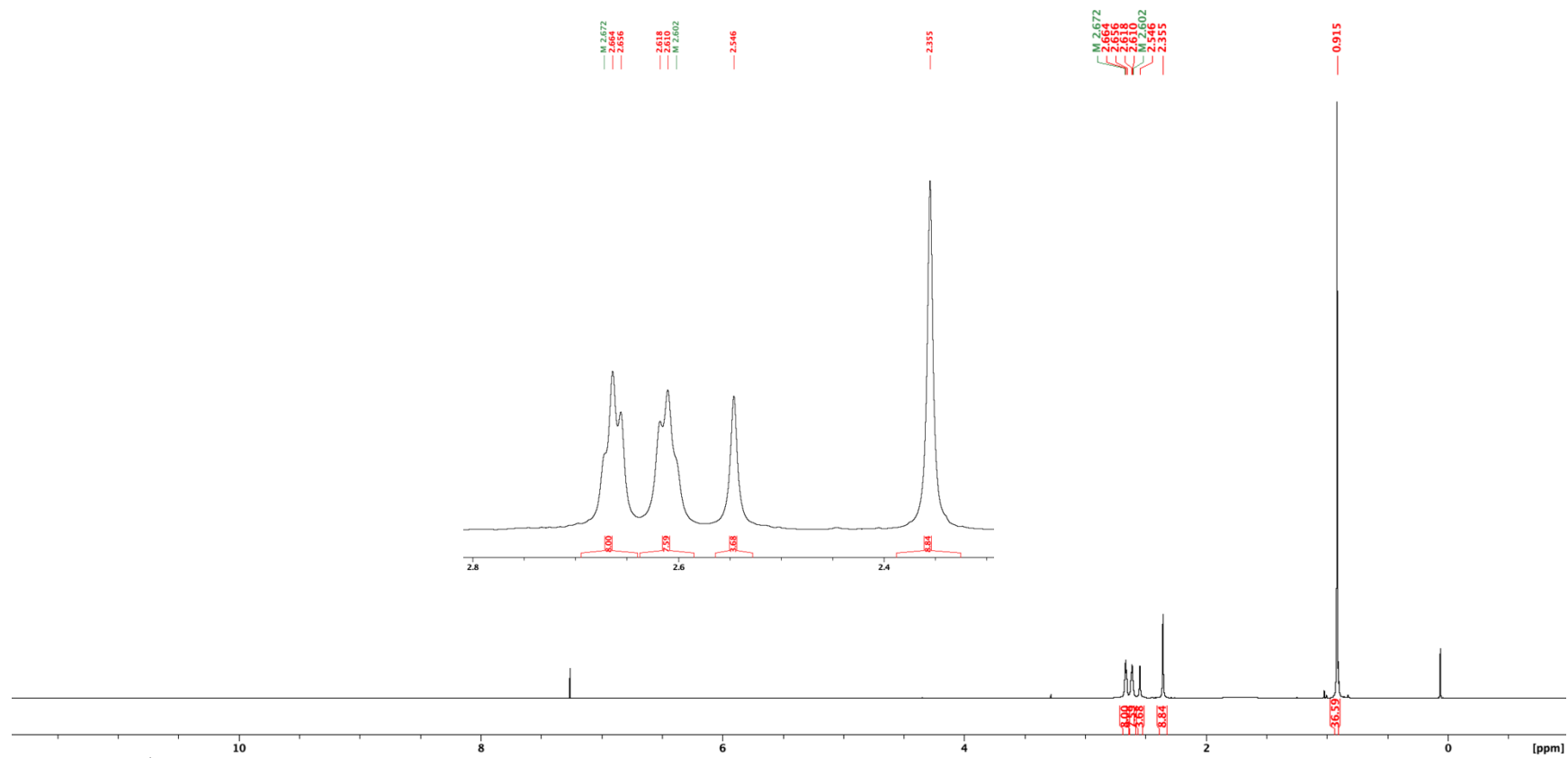
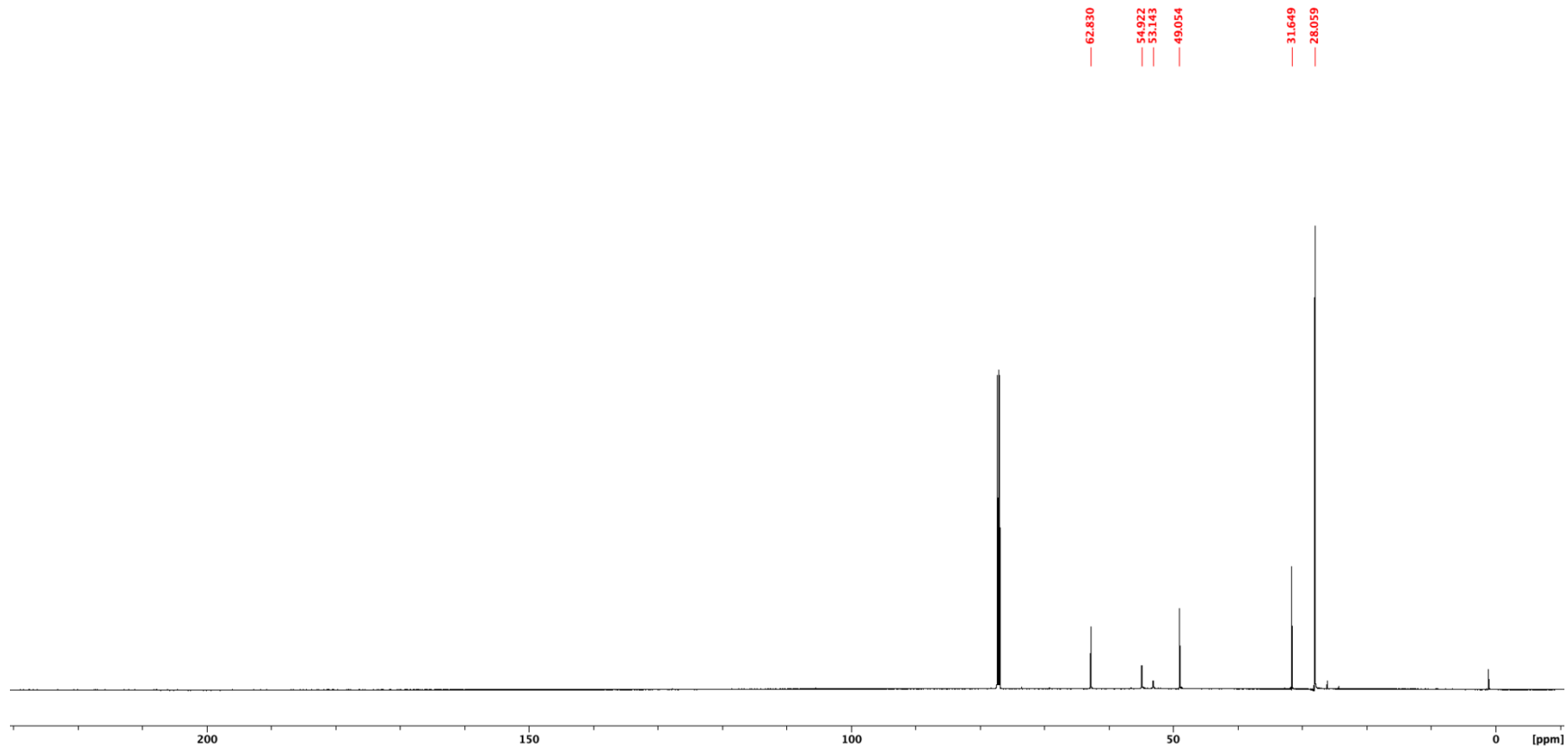
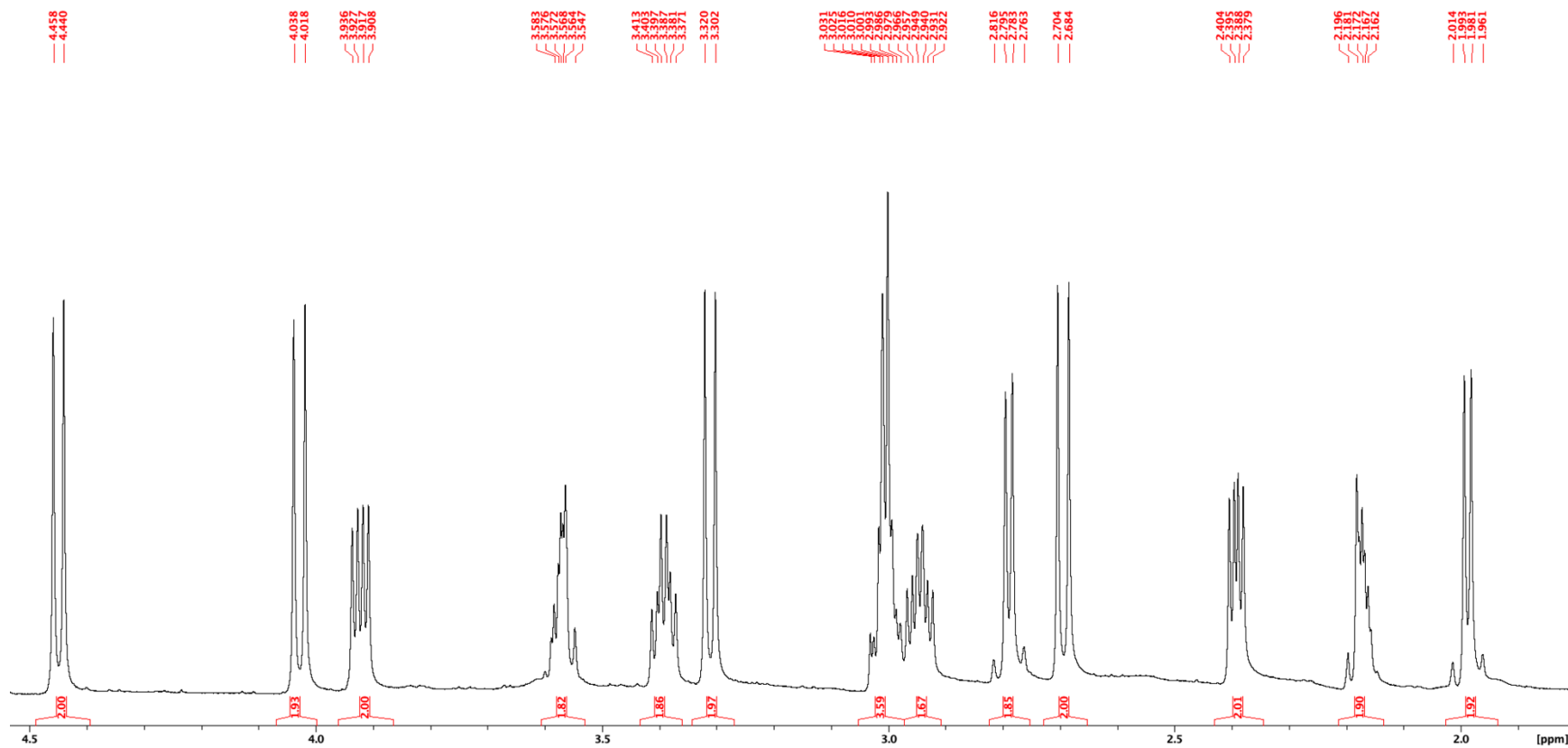


Figure S1. <sup>1</sup>H NMR spectrum (700 MHz, CDCl<sub>3</sub>, 25 °C) of **2**. Inset shows a close-up of the methylene region.

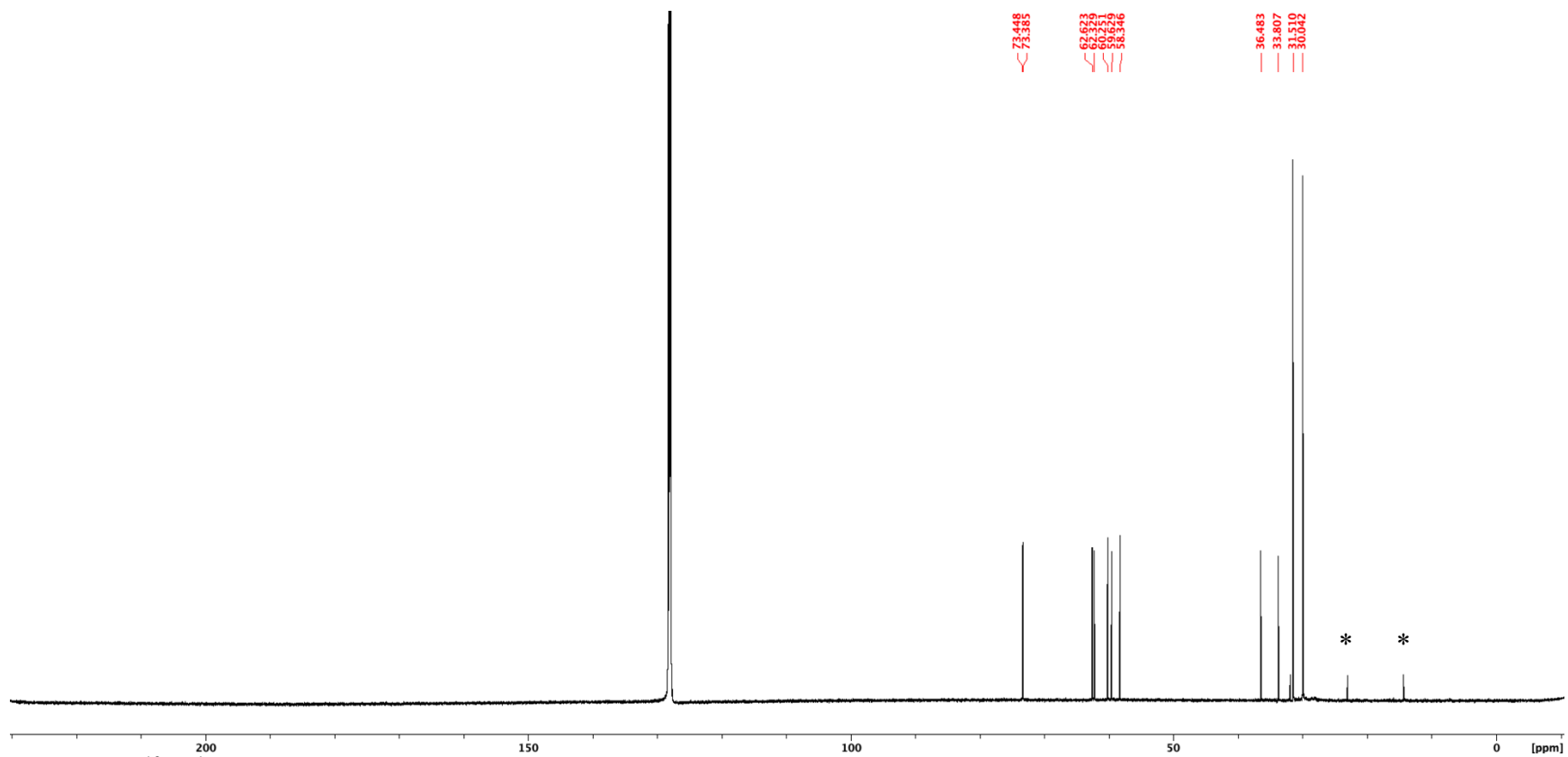


**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (176 MHz,  $\text{CDCl}_3$ , 25 °C) of **2**.

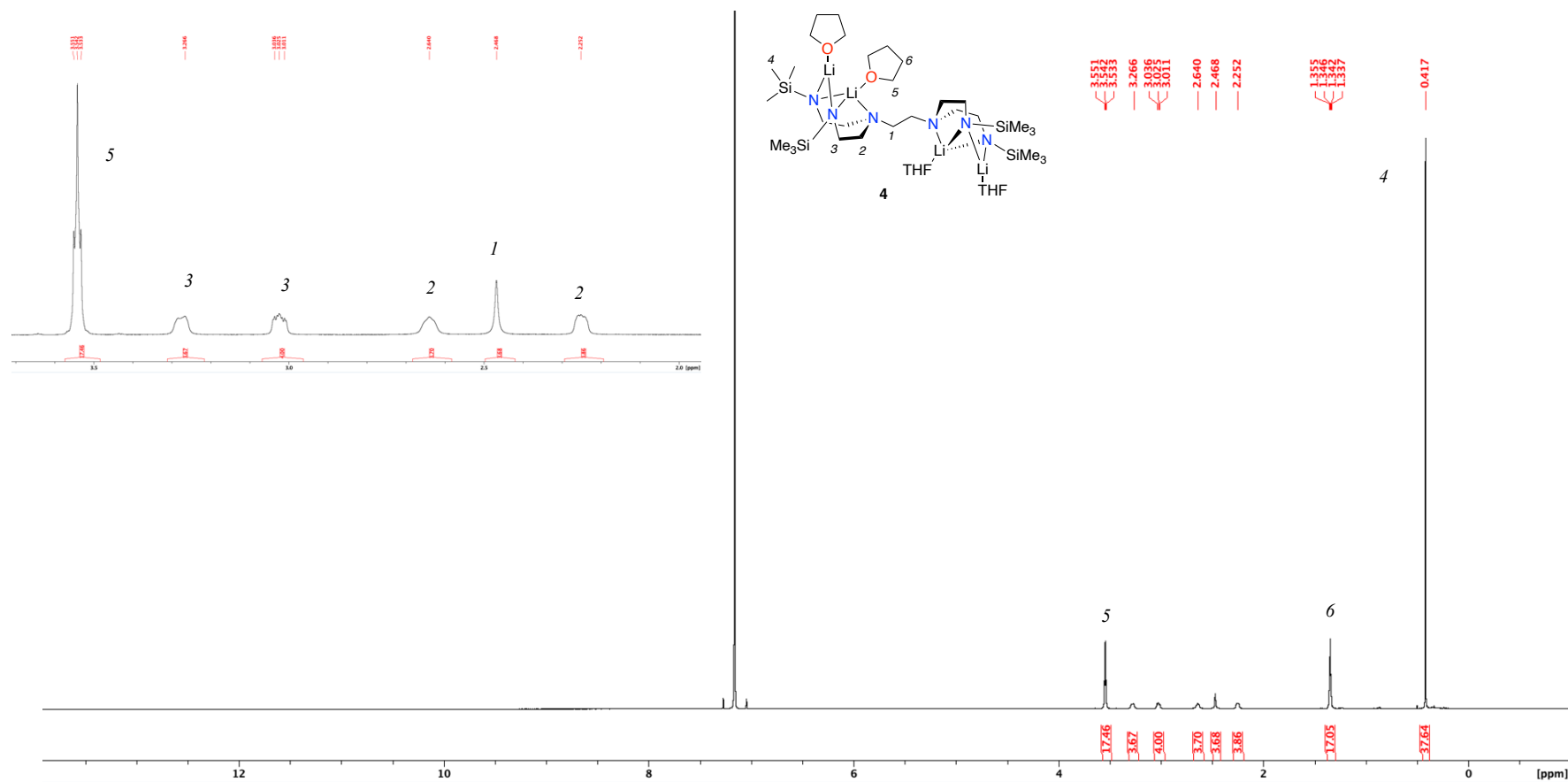




**Figure S4.** Close-up of the methylene region of the  $^1\text{H}$  NMR spectrum (700 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ) of **3**.

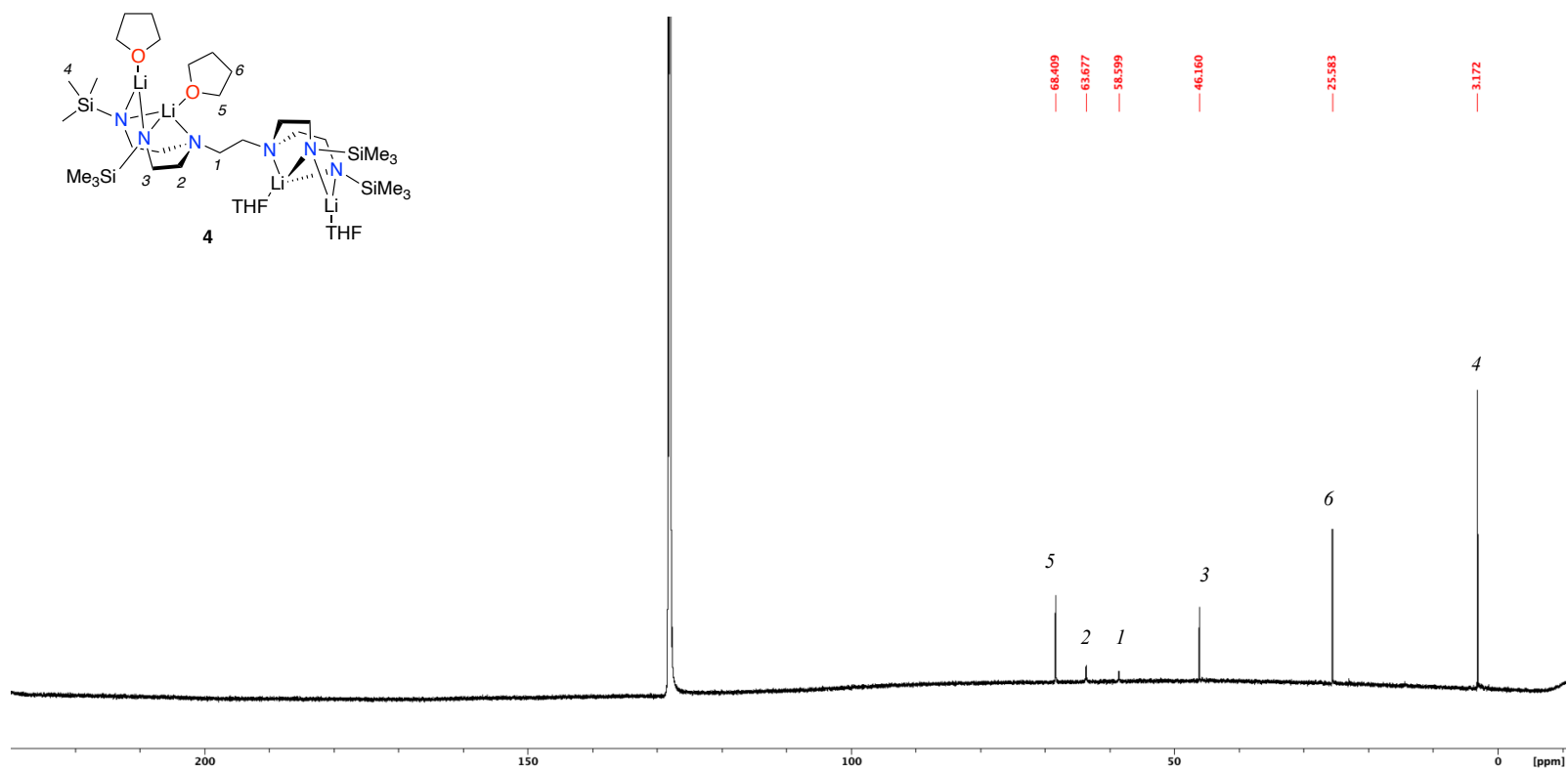


**Figure S5.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (176 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) of **3**. \* indicates residual hexane from recrystallization.

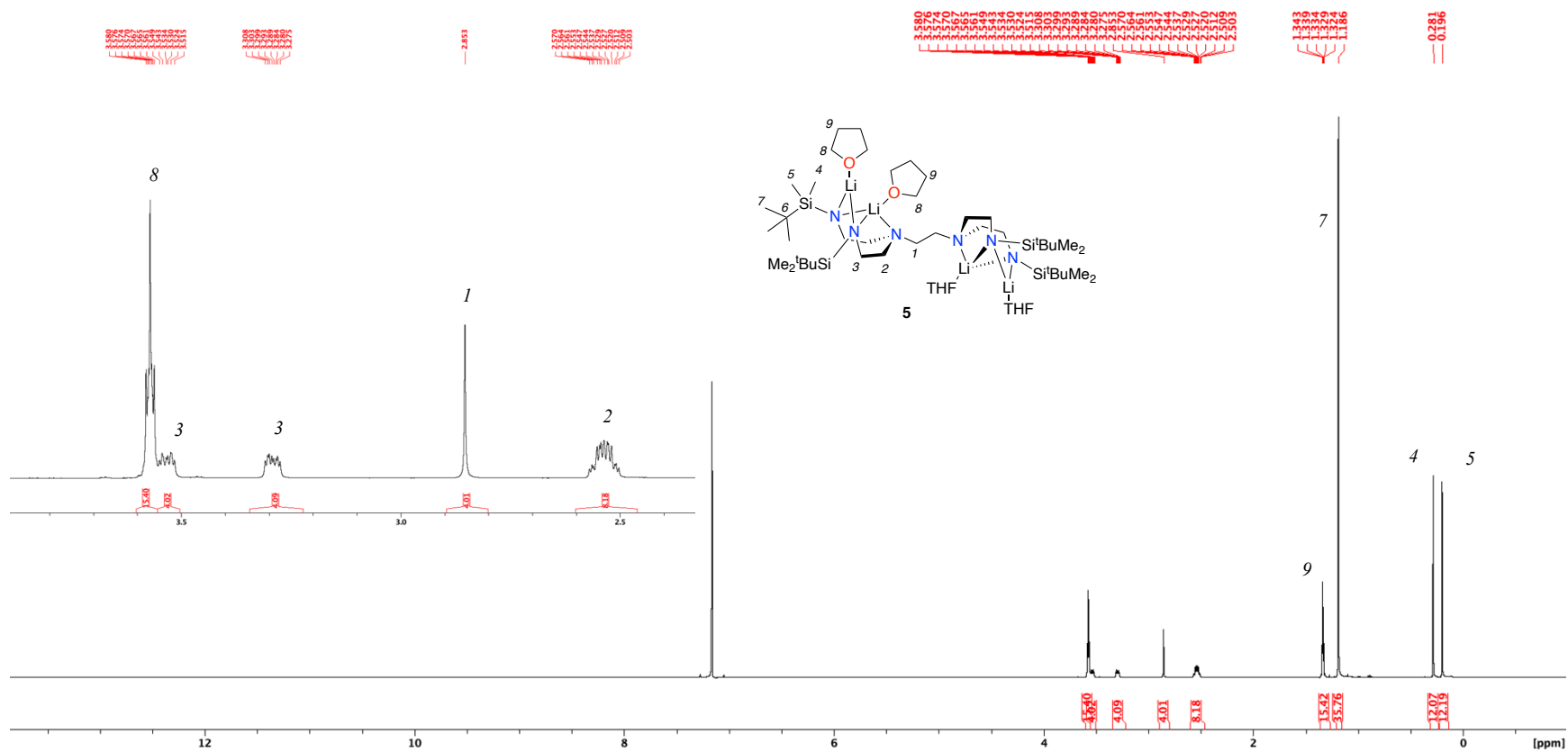


**Figure S6.**  $^1\text{H}$  NMR spectrum (700 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ) of **4**. Inset shows a close-up of the methylene region.

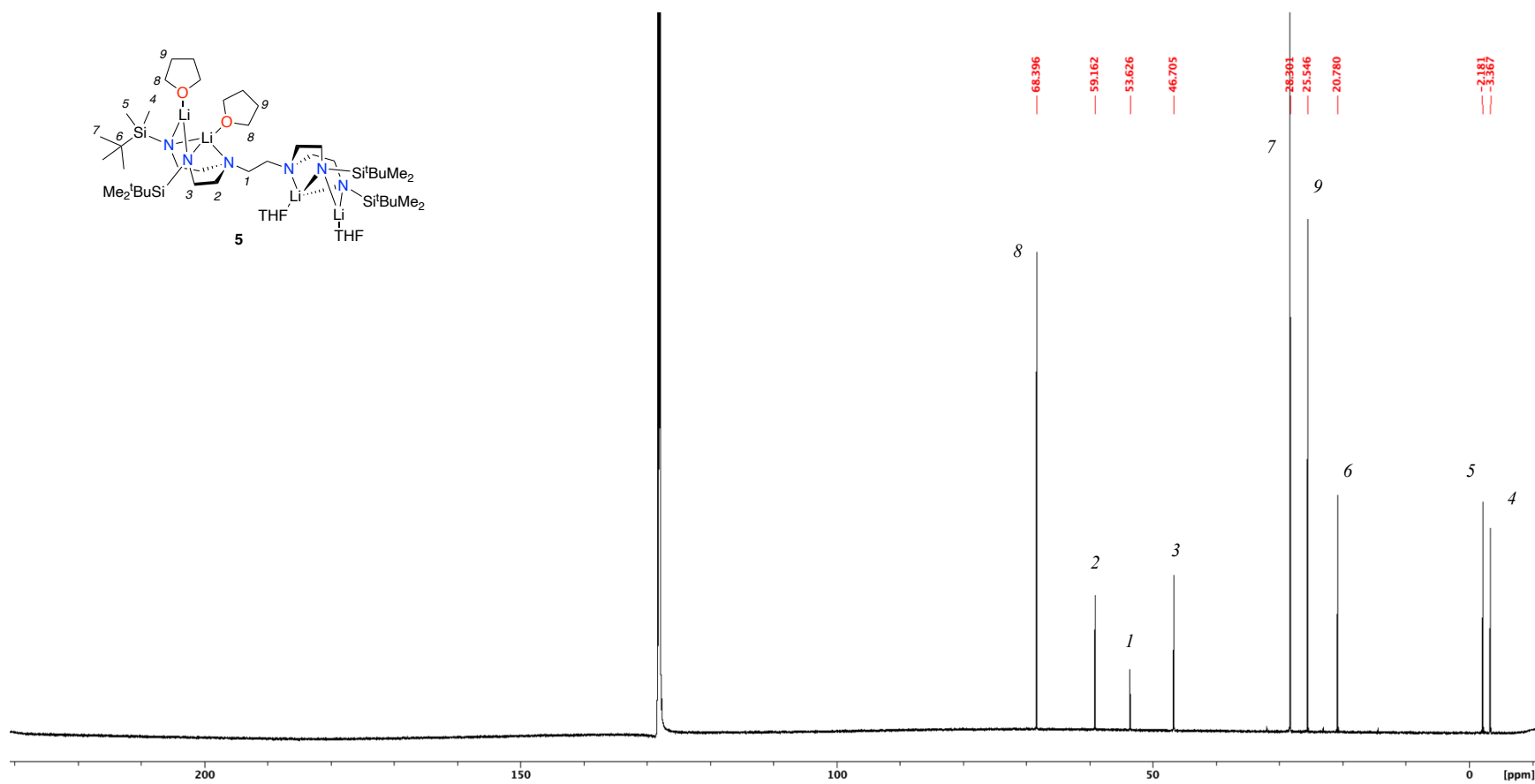




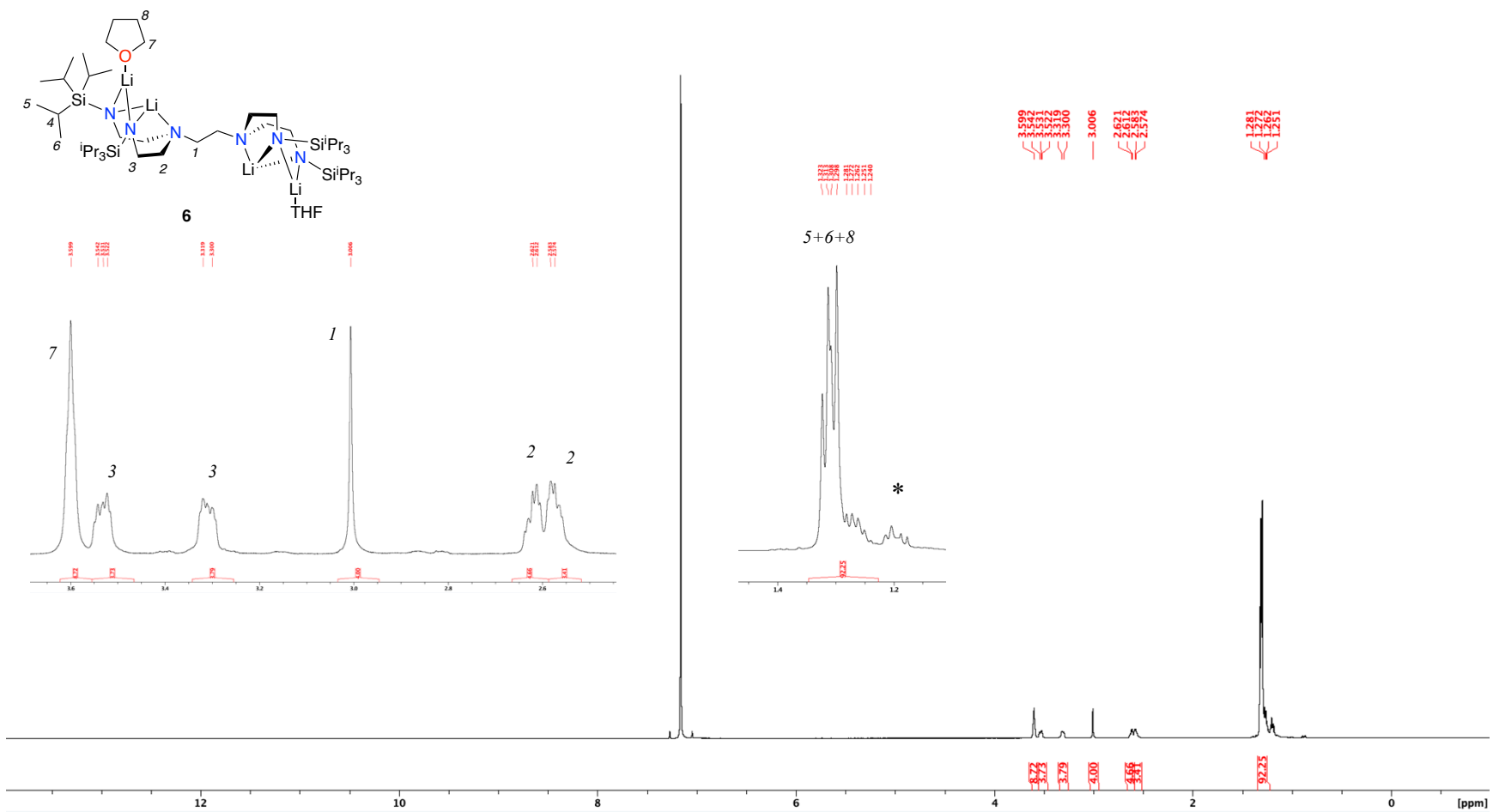
**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (176 MHz,  $\text{C}_6\text{D}_6$ , 25 °C) of **4**.

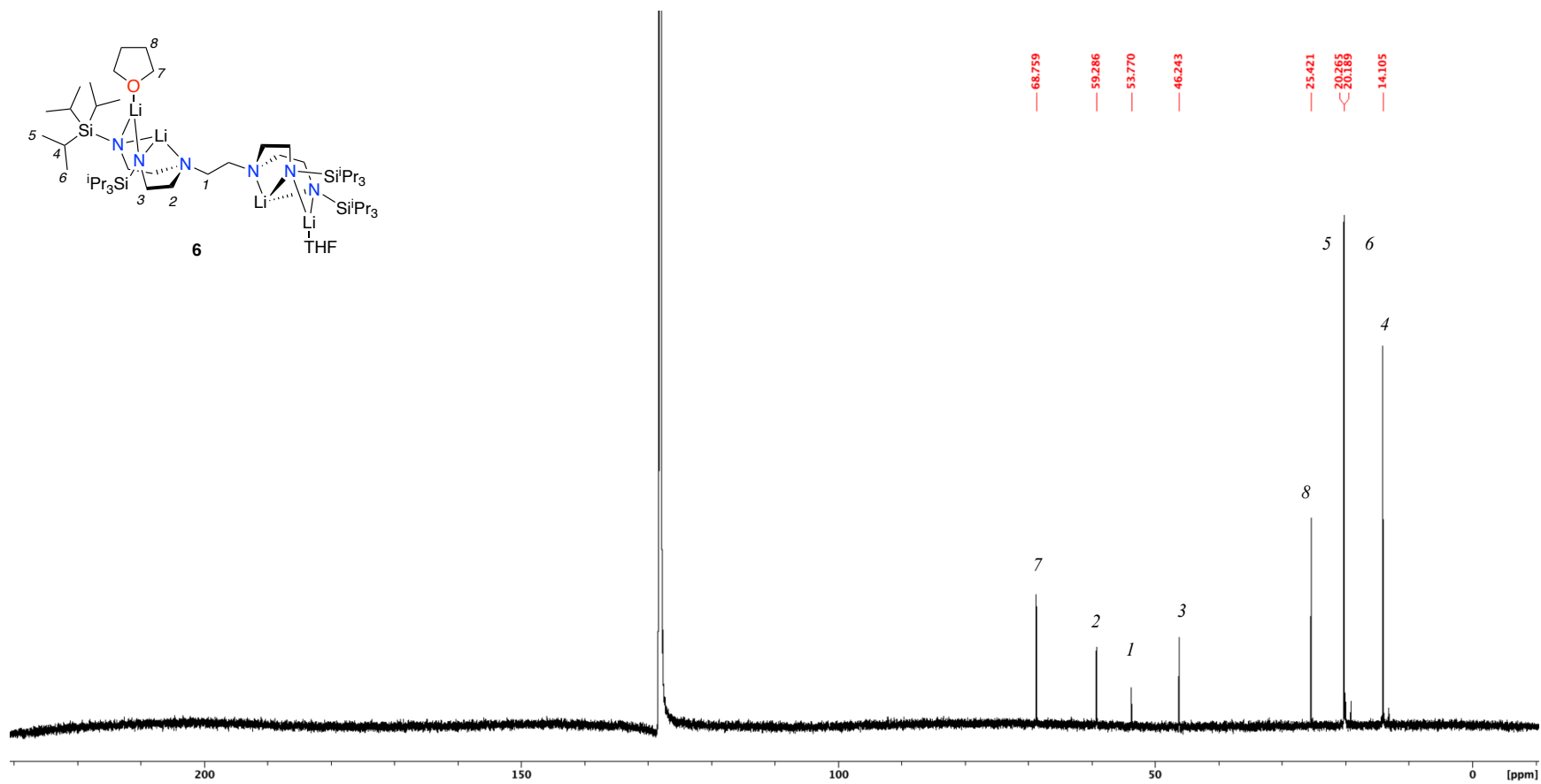


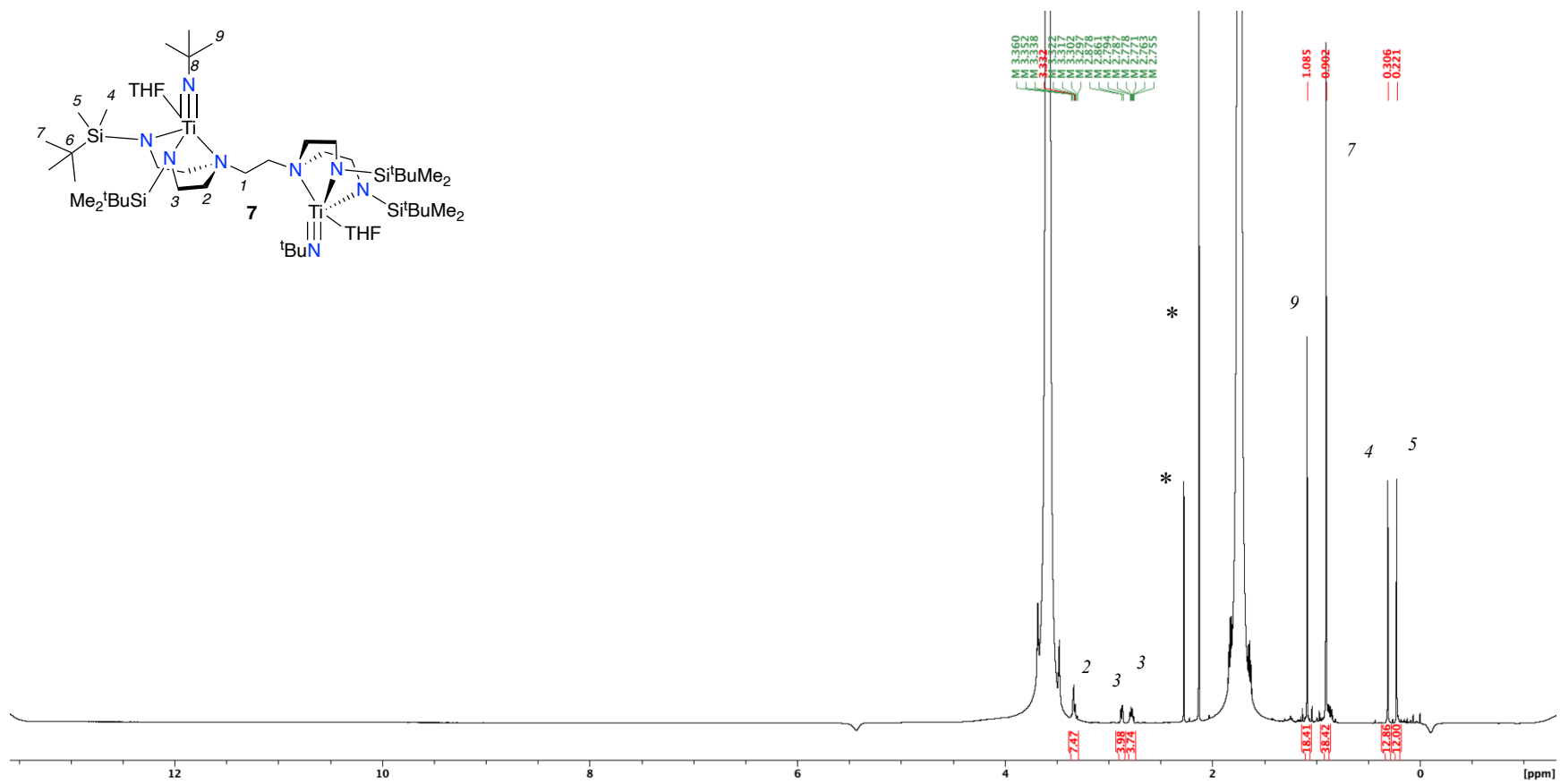
**Figure S8.**  $^1\text{H}$  NMR spectrum (700 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ) of **5**. Inset shows a close-up of the methylene region.



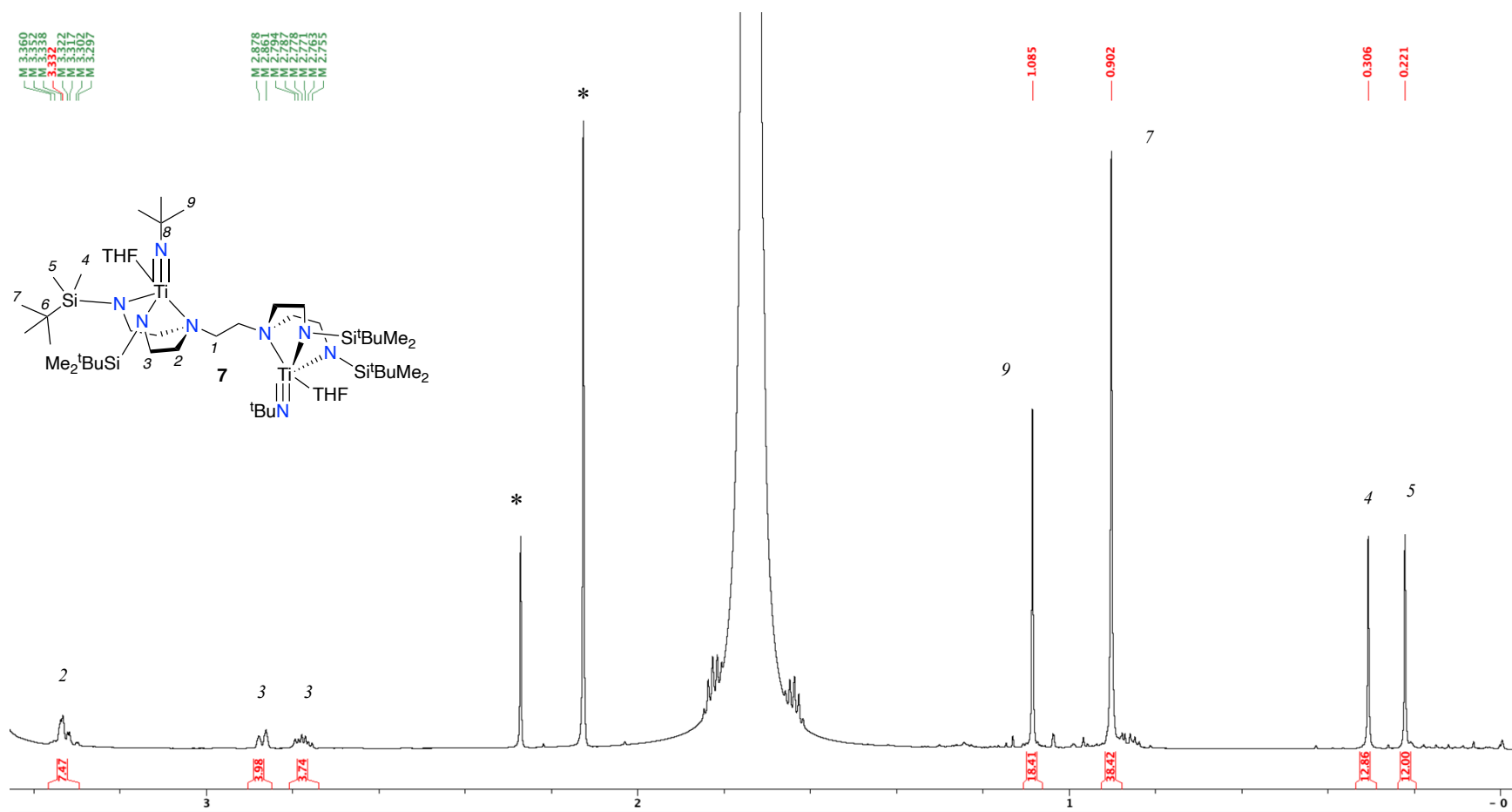
**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (176 MHz,  $\text{C}_6\text{D}_6$ , 25 °C) of **5**.



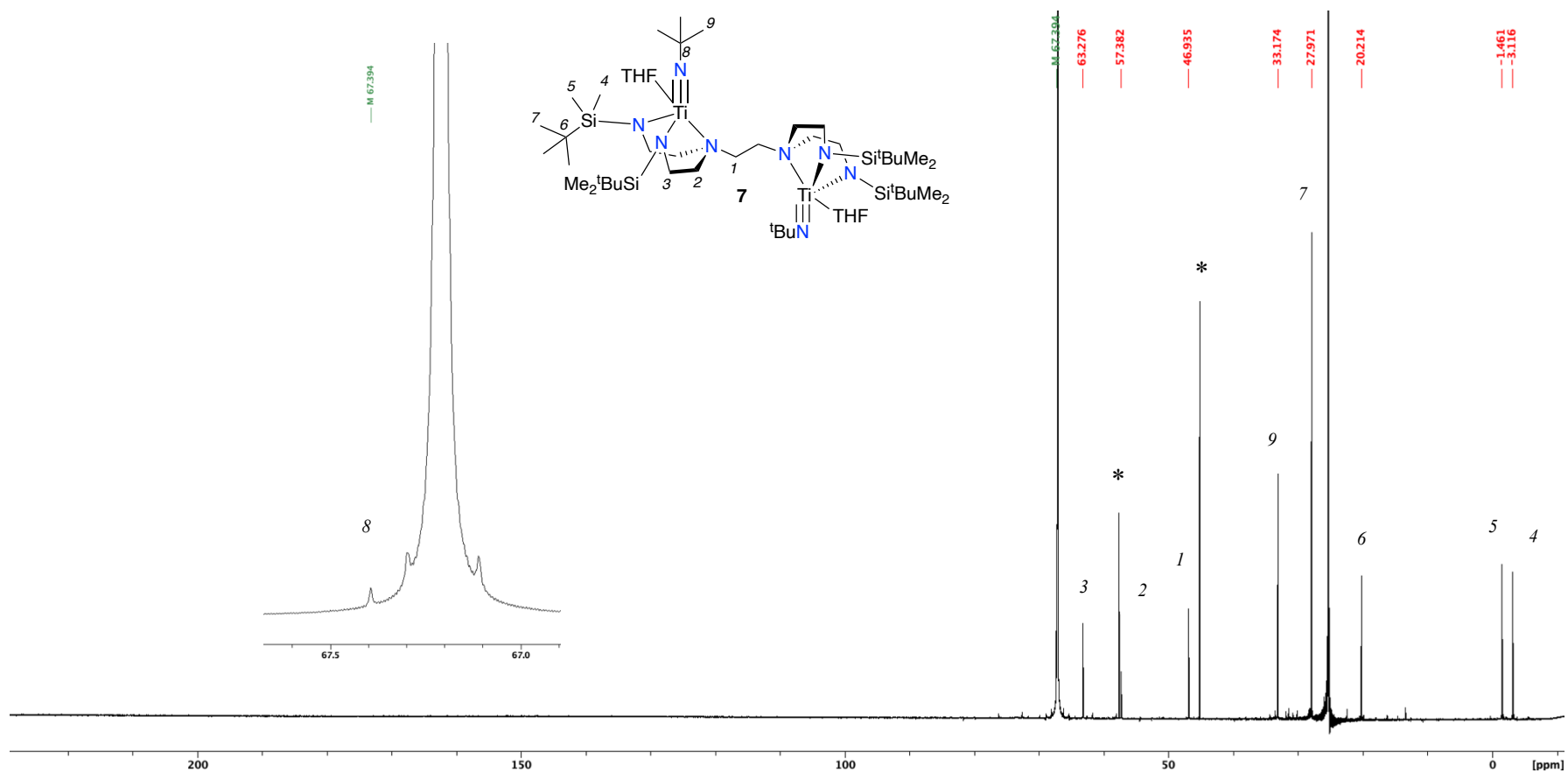




**Figure S12.** No-D <sup>1</sup>H NMR spectrum (700 MHz, THF-H<sub>8</sub>, 25 °C) of **7**.



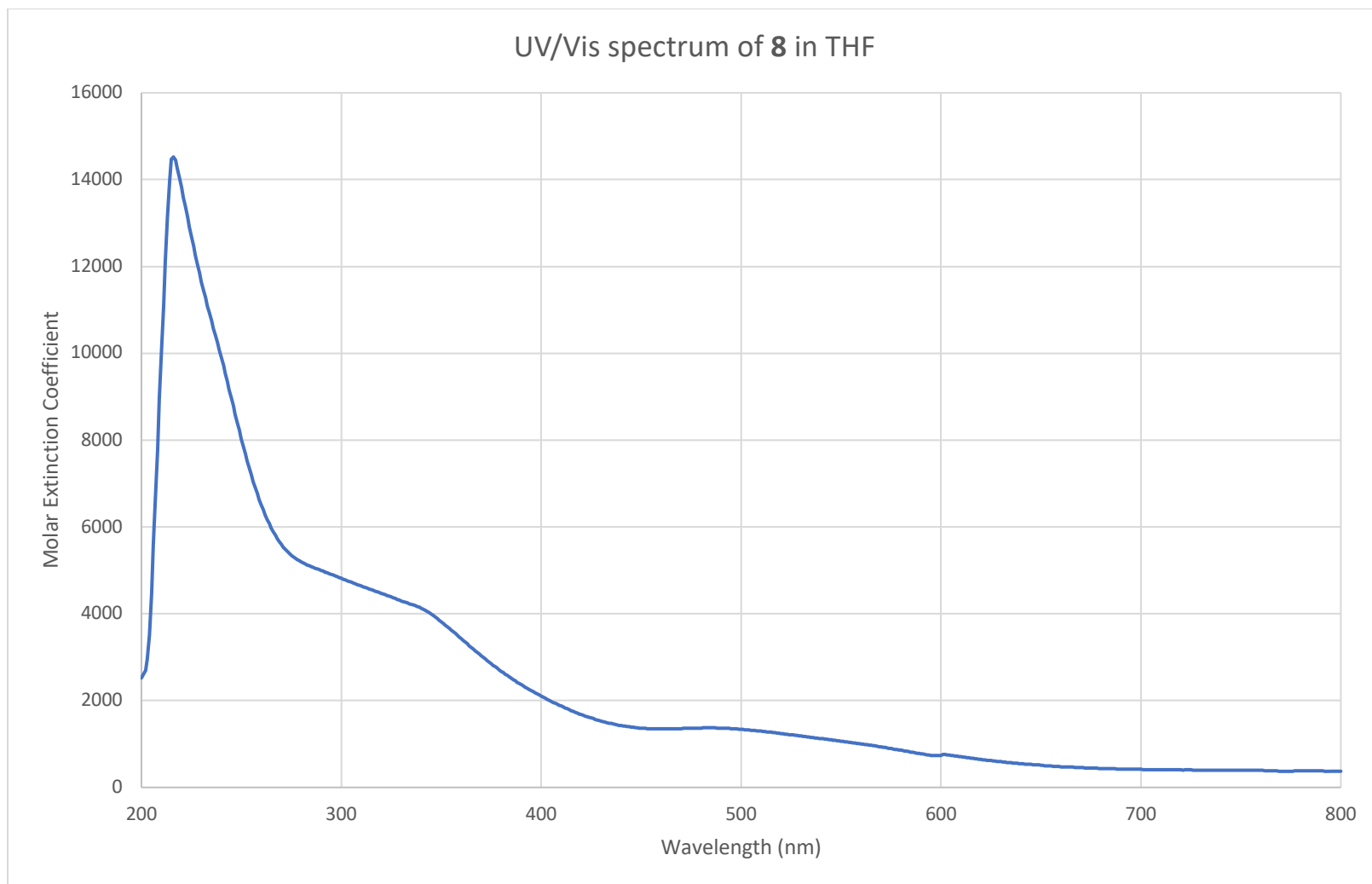
**Figure S13.** Close-up of the No-D <sup>1</sup>H NMR spectrum (700 MHz, THF-H<sub>8</sub>, 25 °C) of **7**. \* indicates free tmeda.



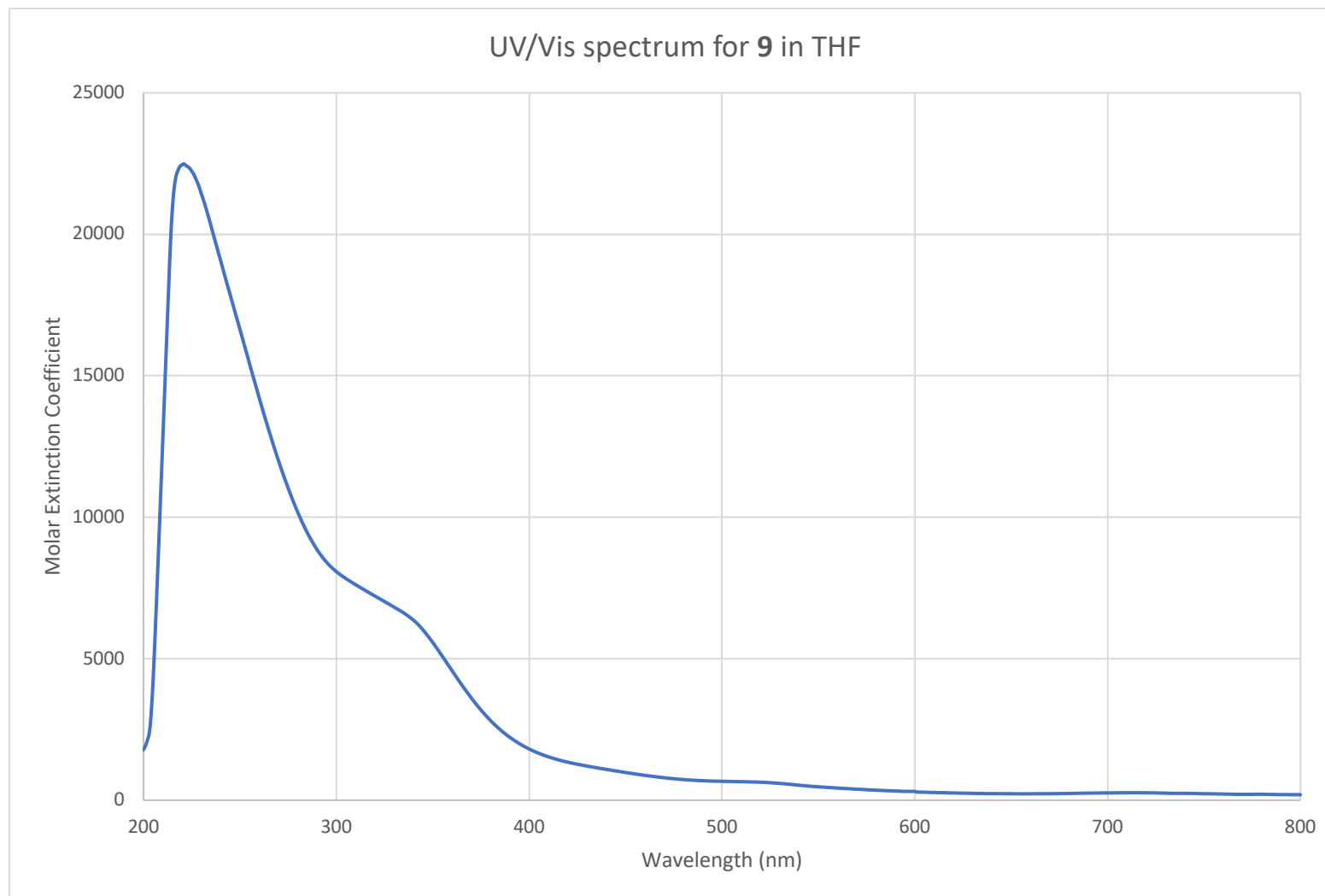
**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (176 MHz, THF- $\text{H}_8$ , 25 °C) of 7. \* indicates free tmeda. Inset shows close-up of resonance for C8.



#### IV. UV/Vis spectrophotometry



**Figure S15.** UV/Vis spectrum of **8** in THF



**Figure S16.** UV/Vis spectrum of **9** in THF

## V. X-ray Crystallography

Diffraction intensities for **3**, **4**, **5**, **6**, **7**, **8** and **9** were collected at low temperature on a Rigaku SynergyS single crystal diffractometer using CuK $\alpha$  radiation, 1.54178 Å. Space groups were determined based on systematic absences (**3**, **6** and **7**) and intensity statistics (**4**, **5**, **8** and **9**). Absorption corrections were applied by SADABS<sup>12</sup>. Structures were solved by direct methods and Fourier techniques and refined on  $F^2$  using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in all structures were refined in calculated positions in a rigid group. Some fragments in **8** and **14** are disordered over two positions. The RIGU option was used in the final refinement of these structures. The crystal data and details of data collections and refinements are given in Tables S1 and S2. All refinements were performed using the SHELXL<sup>13</sup> *via* the OLEX2<sup>14</sup> interface.

CCDC 2365242-2365248 contain the supplementary crystallographic data for this paper.

**Table S1.** Crystallographic data for **3, 4, 5, 6, and 7.**

Compound	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
CCDC Deposition Number	2365242	2365243	2365244	2365245	2365246
Empirical formula	C <sub>30</sub> H <sub>64</sub> N <sub>6</sub> Ti	C <sub>38</sub> H <sub>88</sub> Li <sub>4</sub> N <sub>6</sub> O <sub>4</sub> Si <sub>4</sub>	C <sub>50</sub> H <sub>112</sub> Li <sub>4</sub> N <sub>6</sub> O <sub>4</sub> Si <sub>4</sub>	C <sub>54</sub> H <sub>120</sub> Li <sub>4</sub> N <sub>6</sub> Si <sub>4</sub> O <sub>2</sub>	C <sub>50</sub> H <sub>114</sub> N <sub>8</sub> O <sub>2</sub> Si <sub>4</sub> Ti <sub>2</sub>
Formula weight	556.77	833.26	1001.57	1025.67	1067.65
Temperature/K	173(2)	223(2)	173(2)	173(2)	172.99(10)
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c	P-1	P-1	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a/Å	14.2580(2)	9.1432(2)	10.3186(3)	9.0246(2)	13.8754(3)
b/Å	11.6722(2)	11.1247(4)	11.5334(4)	33.0011(7)	13.7638(2)
c/Å	20.5507(3)	13.5664(5)	13.9949(3)	11.1965(2)	18.1998(3)
α/°	90	100.118(3)	97.960(2)	90	90
β/°	106.841(2)	97.314(2)	98.394(2)	103.588(2)	111.737(2)
γ/°	90	90.882(2)	100.035(3)	90	90
V/Å <sup>3</sup>	3273.41(9)	1346.39(8)	1599.33(8)	3241.23(12)	3228.59(11)
Z	4	1	1	2	2
ρ/ g/cm <sup>-3</sup>	1.130	1.028	1.040	1.051	1.098
μ/ mm <sup>-1</sup>	2.404	1.309	1.171	1.140	3.112
F(000)	1232.0	458.0	554.0	1140.0	1172.0
Crystal size/ mm <sup>3</sup>	0.11 × 0.09 × 0.06	0.2 × 0.14 × 0.1	0.08 × 0.07 × 0.04	0.08 × 0.07 × 0.04	0.3 × 0.2 × 0.04
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.476 to 155.516	6.676 to 155.556	6.476 to 152.332	5.356 to 154.988	6.858 to 151.77
Index ranges	-15 ≤ h ≤ 17, -14 ≤ k ≤ 11, -26 ≤ l ≤ 22	-7 ≤ h ≤ 11, -14 ≤ k ≤ 13, -17 ≤ l ≤ 16	-12 ≤ h ≤ 12, -13 ≤ k ≤ 14, -16 ≤ l ≤ 17	-9 ≤ h ≤ 11, -35 ≤ k ≤ 41, -14 ≤ l ≤ 12	-17 ≤ h ≤ 15, -16 ≤ k ≤ 16, -13 ≤ l ≤ 22
Reflections collected	23810	16558	18236	22732	25746
Independent reflections	6732 [R <sub>int</sub> = 0.0487, R <sub>sigma</sub> = 0.0450]	5494 [R <sub>int</sub> = 0.0301, R <sub>sigma</sub> = 0.0278]	6392 [R <sub>int</sub> = 0.0673, R <sub>sigma</sub> = 0.0679]	6664 [R <sub>int</sub> = 0.0649, R <sub>sigma</sub> = 0.0576]	6443 [R <sub>int</sub> = 0.0442, R <sub>sigma</sub> = 0.0395]
Data/restraints/parameters	6732/0/590	5494/0/253	6392/555/435	6664/0/316	6443/0/343
Goodness-of-fit on F <sup>2</sup>	1.078	1.006	1.058	1.007	1.026
R [I ≥ 2σ(I)] (R1, wR2)	R <sub>1</sub> = 0.0407, wR <sub>2</sub> = 0.0874	R <sub>1</sub> = 0.0630, wR <sub>2</sub> = 0.1799	R <sub>1</sub> = 0.0826, wR <sub>2</sub> = 0.2308	R <sub>1</sub> = 0.0730, wR <sub>2</sub> = 0.1620	R <sub>1</sub> = 0.0470, wR <sub>2</sub> = 0.1004
R (all data) (R1, wR2)	R <sub>1</sub> = 0.0544, wR <sub>2</sub> = 0.1026	R <sub>1</sub> = 0.0735, wR <sub>2</sub> = 0.2018	R <sub>1</sub> = 0.1183, wR <sub>2</sub> = 0.2722	R <sub>1</sub> = 0.1004, wR <sub>2</sub> = 0.1837	R <sub>1</sub> = 0.0615, wR <sub>2</sub> = 0.1197
Largest diff. peak/hole / (e Å <sup>-3</sup> )	0.29/-0.27	0.58/-0.30	0.57/-0.43	0.74/-0.34	0.43/-0.33

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \frac{[\sum (w(F_o^2 - F_c^2)^2)]^{1/2}}{\sum w(F_o^2)^{1/2}}$$

**Table S2.** Crystallographic data for **8** and **9**.

Compound	<b>8</b>	<b>9</b>
CCDC Deposition Number	2365247	2365248
Empirical formula	C <sub>34</sub> H <sub>80</sub> Cl <sub>2</sub> N <sub>6</sub> Si <sub>4</sub> V <sub>2</sub>	C <sub>26</sub> H <sub>59</sub> ClN <sub>3</sub> Si <sub>2</sub> V
Formula weight	858.18	556.33
Temperature/K	170(2)	172.99(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.2464(3)	7.9740(2)
b/Å	12.2692(5)	12.5557(3)
c/Å	17.2053(5)	16.7867(3)
α/°	106.737(3)	99.871(2)
β/°	99.474(2)	98.470(2)
γ/°	100.523(3)	97.611(2)
V/Å <sup>3</sup>	2368.36(14)	1616.14(6)
Z	2	2
ρ/ g/cm <sup>-3</sup>	1.203	1.143
μ/ mm <sup>-1</sup>	5.532	4.155
F(000)	924.0	608.0
Crystal size/ mm <sup>3</sup>	0.08 × 0.07 × 0.04	0.4 × 0.2 × 0.02
Radiation	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.512 to 152.134	5.426 to 152.34
Index ranges	-15 ≤ h ≤ 14, -14 ≤ k ≤ 15, -18 ≤ l ≤ 21	-10 ≤ h ≤ 9, -15 ≤ k ≤ 13, -18 ≤ l ≤ 21
Reflections collected	29776	18382
Independent reflections	9490 [R <sub>int</sub> = 0.0494, R <sub>sigma</sub> = 0.0476]	6426 [R <sub>int</sub> = 0.0433, R <sub>sigma</sub> = 0.0460]
Data/restraints/parameters	9490/676/534	6426/0/311
Goodness-of-fit on F <sup>2</sup>	1.030	1.058
R [I ≥ 2θ (I)] (R1, wR2)	R <sub>1</sub> = 0.0620, wR <sub>2</sub> = 0.1638	R <sub>1</sub> = 0.0325, wR <sub>2</sub> = 0.0786
R (all data) (R1, wR2)	R <sub>1</sub> = 0.0869, wR <sub>2</sub> = 0.1926	R <sub>1</sub> = 0.0452, wR <sub>2</sub> = 0.0932
Largest diff. peak/hole / (e Å <sup>-3</sup> )	1.31/-0.38	0.39/-0.35

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \frac{[\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}}$$

## V. References

- 1 C. Görl, E. Betthausen and H. G. Alt, Di- and trinuclear iron/titanium and iron/zirconium complexes with heterocyclic ligands as catalysts for ethylene polymerization, *Polyhedron*, 2016, **118**, 37–51.
- 2 N. A. Jones, S. T. Liddle, C. Wilson and P. L. Arnold, Titanium(III) alkoxy-N-heterocyclic carbenes and a safe, low-cost route to  $\text{TiCl}_3(\text{THF})_3$ , *Organometallics*, 2007, **26**, 755–757.
- 3 T. S. Lewkebandara, P. H. Sheridan, M. J. Heeg, A. L. Rheingold and C. H. Winter, Terminal and Bridging Imido Complexes from Titanium Tetrachloride and Primary Amines. Implications for the Chemical Vapor Deposition of Titanium Nitride Films, *Inorg Chem*, 1994, **33**, 5879–5889.
- 4 M. T. Hovey, D. T. Cohen, D. M. Walden, P. H. -Y. Cheong and K. A. Scheidt, A Carbene Catalysis Strategy for the Synthesis of Protoilludane Natural Products, *Angewandte Chemie*, 2017, **129**, 9996–9999.
- 5 B. K. Wagnon and S. C. Jackels, Synthesis, characterization, and aqueous proton relaxation enhancement of a manganese(II) heptaaza macrocyclic complex having pendant arms, *Inorg Chem*, 1989, **28**, 1923–1927.
- 6 T. R. Hoye, B. M. Eklov, T. D. Ryba, M. Voloshin and L. J. Yao, No-D NMR (No-Deuterium Proton NMR) Spectroscopy: A Simple Yet Powerful Method for Analyzing Reaction and Reagent Solutions, *Org. Lett*, 2004, **6**, 953–956.
- 7 S. Senthil, D. Fehn, M. R. Gau, A. M. Bacon, P. J. Carroll, K. Meyer and D. J. Mindiola, A Vanadium Methylidene, *J Am Chem Soc*, , DOI:10.1021/jacs.4c01906.
- 8 E. Samuel, Y. Mu, J. F. Harrod, Y. Dromzee and Y. Jeannin, Synthesis and properties of some novel bis(cyclopentadienyl)silyltitanium(III) complexes, *J Am Chem Soc*, 1990, **112**, 3435–3439.
- 9 R. E. H. Kuveke, L. Barwise, Y. Van Ingen, K. Vashisth, N. Roberts, S. S. Chitnis, J. L. Dutton, C. D. Martin and R. L. Melen, An International Study Evaluating Elemental Analysis, *ACS Cent Sci*, 2022, **8**, 855–863.
- 10 F. P. Gabbaï, P. J. Chirik, D. E. Fogg, K. Meyer, D. J. Mindiola, L. L. Schafer and S. L. You, *Organometallics*, 2016, **35**, 3255–3256.
- 11 A. J. Cuellar De Lucio, I. C. Cai, R. J. Witzke, A. N. Desnoyer and T. D. Tilley, Synthesis, Characterization, and Reactivity of Low-Coordinate Titanium(III) Amido Complexes, *Organometallics*, 2022, **41**, 1434–1444.
- 12 G. M. Sheldrick, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, 1998.
- 13 Sheldrick, G. M.; *Acta Cryst*. 2008, **A64**, 112.

- 14 Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* 2009, **42**, 339.