

## Supporting Information

# Synthesis, Structure and Reactivity of Zwitterionic Divalent Rare-Earth Metal Silanides

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### General Remarks

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere drybox containing an atmosphere of purified nitrogen. THF, THF-D<sub>8</sub>, and hexanes were distilled under nitrogen from alkali metals and stored over activated 4 Å molecular sieves prior to use. THF-D<sub>8</sub> (Cambridge Isotope labs.) YbI<sub>2</sub> (Aldrich), EuI<sub>2</sub> (Alfa Aesar), SmI<sub>2</sub> (0.1 M in THF; Aldrich), Bu<sup>t</sup>OLi (Aldrich) and W(CO)<sub>6</sub> (Alfa Aesar) were purchased from commercial sources and used without further purification. Si(SiMe<sub>2</sub>OMe)<sub>4</sub> [1] and BPh<sub>3</sub> [2] were prepared according to literature procedures. The <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, <sup>7</sup>Li and <sup>29</sup>Si NMR spectra were obtained from a Varian Unity Inova

500 and a JOEL 400. All NMR measurements, unless noted otherwise, were carried out at 300 K. The  $^{29}\text{Si}$ -NMR spectra were referenced to TMS ( $\delta = 0$ ),  $^7\text{Li}$ -NMR spectra were referenced to a 0.1 M solution of LiCl in  $\text{D}_2\text{O}$  ( $\delta = 0$ ) and  $^{11}\text{B}$ -NMR spectra were referenced to a 0.1 M solution of  $\text{H}_3\text{BO}_3$  in  $\text{D}_2\text{O}$  ( $\delta = 36$  ppm). The  $^1\text{H}$  NMR spectra were referenced to the residual protonated solvent for  $^1\text{H}$  and the  $^{13}\text{C}$  NMR spectra were referenced to the deuterated solvent peaks.  $^{29}\text{Si}$  NMR spectra were obtained by using the INEPT pulse sequence. IR was performed in Nicolet iS5 single reflection ATR accessory. Elemental Analyses were performed with a Perkin Elmer 2400 Series II CHNS/O Analyzer. Note that the experimentally obtained H values are very close to the theoretical values, while the C values of most of the reported compounds are somewhat lower. We attribute this to the silicon rich character of these compounds resulting in incomplete combustion of carbon due to silicon carbide formation.

## Synthetic Procedures

**[Si(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Yb (Yb-3).** In a Glove box a 25 mL Schlenk flask equipped with a magnetic stir bar was charged with LiO<sup>t</sup>Bu (42 mg, 0.52 mmol), Si(SiMe<sub>2</sub>OMe)<sub>4</sub> (200 mg, 0.52 mmol) and THF (2 mL). After the resulting solution was allowed to stir overnight at room temperature, the solvent and other volatiles were removed under vacuum. The crystalline residue identified by NMR spectroscopy as raw Li-2 was washed with hexanes twice, dried under vacuum and re-dissolved in THF (2 mL). A 20 mL scintillation vial equipped with a magnetic stir bar was charged with YbI<sub>2</sub> (110 mg, 0.26 mmol) and THF (3 mL) and the resulting suspension was stirred for a few hours until a solution had formed. This solution was added to Li-2 dissolved in THF. Yellow crystals precipitated from the reaction mixture upon standing at room temperature overnight. The crystals were isolated by decantation, washed twice with small amounts of THF and dried under vacuum to give 102 mg (52%) of the title compound.  $^1\text{H}$  NMR (THF-D<sub>8</sub>, 400 MHz):  $\delta$  0.37 (s, SiMe<sub>2</sub>, 18 H), 3.47 (s, OCH<sub>3</sub>, 9 H) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (THF-D<sub>8</sub>, 125.7 MHz):  $\delta$  3.5 (SiMe<sub>2</sub>), 50.9 (OMe) ppm.  $^{29}\text{Si}\{\text{H}\}$  NMR (THF-D<sub>8</sub>, 99.3 MHz):  $\delta$  44.5 (SiMe<sub>2</sub>O), -202.9 (SiSi<sub>3</sub>) ppm. - Anal. Calc. for C<sub>18</sub>H<sub>54</sub>O<sub>6</sub>Si<sub>8</sub>Yb (764.34): C, 28.28; H, 7.12. Found: C, 27.91; H, 7.24%.

**[Si(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Eu (Eu-3).** In a Glove box a 25 mL Schlenk flask equipped with a magnetic stir bar was charged with LiO<sup>t</sup>Bu (42 mg, 0.52 mmol), Si(SiMe<sub>2</sub>OMe)<sub>4</sub> (200 mg, 0.52 mmol) and THF (2 mL). After the resulting solution was allowed to stir overnight at room temperature, the

solvent and other volatiles were removed under vacuum. The crystalline residue identified by NMR spectroscopy as raw Li-2 was washed with hexanes twice, dried under vacuum and re-dissolved in THF (2 ml). A 20 mL scintillation vial equipped with a magnetic stir bar was charged with EuI<sub>2</sub> (106 mg, 0.26 mmol) and THF (3 ml) and the resulting suspension was stirred for a few hours until a solution had formed. This solution was added to Li-2 dissolved in THF. Pale-yellow crystals precipitated from the reaction mixture upon standing at room temperature overnight. The crystals were isolated by decantation, washed twice with small amounts of THF and dried under vacuum to give 90 mg (46%) of the title compound. Anal. Calc. for C<sub>18</sub>H<sub>54</sub>O<sub>6</sub>Si<sub>8</sub>Eu (743.26): C, 29.09; H, 7.32. Found: C, 28.53; H, 7.42%.

**[Si(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Sm (Sm-3).** In a Glove box a 25 mL Schlenk flask equipped with a magnetic stir bar was charged with LiO<sup>t</sup>Bu (42 mg, 0.52 mmol), Si(SiMe<sub>2</sub>OMe)<sub>4</sub> (200 mg, 0.52 mmol) and THF (2 ml). After the resulting solution was allowed to stir overnight at room temperature, the solvent and other volatiles were removed under vacuum. The crystalline residue identified by NMR spectroscopy as raw Li-2 was washed with hexanes twice, dried under vacuum and re-dissolved in THF (2 ml). Then 2.6 mL of THF solution of SmI<sub>2</sub> (0.1 M, 0.26 mmol) was added via a syringe resulting in the formation of a dark solution, from which dark-brown crystals precipitated upon standing at room temperature overnight. The crystals were isolated by decantation, washed twice with small amounts of THF and dried under vacuum to give 84 mg (44%) of the title compound. Anal. Calc. for C<sub>18</sub>H<sub>54</sub>O<sub>6</sub>Si<sub>8</sub>Sm (741.66): C, 29.15; H, 7.34. Found: C, 28.05; H, 7.45 %.

**[Ph<sub>3</sub>BSi(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Yb(THF) (Yb-4).** In a Glove box a 20 mL scintillation vial was charged with Yb-3 (200 mg, 0.26 mmol) and dissolved in THF (4 ml). A second 20 mL scintillation vial was charged with BPh<sub>3</sub> (124 mg, 0.52 mmol) and dissolved in THF (2 ml). After combining both solutions dark-yellow crystals precipitated overnight at room temperature. These crystals were isolated by decantation, washed twice with a small amounts of THF and dried under vacuum to give Yb-4 (266 mg, 82%). <sup>1</sup>H NMR (THF-D<sub>8</sub>, 400 MHz, 308 K): δ 0.34 (s, SiMe<sub>2</sub>, 18 H), 1.76 (m, THF, 4 H), 3.61 (s, OCH<sub>3</sub>, 9 H), 3.62 (m, THF, 4 H), 7.33-7.39, 7.52-7.56 (2 m, arom. H, 30 H) ppm. <sup>13</sup>C{H} NMR (THF-D<sub>8</sub>, 125.7 MHz, 308 K): δ 3.2 (SiMe<sub>2</sub>), 26.4 (THF), 51.1 (OMe), 68.2 (THF), 127.7, 129.1, 138.2 (arom. CH) ppm. <sup>29</sup>Si{H} NMR (THF-D<sub>8</sub>, 99.3 MHz, 308 K): δ 44.7 (SiMe<sub>2</sub>O), -132.0 (SiSi<sub>3</sub>) ppm. <sup>11</sup>B NMR (THF-D<sub>8</sub>, 128.3 MHz, 308 K): -8.0 ppm - Anal. Calc. for C<sub>58</sub>H<sub>92</sub>B<sub>2</sub>O<sub>7</sub>Si<sub>8</sub>Yb (1320.457): C, 52.75; H, 7.02. Found: C, 51.64; H, 7.04%.

**[(CO)<sub>5</sub>WSi(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Yb (Yb-5).** In a Glove box a 20 mL scintillation vial was charged with Yb-3 (200 mg, 0.26 mmol) and dissolved in THF (4 ml). A second 20 mL scintillation vial was charged with W(CO)<sub>6</sub> (184 mg, 0.52 mmol) and dissolved in THF (2 ml). Upon combining both solutions, dark orange micro-crystals of Yb-5 precipitated from the reaction mixture overnight at room temperature. The crystalline material was isolated by decantation, washed twice with a small amounts of THF and dried under vacuum (257 mg, 70%). <sup>1</sup>H NMR (THF-D<sub>8</sub>, 400 MHz, 308 K): δ 0.58 (s, SiMe<sub>2</sub>, 18 H), 3.67, (s, OCH<sub>3</sub>, 9 H) ppm. <sup>13</sup>C{H} NMR (THF-D<sub>8</sub>, 125.7 MHz, 328 K): δ 2.0 (SiMe<sub>2</sub>), 52.0 (OMe), 202.0 (CO) ppm. <sup>29</sup>Si{H} NMR (THF-D<sub>8</sub>, 99.3 MHz, 318 K): δ 43.4 (SiMe<sub>2</sub>O), -152.0 (SiSi<sub>3</sub>) ppm. IR (THF): ν<sub>CO</sub> = 2042 cm<sup>-1</sup> (m), 1957 cm<sup>-1</sup> (m), 1907 cm<sup>-1</sup> (vs), 1878 cm<sup>-1</sup> (s). Anal. Calc. for C<sub>28</sub>H<sub>54</sub>O<sub>16</sub>Si<sub>8</sub>YbW<sub>2</sub> (1412.12): C, 23.82; H, 3.85. Found: C, 21.91; H, 3.90%.

## X-ray Crystallography

X-ray diffraction data for all compounds were obtained on a Bruker Smart Apex II CCD diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at either 150 or 100 K. Intensity data were collected using ω-steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All the data were corrected for Lorentz polarization effects. A multi-scan absorption correction was applied using SADABS [3]. Structures were solved by direct methods (SHELXS [4] and SIR2004 [5]) and refined by full-matrix least-squares against *F*<sup>2</sup> (SHELXL [4]). All hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. Complexes Sm-3, Eu-3, and Yb-3 showed some rotational disorder. In Sm-3, this occurred in one independent molecule in the asymmetric unit, with occupancies of approximately 0.6:0.4, while in both Yb-3 and Eu-3 the disorder was seen in the single independent molecule, with occupancies of approximately 0.8:0.2. In the structure Yb-4 the solvent THF molecule has two orientations with a positional disorder of 0.6:0.4 for C31 and C32, respectively. The carbon and oxygen atoms of the minor components were refined with isotropic thermal parameters, and hydrogen atoms were not calculated for the SiMe<sub>2</sub> of the minor components. Crystallographic data for the three structures are listed in Table 1. CCDC-1050381–

1050384 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

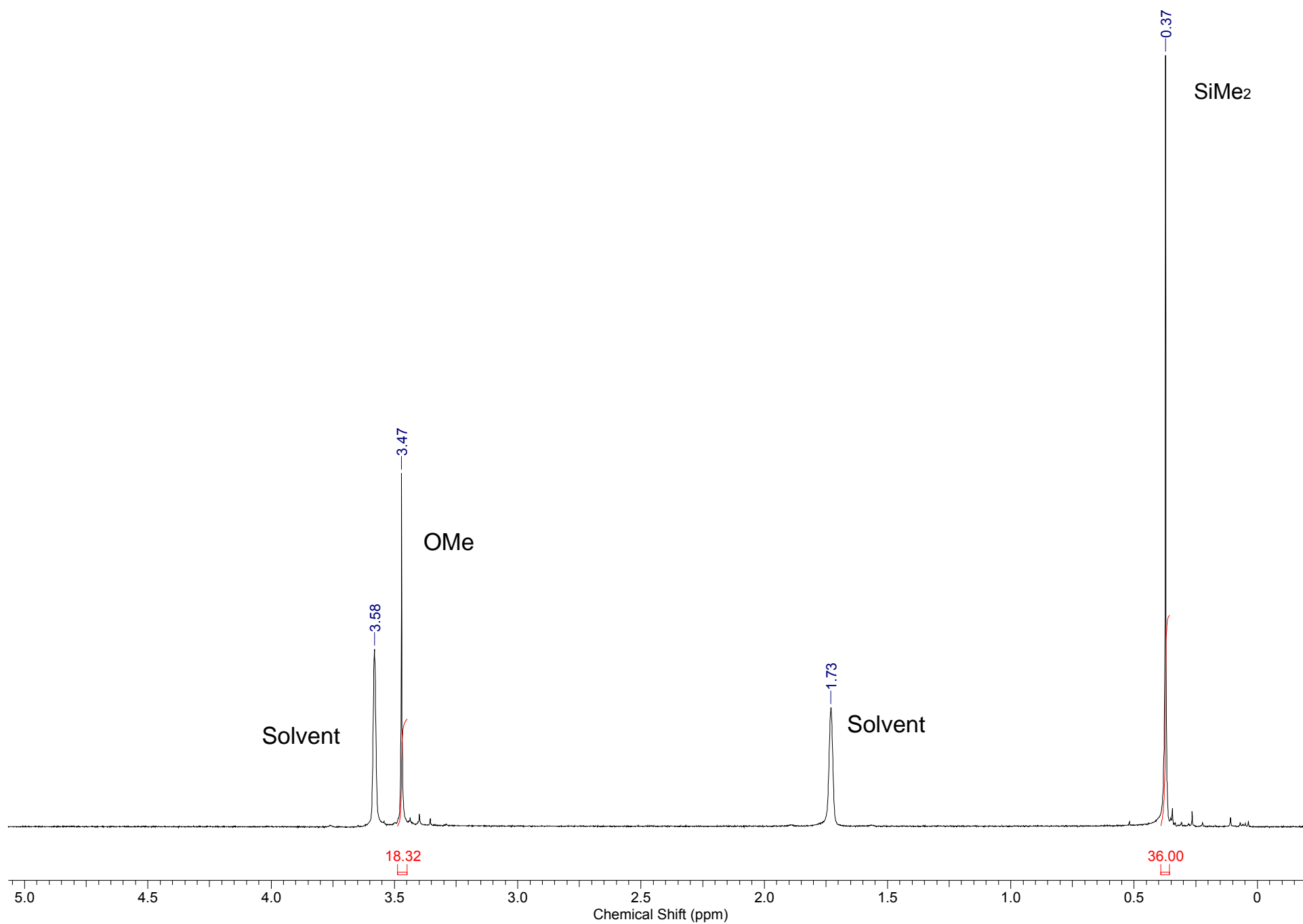
**Table S1.** Crystallographic data for the complexes Sm-3, Yb-3, Eu-3 and Yb-4.

	Sm-3	Yb-3	Eu-3	Yb-4
Formula	C <sub>18</sub> H <sub>54</sub> O <sub>6</sub> Si <sub>8</sub> Sm	C <sub>18</sub> H <sub>54</sub> O <sub>6</sub> Si <sub>8</sub> Yb	C <sub>18</sub> H <sub>54</sub> EuO <sub>6</sub> Si <sub>8</sub>	C <sub>62</sub> H <sub>100</sub> B <sub>2</sub> O <sub>8</sub> Si <sub>8</sub> Yb
Molecular weight	741.68	764.37	743.29	1392.79
Space group	<i>Pbam</i>	<i>Cmca</i>	<i>Cmca</i>	<i>P2<sub>1</sub>/n</i>
a (Å)	16.9527(14)	16.7639(10)	16.8732(14)	12.6349(13)
b (Å)	12.8816(10)	12.7811(8)	12.8843(11)	20.318(2)
c (Å)	16.9068(14)	16.8394(10)	16.9266(14)	13.6729(14)
β (°)				93.8720(12)
Volume (Å <sup>3</sup> )	3692.1(5)	3608.0(4)	3679.8(5)	3501.0(6)
Z	4	4	4	2
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.334	1.407	1.342	1.321
Temperature (K)	150	150	150	100
μ (mm <sup>-1</sup> )	1.876	2.884	1.991	1.521
Reflections collected	42822	21309	19320	42929
Unique reflections ( <i>R</i> <sub>int</sub> )	4541 (0.0227)	2229 (0.0237)	2265 (0.0254)	8419 (0.0433)
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0604	0.0214	0.0236	0.0251
<i>wR</i> <sub>2</sub> (all data)	0.1585	0.0514	0.0590	0.0582

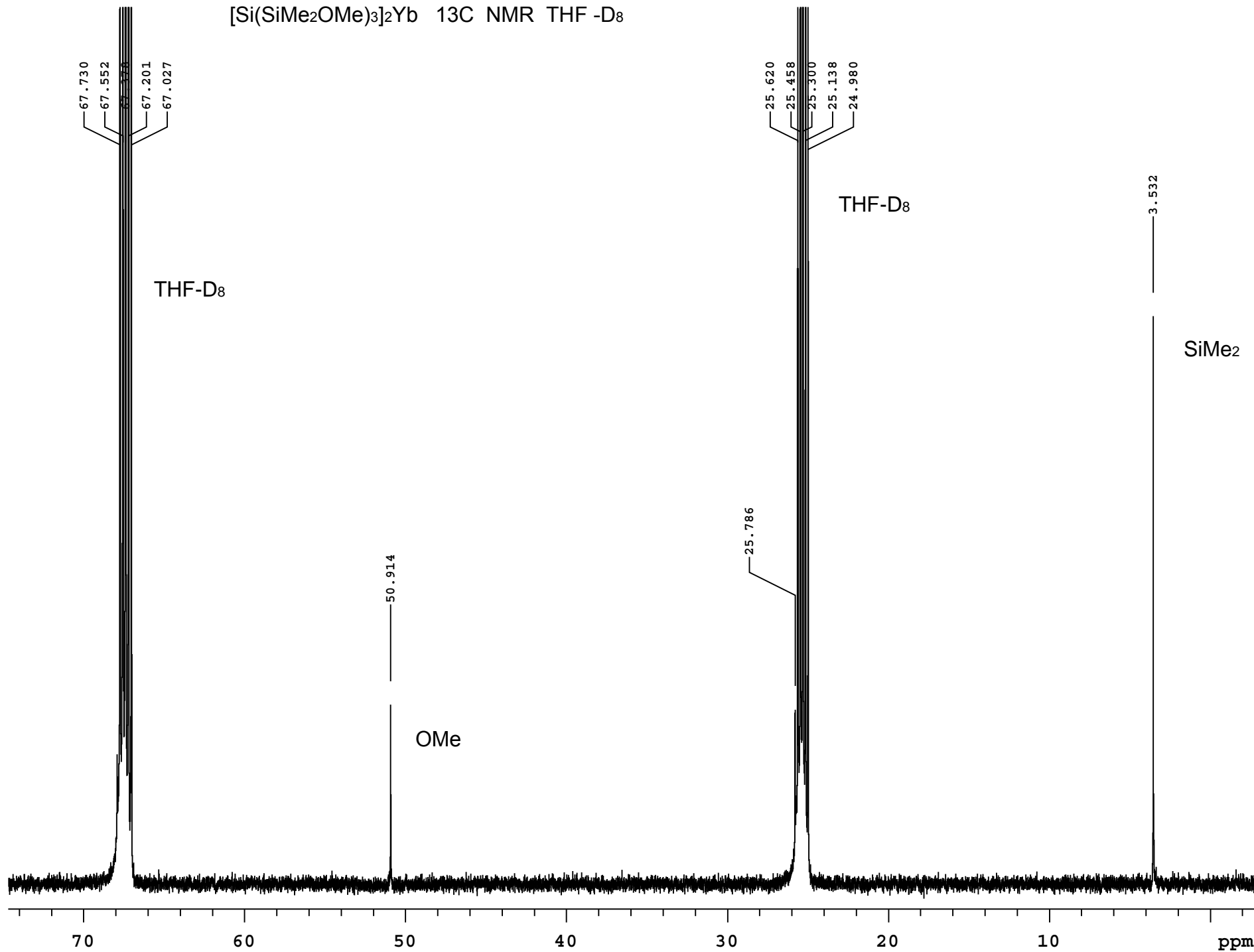
## References

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Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2005**, *38*, 381-388.

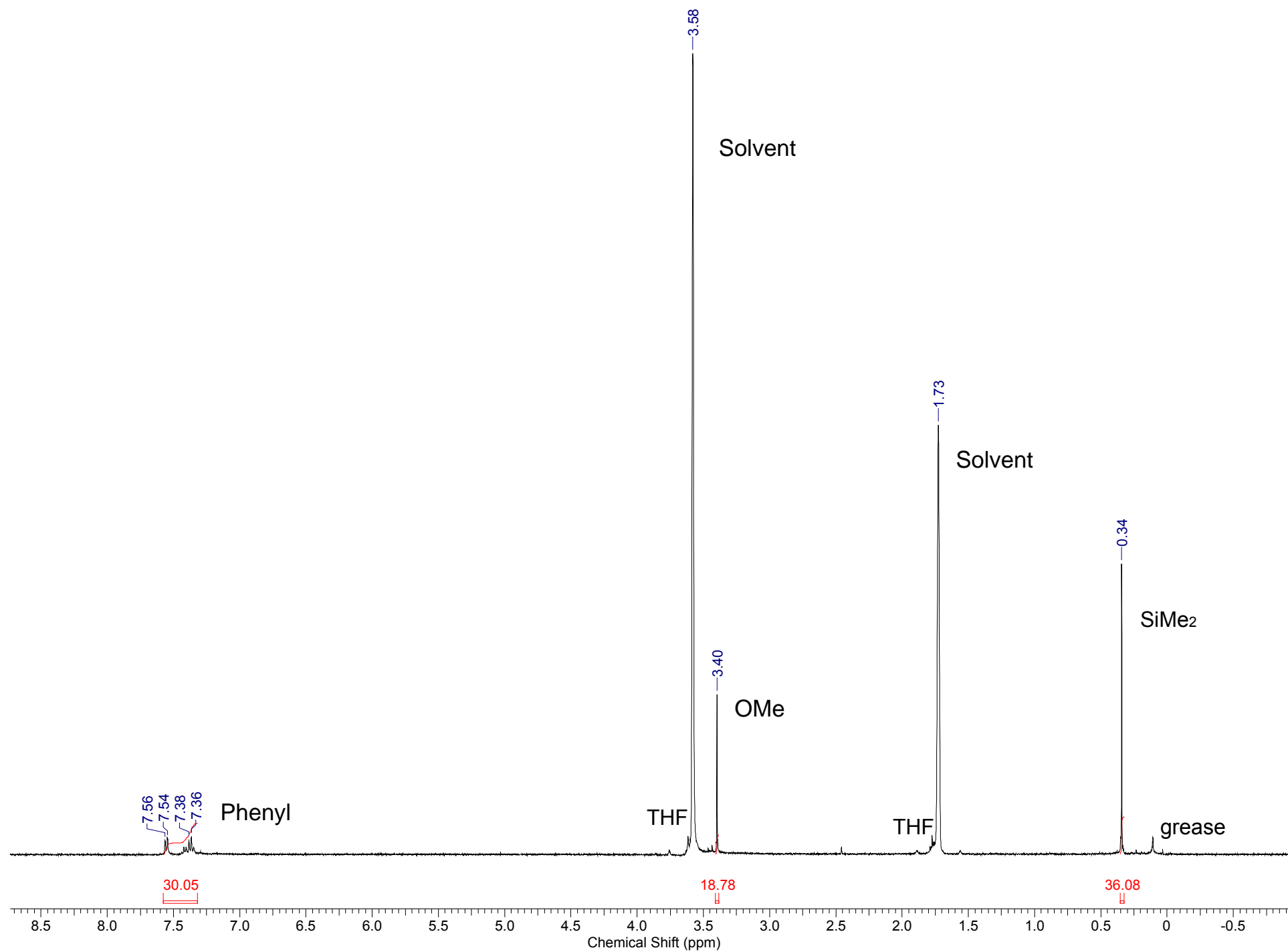
[Si(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Yb 1H NMR THF-D<sub>8</sub>



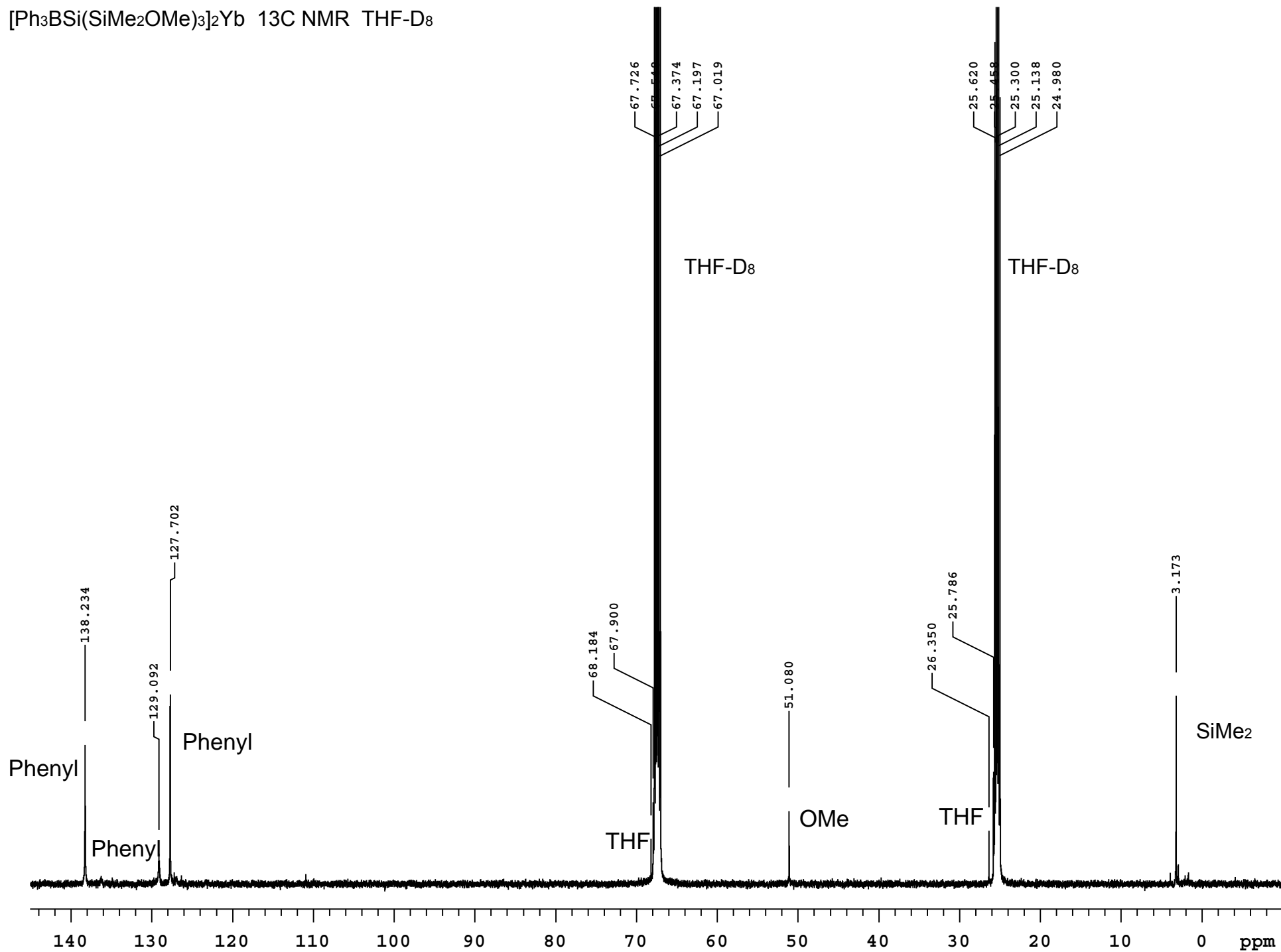
[Si(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Yb <sup>13</sup>C NMR THF -D<sub>8</sub>



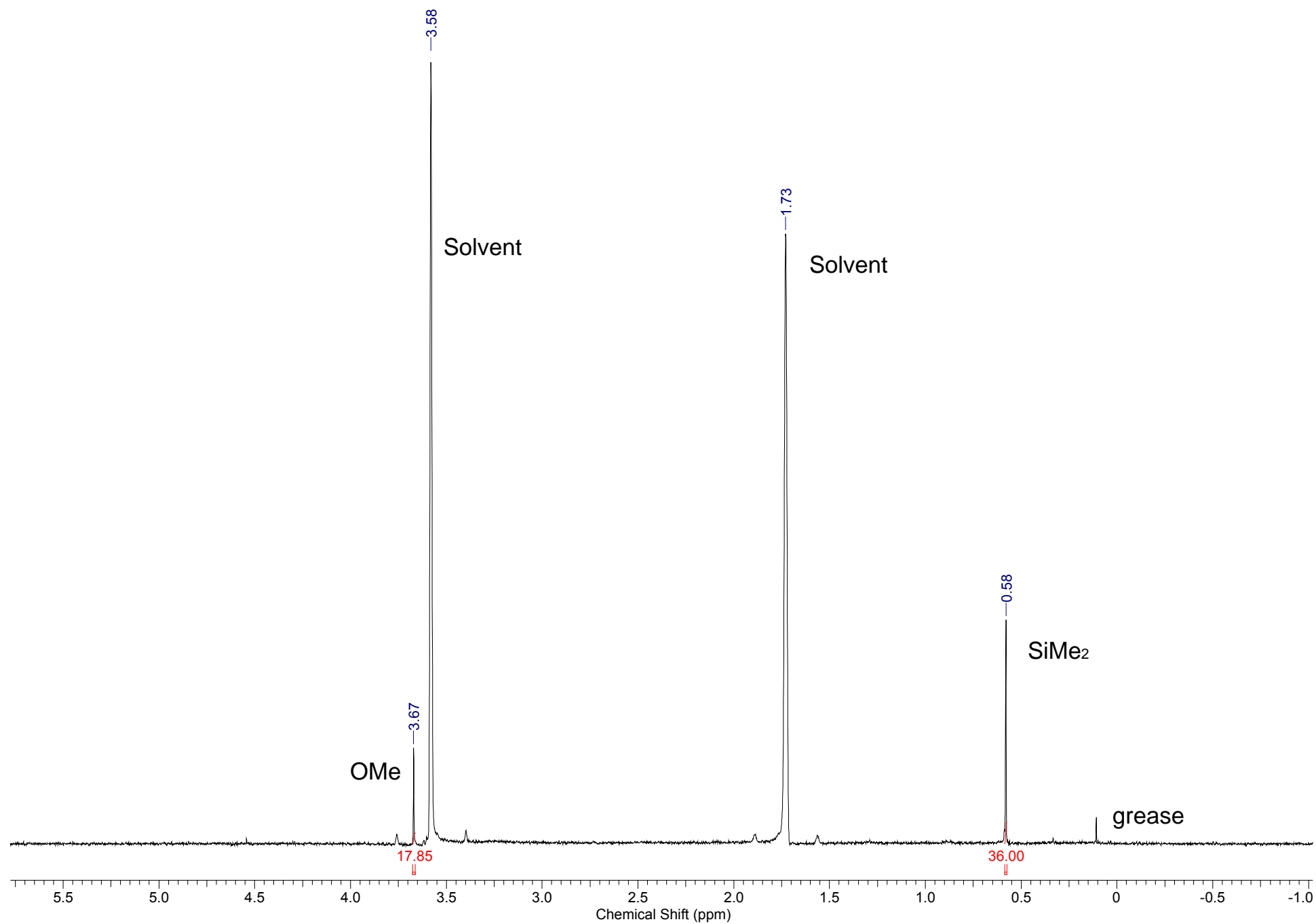




[Ph<sub>3</sub>BSi(SiMe<sub>2</sub>OMe)<sub>3</sub>]<sub>2</sub>Yb <sup>13</sup>C NMR THF-D<sub>8</sub>



$[(\text{CO})_5\text{WSi}(\text{SiMe}_2\text{OMe})_3]_2\text{Yb}$   $^1\text{H}$  NMR THF- $\text{D}_8$



$[(\text{CO})_5\text{WSi}(\text{SiMe}_2\text{OMe})_3]_2 \text{ Yb}$   $^{13}\text{C}$  NMR THF- $\text{D}_8$

