Electronic Supplementary Information

Thorium(IV) Alkyl and Allyl Complexes of a Rigid NON-Donor Pincer Ligand with Flanking 1-Adamantyl Substituents

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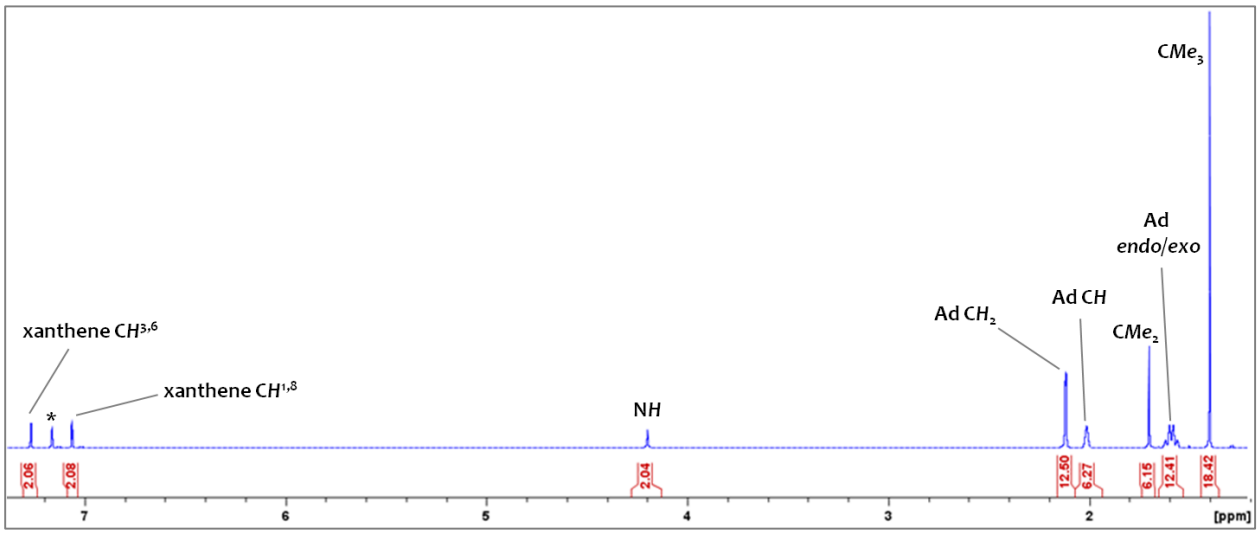
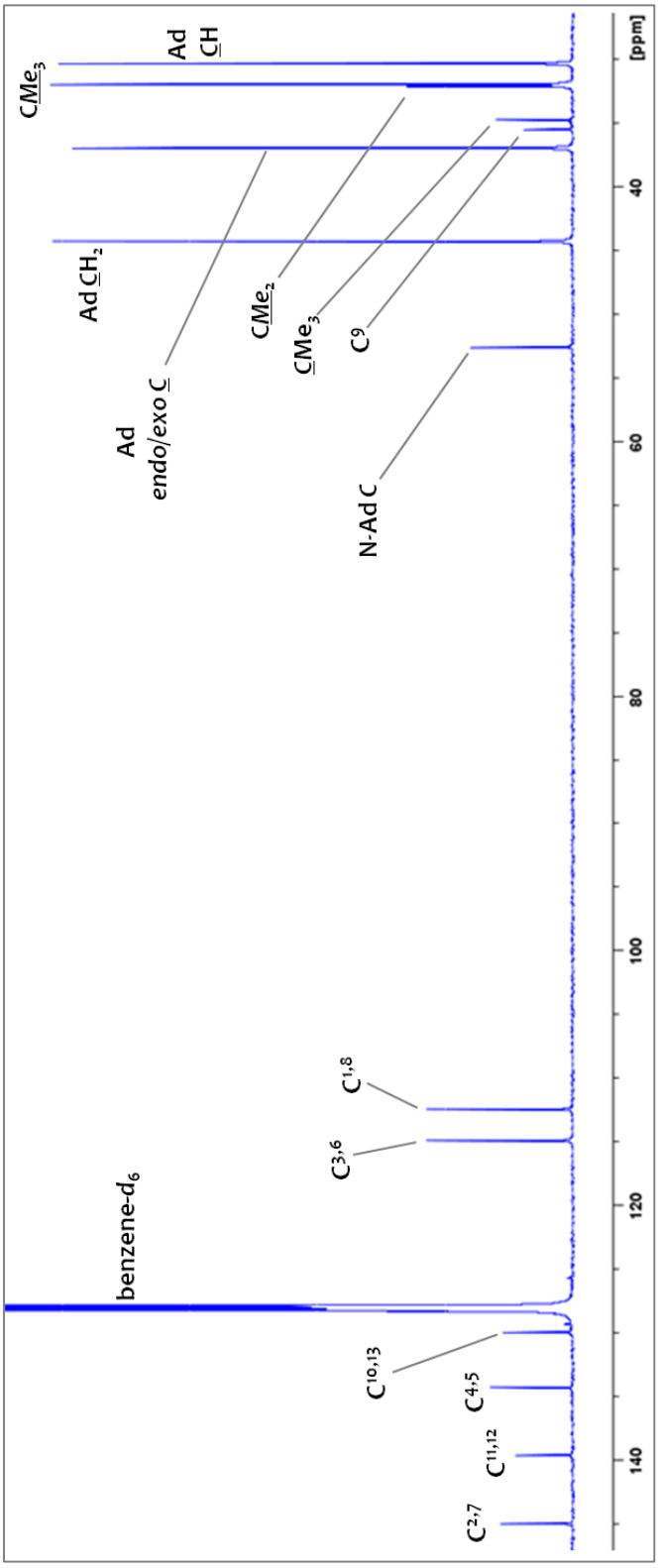
^{1}H NMR spectrum of H_2[XAd] (**1**) in benzene-d_6 (600.1 MHz, 298 K)

* denotes benzene-d_5

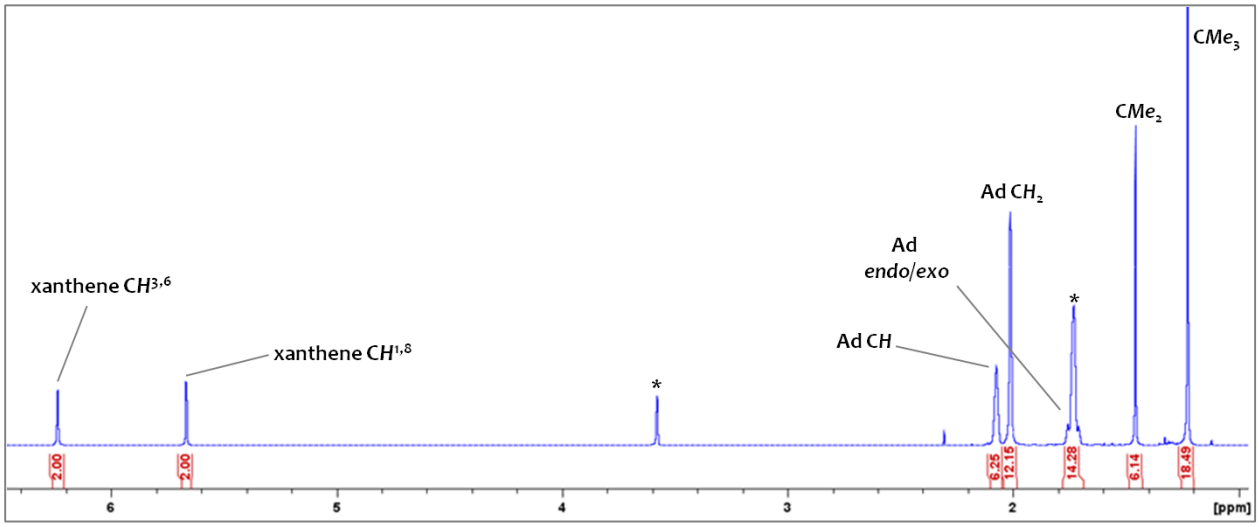


$^{13}C\{^{1}H\}$ NMR spectrum of H_2[XAd] (**1**) in benzene-d_6 (150 MHz, 298 K) - C_6D_6 signal truncated.



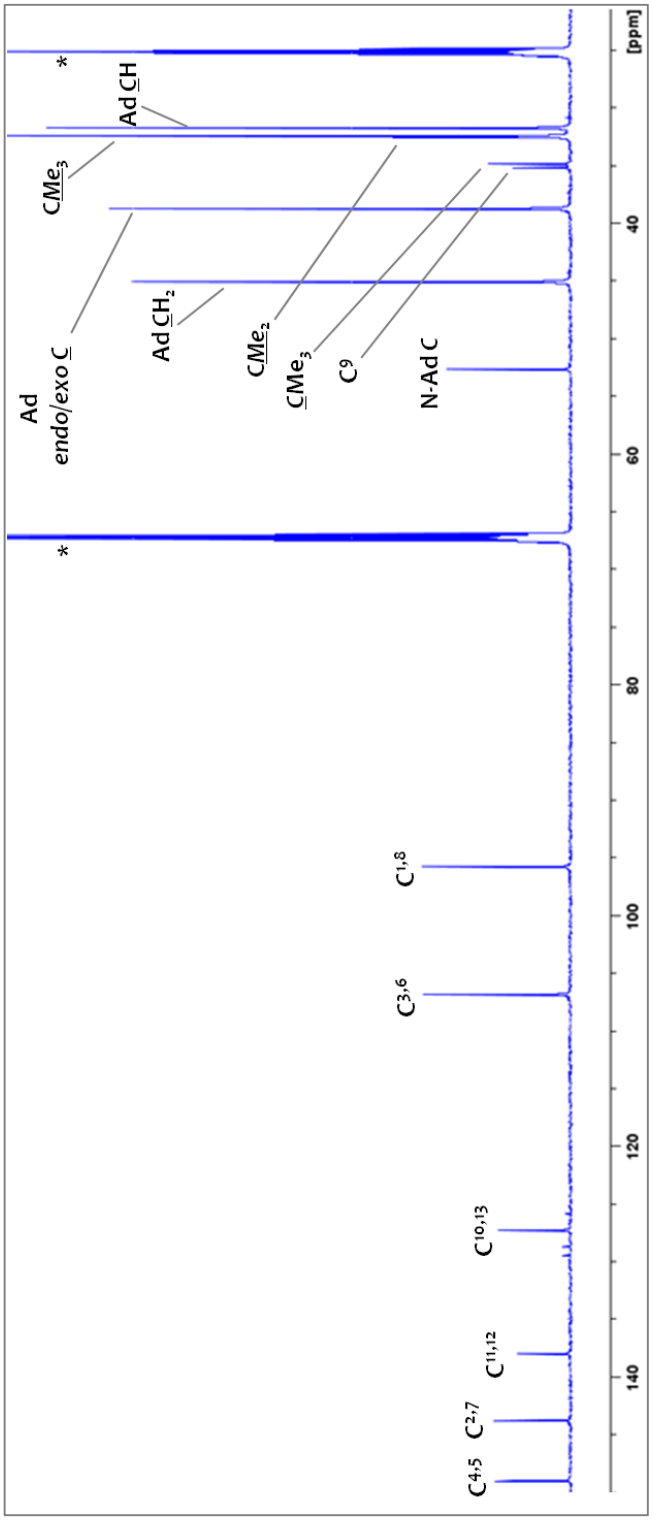
^{1}H NMR spectrum of [{K(THF)$_3$}$_2$(XAd)] (**2a**, *in-situ*) in THF-d_8 (600.1 MHz, 298 K)

* denotes THF-d_7; the CMe_3 signal is truncated.



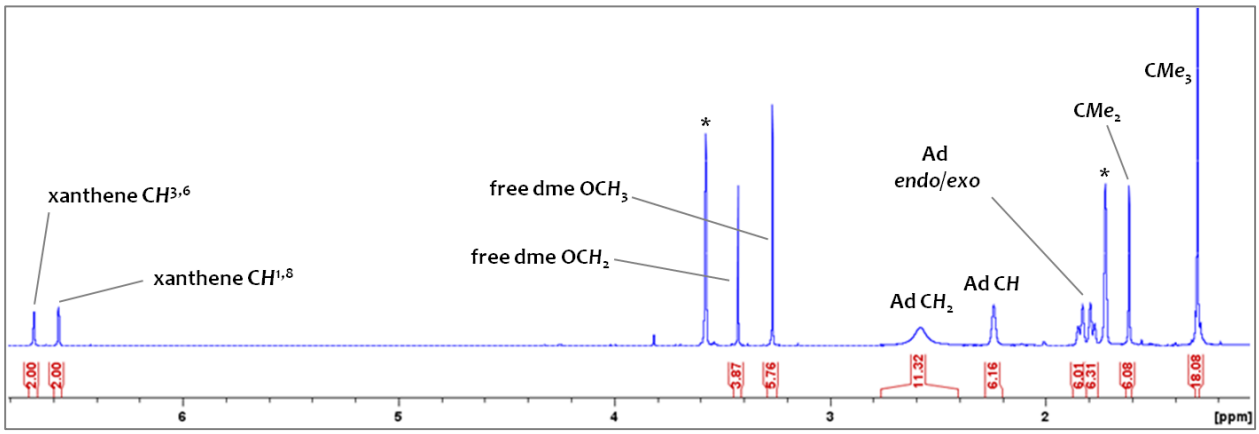
$^{13}C\{^{1}H\}$ NMR spectrum of [{K(THF)$_3$}$_2$(XAd)] (**2a**, *in-situ*) in THF-d_8 (150 MHz, 298 K)

* denotes THF-d_8 (THF-d_8 signals truncated)



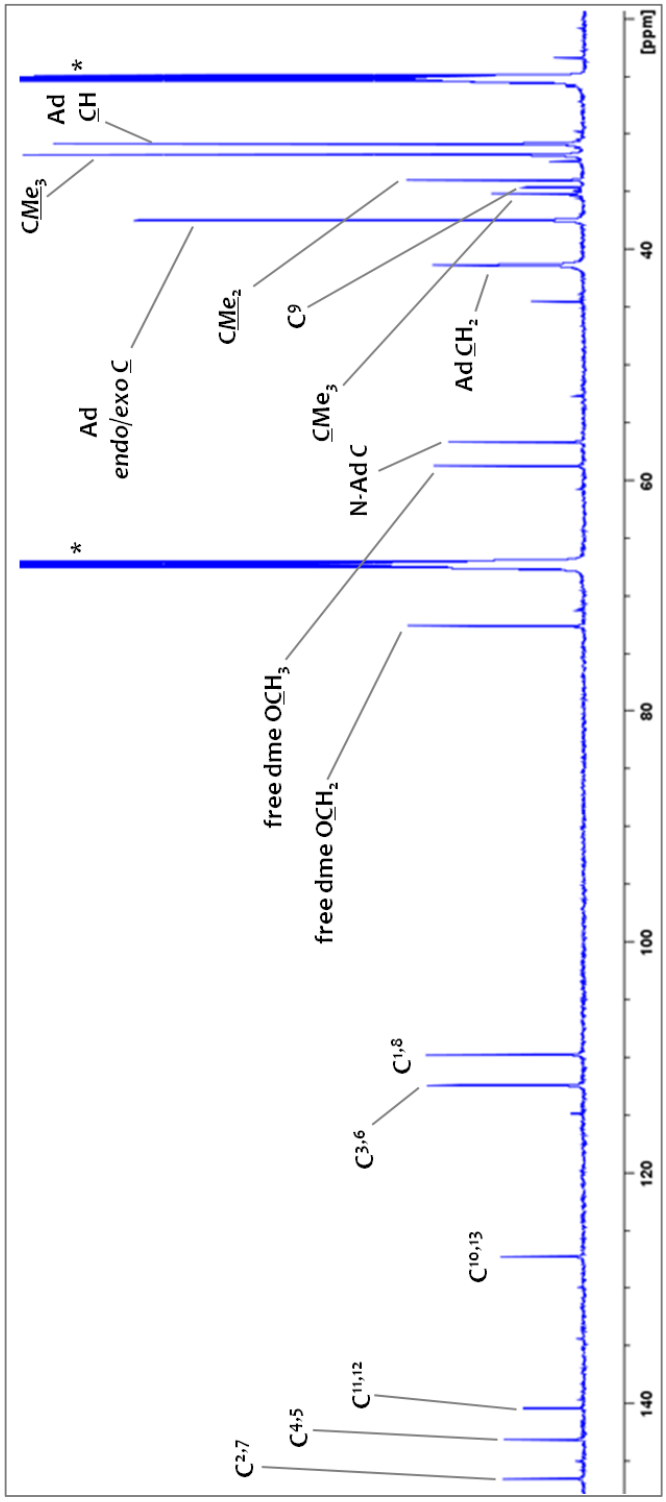
^{1}H NMR spectrum of [(XAd)ThCl$_4$K$_2$]·(dme) (**3**) in THF-d_8 (600.1 MHz, 298 K)

* denotes THF-d_7; the CMe_3 signal is truncated.



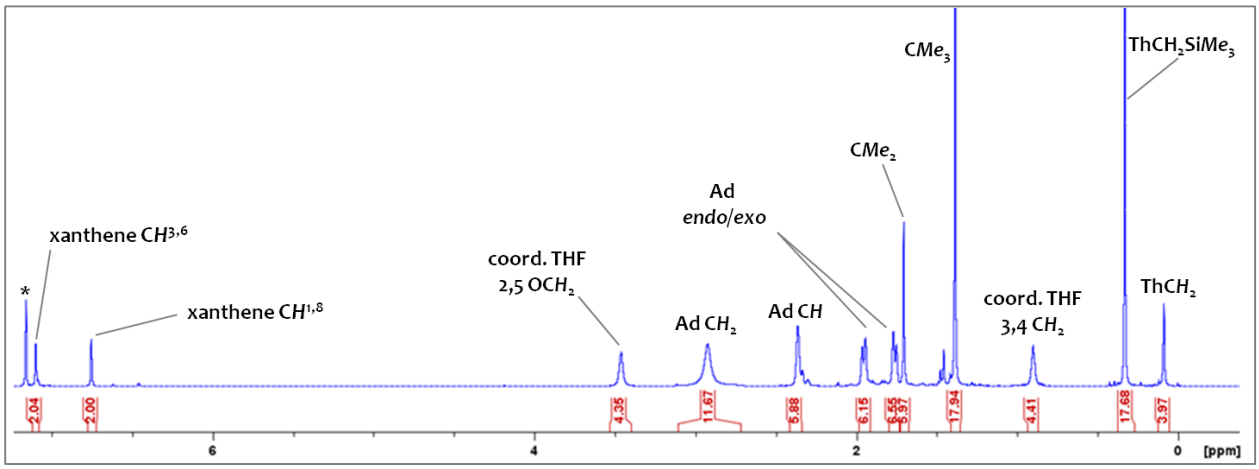
$^{13}C\{^{1}H\}$ NMR spectrum of [(XAd)$ThCl_4K_2$]·(dme) (**3**) in THF-d_8 (150 MHz, 298 K)

* denotes THF-d_8 (THF-d_8 signals truncated)



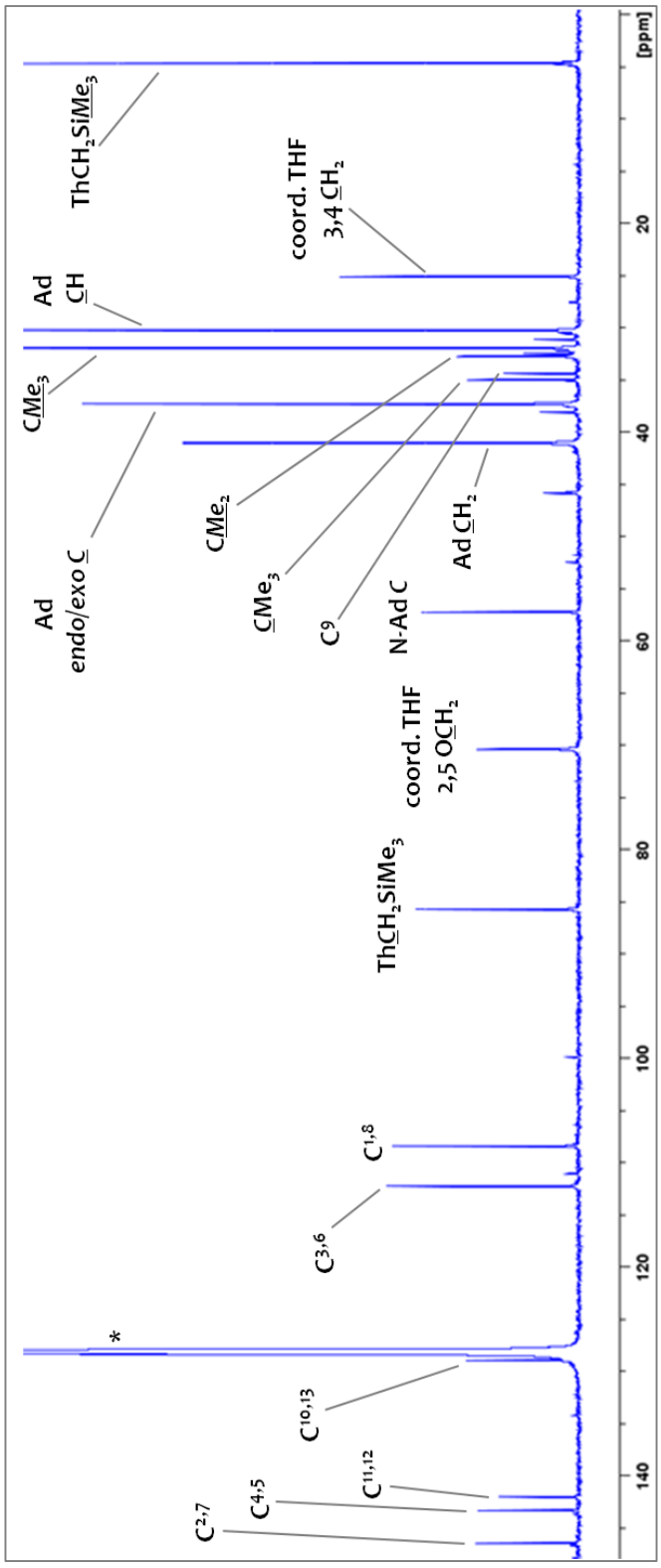
^{1}H NMR spectrum of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in benzene-d_6 (600.1 MHz, 298 K)

* denotes benzene-d_5; the CMe_3 and SiMe_3 signals are truncated.



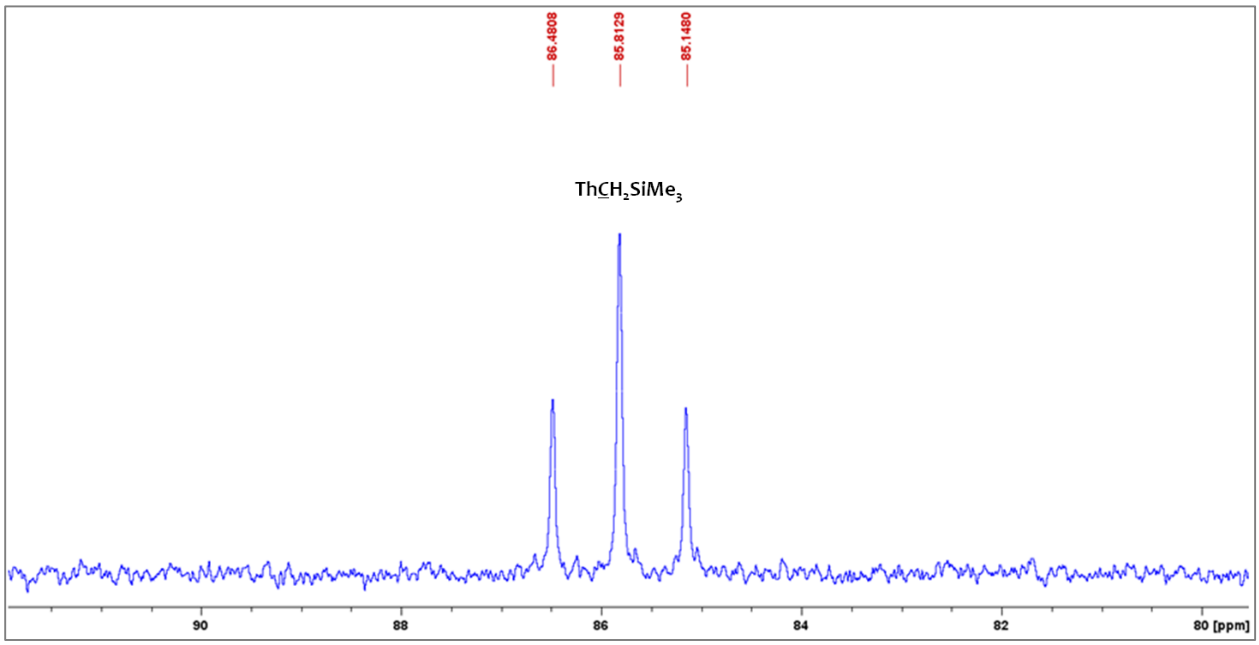
$^{13}C\{^{1}H\}$ NMR spectrum of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in benzene-d_6 (150 MHz, 298 K)

* denotes benzene-d_6; benzene-d_6, CMe_3, and Ad CH peaks are truncated.



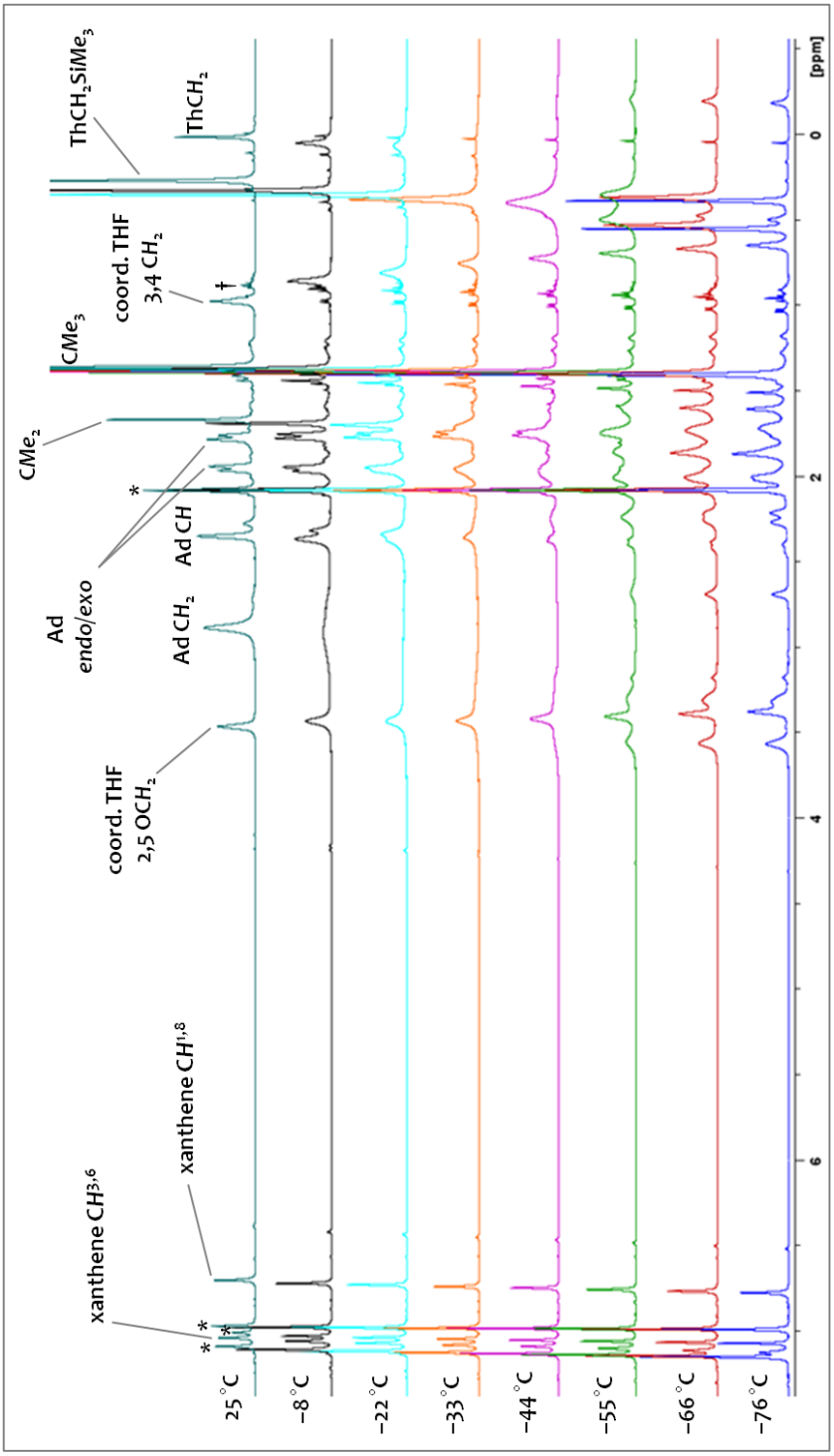
^{13}C NMR spectrum of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in benzene-d_6 (150 MHz, 298 K)

- Proton coupled, Th$\underline{C}H_2SiMe_3$ resonance highlighted



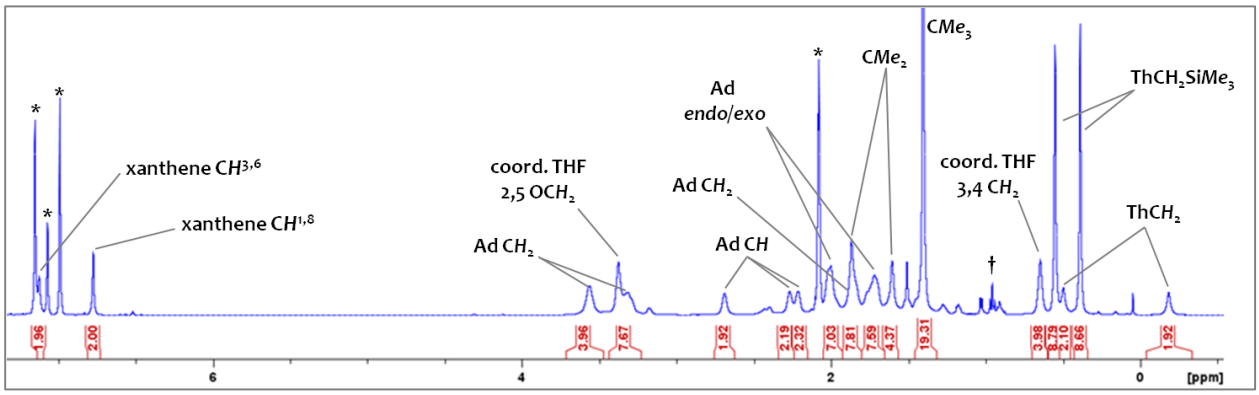
Variable Temperature ^{1}H NMR spectra of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in toluene-d_8 (500.1 MHz, 197–298 K)

* denotes toluene-d_7, † denotes hexanes; the CMe_3 and SiMe_3 signals are truncated.



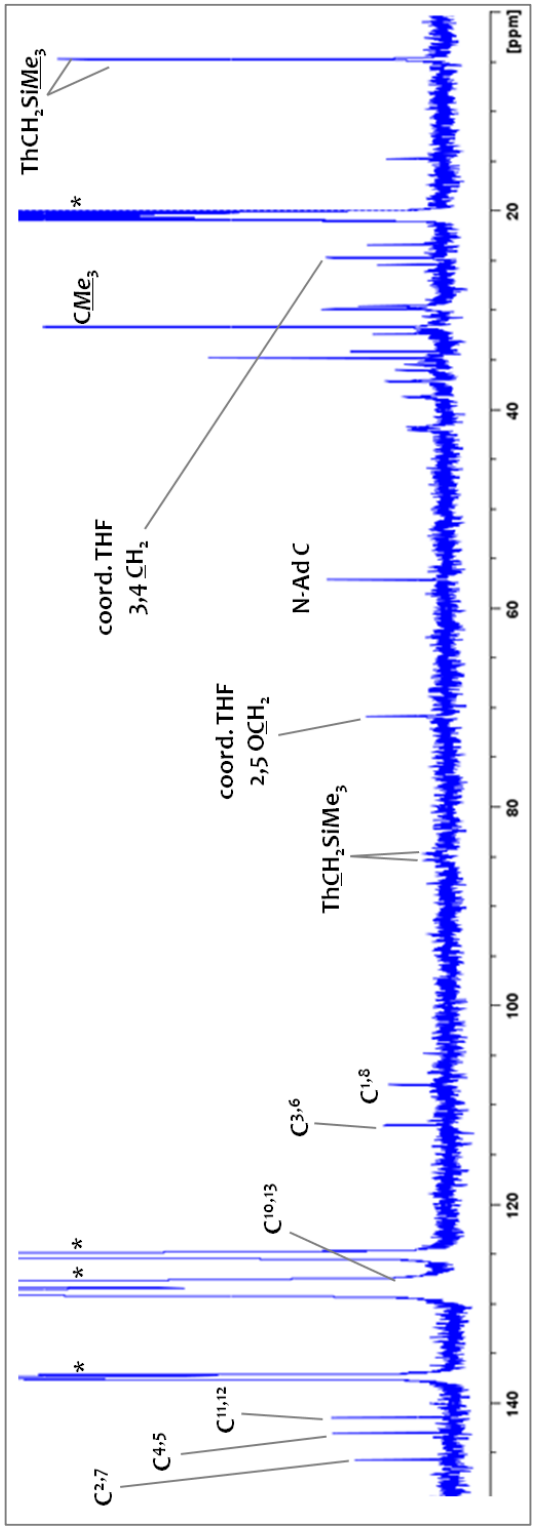
Low T ^{1}H NMR spectrum of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in toluene-d_8 (500.1 MHz, 197 K)

* denotes toluene-d_7, † denotes hexanes; the CMe_3 signal is truncated.



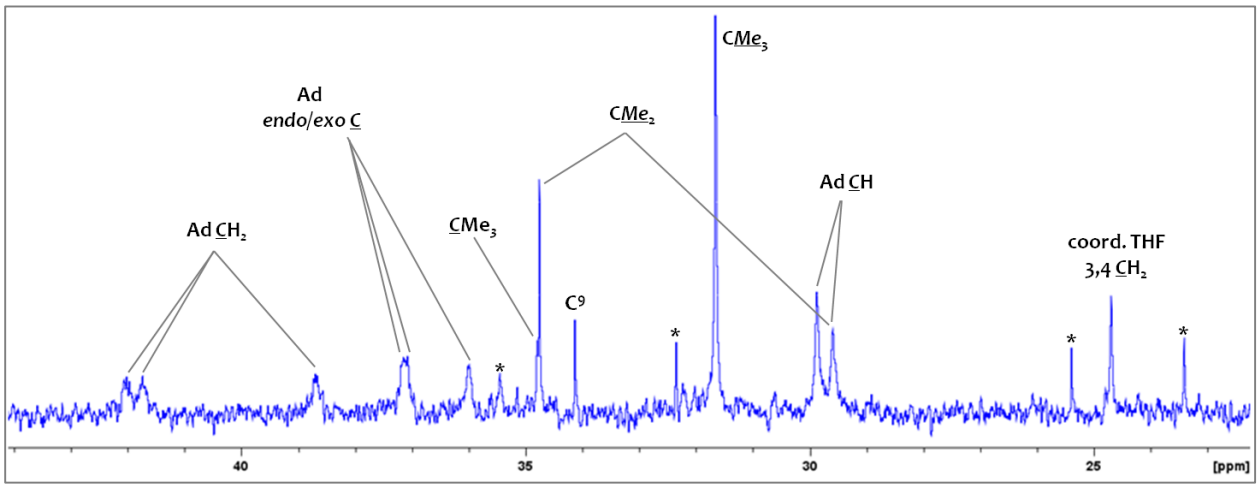
Low T $^{13}C\{^{1}H\}$ NMR spectrum of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in toluene-d_8 (125 MHz, 197 K)

* denotes toluene-d_8; toluene-d_8 signals are truncated. Region between 22 and 44 ppm is expanded on the following page.



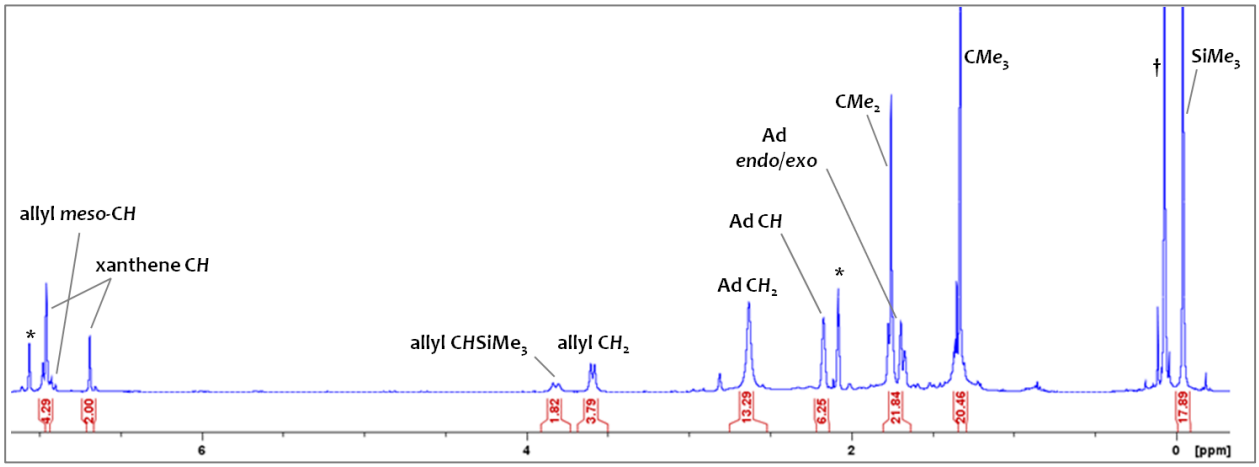
Expanded Region of the Low T $^{13}C\{^{1}H\}$ NMR spectrum of [(XAd)Th(CH_2SiMe_3)$_2$(THF)] (**4**) in toluene-d_8 (125 MHz, 197 K)

* denotes minor impurities (including *n*-hexane at ~ 23 and 32 ppm).



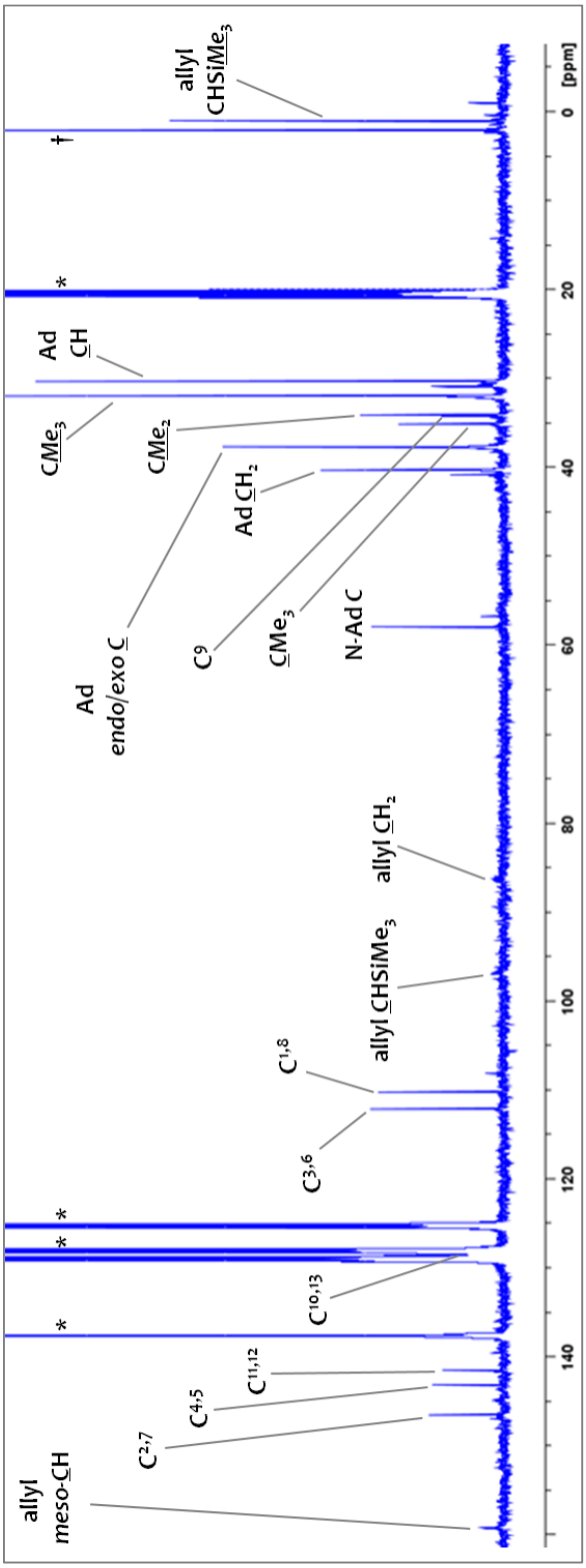
High T ^{1}H NMR spectrum of [(XAd)Th(η^3-allyl^{TMS})$_2$] (**5**) in toluene-d_8 (500.1 MHz, 360 K)

* denotes toluene-d_7, † denotes O(SiMe$_3$)$_2$; the C*Me*$_3$, O(Si*Me*$_3$)$_2$, and Si*Me*$_3$ signals are truncated.



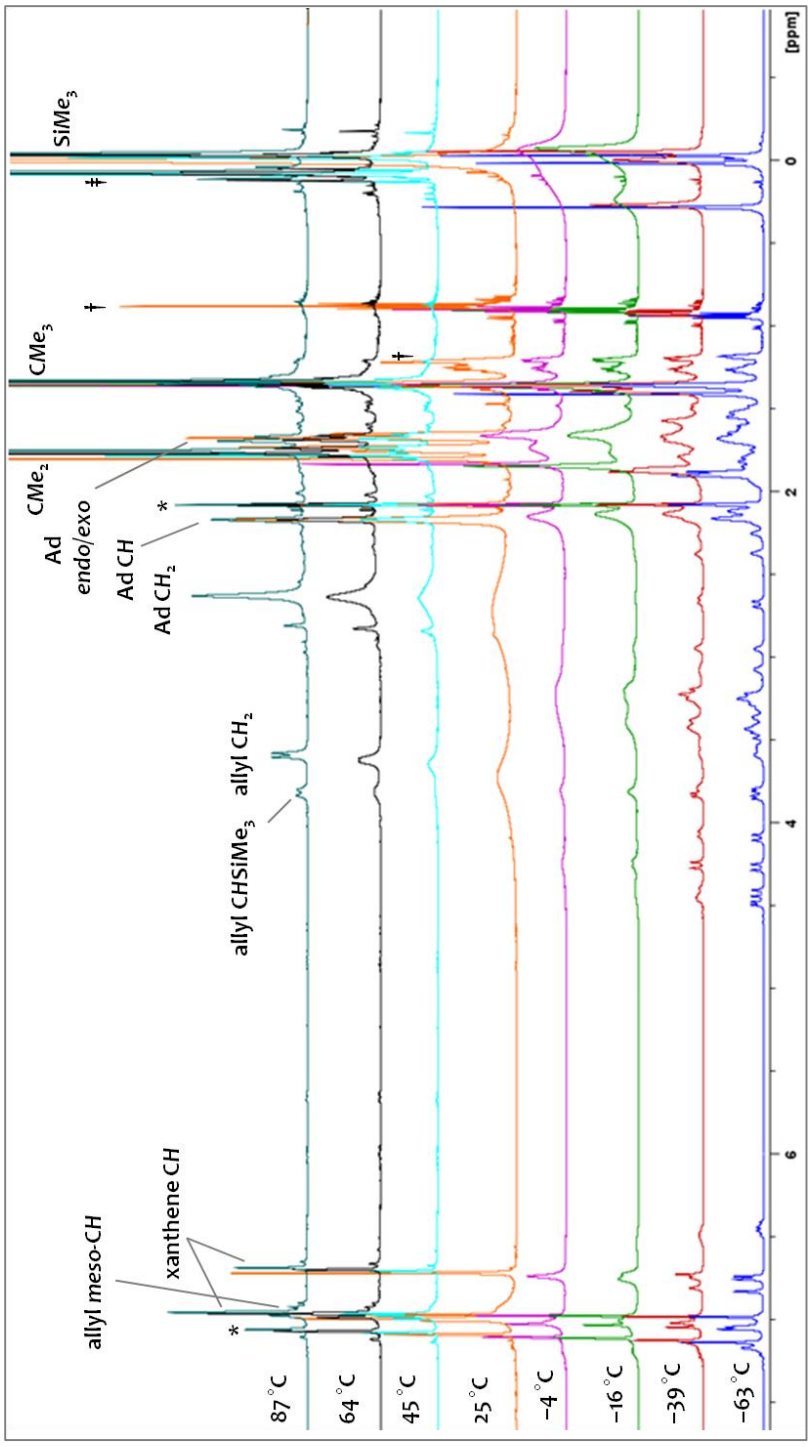
High T $^{13}C\{^{1}H\}$ NMR spectrum of [(XAd)Th(η^3-allyl^{TMS})$_2$] (**5**) in toluene-d_8 (125 MHz, 350 K)

* denotes toluene-d_8, † denotes O(SiMe$_3$)$_2$; toluene-d_8 and O(Si*Me*$_3$)$_2$ peaks are truncated.



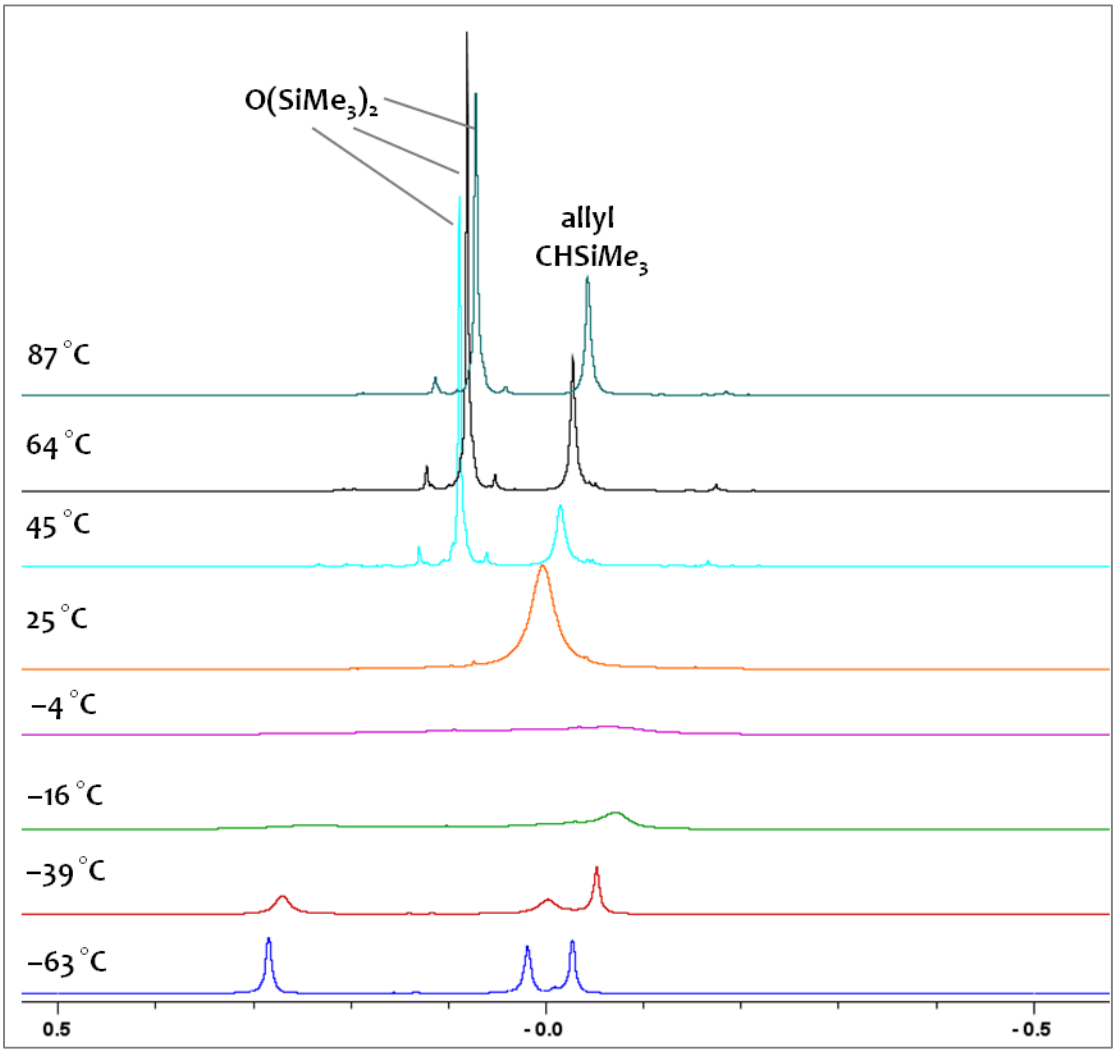
Variable Temperature ^{1}H NMR spectra of [(XAd)Th(η^3-allyl^{TMS})$_2$] (**5**) in toluene-d_8
(500.1 MHz, 210–360 K)

Two separate samples were used for the high- and low temperature experiments. * denotes toluene-d_7, † denotes *n*-pentane, ‡ denotes O(SiMe$_3$)$_2$; the C*Me*$_2$, C*Me*$_3$, O(Si*Me*$_3$)$_2$, and Si*Me*$_3$ signals are truncated.



Variable Temperature ^{1}H NMR spectra of [(XAd)Th(η^3-allyl^{TMS})$_2$] (**5**) in toluene-d_8
(500.1 MHz, 210–360 K)

Silyl region highlighted; two separate samples were used for the high- and low temperature experiments {the sample used for high-temperature experiments contains $O(SiMe_3)_2$}.



Low T ^{1}H NMR spectrum of [(XAd)Th(η^3-allyl^{TMS})$_2$] (**5**) in toluene-d_8 (500.1 MHz, 210 K)

Selected resonances highlighted. * denotes toluene-d_7, † denotes *n*-pentane; the C*Me*$_3$, and Si*Me*$_3$ signals are truncated.