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Supplementary Material

Cerium cyclotrisilazides

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SUPPORTING INFORMATION

Cerium Cyclotrisilazides

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Dedicated to Professor Glen B. Deacon on the occasion of his 85th birthday

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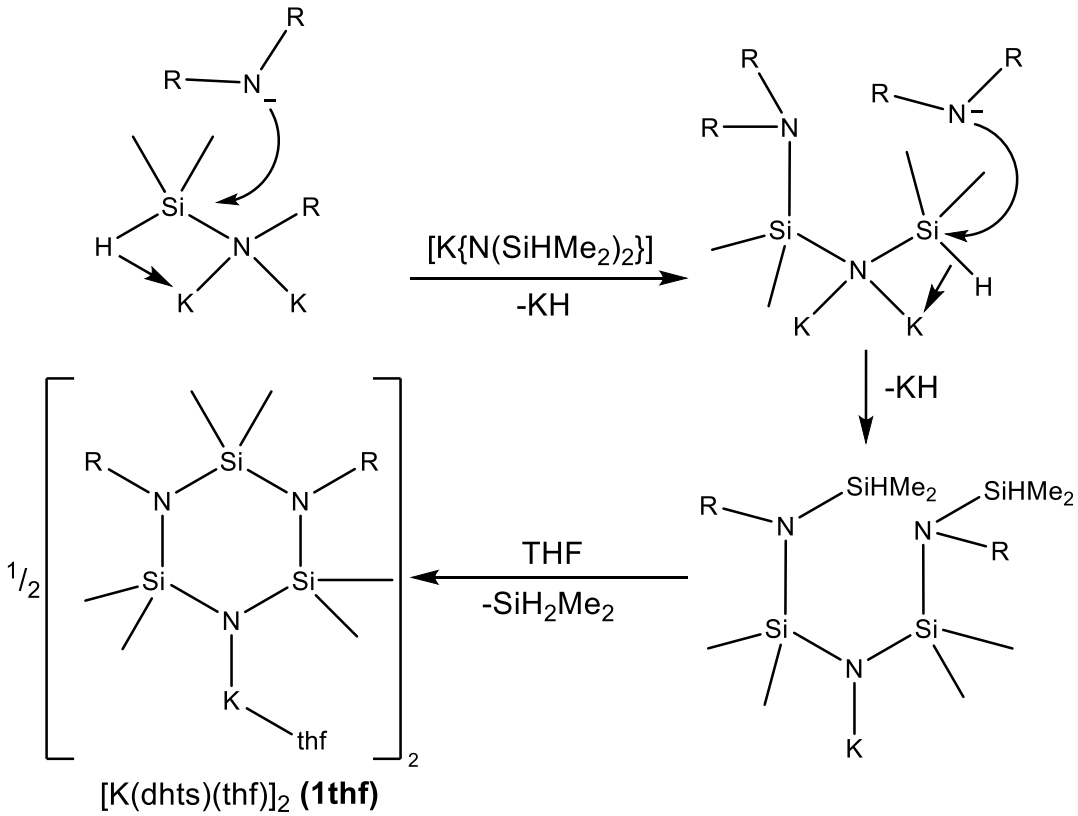
Crystal structure determination

X-ray data: All compounds were examined on a 'Bruker APEX-II CCD' diffractometer. The crystals were mounted on a fibre loop in *n*-paratone crystallography oil. Absorption corrections were completed using Apex II program suite.[1] Structural solutions were obtained by charge flipping (**1thf**)[2] methods or SIR2004 (**2thf, 1tol, 4**)[3] and refined using full matrix least squares methods against F^2 using SHELX2015 or SHELX2008,[4] within the OLEX 2 graphical interface.[5] A list of the parameters are found in Table S1.

Table S1. Data of crystal structures

Complex	$[K(dhts)(thf)]_2$	$Ce(dhts)_3(thf)$	$[K(dhts)(tol)]_2$	$CeCl(dhts)_3$
Complex code	**1thf**	**2thf**	**1tol**	**3**
CCDC number	2123366	2123368	2123367	2123365
Empirical formula	$C_{28}H_{80}K_2N_6O_2Si_{10}$	$C_{34}H_{104}CeN_9OSi_{15}$	$C_{34}H_{80}K_2N_6Si_{10}$	$C_{30}H_{96}CeClN_9Si_{15}$
Formula weight	892.08	1216.73	932.14	1180.20
Temperature/K	99.05	100.15	99.91	100.0
Crystal system	monoclinic	monoclinic	triclinic	trigonal
Space group	$P2_1/c$	$P2_1/c$	P-1	R-3
a/Å	12.9415(9)	20.3484(10)	10.4762(6)	14.2001(5)
b/Å	14.6386(10)	10.7867(5)	11.4891(7)	14.2001(5)
c/Å	14.3830(10)	31.5216(15)	13.2003(8)	54.239(4)
α/°	90.00	90.00	69.9677(8)	90.00
β/°	109.9502(10)	106.0656(10)	70.4786(9)	90.00
γ/°	90.00	90.00	71.1705(9)	120.00
Volume/$Å^3$	2561.3(3)	6648.5(5)	1367.41(14)	9471.7(8)
Z	2	4	1	6
$\rho_{calc}g/cm^3$	1.157	1.216	1.132	1.241
μ/mm^{-1}	0.449	0.988	0.421	1.077
F(000)	968.0	2588.0	504.0	3744.0
Crystal size/mm^3	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.2	0.5 × 0.3 × 0.3	0.4 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)

2Θ range for data collection/°	3.34 to 52.14	3.84 to 56.62	3.394 to 61.112	3.4 to 51.98
Index ranges	-16 ≤ h ≤ 15, -18 ≤ k ≤ 18, -17 ≤ l ≤ 17	-27 ≤ h ≤ 27, -14 ≤ k ≤ 14, -41 ≤ l ≤ 41	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -66 ≤ l ≤ 66
Reflections collected	42008	102190	37927	80818
Independent reflections	5059 [R_{int} = 0.0331, R_{sigma} = 0.0175]	16411 [R_{int} = 0.0519, R_{sigma} = 0.0357]	8373 [R_{int} = 0.0294, R_{sigma} = 0.0236]	4158 [R_{int} = 0.0213, R_{sigma} = 0.0066]
Data/restraints/parameters	5059/12/290	16411/0/580	8373/0/298	4158/12/212
Goodness-of-fit on F^2	1.110	1.030	1.104	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1120	R_1 = 0.0317, wR_2 = 0.0709	R_1 = 0.0276, wR_2 = 0.0741	R_1 = 0.0224, wR_2 = 0.0617
Final R indexes [all data]	R_1 = 0.0459, wR_2 = 0.1214	R_1 = 0.0454, wR_2 = 0.0769	R_1 = 0.0360, wR_2 = 0.0833	R_1 = 0.0240, wR_2 = 0.0634
Largest diff. peak/hole / e $Å^{-3}$	0.84/-0.33	0.88/-0.63	0.48/-0.23	1.83/-0.38



Scheme 1. Possible mechanism of **1thf** formation resulting from nucleophilic attack at the Si–H bond by {N(SiHMe$_2$)$_2$}, eliminating KH (R = SiHMe$_2$). This process likely occurs twice, followed by SiH$_2$Me$_2$ elimination leading to the formation of the dhts ligand. As heating K[N(SiHMe$_2$)$_2$] in THF-D$_8$/C$_6$D$_6$ does not induce such a reaction pathway, and initiation steps is required.

NMR spectra of reported complexes

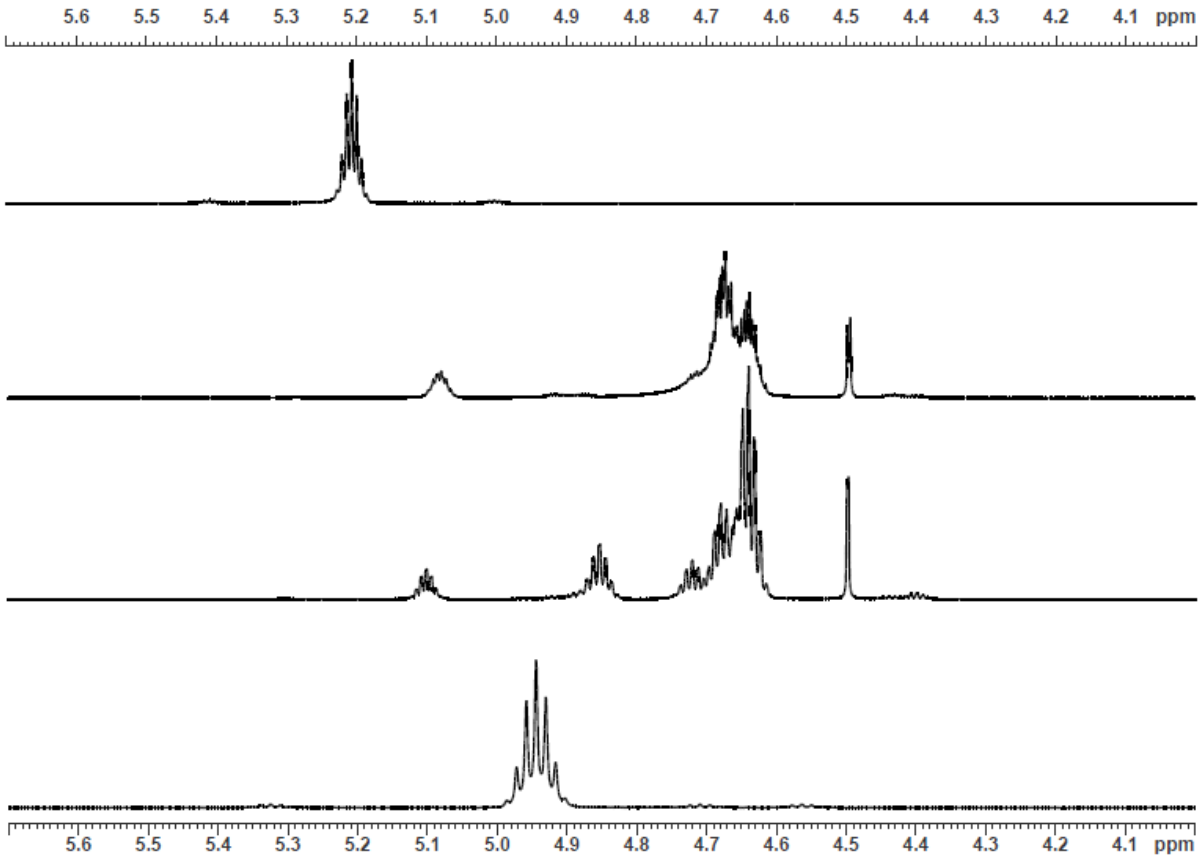


Figure S1.1 ^{1}H NMR spectra (ppm – 4.0 – 5.7 range) of the reaction mixture resulting from K[N(SiMe$_2$H)$_2$] after heating in C_6D_6/THF-D_8 (top), after the addition of HN(SiMe$_2$H)$_2$, after further heating for 24 h, and the isolated dhts complex **1thf** (from top to bottom).

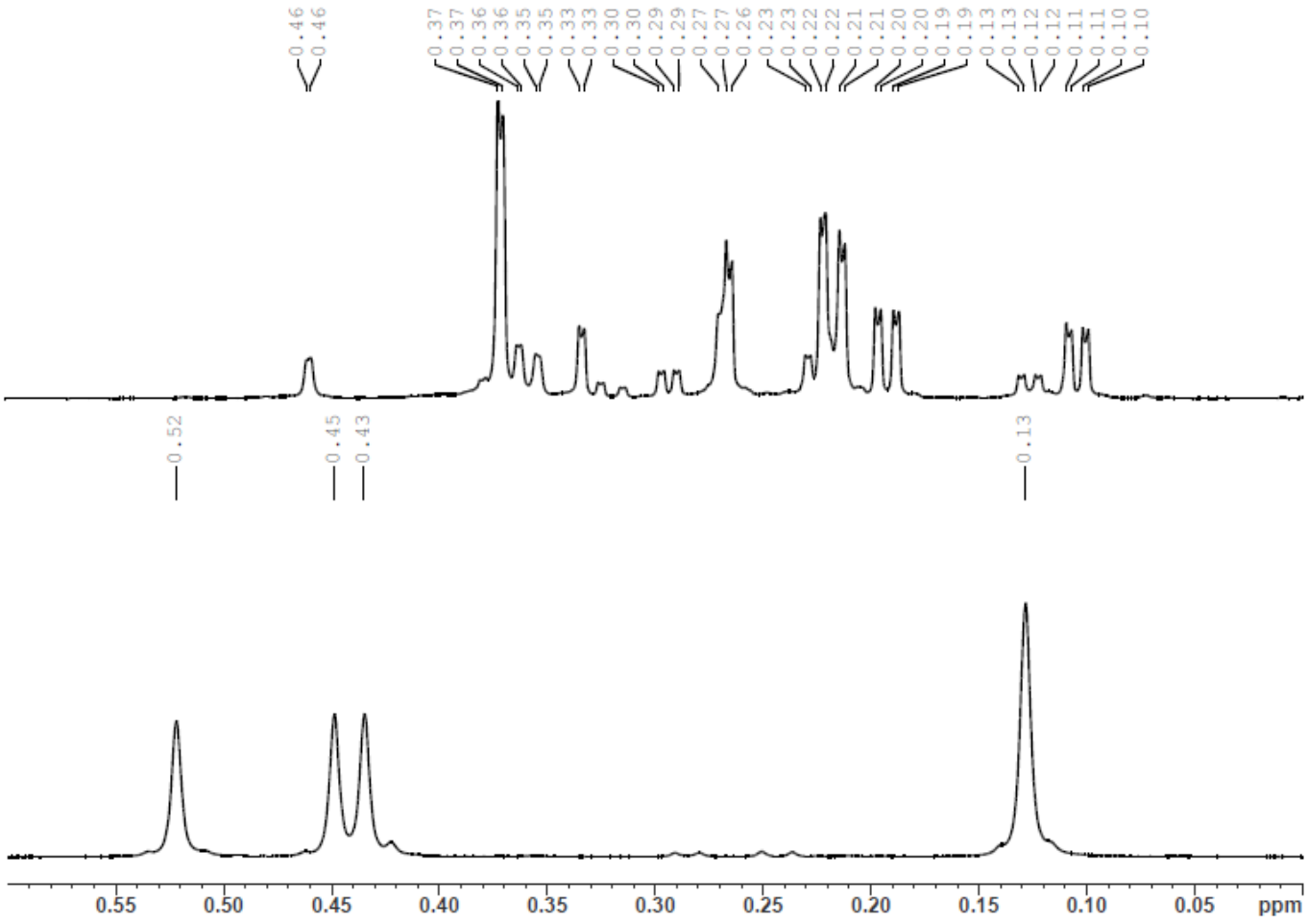


Figure S1.2 ^{1}H NMR spectra (ppm – 0.6 – 0 range) of the reaction mixture after the addition of $HN(SiHMe_2)_2$ and heating (top), and the isolated dhts complex **1thf** (bottom).

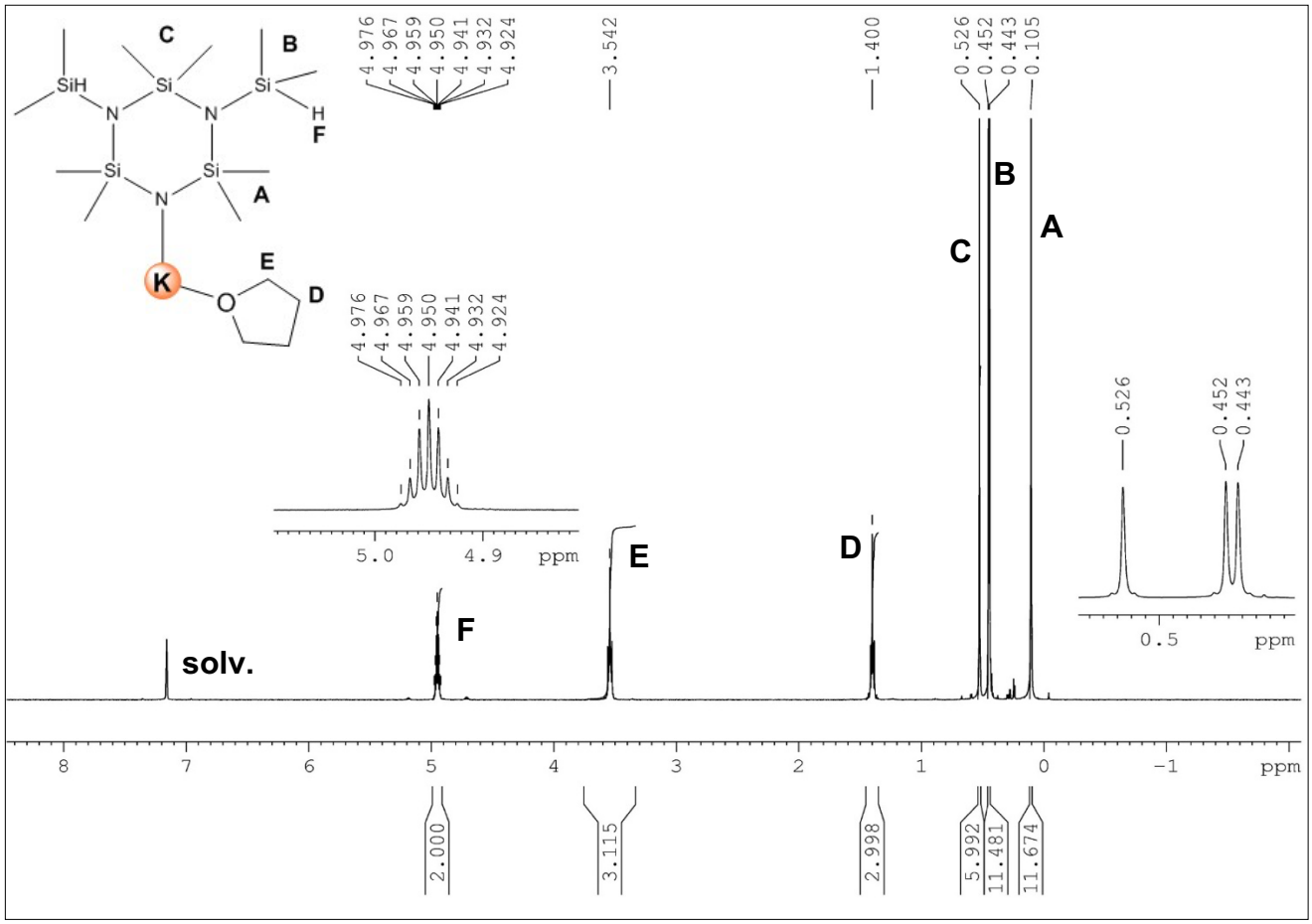


Figure S2. ^{1}H NMR (C_6D_6, 400 MHz, 300 K) of $[K(dhts)(thf)]_2$ (**1thf**).

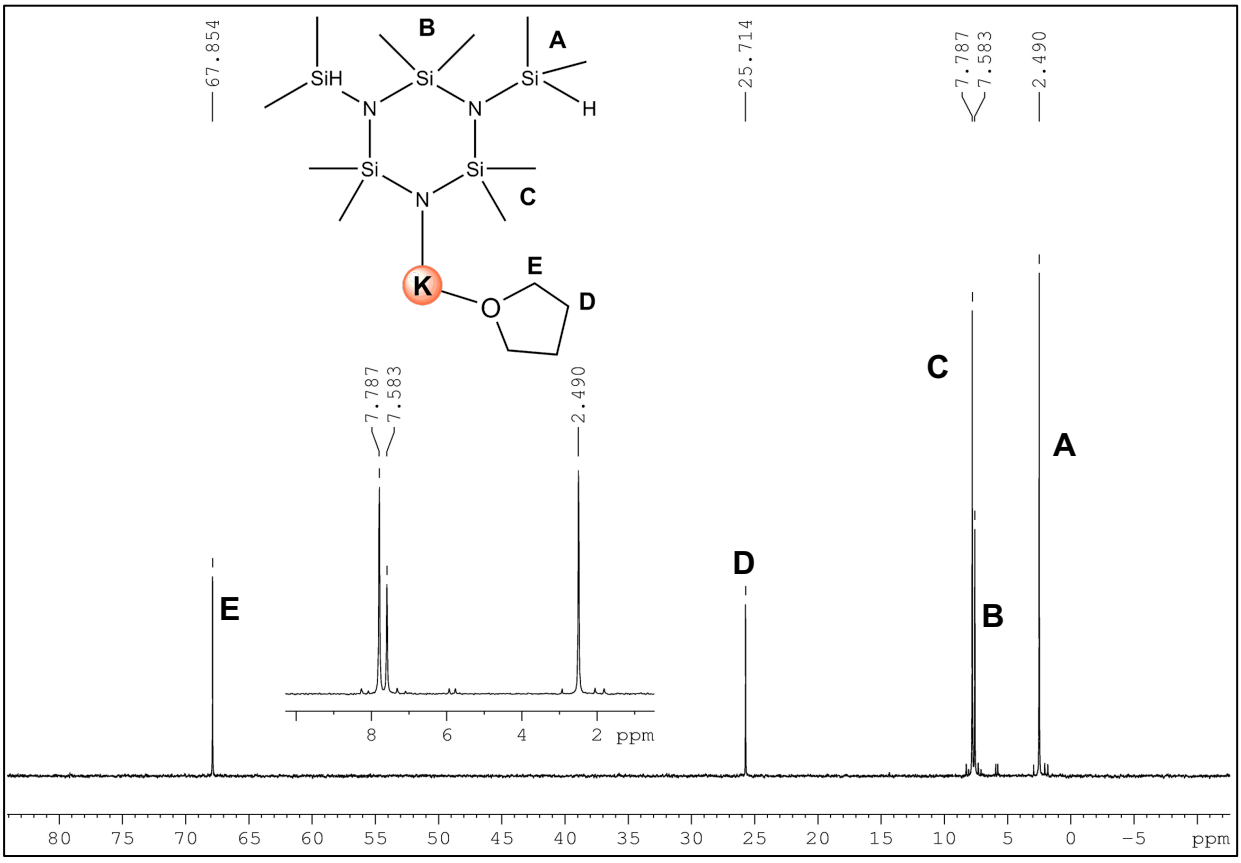


Figure S3. ^{13}C NMR spectrum (C_6D_6, 63 MHz, 300 K) of $[K(dhts)(thf)]_2$ (**1thf**).

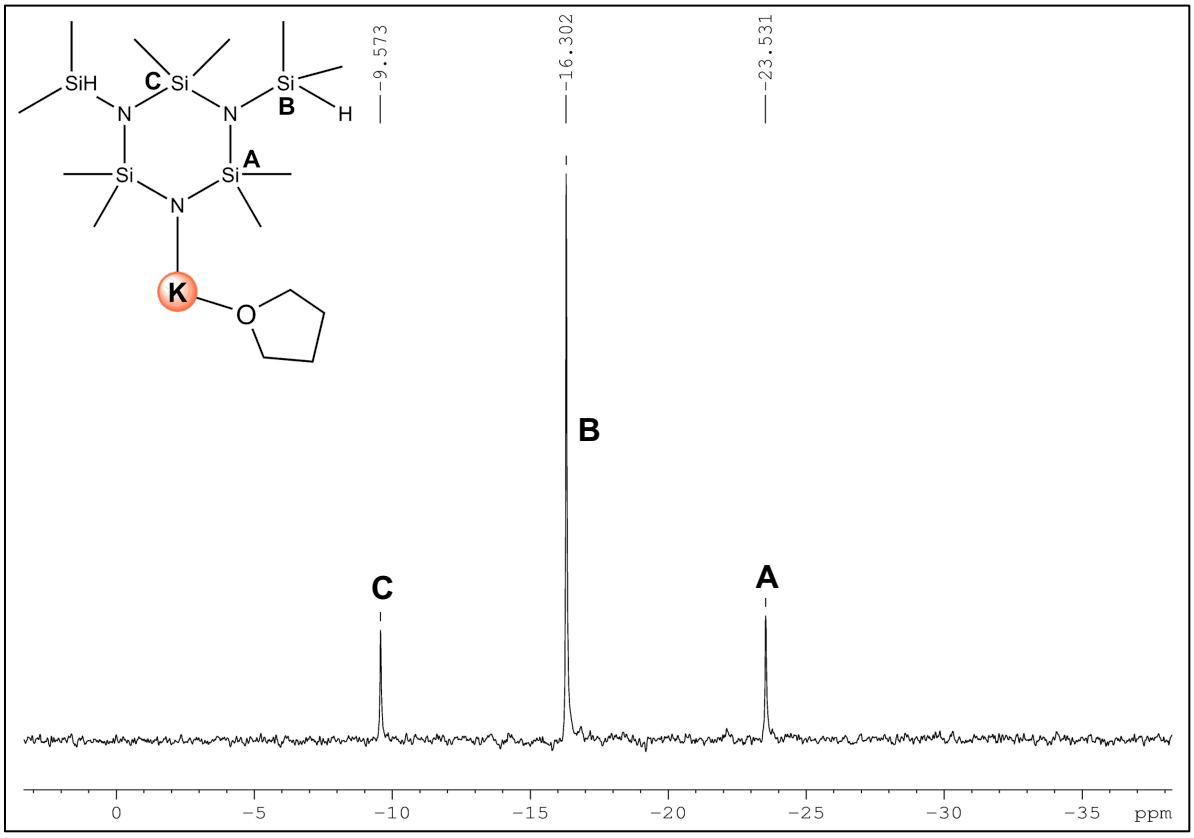
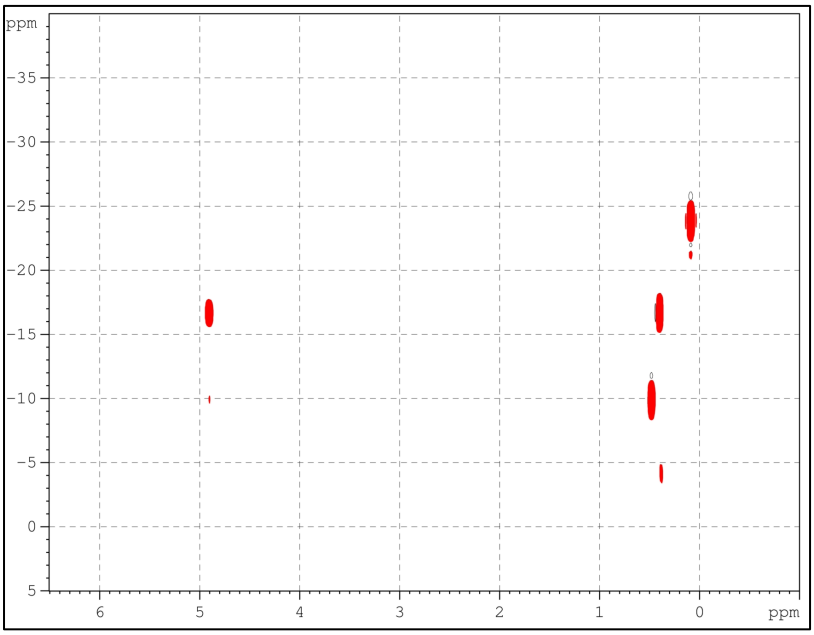


Figure S4. ^{29}Si NMR spectrum (C_6D_6, 50 MHz, 300 K) of $[K(dhts)(thf)]_2$ (**1thf**).



^{1}H NMR peak	^{29}Si NMR peak	assignment
0.09	-24.0	2,6-Si
0.40	-16.8	3,5-Si
0.47	-10	4-Si
4.90	-16.8	3,5-Si

Figure S5. HSQC ^{29}Si-^{1}H spectrum allowing assignment of ^{29}Si NMR.

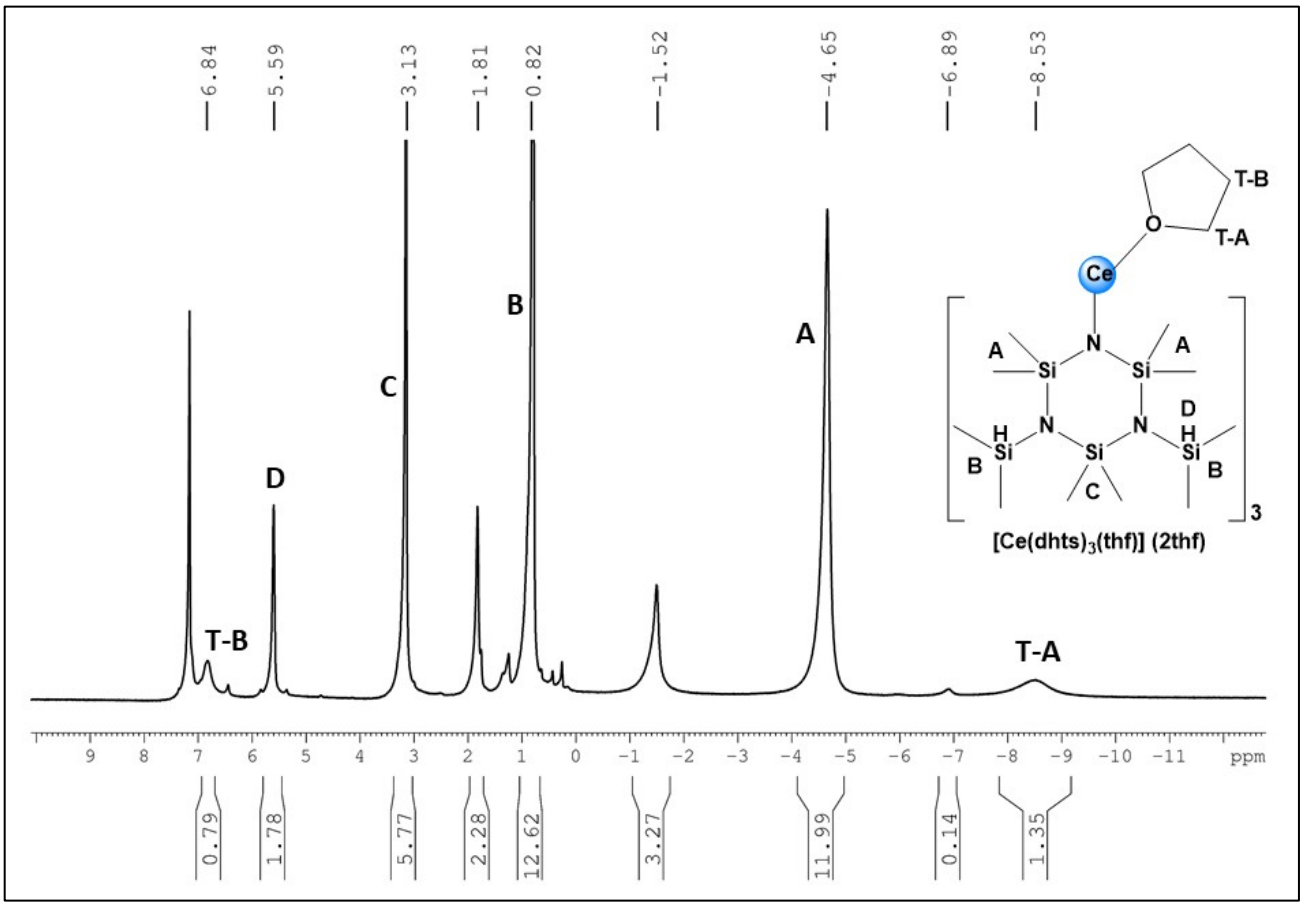


Figure S6. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 300 K) of Ce(dhts)$_3$(thf) (**2thf**) with tentative assignments.

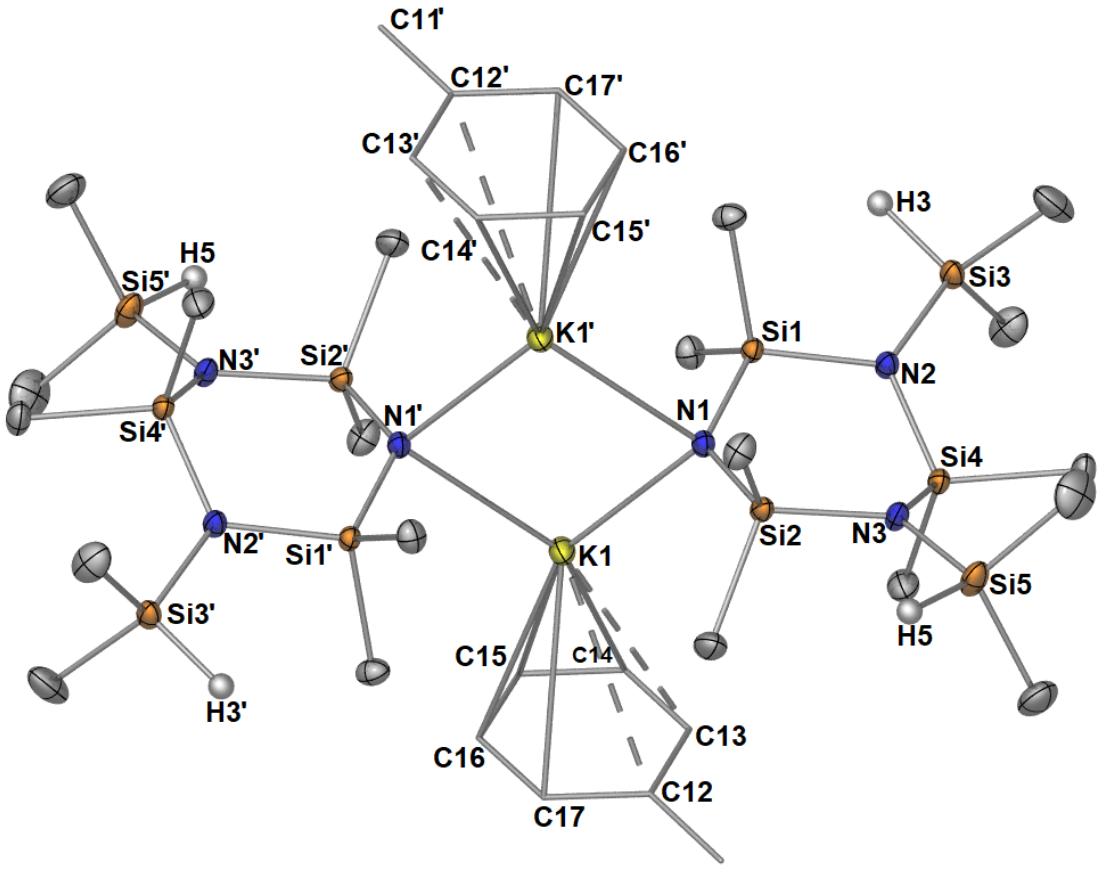


Figure S7. Crystal structure of $[K(dhts)(tol)]_2$ (**1tol**). The molecular structure is shown with ellipsoids at 50% probability level, hydrogen atoms (except for H2 and H4) have been removed for clarity. The toluene ligand is depicted by a wireframe model for clarity. Selected interatomic distances (Å) and angles (°) for **1tol**: K1-N1: 2.8483(9), K1'-N1: 2.6901(9), K1-C12: 3.5513(13), K1-C13:3.5752, K1-C14: 3.4320, K1-C15: 3.2454(12), K1-C16: 3.2039, K1-C17: 3.3532(14), K1-N1-K1': 89.34(3).

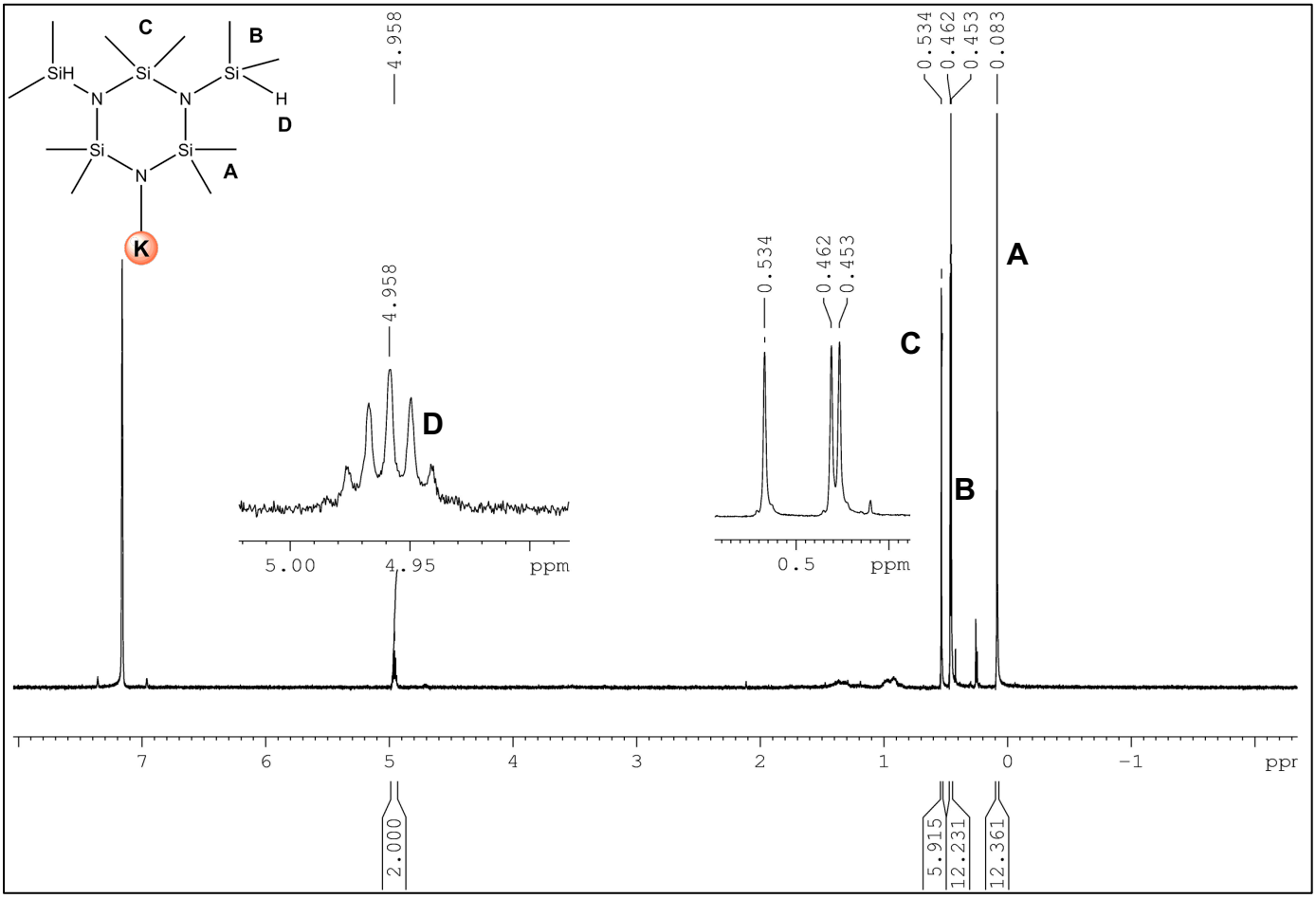


Figure S8. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 300 K) of "[K(dhts)]" obtained from loss of coordinated toluene in $[K(dhts)(tol)]_2$ (**1tol**).

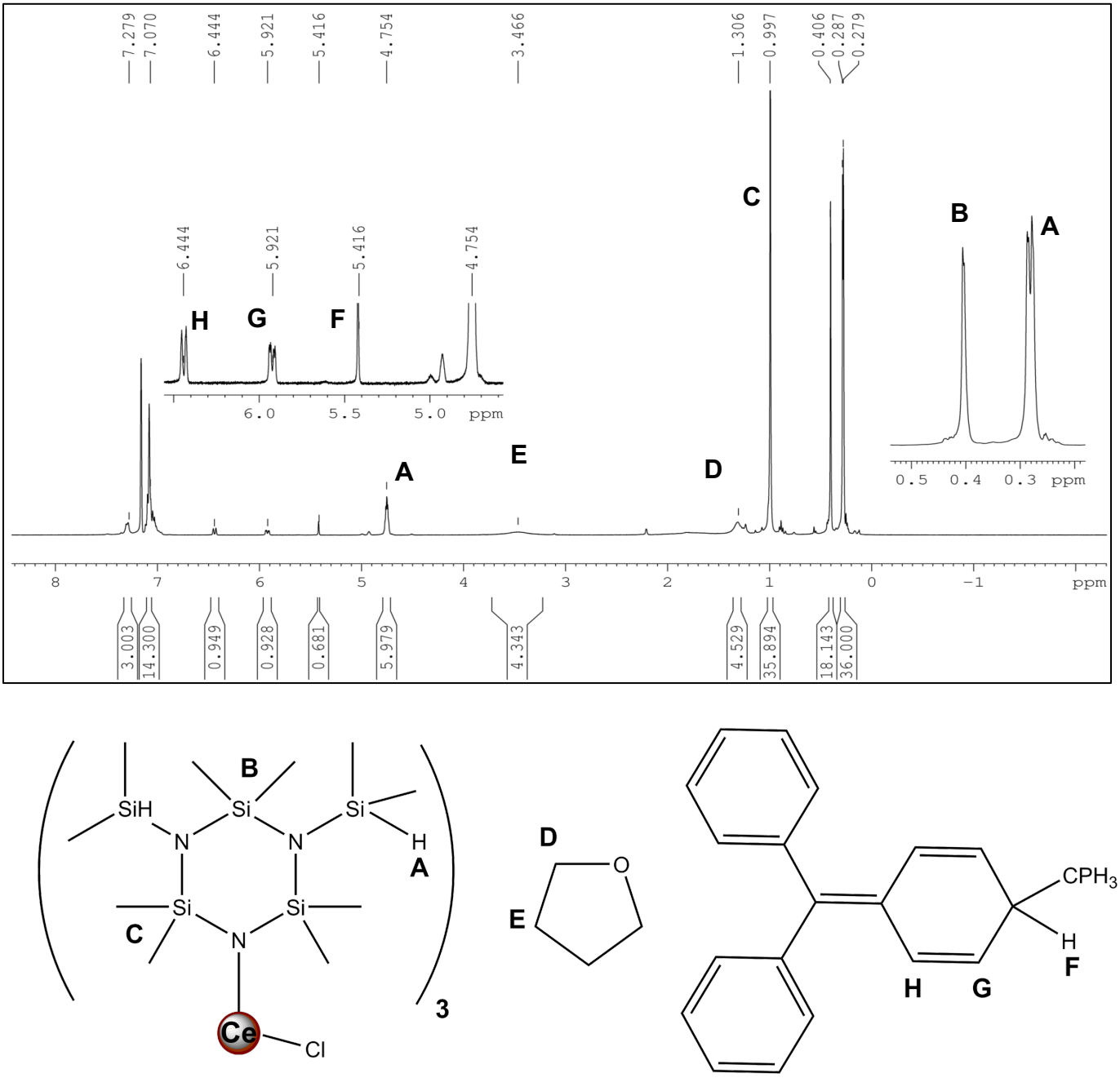


Figure S9. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 300 K) of the reaction mixture between **2thf** and trityl chloride. Integrations for the Gomberg dimer is lower due to poor solubility in C_6D_6.

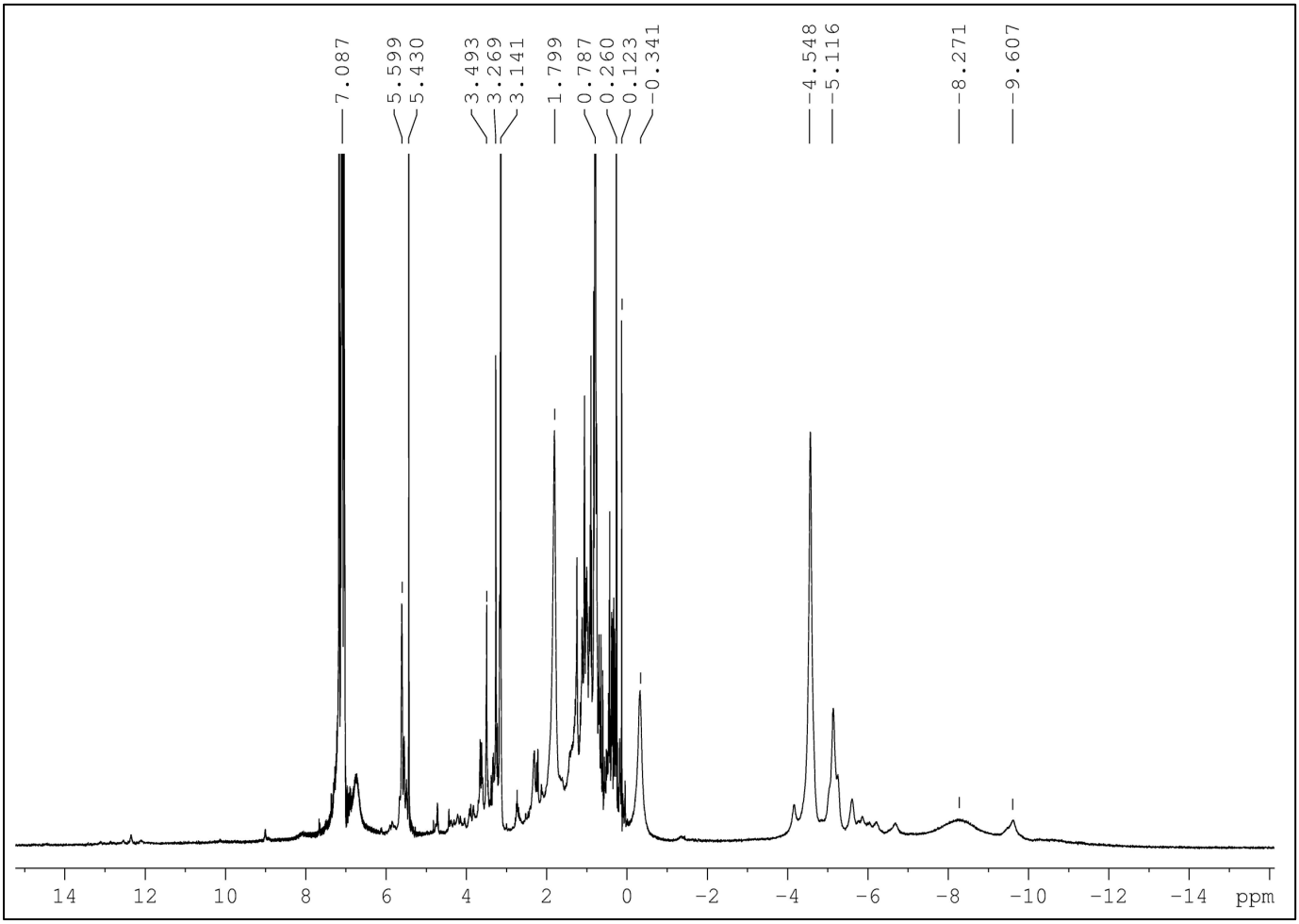


Figure S10. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 300 K) of the reaction mixture between **2thf** and trityl chloride after 24 h indicating complete decomposition.

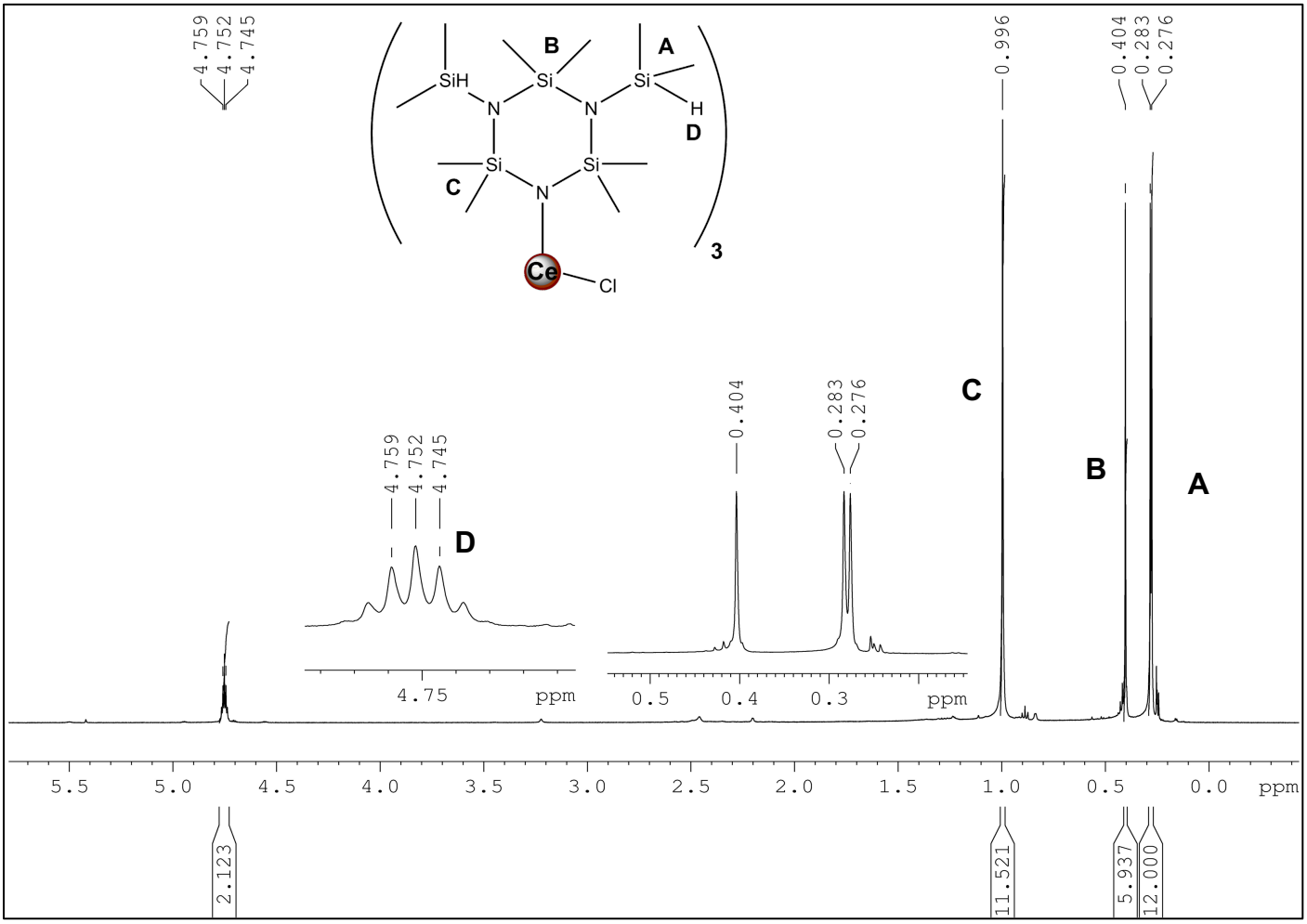


Figure S11. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 300 K) of $CeCl(dhts)_3$ (**3**).

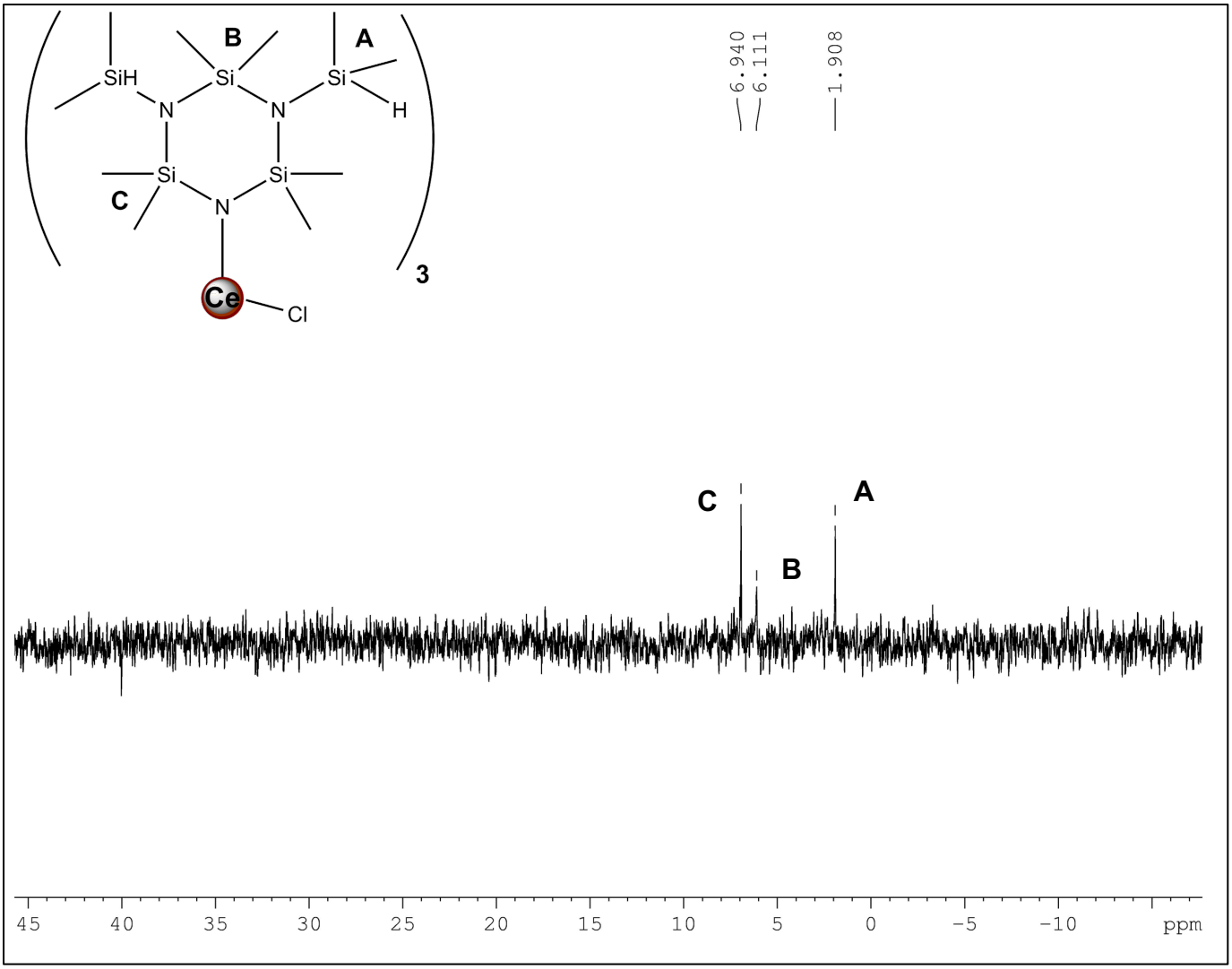


Figure S12. ^{13}C NMR spectrum (C_6D_6, 63 MHz, 300 K) of $CeCl(dhts)_3$ (**3**).

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[1] Apex II Version 2.1, Bruker AXS Ltd., Madison, Wisconsin.

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