Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Donor-stabilized molecular Mg/Al-bimetallic hydrides

Christoph Stuhl, Markus M. Katzenmayer, Cäcilia Maichle-Mössmer and Reiner Anwander*

Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

*To whom correspondence should be addressed. E-mail: reiner.anwander@uni-tuebingen.de

Table of Contents

Table S1. Crystallographic data for compounds **1**, **2**, **3**, **4**, and **5** S3

General procedure for the hydromagnesation of 1-hexene. S4

Table S2. Reaction conditions for hydromagnesation reactions S4

Notes on NMR spectroscopic characterisation S4

Figure S1/S2. NMR spectra of **1** S5

Figure S3/S4. NMR spectra of **2** S6

Figure S5/S6. NMR spectra of **3** S7

Figure S7/S8. NMR spectra of **4** S8

Figure S9. ^{1}H EXSY NMR spectrum of **4** S9

Figure S10-S12. NMR spectra of **5** S9-S10

Figure S13. NMR spectrum of HCp' protonolysis with **1** S11

Figure S14-S16. NMR spectra of reduction of pyridine S11-S12

Figure S17/S18. NMR spectra of hydromagnesation with **1** S13

Figure S19/S20. NMR spectra of hydromagnesation with **3** S14

Figure S21/S22. NMR spectra of hydromagnesation with **4** S15

Table S1. Crystallographic data for compounds **1**, **2**, **3, 4**, and **5**

	1	**2**	**3**	**4**	**5**
formula	$C_{26}H_{60}MgAl_2O_5$	$C_{18}H_{50}MgAl_2O_3$	$C_{14}H_{40}MgAl_2O_4$	$C_{30}H_{84}Al_4Mg_2O_2$	$C_{21}H_{41}AlMgO_2$
M_r [g mol^{-1}]	531.01	392.85	350.73	665.51	376.83
CCDC	1853436	1853437	1853438	1853439	1853440
color	colorless/block	colorless/block	colorless/block	colorless/plate	colorless/plate
crystal dimensions [mm]	0.433 x 0.166 x 0.157	0.718 x 0.506 x 0.456	0.819 x 0.608 x 0.483	0.347 x 0.136 x 0.094	0.287 x 0.282 x 0.218
cryst. syst.	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$Pna2_1$	$P2_1/n$	$P2_1P2_1P2_1$
a [Å]	9.554(3)	22.886(3)	17.8880(4)	10.4747(7)	9.746(5)
b [Å]	12.015(4)	12.4234(17)	8.6400(2)	14.0615(9)	15.225(8)
c [Å]	15.069(5)	18.993(3)	14.9623(3)	15.7685(10)	15.880(9)
α [°]	90.875(6)	90	90	90	90
β [°]	92.171(6)	91.203(5)	90	95.423(4)	90
γ [°]	104.872(6)	90	90	90	90
V [Å^3]	1670.1(10)	5398.9(13)	2312.46(9)	2312.1(3)	2357(2)
Z	2	8	4	2	4
T [K]	100(2)	100(2)	100(2)	100(2)	150(2)
ρ_{calcd} [g cm^{-3}]	1.056	0.967	1.007	0.956	1.062
μ [mm^{-1}]	0.134	0.142	0.162	0.153	0.123
F (000)	588	1760	776	744	832
θ range [°]	1.353/26.498	2.0105/11.34	2.277/28.270	3.416/22.49	2.4495/29.485
unique reflns	6875	11724	5493	5730	5419
observed reflns (I>2σ)	4676	9507	5337	4074	5219
R1/*w*R2 (I>2σ)[a]	0.0859/0.1946	0.0649/0.1533	0.0243/0.0645	0.0449/0.1028	0.0313/0.0837
R1/*w*R2 (all data)[a]	0.1286/0.2143	0.0890/0.1693	0.0253/0.0651	0.10742/0.1173	0.0331/0.0854
GOF[a]	1.064	1.053	1.020	1.027	1.075

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $F_o > 4\sigma(F_o)$. $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

General procedure for the hydromagnesation of 1-hexene. The metal hydrides were weighed into a vial and dissolved or suspended in 0.3 ml toluene-d_8. To increase the solubility of the hydrides **3** and **4** two drops of THF-d_8 were added. 1-Hexene was dissolved in a second vial in 0.3 ml toluene-d_8. The solutions were transferred and combined into a *J. Young* valve NMR sample tube and monitored by ^{1}H NMR spectroscopy. The reactions were heated carefully in steps of 10 °C until a reaction took place at 130 °C. After 16 h the reactions were stopped and in case of **1** heated again for additional 24 h. All reactions produced $[MgH_2]_n$ as a white precipitate.

Table S2. Reaction conditions for hydromagnesation reactions

Substrate	1-hexene	*T* [° C]	time [h]	Yield Mg(*n*-hex)$_2$
1, 20.0 mg, 43.6 µmol	7.34 mg, 87.2 µmol	130	16 h (40 h)	14% (19%)
3, 20.0 mg, 57.1 µmol	9.61 mg, 114 µmol	130	16 h	6%
4, 20.0 mg, 30.1 µmol	10.1 mg, 120 µmol	130	16 h	2%

Notes on NMR spectroscopic characterisation.

Due to the limited solubility of **3** in toluene-d_8 two drops of THF-d_8 were added.

***** residual solvent peak

~ reduced peak intensity

NMR Spectra

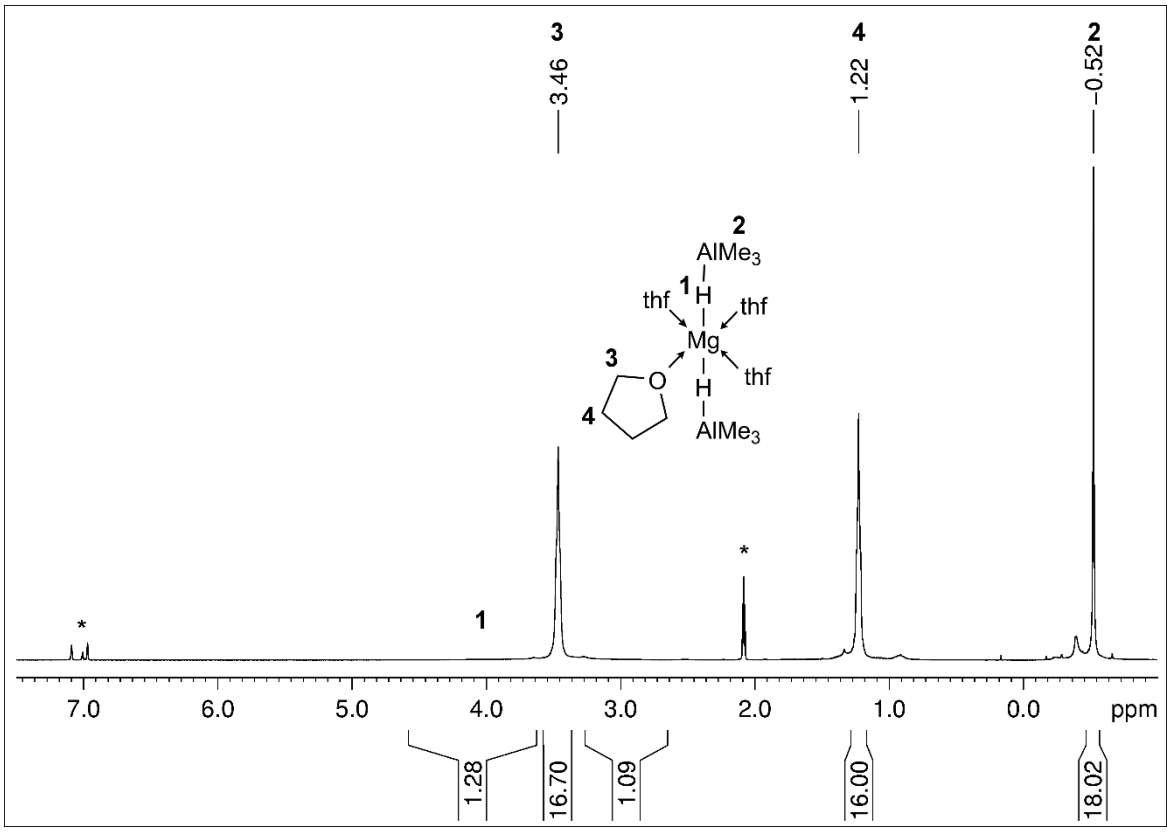

Figure S1. ^{1}H NMR spectrum (400 MHz) of **1** in toluene-d_8 26 at °C.

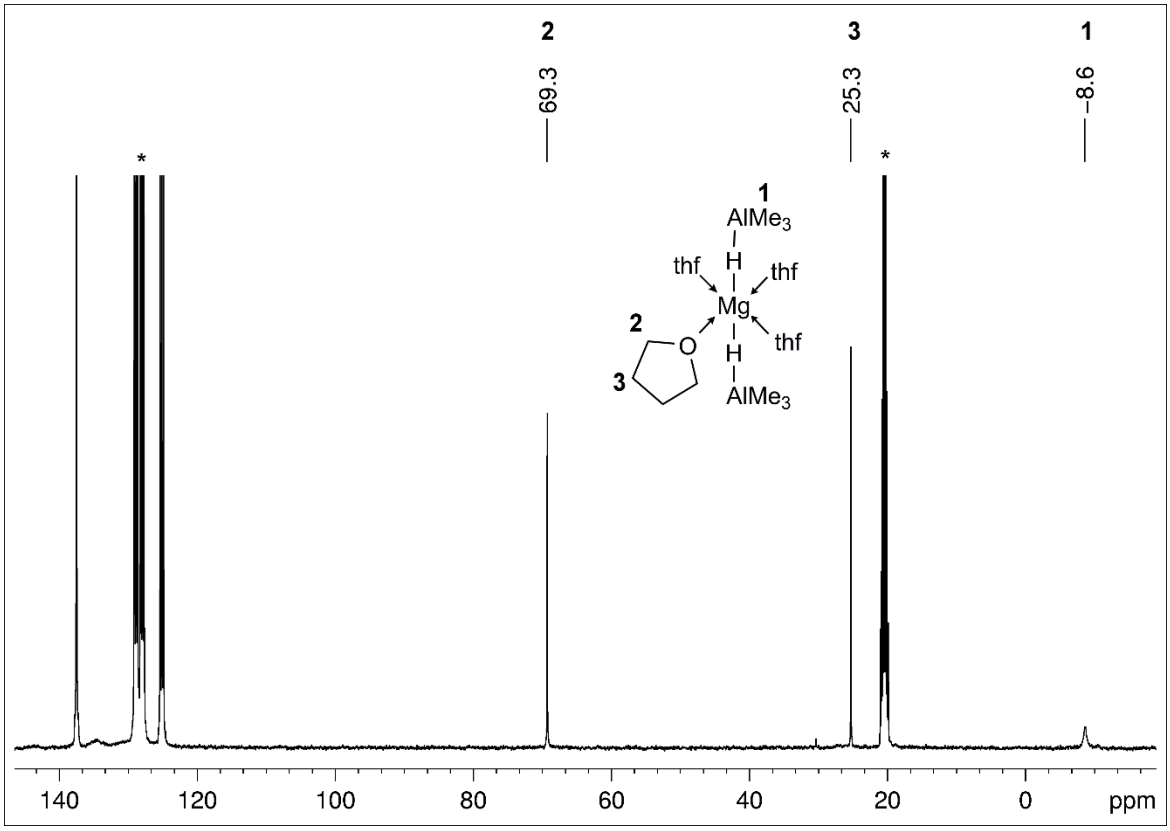

Figure S2. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **1** in toluene-d_8 at 26 °C.

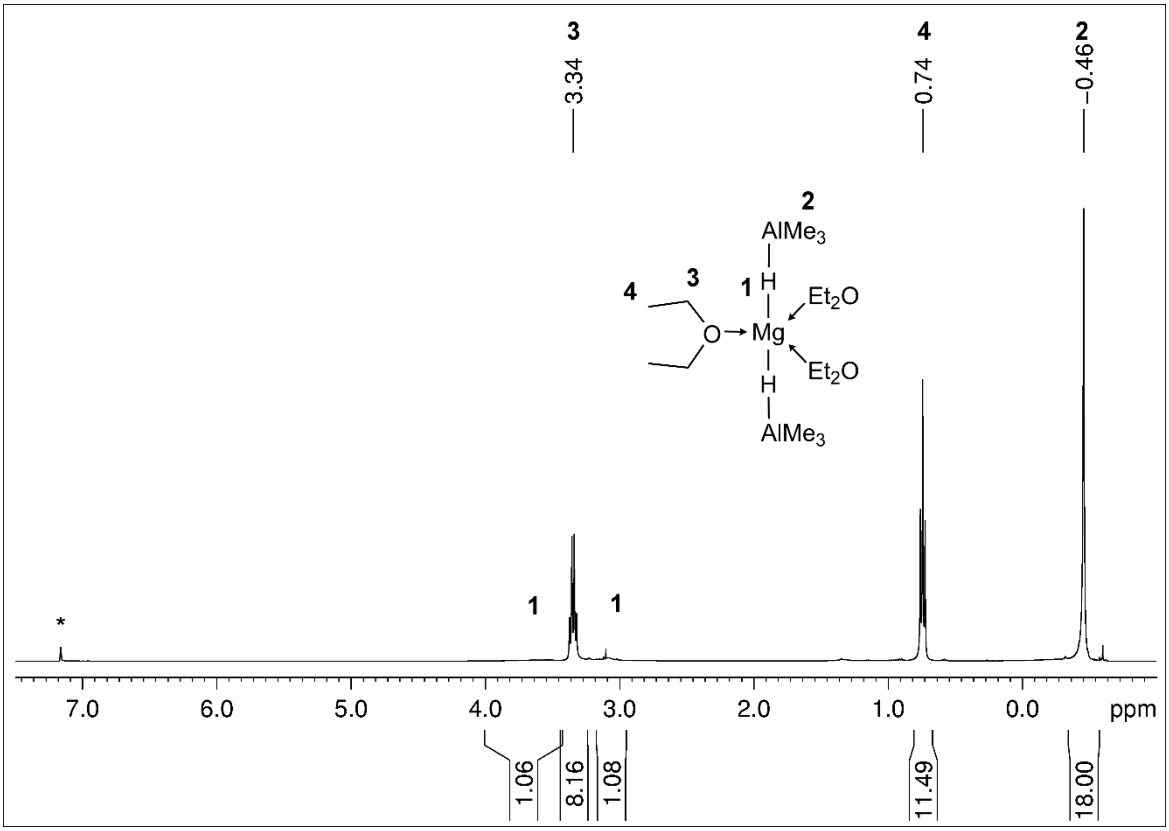

Figure S3. ^{1}H NMR spectrum (400 MHz) of **2** in toluene-d_8 at 26 °C.

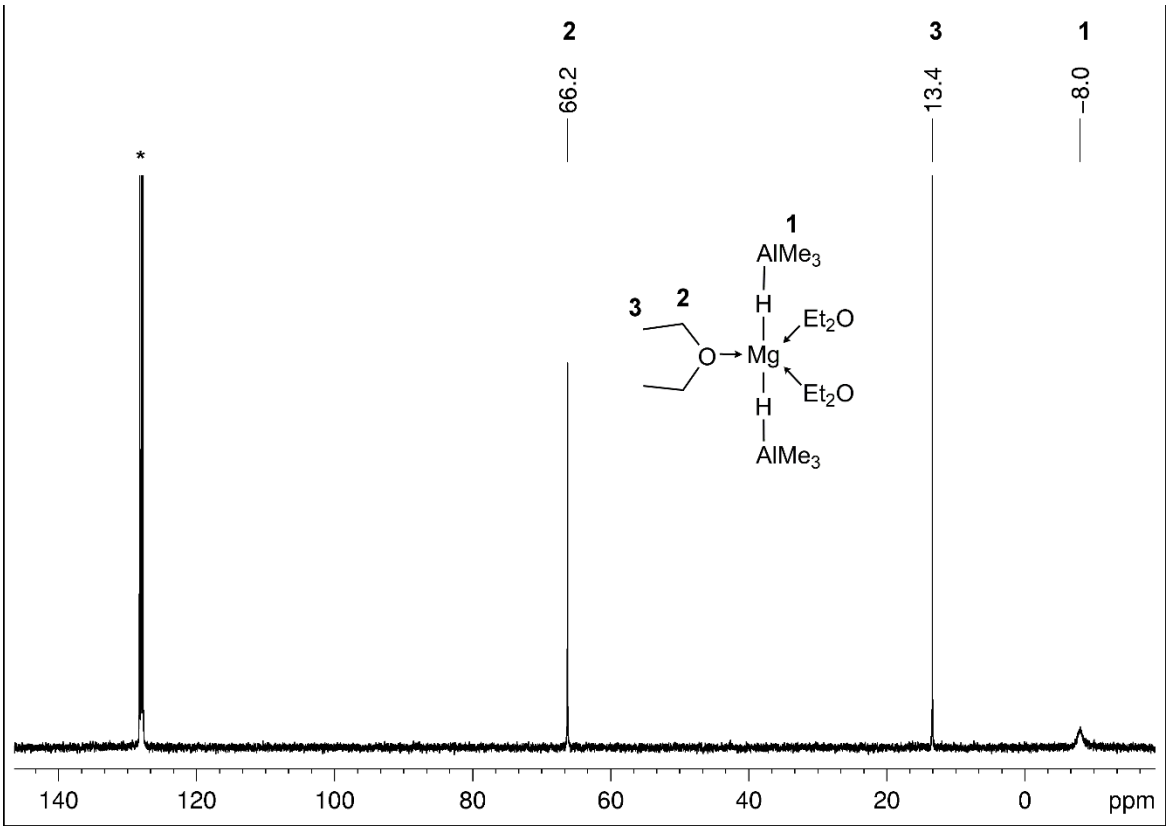

Figure S4. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **2** in toluene-d_8 at 26 °C.

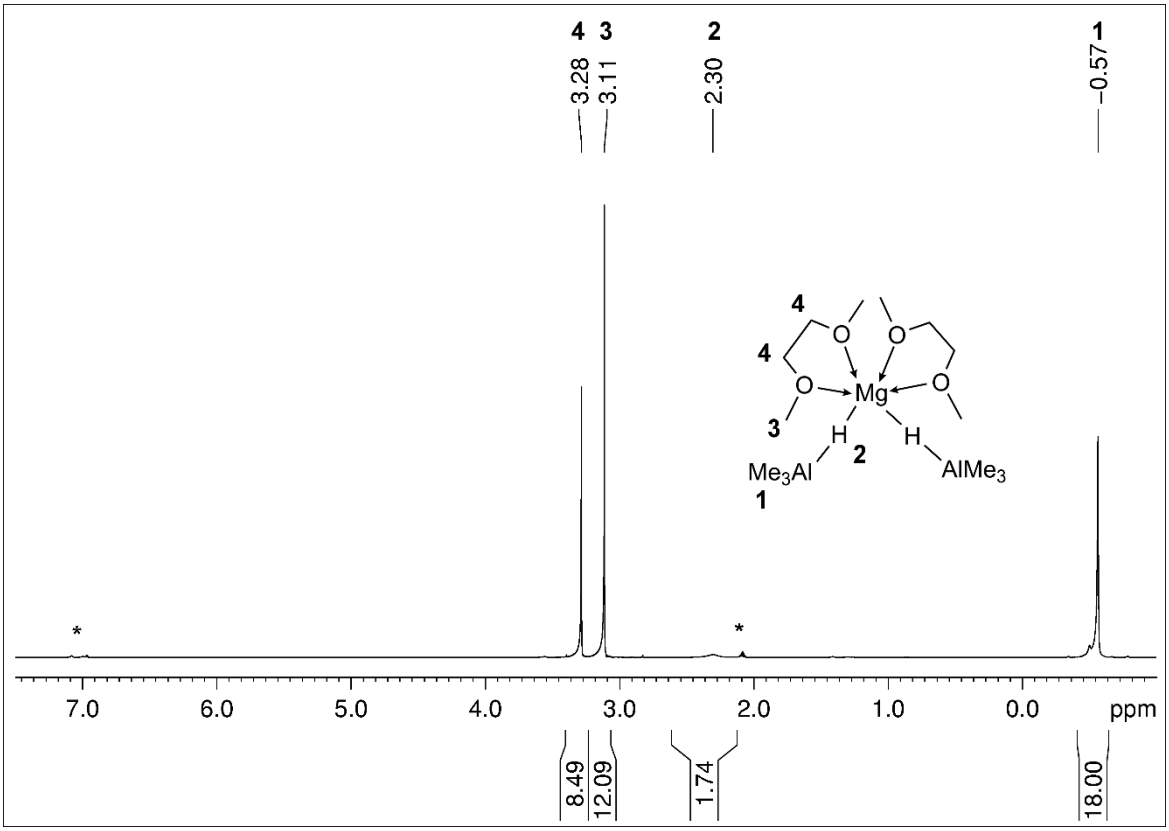

Figure S5. ^{1}H NMR spectrum (400 MHz) of **3** in toluene-d_8 at 26 °C.

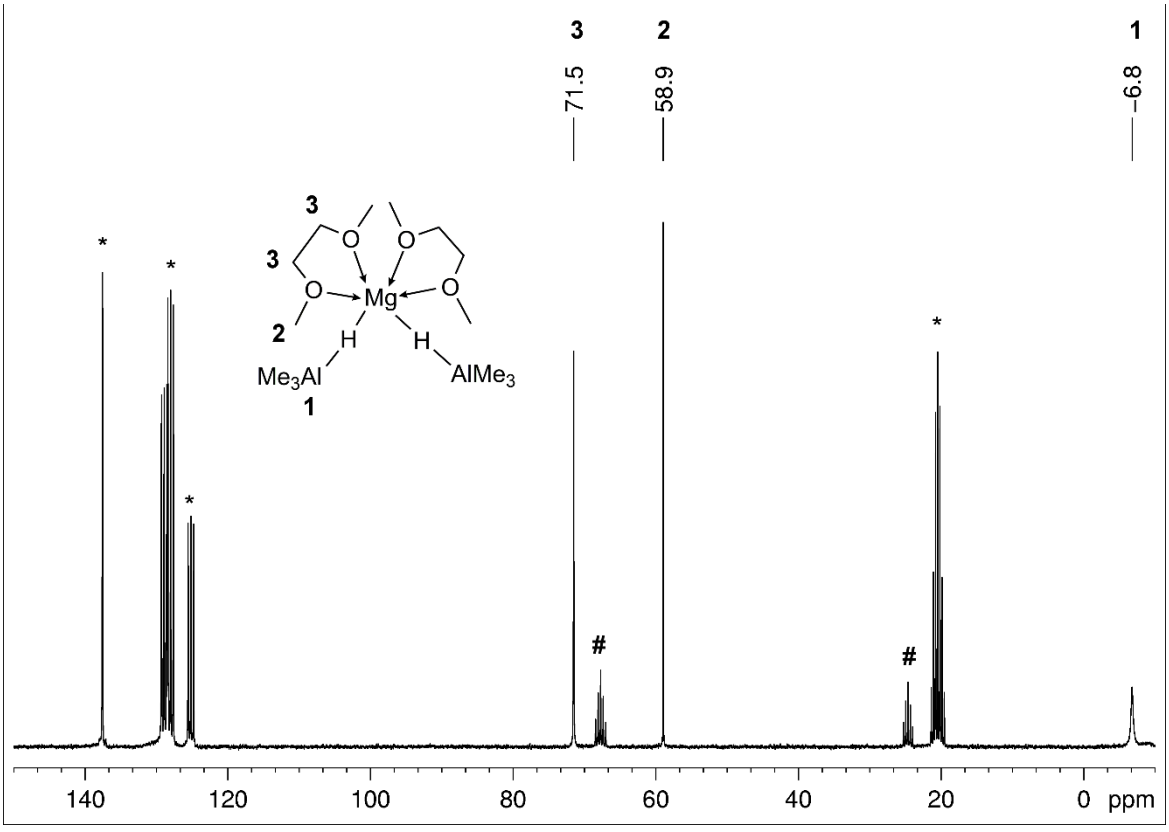

Figure S6. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **3** in toluene-d_8 at 26 °C.

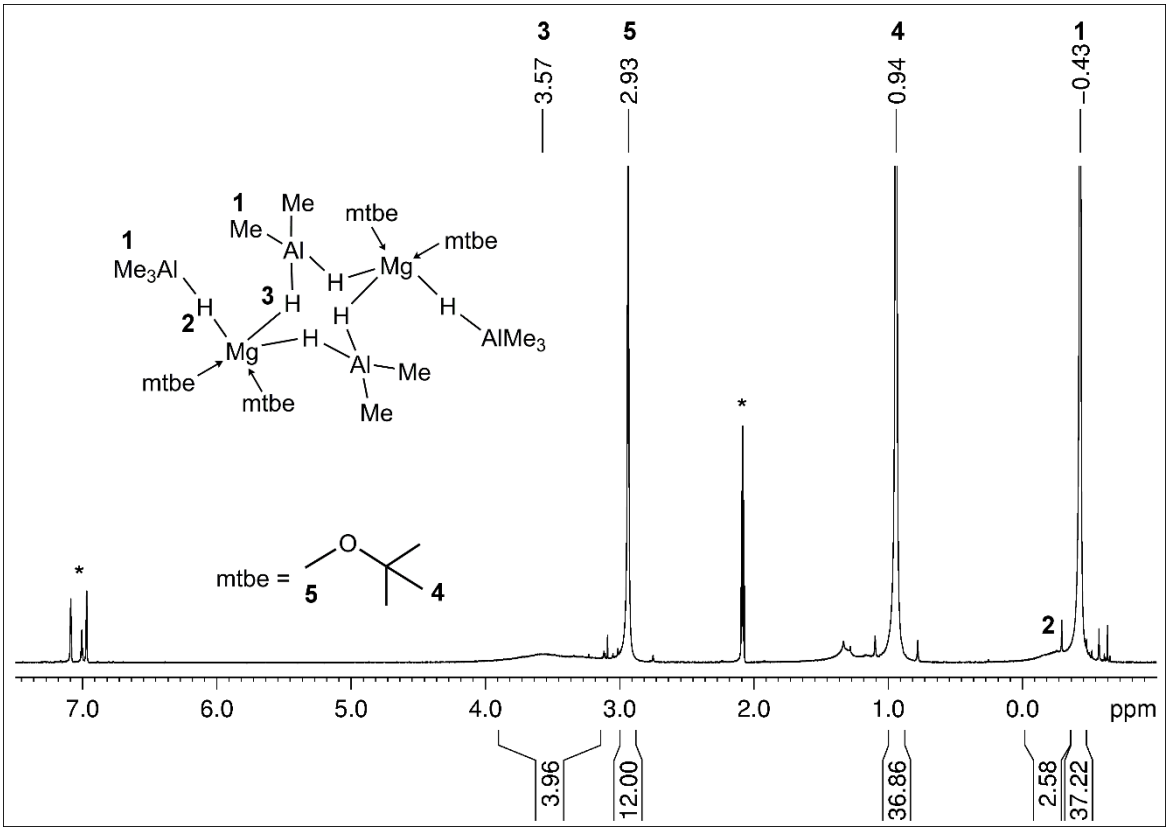

Figure S7. ^{1}H NMR spectrum (400 MHz) of **4** in toluene-d_8 at 26 °C.

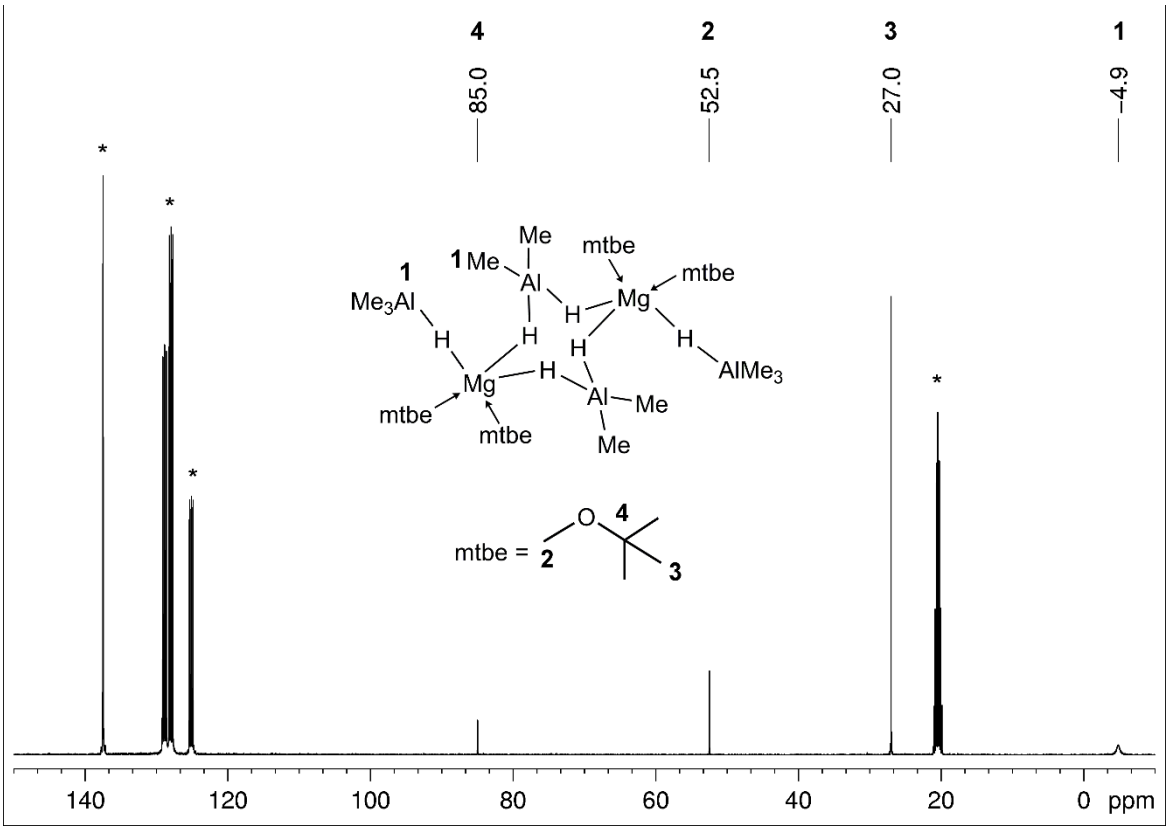

Figure S8. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **4** in toluene-d_8 at 26 °C.

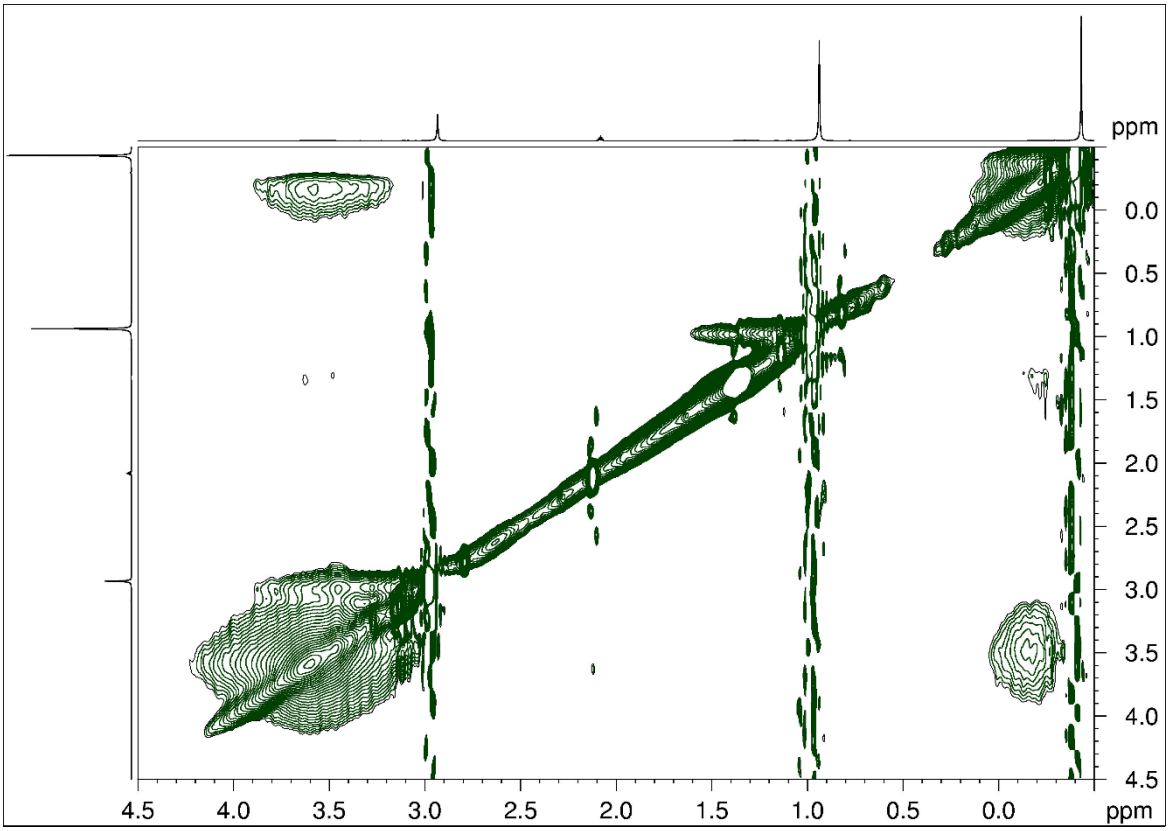

Figure S9. ^{1}H EXSY NMR spectrum (400 MHz) of **4** in toluene-d_8 at 26 °C indicating hydrido exchange.

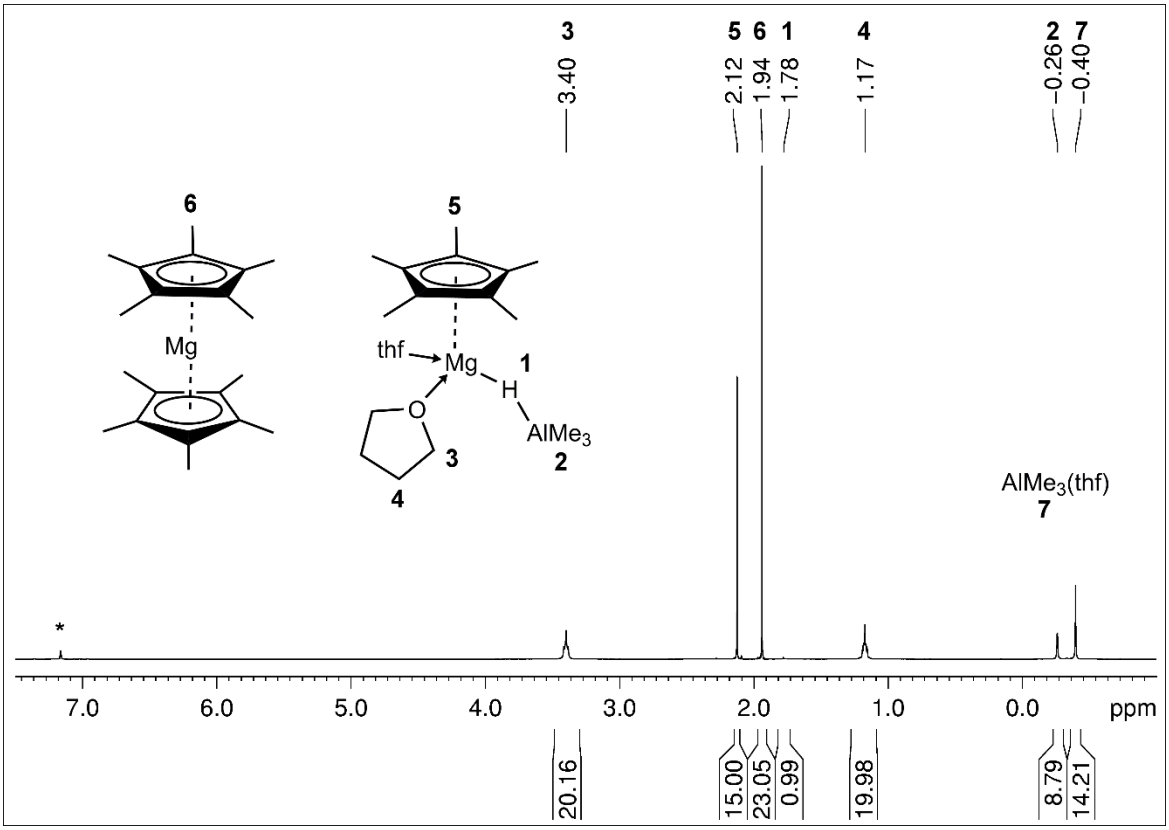

Figure S10. ^{1}H NMR spectrum (400 MHz) of **5** in benzene-d_6 after 1 h at 26 °C.

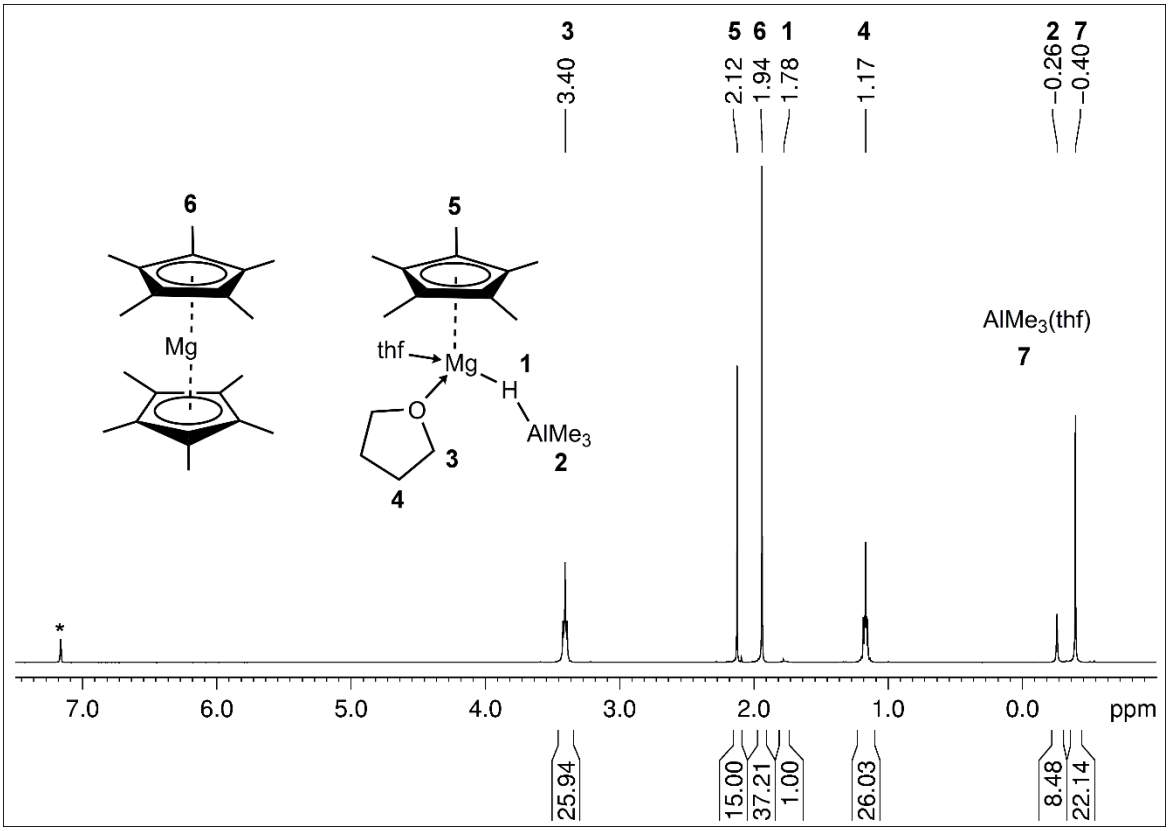

Figure S11. ^{1}H NMR spectrum (400 MHz) of **5** in benzene-d_6 after 16 h at 26 °C.

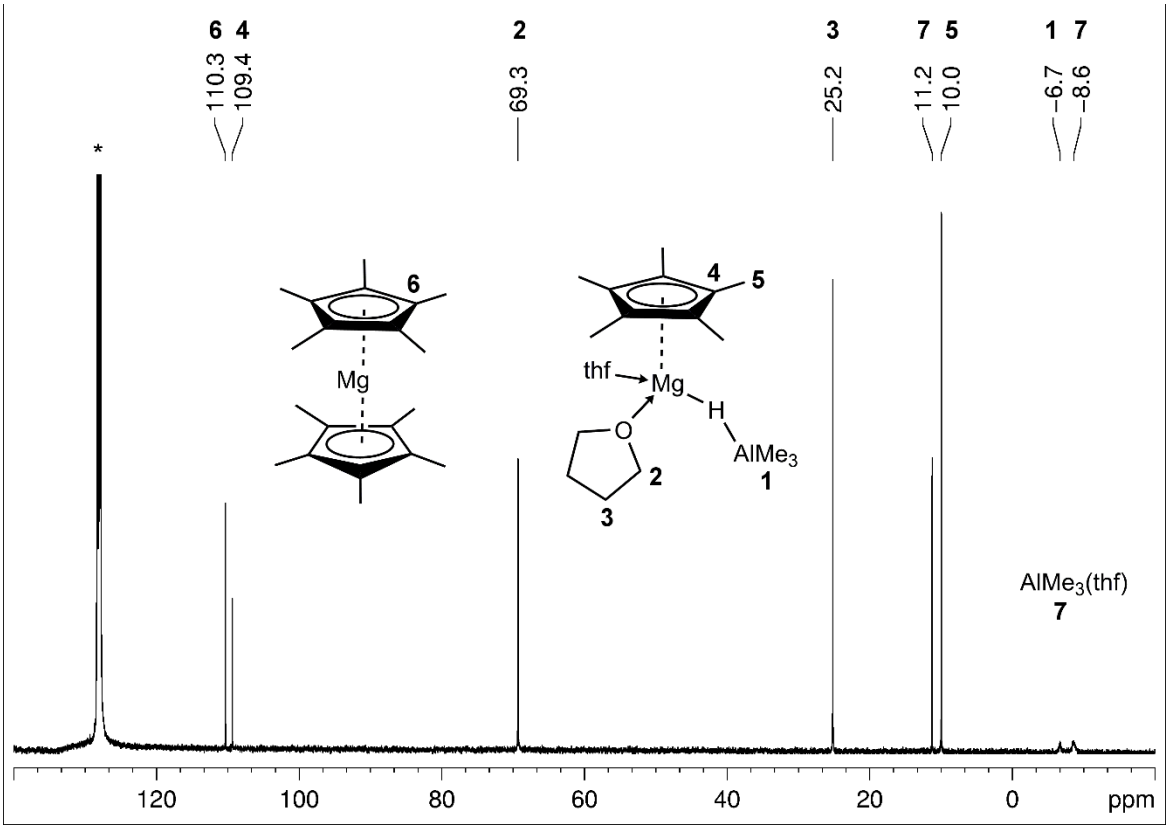

Figure S12. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **5** in benzene-d_6 overnight at 26 °C.

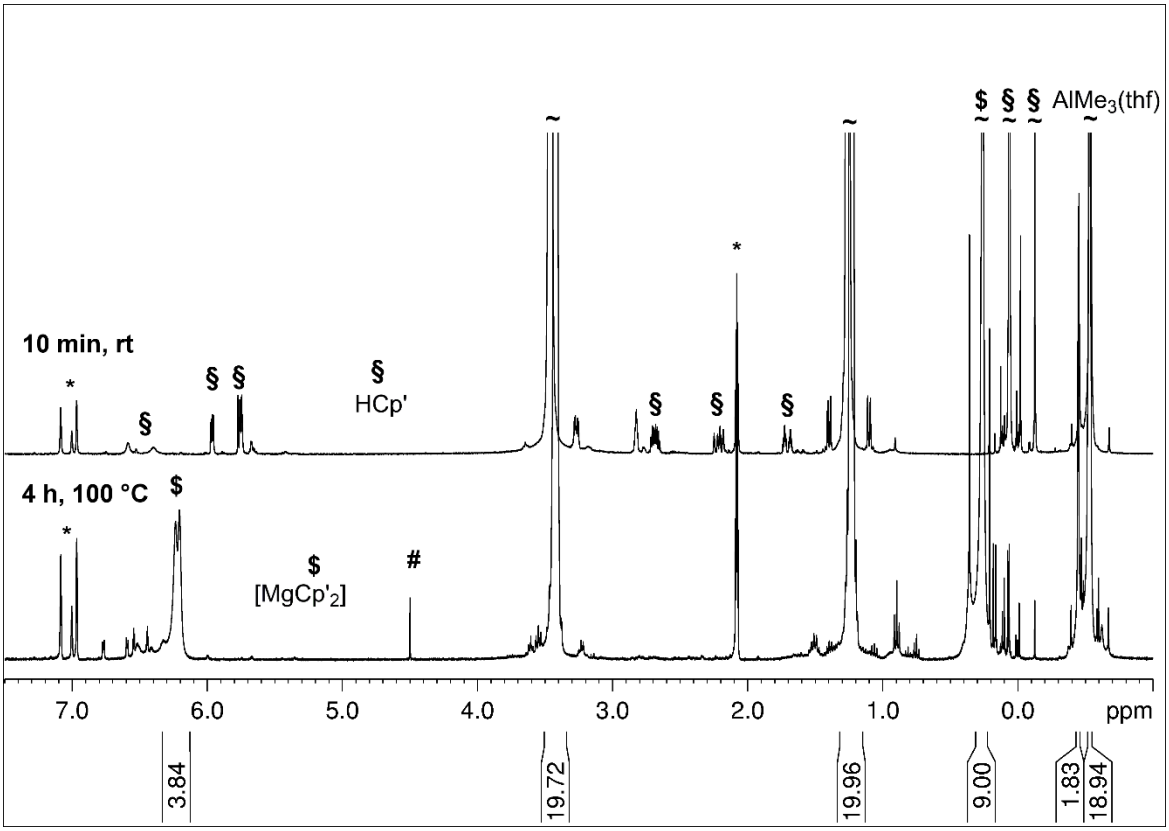

Figure S13. ^{1}H NMR spectra (400 MHz) of the protonolysis of **1** with HCp' in toluene-d_8 illustrating H_2 evolution (#).

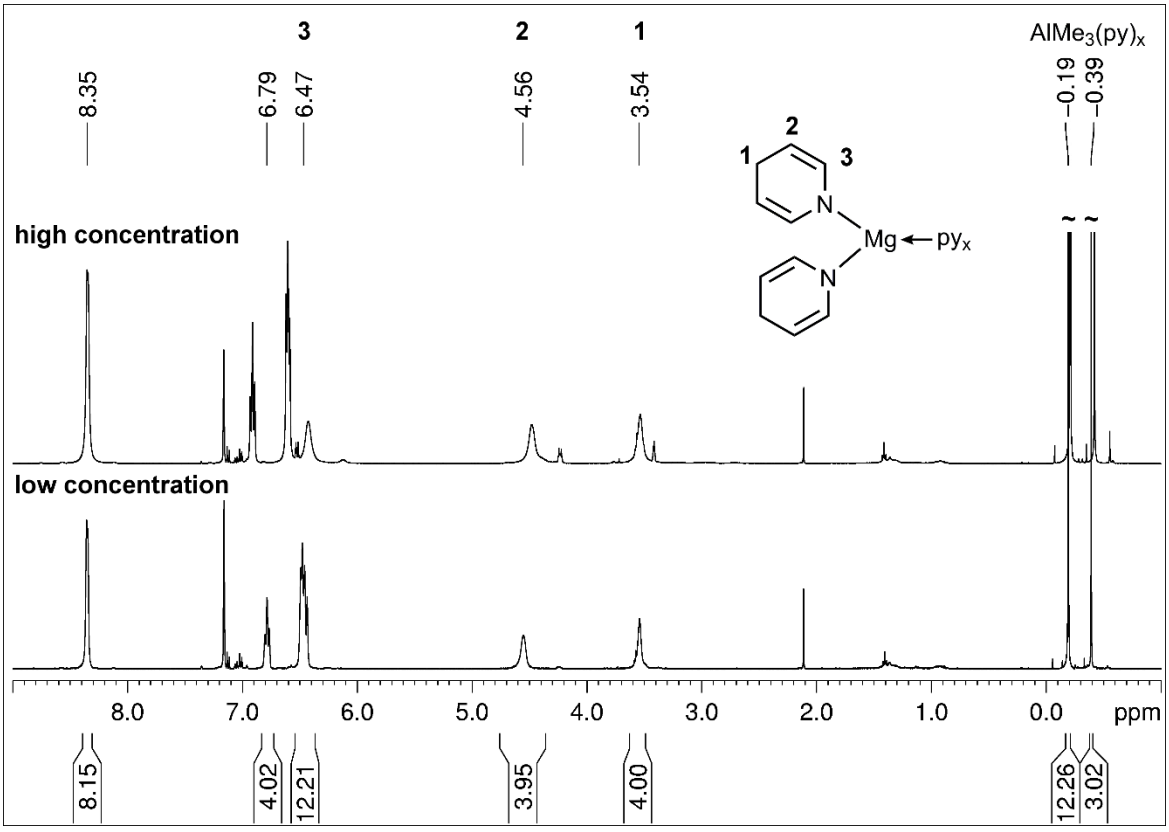

Figure S14. ^{1}H NMR spectrum (400 MHz) of [(py)$_x$Mg(1,4-dihydropyridide)$_2$] in benzene-d_6 at 26 °C.

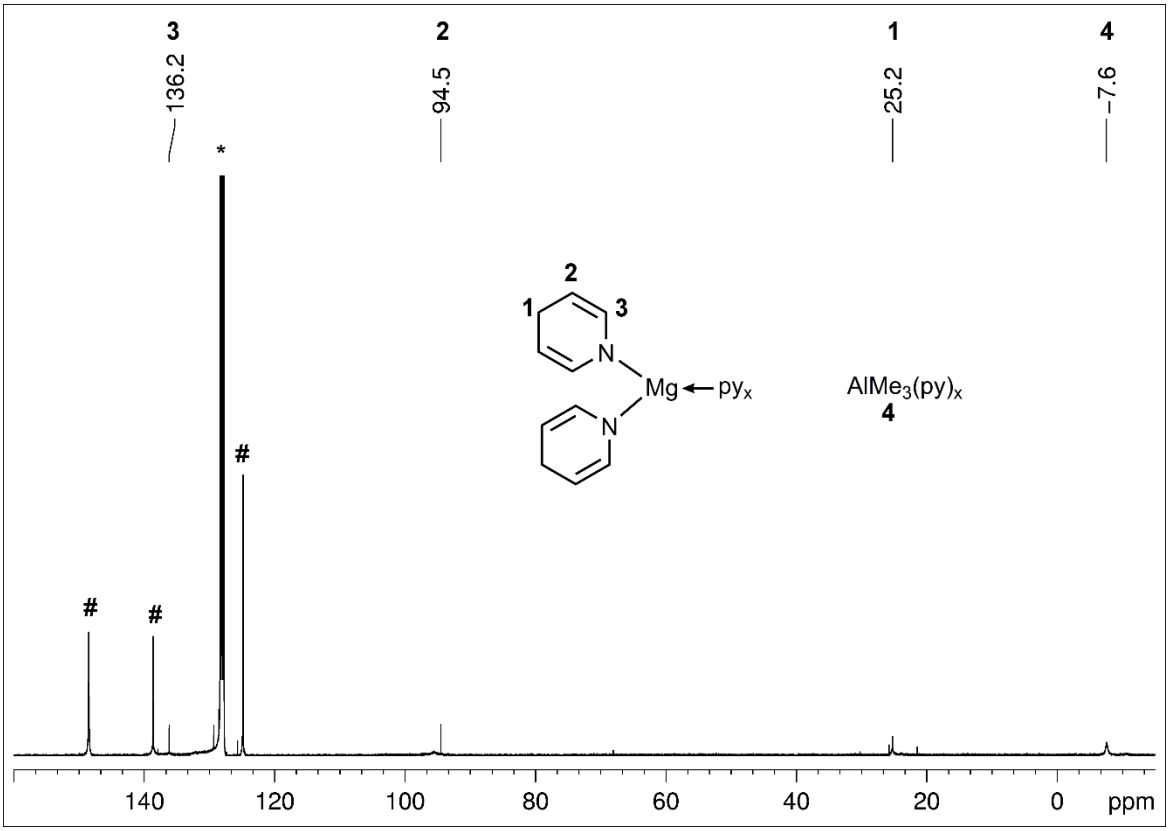

Figure S15. $^{13}C\{^1H\}$ NMR spectrum (101 MHz) of [(py)$_x$Mg(1,4-dihydropyridide)$_2$] in benzene-d_6 at 26 °C. (# pyridine).

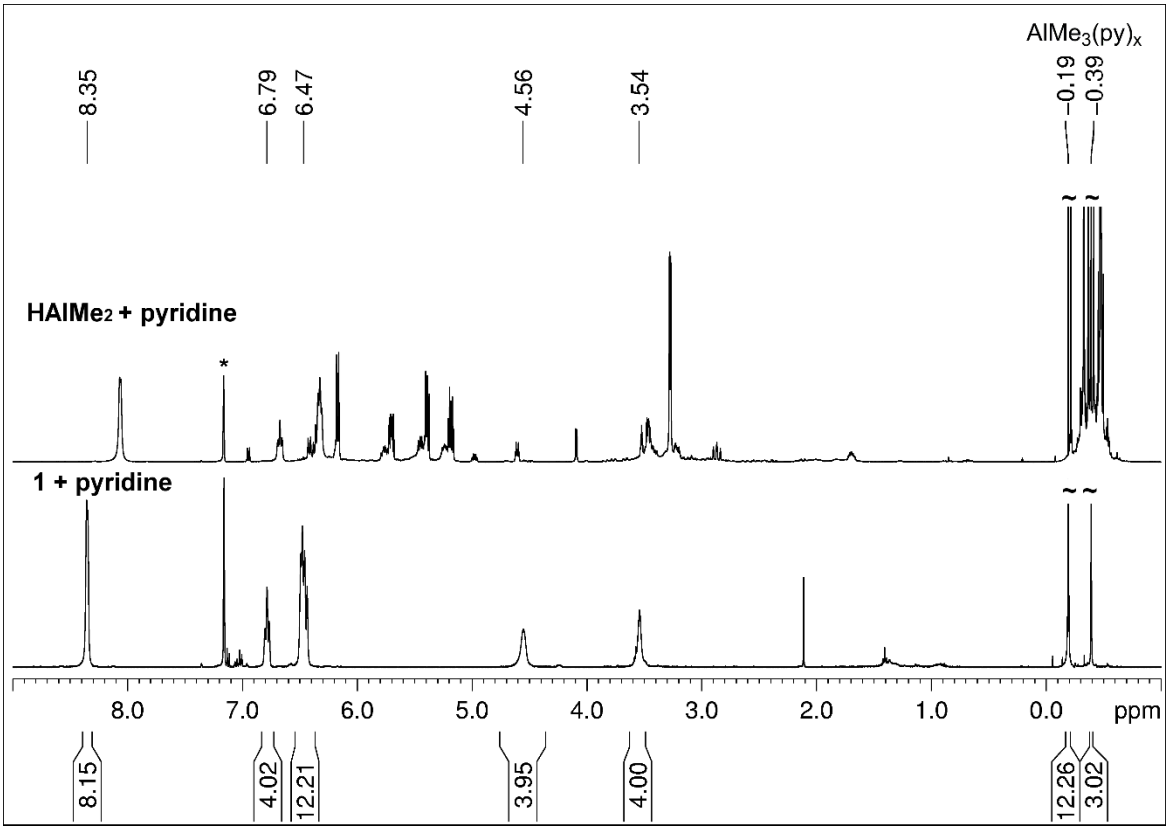

Figure S16. ^1H NMR spectra (400 MHz) of pyridine reduction by **1** and HAlMe$_2$ in benzene-d_6 at 26 °C.

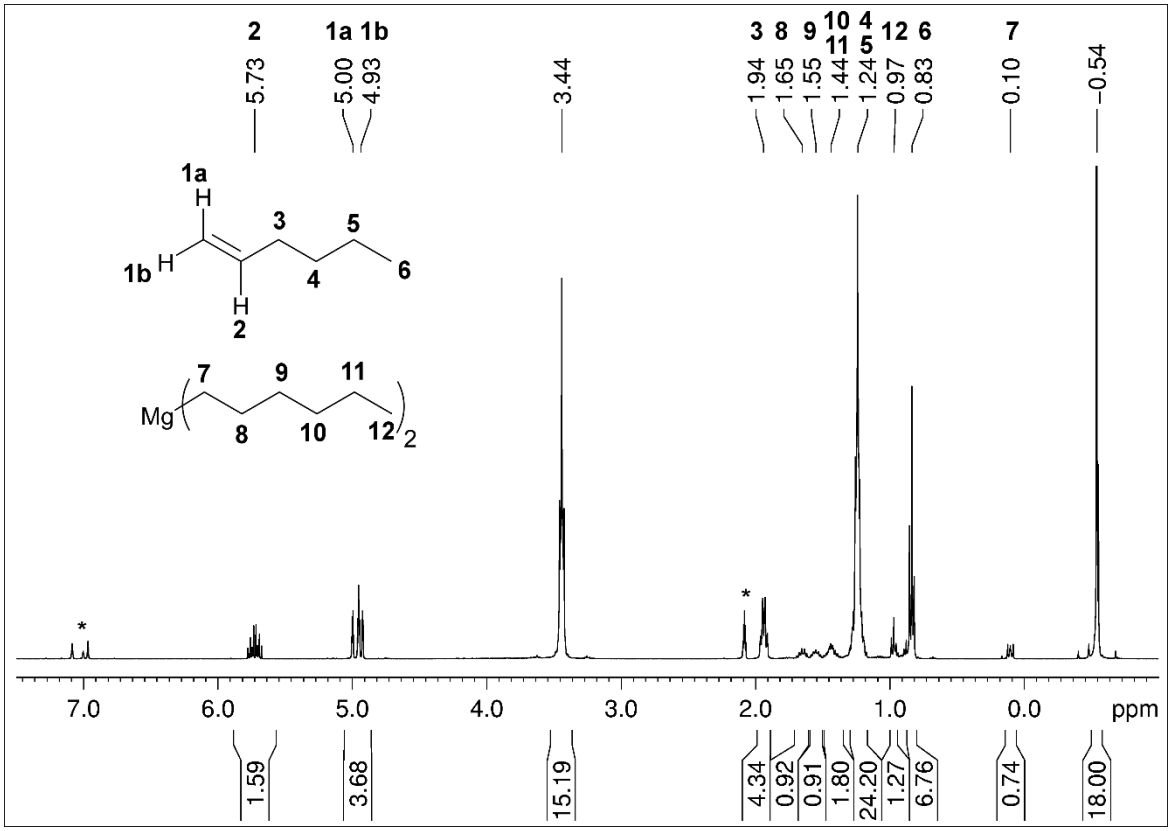

Figure S17. [1]H NMR spectrum (400 MHz) of the hydromagnesation of 1-hexene with **1** in toluene-d_8 at 26°C (40 h, 130 °C).

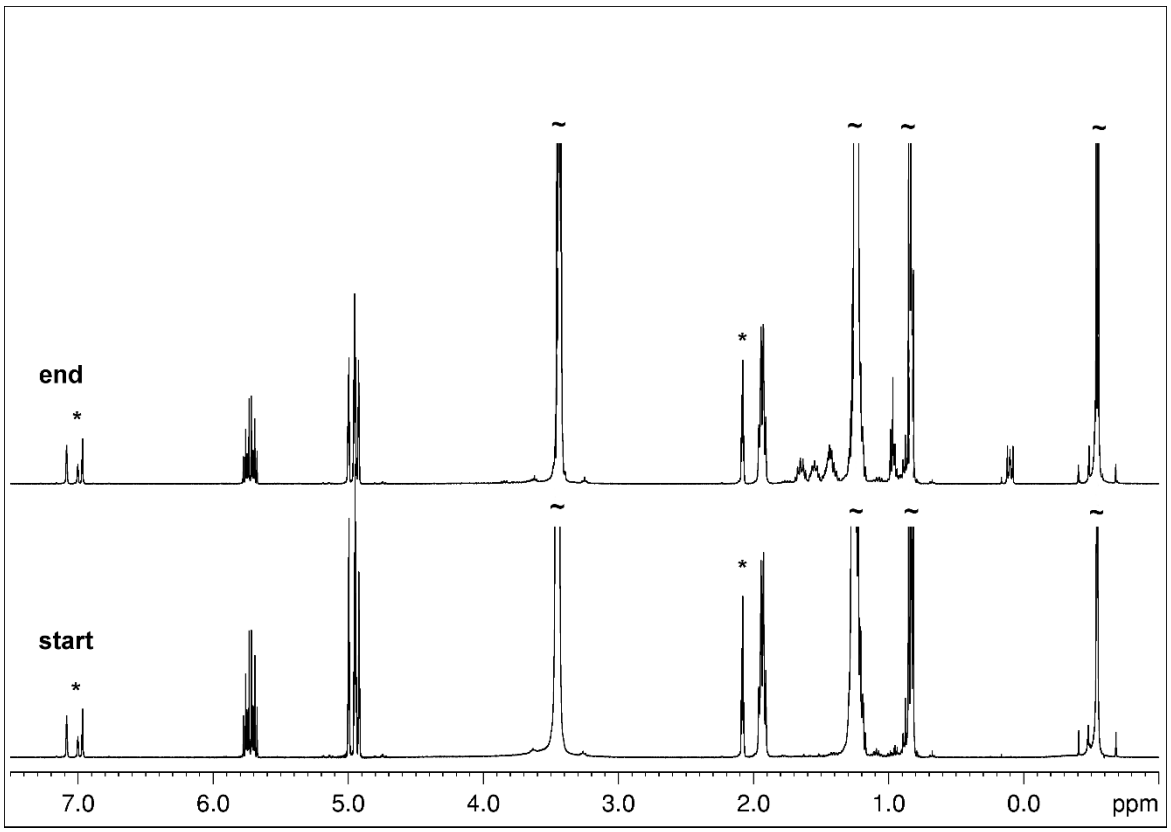

Figure S18. [1]H NMR spectra (400 MHz) of the hydromagnesation of 1-hexene with **1** in toluene-d_8 at 26 °C.

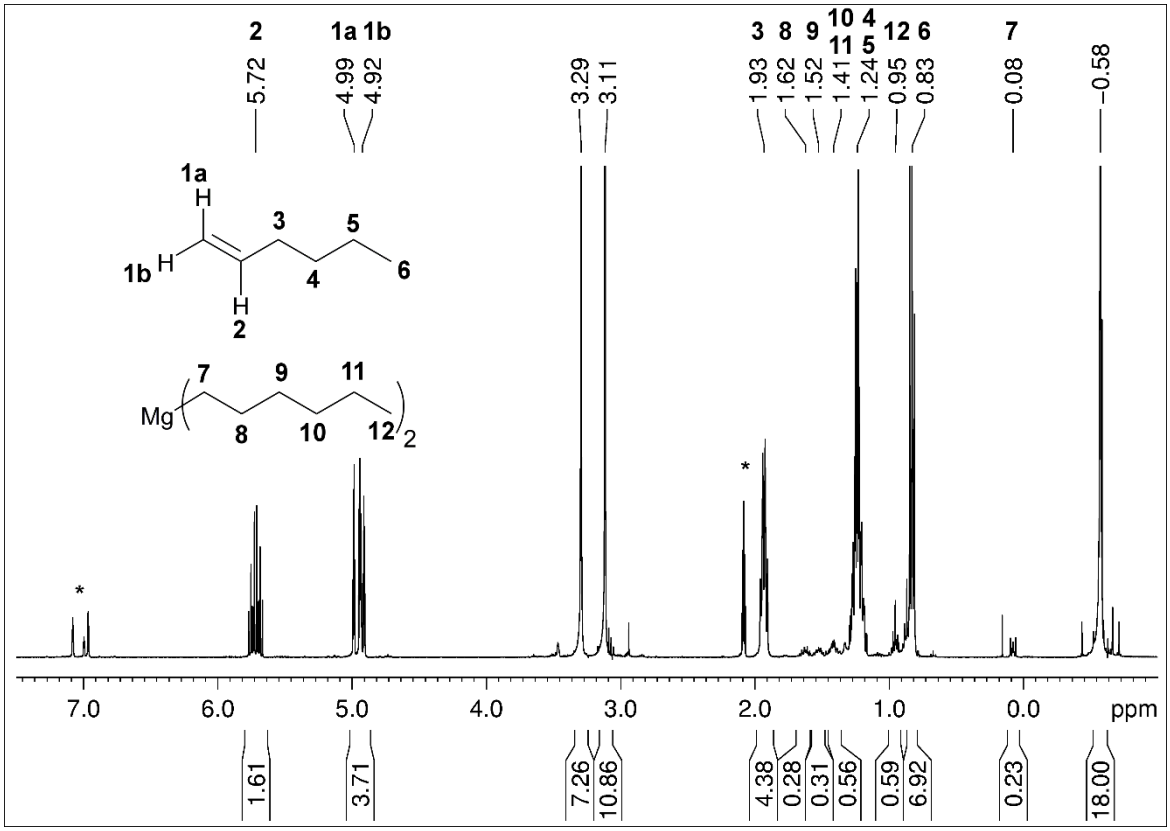

Figure S19. *In situ* ^{1}H NMR spectrum (400 MHz) of the hydromagnesation of 1-hexene with **3** in toluene-d_8 at 26 °C after 16 h at 130 °C.

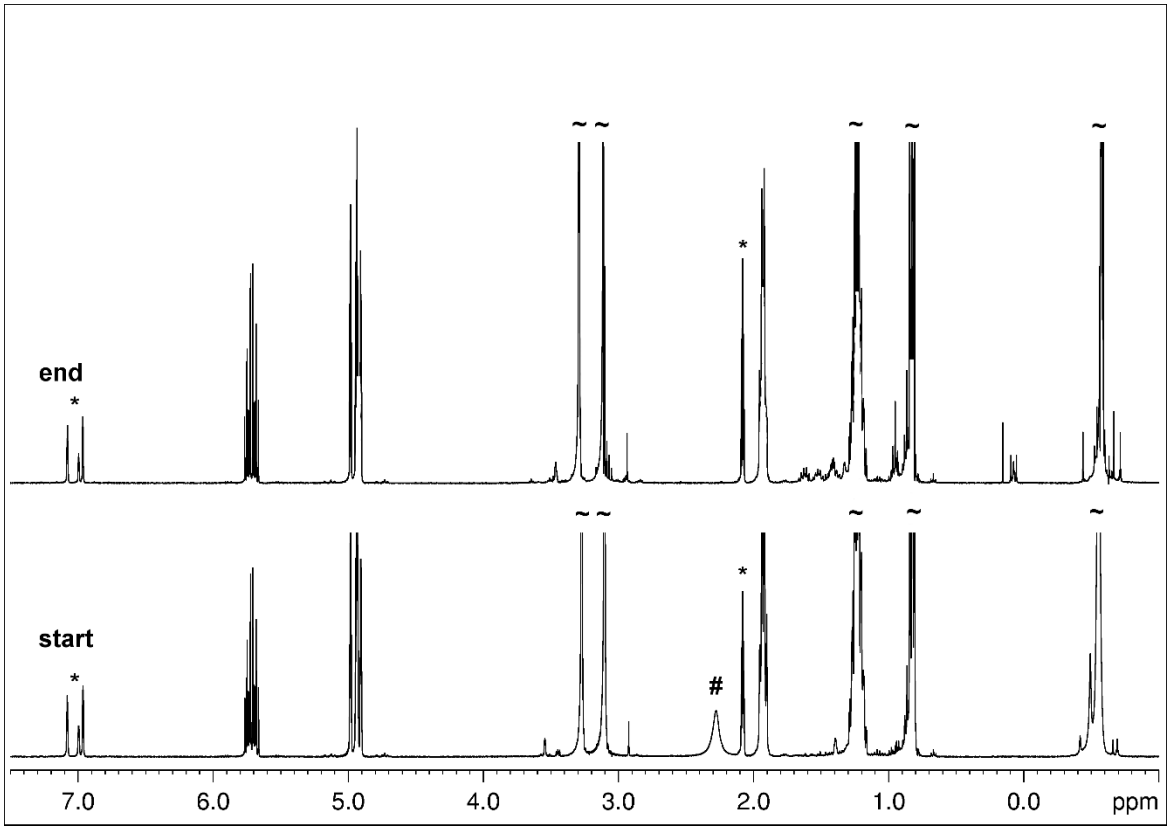

Figure S20. ^{1}H NMR spectra (400 MHz) of the hydromagnesation of 1-hexene with **3** in toluene-d_8 at 26 °C illustrating the decrease of Mg-H-Al species (#) and the product peaks.

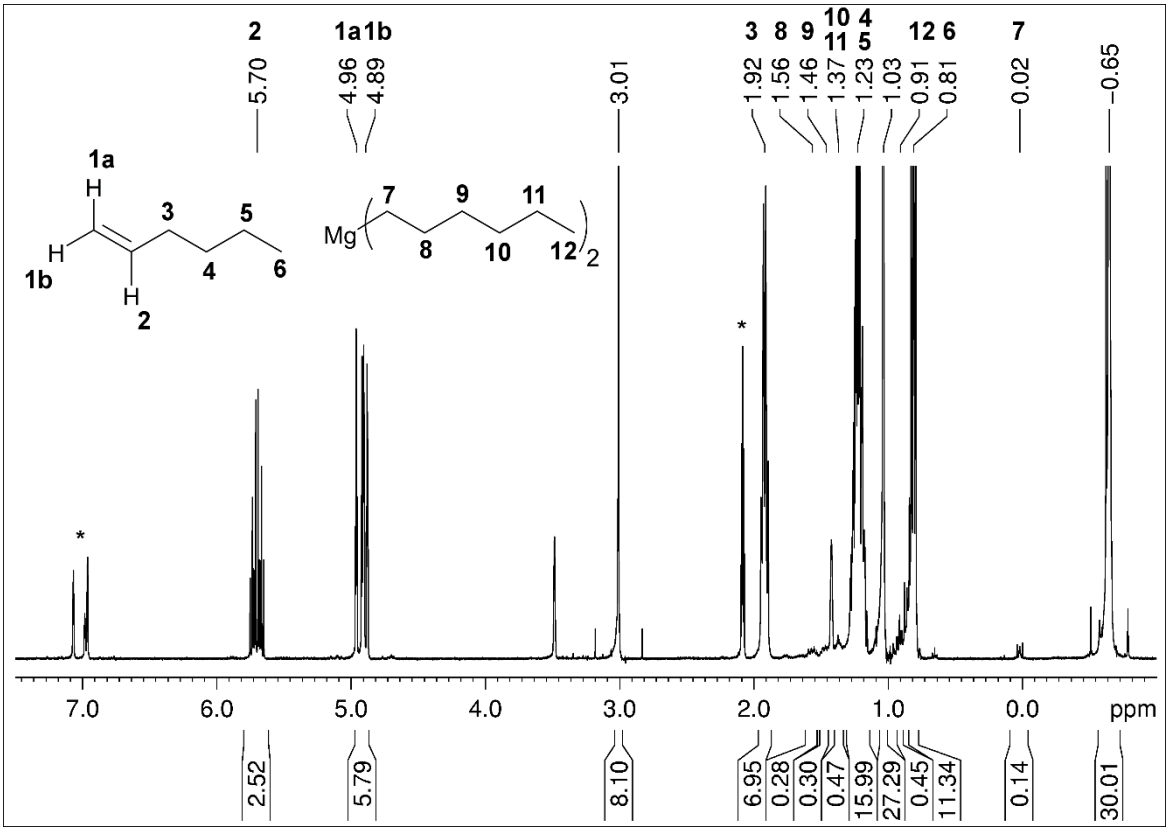

Figure S21. *In situ* ^{1}H NMR spectrum (400 MHz) of the hydromagnesation of 1-hexene with **4** in toluene-d_8 at 26 °C after 16 h at 130 °C.

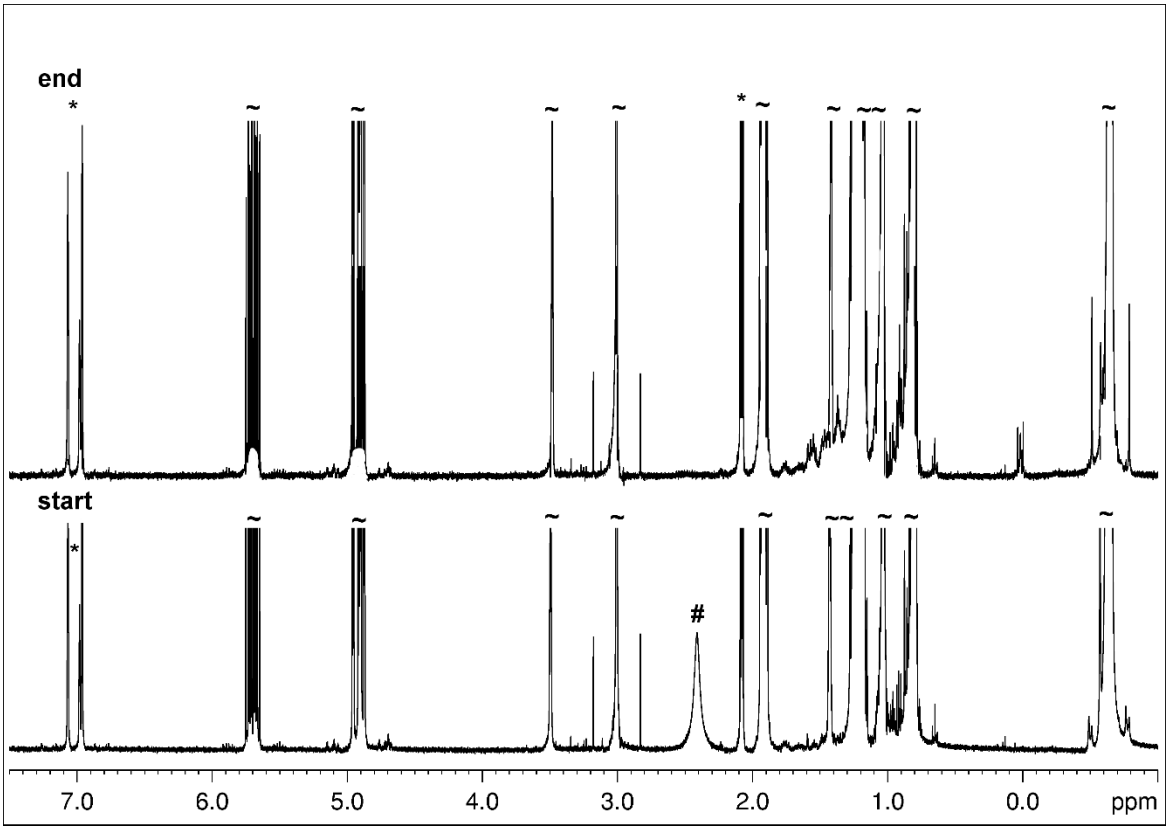

Figure S22. ^{1}H NMR spectra (400 MHz) of the hydromagnesation of 1-hexene with **4** in toluene-d_8 at 26 °C illustrating the decrease of Mg-H-Al species (#) and the product peaks.