Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Alkali Metal and Stoichiometric Effects in Intermolecular Hydroamination Catalysed by Lithium, Sodium and Potassium Magnesiates

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Table S1 Crystallographic data and refinement details for complexes **15** and **16**.

	15	**16**
Empirical formula	$C_{54}H_{108}Mg_2N_6Na_2O_6$	$C_{32}H_{72}Mg_1N_8Na_2$
Mol. Mass	1032.06	639.26
Crystal system	triclinic	Monoclinic
a/ Å	11.6474(5)	10.4760(14)
b/ Å	11.7398(7)	19.224(2)
c/ Å	23.4025(8)	19.864(2)
α/ °	100.805(4)	90
β/ °	94.008(3)	93.733(10)
γ/ °	106.319(4)	90
V/ Å^3	2991.0(2)	3991.9(8)
Z	2	4
λ/ Å	1.5418	0.71073
Measured reflections	43397	19600
Unique reflections	11830	7810
R_{int}	0.0316	0.0781
Observed rflns [I>2σ(I)]	9231	4183
GooF	1.020	1.011
R [on *F*, obs rflns only]	0.0578	0.0711
ωR [on F^2, all data]	0.1752	0.2205
Largest diff. Peak/hole. e/ Å^{-3}	0.486 / -0.363	0.613 / -0.381

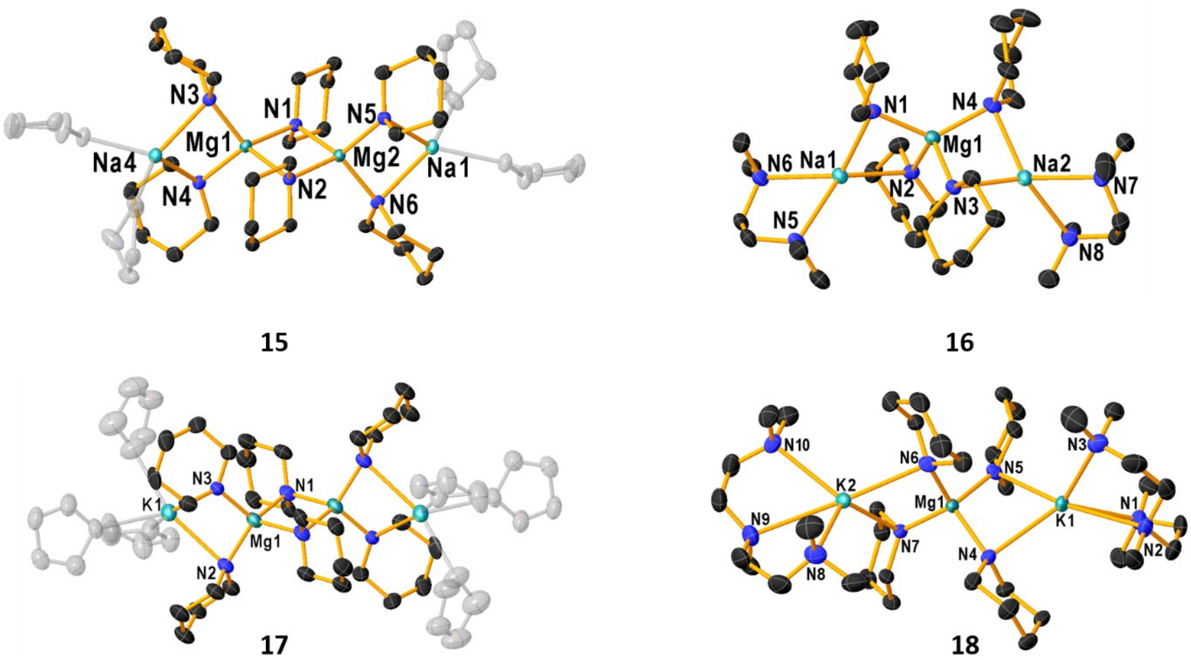

Figure S1 X-ray diffraction structures of **15**-**18**. **17** and **18** provide general connectivity information only, due to poor data quality.

Catalysis - NMR Spectra

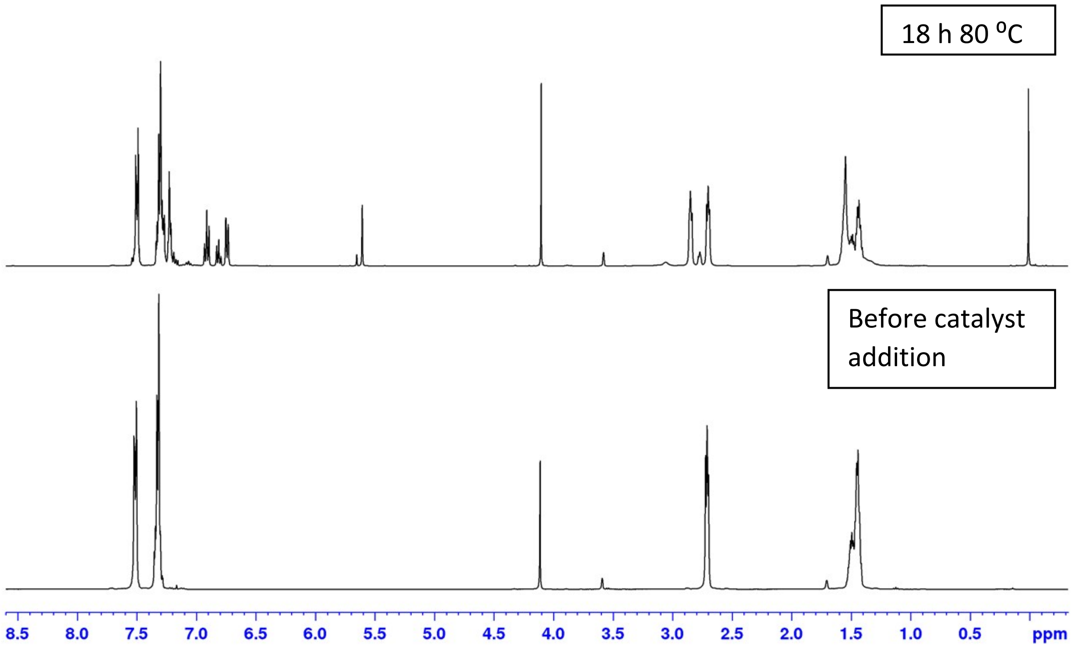

Figure S2 Hydroamination of diphenylacetylene with piperidine, catalysed by $LiMg(CH_2SiMe_3)_3$ (**1**) (5 mol%) in d_8-THF.

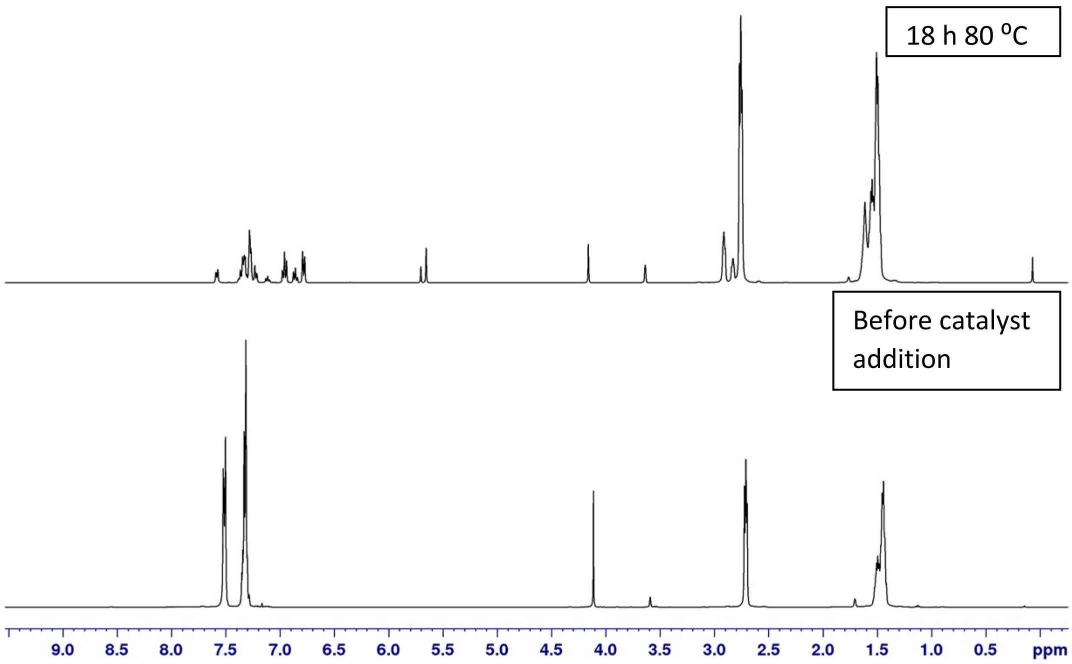

Figure S3 Hydroamination of diphenylacetylene with piperidine, catalysed by $NaMg(CH_2SiMe_3)_3$ (**2**) (5 mol%) in d_8-THF.

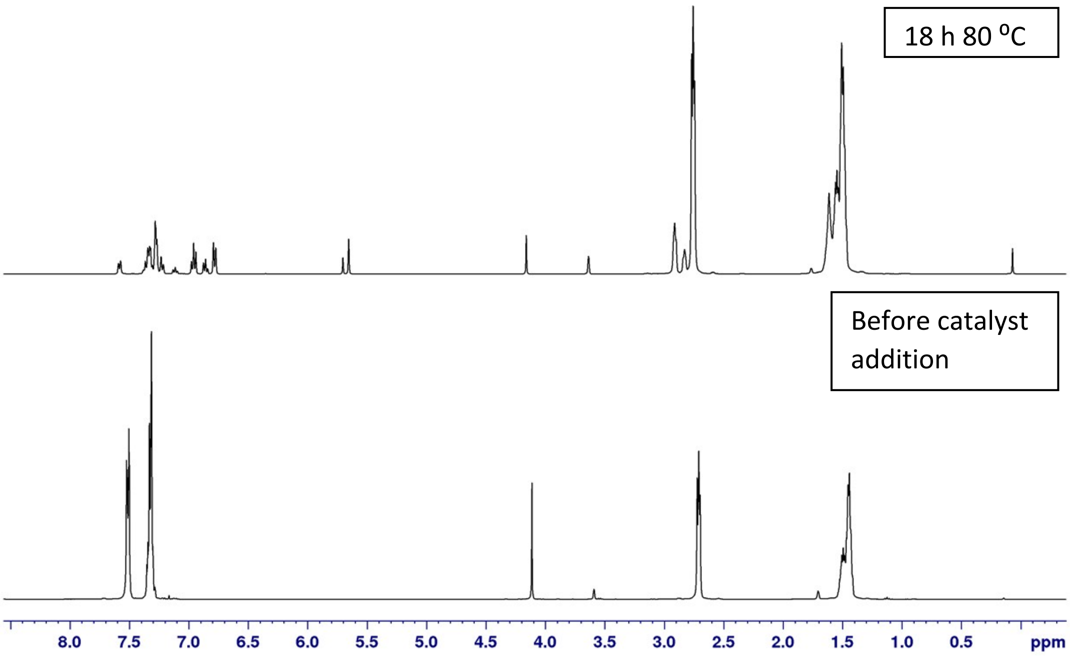

Figure S4 Hydroamination of diphenylacetylene with piperidine, catalysed by $KMg(CH_2SiMe_3)_3$ (**3**) (5 mol%) in d_8-THF.

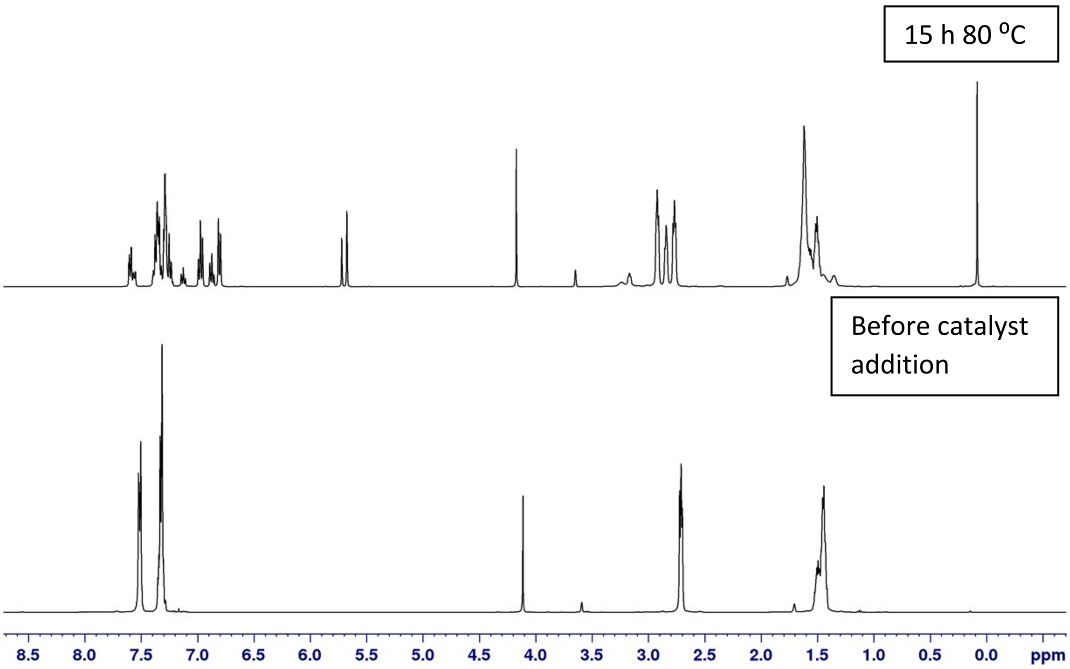

Figure S5 Hydroamination of diphenylacetylene with piperidine, catalysed by $NaMg(CH_2SiMe_3)_3$ (**2**) (10 mol%) in d_8-THF.

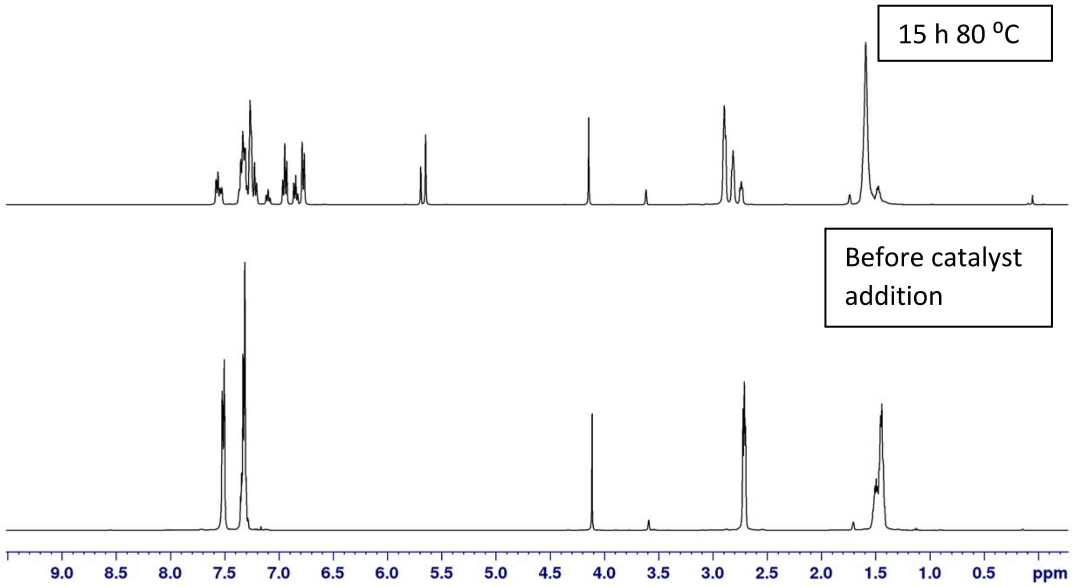

Figure S6 Hydroamination of diphenylacetylene with piperidine, catalysed by $NaMg(CH_2SiMe_3)_3$ (**2**) (2 mol%) in d_8-THF.

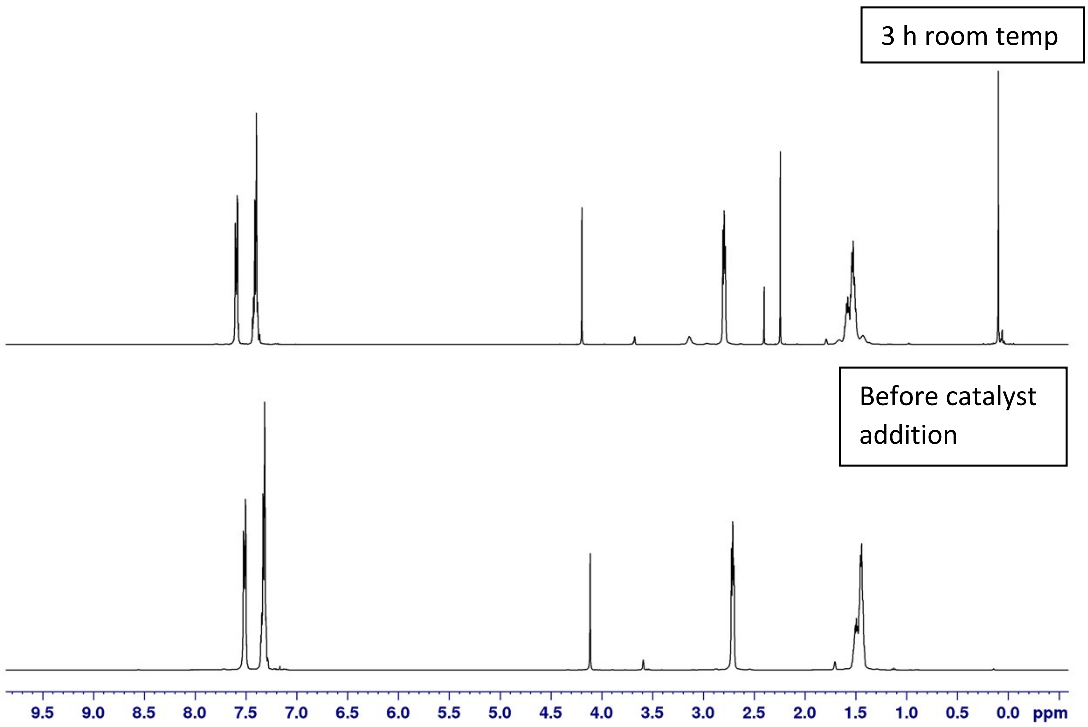

Figure S7 Hydroamination of diphenylacetylene with piperidine, catalysed by $[(TMEDA)_2Li_2Mg(CH_2SiMe_3)_4]$ (**5**) (5 mol%) in d_8-THF.

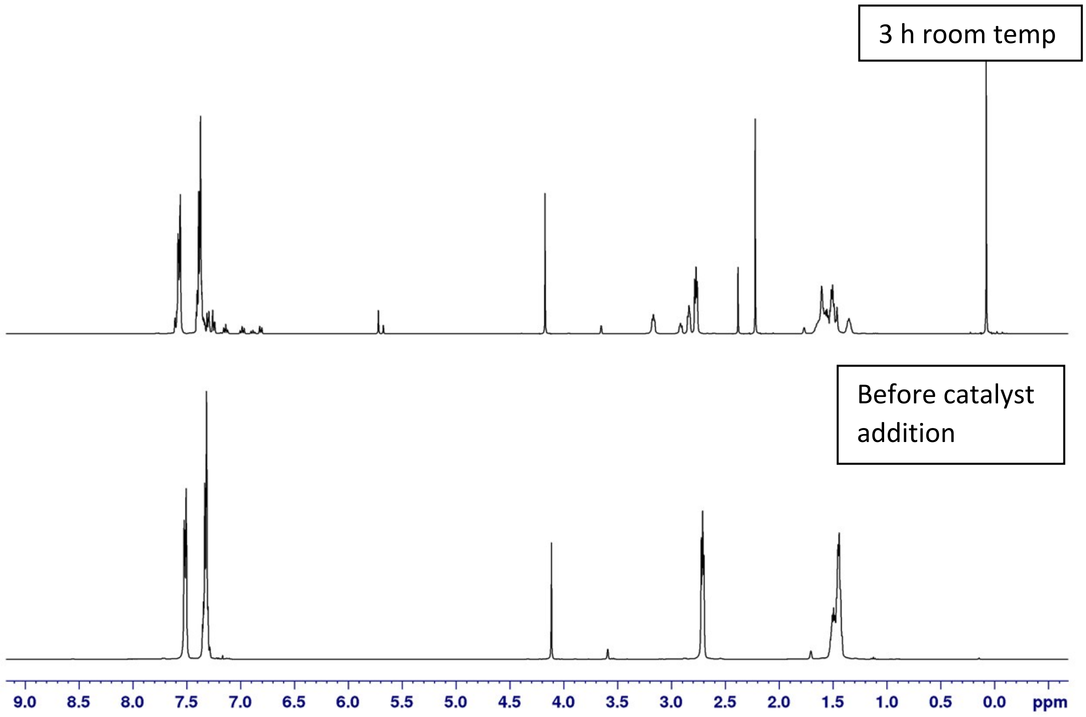

Figure S8 Hydroamination of diphenylacetylene with piperidine, catalysed by $[(TMEDA)_2Na_2Mg(CH_2SiMe_3)_4]$ (**6**) (5 mol%) in d_8-THF.

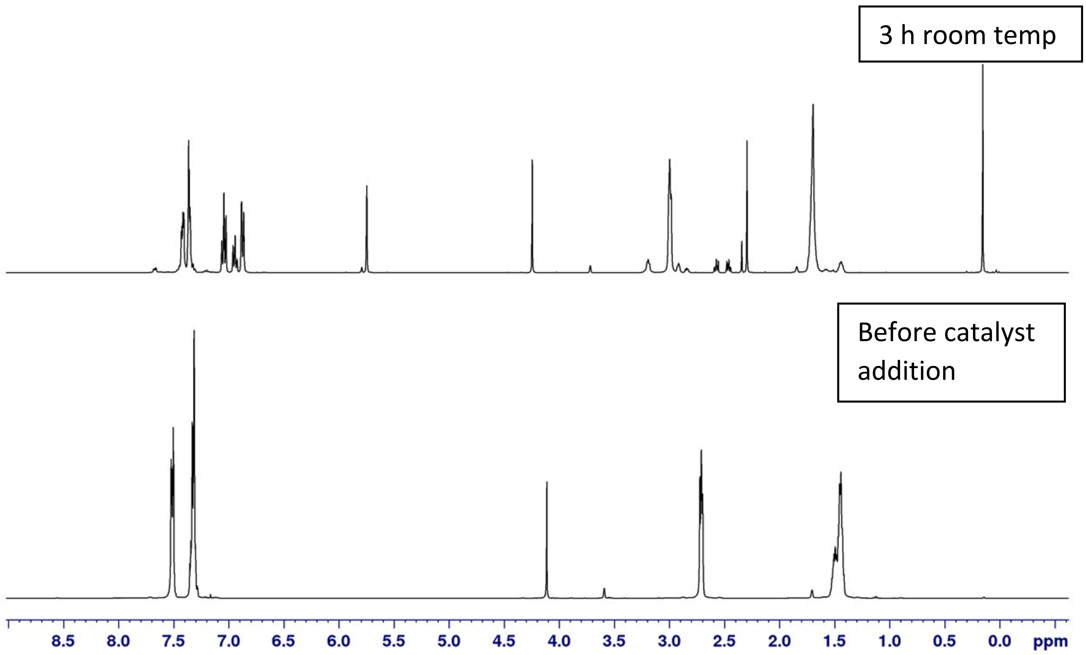

Figure S9 Hydroamination of diphenylacetylene with piperidine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

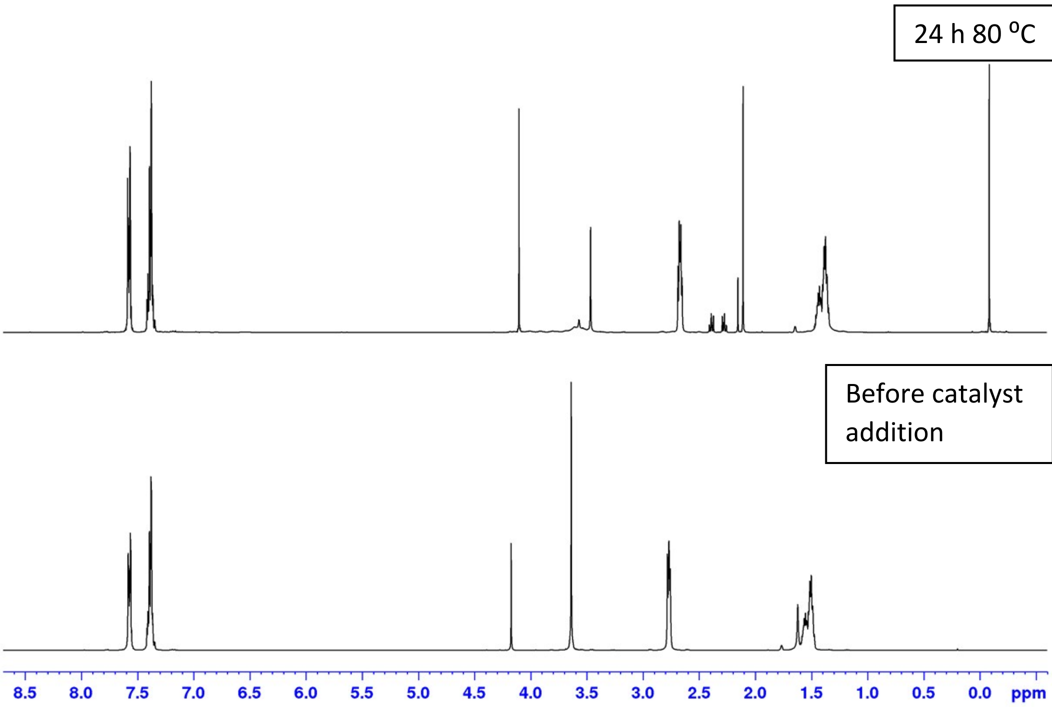

Figure S10 Hydroamination of diphenylacetylene with piperidine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) and 10 mol% of 18-crown-6 in d_8-THF.

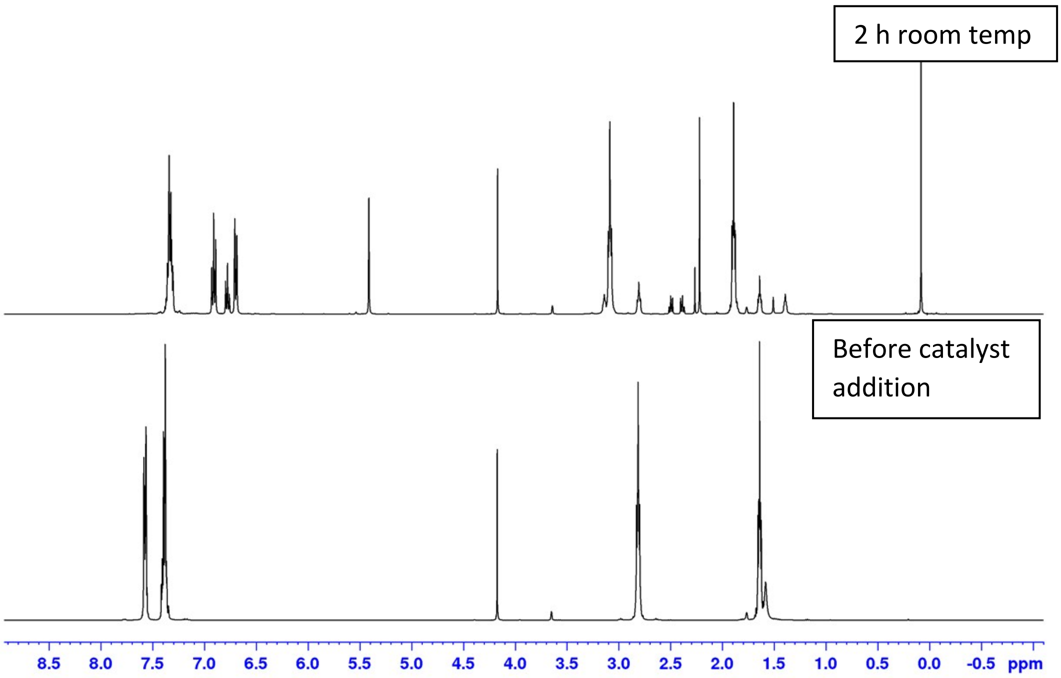

Figure S11 Hydroamination of diphenylacetylene with pyrrolidine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

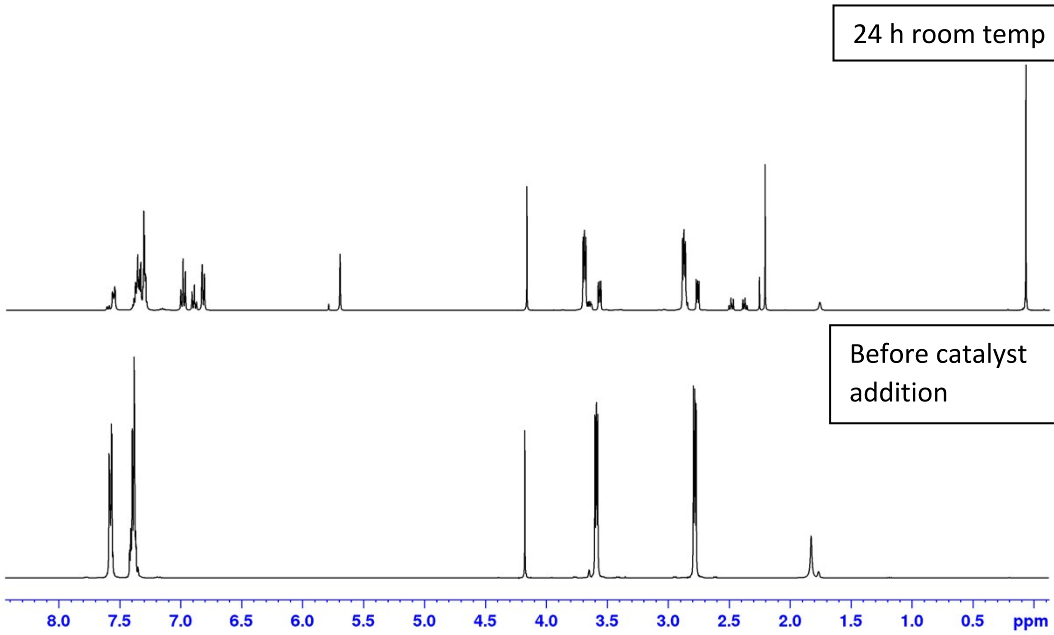

Figure S12 Hydroamination of diphenylacetylene with morpholine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

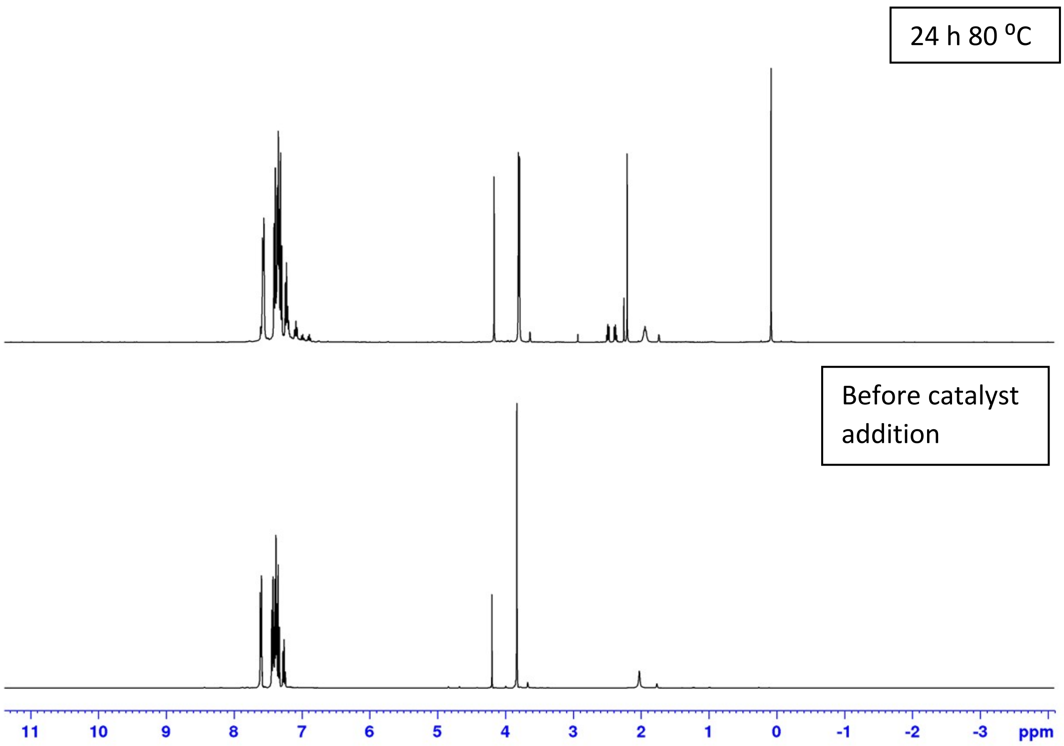

Figure S13 Hydroamination of diphenylacetylene with dibenzylamine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

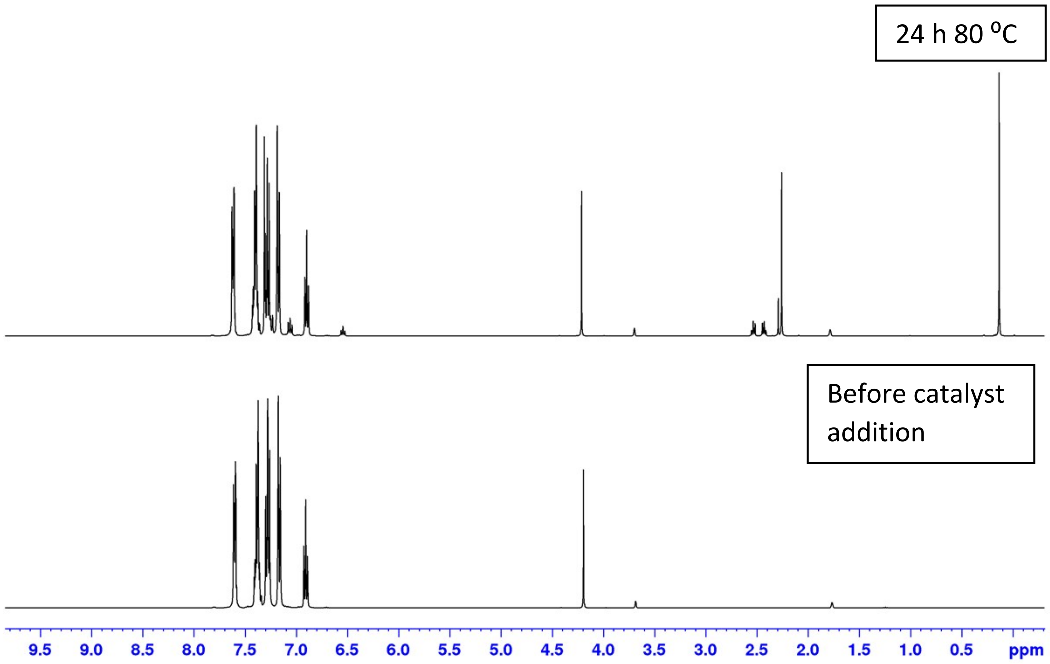

Figure S14 Hydroamination of diphenylacetylene with diphenylamine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

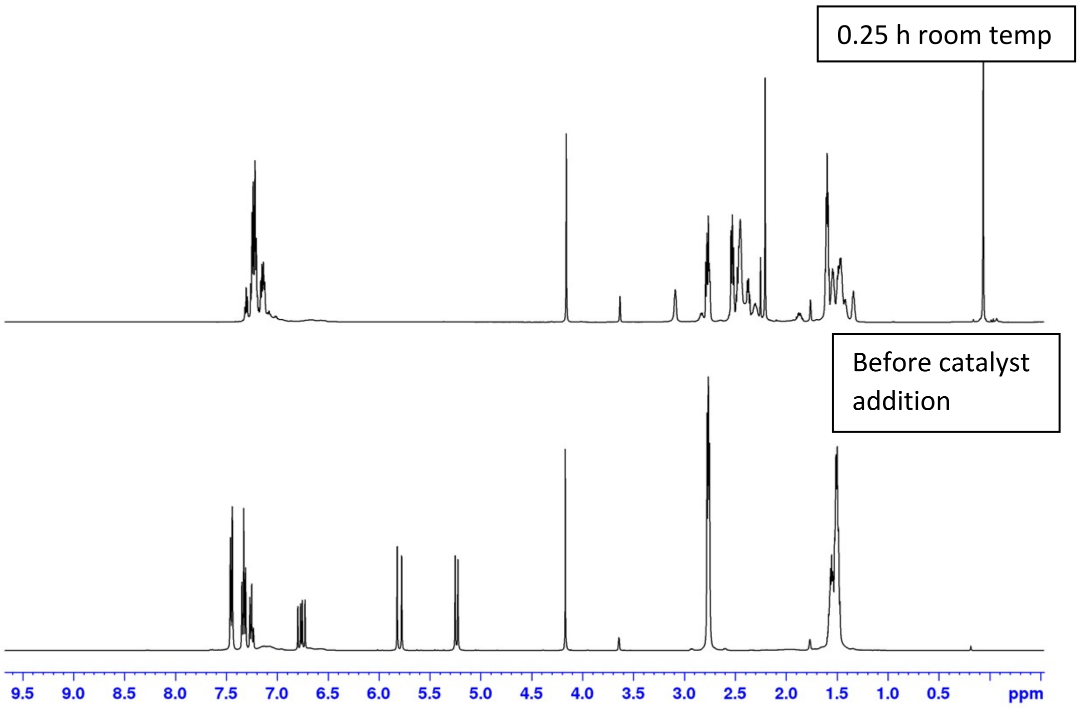

Figure S15 Hydroamination of styrene with piperidine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

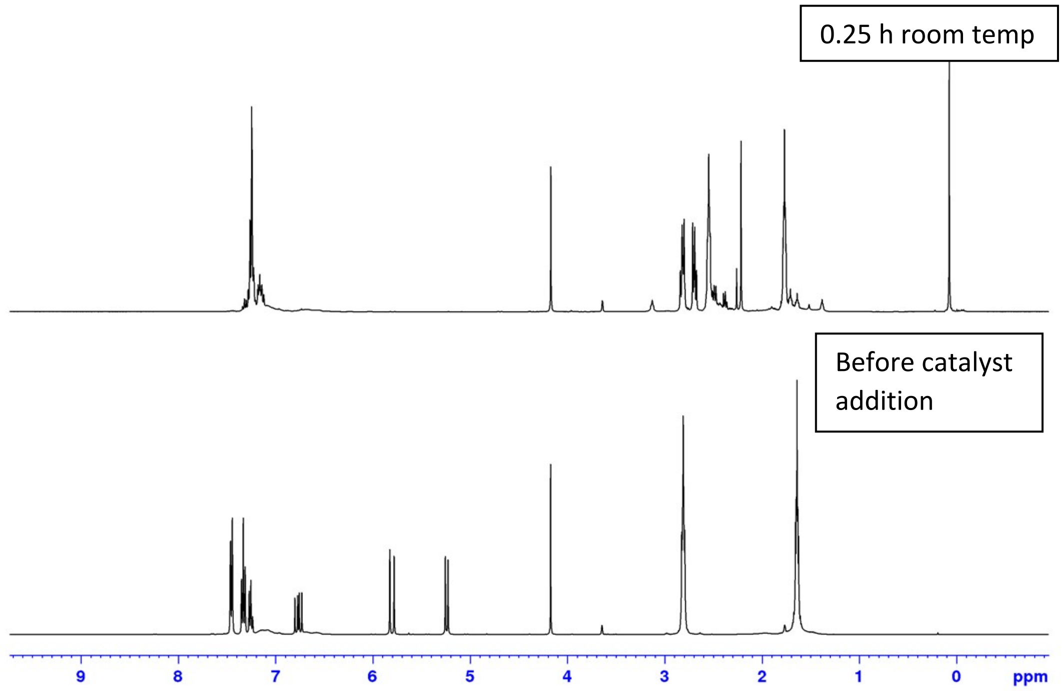

Figure S16 Hydroamination of styrene with pyrrolidine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

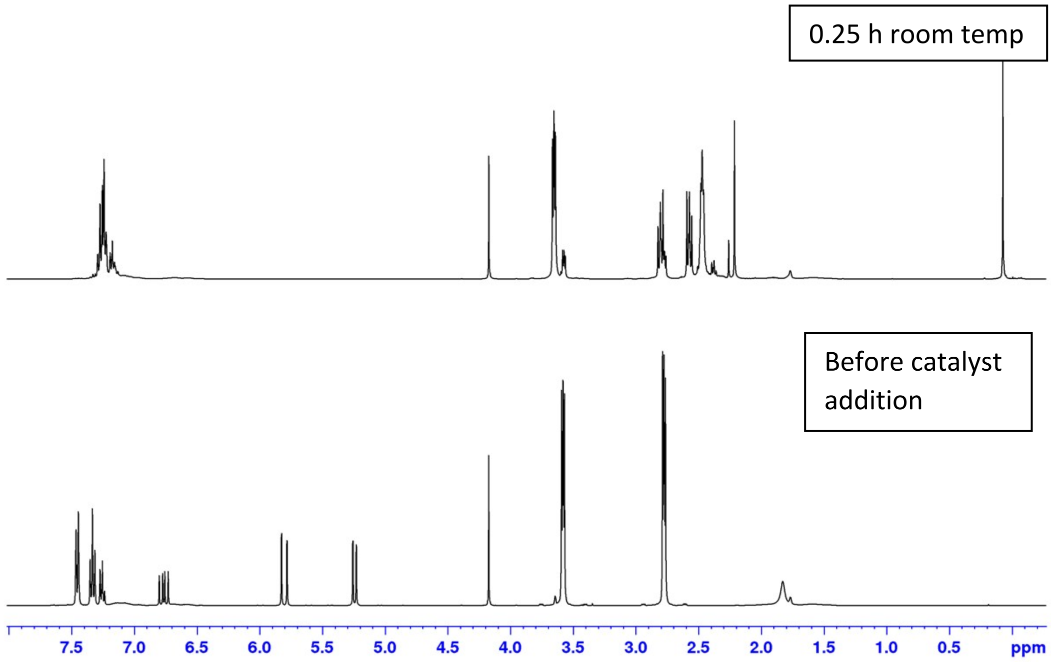

Figure S17 Hydroamination of styrene with morpholine, catalysed by $[(PMDTA)_2K_2Mg(CH_2SiMe_3)_4]$ (**7**) (5 mol%) in d_8-THF.

Amide complexes 15-18 NMR Spectra

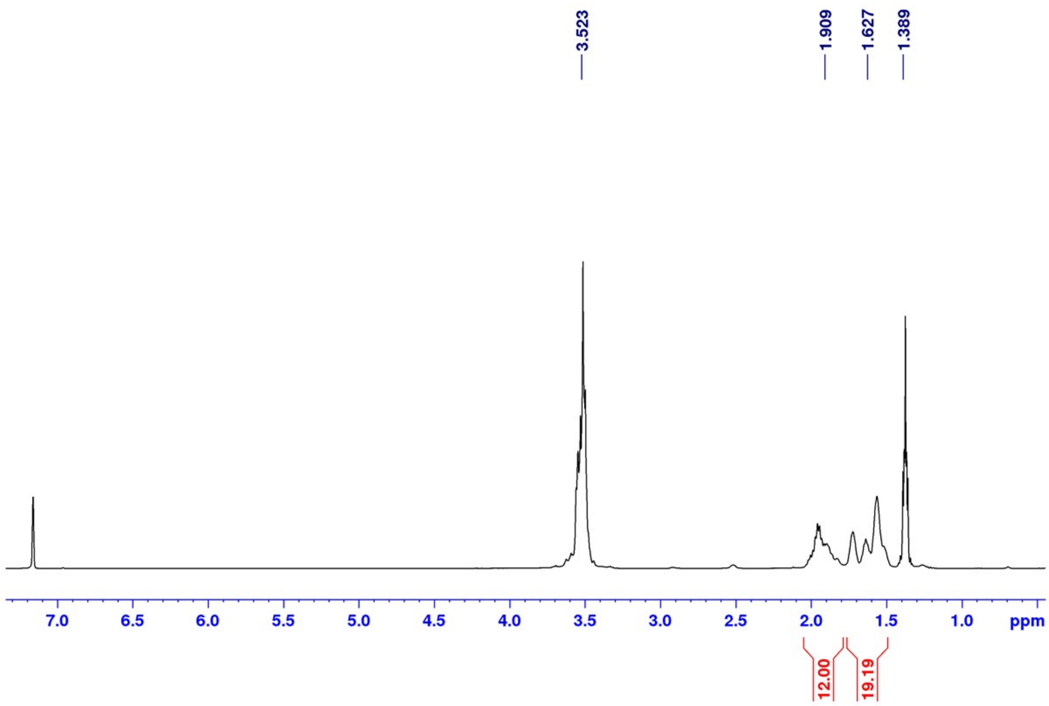

Figure S18 ^{1}H NMR spectrum of $[(THF)_2\{NaMg(NC_5H_{10})_3\}]_2$ (**15**) in C_6D_6.

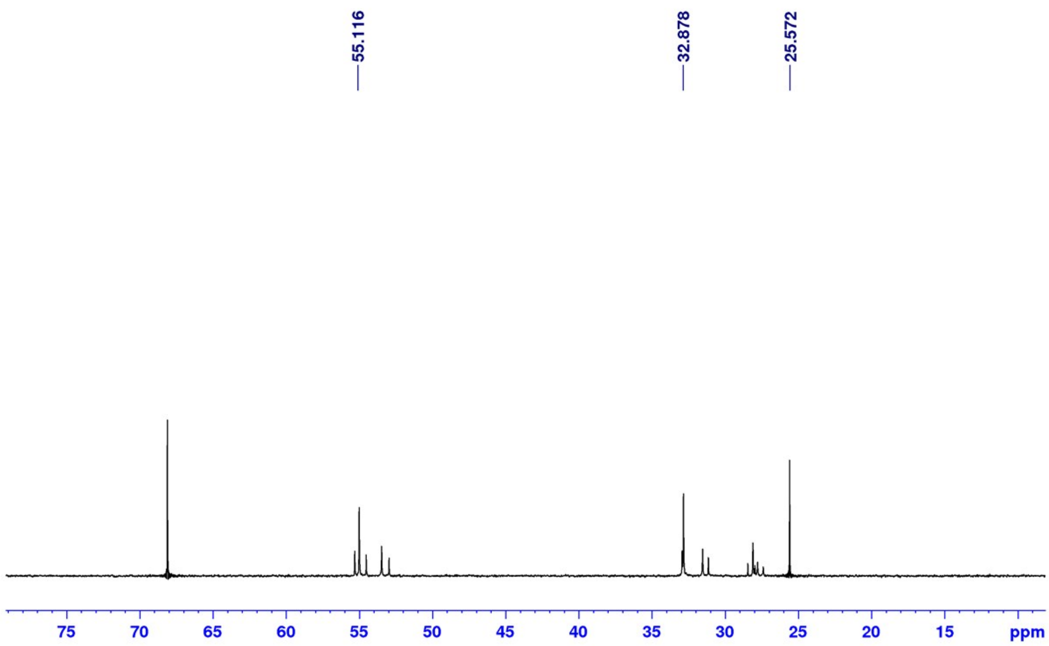

Figure S19 ^{13}C NMR spectrum of $[(THF)_2\{NaMg(NC_5H_{10})_3\}]_2$ (**15**) in C_6D_6.

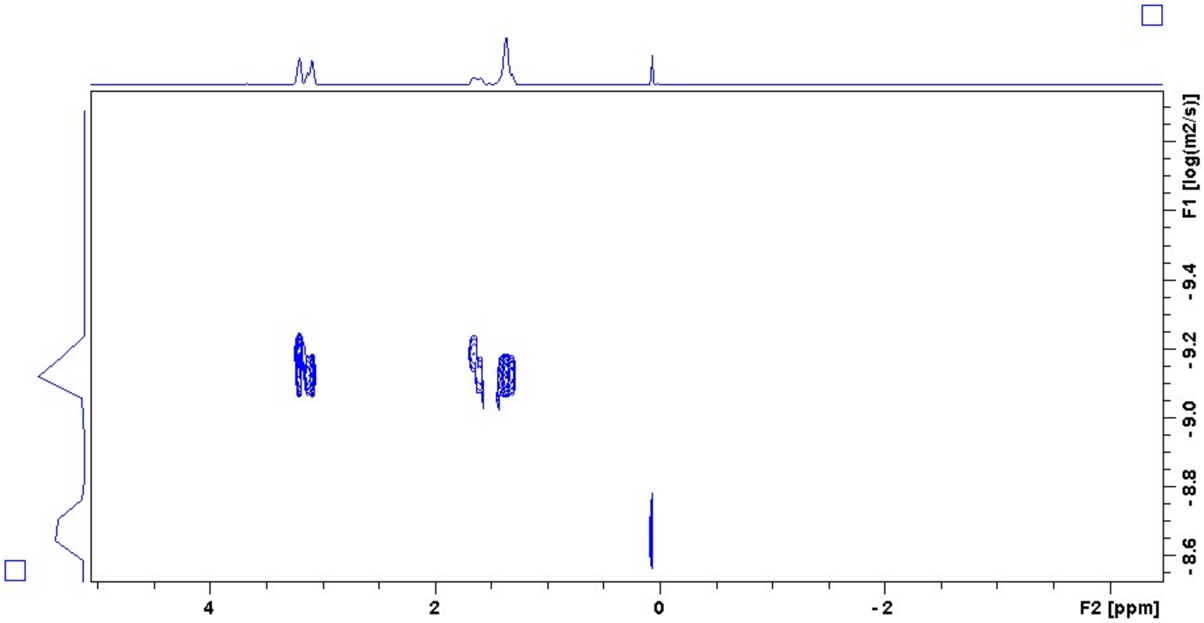

Figure S20 ^{1}H NMR DOSY spectrum of $[(THF)_2\{NaMg(NC_5H_{10})_3\}]_2$ (**15**) in d_8-THF.

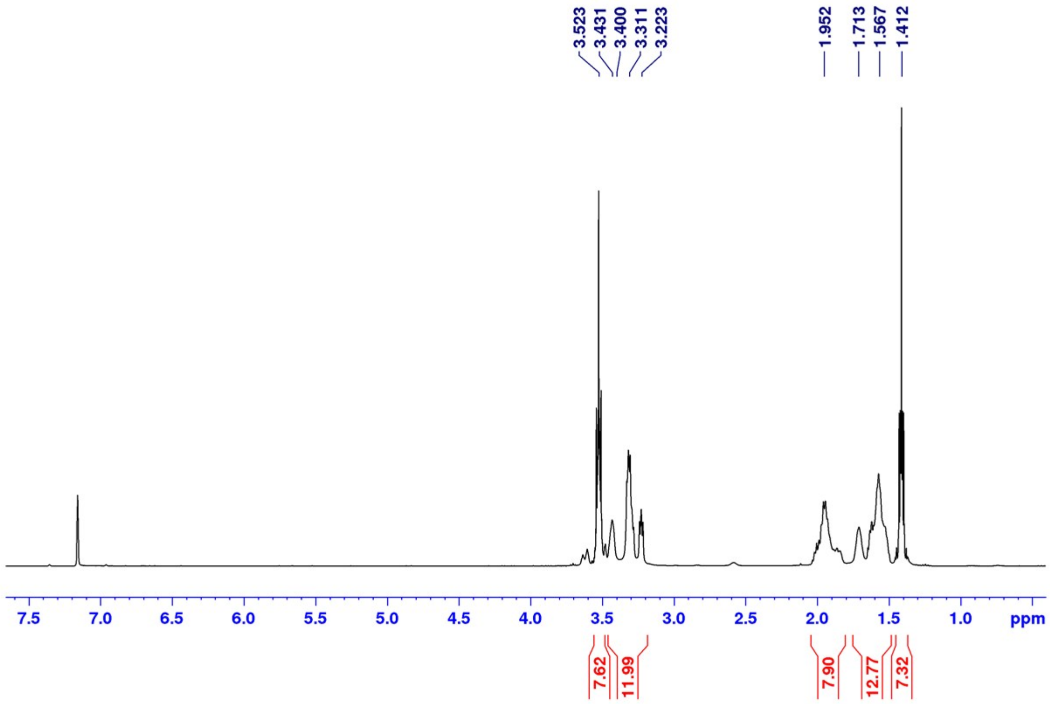

Figure S21 ^{1H} NMR spectrum of $[(THF)_3\{KMg(NC_5H_{10})_3\}]_2$ (**16**) in C_6D_6.

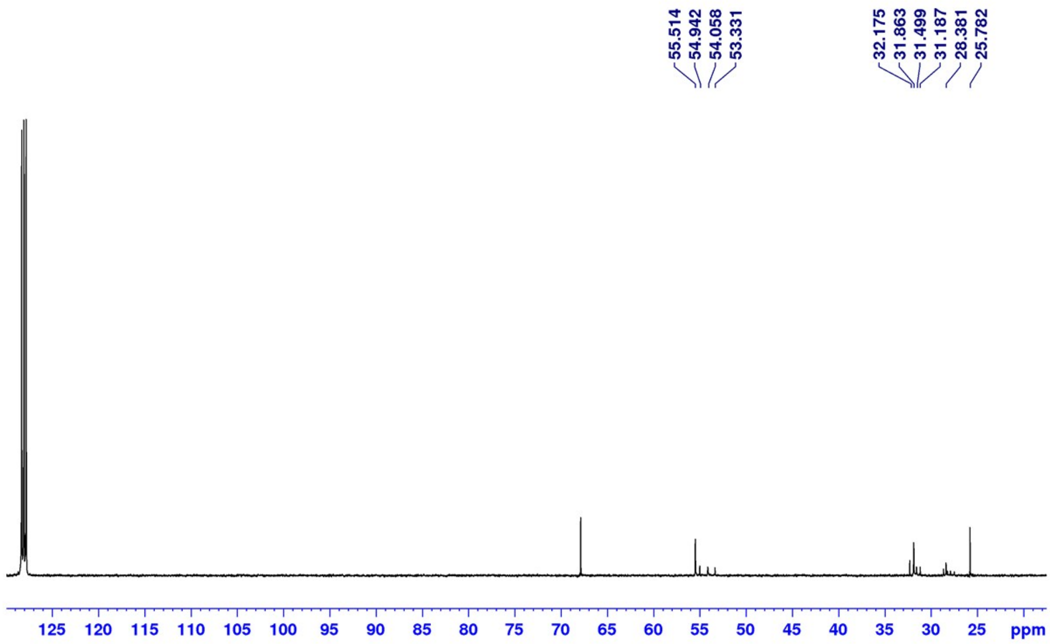

Figure S22 ^{13}C NMR spectrum of $[(THF)_3\{KMg(NC_5H_{10})_3\}]_2$ (**16**) in C_6D_6.

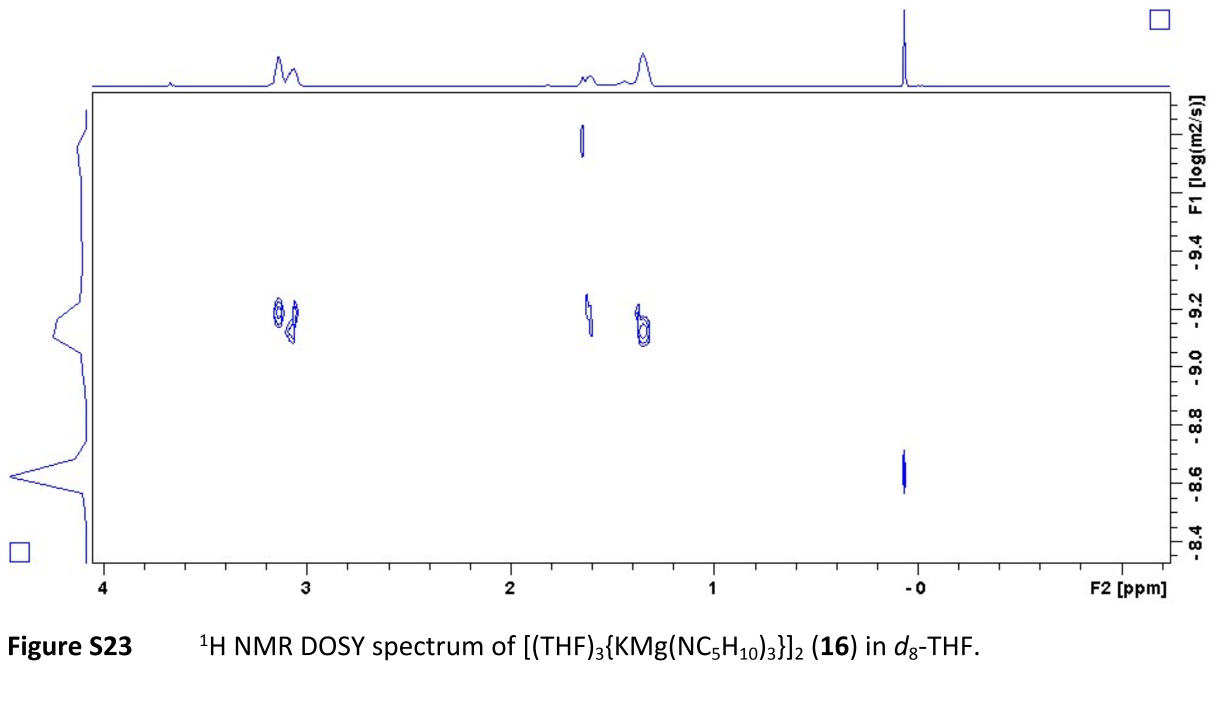

Figure S23 ^{1}H NMR DOSY spectrum of $[(THF)_3\{KMg(NC_5H_{10})_3\}]_2$ (**16**) in d_8-THF.

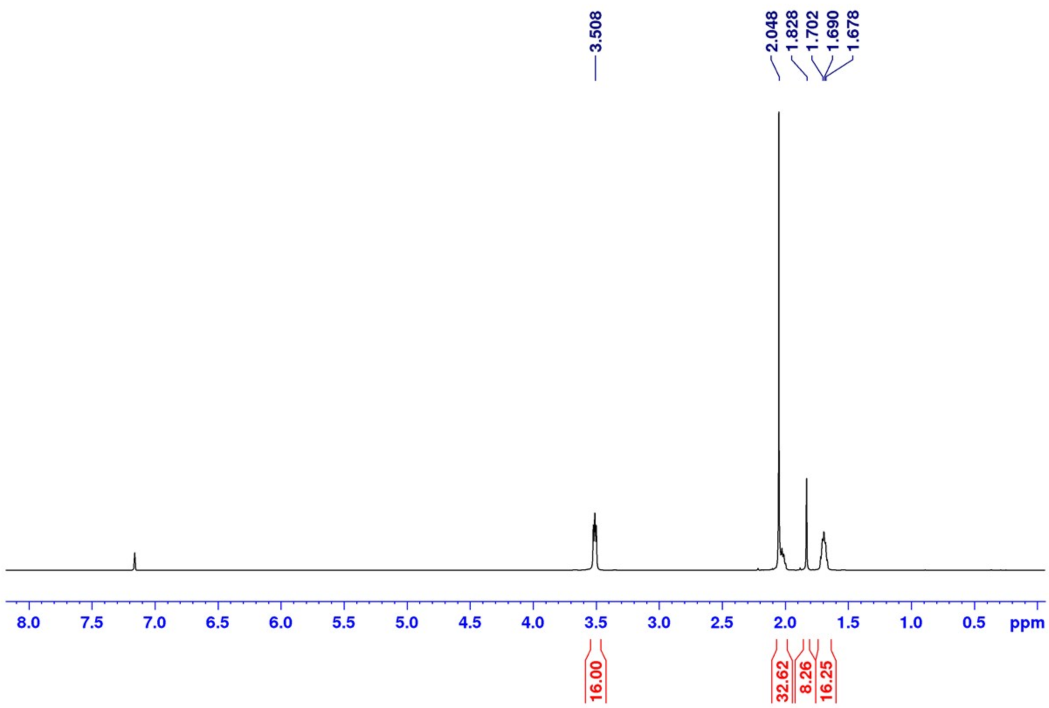

Figure S24 ^{1}H NMR spectrum of $[(TMEDA)_2Na_2Mg(NC_5H_{10})_4]$ (**17**) in C_6D_6.

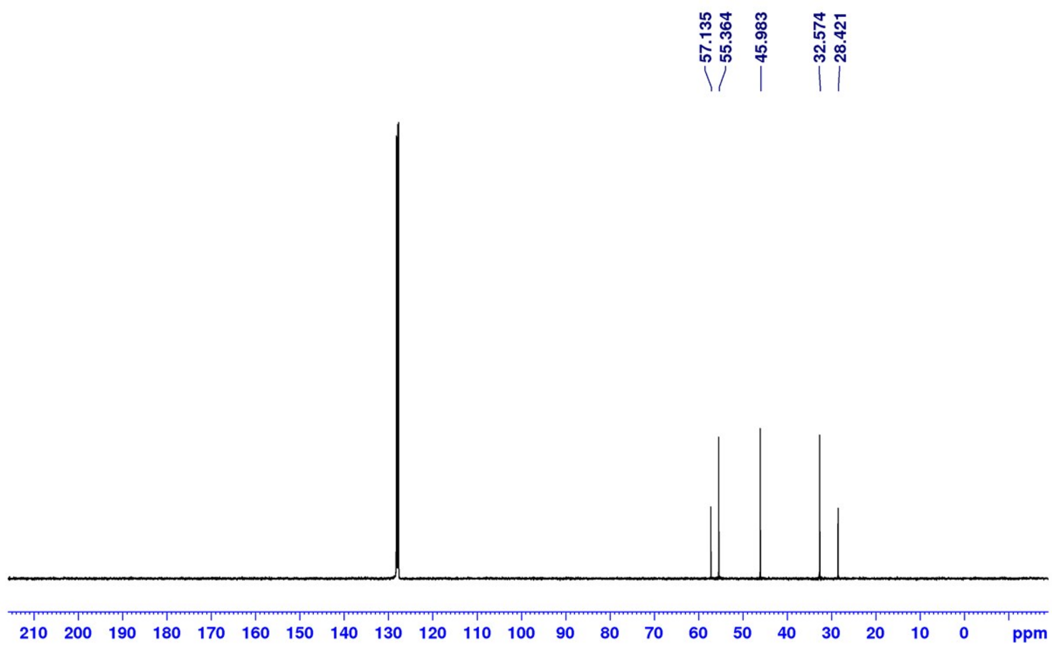

Figure S25 ^{13}C NMR spectrum of $[(TMEDA)_2Na_2Mg(NC_5H_{10})_4]$ (**17**) in C_6D_6.

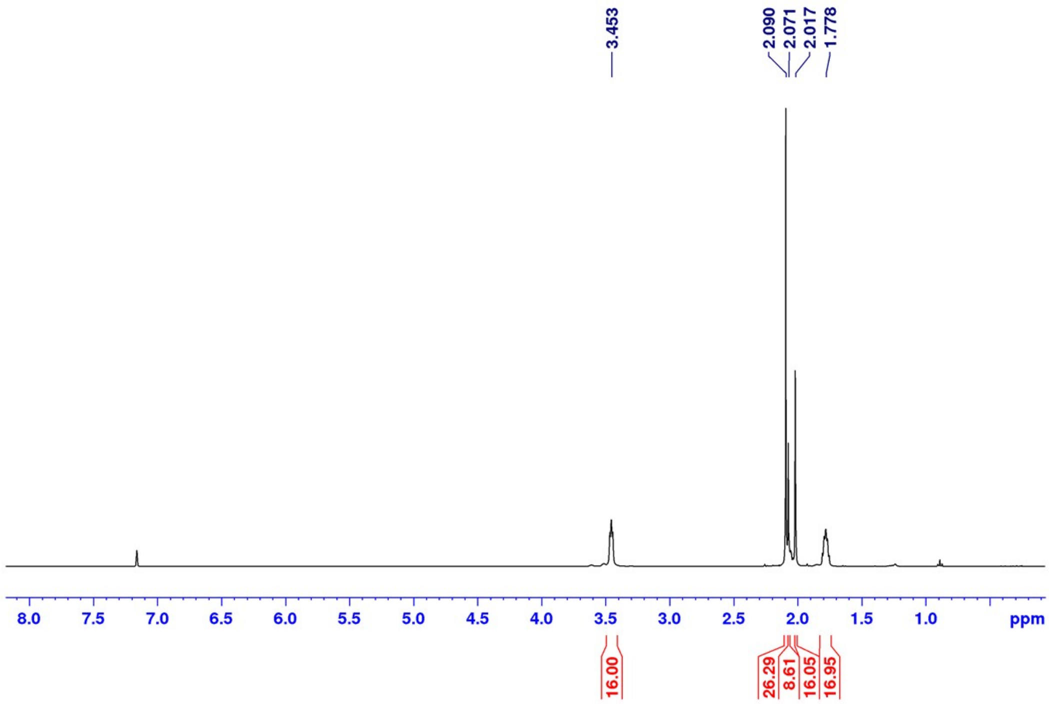

Figure S26 ¹H NMR spectrum of [(PMDETA)$_2$K$_2$Mg(NC$_5$H$_{10}$)$_4$] (**18**) in C_6D_6.

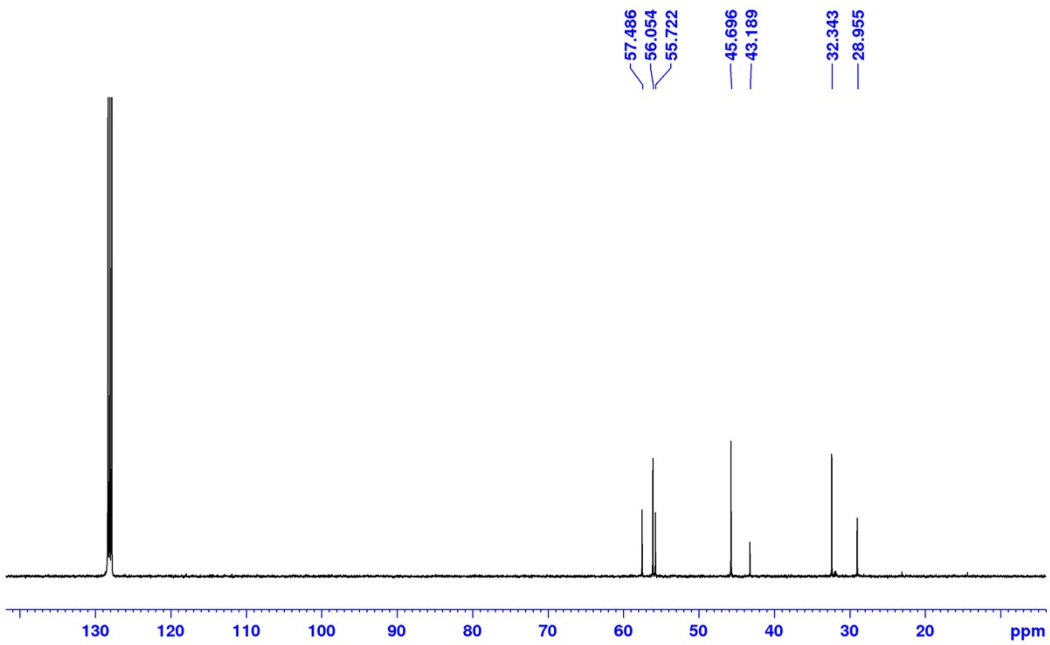

Figure S27 ¹³C NMR spectrum of [(PMDETA)$_2$K$_2$Mg(NC$_5$H$_{10}$)$_4$] (**18**) in C_6D_6.