

Supplementary Information for:

**Cyclopentadienyl-based Mg complexes in the Intramolecular Hydroamination of aminoalkenes:
Mechanistic evidences for a cationic versus neutral magnesium derivatives.**

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Table S1. HSQC ¹H-¹³C spectrum of **2**.

δ ¹ H	δ ¹³ C
5.94	105.4
6.17	110.2
6.75	116.9

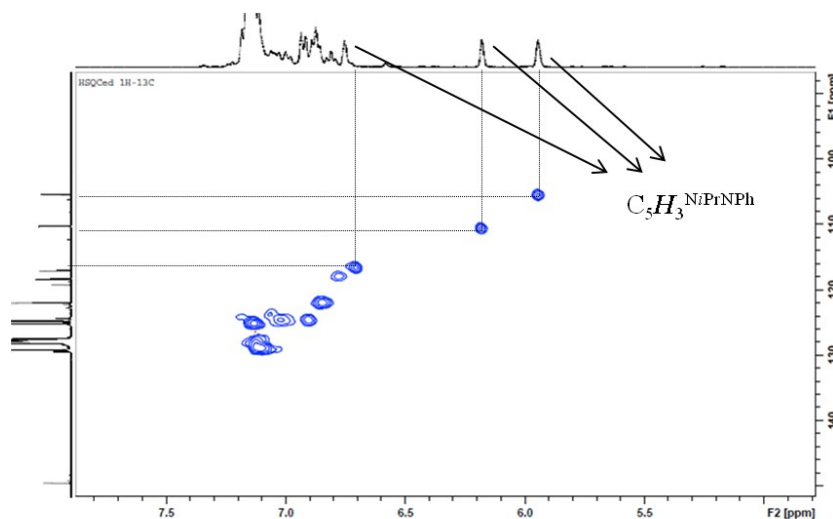


Figure S1. HSQC ¹H-¹³C spectrum of **2**.

Table S2. HMBC ¹H-¹³C spectrum of **2**.

Assignment	δ ¹ H	δ ¹³ C
(CH ₃) ₂ Si	0.63, 0.58	117.5
		105.9
C ₅ H ₃ CH ₂ CH ₂ N(CHMe ₂) ₂	2.42-2.36	110.2
		119.2
C ₅ H ₃ CH ₂ CH ₂ N(CHMe ₂) ₂	1.95	119.2

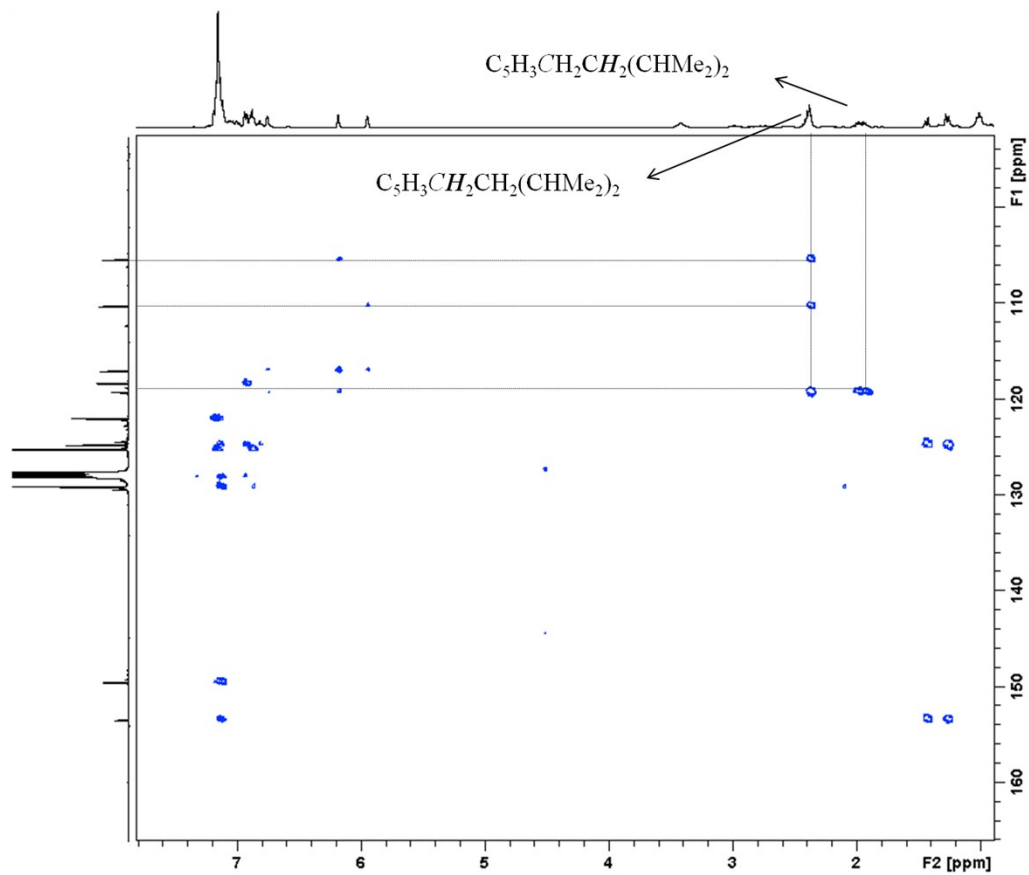


Figure S2. HMBC ^1H - ^{13}C spectrum of **2**.

Diffusion Ordered Spectroscopy (¹H-DOSY) experiments.

According to literature procedures² the internal reference method was employed. Three different patrons were chosen. Tetramethylsilane (SiMe₄, M_w = 88.22), 1,2,3,4-tetraphenylnaphtalene (TPhN, M_w = 432.53) and dendrimer G2O3A12 (DEN, M_w = 1424.23, figure S4). These three patrons and **2** were placed in an NMR tube and 0.5 mL of C₆D₆ was added. After the DOSY experiment was recorded Log D vs Log M_w of patrons was plotted. The molecular weight can be then obtained by interpolating the D value of the desired complex.

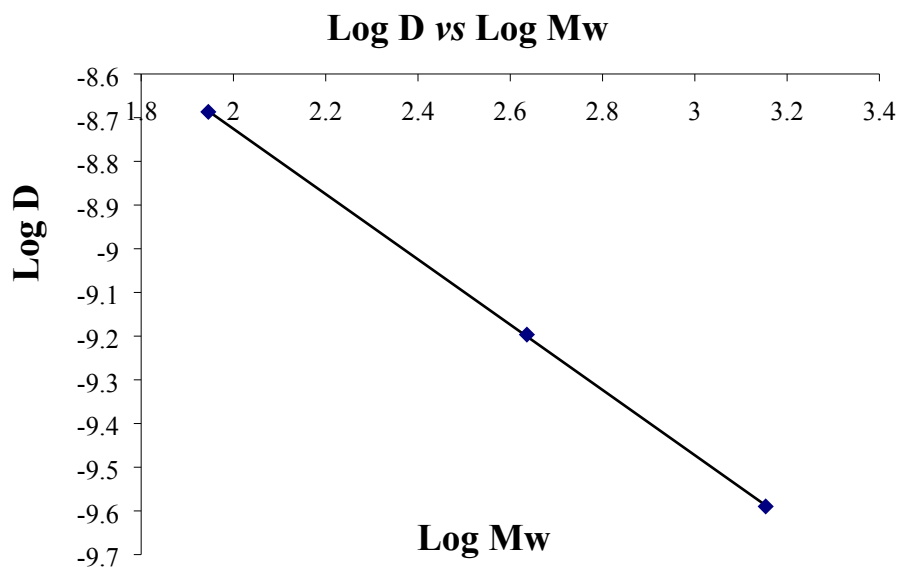


Figure S3. Log D vs Log Mw of **2**.

Table S3: D, Log D, M_w and Log M_w values of three patrons and **2**.

Compound	10 ⁻¹⁰ D (m ² s ⁻¹)	Log D	M _w (g mol ⁻¹)	Log M _w
SiMe ₄	20.6	-8.6868	88.22	1.9455
TPhN	6.36	-9.1965	432.53	2.6360
DEN	2.57	-9.5897	1424.23	3.1536
2	5.84	-9.2334	478.25	2.6797

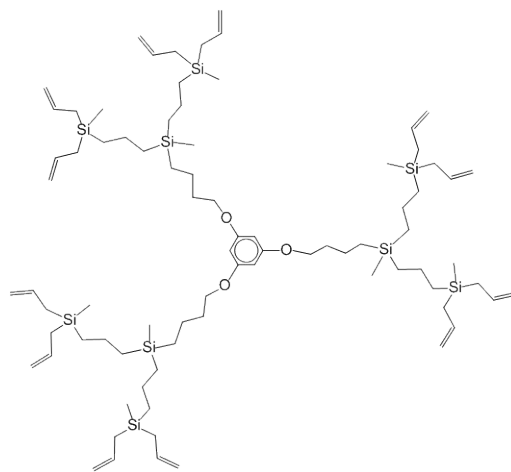


Figure S4. Structure of carborasilane dendrimer G2O3A12.¹

Dendrimer G2O3A12 was synthesized according literature procedure.¹

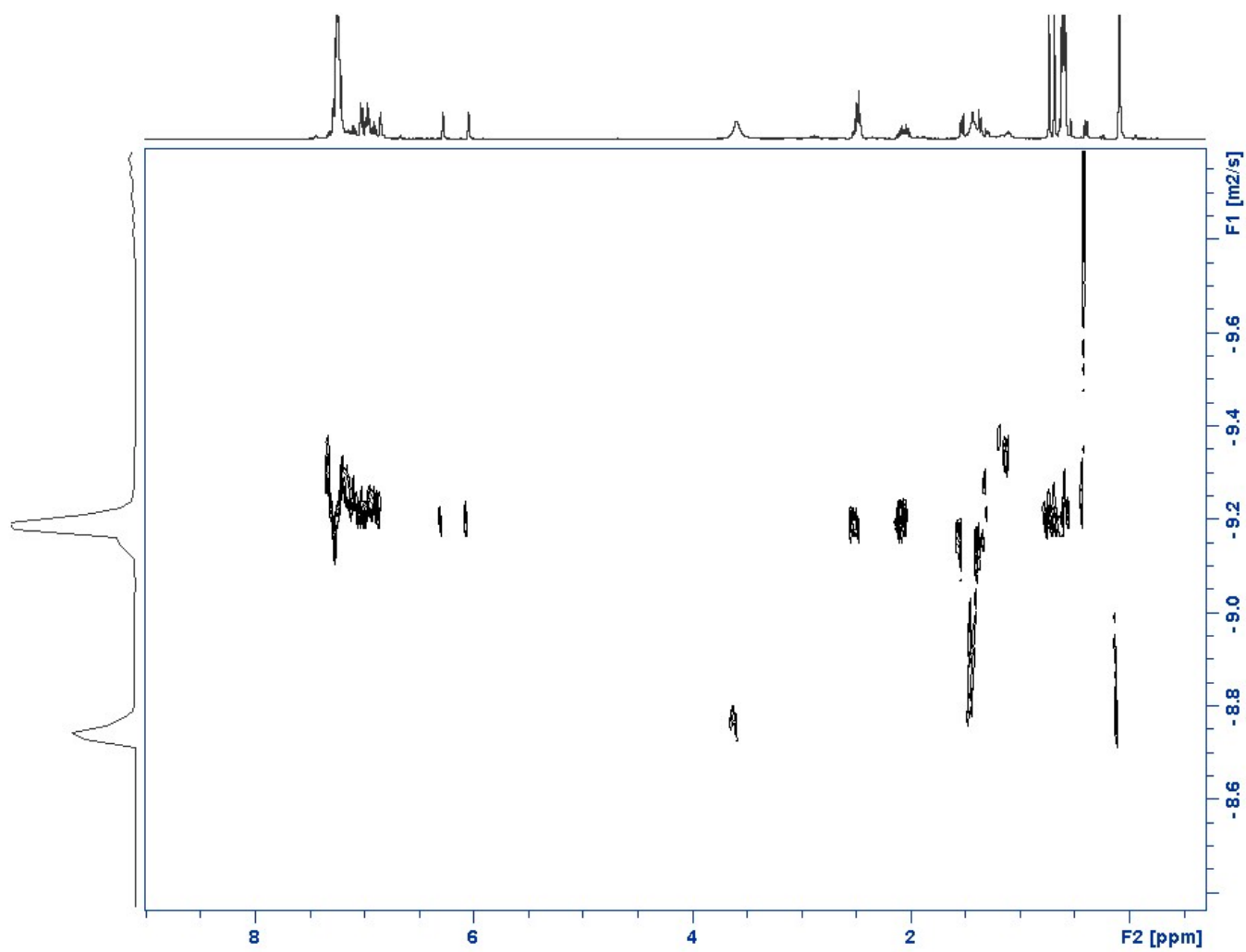


Figure S5. DOSY ¹H of **2** in C₆D₆/THF.

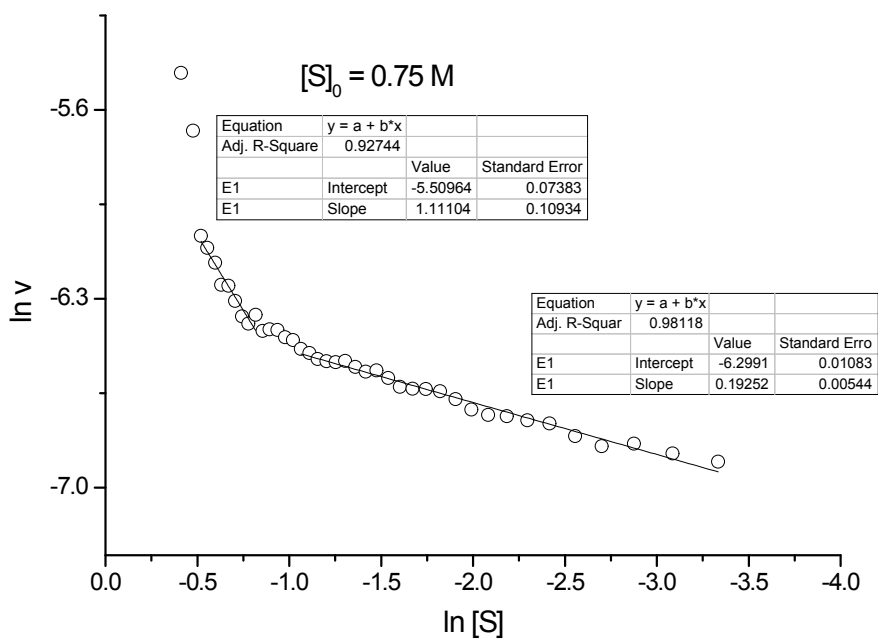


Figure S6. Plot of $\ln v$ versus $\ln S$ for the hydroamination of **A** catalyzed by **2** at 25 °C with $[C]_0 = 20$ mM.

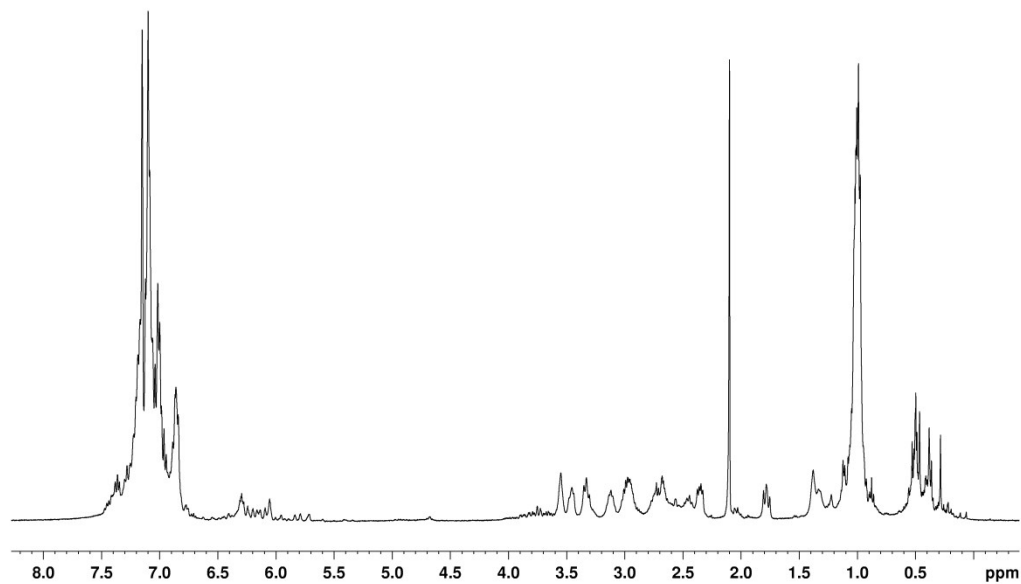


Figure S7. Stoichiometric reaction between **A** and **2** in a ratio 1:1 was carried out at 70 °C.

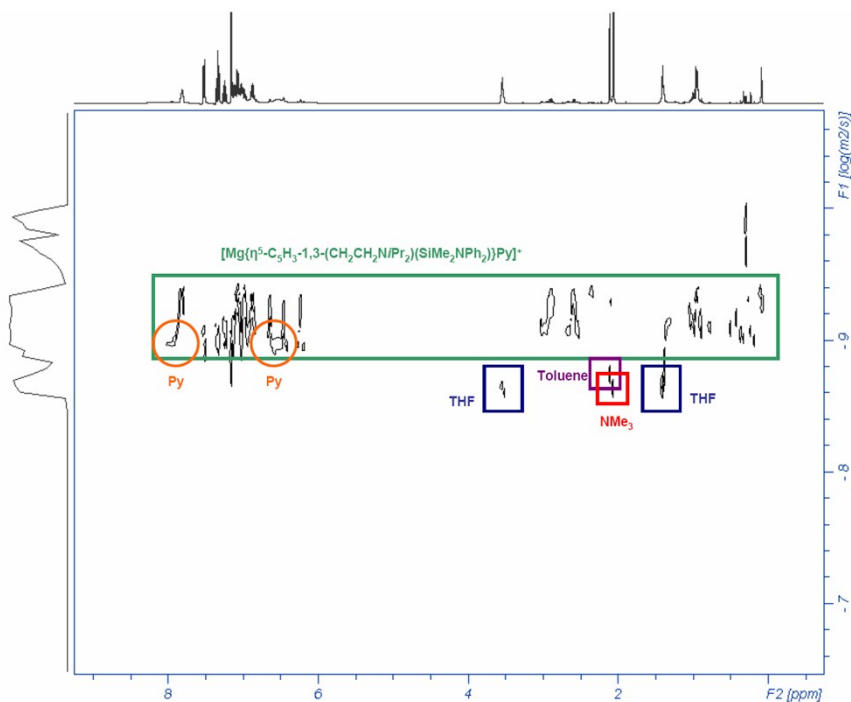


Figure S8. DOSY ^1H of **4** in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{N}$.

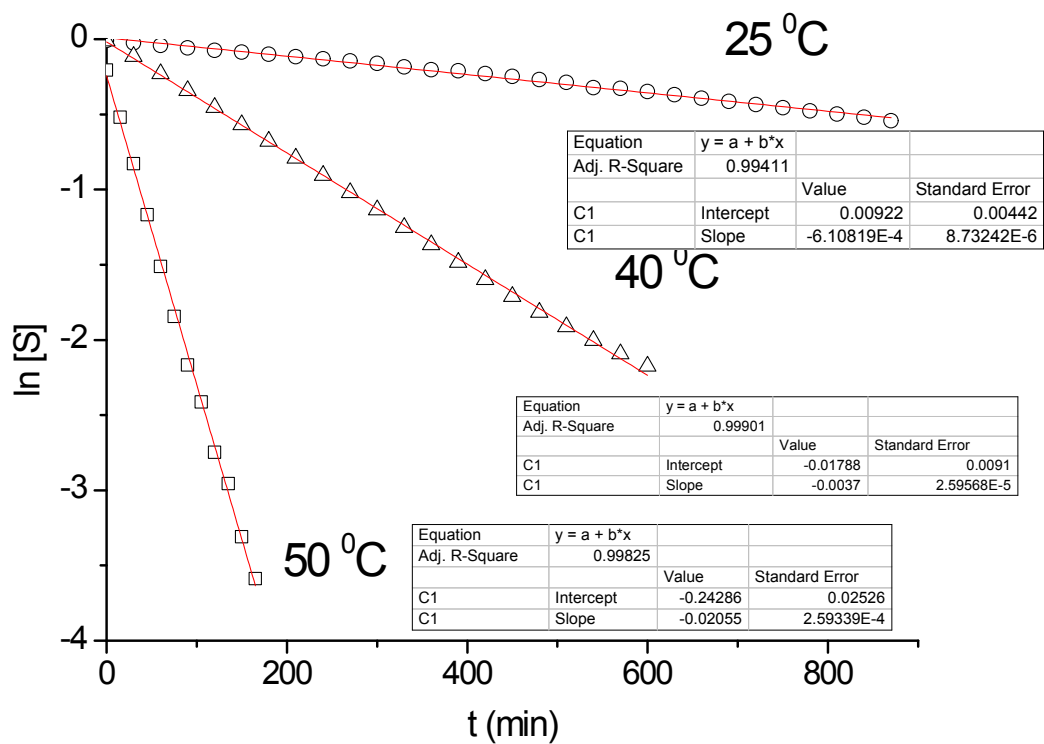


Figure S9. Plot of $\ln S$ versus t for the hydroamination of **A** catalyzed by **4** with $[\text{S}]_0 = 1 \text{ M}$.

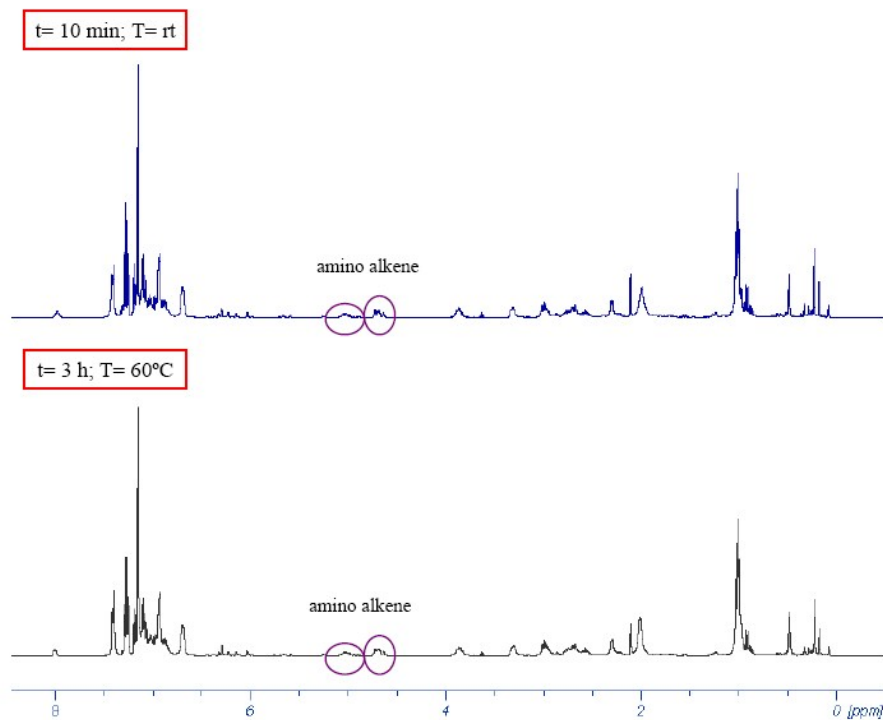


Figure S10. Stoichiometric reaction between **A** and **4** in a ratio 1:1. No reaction was observed.

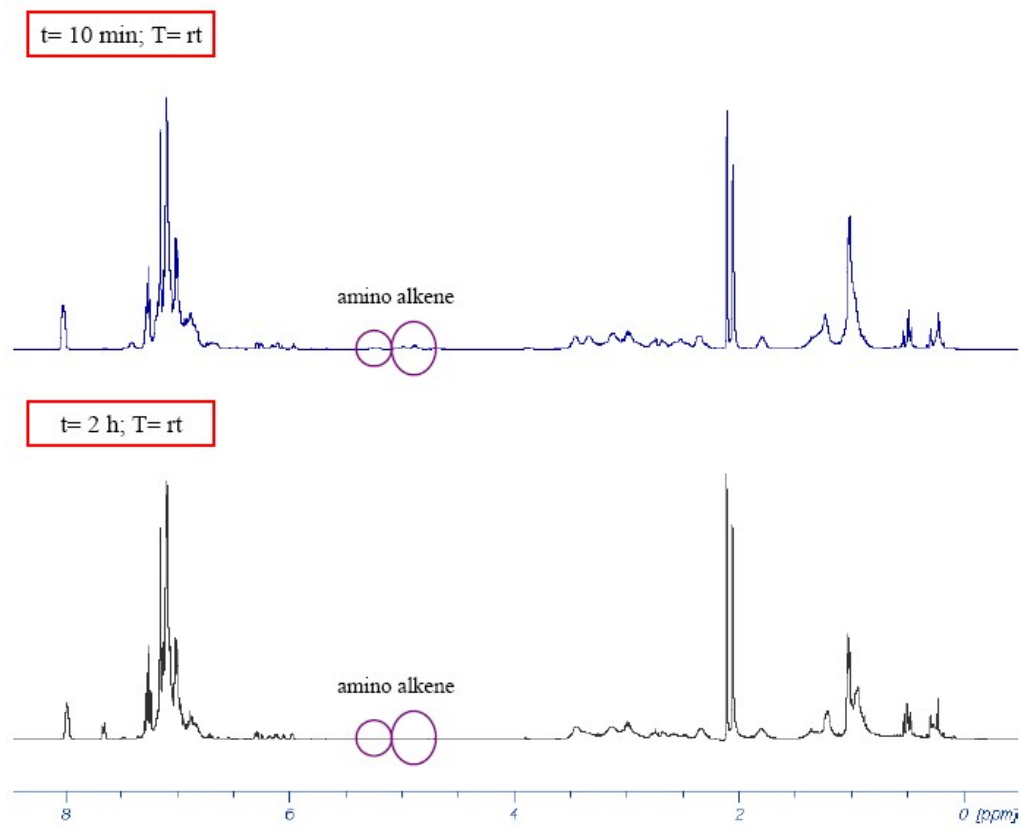


Figure S11. Stoichiometric reaction between **A** and **4** in a ratio 1:2 at rt.

1. Sánchez-Nieves, J., Ortega, P., Muñoz-Fernández, M. A., Gómez R., de la Mata, F. J. *Tetrahedron*, **2010**, *66*, 9203.
2. Li, D., Keresztes, I., Hopson, R. Williard, P. G. *Acc. Chem. Res.* **2009**, *42*, 270.