Supporting Information for

Molecular rare earth metal alumosilicates.

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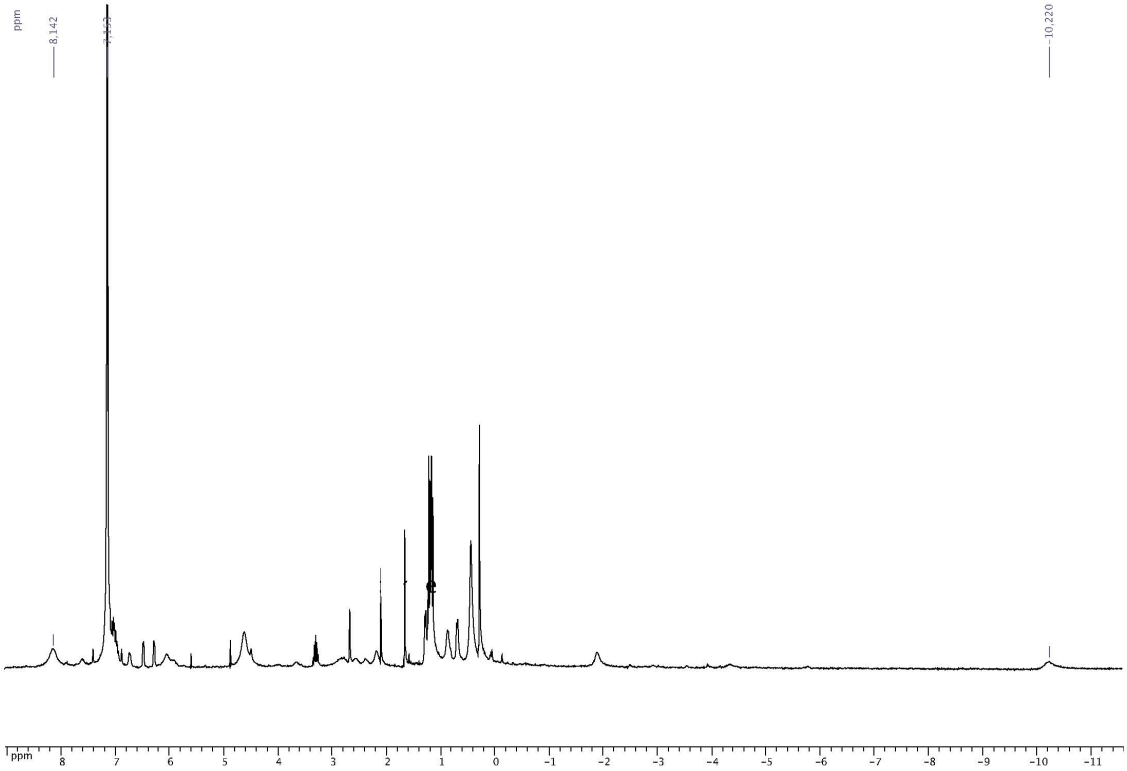

Figure *S1*. ^{1}H NMR of **2**.

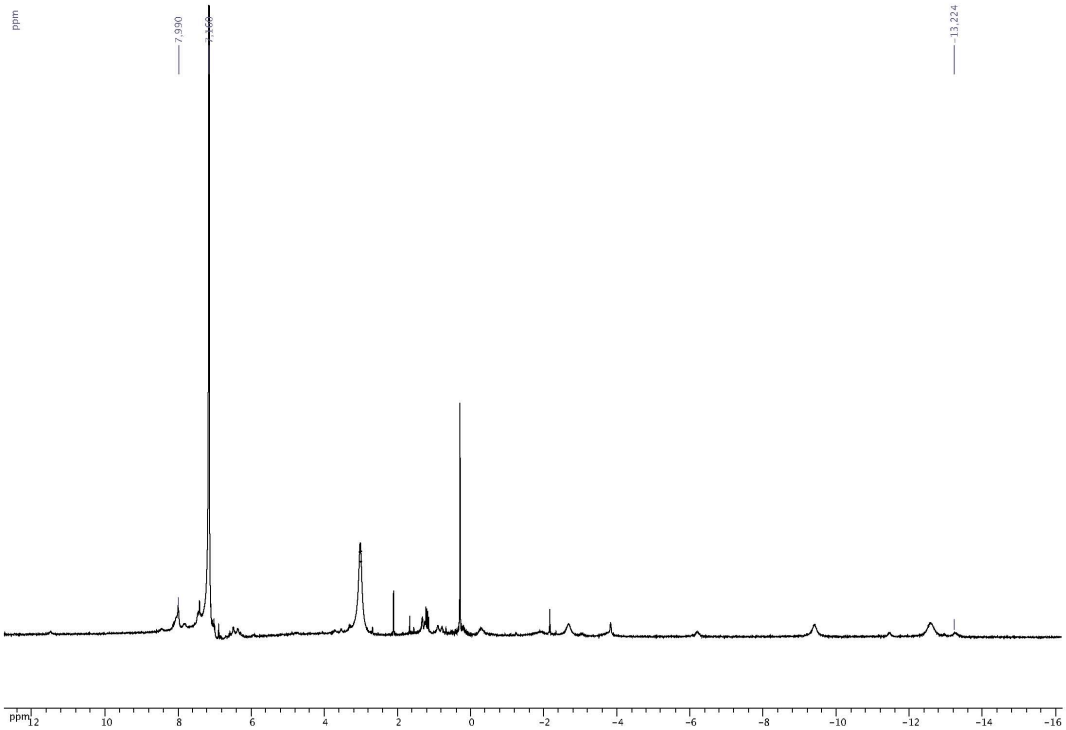

Figure *S2*. ^{1}H NMR of **3**.

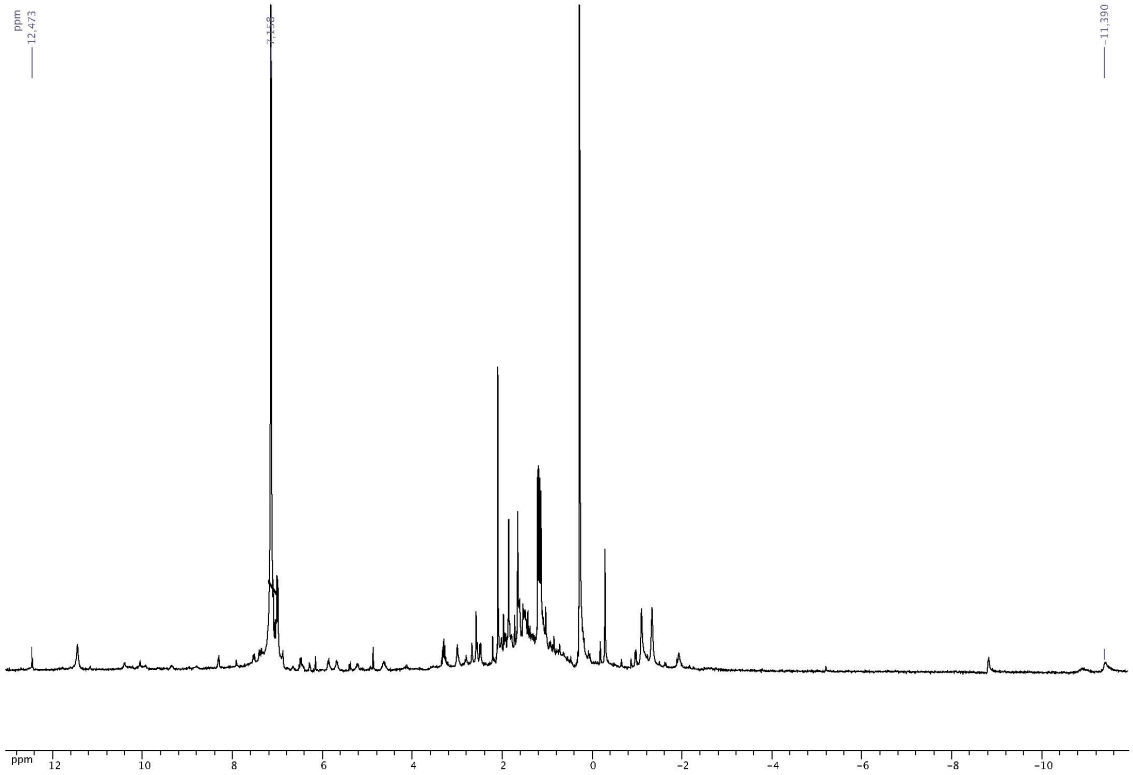

Figure *S3*. ^{1}H NMR of **4**.

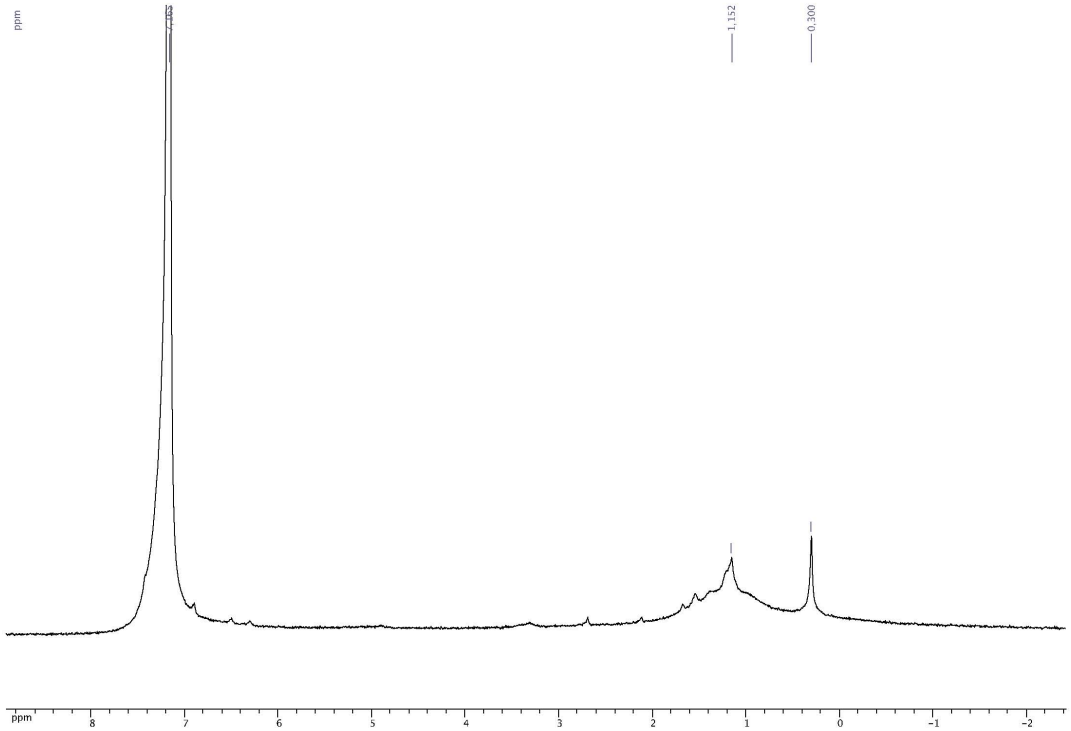

Figure *S4*. ^{1}H NMR of **5**.

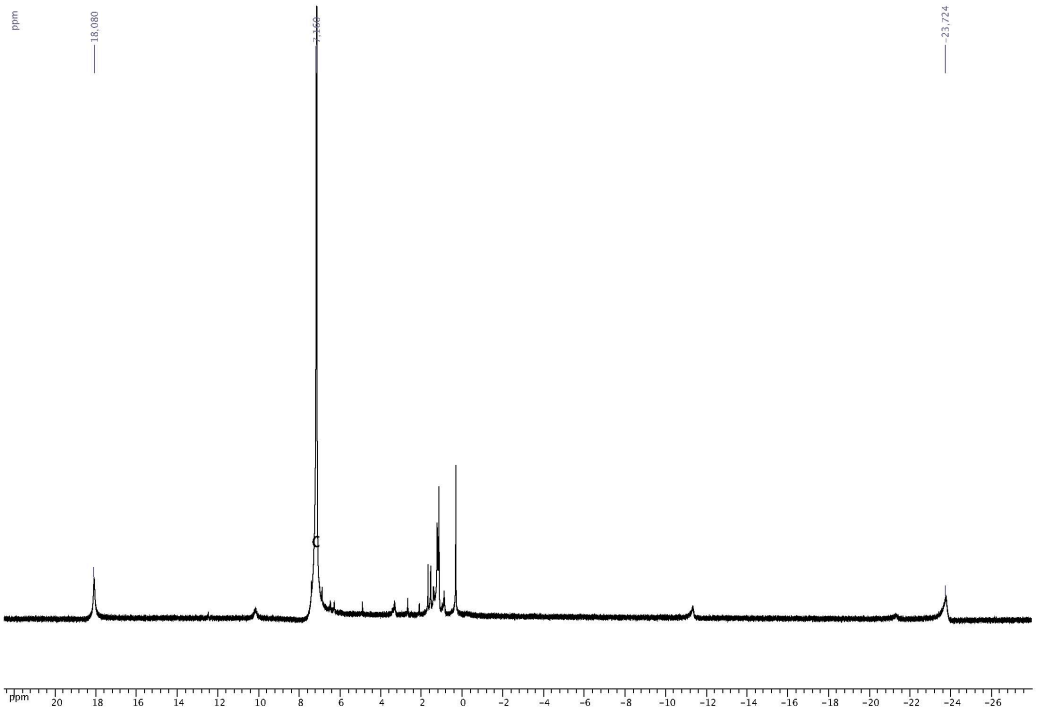

Figure *S5*. ^{1}H NMR of **6**.

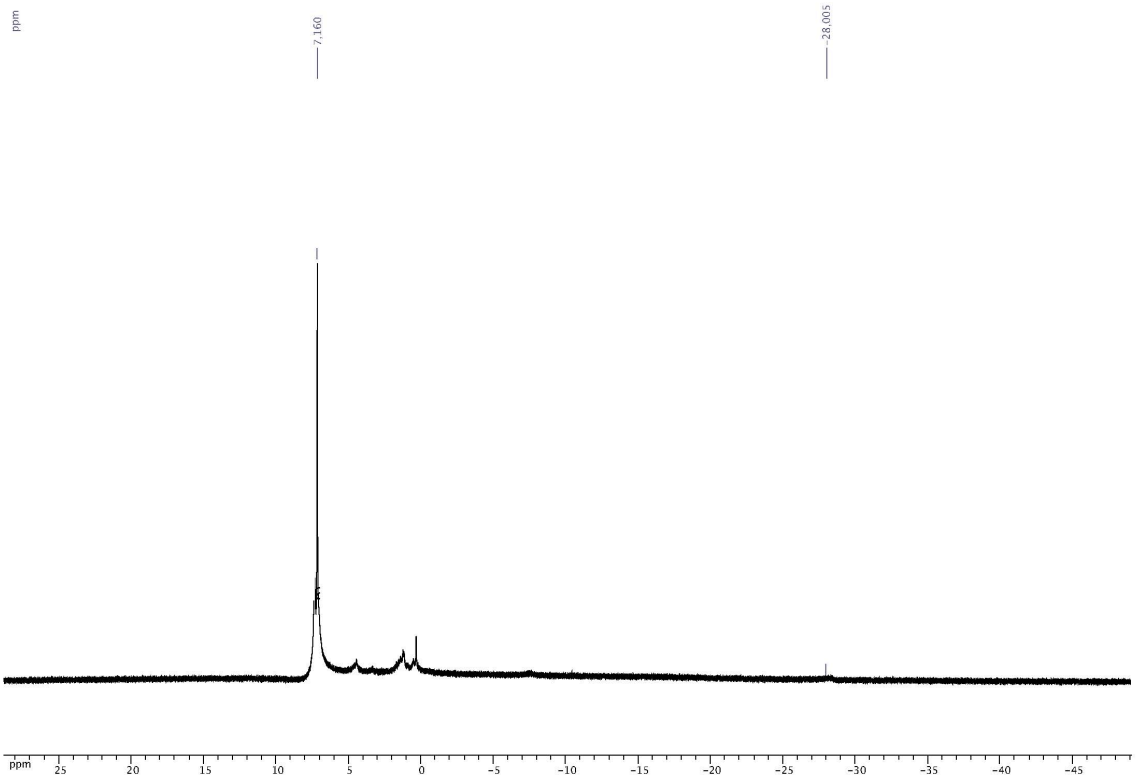

Figure *S6*. ^{1}H NMR of **7**.

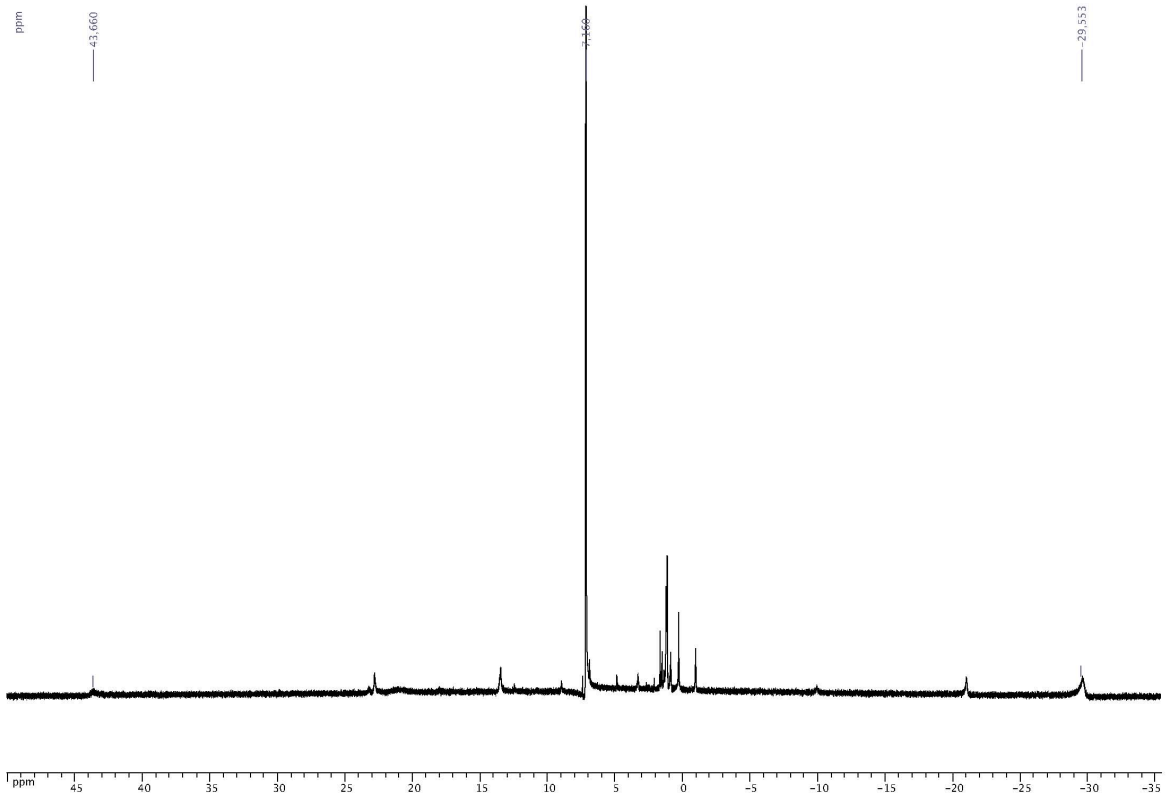

Figure *S7*. ^{1}H NMR of **9**.

Continuous Symmetry and Shape Measures analysis of compound 4

The coordination geometry of Sm1 was calculated using the SHAPE 2.0[1] based on the Continuous Symmetry and Shape Measures (CSM and CShM, respectively) proposed by Avnir *et al.*[2] that considers distortion paths between two ideal symmetries. As a first approach X-ray coordinates of the atom are used to evaluate the deviation of its geometry from the ideal symmetries: square S(SP–4), sawhorse S(SS–4), and tetrahedral S(T–4). Then the deviation from the ideal distortion path between the desired polyhedra is calculated [Δ(T–4, SP–4) ≤ 15% is considered reliable]. Finally, the distortion of the atom is calculated considering it as a percentage using the general coordinate of distortion among the selected ideal polyhedra φ(SP–4→ T–4).[3]

Table *S1*. Values of S(SP–4), S(SS–4), S(T–4), Δ(T–4, SP–4), and (φ(T–4→ SP–4) for Sm1 in **4.**

	1a$_{Sm(1)Cp}$
S(SP–4)[a]	4.49
S(SS–4)[b]	9.58
S(T–4)[c]	18.26
Δ(T–4, SP–4) [d]	6.4
φ(SP–4→ T–4) [e]	34.7

[a] S(SP–4) = square, [b] S(SS–4) = sawhorse, [c] S(T–4) = tetrahedral, [d] Δ(T–4, SP–4) = distortion path deviation, [e] (φ(SP–4→ T–4) = general coordinate of distortion, where SP–4 (0%) y T–4 (100%).

Table *S2*. Selected bond lengths (Å) in compounds **2** – **9**.

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Ln–O(Al)			2.123(2)	2.383(1)	2.372(1)	2.364(1)	2.346(1)	2.331(1)
Ln–O(Si)	2.522(1)	2.548(1)	2.394(2), 2.327(2)	2.127(1)	2.108(1)	2.095(1)	2.092(1)	2.085(1)
Ln–Cp[a]	2.522(1)	2.561(1)	2.460(2)	2.480(1)	2.447(1)	2.398(1)	2.368(1)	2.390(1)
Al–X(Ln)	1.733(1)	1.732(1)	1.703(2)[a]	1.785(1)	1.785(1)	1.784(1)	1.785(1)	1.787(1)
Al–O(Si)	1.725(1)	1.726(1)	1.740(2)[a]	1.703(1)	1.705(1)	1.706(1)	1.704(1)	1.704(1)
Al–N[a]	1.884(1)	1.884(1)	1.917(2)	1.909(1)	1.907(1)	1.907(1)	1.906(1)	1.909(1)
Si–O(Ln)	1.671(1)	1.669(1)	1.631(2)[a]	1.600(1)	1.601(1)	1.600(1)	1.598(1)	1.598(1)
Si–O(Al)	1.610(1)	1.610(1)	1.618(2)[a]	1.644(1)	1.643(1)	1.640(1)	1.639(1)	1.639(1)
Si–O^{t}Bu[a]	1.629(1)	1.628(1)	1.637(2)	1.638(1)	1.640(1)	1.637(1)	1.636(1)	1.638(1)

[a] Average distances.

Table *S3*. Selected bond angles (º) in compounds **2** – **9**.

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Al-O-Si	133.3(1)	133.2(1)	134.0(1)	139.2(1)	138.1(1)	138.4(1)	138.6(1)	138.3(1)
Al-O-Ln	128.3(1)	128.5(1)	133.8(1), 135.3(1)	133.2(1)	133.9(1)	133.4(1)	133.4(1)	133.3(1)
Ln-O-Si	141.8(1)	141.6(1)	122.0(1), 131.4(1)	140.8(1)	140.4(1)	141.1(1)	140.8(1)	140.5(1)
Ln-O-Ln			106.6(1)					
(Si)O-Ln-O(Al)			90.4(1)	84.8(1)	84.1(1)	84.8(1)	85.3(2)	85.5(1)
(Si)O-Ln-O(Si)			74.4(1)					
(Si)O-Al-O	103.3(1)	103.3(1)	111.2(1)[a]	105.1(1)	105.2(1)	105.1(1)	105.1(1)	105.1(1)
(Al)O-Si-O(Ln)	107.4(1)	107.3(1)	112.6(1)[a]	111.4(1)	111.5(1)	111.4(1)	111.3(1)	111.4(1)

[a] Average angles.

References

(1) **SHAPE 2.0** Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools: M. Llunell, D. Casanova, J. Cirera, P. Alemany, and S. Alvarez Universitat de Barcelona, Barcelona, España 2010.

(2) H. Zabrodsky, S. Peleg, D. Avnir, *J. Am. Chem. Soc.* 1992, **114**, 7843–7851; b) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, Coord. *Chem. Rev.* 2005, **249**, 1693–1708.

(3) J. Cirera, P. Alemany, S. Alvarez, *Chem. Eur. J.* 2004, **10**, 190 – 207.