

Reactivity of Dianionic β -diketiminato Lanthanide Amides toward Carbodiimide: Synthesis of γ -amidine-functionalized Dianionic β -diketiminato Lanthanide Amides and New Na/Sm Heterobimetallic Complexes with a γ - amidinate-functionalized Trianionic β -diketiminato Ligand, and Reactivity in Polymerization of L-lactide

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Table 1. Crystallographic data for complexes **1-5**

	1	2	3	4	5
Empirical formula	C ₄₈ H ₇₉ N ₅ Si ₂ Sm	C ₅₁ H ₈₇ N ₅ Si ₂ Yb	C ₄₈ H ₇₉ N ₅ Si ₂ Y	C ₄₈ H ₇₉ N ₅ Si ₂ Gd	C ₅₀ H ₉₁ N ₅ NaO ₄ Si ₂ Sm
Formula weight	932.70	999.48	872.26	940.60	1055.80
Temperature (K)	223(2)	223(2)	200(2)	223(2)	223(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> b c a
Crystal size (mm)	0.09×0.20×0.26	0.20×0.60×0.80	0.25×0.75×0.78	0.20×0.60×0.60	0.15 × 0.30× 0.70
<i>a</i> (Å)	11.5601(11)	11.4354(3)	11.4805(7)	11.5232(2)	12.3799(10)
<i>b</i> (Å)	12.3884(15)	12.4814(3)	12.4211(12)	12.4364(2)	23.828(2)
<i>c</i> (Å)	17.6788(17)	19.2857(5)	17.5400(9)	17.5822(3)	39.619(3)
α (°)	84.091(7)	99.150(2)	84.532(6)	84.5038(14)	90
β (°)	84.872(6)	101.425(2)	82.510(5)	82.1385(15)	90
γ (°)	86.887(9)	92.695(2)	87.367(6)	87.1562(14)	90
<i>V</i> (Å ³)	2490.2(5)	2654.97(13)	2467.2(3)	2482.80(8)	11687.4(17)
<i>Z</i>	2	2	2	2	8
<i>D</i> _{calcd.} (mg cm ⁻³)	1.244	1.250	1.174	1.257	1.200

Absorption	1.262	1.842	1.266	1.419	1.095
coefficient (mm ⁻¹)					
<i>F</i> (000)	984	1052	940	990	4472
θ range (°)	3.00-27.50	3.15-29.43	3.29-29.43	3.33-29.41	3.09-25.00
Reflections	20400/9189	25731/9854	22943 / 9141	95541 / 9195	53353 / 10077
collected / unique	[R(int) = 0.0599]	[R(int) = 0.0625]	[R(int) = 0.0652]	[R(int) = 0.0262]	[R(int) = 0.1379]
Data/restraints/parameters	9189 / 1 / 520	9854 / 6 / 494	9141 / 1 / 523	9195 / 1 / 523	10077 / 6 / 585
Goodness-of-fit on <i>F</i> ²	1.122	1.041	1.030	1.087	1.239
final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0657	0.0374	0.0440	0.0210	0.1152
w <i>R</i> ₂ (all data)	0.0943	0.0904	0.0940	0.0630	0.1754

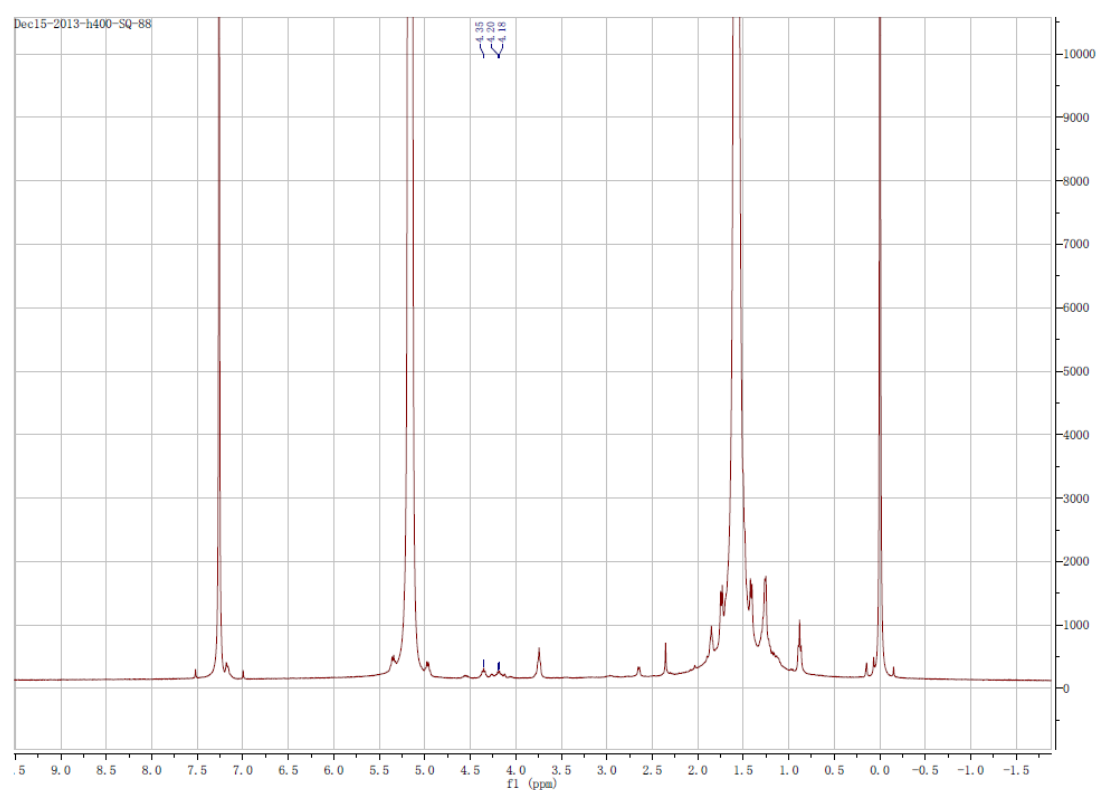


Figure 2. The ¹H NMR spectrum (400 MHz, CDCl₃) of the oligomer of L-lactide initiated by complex **1** after quenching by the addition of wet *n*-hexane. Polymerization conditions:[L-LA]₀/[I]₀ = 10, in toluene, 5 min, 25 °C.

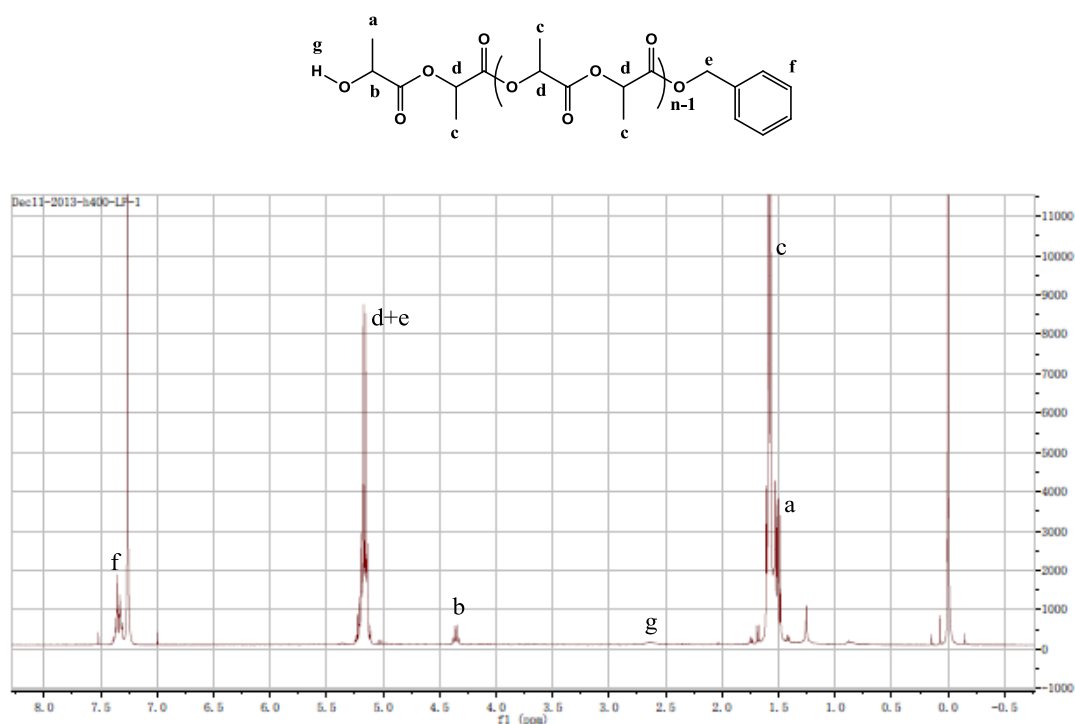


Figure 3. The ¹H NMR spectrum (400 MHz, CDCl₃) of the oligomer of L-lactide initiated by complex **1** in the presence of 100 equiv. of BnOH after quenching by the addition of ethanol containing 5% of HCl. Polymerization conditions: [L-LA]₀/[I]₀ = 2000, in toluene, 30 min, 25 °C.