Supporting Information

Yttrium and Aluminium Complexes bearing Dithiodiolate Ligands: Synthesis and Application in Cyclic Esters Polymerization

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Table of contents

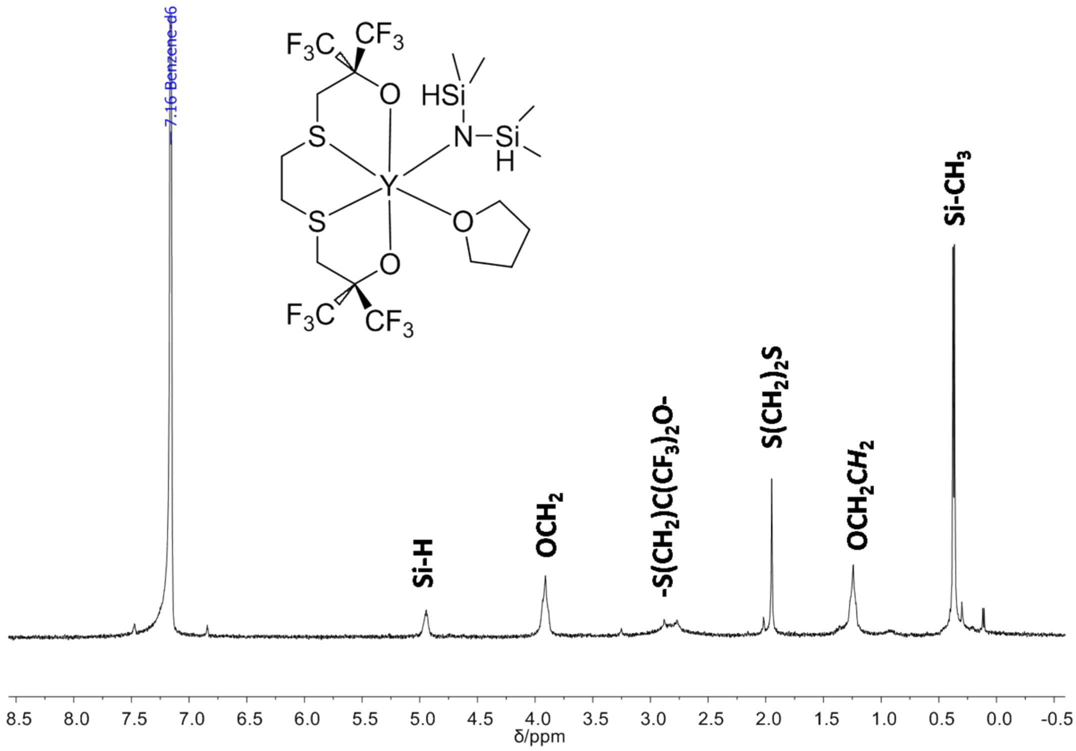


Figure S1. ^1H NMR (250 MHz, C_6D_6, RT) of complex **1**.

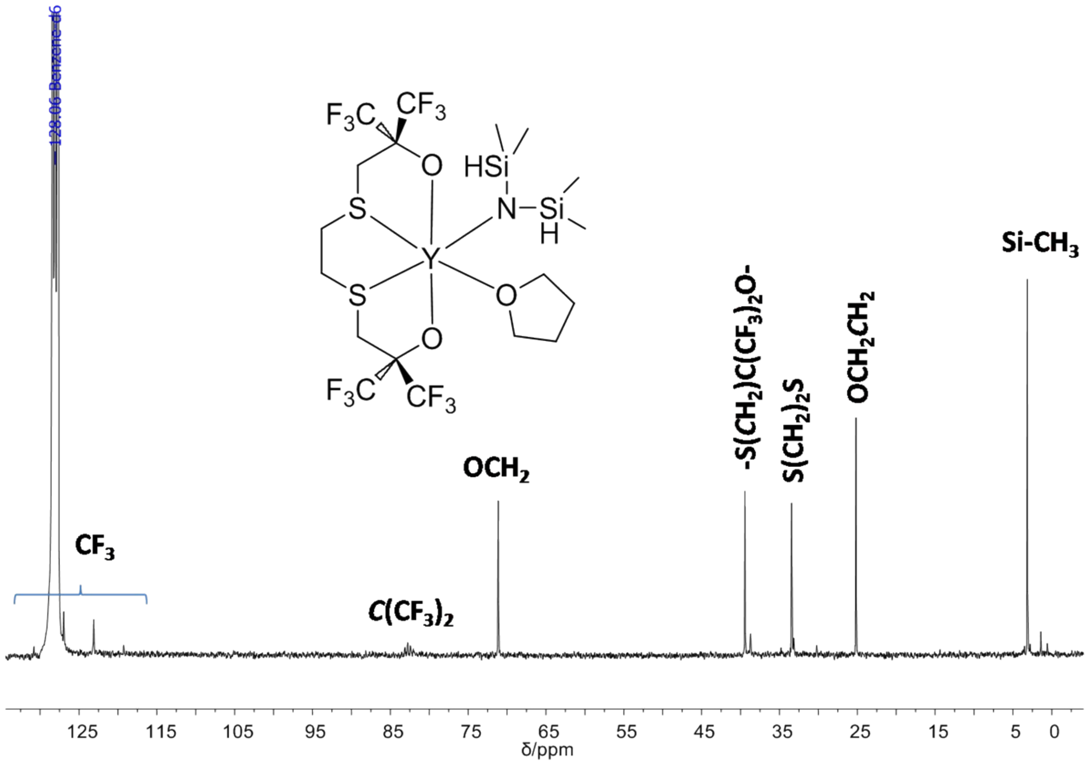


Figure S2. ^{13}C NMR (75.5 MHz, C_6D_6, RT) of complex **1**.

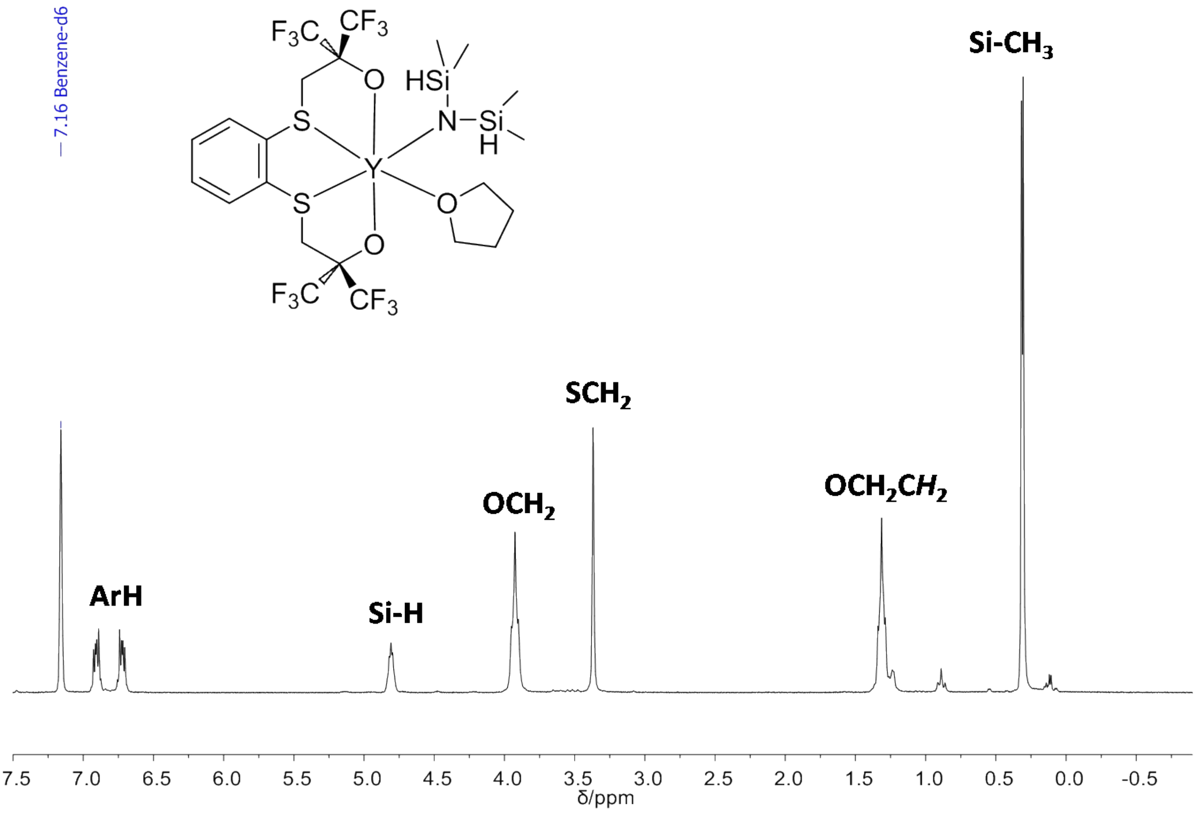


Figure S3. ^{1}H NMR (250 MHz, C_6D_6, RT) of complex **2**

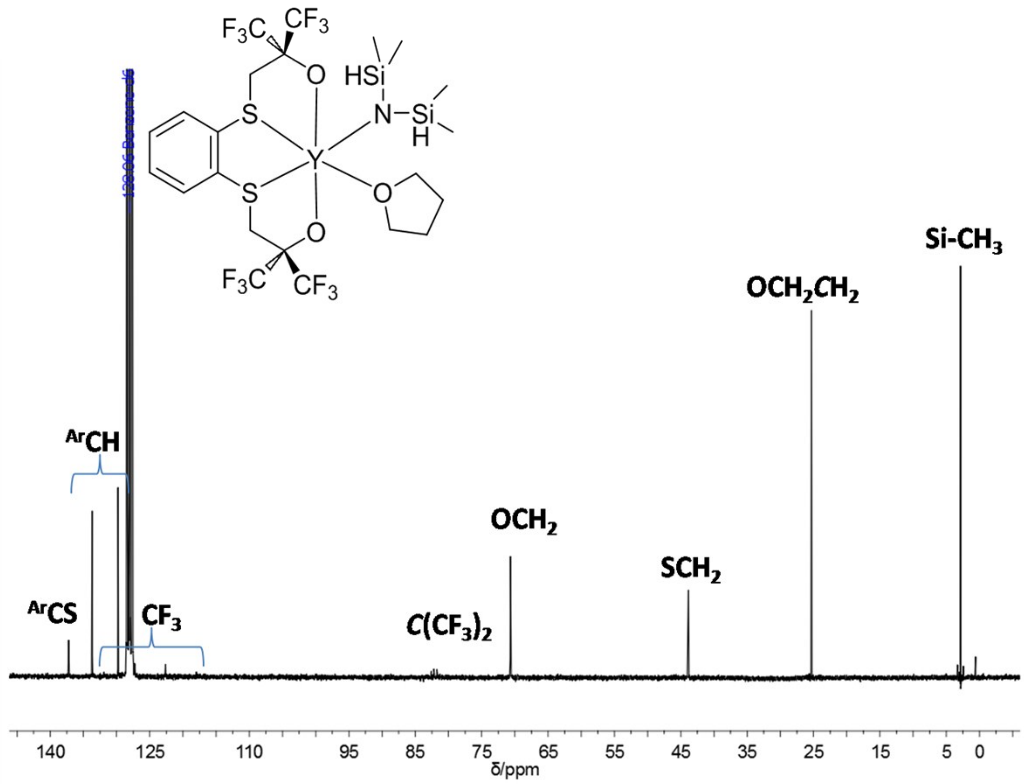


Figure S4. ^{13}C NMR (75.5 MHz, C_6D_6, RT) of complex **2**

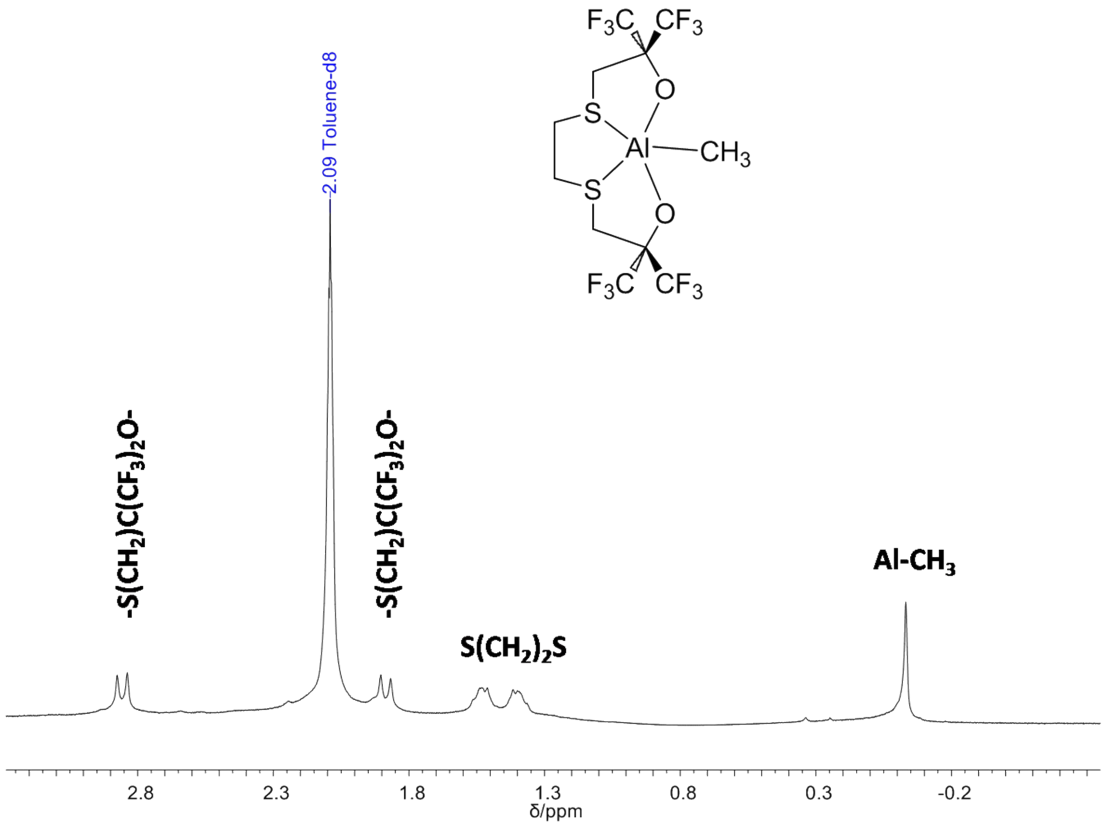


Figure S5. ^{1}H NMR (400 MHz, toluene-d_8, -40 °C) of complex **3**.

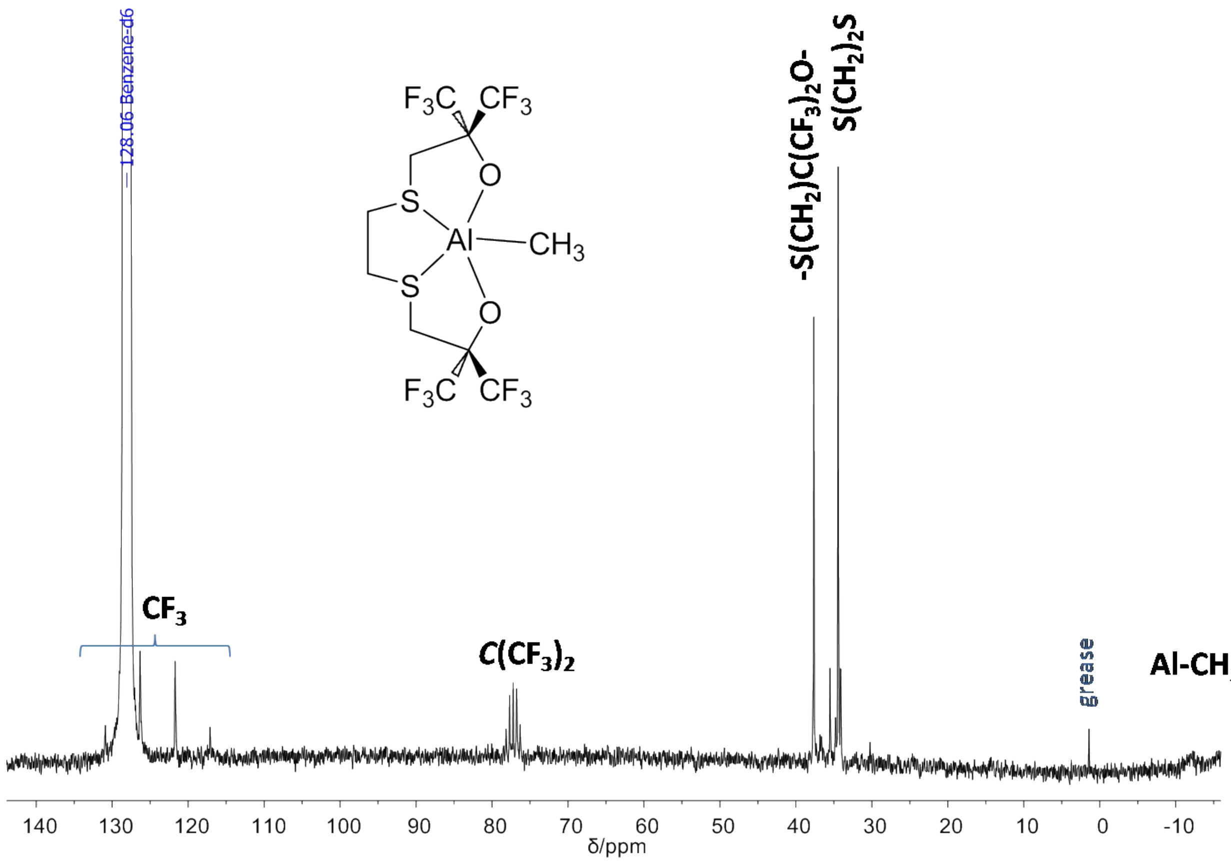


Figure S6. ^{13}C NMR (62.9 MHz, C_6D_6, RT) of complex **3**.

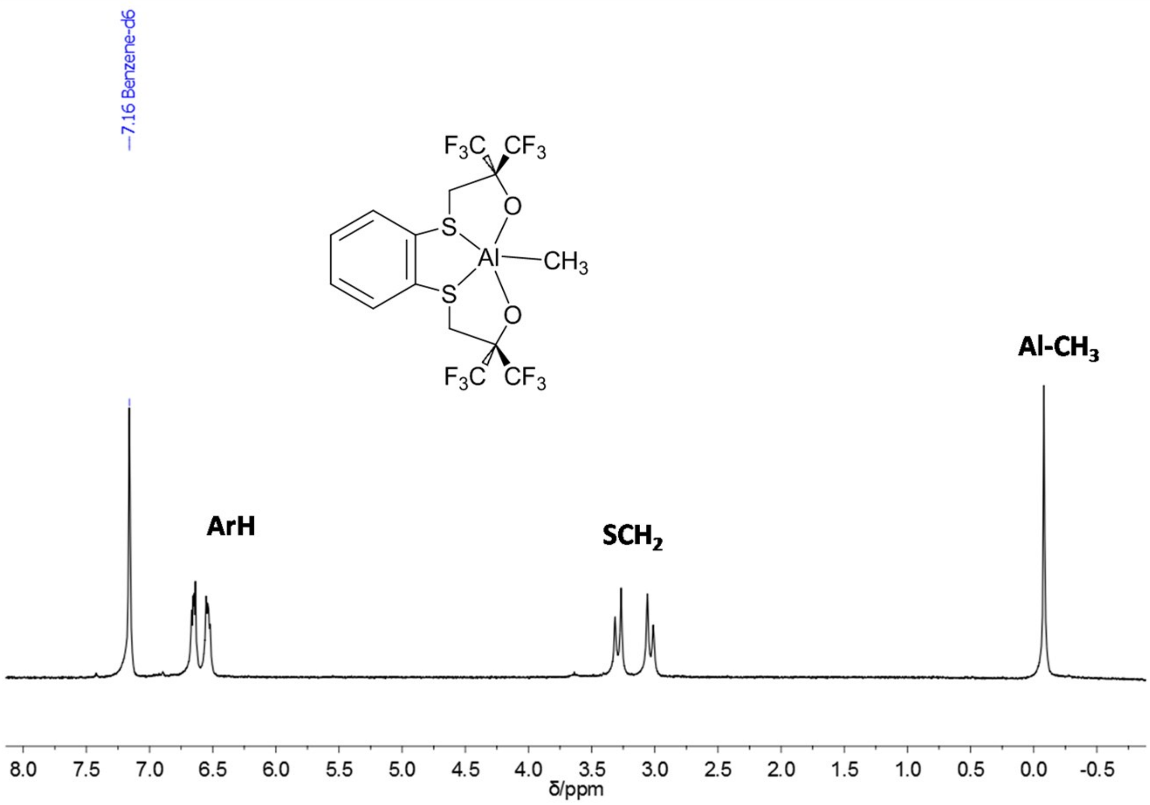


Figure S7. ^{1}H NMR (300 MHz, C_6D_6, RT) of complex **4**.

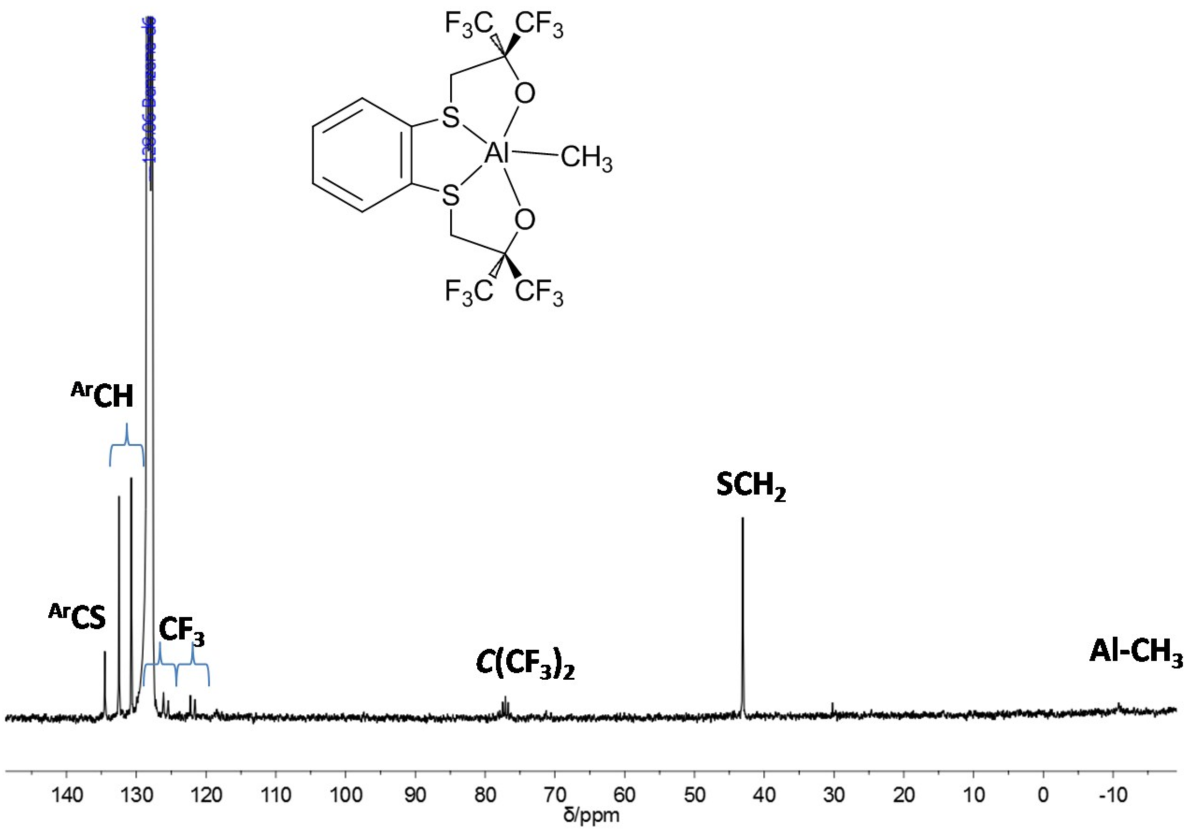


Figure S8. ^{13}C NMR (62.9 MHz, C_6D_6, RT) of complex **4**.

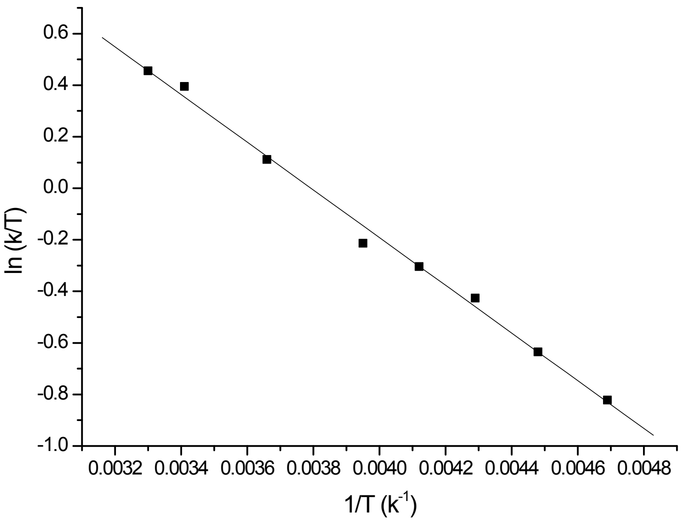


Figure S9. Eyring plot for the temperature-dependent fluxional process for **1**.
A = 3.50988 (0.10865)
B = -925.3615 (27.06213)
R = -0.99744 SD = 0.0359
$\Delta H^{\ddagger}$= 1.84 Kcal/mol $\Delta S^{\ddagger}$= -40.24 cal/mol K
$\Delta G^{\ddagger}$= 13.8 Kcal/mol

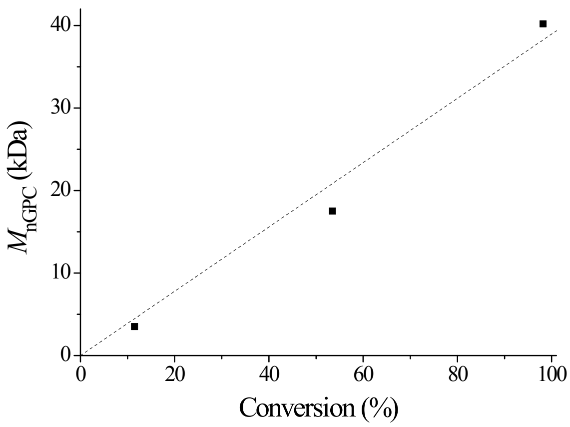


Figure S10. Plot of $M_{n,GPC}$ of the polymer versus conversion. Polymerization of ε-caprolactone by **1** + ^{i}PrOH (1 equiv) at 70 °C.

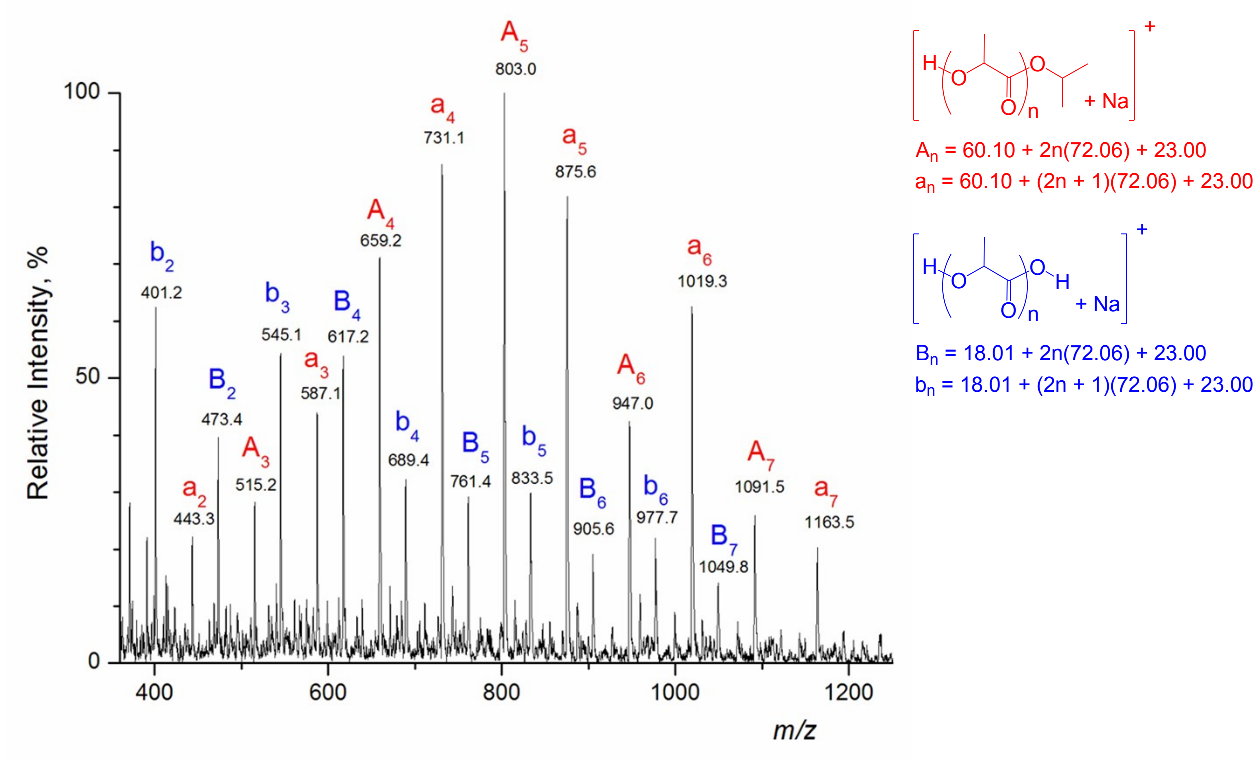


Figure S11. ESI mass spectrum of the oligomerization product of *rac*-lactide by **1** (Table 3, run 13).

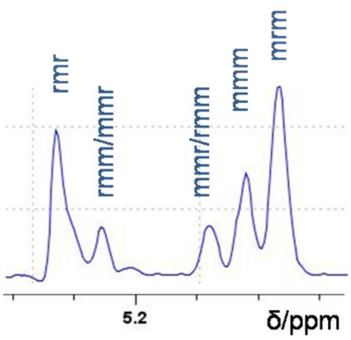


Figure S12. Homonuclear decoupled ^{1}H NMR (600 MHz, $CDCl_3$, RT) of the methine region of heterotactically-enriched PLA prepared with complex **1** (Table 2, run 10).

Table S1. Selected bond lengths (Å) and angles (°) for **2.**

Y1 - O1	2.153(5)	O1 - Y1 - O2	109.26(19)	O1 - Y1 - S1	65.64(13)
Y1 - O2	2.122(5)	O1 - Y1 - O3	83.36(17)	O2 - Y1 - S1	109.22(15)
Y1 - N1	2.253(6)	O2 - Y1 - O3	81.84(18)	O3 - Y1 - S1	148.94(11)
Y1 - O3	2.358(4)	N1 - Y1 - O1	131.0(2)	O1 - Y1 - S2	125.82(13)
Y1 - S1	2.980(2)	N1 - Y1 - O2	118.1(2)	O2 - Y1 - S2	67.02(13)
Y1 - S2	3.046(3)	N1 - Y1 - O3	91.26(19)	O3 - Y1 - S2	142.32(12)
Si1 - N1	1.715(6)	N1 - Y1 - S1	107.27(15)	S1 - Y1 - S2	65.72(6)
Si2 - N1	1.708(6)	N1 - Y1 - S2	85.61(16)	Si2 - N1 - Y1	122.3(3)
Y1···Si1	3.230(3)	Si2 - N1 - Si1	129.2(4)	Si1 - N1 - Y1	108.2(3)
Y1···Si2	3.480(3)				

Table S2. Tetrad probabilities based on Bernoullian Statistic (Th) for a P_r of 0.72 and experimental values (Exp) as obtained by NMR analysis.

Tetrad	**Formula**	**Exp**	**Th**
[*mmm*]	$P_m^2+P_rP_m/2$	0.18	0.18
[*mmr*]	$P_rP_m/2$	0.10	0.10
[*rmm*]	$P_rP_m/2$	0.09	0.10
[*rmr*]	$P_r^2/2$	0.26	0.26
[*mrm*]	$(P_r^2+P_rP_m)/2$	0.37	0.36

Table S3. Polymerization of ε-caprolactone by **4** + ^{i}PrOH. Relationship between M_n of the obtained polymer and the initial mole ratio $[CL]_0$/[**4**-^{i}PrOH]

Run	[ε-CL]/[Al]	Yield[b] (%)	$M_{n,th}$[c] (kDa)	M_n[d,,e] (kDa)	M_w/M_n[d]
14	25	98	2.8	3.1	1.14
15	50	72	4.1	3.5	1.16
16	250	99	28.2	25.7	1.21
17	500	80	45.7	50.2	1.66

[a]**Polymerization conditions:** precatalyst **4**: 10 µmol; ^{i}PrOH: 10 µmol; 10 µL of a 0.1 M toluene solution; toluene: 2 mL; temperature: 70°C; polymerization time: 6h. [b] Determined by ^{1}H NMR ($CDCl_3$, RT). [c]Theoretical molecular masses. [d]Molecular masses and their dispersities as determined by GPC (THF, 35°C) vs. polystyrene standards and corrected by 0.56 factor.

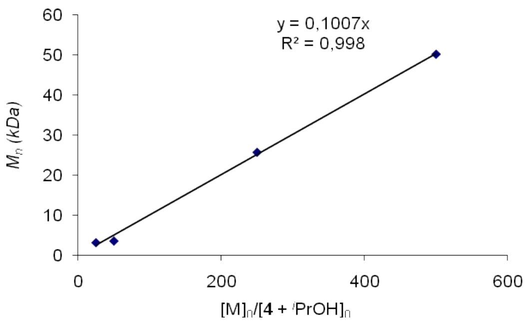
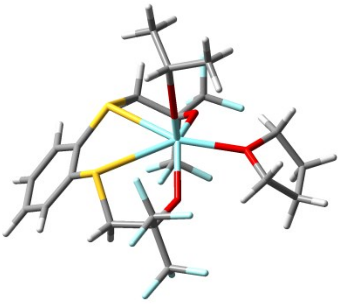


Figure S13. Relationship between M_n of the obtained PCL and the initial mole ratio $[CL]_0$/[**4**-^{i}PrOH] for the polymerization of ε-CL (data reported in Table S3)

Cartesian coordinates and energies of calculated structures

L^{2}YOiPr(THF)



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Multiplicity = 1

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F	4.067197	-2.078685	-1.476364
F	5.208499	-0.214372	-1.222420
F	1.121655	0.819778	-1.353359
F	2.421159	-0.365751	-2.657950
F	3.117824	1.570169	-1.904171
F	-3.923610	-0.492694	-2.443161
F	-4.390326	1.638405	-2.172527
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F	-4.350372	-1.124197	0.153519
F	-5.077163	0.940103	0.346623
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H	0.333236	6.341675	-0.666768
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H	2.763487	5.845048	-0.258163
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E+ ZPE = -3147.288865 A.U.
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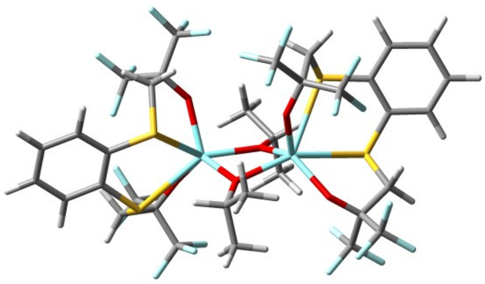
[L^{2}YOiPr]$_2$



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F	2.845269	5.145960	1.246068
F	4.807347	1.469526	0.579077
F	4.327453	2.289955	2.549437
F	5.069832	3.616881	0.963947
F	4.374966	-3.148830	3.215326
F	6.013729	-3.657798	1.841592
F	5.645677	-1.563630	2.398859
F	2.493102	-3.718392	-0.486403

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F	4.265905	-4.867178	0.125246
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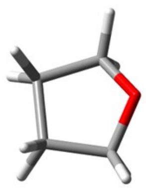
THF



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C	-0.696409	-4.804523	-2.175255
H	1.064531	-3.569148	-1.701605
H	0.206232	-4.147717	-0.231149
C	-1.585944	-3.878955	-3.062014
H	-2.072821	-1.756187	-2.532219
H	-0.425565	-2.012793	-3.206654
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H	-0.003892	-5.425386	-2.769671
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E+ ZPE = -232.333437 A.U.
G = -232.361750 A.U.