Supporting Information

Anilidopyridyl-pyrrolide and -indolide Group 3 Complexes: Highly Active Initiators for the Ring-Opening Polymerization of *rac*-Lactide

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1. Synthesis of percursors A and B. Experimental Details

Compound A. Palladium(II)acetate (50 mg, 0.2 mmol), 2-dicyclohexylphosphino-2,6-dimethoxybiphenyl (0.186 g, 0.4 mmol) N-(t-butoxycarbonyl)-indole-2-boronic acid (1.24 g, 4.75 mmol), 6-bromo-2-pyridine-carboxaldehyde (0.71 g, 3.82 mmol), and K_3PO_4 (2.233 g, 10.5 mmol) were mixed in 10 mL of distilled n-butanol in a 50 mL of schlenk flask under nitrogen atmosphere. The resulting mixture was heated to 82 ^oC and stirred for 2 h. The reaction was followed by TLC. The reaction mixture was allowed to cool to room temperature and then filtered. The solvent was distilled off by rotary evaporation. The crude product was purified via no flash column chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent, obtaining the product as white solid (yield: 86 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ =10.11 (s, 1H; *H*C=O), 8.19 (d, *J*(H,H) = 8.36 Hz, 1H; indole-*H*), 7.95 (m, 2H; indole-*H*), 7.75 (m, 1H; indole-*H*), 7.62 (d, *J*(H,H) =7.3Hz, 1H; Py-*H*), 7.40 (t, 1H; Py-*H*), 7.30 (d, *J*(H,H) = 7.3Hz, 1H; Py-*H*), 6.87 (s, 1H; indole-*H*), 1.35ppm (s, 9H; C(C*H*$_3$)$_3$); ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ=193.72(*C*O), 154.14, 152.34, 150.07, 138.25, 138.04, 137.32, 128.96, 127.62, 125.66, 123.38, 121.42, 120.08, 115.37, 112.37, 84.01(*C*(CH$_3$)$_3$), 27.90 ppm (C(*C*H$_3$)$_3$).

Compound B. To a solution of tert-butyl 2-(6-formylpyridin-2-yl)-1H-indole-1-carboxylate (0.86 g, 2.67mmol) in toluene (20 mL), silica gel 60 (1.60 g, 10 equiv.) was added. After the mixture was refluxed and stirred for 1 h, followed by TLC, the reaction mixture was allowed to cool to room temperature. 2,6-Diisopropylaniline (0.50 g, 2.82 mmol) and molecular sieves were added into the mixture. The resulting mixture was then refluxed for 1 h, followed by TLC. After cooled to room temperature, the solvent was distilled off by rotary evaporation. The crude product was purified via no flash column chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent. After removals of the solvent, affording a light yellow solid (yield: 78 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ = 9.61 (s, 1H; indole-N*H*), 8.36 (s, 1H; *H*C=N), 8.14 (dd, *J*(H,H) = 1.4 Hz, 1H; Ar-*H*), 7.90 (m, 2H; Ar-*H*), 7.67 (d, *J*(H,H) = 8.1Hz, 1H; Ar-*H*), 7.45 (dd, *J*(H,H) = 0.72Hz, 1H; Ar-*H*), 7.24 - 7.09 (m, 6H; Ar-*H*), 3.00 (sept, 2H; C*H*(CH$_3$)$_2$), 1.20 ppm (d, *J*(H,H) = 6.9 Hz, 12H; CH(C*H*$_3$)$_2$); ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 163.16, 153.91, 150.52, 148.72, 137.52, 137.42, 136.71, 136.30, 129.29, 124.68, 123.62, 123.27, 121.56, 121.47, 120.45, 119.70, 111.65, 101.29, 28.18(*C*H(CH$_3$)$_2$), 23.67ppm (CH(*C*H$_3$)$_2$).

2. NMR of Organic and Organometallic Species

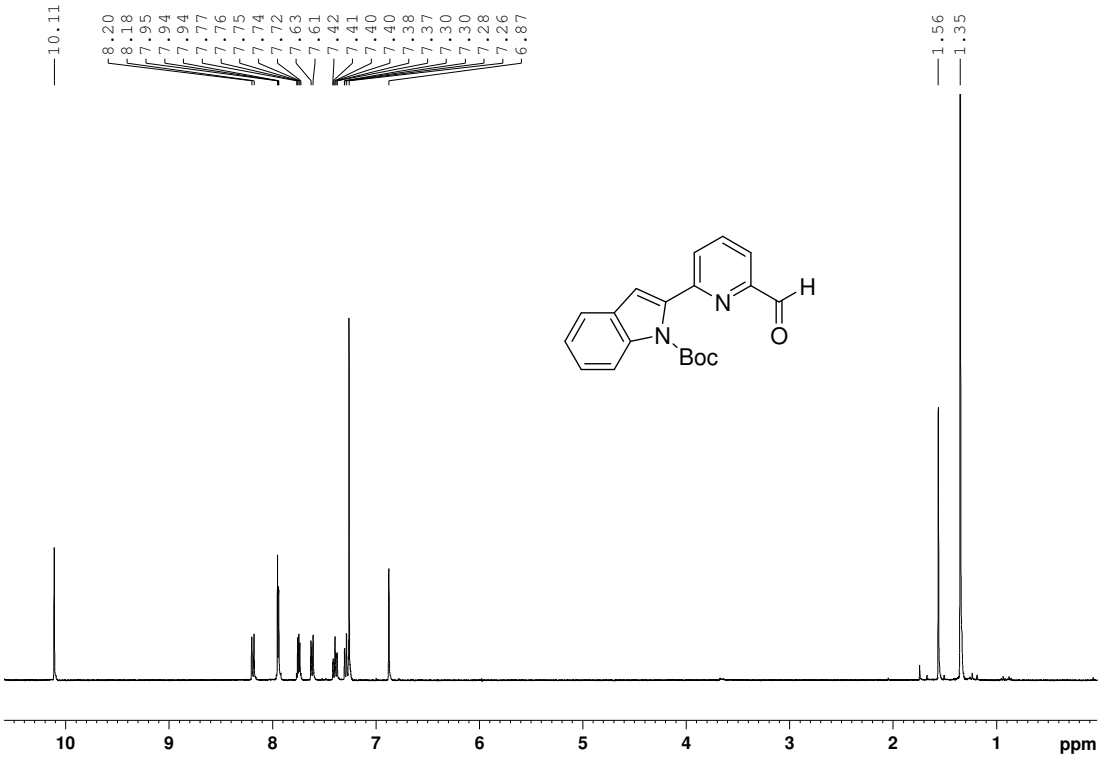

Figure S1. 1H NMR spectrum of compound A (400 MHz, $CDCl_3$; 25 °C)

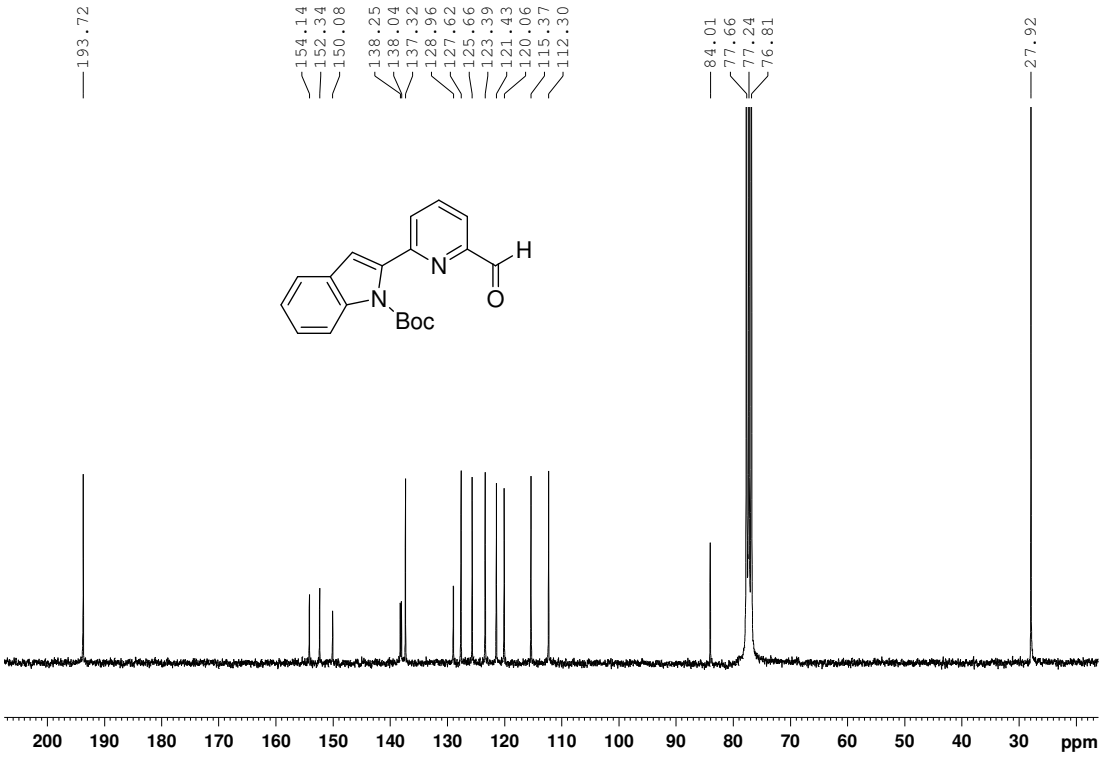

Figure S2. ^{13}C NMR spectrum of compound **A** (300 MHz, $CDCl_3$, 25°C)

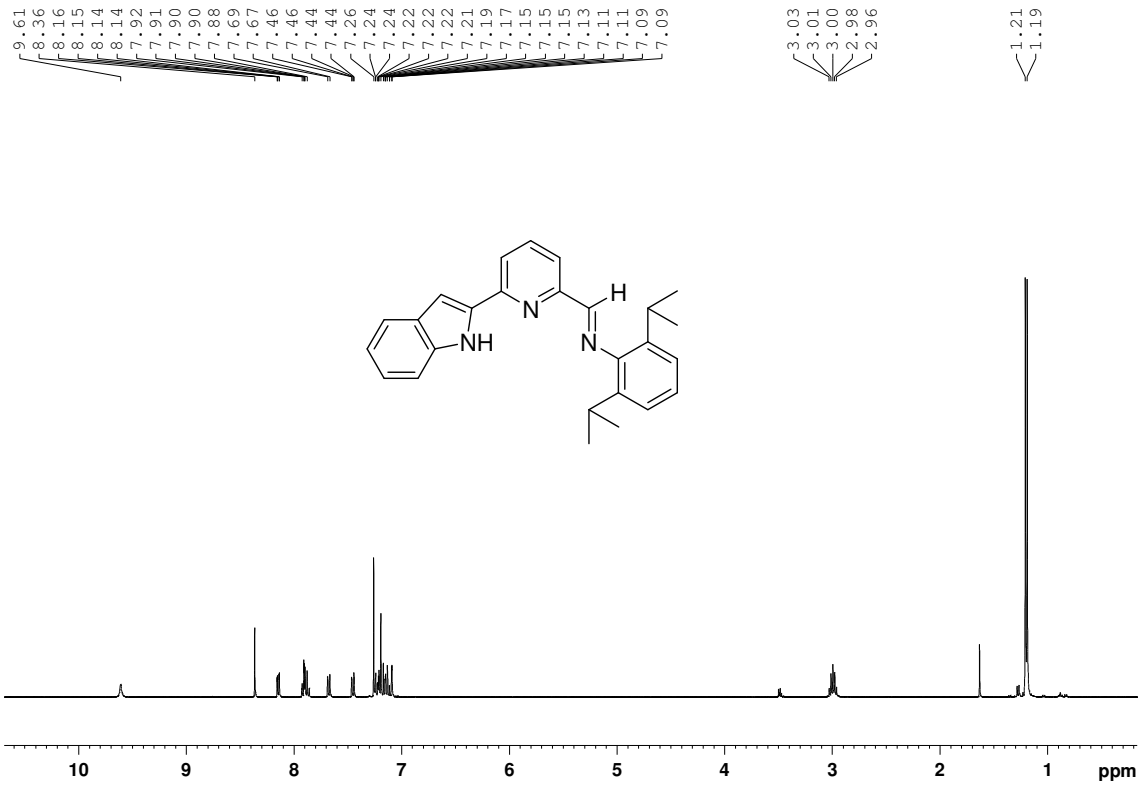

Figure S3.[1]H NMR spectrum of compound **B** (400 MHz, $CDCl_3$, 25°C)

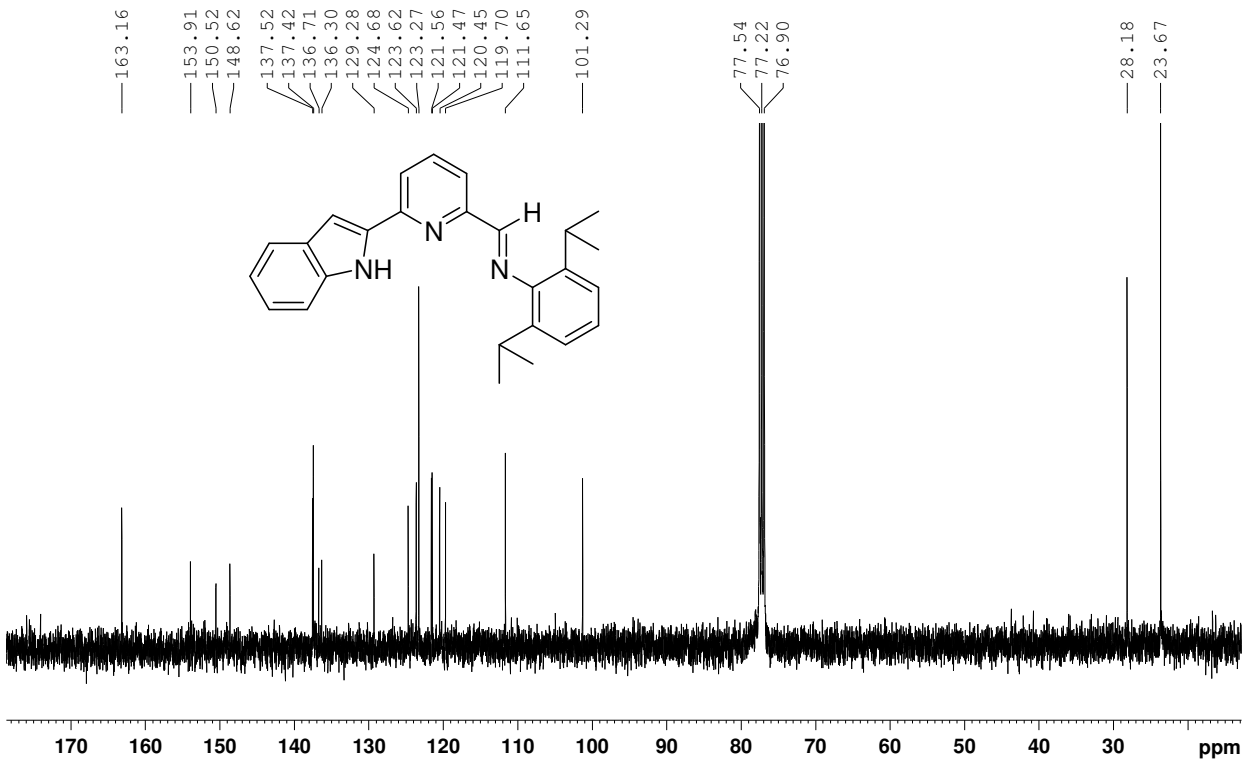

Figure S4.[13]C NMR spectrum of compound **B** (400 MHz, $CDCl_3$, 25°C)

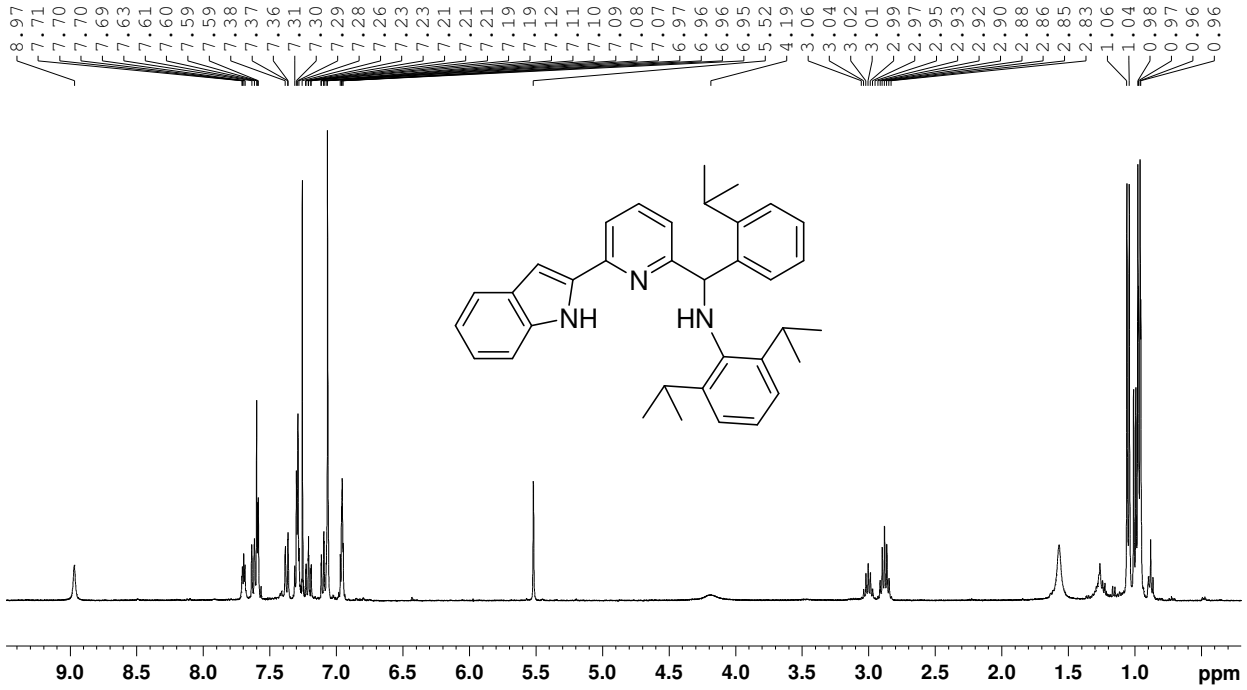

Figure S5. ^{1}H NMR spectrum of proligand $\mathbf{H_2L^2}$ (400 MHz, $CDCl_3$, 25°C)

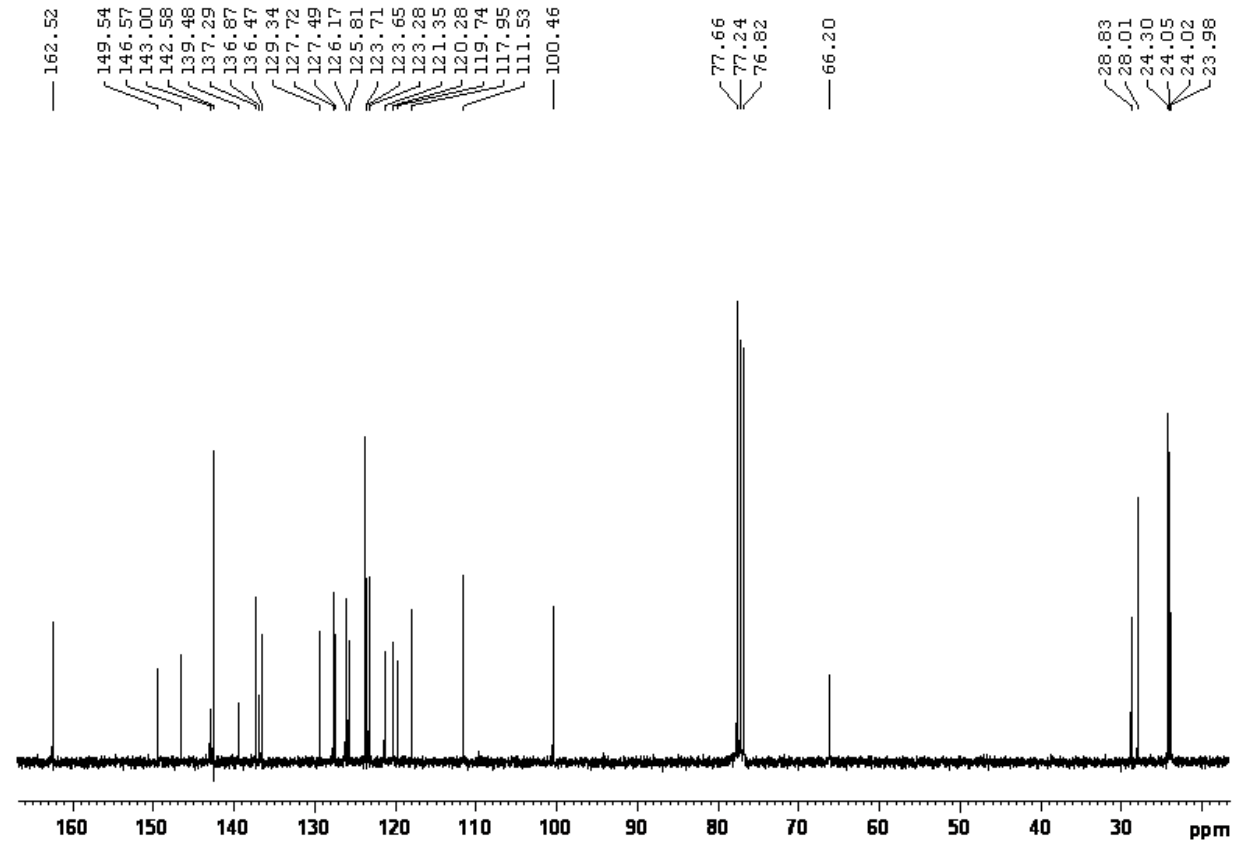

Figure S6. ^{13}C NMR spectrum of proligand $\mathbf{H_2L^2}$ (400 MHz, $CDCl_3$, 25°C)

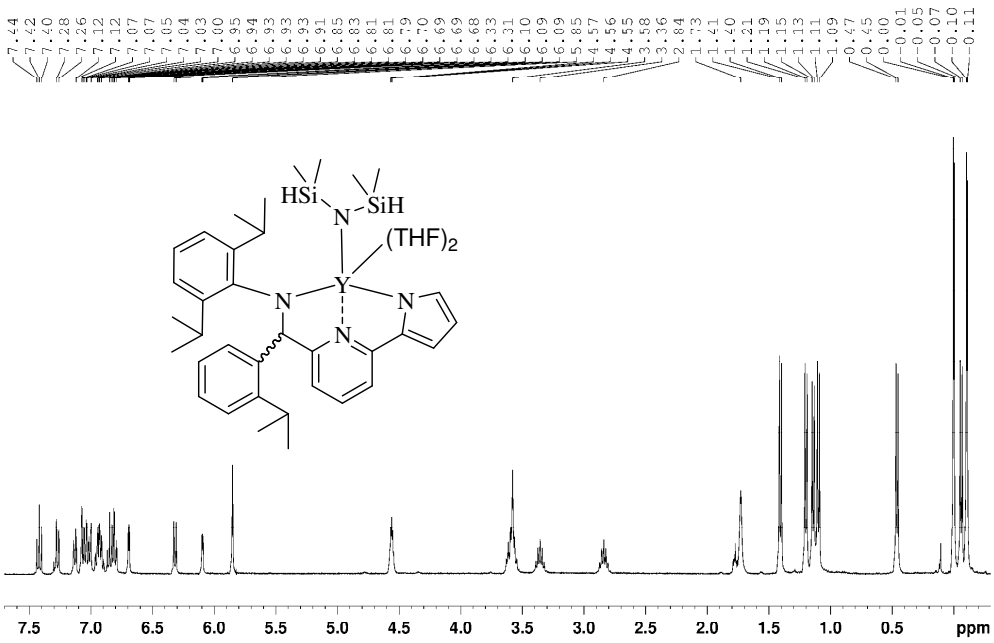

Figure S7. ^{1}H NMR spectrum of Complex **1** (400 MHz, [D_8]THF, 25 ^{0}C)

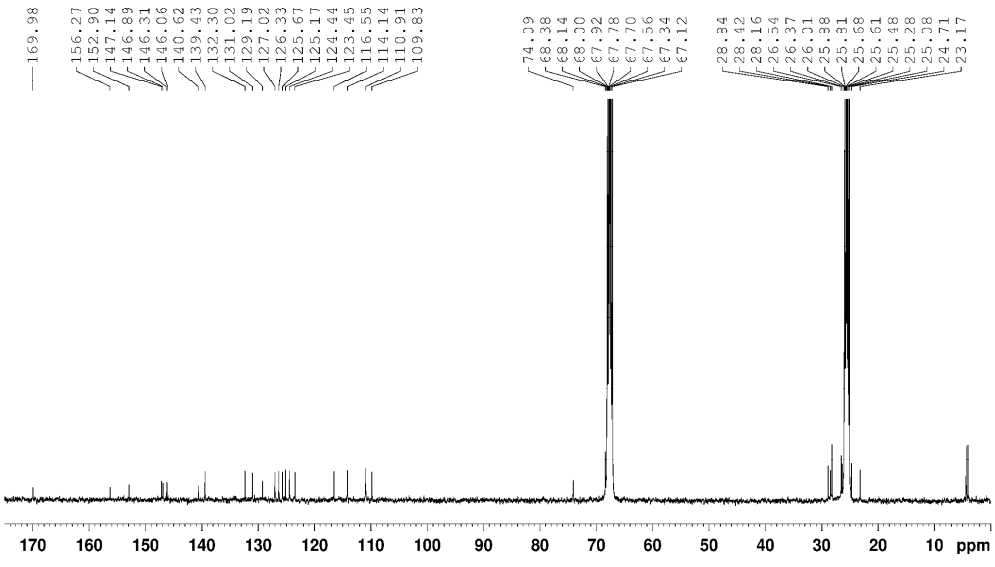

Figure S8.^{13}C NMR spectrum of Complex **1** (100.62 MHz; [D_8]THF, 25 ^{0}C)

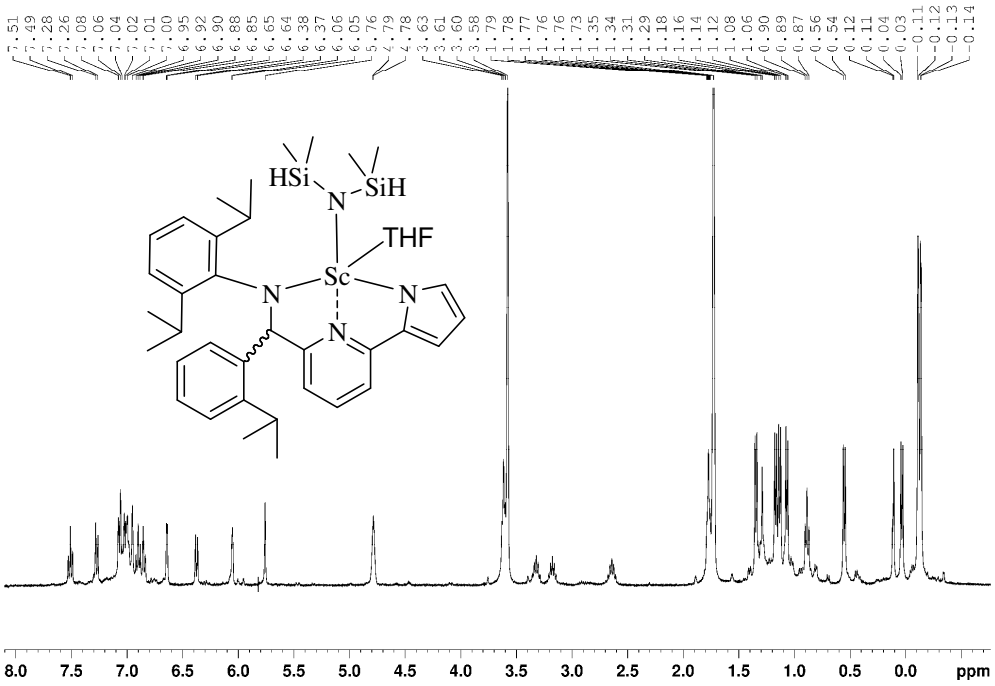

Figure S9.[1]H NMR spectrum of Complex **2**(400MHz, [D_8]THF, 25^{0}C, * pentane, grease)

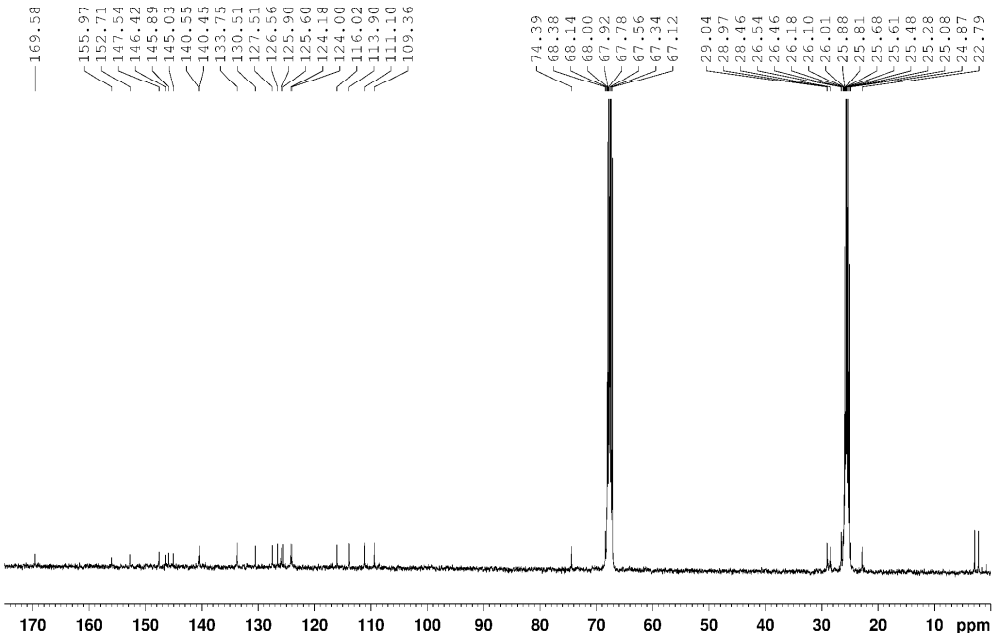

Figure S10.[13]C NMR spectrum of Complex **2** (100.62 MHz, [D_8]THF, 25 ^{0}C)

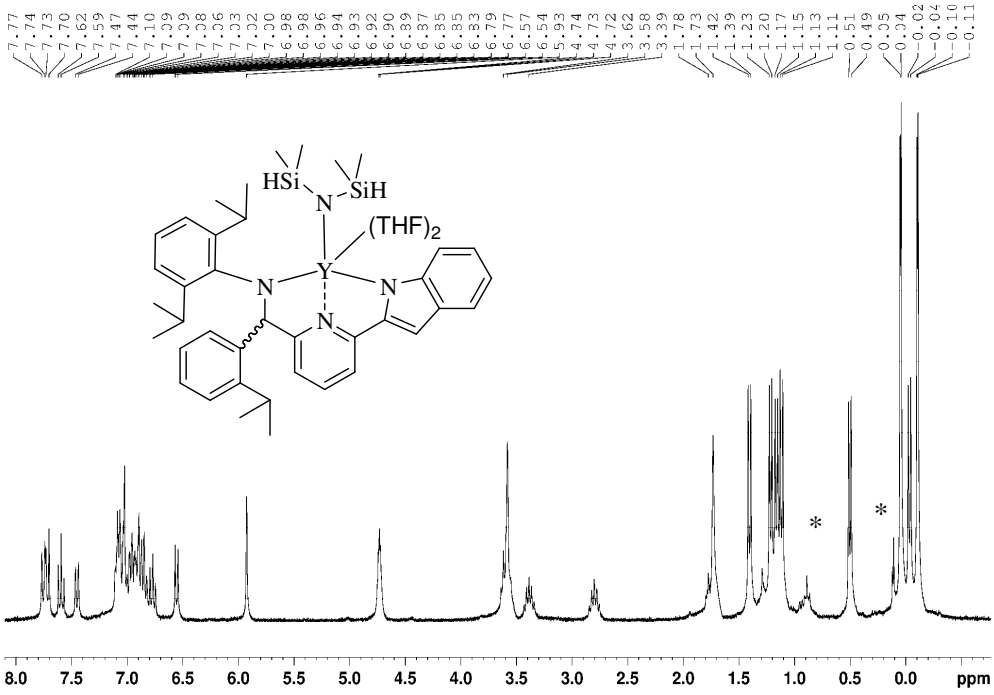

Figure S11. ^{1}H NMR spectrum of Complex **3** (300MHz, [D_8]THF, 25^{0}C; * pentane, grease)

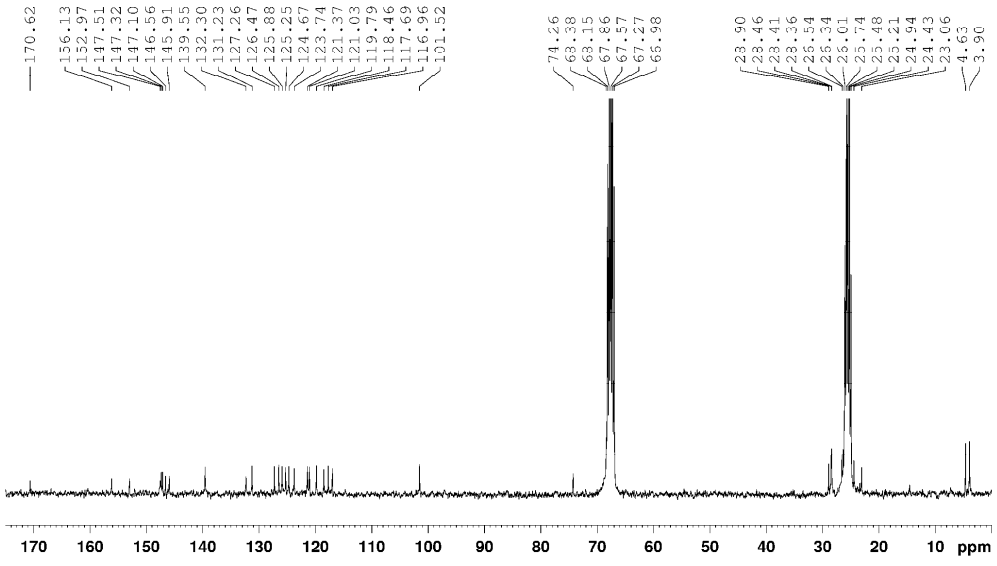

Figure S12. ^{13}C NMR spectrum of Complex **3** (75.47 MHz; [D_8]THF, 25 ^{0}C)

3. Table S1. ROP of rac-Lactide by Initiator 1: Effect of the Monomer-to-Initiator Ratio

run[a]	$[I]_0$	[Mon]/ $[I]_0$	Time[b] (min)	Conv %	Yield (g)	Mn_{th}[c] ($\times 10^3$)	Mn_{GPC}[d] (($\times 10^3$)	PDI	P_r[e]
1	1	20	120	100	0.028	2.9	3.5	1.51	57
2	1	100	20	95	0.146	13.7	14.1	2.01	73
3	1	200	5	89	0.224	25.7	25.4	2.23	77
4	1	400	5	98	0.575	56.5	45.9	2.00	74

[a] General conditions: $[I_0]$ = 0.5 Mm; 2 mL of THF; [b] Reaction times were not optimized. [c] Calculated Mn of PLA (g/mol) = 144.14 × ([rac-LA]/$[I_0]$)×conversion (rac-LA)%. [d] Experimental Mn values (corrected using the Mark–Houwink factor of 0.58) were determined by GPC analysis in THF using polystyrene standards. [e] P_r value is determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum.

4. ^{1}H NMR analysis of polymer chain end groups

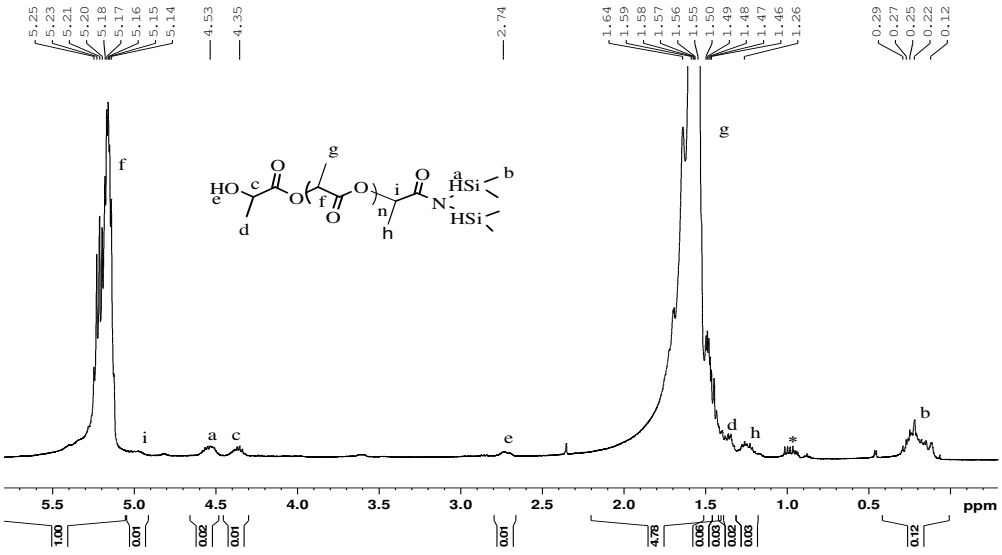

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the oligomers of rac-lactide by initiator **1** (run 1 in Table S1).

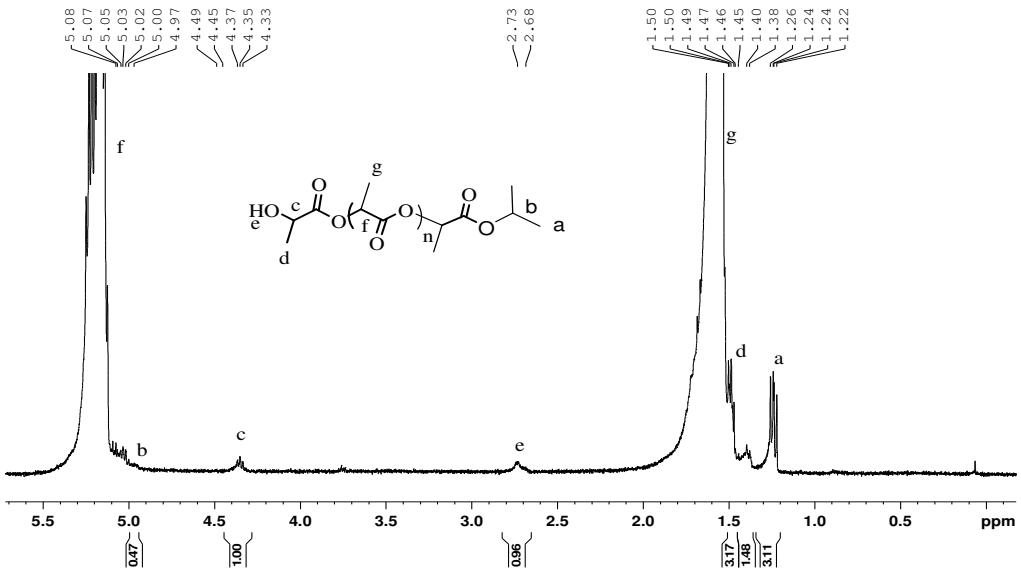

Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the oligomers of rac-lactide by initiator **1** in the presence of 10 equivalents of 2-propanol (run 18 in Table 3).

5. Table S2. Crystallographic Data for 1 and 2

	1	**2**
Chemical formula	$C_{43}\ H_{65}\ N_4\ O_2\ Si_2\ Y_1 \cdot 0.5(C_6H_{14})$	$C_{39}\ H_{57}\ N_4\ O_1\ Si_2\ Sc_1$
Crystal size, mm	0.5 × 0.6 × 0.6	0.1 × 0.2 × 0.3
Crystal habitus, colour	Prism, orange	Prism, yellow
Formula weight	858.17	699.03
Temperature (K)	173	173
λ (Å)	0.71069	0.71069
Crystal system	monoclinic	triclinic
Space group	*P21/c*	*P-1*
a (Å)	12.120(2)	11.195(1)
b (Å)	21.592(2)	13.546(1)
c (Å)	20.208(1)	13.666(1)
α (°)	90	70.99(1)
β (°)	117.44(2)	89.48(1)
γ (°)	90	84.36(1)
Volume ($Å^3$)	4693.5(1)	1949.4(3)
Z	4	2
D_{calcd} ($g \cdot cm^{-3}$)	1.214	1.191
μ (mm^{-1})	1.333	0.285
F(000)	1836	752
Theta range (°)	3.05, 27.51	3.04, 27.50
Reflections collected	37760	33262
Unique observed reflections	10727 [R(int) = 0.0755]	8912 [R(int) = 0.0695]
Goodness-of-fit on F^2	1.018	1.094
Data/parameters	10727/507	8912/434
R1[a], wR2[b] [I>2σ(I)]	0.0641, 0.1253	0.0625, 0.1419
R1[a], wR2[b] (all data)	0.1327, 0.1514	0.1203, 0.1628
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.604, -0.530	0.472, -0.362

[a] $R_1 = \Sigma||Fo|-|Fc|/\Sigma|Fo|$.

[b] $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$