Supporting Information

Stereo Selective Polymerization of *rac*-Lactide Catalyzed by Zwitterionic Calcium complexes

Na Liu, [⊥b] Doudou Liu, [⊥c] Bo Liu,*[a] Hao Zhang*[c] and Dongmei Cui[a]

[a.] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, 5625 Renmin Street, Changchun, 130022, China.*

[b.] *Key Laboratory of Rare and Scattered Elements, Liaoning University, Shenyang, 110036, China.*

[c.] *College of Chemistry & Chemical Engineering, Inner Mongolia University, Hohhot, 010021, China.*

* Corresponding author. E-mail: liubo@ciac.ac.cn. Fax: +86 431 85262774; Tel: +86 431 85262774.

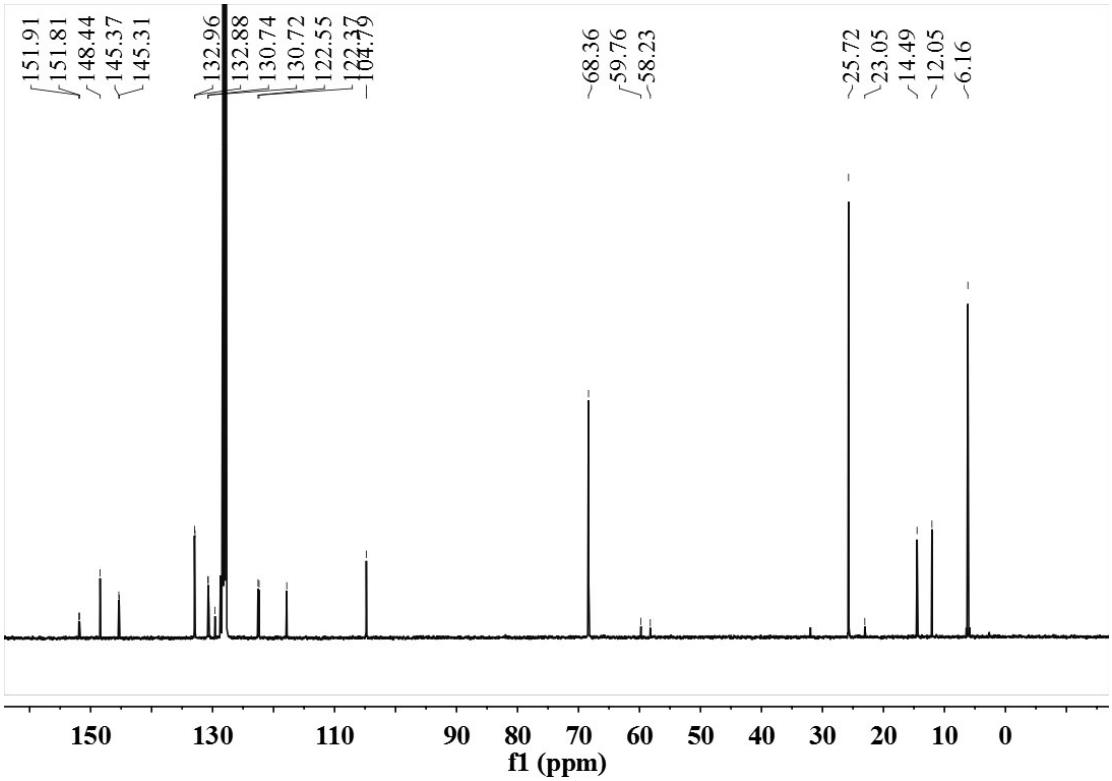

Fig. S1 ^{13}C NMR spectrum (C_6D_6, 100 MHz, 25 °C) of calcium complex **1**.

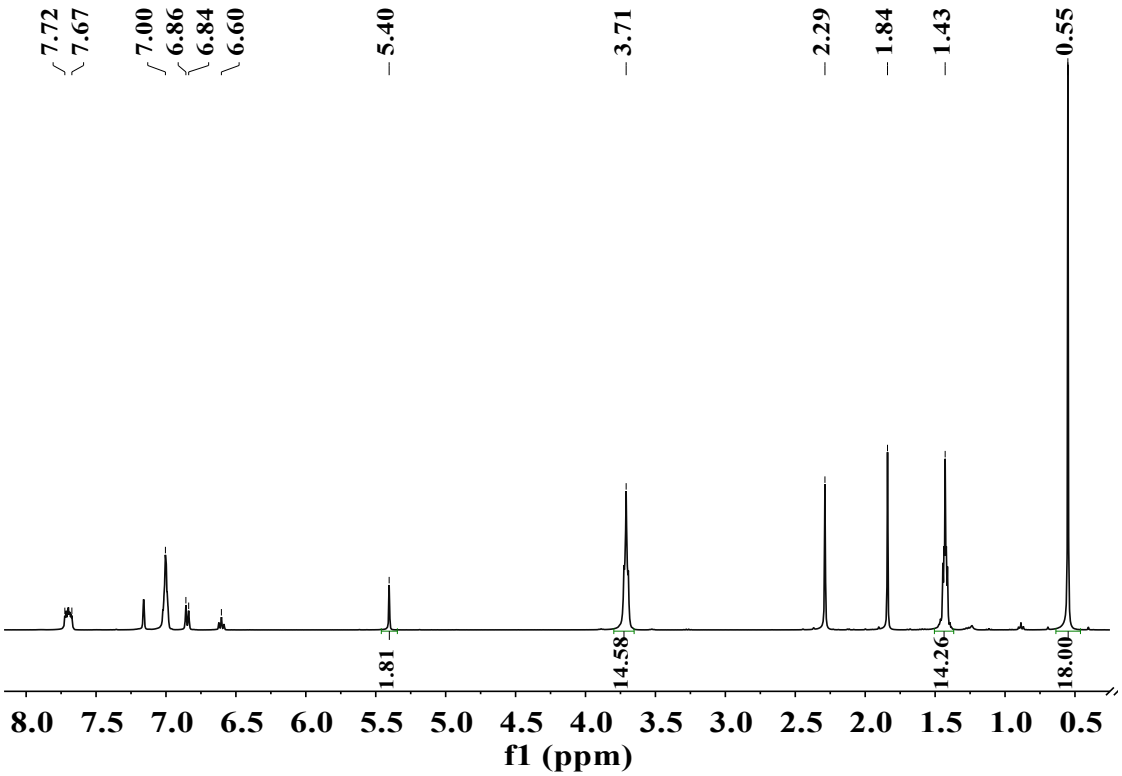

Fig. S2 ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25 °C) of calcium complex **1**.

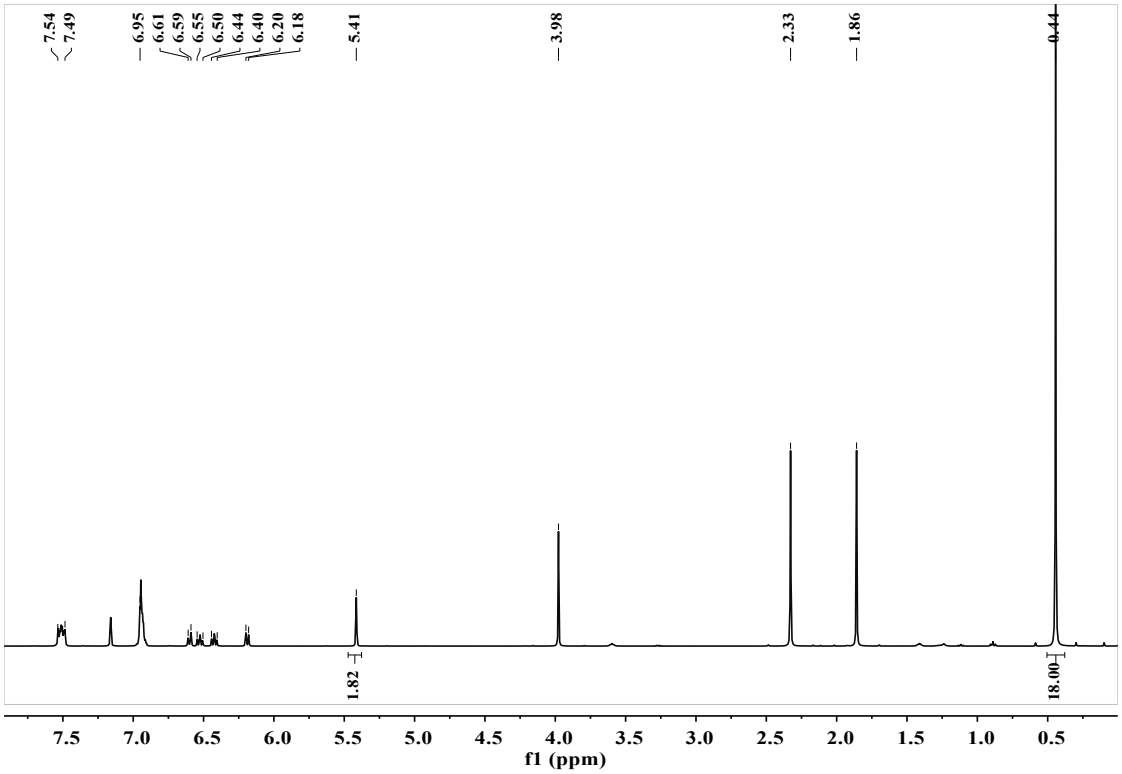

Fig. S3 ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25 ^{o}C) of calcium complex **2**.

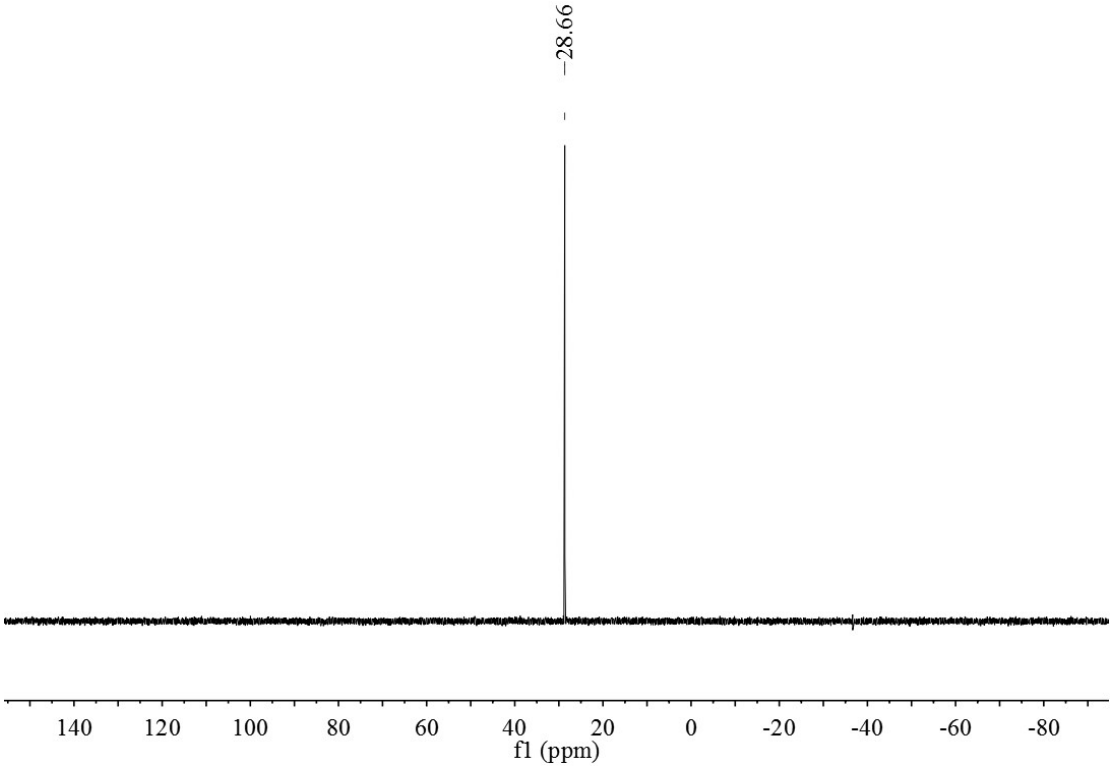

Fig. S4 ^{31}P NMR spectrum (C_6D_6, 162 MHz, 25 ^{o}C) of calcium complex **2**.

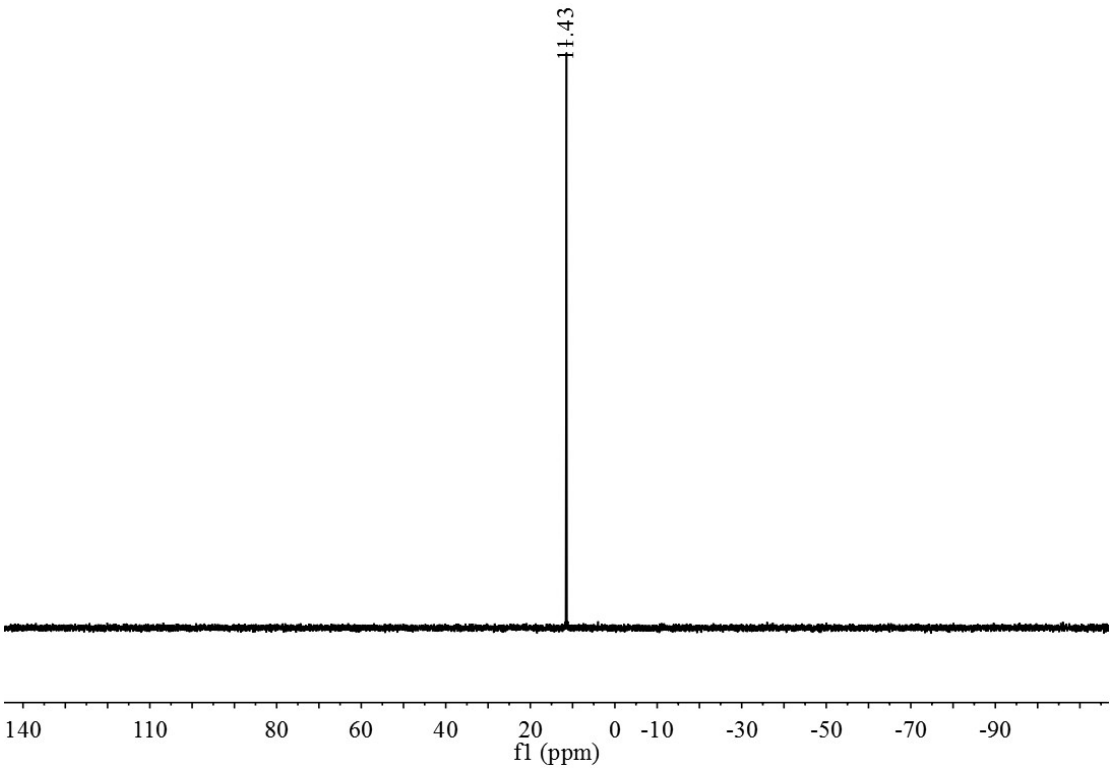

Fig. S5 ^{31}P NMR spectrum (C_6D_6, 162 MHz, 25 ^{o}C) of calcium complex **1**.

Coordination ⟶ uncoordination 8.65 Kcal/mol

Coordination

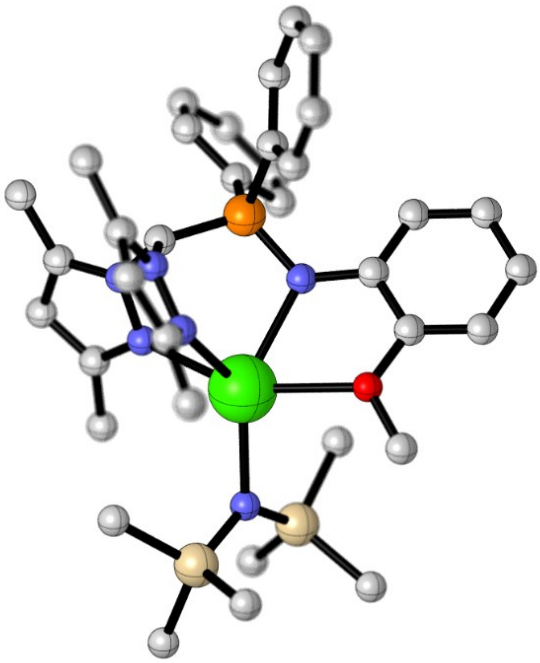

Fig. S6 Optimized structure and free energy (0 kcal/mol) of the O atom of methoxy group coordinated to central metal.

Ca	7.00508100	4.23405500	4.46270600
C	8.76487600	2.18014400	2.65631700
N	9.66638500	2.46045000	3.73228500
N	9.32670900	3.31053200	4.75765400
C	10.36065100	3.31564700	5.59963600
C	11.37756900	2.46342200	5.12788800
H	12.33029100	2.25638900	5.59601700
C	10.35866600	4.14080000	6.84638300
H	9.36487800	4.54924400	7.05034900
H	11.05469000	4.98416000	6.76692200
H	10.66451100	3.54251300	7.71194700
C	10.90698000	1.93452000	3.94095000
C	11.54683600	0.96556400	3.00881800
H	10.82718300	0.21374400	2.67400900
H	12.37758900	0.46151700	3.51068600
H	11.94525900	1.46725800	2.11932100
P	7.37147100	1.21277900	3.09564400
N	6.38732800	1.92671700	4.18972100
Si	7.36220400	7.56196700	5.46659900
C	6.94077200	9.35503000	4.99049900
H	6.82729300	9.47055900	3.90606900
H	7.74117300	10.03325400	5.31462300

H	6.01114400	9.70099400	5.45923200
C	9.07662800	7.22449200	4.70617900
H	9.44727900	6.20638800	4.88549300
H	9.82758500	7.91367100	5.11450100
H	9.05413300	7.36855000	3.61868700
C	7.60622400	7.58476300	7.35909700
H	6.66119700	7.79492300	7.87589400
H	8.32759300	8.35440600	7.66402300
H	7.97891900	6.62370700	7.73869500
C	6.49008700	0.85077700	1.53783500
C	7.14536300	0.35425200	0.40226000
C	5.11533100	1.10737000	1.47904100
C	6.43145400	0.10554700	-0.76772200
H	8.21455000	0.16718900	0.43589600
C	4.40368000	0.86006400	0.30568400
H	4.61114100	1.50993700	2.35321700
C	5.05967000	0.35743200	-0.81661500
H	6.94664400	-0.28015800	-1.64390700
H	3.33681600	1.06443100	0.26915300
H	4.50454200	0.16599200	-1.73153700
C	5.54981200	1.28290700	5.09318700
C	5.27283600	1.95081100	6.31403600

C	4.93937200	0.03197000	4.90907000
C	4.45349000	1.39097300	7.28581200
C	4.11707500	-0.53663700	5.88197300
H	5.11449900	-0.50358000	3.98017400
C	3.87147200	0.13724900	7.07113100
H	4.26223500	1.91358000	8.21687200
H	3.66698200	-1.50910000	5.69900900
H	3.23105100	-0.29464200	7.83490500
O	5.88322800	3.18766500	6.45442300
C	8.00626100	-0.36298100	3.78191600
C	8.54243800	-0.34253000	5.07745600
C	9.07036300	-1.50318700	5.63782900
C	9.05780400	-2.69777400	4.91823500
C	8.51200500	-2.72867300	3.63590500
C	7.98789000	-1.56778000	3.06922000
H	8.53654700	0.58144400	5.64925900
H	9.48434000	-1.47523600	6.64247900
H	9.46468100	-3.60425300	5.35937400
H	8.48731800	-3.65976800	3.07515900
H	7.55295700	-1.60633100	2.07499000
N	7.72517000	4.30760900	2.09512600
C	7.75747500	5.16443800	1.07288500

C	8.61870000	4.68513500	0.06916400
H	8.85054100	5.15864900	-0.87527600
C	6.94374000	6.41667700	1.08009800
H	6.04358200	6.30569500	0.46227400
H	7.51735100	7.25685600	0.67411400
H	6.63110700	6.66852200	2.09794100
C	9.11090100	3.47912300	0.53373300
C	10.08427000	2.53997500	-0.08856300
H	11.10175100	2.94925900	-0.05677700
H	9.83510100	2.36042200	-1.13969200
H	10.08451100	1.58952800	0.45000400
N	8.55149300	3.26634800	1.75954400
N	6.24564700	6.36372100	4.94927500
Si	4.55460900	6.58681700	4.75115600
C	4.03163000	7.87258700	3.44774700
H	4.36273300	8.88409300	3.70808800
H	2.93726500	7.89721000	3.35811400
H	4.43648200	7.63909600	2.45584300
C	3.62445200	7.08892400	6.33707000
H	3.78755600	6.37981700	7.15723200
H	2.54223800	7.15172800	6.16266200
H	3.95501900	8.07441000	6.68968100

C	3.78476200	4.94625800	4.14881900
H	4.20271100	4.62340300	3.18352700
H	2.70644400	5.07448800	3.98877100
H	3.90045700	4.11941800	4.86111800
C	5.61185600	3.92441900	7.64028100
H	4.53413800	4.07488300	7.76674600
H	6.01985200	3.40949300	8.51850800
H	6.09073900	4.89509300	7.50867200

Uncoordination

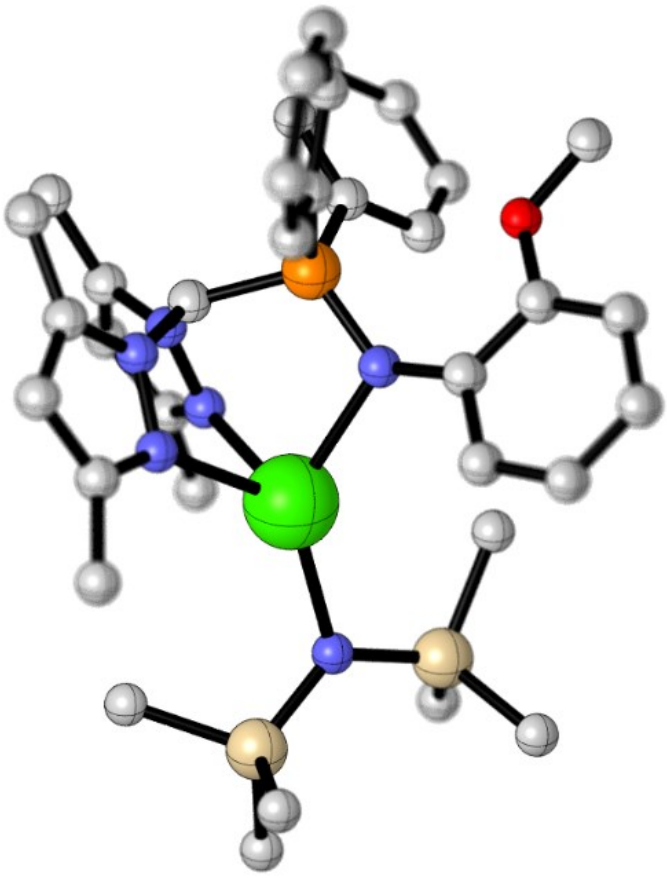

Fig. S7 Optimized structure and calculated free energy (kcal/mol) of the O atom of methoxy group dissociated from central metal.

Ca	7.19272500	4.45883000	4.21663600
C	8.62227200	2.22675900	2.60355800
N	9.60048400	2.44883500	3.62256200
N	9.40878500	3.38800800	4.60921200
C	10.46657400	3.30851700	5.41737300
C	11.35058000	2.31180300	4.96205800
H	12.28715500	2.01173800	5.41210900
C	10.61551700	4.18616700	6.61801200
H	9.70050700	4.74994300	6.81647000
H	11.42838500	4.90941300	6.48245600
H	10.85042500	3.59202700	7.50827300
C	10.77397300	1.78332200	3.82266700
C	11.26137900	0.69419800	2.93147800
H	10.44942600	0.01406800	2.65983100
H	12.04257800	0.12324300	3.44115100
H	11.68914300	1.09445400	2.00514600
P	7.15638900	1.39679800	3.10807600
N	6.33977600	2.22010700	4.26302900
Si	7.53468900	7.56147400	5.70657500
C	7.08062700	9.39954400	5.53433900
H	6.95753100	9.69082100	4.48447600
H	7.86989000	10.03031900	5.96428100

H	6.14804100	9.64208400	6.05854400
C	9.23842700	7.38084700	4.86765100
H	9.60596200	6.34650400	4.82135200
H	10.00382000	7.96584600	5.39416600
H	9.19469500	7.75268500	3.83564200
C	7.77951200	7.26809300	7.57302400
H	6.84494500	7.45954200	8.11522800
H	8.54985100	7.92568400	7.99696400
H	8.06811100	6.23238300	7.79550400
C	6.23667700	1.18685900	1.53975500
C	6.80356300	0.53251500	0.43808900
C	4.96740500	1.76112300	1.41454600
C	6.10121300	0.43356800	-0.76187800
H	7.79810200	0.10350900	0.51778300
C	4.27138700	1.67213600	0.21012100
H	4.53155600	2.27436900	2.26568600
C	4.83403800	1.00455800	-0.87733100
H	6.54717100	-0.08283900	-1.60837200
H	3.28731000	2.12563600	0.12223200
H	4.28860500	0.93377500	-1.81521000
C	5.51240100	1.71055900	5.27052600
C	4.60569200	0.63198500	5.10115300

C	5.52854500	2.32136900	6.53509300
C	3.79329000	0.20151300	6.14842300
C	4.70488700	1.90685200	7.58101200
H	6.22377900	3.14295300	6.70352300
C	3.83745000	0.83861800	7.39059400
H	3.11259700	-0.63065600	6.00057800
H	4.75524300	2.41580900	8.53985300
H	3.19381800	0.49363100	8.19513100
O	4.59122800	0.07798500	3.85426400
C	7.65073900	-0.23859700	3.76602600
C	8.25641100	-0.26815500	5.03015600
C	8.68204900	-1.47619300	5.58026400
C	8.49927900	-2.66793800	4.88120900
C	7.88132300	-2.64811100	3.63084500
C	7.45664300	-1.44201600	3.07695300
H	8.38680900	0.65398200	5.58944600
H	9.14955400	-1.48412000	6.56153600
H	8.82832200	-3.61009500	5.31242800
H	7.72280500	-3.57564000	3.08589700
H	6.95863000	-1.44336200	2.11235400
N	7.83095100	4.41166100	1.88052400
C	7.94735200	5.18630300	0.80153300

C	8.73447100	4.53981800	-0.16756200
H	9.00693800	4.91297100	-1.14553000
C	7.28277400	6.52318600	0.73386200
H	6.41737000	6.50084700	0.06017200
H	7.97306500	7.28510000	0.35576600
H	6.93536800	6.83574400	1.72360500
C	9.08923700	3.31945600	0.38094400
C	9.93314900	2.23138200	-0.18322500
H	10.99359400	2.51265600	-0.17962000
H	9.65160800	2.02010200	-1.21997500
H	9.82042100	1.32347000	0.41295200
N	8.52701100	3.25854600	1.62209600
N	6.43393200	6.44737500	5.00178600
Si	4.73478600	6.64442200	4.84642500
C	4.18852700	8.11092900	3.76412900
H	4.47304200	9.07554900	4.19905000
H	3.09751900	8.11419000	3.63863900
H	4.63642300	8.05675500	2.76385300
C	3.80854100	6.80576500	6.49778800
H	4.00207400	5.94058700	7.14369100
H	2.72318200	6.87666800	6.34917300
H	4.12553600	7.70251200	7.04535300

C	4.02727400	5.10146700	3.96948800
H	4.44995400	4.95967200	2.96327900
H	2.94506200	5.22334800	3.83131700
H	4.16342900	4.17074800	4.53645200
C	3.75951500	-1.03505200	3.61971700
H	2.70123400	-0.78891400	3.78177600
H	3.90718000	-1.30407700	2.57204700
H	4.03501400	-1.88515400	4.25801700

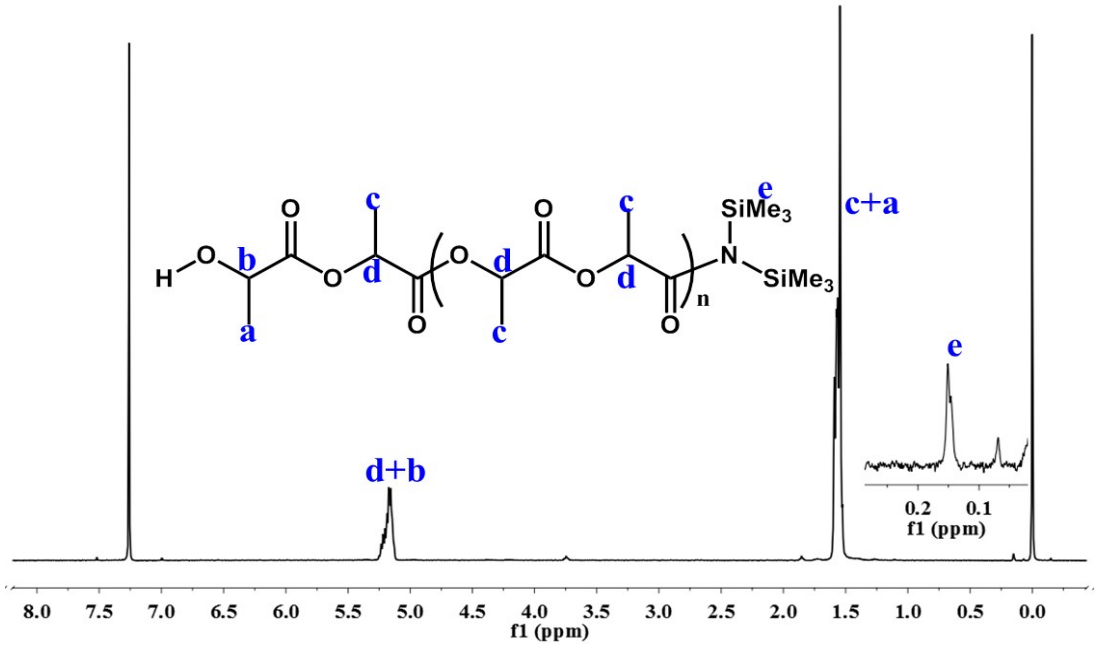

Fig. S8 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 ^{o}C) of the oligomer of the PLA prepared with the catalyst **1** ([*rac*-LA]$_0$/[**1**]$_0$ = 20/1).

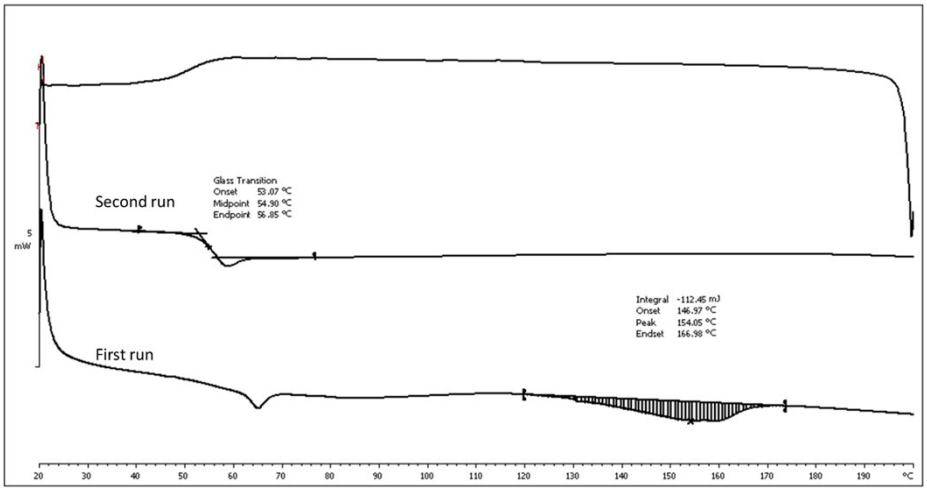

Fig. S9 DSC curve of the resultant PLA catalyzed by catalyst **2** (**Table 2**, entry 8).

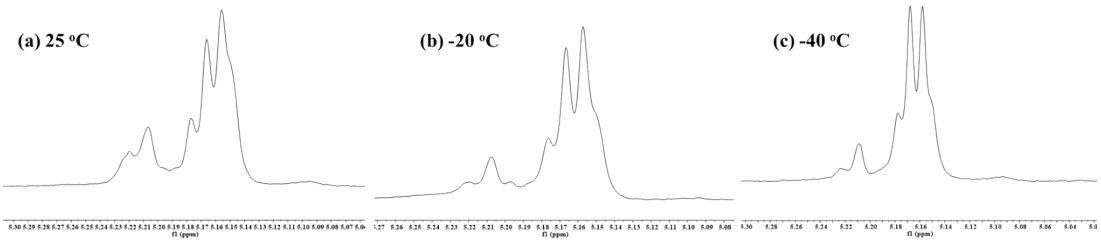

Fig. S10 Methine region of ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) spectra of PLAs generated with **2** at (a) 25 °C (**Table 2**, entry 1); (b) -20 °C (**Table 2**, entry 6); (c) -40 °C (**Table 2**, entry 7).

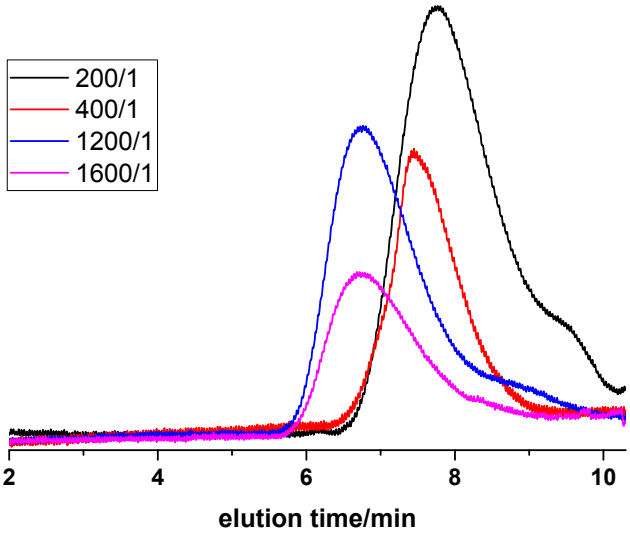

Fig. S11 GPC traces of resultant PLAs by catalyst **2**: black: 200/1 (**Table 2**, entry 1); red: 400/1 (**Table 2**, entry 2); blue: 1200/1 (**Table 2**, entry 3); pink: 1600/1 (**Table 2**, entry 4).

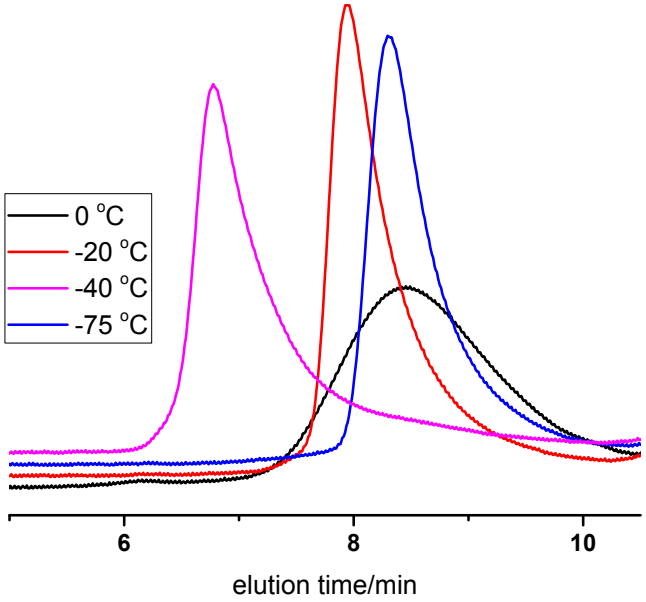

Fig. S12 GPC traces of resultant PLAs by catalyst **2**: black: 0 °C (**Table 2**, entry 5); red: -20 °C (**Table 2**, entry 6); blue: -40 °C (**Table 2**, entry 7); pink: -75 °C (**Table 2**, entry 8).

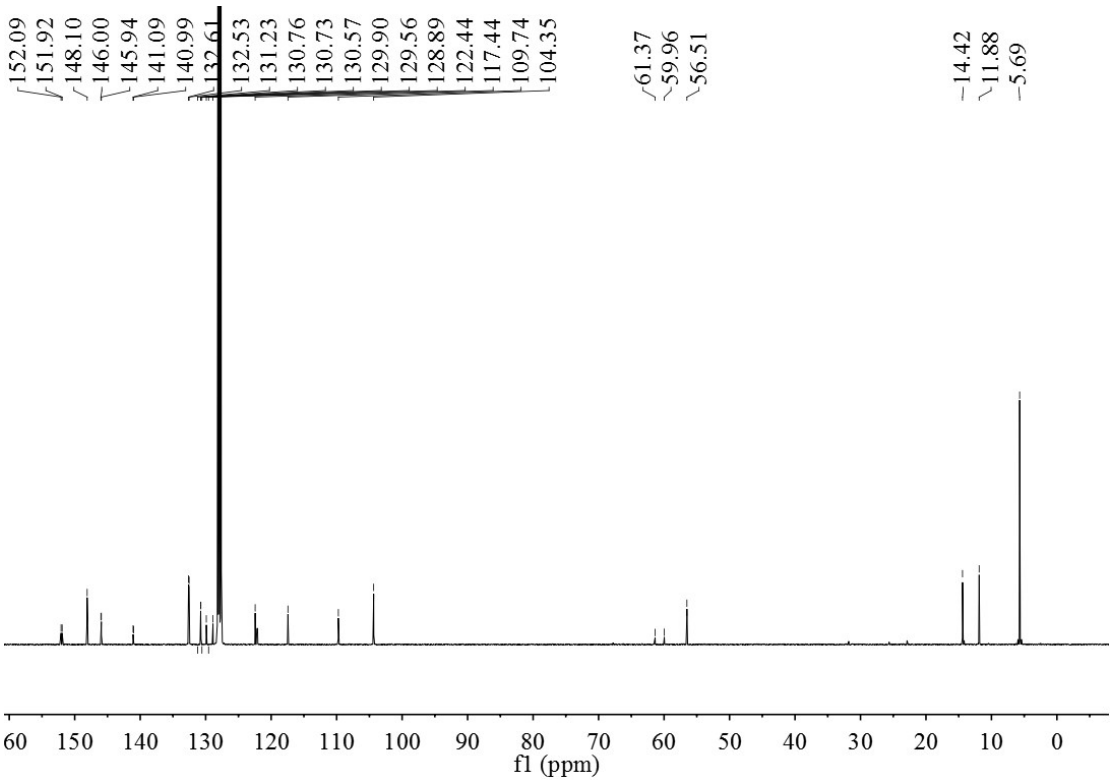

Fig. S13 ^{13}C NMR spectrum (C_6D_6, 100 MHz, 25 °C) of calcium complex **2**.

Table S1 Crystallographic data and structure refinement details for complexes **1** and **2**

	1	**2**
Formula	$C_{39}H_{55}CaN_6OPSi_2$	$C_{36}H_{50}CaN_6OPSi_2$
Fw	750.13	710.05
Wavelength	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	11.2638(9)	9.9377(8)
b (Å)	12.9788(10)	13.2229(10)
c (Å)	17.8234(14)	17.1785(13)
α (°)	93.419(1)	71.337(1)
β (°)	100.831(1)	73.927(1)
γ (°)	95.152(1)	77.882(1)
V ($Å^3$)	2541.05(35)	2036.71(27)
Z	2	2
Absorpt coefficient (mm^{-1})	0.245	0.286
No. of reflec collcd	5661	8369
No. of reflec unique	3552	8115
GOF	0.966	1.026
Dx (g/m^3)	1.149	1.158
μ (mm^{-1})	0.245	0.286
F (0 0 0)	932.0	758.0
θ max, deg	24.998	26.397
R_1	0.0811	0.0601
wR_2	0.2303	0.1875