Supporting Information

Introduction of abnormal N-heterocyclic Carbene as an efficient organocatalyst: Ring opening polymerization of cyclic esters†

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General methods and instrumentation. All manipulations were carried out using standard Schlenk line and glovebox techniques under an atmosphere of dry nitrogen/argon. Solvents were degassed by purging with dinitrogen/argon and dried by conventional method. Toluene and THF was refluxed over sodium/benzophenone and distilled under dry dinitrogen/argon atmosphere. C_6D_6 was dried over sodium/potassium alloy and stored over 4 Å molecular sieves. NMR samples were prepared inside nitrogen filled glovebox. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz and JEOL ECS 400 MHz spectrometers. Chemical shifts (δ) downfield from the reference standard were assigned positive values. GPC measurements were performed on a Waters 515 isocratic high-performance liquid chromatography (HPLC) pump system equipped with a differential Waters 2414 Refractive Index detector using THF (HPLC grade) as an eluant running at 0.3 mL/min. The chromatographic columns HT.3 (WAT 045920) and HT.4 (WAT 045935) were used. Molecular weight and molecular weight distributions were calculated using polystyrene as standard.

Starting materials. ε-CL and δ-VL were purchase from Sigma-Aldrich and dried over freshly ground CaH_2 and distilled before use. *rac*-LA and other reagents were purchased from Sigma-Aldrich and used as received.

General procedure for the ring-opening polymerization (ROP) of cyclic esters. In a single necked tube fitted with standard ground joint, a toluene solution of **1** (0.020 mmol, 10.86 mg, 2.0 mL toluene) and BnOH (0.020 mmol, 2.16 mg) were loaded inside the glovebox at room temperature. The solution was stirred for 2 min, and then cyclicesters (2.0 mmol) was added to the solution and the tube was closed with a glass stopper. The reaction mixture was stirred at 25°C for 1h. The polymerization mixture was quenched by addition of water (0.2 mL) and diluted with dichloromethane and the resultant solution was poured into rapidly stirred methanol (400 mL) solution. The ring-opened polymer was collected as the methanol insoluble white precipitates by filtration and was dried under reduced pressure.

Procedure and result for *in situ* polymerization of cyclic esters. In a Schlenk tube a THF solution of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium hydrochloride salt (0.020 mmol, 12.32 mg, 1.0 mL THF) and potassium trimethylsilyl amide (0.04 mmol, 8 mg, 1.0 mL THF) was added and stirred for 3 h at room temperature. Then to the above solution BnOH (0.020 mmol) was added and stirred for 2 min at room temperature. To the resultant solution appropriate cyclic esters (2.0 mmol) were added to the solution and the reaction mixture was stirred for 1 h at 25 °C. The polymerization mixture was quenched by addition of water (0.2 mL) and diluted with dichloromethane and the resultant solution was poured into rapidly stirred methanol (400 mL) solution. The ring-opened polymer was collected as the methanol insoluble white precipitates by filtration and was dried under reduced pressure.

We tested the activity of *in situ* generated carbene as described above in ring opening polymerization of these three monomers *rac*-LA, ε-CL and δ-VL to test the practicality of the present method for polymerization without isolating the carbene. Despite advances in structural modifications to enhance the stability of N-heterocyclic carbenes and the development of in situ methods for their generation, the use of NHCs is complicated by their extreme air and moisture sensitivity, which necessitates the use of glove-box techniques. The polymerization was performed by in situ generation of the abnormal carbene from its air stable salt using a base bis-potassium trimethylsilylamide in THF and the polymerization compares very well to the results obtained by using the isolated *a*NHC **1**(Table S1).

Table S1. Polymerization Data of Cyclic Esters Using *in situ* generated Abnormal N-Heterocyclic Carbene **1**[a].

M	Solvent	$[M]_0/[1]$ /[BnOH]	Conv. (%)[b]	M_n (NMR)[c]	M_n (theory)[d]	PDI
ε-CL	THF	100/1/1	99	9800	11400	1.12
rac-LA	THF	100/1/1	95	12800	13800	1.18
δ-VL	THF	100/1/1	91	7700	9200	1.11

[a]Typical polymerization reaction: To a solution of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium hydrochloride salt (0.020 mmol, 12.32 mg, 1.0 mL THF) potassium trimethylsilyl amide (0.04 mmol, 8 mg, 1.0 mL THF) was added and stirred for 3h at room temperature. Then to the above solution BnOH (0.020 mmol) was added and stirred for further 2 min at room temperature To the resultant mixture cyclic ester (2 mmol) was added and stirred at room temperature for 1 h at 25 °C. The reaction was terminated by addition of 4 drops of water and exposure to air. [b]Determined by ^{1}H NMR spectroscopy, [c]Determined by ^{1}H NMR spectroscopy,[d]Calculated from $MW_{Monomer} \times$(% Conv.)$\times([M]_0/[BnOH]_0)+MW_{BnOH}$

Kinetic study of polymerization of *rac*-Lactide:

The molecular weights of the ring-opened polymers can be controlled as a function of the monomer-to-initiator ratio (M/I) with consistently narrow polydispersities (PDIs). The plot of molecular weight $[M_n(NMR)]$ versus percent of conversion is presented shows the gradual increase of molecular weight in a linear fashion with progress of the polymerization . This result indicates the controlled nature of polymerization. Also the PDI values remain almost constant during the course of polymerization further supporting the controlled nature of polymerization process (Fig. S1). The

polymerization was performed inside a nitrogen filled glovebox using toluene or THF as solvent. In a single necked tube fitted with standard ground joint, a toluene/THF solution of **1** (0.020 mmol, 10.86 mg, 2.0 mL toluene/THF) and BnOH (0.020 mmol, 2.16 mg) were loaded inside the N_2 filled glovebox at room temperature. The solution was stirred for 2 min, and then *rac*-Lactide (2.0 mmol) was added to the solution and the tube was closed with a glass stopper. The reaction mixture was stirred at 25°C. Kinetic experiments were performed by taking a small amount of aliquots (150µL) from the reaction mixture after a certain time interval and quenched by the addition of water (100 µL). Subsequently, the reaction mixture was dried and checked by ^{1}H NMR spectroscopy and GPC analysis. The conversion as well as the M_n(NMR) at different time interval were determined from the ^{1}H NMR spectroscopy . The relative molecular weight with respect to polystyrene standard and the poly dispersity index (PDI) values were determined from the GPC measurements.
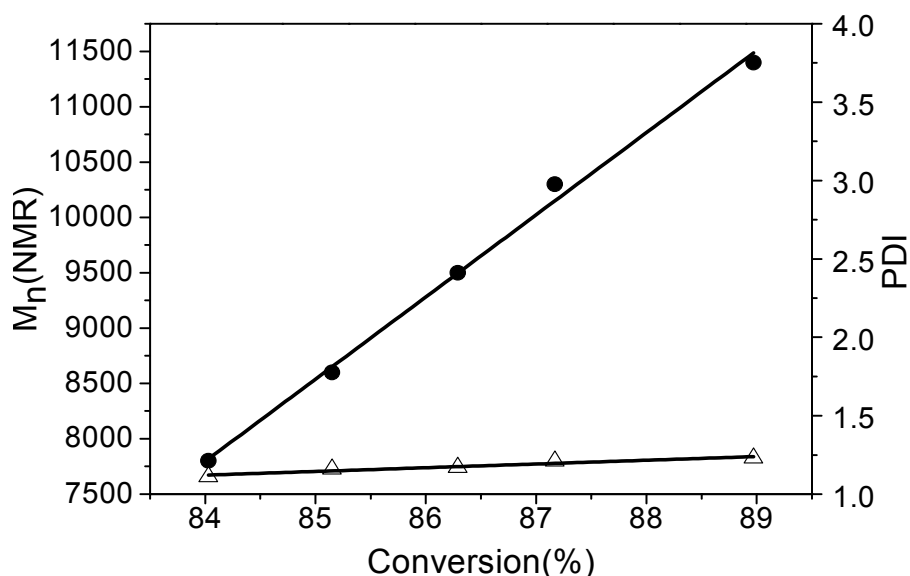

Fig. S1 Plots of M_n (NMR) and PDI (determined by GPC) vs. conversion of *rac*-lactide using **1** as catalyst in THF. The plot with black circles (●) represents to M_n (NMR) values as a function of conversion and the plot with isosceles triangles (Δ) represents to PDI values as a function of conversion.

NMR monitoring stoichiometric reaction:

To gain the further information about the reaction mechanism we performed a number of NMR monitoring experiments. The stoichiometric reaction of **1** with benzyl alcohol (BnOH) reveals the generation of a new resonance at a highly deshielded region of δ 11.5 ppm. This peak disappears when this stoichiometric reaction was performed with deuterated analog of benzyl alcohol (BnOD, Fig. S2). This observation clearly demonstrates that the peak at δ 11.5 ppm belongs to the –OH proton of the benzyl alcohol. A variable temperature study up to 45 °C indicates that on increasing the temperature this hydrogen bonded –OH proton gradually moves towards the shielded region (Fig. S3) indicating weakening of the hydrogen bonding. Further, a ^{1}H–^{13}C HSQC 2D NMR measurement of the stoichiometric reaction mixture of **1** with BnOH reveals no correlation of the resonance at δ 11.5 ppm with any carbon resonance (Fig. S4). All these observations support the formation of a hydrogen bonded adduct between **1** and BnOH.
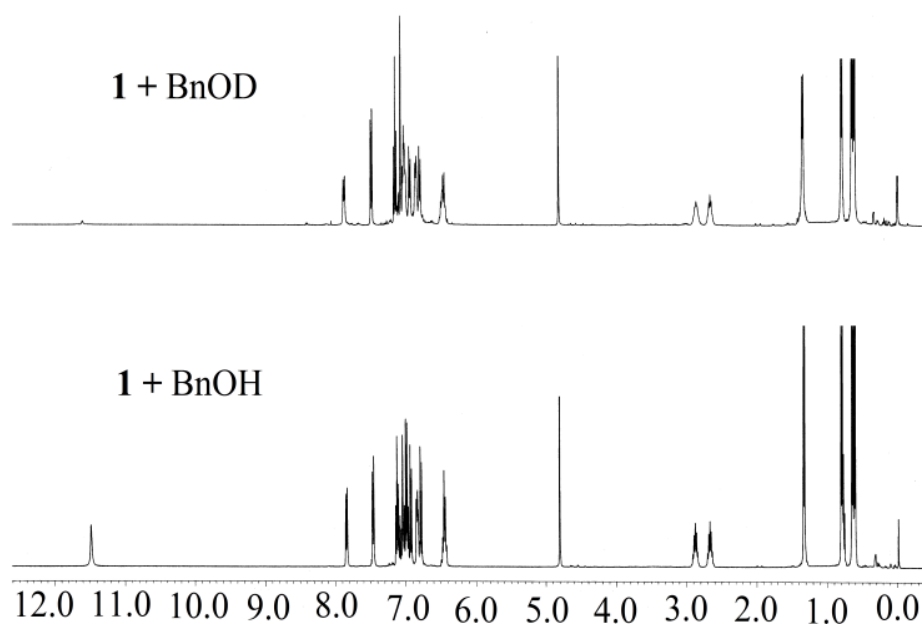
Fig. S2 Plots of ^{1}H NMR spectra of the stoichiometric reaction of **1** with BnOH/D in C$_6$D$_6$. Plot shows disappearance of peak at 11.5 on reaction of **1** with BnOD.
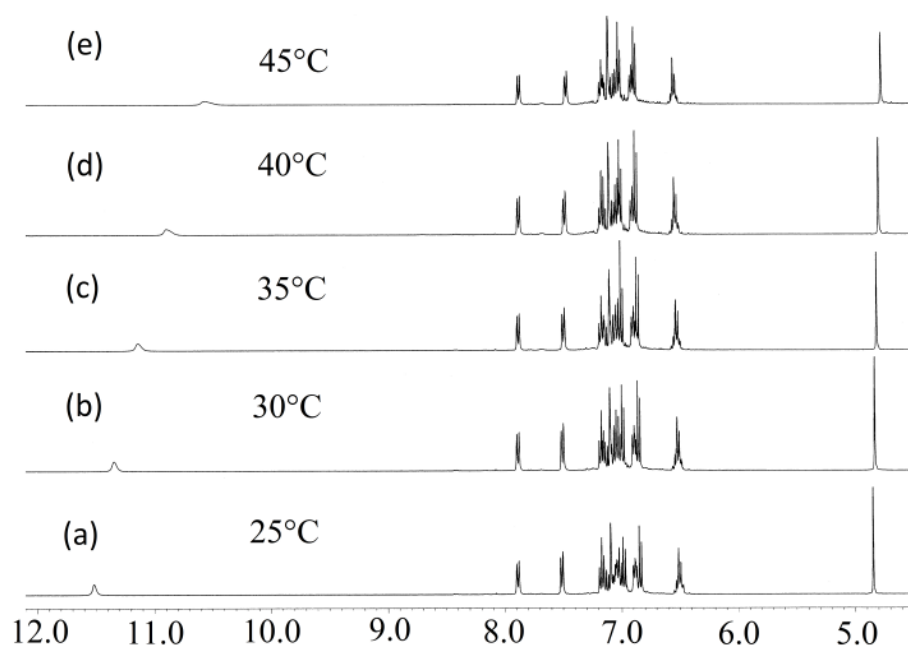
Fig. S3 ^{1}H NMR spectrum of the 1:1 reaction mixture of **1** and BnOH at different temperature; (a) 25 °C; (b) 30 °C; (c) 35 °C; (d) 40 °C; (e) 45 °C revealing gradual shift of peak at δ 11.5 ppm.

SKM-TKS-202A in C6D6
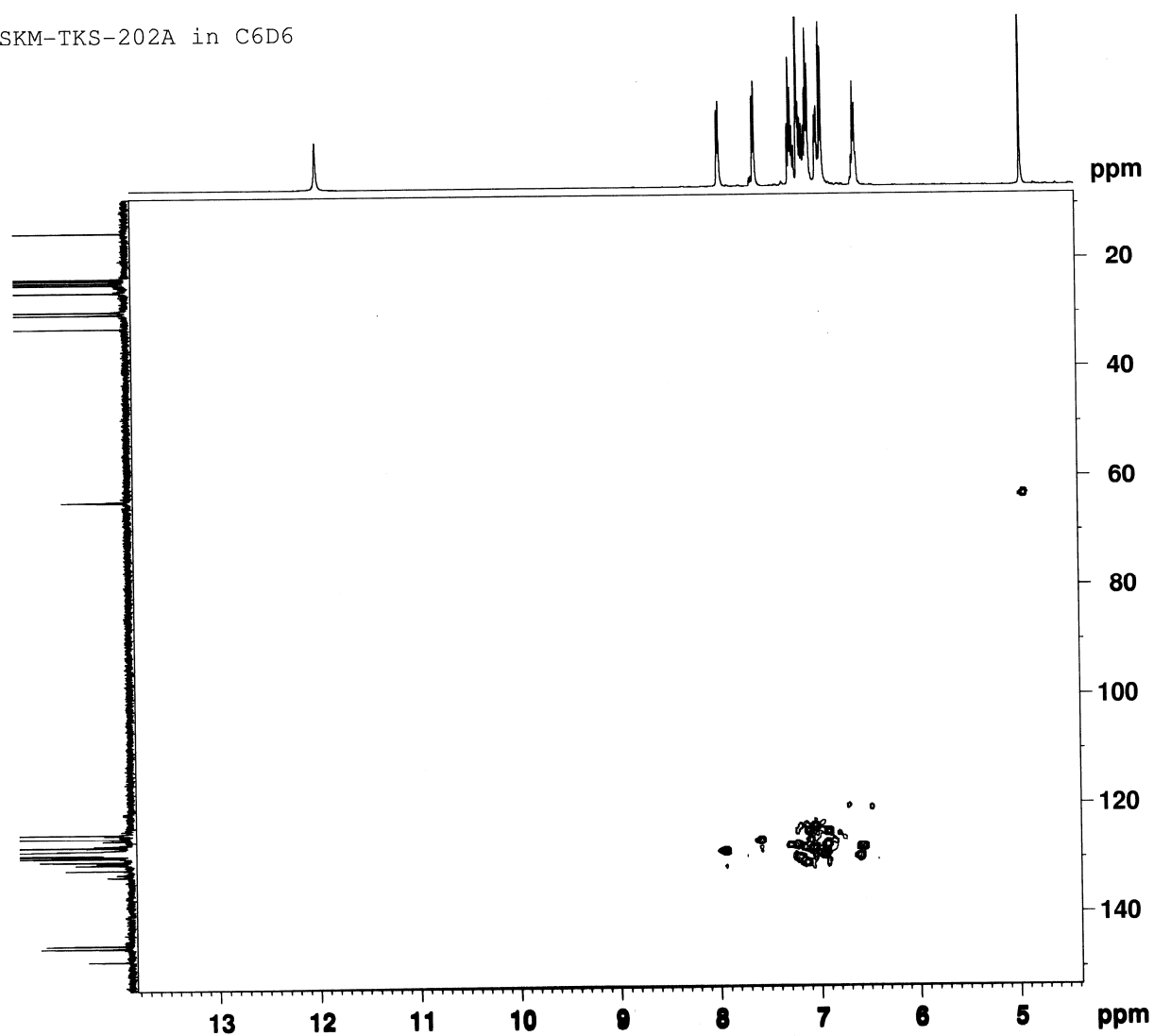
Fig. S4 ^{1}H-^{13}C HSQC spectrum of the (1:1) reaction mixture of **1** and BnOH in benzene-d$_6$ revealing no ^{13}C correlation to the ^{1}H resonance at δ 11.5 ppm.

Controlled addition of monomer and role of benzyl alcohol:

In the present study the role of benzyl alcohol is to act as an initiator for the ring opening polymerization of cyclic esters. Previous studies by Waymouth and Hedrick et al. have demonstrated that the role of benzyl alcohol as an initiator to make linear polyesters using normal N-heterocyclic carbene (*n*NHC) as organocatalyst.[1] It was proposed that the *n*NHC opens the ring by a nucleophilic attack to the cyclic esters involving a zwitterionic intermediate followed by transesterification reaction with benzyl alcohol. The mechanism of *a*NHC catalyzed polymerization of cyclic esters can be depicted as shown in Scheme 1. The cyclic ester monomer undergoes a nucleophilic attack by the hydrogen bonded adduct '**1a**' between **1** and BnOH resulting the ring opened zwitterionic acylimidazole intermediate 'B' (Scheme 1). The slower rate of polymerization in polar solvent THF as compared to toluene (Fig. 1A of main manuscript) can be attributed to this zwitterionic species which might be highly solvated to slow down the rate of polymerization in a polar solvent like THF. This zwitterionic intermediate 'B' is then protonated by benzyl alcohol and the resulting benzyloxy anion (BnO$^-$) attacks the acyl group of acylimidazole intermediate to produce the new hydrogen bonded adduct 'C' between *a*NHC and new hydroxyl terminated ring opened product. An NMR investigation after controlled addition of cyclic ester monomer to reaction mixture of *a*NHC and BnOH was made and monitored to understand the reaction mechanism depicted in Scheme 1. This experiment shows that the hydrogen bonded –OH resonance gradually shifts to high field. For example, after addition of three equiv. of *rac*-lactide monomer, the –OH resonance moves from δ 11.5 ppm to δ 10.3 ppm and to δ 10.2 ppm after eight equivalent addition (Fig. S5). Further addition of more equivalents of monomer continues to show this trend of shifting the hydrogen bonded proton towards high field even after addition of 15 and 25 equivalents of monomer. After 15 equivalents of monomer addition the peak shifts to δ 10.1 ppm and after 25 equivalents of monomer addition this peak moves to δ 9.95 ppm. This shift of the hydrogen bonded resonance may be attributed to the

formation of new hydroxyl terminated product (Scheme S1, for example C and E).   Also it may be

noted that maximum shift (from δ 11.5 ppm to δ 10.3 ppm) takes place at the beginning when benzyl

alcohol is replaced by the ring opened hydroxyl terminated product to form the hydrogen bonded

adduct and this hydroxyl terminated ring opened product plays the role of benzyl alcohol for next

step. Expectedly, when it changes from adduct C to E the NMR shift of the hydrogen bonded adduct

is minimum.

Scheme S1. Plausible mechanism of ring opening polymerization using abnormal carbene **1**.
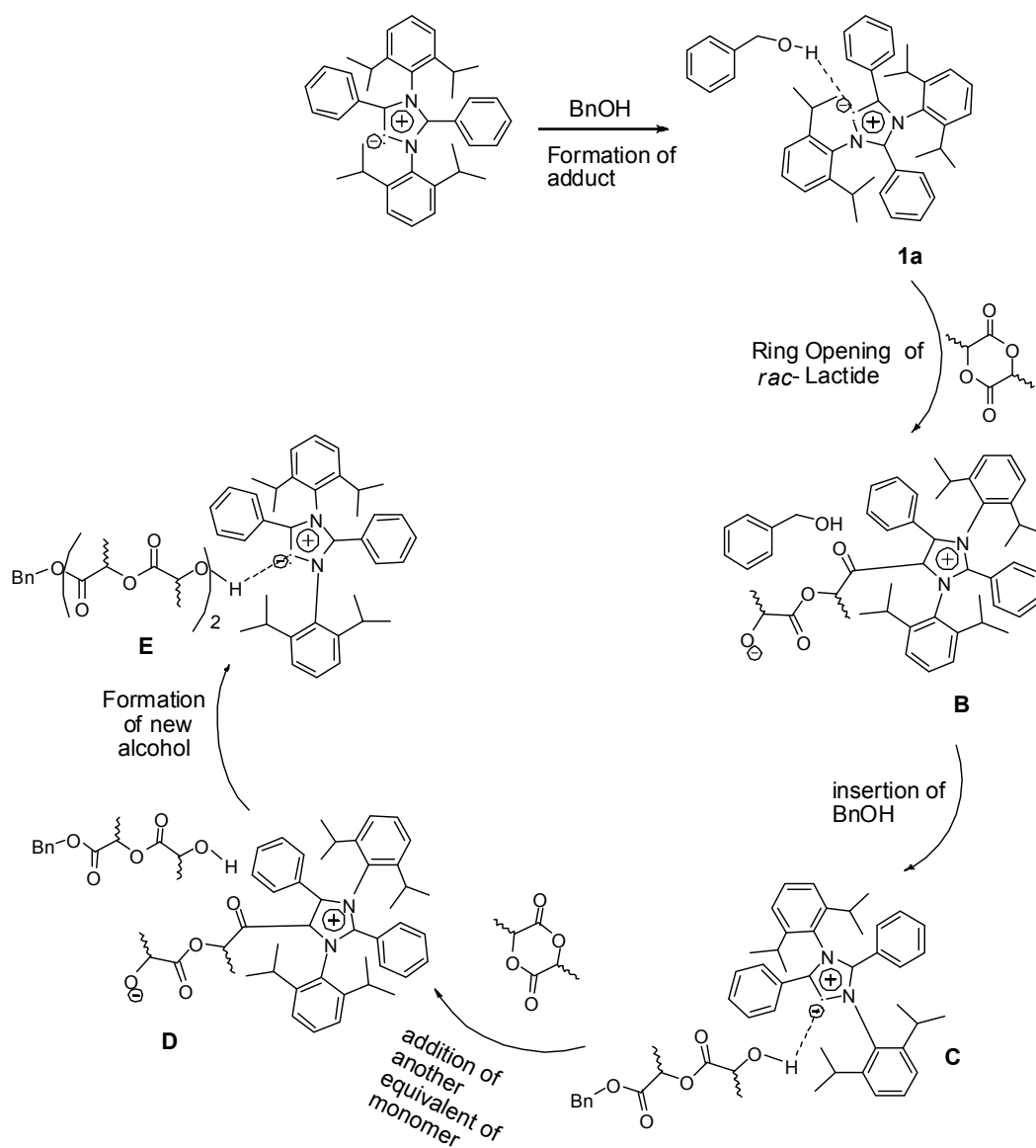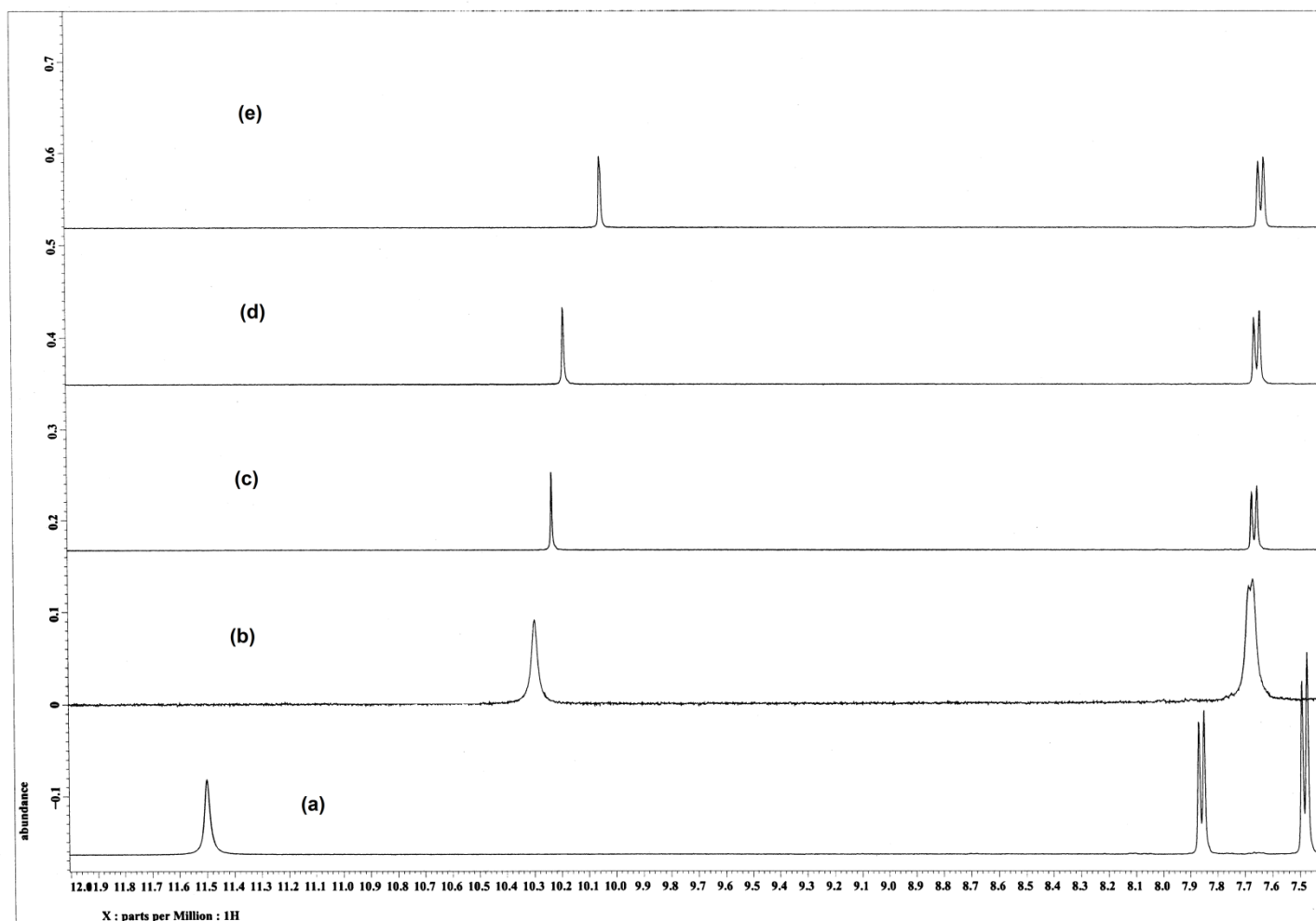
Fig. S5 ^{1}H NMR spectra in benzene-d$_6$: (a) 1:1 reaction mixture of **1** and BnOH ; (b) after addition

of 3 equivalent of *rac*-LA in 1:1 reaction mixture of **1** and BnOH; (c) after addition of 8 equivalent

of *rac*-LA in 1:1 reaction mixture of **1** and BnOH; (d) after addition of 15 equivalent of *rac*-LA in

1:1 reaction mixture of **1** and BnOH; (e) after addition of 25 equivalent of *rac*-LA in 1:1 reaction

mixture of **1** and BnOH.

Determination of kinetic isotope effect:

To gain better understanding of the mechanistic pathway of the polymerization process, we carried out the H/D kinetic isotope effect (KIE) experiment under the same reaction condition using toluene as solvent and the kinetic study of *rac*-lactide was performed (Scheme S2) as described above. In a single necked tube fitted with standard ground joint, a toluene solution of **1** (0.020 mmol, 10.86 mg, 2.0 mL toluene) and BnOD (0.020 mmol, 2.18 mg) were loaded inside the N_2 filled glovebox at room temperature. The solution was stirred for 2 min, and *rac*-lactide (2.0 mmol) was added to the solution and the reaction mixture was stirred at 25°C. Kinetic experiments were performed by taking a small amount of aliquots (150µL) from the reaction mixture after a certain time interval and after quenching by addition of water (100 µL). Subsequently, the reaction mixture was dried and checked by ^1H NMR spectroscopy. The conversion at different time interval was determined from ^1H NMR spectroscopy. The plots of $\ln(C/C_0)$ versus time for the polymerization of *rac*-lactide in the presence of **1** in toluene using BnOH and BnOD at 25 °C results in the k_{obs} values of 0.07363 min^{-1} and 0.01773 min^{-1}, respectively, which translates into a primary KIE of 4.15 (Fig. S6).This observation suggests that hydrogen derived from the -OH group of alcohol is involved in the key step of polymerization.

Scheme S2. Ring opening of *rac*-lactide in the presence of BnOH and BnOD
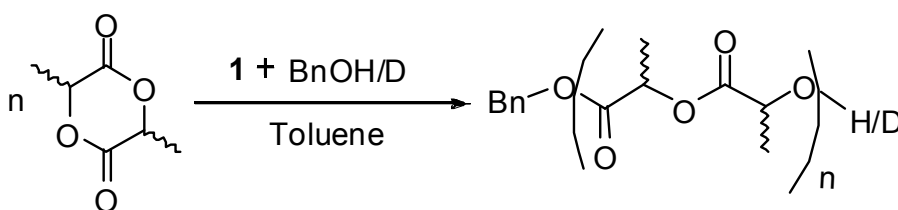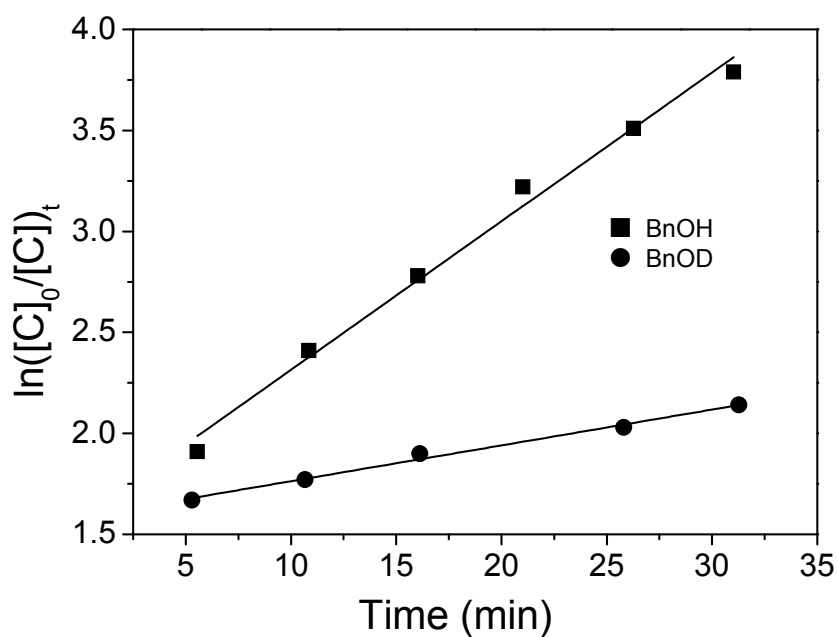
Fig. S6 First order plot for *rac*-lactide (LA) consumption using **1** as catalyst. Conditions: $[LA]_0/[\mathbf{1}]/[BnOH/D] = 100:1:1$, in 2 mL of toluene, 25 °C, 0.15 mL aliquots taken at the given intervals and conversion calculated from ^1H NMR spectroscopy. The kinetic isotope effect (K_H/K_D) = 4.15.
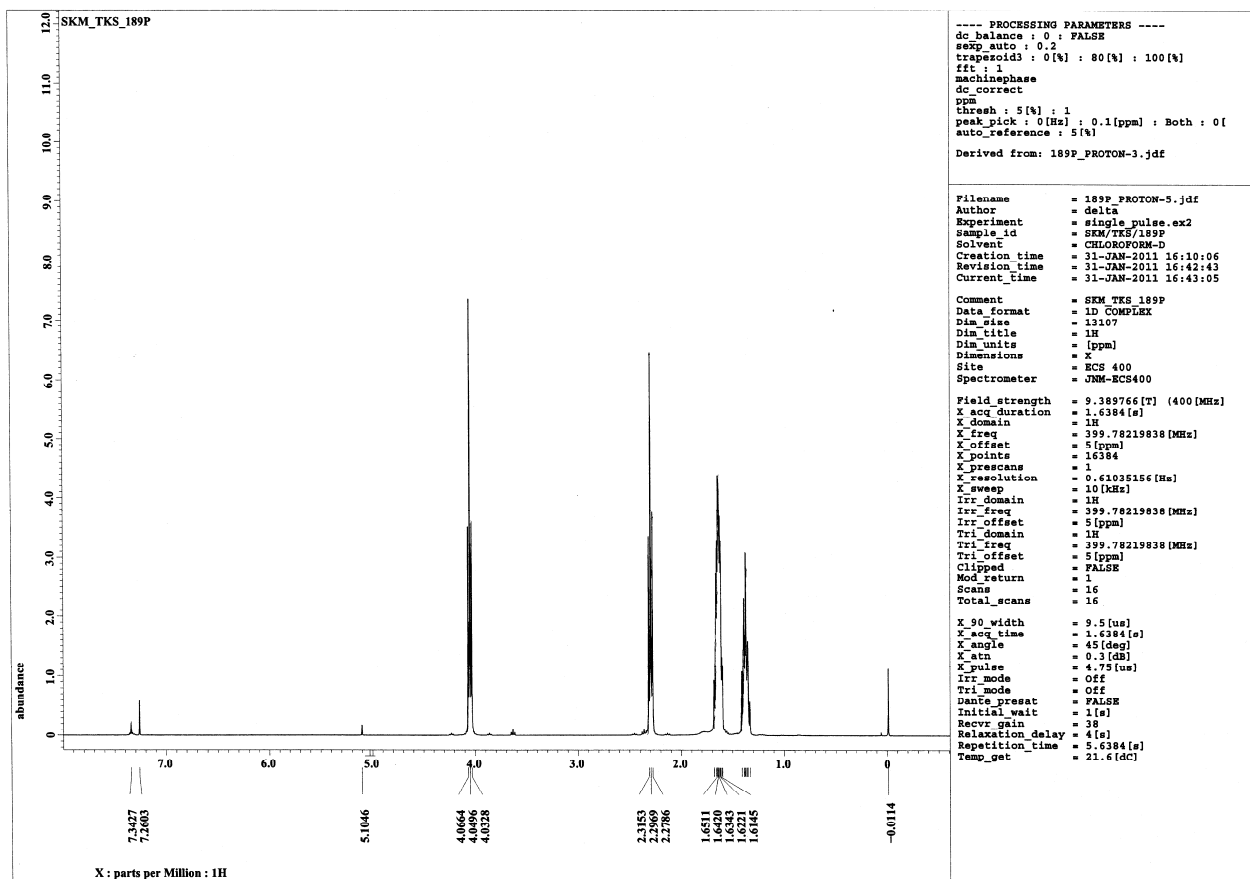
Fig. S7 ^{1}H NMR spectra of polycaprolactone in CDCl$_3$.
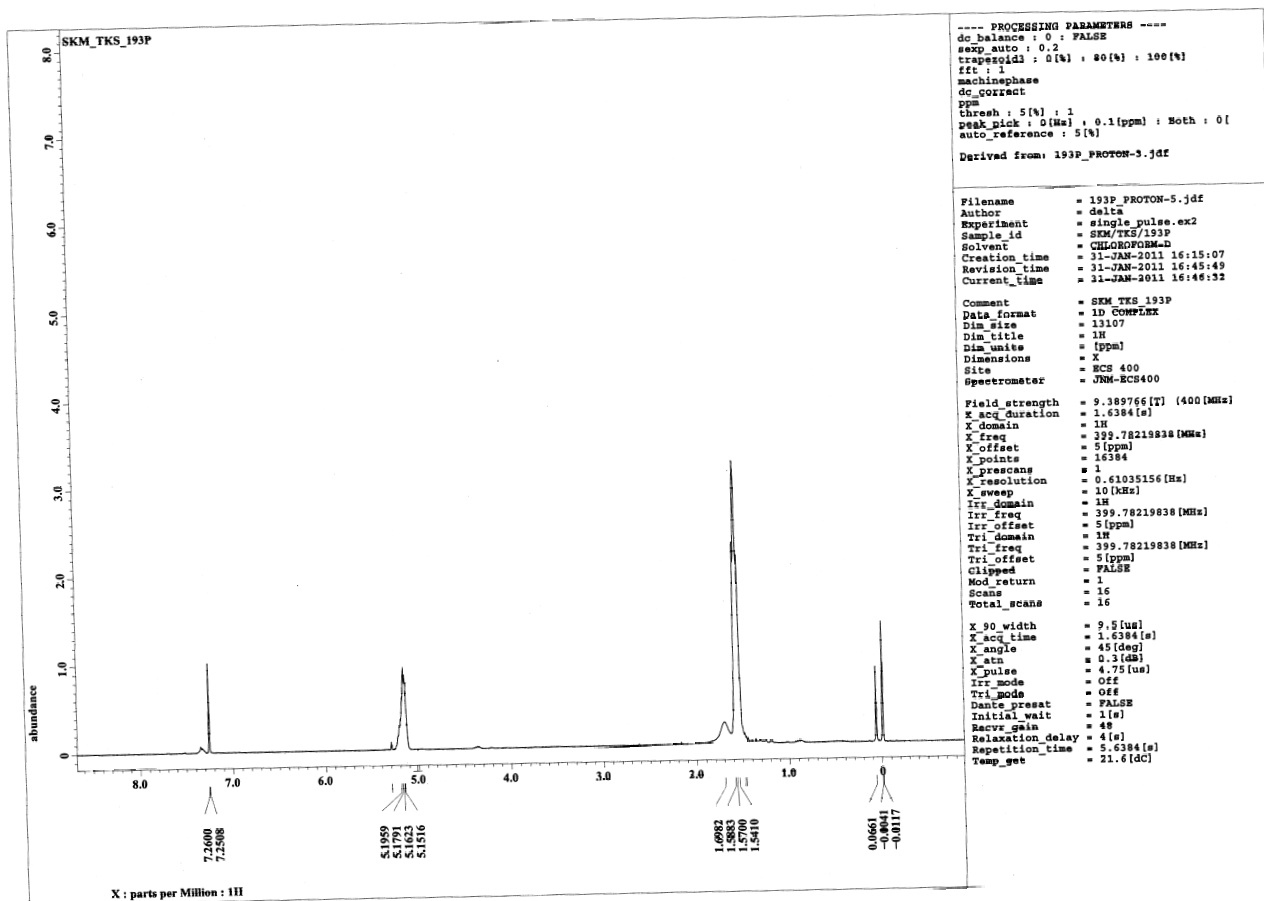
Fig. S8 ^{1}H NMR spectra of poly(*rac*)lactide in CDCl$_3$.
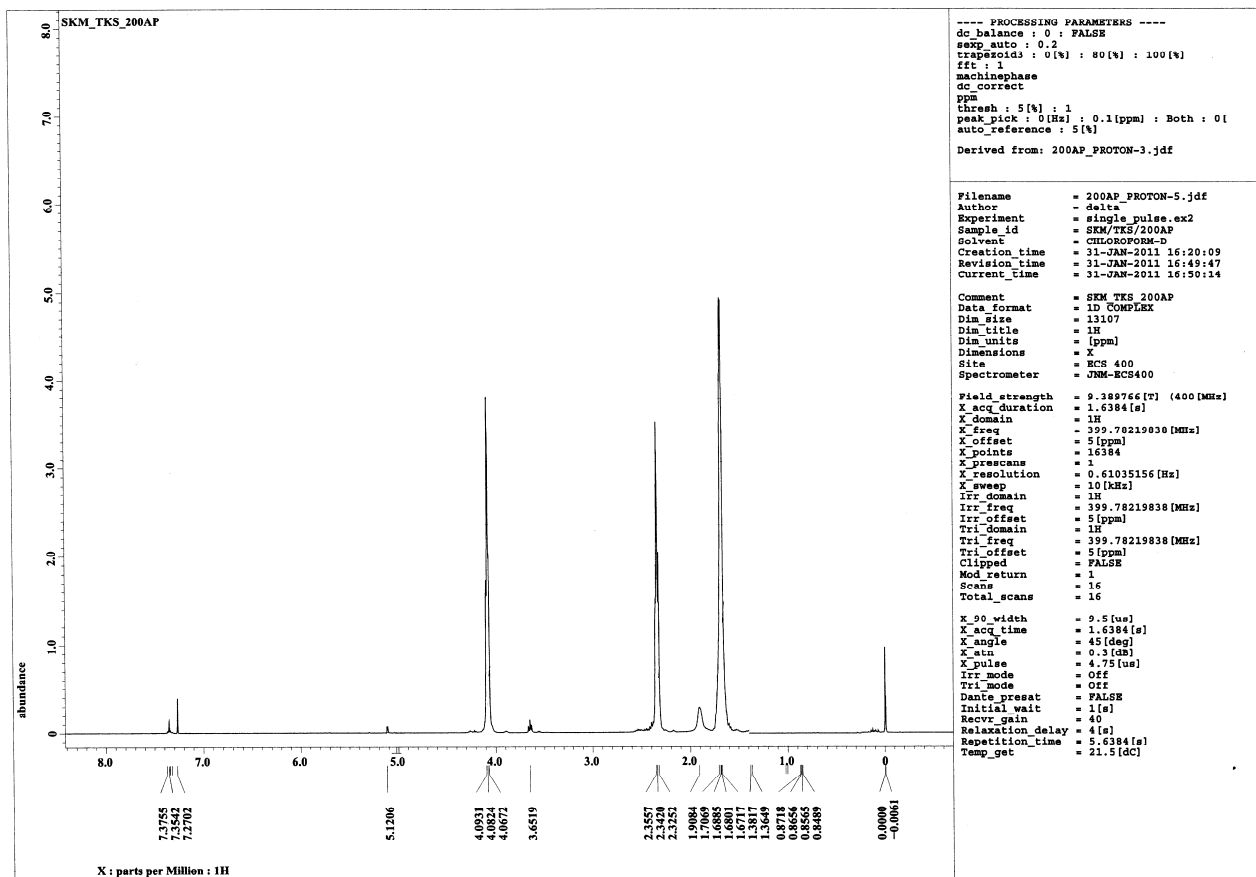
Fig. S9 ^{1}H NMR spectra of poly valerolactone in CDCl$_3$.
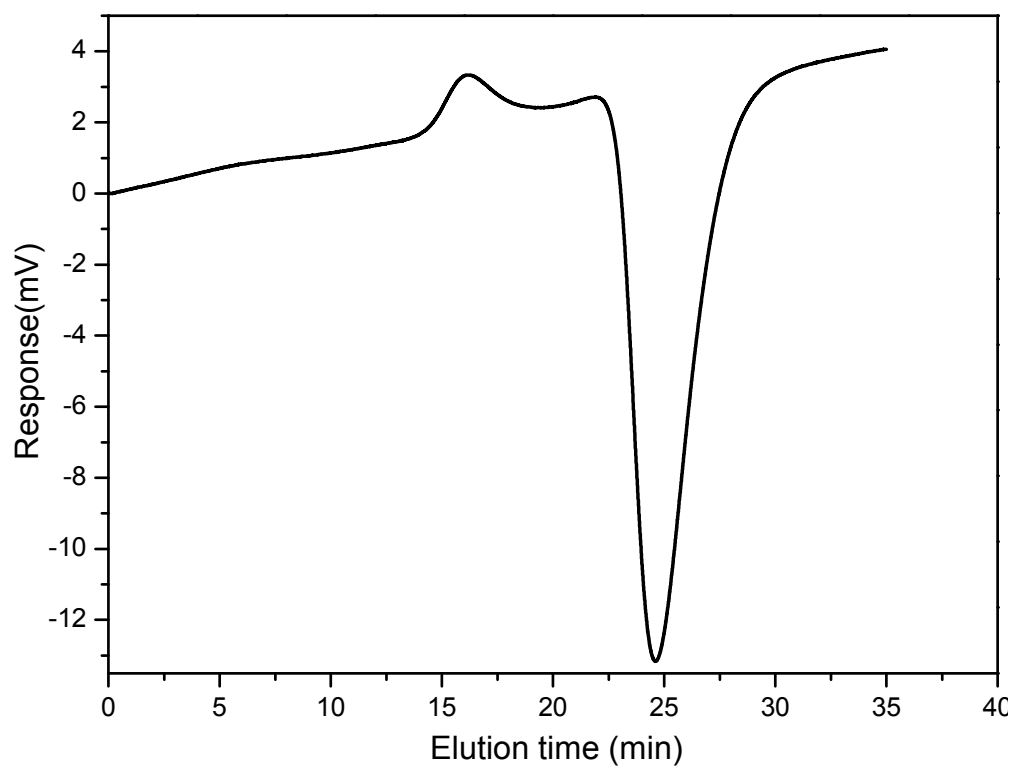
Fig. S10 Typical GPC diagram (THF, 25 °C) for a Poly valero lactone polymer (Table 1, Entry 10).

Table S2. Absolute energies E_e (in hartree) at the BP86/SVP level of theory.

No./Name	E_e	H_{298}	G_{298}	E_{BIG}
1	-1620.927221	-1620.177237	-1620.293253	-1622.578797
2	-1620.948902	-1620.198729	-1620.314965	-1622.601209
BnOH	-346.517545	-346.380321	-346.421070	-346.885329
1a	-1967.470789	-1966.581935	-1966.719581	-1969.483423
2a	-1967.488358	-1966.599085	-1966.738120	-1969.501744

E_e Electronic energy

H_{298} Enthalpy at 298 K

G_{298} Gibbs free energy at 298 K

E_{BIG} Electronic energy at BP86/TZVP level.

Table S3. Cartesian coordinates (Å) of the BP86/SVP optimized structure

No./Name	Coordinates
| 1 | ```
85
xyz
N       -1.19957      -0.78347       0.01560
N        0.83521       0.01623      -0.05813
C       -0.48074       0.39424      -0.00147
C        0.89393      -1.40443      -0.09285
C       -0.40678      -1.93310      -0.01963
C       -1.01087       1.76736       0.01518
C       -2.18292       2.09100      -0.71986
H       -2.68302       1.31718      -1.31715
C       -2.70647       3.39176      -0.70479
H       -3.61439       3.61384      -1.28751
C       -2.07699       4.40666       0.03755
H       -2.48989       5.42769       0.04683
C       -0.91487       4.10302       0.76831
H       -0.41207       4.88523       1.35888
C       -0.38795       2.80302       0.76123
H        0.51438       2.58732       1.34789
C        2.12213      -2.21416      -0.21679
C        3.36504      -1.75988      -0.72950
H        3.48706      -0.71918      -1.05661
C        4.46242      -2.63214      -0.84118
H        5.41355      -2.24988      -1.24587
C        4.35307      -3.97678      -0.45123
H        5.21622      -4.65562      -0.53984
C        3.12292      -4.44504       0.04971
H        3.01724      -5.49803       0.35755
C        2.02727      -3.58099       0.16496
H        1.05813      -3.93742       0.54552
C       -2.64125      -0.87855       0.13760
C       -3.40074      -1.19701      -1.02046
C       -4.79826      -1.31279      -0.87153
H       -5.41625      -1.55677      -1.74936
C       -5.41433      -1.12337       0.37346
H       -6.50861      -1.21336       0.46549
C       -4.63889      -0.82850       1.50325
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H	-5.13201	-0.69856	2.47861
C	-3.23644	-0.70721	1.41523
C	-2.39110	-0.50262	2.67330
H	-1.44346	-0.01284	2.36460
C	-3.04811	0.41427	3.72089
H	-3.34578	1.39000	3.28465
H	-2.33912	0.61278	4.55153
H	-3.95094	-0.04710	4.17472
C	-2.01885	-1.87871	3.27351
H	-2.93026	-2.42062	3.60522
H	-1.35307	-1.75704	4.15450
H	-1.49847	-2.50819	2.52216
C	-2.73834	-1.45954	-2.37427
H	-1.74665	-0.95756	-2.36048
C	-3.52959	-0.88562	-3.56539
H	-4.49600	-1.41139	-3.71762
H	-2.94778	-1.00642	-4.50292
H	-3.75144	0.19534	-3.44003
C	-2.47103	-2.97229	-2.54767
H	-1.82235	-3.33649	-1.72408
H	-1.96231	-3.17112	-3.51512
H	-3.42410	-3.54359	-2.53600
C	1.95063	0.93744	-0.06344
C	2.72398	1.07801	1.12391
C	3.82345	1.96020	1.08353
H	4.44285	2.08799	1.98554
C	4.14394	2.67498	-0.07907
H	5.00805	3.35828	-0.08573
C	3.36625	2.51652	-1.23452
H	3.62848	3.07809	-2.14538
C	2.25716	1.64572	-1.25907
C	2.41193	0.32217	2.41967
H	1.53415	-0.32900	2.22828
C	2.03663	1.28338	3.56950
H	2.87509	1.96682	3.82190
H	1.78938	0.70858	4.48651
H	1.15550	1.90984	3.32054
C	3.58032	-0.59708	2.83816
H	3.84829	-1.30619	2.03025
H	3.30174	-1.18866	3.73530
H	4.48745	-0.00935	3.09590
C	1.45948	1.47684	-2.55452
H	0.60679	0.79948	-2.34160
C	0.87136	2.81668	-3.04563
H	0.24353	3.29651	-2.26797
H	0.23954	2.65373	-3.94387
H	1.67036	3.53426	-3.33050
C	2.30850	0.80328	-3.65548
H	3.17957	1.43146	-3.94000
H	1.69918	0.64415	-4.56995
H	2.69372	-0.18411	-3.32942
2	85		
	xyz		
N	-1.08113	0.12026	-1.11763
N	-0.27946	-0.06239	0.86628
C	0.11913	0.08051	-0.44415
C	-1.68639	-0.11035	1.02028
C	-2.20479	0.00322	-0.26407
C	-2.39683	-0.19037	2.31270
C	-2.00765	-1.10144	3.32565
H	-1.15532	-1.77422	3.15423

C	-2.70352	-1.16007	4.54388
H	-2.38369	-1.87693	5.31680
C	-3.80313	-0.31586	4.77683
H	-4.34747	-0.36443	5.73330
C	-4.20062	0.59370	3.77993
H	-5.05687	1.26492	3.95336
C	-3.50422	0.65941	2.56378
H	-3.81104	1.38359	1.79390
C	-1.14024	0.20217	-2.56088
C	-1.42053	-0.97201	-3.30908
C	-1.47814	-0.85913	-4.71406
H	-1.69289	-1.75478	-5.31815
C	-1.25514	0.36688	-5.35402
H	-1.30272	0.43236	-6.45288
C	-0.96165	1.50855	-4.59546
H	-0.77613	2.46535	-5.10783
C	-0.90037	1.45599	-3.18755
C	-0.53009	2.70667	-2.38950
H	-0.84326	2.53383	-1.33810
C	1.00410	2.89185	-2.37906
H	1.49340	2.00109	-1.93536
H	1.28797	3.78500	-1.78261
H	1.39349	3.03282	-3.41031
C	-1.24805	3.97877	-2.88177
H	-0.91805	4.28060	-3.89843
H	-1.02478	4.82994	-2.20503
H	-2.35052	3.84995	-2.91175
C	-1.57981	-2.34314	-2.65149
H	-1.69426	-2.18330	-1.55977
C	-0.29715	-3.18030	-2.85616
H	-0.11799	-3.38137	-3.93409
H	-0.37990	-4.15979	-2.33847
H	0.59211	-2.65113	-2.45786
C	-2.83225	-3.10068	-3.13504
H	-3.75293	-2.50071	-2.98643
H	-2.94816	-4.05064	-2.57202
H	-2.76747	-3.36694	-4.21159
C	0.67841	-0.07183	1.95084
C	0.85564	1.10456	2.72654
C	1.79942	1.06641	3.77440
H	1.95713	1.96611	4.38992
C	2.54649	-0.08902	4.03779
H	3.27993	-0.09661	4.85999
C	2.36477	-1.23369	3.24918
H	2.96316	-2.13448	3.45642
C	1.42961	-1.25475	2.19395
C	0.11908	2.40905	2.41917
H	-0.68515	2.18010	1.69051
C	1.07536	3.41343	1.73799
H	1.91257	3.69292	2.41288
H	0.53617	4.34558	1.46500
H	1.51387	2.98349	0.81481
C	-0.55340	3.02277	3.66327
H	-1.24227	2.30259	4.14961
H	-1.14163	3.92094	3.37999
H	0.19233	3.34759	4.41963
C	1.28750	-2.50188	1.32042
H	0.31823	-2.42195	0.78445
C	2.39757	-2.52546	0.24517
H	2.33930	-1.61579	-0.38640
H	2.29145	-3.41711	-0.40884

H	3.40370	-2.56556	0.71544
C	1.26149	-3.81346	2.12969
H	2.23444	-4.02051	2.62368
H	1.05194	-4.67250	1.45850
H	0.48025	-3.80104	2.91848
C	-3.60986	-0.04979	-0.71717
C	-4.48287	-1.04213	-0.20332
C	-5.82328	-1.10314	-0.61323
C	-6.32114	-0.18092	-1.55162
C	-5.46530	0.80465	-2.07355
C	-4.12465	0.87243	-1.66163
H	-4.09639	-1.77571	0.52060
H	-6.48264	-1.88394	-0.20166
H	-7.37247	-0.23201	-1.87653
H	-5.84421	1.53311	-2.80799
H	-3.46987	1.65508	-2.07094

BnOH

16
xyz

C	9.02075	-0.00002	-12.97010
C	9.03841	0.00070	-11.56657
C	10.26213	0.00028	-10.86252
C	11.46788	-0.00081	-11.58942
C	11.44995	-0.00149	-12.99621
C	10.22935	-0.00112	-13.69151
H	8.05758	0.00032	-13.50550
H	8.08598	0.00162	-11.00876
H	12.41763	-0.00109	-11.03520
H	12.40111	-0.00232	-13.55301
H	10.21681	-0.00166	-14.79316
C	10.26156	0.00083	-9.34537
H	9.68635	0.89552	-8.99178
H	9.68772	-0.89450	-8.99116
O	11.58968	0.00198	-8.85162
H	11.54309	0.00108	-7.87908

1a

101
xyz

N	0.15616	0.70324	0.02230
N	-1.43170	-0.77198	-0.28271
C	-1.15655	0.56862	-0.36379
C	-0.26473	-1.44621	0.15901
C	0.76494	-0.51359	0.34007
C	-2.07479	1.63866	-0.78990
C	-2.07047	2.89617	-0.13128
H	-1.39176	3.06833	0.71374
C	-2.93381	3.92376	-0.53803
H	-2.91139	4.88844	-0.00711
C	-3.82537	3.72578	-1.60690
H	-4.50273	4.53437	-1.92367
C	-3.84221	2.48518	-2.26808
H	-4.53043	2.31573	-3.11112
C	-2.97862	1.45442	-1.86857
H	-2.99982	0.49803	-2.40651
C	-0.15051	-2.90642	0.35142
C	-1.20880	-3.74120	0.78982
H	-2.19841	-3.31548	1.00422
C	-1.00987	-5.12086	0.96809
H	-1.84803	-5.74752	1.31287
C	0.24619	-5.69846	0.71677
H	0.39838	-6.78075	0.85563
C	1.30788	-4.87829	0.29111
H	2.29880	-5.31680	0.09126

C	1.11708	-3.50101	0.10949
H	1.94893	-2.85817	-0.22392
C	0.91781	1.93787	-0.00001
C	1.12484	2.63288	1.22220
C	1.90457	3.80616	1.17769
H	2.08803	4.36907	2.10567
C	2.45891	4.26466	-0.02640
H	3.06494	5.18465	-0.03703
C	2.25440	3.54717	-1.21191
H	2.71001	3.90505	-2.14870
C	1.48586	2.36354	-1.22805
C	1.33927	1.57038	-2.52698
H	0.62272	0.74347	-2.33976
C	0.75543	2.42767	-3.66916
H	-0.22139	2.87299	-3.38846
H	0.60242	1.80750	-4.57745
H	1.43729	3.25770	-3.95227
C	2.68401	0.91995	-2.92435
H	3.45056	1.69266	-3.14863
H	2.55708	0.30203	-3.83881
H	3.07646	0.26922	-2.11522
C	0.57067	2.11998	2.55358
H	-0.25222	1.40990	2.31955
C	-0.01954	3.23820	3.43605
H	0.76388	3.93502	3.80101
H	-0.50535	2.80142	4.33340
H	-0.78062	3.84213	2.89836
C	1.65050	1.32223	3.31806
H	2.01615	0.47204	2.70940
H	1.23893	0.92088	4.26852
H	2.52055	1.96666	3.56310
C	-2.70603	-1.37794	-0.61088
C	-2.81579	-2.12384	-1.81930
C	-4.06456	-2.71305	-2.10647
H	-4.18117	-3.29726	-3.03308
C	-5.15583	-2.57358	-1.23834
H	-6.12111	-3.04293	-1.48630
C	-5.01705	-1.84002	-0.05227
H	-5.87871	-1.74012	0.62674
C	-3.79421	-1.22844	0.29391
C	-1.65849	-2.30552	-2.80717
H	-0.76576	-1.80005	-2.38478
C	-1.96050	-1.64852	-4.17288
H	-2.84008	-2.11503	-4.66524
H	-1.09447	-1.76907	-4.85666
H	-2.16290	-0.56162	-4.08098
C	-1.29579	-3.79528	-2.99254
H	-1.05392	-4.27979	-2.02636
H	-0.41108	-3.89382	-3.65539
H	-2.12876	-4.36038	-3.46288
C	-3.68710	-0.46288	1.61576
H	-2.66627	-0.03275	1.67886
C	-4.68850	0.71039	1.67953
H	-4.56749	1.39879	0.81933
H	-4.53838	1.29523	2.61106
H	-5.73902	0.34937	1.68219
C	-3.85775	-1.40152	2.83097
H	-4.86445	-1.87059	2.84588
H	-3.74087	-0.83258	3.77712
H	-3.10393	-2.21483	2.83247
O	3.44264	-1.01447	-0.06601

	C	4.16823	-1.38074	1.07593
	H	4.82899	-2.24919	0.82764
	H	3.49284	-1.74835	1.89199
	C	5.05967	-0.28269	1.65688
	C	5.14111	0.98344	1.04781
	C	5.97917	1.98172	1.57823
	C	6.74909	1.72663	2.72604
	C	6.67371	0.46275	3.34234
	C	5.83599	-0.53078	2.81057
	H	4.53149	1.16522	0.14981
	H	6.03167	2.96774	1.08784
	H	7.40710	2.50743	3.14084
	H	7.27272	0.25188	4.24361
	H	5.78351	-1.51991	3.29876
	H	2.46950	-0.76199	0.20765

2a	101			
	xyz			
	N	-1.40915	0.17575	-0.94371
	N	-0.66871	-0.05197	1.06839
	C	-0.29203	0.39168	-0.17450
	C	-2.00060	-0.52087	1.09632
	C	-2.47135	-0.39825	-0.20760
	C	-2.73519	-0.91767	2.31718
	C	-2.20914	-1.83366	3.25977
	H	-1.22047	-2.28212	3.09161
	C	-2.94190	-2.18302	4.40589
	H	-2.51380	-2.89856	5.12575
	C	-4.21326	-1.62905	4.63361
	H	-4.78544	-1.90478	5.53362
	C	-4.74778	-0.71677	3.70592
	H	-5.74017	-0.27042	3.87771
	C	-4.01635	-0.36121	2.56296
	H	-4.43267	0.36464	1.84783
	C	-1.43347	0.46533	-2.36402
	C	-1.22175	-0.59975	-3.28028
	C	-1.25812	-0.29901	-4.65756
	H	-1.09455	-1.10621	-5.38932
	C	-1.48886	1.00673	-5.11014
	H	-1.51095	1.22051	-6.19070
	C	-1.68224	2.04191	-4.18613
	H	-1.85096	3.06800	-4.54973
	C	-1.66123	1.80138	-2.79588
	C	-1.86505	2.97445	-1.83304
	H	-1.86110	2.56720	-0.80050
	C	-0.69758	3.98059	-1.93342
	H	0.27321	3.49454	-1.70566
	H	-0.84476	4.80980	-1.20913
	H	-0.64117	4.43113	-2.94767
	C	-3.22240	3.67830	-2.05015
	H	-3.29003	4.13777	-3.05903
	H	-3.35430	4.49374	-1.30835
	H	-4.08101	2.98350	-1.94008
	C	-0.92404	-2.03178	-2.83275
	H	-1.00509	-2.06613	-1.72668
	C	0.52357	-2.42930	-3.19590
	H	0.67888	-2.43372	-4.29578
	H	0.75397	-3.44925	-2.82159
	H	1.25749	-1.72534	-2.75421
	C	-1.94392	-3.04128	-3.39985
	H	-2.98149	-2.77385	-3.11440
	H	-1.73431	-4.06165	-3.01498

H	-1.89764	-3.09144	-4.50858
C	0.22194	-0.00522	2.21052
C	0.17504	1.11868	3.07439
C	1.05147	1.12987	4.18007
H	1.04146	1.99171	4.86589
C	1.94027	0.07332	4.41370
H	2.61753	0.10466	5.28211
C	1.97470	-1.02180	3.53831
H	2.68318	-1.84296	3.72810
C	1.11791	-1.08993	2.42081
C	-0.73052	2.32088	2.81164
H	-1.40767	2.05534	1.97341
C	0.11711	3.52814	2.35019
H	0.78996	3.87594	3.16349
H	-0.53844	4.38010	2.07047
H	0.74694	3.26148	1.47593
C	-1.61783	2.66766	4.02403
H	-2.23743	1.80256	4.33768
H	-2.30091	3.50627	3.77287
H	-1.01357	2.98980	4.89881
C	1.20014	-2.27821	1.45901
H	0.25603	-2.29865	0.87334
C	2.35548	-2.08204	0.45256
H	2.22349	-1.14467	-0.12326
H	2.39898	-2.92810	-0.26536
H	3.33288	-2.02854	0.97781
C	1.32529	-3.63713	2.17687
H	2.29498	-3.73956	2.70798
H	1.27219	-4.46521	1.43962
H	0.51754	-3.79487	2.92177
C	-3.75206	-0.87247	-0.77265
C	-4.27548	-2.12088	-0.34658
C	-5.48988	-2.60452	-0.85460
C	-6.20691	-1.85976	-1.80863
C	-5.69647	-0.62593	-2.24661
C	-4.48401	-0.13505	-1.73506
H	-3.71214	-2.71941	0.38502
H	-5.87424	-3.57760	-0.50958
H	-7.15824	-2.24214	-2.21131
H	-6.24784	-0.03265	-2.99316
H	-4.10454	0.83474	-2.08376
H	1.10237	1.53729	-0.43717
O	1.79985	2.28129	-0.51130
C	3.04237	1.71409	-0.83324
H	3.41408	1.03371	-0.02136
H	2.98752	1.07635	-1.75467
C	4.10644	2.77473	-1.06209
C	3.83837	4.13776	-0.83133
C	4.83848	5.10727	-1.03150
C	6.12005	4.72772	-1.46435
C	6.39609	3.36706	-1.69789
C	5.39696	2.40144	-1.49818
H	2.83058	4.42197	-0.49501
H	4.61236	6.17051	-0.84741
H	6.90267	5.48733	-1.62195
H	7.39715	3.05768	-2.04033
H	5.62123	1.33692	-1.68603

Computational details: All calculations are performed in Gaussian03 quantum code.[2] The geometries of all the compounds are optimized with the generalized approximation (GGA) to DFT by using the exchange functional of the Becke[3] in addition with the correlation functional of Perdew[4] (BP86). All the atoms are treated with Ahlrich's split valence plus polarization (SVP) basis sets[5] of 6-31G* quality. In all our DFT treatments, the resolution-of-the-identity (RI) approximation (also called "density fitting") for the two electron integrals was employed.[6] The geometries were optimized normally without symmetry constraints. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima or saddle points. Zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies E_e to ground-state energies E_0. The rigid-rotor harmonic approximation was applied for evaluating the thermal and entropic contributions that are needed to derive the enthalpies H_{298} and Gibbs free energies G_{298} at 298 K. For further validation, single-point BP86 calculations were performed at the optimized BP86/SVP geometries employing a larger basis set of triple-ζ quality (TZVP), which is denoted as E_{BIG}. All the figures are made in the Chemcraft visualization software.[7]

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