Supporting information

Modular design of zwitterionic organocatalyst for bulk ring-opening polymerization of cyclic esters

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Contents

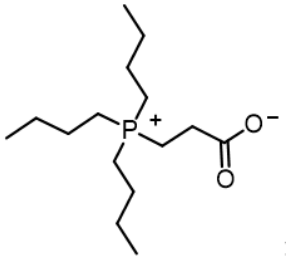
Preparation of the phosphonium carboxybetaine catalysts

Preparation of 3-(tricyclohexylphosphonium) propionate (catalyst **3-Cy**)

3-(tricyclohexylphosphonium) propionate synthesis method: A magneton was added into a 50 mL round-bottomed flask and schlenk operation was performed. Tricyclohexylphosphine (2.80 g, 10 mmol, 1.0 eq) and chloroform solution (10 mL) were added in the inert gas state. In a closed system, acrylic acid (0.7 mL, 10 mmol, 1.0 eq) was slowly added with a syringe under stirring at room temperature, and the solution gradually turned pale yellow. Stirred at room temperature for 24 h, the reaction liquid was concentrated in vacuum and precipitated into a light yellow viscous liquid in ether. By dissolving a small amount of chloroform and washing with ether precipitation three times, the catalyst **3-Cy** was obtained as a white solid by vacuum drying (2.88 g, 82%). Catalyst **3-Bu** was prepared by this method.

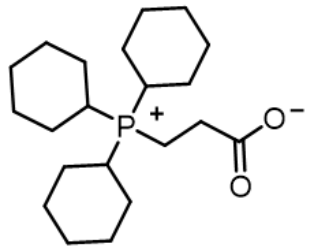
Preparation of 3-(triphenylphosphonium) propionate (catalyst **3-Ph**)

Catalyst **3-Ph** synthesis method: A magneton was added into a 50 mL round-bottom flask and schlenk operation was performed. Triphenylphosphine (2.62 g, 10 mmol, 1.0 eq) and ethyl acetoacetone solution (10 mL, v/v = 4:1) were added in the inert gas state. In a closed system, acrylic acid (0.7 mL, 10 mmol, 1.0 eq) was slowly added with a syringe under stirring at room temperature. After 1 h, white precipitate was slowly produced. Stir at room temperature for 24 h and strain to obtain white solid. After the ethyl ether was washed three times, the ethanol recrystallized and vacuum dried, the catalyst **3-Ph** was a white solid (2.90g, 87%). Catalyst **3-Ph-Me** and **3-Ph-OMe** were prepared by this method.

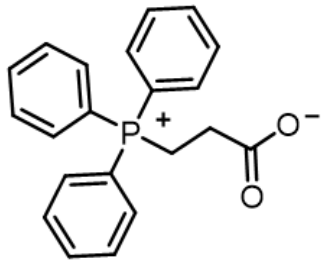


3-(tribubutylphosphonium) propionate (catalyst 3-Bu), Oily liquid, yield: 72%.**^{1}H NMR** (400

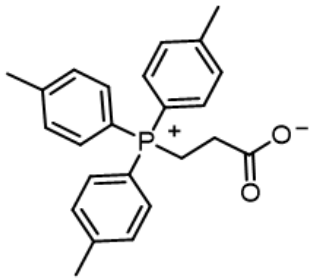
MHz, $CDCl_3$) δ 2.49 (dt, J = 19.9, 6.9 Hz, 2H), 2.28 (dt, J = 11.7, 6.9 Hz, 2H), 2.16 (ddt, J = 12.8, 9.5, 5.3 Hz, 6H), 1.45 (tdd, J = 12.3, 9.5, 6.9 Hz, 12H), 0.90 (t, J = 7.0 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.13, 171.99, 134.99, 134.96, 133.35, 133.25, 130.49, 130.37, 119.69, 118.83, 29.84, 29.79, 20.99, 20.47. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.77.



3-(tricyclohexylphosphonium) propionate (catalyst 3-Cy), White solid, yield: 82%.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 2.64-2.41 (m, 7H), 1.88-1.75 (m, 6H), 1.67-1.64 (m, 6H), 1.52-1.41 (m, 12H), 1.38-1.26 (m, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 172.80, 172.68, 28.70, 28.29, 27.53, 27.49, 26.03, 25.98, 25.86, 25.00, 10.84, 10.39. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 33.46.

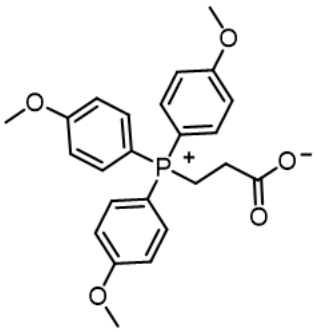


3-(triphenylphosphonium) propionate (catalyst 3-Ph), White solid, yield: 87%.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (m, 3H), 7.61 (m, 12H), 3.53 (m, 2H), 2.55 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.13, 171.99, 134.99, 134.96, 133.35, 133.25, 130.49, 130.37, 119.69, 118.83, 29.84, 29.79, 20.99, 20.47. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.89.

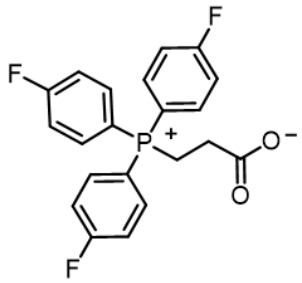


3-(tri (4-methylphenyl) phosphonium) propionate (catalyst 3-Ph-Me), White solid, yield: 85%.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.62 (m, 6H), 7.52 (m, 6H), 3.49, (m, 2H) 2.43 (s, 9H), 2.05 (m,

2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.27, 170.12, 145.00, 144.97, 133.33, 133.22, 130.61, 130.49, 117.23, 116.35, 29.91, 29.86, 21.19, 19.28, 18.77. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 23.09.

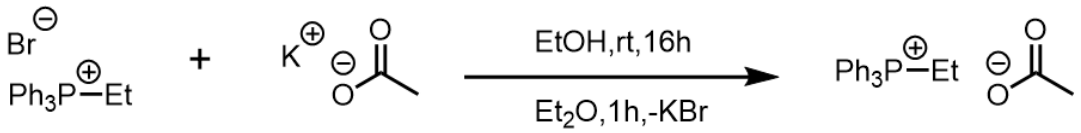


3-(tri (4-methoxyphenyl) phosphonium) propionate (catalyst 3-Ph-OMe), White solid, yield: 89%.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.65 (m, 6H), 7.26 (m, 6H), 3.87 (s, 9H), 3.4 (m, 2H), 2.04 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.26, 171.11, 163.77, 163.74, 135.43, 135.32, 115.81, 115.67, 110.72, 109.79, 55.83, 29.95, 29.91, 19.74, 19.22. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 22.33.



3-(tri (4-fluorophenyl) phosphonium) propionate (catalyst 3-Ph-F), White solid, yield: 51%.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.81 (m, 6H), 7.54 (m, 6H), 3.62 (m, 2H), 2.17 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.66, 171.53, 166.54, 166.51, 164.02, 163.98, 136.51, 136.40, 136.30, 118.69, 118.66, 117.77, 117.74, 117.43, 117.29, 117.21, 117.07, 29.83, 29.78, 20.53, 19.98. **^{31}P NMR** (162 MHz, DMSO-d_6) δ 19.92. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -104.12.

Preparation of ionic pair consisting of phosphonium cation and carboxylate anion



To a dry 25 mL Schlenk flask, ethyl triphenylphosphine bromide (1.11 g, 3 mmol) was added under a nitrogen atmosphere and the salt was dried under reduced

pressure. Dry EtOH (4 mL) was added to give a ca. 0.6 M solution of the salt. Under agitation, a solution of potassium acetate in dry EtOH (1.00 M, 3 mL, 3 mmol) was added slowly over the course of 20 minutes and the resultant mixture was stirred for 16 hours. Then, dry Et_2O (16 mL) was added and the precipitate of KBr was allowed to settle for one hour. Remove the EtOH-Et_2O. The solvent was removed *in vacuo* to yield a syrupy material. Et_2O (8 mL) was added to precipitate the product into a white solid. The ethereal layer was removed and the solid dried to give product as a fine, crystalline powder (1.28 g, 92%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.90 (ddt, 3H), 7.84 – 7.74 (m, 12H), 3.66 – 3.55 (m, 2H), 1.56 (s, 3H), 1.22 (dd, 3H)ppm; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.21, 133.66, 133.56, 130.30, 119.18, 25.98, 18.54, 7.25 ppm; **^{31}P NMR** (162 MHz, DMSO-d_6) δ 28.53.

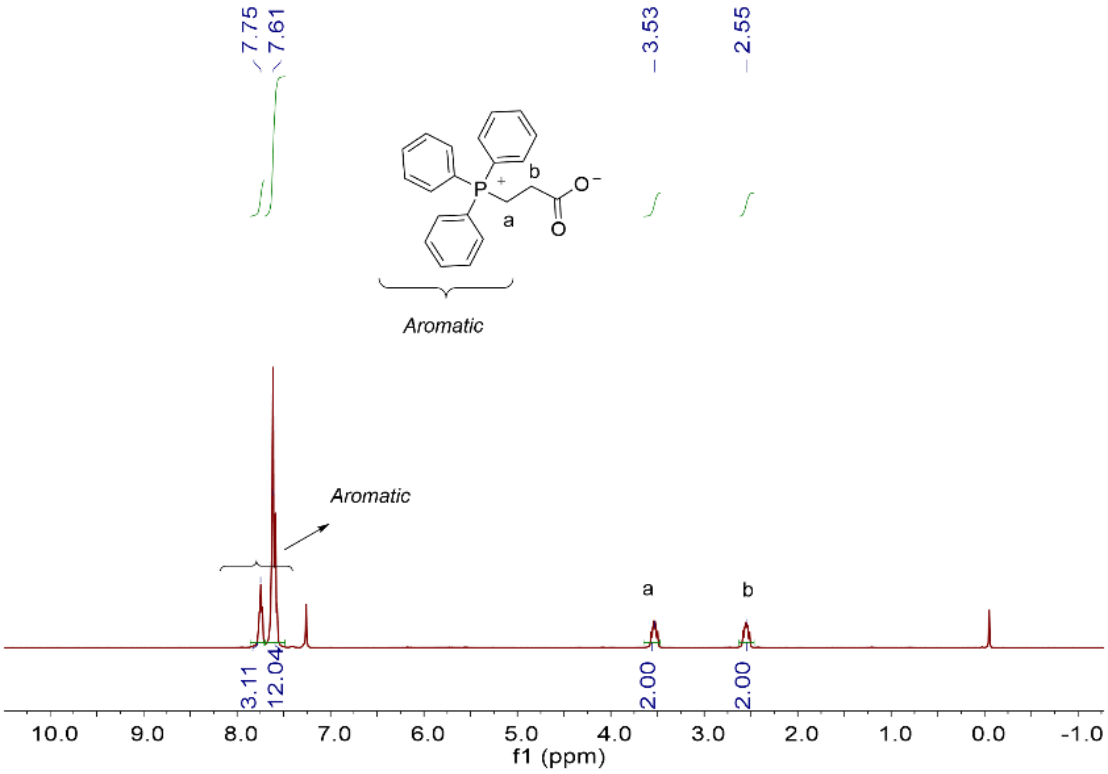


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 3-(triphenylphosphonio) propanoate.

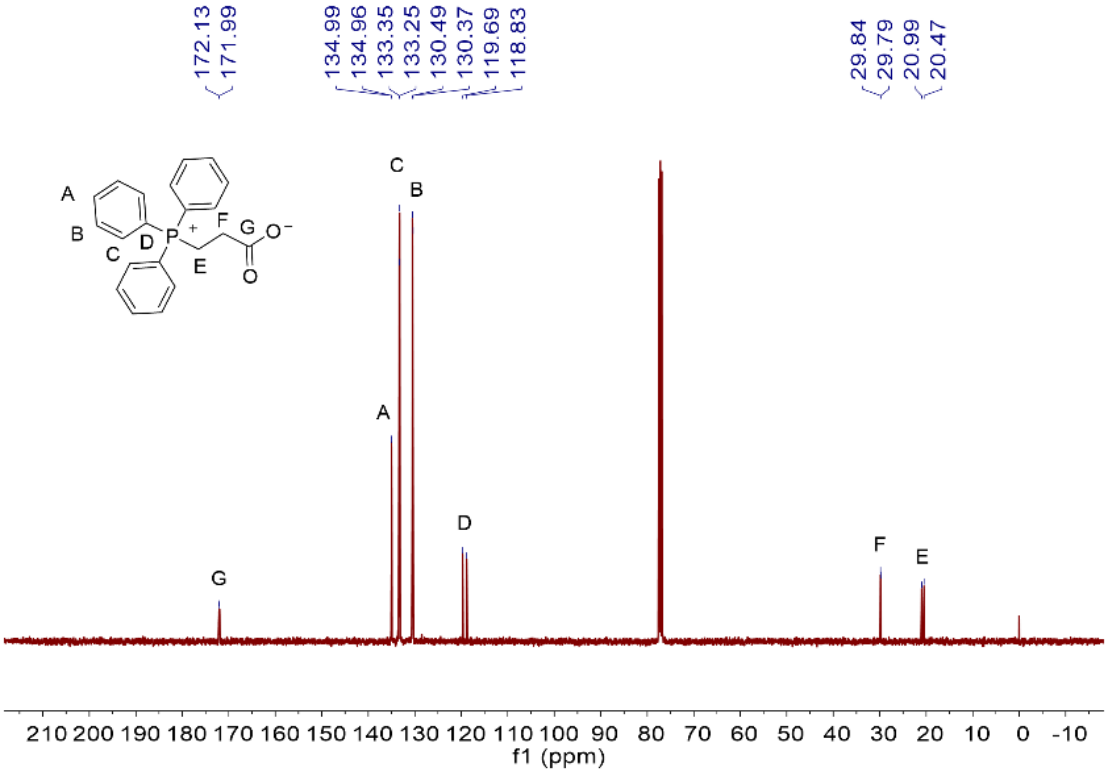


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 3-(triphenylphosphonio) propanoate.

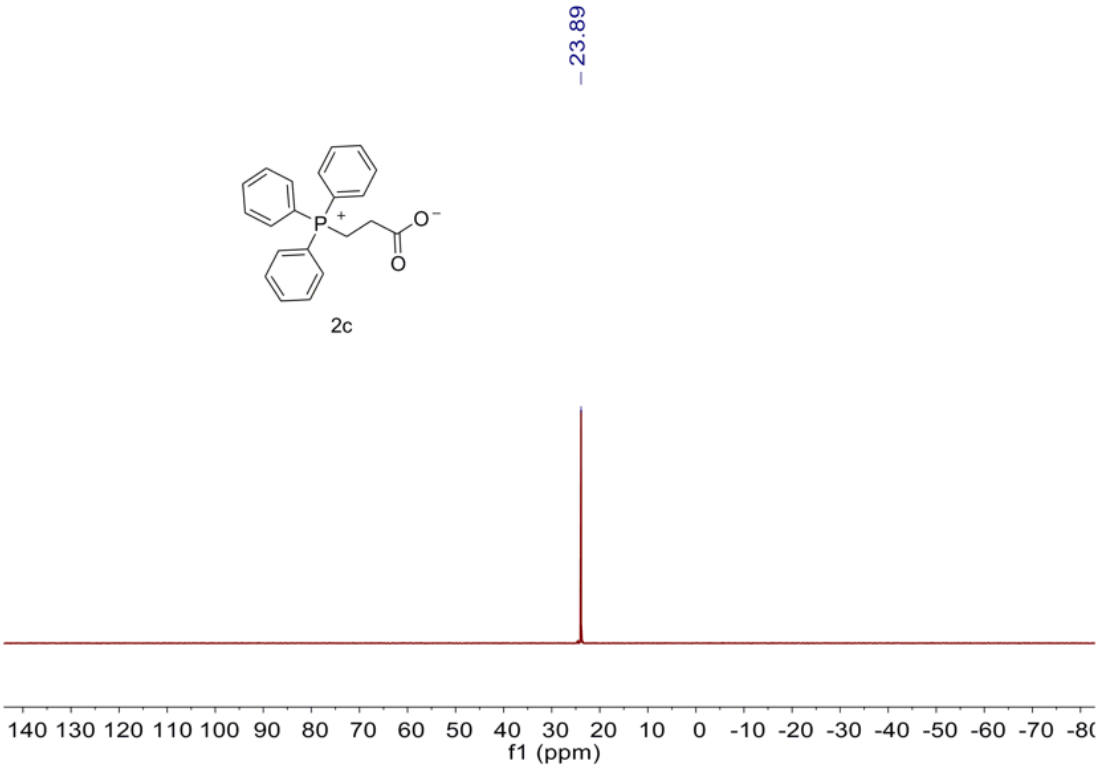


Figure S3. ^{31}P NMR spectrum ($CDCl_3$, 162 MHz) of 3-(triphenylphosphonio) propanoate.

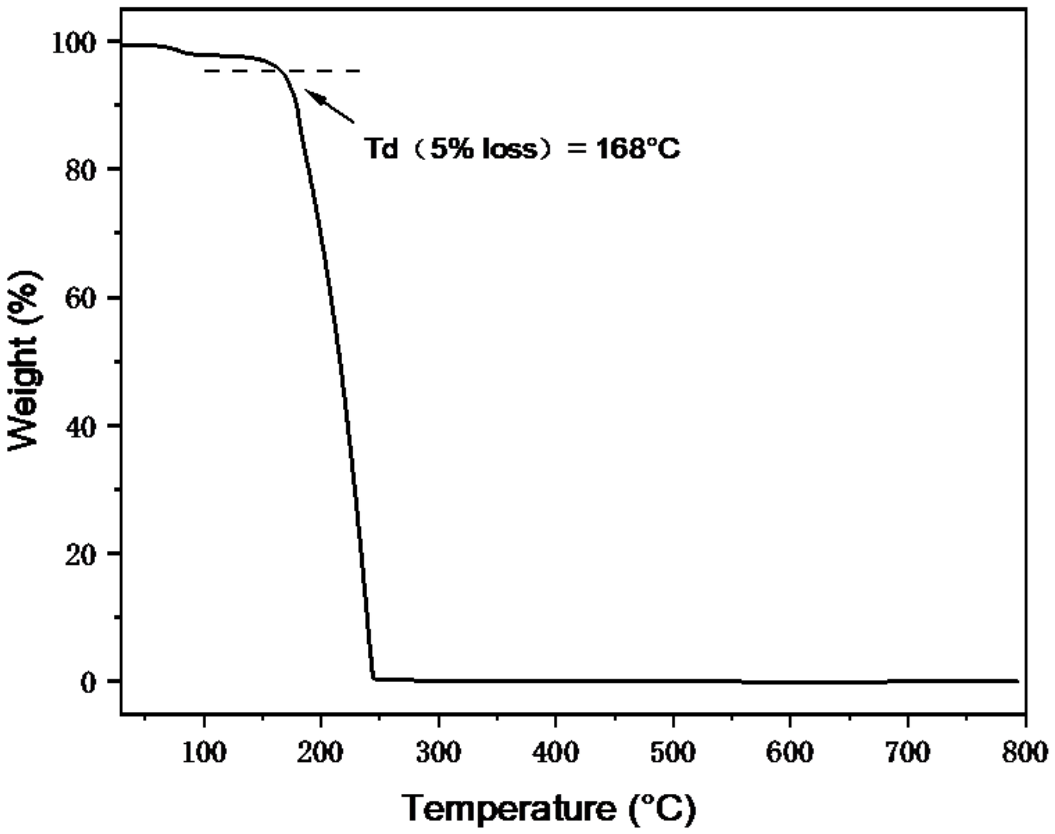


Figure S4. TGA of 3-(triphenylphosphonio) propanoate.

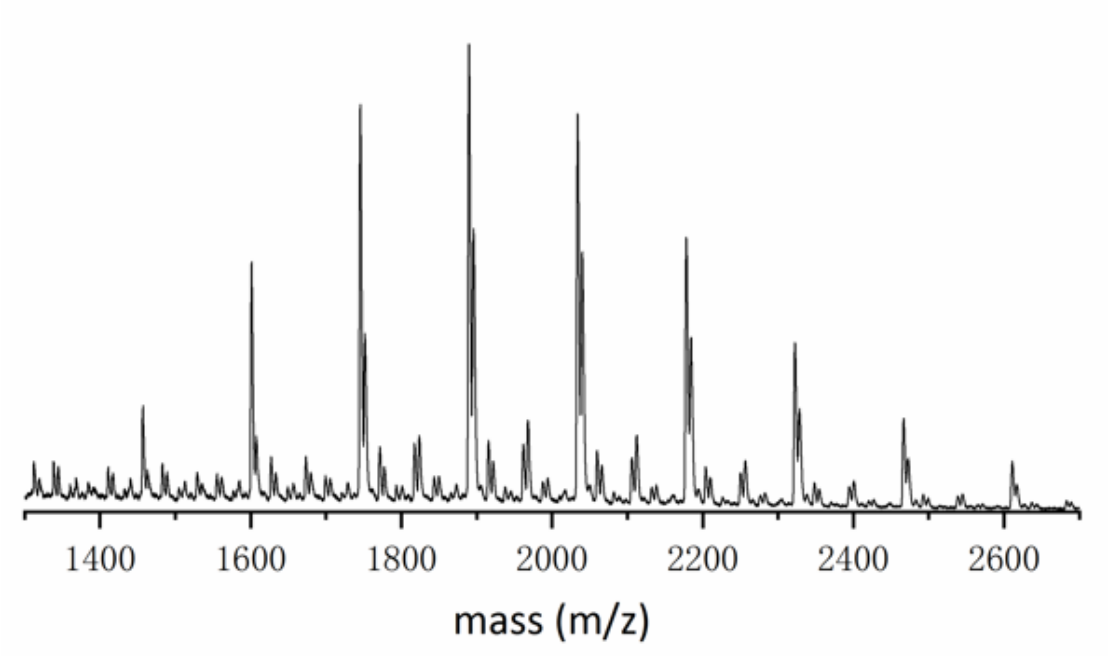
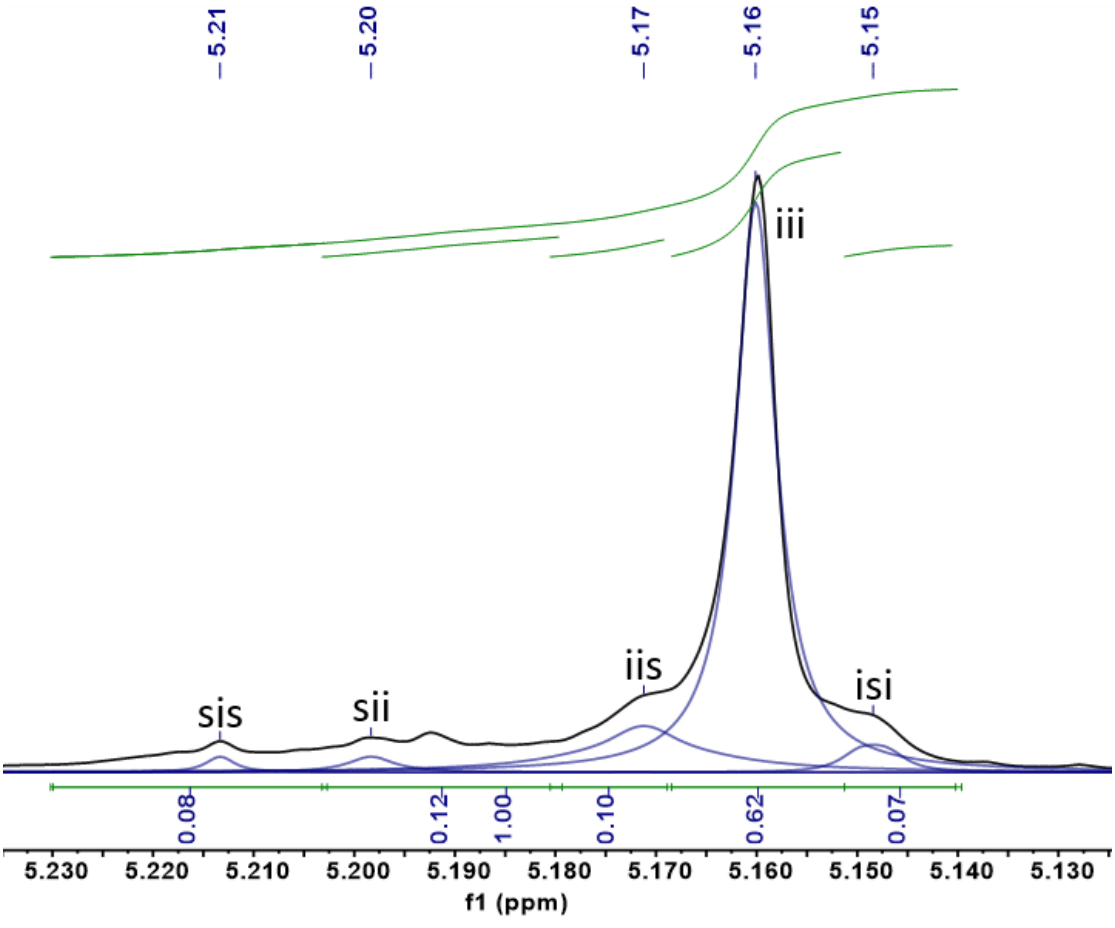


Figure S5. MALDI-TOF MS spectrum of the obtained PLLA ([LLA]/[PPA]/[**3-Ph**] = 25, 140°C, conversion = 70%, $M_{n,\,NMR}$ = 2.3 kg·mol^{-1}, $Đ$ = 1.13).

Figure S6. The isotacticity of PLLA was calculated by ^{1}H NMR spectrum in $CDCl_3$. The isotacticity P_m = 0.72.



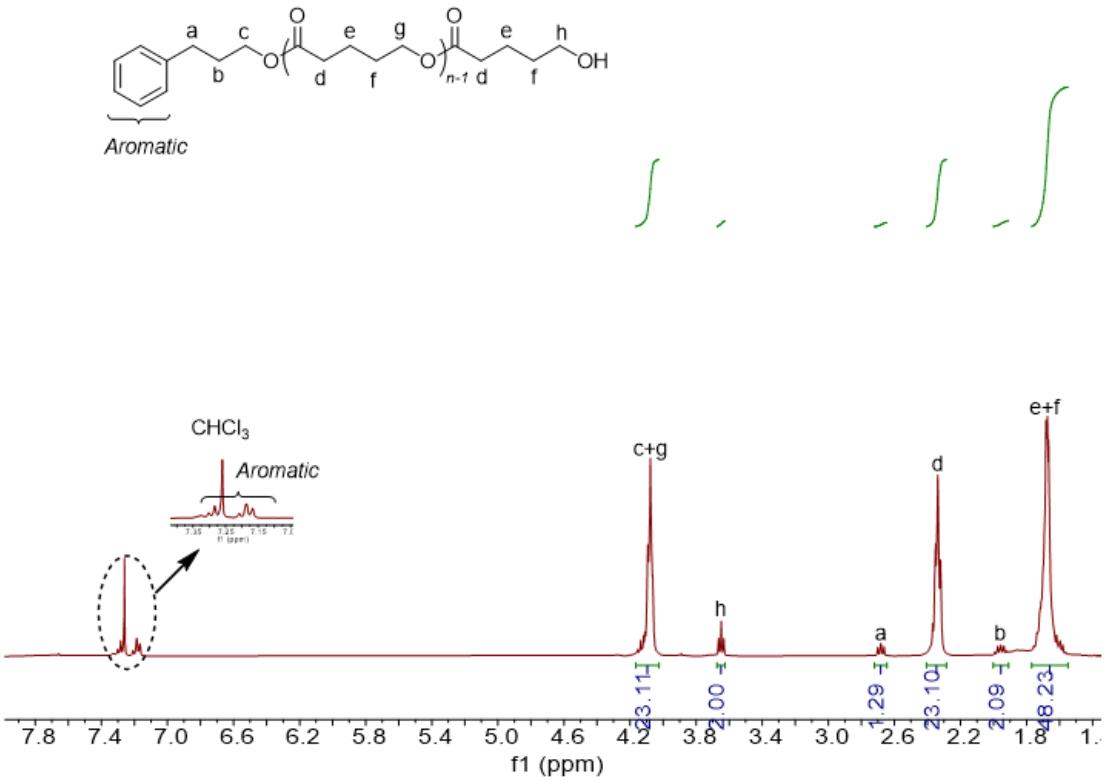


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (*δ*-valerolactone).

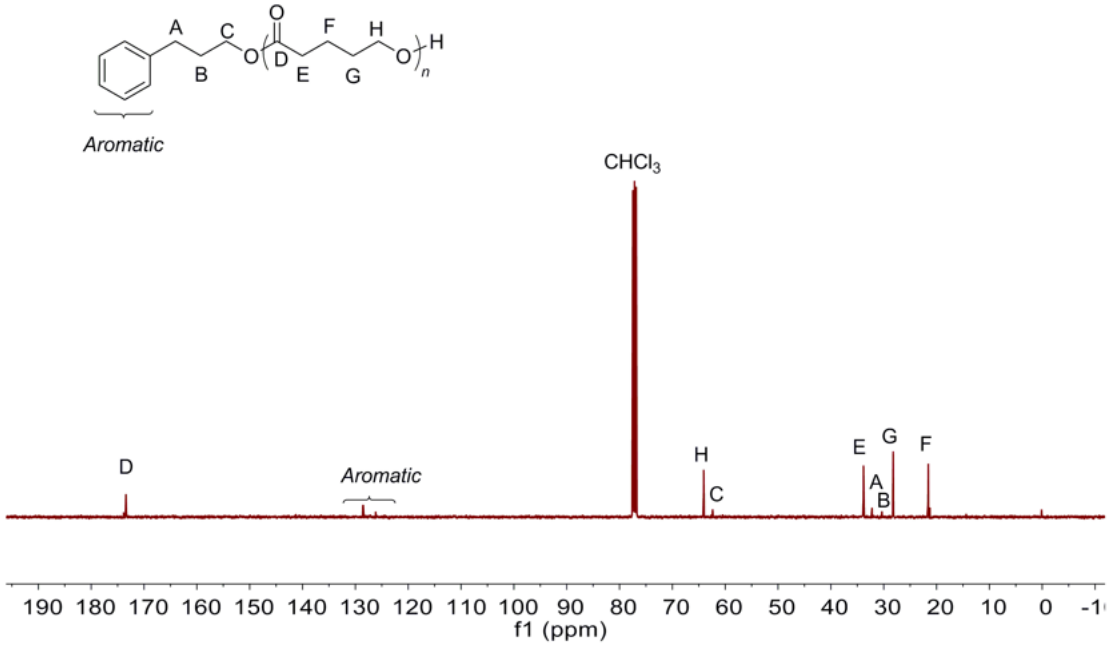


Figure S8. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of poly (*δ*-valerolactone).

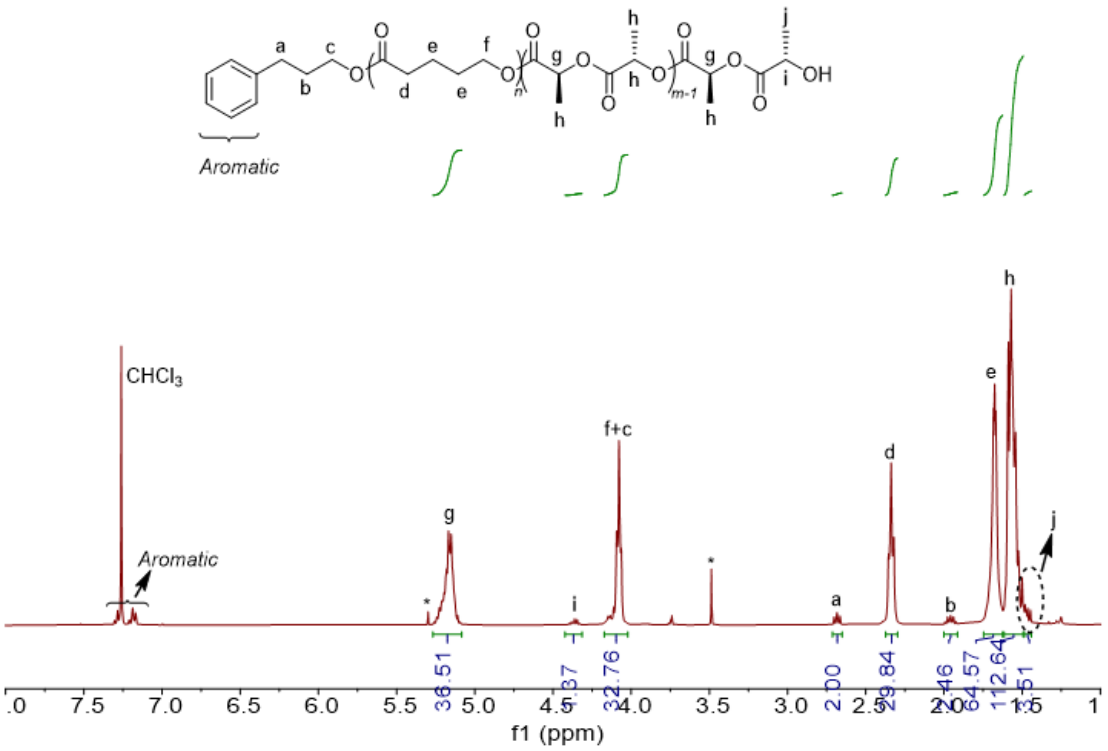


Figure S9. ^{1}H NMR spectrum of PVL-*b*-PLLA in $CDCl_3$.

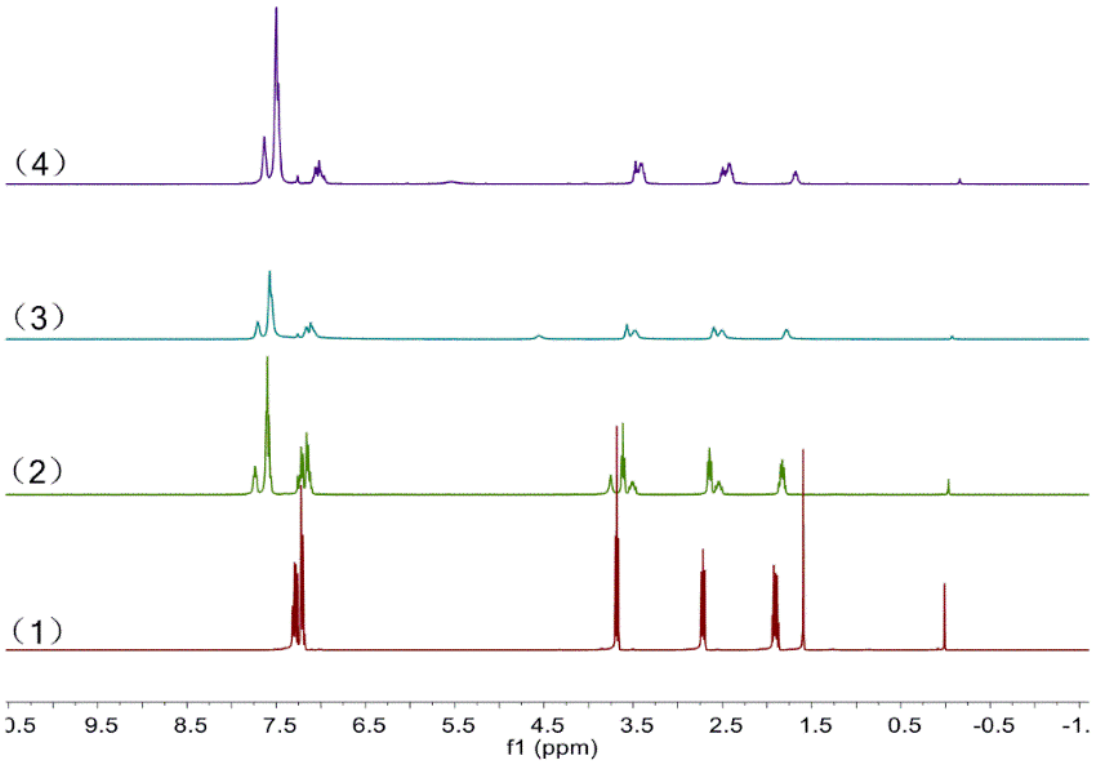


Figure S10. ^{1}H NMR spectrum of PPA in $CDCl_3$ in the presence of varied amounts of 3-(triphenylphosphonio) propanoate (**3-Ph)**: (1) PPA, (2) **3-Ph**/PPA = 0.5/1, (3) **3-Ph**/PPA = 1/1, (4) **3-Ph**/PPA = 2/1.

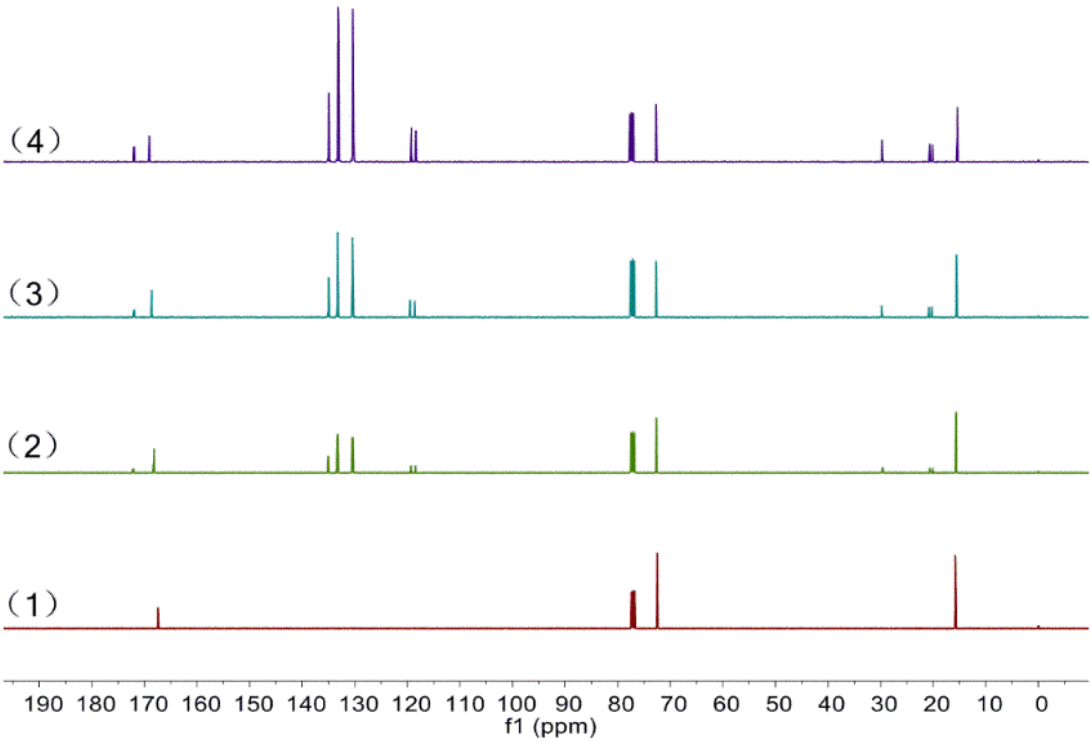


Figure S11. ^{13}C NMR spectrum of LLA in $CDCl_3$ in the presence of varied amounts of 3-(triphenylphosphonio) propanoate (**3-Ph)**: (1) LLA; (2) **3-Ph**/LLA = 0.5/1; (3) **3-Ph**/LLA = 1/1; (4) **3-Ph**/LLA = 2/1.

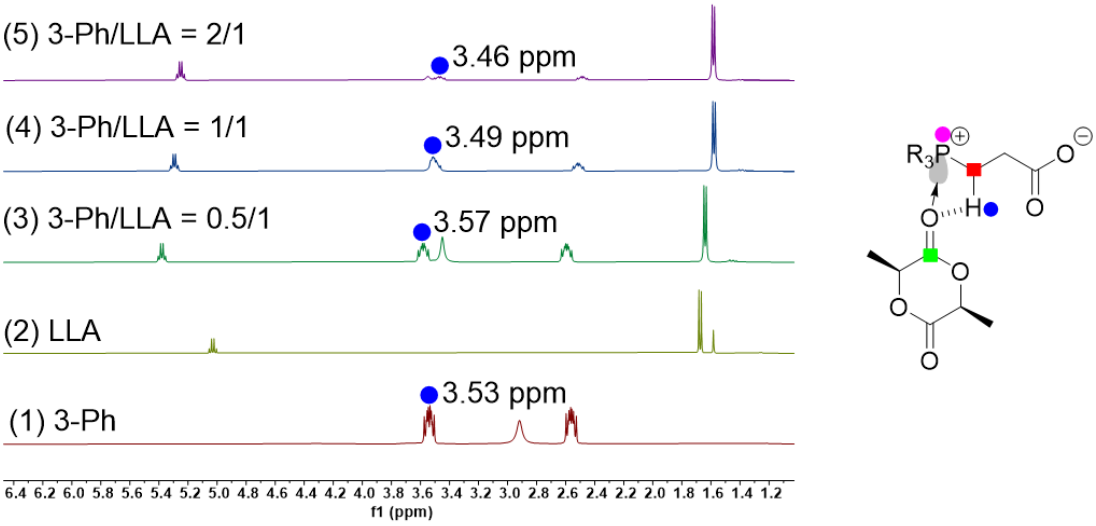


Figure S12. The chemical shifts of the α-C–H proton (blue dots) of **3-Ph** in the ^{1}H NMR spectra ($CDCl_3$) observed in the presence of varied amounts of **3-Ph**: (1) **3-Ph**/LLA = 1/0, (2) **3-Ph**/LLA = 0/1, (3) **3-Ph**/LLA = 0.5/1, (4) **3-Ph**/LLA = 1/1, (5) **3-Ph**/LLA = 2/1.

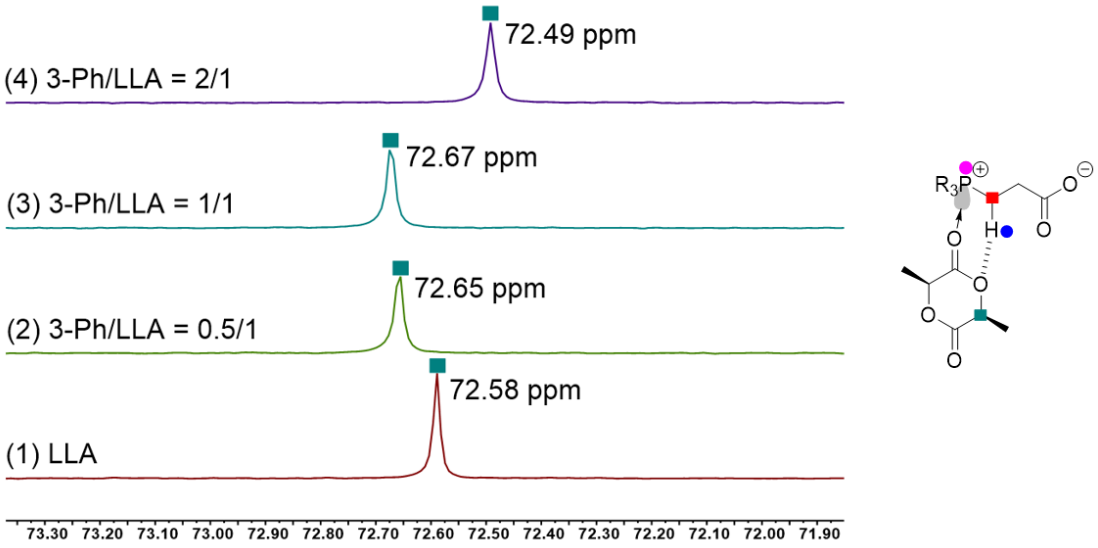


Figure S13. The chemical shifts of the C-H carbon (green dots) of L-LA in the ^{13}C NMR spectra ($CDCl_3$) observed in the presence of incremental amounts of **3-Ph**: (1) LLA; (2) **3-Ph**/ LLA = 0.5/1; (3) **3-Ph**/ LLA = 1/1; (4) **3-Ph**/ LLA = 2/1.

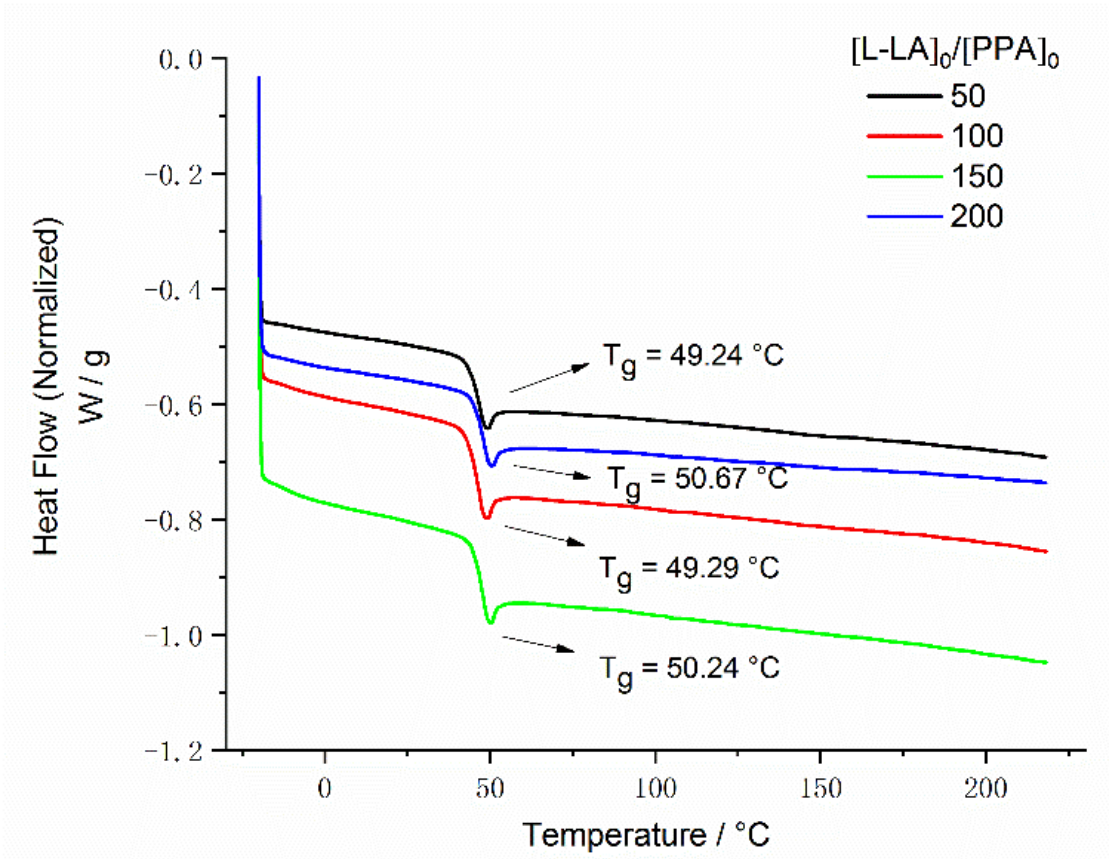


Figure S14. DSC test of PLLA samples with different molecular weights.

Table S1 Thermogravimetric analysis of quaternary phosphine carboxylate **3-R**[a]

Catalyst	**3-Bu**	**3-Cy**	**3-Ph**	**3-Ph-Me**	**3-Ph-OMe**	**3-Ph-F**
$T_{d5\%}$/℃	197	206	168	214	169	188

[a]Measured by TGA; $T_{d5\%}$/°C represents the temperature at 5% mass loss.