Electronic Supplementary Information (ESI) for

Imidodiphosphoric acid as a bifunctional catalyst for the controlled ring-opening polymerization of *δ*-valerolactone and *ε*-caprolactone†

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and Zhenjiang Li*

Preparation of diphenyl phosphoramide 1a. Diphenyl chlorophosphate (2.292 mmol, 0.64 mL) was added into a 50 mL dry round-bottomed flask in a glovebox. Then anhydrous ammonia gas was condensed into the flask at -78 °C (Ca. 10 mL). After 1 h, removing the cold bath and the compound was allowed to warm to room temperature. The compound was concentrated and drynessed under vacuum. The crude product was purified through silica gel column using CH_2Cl_2 as the eluent to get the corresponding diphenyl phosphoramide as white solid.

692 mg, 95% yield;

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.33– 6.41 (m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 129.73 (s), 125.11 (s), 120.33 (d, J = 4.8 Hz)

^{31}P NMR (121 MHz, $CDCl_3$): δ -0.30 (s).

HRMS (ESI-) (*m*/*z*): [M-H] calcd for $C_{24}H_{21}NO_6P_2$, 249.060; found, 249.063

General procedure for synthesis of imidodiphosphoric acid 1b. To a solution of diphenyl chlorophosphate (0.84 mmol, 0.18 mL) and diphenyl phosphoramide (0.764 mmol, 0.19 g) in THF (5 ml) was added sodium hydride (60% dispersion of in mineral oil, 120 mg, 5 mmol) at

room temperature in a glovebox. After being stirred for 24 h at room temperature, 10% aqueous HCl solution and CH_2Cl_2 were injected into the mixture and stirred for 1 h. Separated organic layer was concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (eluent: first 50–100% CH_2Cl_2/hexane; second 3-6% EtOAc/CH_2Cl_2) provided imidodiphosphoric acid which may be salt. The product was dissolved in CH_2Cl_2 and stirred with 3N aqueous HCl for 4 h. The organic layer was separated, extracted with 3N aqueous HCl again, dried over anhydrous $MgSO_4$ and filtered. The concentration of the solution under reduced pressure giving the desired imidodiphosphoric acid as white solid.

877 mg, 65% yield;

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.62–6.71 (m)

^{13}C NMR (75 MHz, CDCl3): δ 150.85–149.68 (m), 129.64 (s), 125.37 (s), 120.88– 120.19 (m).

^{31}P NMR (121 MHz, CDCl3): δ–10.80 (s).

H RMS (ESI-)(m/z): [M-H] calcd for $C_{24}H_{21}NO_6P_2$,480.080;found, 480.073

Procedure for Kinetic Studies. Polymerization was carried out in toluene at 25 °C in a glovebox with a δ-valerolactone (δ-VL) concentration of 1M (275 mg, 2.75 mmol), and a δ-VL/benzyl alcohol/imidodiphosphoric acid molar ratio of 50/1/1 (5.8 μL, 0.055 mmol of benzyl alcohol and 26.5 mg, 0.055 mmol of imidodiphosphoric acid). Aliquots were taken at different times during the polymerization and quenched with a drop of *N*,*N*-Diisopropylethylamine to neutralize the catalyst. The conversion of δ-VL was determined by ^{1}H NMR spectroscopy (300 MHz). Thus, the solvent was evaporated under vacuum. The polymer was recovered by precipitation from $CHCl_3$ in cold hexane/methanol and dried under high vacuum. The poly(δ-

valerolactone) (PVL) samples were analyzed by SEC in THF solution. A similar condition for δ-VL was used for the polymerization of ε-CL. The calculation of conversion (from ^{1}H NMR) was also described (Fig. S1). The conversion of the polymerization (Conv%) is obtained from the integration ratio between the methylene protons neighboring the carbonyl group of the polymer (peaks C) and integral values of both peaks C and the methylene protons belong to the monomer (peak C'). This conversion value increased as the monomer was consumed and the polymer prolonged.

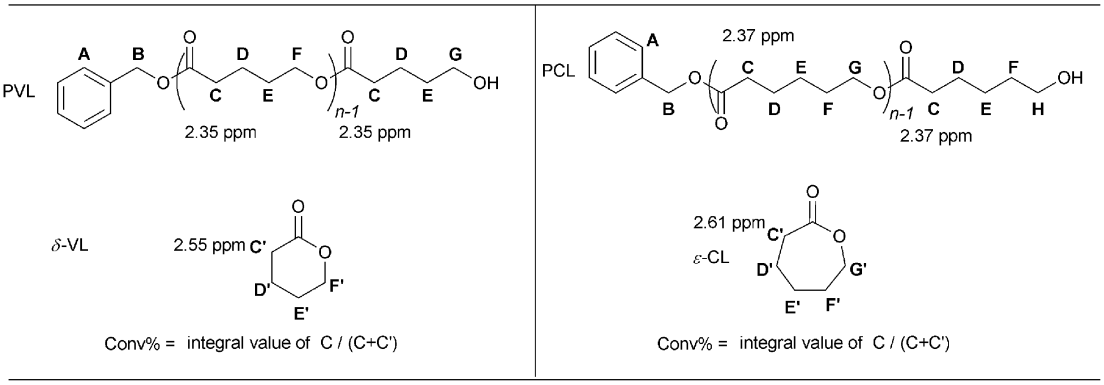

Fig. S1 Calculation method of the monomer conversion from the ^{1}H NMR integral values.

Procedure for synthesis of PCL. In a glovebox, ε-caprolactone (ε-CL) (0.468 mL, 5 mmol, 50 equiv) was disolved in toluene ($[\delta\text{-VL}]_0$ = 1.0 mol L^{-1}) and benzyl alcohol (10.34 μL, 0.1 mmol, 10.81 mg, 1 equiv) was added to the toluene solution. IDPA (0.0481 g, 0.1 mmol, 1 epuiv) was then added to initiate the polymerization. The mixture was stirred for 24 h at 25 °C. An excess of *N,N*-Diisopropylethylamine was added to neutralize the catalyst. The solvent was evaporated under vacuum and the polymer was recovered by precipitation from $CHCl_3$ in methanol and dried within a vacuum drying chamber at 40 °C. Yield, 70.2%; $M_{n\ NMR}$, 5930 g mol^{-1}; M_w/M_n, 1.10. ^{1}H NMR ($CDCl_3$), δ (ppm), 1.26 (m, 2H × n, $(–CH_2CH_2CH_2CH_2CH_2–)_n$), 1.62 (m, 2H × n, $(–CH_2CH_2CH_2O–)_n$), 1.68 (m, 2H × n, $(–COCH_2CH_2–CH_2–)_n$), 2.37 (t, 2H × n,

J = 7.3 Hz, (–OCOCH$_2$CH$_2$–)$_n$), 3.65 (t, 2H, J = 6.6 Hz, –CH$_2$CH$_2$OH), 4.09 (t, 2H × n, J = 6.9 Hz, (–CH$_2$CH$_2$O–)$_n$), 5.12 (s, 2H, ArCH$_2$O), 7.22–7.47 (m, 5H, aromatic).

The selection of initiator. In those previous reported phosphoric-based acid organocatalysis for ROPs, varied alcohols were used as the initiators, as show in Fig. S2. To our knowledge, in IDPA-catalyzed ROPs, alcohols with general type structures such as methanol, benzyl alcohol, and phenylpropyl alcohol, etc. will be suitable for the initiate process. From the MALDI-TOF analyses, residual H_2O can act as the initiator to carry out ring-opening polymerization with IDPA. In this work, benzyl alcohol was selected as initiator because its incorporation as benzylester end group is easily detectable by NMR spectroscopy. In the research of ROPs, benzyl alcohol is the most widely used initiator.

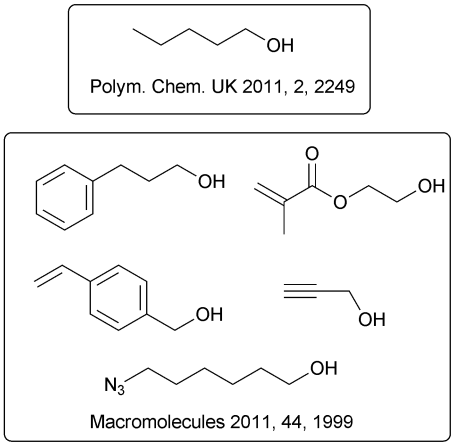

Fig. S2 The selectivity of varied alcohols as initiators.

Supplementary Data

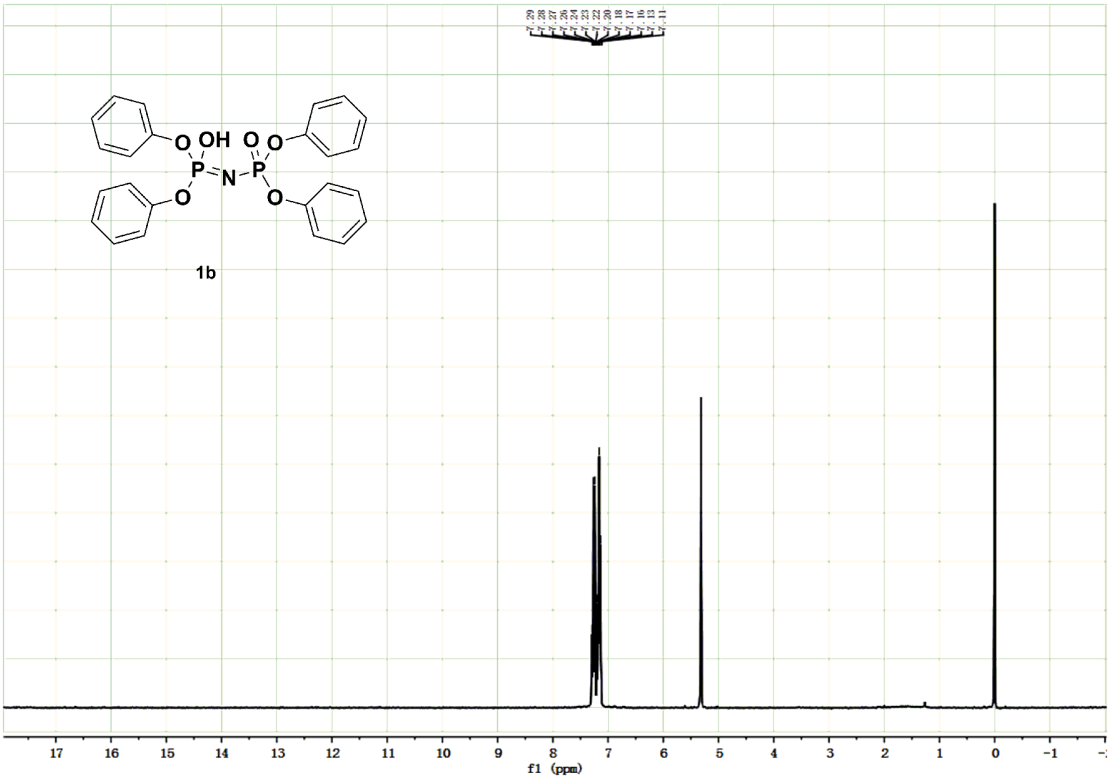

Fig. S3 ^{1}H NMR spectrum of 1b

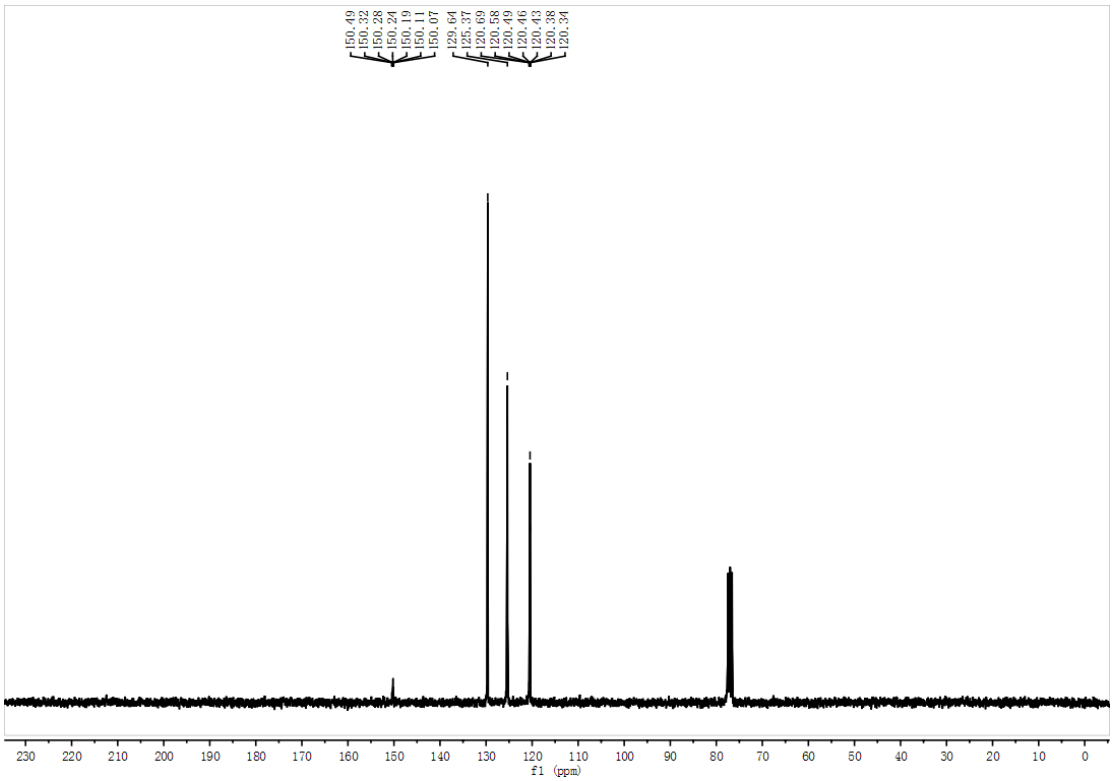

Fig. S4 ^{13}C NMR spectrum of 1b

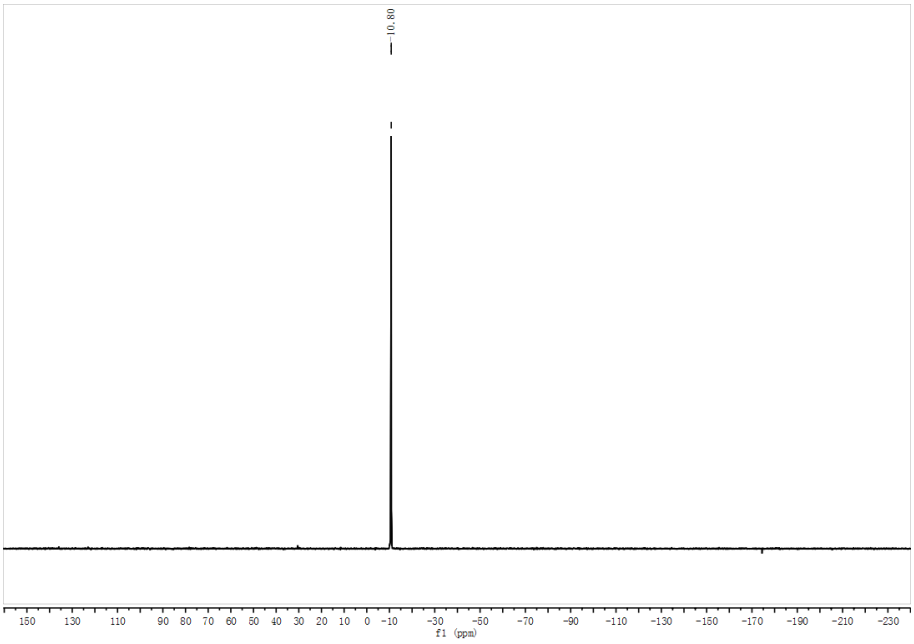

Fig. S5 ^{31}P NMR spectrum of 1b

Mass spectrum

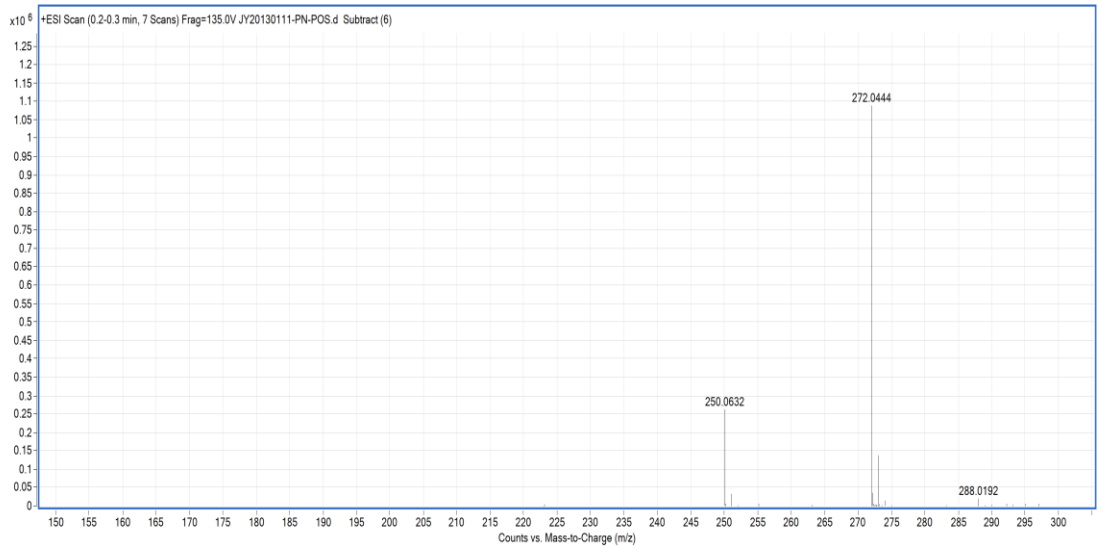

Fig. S6 Mass spectrum of 1a

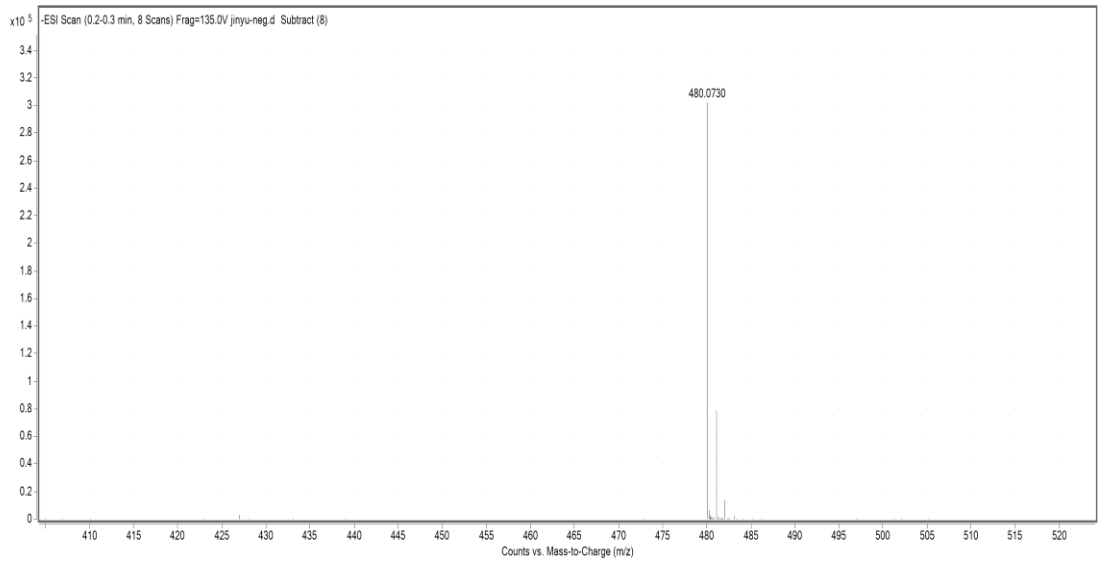

Fig. S7 Mass spectrum of 1b

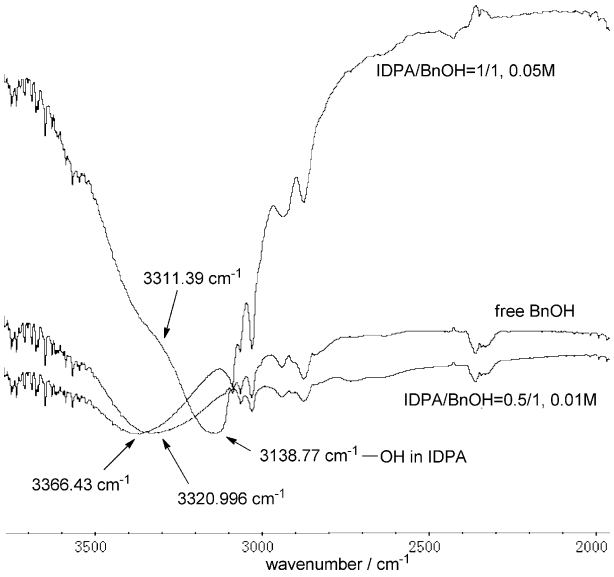

Fig. S8 FT-IR spectroscopy of alcoholic hydroxyl group observed by titration of BnOH with IDPA in toluene.

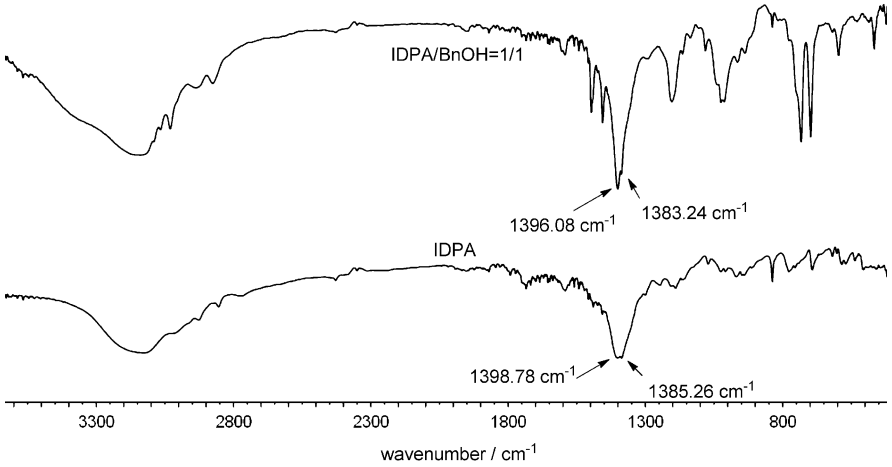

Fig. S9 FT-IR spectroscopy of phosphorus carbonyl observed by titration of BnOH with IDPA in toluene.

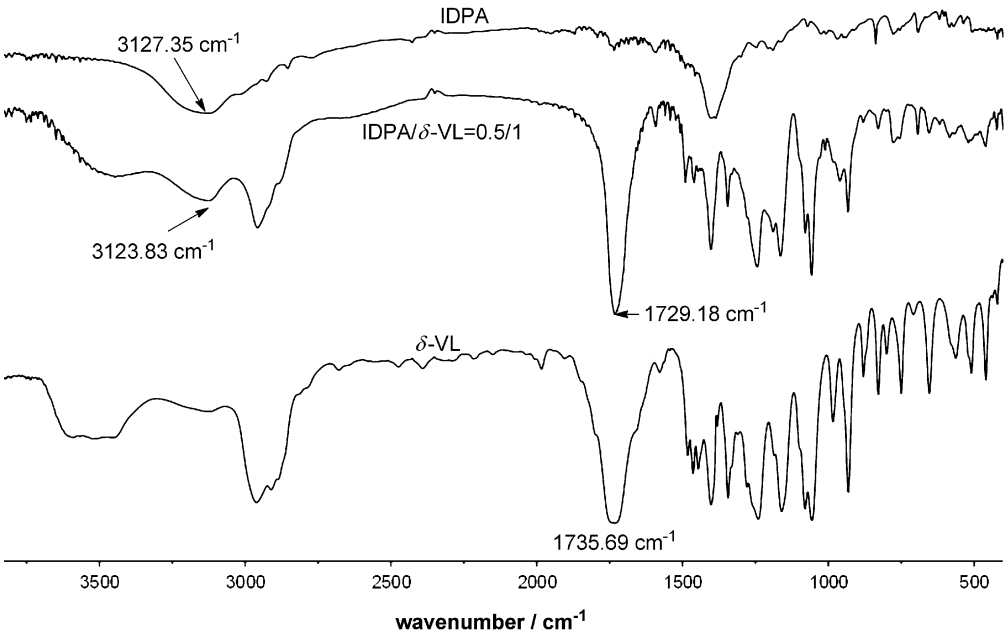

Fig. S10 FT-IR spectroscopy of hydroxyl group in IDPA and carbonyl group in δ-VL observed by titration of δ-VL with IDPA in toluene.