

Electronic Supplementary Information

Efficient and sustainable transformation of gamma-valerolactone into Nylon monomers

Yong Yang, Xurui Wei, Fanxin Zeng, and Li Deng*

Experimental methods

All reagents were obtained from commercial supplier and used without further purification. The yields of products were determined by a Shimadzu GC2010 gas chromatography instrument equipped with a 30 m capillary column (HP-35) and a FID detector or a gas chromatography-mass spectrometer system (Shimadzu QP2010). ¹H NMR spectra was recorded on a Bruker 400 MHz NMR-spectrometer and FT-IR spectroscopy was performed on a Bruker TENSOR 27 FT-IR spectrophotometer.

Catalytic distillation of GVL to methyl pentenoates

The ionic liquid **DIM-TFA** was synthesized according to our previously reported procedure.^[1] 6.8 g (0.1) mole imidazole was dissolved in 25 ml toluene/DMSO mixture (1 : 1) under N₂ atmosphere in a 50 mL flask and 10 mL 10 M NaOH aqueous solution was added. After removal of all water by gradually heating the mixture to 170 °C, the flask was cooled down and 10.7 g (0.05 mol) 1,4-dibromobutane was added dropwise, affording yellow solid mixture of 1, 4-diimidazol-1-yl butane and NaBr. Then the mixture was dissolved by 50 mL chloroform to remove NaBr and purified 1, 4-diimidazol-1-yl butane was obtained by precipitation in water after evaporating chloroform. Then it was dissolved in 30 mL acetonitrile and 0.1 mol 1,3-propanesultone in 10 mL toluene was added slowly with stirring in ice bath. The mixture was heated to 50 °C for 2 h and the zwitterionic precursor was precipitated. After filtration, the resulting precipitate was washed with diethyl ether (20 mL X 3) and dried under vacuum. Finally, equivalent amount of trifluoromethanesulfonic acid was added into the zwitterionic precursor to afford **DIM-TFA**. ¹H NMR (400 MHz, D₂O) for **DIM-TFA** (Figure S1): δ=1.80(s, 2H), 2.22(m, 2H), 2.80(t, 2H), 4.16(d, 2H), 4.27(t, 2H), 7.41(s, 1H), 7.46(s, 1H), 8.74(s, 1H)

To prepare methyl pentenoates, 1.1 g **DIM-TFA** and initial 5 g of GVL were added to a 25 mL flask equipped with condenser and heated to 170 °C. Then a methanol solution containing 20 wt% GVL was injected into the reactor by a syringe pump at a flow rate of 15 mL h⁻¹. Meanwhile, an argon flow of 20 mL min⁻¹ was applied to carry the vapour of esters out of the

reactor. The resulting products were collected and distilled to remove methanol. After removal of methanol, two separated layers could be observed. Then the organic layer containing methyl pentenoates could be isolated from the water layer.

Additionally, we observed that the reaction mixture's color changed from light yellow to dark brown after several hours run. To recover the used **DIM-TFA**, distilled water was added into the reaction residues to dissolve the ionic liquid and remove the insoluble by-product. After extraction with chloroform and evaporating water, the recovered **DIM-TFA** was dried under vacuum. As a result, 95 wt% ionic liquid was recovered from water phase and black viscous by-product were obtained from oil phase. Comparison of the ^1H NMR spectra of the fresh and recovered **DIM-TFA** (Figure S2 and S3) showed no structural change of the ionic liquid. This consisted with the previous thermal gravity results which indicated the ionic liquid was stable below 350 °C.^[1] Moreover, the recovered ionic liquid was able to convert more than 96 % of GVL to pentenoates in another 12 h run (Figure S1b), revealing that the recovered **DIM-TFA** was still active for this reaction. Besides, the FT-IR and ^1H NMR spectra of the viscous by-product (Figure S4 and S5) suggested that it might be generated from the condensation of GVL or pentenoates under acidic condition and also excluded it was derived from **DIM-TFA** since no C-C double bond or imidazole ring was detected. Thus the weight loss of ionic liquid was mainly caused by the operation on a gram-scale. The recovery rate could be improved when scale-up was carried out.

Synthesis of dicarboxylic esters

As a typical procedure of metathesis reactions, 1 g substrates and desired amount of catalyst were added into a 5 mL flask equipped with condenser. The reaction was performed under argon using Schlenk line technique. After the reaction, the resulting mixture was sampled and analyzed by GC or GC-MS. To hydrogenate the unsaturated dicarboxylic esters, the mixture from metathesis reaction was diluted with 20 mL methanol and transferred to an autoclave. The hydrogenation was conducted in the presence of 4 MPa H_2 at 90 °C for 5 h.

Synthesis of Nylon 6,6 from dicarboxylic esters

10 gram of dicarboxylic esters(dimethyladipate : dimethyl pimelate=96:4) obtained from scale-up experiment and vacuum distillation was hydrolyzed using 33 mL 15wt% NaOH aqueous solution at 90 °C. After adjusting the pH to 1~2 with conc. HCl, 7.5 g adipic acid was obtained. According to ^1H NMR analysis (Figure S9), no pimelic acid was observed. To the adipic acid, stoichiometric amount of 1,6-hexanediamine was added at 70 °C with ethanol to precipitate Nylon salt. The salt was heated up to 230 °C with 2 mol% acetic acid for 2h. Then the reaction was performed under vacuum at 270 °C for another 50 min. After cooling down to room temperature, the product was subjected to ^1H NMR (Figure S10) and GPC analysis ($M_n=15370$, $PDI=2.09$).

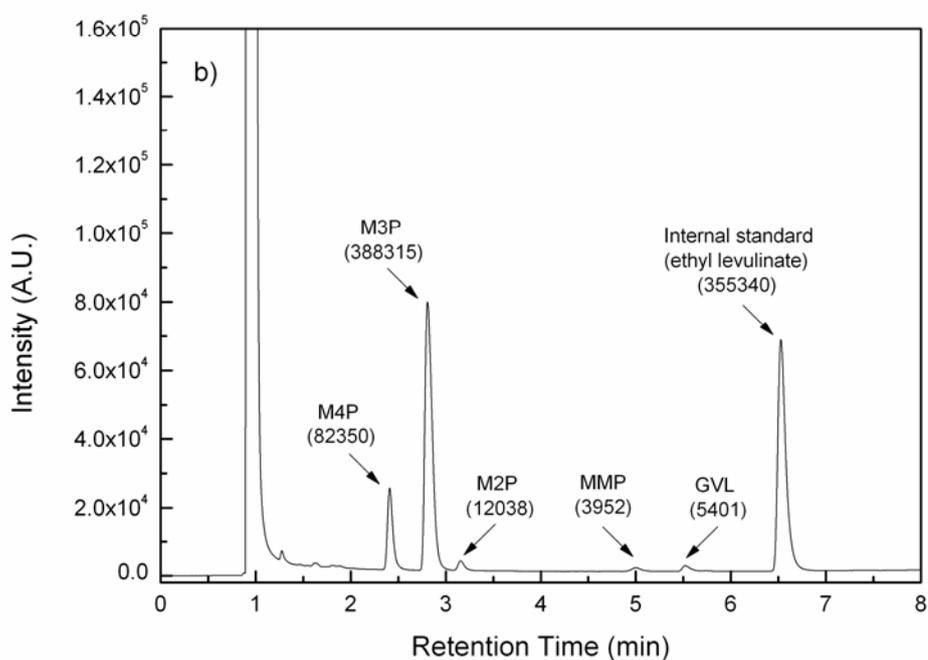
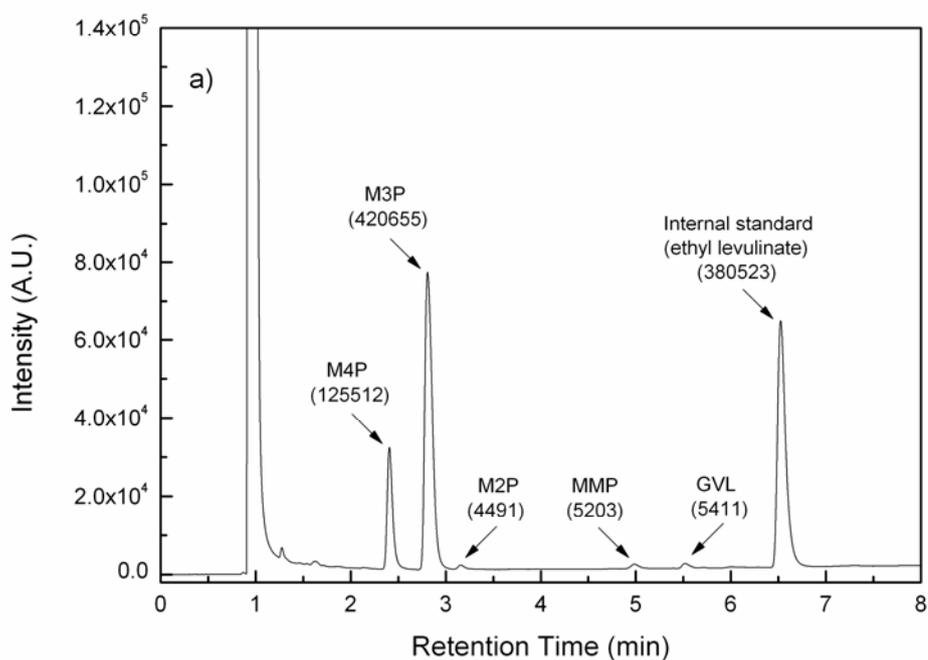


Figure S1. Gas chromatography of the distillate from the catalytic distillation of GVL using (a) fresh and (b) recovered **DIM-TFA**.

(Peak areas are in parenthesis. The response factors of M4P, M3P, M2P and GVL are 1.08, 1.08, 1.16 and 1.33. MMP refers to methyl 4-methoxypentanoate)

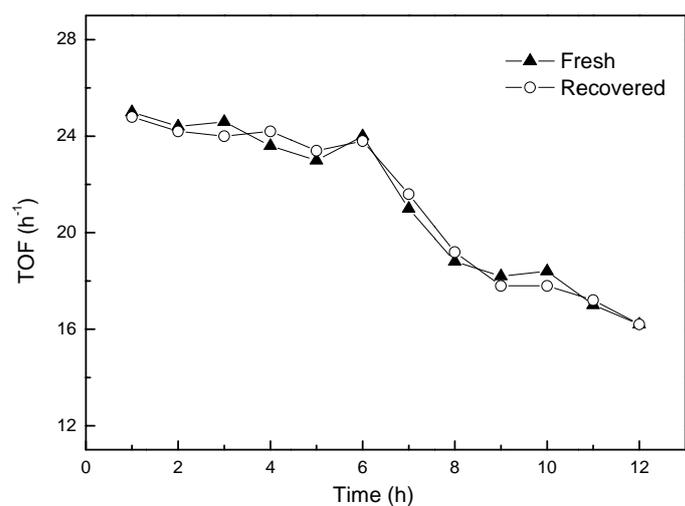


Figure S2. Catalytic distillation of GVL in the presence of fresh and recovered **DIM-TFA**.
 Reaction Conditions: 1.1 g (1.35 mmol) **DIM-TFA**, initial 5 g of GVL, 20 wt% GVL in methanol with a flow rate of 15 mL h⁻¹ (Density: 0.83 Kg L⁻¹), 170 °C. The TOFs were calculated based on the molar amount of pentenoates generated per mole of catalyst per hour.

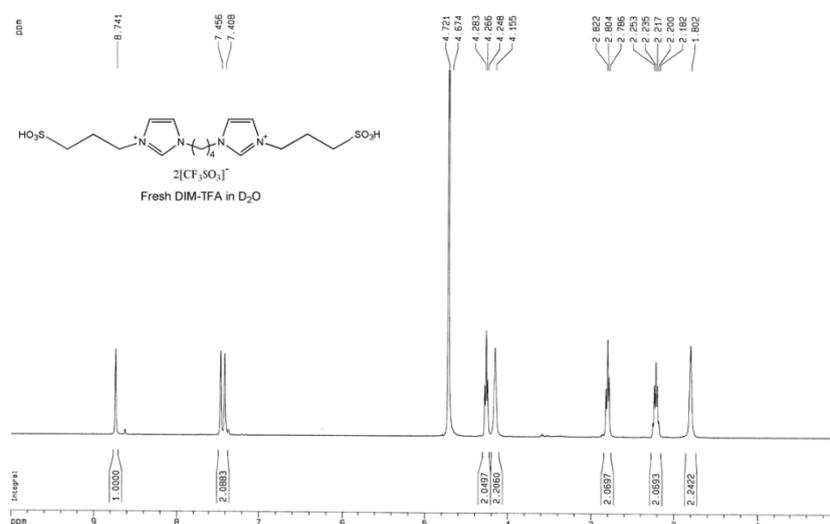


Figure S3. ¹H NMR spectra of fresh **DIM-TFA**.

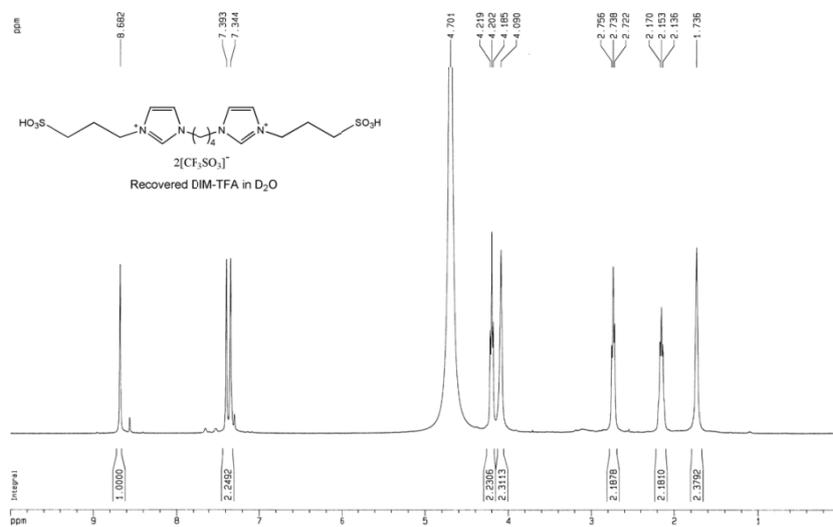


Figure S4. ¹H NMR spectra of recovered DIM-TFA.

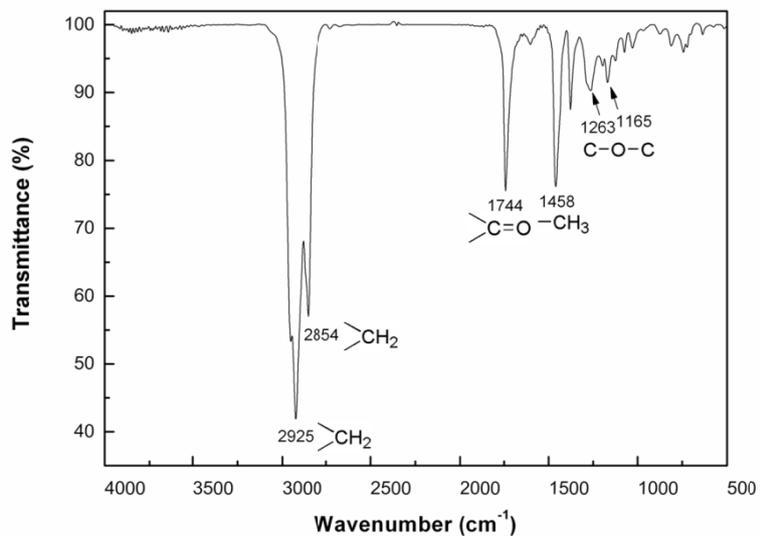


Figure S5. FT-IR spectra of the by-product generated from the catalytic distillation of GVL.

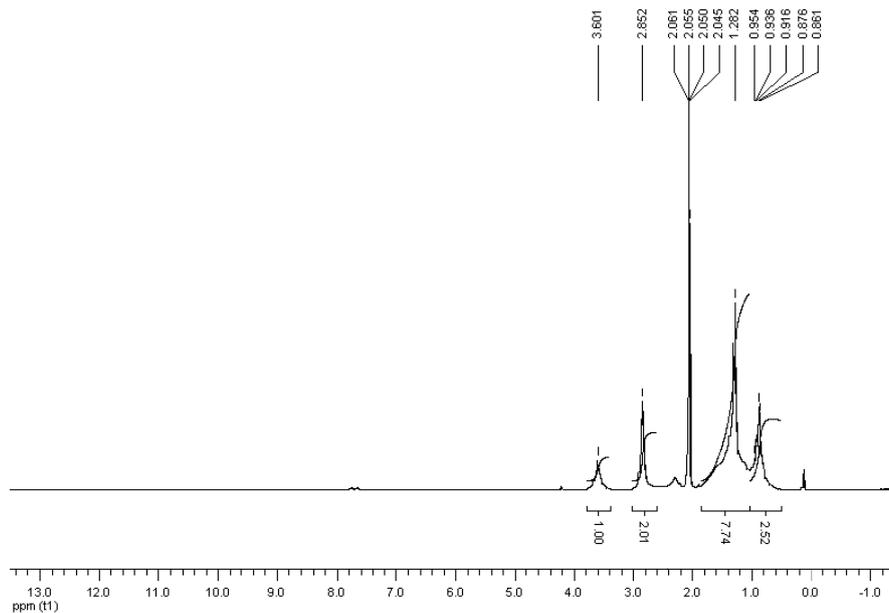
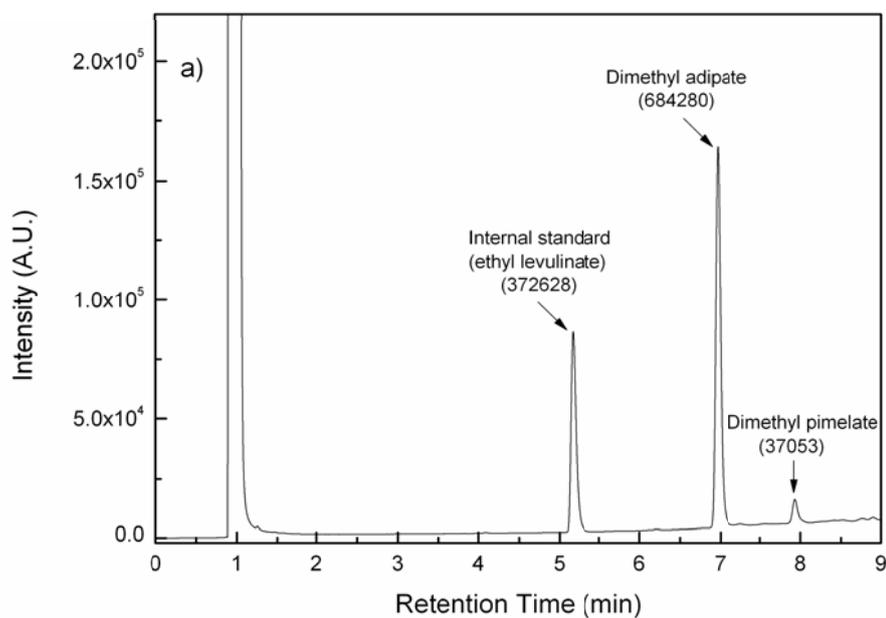


Figure S6. ^1H NMR spectra (in acetone- d_6) of the by-product generated from the catalytic distillation of GVL.



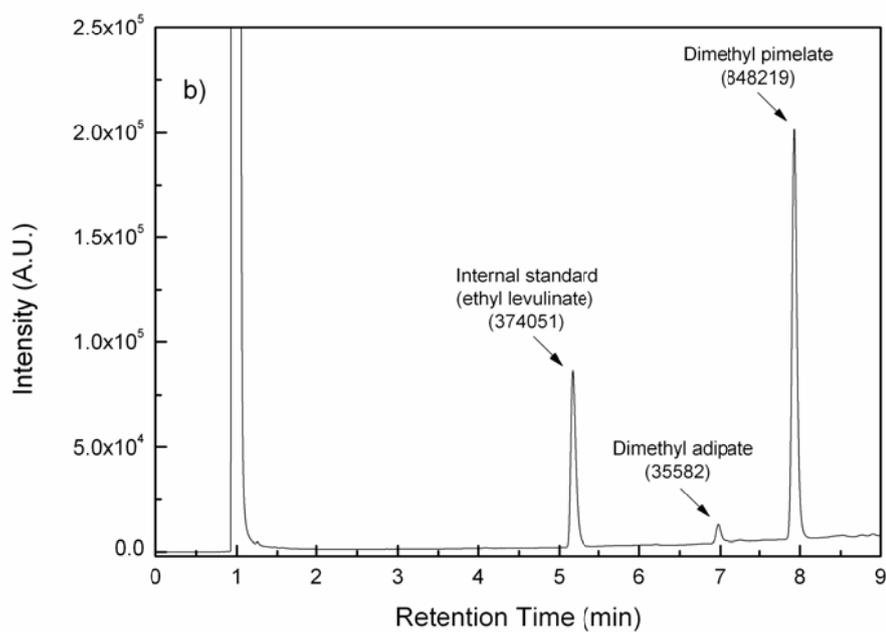
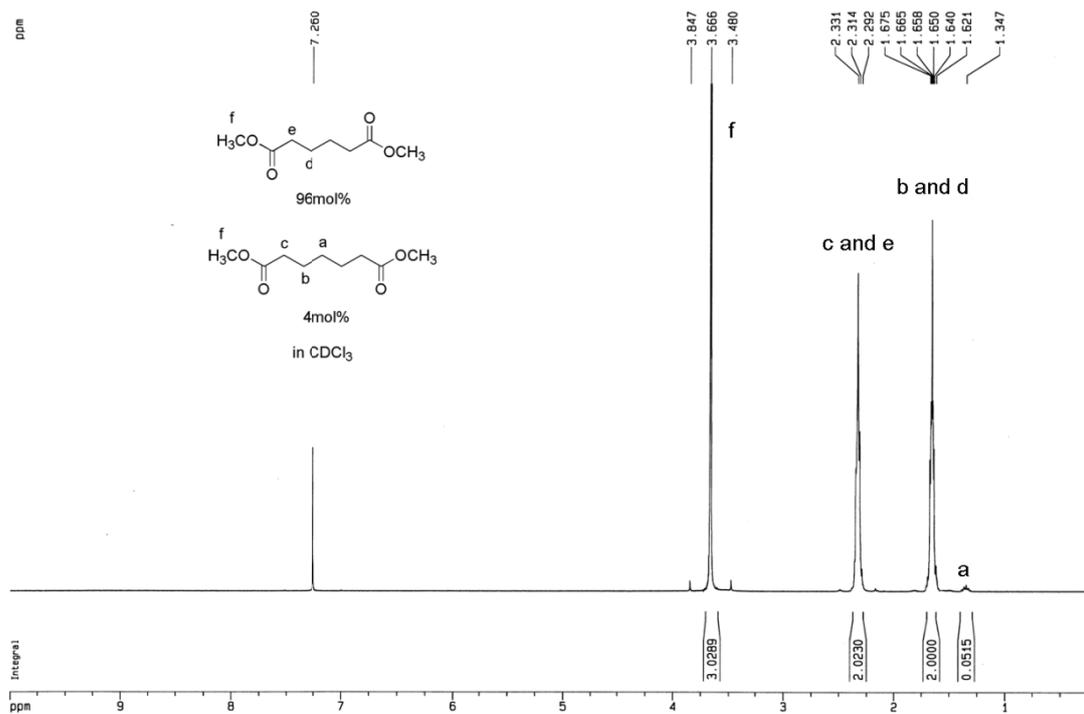


Figure S7. Gas chromatography of the distillates at a) 111 °C and b) 125 °C. (Peak areas are in parenthesis. The response factors of dimethyl adipate and dimethyl pimelate are 1.41 and 1.58)



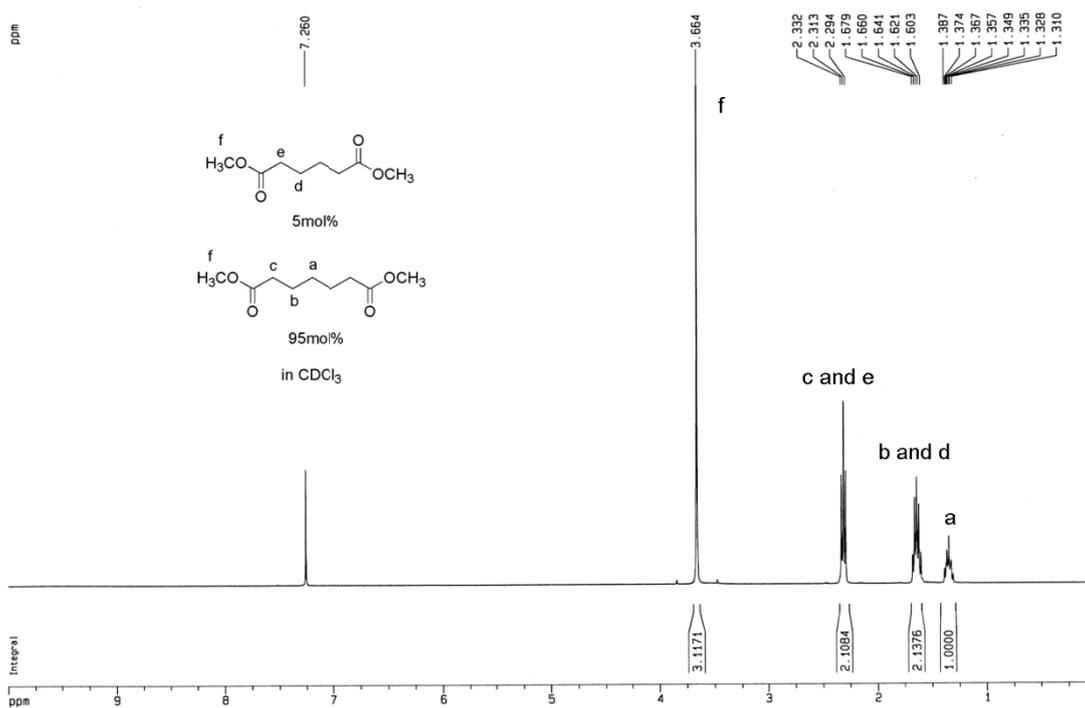


Figure S8. ^1H NMR spectra of the distillates at a) 111 °C and b) 125 °C.

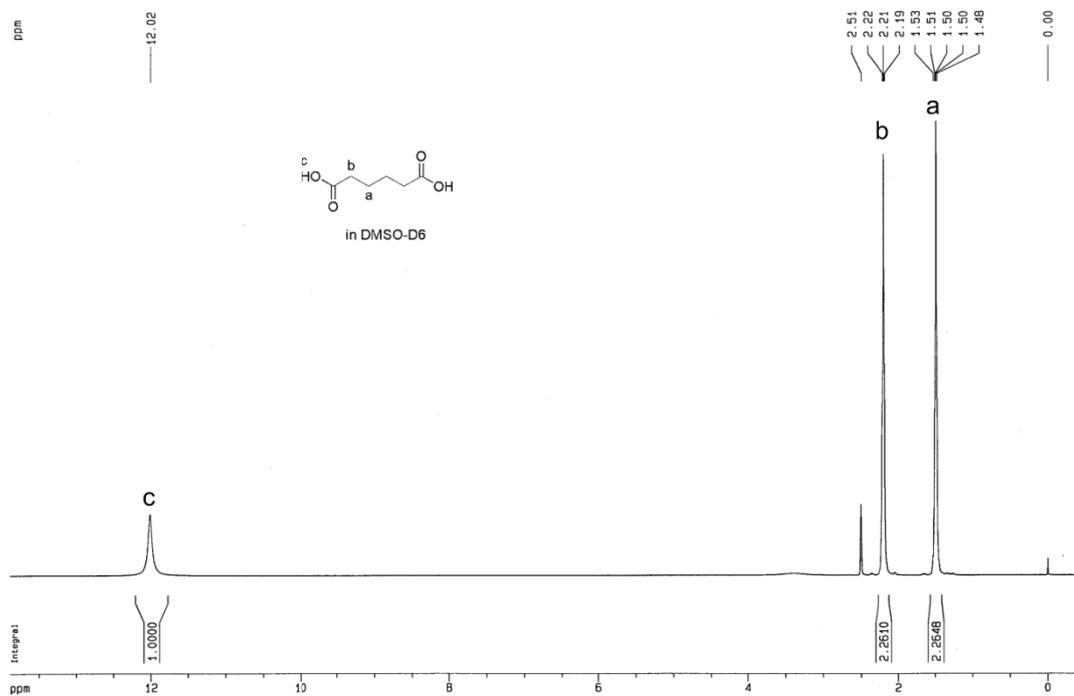


Figure S9. ^1H NMR spectra of the adipic acid obtained via the hydrolysis of dicarboxylic esters.

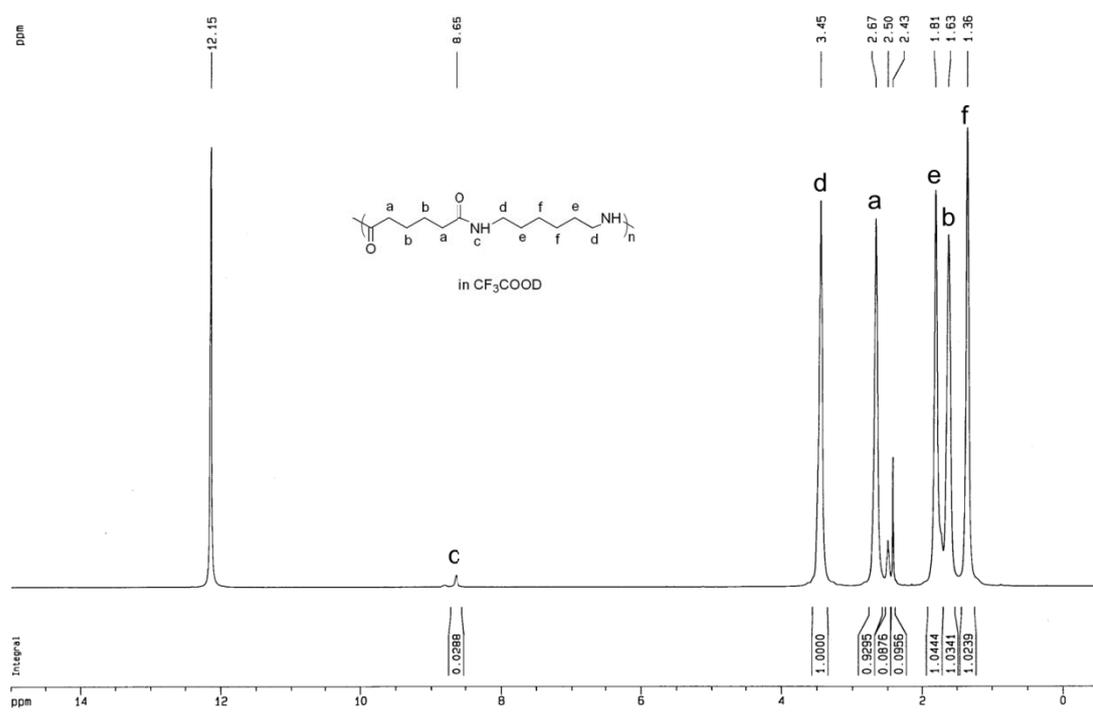


Figure S10. ^1H NMR spectra of the as-prepared Nylon 6,6.