Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Valorization of polycaprolactone for production of nylon-6 monomers

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Methods

1. Chemicals

6-Aminocaproic acid (99%), s-trioxane (99%), cerium (IV) oxide (CeO_2, 99.9%), zirconium (IV) oxide (ZrO_2, 99%), ruthenium on carbon (Ru/C, 5 wt.% Ru) and cerium chloride ($CeCl_3$, 99.9%) were supplied by J&k Scientific Ltd. Ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$, 99%, Ru37-40%), caprolactam (99%), β-hydroxy-isovaleric acid (>96%), platinum on activated carbon (Pt/C, 5% wt.% Pt), palladium on carbon (Pd/C, 5 wt.% Pd), deuterated aqueous ammonia ($ND_3 \cdot D_2O$, 25 wt.%) graphene oxide (GO, >99%), 6-hydroxyhexanoic acid (≥95%), ruthenium on aluminum oxide (Ru/Al_2O_3, 5 wt.% Ru), sodium hydroxide (NaOH, 99%), titanium dioxide nanoparticles (TiO_2, anatase, 99.8%), carbon nanotube (MWCNT, >95%) and silicon dioxide (SiO_2, 99.5%, 15±5nm) were supplied by Beijing Innochem Technology Co., Ltd. Polycaprolactone (Mn 45000, particle), poly(β-hydroxybutyrate) (PHB, ≥98%, powder) and 6-aminohexanamide (99%) were supplied by Shanghai Macklin Biochemical Co., Ltd. 6-Hydroxyhexanamide (≥95%) was supplied by Shanghai Shaoyuan Co., Ltd. Niobium(V) oxide (Nb_2O_5, high purity reagent) was supplied by Sinopharm Chemical Reagent limited corporation. Aqueous ammonia ($NH_3 \cdot H_2O$, 25-28 wt.%) was supplied by Xilong Scientific Co., Ltd. All the above chemicals were used without further purification.

2. Catalysts Preparation

All the supported metal nanocatalysts were prepared by impregnation method in combination with subsequent reduction using H_2. In a typical experiment to prepare 5 wt.% Ru/CeO_2, 500 mg of CeO_2 and 67.6 mg of $RuCl_3.xH_2O$ were loaded into 2 mL of distilled water and stirred at room temperature for 6 h, which was then dried at 60 °C overnight. Subsequently, the dried sample was treated under 10% H_2/Ar at 200 °C for 5 h (ramp rate 5 °C /min) to obtain the desired catalyst Ru/CeO_2. The Ru loading of Ru/CeO_2 was 3.9 wt.%, determined by inductively coupled plasma-optical emission spectrometer (ICP-OES). Similarly, other oxides (ZrO_2, Nb_2O_5, TiO_2, SiO_2) supported Ru catalysts were prepared via changing the supports.

In a typical experiment to synthesize 50 wt.% CeO_2/RGO composite, which was used as support to prepare Ru/CeO_2/RGO trinary catalyst, 40 mg of GO was dispersed in 50 mL of distilled water under the tip sonication for 10 min, and then 2 mL of $CeCl_3$ aqueous solution was dropped into the GO dispersion under sonication within 2 min. Subsequently, 2 mL of NaOH aqueous solution with concentration 3 times higher than that of the $CeCl_3$ used was dropped into the above suspension within 7 min. Finally, the resultant mixture was loaded into a Teflon-lined autoclave and kept at 150 °C for 10 h. After the autoclave was cooled to room temperature, the solid sample was separated via centrifugation, washed with water for three times, and vacuum dried at 60 °C overnight. Using the resultant CeO_2/RGO composite as the support, 5 wt.% Ru /CeO_2/RGO trinary catalyst was also obtained by impregnation reduction.

3. Evaluation of Catalytic Performance

All reactions were performed in a Teflon-lined stainless-steel autoclave (16 mL of the inner volume) equipped with a magnetic stirrer. In a typical experiment, PCL (1 mmol based on the structural unit), $NH_3 \cdot H_2O$ (25-28 wt.%, 3 mL) and catalyst (50 mg, metal/PCL monomer molar ratio 0.02) were successively loaded into the autoclave in a glove box under N_2, and then the autoclave was sealed. Subsequently, the autoclave was moved to an air-bath set at a desired temperature. After reaction, the autoclave was cooled down in an ice water. The catalyst was separated from the reaction system by centrifugation, and the products were then collected via removing aqueous ammonia from the reaction solution by vacuum-rotary evaporation at 60 ºC. The quantitative analysis of the products was conducted by ^1H NMR spectroscopy using s-trioxane as an internal standard and D_2O as solvent.

NMR measurements:

NMR spectra were recorded on Bruker Avance III 400 HD spectrometer equipped with 5 mm pulsed-field-

gradient (PFG) probes. Chemical shifts are given in ppm relative to D_2O or s-trioxane.

For ^1H and ^{13}C NMR analysis, products were dissolved in D_2O and were recorded on Bruker Avance III 400 HD.

Specific calculations are as follows:

$$Yield_i = \frac{Collected\ Product_i(mol)}{theoretical\ Product_i(mol)} \times 100\%$$

$$Conversion = \frac{PCL(input) - PCL(residue)}{PCL(input)} \times 100\%$$

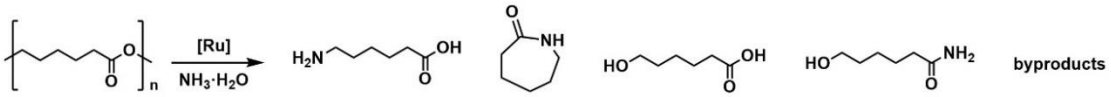
$$Selectivity_i = \frac{Product_i(mol)}{\sum Product(mol)} \times 100\%$$

$$Total\ Yield = \sum Yield$$

In most cases, there was no PCL left, and the recovered catalyst was determined to keep almost unchanged in mass, meaning its conversion is about 100%.

4. Structural Characterization

X-ray diffraction (XRD) was carried out on an X-ray diffractometer (PANalytical, Empyrean, Holland) with Cu Kα radiation, at a scan rate of 7°/min. The morphology of the catalysts was observed using a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan). The ethanol-diluted sample suspension was dropped onto lacey support film for TEM observation. X-ray photoelectron spectroscopy (XPS) was performed on an X-ray Photoelectron spectrometer (ESCALAB250xl, VG, USA) using an Al-Kα radiation source. The binding energy was calibrated by the C 1s peak at 284.8 eV. The Ru content of the catalyst was determined by Inductively Coupled Plasma-Optical Emission Spectrometer (Agilent 5800 VDV ICP-OES). The fresh Ru/CeO_2 (5.35 mg) was digested by aqua regia and inverse aqua regia at 150 °C and filtered by a microporous filtering film for ICP analysis. The Raman spectra were obtained on a HORIBA confocal laser Raman spectrometer (LabRAM HR Evolution, HORIBA) equipped with a 532 nm laser. The Raman spectra were recorded in the spectral range of 200-4000cm^{-1}.



Scheme S1. Possible products of PCL depolymerization.

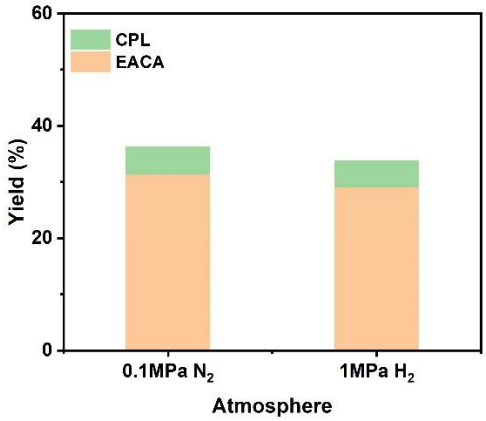


Figure S1. PCL depolymerization with Ru/CeO_2 under different atmosphere. Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; $NH_3 \cdot H_2O$, 3 mL; 18h, 140 °C.

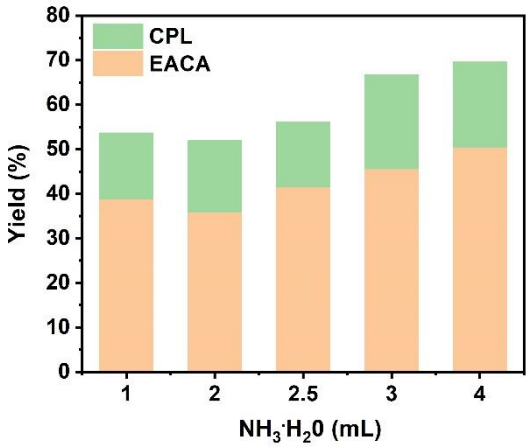


Figure S2. PCL depolymerization using different amount of $NH_3 \cdot H_2O$ over Ru/CeO_2. Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; 18h, 160 °C.

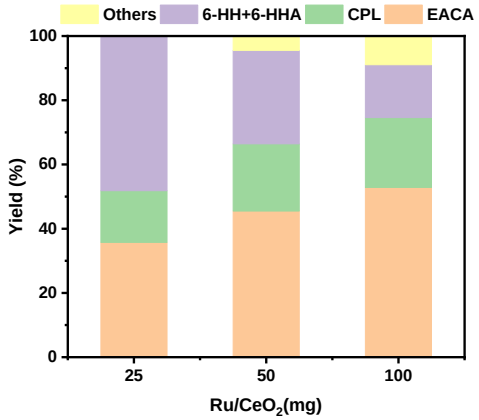


Figure S3. PCL depolymerization over Ru/CeO_2 using different catalyst dosage. Reaction conditions: PCL, 1 mmol; $NH_3 \cdot H_2O$, 3 mL; 18 h, 160 °C.

Note: The decarboxylation of 6-hydroxyhexanoic acid and 6-aminohexanoic acid could occur with high catalyst dosages at 160 °C.

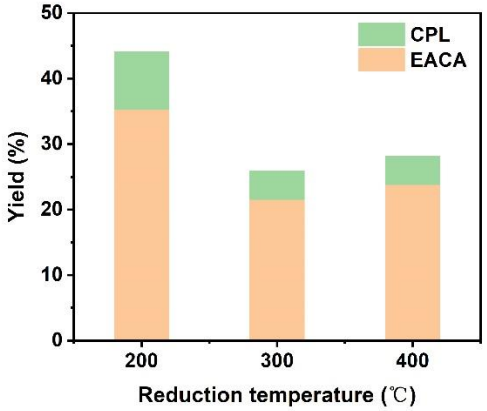


Figure S4. PCL depolymerization over Ru/CeO_2 reduced at different temperatures. Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; $NH_3 \cdot H_2O$, 3 mL; 18 h, 140 °C.

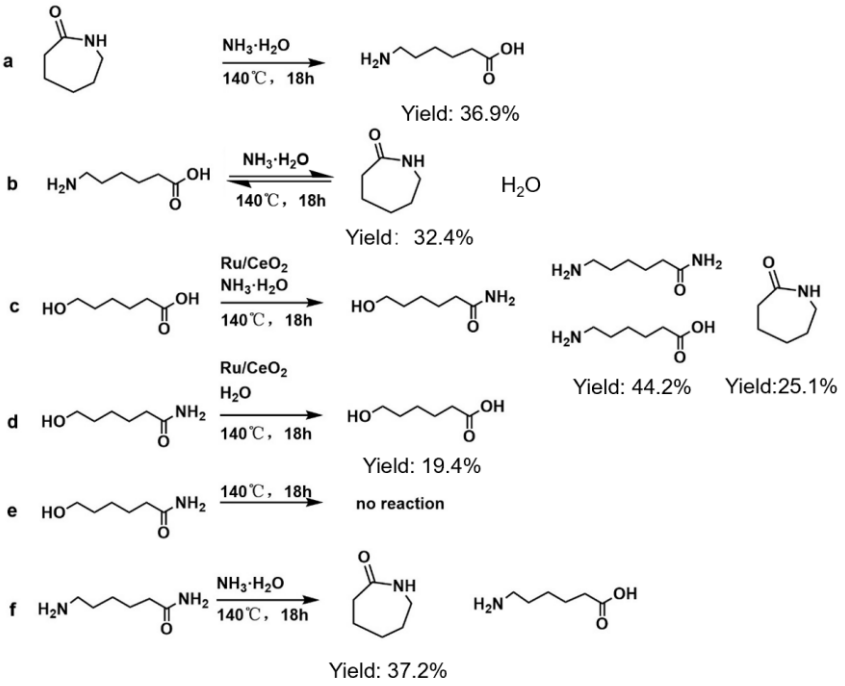


Figure S5. Possible reactions involved in the PCL decomposition. Reaction conditions: (a) caprolactam, 1 mmol; $NH_3{\cdot}H_2O$, 3 mL; 18 h, 140 °C. (b) 6-aminocaproic acid, 1mmol; $NH_3{\cdot}H_2O$, 3 mL; 18 h, 140 °C. (c) 6-hydroxyhexanoic acid, 1mmol; Ru/CeO_2, 50 mg; $NH_3{\cdot}H_2O$, 3 mL; 18 h, 140 °C. (d) 6-hydroxyhexanamide,1mmol; Ru/CeO_2, 50 mg; H_2O, 3mL; 18 h, 140 °C. (e) 6-hydroxyhexanamide,1mmol; 18 h, 140 °C. (f) 6-aminohexanamide, 0.12mmol; $NH_3{\cdot}H_2O$, 1 mL; 18 h, 140 °C.

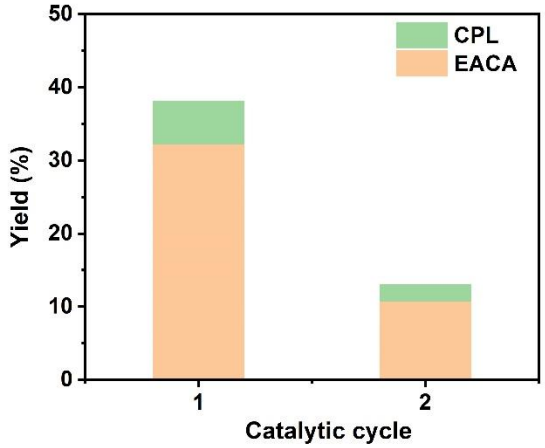


Figure S6. Recycling experiment of Ru/CeO_2 as a catalyst for PCL degradation. Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; $NH_3{\cdot}H_2O$, 3 mL; 140 °C, 18 h for each cycle. Note: The catalyst was separated from the reaction system by centrifugation and washed with water and ethanol for 3 times. After being dried under vacuum, the recovered catalyst was reused for the next run.

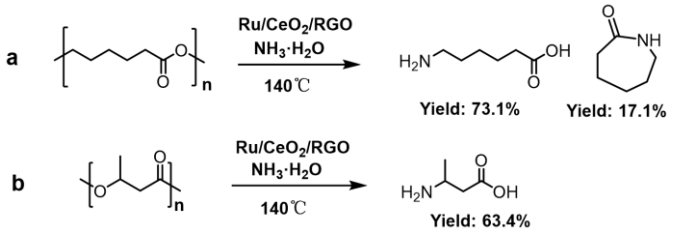


Figure S7. (a) PCL degradation. Reaction conditions: PCL, 0.2 mmol; Ru/CeO2/RGO, 10 mg; $NH_3{\cdot}H_2O$, 1 mL; 140 °C, 144 h. **(b) PHB degradation.** Reaction conditions: PHB, 0.2 mmol; Ru/CeO2/RGO, 10 mg; $NH_3{\cdot}H_2O$, 1 mL; 140 °C, 18 h.

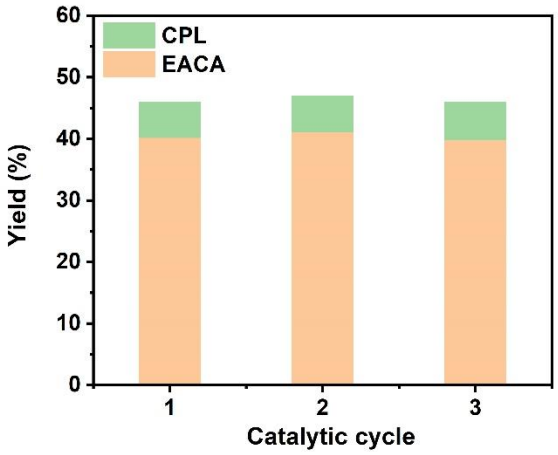


Figure S8. Recycling experiments of $Ru/CeO_2/RGO$ as a catalyst for PCL degradation. Reaction conditions: PCL, 0.2 mmol; $Ru/CeO_2/RGO$, 10 mg; $NH_3 \cdot H_2O$, 1 mL; 140 °C, 18 h for each cycle. Note: The catalyst was separated from the reaction system by centrifugation and washed with water and ethanol for 3 times. After being dried under vacuum, the recovered catalyst was reused for the next run. It is clear that the catalyst remained its activity after reused for 3 times.

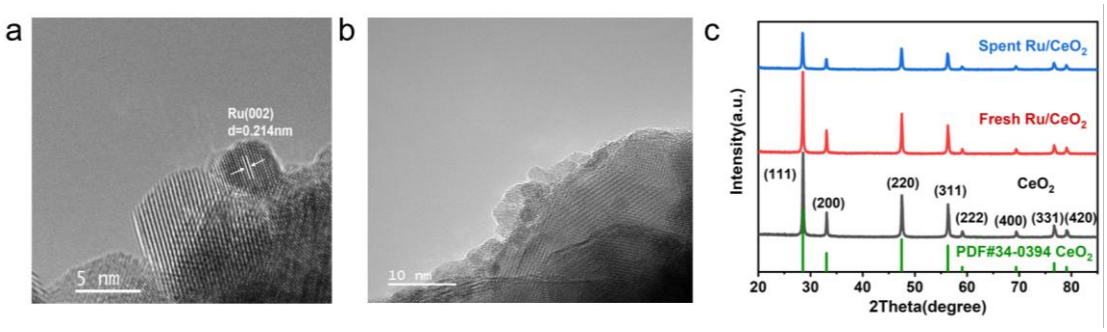


Figure S9. (a-b) TEM images of fresh Ru/CeO_2 catalyst. (c) XRD patterns of various samples.

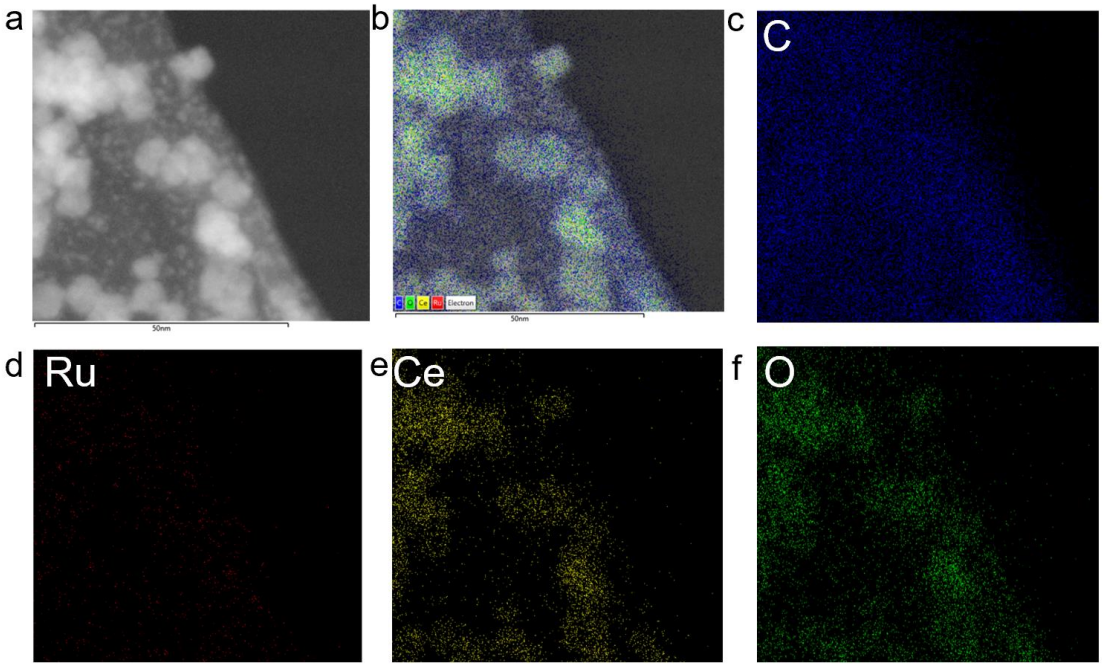


Figure S10. (a-f) EDS images (mapping) of the fresh Ru/CeO_2/RGO catalyst.

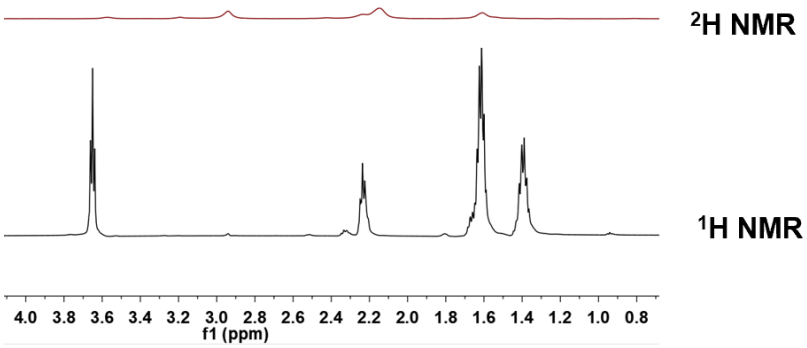


Figure S11. Amination experiment of PCL in $ND_3 \cdot D_2O$. Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; $ND_3 \cdot D_2O$, 1 mL; 140 °C, 18 h. (^2H NMR: H_2O as solvent, ^1H NMR: D_2O as solvent; room temperature).

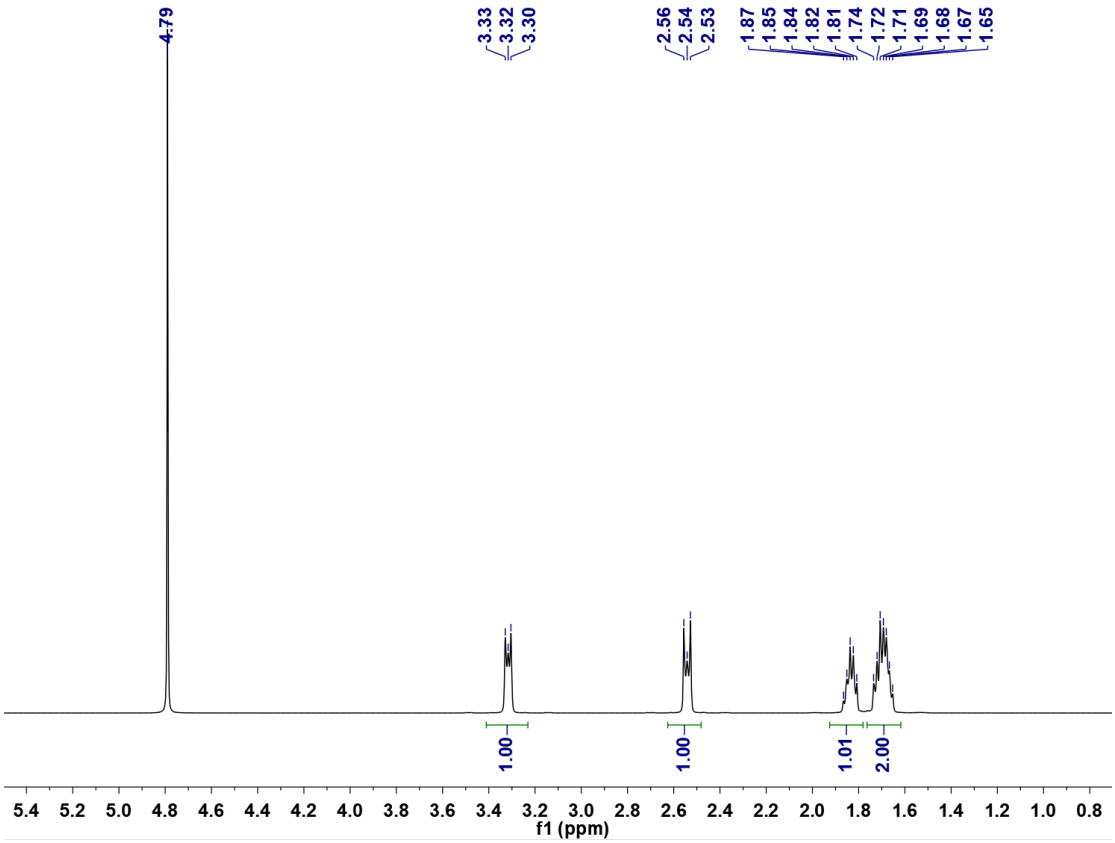


Figure S12. ^{1}H NMR spectrum of commercial caprolactam (D_2O as solvent, 4.79 ppm; room temperature).

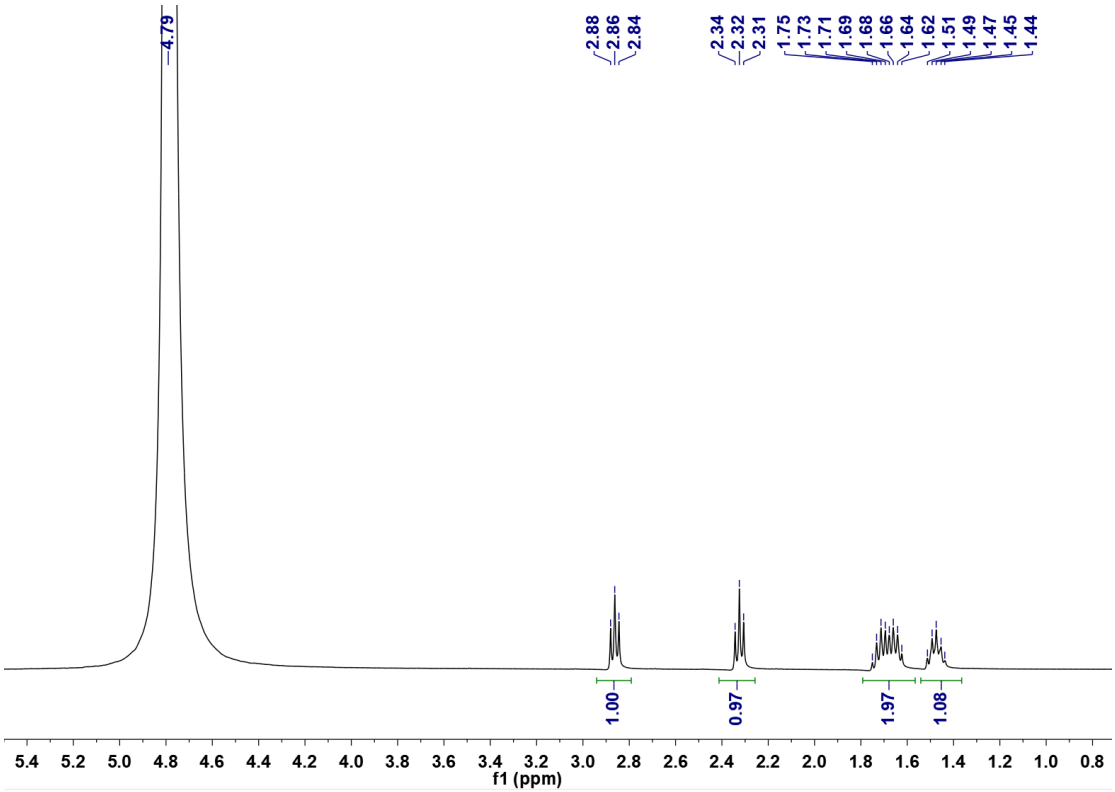


Figure S13. ^{1}H NMR spectrum of commercial 6-aminocaproic acid in $NH_3 \cdot H_2O$ (D_2O as solvent, 4.79 ppm; room temperature).

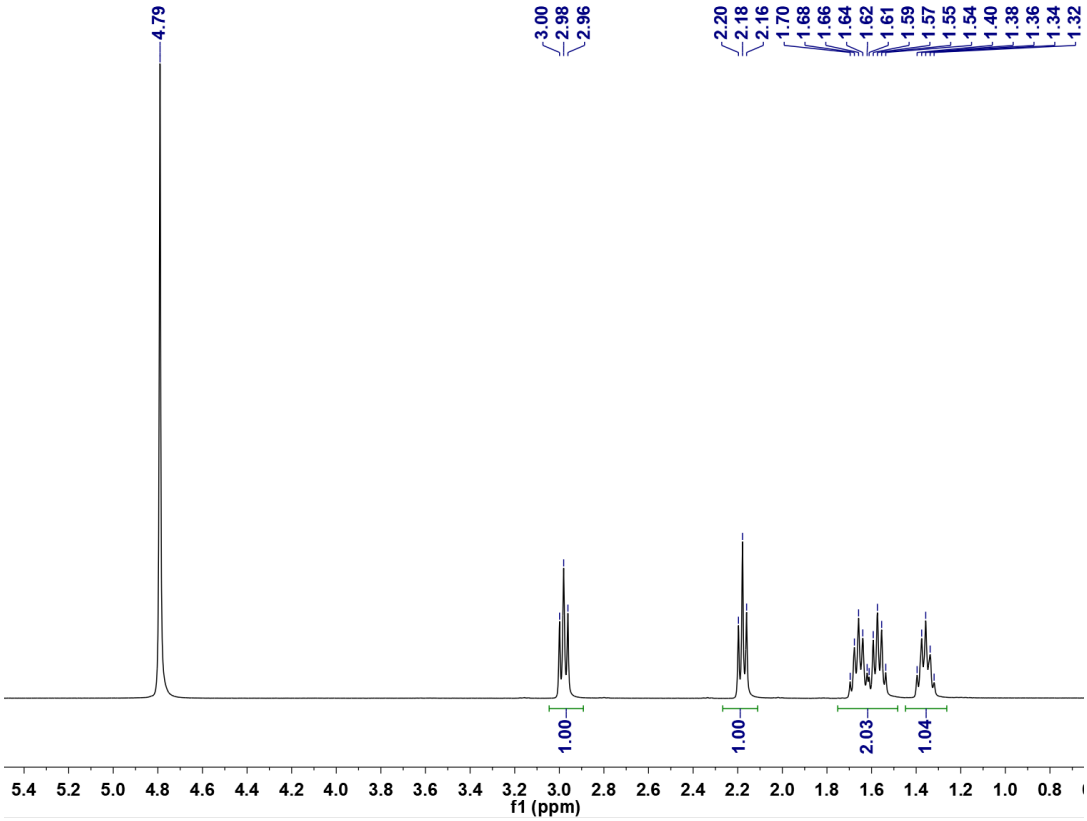


Figure S14. ^{1}H NMR spectrum of commercial 6-aminocaproic acid (D_2O as solvent, 4.79 ppm; room temperature).

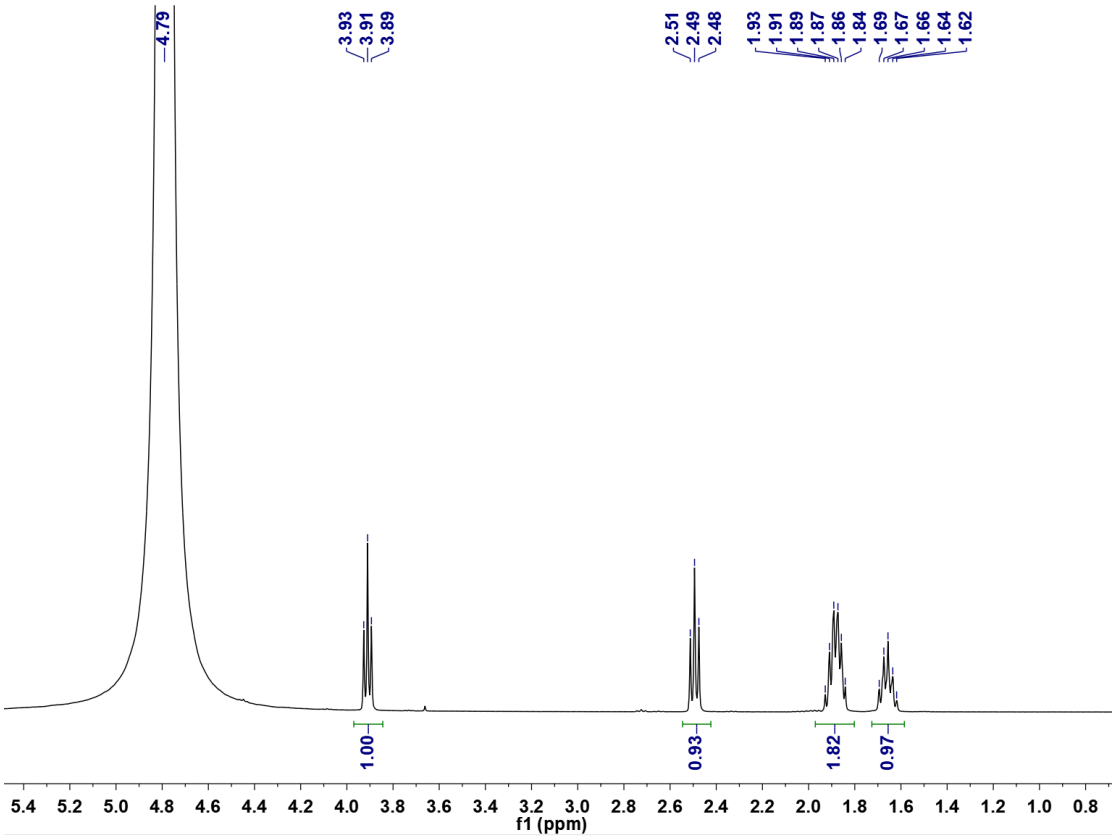


Figure S15. ^{1}H NMR spectrum of commercial 6-hydroxyhexanoic acid in $NH_3 \cdot H_2O$ (D_2O as solvent, 4.79 ppm; room temperature).

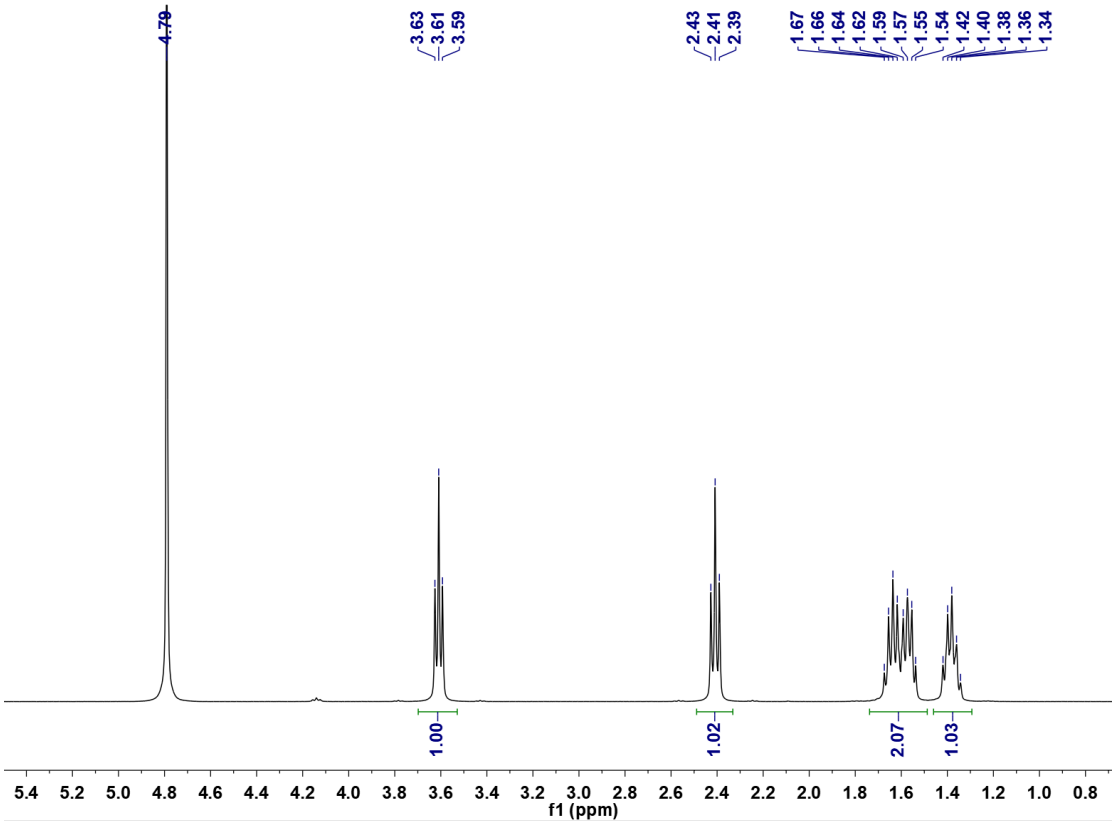


Figure S16. ^{1}H NMR spectrum of commercial 6-hydroxyhexanoic acid (D_2O as solvent, 4.79 ppm; room temperature).

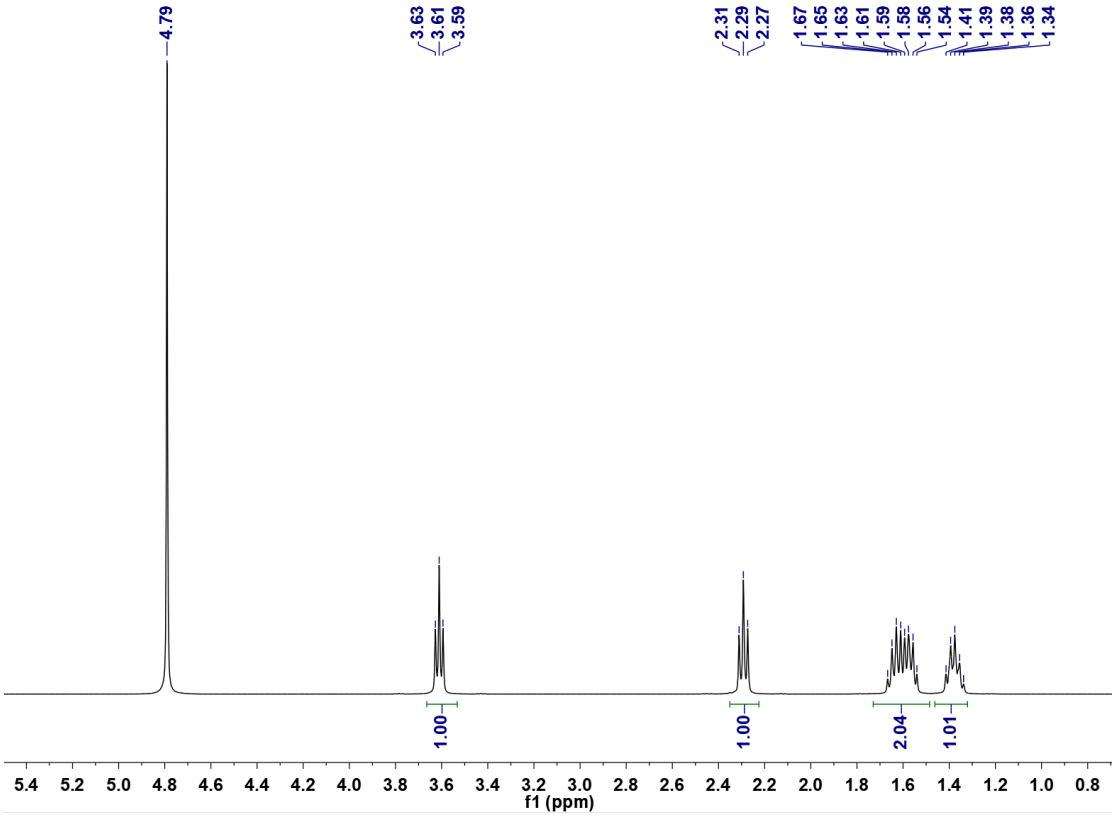


Figure S17. ^{1}H NMR spectrum of commercial 6-hydroxyhexanamide (D_2O as solvent, 4.79 ppm; room temperature).

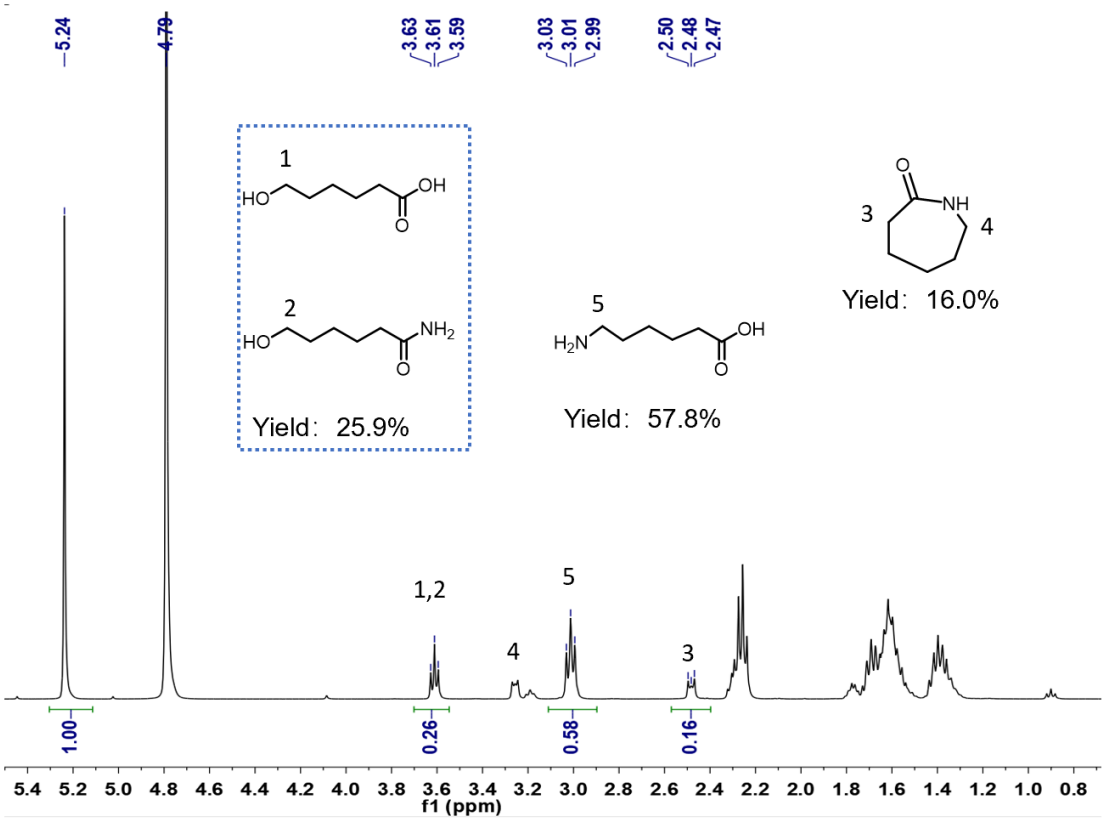


Figure S18. ^{1}H NMR spectrum of the reaction solution of PCL decomposition after spin evaporation treatment (s-trioxane as internal standard, 5.24 ppm; D_2O as solvent, 4.79 ppm; room temperature). Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; $NH_3{\cdot}H_2O$, 3mL; 140 °C, 72h.

Note: From the ^{1}H NMR spectrum, it is clear that 6-hydroxyhexanamide, 6-hydroxyhexanoic acid, 6-aminocaproic acid and caprolactam coexisted in the reaction solution.

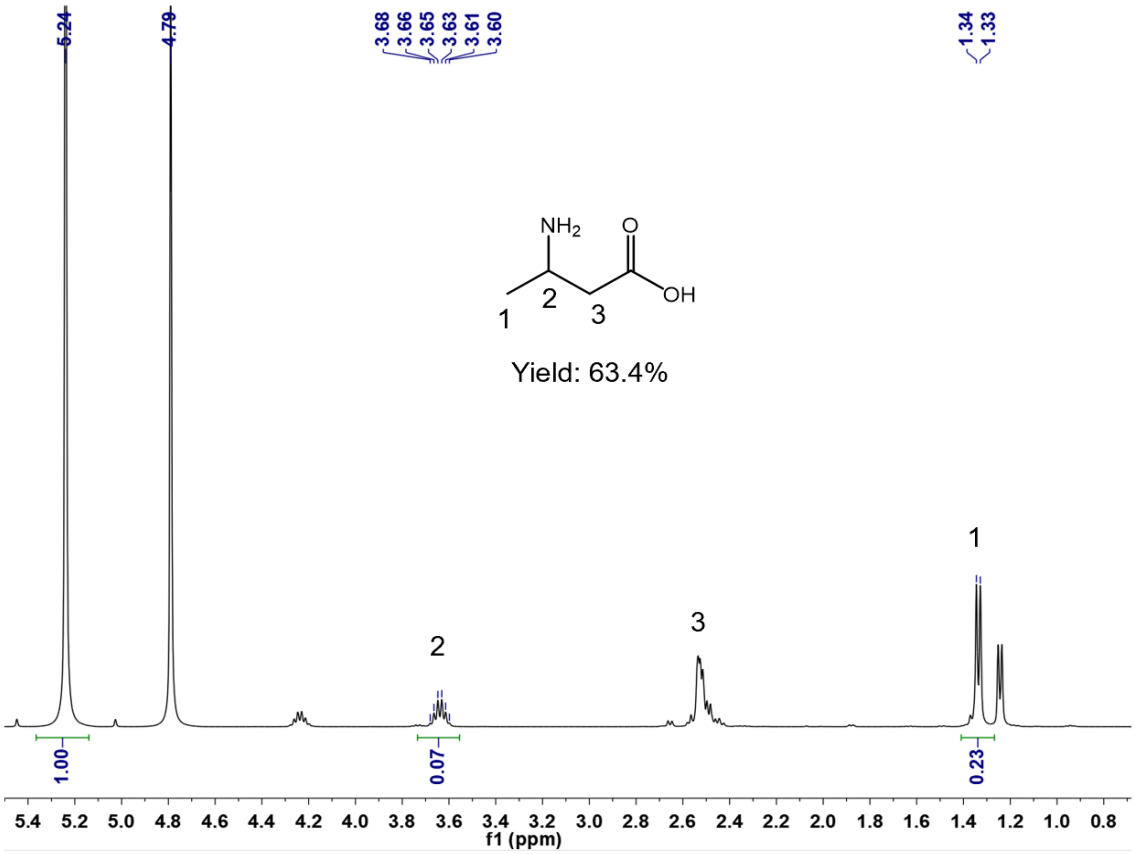


Figure S19. ^{1}H NMR spectrum of the reaction solution of PHB decomposition after spin evaporation treatment (s-trioxane as internal standard, 5.24 ppm; D_2O as solvent, 4.79 ppm; room temperature). Reaction conditions: PHB, 0.2 mmol; Ru/CeO_2/RGO, 10 mg; $NH_3{\cdot}H_2O$, 1mL; 140 °C, 18h.

Note: From the ^{1}H NMR spectrum, it is clear that 3-amino butanoic acid was generated in the reaction solution.

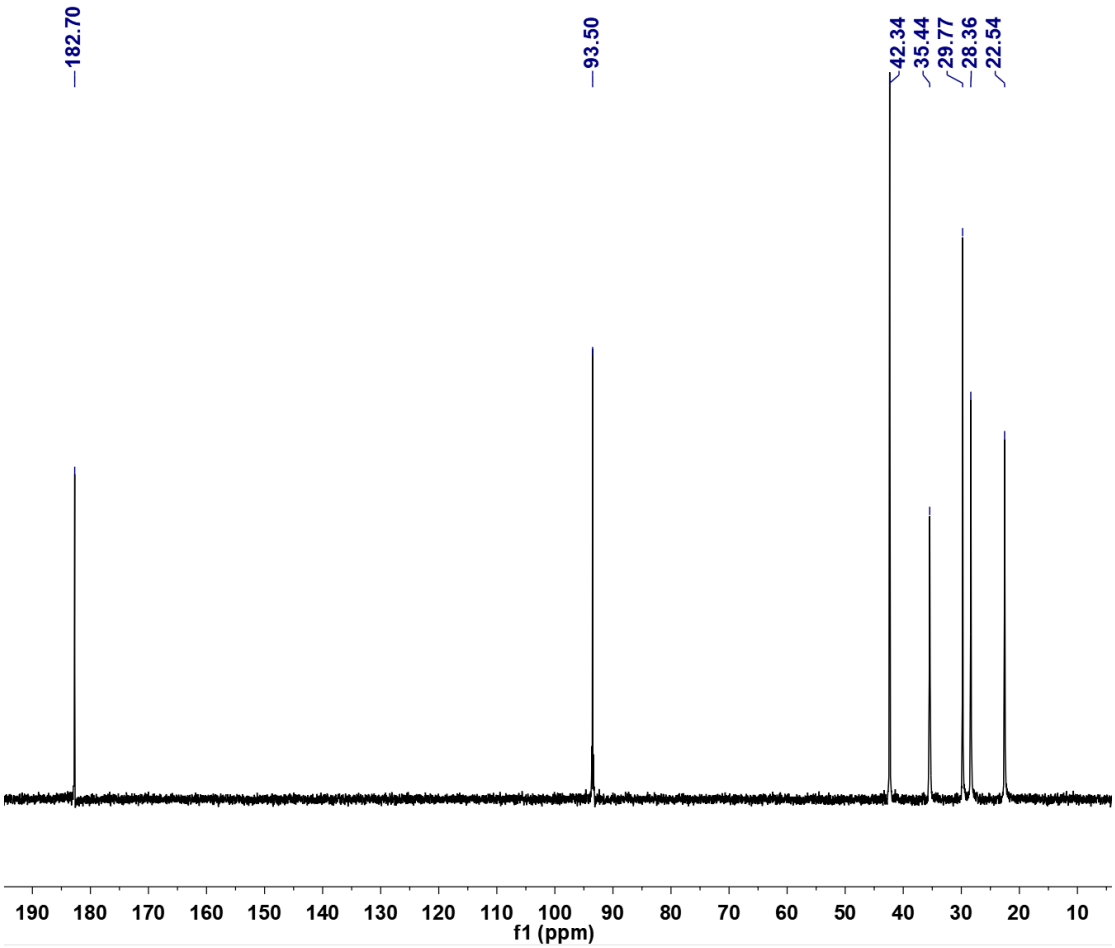


Figure S20. ^{13}C NMR spectrum of commercial caprolactam (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature).

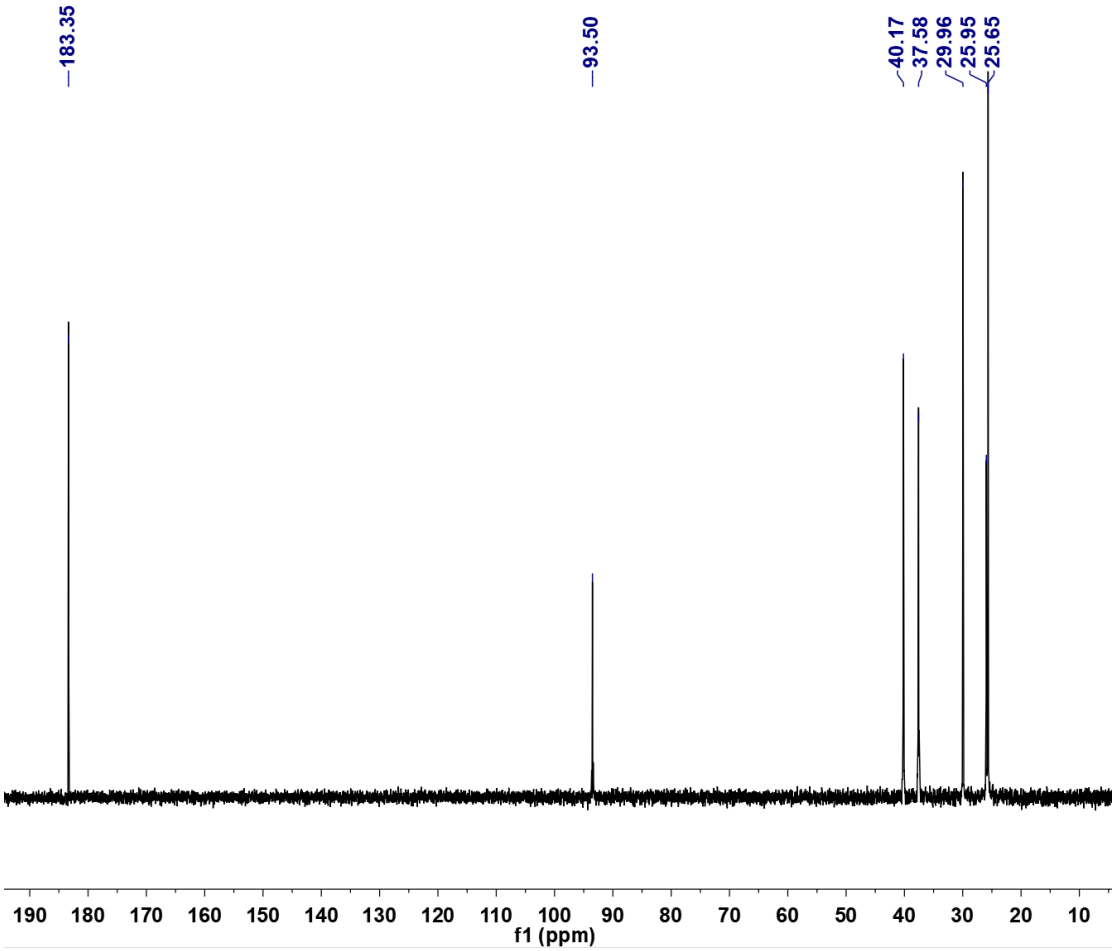


Figure S21. ^{13}C NMR spectrum of commercial 6-aminocaproic acid in $NH_3 \cdot H_2O$ (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature).

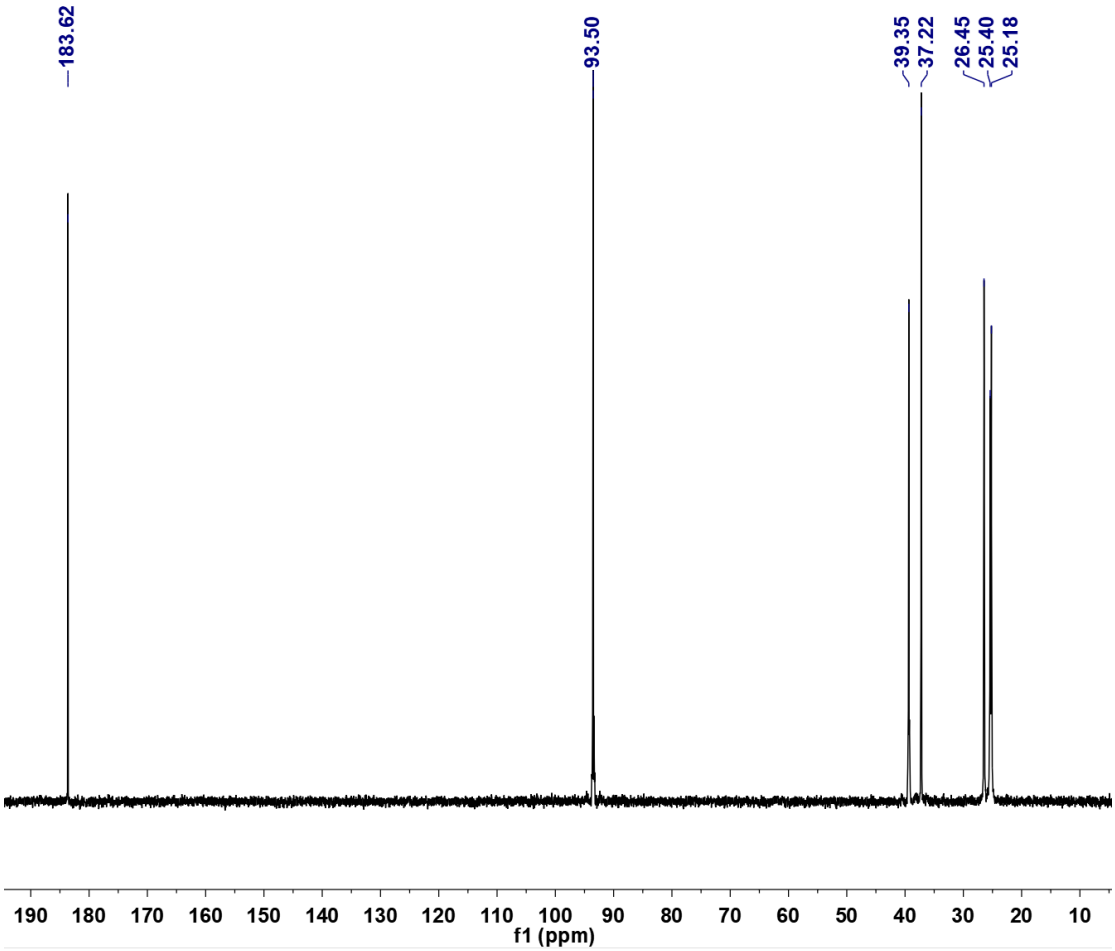


Figure S22. ^{13}C NMR spectrum of commercial 6-aminocaproic acid (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature).

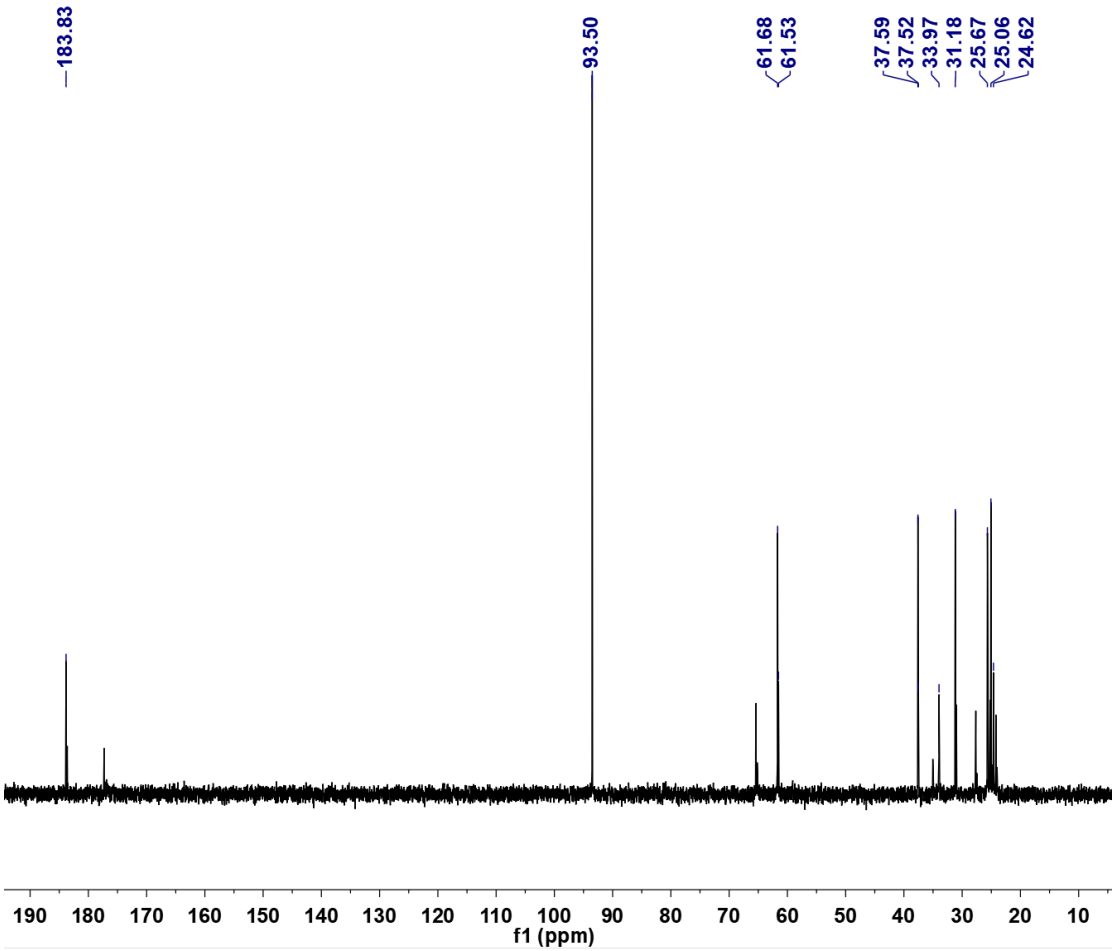


Figure S23. ^{13}C NMR spectrum of commercial 6-hydroxyhexanoic acid in $NH_3 \cdot H_2O$ (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature).

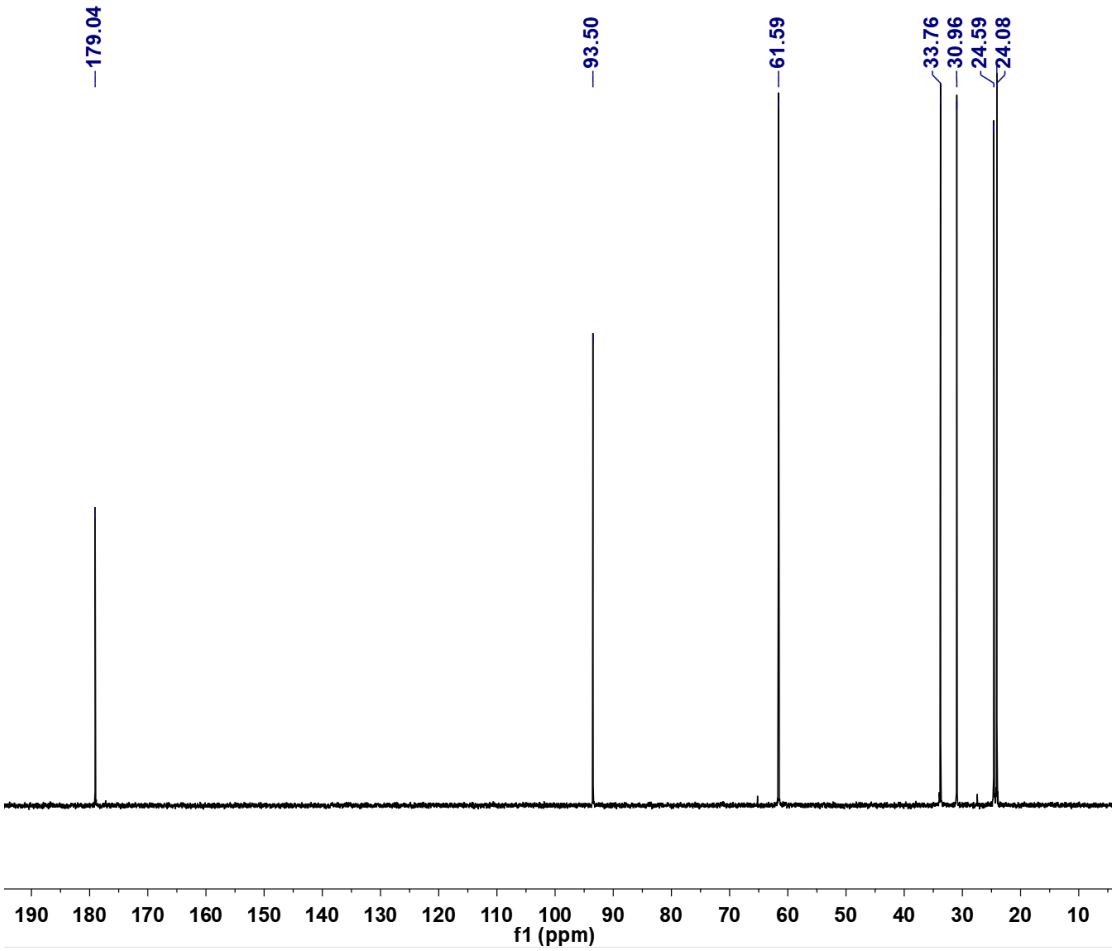


Figure S24. ^{13}C NMR spectrum of commercial 6-hydroxyhexanoic acid (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature).

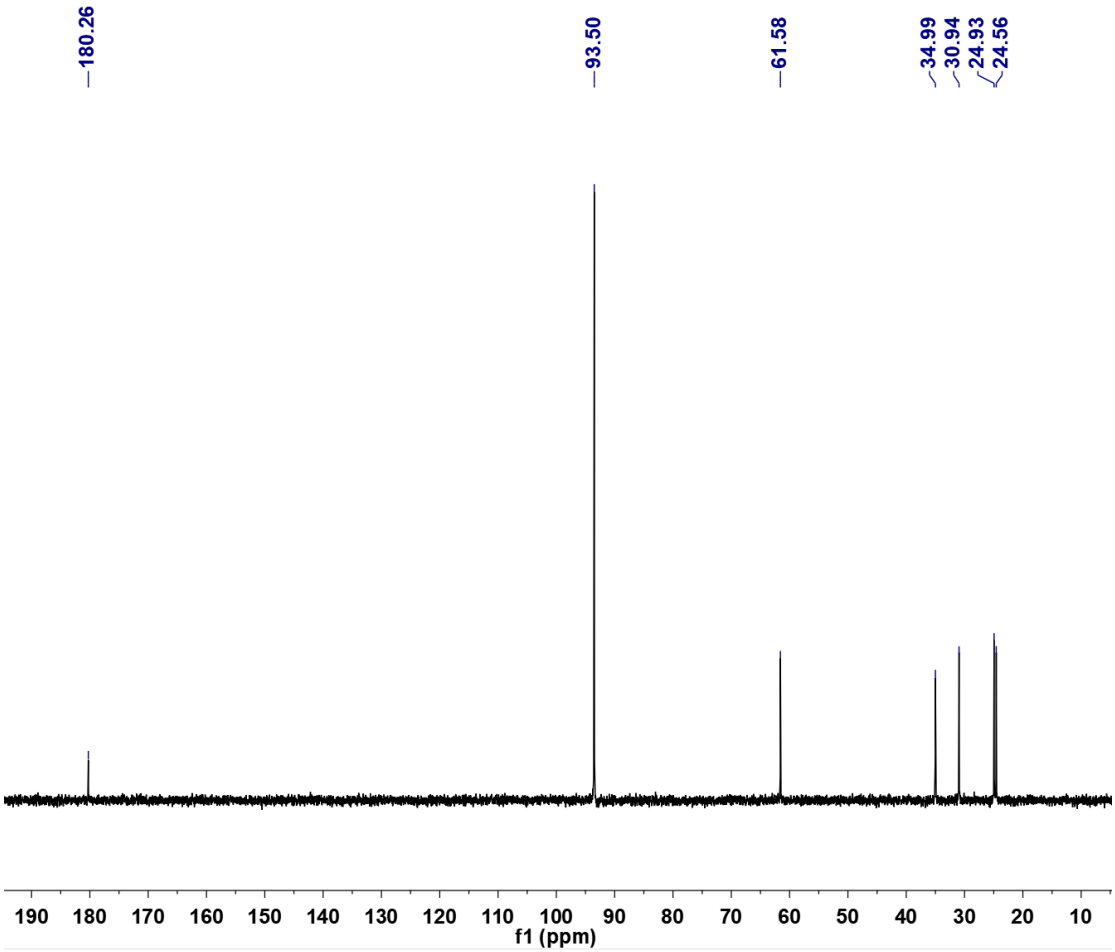


Figure S25. ^{13}C NMR spectrum of commercial 6-hydroxyhexanamide (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature).

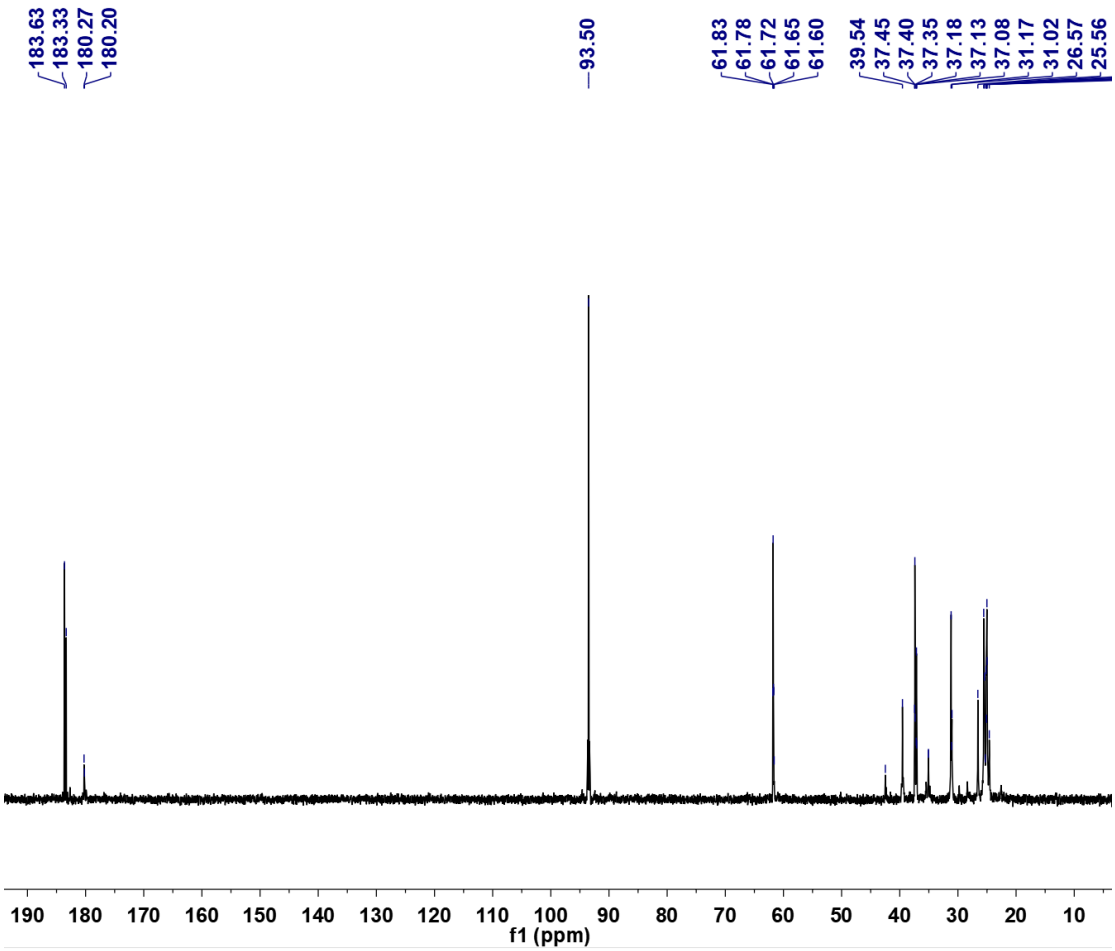


Figure S26. ^{13}C NMR spectrum of the reaction solution of PCL decomposition after spin evaporation treatment (s-trioxane as internal standard, 93.50 ppm; D_2O as solvent; room temperature). Reaction conditions: PCL, 1 mmol; Ru/CeO_2, 50 mg; $NH_3 \cdot H_2O$, 3 mL; 140 °C, 18 h.