

Polyurea-catalyzed cycloaddition of CO₂ and epichlorohydrin: a green approach

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1. Characterization of the Synthesized Polyurea (PU)

1.1. ^1H NMR calculation for the degree of polymerization (DP) of PU

The DP of the PU was determined using end group analysis from ^1H NMR spectroscopy. The integration of the methyl protons (labeled as 5) in urethane moiety served as a reference (3H). DP was evaluated by subtracting the integration obtained of the two protons from the urea nitrogens within the repeating unit from the integration of the NH protons outside the repeating unit using the following equation: $\text{DP} = (\int \text{NH}_{(\text{inside the repeating unit})} - \text{NH}_{(\text{outside the repeating unit})})/2$. Accordingly, the DP was calculated to be 59.

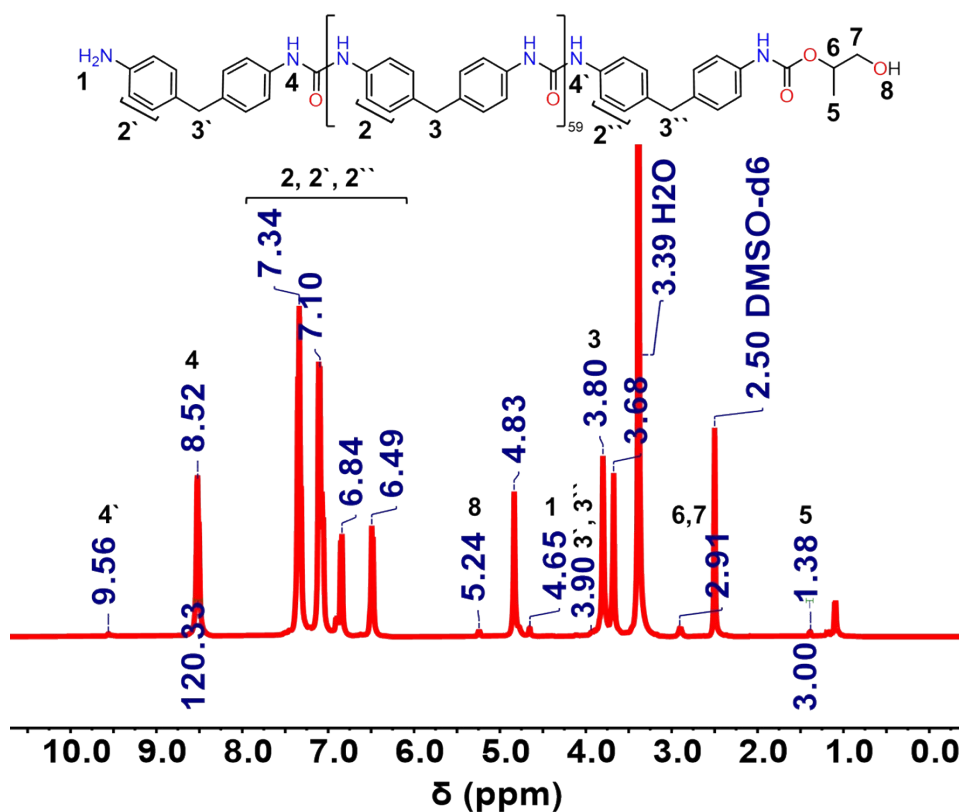


Figure S1. ^1H NMR spectrum of PU in $\text{DMSO-}d_6$.

1.2. ^{13}C NMR of PU

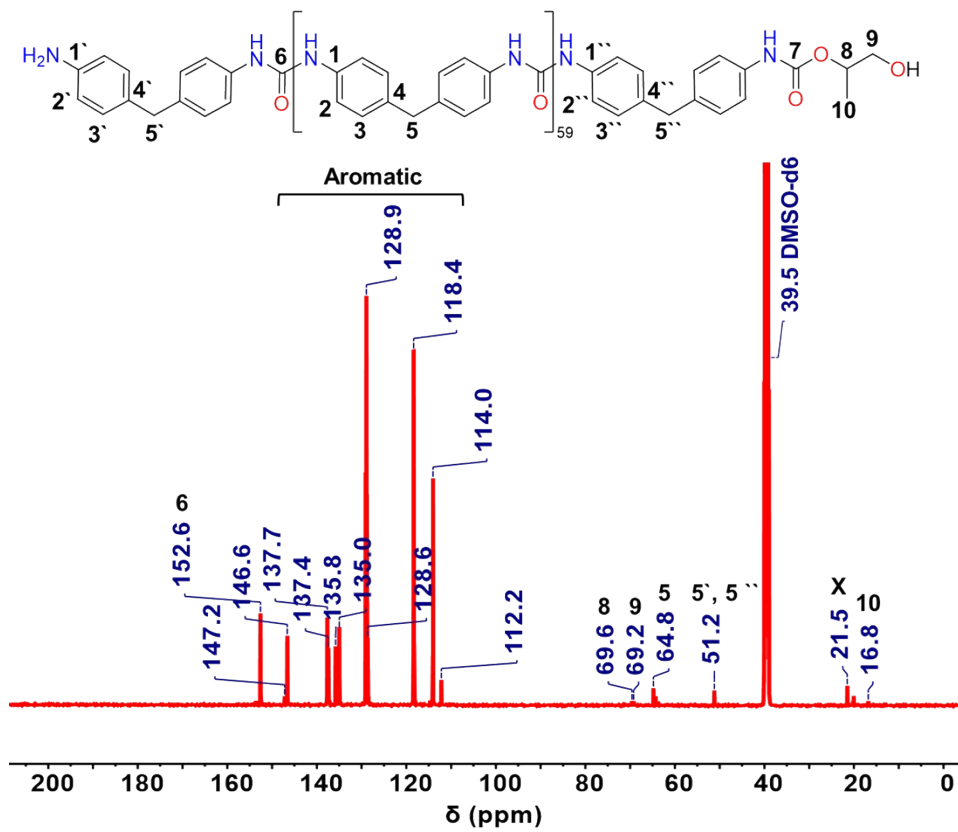


Figure S2. ^{13}C NMR spectrum of PU in $\text{DMSO-}d_6$. X: toluene.

2. ^1H NMR spectra of the cycloaddition reaction

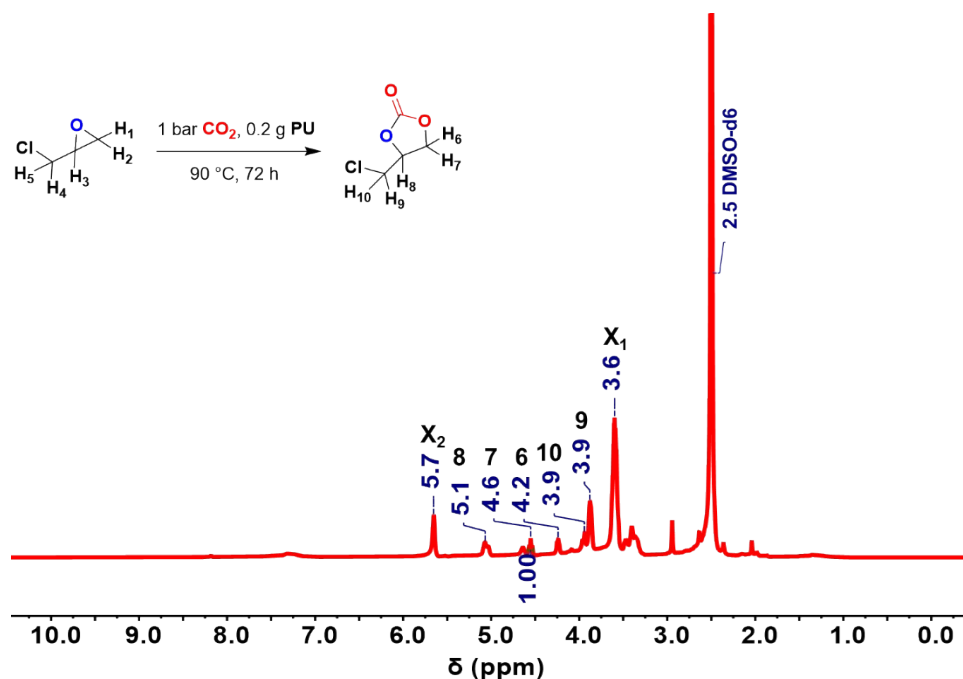


Figure S3. ^1H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

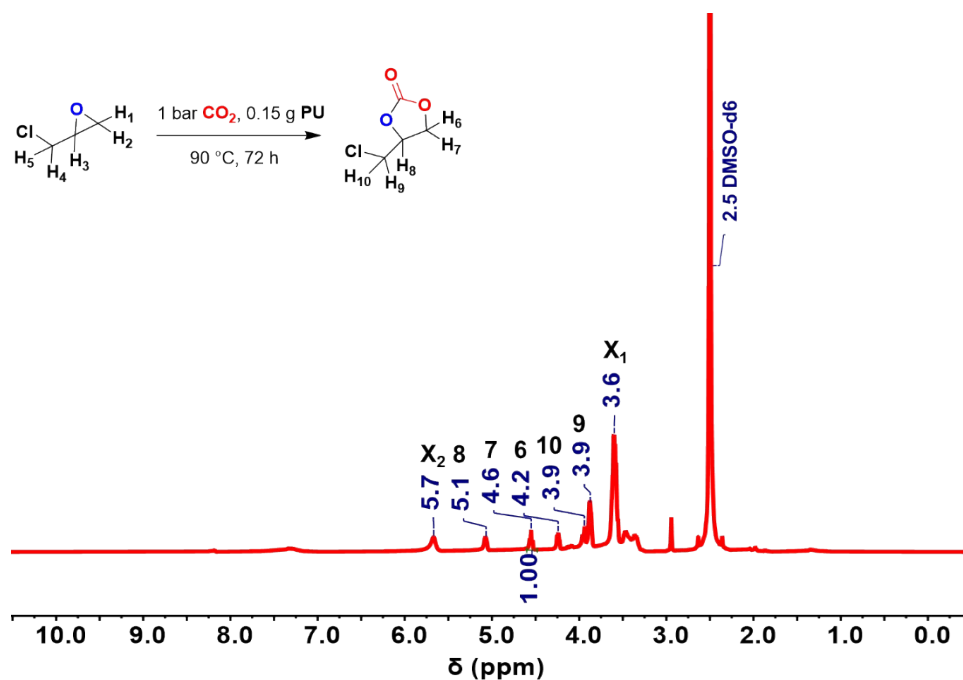


Figure S4. ^1H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

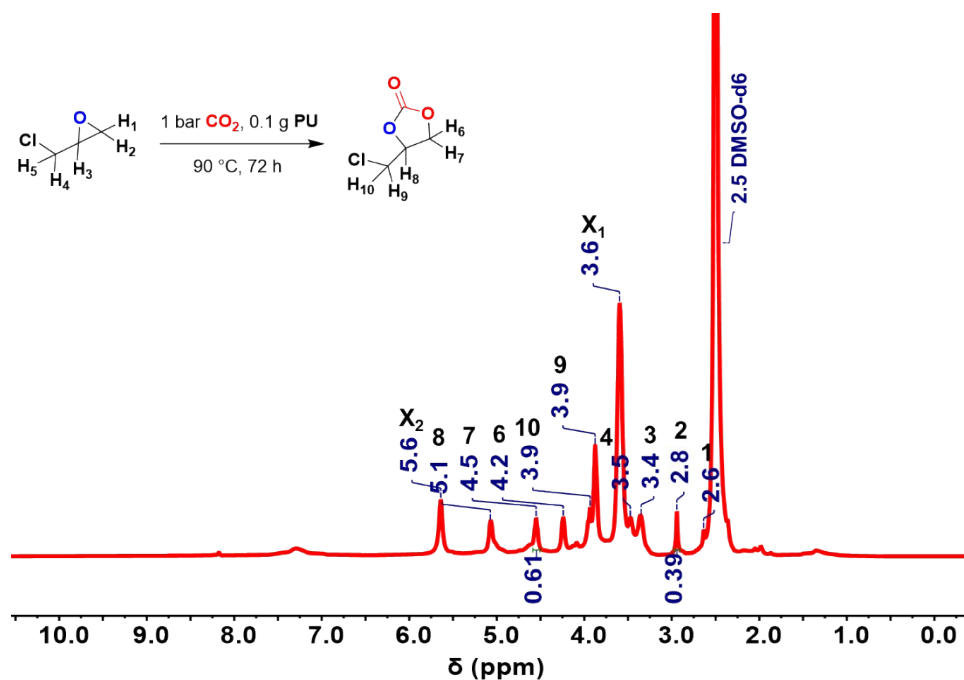


Figure S5. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

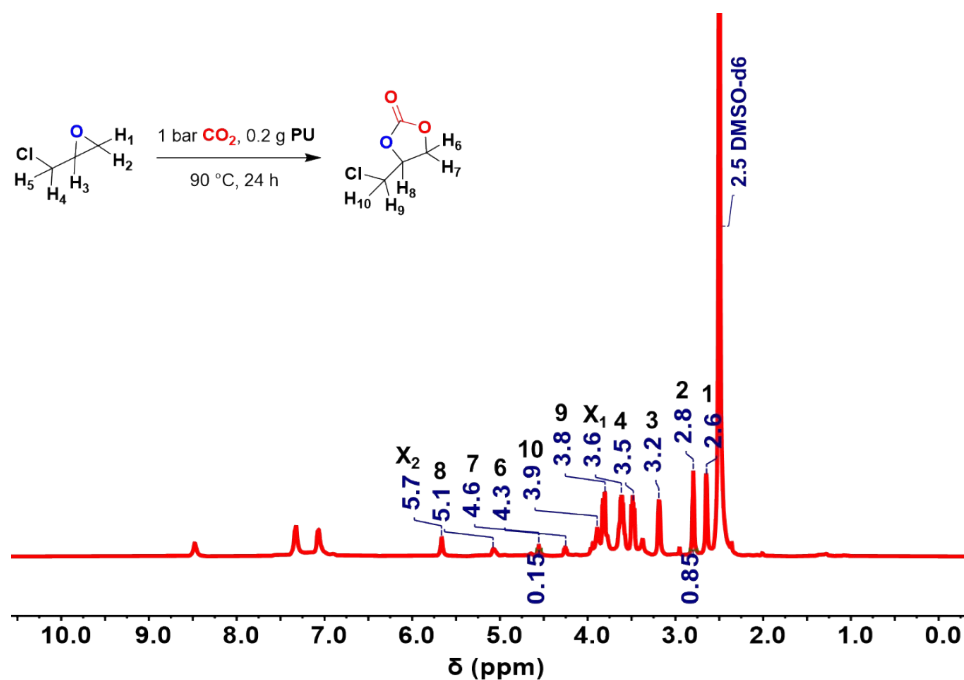


Figure S6. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor). Peaks centered at 7.0, 7.3 and 8.4 corresponding to the PU catalyst.

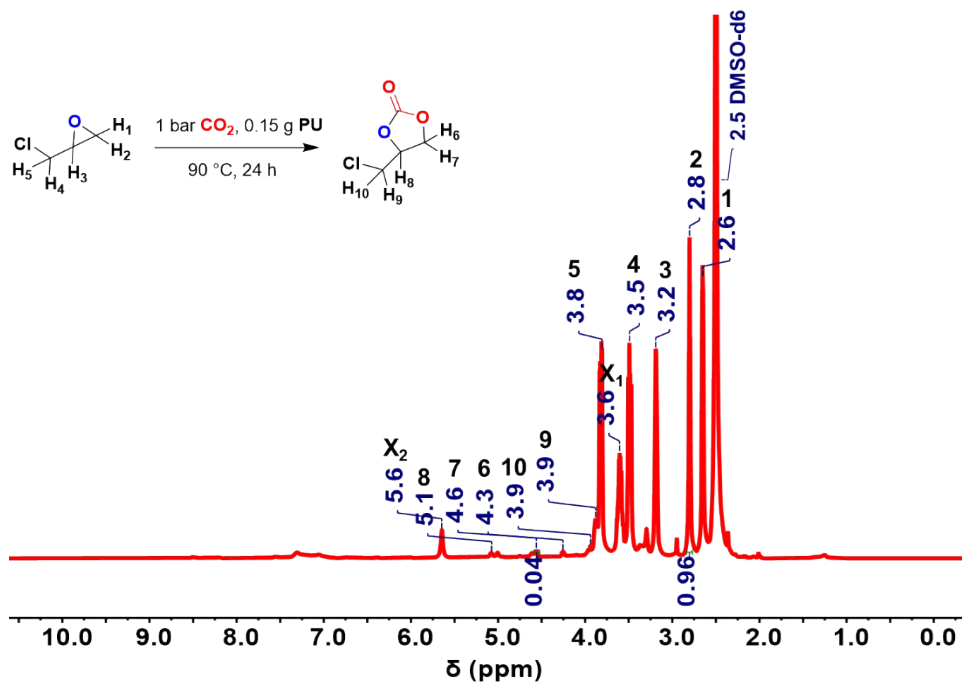


Figure S7. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

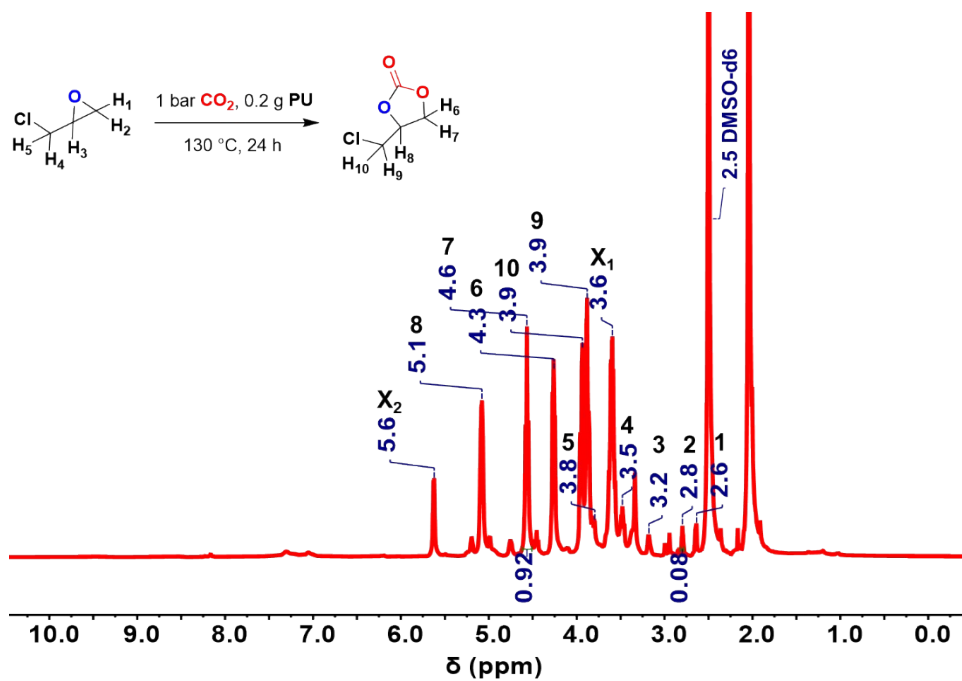


Figure S8. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

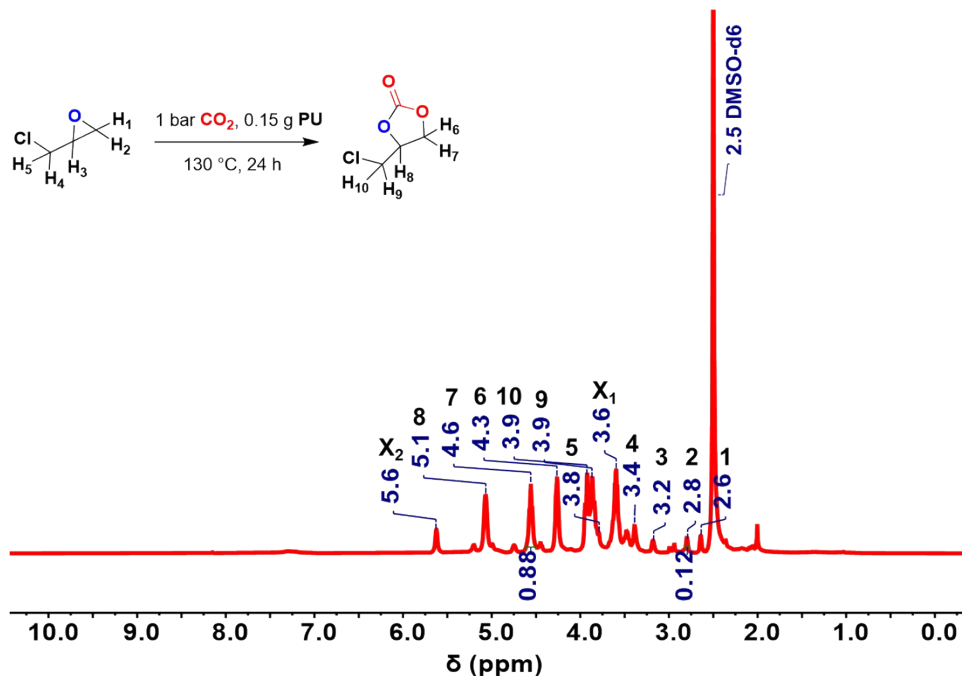


Figure S9. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

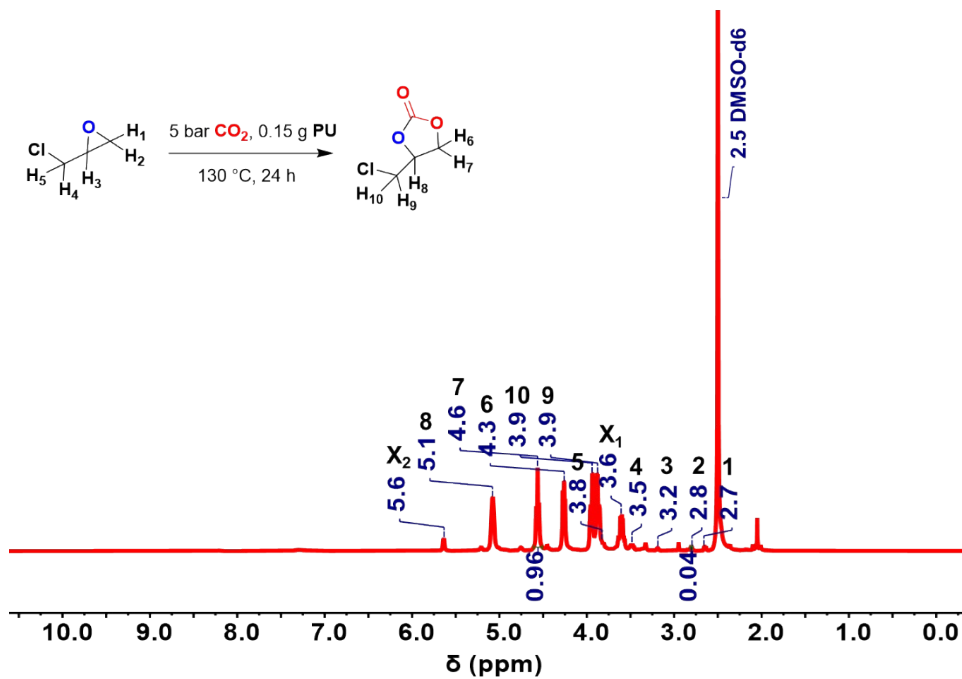


Figure S10. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆, X₁ and X₂: corresponding for the 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

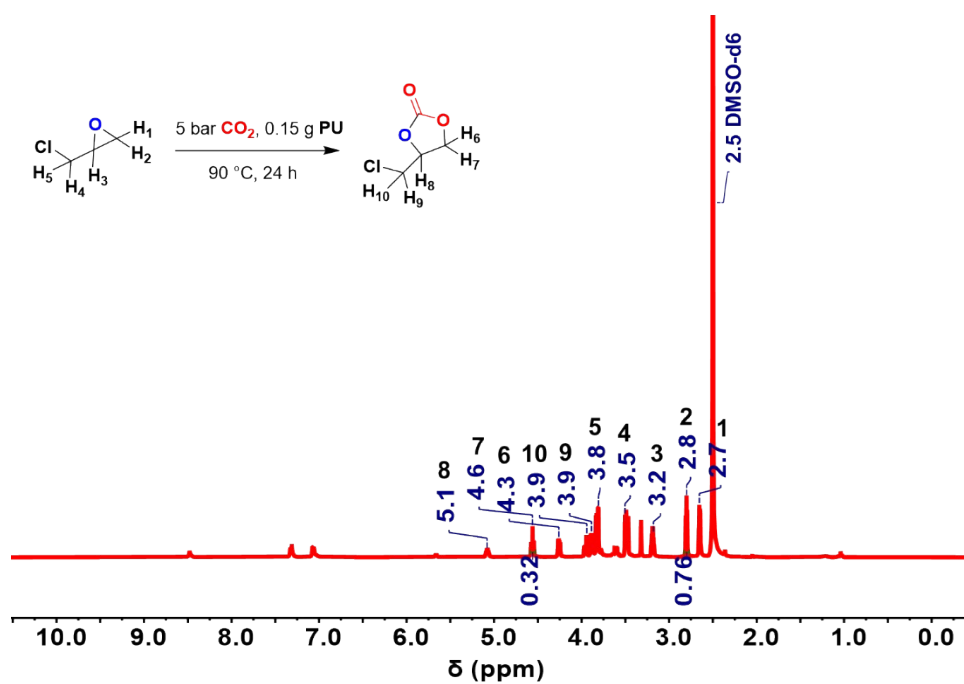


Figure S11. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆. Peaks centered at 7.1, 7.3 and 8.5 corresponding to the PU catalyst.

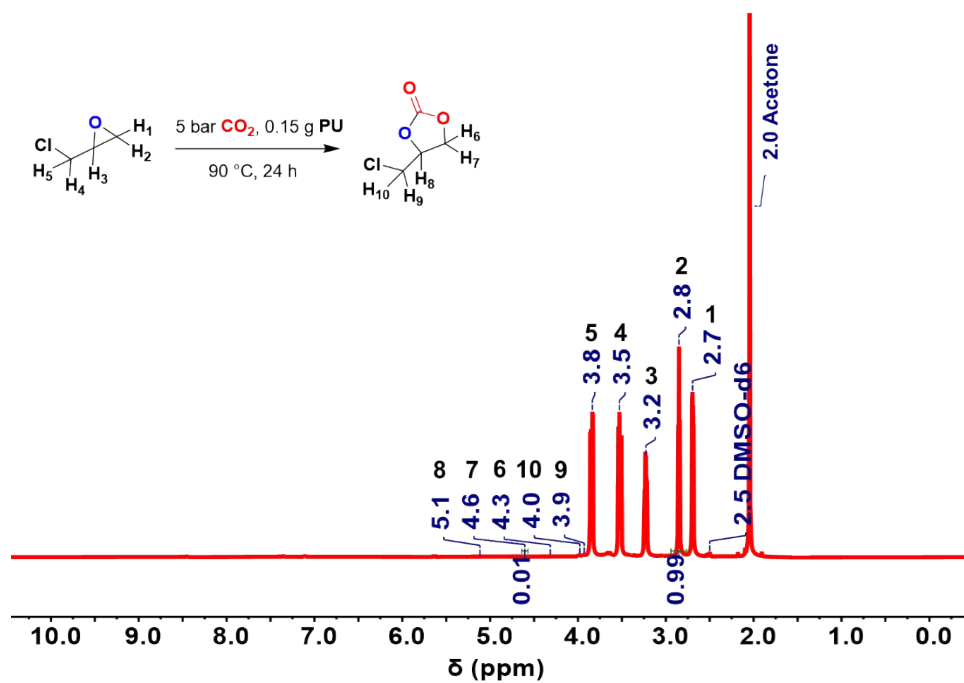


Figure S12. ¹H NMR spectrum of the reaction mixture after the conversion of ECH into its corresponding carbonate in DMSO-*d*₆.

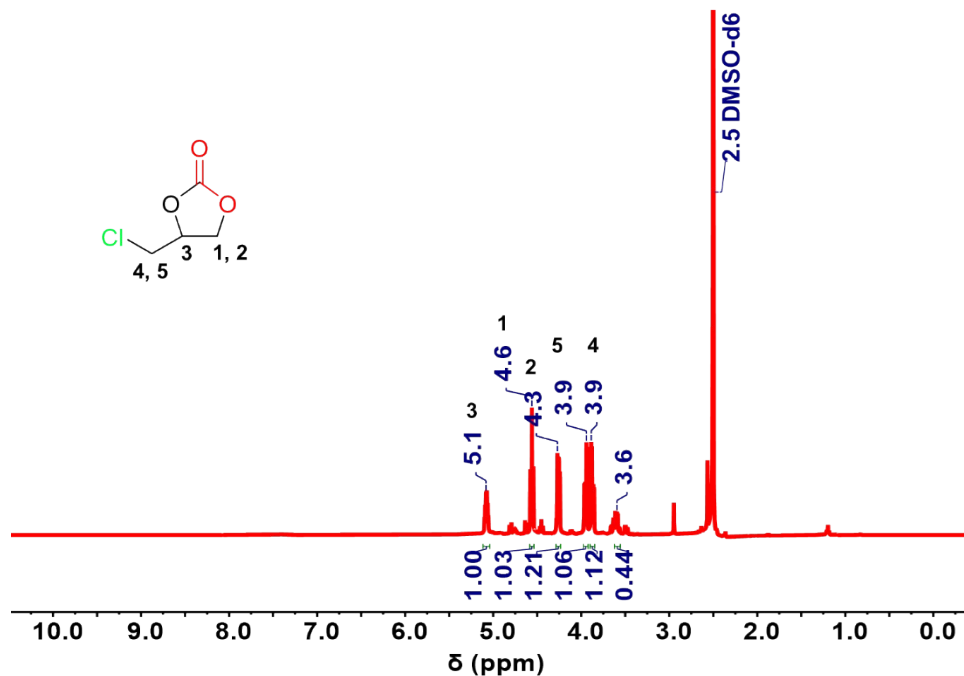


Figure S13. ^1H NMR spectrum of the isolated 4-chloromethyl-2-oxo-1,3-dioxolane in $\text{DMSO-}d_6$, peak at 3.6 corresponds to 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor).

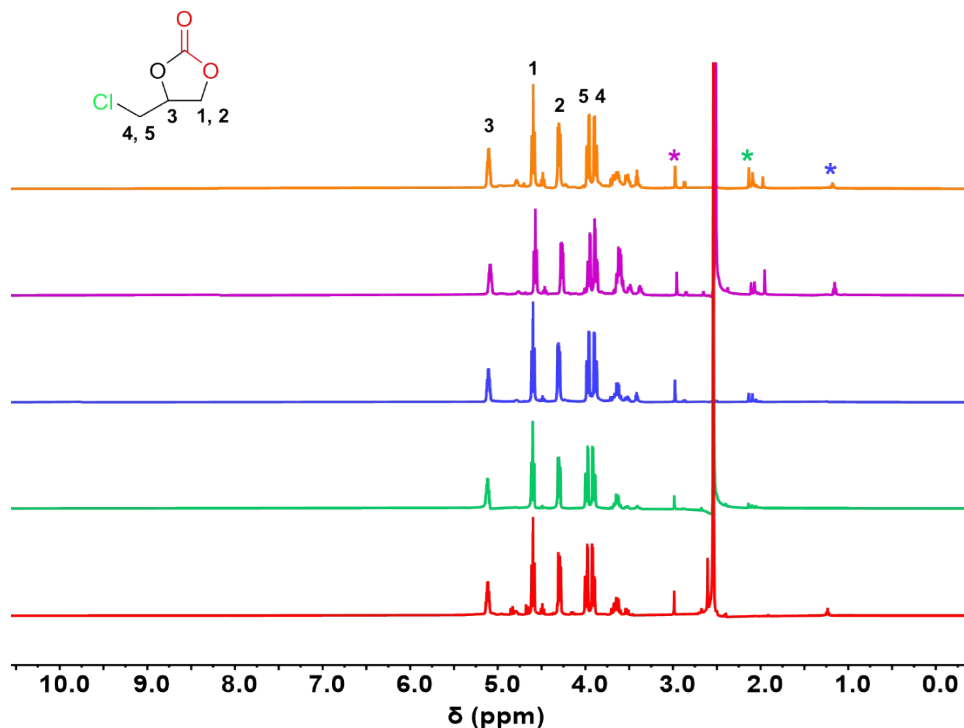


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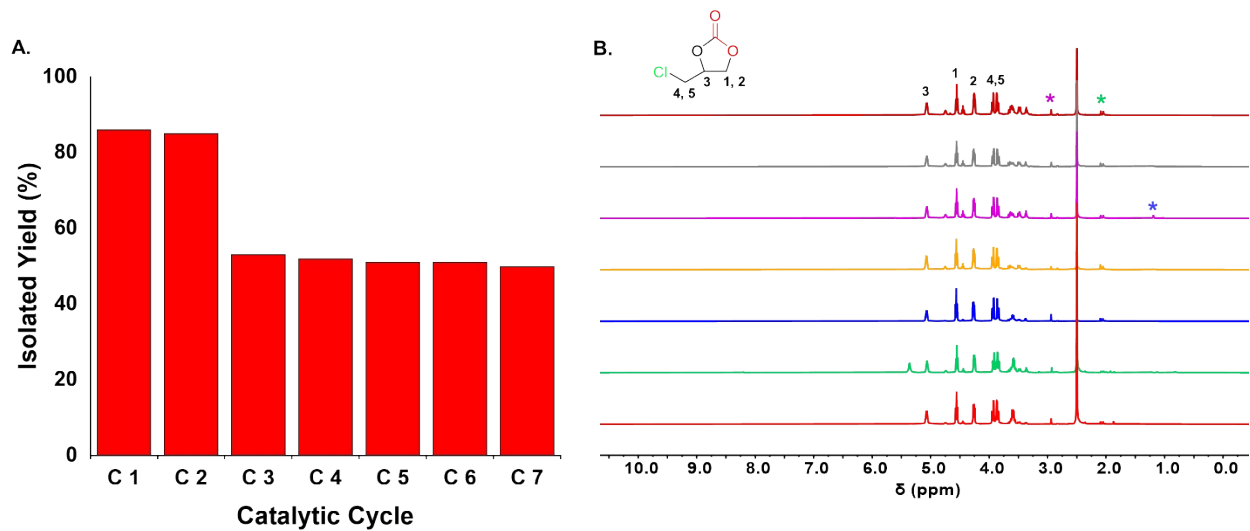
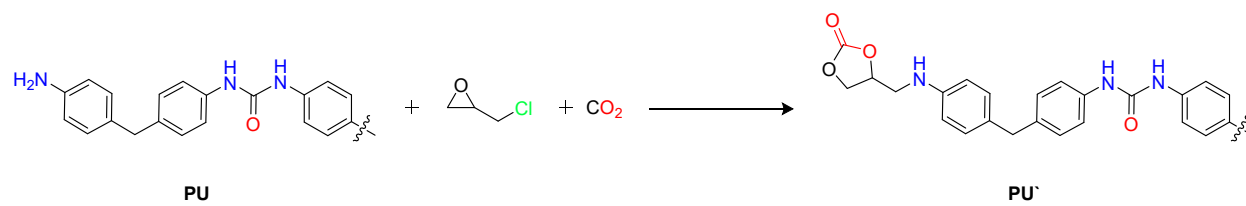


Figure S15. A. The recyclability of **PU** over seven catalytic cycles for the reaction of ECH and CO_2 (second run). **B.** ^1H NMR spectra of the isolated 4-chloromethyl-2-oxo-1,3-dioxolane in $\text{DMSO-}d_6$, peaks at 3.6 and 5.3 correspond to 3-chloropropane-1,2-diol (from the starting material as supplied by the chemical vendor). Peaks labelled with asterisk corresponding to traces of residual solvents used in the isolation process (blue asterisk for hexane, green asterisk for ethyl acetate, and purple asterisk for methanol).

3. Side reaction of PU with ECH



Scheme S1. The side reaction of the **PU** with ECH and CO₂ to produce the **PU'**.

4. DFT-optimized geometries

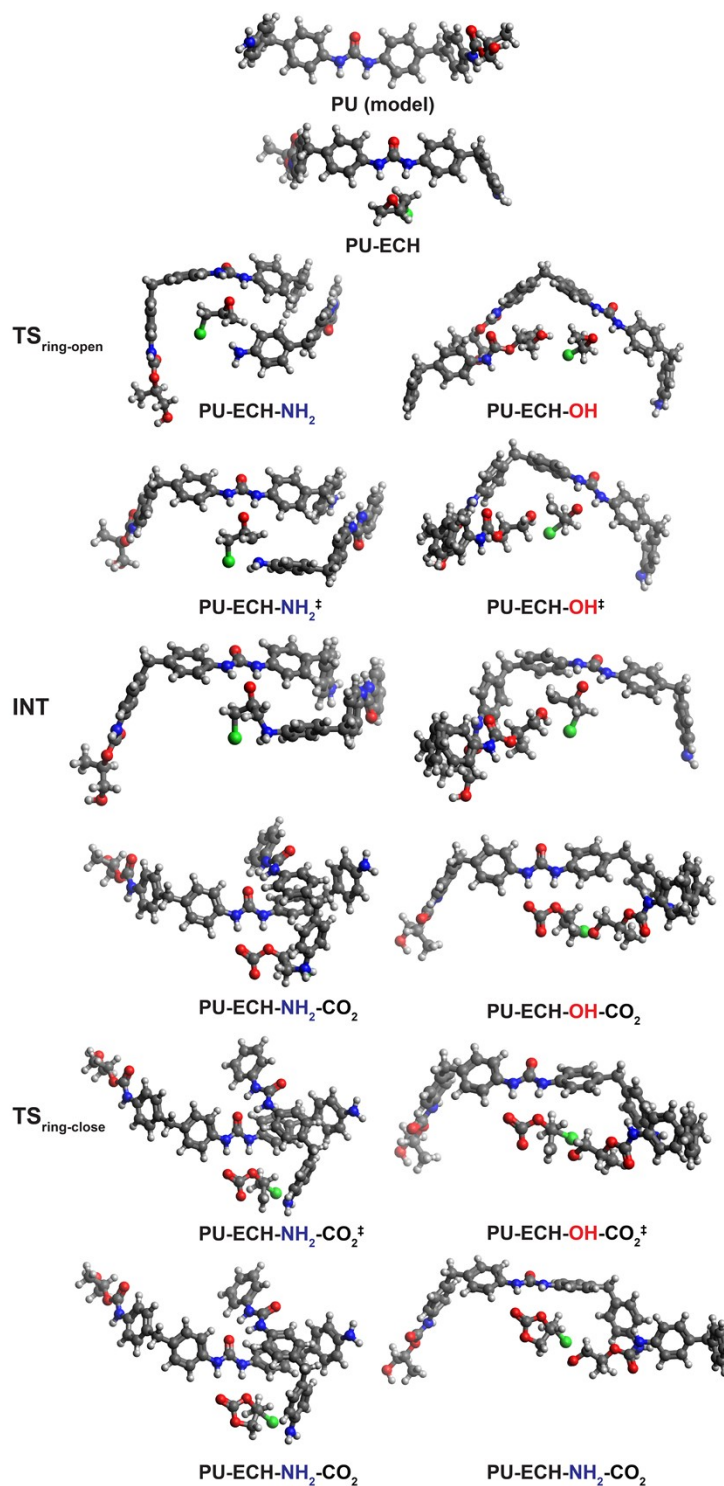


Figure S16. DFT-optimized geometries of all species involved in the calculated reaction profile. Calculations were performed at B3LPY/6-311+G(d)-D3 in DMSO.