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## Green Foundation

1. Poly(cyclohexene carbonate) (PCHC) is a sustainable CO<sub>2</sub>-derived engineering polymer, yet conventional PCHC recycling often requires harsh conditions with little control over monomer selectivity. Here, we introduce the first application of earth-abundant tunable ionic radius lanthanide-organic catalysts that selectively converts PCHC into either of two different monomeric products, each capable of closed-loop chemical recycling: cyclohexene oxide (CHO) or *trans*-cyclohexene carbonate (*trans*-CHC), each delivering >99% purity and near-complete conversion.
2. This approach achieves a rare example of chemodivergence in polymer recycling, allowing precise control over monomer recovery. Additionally, it enables mixed plastic recycling by selectively depolymerize and separate PCHC in the presence of other polymers, demonstrating its compatibility for real-world mixed-plastic waste recycling.
3. This work establishes a novel strategy for CO<sub>2</sub>-based polymer recycling, demonstrating how catalyst-controlled depolymerization provides tunable monomer recovery. These findings can inspire future advancements in catalyst design for plastic recycling.



## ARTICLE

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# Selective Chemodivergent Depolymerization of Poly(Cyclohexene Carbonate) with Lanthanide-Organic Catalysts

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If feasible, introducing chemodiversity into the selective chemical recycling of plastics would provide a resource- and catalyst-efficient means of recovering high-value building blocks from synthetic polymers for diverse recycling applications via straightforward alterations of catalytic conditions. Here we report the application of earth-abundant, readily available lanthanide-organic  $\text{Ln}[\text{N}(\text{TMS})_2]_3$  catalysts to the solventless chemodivergent, non-random back-biting depolymerization of poly(cyclohexenecarbonate) (PCHC) in high selectivity and near-quantitative conversion. Varying the lanthanide ionic radius across the 4f series and modifying the reaction conditions creates an efficient switch in PCHC depolymerization pathway to the corresponding epoxide (cyclohexene oxide; >99% selectivity; >94% yield) or the corresponding cyclic carbonate (*trans*-cyclohexene carbonate; >99% selectivity; 93% yield) monomer, each offering recycling value and closed-loop circularity. Combined experimental and theoretical DFT mechanistic analyses indicate two competing depolymerization pathways: low-energy reversible cyclic carbonate formation and rate-limiting irreversible decarboxylation. These catalysts are recyclable and applicable to plastics mixtures such as PCHC + nylon-6 + polyethylene, enabling sequential monomer capture with a single catalyst in the solvent-free process.

## Green foundation

1. Poly(cyclohexene carbonate) (PCHC) is a sustainable  $\text{CO}_2$ -derived engineering polymer, yet conventional PCHC recycling often requires harsh conditions with little control over monomer selectivity. Here, we introduce the first application of earth-abundant tunable ionic radius lanthanide-organic catalysts that selectively converts PCHC into either of two different monomeric products, each capable of closed-loop chemical recycling: cyclohexene oxide (CHO) or *trans*-cyclohexene carbonate (*trans*-CHC), each delivering >99% purity and near-complete conversion.
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## Introduction

Chemodivergent catalytic processes provide a unique, resource- and catalyst-efficient strategy for expanding product diversity from common starting materials,<sup>1–4</sup> making them ideal to address emerging challenges associated with environmental issues, such as plastics pollution. For decades, escalating

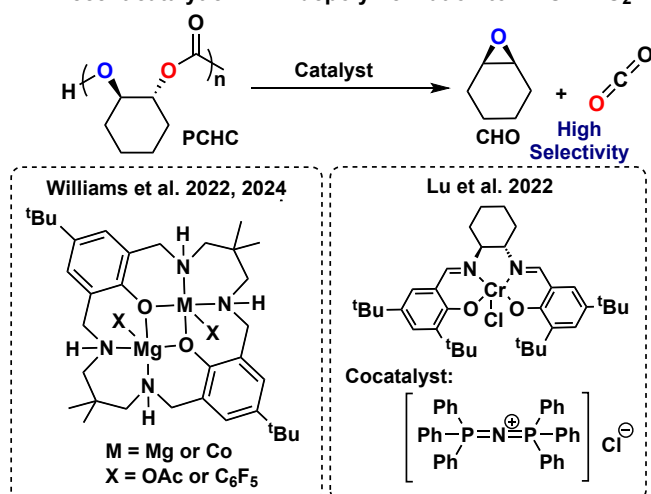
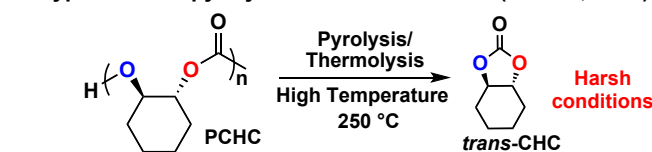
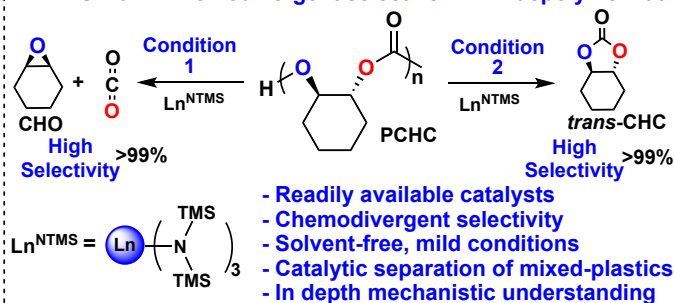
concerns regarding plastic pollution have motivated the need for effective recycling technologies.<sup>5–7</sup> With  $4.5 \times 10^8$  tons of plastics produced annually, great interest has been drawn to chemical recycling processes, which offer the opportunity to reclaim the monomeric units of polymers, thereby enabling closed-loop polymer circularity without compromising materials properties.<sup>8,9</sup> An important class of polymers is polycarbonates, which are high-performance thermoplastics widely used with a 2022 global market surpassing \$22.6B.<sup>10</sup> Aromatic polycarbonates incur a significant production carbon footprint and to date have eluded effective chemical recycling. In contrast, aliphatic polycarbonates prepared from epoxide/ $\text{CO}_2$  ring-opening copolymerization are more attractive

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**Scheme 1.** Overview of PCHC depolymerization to monomers.**A. Recent catalytic PCHC depolymerization to CHO + CO<sub>2</sub>****B. Typical PCHC pyrolysis route to *trans*-CHC (Coates, 2014)****C. This work: Chemodivergent selective PCHC depolymerization**

and have gained attention due to their capture of greenhouse CO<sub>2</sub>, tunable properties, and chemical recyclability to monomers.<sup>11–17</sup>

Among aliphatic polycarbonates, poly(cyclohexene carbonate) (PCHC; **Scheme 1A**) is the most widely used CO<sub>2</sub>-derived polycarbonate. While PCHC is still in the R&D stages, it shows significant promise as a sustainable engineering plastic, reflecting its optical transparency, high tensile strength, and excellent stability/ductility,<sup>18,19</sup> with significant potential in applications such as construction, electronics, automobile, eyewear, and medical equipment. PCHC has also served as a well-established literature benchmark for evaluating the activity and selectivity of aliphatic polycarbonate depolymerization catalysts.<sup>8</sup> The unique chemical recyclability of PCHC lies in its potential depolymerization to yield either of two different monomers: the 5-membered cyclic carbonate *trans*-cyclohexene carbonate (*trans*-CHC) and/or the corresponding epoxide, cyclohexene oxide (CHO), both of which can be re-polymerized to pristine PCHC in closed-loop recycling (**Schemes 1A** and **1B**).<sup>8</sup> Importantly, recovering either monomer offers distinct appeal: epoxides can be readily repolymerized or copolymerized into diverse high-value materials via effective upcycling;<sup>20,21</sup> cyclic carbonates find extensive utilization as aprotic solvents<sup>22</sup> or pharmaceutical intermediates<sup>23</sup>, and are often favored for sequestering greenhouse CO<sub>2</sub>.<sup>24</sup>

Interest in the chemical recycling of PCHC has grown significantly in recent years (see SI **Figure S1**) as a representative CO<sub>2</sub>-derived sustainable polymer. This work demonstrated selective PCHC depolymerization to monomer CHO + CO<sub>2</sub> using well-optimized mono- or bimetallic catalysts (**Scheme 1A**),<sup>25–29</sup> while typically high-temperature PCHC pyrolysis processes (>250 °C) are most effective for the other monomer, *trans*-CHC, as reported by Coates et al. (**Scheme 1B**).<sup>8,21,30,31</sup> Challenges associated with CHO stem from the high kinetic barrier to epoxide formation, requiring elaborate catalyst structures,<sup>32</sup> exemplified by the pioneering studies of Williams et al. using heterodinuclear complexes for efficient CHO + CO<sub>2</sub> recovery. These include a dinuclear Mg(II) catalyst,<sup>25</sup> and heterodinuclear

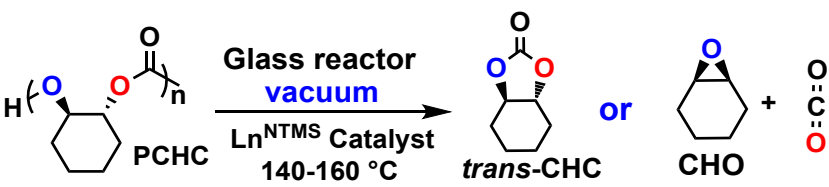
Mg(II)Co(II) catalysts for PCHC depolymerization under solventless conditions.<sup>27,28</sup> Lu et al. reported selective PCHC pyrolysis to CHO + CO<sub>2</sub> using a Cr(III)-Salen catalyst or a PPN-N<sub>3</sub> [bis(triphenylphosphine) iminium azide] cocatalyst at 200 °C.<sup>[26]</sup> While these mono-/dinuclear complexes demonstrate good activity and general selectivity, their preparation involves multiple synthesis/purification steps.

Lanthanide-based catalysts that play a significant role in chemical synthesis, are earth-abundant (La abundance in the earth's crust is comparable to that of Ni and Cu)<sup>33</sup>, kinetically labile, highly electrophilic, structurally tunable, and usually readily available.<sup>34–40</sup> For example, Ln[N(TMS)<sub>2</sub>]<sub>3</sub> complexes (Ln<sup>NTMS</sup>) rapidly and selectively catalyze ketone and aldehyde,<sup>41</sup> ester,<sup>36</sup> as well as amide reductions,<sup>42</sup> and more recently were used in selective and Ln<sup>3+</sup> radius-dependent polyester<sup>43</sup> and nylon-6 depolymerization.<sup>44,45</sup> This motivated us to investigate their potential in polycarbonate deconstruction.

Here we report the rapid, selective, and solventless depolymerization of PCHC using readily available Ln<sup>NTMS</sup> model catalysts (**Scheme 1C**). While not the most active lanthanide-organic catalysts<sup>44,45</sup>, this series allows ready evaluation of Ln<sup>3+</sup> ion size effects, kinetic/mechanistic selectivities, and DFT computational analysis, revealing two discrete and heretofore unrecognized competing depolymerization pathways to produce either of the two different PCHC monomers. An efficient chemodivergence is thereby realized, enabling selective recovery of CHO or *trans*-CHC by simply switching between depolymerization methodologies. Considering the intrinsic values of both monomers, such a catalytic approach is attractive for accessing different recycling/upcycling scenarios via straightforward modifications of reaction conditions. While strict Ln<sup>3+</sup> size chemodivergence is observed in organolanthanide-mediated pyridine C-H borylation vs. dearomatization,<sup>46</sup> such an interplay between catalytic conditions and monomer selectivity in polymer depolymerization processes has never been previously, to our knowledge, achieved and with such selectivity.



## Results and Discussion

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DOI: 10.1039/D5GC01399B**Table 1.** PCHC depolymerization data as a function of the metal ionic radius using  $\text{Ln}^{\text{NTMS}}$  and  $\text{Sc}^{\text{NTMS}}$  catalysts.


Entry <sup>[a]</sup>	Catalyst ( $\text{Ln}^{3+}$ ionic radius)	Total Conv. <sup>[b]</sup> (%)	Monomer Selectivity		TOF <sup>[e]</sup>	
			<i>trans</i> -CHC <sup>[c]</sup> (%)	CHO <sup>[c]</sup> (%)	<i>trans</i> -CHC	CHO
1	$\text{La}^{\text{NTMS}}$ (1.030 Å)	93	-	>99	-	6.2
2	$\text{Sm}^{\text{NTMS}}$ (0.960 Å)	62	25	75	1.03	3.1
3	$\text{Lu}^{\text{NTMS}}$ (0.861 Å)	23	80	20	1.22	0.31
4	$\text{Sc}^{\text{NTMS}}$ (0.745 Å)	8.5	93	7	0.53	0.04
5	No catalyst	<1	>99	-	-	-
6 <sup>[d]</sup>	$\text{La}^{\text{NTMS}}$ (1.030 Å)	93	>99	-	55.8	-

[a] Unless otherwise noted, reactions were performed solventless with 100 mg PCHC under static vacuum in a closed 50 mL Schlenk tube with 5 mol% catalyst at 140 °C for 3 h. See SI for details. [b] From integrating  $^1\text{H}$  NMR of *trans*-CHC (3.0 ppm) + CHO (2.8 ppm) vs. PCHC (4.7–5.0 ppm) reaction mixture in  $\text{d}^8$ -toluene. Note PCHC signals appear as broad features in the 4.6–4.8 ppm range, consistent with literature data.<sup>[25,27]</sup> [c] Product distribution assayed by  $^1\text{H}$  NMR. <sup>[d]</sup> Under dynamic vacuum, 160 °C, 20 min. [e] Estimated TOF (turnover frequency) in units of  $(\text{mol of monomer}) \cdot (\text{mol Cat.})^{-1} \cdot (\text{h})^{-1}$ .

## Catalyst Screening: Lanthanide Ionic Radius Effects

Surprisingly, unlike typical base-initiated depolymerization of aliphatic PCs to the corresponding cyclic carbonates,  $\text{La}^{\text{NTMS}}$  catalyzes PCHC depolymerization to epoxide CHO in high selectivity (>99%) and conversion (93%) under static vacuum at 140 °C in 3 h (Table 1, entry 1). Despite the high basicity of the -NTMS ligands, cyclic carbonate *trans*-CHC, which is the expected product from PCHC via a ring-closing mechanism, is not observed, in contrast to the  $\text{La}^{\text{NTMS}}$ -catalyzed depolymerization of polyesters<sup>33</sup> and polyamides<sup>34</sup> which yield the corresponding cyclic lactones and lactams, respectively, and other base-mediated depolymerizations of  $\text{CO}_2$ -derived PCs<sup>30</sup>. This result suggests a unique catalytic role of the  $\text{Ln}^{3+}$  center.

To further investigate  $\text{Ln}^{3+}$  effects on the current system, a series of homoleptic  $\text{Ln}^{\text{NTMS}}$  precatalysts where  $\text{Ln} = \text{La}, \text{Sm}, \text{Lu}$ , and  $\text{Sc}$  was surveyed under identical solventless, mild depolymerization conditions and static vacuum (Table 1, entries 2–4). Note that under the same reaction conditions, contraction of the  $\text{Ln}^{3+}$  ion radii alters PCHC depolymerization selectivity and rate: large  $\text{La}^{3+}$  exclusively favors rapid epoxide formation,  $\text{Sm}^{3+}$  yields mixed products,  $\text{Lu}^{3+}$  predominantly yields *trans*-CHC, and small  $\text{Sc}^{3+}$  favors exclusive cyclic carbonate formation (*trans*-CHC) at low conversion. Control experiments without a catalyst under identical conditions yield only traces (<1%) of the thermodynamically favored<sup>31</sup> *trans*-CHC product (Table 1, entry 5). This demonstrates a significant catalytic role for the  $\text{Ln}^{\text{NTMS}}$  complexes at this reaction temperature (140–160 °C), with non-catalytic PCHC thermolysis requiring a far higher temperature (250 °C).<sup>31</sup>

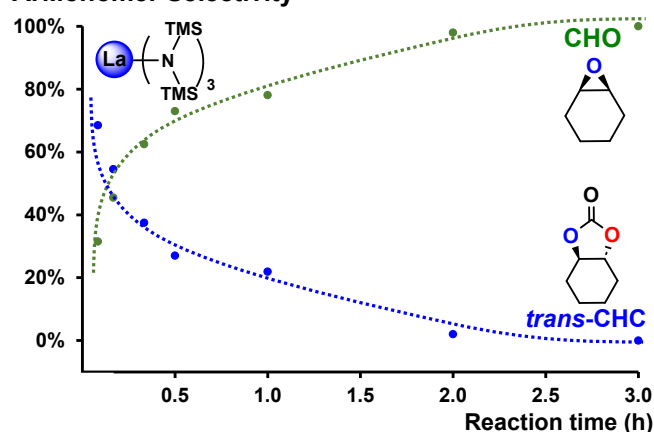
## Kinetic Studies

Considering the apparent dependence of monomer selectivity on the metal ionic radius, combined with a fall in conversion rate as the  $\text{Ln}^{3+}$  ionic radius contracts from  $\text{La}^{3+}$  (1.030 Å) to  $\text{Sc}^{3+}$  (0.745 Å), we hypothesized that *trans*-CHC may play an intermediate role in the reaction pathway. To probe this hypothesis, kinetic studies (Figure 1A) were performed to monitor *trans*-CHC vs. CHO product distribution over the course of the 0–3h reaction using the most active and a moderately active catalyst (Table 1, entries 1 and 2). The data indicate that *trans*-CHC is predominantly produced in the initial stages of reaction, followed by a gradual increase in the CHO monomer content, eventually reaching >99%. We further hypothesized that in a closed reaction system, *trans*-CHC might further undergo conversion to CHO +  $\text{CO}_2$  mediated by  $\text{Ln}^{\text{NTMS}}$ .

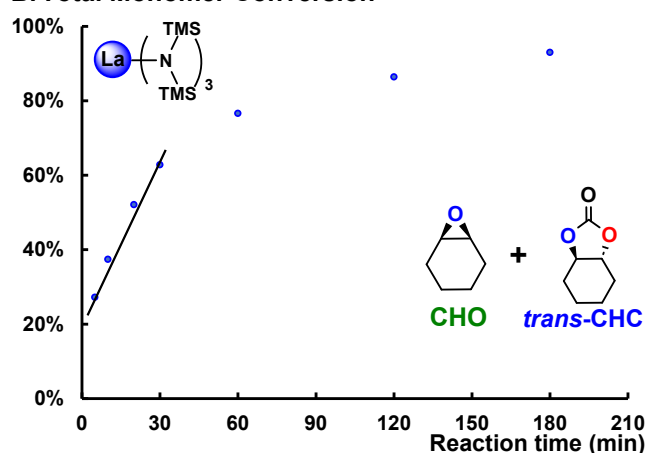
To investigate whether the  $\text{Ln}^{\text{NTMS}}$ -catalyzed PCHC depolymerization proceeds via a back-biting mechanism from hydroxyl end groups or via random chain scissions, total monomer conversion (*trans*-CHC + CHO) was plotted versus time (Figure 1B). A linear increase in monomer yield is observed over the first 30 min (up to ~63 %), followed by saturation. This behavior indicates that the reaction is initially zero-order in [PCHC], suggesting that in the catalyst resting state the polymer is bound to the La center largely at the chain end and depolymerization proceeds with the catalyst walking along the chain. Saturation presumably reflects PCHC depletion and/or catalyst deactivation at chain ends. This kinetic behavior closely resembles profiles previously we previously reported for Nylon-6 depolymerization with Ln-based catalysts.<sup>34,35</sup>



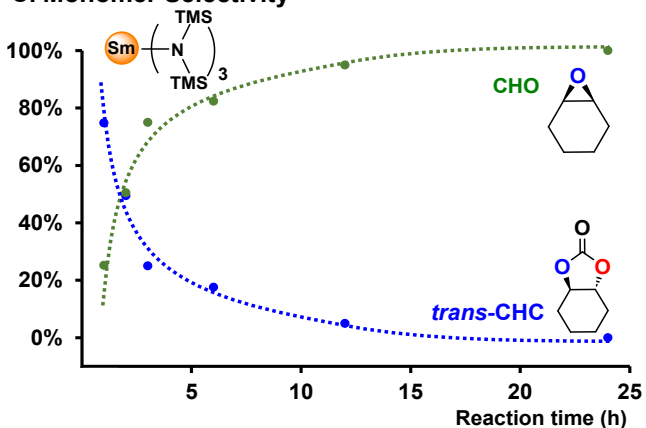
## A. Monomer Selectivity



## B. Total Monomer Conversion



## C. Monomer Selectivity



**Figure 1.** A. Kinetic profile of PCHC depolymerization in a closed reaction system using  $\text{La}^{\text{NTMS}}$  and C.  $\text{Sm}^{\text{NTMS}}$  catalysts under the conditions of Table 1. B. total monomer conversion ( $\text{trans-CHC}$  +  $\text{CHO}$ ) versus reaction time. C. Kinetic profile of PCHC depolymerization in a closed reaction system using  $\text{Sm}^{\text{NTMS}}$ .

Gel Permeation Chromatography (GPC) analysis was also used to examine polymer MW at 0–1.5 h reaction times. The results show a gradual decrease in MW (Figure S7), supporting a back-biting mechanism in which monomers are sequentially eliminated from the polymer chain end in each catalytic cycle, although the observed increase in polydispersity as the reaction

progresses may suggest the presence of a competing random scission mechanism. DOI: 10.1039/D5GC01399B

The respective conversions of  $\text{CHO}$  and  $\text{trans-CHC}$  vs. time were plotted (Figures S8 and S9). The data reveal that the quantity of  $\text{trans-CHC}$  remains relatively constant at a low level (~15–20%) during the early stages of the reaction, followed by the eventual decrease to 0% by the end of the 3-hour kinetic study. Parallel kinetic studies with  $\text{Sm}^{\text{NTMS}}$  reveal that for the smaller  $\text{Ln}^{+3}$  ionic radius, a similar  $\text{CHO}$  selectivity (>99%) is achieved, albeit with a slower approach to equilibrium (Figure 1C).

Mechanistic Studies:  $\text{trans-CHC}$  Reactions

To further probe the reaction pathway and understand the origin of  $\text{Ln}^{\text{NTMS}}$  product selection,  $\text{trans-CHC}$  was synthesized separately and exposed to several  $\text{Ln}^{\text{NTMS}}$  catalysts under identical depolymerization conditions (Table 2), testing the hypothesis that these catalysts should mediate  $\text{CHO}$  formation and at different rates. In agreement with the findings in Table 1,  $\text{Ln}^{\text{NTMS}}$  catalysts having larger ionic radii are more active decarboxylation catalysts for  $\text{CHO}$  formation (Table 2;  $\text{La}^{\text{NTMS}} > \text{Sm}^{\text{NTMS}} > \text{Lu}^{\text{NTMS}} > \text{Sc}^{\text{NTMS}}$ ). Importantly, all of these  $\text{Ln}^{\text{NTMS}}$  catalysts are active in  $\text{trans-CHC}$  polymerization to PCHC, indicating a likely reversible pathway from PCHC to  $\text{trans-CHC}$  depolymerization. Note that in Table 1, depolymerization reactions, the 50 mL Schlenk flask provides a large upper cold zone area for  $\text{CHO}$  condensation/collection, thus displacing the equilibrium towards quantitative  $\text{CHO}$  formation in >99% selectivity in entry 1 with  $\text{La}^{\text{NTMS}}$ . Interestingly, smaller  $\text{Ln}^{+3}$  ionic radii  $\text{Ln}^{\text{NTMS}}$  complexes are more active polymerization catalysts and less active decarboxylation catalysts.  $\text{Sc}^{\text{NTMS}}$ , as the smallest group 3 ion, affords only trace  $\text{CHO}$  product, in good agreement with its sluggish PCHC depolymerization rate (Table 1).

**Table 2.** Product distributions after 3 h for reactions of  $\text{trans-CHC}$  using the indicated amido catalysts.<sup>[a]</sup>

	$\text{trans-CHC}$	$\text{PCHC}$	$\text{CHO}$
Catalyst	$\text{trans-CHC}$ (reagent)	PCHC (polymerization)	$\text{CHO}$ (decarboxylation)
$\text{La}^{\text{NTMS}}$	6%	40%	54%
$\text{Sm}^{\text{NTMS}}$	15%	38%	47%
$\text{Lu}^{\text{NTMS}}$	24%	69%	7%
$\text{Sc}^{\text{NTMS}}$	28%	71%	1%

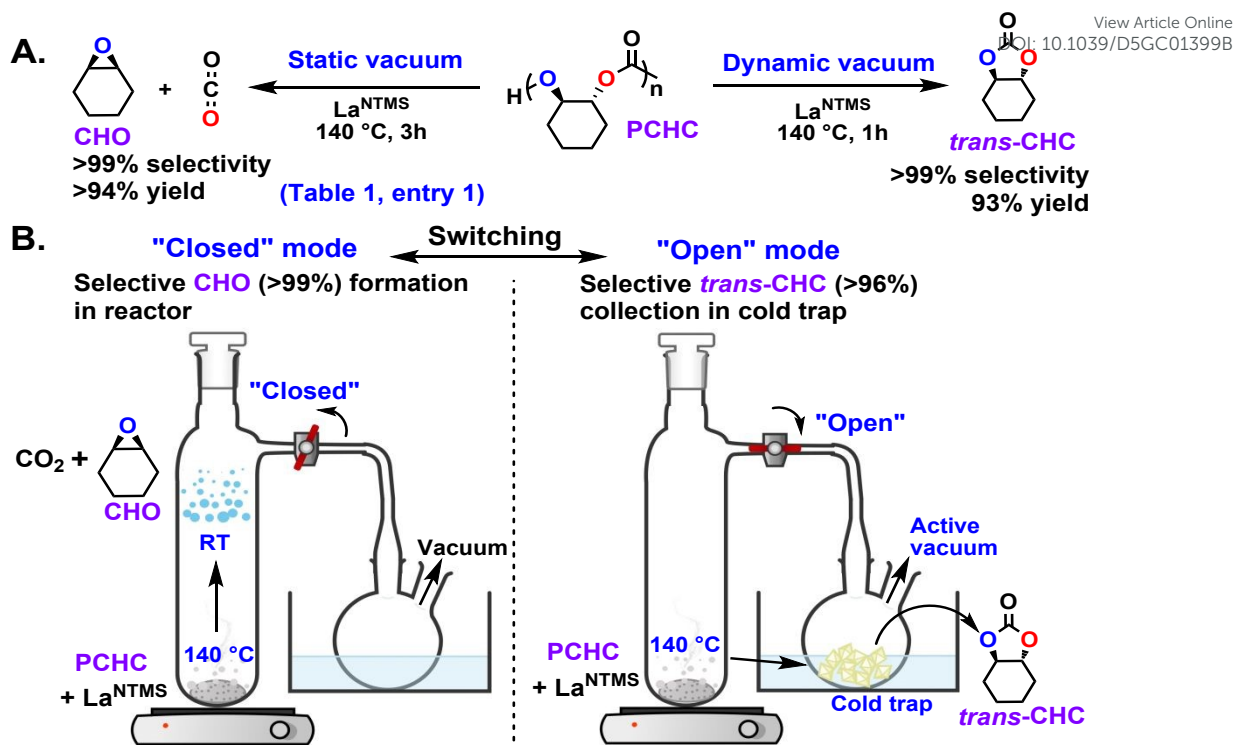
[a] Conditions: reactions performed solventless with 100 mg  $\text{trans-CHC}$  under static vacuum conditions in a closed 5 mL Schlenk tube. The reactor is completely submerged in an oil bath at 140 °C for 3 h. Product distributions determined from the  $^1\text{H}$  NMR integrals of  $\text{trans-CHC}$  (3.0 ppm) +  $\text{CHO}$  (2.8 ppm) vs. PCHC (4.7–5.0 ppm).

## Chemodivergence in PCHC Depolymerization Selectivity

Intrigued by the above results, we find that  $\text{trans-CHC}$  is indeed converted to  $\text{CHO}$  and  $\text{CO}_2$ , but not via direct decarboxylation. Instead,  $\text{trans-CHC}$  first undergoes re-







**Figure 2.** A. Chemodivergent effects of reactor configuration on monomer selectivity in PCHC depolymerization. B. Reactor configured in switchable "Open" and "Closed" modes to yield their respective chemodivergent monomers in high yield and selectivity.

polymerization to PCHC (see results in Table 2), which is then depolymerized to CHO and CO<sub>2</sub>. Furthermore, employing a continuous vacuum and a cold trap might allow isolation of *trans*-CHC, preventing further conversion. Strikingly, when the reaction methodology in Table 1, entry 1 is altered from a closed Schlenk reactor to a reactor under dynamic vacuum, the monomer selectivity of the La<sup>NTMS</sup>-catalyzed PCHC depolymerization is completely reversed (Figure 2A), with the reaction affording *trans*-CHC selectively (>99%) with high conversion (93%) in only 1 h at 140 °C (See Table 1, entry 6 and Table S1, entry 1). The reaction is rapid at 160 °C to reach a 94% yield of *trans*-CHC in only 20 min using 5 mol% La<sup>NTMS</sup>, while a lower catalyst loading (1 mol%) achieves full conversion of *trans*-CHC in 3 h (Table S1, entries 2 and 3).

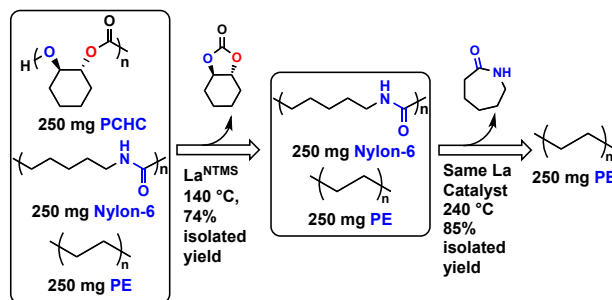
To demonstrate that this chemodivergent monomer selectivity is a truly "switchable" La<sup>NTMS</sup>-catalyzed phenomenon, a reactor was employed (Figure 2B and Figure S15) having a valve linking a Schlenk reactor and a cold trap. When the reactor is in "Open" mode (valve opened), *trans*-CHC is collected in the cold trap under active vacuum with >96% selectivity at 99% conversion. However, when the reactor is switched to "Closed" mode, CHO is formed in the Schlenk tube in >99% selectivity at 96% conversion, consistent with the data in Table 1, entry 1. These results present an unusual example in the field of plastics depolymerization/recycling in which the same catalyst and reaction conditions afford two different polymerizable monomers in high purity and conversion by simply switching between static and dynamic vacuum. Given the distinctive utility of both the present monomers, this chemodivergent catalytic approach offers

an intriguing solution for different recycling and upcycling options via straightforward adjustments in depolymerization conditions.

### Solventless Catalytic Separation of Mixed-Plastics

Since La<sup>NTMS</sup> is also effective for catalytic Nylon-6 depolymerization,<sup>34</sup> we were intrigued by the possibility of catalytically separating plastics mixtures via a simple variation of reaction modality (Scheme 2). Thus, for a mixture containing 250 mg each of PCHC + Nylon-6 + polyethylene in a sublimation reactor, PCHC was first selectively depolymerized to clean *trans*-CHC at 140 °C in 74% isolated yield. Note that ε-caprolactam is not obtained at this temperature, consistent with the inertness of Nylon-6 + La<sup>NTMS</sup> at this relatively low temperature. Next, after collection of the *trans*-CHC, the reaction temperature is elevated to 240 °C (no catalyst

### One Simple Catalyst (La<sup>NTMS</sup>) Separates Three Commercial Plastics



**Scheme 2.** La<sup>NTMS</sup> mediates the clean catalytic separation of PCHC + Nylon-6 + PE mixtures



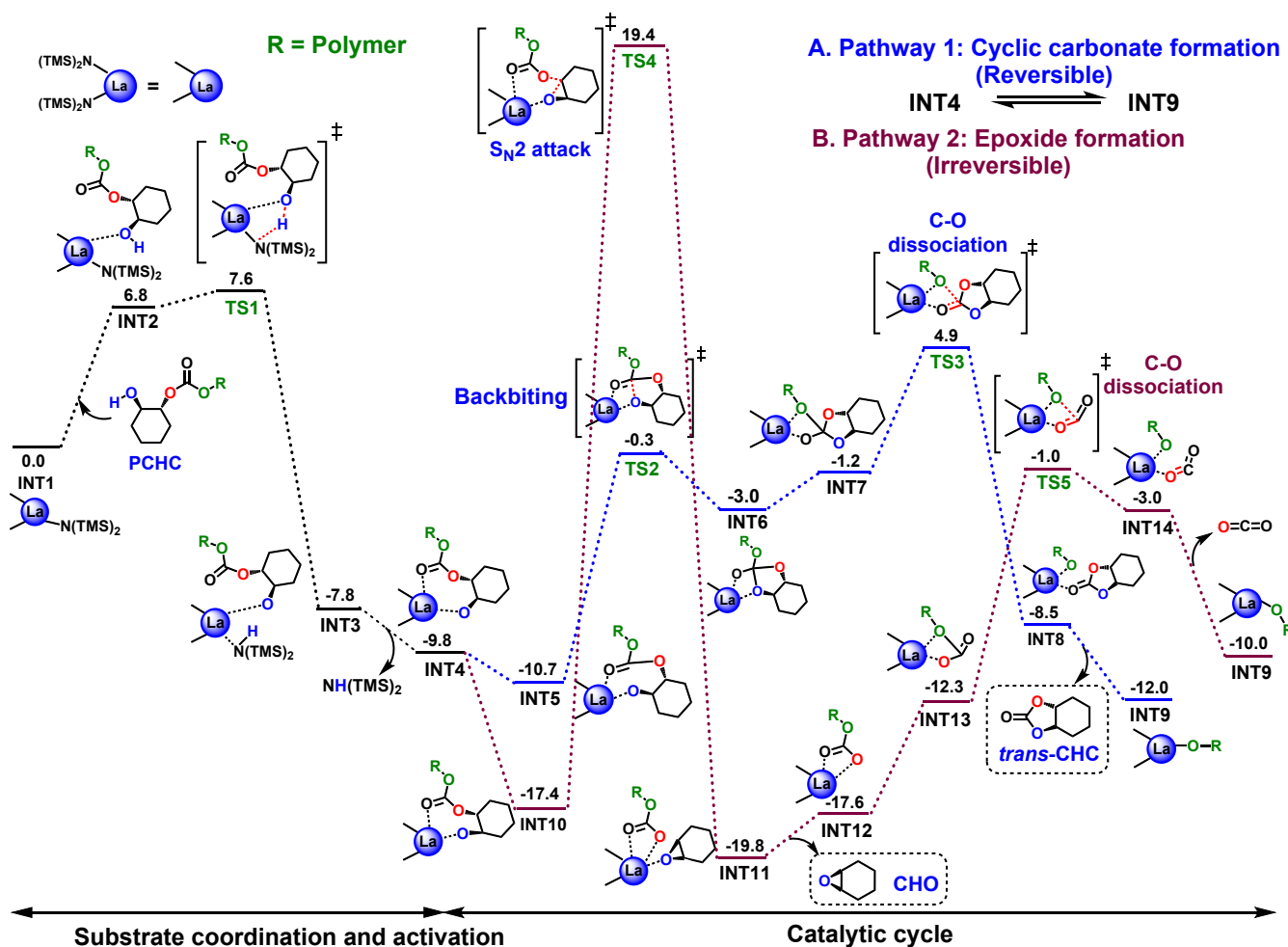
addition), rapidly depolymerizing the Nylon-6 to  $\epsilon$ -caprolactam in 85% isolated yield in 3 h, leaving the residual polyethylene unchanged. Separating PCHC by converting to CHO + CO<sub>2</sub> from a mixed-plastic system was also attempted, although clean conversion of the desired reaction in the presence of nylon-6 and polyolefins is not achieved (~40% of *trans*-CHC still remains, see SI page 20). We attribute this limitation to reduced mass transfer and poorer contact between the formed *trans*-CHC and the catalyst in the solid mixture, which hinders the necessary re-entry of *trans*-CHC into the catalytic cycle.

This model experiment reflects the broad and tunable scope of the inherently cost-effective and readily accessible lanthanide-organic catalysis for polymer recycling and commodity plastics mixture separation. These results highlight not only the recyclability of the catalyst but also its stability and versatility under the reaction conditions. Its ability to promote multiple depolymerization reactions without reactivation shows its robustness and practical utility in chemical recycling. Notably, the only detectable contamination in the recovered monomers originates from the

(TMS)<sub>2</sub>NH ligand, which possesses a lower boiling point than either product and can be readily removed by distillation.

### DFT Mechanistic Analysis

To further probe the origin of the present chemodivergent effects, the mechanism of the La<sup>NTMS</sup>-catalyzed PCHC depolymerization was probed using density functional theory (DFT) to compare and contrast possible reaction pathways, as illustrated in **Figure 3** (see SI for details). The  $\alpha,\omega$ -hydroxy telechelic PCHC (PCHC-OH) monomer was selected as the model to simulate the chain-end initiated depolymerization mechanism, as also proposed for PCHC depolymerization using dinuclear catalysts by Williams et al.<sup>25</sup> Chain-end unzipping vs. random scission mechanisms were also investigated by DFT calculations using both La-NTMS and La-OR potential active species (**Figure S19 and S20**). Results show that in both cases, chain-end unzipping is more kinetically favorable than mid-chain scission. The catalyst-PCHC coordination and activation step, which involves La<sup>3+</sup>-oxygen binding (from INT1 to INT2) followed by proton transfer from PCHC to the -NTMS ligand via TS1 leads to INT3, resembling steps that we mapped in Nylon-6



**Figure 3.** DFT-derived Gibbs free energy profile for the catalyst coordination and activation step, and La<sup>NTMS</sup>-catalyzed PCHC depolymerization cycle including two competing pathways **A.** Cyclic carbonate (*trans*-CHC) formation (blue dotted lines) **B.** Epoxide (CHO) and CO<sub>2</sub> formation (maroon dotted lines). Values were calculated at 140 °C in kcal mol<sup>-1</sup> at the PBE0-D3BJ/def2-TZVP//PBE0-D3BJ/def2-SVP<sup>[47–52]</sup> level of theory, incorporating the SMD solvation model<sup>[53]</sup> of ethylacetate ( $\epsilon = 5.9867$ ). R = Methyl for the calculation.





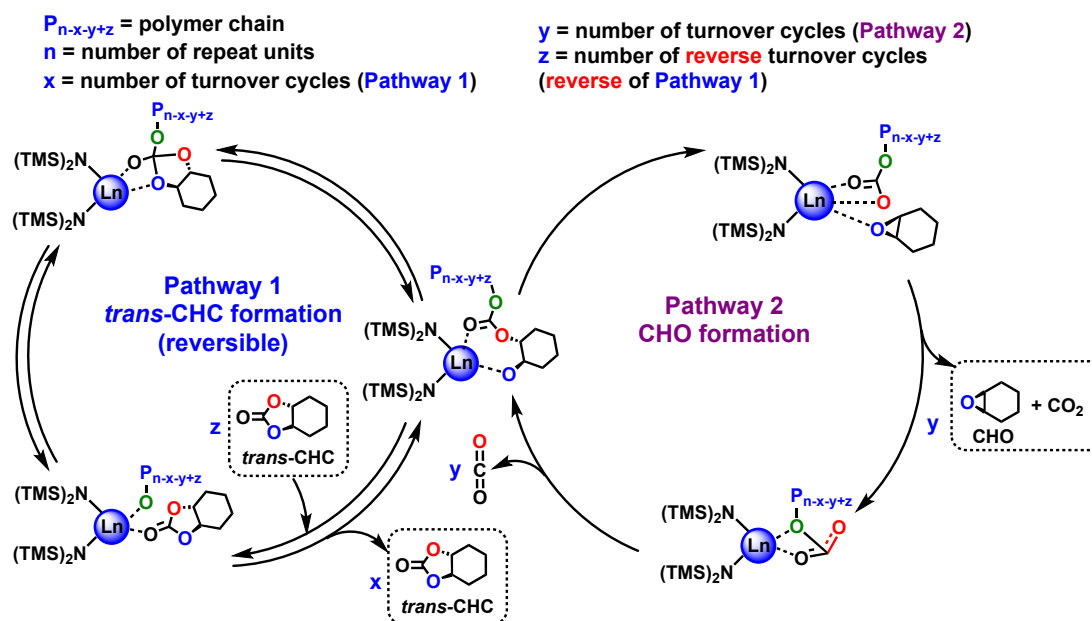
depolymerization.<sup>34,35</sup> Next, the dissociation of  $\text{HN}(\text{TMS})_2$  leads to **INT4**, which initiates the catalytic depolymerization cycle(s). Then, two competing pathways for PCHC depolymerization are examined, with **Pathway 1** producing *trans*-CHC and **Pathway 2** producing  $\text{CHO} + \text{CO}_2$ .

**Pathway 1 (Blue dotted line):** From **INT4**, the polymer undergoes relaxation to **INT5** followed by a two-step addition-elimination reaction (through **TS2** and **TS3**) to generate *trans*-CHC via a “back-biting” process. Note that similar back-biting mechanisms have been proposed in the literature for the depolymerization of various  $\text{CO}_2$ -derived polycarbonates.<sup>21,30</sup> The  $\Delta G$  for the addition step **INT5**  $\rightarrow$  **INT6** is computed to be 7.8 kcal/mol with  $\Delta G^\ddagger = 10.5$  kcal/mol (**TS2**), while the C-O dissociation step (**INT7**  $\rightarrow$  **INT8**) is exergonic with  $\Delta G = -7.4$  kcal/mol and  $\Delta G^\ddagger = 6.0$  kcal/mol. This is followed by the release of *trans*-CHC and formation of **INT9** ( $\Delta G = -3.5$  kcal/mol). The overall computed reaction barrier for **Pathway 1** is 15.6 kcal/mol (**INT5**  $\rightarrow$  **TS3**). However, **INT5** is not the lowest energy intermediate, and as discussed below, the kinetics of **Pathway 1** will be guided by the stability of an intermediate that lies along **Pathway 2** where, from **INT4**, the structure can relax to form **INT10**, yielding a net free energy barrier of 22.3 kcal/mol.

**Pathway 2 (Red dotted line):** From **INT10**, an  $\text{S}_{\text{N}}2$  attack occurs at an adjacent unit via **TS4** ( $\Delta G = -2.4$  kcal/mol;  $\Delta G^\ddagger = 36.8$  kcal/mol). This is followed by the release of monomeric  $\text{CHO}$  and the transition to **INT12** and **INT13**. Subsequent cleavage of the C-O bond via **TS5** then yields **INT14** ( $\Delta G = 9.3$  kcal/mol;  $\Delta G^\ddagger = 11.3$  kcal/mol), followed by  $\text{CO}_2$  release. The formation of  $\text{CHO}$  and  $\text{CO}_2$  occurs with  $\Delta G$  values of 2.2 kcal/mol and  $-7.0$  kcal/mol, respectively. Note that both pathways conclude with **INT9**, where R denotes the remainder of the polymer chain, and this structure can re-enter the catalytic cycle as **INT4**. The overall computed reaction barrier for **Pathway 2** is 36.8 kcal/mol

**Pathway 1 vs Pathway 2** ( $\Delta G^\ddagger = 22.3$  vs 36.8 kcal/mol, respectively) indicates kinetically more favorable *trans*-CHC formation. Furthermore, note that the formation of *cis*-CHC from **Pathway 2** is kinetically less favorable compared to  $\text{CO}_2$  release (**Figure S21**). Additionally, **INT4**, **INT5**, and **INT10** are interchangeable isomeric configurations, with **INT10** being the most stable intermediate, which affects the rates of both **Pathways 1** and **2**. Moreover, **Pathway 1** is found to be a reversible catalytic process with the reverse reaction (**INT9**  $\rightarrow$  **INT4**) featuring an accessible energetic barrier for the rate-determining step (16.9 kcal/mol;  $\Delta G^\ddagger = G_{\text{TS3}} - G_{\text{INT9}}$ ). This is in good agreement with our observation in **Table 2** that the reverse of **Pathway 1** eventually leads to the polymerization of *trans*-CHC to PCHC.

Note that while *trans*-CHC is often considered an intermediate decomposing to  $\text{CHO}$  and  $\text{CO}_2$  as proposed by other authors,<sup>26,30</sup> this study reveals its ability to repolymerize to PCHC in a closed system before further depolymerizing via **Pathway 2** (see **Figure 2**). This alternative pathway is distinctly different from others and, to the best of our knowledge, represents the first instance for the catalytic recycling of  $\text{CO}_2$ -based PCs. These computational results align well with the intriguing chemodivergent selectivity demonstrated in **Figure 2**. Under an active vacuum, *trans*-CHC generated via kinetically favored **Pathway 1** is isolated and removed from the catalytic cycle, preventing the reverse reaction to **INT4** (**Figure 4**). This further inhibits any  $\text{CHO}$  formation via **Pathway 2** under these conditions, in agreement with the high *trans*-CHC selectivity. Conversely, under static vacuum conditions where the *trans*-CHC product is not removed and can re-enter the catalytic cycle in the closed system, the DFT results suggest that the reverse of **Pathway 1** may occur to produce  $\text{CHO}$  via an **INT9**  $\rightarrow$  **INT4**  $\rightarrow$  **Pathway 2** mechanism, in agreement with the present kinetic



**Figure 4.** Simplified dual catalytic cycles for the catalytic depolymerization of PCHC via two competing pathways.

(**INT10**  $\rightarrow$  **TS4**). In comparing these two pathways, both of which proceed from **INT4** to **INT9**, the lower energy barrier of



information in **Figure 1. Pathway 2** is irreversible since the polymerization of epoxides requires excess  $\text{CO}_2$  to yield aliphatic PCs.<sup>11,21,31</sup> Note that the depolymerization of PCHC to CHO and  $\text{CO}_2$  via **Pathway 2** is also strongly favored entropically, primarily driven by the removal of gaseous  $\text{CO}_2$  to shift the reaction equilibrium, a key factor that is not fully captured by DFT,<sup>25</sup> due to the inaccuracy of using the qRRHO approximation to describe the entropy of adsorbed species<sup>36,37</sup> and the limitations of the implicit solvent model for computing solution-phase Gibbs free energies.<sup>38</sup> Furthermore, the calculations imply that **INT11**, which leads to CHO, is -11.4 kcal/mol more favorable than the intermediate that forms *trans*-CHC (**INT8**). This difference in energetic stability may also provide a substantial driving force for the formation of CHO mediated by  $\text{La}^{\text{NTMS}}$ . These DFT results closely align with the present kinetic studies, which clarify the equilibrium dynamics in a three-component system (PCHC, *trans*-CHC, and CHO), and that a constant equilibrium is reached for *trans*-CHC throughout the entire process (see **Figures 1A, 1B** and **Figures S12, S13**).

## Conclusions

We report the solventless and selective depolymerization of PCHC using readily available model  $\text{Ln}^{\text{NTMS}}$  catalysts. Interestingly,  $\text{La}^{\text{NTMS}}$  with the largest  $\text{Ln}^{+3}$  ionic radius participates in the unique chemodivergent monomer selection for PCHC depolymerization in high conversions and rates: dynamic vacuum selectively affords *trans*-CHC (>99% purity at high conversions), while in a closed reaction system, CHO is produced in high selectivity (>99%) and conversion. This chemodivergent PCHC depolymerization selectivity, enabled by a 'switchable' reaction apparatus, provides facile selection of the desired monomer. In addition, this catalytic process can be adapted for the separation of commodity plastics mixtures containing PCHC, nylon-6, and polyethylene in a single-reactor solventless approach, leveraging the versatility of  $\text{La}^{\text{NTMS}}$  in selectively depolymerizing PCHC and nylon-6 to their respective monomers under orthogonal conditions. Regarding the mechanism, the experimental and theoretical analyses reveal a critical role of *trans*-CHC to re-enter the catalytic cycle via a reverse depolymerization pathway, followed by a kinetically more challenging/entropically more favorable CHO formation pathway. Furthermore, we find that while larger  $\text{Ln}^{+3}$  ions favor selective CHO formation in a closed system, smaller  $\text{Ln}^{+3}$  ions/early transition metal ions favor selective *trans*-CHC formation due to the unfavorable decarboxylation step as the  $\text{Ln}^{\text{NTMS}}$  ionic radius contracts. These mechanistic insights highlight the critical role of depolymerization conditions and lanthanide ion identity characteristics in dictating the reaction pathways and outcomes of the depolymerization processes. This knowledge should guide and advance the design of future catalytic processes for selective transformations in plastics recycling.

## Experimental

**Materials and Methods.**  $\text{La}^{\text{NTMS}}$ ,  $\text{Sm}^{\text{NTMS}}$ ,  $\text{Lu}^{\text{NTMS}}$ , and  $\text{Sc}^{\text{NTMS}}$  were purchased from commercial sources and used after purification by recrystallization from pentane. Poly(cyclohexene carbonate) (PCHC) was obtained from Empower Materials (molecular weight range from 150,000 to 200,000, see **Figure S23** for its  $^1\text{H}$ NMR spectrum). All polymers were ground to fine powders and dried under a high vacuum at 60 °C for at least 24 h prior to use. Note that the removal of residual moisture from polymer samples is critical to ensure optimal performance in the depolymerization reactions.

**Physical and Analytical Methods.** NMR spectra were recorded on a Varian Bruker Advance III HD system equipped with a TXO Prodigy probe (500 MHz) spectrometer. Chemical shifts ( $\delta$ ) for  $^1\text{H}$  NMR are referenced to the internal solvent.

**General Procedure A: Depolymerization Reactions under static vacuum (see Figure S24 for example).** In an Argon-filled MBraun glovebox, a 50 mL oven-dried Schlenk tube was charged with a magnetic stir bar, PCHC powder, catalyst, and 2-3 mL of dry toluene. The vessel was sealed tightly, and the polymer and catalyst were thoroughly mixed and dissolved in toluene by stirring at room temperature for approximately 10 min. The Schlenk tube was then carefully evacuated to remove the toluene, sealed to maintain a static vacuum, and heated to the specified temperature with slow magnetic stirring (50-100 rpm) for the specified time. Heating was supplied by a customized aluminum heating block with a fitted hole or by an oil bath for the Schlenk tubes. During the reaction, the products sublime from the hot reaction zone and deposit as liquids on the cold wall of the reactor. After cooling to room temperature, the entire reaction mixture (including products on the cold region and any remaining solid mixture at the bottom of the flask) was dissolved in 3-4 mL of  $\text{d}^8$ -toluene with appropriate sonication. A sample of this solution was withdrawn for NMR analysis. Product distributions and conversions were determined by  $^1\text{H}$  NMR, based on the relative ratios between the integrals for *trans*-CHC (3.0 ppm), CHO (2.8 ppm), and PCHC (4.5-5.0 ppm).

**General Procedure B: Depolymerization Reactions under dynamic vacuum (see Figure S25 for example).** In an Argon-filled MBraun glovebox, a sublimator was charged with a magnetic stir bar, PCHC powder, catalyst, and 2-3 mL of dry toluene. The sublimator was sealed tightly, and the polymer and catalyst were thoroughly mixed and dissolved in toluene by stirring at room temperature for approximately 10 min. The sublimator was then carefully evacuated to remove toluene and heated to the specified temperature with slow magnetic stirring (50-100 rpm) for the specified time. Heating was supplied by an oil bath. The cold finger of the sublimator was cooled to -78 °C using a dry ice/acetone mixture. After cooling to room temperature, the entire reaction mixture (including products on the cold finger and any remaining solid mixture at the bottom of the sublimator) was dissolved in 3-4 mL of  $\text{d}^8$ -toluene with appropriate sonication. A sample of this solution was withdrawn for NMR analysis. Product distributions and



conversions were determined by  $^1\text{H}$  NMR, based on the relative ratios between the integrals for *trans*-CHC (3.0 ppm), CHO (2.8 ppm), and PCHC (4.5–5.0 ppm).

## Conflicts of interest

There are no conflicts to declare.

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**Data availability statement follows:**

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its ESI.

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