

# Cr(III)-Salophen Catalysts: Efficient Single-Component and Binary Systems for Sustainable CO<sub>2</sub>/Cyclohexene Oxide Copolymerization

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# 1. Catalytic assays for the optimization of the copolymerization reaction between CHO and CO<sub>2</sub>

**Table S1. Synthesis of PCHC catalyzed by complexes Cat1 and Cat6 and co-catalysts.<sup>a</sup>**

| Entry | Cat.<br>(0.5 mol%) | Co-cat<br>(0.5 mol%) | % Conv. <sup>b</sup> | % CHC <sup>b</sup> | % Copolymer<br>(% Carbonate linkage) <sup>b</sup> | TON <sup>c</sup> | TOF <sup>d</sup> (h <sup>-1</sup> ) |
|-------|--------------------|----------------------|----------------------|--------------------|---------------------------------------------------|------------------|-------------------------------------|
| 1     | Cat1               | DMAP                 | 83                   | 3                  | 97 (38)                                           | 160              | 6.65                                |
| 2     | Cat2               | DMAP                 | 80                   | 4                  | 96 (40)                                           | 166              | 6.90                                |
| 3     | Cat3               | DMAP                 | 78                   | 6                  | 94 (26)                                           | 156              | 6.48                                |
| 4     | Cat4               | DMAP                 | 86                   | 11                 | 89 (55)                                           | 172              | 7.15                                |
| 5     | Cat5               | DMAP                 | 83                   | 14                 | 86 (65)                                           | 166              | 6.90                                |
| 6     | Cat6               | DMAP                 | 92                   | 4                  | 96 (17)                                           | 183              | 7.65                                |
| 7     | Cat4               | PPNCI                | 85                   | 10                 | 90 (50)                                           | 170              | 7.06                                |
| 8     | Cat5               | PPNCI                | 83                   | 13                 | 87 (69)                                           | 166              | 6.90                                |
| 9     | Cat6               | PPNCI                | 82                   | 9                  | 91 (45)                                           | 164              | 6.81                                |
| 10    | Cat4               | TBAI                 | 34                   | 12                 | 88 (74)                                           | 68               | 2.83                                |
| 11    | Cat5               | TBAI                 | 85                   | 7                  | 93 (53)                                           | 170              | 7.06                                |
| 12    | Cat6               | TBAI                 | 83                   | 6                  | 94 (36)                                           | 166              | 6.90                                |
| 13    | Cat4               | TBAB                 | 83                   | 5                  | 95 (54)                                           | 166              | 6.90                                |
| 14    | Cat5               | TBAB                 | 81                   | 2                  | 98 (18)                                           | 162              | 6.73                                |
| 15    | Cat6               | TBAB                 | 88                   | 8                  | 92 (47)                                           | 176              | 7.31                                |
| 16    | Cat4               | TBAC                 | 82                   | 7                  | 93 (59)                                           | 164              | 6.81                                |
| 17    | Cat5               | TBAC                 | 83                   | 12                 | 88 (66)                                           | 166              | 6.90                                |
| 18    | Cat6               | TBAC                 | 89                   | 5                  | 95 (26)                                           | 178              | 7.40                                |

<sup>a</sup> Reactions were carried out at 100 °C and 8 bar CO<sub>2</sub> pressure for 24 h. <sup>b</sup> Conversion, % of CHC-*trans*, % of PCHC, and % of carbonate linkages determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>c</sup> TON = moles of product/moles of catalyst. <sup>d</sup> TOF = TON/time (h); calculated from total epoxide conversion.

**Table S2. Synthesis of PCHC catalyzed by complexes Cat4 and Cat5 using Toluene.<sup>a</sup>**

| Entry | Cat.<br>(0.5 mol%) | Co-cat.<br>(0.5 mol%) | % Conv. <sup>b</sup> | % CHC <i>trans</i> <sup>b</sup> | % Copolymer<br>(% Carbonate linkage) <sup>b</sup> | TON <sup>c</sup> | TOF <sup>d</sup><br>(h <sup>-1</sup> ) |
|-------|--------------------|-----------------------|----------------------|---------------------------------|---------------------------------------------------|------------------|----------------------------------------|
| 1     | Cat4               | -                     | 68                   | 27                              | 73 (33)                                           | 136              | 5.65                                   |
| 2     | Cat4               | DMAP                  | 71                   | 26                              | 74 (30)                                           | 142              | 5.90                                   |
| 3     | Cat4               | TBAC                  | 14                   | 29                              | 71 (17)                                           | 28               | 1.16                                   |
| 4     | Cat5               | -                     | 69                   | 28                              | 72 (45)                                           | 138              | 5.73                                   |
| 5     | Cat5               | DMAP                  | 75                   | 27                              | 73 (51)                                           | 150              | 6.23                                   |
| 6     | Cat5               | PPNCI                 | 38                   | 20                              | 80 (20)                                           | 76               | 3.16                                   |
| 7     | Cat5               | TBAC                  | 14                   | 29                              | 71 (17)                                           | 28               | 1.16                                   |

<sup>a</sup> Reactions carried out at 100 °C and 8 bar CO<sub>2</sub> pressure for 24 h. <sup>b</sup> Conversion, % of CHC-*trans*, % of PCHC, and % of carbonate linkages determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>c</sup> TON = moles of product/moles of catalyst. <sup>d</sup> TOF = TON/time (h); calculated from total epoxide conversion. <sup>e</sup> Toluene was used as a solvent.

**Table S3. Effect of co-catalyst loading on the synthesis of PCHC by Cat5 and Cat7 - Cat9 with DMAP.<sup>a</sup>**

| Entry | Cat. (mol%) | DMAP mol% | % Conv. <sup>b</sup> | % CHC <i>trans</i> <sup>b</sup> | % Copolymer (% Carbonate linkage) <sup>b</sup> | TON <sup>c</sup> | TOF <sup>d</sup> (h <sup>-1</sup> ) |
|-------|-------------|-----------|----------------------|---------------------------------|------------------------------------------------|------------------|-------------------------------------|
| 1     | Cat7 (0.5)  | 1         | 90                   | 5                               | 95 (48)                                        | 180              | 7.48                                |
| 2     | Cat8 (0.5)  | 1         | 80                   | 12                              | 88 (42)                                        | 160              | 6.65                                |
| 3     | Cat9 (0.5)  | 1         | 81                   | 8                               | 92 (32)                                        | 162              | 6.73                                |
| 4     | Cat5 (1)    | 0.5       | 86                   | 7                               | 93 (54)                                        | 86               | 3.57                                |
| 5     | Cat5 (1)    | 1         | 86                   | 8                               | 92 (63)                                        | 86               | 3.57                                |
| 6     | Cat5 (1)    | 2         | 87                   | 4                               | 96 (45)                                        | 87               | 3.62                                |

<sup>a</sup> Reactions carried out using **Cat5** and DMAP at 8 bar CO<sub>2</sub> pressure for 24 h at 100 °C. <sup>b</sup> Conversion, % of CHC-*trans*, % of PCHC and % of carbonate linkages determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>c</sup> TON = moles of product/moles of catalyst. <sup>d</sup> TOF = TON/time (h); calculated from total epoxide conversion.

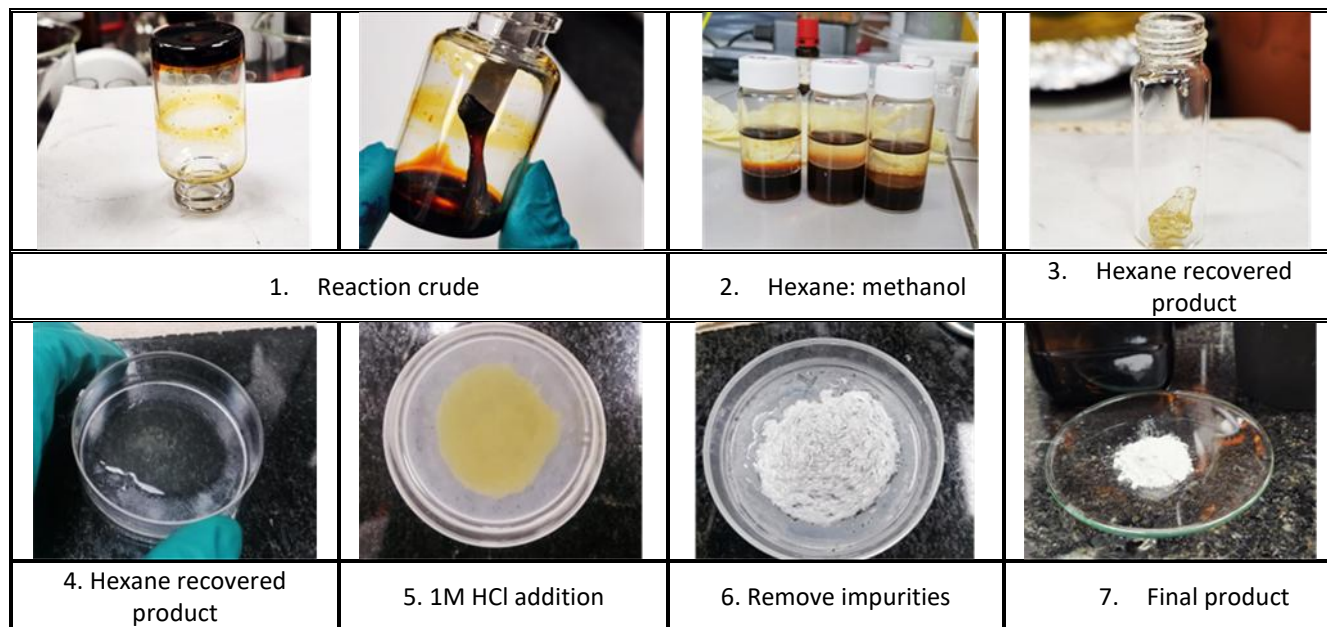
**Table S4. Effect of CO<sub>2</sub> pressure on the synthesis of PCHC by Cat5 and DMAP.<sup>a</sup>**

| Entry | Cat5 mol% | DMAP mol% | Pres. (bar) | % Conv. <sup>b</sup> | % CHC <i>trans</i> <sup>b</sup> | % Copolymer (% Carbonate linkage) <sup>b</sup> | TON <sup>c</sup> | TOF <sup>d</sup> (h <sup>-1</sup> ) |
|-------|-----------|-----------|-------------|----------------------|---------------------------------|------------------------------------------------|------------------|-------------------------------------|
| 1     | 0.5       | -         | 16          | 72                   | 3                               | 97 (56)                                        | 144              | 5.98                                |
| 2     | 1         | -         | 16          | 74                   | 3                               | 97 (58)                                        | 74               | 3.07                                |
| 4     | 0.5       | 1         | 16          | 69                   | 8                               | 92 (67)                                        | 138              | 5.73                                |
| 5     | 1         | -         | 50          | 44                   | 20                              | 80 (48)                                        | 44               | 1.83                                |

<sup>a</sup> Reactions carried out using **Cat5** and DMAP for 24 h at 100 °C. <sup>b</sup> Conversion, % of CHC-*trans*, % of PCHC and % of carbonate linkages determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>c</sup> TON = moles of product/moles of catalyst. <sup>d</sup> TOF = TON/time (h); calculated from total epoxide conversion.

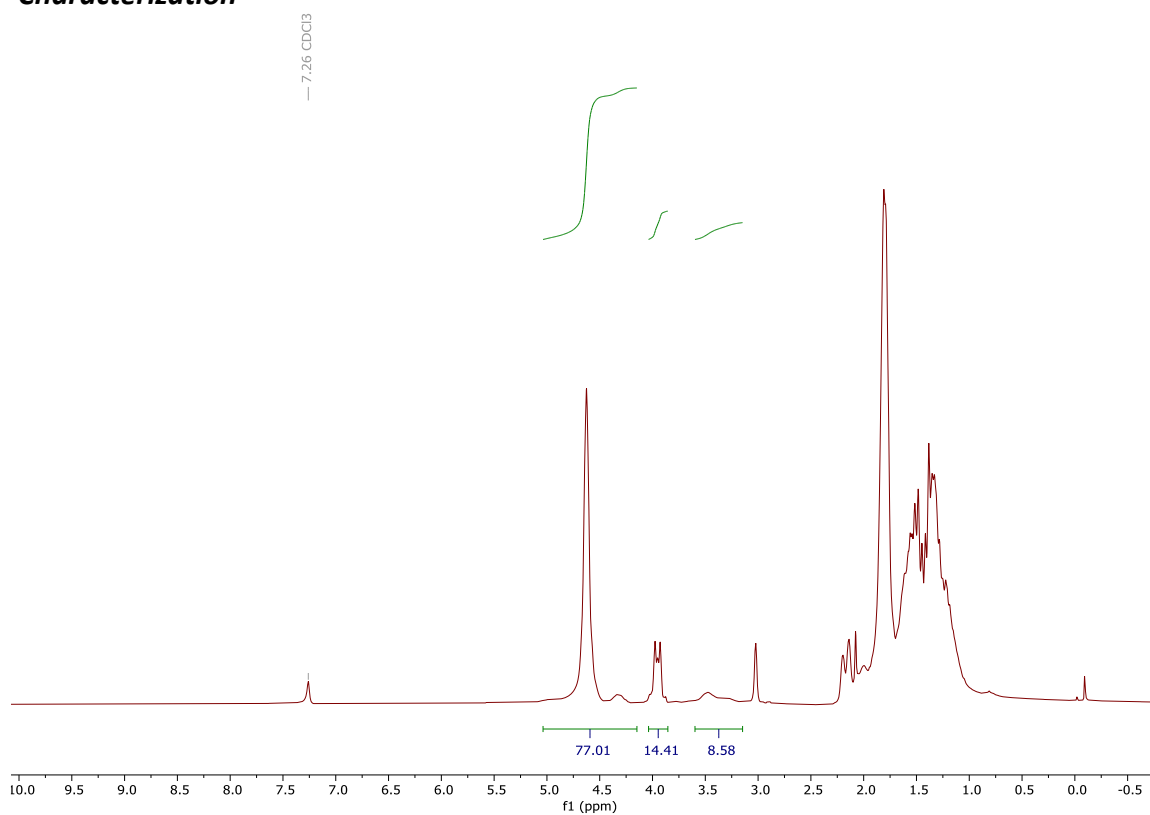
## 2. Characterization and purification of PCHC obtained with Cat5:DMAP

- **Purification**

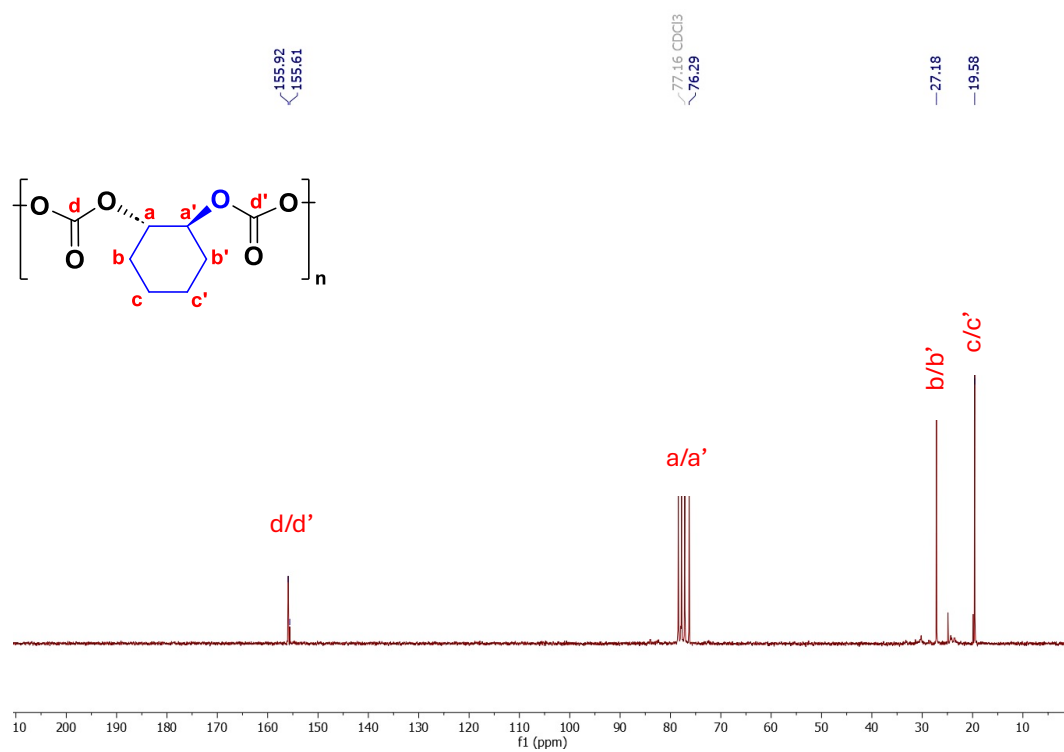


**Figure S1.** PCHC purification steps.

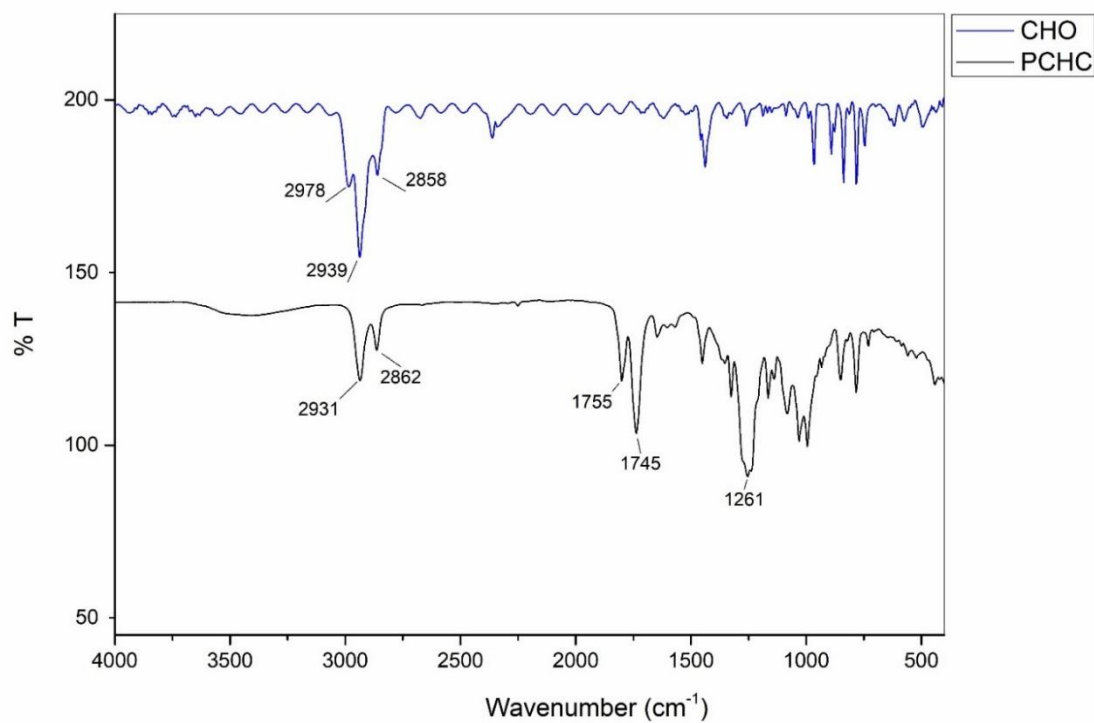
- **Characterization**



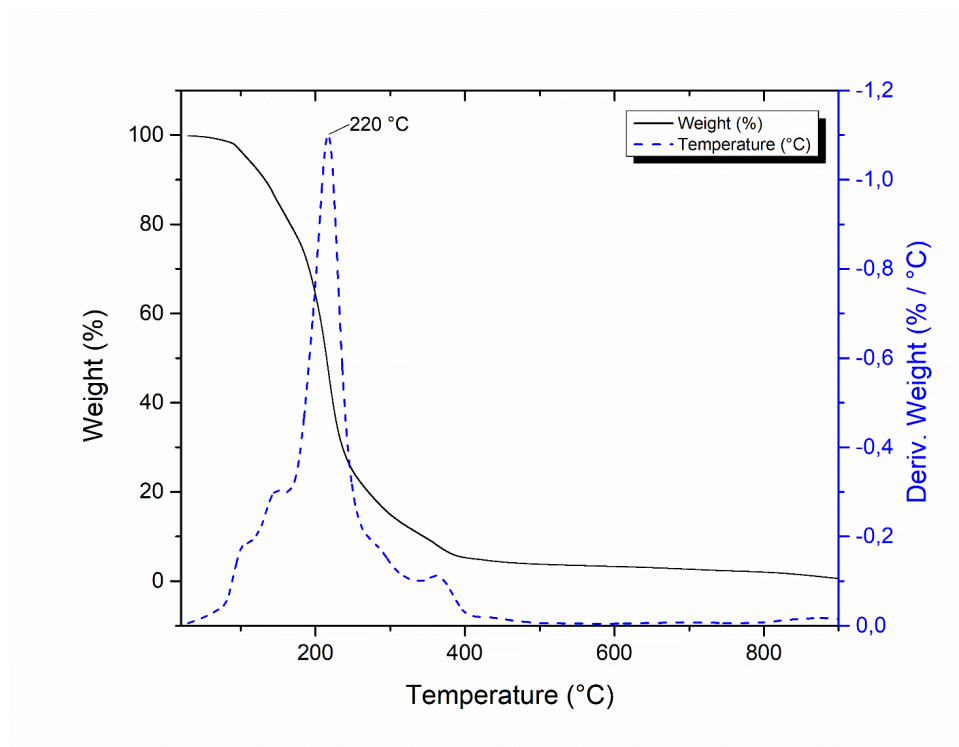
**Figure S2.** <sup>1</sup>H NMR spectrum of reaction crude obtained using Cat5:DMAP in CDCl<sub>3</sub>.



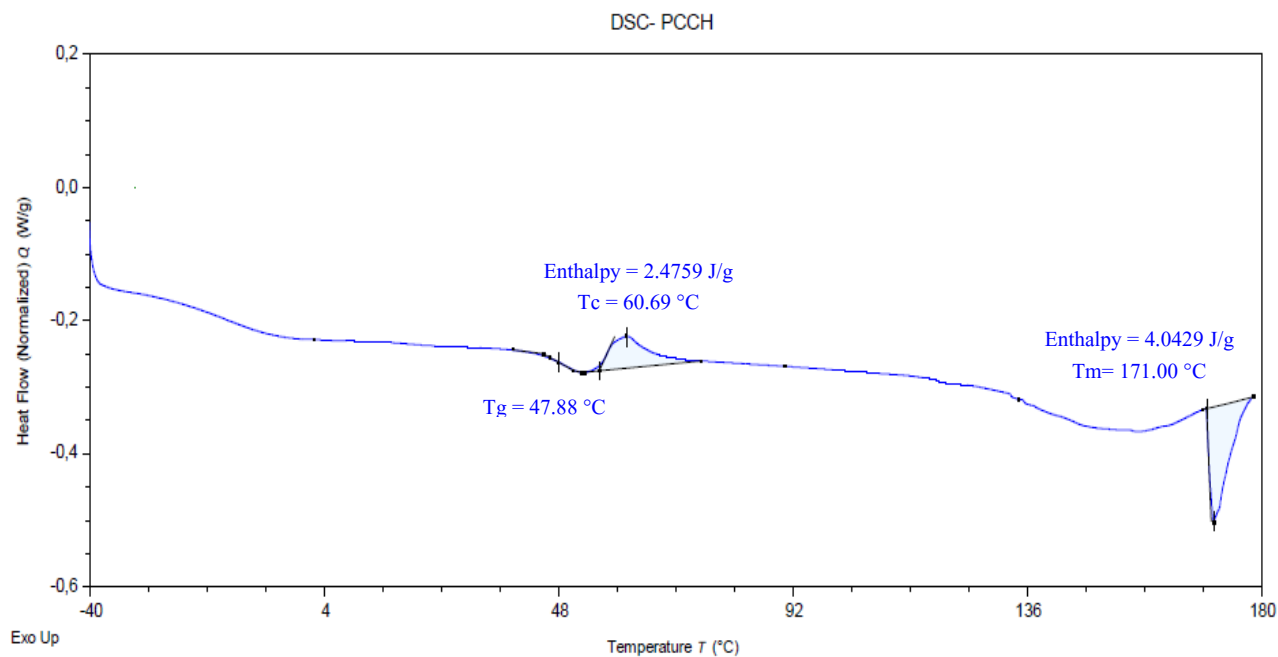
**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of PCHC obtained using **Cat5:DMAP** in  $\text{CDCl}_3$ .



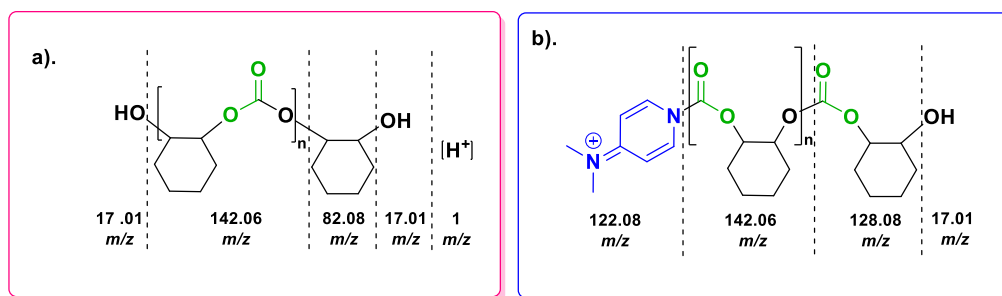
**Figure S4.** FT-IR spectrum of PCHC obtained using the binary catalyst **Cat5:DMAP**.



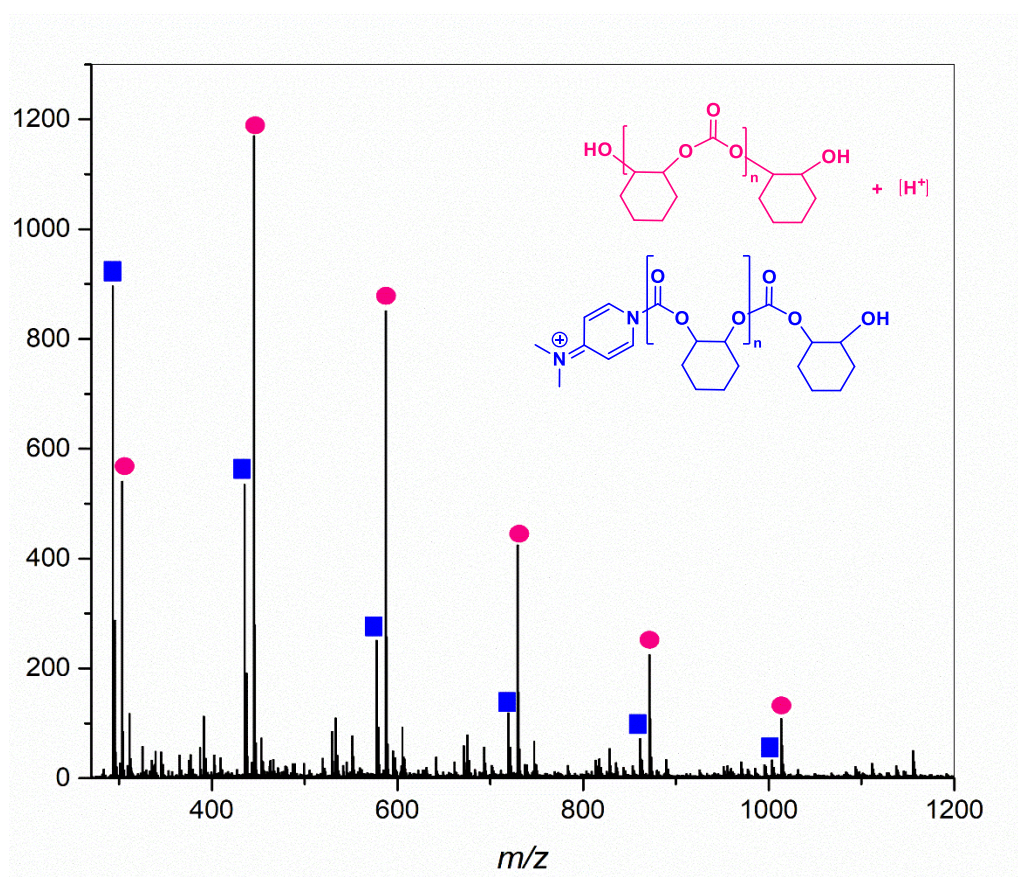
**Figure S5.** Thermogram of PCHC obtained using the binary catalyst **Cat5:DMAP**.



**Figure S6.** DSC curve of PCCH obtained using the binary catalyst **Cat5:DMAP**.



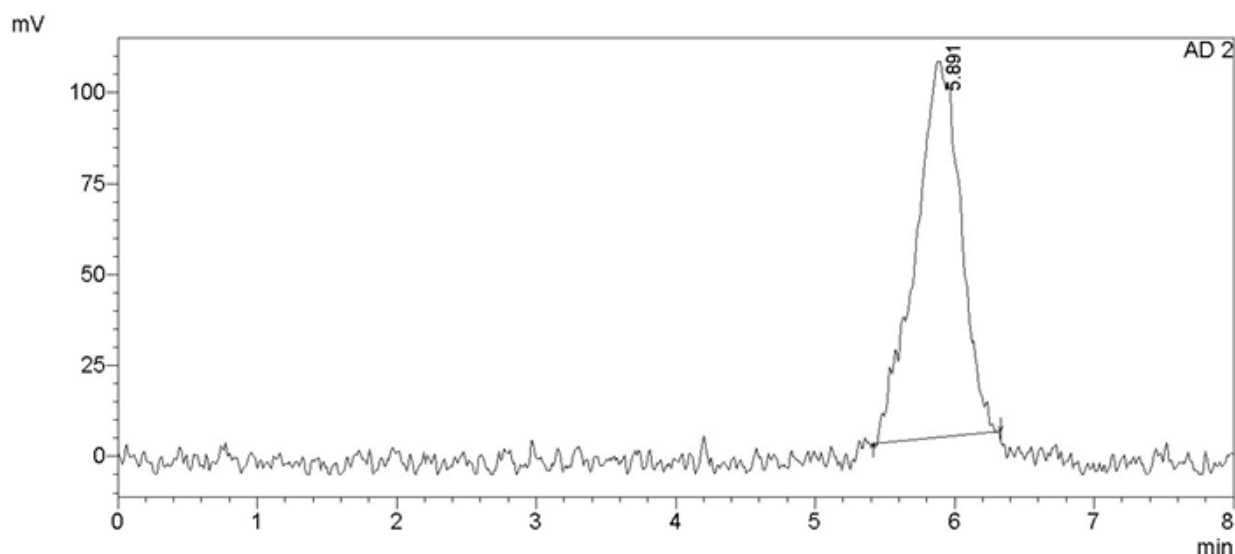
**Figure S7.** Possible structures of PCHC chains determined by HRMS analysis. Possible initiators: a) OH and b) DMAP.



**Figure S8.** HRMS spectrum in acetonitrile of PCHC obtained using the binary catalyst **Cat5:DMAP** by ESI-MS.

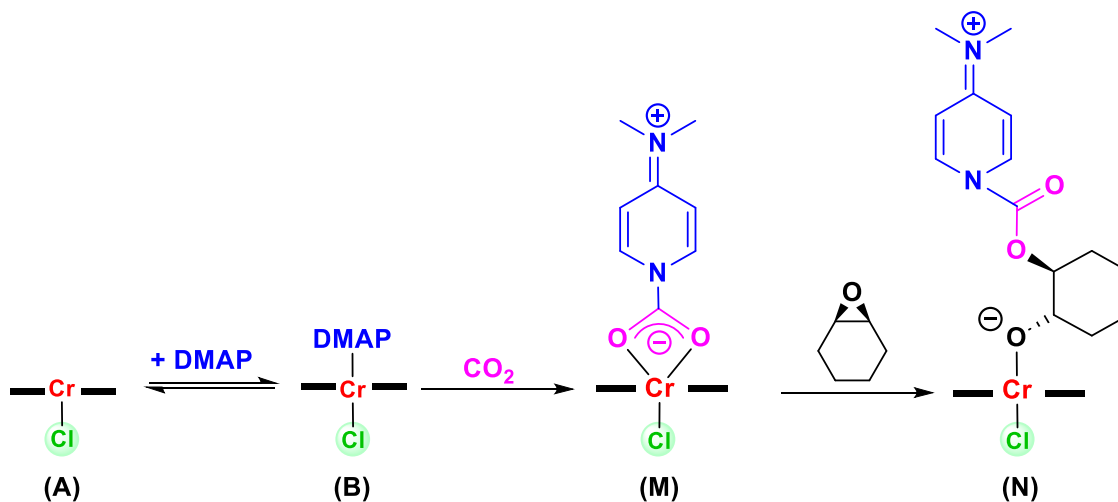
**Table S5. Results of GPC analysis of the polymer obtained with Cat5: DMAP**

| Sample            | Mn(exp) | (Mw/Mn) (PDI) |
|-------------------|---------|---------------|
| <b>Cat5: DMAP</b> | 18.797  | 1.06          |



**Figure S9.** Size exclusion chromatogram (GPC) of the polymer obtained with the **Cat5: DMAP** catalytic system, showing the molecular weight distribution.

### 3. Activation of CO<sub>2</sub> by DMAP



**Scheme S1.** Possible initiation route: activation of CO<sub>2</sub> by DMAP.