

# **Perfluoroaryl Zinc catalysts active in cyclohexene oxide homopolymerization and alternating copolymerization with carbon dioxide**

Yuri C. A. Sokolovicz<sup>1</sup>, Antonio Buonerba<sup>1</sup>, Carmine Capacchione<sup>1</sup>, Samuel Dagorne<sup>2</sup>, Alfonso Grassi<sup>1,\*</sup>

<sup>1</sup> Department of Chemistry and Biology, University of Salerno, Via Giovanni Paolo II, 84084 Fisciano (SA), Italy.

<sup>2</sup> Institute of Chemistry, University of Strasbourg, CNRS, Strasbourg, France.

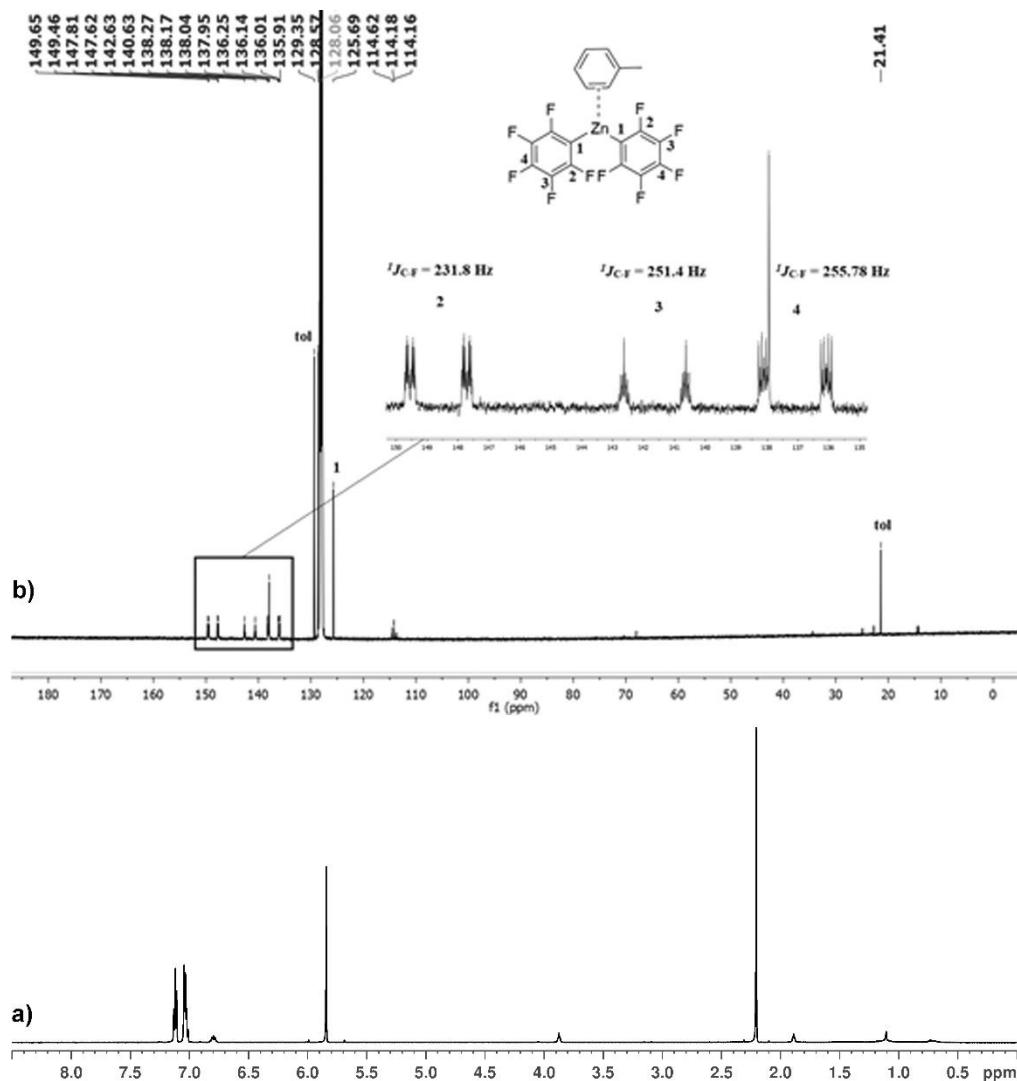
\* Correspondence should be addressed to: A.G. (agrassi@unisa.it; +39 089 969591).

**Table of Contents**

<b>1. Characterization of complexes.....</b>	S3
<b>Figure S1.</b> $^1\text{H}$ (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 25 °C) and $^{13}\text{C}$ (126 MHz, C <sub>6</sub> D <sub>6</sub> , 25°C) NMR spectra of complex <b>1</b> .....	S3
<b>Figure S2.</b> $^1\text{H}$ (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 25 °C) and $^{13}\text{C}$ (151 MHz, tetrachloroethane- $d_2$ , 25°C) NMR spectra of complex <b>2</b> .....	S4
<b>Figure S3.</b> $^{19}\text{F}$ NMR spectrum (282 MHz, C <sub>6</sub> D <sub>6</sub> , 25°C) of complex <b>1</b> .....	S5
<b>Figure S4.</b> $^{19}\text{F}$ NMR spectrum (565 MHz, TCE- $d_2$ , 25°C) of complex <b>2</b> .....	S5
<b>Figure S6.</b> ESI-MS spectrum of complex <b>2</b> .....	S6
<b>2. Characterization of the PCHOs.....</b>	S7
<b>Figure S8.</b> $^1\text{H}$ NMR spectrum (400 MHz, CDCl <sub>3</sub> , 25 °C) of crude reaction mixture containing PCHO from entry <b>2</b> of Table 1.....	S7
<b>Figure S9.</b> $^{13}\text{C}$ NMR spectrum (151 MHz, C <sub>6</sub> D <sub>6</sub> , 25 °C) of PCHO (entry <b>5</b> , Table 1). .....	S7
<b>Figure S10.</b> Magnification of the methine region of the $^{13}\text{C}$ NMR spectrum (151 MHz, C <sub>6</sub> D <sub>6</sub> , 25 °C) of PCHO (entry <b>5</b> , Table 1). .....	S8
<b>Figure S11.</b> Probability (P <sub>m</sub> and P <sub>mm</sub> ) using $^1\text{H}$ and $^{13}\text{C}$ NMR spectra (151 MHz, C <sub>6</sub> D <sub>6</sub> ) of methine region of isolated PCHO (entry <b>5</b> , Table 1). .....	S8
<b>Figure S12.</b> COSY NMR spectrum (400 MHz, CDCl <sub>3</sub> , 25 °C) of PCHO (entry <b>5</b> , Table 1). .....	S9
<b>Figure S13.</b> HSQC NMR spectrum (600 MHz, C <sub>6</sub> D <sub>6</sub> , 25 °C) of PCHO (entry <b>5</b> , Table 1). .....	S10
<b>Figure S14.</b> Magnification of the PCHO diagnostic region from the HSQC NMR spectrum from Figure S13. .....	S10
<b>3. Characterization of the PCHCs by copolymerization CHO-CO<sub>2</sub> promoted by 1/BnOH .....</b>	S11
<b>Figure S15.</b> $^1\text{H}$ NMR spectrum (400 MHz, CDCl <sub>3</sub> , 25 °C) of the crude products resulting from ROCOP of CO <sub>2</sub> with CHO (entry <b>3</b> of Table 2; 77 % ConvCHO Select <sub>PCHC</sub> = 85 %, Select <sub>trans-CHC</sub> = 9 %, Select <sub>PCHO</sub> = 6 %).....	S11

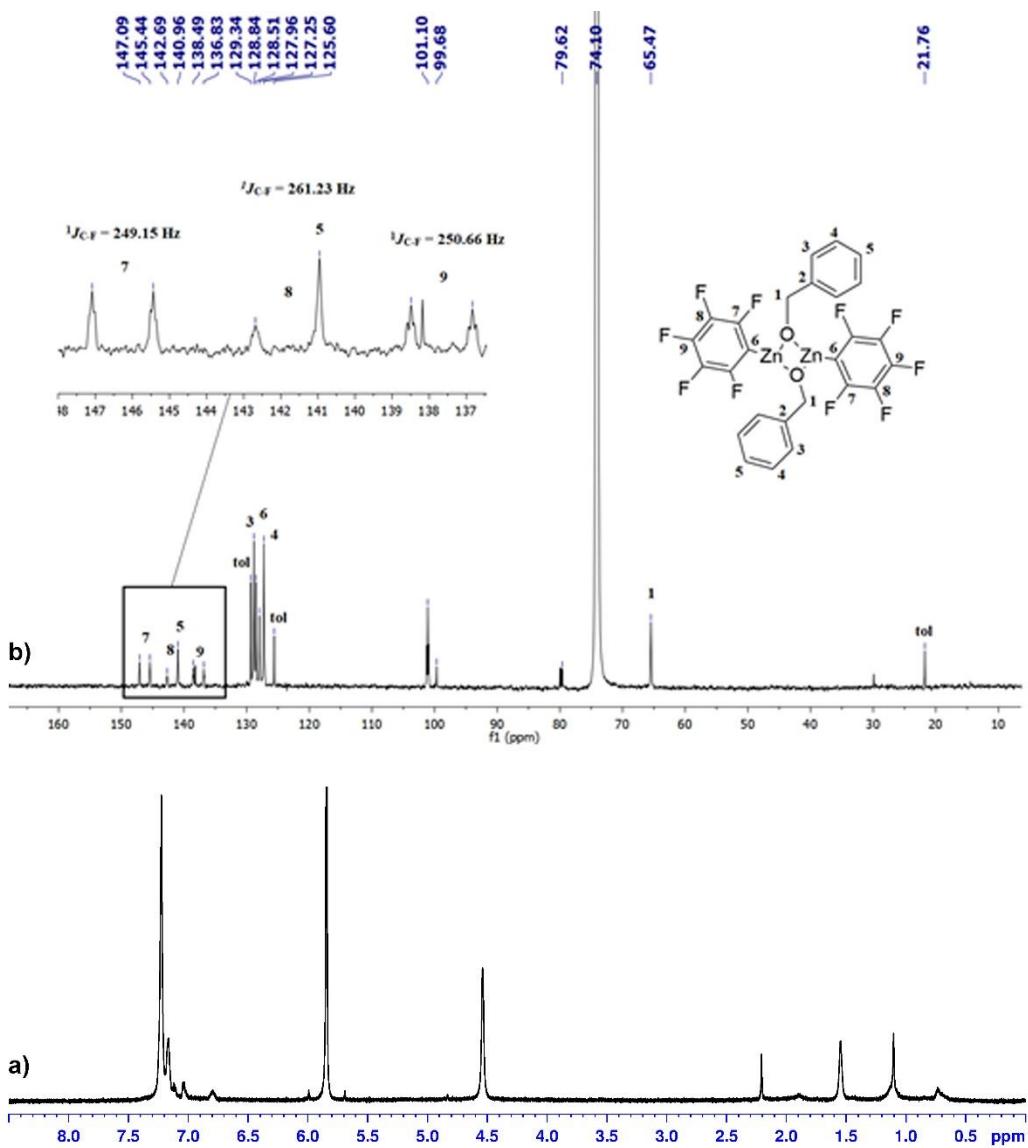
<b>Figure S16.</b> $^{13}\text{C}$ NMR spectrum (101 MHz, 25 °C, $\text{CDCl}_3$ , toluene- $d_8$ ) of the crude reaction mixture resulting from ROCOP of $\text{CO}_2$ with CHO (entry 3 of Table 2; 77 % $\text{Conv}_{\text{CHO}}$ $\text{Select}_{\text{PCHC}} = 85 \%$ , $\text{Select}_{\text{trans-CHC}} = 9 \%$ , $\text{Select}_{\text{PCHO}} = 6 \%$ ).....	S11
<b>Figure S17.</b> $^{13}\text{C}$ NMR spectrum (75 MHz, $\text{C}_6\text{D}_6$ , 25 °C) of PCHC (from entry 5, Table 2).....	S12
<b>Figure S18.</b> $^1\text{H}$ - $^1\text{H}$ COSY NMR (400 MHz, $\text{CDCl}_3$ , 25 °C) of PCHC (entry 5, Table 2).....	S13
<b>4. Characterization of the PCHCs by ROCOP of CHO with <math>\text{CO}_2</math> promoted by complex 2</b> .....	S14
<b>Figure S19.</b> $^1\text{H}$ NMR spectrum (400 MHz, $\text{CDCl}_3$ , 25 °C) of PCHC (entry 1, Table 3).....	S14
<b>Figure S20.</b> $^{13}\text{C}$ NMR spectrum (101 MHz, $\text{CDCl}_3$ , 25 °C) of PCHC (entry 1, Table 3).....	S15
<b>Figure S21.</b> Magnification of $^{13}\text{C}$ NMR spectrum from Figure S24. ....	S15
<b>5. GPC analysis of PCHCs</b> .....	S16
<b>Figure S22.</b> GPC analysis of PCHC (entry 6, Table 2). ....	S16
<b>Figure S23.</b> GPC analysis of PCHC (entry 7, Table 2). ....	S17
<b>Figure S24.</b> GPC analysis of PCHC (entry 9, Table 2). ....	S18
<b>Figure S25.</b> GPC analysis of PCHC (entry 1, Table 3). ....	S19
<b>Figure S26.</b> GPC analysis of PCHC (entry 2, Table 3). ....	S20
<b>Figure S27.</b> GPC analysis of PCHC (entry 3, Table 3). ....	S21
<b>Figure S28.</b> GPC analysis of PCHC (entry 4, Table 3). ....	S22
<b>Figure S29.</b> GPC analysis of PCHC (entry 5, Table 3). ....	S23

## 1. Characterization of complexes



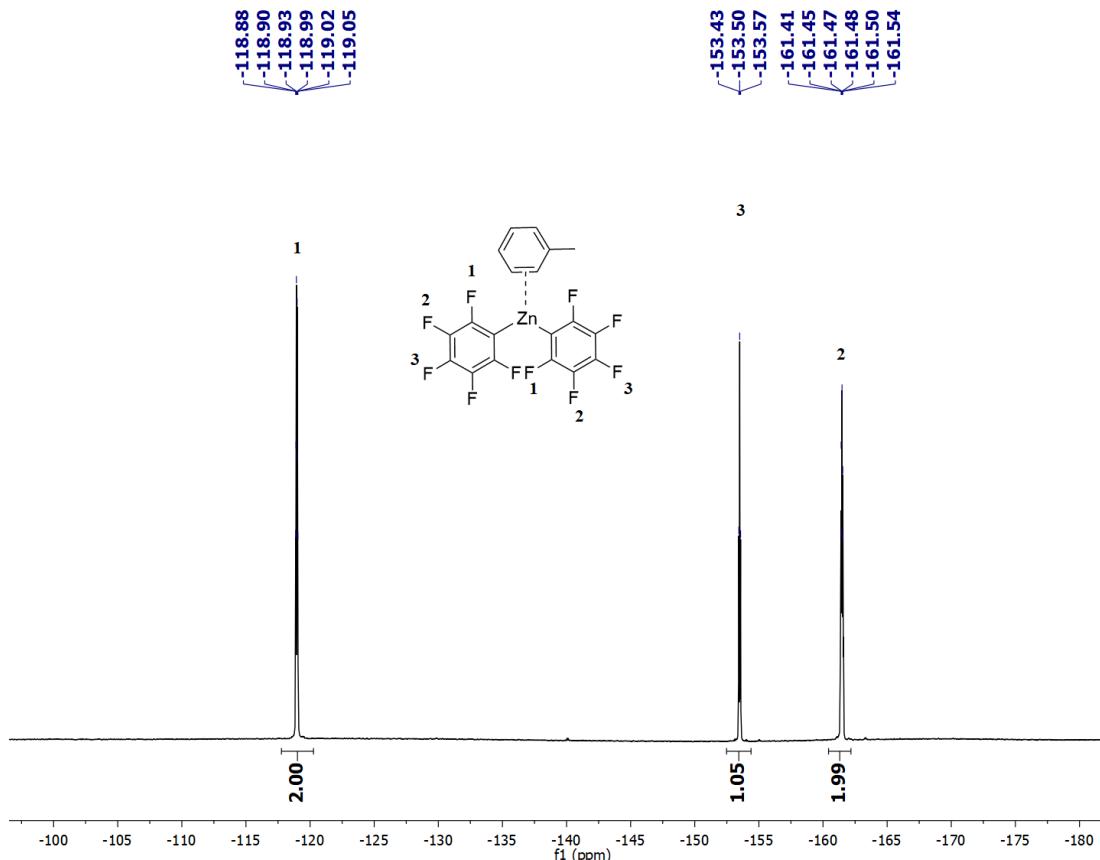
**Figure S1.**  $^1\text{H}$  (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 25 °C) and  $^{13}\text{C}$  (126 MHz,  $\text{C}_6\text{D}_6$ , 25°C) NMR spectra of complex **1**.

Supporting information

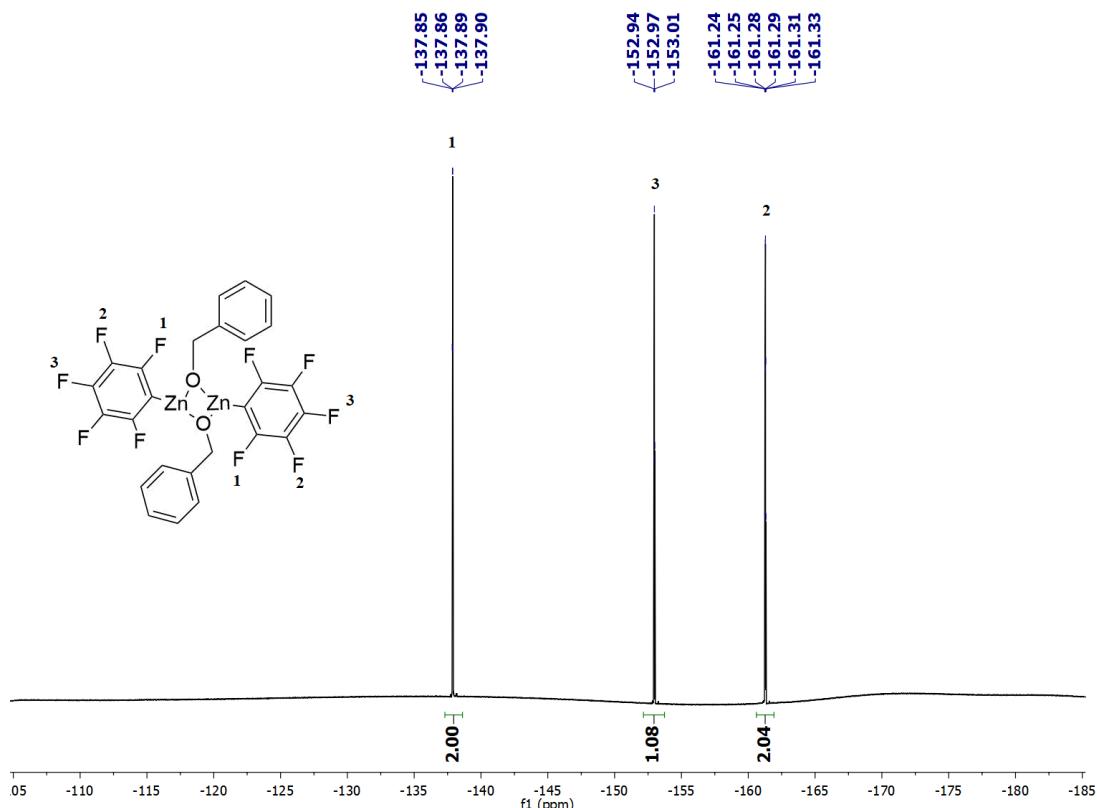


**Figure S2.**  $^1\text{H}$  (600 MHz,  $^{1,1,2,2}\text{-tetrachloroethane-}d_2$ , 25 °C) and  $^{13}\text{C}$  (151 MHz,  $^{1,1,2,2}\text{-tetrachloroethane-}d_2$ , 25 °C) NMR spectra of complex **2**.

Supporting information

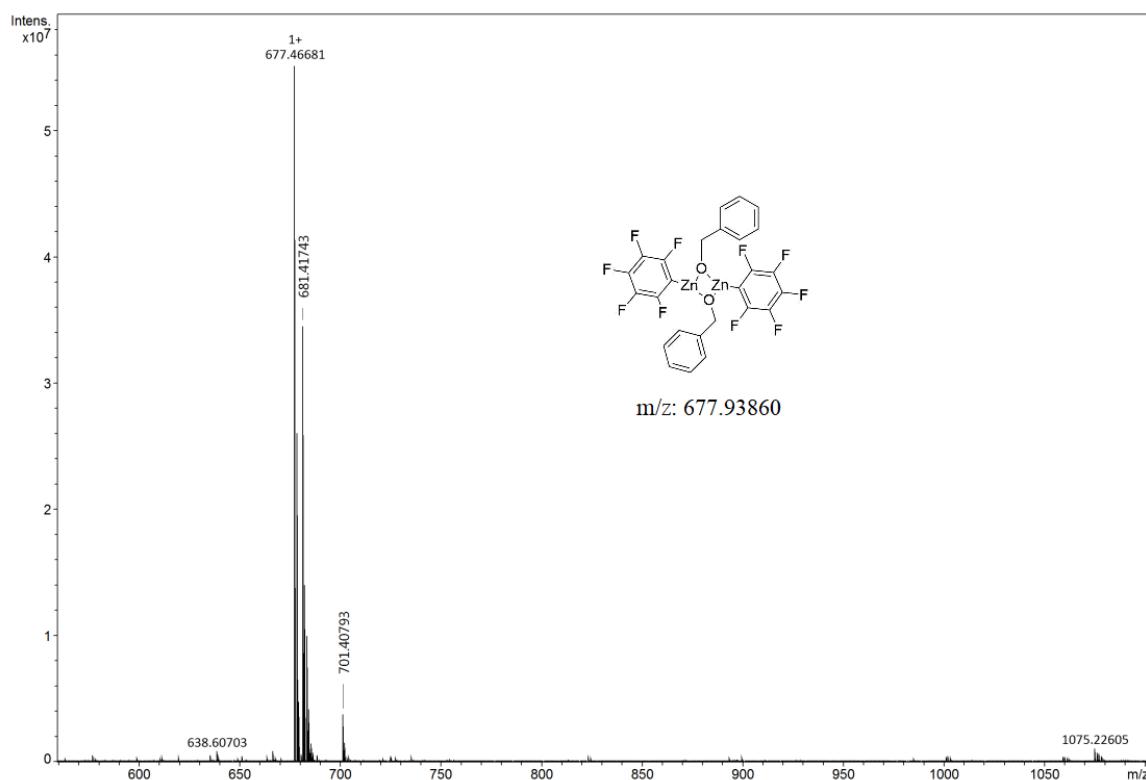


**Figure S3.**  $^{19}\text{F}$  NMR spectrum (282 MHz,  $\text{C}_6\text{D}_6$ , 25°C) of complex 1.



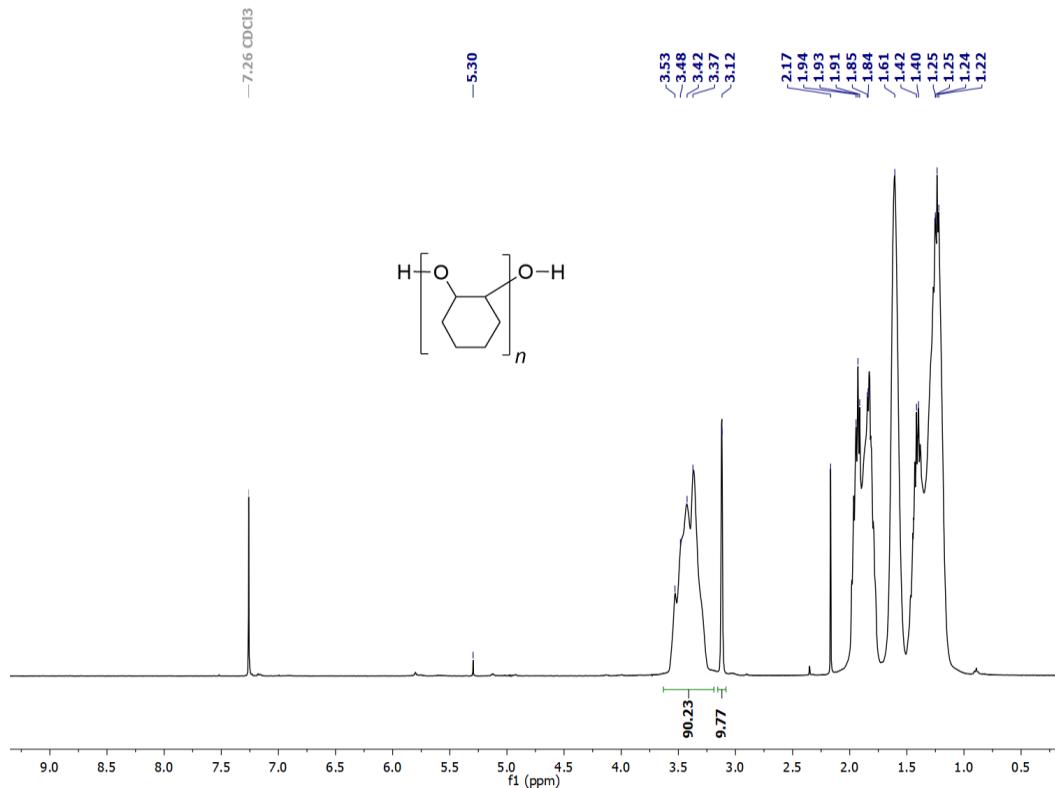
**Figure S4.**  $^{19}\text{F}$  NMR spectrum (565 MHz,  $\text{TCE}-d_2$ , 25°C) of complex 2

## Supporting information

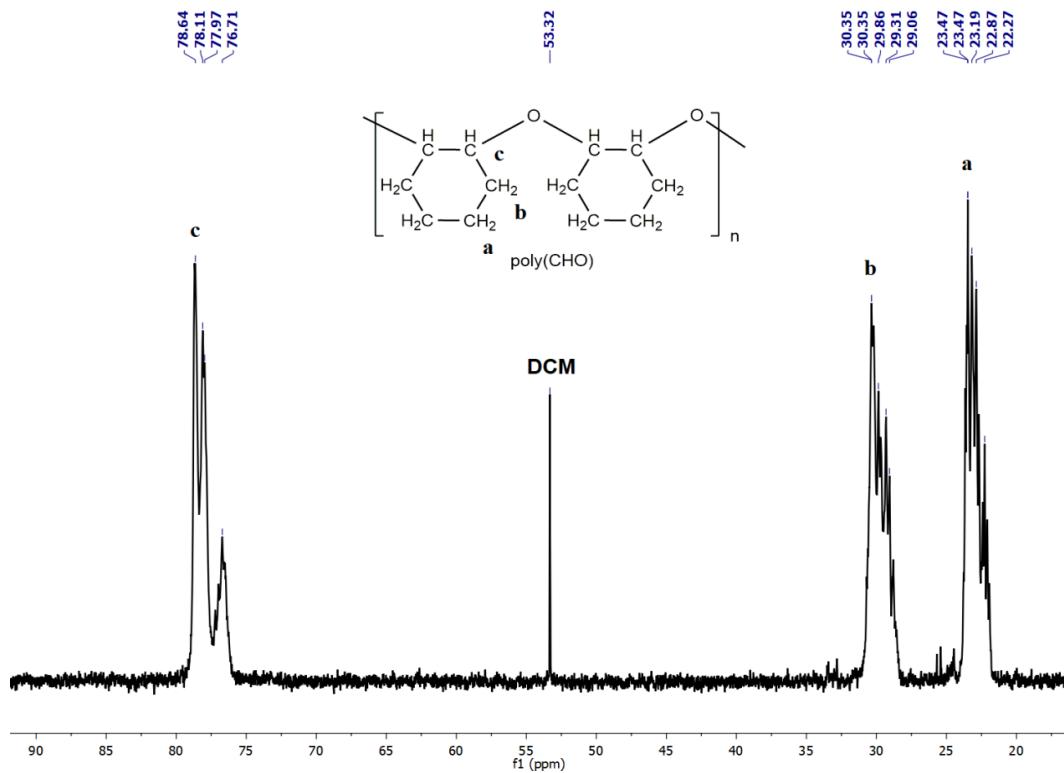


**Figure S6.** ESI-MS spectrum of complex **2**.

## 2. Characterization of the PCHOs

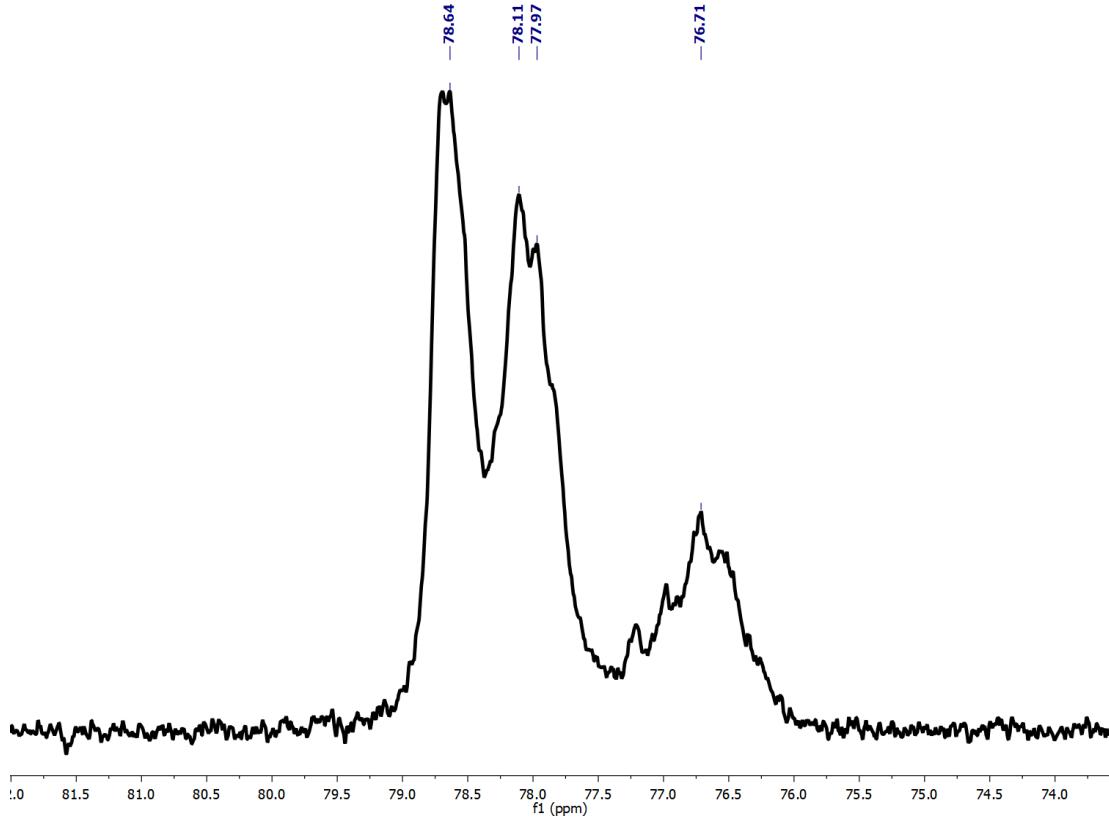


**Figure S8.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C) of crude reaction mixture containing PCHO from entry 2 of Table 1.

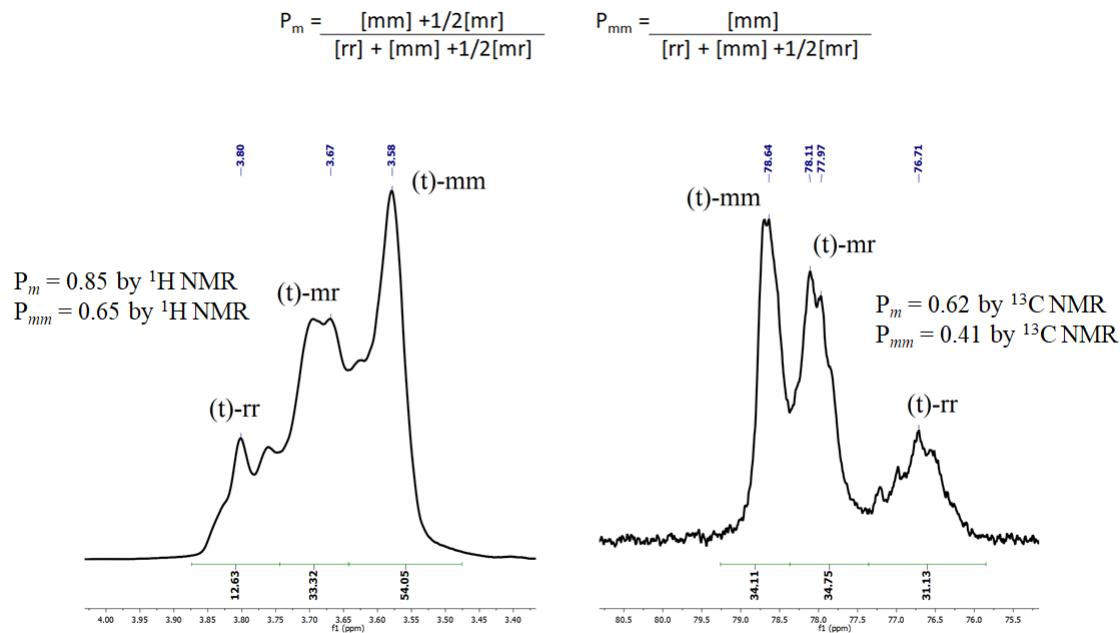


**Figure S9.** <sup>13</sup>C NMR spectrum (151 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) of PCHO (entry 5, Table 1).

## Supporting information

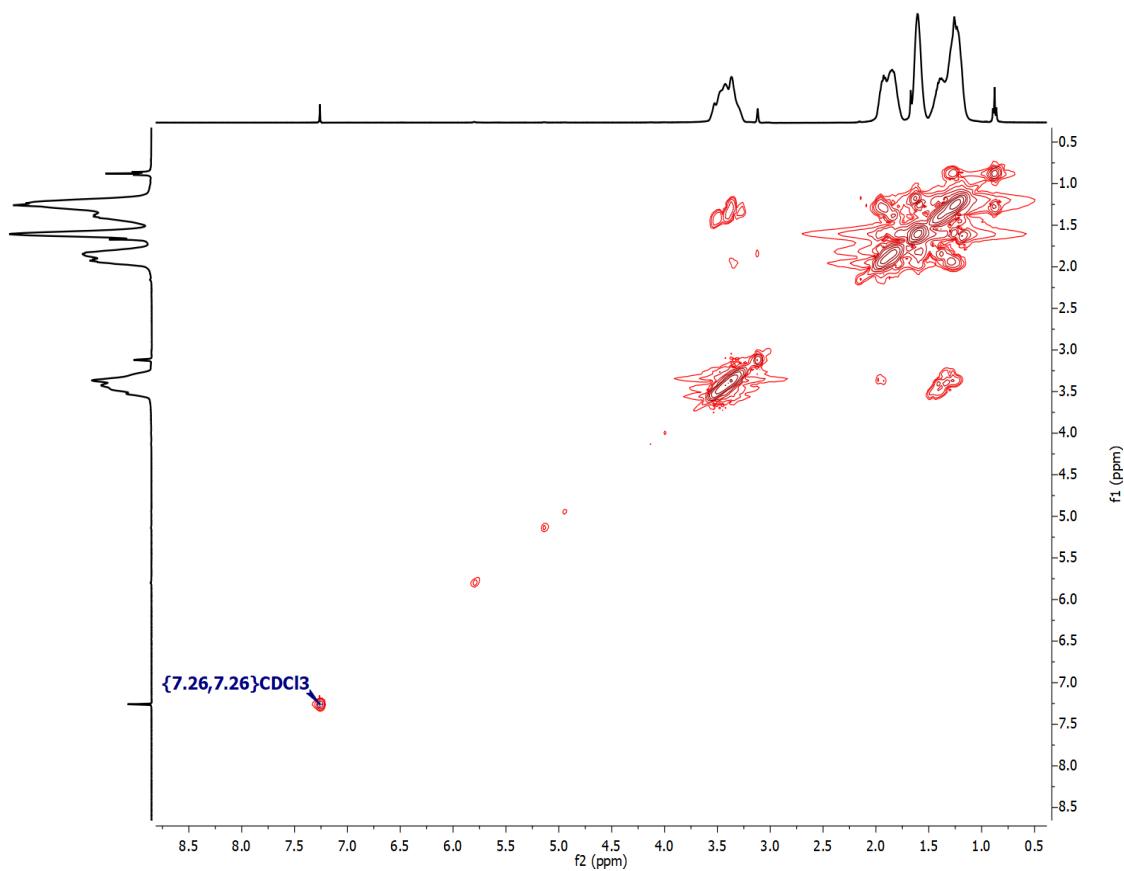


**Figure S10.** Magnification of the methine region of the  $^{13}\text{C}$  NMR spectrum (151 MHz,  $\text{C}_6\text{D}_6$ , 25 °C) of PCHO (entry 5, Table 1).



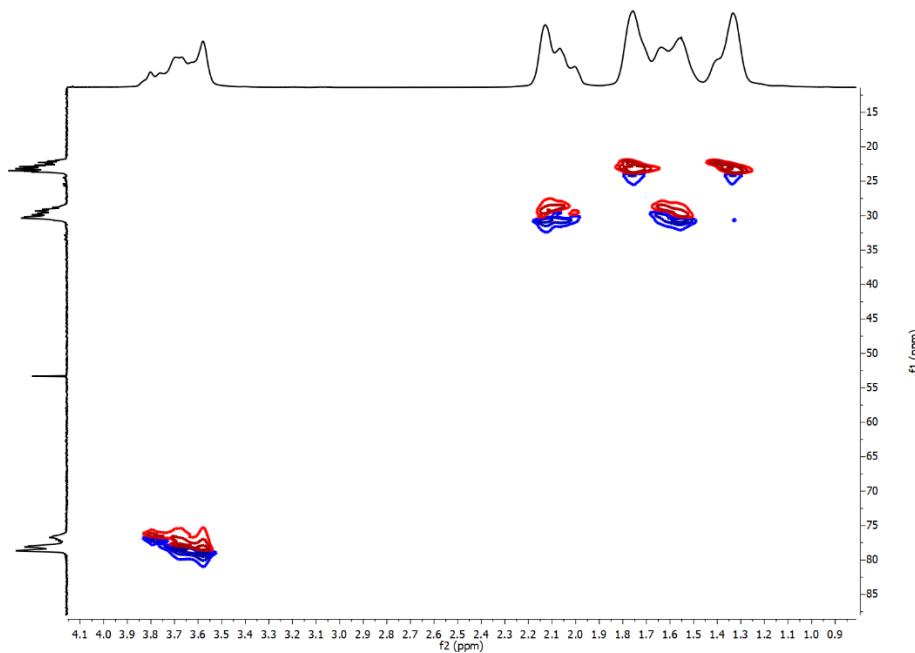
**Figure S11.** Probability ( $P_m$  and  $P_{mm}$ ) using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (151 MHz,  $\text{C}_6\text{D}_6$ ) of methine region of isolated PCHO (entry 5, Table 1).

Supporting information

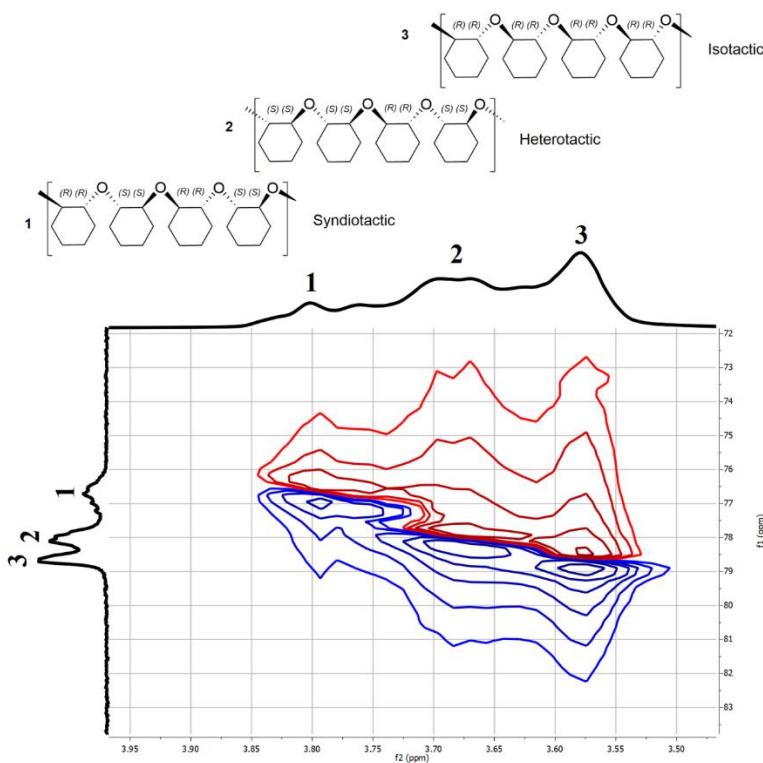


**Figure S12.** COSY NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 °C) of PCHO (entry 5, Table 1).

Supporting information

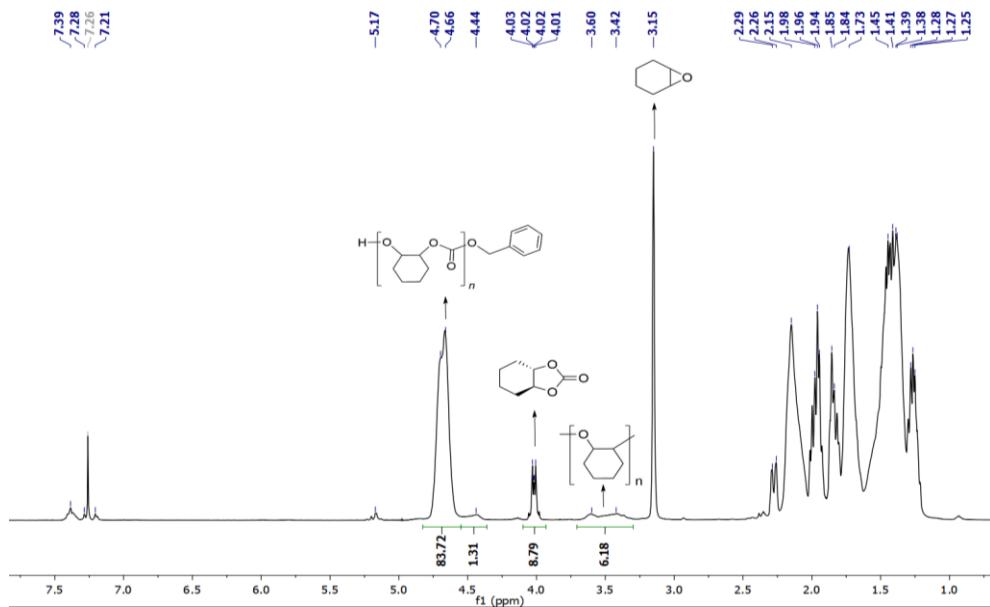


**Figure S13.** HSQC NMR spectrum (600 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) of PCHO (entry 5, Table 1).

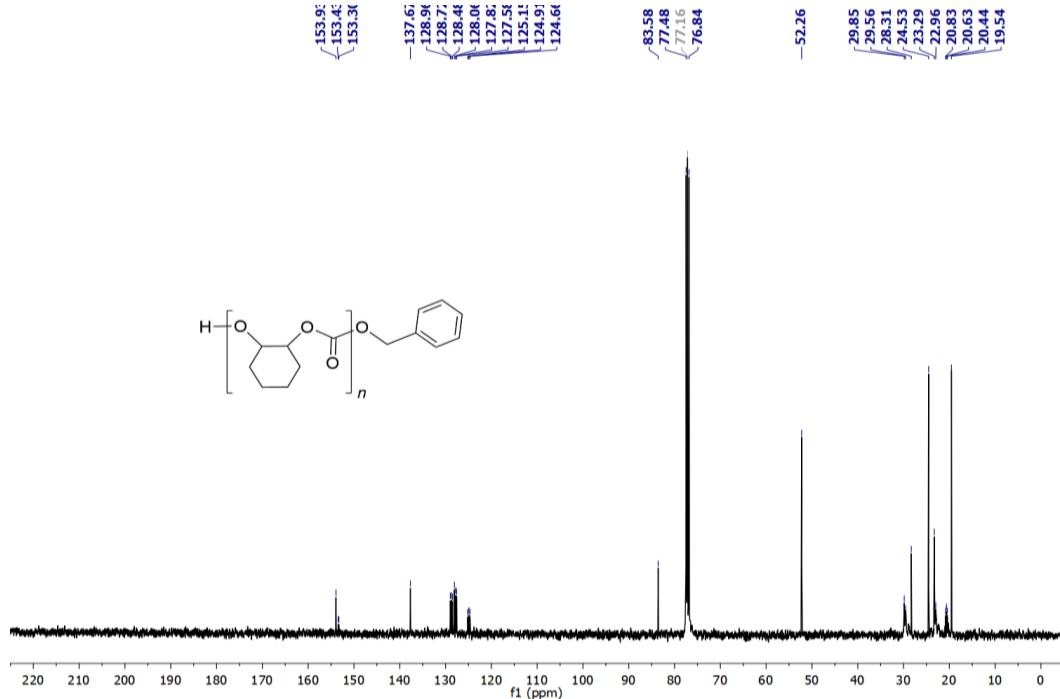


**Figure S14.** Magnification of the PCHO diagnostic region from the HSQC NMR spectrum from Figure S13.

### 3. Characterization of the PCHCs by copolymerization CHO-CO<sub>2</sub> promoted by 1/BnOH

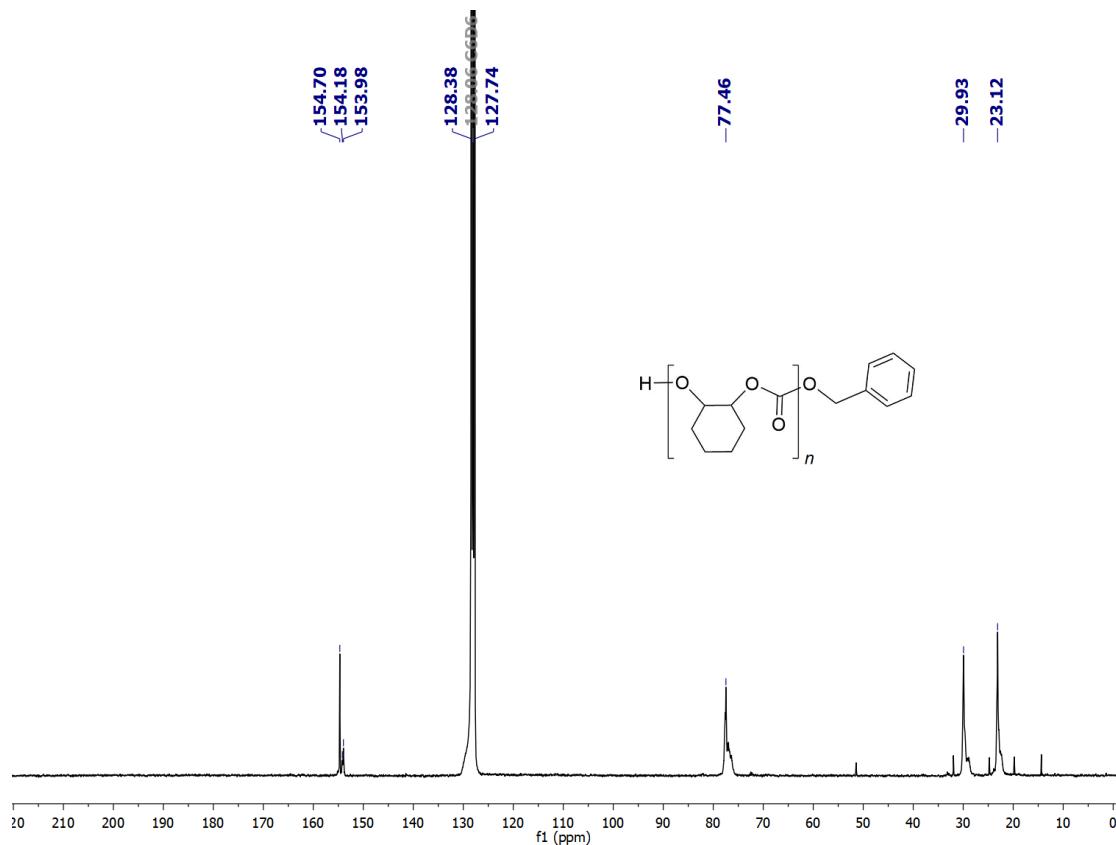


**Figure S15.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25 °C) of the crude products resulting from ROCOP of  $\text{CO}_2$  with CHO (entry 3 of Table 2; 77 %  $\text{Conv}_{\text{CHO}}$   $\text{Select}_{\text{PCHC}} = 85\%$ ,  $\text{Select}_{\text{trans-CHC}} = 9\%$ ,  $\text{Select}_{\text{PCHO}} = 6\%$ ).

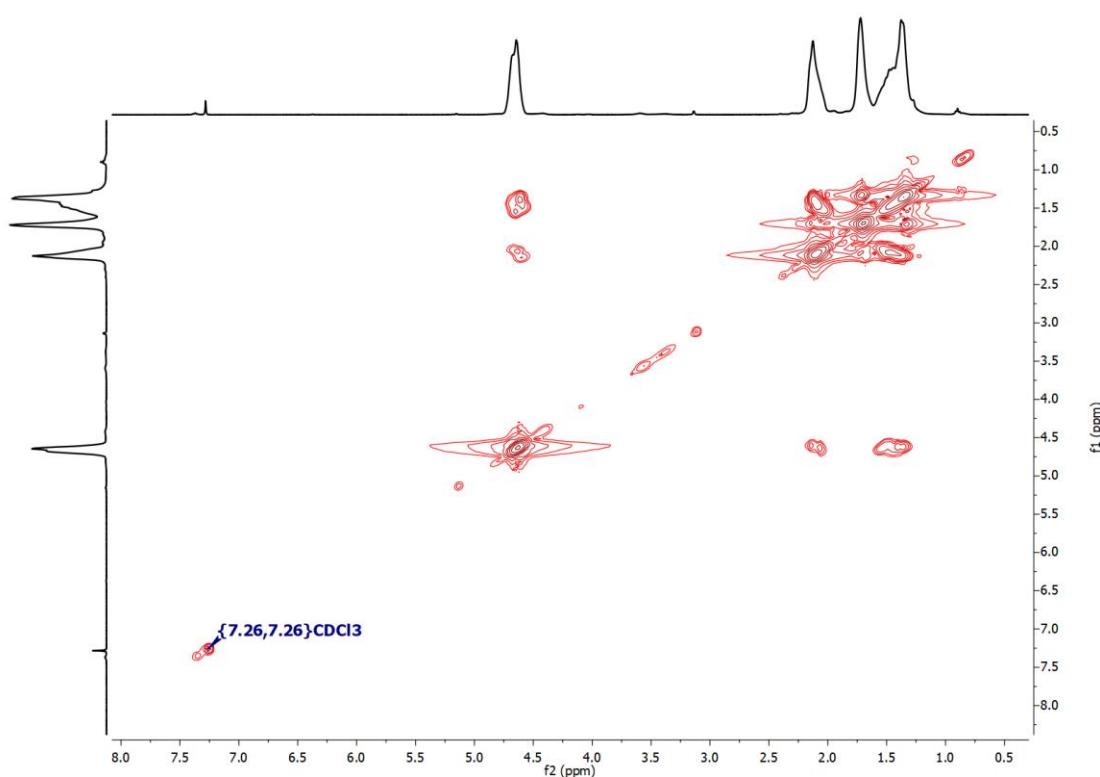


**Figure S16.**  $^{13}\text{C}$  NMR spectrum (101 MHz, 25 °C,  $\text{CDCl}_3$ , toluene- $d_8$ ) of the crude reaction mixture resulting from ROCOP of  $\text{CO}_2$  with CHO (entry 3 of Table 2; 77 %  $\text{Conv}_{\text{CHO}}$   $\text{Select}_{\text{PCHC}} = 85\%$ ,  $\text{Select}_{\text{trans-CHC}} = 9\%$ ,  $\text{Select}_{\text{PCHO}} = 6\%$ ).

Supporting information

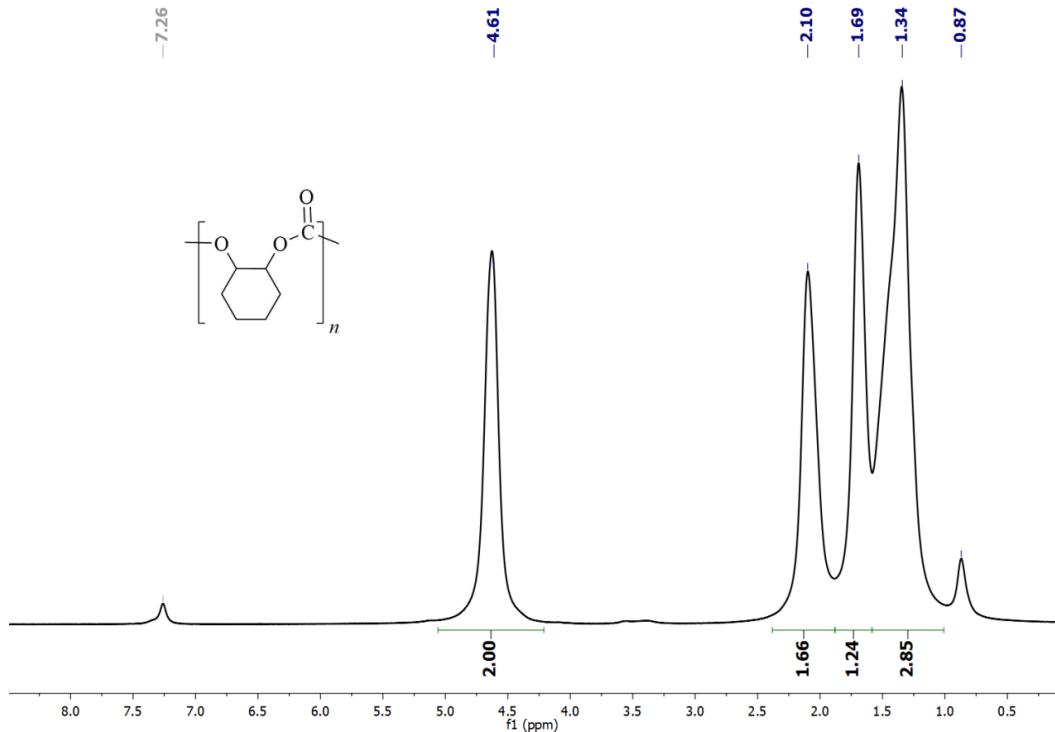


**Figure S17.** <sup>13</sup>C NMR spectrum (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) of PCHC (from entry 5, Table 2).



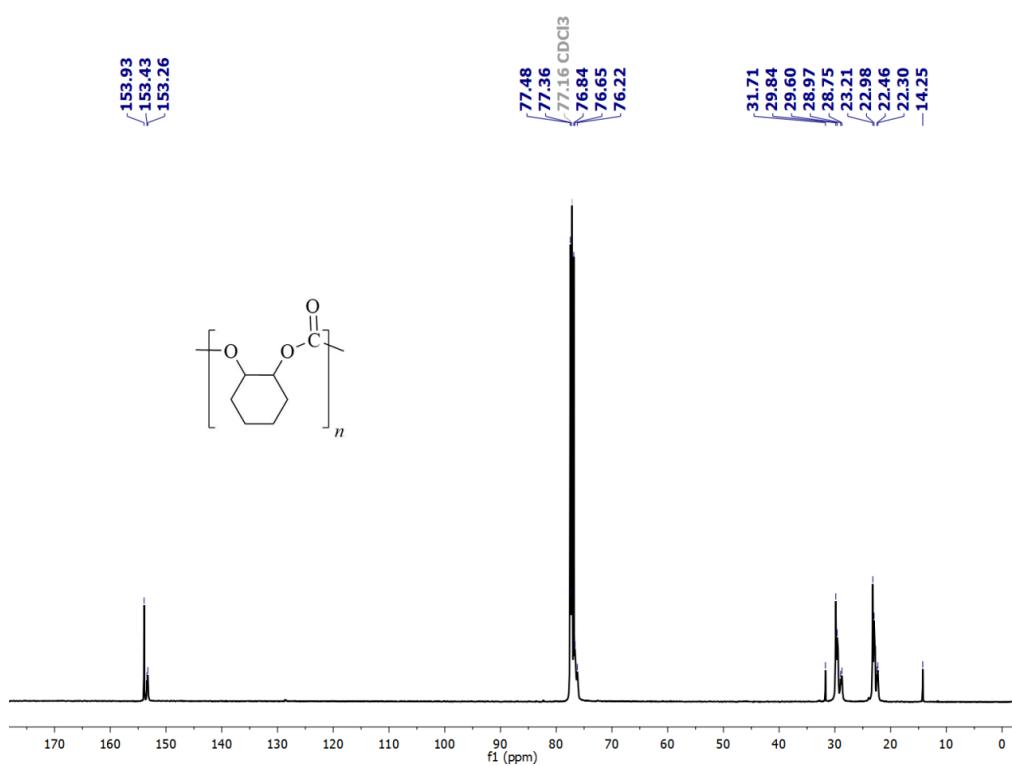
**Figure S18.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) of PCHC (entry 5, Table 2).

#### 4. Characterization of the PCHCs by ROCOP of CHO with CO<sub>2</sub> promoted by complex 2

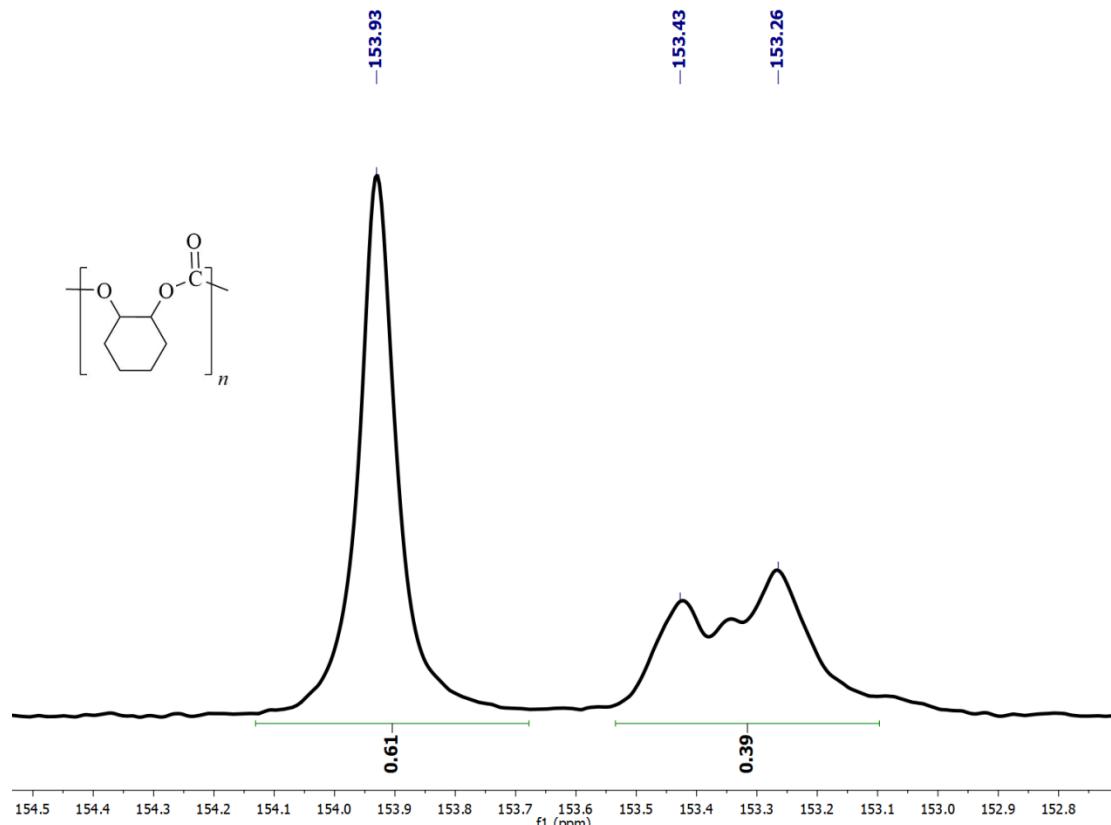


**Figure S19.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25 °C) of PCHC (entry 1, Table 3).

Supporting information

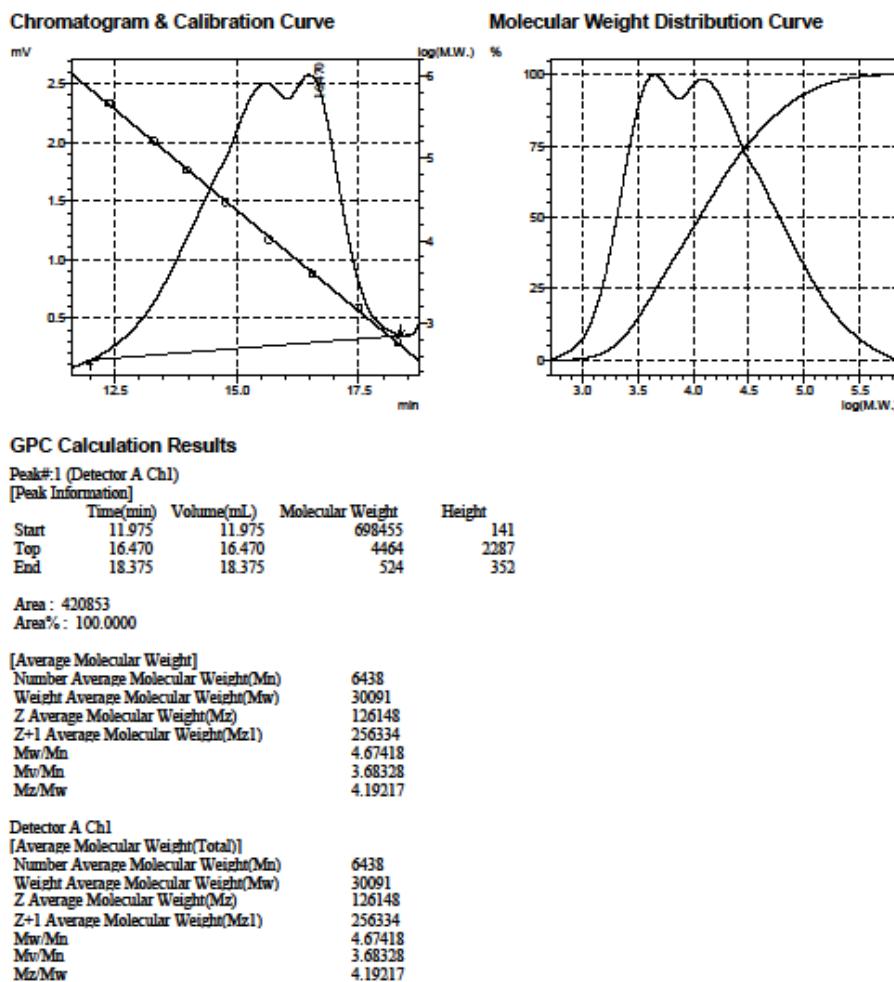


**Figure S20.**  $^{13}\text{C}$  NMR spectrum (101 MHz, CDCl<sub>3</sub>, 25 °C) of PCHC (entry 1, Table 3).



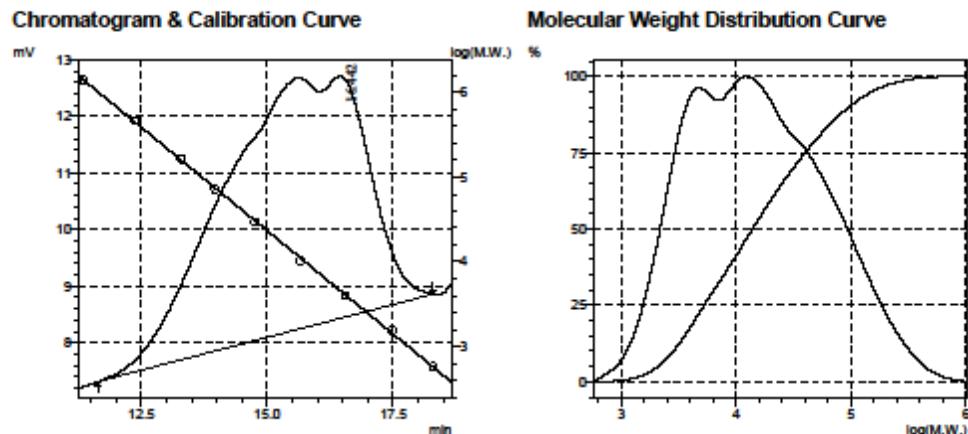
**Figure S21.** Magnification of  $^{13}\text{C}$  NMR spectrum from Figure S24.

## 5. GPC analysis of PCHCs



**Figure S22.** GPC analysis of PCHC (entry 6, Table 2).

## Supporting information



### GPC Calculation Results

#### Peak#1 (Detector A Chl)

##### [Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	11.633	11.633	1025538	7306
Top	16.442	16.442	4604	4281
End	18.292	18.292	576	8852

Area : 881965

Area% : 100.0000

##### [Average Molecular Weight]

Number Average Molecular Weight(Mn)	7222
Weight Average Molecular Weight(Mw)	37417
Z Average Molecular Weight(Mz)	149719
Z+1 Average Molecular Weight(Mz1)	306270
Mw/Mn	5.18077
Mv/Mn	4.08668
Mz/Mw	4.00132

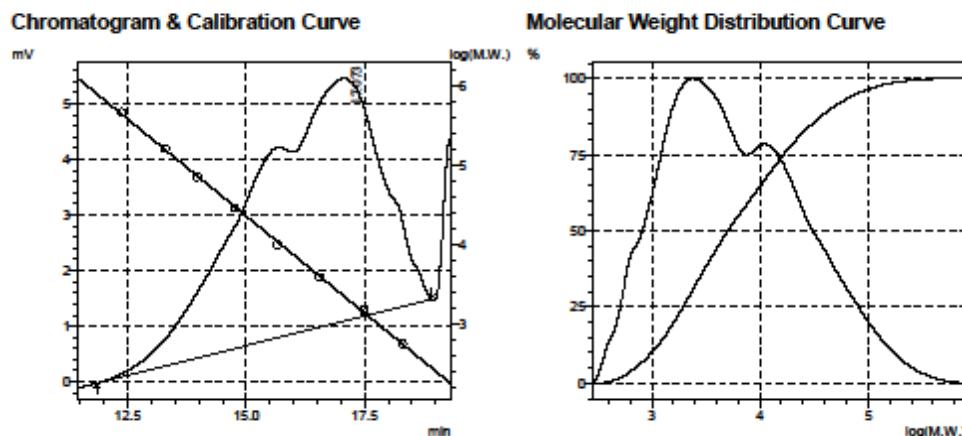
##### Detector A Chl

##### [Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	7222
Weight Average Molecular Weight(Mw)	37417
Z Average Molecular Weight(Mz)	149719
Z+1 Average Molecular Weight(Mz1)	306270
Mw/Mn	5.18077
Mv/Mn	4.08668
Mz/Mw	4.00132

**Figure S23.** GPC analysis of PCHC (entry 7, Table 2).

## Supporting information



### GPC Calculation Results

Peak#1 (Detector A Chl)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	11.850	11.850	803837	-26
Top	17.073	17.073	2266	4364
End	18.917	18.917	285	1480

Area : 854876

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	2623
Weight Average Molecular Weight(Mw)	18262
Z Average Molecular Weight(Mz)	104816
Z+1 Average Molecular Weight(Mz1)	241464
Mw/Mn	6.96269
Mv/Mn	5.15237
Mz/Mw	5.73972

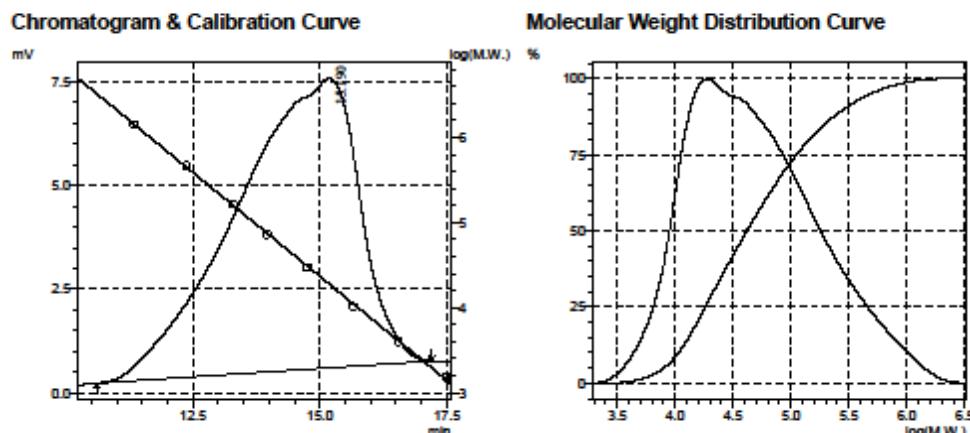
Detector A Chl

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	2623
Weight Average Molecular Weight(Mw)	18262
Z Average Molecular Weight(Mz)	104816
Z+1 Average Molecular Weight(Mz1)	241464
Mw/Mn	6.96269
Mv/Mn	5.15237
Mz/Mw	5.73972

**Figure S24.** GPC analysis of PCHC (entry 9, Table 2).

## Supporting information



### GPC Calculation Results

Peak#1 (Detector A Chl)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	10.608	10.608	3246322	233
Top	15.190	15.190	18807	6963
End	17.208	17.208	1946	771

Area : 1179650

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	25381
Weight Average Molecular Weight(Mw)	115179
Z Average Molecular Weight(Mz)	491535
Z+1 Average Molecular Weight(Mz1)	990055
Mw/Mn	4.53792
Mv/Mn	3.56312
Mz/Mw	4.26756

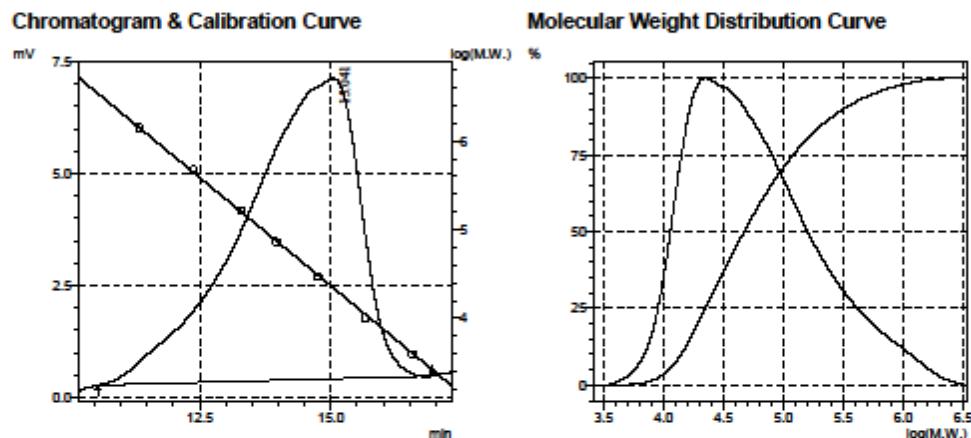
Detector A Chl

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	25381
Weight Average Molecular Weight(Mw)	115179
Z Average Molecular Weight(Mz)	491535
Z+1 Average Molecular Weight(Mz1)	990055
Mw/Mn	4.53792
Mv/Mn	3.56312
Mz/Mw	4.26756

**Figure S25.** GPC analysis of PCHC (entry 1, Table 3).

## Supporting information



### GPC Calculation Results

Peak#1 (Detector A Chl)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	10.558	10.558	3434023	276
Top	15.041	15.041	22257	6710
End	16.942	16.942	2626	482

Area : 1027415

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	32511
Weight Average Molecular Weight(Mw)	133537
Z Average Molecular Weight(Mz)	609158
Z+1 Average Molecular Weight(Mz1)	1232483
Mw/Mn	4.10740
Mv/Mn	3.20781
Mz/Mw	4.56172

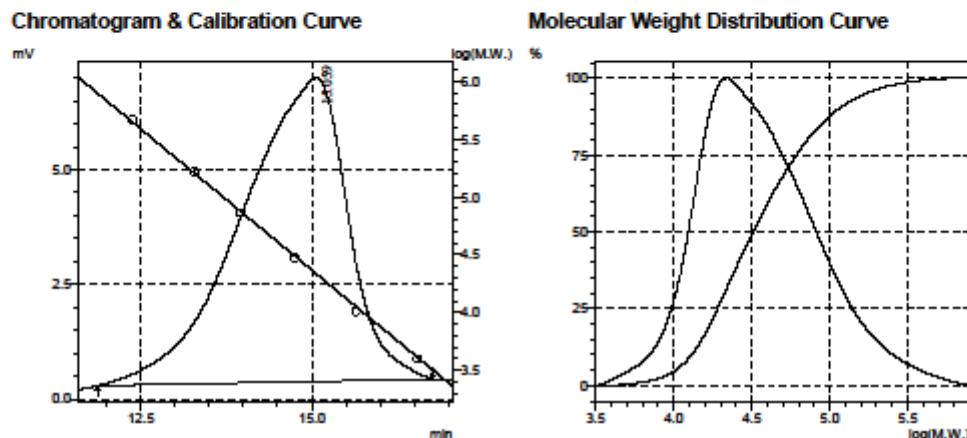
Detector A Chl

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	32511
Weight Average Molecular Weight(Mw)	133537
Z Average Molecular Weight(Mz)	609158
Z+1 Average Molecular Weight(Mz1)	1232483
Mw/Mn	4.10740
Mv/Mn	3.20781
Mz/Mw	4.56172

**Figure S26.** GPC analysis of PCHC (entry 2, Table 3).

## Supporting information



### GPC Calculation Results

#### Peak#1 (Detector A Chl)

##### [Peak Information]

	Time(min)	Volume(mL.)	Molecular Weight	Height
Start	11.867	11.867	788916	291
Top	15.059	15.059	21801	6613
End	16.783	16.783	3137	433

Area : 717373

Area% : 100.0000

##### [Average Molecular Weight]

Number Average Molecular Weight(Mn)	25697
Weight Average Molecular Weight(Mw)	53980
Z Average Molecular Weight(Mz)	133579
Z+1 Average Molecular Weight(Mz1)	268172
Mw/Mn	2.10067
Mv/Mn	1.85824
Mz/Mw	2.47458

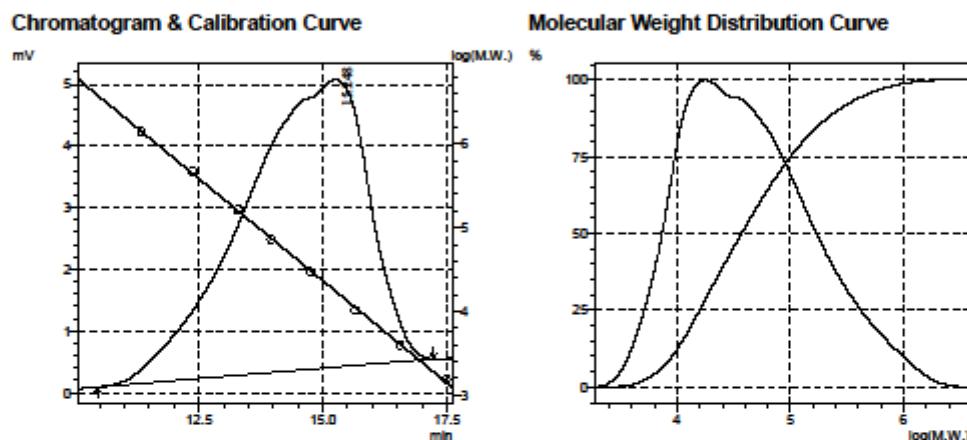
##### Detector A Chl

##### [Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	25697
Weight Average Molecular Weight(Mw)	53980
Z Average Molecular Weight(Mz)	133579
Z+1 Average Molecular Weight(Mz1)	268172
Mw/Mn	2.10067
Mv/Mn	1.85824
Mz/Mw	2.47458

**Figure S27.** GPC analysis of PCHC (entry 3, Table 3).

## Supporting information



### GPC Calculation Results

Peak#1 (Detector A Ch1)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	10.458	10.458	3842613	88
Top	15.248	15.248	17634	4655
End	17.233	17.233	1892	550

Area : 824309

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	22092
Weight Average Molecular Weight(Mw)	107604
Z Average Molecular Weight(Mz)	507290
Z+1 Average Molecular Weight(Mz1)	1076525
Mw/Mn	4.87077
Mv/Mn	3.76623
Mz/Mw	4.71441

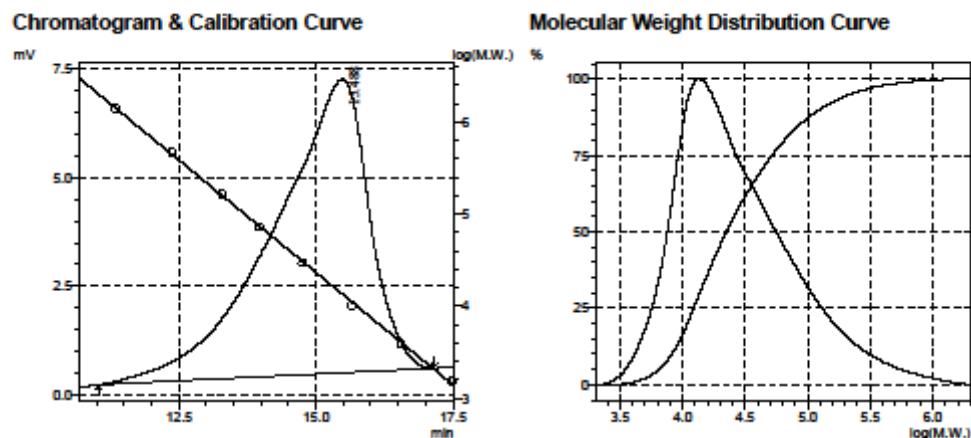
Detector A Ch1

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	22092
Weight Average Molecular Weight(Mw)	107604
Z Average Molecular Weight(Mz)	507290
Z+1 Average Molecular Weight(Mz1)	1076525
Mw/Mn	4.87077
Mv/Mn	3.76623
Mz/Mw	4.71441

**Figure S28.** GPC analysis of PCHC (entry 4, Table 3).

## Supporting information



### GPC Calculation Results

#### Peak#1 (Detector A Chl)

##### [Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	11.033	11.033	2013224	230
Top	15.488	15.488	13453	6759
End	17.167	17.167	2039	610

Area : 813357

Area% : 100.0000

##### [Average Molecular Weight]

Number Average Molecular Weight(Mn)	17440
Weight Average Molecular Weight(Mw)	57839
Z Average Molecular Weight(Mz)	294533
Z+1 Average Molecular Weight(Mz1)	720785
Mw/Mn	3.31649
Mw/Mn	2.62688
Mz/Mw	5.09231

##### Detector A Chl

##### [Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	17440
Weight Average Molecular Weight(Mw)	57839
Z Average Molecular Weight(Mz)	294533
Z+1 Average Molecular Weight(Mz1)	720785
Mw/Mn	3.31649
Mw/Mn	2.62688
Mz/Mw	5.09231

**Figure S29.** GPC analysis of PCHC (entry 5, Table 3).