

## Supporting Information

# Carvacrol- and cardanol-containing 1,3-dioxolan-4-ones as comonomers for the synthesis of functional polylactide-based materials

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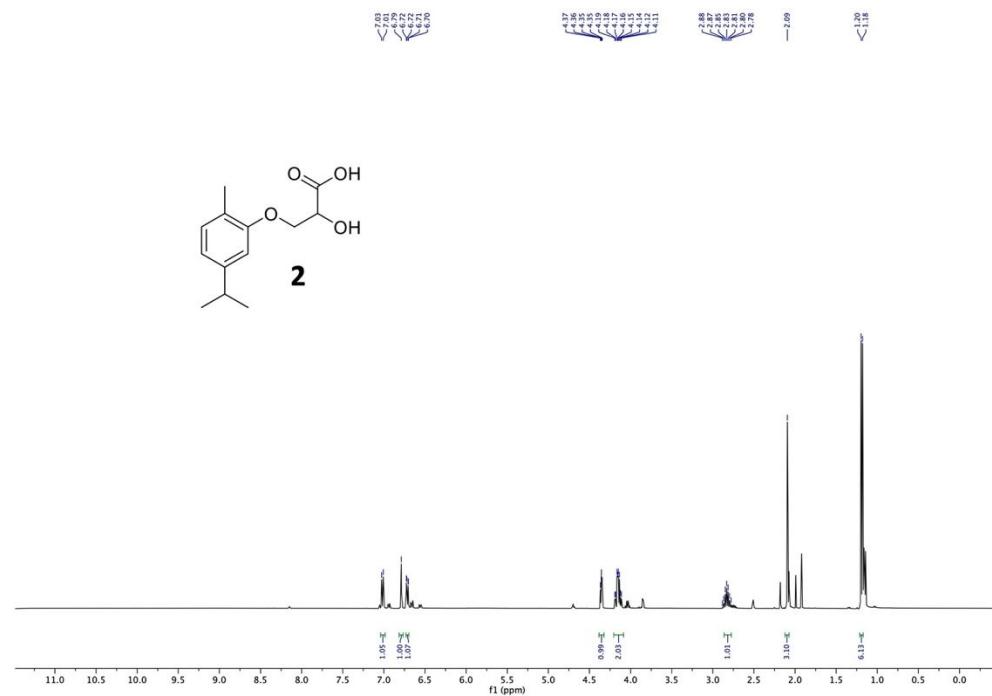
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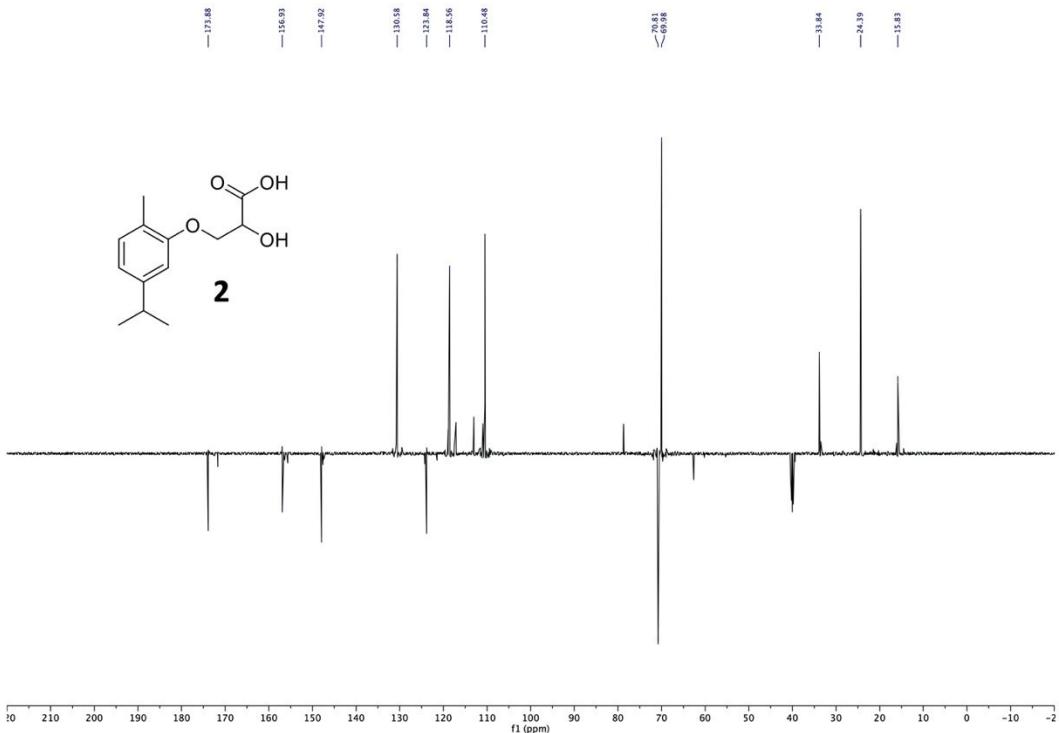
This supporting information file contains 19 pages and 32 figures.

## 1. NMR analyses

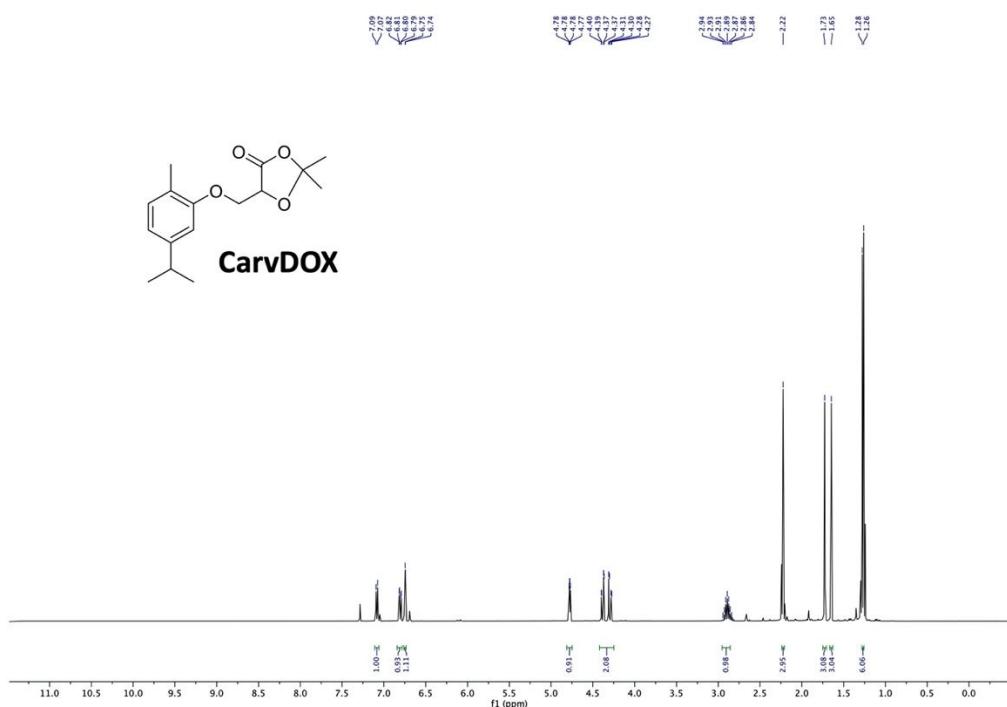
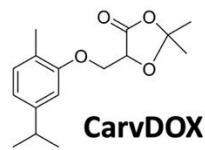
### 1.1 $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of monomers and precursors



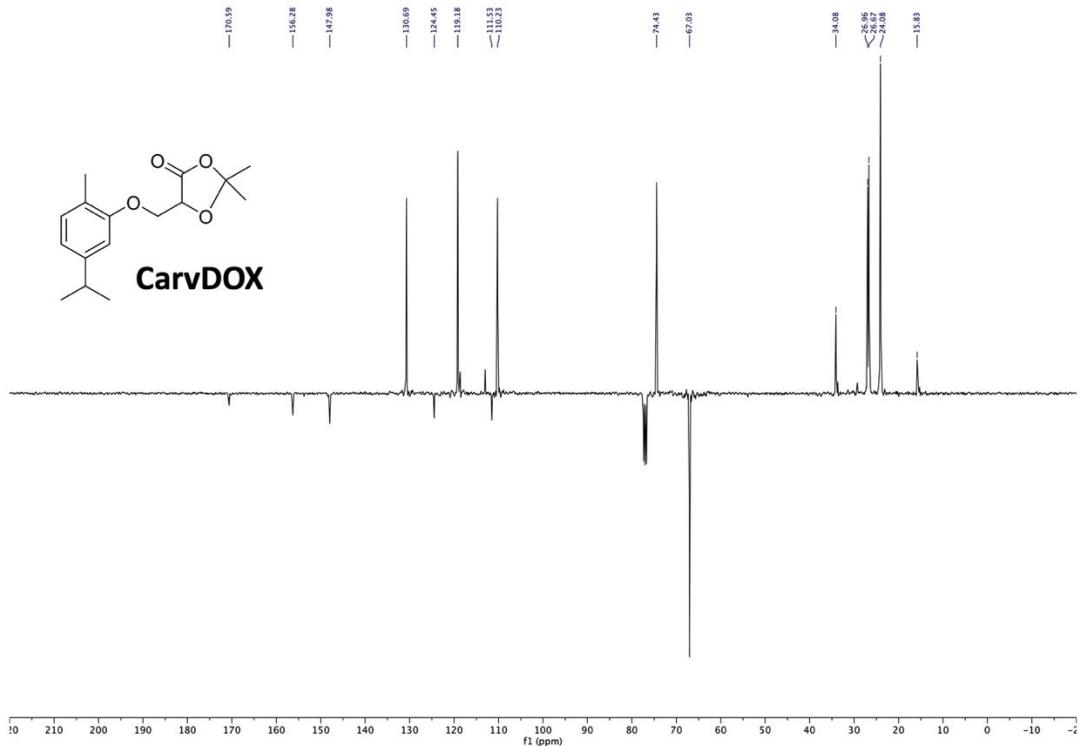
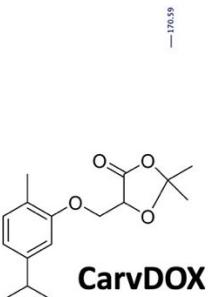
**Figure S 1:**  $^1\text{H}$  NMR spectrum of compound **2**, 400 MHz, DMSO- $\text{d}^6$ .



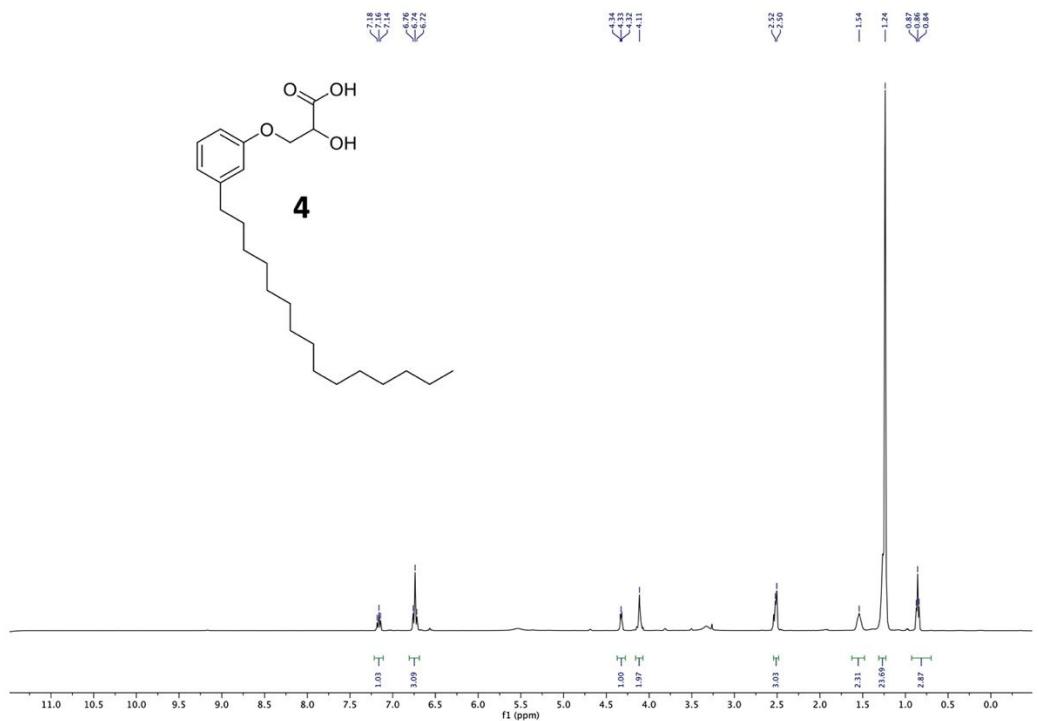
**Figure S 2:**  $^{13}\text{C}$  NMR spectrum of compound **2**, 101 MHz, DMSO-d $^6$ .



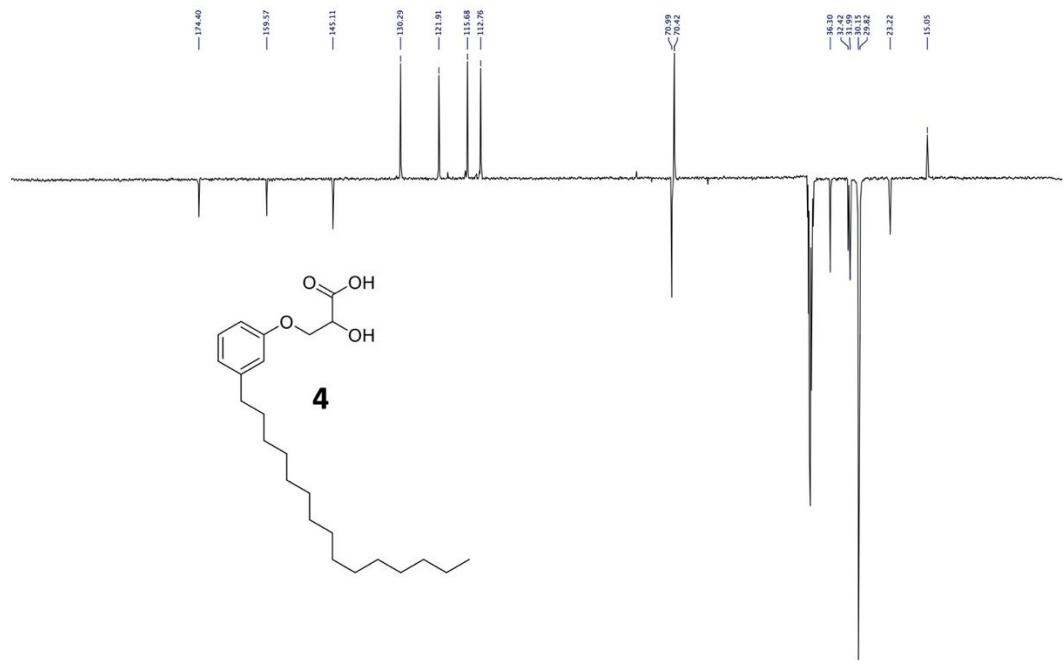
**Figure S 3:**  $^1\text{H}$  NMR spectrum of **CarvDOX**, 400 MHz,  $\text{CDCl}_3$ .



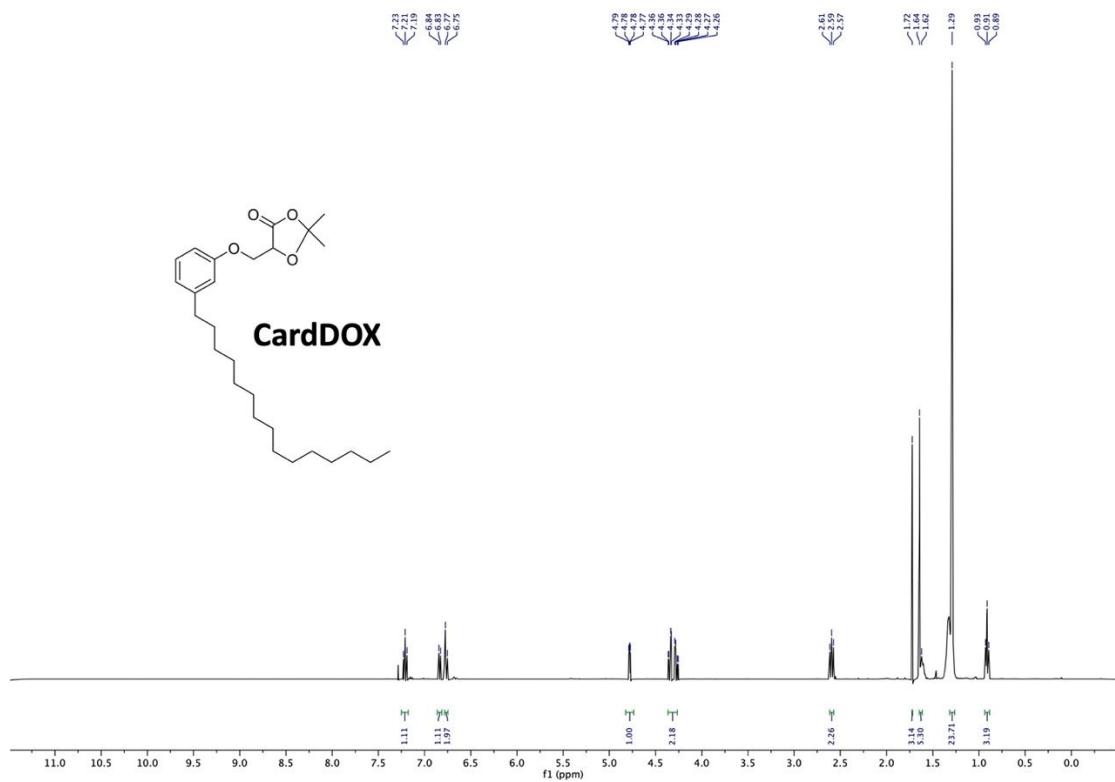
**Figure S 4:**  $^{13}\text{C}$  NMR spectrum of compound **CarvDOX**, 101 MHz,  $\text{CDCl}_3$ .



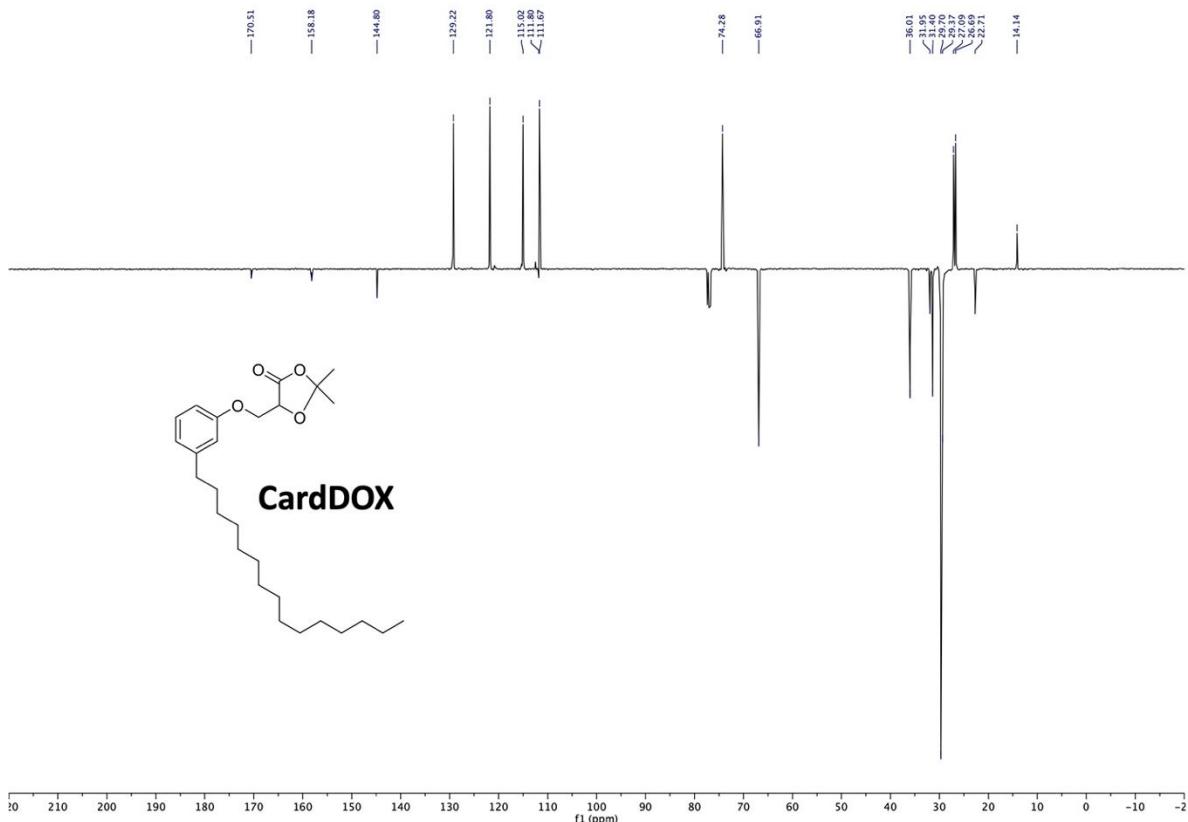
**Figure S 5:**  $^1\text{H}$  NMR spectrum of compound **4**, 400 MHz,  $\text{DMSO-d}_6$ .



**Figure S 6:**  $^{13}\text{C}$  NMR spectrum of compound **4**, 101 MHz,  $\text{DMSO-d}_6$ .

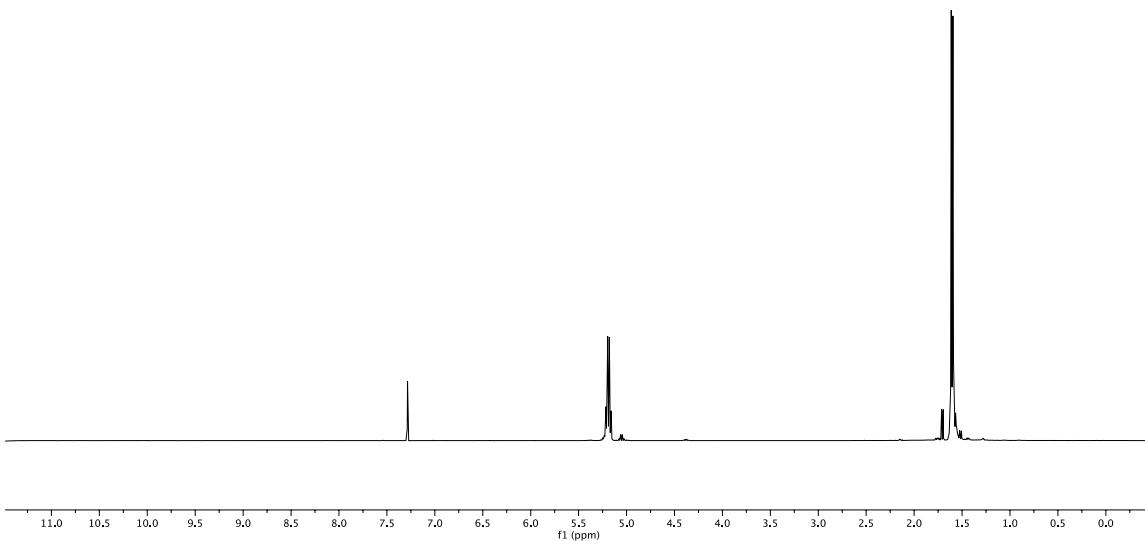


**Figure S 7:**  $^1\text{H}$  NMR spectrum of **CardDOX**, 400 MHz,  $\text{CDCl}_3$ .

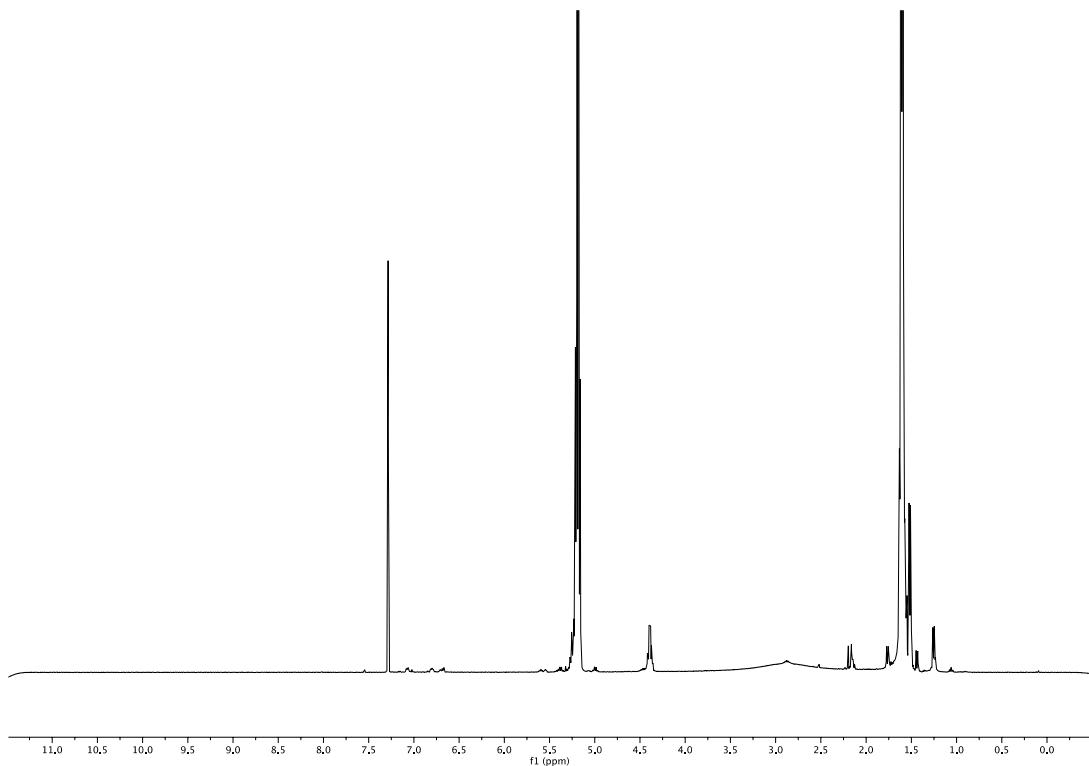


**Figure S 8:**  $^{13}\text{C}$  NMR spectrum of compound **CardDOX**, 101 MHz,  $\text{CDCl}_3$ .

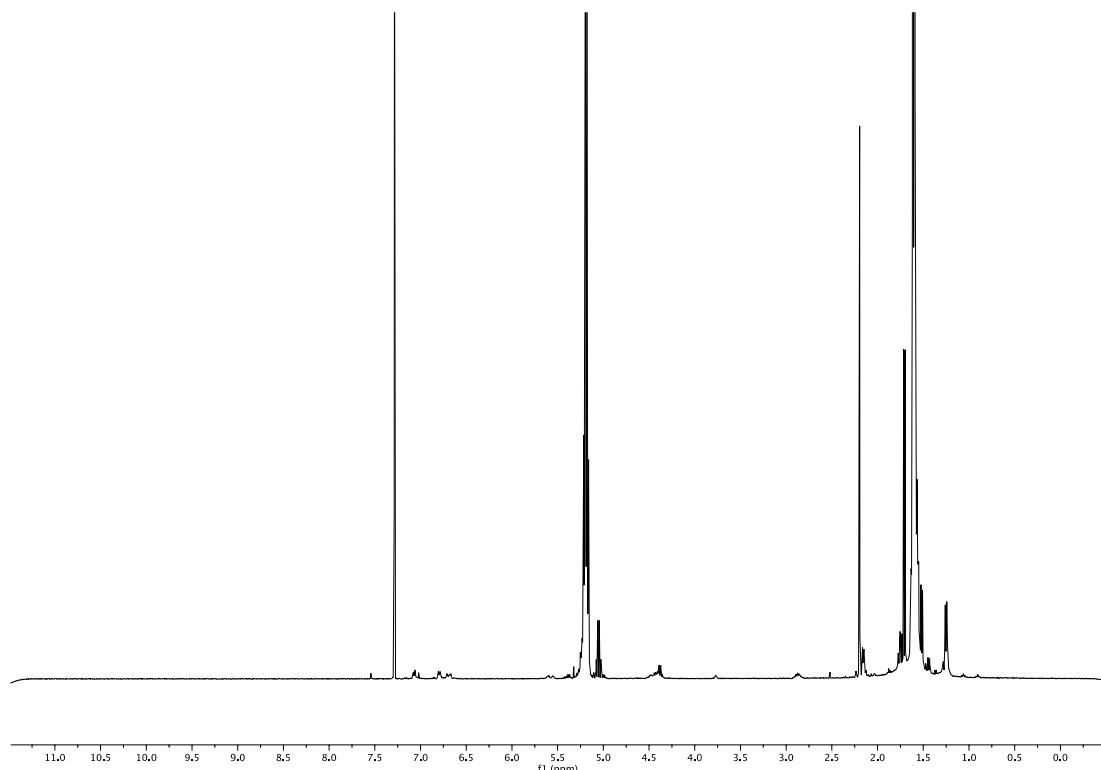
### 1.2 $^1\text{H}$ NMR spectra relative to CarvDOX loading evaluation



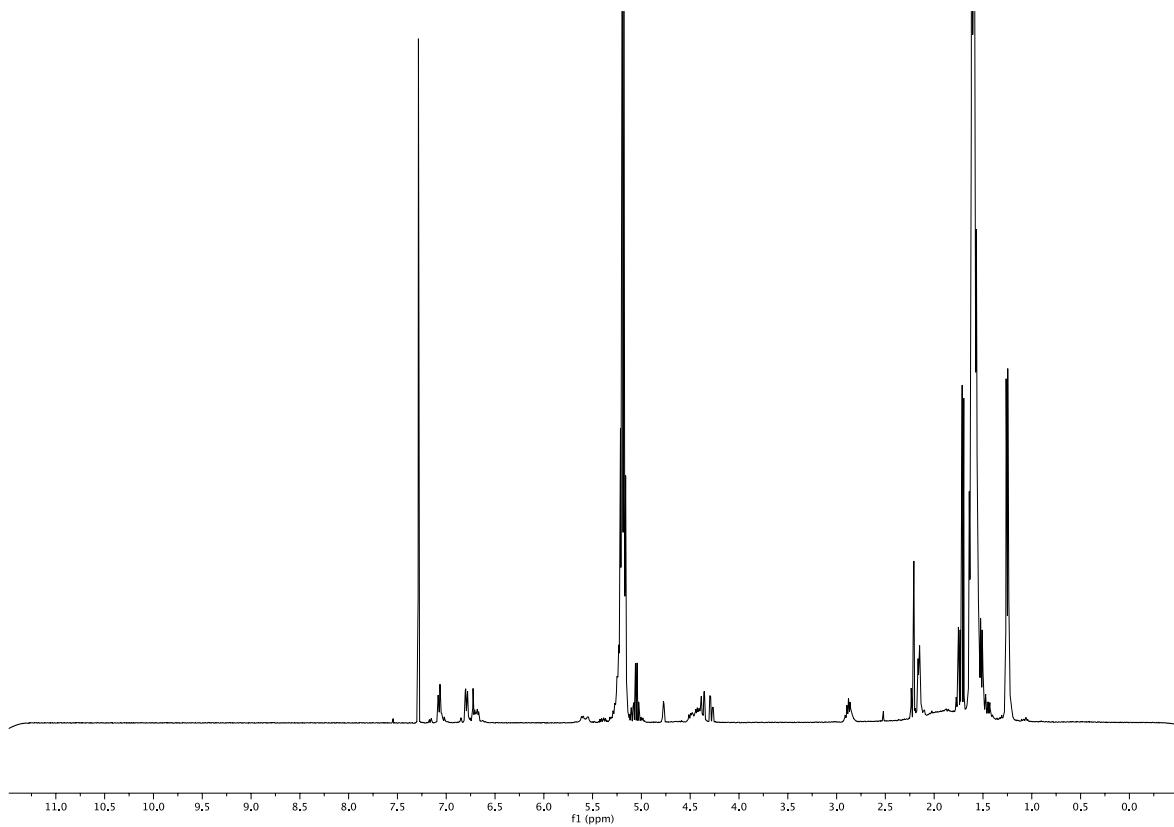
**Figure S 9:**  $^1\text{H}$  NMR spectrum of **PLA**, 400 MHz,  $\text{CDCl}_3$ .



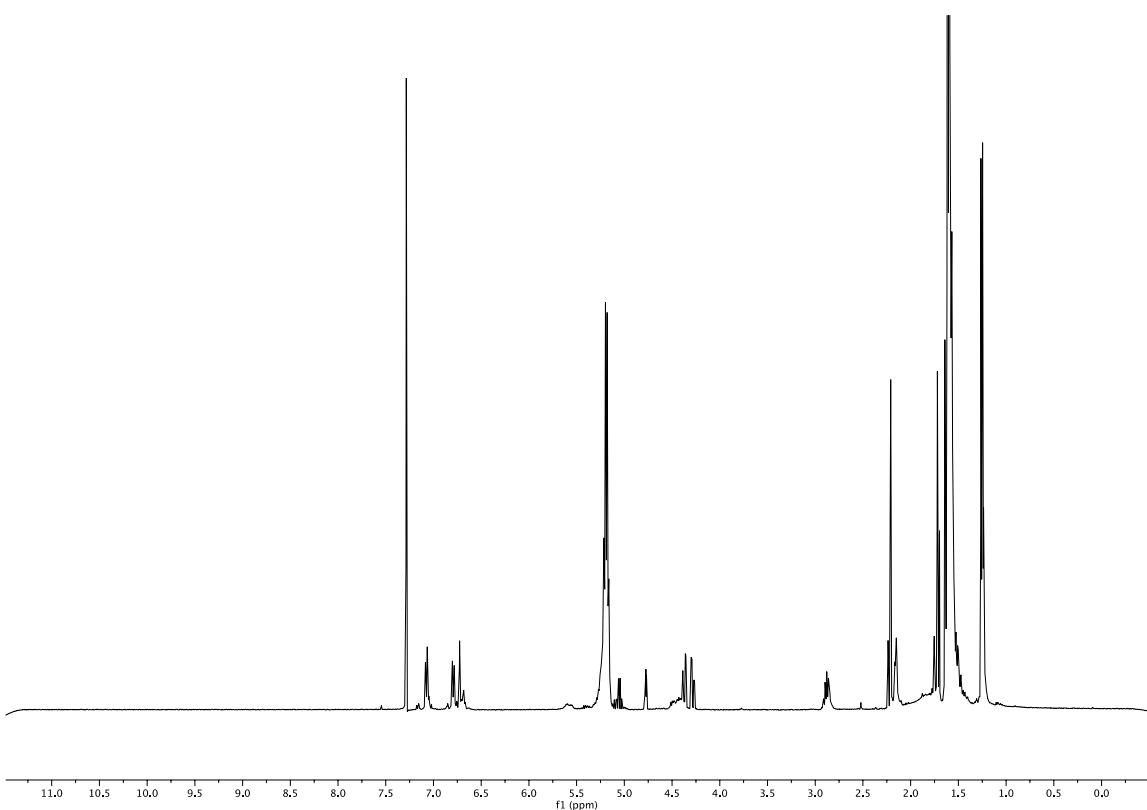
**Figure S 10:**  $^1\text{H}$  NMR spectrum of **PLA-co-Carv2**, 400 MHz,  $\text{CDCl}_3$ .



**Figure S 11:** <sup>1</sup>H NMR spectrum of PLA-co-Carv4, 400 MHz, CDCl<sub>3</sub>.

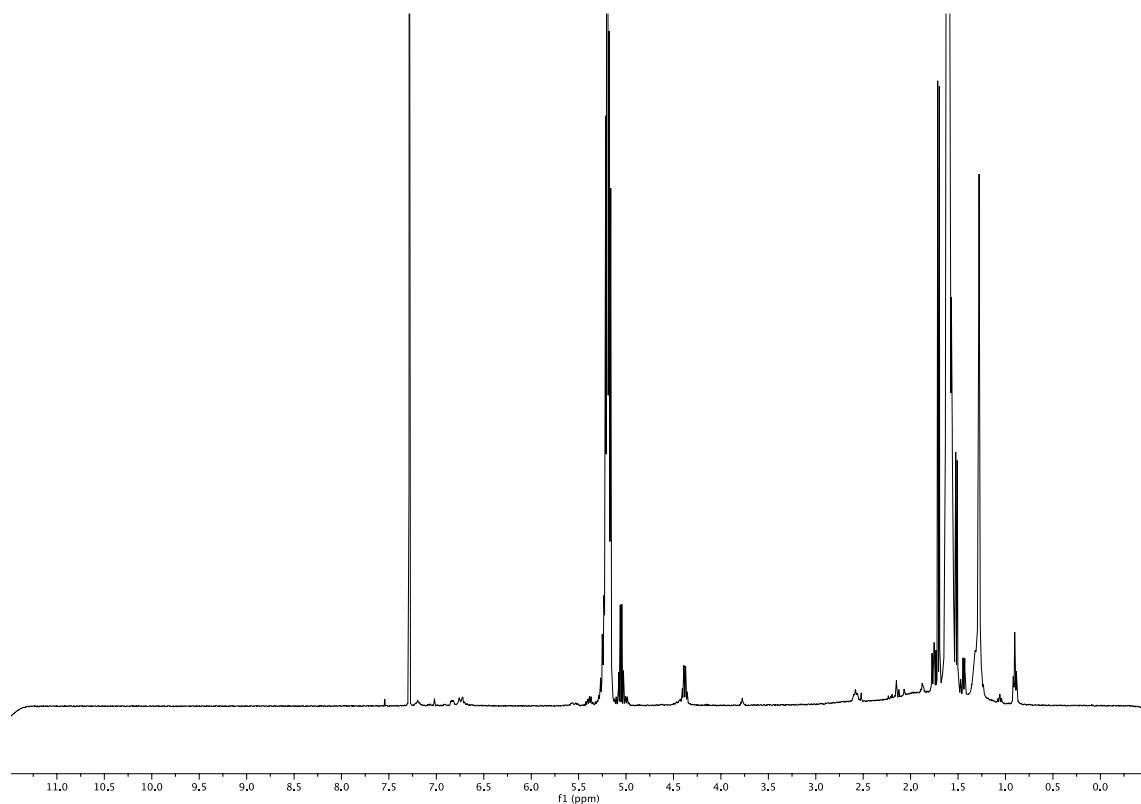


**Figure S 12:** <sup>1</sup>H NMR spectrum of PLA-co-Carv10, 400 MHz, CDCl<sub>3</sub>.

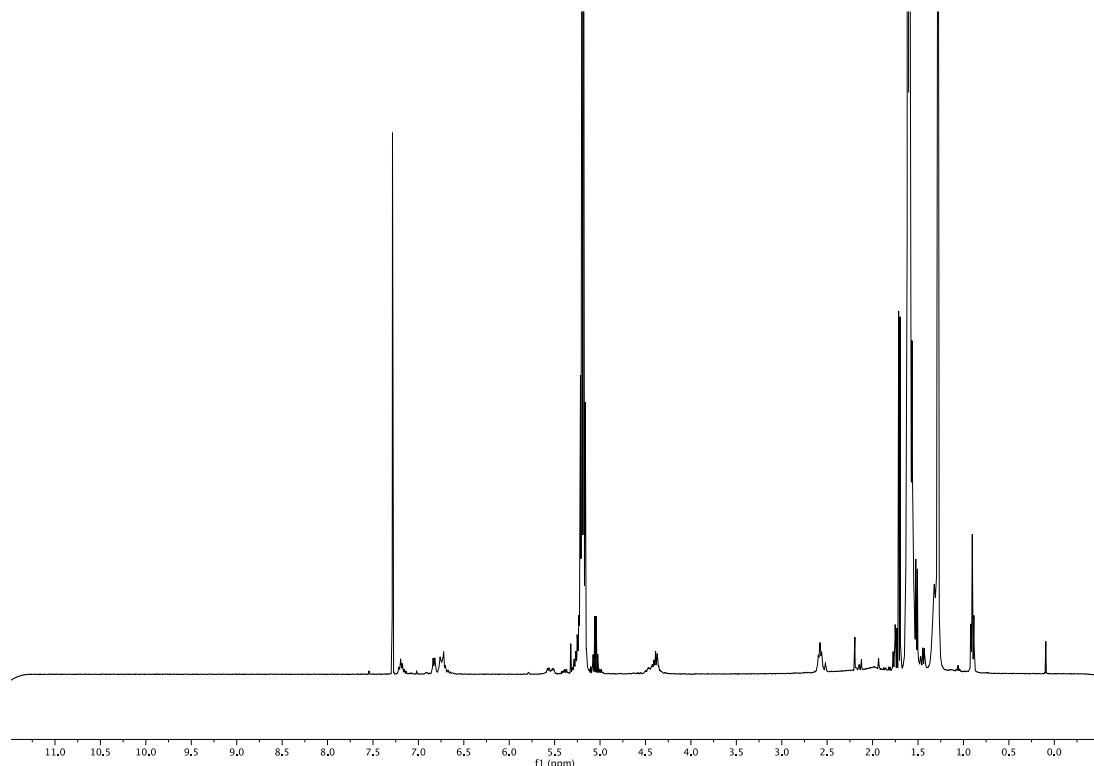


**Figure S 13:** <sup>1</sup>H NMR spectrum of PLA-co-Carv20, 400 MHz,  $\text{CDCl}_3$ .

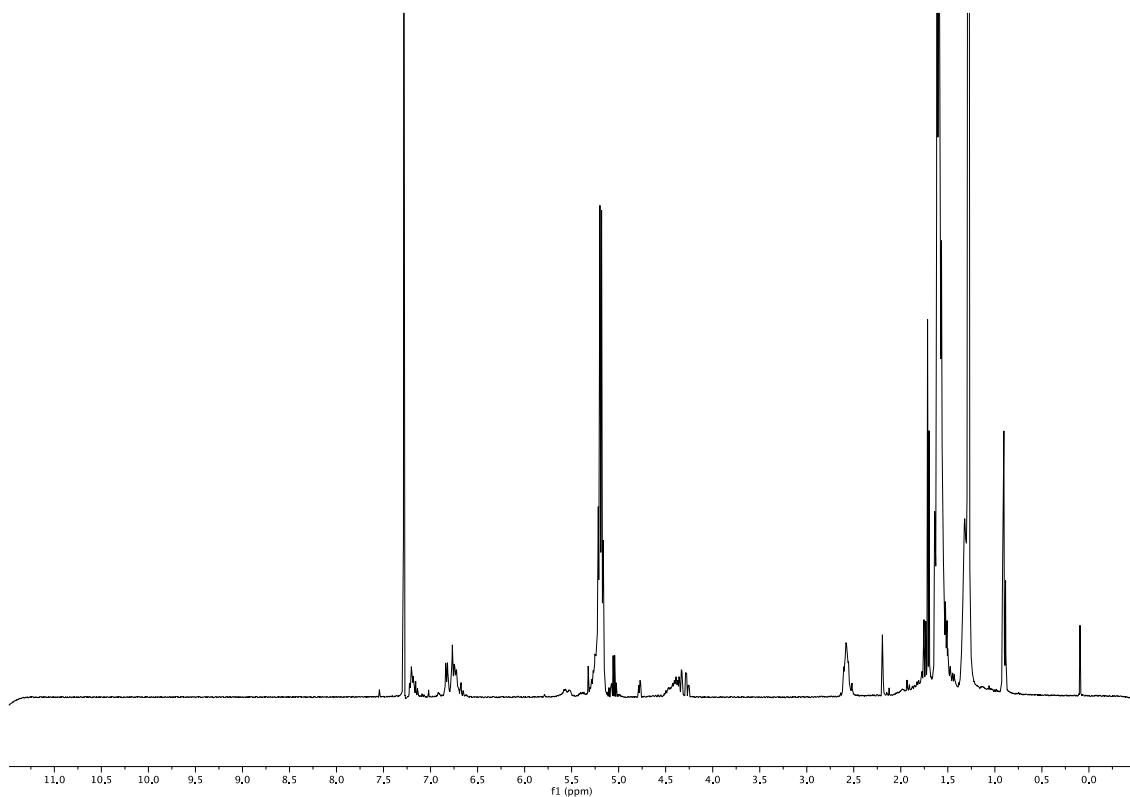
**1.3  $^1\text{H}$  NMR spectra relative to CardDOX loading evaluation**



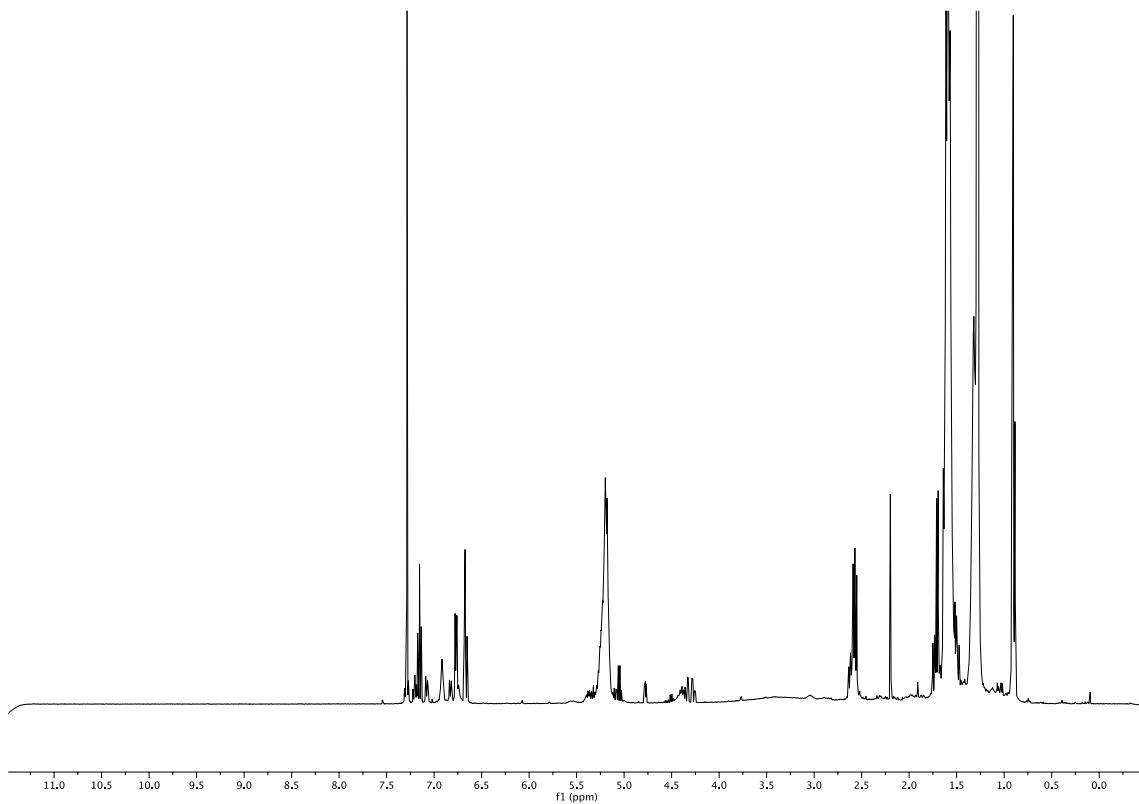
**Figure S 14:**  $^1\text{H}$  NMR spectrum of PLA-co-Card2, 400 MHz,  $\text{CDCl}_3$ .



**Figure S 15:**  $^1\text{H}$  NMR spectrum of PLA-co-Card4, 400 MHz,  $\text{CDCl}_3$ .

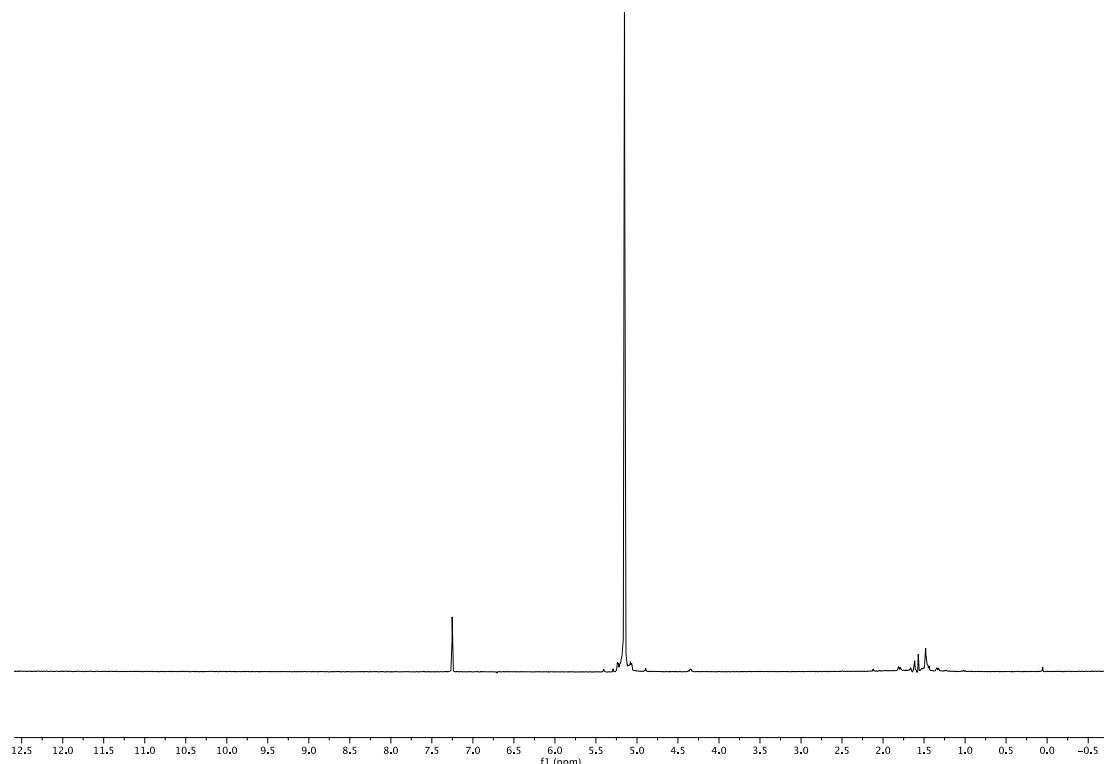


**Figure S 16:** <sup>1</sup>H NMR spectrum of PLA-co-Card10, 400 MHz, CDCl<sub>3</sub>.

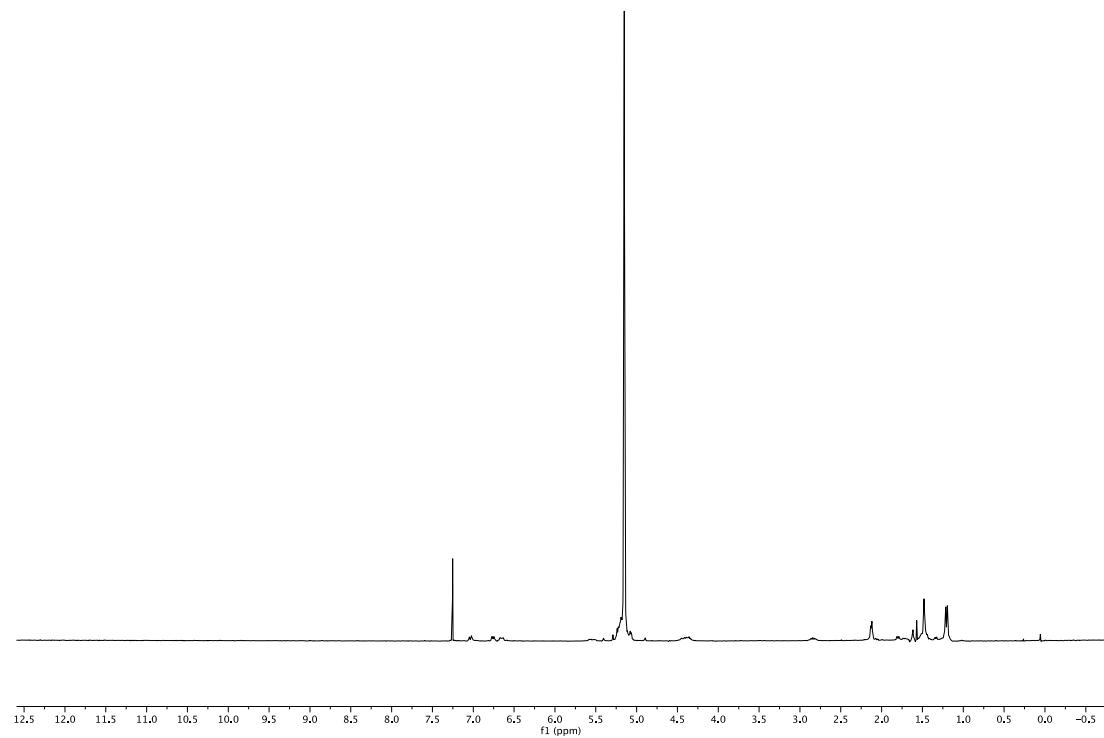


**Figure S 17:** <sup>1</sup>H NMR spectrum of PLA-co-Card20, 400 MHz, CDCl<sub>3</sub>.

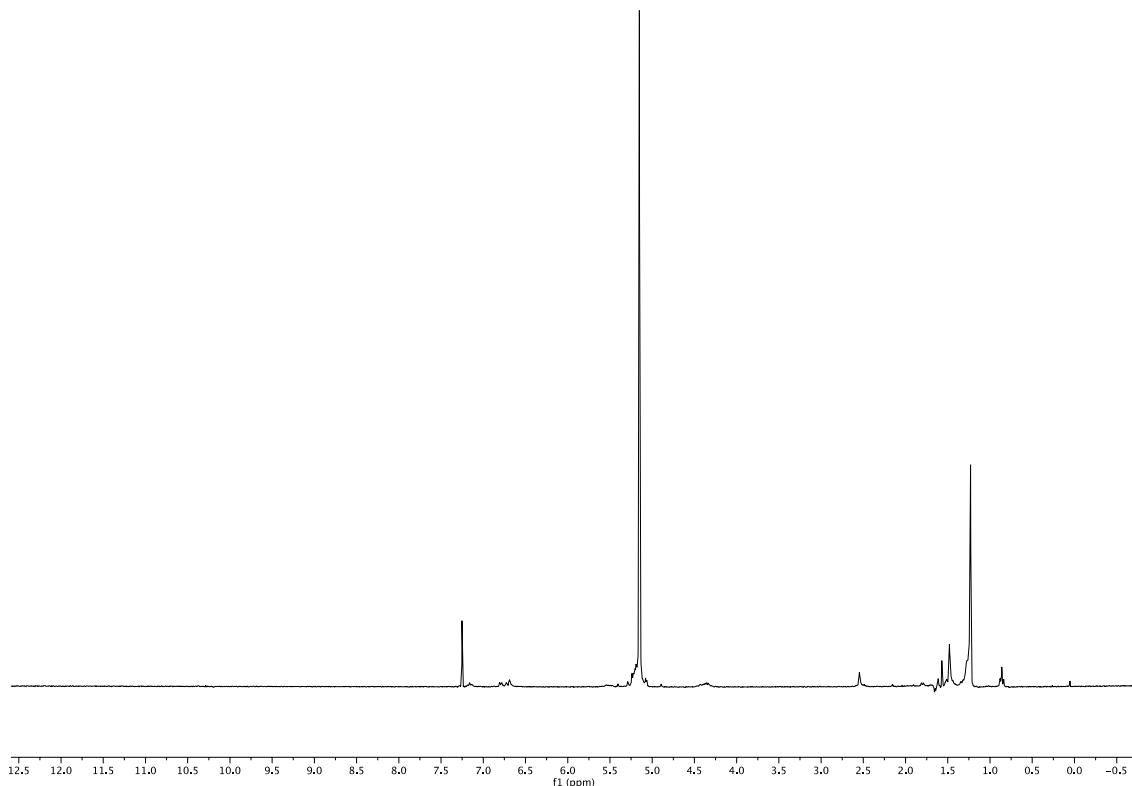
**1.4 Homonuclear decoupled  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  spectra for microstructure determination**



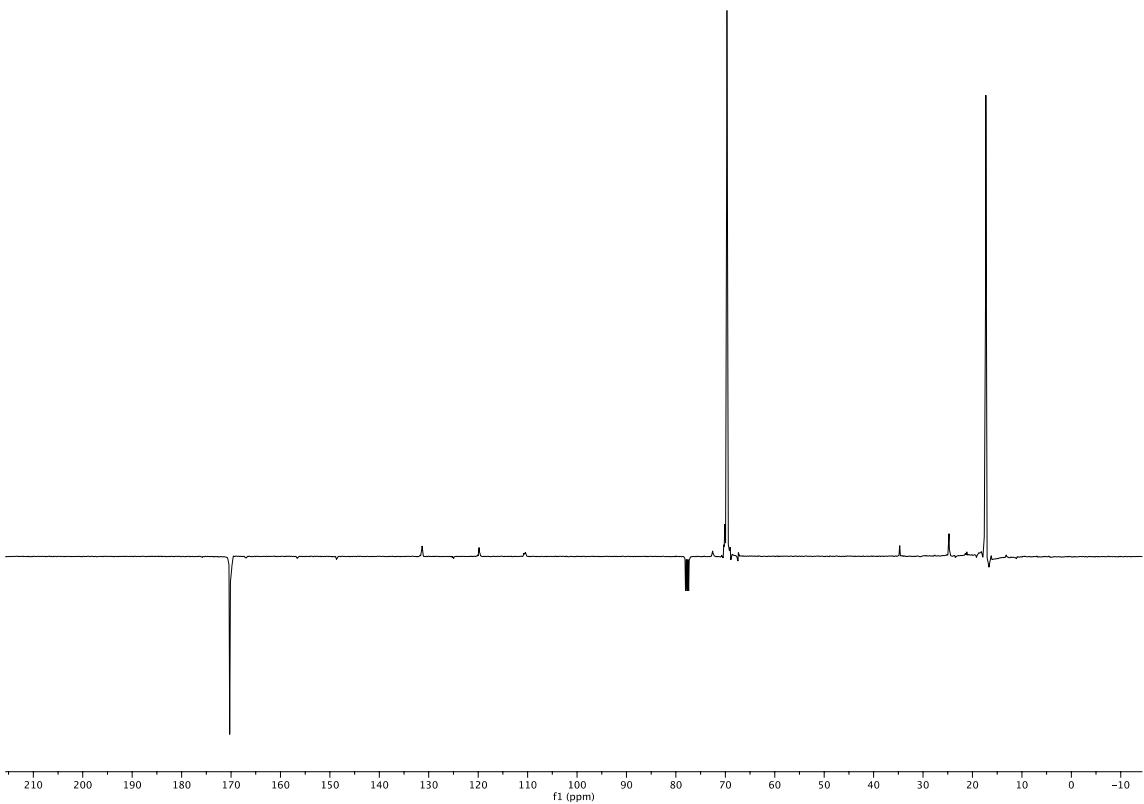
**Figure S 18:** homonuclear decoupled  $^1\text{H}$  NMR spectrum of **PLA**, 300 MHz,  $\text{CDCl}_3$ .



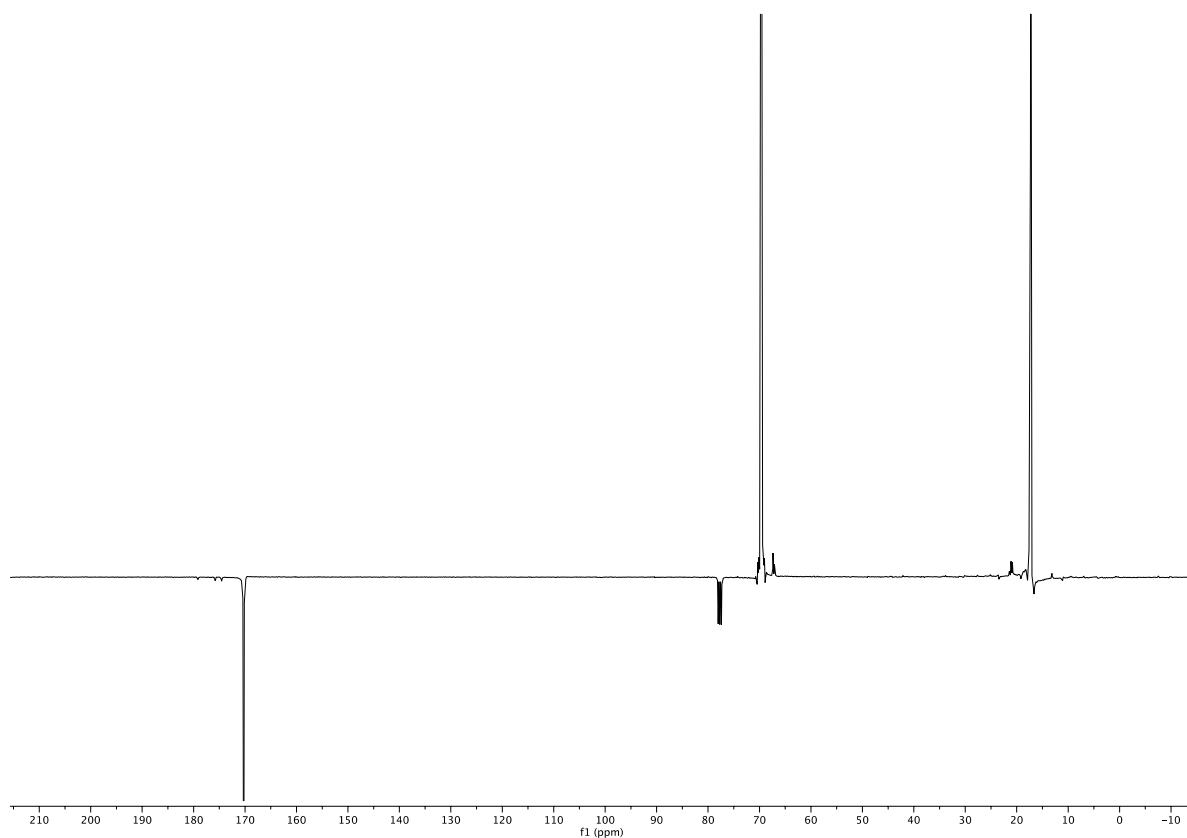
**Figure S 19:** homonuclear decoupled  $^1\text{H}$  NMR spectrum of **PLA-co-Carv10**, 300 MHz,  $\text{CDCl}_3$ .



**Figure S 20:** homonuclear decoupled  $^1\text{H}$  NMR spectrum of **PLA-co-Card10**, 300 MHz,  $\text{CDCl}_3$ .



**Figure S 21:**  $^{13}\text{C}$  NMR spectrum of **PLA-co-Carv10**, 101 MHz,  $\text{CDCl}_3$ .



**Figure S 22:**  $^{13}\text{C}$  NMR spectrum of **PLA-co-Card10**, 101 MHz,  $\text{CDCl}_3$ .

## 2. TGA analyses

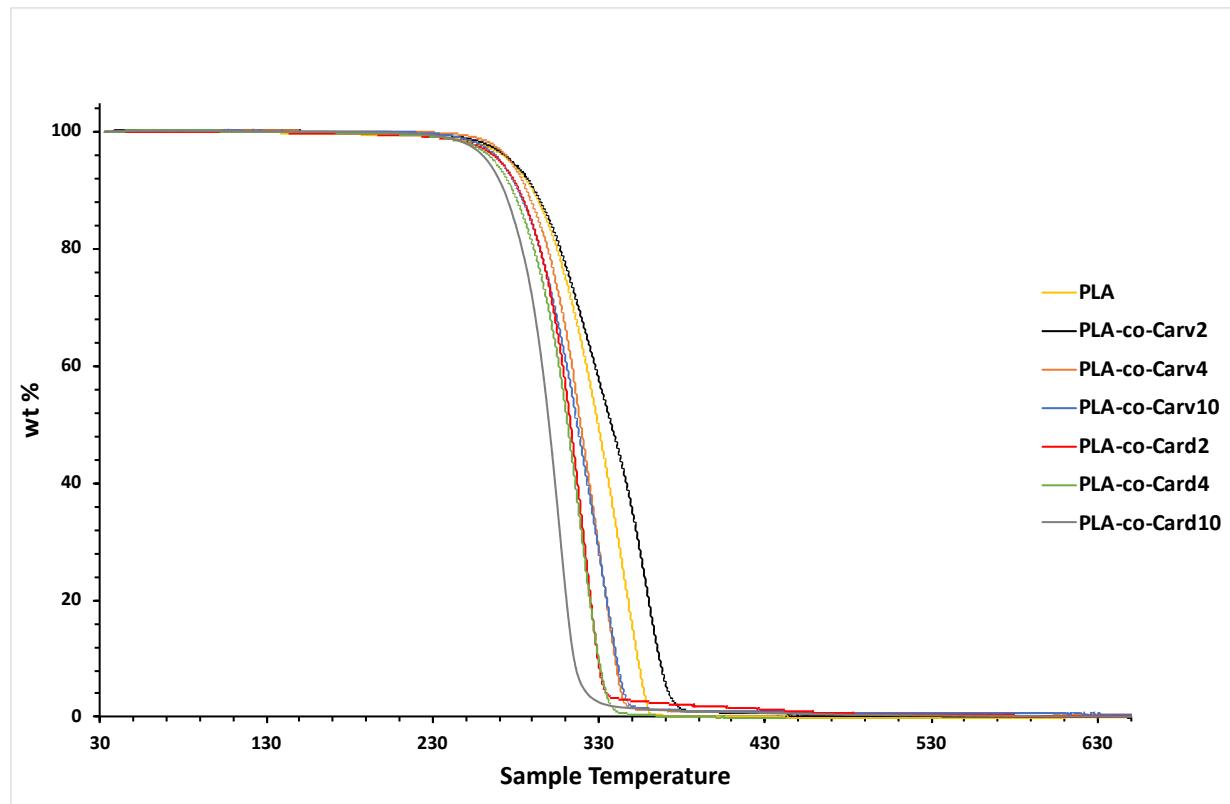


Figure S 23: Superimposed thermal degradation pathways for all samples.

### 3. DSC analyses

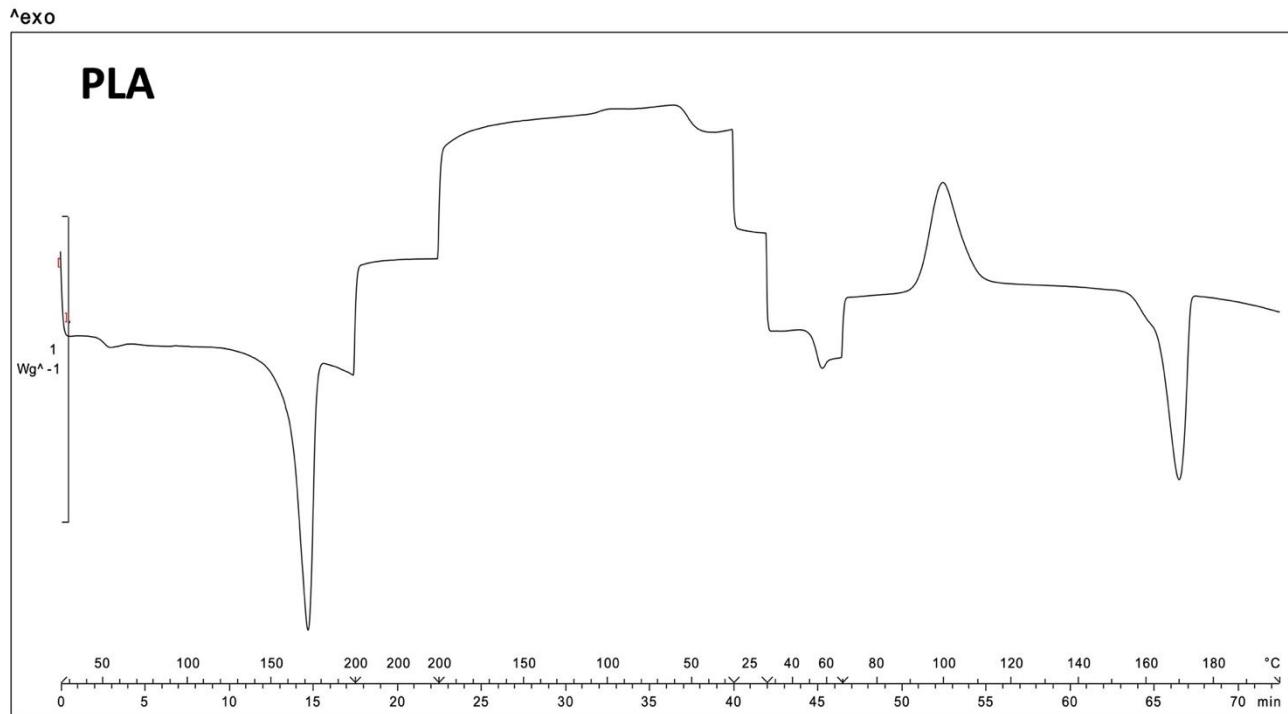


Figure S 24: DSC thermogram of PLA.

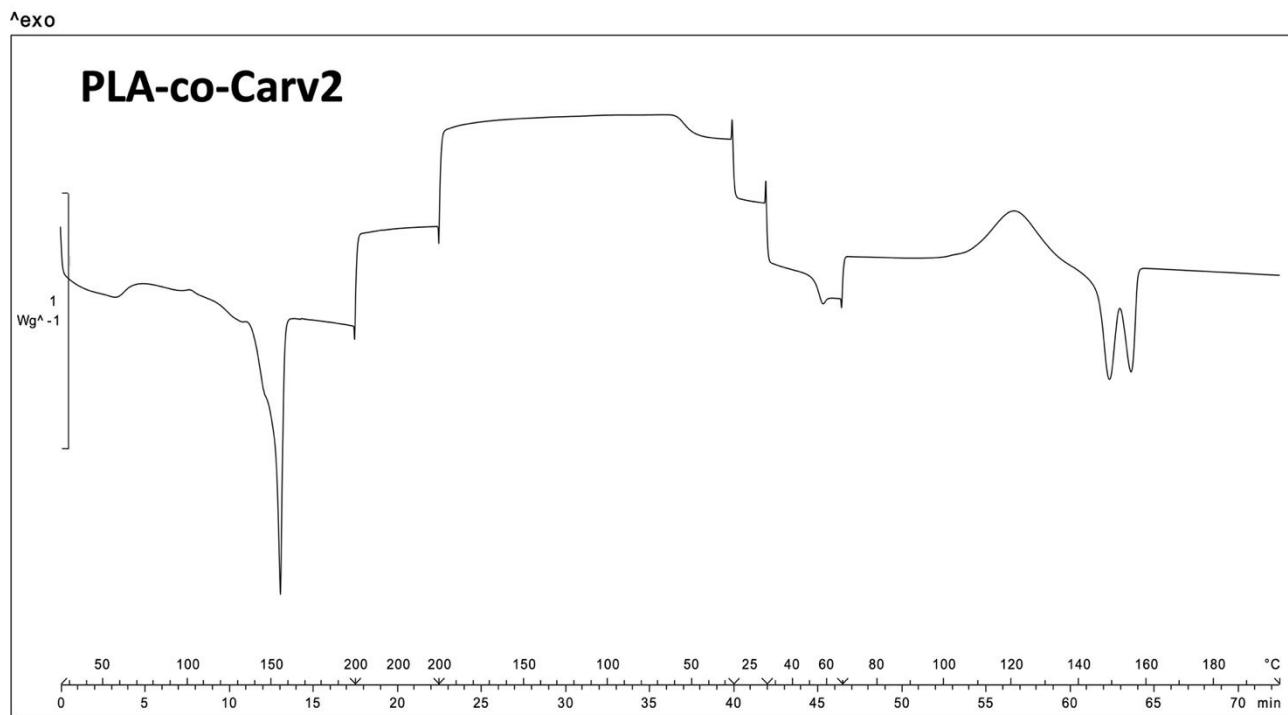


Figure S 25: DSC thermogram of PLA-co-Carv2.

<sup>^</sup>exo

### PLA-co-Carv4

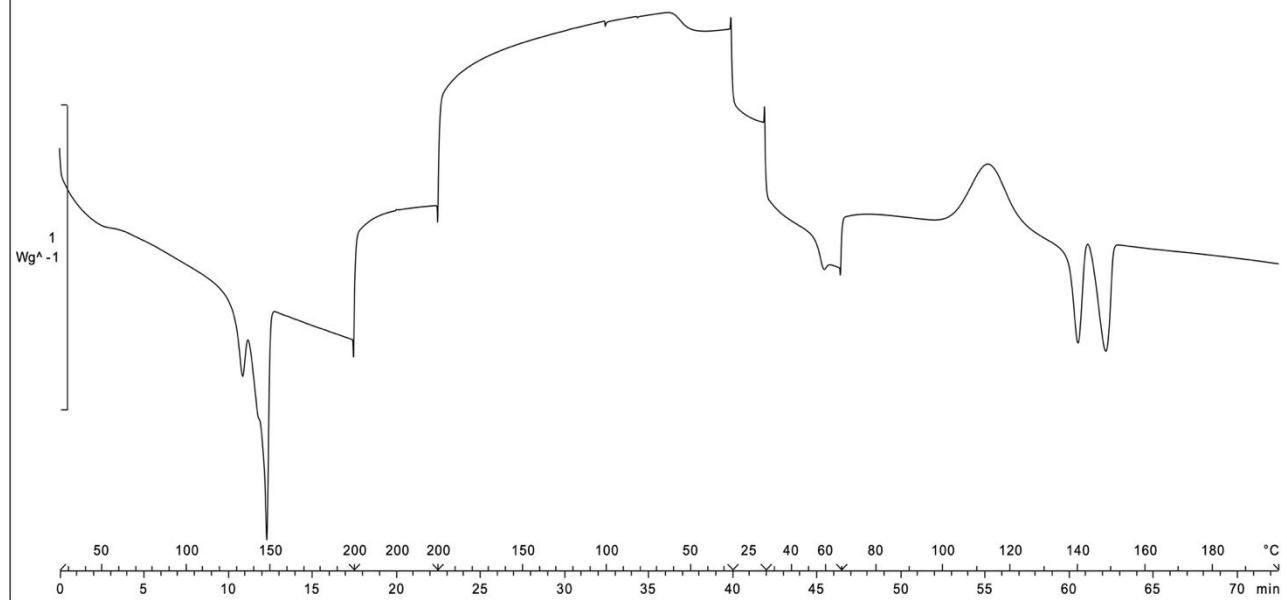


Figure S 26: DSC thermogram of PLA-co-Carv4.

<sup>^</sup>exo

### PLA-co-Carv10

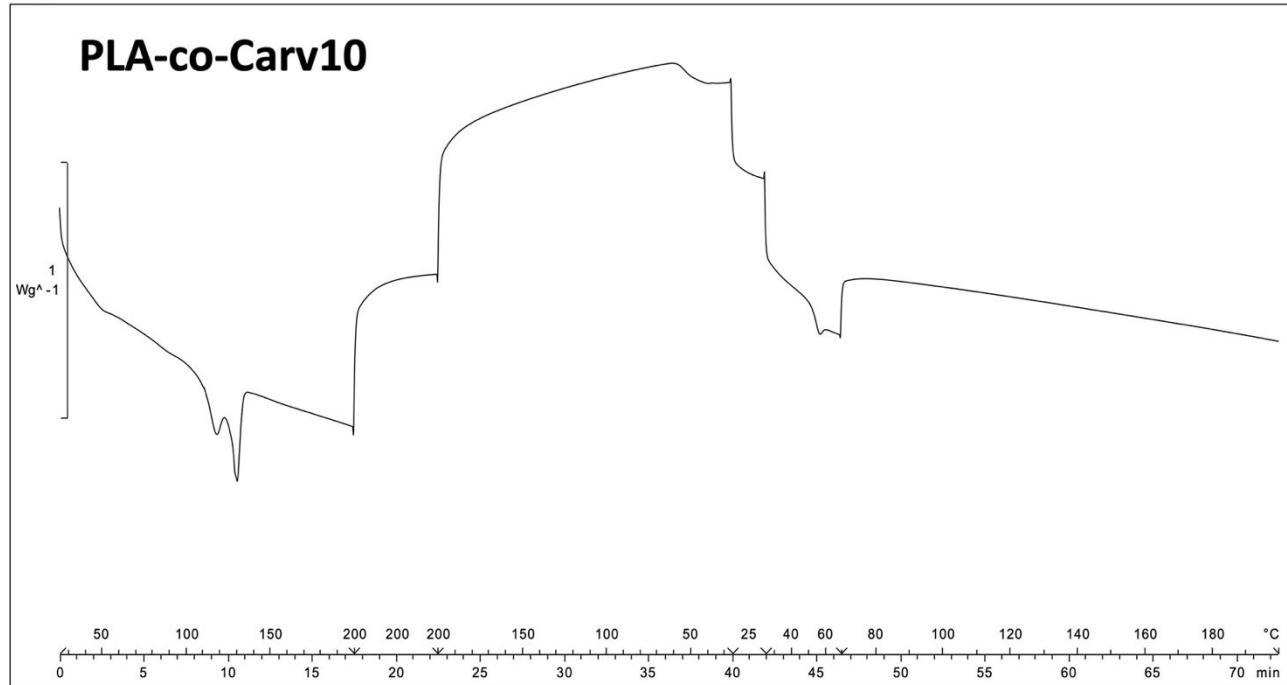


Figure S 27: DSC thermogram of PLA-co-Carv10.

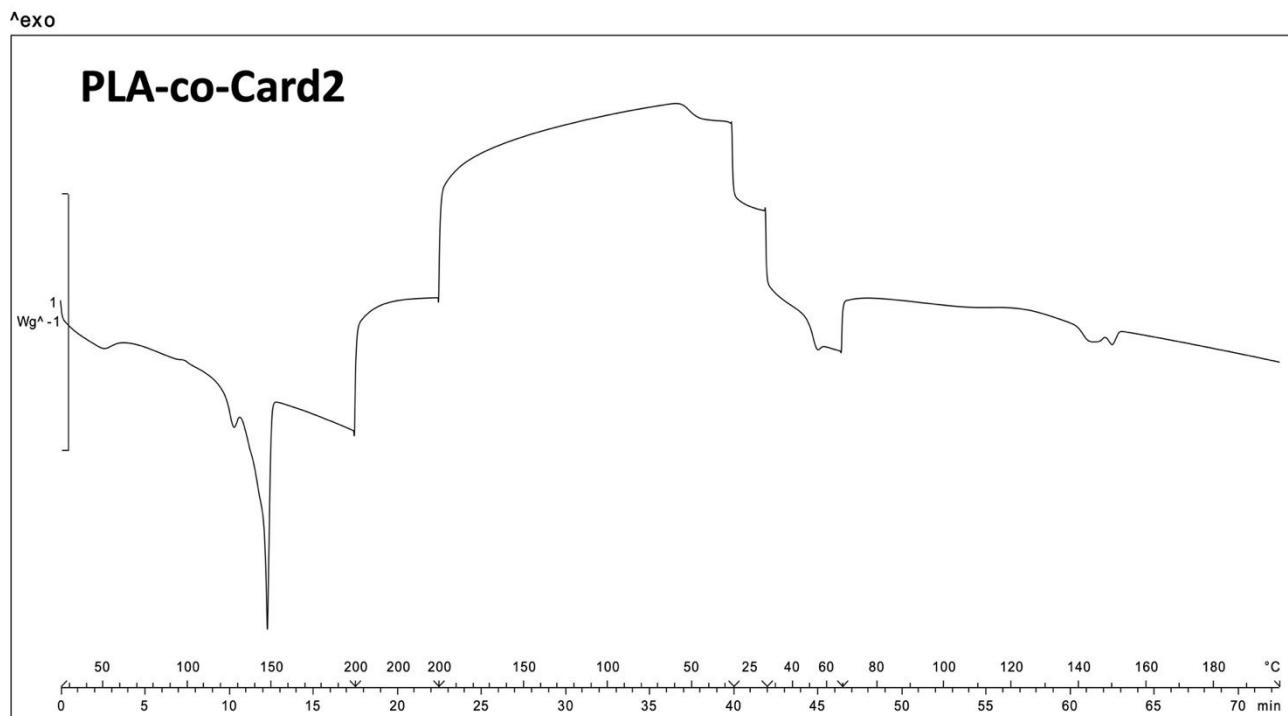


Figure S 28: DSC thermogram of PLA-co-Card2.

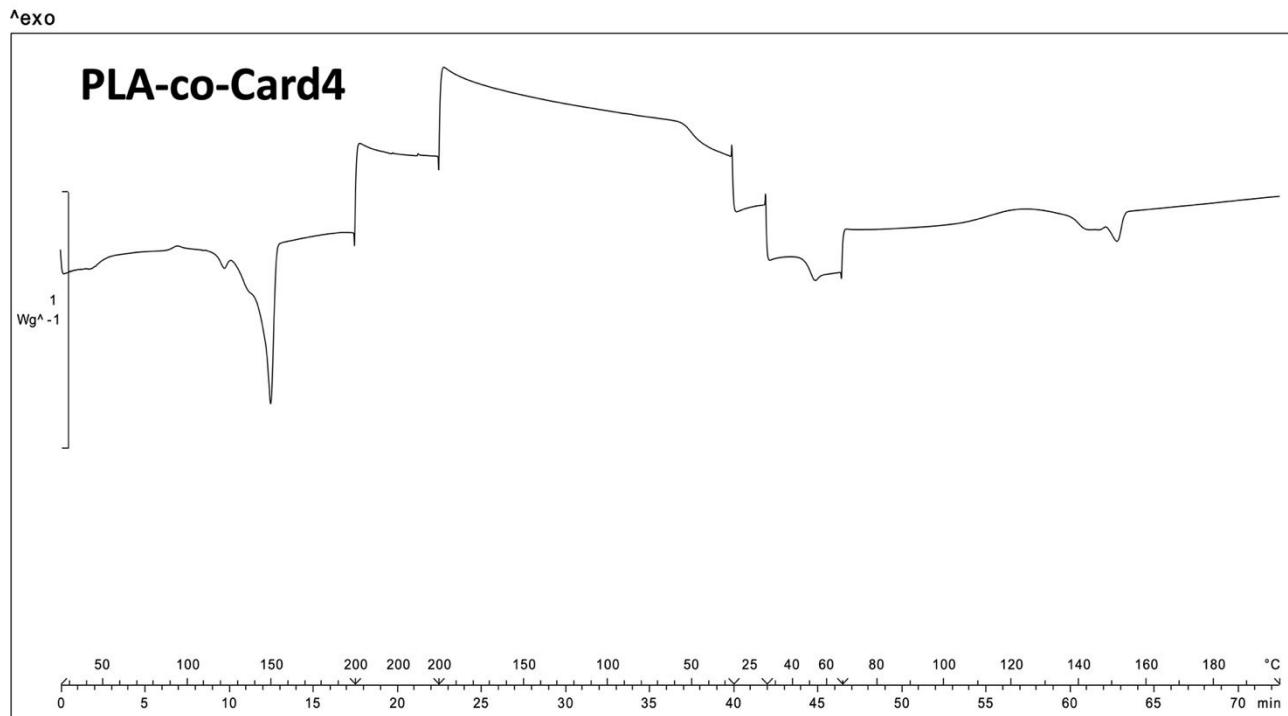


Figure S 29: DSC thermogram of PLA-co-Card4.

<sup>^</sup>exo

## PLA-co-Card10

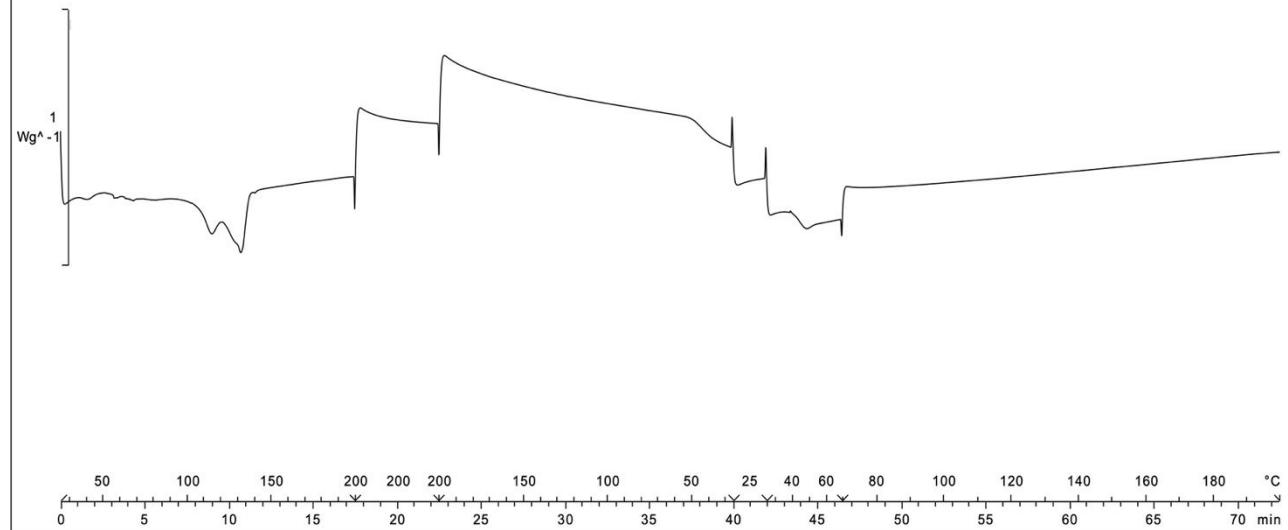
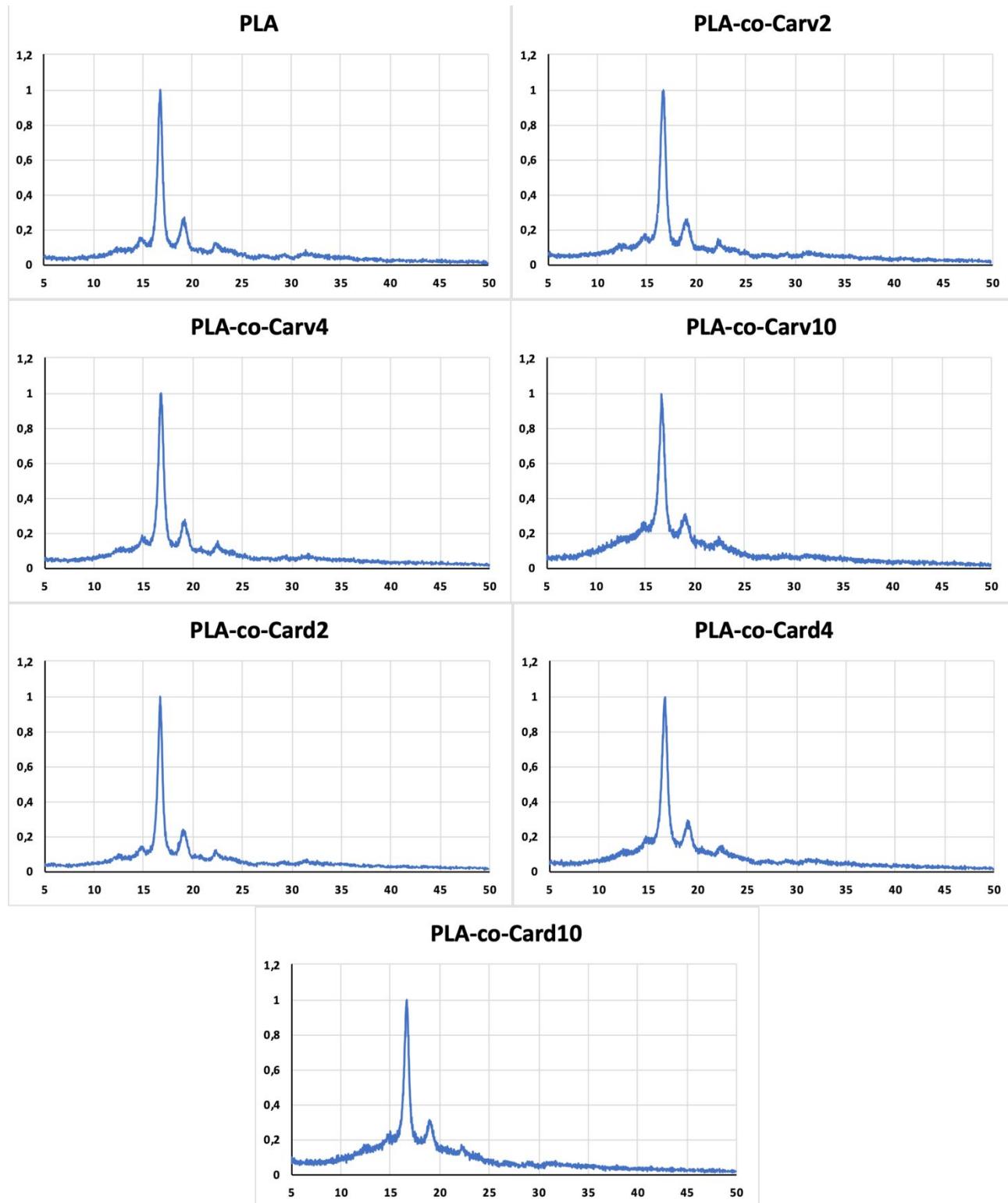


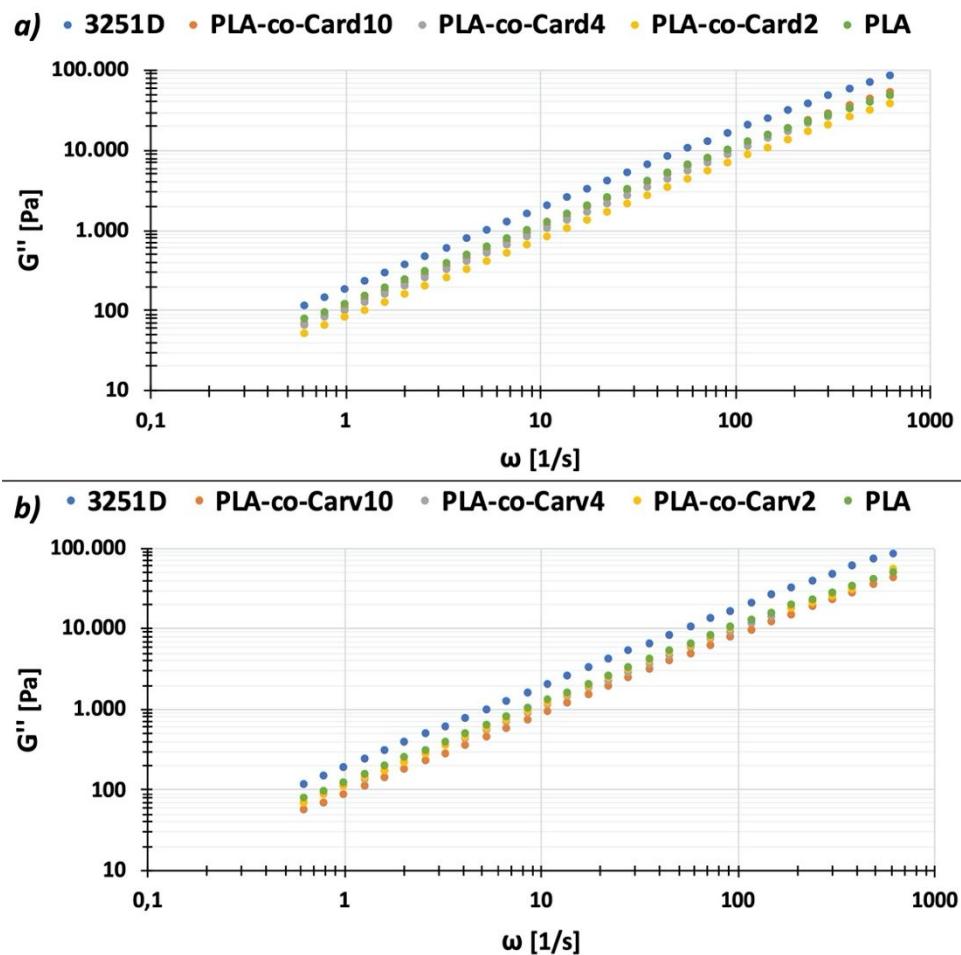
Figure S 30: DSC thermogram of PLA-co-Card10.

#### 4. WAXS analyses



**Figure S 31:** WAXS diffractograms for all samples.

## 5. Loss modulus curves



**Figure S 32:** a) loss modulus curves of cardanol-containing blends compared to Ingeo™ 3251D; b) loss modulus curves of carvacrol-containing blends compared to Ingeo™ 3251D.