

# Supporting Information

## A simple and efficient approach towards photo-sensitive bio-based aliphatic polycarbonate materials

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## Experimental Section

### Materials.

Ethyl chloroformate (97%), 2-mercaptoethanol (98%), benzyl alcohol (BnOH), benzoic acid, 1,5,7-triazabicyclodec-5-ene (TBD, 98%), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), magnesium sulfate ( $\text{MgSO}_4$ ), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,3-bis[3,5-bis(trifluoromethyl)phenyl]thiourea (Schreiner TU, >98.0%) were obtained from Sigma-Aldrich. Triethylamine ( $\text{Et}_3\text{N}$ , 99%) was purchased from Alfa Aesar. Methyl 10-undecenoate was obtained from Nu-Chek Prep, Inc. Cinnamoyl chloride (predominantly trans, 98%) was purchased from TCI Europe. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) was obtained from Wako.

ITERG kindly provided NH-Und-1,3-diol.

All products and solvents (reagent grade) were used as received except otherwise mentioned. The solvents were of reagent grade quality and were purified wherever necessary according to the methods reported in the literature. Flash chromatography was performed on a Grace Reveleris apparatus, employing silica cartridges from Grace. Cyclohexane: ethyl acetate and dichloromethane: methanol gradients were used as eluents depending on the products. The detection was performed through ELSD and UV detectors at 254 nm and 280 nm.

### Characterization.

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively) by using  $\text{CDCl}_3$  as a solvent at room temperature, except otherwise mentioned. Two-dimensional analyses such as  $^1\text{H}$ - $^1\text{H}$  COSY (COReLation SpectroscopY),  $^1\text{H}$ - $^{13}\text{C}$  HSQC (Heteronuclear Single Quantum Spectroscopy) and were also performed. Size Exclusion Chromatography (SEC) analyses were performed in THF (25°C) on a PL GPC50 and with four TSK columns: HXL-L (guard column), G4000HXL (particles of 5 mm, pore size of 200Å, and exclusion limit of 400000 g/mol), G3000HXL (particles of 5 mm, pore size of 75Å, and exclusion limit of 60000 g/mol), G2000HXL (particles of 5 mm, pore size of 20 Å, and exclusion limit of 10000 g/mol) at an elution rate of 1 mL/min. The elution times of the filtered samples were monitored using UV and RI detectors and SEC were calibrated using polystyrene standards. Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -80 to 100°C at 10°C.min<sup>-1</sup> were performed and then the glass transition and melting temperatures were calculated from the second heating run. Thermogravimetric (TGA) analyses were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min<sup>-1</sup> under nitrogen atmosphere from room temperature to 600°C. Dynamic mechanical analyses (DMA) were performed on RSA 3 (TA instrument). The sample temperature was modulated from -50 °C to 150 °C, depending on the sample at a heating rate of 4°C.min<sup>-1</sup>. The measurements were performed in a tension mode at a frequency of 1 Hz, an initial static force of 0.1 N and a strain sweep of 0.04%. Photo-crosslinking were performed using a UV lamp

HAMAMATSU equipped with a LC8 lamp (full power of 4000 mW.cm<sup>-1</sup>) and an A9616-03 filter transmitting in the range 280-400 nm, avoiding the heating of the mixture reaction. The samples were placed at a distance of 9 cm of the UV lamp

#### Synthesis of **NH-Und-1,3-diol**

Methyl 10-undecenoate (1 equiv.), was mixed with 2-amino-1,3-propanediol (1.3 equiv.). TBD (0.05 equiv.) was added to the reaction mixture and heated up at 80°C under a nitrogen flow to remove methanol formed. The reaction mixture was heated for 3h. Depending on the matrix, the reaction mixture might become solid indicating the end of the reaction. The product is then extracted with CHCl<sub>3</sub> and washed 3 times with water. Brine is added in case of emulsion. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum to yield **NH-Und-1,3-diol**. The diol was obtained as white crystals. Yield: 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 6.22 (s, NH), 5.81 (m, 1H), 4.93 (m, 2H), 3.96 (m, 1H), 3.84 (m, 2H), 3.78 (m, 2H), 2.72 (2 OH), 2.24 (t, 2H), 2.04 (q, 2H), 1.65 (m, 2H), 1.38-1.25 (m, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 174.39 (CH<sub>2</sub>-CO-NH), 139.33 (CH<sub>2</sub>=CH-CH<sub>2</sub>), 114.31 (CH<sub>2</sub>=CH-CH<sub>2</sub>), 63.76 (CH-(CH<sub>2</sub>-OH)<sub>2</sub>), 52.49 (CH-(CH<sub>2</sub>-OH)<sub>2</sub>), 36.94 (CH<sub>2</sub>-CO-NH), 33.92 (CH<sub>2</sub>=CH-CH<sub>2</sub>), 29.44-29.02 (CH<sub>2</sub>), 25.84 (CH<sub>2</sub>-CH<sub>2</sub>-CO-NH).

#### Synthesis of **NH-Und-6CC**

In a 500 mL round bottom flask at 0°C equipped with magnetic stirrer, **NH-Und-1,3-diol** (1.0 equiv.) and ethyl chloroformate (4.0 equiv.) were dissolved in 300 mL THF. To the cold reaction mixture, triethylamine (4.0 equiv.) was added dropwise over 10 min. The reaction was allowed to proceed in ice-cold conditions for about 1 hour and then allowed to proceed at room temperature overnight. The precipitated solids were filtered off and the volatiles were removed to result in crude product, which was subjected to flash column chromatography, using a gradient of DCM (100 %) to DCM (95 %) and methanol (5 %) solvent mixture, followed by the removal of volatiles to result in white solid **NH-Und-6CC** as the functional monomer. Yield: 55%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.63 (s, NH), 5.76 (m, 1H), 4.93 (m, 2H), 4.54-4.40 (m, 5H), 2.22 (t, 2H), 1.99 (q, 2H), 1.60 (t, 2H), 1.25 (m, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 174.33 (CH<sub>2</sub>-CO-NH), 148.66 (OCOO), 139.19 (CH<sub>2</sub>=CH-CH<sub>2</sub>), 114.21 (CH<sub>2</sub>=CH-CH<sub>2</sub>), 71.45 (CH-(CH<sub>2</sub>-OCOO)<sub>2</sub>), 40.94 (CH-(CH<sub>2</sub>-OCOO)<sub>2</sub>), 36.14 (CH<sub>2</sub>-CO-NH), 33.81 (CH<sub>2</sub>=CH-CH<sub>2</sub>), 29.34-28.93 (CH<sub>2</sub>), 25.57 (CH<sub>2</sub>-CH<sub>2</sub>-CO-NH).

#### Polymerization of **NH-Und-6CC**

All polymerizations were performed under inert atmosphere (nitrogen) using standard Schlenk, vacuum line, and glovebox techniques. In a 15 mL schlenk flask containing a magnetic stirrer, in glove box, **NH-Und-6CC** (50 equiv.), BnOH (2.0 equiv.) and Schreiner TU (1.0 equiv.) were dissolved in dry DCM ([**NH-Und-6CC**] = 2 mol.L<sup>-1</sup>). To this solution, DBU (1.0 equiv.) was added to initiate polymerization. The reaction mixture was allowed to stir at room temperature. After 5h, the reaction was quenched by the addition of benzoic acid (2 equiv.) and purified by precipitation in cold methanol to yield P(**NH-Und-6CC**). The polymer was obtained as white solid. Yield: 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 5.80 (m, 1H), 4.93 (d, 2H), 4.64-3.93 (m, 5H), 2.24 (m, 2H), 2.01 (q, 2H), 1.62 (m, 2H), 1.28 (m, 10H). SEC (THF, RI): Mn= 5 700 g.mol<sup>-1</sup>, Đ=1.07.

### Synthesis of SH-Cinnamoyl

In a round-bottom flask equipped with magnetic stirrer, cinnamoyl chloride (20 g, 120 mmol) was dissolved in toluene (300 mL). 2-mercaptoethanol (9.3 g, 120 mmol, 1 equiv.) was added and the mixture was stirred under reflux for 2 hours. The solvent was removed on rotary evaporator yielding to **SH-Cinnamoyl** as viscous liquid without further purification. Yield= 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.73 (d, 1H), 7.53 (m, 2H), 7.38 (m, 3H), 6.47 (d, 1H), 4.33 (t, 2H), 2.82 (q, 2H), 1.55 (t, SH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 167.45 (CH-COO-CH<sub>2</sub>), 146.56 (Ph-CH=CH), 133.19-128.31 (Ph), 118.21 (CH=CH-COO), 66.95 (CH-COO-CH<sub>2</sub>), 23.74 (CH<sub>2</sub>-CH<sub>2</sub>-SH)

### Grafting of SH-Cinnamoyl on P(NH-Und-6CC)

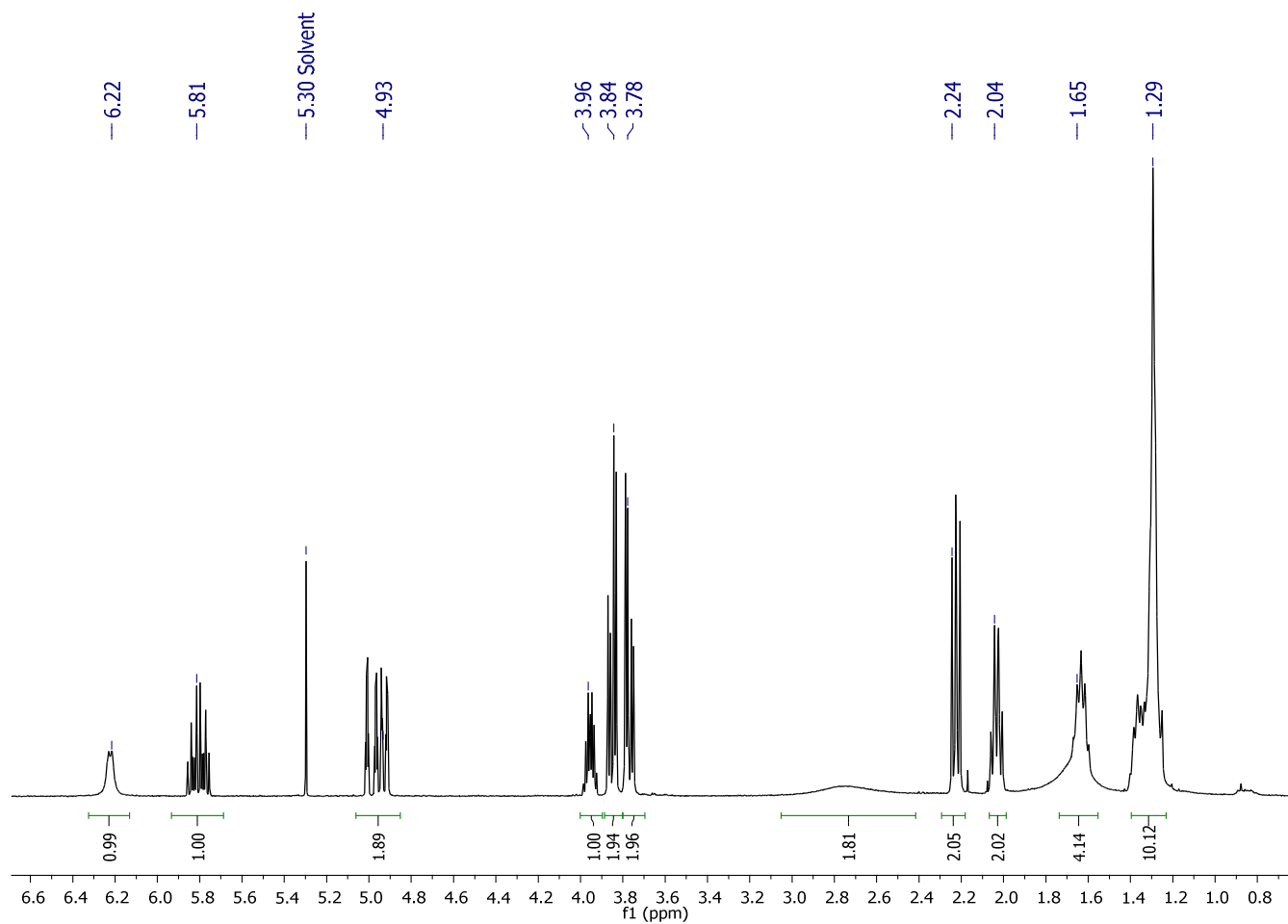
In a round-bottom flask equipped with magnetic stirrer, P(NH-Und-6CC) (1 equiv.), **SH-Cinnamoyl** (3 equiv.) and V70 (1 mol.%) were dissolved in DCM (1 mol.L-1). The reaction was allowed to proceed at 40°C during the appropriate period of time. The solvent was removed to result in c<sub>x</sub>-P(NH-Und-6CC) which was purified by dialysis in methanol (1L for 1g of polymer, 48h, and methanol was changed after 24h). Grafting of cinnamoyl moieties were calculated by <sup>1</sup>H NMR (Figure S14) according to **Error! Reference source not found.**

$$\% \text{ Cinnamoyl} = \frac{\int H_{11}}{\int H_7 + \int H_{11}}$$

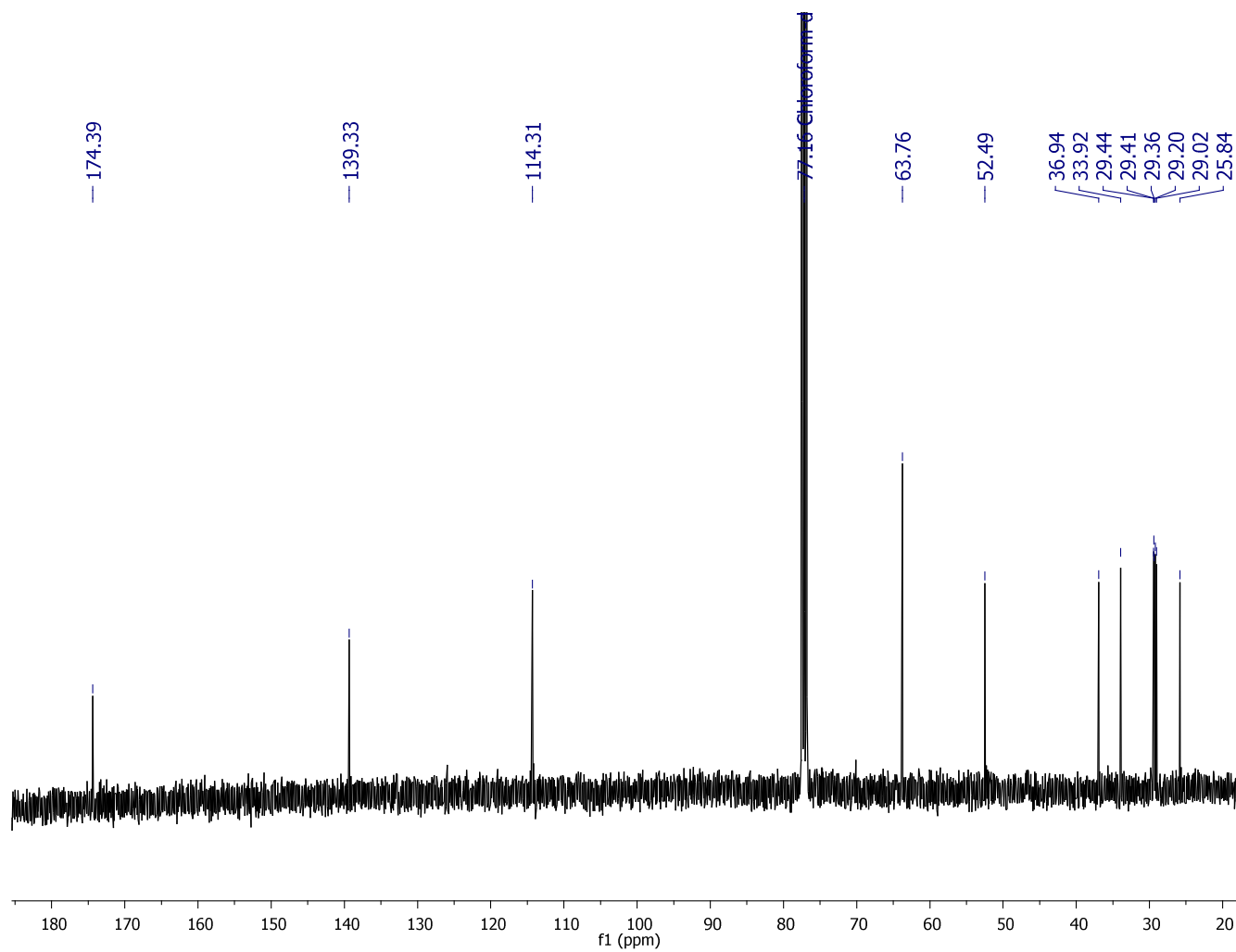
**Equation 1:** Formula used for the calculation of cinnamoyl percentage grafted after the thiol-ene reaction using <sup>1</sup>H NMR integrations of characteristic protons (H<sub>11</sub> and H<sub>7</sub>) in CDCl<sub>3</sub>

### Photo-cross-linking of c<sub>x</sub>-P(NH-Und-6CC)

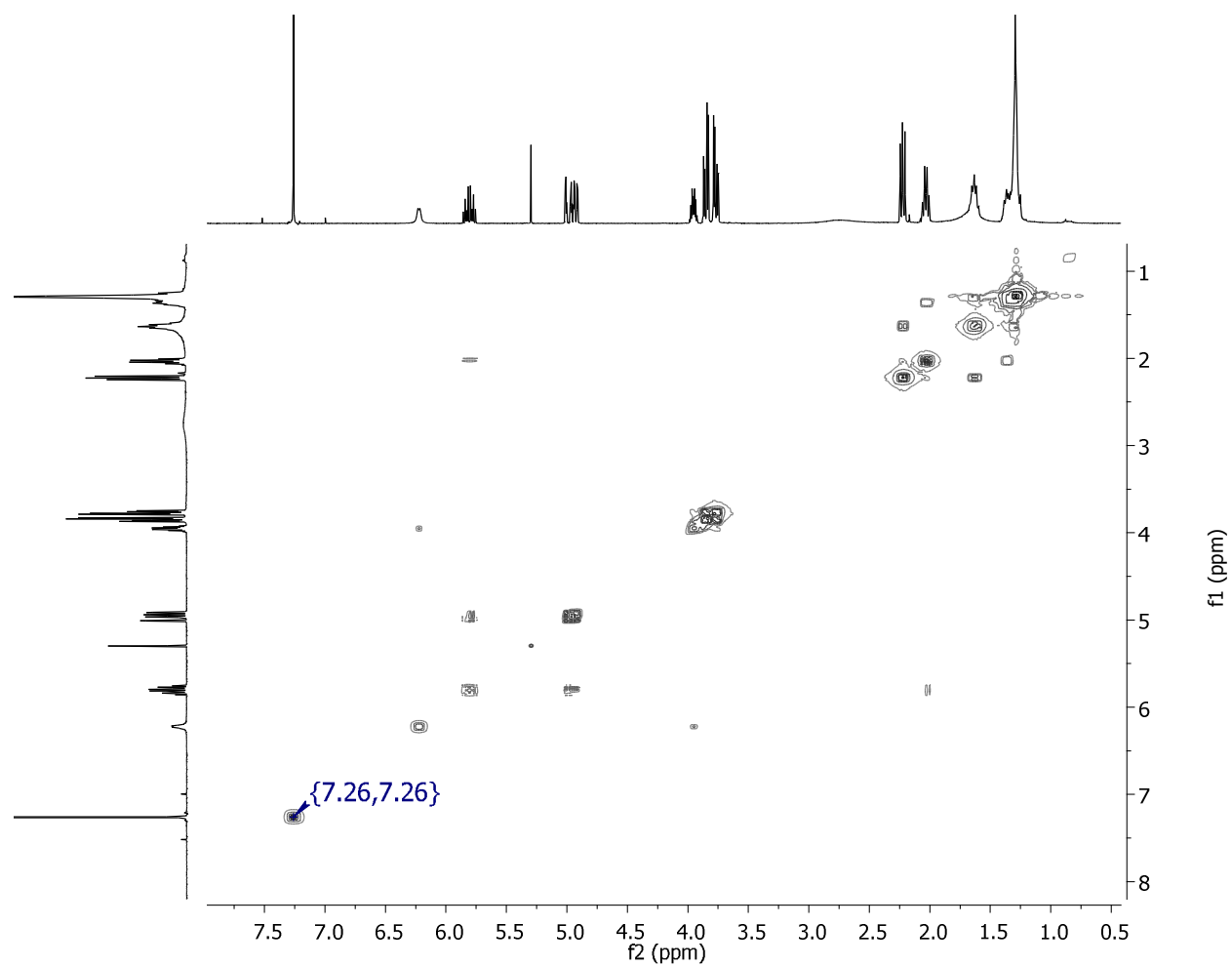
The polymer c<sub>x</sub>-P(NH-Und-6CC) was dissolved in chloroform (CHCl<sub>3</sub>) at 1g.mL<sup>-1</sup> in a vial. After evaporation of the solvent, the films were exposed to UV light at a distance of 9 cm, wavelength λ = 365 nm, for 12 h on each side to form a network structure CL-c<sub>x</sub>-P(NH-Und-6CC) and to ensure uniform curing.



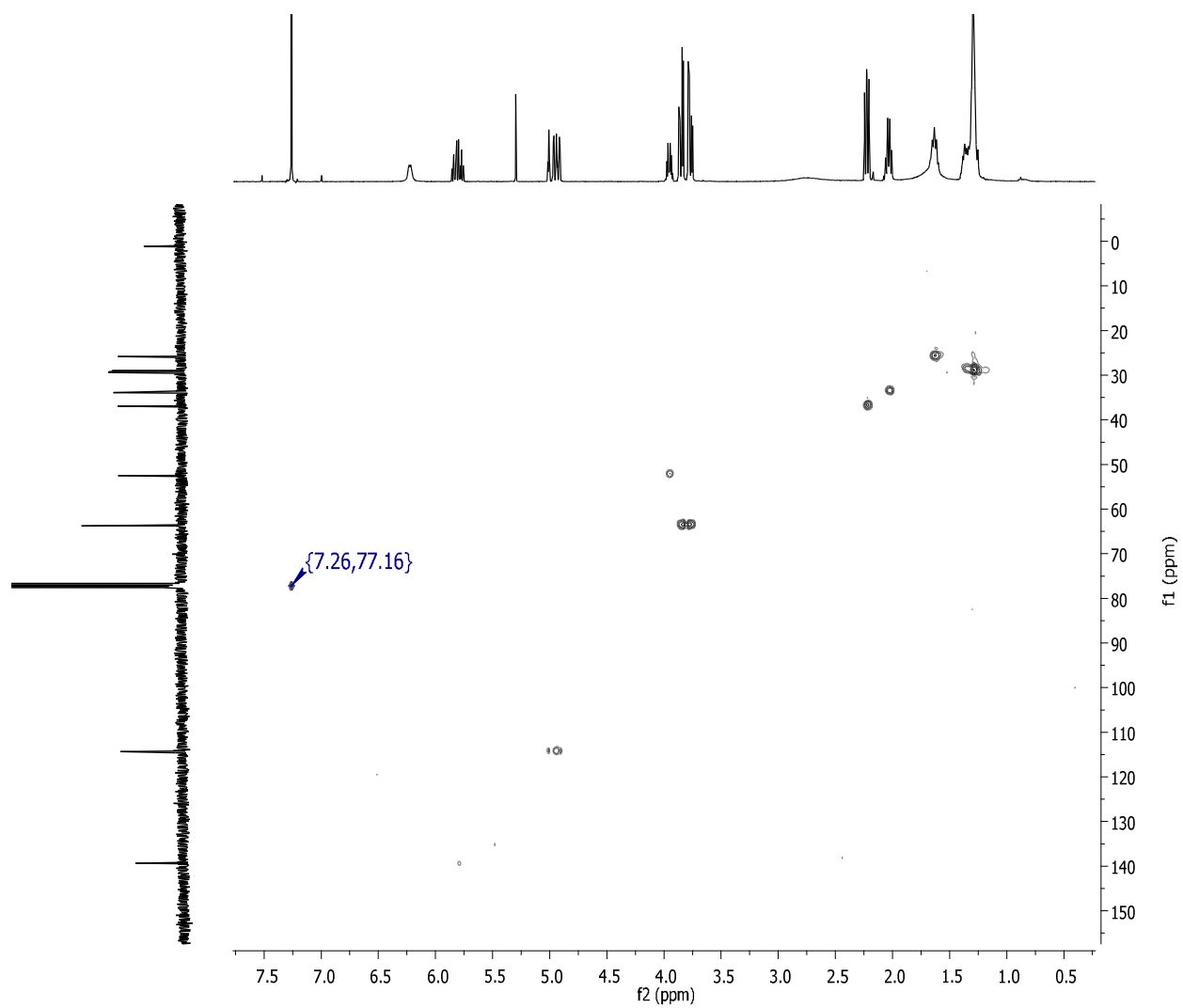
**Figure S1.** <sup>1</sup>H NMR spectrum of NH-Und-1,3-diol in CDCl<sub>3</sub>



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of NH-Und-1,3-diol in  $\text{CDCl}_3$

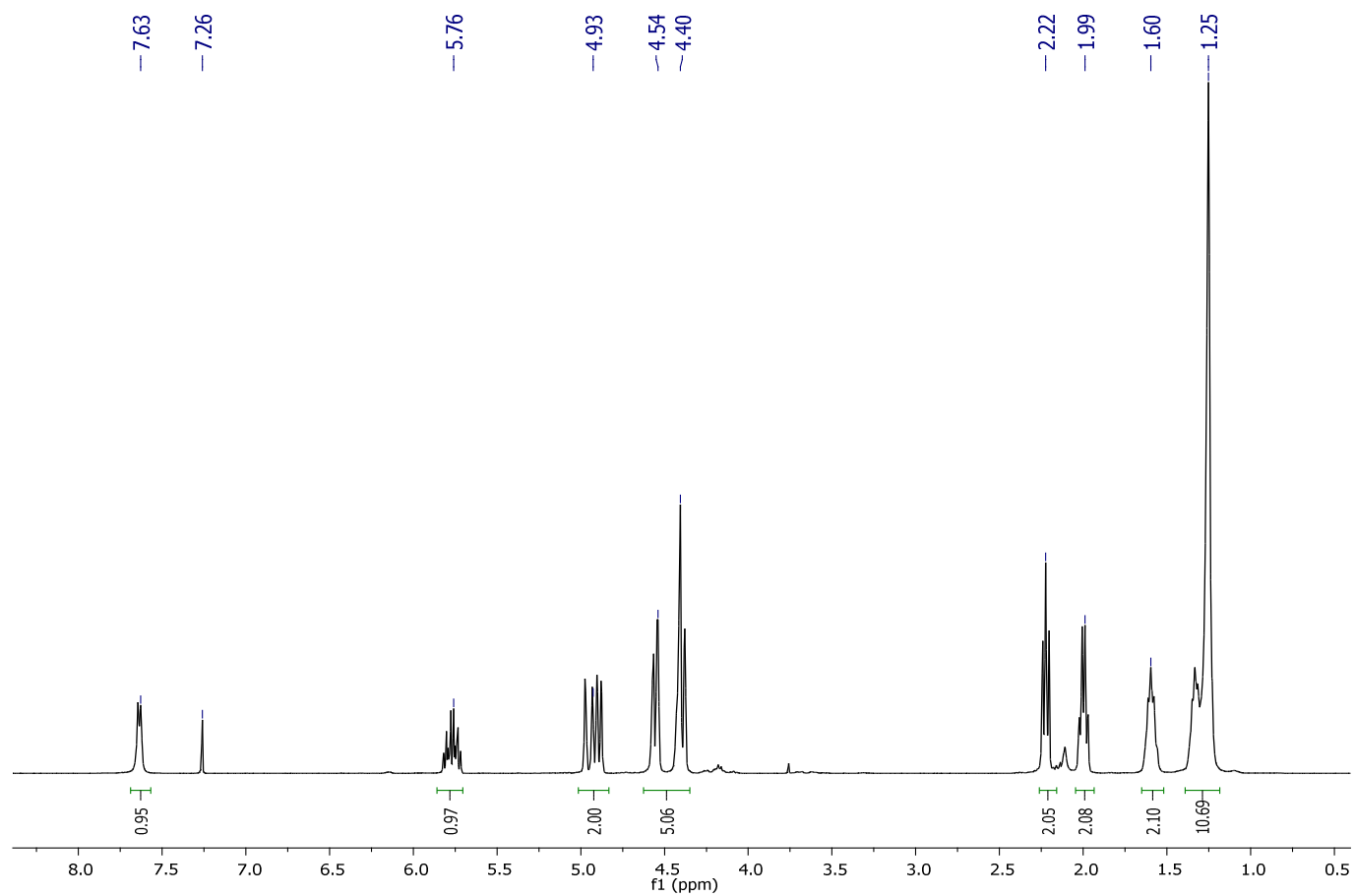


**Figure S3.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of NH-Und-1,3-diol in  $\text{CDCl}_3$

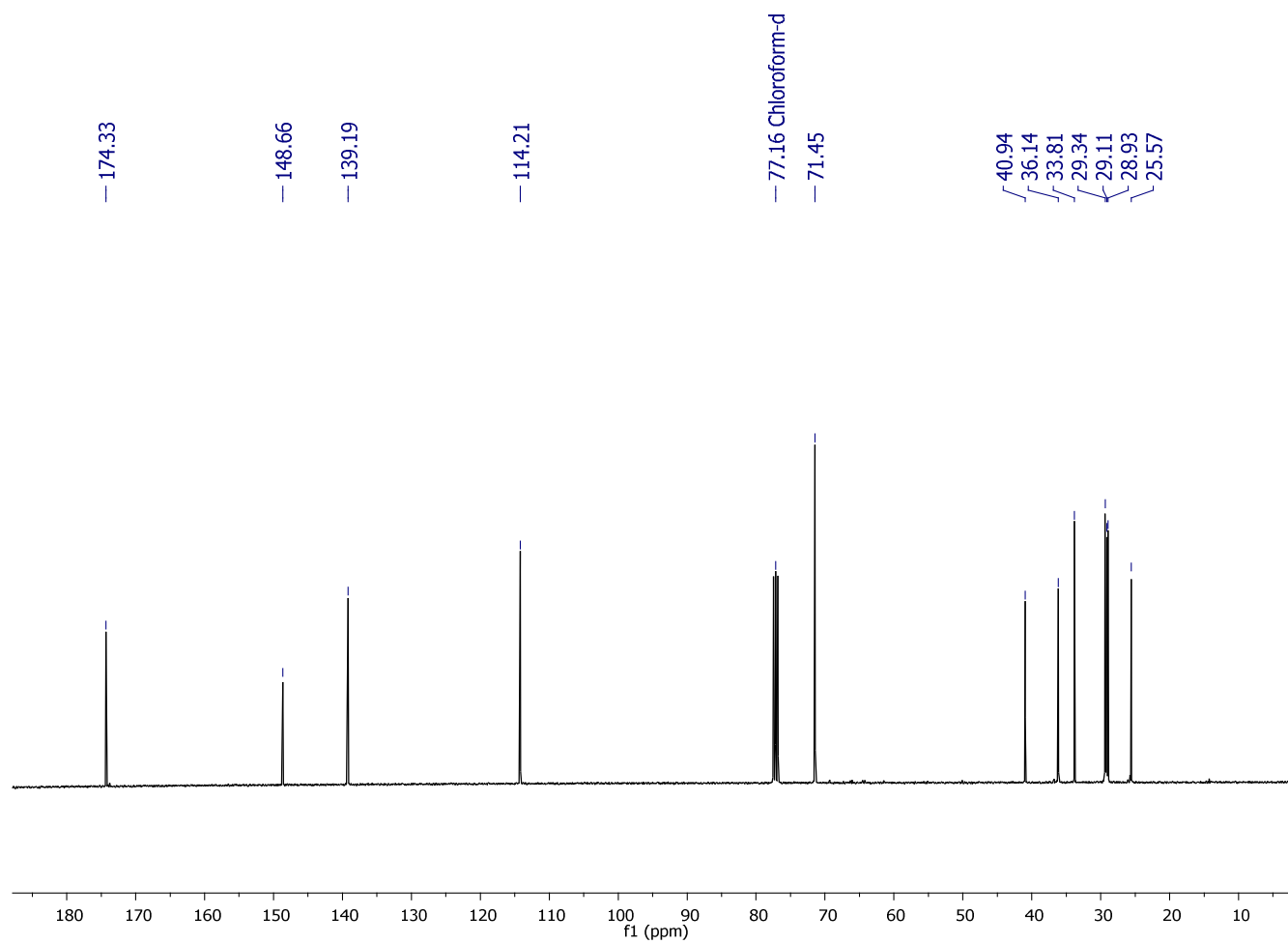


**Figure S4.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of **NH-Und-1,3-diol** in  $\text{CDCl}_3$

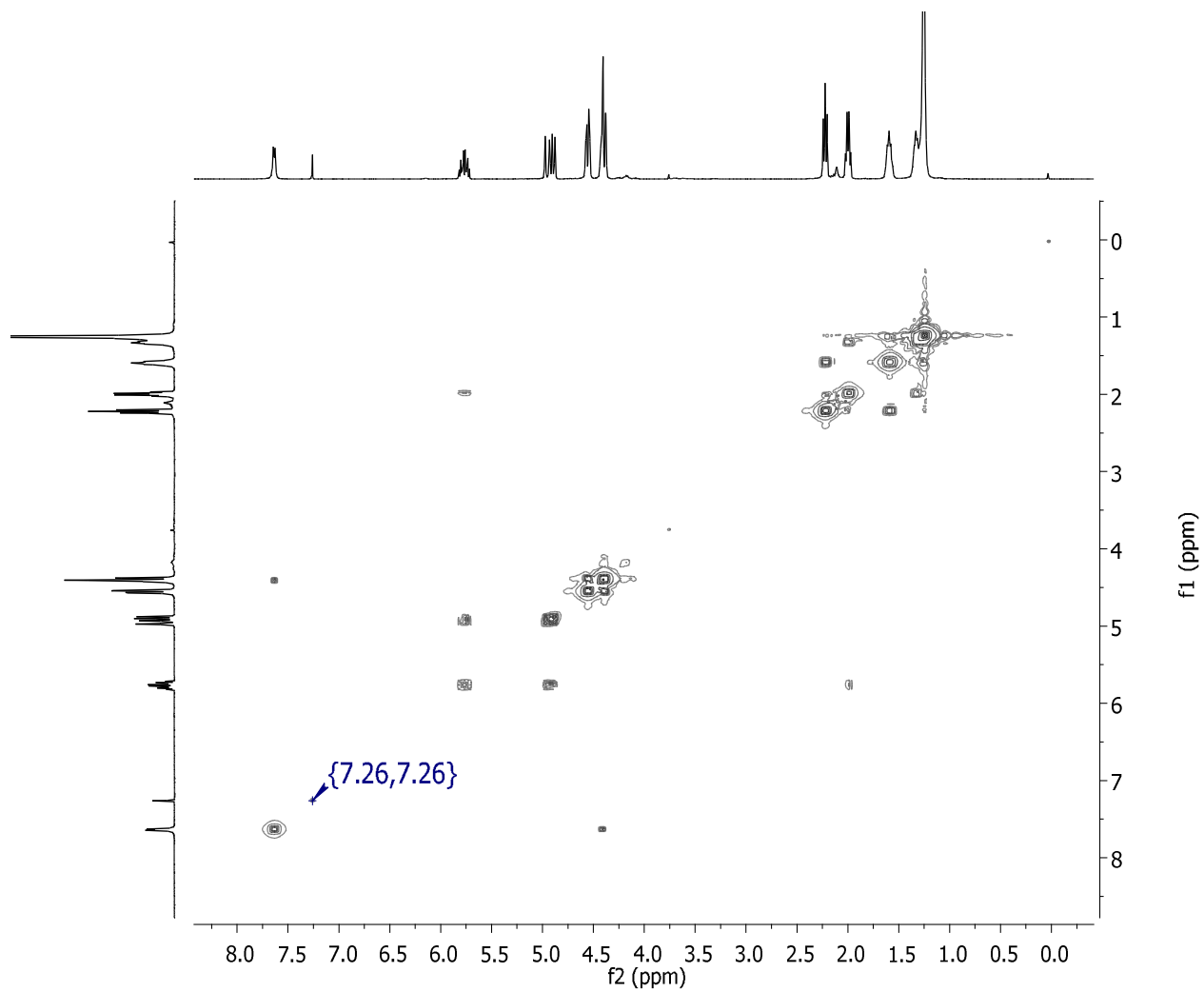




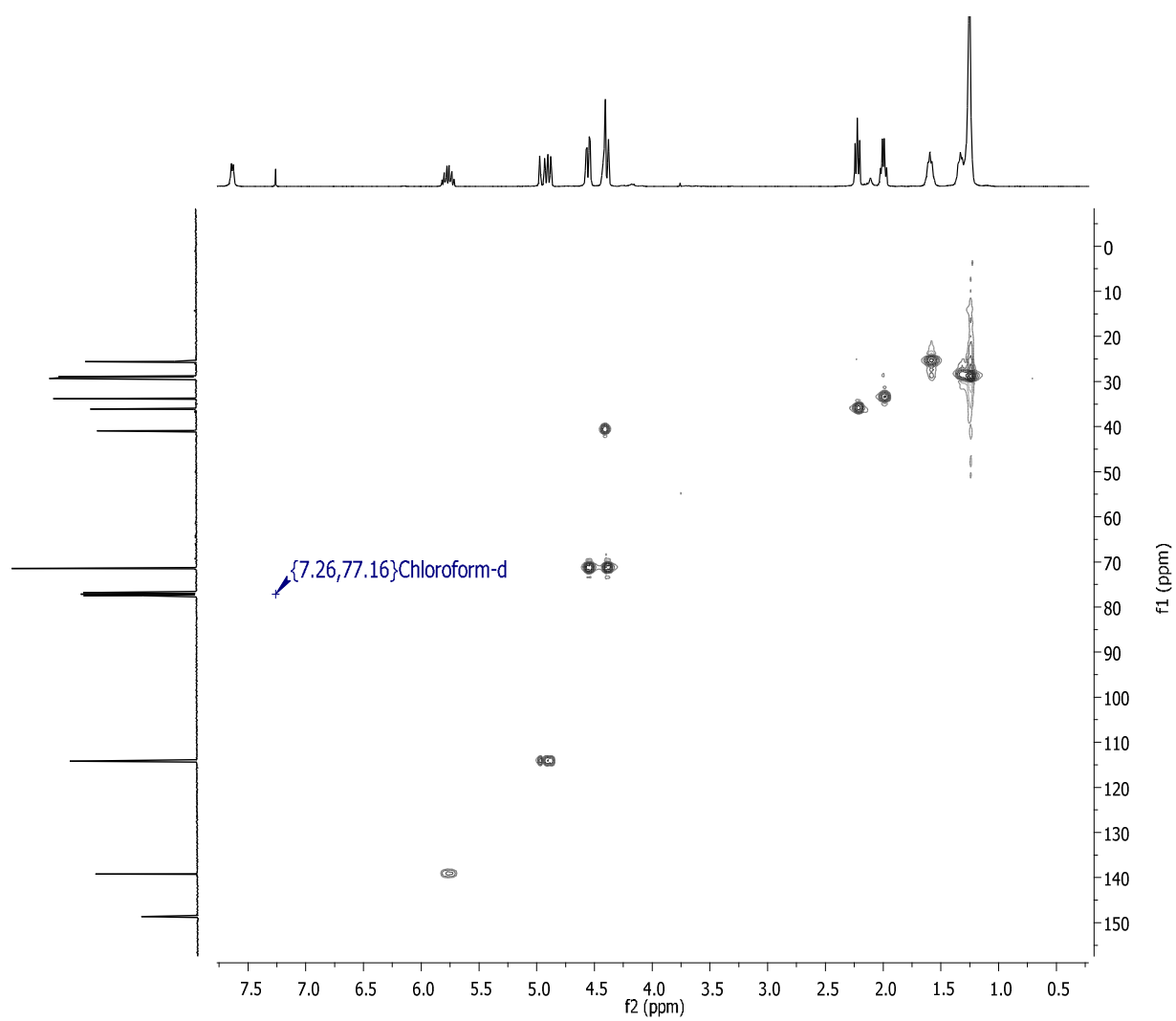
**Figure S5.** <sup>1</sup>H NMR spectrum of NH-Und-6CC in CDCl<sub>3</sub>



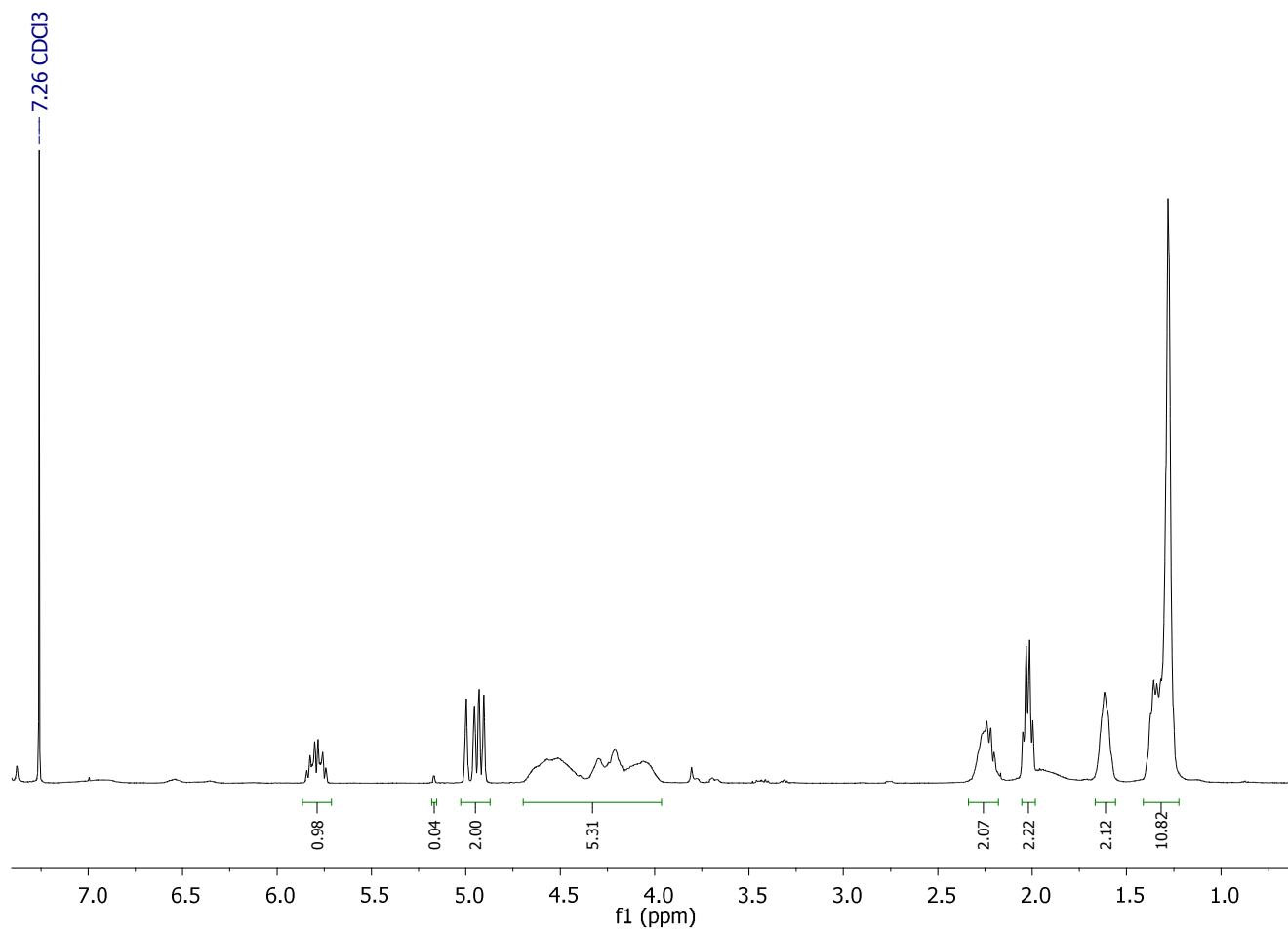
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of NH-Und-6CC in  $\text{CDCl}_3$



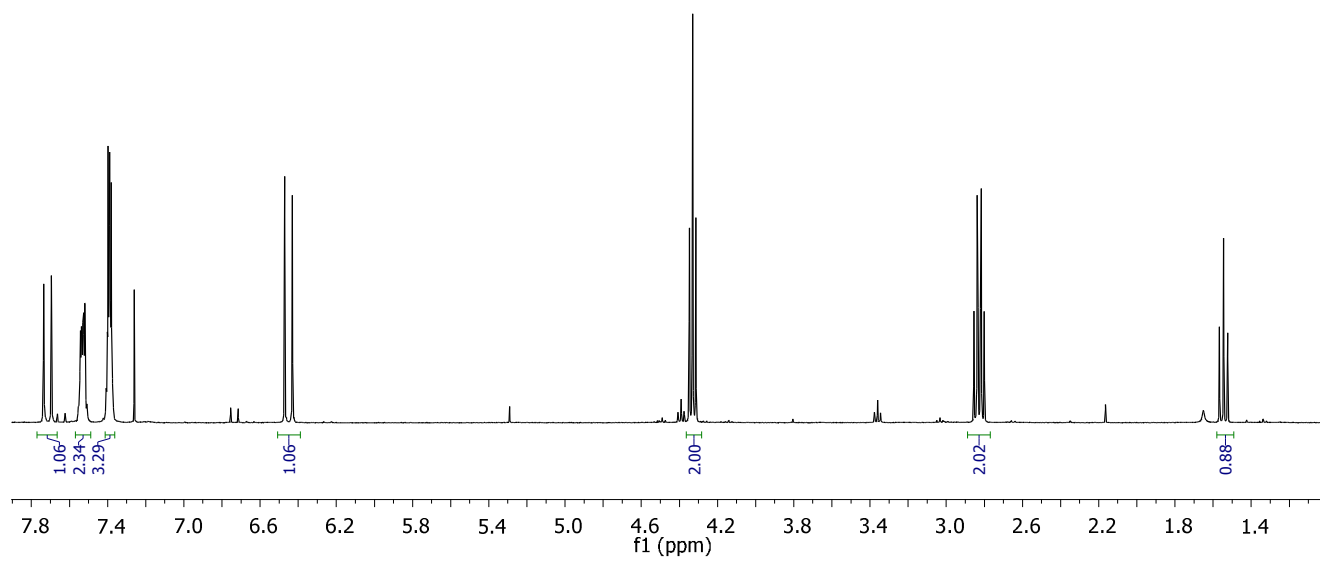
**Figure S7.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **NH-Und-6CC** in  $\text{CDCl}_3$



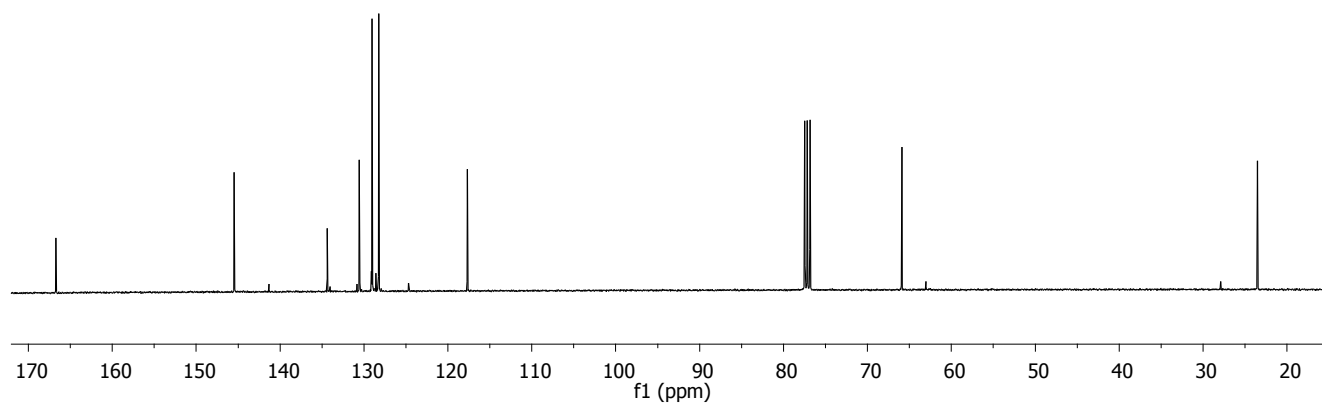
**Figure S8.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of **NH-Und-6CC** in  $\text{CDCl}_3$



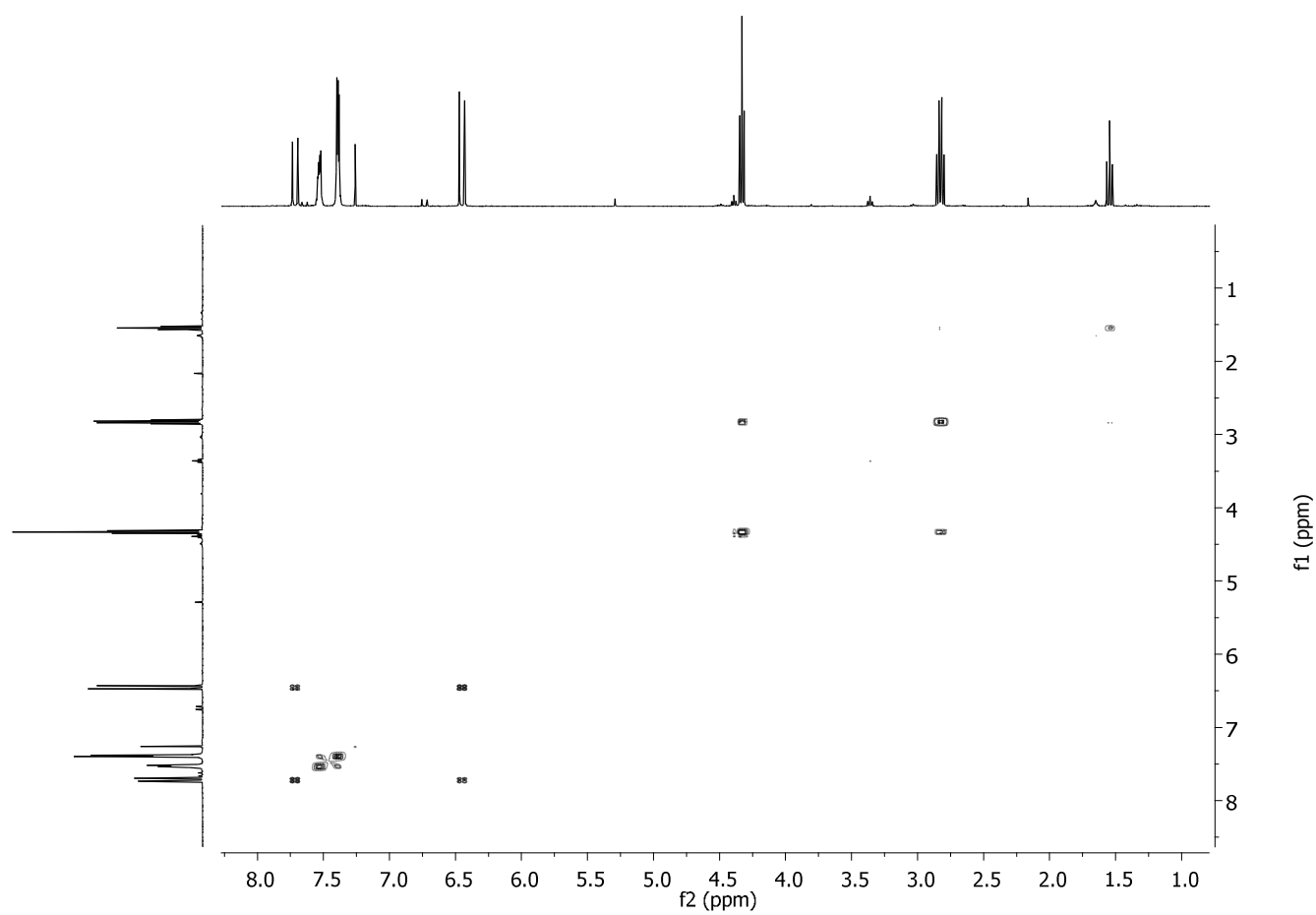
**Figure S9.** <sup>1</sup>H NMR spectrum of P(NH-Und-6CC) in CDCl<sub>3</sub>



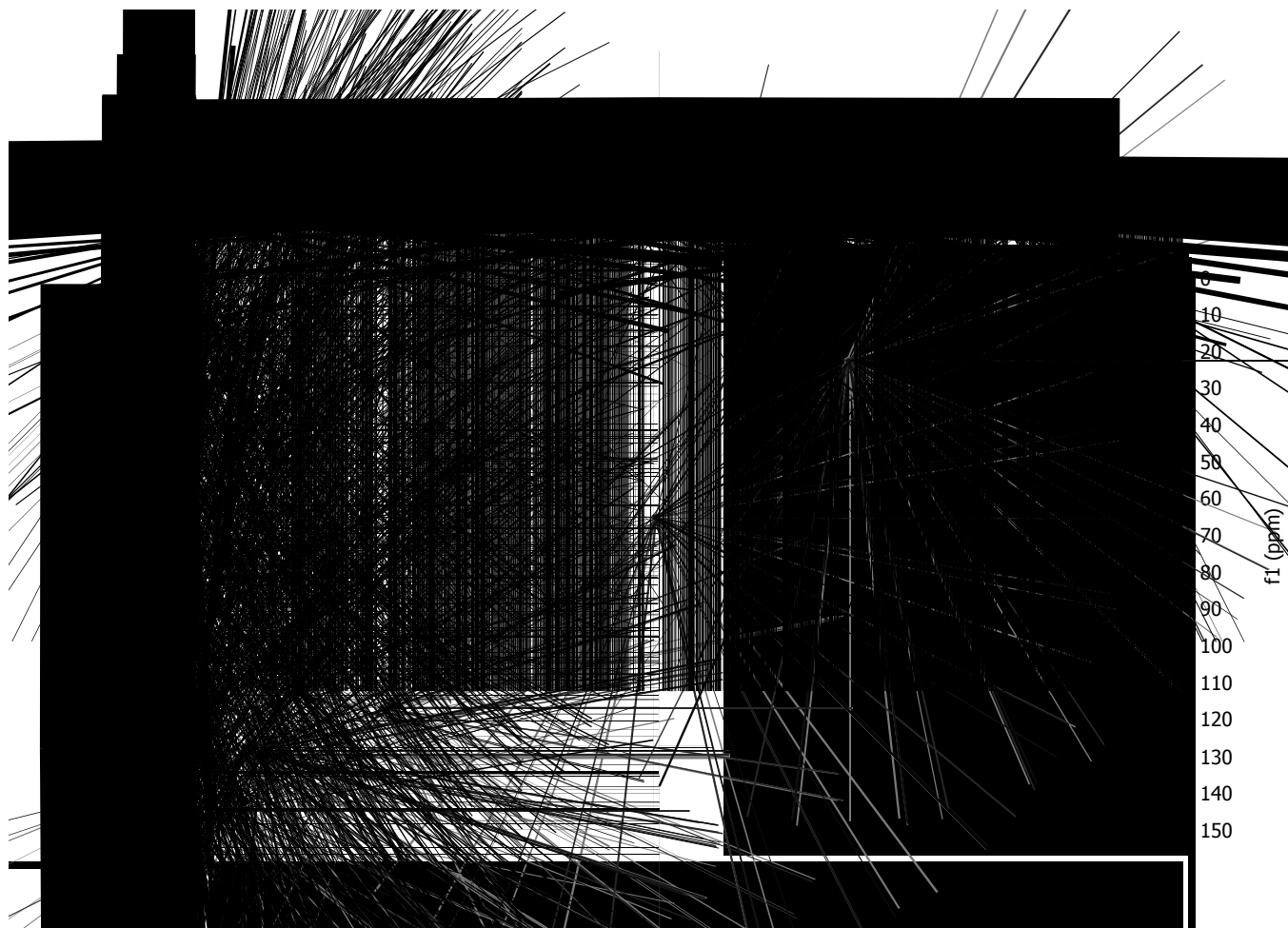
**Figure S10.** <sup>1</sup>H NMR spectrum of SH-Cinnamoyl in CDCl<sub>3</sub>



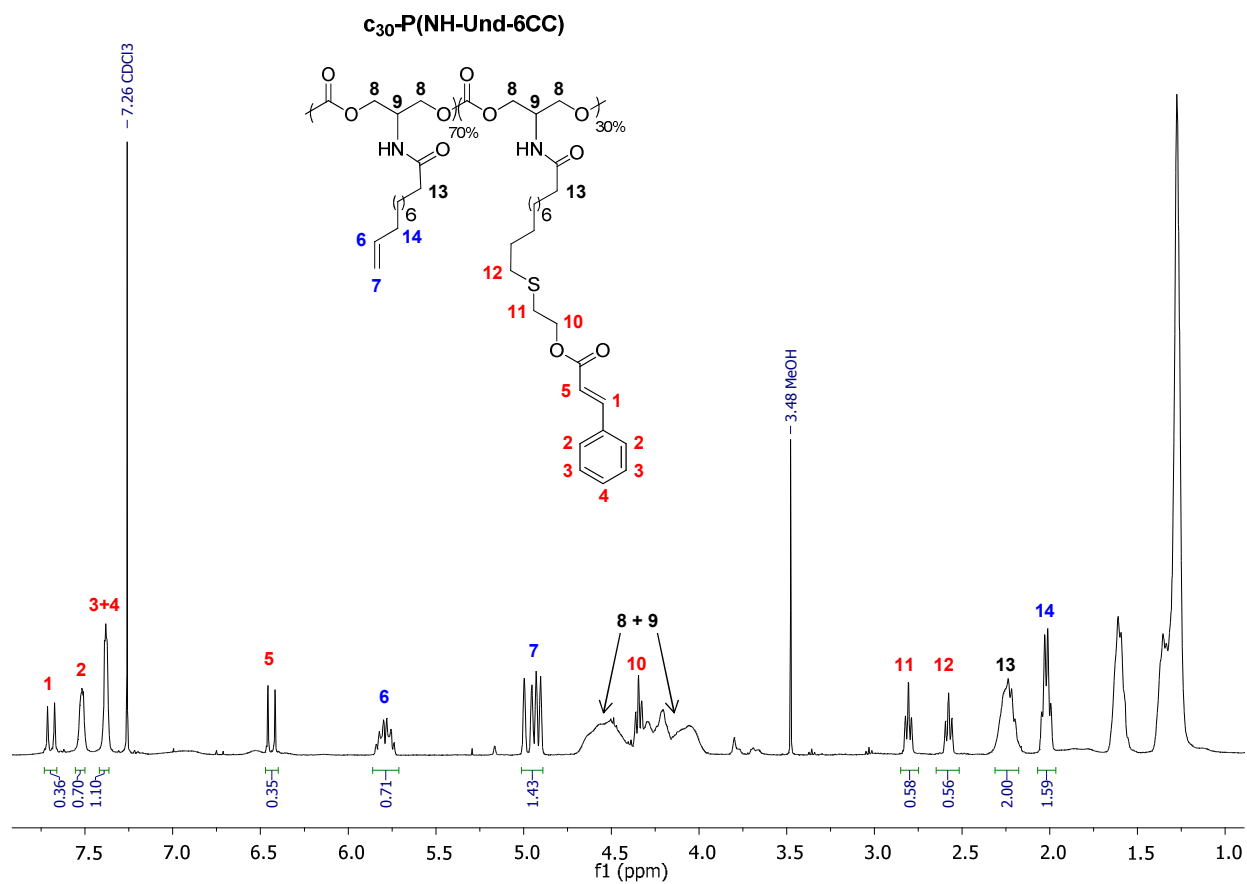
**Figure S11.**  $^{13}\text{C}$  NMR spectrum of **SH-Cinnamoyl** in  $\text{CDCl}_3$



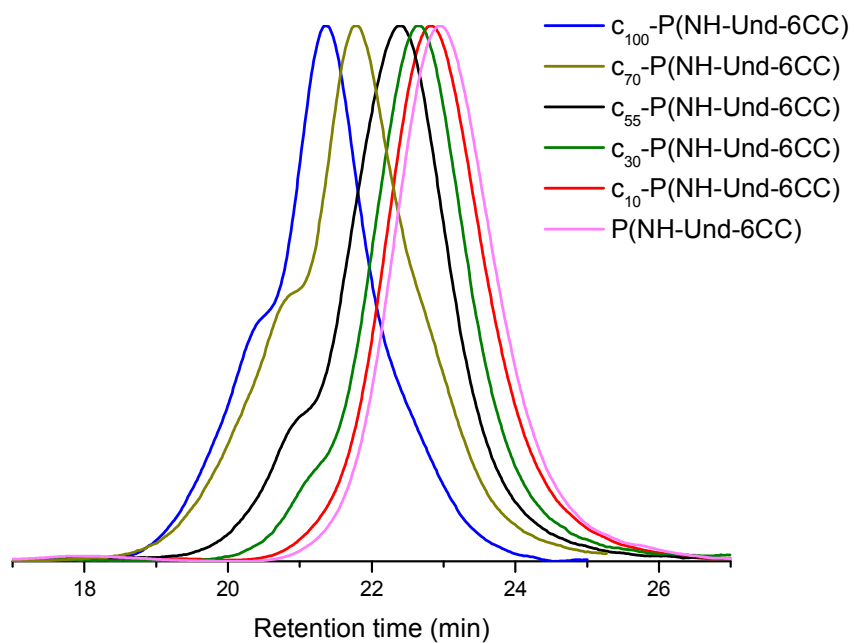
**Figure S12.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **SH-Cinnamoyl** in  $\text{CDCl}_3$



**Figure S13.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of **SH-Cinnamoyl** in  $\text{CDCl}_3$

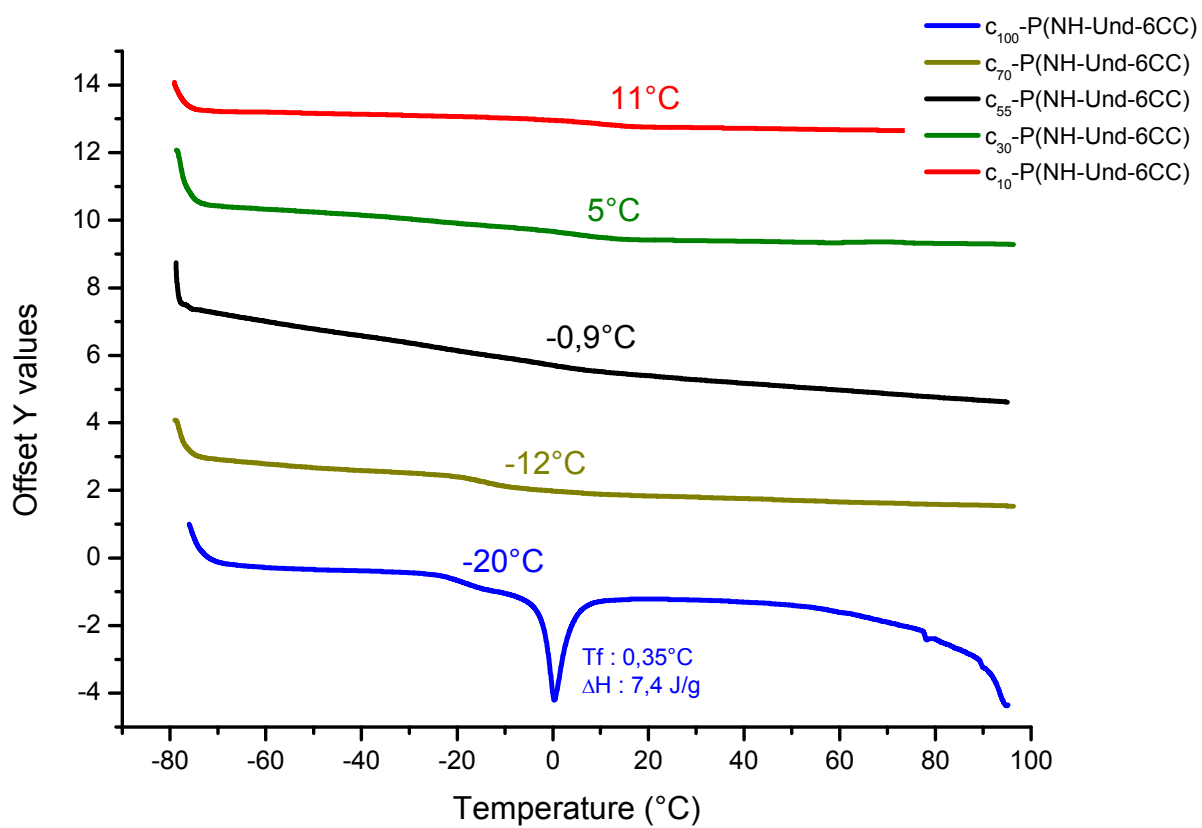


**Figure S14.** <sup>1</sup>H NMR spectrum of cinnamoyl-containing polycarbonate in THF. Example with 30 mol.% of cinnamoyl content grafted on P(NH-Und-6CC)

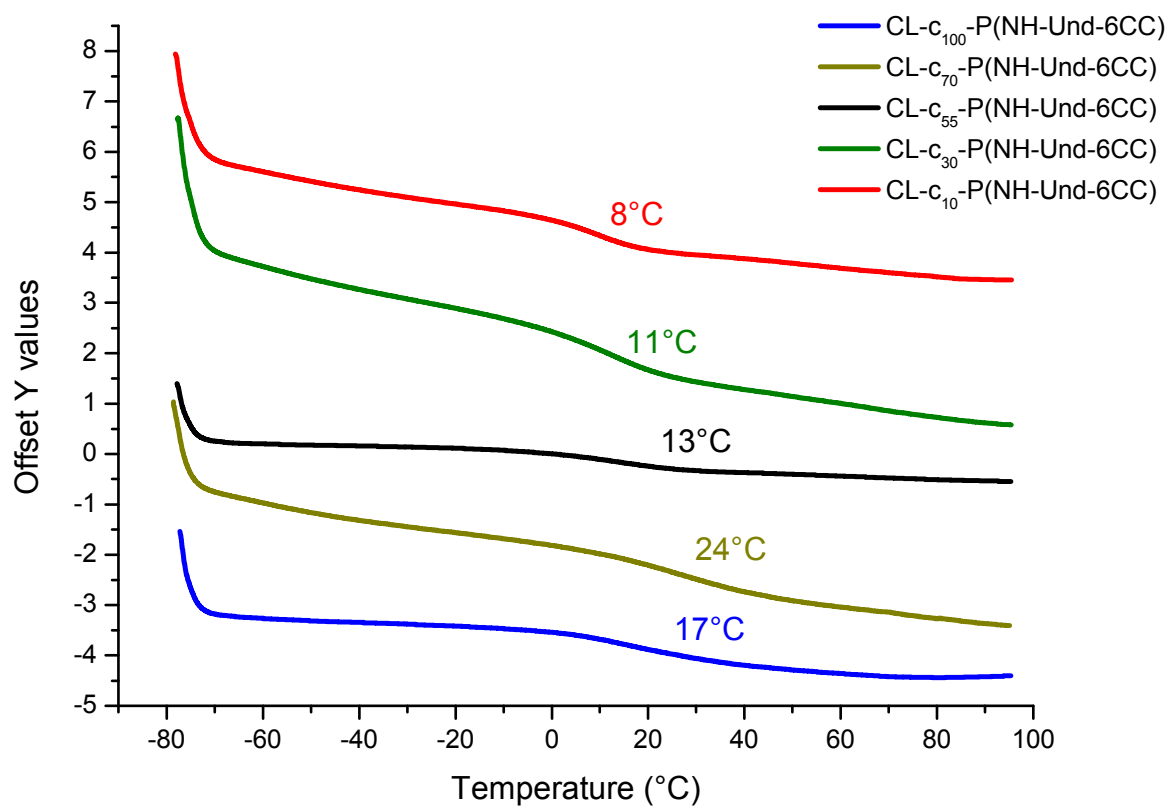


**Figure S15.** SEC traces of cinnamoyl-containing polymers in THF (Polystyrene standards)

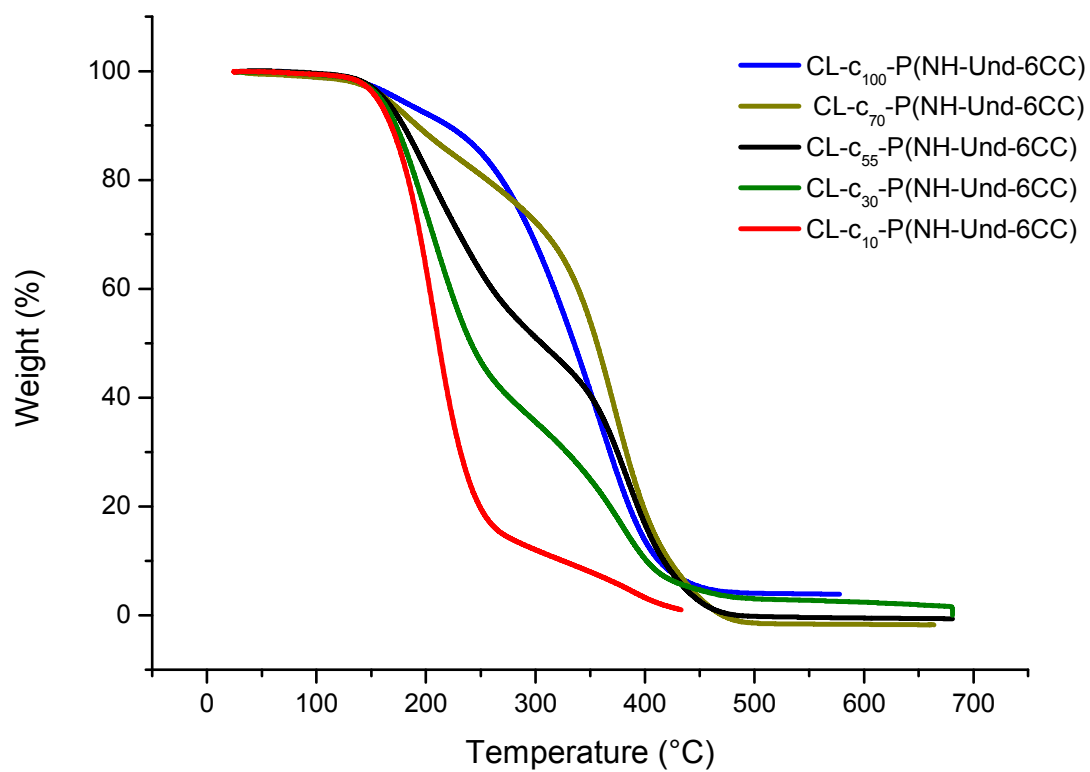




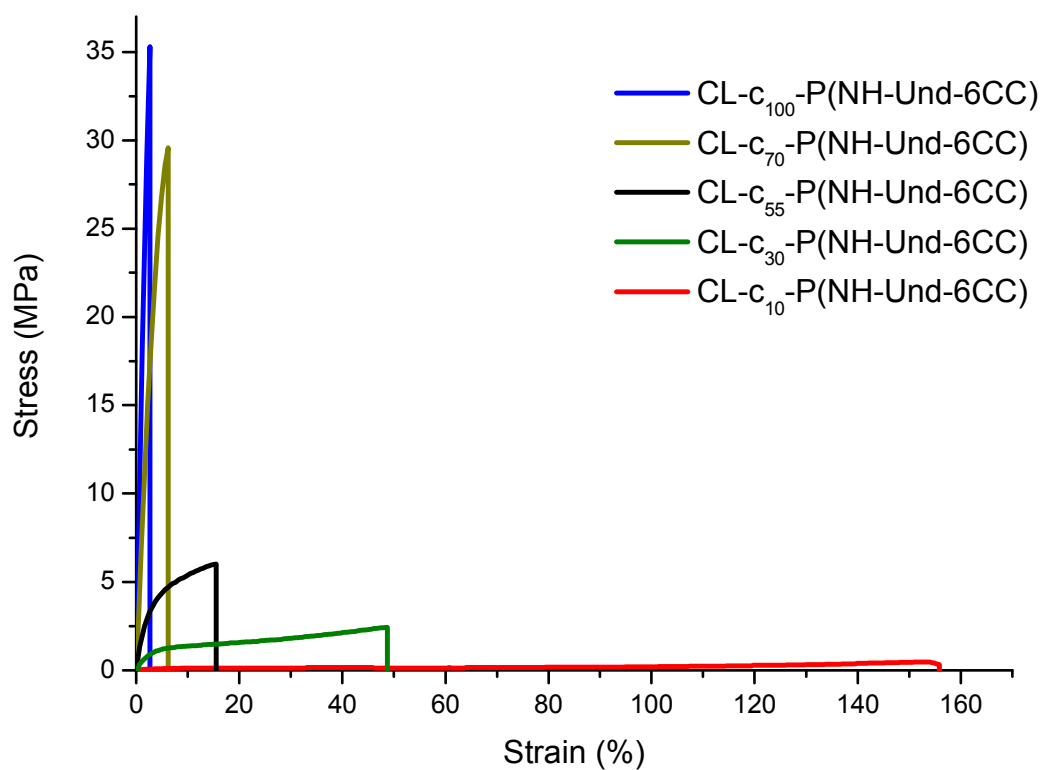
**Figure S16.** Second heating scans of DSC measurement of cinnamoyl-containing polycarbonates



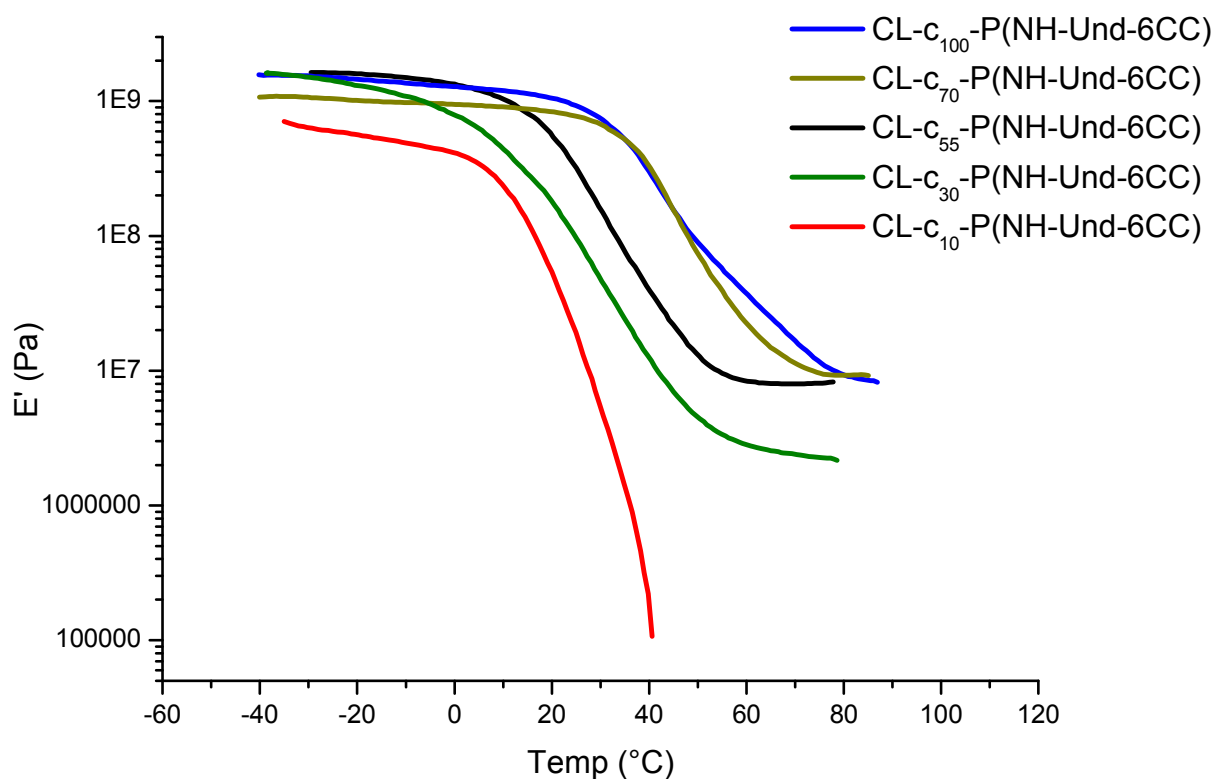
**Figure S17.** Second heating scans of DSC measurement of cross-linked cinnamoyl-containing polycarbonates



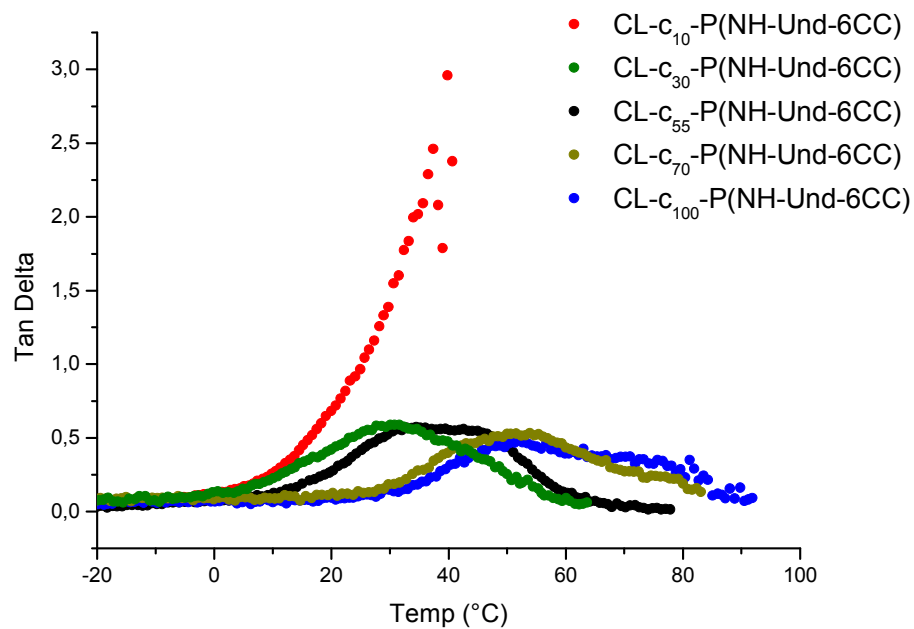
**Figure S18:** TGA analysis of cross-linked cinnamoyl-containing polycarbonates



**Figure S19.** Stress–strain curves at room temperature of the polycarbonate networks prepared with the [2+2] photochemical cyclo-addition of pendant cinnamoyl moieties



**Figure S20.** Thermo-mechanical experiments showing the tensile storage modulus ( $E'$ ) measured using DMA at an oscillation frequency of 1 Hz



**Figure S 21:** Thermo-mechanical experiments showing Tan Delta measured using DMA at an oscillation frequency of 1 Hz