

## Supporting Information

# Synthesis of Polyurethanes Through the Oxidative Decarboxylation of Oxamic Acids: a new gateway toward self-blown foams

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# 1. Experimental section.

## a. Materials.

Dichloromethane (DCM) was dried over activated alumina columns on a PureSolv Solvent Purification System.

Phenyliodine diacetate (PIDA) and oxalyl chloride were supplied by TCI. Trifluoroacetic acid (TFA), 1-hexanol, 1,3,5-trimethylbenzene were supplied by Alfa Aesar. 1,6-diaminohexane, PEG-1500, trimethylolpropane ethoxylate ( $M_n \sim 1014$  g/mol), acetic acid, tert-butanol, butylisocyanate were supplied by Sigma Aldrich. Triethylamine was supplied by Acros Organics. Ethoxylated poly(dimethylsiloxane) (67674-67-3) was supplied by ABCR.

All reagent-grade chemicals were purchased from commercial suppliers and were directly used without further purification unless otherwise indicated.

PEG-1500 and trimethylolpropane ethoxylate were dried using azeotropic distillation with toluene (x3) prior use.

## b. Characterizations.

**$^1\text{H}$  and  $^{13}\text{C}$  Nuclear Magnetic Resonance (NMR)** analysis were performed using either a Bruker Avance III HD 400 spectrometer at 25°C, at 400,2 MHz and 100,7 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  respectively, or a Bruker Avance Neo 400 spectrometer at 25°C, at 400,3 MHz and 100,7 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ( $\delta=7.26$  ppm for  $\text{CDCl}_3$ ,  $\delta=2.50$  ppm for  $\text{DMSO-d}_6$ ).

**Steric Exclusion Chromatography (SEC)** analysis were performed using HFIP as eluent on an Ultimate 3000 system from ThermoScientific equipped with a diode array detector (DAD), a multi-angles laser light scattering detector (MALS) and a differential refractive index detector (dRI) from Wyatt, using two Shodex Asahipack gel column GF310 and GF510 (300 x 7.5 mm for 500 to 300000 Da) at 50 °C at a flow rate of 0.5 mL/min. **The instrument was calibrated with poly(methyl methacrylate) standards.**

**Fourier Transform Infrared (FTIR)** analysis were performed using a Bruker Vertex 70 FTIR spectrometer in ATR mode equipped with a GladiATR diamond with temperature control. The kinetics analysis could be carried out *in-situ* as the reactive systems were deposited directly on the heated diamond. The spectra were acquired using 64 scans and 32 scans for the kinetics analysis.

**Differential Scanning Calorimetry (DSC)** analysis were performed on a DSC Q100 apparatus from TA Instruments. For each sample, two heating cycles from -75 to 200 °C at 10 °C/min were performed. The glass transition temperatures were calculated from the second heating run.

**Thermogravimetric (TGA)** analysis were performed on the TGA-Q500 system from TA Instruments at a heating rate of 10 °C/min under a nitrogen atmosphere from room temperature to 600 °C.

**Compression tests** were conducted using a DMA Q850 apparatus from TA Instruments. The stress required to attain 30% of deformation from the initial thickness of the sample was

measured using a ramp of 100 %/min deformation going up to a strain of 70%, with a preload of 0.02 N.

**Gel content** was measured by weighing a sample of the material, then plunging it in DCM for 24h, and changing the solvent each day until no more weight variation of the sample swollen by the solvent. The sample was then dried and its final mass compared with the initial one.

**Scanning Electron Microscopy (SEM)** images were obtained using a FEI QUANTA 200 microscope in partial vacuum at 50 Pa and 7.00 kV, without metal-plating. For each foam, 2-3 samples were analyzed perpendicularly to the foaming direction at different heights. The morphologies of the foams were then analyzed using the software ImageJ-Fiji by measuring at least 100 cells using the ellipsoidal tool and a combination of plugins and macros to semi-automatize the measurements. The diameter of the cells was averaged between the long and the short length of the ellipses. While it may not be the most accurate way to measure the real cell diameter, as they are 2D image of slices of 3D structures, it was the most accessible for us.<sup>[1]</sup>

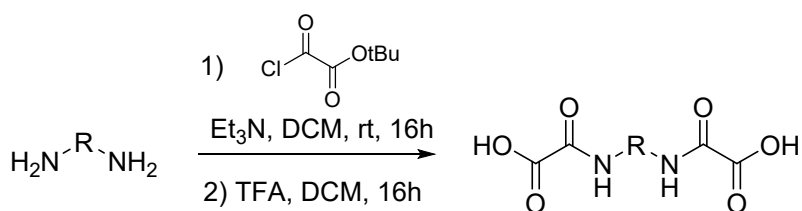
### c. Synthesis of precursors and model molecules.

#### i. Synthesis of bis-oxamic acids

##### Synthesis of tert-butyl-2-chloro-2-oxoacetate:

A mixture of tert-butanol (20.1 mL, 210.0 mmol) in Et<sub>2</sub>O (50.0 mL) was added dropwise to a stirred solution of oxalyl chloride (18.1 mL, 210.8 mmol) in Et<sub>2</sub>O (100.0 mL) at 0 °C under N<sub>2</sub>. The resulting mixture was stirred for 30 min at 0 °C and then 16h at room temperature. The solvent was evaporated to afford 34.59 g of tert-butyl oxalyl chloride as a colorless oil.

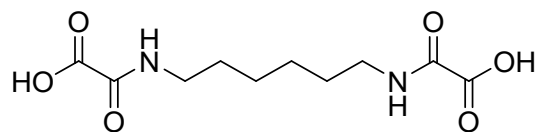
##### Procedure for the preparation of bis-oxamic acids:



The diamine (15.00 mmol, 1 eq.) was dissolved in DCM (100 mL) at 0 °C, under N<sub>2</sub> atmosphere. Triethylamine (36.00 mmol, 2.4 eq.) was added into the mixture followed by addition of tert-butyl-2-chloro-2-oxoacetate (36.00 mmol, 2.4 eq) dropwise. The solution was then stirred at room temperature for at least 16h. The reaction mixture was then washed successively with water (100 mL), and brine (100 mL), dried over sodium sulfate and concentrated under reduced pressure resulting in a crude solid product. The crude product was dissolved in DCM (100 mL) at 0 °C, TFA (150 mmol, 10 eq) was added and the mixture was stirred at room temperature for at least 16h, then concentrated under reduced pressure, washed with diethyl ether then dried under vacuum (12h) to retrieve a white powder.

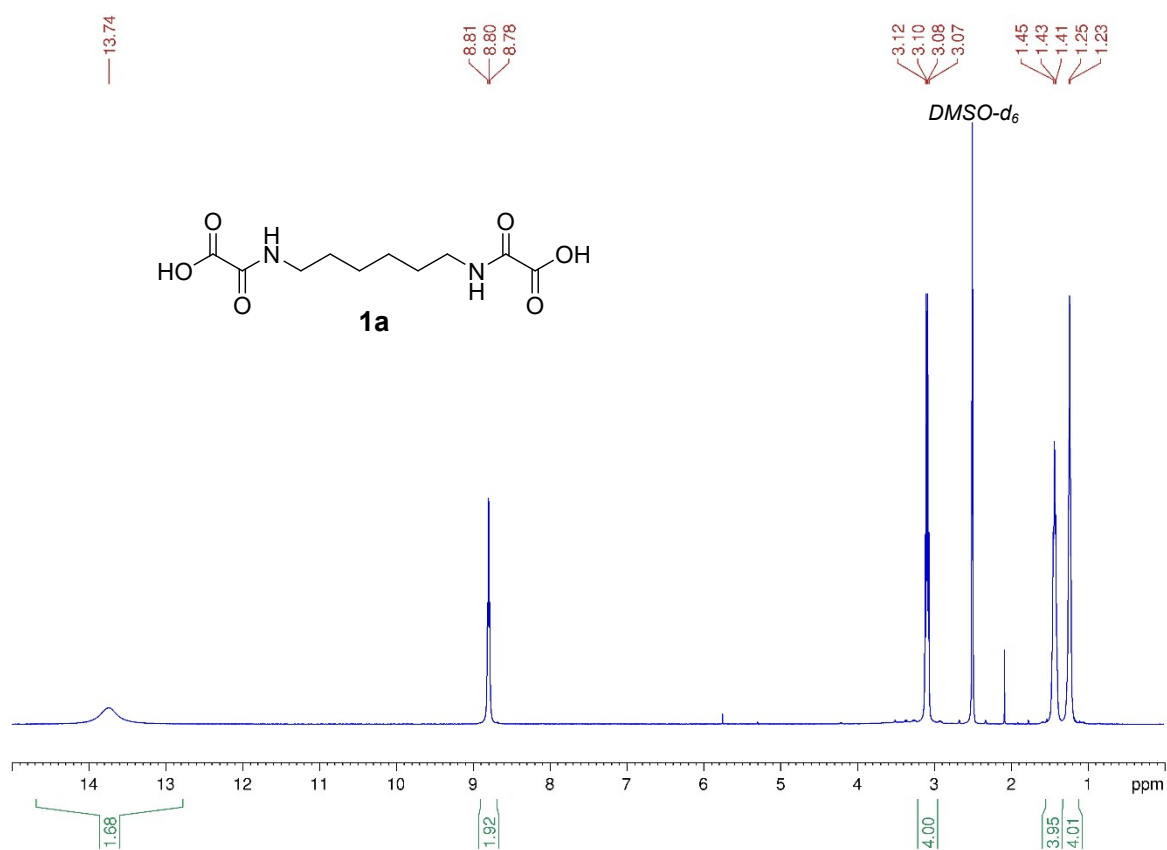
[1] J. Pinto, E. Solórzano, M. A. Rodríguez-Perez, J. A. de Saja, *Journal of Cellular Plastics* **2013**, *49*, 555–575.

**2,2'-(hexane-1,6-diylbis(azanediyl))bis(2-oxoacetic acid) (1a):**

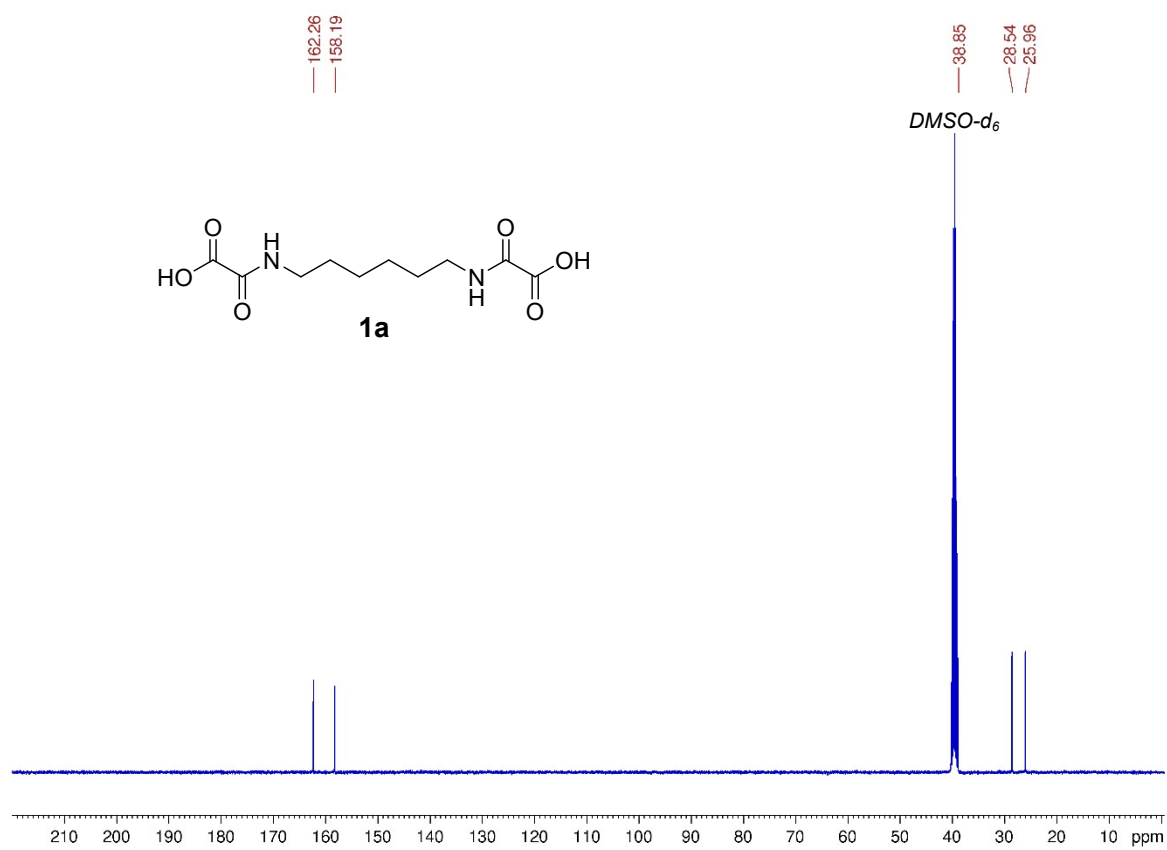


**1a** was obtained through the general procedure in 89% yield as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  : 13.74 (bs, 2H), 8.80 (t, 2H), 3.09 (q, 4H), 1.43 (m, 4H), 1.23 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  : 162.3, 158.2, 38.8, 28.5, 26.0.

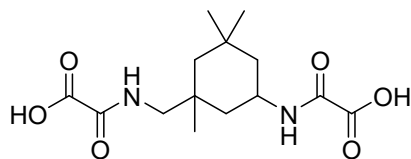
$^1\text{H}$  NMR in  $\text{DMSO-}d_6$  of **1a**:



$^{13}\text{C}$  NMR in  $\text{DMSO-}d_6$  of **1a**:

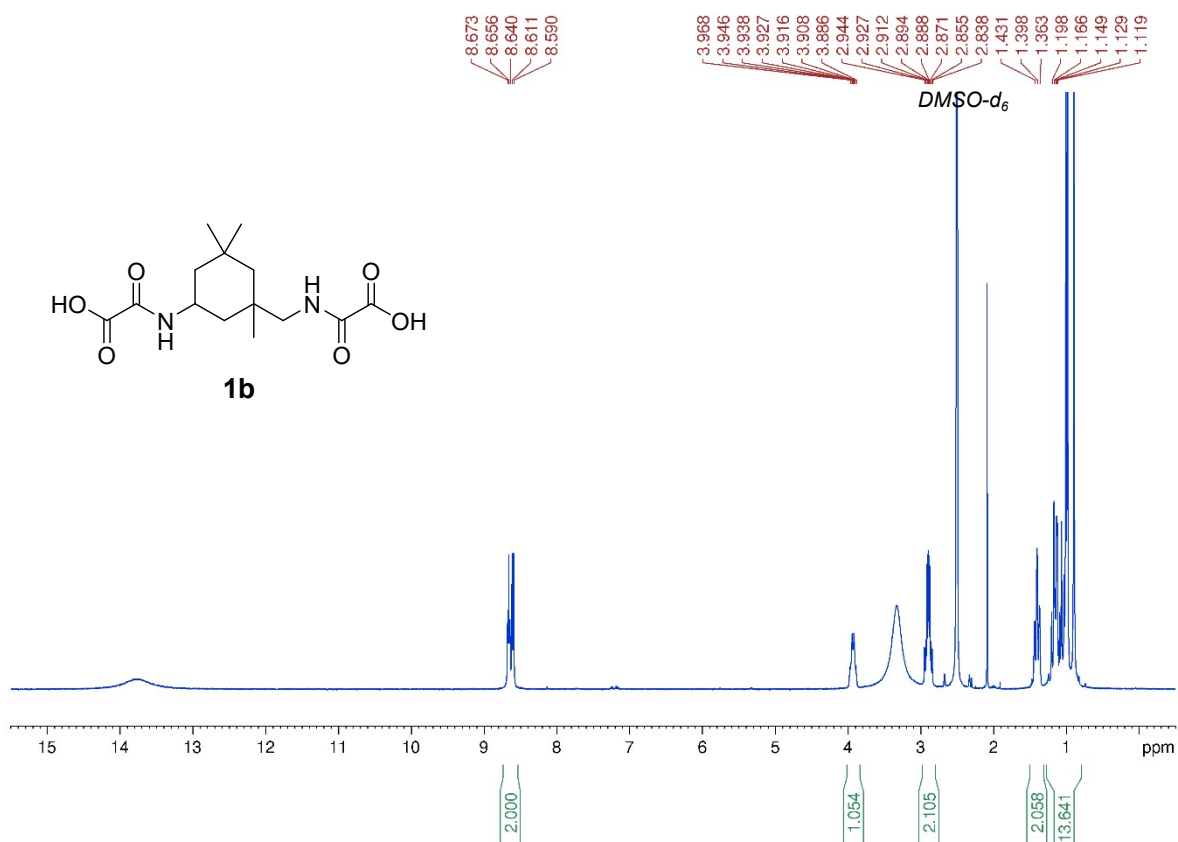


**2-(((5-(carboxyformamido)-1,3,3-trimethylcyclohexyl)methyl)amino)-2-oxoacetic acid (1b):**

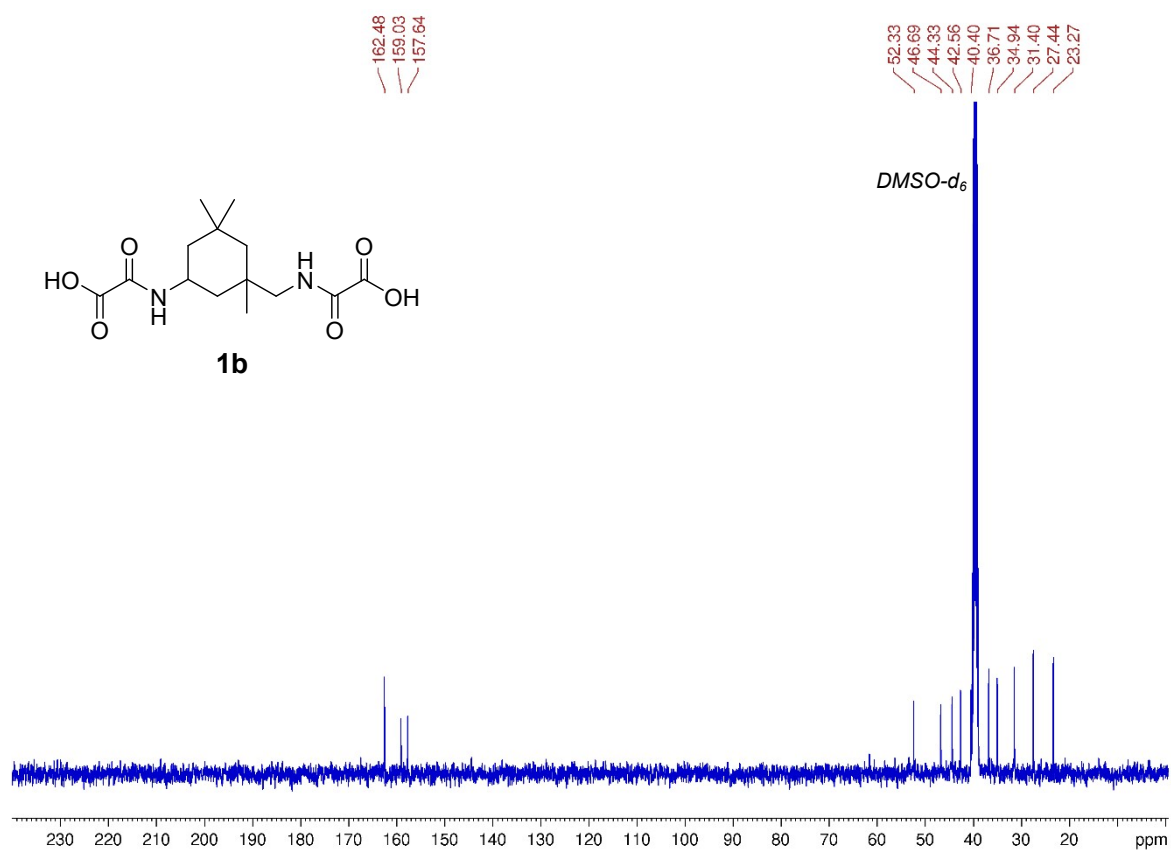


**1b** was obtained through the general procedure in 86% yield as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  : 13.75 (bs, 2H), 8.67-8.59 (m, 2H), 3.97-3.89 (m, 1H), 2.95-2.83 (m, 2H), 1.40 (t,  $J = 10.8$  Hz, 2H), 1.24-0.97 (m, 10H), 0.89 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  : 162.9, 159.5, 158.1, 55.4, 52.8, 47.2, 44.8, 43.0, 40.8, 37.2, 35.4, 31.8, 27.9, 23.7.

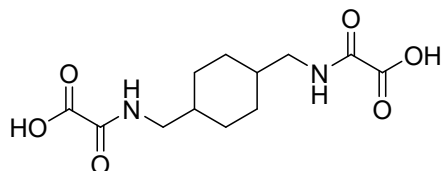
$^1\text{H}$  NMR in  $\text{DMSO-d}_6$  of **1b**:



$^{13}\text{C}$  NMR in  $\text{DMSO-}d_6$  of **1b**:



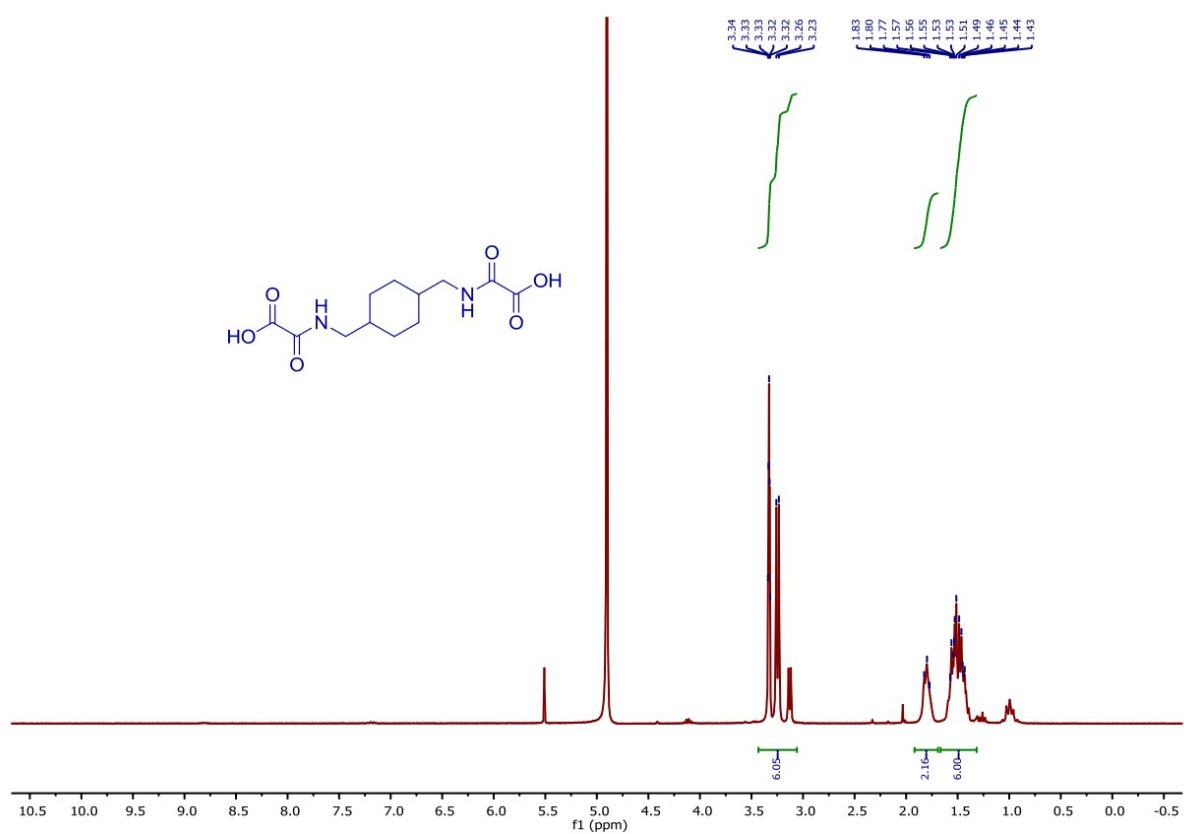
**2,2'-((cyclohexane-1,4-diylbis(methylene))bis(azanediyl))bis(2-oxoacetic acid) (1c):**



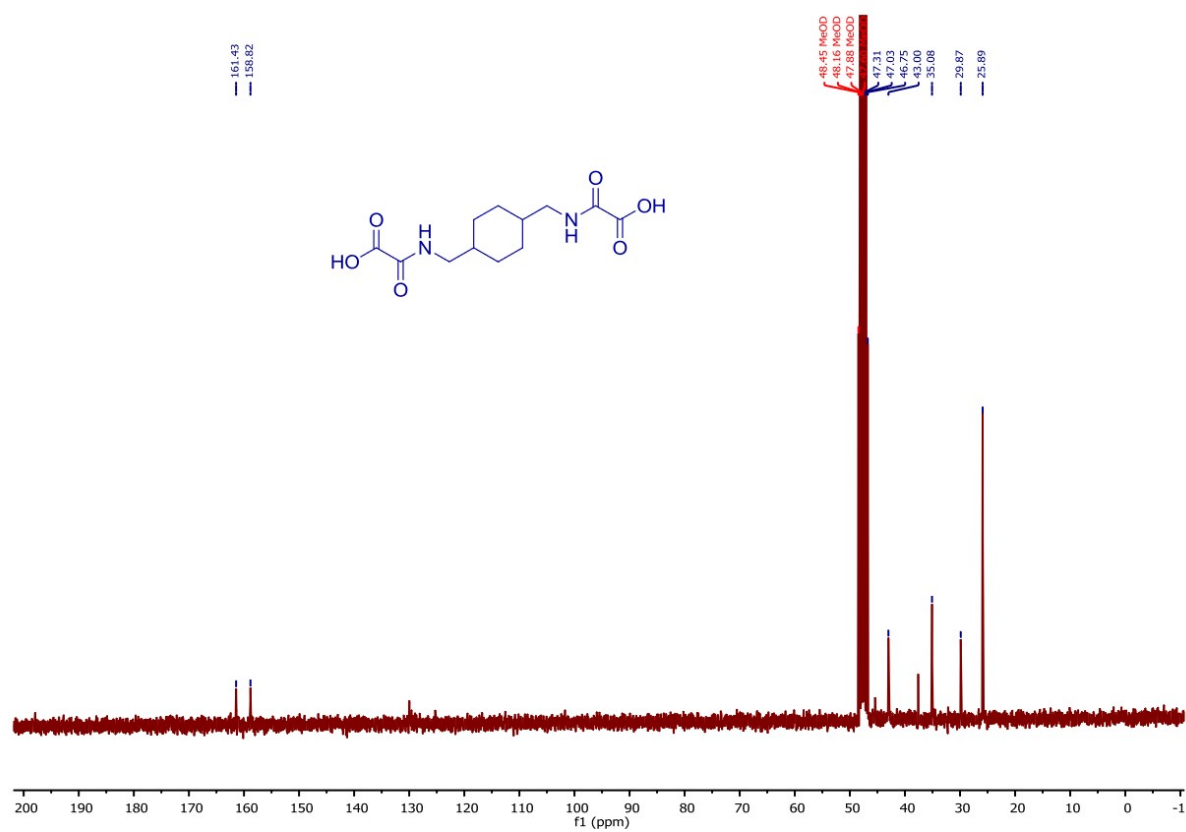
**1c** was obtained through the general procedure in 52% yield as a white solid:  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  3.38-3.07 (m, 6H), 1.91-1.69 (m, 2H), 1.64-1.34 (m, 6H);  $^{13}\text{C}$  NMR (75 MHz, MeOD)  $\delta$  161.43, 158.82, 43.00, 35.08, 29.87, 25.89.s



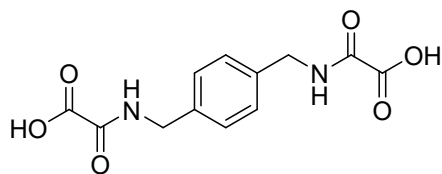
$^1\text{H}$  NMR in MeOD of **1c**:



$^{13}\text{C}$  NMR in MeOD of **1c**:

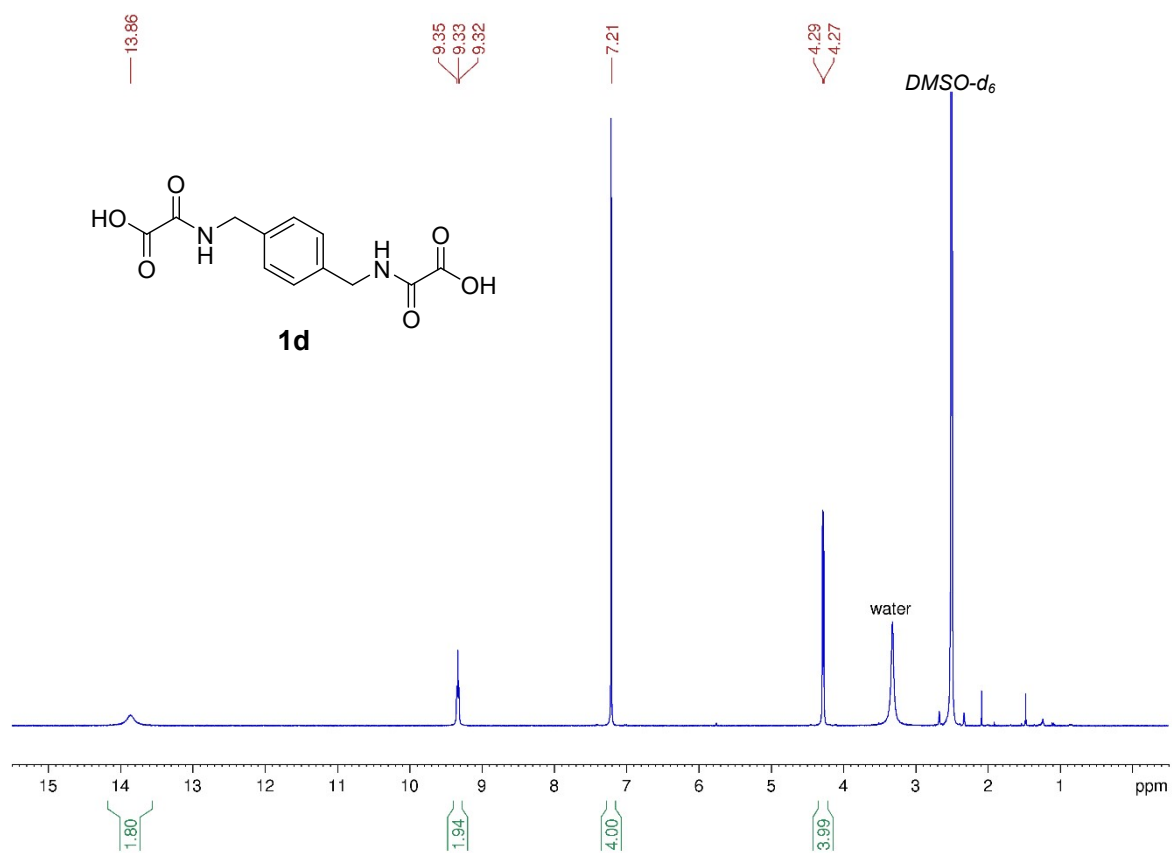


**2,2'-((1,4-phenylenebis(methylene))bis(azanediyl))bis(2-oxoacetic acid) (**1d**):**

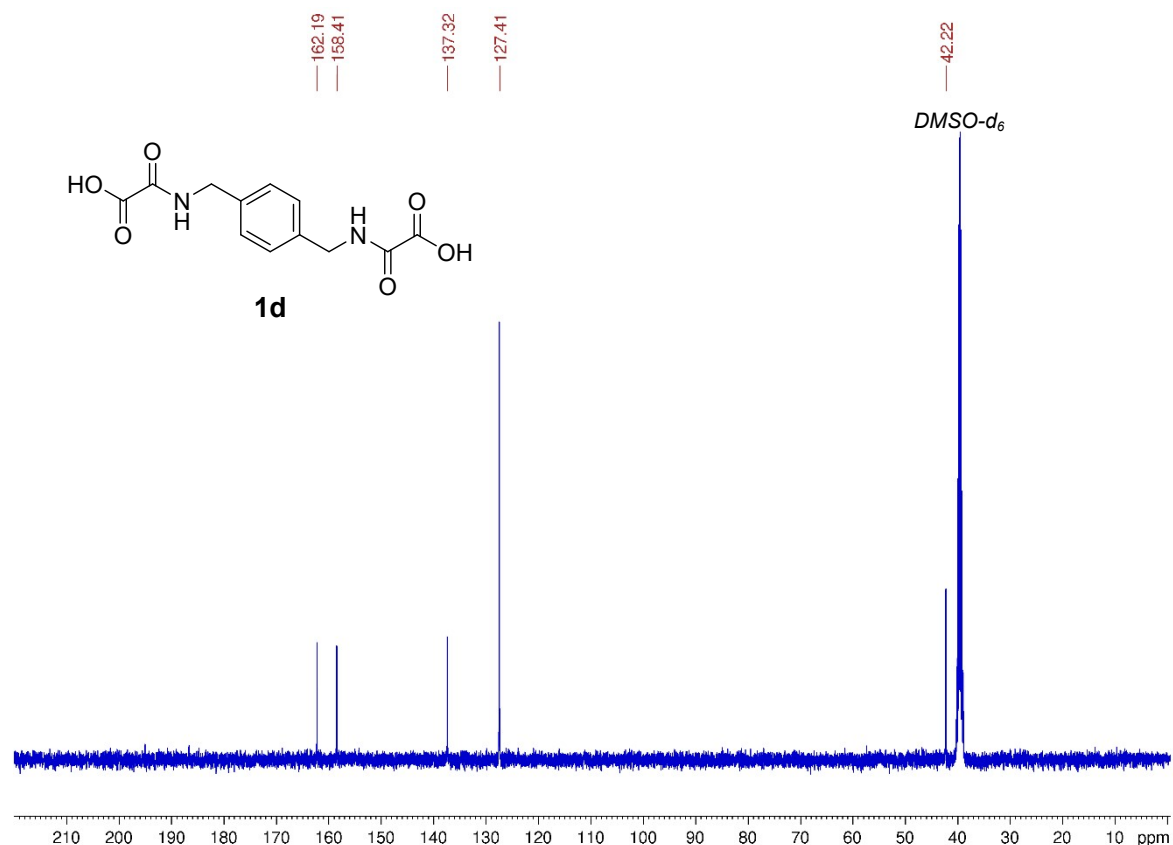


**1d** was obtained through the general procedure in 90% yield as a white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  : 13.86 (bs, 2H), 9.33 (t, 2H), 7.21 (s, 4H), 4.28 (d, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  : 162.19, 158.41, 137.32, 127.41, 42.22.

$^1\text{H}$  NMR in  $\text{DMSO-d}_6$  of **1d**:

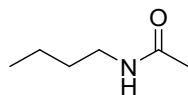


$^{13}\text{C}$  NMR in  $\text{DMSO-d}_6$  of **1d**:



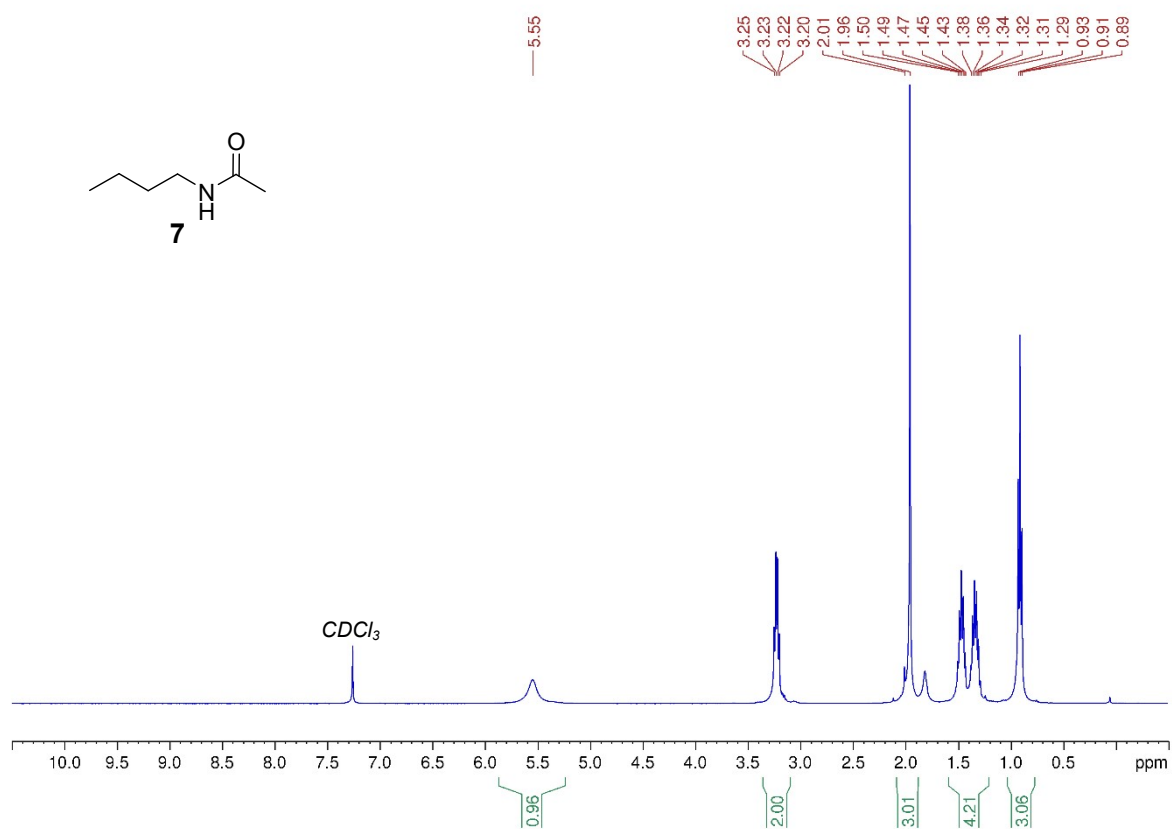
## ii. Synthesis of model molecules

### ***N*-butylacetamide (7):**

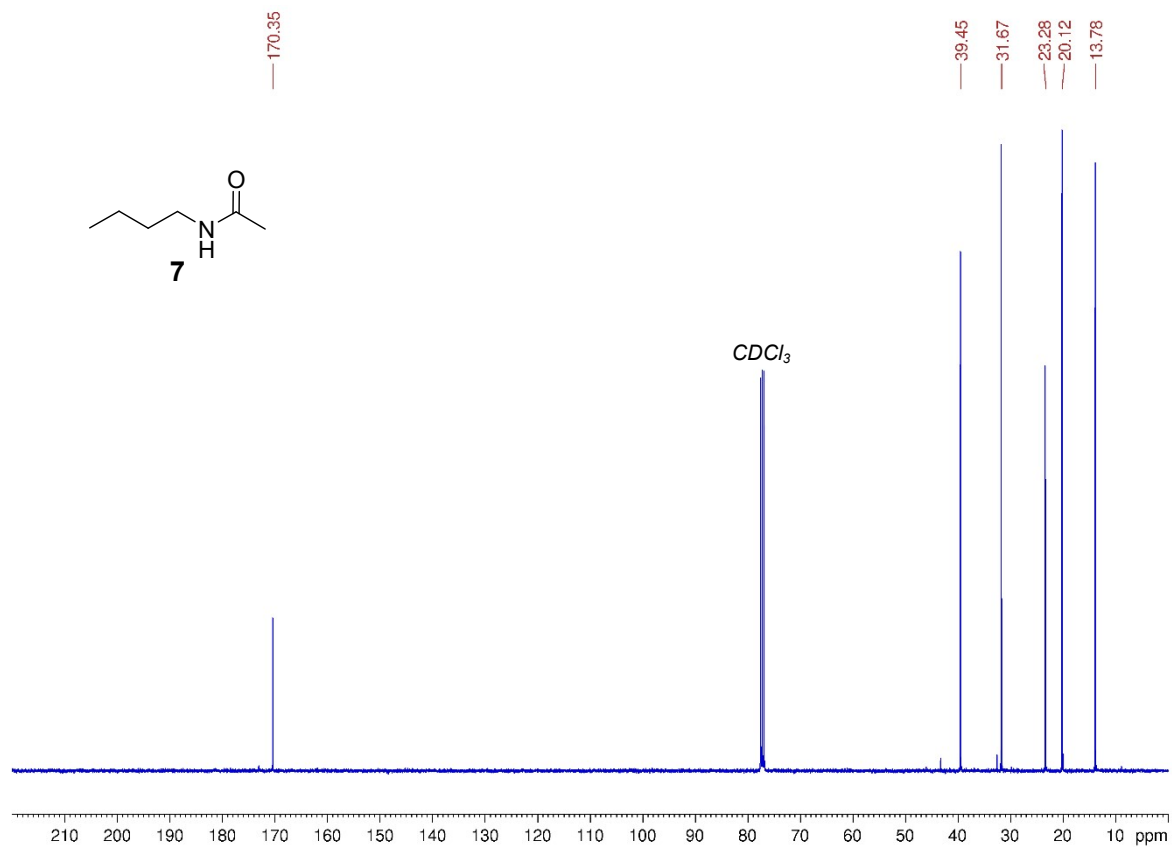


*N*-butylamine (3 mmol) was dissolved in  $\text{CH}_3\text{CN}$  (0.3M). The solution was cooled at  $0^\circ\text{C}$ , then  $\text{Et}_3\text{N}$  (2 eq.) and acetic anhydride (4 eq.) were added. After stirring for 45 min, 2 mL of deionized water were added and the solution was stirred 15 more minutes. The product was diluted with 10 mL of water then extracted with 15 mL of dichloromethane. The organic phase was washed with 1M  $\text{H}_2\text{SO}_4$  (2x15 mL), a saturated solution of  $\text{NaHCO}_3$  (15 mL) and water (15 mL), then dried over  $\text{MgSO}_4$ . The final product was concentrated and dried under reduced pressure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.55 (bs, 1H), 3.22 (q, 2H), 1.96 (s, 3H), 1.47 (m, 2H), 1.34 (m, 2H), 0.91 (t, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.35, 39.45, 31.67, 23.28, 20.12, 13.78.

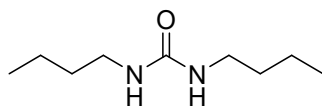
$^1\text{H}$  NMR in  $\text{CDCl}_3$  of **7**:



$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **7**:

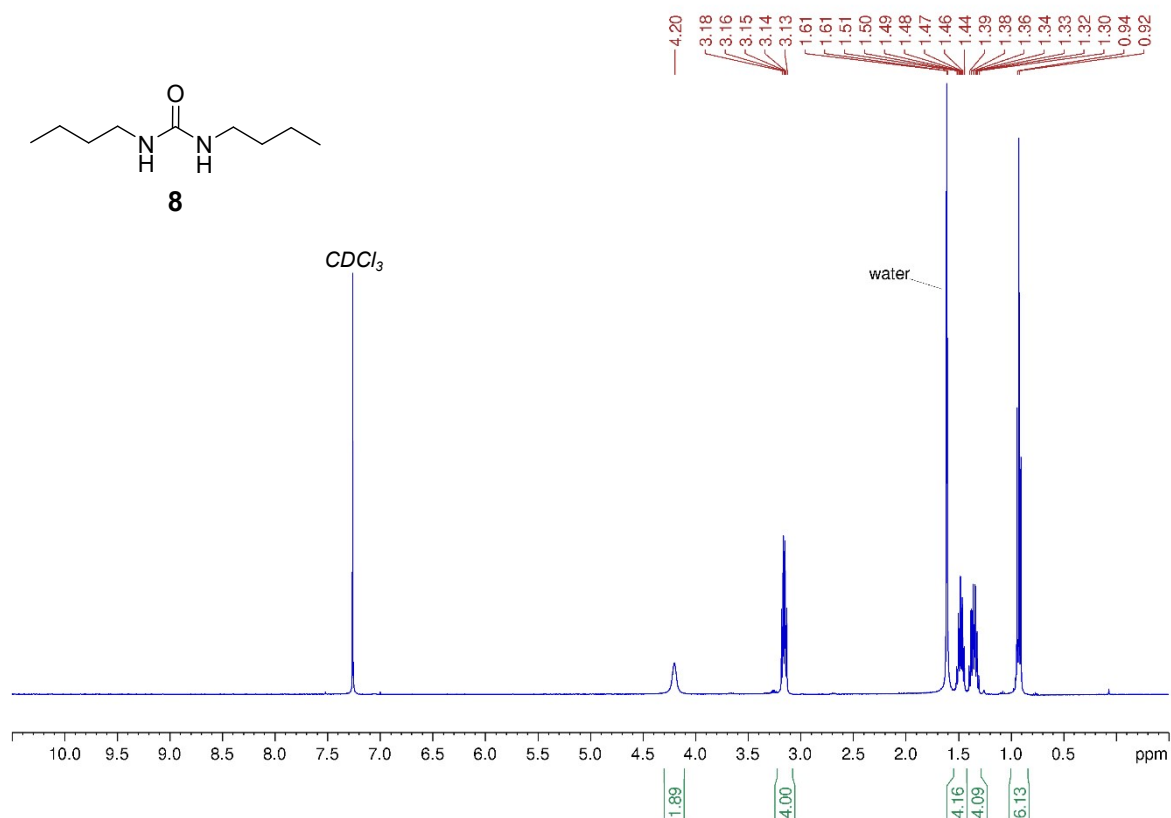


### 1,3-dibutylurea (**8**):

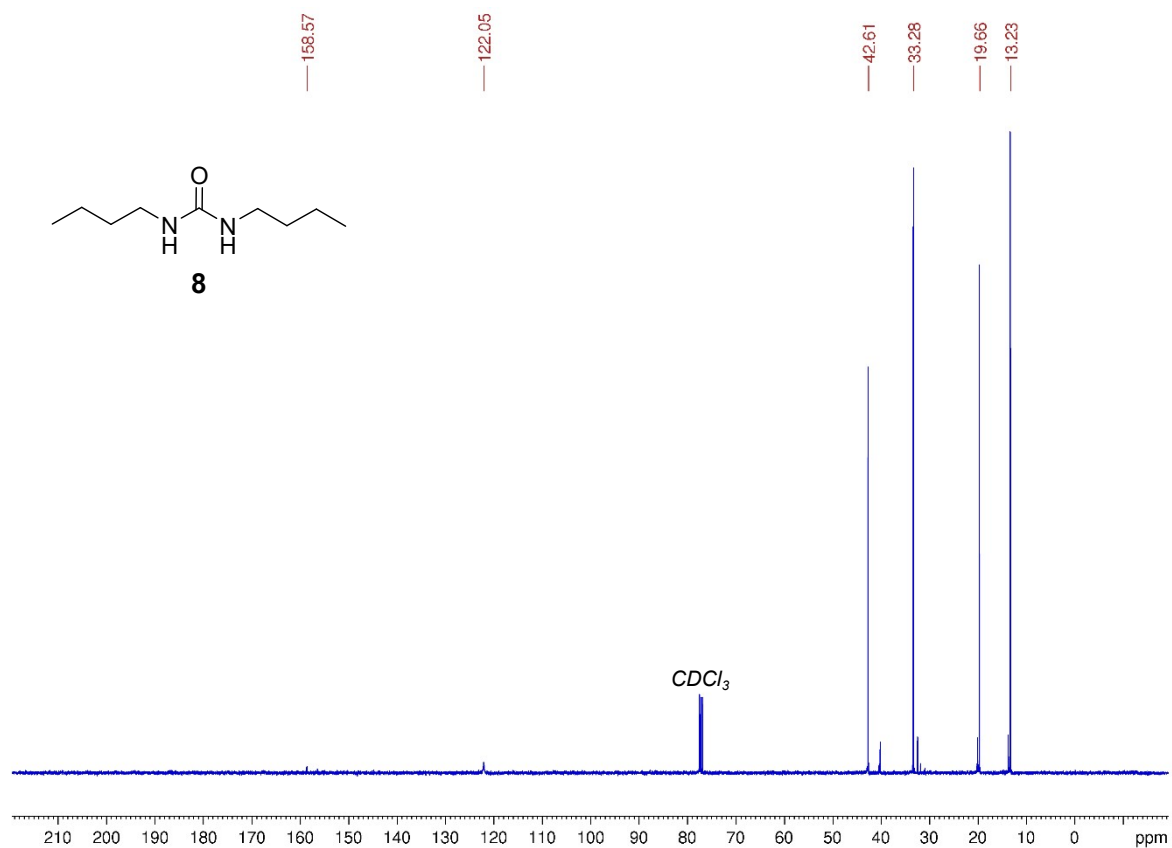


Water (1.0 eq.) and n-butylisocyanate (2.0 eq.) were introduced in a reactor and stirred at 23°C for 12h to give the crude product without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  : 4.20 (bs, 2H), 3.16 (q, 4H), 1.48 (m, 4H), 1.35 (m, 4H), 0.92 (t, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  : 158.57, (122.05), 42.61, 33.28, 19.66, 13.23.

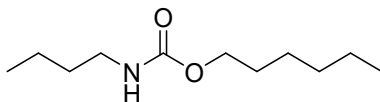
$^1\text{H}$  NMR in  $\text{CDCl}_3$  of **8**:



$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **8**:

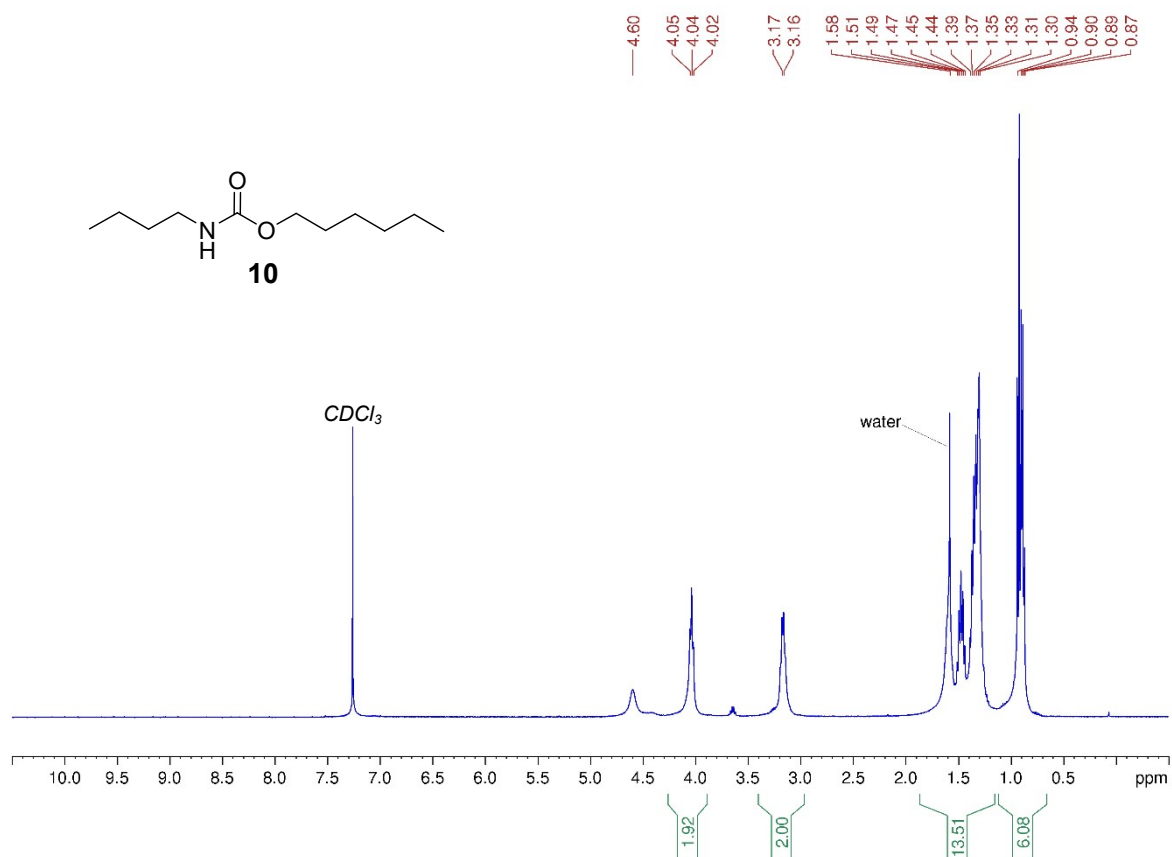


**Hexyl butylcarbamate (10):**

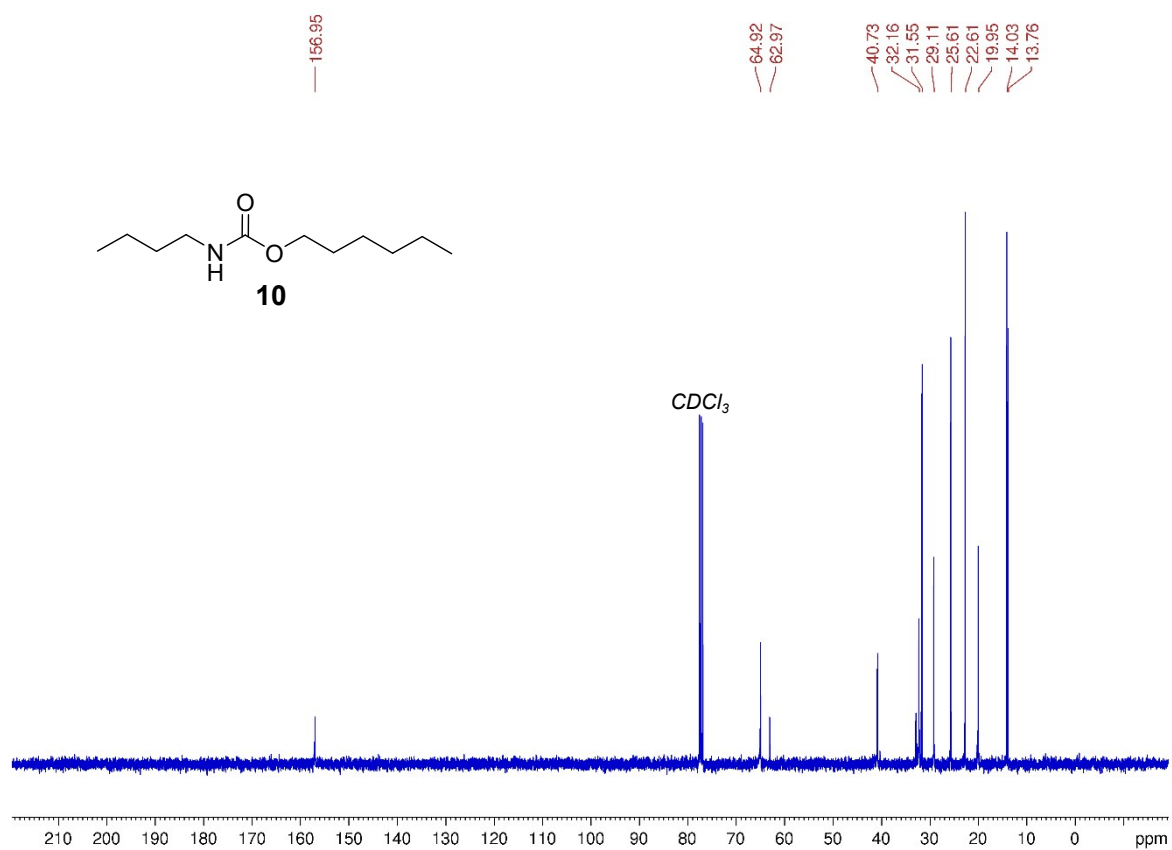


1-hexanol (1.0 eq.) and n-butylisocyanate (1.0 eq.) were introduced in a reactor under  $\text{N}_2$  atmosphere. The mixture was stirred at  $100^\circ\text{C}$  for 6h to give the crude product without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  : 4.60 (bs, 1H), 4.04 (t, 2H), 3.16 (q, 2H), 1.70-1.19 (m, 12H), 0.91 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  : 156.95, 64.91, (62.97), 40.72, 32.16, 31.54, 29.10, 25.61, 22.61, 19.94, 14.03, 13.76.

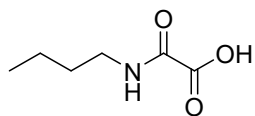
$^1\text{H}$  NMR in  $\text{CDCl}_3$  of **10**:



$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **10**:

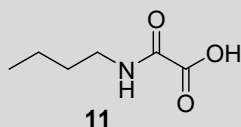


## 2-(butylamino)-2-oxoacetic acid (**11**):



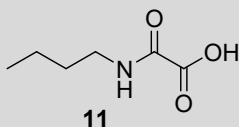
Butylamine (30 mmol, 1 eq.) was dissolved in DCM (60 mL) under nitrogen, triethylamine (90 mmol, 3 eq.) was added into the mixture. The solution was cooled at 0°C before dropwise addition of t-butyl-2-chloro-2-oxo acetate (36 mmol, 1.2 eq.). The solution was then stirred at room temperature for 6 h. The reaction mixture was then washed successively with water (100 mL), and brine (100 mL), dried over sodium sulfate and concentrated under reduced pressure resulting in a crude solid product. The crude product was dissolved in DCM (60 mL), TFA (150 mmol, 5 eq.) was added and the mixture was stirred at room temperature 12h, then concentrated under reduced pressure to afford **11** as a white solid:  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  : 8.79 (t, 1H), 3.11 (q, 2H), 1.43 (m, 2H), 1.26 (m, 2H), 0.86 (t, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  : 160.58, 157.63, 40.34, 30.93, 19.97, 13.62.

$^1\text{H}$  NMR in  $\text{CDCl}_3$  of **11**:

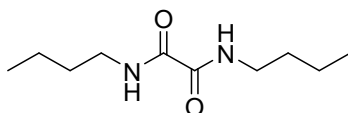




$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **11**:

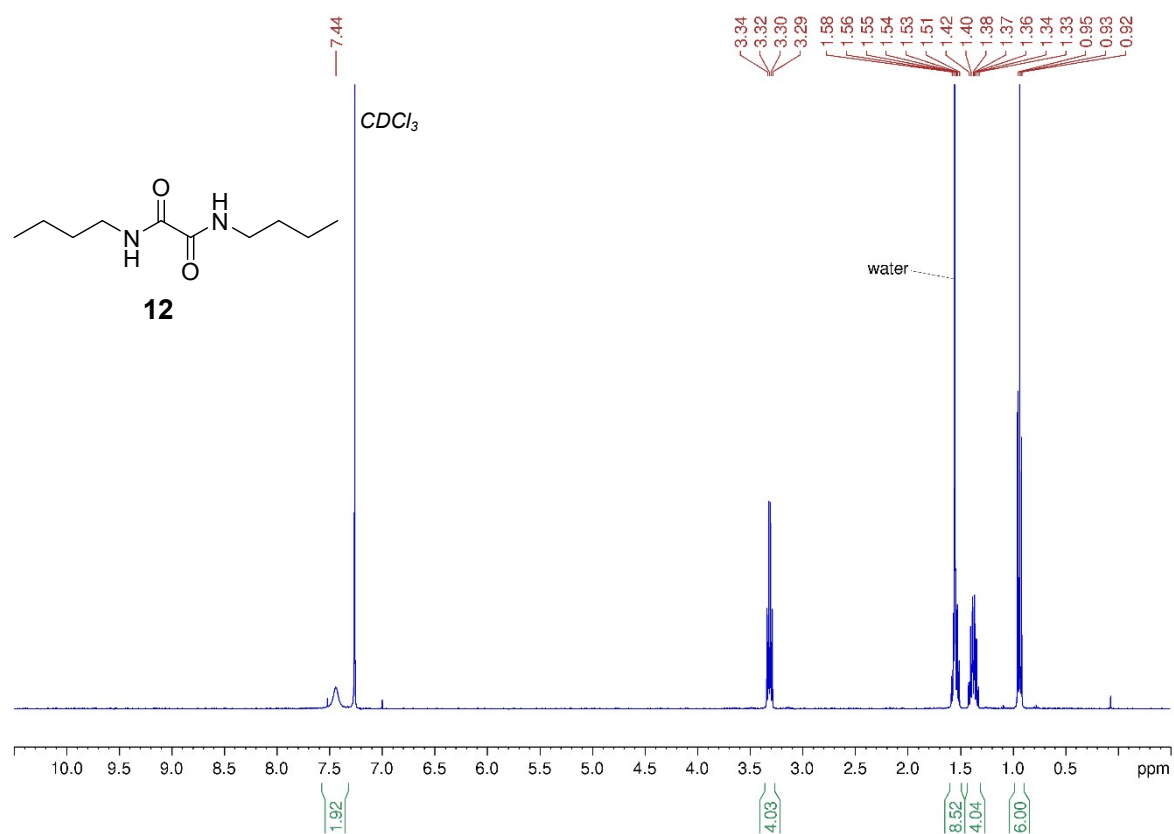


**N<sup>1</sup>,N<sup>2</sup>-dibutyloxalamide (12):**

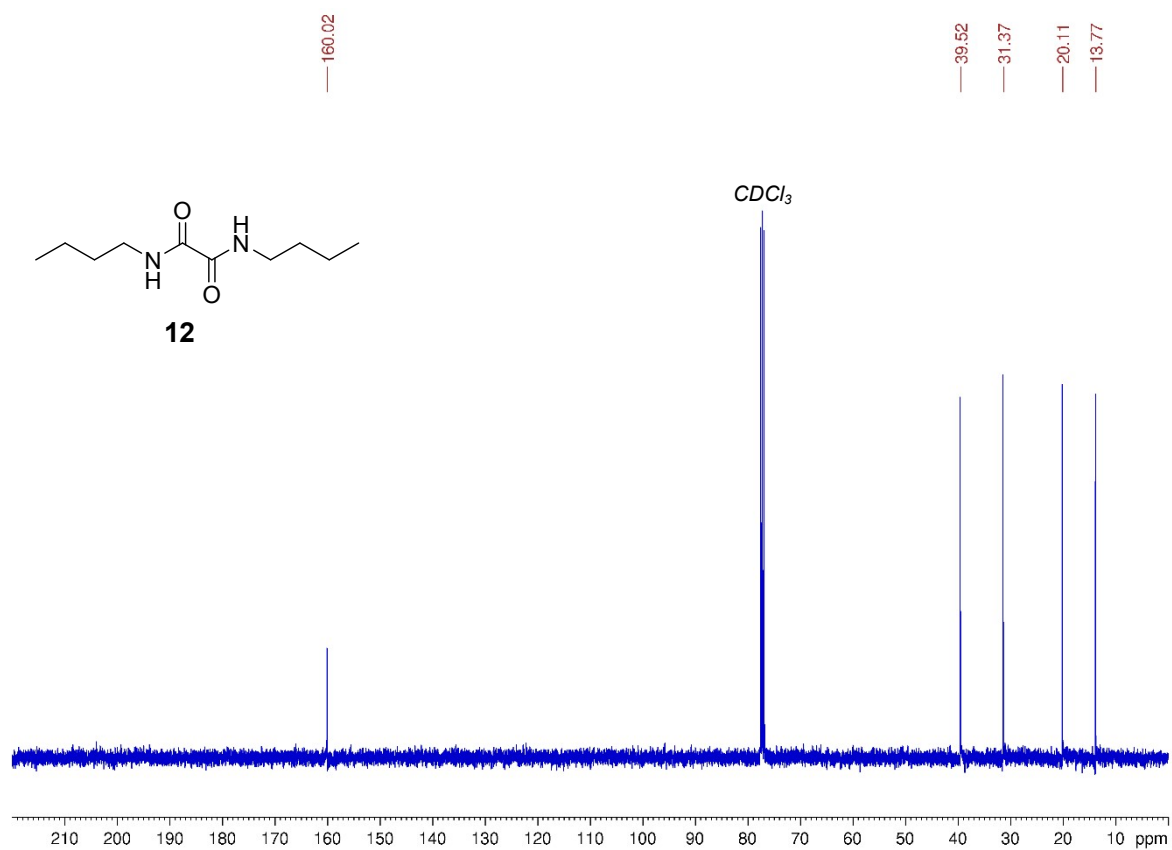


A mixture of oxalyl chloride (5 mmol, 1 eq.) in DCM (5 mL) was added dropwise to a stirred solution of n-butylamine (10 mmol, 2 eq.) in DCM (10 mL) at 0°C under  $\text{N}_2$ . The resulting mixture was stirred for 30 min at 0°C, then 2.5h at room temperature. The resulting solution was washed with water then with brine and dried over  $\text{MgSO}_4$ . It was then concentrated under vacuum and recrystallized with ethyl acetate and dried under heated vacuum to give a white powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  : 7.44 (bs, 2H), 3.31(q, 4H), 1.55 (m, 4H), 1.37 (m, 4H), 0.93 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  : 160.02, 39.52, 31.37, 20.11, 13.77.

$^1\text{H}$  NMR in  $\text{CDCl}_3$  of **12**:



$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  of **12**:



#### d. Procedure for the preparation of thermoplastic polyurethanes.

##### Synthesis of **3a** to **3g**

Bis-oxamic acid (1.0 mmol, 1.0 eq.), PEG-1500 (0.9 eq.) and PIDA (2.4 eq.) were charged into an oven-dried Schlenk tube equipped with a magnetic stirrer, the content was degassed and backfilled with argon. The tube was heated to 70 °C during which the molten polyol helped to solubilize the solid bis-oxamic acid and PIDA. As the reaction progressed, iodobenzene and acetic acid released by PIDA also helped more in homogenizing the reaction mixture. Thereafter, crude polymer, which was highly viscous, was diluted with DCM (2 mL) and precipitated using diethyl ether, then filtered. The obtained PU was dried using vacuum.

##### Synthesis of **PU<sub>ref</sub>**

Hexamethylene diisocyanate (1.0 mmol, 1.0 eq.) and PEG-1500 (1.0 mmol, 1 eq.) were charged into an oven-dried Schlenk tube equipped with a magnetic stirrer, degassed and backfilled with argon. The tube was heated to 70 °C. After 24h, crude polymer, which was highly viscous, was diluted with DCM (2 mL) and precipitated using diethyl ether. The obtained PU was dried using vacuum.

#### e. Procedure for the preparation of polyurethane foams.

##### i. Open reactor

##### Synthesis of **F1** to **F4** and **F6** to **F8**

The triol (1.2 mmol, 0.6 eq.) and ethoxylated poly(dimethylsiloxane) (0.012 g, CAS 67674-67-3) were introduced in a test tube with an inside diameter of 13 mm (see picture below). PIDA (4.4 mmol, 2.2 eq.) and hexamethylene bis-oxamic acid (2 mmol, 1 eq.) were crushed and mixed together, then introduced in the test tube and all the compounds were mixed together. A stirring bar was added into the test tube. It was heated to 100°C in an oil bath, the system started bubbling when the reaction began. A slow intermittent stirring was applied when the system reached a homogenous liquid state and the foam network started to form. The product was cured for 1 hour from the gel time. The foam was obtained after the curing was completed and the test tube cooled down, it was then dried under heated vacuum at 60°C for 4 hours.



ii. Closed reactor

Synthesis of **F5**

The triol (1.2 mmol, 0.6 eq.) and ethoxylated poly(dimethylsiloxane) (0.012 g, CAS 67674-67-3) were introduced in a Schlenk tube with an inside diameter of 13 mm (see picture below). PIDA (4.4 mmol, 2.2 eq.) and hexamethylene bis-oxamic acid (2 mmol, 1 eq.) were crushed and mixed together, then introduced in the Schlenk tube and all the compounds were mixed together. A stirring bar was added into the Schlenk tube. It was heated to 100°C in an oil bath, the system started bubbling when the reaction began. A slow intermittent stirring was applied when the system reached a homogenous liquid state. 20 seconds after the magnetic stirrer was unable to move due to the high viscosity of the mixture, the Schlenk tube was slowly depressurized, and the foam started to rise. After 5 minutes of curing, a vacuum was applied for 5 minutes, then the product was cured for 1 hour under static vacuum. The foam was obtained after curing completion and cooling down the Schlenk tube, it was then dried under heated vacuum at 60 °C for 4 hours.



**f. DFT calculations**

All DFT calculations were performed with the Gaussian 16 software package.<sup>[2]</sup> M06–2X exchange-correlation functional<sup>[3]</sup> was used with a high-quality triple- $\zeta$  def2-TZVP basis set for molecular structure optimization. All structures were optimized in gas phase at 298 °K. Frequency calculations were performed to insure that there is no imaginary frequency for local minima. The connectivity between stationary points was established by Intrinsic Reaction Coordinate computations (IRC).

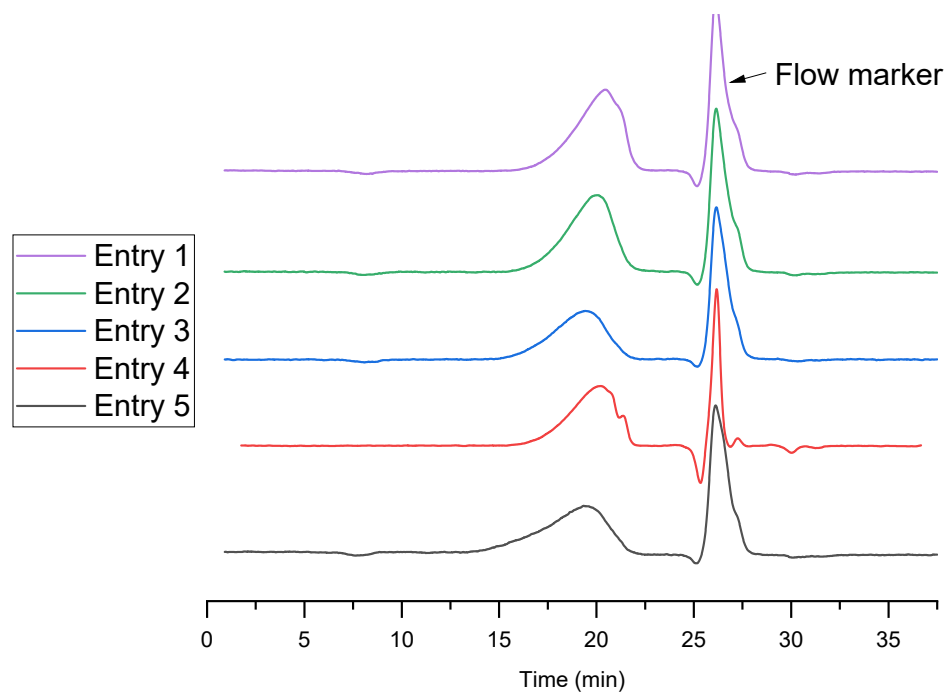
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[2] Gaussian 16, Revision **B.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

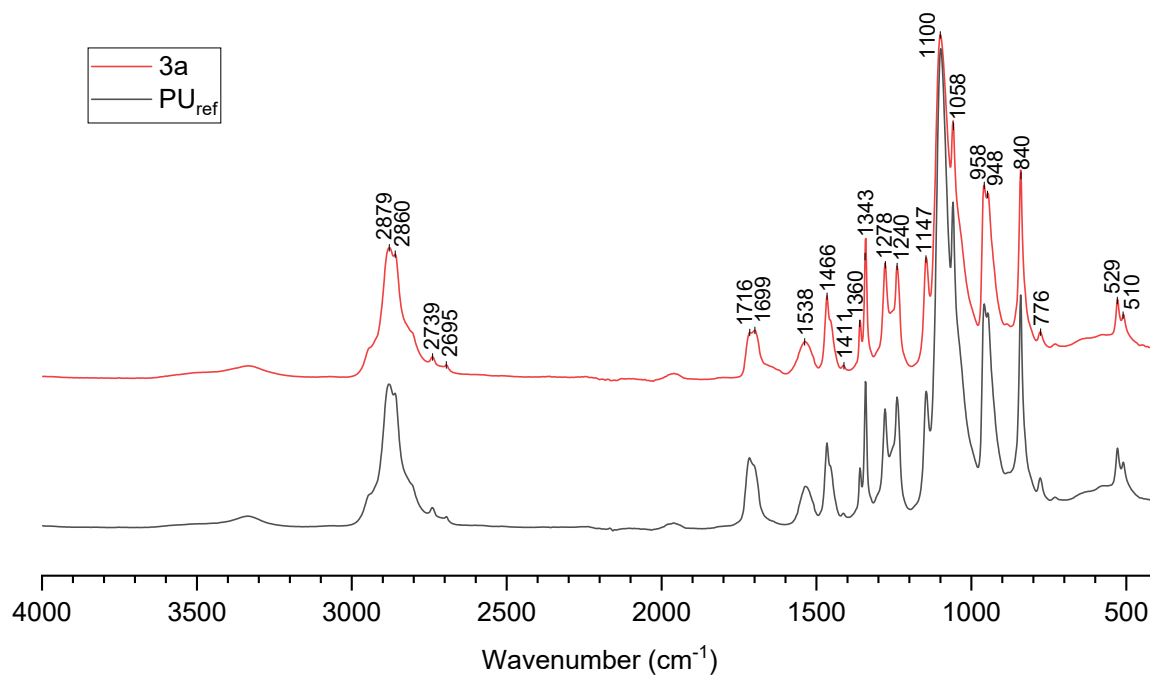
[3] a) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101: 1. b) Y. Zhao, D. G. Truhlar *Theor. Chem. Acc.* **2008**, *120*, 215.

## 2. Supplementary data.

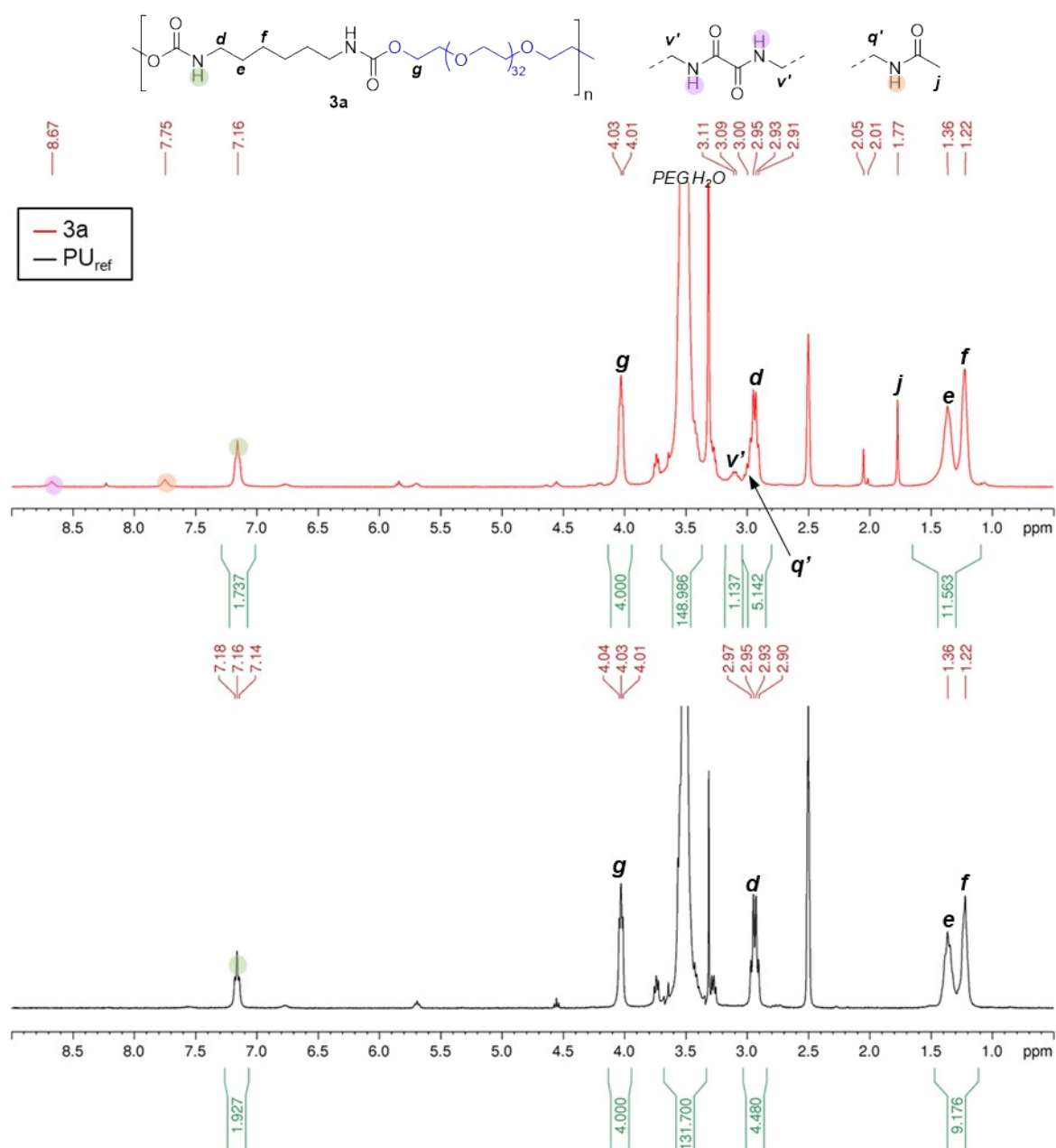
### a. Synthesis of thermoplastic polyurethanes



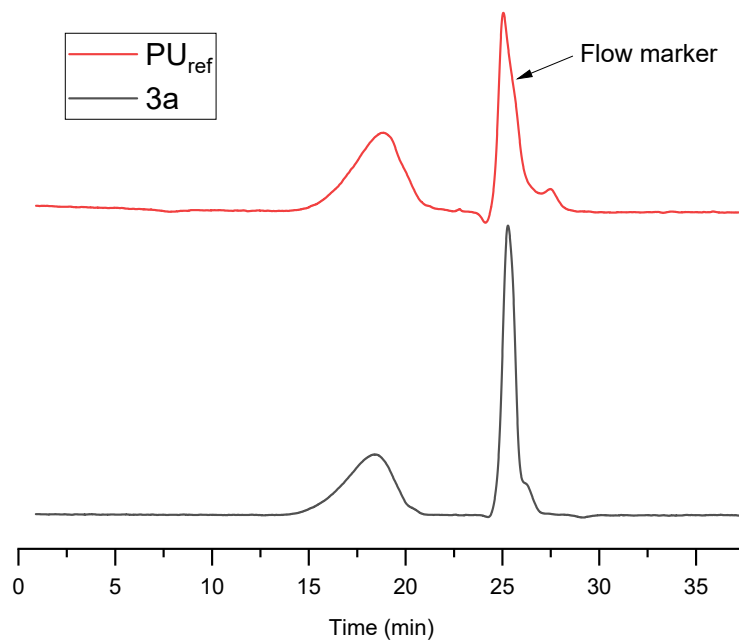
**Figure S1:** SEC traces (in HFIP) of PU 3a synthesized under various conditions (Table 1).



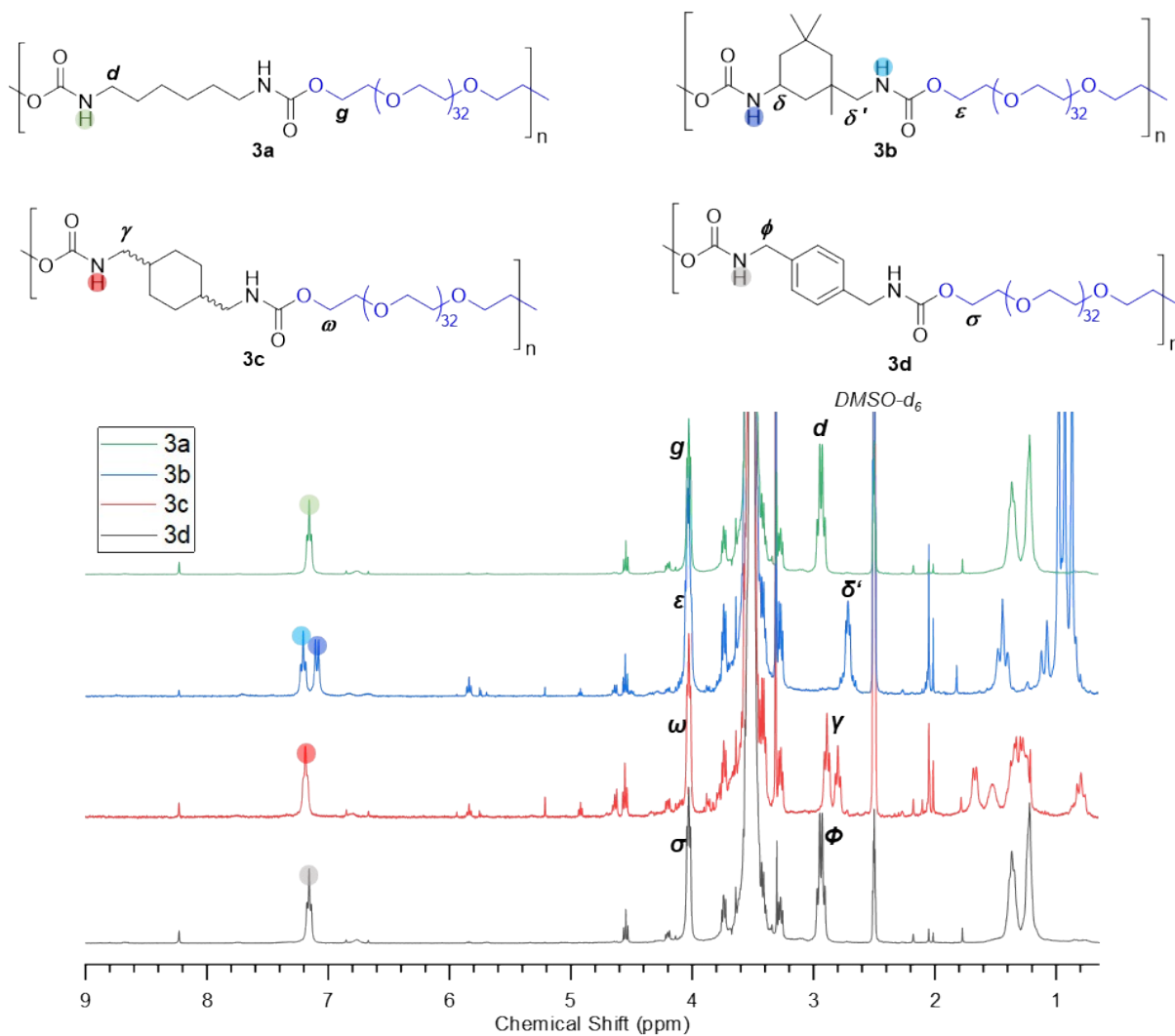
**Figure S2:** FTIR spectra of PU 3a compared to PU<sub>ref</sub>.



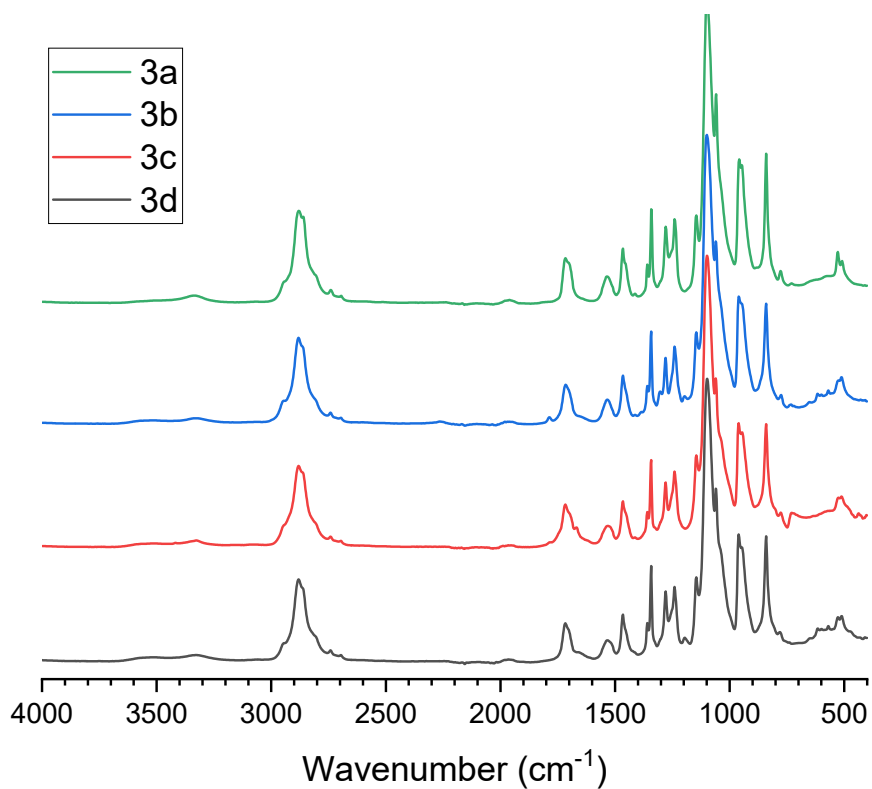
**Figure S3:**  $^1\text{H}$  NMR spectra (in  $\text{DMSO-d}_6$ ) comparison of **3a** and  $\text{PU}_{\text{ref}}$ .



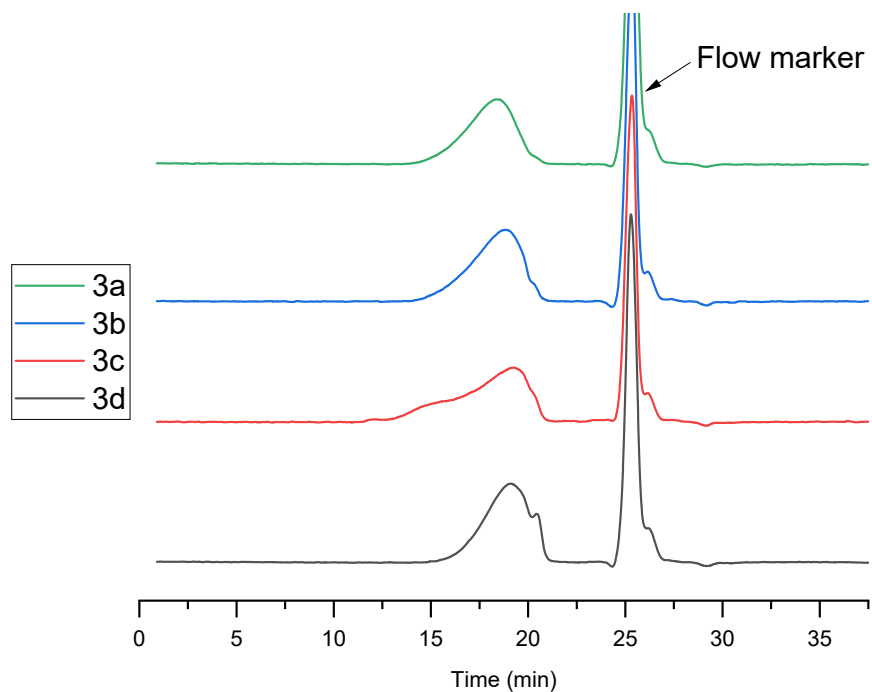
**Figure S4:** SEC traces (in HFIP) comparison of PU **3a** and **PU<sub>ref</sub>**.



**Figure S5:**  $^1\text{H}$  NMR spectra (in  $\text{DMSO-d}_6$ ) of PUs **3a-d**.

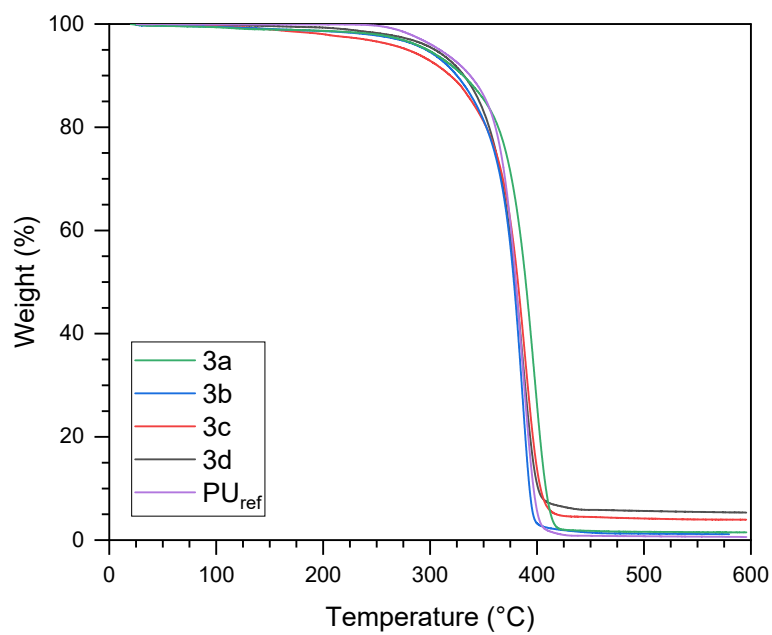


**Figure S6:** FTIR spectra of PUs **3a-d**.

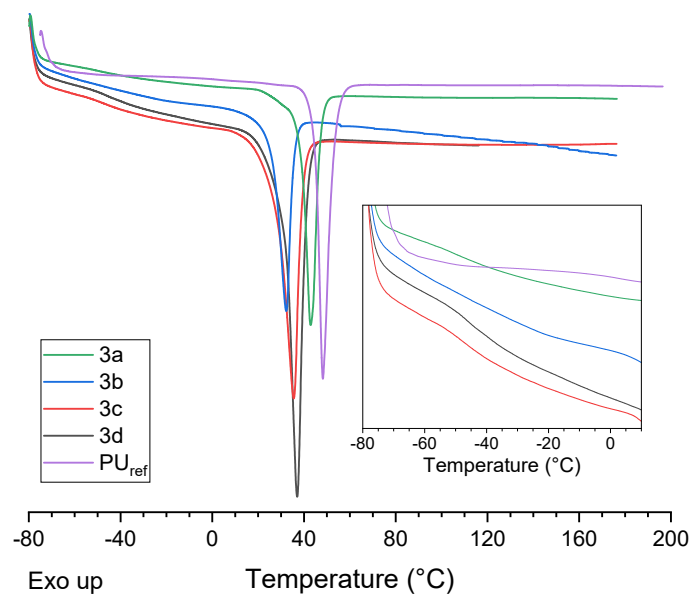


**Figure S7:** SEC traces (in HFIP) of PUs **3a-d**.



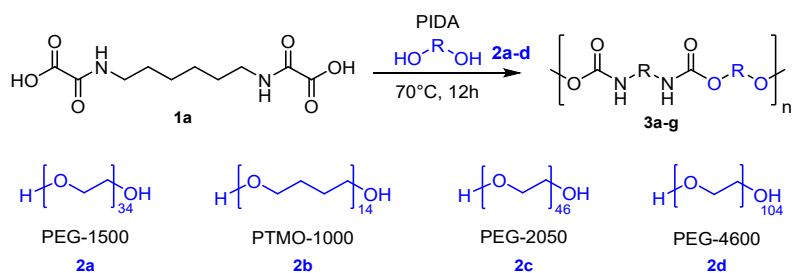


**Figure S8:** TGA thermogram of PUs **3a-d** and **PU<sub>ref</sub>**.

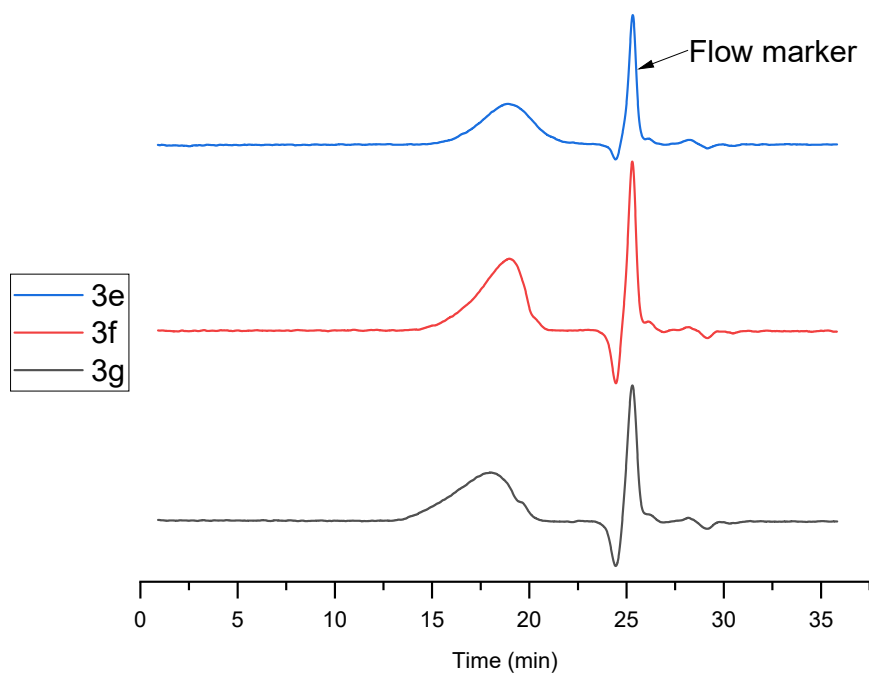


**Figure S9:** DSC thermogram (second heating cycle) of PUs **3a-d** and **PU<sub>ref</sub>**.

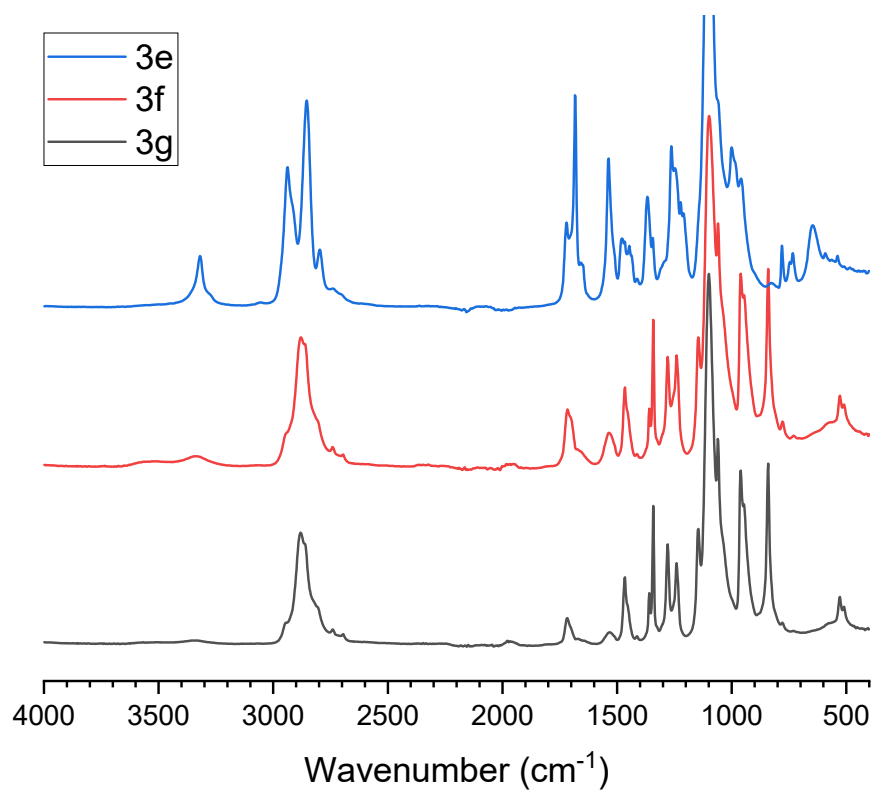
**Table S1:** Synthesis of thermoplastic PUs **3e-g** from bis-oxamic acids **1a** and diols **2b-d**, using PIDA-mediated oxidative decarboxylation.



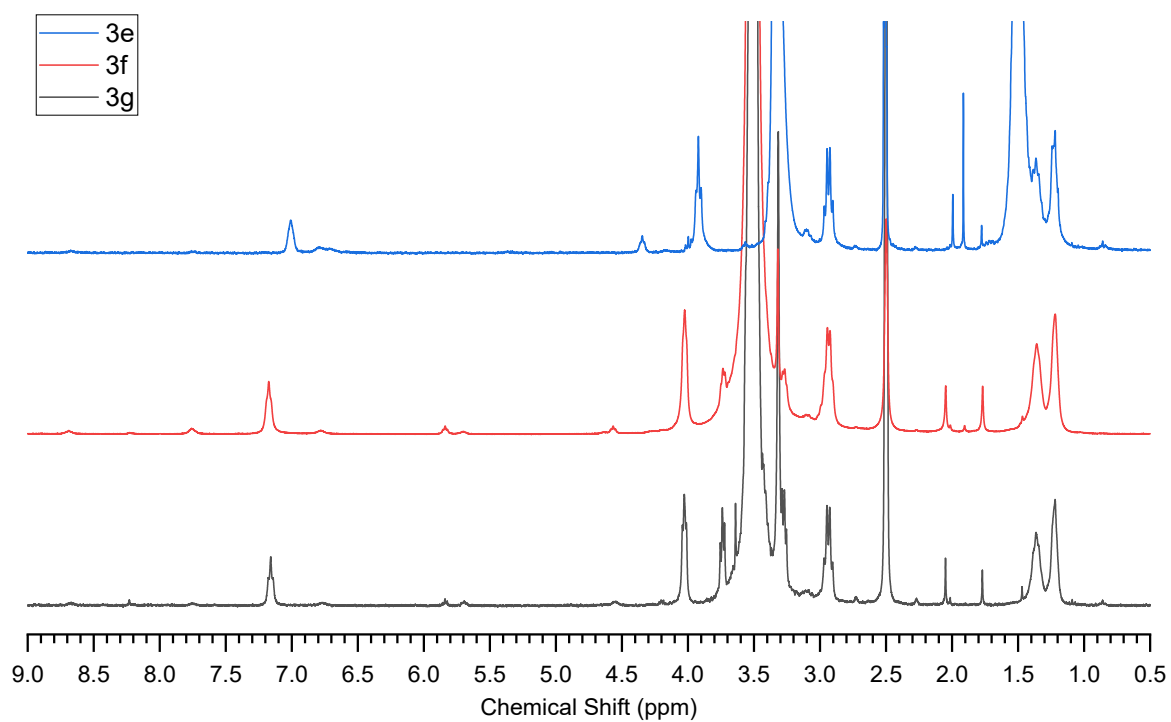
<b>1a-d</b>	<b>Diol</b>	<b>PU</b>	<b>M<sub>n</sub></b> [g/mol]	<b>M<sub>w</sub></b> [g/mol]	<b>Đ</b>	<b>T<sub>d5%</sub></b> [°C]	<b>T<sub>g</sub></b> [°C]	<b>T<sub>m</sub></b> [°C]
<b>1a</b>	<b>2b</b>	3e	21900	48500	2.2	321	-	39.2
<b>1a</b>	<b>2c</b>	3f	35900	64400	1.8	-	-	39.8
<b>1a</b>	<b>2d</b>	3g	56400	114000	2.0	332	-	52.7



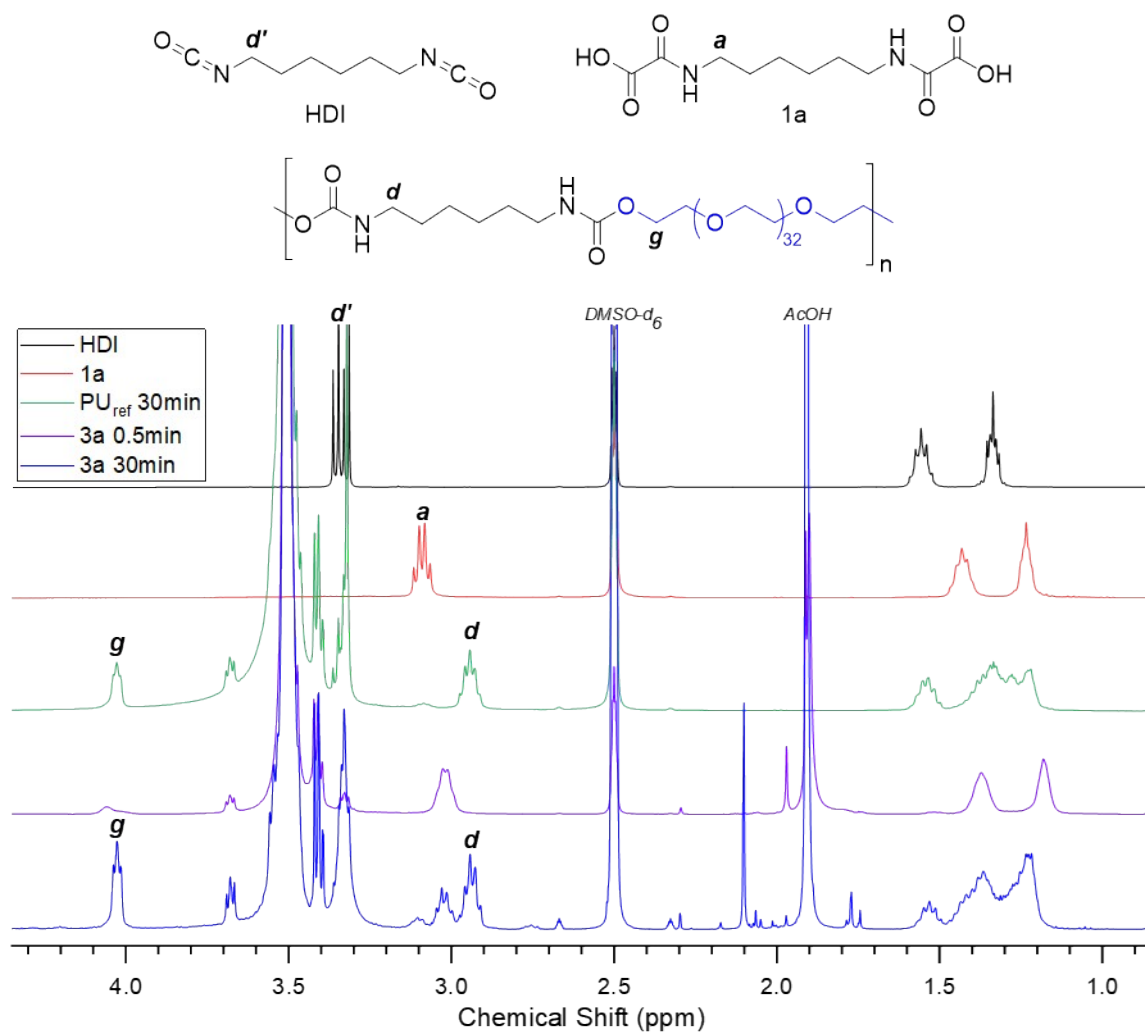
**Figure S10:** SEC traces (in HFIP) of PU **3e-g**.



**Figure S11:** FTIR spectra of PUs **3e-g**.

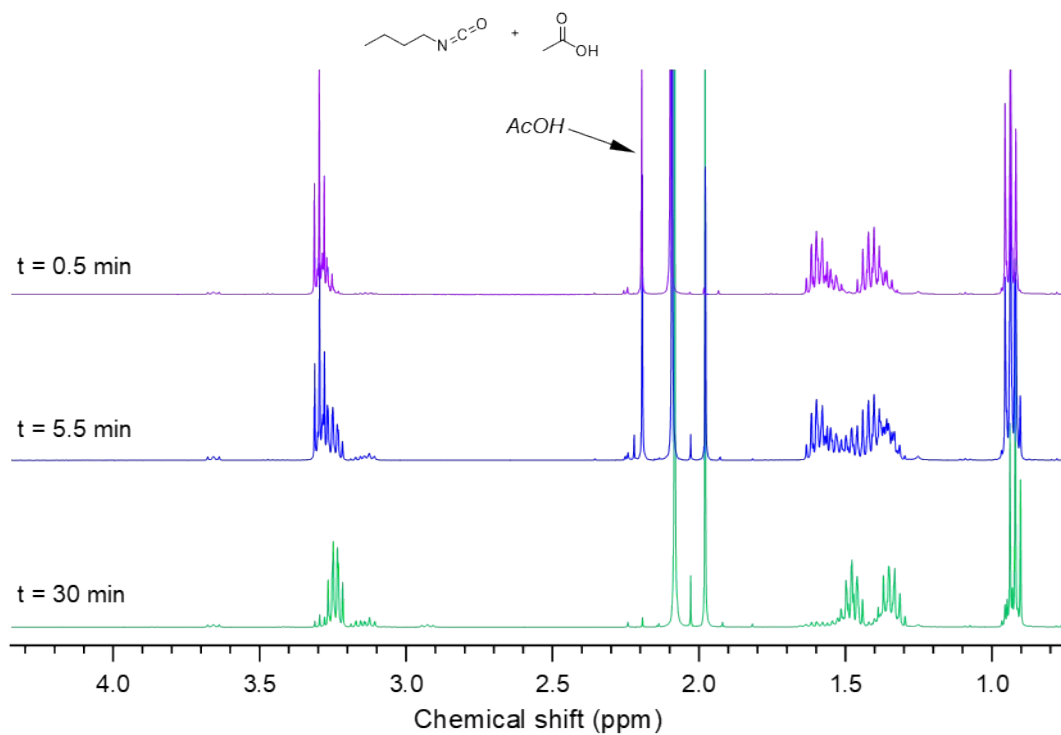


**Figure S12:** <sup>1</sup>H NMR spectra (in DMSO-d<sub>6</sub>) of PUs **3e-g**.

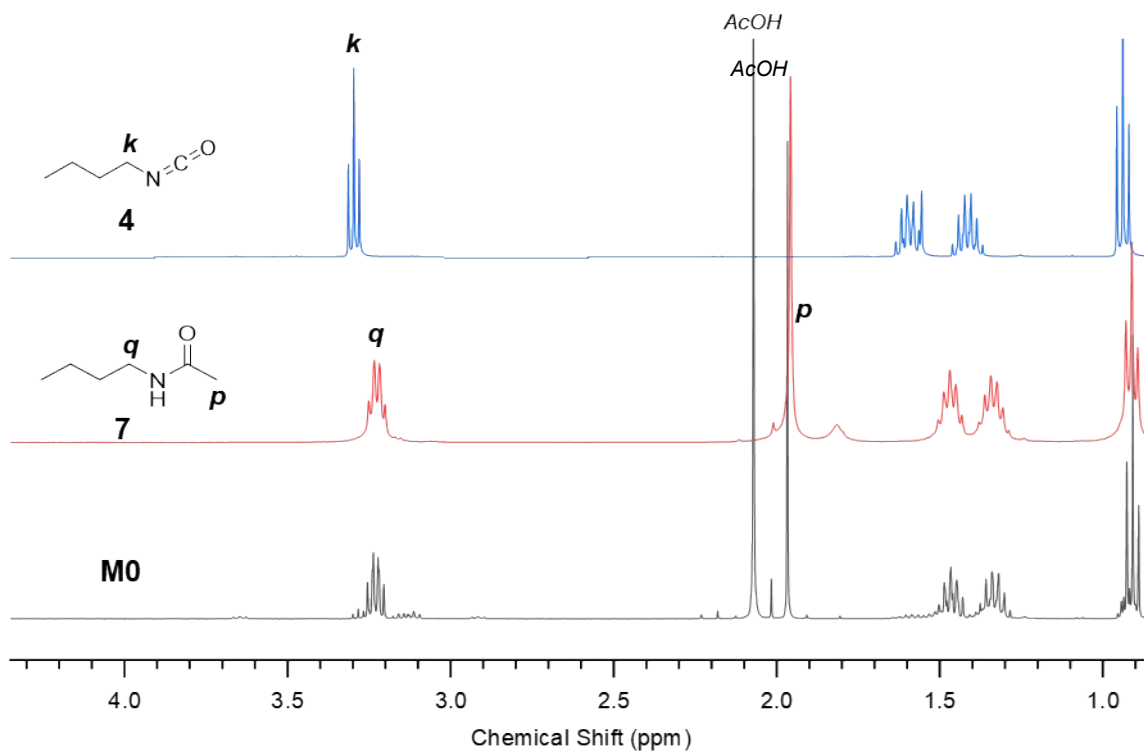


**Figure S13:** <sup>1</sup>H NMR spectra (in DMSO-d<sub>6</sub>) of the formation of isocyanate and urethane during the synthesis of **3a**.

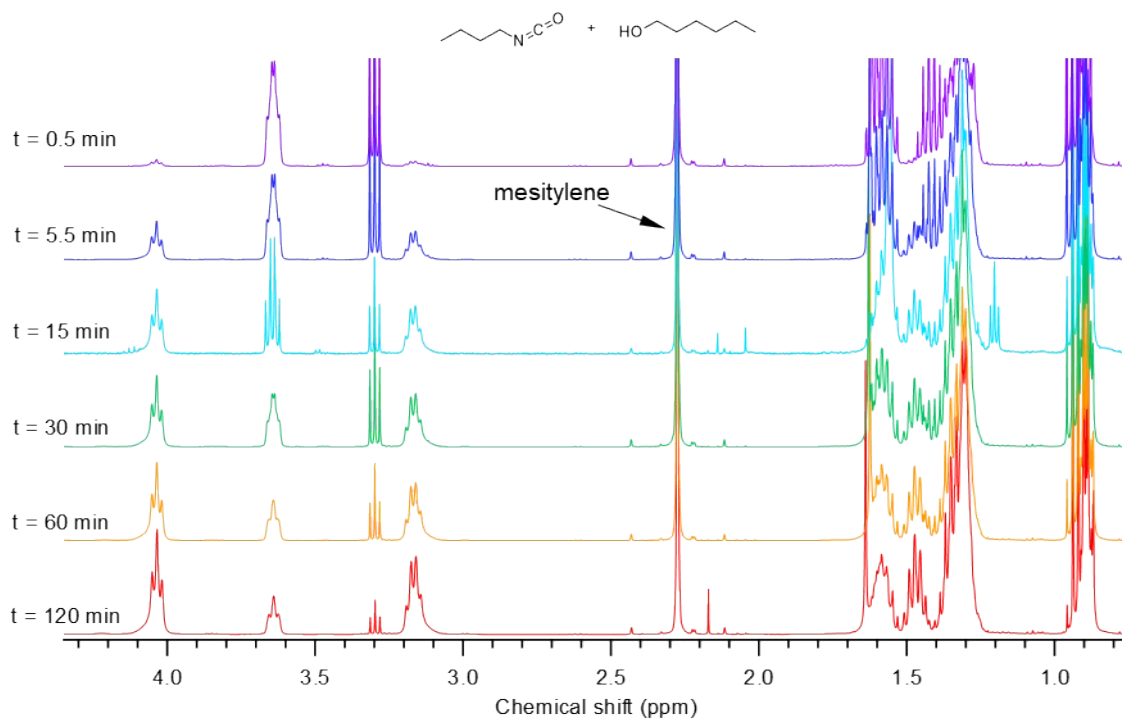
### c. Model reactions



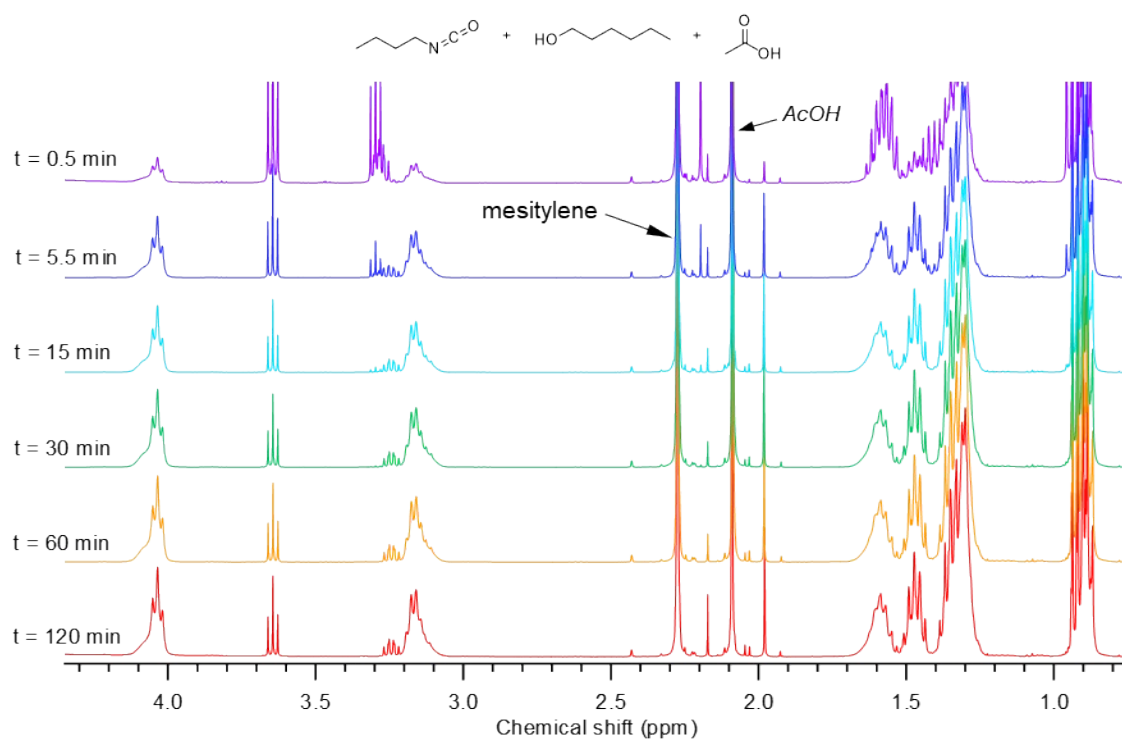
**Figure S14:** <sup>1</sup>H NMR (in CDCl<sub>3</sub>) kinetics of the model reaction **M0**.



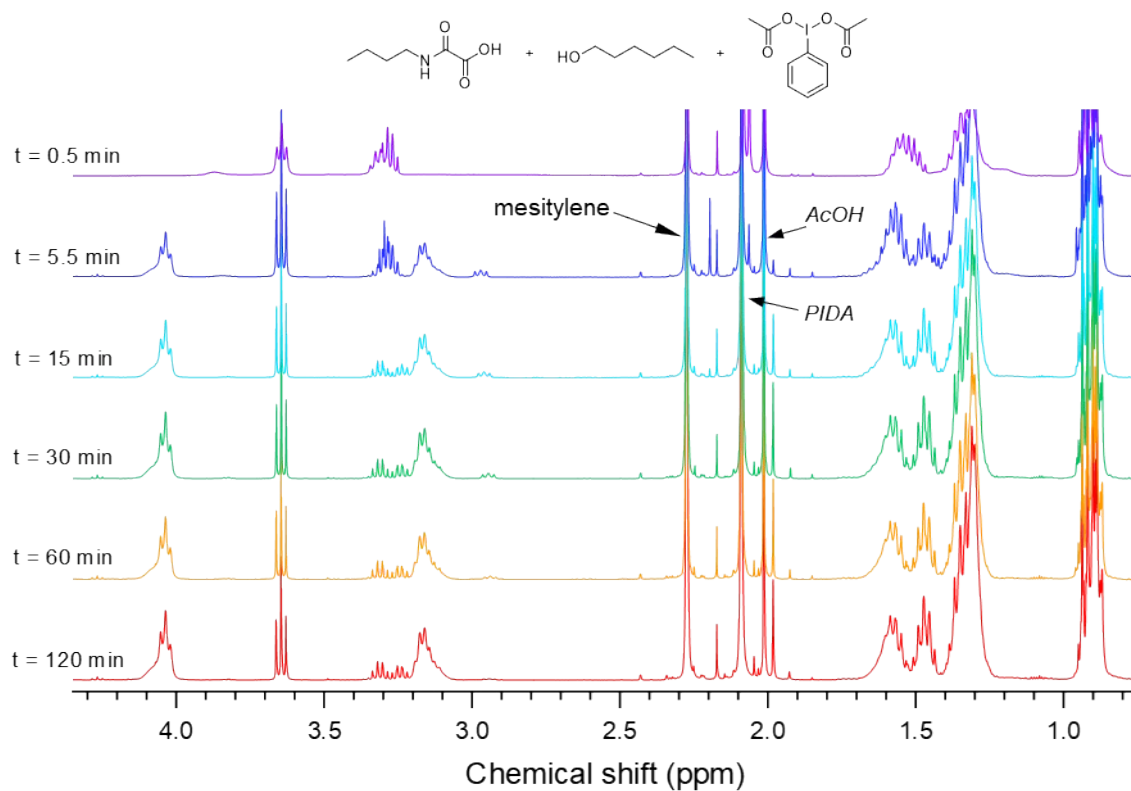
**Figure S15:** <sup>1</sup>H NMR (in CDCl<sub>3</sub>) spectra comparing **M0** to **4** and **7**.



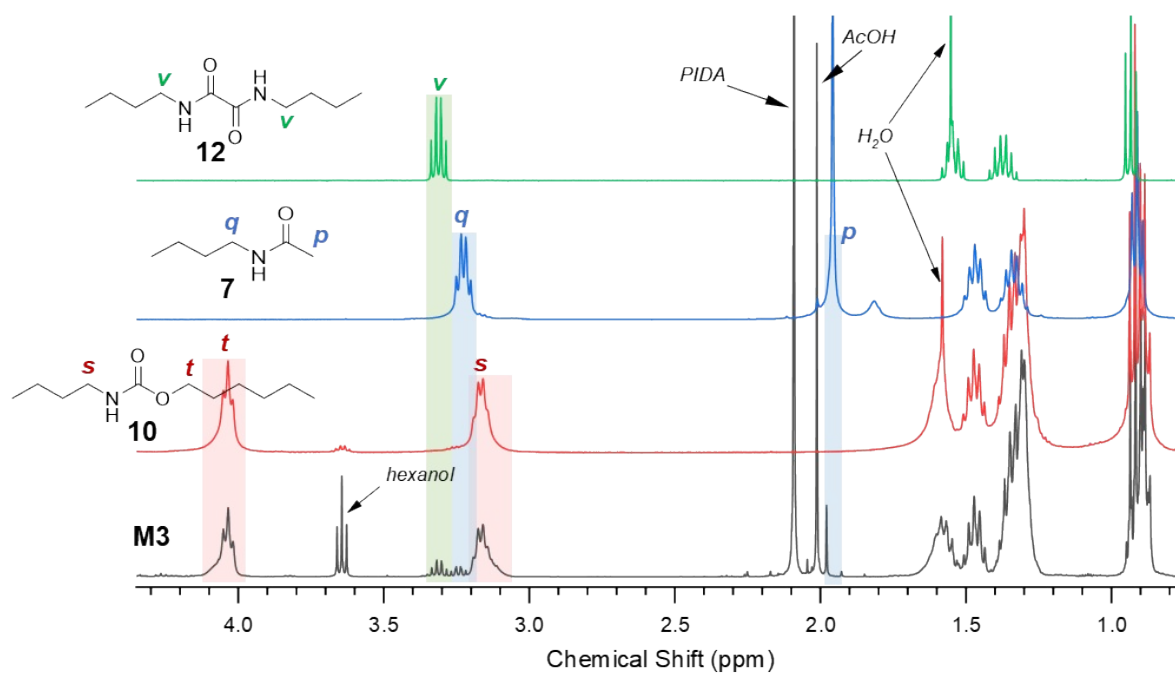
**Figure S16:**  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) kinetics of the model reaction **M1** using the isocyanate pathway at  $70^\circ\text{C}$  in bulk.



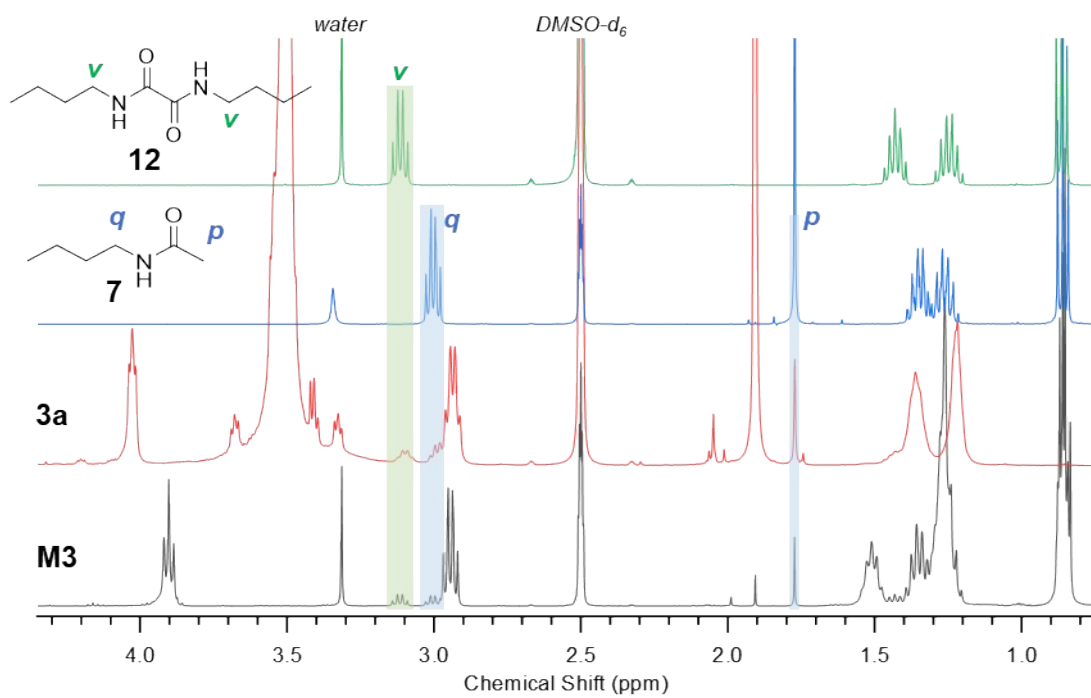
**Figure S17:**  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) kinetics of the model reaction **M2** using the isocyanate pathway in presence of AcOH at  $70^\circ\text{C}$  in bulk.



**Figure S18:**  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) kinetics of the model reaction **M3** using the oxamic acid pathway at  $70^\circ\text{C}$  in bulk.



**Figure S19:**  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) spectra comparing **M3** to **7**, **10** and **12**.

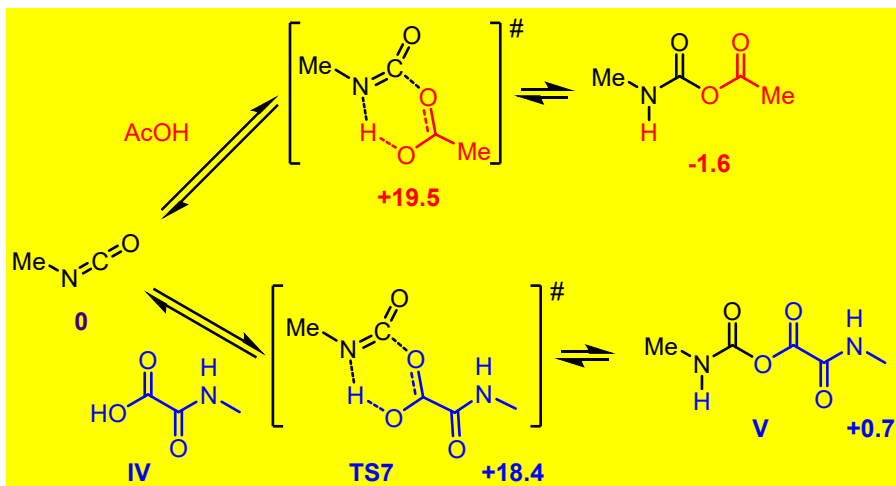


**Figure S20:** <sup>1</sup>H NMR spectra (in DMSO-d<sub>6</sub>) comparison of **3a**, **M3**, **7** and **12**.



## e. DFT Calculations

All the computed structures are available on request. This Supporting information contains free Gibbs energies and cartesian coordinates of all structures discussed below.



**Figure S21:** Comparison of the addition of acetic acid and methyl oxamic acid onto methyl isocyanate

### Coordinates of computed structures

#### *N*-Methyloxamic acid IV

O	-2.1402000	0.65165900	-0.00025200
H	-2.98663600	0.18050300	-0.00051200
C	-1.17694200	-0.25698600	-0.00001800
O	-1.35629200	-1.44378000	0.00006500
C	0.22655300	0.38307500	0.00021500
O	0.38583400	1.57899500	0.00020700
N	1.18483900	-0.55884000	0.00042000
H	0.87492300	-1.51839700	0.00013800
C	2.59289200	-0.23184700	-0.00033800
H	3.08349900	-0.63043700	0.88781900
H	3.08271900	-0.63191600	-0.88829100
H	2.68187100	0.85167000	-0.00141400

#### TS7

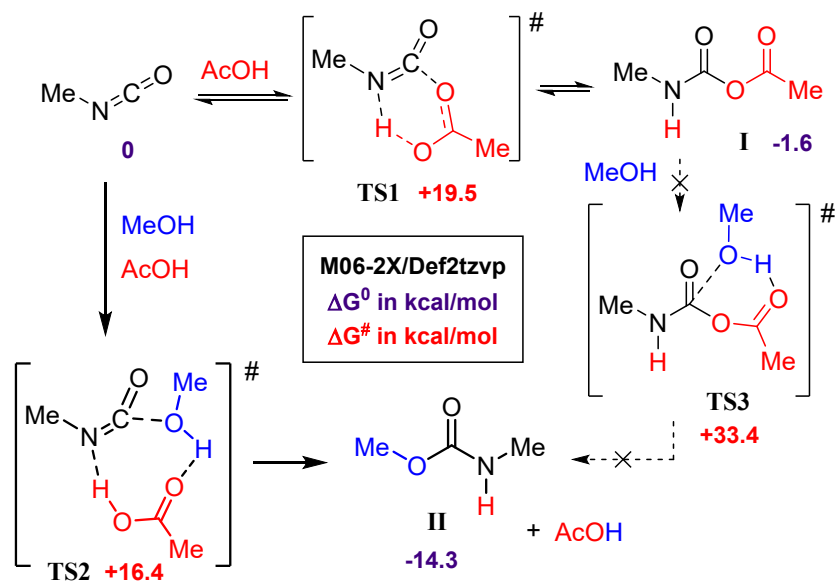
C	3.84904200	-0.72289700	0.00002000
H	4.08079100	-1.31170800	-0.88590500
H	4.08065900	-1.31205200	0.88575000
H	4.46040200	0.17815800	0.00024100
N	2.42076400	-0.39396500	-0.00000700
C	2.09326600	0.82935000	0.00000100
O	2.31772600	1.96706500	0.00002000
O	0.26157900	-1.52716200	-0.00003100
H	1.37347900	-1.18888600	-0.00004500
C	-0.35588900	-0.43003800	-0.00002100
O	0.19475100	0.69503100	-0.00002600
C	-1.89720000	-0.48796600	0.00000400
O	-2.48770700	-1.54024200	0.00004000

C	-3.90520100	0.86407900	0.00001100
H	-4.16088900	1.92002700	0.00012700
H	-4.33210300	0.38658500	-0.88229100
H	-4.33207300	0.38639800	0.88222600
N	-2.46470800	0.72790000	-0.00001900
H	-1.85756100	1.53122500	-0.00003400

#### Product V

C	-3.83960900	-0.86792500	-0.00024900
H	-4.29007200	-0.41785100	0.88394200
H	-4.03601300	-1.93658700	-0.00192900
H	-4.29034500	-0.41504500	-0.88284600
N	-2.40305500	-0.66692300	-0.00030900
C	-1.93032100	0.58426700	0.00019000
O	-2.57020600	1.59001400	0.00039800
O	0.16466300	-1.43623300	0.00031000
H	-1.75768400	-1.43977400	0.00000700
C	0.37316500	-0.25074100	0.00022000
O	-0.52279700	0.72430100	0.00019600
C	1.80906800	0.32151500	-0.00006000
O	2.03734500	1.50481700	-0.00029500
C	4.13952200	-0.32954800	-0.00026300
H	4.39331900	0.25803600	0.88220400
H	4.71518000	-1.25086700	-0.00060900
H	4.39287300	0.25842700	-0.88259300
N	2.72913800	-0.65534700	-0.00002200
H	2.40715900	-1.60904800	0.00024100

## Structures computed in Scheme 2



Compounds	Sum of electronic and thermal Free Energies (Hartrees)	Energy difference (kcal/mol)
<b>MeNCO</b>	-207.960613	0
<b>MeOH</b>	-115.686137	-
<b>AcOH</b>	-229.053419	-
<b>TS1</b>	-436.982910	+19.5
<b>I</b>	-437.016621	-1.6
<b>TS2</b>	-552.674215	+16.4
<b>II</b>	-323.669483	-14.3
<b>TS3</b>	-552.646996	+33.4

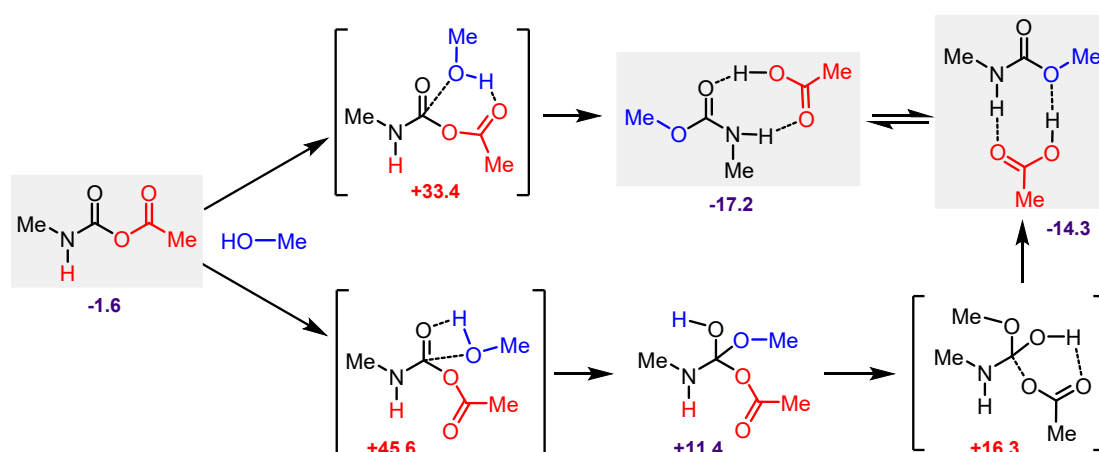
## Coordinates of computed structures

<b>MeNCO</b>				H	-1.14422100	-0.74983000	0.00011900
C	-1.73957000	0.15896800	0.00021100	<b>TS1</b>			
H	-1.96076300	0.62795400	0.95807800	C	-2.62430000	-1.04860400	-0.00012000
H	-2.44531600	-0.65141500	-0.15988100	H	-2.78887100	-1.65904800	0.88704600
H	-1.86372300	0.89383600	-0.79402300	H	-2.78563900	-1.66690200	-0.88239100
N	-0.40777600	-0.37410500	-0.00122400	H	-3.34298200	-0.22973100	-0.00507200
C	0.73965000	-0.05698900	-0.00008200	N	-1.24725900	-0.55255400	-0.00013900
O	1.89047000	0.14206000	0.00045300	C	-1.08547300	0.70531300	0.00002100
<b>AcOH</b>				O	-1.49857100	1.79394100	0.00001500
O	0.78825200	-1.02706600	0.00020000	O	1.07964800	-1.32417300	0.00026700
H	1.72701900	-0.79092200	0.00051000	H	-0.02357200	-1.20303300	0.00012800
C	0.08980300	0.12593200	-0.00042000	C	1.51605500	-0.12167100	0.00022200
O	0.62365300	1.19811600	0.00004200	O	0.76291100	0.87487600	0.00018700
C	-1.38846400	-0.12349900	-0.00003100	C	3.00019100	0.06498700	-0.00020900
H	-1.65748300	-0.70877700	-0.87882600	H	3.41495000	-0.42173300	-0.88251400
H	-1.65717100	-0.70790100	0.87945400	H	3.24914700	1.12116500	0.00418800
H	-1.91564000	0.82460100	-0.00036800	H	3.41703300	-0.43013700	0.87635500
<b>MeOH</b>				<b>I</b>			
C	0.66158200	-0.02048600	0.00001700	C	2.72907800	-0.76797600	-0.00014700
H	1.08188900	0.98328700	-0.00109300	H	3.16933300	-0.30534200	-0.88319800
H	1.02134700	-0.54371200	0.89079300	H	2.95325200	-1.83131000	-0.00032000
H	1.02123400	-0.54561400	-0.88968000	H	3.16943800	-0.30566100	0.88302500
O	-0.74371800	0.12234800	-0.00003000	N	1.28905100	-0.60419300	-0.00001800

C	0.77921900	0.63244900	0.00000800	O	-1.09213000	-0.71623100	0.00002100
O	1.39885200	1.65559400	0.00026000	C	-2.34913300	-0.04911900	-0.00004600
O	-1.24448700	-1.44404500	0.00029600	H	-2.45004900	0.57606400	-0.88597000
H	0.65913200	-1.39093500	-0.00040000	H	-3.10014200	-0.83383600	-0.00055300
C	-1.51828600	-0.27572800	0.00006200	H	-2.45051500	0.57534000	0.88634100
O	-0.62094200	0.73713000	-0.00020600	N	1.12317100	-0.61792200	-0.00004000
C	-2.91039900	0.27760600	-0.00012400	H	1.03187700	-1.61875900	-0.00005500
H	-3.62426600	-0.53953700	0.00037400	O	-0.09668200	1.30977100	0.00003700
H	-3.04760800	0.90779600	0.87799100	C	2.42707200	0.00231500	0.00002600
H	-3.04768800	0.90680600	-0.87894200	H	2.99581700	-0.27587600	-0.88821600
				H	2.27860400	1.07915600	-0.00013500
				H	2.99565200	-0.27563300	0.88845400
<b>TS2</b>				<b>TS3</b>			
C	1.31696500	2.56533700	0.11349100	C	2.59828300	-1.48222300	-0.46587000
H	0.47216400	3.09145200	0.55455100	H	3.07701900	-1.51322100	0.50956500
H	1.55831900	3.03723600	-0.83970700	H	3.11241800	-0.74678500	-1.09074900
H	2.17669700	2.65308200	0.77881200	H	2.67644000	-2.46455800	-0.92609100
N	0.92542200	1.16504200	-0.09778900	N	1.18470800	-1.17310300	-0.27884400
C	1.85605500	0.33099500	-0.00895900	C	0.92611700	-0.03818000	0.44561800
O	2.96329900	0.00428900	0.18591900	O	1.50143100	0.40394900	1.37506700
O	-1.68402000	1.06919100	-0.25493500	O	-1.53190500	0.04982500	-1.20505700
H	-0.65714900	1.01146900	-0.24830800	H	0.60786700	-1.27402800	-1.10170500
C	-2.23088800	-0.08249000	0.02597000	C	-1.71638600	-0.33503100	-0.02057200
O	-1.59560600	-1.11233800	0.19707600	O	-0.81823900	-0.30116800	0.87017600
C	-3.72654600	-0.03553700	0.12013800	C	-3.05828900	-0.88469500	0.36960900
H	-4.01456500	0.67189000	0.89723900	H	-3.21421100	-0.78322100	1.43985200
H	-4.13207100	0.33116700	-0.82242900	H	-3.84302300	-0.38980400	-0.19663600
H	-4.11694800	-1.02312600	0.34248700	H	-3.06872400	-1.94630700	0.11642600
C	1.50532500	-2.45435800	0.08388400	C	0.30721100	2.41254400	-0.09459100
H	1.24008500	-3.29406500	-0.55848700	H	1.15420000	2.64892200	0.54331200
H	2.58554300	-2.32334300	0.08412000	H	0.20981000	3.15118500	-0.88754900
H	1.16295300	-2.64419100	1.10229300	H	-0.60145900	2.37634400	0.50881600
O	0.93528800	-1.26291100	-0.43092600	O	0.55129600	1.14469500	-0.69811100
H	-0.03012500	-1.19640000	-0.19025800	H	-0.36556400	0.74028700	-1.10509900
<b>II</b>							
C	-0.02009500	0.10525100	0.00001100				

### Additional computed pathways

All computational data are available on request

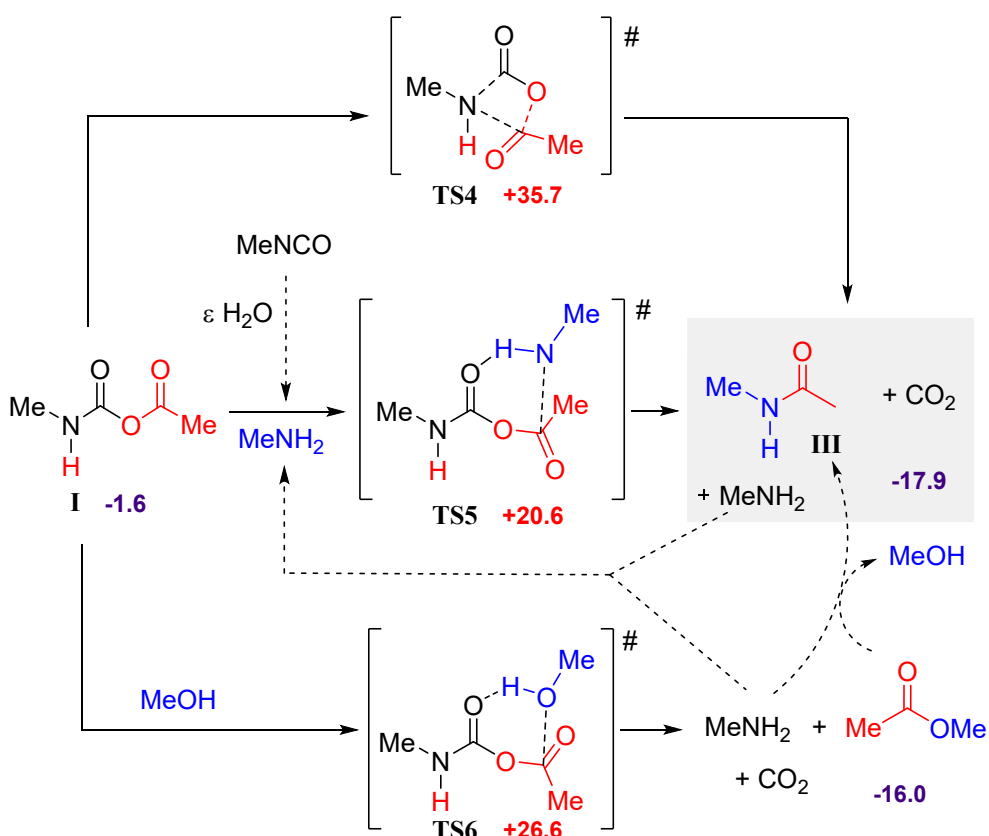


**Figure S22:** Additional pathways starting with NCA

### Pathways toward the amide formation

The proposed synthesis of amide **III** involves a 1,3-acyl transfer shift proceeding through **TS4**, coupled with a subsequent decarboxylation (Figure S22). However, this pathway is computationally predicted

to have a prohibitively high energy barrier, rendering it unattainable without catalysis.<sup>[4]</sup> An alternative and more practical route entails the attack of an amine on the acetyl moiety (via **TS5**), leading to the formation of amide **III** and CO<sub>2</sub> after decarboxylation. This process allows for the regeneration of the amine, which can then reenter into the catalytic cycle. The initial generation of the amine may be achieved through either the hydrolysis of the isocyanate by residual water traces or the attack of an alcohol on NCA **I** via **TS6**, resulting in an amine and an ester (MeCO<sub>2</sub>Me), that could potentially react again to yield amide **III**. While the reaction of NCA **I** with acetic acid to produce Ac<sub>2</sub>O and MeNH<sub>2</sub> (alongside CO<sub>2</sub>) is feasible, it is found to be less favorable (vide infra). The computational analysis suggests that a self-sustaining formation of the amide represents a more favorable pathway compared to the conventionally accepted 1,3-acyl shift. It is noteworthy that the potential formation of ureas, arising from the reaction between MeNH<sub>2</sub> and the isocyanate, is plausible. Upon comparing the NMR spectrum of the model reaction **M0** with that of the model urea **8** (di-n-butylurea, vide infra), we cannot entirely rule out the presence of minute amount of the urea, supporting the catalytic cycle below.



**Figure S23:** DFT calculations for a pathway toward amide formation

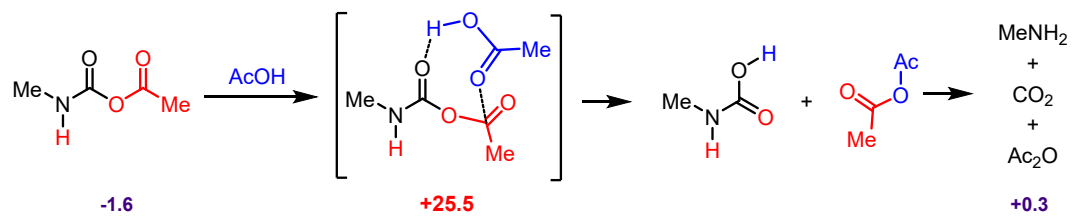
Compounds	Sum of electronic and thermal Free Energies (Hartrees)	Energy difference (kcal/mol)
<b>I</b>	-437.016621	-1.6
<b>MeNH<sub>2</sub></b>	-95.801131	-
<b>TS4</b>	-436.957253	+35.7
<b>TS5</b>	-532.785027	+20.6
<b>TS6</b>	-552.657858	+26.6
<b>III</b>	-248.436929	-17.9
<b>AcOMe</b>	-268.321384	-16.0
<b>CO<sub>2</sub></b>	-188.605639	-

#### Coordinates of computed structures

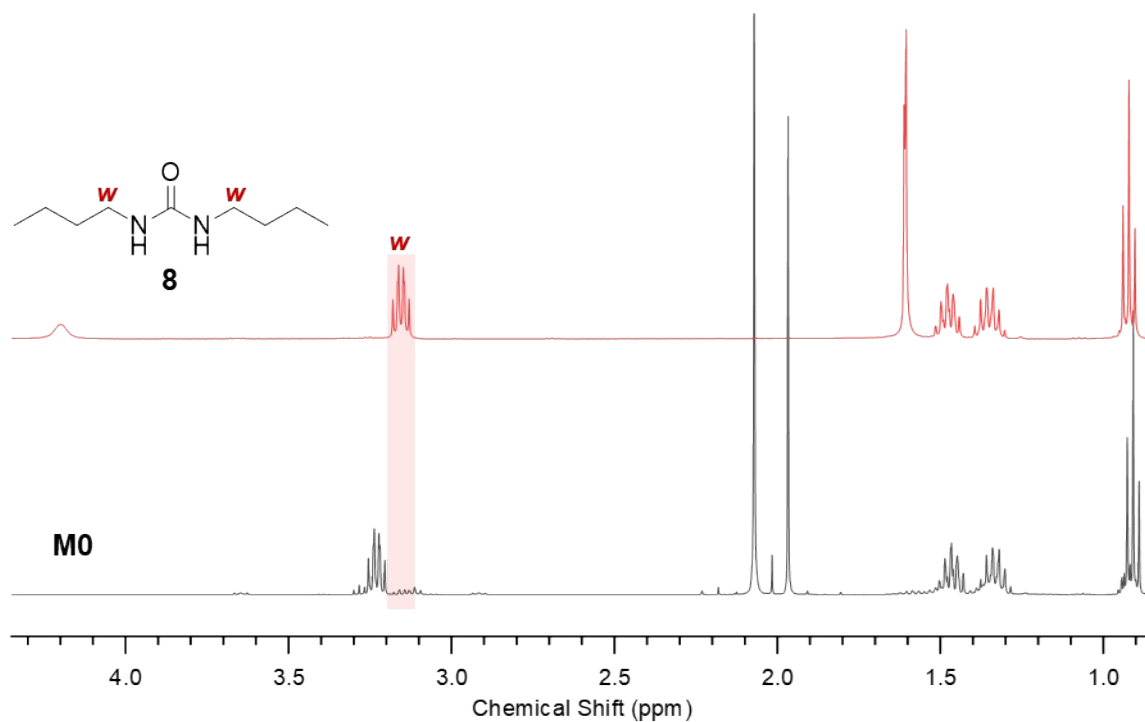
[4] Y.-Y. Jiang, T.-T. Liu, R.-X. Zhang, Z.-Y. Xu, X. Sun, S. Bi, J. Org. Chem. 2018, 83, 2676–2685.

<b>AcOMe</b>				O	-1.18281800	-0.40008000	1.47271800
O	-1.57867600	-0.85239900	0.00004700	H	2.55762000	-1.52079700	0.00633500
C	-0.60102300	-0.16658100	-0.00003300	C	-1.25909500	-0.56835900	0.27943000
C	-0.64184300	1.34142800	-0.00001900	O	0.31854800	-0.90818100	-0.46882500
H	-0.14063400	1.74439300	0.88032200	C	-2.01818000	-1.70222900	-0.36572500
H	-0.14143500	1.74463800	-0.88064600	H	-1.70125400	-2.62497500	0.11367600
H	-1.68230600	1.64800400	0.00044600	H	-3.08363700	-1.55952900	-0.17598500
C	1.79871700	0.01804900	0.00005400	H	-1.83115300	-1.77084100	-1.43502000
H	1.86939800	0.64307100	-0.89121400	C	-2.54956300	1.59339200	0.04189000
H	1.86999700	0.64181600	0.89211500	H	-3.50306200	1.08191300	-0.08020500
H	2.61935400	-0.69372300	-0.00076900	H	-2.58323000	2.56118700	-0.45349300
O	0.61249100	-0.75829800	-0.00008000	H	-2.33982000	1.71899300	1.10037400
				N	-1.46403600	0.78037400	-0.52307300
				H	-1.59905200	0.57778300	-1.51015800
				H	-0.49058800	1.22712500	-0.40956700
<b>CO<sub>2</sub></b>							
C	0.00000000	0.00000000	0.00000000				
O	0.00000000	0.00000000	1.15456600				
O	0.00000000	0.00000000	-1.15456600				
<b>MeNH<sub>2</sub></b>							
C	-0.70546300	-0.00000700	0.01783200				
H	-1.11259600	0.87780300	-0.48394000				
H	-1.07103400	-0.00070200	1.05124000				
H	-1.11276300	-0.87702000	-0.48520300				
N	0.74738700	-0.00000600	-0.12111600				
H	1.14871400	0.81266000	0.32936200				
H	1.14874900	-0.81265800	0.32935800				
<b>III</b>							
C	-1.96220600	-0.10997700	0.00010700				
H	-2.50873300	-0.43220200	-0.88724600				
H	-1.89295100	0.97481600	-0.00161000				
H	-2.50746900	-0.42939400	0.88927200				
N	-0.61236600	-0.62843000	-0.00017900				
O	0.41335600	1.38791600	-0.00000800				
H	-0.47084100	-1.62356300	0.00000500				
C	0.48475600	0.17733000	-0.00013500				
C	1.80598000	-0.56184800	0.00008000				
H	1.88811500	-1.19746500	-0.88251000	<b>TS6</b>			
H	1.88890900	-1.19514400	0.88427100	C	-3.53152900	0.07930200	0.03290100
H	2.61150300	0.16560100	-0.00117700	H	-3.41190700	1.15014600	0.17812500
				H	-3.76734500	-0.37582400	0.99650100
				H	-4.35322900	-0.09696800	-0.65790100
<b>TS4</b>				N	-2.31400800	-0.46041800	-0.53370000
N	0.41261700	0.51142700	0.59744600	C	-1.09340100	-0.04834900	-0.15231100
C	1.01355800	-0.69633500	-0.07334100	O	-0.98220900	0.88281900	0.68861800
O	2.16656500	-0.97928400	0.00728400	O	1.12549200	-1.27041700	1.32406900
O	-1.40316300	0.78704800	-1.04722000	H	-2.34014800	-1.27710700	-1.11928600
C	-1.06979000	0.05053500	-0.17472300	C	1.34507000	-0.72284400	0.30231800
O	-0.00023000	-1.20125700	-0.66274000	O	-0.08470100	-0.62697600	-0.70951700
C	-1.95263400	-0.61313700	0.84132600	C	2.38124500	-1.03741600	-0.72908600
H	-2.65055300	-1.25090700	0.30165500	H	2.25283800	-0.45912000	-1.63758100
H	-1.39117100	-1.22218400	1.54589100	H	3.36073900	-0.85115600	-0.28956500
H	-2.51448900	0.15901800	1.36628500	H	2.28863400	-2.09671800	-0.95942500
C	0.97684000	1.78964000	0.15590100	C	1.69835800	1.82122600	-0.50466300
H	0.60057300	2.59196100	0.78555800	H	2.75095900	1.72791200	-0.76540800
H	2.06367700	1.74305500	0.20504900	H	1.07635900	1.58423200	-1.37100800
H	0.64749100	1.95092600	-0.86955200	H	1.49993900	2.84317700	-0.18319500
H	0.44294400	0.41187500	1.60943200	O	1.40653100	0.94964000	0.57942100
				H	0.32185900	1.04231200	0.78897000
<b>TS5</b>							
C	3.62248700	0.31927700	0.23353100				
H	4.53844800	-0.17622900	-0.08350900				
H	3.68713100	0.54214600	1.30103100				
H	3.52113200	1.25835700	-0.30526800				
N	2.49030800	-0.52175000	-0.07919300				
C	1.24262400	-0.02512600	-0.23986200				
O	1.04101100	1.20485700	-0.19738500				

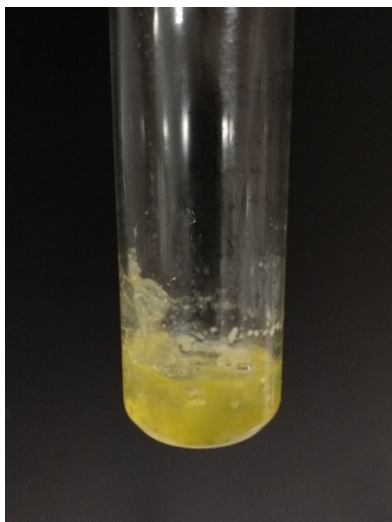
Additional pathways for the attack with AcOH



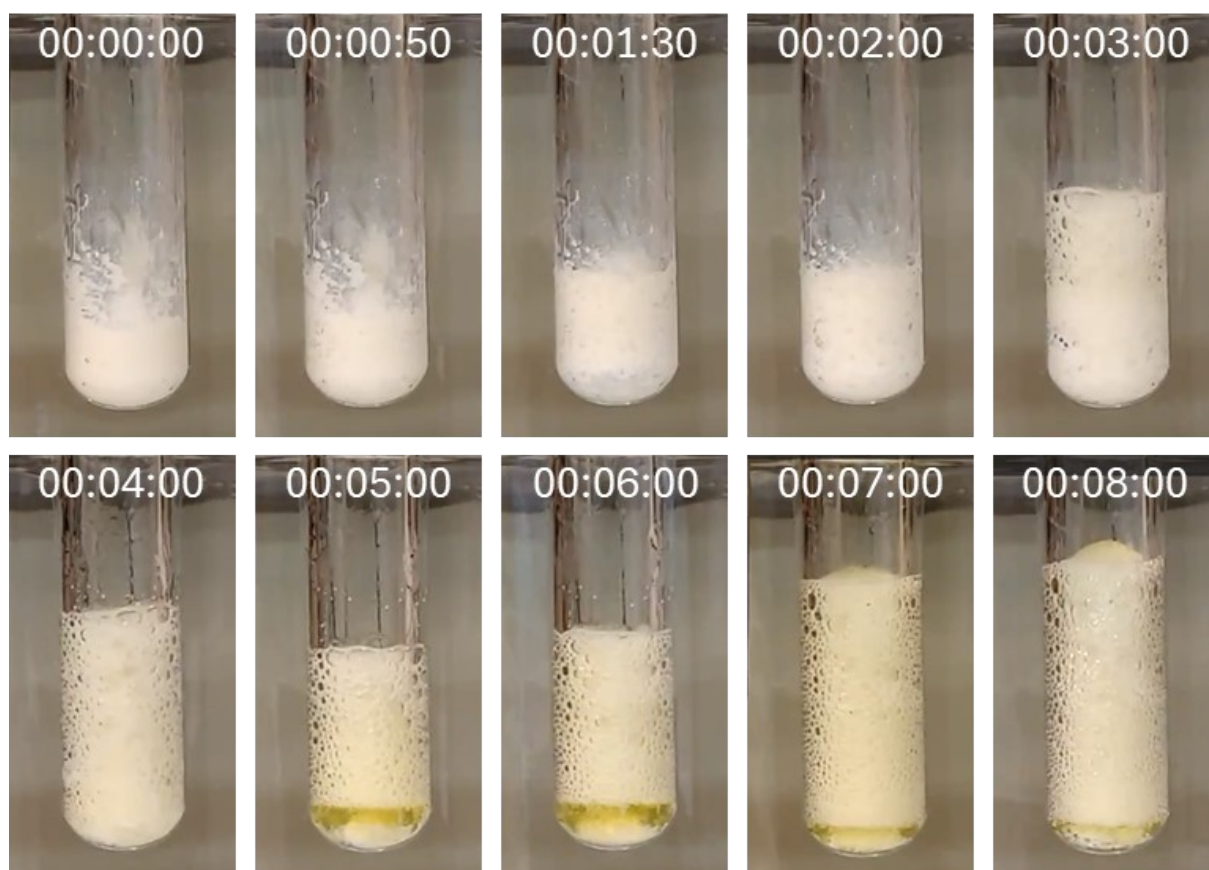
Comparison of the NMR spectra (CDCl<sub>3</sub>) of the reaction **M0** and of the urea **8**



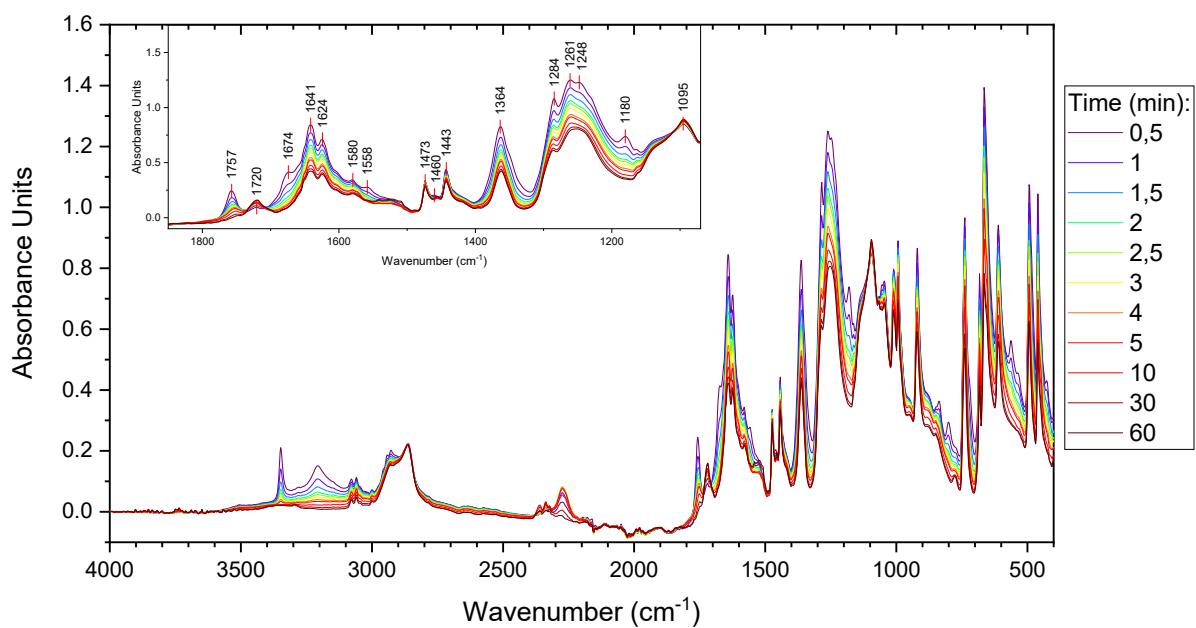
## f. Foam synthesis



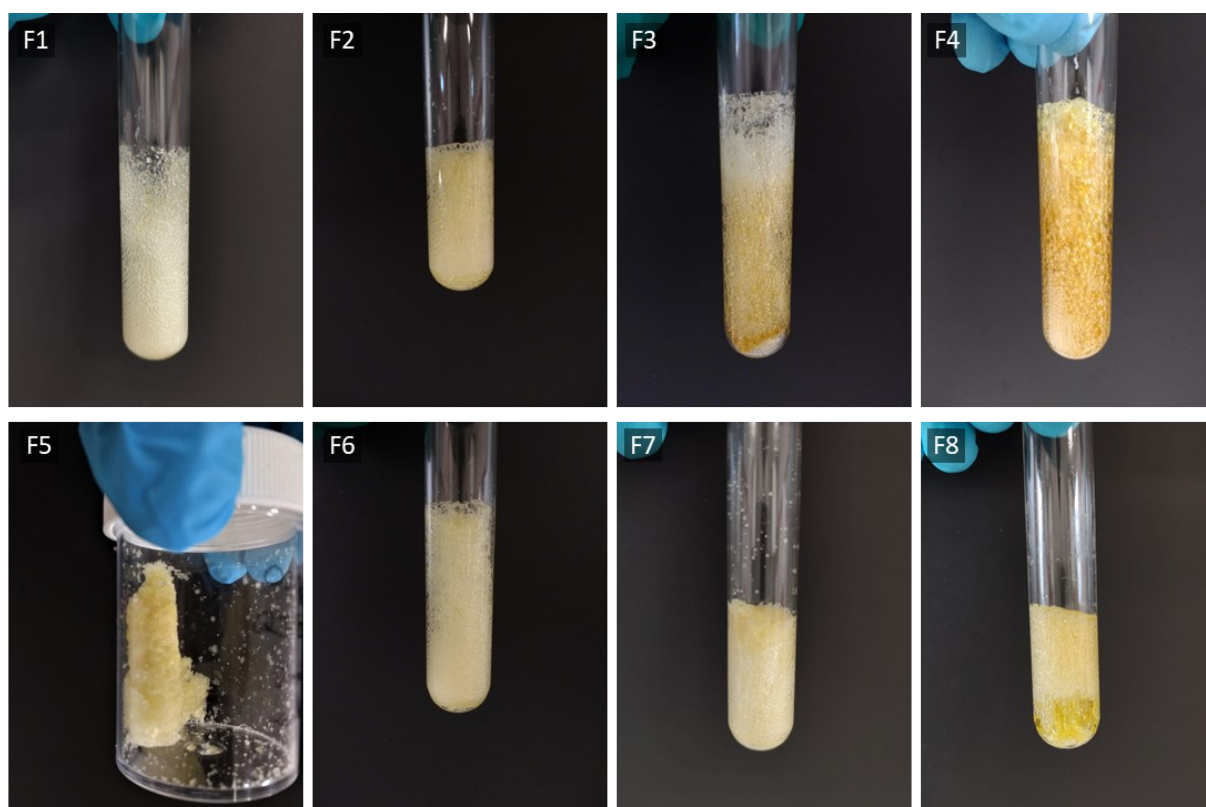
**Figure S24:** Foam production tentative at 70°C.



**Figure S25:** Evolution of the foaming reaction of F1 at 100°C

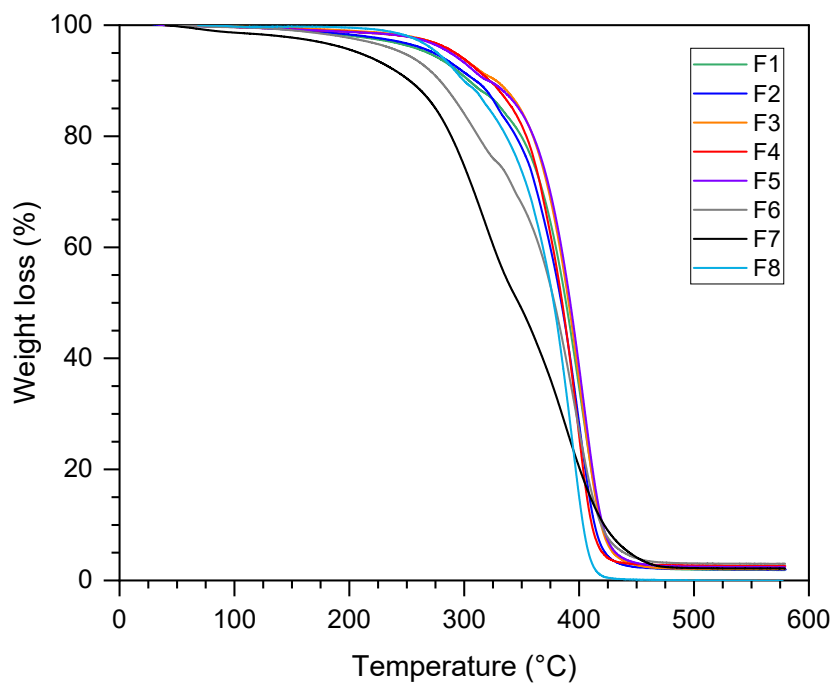


**Figure S26:** FTIR kinetic analysis of the foaming reaction of **F1** at 100°C.

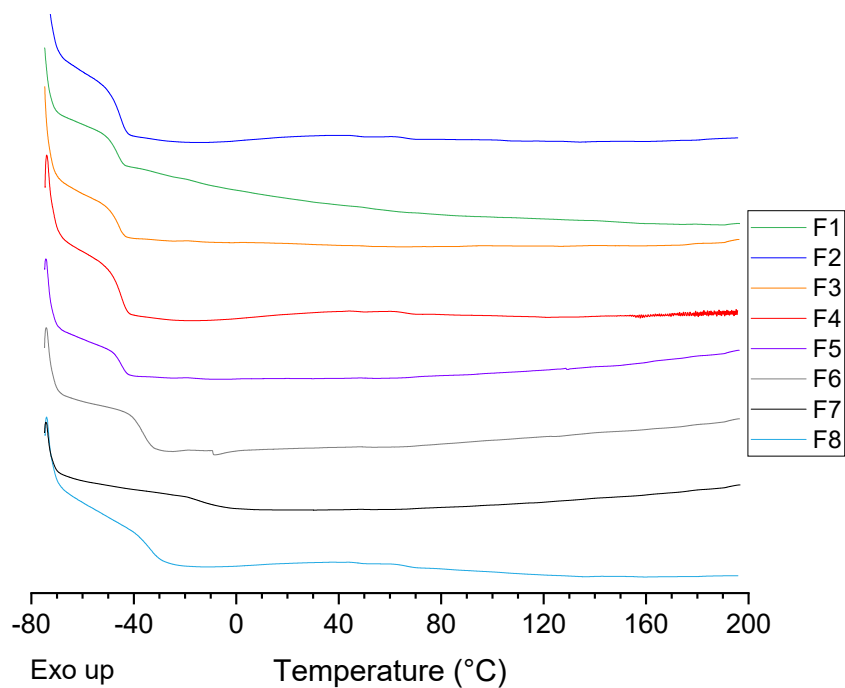


**Figure S27:** Photographs of PU foams **F1-8**.

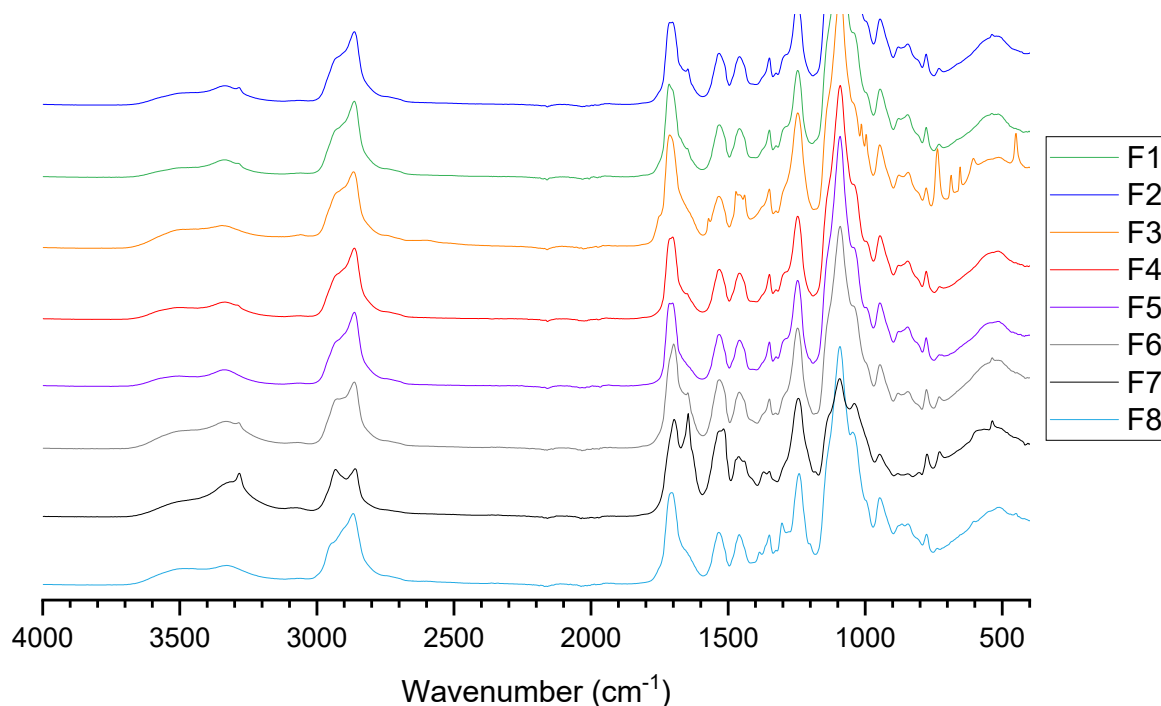




**Figure S28:** TGA thermograms of PU foams **F1-8**.



**Figure S29:** DSC thermograms (second heating cycle) of PU foams **F1-8**.

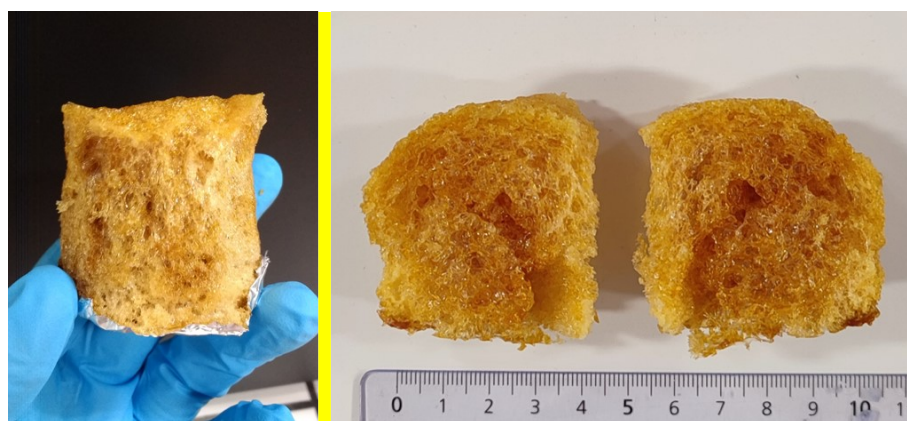


**Figure S30:** FTIR spectra of PU foams **F1-8**.

### g. Scale-up of the foam synthesis

Larger pieces of foam were obtained by reacting larger amounts of triol and hexamethylene bis-oxamic acid in a home-made open reactor fabricated with aluminium foil.

The triol (12 mmol, 0.6 eq.) and ethoxylated poly(dimethylsiloxane) (0.12 g) were introduced in the open reactor. PIDA (44 mmol, 2.2 eq.) and hexamethylene bis-oxamic acid (20 mmol, 1 eq.) were crushed and combined, then introduced in the open reactor and all the compounds were mixed together. The reactor was introduced in an oven pre-heated at 115 °C. After 1h30 of curing, a foam was obtained as represented on the picture below. It was dried under heated vacuum at 60°C for 4 hours. According to DSC and TGA measurements,  $T_g = -45.1$  °C, and  $T_{d5\%} = 294$  °C, respectively, in close agreement with the values reported for the previous foams.



**Figure S31:** Picture of the foam obtained by scaling-up the aforementioned process