# Functional Regioregular (Poly)urethanes from Soft Nucleophiles and Cyclic Iminocarbonates

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## Materials and methods

### *Chemicals*

Glacial acetic acid, octanoic acid (98%), benzoic acid (99%), acrylic acid (99%), levulenic acid (98%), L-leucic acid (98%), 3-butenenoïc acid (97%), coumalic acid (97%), glycolic acid (98%), 2,2-bis-(hydroxymethyl)propionic acid (98%), itaconic acid (99 %), succinic acid (99%), terephthalic acid (98%), D,L-malic acid (99%), sulfuryl chloride (97%), were purchased from Sigma Aldrich and used without any further purification. Ethyl formate (98%), triethylamine (99%), phosphorous oxychloride (99%), *n*-butyl isocyanide (98%), cesium carbonate (99.5% for analysis, anhydrous), potassium carbonate (99%, for analysis, anhydrous), magnesium sulfate (99%, extra pure, dried), acetonitrile (99.9%, extra dry) and dichloromethane (> 99%, extra dry) were purchased from Acros Organics and used without further purification. 2-Methylpropane-1,2-diol (95%) was purchased from ABCR and used without further purification. 1,4-Diaminobutane (98%) was purchased from Alfa Aesar and used with further purification. *Tert*-butyl methyl ether (MTBE, extra pure, SRL) and Ethyl acetate (EtOAc, 99.8%) were purchased from Fisher Chemical and used without further purification. Heptane was purchased from Fisher Chemical and distilled prior to use. Celite was purchased from Chem-Lab NV. Deuterated chloroform ($CDCl_3$, 99.8% D) and dimethylsulfoxide (DMSO-$d_6$, 99.8% D) were purchased from Eurisotop. DMSO (> 99.5%, Aldrich) was dried onto molecular sieves 3 Å prior to use.

### *Characterization techniques*

*Mass Spectrometry.* High resolution mass spectrometry (HRMS) samples of the model carbamates were prepared by dissolving 0.1-5 mg of the compound in $CH_3CN/H_2O$ and further diluted to a concentration of $10^{-5}$-$10^{-6}$ M. Formic acid (0.1%) was added prior to injection. 10 µL of each sample was injected using the CapLC system (Waters, Manchester, UK) and electrosprayed using a standard electrospray source. Samples were injected with an interval of 3 minutes. Positive ion mode accurate mass spectra were acquired using a Q-TOF II instrument (Waters, Manchester, UK). The MS was calibrated prior to use with a 0.1% $H_3PO_4$ solution. The spectra were lock mass corrected using the known mass of the nearest $H_3PO_4$ cluster or a known background ion. Analytes were detected as protonated or as a sodium adduct. All measured masses are within a difference of 5 ppm compared to the calculated mass unless specified otherwise.

*NMR spectroscopy.*

$^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker Avance 400 MHz spectrometers in the Fourier transform mode at 303 K (unless stated otherwise), using the non or partly deuterated solvent as internal standard ($^1H$: $\delta$ = 7.26 ppm, $^{13}C$: $\delta$ = 77.16 ppm for $CDCl_3$ and $^1H$: $\delta$ = 2.50 ppm, $^{13}C$: $\delta$ = 39.52 ppm for DMSO-$d_6$). 16 Scans were recorded for $^1H$ spectra and 512 scans for $^{13}C$ spectra. Chemical

shifts ($\delta$) are given in ppm and coupling constants ($J$) are reported in Hertz (Hz). Multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), br s (broad singlet) and m (multiplet) or combinations thereof.

*Size Exclusion Chromatography.*

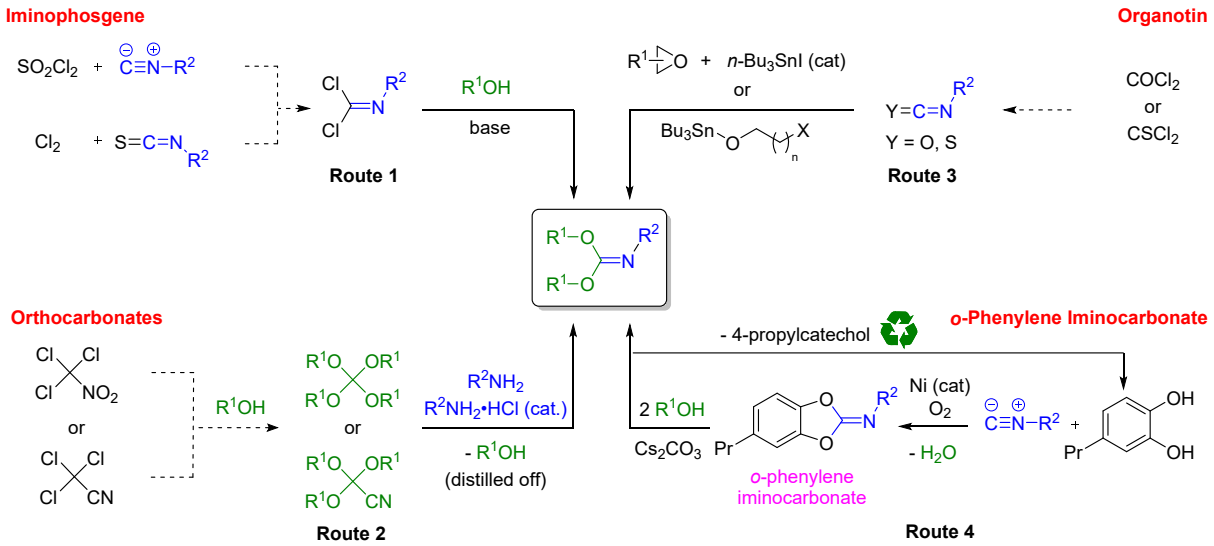
The molecular weight ($M_n$ and $M_w$) and the dispersity (Đ) of the polyurethanes were determined by size exclusion chromatography (SEC) in DMF containing LiBr (0.025 mol/L) at 55 °C and a flow rate: 1 mL/min) with a Waters chromatograph equipped with two columns dedicated to the analysis of low molar mass samples (PSS gram analytical 100 Å, separation range 300-60000 Da) and a pre column (100 Å), a dual λ absorbance detector (Waters 2487) and a refractive index detector (Waters 2414). A previously established PS calibration curve was used.

*Dynamic scanning calorimetry (DSC).*

DSC analysis was performed on a DSC 250 (TA Instruments). All the experiments were performed under nitrogen flow. 4–6 mg of polymers were introduced in hermetic aluminum pans. Polymers were cooled to -80°C and then heated at a rate of 5°C/min. The temperature modulated segment was set with an amplitude of 1 °C with a period of 60 seconds.

## General Synthesis Methods For Iminocarbonates

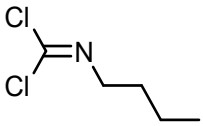
Although iminocarbonates have attracted the attention of organic chemists for decades, only a limited number of methods to synthesize them are known. The most general strategy involves an addition-elimination reaction of alcoholates on iminophosgenes (Scheme S1, Route 1).[3] Other less-applied approaches rely on orthocarbonates (Scheme S1, Route 2)[4] or organotin reactants in combination with isocyanates or isothiocyanates (Scheme S1, Route 3).[5] We recently reported an oxidative Ni-catalyzed reaction of isocyanides with catechols providing bench stable *o*-phenylene iminocarbonates (Scheme S1, Route 4). These platform molecules were easily transferred into dialkyl iminocarbonates *via* $S_NAE$ with alcohols, however only in a moderate yield of 30 to 40%.




**Scheme S1.** Synthetic approaches to the fabrication of cyclic iminocarbonates

**Experimental protocols**

Synthesis of *n*-butylcarbonimidic dichloride

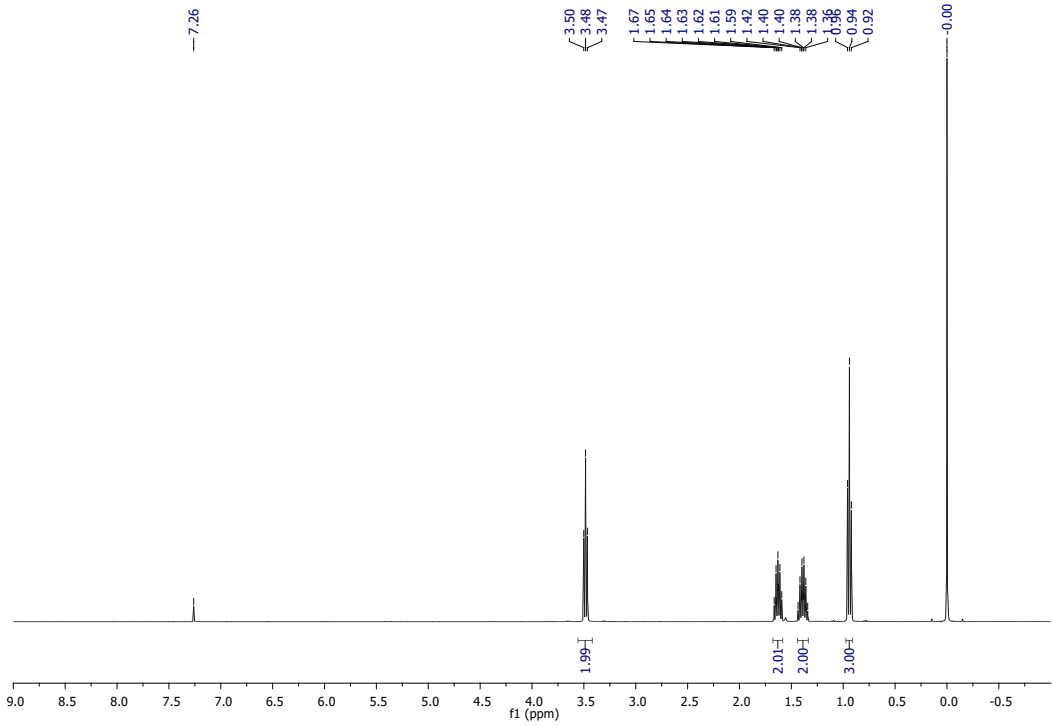


A flame-dried round-bottomed flask of 250 mL equipped with a stir bar was charged under argon atmosphere with *n*-butylisocyanide (5 mL, 45.8 mmol, 1.0 equiv) and DCM (60 mL, dry). The solution was cooled to -40 °C before a solution of sulfuryl chloride (50.2 mmol, 1.05 equiv) in DCM (15 mL, dry) was added dropwise. The reaction mixture was stirred further at -40 °C for 5 min and subsequently at room temperature for 15 min. The solvent was removed under reduced pressure without heating (*ca* 100 mbar) to afford the crude iminophosgene. Purification by vacuum distillation (80 °C, 40 mbar) afforded the title compound (4.75 g, 30.8 mmol, 65%) as a colorless liquid. The spectral data match those reported in the literature.[1]

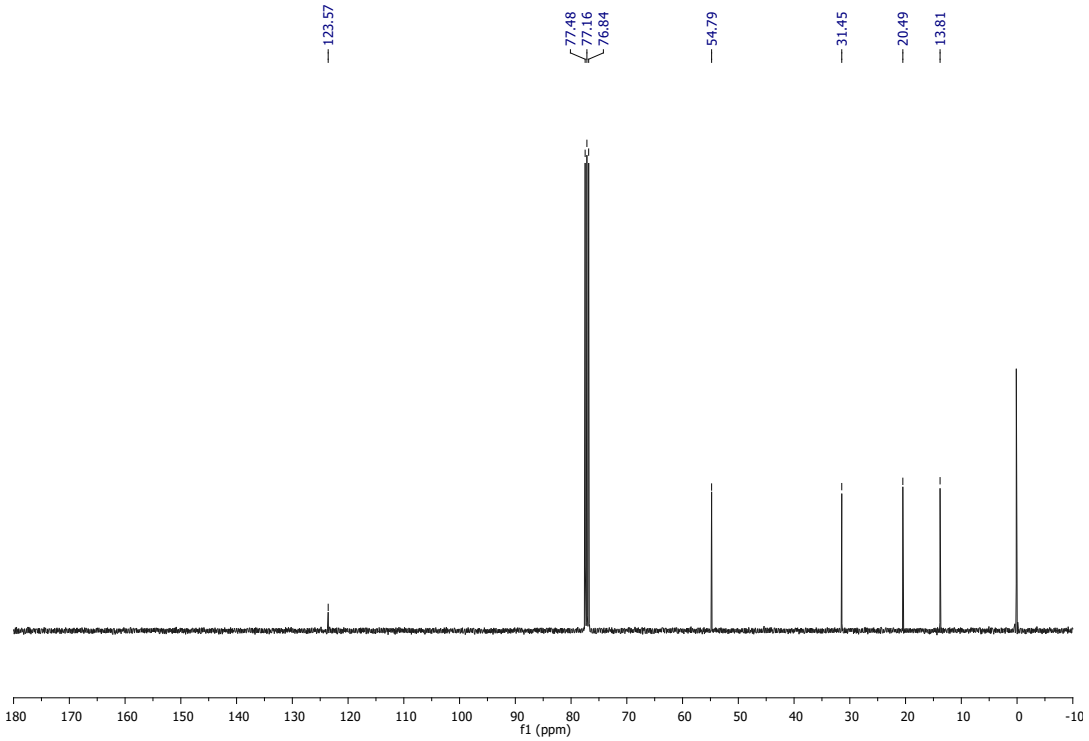
**$^1$H NMR (400 MHz, $CDCl_3$):** δ (in ppm) = 0.94 (t, 3H, *J* = 7.4 Hz), 1.44 - 1.34 (m, 2H), 1.67 - 1.59 (m, 2H), 3.48 (t, 2H, *J* = 7.0 Hz).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ (in ppm) = 13.8 ($CH_3$), 20.5 ($CH_2$), 31.5 ($CH_2$), 54.8 ($CH_2$), 123.6 (C).

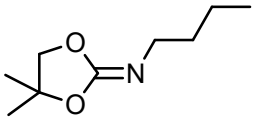
$^1$H NMR (400 MHz, $CDCl_3$):



$^{13}$C NMR (101 MHz, $CDCl_3$):




Synthesis of *N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (mixture of *Z* and *E* isomers, **1**)



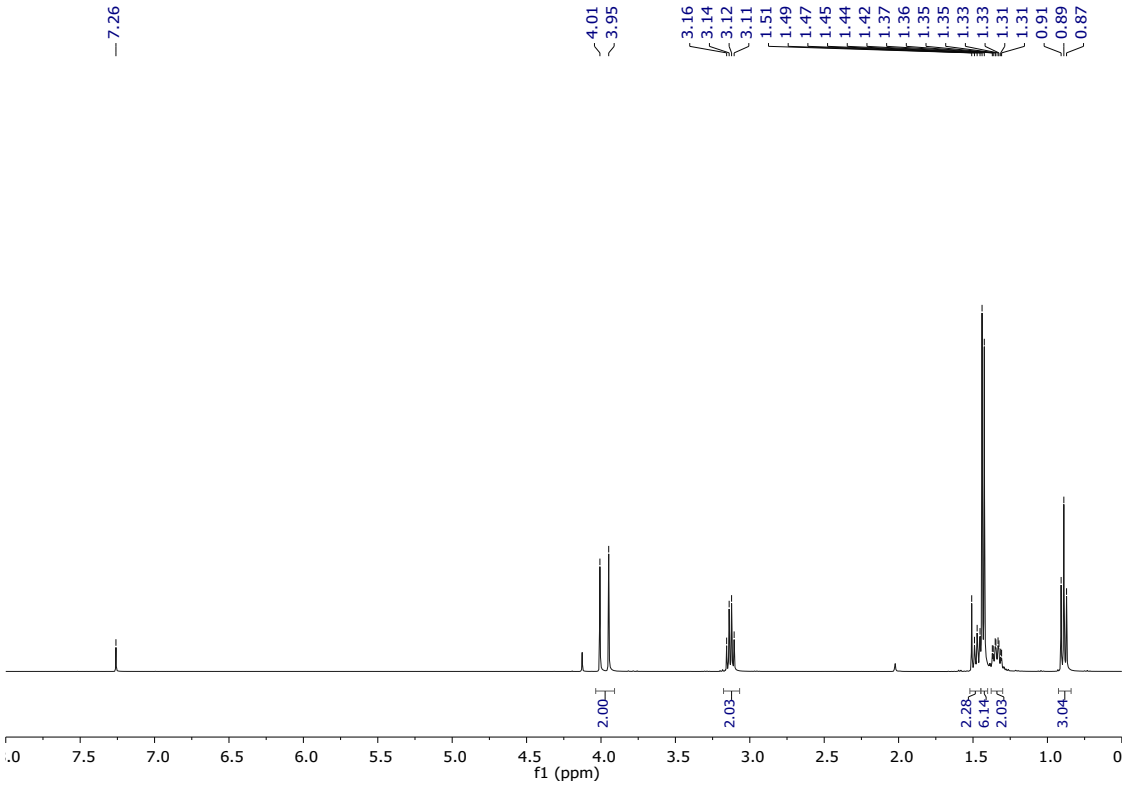
A flame-dried round-bottomed flask of 250 mL equipped with a stir bar was charged under argon atmosphere with 2-methylpropane-1,2-diol (10.8 g, 120 mmol, 1.0 equiv), $Cs_2CO_3$ (82.1 g, 252 mmol, 2.1 equiv) and acetonitrile (100 mL, dry). Subsequently, a solution of *n*-butylcarbonimidic dichloride (22 g, 144 mmol, 1.2 equiv) in acetonitrile (20 mL, dry) was added at room temperature. The reaction mixture was refluxed in an oil bath for 24 h. The reaction mixture was allowed to cool to room temperature. MTBE (50 mL) was added and the resulting orange suspension was filtered through Celite®. The obtained solution was concentrated under reduced pressure to afford an orange liquid. The product was purified by distillation using a Vigreux column (94 °C, 4 mbar), which provided a *ca* 1:1 mixture of diastereoisomers (14.8 g, 86.4 mmol, 72%) as a colorless liquid. Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ (in ppm) = 0.89 (t, 3H, *J* = 7.3 Hz), 1.37 - 1.31 (m, 2H), 1.42 (s, 3H), 1.44 (s, 3H), 1.51 - 1.45 (m, 2H), 3.12 (t, 1H, *J* = 6.8 Hz), 3.14 (t, 1H, *J* = 6.8 Hz), 3.95 (s, 1H), 4.01 (s, 1H).

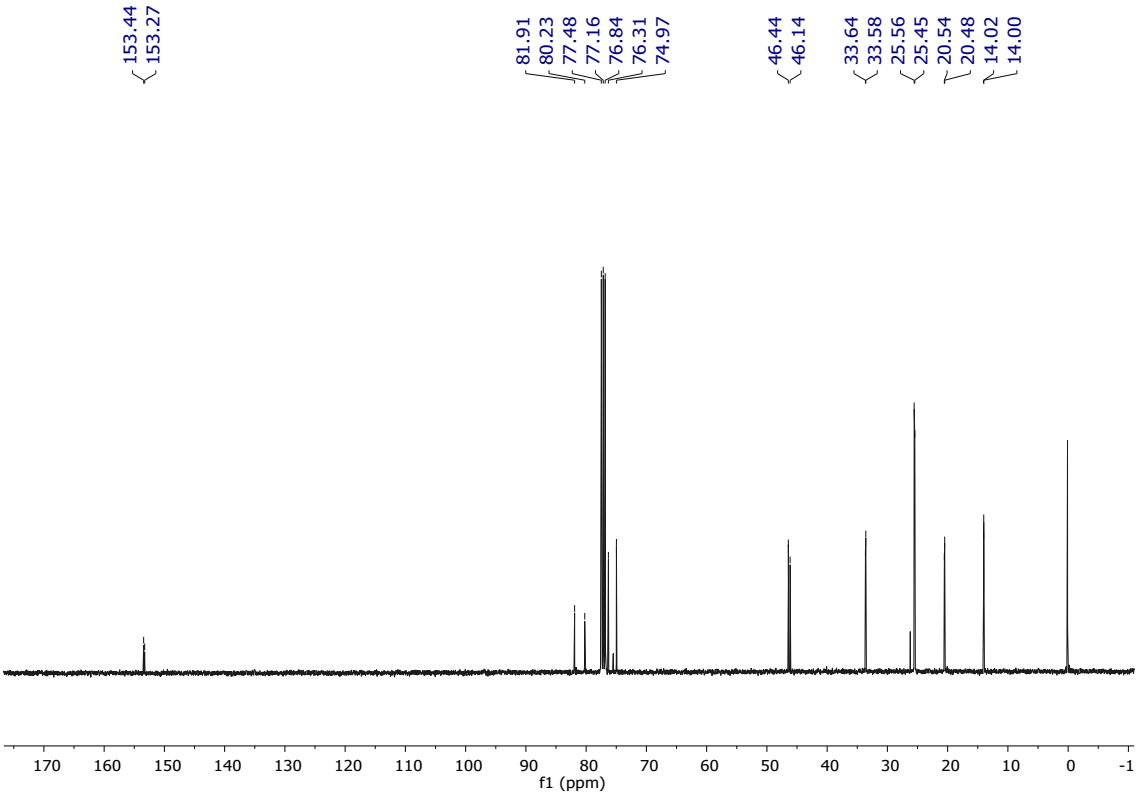
**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ (in ppm) = 14.0 ($CH_3$), 14.0 ($CH_3$), 20.5 ($CH_2$), 20.5 ($CH_2$), 25.5 ($CH_3$), 25.6 ($CH_3$), 33.6 ($CH_2$), 33.6 ($CH_2$), 46.1 ($CH_2$), 46.4 ($CH_2$), 75.0 ($CH_2$), 76.3 ($CH_2$), 80.2 (C), 81.9 (C), 153.3 (C), 153.5 (C).

**HRMS(ESI+):** m/z calcd. for $C_9H_{18}N_1O_2$ $[M + H]^+$ 172.1332, found 172.1330.

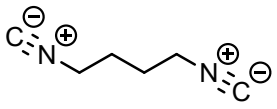
$^{1}$H NMR (400 MHz, $CDCl_3$):




$^{13}$C NMR (101 MHz, $CDCl_3$):



Synthesis of 1,4-diisocyanobutane



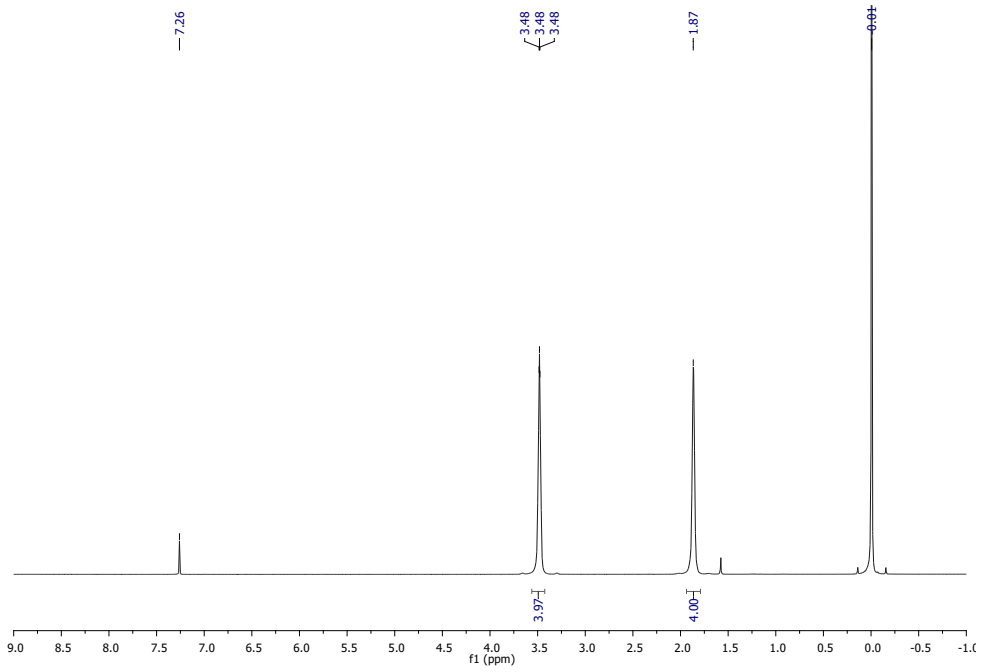
A 100 mL round-bottomed flask equipped with a stir bar was charged with butane-1,4-diamine (10.5 mL, 100 mmol, 1.0 equiv) and ethyl formate (40.4 mL, 500 mmol, 5.0 equiv). The flask was equipped with a reflux condenser, placed in an oil bath and refluxed overnight. The reaction mixture was concentrated *in vacuo* to get the crude diformamide. After freeze-drying of this solid, the crude *N*,*N*′-(butane-1,4-diyl)diformamide was used in the next step without further purification.

An oven-dried 250 mL round-bottomed flask equipped with a stir bar was cooled to room temperature under argon. Then it was charged with *N*,*N*′-(butane-1,4-diyl)diformamide (7.2 g, 50 mmol, 1.0 equiv), triethylamine (42.0 mL, 300 mmol, 6.0 equiv) and dichloromethane (50 mL, dry). The resulting mixture was cooled to 0 °C. Then, freshly distilled phosphorous oxychloride (13 mL, 140 mmol, 2.8 equiv) was added dropwise at 0 °C over 30 minutes. The resulting red slurry was stirred at room temperature for 3 h under argon atmosphere. The reaction mixture was poured onto a mixture of aqueous potassium carbonate (28 g in 200 mL of $H_2O$) and ice water (200 g). The biphasic mixture was stirred at room temperature for 30 min. The layers were separated and the aqueous layer was extracted with dichloromethane (50 mL, 3 x). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Manual flash chromatography on silica gel using a heptane / ethyl acetate gradient (100:0 to 50:50) afforded the title compound (2.2 g, 20.4 mmol, 40%) as a yellow liquid. Remark: This compound is unstable under air atmosphere at room temperature, therefore this product is stored under argon in the freezer. Known compound, however no spectroscopic data have been reported in the literature.

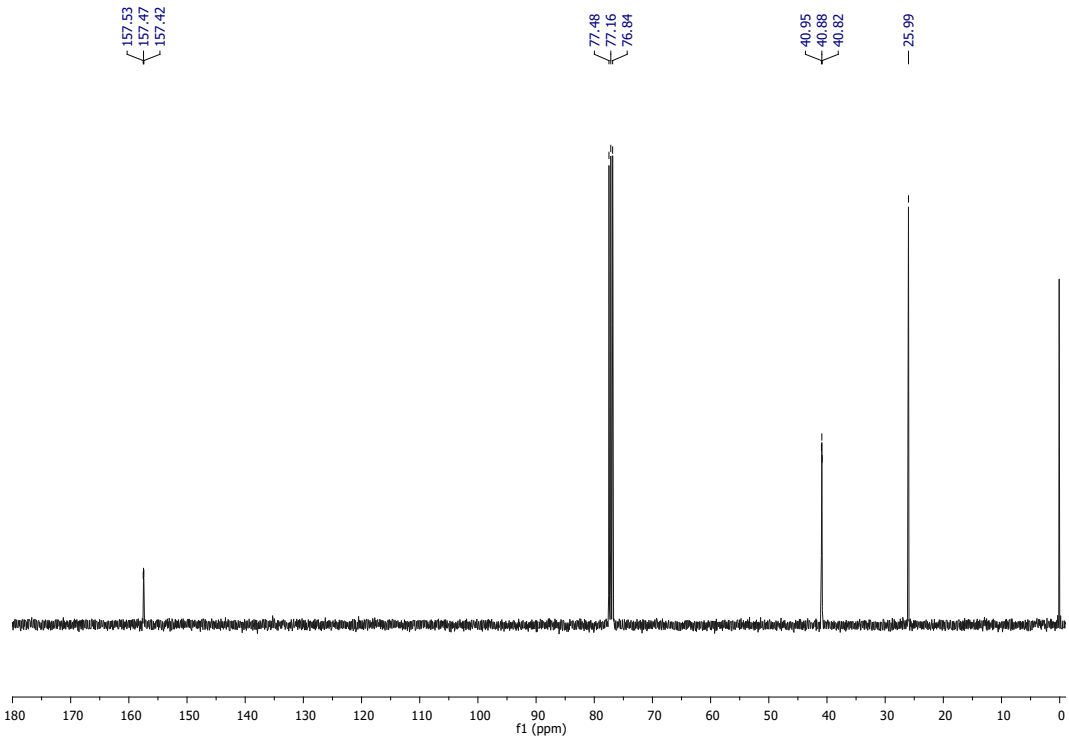
**$^1$H NMR (400 MHz, $CDCl_3$):** δ (in ppm) = 1.86 (br s, 4H), 3.49 - 3.47 (m, 4H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ (in ppm) = 26.0 ($CH_2$), 40.9 (t, $J_{C,N}$ = 6.6 Hz, $CH_2$), 157.5 (t, $J_{C,N}$ = 5.4 Hz, C).

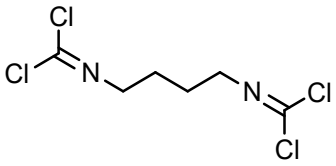
$^1$H NMR (400 MHz, $CDCl_3$):



$^{13}$C NMR (101 MHz, $CDCl_3$):




Synthesis of butane-1,4-diyldicarbonimidic tetrachloride

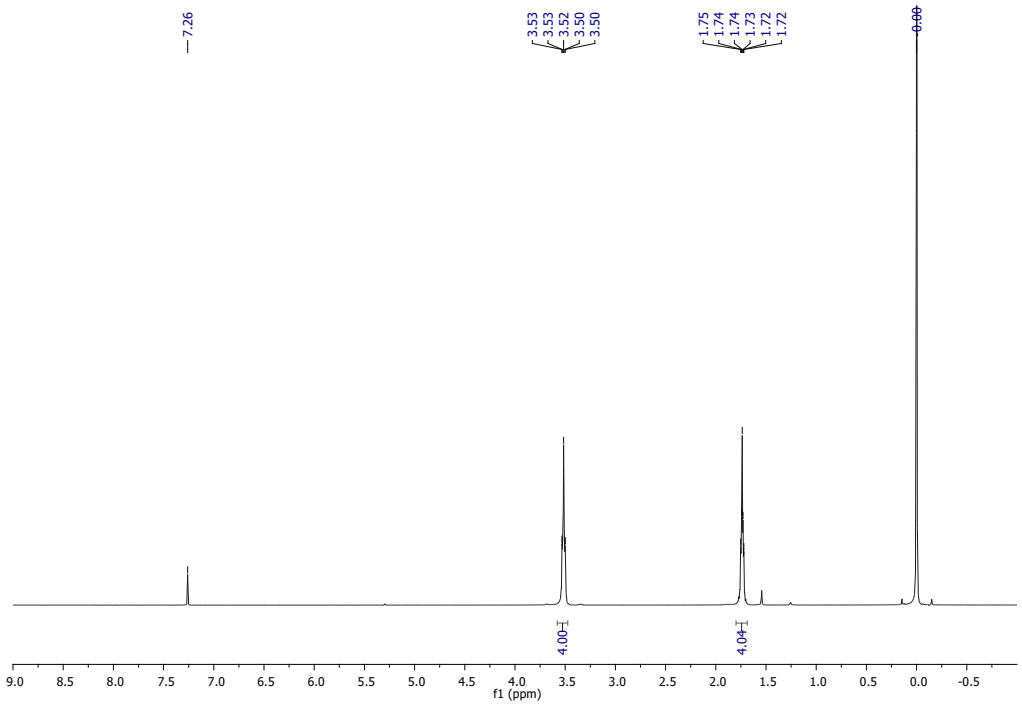



A flame-dried round-bottomed flask of 100 mL equipped with a stir bar was charged under argon atmosphere with 1,4-diisocyanobutane (2.09 g, 19.3 mmol, 1.0 equiv) and DCM (20 mL, dry). The solution was cooled to -40 °C (using acetonitrile/liquid nitrogen bath) before a solution of sulfuryl chloride (3.2 mL, 39.6 mmol, 2.05 equiv) in DCM (10 mL, dry) was added dropwise over 15 minutes. The reaction mixture was stirred further at -40 °C for 5 min and subsequently at room temperature for 15 min. The solvent was removed under reduced pressure without heating (*ca* 100 mbar) to afford the crude diiminophosgene (4.4 g, 17.6 mmol, 91%) as an orange liquid, which was used without further purification. The spectral data match those reported in the literature.[1,2]

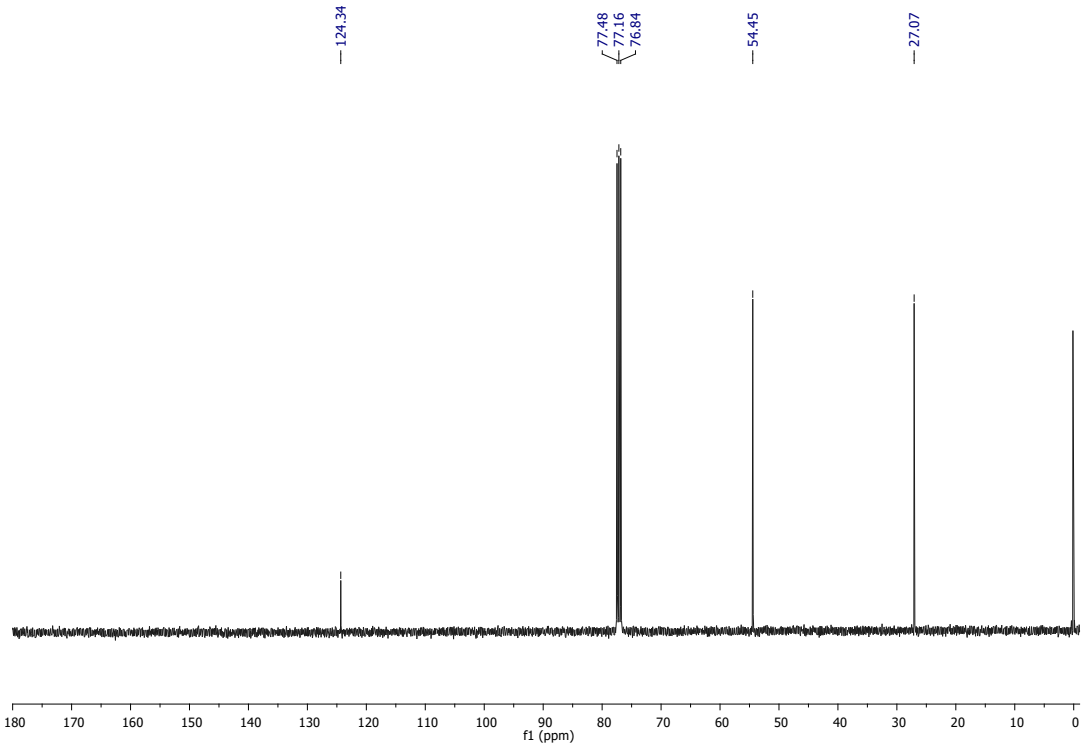
**$^1$H NMR (400 MHz, $CDCl_3$):** δ (in ppm) = 1.84 - 1.64 (m, 4H), 3.64 - 3.38 (m, 4H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ (in ppm) = 27.1 ($CH_2$), 54.5 ($CH_2$), 124.3 (C).

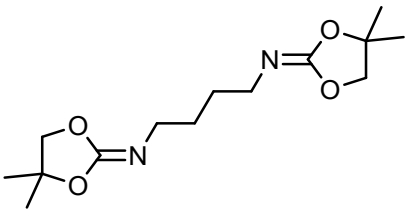
$^{1}H$ NMR (400 MHz, $CDCl_3$):




$^{13}C$ NMR (101 MHz, $CDCl_3$):



Synthesis of *N,N*-bis(4,4-dimethyl-1,3-dioxolan-2-ylidene)butane-1,4-diamine (mixture of *Z* and *E* isomers, **6**)



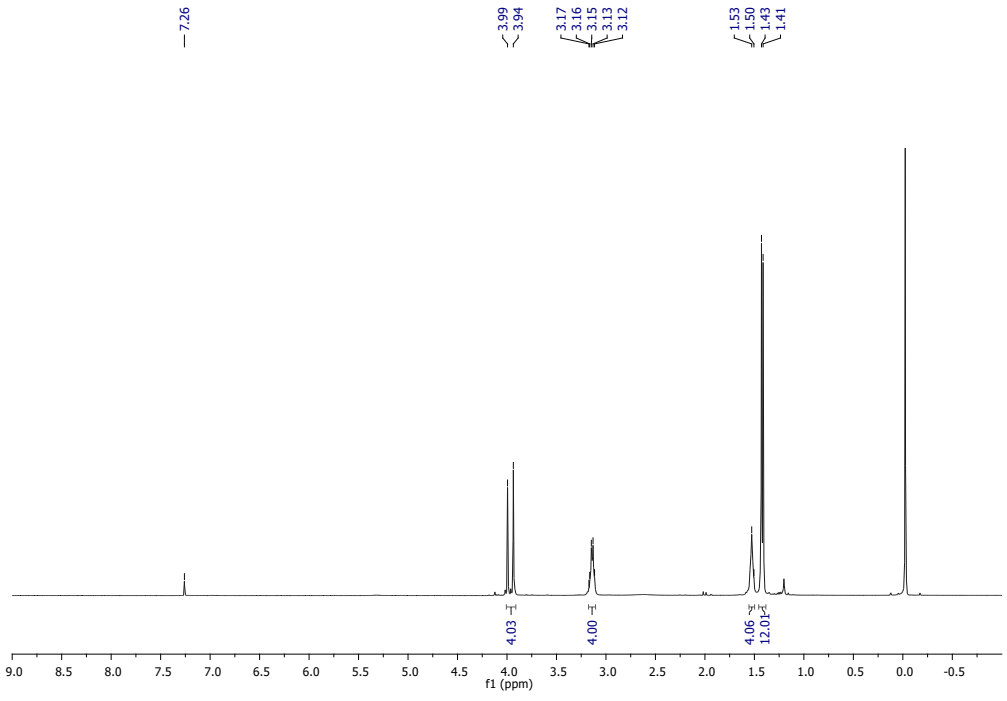
A flame-dried three-necked flask of 1 L, equipped with a reflux condenser and overhead stirrer was charged under argon atmosphere with 2-methylpropane-1,2-diol (8.3 mL, 92 mmol, 2.05 equiv), $Cs_2CO_3$ (61.6 g, 252 mmol, 2.1 equiv) and acetonitrile (120 mL, dry). Subsequently, a solution of butane-1,4-diyldicarbonimidic tetrachloride (11,3 g, 45 mmol, 1.0 equiv) in acetonitrile (10 mL, dry) was added at room temperature. The reaction mixture was refluxed in an oil bath (at 80 °C) for 20 h. The reaction mixture was allowed to cool to room temperature. MTBE (50 mL) was added and the resulting orange suspension was filtered through Celite®. The obtained solution was concentrated under reduced pressure to afford an orange liquid. The mixture was treated with a mixture of water and EtOAc (50 mL, 1:1) and the layers were separated. The product was purified by flash column chromatography on silica gel (heptane/$Et_3N$ (85:15), then heptane/EtOAc/$Et_3N$ (75:10:15), then heptane/EtOAc/$Et_3N$ (50:35:15)). A recrystallization with heptane/EtOAc (95:5) afforded the title compound (6.3 g, 22.2 mmol, 49%) as a mixture of diastereoisomers as a white solid. Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ (in ppm) = 1.41 (s, 6H), 1.43 (s, 6H), 1.54 - 1.50 (m, 4H), 3.17 - 3.12 (m, 4H), 3.94 (s, 2H), 3.99 (s, 2H).

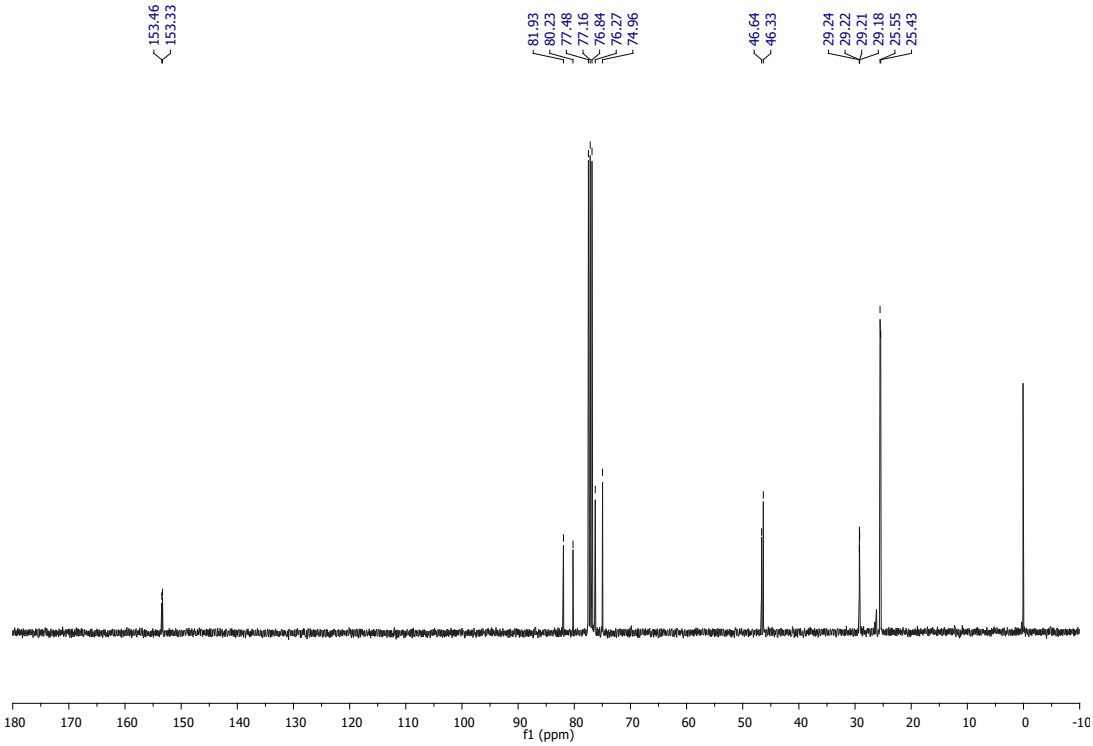
**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ (in ppm) = 25.5 ($CH_3$), 25.6 ($CH_3$), 29.2 ($CH_2$), 29.2 ($CH_2$), 29.2 ($CH_2$), 29.2 ($CH_2$), 46.3 ($CH_2$), 46.6 ($CH_2$), 75.0 ($CH_2$), 76.3 ($CH_2$), 80.2 (C), 82.0 (C), 153.3 (C), 153.5 (C).

**HRMS(ESI+):** m/z calcd. for $C_{14}H_{25}N_2O_4$ $[M + H]^+$ 285.1815, found 285.1816.

$^1$H NMR (400 MHz, $CDCl_3$):



$^{13}C$ NMR (101 MHz, $CDCl_3$):



***Results***

*Kinetic study of the ring-opening of N-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**) by glacial acetic acid and benzoic acid. Time evolution of $^{1}H$ NMR spectra.*

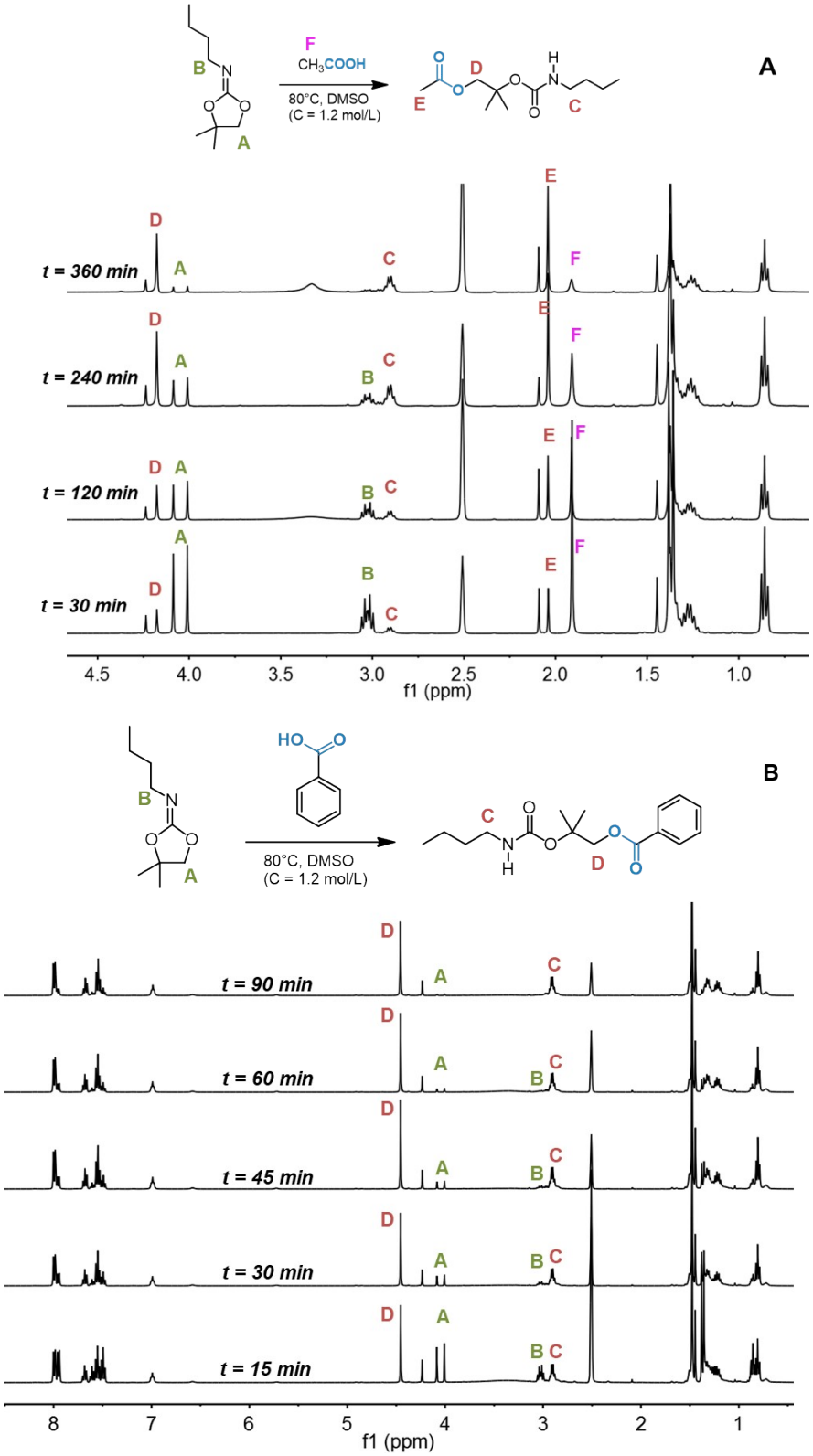


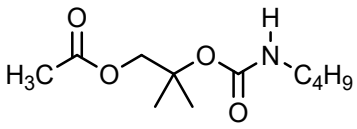

**Figure S1:** Time evolution of the ring-opening of *N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**) with A) acetic acid and B) benzoic acid at T = 80 °C in DMSO-$d_6$ ( = 1.2 mol/L).

*Synthesis of carbamates **2** from **1** and carboxylic acids*

*General experimental procedure A*:

*N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**, 0.964 g, 5.1 mmol, 1.0 equiv) was introduced in a flame dried glass tube equipped with a three-way stop cap. Then, the acid (5.1 mmol, 1.0 equiv) and DMSO (3 mL, dry) were added under $N_2$ flow. The reaction was allowed to stir at 80 °C for 18 h. The reaction medium was then cooled to room temperature and diluted with water (20 mL). The water layer was extracted with diethyl ether (3 x 10 mL). The organic phases were then reassembled and dried over anhydrous $MgSO_4$. After removal of the solvent *in vacuo*, the crude carbamate **2** was purified by flash chromatography using the indicated eluent.

*2-[(butylcarbamoyl)oxy]-2-methylpropyl acetate* (**2a**)



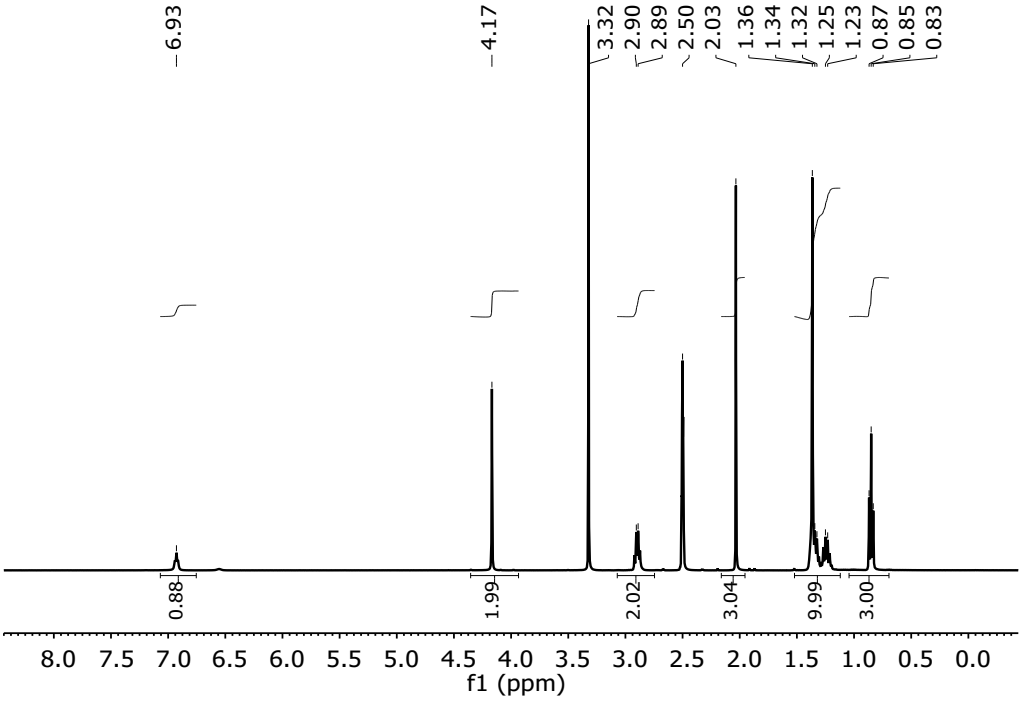
Prepared according to the general experimental procedure A using glacial acetic acid (0.295 mL, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 96%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 90/10). The product was obtained as colorless oil with yield of 92% (1.084 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.85 (t, 3H, *J* = 7.2 Hz), 1.23 (m, 2H), 1.34 (m, 2H), 1.36 (s, 6H), 2.03 (s, 3H), 2.9 (q, 2H, *J* = 6.6 Hz), 4.17 (s, 2H), 6.93 (t, 1H, *J* = 5.8 Hz).

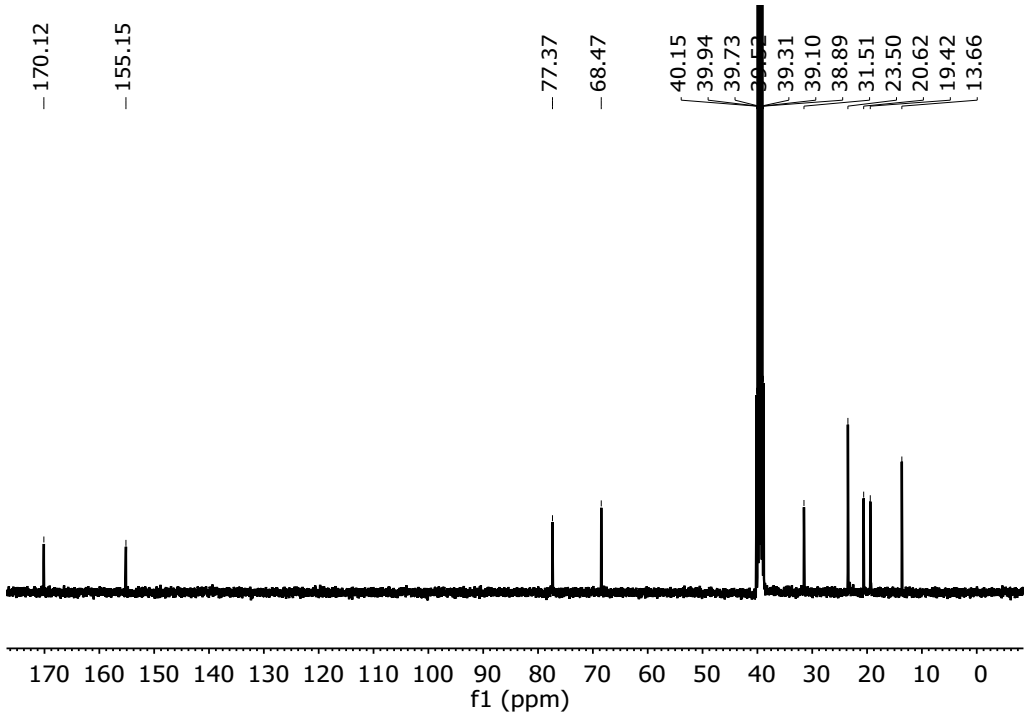
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.6, 19.4, 19.4, 20.6, 23.5, 31.5, 68.5, 77.4, 156.1, 170.1.

**HRMS(ESI+):** m/z calcd. for $C_{11}H_{21}NO_4Na$ $[M + Na]^+$ 254.1362, found 254.1355.

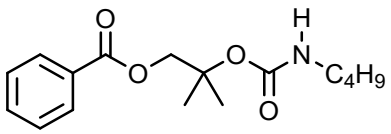
$^1$H NMR (400 MHz, DMSO-$d_6$):



$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*2-[(butylcarbamoyl)oxy]-2-methylpropyl benzoate* (**2b**)



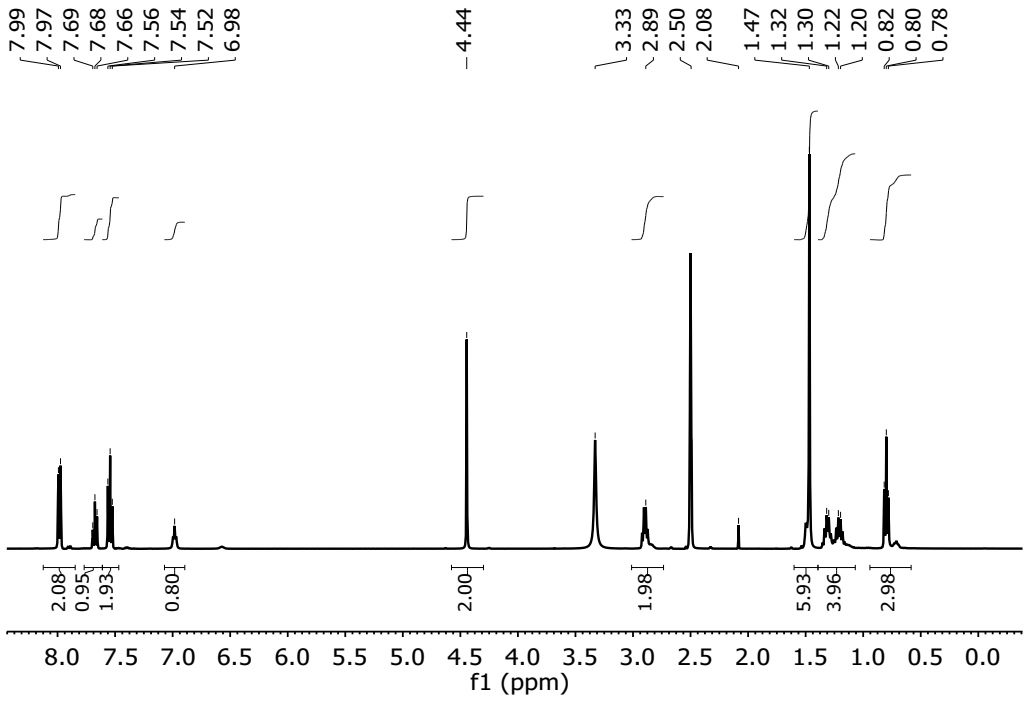
Prepared according to the general experimental procedure A using benzoic acid (622 mg, 5.1 mmol, 1.0 equiv). The crude $^{1}$H NMR indicated a 99% conversion of **1** and a selectivity of 93%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 90/10). The product was obtained as a white solid with a yield of 88% (1.315 g). Unknown compound according to a SciFinder search.

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.80 (t, 3H, *J* = 7.2 Hz), 1.20 (m, 2H), 1.30 (m, 2H), 1.47 (s, 6H), 2.89 (q, 2H, *J* = 6.6 Hz), 4.44 (s, 2H), 6.97 (t, 1H, *J* = 5.8 Hz), 7.52 - 7.56 (t, 2H, *J* = 7.7 Hz), 7.66 - 7.69 (t, 1H, *J* = 7.4 Hz), 7.94 - 7.97 (d, 2H, *J* = 7.1 Hz).

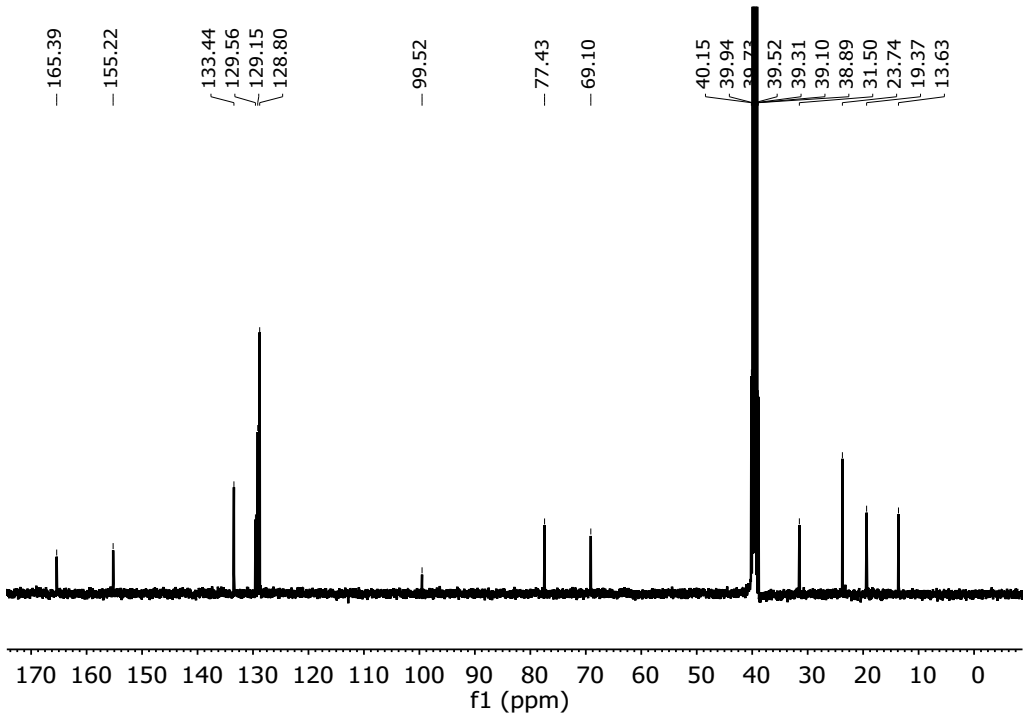
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.6, 19.4, 23.8, 31.5, 69.1, 77.4, 99.5, 128.8, 129.1, 129.5, 133.4, 155.2, 165.4.

**HRMS(ESI+):** m/z calcd. for $C_{16}H_{23}NO_4Na$ $[M + Na]^+$ 316.1519 , found 316.1511.

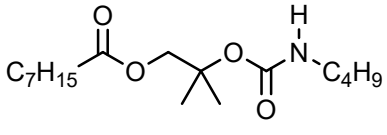
$^{1}$H NMR (400 MHz, DMSO-$d_6$):




$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*2-[(butylcarbamoyl)oxy]-2-methylpropyl octanoate* (**2c**)




Prepared according to the general experimental procedure A using octanoic acid (0.808 mL, 5.1 mmol, 1.0 equiv). The crude $^{1}$H NMR indicated a 97% conversion of **1** and a selectivity of 93%. Purification

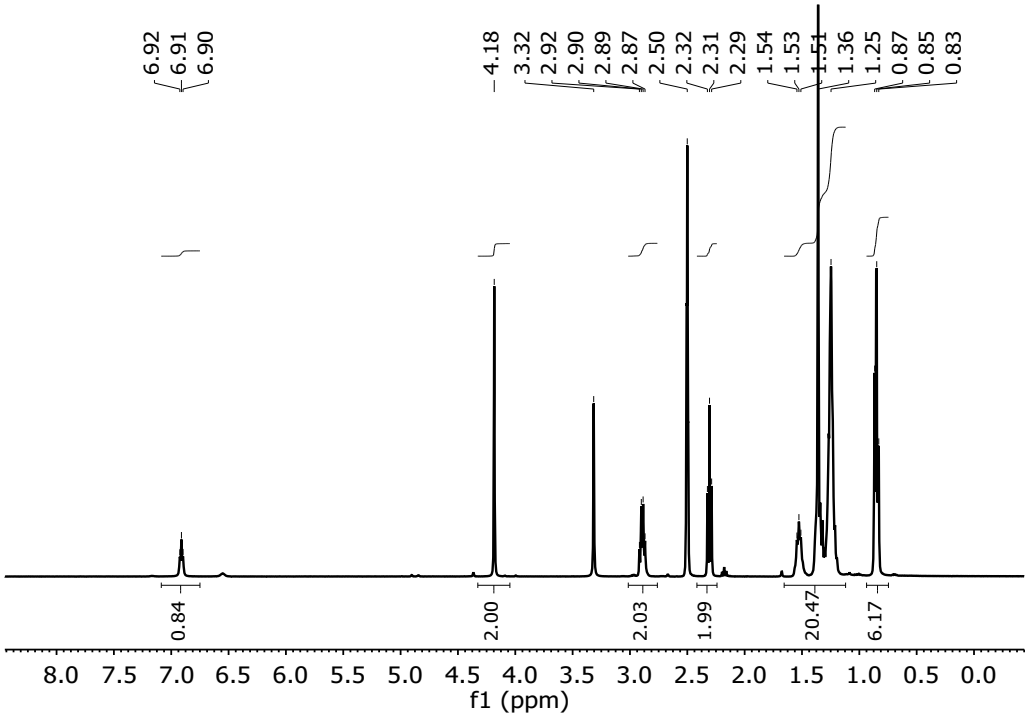
by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 90/10). Product obtained as a colorless oil with a yield of 90% (1.446 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.85 (2 x t, 6H, *J* = 7.2 Hz), 1.25 - 1.36 (m, 20H), 1.53 (q, 2H, *J* = 7.4 Hz), 2.31 (t, 2H, *J* = 7.3 Hz), 2.89 (q, 2H, *J* = 6.6 Hz), 4.18 (s, 2H), 6.91 (t, 1H, *J* = 5.8 Hz).

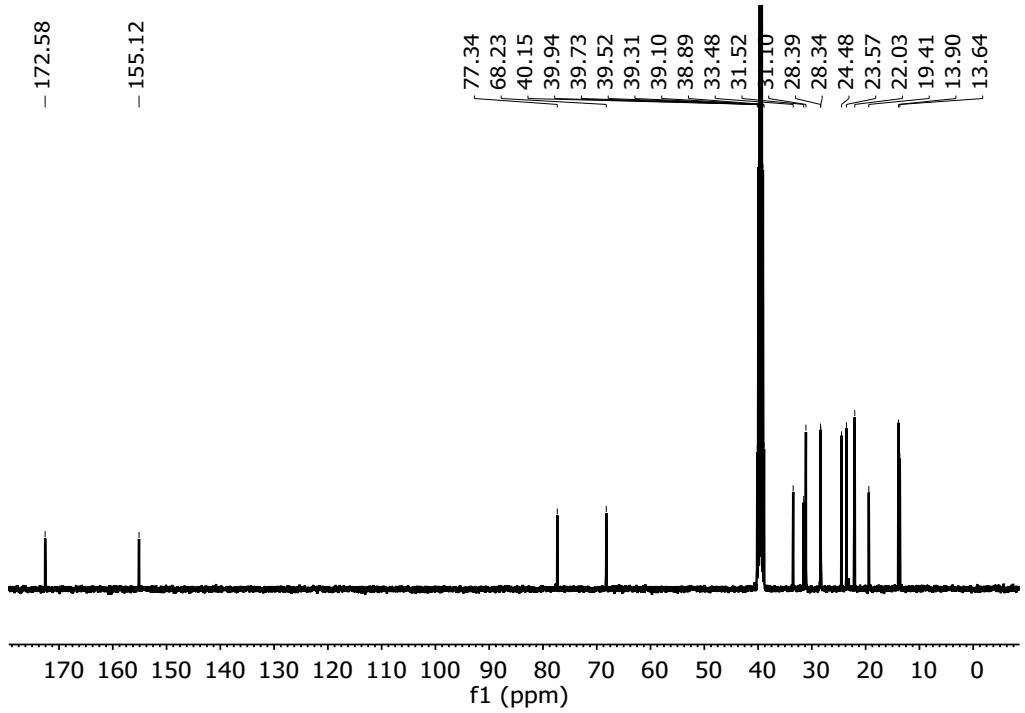
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.6, 13.9, 19.4, 22.0, 24.1, 24.5, 28.3, 28.4, 31.1, 31.5, 33.5, 68.2, 77.3, 155.1, 172.6. Note that a methylene signal at 39.3 ppm is masked by DMSO-$d_6$. This signal was evidenced by a $^{13}$C DEPT-135 NMR experiment.

**HRMS(ESI+):** m/z calcd. for $C_{17}H_{33}NO_4Na$ $[M + Na]^+$ 338.2302 g/mol, found 338.2301 g/mol.

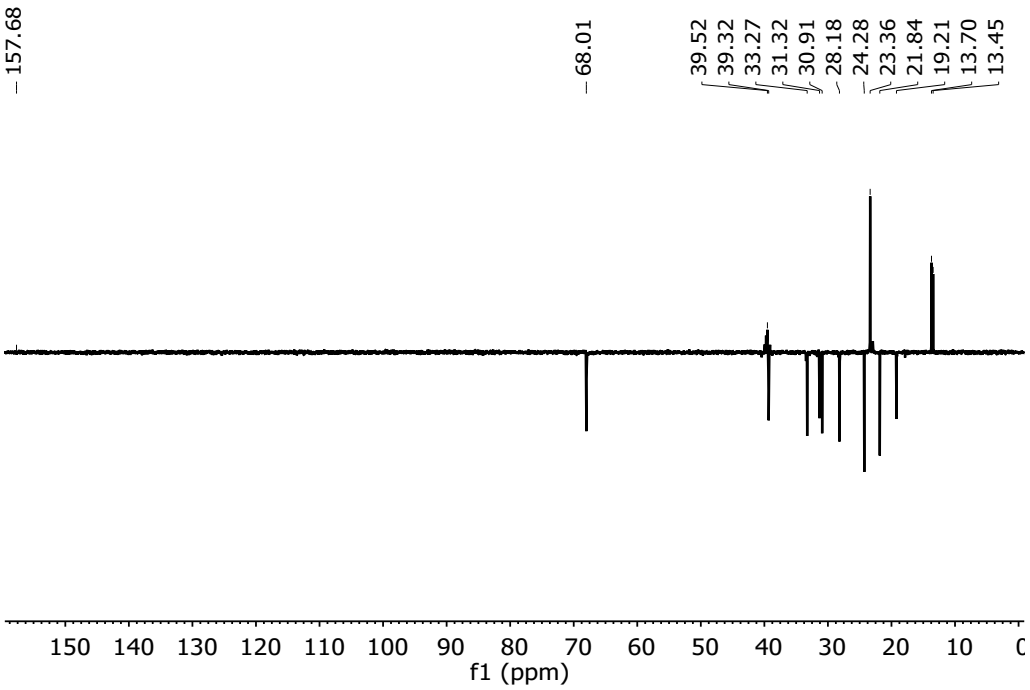
$^1$H NMR (400 MHz, DMSO-$d_6$):



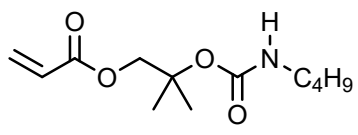
$^{13}$C NMR (101 MHz, DMSO-$d_6$):




$^{13}$C DEPT-135 (101 MHz, DMSO-$d_6$)




*2-[(butylcarbamoyl)oxy]-2-methylpropyl acrylate* (**2d**)




Prepared according to the general experimental procedure A using acrylic acid (0.35 mL, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 90%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc

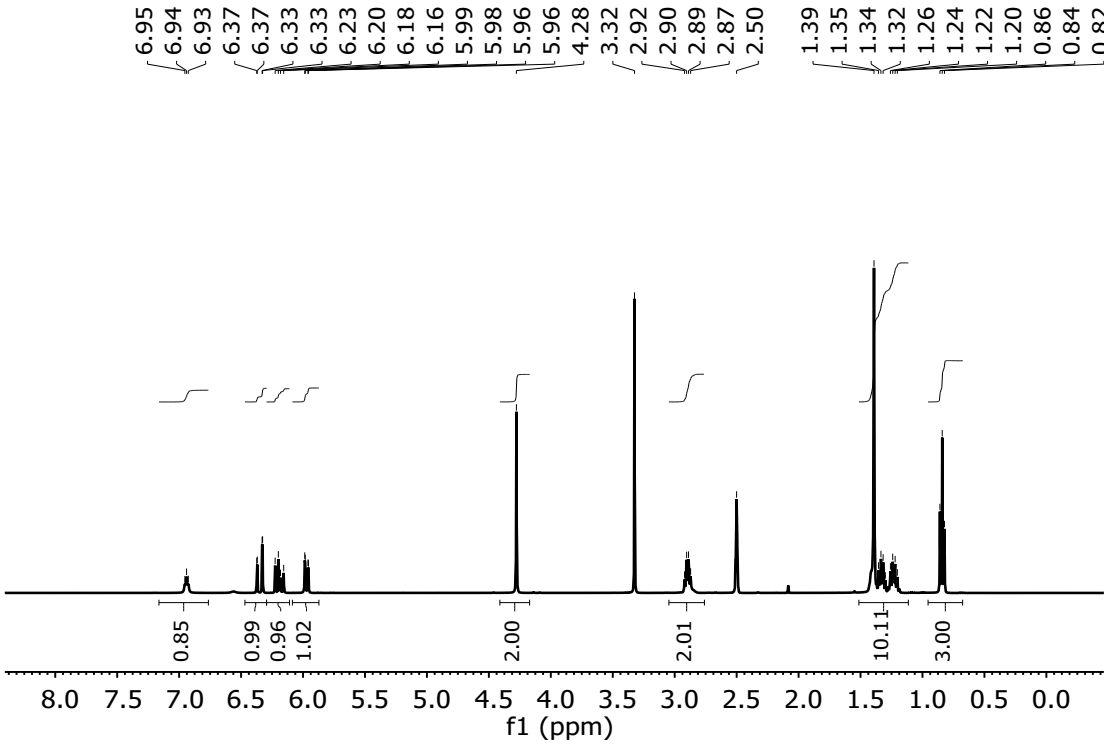
= 90/10). The product was isolated as colorless oil with a yield of 85% (1.053 g). Unknown compound according to a SciFinder search.

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.84 (t, 3H, *J* = 7.2 Hz), 1.20 - 1.39 (m, 10H), 2.89 (q, 2H, *J* = 6.6 Hz), 4.28 (s, 2H), 5.96 - 5.99 (dd, 1H, *J* = 17.3 Hz ), 6.16 - 6.23 (dd, 1H, *J* = 10.5 Hz), 6.33 - 6.37 (dd, 1H, *J* = 1.5 Hz), 6.94 (t, 1H, *J* = 5.8 Hz).

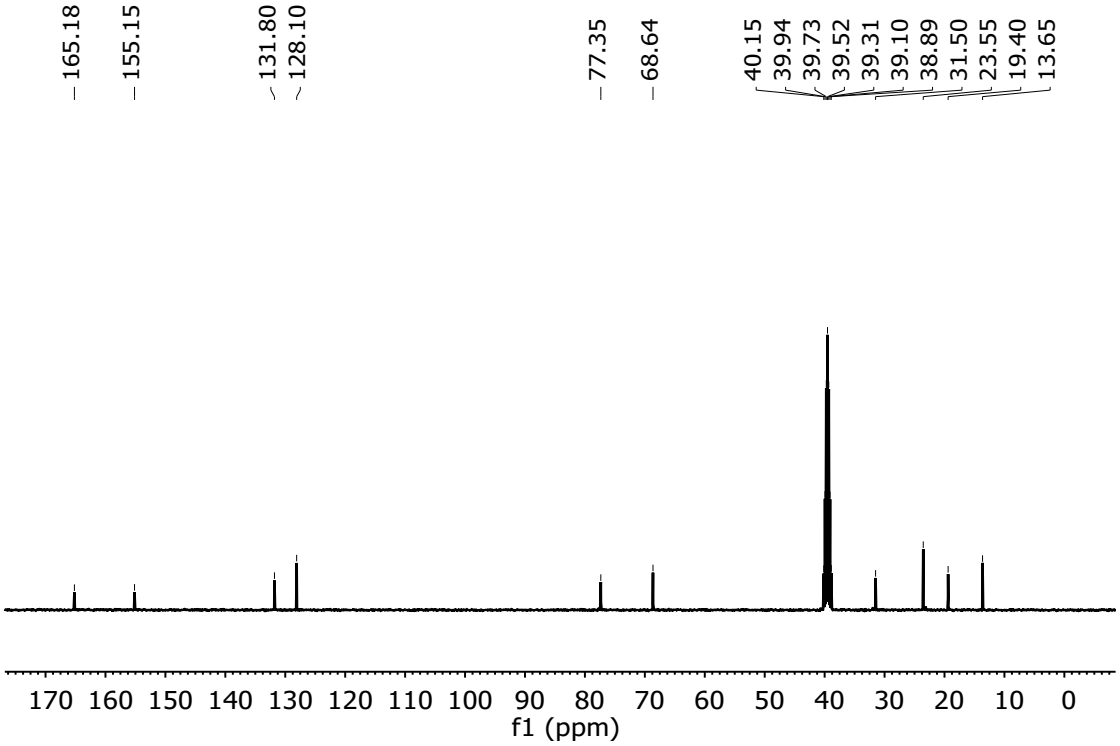
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.6, 19.4, 23.5, 31.5, 68.6, 77.3, 128.1, 131.8, 155.1, 165.2.

**HRMS(ESI+):** m/z calcd. for $C_{12}H_{21}NO_4Na$ $[M + Na]^+$ 266.1363, found 266.1361.

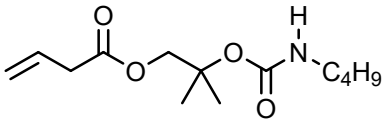
$^{1}$H NMR (400 MHz, DMSO-$d_6$):



$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*2-[(butylcarbamoyl)oxy]-2-methylpropyl but-3-enoate* (**2e**)



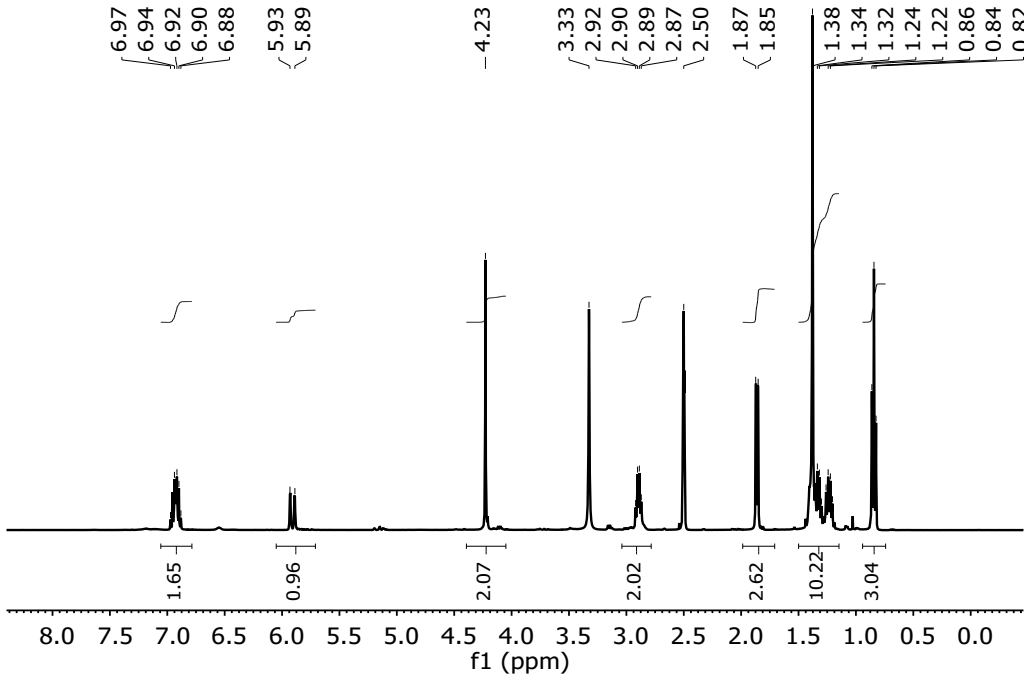
Prepared according to the general experimental procedure A using 3-butenoic acid (0.433 mL, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 88%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 90/10). The product was isolated as colorless oil with a yield of 82% (1.074 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.84 (t, 3H, *J* = 7.2 Hz), 1.22 - 1.38 (m, 10H), 1.87 (dd, 2H, *J* = 6.9, 1.7 Hz), 2.89 (q, 2H, *J* = 6.6 Hz), 4.23 (s, 2H), 5.93 (d, 1H, *J* = 1.7 Hz), 6.88 - 6.97 (m, 2H).

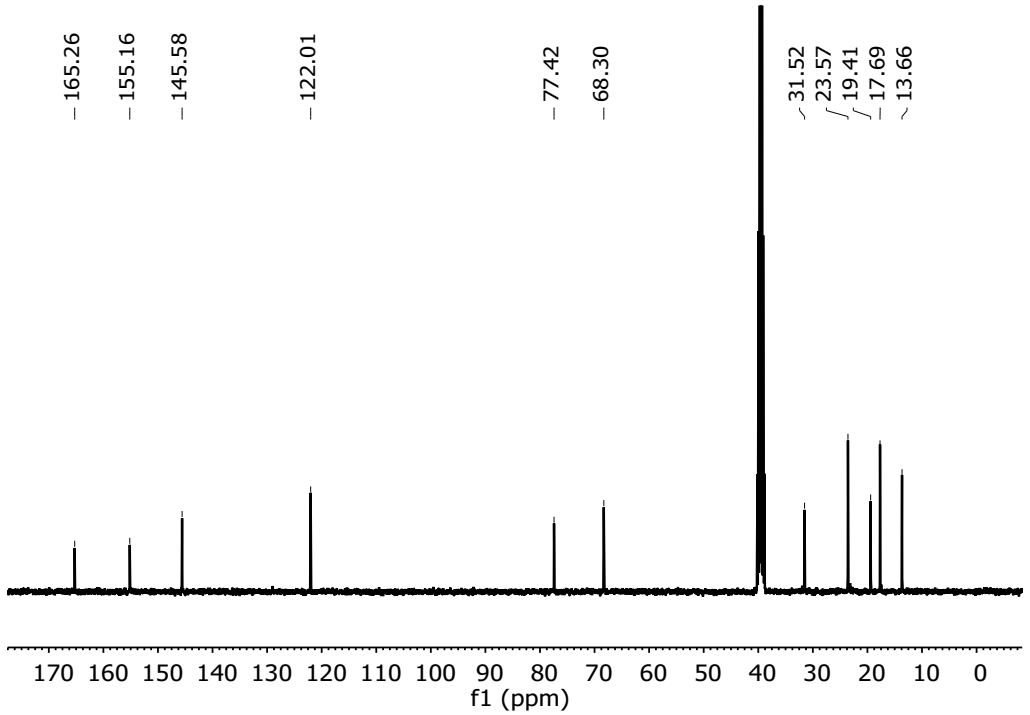
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 14.1, 18.2, 19.9, 24.0, 32.0, 68.8, 77.9, 122.5, 146.0, 155.6, 165.7.

**HRMS(ESI+):** m/z calcd. for $C_{13}H_{23}NO_4Na$ $[M + Na]^+$ 280.1519 g/mol, found 280.1514 g/mol.

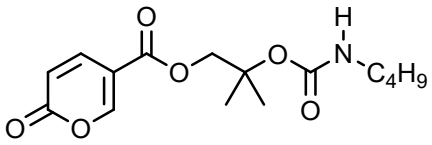
$^{1}$H NMR (400 MHz, DMSO-$d_6$):




$^{13}$C NMR (101 MHz, DMSO-$d_6$):



*2-[(butylcarbamoyl)oxy]-2-methylpropyl 2-oxo-2H-pyran-5-carboxylate* (**2f**)



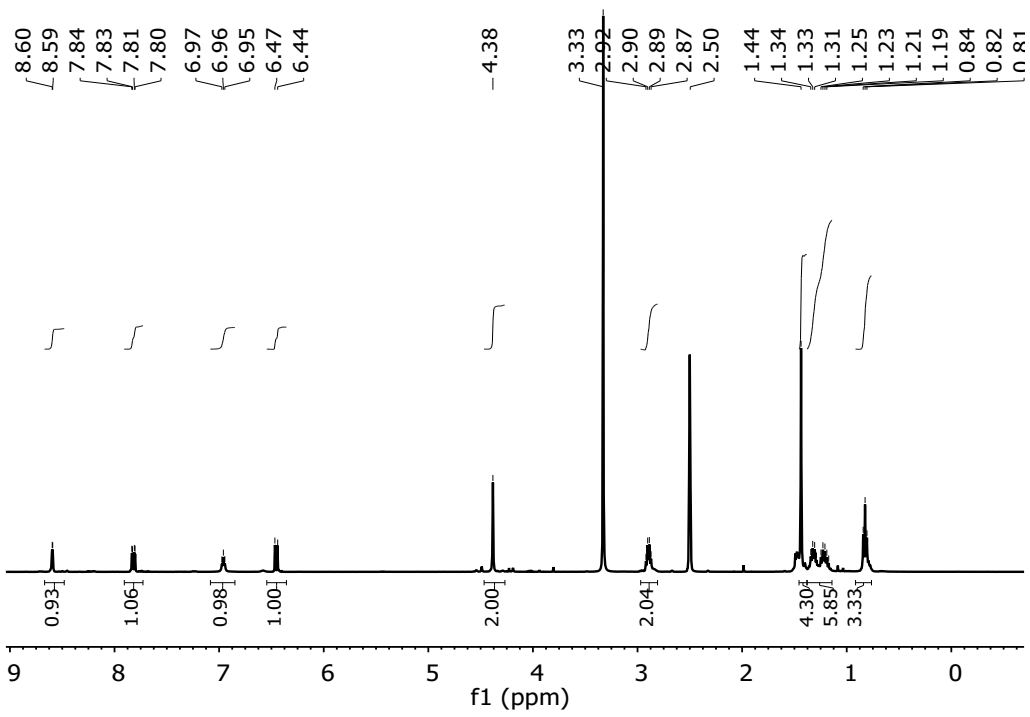
Prepared according to the general experimental procedure A using coumalic acid (714 mg, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 92%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 80/20). The product was isolated as white solid with a yield of 77% (1.22 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.82 (t, 3H, *J* = 7.2 Hz), 1.19 - 1.44 (m, 10H), 2.90 (q, 2H, *J* = 6.6 Hz), 4.38 (s, 2H), 6.47 (dd, 1H, *J* = 1.1 Hz), 6.96 (t, 1H, *J* = 5.8 Hz), 7.80 - 7.84 (dd, 1H, *J* = 2.7 Hz), 8.60 (d, 1H, *J* = 1.7 Hz).

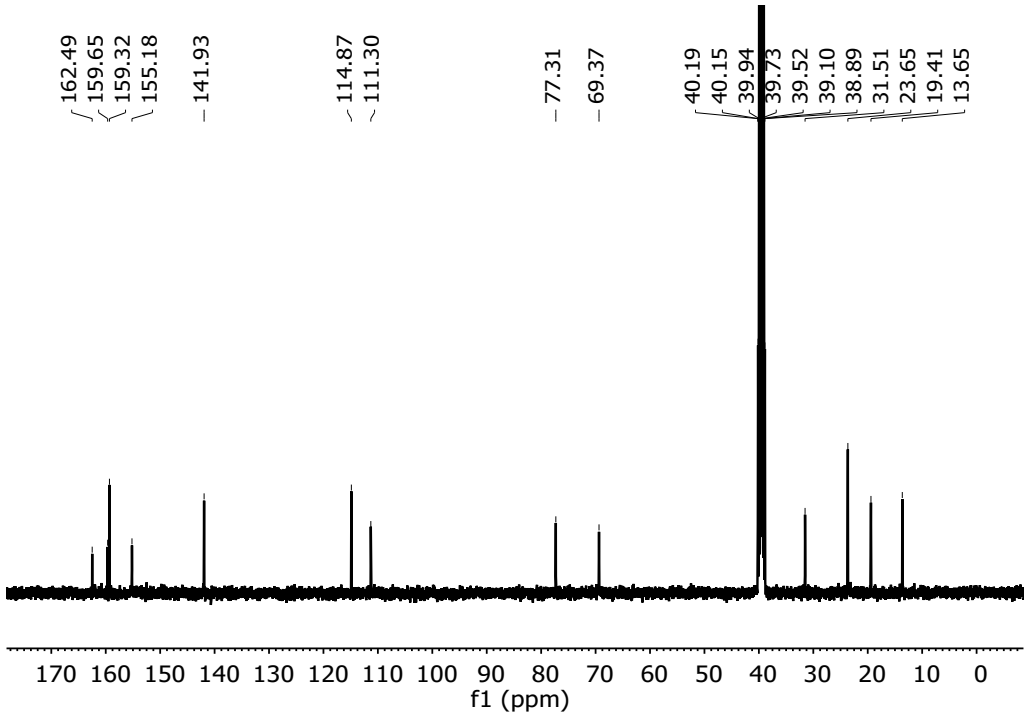
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.6, 19.4, 23.6, 31.5, 69.3, 77.3, 111.3, 114.9, 141.9, 155.1, 159.3, 159.6, 162.5.

**HRMS(ESI+):** m/z calcd. for $C_{15}H_{22}NO_6$ $[M + H]^+$ 312.1442, found 312.1440.

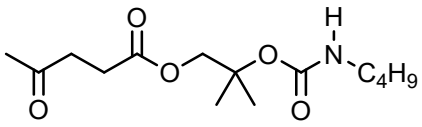
$^1$H NMR (400 MHz, DMSO-$d_6$):



$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*2-[(butylcarbamoyl)oxy]-2-methylpropyl 4-oxopentanoate* (**2g**)



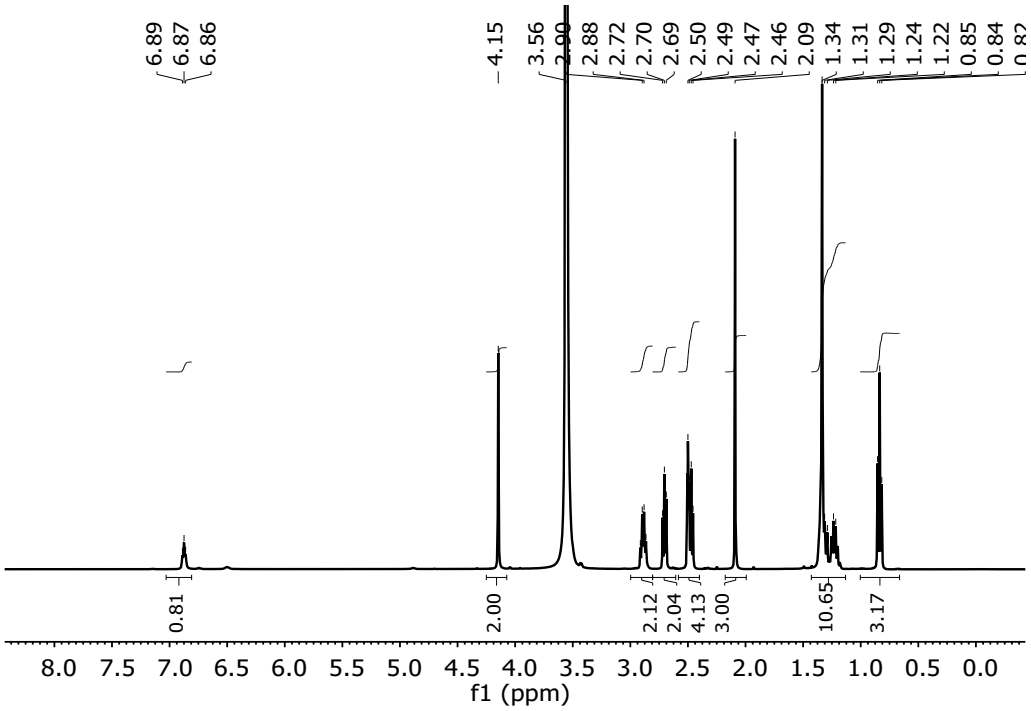
Prepared according to the general experimental procedure A using levulinic acid (592 mg, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 92%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 80/20). The product was isolated as colorless oil with a yield of 72% yield (1.053 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.84 (t, 3H, *J* = 7.2 Hz), 1.22 - 1.34 (m, 10H), 2.09 (s, 3H) 2.48 (t, 2H, *J* = not determined due tooverlay with the DMSO signal), 2.70 (t, 2H, *J* = 5.4 Hz), 2.88 (q, 2H, *J* = 6.6 Hz), 4.15 (s, 2H), 6.87 (t, 1H, *J* = 5.8 Hz).

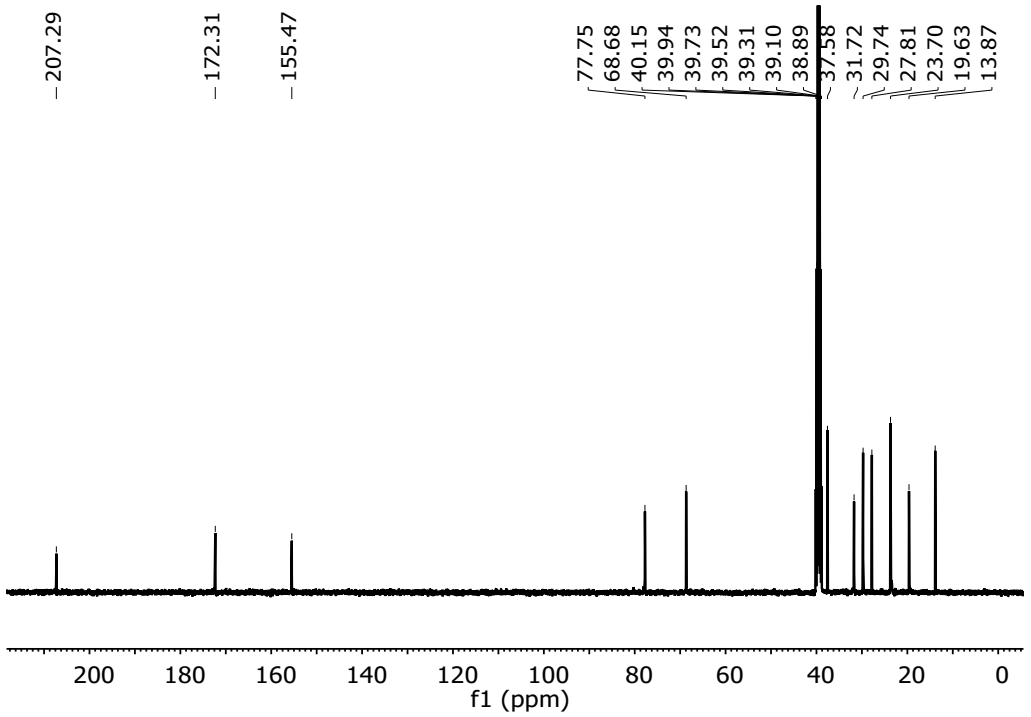
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.9, 19.6, 23.7, 27.8, 29.7, 31.7, 37.6, 68.7, 77.7, 155.5, 172.3, 207.3.

**HRMS(ESI+):** m/z calcd. for $C_{14}H_{25}NO_5Na$ $[M + Na]^+$ 310.1625, found 310.1618.

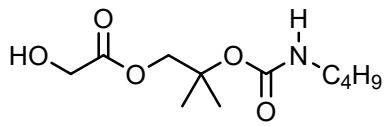
$^{1}$H NMR (400 MHz, DMSO-$d_6$):




$^{13}$C NMR (101 MHz, DMSO-$d_6$):



*2-[(butylcarbamoyl)oxy]-2-methylpropyl 2-hydroxyacetate* (**2h**)



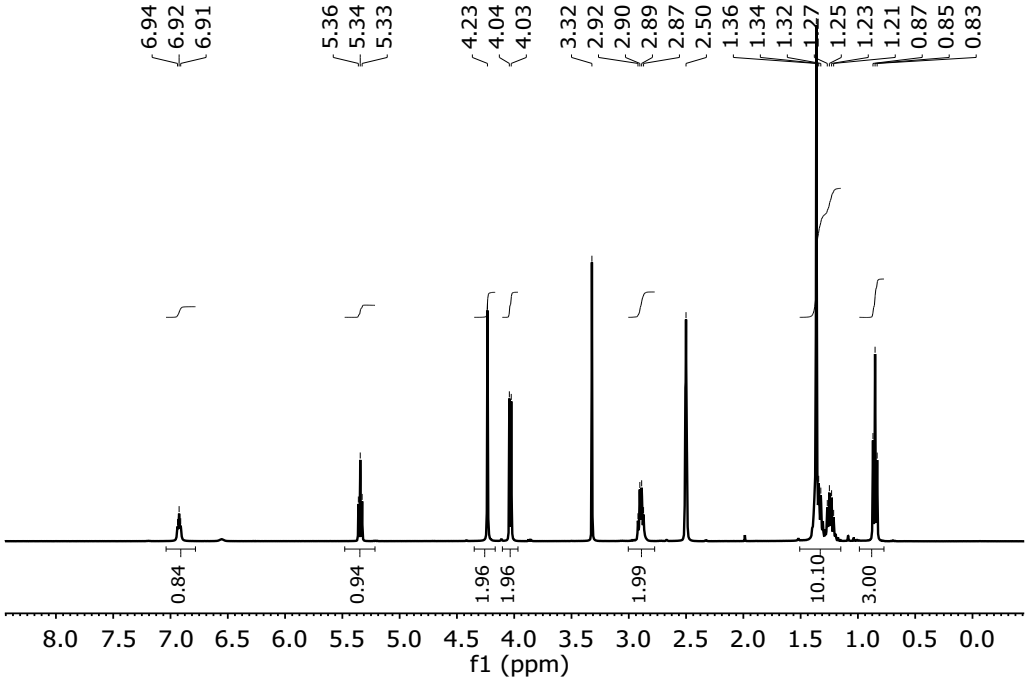
Prepared according to the general experimental procedure A using glycolic acid (387 mg, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 99%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = 70/30). The product was isolated as a colorless oil with a yield of 69% (869 mg). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.85 (t, 3H, *J* = 7.2 Hz), 1.21 - 1.36 (m, 10H), 2.89 (q, 2H, *J* = 6.6 Hz), 4.04 (d, 2H, *J* = 6.6 Hz), 4.23 (s, 2H), 5.34 (t, 1H, *J* = 6.6 Hz), 6.92 (t, 1H, *J* = 5.8 Hz).

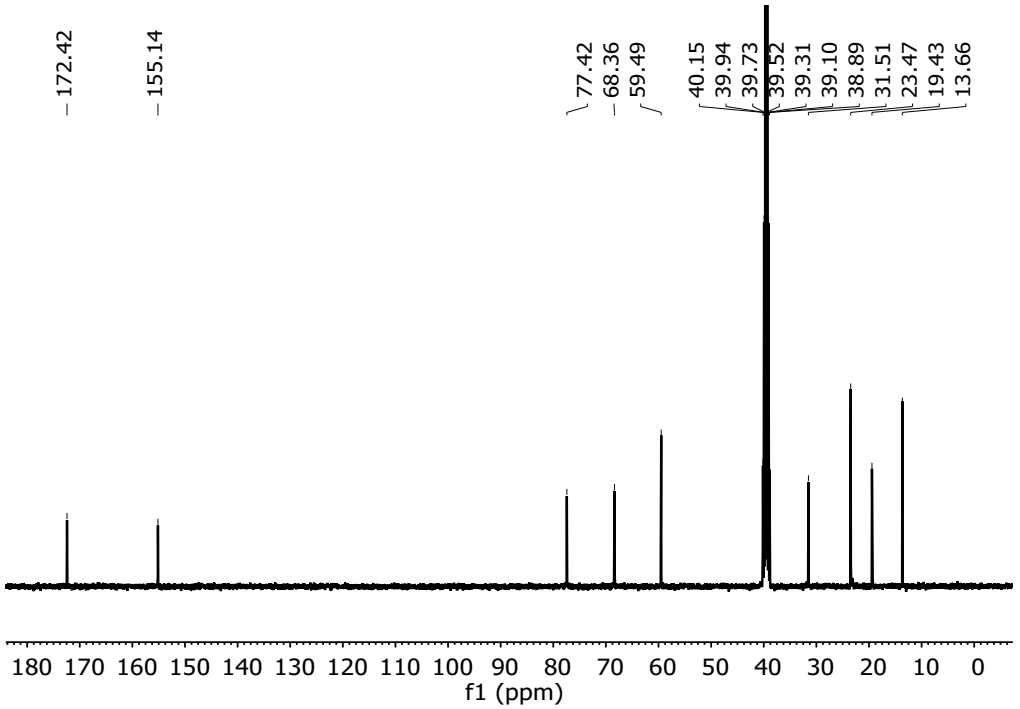
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.7, 19.5, 23.5, 31.5, 59.5, 68.3, 77.4, 155.1, 172.4.

**HRMS(ESI+):** m/z calcd. for $C_{11}H_{21}NO_5Na$ $[M + Na]^+$ 270.1312, found 270.1318.

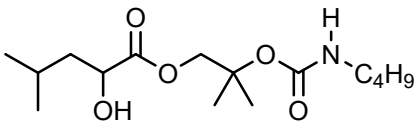
$^1$H NMR (400 MHz, DMSO-$d_6$):



$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*2-[(butylcarbamoyl)oxy]-2-methylpropyl 2-hydroxy-4-methylpentanoate* (**2i**)



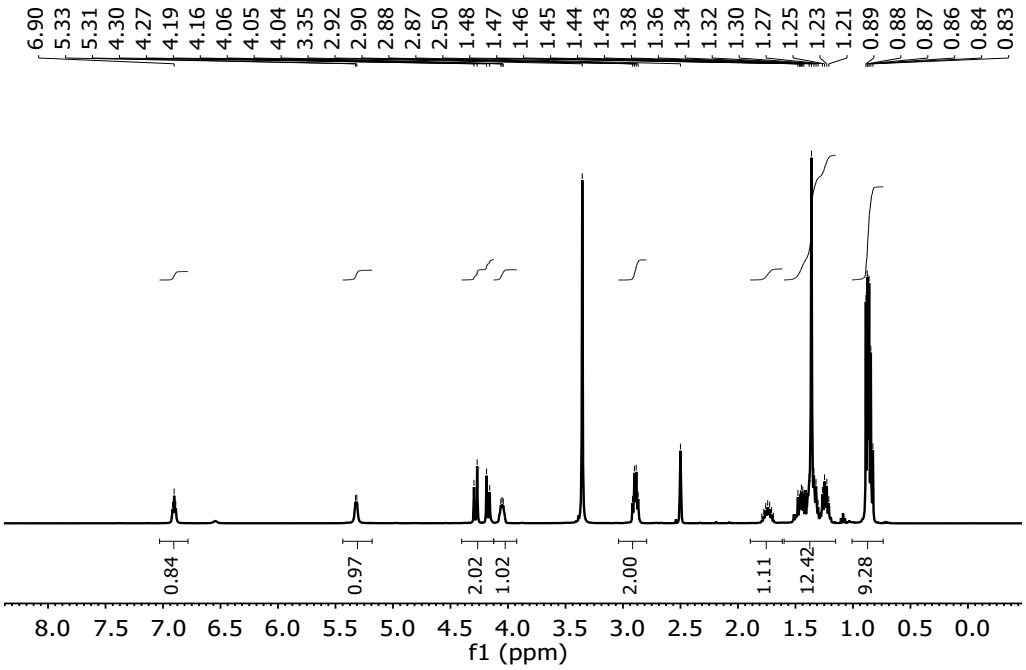

Prepared according to the general experimental procedure A using L-leucic acid (674 mg, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 91%. Purification by silica flash chromatography ($SiO_2$, eluent : petroleum ether/EtOAc = gradient from 90/10 to 70/30). The product was isolated as a colorless oil with a yield of 59% (911 mg) yield. Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.83 - 0.89 (m, 9H), 1.21 - 1.48 (m, 12H), 1.69 - 1.79 (m, 1H), 2.88 (q, 2H, *J* = 6.6 Hz), 4.04 (m, 1H), 4.16 - 4.30 (q, 2H, *J* = 3.4 Hz), 5.31 (d, 1H, *J* = 0.4 Hz), 6.90 (t, 1H, *J* = 5.8 Hz).

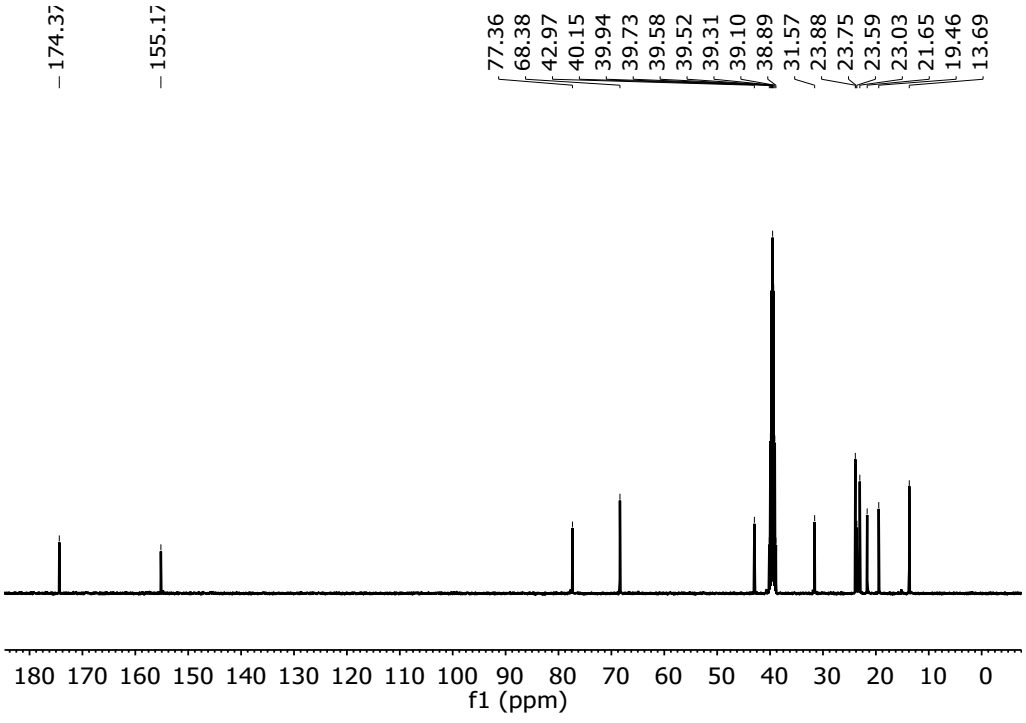
**$^{13}$C NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 13.7, 19.5, 21.7, 23.0, 23.6, 23.8, 29.9, 31.6, 40.1, 43.0, 68.4, 77.4, 155.2, 174.4.

**HRMS(ESI+):** m/z calcd. for $C_{15}H_{29}NO_5Na$ $[M + Na]^+$ 326.1938, found 326.1930.

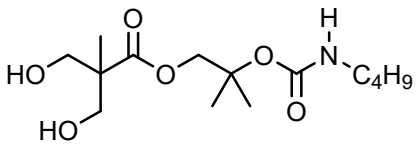
$^{1}$H NMR (400 MHz, DMSO-$d_6$):




$^{13}$C NMR (101 MHz, DMSO-$d_6$):



*2-[(butylcarbamoyl)oxy]-2-methylpropyl 3-hydroxy-2-(hydroxymethyl)propanoate* (**2j**)



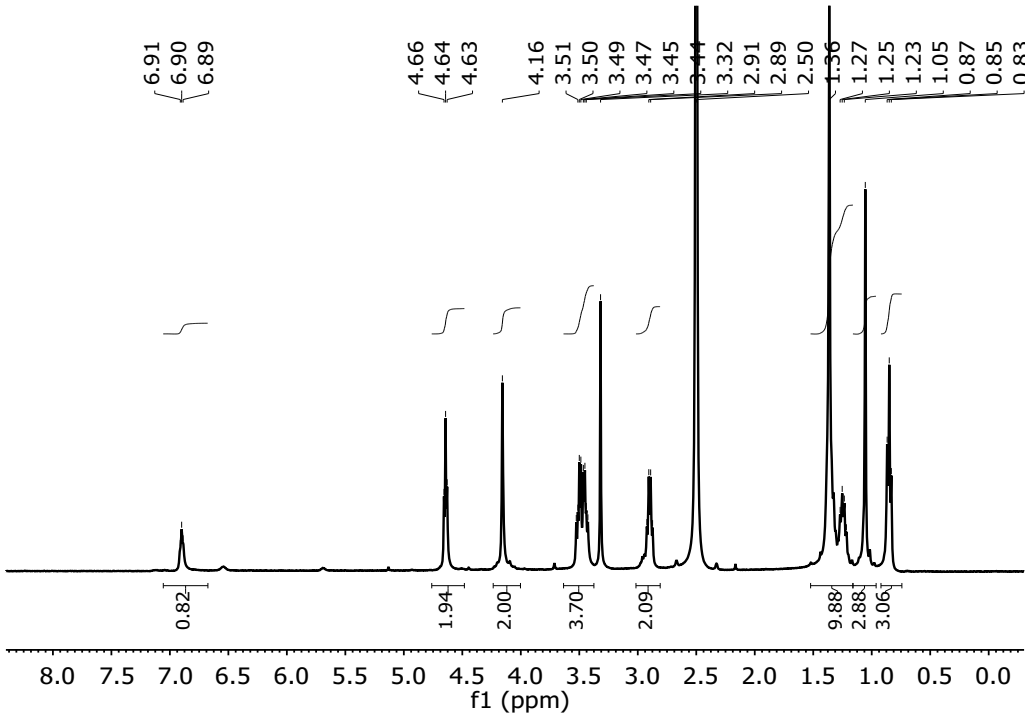

Prepared according to the general experimental procedure A using 2,2-bis-(hydroxymethyl)propionic acid (684 mg, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 98% conversion of **1** and a selectivity of 94%. Purification by silica flash chromatography ($SiO_2$, eluent : EtOAc/MeOH = 80/20). The product was isolated as yellow oil with a yield of 78% (1.21 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.85 (t, 3H, *J* = 7.2 Hz), 1.05 (s, 3H), 1.23 - 1.36 (m, 10H), 2.91 (q, 2H, *J* = 6.6 Hz), 3.45 - 3.50 (m, 4H), 4.16 (s, 2H), 4.64 (t, 2H, *J* = 0.4 Hz), 6.90 (t, 1H, *J* = 5.8 Hz).

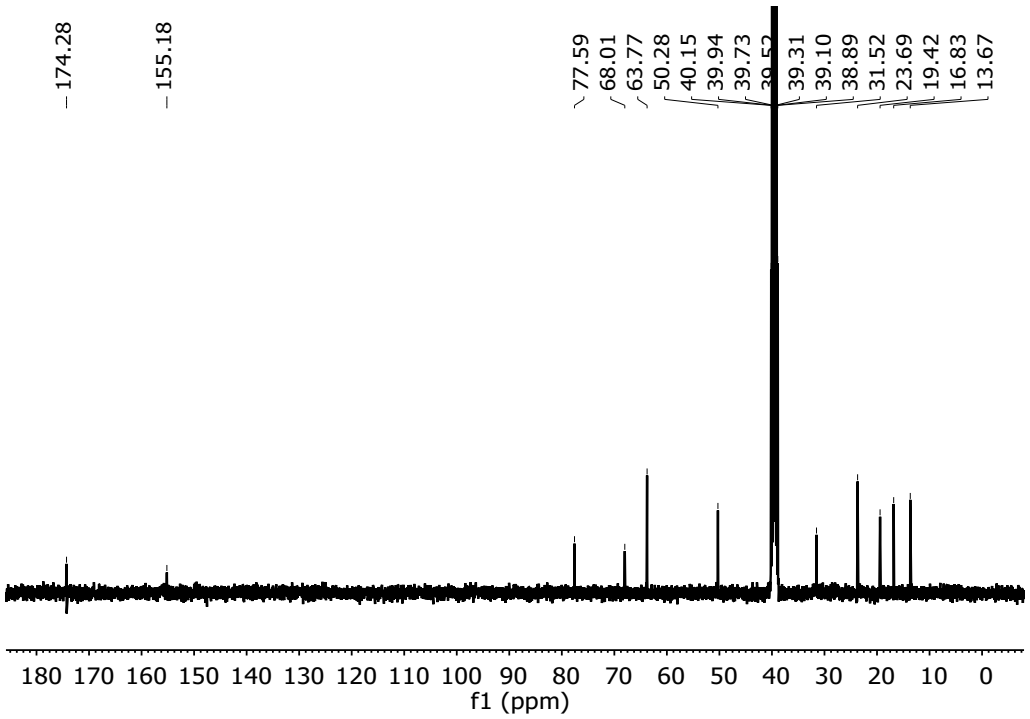
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.7, 16.8, 19.4, 23.7, 31.5, 50.3, 63.8, 68.0, 77.6, 155.2, 174.3.

**HRMS(ESI+):** m/z calcd. for $C_{14}H_{27}NO_6Na$ $[M + Na]^+$ 328.1731, found 328.1740.

$^1$H NMR (400 MHz, DMSO-$d_6$):



$^{13}C$ NMR (101 MHz, DMSO-$d_6$):



*Alcoholysis of cyclic iminocarbonates in the presence of DBU or methanesulfonic acid.*

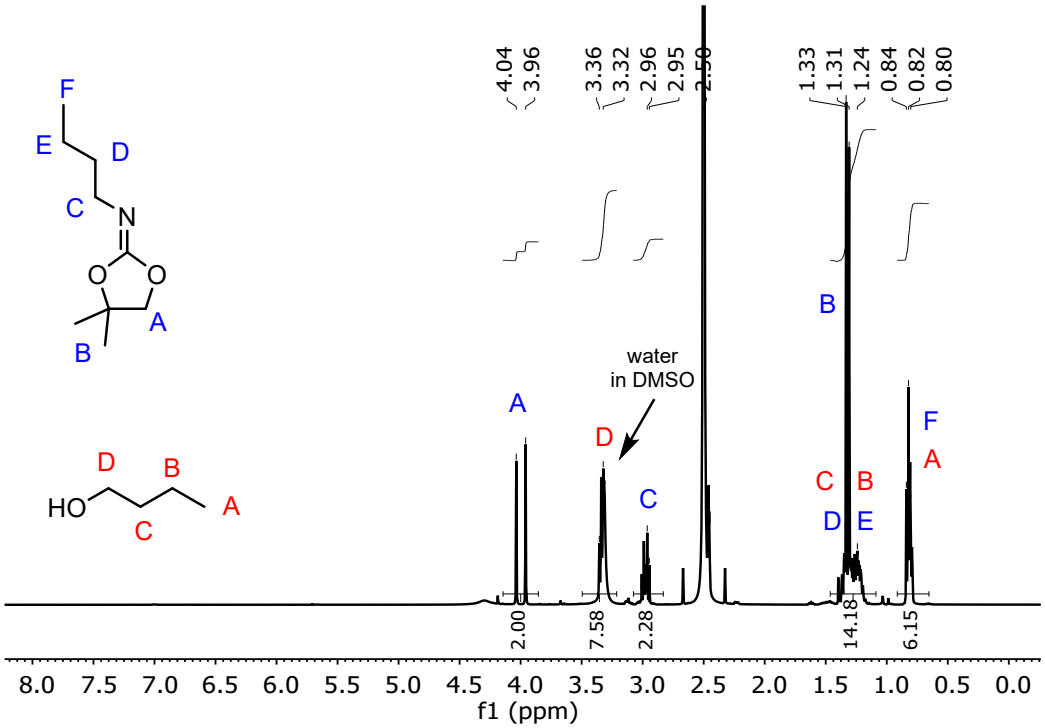



**Figure S2**. $^{1}$H NMR spectrum in DMSO-$d_6$ of the obtained crude sample when *N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**)is treated with *n*-butanol in the presence of DBU at 80 °C for 18 h. No conversion of **1** was observed.

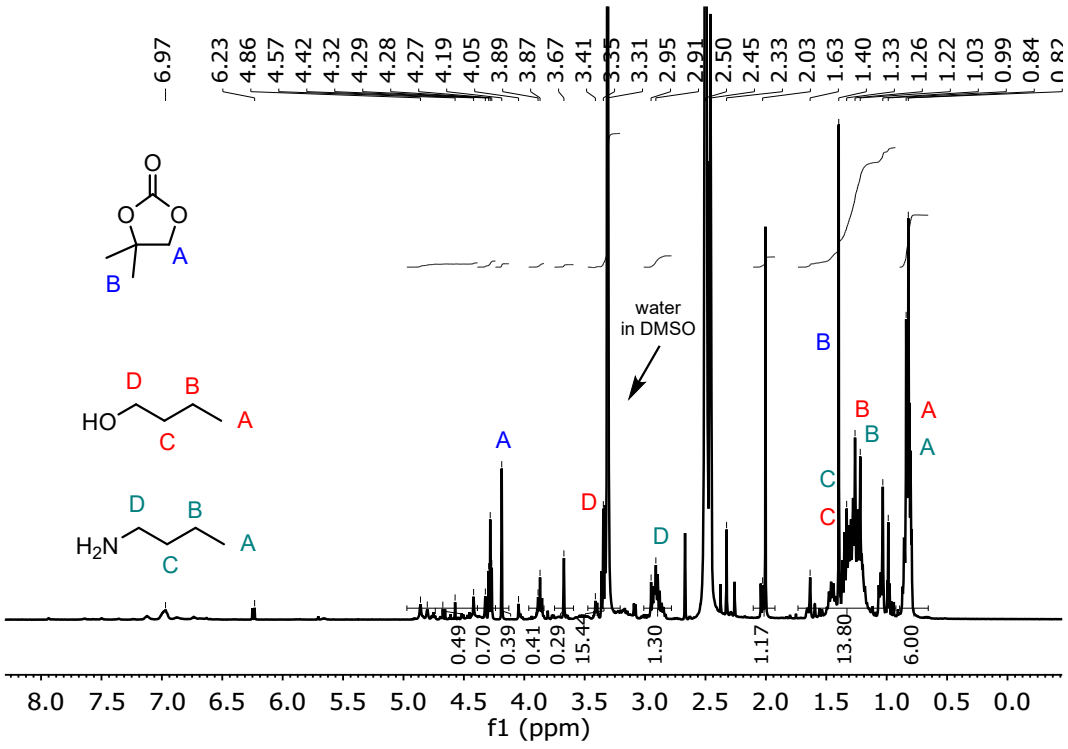


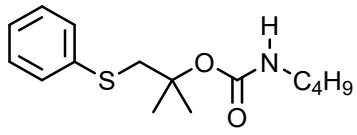

**Figure S3**. $^{1}$H NMR spectrum in DMSO-$d_6$ of the obtained crude sample when *N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**)is treated with *n*-butanol in the presence of methanesulfonic acid at 80 °C for 18 h.

*Synthesis of model carbamates from **1** and sulfur nucleophiles (**5a-c**)*

*General experimental procedure B*:

*N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**, 0.964 g, 5.1 mmol, 1.0 equiv) was introduced in a flame dried glass tube equipped with a three-way stop cap. Then, the thiol (5.1 mmol, 1.0 equiv) and DMSO (3 mL, dry) were added under $N_2$ flow. The solution was degassed for 10 min by bubbling of $N_2$ prior to reaction at 80 °C for 18 h. The reaction medium was then cooled to room temperature and diluted with 20 mL of water. The water layer was extracted with diethyl ether (3 x, 10 mL). The organic phases were then reassembled and dried over anhydrous $MgSO_4$. After removal of the solvent *in vacuo*, the crude carbamate was purified by flash chromatography using the indicated eluent.

*2-methyl-1-(phenylsulfanyl)propan-2-yl butylcarbamate (**5a**)*



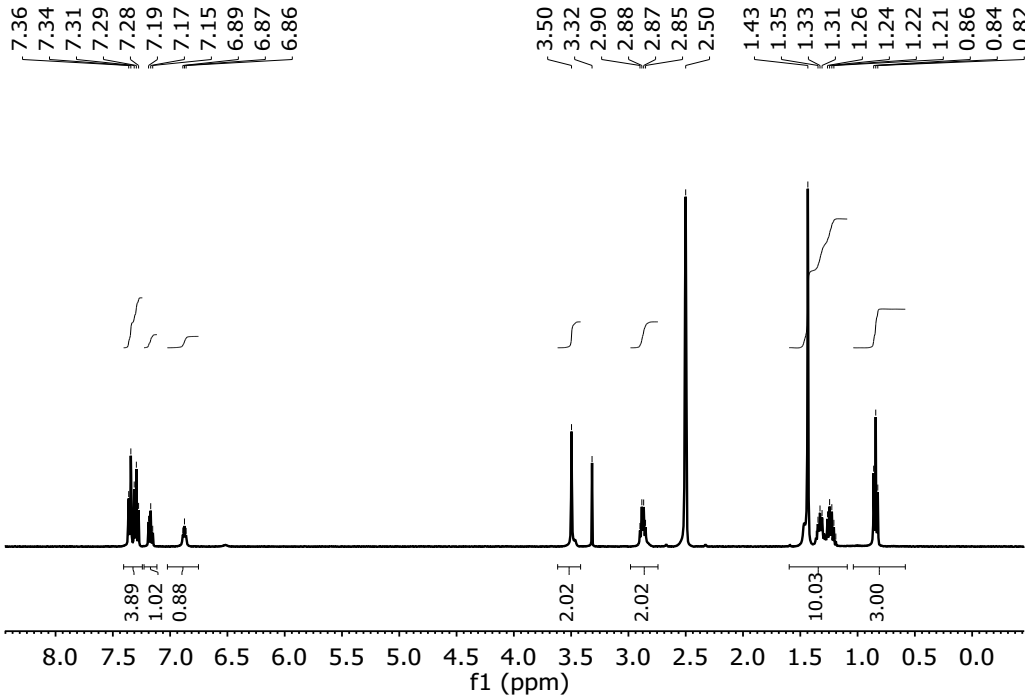
Prepared according to the general experimental procedure B using thiophenol (561 mg, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 99% conversion of **1** and a selectivity of 99%. Purification by silica flash chromatography ($SiO_2$, eluent : EtOAc/petroleum ether = 90/10). The product was isolated as a clear oil with a yield of 88% (1.26 g). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.82 (t, 3H, *J* = 7.2 Hz), 1.21 - 1.43 (m, 10H), 2.87 (t, 2H, *J* = 6.5 Hz), 3.50 (s, 2H), 6.87 (t, 1H, *J* = 5.7 Hz), 7.17 (t, 1H, *J* = 7.2 Hz), 7.28 - 7.36 (m, 4H).

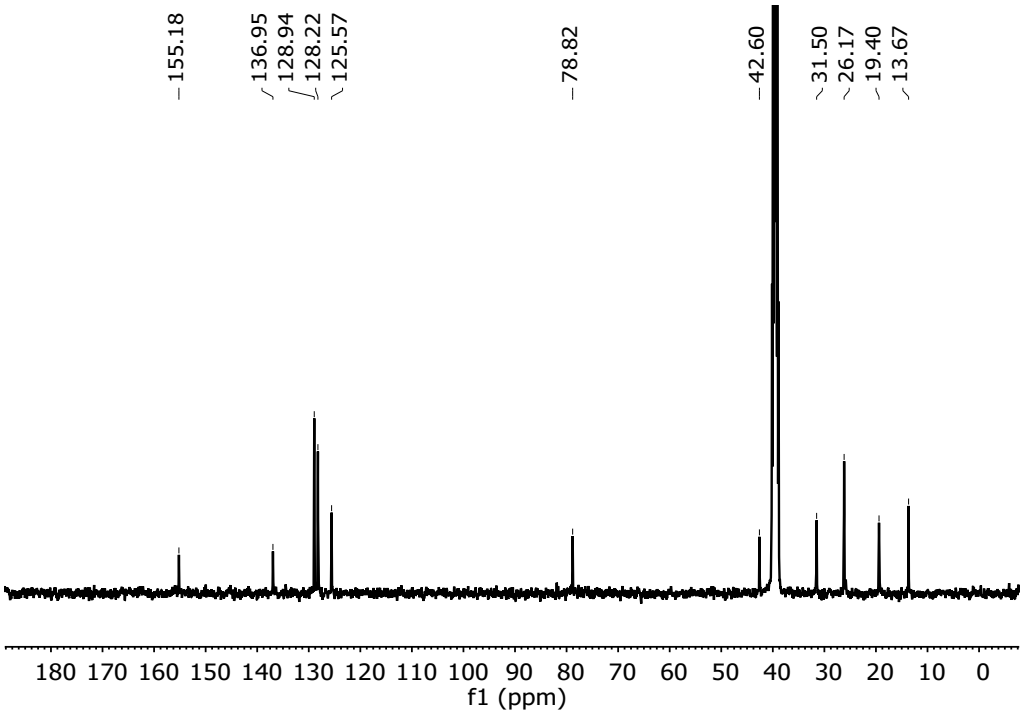
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.7, 19.4, 26.2, 31.5, 42.6, 78.8, 125.6, 128.2, 128.9, 136.9, 155.2.

**HRMS(ESI+):** m/z calcd. for $C_{15}H_{24}NO_2S$ $[M + H]^+$ 282.1522, found 282.1525.

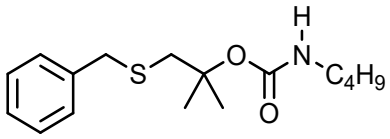
$^1$H NMR (400 MHz, DMSO-$d_6$):



$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*1-(benzylsulfanyl)-2-methylpropan-2-yl butylcarbamate (**5b**)*



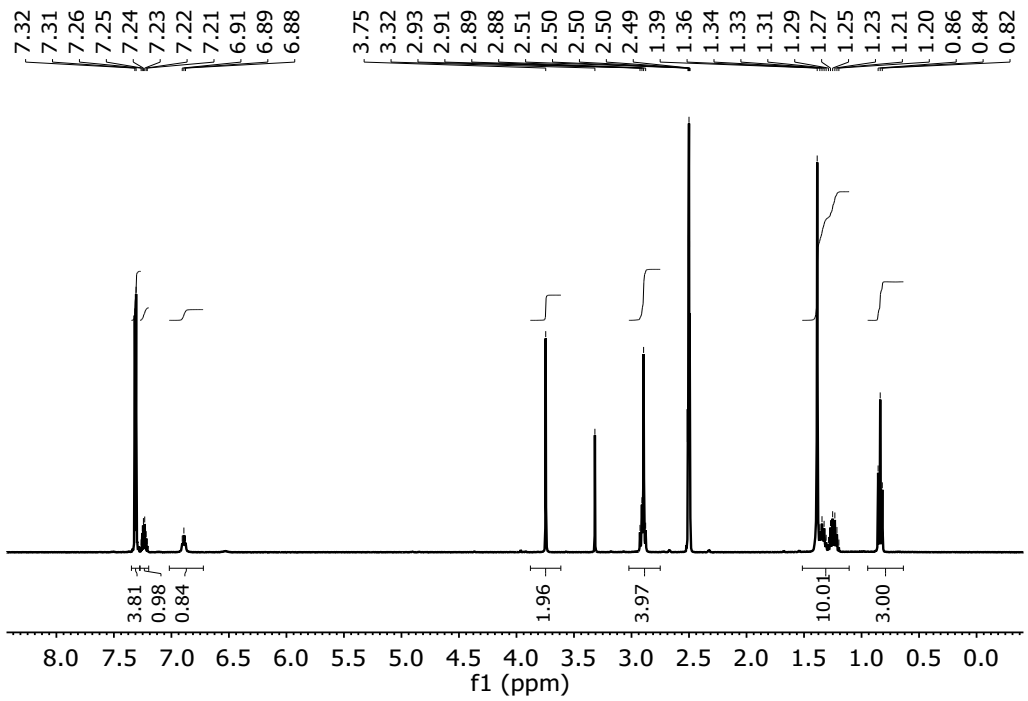

Prepared according to the general experimental procedure B using benzyl mercaptan (0.597 mL, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 77% conversion of **1** and a selectivity of 90%. Purification by silica flash chromatography ($SiO_2$, eluent : EtOAc/petroleum ether = 90/10). The product was isolated as a clear colorless oil with yield of 56% (842 mg). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.84 (t, 3H, *J* = 7.2 Hz), 1.20 - 1.39 (m, 10H), 2.88 - 2.93 (s + q, 4H), 3.75 (s, 2H), 6.89 (t, 1H, *J* = 5.8 Hz), 7.21 - 7.26 (m, 1H), 7.31 (d, 4H, *J* = 4.4 Hz).

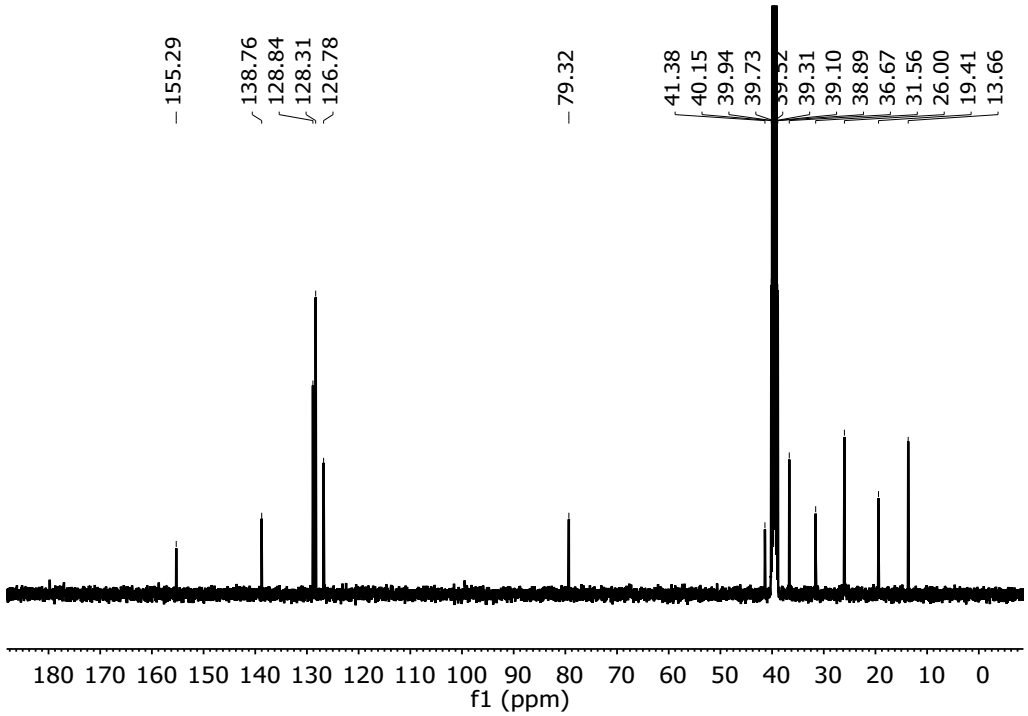
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.7, 19.4, 26.0, 31.6, 36.7, 38.9, 41.4, 79.3, 126.8, 128.3, 128.8, 138.8, 155.3.

**HRMS(ESI+):** m/z calcd. for $C_{16}H_{25}NO_2SNa$ $[M + Na]^+$ 318.1498, found 318.1496.

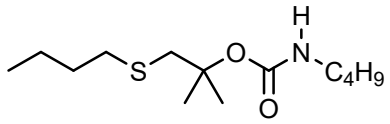
$^{1}$H NMR (400 MHz, DMSO-$d_6$):




$^{13}$C NMR (101 MHz, DMSO-$d_6$):



*1-(butylsulfanyl)-2-methylpropan-2-yl butylcarbamate (**5c**)*



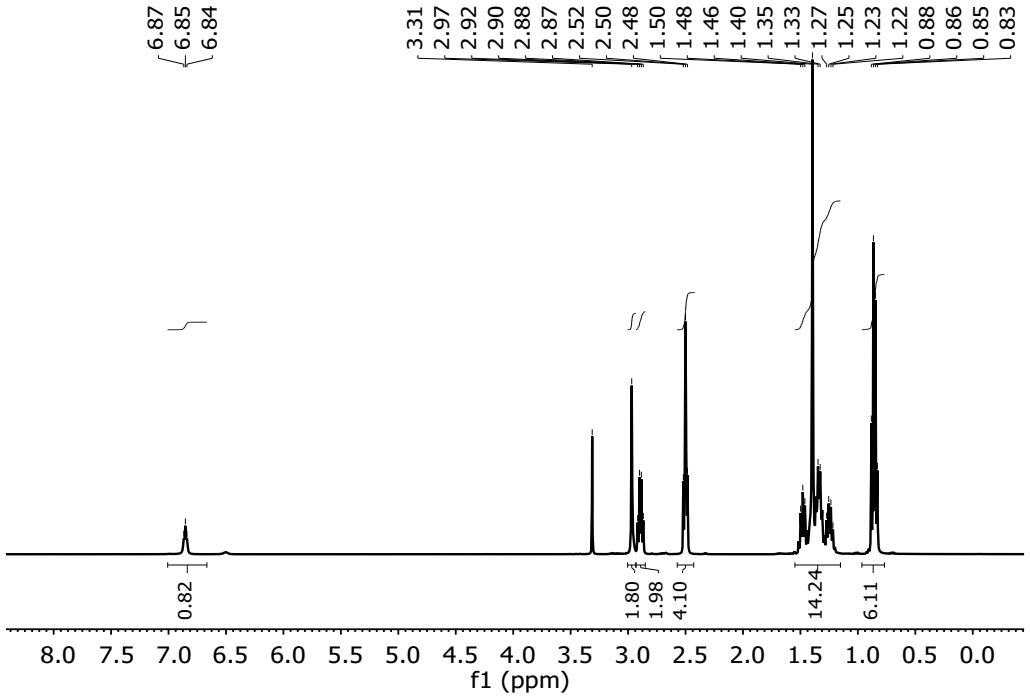
Prepared according to the general experimental procedure B using 1-butanethiol (0.546 mL, 5.1 mmol, 1.0 equiv). The crude $^1$H NMR indicated a 52% conversion of **1** and a selectivity of 63%. Purification by silica flash chromatography ($SiO_2$, eluent : EtOAc/petroleum ether = 90/10). The product was isolated as a clear colorless oil with a yield of 31% (402 mg). Unknown compound according to a SciFinder search.

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ (in ppm) = 0.83 - 0.88 (m, 6H), 1.22 - 1.50 (m, 14H), 2.5 (2H, overlay with DMSO), 2.89 (q, 2H, *J* = 6.6 Hz), 2.97 (s, 2H), 6.84 (t, 1H, *J* = 5.8 Hz).

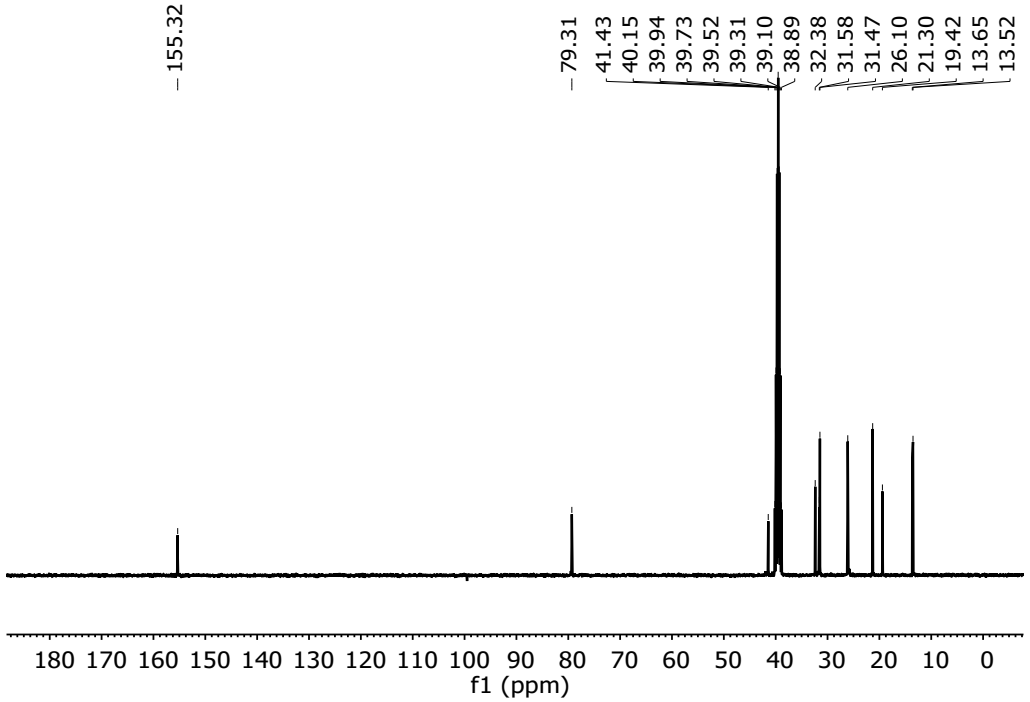
**$^{13}$C NMR (101 MHz, DMSO-$d_6$):** δ (in ppm) = 13.5, 13.6, 19.4, 21.3, 26.1, 31.5, 31.6, 32.4, 41.3, 79.3, 155.3.

**HRMS(ESI+):** m/z calcd. for $C_{13}H_{27}NO_2SNa$ $[M + Na]^+$ 284.1655, found 284.1658.

$^1$H NMR (400 MHz, DMSO-$d_6$):



$^{13}$C NMR (101 MHz, DMSO-$d_6$):




*Synthesis of polyurethanes by step-growth copolymerization of dicarboxylic acids (**7**) and N,N-bis(4,4-dimethyl-1,3-dioxolan-2-ylidene)butane-1,4-diamine (**6**).*

*Polymer synthesis - Experimental procedure*. In a representative experiment, succinic acid (**7a**) and product **6** were vacuum dried for 24 h at 40 °C under vacuum in two separate glass tubes. Then, DMSO (dry) was added within each vials to obtain solutions with a concentration of 1.4 mol/L. Each solution was transferred into a second glass tube containing molecular sieves 3 Å for further drying of the monomers. After 24 h, equal volumes of each monomer solution were mixed into a flame dried glass tube under $N_2$ flow. The polymerization was left at 80 °C for 24 h. After polymerization, the crude sample was analyzed by $^1$H NMR spectroscopy and by SEC characterization before precipitation in diethyl ether. The purified polymer was finally vacuum dried prior structural characterization via $^1$H and $^{13}$C NMR spectroscopy. This protocol was applied for the synthesis of all polymers, including those synthesized between **6** and dithiols **8a-c**, by adapting the quantities of each of the comonomers to respect the stoichiometry.

*NMR Characterizations of the polymers*

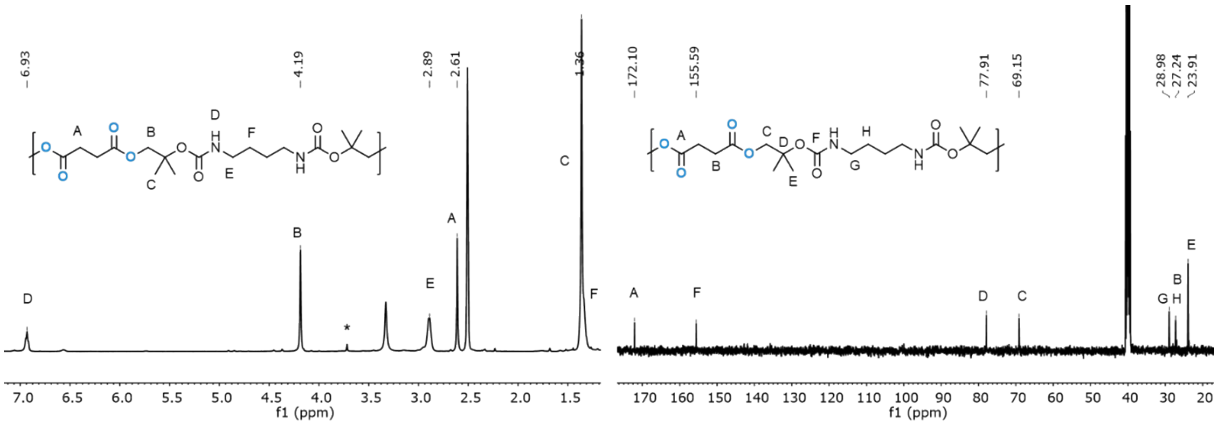



**Figure S4:** $^{1}$H NMR (400 MHz, DMSO-$d_6$, 303 K) (left) and $^{13}$C NMR (101 MHz, DMSO-$d_6$, 303 K) (right) spectra of a polyurethane synthesized by step-growth copolymerization of cyclic bisiminocarbonate 6 with succinic acid (**7a**). * Impurity present in cyclic bisiminocarbonate **6**.

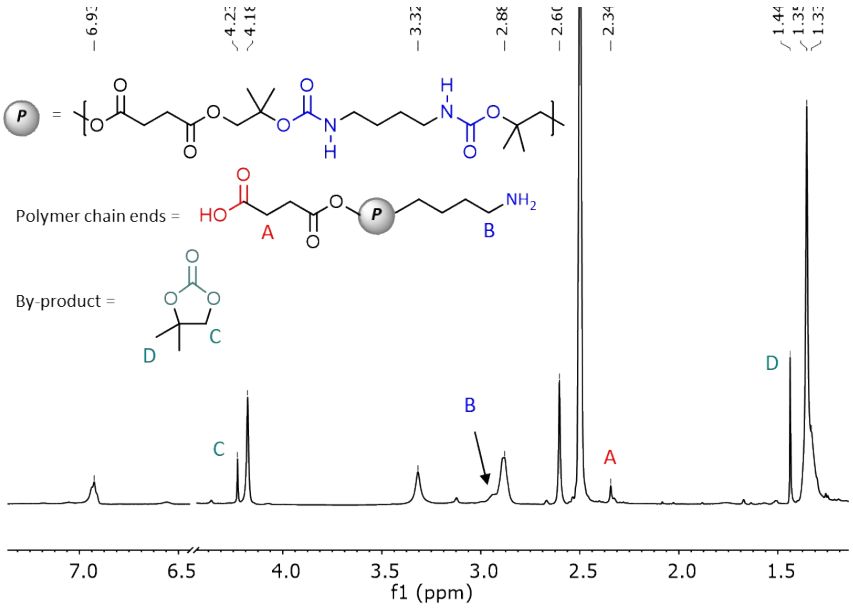



**Figure S5:** $^{1}$H NMR structural characterization of crude polyurethane ($M_w$ = 4,400 g/mol) synthesized by step-growth copolymerization of cyclic bisiminocarbonate **6** with succinic acid (**7a**) in DMSO (C = 0.7 mol/L) at 80 °C for 24 h (*cfr.* Table 1, entry 1 of the main manuscript). Identification of the chain ends of the crude polyurethane synthesized from *N*,*N*-bis(4,4-dimethyl-1,3-dioxolan-2-ylidene)butane-1,4-diamine (**6**) and succinic acid (**7a**) in DMSO after simple drying of the comonomers under vacuum.

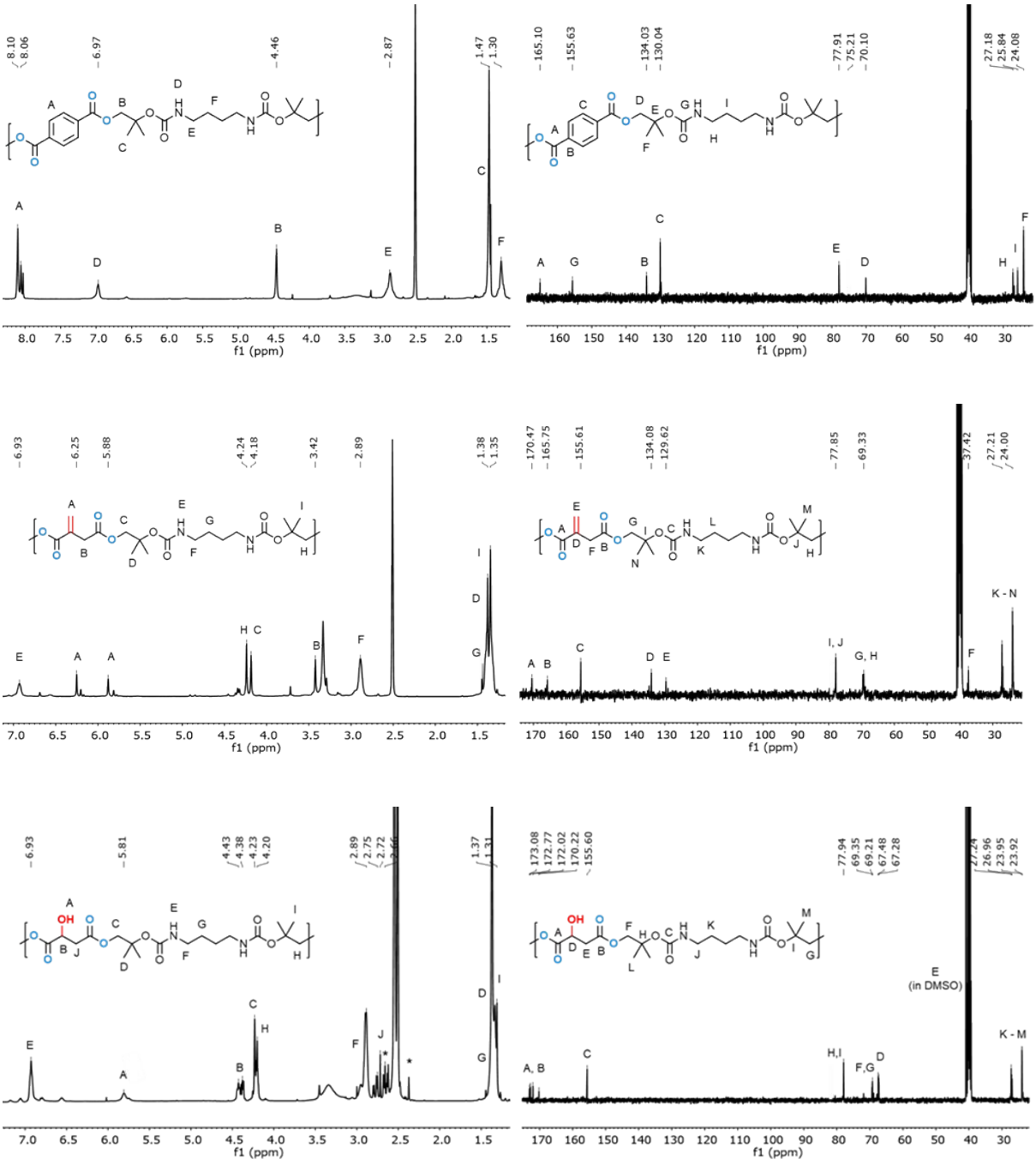



**Figure S6:** $^{1}$H (400 MHz, DMSO-$d_6$, 303 K) and $^{13}$C NMR (101 MHz, DMSO-$d_6$, 303 K) spectra of polyurethanes synthesized by step-growth copolymerization of cyclic bisiminocarbonate **6** and terephthalic (**7b**) (top), itaconic (**7c**) (middle) or d,l-malic acid (**7d**) (bottom) (*cfr.* polymers in Table 1, entries 6, 9 and 12).

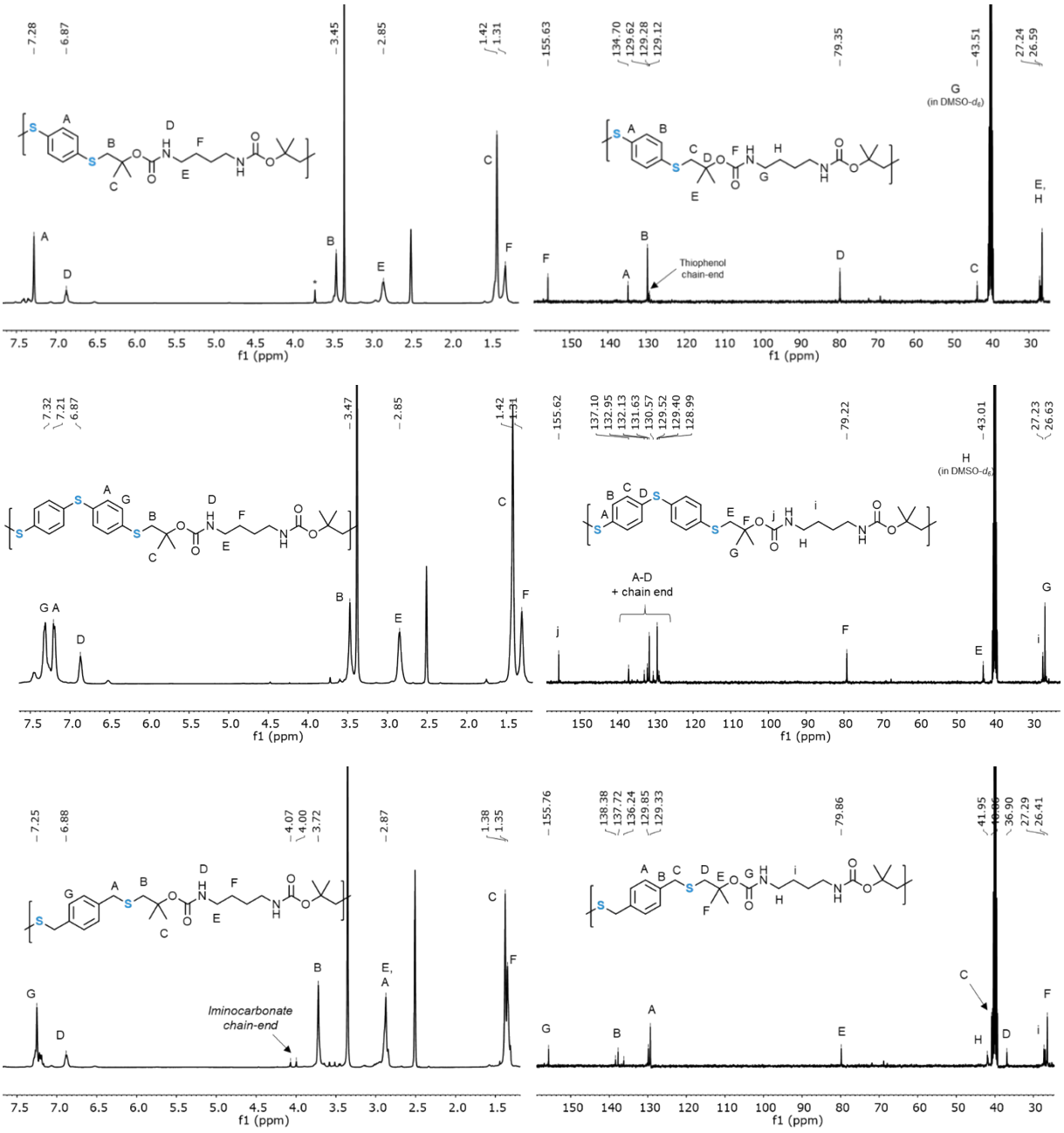



**Figure S7:** $^{1}$H (400 MHz, DMSO-$d_6$, 303 K) and $^{13}$C NMR (101 MHz, DMSO-$d_6$, 303 K) spectra of polyurethanes synthesized from the step-growth copolymerization of cyclic bisiminocarbonate **6** and 1,4-benzenedithiol (**8a**, top), 4,4'-thiobisbenzenethiol (**8b**, middle) or 1,4-benzenedimethanethiol (**8c**, bottom).

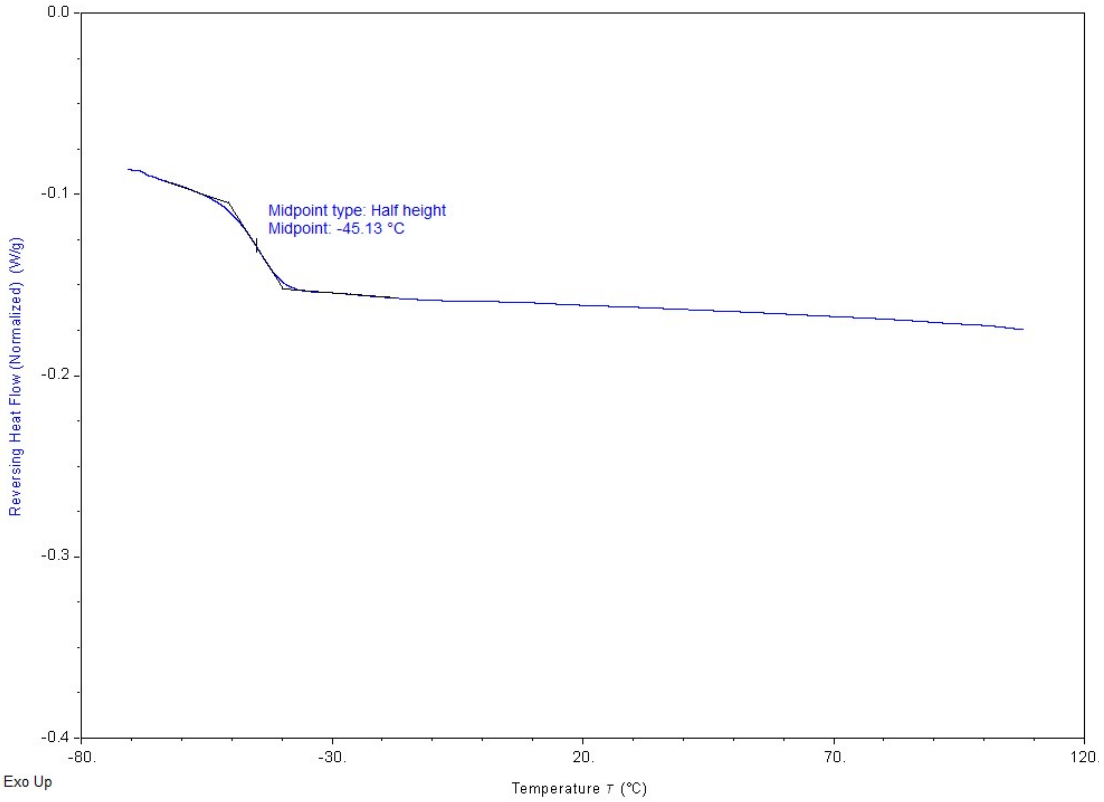



**Figure S8:** Reversing heat flow by modulated DSC of **P3**.

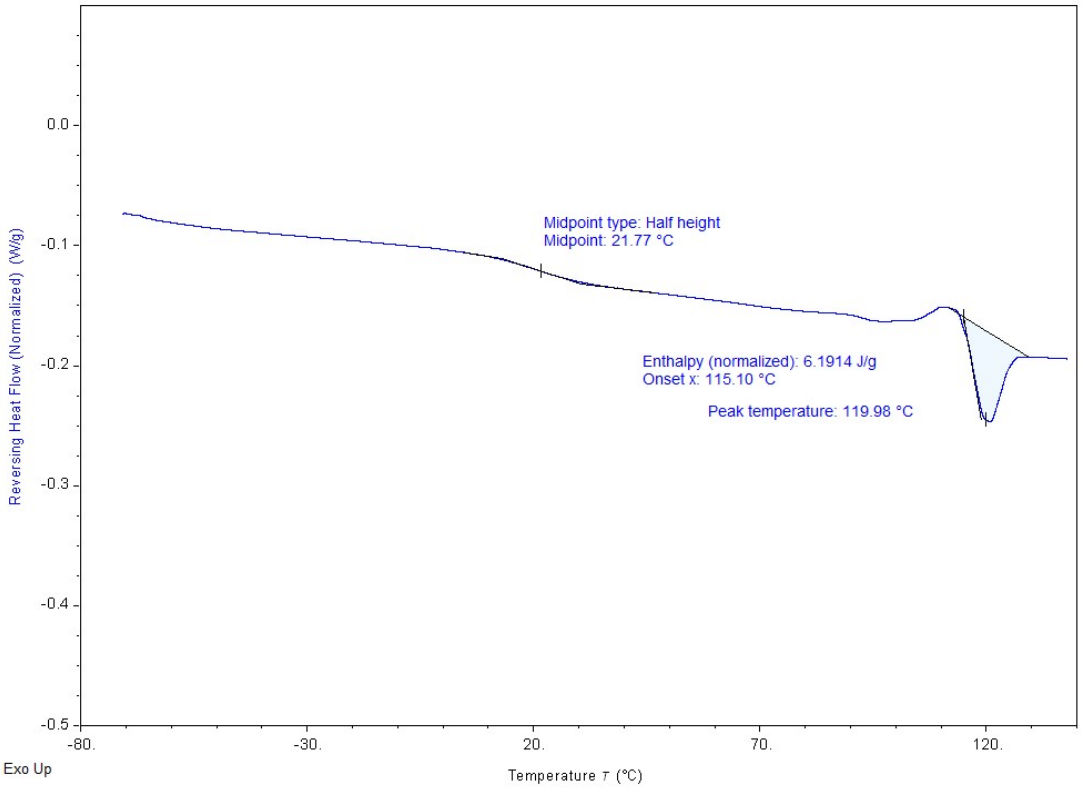



**Figure S9:** Reversing heat flow by modulated DSC of **P6**.

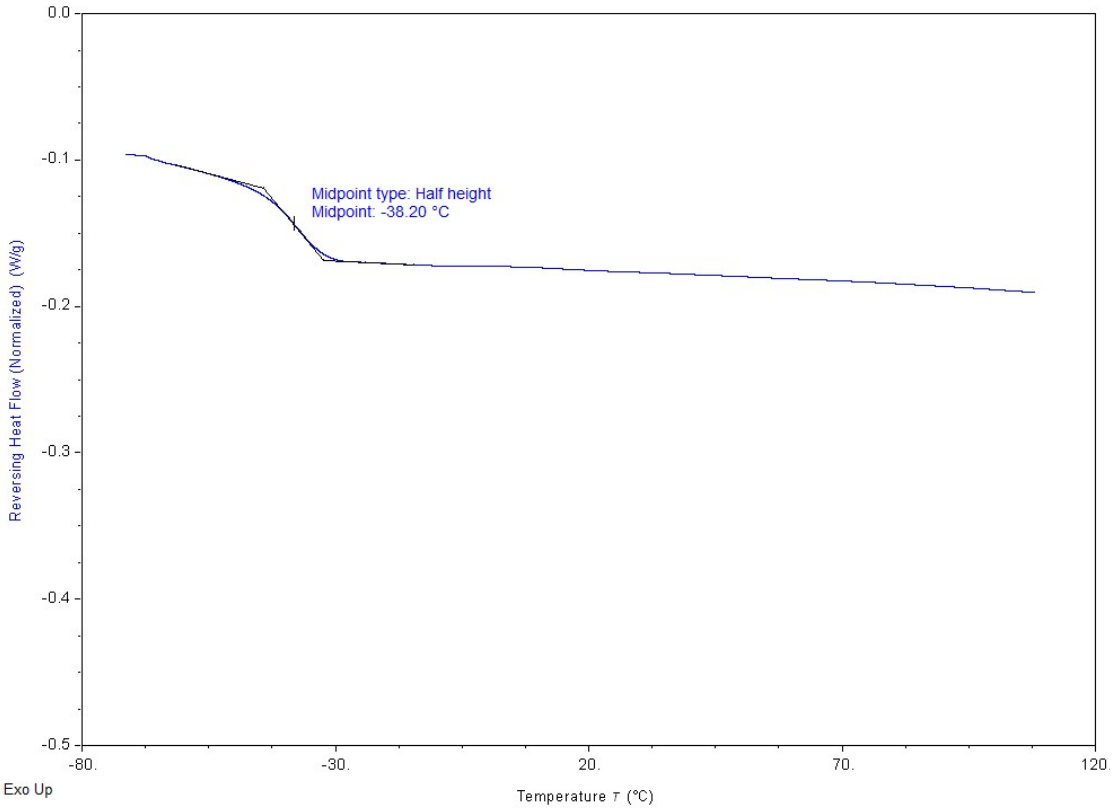



**Figure S10:** Reversing heat flow by modulated DSC of **P9**.

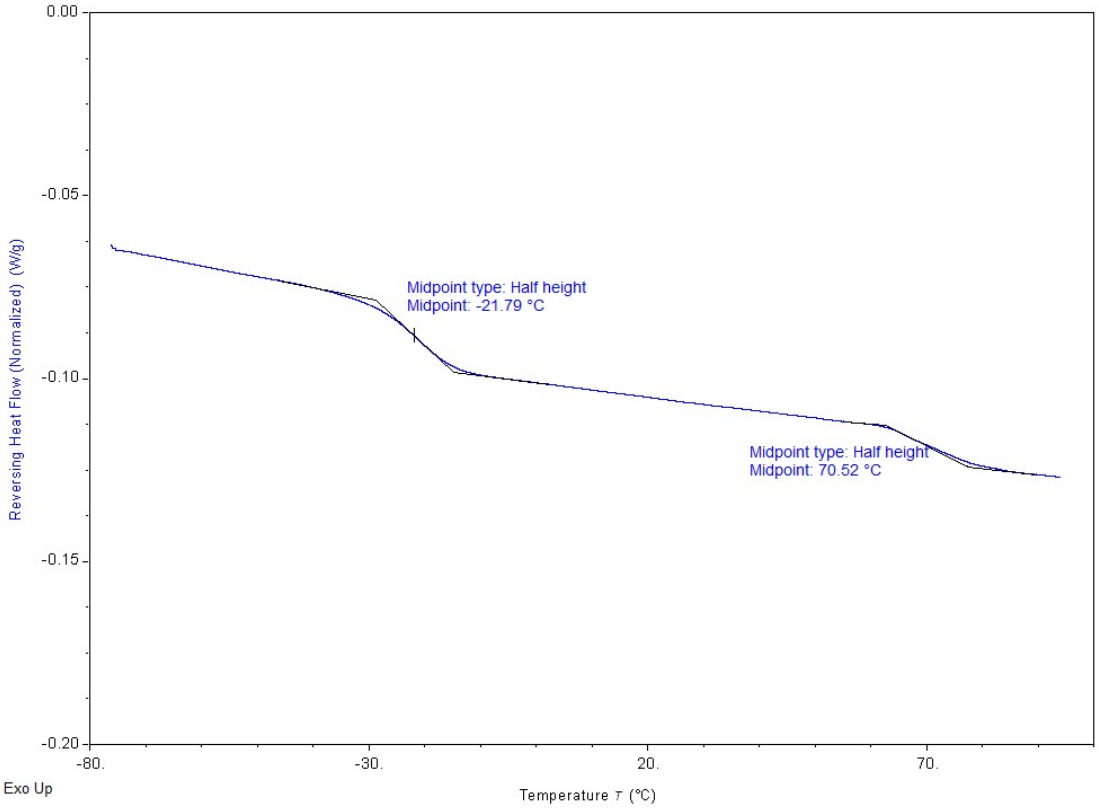



**Figure S11:** Reversing heat flow by modulated DSC of **P13**.

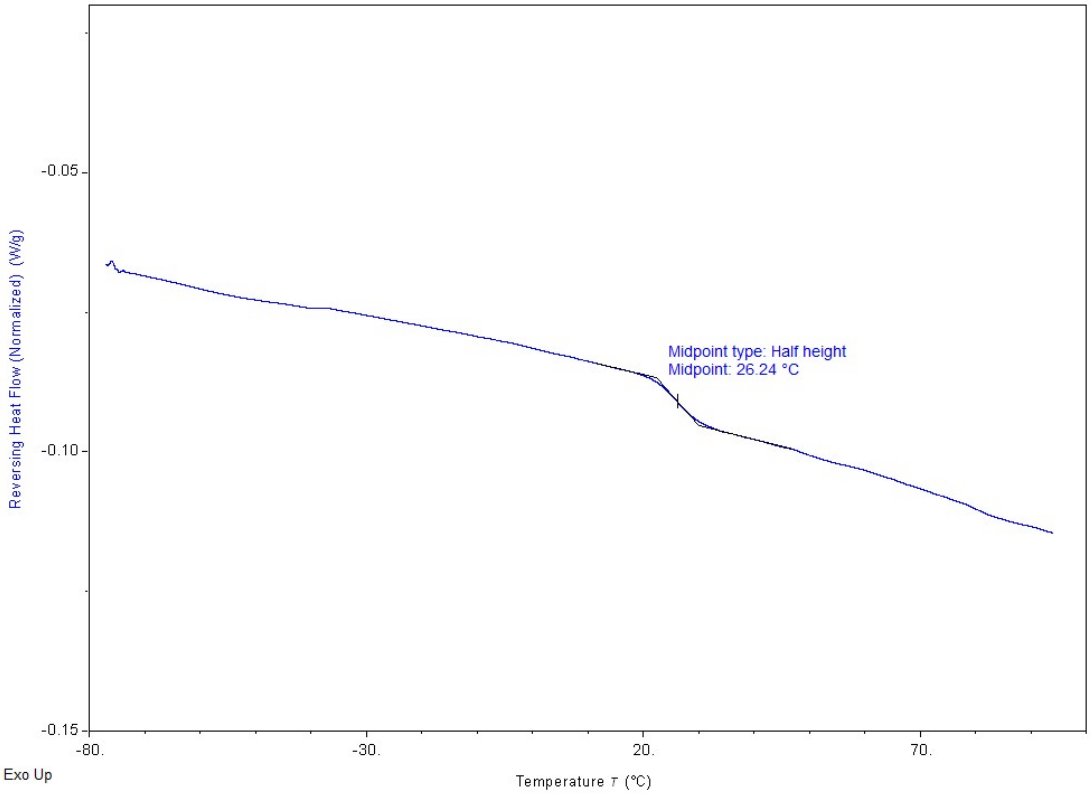



**Figure S12:** Reversing heat flow by modulated DSC of **P14**.

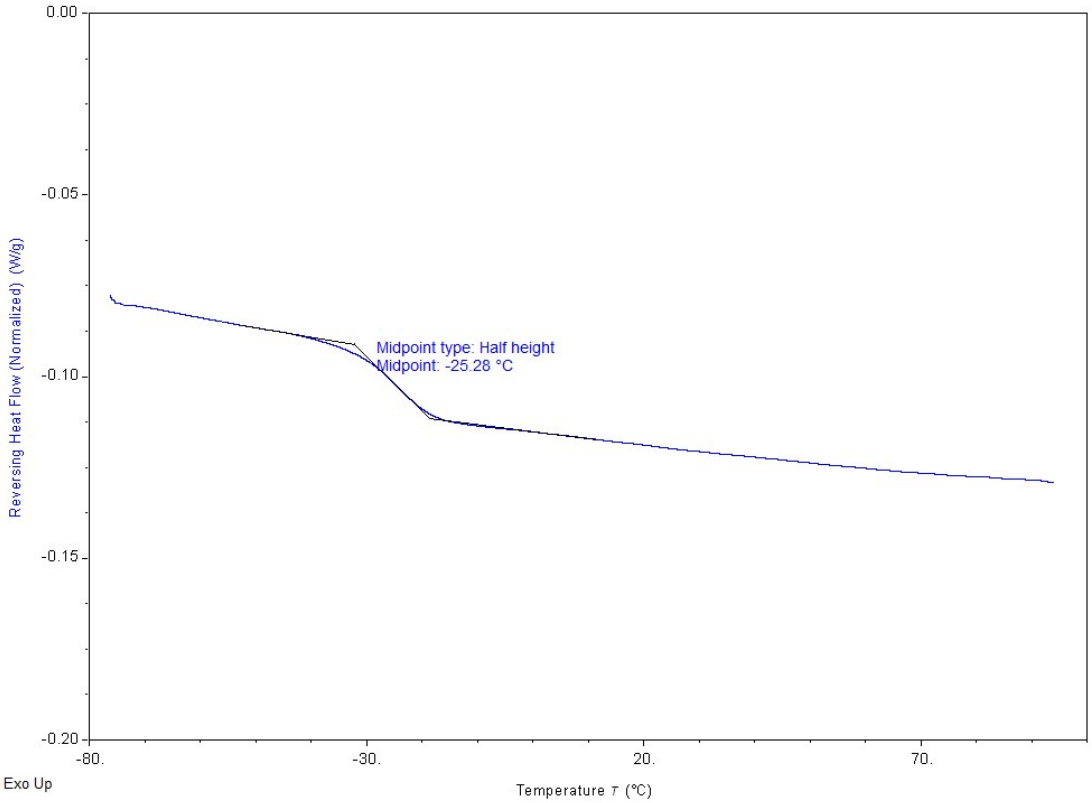



**Figure S13:** Reversing heat flow by modulated DSC of **P15**.

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