Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

2-Amino-1,3-propane diols: A versatile platform for the syntheses of aliphatic cyclic carbonate monomers.

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Materials and methods

Materials

Unless, specifically mentioned, all materials were purchased from Sigma-Aldrich or TCI or Merck. All solvents were of analytical grade, purchased from Fisher Scientific or J. T. Baker and used as received. Benzyl alcohol, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), (-) sparteine were distilled from CaH_2 under dry N_2 and transferred to glove box. *N*-(3,5-Trifuluoromethyl)phenyl-*N*′-cyclohexylthiourea (TU) catalyst was prepared as described elsewhere.[1] Before transferring into glove box, monomers and other reagents were dried extensively by freeze drying process under high vacuum.

Nuclear magnetic resonance (NMR) spectroscopy

The ^{1}H- and ^{13}C-NMR spectra of monomers and polymers were recorded using a Bruker Avance 400 spectrometer, and operated at 400 and 100 MHz respectively, with the solvent proton signal as the internal reference standard.

Molecular weight determination by size exclusion chromatography (SEC)

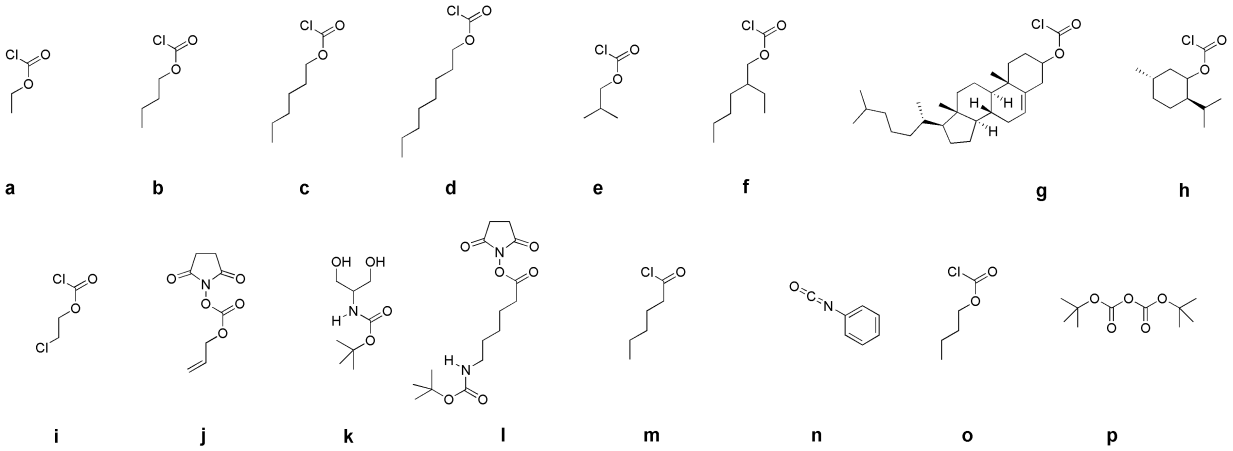
SEC was conducted using THF as the eluent for monitoring the polymer conversion and also for the determination of polystyrene equivalent molecular weights of the macro-transfer agents. THF-SEC was recorded on a Waters 2695D (Waters Corporation, USA) Separation Module equipped with an Optilab rEX differential refractometer (Wyatt Technology Corporation, U.S.A.) and Waters HR-4E as well as HR 1 columns (Waters Corporation, USA). The system was equilibrated at 30 °C in THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known concentration (ca. 3 mg/mL)

and an injection volume of 100 µL was used. Data collection and analysis were performed using the Astra software (Wyatt Technology Corporation, USA; version 5.3.4.14). The columns were calibrated with series of polystyrene standards ranging from Mp = 360 Da to Mp = 778 kDa (Polymer Standard Service, USA).

Monomer synthesis:

Synthesis of functional diols (1 a-p)

Except for **1k** (Sigma Aldrich 98%), all other diols were synthesized using one of the following general procedure by using the reacting the corresponding commercially available electrophile (**SI. Figure 1**).



SI. Figure 1. List of electrophiles (or starting materials) used in this study to prepare functional diols

General procedure for reaction of 2-amino-1,3-propane diols with chloroformates:[2]

Representative example: Synthesis of isobutyl 1,3-dihydroxypropan-2-ylcarbamate (**1e**)

In a 1 L round bottom flask with magnetic stir bar, serinol (10.0 g) and Na_2CO_3 (25.0 g) were dissolved in the mixture of DI water (250 mL) and THF (150 mL). The reaction mixture was allowed to cool in ice-bath for about 15 – 30 min. Isobutyl chloroformate (14.0 mL) was added in one portion and the reaction was allowed to proceed in ice-cold conditions for 1-2 h, followed by ~ 14 h at room temperature. The product was extracted into ethyl acetate (4 x 200 mL) and the combined organic fractions were dried over Na_2SO_4 and the volatiles were removed under vaccuo to yield **1e** as the crystalline solid (18.2 g, 88.9 %).

The following procedure was generally followed to prepare compounds **1a-i** and **1o**. Typical isolated yields ~ 70 - 98%. Except for **1a,** additional ethyl acetate extractions (8 x 200 mL) were necessary to improve the yield.

Synthesis of allyl-1,3-dihydroxypropan-2-ylcarbamate (**1j**):

To a 500 mL round bottom flask equipped with magnetic stirrer, serinol (5.1 g, 0.056 mol, 1.1 equiv.) and sodium carbonate (12.5 g) were dissolved in THF-DI water mixture (~ 150 mL, 1:1 v/v). The reaction mixture was allowed to equilibrate at ice-cold conditions for about 30 min and to this N-(allyloxycarbonyloxy) succinimide (10 g, 0.05 mol, 1.0 equiv.) was added in one portion. The reaction was allowed to proceed in ice-cold conditions for about 1-2 hours and then allowed to proceed at room temperature for 15 hours. The product was extracted into ethyl acetate (200 mL x 4) and the combined organic layers were dried with sodium sulphate followed by the removal of volatiles to result in white solid (8.5g, 95%) as the product.

Synthesis of tert-butyl 5-(1,3-dihydroxypropan-2-ylcarbamoyl)pentylcarbamate (**1l**):

In a 500 mL round bottom flask with magnetic stir bar, 6-(Boc-amino)caproic acid N-succinimidyl ester (5.0 g, Sigma Aldrich (≥ 98.0%)) and serinol (1.7 g) were dissolved in the mixture of DI water (125 mL) and acetonitrile (125 mL). About 20 drops of triethyl amine were added to the reaction mixture and the reaction was allowed to proceed under nitrogen at room temperature for 15 hours. Another 100 mL of DI water was added to the reaction mixture and the product was extracted into ethyl acetate (6 x 200 mL). The final product was a white solid. (3.7 g, 79.8 %).

Reaction of 2-amino-1,3-propane diols with isocyanates:

Synthesis of 1-(1,3-dihydroxypropan-2-yl)-3-phenylurea (**1n**)

In a 250 mL round bottom flask equipped with magnetic stirrer, phenylisocyanate (3.0 g, 0.025 mol, 1.0 equiv.) was dissolved in THF (100 mL). To this solution, serinol (2.5 g, 0.027 mol, 1.1 equiv.) DI water (~ 50 mL) was added drop-wise over 30 min and white solid, precipitated out of the solution. The reaction mixture was allowed to stir at RT for additional 2 hours and the precipitated solids were isolated and washed with ice-cold diethyl ether followed by vacuum drying to result in white solid (3.6 g, 69 %) as the product.

Synthesis of tert-butyl 1,3-dihydroxy-2-methylpropan-2-ylcarbamate (**1o**)[3]

In a 250 mL round bottom flask equipped with magnetic stirrer, 2-amino-2-methyl-1,3-propane diol (5.3 g, 0.050 mol, 1.0 equiv.) was dissolved in methanol (135 mL) and triethylamine (15 mL) mixture. To this solution di-tert-butyl dicarbonate (13.3 g, 0.061 mol. 1.2 equiv.) was added in one portion. The reaction was allowed proceed at RT, followed by the removal of volatiles

using rotavapor. The crude reaction mixture was dissolved in 100 mL DI water and the product was extracted into ethyl acetate (4 x 200 mL) and dried over Na_2SO_4 and concentrated in vacuuo to the product as a white solid (8.3 g, 80.6 %) as the product.

General procedure for intramolecular cyclization of functional diols:

Representative example: Synthesis of allyl-2-oxo-1,3-dioxan-5-ylcarbamate (**2j**)

In a 250 mL round bottom flask, equipped with magnetic stirrer, allyl-1,3-dihydroxypropan-2-ylcarbamate (5.0 g, 28.5 mmol, 1.0 equiv.) and ethyl chloroformate (2.7 mL, ~ 4.0 equiv) were dissolved in 125 mL THF. The reaction mixture was allowed to equilibrate at ice-cold conditions for 30 min. To the cold reaction mixture, triethylamine (4.0 mL, ~ 4.0 equiv.) was added dropwise over 15 min. The reaction was allowed to proceed in ice-cold conditions for about 1-2 hours and then allowed to proceed at room temperature for 15 hours. The precipitated solids were filtered off and the volatiles were removed to result in crude product, which was subjected to flash column chromatography, using a gradient of DCM (100 %) to DCM (80 %) and ethyl acetate (20 %)solvent mixture, followed by the removal of volatiles to result in white crystalline solid as the functional monomer (2.48g, 49%)

The following procedure was generally followed to prepare compounds **2a-q.** Typical isolated yields after flash column chromatography was ~ 45 – 70 %.

General procedure for homopolymerization:

*Representative example – enrty 6; table 1:*In a 7 mL vial containing a magnetic stir bar, in glove box, **2k** (104 mg, 479 µmol, 19.7 equiv.), and BzOH (2.5 µL, 2.6 mg, 24.2 µmol, 1.0 equiv.),

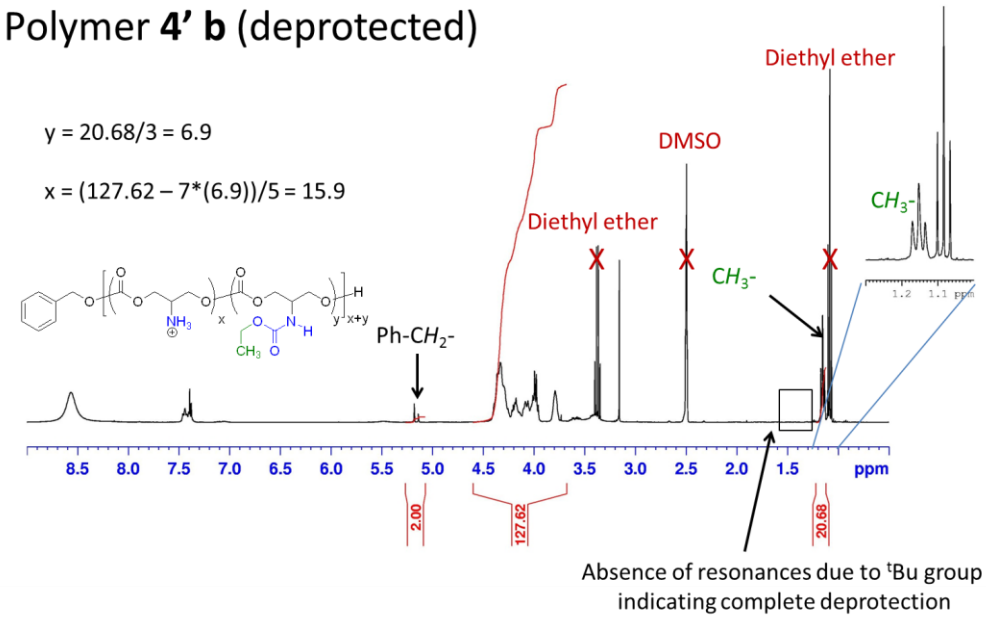
were dissolved in DCM (1.0 mL). To this solution, DBU (3.6 µL, 3.7 mg, 24.2 µmol., 1.0 equiv.) was added to initiate polymerization. The reaction mixture was allowed to stir at room temperature. After 180 s (3 min), the reaction was quenched by the addition of about 10 mg of benzoic acid.

*General procedure for copolymerization of **2a** and **2k**:*

*Representative example – synthesis of **4a**:* In a 7 mL vial containing a magnetic stir bar, in glove box, **2k** (467 mg, 2.150 mmol, 22.1 equiv.), **2a** (56.3 mg, 0.298 mmoles, 3.1 equiv.) and BzOH (10.0 microliters, 10.5 mg, 97.1 micromoles, 1.0 equiv.) and TU (36.1 mg, 97.5 micromoles, 1.0 equiv.) were dissolved in dichloromethane (5.0 mL). To this solution, (-)-sparteine (22.3 microliters, 22.7 mg, 97.0 micromole, 1.0 equiv.) was added to initiate polymerization. The reaction mixture was allowed to stir at room temperature. After 4 hours, the reaction was quenched by the addition of about 20 mg of benzoic acid.

General procedure for deprotection of polymers

Typically, polymer was dissolved in CH_2Cl_2, to which trifluoroacetic acid (TFA, ~10 equiv. with respect to ^{t}Boc groups) was added drop-wise and the reaction mixture was allowed to stir for 1 hr at room temperature, after which the solvent and excess TFA were removed by bubbling N_2 gas and the residual volatiles were removed in vacuum. Isolated yields were generally over 90 %. A representative example of deprotected polymer (**4' b**, **Table 2**) is provided below

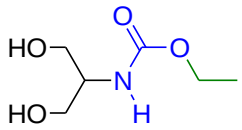


References:

1. Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L., *Macromolecules* **2006**, *39*, 7863-7871
2. Hu, X.; Chen, X.; Xie, Z.; Cheng, H.; Jing, X., *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7022-7032.
3. Kang, J.-H.; Chung, H.-E.; Kim, S. Y.; Kim, Y.; Lee, J.; Lewin, N. E.; Pearce, L. W.; Blumberg, P. M.; Marquez, V. E. *Bioorg. Med. Chem* **2003**, *11*, 2529 – 2539

Characterization data for functional 1,3-diols:

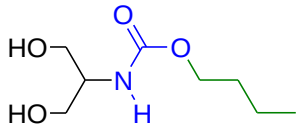
ethyl 1,3-dihydroxypropan-2-ylcarbamate **(1a):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.94 – 5.65 (br. m, 1H, NH), 4.09 (q, *J*= 7.0 Hz, 2H, OH), 3.94 – 3.60 (m, 7H, C*H*$_2$OH, C*H* $(CH_2OH)_2$ and O*H*), 1.23 (t, *J* = 7.0 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 157.36, 62.41, 61.33, 53.60, 14.63

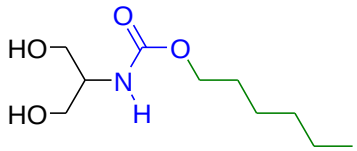
butyl 1,3-dihydroxypropan-2-ylcarbamate **(1b):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.63 (d, *J* = 7.4 Hz, 1H, NH), 4.55 (br. s, 2H, OH), 3.91 (t, *J* = 6.6 Hz, 2H, CH_2), 3.50 – 3.26 (m, 5H, C*H*$_2$OH and C*H* $(CH_2OH)_2$), 1.57 – 1.44 (m, 2H, C*H*$_2$$CH_2CH_3$), 1.39 - 1.24 (m, 2H, C*H*$_2$$CH_3$), 0.88 (t, *J* = 7.4 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 156.27, 63.42, 60.57, 54.88, 30.91, 18.77, 13.74

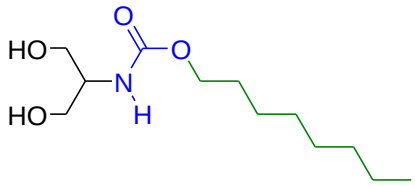
hexyl 1,3-dihydroxypropan-2-ylcarbamate **(1c):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.64 (d, *J* = 7.4 Hz, 1H, NH), 4.55 (t, *J* = 5.4 Hz, 2H, OH), 3.90 (t, *J* = 6.6 Hz, 2H, CH_2), 3.48 – 3.30 (m, 5H, C*H*$_2$OH and C*H* ($CH_2OH)_2$), 1.51 (quin. *J* = 7.0 Hz, 2H, CH_2), 1.37 – 1.18 (m, 6H, CH_2), 0.86 (t, *J* = 7.0 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 156.20, 63.66, 60.50, 54.84, 31.32, 25.50, 22.18, 14.02

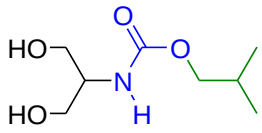
octyl 1,3-dihydroxypropan-2-ylcarbamate **(1d):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.63 (d, *J* = 7.4 Hz, 1H, NH), 4.55 (t, *J* = 5.2 Hz, 2H, OH), 3.90 (t, *J* = 6.6 Hz, 2H, CH_2), 3.50 – 3.27 (m, 5H, C*H*$_2$OH and C*H* ($CH_2OH)_2$), 1.51 (quin. *J* = 7.0 Hz, 2H, CH_2), 1.41 – 1.14 (m, 10H, CH_2), 0.85 (t, *J* = 7.0 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 156.20, 63.66, 60.50, 54.84, 31.32, 25.50, 22.18, 14.02

isobutyl 1,3-dihydroxypropan-2-ylcarbamate **(1e):**

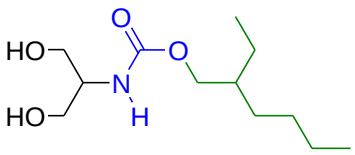


^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.65 (d, *J* = 7.4 Hz, 1H, NH), 4.56 (t, *J* = 5.2 Hz, 2H,

OH), 3.70 (d, *J* = 6.6 Hz, 2H, CH_2), 3.50 – 3.30 (m, 5H, C*H*$_2$OH and C*H* ($CH_2OH)_2$), 1.90 – 1.73 (m, 1H, C*H*($CH_3)_2$), 0.87(d, *J* = 6.6 Hz, 6H($CH_3)_2$)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 156.29, 65.76, 63.53, 54.87, 23.75, 19.05

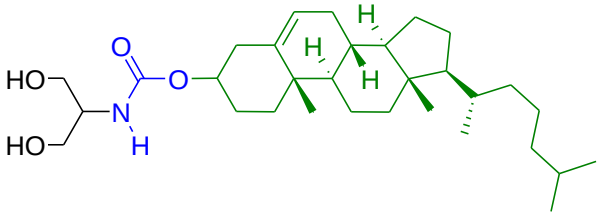
2-ethylhexyl 1,3-dihydroxypropan-2-ylcarbamate **(1f):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.63 (d, *J* = 7.4 Hz, 1H, NH), 4.56 (br. m, 2H, OH), 3.92 – 3.75 (m, 2H), 3.50 – 3.26 (m, 5H, C*H*$_2$OH and C*H* ($CH_2OH)_2$), 1.14 – 1.57 (m, 9H, C*H*OC=O and C*H*$_2$) 0.95 – 0.76 (m, 6H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 156.33, 65.82, 60.49, 54.86, 38.66, 29.85, 28.47, 23.20, 22.57, 14.02, 10.90

cholesteryl 1,3-dihydroxypropan-2-ylcarbamate **(1g):**

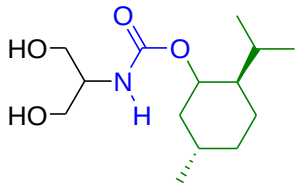


^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.92-5.50 (br. m, 1H, NH), 5.45 – 5.25 (br. m, 1H,

C=C*H*), 4.71 – 4.29 (br. m, 1H, C*H*OC=O) 4.18 – 3.30 (m, 7H), 2.46-2.17 (m, 2H), 2.10 – 0.75 (m, 38H), 0.66 (s, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.82, 139.79, 122.75, 74.97, 64.50, 56.79, 56.32, 53.50, 50.06, 42.42, 39.86, 39.63, 38.61, 37.08, 36.65, 36.32, 35.97, 32.01, 31.96, 28.38, 28.23, 28.13, 24.42, 24.05, 22.97, 22.67, 21.18, 19.48, 18.85, 11.99

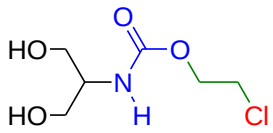
(2R,5S)-2-isopropyl-5-methylcyclohexyl 1,3-dihydroxypropan-2-ylcarbamate **(1h):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.55 (d, *J* = 7.4 Hz, 1H, NH), 4.61 – 4.31 (br. m, 2H, OH), 4.46 – 4.31 (m, 1H, C*H*OC=O), 3.50 – 3.27 (m, 5H, C*H*$_2$OH and C*H* ($CH_2OH)_2$), 2.00 – 1.82 (m, 2H), 1.73 – 1.53 (m, 2H), 1.51 – 1.13 (m, 2H), 1.10 – 0.78 (m, 9H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 155.97, 72.75, 60.50, 60.48, 54.78, 47.03, 41.43, 33.92, 31.00, 25.67, 23.08, 22.05, 20.69, 16.33

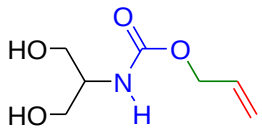
2-chloroethyl 1,3-dihydroxypropan-2-ylcarbamate **(1i):**



^{1}H NMR (400 MHz, D_2O, δ, ppm): 4.29 (t, J = 5.4 Hz, 2H, C*H*$_2$OC=O), 3.5 – 3.5 (m, 7H, C*H*$_2$Cl, C*H*$_2$OH and C*H* ($CH_2OH)_2$)

^{13}C NMR (100 MHz, D_2O, δ, ppm): 158.00, 64.99, 60.72, 54.23, 42.48

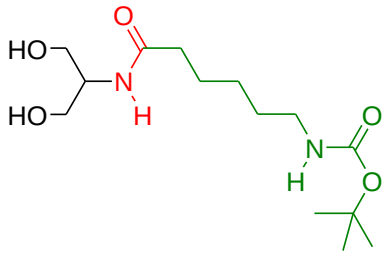
allyl 1,3-dihydroxypropan-2-ylcarbamate **(1j):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.80 (d, *J* = 7.4 Hz, 1H, NH), 5.96 – 5.83 (m, 1H, C*H*=CH_2), 5.32 – 5.12 (m, 2H, CH=C*H*$_2$), 4.58 (t, *J* = 5.4 Hz, 2H, OH), 4.50 – 4.38 (m, 2H, C*H*$_2$CH=CH_2), 3.50– 3.27 (m, 5H, C*H*$_2$OH and C*H* ($CH_2OH)_2$)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 155.86, 133.88, 117.00, 64.32, 60.57, 55.02

tert-butyl 5-(1,3-dihydroxypropan-2-ylcarbamoyl)pentylcarbamate **(1l):**

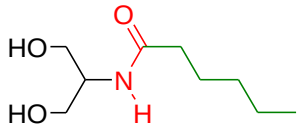


^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.44 (d, *J* = 8.0 Hz, 1H, NH), 6.76 (t, *J* = 5.4 Hz, 1H, NH), 4.58 (t, *J* = 5.4 Hz, 2H, OH), 3.63 – 3.74 (m, 1H), 3.37 (t, *J* = 5.4 Hz, 4H, C*H*$_2$OH), 2.87

(q, *J* = 6.6 Hz, 2H, CH_2), 2.05 (t, *J* = 7.4 Hz, 2H, CH_2), 1.13 – 1.55 (m, 15H, $(CH_2)_3$ and $C(CH_3)_3$)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 172.13, 155.64, 77.37, 60.25, 52.78, 35.44, 29.39, 28.34, 26.07, 25.29, 25.16

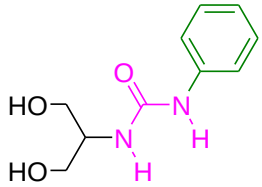
N-(1,3-dihydroxypropan-2-yl)hexanamide **(1m):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.45 (d, *J* = 8.0 Hz, 1H, NH), 4.59 (br. t, 2H, OH), 3.75 – 3.61 (m, 1H), 3.45 – 3.30 (m, 4H, C*H*$_2$OH), 2.06 (t, *J* = 7.4 Hz, 2H, CH_2), 1.47 (quin., *J* = 7.4 Hz, 2H, CH_2), 1.33 – 1.14 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 172.22, 60.27, 52.79, 35.45, 30.98, 25.11, 22.00, 13.98

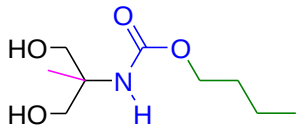
1-(1,3-dihydroxypropan-2-yl)-3-phenylurea **(1n):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.61 (br. s, 1H, NH), 7.36 (m, 2H, Ph), 7.21 (m, 2H, Ph), 6.87 (tt, J^{1}= 7.4 Hz, J^{2}= 1.0 Hz, 1H, Ph), 6.07 (d, J = 8.2 Hz, 1H, NH), 4.75 (t, J = 5.2 Hz, 2H, OH), 3.68 – 3.56 (m, 1H), 3.56 – 3.33 (m, 4H, CH_2OH)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 155.05, 140.65, 128.77, 121.00, 117.48, 60.15, 52.42

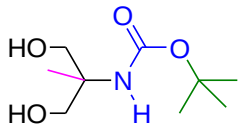
butyl 1,3-dihydroxy-2-methylpropan-2-ylcarbamate **(1o):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.23 (br. s, 1H, NH), 4.58 (br.s, 2H, OH), 3.89 – 3.86 (t, 2H, CH_2OC=O), 3.44 – 3.34 (m, 4H, CH_2OH), 1.535 – 1.501 (m, 2H, CH_2CH$_2$CH$_3$), 1.36 – 1.27 (m, 2H, CH$_2$CH_2CH$_3$), 1.10 (s, 3H, CH$_3$), 0.90 – 0.86 (t, J = 7.4 Hz, 3H, CH$_2$CH$_2$CH_3)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 155.14, 63.50, 63.01, 56.95, 30.75, 18.67, 18.46, 10.65

tert-butyl 1,3-dihydroxy-2-methylpropan-2-ylcarbamate **(1p):**



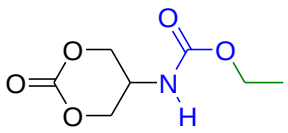
^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 5.89 (br. s, 1H, NH), 4.60 (t, J = 5.8 Hz, 2H, OH), 3.50– 3.25 (m, 4H, CH_2OH), 1.36 (s, 9H, C(CH$_3$)$_3$), 1.09 (s, 3H CH$_3$)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 154.67, 77.56, 63.69, 56.80, 28.29, 18.42

Electronic Supplementary Material (ESI) for Polymer Chemistry

Characterization data for functional cyclic carbonate monomers:

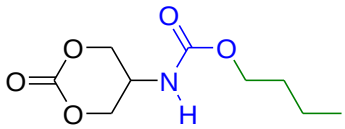
***ethyl 2-oxo-1,3-dioxan-5-ylcarbamate* (2a):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.20 – 5.75 (br. m, 1H, NH), 4.65 – 4.32 (m, 4H, $CH_2OC{=}O(O)$), 4.25 – 4.0 (m, 3H, $CH_3CH_2OC{=}O$ and C*H*), 1.24 (t, *J* = 7.0 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.36, 148.07, 71.13, 61.16, 42.63, 14.60

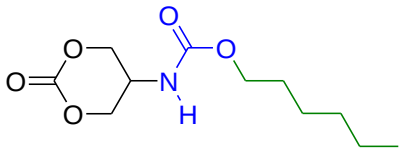
***butyl 2-oxo-1,3-dioxan-5-ylcarbamate* (2b):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.73 (br. m, 1H, NH), 4.63 – 4.34 (m, 4H, $CH_2OC{=}O(O)$), 4.24 – 4.15 (3.91 (t, *J* = 6.6 Hz, 2H, CH_2), 4.08 (t, J = 6.8 Hz, 2H, $NHO{=}COCH_2$), 1.66 – 1.54 (m, 2H, $CH_2\ CH_2CH_3$), 1.44 – 1.30 (m, 2H, $CH_2\ CH_3$), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.35, 147.79, 71.16, 65.64, 42.74, 31.00, 19.12, 13.83

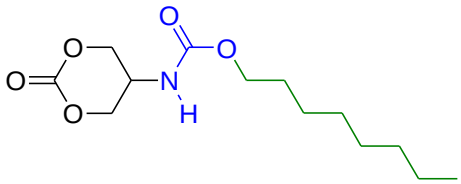
hexyl 2-oxo-1,3-dioxan-5-ylcarbamate **(2c):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.82 (br. s, 1H, NH), 4.65 – 4.35 (m, 4H, $CH_2OC{=}O(O)$), 4.23 – 4.13 (m, 1H, CH), 4.07 (t, *J* = 6.8 Hz, 2H, OCH_2CH_2), 1.60 (quin. *J* = 7.0 Hz, 2H, $OCH_2CH_2CH_2$), 1.40 – 1.15 (m, 6H, $(CH_2)_3CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.39, 147.86, 71.14, 65.92, 42.77, 31.52, 28.95, 25.55, 22.63, 14.09

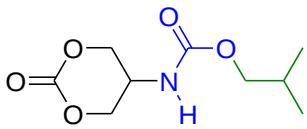
octyl 2-oxo-1,3-dioxan-5-ylcarbamate **(2d):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.84 (br. d, 1H, NH), 4.64 – 4.31 (m, 4H, $CH_2OC{=}O(O)$), 4.25 – 4.13 (m, 1H, CH), 4.06 (t, *J* = 6.8 Hz, 2H, OCH_2CH_2), 1.60 (quin. *J* = 7.0 Hz, 2H, $OCH_2CH_2CH_2$), 1.40 – 1.15 (m, 10H, $(CH_2)_5CH_3$), 0.86 (t, *J* = 7.0 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.39, 147.90, 71.15, 65.90, 42.71, 31.86, 29.31, 29.28, 28.97, 25.84, 22.73, 14.20

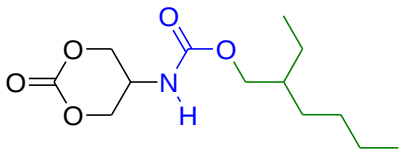
isobutyl 2-oxo-1,3-dioxan-5-ylcarbamate **(2e):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.98 (br. d, 1H, NH), 4.66 – 4.32 (m, 4H, $CH_2OC{=}O(O)$), 4.26 – 4.12 (m, 3H, $CH_2(CH_2)CHNH$), 3.84 (d, *J* = 6.6 Hz, 2H, $O{=}COCH_2CH(CH_3)_2$), 1.89 (sept. *J* = 6.6 Hz, 1H, $O{=}COCH_2CH(CH_3)_2$), 0.90 (t, *J* = 6.6 Hz, 6H, *J* = 6.6 Hz, 2H, $CH(CH_3)_2$))

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.48, 148.02, 71.70, 71.12, 42.66, 27.98, 19.06

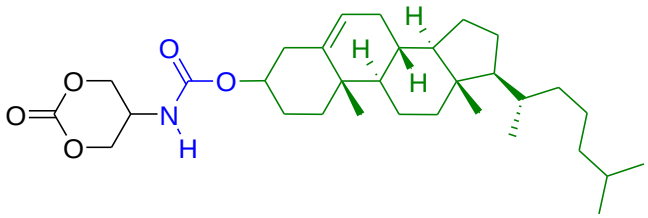
2-ethylhexyl 2-oxo-1,3-dioxan-5-ylcarbamate **(2f):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.76 (d, *J* = 6.4 Hz. 1H, NH), 4.65 – 4.30 (m, 4H, $CH_2OC{=}O(O)$), 4.25 – 4.11 (m, 1H, $CH_2(CH_2)CHNH$), 4.10 – 3.88 (m, 2H, $O{=}COCH_2CH(CH_2)CH_2$), 1.66 – 1.44 (m, 1H, $O{=}COCH_2CH(CH_2)CH_2$), 1.40 – 1.17 (m, 8H, $O{=}COCH_2CH(CH_2\ CH_3)(CH_2)_3CH_3$), 0.95 – 0.80 (m, 6H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.48, 147.85, 71.15, 68.11, 42.73, 39.02, 30.32, 29.00, 23.69, 23.06, 14.16, 11.07

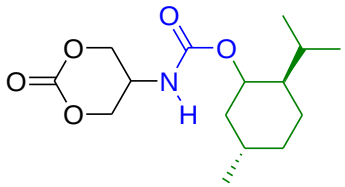
***cholestryl 2-oxo-1,3-dioxan-5-ylcarbamate* (2g):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.59 (br. d, *J* = 7.0 Hz, 1H, NH), 5.43 – 5.32 (m, 1H, C=C*H*), 4.68 – 4.32 (m, 5H), 4.27 – 4.14 (m, 1H), 2.43-2.21 (m, 2H), 2.10 – 0.78 (m, 38H), 0.67 (s, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 155.67, 147.75, 139.60, 122.93, 75.52, 71.18, 56.78, 56.23, 50.07, 42.69, 42.41, 39.81, 39.62, 38.54, 37.01, 36.64, 36.28, 35.91, 31.99, 31.93, 28.35, 38.16, 28.12, 24.39, 23.94, 22.96, 22.69, 31.14, 19.45, 18.83, 11.97

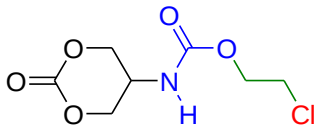
***(2R,5S)-2-isopropyl-5-methylcyclohexyl 2-oxo-1,3-dioxan-5-ylcarbamate* (2h):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.40 – 5.25 (br. m, 1H, NH), 4.65 – 4.50 (m, 3H), 4.49 – 4.34 (m, 2H), 4.26 – 4.15 (m, 1H), 2.09 – 1.79 (m, 2H), 1.73 – 1.59 (m, 2H), 1.55 – 1.27 (m, 2H), 1.12 – 0.80 (m, 9H, CH_3), 0.77 (t, *J* = 6.8 Hz, 3H, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 155.89, 147.57, 75.92, 71.22, 71.19, 47.34, 42.76, 41.37, 34.24, 31.50, 26.31, 23.48, 22.14, 22.21, 16.47

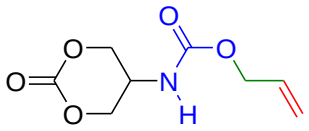
***2-chloroethyl 2-oxo-1,3-dioxan-5-ylcarbamate* (2i):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.18 (br. d, *J* = 5.4 Hz, 1H, NH), 4.60 – 4.18 (m, 6H, C*H*$_2$OC=O(O) and OC*H*$_2$CH$_2$Cl), 4.04 – 3.94 (m, 1H, C*H*CH$_2$OC=O(O)), 3.80 (t, J = 5.4 Hz, 2H, OCH$_2$C*H*$_2$Cl)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 155.76, 147.39, 69.94, 64.40, 43.12, 42.22

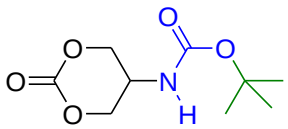
***allyl 2-oxo-1,3-dioxan-5-ylcarbamate* (2j):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.05 (d, *J* = 5.4 Hz, 1H, NH), 6.00 – 5.82 (m, 1H, C*H*=CH$_2$), 5.35 – 5.14 (m, 2H, CH=C*H*$_2$), 4.65 – 4.22 (m, 6H, C*H*$_2$OC=O(O) and C*H*$_2$CH=CH$_2$), 4.04 – 3.93 (m, 1H, C*H*CH$_2$OC=O(O)), 2.43-2.21 (m, 2H), 2.10 – 0.78 (m, 38H), 0.67 (s, 3H, CH$_3$)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 155.88, 147.40, 133.45, 117.30, 70.07, 64.70, 42.19

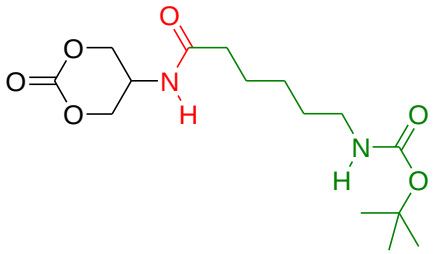
tert-butyl 2-oxo-1,3-dioxan-5-ylcarbamate **(2k):`**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.47 (br. d, *J* = 6.4 Hz, 1H, NH), 4.60 – 4.32 (m, 4H, C*H*$_2$OC=O(O)), 4.18 – 4.06 (m, 1H, C*H*CH$_2$OC=O(O)), 1.43 (s, 9H, $(CH_3)_3$)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 155.27, 147.84, 80.85, 71.18, 42.37, 28.36

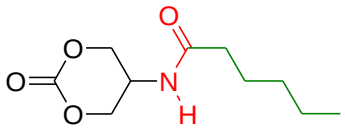
tert-butyl 5-(2-oxo-1,3-dioxan-5-ylcarbamoyl)pentylcarbamate **(2l):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.57 (d, *J* = 6.6 Hz, 1H, NH), 4.85 – 4.35 (m, 5H, C*H*$_2$OC=O(O) and NH), 4.35 – 3.45 (m, 1H, C*H*CH$_2$OC=O(O)), 3.08 (q, *J* = 6.4 Hz, 2H, $(CH_2)_3$C*H*$_2$NHC=O(O)C$(CH_3)_3$), 2.33 – 2.16 (m, 2H, (NH)O=CC*H*$_2$ $(CH_2)_3$CH$_2$NH) 1.71 - 1.23 (m, 15H, (NH)O=CCH$_2$ (C*H*$_2$)$_3$CH$_2$NHC=O(O)C(C*H*$_3$)$_3$)

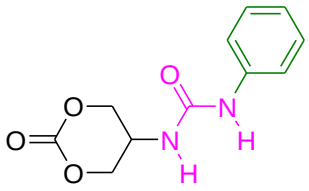
^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 175.06, 156.15, 148.64, 79.19, 71.39, 410.6, 40.40, 35.97, 29.75, 28.53, 26.38, 25.12

N-(2-oxo-1,3-dioxan-5-yl)hexanamide **(2m):**



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.58 (br. d, *J* = 6.6 Hz, 1H, NH), 4.65 – 4.00 (m, 5H, C*H*$_2$OC=O(O) and 1H, C*H*CH$_2$OC=O(O)), 2.24 (t, *J* = 7.4 Hz, 2H, NHC=OC*H*$_2$ (CH$_2$)$_3$CH$_3$), 1.71 - 1.52 (m, 2H, NHC=OCH$_2$C*H*$_2$(CH$_2$)$_2$CH$_3$), 1.38 – 1.17 (m, 4H, NHC=OCH$_2$CH$_2$(C*H*$_2$)$_2$CH$_3$), 0.87 (t, *J* = 7.0, 3H, CH$_3$)

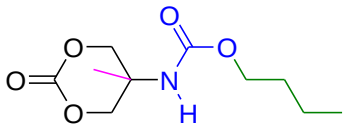
1-(2-oxo-1,3-dioxan-5-yl)-3-phenylurea **(2n):**



^{1}H NMR (400 MHz, DMSO-d$_6$, δ, ppm): 8.49 (s, 1H, NH), 7.46 – 6.84 (m, 6H, Ph and NH), 4.71 – 4.27 (m, 4H, C*H*$_2$OC=O(O)), 4.22 – 4.11 (m, 1H, C*H*CH$_2$OC=O(O))

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 154.85, 147.47, 139.93, 128.81, 121.60, 117.84, 71.26, 40.95

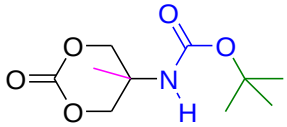
butyl 5-methyl-2-oxo-1,3-dioxan-5-ylcarbamate **(2o):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 5.29 (br. s, 1H, NH), 4.64 - 4.17 (m, 4H, CH_2OC=O(O)), 4.04 (t, *J* = 6.0, 2H, NH(O=)COCH_2), 1.62 – 1.55 (m, 2H, NH(O=)COCH$_2$CH_2), 1.40 – 1.31 (m, 5H, CH$_2$*CH*$_2$CH$_3$ and CH$_3$), 0.92 (t, *J* = 7.6, 3H, CH$_2$CH$_2$CH_3)

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 155.43, 147.71, 73.75, 65.16, 47.88, 30.97, 19.15, 18.39, 13.83

tert-butyl 5-methyl-2-oxo-1,3-dioxan-5-ylcarbamate **(2p):**



^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.21 (br. s, 1H, NH), 4.65 – 4.21 (m, 4H, CH_2OC=O(O)), 1.39 (s, 9H, C(CH$_3$)$_3$), 1.17 (s, 3H, CH$_3$)

^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 154.87, 147.44, 78.53, 72.53, 47.06, 28.17, 17.55