Electronic supplementary materials *Mendeleev Commun.*, 2018, **28**, 629–631

Ring-opened 4-hydroxy-δ-valerolactone subunit as a key structural fragment of polyesters that degrade without acid formation

Ilya E. Nifant'ev, Andrey V. Shlyakhtin, Vladimir V. Bagrov, Roman N. Ezhov, Boris A. Lozhkin, Andrei V. Churakov and Pavel V. Ivchenko

CONTENTS

General experimental remarks. Synthetic experiments were performed using standard laboratory equipment. Synthesis of BHT-Mg polymerization catalyst **2** and copolymerization were performed in argon atmosphere. L-glutamic acid, *D*-xylose, 3,4-dihydro-2*H*-pyran, BnBr, Me_2NH (33% aq.), NaH (60% suspension in mineral oil) were used as purchased (Aldrich). Diethyl ether, THF, benzene and toluene were refluxed with Na/benzophenone and distilled prior to use. Pentane and hexanes were refluxed over Na/K alloy for 12 hours, and then distilled. CH_2Cl_2 was washed with aqueous Na_2CO_3, stirred with $CaCl_2$ powder, refluxed over CaH_2 for 8 h and distilled. ε-Caprolactone was distilled under reduced pressure and stored under argon.

$CDCl_3$ (Cambridge Isotope Laboratories, Inc., D 99.8 %) was distilled over P_2O_5 and stored over 4 Å molecular sieves. DMSO-d_6 and acetone-d_6 (Cambridge Isotope Laboratories, Inc., D 99.5 %) were used as purchased. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks. Size exclusion chromatography (SEC) analysis of polymer samples was performed at 40 °C using Agilent PL-GPC 220 gel permeation chromatograph equipped with PLgel column, with THF as eluent (1 mL/min) and polystyrene standards. Elemental analysis (C, H, O) was made on a Perkin Elmer Series II CHNS/O Analyzer 2400.

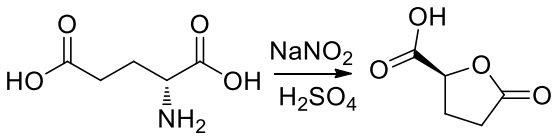
TBD and BHT–Mg catalyst $[(\mu\text{-}PhCH_2O)Mg(BHT)(THF)]_2$ were prepared according to previously reported procedures: I. Nifant'ev , A. Shlyakhtin, V. Bagrov, B. Lozhkin, G. Zakirova, P. Ivchenko and O. Legon'kova, *Reac. Kinet. Mech. Cat.,* 2016, **117**, 447; I.E. Nifant'ev, A.V. Shlyakhtin, V.V. Bagrov, M.E. Minyaev, A.V. Churakov, S.G. Karchevsky, K.P. Birin and P.V. Ivchenko, *Dalton Trans.*., 2017, **46**, 12132.

S2. Synthesis and characterization of comonomers 1a,b

S2.1. Preparation of (*R*)-4-benzyloxy-δ-valerolactone (1a)

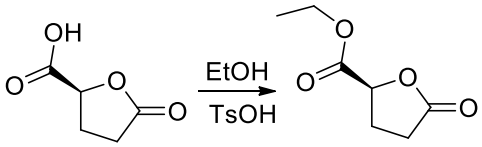
(*R*)-4-Benzyloxy-δ-valerolactone (IUPAC name: (*R*)-5-(benzyloxy)tetrahydro-2*H*-pyran-2-one) **1** was prepared in 8 stages from *L*-glutamic acid. The overall yield was 13.6%.

(*S*)-5-Oxotetrahydrofuran-2-carboxylic acid



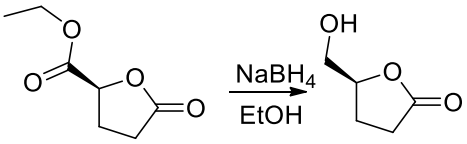
L-Glutamic acid (73.5 g, 0.5 mol) was suspended in water (500 mL). Solution of $NaNO_2$ (42 g, 0.6 mol) in water (300 mL) and 1*M* H_2SO_4 (300 mL) were added simultaneously within one hour. After 16 h of stirring, the water was evaporated at 40 °C under reduced pressure. A paste-like residue was extracted with boiling acetone (5×200 mL), the combined extracts were evaporated. The residue was used without porification.

Ethyl (*S*)-5-oxotetrahydrofuran-2-carboxylate



(*S*)-5-Oxotetrahydrofuran-2-carboxylic acid was dissolved in ethanol (130 mL) and benzene (250 mL), *p*-TsOH monohydrate (2 g) was added. The mixture was refluxed for 5 h. The solvents were removed under ambient pressure. Benzene (200 mL) was added, the solution was washed with water (150 mL), 10% aq. Na_2CO_3 (100 mL) and water (150 mL); dried over Na_2SO_4 and evaporated under reduced pressure. The product was separated by distillation *in vacuo*, the yield was 47.4 g (60%). ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz): δ 4.89 (m, 1H, H^2); 4.2 (qd, 2H, OCH_2CH_3); 2.20–2.60 (m, 4H, H^3 & H^4); 1.25 (t, 3H, OCH_2CH_3).

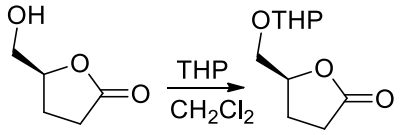
(*S*)-5-(Hydroxymethyl)dihydrofuran-2(3*H*)-one



Ethyl (*S*)-5-oxotetrahydrofuran-2-carboxylate (47.4 g, 0.3 mol) was added to the suspension of $NaBH_4$ (11.4 g, 0.3 mol) in EtOH (150 mL) keeping the temperature of the reaction mixture 20-

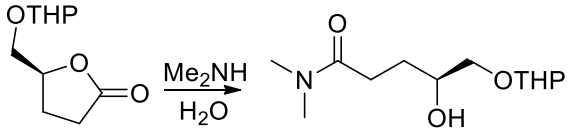
25 °C. After 1 hour of stirring, the mixture was poured into water (200 mL), EtOH was removed under reduced pressure. The aqueous solution was washed by AcOEt (3×150 mL) and evaporated under reduced pressure. A paste-like residue was extracted with acetone (5×100 mL), the combined extracts were dried over Na_2SO_4 and evaporated. The product was purified by column chromatography using EtOH/$CHCl_3$ 1:20 mixture (by volume) as eluent. The yield was 13.9 g (40%), viscous pale-yellow liquid. ^{1}H NMR (DMSO-d_6, 20 °C, 400 MHz): δ 4.59 (m, 1H); 3.85 (dd, 1H); 3.6 (dd, 1H); 2.98 (s, 1H, OH); 2.42–2.65 (m, 2H); 2.03-2.30 (m, 2H).

(5*S*)-5-[(Tetrahydropyran-2-yloxy)methyl]dihydrofuran-2(3*H*)-one



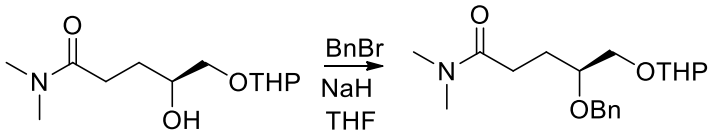
Pyridinium tosylate (PPTS, 1.27 g, 5 mmol) and 3,4-dihydro-2*H*-pyran (10.9 g, 0.13 mol) were added dropwise at 0 °C to the solution of (*S*)-5-(hydroxymethyl)dihydrofuran-2(3*H*)-one (13.9 g, 0.12 mol) in CH_2Cl_2 (250 mL). After 16 h of stirring at room temperature, the mixture was washed by satureted aq. $NaHCO_3$ (100 mL) and brine (100 mL). Organic phase was dried over Na_2SO_4, and evaporated under reduced pressure. The yield was 22.8 g (95%), viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz): δ 4.53–4.73 (m, 2H); 3.4–4.0 (m, 4H); 2.35–2.70 (m, 2H); 1.98–2.34 (m, 2H); 1.35–1.85 (m, 6H).

(4*S*)-4-Hydroxy-*N*,*N*-dimethyl-5-(tetrahydropyran-2-yloxy)pentanamide



Dimethylamine (33% aq., 51.3 g, 1.1 mol) was added to a solution of (5*S*)-5-[(tetrahydropyran-2-yloxy)methyl]dihydrofuran-2(3*H*)-one (22.8 g, 0.11 mol) in THF (80 mL). After 16 h of stirring at room temperature, the mixture was evaporated under reduced pressure. The yield was 25.6 g (95%), viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz): δ 4.57 (m, 1H); 3.37–3.95 (m, 5H); 3.02 (s, 3H, N–Me); 2.94 (s, 3H, N–Me), 2.51 (t, 2H); 1.45–1.95 (m, 8H).

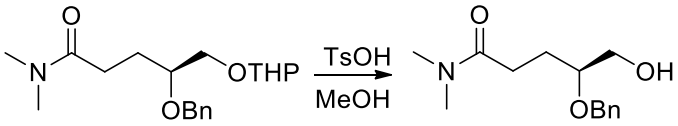
(4*S*)-4-Benzyloxy-*N*,*N*-dimethyl-5-(tetrahydropyran-2-yloxy)pentanamide



The product of the previous stage (25.6 g, 0.1 mol) in THF (50 mL) was added dropwise to a suspension of NaH (2.64 g of 60% suspension in mineral oil, 0.11 mol) in THF (200 mL) at 0 °C.

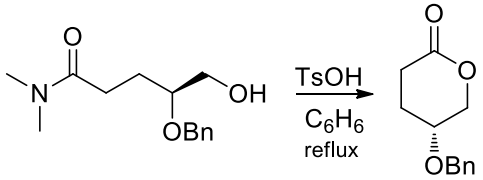
After the end of hydrogen evolution, BnBr (17.1 g, 0.1 mol) was added. After 16 h of stirring at room temperature, the mixture was poured into saturated aq. NH_4Cl (250 mL). The solution was extracted with ether (2×200 mL), the combined organic phase was washed with water (2×200 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The yield was 30.1 g (90%), viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz): δ 7.25–7.4 (m, 5H, arom.); 4.75 (dd, 1H); 4.57 (dd, 1H); 4.65 (m, 1H); 3.45–3.95 (m, 5H); 2.94 (d, 6H, $N(Me)_2$); 2.27–2.50 (m, 2H); 1.45–2.05 (m, 8H).

(*S*)-4-Benzyloxy-5-hydroxy-*N*,*N*-dimethylpentanamide



The product of the previous stage (30.1 g, 0.09 mol) was dissolved in MeOH (150 mL), TsOH (1.55 g, 10% mol) was added. After 16 h at room temperature, the solution was evaporated under reduced pressure, and the residue was dried *in vacuo* with stirring. The yield was ~90% (NMR), viscous yellow liquid. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz): δ 7.25–7.4 (m, 5H, arom.); 4.58 (q, 2H); 3.63 (m, 3H); 2.97 (br.s, 6H, $N(Me)_2$); 2.37–2.57 (m, 2H); 1.97–2.05 (m, 2H).

(*R*)-5-(Benzyloxy)tetrahydro-2*H*-pyran-2-one



The product of the previous stage (20.3 g, 0.08 mol) was dissolved in benzene (120 mL), *p*-TsOH (13.7 g, 0.08 mol) was added. The mixture was refluxed for 3 h, cooled, washed with saturated aq. $NaHCO_3$ (2×100 mL) and water (2×100 mL). The organic phase was dried over Na_2SO_4, and evaporated under reduced pressure. The product was purified by column chromatography (hexane/AcOEt 2:1 by volume as an eluent) and recrystallized from hexane/AcOEt 1:1. The yield was 11.5 g (70%), colorless crystals. Calculated for $C_{12}H_{14}O_3$, %: C, 69.88; H, 6.84; O, 23.27. Found, %: C, 69.80; H, 6.89; O, 23.31. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 7.25-7.4 (m, 5H, arom.), 4.57 (s, 2H, OCH_2Ph), 4.38-4.48 (m, 1H, **1**), 4.29 (dd, 1H, **1**, ^1J = 12.13 Гц, ^2J = 3.03 Гц), 3.82 (quin, 1H, C*H*-OCH_2Ph, ^1J = 3.85 Гц) ,2.67-2.83 (m, 1H, **3**), 2.45-2.57 (m, 1H, **3**), 1.97-2.17 (m, 2H, **2**). ^{13}C NMR ($CDCl_3$, 101 MHz, 20 °C); δ 170.65; 137.63; 128.65; 128.48; 128.05; 127.93; 127.67; 70.80; 70.59; 69.11; 26.39, 24.71.

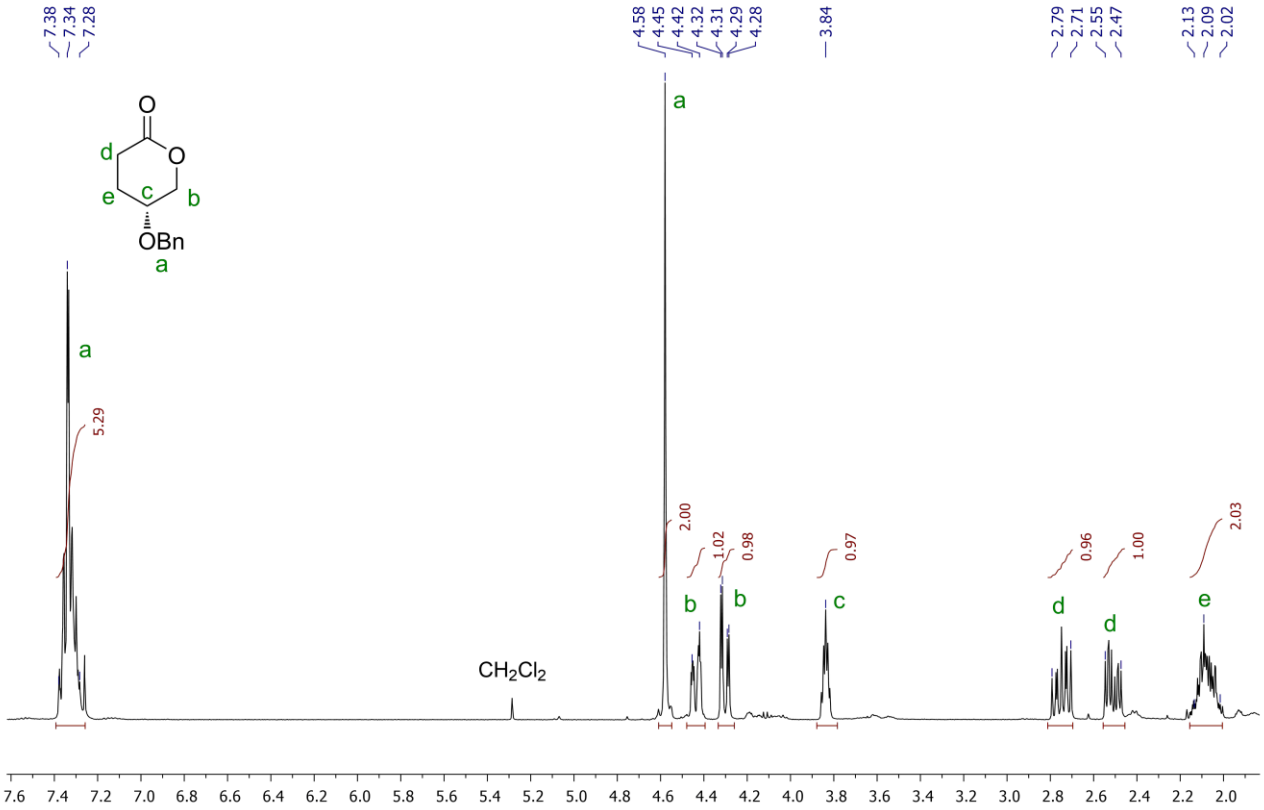


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 20 °C) of **1a**

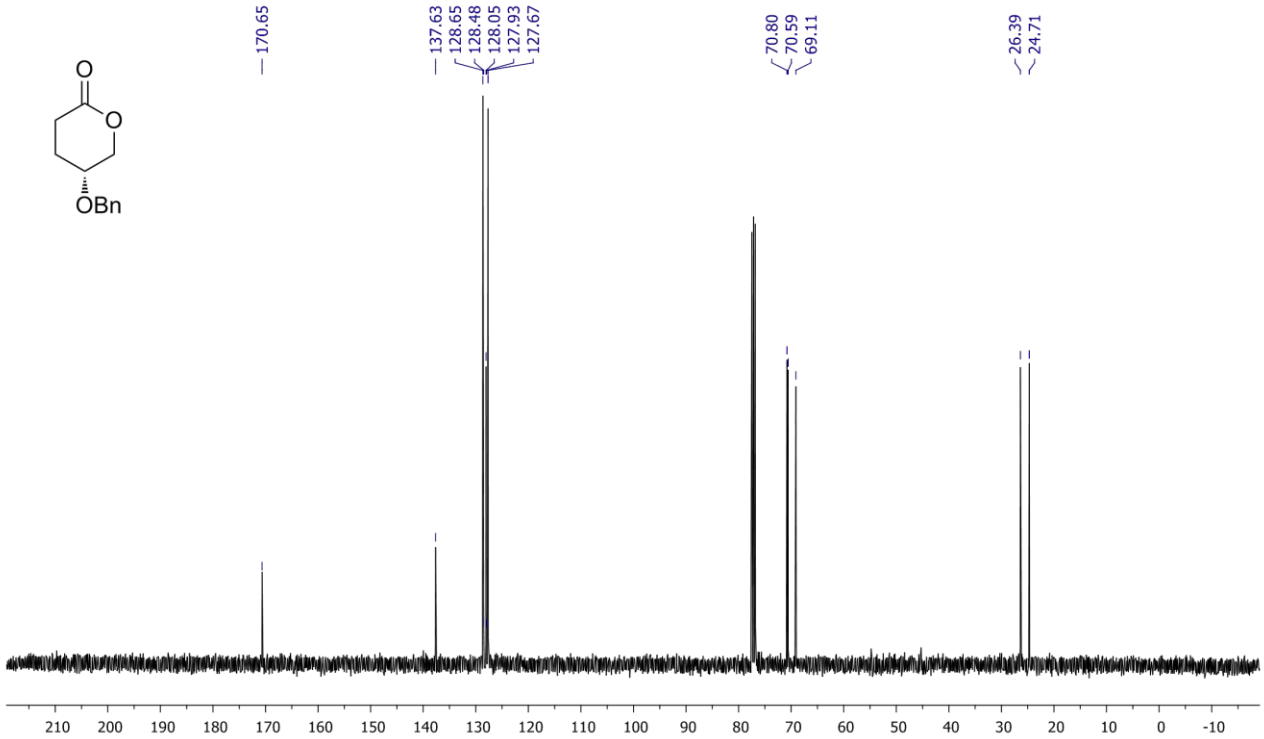
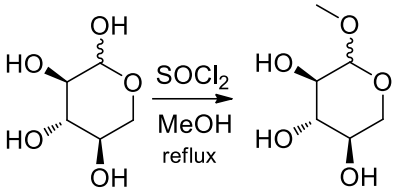


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz, 20 °C) of **1a**

S2.2. Preparation of (2*R*,4*S*)-2,4-bis(benzyloxy)-δ-valerolactone (1b)

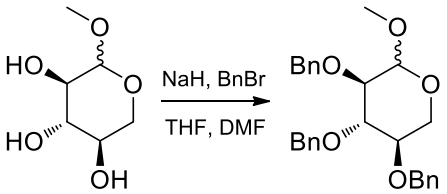
(2*R*,4*S*)-2,4-Bis(benzyloxy)-δ-valerolactone (IUPAC name: (3*R*,5*S*)-3,5-bis(benzyloxy)tetrahydro-2*H*-pyran-2-one) **1b** was prepared in 6 stages from *L*-glutamic acid. The overall yield was 36%.

(3*R*,4*S*,5*R*)-2-Methoxytetrahydro-2*H*-pyran-3,4,5-triol



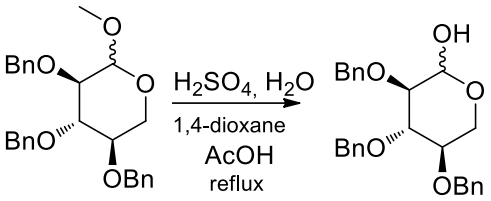
1% HCl solution in MeOH was prepared by slow addition of $SOCl_2$ (5 mL, 69 mmol) to MeOH (250 mL) at 0 °C. *D*-Xylose (25.0 g, 0.17 mol) was added, the mixture was refluxed for 4 h, cooled, neutralized with $NaHCO_3$ (17.5 g, 0.21 mol) and evaporated under reduced pressure. The residue was dissolved in EtOH (200 mL), the solution was evaporated to one half of the initial volume, toluene (100 mL) was added, and evaporated to dryness. The residue was used in next stage of the synthesis without purification.

(3*R*,4*S*,5*R*)-3,4,5-Tris(benzyloxy)-2-methoxytetrahydro-2*H*-pyran



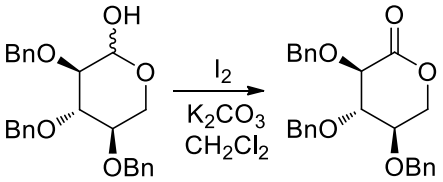
The solution of the product obtained above in DMF (500 mL) was added within 2 h to ice-cooled suspension of NaH (60% in mineral oil, 34 g, 0.85 mol) in THF (100 mL). After 1 h at the end of addition, BnBr (74 mL, 0.61 mol) was added. After 16 h of stirring at room temperature, the mixture was treated with 10% NH_4Cl (150 mL), diluted by water (2 L) and extracted with AcOEt (3×200 mL). The combined organic phase was washed with water, brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue (74 g) was used in next stage of the synthesis without purification.

(3*R*,4*S*,5*R*)-3,4,5-Tris(benzyloxy)tetrahydro-2*H*-pyran-2-ol



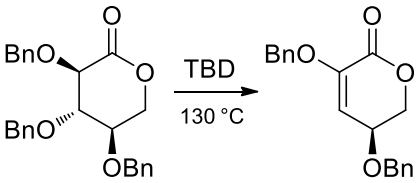
The product of the previous stage was dissolved in the mixture of 1*M* H_2SO_4 (210 mL), AcOH (240 mL) and 1,4-dioxane (220 mL). The mixture was refluxed for 10 h, cooled, then water (800 mL) and hexane (100 mL) were added. The mixture was stirred for 10 min, the precipitate was filtered off and washed with hexane (200 mL). The product was recrystallized from MeOH. The yield was 51.1 g (71%), beige crystalline powder. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 7.27-7.38 (m, 15H, arom.), 5.11 (m, 1H); 4.64–4.88 (m, 6H); 3.50–3.87 (m, 5H).

(3*R*,4*S*,5*R*)-3,4,5-Tris(benzyloxy)tetrahydro-2*H*-pyran-2-one



(3*R*,4*S*,5*R*)-3,4,5-Tris(benzyloxy)tetrahydro-2*H*-pyran-2-ol (51 g, 0.12 mol) was dissolved in CH_2Cl_2 (500 mL). K_2CO_3 (49.8 g, 0.36 mol) and I_2 (91.4 g; 0.36 mol) were added. After 16 h of stirring, the mixture was treated with 10% $Na_2S_2O_3$. The organic phase was separated, the aqueous phase was extracted with CH_2Cl_2 (3×200 mL). The combined organic fraction was dried over Na_2SO_4 and evaporated under reduced pressure. The product was recrystallized from MeOH. The yield was 35.1 g (70%), colorless crystalline powder. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 7.25-7.53 (m, 15H, arom.); 5.07 (d, 1H); 4.7 (d, 2H, OCH_2Ph); 4.58 (q, 2H, OCH_2Ph); 4.63 (d, 1H, OCH_2Ph); 4.40–4.47 (m, 1H); 4.29–4.36 (m, 1H); 4.18 (d, 1H, OCH_2Ph); 3.94 (m, 1H); 3.82 (m, 1H).

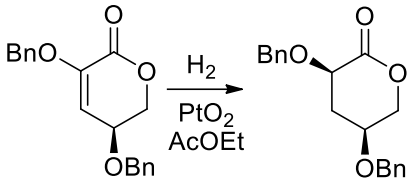
(*S*)-3,5-Bis(benzyloxy)-5,6-dihydro-2*H*-pyran-2-one



The mixture of (3*R*,4*S*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-one (27 g, 65 mmol) and TBD (0.45 g, 3.2 mmol, 5% mol) was heated at 130 °C for 3 h under argon. After cooling, CH_2Cl_2 (50 mL) was added, the mixture was washed with aq. AcOH. The organic phase was separated, evaporated under reduced pressure, the product was purified using column

chromatography (benzene/AcOEt 10:1 as an eluent). The yield was 19.2 g (95%), pale yellow waste. Calculated for $C_{19}H_{18}O_4$, %: C, 73.53; H, 5.85; O, 20.62. Found, %: C, 73.56; H, 5.71; O, 20.73. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 7.27-7.46 (m, 15H, arom.); 5.78 (m, 1H, CH); 4.94 (s, 2H, OCH_2Ph); 4.50–4.59 (m, 1H, CH-OBn); 4.54 (s, 2H, OCH_2Ph); 4.36–4.44 (m, 1H, CH_2O); 4.19–4.27 (m, 1H, CH_2O).

(3*R*,5*S*)-3,5-Bis(benzyloxy)tetrahydro-2*H*-pyran-2-one



(*S*)-3,5-Bis(benzyloxy)-5,6-dihydro-2*H*-pyran-2-one (5 g, 16 mmol) was dissolved in MeOH (50 mL), PtO_2 (5 mol%) was added. Hydrogen gas was bubbled through the vigorously stirred solution for 3 h. The solution was passed through celite and evaporated. The product was recrystallized from MeOH. The yield was 3.85 g (77%), colorless crystals. Calculated for $C_{19}H_{20}O_4$, %: C, 73.06; H, 6.45; O, 20.49. Found, %: C, 73.15; H, 6.50; O, 20.35. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 7.25-7.45 (m, 10H, arom. H); 4.98 (d, 1H, ^1J = 11.7 Hz); 4.63 (d, 1H, ^1J = 11.7 Hz); 4.53 (m, 2H); 4.43 (dd, 1H, ^1J = 12.2 Hz, ^2J = 2.5 Hz); 4.14 (dd, 1H, ^1J = 12.2 Hz, ^2J = 2.9 Hz); 4.01 (dd, 1H, ^2J = 10.3 Hz, ^2J = 8.3 Hz); 3.91 (m, 1H); 2.60–2.67 (m, 1H); 2.06 (m, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz, 20 °C): δ 171.45; 137.41; 137.37; 128.62; 128.09; 128.04; 127.75; 72.51; 70.62; 70.35; 69.70; 68.58; 33.53.

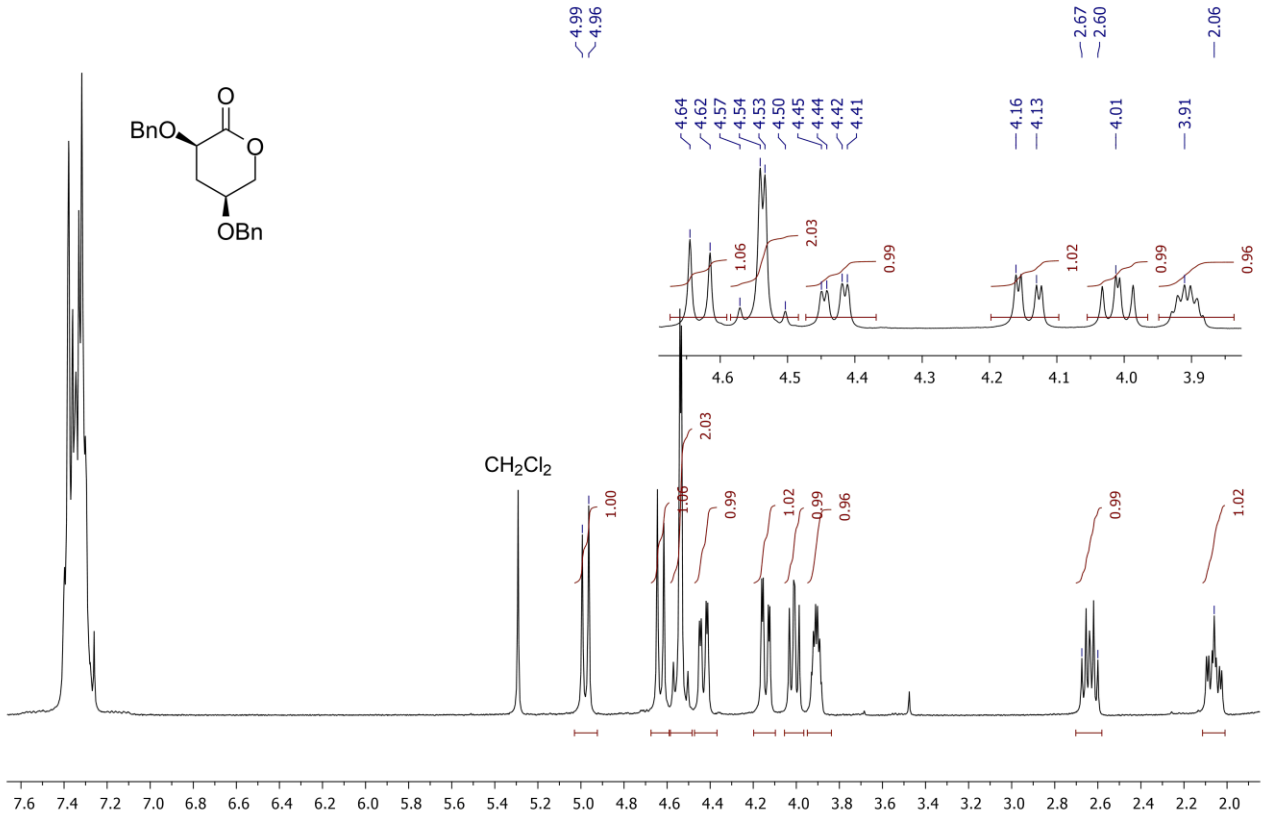


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 20 °C) of **1b**

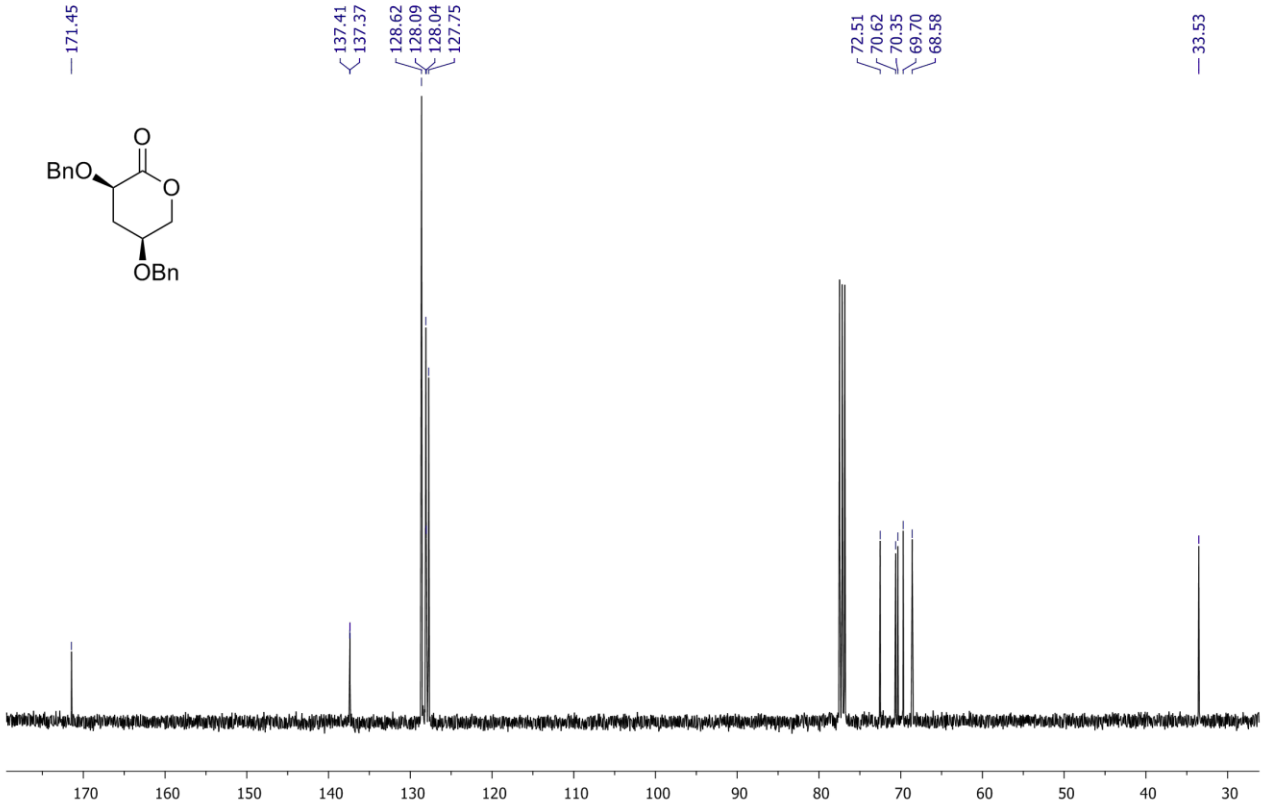


Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz, 20 °C) of **1b**

S3. X-ray analysis of 1b

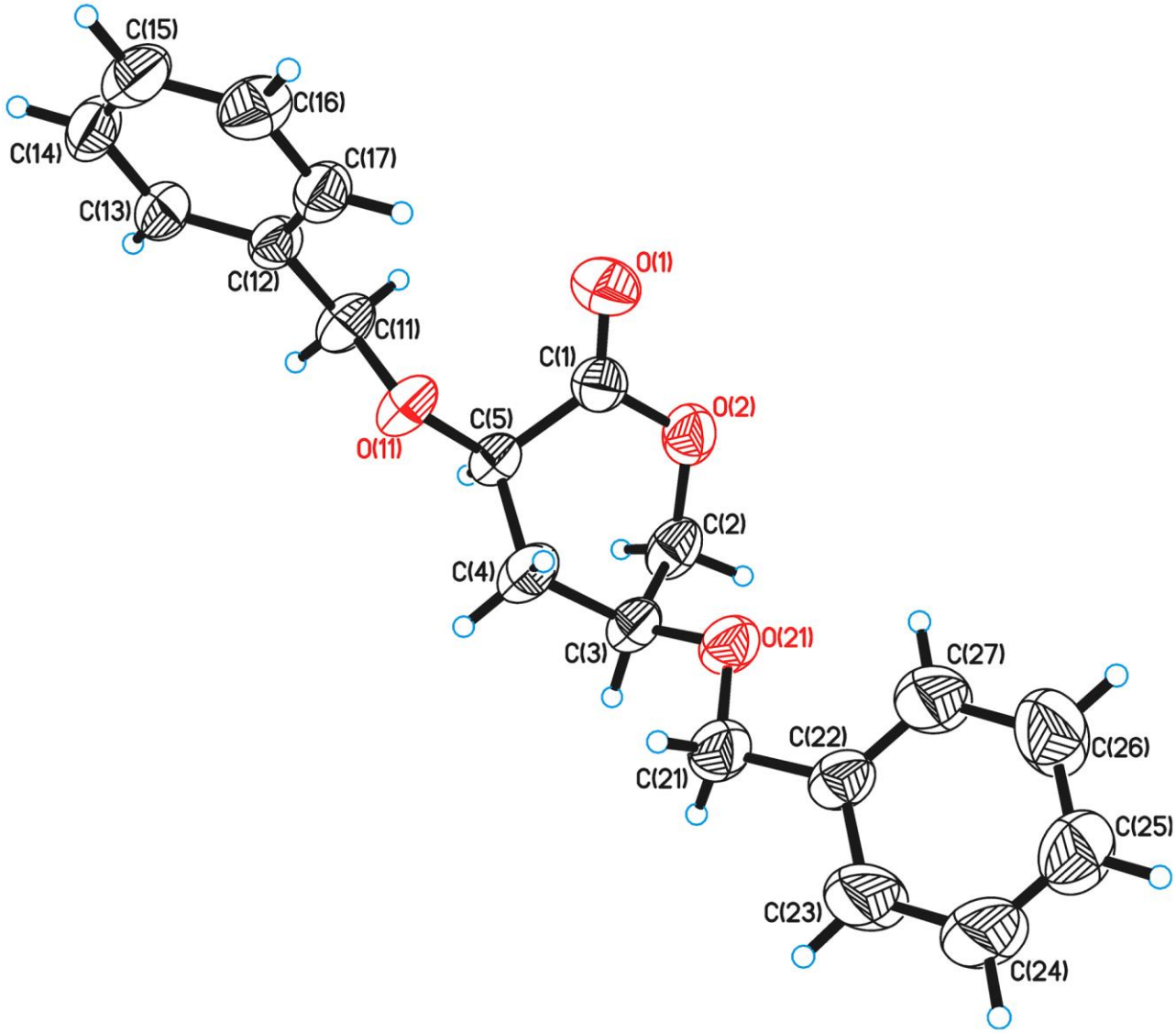


Figure S5. Molecular structure of **1b**

Table S1. Crystal data, data colection, structure solution and refinement parameters for **1b**

Empirical formula	C19H20O4
Formula weight	312.35
Color, habit	colourless prism
Crystal size, mm	0.60 × 0.40 × 0.40
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions:	
a, A	11.153(4)
b, A	5.579(2)
c, A	13.192(3)
alpha, deg	90
beta, deg	92.63(2)
gamma, deg	90
Volume, A^3	820.0(5)
Z	2
Calculated density, g cm^{-3}	1.265
Absorption coefficient, mm^{-1}	0.716
F(000)	332
Diffractometer	Enraf-Nonius CAD4
Temperature, K	295(2)
Radiation, (λ, Å)	graphite monochromatized CuK\a (1.54178)
Scan mode	ω
Scan width, deg	1.0 + 0.15tan(theta)
Scan rate, deg min^{-1}	variable
θ range, deg	3.35 to 75.03
Limiting indices	-13<=h<=13, -6<=k<=6, -16<=l<=16
Reflections collected / unique	6462 / 3351 [R(int) = 0.0290]
Completeness to θ	75.03 99.8 %
Reflections with I>2σ(I)	3186
Absorption correction	Semi-empirical from equivalents
Min. and Max. transmission	0.6731 and 0.7626
Solution method	Direct methods[1]
Refinement method	Full-matrix least-squares[2] on F^2
Hydrogen treatment	All H atoms were placed in calc. positions and refined using a riding model
Data / restraints / parameters	3351 / 1 / 209
Goodness-of-fit on F^2	1.050
Final R indices [I>2 σ (I)]	R_1 = 0.0401, wR_2 = 0.1078
R indices (all data)	R_1 = 0.0418, wR_2 = 0.1100
Absolute structure parameter	0.04(18)
Extinction coefficient	0.0184(17)
Largest diff. peak and hole, e/A^3	0.166 and -0.164

[1] G.M.Sheldrick, *Acta Cryst.*, 1990, **A46**, 467 (SHELXS-97)
[2] SHELXL-97, Program for the Refinement of Crystal Structures. University of Gottingen, 1997

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **1b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
O(1)	2868(2)	6511(2)	927(2)	94(1)	C(14)	-2587(2)	6661(4)	1443(1)	70(1)
O(2)	4308(1)	3820(3)	891(1)	67(1)	C(15)	-2276(2)	8644(4)	1994(1)	74(1)
O(11)	1331(1)	3510(2)	1859(1)	61(1)	C(16)	-1082(2)	9116(3)	2256(2)	73(1)
O(21)	5262(1)	1879(2)	2829(1)	64(1)	C(17)	-208(1)	7558(3)	1953(1)	62(1)
C(1)	3182(2)	4500(3)	1091(1)	58(1)	C(21)	5421(2)	835(4)	3803(1)	73(1)
C(2)	4618(2)	1365(4)	1122(1)	64(1)	C(22)	6539(2)	1864(3)	4329(1)	64(1)
C(3)	4374(1)	728(3)	2200(1)	57(1)	C(23)	7037(3)	743(6)	5168(2)	130(1)
C(4)	3094(2)	1455(4)	2446(1)	70(1)	C(24)	8074(3)	1596(7)	5662(2)	127(1)
C(5)	2415(1)	2569(3)	1539(1)	49(1)	C(25)	8626(2)	3448(6)	5327(2)	99(1)
C(11)	451(1)	3875(3)	1050(1)	60(1)	C(26)	8161(3)	4593(7)	4483(2)	123(1)
C(12)	-501(1)	5531(3)	1403(1)	52(1)	C(27)	7103(2)	3785(5)	3992(2)	96(1)
C(13)	-1707(1)	5077(3)	1150(1)	60(1)					

Table S3. Bond lengths [Å] for **1b**

O(1)-C(1)	1.192(2)	C(4)-H(4B)	0.9700	C(17)-H(17)	0.9300
O(2)-C(1)	1.349(2)	C(5)-H(5)	0.9800	C(21)-C(22)	1.512(3)
O(2)-C(2)	1.442(2)	C(11)-C(12)	1.498(2)	C(21)-H(21A)	0.9700
O(11)-C(5)	1.4004(17)	C(11)-H(11A)	0.9700	C(21)-H(21B)	0.9700
O(11)-C(11)	1.4316(17)	C(11)-H(11B)	0.9700	C(22)-C(27)	1.330(3)
O(21)-C(21)	1.4148(19)	C(12)-C(17)	1.375(2)	C(22)-C(23)	1.367(3)
O(21)-C(3)	1.416(2)	C(12)-C(13)	1.393(2)	C(23)-C(24)	1.385(4)
C(1)-C(5)	1.512(2)	C(13)-C(14)	1.389(3)	C(23)-H(23)	0.9300
C(2)-C(3)	1.503(2)	C(13)-H(13)	0.9300	C(24)-C(25)	1.291(4)
C(2)-H(2A)	0.9700	C(14)-C(15)	1.360(3)	C(24)-H(24)	0.9300
C(2)-H(2B)	0.9700	C(14)-H(14)	0.9300	C(25)-C(26)	1.366(4)
C(3)-C(4)	1.533(2)	C(15)-C(16)	1.385(3)	C(25)-H(25)	0.9300
C(3)-H(3)	0.9800	C(15)-H(15)	0.9300	C(26)-C(27)	1.394(4)
C(4)-C(5)	1.5200(19)	C(16)-C(17)	1.380(2)	C(26)-H(26)	0.9300
C(4)-H(4A)	0.9700	C(16)-H(16)	0.9300	C(27)-H(27)	0.9300

Table S4. Bond angles [°] for **1b**

C(1)-O(2)-C(2)	116.27(13)	C(14)-C(13)-C(12)	120.29(16)
C(5)-O(11)-C(11)	113.60(11)	C(14)-C(13)-H(13)	119.9
C(21)-O(21)-C(3)	113.58(14)	C(12)-C(13)-H(13)	119.9
O(1)-C(1)-O(2)	119.82(17)	C(15)-C(14)-C(13)	119.99(16)
O(1)-C(1)-C(5)	125.08(17)	C(15)-C(14)-H(14)	120.0
O(2)-C(1)-C(5)	115.09(13)	C(13)-C(14)-H(14)	120.0
O(2)-C(2)-C(3)	111.84(14)	C(14)-C(15)-C(16)	120.47(16)
O(2)-C(2)-H(2A)	109.2	C(14)-C(15)-H(15)	119.8
C(3)-C(2)-H(2A)	109.2	C(16)-C(15)-H(15)	119.8
O(2)-C(2)-H(2B)	109.2	C(17)-C(16)-C(15)	119.46(17)
C(3)-C(2)-H(2B)	109.2	C(17)-C(16)-H(16)	120.3
H(2A)-C(2)-H(2B)	107.9	C(15)-C(16)-H(16)	120.3
O(21)-C(3)-C(2)	107.17(14)	C(12)-C(17)-C(16)	121.11(16)
O(21)-C(3)-C(4)	112.86(14)	C(12)-C(17)-H(17)	119.4
C(2)-C(3)-C(4)	110.40(13)	C(16)-C(17)-H(17)	119.4
O(21)-C(3)-H(3)	108.8	O(21)-C(21)-C(22)	109.04(15)

C(2)-C(3)-H(3)	108.8	O(21)-C(21)-H(21A)	109.9
C(4)-C(3)-H(3)	108.8	C(22)-C(21)-H(21A)	109.9
C(5)-C(4)-C(3)	112.14(12)	O(21)-C(21)-H(21B)	109.9
C(5)-C(4)-H(4A)	109.2	C(22)-C(21)-H(21B)	109.9
C(3)-C(4)-H(4A)	109.2	H(21A)-C(21)-H(21B)	108.3
C(5)-C(4)-H(4B)	109.2	C(27)-C(22)-C(23)	117.3(2)
C(3)-C(4)-H(4B)	109.2	C(27)-C(22)-C(21)	123.07(15)
H(4A)-C(4)-H(4B)	107.9	C(23)-C(22)-C(21)	119.61(19)
O(11)-C(5)-C(1)	111.24(12)	C(22)-C(23)-C(24)	121.6(3)
O(11)-C(5)-C(4)	108.78(11)	C(22)-C(23)-H(23)	119.2
C(1)-C(5)-C(4)	109.19(13)	C(24)-C(23)-H(23)	119.2
O(11)-C(5)-H(5)	109.2	C(25)-C(24)-C(23)	120.9(2)
C(1)-C(5)-H(5)	109.2	C(25)-C(24)-H(24)	119.5
C(4)-C(5)-H(5)	109.2	C(23)-C(24)-H(24)	119.5
O(11)-C(11)-C(12)	109.13(12)	C(24)-C(25)-C(26)	119.0(2)
O(11)-C(11)-H(11A)	109.9	C(24)-C(25)-H(25)	120.5
C(12)-C(11)-H(11A)	109.9	C(26)-C(25)-H(25)	120.5
O(11)-C(11)-H(11B)	109.9	C(25)-C(26)-C(27)	120.6(3)
C(12)-C(11)-H(11B)	109.9	C(25)-C(26)-H(26)	119.7
H(11A)-C(11)-H(11B)	108.3	C(27)-C(26)-H(26)	119.7
C(17)-C(12)-C(13)	118.66(15)	C(22)-C(27)-C(26)	120.6(2)
C(17)-C(12)-C(11)	121.07(14)	C(22)-C(27)-H(27)	119.7
C(13)-C(12)-C(11)	120.24(15)	C(26)-C(27)-H(27)	119.7

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + ... + 2 hkab U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	91(1)	56(1)	132(1)	15(1)	-11(1)	-3(1)
O(2)	54(1)	86(1)	60(1)	12(1)	4(1)	-5(1)
O(11)	47(1)	87(1)	48(1)	-4(1)	-4(1)	20(1)
O(21)	58(1)	78(1)	54(1)	7(1)	-6(1)	4(1)
C(1)	58(1)	56(1)	60(1)	1(1)	-5(1)	-2(1)
C(2)	49(1)	87(1)	56(1)	-6(1)	5(1)	12(1)
C(3)	45(1)	68(1)	58(1)	2(1)	-1(1)	10(1)
C(4)	49(1)	109(1)	54(1)	20(1)	5(1)	20(1)
C(5)	43(1)	58(1)	47(1)	-2(1)	1(1)	8(1)
C(11)	50(1)	76(1)	53(1)	-5(1)	-10(1)	11(1)
C(12)	45(1)	61(1)	50(1)	6(1)	-4(1)	5(1)
C(13)	48(1)	68(1)	63(1)	5(1)	-8(1)	0(1)
C(14)	43(1)	93(1)	74(1)	13(1)	-1(1)	7(1)
C(15)	61(1)	86(1)	74(1)	8(1)	5(1)	26(1)
C(16)	75(1)	65(1)	77(1)	-8(1)	-6(1)	14(1)
C(17)	49(1)	63(1)	73(1)	-2(1)	-6(1)	2(1)
C(21)	61(1)	96(1)	60(1)	17(1)	-5(1)	-1(1)
C(22)	62(1)	79(1)	51(1)	6(1)	-1(1)	10(1)
C(23)	150(3)	129(2)	105(2)	60(2)	-69(2)	-55(2)
C(24)	140(3)	127(2)	107(2)	38(2)	-71(2)	-29(2)
C(25)	95(2)	119(2)	81(1)	-5(1)	-23(1)	-14(2)
C(26)	130(2)	142(3)	95(2)	28(2)	-29(2)	-59(2)
C(27)	108(2)	102(2)	75(1)	23(1)	-25(1)	-15(1)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1b**

	x	y	z	U(eq)
H(2A)	5462	1115	1009	77
H(2B)	4158	312	666	77
H(3)	4458	-1010	2285	69
H(4A)	2663	51	2665	85
H(4B)	3129	2594	3002	85
H(5)	2243	1329	1026	59
H(11A)	95	2353	846	72
H(11B)	827	4564	468	72
H(13)	-1923	3707	784	72
H(14)	-3389	6365	1263	84
H(15)	-2868	9690	2196	88
H(16)	-872	10473	2633	87
H(17)	594	7883	2124	74
H(21A)	5499	-890	3741	87
H(21B)	4728	1171	4199	87
H(23)	6672	-624	5413	156
H(24)	8377	824	6244	153
H(25)	9330	3993	5655	119
H(26)	8553	5924	4233	148
H(27)	6790	4596	3423	115

Table S7. Torsion angles [deg] for **1b**

C(2)-O(2)-C(1)-O(1)	179.30(17)	C(17)-C(12)-C(13)-C(14)	0.6(2)
C(2)-O(2)-C(1)-C(5)	0.58(18)	C(11)-C(12)-C(13)-C(14)	-177.47(15)
C(1)-O(2)-C(2)-C(3)	-53.68(18)	C(12)-C(13)-C(14)-C(15)	-1.2(3)
C(21)-O(21)-C(3)-C(2)	-159.19(15)	C(13)-C(14)-C(15)-C(16)	0.8(3)
C(21)-O(21)-C(3)-C(4)	79.06(18)	C(14)-C(15)-C(16)-C(17)	0.1(3)
O(2)-C(2)-C(3)-O(21)	-72.76(16)	C(13)-C(12)-C(17)-C(16)	0.2(2)
O(2)-C(2)-C(3)-C(4)	50.5(2)	C(11)-C(12)-C(17)-C(16)	178.32(16)
O(21)-C(3)-C(4)-C(5)	120.97(16)	C(15)-C(16)-C(17)-C(12)	-0.6(3)
C(2)-C(3)-C(4)-C(5)	1.1(2)	C(3)-O(21)-C(21)-C(22)	168.88(14)
C(11)-O(11)-C(5)-C(1)	79.39(16)	O(21)-C(21)-C(22)-C(27)	12.7(3)
C(11)-O(11)-C(5)-C(4)	-160.30(15)	O(21)-C(21)-C(22)-C(23)	-164.5(3)
O(1)-C(1)-C(5)-O(11)	-7.4(2)	C(27)-C(22)-C(23)-C(24)	1.3(5)
O(2)-C(1)-C(5)-O(11)	171.27(12)	C(21)-C(22)-C(23)-C(24)	178.7(3)
O(1)-C(1)-C(5)-C(4)	-127.45(19)	C(22)-C(23)-C(24)-C(25)	-2.1(7)
O(2)-C(1)-C(5)-C(4)	51.20(17)	C(23)-C(24)-C(25)-C(26)	1.2(6)
C(3)-C(4)-C(5)-O(11)	-171.17(16)	C(24)-C(25)-C(26)-C(27)	0.3(6)
C(3)-C(4)-C(5)-C(1)	-49.6(2)	C(23)-C(22)-C(27)-C(26)	0.1(4)
C(5)-O(11)-C(11)-C(12)	-162.94(14)	C(21)-C(22)-C(27)-C(26)	-177.2(3)
O(11)-C(11)-C(12)-C(17)	43.7(2)	C(25)-C(26)-C(27)-C(22)	-0.9(5)
O(11)-C(11)-C(12)-C(13)	-138.20(15)		

S4. Copolymerization experiments and copolymer characteristics

S4.1. Copolymerization procedure

Copolymer 3a (run 2, Table 1, main text). A preheated glass ampoule was equipped with a magnetic stir bar and a septum and then filled with dry argon. Catalyst **2** (0.0773 mmol) in toluene (1 mL) was added to cooled to 0 °C solution containing **1a** (75.6 mg, 0.367 mmol), εCL (795 mg, 6.96 mmol) THF (2.4 ml) and toluene (2.7 ml). After 1 hour of stirring, a 5-fold excess of acetic acid was injected into the ampoule to neutralize the catalyst and stop the process. The monomer conversion was determined using ^{1}H NMR spectroscopy by integration of the monomer $CH_2OC=O$ (δ = 4.20 ppm) and polymer $CH_2OC=O$ (δ = 4.05 ppm) resonance signals. The polymer was precipitated from the resulting solution with a 10-fold volume excess of diethyl ether. The polymer was filtered, washed with diethyl ether and dried under vacuum.

For run 4 (Table 1, main text), reagent and solvent loading: **2** (0.0773 mmol), **1b** (114 mg, 0.367 mmol), εCL, (795 mg, 6.96 mmol), THF (2.3 ml), toluene (3.67 ml).

Copolymer 3b (run 3, Table 1, main text), reagent and solvent loading: **2** (0.0773 mmol), **1b** (151 mg, 0.733 mmol), εCL (730 mg, 6.6 mmol), THF (2.4 ml), toluene (3.67 ml).

For run 5 (Table 1, main text), reagent and solvent loading: **2** (0.0773 mmol), **1b** (229 mg, 0.733 mmol), εCL (730 mg, 6.6 mmol), THF (2.3 ml), toluene (3.67 ml).

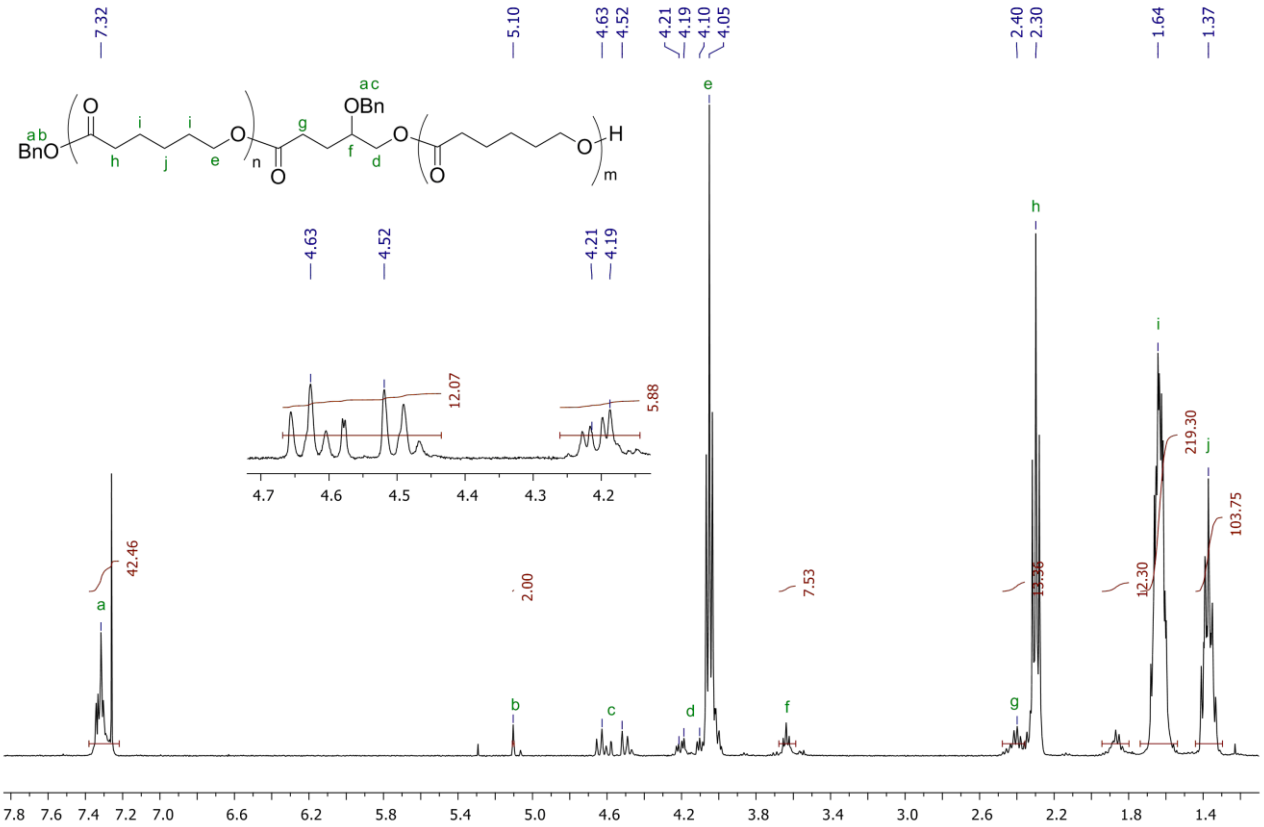


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 20 °C) of copolymer **3a** (45:5, Table 1, run 1)

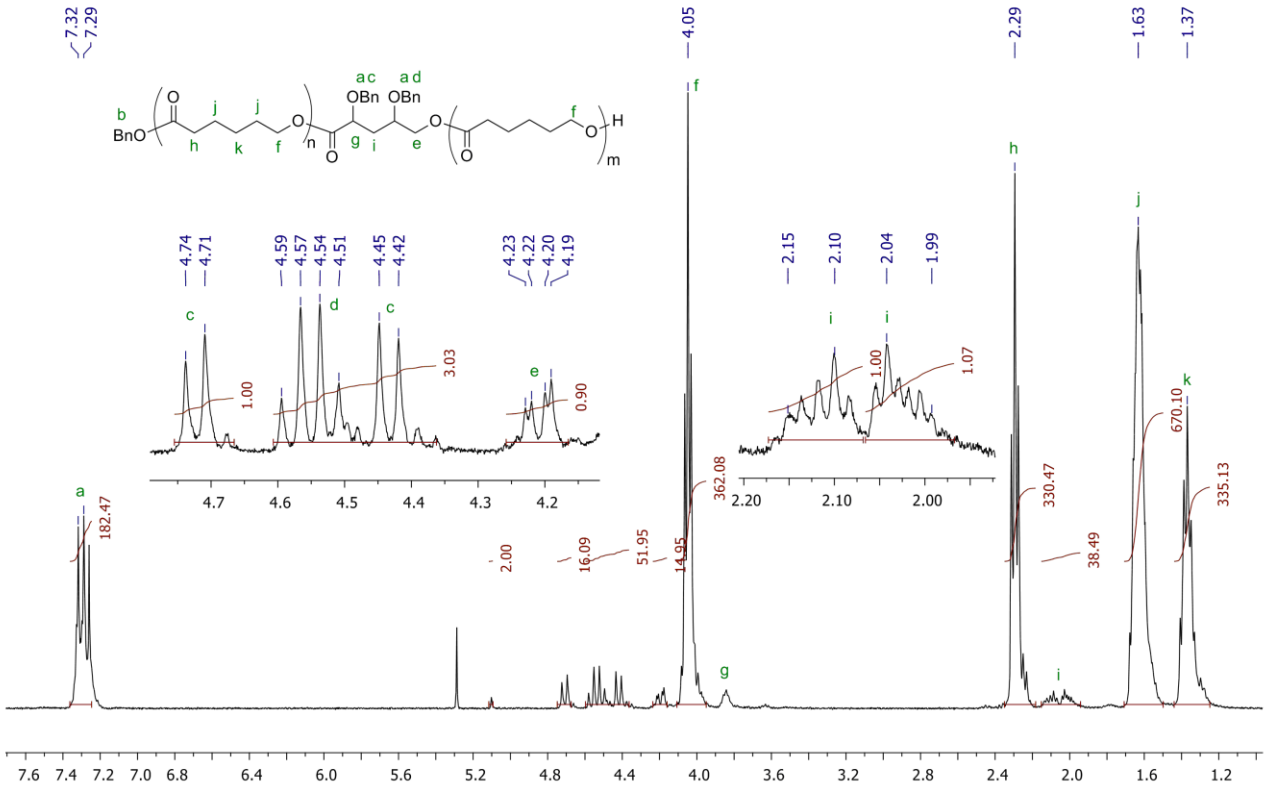


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 20 °C) of copolymer **3b** (90:10, Table 1, run 3)

S4.3. Debenzylation. Polymer **3** sample (~1 g) was placed into two-necked flack equipped with magnetic stirring bar and glass capillary inlet. THF (10 mL) and 5% Pd/C (100 mg) were added. Hydrogen was bubbled through the stirred reaction mixture within 6 h. The mixture was filtered through celite, and evaporated under reduced pressure yielding the product. This product was washed with Et_2O and dried *in vacuo*. The typical yield was ~95%.

Representative examples of NMR spectra are given below

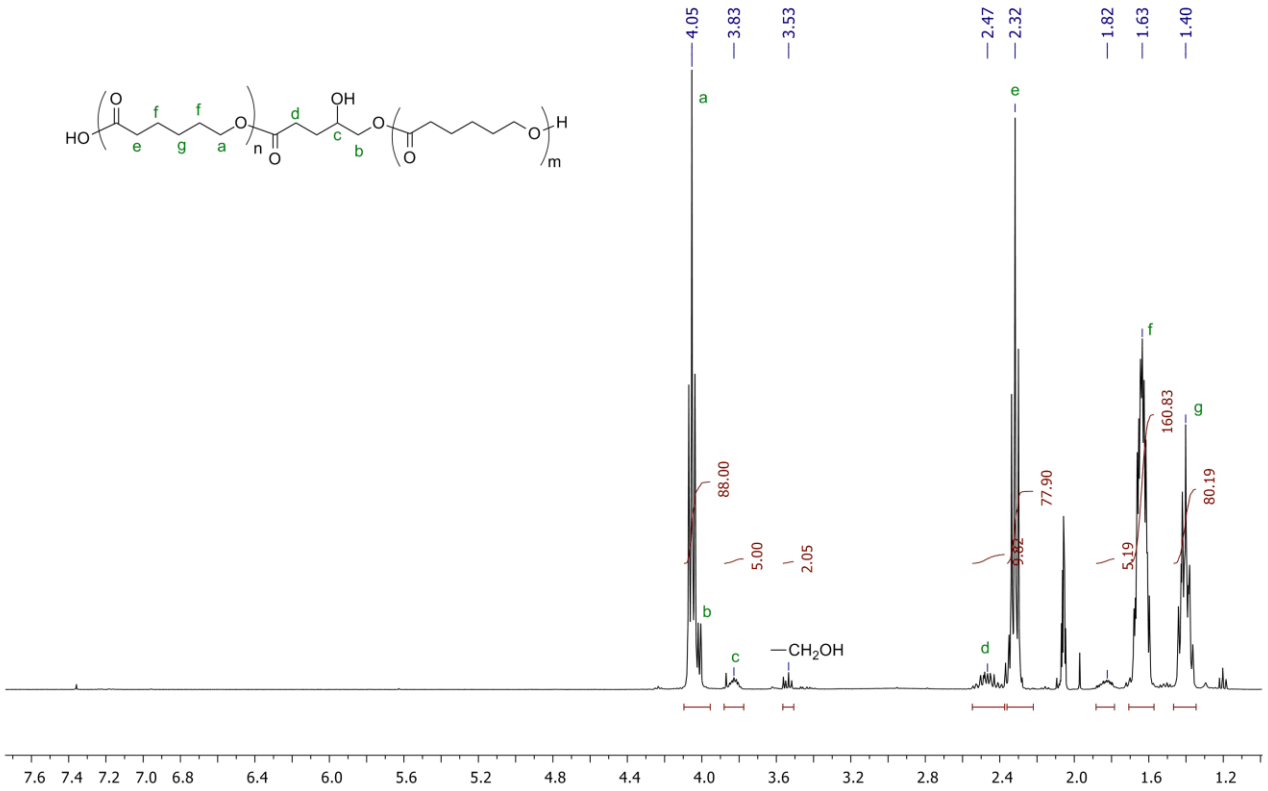


Figure S8. ^{1}H NMR (acetone-d_6, 400 MHz, 20 °C) of copolymer **4a** (45:5, Table 1, run 1)

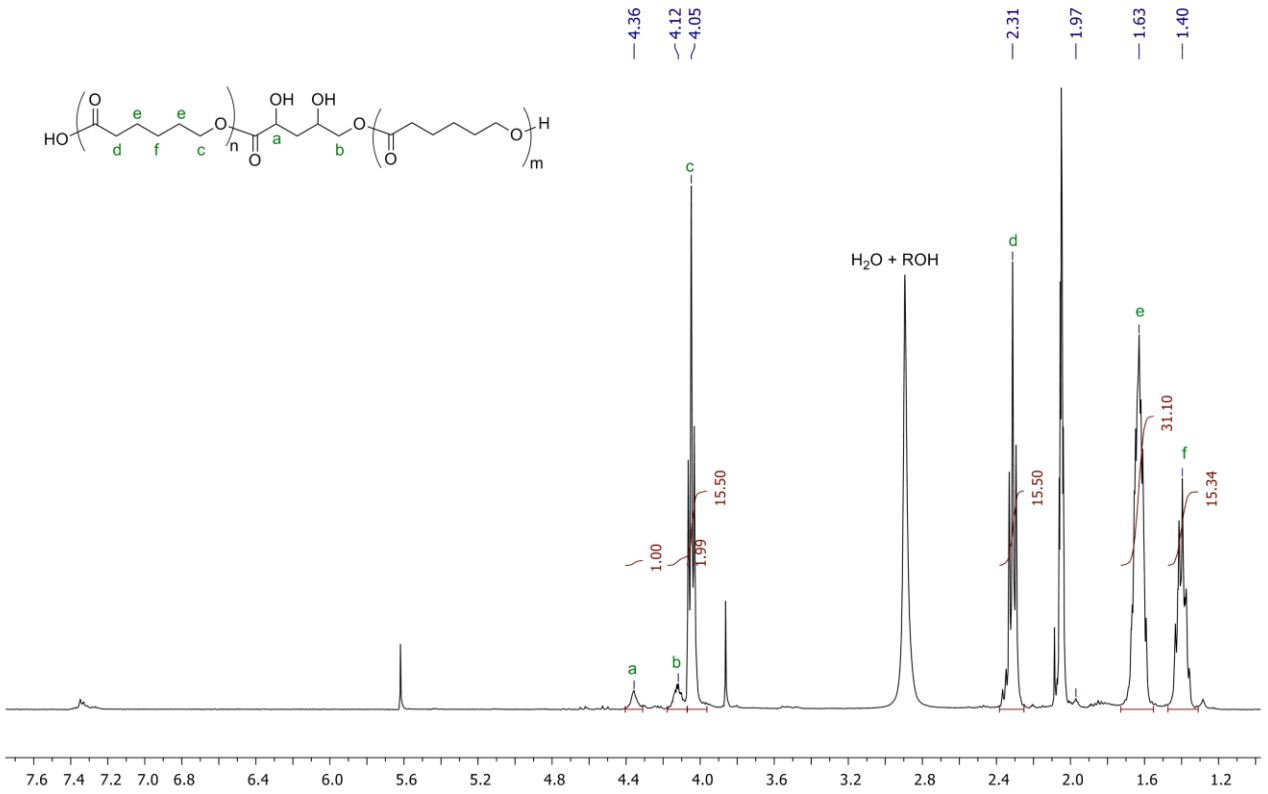


Figure S9. ^{1}H NMR (acetone-d_6, 400 MHz, 20 °C) of copolymer **4b** (90:10, Table 1, run 3)

S5. Copolymer degradation

Copolymer **4** (40 mg) were dissolved in $CDCl_3$ (0.65 mL). The resulting clear solution was placed into 5 mm NMR tube. $MeSO_3H$ or TBD (5% mol/mol) were introduced into the sample. NMR spectra were recorded after 1, 2, 4 and 8 h. The conversion of copolymer was estimated by integration of characteristic signals in ^1H NMR spectra.

Fragments of ^1H NMR spectra for copolymer **4a** degradation are shown below (Figure S10). Copolymer **4b** degradation spectra are provided in the main text.

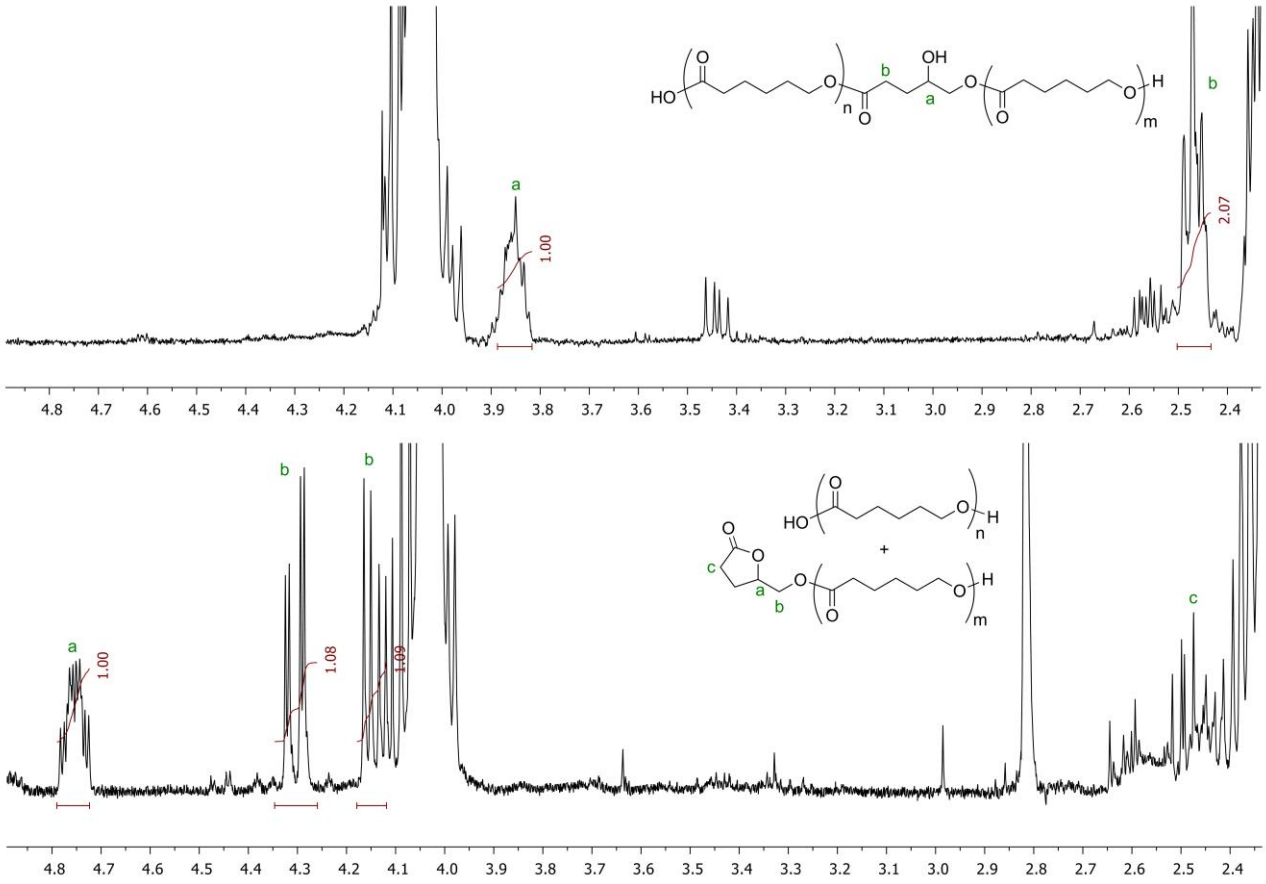


Figure S10. Fragments of ^1H NMR spectra ($CDCl_3$, 400 MHz, 20 °C) of copolymer **4a** (90:10, Table 1, run 2) before and after the reaction with $MeSO_3H$