Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Organic carboxylate salt-enabled alternative synthetic routes for bio-functional cyclic carbonates and aliphatic polycarbonates

Yuya Watanabe,[a] *Shunya Takaoka,*[a] *Yuta Haga,*[a] *Kohei Kishi,*[a] *Shunta Hakozaki,*[a] *Atsushi Narumi,*[a] *Takashi Kato,*[b] *Masaru Tanaka,*[c] *and Kazuki Fukushima*[*,a,b,d]

[a]*Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, JAPAN*

[b]*Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN*

[c]*Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, JAPAN*

[d]*Japan Science and Technology Agency (JST), PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, JAPAN*

Contents:

Experimental Section

Materials

Reagents and solvents were purchased from Sigma-Aldrich Japan (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), FUJIFILM Wako Chemicals (Osaka, Japan), and Tokyo Chemical Industry (Tokyo, Japan) and used as received unless specified otherwise. 1-Bromo-3-methoxypropane was acquired from Oakwood Chemical (Estill, SC, USA). Dehydrated tetrahydrofuran (THF) and CH_2Cl_2 were supplied by a solvent supply system (Kanto Chemical). 1-(3,5-Bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (TU) was prepared as reported previously.[S1] Benzyl alcohol (BnOH) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were vacuum distilled over CaH_2 and stored in a nitrogen-filled glovebox. 1-Pyrenebutanol (PB) and TU were also dehydrated over CaH_2 and stored in the glovebox.

Methods

^1H and ^{13}C NMR spectra were acquired on JEOL 500MHz JNM-ECX and JNM-ECX400SL instruments operated at 500 and 400 MHz for ^1H and at 125 and 100 MHz for ^{13}C. Size-exclusion chromatography (SEC) in THF was performed at 40 °C using an integrated Malvern Viscotek TDAmax SEC unit equipped with three TSK-gel (one G2000HHR and two GMHHR-H) columns connected in series, a right-angle light scattering detector, a refractive index (RI) detector, a viscometer detector, and a ultraviolet (UV) detector (Viscotec UV detector 2600). The obtained M_n and $Đ_M$ values were calibrated using polystyrene (PS) standards with molar masses ranging between 580 and 3.64 ×10^5 g mol^{-1}. The measurement of **2b** was performed using an integrated Tosoh HLC-8220 SEC unit equipped with three TSK-gel columns (super AW5000, super AW4000, and super AW3000) connected in series and an RI detector at 30 °C. Calibration was performed using PS standards (2500 to 1.1 × 10^6 g mol^{-1}).

Solubility testing of bis-MPA salts

Bis-MPA (268 mg, 2.0 mmol) and nitrogen bases (2.0 mmol) were mixed in an organic solvent (10 mL) at 25 °C. Eight commercially available nitrogen bases were used for this purpose (Scheme S1). The solubilities of the bis-MPA salts were visually evaluated, as summarized in Table S1.

Scheme S1. Formation of bis-MPA organic salts with nitrogen bases **B1**–**B8**.

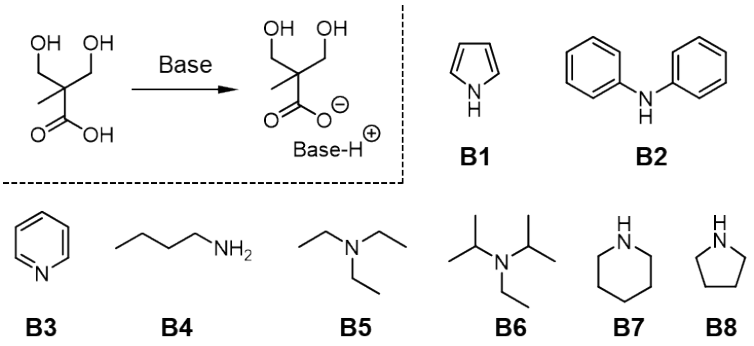


Table S1. Solubilities of bis-MPA salts with various nitrogen bases.[a]

Base		**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**
pK_a (H_2O)[b]		–3.8	0.78	5.23	10.59	10.65	10.98	11.22	11.27
Solvent	**ε**[c]								
Toluene	2.38	–	–	–	–	–	–	–	–
Et_2O	4.33	–	–	–	–	–	–	–	–
$CHCl_3$	4.81	–	–	–	+	+	+	+	+
EtOAc	6.02	–	–	–	–	ps	–	–	–
THF	7.58	–	–	–	ps	+	+	–	–
CH_2Cl_2	8.93	–	–	–	ps	+	+	–	+
Acetone	20.7	–	–	–	+	+	+	–	ps
CH_3CN	37.5	–	–	–	ps	+	+	–	–

[a][bis-MPA] = 0.2 M. +: soluble, ps: phase-separated, –: insoluble as a powder precipitate. [b]Retrieved from Refs. S2–S6. [c]Dielectric constant.

Notes for Table S1

The difference in pK_a between the acid and base ($\Delta pK_a = pK_{a\,[base]} - pK_{a\,[acid]}$) strongly correlates with the charge state of the acid-base complex. At $\Delta pK_a < -1$, it exists as a non-ionized cocrystal, while at $\Delta pK_a > 4$, it is an ionized salt.[S7] Although the pK_a of bis-MPA has not been reported previously, its value is expected to be approximately 4 based on the data for similar carboxylic acids. The bis-MPA salts with **B4**–**B8** exhibited good solubility in organic solvents, suggesting their dissolution in the form of ionic pairs. Nevertheless, there is no clear correlation between the utilized solvents and the pK_a values of the amines.

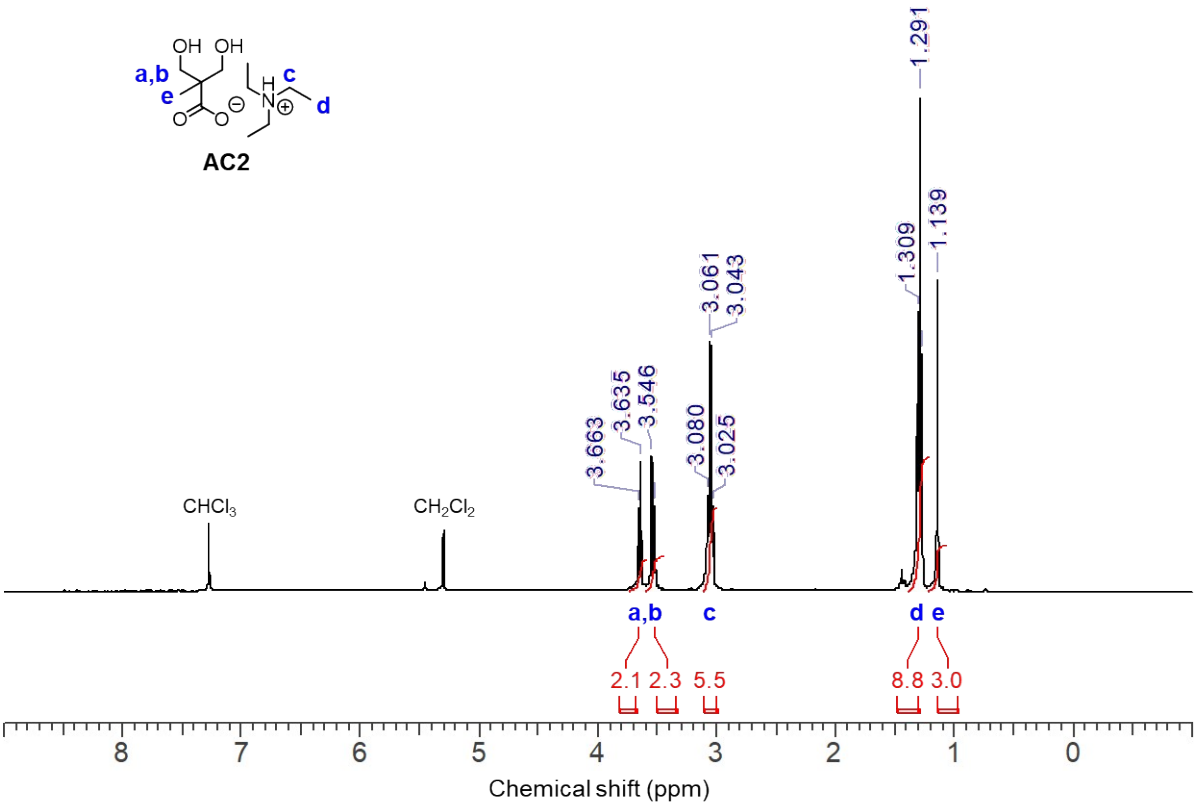
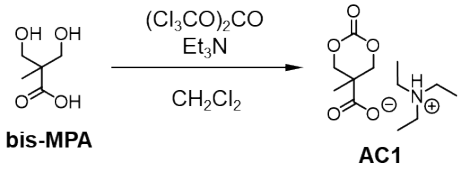


Figure S1. ^{1}H NMR spectrum of the bis-MPA salt with **B5** (**AC2**) formed in CH_2Cl_2 (400 MHz, $CDCl_3$).

Direct cyclization of bis-MPA: Formation of AC1



Bis-MPA (5.45 g, 40 mmol) was mixed with triethylamine (TEA; 20 mL, 140 mmol) and CH_2Cl_2 (80 mL) under a nitrogen atmosphere. The solution was chilled in a dry ice/2-propanol bath to approximately –75 °C followed by the dropwise addition of a CH_2Cl_2 solution (20 mL) of triphosgene (4.78 g, 16 mmol) using an addition funnel. The reaction mixture was stirred under the chilled conditions for 90 min and then under ambient conditions for 2 h. After the precipitates comprising the byproduct triethylammonium chloride ($TEAH^+Cl^-$) were filtered out, the filtrate was evaporated and dried under vacuum to obtain **AC1**. Alternatively, hexane (200 mL) was gradually added to the filtrate to form the precipitates of $TEAH^+Cl^-$. **AC1** was obtained from the filtrate after vacuum drying (7.4 g, 71%). Note that THF was not an appropriate solvent for this reaction. The concomitant formation of an insoluble $TEAH^+Cl^-$ salt in THF might negatively affect cyclization, confirming the formation of oligomers. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.69 (d, *J* = 10.5 Hz, 2H, C*H*$_a$H$_b$), 4.15 (d, *J* = 10.5 Hz, 2H, CH$_a$*H*$_b$), 3.06 (q, *J* = 7.3 Hz, 6H, NHC*H*$_2$), 1.32–1.24 (m, 12H, C*H*$_3$).

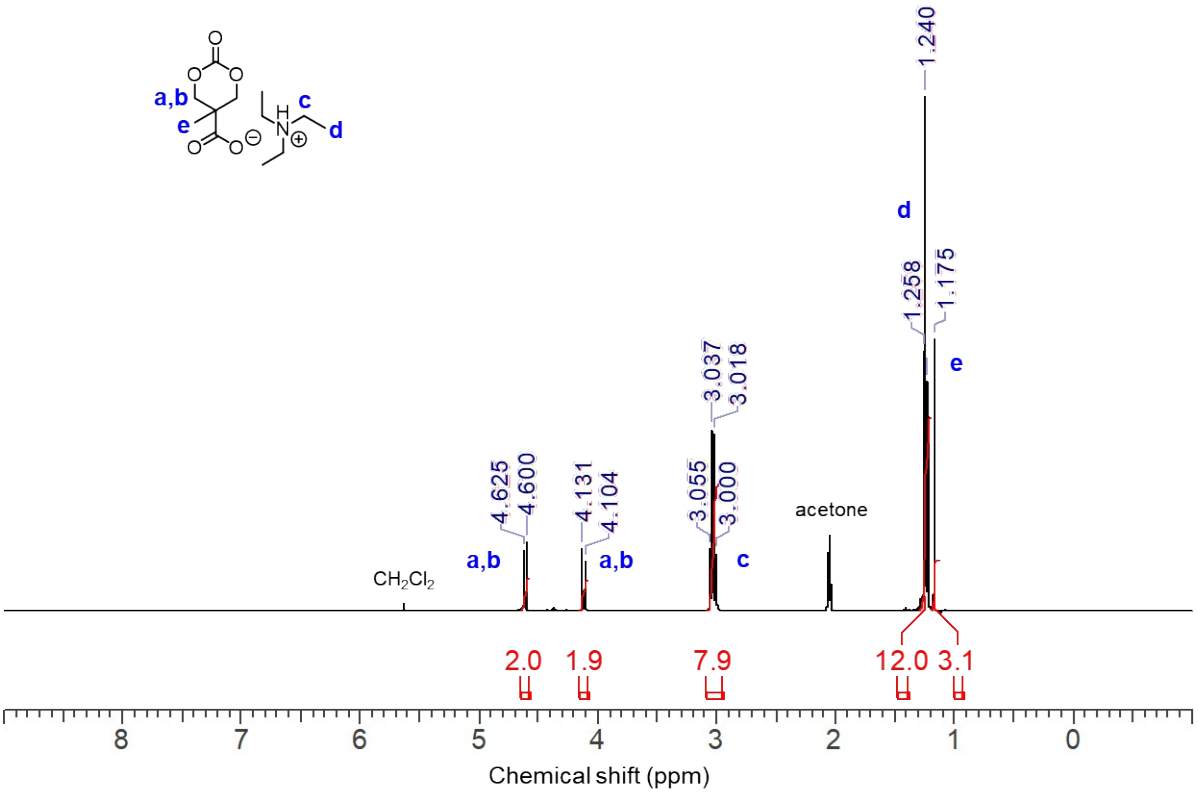


Figure S2. ^{1}H NMR spectrum of **AC1** including more than 1 equivalent of triethylammonium relative to carboxylate (400 MHz, acetone-d_6).

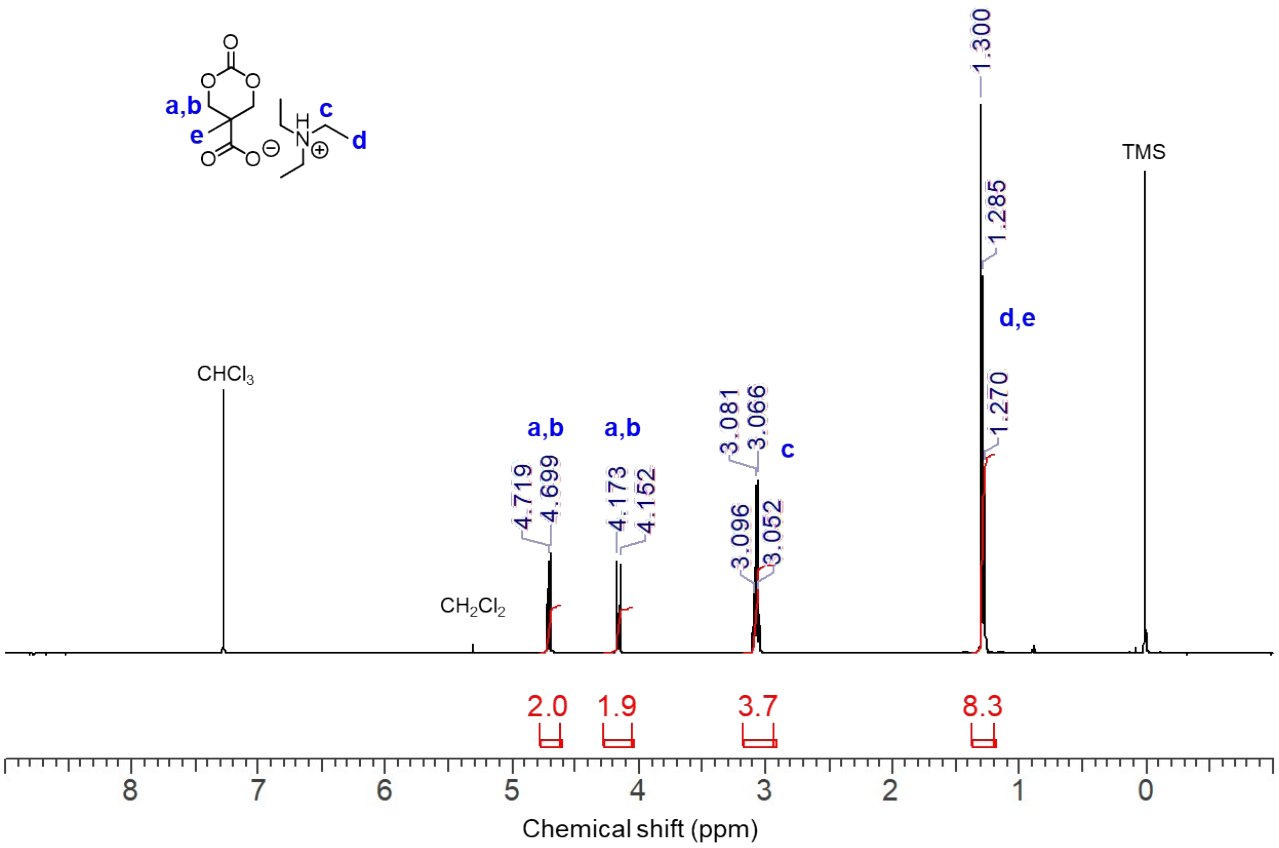
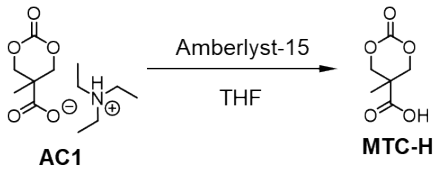


Figure S3. ^{1}H NMR spectrum of **AC1** including less than 1 equivalent of triethylammonium relative to carboxylate (400 MHz, $CDCl_3$).

Formation of MTC-H



By treatment of AC1 with an ion exchange resin. AC1 (2.0 g, 7.6 mmol) was dissolved in dry THF and stirred with Amberlyst-15 (1.6 g) at 25 °C for 2 h. After the resin was filtered out, the filtrate was evaporated at a reduced pressure. The obtained residue was washed with CH_2Cl_2 to form a pale yellowish solid (1.1 g, 89%). The ^{1}H NMR spectrum matched that reported in the literature.[S8] ^{1}H NMR (400 MHz, acetone-d_6, δ): 4.67 (d, J = 10.9 Hz, 2H, C$\underline{H_a}$H$_b$), 4.36 (d, J = 10.4 Hz, 2H, CH$_a$$\underline{H_b}$), 1.32 (m, 12H, C$\underline{H_3}$).

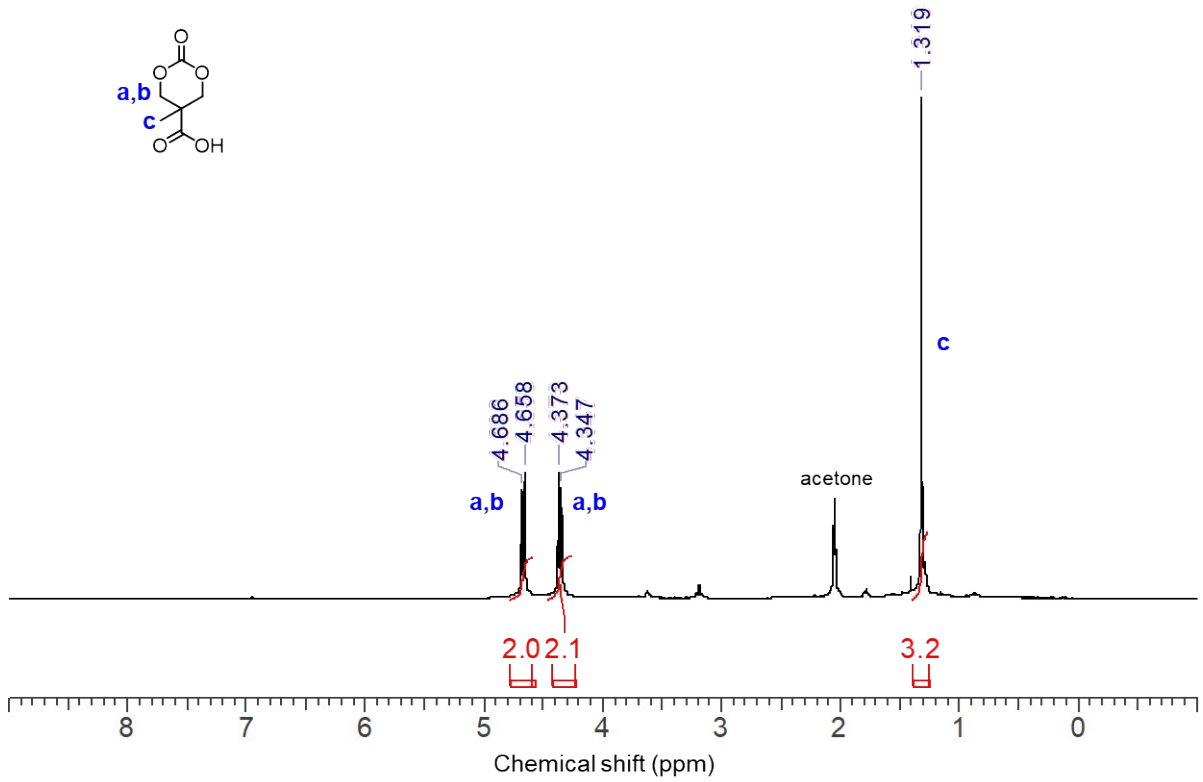
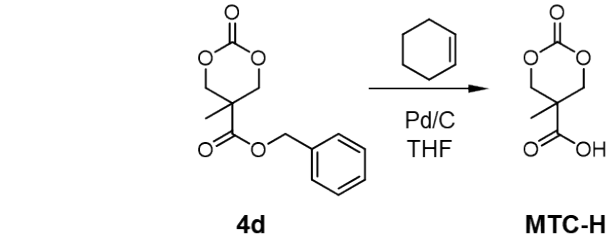


Figure S4. ^{1}H NMR spectrum of MTC-H obtained by the treatment of **AC1** with an ion exchange resin (400 MHz, acetone-d_6)

By catalytic hydrogenolysis. 1d (8.0 g, 32 mmol), which was preliminarily synthesized as described elsewhere,[S8] was dissolved in THF (160 mL), and the resulting solution was degassed. Pd/C (10 wt.%; 2.0 g) was dispersed in the solution, which was further degassed. Cyclohexene (32.5 mL, 320 mmol) was added to the reaction mixture and stirred at 60 °C for 24 h. Afterward, the solution was degassed, and the insoluble part was removed using a glass filter with celite. The filtrate was evaporated, dried under vacuum, and washed with CH_2Cl_2 to form a white solid (4.7 g, 91%). The obtained ^{1}H NMR spectrum matched that

reported in the literature.[S7]

Scheme S2. Formation of MTC-H by the catalytic transfer hydrogenolysis of the benzyl-functionalized cyclic carbonate (**4d**).



4d **MTC-H**

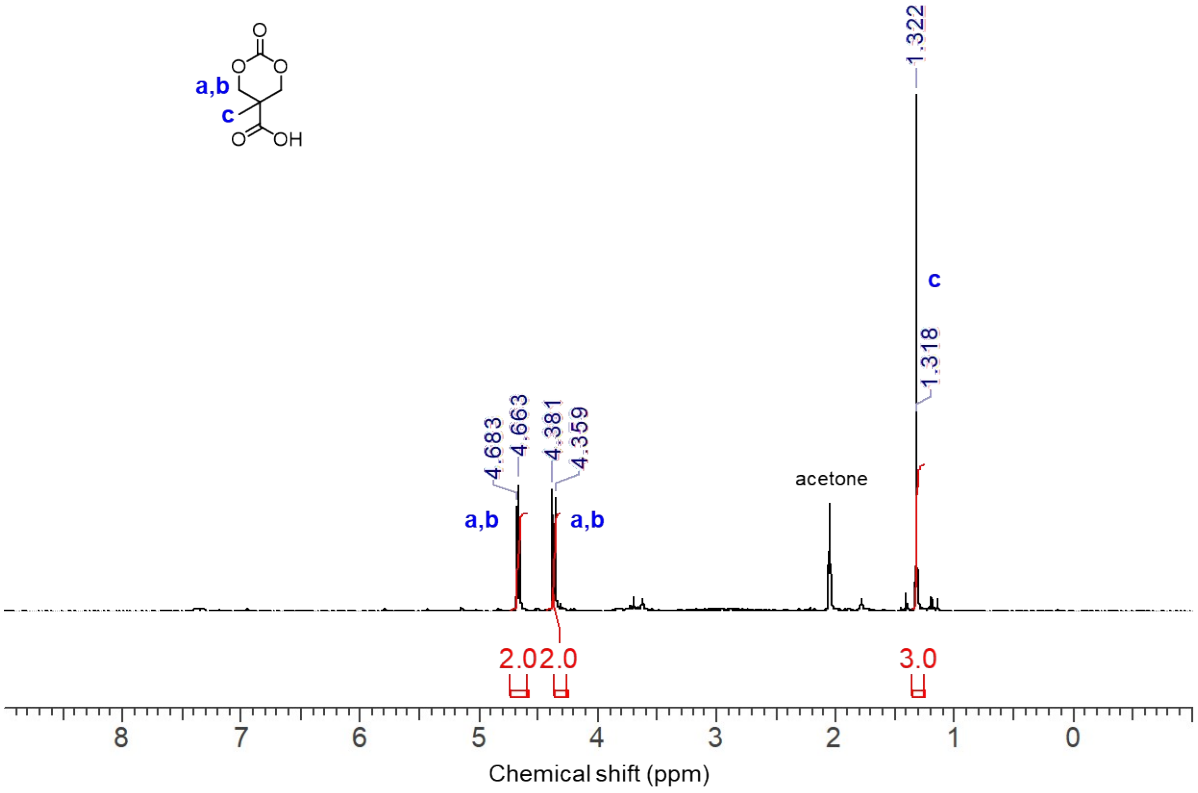
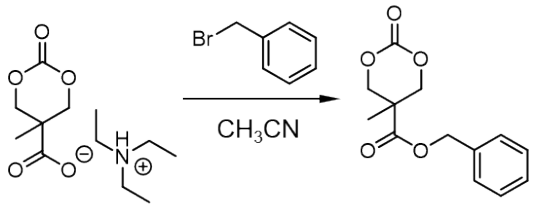


Figure S5. ^{1}H NMR spectrum of MTC-H obtained by hydrogenolysis (500 MHz, acetone-d_6).

Optimization of the reaction conditions for the esterification of AC1 with benzyl bromide

AC1 (260 mg, 1.0 mmol) was dissolved in acetonitrile (0.67 mL) followed by the addition of benzyl bromide (0.145 mL, 1.22 mmol). The resultant mixture was stirred at 25 °C for a predetermined time. An aliquot was taken at certain time points to monitor the product formation by ^{1}H NMR. The obtained results are summarized in Table S2.

Scheme S3. Esterification of **AC1** with benzyl bromide for optimizing the reaction conditions.



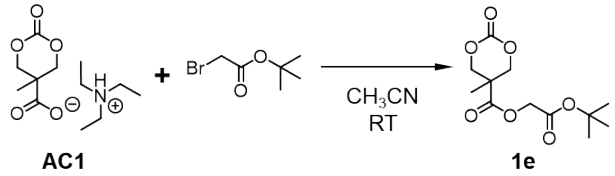
AC1 **1d**

Table S2. Esterification of **AC1** with benzyl bromide (BnBr) under various conditions.

Run	[AC1] (M)	BnBr (equiv.)	Temperature (°C)	Time (h)	Conversion[a] (%)
1	0.25	1.0	RT	24	74
2	0.5	1.0	RT	24	77
3	1.0	1.0	RT	24	82
4	1.5	1.0	RT	24	83
5	0.25	1.2	RT	13	87
6	0.25	1.5	RT	13	92
7	0.25	1.7	RT	13	89
8	0.25	2.0	RT	13	88
9	0.25	1.0	40	24	84
10	0.25	1.0	50	24	85
11	0.25	1.0	60	24	84

[a]Determined by ^{1}H NMR.

Synthesis of functionalized cyclic carbonates 1 from AC1 through esterification with alkyl bromides



AC1 1e

Typical procedure: Synthesis of 1e. AC1 (1.0 g, 3.8 mmol) was mixed with *tert*-butyl bromoacetate (0.7 mL, 4.6 mmol) in acetonitrile (2.6 mL) and stirred at 25 °C. The product formation was monitored by ^{1}H NMR. The reaction mixture was concentrated under a reduced pressure, and the obtained residue was dispersed in THF to filter out precipitates. The filtrate was concentrated, and the residue was dissolved in CH_2Cl_2 and washed with brine twice. The organic layer was dried over $MgSO_4$, evaporated, and dried under vacuum at 25 °C. The residue was purified by column chromatography using a mixed solvent of EtOAc and hexane (6:4, v/v) followed by recrystallization from toluene to obtain a white solid as **1e** (0.23 g, 22%). The ^{1}H NMR spectrum matched that reported in the literature.[S9] ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.76 (d, *J* = 10.8 Hz, 2H, C$\underline{H_a}$H$_b$OCO), 4.60 (s, 2H, C$\underline{H_2}$CO), 4.25 (d, *J* = 10.8 Hz, 2H, CH$_a\underline{H_b}$OCO), 1.49 (s, 9H, *tert*-Bu), 1.44 (s, 3H, C$\underline{H_3}$).

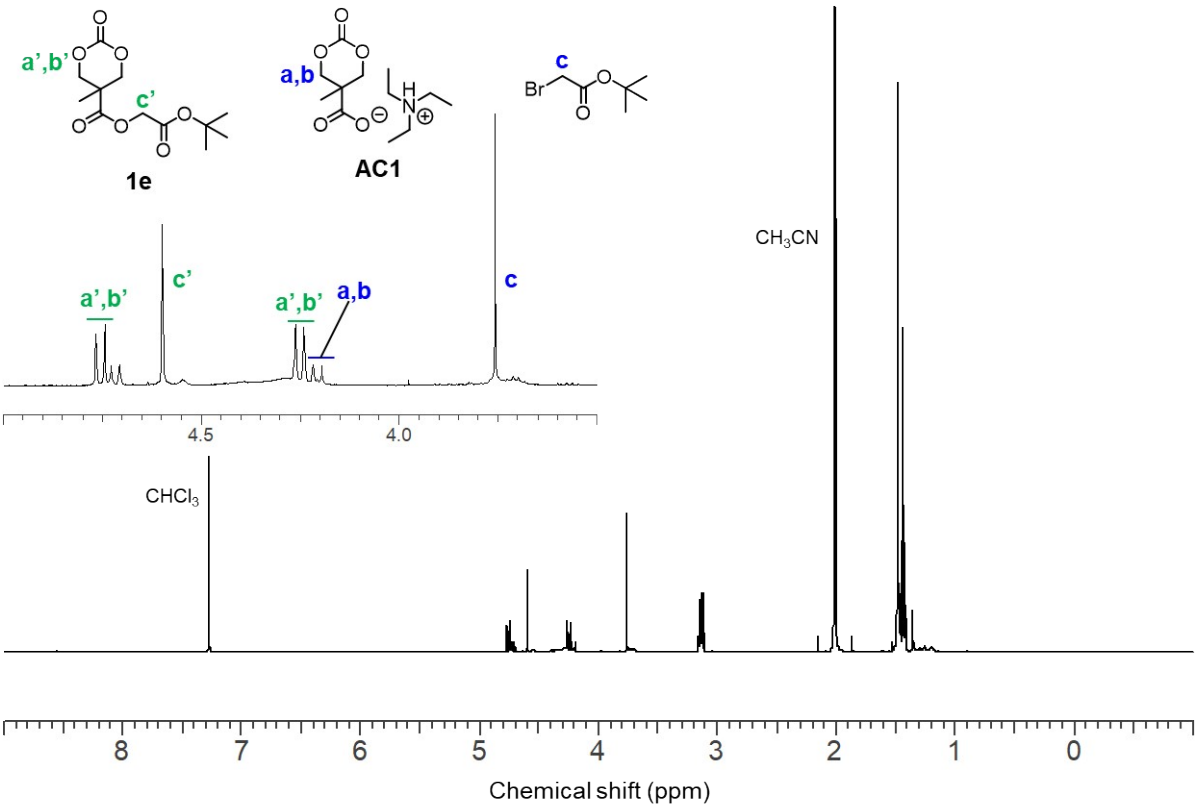


Figure S6. ^{1}H NMR spectrum of the reaction mixture showing the formation of **1e** at 6 h (500 MHz, $CDCl_3$). Inset: expanded region between 3.5 and 5.0 ppm.

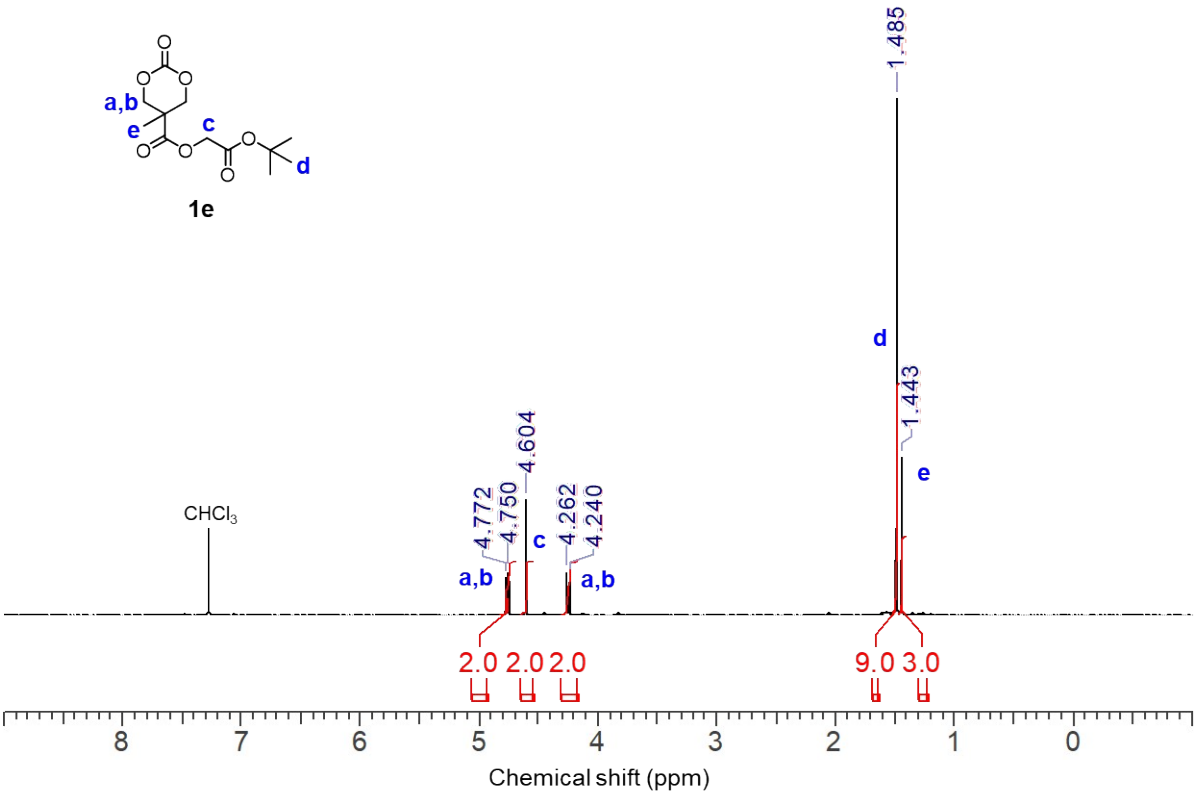
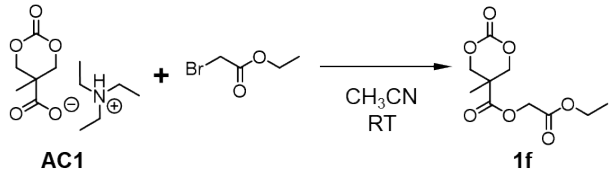


Figure S7. ^{1}H NMR spectrum of **1e** derived from **AC1** (500 MHz, $CDCl_3$).



AC1 **1f**

1f. The reaction was performed as described above for **1e**, using ethyl bromoacetate (0.51 mL, 4.6 mmol). The product formation was monitored by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.77 (d, *J* = 11.3 Hz, 2H, C$\underline{H_a}$H$_b$OCO), 4.72 (s, 2H, C$\underline{H_2}$CO), 4.28–4.21 (m, 6H, CH$_a\underline{H_b}$OCO, C$\underline{H_2}$CH$_3$), 1.43 (s, 3H, C$\underline{H_3}$), 1.30 (t, *J* = 11.3 Hz, 3H, CH$_2$C$\underline{H_3}$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.6, 166.8, 147.2, 72.7, 61.8, 61.5, 40.1, 17.4, 14.0.

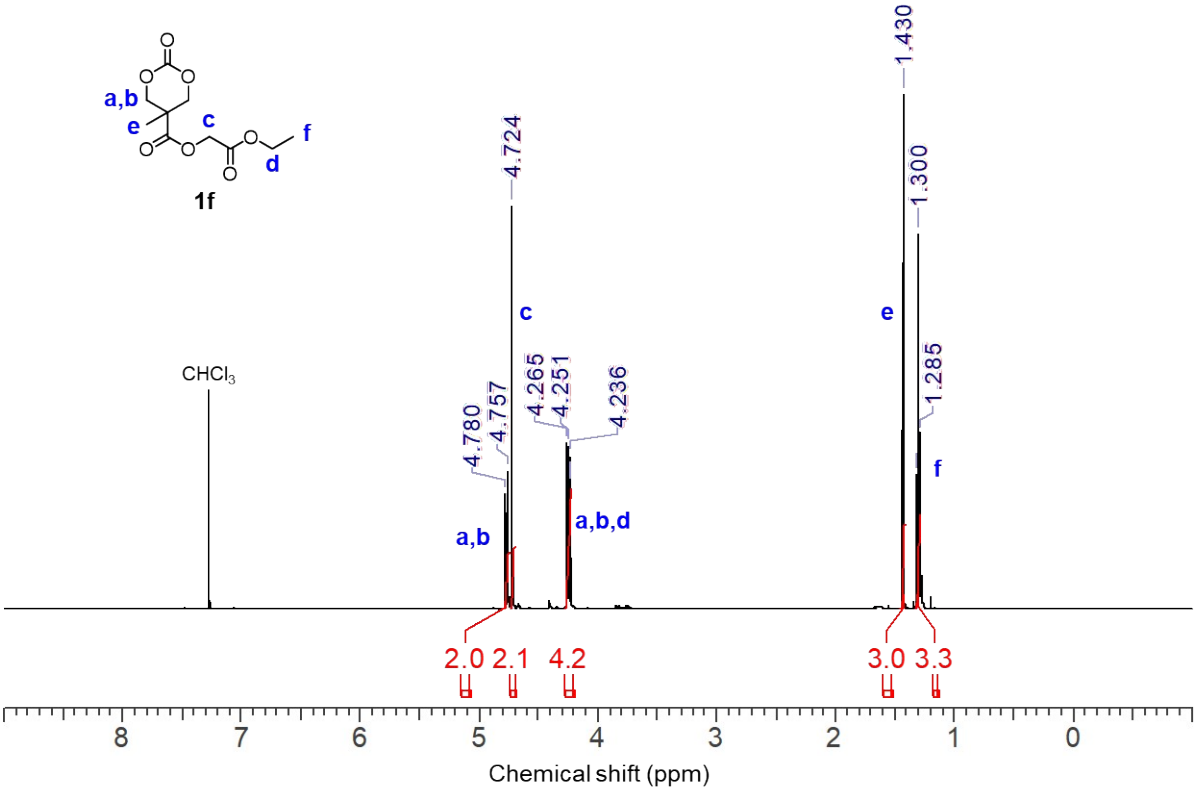


Figure S8. ^{1}H NMR spectrum of **1f** derived from **AC1** (500 MHz, $CDCl_3$).

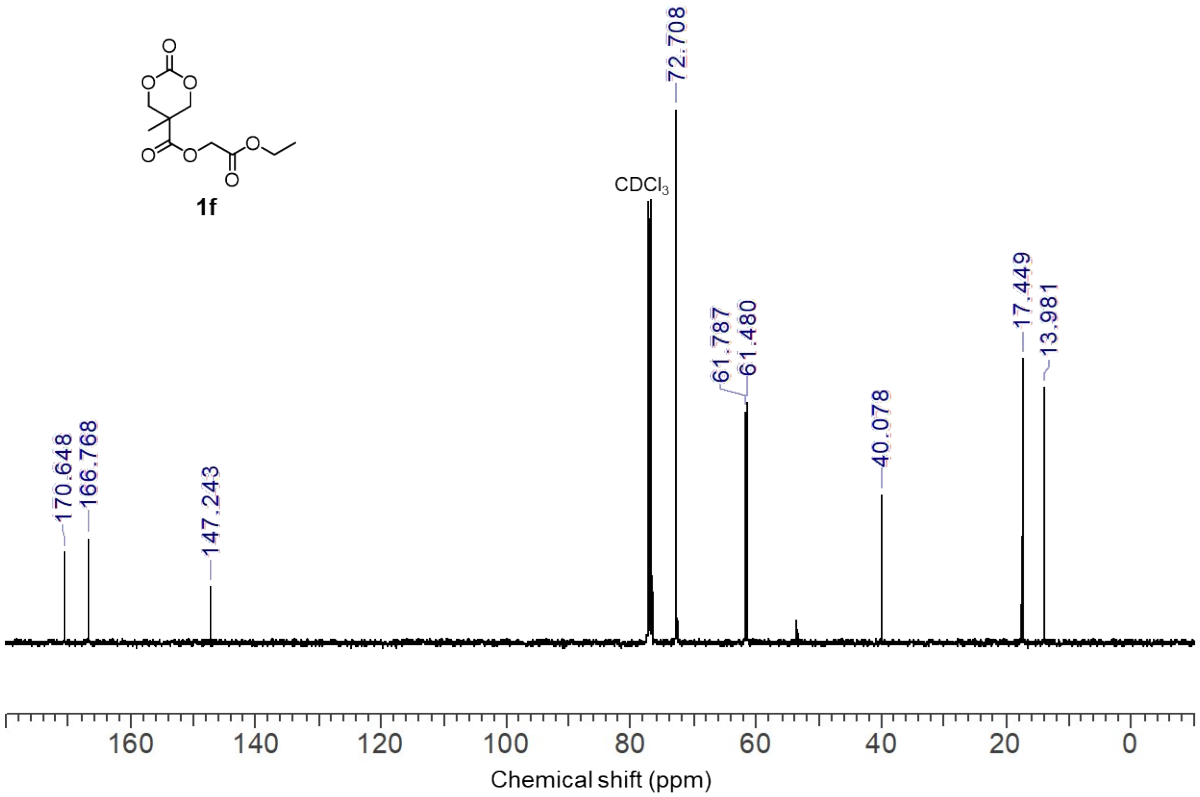
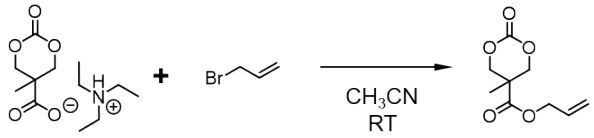
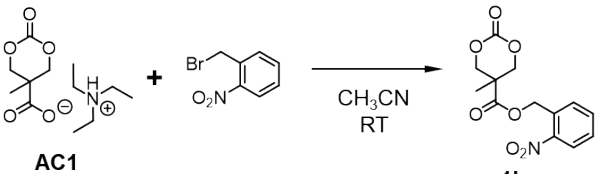


Figure S9. ^{13}C NMR spectrum of **1f** (100 MHz, $CDCl_3$).



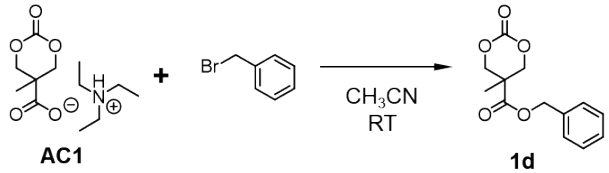
AC1 **1g**

1g. The reaction was performed as described above for **1e**, using allyl bromide (0.40 mL, 4.7 mmol). The product formation was monitored by ^{1}H NMR. The crude product was purified by column chromatography using a mixture of ethyl acetate and hexane (8:2, v/v) to produce a white solid as **1g** (119 mg, 16%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S10,S11] ^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.97–5.84 (m, 1H), 5.40–5.27 (m, 2H, CHC$\underline{H_2}$), 4.75–4.66 (m, 4H, OC$\underline{H_2}$CH, CH_aH$_b$OCOO), 4.21 (d, J = 11.0 Hz, 2H, CH$_a\underline{H_b}$OCOO), 1.35 (s, 3H, C$\underline{H_3}$).



AC1 **1h**

1h. The reaction was performed as described above for **1e**, using 2-nitrobenzyl bromide (996 mg, 4.6 mmol). The product formation was monitored by ^{1}H NMR.



1d. The reaction was performed as described above for **1e**, using **AC1** (2.48 g, 9.5 mmol), acetonitrile (6.4 mL), and benzyl bromide (1.4 mL, 11.5 mmol). The product formation was monitored by ^{1}H NMR. The crude product was purified by column chromatography using a mixture of ethyl acetate and hexane (6:4, v/v). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S8] ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.43–7.32 (m, 5H, Ar-*H*), 5.23 (s, 2H, PhC*H*$_2$), 4.72 (d, *J* = 10.8 Hz, 2H, C*H*$_a$H$_b$OCOO), 4.22 (d, *J* = 10.8 Hz, 2H, CH$_a$*H*$_b$OCOO), 1.35 (s, 3H, C*H*$_3$).

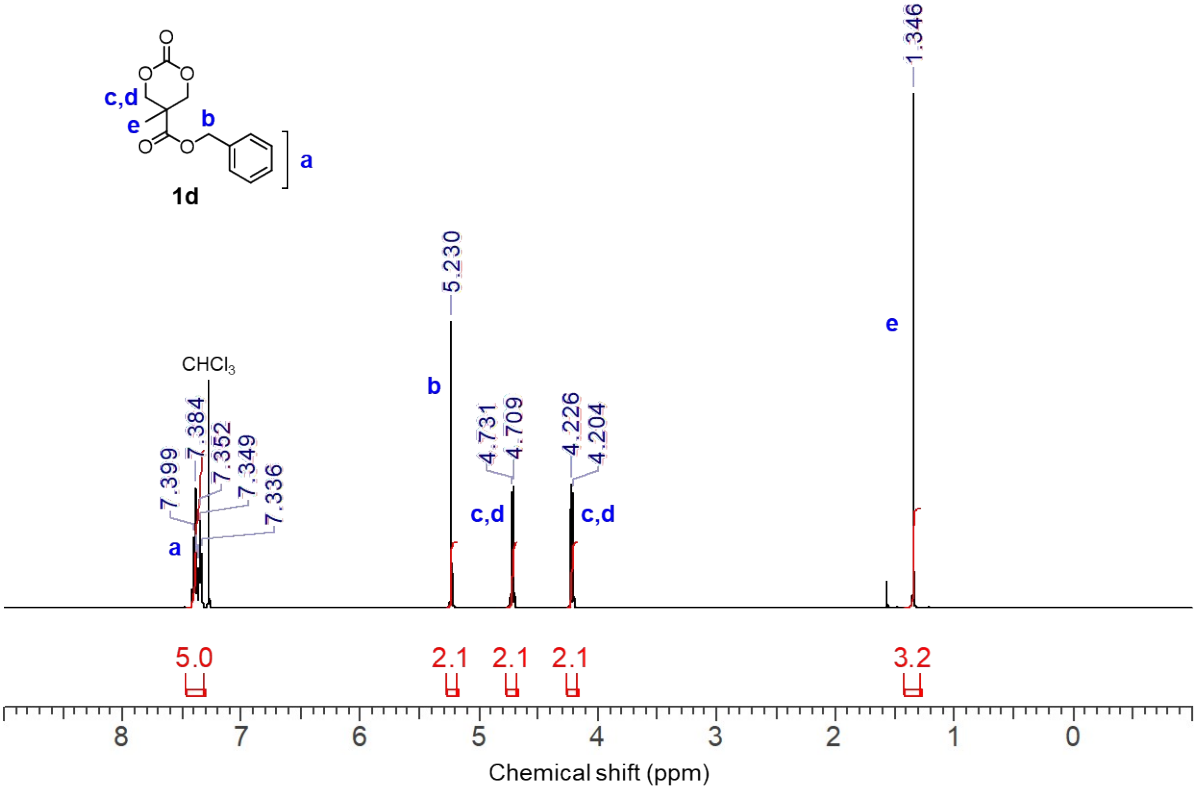
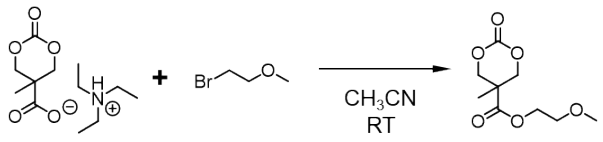


Figure S10. ^{1}H NMR spectrum of **1d** derived from **AC1** (500 MHz, $CDCl_3$).



AC1 **1a**

1a. The reaction was performed as described above for **1e**, using **AC1** (261 mg, 1.0 mmol), acetonitrile (0.67 mL), and 2-bromoethyl methyl ether (0.114 mL, 1.2 mmol). The product formation was monitored by ^{1}H NMR.

1b. The reaction was performed as described above for **1a**, using tetrahydrofurfuryl bromide (0.130 mL, 1.2 mmol). The product formation was monitored by ^{1}H NMR. However, no reaction occurred after 10 days.

1c. The reaction was performed as described above for **1a**, using 1-bromo-3-methoxypropane (0.135 mL, 1.2 mmol). The product formation was monitored by ^{1}H NMR.

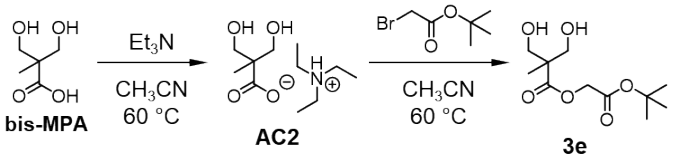
1i. The reaction was performed as described above for **1a**, using 1-bromobutane (0.130 mL, 1.2 mmol). The product formation was monitored by ^{1}H NMR.

1j. The reaction was performed as described above for **1a**, using 1-bromo-4-methoxybutane (0.155 mL, 1.2 mmol). The product formation was monitored by ^{1}H NMR.

1k. The reaction was performed as described above for **1a**, using 1-bromo-2-methylpropane (0.130 mL, 1.2 mmol). The product formation was monitored by ^{1}H NMR. However, no reaction occurred after 24 h.

1l. The reaction was performed as described above for **1a**, using bromoacetaldehyde dimethylacetal (0.160 mL, 1.0 mmol). The product formation was monitored by ^{1}H NMR. However, no reaction occurred after 2 days.

Synthesis of bis-MPA esters 3 through esterification of AC2 and alkyl bromides



Typical procedure: Synthesis of 3e. Bis-MPA (10.1 g, 74 mmol) and TEA (7.6 g, 76 mmol) were dissolved in acetonitrile (250 mL) at 60 °C for 1 h. An acetonitrile solution (50 mL) of *tert*-butyl bromoacetate (14.8 g, 76 mmol) was slowly added to the reaction mixture, which was continuously stirred at 60 °C for 24 h. The resulting solution was concentrated, dissolved in EtOAc (50 mL), and extracted with brine twice. The organic layer was dried over $MgSO_4$, evaporated, and dried under vacuum to obtain a transparent oil as **3e** (15.6 g, 85%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S9] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.63 (s, 2H, OC*H*$_2$CO), 3.82 (s, 4H, C*H*$_2$OH), 3.09–2.97 (br, 2H, O*H*), 1.49 (s, 9H, *tert*-Bu), 1.20 (s, 3H, C*H*$_3$).

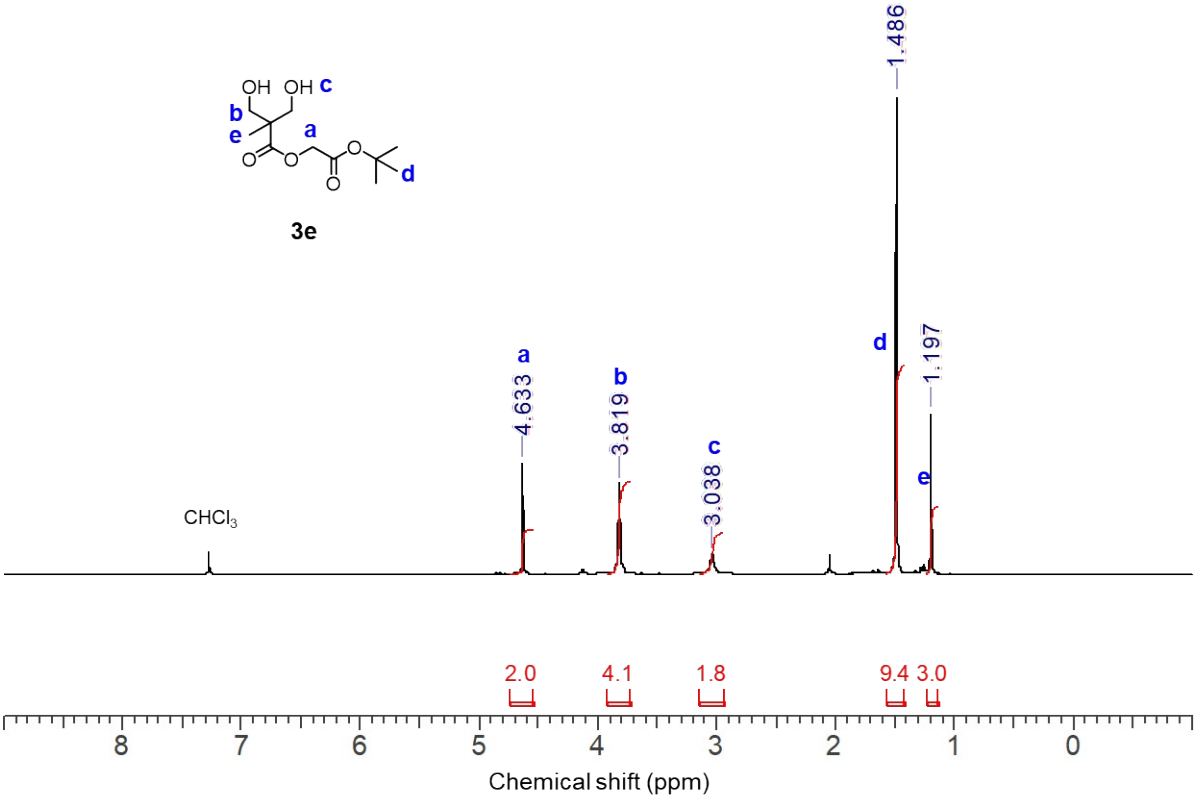
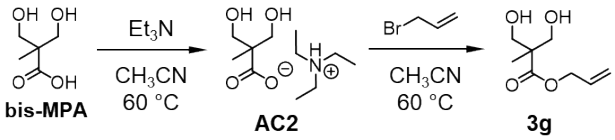


Figure S11. ^{1}H NMR spectrum of **3e** derived from **AC2** (400 MHz, $CDCl_3$).



3g. The reaction was performed as described above for **3e**, using allyl bromide (9.1 g, 75 mmol) to produce **3g** (9.7 g, 75%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S11] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.01–5.87 (m, 1H, C*H*=CH_2), 5.36 (d, 1H, *J* = 17.4 Hz, CH=CH_aH$_b$), 5.27 (d, 1H, *J* = 10.5 Hz, CH=C$H_a$$H_b$), 4.68 (d, 2H, *J* = 5.5 Hz, COOCH_2), 3.94 (d, 2H, *J* = 11.4 Hz, CH_aH$_b$OH), 3.74 (d, 2H, *J* = 11.4 Hz, C$H_a$$H_b$OH), 3.08–2.90 (br, 2H, O*H*), 1.09 (s, 3H, CH_3).

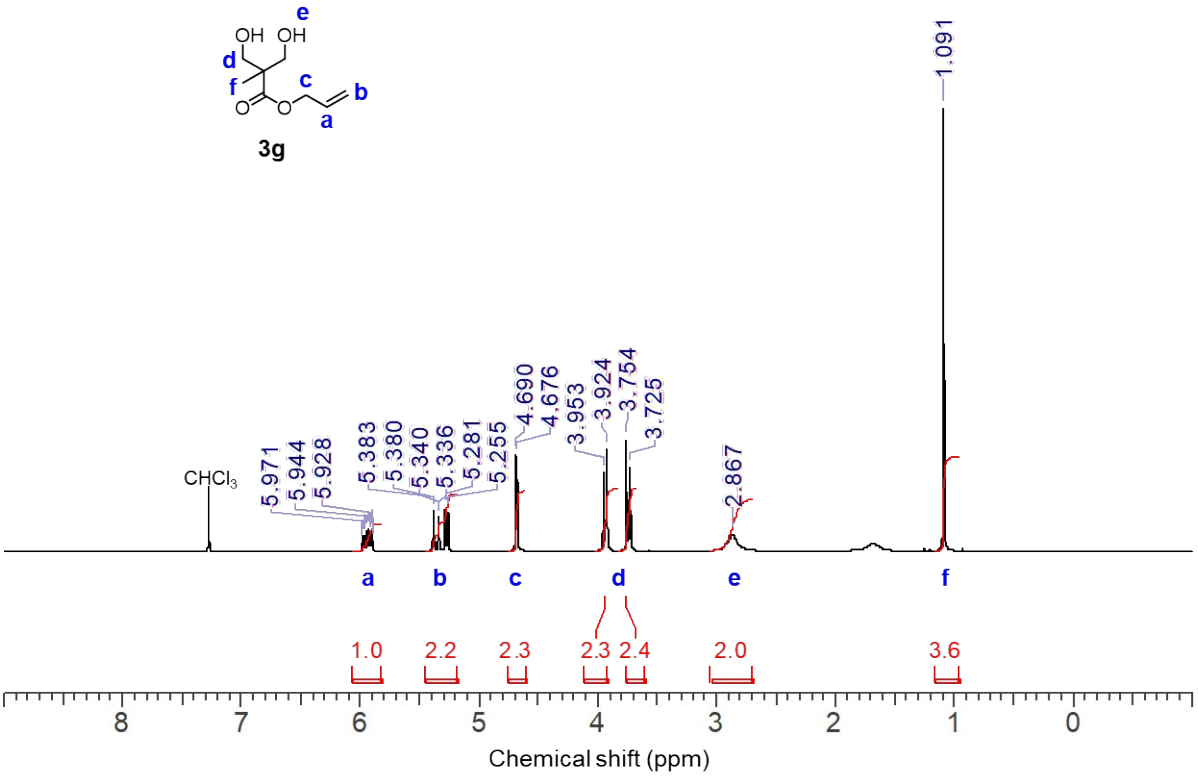
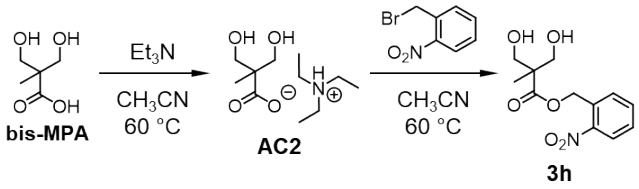


Figure S12. ^{1}H NMR spectrum of **3g** derived from **AC2** (400 MHz, $CDCl_3$).



3h. The reaction was performed as described above for **3e**, using 2-nitrobenzyl bromide (16.4 g, 7.6 mmol) to produce **3h** (15.9 g, 79%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S12] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.12 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.73–7.66 (m, 2H, Ar-*H*), 7.57–7.47 (m, 1H, Ar-*H*), 5.61 (s, 2H, Ar-C*H*$_2$), 3.99 (dd, 2H, *J* = 11.1, 6.6 Hz, C*H*$_a$H$_b$OH), 3.78 (dd, 2H, *J* = 11.6, 6.1 Hz, CH$_a$*H*$_b$OH), 2.82 (t, 2H, *J* = 6.3 Hz, O*H*), 1.12 (s, 3H, C*H*$_3$).

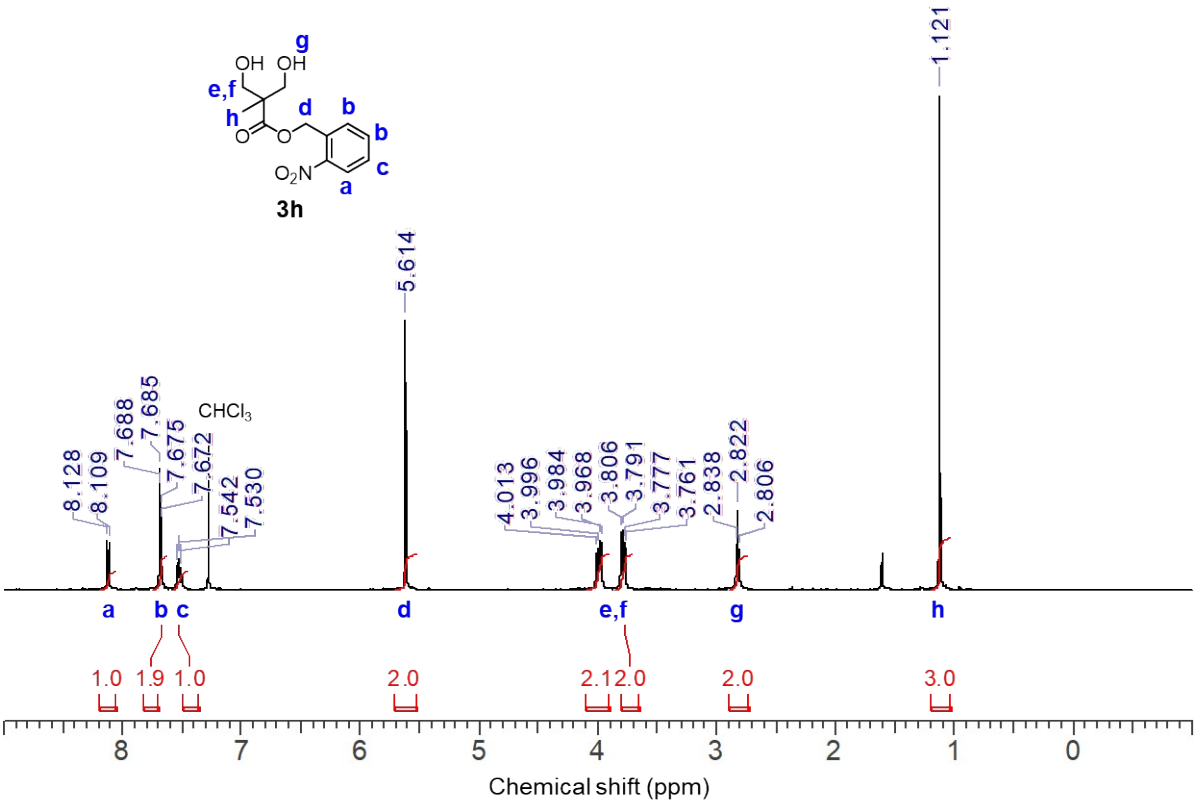
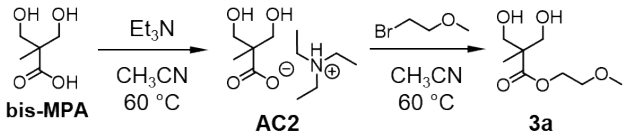


Figure S13. ^{1}H NMR spectrum of **3h** derived from **AC2** (400 MHz, $CDCl_3$).



3a. The reaction was performed as described above for **3e**, using bis-MPA (1.0 g, 7.3 mmol), TEA (0.76 g, 7.5 mmol), 2-bromoethyl methyl ether (1.04 g, 7.5 mmol), and a certain volume of acetonitrile to maintain the same concentration. The reaction was run for 72 h (0.45 g, 32%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S13] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.34 (t, *J* = 4.8 Hz, 2H, OCOC$\underline{H_2}$), 3.85 (d, *J* = 11.4 Hz, 2H, C$\underline{H_a}$CH$_b$OH), 3.73 (d, *J* = 11.4 Hz, 2H, CH$_a$C$\underline{H_b}$OH), 3.63 (t, *J* = 4.8 Hz, 2H, C$\underline{H_2}$O), 3.39 (s, 3H, OC$\underline{H_3}$), 1.11 (s, 3H, C$\underline{H_3}$).

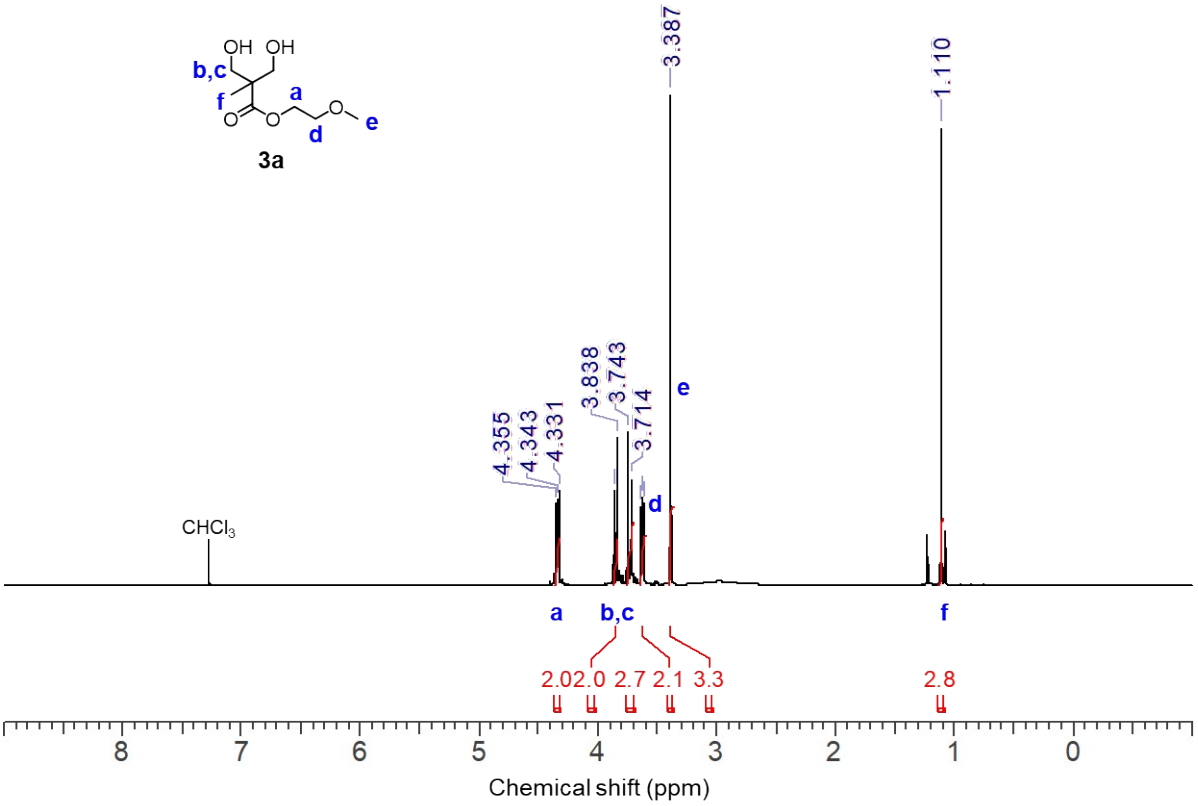
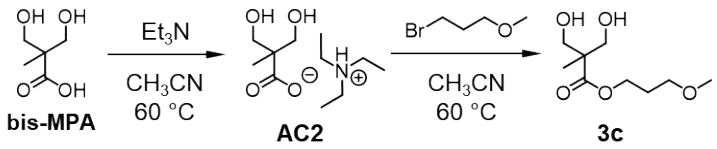


Figure S14. ^{1}H NMR spectrum of **3a** derived from **AC2** (400 MHz, $CDCl_3$).



3c. The reaction was performed as described above for **3a**, using 1-bromo-3-methoxypropane (1.15 g, 7.5 mmol) to produce **3c** (0.49 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.30 (t, *J* = 6.0 Hz, 2H, OCOC*H*$_2$), 3.87 (d, *J* = 11.4 Hz, 2H, C*H*$_a$CH$_b$OH), 3.72 (d, *J* = 11.4 Hz, 2H, CH$_a$C*H*$_b$OH), 3.52 (t, *J* = 5.7 Hz, 2H, C*H*$_2$O), 3.34 (s, 3H, OC*H*$_3$), 1.95 (quin, *J* = 5.8 Hz, 2H, C*H*$_2$), 1.07 (s, 3H, C*H*$_3$).

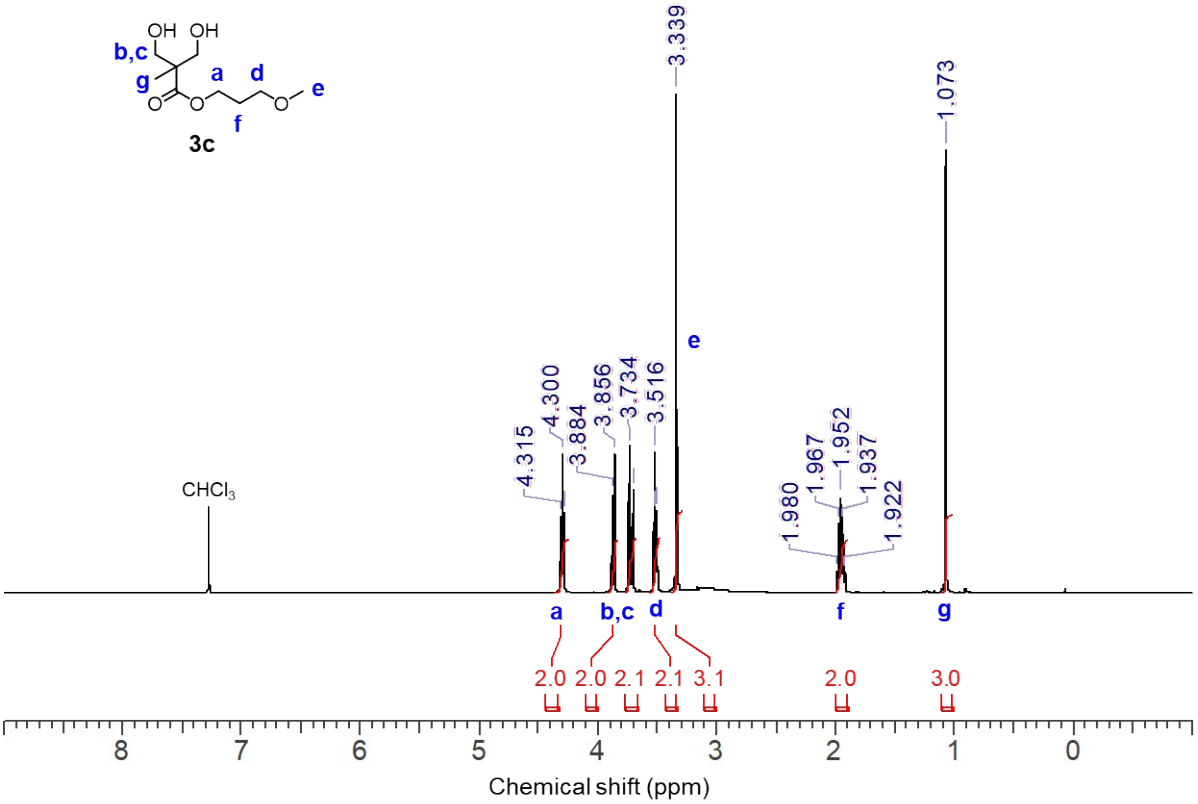
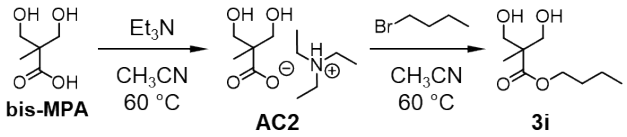


Figure S15. ^{1}H NMR spectrum of **3c** derived from **AC2** (400 MHz, $CDCl_3$).



3i. The reaction was performed as described above for **3a**, using 1-bromobutane (1.03 g, 7.5 mmol) to produce **3i** (0.72 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.18 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 3.92 (d, *J* = 11.0 Hz, 2H, C*H*$_a$H$_b$OH), 3.72 (d, *J* = 11.0 Hz, 2H, CH$_a$*H*$_b$OH), 3.03–2.79 (br, 2H, O*H*), 1.71–1.59 (m, 2H, OCH$_2$C*H*$_2$), 1.46–1.35 (m, 2H, C*H*$_2$CH$_3$), 1.06 (s, 3H, C*H*$_3$), 0.95 (t, *J* = 7.3 Hz, 3H, CH$_2$C*H*$_3$).

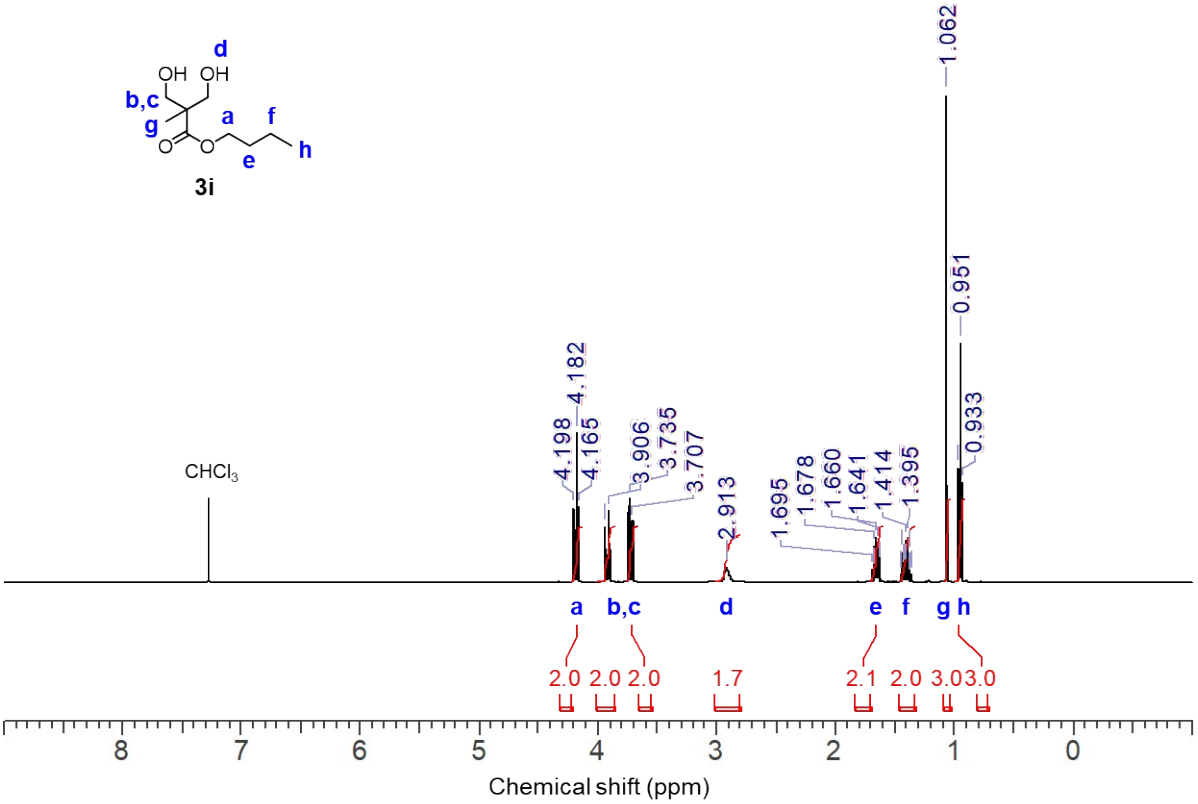
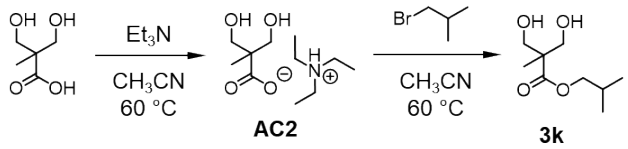


Figure S16. ^{1}H NMR spectrum of **3i** derived from **AC2** (400 MHz, $CDCl_3$).



3k. The reaction was performed as described above for **3a**, using 1-bromo-2-methylpropane (1.03 g, 7.5 mmol) with a longer reaction time of 190 h (0.40 g, 29%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.99–3.89 (m, 4H, OC$\underline{H_2}$, C$\underline{H_a}$H$_b$OH), 3.73 (d, *J* = 11.0 Hz, 2H, CH$_a$$\underline{H_b}$OH), 2.94–2.83 (br, 2H, O$\underline{H}$), 2.06–1.93 (m, 1H, C$\underline{H}$), 1.08 (s, 3H, C$\underline{H_3}$), 0.96 (d, *J* = 6.4 Hz, 6H, CHC$\underline{H_3}$).

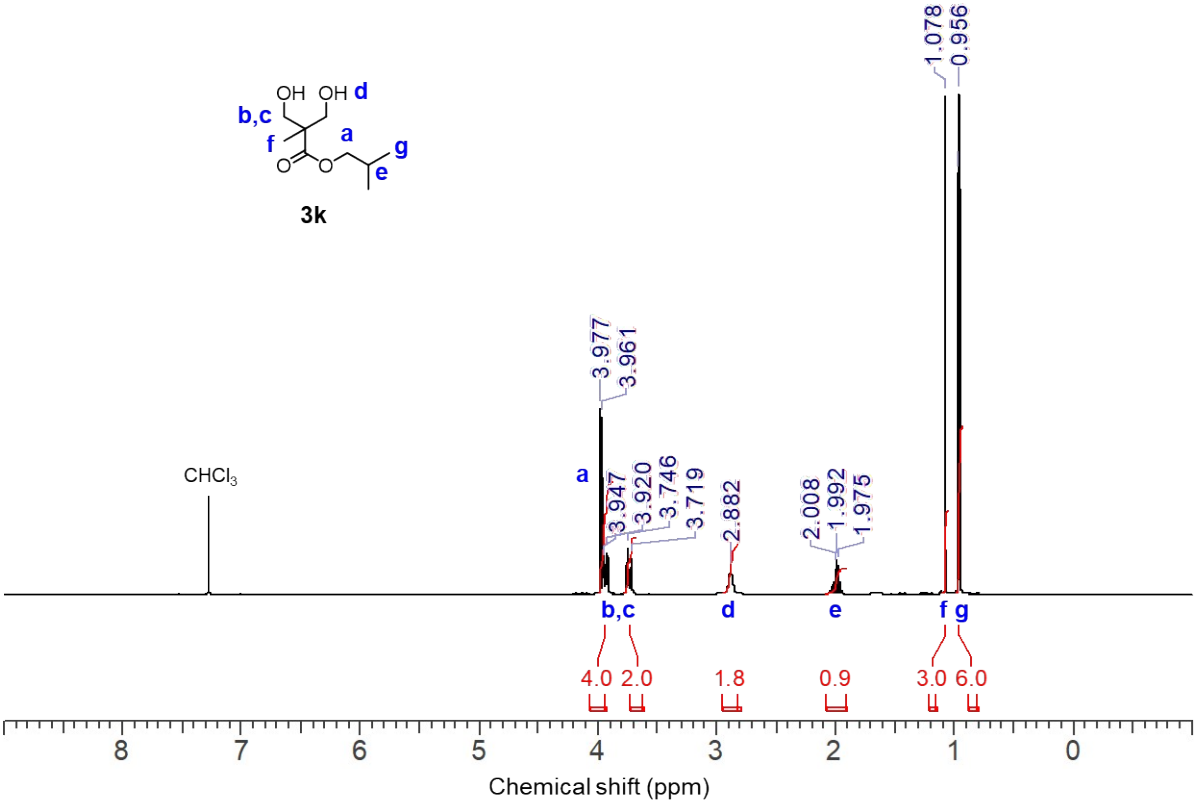
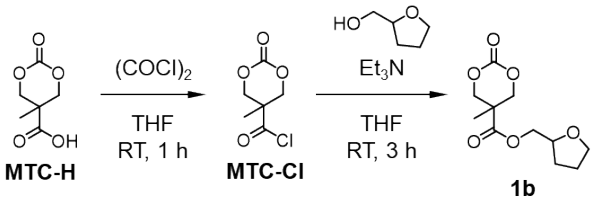


Figure S17. ^{1}H NMR spectrum of **3k** derived from **AC2** (400 MHz, $CDCl_3$).

Synthesis of 1b from MTC-H



MTC-H (1.0 g, 6.2 mmol) derived from **AC1** was dissolved in dry THF (40 mL) under a nitrogen atmosphere. Oxalyl chloride (1.18 g, 9.3 mmol) was dissolved in dry THF (15 mL) and slowly added to the MTC-H solution through an addition funnel. The obtained mixture was stirred at 25 °C for 1 h, degassed, and evaporated. The residue was dried under vacuum and used in the subsequent reaction without purification (MTC-Cl). Tetrahydrofurfuryl alcohol (0.64 g, 6.2 mmol) was dehydrated by CaH_2 in dry THF (15 mL) and then mixed with TEA (0.68 g, 6.8 mmol) after removing CaH_2 usiing a syringe filter (pore size: 0.45 μm; PTFE). MTC-Cl was dissolved in dry THF (20 mL) followed by the slow addition of the THF solution of the alcohol over 30 min. The obtained mixture was stirred at 25 °C for 3 h, filtered to remove precipitates, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate as an eluent to obtain a clear oil as **1b** (0.65 g, 43 %). ^{1}H NMR (400 MHz, acetone-d_6, δ): 4.67 (d, J = 10.4 Hz, 2H, C$\underline{H_a}$H$_b$), 4.38 (d, J = 10.4 Hz, 2H, CH$_a$$\underline{H_b}$), 4.23–4.02 (m, 3H, COOC$\underline{H_2}$, COOCH$_2$C$\underline{H}$), 3.86–3.63 (m, 2H, CHOC$\underline{H_2}$), 2.03–1.61 (m, 4H, CHC$\underline{H_2}$, CHCH$_2$C$\underline{H_2}$), 1.31 (s, 3H, C$\underline{H_3}$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.0, 147.4, 76.0, 72.9, 68.4, 67.6, 40.2, 27.8, 25.6, 17.5.

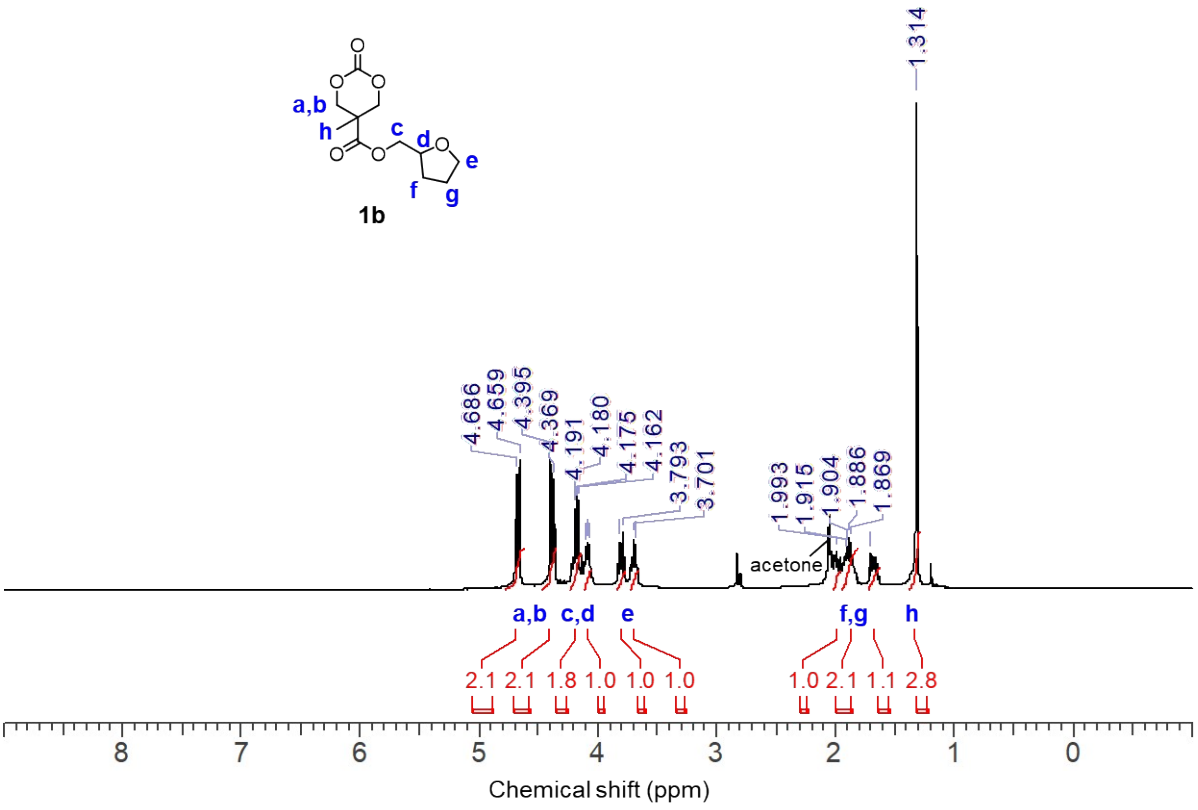


Figure S18. ^{1}H NMR spectrum of **1b** derived from MTC-H (400 MHz, acetone-d_6).

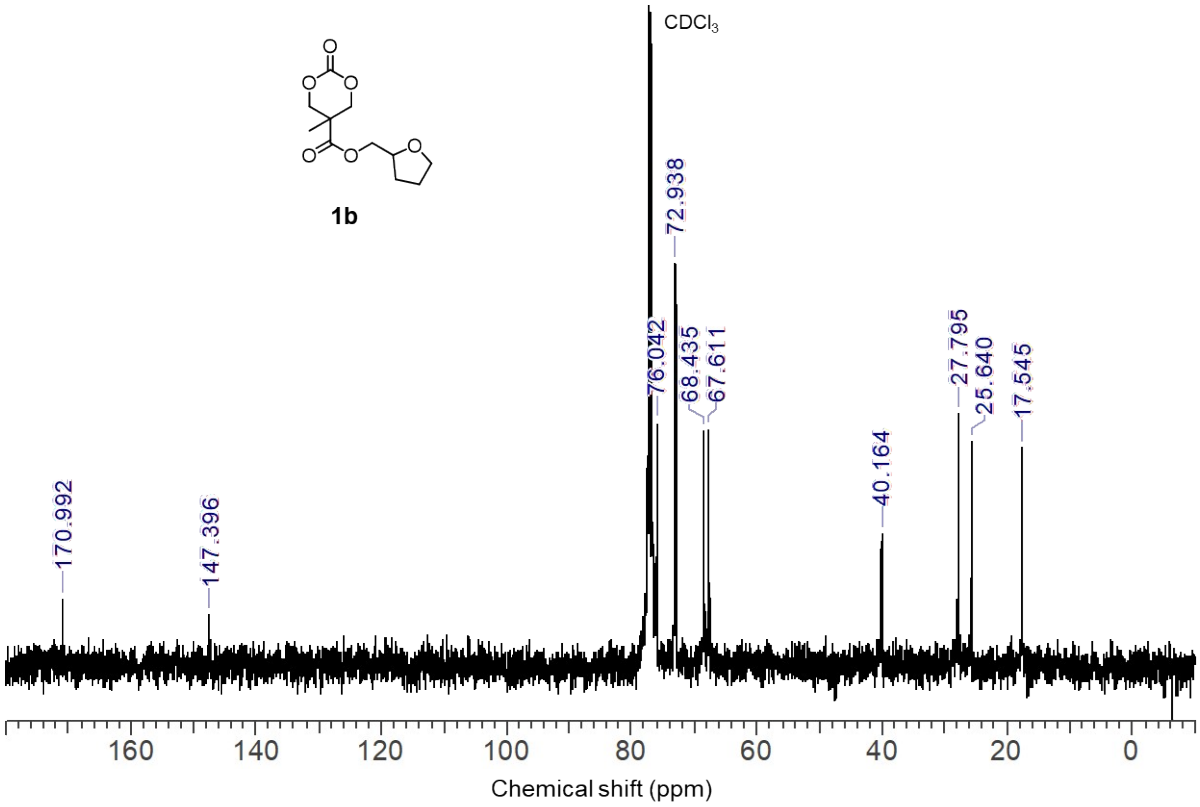
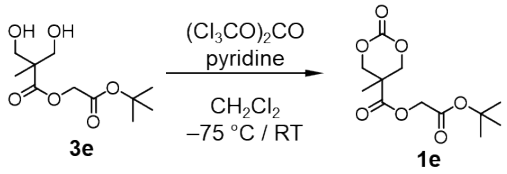


Figure S19. ^{13}C NMR spectrum of **1b** derived from MTC-H (100 MHz, $CDCl_3$).

Cyclization of bis-MPA esters 3 for synthesis of 1



Typical procedure: Synthesis of 1e. 3e (12.5 g, 50 mmol) was dissolved in dry CH_2Cl_2, and the resulting solution was chilled in a dry ice/2-propanol bath at approximately –75 °C. After pyridine (23.9 g, 0.3 mol) previously dehydrated over KOH was added to the flask, a dry CH_2Cl_2 solution (100 mL) of triphosgene (7.46 g, 25 mmol) was added dropwise to the mixtureover 1.5 h under a nitrogen atmosphere. The reaction mixture was warmed to 25 °C and stirred for 2 h. The reaction was terminated by the addition of a saturated NH_4Cl aqueous solution, and the organic layer was successively extracted with a 1 N HCl aqueous solution, a saturated $NaHCO_3$ aqueous solution, and brine. The organic layer was dried over $MgSO_4$, evaporated, and dried under vacuum to form a white solid, which was recrystallized from toluene (9.0 g, 65%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S9] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.76 (d, *J* = 10.9 Hz, 2H, C$\underline{H_a}$CH$_b$OCO), 4.60 (s, 2H, OC$\underline{H_2}$CO), 4.25 (d, *J* = 10.9 Hz, 2H, CH$_a$C$\underline{H_b}$OCO), 1.48 (s, 9H, *tert*-Bu), 1.44 (s, 3H, C$\underline{H_3}$).

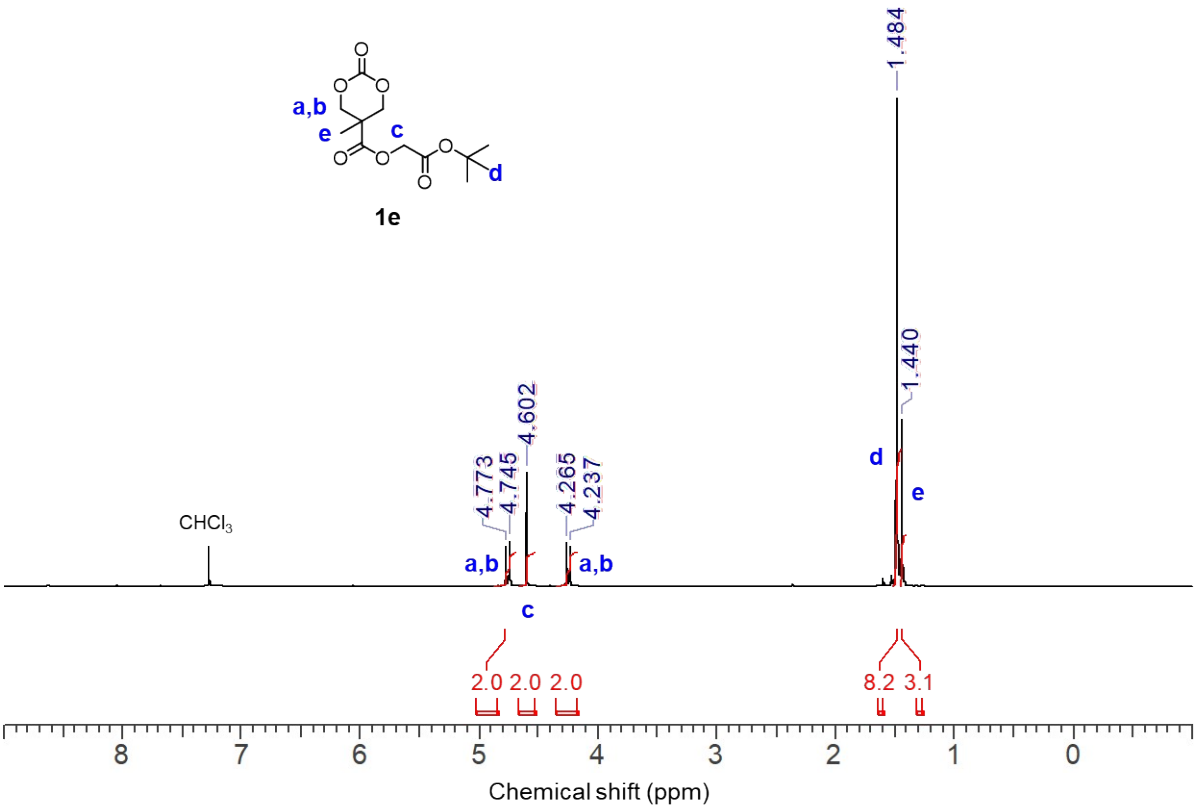
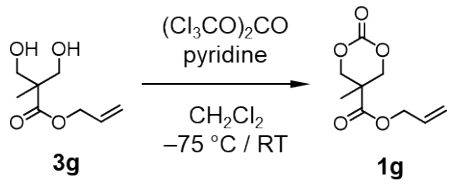


Figure S20. ^{1}H NMR spectrum of **1e** prepared from **3e** (400 MHz, $CDCl_3$).



1g. The reaction was performed as described above for **1e**, using **3g** (4.4 g, 25 mmol), pyridine (11.9 g, 0.15 mol), triphosgene (3.74 g, 12.6 mmol), and a certain volume of dry CH_2Cl_2 to maintain the same concentration (4.2 g, 83%). The obtained ^{1}H NMR spectrum matched that reported in the literature.[S10,S11] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.99–5.84 (m, 1H, C*H*=CH_2), 5.41–5.26 (m, 2H, CH=C*H*$_2$), 4.78–4.62 (m, 3H, OCOC*H*$_2$, C*H*$_a$H$_b$OCOO), 4.22 (d, 2H, *J* = 10.9 Hz, CH$_a$*H*$_b$OCOO), 1.37 (s, 3H, C*H*$_3$).

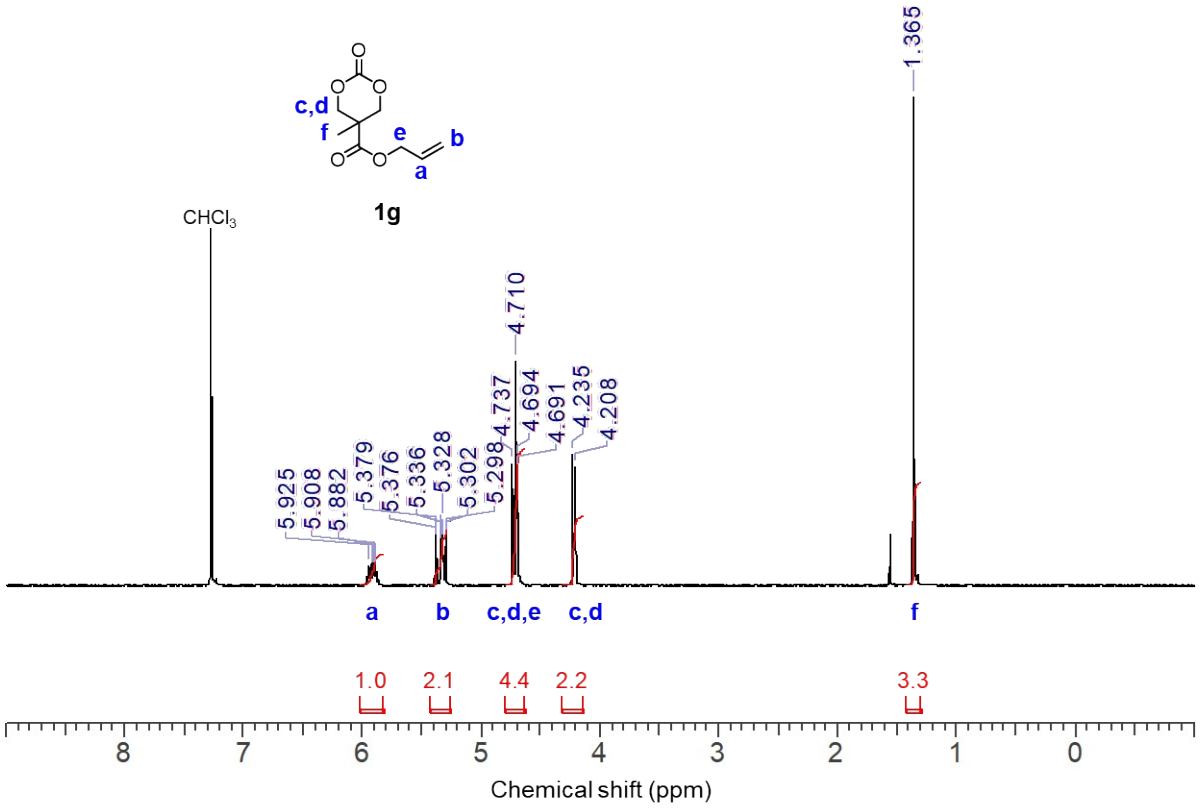
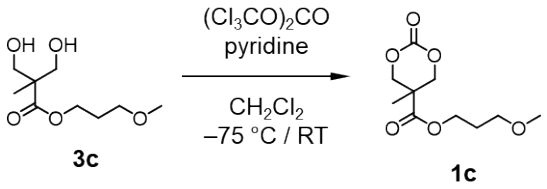


Figure S21. ^{1}H NMR spectrum of **1g** prepared from **3g** (400 MHz, $CDCl_3$).



1c. The reaction was performed as described above for **1e**, using **3c** (1.06 g, 4.9 mmol), pyridine (2.3 g, 29 mol), triphosgene (0.72 g, 2.4 mmol), and a certain volume of dry CH_2Cl_2 to maintain the same concentration. The crude product was purified by silica gel column chromatography using EtOAc as an eluent (0.76 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.70 (d, 2H, *J* = 10.5 Hz, CH_aH$_b$OCOO), 4.32 (t, 2H, *J* = 6.4 Hz, OCOCH_2), 4.221 (d, 2H, *J* = 11.0 Hz, CH_aH$_b$OCOO), 3.45 (t, 2H, *J* = 6.2 Hz, OCH_2), 3.34 (s, 3H, OCH_3), 1.94 (quin, *J* = 6.3 Hz, 2H, CH_2), 1.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.0, 147.4, 73.0, 68.7, 63.5, 58.7, 40.1, 28.7, 17.5.

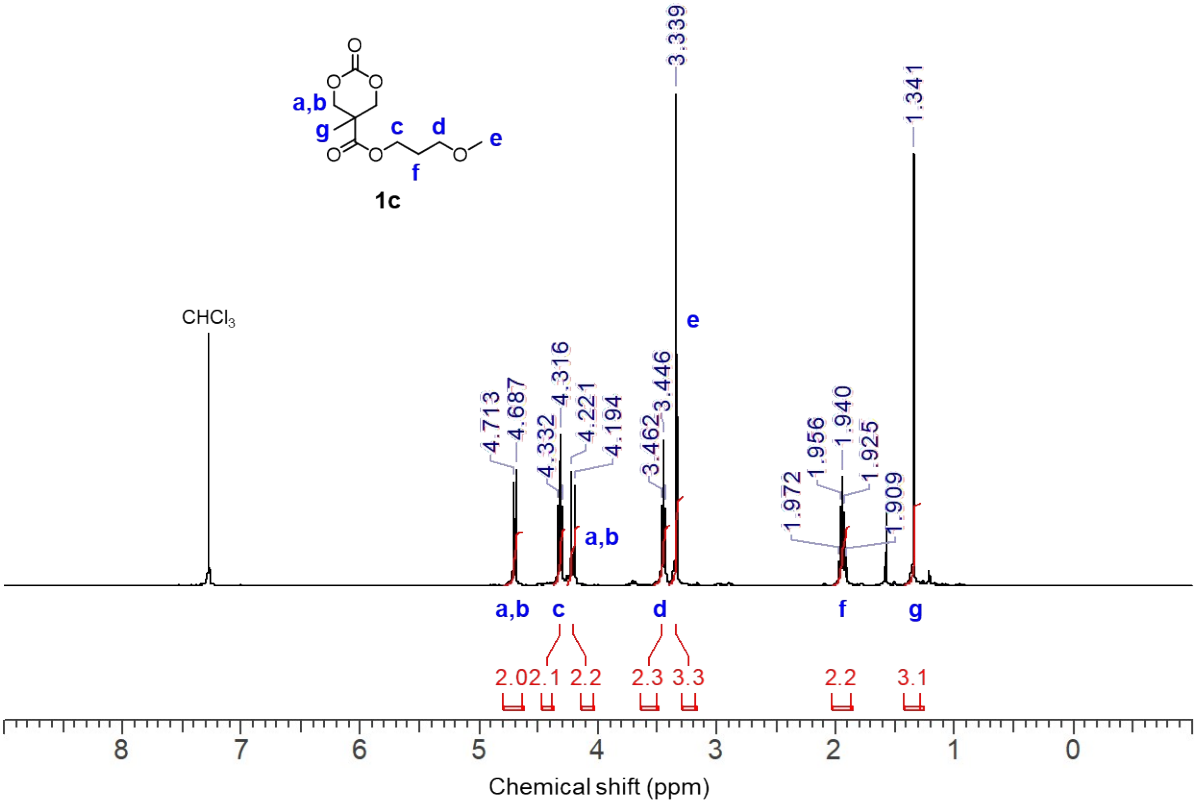


Figure S22. ^{1}H NMR spectrum of **1c** prepared from **3c** (400 MHz, $CDCl_3$).

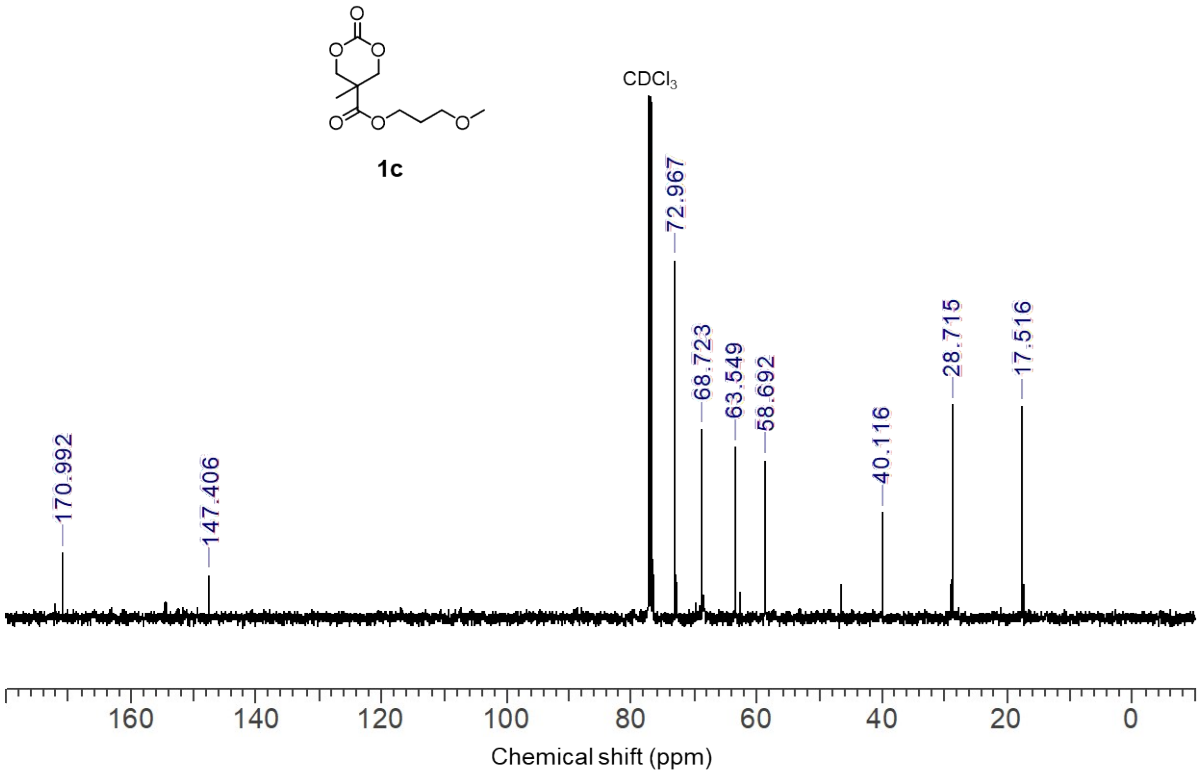
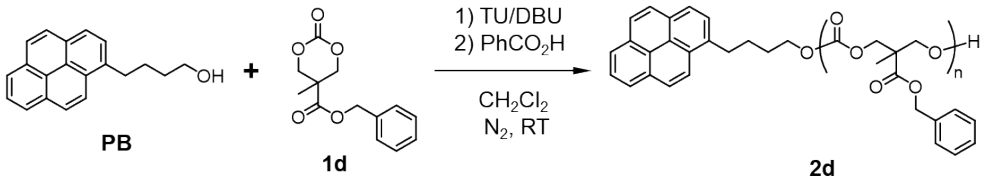


Figure S23. ^{13}C NMR spectrum of **1c** prepared from **3c** (100 MHz, $CDCl_3$).

Organocatalytic ring-opening polymerization of functionalized cyclic carbonates 1



Typical procedure: Ring-opening polymerization (ROP) of 1d. 1d (255 mg, 1.0 mmol) was dissolved in dry CH_2Cl_2 (1.0 mL) and dehydrated by CaH_2 for 30 min prior to polymerization. After CaH_2 was removed using a syringe filter (pore size: 0.45 μm; PTFE), PB (5.5 mg, 0.02 mmol), TU catalyst (18 mg, 0.05 mmol), and DBU (7.3 mg, 0.05 mmol) were added to the monomer solution. The resulting mixture was stirred for 5.5 h at 25 °C, quenched with benzoic acid, and precipitated in 2-propanol to form a clear viscous material as **2d**. SEC (THF, 40 °C, PS standards): M_n 14,400 g mol^{-1}, $Đ_M$ 1.25. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.37–7.28 (m, 350H, Ar-*H*), 5.13 (s, 141H, Ar-C*H*$_2$), 4.34–4.22 (m, 273H, C*H*$_2$), 1.23 (s, 214H, C*H*$_3$).

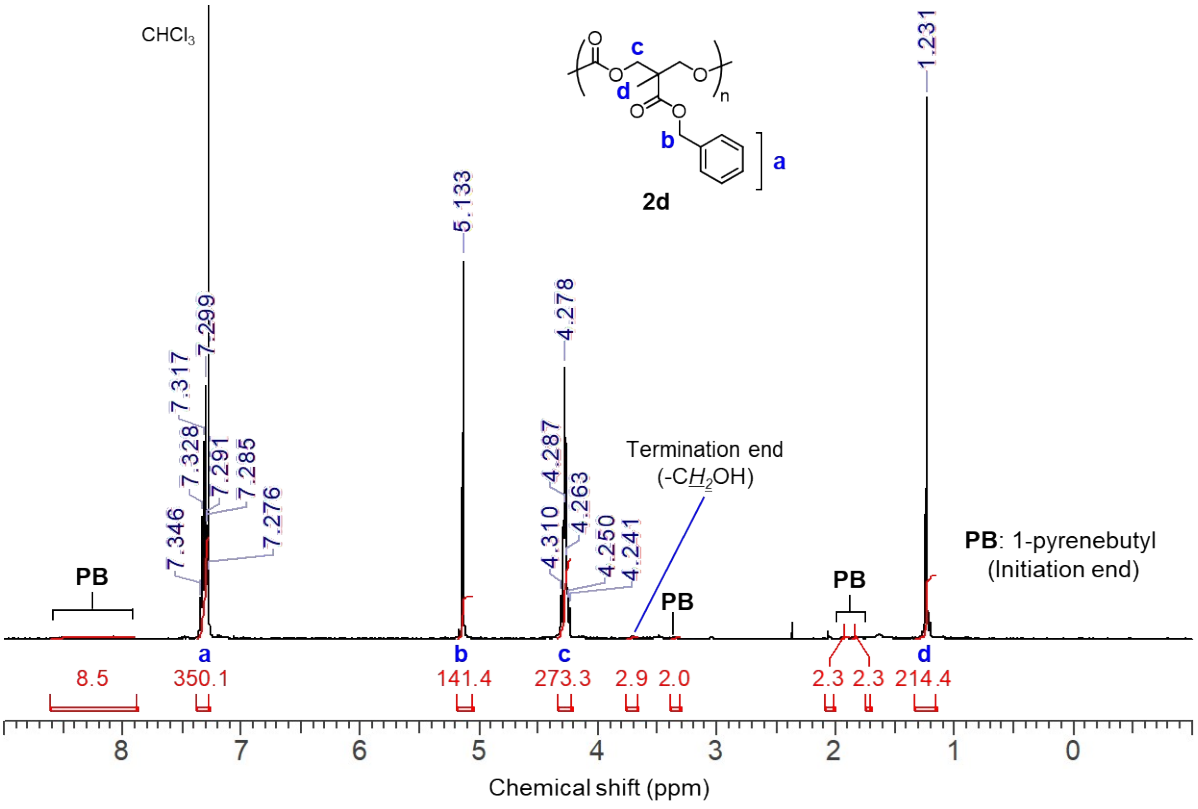
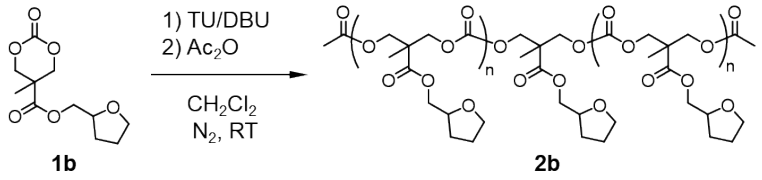


Figure S24. ^{1}H NMR spectrum of **2d** (500 MHz, $CDCl_3$).



ROP of 1b. Polymerization was performed as described above for **1d** without initiator, using **1b** (300 mg, 1.23 mmol), TU (22 mg, 0.06 mmol), DBU (14 mg, 0.06 mmol), and dry CH_2Cl_2 (2 mL). The reaction was quenched with acetic anhydride (25 mg, 0.24 mmol) at 34 h (225 mg, 75%). SEC (THF, 40 °C, PS standards): M_n 11,000 g mol^{-1}, $Đ_M$ 1.12. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.38–4.25 (m, 121H, OCOOC*H*$_2$), 4.20–4.07 (m, 97H, COOC*H*$_2$, OC*H*), 3.90–3.74 (m, 65H, OC*H*$_2$), 2.06 (s, 6H, COC*H*$_3$), 2.05–1.84 (m, 97H, C*H*$_2$), 1.68–1.58 (m, 36H, C*H*$_2$), 1.28 (s, 93H, C*H*$_3$).

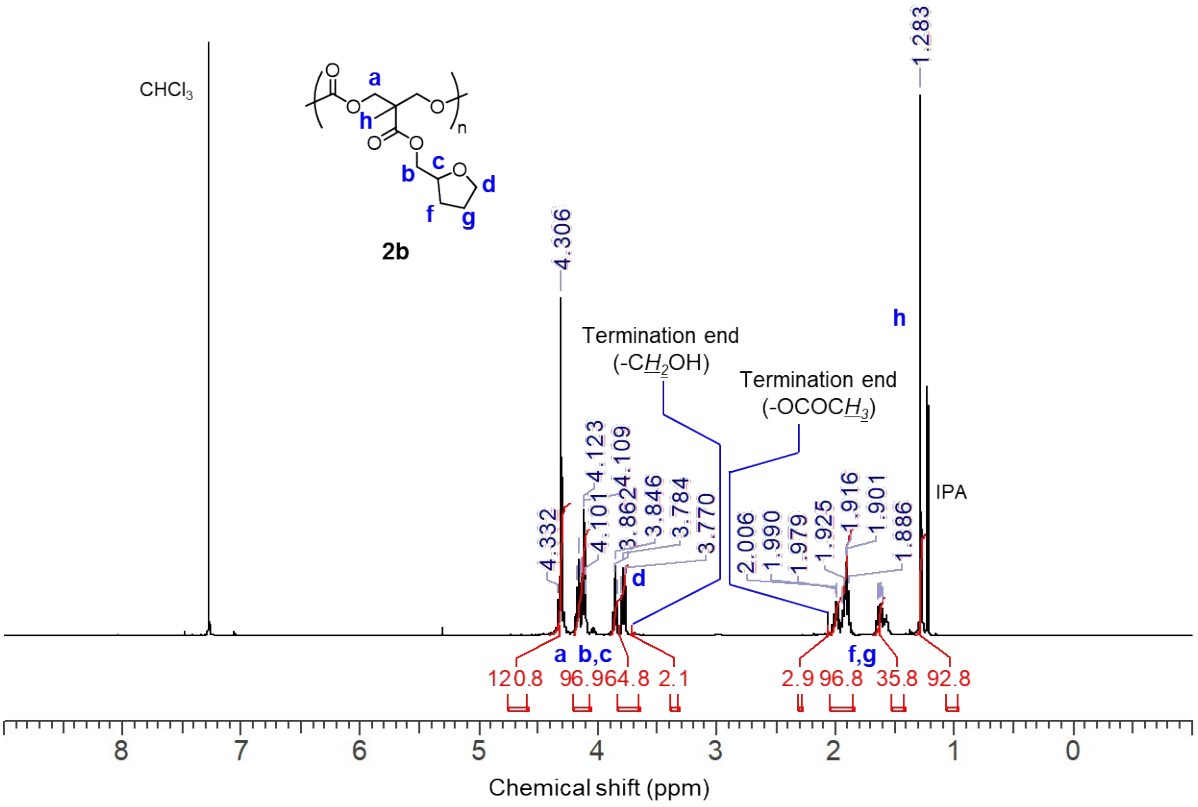
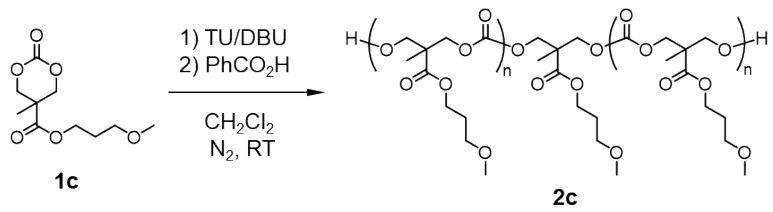


Figure S25. ^{1}H NMR spectrum of **2b** (500 MHz, $CDCl_3$).



ROP of 1c. Polymerization was performed as described above for **1d** without initiator, using **1c** (301 mg, 1.3 mmol), TU (9.6 mg, 0.026 mmol), DBU (4.0 mg, 0.026 mmol), and dry CH_2Cl_2 (1.3 mL). The reaction was finished in 2 h (243 mg, 81%). SEC (THF, 40 °C, PS standards): M_n 14,000 g mol^{-1}, $Đ_M$ 1.09. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.38–4.17 (m, 195H, C*H*$_2$OCOO, OCOC*H*$_2$), 3.43 (t, 67H, *J* = 6.0 Hz, OC*H*$_2$), 3.33 (s, 105H, OC*H*$_3$), 1.95–1.85 (m, 69H, C*H*$_2$), 1.26 (s, 107H, C*H*$_3$).

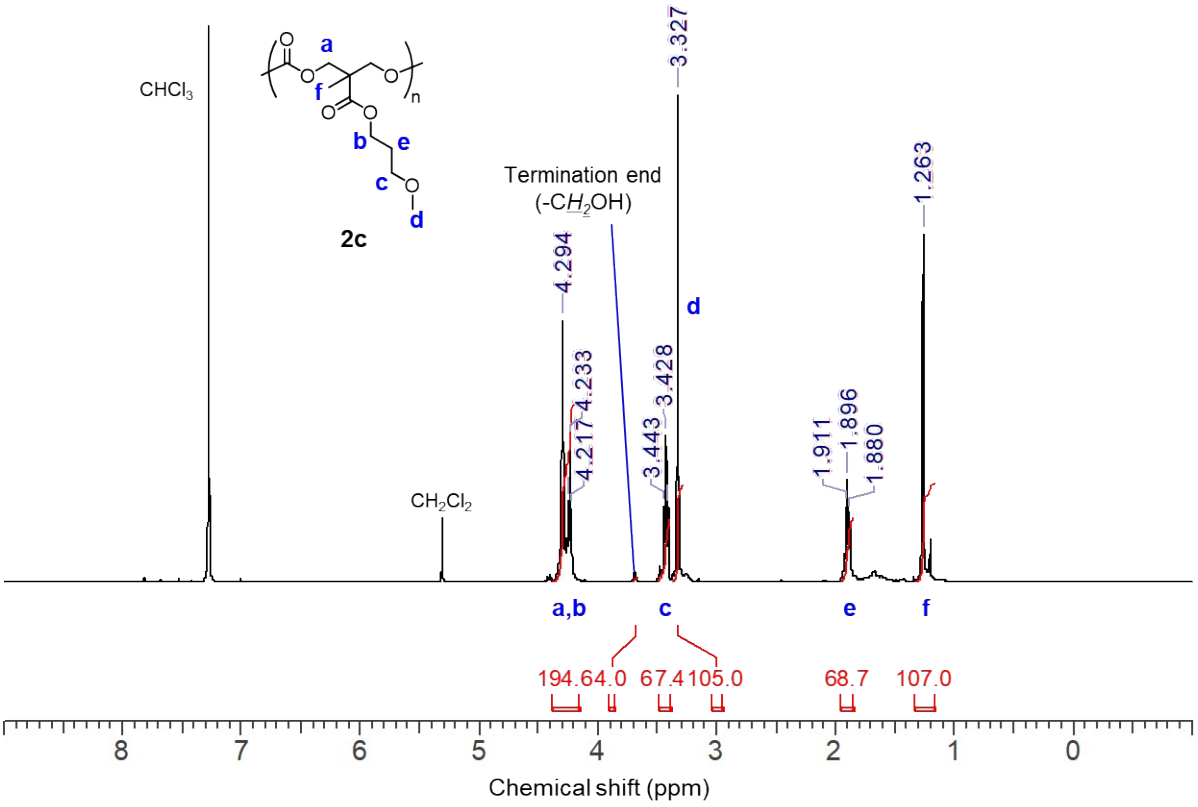
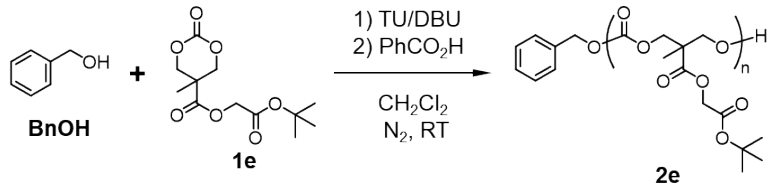


Figure S26. ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$).



ROP of 1e. Polymerization was performed as described above for **1d**, using BnOH (2.9 mg, 0.036 mmol), **1e** (1.0 g, 3.6 mmol), TU (67 mg, 0.18 mmol), DBU (28 mg, 0.18 mmol), and dry CH_2Cl_2 (4.0 mL). The reaction was finished in 1.5 h (0.73 g, 73%). SEC (THF, 40 °C, PS standards): M_n 9,700 g mol^{-1}, $Đ_M$ 1.26. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.54 (s, 78H, OC*H*$_2$CO). 4.43–4.27 (m, 163H, C*H*$_2$), 1.47 (s, 376H, *tert*-Bu), 1.34 (s, 128H, C*H*$_3$).

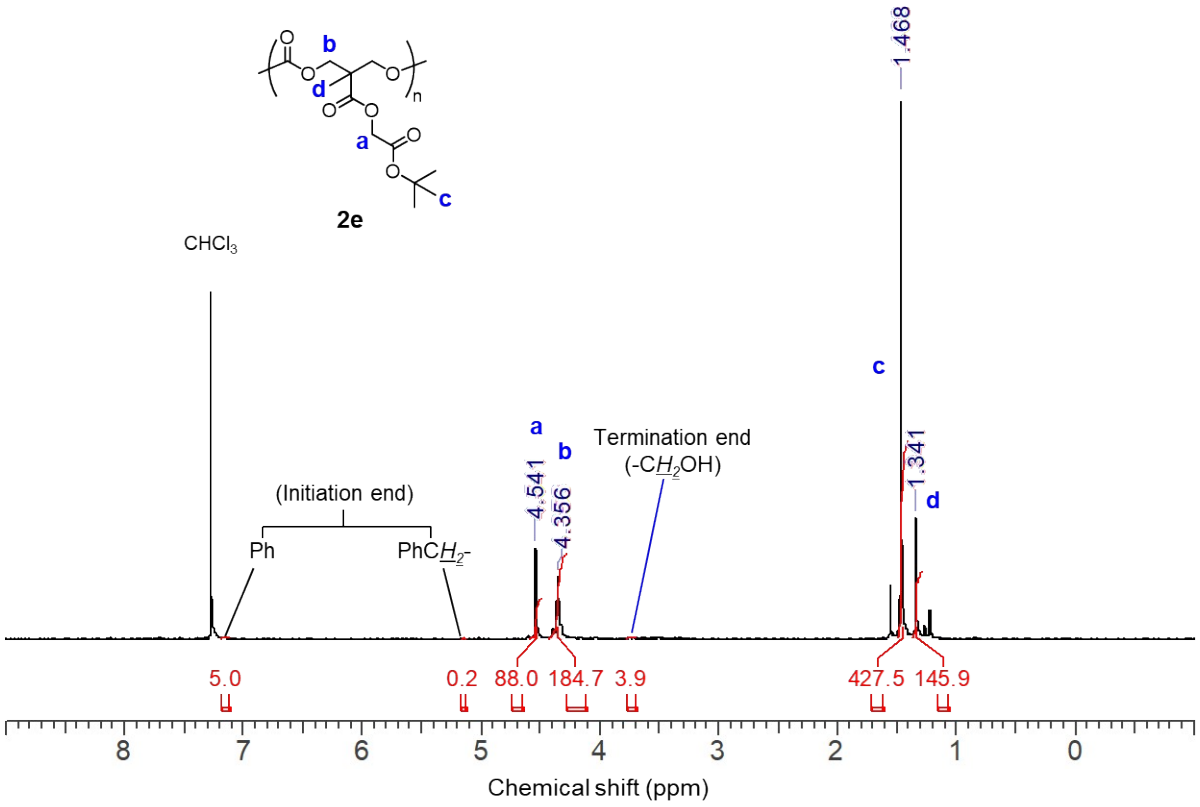
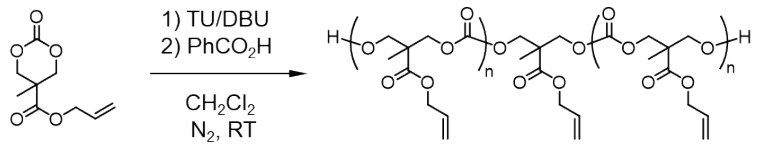


Figure S27. ^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$).



1g **2g-i**

ROP of 1g (i). Polymerization was performed as described above for **1c**, using **1g** prepared from **3g** (800 mg, 4.0 mmol), TU (30 mg, 0.08 mmol), DBU (12 mg, 0.08 mmol), and dry CH_2Cl_2 (4.0 mL). The reaction was finished in 1 h (694 mg, 85%). SEC (THF, 40 °C, PS standards): M_n 23,600 g mol^{-1}, $Đ_M$ 1.12. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.95–5.83 (m, 105H, C*H*=CH_2), 5.36–5.21 (m, 241H, CH=C*H*$_2$), 4.64 (d, 218H, *J* = 5.6 Hz, COOC*H*$_2$), 4.37–4.25 (m, 425H, C*H*$_2$OCOO), 1.28 (s, 333H, C*H*$_3$).

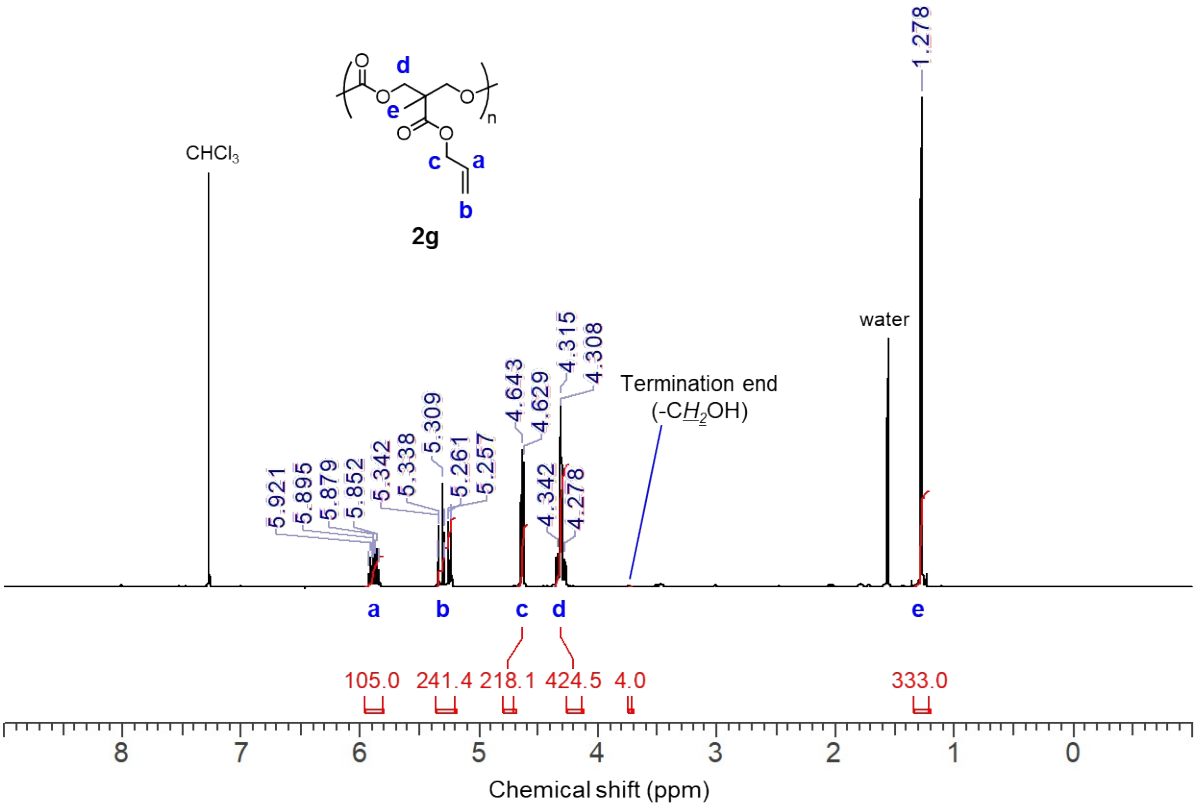
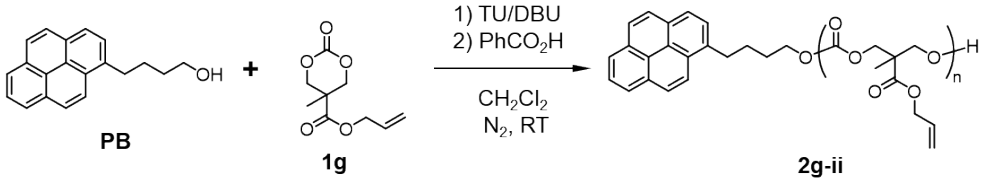


Figure S28. ^{1}H NMR spectrum of **2g-i** (400 MHz, $CDCl_3$).



ROP of 1g (ii). Polymerization was performed as described above for **1d**, using **1g** prepared from **AC1** (111 mg, 0.56 mmol), PB (3.0 mg, 0.011 mmol), TU (10 mg, 0.028 mmol), DBU (4.1 mg, 0.027 mmol), and dry CH_2Cl_2 (0.4 mL). The reaction mixture was stirred for 8.5 h. SEC (THF, 40 °C, PS standards): M_n 13,200 g mol^{-1}, $Đ_M$ 1.56. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.95–5.83 (m, 56H, C*H*=CH_2), 5.36–5.21 (m, 115H, CH=C*H*$_2$), 4.64 (d, 118H, J = 5.6 Hz, COOC*H*$_2$), 4.37–4.25 (m, 300H, C*H*$_2$OCOO), 1.28 (s, 181H, C*H*$_3$).

Estimation of degrees of polymerization (DPs) of resultant polymers. The DPs of the resultant polycarbonates were estimated from the integral values of the polymer main chains and the termination end groups in the ^{1}H NMR spectra. The signals for methylene neighboring hydroxy terminal groups and for acetyl terminal groups appear around 3.7 and 2.1 ppm, respectively. When alcohol initiators were used, NMR signals for the initiation end can be observed. However, the integral values were often less than those of the termination end, indicating concomitant initiation by impurities such as water and decarbonylated (or unreacted) diols derived from monomers. We assumed that the polymer chains initiated by the impurities have termination ends at both ends. In this case, the integral values of the termination end were regarded as the sum of those for polymer chains with single and double termination ends.

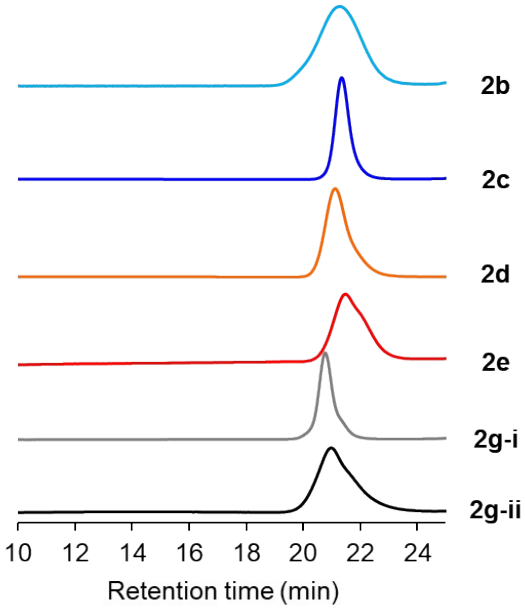


Figure S29. SEC traces of ROP products (THF, 40 °C).

Note for Fig. S29.

Measurements of **2b** were performed using a different SEC system with a different set of columns and settings.

Platelet adhesion tests

Platelet adhesion tests were performed using spin-coated substrates as described elsewhere.[S13,S14] Briefly, the synthesized polymers were immersed in Miili-Q water for 24 h to eluviate water-soluble impurities and dried under vacuum prior to spin coating. Afterwards, $CHCl_3$ solutions of the polymers with concentrations of 0.2 wt./v% (40 μL) were spin-coated on poly(ethylene terephthalate) (PET) sheets (φ: 14 mm; thickness: 125 μm; Mitsubishi Plastics, Tokyo, Japan) at 500 rpm for 5 s, 2000 rpm for 10 s, a slope of 5 s, 4000 rpm for 5 s, and a slope of 4 s. The spin-coated substrates were dried in air for 10 min and re-coated via the same procedure.

The polymer-coated substrates, which were cut into squares with sizes of 8 mm, were sterilized by UV light on a clean bench for 2 h before use. Human whole blood purchased from Bizcom Japan (Tokyo, Japan) was centrifuged to obtain platelet-rich plasma (PRP) and platelet-poor plasma (PPP). The PRP and PPP were mixed to prepare platelet suspension plasma with a platelet concentration of 4×10^7 cells cm^{-2}. This plasma (200 μL) was applied to the polymer-coated substrates, which were subsequently incubated for 1 h at 37 °C. After washing with phosphate-buffered saline (PBS) twice, the substrates were immersed in a PBS solution containing 1 wt.% glutaraldehyde for 2 h at 37 °C to fix the adherent platelets. The fixed samples were immersed in PBS for 10 min and then twice in a 1:1 mixture of PBS and Milli-Q water for 8 min. The immersed samples were washed with Milli-Q water and dried in air overnight. The air-

dried samples were sputter-coated with Pt–Pd (JFC-1200, JEOL) prior to observations by scanning electron microscopy (SEM; VE-9800, KEYENCE, Tokyo, Japan) conducted at accelerating voltages of 3–5 keV. The tests for **2b** and **2c** were conducted independently, using different platelet suspensions.

During SEM observations, at least five images were randomly captured for each sample. Representative images of the platelets adhered to the polymer-coated substrates are shown in Figure S30. The adhered platelets were visually counted and then averaged to calculate the cell numbers per square centimeter for a quantitative analysis (Figure 4). For the evaluation of **2b**, two substrates were used for each polymer. The average cell numbers were calculated from the counted values in 10 images (2 substrates × 5 images). The same tests were repeated two more times to verify the reproducibility of the obtained data (see Figure 4a). For the evaluation of **2c**, three substrates were used for each polymer, and the average cell numbers were computed from 15 images (3 substrates × 5 images). The obtained results are summarized in Figure 4b. All data points were represented as the mean ± standard deviation. Statistical analyses included the analysis of variance (F-test) and Student's t-test conducted using Microsoft Excel in Microsoft 365. In all tests, $p < 0.05$ was used as a statistical significance criterion.

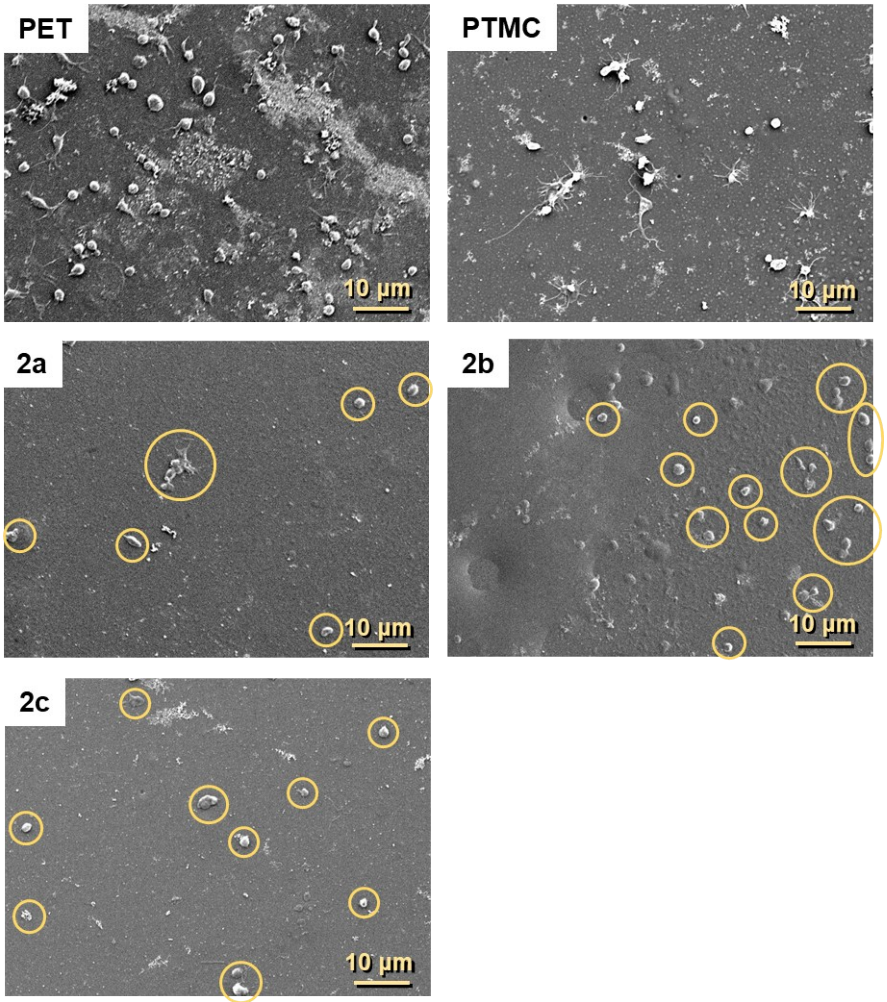


Figure S30. Representative SEM images of the platelets adhered to the polymer substrates. The circles highlight the adhered platelets on **2a**–**2c**.

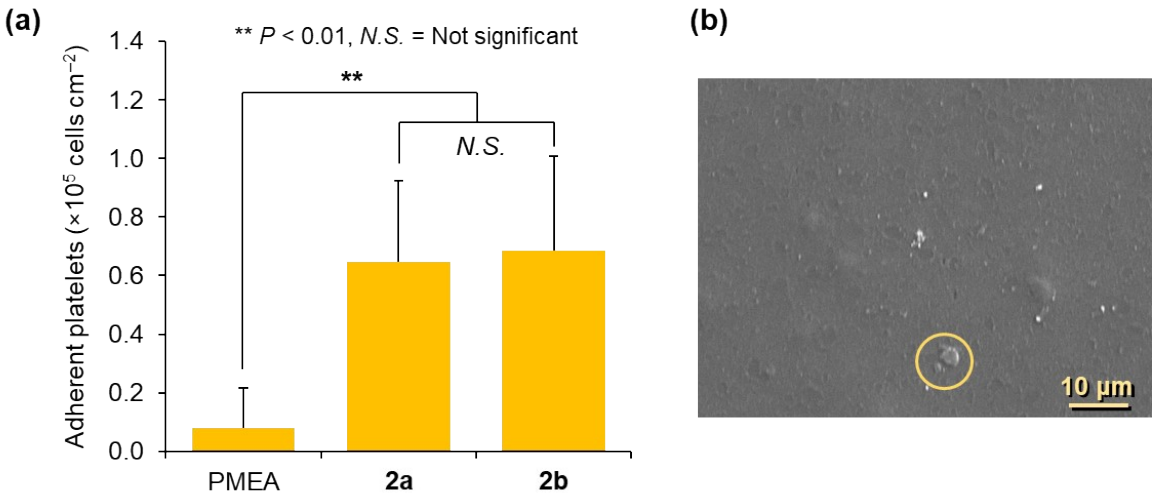


Figure S31. (a) Numbers of adherent platelets on the polymer-coated substrates displayed as mean values with standard deviations (n = 10; 2 substrates × 5 points per polymer). PMEA: poly(2-methoxyethyl acrylate). (b) Representative SEM image of the platelets adhered to PMEA. The circle highlights the adhered platelets.

Note for Fig. S31a.

PMEA (M_n 22 kg mol^{-1}, $Đ_M$ 2.8) was synthesized by free-radical polymerization and dissolved in methanol (0.2 wt./v%) for spin-coating on the PET sheets as previously reported.[S13]

References

S1. R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. Li, C. G. Wade, R. M. Waymouth, and J. L. Hedrick, *Macromolecules*, 2006, **39**, 7863–7871.

S2. Y. Chiang and E. B. Whipple, *J. Am. Chem. Soc.*, 1963, **85**, 2763–2767.

S3. D. Dolman and R. Stewart, *Can. J. Chem*., 1967, **45**, 903–910.

S4. A. Albert, R. Goldacre and J. Phillips, *J. Chem. Soc.*, 1948, 2240–2249.

S5. H. K. Hall, *J. Am. Chem. Soc.*, 1957, **79**, 5441–5444.

S6. D. D. Perrin, *Dissociation constants of organic bases in aqueous solution*, Butterworths, London, 1965, Supplement 1972.

S7. A. J. Cruz-Cabeza, *CrystEngComm*, 2012, **14**, 6362–6365.

S8. R. C. Pratt, F. Nederberg, R. M. Waymouth and J. L. Hedrick, *Chem. Commun.*, 2008, 114–116.

S9. C. Bartolini, L. Mespouille, I. Verbruggen, R. Willem and P. Dubois, *Soft Matter*, 2011, **7**, 9628–9637.

S10. D. P. Sanders, K. Fukushima, D. J. Coady, A. Nelson, M. Fujiwara, M. Yasumoto and J. L. Hedrick, *J. Am. Chem. Soc.* 2010, **132**, 14724–14726.

S11. S. Tempelaar, L. Mespouille, P. Dubois and A. P. Dove, *Macromolecules*, 2011, **44**, 2084–2091.

S12. Z. Xie, X. Hu, X. Chen, J. Sun, Q. Shi and X. Jing, *Biomacromolecules*, 2008, **9**, 376–380.

S13. K. Fukushima, Y. Inoue, Y. Haga, T. Ota, K. Honda, C. Sato and M. Tanaka, *Biomacromolecules*, 2017, **18**, 3834–3843.

S14. V. Montagna, J. Takahashi, M.-Y. Tsai, T. Ota, N. Zivic, S. Kawaguchi, T. Kato, M. Tanaka, H. Sardon and K. Fukushima, *ACS Biomater. Sci. Eng.*, 2021, **7**, 472–481.