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Supplementary Information for

Organocatalyzed ring-opening reactions of *γ*-carbonyl-substituted *ε*-caprolactones

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Contents:

Experimental section

Materials

Ethyl 4-oxocyclohexanecarboxylate (**3**; 98%), diphenyl phosphate (DPP; 99.0%), benzyl alcohol (**A_3**, >99.0%), and ε-caprolactone (CL; 98.0%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). 2-methoxyethanol (**A_2**, 99.8%), 2-methoxyethylamine (2MEA; 99.0%), Amberyst-15® (dry, moisture < 1.5%), *m*-chloroperoxybenzoic acid (*m*CPBA; 77%), 1-pyrenebutanol (**A_1**; 99%), 4-dodecylbenzenesulfonic acid (DBSA; 95%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; 98%), and (–)-sparteine (SP; 99%) were purchased from Sigma-Aldrich Japan (Tokyo, Japan). 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 99.0%) was purchased from Kanto Chemical (Tokyo, Japan). Triethylamine (99.0%), *p*-toluenesulfonic acid monohydrate (PTSA; 99.0%), and stannous 2-ethyl hexanoate ($Sn(Oct)_2$; 96%) were purchased from Wako Pure Chemical (Tokyo, Japan). Dehydrated tetrahydrofuran (THF) and dichloromethane were supplied by a solvent supply system (Kanto Chemical, water content < 10 ppm). 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (TU) was synthesized as reported in a previous study[S1] and dried using calcium hydride (CaH_2). CL, benzyl alcohol, DBU, and SP were distilled over CaH_2 before use.

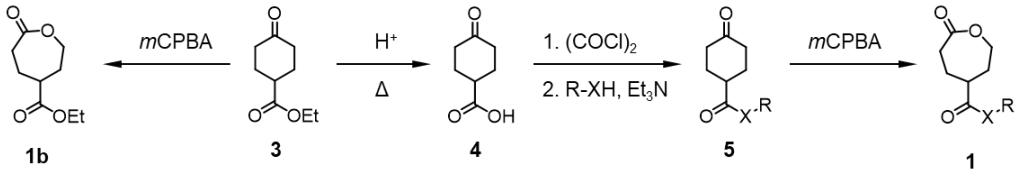
Methods

^1H and ^{13}C NMR spectroscopies were performed on JEOL JNM-ECA 400 and JNM-EC500 operating at 400/100 and 500/125 MHz, respectively. Size exclusion chromatography (SEC) in THF was performed at 30 °C with a flow rate of 1.0 mL min^{-1} using an integrated SEC unit of Tosoh HLC-8220 GPC equipped with three TSK-gel columns connected in series (super AW5000, AW4000, and AW3000) and a refractive index (RI) detector. The number-average molecular weight (M_n) and molar-mass dispersity ($Đ_M$) were calibrated using polystyrene (PS) standards (Tosoh TSK Standard Polystyrene; M_w = 2.6 × 10^3, 6.0 × 10^3, 1.0 × 10^4, 1.8 × 10^4, 9.6 × 10^4, 1.9 × 10^5, 4.3 × 10^5, 7.1 × 10^5, and 1.1 × 10^6 g mol^{-1}). The SEC measurement in DMF containing 10 mM LiBr, was also conducted at 40 °C with a flow rate of 1.0 mL min^{-1} using a Tosoh HPLC HLC-8220 system equipped with RI and ultraviolet detectors and four TSK-gel columns consecutively connected (*α*-M, *α*-4000, *α*-3000, and *α*-2500). The same PS standards were used for the calculation of M_n and $Đ_M$. Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded using a HORIBA spectrometer FT-720 in transmission mode. Specimens were prepared by solvent-casting on a KBr plate.

Synthesis of γ-carbonyl-functionalized ε-caprolactones

The synthesis procedure for **1** followed in this study is provided in a previous report,[S2] modifying a step in the synthesis of **5**.

Scheme S1. Synthesis of γ-carbonyl functionalized seven-membered lactones **1a**–**c**.



1a, 5a:
X = O, R = -$(CH_2)_2OCH_3$
1c, 5c:
X = NH, R = -$(CH_2)_2OCH_3$

Synthesis of 4-oxocyclohexanecarboxylic acid (4)

Compound **3** (5.00 g, 29.0 mmol) was dispersed in a 2% H_2SO_4 aqueous solution (100 mL), and the mixture was refluxed for 5 h. Then, the reaction mixture was washed with ethyl acetate (100 mL) twice. The organic layer was dried over $MgSO_4$ and evaporated. The residue was then dispersed in hexane (150 mL) for 1 h and filtered. After vacuum drying, white solid was obtained as **4** (3.76 g, 84.2%), and the product was used directly in the subsequent step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88–2.77 (m, C*H*, 1H), 2.57–2.47 (m, COC*H*$_a$H$_b$, 2H), 2.44–2.33 (m, COCH$_a$*H*$_b$, 2H), 2.31–2.21 (m, C*H*$_a$H$_b$, 2H), 2.14–2.01 (m, CH$_a$*H*$_b$, 2H).

Synthesis of 2-methoxyethyl 4-oxocyclohexanecarboxylate (5a)

A few drops of DMF were added to a solution of **4** (5.68 g, 40.0 mmol) in dehydrated THF (100 mL). Then, oxalyl chloride (4.2 mL, 48 mmol) was added dropwise to the solution at room temperature, and the mixture was stirred for 1 h under a N_2 atmosphere to form the acid chloride intermediate. Subsequently, a solution of 2-methoxyethanol (3.04 g, 40 mmol) and trimethylamine (2.4 equiv. to alcohol) in dehydrated THF (35 mL), which was previously further dried over CaH_2, was gradually added to the intermediate solution for 20 min, and the reaction mixture was stirred for another 1 h. After N_2 bubbling of the mixture to remove excess oxalyl chloride for 30 min, the precipitate was filtered out, and the filtrate was concentrated in vacuum. The concentrate was then dissolved in ethyl acetate and stirred with Amberyst-15 (4.0 g) for 1 h. The resin was filtered out, and the filtrate was dried in vacuum to obtain yellowish brown oil as **5a** (7.6 g, 95.0%). The product was used directly in the subsequent step without further purification. ^{1}H NMR (500MHz, $CDCl_3$): δ 4. 29 (t, *J* = 4.53 Hz, COOC*H*$_2$, 2H), 3.62 (t, *J* = 4.53 Hz, OC*H*$_2$, 2H), 3.40 (s, C*H*$_3$, 3H), 2.83–2.75 (m, C*H*, 1H), 2.52–2.42 (m, COC*H*$_a$H$_b$, 2H), 2.41–2.28 (m, COCH$_a$*H*$_b$, 2H), 2.27–2.17 (m, C*H*$_a$H$_b$, 2H), 2.09–1.95 (m, CH$_a$*H*$_b$, 2H).

Synthesis of 2-methoxyethyl 7-oxooxepane-4-carboxylate (1a)

A solution of *m*CPBA (18.1 g, 105 mmol) dissolved in chloroform (126 mL) was added to a chloroform solution (63 mL) of **5a** (12.6 g, 63 mmol), and the mixture was then heated at 65 °C for 2 h. The precipitate was filtered, and the filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (200 mL). The organic layer was dried over $MgSO_4$ and evaporated in

vacuum. The residue was purified using column chromatography using a mixture of ethyl acetate and hexane (5:1) as an eluent, followed by vacuum distillation over CaH_2 (0.5 mmHg, 150 °C) to obtain clear oil as **1a** (5.8 g, 42.6%). ^{1}H NMR (500MHz, $CDCl_3$): δ 4.41–4.34 (m, $COOC\underline{H_a}H_{b(ring)}$, 1H), 4.26 (t, *J* = 4.53 Hz, $COOC\underline{H_2}$, 2H), 4.22–4.14 (m, $COOCH_a\underline{H_{b(ring)}}$, 1H), 3.58 (t, *J* = 4.53 Hz, $OC\underline{H_2}$, 2H), 3.37 (s, $C\underline{H_3}$, 3H), 2.82–2.71 (m, CH, $COC\underline{H_a}H_b$, 2H), 2.64–2.57 (m, $COCH_a\underline{H_b}$, 1H), 2.22–2.15 (m, $COOCH_2\underline{H_a}H_{b(ring)}$, 1H), 2.14–2.05 (m, $COOCH_2H_a\underline{H_{b(ring)}}$, $COCH_2\underline{H_a}H_{b(ring)}$, 2H), 2.01–1.92(m, $COCH_2H_a\underline{H_{b(ring)}}$, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 173.5, 70.2, 66.5, 63.7, 58.9, 43.8, 32.0, 31.3, 24.7.

Synthesis of ethyl 7-oxooxepane-4-carboxylate (1b)

Compound **1b** was prepared using the same procedure as that of **1a** and purified by column chromatography using a mixture of ethyl acetate and n-hexane (3:7) as an eluent (3.22g 54%). ^{1}H NMR (500MHz, $CDCl_3$): δ 4.42–4.34 (m, $COOC\underline{H_a}H_{b(ring)}$, 1H), 4.24–4.11 (m, $COOCH_a\underline{H_{b(ring)}}$, $OC\underline{H_2}$, 3H), 2.83–2.76 (m, $COC\underline{H_a}H_{b(ring)}$, 1H), 2.70 (sep, *J* = 4.13 Hz, $C\underline{H}$, 1H), 2.66–2.59 (m, $COCH_a\underline{H_{b(ring)}}$, 1H), 2.23–2.07 (m, $COOCH_2\underline{H_{2(ring)}}$, $COCH_2\underline{H_a}H_{b(ring)}$, 3H), 2.02–1.93 (m, $COCH_2H_a\underline{H_{b(ring)}}$, 1H), 1.28 (t, *J* = 7.23 Hz, $C\underline{H_3}$, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.8, 172.9, 66.5, 60.7, 38.5, 31.8, 28.9, 25.6, 14.3.

Synthesis of *N*-(2-methoxyethyl)-4-oxocyclohexanecarboxamide (5c)

Compound **5c** was prepared by the same procedure as that of **5a** using 2-methoxyethylamide instead of 2-methoxyethanol. (8.8 g, 88.4%). ^{1}H NMR (400MHz, $CDCl_3$): δ 5.99-5.81 (br, $N\underline{H}$, 1H), 3.48 (s, $NHC\underline{H_2}$, $OC\underline{H_2}$, 4H), 3.38 (s, $C\underline{H_3}$, 3H), 2.65–2.48 (m, $COC\underline{H_a}H_b$, $C\underline{H}$, 3H), 2.42–2.29 (m, $COH_a\underline{H_b}$, 2H), 2.25–2.12 (m, $COCH_2\underline{H_a}H_b$, 2H), 2.11–1.95 (m, $COCH_2H_a\underline{H_b}$, 2H).

Synthesis of *N*-(2-methoxyethyl)-7-oxooxepane-4-carboxamine (1c)

A solution of *m*CPBA (6.38 g, 37 mmol) in chloroform (66 mL) was added to a chloroform solution (63 mL) of **5c** (4.4 g, 22 mmol), and the mixture was heated at 65 °C for 2 h. Then, the precipitate was filtered, and the filtrate was evaporated in vacuum. Diethyl ether was added to the residue, and the mixture was stirred and filtered. The residue was then recrystallized from toluene to form **1c** (2.3 g, 48.4%). ^{1}H NMR (500MHz, $CDCl_3$): δ 5.98–5.83(s, $N\underline{H}$, 1H), 4.55–4.43 (m, $COOC\underline{H_a}H_b$, 1H), 4.24–4.13 (m, $COOH_a\underline{H_b}$, 1H), 3.46 (s, $NHC\underline{H_2}$, $OC\underline{H_2}$, 4H), 3.36 (s, $C\underline{H_3}$, 3H), 2.95–2.85 (m, $COC\underline{H_a}H_b$, 1H), 2.67–2.56 (m, $COH_a\underline{H_b}$, 1H), 2.46 (sep, *J* = 4.62 Hz, $C\underline{H}$, 1H), 2.18–2.00 (m, $COOCH_2C\underline{H_2}$, $COCH_2C\underline{H_a}H_b$, 3H), 1.99–1.87 (m, $COCH_2H_a\underline{H_b}$, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.2, 173.6, 70.9, 66.8, 58.7, 45.9, 39.1, 32.2, 32.0, 25.7.

General procedure for ring-opening reactions of 1

In a nitrogen-filled glove box, **1** (1.0 mmol), $\mathbf{A_1}$ (2.74 mg, 0.01 mmol), and a catalyst were dissolved in a dehydrated solvent (CH_2Cl_2 or toluene). The reaction mixture was stirred until

nearly full conversion of **1** was confirmed through ^{1}H NMR spectroscopy. The reaction was terminated by triethylamine and benzoic acid for acidic and basic catalysts. The reaction mixture was precipitated in hexane, and the precipitated product was characterized using ^{1}H and ^{13}C NMR, SEC, and FT-IR.

General procedure for ring-opening reactions of 1 with equimolar alcohols

The equimolar ring-opening reactions were conducted using the same protocol as that of the ROP of **1**, and equimolar alcohols $\mathbf{A_x}$ relative to the monomer **1** were used. The reaction mixture was stirred until nearly full conversion of **1** was confirmed through ^{1}H NMR spectroscopy. To remove the catalyst for subsequent characterizations by ^{1}H and ^{13}C NMR, SEC, and FT-IR, the selected products were purified by column chromatography using ethyl acetate and hexane (1:1) and silica gels.

Screening of catalysts for the ring-opening polymerization (ROP) of CL

In a nitrogen-filled glove box, CL (228 mg, 2.0 mmol), $\mathbf{A_1}$ (5.48 mg, 0.02 mmol), and a catalyst (0.02 mmol) were dissolved in 2 mL of a dehydrated solvent (DCM or toluene). The monomer concentration is set as 1 M, and the ratio of the monomer, initiator, and catalyst is 100:1:1 in all entries. For the PTSA-catalyzed ROP, no initiator was used because it was the monohydrate and the hydrated water can serves as the initiator. The reaction mixture was stirred at room temperature until nearly full conversion of CL was confirmed through ^{1}H NMR spectroscopy. The reaction was terminated by triethylamine and benzoic acid for acidic and basic catalysts. The reaction mixture was precipitated in hexane, and the precipitated product was characterized using ^{1}H NMR and SEC.

Density functional theory (DFT) calculations

The stability and reactivity of the ring-opened structure of **1a-O** were estimated by DFT calculations using a simpler structure of **1a-O** as **1a'-O** (Fig. S3a). The DFT calculations were conducted using the Gaussian09 package[S3] with the B3LYP/6-31G(d) basis set[S4–S6]. A hydrogen atom was abstracted from the hydroxyl group in the optimized structure of **1a'-O**. Then, the structure of the anion form was optimized (Fig. S3b, left). After the optimization, a five-membered ring structure was formed (Fig. S3b, right). After the optimization of a cation form, where a hydrogen atom was added to a carbonyl oxygen atom, the hydrogen atom was directed to the oxygen atom at the hydroxyl group but the ring structure was not formed (Fig. S3c). These results suggest that the anion is more favorable to forming the ring structure than the cation. As shown in Fig. S3d, the ring structure was not formed upon adding methylene between ester and O^{-}, indicating that the formation of a six-membered ring is less favorable than that of a five-membered ring.

Supplementary Table and Figures

Table S1. ROPs of CL with different organocatalysts.

Entry[a]	Catalysts	Solvent	Time (h)	Conv.[b] (%)	M_n[c] (kg mol^{-1})	$Đ_M$[c]
1[d]	PTSA	CH_2Cl_2	28	>99	21.3	1.28
2[e]	TBD	CH_2Cl_2	>48	46	6.2	1.04
3[d]	DPP	toluene	23	>99	21.0	1.06
4[d]	DPP	CH_2Cl_2	27	79	19.1	1.04

[a]The ROP was conducted at room temperature (20–25 °C). [CL] = 1.0 M, CL/**A**$_1$/Cat. = 100/1/1. [b]Monomer conversion was determined by ^{1}H NMR. [c]Determined by SEC (THF, 30 °C) using polystyrene standards for calibration. PTSA, *p*-toluenesulfonic acid; TBD, 1,5,7-triazabicylclo[4.4.0]dec-5-ene; DPP, diphenyl phosphate. [d]The reaction was quenched by triethylamine. [e]The reaction was quenched by benzoic acid.

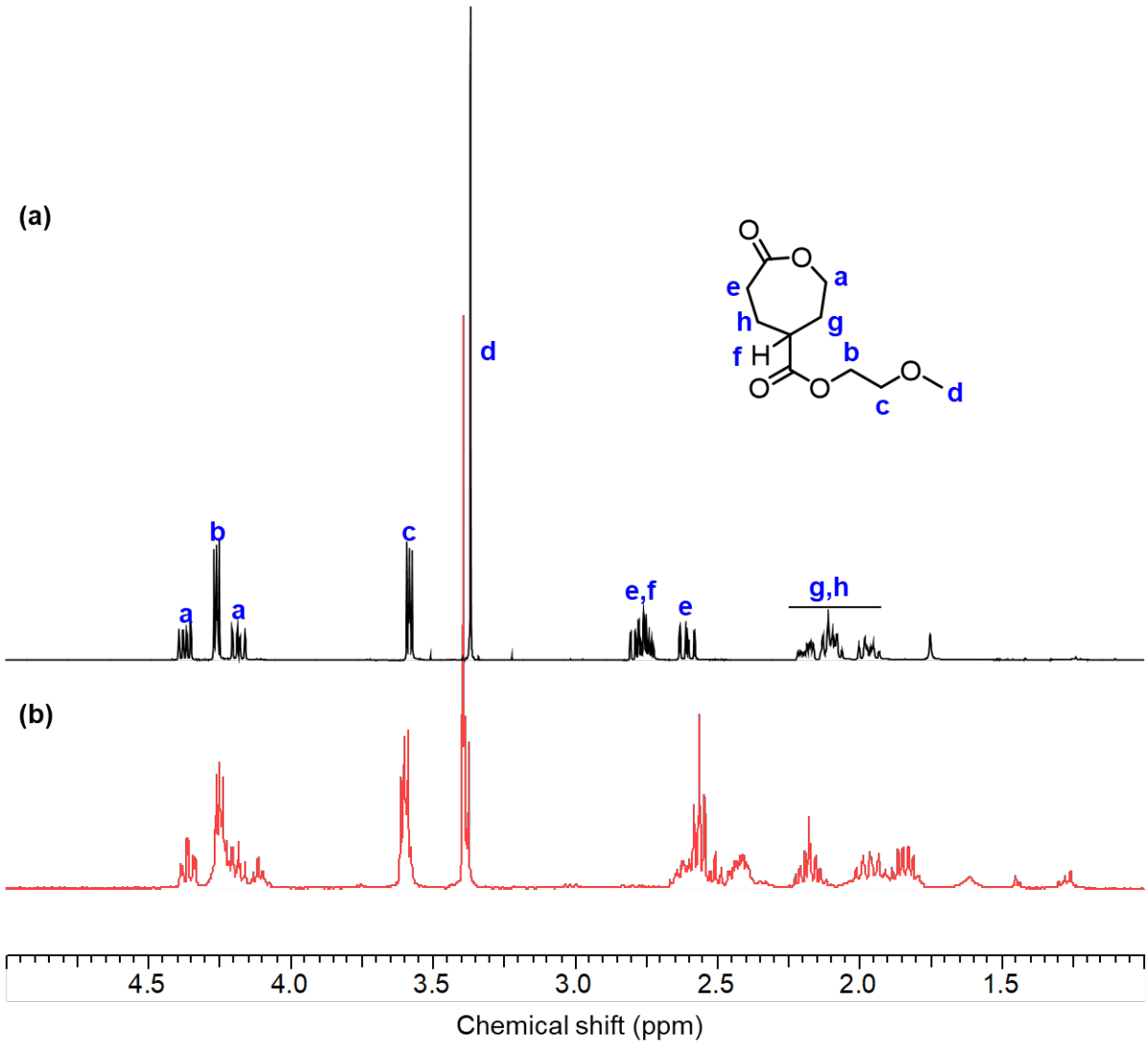


Fig. S1 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) **1a** and (b) the reaction mixture of run 1 in Table 1.

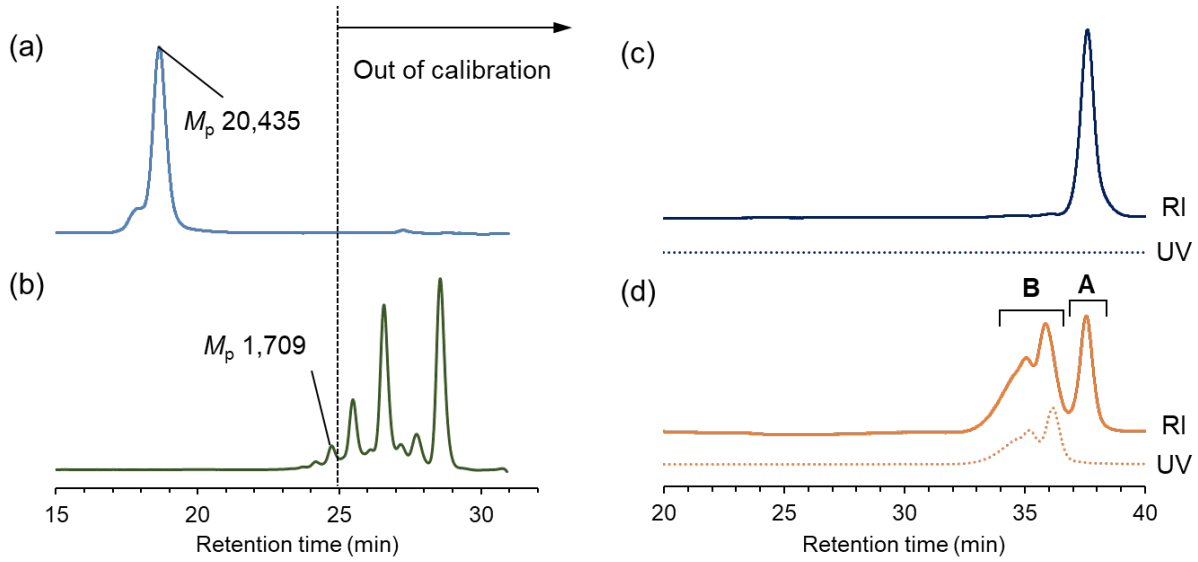


Fig. S2 SEC traces using THF (a, b) and DMF containing 10 mM LiBr (c, d) as eluent: PCL obtained by entry 4 in Table S1(a), a ring-opening reaction product of run 2 in Table 1 (b), **1a** (c) and a ring-opening reaction product of run 4 in Table 1 (d). The curves of (a) and (b) are obtained from RI detector, and those of (c) and (d) include RI and UV detectors. M_p values in (a) and (b) indicate peak top molecular weights calibrated based on polystyrene standards. Fractions A and B are designated as a UV-undetectable and UV-detectable parts in (d).

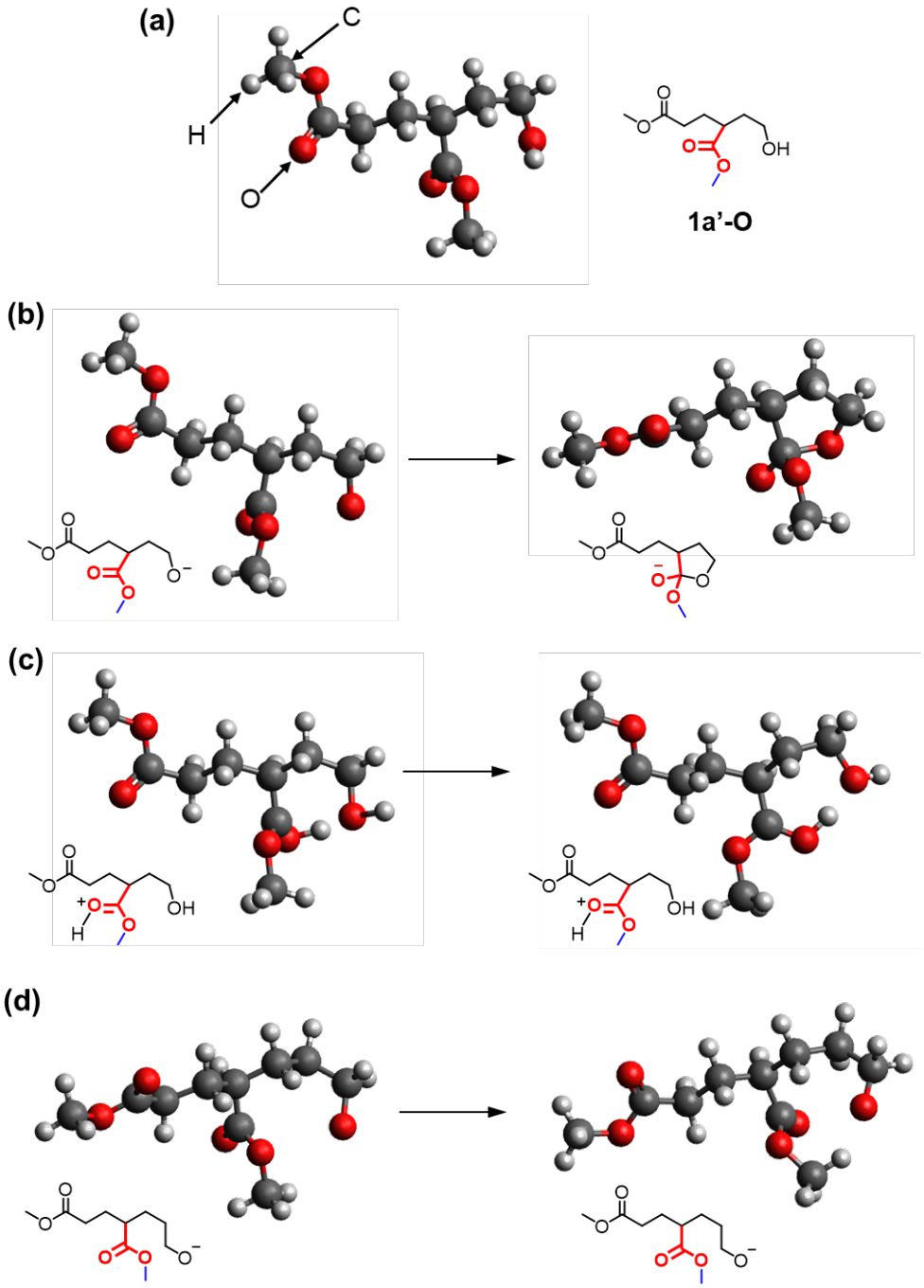


Fig. S3 DFT calculations to evaluate the reactivity and stability of the model compound **1a'-O** (a) in the anion (b) and cation (c) forms, and (d) its analogue with additional methylene between the ester side group and O^{-}. (b–d): Initial (left) and optimized (right) structures.

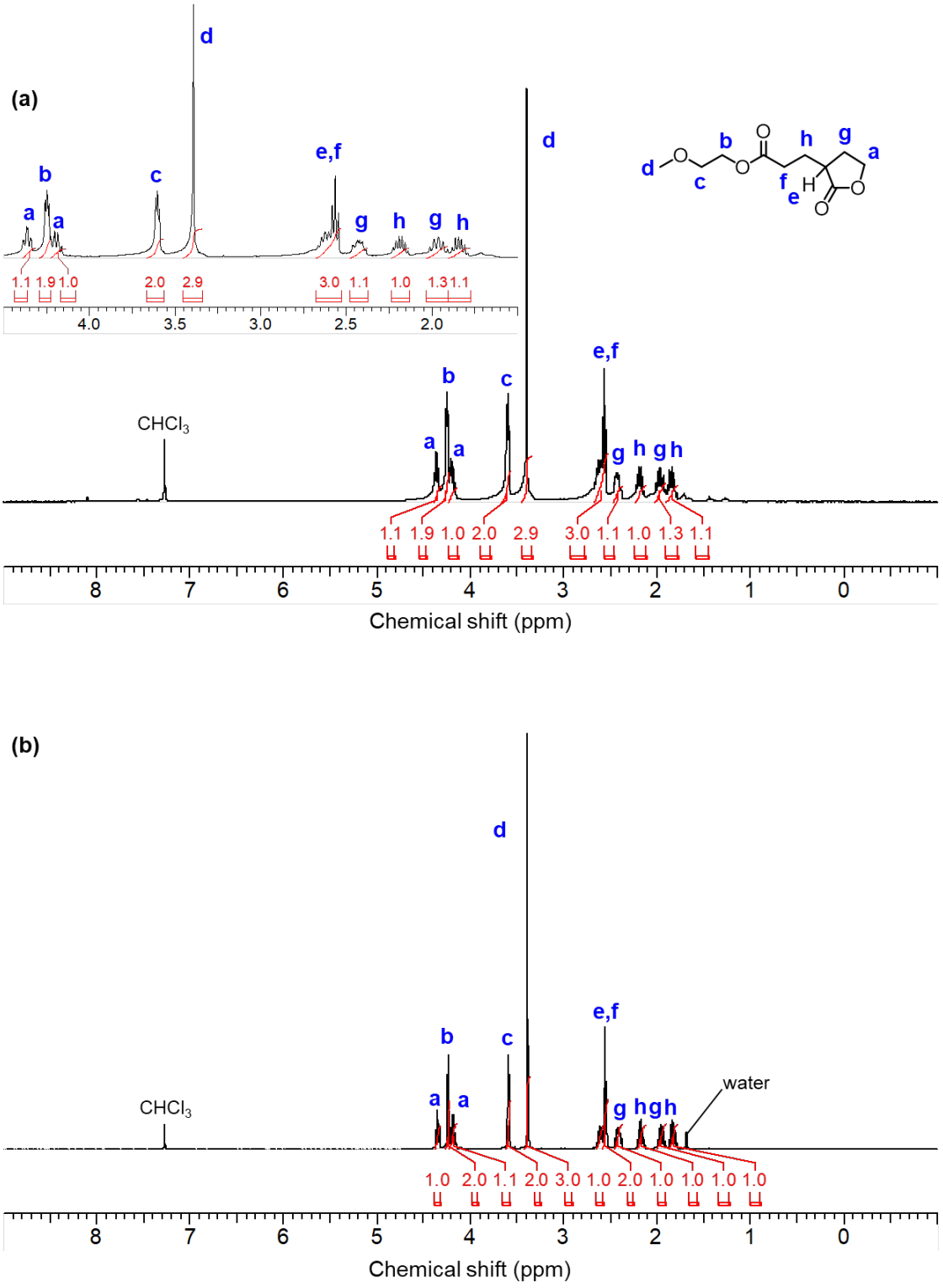


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the products of the 1:1 reaction of **1a** and $\mathbf{A_2}$: crude product (a) and after purification by column chromatography (b). The insert of (a) shows the expanded region.

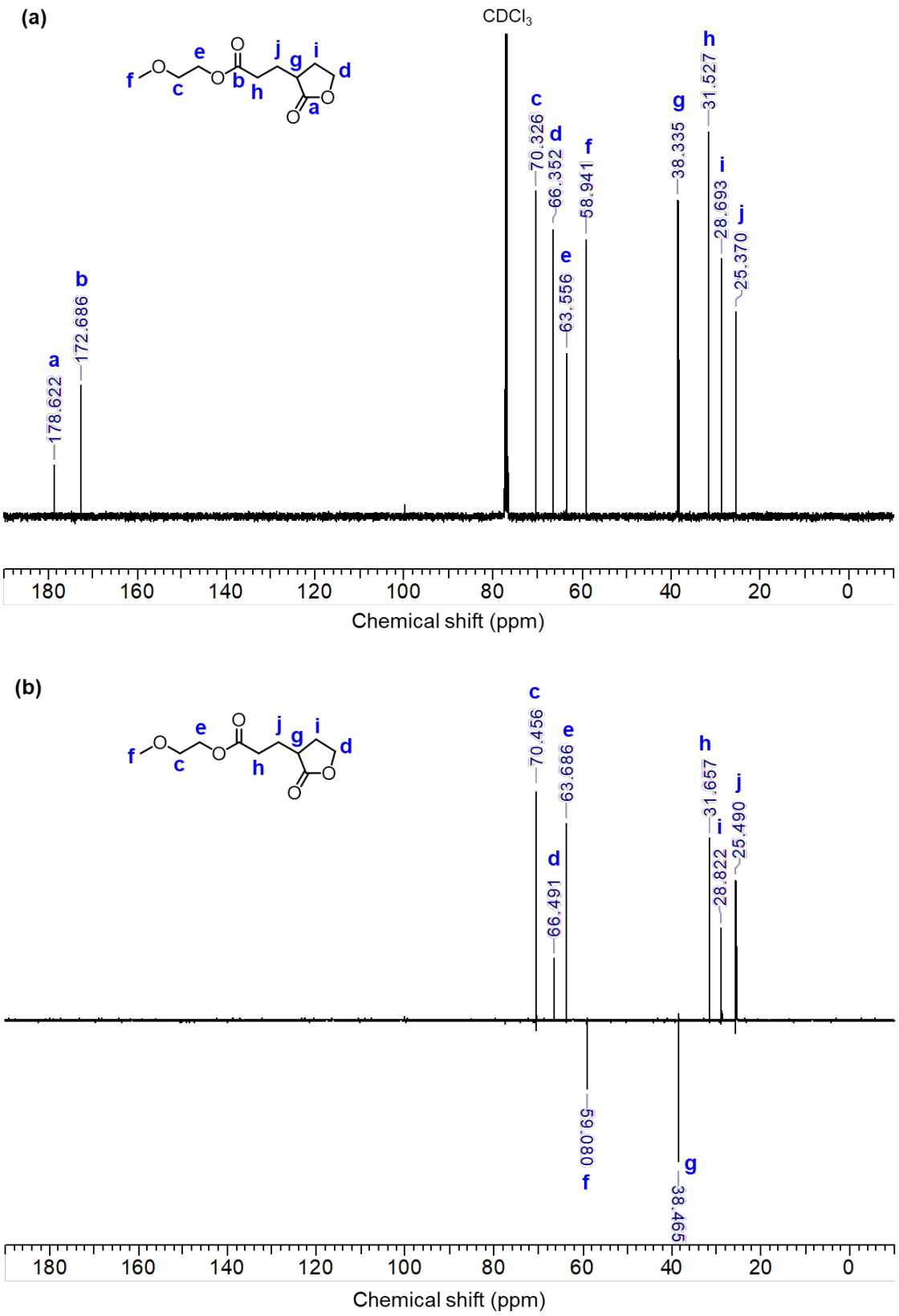


Fig. S5 ^{13}C NMR spectra of **2a** (125 MHz, $CDCl_3$). (a) full spectrum and (b) DEPT-135.

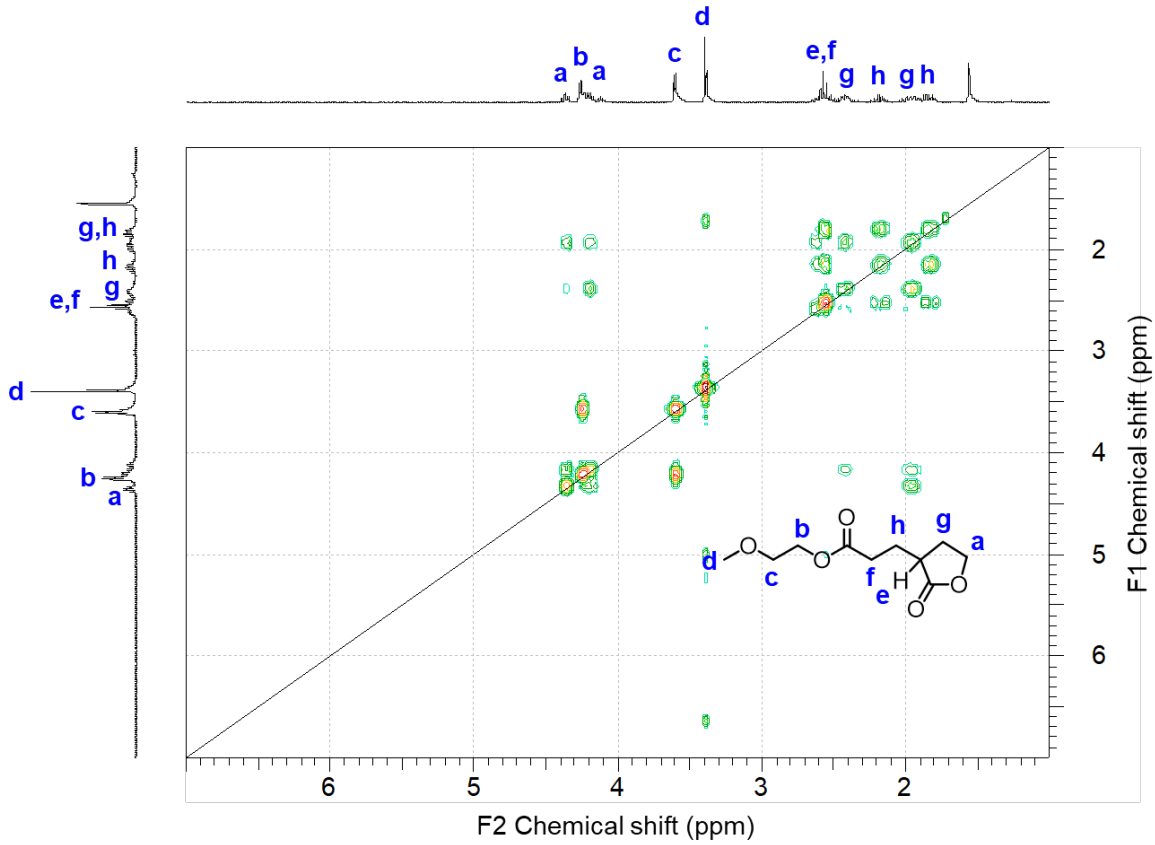


Fig. S6 Expanded region of the $^{1}H–^{1}H$ COSY spectrum (500 MHz) of **2a** in $CDCl_3$.

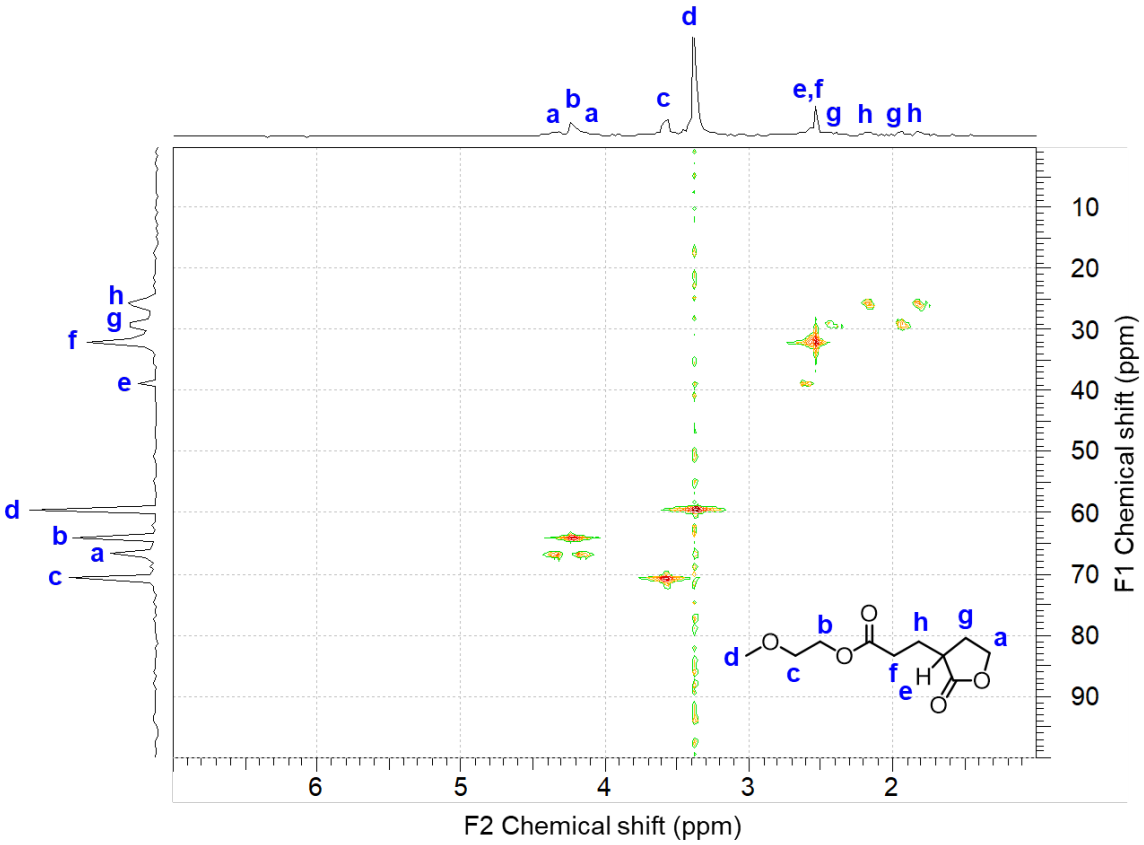


Fig. S7 Expanded region of the $^{1}H–^{13}C$ HMQC spectrum of **2a** in $CDCl_3$.

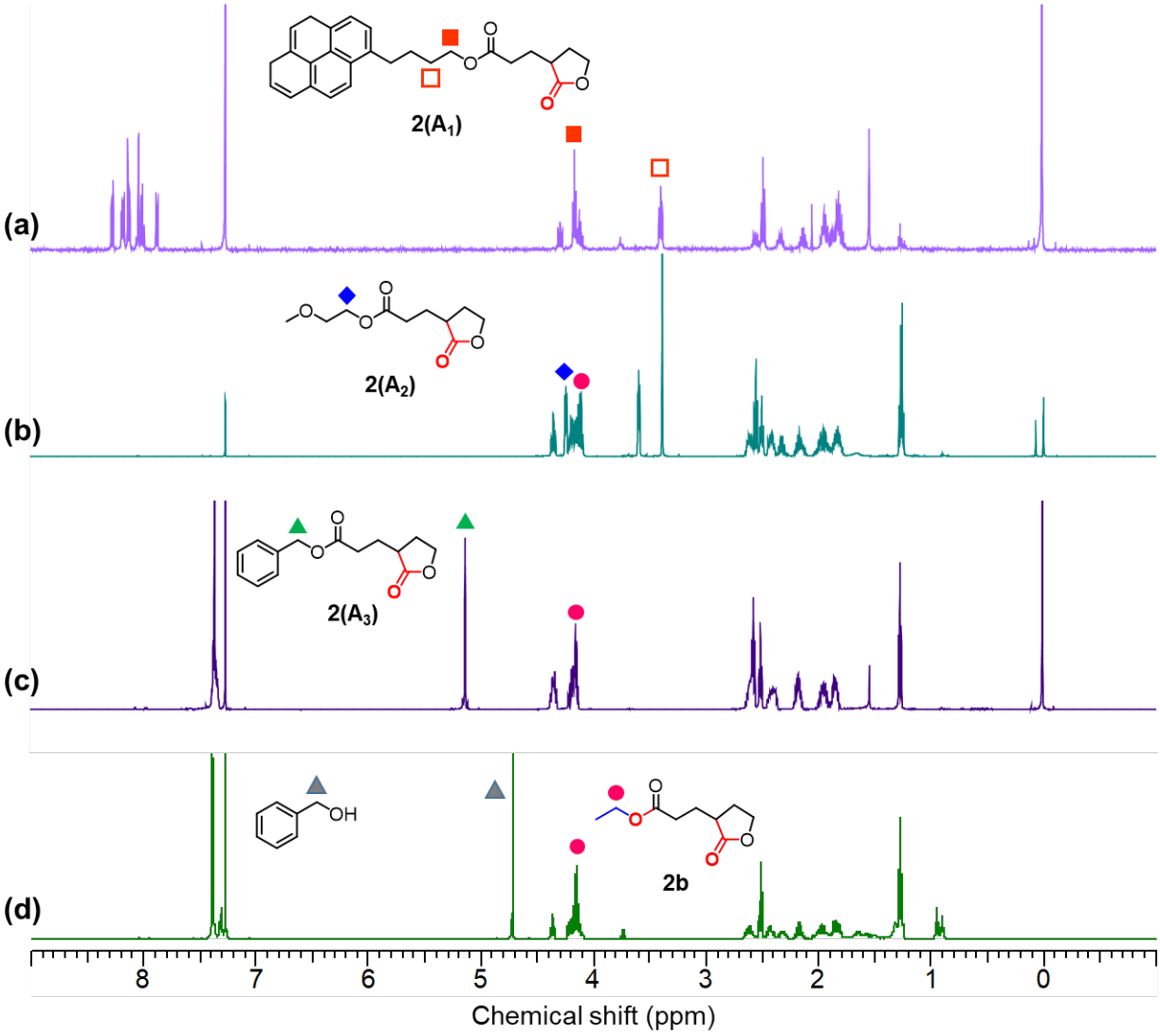


Fig. S8 ^{1}H NMR spectra (500 MHz) of the equimolar reaction mixtures of **1b** and $\mathbf{A_x}$ in $CDCl_3$: (a) run 1, (b) run 2, (c) run 3, and (d) run 8 in Table 2.

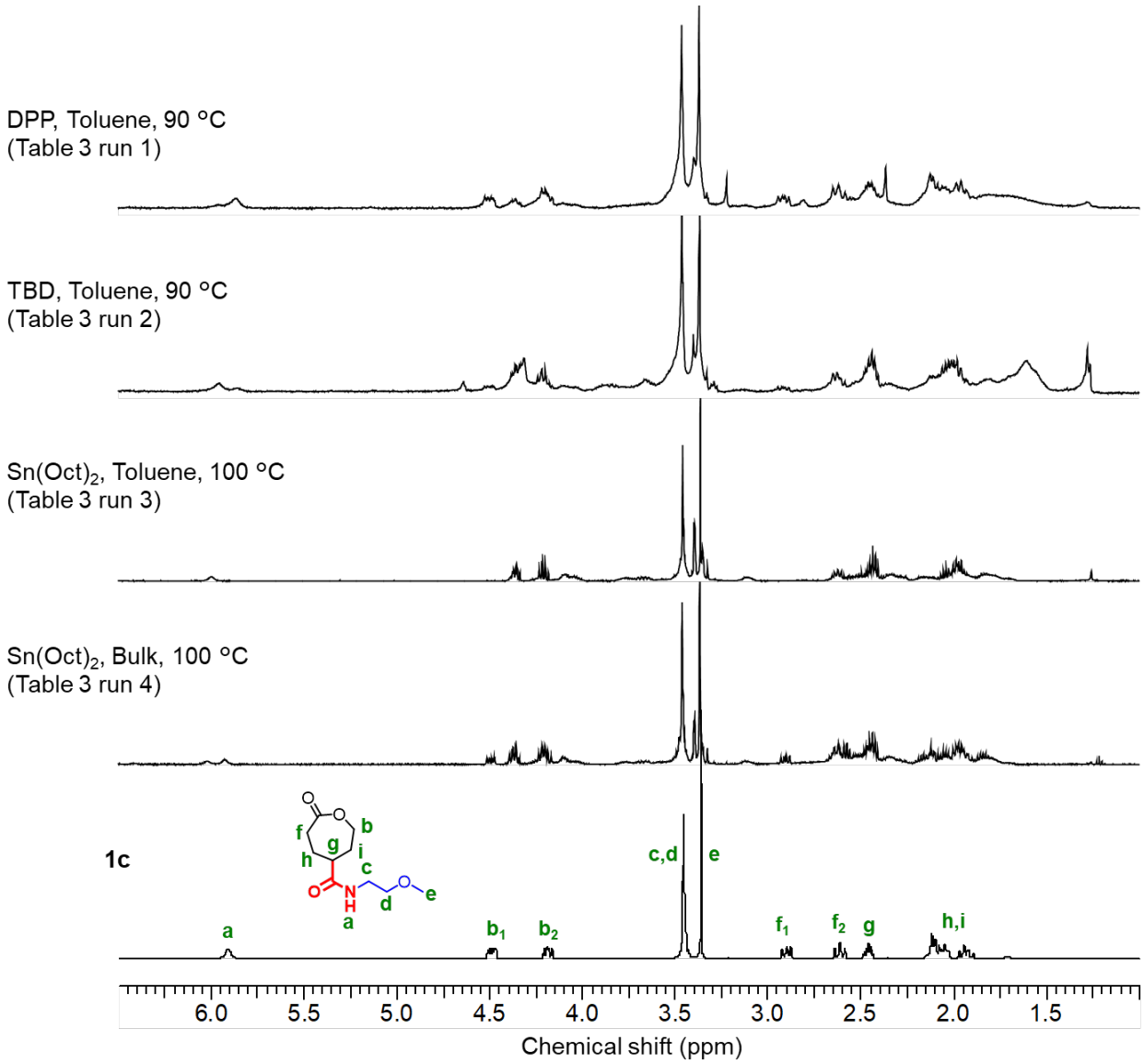


Fig. S9 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the reaction mixture of **1c** treated with different catalysts.

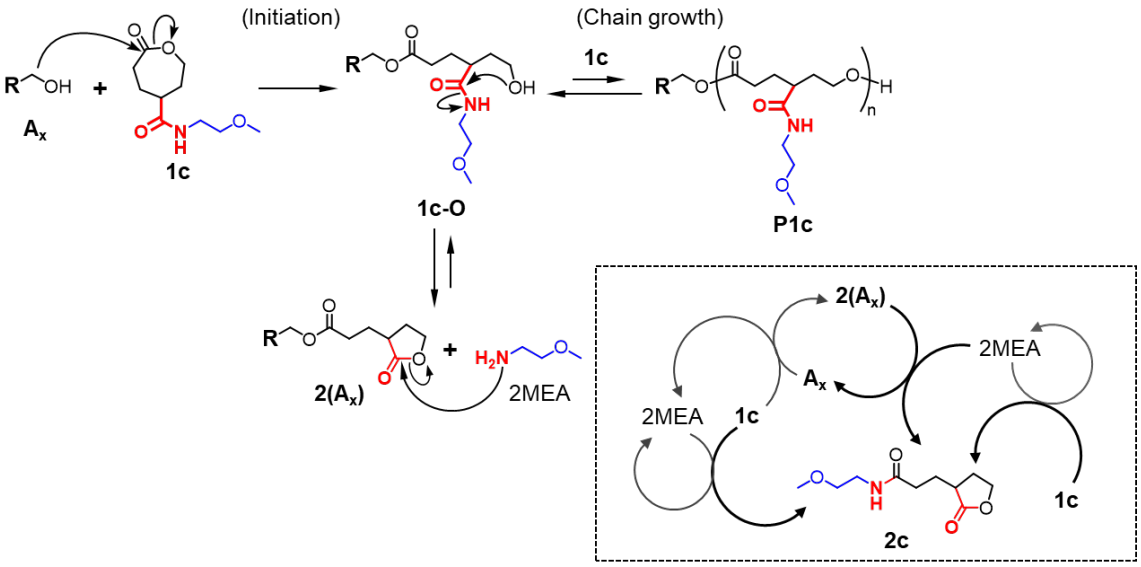


Fig. S10 Plausible mechanism of the ring-opening reaction of **1c**. 2MEA: 2-methoxyethylamine.

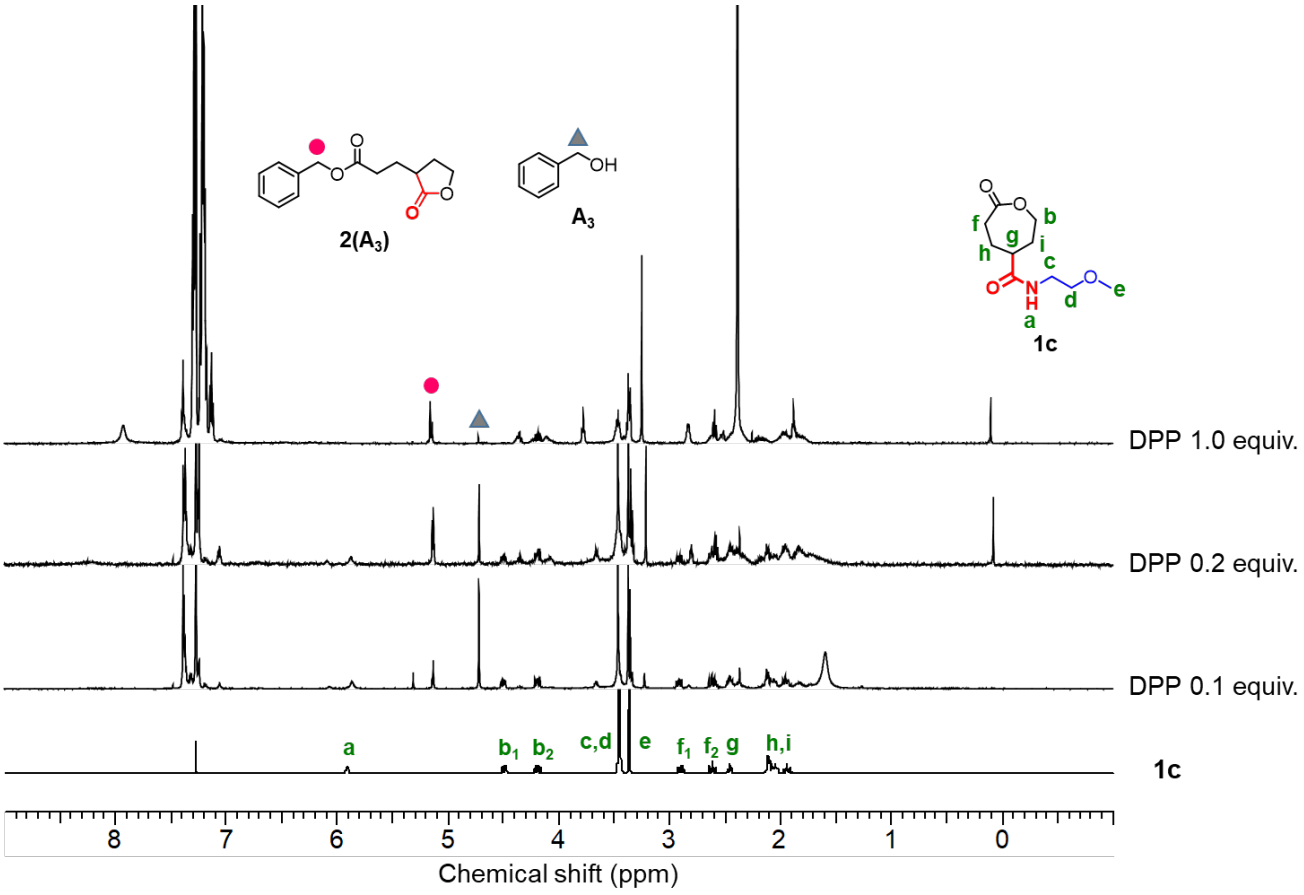


Fig. S11 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the equimolar reaction mixtures of **1c** and **A_3** in the presence of different loadings of DPP.

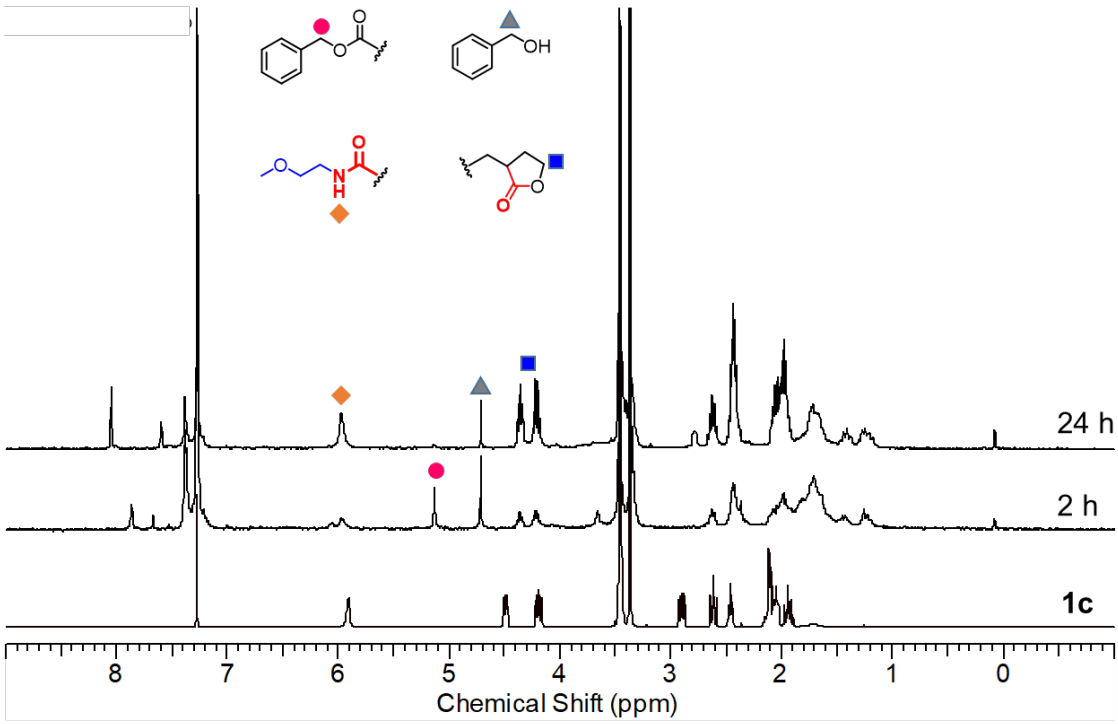


Fig. S12 Time course of the ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the equimolar reaction mixtures of **1c** and **A_3** in the presence of TU/DBU.

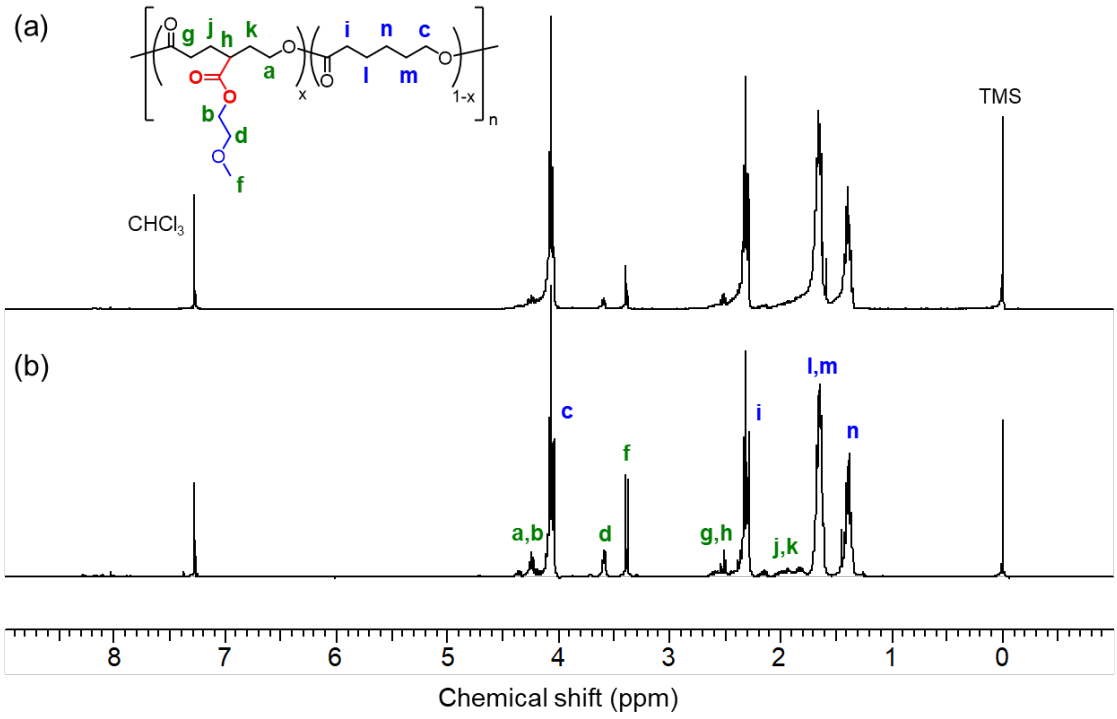
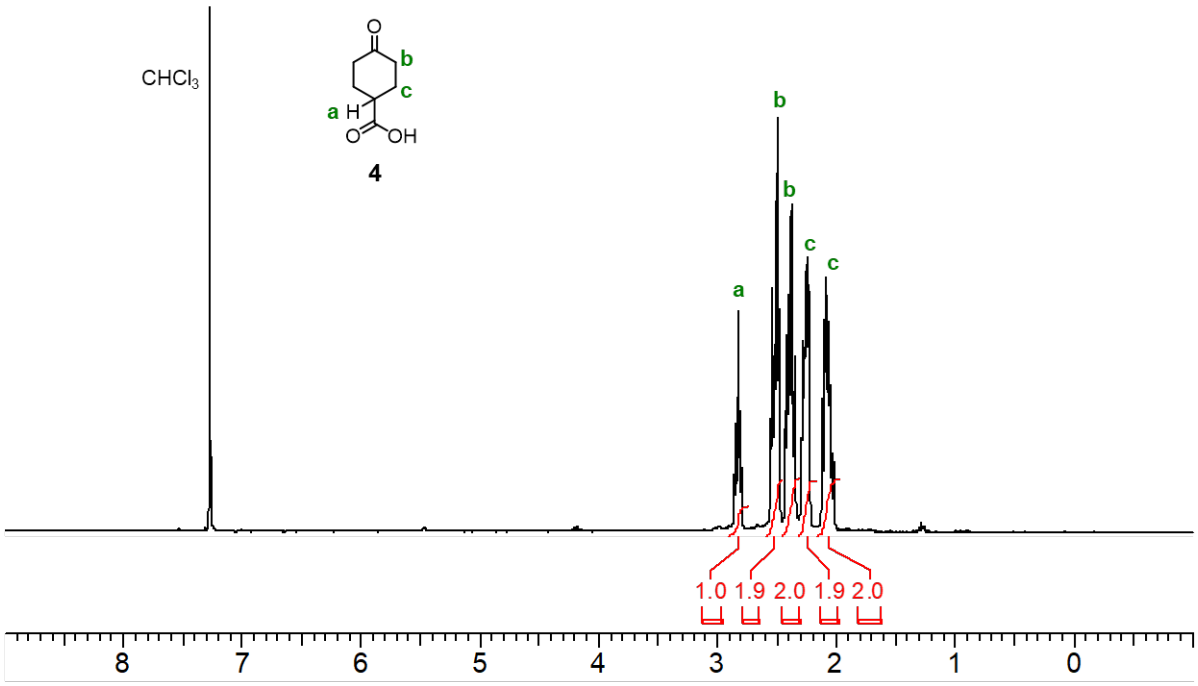


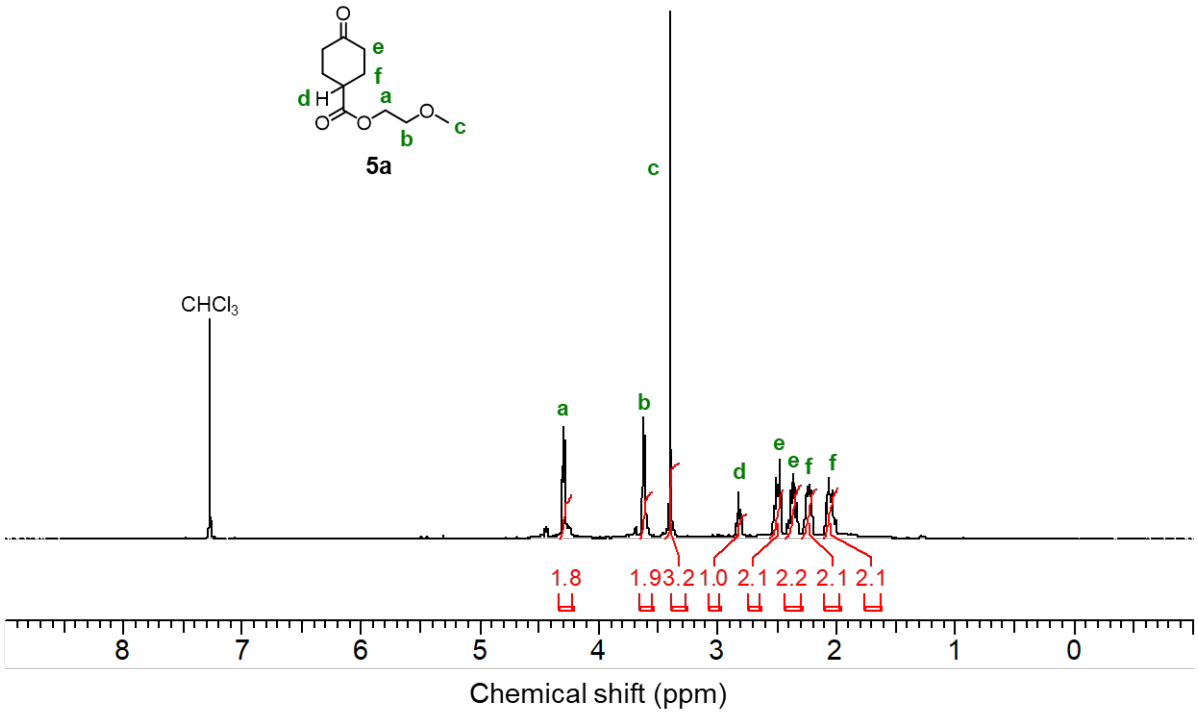
Fig. S13 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the copolymers of **1a** and CL with x = (a) 0.07 and (b) 0.16.

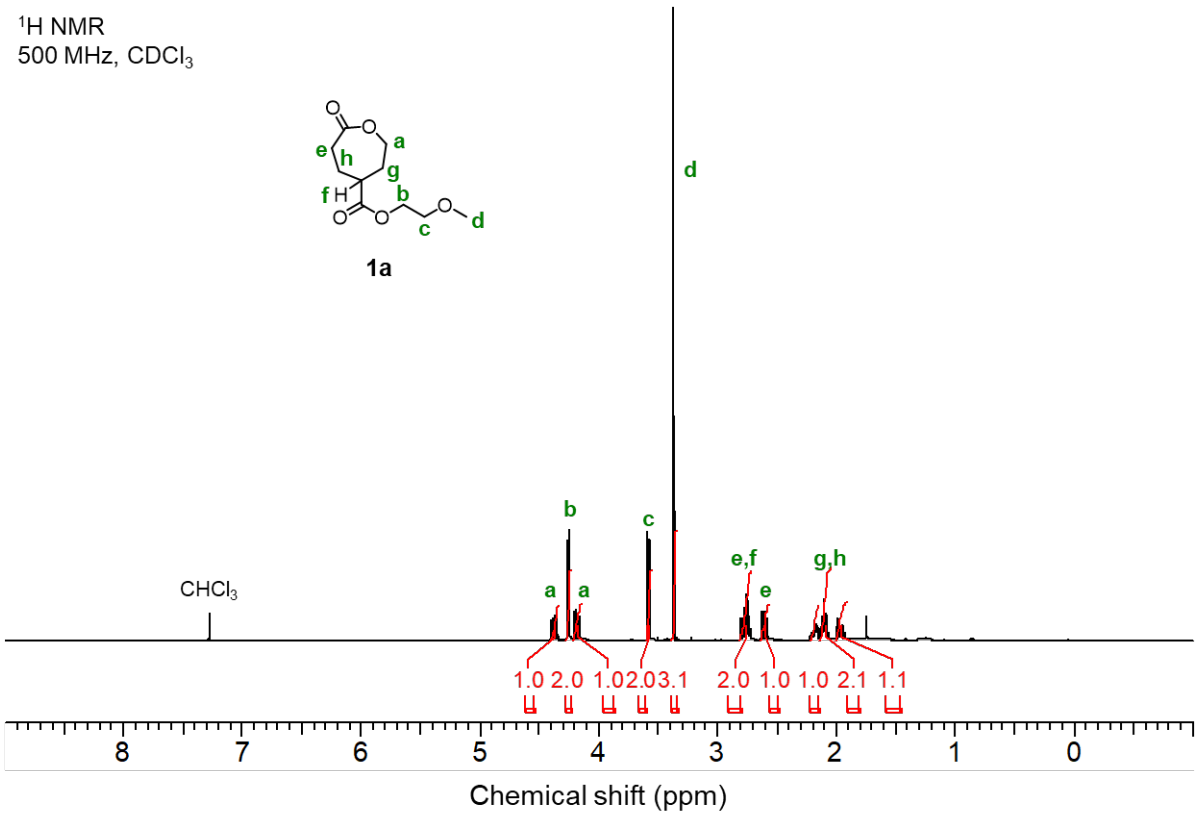
NMR galleries

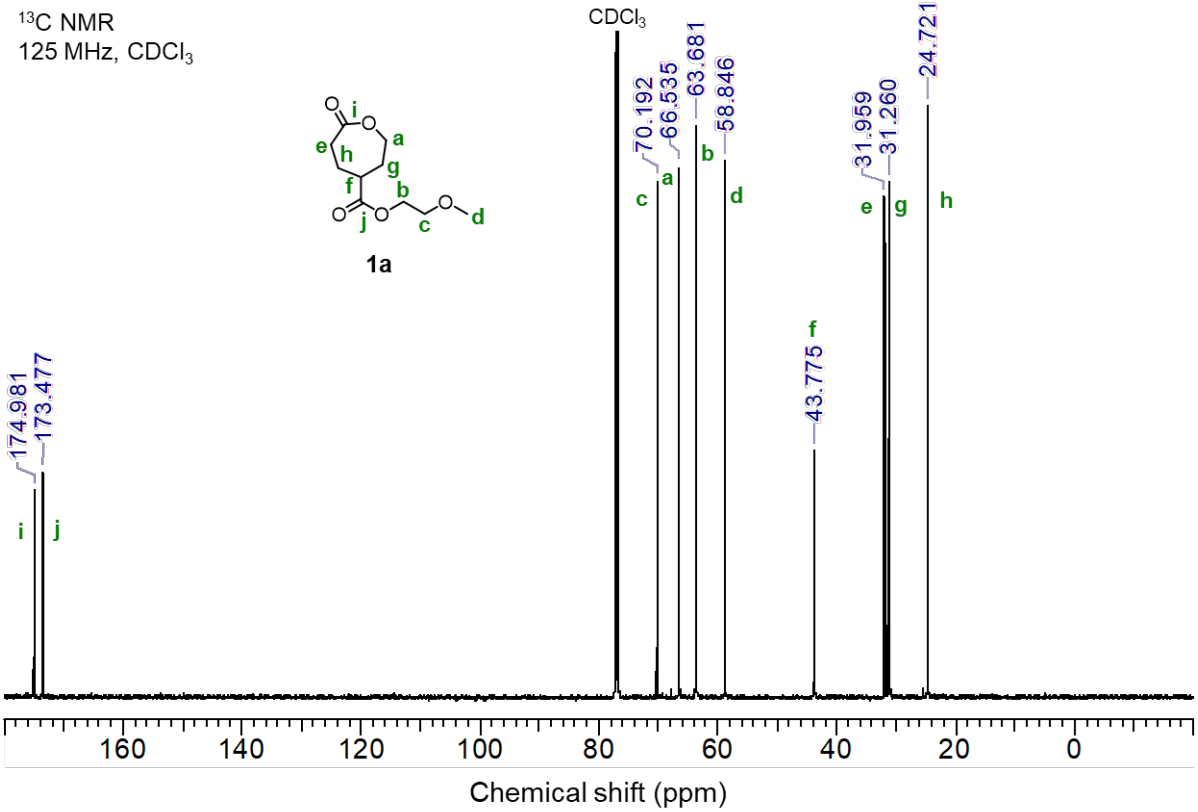
^{1}H NMR
400 MHz, $CDCl_3$

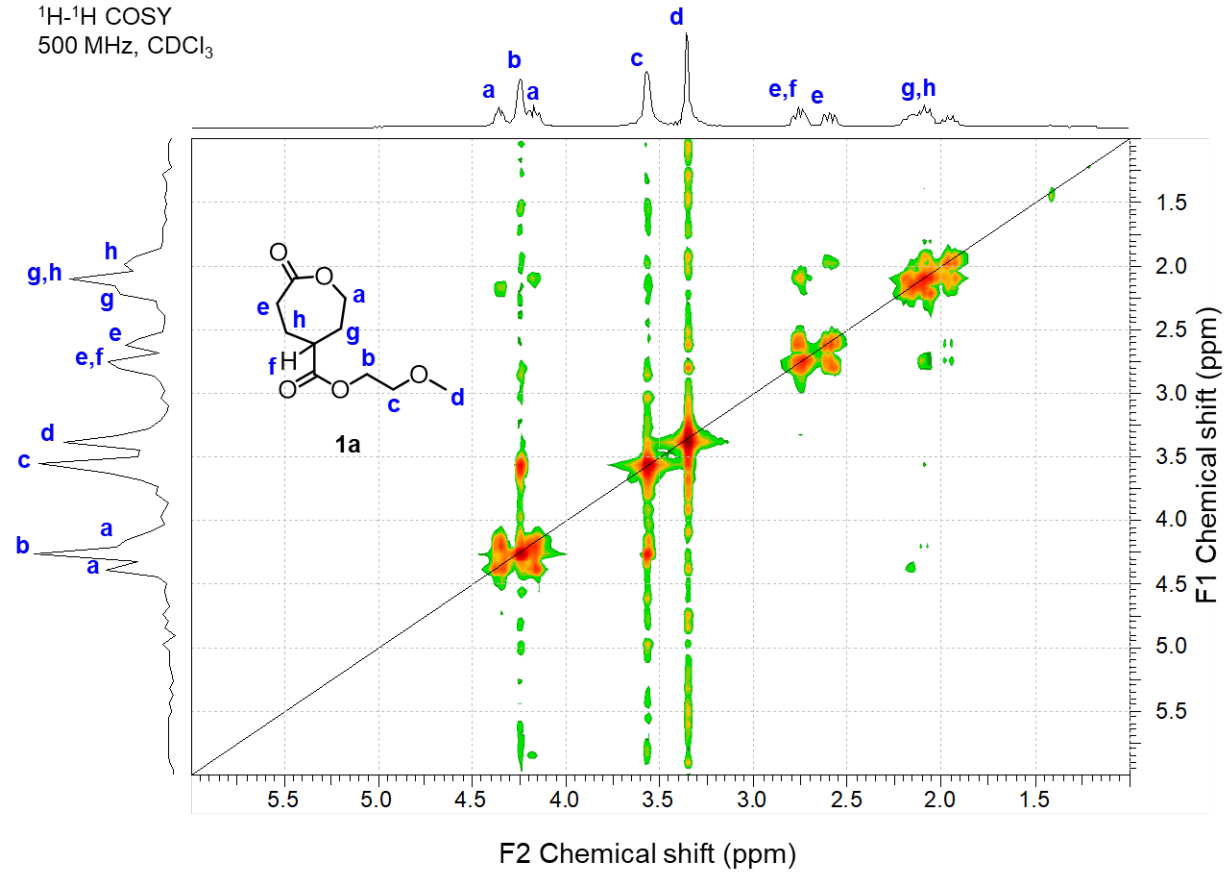


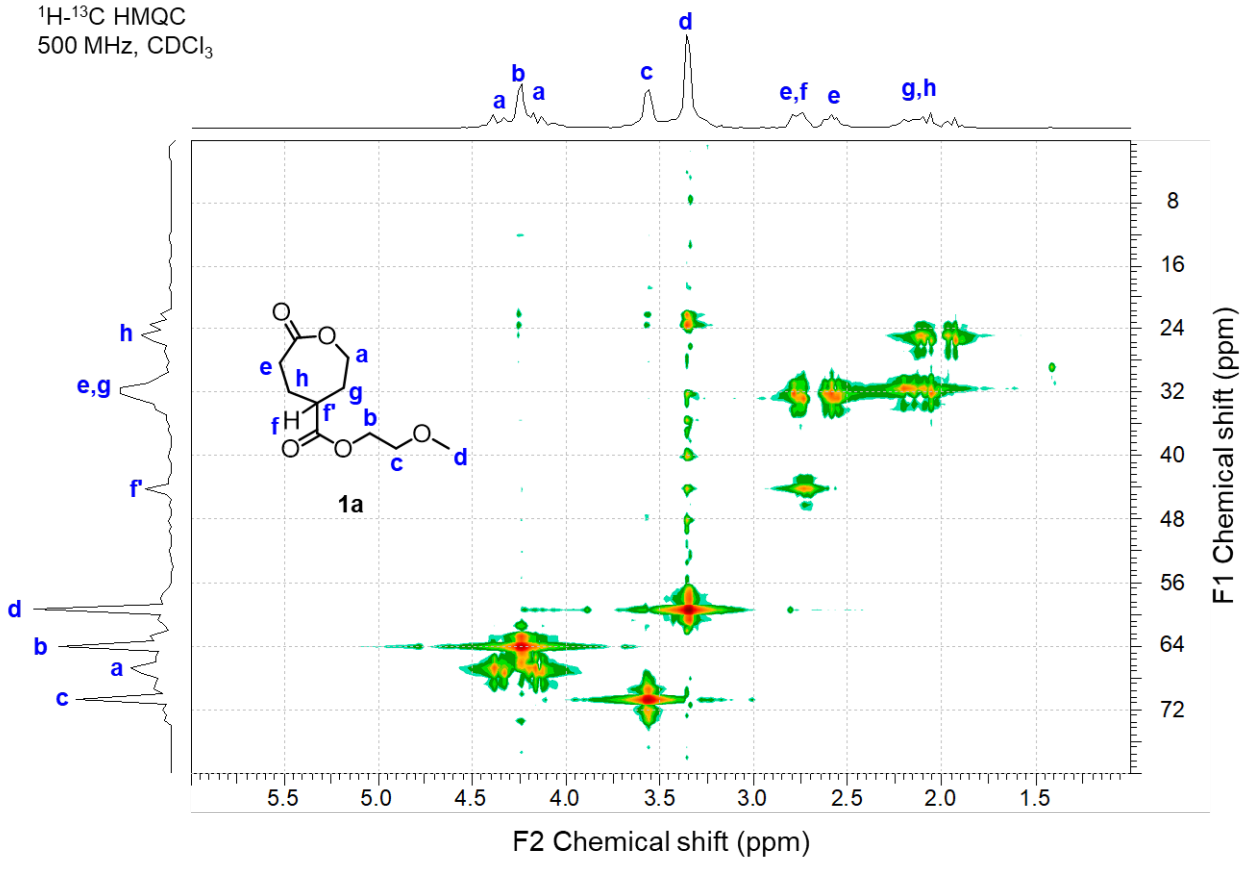
^{1}H NMR
500 MHz, $CDCl_3$



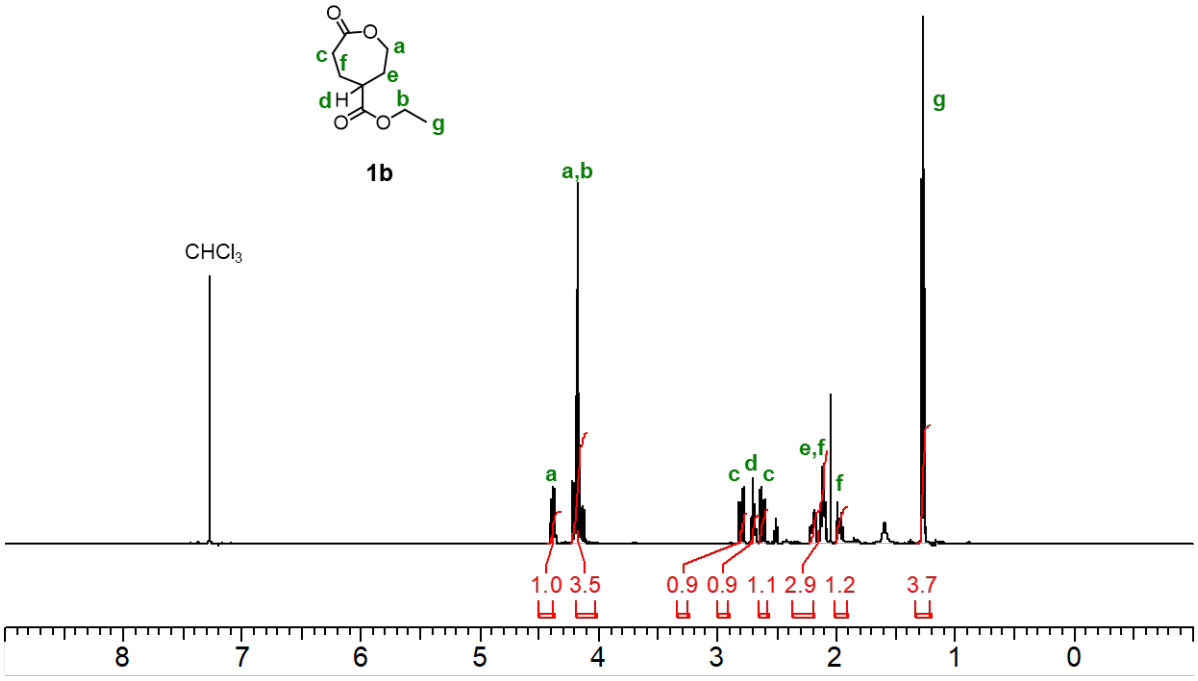

1H NMR
500 MHz, CDCl3
1a
CHCl3
1.0 2.0 1.0 2.0 3.1 2.0 1.0 1.0 2.1 1.1
Chemical shift (ppm)


13C NMR
125 MHz, CDCl3
1a
CDCl3
174.981
173.477
70.192
66.535
63.681
58.846
43.775
31.959
31.260
24.721
Chemical shift (ppm)

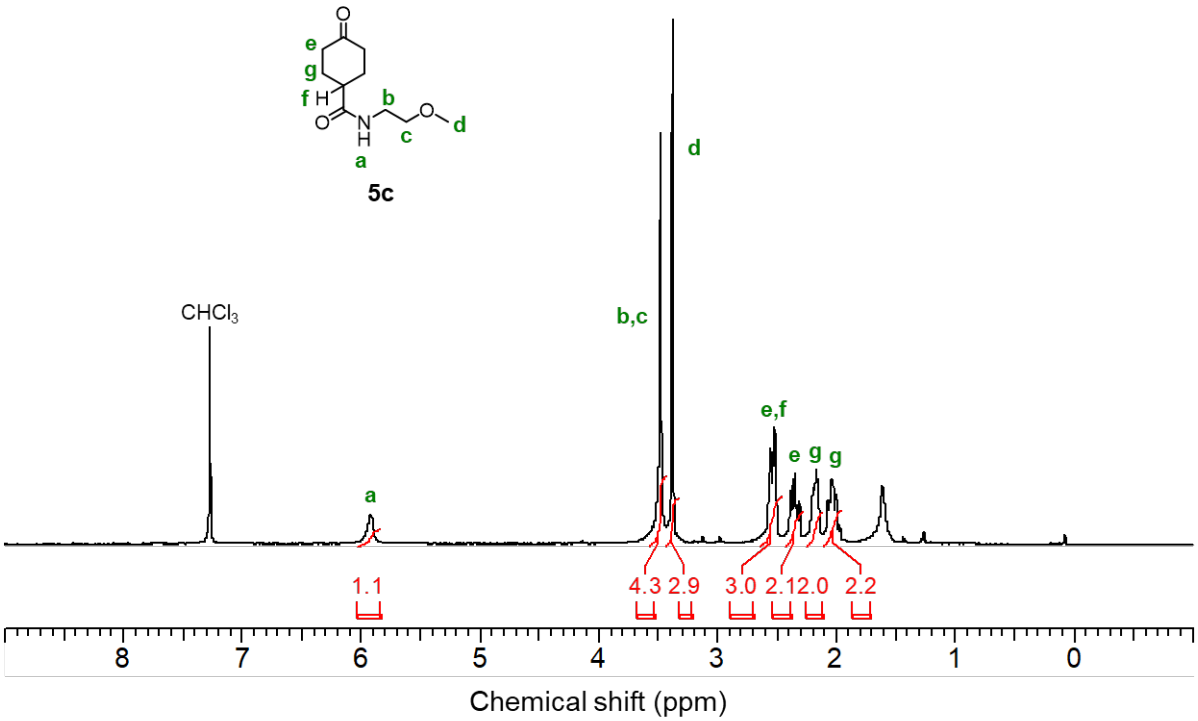

^{1}H-^{1}H COSY
500 MHz, $CDCl_3$
a
b
a
c
d
e,f
e
g,h
h
g
e
f
d
c
b
a
1a
F1 Chemical shift (ppm)
F2 Chemical shift (ppm)


^{1}H-^{13}C HMQC
500 MHz, $CDCl_3$
a
b
a
c
d
e,f
e
g,h
h
e,g
f'
d
b
a
c
1a
F1 Chemical shift (ppm)
F2 Chemical shift (ppm)

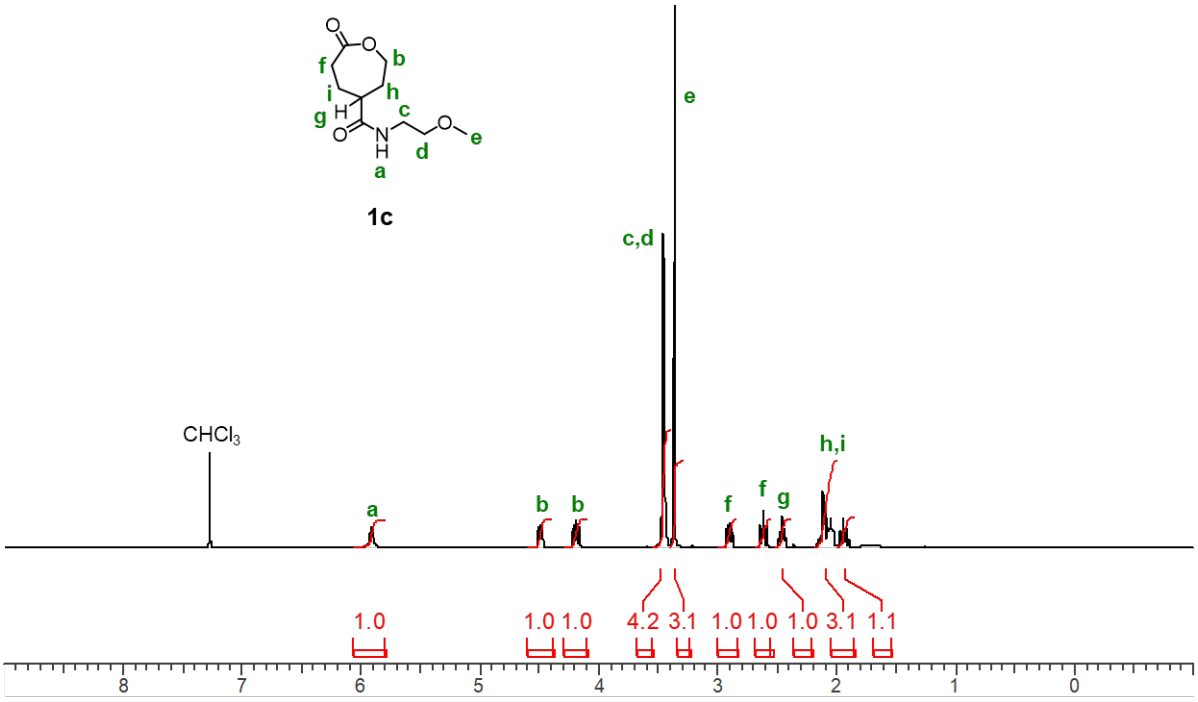
^{1}H NMR
500 MHz, $CDCl_3$



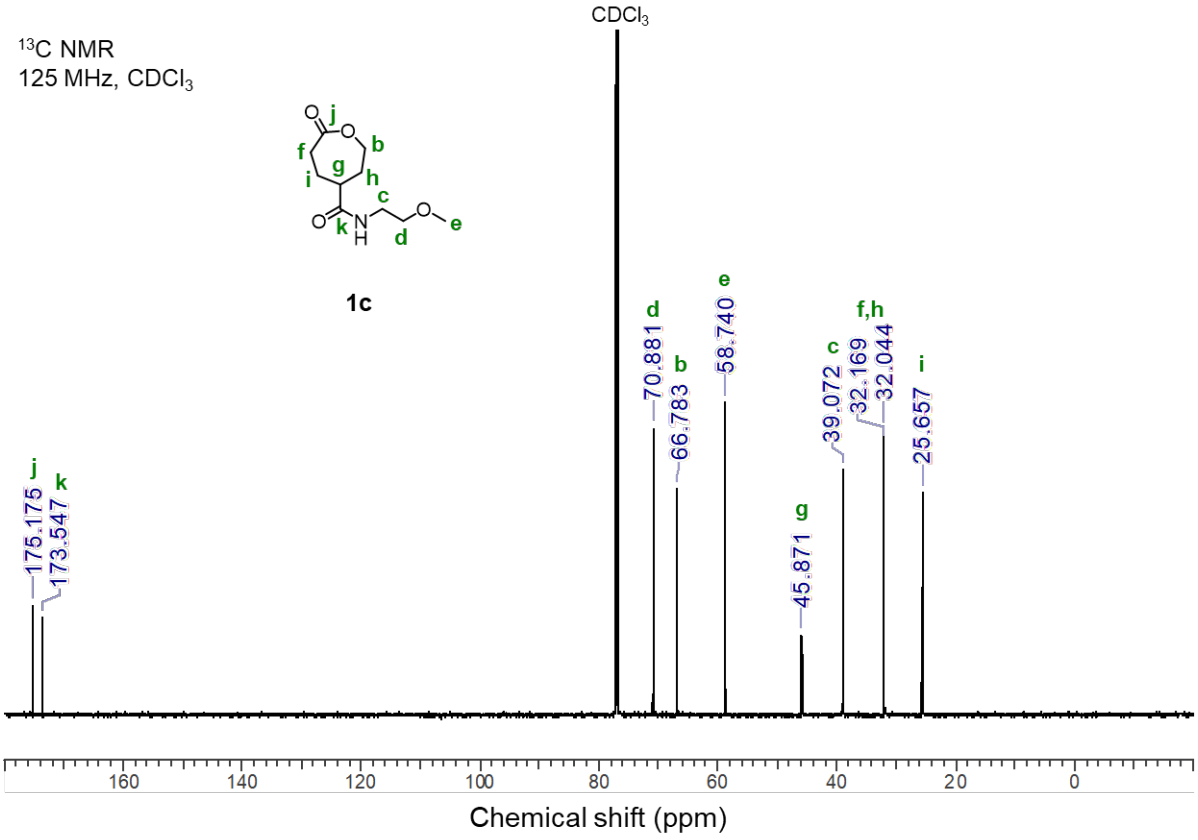
^{1}H NMR
400 MHz, $CDCl_3$



^{1}H NMR
500 MHz, $CDCl_3$



^{13}C NMR
125 MHz, $CDCl_3$



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