

COMMUNICATION

Poly(hydroxyurethane): Catalytic Applicability for the Cyclic Carbonate Synthesis from Epoxides and CO₂Suguru Motokucho*^a and Hiroshi Morikawa^bReceived 00th January 20xx,
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We have developed a synthetic methodology using poly(hydroxyurethane) as an organocatalyst for the chemical fixation of CO₂ into epoxides, leading to the formation of five-membered cyclic carbonates with remarkably high selectivity and yields. The catalyzed reaction was applicable to various epoxides.

Polyurethanes are industrially manufactured by the reaction between polyfunctional isocyanates and polyols. Isocyanates prepared from toxic phosgene are extremely harmful for both humans and the environment. Therefore, poly(hydroxyurethane)s (PHUs) can replace polyurethanes because their synthetic procedure is environmentally benign. PHUs (also called non-isocyanate polyurethanes) are easily produced via the aminolysis reactions of five-membered cyclic carbonates (5CCs) without formation of by-products (Figure 1).^{1,2} In addition, PHUs have been studied as potential coating materials, adhesives, and resins for three-dimensional printing applications, owing to their unique properties.^{1–6} 5CCs, the key reagent for PHU synthesis, are produced by the cycloaddition reaction of epoxides and carbon dioxide (CO₂) (Figure 1);^{7–10} they are also used as electrolytes in lithium ion batteries.¹¹ The efficient transformation of CO₂, which is an industrial waste, into value-added reagents is a critical research objective for sustainable chemistry and environmental preservation. CO₂ is a renewable, inexhaustible, cheap, and nontoxic resource, which allows synthetic flow of PHUs through 5CC products with high atom economy. As of today, various metal-based and organic catalysts have been developed for 5CC synthesis.^{7–10} Among them, organocatalysts are preferred because of their low cost, low toxicity, and versatile molecular design that allows the

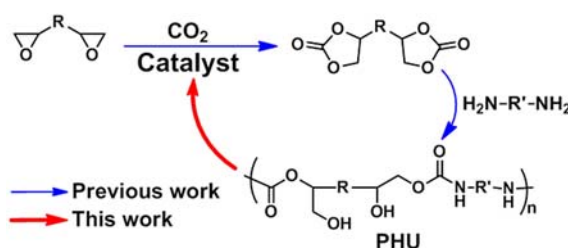
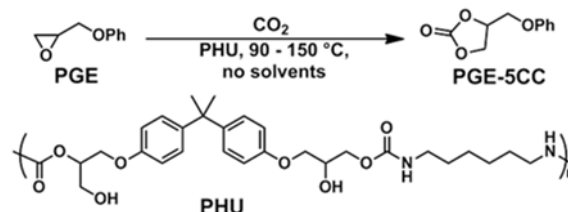


Figure 1 PHU synthetic flow from epoxide through 5CC.

control of the activity.^{12–14} Recently, we have found that traditional polyurethane can be used as an organocatalyst for manufacturing 5CCs from epoxides and CO₂,¹⁵ which stimulated the development of various polyurethane structures. In this study, we examine the applicability of PHU as a catalyst in the synthesis of 5CCs (Scheme 1).

Figure 1 illustrates a simple but innovative concept of this study. 5CC derivatives are precursors for PHU production; therefore, the use of PHU as a catalyst for 5CC synthesis can help to build a material circulation involving 5CC and PHU without any synthetic catalysts. In other words, the polymer catalyzes the formation of the monomer serving as its own precursor, which is reported for the first time here. Notably, this reaction is performed under halogen-free and metal-free conditions, which are required for the industrial manufacturing of 5CCs.¹⁶

We selected phenyl glycidyl ether (PGE) as the epoxide substrate. The mixture of PGE and PHU reacted under 5.2 MPa CO₂ pressure in the absence of any organic solvents (Scheme 1).

Scheme 1 PHU-catalyzed PGE-5CC synthesis through the reaction of PGE with CO₂.

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The molar ratio of PHU urethane moieties to PGE was varied from 0.01 to 0.40 (the most frequently used value was 0.20); these numbers are equivalent to catalyst amounts of 1–40 mol%. PHU is soluble in PGE at temperatures higher than 90 °C under atmospheric pressure; therefore, the reaction was expected to proceed homogeneously under these conditions.

After a specified time, the reaction mixture was analyzed by performing ^1H nuclear magnetic resonance ($^1\text{H-NMR}$) measurements of the CDCl_3 solution, estimating both the conversion of PGE as the consumption and its selectivity from PGE to **PGE-5CC**¹⁷ in the reaction mixture (Figure S1, Equations S2 and S3). Finally, the reaction mixture was separated into diethyl ether-soluble components and insoluble solids. The former contained a mixture of PGE and **PGE-5CC** and was purified to isolate pure **PGE-5CC**. In contrast, the insoluble solid consisted of recovered PHU.

Table 1 lists the various parameters of the reactions, such as conversion, selectivity, and isolated yield of **PGE-5CC**¹⁸, performed under different conditions. Notably, the **PGE-5CC** selectivity in each reaction (Entries 1–11 in Table 1) was extremely high (>99%) without forming any by-products, which was consistent with the similar values of conversion and isolated yield. At 90 °C, increasing the molar ratio from 0.01 to 0.40 increased both the conversion and yield. Surprisingly, 96% conversion and 93% isolated yield were achieved at the ratio of 0.40 (Entry 7) despite a relatively mild temperature of 90 °C, confirming the high catalytic activity of PHU. Reactions at temperatures above 90 °C were also performed at a fixed catalyst ratio of 0.20. At 120 °C, the carbonation reaction achieved the highest yield of 97% after 16 h (Entry 10). Further increase in the temperature to 150 °C resulted in 82% yield (Entry 11) after only 4 h of reaction.

Table 1 Effects of the reaction conditions^a on the synthesis of **PGE-5CC**.

Entry	Temp ./ °C	Catalyst ratio ^b	Time / h	Conversion ^{c, d} /%	Selectivity ^{c, e} /%	Isolated yield ^f /%
1	90	0.01	16	trace	>99	2
2	90	0.05	16	18	>99	14
3	90	0.10	16	31	>99	26
4	90	0.20	4	8	>99	6
5	90	0.20	11	28	>99	26
6	90	0.20	16	50	>99	46
7	90	0.40	16	96	>99	93
8	120	0.20	4	31	>99	27
9	120	0.20	11	95	>99	91
10	120	0.20	16	quant.	>99	97
11	150	0.20	4	83	>99	82

^aUnder 5.2 MPa CO_2 . ^bMolar ratio of [urethane moiety of PHU]₀/[PGE].

^cDetermined from $^1\text{H-NMR}$ analysis of the reaction mixture. ^dConsumption of PGE.

^eFrom PGE to **PGE-5CC**. ^fAfter the purification via SiO_2 column chromatography.

In contrast to the isolated **PGE-5CC**, high yields of recovered PHU solids were obtained from the reactions conducted over the temperature range 90–150 °C (Table S1), indicating that PHU could be easily separated from the reaction mixture. These solids were analyzed by $^1\text{H-NMR}$, Fourier-transform infrared (FT-IR) spectroscopy, and gel permeation chromatography

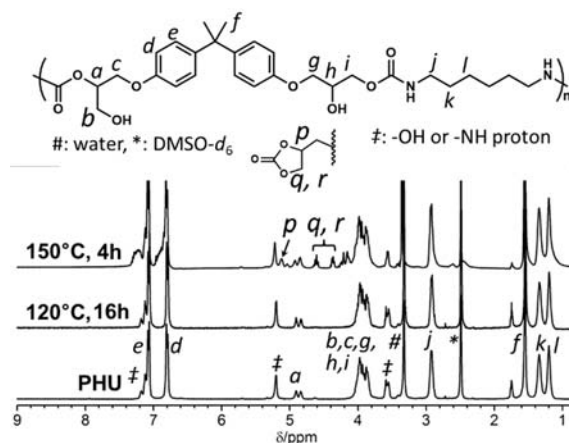
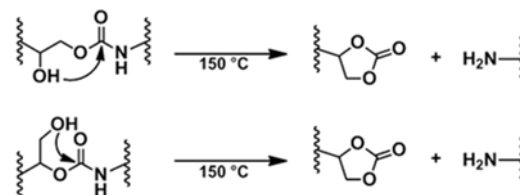


Figure 2 $^1\text{H-NMR}$ spectra of the pristine PHU and the PHU recovered by filtration (in DMSO-d_6).

(GPC); the obtained data were compared with the parameters of the pristine PHU. No changes in the $^1\text{H-NMR}$ spectra were observed for the samples treated at 90 and 120 °C. In contrast, new peaks at 5.1–4.4 ppm appeared after the treatment at 150 °C, which were assigned to the protons (*p*, *q*, *r*) of 5CC moieties (Figures 2 and S2). In this case, the yield of 5CC moieties produced from hydroxyurethane linkage (Scheme 2), as estimated from the intensity ratio of signals *q*, *k*, and *l*, was 24%. This observation was in good agreement with the results of FT-IR and GPC measurements. The obtained FT-IR spectra (Figure S3) show a characteristic peak at 1806 cm^{-1} , which is assigned to the carbonyl groups of 5CC moieties in the sample treated at 150 °C. In the corresponding GPC profiles (Figure S4), the number- and weight-average molecular weights noticeably decreased for the PHU sample treated at 150 °C (Table S2), but not for the samples treated at 90 and 120 °C. The observed temperature dependency presumably originated from the thermal decomposition of PHU urethane moieties leading to 5CC formation, as was reported previously (Scheme 2).^{19,20} These results indicate that temperatures below 120 °C are favorable for the recovery of PHU without degradation.

The described PHU-catalyzed reaction was performed for various substituted epoxides, resulting in the formation of different 5CCs (**5CC-1** to **5CC-10**) with relatively high yield (Figure 3). For optically active **5CC-9** and **5CC-10**, the stereochemical configuration was maintained during the entire reaction (Scheme S1). In addition to monofunctional 5CCs, bifunctional **5CC-11** and **5CC-12** were produced from the corresponding diepoxides. Bisphenol A-based **5CC-12** is a well-known starting compound for PHU synthesis,^{1,2,21,22} and it allows the implementation of the cycle outlined in Figure 1. The



Scheme 2 Thermal decomposition reaction of the hydroxyurethane linkage in the main chain.

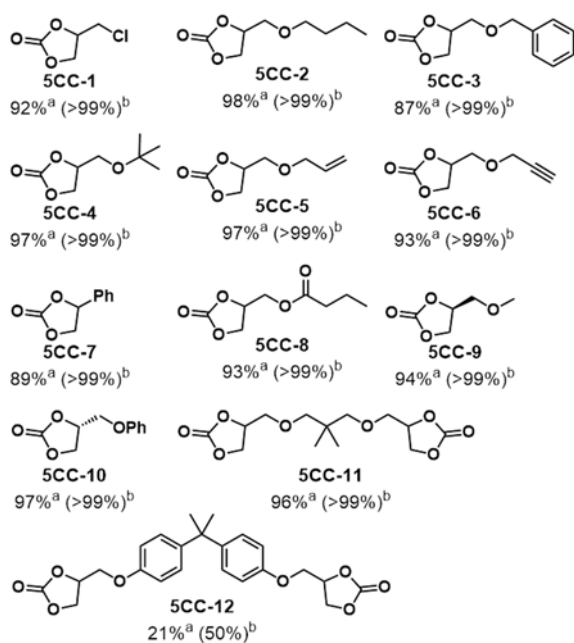
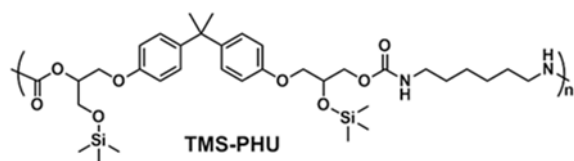


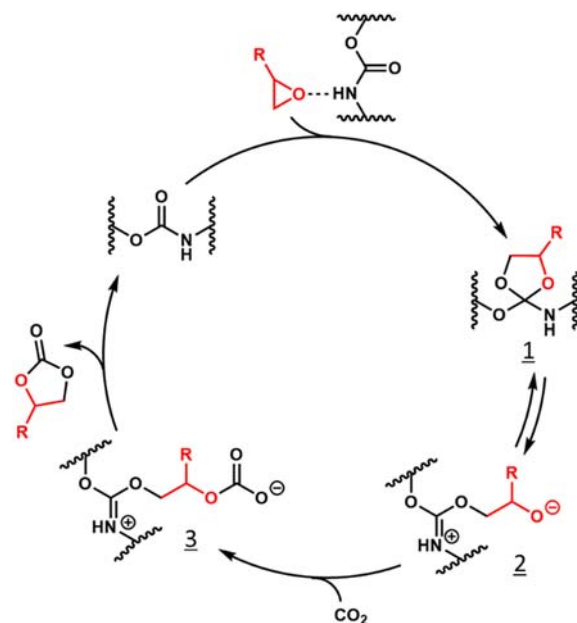
Figure 3 Syntheses of 5CCs from various epoxides. Reaction conditions: 120 °C, 5.2 MPa CO₂, 16 h, 5.0 mmol epoxide, [PHU urethane groups]₀/[epoxide]₀ = 0.20. ^aisolated yield, ^bconversion of epoxy moieties in the reaction.



Scheme 3 Chemical structure of TMS-PHU.

polymerization of **5CC-12** obtained in this study was conducted with 1,6-hexamethylenediamine for the preparation of PHU.²¹ The reaction successfully produced PHU as a white solid with 87% yield, which was confirmed after obtaining ¹H-NMR spectrum and GPC profile similar to that of the pristine PHU (Figures S5 and S6). These results indicate achievement of the concept shown in Figure 1.

To elucidate the interaction between PGE and urethane moiety of PHU at the initial stage of the reaction, ¹H-NMR spectra of PHU in the presence and absence of PGE were measured in DMSO-*d*₆ at 25 °C (Figure S7). Addition of 2 equivalent (molar ratio) of PGE to the urethane moiety resulted in the shift of chemical shift values of the N-H and O-H protons of PHU from 5.230 and 4.869 to 5.264 and 4.912 ppm, respectively in comparison to the ¹H-NMR spectra of PHU. We also measured ¹H-NMR spectra of PGE and a modified PHU, i.e., a hydroxy group-protecting combination of PHU with trimethylsilyl ether (denoted as TMS-PHU, Scheme 3). The chemical shift value of the N-H proton of TMS-PHU shifted from 4.725 to 4.738 ppm in CDCl₃ owing to the presence of PGE (Figure S8). The change in the chemical shift values indicates the formation of a hydrogen bond between the NH proton of the urethane moiety and the oxygen atom of the epoxide, which



Scheme 4. Plausible reaction mechanism for the urethane-catalyzed 5CC synthesis through the reaction of epoxide with CO₂.

influenced the electronic density distribution of the urethane moiety. This consideration of formation of hydrogen bond is supported by similar ¹H-NMR analyses in previous studies.^{10,23} In these studies, the epoxide was reported to be activated by the hydrogen bonds for the synthesis of 5CCs.

From the results of Scheme S1 and the aforementioned ¹H-NMR analyses (Figures S7 and S8), a plausible mechanism of the PHU-catalyzed 5CC formation reaction is illustrated in Scheme 4. First, the epoxide is activated by the hydrogen bond through the NH proton of urethane moiety. A cyclic compound (1) is then formed owing to the reaction between the epoxide and the carbonyl group of urethane moiety, followed by a ring-opening reaction resulting in the formation of zwitterionic species involving alkoxide ion (2). Subsequently, it reacts with CO₂ to form corresponding carbonate anion (3). Finally, (3) undergoes a ring-closure reaction causing the release of urethane moiety and the formation of the desired 5CC. Jiang *et al.* have reported synthesis of 5CC from epoxide and CO₂, catalyzed by *N,N*-dimethylformamide (DMF) in the absence of nucleophiles such as chloride ion.²⁴ In that study, DMF reacts with epoxide to form cyclic species, followed by a ring-opening and subsequent ring-closure reactions. The reaction mechanism shown in Scheme 4 is in good agreement with the DMF-catalyzed reaction mechanism.

Finally, to examine the effect of the PHU structure on this reaction, TMS-PHU was selected. As a preliminary experiment, the reaction of PGE with CO₂ was performed using TMS-PHU¹⁸ instead of PHU (Scheme 1) under the conditions specified in Entry 6 of Table 1. After the reaction, TMS-PHU solid was successfully recovered by re-precipitation into diethyl ether. ¹H-NMR and GPC analyses revealed that the recovered TMS-PHU did not decompose (e.g., via desilylation) during the reaction, indicating that its original structure was well preserved (Figures S9 and S10; Table S3). After performing the evaluation and

purification procedures that were similar to those conducted using PHU, the conversion of PGE and isolated yield of **PGE-5CC** in the TMS-PHU catalyzed reaction were 52% and 49%, respectively. These values are very close to those obtained using PHU catalyst (Entry 6), which indicates that the urethane group of TMS-PHU exhibited sufficient catalytic activity for the cyclic carbonate synthesis. This result suggests that the catalytic activity of the urethane moiety in the original PHU is much higher than that of its hydroxy functional group (Scheme 1). However, PHU and TMS-PHU are inherently different in terms of hydrophobicity and main chain mobility, which presumably affect their catalytic activities. Therefore, a further study on the structural dependency of PHU on the reaction behavior is currently ongoing.

In summary, PHU effectively catalyzed the reactions of PGE and other epoxides with CO₂ to produce various 5CCs with very high yields. This is the first demonstration of the chemical transformation of CO₂ by PHU, which may assist in conducting further studies related to petroleum- and bio-based polyurethane^{1,2,7-10}-catalyzed reactions and their practical applications.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

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Supplementary Information

Poly(hydroxyurethane): Catalytic Applicability for the Cyclic Carbonate Synthesis from Epoxides and CO₂

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1. Materials and methods

Poly(hydroxyurethane)¹⁾ (PHU (HPU A-0110)) and modified PHU containing a trimethylsilyl protecting group (TMS-PHU (HPU A0110-TMS)) were supplied by Dainichiseika Color & Chemicals Mfg. Co., Ltd. (Tokyo, Japan). Phenyl glycidyl ether (PGE) and other epoxides were purchased from TCI (Tokyo, Japan). Butyric acid glycidyl ester used as a precursor of 5CC-8 was prepared as described in the literature²⁾. 18-Crown-6 was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and used without further purification. All reagents and solvents were of reagent grade and used as received unless stated otherwise.

¹H and ¹³C nuclear magnetic resonance (NMR) spectra (400 MHz ¹H and 100 MHz ¹³C) were recorded on a JNM-GX400 spectrometer (JEOL, Ltd., Japan) in CDCl₃ or dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) at room temperature (approximately 20 °C), and chemical shifts were determined using tetramethylsilane as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FTIR 460 KY Plus spectrometer (Tokyo, Japan), and transmission spectra were obtained using KBr discs. The number- and weight-average molecular weights (*M*_n and *M*_w, respectively) and polydispersity index (*D* = *M*_w/*M*_n) values of polymer samples were estimated by gel permeation chromatography (GPC) using a JASCO (JASCO Corp., Japan) high-performance liquid chromatography system (pump: PU-2060; reflective index detector: RI-2031; column oven: CO-4060) equipped with a polystyrene gel column (SB-804 HQ; Shodex Co. Ltd., Japan). Dimethylformamide (DMF) eluent containing 10 mmol/L LiBr was passed at a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards. Optical rotations were measured in the 50-mm length cell of a JASCO P-2200 digital polarimeter at a temperature of 21 °C and the average value was calculated from the results of ten independent measurements.

2. Synthesis and characterization

Synthesis of PGE-5CC and separation of PHU: In a typical procedure, 750 mg (5.00 mmol) PGE was added to a mixture of 277 mg (1.00 mmol) PHU and 6.6 mg (0.025 mmol) 18-crown-6 in a 200-mL autoclave. After pouring liquid CO₂, the autoclave was sealed and weighed on an electronic balance BPS6K01 (Asone, Japan; resolution: 0.1 g; capability: 6.000 kg) to calculate the weight of CO₂ in the reactor set to 39.0 g (890 mmol). Subsequently, the autoclave was heated to 120 °C for 16 h, cooled, and depressurized by venting the reactor bulb. Using an aliquot of the reaction mixture, a CDCl₃ solution for ¹H-NMR studies was prepared by removing the insoluble PHU fraction. The conversion of PGE and its selectivity for **PGE-5CC** production were estimated using the NMR singlet signal of 18-crown-6 as an internal standard.

The reaction mixture was dissolved in tetrahydrofuran and poured into a large amount of diethyl ether to precipitate a white solid. After filtration, the obtained solid was dried under vacuum at 40 °C for 20 h to recover PHU (269 mg), which was examined by ¹H-NMR, FT-IR, and GPC techniques. The filtrate was concentrated, and the crude product was purified by SiO₂ column chromatography (eluent: hexane/ethyl acetate = 4/1, v/v) to obtain 942 mg (4.85 mmol) **PGE-5CC** as a white solid corresponding to 97% yield.

The reaction, purification, and analysis steps were individually performed to evaluate the effects of variations in the reaction time (4–16 h) and temperature (90–150 °C) on the PGE conversion and its selectivity for **PGE-5CC** production.

Estimation of the molar ratio of urethane groups ([urethane groups]₀) to PGE: The molar amount of PHU urethane groups was estimated by the following equation:

$$[\text{urethane groups}]_0 = \frac{[\text{weight of PHU (g)}]}{[\text{molecular weight of PHU repeating unit [544.64]}]} \times 2 \quad (\text{S1})$$

From the molar amounts of urethane groups and PGE, the molar ratio [urethane groups]₀/[PGE]₀ was determined.

Reactions of substituted epoxides with CO₂: Synthesis of **5CC-1** is given as an example here. First, 471 mg (5.09 mmol) epichlorohydrin was added to a mixture of 277 mg (1.00 mmol) PHU and 6.6 mg (0.025 mmol) 18-crown-6 in a 200-mL autoclave. The reaction was performed following the **PGE-5CC** synthesis procedure described above. After the reaction, the resulting crude product was purified by SiO₂ column chromatography (eluent: hexane/ethyl acetate = 7/1, v/v) to obtain 640 mg (4.68 mmol) **5CC-1** as a colorless oil with a 92% yield.

Reaction of PGE with CO₂ using TMS-PHU catalyst: A reaction similar to the PHU-catalyzed process was also performed in this study. 750 mg (5.00 mmol) PGE was added to a mixture of 350 mg (1.00 mmol) TMS-PHU and 6.6 mg (0.025 mmol) 18-crown-6 in a 200 mL autoclave. The autoclave filled with pressured CO₂ (5.2 MPa) was heated to 90 °C for 16 h. After the reaction, ¹H-NMR measurements were performed to estimate the conversion of PGE and selectivity for **PGE-5CC** production using an aliquot of the reaction mixture. The mixture was then re-precipitated from the CHCl₃ solution thrice using diethyl ether three times to recover 270 mg of TMS-PHU as a white solid. The resulting diethyl ether solution was concentrated, and the crude product was purified by SiO₂ column chromatography (eluent: hexane/ethyl acetate = 4/1, v/v) to obtain 476 mg (2.45 mmol) **PGE-5CC** as a white solid corresponding to a 49% yield.

Synthesis of PHU from the reaction of 5CC-12 and 1,6-hexamethylenediamine: 1,6-hexamethylenediamine (1.16 g, 10 mmol) was added to a solution of **5CC-12** (4.28 g, 10 mmol) in DMF (20 mL) under nitrogen atmosphere. The mixture was stirred for 24 h at 100 °C. The reaction mixture was poured into 450 mL of diethyl ether resulting in the precipitate of a white solid. The precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo* at 50 °C to give PHU as a white solid (4.77 g, 87 % yield). The obtained PHU exhibited ¹H-NMR spectrum and GPC profile very similar to that of the PHU supplied by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

$M_n = 1.02 \times 10^4$, $M_w = 2.18 \times 10^4$, $D = 2.14$.

¹H-NMR spectrum and GPC profile were shown in **Figure S5** and **S6**.

3. Estimations of PGE conversion and selectivity by $^1\text{H-NMR}$ (see Figure S1)

The conversion of PGE and selectivity for **PGE-5CC** production were estimated via the following equations:

$$\text{Conversion of PGE (\%)} = \left(1 - \frac{f/200}{X/24}\right) \times 100 \quad (\text{S2})$$

$$\text{Selectivity of the reaction for the production of PGE-5CC (\%)} = \frac{F/200}{X/24} / \left(1 - \frac{f/200}{X/24}\right) \times 100 \quad (\text{S3})$$

where f = integral ratio of PGE methine protons (from Figure S1)

F = integral ratio of **PGE-5CC** methine protons (from Figure S1)

X = integral ratio of 18-crown-6 used as an internal standard.

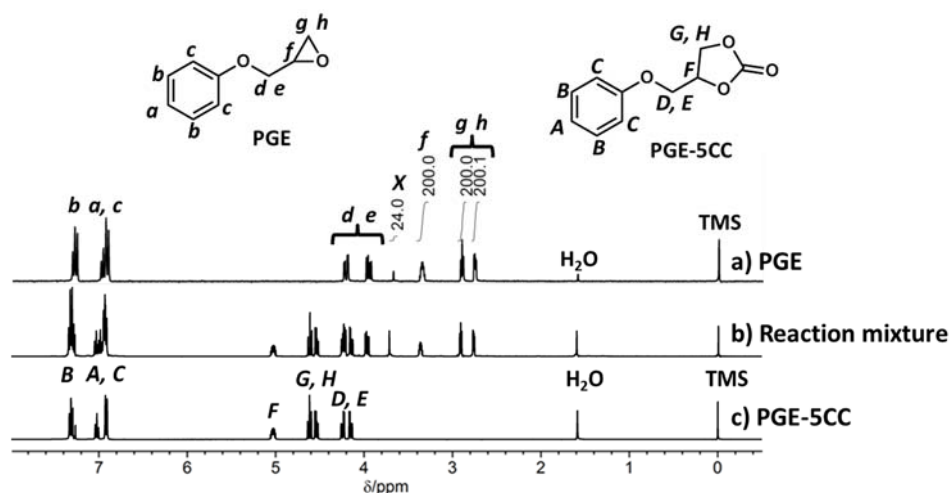


Figure S1. $^1\text{H-NMR}$ (CDCl_3) spectra of a) PGE, b) the reaction mixture, and c) **PGE-5CC**. Reaction conditions: 90 $^\circ\text{C}$, 16 h, and 5.2 MPa CO_2 pressure in the presence of PHU ($[\text{urethane groups}]_0/[\text{PGE}]_0 = 0.20$). Signal X is generated by 18-crown-6.

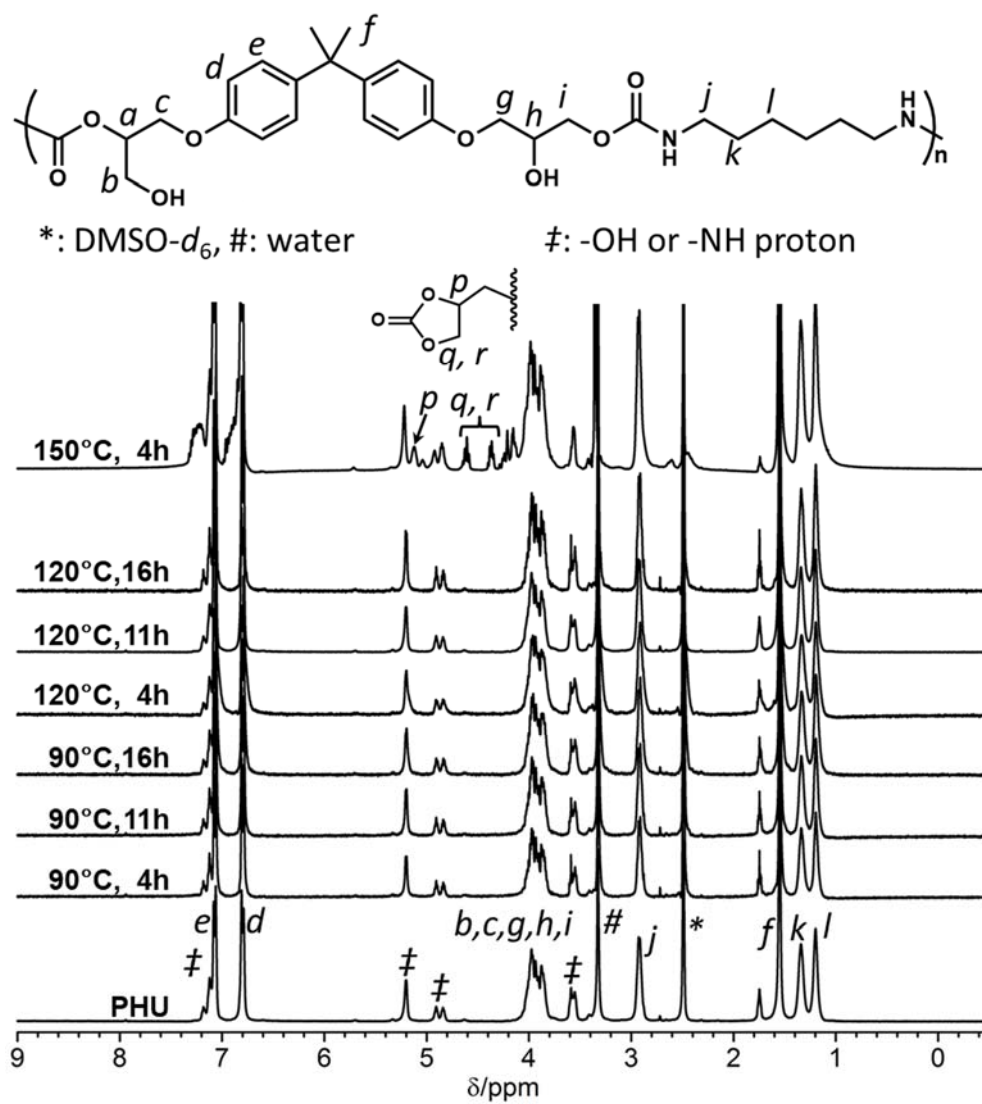


Figure S2. $^1\text{H-NMR}$ (DMSO- d_6) spectra of the pristine PHU and PHU after the reaction by filtration.

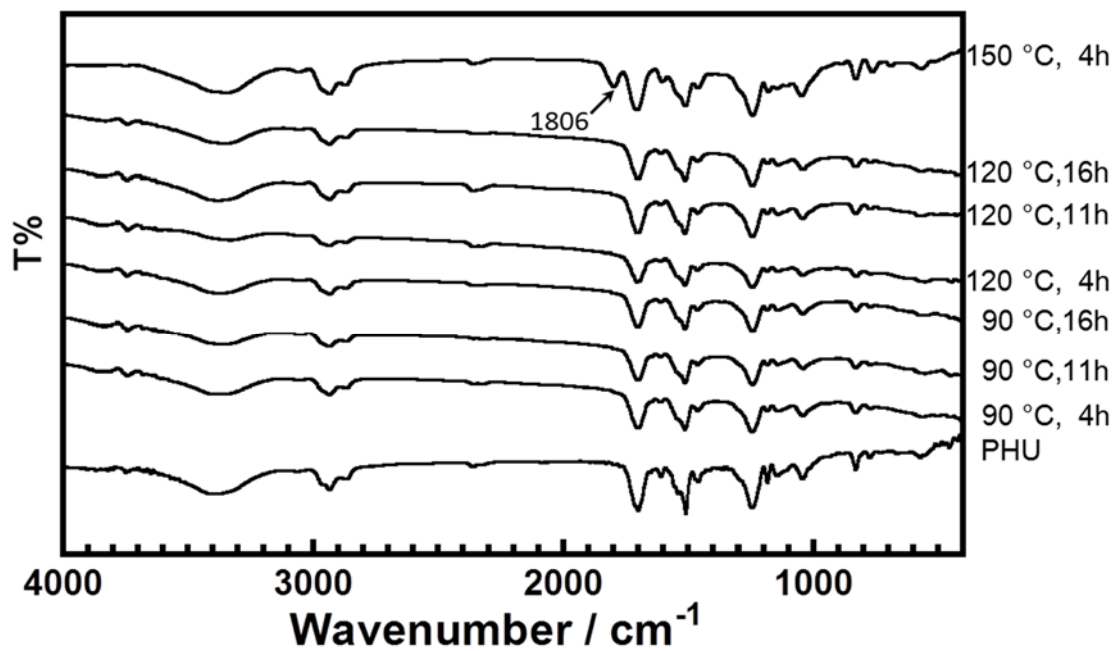


Figure S3. FT-IR spectra of the pristine PHU and PHU after the reaction by filtration.

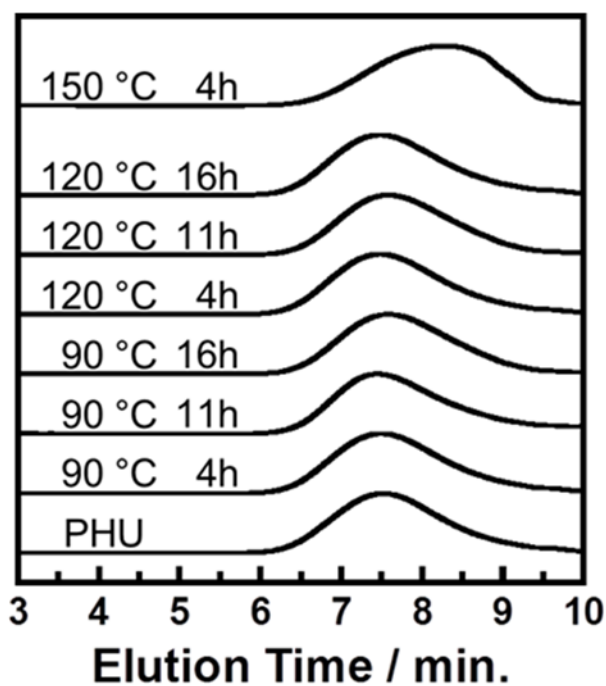


Figure S4. GPC profiles of the pristine and recovered PHU. DMF was used as the eluent.

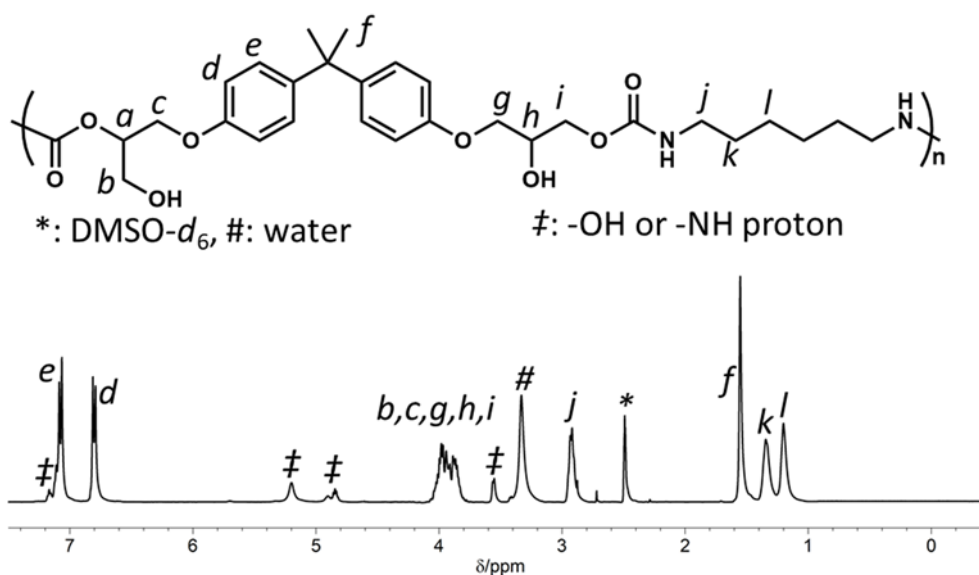


Figure S5. $^1\text{H-NMR}$ (DMSO- d_6) spectrum of the PHU synthesized from **5CC-12** and 1,6-hexamethylenediamine.

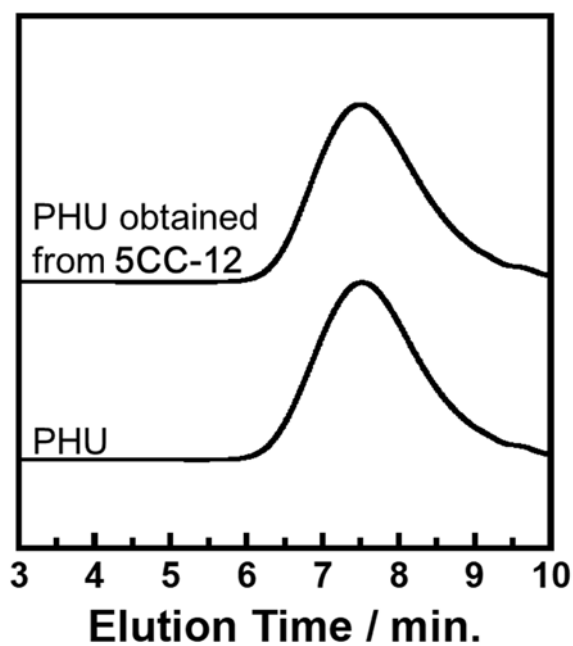


Figure S6. GPC profiles of the pristine PHU and PHU synthesized from **5CC-12** and 1,6-hexamethylenediamine.

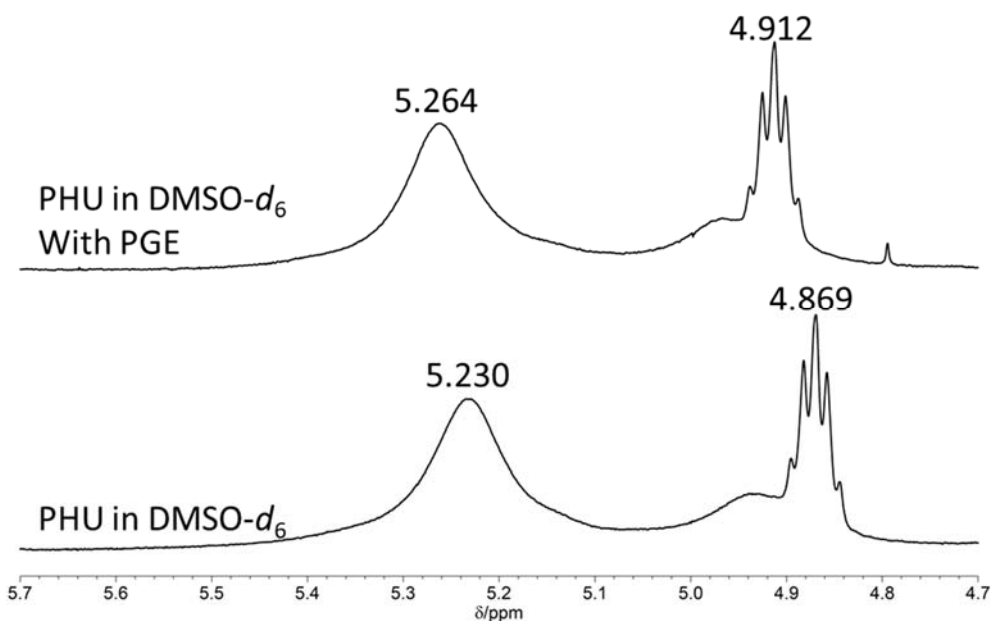


Figure S7. $^1\text{H-NMR}$ (400 MHz) spectra of PHU (0.32 mmol of urethane moiety) and the mixture of PGE (0.64 mmol) and PHU (0.32 mmol) in 0.8 mL of $\text{DMSO-}d_6$.

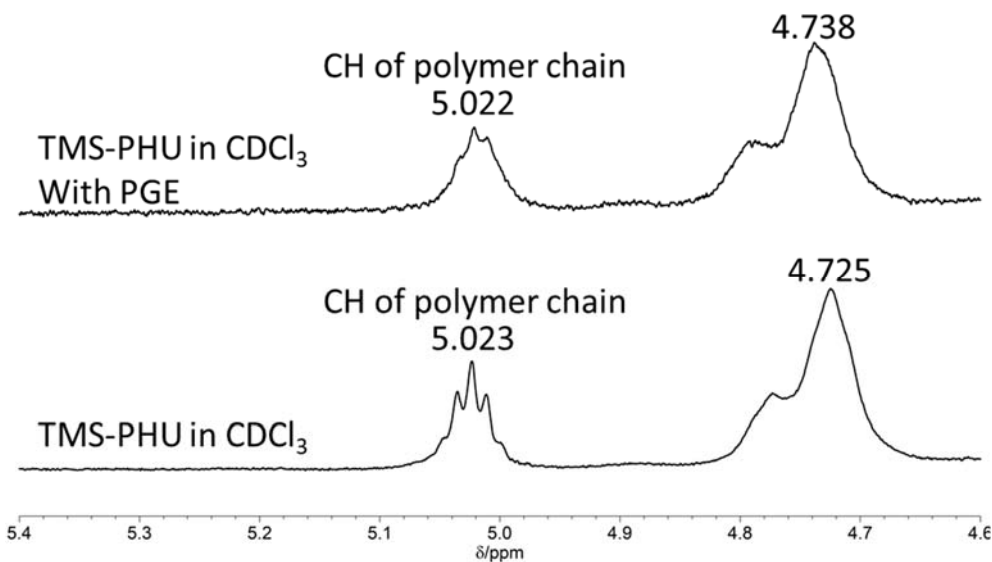


Figure S8. $^1\text{H-NMR}$ (400 MHz) spectra of TMS-PHU (0.32 mmol of urethane moiety) and the mixture of PGE (0.64 mmol) with TMS-PHU (0.32 mmol) in CDCl_3 .

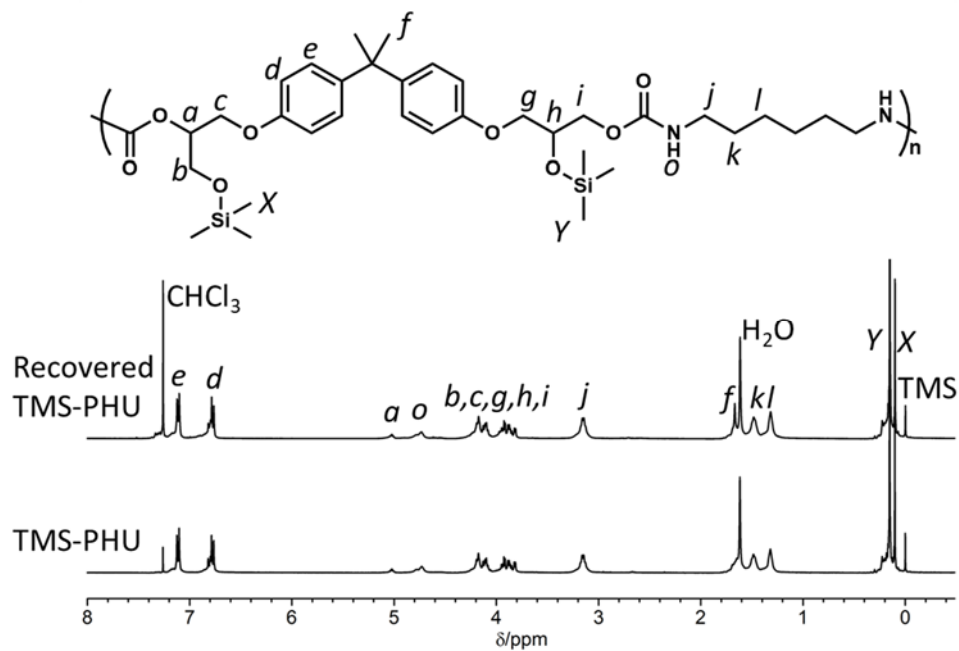


Figure S9. $^1\text{H-NMR}$ (CDCl_3) spectra of the pristine TMS-PHU and the TMS-PHU recovered after reaction by filtration.

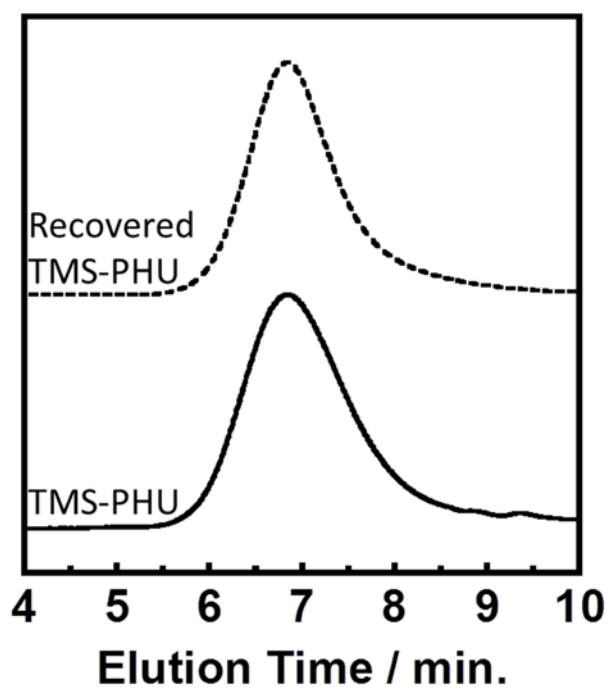


Figure S10. GPC profiles of the pristine and recovered TMS-PHU. DMF was used as the eluent.

Table S1. Weights of the added and recovered PHU.

Entry	Temp. / °C	Time / h	PHU weight / g	Weight of recovered PHU / g
4	90	4	0.275	0.267
5	90	11	0.274	0.269
6	90	16	0.275	0.263
8	120	4	0.277	0.266
9	120	11	0.282	0.273
10	120	16	0.277	0.269
11	150	4	0.277	0.220

The entry numbers correspond to those of Table 1 in the main file.

Table S2. M_n , M_w , and D (M_w/M_n) values of the added and recovered PHU.

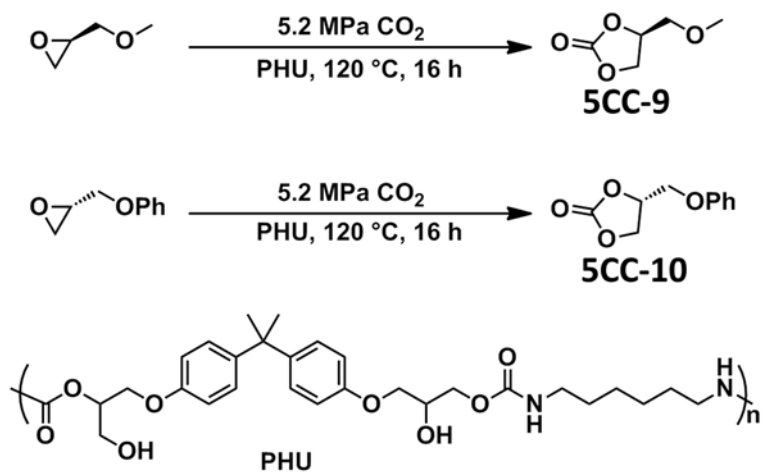
	$M_n / 10^4$	$M_w / 10^4$	D
PHU	1.03	2.19	2.13
Entry 11 (150 °C, 4 h)	0.34	0.87	2.59

M_n : number-average molecular weight; M_w : weight-average molecular weight; D : dispersity defined as M_w/M_n . The samples are identical to those analyzed in Figure S4.

Table S3. M_n , M_w , and D (M_w/M_n) values of the added and recovered TMS-PHU.

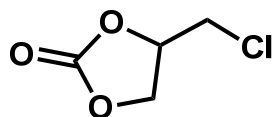
	$M_n / 10^4$	$M_w / 10^4$	D
TMS-PHU	2.33	4.55	1.95
Recovered TMS-PHU	2.25	4.44	1.97

M_n : number-average molecular weight; M_w : weight-average molecular weight; D : dispersity defined as M_w/M_n . The samples are identical to those analyzed in Figure S6.

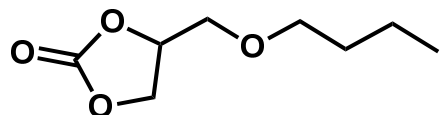


Scheme S1. PHU-catalyzed syntheses of 5CCs (**5CC-9** and **5CC-10**) through the reaction of optically active epoxides and CO₂.

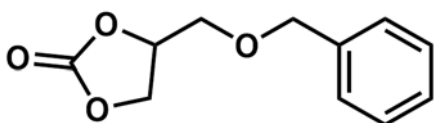
4. Characterization of 5CCs



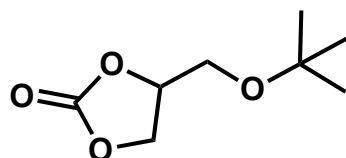
4-(chloromethyl)-1,3-dioxolan-2-one (5CC-1)^{3, 4)}: Colorless oil; ¹H-NMR (400 MHz, CDCl₃): δ 5.00–4.94 (m, 1H), 4.60 (dd, *J* = 8.4, 8.8 Hz, 1H), 4.42 (dd, *J* = 5.6, 8.8 Hz, 1H), 3.81–3.70 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 154.0, 74.2, 67.0, 43.5.



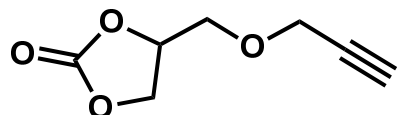
4-(butoxymethyl)-1,3-dioxolan-2-one (5CC-2)⁵⁾: Colorless oil; ¹H-NMR (400 MHz, CDCl₃): δ 4.84–4.81 (m, 1H), 4.53–4.48 (m, 1H), 4.39 (dd, *J* = 6.0, 7.2 Hz, 1H), 3.70–3.66 (m, 1H), 3.62–3.58 (m, 1H), 3.51 (dd, *J* = 8.4, 8.4 Hz, 2H), 1.61–1.52 (m, 2H), 1.41–1.32 (m, 2H), 0.92 (t, *J* = 6.8 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 155.0, 75.1, 71.7, 69.5, 66.2, 31.4, 19.0, 13.7.



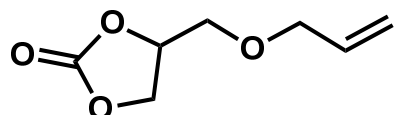
4-((benzyloxy)methyl)-1,3-dioxolan-2-one (5CC-3)^{4, 5)}: White solid; ¹H-NMR (400 MHz, CDCl₃): δ 7.36–7.31 (m, 5H), 4.84–4.78 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.48 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.38 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.73–3.60 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 154.9, 137.0, 128.5, 128.0, 127.7, 74.9, 73.6, 68.8, 66.2.



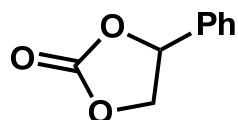
4-(tert-butoxymethyl)-1,3-dioxolan-2-one (5CC-4)³⁾: Colorless oil; ¹H-NMR (400 MHz, CDCl₃): δ 4.82–4.76 (m, 1H), 4.49 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.39 (dd, *J* = 8.0, 8.4 Hz, 1H), 3.65–3.51 (m, 2H), 1.20 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃): δ 155.2, 75.1, 73.7, 66.4, 61.2, 27.2.



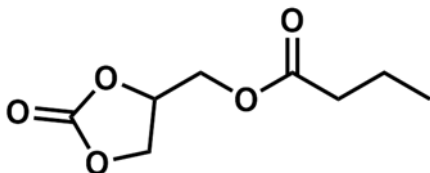
4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (5CC-5)⁵⁾: Colorless oil; ¹H-NMR (400 MHz, CDCl₃): δ 4.89–4.84 (m, 1H), 4.52 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.41 (dd, *J* = 6.0, 8.4 Hz, 1H), 4.30–4.19 (m, 2H), 3.82–3.73 (m, 2H), 2.51 (t, *J* = 2.3 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 154.8, 78.5, 75.6, 74.6, 68.4, 66.2, 58.8.



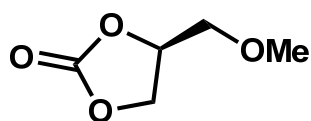
4-((allyloxy)methyl)-1,3-dioxolan-2-one (5CC-6)^{3, 4)}: Colorless oil; ¹H-NMR (400 MHz, CDCl₃): δ 5.91–5.83 (m, 1H), 5.32–5.22 (m, 2H), 4.85–4.81 (m, 1H), 4.51 (dd, *J* = 8.2, 8.2 Hz, 1H), 4.40 (dd, *J* = 6.0, 8.4 Hz, 1H), 4.08–4.05 (m, 2H), 3.70 (dd, *J* = 4.0, 11.2 Hz, 1H), 3.62 (dd, *J* = 4.0, 11.2 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 154.9, 133.6, 117.9, 75.0, 72.6, 68.8, 66.2.



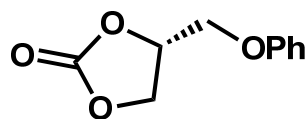
4-Phenyl-1,3-dioxolan-2-one (5CC-7)³⁻⁵: White solid; ¹H-NMR (400 MHz, CDCl₃): δ 7.46–7.35 (m, 5H), 5.68 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.80 (dd, *J* = 8.0, 8.4 Hz, 1H), 4.35 (dd, *J* = 8.0, 8.4 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 154.8, 135.7, 129.7, 129.2, 125.8, 78.0, 71.1.



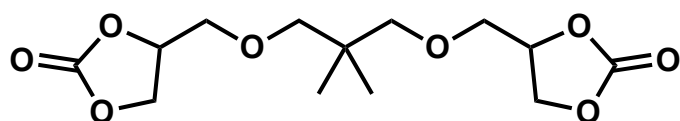
(2-oxo-1,3-dioxolan-4-yl)methyl butyrate (5CC-8)⁶: Colorless oil; ¹H-NMR (400 MHz, CDCl₃): δ 4.99–4.94 (m, 1H), 4.58 (dd, *J* = 8.7, 8.5 Hz, 1H), 4.40–4.25 (m, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.71–1.62 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 173.0, 154.5, 73.8, 65.9, 62.7, 35.6, 18.1, 13.4.



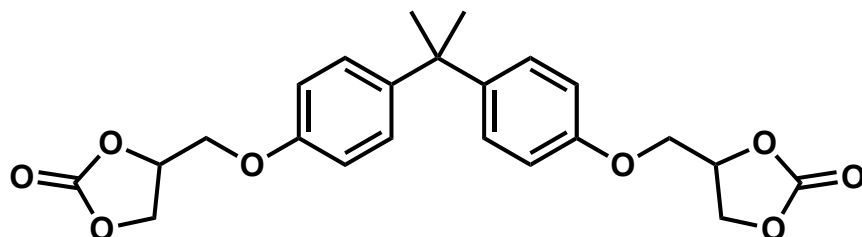
(S)-4-(methoxymethyl)-1,3-dioxolan-2-one (5CC-9)⁷: Colorless oil; ¹H-NMR (400 MHz, CDCl₃) δ 4.84–4.79 (m, 1H), 4.50 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.38 (dd, *J* = 6.0, 8.0 Hz, 1H), 3.65 (dd, *J* = 4.0, 10.8 Hz, 1H), 3.57 (dd, *J* = 3.6, 10.8 Hz, 1H), 3.43 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 154.9, 75.0, 71.2, 65.9, 59.2. [*a*]_D²¹ = -35.3 (*c* = 1.0, EtOH) [lit.7 [*a*]_D²⁴ = -36.5 (*c* = 1.0, EtOH, >98% ee (*S*))].



(R)-4-(phenoxy)methyl-1,3-dioxolan-2-one (5CC-10)⁴: White solid; ¹H-NMR (400 MHz, CDCl₃) δ 7.28 (t, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.03–4.98 (m, 1H), 4.58 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.50 (dd, *J* = 6.0, 8.8 Hz, 1H), 4.24 (dd, *J* = 4.0, 10.8 Hz, 1H), 4.10 (dd, *J* = 3.6, 10.8 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 157.7, 154.7, 129.6, 121.8, 114.5, 74.2, 66.8, 66.1. [*a*]_D²¹ = +18.0 (*c* = 1.0, EtOH) [lit.4 [*a*]_D²⁰ = +18.3 (*c* = 1.2, EtOH; 99% ee (*R*))].



4,4'-(((2,2-dimethylpropane-1,3-diyl)bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (5CC-11)¹: White solid; ¹H-NMR (400 MHz, CDCl₃) δ 4.85–4.82 (m, 2H), 4.54–4.36 (m, 4H), 3.73–3.70 (m, 2H), 3.60–3.57 (m, 2H), 3.29–3.23 (m, 4H), 0.88 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃, mixture of stereoisomers): δ 155.1, 76.7, 76.6, 75.2, 70.3, 70.0, 66.1, 36.2, 21.8.



4,4'-(((propane-2,2-diyl)bis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (5CC-12)¹: White solid; ¹H-NMR (400 MHz, CDCl₃): δ 7.14 (d, *J* = 8.8 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 4H), 5.04–4.98 (m, 2H), 4.60 (dd, *J* = 8.5, 8.5 Hz, 2H), 4.52 (dd, *J* = 5.9, 8.5 Hz, 2H), 4.23 (dd, *J* = 4.3, 10.6 Hz, 2H),

4.12 (dd, $J = 3.5, 10.7$ Hz, 2H), 1.63 (s, 6H). ^{13}C -NMR (100 MHz, CDCl_3): δ 155.4, 154.4, 144.1, 127.7, 113.8, 73.9, 66.7, 66.0, 41.6, 30.7.

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