

# Improved Synthesis of Unsymmetrical Carbonate Derivatives Using Calcium Salts

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**Supporting Information** 

**ABSTRACT:** An effective synthetic method for unsymmetrical carbonate species has been developed. Calcium oxide and calcium hydroxide were found to be highly effective for this reaction, affording unsymmetrical carbonates in high yield and purity. Calcium chloride, which is a coproduct, serves as a water scavenger that can be easily removed. Additional drying processes and complicated purification steps are not necessary in this reaction. This improved process is important in terms of green sustainable chemistry principles.

**KEYWORDS:** *unsymmetrical carbonate synthesis, effective dry process, sustainability, green chemistry* 

# INTRODUCTION

Carbonate derivatives are key compounds for electrolytes in lithium ion batteries,<sup>1-6</sup> as shown in Figure 1. Among them, unsymmetrical carbonates are employed as main electrolyte solvents because of their low viscosities.<sup>7</sup> Fluorine-containing carbonates, such as compounds 1a and 4, are particularly stable at high voltages.<sup>8</sup> Furthermore, high purity of the products is required to achieve large capacities and low electric resistances.<sup>3</sup>

Conventional synthetic methods for unsymmetrical carbonate species<sup>8,11-13</sup> are shown in Scheme 1. Method A, the ester exchange reaction, is normally carried out under acidic or catalytic conditions. This transesterification affords low yields, where the symmetric starting material is recovered because of the reversibility of the reaction. On the other hand, in Method B, organic amines are typically utilized to capture hydrogen chloride gas. However, in industrial processes, these methods are associated with several drawbacks, as summarized below:<sup>9</sup>

- The conversion is low (Method A).
- Washing processes are required to remove ammonium salts.
- Said washing processes result in the loss of target compounds and generation of symmetric byproducts due to transesterifications. These transesterifications are caused by alcohol species generated from alkyl haloformates and water.
- In many cases, removal of the amine from the target compound is difficult because of their similar boiling points.
- In industrial processes, the washing process with acidic aqueous solution has the possibility to be unsuitable for

these cases because of the transesterification and loss of desired compounds.

Unsymmetrical chain carbonates are generally more predisposed to decompose than symmetric carbonate species under conditions of high humidity and heat because of their electronic bias.<sup>9,10</sup> This unsymmetrical state is caused by the difference in the leaving abilities of the two alkoxides. Therefore, anhydrous synthetic methods are required for such unsymmetrical carbonate derivatives. Two kinds of reaction processes, using organic or inorganic bases, are regarded as improved reaction conditions to circumvent these problems.

# RESULTS AND DISCUSSION

Process Using Organic Bases. As a solution to the problems of conventional methods, removable amines with high boiling points and direct purification by distillation can be employed (Table 1). Triethylamine was thus tested in a preliminary study. In this case, high conversion and selectivity were obtained, but the boiling points of this amine and product 1a are almost the same (entry 1). In addition, a washing step for the removal of triethylamine hydrochloride is required. Therefore, the reaction yield is very low. Tributylamine was then selected for this reaction (entry 2). This amine afforded high conversion and a homogeneous reaction mixture as a result of the high solubility of tributylamine hydrochloride in several solvents.<sup>14</sup> The operation of purification is easy to perform, which is a benefit for process chemistry. However, the selectivity and the isolated yield of this reaction were significantly reduced, as it was very difficult to isolate 1a from its mixture with 2 because of their similar boiling points. Therefore, we considered that these processes using amines are not suitable for industrial carbonate synthesis in terms of high purity and yield. Further studies of this type of system were thus not pursued.

A plausible mechanism for the observed undesired reactions is shown in Scheme 2. In a previous report, tertiary amines and methyl chloroformate were found to generate trialkylmethylammonium chloride and carbon dioxide.<sup>15</sup> Path (i) is the desired reaction, while path (ii) affords reduced selectivity due to the generation of methanol following the production of ammonium salts and the hydrolysis of methyl chloroformate.<sup>16</sup> Triethylamine favors the fast path (i) and good selectivity.

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Figure 1. Carbonate species employed in lithium ion batteries.





Otherwise, in the reaction with tributylamine, we believe that the reactivity of a tributylacylammonium intermediate with trifluoroethanol is low because of its bulky structure, so path (ii) predominates.

Process Using Inorganic Bases. As another class of easily removable reagents, solid bases such as inorganic salts were considered. Sodium hydroxide and potassium carbonate were examined in the neat state for the synthesis of carbonate 1a (Table 2). Inorganic bases are normally suitable for industrial and green chemistry processes because they are inexpensive and easily available. They are typically used for hydrolysis; therefore, the reaction mixture was analyzed quickly. Although the reaction time was short, the inorganic salts tested afforded inadequate conversions (entries 1 and 2). On the other hand, excess potassium carbonate afforded high conversion (entry 3). However, water present in the starting materials promotes this reaction, triggering also decomposition reactions such as disproportionation. As a result, symmetric byproducts are generated, leading to rather low isolated yields. Moreover, compound 2 inhibits the efficient purification of 1a by distillation in this reaction because they have the same boiling

#### Table 1. Use of Different Organic Amines

point. Therefore, an additional drying agent was used to reduce the moisture content. Molecular sieves were able to improve the selectivity (entry 4); however, this additional solid adsorbent caused stirring difficulties and decreased both the conversion and yield.

Scheme 3 shows the side reactions believed to occur in this process. Different decomposition reactions may proceed because of the presence of water. Potassium carbonate and water afford potassium hydroxide according to reaction (A). As shown reactions (B), water causes the hydrolysis of compound 6 and the generation of methanol. Then water is regenerated by the neutralization between hydrogen chloride and potassium carbonate. The hydroxide anion triggers proton abstraction and the regeneration of water. This water reacts with a potassium carbonate molecule again through reaction (A). As a result, alkoxides are generated in several steps, which subsequently produce symmetrical carbonates. In addition, the methoxide anion is more reactive than trifluoroethoxide because of its electron density. In fact, starting materials 6 and 7a were found to contain water at 480 and 1100 ppm, respectively, as measured with a Karl Fischer moisture meter. This moisture is believed to be the cause of the undesired reactions.

New Anhydrous Method with Calcium Species. Next, we examined an effective method under anhydrous and basic conditions without any additional solid drying agent. Our proposal is shown in Scheme 4. First, calcium oxide quickly reacts with  $H_2O$  from the reaction system, accompanied by heat generation. Second, the main reaction is assisted by calcium hydroxide as a strong base. Third, calcium chloride removes  $H_2O$  from the reaction system as a hydrate. Finally, the  $H_2O$  molecule is partially absorbed by calcium oxide again. Therefore, the calcium species works as both an accelerator of

|       | MeO CI + HO CF <sub>3</sub><br>(1.0 eq.) (1.0 eq.) | base (1.0 eq.)<br>CH <sub>2</sub> Cl <sub>2</sub> (1.0 M)<br>room temperature |                               |                      | O<br>O<br>CF         |
|-------|--|---|-------------------------------|----------------------|----------------------|
|       | 6a 7a  | 18 h  | 1a                            | 2<br>90 °C           | 8a                   |
|       |  |   |                               |                      |                      |
| entry | base   | bp (°C)   | conv. (%) <sup><i>a</i></sup> | 1a:2:8a <sup>b</sup> | yield of $1a (\%)^c$ |
| 1     | triethylamine                                      | 89  | 100                           | 93:6:1               | 51                   |
| 2     | tributylamine                                      | 216   | 100                           | 72:26:2              | 43                   |

<sup>a</sup>The conversion refers to the consumption of 7a, as determined by the GC area %. <sup>b</sup>Determined from the GC area %. <sup>c</sup>Isolated yields.

Scheme 2. Plausible Mechanism for the Reduction in the Reaction Selectivity



Table 2. Use of Different Inorganic Bases

|       | MeO CI <sup>+</sup> HO CF <sub>3</sub><br>(1.0 eq.) (1.0 eq.)<br>6a 7a | base<br>additive<br>neat<br>room temperature<br>2 minutes<br>1a |                               | e <sup>+</sup> F <sub>3</sub> C 0 8a | CF3                    |
|-------|--|---|-------------------------------|--------------------------------------|------------------------|
| entry | base   | additive  | conv. (%) <sup><i>a</i></sup> | 1a:2:8a <sup>b</sup>                 | yield of $1a \ (\%)^c$ |
| 1     | NaOH (1.0 equiv)   | none  | 68                            | -                                    | -                      |
| 2     | $K_2CO_3$ (1.0 equiv)  | none  | 79                            | -                                    | -                      |
| 3     | $K_2CO_3$ (2.0 equiv)  | none  | 99                            | 49:40:11                             | trace                  |
| 4     | $K_2CO_3$ (2.0 equiv)  | $MS4A^d$  | 80                            | 80:17:3                              | trace                  |

<sup>*a*</sup>The conversion refers to the consumption of 7a, as determined by the GC area %. <sup>*b*</sup>Determined from the GC area %. <sup>*c*</sup>Isolated yields. <sup>*d*</sup>MS4A refers to 4Å molecular sieves. The mass of MS4A was equal to the mass of 7a in this reaction.





the key reaction and a water scavenger. In these points, calcium species have the advantage over other inorganic bases such as potassium carbonate.

Calcium oxide and calcium hydroxide were applied in the present system (Table 3). The former was found to be suitable for this reaction, affording excellent selectivity, but the reaction

was very slow (entries 1 and 2). From these results, we concluded that solid reagents hinder the stirring and slow down the removal of water in the late stages of the reaction. Dodecane was used as a nonreactive diluent to improve the stirring and conversion (entry 3). However, the reaction time was still very long. The key to this reaction is the generation of

## Scheme 4. Proposed Method Involving a Calcium Cycle



#### Table 3. Use of Different Calcium Species

|       | MeO CI +<br>(1.0 eq.)<br>6a | HO CF <sub>3</sub> Ca-base (1.0 eq.)<br>(1.0 eq.) 0 °C<br>7a | MeO CF3           | * MeO OMe +<br>2              | 0<br>F₃C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | `CF₃                 |
|-------|-----------------------------|--|-------------------|-------------------------------|--|----------------------|
| entry | Ca base                     | solvent  | time              | conv. (%) <sup><i>a</i></sup> | 1a:others <sup>b</sup>                         | yield of $1a (\%)^c$ |
| 1     | CaO                         | none   | 1 h               | 78                            | >99:1  | _                    |
| 2     | CaO                         | none   | 3 days            | 96                            | >99:1  | -                    |
| 3     | CaO                         | dodecane   | 3 days            | 99                            | >99:1  | 85                   |
| 4     | CaO                         | dodecane   | 27 h <sup>d</sup> | 99                            | 95:5   | 79                   |
| 5     | $Ca(OH)_2$                  | dodecane   | 20 h              | >99                           | >99:1  | 92                   |
| 6     | $Ca(OH)_2$                  | 1a   | 20 h              | 93 <sup>e</sup>               | >99:1  | 89                   |

"The conversion refers to the consumption of 7a, as determined by the GC area %. <sup>b</sup>The ratio was determined by the GC area %. <sup>c</sup>Isolated yield. "0.1 equiv of water was added to the mixture to accelerate the reaction. <sup>e</sup>The conversion and 1a:others ratio were calculated using the following equations: conv. (%) =  $(A_{1a} - B_{1a} + A_2 + A_{8a})/B_{7a} \times 100$  and 1a:others =  $(A_{1a} - B_{1a})/(A_2 + A_{8a})$ , where A is the GC area % in the reaction mixture and B is the GC area % before addition of the Ca base.

#### Table 4. Substrate Scope

|       | R <sup>1</sup> (<br>R <sup>1</sup> | $ \begin{array}{c} O \\ O \\ \hline CI \end{array}^+ R^2 OH \\ = Me (6) \\ Et (6') \end{array} $ | Ca(OH) <sub>2</sub> (1.0 eq<br>dodecane (1.0 M<br>0 °C<br>overnight | $\begin{array}{c} \textbf{A} \textbf{A} \textbf{A} \textbf{A} \textbf{A} \textbf{A} \textbf{A} A$ | + $R^{1}OOR^{1}$<br>$R^{1} = Me(2)$<br>Et (2') | + 0<br>R <sup>2</sup> O OR <sup>2</sup><br>8a-d |                      |
|-------|------------------------------------|--|---|---|--|---|----------------------|
| entry | $\mathbb{R}^1$                     | R <sup>2</sup> OH  | [   | product   | conv. (%) <sup><i>a</i></sup>                  | product:others <sup>b</sup>                     | yield of $1a (\%)^c$ |
| 1     | Me (6)                             | 2,2,2-trifluoroet  | hanol (7 <b>a</b> )   | 1a  | >99  | >99:1   | 92                   |
| 2     | Et (6')                            | 2,2,2-trifluoroet  | hanol (7 <b>a</b> )   | 1a'   | >99  | >99:1   | 89                   |
| 3     | Me (6)                             | ethanol (7b)   |   | 1b  | 89   | >99:1   | 79                   |
| 4     | Me (6)                             | allyl alcohol (70  | :)  | 1c  | 92   | >99:1   | 81                   |
| 5     | Me (6)                             | phenol (7d)  |   | 1d  | 90   | 97:3  | 77 <sup>d</sup>      |

<sup>*a*</sup>The conversion refers to the consumption of 7a-d, as determined by the GC area %. <sup>*b*</sup>The ratio was determined by the GC area %. <sup>*c*</sup>Isolated yields. <sup>*d*</sup>Dichloromethane was used instead of dodecane for the isolation step.

calcium hydroxide. A small amount of water was thus added to the mixture to accelerate the reaction (entry 4). Such water addition shortened the reaction time, albeit with reduced selectivity toward 1a. Next, we found that calcium hydroxide presents adequate basicity and water removal ability for this reaction (entry 5). This calcium species was revealed as the most suitable reagent for the synthesis of 1a, affording short reaction times, high conversions, and excellent selectivity without the addition of water.

Moreover, if the target compound could be used as the solvent, the possibility of contamination would be completely eliminated. This is an important standpoint in process chemistry. Indeed, the target molecule 1a could be employed as the solvent (Table 3, entry 6). This was possible because of the completely dry conditions obtained using calcium species. For example, base-sensitive solvents such as 1a cannot be used

under wet conditions. Under the present improved conditions, DMC is not generated and the target compound can be easily separated. Furthermore, the product is kept dry without the need for any additional drying process.

Substrate Scope and Applications. Various substrates were examined under the newly developed reaction conditions (Table 4). The reaction was also suitable for other fluorine-containing unsymmetrical carbonates (entry 2). Moreover, these conditions could also be applied to general alkyl and aromatic alcohols without any side reactions such as disproportionation and polymerization (entries 3-5). As a result, fluorine-containing carbonate species, which are more water-sensitive than non-fluorine-containing carbonates, are particularly favored in this system. The boiling points of the alcohols were not too similar to those of the products; therefore, all of the products could be easily isolated by

distillation under dry conditions and directly used in lithium ion batteries without additional drying processes.

Carbonate species are useful not only as electrolytes but also as versatile building blocks.<sup>16,17</sup> Glycerol carbonate exhibits broad reactivity due to the presence of both a hydroxyl group and a 2-oxo-1,3-dioxolane group, and thus, it has been studied and employed in several emerging applications from solvents to polymers.<sup>15</sup> This molecule was therefore targeted as another application of the present reaction (Scheme 5). The desired compound **10** was obtained in high yield by esterification and transesterification reactions involving thermal methanol elimination.



Scaled-Up Process. Moreover, this reaction was performed at kilogram scale, as indicated in Table 5. In the case of



| N.     | <b>6</b><br>(1.0 eq.) | <b>7a</b><br>(1.0 eq.) | 22 h                              | 1a      | 0.3                    |
|--------|-----------------------|------------------------|-----------------------------------|---------|------------------------|
| entry  | v solvent             |                        | purification                      |         | yield (%) <sup>a</sup> |
| 1<br>2 | dodecane<br>1a        | filtratio<br>distilla  | on, separation, and disti<br>tion | llation | 85<br>82 <sup>b</sup>  |

"Isolated yields. <sup>b</sup>The yield was calculated without considering the amount of **1a** used as the solvent. The details of the procedure are described in the Experimental Section.

the dodecane solution, the product was easily isolated by distillation from the filtrate crude solution (entry 1). The target carbonate **1a** was also suitable for scale-up as the solvent instead of dodecane (entry 2). In this case, only distillation was required for product purification.

## CONCLUSIONS

An effective synthesis of unsymmetrical carbonates was developed that affords high conversion and selectivity. The key to the success of this process is the use of calcium oxide or calcium hydroxide. These calcium species are easy to obtain and separate after the reaction and can be reused in the total demand of calcium. This reaction method is more suitable for water-sensitive fluorine-containing carbonates than for hydrocarbon carbonates. In addition, this process offers good atom economy, as the key reaction and drying steps are performed at the same time. Thus, this efficient reaction has great potential in sustainable chemistry processes.

### EXPERIMENTAL SECTION

**General Information.** Starting materials, reagents, and solvents were obtained from commercial suppliers and used without further purification. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were measured on a JEOL RESONANCE ECZ-400S 400 MHz FT NMR spectrometer in the specified deuterated solvent. The chemical shifts ( $\delta$ ) of the <sup>1</sup>H NMR spectra are

reported in parts per million using an internal standard (TMS) or residual solvent (CHCl<sub>3</sub>: 7.26 ppm). Data are reported as follows: chemical shift (multiplicity, coupling constant, integration). Multiplicities are denoted as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, tt = triplet of triplets, q = quartet, dq = doublet of quartets, qd = quartet of doublets, and m = multiplet. Chemical shifts of proton-decoupled <sup>13</sup>C NMR spectra are reported in parts per million from the central signal of CDCl<sub>3</sub> (77.0 ppm). Gas chromatography (GC) analysis was performed on a SHIMAZU GC-2010 Plus system with a DB-624 column (Agilent Technology, part no. 123-1364, column length 60 m, inner diameter 0.320 mm, film thickness 1.80  $\mu$ m).

**GC Method.** Injection mode, split; vaporization chamber temperature, 200 °C; carrier gas, helium; control mode, linear velocity; pressure, 122.6 kPa; split ratio, 50.0; column temperature, 40.0 to 250.0 °C at 10 °C/min.

Synthesis of Methyl 2,2,2-Trifluoroethyl Carbonate (1a). General Procedure Using an Amine. 2,2,2-Trifluoroethanol (7a) (0.93 mL, 12.9 mmol) was dissolved in dichloromethane (130 mL), and methyl chloroformate (6) (1.0 mL, 12.9 mmol) was added to the solution. The mixture was cooled to 0 °C and stirred for 15 min. Tributylamine (0.46 mL, 1.94 mmol) was then added dropwise, and the mixture was slowly warmed to 25 °C. After stirring overnight, the reaction mixture was analyzed by GC.

General Procedure Using Calcium Salts for Chain Carbonates. 7a (9.31 mL, 129 mmol) was dissolved in dodecane (130 mL), and 6 (10 mL, 129 mmol) was added to the solution. The mixture was cooled to 0 °C and stirred for 15 min. Calcium hydroxide (4.81 g, 65 mmol) was then added in portions, and the mixture was slowly warmed to 25 °C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. Methyl 2,2,2-trifluoroethyl carbonate (1a) was obtained as a colorless oil (18.8 g, 92%).

*Kilogram-Scale Synthesis Using Dodecane as the Solvent.* **7a** (1.30 kg, 13.0 mol) was dissolved in dodecane (2.0 L), and **6** (1.23 kg, 13.0 mol) was added to the solution. The mixture was cooled to 0  $^{\circ}$ C and stirred for 45 min. Calcium hydroxide (482 g, 6.5 mol) was then added in portions, and the mixture was slowly warmed to 25  $^{\circ}$ C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. **1a** was obtained as a colorless oil (1.73 kg, 85%).

Kilogram-Scale Synthesis Using the Target Compound as the Solvent. 7a (1.30 kg, 13.0 mol) was dissolved in 1a (2.0 kg, 12.7 mol), and 6 (1.23 kg, 13.0 mol) was added to the solution. The mixture was cooled to 0 °C and stirred for 45 min. Calcium hydroxide (482 g, 6.5 mol) was then added in portions, and the mixture was slowly warmed to 25 °C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. 1a was obtained as a colorless oil (3.67 kg). The yield was calculated without considering the amount of 1a used as the solvent (1.67 kg, 82%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.48–4.40 (m, 2H), 3.75– 3.77 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 154.56, 122.64 (q,  $J_{C-F}$  = 278.8 Hz), 63.23 (q,  $J_{C-F}$  = 37.4 Hz), 55.33 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ –75.00 to –75.24 (m).

Ethyl 2,2,2-Trifluoroethyl Carbonate (1a'). 7a (9.32 mL, 129 mmol) was dissolved in dodecane (130 mL), and

ethyl chloroformate (6') (12 mL, 129 mmol) was added to the solution. The mixture was cooled to 0 °C and stirred for 15 min. Calcium hydroxide (4.81 g, 65 mmol) was then added in portions, and the mixture was slowly warmed to 25 °C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. Ethyl 2,2,2-trifluoroethyl carbonate (1a') was obtained as a colorless oil (19.8 g, 89%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.43 (qd, J = 8.3, 1.3 Hz, 2H), 4.15–4.21 (m, 2H), 1.25 (tt, J = 7.2, 1.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  156.03, 124.79 (q,  $J_{C-F}$  = 278.8 Hz), 67.27, 65.19 (q,  $J_{C-F}$  = 36.8 Hz), 15.83. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  –74.87 to –74.91 (m).

Ethyl Methyl Carbonate (1b). Ethanol (7b) (7.52 mL, 129 mmol) was dissolved in dodecane (130 mL), and 6 (10 mL, 129 mmol) was added to the solution. The mixture was cooled to 0 °C and stirred for 15 min. Calcium hydroxide (4.81 g, 65 mmol) was then added in portions, and the mixture was slowly warmed to 25 °C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. Ethyl methyl carbonate (1b) was obtained as a colorless oil (10.6 g, 79%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.95–4.01 (m, 2H), 3.55 (t, *J* = 1.8 Hz, 3H), 1.09 (td, *J* = 7.2, 1.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  155.36, 63.42, 53.95, 13.70.

Allyl Methyl Carbonate (1c). Allyl alcohol (7c) (8.83 mL, 129 mmol) was dissolved in dodecane (130 mL), and 6 (10 mL, 129 mmol) was added to the solution. The mixture was cooled to 0 °C and stirred for 15 min. Calcium hydroxide (4.81 g, 65 mmol) was then added in portions, and the mixture was slowly warmed to 25 °C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. Allyl methyl carbonate (1c) was obtained as a colorless oil (10.7 g, 81%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.74–5.84 (m, 1H), 5.20 (dq, J = 17.0, 1.4 Hz, 1H), 5.11 (dq, J = 10.4, 1.2 Hz, 1H), 4.46–4.48 (m, 2H), 3.63 (t, J = 1.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  155.24, 131.44, 118.16, 67.98, 54.29.

Methyl Phenyl Carbonate (1d). Phenol (7d) (12.1 g, 129 mmol) was dissolved in dichloromethane (130 mL), and 6 (10 mL, 129 mmol) was added to the solution. The mixture was cooled to 0  $^{\circ}$ C and stirred for 15 min. Calcium hydroxide (4.81 g, 65 mmol) was then added in portions, and the mixture was slowly warmed to 25  $^{\circ}$ C. After stirring overnight, the reaction mixture was filtered, and the filtrate was analyzed by GC and distilled under reduced pressure. Methyl phenyl carbonate (1d) was obtained as a colorless oil (15.1 g, 77%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35–7.39 (m, 2H), 7.18– 7.24 (m, 3H), 3.84 (t, *J* = 1.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  153.95, 150.89, 129.15, 125.68, 120.72, 54.89.

**Glycerol 1,2-Carbonate (10).** Glycerol (9) (11.9 g, 129 mmol) was dissolved in toluene (130 mL), and 6 (10 mL, 129 mmol) was added to the solution. The mixture was cooled to 0 °C and stirred for 15 min. Calcium hydroxide (4.81 mg, 65 mmol) was added in portions. After 6 h of stirring and slow warming to room temperature, the reaction mixture was stirred under reflux for 24 h in a Dean–Stark apparatus. The resulting mixture was filtered at 25 °C, and the filtrate was analyzed by GC and distilled under vacuum. Glycerol 1,2-carbonate (10) was obtained as a colorless oil (11.0 g, 72%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.82–4.78 (m, 1H), 4.53– 4.44 (m, 2H), 3.99–3.70 (m, 2H). <sup>13</sup>C NMR (101 MHz, acetone- $d_6$ ):  $\delta$  155.95, 77.42, 66.18, 61.41.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.9b00087.

NMR spectra of the compounds (PDF)

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The manuscript was written through contributions from all of the authors, and all of the authors approved the final version of the manuscript.

# Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

DMC, dimethyl carbonate; EMC, ethyl methyl carbonate; EC, ethylene carbonate; NMR, nuclear magnetic resonance

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