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Selective Synthesis of Carbonates from Glycerol, CO_2, and Alkyl Halides Using *tert*-Butyltetramethylguanidine

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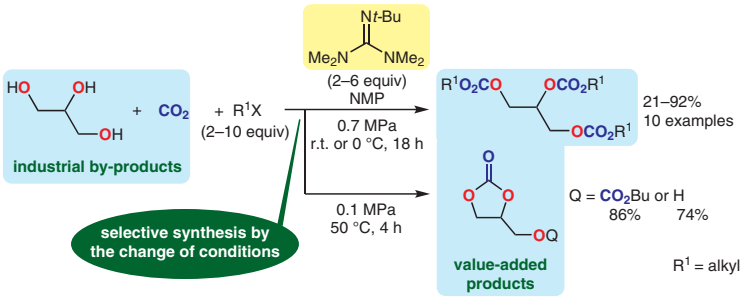

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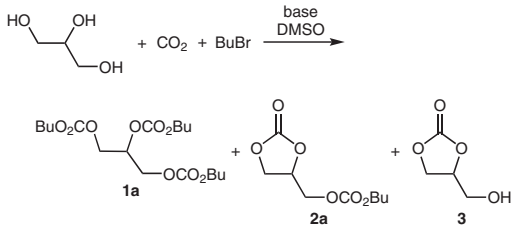
Abstract Herein, we describe the guanidine-promoted synthesis of carbonates from glycerol, CO_2, and alkyl halides. Specifically, a linear tricarbonate (1,2,3-tri-*O*-butoxycarbonylglycerol), a dicarbonate [butyl (2-oxo-1,3-dioxolan-4-yl)methyl carbonate] containing a linear and a cyclic moiety, and a cyclic monocarbonate (4-hydroxymethyl-2-oxo-1,3-dioxolan) were selectively obtained in good yields, which were strongly affected by the steric bulkiness of the guanidine group substituents. The developed method exhibits the advantages of high efficiency and mild conditions, thus being a powerful tool for the synthesis of value-added products from industrial by-products.

Key words carbon dioxide, glycerol, carbonates, guanidines

The progressing global climate change requires the development of efficient CO_2-utilization methods to decrease the atmospheric concentration of this greenhouse gas, which can be used as a carbon source. It is currently recognized as an attractive and versatile reagent in organic synthesis because of its low cost and environmental friendliness.[1] Moreover, the ever-increasing global production of glycerol as a side-product of the biodiesel industry also necessitates the search for suitable utilization methods, e.g., those employing glycerol as the starting material for high value-added products or as a green solvent.[2] Therefore, the simultaneous conversion of both CO_2 and glycerol to valuable products is doubly advantageous from environmental and economic perspectives, since two wastes are utilized at the same time.

Organic carbonates obtained from glycerol or/and CO_2 are an important class of biomass-based valuable products.[3] Besides the widely used cyclic monocarbonate of glycerol (4-hydroxymethyl-2-oxo-1,3-dioxolan or glycerol carbonate),[4] linear tricarbonates (1,2,3-tri-*O*-alkoxycarbonylglycerol)[5] and dicarbonates [alkyl (2-oxo-1,3-dioxolan-4-yl)methyl carbonate] containing a linear and a cyclic moiety[6] are also known, being used as refrigeration oils, biomaterials for tissue engineering, adjuvants for agrochemicals, electrolyte solvents for Li-ion batteries and display devices, and coating films. In particular, these tri- and dicarbonates have high potential as starting materials for degradable aliphatic polycarbonates. Although several catalytic syntheses of the above cyclic monocarbonate from glycerol and CO_2

Table 1 Base-Promoted Synthesis of Carbonates from Glycerol, CO_2, and *n*-Butyl Bromide[a]



Entry	Base[b]	NMR ratio **1a**/**2a**/**3**
1	DBU	1:76:23
2	A	50:41:9
3	B	62:36:2
4	C	50:46:4
5	D	22:77:1
6[c]	E	0:12:88

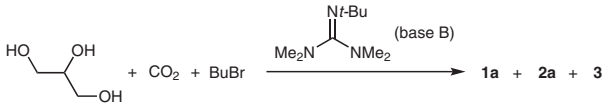
[a] *Reaction conditions*: glycerol (1 mmol) was treated with *n*-BuBr (3.3 mmol) in dimethyl sulfoxide (DMSO; 3 mL) under an atmosphere of CO_2 (0.7 MPa) in the presence of a base (3.3 mmol) at 25 °C for 18 h. **1a**, **2a**, and **3** were given mainly from glycerol.
[b] A: *N*-*tert*-butyl-*N*′,*N*′-dimethylacetamidine, B: 2-*tert*-butyl-1,1,3,3-tetramethylguanidine, C: 2-cyclohexyl-1,1,3,3-tetramethylguanidine, D: 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, and E: 2-phenyl-1,1,3,3-tetramethylguanidine.
[c] Recovery of glycerol: about 39% NMR yield.

have already been reported, the corresponding yields did not exceed 35% even under harsh conditions in the presence of dehydration agents.[7] In addition, some reports claim that glycerol carbonate can be efficiently prepared from glycerol and CO_2 by noncatalytic methods, e.g., by using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)–dibromomethane–ionic liquid or silver complex–propargylic alcohol systems.[8] However, to the best of our knowledge, the direct synthesis of the above tricarbonates and dicarbonates from glycerol and CO_2 has not been reported. In particular, the environmentally benign synthesis of linear tricarbonates presents a significant challenge. For example, transesterification of dialkyl carbonates with glycerol in the presence of potassium carbonate, a typical ecofriendly method of carbonates synthesis, was reported to exclusively afford the thermodynamically most stable five-membered cyclic carbonates.[3a] Therefore, tricarbonates are commonly prepared by using reactive haloformate esters derived from hazardous phosgene,[5a,c] which inspired us to develop a facile method of selectively preparing linear tricarbonates from two industrial by-products, CO_2 and glycerol.

A number of methods for dialkyl carbonate synthesis using CO_2 instead of phosgene as the carbon source have been developed. Among them, carboxylation of alcohols with CO_2 utilizing alkyl halides has been achieved in the presence of inorganic or strong organic bases under mild conditions.[9] Since the base-promoted reaction proceeds through the alkylation of the carbonate salt intermediate formed from CO_2, alcohol, and the base, the product yield is significantly affected by the basicity and nucleophilicity of the organic base. Nevertheless, only DBU[9a] and 2-cyclohexyl-1,1,3,3-tetramethylguanidine[9c] have been identified as useful strong organic bases for the above synthesis. Although a convenient synthesis of ethylene carbonates from CO_2 and 1,2-diols using alkyl halides in the presence of DBU has been reported,[9h] the DBU-assisted procedure has not been successfully applied to the synthesis of linear dicarbonates of 1,2-diols except for the case of *trans*-cyclohexanediol, which does not readily undergo cyclization because of the inherent steric repulsion. On the other hand, we have already tackled the utilization of CO_2 and glycerol, succeeding in the synthesis of glycerol carbonate from glycerol using sulfur[10] and selenium[11] as well as employing the DBU-catalyzed reaction of CO_2 with aminobenzonitrile.[12] Herein, we report a selective base-promoted synthesis of linear tricarbonates from glycerol, CO_2, and alkyl halides under mild conditions.

The synthesis of linear tributylcarbonate **1a** from glycerol, CO_2, and *n*-butyl bromide in the presence of several strong organic bases was investigated as a model reaction (Table 1). The use of DBU afforded dicarbonate **2a** containing a linear and a cyclic moiety as the major product, along with traces of **1a** (entry 1). As DBU is known to be alkylated by *n*-butyl bromide during the preparation of dialkyl carbonates,[9a] the reaction was carried out with a more bulky and less nucleophilic acetamidine (base A), which resulted in the formation of **1a** in preference to **2a** (entry 2). Furthermore, the use of *tert*-butyltetramethylguanidine (base B,

Table 2 Guanidine-Promoted Synthesis of **1a**: Screening of Reaction Conditions[a]



Entry	Base (mmol)	CO_2 (MPa)	Temp (°C)	Solvent	Amount of solvent (mL)	*n*-BuBr (mmol)	NMR ratio **1a**/**2a**/**3**
1	3.3	0.7	25	DMSO	3	3.3	62:36:2
2	3.3	0.1	25	DMSO	3	3.3	33:60:7
3	3.3	1.7	25	DMSO	3	3.3	57:40:3
4	3.3	0.7	50	DMSO	3	3.3	49:47:4
5	3.3	0.7	0	NMP	3	3.3	40:51:9
6	3.3	0.7	25	NMP	3	3.3	70:28:2
7	3.3	0.7	25	MeCN	3	3.3	2:66:32
8	3.3	0.7	25	THF	3	3.8	7:76:17
9	3.3	0.7	25	none	–	3.3	33:58:9
10	3.3	0.7	25	NMP	1	3.3	81:18:1
11	6	0.7	25	NMP	1	6	90:10:0
12	6	0.7	25	NMP	1	10	93[b]:7:0

[a] *Reaction conditions*: glycerol (1 mmol), reaction time (18 h). **1a**, **2a**, and **3** were given mainly from glycerol.
[b] Isolated yield: 89%.

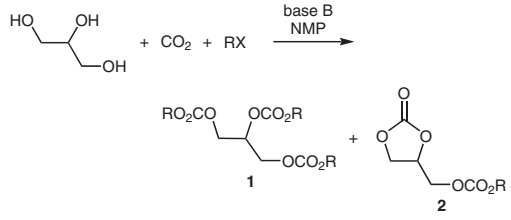
expected to be stronger than base A) increased the yield of **1a**, with the **1a**/**2a** molar ratio decreasing with decreasing steric bulkiness of the guanidine substituents (entries 3–5). Moreover, the above ratio was also strongly affected by the basicity of the substituted guanidines (entry 6). Considering the scope of the alkylating reagent, *n*-butyl chloride was inferior to *n*-butyl bromide, affording compound **3** and unreacted glycerol instead of compounds **1a** and **2a** under the tested conditions.

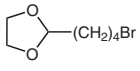
With the base B in hand, we proceeded to optimize other reaction conditions (Table 2), showing that the use of pressurized CO_2 could effectively increase the yield of **1a**, whereas a further increase in pressure from 0.7 to 1.7 MPa had no beneficial effect (entries 1–3). Similarly, temperatures higher or lower than 25 °C also resulted in lower molar ratios of **1a** (entries 1, 4, and 5), which were also considerably influenced by the choice of solvent. Thus, *N*-methylpyrrolidinone and dimethyl sulfoxide were more suitable solvents than acetonitrile and tetrahydrofuran (entries 1 and 6–8), even though carbonates were obtained even under solvent-free conditions (entry 9). Moreover, decreasing the solvent volume from 3 to 1 mL increased the **1a**/**2a** ratio (entries 6 and 10), with a similar effect achieved by using an excess of *n*-butyl bromide and base (entries 10–12). Consequently, the optimized mild conditions allowed **1a** to be efficiently prepared from glycerol and CO_2 in the presence of an alkylated guanidine.

Subsequently, the optimized conditions were used to investigate the scope of alkyl halides (Table 3).[13] *n*-Butyl bromide, *sec*-butyl halides, dodecyl bromide, allyl bromide, and benzyl bromide smoothly reacted with glycerol in an atmosphere of pressurized CO_2 to furnish the corresponding trialkylcarbonates **1a–e** in good to high yields (entries 1–6). Notably, better results were obtained for *sec*-butyl iodide than for the corresponding bromide because of the decreased yield of dicarbonate **2b** observed in the former case (entries 2 and 3). Reactions with allyl and benzyl bromides were performed at low temperature to suppress the production of **2d** and **2e**, affording the desired tricarbonates in high yields (entries 5 and 6). In particular, the reaction was applicable to alkyl bromides bearing ester, cyano, and acetal groups, thus allowing the direct synthesis of functionalized tricarbonates **1f–h** (entries 7–9) that are difficult to prepare from the corresponding haloformate esters. Moreover, although terminal alkyne groups were not tolerated, compound **1j**, featuring an internal alkyne moiety, was obtained in moderate yield along with **2j** (entries 10 and 11). However, no desired tricarbonates were obtained in the cases of *tert*-butyl iodide and ethyl 3-bromopropionate because of the competing elimination of hydrogen halides from these species (entries 12 and 13). Moreover, a poor yield was also observed for 2-bromoethyl methyl ether owing to the competing formation of **2k** (entry 14). Thus, several tricarbonates were directly synthesized from glycerol, CO_2, and alkyl halides by using *tert*-butyltetramethylguanidine as a promoter.

The above reaction was further applied to the synthesis of cyclic carbonates from glycerol, CO_2, and *n*-butyl bromide. Thus, the synthesis of **2a** was investigated under the conditions optimized for the preparation of **1a** (Table 4), with the slow addition of *n*-butyl bromide in an atmosphere of CO_2 (0.1 MPa) at 25 °C over 18 hours leading to the relatively selective production of **2a** (entry 1). Furthermore, an even higher selectivity was observed when the reaction mixture was heated at 50 °C for four hours (entry 2).[14] Subsequently, the synthesis of **3** was attempted. A decrease in the amount of *n*-butyl bromide and guanidine to four equivalents caused a decrease in the **2a**/**3** ratio (entry 3), with a further decrease to two equivalents resulting in the highly selective formation of **3** (entry 4). Thus, cyclic carbonates could be selectively obtained only by changing the reaction conditions.

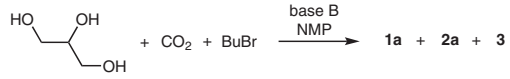
Table 3 Guanidine-Promoted Synthesis of Tricarbonates **1**: Scope of Alkyl Halides[a]



Entry	RX	1	Yield (%)
1	*n*-BuBr	**1a**	89
2	*s*-BuBr	**1b**	61
3	*s*-BuI	**1b**	82
4	n-$C_{12}H_{25}Br$	**1c**	81
5[b]	CH_2=$CHCH_2Br$	**1d**	92
6[b]	$PhCH_2Br$	**1e**	90
7	$EtOC(O)(CH_2)_3Br$	**1f**	81
8	$NC(CH_2)_4Br$	**1g**	81
9		**1h**	79
10[b]	$HC{\equiv}CCH_2Br$	(**1i**)	0[c]
11[b]	$MeC{\equiv}CCH_2Br$	**1j**	45[d]
12	*t*-BuI		0
13	$EtOC(O)(CH_2)_2Br$		0
14	$MeO(CH_2)_2Br$	**1k**	21[e]

[a] *Reaction conditions*: glycerol (1 mmol), CO_2 (0.7 MPa), alkyl halide (10 mmol), NMP (1 mL), base B (6 mmol), 25 °C, 18 h.
[b] 0 °C.
[c] Compound **2i**: 49%. Recovery of glycerol: 0%.
[d] Compound **2j**: 47%.
[e] Compound **2k**: 76%.

Table 4 Guanidine-Promoted Synthesis of **2a** and **3**: Screening of Reaction Conditions[a]



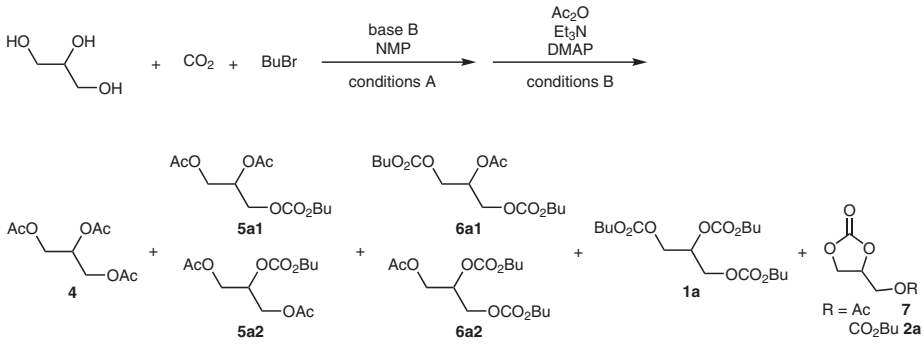
Entry	Base (mmol)	*n*-BuBr (mmol)	Temp (°C)	Time (h) total, drop/stir[b]	NMR ratio **1a**/**2a**/**3**
1	6	6	25	18, 6/12	33:67:0
2	6	6	50	4, 3/1	0:95[c]:5
3	4	4	50	4, 3/1	0:80:20
4	2	2	50	4, 3/1	0:8:92[d]

[a] *Reaction conditions*: glycerol (1 mmol), CO_2 (0.1 MPa), NMP (1 mL).
[b] Total time: the sum of "drop" and "stir" times. Drop: time required for the dropwise addition of *n*-BuBr into an NMP solution of glycerol and base B in an atmosphere of CO_2. Stir: time of stirring the reaction mixtures after the dropwise addition of *n*-BuBr.
[c] Isolated yield: 86%.
[d] Isolated yield: 74%.

The reaction of glycerol with CO_2 (0.7 MPa) and *n*-BuBr (2.2 equiv) in the presence of base B (2.2 equiv) was quenched after three hours to observe the reaction intermediates (conditions A, entry 2, Table 5). Notably, the gas-chromatographic (GC) analysis of the resulting mixtures showed the production of only cyclic carbonates **2a** and **3** along with **1a**, which was ascribed to the conversion of linear carbonates to cyclic ones during the GC measurements. Therefore, the unreacted hydroxyl groups in the resulting mixtures were protected by treatment with acetic anhydride (conditions B, Table 5). As shown in Table 5, the guanidine-promoted reaction (conditions A) followed by acetylation (conditions B) afforded some carbonates. Entries 1–3 reveal the formation of linear monocarbonates **5a1** and **5a2**, which were then converted into the corresponding linear dicarbonates **6a1** and **6a2** and the tricarbonate **1a**.

Thus, the studied reaction was concluded to proceed through the formation of carbonate salt **8** from glycerol, CO_2, and guanidine, with its subsequent transformations affording linear monocarbonates **5'** that were further converted to **6'** and finally to **1** (Scheme 1). According to the proposed mechanism, **5'** cyclizes to **3**, which is further carboxylated to afford **2**. In a similar manner, the cyclization of **6'** gives **2**. In this cyclization, even if six-membered cyclic carbonates were formed, it is considered that the six-membered carbonates were isomerized to five-membered ones to give **2** and **3** excusively.[15] In addition, the **5a1** and **6a1** ratios exceeded the **5a2** and **6a2** ones (entries 1–3, Table 5), indicating that the 1- and 3-hydroxyl groups of glycerol were carboxylated more smoothly than the 2-hydroxyl one. Moreover, the formation of cyclic carbonates **2a** and **7** was favored by increasing the temperature (entries 2 and 4) and the amount of base (entries 4–6). However, the amount of base did not affect the yield of cyclic carbonates at 25 °C (entries 2 and 7). Accordingly, the combination of reaction temperature and amount of base had a considerable effect on the cyclization step. As described above, linear tricarbonates could be selectively produced (entry 12, Table 2) in an atmosphere of pressurized CO_2 by using excessive

Table 5 GC Analysis of Intermediates Observed in the Guanidine-Promoted Syntheses of Carbonates[a]

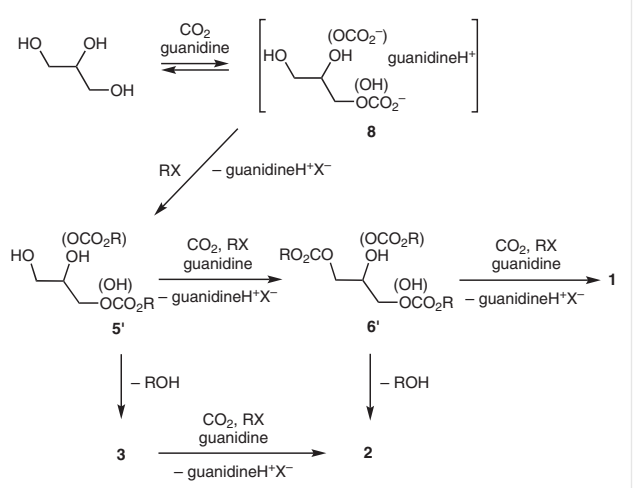


Entry	Base (mmol)	Temp (°C)	Time (h)	GC ratio **4**/**5a1**/**5a2**/**6a1**/**6a2**/**1a**/**7**/**2a**
1	2.2	25	0.3	20:37:8:15:14:4:1:1
2	2.2	25	3	12:37:5:22:15:7:1:1
3	2.2	25	18	3:18:2:33:18:23:0:3
4	2.2	50	3	8:21:4:22:15:14:6:10
5	3.3	50	3	4:4:1:8:5:31:8:39
6	4.4	50	3	1:1:0:1:2:39:8:48
7	3.3	25	3	8:25:8:25:21:12:0:1

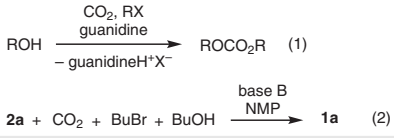
[a] *Reaction conditions*: A: glycerol (1 mmol), CO_2 (0.7 MPa), *n*-BuBr (2.2 mmol), NMP (1 mL); B: Ac_2O (3 mmol), Et_3N (3 mmol), DMAP (0.05 mmol), r.t., 2 h.

amounts of base to promote the formation of carbonate salts, with other parameters corresponding to room temperature, medium concentration, and excess alkyl halides to suppress intramolecular cyclization.

Alcohols produced in the cyclization step reacted with CO_2 and alkyl halides in the presence of guanidine, affording dialkyl carbonates as by-products, e.g., dibutyl carbonate (entry 2, Table 4; equation 1, Scheme 2). In addition, when carboxylation of **2a** was carried out by addition of *n*-butyl alcohol under the conditions of entry 12 (Table 2) to investigate the possibility of converting **2** into **1**, compound **1a** was obtained in only about 5% yield (equation 2, Scheme 2), which showed that **2a** was only marginally converted into **1a** even under these conditions containing alcohols.



Scheme 1 Plausible mechanism of carbonate formation



Scheme 2 *Reaction conditions*: **2a** (1 mmol), CO_2 (0.7 MPa), *n*-BuBr (10 mmol), *n*-BuOH (3 mmol), base B (6 mmol), NMP (1 mL), 25 °C, 18 h

The large influence of the choice of base on the yield of **1** (Table 1) was ascribed to the effective formation of carbonate salts in the presence of strong bases. Moreover, the bulkiness of the guanidinium cation increased the nucleophilicity of the carbonate anion, promoting the carboxylation of the remaining 2-hydroxyl group in **6'** and also hindering the electrophilic attack of alkyl halides on the guanidine moiety. Thus, base B enabled the efficient formation of more nucleophilic glycerol carbonate salts even at room temperature, suppressing cyclization and facilitating the formation of linear tricarbonates.

In conclusion, the described reaction was proven to be useful for the direct synthesis of linear and cyclic carbonates from widely available inexpensive building blocks, glycerol and CO_2, with this study being the first-time report of such direct synthesis. The developed method is particularly useful because it allows the efficient synthesis of value-added products from two industrial by-products at ambient temperature and CO_2 pressure, additionally featuring the advantages of high selectivity, high yields, broad applicability, and mild conditions.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610027.

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(13) **General Procedure for the Synthesis of Linear Tricarbonates 1 Using Base B**

A stainless steel autoclave was charged with glycerol (1 mmol), base B (6 mmol), and NMP (1 mL), flushed three times with CO_2, and finally charged with CO_2 to 0.7 MPa at room temperature. The obtained mixture was magnetically stirred at 25 °C for 1 h, and an alkyl halide (10 mmol) was added at room temperature after CO_2 evacuation, followed by repeated CO_2 flushing/charging to 0.7 MPa. The reaction mixture was magnetically stirred at 25 °C for 18 h under 0.7 MPa pressure of CO_2. After EtOAc was added to the resulting mixture to precipitate the dissolved salt, the salt was removed with a Buchner funnel and washed with EtOAc. The combined filtrate was concentrated in vacuo, and the obtained product ratios were determined by ^{1}H NMR spectroscopic measurements. The crude product was purified by silica gel column chromatography, affording linear tricarbonates **1**.

1,2,3-Tri-*O*-(2-butynyloxy)carbonylglycerol (1j)

IR (neat): 2959, 2924, 2323, 2241, 1756, 1442, 1384, 1237, 1156, 961, 923, 789 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.87 (t, *J* = 2.4 Hz, 9 H), 4.32 (dd, *J* = 12.0, 6.0 Hz, 2 H), 4.44 (dd, *J* = 12.0, 4.8 Hz, 2 H), 4.70–4.73 (m, 6 H), 5.12–5.15 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 3.59, 56.61, 56.72, 65.26, 72.12, 72.20, 72.71, 84.45, 84.54, 153.74, 154.16 ppm. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}NaO_9$ [M + Na]$^+$: 403.1005; found: 403.1004.

(14) **General Procedure for the Synthesis of Cyclic Carbonates (2a and 3) Using Base B**

Glycerol (1 mmol), base B (2 or 6 mmol), and NMP (1 mL) were added to a glass vessel connected to an injection port equipped with a three-way cock. The vessel was charged with CO_2 from a balloon, and it was stirred at 25 °C for 1 h. An alkyl bromide (2 or 6 mmol) was added dropwise at 50 °C for 3 h under 0.1 MPa of CO_2 pressure and further stirred for another 1 h. The workup and purification were the same as those reported in the general procedure for the synthesis of compound **1**.

2-Butynyl (2-oxo-1,3-dioxolan-4-yl)methyl carbonate (2j)

IR (neat): 2960, 2925, 2322, 2241, 1798, 1758, 1394, 1267, 1170, 1088, 1053, 951, 789, 772 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.87 (t, 1.8 Hz, 3 H), 4.33 (dd, *J* = 12.6, 4.2 Hz, 1 H), 4.36 (dd, *J* = 9.0, 6.6 Hz, 1 H), 4.45 (dd, *J* = 12.6, 4.2 Hz, 1 H), 4.57 (t, *J* = 9.0 Hz, 1 H), 4.73 (q, *J* = 1.8 Hz, 2 H), 4.92–4.96 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 3.63, 56.98, 65.71, 66.09, 71.96, 73.24, 84.83, 154.05, 154.13 ppm. HRMS (ESI): *m/z* calcd for $C_9H_{10}NaO_6$ [M + Na]$^+$: 237.0375; found: 237.0368.

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