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# Hydroxyl-Functionalized Imidazoles: Highly Active Additives for the Potassium Iodide-Catalyzed Synthesis of 1,3-Dioxolan-2-one Derivatives from Epoxides and Carbon Dioxide

Thomas Werner,\* Nils Tenhumberg, and Hendrik Büttner<sup>[a]</sup>

Dedicated to Prof. Dr. Armin Börner on the occasion of his 60<sup>th</sup> birthday.

4(5)-(Hydroxymethyl)imidazole and potassium iodide were identified as an efficient catalyst system for the cycloaddition of epoxides and carbon dioxide producing 1,3-dioxolan-2-one derivatives under solvent-free conditions. The high activity of the catalyst system even at 60 °C was probably due to synergistic effects between potassium iodide and the substituted imidazole. Various functionalized and nonfunctionalized termi-

# Introduction

Global climate change is closely connected to the emission of anthropogenic greenhouse gases. CO<sub>2</sub> has been identified as a major contributor to these emissions. In addition to the reduction in the CO<sub>2</sub> output, the use of CO<sub>2</sub> as a synthetic building block is the central point of the overall CO<sub>2</sub> management strategy.<sup>[1]</sup> Hence, the use of CO<sub>2</sub> as a C<sub>1</sub> building block in organic synthesis and industrial processes has recently been given great attention and is widely studied in current research.<sup>[2]</sup> One of the most efficient methods for the chemical fixation of  $CO_2$  is the coupling reaction of epoxides and  $CO_2$ producing cyclic carbonates. These carbonates can be used as aprotic polar solvents, as intermediates for organic and polymeric synthesis, and as electrolytes for lithium-ion batteries.<sup>[3]</sup> Various homo- and heterogeneous catalysts and catalytic systems have been developed for this transformation.<sup>[4]</sup> However, many of these catalyst systems suffer from low catalyst stability or reactivity, require solvents, co-catalysts, or harsh reaction conditions. Alkali metal salts are the most promising catalysts for this reaction because they are abundant, inexpensive, and nontoxic. The addition of cocatalysts or solvents is usually necessary to improve the catalytic efficiency because of the low solubility and activity of these salts.<sup>[5]</sup> Furthermore, there have been frequent reports on the synergistic effect related to the presence of hydrogen bond donors such as cellulose,  $^{[6]}\beta$ -cyclodextrin,<sup>[7]</sup> amino acids,<sup>[8]</sup> and amino alcohols<sup>[9]</sup> acting as cocata-

 [a] Dr. T. Werner, Dr. N. Tenhumberg, H. Büttner Leibniz-Institut für Katalyse e. V. an der Universität Rostock Albert-Einstein-Strasse 29a 18059 Rostock (Germany) E-mail: thomas.werner@catalysis.de
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nal epoxides as well as internal epoxides were converted into the corresponding cyclic carbonates in high yields (up to 99%) under mild reaction conditions within a short reaction time. Compared with the previously reported amino alcohols e.g. triethanolamine based catalyzed synthesis of cyclic carbonates, the catalyst system described herein demonstrates a higher activity toward a broad substrate scope

lysts in the cycloaddition of CO<sub>2</sub> to epoxides. The development of catalyst systems for the coupling reaction of epoxides and CO<sub>2</sub>, at temperatures below 100 °C, low pressures, and short reaction times, with readily available, inexpensive nontoxic reagents is still an attractive topic.<sup>[10]</sup> Methods using organocatalysts under mild reaction conditions (e.g., at room temperature) are rare and usually require long reaction times or involve metal complexes as cocatalysts. We recently reported the use of the combination of KI and triethanolamine (TEA) as a catalyst system for the synthesis of cyclic carbonates at 90 °C within a short reaction time of 2 h.<sup>[11]</sup> However, the use of this catalyst system seems to be limited to the conversion of short-chain epoxides under the chosen reaction conditions. Long-chain epoxides, such as 1,2-epoxyhexane and 1,2-epoxyoctane, were converted into the corresponding carbonates only in moderate vields.

Herein, we report the use of commercially available imidazoles and hydroxyl-functionalized imidazoles in combination with readily available KI as a simple and efficient catalyst system for the synthesis of cyclic carbonates under mild and solvent-free reaction conditions. In contrast to KI/TEA, this new catalyst system is also suitable for the conversion of long-chain epoxides into the corresponding carbonates in good to excellent yields.

# **Results and Discussion**

In our initial studies, the conversion of 1,2-butylene oxide (**1 a**) and CO<sub>2</sub> to 1,2-butylene carbonate (**2 a**) served as a model reaction for the screening of various additives in combination with KI (Table 1). To identify a new efficient catalytic system, comparatively mild reaction conditions  $[T=90^{\circ}C, p(CO_2)=$ 



10 bar (1 bar = 100 kPa)] were chosen. In an initial screening, we found that cyclic amines such as pyrrolidine (**3 b**) and 1,8-diazabicyclo[5.4.0]undec-7-ene (**3 c**) demonstrate higher activity than aliphatic amines (Table 1, entries 2–4). The use of imidazole (**3 d**) and benzimidazole (**3 e**) results in the formation of carbonate **2 a** in excellent yields (96 and 97%, respectively; Table 1, entries 5 and 6).

In further investigations, different hydroxyl- and carboxylfunctionalized imidazole derivatives 3h-m as well as the amino acid L-proline (3 g) were studied as additives (Table 2). We envisioned a synergistic effect due to hydrogen bonding between the oxirane and the hydroxyl functionality of the additives 3h-m. Quantitative conversions of epoxide 1a and excellent yields (up to 99%) were obtained with various additives (Table 2), which is notable because the reaction is performed with a transition-metal-free catalyst system under mild and solvent-free conditions. Reaction temperatures above 100°C and longer reactions times are usually required.<sup>[5,7,12]</sup> To demonstrate a better distinction of the activity of various additives, the reaction was performed at a lower temperature (80°C). These results indicate that in contrast to unsubstituted imidazoles, substituted imidazoles with an additional hydroxyl group were more active (Table 2, entries 1-5). If KCl or KBr is used instead of KI, the yields were 2 and 6%, respectively.

Notably, 4(5)-(hydroxymethyl)imidazole (**3 h**) and 1*H*-benzimidazole-2-methanol (**3 l**) demonstrated the same high catalytic activity for the conversion of the model substrate **1 a** and  $CO_2$ into the cyclic carbonate **2 a** as did the previously reported KI/ TEA (**3 n**) system (Table 2, entries 4, 8, and 10). In addition, **3 g** 



[a] Reaction conditions: 25 mmol of **1a**, 2.0 mol% Kl, 2.0 mol% additive **3**, T=80 or 90 °C,  $p(CO_2)=10$  bar, t=3 h; [b] Determined from GC analysis with hexadecane as internal standard. Selectivity toward cyclic carbonate was  $\geq$  99%; [c] In the absence of Kl, the yield of **2a** was 0% at 80 and 90 °C, respectively; [d] 2 mol% KCl, 2% yield of **2a**; [e] 2 mol% KBr, 6% yield of **2a**.

was found to be a suitable additive for the synthesis of cyclic carbonates under the chosen reaction conditions (Table 2, entry 3), which is notable because the synthesis of cyclic carbonates with use of catalytic amounts of KI and amino acids is commonly performed at higher temperatures.<sup>[8]</sup>

We further explored the effect of the reaction parameters in our model reaction using **3h** as an additive. The effect of the reaction temperature on the yield of carbonate **2a** was studied in the temperature range of 25–90 °C (Figure 1). Low conversions were observed at temperatures up to 50 °C. The yield of carbonate **2a** increased considerably up to 74% at 70 °C. A quantitative conversion of epoxide **1a** to carbonate **2a** occurred at 90 °C within a short reaction time of 3 h. At low temperatures (between 50 and 70 °C), **3n** was found to be slightly more active than **3h**.

The dependence of the yield of carbonate 2a on the reaction time at an initial CO<sub>2</sub> pressure of 10 bar and 90 °C is shown in Figure 2. The conversion of epoxide 1a to product 2a proceeded quickly within the first 60 min. Notably, after 30 min, more than half of the epoxide 1a was converted into



**Figure 1.** Effect of the reaction temperature. Reaction conditions: 25 mmol of **1 a**, 2.0 mol% Kl, 2.0 mol% **3 h** or **3 n**,  $p(CO_2) = 10$  bar, t = 3 h.



**Figure 2.** Effect of the reaction time. Reaction conditions: 25 mmol of 1 a, 2.0 mol % KI, 2.0 mol % **3h** or **3n**, T=90 °C,  $p(CO_2)=10$  bar.

carbonate **2a**. Within 60 min, a high yield (82%) was obtained. After 120 min, the yield increased up to 98%.

Consequently, further investigations were performed within a short reaction time of 2 h. With respect to the yield of carbonate **2a**, no significant difference was observed between the additives **3h** and **3n** at different reaction times. The effect of the catalyst concentration is shown in Figure 3. The best result is obtained with equivalent amounts of KI and **3h** or **3n**, respectively. As expected, the yield of carbonate **2a** increases with the increase in the concentration of the catalyst. An 80% yield of product **2a** was obtained with 1 mol% of a 1:1 mixture of KI and an additive**3n**. An excellent yield (99%) was obtained with a catalyst concentration of 2 mol% KI and 2 mol% **3h**. In the absence of either KI or additive **3h** and **3n**, the desired carbonate **2a** was not obtained. Notably, at low catalyst loadings (0.5 mol%), **3h** demonstrated a significantly higher activity than did **3n**.

So far, the coupling reaction of epoxide 1a and  $CO_2$  was performed under an initial  $CO_2$  pressure of 10 bar. Pressure is a significant parameter with respect to safety concerns and connected costs, especially for industrial plants. Hence, the conversion at low pressures is desirable. To investigate the effect of





**Figure 3.** Effect of the catalyst concentration. Reaction conditions: 25 mmol of 1 a, 0–2.0 mol% Kl, 0–2.0 mol% 3 h or 3 n, Kl/additive = 1:1, T = 90°C,  $p(CO_2)$  = 10 bar, t = 2 h.

pressure, the conversion of **1a** was examined at 2–10 bar  $CO_2$  pressure and under isobaric conditions (Figure 4). In the pressure range of 5–10 bar, there was no notable effect of pressure on the yield of **2a**. These results indicate that the synthesis of carbonate **2a** had already been performed in high yields ( $\geq$  87%) with a constant low pressure ( $\geq$  3 bar). However, by performing the reaction at extremely low pressures ( $\leq$  2 bar), conversions and yields decreased significantly below 16%.



**Figure 4.** Effect of CO<sub>2</sub> pressure. Reaction conditions: 25 mmol of 1 a, 2.0 mol% Kl, 2.0 mol% **3 h** or **3 n**, T=90 °C, t=2 h.

No significant difference was observed between **3h** and **3n** at different reaction pressures. As a result of the optimization of the reaction conditions, both additives **3h** and **3n** demonstrate a similar catalytic activity for the conversion of the model compound **1a** into the corresponding cyclic carbonate **2a**.

To extend the scope of the developed catalyst system, various epoxides **1** were converted into the corresponding carbonates **2** with use of the catalyst system KI/**3 h** under optimized reaction conditions (Table 3). Analytically pure products were obtained through simple filtration over silica gel, followed by the removal of all volatiles in vacuum. High yields ( $\geq$  87%) of the cyclic carbonates **2** were obtained through the conversion

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Table 3.	Screening of functionalized imidazole 1-2  mol $R^1$ $R^2$ + $CO_2$ 1-2  mol 1-2  mol $60-90^{\circ}\text{C}$ , $p(\text{C})$ 2-24  h, so 1	additives. <sup>[a]</sup> ol% KI <b>3h</b> or <b>3n</b> CO <sub>2</sub> ) = 10 bar Ivent free		D R <sup>2</sup>
Entry	Product <b>2</b>	Product 2		d <sup>[b]</sup> [%] Kl/ <b>3 h</b>
1		2a	95 88 <sup>[d]</sup>	97 (99) <sup>[c]</sup> 97 <sup>[d]</sup>
2	Me	2 b	95	97
3	Bu	2c	55	92
4	Hex	2 d	10 15 <sup>[d]</sup>	74 92 <sup>[d]</sup>
5	Ph ,0	2e	79 61 <sup>[d]</sup>	90 83 <sup>[d]</sup>
6	c C	2 f	79	87
7	CI	2 g	70 48 <sup>[d]</sup>	87 94 <sup>[d]</sup>
8		2 h	84	90
9		2i	59	93
10	Me	2j	91 99 <sup>[d]</sup>	90 99 <sup>[d]</sup>
11	PhoO	2 k	97 98 <sup>[d]</sup>	93 99 <sup>[d]</sup>
12		21	2 27 <sup>[e]</sup>	4 78 <sup>[e]</sup>
13	H <sub>3</sub> C(CH <sub>2</sub> )7 (CH <sub>2</sub> )7 OCH <sub>3</sub>	2 m	8 <sup>[f]</sup>	5 <sup>[f]</sup>
[a] Reaction conditions: 25 mmol of 1, 2.0 mol% Kl, 2.0 mol% <b>3h</b> or <b>3n</b> . $T = 90 \degree C$ .				



of both nonfunctionalized and functionalized terminal epoxides (Table 1, entries 1–11). The previously reported results for the catalyst system KI/**3 n** are compared with the obtained results of both catalyst systems (see Table 3). During the optimization of reaction conditions, no remarkable effect was observed for the conversion of short-chain epoxides, such as the model compound **1a** and propylene oxide (**1b**). The corresponding cyclic carbonates **2a** and **2b** were isolated in high yields (97 and 95%) using both additives, respectively (Table 3, entries 1 and 2). However, for most of the epoxides 1, a slightly higher yield was obtained with KI/3h as a catalyst. A notable effect was observed for the conversion of long-chain epoxides such as 1,2-epoxyhexane (1 c), 1,2-epoxyoctane (1 d), and 1,2-epoxy-5hexene (1i). Compared with the catalyst system KI/ 3n, significantly higher yields (up to 93%) were obtained for the corresponding carbonates 2c, 2d, and 2i with KI/3h (Table 3, entries 3, 4, and 9). We assume that this is due to the lower solubility of 3n in apolar substrates. In contrast, the same substrate effect was less significant for 3h owing to the lower polarity of 3h. Cyclohexene oxide (1l) and epoxidized methyl oleate (1 k) were tested as representatives of internal epoxides. Internal epoxides are usually less reactive than terminal epoxides owing to steric hindrance.[17-20] Under optimized reaction conditions, both catalyst systems demonstrated only a low activity for the conversion of 11. However, under more rigorous reaction conditions [T = 120 °C,  $p(CO_2) = 50$  bar, t = 6 h], cyclohexene oxide (1 l) was converted into the corresponding carbonate 21 in a high yield (78%) with KI/3h as a catalyst, whereas only a moderate yield (27%) was obtained with KI/ 3n (Table 3, entry 12). The conversion of 1m into the corresponding carbonate was studied under our standard reaction conditions used for the synthesis of carbonated fatty acid esters. Oleochemical carbonates can be used in various applications, such as the production of potential industrial lubricants, fuel additives, polymer plasticizers, and starting materials for polyesters and polycarbonate materials.<sup>[14]</sup> However, the desired cyclic carbonate 2m was formed only in low amounts (Table 3, entry 13). In general, the catalyst system KI/3h demonstrates a broader substrate scope than KI/3 n. The feasibility of catalyst recycling was demonstrated for the model reaction under our standard reaction conditions. In this case, 2a was separated from the catalyst by Kugelrohr distillation. The reused catalyst led to excellent yield (99%) in the second cycle (entry 1).

Furthermore, we converted a number of selected epoxides into the corresponding cyclic carbonates at a lower temperature (60 °C) and only 1 mol% catalyst (Table 3, entries 1, 4, 5, 7, 10, and 11). Even though the reaction time had to be increased to 24 h, high yields (up to 99%) were obtained under these mild reaction conditions (entries 10 and 11). The catalyst

system KI/**3 h** again demonstrated higher activity than KI/**3 n**. The general mechanism for the conversion of  $CO_2$  with ep-

oxide producing cyclic carbonates is well recognized and involves three main elementary steps: epoxide ring opening,  $CO_2$  insertion, and ring closure to form the five-membered cyclic carbonate. The availability of a dissolved halogen anion usually plays a crucial role in this reaction mechanism. Unfortunately, any attempt to isolate a catalytically active species from KI and **3h** failed. NMR investigations to explain the interaction

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between **3h** and KI were not successful. However, imidazolium halides have already been described as a suitable catalyst for the synthesis of cyclic carbonates.<sup>[15]</sup> Moreover, we recently found that the combination of KI and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene serves as an effective catalyst system for the conversion of epoxides and CO<sub>2</sub> into cyclic carbonates.

Herein, we demonstrated that the reaction of the carbene and KI in the presence of CO<sub>2</sub> and small amounts of H<sub>2</sub>O yields the corresponding imidazolium iodide, which acts as a catalyst in this reaction.<sup>[16]</sup> Therefore, we assumed that the reaction of KI and 3h could also yield the corresponding 4-(hydroxymethyl)-1H-imidazol-3-ium iodide (4). Therefore, we proposed the putative reaction mechanism shown in Scheme 1. The free hydroxyl function of the insitu formed imidazolium iodide 4 could activate the epoxide. The activation of the epoxide by a hydrogen bond donor accelerates the conversion with CO<sub>2</sub>. Nucleophilic ring opening of the epoxide by the iodide leads to the corresponding halohydrin anion. Subsequent CO<sub>2</sub> insertion and ring closing liberates the desired cyclic carbonate. The corresponding halohydrin was detected by using GC-MS after the aqueous workup of the reaction mixture. In this case, 2a was converted in the presence of 50 mol% catalyst under an argon atmosphere.

A sample of **4** was synthesized from **3h** and aqueous hydrogen iodide (Scheme 2). The catalytic activity of 4 was proved in the coupling reaction of **1 a** and CO<sub>2</sub> under the reaction conditions summarized in Table 3. With 4 as a catalyst, we could convert epoxide 1 a into carbonate 2 a in 93% yield. This result was comparable to the yield obtained with the catalyst system



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89% yield

KHCO-

Scheme 2. Synthesis of the postulated active species 4.

KI/3h. Therefore, we suggest that 4 is the catalytically active species of the catalyst system KI/3 h. The addition of 25 mol% H<sub>2</sub>O under the standard reaction conditions had no significant effect on the reaction outcome, and product 2a was isolated in 91% yield.

The formation of 4 from 3h and KI under the standard reaction conditions most probably occurred in the presence of H<sub>2</sub>O and CO<sub>2</sub> (Scheme 3). Tertiary amines form ammonium hydrogen carbonates in the presence of CO<sub>2</sub> and H<sub>2</sub>O in a reversible reaction.<sup>[17]</sup> In a first step, we assume that the corresponding 4-(hydroxymethyl)-1H-imidazol-3-ium hydrogen carbonate (5) is formed by the reaction of **3h** and CO<sub>2</sub> in the presence of small amounts of H<sub>2</sub>O. Subsequent exchange of the anion yields 4, along with the formation of potassium hydrogen carbonate as a byproduct. Notably, the postulated reaction shown in Scheme 3 is an equilibrium reaction. This is most probably the reason why we could not synthesize 4 from 3h and KI or isolate 4 under CO<sub>2</sub>-free conditions.

+ H<sub>2</sub>O но



that the developed catalyst system demonstrated higher activity than did the previously reported KI/triethanolamine system. In addition, a plausible explanation for the high activity of the catalyst system and the interaction of the additive 4(5)-(hydroxylmethyl)imidazole and KI was proposed. Overall, we assume that this simple system is of general interest for the synthesis of 1,3-dioxolan-2-one derivatives from epoxides and CO<sub>2</sub>.



Scheme 1. Proposed reaction mechanism for the conversion of epoxides 1 into the corresponding carbonates 2 with the catalyst system KI/3 h.

# **Experimental Section**

All coupling reactions were performed in a 45 mL stainless steel reactor equipped with a magnetic stirrer. Epoxidized methyl oleate (1 k) was prepared according to the method of Behr et al.<sup>[18]</sup> All other starting materials were purchased from commercial sources and used without further purification.

#### Synthesis of 4

Aqueous hydrogen iodide (1.12 g, 5.0 mmol, 57 wt%) was added slowly to a solution of **3h** (0.491 g, 5.0 mmol) in 1,4-dioxane (10 mL). The reaction mixture was stirred at 25 °C for 20 h. Then, the reaction mixture was extracted with ethyl acetate (10 mL) and washed with H<sub>2</sub>O (10 mL). The aqueous phase was concentrated through evaporation, and the crude product was dried at 60 °C in vacuum for 6 h. Compound **4** (1.00 g, 0.445 mmol, 89.0%) was isolated as a colorless solid. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 22 °C):  $\delta$  = 4.49 (d, <sup>3</sup>*J*<sub>H,H</sub> = 8.6 Hz, 2H), 7.51 (s, 1H), 8.95 (d, <sup>3</sup>*J*<sub>H,H</sub> = 1.3 Hz, 2H), 10.8–15.2 ppm (broad s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>, 22 °C):  $\delta$  = 55.33 (CH<sub>2</sub>), 116.09 (CH), 133.84 (CH), 134.32 ppm (CH); elemental analysis calcd (%) for C<sub>4</sub>H<sub>7</sub>IN<sub>2</sub>O (*M* = 226.02 gmol<sup>-1</sup>): C 21.26, H 3.12, I 56.15, N 12.39; found: C 20.93, H 3.1, I 56.4, N 12.34.

## Synthesis of 1 m<sup>[18]</sup>

 $Ru(acac)_3$  (acac = acetylacetonato; 80.0 mg, 0.20 mmol), dipicolinic acid (668 mg, 4.0 mmol), and methyl oleate (11.8 g, 40 mmol) were dissolved in acetonitrile (160 mL). After the addition of hydrogen peroxide (35% aq, 12.8 g, 132 mmol), the mixture was stirred at 25 °C for 4 h. The resulting mixture was extracted with cyclohexane (4×200 mL). The collected cyclohexane phases were concentrated up to 100 mL and washed with H<sub>2</sub>O (50 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>, and all volatiles were evaporated under reduced pressure. The pure product 1m (12.08 g, 37.7 mmol, 96%) was obtained as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta \!=\! 0.88$  (t,  ${}^{3}J_{\text{H,H}} \!=\! 6.7$  Hz, 3 H), 1.23–1.54 (m, 24 H), 1.57-1.67 (m, 2H), 2.30 (t, <sup>3</sup>J<sub>H,H</sub>=7.5 Hz, 2H), 2.86-2.92 (m, 2H), 3.66 ppm (s, 3 H);  ${}^{13}C{}^{1}H$  NMR (75 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 14.07$ (CH3), 22.63 (CH2), 24.86 (CH2), 26.52 (CH2), 26.57 (CH2), 27.76 (CH2), 27.80 (CH<sub>2</sub>), 29.00 (CH<sub>2</sub>), 29.15 (CH<sub>2</sub>), 29.19 (CH<sub>2</sub>), 29.30 (CH<sub>2</sub>), 29.50 (CH<sub>2</sub>), 29.52 (CH<sub>2</sub>), 31.82 (CH<sub>2</sub>), 34.02 (CH<sub>2</sub>), 51.42 (OCH<sub>3</sub>), 57.15 (CH), 57.20 (CH), 174.23 ppm (C=O); MS (EI): m/z (%): 281 (1) [M-OCH<sub>3</sub>], 264 (1), 199 (14)  $[C_{11}H_{19}O_3]$ , 171 (17), 155 (100)  $[C_{10}H_{19}O]$ , 153 (20), 139 (19), 127 (23), 121 (10), 109 (26), 97 (34), 87 (32), 83 (32), 74 (54), 69 (46), 55 (63), 43 (29), 41 (35).

#### General procedure (GP1) for the synthesis of cyclic carbonates 2

The reactor was charged with KI (2 mol%), **3h** (2 mol%), and epoxide **1** (25.0 mmol). The reactor was sealed and charged with CO<sub>2</sub> to a pressure of 10 bar at 23 °C until the equilibrium was reached. Then, the reactor was heated to 90 °C and the reaction mixture stirred for 2 h. The reactor was cooled to ambient temperature, and CO<sub>2</sub> was released slowly over a period of 10 min. The crude product was filtered over silica gel with dichloromethane as a solvent. After removal of all volatiles under vacuum, the pure cyclic carbonate **2** was obtained.

# 4-Ethyl-1,3-dioxolan-2-one (2 a)<sup>[19]</sup>

According to GP1, **1a** (1.81 g, 25.0 mmol) was converted into **2a** in the presence of KI (84 mg, 0.51 mmol) and **3h** (49.0 mg, 0.50 mmol). After removal of all volatiles, **2a** (2.83 g, 24.3 mmol, 97%) was obtained as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23°C):  $\delta = 1.02$  (t,  ${}^{3}J_{H,H} = 7.5$  Hz, 3H), 1.69–1.87 (m, 2H), 4.08 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.0$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.9$  Hz, 1H), 4.63–4.70 ppm (m, 1H);  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 8.4$  (CH<sub>3</sub>), 26.9 (CH<sub>2</sub>), 69.0 (CH<sub>2</sub>), 78.0 (CH), 155.16 ppm (C=O); MS (EI): m/z (%): 116 [ $M^{+}$ ] (2), 87 [ $M^{+} - C_{2}H_{5}$ ] (79), 57 (14), 43 (100), 39 (14).

# 4-Methyl-1,3-dioxolan-2-one (2b)<sup>[19]</sup>

According to GP1, **1b** (1.45 g, 25.0 mmol) was converted into **2b** in the presence of KI (83 mg, 0.50 mmol) and **3h** (49 mg, 0.50 mmol). After removal of all volatiles, **2b** (2.48 g, 24.3 mmol, 97%) was obtained as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 1.48$  (d,  ${}^{3}J_{H,H} = 6.3$  Hz, 3H), 4.02 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.2$  Hz, 1H), 4.55 (dd,  ${}^{3}J_{H,H} = 8.4$  Hz,  ${}^{2}J_{H,H} = 7.7$  Hz, 1H), 4.80-4.91 ppm (m, 1H);  ${}^{13}C{}^{1}H$  NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 19.3$  (CH<sub>3</sub>), 70.6 (CH<sub>2</sub>), 73.5 (CH), 155.0 ppm (C=O); MS (EI): *m/z* (%): 102 (7) [*M*<sup>+</sup>], 87 (25) [*M*<sup>+</sup>-CH<sub>3</sub>], 57 (100), 43 (78).

## 4-Butyl-1,3-dioxolan-2-one (2 c)[19]

According to GP1, **1 c** (2.51 g, 25.1 mmol) was converted into **2 c** in the presence of KI (83.5 mg, 0.50 mmol) and **3 h** (49.1 mg, 0.50 mmol). After removal of all volatiles, **2 c** (3.31 g, 22.9 mmol, 92%) was obtained as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 0.91$  (t,  ${}^{3}J_{\rm H,\rm H} = 7.1$  Hz, 3 H), 1.28–1.49 (m, 4H), 1.62–1.86 (m, 2 H), 4.06 (dd,  ${}^{3}J_{\rm H,\rm H} = 8.3$  Hz,  ${}^{2}J_{\rm H,\rm H} = 7.2$  Hz, 1 H), 4.52 (dd,  ${}^{3}J_{\rm H,\rm H} = 8.3$  Hz,  ${}^{2}J_{\rm H,\rm H} = 7.9$  Hz, 1 H), 4.65–4.74 ppm (m, 1 H);  ${}^{13}$ C[<sup>1</sup>H NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 13.69$  (CH<sub>3</sub>), 22.14 (CH<sub>2</sub>), 26.33 (CH<sub>2</sub>), 33.44 (CH<sub>2</sub>), 69.32 (CH<sub>2</sub>), 77.00 (CH), 155.04 ppm (C=O); MS (EI): *m/z* (%): 87 (64), 86 (15), 71 (27), 58 (63), 57 (60), 56 (24), 55 (24), 44 (29), 43 (100), 51 (50), 39 (25).

# 4-Hexyl-1,3-dioxolan-2-one (2d)<sup>[20]</sup>

According to GP1, **1d** (3.23 g, 25.2 mmol) was converted into **2d** in the presence of KI (83.0 mg, 0.50 mmol) and **3h** (49.2 mg, 0.50 mmol). After removal of all volatiles, **2d** (3.19 g, 18.5 mmol, 74%) was obtained as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 0.87$  (t,  ${}^{3}J_{\text{H,H}} = 6.9$  Hz, 3H), 1.24–1.48 (m, 8H), 1.64–1.71 (m, 1H), 1.74–1.84 (m, 1H), 4.05 (dd,  ${}^{3}J_{\text{H,H}} = 8.4$  Hz,  ${}^{2}J_{\text{H,H}} = 7.2$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{\text{H,H}} = 8.4$  Hz,  ${}^{2}J_{\text{H,H}} = 7.2$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{\text{H,H}} = 8.4$  Hz,  ${}^{2}J_{\text{H,H}} = 7.2$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{\text{H,H}} = 8.4$  Hz,  ${}^{2}J_{\text{H,H}} = 7.2$  Hz, 1H), 4.52 (dd,  ${}^{3}J_{\text{H,H}} = 8.4$  Hz,  ${}^{2}J_{\text{H,H}} = 7.9$  Hz, 1H), 4.66–4.73 ppm (m, 1H);  ${}^{13}\text{C}{}^{1}\text{H}$  NMR (100 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 13.88$  (CH<sub>3</sub>), 22.35 (CH<sub>2</sub>), 24.21 (CH<sub>2</sub>), 28.68 (CH<sub>2</sub>), 31.40 (CH<sub>2</sub>), 33.76 (CH<sub>2</sub>), 69.32 (CH<sub>2</sub>), 77.00 (CH), 155.03 ppm (C=O); MS (EI): *m/z* (%): 173(1) [*M*<sup>+</sup>], 110 (5), 95 (29), 87 (18) [*M*<sup>+</sup>-C<sub>6</sub>H<sub>13</sub>], 85 (13) [*M*<sup>+</sup>-C<sub>6</sub>H<sub>13</sub>], 81 (83), 68 (50), 58 (54), 57 (54), 55 (54), 43 (100), 41 (66), 39 (25).

#### 4-Phenyl-1,3-dioxolan-2-one (2e)[19]

According to GP1, styrene oxide (3.02 g, 25.1 mmol) was converted into **2e** in the presence of KI (84 mg, 0.51 mmol) and **3h** (49 mg, 0.50 mmol). After removal of all volatiles, **2e** (3.73 g, 22.7 mmol, 90%) was obtained as a colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22°C):  $\delta = 4.36$  (dd,  ${}^{3}J_{\rm H,H} = 8.6$  Hz,  ${}^{2}J_{\rm H,H} = 7.9$  Hz, 1H), 4.81 (dd,  ${}^{3}J_{\rm H,H} = 8.5$  Hz,  ${}^{2}J_{\rm H,H} = 8.3$  Hz, 1H), 5.69 (t,  ${}^{3}J_{\rm H,H} = 8.0$  Hz, 1H), 7.36–7.50 ppm

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(m, 5H);  ${}^{13}C{}^{1}H{}$  NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta$  = 71.1 (CH<sub>2</sub>), 78.0 (CH), 125.8 (CH), 129.2 (2×CH), 129.7 (2×CH), 135.8 (C), 154.8 ppm (C=O); MS (EI): *m/z* (%): 164 (78) [*M*<sup>+</sup>], 119 (14), 105 (31), 91 (72), 90 (100), 89 (35), 78 (67), 77 (23), 65 (17), 51 (19).

#### 4-(4-Chlorophenyl)-1,3-dioxolan-2-one (2 f)<sup>[21]</sup>

According to GP1, 2-(4-chlorophenyl)oxirane (3.87 g, 25.0 mmol) was converted into **2 f** in the presence of KI (83.3 mg, 0.50 mmol) and **3h** (49.5 mg, 0.50 mmol). After removal of all volatiles, **2 f** (4.30 g, 21.7 mmol, 87%) was obtained as a colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta$ =4.31 (dd, <sup>3</sup>J<sub>H,H</sub>=8.6 Hz, <sup>2</sup>J<sub>H,H</sub>=7.8 Hz, 1 H), 4.81 (dd, <sup>3</sup>J<sub>H,H</sub>=8.6 Hz, <sup>2</sup>J<sub>H,H</sub>=8.3 Hz, 1 H), 5.66 (t, <sup>3</sup>J<sub>H,H</sub>=8.0 Hz, 1 H) 7.30–7.33 (m, 2 H), 7.41–7.45 ppm (m, 2 H); <sup>13</sup>C[<sup>1</sup>H) NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta$ =70.96 (CH), 77.20 (CH), 127.23 (2×CH), 129.49 (2×CH), 134.25 (C), 135.76 (C–Cl), 154.48 ppm (C=O); MS (EI): *m/z* (%): 198 (81) [*M*<sup>+</sup>], 163 (15), 139 (30), 124 (100), 119 (26), 112 (60), 89 (99), 75 (22), 63 (22), 50 (14).

#### 4-(Chloromethyl)-1,3-dioxolan-2-one (2g)<sup>[19]</sup>

According to GP1, epichlorohydrin (2.32 g, 25.1 mmol) was converted into **2g** in the presence of KI (83.3 mg, 0.50 mmol) and **3h** (49.3 mg, 0.50 mmol). After workup, **2g** (2.99 g, 21.9 mmol, 87%) was obtained as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$ =3.69–3.83 (m, 2H), 4.40 (dd, <sup>3</sup>J<sub>H,H</sub>=8.8 Hz, <sup>2</sup>J<sub>H,H</sub>=5.8 Hz, 1H), 4.59 (dd, <sup>3</sup>J<sub>H,H</sub>=8.8 Hz, <sup>2</sup>J<sub>H,H</sub>=8.2 Hz, 1H), 4.94–5.02 ppm (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$ =43.56 (CH<sub>2</sub>), 66.94 (CH<sub>2</sub>), 74.18 (CH), 154.08 ppm (C=O); MS (EI): *m/z* (%): 136 (1) [*M*<sup>+</sup>], 87 (100) [C<sub>3</sub>H<sub>3</sub>O<sub>3</sub><sup>+</sup>], 62 (5), 57 (5), 49 (9), 43 (26).

# 4-Vinyl-1,3-dioxolan-2-one (2h)<sup>[10]</sup>

According to GP1, butadiene monoxide (1.73 g, 24.6 mmol) was converted into **2h** in the presence of KI (83.4 mg, 0.50 mmol) and **3h** (49.6 mg, 0.50 mmol). After removal of all volatiles, **2h** (2.55 g, 22.3 mmol, 91%) was obtained as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 4.15$  (dd, <sup>2</sup> $J_{H,H} = 8.5$  Hz, <sup>3</sup> $J_{H,H} = 7.5$  Hz, 1H), 4.60 (dd, <sup>2</sup> $J_{H,H} = 8.5$  Hz, <sup>3</sup> $J_{H,H} = 8.1$  Hz, 1H), 5.09–5.16 (m, 1H), 5.42–5.53 (m, 1H), 5.84–5.96 ppm (m, 1H); <sup>13</sup>C[<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 69.01$  (CH<sub>2</sub>), 77.29 (CH), 121.22 (CH<sub>2</sub>), 132.09 (CH), 154.71 ppm (C=O); MS (EI): *m/z* (%): 69 (7), 55 (9), 42 (100), 39 (51).

## 4-(But-3-enyl)-1,3-dioxolan-2-one (2i)<sup>[10]</sup>

According to GP1, **1i** (2.47 g, 25.2 mmol) was converted into **2i** in the presence of KI (84 mg, 0.51 mmol) and **3h** (50 mg, 0.51 mmol). After removal of all volatiles, **2i** (3.34 g, 23.5 mmol, 93%) was obtained as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 1.72-1.83$  (m, 1 H), 1.87–1.99 (m, 1 H), 2.12–2.30 (m, 2 H), 4.08 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.4 Hz, <sup>2</sup>J<sub>H,H</sub> = 7.2 Hz, 1 H), 4.53 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.4 Hz, <sup>2</sup>J<sub>H,H</sub> = 7.9 Hz, 1 H), 4.68–4.78 (m, 1 H), 5.03–5.12 (m, 2 H), 5.72–5.85 ppm (m, 1 H); 1<sup>3</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 28.6$  (CH<sub>2</sub>), 33.0 (CH<sub>2</sub>), 69.3 (CH<sub>2</sub>), 76.3 (CH), 116.4 (CH<sub>2</sub>), 136.0 (CH), 154.9 ppm (C=O); MS (EI): *m/z* (%): 101 (8), 83 (21), 80 (28), 67 (19), 54 (100), 43 (99), 41 (50, 39 (53).

# (2-Oxo-1,3-dioxolan-4-yl)methyl methacrylate (2j)<sup>[10]</sup>

According to GP1, glycidyl methacrylate (3.56 g, 25.0 mmol) was converted into **2j** in the presence of KI (84 mg, 0.51 mmol) and **3h** (50 mg, 0.51 mmol). After removal of all volatiles, **2j** (4.18 g,

22.5 mmol, 90%) was obtained as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 1.94$  (dd, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 3 H), 4.29–4.37 (m, 2 H), 4.43 (dd, <sup>3</sup>J<sub>H,H</sub> = 12.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.1 Hz, 1 H), 4.58 (t, <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz, 1 H), 4.95–5.02 (m, 1 H), 5.64 (m, 1 H), 6.13–6.15 ppm (m, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 18.1$  (CH<sub>3</sub>), 63.4 (CH<sub>2</sub>), 66.0 (CH<sub>2</sub>), 73.8 (CH), 127.2 (CH<sub>2</sub>), 135.1 (C), 154.4 (C=O), 166.6 ppm (C=O); MS (EI): *m/z* (%): 186 (24) [*M*<sup>+</sup>], 69 (100), 68 (38), 41 (50), 39 (24).

#### 4-(Phenoxymethyl)-1,3-dioxolan-2-one (2k)<sup>[10]</sup>

According to GP1, glycidyl phenyl ether (3.76 g, 25.0 mmol) was converted into **2k** in the presence of KI (83.7 mg, 0.50 mmol) and **3h** (50.0 mg, 0.51 mmol). After removal of all volatiles, **2k** (4.53 g, 23.3 mmol, 93%) was obtained as a colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$ =4.15 (dd, <sup>3</sup>J<sub>H,H</sub>=10.6 Hz, <sup>2</sup>J<sub>H,H</sub>=3.6 Hz, 1H), 4.25 (dd, <sup>3</sup>J<sub>H,H</sub>=10.6 Hz, <sup>2</sup>J<sub>H,H</sub>=4.2 Hz, 1H), 4.52–4.65 (m, 2H), 5.00–5.06 (m, 1H), 6.90–6.94 (m, 2H), 7.00–7.05 (m, 1H), 7.27–7.35 ppm (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$ =66.19 (CH<sub>2</sub>), 66.81 (CH<sub>2</sub>), 74.09 (CH), 114.55 (2×CH), 121.94 (CH), 129.66 (2×CH), 154.65 (C), 157.70 ppm (C=O); MS (EI): *m/z* (%): 194 (71), 107 (100), 94 (73), 79 (27), 77 (89), 66 (16), 65 (21), 51 (18), 39 (15).

#### Cyclohexene oxide carbonate (21)<sup>[20]</sup>

According to GP1, cyclohexene oxide (1I) (2.47 g, 25.1 mmol) was converted into 2I in the presence of KI (83 mg, 0.50 mmol) and 3h (49 mg, 0.50 mmol) at 120 °C and a CO<sub>2</sub> pressure of 50 bar over a period of 6 h. After removal of all volatiles, 2I (2.80 g, 19.7 mmol, 78%) was obtained as a colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta$  = 1.36–1.48 (m, 2H), 1.57–1.69 (m, 2H), 1.87–1.95 (m, 4H), 4.65–4.72 ppm (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta$  = 19.1 (2×CH<sub>2</sub>), 26.7 (2×CH<sub>2</sub>), 75.7 (2×CH), 155.3 ppm (C=O); MS (EI): *m/z* (%): 142 (1) [*M*<sup>+</sup>], 97 (14), 83 (39) [C<sub>6</sub>H<sub>11</sub><sup>+</sup>], 80 (32), 70 (43), 69 (100) [C<sub>5</sub>H<sub>9</sub><sup>+</sup>], 57 (47), 55 (80), 54 (48), 42 (77), 41 (88).

# Carbonated methyl oleate (2 m)<sup>[22]</sup>

According to GP1, epoxidized methyl oleate (1m) (1.56 g, 5.0 mmol) was converted into 2 m in the presence of Kl (16.6 mg, 0.10 mmol) and 3 h (9.8 mg, 0.10 mmol) at 100 °C and a CO<sub>2</sub> pressure of 50 bar over a period of 16 h. After the reaction, the reactor was cooled to ambient temperature and CO<sub>2</sub> was released slowly. Hexadecane (400 mg) was added as an internal standard, and the reaction mixture was diluted with dichloromethane (10 mL). The catalyst was removed by purification of the reaction mixture was analyzed by using 7890A-GC (Agilent). Pure samples of *cis*- and *trans*-carbonated methyl oleate (2 m) were obtained by purification of the reaction mixture over silica gel column chromatography using cyclohexane/ethyl acetate (10:1) as an eluent.

*cis*-Carbonated methyl oleate: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  = 0.88 (t, <sup>3</sup>*J*<sub>H,H</sub> = 6.8 Hz, 3 H), 1.22−1.44 (m, 20 H), 1.46−1.75 (m, 6 H), 2.30 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, 2 H), 3.67 (s, 3 H), 4.58−4.66 ppm (m, 2 H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta$  = 14.05 (CH<sub>3</sub>), 22.60 (CH<sub>2</sub>), 24.78 (CH<sub>2</sub>), 25.51 (CH<sub>2</sub>), 25.56 (CH<sub>2</sub>), 28.83 (CH<sub>2</sub>), 28.86 (CH<sub>2</sub>), 28.89 (CH<sub>2</sub>), 28.95 (CH<sub>2</sub>), 28.99 (CH<sub>2</sub>), 29.11 (CH<sub>2</sub>), 29.20 (CH<sub>2</sub>), 29.28 (CH<sub>2</sub>), 31.75 (CH<sub>2</sub>), 33.96 (CH<sub>2</sub>), 51.45 (OCH<sub>3</sub>), 79.88 (CH), 79.93 (CH), 154.75 (C=O), 174.18 ppm (C=O); MS (EI): *m/z* (%): 357 (1), 325 (34), 294 (9), 262 (20), 239 (64), 221 (10), 181 (13), 164 (16), 155 (38), 135 (26), 121 (34), 109 (47), 95 (77), 81 (78), 69 (59), 55 (100), 43 (56), 41

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(56); HRMS (ESI): m/z calcd for  $C_{20}H_{36}O_5$ : 357.26355 [ $MH^+$ ]; found: 357.26339.

*trans*-Carbonated methyl oleate: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 0.85$  (t, <sup>3</sup> $J_{H,H} = 6.8$  Hz, 3 H), 1.19–1.50 (m, 20 H), 1.54–1.75 (m, 6H), 2.28 (t, <sup>3</sup> $J_{H,H} = 7.5$  Hz, 2H), 3.64 (s, 3H), 4.17–4.24 ppm (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 22 °C):  $\delta = 13.97$  (CH<sub>3</sub>), 22.50 (CH<sub>2</sub>), 24.48 (CH<sub>2</sub>), 24.52 (CH<sub>2</sub>), 24.69 (CH<sub>2</sub>), 28.79 (CH<sub>2</sub>), 28.84 (2×CH<sub>2</sub>), 29.00 (CH<sub>2</sub>), 29.05 (CH<sub>2</sub>), 29.19 (CH<sub>2</sub>), 31.66 (CH<sub>2</sub>), 33.67 (CH<sub>2</sub>), 33.68 (CH<sub>2</sub>), 33.85 (CH<sub>2</sub>), 51.34 (OCH<sub>3</sub>), 81.87 (CH), 81.91 (CH), 154.60 (C= O), 174.05 ppm (C=O); MS (EI): *m/z* (%): 357 (1), 325 (35), 294 (7), 262 (17), 241 (25), 239 (32), 221 (18), 181 (11), 164 (14), 155 (24), 135 (25), 121 (34), 109 (55), 95 (86), 81 (83), 69 (60), 55 (100), 43 (55), 41 (56); HRMS (ESI): *m/z* calcd for C<sub>20</sub>H<sub>36</sub>O<sub>5</sub>: 357.26355 [*M*<sup>+</sup> -H]; found: 357.26334.

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