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Selective pyrolysis of bifunctional compounds: gas-phase elimination of carbonate–ester functionalities

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Abstract

Compounds containing both carbonate and ester functionalities were synthesized and then subjected to online-GC gas-phase pyrolysis. The carbonate groups were cleaved selectively in all elimination reactions. The end products of the reaction were found to be affected by the nature of the substrate. The presence of hydrogen and carbonyl substituents on the carbon β to the carbonate group resulted in further product decomposition through a concerted six-membered transition state. Results from flash vacuum pyrolysis (FVP) and analysis of the GC data indicate that the cleavage of the carbonate group is fast, and that the slower secondary decomposition reactions are independent of the presence of the carbonate group. Spectroscopic analyses of the products are reported.

Keywords: Online-GC gas-phase pyrolysis; Selectivity; Carbonate–ester bifunction

1. Introduction

Gas-phase pyrolyses have been utilized as economic and efficient methodologies in alternative and selective syntheses.[1–7] These reactions were used successfully in the preparation of 2-glucosyl-1,2,4-triazole-3(2*H*)-thione, which is a biologically important compound.[1] A novel heterocyclic ring system, benzo[1,2-*b*]cinnoline has also been synthesized by the gas-phase pyrolysis of benzotriazole derivatives.[2] Besides, flash vacuum pyrolysis (FVP) technique was used effectively to functionalize alkynes and various related systems, and to convert substituted phosphorus ylides into 1,3-diene derivatives; all these compounds being useful precursors for organic synthesis.[6,7]

Ester and carbonate moieties are used extensively in the protection of hydroxyl groups.[8] The selective removal of either the ester or carbonate group when both are present in the same molecule could be problematic because of their similar reactivity. Pyrolysis of carbonates, thiocarbonates, esters, and thioesters has been reported.[9–11] The studies show that the carbonate and ester groups have different thermal stability, that the pyrolytic reactions of the carbonate group are about 10-fold faster than ester pyrolysis, and that these reactions proceed by a concerted cis-elimination pathway. Exploiting the difference in the thermal stability of the ester and carbonate groups, we report in this work the utility of gas-phase pyrolysis as an alternative route in the selective deprotection of compounds containing both carbonate and ester functionalities. The pyrolytic reactions were preformed using an online-GC pyrolyzer. Where appropriate, FVP was used to separate the constituents of the pyrolyzates.

2. Results and discussion

The hydroxycarbonate and the carbonate–ester compounds under study were synthesized starting with substituted 1,3-diol precursors (**1**–**7**)**a**. The diols were cyclized into the carbonate derivatives (**1**–**7**)**b** using ethyl chloroformate in tetrahydrofuran (THF) in the presence of Et_3N. The cyclic carbonate compounds were opened by an acid catalyst in ethanol to obtain acyclic hydroxycarbonate compounds (**1**–**7**)**c**. The

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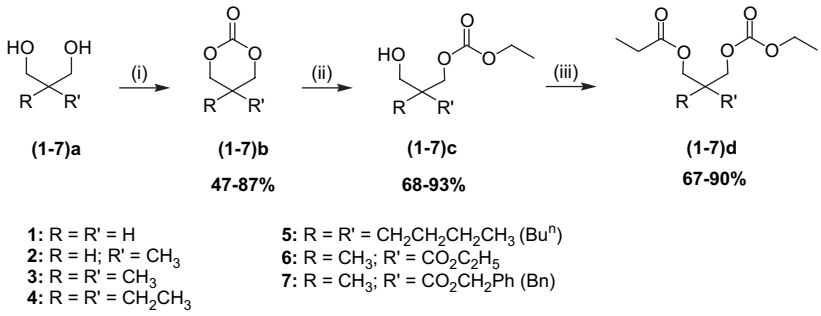
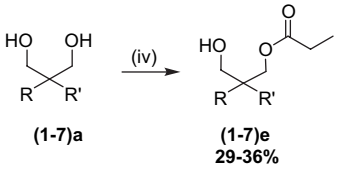


Scheme 1. Synthesis of carbonate–ester bifunctional compounds: (i) ethyl chloroformate, Et_3N/THF; (ii) ethanol/TFA, (iii) propanoic anhydride/DMAP.

hydroxyl group subsequently was acylated with propanoic anhydride in presence of DMAP as catalyst to produce the target carbonate–ester compounds (**1**–**7**)**d** as shown in Scheme 1.

On the other hand, the hydroxymonoesters were prepared by reacting the diols (**1**–**7**)**a** with propanoic anhydride in a 1:1 ratio using THF as solvent and DMAP as catalyst. The hydroxyalkyl ester product was isolated by column chromatography with 20% ethyl acetate in petroleum ether as eluent (Scheme 2).



Scheme 2. Synthesis of hydroxyesters: (iv) propanoic anhydride, DMAP/THF.

Carbonate, carbonate–ester, and ester compounds (**c**, **d**, **e**) were first injected in the gas chromatograph and the retention times were recorded for each set of compounds. The online-GC pyrolyzer was then used to perform the gas-phase pyrolysis reactions. An internal standard (chlorobenzene, 1,3-dichlorobenzene, or 1,2,4-trichlorobenzene) was added to the carbonate–ester compounds (**1**–**7**)**d**, the temperature of the pyrolyzer raised incrementally, and pyrolysis was monitored by GC. In all cases, thermal decomposition started at >500 °C. Peak heights of the ester compounds gradually increased with temperature (Fig. 1). The pyrolytic reactions were deemed complete when the peaks for the starting carbonate–ester compounds disappeared at ca. 700 °C. No hydroxycarbonate peaks were detected in the GC for any substrate, which indicated that the pyrolytic reactions are highly selective.

The rate coefficients (k, s^{-1}) and Arrhenius parameters of compounds (**1**–**7**)**d** are shown in Table 1. Kinetic analysis was conducted at the temperature range 840–953 K. Rate constants were calculated and plotted against $1/T$. The Arrhenius plots were strictly linear; an example is shown in Figure 2 for substrate **3d**. The activation energy (E_a, kJ mol^{-1}) calculated from the slope of the plot, the Arrhenius log A (s^{-1}), and the first-order-rate constant (k, s^{-1}) at 900 K are given in Table 1. The kinetic data show little difference in rate coefficients. The products of pyrolysis, however, were clearly affected by the nature of the substrates. When the R and R′ substituents are methyl, ethyl, or butyl groups only ester compounds are formed. Initial pyrolysis proceeds through a cyclic six-membered transition state, which is the preferred pyrolytic reaction pathway (Scheme 3),[10,12] and subsequent secondary decomposition leads to loss of a stable CO_2 fragment and formation of the hydroxyester product.

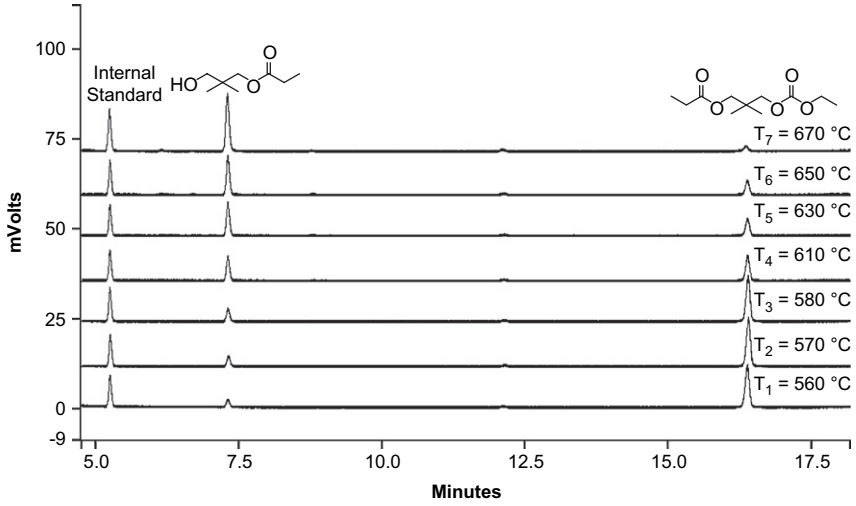


Figure 1. GC gas-phase pyrolysis chromatograms of **3d** as function of reaction temperature.

Table 1
Rate coefficients (k, s^{-1}) and Arrhenius parameters of reactions of compounds (**1**–**7**)**d**

Compound	T/K	k/s^{-1}	log A/s^{-1}	E_a/kJ mol^{-1}	$k_{900\ K}$/s^{-1}
1d	843.15	1.5	12.3±0.3	196.4±5.6	8.4
	853.15	2.0			
	873.15	3.5			
	883.15	4.9			
	893.15	7.5			
	923.15	16.1			
2d	833.15	1.5	8.4±0.3	131.5±2.2	6.2
	853.25	2.4			
	883.15	4.3			
	893.15	5.3			
	903.15	6.8			
	913.15	8.0			
	933.15	11.0			
	953.15	17.3			
3d	833.15	1.1	9.4±0.2	149.4±4.3	6.0
	848.15	1.9			
	863.15	2.5			
	878.15	3.9			
	893.15	5.1			
	908.15	7.0			
	923.15	9.8			
4d	843.15	0.3	14.3±0.5	238.9±8.3	2.6
	858.15	0.5			
	888.15	1.9			
	918.15	5.3			
	933.15	7.0			
	948.15	13.6			
5d	848.15	1.5	11.7±0.2	187.8±3.5	7.0
	878.15	3.6			
	893.15	5.9			
	908.15	8.8			
	923.15	13.3			
6d	848.15	0.5	13.5±0.5	224.6±8.3	2.9
	863.15	0.8			
	938.15	1.1			
	953.15	1.5			
7d	878.15	1.5	13.7±0.31	227.4±5.3	3.2
	893.15	2.4			
	908.15	4.3			
	953.15	17.0			

For compounds **1d** and **2d**, even when the reaction shows selectivity in cleavage of the carbonate group, the GC chromatograms still show minor peaks at relatively high reaction temperature. The common feature of these two sets of compounds is that they have H at the β-carbon to an ester group, which is reported in the literature to facilitate further slow pyrolysis through a concerted six-membered transition state as the preferred reaction pathway (Scheme 4, R=H).[12] Kinetically, for compounds **1d** and **2d** the fast pyrolytic reaction step is the cleavage of the carbonate group and the slower step is the elimination of the β-hydrogen. This seemed obvious to us because at the initial stages of the pyrolysis we detect only the peaks corresponding to the hydroxyester compounds resulting from the elimination of the carbonate groups.

To confirm the proposed β-hydrogen elimination pathway, flash vacuum pyrolysis (FVP) was carried out on the carbonate–ester compounds **1d** and **2d**, from which the hydroxyester compounds **1e** and **2e** were obtained at 650 and

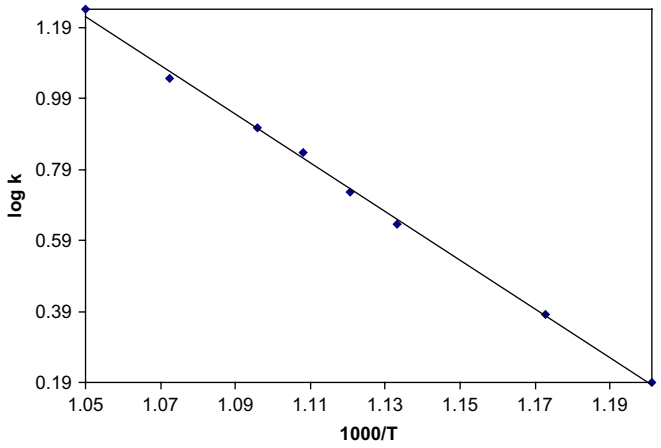
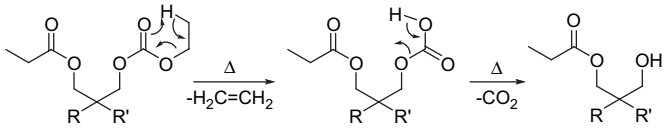
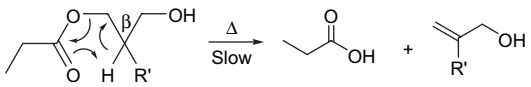


Figure 2. Arrhenius plot for **3d**.



Scheme 3. Pyrolysis of compounds (**1**–**5**)**d**.



Scheme 4. Ester pyrolysis by elimination of β-hydrogen.

680 °C, respectively. The products from FVP were isolated and analyzed by NMR and MS. Further pyrolysis of the hydroxyesters gave the alkene and carboxylic acid observed for the (slower) secondary pyrolytic reaction. Since both carbonate–ester compounds and hydroxyester compounds gave the same reaction products, the proposed mechanism of ester pyrolysis does not require the presence of the carbonate group. For compounds **1d** and **1e** the alkene fragment is allyl alcohol and the acid is propanoic acid. Compounds **2d** and **2e** formed 2-methylprop-2-en-1-ol and propanoic acid. Authentic samples and the pyrolyzate fragments gave the same GC retention times.

In the case of compounds **6d** and **7d**, the presence of a carbonyl group at the β-carbon affects the pyrolysis pathway. Initially (lower temperature), the reactions proceed by the selective elimination of the carbonate group. With the increase of temperature, new peaks indicative of secondary decomposition begin to appear. At 665 °C, compound **6d** shows starting material, ester compound, and product peaks; at 695 °C, only the starting material and the product peaks are present; at 710 °C, the starting material and the hydroxyester compound peaks disappear. Pyrolysis of compound **7d** follows the same pattern (Figs. 3 and 4). Analyzing the GC chromatograms of the products of reaction of compounds **6d** and **7d**, we conclude that the reactions commence by the elimination of the carbonate group, followed by secondary pyrolytic reaction involving a cyclic six-membered transition state, in which the hydroxyl and the carbonyl groups play noticeable roles. The proposed

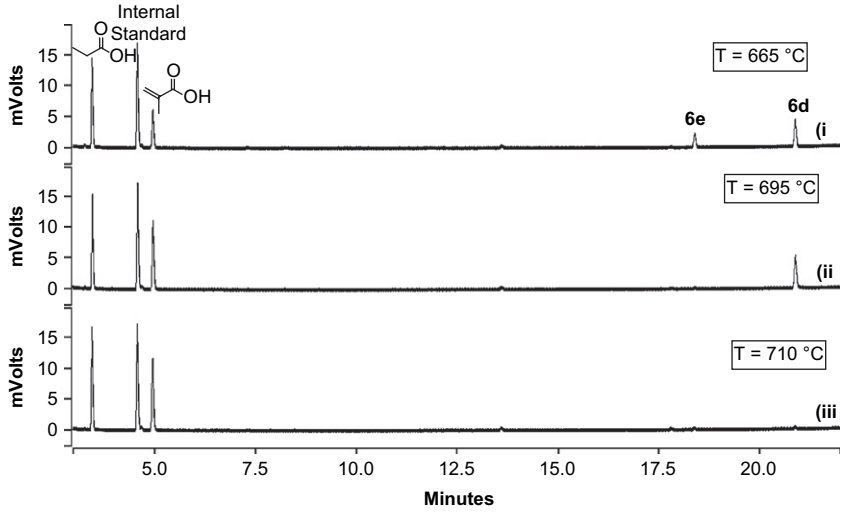


Figure 3. Gas-phase pyrolysis chromatograms of reaction of **6d** as function of reaction temperature.

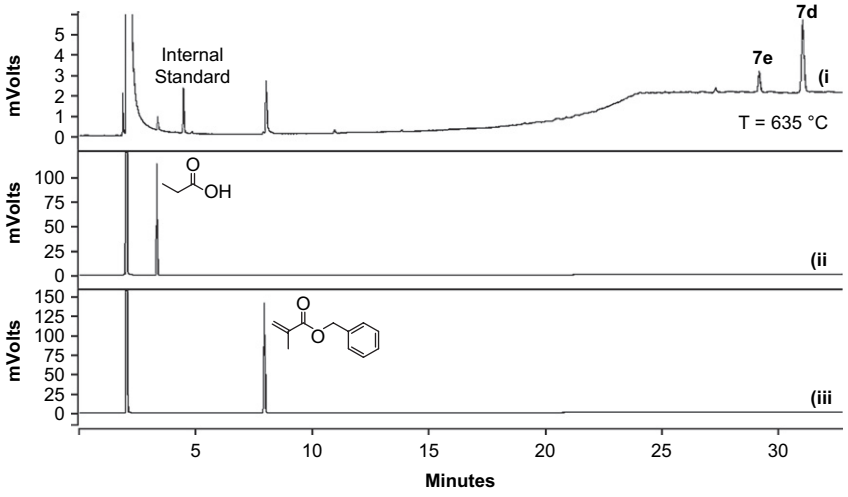


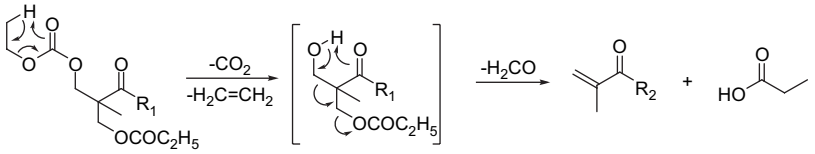
Figure 4. (i) Gas-phase pyrolysis chromatograms of compound **7d** at 635 °C; (ii) chromatogram of propanoic acid; (iii) chromatogram of benzyl methacrylate.

reaction mechanism is shown in Scheme 5. The pyrolytic reaction of compound **6d** gave methacrylic acid and propanoic acid, the ethyl ester group being unstable under the conditions of reaction, whereas compound **7d** resulted in the formation of benzyl methacrylate and propanoic acid, because the benzyl ester is much more stable than the ethyl ester.

Flash vacuum pyrolysis has been carried out for compounds **6d** and **7d** and **6e** and **7e** at 750 °C to ensure complete pyrolysis of the compounds. The products of pyrolysis were separated by column chromatography and full spectral data were recorded. The data confirmed the suggested products. The same procedure of authentication used for compounds **1d** and **2d** was employed for compounds **6d** and **7d** and **6e** and **7e**: validation by GC retention times of benzyl methacrylate, methacrylic acid, and propanoic acid (Figs. 3 and 4).

3. Conclusion

Carbonate–ester bifunctional compounds were synthesized and then pyrolyzed in order to investigate the selective removal of one group or the other as a strategy toward selective deprotection. The results indicate that gas-phase pyrolysis



$R_1 = OC_2H_5$ or OBn
R_2 = OH or OBn

Scheme 5. FVP of compounds (**6**–**7**)**d** at 750 °C.

favors removal of the carbonate groups; the reactions being monitored using GC retention times of synthetic authentic samples of substrates and products. The kinetic data in Table 1 reveal small differences in rate coefficients. The most reactive substrates were the unsubstituted compound (**1d**) and that with the longest alkyl chain (**5d**). The shorter alkyl chains and the alkyl and benzyl carboxylate groups of compounds (**4d**, **6d**, **7d**) reduced reactivities threefold compared to **1d**; the effect of the alkyl groups in **2d** and **3d** was smaller. However, the nature of the products of pyrolysis was affected by the nature of the substrate. Hydrogen and carbonyl substituents on the β-carbon resulted in secondary decomposition of the reaction products. FVP was employed to separate and isolate the constituents of the pyrolyzates. Authentic samples were used to confirm and establish the retention times of the products of the gas-phase pyrolysis reactions. The accepted reaction mechanism involves a cyclic six-membered transition state, which is the dominant reaction pathway in this type of gas-phase pyrolytic reactions.[9] Work is in progress on the alternative biocatalytic selective deprotection of carbonate–ester bifunctional compounds.

4. Experimental section

4.1. General

All chemicals including compounds (**1**–**5**)**a** were purchased from Aldrich and used as-received unless otherwise indicated. ^{1}H NMR spectra were recorded on a BRUKER DPX 400 MHz Superconducting NMR spectrometer. Mass spectra were measured on Vg Auto-Spes-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LC–MS using Agilent 1100 series LC/MSD with an API-ES/APCI Ionization Mode, Positive/Negative Polarity, Autosampler, Quaternary Pump and Agilent Chemstation Software. Microanalyses were performed on LECO CHNS-932 Elemental Analyser. GC analyses were performed on Varian GC CP-3800 with FID Detector, Capillary Injector Port, and Varian Star 5.51 Chromatography Workstation Software. Pyrolysis was carried out using SGE Pyrojector II on-line pyrolyzer (continuous mode) with temperature range 0–900 °C under non-oxidizing conditions. The hot zone is a quartz glass liner with 60 mm length and 2 mm internal diameter.

4.2. Kinetic measurements

A stock solution (4 mL) was prepared by dissolving 6–10 mg of the substrate in acetonitrile as solvent to give a concentration of 1000–2000 ppm. An internal standard was then added, the amount being adjusted to give the desired peak area ratio of substrate to standard (2.5:1). The solvent and the internal standard are selected such that both are stable under the conditions of pyrolysis, and because they would not react with either substrate or product. The internal standards used in this study are chlorobenzene, 1,3-dichlorobenzene or 1,2,4-trichlorobenzene. Each solution was filtered to ensure that a homogeneous solution is obtained. The weight ratio of the substrate with respect to the internal standard was calculated from the ratio of the substrate peak area to the peak area of the internal standard. The kinetic rate was obtained by tracing the rate of disappearance of the substrate with respect to the internal standard as follows: 1 μL of the solution is injected in the pyrolyzer, which is set at non-pyrolysis conditions to get the initial ratio of the sample to the internal standard A_0 (standardization value). The sample was then passed through GC (oven temperature: 140–200 °C, flow rate: 1–1.5 mL/min, injection port temperature: 250 °C, and FID detector temperature: 300 °C). The GC column used was SUPELCO SPB-20 fused silica capillary column (30 m length, 0.32×0.25 μm film thickness). This procedure is repeated after each 10–15 °C rise in the temperature of the pyrolyzer until ≥90% pyrolysis takes place. The relative ratios of the integration values of the sample and the internal standard (A) at the pyrolysis temperature are then determined. The rate coefficients were calculated using the expression for a first-order reaction: $kt=\ln(A_0/A)$. The Arrhenius parameters were obtained from a plot of $\log k$ against $1/T$ (K). The residence time (t) was calculated from the relation $t=PVT_m/P_mTG$, where P is the atmospheric pressure, V is the volume of the reactor, T_m is room temperature (K), T is the reactor temperature (K) and G is the carrier gas flow rate (mL/s).[16,17]

4.3. Flash vacuum pyrolysis (FVP)

The apparatus used has been described in recent publications.[4] The sample was volatilized from a tube in a Büchi Kugelrohr oven through a 30×2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 750 °C, the temperature being monitored by a Pt/Pt–13%Rh thermocouple situated at the center of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions the contact time in the hot zone was estimated to be ∼10 ms. The different zone samples of the products collected in the U-shaped trap were analyzed by ^{1}H NMR, LC–MS, and GC–MS. Relative and percent yields were determined from GC and compared with authentic samples.

4.4. Synthesis

4.4.1. Ethyl 2,2-bis(hydroxymethyl)propanoate (*6a*)

Bis(hydroxymethyl)propanoic acid (10 g, 74.6 mmol) was dissolved in (50 mL) ethanol and a few drops of H_2SO_4 were added. The reaction mixture was refluxed. After 3 h, the reaction mixture was cooled and ethanol was evaporated. The residue was dissolved in ethyl acetate and washed with sodium bicarbonate solution followed by water. Following the extraction, the organic layer was dried over anhydrous sodium sulfate, filtered, and then evaporated to obtain **6a** as a colorless oil (9.3 g, 77% yield); MS: m/z 162 ($M^{+\bullet}$); ^{1}H NMR ($CDCl_3$)

ppm: 1.07 (s, 3H, CH_3), 1.31 (t, J=7.2 Hz, 3H, CH_3), 3.04 (br s, 1H, OH), 3.72 (d, J=10.8 Hz, 2H, CH_2), 3.91 (d, J=10.8 Hz, 2H, CH_2), 4.23 (q, J=7.2 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.7 (CH_3), 17.7 (CH_3), 49.6 (CH), 69.7 (OCH_2), 68.9 ($2OCH_2$), 176.6 (OC=O). Anal. Calcd for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 51.51; H, 8.79.

*4.4.2. Benzyl 2,2-bis(hydroxymethyl)propanoate (**7a**)*

Compound **7a** was synthesized according to the literature procedure,[13] and was obtained as white crystals (13.4 g, 80% yield); mp: 75 °C; MS: *m/z* 224 ($M^{+\bullet}$); ^{1}H NMR ($CDCl_3$) ppm: 1.11 (s, 3H, CH_3), 2.95 (s, 2H, 2OH), 3.76 (d, J=11.3 Hz, 2H, OCH_2), 3.97 (d, J=11.2 Hz, 2H, OCH_2), 5.24 (s, 2H, OCH_2), 7.34–7.43 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) ppm: 17.7 (CH_3), 49.8 (CH), 67.3 (OCH_2), 68.9 ($2OCH_2$), 128.5 (ArC), 128.9 (ArC), 129.2 (ArC), 136.2 (ArC), 176.3 (OC=O). Anal. Calcd for $C_7H_{14}O_4$: C, 64.27; H, 7.19. Found: C, 63.70; H, 7.00.

*4.4.3. General procedure for synthesis of cyclic carbonates (**1–7**)**b***

The cyclic carbonate compounds were prepared according to the literature procedures.[13,14]

*4.4.3.1. 1,3-Dioxan-2-one (**1b**).*[14] White crystals (9.3 g, 70% yield); mp: 47–48 °C; MS: *m/z* 102 (M^+, 100%) and 57 (87%); ^{1}H NMR ($CDCl_3$) ppm: 2.17 (quin, J=5.7 Hz, 2H, CH_2), 4.48 (t, J=5.7 Hz, 4H, $2CH_2$). Anal. Calcd for $C_4H_6O_3$: C, 47.06; H, 5.92. Found: C, 46.81; H, 6.34.

*4.4.3.2. 5-Methyl-1,3-dioxan-2-one (**2b**).* Colorless oil (59% yield); MS: *m/z* 116 (M^+, 34%), 75 (47%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.02 (d, J=6.8 Hz, 3H, CH_3), 2.34–2.38 (m, 1H, CH), 4.05 (t, J=10.1 Hz, 2H, OCH_2), 4.38 (d, J=10.6, 4.3 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 12.4 (CH_3), 26.8 (CH), 73.7 ($2OCH_2$), 149.1 (OC=OO).

*4.4.3.3. 5,5-Dimethyl-1,3-dioxan-2-one (**3b**).* White crystals (66% yield); mp: 96–97 °C; MS *m/z* 130 (M^+, 10%), 101 (14%), 86 (76%), 71 (20%), 56 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.15 (s, 6H, $2CH_3$), 4.10 (s, 4H, $2CH_2$). ^{13}C NMR ($CDCl_3$) ppm: 21.6 ($2CH_3$), 28.9 (C), 78.1 ($2OCH_2$), 148.7 (OC=OO). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.36; H, 7.63.

*4.4.3.4. 5,5-Diethyl-1,3-dioxan-2-one (**4b**).* White crystals (70% yield); mp: 49–50 °C; MS: *m/z* 159 (M^++1, 5%), 84 (60%), 69 (100%), 55 (68%); ^{1}H NMR ($CDCl_3$) ppm: 0.92 (t, J=7.6 Hz, 6H, $2CH_3$), 1.50 (q, J=7.6 Hz, 4H, $2CH_2$), 4.15 (s, 4H, $2OCH_2$). ^{13}C NMR ($CDCl_3$) ppm: 7.7 ($2CH_3$), 23.2 ($2CH_2$), 34.1 (C), 75.5 ($2OCH_2$), 149.2 (OC=OO). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.42; H, 8.85.

*4.4.3.5. 5,5-Dibutyl-1,3-dioxan-2-one (**5b**).* Colorless oil (62% yield); MS: *m/z* 213 (M^+–1, 5%), 157 (7%), 140 (18%), 110 (7%), 97 (30%), 83 (64%), 70 (47%), 56 (100%); ^{1}H NMR ($CDCl_3$) ppm: 0.94 (t, J=7.1 Hz, 6H, $2CH_3$), 1.24–1.63 (m, 12H, $6CH_2$), 4.14 (s, 4H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.5 ($2CH_3$), 23.7 ($2CH_2$), 25.5 ($2CH_2$), 30.9 ($2CH_2$), 33.9 (C), 76.0 ($2OCH_2$), 159.0 (OC=OO). Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 66.46; H, 10.36.

*4.4.3.6. Ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (**6b**).* White crystals (78% yield); mp: 51 °C; MS: *m/z* 189 (M^++1, 54%), 157 (27%), 143 (40%), 127 (10%), 115 (95%), 99 (75%), 86 (60%), 72 (92%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.33 (t, J=7.1 Hz, 3H, CH_3), 1.36 (s, 3H, CH_3), 4.22 (d, J=10.6 Hz, 2H, CH_2), 4.28 (q, J=7.1 Hz, 2H, CH_2), 4.72 (d, J=10.6 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.4 (CH_3), 18.0 (CH_3), 40.5 (C), 62.7 (OCH_2), 73.4 ($2OCH_2$), 147.9 (OC=OO), 171.5 (OC=O). Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 50.65; H, 6.34.

*4.4.3.7. Benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (**7b**).*[13] White crystals (85% yield); mp: 75 °C; MS: *m/z* 250 (M^+, 2%), 144 (5%), 107 (18%), 100 (30%), 91 (100%), 85 (11%), 77 (8%), 65 (11%); ^{1}H NMR ($CDCl_3$) ppm: 1.35 (s, 3H, CH_3), 4.23 (d, J=10.8 Hz, 2H, CH_2), 4.73 (d, J=10.8 Hz, 2H, CH_2), 5.24 (s, 2H, CH_2), 7.35–7.43 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) ppm: 18.0 (CH_3), 40.6 (C), 68.3 (OCH_2), 73.3 ($2OCH_2$), 128.6 (ArC), 129.1 (ArC), 129.2 (ArC), 135.1 (ArC), 147.8 (OC=OO), 171.3 (OC=O).

*4.4.4. General procedure for the synthesis of open-ring carbonates (**1–7**)**c***

Compounds (**1–7**)**b** (2 g) were dissolved in ethanol (30 mL) and few drops of trifluoroacetic acid (TFA) were added, while the mixture is being stirred at room temperature. After addition was completed, ethanol was evaporated and the residue was dissolved in ethyl acetate. The organic layer was extracted with sodium bicarbonate solution and water, then dried with anhydrous sodium sulfate and ethyl acetate was finally evaporated to recover the pure compound.[15]

*4.4.4.1. Ethyl (3-hydroxypropyl) carbonate (**1c**).* Colorless oil (72% yield); MS: *m/z* 131 (50%), 103 (100%), 59 (50%); ^{1}H NMR ($CDCl_3$) ppm: 1.32 (t, J=7.2 Hz, 3H, CH_3), 1.69 (br s, 1H, OH), 1.94 (quin, J=6.0 Hz, 2H, CH_2), 3.77 (t, J=6.0 Hz, 2H, OCH_2), 4.23 (q, J=7.2 Hz, 2H, OCH_2), 4.29 (t, J=6.0 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.8 (CH_3), 32.2 (CH_2), 59.6 (OCH_2), 64.7 (OCH_2), 65.3 (OCH_2), 156.1 (OC=OO).

*4.4.4.2. Ethyl (3-hydroxy-2-methylpropyl) carbonate (**2c**).* Colorless oil (68% yield); MS: *m/z* 162 (M^+, 1%), 135 (10%), 117 (100%), 73 (44%), 57 (72%); ^{1}H NMR ($CDCl_3$) ppm: 0.96 (d, J=7.0 Hz, 3H, CH_3), 1.30 (t, J=7.1 Hz, 3H, CH_3), 1.99–2.04 (m, 1H, CH), 2.33 (br s, 1H, OH), 3.50–3.59 (m, 2H, OCH_2), 4.12 (d, J=5.9 Hz, 2H, OCH_2), 4.19 (q, J=7.1 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.0 (CH_3), 14.8 (CH_3), 35.9 (CH), 64.7 (OCH_2), 70.0 ($2OCH_2$), 156.2 (OC=OO). Anal. Calcd for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 50.93; H, 8.70.

*4.4.4.3. Ethyl (3-hydroxy-2,2-dimethylpropyl) carbonate (**3c**).* Colorless oil (82% yield); MS: *m/z* 152 (20%), 91 (100%), 73 (60%), 69 (58%), 56 (95%); ^{1}H NMR ($CDCl_3$) ppm: 0.96 (s, 6H, $2CH_3$), 1.34 (t, J=7.1 Hz, 3H, CH_3), 2.16 (br s, 1H, OH), 3.38 (s, 2H, OCH_2), 4.01 (s, 2H, OCH_2), 4.23 (q, J=7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.8 (CH_3), 21.9 ($2CH_3$), 37.1 (C), 64.8 (OCH_2), 68.6 (OCH_2), 73.6 (OCH_2), 156.5 (OC═OO). Anal. Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 53.53; H, 9.28.

*4.4.4.4. Ethyl [2-ethyl-2-(hydroxymethyl)butyl] carbonate (**4c**).* Colorless oil (89% yield); MS: *m/z* 187 (20%), 173 (10%), 159 (25%), 97 (100%), 83 (75%), 69 (25%), 55 (65%); ^{1}H NMR ($CDCl_3$) ppm: 0.86 (t, J=7.5 Hz, 6H, $2CH_3$), 1.24–1.39 (m, 7H, CH_3, $2CH_2$), 2.14 (br s, 1H, OH), 3.39 (s, 2H, OCH_2), 4.05 (s, 2H, OCH_2), 4.23 (q, J=7.1 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 7.5 ($2CH_3$), 14.8 (CH_3), 22.3 ($2CH_2$), 41.9 (C), 64.7 (OCH_2), 64.9 (OCH_2), 69.9 (OCH_2), 156.6 (OC═OO). Anal. Calcd for $C_{10}H_{20}O_4$: C, 58.80; H, 9.87. Found: C, 58.95; H, 10.08.

*4.4.4.5. 2-Butyl-2-(hydroxymethyl)hexyl ethyl carbonate (**5c**).* Colorless oil (69% yield); MS: *m/z* 243 (34%), 229 (32%), 215 (60%), 201 (20%), 171 (30%), 153 (92%), 140 (100%), 111 (40%), 97 (95%), 83 (100%), 69 (70%), 55 (70%); ^{1}H NMR ($CDCl_3$) ppm: 0.93 (t, J=7.2 Hz, 6H, $2CH_3$), 1.18–1.35 (m, 15H, CH_3, $6CH_2$), 2.02 (1H, OH), 3.39 (s, 2H, OCH_2), 4.04 (s, 2H, OCH_2), 4.23 (q, J=7.2 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 14.4 ($2CH_3$), 14.7 (CH_3), 23.9 ($2CH_2$), 25.1 ($2CH_2$), 30.9 ($2CH_2$), 41.6 (C), 64.5 (OCH_2), 65.1 (OCH_2), 70.5 (OCH_2), 156.4 (OC═OO). Anal. Calcd for $C_{14}H_{28}O_4$: C, 64.58; H, 10.84. Found: C, 64.51; H, 11.11.

*4.4.4.6. Ethyl 3-[(ethoxycarbonyl)oxy]-2-(hydroxymethyl)-2-methylpropanoate (**6c**).* Colorless oil (88% yield); MS: *m/z* 234 (M^+, 7%), 189 (60%), 115 (40%), 99 (50%), 69 (100%), 57 (80%); ^{1}H NMR ($CDCl_3$) ppm: 1.24 (s, 3H, CH_3), 1.28–1.35 (m, 6H, $2CH_3$), 2.52 (t, J=6.9 Hz, 1H, OH), 3.73 (d, J=6.6 Hz, 2H, OCH_2), 4.20–4.24 (m, 4H, $2OCH_2$), 4.27 (d, J=11.2 Hz, 1H, OCH), 4.45 (d, J=10.9 Hz, 1H, OCH). ^{13}C NMR ($CDCl_3$) ppm: 14.6 (CH_3), 14.8 (CH_3), 18.1 (CH_3), 48.7 (C), 61.8 (OCH_2), 64.9 (OCH_2), 65.4 (OCH_2), 69.4 (OCH_2), 155.9 (OC═OO), 174.8 (OC═O). Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.14; H, 7.77.

*4.4.4.7. Benzyl 3-[(ethoxycarbonyl)oxy]-2-(hydroxymethyl)-2-methylpropanoate (**7c**).* Colorless oil (93% yield); MS: *m/z* 296 (M^+, 27%), 279 (30%), 189 (40%), 131 (40%), 91 (100%), 72 (40%); ^{1}H NMR ($CDCl_3$) ppm: 1.26 (s, 3H, CH_3), 1.32 (t, J=7.1 Hz, 3H, CH_3), 2.47 (br s, 1H, OH), 3.76 (d, J=5.7 Hz, 2H, OCH_2), 4.20 (q, J=7.1 Hz, 2H, CH_2), 4.30 (d, J=10.9 Hz, 1H, CH), 4.46 (d, J=11.1 Hz, 1H, CH), 5.21 (s, 2H, CH_2), 7.35–7.39 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) ppm: 14.8 (CH_3), 18.0 (CH_3), 48.9 (C), 65.0 (OCH_2), 65.4 (OCH_2), 67.3 (OCH_2), 69.4 (OCH_2), 128.5 (ArCH), 128.9 (ArCH), 128.2 (ArCH), 136.1 (ArC), 155.9 (OC═OO), 174.6 (OC═O). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.53; H, 6.99.

*4.4.5. General procedure for the synthesis of carbonate–ester compounds (**1–7**)**d***

Compounds (**1–7**)**c** (1 g) were dissolved in dry THF (10 mL) with 5% by weight of DMAP. Propanoic anhydride [1.5 equiv] was added, while the reaction mixture was stirred at room temperature. After the reaction was completed, the THF was evaporated and the residue dissolved in ethyl acetate and extracted with sodium bicarbonate solution and water. The organic layer was dried with anhydrous sodium sulfate, and ethyl acetate was then evaporated to obtain the pure product.

*4.4.5.1. 3-(Ethoxycarbonyloxy)propyl propanoate (**1d**).* Colorless oil (90% yield); MS: *m/z* 131 (25%), 115 (80%), 97 (25%), 83 (30%), 69 (62%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.16 (t, J=7.6 Hz, 3H, CH_3), 1.33 (t, J=7.1 Hz, 3H, CH_3), 2.03 (quin, J=6.2 Hz, 2H, CH_2), 2.35 (q, J=7.6 Hz, 2H, CH_2), 4.20–4.25 (m, 6H, $3OCH_2$). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 14.8 (CH_3), 28.1 (CH_2), 28.6 (CH_2), 61.1 (OCH_2), 64.6 (OCH_2), 64.9 (OCH_2), 155.7 (OC═OO), 175.0 (OC═O). Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.60; H, 7.92.

*4.4.5.2. 3-[(Ethoxycarbonyl)oxy]-2-methylpropyl propanoate (**2d**).* Colorless oil (67% yield); MS: *m/z* 145 (12%), 129 (95%), 117 (25%), 72 (9%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.03 (d, J=6.9 Hz, 3H, CH_3), 1.16 (t, J=7.6 Hz, 3H, CH_3), 1.33 (t, J=7.1 Hz, 3H, CH_3), 2.20–2.25 (m, 1H, CH), 2.36 (q, J=7.6 Hz, 2H, CH_2), 4.02–4.15 (m, 4H, $2OCH_2$), 4.22 (q, J=7.1 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 14.3 (CH_3), 14.8 (CH_3), 28.1 (CH), 33.1 (CH_2), 64.6 (OCH_2), 66.0 (OCH_2), 69.7 (OCH_2), 155.8 (OC═OO), 175.0 (OC═O). Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.23; H, 8.54.

*4.4.5.3. 3-[(Ethoxycarbonyl)oxy]-2,2-dimethylpropyl propanoate (**3d**).* Colorless oil (87% yield); MS: *m/z* 232 (M^+, 8%), 208 (50%), 143 (48%), 105 (54%), 91 (80%), 77 (52%), 69 (70%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 0.98 (s, 6H, $2CH_3$), 1.15 (t, J=7.6 Hz, 3H, CH_3), 1.33 (t, J=7.1 Hz, 3H, CH_3), 2.37 (q, J=7.6 Hz, 2H, CH_2), 3.92 (s, 2H, OCH_2), 3.98 (s, 2H, OCH_2), 4.21 (q, J=7.1 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 14.8 (CH_3), 22.2 ($2CH_3$), 28.1 (CH_2), 35.2 (C), 64.6 (OCH_2), 69.4 (OCH_2), 73.1 (OCH_2), 155.8 (OC═OO), 174.9 (OC═O). Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.90; H, 8.92.

*4.4.5.4. 2-[(Ethoxycarbonyl)oxy]methyl-2-ethylbutyl propanoate (**4d**).* Colorless oil (83% yield); MS: *m/z* 260 ($M^{+\bullet}$); ^{1}H NMR ($CDCl_3$) ppm: 0.85 (t, J=7.5 Hz, 6H, $2CH_3$), 1.16 (t, J=7.6 Hz, 3H, CH_3), 1.31–1.40 (m, 7H, CH_3, $2CH_2$), 2.36 (q, J=7.6 Hz, 2H, CH_2), 3.96 (s, 2H, OCH_2), 4.02 (s, 2H, OCH_2), 4.20 (q, J=7.2 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 7.6 ($2CH_3$), 9.7 (CH_3), 14.8 (CH_3), 23.4 ($2CH_2$), 28.2

(CH_2), 40.2 (C), 64.6 (OCH_2), 65.8 (OCH_2), 69.8 (OCH_2), 155.8 (OC═OO), 174.9 (OC═O). Anal. Calcd for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 60.38; H, 9.37.

*4.4.5.5. 2-Butyl-2-[(2-ethoxy-2-oxoethoxy)methyl]hexyl propanoate (**5d**).* Colorless oil (82% yield); MS: *m/z* 243 (24%), 227 (60%), 213 (35%), 139 (40), 97 (70%), 83 (77%), 69 (54%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 0.92 (t, *J*=7.2 Hz, 6H, $2CH_3$), 1.16 (t, *J*=7.6 Hz, 3H, CH_3), 1.20–1.35 (m, 15H, CH_3, $6CH_2$), 2.36 (q, *J*=7.6 Hz, 2H, CH_2), 3.94 (s, 2H, OCH_2), 3.95 (s, 2H, OCH_2), 4.21 (q, *J*=7.2 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 14.4 ($2CH_3$), 14.8 (CH_3), 23.9 ($2CH_2$), 25.3 ($2CH_2$), 28.2 (CH_2), 31.3 ($2CH_2$), 40.1 (C), 64.5 (OCH_2), 66.5 (OCH_2), 70.3 (OCH_2), 155.8 (OC═OO), 174.8 (OC═O). Anal. Calcd for $C_{17}H_{32}O_5$: C, 64.53; H, 10.19. Found: C, 64.97; H, 10.50.

*4.4.5.6. Ethyl 3-[(ethoxycarbonyl)oxy]-2-methyl-2-[(propionyloxy)methyl]propanoate (**6d**).* Colorless oil (88% yield); MS: *m/z* 291 (M^++1, 35%), 245 (40%), 217 (68%), 201 (47%), 144 (40%), 114 (64%), 99 (64%), 99 (52%), 69 (43%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.15 (t, *J*=7.6 Hz, 3H, CH_3), 1.26–1.34 (m, 9H, $3CH_3$), 2.35 (t, *J*=7.6 Hz, 3H, CH_3), 4.18–4.37 (m, 8H, $4OCH_2$). ^{13}C NMR ($CDCl_3$) ppm: 9.6 (CH_3), 14.6 (CH_3), 14.8 (CH_3), 27.9 (CH_2), 46.8 (C), 61.8 (OCH_2), 64.8 (OCH_2), 65.7 (OCH_2), 68.9 (OCH_2), 155.4 (OC═OO), 173.1 (OC═O), 174.4 (OC═O). Anal. Calcd for $C_{13}H_{22}O_7$: C, 53.78; H, 7.64. Found: C, 54.20; H, 7.77.

*4.4.5.7. Benzyl 3-[(ethoxycarbonyl)oxy]-2-methyl-2-[(propionyloxy)methyl]propanoate (**7d**).* Colorless oil (80% yield); MS: *m/z* 352 (M^+, 15%), 279 (28%), 263 (55%), 245 (72%), 205 (44%), 189 (80%), 173 (83%), 128 (67%), 107 (56%), 92 (100%), 65 (84%), 57 (76%); ^{1}H NMR ($CDCl_3$) ppm: 1.10 (t, *J*=7.6 Hz, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.32 (t, *J*=7.1 Hz, 3H, CH_3), 2.24–2.30 (m, 2H, CH_2), 4.16–4.38 (m, 6H, $3OCH_2$), 5.19 (s, 2H, OCH_2), 7.33–7.40 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) ppm: 9.6 (CH_3), 14.8 (CH_3), 18.3 (CH_3), 27.9 (CH_2), 47.0 (C), 64.9 (OCH_2), 65.8 (OCH_2), 67.4 (OCH_2), 68.9 (OCH_2), 128.6 (ArCH), 128.9 (ArCH), 129.2 (ArCH), 136.1 (ArC), 155.4 (OC═OO), 173.0 (OC═O), 174.4 (OC═O). Anal. Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 61.44; H, 7.14.

*4.4.6. General procedure for the synthesis of ester compounds (**1–7**)**e***

Compounds (**1–7**)**a** (1 g) were dissolved in dry THF (10 mL) with 5% by weight of DMAP. Propanoic anhydride [1:1 mole ratio] was added and the reaction was let to stir at room temperature. After the reaction was completed, the THF was evaporated and the residue dissolved in ethyl acetate and extracted with sodium bicarbonate solution and water. The organic layer dried with anhydrous sodium sulfate, and ethyl acetate was then evaporated. The mono-acetate product was separated using silica gel flash column chromatography, eluting with 20% ethyl acetate/petroleum ether.

*4.4.6.1. 3-Hydroxypropyl propanoate (**1e**).* Colorless oil (29% yield); MS: *m/z* 111 (10%), 97 (20%), 81 (42%), 69 (90%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 1.13 (t, *J*=7.6 Hz, 3H, CH_3), 1.86 (quin, *J*=6.2 Hz, 2H, CH_2), 2.33 (q, *J*=7.6 Hz, 2H, CH_2), 3.68 (t, *J*=6.0 Hz, 2H, CH_2), 4.22 (t, *J*=6.2 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 28.1 (CH_2), 32.3 (CH_2), 59.7 (OCH_2), 61.8 (OCH_2), 175.6 (OC═O).

*4.4.6.2. 3-Hydroxy-2-methylpropyl propanoate (**2e**).* Colorless oil (32% yield); MS: *m/z* 146 (M^+, 4%), 97 (25%), 74 (30%), 69 (44%), 57 (100%); ^{1}H NMR ($CDCl_3$) ppm: 0.94 (d, *J*=7.0 Hz, 3H, CH_3), 1.14 (t, *J*=7.6 Hz, 3H, CH_3), 1.96–2.00 (m, H, CH), 2.22 (br s, 1H, OH), 2.34 (q, *J*=7.6 Hz, 2H, CH_2), 3.48–3.54 (m, 2H, OCH_2), 4.03–4.12 (m, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 14.0 (CH_3), 28.1 (CH_2), 36.0 (CH_2), 64.9 (OCH_2), 66.6 (OCH_2), 175.7 (OC═O). Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 56.35; H, 9.78.

*4.4.6.3. 3-Hydroxy-2,2-dimethylpropyl propanoate (**3e**).* Colorless oil (30% yield); MS: *m/z* 143 (10%), 129 (10%), 97 (40%), 81 (50%), 69 (100%), 57 (95%); ^{1}H NMR ($CDCl_3$) ppm: 0.94 (s, 6H, $2CH_3$), 1.18 (t, *J*=7.6 Hz, 3H, CH_3), 2.23 (br s, 1H, OH), 2.39 (q, *J*=7.6 Hz, 2H, CH_2), 3.31 (s, 2H, OCH_2), 3.96 (s, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.8 (CH_3), 22.1 ($2CH_3$), 28.2 (CH_2), 37.0 (C), 68.8 (OCH_2), 69.8 (OCH_2), 175.8 (OC═O).

*4.4.6.4. 2-Ethyl-2-(hydroxymethyl)butyl propanoate (**4e**).* Colorless oil (34% yield); MS: *m/z* 84 (100%), 69 (40%), 57 (90%); ^{1}H NMR ($CDCl_3$) ppm: 0.84 (t, *J*=7.6 Hz, 6H, $2CH_3$), 1.16 (t, *J*=7.6 Hz, 3H, CH_3), 1.21–1.33 (m, 4H, $2CH_2$), 2.31 (br s, 1H, OH), 2.38 (q, *J*=7.6 Hz, 2H, CH_2), 3.32 (s, 2H, OCH_2), 3.99 (s, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 7.5 ($2CH_3$), 9.8 (CH_3), 22.6 ($2CH_2$), 28.2 (CH_2), 41.8 (C), 64.8 (OCH_2), 66.5 (OCH_2), 175.9 (OC═O). Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. Found: C, 62.90; H, 10.93.

*4.4.6.5. 2-Butyl-2-(hydroxymethyl)hexyl propanoate (**5e**).* Colorless oil (31% yield); MS: *m/z* 244 (M^+, 20%), 140 (100%); ^{1}H NMR ($CDCl_3$) ppm: 0.93 (t, *J*=7.2 Hz, 6H, $2CH_3$), 1.18 (t, *J*=7.6 Hz, 3H, CH_3), 1.20–1.33 (m, 12H, $6CH_2$), 2.25 (t, *J*=6.8 Hz, 1H, OH), 2.39 (q, *J*=7.6 Hz, 2H, CH_2), 3.33 (d, *J*=6.8 Hz, 2H, OCH_2), 4.00 (s, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) ppm: 9.8 (CH_3), 14.6 ($2CH_3$), 24.1 ($2CH_2$), 25.3 ($2CH_2$), 28.2 (CH_2), 30.6 ($2CH_2$), 41.7 (C), 65.6 (OCH_2), 67.2 (OCH_2), 175.9 (OC═O). Anal. Calcd for $C_{14}H_{28}O_3$: C, 68.81; H, 11.55. Found: C, 68.56; H, 11.79.

*4.4.6.6. Ethyl 3-hydroxy-2-methyl-2-[(propionyloxy)methyl]-propanoate (**6e**).* Colorless oil (36% yield); MS: *m/z* 218 (M^+, 40%), 201 (65%), 173 (64%), 145 (65%), 114 (84%), 99 (56%), 86 (45%), 69 (100%), 57 (87%); ^{1}H NMR ($CDCl_3$) ppm: 1.12 (t, *J*=7.5 Hz, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.25 (t, *J*=7.1 Hz, 3H, CH_3), 2.33 (q, *J*=7.6 Hz, 2H, CH_2), 2.84 (br s, 1H, OH), 3.65 (dd, *J*=11.5, *J*=6.3 Hz, 2H, OCH_2), 4.14–4.21 (m, 3H, OCH, OCH_2), 4.30 (d,

J=11.1 Hz, 1H, OCH). ^{13}C NMR ($CDCl_3$) ppm: 9.7 (CH_3), 14.7 (CH_3), 18.1 (CH_3), 28.1 (CH_2), 48.6 (C), 61.6 (OCH_2), 65.5 (OCH_2), 66.3 (OCH_2), 175.1 (OC═O), 175.2 (OC═O). Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.50; H, 8.48.

*4.4.6.7. Benzyl 3-hydroxy-2-methyl-2-[(propionyloxy)methyl]-propanoate (**7e**).* Colorless oil (32% yield); MS: *m*/*z* 280 (M^+, 62%), 262 (65%), 180 (45%), 172 (100%), 130 (15%), 106 (45%), 91 (100%), 57 (70%); ^{1}H NMR ($CDCl_3$) ppm: 1.11 (t, J=7.6 Hz, 3H, CH_3), 1.25 (s, 3H, CH_3), 2.30 (q, J=7.6 Hz, 2H, CH_2), 2.54 (t, J=6.9 Hz, 1H, OH), 3.66–3.76 (m, 2H, OCH_2), 4.25 (d, J=11.2 Hz, 1H, OCH), 4.37 (d, J=11.2 Hz, 1H, OCH), 5.22 (d, J=12.4 Hz, 1H, OCH), 5.18 (d, J=12.4 Hz, 1H, OCH), 7.35–7.40 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) ppm: 9.6 (CH_3), 18.1 (CH_3), 27.9 (CH_2), 48.8 (C), 65.5 (OCH_2), 66.3 (OCH_2), 67.3 (OCH_2), 128.6 (ArCH), 128.9 (ArCH), 129.2 (ArCH), 136.2 (ArC), 174.9 (OC═O), 175.2 (OC═O). Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 63.92; H, 7.48.

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