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One Approach to Cyclic Carbonates via a Three-Component Cyclization of Phenacyl Bromide, CO_2, and Aldehyde

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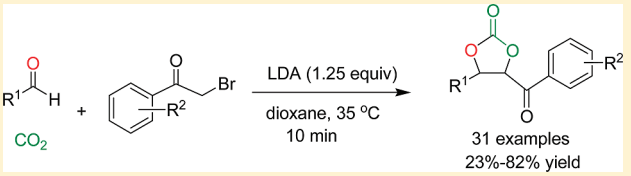
Supporting Information

ABSTRACT: A three-component cyclization reaction was designed for synthesizing cyclic carbonates in a single operation from phenacyl bromide, CO_2, and aldehyde in the presence of lithium diisopropylamide (LDA). These novel reactions were achieved under extremely mild conditions to generate the target products in moderate to good yields within 10 min.



INTRODUCTION

The chemistry of CO_2 has received much attention from the viewpoint of carbon resources and environmental problems in the past decade.[1] Cyclic carbonates, as one of the products of CO_2 chemistry, are attractive and important compounds in a variety of chemical research fields,[2] such as polar aprotic solvents and intermediates in organic synthesis that can be used for the protection of 1,2- and 1,3-diols[3] and the construction of structurally complex molecules.[4] Biologically active molecules that contain a cyclic carbonate component have also been isolated from various kinds of natural sources.[5] Cyclic carbonates can be normally synthesized by a cycloaddition reaction of CO_2 with epoxides in the presence of various activating reagents.[6] Although numerous synthetic methods for the syntheses of carbonates have been documented in the literature, they have the limitation of depending upon the initial epoxide substrate.

Recently, He et al. reported an environmentally benign synthesis of styrene carbonate directly from styrene and CO_2 catalyzed by a binary system composed of sodium phosphotungstate and *n*-Bu_4NBr using 30% H_2O_2 as an oxidant.[7] We have recently disclosed that dioxo(tetraphenylporphyrinato)ruthenium(VI) and quaternary onium salts can be used as effective catalysts to initiate a three-component reaction of olefin, O_2, and CO_2 at ambient temperature under low pressure for producing cyclic carbonates.[8] Although these findings furnish a simple and more cost-effective pathway for the environmentally benign chemical fixation of CO_2 to produce cyclic carbonates, the method requires harsh reaction conditions such as relatively high pressure, high temperature, and long reaction time, using toxic or costly reagents and requiring a tedious workup for separation despite a few efficient methods exploited up to now.[6c,d,9] For extending the applications of cyclic carbonates, it is desirable to develop new methodology that can operate under mild conditions. We take note of the Darzens reaction,[10] which is traditionally carried out in the presence of strong base and mechanistically includes an aldol reaction of an α-halo carbonyl compound with an aldehyde to form a C−C bond followed by an intramolecular cyclization of the intermediate halohydrin compound to form an epoxide. Considering the same anionic intermediate in the mechanism of the Darzens reaction and the mechanism of cyclic carbonate synthesis,[6d,11] we have designed a three-component cyclization reaction for cyclic carbonate synthesis in an one-pot reaction from phenacyl bromide, CO_2, and aldehyde using LDA as a base. This new strategy for cyclic carbonate synthesis avoids the rigorous reaction conditions of high pressure, high temperature, and long reaction time, generating trans cyclic carbonates from phenacyl bromide, CO_2, and aldehyde.

RESULTS AND DISCUSSION

We set out to access the scope and limitations of the reactions using phenacyl bromide, CO_2, and benzaldehyde as the model substrate in the presence of strong bases such as *n*-BuLi, KO-*tert*-Bu, LDA, Cs_2CO_3, etc. After we screened the bases, LDA was found to be the best choice to initiate this reaction. Then, solvent effects were investigated. The results given in Table 1 demonstrated that 1,4-dioxane is the best medium for cyclic carbonate formation (entry 2). The yield of cyclic carbonate slightly decreased in tetrahydrofuran (THF) (entry 1). Reactions in other dry solvents, including dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), were less suitable and gave extremely low yields (entries 3−6). In contrast, these solvents give higher yields of epoxide (entries 5 and 6). These observations could be explained in terms of the effect of the polarity of solvent: the less the polarity of the solvent, the more cyclic carbonate produced. This is attributed to the higher nucleophilicity of an oxygen anion in a less polar solvent.

The temperature effect was then investigated in pursuit of the optimum reaction conditions (Table 2). The yield of cyclic carbonate increased when the temperature was raised from 15 to 35 °C (entries 1−3). The best yield of 68% was obtained at 35 °C. However, the yield of target product decreased when the temperature was over 35 °C (entry 4). In contrast, the reaction ceased at 0 °C (entry 5).

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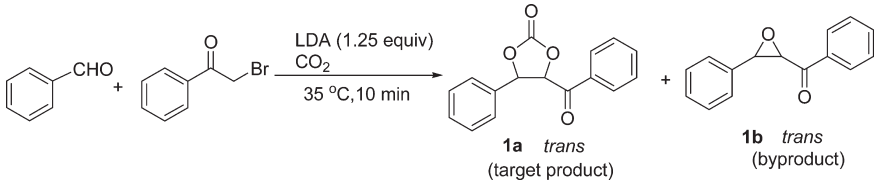
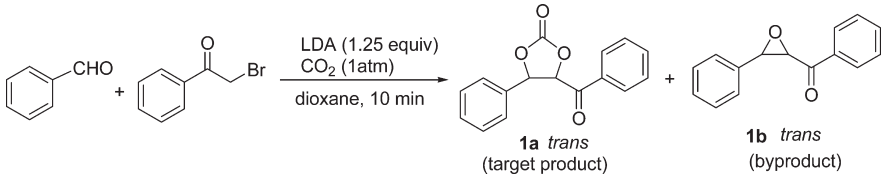
Table 1. Effect of Solvent on the Cyclic Carbonate Synthesis[a]



			yield[c] (%)	
entry	solvent	conv[b] (%)	**1a**	**1b**
1	THF	90	62	21
2	1,4-dioxane	92	68	18
3	*n*-butyl ether	42	21	16
4	acetonitrile	35	17	14
5	DMSO	62	5	42
6	DMF	58	4	47

[a] Reactions were carried out at 35 °C with 2 mmol of benzaldehyde and 4 mmol of phenacyl bromide, under an atmosphere of CO_2 (1 atm) over 10 min after LDA addition. [b] Conversion based on the benzaldehyde. [c] Isolated yield after column chromatography.

Table 2. Effect of Temperature on the Yield of Polysubstituted Cyclic Carbonate[a]



			yield[c] (%)	
entry	temp (°C)	conv[b] (%)	**1a**	**1b**
1	15	42	28	8
2	25	58	38	11
3	35	92	68	18
4	45	94	61	25
5	0	0	0	0

[a] Reactions were carried out with 2 mmol of benzaldehyde and 4 mmol of phenacyl bromide, under an atmosphere of CO_2 (1 atm) over 10 min after LDA addition. [b] Conversion based on the benzaldehyde. [c] Isolated yield after column chromatography.

To further extend the scope of the substrate, various substituted aldehydes and substituted phenacyl bromides were introduced into this three-component reaction, affording the corresponding cyclic carbonates. The results are summarized in Table 3. Clearly, the substituted groups with various electronic characters on the phenyl ring of the aldehydes and phenacyl bromides influenced the reaction activities and selectivities (entries 1−24). We note that the substrates with an electron-donating group on the phenyl ring have a selectivity toward formation of cyclic carbonates higher than for those bearing an electron-withdrawing group (entries 2−7 vs entries 8−16). Treatment of an aromatic aldehyde having a 2-CH_3 group with phenacyl bromide gave the corresponding product in 81% yield and 100% selectivity (entry 6). However, the aldehyde with the NO_2 group can only be converted to the corresponding cyclic carbonate in both low yield and selectivity (entries 14−16). Interestingly, the same groups substituted at a different position on the phenyl ring of the aldehyde also influence the reaction activities and selectivities (entries 2 and 3, entries 4−6, entries 8−10, and entries 14−16). It can be seen that the aromatic aldehydes with ortho-substituted groups show higher reactivity and selectivity due to their higher cation charge and stereochemical effects (entries 3, 6, 8, and 17−20). In contrast, the fatty aldehydes gave low yield and selectivity (entries 25−29). It is worth pointing out that cinnamaldehyde and 2-furaldehyde can uniquely produce the corresponding cyclic carbonates (entries 30 and 31). On the other hand, when ethyl 2-bromoacetate was used instad of phenacyl bromide, this type of reaction could not occur; when 1-bromoacetone or 2-bromo-*N*-phenylacetamide was used instad of phenacyl bromide, the relevant epoxide could be found in the products, but the target product of cyclic carbonate could not be found. Obviously, the phenyl ring of phenacyl bromides plays a key factor in this reaction because it can stabilize the carbanion intermediate, allowing the reaction to take place (vide infra).

On the basis of the experimental results described above, we propose a plausible reaction mechanism (Scheme 1). The first step of the mechanism is an aldol reaction: the LDA deprotonates the phenacyl bromide, resulting in carbanion **A**. The carbon anion of **A** then attacks the carbonyl group of the aldehyde, yielding intermediate **B**. The oxygen anion of **B** then attacks the

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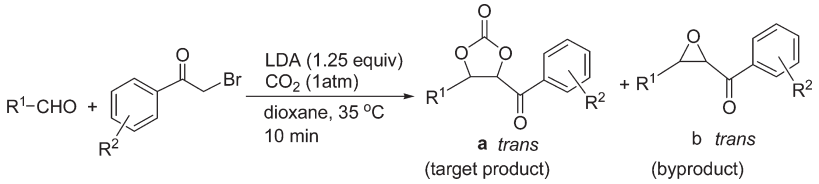
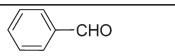
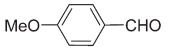
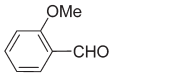
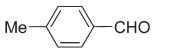
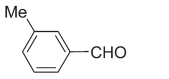
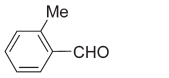
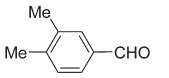
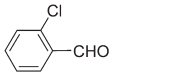
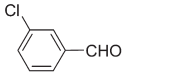
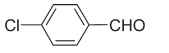
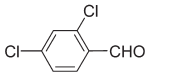
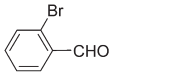
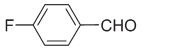
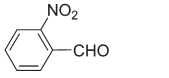
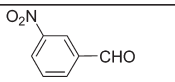
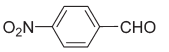
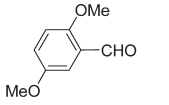
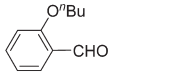
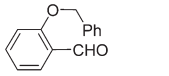
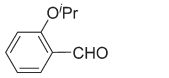
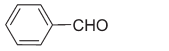
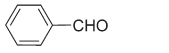
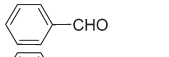
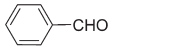
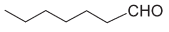
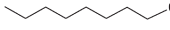
Table 3. Effect of Substituent for the Yield of Cyclic Carbonate[a]



Entry	Aldehyde	R^2	Conv[b] (%)	Yield[c](%) a	Yield[c](%) b
1		H	92	68	18
2		H	28	23	0
3		H	94	81	8
4		H	58	45	6
5		H	92	75	15
6		H	91	81	0
7		H	62	54	6
8		H	93	68	16
9		H	89	58	28
10		H	96	73	19
11		H	91	52	36
12		H	90	67	17
13		H	85	61	19
14		H	96	58	28
15		H	89	33	36
16		H	92	29	23
17		H	89	77	8
18		H	92	80	6
19		H	93	81	8
20		H	94	82	5
21		4-MePh	75	62	6
22		4-ClPh	87	62	18
23		4-BrPh	91	63	21
24		4-MePh	31	27	0
25		H	86	37	16
26		H	84	40	15
27		H	87	42	15
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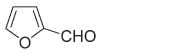
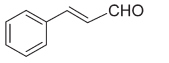
30		H	92	56	
31		H	93	51	

[a] Reactions were carried out at 35 °C with 2 mmol of aldehyde and 4 mmol of substituted phenacyl bromide, under an atmosphere of CO_2 (1 atm) over 10 min after LDA addition. [b] Conversion based on the benzaldehyde. [c] Isolated yield after column chromatography.

carbon of CO_2 to form the new intermediate **C**. Then, the intramolecular cyclization of **C** via oxygen anion attack at the α-carbon of the carbonyl led to formation of the product **a** accompanied by the departure of Br^-. On the other hand, when the oxygen anion of intermediate **B** directly attacks the α-carbon of carbonyl, the byproduct **b** is produced under the reaction conditions.

In summary, we have discovered a new and concise method to fabricate the trans cyclic carbonates via a three-component cyclization reaction of substituted phenacyl bromide, CO_2, and various aldehydes in the presence of LDA under extremely mild conditions in good yields within 10 min. This robust methodology provides a new route to cyclic carbonates via aldehydes and a good example of utilizing CO_2 as a building block in organic synthesis. The products also enrich the family of cyclic carbonates.

EXPERIMENTAL SECTION

General Procedure for the Preparation of Cyclic Carbonates. Carbon dioxide was bubbled into the solution of phenacyl bromide (0.8 g, 4 mmol) with various aldehydes (2 mmol) in anhydrous dioxane (5 mL). Then LDA (2.5 mL, 1 M) was added dropwise by syringe to the above solution at 35 °C over 2.5 min with vigorous stirring. The reaction was allowed to proceed at 35 °C with constant bubbling of carbon

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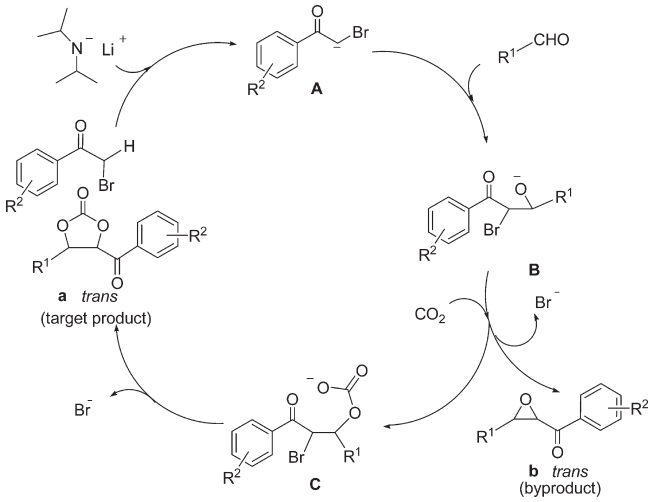
Scheme 1. Proposed Mechanism for Polysubstituted Cyclic Carbonate Synthesis



dioxide and stirring for 10 min. The reaction mixture was quenched with water and extracted with ethyl acetate (10 mL × 3), and the extracts were dried over anhydrous magnesium sulfate. The solvent was evaporated under vacuum. The crude residue was purified by column chromatography (12/1 petroleum ether (60−90 °C)/EtOAc), affording the pure target product and byproduct. This procedure was followed for all the reactions given in Table 3. The known compounds were identified by comparison of their spectra with those of authentic samples.[2b] The unknown compounds listed in Table 3 were properly characterized by ^{1}H and ^{13}C NMR and HRMS:

4-(2-Methoxyphenyl)-5-benzoyl-1,3-dioxolan-2-one (3a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J = 8.1 Hz, 2H), 7.67 (t, J = 7.5, 7.2 Hz, 1H), 7.52 (t, J = 7.8, 7.5 Hz, 2H), 7.49−7.38 (m, 2H), 7.04 (t, J = 7.8, 7.5 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.03 (d, J = 5.7 Hz, 1H), 5.71 (d, J = 5.7 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 156.5, 153.8, 134.6, 133.8, 131.0, 129.2, 128.9, 127.7, 123.9, 121.0, 110.9, 79.7, 77.0, 55.3. HRMS (ESI): m/z calcd for $C_{17}H_{14}O_5$ $[M + NH_4]^+$ 316.1179, found 316.1180.

4-(4-Methylphenyl)-5-benzoyl-1,3-dioxolan-2-one (4a; 4-*p*-Tolyl-1,3-dioxolan-2-one). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.31−7.23 (m, 4H), 5.85 (d, J = 5.7 Hz, 1H), 5.61 (d, J = 5.7 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.2, 153.2, 140.0, 134.9, 133.2, 132.5, 129.9, 129.2, 129.0, 126.0, 81.8, 79.1, 21.2. HRMS (ESI): m/z calcd for $C_{17}H_{14}O_4$ $[M + NH_4]^+$ 300.1230, found 300.1235.

4-(3-Methylphenyl)-5-benzoyl-1,3-dioxolan-2-one (5a; *m*-Tolyl-1,3-dioxolan-2-one). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.00 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 8.0, 7.6 Hz, 2H), 7.39−7.36 (m, 3H), 7.30 (d, J = 7.6 Hz, 1H), 6.20 (d, J = 5.6 Hz, 1H), 5.96 (d, J = 5.6 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 193.0, 154.2, 139.8, 137.0, 135.4, 134.5, 131.3, 129.98, 129.95, 129.8, 128.1, 124.6, 82.1, 80.1, 21.4. HRMS (ESI): m/z calcd for $C_{17}H_{14}O_4$ $[M + NH_4]^+$ 300.1230, found 300.1224.

4-(2-Methylphenyl)-5-benzoyl-1,3-dioxolan-2-one (6a; *o*-Tolyl-1,3-dioxolan-2-one). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.8 Hz, 1H), 7.49−7.42 (m, 3H), 7.33−7.30 (m, 2H), 7.21−7.18 (m, 1H), 6.22 (d, J = 5.4 Hz, 1H), 5.66 (d, J = 6.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.1, 153.2, 135.7, 134.8, 133.5, 133.1, 131.2, 129.6, 129.2, 128.9, 126.9, 125.7, 81.1, 76.1, 18.9. HRMS (ESI): m/z calcd for $C_{17}H_{14}O_4$ $[M + NH_4]^+$ 300.1230, found 300.1228.

4-(3,4-Dimethylphenyl)-5-benzoyl-1,3-dioxolan-2-one (7a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.19−7.11 (m, 3H), 5.80 (d, J = 6.0 Hz, 1H), 5.61 (d, J = 5.7 Hz, 1H), 2.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.2, 153.2, 138.6, 137.8, 134.8, 133.2, 132.8, 130.4, 129.2, 128.9, 127.1, 123.5, 81.7, 79.1, 19.7, 19.5. HRMS (ESI): m/z calcd for $C_{18}H_{16}O_4$ $[M + NH_4]^+$ 314.1387, found 314.1384.

4-(2-Chlorophenyl)-5-benzoyl-1,3-dioxolan-2-one (8a). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.08 (d, J = 8.0 Hz, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.67−7.65 (m, 1H), 7.57 (d, J = 8.0, 7.6 Hz, 2H), 7.54−7.49 (m, 3H), 6.37 (d, J = 4.8 Hz, 1H), 6.30 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 192.7, 154.1, 135.6, 134.6, 134.4, 133.1, 132.1, 131.2, 130.2, 129.8, 129.2, 128.8, 80.4, 77.2. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClO_4$ $[M + NH_4]^+$ 320.0684, found 320.0681.

4-(3-Chlorophenyl)-5-benzoyl-1,3-dioxolan-2-one (9a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.8 Hz, 1H), 7.39−7.18 (m, 6H), 5.84 (d, J = 6.3 Hz, 1H), 5.49 (d, J = 6.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.9, 152.7, 137.3, 135.0, 134.9, 132.9, 130.5, 129.7, 129.2, 128.9, 125.9, 124.0, 81.4, 77.8. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClO_4$ $[M + NH_4]^+$ 320.0684, found 320.0677.

4-(4-Chlorophenyl)-5-benzoyl-1,3-dioxolan-2-one (10a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.6 Hz, 2H), 7.70−7.67 (t, J = 7.2, 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.45 (dd, J = 6.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 6.00 (d, J = 6.4 Hz, 1H), 5.53 (d, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 152.7, 135.9, 135.1, 134.1, 133.3, 129.6, 129.4, 129.1, 127.3, 81.9, 78.2. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClO_4$ $[M + NH_4]^+$ 320.0684, found 320.0687.

4-(2,4-Dichlorophenyl)-5-benzoyl-1,3-dioxolan-2-one (11a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.46−7.31 (m, 4H), 7.29 (m, 1H), 6.27 (d, J = 4.5 Hz, 1H), 5.63 (d, J = 4.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2, 152.8, 136.2, 134.9, 133.1, 132.3, 132.1, 130.1, 129.3, 129.0, 128.4, 128.0, 79.6, 75.4. HRMS (ESI): m/z calcd for $C_{16}H_{10}Cl_2O_4$ $[M + NH_4]^+$ 354.0294, found 354.0299.

4-(2-Bromophenyl)-5-benzoyl-1,3-dioxolan-2-one (12a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 8.1 Hz, 2H), 7.64−7.57 (m, 2H), 7.51−7.40 (m, 5H), 6.34 (d, J = 4.5 Hz, 1H), 5.72 (d, J = 4.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.4, 153.1, 135.1, 134.8, 133.4, 133.3, 131.0, 129.3, 128.9, 128.2, 127.3, 120.7, 79.7, 77.4. HRMS (ESI): m/z calcd for $C_{16}H_{11}BrO_4$ $[M + NH_4]^+$ 364.0179, found 364.0175.

4-(4-Fluorophenyl)-5-benzoyl-1,3-dioxolan-2-one (13a). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.00 (m, J = 8.1 Hz, 2H), 7.75−7.64 (m, 3H), 7.57 (t, J = 7.5, 7.8 Hz, 2H), 7.29 (t, J = 8.4 Hz, 8.7 Hz, 2H), 6.24 (d, J = 6.0 Hz, 1H), 6.06 (d, J = 5.7 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 193.0, 165.9, 162.6, 154.1, 135.5, 134.7, 133.3, 133.2, 130.3, 130.2, 130.1, 129.9, 117.1, 116.8, 82.2, 79.6. HRMS (ESI): m/z calcd for $C_{16}H_{11}FO_4$ $[M + NH_4]^+$ 304.0980, found 304.0978.

4-(2-Nitrophenyl)-5-benzoyl-1,3-dioxolan-2-one (14a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 z, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 4.2 Hz, 2H), 7.70−7.63 (m, 2H), 7.53 (t, J = 7.8, 7.5 Hz, 2H), 6.71 (d, J = 3.9 Hz, 1H), 5.74 (d, J = 3.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.1, 153.2, 145.8, 135.2, 134.8, 133.6, 133.4, 130.3, 129.4, 129.0, 126.8, 125.9, 79.4, 75.2. HRMS (ESI): m/z calcd for $C_{16}H_{11}NO_6$ $[M + NH_4]^+$ 331.0925, found 331.0932.

4-(3-Nitrophenyl)-5-benzoyl-1,3-dioxolan-2-one (15a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.30 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 7.5 Hz, 2H), 7.88 (d, J = 8.1 Hz, 1H), 7.74−7.70 (m, 2H), 7.59−7.53 (m, 2H), 6.23 (d, J = 6.3 Hz, 1H), 5.71 (dd, J = 1.8, 6.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.9, 152.3, 148.4, 137.5, 135.1, 133.0, 132.0, 130.5, 129.4, 129.0, 124.4, 121.0, 81.6, 77.5. HRMS (ESI): m/z calcd for $C_{16}H_{11}NO_6$ $[M + NH_4]^+$ 331.0925, found 331.0929.

4-(4-Nitrophenyl)-5-benzoyl-1,3-dioxolan-2-one (16a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (dd, J = 1.8, 8.7 Hz, 2H), 7.98 (d, J =

8.7 Hz, 2H), 7.64 (t, J = 9.0, 8.7 Hz, 3H), 7.51 (t, J = 8.4, 7.5 Hz, 2H), 6.18 (d, J = 6.9 Hz, 1H), 5.53 (d, J = 6.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.9, 152.3, 148.4, 142.4, 135.2, 133.1, 129.5, 129.1, 126.7, 124.4, 81.6, 77.4. HRMS (ESI): m/z calcd for $C_{16}H_{11}NO_6$ $[M + NH_4]^+$ 331.0925, found 331.0928.

4-Benzoyl-5-(2,5-dimethoxyphenyl)-1,3-dioxolan-2-one (17a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 7.5, 6.9 Hz, 1H), 7.50 (t, J = 7.5, 7.2 Hz, 2H), 6.94−6.83 (m, 3H), 5.95 (d, J = 5.4 Hz, 1H), 5.71 (d, J = 5.4 Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.6, 153.7, 153.6, 150.2, 134.6, 133.7, 129.0, 128.9, 124.7, 115.2, 113.2, 111.9, 79.6, 76.6, 55.8, 55.5. HRMS (ESI): m/z calcd for $C_{18}H_{16}O_6$ $[M + NH_4]^+$ 346.1285, found 346.1279.

4-Benzoyl-5-(2-butoxyphenyl)-1,3-dioxolan-2-one (18a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 2H), 7.65−7.60 (m, 1H), 7.49−7.44 (m, 2H), 7.43−7.29 (m, 2H), 6.99−6.92 (m, 2H), 5.99 (d, J = 5.1 Hz, 1H), 5.74 (d, J = 5.1 Hz, 1H), 3.96−3.89 (m, 2H), 1.63−1.54 (m, 2H), 1.39−1.29 (m, 2H), 0.90 (t, J = 7.5, 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3, 156.3, 153.6, 134.5, 133.4, 131.1, 129.0, 128.8, 128.0, 123.4, 120.4, 111.6, 79.6, 76.9, 67.9, 30.6, 18.9, 13.5. HRMS (ESI): m/z calcd for $C_{20}H_{20}O_5$ $[M + NH_4]^+$ 358.1649, found 358.1642.

4-Benzoyl-5-(2-(benzyloxy)phenyl)-1,3-dioxolan-2-one (19a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, J = 7.8 Hz, 2H), 7.61−7.56 (m, 1H), 7.43−7.34 (m, 4H), 7.27−7.20 (m, 5H), 7.04−6.98 (m, 2H), 6.13 (d, J = 5.1 Hz, 1H), 5.70 (d, J = 5.1 Hz, 1H), 5.00 (dd, J = 11.7, 24.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.1, 155.7, 153.6, 135.5, 134.5, 133.6, 130.9, 129.1, 128.8, 128.6, 128.3, 127.9, 127.6, 124.2, 121.2, 112.3, 79.7, 76.5, 70.4. HRMS (ESI): m/z calcd for $C_{23}H_{18}O_5$ $[M + NH_4]^+$ 392.1492, found 392.1490.

4-Benzoyl-5-(2-isopropoxyphenyl)-1,3-dioxolan-2-one (20a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, J = 8.4 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.49−7.45 (t, J = 7.8, 7.5 Hz, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 6.3 Hz, 1H), 6.97−6.93 (m, 2H), 5.97 (d, J = 5.7 Hz, 1H), 5.73 (d, J = 5.7 Hz, 1H), 4.63 (t, J = 6.0, 6.3 Hz, 1H), 1.30 (d, J = 6.0 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.4, 155.1, 153.8, 134.5, 133.5, 131.0, 129.1, 128.9, 128.5, 124.3, 120.2, 112.6, 79.7, 77.2, 70.3, 21.7, 21.2. HRMS (ESI): m/z calcd for $C_{19}H_{18}O_5$ $[M + NH_4]^+$ 344.1492, found 344.1486.

4-Phenyl-5-(4-methylbenzoyl)-1,3-dioxolan-2-one (21a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, J = 8.1 Hz, 2H), 7.42−7.39 (m, 5H), 7.27 (d, J = 8.4 Hz, 2H), 5.88 (d, J = 6.3 Hz, 1H), 5.60 (d, J = 6.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.5, 153.2, 146.2, 135.5, 130.6, 129.7, 129.4, 129.3, 129.2, 125.9, 81.6, 79.0, 21.7. HRMS (ESI): m/z calcd for $C_{17}H_{14}O_4$ $[M + NH_4]^+$ 300.1230, found 300.1227.

4-Phenyl-5-(4-chlorobenzoyl)-1,3-dioxolan-2-one (22a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2H), 7.49−7.41 (m, 7H), 5.99 (d, J = 6.6 Hz, 1H), 5.55 (d, J = 6.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.1, 152.9, 141.6, 135.4, 131.6, 130.7, 129.9, 129.4, 129.3, 125.9, 81.9, 78.8. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClO_4$ $[M + NH_4]^+$ 320.0684, found 320.0680.

4-Phenyl-5-(4-bromobenzoyl)-1,3-dioxolan-2-one (23a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.49−7.42 (m, 5H), 6.01 (d, J = 5.7 Hz, 1H), 5.52 (d, J = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.4, 152.8, 135.5, 132.5, 132.1, 130.8, 130.6, 129.9, 129.4, 125.9, 82.0, 78.8. HRMS (ESI): m/z calcd for $C_{16}H_{11}BrO_4$ $[M + NH_4]^+$ 364.0179, found 364.0183.

4-Phenyl-5-(4-methoxybenzoyl)-1,3-dioxolan-2-one (24a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.7 Hz, 2H), 7.46−7.39 (m, 5H), 6.95 (d, J = 8.7 Hz, 2H), 5.94 (d, J = 6.3 Hz, 1H), 5.57 (d, J = 6.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.3, 164.8, 153.2, 135.6, 131.7, 129.7, 129.2, 126.2, 125.9, 114.2, 81.6, 79.0, 55.6. HRMS (ESI): m/z calcd for $C_{17}H_{14}O_5$ $[M + NH_4]^+$ 316.1179, found 316.1178.

4-Benzoyl-5-pentyl-1,3-dioxolan-2-one (25a). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.92 (d, J = 5.4 Hz, 2H), 7.62−7.57 (m, 1H), 7.49−7.44 (m, 2H), 5.81 (d, J = 4.8 Hz, 1H), 4.84−4.79 (m, 1H), 1.87−1.79 (m, 2H), 1.42−1.30 (m, 2H), 1.27−1.17 (m, 4H), 0.77−0.73 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 153.3, 134.6, 133.4, 129.1, 128.9, 79.7, 78.4, 33.9, 31.0, 23.9, 22.2, 13.7. HRMS (ESI): m/z calcd for $C_{15}H_{18}O_4$ $[M + NH_4]^+$ 280.1543, found 280.1546.

4-Benzoyl-5-hexyl-1,3-dioxolan-2-one (26a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.67 (t, J = 7.8, 6.3 Hz, 1H), 7.54 (t, J = 7.5, 7.8 Hz, 2H), 5.34 (d, J = 5.1 Hz, 1H), 5.00−4.95 (m, 1H), 1.93−1.80 (m, 2H), 1.54−1.29 (m, 8H), 0.89 (t, J = 6.3, 5.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 153.3, 134.8, 133.5, 129.2, 129.0, 79.9, 78.4, 34.1, 31.4, 28.7, 24.3, 22.4, 13.9. HRMS (ESI): m/z calcd for $C_{16}H_{20}O_4$ $[M + NH_4]^+$ 294.1700, found 294.1697.

4-Benzoyl-5-octyl-1,3-dioxolan-2-one (27a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 5.4 Hz, 2H), 7.69−7.64 (m, 1H), 7.55−7.50 (m, 2H), 5.34 (d, J = 5.4 Hz, 1H), 4.99−4.94 (m, 1H), 1.92−1.79 (m, 2H), 1.56−1.27 (m, 12H), 0.90−0.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 153.3, 134.7, 133.5, 129.2, 129.0, 79.9, 78.4, 34.1, 31.7, 29.2, 29.0, 28.9, 24.4, 22.5, 14.0. HRMS (ESI): m/z calcd for $C_{18}H_{24}O_4$ $[M + NH_4]^+$ 322.2013, found 322.2006.

4-Benzoyl-5-nonyl-1,3-dioxolan-2-one (28a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 7.8 Hz, 2H), 7.69−7.64 (m, 1H), 7.55−7.50 (m, 2H), 5.35 (d, J = 5.4 Hz, 1H), 4.99−4.93 (m, 1H), 1.92−1.79 (m, 2H), 1.51−1.42 (m, 2H), 1.26 (m, 12H), 0.90−0.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 153.3, 134.7, 133.5, 129.2, 129.0, 79.9, 78.4, 34.1, 31.7, 29.3, 29.2, 29.1, 28.9, 24.3, 22.6, 14.0. HRMS (ESI): m/z calcd for $C_{19}H_{26}O_4$ $[M + NH_4]^+$ 336.2169, found 336.2173.

4-Benzoyl-5-undecyl-1,3-dioxolan-2-one (29a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.67 (t, J = 6.9, 7.2 Hz, 1H), 7.53 (t, J = 6.3, 7.5 Hz, 2H), 5.34 (d, J = 5.4 Hz, 1H), 4.97 (t, J = 2.4, 2.7 Hz, 1H), 1.92−1.83 (m, 2H), 1.54−1.46 (m, 2H), 1.38−1.26 (m, 16H), 0.90−0.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 153.3, 134.7, 133.5, 129.2, 129.0, 79.9, 78.4, 34.1, 31.8, 29.5, 29.4, 29.3, 28.9, 24.4, 22.6, 14.0. HRMS (ESI): m/z calcd for $C_{21}H_{30}O_4$ $[M + NH_4]^+$ 364.2482, found 364.2484.

4-(Furan-2-yl)-5-benzoyl-1,3-dioxolan-2-one (30a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 7.2 Hz, 2H), 7.61−7.59 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 1.2 Hz, 1H), 7.45 (t, J = 7.8, 7.5 Hz, 2H), 6.63 (d, J = 2.7 Hz, 1H), 6.42 (dd, J = 1.8, 2.7 Hz, 1H), 6.03 (d, J = 6.0 Hz, 1H), 5.90 (d, J = 5.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.3, 152.7, 146.2, 144.8, 134.8, 132.6, 128.9, 128.8, 112.6, 110.9, 77.8, 71.9. HRMS (ESI): m/z calcd for $C_{14}H_{10}O_5$ $[M + NH_4]^+$ 276.0866, found 276.0872.

4-Styryl-5-benzoyl-1,3-dioxolan-2-one (31a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 7.8 Hz, 1H), 7.52 (t, J = 8.4, 7.5 Hz, 2H), 7.43−7.31 (m, 5H), 6.78 (d, J = 15.6 Hz, 1H), 6.30 (dd, J = 7.5, 15.6 Hz, 1H), 5.56 (d, J = 6.0 Hz, 1H), 5.48 (t, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.0, 153.1, 137.0, 134.8, 134.5, 133.1, 129.1, 129.0, 128.7, 127.0, 121.7, 79.8, 78.9. HRMS (ESI): m/z calcd for $C_{18}H_{14}O_4$ $[M + NH_4]^+$ 312.1230, found 312.1224.

■ ASSOCIATED CONTENT

Supporting Information. Figures and text giving characterization data and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, 153–155. (b) Yoshida, M.; Ihara, M. *Chem. Eur. J.* **2004**, *10*, 2886–2893. (c) Eghbali, N.; Li, C.-J. *Green Chem.* **2007**, *9*, 213–215.

(2) (a) Schffner, B.; Schffner, F.; Verevkin, S. P.; Brner, A. *Chem. Rev.* **2010**, *110*, 4554–4581. (b) North, M.; Pasquale, R.; Young, C. *Green Chem.* **2010**, *12*, 1514–1539.

(3) (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999; p 241. (b) Willis, M. C.; Cutting, G. A.; John, M. P. *Synlett* **2004**, 1195–1198.

(4) Davidson, J. E. P.; Anderson, E. A.; Buhr, W.; Harrison, J. R.; O, Sullivan, P. T.; Collins, I.; Green, R. H.; Holmes, A. B. *Chem. Commun.* **2000**, 629–630.

(5) (a) Mizobuchi, S.; Mochizuki, J.; Soga, H.; Tanba, H.; Inoue, H. *J. Antibiot.* **1986**, *39*, 1776–1778. (b) Chatterjee, S.; Reddy, G. C. S.; Franco, C. M. M.; Rupp, R. H.; Ganguli, B. N.; Fehlhaber, H. W.; Hans, W.; Kogler, H. *J. Antibiot.* **1987**, *40*, 1368–1374. (c) Patel, M.; Conover, M.; Horan, A.; Loebenberg, D.; Marquez, J.; Mierzwa, R.; Puar, M. S.; Yarborough, R.; Waitz, J. A. *J. Antibiot.* **1988**, *41*, 794–797.

(6) (a) Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951–976. (b) Sakakura, T.; Kohno, K. *Chem. Commun.* **2009**, 1312–1330. (c) Salvatore, R. N.; Shin, S. I.; Nagle, A. S.; Jung, K. W. *J. Org. Chem.* **2001**, *66*, 1035–1037. (d) North, M.; Pasquale, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2946–2948. (e) Yan, P.; Jing, H. W. *Adv. Synth. Catal.* **2009**, *351*, 1325–1332. (f) Jin, L.; Huang, Y.; Jing, H.; Chang, T.; Yan, P. *Tetrahedron: Asymmetry* **2008**, *19*, 1947–1953. (g) Sun, J. M.; Fujita, S. I.; Arai, M. *J. Organomet. Chem.* **2005**, *690*, 3490–3497.

(7) Wang, J. L.; Wang, J. Q.; He, L. N.; Dou, X. Y.; Wu, F. *Green Chem.* **2008**, *10*, 1218–1223.

(8) Bai, D. S.; Jing, H. W. *Green Chem.* **2010**, *12*, 39–41.

(9) Melendez, J.; North, M.; Villuendas, P. *Chem. Commun.* **2009**, 2577–2579.

(10) (a) Tanaka, K.; Shiraishi, R. *Green Chem.* **2001**, *3*, 135–136. (b) Akiyama, T.; Suzuki, T.; Mori, K. *Org. Lett.* **2009**, *11*, 2445–2447. (c) Ghosh, A. K.; Kim, J.-H. *Org. Lett.* **2004**, *6*, 2725–2728.

(11) (a) Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732–3734. (b) Berkessel, A.; Brandenburg, M. *Org. Lett.* **2006**, *8*, 4401–4404. (c) Chang, T.; Jing, H.; Jin, L.; Qiu, W. *J. Mol. Catal. A: Chem.* **2007**, *264*, 241–247. (d) Caló, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561–2563.