One-Pot Synthesis of Cyclic Carbonates from Aldehydes, Sulfur Ylide, and CO_2

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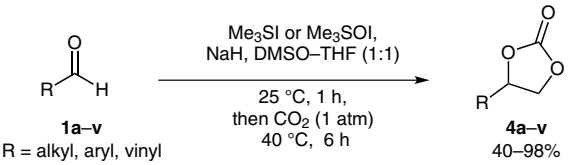
Abstract: Treatment of aldehydes with sulfur ylide (CH_2=$SOMe_2$ or CH_2=SMe_2), in the presence of CO_2 (1 atm) bubbled sequentially under mild conditions, produces cyclic carbonates in preparative yields. Sodium iodide formed in situ promotes the reaction between epoxide as intermediate and CO_2 at ambient conditions, thus constituting a powerful metal-free synthesis of organic cyclic carbonates directly from aldehydes.

Key words: cyclization, epoxides, insertion, carbon dioxide, cyclic carbonates

Carbon dioxide is one of the major constituents of greenhouse gases, and to control its rapidly increased concentration in atmosphere is a major challenge for scientific communities.[1] Global-warming concern has dramatically increased interest in using CO_2 as a feedstock for the preparation of value-added chemicals.[1j] Although CO_2 is an attractive nonhazardous C_1 synthon in abundance, its utilization in chemical transformations remains challenging because of its high thermodynamic stability and low chemical reactivity.[2] In particular, the synthesis of low-energy target molecules (e.g., organic carbonates) represents a promising alternative to overcome this thermodynamics. Organic cyclic carbonates are biodegradable chemicals that find tremendous applications as electrolytic materials in lithium ion batteries, polar aprotic solvents, intermediates in the production of pharmaceuticals and fine chemicals, as well as for developing engineered polymeric materials.[3] Biologically active molecules that contain a cyclic carbonate moiety have also been isolated from various natural sources.[4] In literature, cyclic carbonates are generally prepared by the cycloaddition of CO_2 with epoxides in the presence of many activating reagents such as quaternary ammonium salts,[5a–c] azaphosphatranes,[5d] metal–salen complexes derived from Al, Zn, Mg, and other first-row transition metals.[6] Other methods of their synthesis include the reaction of CO_2 with styrenes,[7] propargyl alcohols,[8] allyl alcohols,[9] diols,[10] or halohydrins.[11] Although these reported methods provide a simple route for the environmentally benign chemical fixation of CO_2 to produce cyclic carbonates, these have certain limitations such as dependence on epoxides as starting materials, use of toxic or costly reagents, relatively high pressure and temperature, often requiring a tedious work-up procedure for their isolation. Sulfur ylides have been widely employed in the conversion of aldehydes into epoxides (Corey–Chaykovsky reaction) in organic synthesis, thereby serving as C_1 carbon source under ambient conditions.[12] In this note, we wish to disclose an efficient and metal-free, one-pot procedure for the synthesis of organic cyclic carbonates by the sequential reaction of aldehydes with sulfur ylides (CH_2=$SOMe_2$ or CH_2=SMe_2) followed by its reaction with CO_2 (1 atm) in the absence of heavy-metal additives under ambient conditions (Scheme 1).



Scheme 1 Synthesis of cyclic carbonates from aldehydes, sulfur ylide, and CO_2

Preliminary experiments have shown that when all the three components (aldehyde, sulfur ylide, and CO_2) were treated together at 25 °C in DMSO, a stable, colorless adduct[12] (mp 135–137 °C) was obtained instantaneously due to the preferential reaction of sulfur ylide with CO_2. It was then reasoned that CO_2 could be bubbled sequentially after the in situ formation of epoxide from aldehyde and sulfur ylide.

The CO_2 insertion into epoxide can be further facilitated by NaI as promoter formed in the reaction. However, when CO_2 (1 atm) was bubbled into the reaction mixture at 25 °C after one hour (by which time the complete formation of epoxide has taken place), only epoxide **2a** was isolated in 95% yield (Table 1, entry 1). At 40 °C, it gave the desired cyclic carbonate **4a** (30%) along with significant amount of iodo alcohol **3a** (65%). Subsequently it was found that the yield of **4a** was, however, dependent linearly on temperature (Table 1, entries 3–5). At this stage, it was thought that by reducing the polarity of the solvent, the nucleophilicity of the iodo alkoxide **3** (Scheme 2) could be increased for its reaction with CO_2 so as to maximize the yield of **4a**.[11] Thus, when the reaction was carried out with a relatively low polar solvent system (DMSO–THF, 1:1) at 25 °C under CO_2 (1 atm), no cyclic carbonate was observed; only epoxide **2a** was again obtained in 96% yield. Finally, at 40 °C, a dramatic improvement in yield of **4a** (94%) was achieved with the

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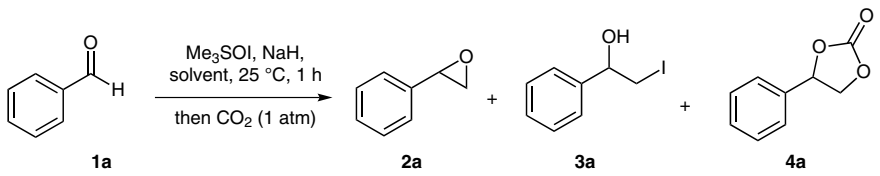
Table 1 Optimization Parameters for Cyclic Carbonates[a]



Entry	Solvent	Temp (°C)	Time (h)	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	DMSO	25	12	95	–	–
2	DMSO	40	12	–	65	30
3	DMSO	60	12	–	53	41
4	DMSO	80	12	–	23	71
5	DMSO	100	12	–	–	87
6	DMSO–THF(1:1)	25	12	96	–	–
7	DMSO–THF(1:1)	40	6	–	–	94

[a] Aldehyde (3 mmol), NaH (3.3 mmol), Me_3SOI (3.3 mmol), solvent (20 mL).
[b] Isolated yield after column chromatographic purification.

same solvent system Table 1, entry 7). Unfortunately, other bases (KOH, NaOH, KO*t*-Bu)[13] were not as effective as NaH. With the optimized reaction conditions in hand,[16] we then examined the substrate scope of the reaction (Table 2). Even lower members of cyclic carbonates of commercial importance (**4b** and **4c**) can be prepared in moderate to good yields. Further, aldehydes bearing halo, cyano, nitro, methoxy, and methylene dioxy groups on the aromatic nucleus and functionalized aliphatic aldehydes underwent this sequential reaction smoothly to afford the corresponding cyclic carbonates **4a**–**v** in high yields. Among the substrates screened, aldehdyes with halo **4k**–**n** and cyano **4t** substituents on the aromatic nucleus were found to be the best substrates for this methodology.

Volatile aliphatic and conjugated aldehydes[14] were also converted into the corresponding cyclic carbonates **4b**–**h** in high yields (Table 2, entries 2–8). Also, chiral amino aldehyde **1u** gave the corresponding cyclic carbonate **4u** efficiently under the reaction conditions (Table 2, entry 21). Cyclic carbonates **4a**–**v** have exhibited a strong IR absorption in the range 1792–1822 cm^{-1} due to the C=O stretching vibration of the cyclic carbonate moiety.

Table 2 Cyclic Carbonates from Aldehydes and CH_2=$SOMe_2$ or CH_2=SMe_2 with CO_2[a]

Entry	Aldehydes **1**	Yield of cyclic carbonates (%)[b]
1	benzaldehyde (**1a**)	**4a** 94
2	acetaldehyde (**1b**)	**4b** 40
3	propionaldehyde (**1c**)	**4c** 65
4	isobutyraldehyde (**1d**)	**4d** 73
5	*n*-pentanal (**1e**)	**4e** 89

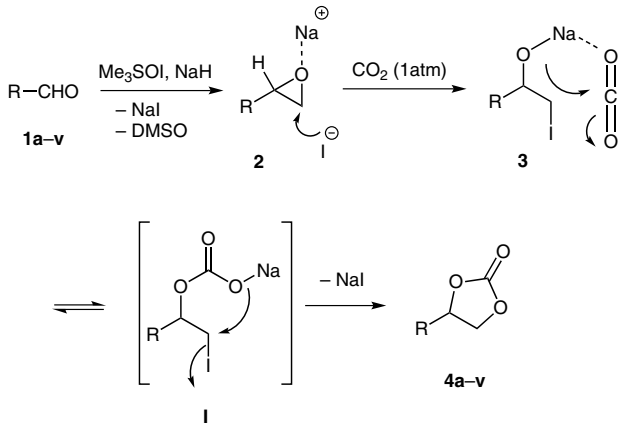
Table 2 Cyclic Carbonates from Aldehydes and CH_2=$SOMe_2$ or CH_2=SMe_2 with CO_2[a] (continued)

Entry	Aldehydes **1**	Yield of cyclic carbonates (%)[b]
6	*n*-heptanal (**1f**)	**4f** 94
7[b]	acrolein (**1g**)	**4g** 65
8[b]	cinnamaldehyde (**1h**)	**4h** 98
9	2-methoxybenzaldehyde (**1i**)	**4i** 85
10	3,4,5-trimethoxybenzaldehyde (**1j**)	**4j** 90
11	4-fluorobenzaldehyde (**1k**)	**4k** 90
12	4-chlorobenzaldehyde (**1l**)	**4l** 87
13	2-bromobenzaldehyde (**1m**)	**4m** 96
14	4-trifluoromethylbenzaldehyde (**1n**)	**4n** 98
15	2-nitrobenzaldehyde (**1o**)	**4o** 79
16	3-nitrobenzaldehyde (**1p**)	**4p** 75
17	piperonal (**1q**)	**4q** 86
18	3-benzyloxy-1-propanal (**1r**)	**4r** 80
19	3-phenylpropanal (**1s**)	**4s** 77
20	3,4-$(OMe)_2$-2-CN-phenyl-propanal (**1t**)	**4t** 83
21	(*S*)-(α-NHBoc)-3-phenyl-propanal (**1u**)	**4u** 79
22	4-thiomethylbenzaldehyde (**1v**)	**4v** 90

[a] Reaction conditions: aldehyde (3 mmol), NaH (3.3 mmol), Me_3SOI (3.3 mmol), DMSO (10 mL), THF (10 mL), 25 °C, 1 h, then CO_2 bubbling 40 °C, 6 h.
[b] Dimethylsulfonium methylide was used instead of dimethyloxosulfonium methylide.

For comparative studies, it was of interest to investigate the effect of temperature on cycloaddition of styrene epoxide with CO_2 using various alkali metal iodides. Thus, when styrene epoxide was treated with CO_2 (1.0133 bar) in the presence of NaI (100 mol%) in DMSO–THF (1:1) at 25 °C for 12 hours, no reaction took place. However, when the same reaction was carried out at 40 °C for six hours, the corresponding styrene cyclic carbonate was obtained in 95% yield. Also, other alkali metal iodides (KI and LiI, in stoichiometric amount) under the same reaction conditions, could be employed to give the styrene cyclic carbonate in 73% and 83% yield, respectively. NaI could also be used in catalytic amount (10 mol%) to give styrene cyclic carbonate in 91% yield, although it took 38 hours to completion. From the above investigations, we strongly believe that a slightly higher temperature (40 °C) is needed for the activation of styrene epoxide by alkali metal iodide.

Based on the above observations, a probable mechanistic pathway for the formation of cyclic carbonates is shown in Scheme 2.[15] Firstly, aldehydes **1a**–**v** react with sulfur ylide (generated in situ from $O{=}SMe_3I$ and NaH in DMSO) to form epoxide **2** which was isolated and characterized. Subsequently, NaI formed in situ in the reaction medium promotes the regioselective ring opening of epoxide **2** to give iodo alkoxide complex **3** (confirmed by isolation and characterization of iodoalcohol **3a**, see Table 1). This is followed by its simultaneous insertion with CO_2 producing the intermediate **I**, cyclization of which results in the formation of cyclic carbonates **4a**–**v**.



Scheme 2 Pathway for the formation of cyclic carbonates from aldehydes, sulfur ylide, and CO_2

In summary, we have described, for the first time, a novel 'one-pot' procedure that involves reaction of aldehydes **1a**–**v** with sulfur ylides, followed by CO_2 insertion in a sequential fashion leading to the high-yield synthesis of cyclic carbonates **4a**–**v**. The salient features of the methodology are as follows: (1) unprecedented one-pot synthesis of organic cyclic carbonates directly from aldehydes; (2) inexpensive and commercially available starting materials; (3) metal-free synthesis; (4) water-soluble NaI acts as a promoter; (5) milder reaction conditions; (6) functional-group tolerance; and (7) high yields of cyclic carbonates.

Acknowledgment

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(12) (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353. (b) Melting point was found to be in agreement with the reported value.
(13) (a) Ylide generation failed with NaOH. (b) Diol was obtained in 48% yield with KOH. (c) Trace amount (5%) of epoxide was obtained using KO*t*-Bu as base.
(14) Dimethylsulfonium methylide was used instead of dimethyloxosulfonium methylide.
(15) North, M.; Pasquale, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 2946.
(16) **General Description**
Solvents were purified and dried by standard procedures before use; PE of boiling range 60–80 °C was used. Melting points are uncorrected and recorded on a Buchi B-542 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-200 spectrometer unless mentioned otherwise. Elemental analysis was carried out on a Carlo Erba CHNS-O analyzer. Infrared spectra were recorded on Shimadzu FTIR-8400 spectrometer and absorption is expressed in cm^{-1}. HRMS data for new compounds were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Purification was done using column chromatography (230–400 mesh).
General Experimental Procedure for the Preparation of Cyclic Carbonates 4a–v
NaH (0.132 g, 3.3 mmol; previously washed with anhydrous PE to remove oil) was taken in an oven-dried three-necked flask, followed by addition of anhydrous DMSO (10 mL) through a septum to it, and the whole slurry was stirred at 25 °C under N_2 atmosphere. Solid Me_3SOI (0.726 g, 3.3 mmol) was added to the slurry with stirring over a period of 5 min via a solid addition funnel until it becomes a homogeneous solution. A solution of aldehyde **1a–v** (3 mmol), dissolved in anhydrous THF (10 mL), was added dropwise to the reaction mixture. After 1 h, CO_2 (1 atm) was then bubbled slowly via a needle into the reaction mixture, (after ascertaining that aldehyde was completely converted into epoxide, monitored by TLC) at 40 °C, for 6 h. Water (10 mL) was added to quench the reaction. It was then extracted with EtOAc (3 × 20 mL); the organic layer was washed with brine and dried over anhydrous Na_2SO_4 and the solvent concentrated, product purified by silica gel column chromatography (100–200 mesh) using PE and EtOAc (70:30) as eluent to afford pure cyclic carbonates **4a–v**.
4-Phenyl-1,3-dioxolan-2-one (4a)
Yield 94% (463 mg, 2.82 mmol); colorless solid; mp 53–54 °C (lit. mp 51–53 °C). IR ($CHCl_3$): ν_{max} = 769, 1068, 1168, 1328, 1458, 1812 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.29 (t, *J* = 7.9 Hz, 1 H), 4.77 (t, *J* = 7.9 Hz, 1 H), 5.64 (t, *J* = 7.9 Hz, 1 H), 7.32–7.42 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.9, 77.8, 125.7, 129.0, 129.4, 135.8, 154.6. Anal. Calcd (%) for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.84; H, 4.90.
4-Methyl-1,3-dioxolan-2-one (4b)
Yield 40% (122.5 mg, 1.2 mmol); colorless oil; IR ($CHCl_3$): ν_{max} = 711, 776, 1051, 1120, 1183, 1354, 1389, 1793 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.49 (d, *J* = 6.1 Hz, 3 H), 4.02 (dd, *J* = 8.2, 1.0 Hz, 1 H), 4.55 (t, *J* = 8.0 Hz, 1 H), 4.77–4.94 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 70.4, 73.4, 154.8. Anal. Calcd (%) for $C_4H_6O_3$: C, 47.06; H, 5.92. Found: C, 47.04; H, 5.91.
4-Ethyl-1,3-dioxolan-2-one (4c)
Yield 65% (226.4 mg, 1.95 mmol); colorless oil. IR ($CHCl_3$): ν_{max} = 1060, 1177, 1377, 1797 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.4 Hz, 3 H), 1.72–1.87 (m, 2 H), 4.1 (dd, *J* = 8.2, 1.5 Hz, 1 H), 4.55 (t, *J* = 8.2 Hz, 1 H), 4.63–4.73 (m, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.9, 26.2, 68.5, 77.6, 154.6. Anal. Calcd (%) for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.75; H, 6.91.
4-Isopropyl-1,3-dioxolan-2-one (4d)
Yield 73% (285 mg, 2.19 mmol); colorless oil. IR ($CHCl_3$): ν_{max} = 1075, 1175, 1392, 1789 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.8 Hz, 3 H), 1.04 (d, *J* = 6.5 Hz, 3 H), 1.90–2.00 (m, 1 H), 4.12–4.18 (m, 1 H), 4.37–4.53 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.4, 16.8, 31.4, 67.2, 80.9, 154.6. HRMS (ESI$^+$): *m/z* = calcd for $(C_6H_{10}O_3)^+$ [M + H]$^+$: 131.0709; found: 131.0708. Anal. Calcd (%) for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.40; H, 7.71.
4-Butyl-1,3-dioxolan-2-one (4e)
Yield 89% (384.9 mg, 2.6 mmol); gum. IR ($CHCl_3$): ν_{max} = 1066, 1173, 1797 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88–0.95 (m, 3 H), 1.23–1.40 (m, 3 H), 1.68–1.80 (m, 3 H), 4.05 (dd, *J* = 8.2, 1.0 Hz, 1 H), 4.51 (t, *J* = 8.2 Hz, 1 H), 4.62–4.76 (m, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 22.2, 26.4, 33.6, 69.3, 76.9, 154.9. Anal. Calcd (%) for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.34; H, 8.38%.
4-Hexyl-1,3-dioxolan-2-one (4f)
Yield 94% (486 mg, 2.82 mmol); gum. IR ($CHCl_3$): ν_{max} = 772, 1065, 1170, 1802 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86–0.93 (m, 3 H), 1.30–1.49 (m, 8 H), 1.69–1.80 (m, 2 H), 4.06 (t, *J* = 7.2 Hz, 1 H), 4.51 (t, *J* = 8.0 Hz, 1 H), 4.62–4.76 (m, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 22.4, 24.3, 28.7, 31.4, 33.8, 69.2, 76.8, 154.8. Anal. Calcd (%) for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.73; H, 9.40.
4-Vinyl-1,3-dioxolan-2-one (4g)
Yield 65% (222.5 mg, 1.95 mmol); yellow oil. IR ($CHCl_3$): ν_{max} = 772, 991, 1060, 1168, 1385, 1510, 1805 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.17 (t, *J* = 7.8 Hz, 1 H), 4.61 (t, *J* = 8.4 Hz, 1 H), 5.12 (dd, *J* = 14.9, 7.5 Hz, 1 H), 5.48 (t, *J* = 16.5 Hz, 2 H), 5.83–6.0 (m, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 68.8, 76.8, 120.9, 132.2, 154.2. HRMS (ESI$^+$): *m/z* calcd for $(C_5H_6O_3)^+$ [M + H]$^+$: 115.0396; found: 115.0392; Anal. Calcd (%) for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.61; H, 5.32.
(*E*)-4-Styryl-1,3-dioxolan-2-one (4h)
Yield 98% (559 mg, 2.94 mmol); colorless solid; mp 115–116 °C. IR ($CHCl_3$): ν_{max} = 1049, 1070, 1168, 1648, 1800 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.23 (t, *J* = 8.0 Hz, 1 H), 4.64 (t, *J* = 8.2 Hz, 1 H), 5.26 (q, *J* = 7.9 Hz, 1 H), 6.15 (dd, *J* = 15.7, 7.7 Hz, 1 H), 6.73 (d, *J* = 15.7 Hz, 1 H), 7.26–7.40 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 69.2, 77.6, 122.4, 126.9, 128.8, 129.0, 134.8, 136.6, 154.4. HRMS (ESI$^+$): *m/z* calcd for $(C_{11}H_{10}O_3)^+$ [M + Na]$^+$: 213.0527; found: 213.0522. Anal. Calcd (%) for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.41; H, 5.33.
4-(2-Methoxyphenyl)-1,3-dioxolan-2-one (4i)
Yield 85% (495 mg, 2.55 mmol); gum. IR ($CHCl_3$): ν_{max} = 757, 1076, 1166, 1249, 1494, 1812 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 4.25 (dd, *J* = 8.4, 1.1 Hz, 1 H), 4.82 (t, *J* = 8.4 Hz, 1 H), 5.81 (t, *J* = 8.0 Hz, 1 H), 6.90–7.04 (m, 2 H), 7.32–7.38 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 70.5, 74.7, 110.5, 120.9, 124.9, 126.1, 130.3, 154.9, 156.1. Anal. Calcd (%) for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.79; H, 5.14.
4-(3,4,5-Trimethoxyphenyl)-1,3-dioxolan-2-one (4j)

Yield 90% (686 mg, 2.7 mmol); brown solid; mp 133–134 °C. IR ($CHCl_3$): ν_{max} = 1068, 1125, 1243, 1510, 1796 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 3.88 (s, 6 H), 4.31 (t, *J* = 8.3 Hz, 1 H), 4.78 (t, *J* = 8.4 Hz, 1 H), 5.60 (t, *J* = 7.9 Hz, 1 H), 6.54 (s, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.1, 60.7, 71.1, 78.0, 102.6, 131.2, 138.8, 153.8, 154.5. HRMS (ESI^+): *m/z* calcd for $(C_{12}H_{14}O_6)^+$ $[M + H]^+$: 255.0869; found: 255.0855. Anal. Calcd (%) for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.62; H, 5.50.

4-(4-Fluorophenyl)-1,3-dioxolan-2-one (4k)

Yield 90% (492 mg, 2.7 mmol); colorless solid; mp 91–92 °C. IR ($CHCl_3$): ν_{max} = 773, 840, 1069, 1161, 1210, 1385, 1514, 1818 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.31 (t, *J* = 8.2 Hz, 1 H), 4.80 (t, *J* = 8.3 Hz, 1 H), 5.66 (t, *J* = 8.0 Hz, 1 H), 7.08–7.19 (m, 2 H), 7.32–7.40 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 71.0, 77.3, 116, 116.5, 127.9, 128.0, 131.6, 154.4, 160.84, 165.8. Anal. Calcd (%) for $C_9H_7FO_3$: C, 59.35; H, 3.87. Found: C, 59.37; H, 3.86.

4-(4-Chlorophenyl)-1,3-dioxolan-2-one (4l)

Yield 87% (518 mg, 2.61 mmol); colorless solid; mp 70–71 °C (lit. mp 68–69 °C). IR ($CHCl_3$): ν_{max} = 770, 829, 1071, 1167, 1384, 1494, 1816 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.29 (t, *J* = 8.4 Hz, 1 H), 4.80 (t, *J* = 8.4 Hz, 1 H), 5.65 (t, *J* = 7.8 Hz, 1 H), 7.28–7.33 (m, 2 H), 7.36–7.44 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.9, 77.1, 127.2, 129.4, 134.4, 135.7, 154.3. Anal. Calcd (%) for $C_9H_7ClO_3$: C, 54.43; H, 3.55. Found: C, 54.37; H, 3.56.

4-(2-Bromophenyl)-1,3-dioxolan-2-one (4m)

Yield 96% (700 mg, 2.88 mmol); gum. IR ($CHCl_3$): ν_{max} = 763, 969, 1072, 1125, 1159, 1208, 1473, 1817 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.24 (dd, *J* = 6.8, 1.7 Hz, 1 H), 4.99 (t, *J* = 8.4 Hz, 1 H), 5.94 (t, *J* = 8.0 Hz, 1 H), 7.28–7.39 (m, 1 H), 7.43–7.62 (m, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.4, 76.3, 120.1, 126.0, 128.1, 130.4, 132.96, 136.3, 154.3. Anal. Calcd (%) for $C_9H_7BrO_3$: C, 44.47; H, 2.90. Found: C, 44.45; H, 2.86.

4-[4-(Trifluoromethyl)phenyl]-1,3-dioxolan-2-one (4n)

Yield 98% (683 mg, 2.94 mmol); gum. IR ($CHCl_3$): ν_{max} = 771, 844, 1071, 1167, 1264, 1327, 1426, 1822 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.30 (t, *J* = 7.8 Hz, 1 H), 4.85 (t, *J* = 8.4 Hz, 1 H), 5.74 (t, *J* = 7.9 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.70–7.74 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.8, 76.8, 126.0, 126.2, 126.3, 126.4, 139.9, 154.2. HRMS (ESI^+): *m/z* calcd for $(C_{10}H_7F_3O_3)^+$ $[M + H]^+$: 233.0426; found: 233.0426. Anal. Calcd (%) for $C_{10}H_7F_3O_3$: C, 51.74; H, 3.04. Found: C, 51.71; H, 3.06.

4-(2-Nitrophenyl)-1,3-dioxolan-2-one (4o)

Yield 79% (496 mg, 2.37 mmol); brown solid; mp 95–96 °C. IR ($CHCl_3$): ν_{max} = 1073, 1167, 1350, 1527, 1819 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.27 (dd, *J* = 9.0, 3.3 Hz, 1 H), 5.17 (t, *J* = 8.9 Hz, 1 H), 6.28 (dd, *J* = 8.7, 2.7 Hz, 1 H), 7.60–7.68 (m, 1 H), 7.83 (d, *J* = 4.0 Hz, 2 H), 8.26 (d, *J* = 8.2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 71.2, 74.3, 125.6, 126.2, 129.9, 134.1, 135.1, 145.9, 154.2 Anal. Calcd (%) for $C_9H_7NO_5$: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.71; H, 3.35; N, 6.66.

4-(3-Nitrophenyl)-1,3-dioxolan-2-one (4p)

Yield 75% (470 mg, 2.25 mmol); brown solid; mp 97–98 °C. IR ($CHCl_3$): ν_{max} = 1071, 1166, 1349, 1530, 1805 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.35 (dd, *J* = 8.7, 1.1 Hz, 1 H), 4.91 (t, *J* = 8.5 Hz, 1 H), 5.81 (t, *J* = 7.8 Hz, 1 H), 7.64–7.78 (m, 2 H), 8.24–8.33 (m,2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.7, 76.3, 120.9, 124.5, 130.5, 131.4, 138.2, 148.6, 153.8. HRMS (ESI^+): *m/z* calcd for $(C_9H_7NO_5)^+$ $[M + Na]^+$: 232.0221; found: 232.0214. Anal. Calcd (%) for $C_9H_7NO_5$: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.72; H, 3.34; N, 6.68.

4-{Benzo[*d*][1,3]dioxol-5-yl}-1,3-dioxolan-2-one (4q)

Yield 86% (537 mg, 2.58 mmol); gum. IR ($CHCl_3$): ν_{max} = 1070, 1164, 1251, 1505, 1791 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.32 (t, *J* = 8.4 Hz, 1 H), 4.75 (t, *J* = 8.5 Hz, 1 H), 5.58 (t, *J* = 8.0 Hz, 1 H), 6.01 (s, 2 H), 6.84 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 71.0, 78.0, 101.5, 106.1, 108.6, 120.3, 129.2, 148.5, 148.8, 154.6. Anal. Calcd (%) for $C_{10}H_8O_5$: C, 57.70; H, 3.87. Found: C, 57.72; H, 3.84.

4-[2-(Benzyloxy)ethyl]-1,3-dioxolan-2-one (4r)

Yield 80% (533 mg, 2.4 mmol); gum. IR ($CHCl_3$): ν_{max} = 1061, 1173, 1364, 1454, 1794 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.02–2.10 (m, 2 H), 3.58–3.65 (m, 2 H), 4.17 (dd, *J* = 8.4, 1.0 Hz, 1 H), 4.47–4.52 (m, 3 H), 4.79–4.93 (m, 1 H), 7.29–7.40 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.0, 33.9, 61.5, 65.3, 69.1, 69.6, 73.1, 73.3, 75.0, 127.5, 127.8, 128.3, 128.4, 137.5, 154.7. Anal. Calcd (%) for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.82; H, 6.31.

4-Phenethyl-1,3-dioxolan-2-one (4s)

Yield 77% (444 mg, 2.31 mmol); gum. IR ($CHCl_3$): ν_{max} = 1061, 1165, 1796 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.94–2.17 (m, 2 H), 2.72–2.91 (m, 2 H), 4.01 (dd, *J* = 8.3, 1.1 Hz, 1 H), 4.44 (t, *J* = 8.2 Hz, 1 H), 4.62–4.68 (m, 1 H), 7.15–7.34 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.8, 35.6, 69.1, 75.8, 126.5, 128.3, 128.7, 139.6, 154.6. Anal. Calcd (%) for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.71; H, 6.26.

4,5-Dimethoxy-2-(2-oxo-1,3-dioxolan-4-yl)benzonitrile (4t)

Yield 83% (690.42, 2.49 mmol); gum. IR ($CHCl_3$): ν_{max} = 1064, 1168, 1270, 1516, 1793, 2218 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.09 (q, *J* = 7.8 Hz, 1 H), 2.89–2.98 (m, 1 H), 3.89 (s, 3 H), 3.94 (s, 3 H), 4.14 (dd, *J* = 8.3, 1.6 Hz, 1 H), 4.54 (t, *J* = 8.2 Hz, 1 H), 4.62–4.73 (m, 1 H), 6.80 (s, 1 H), 7.03 (s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.5, 35.0, 56.1, 69.0, 75.6, 103.0, 112.3, 114.2, 118.0, 138.1, 147.9, 152.9, 154.5. HRMS (ESI^+): *m/z* calcd for $(C_{14}H_{15}NO_5)^+$ $[M + H]^+$: 278.1023; found: 278.1026. Anal. Calcd (%) for $C_{14}H_{15}NO_5$ C, 60.64; H, 5.45; N, 5.05. Found: C, 60.60; H, 5.40; N, 5.10.

***tert*-Butyl {(*S*)-1-[(*S*)-2-Oxo-1,3-dioxolan-4-yl]-2-phenylethyl}carbamate (4u)**

Yield 79% (728 mg, 2.37 mmol); colorless solid; mp 148–149 °C. IR ($CHCl_3$): ν_{max} = 1061, 1169, 1249, 1366, 1689, 1800 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.40 (s, 9 H), 2.82–2.89 (m, 2 H), 4.09 (m, 1 H), 4.28–4.44 (m, 2 H), 4.67 (m, 2 H), 7.22–7.33 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.2, 38.5, 52.8, 66.5, 76.1, 80.4, 127.1, 128.88, 129.2, 136.4, 154.6, 155.9. Anal. Calcd (%) for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.57; H, 6.91; N, 4.60.

4-[4-(Methylthio)phenyl]-1,3-dioxolan-2-one (4v)

Yield 90% (573 mg, 2.73 mmol); yellow solid; mp 55–57 °C. IR ($CHCl_3$): ν_{max} = 817, 895, 1062, 1173, 1384, 1514, 1767 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 4.30 (t, *J* = 8.1 Hz, 1 H), 4.76 (t, *J* = 8.2 Hz, 1 H), 5.61 (t, *J* = 8.0 Hz, 1 H), 7.27 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0, 70.7, 77.5, 125.8, 131.9, 140.7, 154.5. Anal. Calcd (%) for $C_{10}H_{10}SO_3$: C, 57.13; H, 4.79. Found: C, 57.17; H, 4.86. HRMS (ESI^+): *m/z* calcd for $(C_{10}H_{10}O_3S)^+$ $[M + H]^+$: 211.0429; found: 211.0441.

2-Iodo-1-phenylethan-1-ol (3a)

Gum. IR ($CHCl_3$): ν_{max} = 699, 1054, 1174, 1452, 3404 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.44 (br s, 1 H), 3.33–3.52 (m, 2 H), 4.80–4.84 (m, 1 H), 7.31–7.38 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1502, 74.0, 125.7, 128.3, 128.6, 141.1. Anal. Calcd (%) for C_8H_9IO: C, 38.74; H, 3.66. Found: C, 38.70; H, 3.63.