**3,5,6-Trimethoxyphthalide (31).** A solution of benzamide **31** (100 mg, 0.34 mmol) and a catalytic amount of TsOH in 2.5 mL of anhydrous THF was stirred at reflux overnight under an atmosphere of $N_2$; then the cooled reaction mixture was washed with saturated $NaHCO_3$ (2×) and with brine, dried over $Na_2SO_4$, and concentrated to a solid. Recrystallization in $Et_2O$/hexanes afforded a shiny white solid, 70 mg (92%), mp 134-135 °C; IR ($CHCl_3$) 1745, 1605, 1500, 1050 $cm^{-1}$; NMR (250 MHz, $CDCl_3$) δ 3.82 (s, 3 H), 3.96 (s, 3 H), 5.20 (s, 2 H), 6.46 (s, 1 H); $M^+$ 224.0690 (theory 224.0684).

**Acknowledgment.** This work was supported by the National Science Foundation (CHE-8306687) and the National Institutes of Health (CA 39717). The Bruker WM-250 spectrometer used in this work was purchased with funds from the National Science Foundation and the Montedison Group of Milan. The Kratos mass spectrometer was purchased with funds from the Department of Health and Human Services, Division of Research Resources.

**Registry No.** 1, 80455-68-1; **3b**, 105518-04-5; **4a**, 65489-47-6; **4b**, 105518-05-6; **5**, 24953-73-9; **9**, 77220-15-6; **10**, 103548-65-8; **11a**, 105518-06-7; **11b**, 103548-64-7; **12**, 103548-66-9; **13**, 104422-97-1; **15**, 824-46-4; **16**, 2880-58-2; **17**, 105518-07-8; **19**, 105518-08-9; **20**, 105518-09-0; **21**, 490-64-2; **21** (chloride), 42833-66-9; **22**, 20029-76-9; **23**, 38156-66-0; **24**, 105518-10-3; **31**, 105518-11-4; **32**, 105518-12-5; **33**, 105518-13-6; **34**, 105518-14-7; 3,4,6-trimethoxybenzonitrile, 14894-77-0; 1,2,4-trimethoxybenzene, 135-77-3; dimethyl acetylenedicarboxylate, 762-42-5.

# General Scope of 1,3-Dioxolanation of α,β-Unsaturated Aldehydes with 1,2-Bis((trimethylsilyl)oxy)ethane and Trimethylsilyl Trifluoromethanesulfonate

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1,3-Dioxolanation of α,β-unsaturated aldehydes with 1,2-bis((trimethylsilyl)oxy)ethane in the presence of trimethylsilyl trifluoromethanesulfonate as catalyst has been systematically investigated. These silylated reagents readily acetalize aliphatic, highly conjugated aliphatic, and aromatic enals. Under the mild, aprotic conditions of the reaction, olefins do not rearrange or isomerize, and the acid-sensitive propionyloxy, (tetrahydropyranyl)oxy, and vinyl ether moieties are relatively stable. Aromatic bromide, furan, thiophene, and nitro functionalities are also inert. The only limitation found is in the case of 4-(dimethylamino)cinnamaldehyde, which did not afford a detectable amount of the corresponding dioxolane.

The 1,3-dioxolane moiety is one of the most frequently used protecting groups for carbonyl compounds.[1] For our work in the total synthesis of natural products, we required an efficient method to convert α,β-unsaturated aldehydes to the corresponding 1,3-dioxolanes under mild conditions with reagents compatible with various functional groups. A trimethylsilyl trifluoromethanesulfonate ($Me_3SiOTf$) catalyzed dioxolanation of ketones using 1,2-bis((trimethylsilyl)oxy)ethane (BTSE) under aprotic conditions has been reported by Noyori et al.[2] To our knowledge, no systematic study on the use of these reagents to protect α,β-unsaturated aldehydes has been reported. Herein, we disclose the scope and limitations of the procedure for the protection of α,β-unsaturated aldehydes. Our results should be of significance to the synthetic community.

## Results and Discussion

Addition of an enal to a solution of BTSE (1.2 equiv) and a catalytic amount (0.01 equiv) of $Me_3SiOTf$ in dichloromethane at −78 °C provided the corresponding unsaturated dioxolane, generally in good-to-excellent yield (Scheme I). The reaction proceeded rapidly (3-4 h) for most substrates. Both acyclic (e.g., **1a**) and cyclic enals (e.g., **1b**, with the C=C double bond endocyclic) gave the corresponding acetals readily. Neither the terminal C=C double bond in **1a** nor the isopropenylic C=C double bond in **1b** shifted to the more thermodynamically stable position under the reaction conditions. This is consistent with results obtained in a β,γ-enone system reported previously.[2]

Elongation of the conjugated system of enals by one C=C double bond, as in **1c**, or with a phenyl group, as in **1d**, did not significantly influence the reaction rate. Both of these substrates gave the corresponding dioxolanes in excellent yield within 4 h at −78 °C. Extensive conjugation of the enal moiety with additional C=C double bonds as in **1e** did not substantially retard acetalization.

The acid-sensitive allylic propionyloxy and (tetrahydropyranyl)oxy groups in **1f** and **1g**, respectively, were relatively inert toward the acetalization reagents at −78 °C. However, loss of the tetrahydropyranyl (THP) group in **2g** occurred when the reaction mixture was warmed to room temperature. In order to obtain a respectable yield of **2g**, it was necessary to react **1g** with only a slight excess (1.05 equiv) of BTSE at −78 °C for 24 h. Note that attempted acetalization of **1g** by typical methods using ethylene glycol in the presence of various catalysts, such as *p*-toluenesulfonic acid, pyridinium *p*-toluenesulfonate,[3]

† Research Fellow of the Alfred P. Sloan Foundation, 1986-1988.
‡ Summer Research Fellow.

(1) For general methods to prepare 1,3-dioxolanes, see: (a) Greene, T. W. *Protective Groups in Organic Syntehsis*, Wiley: New York, 1981; p 124. (b) Loewenthal, H. J. E. In *Protective Groups in Organic Chemistry*; McOmie, J. F. W., Ed., Plenum: London and New York, 1973; Chapter 9.

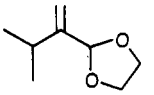
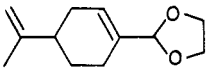
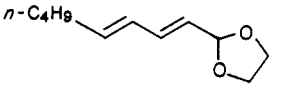
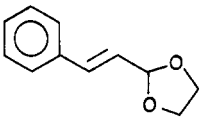
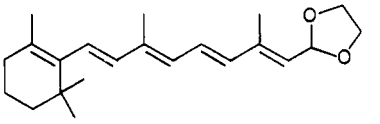
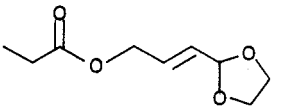
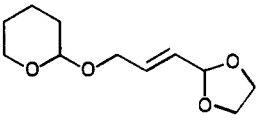
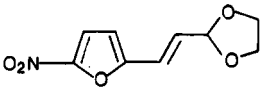
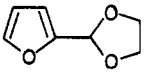
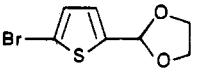
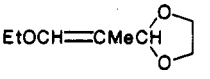
(2) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357.

(3) For the use of pyridinium *p*-toluenesulfonate as an efficient catalyst for the formation of dioxolane-type acetals, see: Sterzycki, R. *Synthesis*, **1979**, 724.

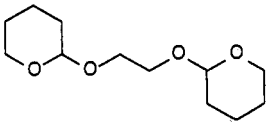
0022-3263/87/1952-0188$01.50/0 

**Scheme I**

α,β-unsaturated enal + $\begin{matrix}\text{OSiMe}_3\\ \text{OSiMe}_3\end{matrix}$ (1) $\xrightarrow[CH_2Cl_2]{Me_3SiOTf}$ α,β-unsaturated 1,3-dioxolane (2) + $(Me_3Si)_2O$

| | | yield, % | |
|---|---|---|---|
| a | 2-isopropylacrolein | 82 |  |
| b | (*S*)-(−)-perillaldehyde | 79 |  |
| c | *trans,trans*-2,4-nonadienal | 96 |  |
| d | *trans*-cinnamaldehyde | 91 |  |
| e | *trans*-retinal | 74 |  |
| f | *trans*-4-(propionyloxy)crotonaldehyde | 84 |  |
| g | *trans*-4-((tetrahydropyranyl)oxy)crotonaldehyde | 78 |  |
| h | 5-nitro-2-furanacrolein | 93 |  |
| i | 2-furaldehyde | 56 (99, crude) |  |
| j | 5-bromo-2-thiophenecarboxaldehyde | 100 |  |
| k | 3-ethoxymethacrolein | 40-50 |  |

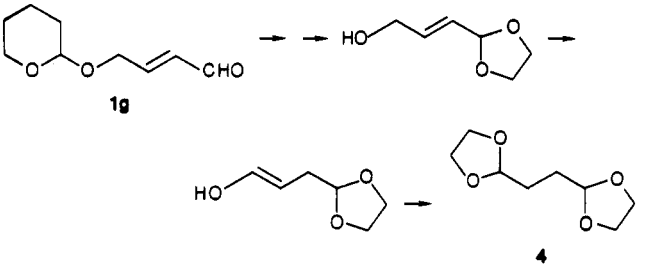
or Amberlyst 15 ion-exchange resin,[4] gave complex mixtures of products, as indicated by thin-layer chromatography. Two major components were isolated and characterized as 1,2-bis((tetrahydropyranyl)oxy)ethane (**3**)[5] and bis(dioxolane) **4**.[6] Compound **3** presumably arose by



**3**

transfer of THP groups from two molecules of **1g** to the dioxolanation reagent, ethylene glycol. Compound **4** apparently also originated from **1g** and ethylene glycol via an unexpected protection–deprotection–double bond migration sequence, as depicted in Scheme II.

**Scheme II**

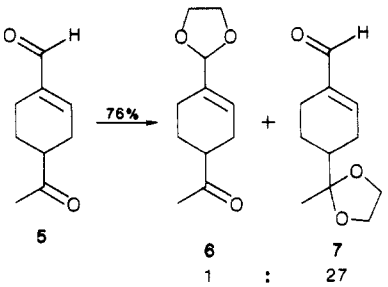


**1g** **4**

5-Nitro-2-furanacrolein (**1h**) was converted to the corresponding acetal **2h** with BTSE and $Me_3SiOTf$ in very high yield (93%); however, it was necessary to modify the typical procedure due to the poor solubility of **1h** in dichloromethane at −78 °C. Thus, **1h** was placed in the reaction flask before adding dichloromethane, $Me_3SiOTf$, and BTSE. The reaction mixture was stirred at −78 °C for 3 h and then at room temperature for 14 h. The solid **1h** gradually disappeared, and the product **2h** was purified by crystallization. It was found that the nitrofuranyl nu-

(4) Dann, A. E.; Davis, J. B.; Nagler, M. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 158.
(5) This product was compared to an authentic sample independently synthesized from ethylene glycol and dihydropyran.
(6) Chastrette, F.; Hassambay, M.; Chastrette, M. *Bull. Soc. Chim. Fr.* **1976**, 601.

**Scheme III**




cleus is stable under these reaction conditions.

We have extended this dioxolanation procedure to two "pseudo" enal substrates, 2-furaldehyde (**1i**) and 5-bromo-2-thiophenecarboxaldehyde (**1j**).[7] Although **1i** was converted in 99% yield to the corresponding acetal **2i**, microdistillation of the products afforded only a 56% yield of pure **2i**. Similarly, thiophene **1j** was quantitatively converted to **2j**. Spectroscopic and chromatographic analysis of the product **2j** indicated high purity, making further purification unnecessary.

Upon observing the remarkable stability of the various functional groups in compounds **1a–1j** toward the reagents BTSE and $Me_3SiOTf$, we decided to explore the limitations of this dioxolanation method. Thus, 3-ethoxymethacrolein (**1k**), which contains a vinyl alkyl ether moiety, reacted to the extent of only 50% to give **2k**, even after 17 h at room temperature. There was no indication that the vinyl ethyl ether functionality in **1k** was destroyed under these conditions. Attempts to separate **2k** from unreacted **1k** were unsuccessful.

Acetalization of 4-(dimethylamino)cinnamaldehyde, which bears a tertiary amino group as well as an enal moiety, also afforded information regarding the limitations of the method. Treatment of this aldehyde with BTSE in the presence of 1.1 equiv of $Me_3SiOTf$ for 44 h at room temperature gave a black-green, tarry product mixture consisting mostly of starting material. The desired dioxolane could not be detected in this mixture by $^1H$ NMR.

The "bulky-proton" containing reagents, BTSE and $Me_3SiOTf$, have been shown to provide remarkable selectivity in the monoketalization of dicarbonyl compounds in which the two carbonyl groups have different steric environments.[8] However, dioxolanation of acetyl enal **5** with 1 equiv of BTSE in the presence of 0.05 equiv of $Me_3SiOTf$ at −78 °C provided in 76% yield a mixture of **6** and **7** in the ratio of 1:27 (Scheme III). This result indicates that, in the absence of significant steric bias, ketalization of a saturated carbonyl group is easier than acetalization of an enal functionality by these reagents. Ketal **7** was identified by its $^1H$ NMR spectral properties. Acetal **6** was identified by comparison of its $^1H$ NMR spectral properties and its GC retention time with those of an authentic sample prepared by osmylation[9] of dioxolane **2b** followed by $Pb(OAc)_4$ cleavage.[10]

## Conclusion

We have demonstrated that conjugated enals, dienals, polyenals, and aromatic enals can be protected as their 1,3-dioxolanes with BTSE and $Me_3SiOTf$ in good-to-excellent yields. A wide range of functional groups, including the propionyloxy, (tetrahydropyranyl)oxy, nitro, furan, thiophene, and ethoxyvinyl moieties, are compatible with these reagents. By this procedure ketalization of a nonconjugated ketone is easier than acetalization of an enal in the absence of significant steric bias. A limitation of the procedure is that, in the presence of amino groups, dioxolanation is difficult or impossible.

## Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Dichloromethane and pyridine were dried and distilled over $CaH_2$. For column chromatography, 63–200-μm silica gel (E. Merck #7734) was used. Analytical TLC was performed on precoated plates purchased from Analtech, Inc. (silica gel GHLF) using UV light and/or 2.5% phosphomolybdic acid in ethanol with heating for visualization. Mixtures of ethyl acetate and hexanes, dried and distilled over $CaH_2$, were used as eluants. Distillations were carried out in a micro still apparatus purchased from Kontes Scientific Glass/Instruments. The temperatures provided below are the bath temperatures at which the desired products were collected, and not necessarily the actual boiling points. Infrared spectra (IR) were measured on a Perkin-Elmer 599B spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601 $cm^{-1}$ absorption. IR absorption intensities are designated using the following abbreviations: s, strong; m, medium; w, weak. $^1H$ NMR spectra were obtained on a Varian CFT-20 spectrometer using chloroform-*d* as solvent and tetramethylsilane as an internal standard. NMR multiplicities are recorded by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra were obtained with a VG Analytical 70-S mass spectrometer. Melting points were determined on a Büchi 510K melting point apparatus and are uncorrected. GC analyses were performed on a Hewlett-Packard 5794A instrument equipped with a 12.5-m cross-linked methylsilicone gum capillary column (0.2-mm i.d.). Elemental analyses were carried out by Mic Anal, Tucson, AZ.

**General Procedure.** The experimental procedure is a slight modification of that reported by Noyori and co-workers.[2] In a typical experiment, $Me_3SiOTf$ (0.01 equiv) was added into a reaction flask containing dry dichloromethane (1 mL/mmol of enal) under $N_2$. The mixture was cooled to −78 °C. 1,2-Bis((trimethylsilyl)oxy)ethane (1.2 equiv) was then added into the reaction flask followed by injection of the enal (1.0 equiv; in general, 100–400 mg). The reaction was monitored by TLC and quenched at −78 °C by adding dry pyridine (0.25 equiv). The reaction mixture was poured into a saturated $NaHCO_3$ aqueous solution and extracted several times with dichloromethane. The combined organic layers were washed with saturated NaCl aqueous solution and dried over a 1:1 mixture of $K_2CO_3$ and $MgSO_4$. After the solution was concentrated, the residue was purified by microdistillation, column chromatography, or crystallization.

**1,3-Dioxolane of 2-Isopropylacrolein (2a).** The reactants were stirred at −78 °C for 3 h. After workup, microdistillation (68–72 °C/101 mm) afforded **2a** in 82% yield: $R_f$ 0.28 (10% EtOAc in hexanes); $^1H$ NMR δ 5.26 (s, 2 H), 5.06 (s, 1 H), 3.95 (m, 4 H), 2.41 (m, 1 H), 1.09 (d, 6 H, $J$ = 6.8); IR (neat) 3079 (w, =CH), 2959 (s), 2869 (s), 1648 (m, C=C), 1088 (s, CO) $cm^{-1}$. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.53; H, 10.25.

**1,3-Dioxolane of (*S*)-(−)-Perillaldehyde (2b).** The reactants were stirred at −78 °C for 3 h. After workup, microdistillation (60 °C/0.4 mm) afforded **2b** in 79% yield: $R_f$ 0.32 (10% EtOAc in hexanes); $^1H$ NMR δ 5.94 (br s, 1 H), 5.13 (s, 1 H), 4.72 (br s, 2 H), 3.95 (m, 4 H), 2.41–1.27 (m, 7 H), 1.73 (br s, 3 H); IR (neat) 3076 (m, =CH), 2906 (s), 1677 (m, C=C), 1640 (m, C=C), 1438 (m), 1373 (m), 1308 (m), 1178 (s, CO), 933 (s) $cm^{-1}$. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.51; H, 9.45.

**1,3-Dioxolane of *trans,trans*-2,4-Nonadienal (2c).** The reactants were stirred at −78 °C for 3 h. After workup, microdistillation (104–115 °C/6 mm) afforded **2c** in 96% yield: $R_f$ 0.29 (10% EtOAc in hexanes); $^1H$ NMR δ 6.44–5.11 (m, 5 H), 3.94 (m, 4 H), 2.06 (br q, 2 H), 1.33 (m, 4 H), 0.88 (br t, 3 H); IR (neat) 2960 (s), 2921 (s), 1662 (m, C=C), 1390 (m), 1254 (m), 1147 (s,

(7) For a discussion of the aromatic characteristics of furan and thiophene rings, see: Acheson, R. M. *An Introduction to the Chemistry of Heterocyclic Compounds*, 3rd ed.; Wiley: New York 1976; pp 174–9.
(8) Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1985**, *50*, 3946.
(9) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *23*, 1973.
(10) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; pp 360–3.

CO), 1060 (s, CO), 993 (s), 848 (m) $cm^{-1}$. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.79; H, 9.82.

**1,3-Dioxolane of *trans*-Cinnamaldehyde (2d).**[11a] The reactants were stirred at −78 °C for 4 h. After workup, microdistillation (114 °C/0.3 mm, lit.[11a] 84 °C/0.1 mm) afforded **2d** in 91% yield: $R_f$ 0.21 (10% EtOAc in hexanes); $^1H$ NMR δ 7.34 (m, 5 H), 6.78 (d, 1 H, $J$ = 16.0), 6.15 (dd, 1 H, $J$ = 5.8, 16.0), 5.42 (d, 1 H, $J$ = 5.8), 3.98 (m, 4 H); IR (melt) 3054 (m, =CH), 3024 (m, =CH), 2950 (s), 2904 (s), 1948 (w), 1877 (w), 1794 (w), 1658 (m, C=C), 1598 (m, C=C), 1578 (m, C=C), 1495 (s), 1452 (s), 1393 (s), 1143 (s, CO), 1068 (s, CO), 953 (s), 753 (s, =CH), 698 (s, =CH) $cm^{-1}$.

**1,3-Dioxolane of *trans*-Retinal (2e).** The reactants were stirred at −78 °C for 4 h. After workup, the crude product was chromatographed through silica gel ($Et_2O$ as eluent), and the volatile components were removed by rotovapping followed by oil pump evacuation (25 °C, 2.5 h, 0.1 mm). Dioxolane **2e** was obtained as a viscous red oil in 74% yield: $R_f$ 0.28 (10% EtOAc in hexanes); $^1H$ NMR δ 6.90–5.12 (m, 7 H), 3.97 (m, 4 H), 2.34–1.06 (m, 6 H), 1.96 (s, 6 H), 1.71 (s, 3 H), 1.02 (s, 6 H); IR (neat) 3040 (w, =CH), 2921 (s), 1657 (m, C=C), 1630 (m, C=C), 1574 (m), 1450 (m), 1386 (m), 1361 (m), 1145 (s, CO), 1061 (s, CO), 970 (s), 846 (s) $cm^{-1}$; exact mass calcd for $C_{22}H_{32}O_2$ 328.2402, found 328.2393.

**1,3-Dioxolane of *trans*-4-(Propionyloxy)crotonaldehyde (2f).** The reactants were stirred at −78 °C for 4 h. After workup, chromatography on a silica gel column using 20% EtOAc in hexanes as eluent afforded **2f** as a colorless liquid in 84% yield: $R_f$ 0.42 (40% EtOAc in hexanes); $^1H$ NMR δ 6.05 (dt, 1 H, $J$ = 15.5, 4.8), 5.73 (ddt, 1 H, $J$ = 15.5, 5.1, 0.9), 5.28 (d, 1 H, $J$ = 5.1), 4.62 (dd, 2 H, $J$ = 4.8, 0.9), 3.93 (m, 4 H), 2.36 (q, 2 H, $J$ = 7.3), 1.15 (t, 3 H, $J$ = 7.3); IR (neat) 2985 (s), 2890 (s), 1735 (s, C=O), 1686 (m, C=C), 1465 (m), 1350 (s), 1180 (s, CO), 1060 (s, CO), 973 (s), 815 (m) $cm^{-1}$. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.83; H, 7.73.

**1,3-Dioxolane of *trans*-4-((Tetrahydropyranyl)oxy)crotonaldehyde (2g).** Aldehyde **1g** was stirred with BTSE (1.05 equiv) and $Me_3SiOTf$ in dichloromethane at −78 °C for 24 h. After workup, the crude product was chromatographed on a silica gel column using 30% EtOAc in hexanes as eluent. Dioxolane **2g** was obtained as a colorless liquid in 78% yield: $R_f$ 0.38 (40% EtOAc in hexanes); $^1H$ NMR δ 6.13–5.44 (m, 2 H), 5.28 (d, 1 H, $J$ = 5.3), 4.64 (br s, 1 H), 4.38–3.28 (m, 8 H), 1.93–1.33 (m, 6 H); IR (neat) 2946 (s), 2866 (s), 1680 (w, C=C), 1388 (s), 1349 (s), 1128 (s, CO), 1025 (s, CO), 965 (s), 908 (s), 874 (m), 819 (m) $cm^{-1}$. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.47; H, 8.69.

**1,3-Dioxolane of 5-Nitro-2-furanacrolein (2h).** The reactants were stirred at −78 °C for 3 h, then at room temperature for 14 h. Because of the poor solubility of **1h**, the reagents were added to the enal in dichloromethane (inverse order). After workup, recrystallization from ether afforded **2h** in 93% yield: mp 69.5–70.0 °C; $R_f$ 0.29 (40% EtOAc in hexanes); $^1H$ NMR δ 7.30 (d, 1 H, $J$ = 3.8), 6.77–6.31 (m, 3 H), 5.48 (d, 1 H, $J$ = 3.6), 4.00 (m, 4 H); IR ($CCl_4$) 2956 (w), 2885 (m), 1524 (w, C=C), 1488 (s, N=O), 1352 (s, N=O), 1241 (m), 1144 (s, CO), 1021 (m, CO), 964 (s) $cm^{-1}$. Anal. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30. Found: C, 51.40; H, 4.16.

**1,3-Dioxolane of 2-Furaldehyde (2i).**[11b] The reactants were stirred at −78 °C for 3.5 h to provide crude **2i** in 99% yield. Microdistillation (60 °C/0.35 mm, lit.[11b] 93 °C/13 mm) afforded pure **2i** in 56% yield, with the remainder decomposing: $R_f$ 0.16 (10% EtOAc in hexanes); $^1H$ NMR δ 7.41 (dd, 1 H, $J$ = 1.8–0.9), 6.39 (m, 2 H), 5.92 (s, 1 H ), 4.06 (m, 4 H); IR (neat) 3125 (m, =CH), 2960 (s), 2894 (s), 1604 (m, C=C), 1505 (m), 1357 (s), 1227 (s), 1157 (s, CO), 1075 (s, CO), 937 (s), 890 (s), 750 (s) $cm^{-1}$.

**1,3-Dioxolane of 5-Bromo-2-thiophenecarboxaldehyde (2j).**[11c] The reactants were stirred at −78 °C for 20 h. After workup, the crude product was chromatographed through silica gel ($Et_2O$ as eluent), and the volatile components were removed by rotovapping followed by oil pump evacuation (25 °C, 2.0 h, 0.1 mm). Dioxolane **2j** was obtained in quantitative yield: $R_f$ 0.54 (40% EtOAc in hexanes); $^1H$ NMR δ 6.92 (s, 2 H), 6.01 (s, 1 H), 4.04 (m, 4 H); IR (neat) 3098 (w, =CH), 2960 (s), 2888 (s), 1670 (m, C=C), 1553 (m, C=C), 1444 (s), 1381 (s), 1205 (s), 1057 (s, CO), 956 (s), 805 (s) $cm^{-1}$.

**1,3-Dioxolane of 3-Ethoxymethacrolein (2k).** The reactants were stirred at −78 °C for 4 h and then at room temperature for 17 h. NMR analysis of the crude mixture showed 50% conversion to the desired product. Microdistillation gave a mixture of **2k** and unreacted **1k**: $^1H$ NMR (**2k**) δ 6.23 (br s, 1 H), 5.07 (s, 1 H), 3.93 (m, 4 H), 3.82 (q, 2 H, $J$ = 7.0), 1.58 (d, 3 H, $J$ = 1.3), 1.24 (t, 3 H, $J$ = 7.0); exact mass calcd for $C_8H_{14}O_3$ 158.0943, found 158.0940.

**1,3-Dioxolanes of 4-Acetylcyclohex-1-ene-1-carboxaldehyde (6 and 7).** Compound **5** (1.02 equiv) was stirred with $Me_3SiOTf$ (0.05 equiv) and BTSE (1.00 equiv) in dichloromethane at −78 °C for 20 h. After workup, a mixture of dioxolanes was obtained in 76% yield. The ratio of **6** to **7** by GC was 1:27. Dioxolane **6** was identified by GC and $^1H$ NMR comparison with an authentic sample: GC retention time 10.69 min (125 °C); $^1H$ NMR δ 5.93 (br s, 1 H), 5.12 (s, 1 H), 3.94 (m, 4 H), 2.17 (s, 3 H). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.25; H, 8.34. Dioxolane **7**: GC retention time 10.18 min (125 °C); $^1H$ NMR δ 9.43 (s, 1 H), 6.79 (m, 1 H), 3.95 (br s, 4 H), 1.30 (s, 3 H); exact mass calcd for $C_{10}H_{13}O_3$ ($M^+ - CH_3$) 181.0865, found 181.0873.

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(11) Known compound: (a) Davis, H. A.; Brown, R. K. *Can. J. Chem.* **1971**, *49*, 2563. (b) Hinz, A.; Meyer, G.; Schücking, G. *Chem. Ber.* **1943**, *76*, 676. (c) Johnson, A. L. *J. Org. Chem.* **1976**, *41*, 1320.