JOC*Note*

Fluoride-Assisted Regioselective Conversion of Functionalized Furans to α-Substituted γ-Hydroxybutenolides Using Singlet Oxygen

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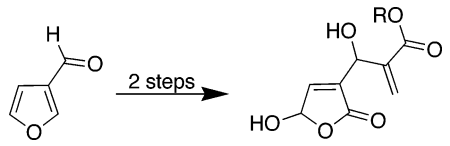
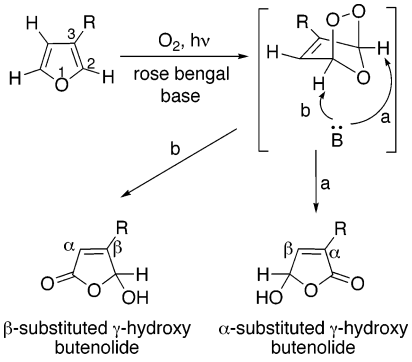


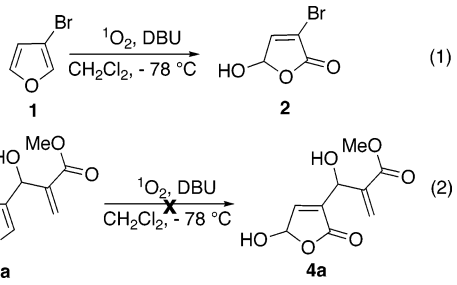
A facile synthesis of α-substituted γ-hydroxybutenolides from 3-furfural was achieved using a Baylis−Hillman reaction followed by singlet oxygen oxidation. The regioselectivity of this conversion was controlled by using TBAF.

The γ-hydroxybutenolide moiety is frequently observed in bioactive natural products. The α-substituted γ-hydroxybutenolides have found utility as antimicrobial compounds, while the β-substituted γ-hydroxybutenolides are known to have anticancer or anti-inflammatory properties.[1] This has prompted ongoing interest in the development of facile and selective synthetic methods for rapidly accessing diverse and highly functionalized analogues of this class of structures.[2] Photooxidative conversion of furans to α- or β-substituted γ-hydroxybutenolides (Scheme 1), among other transformations amenable to practical combinatorial synthesis, has in particular received significant attention due to the mild and green nature of this transformation from readily available starting materials.[3] The use of a simple alkyl amine base to confer regioselectivity for the β-substituted γ-hydroxybutenolides in this transformation is an established strategy;[3d] however, the selectivity for the α-substituted γ-hydroxybutenolide has met with considerable challenges. Most recently, Aquino and co-workers reported the first example of a regioselective conversion of a bromo-furan to the α-substituted γ-hydroxybutenolide using DBU (eq 1).[3f] This method, however, resulted in complex mixtures of products when we applied it to more functionalized furans such as **3a** (eq 2).

SCHEME 1



We have previously reported using the Baylis−Hillman reaction for synthesizing 3-hydroxyacrylate furans, from 3-furfural and a range of acrylates, and their subsequent conversion selectively to the β-substituted γ-hydroxybutenolides using Hünig's base.[4] Herein, we report a regioselective conversion of these highly functionalized furans to α-substituted γ-hydroxybutenolide by simply switching the base to TBAF during the photooxidation reaction. Nucleophilic halides have been shown to catalyze the alkylation of butenolides masked as alkoxyfurans.[5] In this Note, the use of a fluoride anion is proposed to exert its effect on the regioselectivity for α-substituted γ-hydroxybutenolide through H-bonding to the 3′-hydroxy group in close proximity.



The Baylis−Hillman reaction was found to be an economic and mild method for synthesizing 3-hydroxyacrylate furans with moderate yields between 30 and 70% (unreacted starting materials recovered).[4] From our previous mechanistic studies of the photooxidation reaction of the 3-hydroxyacrylate furans in the presence of Hünig's base, the key intermediate observed by NMR was a salt, **5**, formed between the ammonium cation and an open-ring, butenolide anion (Scheme 2). The formation of the final butenolide required protonation as a separate step. This led us to examine the effect of quaternary ammonium salts in the photooxidation reaction. It was hypothesized that different salts may prefer different pathways of the endoperoxide opening.

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(1) For recent examples of α- or β-substituted bioactive butenolides found in nature, see: (a) Wright, A. D.; Nys, R. D.; Angerhofer, C. K.; Pezzuto, J. M.; Gurrath, M. *J. Nat. Prod.* **2006**, *69*, 1180−1187. (b) Keyzers, R. A.; Davies-Coleman, M. T. *Chem. Soc. Rev.* **2005**, *34*, 355−365. (c) Charan, R. D.; McKee, T. C.; Boyd, M. R. *J. Org. Chem.* **2001**, *64*, 661−663.

(2) For recent reviews of synthetic routes to butenolides, see: (a) Brückner, R. *Curr. Org. Chem.* **2001**, *5*, 679−718. (b) Carter, N. B.; Nadany, A. E.; Sweeney, J. B. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2324−2342.

(3) For initial work in photooxidative conversion of furans to γ-hydroxybutenolides, see: (a) Grimminger, W.; Kraus, W. *Lieb. Ann. Chem.* **1979**, *10*, 1571−1576. (b) Brownbridge, P.; Chan, T. H. *Tetrahedron Lett.* **1980**, *21*, 3431−3434. (c) Katsumura, S.; Hori, K.; Fugiwara, S.; Isoe, S. *Tetrahedron Lett.* **1985**, *26*, 4625−4628. (d) Kernan, M. R.; Faulkner, D. J. *J. Org. Chem.* **1988**, *53*, 2773−2776. For a recent summary of the use of singlet oxygen in biomimetic syntheses, see: (e) Margaros, I.; Montagnon, T.; Tofi, M.; Pavlakos, E.; Vassilikogiannakis, G. *Tetrahedron* **2006**, *62*, 5308−5317. For a very recent example of regioselective synthesis of γ-hydroxybutenolides, see: (f) Aquino, M.; Bruno, I.; Riccio, R.; Gomez-Paloma, L. *Org. Lett.* **2006**, *8*, 4831−4834.

(4) Patil, S. N.; Liu, F. *Org. Lett.* **2007**, *9*, 195−198.

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SCHEME 2

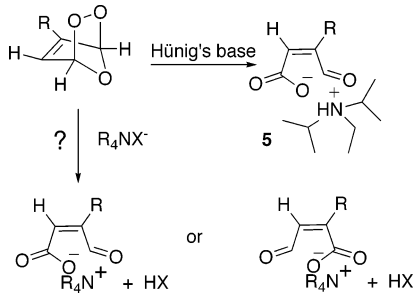
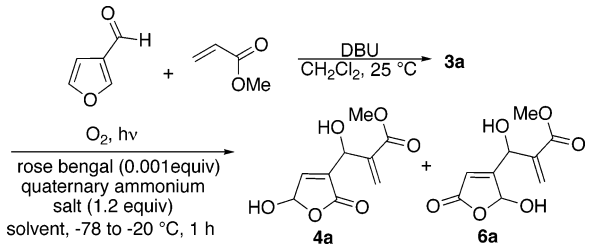


TABLE 1. Effects of Quaternary Ammonium Salts and Solvents on the Conversion of 3a to 4a and 6a



entry	quaternary ammonium salt[a]	solvent	ratio **4a**/**6a**[b]
1	TBAH in MeOH[c]	MeOH	0:1
2	TBAC	MeOH	1:13
3	TBAF in THF[c]	MeOH	5:1
4	TBAI	THF	complex mixture
5	TBAC	THF	complex mixture
6	TBAF in THF	THF	3:1
7	TBAF in THF	DCM	7:1

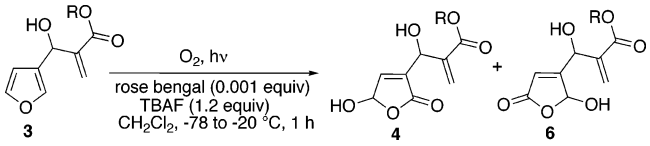
[a] Abbreviations: tetrabutylammonium hydroxide (TBAH), tetrabutylammonium iodide (TBAI), tetrabutylammonium chloride (TBAC), and tetrabutylammonium fluoride (TBAF). [b] Ratio was determined by NMR. [c] These reagents were commercially available as solutions.

When a series of tetrabutylammonium salts was applied (Table 1), the usual regioselectivity for the β-substituted γ-hydroxybutenolide was observed for TBAH and TBAC in methanol, while this selectivity was reversed with TBAF, which provided, interestingly, α-substituted γ-hydroxybutenolide as the major isomer.

As this preference for the α-isomer of γ-hydroxybutenolide controlled by a salt in singlet oxygen oxidation is unprecedented, we sought to examine the role of TBAF in this reaction further. A panel of quaternary ammonium fluorides, including tetraethylammonium fluoride (TEAF), tetrahexylammonium fluoride (THAF), and TBAF, was applied to the photooxidation reaction of **3a** in dichloromethane. The selectivity for the α-isomer of γ-hydroxybutenolide was consistently observed for all three fluorides, with the regioselectivity ratio reduced to around 2 or 4:1 in the TEAF or THAF case. This suggested that the regioselectivity was dependent on the fluoride anion and that the bulkiness of the alkyl ammonium cation had only a minor effect in determining the deprotonation pathway of the endoperoxide.

We then investigated the scope and substrate effect of this fluoride-assisted, regioselective conversion of furans to butenolides with TBAF as the fluoride source. A group of highly functionalized furans, **3a**−**h**, synthesized as the BH adducts of 3-furfural with a variety of acrylates, was subjected to this reaction in the presence of 1.2 equiv of TBAF in dichloromethane (Table 2). These substrates differed from one another

TABLE 2. TBAF-Assisted Regioselective Conversion of 3 to 4 and 6



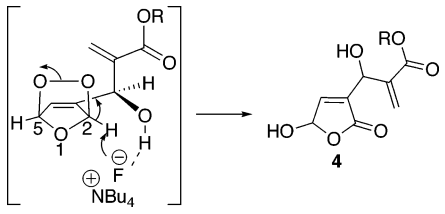
entry	furan	R	%yield[a] 4/6
1	**3a**	Me	84:12
2	**3b**	Et	86:11
3	**3c**	Butyl	95:0
4	**3d**	dodecyl	91:3
5	**3e**	2-chloroethyl	92:3
6	**3f**	Allyl	87:11
7	**3g**	benzyl	89:0
8	**3h**	cinnamyl	90:4

[a] Isolated yields.

only in the ester group of the hydroxy acrylate side chain attached to the furan core. The side chain variation on the furan core was influential on the regioselectivity of the photooxidation. The bulkiness of the side chain seemed to somewhat enhance the regioselectivity ratio for the α-isomer, even though the deprotonation site leading to the α-isomer must be at the sterically more hindered proton. For example, the regioselectivity ratio for **3a** (entry 1, Table 2) was 7:1, while that for **3h**, which has a larger cinnamyl side chain (entry 8, Table 2), was 23−25:1. In the case of **3g** (entry 7, Table 2), the α-isomer was the sole γ-hydroxybutenolide isolated.

Initially, the isolated yields of butenolides **4a**−**h** from this transformation were only moderate between 30 and 60%. This was inconsistent with the proton NMR spectra of the crude mixtures of the reactions that indicated nearly quantitative deprotonation of the endoperoxide to reach the salt intermediate. It was hypothesized that the subsequent protonation step may not have proceeded efficiently. Optimization of the purification step revealed that DOWEX acidic resins would suffice in protonating the salt intermediate and furnish the desired butenolides in high yields without aqueous workup. The utility of these resins in TBAF workup was also highlighted by a recent report on the synthesis of halichondrin.[6]

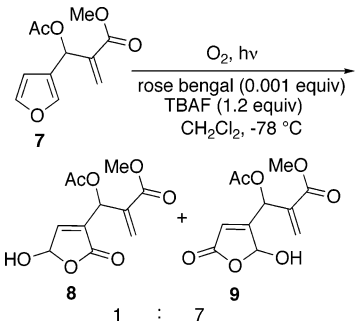
This fluoride-based regioselectivity prompted us to investigate further the possible mechanism behind this preferred deprotonation path in opening the endoperoxide intermediate. It was postulated that the secondary hydroxy group could guide the



incoming fluoride through H-bonding toward the H2 proton for deprotonation, which would lead to the regioselective formation of the α-substituted γ-hydroxybutenolides. To test this hypothesis, the hydroxy group of **3a** was protected as an acetate to provide **7**, which was then subjected to the photooxidation in the presence of TBAF (Scheme 3). The regioselectivity for the α-isomer, **8**, was in this case lost, in the absence of this

(6) Kaburagi, Y.; Kishi, Y. *Org. Lett.* **2007**, *9*, 723−726.

SCHEME 3



H-bonding group, and the β-substituted γ-hydroxybutenolide, **9**, became the predominant isomer. Presumably, in the absence of the H-bond donor, the preferred deprotonation site would be the less hindered H5, as seen in our previous study with a bulky Hünig's base, to form the β-substituted butenolide.[4] The relationship seen in the **3a**−**h** series between the bulkiness of the side chain and the regioselectivity ratio for the α-isomer through the more hindered deprotonation pathway supports indirectly this postulate, as the transition state could be more conformationally rigidified in the presence of a bulkier side chain to facilitate a stronger H-bonding interaction between the fluoride anion and the 3′-hydroxy group.

In conclusion, this work illustrates the utility of using a simple reagent, TBAF, to control the regioselective formation of α-substituted γ-hydroxybutenolides from highly functionalized 3′-hydroxyacrylate furans using singlet oxygen. The role of TBAF in conferring the regioselectivity is attributed to the H-bonding interaction between the fluoride anion and the OH group in close proximity to bias one of the two deprotonation pathways from the key endoperoxide intermediate formed upon photooxidation. This selective and facile synthesis presents an efficient entry to functionalized butenolides as useful synthons for further transformations.

Experimental Section

General Procedure for the Preparation of Baylis−Hillman Adducts. DBU (475 mg, 3.12 mmol) was added to a stirred solution of an acrylate (3.75 mmol) and 3-furfural (300 mg, 3.12 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred under nitrogen at room temperature for 2 days. Upon finishing, dichloromethane (15 mL) was added to the reaction mixture and neutralized with 1 N HCl, followed by washing with water and brine. The organic layer thus obtained was dried over Na_2SO_4, filtered, and evaporated to provide a crude mixture for further purification by column chromatography (petroleum ether/ethyl acetate 2:1) to afford the Baylis−Hillman adduct as a colorless oil.

Methyl 2-(Furan-3yl(hydroxy)methyl)acrylate (3a). Yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (d, J = 4.0 Hz, 1H), 3.76 (s, 3H), 5.50 (d, J = 4.0 Hz, 1H), 5.87 (s, 1H), 6.30 (s, 1H), 6.35 (s, 1H), 7.37−7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 66.2, 109.5, 126.4, 127.0, 140.3, 141.7, 144.1, 167.8; IR (thin film/NaCl) 1719 cm^{-1}; ESI [M + Na$^+$]: 205.047658, calcd for $(C_9H_{10}O_4Na)^+$: 205.047679.

Ethyl 2-(Furan-3-yl(hydroxy)methyl)acrylate (3b). Yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 2H), 3.12 (bs, 1H), 4.22 (q, J = 7.1 Hz, 2H), 5.50 (s, 1H), 5.85 (s, 1H), 6.30 (s, 1H), 6.36−6.35 (m, 1H), 7.39−7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 61.5, 67.3, 109.5, 126.1, 127.2, 140.3, 142.0, 143.8, 166.9; IR (thin film/NaCl) 3411, 1712 cm^{-1}; ESI [M + Na$^+$]: 219.062522, calcd for $(C_{10}H_{12}O_4Na)^+$: 219.063329.

Butyl 2-(Furan-3-yl(hydroxy)methyl)acrylate (3c). Yield: 49%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91−0.94 (m, 3H), 1.41−1.36 (m, 2H), 1.67−1.60 (m, 2H), 3.09 (d, J = 6.3 Hz, 1H), 4.17 (t, J = 6.6 Hz, 2H), 5.51 (d, J = 6.3 Hz, 1H), 5.85 (s, 1H), 6.30 (s, 1H), 6.36 (d, J = 0.8 Hz, 1H), 7.37 (s, 1H), 7.38 (d, J = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.6, 31.0, 65.4, 67.4, 109.5, 126.2, 127.2, 140.3, 142.0, 143.8, 166.9; IR (thin film/NaCl) 1719 cm^{-1}; ESI [M + Na$^+$]: 247.095717, calcd for $(C_{12}H_{16}O_4Na)^+$: 247.094629.

Dodecyl 2-(Furan-3-yl(hydroxy)methyl)acrylate (3d). Yield: 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.26 (s, 18H), 1.66−1.54 (m, 2H), 3.12 (d, J = 6.3 Hz, 1H), 4.15 (t, J = 6.6 Hz, 2H), 5.51 (d, J = 6.1 Hz, 1H), 5.85 (s, 1H), 6.29 (s, 1H), 6.36 (s, 1H), 7.38−7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 23.2, 26.2, 26.4, 29.0, 29.7, 29.8, 29.9, 30.0, 30.1, 32.4, 65.7, 67.3, 109.6, 126.1, 127.2, 140.3, 142.1, 143.7, 166.9; IR (thin film/NaCl) 2929, 2855, 1718 cm^{-1}; ESI [M + Na$^+$]: 359.219551, calcd for $(C_{20}H_{32}O_4Na)^+$: 359.219830.

Benzyl 2-(Furan-3-yl(hydroxy)methyl)acrylate (3g). Yield: 47%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 1H), 5.20 (s, 2H), 5.54 (s, 1H), 5.90 (s, 1H), 6.36−6.34 (m, 2H), 7.38−7.28 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.9, 67.3, 109.5, 126.7, 127.5, 128.2, 128.6, 128.9, 129.1, 135.9, 140.4, 141.8, 143.8, 166.6; IR (thin film/NaCl) 3055, 2985, 1717 cm^{-1}; ESI [M + Na$^+$]: 281.078810, calcd for $(C_{15}H_{14}O_4Na)^+$: 281.078979.

General Procedure for Singlet Oxygen Oxidation Reaction. To a mixture of a Baylis−Hillman adduct (0.30 mmol) and Rose Bengal (3 mg, 0.003 mmol) in anhydrous dichloromethane (70 mL) was added tetrabutylammonium fluoride, 1.0 M solution in tetrahydrofuran (0.36 mmol). The reaction mixture was then exposed to singlet oxygen (generated from air with a 150 W flood light) at −78 °C for 1 h. The reaction mixture was then warmed to −20 °C, and the solvent was removed under vacuum at room temperature. The crude mixture as solution in acetonitrile (2 mL) was then passed through Poly Prep columns containing a prefilled AG50W-X8 (H^+) resin of ion exchange capacity 3.4 (nominal mequiv/2 mL of resin) using 8 mL of acetonitrile. The residue, after the protonation step, was filtered through silica gel to remove trace impurities (silica gel, 60 Å, 0.06−0.2 mm, 70−230 mesh) and further purified by flash column chromatography to afford the butenolide as a colorless oil.

Methyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)-methyl)acrylate (4a). Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.33 (s, 1H), 6.05 (s, 1H), 6.14 (s, 1H), 6.43 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 66.7, 97.7, 129.0, 138.1, 138.3, 146.4, 166.8, 170.5; IR (thin film/NaCl) 3421, 1759, 1715 cm^{-1}; ESI [M + Na$^+$]: 237.037562, calcd for $(C_9H_{10}O_6$-Na)$^+$: 237.037508.

Ethyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)-methyl)acrylate (4b). Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 5.31 (s, 1H), 6.03 (bs, 1H), 6.12 (s, 1H), 6.42 (s, 1H), 7.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 62.0, 66.4, 66.5, 97.8, 128.5, 128.8, 138.1, 138.6, 146.6, 166.4, 170.7; IR (thin film/NaCl) 1766, 1712 cm^{-1}; ESI [M + Na$^+$]: 251.053500, calcd for $(C_{10}H_{12}O_6Na)^+$: 251.053158.

Butyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)-methyl)acrylate (4c). Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 3H), 1.44−1.34 (m, 2H), 1.69−1.62 (m, 2H), 4.0−3.9 (bs, 1H), 4.17 (t, J = 6.6 Hz, 2H), 4.9−4.7 (bs, 1H), 5.31 (s, 1H), 6.02 (s, 1H), 6.13 (s, 1H), 7.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.6, 30.9, 65.8, 66.6, 97.8, 128.6, 138.2, 138.6, 146.4, 166.5, 170.6; IR (thin film/NaCl) 1767, 1709 cm^{-1}; ESI [M + Na$^+$]: 279.086116, calcd for $(C_{12}H_{16}O_6Na)^+$: 279.084458.

Dodecyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)-methyl)acrylate (4d). Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.4−1.2 (m, 18 H), 1.8−1.5 (m, 2H),

3.9−3.7 (bs, 1H), 4.16 (t, J = 6.74 Hz, 2H), 5.32 (s, 1H), 6.02 (s, 1H), 6.13 (s, 1H), 6.41 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 23.2, 26.4, 28.9, 29.7, 29.8, 29.98, 30.05, 30.1, 32.4, 66.1, 65.0, 97.7, 128.6, 138.4, 138.5, 146.0, 166.5, 170.2; IR (thin film/NaCl) 1765, 1717 cm^{-1}; ESI [M + Na$^+$]: 319.209785, calcd for $(C_{20}H_{32}O_6Na)^+$: 319.209659.

2-Chloroethyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)methyl)acrylate (4e). Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (t, J = 5.6 Hz, 2H), 4.43−4.40 (m, 2H), 5.36 (s, 1H), 6.10 (s, 1H), 6.16 (s, 1H), 6.51 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0, 65.1, 66.6, 98.1, 129.7, 138.2, 146.0, 165.7, 170.3; IR (thin film/NaCl) 3409, 1764, 1710 cm^{-1}; ESI [M + Na$^+$]: 287.010534, calcd for $(C_{10}H_{11}O_6ClNa)^+$: 287.011236.

Allyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)methyl)acrylate (4f). Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (dt, J = 5.8, 1.3 Hz, 2H), 5.36−5.27 (m, 3H), 5.93 (ddt, J = 17.2, 10.4, 5.9 Hz, 1H), 6.06 (s, 1H), 6.12 (s, 1H), 6.46 (s, 1H), 7.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.4, 66.8, 97.7, 119.5, 129.0, 132.0, 138.1, 138.4, 146.3, 166.0, 170.4; IR (thin film/NaCl) 1767, 1718 cm^{-1}; ESI [M + Na$^+$]: 263.052578, calcd for $(C_{11}H_{12}O_6Na)^+$: 263.053158.

Benzyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)methyl)acrylate (4g). Yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (d, J = 4.2 Hz, 2H), 5.33 (s, 1H), 6.03 (s, 1H), 6.05 (s, 1H), 6.46 (s, 1H), 7.02 (s, 1H), 7.30−7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.4, 67.5, 97.7, 128.7, 128.8, 129.0, 129.1, 129.2, 135.6, 138.4, 146.5, 166.0, 170.5; IR (thin film/NaCl) 1767, 1709 cm^{-1}; ESI [M + Na$^+$]: 313.069581, calcd for $(C_{15}H_{14}O_6Na)^+$: 313.068808.

Cinnamyl 2-(Hydroxy(5-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)methyl)acrylate (4h). Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (d, J = 5.5 Hz, 2H), 5.34 (s, 1H), 6.06 (s, 1H), 6.10 (s, 1H), 6.28 (dt, J = 15.4, 6.6 Hz, 1H), 6.48 (s, 1H), 6.67 (d, J = 15.8 Hz, 1H), 7.11 (s, 1H), 7.38−7.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.0, 66.4, 98.5, 122.8, 127.1, 128.7, 128.9, 129.1, 135.3, 136.4, 138.0, 138.7, 146.9, 166.1, 170.9; IR (thin film/NaCl) 1769, 1709 cm^{-1}; ESI [M + Na$^+$]: 339.084760, calcd for $(C_{17}H_{16}O_6Na)^+$: 339.084458.

Methyl 2-(Acetoxy(furan-3-yl)methyl)acrylate (7). Yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 2H), 3.75 (s, 1H), 5.92 (s, 1H), 6.36 (s, 1H), 6.38 (s, 1H), 6.66 (s, 1H), 7.36 (s, 1H), 7.42−7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.6, 66.4, 109.9, 123.7, 126.2, 139.6, 141.7, 143.8, 165.9, 169.9; ESI [M + Na$^+$]: 247.057789, calcd for $(C_{11}H_{12}O_5Na)^+$: 247.058243.

Methyl 2-(Acetoxy(2-hydroxy-5-oxo-2,5-dihydrofuran-3-yl)methyl)acrylate (9). Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 1H), 3.81 (s, 1H), 6.04 (s, 1H), 6.11 (s, 1H), 6.30 (s, 1H), 6.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 53.2, 66.4, 68.2, 98.8, 120.5, 121.7, 128.7, 130.3, 169.8; ESI [M + Na$^+$]: 279.047662, calcd for $(C_{11}H_{12}O_7Na)^+$: 279.048073.

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Supporting Information Available: NMR spectra of **3a**−**h**, **4a**−**h**, **7**, and **9** and ^{1}H NMR spectra of the product mixtures of the singlet oxygen oxidation of furans after ion exchange and filtering. This material is available free of charge via the Internet at http://pubs.acs.org.

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