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Regiocontrolled Synthesis of γ-Hydroxybutenolides via Singlet Oxygen-Mediated Oxidation of 2-Thiophenyl Furans

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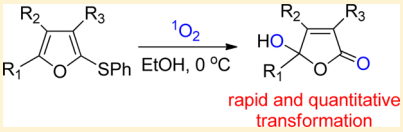
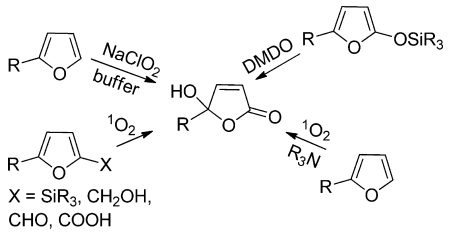
Supporting Information

ABSTRACT: Photooxygenation of 2-thiophenyl-substituted furans in ethanol leads to the rapid, regiocontrolled, and quantitative synthesis of γ-hydroxybutenolides. The carbonyl group in butenolide holds the position of thiophenyl moiety in reacting furans. Decomposition of the initially formed [4 + 2] endoperoxide into products through a radical chain mechanism is proposed, as the fate of thiophenyl moiety is its transformation into ethyl phenylsulfenate (PhS-OEt) and diphenyldisulfide. Under the reaction conditions, the sulfenate is fast oxidized into the corresponding sulfinate.



The γ-hydroxybutenolide moiety [5-hydroxyfuran-2(5*H*)-ones] appears as an essential unit in a vast variety of bioactive natural products and other substances of biomedical significance. They can be either unsubstituted (hydrogen) at the γ-position (e.g., dysidiolide,[1] manoalide,[2] cacospongionolides,[3] etc.) or substituted (e.g., PD 156707,[4] caribenol A,[5] annomolon A,[6] etc.). As a consequence, several methodologies for the construction of this class of compounds have been developed, including acid-catalyzed inter or intramolecular condensation,[7] Knoevenagel condensation,[8] selective reduction of substituted maleic anhydrides,[9] carbonylative oxidative cycloaddition among aldehydes and alkynes,[10] and acid-catalyzed annulation of alkynes with α-keto acids.[11] Yet, the most common and straightforward approach relies on suitable furan oxidation by various means (Scheme 1), such as

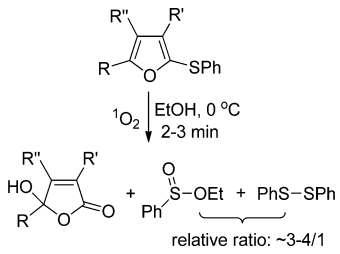
Scheme 1. Protocols for the Synthesis of γ-Hydroxybutenolides Using Furans as Precursors and a Suitable Oxidant



treatment of 2-trialkylsilyloxyfurans with dimethyldioxirane,[12] $NaClO_2$-mediated oxidation of simple furans,[13] oxidation with $K_2Cr_2O_7$,[14] and by using singlet molecular oxygen ($^1O_2$) as a green oxidant. The known protocols for the synthesis of γ-hydroxybutenolides utilizing $^1O_2$ are (1) photooxygenation of furans having at least one nonsubstituted *ortho*-position, in the presence of a hindered base,[15] where the initially formed [4 + 2] endoperoxide (ozonide) yields product(s) via a Kornblum-DeLaMare rearrangement; (2) photooxygenation of 2-trialkylsilylfurans,[16] where the [4 + 2] silyl endoperoxide undergoes ring opening rearrangement followed by hydrolysis; and (3) photooxygenation of furans bearing at the *ortho*-position a hydroxyalkyl group, an aldehyde, or a carboxylate.[17]

In this manuscript, we present a new and highly efficient protocol for the synthesis of γ-hydroxybutenolides, using the easily synthesized 2-thiophenyl-substituted furans as precursors (Table 1). Methylene Blue-sensitized photooxygenation of these compounds in ethanol as solvent at 0 °C provides after 2−3 min of irradiation (0.2−0.3 mmol scale) their clean and quantitative transformation into γ-hydroxybutenolides (Scheme 2). A protic solvent, such as ethanol or methanol, is essential as

Scheme 2. Photooxygenation of 2-Thiophenyl Furans in Ethanol



will be analyzed in the following mechanistic discussion. In nonprotic solvents (DCM, chloroform), a mixture of products is formed. The fate of thiophenyl moiety in reacting furans is its final transformation into ethyl phenylsulfinate [PhS(O)-OEt] and diphenyldisulfide (PhSSPh) in a relative ratio sulfinate/disulfide ~4/1 to 3/1 for all substrates examined. The side products were isolated and characterized by comparison with an authentic sample for disulfide and to the known spectroscopic data of the sulfinate esters (methyl or ethyl, depending on the solvent used).[18] Note that in contrast to our photooxygenation results of 2-substituted thiofurans, the

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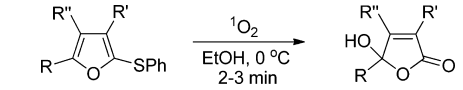
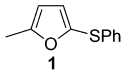
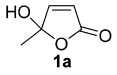
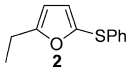
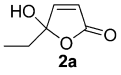
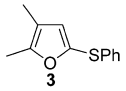
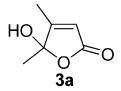
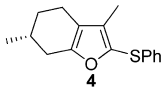
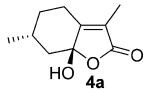
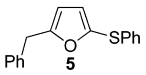
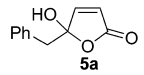
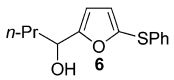
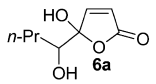
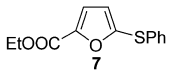
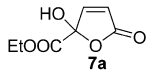
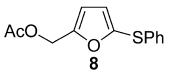
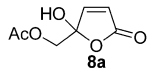
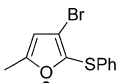
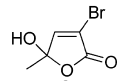
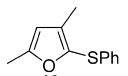
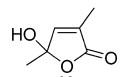
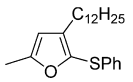
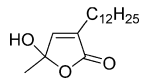
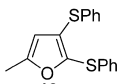
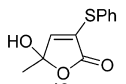
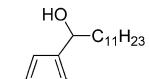
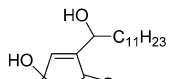
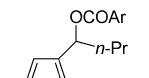
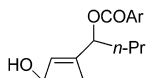
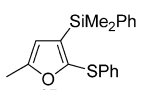
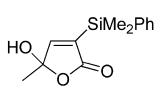
Table 1. Synthesis of γ-Hydroxybutenolides via Photooxygenation of 2-Thiophenyl Furans in Ethanol



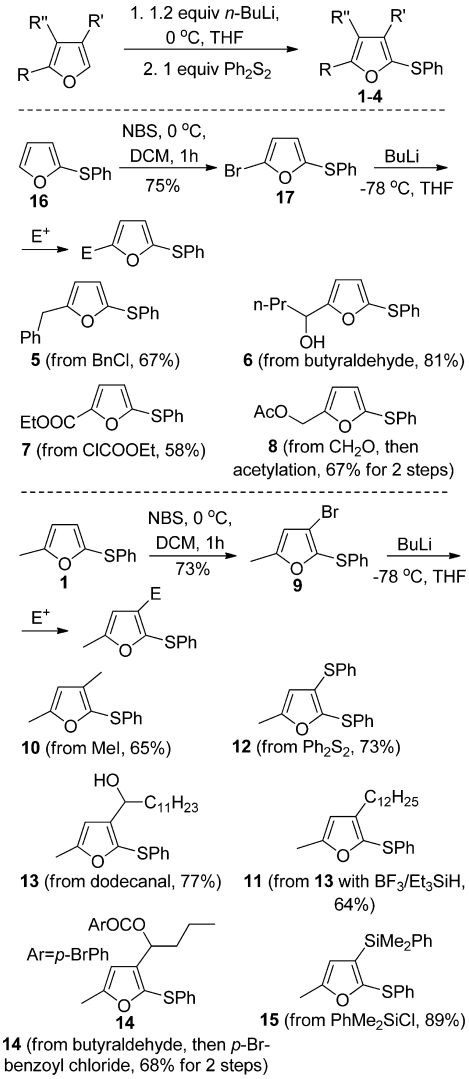
Furan	Product	Isolated yield (%)
 **1**	 **1a**	75%
 **2**	 **2a**	72%
 **3**	 **3a**	74%
 **4**	 **4a**	65%
 **5**	 **5a**	68%
 **6**	 **6a**	73%[a]
 **7**	 **7a**	62%
 **8**	 **8a**	69%
 **9**	 **9a**	71%
 **10**	 **10a**	72%
 **11**	 **11a**	71%
 **12**	 **12a**	66%
 **13**	 **13a**	70%[b]
 **14** Ar = *p*-Bromophenyl	 **14a**	68%[b]
 **15**	 **15a**	74%

[a]Mixture of diastereomers (~50/50). [b]Mixture of diastereomers (~55/45).

reaction of singlet oxygen with 2,5-bis-thiophenylfuran derivatives in methanol affords *O*-methyl-*S*-phenyl thiomaleates.[19]

In Table 1, we present the scope and generality of this method for the synthesis of a series of γ-hydroxybutenolides, using suitably substituted 2-thiophenylfurans whose syntheses is presented in Scheme 3. Substrates **1**–**4** were obtained by direct lithiation of the corresponding furans with *n*-BuLi followed by quenching with PhSSPh in ~60–75% yield.[20] Substrates **5**–**8** were synthesized as follows: *ortho*-bromination of 2-(phenylthio)furan, **16**, with 1 equiv of NBS in dry DCM at 0 °C for 1 h afforded 2-bromo-5-(phenylthio)furan (**17**) in 75% yield. The bromofuran **17** was treated with *n*-BuLi (−78 °C, 30 min, THF) and then quenched with benzyl bromide (to produce **5**, 67% yield), with butyraldehyde (to produce **6**, 81% yield), with ethyl chloroformate (to produce **7**, 58% yield), and with paraformaldehyde to produce (5-(phenylthio)furan-2-yl)methanol (**18**) in 70% yield. Subsequently, **18** was acetylated with Ac_2O to form **8** in 95% yield. Substrates **9**–**15** were synthesized as follows: bromination of **1** with 1 equiv of NBS in dry DCM at 0 °C for 1 h, afforded bromofuran **9**[20] in 73%

Scheme 3. Synthesis of the 2-Thiophenyl-Substituted Furans Used in This Study



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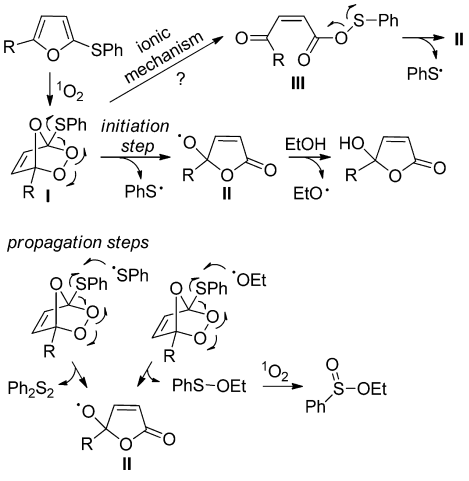
yield. The bromofuran was transmetalated with *n*-BuLi (−78 °C, 30 min, THF) and then quenched with CH_3I to produce **10** (65% yield), with PhSSPh to produce **12** (73% yield), with $PhMe_2SiCl$ to produce **15** (89% yield), and with dodecanal to produce **13** (77% yield). Reduction of **13** with BF_3/Et_3SiH afforded **11** in 64% yield. Finally, furan **14** was prepared in 68% overall yield by quenching transmetalated **9** with butyraldehyde to form **19**,[20] followed by esterification with *p*-bromobenzoyl chroride (Et_3N, 4-DMAP, DCM).

After photooxygenation, the desired γ-hydroxybutenolides were purified by column chromatography and the isolated yields ranged between 62 and 75%. The reaction tolerates as series of functionalities in furan side chains such as alcohol, esters, thioether, halide, or silyl group. Although the photooxygenation of 2-thiophenylfurans is quantitative and clean, the lower isolated yields of products probably reflects the partial tendency of cyclic butenolides to isomerize into *trans*-keto acids while in silica gel. The current protocol has the advantage that not only the directing thiophenyl moiety can be easily introduced at the *ortho* position of the furan ring, but it also directs bromination of furans, so it is feasible to achieve the regiocontrolled synthesis of a series of γ-hydroxybutenolides, such as **9a**−**15a**.

A useful observation in terms of mechanistic discussion was that after ∼1 min of photooxygenation of the model compound **1** (Table 1) in ethanol, the sulfenate ester PhS-OEt[21] can be detected by ^{1}H NMR (see Supporting Information) in 1:2 to 1:3 relative ratio compared with ethyl phenylsulfinate, but after an additional 1−2 min of irradiation, it had been completely oxidized into the corresponding sulfinate, which as noted above is the final fate of the thiophenyl moiety of all reacting furans in our studies, along with diphenyldisulfide. Therefore, we consider ethyl phenylsulfenate (PhSOEt) as a primary reaction product. The formation of byproduct PhSSPh dictates a free radical decomposition pathway of the initially formed endoperoxide **I**, shown in Scheme 4. After cleavage of C−S and O−O bonds in **I**, the resulting butenyloxy radical **II** abstracts a hydrogen atom from the protic solvent to generate the γ-hydroxybutenolide. The ethoxy as well as the thiophenyl radicals lead to **II** through the depicted propagation steps (Scheme 2) and to the observed side products ethyl phenylsulfenate (PhSOEt) and diphenyldisulfide (PhSSPh). Oxidation of PhSOEt under the reaction conditions by singlet oxygen generates ethyl phenylsulfinate.[22] Note that PhS-OEt or PhS(O)-OEt do not arise from PhSSPh under the reaction conditions, as verified by an independent experiment. In our hands, diphenyldisulfide was inert against $^1O_2$, as already well established in the literature.[23] The possibility that persulfenate ester **III** is formed, through a mechanism analogous to the photooxygenation of silylfurans,[16a] followed by radical scission of the O−S bond (initiation) and subsequent propagation steps cannot be excluded. A complete ionic mechanism (ethanol attack on sulfur of intermediate **I** to form ethyl phenylsulfenate accompanied by peroxide opening to form hydroxybutenolide) is less likely to occur, as formation of side product diphenyldisulfide cannot be justified. In addition, thiophenol (formed by any ionic pathway) was excluded as precursor of diphenyldisulfide, as in separate experiment (methylene-blue sensitized photooxygenation of thiophenol in ethanol for 5 min) no such transformation was noticed.

In conclusion, we have shown herein a novel and quite simple method for the quantitative formation of γ-hydrobutenolides via photooxygenation of 2-thiophenylfurans in ethanol. A radical-chain decomposition of the initially formed [4 + 2] endoperoxide is proposed as the most rational mechanism. The reacting furans can be easily synthesized from simple precursors. Our protocol adds a new and useful application of furan photooxygenation in synthetic organic chemistry.[24]

Scheme 4. Possible Mechanisms for the Formation of γ-Hydroxybutenolide via Photooxygenation of a 2-Thiophenyl-Substituted Furan in Ethanol



EXPERIMENTAL SECTION

General. The reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F-254). Flash column chromatography was carried out on SiO_2 (silica gel 60, particle size 0.040−0.063 mm). NMR spectra were recorded on 300 and 500 MHz instruments. High resolution mass spectra (HRMS) were recorded using ESI-Orbitrap and TOF-ESI techniques.

Spectroscopic Data of Synthesized Furans. *2-Methyl-5-(phenylthio)furan (**1**):*[20] Colorless oil (1.82 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.27−7.22 (m, 2H), 7.19−7.13 (m, 3H), 6.67 (d, J = 3.0 Hz, 1H), 6.08 (dq, J_1 = 3.0 Hz, J_2 = 1.0 Hz, 1H), 2.33 (d, J = 1.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 156.8, 140.2, 137.0, 129.0 (2C), 127.0 (2C), 126.0, 121.2, 108.1, 14.1.

*2-Ethyl-5-(phenylthio)furan (**2**).* Colorless oil (0.34 g, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.25−7.22 (m, 2H), 7.18−7.13 (m, 3H), 6.68 (d, J = 3.0 Hz, 1H), 6.09 (d, J = 3.0 Hz, 1H), 2.68 (q, J = 7.5 Hz, 2H), 1.24 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 162.4, 140.0, 137.2, 129.0 (2C), 126.9 (2C), 126.0, 121.0, 106.5, 21.8, 11.9. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}OS$ + H, 205.0687; found, 205.0679.

*2,3-Dimethyl-5-(phenylthio)furan (**3**).* Colorless oil (0.26 g, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.26−7.21 (m, 2H), 7.19−7.12 (m, 3H), 6.55 (br s, 1H), 2.24 (br s, 3H), 1.96 (br s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 152.3, 138.5, 137.2, 128.9 (2C), 126.9 (2C), 125.9, 123.3, 116.5, 11.8, 9.8. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}OS$ + H, 205.0687; found, 205.0679.

*(R)-3,6-Dimethyl-2-(phenylthio)-4,5,6,7-tetrahydrobenzofuran (**4**).* Colorless oil (0.065 g, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.26−7.21 (m, 2H), 7.14−7.08 (m, 3H), 2.69 (dd, J_1 = 17.5 Hz, J_2 = 5.5 Hz, 1H), 2.46−2.32 (m, 2H), 2.19 (dd, J_1 = 17.5 Hz, J_2 = 9.5 Hz, 1H), 2.02 (s, 3H), 1.98−1.91 (m, 1H), 1.89−1.82 (m, 1H), 1.44−1.34 (m, 1H), 1.08 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 154.2, 137.8, 135.7, 129.5, 128.9 (2C), 126.4 (2C), 125.6, 119.2, 31.5, 31.0, 29.4, 21.4, 20.2, 9.3. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}OS$ + H, 259.1157; found, 259.1149.

*2-(Phenylthio)furan (**16**):*[25] Colorless oil (1.15 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.59 (m, 1H), 7.28−7.17 (m, 5H), 6.76

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(m, 1H), 6.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 146.5, 142.9, 136.3, 129.0 (2C), 127.4 (2C), 126.3, 119.5, 111.8.

*2-Bromo-5-(phenylthio)furan (**17**).* Colorless oil (0.95 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.30−7.19 (m, 5H), 6.72 (d, J = 3.0 Hz, 1H), 6.40 (d, J = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 145.2, 135.5, 129.2 (2C), 127.8 (2C), 126.7, 125.3, 122.3, 113.7. MS (EI): 256 (M^+, 22%), 254 (M^+, 22%), 175 (42%), 147 (100%).

*2-Benzyl-5-(phenylthio)furan (**5**).* Colorless oil (0.090 g, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.38−7.33 (m, 2H), 7.30−7.26 (m, 5H), 7.22−7.18 (m, 3H), 6.71 (br s, 1H), 6.10 (br s, 1H), 4.03 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 159.2, 141.1, 137.3, 136.8, 128.9 (2C), 128.7 (2C), 128.5 (2C), 127.0 (2C), 126.6, 126.0, 120.9, 108.7, 34.9. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}OS$ + H, 267.0844; found, 267.0836.

*1-(5-(Phenylthio)furan-2-yl)butan-1-ol (**6**).* Colorless oil (0.104 g, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.29−7.13 (m, 5H), 6.70 (d, J = 3.5 Hz, 1H), 6.31 (d, J = 3.5 Hz, 1H), 4.67 (t, J = 7.0 Hz, 1H), 1.85−1.77 (m, 2H), 1.52−1.28 (m, 2H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.3, 141.9, 136.4, 129.0 (2C), 127.2 (2C), 126.2, 120.5, 107.8, 67.7, 37.5, 18.6, 13.8. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_2S$ + H − H_2O, 231.0844; found, 231.0845.

*Ethyl 5-(Phenylthio)furan-2-carboxylate (**7**).* Colorless oil (0.072 g, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.29−7.21 (m, 5H), 7.17 (d, J = 3.5 Hz, 1H), 6.66 (d, J = 3.5 Hz, 1H), 4.35 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 158.0, 149.4, 147.2, 133.7, 129.3 (2C), 129.2 (2C), 127.3, 119.0, 118.9, 61.1, 14.2. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}O_3S$ + H, 249.0585; found, 249.0580.

*(5-(Phenylthio)furan-2-yl)methanol (**18**).*[26] Colorless oil (0.090 g, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.28−7.13 (m, 5H), 6.71 (d, J = 3.5 Hz, 1H), 6.38 (d, J = 3.5 Hz, 1H), 4.61 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 158.1, 143.0, 136.0, 129.1 (2C), 127.6 (2C), 126.4, 120.5, 109.7, 57.7.

*(5-(Phenylthio)furan-2-yl)methyl Acetate (**8**).* Colorless oil (0.103 g, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.27−7.14 (m, 5H), 6.70 (d, J = 3.5 Hz, 1H), 6.47 (d, J = 3.5 Hz, 1H), 5.04 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 170.5, 153.4, 144.1, 135.7, 129.1 (2C), 127.9 (2C), 126.5, 120.2, 112.2, 58.1, 20.8. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}O_3S$ + H, 249.0585; found, 249.0580.

*3-Bromo-5-methyl-2-(phenylthio)furan (**9**):*[20] Colorless oil (1.22 g, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.58−7.54 (m, 2H), 7.48−7.44 (m, 3H), 6.22 (s, 1H), 1.66 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 156.7, 140.0, 135.3, 129.1 (2C), 127.8 (2C), 126.6, 111.8, 111.7, 14.2.

*3,5-Dimethyl-2-(phenylthio)furan (**10**).* Colorless oil (0.074 g, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.25−7.08 (m, 5H), 6.04 (br s, 1H), 2.32 (br s, 3H), 2.11 (br s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.6, 137.5, 136.2, 131.0, 128.9 (2C), 126.3 (2C), 125.6, 110.2, 14.0, 11.1. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}OS$ + H, 205.0687; found, 205.0679.

*3-Dodecyl-5-methyl-2-(phenylthio)furan (**11**).* Colorless oil (0.058 g, 64% yield from **13**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.25−7.21 (m, 2H), 7.14−7.07 (m, 3H), 6.03 (br s, 1H), 2.46 (t, J = 7.5 Hz, 2H), 2.30 (br s, 3H), 1.52−1.46 (m, 2H), 1.32−1.18 (m, 18H), 0.89 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.7, 137.8, 135.9, 135.8, 128.9 (2C), 126.3 (2C), 125.6, 109.0, 31.9, 30.0, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.7, 22.7, 14.1, 14.1. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{34}OS$ + H, 359.2409; found, 359.2412.

*5-Methyl-2,3-bis(phenylthio)furan (**12**).* White solid (0.076 g, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.31−7.17 (m, 10H), 6.08 (br s, 1H), 2.31 (br s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 156.6, 143.0, 135.6, 129.1 (2C), 129.0 (2C), 128.9 (2C), 128.2 (2C), 128.2, 126.5, 126.4, 125.6, 111.7, 14.1. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}OS_2$ + H, 299.0564; found, 299.0555.

*1-(5-Methyl-2-(phenylthio)furan-3-yl)dodecan-1-ol (**13**).* Colorless oil (0.195 g, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.26−7.22 (m, 2H), 7.16−7.11 (m, 3H), 6.18 (br s, 1H), 4.77 (t, J = 7.0 Hz, 1H), 2.32 (d, J = 1.0 Hz, 3H), 1.82−1.75 (m, 1H), 1.64−1.58 (m, 1H), 1.35−1.16 (m, 18H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 156.5, 137.6, 137.0, 136.6, 129.0 (2C), 126.9 (2C), 126.1, 106.3, 67.1, 37.5, 31.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 25.6, 22.7, 14.1, 14.1. HRMS (TOF-ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{34}O_2S$ + H − H_2O, 357.2252; found, 357.2260.

*1-(5-Methyl-2-(phenylthio)furan-3-yl)butan-1-ol (**19**).*[20] Colorless oil (0.135 g, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.26−7.10 (m, 5H), 6.18 (s, 1H), 4.78 (t, J = 7.0 Hz, 1H), 2.32 (s, 3H), 1.82−1.54 (m, 2H), 1.40−1.30 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 156.5, 137.6, 136.9, 136.5, 129.1 (2C), 126.8 (2C), 126.1, 106.3, 66.8, 39.6, 18.8, 14.1, 13.8.

*1-(5-Methyl-2-(phenylthio)furan-3-yl)butyl 4-Bromobenzoate (**14**).* White solid (0.068 g, 58% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.84 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.24−7.07 (m, 5H), 6.19 (s, 1H), 6.08 (t, J = 7.0 Hz, 1H), 2.31 (s, 3H), 2.04−1.94 (m, 1H), 1.82−1.72 (m, 1H), 1.40−1.25 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.9, 156.4, 138.0, 136.4, 133.4, 131.6 (2C), 131.1 (2C), 129.3, 128.9 (2C), 127.9, 127.2 (2C), 126.1, 106.9, 70.1, 37.2, 18.6, 14.1, 13.7. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}BrO_3S$ + H − p-bromobenzoic acid, 245.1000; found, 245.0997.

*Dimethyl(5-methyl-2-(phenylthio)furan-3-yl)(phenyl)silane (**15**).* Colorless oil (0.078 g, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.53−7.50 (m, 2H), 7.35−7.30 (m, 3H), 7.23−7.12 (m, 3H), 7.05−7.01 (m, 2H), 5.99 (d, J = 1.5 Hz, 1H), 2.29 (s, 3H), 0.51 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 156.3, 145.2, 137.9, 137.3, 133.9 (2C), 129.0, 128.9 (2C), 128.6, 127.7 (2C), 126.8 (2C), 125.8, 113.1, 13.7, −2.1. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}OSSi$ + H, 325.1082; found, 325.1087.

Photooxygenation of 2-Thiophenyl Furans. In a vial the appropriate 2-thiophenylfuran (∼0.2 mmol) is dissolved in ethanol (1 mL). Methylene blue is added (concentration ∼10^{-3} to 10^{-4} M) and the solution is irradiated with visible light using a 300 W xenon lamp, under a constant flow (bubbling) of oxygen gas. After substrate consumption (typically 2−3 min), the solvent is evaporated and the residue is chromatographed to provide the γ-hydroxybutenolides. The byproducts (diphenyldisulfide and ethyl phenylsulfinate) can also be isolated.

Ethyl Phenylsulfinate.[18a] ^{1}H NMR (500 MHz, $CDCl_3$): 7.73−7.70 (m, 2H), 7.56−7.52 (m, 3H), 4.12 (dq, J_1 = 11.5 Hz, J_2 = 7.0 Hz, 1H), 3.73 (dq, J_1 = 11.5 Hz, J_2 = 7.0 Hz, 1H), 1.28 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 144.8, 132.0, 129.0 (2C), 125.2 (2C), 61.0, 15.5.

Methyl Phenylsulfinate.[18b] Formed if methanol is used as solvent. ^{1}H NMR (500 MHz, $CDCl_3$): 7.73−7.70 (m, 2H), 7.56−7.52 (m, 3H), 3.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 143.9, 132.2, 129.1 (2C), 125.4 (2C), 49.6.

Spectroscopic Data of γ-Hydroxybutenolides. *5-Hydroxy-5-methylfuran-2(5H)-one (**1a**):*[17a] Colorless oil (0.024 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.26 (d, J = 5.5 Hz, 1H), 6.08 (d, J = 5.5 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 170.9, 155.3, 122.4, 106.6, 24.4.

*5-Ethyl-5-hydroxyfuran-2(5H)-one (**2a**).*[27] Colorless oil (0.016 g, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.22 (d, J = 5.5 Hz, 1H), 6.11 (d, J = 5.5 Hz, 1H), 2.04−1.93 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 170.9, 154.2, 123.3, 108.8, 30.6, 7.6.

*5-Hydroxy-4,5-dimethylfuran-2(5H)-one (**3a**):*[7b] Colorless oil (0.012 g, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 5.75 (q, J = 1.5 Hz, 1H), 2.09 (d, J = 1.5 Hz, 3H), 1.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 170.7, 168.0, 117.1, 106.7, 23.3, 12.4.

*(6R,7aR)-7a-Hydroxy-3,6-dimethyl-5,6,7,7a-tetrahydrobenzofuran-2(4H)-one (**4a**):*[28] Colorless oil (0.012 g, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 2.70−2.65 (m, 1H), 2.40−2.32 (m, 2H), 2.02−1.94 (m, 2H), 1.80 (d, J = 1.0 Hz, 3H), 1.29−1.23 (m, 1H), 1.06−0.98 (m, 1H), 0.97 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 172.2, 160.3, 121.4, 103.4, 45.9, 35.0, 29.1, 24.3, 21.1, 8.2.

*5-Benzyl-5-hydroxyfuran-2(5H)-one (**5a**).* Colorless oil (0.012 g, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.36−7.26 (m, 5H), 7.20 (d, J = 5.5 Hz, 1H), 6.06 (d, J = 5.5 Hz, 1H), 3.26 (d, J = 14.0 Hz, 1H), 3.21 (d, J = 14.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 170.0,

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153.8, 132.8, 130.5 (2C), 128.7 (2C), 127.8, 123.7, 106.8, 44.2. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}O_3$ + H, 191.0708; found, 191.0712.

*5-Hydroxy-5-(1-hydroxybutyl)furan-2(5H)-one (**6a**, Equimolar Mixture of Two Diastereomers).* Colorless oil (0.013 g, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.25 (d, J = 5.5 Hz, 1H of first diastereomer), 7.24 (d, J = 5.5 Hz, 1H of second diastereomer), 6.20 (d, J = 5.5 Hz, 1H of first diastereomer), 6.19 (d, J = 5.5 Hz, 1H of second diastereomer), 3.79 (m, 1H from each diastereomer), 1.65−1.36 (m, 4H from each diastereomer), 0.93 (t, J = 7.5 Hz, 3H from each diastereomer). ^{13}C NMR (125 MHz, $CDCl_3$): 170.7 and 170.3 (two diastereomers), 152.2 and 151.9 (two diastereomers), 125.0 and 124.7 (two diastereomers), 108.7 and 108.2 (two diastereomers), 74.5 and 74.2 (two diastereomers), 33.1 and 33.0 (two diastereomers), 19.0 and 18.8 (two diastereomers), 13.8 and 13.8 (two diastereomers). HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_8H_{12}O_4$ + H − H_2O, 155.0708; found, 155.0707.

*Ethyl 2-Hydroxy-5-oxo-2,5-dihydrofuran-2-carboxylate (**7a**).* Colorless oil (0.010 g, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.19 (d, J = 5.5 Hz, 1H), 6.33 (d, J = 5.5 Hz, 1H), 4.33 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 169.6, 167.0, 149.7, 125.4, 100.6, 64.3, 13.9. HRMS (TOF-ESI) m/z: $[M - H]^-$ Calcd for $C_7H_8O_5$ − H, 171.0294; found, 171.0302.

*(2-Hydroxy-5-oxo-2,5-dihydrofuran-2-yl)methyl Acetate (**8a**):*[17a] Colorless oil (0.012 g, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.25 (d, J = 5.5 Hz, 1H), 6.22 (d, J = 5.5 Hz, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.22 (d, J = 11.5 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 170.7, 169.5, 151.7, 124.7, 104.7, 65.1, 20.6.

*3-Bromo-5-hydroxy-5-methylfuran-2(5H)-one (**9a**).* Colorless oil (0.014 g, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.34 (s, 1H), 1.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.0, 151.5, 115.9, 105.9, 24.7. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_5H_5BrO_3$ + H, 192.9500; found, 192.9505.

*5-Hydroxy-3,5-dimethylfuran-2(5H)-one (**10a**):*[7b] Colorless oil (0.012 g, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 6.86 (q, J = 1.5 Hz, 1H), 1.91 (d, J = 1.5 Hz, 3H), 1.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 171.8, 147.6, 131.7, 104.2, 24.7, 10.3.

*3-Dodecyl-5-hydroxy-5-methylfuran-2(5H)-one (**11a**).* White solid (0.026 g, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 6.81 (t, J = 1.5 Hz, 1H), 2.31 (td, J_1 = 7.5 Hz, J_2= 1.5 Hz, 2H), 1.67 (s, 3H), 1.55−1.50 (m, 2H), 1.36−1.22 (m, 18H), 0.86 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 171.8, 146.9, 136.1, 104.5, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 27.1, 24.8, 24.8, 22.7, 14.1. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{17}H_{30}O_3$ + H, 283.2273; found, 283.2275.

*5-Hydroxy-5-methyl-3-(phenylthio)furan-2(5H)-one (**12a**).* Colorless oil (0.015 g, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.58−7.55 (m, 2H), 7.47−7.43 (m, 3H), 6.23 (s, 1H), 1.66 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 167.4, 140.8, 136.2, 134.4 (2C), 130.0 (2C), 129.9, 128.8, 105.7, 25.0. HRMS (TOF-ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}O_3S$ + H, 223.0429; found, 223.0425.

*5-Hydroxy-3-(1-hydroxydodecyl)-5-methylfuran-2(5H)-one (**13a**, Mixture of Two Diastereomers in 55/45 Relative Ratio).* Colorless oil (0.026 g, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.02 (d, J = 1.5 Hz, 1H of major diastereomer), 6.98 (d, J = 1.5 Hz, 1H of minor diastereomer), 4.43 (m, 1H from each diastereomer), 1.78−1.62 (m, 2H from each diastereomer), 1.69 (s, 3H of minor diastereomer), 1.68 (s, 3H of major diastereomer), 1.35−1.20 (m, 18H from each diastereomer), 0.87 (t, J = 7.0 Hz, 3H from each diastereomer). ^{13}C NMR (125 MHz, $CDCl_3$): 170.9 and 170.5 (two diastereomers), 147.8 and 147.8 (two diastereomers), 137.7 and 137.0 (two diastereomers), 105.4 and 105.1 (two diastereomers), 67.1 and 65.9 (two diastereomers), 35.2 and 34.9 (two diastereomers), 31.9 (two overlapping diastereomers), 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3 (overlapping peaks from each and the two diastereomers), 25.4 and 25.2 (two diastereomers), 24.5 and 24.3 (two diastereomers), 22.7 (two overlapping diastereomers), 14.1 (two overlapping diastereomers). HRMS (TOF-ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{30}O_4$ + H − H_2O, 281.2117; found, 281.2109.

*1-(5-Hydroxy-5-methyl-2-oxo-2,5-dihydrofuran-3-yl)butyl 4-Bromobenzoate (**14a**, Mixture of Two Diastereomers in 55/45 Relative Ratio).* Colorless oil (0.021 g, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.93 (d, J = 8.5 Hz, 2H of first diastereomer), 7.91 (d, J = 8.5 Hz, 2H of second diastereomer), 7.61 (d, J = 8.5 Hz, 2H from each diastereomer), 7.00 (br s, 1H of first diastereomer), 6.96 (br s, 1H of second diastereomer), 5.80−5.76 (m, 1H from each diastereomer), 2.02−1.91 (m, 2H from each diastereomer), 1.70 (s, 3H from each diastereomer), 1.48−1.40 (m, 2H from each diastereomer), 0.97 (t, J = 7.5 Hz, 3H of first diastereomer), 0.96 (t, J = 7.5 Hz, 3H of second diastereomer). ^{13}C NMR (125 MHz, $CDCl_3$): 168.4 and 168.2 (two diastereomers), 165.1 and 164.9 (two diastereomers), 147.9 and 147.7 (two diastereomers), 135.1 and 135.0 (two diastereomers), 132.0 and 131.9 (2C of two diastereomers), 131.2 (2C of two ovelapping diastereomers), 128.8 and 128.7 (two diastereomers), 128.4 and 128.3 (two diastereomers), 104.5 and 104.2 (two diastereomers), 69.6 and 69.2 (two diastereomers), 34.9 and 34.8 (two diastereomers), 24.8 and 24.5 (two diastereomers), 18.4 and 18.4 (two diastereomers), 13.7 and 13.7 (two diastereomers). HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}BrO_5$ + H, 369.0338; found, 369.0331.

*3-(Dimethyl(phenyl)silyl)-5-hydroxy-5-methylfuran-2(5H)-one (**15a**).* Colorless oil (0.028 g, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.60−7.56 (m, 2H), 7.42−7.38 (m, 3H), 7.17 (s, 1H), 1.64 (s, 3H), 0.55 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.8, 163.5, 135.3, 135.0, 134.0 (2C), 129.9, 128.1 (2C), 105.8, 24.3, −3.6, −3.7. HRMS (ESI-Orbit trap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}SiO_3$ + H − H_2O, 231.0841; found, 231.0845.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00660.

Copies of ^{1}H and ^{13}C NMR of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Takahashi, M.; Dodo, K.; Sugimoto, Y.; Aoyagi, Y.; Yamada, Y.; Hashimoto, Y.; Shirai, R. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2571.

(2) Potts, B. C. M.; Faulkner, D. J. *J. Nat. Prod.* **1992**, *55*, 1701.

(3) Cheung, A. K.; Murelli, R.; Snapper, M. L. *J. Org. Chem.* **2004**, *69*, 5712.

(4) Holtke, C.; Law, M. P.; Wagner, S.; Kopka, K.; Faust, A.; Breyholz, H. J.; Schober, O.; Bremer, C.; Riemann, B.; Schafers, M. *Bioorg. Med. Chem.* **2009**, *17*, 7197.

(5) Liu, L.-Z.; Han, J.-C.; Yue, G.-Z.; Li, C.-C.; Yang, Z. *J. Am. Chem. Soc.* **2010**, *132*, 13608.

(6) Son, J. K.; Kim, D. H.; Woo, M. H. *J. Nat. Prod.* **2003**, *66*, 1369.

(7) (a) Parker, A. N.; Lock, M. J.; Hutchison, J. M. *Tetrahedron Lett.* **2013**, *54*, 5322. (b) Lee, B. T.; Schrader, T. O.; Martin-Matute, B.; Kauffman, C. R.; Zhang, P.; Snapper, M. L. *Tetrahedron* **2004**, *60*, 7391.

DOI: 10.1021/acs.joc.6b00660
J. Org. Chem. XXXX, XXX, XXX−XXX

(8) Lamberth, C.; Godineau, E.; Smejkal, T.; Trah, S. *Tetrahedron Lett.* **2012**, *53*, 4117.
(9) Deore, P. S.; Batwal, R. U.; Argade, N. P. *Synthesis* **2015**, *47*, 485.
(10) Miura, H.; Takeuchi, K.; Shishido, T. *Angew. Chem., Int. Ed.* **2016**, *55*, 278.
(11) Mao, W.; Zhu, C. *Chem. Commun.* **2016**, *52*, 5269.
(12) (a) Boukouvalas, J.; Lachance, N. *Synlett* **1998**, *1998*, 31. (b) Boukouvalas, J.; Loach, R. P. *J. Org. Chem.* **2008**, *73*, 8109.
(13) (a) Clive, D. L. J.; Minaruzzaman; Ou, L. *J. Org. Chem.* **2005**, *70*, 3318. (b) Lykakis, I. N.; Zaravinos, I.-P.; Raptis, C.; Stratakis, M. *J. Org. Chem.* **2009**, *74*, 6339.
(14) Erharuyi, O.; Adhikari, A.; Falodun, A.; Imad, R.; Choudhary, M. I. *Tetrahedron Lett.* **2016**, *57*, 2201.
(15) (a) Kernan, M. R.; Faulkner, D. J. *J. Org. Chem.* **1988**, *53*, 2773. (b) Patil, S. N.; Liu, F. *Org. Lett.* **2007**, *9*, 195. (c) Aquino, M.; Bruno, I.; Riccio, R.; Gomez-Paloma, L. *Org. Lett.* **2006**, *8*, 4831.
(16) (a) Adam, W.; Rodriguez, A. *Tetrahedron Lett.* **1981**, *22*, 3505. (b) Sofikiti, N.; Tofi, M.; Montagnon, T.; Vassilikogiannakis, G.; Stratakis, M. *Org. Lett.* **2005**, *7*, 2357. (c) Helliwell, M.; Karim, S.; Parmee, E. R.; Thomas, E. J. *Org. Biomol. Chem.* **2005**, *3*, 3636. (d) Noutsias, D.; Vassilikogiannakis, G. *Org. Lett.* **2012**, *14*, 3565.
(17) (a) Heugebaert, T. S. A.; Stevens, C. V.; Kappe, C. O. *ChemSusChem* **2015**, *8*, 1648. (b) Noutsias, D.; Kouridaki, A.; Vassilikogiannakis, G. *Org. Lett.* **2011**, *13*, 1166. (c) Feringa, B. L. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 469. (d) Lee, G. C. M.; Syage, E. T.; Harcourt, D. A.; Holmes, J. M.; Garst, M. E. *J. Org. Chem.* **1991**, *56*, 7007. (e) White, J. D.; Carter, J. P.; Kezar, H. S. *J. Org. Chem.* **1982**, *47*, 929.
(18) (a) For ethyl phenylsulfinate: Xia, M.; Chen, S.; Bates, D. K. *J. Org. Chem.* **1996**, *61*, 9289. (b) For methyl phenylsulfinate: Wei, J.; Sun, Z. *Org. Lett.* **2015**, *17*, 5396.
(19) Arroyo, Y.; Rodriguez, J. F.; Sanz-Tejedor, A.; Santos, M. *Tetrahedron Lett.* **2002**, *43*, 9129.
(20) Nolan, S. M.; Cohen, T. *J. Org. Chem.* **1981**, *46*, 2473.
(21) Ethyl phenylsulfenate has characteristic absorptions in the ^{1}H NMR at 3.86 (q, J = 7.0 Hz, 2H) and 1.27 (t, J = 7.0 Hz, 3H): Taira, K.; Mock, W. L.; Gorenstein, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 7831.
(22) The photooxygenation of ethyl sulfenate and sulfenates in general is very fast and generates the corresponding sulfinates: (a) Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952. (b) Clennan, E. L.; Chen, M.-F. *J. Org. Chem.* **1995**, *60*, 6444. (c) Pasto, D. J.; Cottard, F.; Horgan, S. *J. Org. Chem.* **1993**, *58*, 4110.
(23) Concerning the photooxygenation of disulfides, see: Clennan, E. L.; Wang, D.; Clifton, C.; Chen, M.-F. *J. Am. Chem. Soc.* **1997**, *119*, 9081.
(24) Montagnon, T.; Kalaitzakis, D.; Triantafyllakis, M.; Stratakis, M.; Vassilikogiannakis, G. *Chem. Commun.* **2014**, *50*, 15480.
(25) Wong, Y.-C.; Jayanth, T. J.; Cheng, C.-H. *Org. Lett.* **2006**, *8*, 5613.
(26) Chuang, C.-T.; Yen, C.-H.; Wu, H.-J. *J. Chin. Chem. Soc.* **1998**, *45*, 789.
(27) Bagal, S. K.; Adlington, R. M.; Brown, R. A. B.; Baldwin, J. E. *Tetrahedron Lett.* **2005**, *46*, 4633.
(28) Horinaka, A.; Naya, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1964.

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J. Org. Chem. XXXX, XXX, XXX−XXX