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Synthesis and Photocatalytic Reactivity of Vinylsulfonium Ylides

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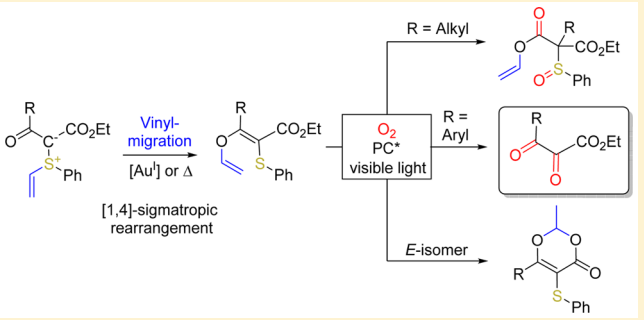
Supporting Information

ABSTRACT: Although sulfur ylides are textbook reagents in organic synthesis, surprisingly little variation of substituents on sulfur is usually observed. In particular, vinylsulfonium ylides have been neglected so far. Herein, we present a study on their synthesis and reactivity, including interesting behavior under photocatalytic conditions.



INTRODUCTION

Sulfur ylides continue to be important synthetic intermediates since their introduction in organic synthesis more than half a century ago. They are often the default reagents for the formation of small-sized carbo- or heterocycles,[1] most prominently via the Corey–Chaykovsky–Johnson[2] family of reactions. Such classical processes are based on the carbenoid-type reactivity of sulfur ylides. Many additional rearrangements[3] involving sulfur ylides have been reported.

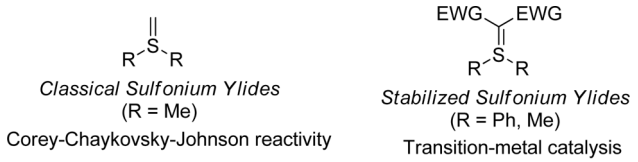
Recently, we and others have reported that sulfur ylides are particularly versatile substrates for noble transition metal catalysis, particularly gold(I).[4,5] Yet, most sulfur ylides employed in those works possess very little structural diversity regarding the substituents carried by sulfur itself; in fact, almost invariably, aromatic (Ph) or simple methyl groups are used. On one hand, this lack of functionality is related to the number of reactions which ultimately lead to a loss of the sulfide moiety during the reaction, with any substituents on sulfur thus ending up among the byproducts. On the other hand, sulfur ylides are generally prepared through deprotonation of sulfonium salts[6] or the reaction of carbenes[7] with sulfides, all methods which might not lend themselves to dramatic structural variation.

During our investigation of synthesis and reactivity of different sulfonium ylides,[8] we were interested in cases in which the substituent on sulfur is unsaturated but not aromatic (Scheme 1). While vinylsulfonium salts have been exploited as versatile two-carbon homologating agents,[9] vinylsulfonium ylides have been neglected so far. Herein, we present a study on the synthesis and reactivity of vinylsulfonium ylides, including interesting behavior under photocatalytic[10] conditions.

RESULTS AND DISCUSSION

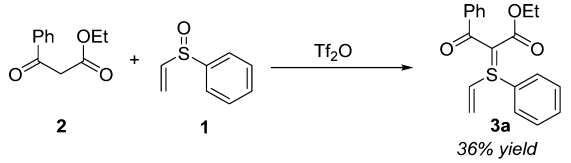
In our design, a phenyl substituent was employed to enhance the stability of the ylide.[11] Preparation of the lead compound **3a** was envisaged through direct coupling of commercially available phenyl vinylsulfoxide **1** and the corresponding

Scheme 1. Comparison of Different Families of Sulfonium Ylides



β-ketoester **2** by electrophilic activation (Scheme 2).[8,12] Even though several side reactions could be anticipated,[13] the desired vinylsulfonium ylide **3a** was easily obtained when

Scheme 2. Preparation of Vinylsulfonium Ylide 3[a]



[a]Yields refer to isolated material. Reactions were conducted on a 5.0 mmol scale, ketoester (1.0 equiv), phenyl vinylsulfoxide (1.0 equiv), Tf_2O (1.1 equiv), DCM (0.1 M), −78 °C to rt, 12 h.

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Tf_2O was employed as activating agent, although in a modest 36% yield.

With the desired vinylsulfonium ylide in hand, we turned to the examination of its reactivity. Given our prior experience with gold catalysis,[5a−e] we naturally started our investigations in that direction. Treatment of ylide **3a** with 5 mol % of the Echavarren catalyst[14] **4** in toluene resulted in clean and full conversion into a new product. Remarkably, no carbon−carbon bond was formed, in contrast to what we had previously observed on substrates carrying distal olefins.[5a−c] Instead, the vinyl ether **5a** was formed in what appears to be a *S*- to *O*-vinyl migration. The structure was unambiguously assigned as (*Z*)-**5a** by X-ray analysis (Figure 1).

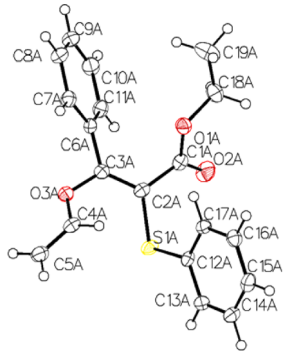
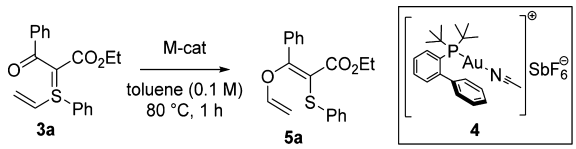


Figure 1. Crystal structure of vinyl ether **5a**. Ellipsoids are drawn at 50% probability (see the Supporting Information for details).

Intrigued by this reaction, we further investigated the action of different noble metal catalysts on **3a** (Table 1). Surprisingly,

Table 1. Rearrangement of Vinylsulfonium Ylide 3a



entry[a]	catalyst (mol %)	yield[b]
1	**4** (4.1)	quant.
2	**4** (1.0)	98 (97)[c,d]
3	$PtCl_2$ (4.1)	76
4	$PtCl_4$ (6.4)	90
5	$PdCl_2$ (6.1)	quant.
6	$Pd(ACN)_2Cl_2$ (6.3)	98
7	CuI (5.0)	trace
8	[e]	92[f]

[a]Reactions were run on ca. 0.1 mmol scale under argon atmosphere. [b]Yield determined by ^1H NMR analysis (internal standard). [c]Isolated yield in parentheses. [d]Yield was reproducible on a 1.7 mmol scale using 2 mol % of catalyst **4**. [e]At 180 °C, 3 h, MW irradiation. [f]Mixture of configurational isomers in a ratio of *Z*/*E* = 1.5:1.

very little dependence on the nature of the catalyst was observed, and other late transition metal salts such as $PdCl_2$, $PtCl_2$, or $PtCl_4$ all catalyzed the reaction with appreciable levels of efficiency (Table 1, entries 3−6). Conversely, CuI did not show any catalytic activity. The observation of equally successful reaction outcomes with π-acidic metals is informative from a mechanistic standpoint (vide infra). In 2010, we reported a related reaction for diphenylsulfonium ylides.[8a] In that reaction, a phenyl group was transferred to oxygen upon microwave irradiation, in what is an example of the Smiles rearrangement.[15] Following this thermal activation procedure for **3a**, the reaction also took place smoothly; however, under these conditions, double bond isomerization is observed and the product was obtained as a mixture of *E*- and *Z*-isomers. For this transformation, mechanisms have to be considered for both the catalytic and thermal variants.

In the presence of a π-Lewis acid catalyst, activation of the vinyl group and subsequent 5-exo-trig or 6-endo-trig cyclization is feasible (Scheme 3, left). In the first case, simple elimination of the sulfonium moiety in **6** delivers the vinyl ether, whereas in the latter case, a metal carbene **7** could be formed, which after formal elimination and protodeauration will afford the same product. We reasoned that differentiation between these two pathways might be achieved by a labeling experiment.

As vinylsulfoxides have been reported to undergo metalation α to sulfur,[16] α-deuterated sulfoxide *d*-**1** appeared to be a readily accessible labeled derivative. Indeed, deprotonation with LDA and subsequent quenching with deuterium oxide gave the desired labeled compound *d*-**3a** with 90% deuterium incorporation (Scheme 4). Conversion to the sulfur ylide proceeded as described previously, setting the stage for the vinyl transfer step. In the event, catalytic rearrangement of *d*-**3a** produced regioisomer *d*-(*Z*)-**5a** exclusively, ruling out possible six-membered cyclic intermediates.

Remarkably, the thermal variant also led to the labeled regioisomer *d*-**5a**, ruling out an otherwise mechanistically appealing [3,3] sigmatropic rearrangement (Scheme 3, right). In these cases, a Smiles-like addition−elimination mechanism seems very unlikely due to the instability of a theoretical methylide intermediate. Nevertheless, in a concerted process, this would be akin to a vinylic S_N2 reaction.[17] Since an S_N2 σ mechanism would be prohibited by the impossibility of forming an all-in-plane transition state within a cyclic structure, a concerted S_N2 π mechanism could be operative. This is further re-inforced by the fact that "hard" oxygen-based nucleophiles have been shown to prefer S_N2 π pathways in calculations.[17b] A concerted mechanism is also known in some cases of the related Smiles rearrangement[15c] and has also been suggested recently for the sulfur to oxygen migration in the Julia−Kocienski reaction.[18] Furthermore, a concerted process would also be an example of a [1,4]-sigmatropic rearrangement[19] with an aromatic transition state (Figure 2).[20]

Inspired by the rise of photocatalysis in recent years, we investigated how a divinyl ether such as **5a** would react under SET oxidation. Vinyl ether **5a** was consequently subjected to LED irradiation using the standard $[Ru(bpy)_3]^{2+}$ catalyst. Surprisingly, in the presence of common oxidative or reductive quenchers, no reaction except isomerization of the double bond was observed (Table 2). After additional investigation, it was found that when the solution was not degassed or oxygen was allowed to enter the reaction, full conversion of the starting material was observed. The main product under these oxidative conditions was identified to be α,β-diketoester **8a** (Table 2).[21] The conversion was not limited to the use of a ruthenium photocatalyst, as other common catalysts such as $[Ir(dtbbpy)(ppy)_2][PF_6]$ and eosin Y displayed very similar reactivity (Table 2, entries 4 and 5).

Lowering the polarity of the solvent composition proved to be beneficial (Table 2, entry 6). Furthermore, the reaction time was greatly reduced when a gentle stream of oxygen was applied (entry 7).

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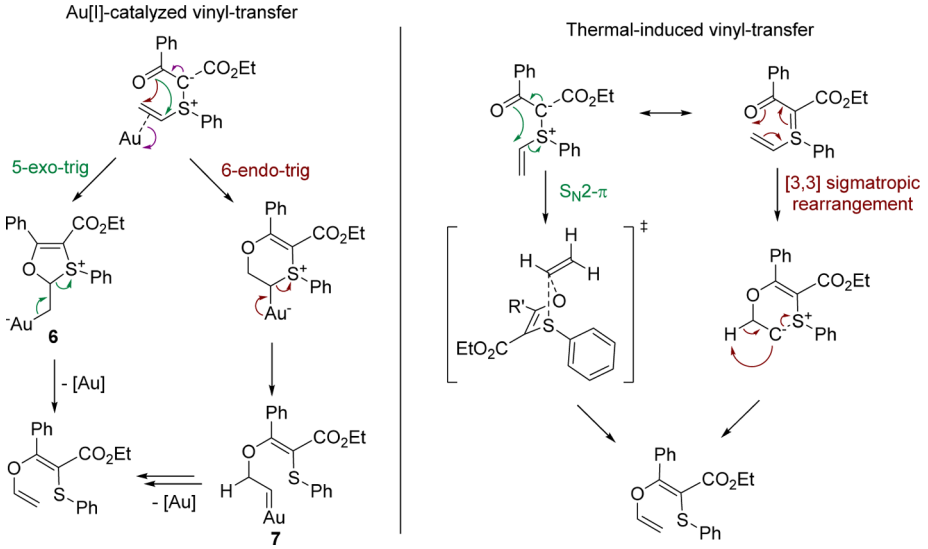
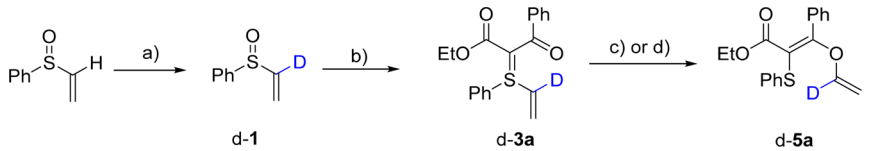
Scheme 3. Possible Mechanistic Pathways for the Rearrangement of Vinylsulfonium Ylides: Au(I)-Catalyzed Reaction (Left) and Thermal Reaction (Right)



Scheme 4. Deuterium-Labeling Experiment[a]



[a]Conditions: (a) LDA (1.1 equiv), THF, −78 °C, 15 min then D_2O, 23%; (b) ethyl benzoylacetate (1.0 equiv), Tf_2O (1.1 equiv), DCM, −78 °C to rt, 12 h, 28%; (c) [JohnPhosAuACN]SbF_6 (2 mol %), toluene, 70 °C, 1 h, 95%; (d) toluene, 180 °C, 3 h, MW, 88% as mixture of *E*/*Z* isomers in a ratio of 1.4:1.

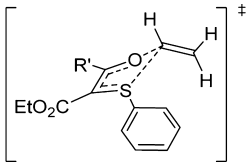
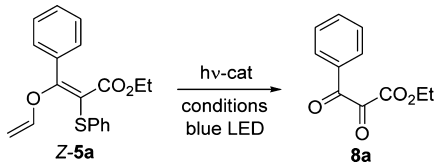


Figure 2. Proposed transition state of the [1,4]-sigmatropic rearrangement.

We then turned our attention to the generality of this reaction, and results are summarized in Scheme 5. Halo-substituted substrate (*Z*)-**5b** reacted in similar fashion, and the corresponding tricarbonyl compound **8b** was obtained in good yield. Subjecting the product of phenyl transposition **9a**[8a] to these photocatalytic conditions revealed that the reaction was not restricted to vinyl ethers, although lower yields were observed. Alongside the products, phenyl benzoate **10** was isolated in 19% yield. In similar way, the methoxy-substituted aryl ether **9b** was prepared and subjected to the photocatalytic oxidation conditions. Gratifyingly, the product was obtained in good yield after extended reaction time, along with the oxidized sulfoxides **11** in 8% combined yield as side products.

Surprisingly, changing what was originally the ketoester residue from *aryl* to *alkyl* resulted in a complete change in reaction outcome. Instead of oxidation to a tricarbonyl compound, the vinyl malonate **12a**, where the *t*-butyl substituent has been lost, was obtained from vinyl ether (*Z*)-**5c**. A sterically demanding environment appears to facilitate the loss of the *t*-butyl moiety. In order to assess the influence of the double bond geometry of the starting material, the two isopropyl-containing

Table 2. Screening of Conditions for the Photocatalytic Oxidation of Vinyl Ether 5a



entry[a]	catalyst[b]	solvent	condition	time (h)	yield[b]
1[c]	[Ru]	ACN	argon	6	nr
2[d]	[Ru]	ACN	argon	14	nr
3	[Ru]	ACN	open flask	12	31
4	[Ir]	ACN	open flask	12	58[e]
5	eosin Y[f]	ACN	open flask	12	53[e]
6	[Ru]	5:1 $CHCl_3$/ACN	open flask	12	57
7	[Ru]	5:1 $CHCl_3$/ACN	O_2 stream	2	65

[a]All reactions carried out on a 0.01 mol scale with a concentration of 0.05 M, irradiation with blue LED (440−480 nm); yield refers to isolated material unless stated otherwise. [b]Catalyst loading of 3 mol % unless stated otherwise; [Ru] = $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$, [Ir] = $[Ir(dtbbpy)(ppy)_2][PF_6]$. [c]*m*-Dinitrobenzene (1.2 equiv). [d]Diisopropylethylamine (2 equiv). [e]Yield determined by ^1H NMR (internal standard) of the crude mixture. [f]Eosin Y (1 equiv), irradiation with green light at 550 nm, 110 W.

isomers (*Z*)-**5d** and (*E*)-**5d** (obtained by thermal rearrangement of the corresponding ylide) were separated and independently submitted to photocatalytic oxidation. While (*Z*)-**5d** mimics the behavior of its *t*-butyl analogue (*Z*)-**5c**, yielding a vinyl ester (still carrying the isopropyl substituent and,

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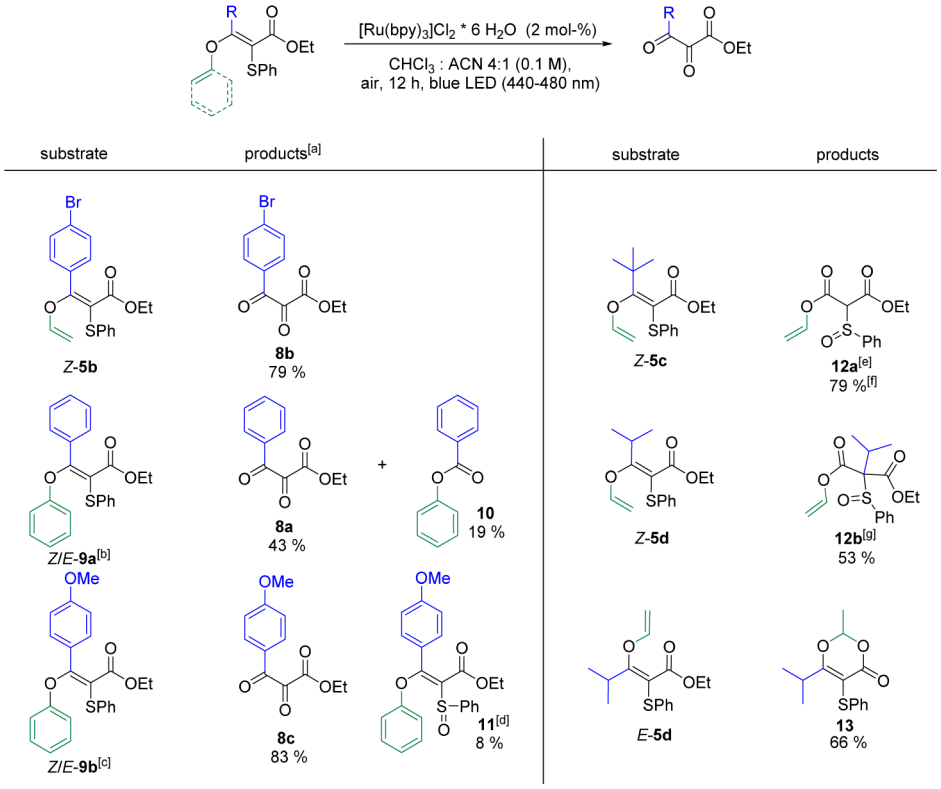
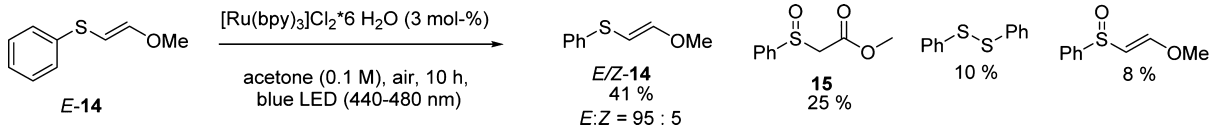
Scheme 5. Scope of the Photocatalytic Oxidation[a]



[a]Reactions were carried out on a 0.05−0.15 mmol scale. All reported yields refer to isolated material: [a] α,β-diketoesters were obtained as a mixture of diketone and hydrate in varying ratios (see Supporting Information for more information); [b] Z/E = 3.5:1, reaction was run in ACN; [c] Z/E = 1.3:1; [d] isomers with a ratio of 1.7:1; [e] dr 1:1; [f] 70% conversion. Yield is based on unreacted starting material [g] obtained as a single diastereomer.

Scheme 6. Photocatalytic Oxidations of Surrogate (*E*)-14



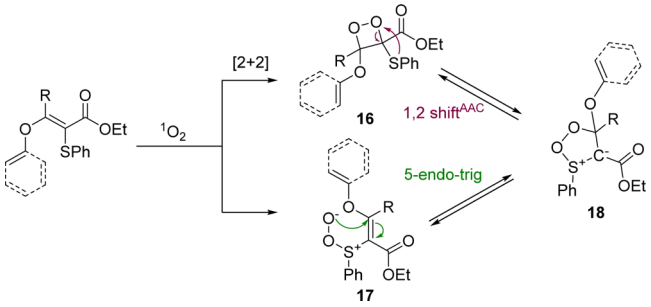
strikingly, as a single diastereomer **12b**), the opposite isomer gave the cyclized 1,3-dioxin-4-one **13** as major product (66%).

To gain additional insight on the mechanism of these reactions, surrogate (*E*)-**14** (Scheme 6) was synthesized according to a literature procedure.[22] Its photocatalytic oxidation produced sulfoxide ester **15** as a main product, incorporating two additional oxygen atoms. The lower efficiency of this transformation indicates a crucial role of the electron-withdrawing functionality adjacent to the thioether of the parent compounds **5**.

It is known that $[Ru(bpy)_3]^{2+}$ can serve as sensitizer for the generation of singlet oxygen with very high quantum yields.[23] Reactions of singlet oxygen with organic molecules have been widely reported in the literature.[24] One plausible mechanism would be a [2 + 2] cycloaddition with the internal double bond to yield 1,2-dioxetane **16**, which could undergo ring expansion to a endoperoxy sulfonium ylide **18**[25] (Scheme 7). Alternatively, the same intermediate could derive from an attack on sulfur[26] followed by a 5-endo-trig cyclization. These products could also be generated by a sequential single-electron transfer.

In Scheme 8, plausible pathways from intermediate **18** to the observed products are presented. In pathway A, generation of an unstable epoxide[25] and hydrolysis followed by elimination of

Scheme 7. Proposed Reaction with Singlet Oxygen to Endoperoxide Sulfonium Ylide 18



sulfenic acid[27] might account for the dominant formation of diketoester **8**.

The formation of sulfoxide esters **12a** and **12b** as well as **15** seemed to result from a 1,2-alkyl and hydride shift,[28] respectively (Scheme 8, pathway B). Corroborating evidence for the proposal that the formation of **12a** and **12b** as well as **15** might be a concerted process is given by the fact that no vinylic esters were isolated without concomitant oxidation to the

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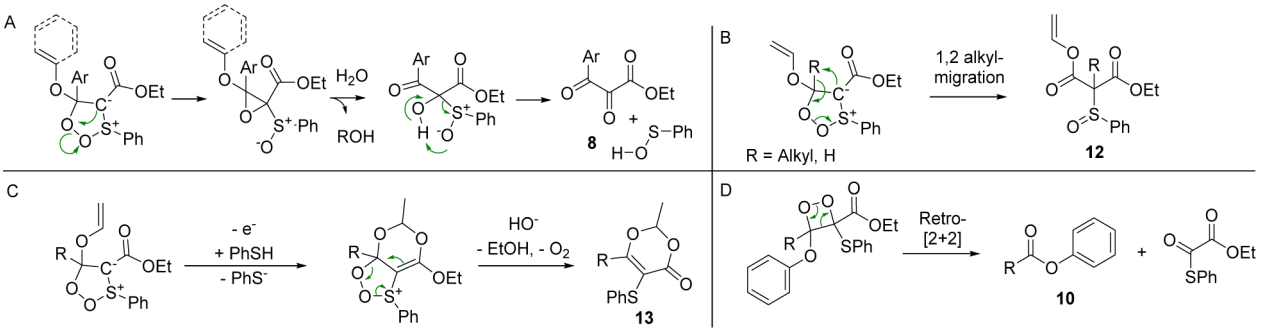
Scheme 8. Different Pathways Depending on Substitution Pattern



respective sulfoxides. Additionally, the fact that **12b** is obtained as a single diastereomer could be the result of restricted rotation. For the reaction of (*E*)-**5d**, the vinyl substituent and the carbonyl group of the ester seem to be in perfect arrangement for cyclization. Even though oxygen is not necessarily incorporated in the product, only traces thereof are observed when the reaction is carried out in the absence of oxygen. From common intermediate **18**, a radical cyclization with abstraction of hydrogen from thiophenol and hydrolysis are feasible (Scheme 8, pathway C), although this pathway could be operative starting with (*E*)-**5d** directly, as well. The phenyl ester **10** is quite likely the retro-[2 + 2] product of the 1,2-dioxetane intermediate **18**[24,29] (Scheme 8, pathway D).

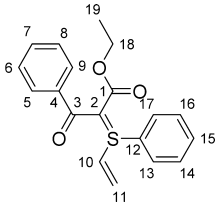
CONCLUSIONS

In summary, we have presented the first synthesis of a new class of sulfonium ylides bearing a *S*-vinyl substituent starting from commercially available phenyl vinylsulfoxide. These compounds undergo an interesting stereoselective gold-catalyzed *S*- to *O*-vinyl shift under mild conditions. This rearrangement and its thermal variant were investigated by deuterium-labeling experiments, supporting the intermediacy of five-membered cyclic intermediates. The use of a photocatalyst in combination with oxygen and visible light enabled the transformation of the resulting vinyl ethers into different oxidation or cyclization products depending on the substitution pattern. Aromatic substituents led mainly to the formation of tricarbonyl compounds, whereas secondary or tertiary alkyl moieties triggered a different behavior that resulted in group migrations and fragmentations. These unusual transformations highlight the versatility and bountiful reactivity that can be expected from modulating substitution patterns in sulfonium ylides.

EXPERIMENTAL SECTION

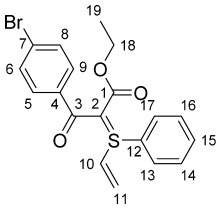
General Procedure for the Synthesis of Vinylsulfonium Ylides. In a flame-dried flask, *β*-ketoester (5 mmol) and phenyl vinylsulfoxide (0.67 mL, 5 mmol) in dry CH_2Cl_2 (50 mL) were cooled to −78 °C and treated with trifluoromethanesulfonic anhydride (1.11 mL, 1.86 g, 5.5 mmol). The mixture was stirred for 1 h at this temperature before the acetone bath was removed, and the reaction was stirred for 11 h at room temperature. It was quenched with a saturated potassium carbonate solution (15 mL) and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The crude mixture was purified by column chromatography over silica gel (heptane/ethyl acetate = 1/1).

*Ethyl 3-Oxo-3-phenyl-2-(phenyl(vinyl)sulfanylidene)propanoate (**3a**):*



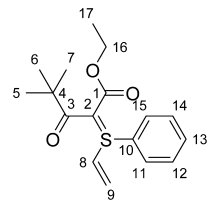
Brown oil (10 mmol scale, 1.120 g, 34% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70−7.63 (m, 2H), 7.55−7.48 (m, 5H), 7.45 (dd, J = 16.8, 9.0 Hz, 1H), 7.39−7.29 (m, 3H), 6.31 (dd, J = 16.8, 1.1 Hz, 1H), 6.19 (dd, J = 9.0 1.1 Hz, 1H), 3.94 (m, 2H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 190.0, 166.3, 143.0, 131.6, 131.1, 131.0, 130.0, 129.5, 128.0, 127.8, 127.5, 127.1, 59.6, 14.1; HRMS (ESI+) calcd for $C_{19}H_{18}O_3S$ ([M + Na]$^+$) 349.0869, found 349.0867; IR (neat, cm^{-1}) 3070, 2972, 1645, 1543, 1331, 1276, 1151, 1065, 726, 696.

*Ethyl 3-(4-Bromophenyl)-3-oxo-2-(phenyl(vinyl)sulfanylidene)-propanoate (**3b**):*



Brown oil (5.3 mmol scale, 0.530 g, 25% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67−7.60 (m, 2H), 7.54−7.37 (m, 8H), 6.30 (dd, J = 16.8, 1.2 Hz, 1H), 6.19 (dd, J = 9.0, 1.2 Hz, 1H), 4.02−3.89 (m, 2H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 188.6, 165.9, 141.7, 131.3, 131.2, 130.5, 130.0, 129.5, 127.6, 127.1, 123.7, 76.7, 59.7, 14.2; HRMS (ESI+) calcd for $C_{19}H_{17}O_3SBr$ ([M + Na]$^+$) 428.9954, found 428.9961; IR (neat, cm^{-1}) 2977, 1650, 1554, 1328, 1278, 1059, 747, 696.

*Ethyl 4,4-Dimethyl-3-oxo-2-(phenyl(vinyl)sulfanylidene)-pentanoate (**3c**):*



White crystals (5.1 mmol scale, 0.272 g, 18% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54−7.40 (m, 5H), 7.26 (dd, J = 16.8, 9.0 Hz, 1H), 6.22 (dd, J = 16.8, 1.0 Hz, 1H), 6.11 (dd, J = 9.0, 1.0 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.32 (s, 9H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 199.3, 165.3, 132.3, 130.5, 130.4, 129.7, 129.3, 126.1, 76.9, 59.4, 43.3, 27.1, 14.6; HRMS (ESI+) calcd for $C_{17}H_{22}O_3S$ ([M + Na]$^+$) 329.1182, found 329.1171; IR (neat, cm^{-1}) 3081, 2976, 1672, 1573, 1312, 1057, 745.

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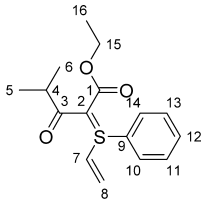
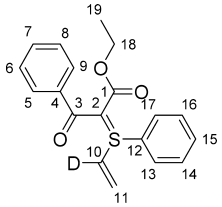
*Ethyl 4-Methyl-3-oxo-2-(phenyl(vinyl)sulfanylidene)pentanoate (**3d**):*



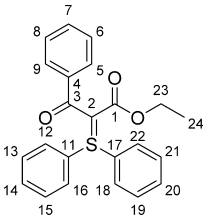
Brown oil (5.0 mmol scale, 0.334 g, 23% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51−7.41 (m, 5H), 7.32 (dd, J = 16.8, 9.1 Hz, 1H), 6.14 (dd, J = 16.8, 1.0 Hz, 1H), 6.09 (dd, J = 9.0, 1.0 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.82 (sep, J = 6.8 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H), 1.07 (dd, J = 6.8 1.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 198.0, 166.1, 131.8, 130.6, 130.5, 129.7, 128.4, 126.4, 75.4, 59.5, 36.1, 19.7, 19.5, 14.7; HRMS (ESI+) calcd for $C_{16}H_{20}O_3S$ ([M + Na]$^+$) 315.1025, found 315.1015; IR (neat, cm^{-1}) 3077, 2930, 1665, 1577, 1378, 1282, 1056, 746, 632.

*Ethyl 3-Oxo-3-phenyl-2-(phenyl(vinyl-1-d)sulfanylidene)-propanoate (d-**3a**):*



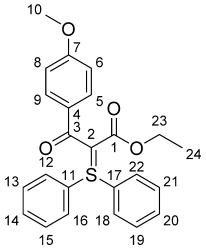
Light brown oil (1.3 mmol scale, 0.117 g, 28% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.69−7.61 (m, 2H), 7.55−7.47 (m, 5H), 7.37−7.29 (m, 3H), 6.30 (s, 1H), 6.19 (s, 1H), 4.00−3.87 (m, 2H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 190.0, 166.3, 142.9, 131.5, 131.1, 130.9, 129.9, 129.5, 127.8, 127.4, 127.1, 76.5, 59.6, 14.1; HRMS (ESI+) calcd for $C_{19}H_{17}DO_3S$ ([M + Na]$^+$) 350.0932, found 350.0928; IR (neat, cm^{-1}) 3059, 2980, 1650, 1553, 1323, 1280, 1060, 725.

*Ethyl 2-(Diphenylsulfanylidene)-3-oxo-3-phenylpropanoate (SM of **9a**):*[8a]



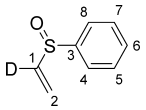
Diphenyl sulfoxide was used as reagent; white solid (5.2 mmol scale, 1.490 g, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75−7.67 (m, 4H), 7.58−7.45 (m, 8H), 7.38−7.28 (m, 3H), 3.91 (q, J = 7.1 Hz, 2H), 0.87 (t, J = 7.1 Hz, 3H).

*Ethyl 2-(Diphenylsulfanylidene)-3-(4-methoxyphenyl)-3-oxopropanoate (SM of **9b**):*[4d]



The compound was prepared according to reference 4d; white solid (3.1 mmol scale, 1.206 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74−7.66 (m, 4H), 7.56 (d, J = 8.8 Hz, 2H), 7.53−7.45 (m, 6H), 6.83 (d, J = 8.8 Hz, 2H), 3.95 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 189.0, 166.6, 161.2, 135.4, 131.5, 130.6, 130.3, 129.9, 129.8, 112.8, 75.2, 59.6, 55.5, 14.4; HRMS (ESI+) calcd for $C_{24}H_{22}O_4S$ ([M + Na]$^+$) 429.1131, found 429.1131; IR (neat, cm^{-1}) 1665, 1323, 1249, 1055, 746.

*Preparation of Phenyl-(vinyl-1-d)sulfoxide (d-**1**).*[30]

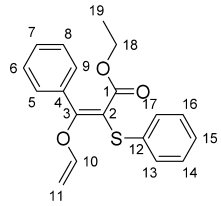


To a −78 °C solution of diisoproylamine (0.85 mL, 6.06 mmol, 1.21 equiv) in 20 mL dry THF was added *n*-BuLi solution (15% in hexane, 3.5 mL, 5.6 mmol, 1.12 equiv). The reaction was stirred for 30 min at this temperature, and a solution of phenyl vinylsulfoxide (0. 67 mL, 5.01 mmol) in 10 mL of dry THF was added dropwise. After an additional 30 min, the reaction was allowed to warm to room temperature for 10 min. The reaction was quenched by the addition of D_2O (1 mL) and diluted with H_2O (5 mL), and the organics were extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography over silica gel (heptane/ethyl acetate) afforded deuterated phenyl vinylsulfoxide in a ratio of *d*-**1**/**1** = 10:1: colorless liquid (0.150 g, 20% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.65−7.58 (m, 2H), 7.54−7.46 (m, 3H), 6.19 (t, J = 2.3 Hz, 1H), 5.88 (s br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.5, 142.9 (t, J = 27.1 Hz), 131.3, 129.6, 124.8, 120.6; HRMS (ESI+) calcd for C_8H_7DOS ([M + Na]$^+$) 176.0251, found 176.0245; IR (neat, cm^{-1}) 1443, 1084, 1045, 750, 694.

General Procedure for the Vinyl Migration. *Method A.* To a solution of vinylsulfonium ylide (1 mmol) in dry toluene (10 mL) was added Echavarren catalyst **4** (2−5 mol %), and the reaction was heated to 70 °C for 1 h. Removal of the volatiles in vacuo and consequent flash chromatography over silica gel using ethyl acetate afforded vinyl ethers.

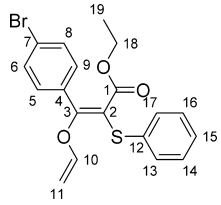
Method B.[8a] In a microwave tube, sulfonium ylide (1 mmol) was dissolved in dry toluene (10 mL) and subjected to microwave irradiation to 180 °C for 3 h. The bright yellow solution was concentrated under reduced pressure, and flash chromatography over silica gel (heptane/ethyl acetate = 10/1) afforded the products as a mixture of double bond isomers.

*Ethyl (Z)-3-Phenyl-2-(phenylthio)-3-(vinyloxy)acrylate (**5a**):*



Pale yellow oil. Method A: 1.7 mmol scale, 0.555 g, 97% yield. Method B: 0.1 mmol scale, 0.030 g, 92% yield as mixture of *Z*/*E* isomers in a ratio of 1.5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46−7.35 (m, 7H), 7.30−7.24 (m, 2H), 7.22−7.16 (m, 1H), 6.26 (dd, J = 13.7, 6.1 Hz, 1H), 4.67 (dd, J = 13.7, 2.1 Hz, 1H), 4.62 (dd, J = 6.1, 2.1 Hz, 1H), 3.81 (q, J = 7.1 Hz, 2H), 0.80 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.4, 161.1, 147.6, 135.0, 133.9, 130.2, 129.9, 129.0, 128.9, 128.6, 126.8, 112.1, 95.1, 61.4, 13.6; HRMS (ESI+) calcd for $C_{19}H_{18}O_3S$ ([M + Na]$^+$) 349.0869, found 349.0863; IR (neat, cm^{-1}) 3059, 2981, 1714, 1583, 1271, 1140, 1050, 741, 696.

*Ethyl (Z)-3-(4-Bromophenyl)-2-(phenylthio)-3-(vinyloxy)acrylate (**5b**):*



Pale yellow solid. Method A: 1.24 mmol scale, 0.404 g, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55−7.50 (m, 2H), 7.44−7.38 (m, 2H), 7.33−7.24 (m, 4H), 7.24−7.18 (m, 1H), 6.25 (dd, J = 13.7, 6.2 Hz, 1H), 4.65 (dd, J = 13.7, 2.2 Hz, 1H), 4.29 (dd, J = 6.2,

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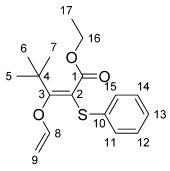
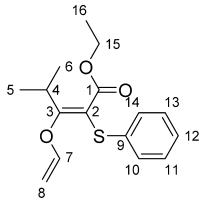
2.2 Hz, 1H), 3.83 (q, J = 7.1 Hz, 2H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.0, 158.7, 147.6, 134.3, 132.8, 131.9, 130.4, 130.4, 129.1, 127.2, 124.6, 113.9, 95.4, 61.6, 13.7; HRMS (ESI+) calcd for $C_{19}H_{17}O_3SBr$ ([M + Na]$^+$) 428.9954, found 428.9950; IR (neat, cm^{-1}) 3072, 2987, 1719, 1580, 1259, 1134, 1054, 739, 689.

*Ethyl (Z)-4,4-Dimethyl-2-(phenylthio)-3-(vinyloxy)pent-2-enoate (**5c**):*



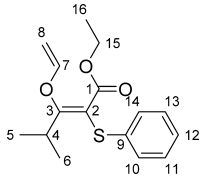
Colorless oil. Method A: 0.26 mmol scale, 0.075 g, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42−7.37 (m, 2H), 7.30−7.20 (m, 3H), 6.38 (dd, J = 13.8, 6.3 Hz, 1H), 4.54 (dd, J = 13.8, 2.0 Hz, 1H), 4.23 (dd, J = 6.3, 2.0 Hz, 1H), 3.91 (q, J = 7.2 Hz, 2H), 1.22 (s, 9H), 1.06 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.3, 164.3, 151.2, 133.3, 131.7, 128.8, 127.6, 114.6, 90.9, 61.4, 39.6, 28.4, 13.8; HRMS (ESI+) calcd for $C_{17}H_{22}O_3S$ ([M + Na]$^+$) 329.1182, found 329.1182; IR (neat, cm^{-1}) 2963, 2871, 1721, 1633, 1585, 1239, 1151, 1043, 740, 690.

*Ethyl (Z)-4-Methyl-2-(phenylthio)-3-(vinyloxy)pent-2-enoate ((Z)-**5d**):*



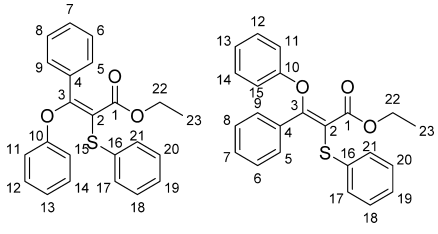
Colorless oil. Method A: 0.1 mmol scale, 0.026 g, 91% yield. Method B: 0.54 mmol scale, 0.120 g, 76% yield as mixture of Z/E isomers in a ratio of 1.6:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29−7.23 (m, 4H), 7.20−7.14 (m, 1H), 6.43 (dd, J = 13.8, 6.1 Hz, 1H), 4.57 (dd, J = 13.8, 2.1 Hz, 1H), 4.26 (dd, J = 6.1, 2.1 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.34 (sep, J = 6.8 Hz, 1H), 1.18 (d, J = 6.8 Hz, 6H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.1, 166.6, 150.6, 135.7, 129.0, 128.5, 126.4, 111.1, 92.0, 61.6, 33.2, 19.9, 13.9; HRMS (ESI+) calcd for $C_{16}H_{20}O_3S$ ([M + Na]$^+$) 315.1025, found 315.1010; IR (neat, cm^{-1}) 2972, 2874, 1708, 1635, 1583, 1231, 1144, 1052, 740, 691.

*Ethyl (E)-4-Methyl-2-(phenylthio)-3-(vinyloxy)pent-2-enoate ((E)-**5d**):*



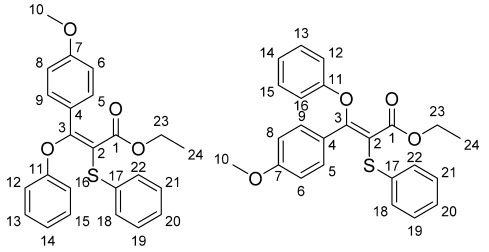
Obtained by chromatographic separation. Method B: 0.54 mmol scale, 0.045 g, 29% yield, 76% yield as mixture of Z/E isomers in a ratio of 1.6:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32−7.23 (m, 4H), 7.19−7.14 (m, 1H), 6.30 (dd, J = 13.7, 6.1 Hz, 1H), 4.67 (dd, J = 13.7, 2.1 Hz, 1H), 4.30 (dd, J = 6.1, 2.1 Hz, 1H), 4.08 (q, J = 7.1 Hz, 2H), 3.59 (sep, J = 6.8 Hz, 1H), 1.13 (d, J = 6.8 Hz, 6H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.6, 166.1, 150.4, 135.9, 129.1, 127.8, 126.3, 108.3, 93.4, 61.5, 32.3, 19.7, 14.1; HRMS (ESI+) calcd for $C_{16}H_{20}O_3S$ ([M + Na]$^+$) 315.1025, found 315.1010.

*Ethyl 3-Phenoxy-3-phenyl-2-(phenylthio)acrylate (**9a**):*[8a]



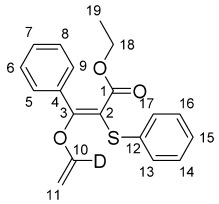
Colorless oil. Method B: 0.37 mmol, 0.129 g, 92% yield as mixture of Z/E isomers in a ratio of 3.3:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92−7.57 (m, 0.6H), 7.48−7.39 (m, 4.6H), 7.34−7.15 (m, 11.2H), 7.02−6.87 (m, 3.9H), 4.06 (q, J = 7.1 Hz, 0.6H), 3.86 (q, J = 7.1 Hz, 2H), 0.99 (t, J = 7.1 Hz, 0.9H), 0.85 (t, J = 7.1 Hz, 3H).

*Ethyl 3-(4-Methoxyphenyl)-3-phenoxy-2-(phenylthio)acrylate (**9b**):*



Yellow solid. Method B: 0.98 mmol scale, 0.380 g, 95% yield as mixture of Z/E isomers in a ratio of 1.33:1. Z-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59−7.53 (d, J = 9 Hz, 2H), 7.45−7.35 (m, 2H), 7.34−7.14 (m, 5H), 7.01−6.86 (m, 3H), 6.81−6.74 (m, 2H), 3.90 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.8, 160.9, 158.9, 156.2, 134.5, 130.5, 129.6, 129.2, 129.0, 127.0, 126.3, 123.0, 117.9, 114.9, 113.9, 61.5, 55.4, 13.8. E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45−7.35 (m, 4H), 7.34−7.14 (m, 5H), 7.01−6.86 (m, 3H), 6.81−6.74 (m, 2H), 4.06 (q, J = 7.1 Hz, 2H), 3.75 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.6, 161.0, 160.8, 156.6, 136.1, 131.6, 130.5, 129.5, 128.0, 126.4, 124.8, 122.9, 118.1, 114.9, 113.6, 61.5, 55.3, 14.0; HRMS (ESI+) calcd for $C_{24}H_{22}O_4S$ ([M + Na]$^+$) 429.1131, found 429.1134; IR (neat, cm^{-1}) 1713, 1249, 1198, 1174, 1044, 1026, 740.

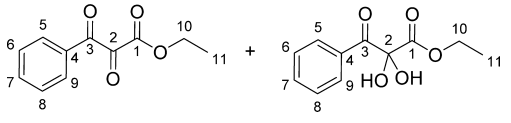
*Ethyl (Z)-3-Phenyl-2-(phenylthio)-3-((vinyl-1-d)oxy)acrylate (d-**5a**):*



Pale yellow oil. Method A: 0.09 mmol scale, 0.029 g, 95% yield. Method B: 0.04 mmol scale, 88% yield (^{1}H NMR) as mixture of E:Z isomers in a ratio of 1.4:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46−7.35 (m, 7H), 7.30−7.24 (m, 2H), 7.22−7.16 (m, 1H), 4.66 (q, J = 1.9 Hz, 1H), 4.26 (d, J = 1.9 Hz, 1H), 3.81 (q, J = 7.1 Hz, 2H), 0.80 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.4, 161.0, 147.4 (t, J = 28.4 Hz), 134.9, 133.8, 130.2, 129.9, 129.0, 128.9, 128.6, 126.8, 112.1, 94.9, 61.3, 13.6; HRMS (ESI+) calcd for $C_{19}H_{17}DO_3S$ ([M + Na]$^+$) 350.0932, found 350.0927; IR (neat, cm^{-1}) 3058, 2980, 1716, 1584, 1149, 1056, 740, 697.

General Procedure for the Photocatalytic Oxidation. In a glass vial, the respective substrate (0.05−0.15 mmol) was dissolved in $CHCl_3$/ACN 4:1 (0.05 M), treated with $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ (2 mol %), irradiated with a blue LED light bulb (8 W), and stirred without a lid for 12 h. Water was added (2 mL), and the reaction was extracted twice with CH_2Cl_2. Drying over anhydrous sodium sulfate and removal of the solvent under reduced pressure afforded crude product which was purified by column chromatography over silica gel (heptane/ethyl acetate = 5/1).

*Ethyl 2,3-Dioxo-3-phenylpropanoate (**8a**):*[31]



Yellow oil. From **5a**: 0.082 mmol scale, 0.011 g, 65% yield. From **9a**: 0.080 mmol scale, 0.007 g, 43% yield (reaction performed in 100% ACN); mixture of hydrate and keto form in a ratio of 5.3:1. Hydrate: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.07 (d, J = 8.2 Hz, 2H), 7.65−7.61 (m, 1H), 7.50−7.45 (m, 2H), 5.28 (s br, 2H), 4.22 (q, J = 7.1 Hz, 2H),

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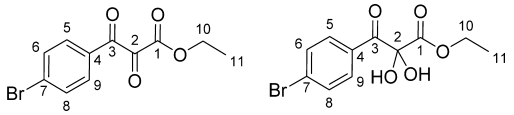
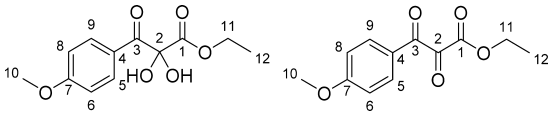
1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.7, 170.0, 134.7, 131.5, 130.3, 128.9, 91.7, 63.3, 13.7. Ketone: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00 (d, J = 8.0 Hz, 2H), 7.73−7.69 (m, 1H), 7.57−7.53 (m, 2H), 4.43 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 190.3, 183.9, 160.7, 135.6, 131.7, 130.1, 129.3, 63.4, 14.1; HRMS (ESI+) calcd for $C_{11}H_{10}O_4$ ([M + MeOH + Na]$^+$) 261.0733, found 261.0721; IR (neat, cm^{-1}) 3062, 2934, 1736, 1690, 1237, 1131, 718.

*Ethyl 3-(4-Bromophenyl)-2,2-dihydroxy-3-oxopropanoate (**8b**):*



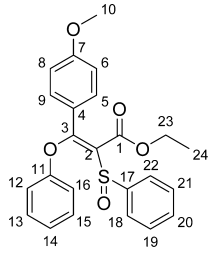
White crystals. From **5b**: 0.222 mmol scale, 0.050 g, 79% yield; mixture of hydrate and keto form in a ratio of 2.1:1. Hydrate: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.94 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 5.23 (s br, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 190.9, 169.8, 132.4, 131.7, 130.4, 130.3, 91.7, 63.6, 13.9. Ketone: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.88 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 189.1, 183.3, 160.7, 132.8, 131.5, 131.5, 130.4, 63.6, 14.1;HRMS (ESI+) calcd for $C_{11}H_9O_4Br$ ([M + Na]$^+$) 306.9576, found 306.9569; IR (neat, cm^{-1}) 2983, 1737, 1585, 1238, 1141, 1010, 751.

*Ethyl 3-(4-Methoxyphenyl)-2,3-dioxopropanoate (**8c**):*[31]



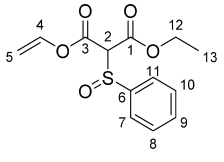
Pale yellow oil. From **9b**: 0.12 mmol scale, 0.024 g, 83% yield; mixture of hydrate and ketoform in a ratio of 2.1:1. Hydrate: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.06 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 5.29 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 189.9, 170.4, 164.9, 132.9, 124.3, 114.2, 91.6, 63.3, 55.7, 13.9. Ketone: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 4.42 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 188.4, 184.1, 165.7, 161.1, 132.8, 124.8, 114.7, 63.3, 55.9, 14.1; HRMS (ESI+) calcd for $C_{12}H_{12}O_5$ ([M + Na + MeOH]$^+$) 291.0839, found 291.0843; IR (neat, cm^{-1}) 3410 (br), 1740, 1679, 1598, 1247, 1093, 848.

*Ethyl 3-(4-Methoxyphenyl)-3-phenoxy-2-(phenylsulfinyl)acrylate (**11**):*



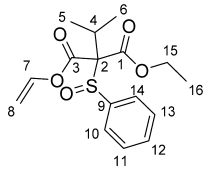
Pale yellow oil. From **9b**: 0.12 mmol scale, 0.004 g, 8% yield; mixture of isomers in a ratio of 1.7:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.79−7.72 (m, 1.7H), 7.67−7.58 (m, 2.2H), 7.52−7.38 (m, 6.6H), 7.25−7.15 (m, 3.1H), 7.04−6.86 (m, 6.0H), 6.76 (d, J = 8.8 Hz, 2.1H), 4.04−3.86 (m, 3.2H), 3.80 (s, 1.7H), 3.74 (s, 3.0H), 0.91−1.00 (m, 4.7H); HRMS (ESI+) calcd for $C_{24}H_{22}O_5S$ ([M + Na]$^+$) 445.1080, found 445.1083.

*1-Ethyl 3-Vinyl-2-(phenylsulfinyl)malonate (**12a**):*



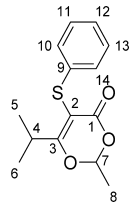
Yellow oil. From **5c**: 0.14 mmol scale, 0.030 g, 79% yield; mixture of diastereomers in a ratio of 1:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.78−7.72 (m, 4H), 7.58−7.51 (m, 6H), 7.25 (dd, J = 13.8, 6.2 Hz, 1H), 6.99 (dd, J = 13.8, 6.2 Hz, 1H), 4.98 (dd, J = 13.8, 2.1 Hz, 1H), 4.84 (dd, J = 13.8, 2.1 Hz, 1H), 4.71 (dd, J = 6.2, 2.1 Hz, 1H), 4.62 (dd, J = 6.2, 2.1 Hz, 1H), 4.51 + 4.51 (2 s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 4.06 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 162.4, 161.9, 160.1, 159.5, 141.2, 141.1, 141.0, 140.6, 132.7, 132.7, 129.5, 129.4, 125.5, 125.4, 100.2 (2C), 75.9, 75.8, 63.4, 63.1, 14.1, 13.9; HRMS (ESI+) calcd for $C_{13}H_{14}O_5S$ ([M + Na]$^+$) 305.0454, found 305.0451; HRMS (ESI−) calcd for $C_{13}H_{14}O_5S$ ([M − H$^+$]$^-$) 281.0489, found 281.0490.

*1-Ethyl 3-Vinyl-2-isopropyl-2-(phenylsulfinyl)malonate (**12b**):*



Colorless oil. From (*Z*)-**5d**: 0.1 mmol scale, 0.017 g, 53% yield; single diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.80−7.74 (m, 2H), 7.51−7.44 (m, 3H), 7.27 (dd, J = 13.9, 6.2 Hz, 1H), 5.00 (dd, J = 13.9, 2.0 Hz, 1H), 4.73 (dd, J = 6.2, 2.0 Hz, 1H), 3.84 (dq, J = 10.7, 7.1 Hz, 1H), 3.47 (dq, J = 10.7, 7.1 Hz, 1H), 2.95 (sep, J = 6.9 Hz, 1H), 1.25 (dd, J = 10.2, 6.9 Hz, 6H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.6, 163.3, 141.1, 140.6, 131.8, 128.7, 126.5, 99.9, 83.7, 61.8, 29.9, 19.3, 17.7, 13.7; HRMS (ESI+) calcd for $C_{16}H_{20}O_5S$ ([M + Na]$^+$) 347.0924, found 347.0925; IR (neat, cm^{-1}) 2977, 1724, 1241, 1140, 1084, 751, 595.

*6-Isopropyl-2-methyl-5-(phenylthio)-4H-1,3-dioxin-4-one (**13**):*



Colorless oil. From (*E*)-**5d**: 0.05 mmol, 0.009 g, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30−7.20 (m, 5H), 7.19−7.12 (m, 1H), 5.67 (q, J = 5.2 Hz, 1H), 3.60 (sep, J = 6.9 Hz, 1H), 1.73 (d, J = 5.2 Hz, 3H), 1.13 (dd, J = 6.8, 5.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 185.0, 161.8, 136.2, 129.2, 127.1, 126.2, 99.0, 98.4, 31.3, 19.9, 19.5, 19.0; HRMS (ESI+) calcd for $C_{14}H_{16}O_3S$ ([M + Na]$^+$) 287.0718, found 287.0713; IR (neat, cm^{-1}) 2975, 1741, 1566, 1327, 1113, 1022, 740.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01073.

X-ray analysis and NMR spectra (PDF)

X-ray data (CIF)

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Notes

The authors declare no competing financial interest.

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