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Visible-Light-Driven *Z*-Selective Reaction of Methyl Ketones with DMSO: A Mild Synthetic Approach to Methylthio-Substituted 1,4-Enedione Promoted by Selectfluor™

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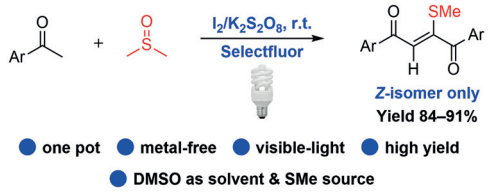

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Abstract Here we disclose a simple, visible-light-driven *Z*-selective synthesis of methylthio-substituted 1,4-enedione in a single step promoted by Selectfluor. Dimethyl sulfoxide is used as both the 'thio' source and the solvent. Molecular iodine and potassium persulfate are used as catalyst and oxidant, respectively. White light (CFL-30W) is used as the light source. The proposed mechanism involves a Kornblum reaction followed by aldol reaction.

Key words visible light, Selectfluor, 1,4-enedione, *Z*-selective

Visible-light photocatalysis has attracted a lot of attention from organic synthetic chemists over the past decade,[1] and many pharmaceuticals and natural products have been synthesized by using this strategy.[2] Currently this area is a hot topic in organic synthesis due to its many advantages. Unlike thermal reactions, photochemical reactions occur under mild conditions at ambient temperature. In addition, light is inexpensive, abundant, environmentally benign, and renewable source of energy. However, problems arise because most organic molecules do not absorb light in the visible region, which restricts the use of photochemical reactions. This fact has encouraged the development of photocatalysts for visible-light-promoted organic transformations. Photocatalysts absorb visible light from the source and use the energy gained for the transfer of a single electron either to or from organic molecules to begin a chemical reaction. Ruthenium and iridium complexes are commonly employed as photocatalysts for photochemical reactions,[3] but these are highly toxic in nature, which restricts their application on a large scale. Organic photocatalysts have recently been used as alternatives to transition-metal-based photocatalysts because the former are cheap and nontoxic compared to metal photocatalysts.[4] Eosin Y and rose bengal dyes are examples of two such organo photocatalysts that are widely used in current synthetic chemistry.[5] Selectfluor is often used as a fluorinating agent,[6] and for other purposes,[7] in organic synthesis. Lei and Jin's group very recently noted that Selectfluor can also be used to effectively promote photochemical reactions.[8]

The 1,4-enedione moiety is an important group that is present in many bioactive natural products, marine products, sesquiterpenes, and steroids, and in antitumor and antifungal agents (Figure 1).[9] The group is also used in synthetic precursors.[10] Various methods have been developed for the synthesis of 1,4-enedione derivatives.[11] Pan[12a] and our group[12b] developed methods for obtaining methylthio-substituted 1,4-enedione (mixture of *E*- and *Z*-isomers) via

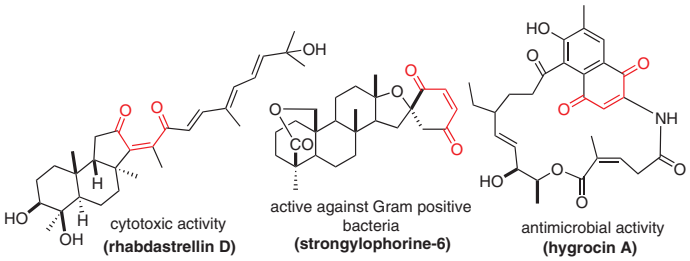

Figure 1 Bioactive compounds having a 1,4-enedione moiety

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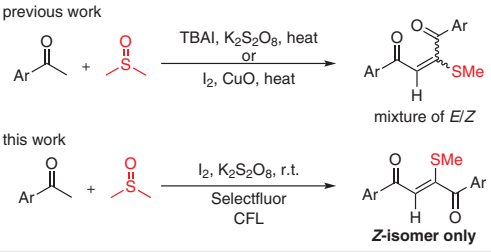
the self-dimerization of acetophenones under heating. The α-functionalization of methyl ketones has many applications in the synthesis of natural products and pharmaceuticals. Formation of C–C, C–N, and C–O bonds α- to the carbonyl group were recently developed by different research groups.[13] However, C–S bond formation α- to the carbonyl group is less studied,[14] even though sulfides are important building blocks in many fields of chemistry and biology, especially in the pharmaceutical industries.[15] Nowadays DMSO is used as a safe, economic and efficient source of the methylthio moiety in organic synthesis.[16] This functional group is introduced to organic molecules via C–H functionalization using transition-metal or metal-free catalysts.[14b,17] However, organic syntheses performed under metal-free conditions have gained much interest because of their less toxic, inexpensive and air-tolerant nature.[18] Herein, we report a visible-light-driven reaction of methyl ketones in DMSO at room temperature to synthesize 2-methylthio-1,4-enedione compounds promoted by Selectfluor in the presence of iodine as catalyst and potassium persulfate as oxidant (Scheme 1). Unlike the previous reports,[12] this reaction is 100% stereoselective, giving the *Z*-isomer exclusively under mild conditions.



Scheme 1 Visible-light-promoted 1,4-enedione synthesis

In a continuation of our previous work,[12b] we attempted to introduce a fluorine atom into the 1,4-enedione product in a one-pot process. Thus, we treated the reaction mixture of acetophenone, DMSO, TBAI, and $K_2S_2O_8$ with Selectfluor (1 equiv) as fluorinating agent under microwave irradiation

Table 1 Optimization of the Reaction Conditions[a]

Entry	Catalyst (mol%)	Oxidant (equiv)	Photocatalyst/ promoter (equiv)	Light source	Time (h)	Yield of **3** (%)[b]
1	TBAI (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	CFL (25 W)	30	75
2	TBAI (5)	$K_2S_2O_8$ (0.5)	–	CFL (25 W)	30	–
3	TBAI (5)	$K_2S_2O_8$ (0.5)	eosin Y (0.1)	CFL (25 W)	30	–
4	TBAI (5)	$K_2S_2O_8$ (0.5)	rose bengal (0.1)	CFL (25 W)	30	–
5	TBAI (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	white LED (25 W)	30	–
6	TBAI (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	blue LED (25 W)	30	–
7	TBAI (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	UV lamp (25 W)[c]	30	–
8	TBAI (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	sunlight	36	trace
9	TBAI (5)	–	Selectfluor (1)	CFL (25 W)	30	–
10	TBAI (5)	TBHP (0.5)	Selectfluor (1)	CFL (25 W)	30	–
11	TBAI (5)	Oxone (0.5)	Selectfluor (1)	CFL (25 W)	30	–
12	–	$K_2S_2O_8$ (0.5)	Selectfluor (1)	CFL (25 W)	30	–
13	I_2 (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	CFL (25 W)	30	78
14	**I_2 (5)**	**$K_2S_2O_8$ (0.5)**	**Selectfluor (1)**	**CFL (30W)**	**30**	**86**
15	I_2 (5)	$K_2S_2O_8$ (0.5)	Selectfluor (0.5)	CFL (30 W)	30	45
16	I_2 (5)	$K_2S_2O_8$ (0.5)	Selectfluor (2)	CFL (30 W)	30	86
17	I_2 (5)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	CFL (30 W)	40	84
18	I_2 (5)	$K_2S_2O_8$ (1)	Selectfluor (1)	CFL (30 W)	30	85
19	I_2 (10)	$K_2S_2O_8$ (0.5)	Selectfluor (1)	CFL (30 W)	30	82

[a] All the reactions were performed by taking 1 mmol of **1** and 2 mL of DMSO. DMSO here acts as reagent as well as solvent.
[b] Yields are for the isolated products.
[c] UV lamp of 280 nm and 365 nm wavelength were used.

and thermal conditions at 120 °C. However, only the usual two 1,4-enedione isomers were formed and no fluorination was observed. We then performed the reaction at room temperature for 48 h, but no reaction occurred. Then the same reaction was carried out under white light (CFL, 25 W) at room temperature for 30 h. Although the reaction occurred nicely, we did not observe any fluorination; the *Z*-isomer of methylthio substituted 1,4-enedione was isolated exclusively. To confirm the role of Selectfluor, we performed the reaction under the same white light but in the absence of Selectfluor. However, this time no reaction was observed. This positive role of Selectfluor encouraged us to study the process in more detail (Table 1). The reaction was also tried with different light sources such as white/blue LED, UV lamp and in sunlight (entries 5–8); however, only under sunlight was any trace of product observed. Without $K_2S_2O_8$ or with different oxidants such as TBHP and oxone, no reaction was observed (entries 9–11). We also checked the reaction by increasing the loading of oxidant and iodine catalyst but did not obtain any better results (entries 18 and 19). When we reduced the loading of Selectfluor, a clear reduction in the yield was observed with 0.5 equiv of Selectfluor. In contrast, no improvement was noted with increased loading of Selectfluor (entries 15 and 16).

After optimizing the reaction conditions, we then started screening of substrates for the reaction (Figure 2). A variety of aromatic and heteroaromatic methyl ketones were employed for the reaction and, in each case, we obtained very good yield of the *Z*-isomer of the product. The *ortho*-, *meta*-, and *para*-substituted aryl methyl ketones gave similar product yields. Electron-withdrawing or -donating groups on the phenyl ring did not affect the yield of the reaction, but no reaction was observed with aliphatic ketones.

The mechanism for the formation of **3** is proposed based on previous reports[8] and on the results of our study (Table 1 and Scheme 2). It is clear that the reaction leading to the formation of **3** proceeds through a radical pathway, which was established by carrying out a reaction in the presence of BHT (1.5 equiv), in which only a trace of product was obtained (Scheme 2a). When the reaction was performed in solvents other than DMSO, no reaction was observed after 30 h (Scheme 2b), which indicates the possibility of an initial Kornblum reaction. We then attempted a cross reaction between phenylglyoxal (the probable Kornblum product) and 4-bromoacetophenone under the optimized conditions. We detected the presence of both the cross-product and self-condensed product of 4-bromoacetophenone in the crude product mixture, which were confirmed from HRMS analysis (Scheme 2c). This reaction suggests the in situ generation of arylglyoxal in the reaction. However, the reaction of phenylglyoxal with acetophenone did not proceed in the absence of iodine (Scheme 2d) and, hence, it is concluded that besides Kornblum reaction, iodine is also required in the subsequent reaction step(s). When the same reaction was carried out under the optimized conditions but without Selectfluor, the reaction ended with the formation of simple 1,4-enedione rather than the methylthio sub-

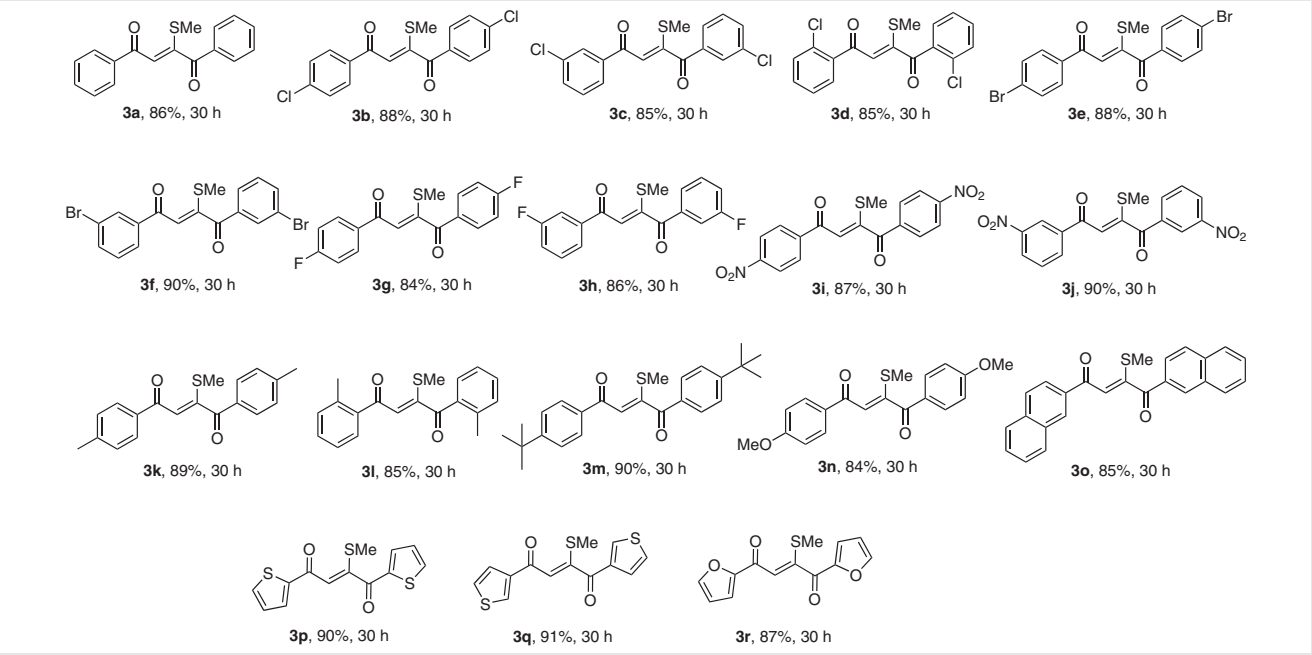
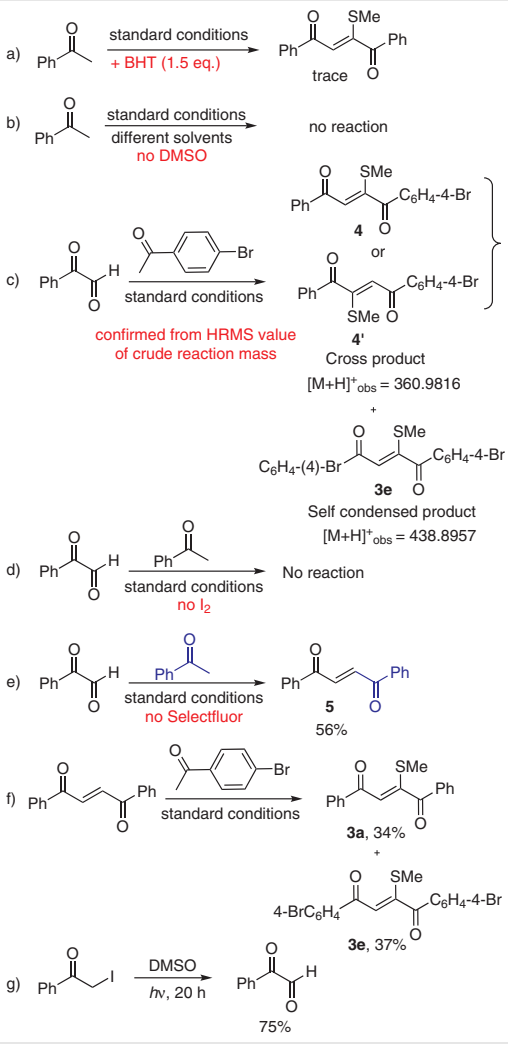
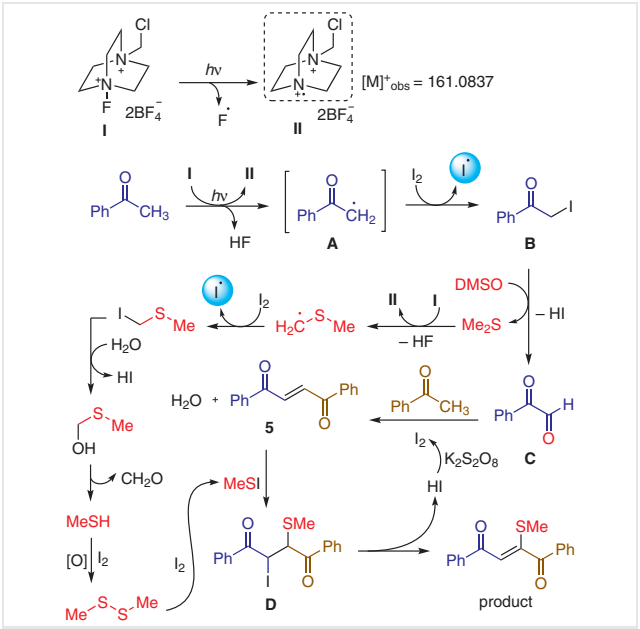


Figure 2 Substrate scope of the reaction. *Reagents and conditions*: methyl ketone (1 mmol), DMSO (2 mL), I_2 (5 mol%, 13 mg), $K_2S_2O_8$ (0.5 equiv, 135 mg) and Selectfluor (1 mmol, 354 mg) under CFL-30 W at room temperature. Products were purified by column chromatography using silica gel (100–200 mesh) and yields are for the isolated products.

stituted 1,4-enedione (Scheme 2e). This indicates that the Selectfluor is required to generate the –SMe group. When simple 1,4-enedione was treated with 4-bromoacetophenone under the standard conditions, a mixture of **3a** and **3e** was formed (Scheme 2f). The purpose of using 4-bromoacetophenone in this reaction is to generate the -SMe group through Kornblum reaction. This reaction suggests the formation of intermediate **5**. We also checked the reaction of phenacyl iodide (a probable intermediate) in DMSO under photoirradiation and found most of the staring material was converted into phenylglyoxal after 20 h of reaction (Scheme 2g). We therefore proposed a mechanism in which acetophenone first loses a hydrogen atom by reaction with Selectfluor, giving the radical **A**, which reacts with iodine to give phenacyl iodide **B**.[19] The intermediate **B** then undergoes Kornblum reaction[20] under visible light at room temperature, giving phenylglyoxal **C**, which then reacts with another molecule of acetophenone in the presence of iodine to give the dehydrated aldol intermediate **5**.[12b] The eliminated dimethyl sulfide from the Kornblum reaction in turn produces $MeSCH_2OH$ in the presence of Selectfluor and iodine, which then decomposes to MeSH and formaldehyde. The MeSH is then oxidized to dimethyl disulfide by iodine.[21] Dimethyl disulfide subsequently reacts with iodine to form MeSI,[21b,22] which undergoes ionic addition onto the C=C double bond of **5** to give **D**. This intermediate then releases a molecule of hydroiodic acid to furnish the desired product (Scheme 3).



Scheme 2 Control experiments



Scheme 3 Plausible mechanism

In summary, we have successfully developed an efficient visible-light-promoted methodology to synthesize 2-methylthio-1,4-enedione in a single step, *Z*-selectively, using DMSO as the 'thio' source. Salient features of the reaction are that Selectfluor is used to promote the photochemical reaction and that the reaction is highly diastereoselective. The mechanism is not yet fully understood, in particular with respect to how the Selectfluor induces high selectivity, and further studies are ongoing in our laboratory. A bioassay of the synthesized compounds is also in progress and the results will be published in due course.

All the commercially available reagents were used as received. Melting points were determined in open capillary tubes with a Büchi-540 micro melting point apparatus and are uncorrected. HRMS data were recorded after electrospray ionization with a Q-TOF mass analyzer (Waters). NMR spectra were recorded with Bruker-500 (125) MHz and Jeol-400 (100) MHz NMR spectrometers with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are measured in hertz (Hz). All the experiments were monitored by thin-layer chromatography (TLC) on

precoated silica gel plates (Merck) and visualized under a UV lamp at 254 nm for UV active materials. Further visualization was achieved by exposure to iodine vapor. Column chromatography was performed on silica gel (100–200 mesh, Merck) using EtOAc/hexane as eluent.

Synthesis of 3a; Typical Procedure

To a 10 mL round-bottom flask equipped with a magnetic stir bar, acetophenone (1 mmol, 120 mg), DMSO (2 mL), I_2 (5 mol %, 13 mg), $K_2S_2O_8$ (0.5 equiv, 135 mg) and Selectfluor (1 mmol, 354 mg) were added. The reaction mixture was then stirred under irradiation with 30 W white CFL (kept at a distance of ca. 8 cm from the flask) at r.t. After the completion of the reaction (monitored by TLC) the crude mixture was poured into cold water (30 mL). The organic fraction was then extracted with EtOAc (2 × 20 mL). The solvent was removed under reduced pressure and the crude product was purified by column chromatography using silica gel (100–200 mesh; petroleum ether/EtOAc) to obtain pure product.

(*Z*)-2-(Methylthio)-1,4-diphenylbut-2-ene-1,4-dione (3a)[12]

Yield: 121 mg (86%); yellow solid; mp 70–71 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–8.06 (m, 2 H), 7.95–7.93 (m, 2 H), 7.70–7.65 (m, 1 H), 7.56–7.52 (m, 3 H), 7.47–7.43 (m, 2 H), 7.09 (s, 1 H), 2.16 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 188.2, 160.6, 137.9, 134.8, 132.7, 130.0, 129.1, 128.6, 128.1, 116.0, 15.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{17}H_{14}O_2S$: 283.0787; found: 283.0789.

(*Z*)-1,4-Bis(4-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (3b)[12]

Yield: 155 mg (88%); yellow solid; mp 124–126 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01–7.99 (m, 2 H), 7.89–7.86 (m, 2 H), 7.53–7.50 (m, 2 H), 7.44–7.41 (m, 2 H), 7.03 (s, 1 H), 2.16 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.5, 186.8, 160.8, 141.6, 139.2, 136.0, 133.1, 131.3, 129.6, 129.4, 129.0, 115.6, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}C_{l2}O_2S$: 351.0008; found: 351.0012.

(*Z*)-1,4-Bis(3-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (3c)[12b]

Yield: 149 mg (85%); yellow solid; mp 174–176 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (m, 1 H), 7.94–7.90 (m, 2 H), 7.82–7.80 (m, 1 H), 7.66–7.64 (m, 1 H), 7.52–7.48 (m, 2 H), 7.42–7.39 (m, 1 H), 7.02 (s, 1 H), 2.17 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.4, 186.7, 161.0, 139.2, 136.2, 135.6, 134.9 (2C), 132.7, 130.5, 130.0, 129.5, 128.2, 126.1, 115.6, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}C_{l2}O_2S$: 351.0008; found: 351.0011.

(*Z*)-1,4-Bis(2-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (3d)[12b]

Yield: 149 mg (85%); yellow solid; mp 88–90 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 1 H), 7.54–7.48 (m, 3 H), 7.42–7.38 (m, 1 H), 7.37–7.34 (m, 2 H), 7.33–7.29 (m, 1 H), 6.82 (s, 1 H), 2.38 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.2, 189.8, 159.9, 138.9, 135.4, 133.8, 133.6, 132.1, 132.0, 131.4, 131.2, 130.3, 130.2, 127.1 (2C), 122.2, 16.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}C_{l2}O_2S$: 351.0008; found: 351.0010.

(*Z*)-1,4-Bis(4-bromophenyl)-2-(methylthio)but-2-ene-1,4-dione (3e)[12b]

Yield: 194 mg (88%); yellow solid; mp 124–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.90 (m, 2 H), 7.81–7.78 (m, 2 H), 7.70–7.67 (m, 2 H), 7.61–7.58 (m, 2 H), 7.01 (s, 1 H), 2.16 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 187.0, 160.9, 136.4, 133.5, 132.6, 132.0, 131.3, 130.6, 129.6, 128.0, 115.5, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}Br_2O_2S$: 438.8998; found: 438.9001.

(*Z*)-1,4-Bis(3-bromophenyl)-2-(methylthio)but-2-ene-1,4-dione (3f)[12b]

Yield: 198 mg (90%); yellow gum.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 8.06 (m, 1 H), 7.98–7.96 (m, 1 H), 7.86–7.85 (m, 1 H), 7.81–7.80 (m, 1 H), 7.68–7.66 (m, 1 H), 7.44–7.41 (m, 1 H), 7.36–7.33 (m, 1 H), 7.00 (s, 1 H), 2.17 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.3, 186.6, 161.0, 139.4, 137.8, 136.4, 135.6, 132.4, 131.1, 130.7, 130.3, 128.6, 126.6, 123.5, 123.0, 115.5, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}Br_2O_2S$: 438.8998; found: 438.9001.

(*Z*)-1,4-Bis(4-fluorophenyl)-2-(methylthio)but-2-ene-1,4-dione (3g)[12b]

Yield: 134 mg (84%); yellow gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.08 (m, 2 H), 7.99–7.95 (m, 2 H), 7.23–7.19 (m, 2 H), 7.15–7.11 (m, 2 H), 7.03 (s, 1 H), 2.16 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2, 186.6, 166.8 (d, *J* = 258.2 Hz), 165.5 (d, *J* = 254.8 Hz), 160.6, 134.1 (d, *J* = 2.9 Hz), 132.8 (d, *J* = 9.6 Hz), 131.3 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 9.2 Hz), 116.5 (d, *J* = 22.2 Hz), 115.8 (d, *J* = 21.7 Hz), 115.6, 15.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}F_2O_2S$: 319.0599; found: 319.0603.

(*Z*)-1,4-Bis(3-fluorophenyl)-2-(methylthio)but-2-ene-1,4-dione (3h)[12b]

Yield: 137 mg (86%); yellow gum.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.81 (m, 1 H), 7.74–7.72 (m, 1 H), 7.69–7.67 (m, 1 H), 7.63–7.60 (m, 1 H), 7.53–7.48 (m, 1 H), 7.43–7.34 (m, 1 H), 7.24–7.20 (m, 1 H), 7.00 (s, 1 H), 2.15 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.6, 186.8, 163.1 (d, *J* = 248 Hz), 163.0 (d, *J* = 248 Hz), 161.0, 139.5 (d, *J* = 6.4 Hz), 136.9 (d, *J* = 6.4 Hz), 131.1 (d, *J* = 7.3 Hz), 130.5 (d, *J* = 7.3 Hz), 126.1 (d, *J* = 2.7 Hz), 123.8 (d, *J* = 2.7 Hz), 122.2 (d, *J* = 21.8 Hz), 119.9 (d, *J* = 21.8 Hz), 116.3 (d, *J* = 22.7 Hz), 115.8, 115.0 (d, *J* = 22.7 Hz), 15.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}F_2O_2S$: 319.0599; found: 319.0602.

(*Z*)-2-(Methylthio)-1,4-bis(4-nitrophenyl)but-2-ene-1,4-dione (3i)[12]

Yield: 162 mg (87%); yellow solid; mp 188–190 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40–8.39 (m, 2 H), 8.32–8.30 (m, 2 H), 8.26–8.24 (m, 2 H), 8.09–8.08 (m, 2 H), 7.08 (s, 1 H), 2.19 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.9, 186.2, 161.9, 151.3, 150.1, 142.1, 138.8, 130.9, 129.1, 124.4, 124.0, 115.7, 15.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}N_2O_6S$: 373.0489; found: 373.0493.

(*Z*)-2-(Methylthio)-1,4-bis(3-nitrophenyl)but-2-ene-1,4-dione (3j)[12b]

Yield: 167 mg (90%); yellow gum.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.88 (s, 1 H), 8.73 (s, 1 H), 8.56–8.55 (m, 1 H), 8.41 (m, 2 H), 8.31–8.30 (m, 1 H), 7.82–7.79 (m, 1 H), 7.72–7.69 (m, 1 H), 7.13 (s, 1 H), 2.21 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.4, 185.5, 161.6, 148.8, 148.4, 138.8, 135.9, 135.3, 133.8, 130.7, 130.1, 129.1, 127.2, 124.4, 122.8, 115.3, 15.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{12}N_2O_6S$: 373.0489; found: 373.0492.

(*Z*)-2-(Methylthio)-1,4-di-*p*-tolylbut-2-ene-1,4-dione (3k)[12b]

Yield: 138 mg (89%); yellow solid; mp 111–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.2 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 7.07 (s, 1 H), 2.45 (s, 3 H), 2.39 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 187.9, 160.3, 146.1, 143.4, 135.3, 132.4, 130.1, 129.8, 129.3, 128.1, 115.8, 21.8, 21.6, 15.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}O_2S$: 311.1100; found: 311.1108.

(*Z*)-2-(Methylthio)-1,4-di-*o*-tolylbut-2-ene-1,4-dione (3l)[12b]

Yield: 132 mg (85%); yellow solid; mp 93–95 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88–7.86 (m, 1 H), 7.54–7.48 (m, 2 H), 7.35–7.31 (m, 3 H), 7.24–7.19 (m, 2 H), 6.79 (s, 1 H), 2.68 (s, 3 H), 2.54 (s, 3 H), 2.20 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.6, 192.3, 160.9, 141.1, 138.7, 138.0, 133.9, 133.5, 133.0, 132.5, 131.7, 131.0, 128.4, 126.1, 125.6, 120.1, 22.0, 20.8, 15.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}O_2S$: 311.1100; found: 311.1105.

(*Z*)-1,4-Bis(4-(*tert*-butyl)phenyl)-2-(methylthio)but-2-ene-1,4-dione (3m)[12b]

Yield: 177 mg (90%); brown gum.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.3 Hz, 2 H), 7.91 (d, *J* = 8.1 Hz, 2 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.1 Hz, 2 H), 7.10 (s, 1 H), 2.19 (s, 3 H), 1.38 (s, 9 H), 1.35 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.6, 188.0, 160.3, 158.9, 156.4, 135.3, 132.4, 130.1, 128.0, 126.1, 125.6, 116.0, 35.4, 35.1, 31.1, 31.0, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{30}O_2S$: 395.2039; found: 395.2039.

(*Z*)-1,4-Bis(4-methoxyphenyl)-2-(methylthio)but-2-ene-1,4-dione (3n)[12]

Yield: 144 mg (84%); yellow solid; mp 109–111 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07–8.05 (m, 2 H), 7.97–7.95 (m, 2 H), 7.08 (s, 1 H), 7.02–7.00 (m, 2 H), 6.96–6.94 (m, 2 H), 3.93 (s, 3 H), 3.88 (s, 3 H), 2.17 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.5, 186.9, 164.8, 163.1, 159.9, 132.5, 130.9, 130.3, 127.9, 115.7, 114.3, 113.8, 55.6, 55.4, 15.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}O_4S$: 343.0999; found: 343.1000.

(*Z*)-2-(Methylthio)-1,4-di(naphthalen-2-yl)but-2-ene-1,4-dione (3o)[12b]

Yield: 162 mg (85%); yellow solid; mp 127–129 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (s, 1 H), 8.44 (s, 1 H), 8.17–8.15 (m, 1 H), 8.09–8.07 (m, 1 H), 7.98–7.97 (m, 2 H), 7.92–7.88 (m, 3 H), 7.86–7.84 (m, 1 H), 7.67–7.64 (m, 1 H), 7.59–7.55 (m, 2 H), 7.52–7.49 (m, 1 H), 7.35 (s, 1 H), 2.21 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.9, 188.1, 160.7, 136.3, 135.3, 135.1, 133.4, 132.5, 132.4, 132.2, 129.9, 129.6, 129.5, 129.4, 129.2, 128.6, 128.3, 127.9, 127.7, 127.2, 126.7, 124.0, 123.8, 116.2, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{18}O_2S$: 383.1100; found: 383.1103.

(*Z*)-2-(Methylthio)-1,4-di(thiophen-2-yl)but-2-ene-1,4-dione (3p)[12]

Yield: 132 mg (90%); yellow solid; mp 122–124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.80 (m, 2 H), 7.69–7.63 (m, 2 H), 7.22–7.20 (m, 1 H), 7.13–7.11 (m, 1 H), 7.02 (s, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.7, 180.7, 159.1, 145.2, 142.0, 137.1, 136.6, 133.8, 131.1, 128.9, 128.2, 116.6, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}O_2S_3$: 294.9916; found: 294.9924.

(*Z*)-2-(Methylthio)-1,4-di(thiophen-3-yl)but-2-ene-1,4-dione (3q)[12b]

Yield: 134 mg (91%); yellow solid; mp 90–92 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.22 (m, 1 H), 8.03–8.02 (m, 1 H), 7.66–7.65 (m, 1 H), 7.60–7.58 (m, 1 H), 7.43–7.41 (m, 1 H), 7.34–7.32 (m, 1 H), 6.96 (s, 1 H), 2.19 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.3, 182.4, 160.0, 142.9, 140.2, 136.8, 131.4, 127.6, 127.2, 127.1, 126.6, 117.0, 15.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}O_2S_3$: 294.9916; found: 294.9918.

(*Z*)-1,4-Di(furan-2-yl)-2-(methylthio)but-2-ene-1,4-dione (3r)[12b]

Yield: 114 mg (87%); yellow solid; mp 152–154 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (s, 1 H), 7.62 (s, 1 H), 7.40 (d, *J* = 3.5 Hz, 1 H), 7.28 (d, *J* = 3.4 Hz, 1 H), 7.11 (s, 1 H), 6.70–6.69 (m, 1 H), 6.61–6.60 (m, 1 H), 2.29 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.4, 176.7, 158.1, 153.3, 150.6, 149.3, 146.1, 123.1, 116.9, 116.7, 112.9, 112.6, 15.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}O_4S$: 263.0373; found: 263.0377.

(*E*)-1,4-Diphenylbut-2-ene-1,4-dione (5)[12b]

Yield: 132 mg (56%); yellow solid; mp 103–105 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08–8.06 (m, 4 H), 8.02 (s, 2 H), 7.66–7.63 (m, 2 H), 7.56–7.52 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.7, 136.8, 135.0, 133.8, 128.8 (2C).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{12}O_2$: 237.0910; found: 237.0914.

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Supporting Information

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