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Iron-Mediated Oxidative C–H Alkylation of *S,S*-Functionalized Internal Olefins *via* C(sp^2)–H/C(sp^3)–H Cross-Coupling

Quannan Wang,[a,b] Jiang Lou,[a,b] Ping Wu,[a,b] Kaikai Wu,[a] and Zhengkun Yu[a,c,*]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China
Fax: (+86)-411-8437-9227; e-mail: zkyu@dicp.ac.cn
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[c] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China

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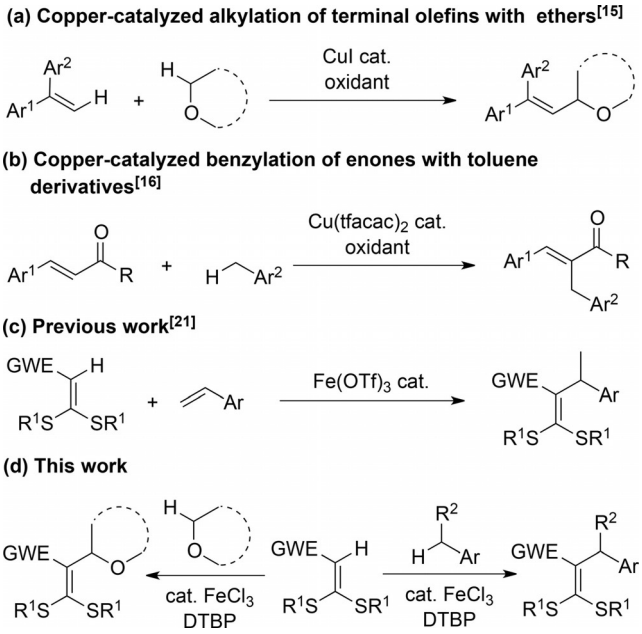
Abstract: Mediated by a catalytic amount of $FeCl_3$, the C–H alkylation of *S,S*-functionalized internal olefins, i.e., α-oxo ketene dithioacetals and their analogues, was efficiently achieved using simple ethers and toluene derivatives as the coupling partners, di-*tert*-butyl peroxide (DTBP) as the oxidant, and DABCO·6H_2O as the additive. The alkylthio functionality is essential for the internal olefinic C–H bond to undergo such an alkylation with the *O*-adjacent C(sp^3)–H bonds of the ethers and the benzylic C–H bonds of the toluene derivatives, respectively. Tetrasubstituted olefins were thus synthesized and further transformed to highly substituted pyrazoles and isoxazoles. The strategy to activate an internal olefinic C–H bond by polarizing its parent olefinic C=C bond with both the dialkylthio group and an electron-withdrawing functionality was investigated. The mechanistic studies suggest a radical pathway for the C(sp^2)–H/C(sp^3)–H cross-coupling reactions. The present protocol provides a convenient route to tetrasubstituted olefins.

Keywords: alkylation; C–H functionalization; C–H/C–H cross-coupling; internal olefins; iron

Introduction

Multisubstituted olefin motifs are abundant in numerous natural products, pharmaceuticals, and functional materials.[1] Considerable efforts have been made to synthesize multisubstituted olefins, and transition metal-catalyzed cross-coupling has proven to be one of the most useful synthetic methods in this area.[2] Although vinyl halides,[3] vinyl pseudohalides such as vinylboronic acids and boronates,[4] vinyl-metals such as vinylzirconium,[4a] vinylzinc,[4c,5a] vinylmagnesium,[5b] and vinylaluminum[5c] compounds, and other reagents[6] can be utilized for this purpose, more concise and alternative methods have been strongly desired. Recently, direct C–H functionalization has emerged as an important method for the construction of a C–C bond owing to atom economy, operational simplicity, and environmental friendliness.[7] In this regard, cross-dehydrogenative-coupling (CDC)[8] has been paid particular attention, and transition metal-catalyzed oxidative C(sp^3)–H functionalizations of ethers, toluene derivatives, cycloalkanes, and common alkanes have been documented.[9] However, oxidative C(sp^2)–H alkylation of olefins remains challenging and only limited examples have recently been reported. Yu, et al. reported palladium-catalyzed CDC reactions of terminal olefins *via* directed C(sp^3)–H activation.[10] Sanford, et al. realized pyridine-directed, palladium-catalyzed aerobic C(sp^3)–H bond cleavage to establish an olefinic C(sp^2)–C(sp^3) bond.[11] Wang and co-workers documented copper/organo-catalyzed asymmetric oxidative cross-coupling reactions between tertiary amines and olefins using molecular oxygen as the oxidant.[12] Liu, et al. synthesized 1*H*-indenes through DDQ-mediated cross-coupling between vinylic C(sp^2)–H bonds and benzylic C(sp^3)–H bonds.[13] Wei and co-workers have achieved a copper-catalyzed oxidative direct alkylation of styrenes with unactivated alkanes.[14] Lei, et al. developed Cu(I)-catalyzed oxidative cross-coupling between terminal olefinic C–H bonds and C(sp^3)–H bonds of simple ethers for the synthesis of allylic ethers (Scheme 1a).[15] Toluene derivatives were also employed for similar transformations of enone derivatives (Scheme 1b).[16] Transition metal-catalyzed oxidative cross-coupling of comuarins and flavones with unactivated C(sp^3)–H bonds were



Scheme 1. Oxidative C–H alkylation of olefins.

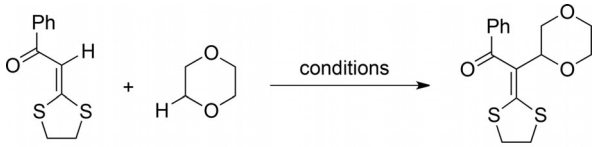
recently reported.[17] Unfortunately, work on transition metal-catalyzed oxidative alkylation of olefins has been focused on terminal olefinic C(sp^2)–H bonds, implicating that direct C–H alkylation of internal olefins still remains a challenge due to the steric hindrance and electronic impact from the internal olefin substrates.

During the ongoing investigation of the reactivities of internal olefins, we have recently developed a strategy to activate internal olefinic C–H bonds.[18,19] Introduction of an electron-withdrawing group such as carbonyl, ester, or cyano, and one or two electron-donating alkylthio functionalities to the two ends of an olefinic C=C bond can intrinsically polarize the carbon-carbon double bond and thus activate its olefinic C–H bond. In this regard, we successfully prepared tetrasubstituted olefins through transition metal-catalyzed oxidative C–H functionalization of ketene dithioacetals[20] as the polarized internal olefin substrates,[18b,e,f] and an iron-catalyzed alkylation method was also established with styrenes as the coupling partners (Scheme 1c).[21] Due to the advantages of iron catalysis in C–H functionalization,[8e,9e,22] we reasonably envisioned that simple iron salts might be applied as the catalysts or mediators in the CDC reactions of such internal olefinic C–H bonds. Herein, we disclose the $FeCl_3$-mediated oxidative C–H alkylation of ketene dithioacetals with simple ethers and toluene derivatives for the synthesis of tetrasubstituted olefins (Scheme 1d).[23]

Results and Discussion

Initially, the reaction of α-benzoyl ketene dithioacetal **1a** and 1,4-dioxane (**2a**) was conducted to screen the reaction conditions (Table 1). In the presence of 10 mol% $FeCl_3$ and 2 equivalents of di-*tert*-butyl peroxide (DTBP) as the oxidant, the reaction was performed in 1,4-dioxane (2 mL) at 120 °C for 24 h under a nitrogen atmosphere, forming the target C–H alkylation product **3a** in 9% yield (Table 1, entry 1). Addition of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (10 mol%) obviously enhanced the yield to 40%, and use of 5 mol% $FeCl_3$ remarkably improved the yield to 67% (Table 1, entries 2 and 3). Moreover, replacement of DBU by 1,4-diaza[2.2.2]bicyclooctane hydrate (DABCO·6 H_2O) further increased the product yield (69%), presumably due to its better stabilization of the iron(III) salt mediator during the reaction (Table 1, entry 4). Elevating the reaction temperature to 130 or 140 °C resulted in **3a** in 85–86% yields (Table 1, entries 5 and 6). The reaction could not efficiently occur in benzene, and did not occur in both DMF and DMSO (Table 1, entries 7–9). An air atmos-

Table 1. Screening of the reaction conditions.[a]



1a **2a** **3a**

Entry	$FeCl_3$ [mol%]	Additive [mol%]	Solvent	T [°C]	Yield[b] [%]
1	10		1,4-dioxane	120	9
2	10	DBU	1,4-dioxane	120	40
3	5	DBU	1,4-dioxane	120	67
4	5	DABCO·6 H_2O	1,4-dioxane	120	69
5	5	DABCO·6 H_2O	1,4-dioxane	130	86
6	5	DABCO·6 H_2O	1,4-dioxane	140	85
7[c]	5	DABCO·6 H_2O	benzene	130	59
8[c]	5	DABCO·6 H_2O	DMF	130	0
9[c]	5	DABCO·6 H_2O	DMSO	130	0
10[d]	5	DABCO·6 H_2O	1,4-dioxane	130	71
11[e]	5	DABCO·6 H_2O	1,4-dioxane	130	92 (80)[f]
12[e]	0	DABCO·6 H_2O	1,4-dioxane	130	0
13[g]	5	DABCO·6 H_2O	1,4-dioxane	130	0

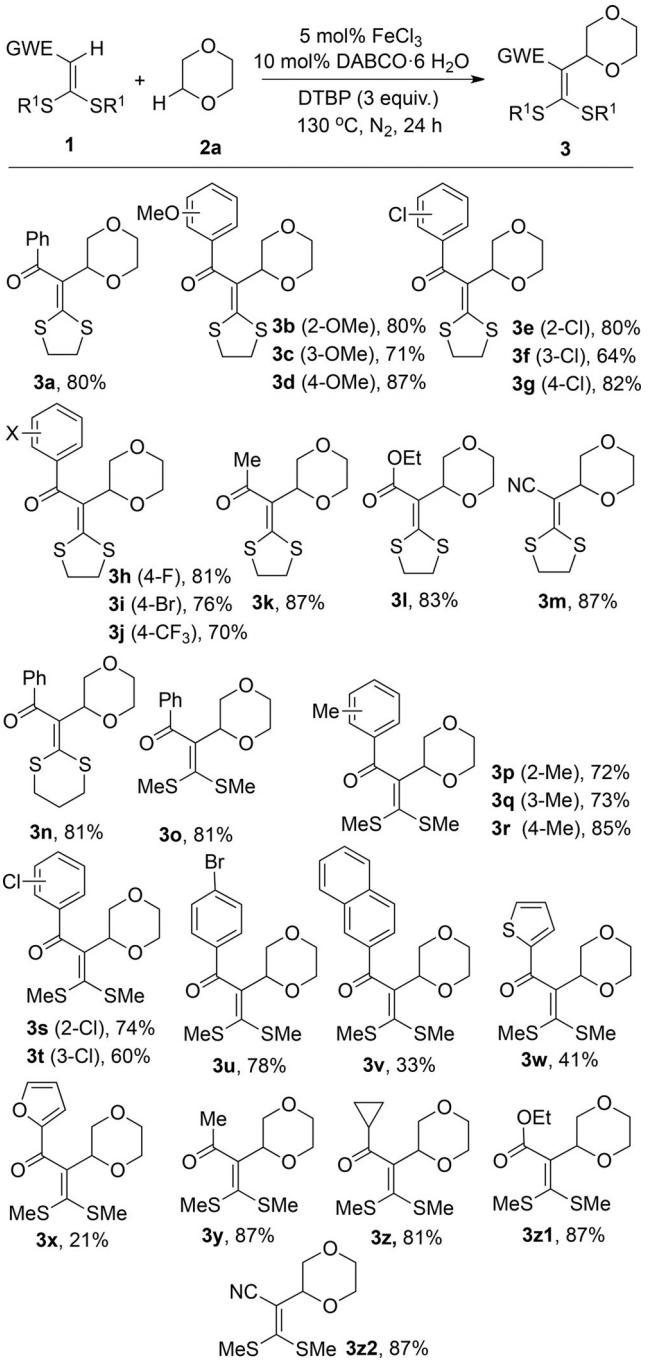
[a] *Conditions:* **1a** (0.3 mmol), additive (0.03 mmol), DTBP (0.6 mmol), solvent (2 mL), in a 25-mL sealed tube, 0.1 MPa N_2, 24 h.
[b] Determined by GC analysis with mesitylene as the internal standard.
[c] Using 1,4-dioxane (3 mmol).
[d] Under an air atmosphere.
[e] Using 3 equiv. DTBP.
[f] Isolated yield given in parentheses.
[g] Without DTBP.

phere deteriorated the reaction efficiency to give **3a** in 71% yield, and the best yield (92%) was obtained in the case of using 3 equiv. DTBP as the oxidant (Table 1, entries 10 and 11). It was noted that without either $FeCl_3$ or the oxidant the reaction did not happen. Product **3a** was not dectected in the reaction mixture of **1a** and **2a** by GC analysis in the absence of the $FeCl_3$ catalyst, revealing that DTBP itself could not promote the desired reaction without the catalyst (Table 1, entries 12 and 13).

Under the optimal conditions the scope of ketene dithioacetals **1** was investigated by means of their reactions with 1,4-dioxane (**2a**) (Table 2). Cyclic α-benzoyl ketene dithioacetal (**1a**) reacted with **2a** to afford the target product **3a** in 80% isolated yield. In a similar fashion, the reactions of methoxy- and chloro-substituted aroyl ketene dithioacetals with **2a** gave products **3b–3g** (64–87%). It is noted that 3-MeO and 3-Cl substituents exhibited a negative impact on the reaction efficiency. The *para*-substituents, i.e., 4-F, 4-Br, and 4-CF_3 on the aroyl moiety, demonstrated various electronic effects, leading to products **3h–3j** in 70–81% yields. Acetyl, ester, and cyano functionalized ketene dithioacetals also efficiently underwent the reactions to generate **3k–3m** (83–87%). Enlarging the dithioalkyl ring of **1** or using the open-chain ketene dithioacetal substrates did not affect the formation of the target products **3n** (81%) and **3o** (81%). In the cases of using the open-chain methyl-substituted α-benzoyl ketene di(methyl-thio)acetals products **3p–3r** (72–85%) were obtained, showing a steric effect from the 2-methyl substituent. The open-chain α-chlorobenzoyl ketene dithioacetals exhibited a reactivitiy lower than that of their cyclic analogues, forming **3s** (74%) and **3t** (60%), respectively. However, 4-Br-substituted di(methylthio)acetal exhibited a reactivity similar to its cyclic analogue to produce **3u** in 78% yield. Bulky α-(2-naphthoyl) and α-heteroaroyl (e.g., 2-furoyl and 2-thienoyl) ketene dithioacetals reacted with **2a** less efficiently, only yielding **3v–3x** in 21–41% yields. For the open-chain acetyl, cyclopropylcarbonyl, ester or cyano functionalized ketene di(methylthio)-acetals their oxidative C–H/C–H cross-coupling reactions with **2a** efficiently proceeded to afford **3y–3z2** in 81–87% yields. It is noteworthy that 1,4-dioxane acted as both the reactant and solvent for the reactions. The molecular structure of the tetrasubstituted olefin product **3a** was further confirmed by the X-ray single crystallographic structural analysis (Figure 1).[24]

Next, the generality of the protocol was explored by using various ethers **2** as the coupling partners (Table 3). With cyclic α-oxo and α-cyano ketene dithioacetals as the internal olefin substrates their reactions with tetrahydrofuran (THF) afforded **4a** (83%), **4b** (88%), and **4c** (70%), respectively. In comparison to the corresponding reactions of the same olefin substrates with 1,4-dioxane (**2a**) as shown in Table 2, the formation of **4a** and **4b** was superior to that of **3a** (80%) and **3k** (87%), while the generation of **4c** was inferior to that of **3m** (87%). The reaction of α-acetyl ketene di(methylthio)acetal with THF efficiently formed **4e** in 93% yield, whereas in other cases THF reacted less efficiently than **2a** to give **4d** (70%) and

Table 2. Scope of ketene dithioacetals **1**.[a]



[a] *Conditions:* **1** (0.5 mmol), **2a** (3 mL), $FeCl_3$ (0.025 mmol), DABCO·6H_2O (0.05 mmol), DTBP (1.5 mmol), 130 °C, in a 25-mL sealed tube, 0.1 MPa N_2, 24 h. Yields refer to the isolated products.

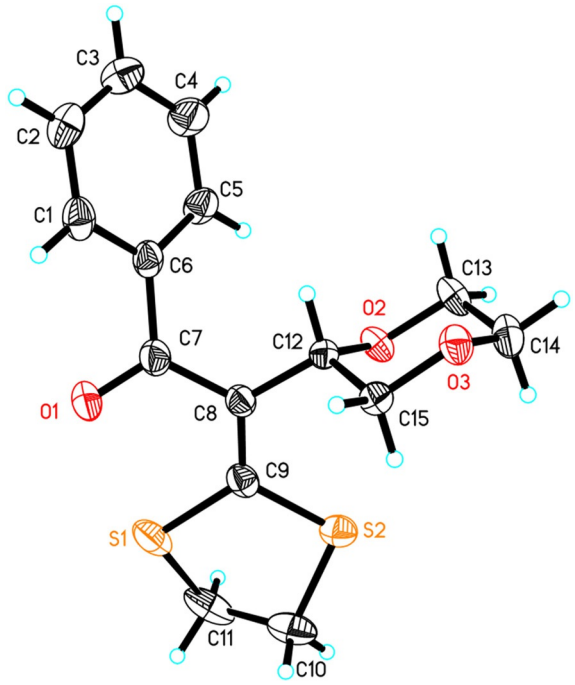
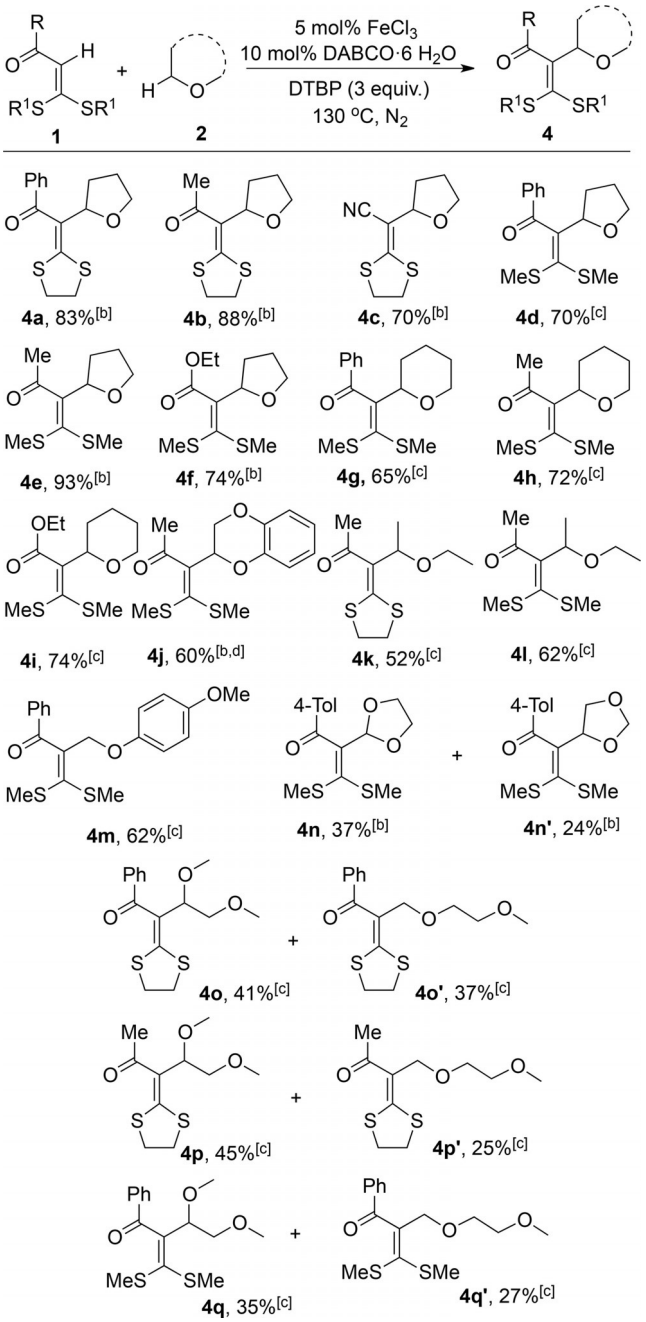


Figure 1. Molecular structure of compound **3a**.

4f (74%) over a longer period of 48 h. The reactivity of tetrahydropyran (THP) was lower than that of THF and its reactions with α-oxo ketene di(methylthio)acetals only produced **4g** (65%), **4h** (72%), and **4i** (74%) in moderate yields. 1,4-Benzodioxane also exhibited a lower reactivity than aliphatic 1,4-dioxane to react with α-acetyl ketene di(methylthio)acetal to form **4j** (60%). Acyclic ethers, e.g., diethyl ether, could undergo the oxidative cross-coupling reaction *via* its methylene C–H bond, affording **4k** (52%) and **4l** (62%), respectively. 1,4-Dimethoxybenzene showed a moderate reactivity to form **4m** (62%), while anisole did not undergo the desired reaction under the stated conditions, which is presumably attributed to the negative electronic effect from the ether substrate. Two kinds of C(sp^3)–H bonds are present in 1,3-dioxolane which participated in the reaction to generate two separable isomers **4n** (37%) and **4n′** (24%), demonstrating that the *O*,*O*-methylene C–H bond is more reactive than the *O*-methylene C–H bond. Glycol dimethyl ether reacted with the cyclic α-benzoyl ketene acetal, also affording two regioisomers **4o** (41%) and **4o′** (37%). Similar results were obtained from the reactions of α-acetyl and α-benzoyl ketene dithioacetals, yielding **4p** (45%) and **4p′** (25%), and **4q** (35%) and **4q′** (27%), respectively, revealing that the *O*-methylene C–H bond is more reactive than the methoxy C–H in glycol dimethyl ether.

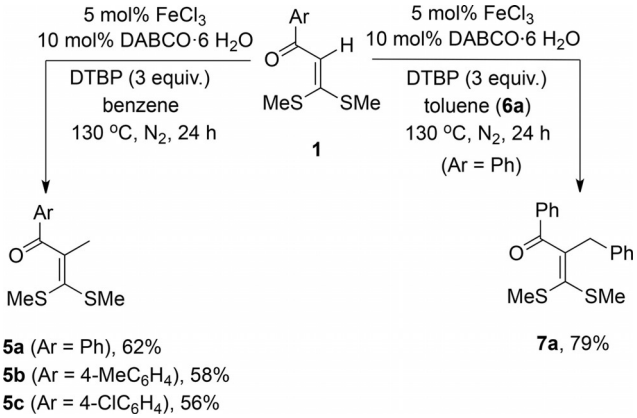
During the screening of conditions for the reactions of **1** with **2**, control experiments were performed in the absence of **2** in benzene or toluene solvent under the standard conditions (Scheme 2). In benzene α-

Table 3. Scope of ethers **2**.[a]



[a] *Conditions:* **1** (0.5 mmol), **2** (3 mL), $FeCl_3$ (0.025 mmol), DABCO·6H_2O (0.05 mmol), DTBP (1.5 mmol), 130 °C, in a 25-mL sealed tube, 0.1 MPa N_2, 24–48 h. Yields refer to the isolated products.
[b] For 24 h.
[c] For 48 h.
[d] 1.5 mmol of ether in benzene (3 mL).

aroyl ketene dithioacetal substrates underwent olefinic C(sp^2)–H methylation to form **5a–5c** (56–62%) with DTBP as the methylating agent,[25] while in toluene benzylation occurred to yield olefinic C(sp^2)–H benzylation product **7a** (79%). Thus, C–H benzylation of

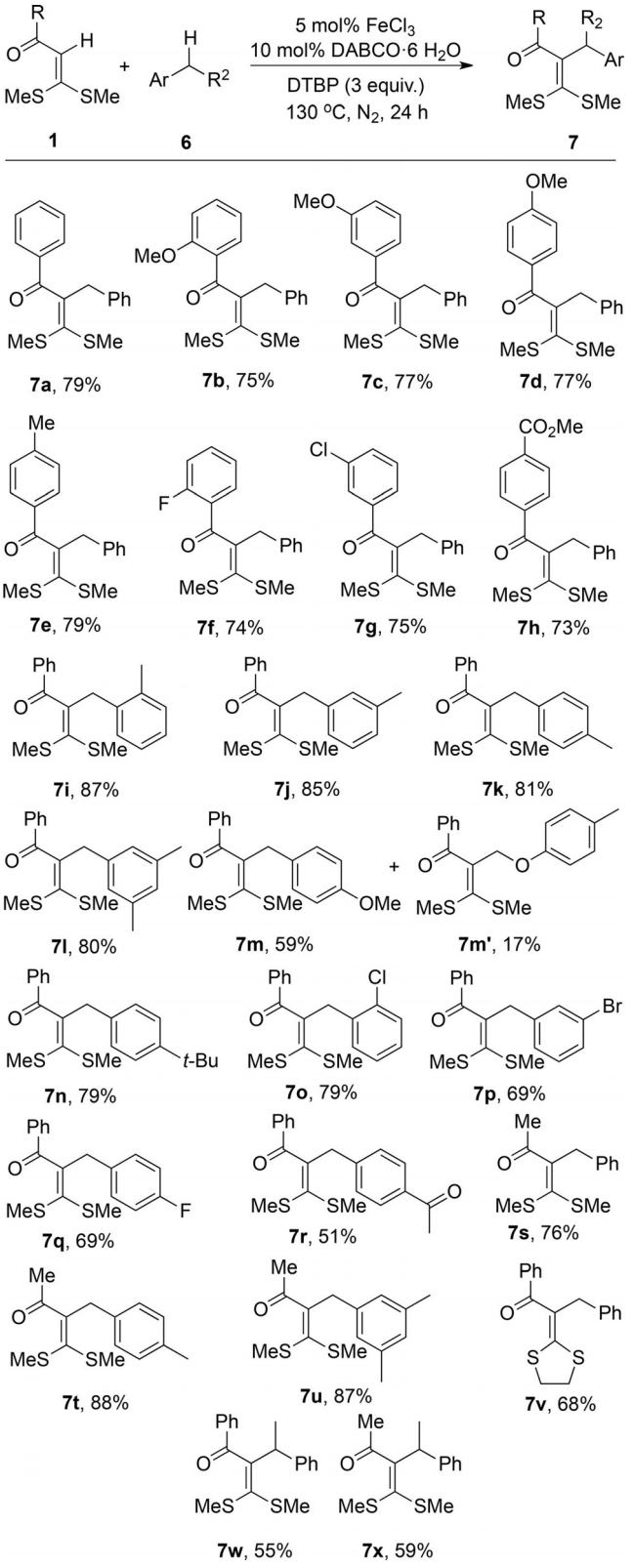


Scheme 2. Reactions of **1** in the absence of ethers.

α-oxo ketene dithioacetals **1** was investigated by replacement of the ether substrates with toluene derivatives as the coupling partners (Table 4). The reactions took place efficiently with toluene and its analogues to afford the C–H benzylated olefin products **7a–7h** (73–79%). Both electron-donating and electron-withdrawing groups such as MeO, Me, F, Cl, and CO_2Me were tolerated on the aroyl moieties of the internal olefin substrates, and no obvious steric effect was observed. Multimethyl-substituted toluene derivatives such as *o*-, *m*-, and *p*-xylenes, and mesitylene efficiently reacted with α-benzoyl ketene di(methylthio)acetal to form the benzylation products **7i–7l** (80–87%). The reaction of 4-methoxytoluene gave two separable regioisomers **7m** (59%) and **7m′** (17%), revealing that the benzylic C–H bond is more reactive than the methoxy C–H bond in the substituted toluene substrate. 4-*tert*-Butyl- and 2-chlorotoluenes also reacted with the internal olefin, yielding **7n** (79%) and **7o** (79%), respectively. However, 3-Br, 4-F, and 4-acetyl substituted toluene derivatives exhibited a moderate reactivity, and their reactions produced **7p–7r** in 51–69% yields. Both acyclic α-acetyl and cyclic α-benzoyl ketene dithioacetals reacted well with toluene and its derivatives to give **7s–7v** (68–88%). Unexpectedly, ethylbenzene could demonstrate a moderate reactivity to form the relatively sterically hindered benzylation products **7w** and **7x** (55–59%). These results have supplemented the previous work on C–H benzylation of electron-rich arenes[26] and activated olefins[22c] through iron-catalyzed oxidative C–H/C–H cross-coupling.

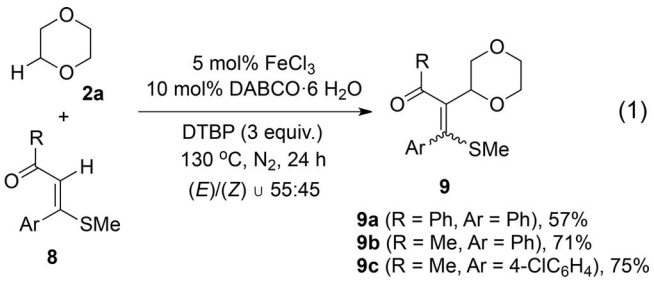
In order to further probe into the C–H bond reactivity of the polarized internal olefins, the impact of alkylthio(s) was investigated. Reacting α-acetyl and α-benzoyl ketene (methylthio)acetals **8** with 1,4-dioxane (**2a**) under the standard conditions gave the oxidative C(sp^2)–H/C(sp^3)–H cross-coupling products **9a–9c** in 57–75% yields [Eq. (1)]. As compared to the corresponding di(methylthio)acetals, these monothioacetal substrates exhibited a lower reactivity to

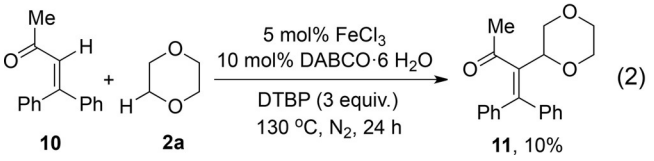
Table 4. C–H benzylation of α-oxoketene dithioacetals **1**.[a]



[a] *Conditions:* **1** (0.5 mmol), **6** (3 mL), $FeCl_3$ (0.025 mmol), DABCO·6H_2O (0.05 mmol), DTBP (1.5 mmol), 130 °C, in a 25-mL sealed tube, 0.1 MPa N_2, 24 h. Yields refer to the isolated products.

2a. In the case of using 4,4-diphenyl-but-3-enone (**10**) as the internal olefin substrate, the desired reaction could not effectively occur under the stated conditions, only forming the target product **11** in 10% yield [Eq. (2)]. These results have unambiguously demonstrated that the alkylthio functionality is necessary for the C–H functionalization of internal olefins **1**.[18b,e,f]

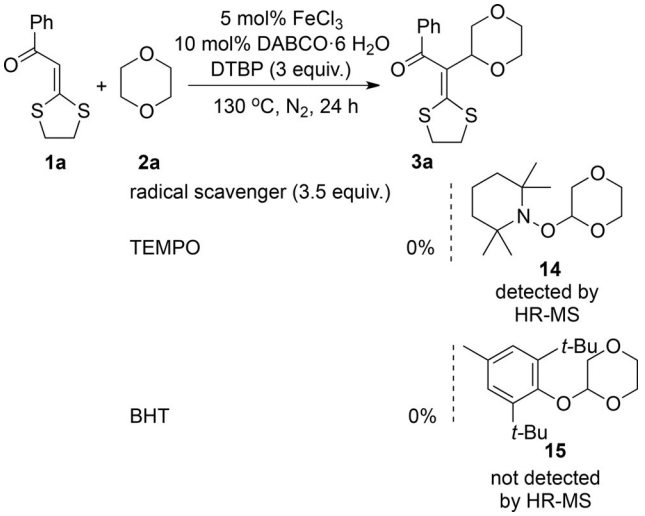




Then, the potential applications of the target tetrasubstituted olefin products were explored (Scheme 3). Treatment of **3o**, **3y**, **3z**, and **7s** with an excess amount of hydrazine hydrate (10 equiv.) in refluxing toluene afforded multisubstituted pyrazole derivatives **12a**–**12d** in excellent yields (87–96%).

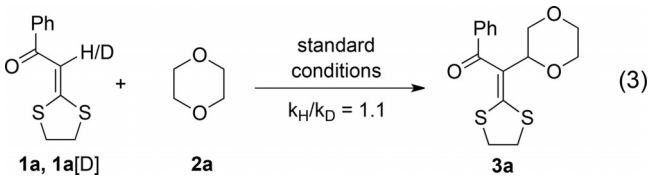
The reactions of **3y**, **3z**, and **4e** with hydroxylamine (6 equiv.) in refluxing ethanol gave fully substituted isoxazoles **13a**–**13c** (54–56%). These results have depicted the potential applications of the resultant tetrasubstituted olefins in the synthesis of trisubstituted pyrazoles[27] and fully functionlized isoxazoles.

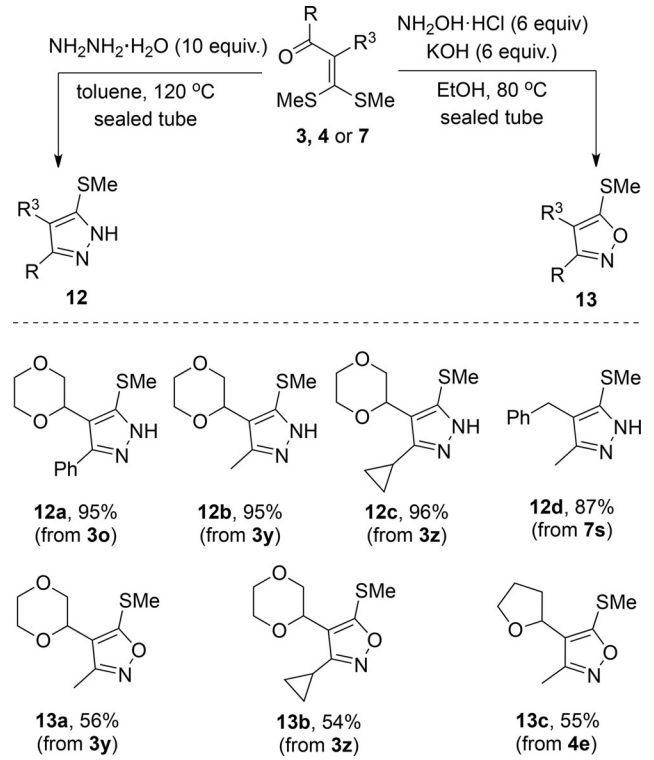
Additional control experiments were carried out to probe into the reaction mechanism. Introduction of a radical scavenger such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-*di*-*tert*-butyl-4-methylphenol (BHT) (3.5 equiv.) to the reaction of α-oxo ketene dithioacetal **1a** and 1,4-dioxane (**2a**) completely inhibited the oxidative C–H/C–H cross-coupling reaction (Scheme 4), suggesting that a radical pathway



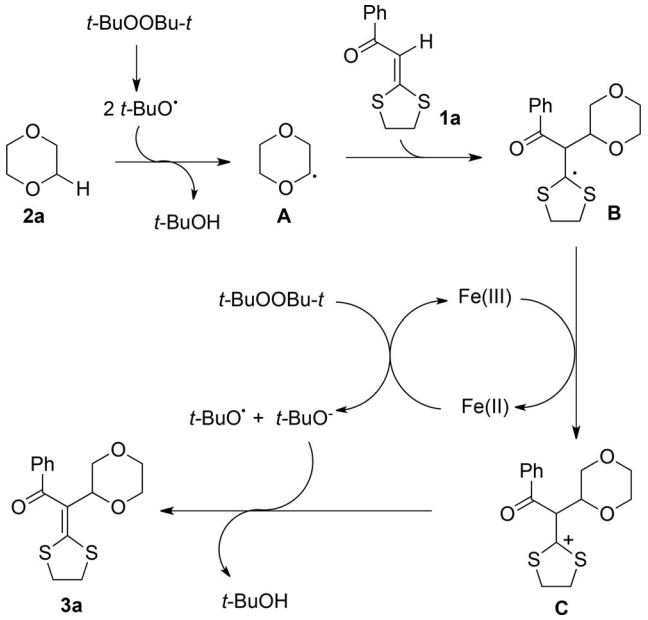
Scheme 4. Radical trapping experiments.

is involved in the catalytic cycle. The alkyl-scavenger adduct **14** was detected in the reaction mixture of **1a** with **2a** by HR-MS determination, but it was not successfully isolated (see the Supporting Information). The kinetic isotope effect (KIE) experiments were also conducted under the standard conditions by means of the reactions of **1a** and its deuterated form **1a**[D] with **2a** [Eq. (3)]. A secondary isotope effect was observed with $k_H/k_D = 1.1$, which implicates that the internal olefinic C(sp^2)–H bond cleavage is not involved in the rate-determining step in the overall catalytic cycle (see the Supporting Information for details).





Scheme 3. Synthetic applications of tetrasubstituted olefins.



Scheme 5. Proposed mechanism.

A plausible mechanism is proposed in Scheme 5. Initially, the homolytic cleavage of DTBP generates two *tert*-butoxy radicals. Subsequent interaction of ether **2a** with a *tert*-butoxy radical yields the new radical species **A** with release of *tert*-butyl alcohol by hydrogen abstraction from the C–H bond adjacent to the ether oxygen atom. Addition of radical **A** to the internal olefinic C=C bond of α-oxo ketene dithioacetal **1a** results in radical **B** which then reacts with the high valent Fe(III) salt to form cationic species **C** and the low valent Fe(II) species through a single electron transfer (SET) process. Oxidation of the Fe(II) species with DTBP regenerates the Fe(III) mediator, and produces *tert*-butoxy anion as well asthe *tert*-butoxy radical species. The alkylthio functionalities may help to stabilize the cationic species **C** due to their electron-donating property. Abstraction of a proton from species **C** by the basic *tert*-butoxy anion generated from DTBP affords the target product **3a**.

Conclusions

In summary, the iron-mediated oxidative C–H alkylation of *S,S*-functionalized internal olefins has been efficiently realized by means of simple ethers and toluene derivatives as the cross-coupling partners. Tetrasubstituted olefins were thus synthesized and efficiently applied for the preparation of trisubstituted NH-pyrazoles and fully functionalized isoxazoles. The present synthetic protocol provides a convenient route to fully functionalized olefins.

Experimental Section

General Considerations

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a 400 MHz spectrometer and all chemical shift values refer to $CDCl_3$ [δ(^{1}H), 7.26 ppm and δ(^{13}C), 77.16 ppm]. X-Ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The HR-MS data were obtained by ESI on a GC-TOF mass spectrometer. Column chromatographic purifications were performed on silica gel. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

General Procedure for the C–H Alkylation of Ketene Dithioacetals 1 with Ethers 2

Under a nitrogen atmosphere, a mixture of α-oxo ketene dithioacetal **1** (0.5 mmol), $FeCl_3$ (4 mg, 0.025 mmol), DABCO·6H_2O (11 mg, 0.05 mmol), and DTBP (219 mg, 1.5 mmol) in 1,4-dioxane (**2a**) (3 mL) was stirred in a 25-mL sealed tube at 130 °C for 24 h. After being cooled to ambient temperature, the mixture was evaporated of all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography [eluent: petroleum ether (60–90 °C)/ethyl acetate = 4:1, v/v] to afford the target product **3** or **4**.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (3a): yield: 123 mg (80%); pale yellow solid; mp 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.69 (d, J = 7.1 Hz, 2H, aromatic CH), 7.48 (t, 1H, aromatic CH), 7.40 (t, 2H, aromatic CH), 4.71 (dd, J = 10.5 and 3.0 Hz, 1H, O*CH*CH_2O), 4.12 and 3.89 (m each, 1:1H, OCH*C*H_2O), 3.72 (m, 2H, $CH_2OCH_2CH_2O$), 3.62 (m) and 3.53 (dd, J = 11.7, 2.9 Hz) (1:1H, $CHOCH_2CH_2O$), 3.42, 3.31 and 3.16 (m, 1:2:1H, S*C*H_2*C*H_2S); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.2 (Cq, C=O), 163.1 and 138.6 (Cq), 131.8, 128.5, and 128.4 (aromatic CH), 121.9 (Cq), 76.7 (O*CH*CH_2O), 67.2 (OCH*C*H_2O), 66.7 and 65.7 (O*C*H_2*C*H_2O), 37.4 and 37.2 (S*C*H_2*C*H_2S); HR-MS (ESI): m/z = 309.0617, calcd. for $C_{15}H_{16}O_3S_2$ $[M+H]^+$: 309.0619.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-(2-methoxyphenyl)ethanone (3b): yield: 133 mg (80%); pale yellow solid; mp 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.34 (m, 1H, aromatic CH), 7.18 (d, J = 7.4 Hz, 1H, aromatic CH), 6.95 (t, 1H, aromatic CH), 6.89 (d, J = 8.3 Hz, 1H, aromatic CH), 4.50 (dd, J = 10.6 and 3.0 Hz, 1H, O*CH*CH_2O), 4.08 (t) and 3.85 (d, J = 10.7 Hz) (1:1H, OCH*C*H_2O), 3.78 (s, 3H, OCH_3), 3.67 (m, 2H, $CH_2OCH_2CH_2O$), 3.57 (m) and 3.45 (dd, J = 11.6 and 3.0 Hz) (1:1H, $CH_2OCH_2CH_2O$), 3.38 and 3.18 (m each, 2H, S*C*H_2*C*H_2S); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.8 (Cq, C=O), 168.4 (Cq), 156.1 (Cq), 131.0 (aromatic CH), 129.9 (Cq), 128.2 (aromatic CH), 122.3 (Cq), 120.8 and 111.0 (aromatic CH), 76.2 (O*CH*CH_2O), 67.1 (OCH*C*H_2O), 66.3 and 65.5 (O*C*H_2*C*H_2O), 55.5 (OCH_3), 37.3 and 36.9 (S*C*H_2*C*H_2S); HR-MS (ESI): m/z = 339.0729, calcd. for $C_{16}H_{18}O_4S_2$ $[M+H]^+$: 339.0725.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-(3-methoxyphenyl)ethanone (3c): yield: 122 mg (71%); pale yellow solid; mp 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C,

TMS): δ = 7.22 (m, 2H, aromatic CH), 7.16 (d, J = 2.4 Hz, 1H, aromatic CH), 6.95 (m, 1H, aromatic CH), 4.65 (dd, J = 10.5 and 3.1 Hz, 1H, O*CH*CH$_2$O), 4.06 (m) and 3.80 (dd, J = 13.5, 5.1 Hz) (1:1H, OCH*CH$_2$*O), 3.73 (s, 3H, OCH$_3$), 3.65 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.55 (m) and 3.45 (dd, J = 11.7 and 3.0 Hz) (1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.36, 3.25 and 3.09 (m each, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 192.8 (Cq, C=O), 163.7, 159.5 and 139.9 (Cq), 129.4 (aromatic CH), 121.8 (Cq), 120.9 (s), 118.3 and 112.6 (aromatic CH), 76.5 (O*CH*CH$_2$O), 67.2 (OCH*CH$_2$*O), 66.6 and 65.7 (O*CH$_2$CH$_2$*O), 55.37 (OCH$_3$), 37.4 and 37.2 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 339.0724, calcd. for $C_{16}H_{18}O_4S_2$ $[M+H]^+$: 339.0725.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)ethanone (3d): yield: 147 mg (87%); pale yellow solid; mp 103–105 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.75 (d, J = 8.7 Hz, 2H, aromatic CH), 6.88 (d, J = 8.7 Hz, 2H, aromatic CH), 4.65 (dd, J = 10.3, 2.6 Hz, 1H, O*CH*CH$_2$O), 4.02 (t) and 3.79 (m) (1:4H, OCH$_3$ and OCH*CH$_2$*O), 3.71 and 3.59 (m each, 2:2H, O*CH$_2$CH$_2$*O), 3.38, 3.28 and 3.13 (m, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 192.6 (Cq, C=O), 163.0 (Cq of Ph), 156.9 (Cq), 131.4 (aromatic CH), 130.5 (Cq), 122.5 (Cq), 113.6 (aromatic CH), 77.2 (O*CH*CH$_2$O), 67.1 (OCH*CH$_2$*O), 67.0 and 65.7 (O*CH$_2$CH$_2$*O), 55.4 (OCH$_3$), 37.4 and 37.4 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 339.0719, calcd. for $C_{16}H_{18}O_4S_2$ $[M+H]^+$: 339.0725.

1-(2-Chlorophenyl)-2-(1,4-dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)ethanone (3e): yield: 137 mg (80%); pale yellow solid; mp 130–131 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.38 (dd, J = 7.9 and 1.2 Hz, 1H, aromatic CH), 7.30 (m, 2H, aromatic CH), 7.21 (dd, J = 7.4 and 1.6 Hz, 1H, aromatic CH), 4.45 (dd, J = 10.6 and 3.1 Hz, 1H, O*CH*CH$_2$O), 4.04 (t) and 3.84 (d, J = 8.8 Hz) (1:1H, OCH*CH$_2$*O), 3.64 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.59 (m) and 3.50 (dd, J = 11.7 and 2.9 Hz) (1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.42 and 3.23 (m each, 2:2H, S*CH$_2$CH$_2$*S); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 189.4 (Cq, C=O), 171.4, 139.7 and 130.6 (Cq), 130.4, 129.8, 127.8 and 126.9 (aromatic CH), 121.1 (Cq), 76.0 (O*CH*CH$_2$O), 67.2 (OCH*CH$_2$*O), 66.2 and 65.6 (O*CH$_2$CH$_2$*O), 37.6 and 37.1 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 343.0232, calcd. for $C_{15}H_{15}O_3S_2Cl$ $[M+H]^+$: 343.0229.

1-(3-Chlorophenyl)-2-(1,4-dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)ethanone (3f): yield: 109 mg (64%); pale yellow solid; mp 125–127 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.69 (s, 1H, aromatic CH), 7.57 (d, J = 7.6 Hz, 1H, aromatic CH), 7.46 (d, J = 8.0 Hz, 1H, aromatic CH), 7.36 (t, 1H, aromatic CH), 4.68 (dd, J = 10.5 and 2.9 Hz, 1H, O*CH*CH$_2$O), 4.14 (t) and 3.91 (d, J = 9.4 Hz) (1:1H, OCH*CH$_2$*O), 3.74 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.63 (m) and 3.53 (dd, J = 11.7 and 2.7 Hz) (1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.46, 3.36 and 3.20 (m each, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 191.6 (Cq, C=O), 165.2, 140.5 and 134.6 (Cq), 131.7, 129.8, 128.6 and 126.6 (aromatic CH), 121.5 (Cq), 76.6 (O*CH*CH$_2$O), 67.4 (OCH*CH$_2$*O), 66.7 and 65.8 (O*CH$_2$CH$_2$*O), 37.5 and 37.4 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 342.0230, calcd. for $C_{15}H_{15}O_3S_2Cl$ $[M+H]^+$: 343.0229.

1-(4-Chlorophenyl)-2-(1,4-dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)ethanone (3g): yield: 140 mg (82%); pale yellow solid; mp 149–151 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.66 (d, J = 8.3 Hz, 2H, aromatic CH), 7.39 (d, J = 8.3 Hz, 2H, aromatic CH), 4.65 (dd, J = 10.4 and 2.8 Hz, 1H, O*CH*CH$_2$O), 4.11 (t) and 3.88 (d, J = 9.4 Hz) (1:1H, OCH*CH$_2$*O), 3.73 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.62 and 3.53 (m each, 1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.43, 3.33 and 3.18 (m each, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 192.1 (Cq, C=O), 163.2, 138.2 and 136.9 (Cq), 130.2 and 128.8 (aromatic CH), 121.7 (Cq), 76.8 (O*CH*CH$_2$O), 67.3 (OCH*CH$_2$*O), 66.8 and 65.8 (O*CH$_2$CH$_2$*O), 37.5 and 37.3 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 343.0232, calcd. for $C_{15}H_{15}O_3S_2Cl$ $[M+H]^+$: 343.0229.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)ethanone (3h): yield: 133 mg (81%); pale yellow solid; mp 135–137 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.76 (dd, J = 8.6 and 5.5 Hz, 2H, aromatic CH), 7.09 (t, 2H, aromatic CH), 4.66 (dd, J = 10.4 and 3.0 Hz, 1H, O*CH*CH$_2$O), 4.10 (t) and 3.88 (d, J = 10.0 Hz) (1:1H, OCH*CH$_2$*O), 3.71 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.64 (m) and 3.55 (dd, J = 11.7 and 2.9 Hz) (1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.43, 3.33 and, 3.17 (m each, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 192.0 (Cq, C=O), 165.1 (d, J = 253.3 Hz, Cq of Ph), 161.7 (Cq), 134.6 (d, J = 3.1 Hz, Cq of Ph), 131.4 (d, J = 9.1 Hz, aromatic CH), 121. 9 (Cq), 115.6 (d, J = 21.8 Hz, aromatic CH), 76.9 (O*CH*CH$_2$O), 67.3 (OCH*CH$_2$*O), 66.8 and 65.8 (O*CH$_2$CH$_2$*O), 37.5 and 37.3 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 327.0517, calcd. for $C_{15}H_{15}O_3S_2F$ $[M+H]^+$: 327.0525.

1-(4-Bromophenyl)-2-(1,4-dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)ethanone (3i): yield: 146 mg (76%); pale yellow solid; mp 141–143 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.56 (q, J = 8.5 Hz, 4H, aromatic CH), 4.64 (dd, J = 10.4 and 2.9 Hz, 1H, O*CH*CH$_2$O), 4.10 (t) and 3.87 (d, J = 9.3 Hz) (1:1H, OCH*CH$_2$*O), 3.71 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.61 (m) and 3.52 (dd, J = 11.7 and 2.8 Hz) (1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.42, 3.32 and 3.17 (m each, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 192.2 (Cq, C=O), 163.5 and 137.4 (Cq), 131.8 and 130.3 (aromatic CH), 126.7 and 121.7 (Cq), 76.8 (O*CH*CH$_2$O), 67.4 (OCH*CH$_2$*O), 66.8 and 65.8 (O*CH$_2$CH$_2$*O), 37.6 and 37.4 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 386.9722, calcd. for $C_{15}H_{15}O_3S_2Br$ $[M+H]^+$: 386.9724.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)-1-[4-(trifluoromethyl)phenyl]ethanone (3j): yield: 132 mg (70%); pale yellow solid; mp 133–135 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.78 (d, J = 8.0 Hz, 2H, aromatic CH), 7.69 (d, J = 8.1 Hz, 2H, aromatic CH), 4.65 (dd, J = 10.5 and 2.9 Hz, 1H, O*CH*CH$_2$O), 4.15 (t) and 3.91 (d, J = 9.6 Hz) (1:1H, OCH*CH$_2$*O), 3.72 (m, 2H, CH$_2$O*CH$_2$*CH$_2$O), 3.63 and 3.52 (m each, 1:1H, CH$_2$OCH$_2$*CH$_2$*O), 3.47, 3.37 and 3.22 (m, 1:2:1H, S*CH$_2$CH$_2$*S); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 191.6 (Cq, C=O), 166.7 and 142.2 (Cq), 133.0 (q, J = 32.7 Hz, Cq of Ph), 128.7 (aromatic CH), 125.5 (q, J = 3.7 Hz, aromatic CH), 123.8 (q, J = 272.6 Hz, CF$_3$), 121.3 (Cq), 76.5 (O*CH*CH$_2$O), 67.4 (OCH*CH$_2$*O), 66.6 and 65.8 (O*CH$_2$CH$_2$*O), 37.5 and 37.4 (S*CH$_2$CH$_2$*S); HR-MS (ESI): m/z = 377.0491, calcd. for $C_{16}H_{15}O_3S_2F_3$ $[M+H]^+$: 377.0493.

1-(1,4-Dioxan-2-yl)-1-(1,3-dithiolan-2-ylidene)propan-2-one (3k): yield: 107 mg (87%); white solid; mp 119–121 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 4.83 (dd, J = 10.7 and 3.1 Hz, 1H, O*CH*CH$_2$O), 3.93 (m, 2H, OCH*CH$_2$*O), 3.84, 3.73 and 3.63 (m, 1:2:1H, O*CH$_2$CH$_2$*O),

3.34 and 3.20 (m each, 2:2H, SCH_2CH_2S), 2.36 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.2 (Cq, C=O), 166.3 and 121.5 (Cq), 77.0 (O$CH$$CH_2$O), 67.5 (OCH$CH_2$O), 66.8 and 65.8 (O$CH_2CH_2$O), 38.0 and 36.2 (S$CH_2CH_2$S), 28.9 (CO$CH_3$); HR-MS (ESI): m/z = 247.0454, calcd. for $C_{10}H_{14}O_3S_2$ $[M+H]^+$: 247.0463.

Ethyl 2-(1,4-dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)acetate (3l): yield: 114 mg (83%); white solid; mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.81 (dd, J = 10.3 and 2.8 Hz, 1H, O$CH$$CH_2$O), 4.16 (dd, J = 13.0 and 5.9 Hz, 2H, OCH_2CH_3), 3.73 (m, 6H, $CH_2OCH_2CH_2$O), 3.32 and 3.19 (m, 2:2H, SCH_2CH_2S), 1.25 (t, 3H, OCH$_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 165.2 (Cq, C=O), 165.1 and 113.0 (Cq), 75.3 (O$CH$$CH_2$O), 67.2 (OCH$CH_2$O), 66.6 and 65.8 (O$CH_2CH_2$O), 60.6 (O$CH_2CH_3$), 37.5 and 37.1 (S$CH_2CH_2$S), 14.3 (OCH$_2CH_3$); HR-MS (ESI): m/z = 277.0567, calcd. for $C_{11}H_{16}O_4S_2$ $[M+H]^+$: 277.0568.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithiolan-2-ylidene)acetonitrile (3m): yield: 100 mg (87%); white solid; mp 122–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.30 (dd, J = 10.0 and 2.8 Hz, 1H, O$CH$$CH_2$O), 3.80, 3.69 and 3.63 (m each, 3:2:1H, $CH_2OCH_2CH_2$O), 3.56 (m, 4H, SCH_2CH_2S); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.8, 116.9 and 94.3 (Cq), 75.3 (O$CH$$CH_2$O), 68.5 (OCH$CH_2$O), 66.9 and 66.1 (O$CH_2CH_2$O), 39.6 and 38.3 (S$CH_2CH_2$S); HR-MS (ESI): m/z = 252.0120, calcd. for $C_9H_{11}NO_2S_2$ $[M+Na]^+$: 252.0120.

2-(1,4-Dioxan-2-yl)-2-(1,3-dithian-2-ylidene)-1-phenylethanone (3n): yield: 130 mg (81%); pale yellow solid; mp 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94 (d, J = 7.5 Hz, 2H, aromatic CH), 7.53 (t, 1H, aromatic CH), 7.43 (t, 2H, aromatic CH), 4.85 (dd, J = 9.1 and 4.1 Hz, 1H, O$CH$$CH_2$O), 3.77 and 3.69 (m each, 2:2H, $CH_2OCH_2CH_2$O), 3.59 and 3.51 (m each, 1:1H, $CH_2OCH_2CH_2$O), 2.98 (m, 2H, SCH_2), 2.74 (m, 2H, SCH_2), 2.09 (m, 2H, $SCH_2CH_2CH_2$S); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 195.0 (Cq, C=O), 138.6, 137.7 and 134.4 (C=CCH), 133.2, 129.5 and 128.6 (aromatic CH), 75.6 (O$CH$$CH_2$O), 68.2 (OCH$CH_2$O), 66.9 and 66.0 (O$CH_2CH_2$O), 29.1 and 28.8 ($SCH_2$), 23.92 ($SCH_2CH_2CH_2$S); HR-MS (ESI): m/z = 323.0774, calcd. for $C_{16}H_{18}O_3S_2$ $[M+H]^+$: 323.0776.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (3o): yield: 125 mg (81%); white solid; mp 111–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.91 (d, J = 7.6 Hz, 2H, aromatic CH), 7.53 (t, 1H, aromatic CH), 7.44 (t, 2H, aromatic CH), 5.05 (dd, J = 10.2 and 2.5 Hz, 1H, O$CH$$CH_2$O), 3.83, 3.68 and 3.48 (m each, 1:4:1H, $CH_2OCH_2CH_2$O), 2.35 (s, 3H, SCH_3), 2.04 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS)δ 194.7 (Cq, C=O), 143.4, 137.6 and 137.2 (Cq), 133.1 (aromatic CH), 129.4 and 128.4 (aromatic CH), 76.6 (O$CH$$CH_2$O), 68.7 (OCH$CH_2$O), 66.8 and 66.1 (O$CH_2CH_2$O), 17.1 ($SCH_3$), 16.4 ($SCH_3$); HR-MS (ESI): m/z = 311.0774 calcd. for $C_{15}H_{18}O_3S_2$ $[M+H]^+$: 311.0776.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)-1-*o*-tolylprop-2-en-1-one (3p): yield: 117 mg (72%); white solid; mp 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.69 (d, J = 7.6 Hz, 1H, aromatic CH), 7.33 (t, 1H, aromatic CH), 7.20 (t, 2H, aromatic CH), 5.03 (dd, J = 10.0 and 2.9 Hz, 1H, O$CH$$CH_2$O), 3.79 (m, 4H, $CH_2OCH_2CH_2$O), 3.63 and 3.53 (m each, 1:1H, $CH_2OCH_2CH_2$O), 2.60 (s, 3H, SCH_3), 2.32 (s, 3H, SCH_3), 1.89 (s, 3H, Ph-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.6 (Cq, C=O), 145.5, 134.0, 137.9 and 137.8 (Cq) 131.6, 131.6, 131.2 and 125.1 (aromatic CH), 76.9 (O$CH$$CH_2$O), 68.8 (OCH$CH_2$O), 66.8 and 66.1 (O$CH_2CH_2$O), 21.5 (Ph-$CH_3$), 16.7 ($SCH_3$), 16.4 ($SCH_3$); HR-MS (ESI): m/z = 325.0930, calcd. for $C_{16}H_{20}O_3S_2$ $[M+H]^+$: 325.0932.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)-1-*m*-tolylprop-2-en-1-one (3q): yield: 118 mg (73%); white solid; mp 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.76 (s, 1H, aromatic CH), 7.68 (d, J = 6.9 Hz, 1H, aromatic CH), 7.33 (q, J = 7.5 Hz, 2H, aromatic CH), 5.05 (dd, J = 10.2 and 2.6 Hz, 1H, O$CH$$CH_2$O), 3.83 (dd, J = 11.5 and 2.4 Hz), 3.68 (m) and 3.49 (m) (1:4:1H, $CH_2OCH_2CH_2$O), 2.40 (s, 3H, SCH_3), 2.36 (s, 3H, SCH_3), 2.06 (s, 3H, Ph-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 194.9 (Cq, C=O), 143.6, 138.3, 137.5 and 136.9 (Cq), 134.1 (aromatic CH), 129.5 (aromatic CH), 128.3 (aromatic CH), 127.1 (aromatic CH), 76.6 (O$CH$$CH_2$O), 68.7 (OCH$CH_2$O), 66.8 and 66.1 (O$CH_2CH_2$O), 21.5 (Ph-$CH_3$), 17.2 ($SCH_3$), 16.4 ($SCH_3$); HR-MS (ESI): m/z = 325.0934, calcd. for $C_{16}H_{20}O_3S_2$ $[M+H]^+$: 325.0932.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)-1-(*p*-tolyl)-prop-2-en-1-one (3r): yield: 138 mg (85%); white solid; mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.81 (d, J = 8.1 Hz, 2H, aromatic CH), 7.24 (t, 2H, aromatic CH), 5.04 (dd, J = 10.2 and 2.8 Hz, 1H, O$CH$$CH_2$O), 3.81 (dd, J = 11.5 and 2.6 Hz), 3.65 (m) and 3.47 (m) (1:4:1H, $CH_2OCH_2CH_2$O), 2.39 (s, 3H, Ph-CH_3), 2.34 (s, 3H, SCH_3), 2.08 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 194.3 (Cq, C=O), 144.0, 143.5, 136.8 and 135.1 (Cq), 129.5 and 129.2 (aromatic CH), 76.5 (O$CH$$CH_2$O), 68.6 (OCH$CH_2$O), 66.7 and 66.0 (O$CH_2CH_2$O), 21.8 (Ph-$CH_3$), 17.1 ($SCH_3$), 16.3 ($SCH_3$); HR-MS (ESI): m/z = 325.0935, calcd. for $C_{16}H_{20}O_3S_2$ $[M+H]^+$: 325.0932.

2-(1,4-Dioxan-2-yl)-1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (3s): yield: 128 mg (74%); white solid; mp 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.76 (d, J = 7.6 Hz, 1H, aromatic CH), 7.42 (d, J = 7.8 Hz, 1H, aromatic CH), 7.36 (dd, J = 10.7 and 4.3 Hz, 1H, aromatic CH), 7.28 (t, 1H, aromatic CH), 5.02 (dd, J = 9.1 and 3.9 Hz, 1H, O$CH$$CH_2$O), 3.79 (m, 4H, $CH_2OCH_2CH_2$O), 3.64 (dd, J = 11.6 and 2.1 Hz) and 3.55 (m) (1:1H, $CH_2OCH_2CH_2$O), 2.33 (s, 3H, SCH_3), 1.91 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.8 (Cq, C=O), 144.2, 140.4, 137.6 and 133.8 (Cq), 132.1, 131.4, 131.1and 126.1 (aromatic CH), 76.9 (O$CH$$CH_2$O), 68.6 (OCH$CH_2$O), 66.8 and 66.1 (O$CH_2CH_2$O), 16.7 ($SCH_3$), 16.4 ($SCH_3$); HR-MS (ESI): m/z = 345.0387, calcd. for $C_{15}H_{17}O_3S_2Cl$ $[M+H]^+$: 345.0386.

1-(3-Chlorophenyl)-2-(1,4-dioxan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (3t): yield: 104 mg (60%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.89 (s, 1H, aromatic CH), 7.76 (d, J = 7.7 Hz, 1H, aromatic CH), 7.49 (m, 1H, aromatic CH), 7.38 (t, 1H, aromatic CH), 5.04 (dd, J = 10.2 and 2.8 Hz, 1H, O$CH$$CH_2$O), 3.82 (dd, J = 11.5 and 2.7 Hz), 3.68 (m) and 3.49 (m) (1:4:1H, $CH_2OCH_2CH_2$O), 2.35 (s, 3H, SCH_3), 2.05 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.5 (Cq, C=O), 142.8, 139.4, 138.0 and 134.8 (Cq), 139.8, 129.8, 129.1 and 127.6 (aromatic CH), 76.6 (O$CH$$CH_2$O), 68.6

(OCHCH_2O), 66.8 and 66.1 (OCH_2CH_2O), 17.1 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 345.0389, calcd. for $C_{15}H_{17}O_3S_2Cl$ $[M+H]^+$: 345.0386.

1-(4-Bromophenyl)-2-(1,4-dioxan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (3u): yield: 152 mg (78%); white solid; mp 131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.76 (m, 2H, aromatic CH), 7.57 (d, J = 7.0 Hz, 2H, aromatic CH), 5.03 (d, J = 10.1 Hz, 1H, OCHCH$_2$O), 3.81 (d, J = 11.5 Hz), 3.66 (m), and 3.47 (t, J = 11.5 Hz) (1:4:1H, $CH_2OCH_2CH_2O$), 2.34 (s, 3H, SCH_3), 2.05 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.7 (Cq, C=O), 142.8, 137.6 and 136.5 (Cq), 131.7 and 130.8 (aromatic CH), 128.3 (Cq), 76.5 (OCHCH$_2$O), 68.5 (OCHCH_2O), 66.7 and 66.0 (OCH_2CH_2O), 17.1 (SCH_3), 16.3 (SCH_3); HR.MS (ESI): m/z = 388.9883, calcd. for $C_{15}H_{17}O_3S_2Br$ $[M+H]^+$: 388.9881.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)-1-(naphthalen-2-yl)prop-2-en-1-one (3v): yield: 60 mg (33%); pale yellow solid; mp 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.42 (s, 1H, aromatic CH), 8.01 (m, 2H, aromatic CH), 7.88 (m, 2H, aromatic CH), 7.56 (m, 2H, aromatic CH), 5.14 (dd, J = 10.2 and 2.8 Hz, 1H, OCHCH$_2$O), 3.90 (dd, J = 11.5 and 2.6 Hz), 3.70 (m) and 3.51 (m) (1:4:1H, $CH_2OCH_2CH_2O$), 2.39 (s, 3H, SCH_3), 2.05 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 194.8 (Cq, C=O), 143.6, 137.4, 135.8, 135.1 and 132.7 (Cq), 131.6, 129.9, 128.5, 128.4, 127.9, 126.7 and 124.7 (aromatic CH), 76.8 (OCHCH$_2$O), 68.8 (OCHCH_2O), 66.8 and 66.1 (OCH_2CH_2O), 17.2 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 361.0936, calcd. for $C_{19}H_{20}O_3S_2$ $[M+H]^+$: 361.0932.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (3w): yield: 64 mg (41%); pale yellow solid; mp 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.64 (d, J = 4.9 Hz, 1H, aromatic CH), 7.58 (d, J = 3.7 Hz, 1H, aromatic CH), 7.09 (m, 1H, aromatic CH), 5.01 (dd, J = 10.2 and 2.8 Hz, 1H, OCHCH$_2$O), 3.65 (m, 6H, $CH_2OCH_2CH_2O$), 2.35 (s, 3H, SCH_3), 2.12 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 186.9 (Cq, C=O), 145.1, 143.0 and 138.7 (Cq), 134.3, 134.1 and 128.1 (aromatic CH), 76.2 (OCHCH$_2$O), 68.6 (OCHCH_2O), 66.8 and 66.0 (OCH_2CH_2O), 17.5 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 317.0339, calcd. for $C_{13}H_{16}O_3S_3$ $[M+H]^+$: 317.0340.

2-(1,4-Dioxan-2-yl)-1-(furan-2-yl)-3,3-bis(methylthio)-prop-2-en-1-one (3x): yield: 31 mg (21%); pale yellow solid: mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60 (s, 1H, aromatic CH), 7.10 (d, J = 3.5 Hz, 1H, aromatic CH), 6.53 (dd, J = 3.1 and 1.1 Hz, 1H, aromatic CH), 5.01 (dd, J = 10.2 and 2.8 Hz, 1H, OCHCH$_2$O), 3.74 (m, 4H, $CH_2OCH_2CH_2O$), 3.61 and 3.51 (m each, 1:1H, $CH_2OCH_2CH_2O$), 2.35 (s, 3H, SCH_3), 2.14 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 182.3 (Cq, C=O), 153.3 (Cq), 147.1 (aromatic CH), 142.1 (Cq), 139.4 (Cq), 119.2 (aromatic CH), 112.5 (aromatic CH), 76.4 (OCHCH$_2$O), 68.7 (OCHCH_2O), 66.9 and 66.1 (OCH_2CH_2O), 17.8 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 301.0569, calcd. for $C_{13}H_{16}O_4S_2$ $[M+H]^+$: 301.0568.

3-(1,4-Dioxan-2-yl)-4,4-bis(methylthio)but-3-en-2-one (3y): yield: 108 mg (87%); white solid; mp 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.87 (dd, J = 10.2, 3.0 Hz, 1H, OCHCH$_2$O), 3.60 (m, 6H, $CH_2OCH_2CH_2O$), 2.34 (s, 3H, SCH_3), 2.27 (s, 3H, SCH_3), 2.21 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 202.8 (Cq, C=O), 146.7 and 134.0 (Cq), 76.3 (OCHCH$_2$O), 68.2 (OCHCH_2O), 66.6 and 66.0 (OCH_2CH_2O), 32.3 (CH_3CO), 17.3 (SCH_3), 16.3 (SCH_3); HR-MS (ESI): m/z = 249.0617, calcd. for $C_{10}H_{16}O_3S_2$ $[M+H]^+$: 249.0619.

1-Cyclopropyl-2-(1,4-dioxan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (3z): yield: 111 mg (81%); pale yellow solid; mp 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.89 (dd, J = 10.1 and 3.0 Hz, 1H, OCHCH$_2$O), 3.73 (dd, J = 8.1 and 2.0 Hz), 3.68 (dd, J = 11.5 and 2.9 Hz) and 3.56 (m) (2:1:3H, $CH_2OCH_2CH_2O$), 2.30 (s, 3H, SCH_3), 2.24 (s, 3H, SCH_3), 2.09 (m, 1H, CH_2CHCH_2), 1.17 and 0.96 (m, 2H, $CHCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 204.6 (Cq, C=O), 146.6 and 136.2 (Cq), 76.2 (OCHCH$_2$O), 68.6 (OCHCH_2O), 66.8 and 66.1 (OCH_2CH_2O), 23.2 (CH_2CHCH_2), 17.4 (SCH_3), 16.4 (SCH_3), 12.8 and 12.3 ($CHCH_2CH_2$); HR-MS (ESI): m/z = 275.0775, calcd. for $C_{12}H_{18}O_3S_2$ $[M+H]^+$: 275.0776.

Ethyl 2-(1,4-dioxan-2-yl)-3,3-bis(methylthio)acrylate (3z1): yield: 121 mg (87%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.79 (t, 1H, OCHCH$_2$O), 4.17 (m, 2H, OCH_2CH$_3$), 3.64, 3.56 and 3.46 (m each, 2:3:1H, $CH_2OCH_2CH_2O$), 2.23 (s, 3H, SCH_3), 2.17 (s, 3H, SCH_3), 1.23 (t, 3H, OCH$_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 165.8 (Cq, C=O), 138.4 and 137.6 (Cq), 75.2 (OCHCH$_2$O), 68.1 (OCHCH_2O), 66.5 and 65.7 (OCH_2CH_2O), 61.0 (OCH_2CH$_3$), 17.2 (SCH_3), 16.0 (SCH_3), 14.0 (OCH$_2CH_3$); HR-MS (ESI): m/z = 279.0725, calcd. for $C_{13}H_{14}O_2S_2$ $[M+H]^+$: 279.0725.

2-(1,4-Dioxan-2-yl)-3,3-bis(methylthio)acrylonitrile (3z2): yield: 101 mg (87%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.74 (dd, J = 10.2 and 2.8 Hz, 1H, OCHCH$_2$O), 3.70 (m, 6H, $CH_2OCH_2CH_2O$), 2.47 and 2.44 (s each, 3:3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 161.0, 115.9 and 111.6 (Cq), 73.5 (OCHCH$_2$O), 68.4 (OCHCH_2O), 66.8 and 65.9 (OCH_2CH_2O), 18.3 (SCH_3), 17.7 (SCH_3); HR-MS (ESI): m/z = 232.0462, calcd. for $C_9H_{13}NO_2S_2$ $[M+H]^+$: 232.0460.

2-(1,3-Dithiolan-2-ylidene)-1-phenyl-2-(tetrahydrofuran-2-yl)ethanone (4a): yield: 121 mg (83%); pale yellow solid; mp 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.68 (m, 2H, aromatic CH), 7.41 (m, 3H, aromatic CH), 4.83 (m, 1H, OCHCH$_2$), 4.02 and 3.71 (m each, 1:1H, OCH_2CH$_2$), 3.41, 3.28 and 3.13 (m each, 1:2:1H, SCH_2CH_2S), 2.17 and 1.91 (m each, 1:3H, OCHCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.6 (Cq, C=O), 160.6 and 139.0 (Cq), 131.3, 128.5 and 128.2 (aromatic CH), 124.9 (Cq), 79.6 (OCHCH$_2$), 67.9 (OCH_2CH$_2$), 37.4 and 36. 9 (SCH_2CH_2S), 29.8 (CHCH_2CH$_2$), 26.6 (CHCH$_2CH_2$); HR-MS (ESI): m/z = 293.0671, calcd. for $C_{15}H_{16}O_2S_2$ $[M+H]^+$: 293.0670.

1-(1,3-Dithiolan-2-ylidene)-1-(tetrahydrofuran-2-yl)propan-2-one (4b): yield: 101 mg (88%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.94 (dd, J = 9.4 and 6.3 Hz, 1H, OCHCH$_2$), 4.05 and 3.77 (m each, 1:1H, OCH_2CH$_2$), 3.28 and 3.10 (m each, 2:2H, SCH_2CH_2S), 2.21 (s, 3H, COCH_3), 1.99 (m, 4H, CHCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.3 (Cq, C=O), 162.9 and 124.3 (Cq), 79.6 (OCHCH$_2$), 67.6 (OCH_2CH$_2$), 37.5 and 36.2 (SCH_2CH_2S), 23.0 (CHCH_2CH$_2$), 28.5 (CHCH$_2CH_2$),

26.4 ($CO\mathit{CH_3}$); HR-MS (ESI): m/z = 231.0516, calcd. for $C_{10}H_{14}O_2S_2$ $[M+H]^+$: 231.0513.

2-(1,3-Dithiolan-2-ylidene)-2-(tetrahydrofuran-2-yl)-acetonitrile (4c): yield: 75 mg (70%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.58 (t, 1 H, $O\mathit{CH}CH_2$), 3.96 and 3.79 (dd each, 1:1 H, $O\mathit{CH_2}CH_2$), 3.51 (m, 4 H, $S\mathit{CH_2CH_2}S$), 2.04 (m, 4 H, $CH\mathit{CH_2CH_2}$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 163.4 (Cq, *C*N), 117.5 and 99.2 (Cq), 78.8 ($O\mathit{CH}CH_2$), 68.7 ($O\mathit{CH_2}CH_2$), 39.4 and 37.9 ($S\mathit{CH_2CH_2}S$), 31.2 and 26.0 ($CH\mathit{CH_2CH_2}$); HR-MS (ESI): m/z = 214.0359, calcd. for $C_9H_{11}NOS_2$ $[M+H]^+$: 214.0360.

3,3-Bis(methylthio)-1-phenyl-2-(tetrahydrofuran-2-yl)prop-2-en-1-one (4d): yield: 103 mg (70%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.93 (d, J = 8.1 Hz, 2 H, aromatic CH), 7.48 (m, 3 H, aromatic CH), 5.23 (t, 1 H, $O\mathit{CH}CH_2$), 3.63 (dq, J = 22.1 and 7.6 Hz, 2 H, $O\mathit{CH_2}CH_2$), 2.33 (s, 3 H, SCH_3), 2.24 and 2.07 (m each, 1:4 H, SCH_3 and $OCH\mathit{CH_2}CH_2$), 1.83 (m, 2 H, $CH_2\mathit{CH_2}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 195.8 (Cq, C=O), 148.9, 137.6 and 133.4 (Cq), 133.0 (aromatic CH), 129.2 (aromatic CH), 128.5 (aromatic CH), 79.2 ($O\mathit{CH}CH_2$), 68.9 ($O\mathit{CH_2}CH_2$), 31.9 ($CH\mathit{CH_2}CH_2$), 26.2 ($CHCH_2\mathit{CH_2}$), 17.1 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): m/z = 295.0828, calcd. for $C_{14}H_{16}O_2S_2$ $[M+H]^+$: 295.0826.

4,4-Bis(methylthio)-3-(tetrahydrofuran-2-yl)but-3-en-2-one (4e): yield: 108 mg (93%); white solid; mp 50–51 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.00 (t, 1 H, $O\mathit{CH}CH_2$), 3.71 (t, 2 H, $O\mathit{CH_2}CH_2$), 2.34 (s, 3 H, $CO\mathit{CH_3}$), 2.25 (s, 3 H, SCH_3), 2.20 (s, 3 H, SCH_3), 2.15 and 1.85 (m each, 1:3 H, $CH\mathit{CH_2CH_2}$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 203.9 (Cq, C=O), 152.5 and 130.2 (Cq), 79.0 ($O\mathit{CH}CH_2$), 68.8 ($O\mathit{CH_2}CH_2$), 32.4 ($CH\mathit{CH_2}CH_2$), 31.8 ($CHCH_2\mathit{CH_2}$), 26.1 ($CO\mathit{CH_3}$), 17.3 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): m/z = 233.0668, calcd. for $C_{10}H_{16}O_2S_2$ $[M+H]^+$: 233.0670.

Ethyl 3,3-bis(methylthio)-2-(tetrahydrofuran-2-yl)-acrylate (4f): yield: 97 mg (74%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.05 (t, J = 7.4 Hz, 1 H, $O\mathit{CH}CH_2$), 4.24 (m, 2 H, $O\mathit{CH_2}CH_3$), 3.77 (m, 2 H, $O\mathit{CH_2}CH_2$), 2.28 (s, 3 H, SCH_3), 2.25 (s, 3 H, SCH_3), 2.14 and 1.89 (m each, 1:3 H, $OCH\mathit{CH_2}CH_2$), 1.30 (t, J = 7.1 Hz, 3 H, $OCH_2\mathit{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.9 (Cq, C=O), 143.5 and 135.2 (Cq), 78.2 ($O\mathit{CH}CH_2$), 69.1 ($O\mathit{CH_2}CH_2$), 61.0 ($O\mathit{CH_2}CH_3$), 32.0 ($CH\mathit{CH_2}CH_2$)and 26.3 ($CHCH_2\mathit{CH_2}$), 17.5 (SCH_3), 16.2 (SCH_3), 14.2 ($OCH_2\mathit{CH_3}$); HR-MS (ESI): m/z = 263.0774, calcd. for $C_{11}H_{18}O_3S_2$ $[M+H]^+$: 263.0776.

3,3-Bis(methylthio)-1-phenyl-2-(tetrahydro-2*H*-pyran-2-yl)prop-2-en-1-one (4g): yield: 100 mg (65%); colorless liquid. ^{1}H NMR NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.95 (d, J = 7.4 Hz, 2 H, aromatic CH), 7.53 (t, 1 H, aromatic CH), 7.44 (t, 2 H, aromatic CH), 4.71 (dd, J = 10.9 and 2.5 Hz, 1 H, $O\mathit{CH}CH_2$), 3.90 and 3.46 (m each, 1:1 H, $O\mathit{CH_2}CH_2$), 2.34 (s, 3 H, SCH_3), 2.04 (s, 3 H, SCH_3), 1.72 and 1.49 (m each, 3:3 H, $CH\mathit{CH_2CH_2CH_2}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 195.3 (Cq, C=O), 148.4, 137.7 and 134.3 (Cq), 133.0, 129.6 and 128.4 (aromatic CH), 78.6 ($O\mathit{CH}CH_2$), 68.7 ($O\mathit{CH_2}CH_2$), 30.4 ($CH\mathit{CH_2}CH_2CH_2$), 25.5 ($CHCH_2\mathit{CH_2}CH_2$), 23.7 ($CHCH_2CH_2\mathit{CH_2}$), 17.2 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): m/z = 309.0980, calcd. for $C_{16}H_{20}O_2S_2$ $[M+H]^+$: 309.0983.

4,4-Bis(methylthio)-3-(tetrahydro-2*H*-pyran-2-yl)but-3-en-2-one (4h): yield: 89 mg (72%); white solid; mp 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.57 (dd, J = 8.8 and 4.7 Hz, 1 H, $O\mathit{CH}CH_2$), 3.92 (dd, J = 11.1 and 3.6 Hz) and 3.40 (m) (1:1 H, $O\mathit{CH_2}CH_2$), 2.34 (s, 3 H, $CO\mathit{CH_3}$), 2.26 (s, 3 H, SCH_3), 2.21 (s, 3 H, SCH_3), 1.90 and 1.52 (m, 1:5 H, $CH\mathit{CH_2CH_2CH_2}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 203.3 (Cq, C=O), 152.0 and 130.6 (Cq), 78.4 ($O\mathit{CH}CH_2$), 68.6 ($O\mathit{CH_2}CH_2$), 32.4 ($CO\mathit{CH_3}$), 30.2 ($CH\mathit{CH_2}CH_2CH_2$), 25.5 ($CHCH_2\mathit{CH_2}CH_2$), 23.4 ($CHCH_2CH_2\mathit{CH_2}$), 17.4 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): m/z = 247.0824, calcd. for $C_{11}H_{18}O_2S_2$ $[M+H]^+$: 247.0826.

Ethyl 3,3-bis(methylthio)-2-(tetrahydro-2*H*-pyran-2-yl)-acrylate (4i): yield: 102 mg (74%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.58 (dd, J = 11.2 and 1.8 Hz, 1 H, $O\mathit{CH}CH_2$), 4.27 (m, 2 H, $O\mathit{CH_2}CH_3$), 3.96 (dd, J = 10.9 and 2.8 Hz) and 3.44 (m) (1:1 H, $O\mathit{CH_2}CH_2$), 2.29 (s, 3 H, SCH_3), 2.24 (s, 3 H, SCH_3), 1.78 and 1.51 (m each, 2:4 H, $CH\mathit{CH_2CH_2CH_2}CH_2$), 1.31 (t, 3 H, $OCH_2\mathit{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.7 (Cq, C=O), 143.2 and 135.2 (Cq), 77.6 ($O\mathit{CH}CH_2$), 68.7 ($O\mathit{CH_2}CH_2$), 61.1 ($O\mathit{CH_2}CH_3$), 30.2 ($CH\mathit{CH_2}CH_2CH_2$), 25.5 ($CHCH_2\mathit{CH_2}CH_2$), 23.5 ($CHCH_2CH_2\mathit{CH_2}$), 17.5 (SCH_3), 16.1 (SCH_3), 14.3 ($OCH_2\mathit{CH_3}$); HR-MS (ESI): m/z = 277.0935, calcd. for $C_{12}H_{20}O_3S_2$ $[M+H]^+$: 277.0932.

3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-2-yl)-4,4-bis(methylthio)but-3-en-2-one (4j): yield: 89 mg (60%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.85 (m, 4 H, aromatic CH), 5.46 (dd, J = 9.0 and 2.6 Hz, 1 H, $O\mathit{CH}CH_2O$), 4.25 (dd, J = 11.4 and 2.6 Hz) and 4.13 (dd, J = 11.4 and 9.0 Hz) (1:1 H, $OCH\mathit{CH_2}O$), 2.49 (s, 3 H, SCH_3), 2.36 (s, 3 H, SCH_3), 2.32 (s, 3 H, $CO\mathit{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 202.2 (Cq, C=O), 144.1, 143.0, 142.9 and 137.5 (Cq), 121.9, 121.6, 117.4 and 117.3 (aromatic CH), 74.1 ($O\mathit{CH}CH_2O$), 65.8 ($OCH\mathit{CH_2}O$), 32.4 ($CO\mathit{CH_3}$), 17.3 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 297.0622, calcd. for $C_{14}H_{16}O_3S_2$ $[M+H]^+$: 297.0619.

3-(1,3-Dithiolan-2-ylidene)-4-ethoxypentan-2-one (4k): yield: 60 mg (52%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.69 (q, J = 6.7 Hz, 1 H, $CH_3\mathit{CH}O$), 3.41 and 3.2 (m each, 1:3 H, $CH_3\mathit{CH_2}O$ and $S\mathit{CH_2}$), 3.22 (m, 2 H, SCH_2), 2.32 (s, 3 H, $CO\mathit{CH_3}$), 1.46 (d, J = 6.7 Hz, 3 H, $\mathit{CH_3}CHO$), 1.18 (t, 3 H, $\mathit{CH_3}CH_2O$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 194.2 (Cq, C=O), 162.6 and 126.3 (Cq), 76.5 ($CH_3\mathit{CH}O$), 64.1 ($CH_3\mathit{CH_2}O$), 37.9 and 36.1 ($S\mathit{CH_2CH_2}S$), 28.5 ($CO\mathit{CH_3}$), 19.8 ($\mathit{CH_3}CHO$), 15.4 ($\mathit{CH_3}CH_2O$); HR-MS (ESI): m/z = 255.0487, calcd for $C_{10}H_{17}O_2S_2$ $[M+Na]^+$: 255.0489.

3-[Bis(methylthio)methylene]-4-ethoxypentan-2-one (4l): yield: 73 mg (62%); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.75 (q, J = 6.6 Hz, 1 H, $CH_3\mathit{CH}O$), 3.47 (m, 2 H, $CH_3\mathit{CH_2}O$), 2.33 (s, 3 H, $CO\mathit{CH_3}$), 2.28 (s, 3 H, SCH_3), 2.24 (s, 3 H, SCH_3), 1.31 (d, J = 6.6 Hz, 3 H, $\mathit{CH_3}CHO$), 1.14 (t, 3 H, $\mathit{CH_3}CH_2O$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 203.1 (Cq, C=O), 152.4 and 132.6 (Cq), 75.2 ($CH_3\mathit{CH}O$), 64.6 ($CH_3\mathit{CH_2}O$), 32.0 ($CO\mathit{CH_3}$), 20.4 ($\mathit{CH_3}CHO$), 17.4 (SCH_3), 16.3 (SCH_3), 15.3 ($\mathit{CH_3}CH_2O$); HR-MS (ESI): m/z = 257.0640, calcd for $C_{10}H_{18}O_2S_2$ $[M+Na]^+$: 257.0646;.

2-[(4-Methoxyphenoxy)methyl]-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (4m): yield: 112 mg (62%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.91 (d,

J=7.2 Hz, 2H, aromatic CH), 7.54 (t, 1H, aromatic CH), 7.44 (t, 2H, aromatic CH), 6.78 (m, 4H, aromatic CH), 4.99 (s, 2H, OCH_2), 3.74 (s, 3H, OCH_3), 2.39 and 2.11 (s each, 3:3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 196.3 (Cq, C=O), 154.2, 152.5, 142.9 and 141.3 (Cq), 137.7 (C=CCH), 133.1, 129.3, 128.5, 116.2 and 114.6 (aromatic CH), 68.9 (OCH_2), 55.8 (OCH_3), 17.2 and 16.7 (SCH_3); HR-MS (ESI): m/z=383.0747, calcd for $C_{19}H_{20}O_3S_2$ $[M+Na]^+$: 383.0752.

2-(1,3-Dioxolan-2-yl)-3,3-bis(methylthio)-1-(*p*-tolyl)-prop-2-en-1-one (4n): yield: 57 mg (37%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.86 (d, J= 8.1 Hz, 2H, aromatic CH), 7.25 (d, J=7.8 Hz, 2H, aromatic CH), 6.13 (s, 1H, OCHO), 3.81 (m, 4H, OCH_2CH_2O), 2.40 (s, 3H, SCH_3), 2.37 (s, 3H, SCH_3), 2.14 (s, 3H, Ph-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=193.8 (Cq, C= O), 144.2, 143.3, 140.7 and 134.7 (Cq), 129.7 (aromatic CH), 129.3 (aromatic CH), 101.4 (OCHO), 65.5 (OCH_2CH_2O), 21.9 (Ph-CH_3), 17.1 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z=311.0775, calcd. for $C_{15}H_{18}O_3S_2$ $[M+H]^+$: 311.0776.

2-(1,3-Dioxolan-4-yl)-3,3-bis(methylthio)-1-(*p*-tolyl)-prop-2-en-1-one (4n′): yield: 38 mg (24%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.84 (d, J= 8.2 Hz, 2H, aromatic CH), 7.27 (d, J=7.9 Hz, 2H, aromatic CH), 5.37 (t, 1H, O$CH$$CH_2$O), 4.84 and 4.73 (s each, 1:1H, OCH_2O), 4.21 (dd, J=8.3 and 6.9 Hz) and 3.97 (dd, J=8.3 and 7.1 Hz) (1:1H, OCHCH_2O), 2.41 (s, 3H, Ph-CH_3), 2.37 (s, 3H, SCH_3), 2.12 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=194.7 (Cq, C=O), 144.9, 144.4, 136.1 and 134.9 (Cq), 129.5 and 129.4 (aromatic CH), 95.9 (OCH_2O), 75.6 (O$CH$$CH_2$O), 69.2 (OCH$CH_2$O), 21.9 (Ph-$CH_3$), 17.2 ($SCH_3$), 16.4 ($SCH_3$); HR-MS (ESI): m/z= 311.0779, calcd. for $C_{15}H_{18}O_3S_2$ $[M+H]^+$: 311.0776.

2-(1,3-Dithiolan-2-ylidene)-3,4-dimethoxy-1-phenylbutan-1-one (4o): yield: 64 mg (41%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.59 (m, 2H, aromatic CH), 7.44 (m, 3H, aromatic CH), 4.59 (dd, J=8.2 and 4.3 Hz, 1H, CHOCH_3), 3.79 (dd, J=10.4 and 8.2 Hz) and 3.45 (m) (1:1H, CH_2OCH_3), 3.40 and 3.34 (m each, 4:1H, OCH_3 and SCH_2), 3.27 and 3.16 (m each, 4:1H, OCH_3 and SCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=194.0 (Cq, C=O), 161.7 and 139.5 (Cq), 131.2, 128.5 and 128.1 (aromatic CH), 122.3 (Cq), 81.0 (CHOCH_3), 72.9 (CH_2OCH_3), 59.0 (OCH_3), 57.0 (OCH_3), 37.5 and 37.4 (SCH_2CH_2S); HR-MS (ESI): m/z=333.0594, calcd. for $C_{15}H_{18}O_3S_2$ $[M+Na]^+$: 333.0595.

2-(1,3-Dithiolan-2-ylidene)-3-(2-methoxyethoxy)-1-phenylpropan-1-one (4o′): yield: 58 mg (37%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.76 (m, 2H, aromatic CH), 7.42 (m, 3H, aromatic CH), 4.34 (s, 2H, CH_2OCH_2CH_2), 3.59 (s, 4H, OCH_2CH_2O), 3.38 (m, 7H, OCH_3 and SCH_2CH_2S); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 191.9 (Cq, C=O), 172.3 and 139.2 (Cq), 131.0, 128.3 and 128.1 (aromatic CH), 121.1 (Cq), 71.8 (CH_2OCH_2CH_2), 71.4 (CH$_2$OCH_2CH$_2$), 69.3 (CH$_2$OCH$_2$$CH_2$), 59.1 ($OCH_3$), 38.9 and 36.0 (S$CH_2CH_2$S); HR-MS (ESI): m/z=333.0596, calcd. for $C_{15}H_{18}O_3S_2$ $[M+H]^+$: 333.0595.

3-(1,3-Dithiolan-2-ylidene)-4,5-dimethoxypentan-2-one (4p): yield: 56 mg (45%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=4.65 (dd, J=8.5, 3.9 Hz, 1H, CHOCH_3), 3.78 (m, 1H), and 3.39 (dd, J=10.4 and 3.9 Hz) (1:1H, CH_2OCH_3), 3.34 (s, 3H, OCH_3), 3.30 (m, 2H, SCH_2), 3.25 (s, 3H, OCH_3), 3.17 (m, 2H, SCH_2), 2.27 (s, 3H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 193.9 (Cq, C=O), 165.5 and 121.6 (Cq), 81.7 (CHOCH_3), 73.4 (CH_2OCH_3), 59.2 (OCH_3), 56.8 (OCH_3), 37.9 and 36.2 (SCH_2CH_2S), 28.5 (COCH_3); HR-MS (ESI): m/z= 271.0438, calcd. for $C_{10}H_{16}O_3S_2$[M+Na]$^+$: 271.0439.

3-(1,3-Dithiolan-2-ylidene)-4-(2-methoxyethoxy)-butan-2-one (4p′): yield: 31 mg (25%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=4.52 (s, 2H, CH_2OCH_2CH_2), 3.63 and 3.56 (m each, 2:2H, SCH_2CH_2S), 3.38 (m, 5H, OCH_3 and CH$_2$OCH_2CH$_2$), 3.32 (m, 2H, CH$_2$OCH$_2$$CH_2$), 2.34 (s, 3H, CO$CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=194.5 (Cq, C=O), 167.4 and 121.4 (Cq), 72.0 (CH_2OCH_2CH_2), 71.4 (CH$_2$OCH_2CH$_2$), 69.0 (CH$_2$OCH$_2$$CH_2$), 59.1 ($OCH_3$), 39.3 and 35.8 (S$CH_2CH_2$S), 27.2 (CO$CH_3$); HR-MS (ESI): m/z=271.0434, calcd. for $C_{10}H_{16}O_3S_2$ $[M+Na]^+$: 271.0439.

2-[Bis(methylthio)methylene]-3,4-dimethoxy-1-phenylbutan-1-one (4q): yield: 54 mg (35%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.85 (d, J= 7.3 Hz, 2H, aromatic CH), 7.47 (t, 1H, aromatic CH), 7.38 (t, 2H, aromatic CH), 4.83 (dd, J=7.0 and 4.7 Hz, 1H, CHOCH_3), 3.48 (dd, J=10.2 and 7.1 Hz) and 3.40 (m) (1:4H, CH_3OC$H$$CH_2$ and OCH_3), 3.22 (s, 3H, OCH_3), 2.30 (s, 3H, SCH_3), 2.04 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=194.7 (Cq, C=O), 144.4, 138.5 and 137.3 (Cq), 133.0, 129.1 and 128.4 (aromatic CH), 80.8 (CHOCH_3), 74.0 (CHCH_2OCH_3), 59.0 (OCH_3), 58.1 (OCH_3), 17.1 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z= 335.0755, calcd. for $C_{15}H_{20}O_3S_2$ $[M+Na]^+$: 335.0752.

2-[(2-Methoxyethoxy)methyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (4q′): yield: 42 mg (27%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.91 (d, J=7.6 Hz, 2H, aromatic CH), 7.53 (t, 1H, aromatic CH), 7.44 (t, 2H, aromatic CH), 4.56 (s, 2H, CH_2OCH_2CH_2), 3.59 and 3.43 (m each, 2:2H, OCH_2CH_2O), 3.26 (s, 3H, OCH_3), 2.36 (s, 3H, SCH_3), 2.08 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=196.5 (Cq, C=O), 143.4, 140.7 and 137.5 (Cq), 133.0, 129.3 and 128.5 (aromatic CH), 71.8 (CH_2OCH_2CH_2), 71.0 (CH$_2$OCH_2CH$_2$), 70.2 (CH$_2$OCH$_2$$CH_2$), 59.1 ($OCH_3$), 17.2 ($SCH_3$), 16.6 ($SCH_3$); HR-MS (ESI): m/z=335.0752, calcd. for $C_{15}H_{20}O_3S_2$ $[M+Na]^+$: 335.0752.

Typical Procedure for the Methylation of Ketene Dithioacetals 1

Under a nitrogen atmosphere, a mixture of α-oxo ketene dithioacetal **1** (0.5 mmol), $FeCl_3$ (4 mg, 0.025 mmol), DABCO·6H_2O (11 mg, 0.05 mmol), and DTBP (219 mg, 1.5 mmol) in benzene (3 mL) was stirred in a 25-mL sealed tube at 130 °C for 24 h. After being cooled to ambient temperature, the mixture was evaporated of all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate=40:1, v/v) to afford the target product **5**.

2-Methyl-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (5a): yield: 74 mg (62%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.86 (m, 2H, aromatic CH), 7.56 (t, 1H, aromatic CH), 7.46 (t, 2H, aromatic CH), 2.36 (s, 3H, SCH_3), 2.20 (s, 3H, C=CCH_3), 2.05 (s, 3H,

SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 197.5$ (Cq, C=O), 143.6 (*C*SMe), 136.3 (Cq of Ph), 133.5 (C=*C*CH_3), 133.3, 129.1 and 128.7 (aromatic CH), 20.1 (C=C*CH_3*), 17.2 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): $m/z =$ 239.0561, calcd. for $C_{12}H_{14}OS_2$ $[M+H]^+$: 239.0564.

2-Methyl-3,3-bis(methylthio)-1-(*p*-tolyl)prop-2-en-1-one (5b): yield: 73 mg (58%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.77$ (d, $J = 8.2$ Hz, 2H, aromatic CH), 7.26 (m, 2H, aromatic CH), 2.41 (s, 3H, Ph-*C*H_3), 2.35 (s, 3H, SCH_3), 2.18 (s, 3H, C=C*C*H_3), 2.07 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 197.3 (Cq, C=O), 144.2, 143.9 and 133.6 (Cq), 132.3 (Cq), 129.5 and 129.3 (aromatic CH), 21.8 (Ph-*C*H_3), 20.1 (C=C*C*H_3), 17.3 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): $m/z =$ 253.0724, calcd. for $C_{13}H_{16}OS_2$ $[M+H]^+$: 253.0721.

1-(4-Chlorophenyl)-2-methyl-3,3-bis(methylthio)-prop-2-en-1-one (5c): yield: 76 mg (56%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.79$ (d, $J =$ 8.5 Hz, 2H, aromatic CH), 7.43 (d, $J = 8.5$ Hz, 2H, aromatic CH), 2.35 (s, 3H, SCH_3), 2.18 (s, 3H, C=C*C*H_3), 2.05 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 196.3$ (Cq, C=O), 142.8, 139.6, 134.8 and 134.3 (Cq), 130.4 and 129.1 (aromatic CH), 20.1 (C=C*C*H_3), 17.3 (SCH_3), 16.2 (SCH_3); HR-MS (ESI): $m/z = 273.0175$ calcd. for $C_{12}H_{13}ClOS_2$ $[M+H]^+$: 273.0175.

Typical Procedure for the C–H Alkylation of Ketene Dithioacetals 1 with Toluene Derivatives 6

Under a nitrogen atmosphere, a mixture of α-oxo ketene dithioacetal **1** (0.5 mmol), $FeCl_3$ (4 mg, 0.025 mmol), DABCO·6H_2O (11 mg, 0.05 mmol), and DTBP (219 mg, 1.5 mmol) in toluene derivative **6** (3 mL) was stirred in a 25-mL sealed tube at 130 °C for 24 h. After being cooled to ambient temperature, the mixture was evaporated of all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography [eluent: petroleum ether (60–90 °C)/ethyl acetate = 100:1, v/v] to afford the target product **7**.

2-Benzyl-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7a): yield: 124 mg (79%); white solid; mp 60–62 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.59$ (d, $J =$ 7.4 Hz, 2H, aromatic CH), 7.43 (t, 1H, aromatic CH), 7.30 (t, 2H, aromatic CH), 7.17 (m, 5H, aromatic CH), 4.09 (s, 2H, Ph*C*H_2), 2.39 and 2.00 (s each, 3:3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 197.3$ (Cq, C=O), 146.0, 137.7, 137.6 and 136.4 (Cq), 132.7, 129.2, 128.9, 128.6, 128.3 and 126.5 (aromatic CH), 40.86 (Ph*C*H_2), 17.1 and 16.5 (SCH_3); HR-MS (ESI): $m/z = 315.0878$, calcd. for $C_{18}H_{18}OS_2$ $[M+H]^+$: 315.0877.

2-Benzyl-1-(2-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (7b): yield: 123 mg (75%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.34$ (m, 2H, aromatic CH), 7.21 (m, 4H, aromatic CH), 7.15 (m, 1H, aromatic CH), 6.85 (dd, $J = 7.8$, 5.3 Hz, 2H, aromatic CH), 4.08 (s, 2H, Ph*C*H_2), 3.69 (s, 3H, OCH_3), 2.35 (s, 3H, SCH_3), 1.95 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 195.8$ (Cq, C=O), 158.6, 148.5, 138.6 and 137.2 (Cq), 133.2, 130.8 and 129.2 (aromatic CH), 128.7 (Cq), 128.4, 126.2, 120.1 and 111.5 (aromatic CH), 55.5 (OCH_3), 40.3 (Ph*C*H_2), 16.93 (SCH_3), 16.6 (SCH_3); HR-MS (ESI): $m/z = 345.0982$, calcd. for $C_{19}H_{20}O_2S_2$ $[M+H]^+$: 345.0983.

2-Benzyl-1-(3-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (7c): yield: 132 mg (77%); pale yellow liquid.^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.15$ (m, 8H, aromatic CH), 6.98 (m, 1H, aromatic CH), 4.08 (s, 2H, Ph*C*H_2), 3.73 (s, 3H, OCH_3), 2.39 (s, 3H, SCH_3), 2.01 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 197.1 (Cq, C=O), 159.6, 146.1, 139.0, 137.8, 136.3 (Cq), 129.2, 128.6, 126.6, 121.8, 119.7 and 112.4 (aromatic CH), 55.4 (OCH_3), 40.9 (Ph*C*H_2), 17.1 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): $m/z = 345.0982$, calcd. for $C_{19}H_{20}O_2S_2$ $[M+H]^+$: 345.0983.

2-Benzyl-1-(4-methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (7d): yield: 132 mg (77%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.59$ (d, $J =$ 8.8 Hz, 2H, aromatic CH), 7.15 (m, 5H, aromatic CH), 6.79 (d, $J = 8.9$ Hz, 2H, aromatic CH), 4.07 (s, 2H, Ph*C*H_2), 3.80 (s, 3H, OCH_3), 2.38 (s, 3H, SCH_3), 2.06 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 196.1$ (Cq, C=O), 163.3, 146.2, 137.8 and 134.9 (Cq), 131.4 (aromatic CH), 130.2 (Cq), 129.1, 128.5, 126.5 and 113.5 (aromatic CH), 55.5 (OCH_3), 40.8 (Ph*C*H_2), 17.1 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): $m/z = 345.0979$, calcd. for $C_{19}H_{20}O_2S_2$ $[M+H]^+$: 345.0983.

2-Benzyl-3,3-bis(methylthio)-1-(*p*-tolyl)prop-2-en-1-one (7e): yield: 130 mg (79%); colorless liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.51$ (d, $J = 8.1$ Hz, 2H, aromatic CH), 7.20 (m, 4H, aromatic CH), 7.13 (m, 3H, aromatic CH), 4.08 (s, 2H, Ph*C*H_2), 2.39 (s, 3H, PhCH_3), 2.34 (s, 3H, SCH_3), 2.04 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1967.0$ (Cq, C=O), 146.1, 143.5, 137.8, 135.6 and 134.9 (Cq), 129.1, 129.0, 128.5 and 126.5 (aromatic CH), 40.8 (Ph*C*H_2), 21.8 (PhCH_3), 17.1 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): $m/z = 329.1034$, calcd. for $C_{19}H_{20}OS_2$ $[M+H]^+$: 329.1034.

2-Benzyl-1-(2-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (7f): yield: 123 mg (74%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.38$ (m, 1H, aromatic CH), 7.31 (m, 1H, aromatic CH), 7.23 (m, 4H, aromatic CH), 7.16 (m, 1H, aromatic CH), 7.03 (m, 2H, aromatic CH), 4.12 (s, 2H, Ph*C*H_2), 2.38 (s, 3H, SCH_3), 1.97 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 193.5$ (Cq, C=O), 161.2 (d, $J = 256.8$ Hz, Cq of Ph), 146.9 (Cq), 139.4 (d, $J = 2.4$ Hz, Cq), 138.0 (Cq), 133.6 (d, $J = 8.8$ Hz, aromatic CH), 130.5, 129.2 and 128.6 (aromatic CH), 127.60 (d, $J = 10.3$ Hz, Cq), 126.5 (aromatic CH), 123.8 (d, $J =$ 3.7 Hz, aromatic CH), 116.4 (d, $J = 22.2$ Hz, aromatic CH), 40.4 (Ph*C*H_2), 17.0 (SCH_3), 16.6 (SCH_3); HR-MS (ESI): $m/z = 333.0783$, calcd. for $C_{18}H_{17}FOS_2$ $[M+H]^+$: 333.0783.

2-Benzyl-1-(3-chlorophenyl)-3,3-bis(methylthio)-prop-2-en-1-one (7g): yield: 130 mg (75%); white solid; mp 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.55$ (s, 1H, aromatic CH), 7.38 (m, 2H, aromatic CH), 7.18 (m, 6H, aromatic CH), 4.08 (s, 2H, Ph*C*H_2), 2.40 (s, 3H, SCH_3), 2.00 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 195.9$ (Cq, C=O), 145.2, 139.5, 137.5, 137.4 and 134.5 (Cq), 132.4, 129.4, 129.0, 128.7, 126.8 and 126.7 (aromatic CH), 40.9 (Ph*C*H_2), 17.0 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): $m/z = 349.0484$, calcd. for $C_{18}H_{17}ClOS_2$ $[M+H]^+$: 349.0488.

Methyl 4-[2-benzyl-3,3-bis(methylthio)acryloyl]benzoate (7h): yield: 136 mg (73%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94 (d, J = 8.5 Hz, 2H, aromatic CH), 7.56 (d, J = 8.4 Hz, 2H, aromatic CH), 7.16 (m, 5H, aromatic CH), 4.10 (s, 2H, PhCH_2), 3.89 (s, 3H, OCH_3), 2.39 (s, 3H, SCH_3), 1.94 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.7 (Cq, C=O), 166.4 (Cq, C=O), 145.4, 141.6, 137.9 and 137.5 (Cq of Ph), 133.1 (Cq), 129.4, 129.1, 128.7, 128.5 and 126.7 (aromatic CH), 52.5 (OCH_3), 41.0 (PhCH_2), 16.9 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 373.0931, calcd. for $C_{20}H_{20}O_3S_2$ $[M+H]^+$: 373.0932.

2-(2-Methylbenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7i): yield: 142 mg (87%); colorless solid; mp 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.64 (d, J = 7.4 Hz, 2H, aromatic CH), 7.45 (t, 1H, aromatic CH), 7.32 (t, 2H, aromatic CH), 7.16 (m, 1H, aromatic CH), 7.03 (m, 3H, aromatic CH), 4.08 (s, 2H, PhCH_2), 2.40 (s, 3H, SCH_3), 2.26 (s, 3H, Ph-CH_3), 2.08 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.9 (Cq, C=O), 146.0, 137.1, 136.5, 135.7 and 135.1 (Cq), 132.8, 130.3, 129.7, 128.8, 128.3, 126.7 and 126.1 (aromatic CH), 37.8 (PhCH_2), 20.0 (Ph-CH_3), 17.3 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 329.1029, calcd. for $C_{19}H_{20}OS_2$ $[M+H]^+$: 329.1034.

2-(3-Methylbenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7j): yield: 140 mg (85%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62 (m, 2H, aromatic CH), 7.44 (t, 1H, aromatic CH), 7.32 (t, 2H, aromatic CH), 7.09 (t, 1H, aromatic CH), 6.97 (m, 3H, aromatic CH), 4.08 (s, 2H, PhCH_2), 2.40 (s, 3H, SCH_3), 2.23 (s, 3H, Ph-CH_3), 2.02 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 197.3 (Cq, C=O), 145.9, 138.0, 137.5, 137.4 and 136.1 (Cq),132.6, 129.9, 128.9, 128.3, 128.1, 127.2 and 126.0 (aromatic CH), 40.7 (PhCH_2), 21.3 (Ph-CH_3), 17.0 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 329.1035, calcd. for $C_{19}H_{20}OS_2$ $[M+H]^+$: 329.1034.

2-(4-Methylbenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7k): yield: 133 mg (81%); white solid; mp 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62 (d, J = 7.3 Hz, 2H, aromatic CH), 7.45 (t, 1H, aromatic CH), 7.31 (dd, J = 20.4 and 12.8 Hz, 2H, aromatic CH), 7.04 (dd, J = 29.4 and 7.9 Hz, 4H, aromatic CH), 4.06 (s, 2H, PhCH_2), 2.39 (s, 3H, SCH_3), 2.26 (s, 3H, Ph-CH_3), 2.01 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 197.3 (Cq, C=O), 146.2, 137.6, 136.1, 135.9 and 134.6 (Cq), 132.6 (s), 129.2, 129.0, 128.9 and 128.2 (aromatic CH), 40.4 (PhCH_2), 21.1 (Ph-CH_3), 17.0 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 329.10354, calcd. for $C_{19}H_{20}OS_2$ $[M+H]^+$: 329.1034.

2-(3,5-Dimethylbenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7l): yield: 137 mg (80%); white solid; mp 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.63 (d, J = 7.5 Hz, 2H, aromatic CH), 7.45 (t, 1H, aromatic CH), 7.31 (dd, J = 20.2, 12.6 Hz, 2H, aromatic CH), 6.77 (d, J = 8.7 Hz, 3H, aromatic CH), 4.02 (s, 2H, PhCH_2), 2.40 (s, 3H, SCH_3), 2.19 (s, 6H, Ph-CH_3), 2.02 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 197.4 (Cq, C=O), 146.2, 137.9, 137.6, 137.4 and 135.9 (Cq), 132.6, 129.0, 128.2, 128.1 and 127.0 (aromatic CH), 40.7 (PhCH_2), 21.3 (Ph-CH_3), 17.0 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z = 343.1194, calcd. for $C_{20}H_{22}OS_2$ $[M+H]^+$: 343.1194.

2-(4-Methoxybenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7m): yield: 101 mg (59%); white solid; mp 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62 (m, 2H, aromatic CH), 7.46 (t, 1H, aromatic CH), 7.32 (dd, J = 18.6 and 11.0 Hz, 2H, aromatic CH), 7.11 (d, J = 8.6 Hz, 2H, aromatic CH), 6.75 (d, J = 8.6 Hz, 2H, aromatic CH), 4.05 (s, 2H, PhCH_2), 3.74 (s, 3H, OCH_3), 2.41 (s, 3H, SCH_3), 2.02 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 197.4 (Cq, C=O), 158.2, 146.4, 137.6 and 135.8 (Cq), 132.7 and 130.1 (aromatic CH), 129.8 (Cq), 128.9, 128.3 and 114.0 (aromatic CH), 55.3 (OCH_3), 39.9 (PhCH_2), 17.0 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 345.0984, calcd. for $C_{19}H_{20}O_2S_2$ $[M+H]^+$: 345.0983.

3,3-Bis(methylthio)-1-phenyl-2-[(*p*-tolyloxy)methyl]prop-2-en-1-one (7m′): yield: 30 mg (17%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.92 (m, 2H, aromatic CH), 7.54 (t, 1H, aromatic CH), 7.44 (t, 2H, aromatic CH), 7.02 (d, J = 8.4 Hz, 2H, aromatic CH), 6.75 (d, J = 8.5 Hz, 2H, aromatic CH), 5.01 (s, 2H, PhOCH_2), 2.39 (s, 3H, SCH_3), 2.25 (s, 3H, Ph-CH_3), 2.11 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 196.3 (Cq, C=O), 156.3, 142.9, 141.4 and 137.7 (Cq), 133.0 (aromatic CH), 130.5 (Cq), 129.9, 129.3, 128.5 and 114.9 (aromatic CH), 68.3 (PhOCH_2), 20.6 (PhCH_3), 17.2 (SCH_3), 16.7 (SCH_3); HR-MS (ESI): m/z = 367.0803, calcd. for $C_{19}H_{20}O_2S_2$ $[M+Na]^+$: 367.0802.

2-[4-(*tert*-Butyl)benzyl]-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7n): yield: 146 mg (79%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.29 (m, 9H, aromatic CH), 4.03 (s, 2H, PhCH_2), 2.37 (s, 3H, SCH_3), 1.98 (s, 3H, SCH_3), 1.22 (s, 9H, C$(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 197.5 (Cq, C=O), 149.3, 146.4, 137.6 and 135.7 and 134.6 (Cq), 132.6, 129.0, 128.8, 128.1 and 125.5 (aromatic CH), 40.3 (PhCH_2), 34.4 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 17.0 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 371.1497, calcd. for $C_{22}H_{26}OS_2$ $[M+H]^+$: 371.1503.

2-(2-Chlorobenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7o): yield: 138 mg (79%); white solid; mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.69 (d, J = 7.5 Hz, 2H, aromatic CH), 7.43 (t, 1H, aromatic CH), 7.27 (m, 4H, aromatic CH), 7.05 (m, 2H, aromatic CH), 4.19 (s, 2H, PhCH_2), 2.37 (s, 3H, SCH_3), 2.07 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.5 (Cq, C=O), 144.3, 137.0, 136.5, 135.2 and 134.2 (Cq), 132.9, 131.3, 129.4, 128.8, 128.3, 128.1 and 126.90 (aromatic CH), 38.0 (PhCH_2), 17.2 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 349.0490, calcd. for $C_{18}H_{17}ClOS_2$ $[M+H]^+$: 349.0488.

2-(3-Bromobenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7p): yield. 135 mg (69%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.63 (m, 2H), 7.46 (m, 1H, aromatic CH), 7.36 (dd, J = 12.3 and 4.5 Hz, 3H, aromatic CH), 7.27 (m, 1H, aromatic CH), 7.07 (m, 2H, aromatic CH), 4.05 (s, 2H, PhCH_2), 2.39 (s, 3H, SCH_3), 2.04 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.9 (Cq, C=O), 144.6, 140.0, 137.6 and 137.3 (Cq), 132.8, 132.1, 130.1, 129.6, 128.9, 128.4 and 127.8 (aromatic CH), 122.5 (Cq), 40.2 (PhCH_2), 17.1 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z = 392.9988, calcd. for $C_{18}H_{17}BrOS_2$ $[M+H]^+$: 392.9982.

2-(4-Fluorobenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7q): yield: 113 mg (69%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.58 (m, 2H,

aromatic CH), 7.45 (t, 1H, aromatic CH), 7.32 (t, 2H, aromatic CH), 7.14 (dd, J=8.5 and 5.5 Hz, 2H, aromatic CH), 6.88 (dd, J=12.1 and 5.3 Hz, 2H, aromatic CH), 4.04 (s, 2H, PhCH_2), 2.38 (s, 3H, SCH_3), 2.01 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=197.2 (Cq, C=O), 161.0 (d, J=244.6 Hz, Cq of Ph), 145.5, 137.5 and 136.7 (Cq), 133.5 (d, J=3.2 Hz, Cq of Ph), 132.8 (aromatic CH), 130.6 (d, J=7.9 Hz, aromatic CH), 128.88 and 128.35 (aromatic CH), 115.4 (d, J=21.3 Hz, aromatic CH), 39.9 (PhCH_2), 17.0 (SCH_3), 16.4 (SCH_3); HR-MS (ESI): m/z=333.0783, calcd. for $C_{18}H_{17}FOS_2$ $[M+H]^+$: 333.0783.

2-(4-Acetylbenzyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7r): yield: 92 mg (51%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.75 (d, J=8.3 Hz, 2H, aromatic CH), 7.55 (m, 2H, aromatic CH), 7.40 (dd, J=10.5 and 4.3 Hz, 1H, aromatic CH), 7.25 (m, 4H, aromatic CH), 4.08 (s, 2H, PhCH_2), 2.48 (s, 3H, SCH_3), 2.35 (s, 3H,COCH_3), 1.97 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=197.9 (Cq, C=O), 196.9 (Cq, C=O), 144.3 (*C*SMe), 143.5, 138.0 and 137.4 (Cq of Ph), 135.5 (C=CCH_2), 132.9, 129.4, 128.9, 128,8 and 128.4 (aromatic CH), 40.7 (PhCH_2), 26.7 (COCH_3), 17.2 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z=357.0987, calcd. for $C_{20}H_{20}O_2S_2$ $[M+H]^+$: 357.0983.

3-Benzyl-4,4-bis(methylthio)but-3-en-2-one (7s): yield: 96 mg (76%); colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.34 (t, 2H, aromatic CH), 7.25 (m, 3H, aromatic CH), 4.05 (s, 2H, PhCH_2), 2.42 and 2.39 (s each, 3:3H, SCH_3 and COCH_3), 2.21 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 204.1 (Cq, C=O), 148.1, 138.0 and 136.5 (Cq), 128.7, 128.6 and 126.5 (aromatic CH), 40.0 (PhCH_2), 31.1 (COCH_3), 17.5 (SCH_3), 16.7 (SCH_3); HR-MS (ESI): m/z=253.0723, calcd. for $C_{13}H_{16}OS_2$ $[M+H]^+$: 253.0721.

3-(4-Methylbenzyl)-4,4-bis(methylthio)but-3-en-2-one (7t): yield: 117 mg (88%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.06 (q, J=8.1 Hz, 4H, aromatic CH), 3.93 (s, 2H, PhCH_2), 2.35 (s, 3H, SCH_3), 2.32 and 2.30 (s each, 3:3H, Ph-CH_3 and COCH_3), 2.15 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=204.3 (Cq, C=O), 148.5, 136.1, 136.0 and 134.8 (Cq), 129.4 and 128.5 (aromatic CH), 39.6 (PhCH_2), 31.2 (COCH_3), 21.1 (Ph-CH_3), 17.5 (SCH_3), 16.7 (SCH_3); HR-MS (ESI): m/z=267.0877, calcd. for $C_{14}H_{18}OS_2$ $[M+H]^+$: 267.0877.

3-(3,5-Dimethylbenzyl)-4,4-bis(methylthio)but-3-en-2-one (7u): yield: 122 mg (87%); pale yellow solid; mp 53–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=6.83 (s, 1H, aromatic CH), 6.76 (s, 2H, aromatic CH), 3.91 (s, 2H, PhCH_2), 2.36 and 2.33 (s each, 3:3H, SCH_3 and Ph-CH_3), 2.27 (s, 6H, COCH_3 and Ph-CH_3), 2.15 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=204.4 (Cq, C=O), 148.5, 138.2, 137.8 and 136.1 (Cq), 128.3 and 126.5 (aromatic CH), 40.0 (PhCH_2), 31.3 (COCH_3), 21.4 (Ph-CH_3), 17.5 (SCH_3), 16.8 (SCH_3); HR-MS (ESI): m/z=281.1037, calcd. for $C_{15}H_{20}OS_2$ $[M+H]^+$: 281.1034.

2-(1,3-Dithiolan-2-ylidene)-1,3-diphenylpropan-1-one (7v): yield: 106 mg (68%); pale yellow solid; mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.52 (m, 3H, aromatic CH), 7.35 (m, 5H, aromatic CH), 7.20 (d, J=7.3 Hz, 2H, aromatic CH), 4.14 (s, 2H, PhCH_2), 3.45 (m, 4H, SCH_2CH_2S); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=193.6 (Cq, C=O), 164.4, 139.8, 138.8 (Cq of Ph), 130.6, 128.5, 128.2, 128.1, 127.6 and 126.2 (aromatic CH), 122.9 (Cq), 40.4 (PhCH_2), 39.2 and 36.4 (SCH_2CH_2S); HR-MS (ESI): m/z=313.0728, calcd. for $C_{18}H_{16}OS_2$ $[M+H]^+$: 313.0721.

2-[Bis(methylthio)methylene]-1,3-diphenylbutan-1-one (7w): yield: 90 mg (55%); yellow solid; mp 62–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.61 (d, J=7.4 Hz, 2H, aromatic CH), 7.41 (t, 1H, aromatic CH), 7.27 (dd, J=15.2 and 7.6 Hz, 4H, aromatic CH), 7.15 (t, 2H, aromatic CH), 7.07 (t, 1H, aromatic CH), 4.74 (q, J=7.3 Hz, 1H, CHCH$_3$), 2.32 (s, 3H, SCH_3), 2.00 (s, 3H, SCH_3), 1.49 (d, J=7.3 Hz, 3H, CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=196.0 (Cq, C=O), 150.9, 142.8, 137.6 and 133.3 (Cq), 132.7, 129.1, 128.3, 128.2, 128.1, and 126.5 (aromatic CH), 43.8 (PhCH), 19.4 (CHCH_3), 17.1 (SCH_3), 16.4 (s); HR-MS (ESI): m/z=329.1035, calcd. for $C_{19}H_{20}OS_2$ $[M+H]^+$: 329.1034.

3-[Bis(methylthio)methylene]-4-phenylpentan-2-one (7x): yield: 87 mg (59%); white solid; mp 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.25 (m, 5H, aromatic CH), 4.65 (q, J=7.2 Hz, 1H, C=CCH), 2.33 and 2.26 (s each, 3:3H, SCH_3 and COCH_3), 1.86 (s, 3H, SCH_3), 1.49 (d, J=7.2 Hz, 3H, CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=204.4 (Cq, C=O), 155.3, 142.1 and 130.3 (Cq), 128.6, 127.8 and 126.8 (aromatic CH), 42.7 (PhCH_2), 32.2 (COCH_3), 18.2 (CHCH_3), 17.4 (SCH_3), 16.5 (SCH_3); HR-MS (ESI): m/z=267.0874, calcd for $C_{14}H_{18}OS_2$ $[M+H]^+$: 267.0877.

2-(1,4-Dioxan-2-yl)-3-(methylthio)-1,3-diphenylprop-2-en-1-one (9a): yield: 97 mg (57%); white solid; mp 137–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) (for *E*-isomer): δ=7.62 (m, 2H, aromatic CH), 7.49 (m, 2H, aromatic CH), 7.31 (m, 1H, aromatic CH), 7.18 (t, 2H, aromatic CH), 7.04 (m, 3H, aromatic CH), 5.10 (dd, J=10.2 and 2.7 Hz, 1H, OCHCH$_2$O), 4.06 (dd, J=11.5 and 2.7 Hz) and 3.65 (m) (1:5H, $CH_2OCH_2CH_2$O), 1.85 (s, 3H, SCH_3); (for *Z*-isomer): δ=8.11 (m, 2H, aromatic CH), 7.57 (t, 1H, aromatic CH), 7.49 (m, 3H, aromatic CH), 7.40 (m, 1H, aromatic CH), 7.04 (m, 3H, aromatic CH), 4.35 (dd, J=10.0 and 2.9 Hz, 1H, OCHCH$_2$O), 3.65 (m, 6H, $CH_2OCH_2CH_2$O), 1.62 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) (for *E*-isomer): δ=197.1 (Cq, C=O) [190.0 for *Z*-isomer], 143.2 (Cq) [141.62 for *Z*-isomer], 137.9 (Cq) [137.8 for *Z*-isomer], 136.0 (Cq) [136.2 and 135.6 for *Z*-isomer], 132.6, 129.8, 129.3, 128.4, 128.1 and 127.8 (aromatic CH) [133.1, 129.4, 129.0, 128.8, 128.9 and 128.5 for *Z*-isomer], 76.6 (OCHCH$_2$O) [76.3 for *Z*-isomer], 69.2 (s), 68.6 (CH_2OCH$_2$CH$_2$O) [69.2 for *Z*-isomer], 67.0 and 66.2 (CH$_2$OCH_2CH_2O) [66.5 and 65.9 for *Z*-isomer], 15.6 (SCH_3) [15.4 for *Z*-isomer]; HR-MS (ESI): m/z=341.1211, calcd. for $C_{20}H_{20}O_3S$ $[M+H]^+$: 341.1211.

3-(1,4-Dioxan-2-yl)-4-(methylthio)-4-phenylbut-3-en-2-one (9b): yield: 99 mg (71%); white solid; mp 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) (for *E*-isomer): δ=7.39 (m, 3H, aromatic CH), 7.27 (m, 2H, aromatic CH), 4.18 (dd, J=10.3 and 2.7 Hz, 1H, OCHCH$_2$O), 3.87, 3.67 and 3.51 (m each, 2:2:2H, $CH_2OCH_2CH_2$O), 2.54 (s, 3H, SCH_3), 1.79 (s, 3H, COCH_3); (for *Z*-isomer): δ=7.39 (m, 3H, aromatic CH), 7.27 (m, 2H, aromatic CH), 4.95 (dd, J=9.9 and 3.0 Hz, 1H, OCHCH$_2$O), 3.87, 3.67 and 3.51 (m each, 2:2:2H, $CH_2OCH_2CH_2$O), 1.86 (s, 3H, SCH_3), 1.76 (s, 3H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) (for

E-isomer): δ = 203.3 (Cq, C=O) [203.8 for *Z*-isomer], 141.8 (Cq) [142.1 for *Z*-isomer], 137.4 (Cq) [138.6 for *Z*-isomer], 135.4 (Cq) [136.3 for *Z*-isomer], 128.7, 128.6 and 128.5 (aromatic CH) [129.3, 128.8 and 128.7 for *Z*-isomer], 75.7 (O*C*HCH$_2$O) [76.6 for *Z*-isomer], 68.5 (OCHCH$_2$O) [67.9 for *Z*-isomer], 66.5 and 65.8 (O*C*H$_2$*C*H$_2$O) [66.8 and 66.0 for *Z*-isomer], 31.9 (CO*C*H$_3$) [32.0 for *Z*-isomer], 15.4 (SCH$_3$); HR-MS (ESI): *m/z* = 279.1048, calcd. for $C_{15}H_{18}O_3S$ [*M*+H]$^+$: 279.1055.

4-(4-Chlorophenyl)-3-(1,4-dioxan-2-yl)-4-(methylthio)but-3-en-2-one (9c): yield: 117 mg (75%); white solid; mp 86–88 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS) (for *E*-isomer): δ = 7.37 (d, *J* = 8.3 Hz, 2H, aromatic CH), 7.21 (d, *J* = 8.3 Hz, 2H, aromatic CH), 4.08 (dd, *J* = 10.3 and 2.8 Hz, 1H, O*C*HCH$_2$O), 3.86 (dd, *J* = 11.4 and 2.8 Hz) and 3.75 (m) (1:1H, *C*H$_2$OCH$_2$CH$_2$O), 3.54 (m, 4H, O*C*H$_2$*C*H$_2$O), 2.48 (s, 3H, SCH$_3$), 1.76 (s, 3H, CO*C*H$_3$); (for *Z*-isomer): δ = 7.30 (d, *J* = 8.4 Hz, 2H, aromatic CH), 7.16 (d, *J* = 8.4 Hz, 2H, aromatic CH), 4.89 (dd, *J* = 10.1 and 2.9 Hz, 1H, O*C*HCH$_2$O), 3.75 (m, 2H, *C*H$_2$OCH$_2$CH$_2$O), 3.54 (m, 4H, O*C*H$_2$*C*H$_2$O), 1.82 (s, 3H, SCH$_3$), 1.78 (s, 3H, CO*C*H$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS) (for *E*-isomer): δ = 203.4 (Cq, C=O) [203.8 for *Z*-isomer], 139.8 (Cq) [140.5 for *Z*-isomer], 138.4 and 134.8 (Cq) [139.9 and 135.0 for *Z*-isomer], 134.0 (Cq) [134.8 for *Z*-isomer], 130.1 and 129.1 (aromatic CH) [130.8 and 129.0 for *Z*-isomer], 75.6 (O*C*HCH$_2$O) [76.5 for *Z*-isomer], 68.5 (O*C*HCH$_2$O) [68.0 for *Z*-isomer], 66.6 and 65.9 (O*C*H$_2$*C*H$_2$O) [66.9 and 66.1 for *Z*-isomer], 31.9 (CO*C*H$_3$) [32.3 for *Z*-isomer], 15.60 (SCH$_3$); HR-MS (ESI): *m/z* = 313.0670, calcd. for $C_{15}H_{18}ClO_3S$ [*M*+H]$^+$: 313.0665.

3-(1,4-Dioxan-2-yl)-4,4-diphenylbut-3-en-2-one (11): yield: 16 mg (10%); white solid; mp 94–96 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.31 (m, 3H, aromatic CH), 7.20 (m, 5H, aromatic CH), 7.17 (m, 2H, aromatic CH), 4.39 (dd, *J* = 10.2 and 2.7 Hz, 1H, O*C*HCH$_2$O), 3.90 (dd, *J* = 11.5 and 10.3 Hz) and 3.69 (d, *J* = 10.4 Hz) (1:1H, OCH*C*H$_2$O), 3.55 (m, 4H, O*C*H$_2$*C*H$_2$O), 1.86 (s, 3H, CO*C*H$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 206.9 (Cq, C=O), 144.9 (*C*SMe), 140.3 and 139.8 (Cq of Ph), 138.5 (C=*C*CH), 129.4, 129.0, 128.8, 128.7, 128.6 and 128.2 (aromatic CH), 77.0 (O*C*HCH$_2$O), 68.9 (*C*H$_2$OCH$_2$CH$_2$O), 66.6 and 66.1 (O*C*H$_2$*C*H$_2$O), 32.7 (CO*C*H$_3$); HR-MS (ESI): *m/z* = 309.1491, calcd. for $C_{20}H_{20}O_3$ [*M*+H]$^+$: 309.1491.

General Procedure for the Synthesis of Trisubstituted Pyrazoles 12

A mixture of **3** or **7** (0.2 mmol) and NH$_2$NH$_2$·H$_2$O (114 mg, 2.0 mmol, 85% aqueous) in toluene (2 mL) was stirred in a 10-mL sealed tube at 120 °C for 24 h. After being cooled to ambient temperature, the mixture was evaporated of all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: dichloromethane) to afford the target product.

4-(1,4-Dioxan-2-yl)-5-(methylthio)-3-phenyl-1*H*-pyrazole (12a): yield: 52 mg (95%); white solid; mp 149–151 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.45 (m, 5H, aromatic CH), 4.72 (dd, *J* = 10.7 and 2.8 Hz, 1H, O*C*HCH$_2$O), 3.99 (t) and 3.89 (d, *J* = 11.3 Hz) (1:1H, OCH*C*H$_2$O), 3.80 (m), 3.70 (d, *J* = 5.8 Hz) and 3.60 (dd, *J* = 11.7 and 2.7 H)(1:2:1H, O*C*H$_2$*C*H$_2$O), 2.44 (s, 3H, SCH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 145.8, 144.8 and 130.1 (Cq), 129.0, 128.8 and 128.7 (aromatic CH), 114.5 (Cq), 70.9 (O*C*HCH$_2$O), 69.0 (OCH*C*H$_2$O), 67.4 and 66.2 (O*C*H$_2$*C*H$_2$O), 16.7 (SCH$_3$); HR-MS (ESI): *m/z* = 277.1008, calcd. for $C_{14}H_{16}N_2O_2S$ [*M*+H]$^+$: 277.1011.

4-(1,4-Dioxan-2-yl)-3-methyl-5-(methylthio)-1*H*-pyrazole (12b): yield: 41 mg (95%); white solid; mp 88–90 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.72 (s, 1H, *NH*), 4.67 (dd, *J* = 10.4 and 3.0 Hz, 1H, O*C*HCH$_2$O), 3.75 (m, 6H, O*C*H$_2$*C*H$_2$O*C*H$_2$), 2.40 (s, 3H, SCH$_3$), 2.33 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 143.5, 141.2 and 115.2 (Cq), 71.4 (O*C*HCH$_2$O), 70.0 (OCH*C*H$_2$O), 67.4 and 66.4 (O*C*H$_2$*C*H$_2$O), 17.5 (SCH$_3$), 11.1 (CH$_3$); HR-MS (ESI): *m/z* = 215.0851, calcd. for $C_9H_{14}N_2O_2S$ [*M*+H]$^+$: 215.0854.

3-Cyclopropyl-4-(1,4-dioxan-2-yl)-5-(methylthio)-1*H*-pyrazole (12c): yield: 46 mg (96%); white solid; mp 128–130 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.26 (s, 1H, *NH*), 4.71 (dd, *J* = 10.6 and 2.7 Hz, 1H, O*C*HCH$_2$O), 3.75 (m, 6H, O*C*H$_2$*C*H$_2$O*C*H$_2$), 2.35 (s, 3H, SCH$_3$), 1.94 (m, 1H, CH$_2$*C*HCH$_2$), 0.82 and 0.63 (m each, 3:1H, CH$_2$*C*HCH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 147.2, 142.9 and 115.9 (Cq of pyrazole), 71.3 (O*C*HCH$_2$O), 69.9 (OCH*C*H$_2$O), 67.4 and 66.4 (O*C*H$_2$*C*H$_2$O), 17.3 (SCH$_3$), 7.5 (CH$_2$*C*HCH$_2$), 6.7 and 6.6 (*C*H$_2$CH*C*H$_2$); HR-MS (ESI): *m/z* = 241.1012, calcd. for $C_{11}H_{16}N_2O_2S$ [*M*+H]$^+$: 241.1011.

4-Benzyl-3-methyl-5-(methylthio)-1*H*-pyrazole (12d): yield: 38 mg (87%); colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.65 (s, 1H, *NH*), 7.21 (m, 5H, aromatic CH), 3.82 (s, 2H, Ph*C*H$_2$), 2.35 (s, 3H, SCH$_3$), 2.19 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 142.7, 141.7 and 140.5 (Cq), 128.5, 128.3 and 126.1 (aromatic CH), 118.3 (Cq), 29.3 (Ph*C*H$_2$), 17.6 (SCH$_3$), 10.9 (CH$_3$); HR-MS (ESI): *m/z* = 219.0956, calcd. for $C_{12}H_{14}N_2S$ [*M*+H]$^+$: 219.0956.

General Procedure for the Synthesis of Isoxazoles 13

A mixture of **3** (50 mg, 0.2 mmol), NH$_2$OH·HCl (83 mg, 1.2 mmol), and KOH (79 mg, 1.2 mmol, 85%) in EtOH (2 mL) was stirred in a 10-mL sealed tube at 120 °C for 24 h. After being cooled to ambient temperature, the mixture was evaporated of all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography [eluent: petroleum ether (60–90 °C)/ethyl acetate = 10:1, v/v] to afford the target product.

4-(1,4-Dioxan-2-yl)-3-methyl-5-(methylthio)isoxazole (13a): yield: 24 mg (56%); colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 4.53 (dd, *J* = 8.0 and 5.5 Hz, 1H, O*C*HCH$_2$O), 3.76 (m, 6H, O*C*H$_2$*C*H$_2$O*C*H$_2$), 2.55 (s, 3H, SCH$_3$), 2.30 (s, 3H, *C*H$_3$C=N); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 163.7, 159.8 and 112.6 (Cq of isoxazole), 70.1 (O*C*HCH$_2$O), 69.3 (OCH*C*H$_2$O), 67.2 and 66.4 (O*C*H$_2$*C*H$_2$O), 14.9 (SCH$_3$), 11.1 (*C*H$_3$C=N); HR-MS (ESI): *m/z* = 216.0690, calcd. for $C_9H_{13}NO_3S$ [*M*+H]$^+$: 216.0694.

3-Cyclopropyl-4-(1,4-dioxan-2-yl)-5-(methylthio)isoxazole (13b): yield: 26 mg (54%); white solid; mp 71–73 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 4.65 (dd, *J* = 10.4 and 2.9 Hz, 1H, O*C*HCH$_2$O), 3.78 (m, 6H, O*C*H$_2$*C*H$_2$O*C*H$_2$), 2.55 (s, 3H, SCH$_3$), 1.94 (m, 1H, CH$_2$*C*HCH$_2$), 1.08 and 0.94 (m each, 1:3H, *C*H$_2$CH*C*H$_2$);

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 165.0, 163.7 and 113.1 (Cq of isoxazole), 70.1 (O*C*HCH$_2$O), 69.5 (OCH*C*H$_2$O), 67.3 and 66.4 (O*C*H$_2$*C*H$_2$O), 14.9 (SCH_3), 8.5 (CH$_2$*C*HCH$_2$), 7.3 and 6.5 (*C*H$_2$CH*C*H$_2$); HR-MS (ESI): *m/z* = 242.0854, calcd. for $C_{11}H_{15}NO_3S$ $[M+H]^+$: 242.0851.

3-Methyl-5-(methylthio)-4-(tetrahydrofuran-2-yl)isoxazole (13c): yield: 22 mg (55%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.74 (dd, *J* = 8.6 and 6.7 Hz, 1H, O*C*HCH$_2$), 4.02 and 3.84 (m each,1:1H, O*C*H$_2$CH$_2$), 2.55 (s, 3H, SCH_3), 2.25 (s, 3H, *C*H$_3$C=N), 2.08 and 1.85 (m each, 3:1H, OCHC*H*$_2$C*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 162.2, 159.7 and 116.6 (Cq of isoxazole), 72.5 (O*C*HCH$_2$), 68.6 (O*C*H$_2$CH$_2$), 32.1 and 26.6 (OCH*C*H$_2$*C*H$_2$), 15.1 (SCH_3), 11.0 (*C*H$_3$C=N); HR-MS (ESI): *m/z* = 200.0741 calcd. for $C_9H_{13}NO_2S$ $[M+H]^+$: 200.0745.

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References

[1] E.-I. Negishi, Z. H. Huang, G. W. Wang, S. Mohan, C. Wang, H. S. Hattori, *Acc. Chem. Res.* **2008**, *41*, 1474.

[2] a) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009; b) X. J. Shang, Z. Q. Liu, *Chem. Soc. Rev.* **2013**, *42*, 3253.

[3] a) Y. H. Takeda, M. Shimizu, T. Hiyama, *Angew. Chem.* **2007**, *119*, 8813; *Angew. Chem. Int. Ed.* **2007**, *46*, 8659; b) S. G. Newman, M. Lautens, *J. Am. Chem. Soc.* **2010**, *132*, 11416.

[4] a) Y. Nishihara, M. Miyasaka, M. Okamoto, H. Inoue, E. Takahashi, K. Tanemura, K. Takagi, *J. Am. Chem. Soc.* **2007**, *129*, 12634; b) M. Shimizu, I. Nagao, Y. Tomioka, T. Hiyama, *Angew. Chem.* **2008**, *120*, 8216; *Angew. Chem. Int. Ed.* **2008**, *47*, 8096; c) C. Wang, T. Tobrman, Z. Q. Xu, E.-I. Negishi, *Org. Lett.* **2009**, *11*, 4092.

[5] a) X. Bresser, P. Knochel, *Angew. Chem.* **2011**, *123*, 1954; *Angew. Chem. Int. Ed.* **2011**, *50*, 1914; b) R. Egris, M. Villacampa, J. C. Menéndez, *Chem. Eur. J.* **2009**, *15*, 10930; c) K. Akiyama, F. Gao, A. H. Hoveyda, *Angew. Chem.* **2010**, *122*, 429; *Angew. Chem. Int. Ed.* **2010**, *49*, 419–423.

[6] a) K. Itami, Y. Ohashi, J.-i. Yoshida, *J. Org. Chem.* **2005**, *70*, 2778; b) M. Movassaghi, A. E. Ondrus, *J. Org. Chem.* **2005**, *70*, 8638; c) C. L. Sun, Y. Wang, X. Zhou, Z. H. Wu, B. J. Li, B. T. Guan, Z. J. Shi, *Chem. Eur. J.* **2010**, *16*, 5844; d) Y. Ashida, Y. Sato, T. Ueno, K. Suzuki, K.-I. Kai, H. Nakatsuji, Y. Tanabe, *Chem. Eur. J.* **2015**, *21*, 5934.

[7] For selected recent reviews on C–H activation (functionalization), see: a) L. Yang, H. M. Huang, *Chem. Rev.* **2015**, *115*, 3468; b) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498; c) T. Gensch, M. N. Hopkinson, F. Glorius, J. W. Delord, *Chem. Soc. Rev.* **2016**, *45*, 2900.

[8] a) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335; b) C. Liu, H. Zhang, W. Shi, A. W. Lei, *Chem. Rev.* **2011**, *111*, 1780; c) F. Jia, Z. P. Li, *Org. Chem. Front.* **2014**, *1*, 194; d) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem.* **2014**, *126*, 76; *Angew. Chem. Int. Ed.* **2014**, *53*, 74; e) R. Vanjari, K. N. Singh, *Chem. Soc. Rev.* **2015**, *44*, 8062; f) L. Y. Lv, Z. P. Li, *Top. Curr.Chem.* **2016**, *374*, 38.

[9] For selected recent reports on transition metal-catalyzed oxidative C(sp^3)–H functionalization, see: a) Z. P. Li, L. Cao, C. J. Li, *Angew. Chem.* **2007**, *119*, 6625; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505; b) Y. H. Zhang, C. J. Li, *Eur. J. Org. Chem.* **2007**, 4654; c) Z. P. Li, R. Yu, H. J. Li, *Angew. Chem.* **2008**, *120*, 7607; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497; d) K. Z. Li, G. Y. Tan, J. S. Huang, F. J. Song, J. S. You, *Angew. Chem.* **2013**, *125*, 13180; *Angew. Chem. Int. Ed.* **2013**, *52*, 12942; e) D. Liu, C. Liu, H. Li, A. W. Lei, *Angew. Chem.* **2013**, *125*, 4549; *Angew. Chem. Int. Ed.* **2013**, *52*, 4453; f) W. T. Wei, M.-B. Zhou, J. H. Fan, W. Liu, R.-J. Song, Y. Liu, M. Hu, P. Xie, J. H. Li, *Angew. Chem.* **2013**, *125*, 3726; *Angew. Chem. Int. Ed.* **2013**, *52*, 3638; g) A. Modak, U. Dutta, R. Kancherla, S. Maity, M. Bhadra, S. M. Mobin, D. Maiti, *Org. Lett.* **2014**, *16*, 2602; h) K. Z. Li, Q. Wu, J. B. Lan, J. S. You, *Nat. Commun.* **2015**, *6*, 8404; i) M. Hu, J. H. Fan, Y. Liu, X. H. Ouyang, R. J. Song, J. H. Li, *Angew. Chem.* **2015**, *127*, 9713; *Angew. Chem. Int. Ed.* **2015**, *54*, 9577; j) M. Brzozowski, J. A. Forni, G. P. Savage, A. Polyzos, *Chem. Commun.* **2015**, *51*, 334; k) S. Tang, P. Wang, H. R. Li, A. W. Lei, *Nat. Commun.* **2016**, *7*, 11676; l) H. Aruri, U. Singh, M. Kumar, S. Sharma, S. K. Aithagani, V. K. Gupta, S. Mignan, R. A. Vishwakarma, P. P. Singh, *J. Org. Chem.* **2017**, *82*, 1000.

[10] a) S. H. Li, G. Cheng, C. G. Feng, W. Gong, J. Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 5267; b) H. Jiang, J. He, T. Liu, J. Q. Yu, *J. Am. Chem. Soc.* **2016**, *138*, 2055.

[11] K. J. Stowers, K. C. Fortner, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 6541.

[12] G. Zhang, Y. X. Ma, S. L. Wang, Y. H. Zhang, R. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 12334.

[13] H. Wang, Y. L. Zhao, L. Li, S. S. Li, Q. Liu, *Adv. Synth. Catal.* **2014**, *356*, 3157.

[14] Y. F. Zhu, Y. Y. Wei, *Chem. Sci.* **2014**, *5*, 2379.

[15] D. Liu, C. Liu, H. Li, A. W. Lei, *Chem. Commun.* **2014**, *50*, 3623.

[16] G. P. Qin, X. N. Chen, L. Yang, H. M. Huang, *ACS Catal.* **2015**, *5*, 2882.

[17] a) B. Niu, W. N. Zhao, Y. C. Ding, Z. G. Bian, C. U. Pittman, A. H. Zhou, H. B. Ge, *J. Org. Chem.* **2015**, *80*, 7251; b) B. A. Mir, A. Banerjee, S. K. Santra, S. Rajamanickam, B. K. Patel, *Adv. Synth. Catal.* **2016**, *358*, 3471; c) L. Y. Dian, H. Zhao, D. Z. Negrerie, Y. F. Du, *Adv. Synth. Catal.* **2016**, *358*, 2422.

[18] a) H. F. Yu, Z. K. Yu, *Angew. Chem.* **2009**, *121*, 2973; *Angew. Chem. Int. Ed.* **2009**, *48*, 2929; b) H. F. Yu, W. W. Jin, C. L. Sun, J. P. Chen, W. M. Du, S. B. He, Z. K. Yu, *Angew. Chem.* **2010**, *122*, 5928; *Angew. Chem. Int. Ed.* **2010**, *49*, 5792; c) W. W. Jin, W. M. Du, Q. Yang, H. F. Yu, J. P. Chen, Z. K. Yu, *Org. Lett.* **2011**, *13*, 4272; d) Z. F. Mao, F. Huang, H. F. Yu, J. P. Chen,

Z. K. Yu, Z. Q. Xu, *Chem. Eur. J.* **2014**, *20*, 3439; e) W. W. Jin, Q. Yang, P. Wu, J. P. Chen, Z. K. Yu, *Adv. Synth. Catal.* **2014**, *356*, 2097; f) X. G. Yang, Z. Q. Liu, C. L. Sun, J. P. Chen, Z. K. Yu, *Chem. Eur. J.* **2015**, *21*, 14085; g) P. Wu, L. D. Wang, K. K. Wu, Z. K. Yu, *Org. Lett.* **2015**, *17*, 868; h) X. G. Yang, K. K. Wu, P. Wu, J. P. Chen, C. L. Sun, Z. K. Yu, *Chem. Eur. J.* **2015**, *21*, 9323; i) T. L. Guo, Q. B. Jiang, Z. K. Yu, *Adv. Synth. Catal.* **2016**, *358*, 3450.

[19] L. D. Wang, W. He, Z. K. Yu, *Chem. Soc. Rev.* **2013**, *42*, 599.

[20] L. Pan, X. H. Bi, Q. Liu, *Chem. Soc. Rev.* **2013**, *42*, 1251.

[21] Q. Yang, P. Wu, J. P. Chen, Z. K. Yu, *Chem. Commun.* **2014**, *50*, 6337.

[22] For selected recent reports on iron-catalyzed C–H functionalization, see: a) C. L. Sun, B. J. Li, Z. J. Shi, *Chem. Rev.* **2011**, *111*, 1293; b) J. H. Fan, M. B. Zhou, Y. Liu, W. T. Wei, X. H. Ouyang, R. J. Song, J. H. Li, *Synlett* **2014**, *25*, 657; c) L. IIies, T. Matsubara, S. Ichikawa, S. Asako, E. Nakamura, *J. Am. Chem. Soc.* **2014**, *136*, 13126; d) I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 3170.

[23] During the review period a communication on DTBP-promoted C–H alkylation of α-oxo ketene dithioacetals was published online. See: J. W. Wen, F. Zhang, W. Y. Shi, A. W. Lei, *Chem. Eur. J.* **2017**, DOI:10.1002/chem.201701664.

[24] CCDC 1486033 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[25] a) Q. Dai, J. T. Yu, Y. Jiang, S. J. Guo, H. T. Yang, J. Cheng, *Chem. Commun.* **2014**, *50*, 3865; b) N. B. Zhu, J. G. Zhao, H. L. Bao, *Chem. Sci.* **2017**, *8*, 2081; c) P. Z. Zhang, J. A. Li, L. Zhang, A. Shoberu, J. P. Zou, W. Zhang, *Green Chem.* **2017**, *19*, 919.

[26] Y. Z. Li, B. J. Li, X. Y. Lu, S. Lin, Z. J. Shi, *Angew. Chem.* **2009**, *121*, 3875; *Angew. Chem. Int. Ed.* **2009**, *48*, 3817.

[27] W. W. Jin, H. F. Yu, Z. K. Yu, *Tetrahedron Lett.* **2011**, *52*, 5884.

