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One-pot synthesis of symmetric 1,7-dicarbonyl compounds *via* a tandem radical addition–elimination–addition reaction†

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A novel approach to synthesize symmetric 1,7-dicarbonyl compounds *via* a tandem radical addition–elimination–addition reaction of *S*-carbonylmethyl xanthates with allylmethylsulfone and its analogues has been developed. Radicals were produced from *S*-carbonylmethyl xanthates by adding dilauroyl peroxide and reacted with allylmethylsulfone or analogues to generate terminal olefins as intermediates. The excessive radicals reacted with the intermediate olefins immediately to give adducts of symmetric 1,7-dicarbonyl compounds. This is an efficient method to synthesize 1,7-dicarbonyl compounds under mild conditions.

Introduction

Symmetric 1,7-dicarbonyl compounds are key intermediates in the synthesis of natural compounds and drug candidates in medicinal chemistry. Some symmetric 1,7-dicarbonyl compounds and analogues show anticancer,[1] antitumor,[2] antithrombosis,[3] and neuroprotection activities.[4] Symmetric 1,7-dicarbonyl compounds have been widely applied in the synthesis of cycloheptene derivatives *via* intramolecular reductive coupling[5a] or *via* acetalization and disproportationation,[5b] in the synthesis of cyclohexanone derivatives *via* the intramolecular Dieckmann condensation,[6] and in the synthesis of seven-membered cyclic ketones[7a] and eight-membered cyclic diketones.[7b] As a result, several methods to synthesize 1,7-dicarbonyl compounds have been developed. Pioneering works on the synthesis of 1,7-dicarbonyl compounds involved Michael addition reactions of nitroalkanes, aliphatic ketones, or esters with α,β-unsaturated carbonyl compounds,[8] coupling reactions of 1,5-dihaloalkane bis-Grignard reagents (or bis-zinc reagents) with acyl chlorides or benzimidazolium salts,[9] and Friedel–Crafts acylation of pentanedioic chloride with arenes.[10] However, these methods showed some drawbacks such as harsh reaction conditions, limited group tolerance, or low regioselectivity in the Friedel–Crafts acylation. Thus, it is important to develop a more facile method to prepare 1,7-dicarbonyl compounds.

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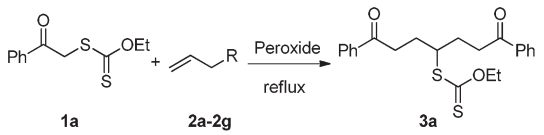
† Electronic supplementary information (ESI) available: Analytic data of known compounds **1** and **2**, copies of ^{1}H and ^{13}C NMR spectra of unknown intermediates of **1** and **2**, and products **3**. See DOI: 10.1039/c3ra42932f

Compounds with a xanthate group are useful intermediates in organic synthesis because the xanthate group is generally maintained after reactions with olefins.[11] Meanwhile, the xanthate group can be converted to hydrogen,[12] thiol,[13] sulfonic acid,[14] halogen, or azide, which can be further converted to an amino group.[15] It has been reported that the reactions of xanthates with allylalkylsulfones[15a,16] or vinylalkyl(phenyl)sulfones[17] generate terminal olefins or olefins, respectively, *via* a radical addition and a subsequent radical rearrangement and elimination of alkanesulfonyl or benzenesulfonyl radicals. It is well-known that xanthates readily undergo the radical addition with various terminal olefins.[11,18] To the best of our knowledge, no example has been reported on the tandem radical addition–elimination–addition of two molecules of xanthates with allylmethylsulfone and analogues to construct symmetric organic compounds. Herein, we designed and present a tandem radical addition–elimination–addition reaction of *S*-carbonylmethylxanthates with allylmethylsulfone and its analogues to prepare symmetric 1,7-dicarbonyl derivatives.

Results and discussion

We designed a reaction of *S*-carbonylmethylxanthates and allylmethylsulfone that would generate 3-butenylcarbonyl intermediates, which would further react with the second molecule of *S*-carbonylmethylxanthates to give rise to symmetric 1,7-dicarbonyl compounds. To achieve the tandem reaction, *O*-ethyl *S*-2-phenyl-2-oxoethylxanthate (**1a**) and allylmethylsulfone (**2a**) were first selected to optimize the reaction conditions. When the reaction was initiated by dilauryl peroxide (DLP), xanthate **1a** and sulfone **2a** reacted in a molar

Table 1 Optimization of the reaction of xanthate **1a** with allylmethylsulfone (**2a**) and its analogues



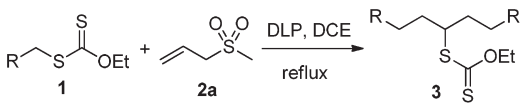
1a 2a-2g 3a

Entry	2	R	Molar ratio **1a** : **2**	Initiator (equiv. *vs.* **1a**)	Solvent	Isolated yield (%)
1	**2a**	$MeSO_2$	2 : 1	DLP (0.45)	DCE	75
2	**2a**	$MeSO_2$	2.2 : 1	DLP (0.45)	DCE	81
3	**2a**	$MeSO_2$	3 : 1	DLP (0.45)	DCE	78
4	**2a**	$MeSO_2$	2.2 : 1	BPO (0.50)	DCE	36
5	**2a**	$MeSO_2$	2.2 : 1	AIBN (1.0)	DCE	trace
6	**2a**	$MeSO_2$	2.2 : 1	DLP (0.45)	EA	75
7	**2a**	$MeSO_2$	2.2 : 1	DLP (0.45)	C_6H_5Cl	75
8	**2b**	$EtSO_2$	2.2 : 1	DLP (0.45)	DCE	75
9	**2c**	$PhSO_2$	2.2 : 1	DLP (0.70)	DCE	65
10	**2d**	*n*-BuSO	2.2 : 1	DLP (0.45)	DCE	60
11	**2e**	PhSO	2.2 : 1	DLP (0.45)	DCE	40
12	**2f**	*n*-BuS	2.2 : 1	DLP (0.45)	DCE	49
13	**2g**	PhS	2.2 : 1	DLP (0.45)	DCE	27
14	**2h**	AcS	2.2 : 1	DLP (0.45)	DCE	50

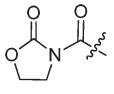
ratio of 2 : 1 in refluxing 1,2-dichloroethane (DCE) to produce the expected product *O*-ethyl-*S*-(1,7-diphenyl-1,7-dioxoheptan-4-yl) xanthate (**3a**) in a yield of 75% (Table 1, entry 1). The yield was improved to 81% when the molar ratio was increased to 2.2 : 1 (Table 1, entry 2). Further increasing the molar ratio to 3 : 1 resulted in the decrease of the yield to 78% (Table 1, entry 3). However, benzoyl peroxide (BPO) and azodiisobutyronitrile (AIBN) diminished the yield (Table 1, entries 4 and 5). The solvent screening revealed that dichloroethane (DCE) shows better efficiency than ethyl acetate (EA) and chlorobenzene (Table 1, entries 2, 6, and 7). To evaluate the effect of the substituent in the allylsulfones, allyl ethylsulfone (**2b**) and allyl phenylsulfone (**2c**) were prepared and tested as the olefin precursors instead of sulfone **2a**. Both sulfones **2b** and **2c** gave rise to xanthate **3a** in lower yields than the sulfone **2a** (Table 1, entries 8 and 9). When allyl phenylsulfone (**2c**) was used, the reaction consumed more DLP (Table 1, entry 9). To extend the tandem reaction, a variety of sulfone analogues, including representative aliphatic and aromatic allylsulfoxides (**2d** and **2e**), allylthioethers (**2f** and **2g**), and allyl thioacetate (**2h**), were tested (Table 1, entries 10–14). The adduct xanthate **3a** was obtained in low to satisfactory yields. The results indicate that all allylic sulfur derivatives can be used as the precursors of the C3 moiety in the tandem radical reaction for the synthesis of the 1,7-dicarbonyl compound. But allylsulfones, especially allylmethylsulfone (**2a**), are more efficient precursors than allylsulfoxides, allylthioethers, and allyl thioacetate.

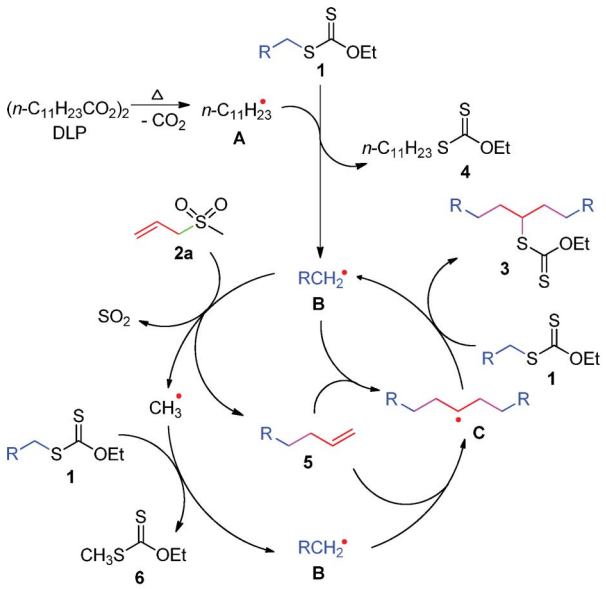
Different xanthates **1** were readily obtained *via* the reaction of potassium *O*-ethyl xanthate and the corresponding halomethylcarbonyl compounds, including representative aliphatic and aromatic bromo/chloromethyl ketones, chloroacetates, chloroacetamides, and chloroacetonitrile.[19–24] They reacted with the best precursor of the C3 moiety, allylmethylsulfone (**2a**), to afford the corresponding symmetric 1,7-dicarbonyl compounds under the optimal conditions (Table 2). The results indicate that 1,7-dicarbonyl compounds, including 1,7-diketones (Table 2, entries 1–4), 1,7-heptanedioates (Table 2, entries 5–9), 1,7-heptanediamides (Table 2, entries 10–12), and 1,7-heptanedinitrile (Table 2, entry 13), were obtained in satisfactory to good yields except for di(4-nitrophenyl) 1,7-heptanedioate (**3h**) and *N*,*N*,*N*′,*N*′-tetraphenyl 1,7-heptanediamide (**3j**) (Table 2, entries 8 and 10), which were obtained in relatively low yields.

Table 2 Synthesis of symmetric 1,7-dicarbonyl compounds *via* tandem radical reactions



1 2a 3

Entry	Xanthate	R	Time (h)	Isolated yield (%)
1	**1a**	PhCO	15	81
2	**1b**	4-$MeOC_6H_4CO$	15	78
3	**1c**	MeCO	15	72
4	**1d**	$ClCH_2CO$	15	65
5	**1e**	EtO_2C	8	71
6	**1f**	PhO_2C	8	69
7	**1g**	4-$ClC_6H_4O_2C$	8	84
8	**1h**	4-$O_2NC_6H_4O_2C$	20	40
9	**1i**	BnO_2C	8	69
10	**1j**	Ph_2NCO	20	35
11	**1k**	Ph(Ms)NCO	15	69
12	**1l**		15	79
13	**1m**	CN	15	51



Scheme 1 Possible mechanism of the tandem radical addition–elimination–addition reaction.

Previous reports show that it is harmful for the radical addition of xanthates with olefins when the molecules contain an amino group. The common solution to the problem is to protect the amino group.[11] When the protecting group is diphenyl, the reaction gives the product in a low yield. However, when changing the protecting group to a methanesulfonyl or alkoxycarbonyl group, the yields increase obviously, revealing that the electron-withdrawing protecting groups are beneficial for the tandem reaction. These decrease the alkalinity of the nitrogen atom, resulting in an increase of the electrophilicity of the aminocarbonylmethyl radicals (Table 2, entries 10–12).

The cyano group is a potential carbonyl group, a precursor of the carbonyl, carboxylic acid, carboxylate, or amide groups. Thus, introducing the cyano group into the molecule is very important in organic synthesis. When submitting xanthate **1m** to the tandem reaction, we successfully produced the target product *S*-(1,5-dicyanopentan-3-yl) *O*-ethyl carbonodithioate (**3m**) in a moderate yield of 51% (Table 2, entry 13).

The proposed mechanism of the tandem reaction is shown in Scheme 1. DLP dissociates into the undecyl radical (**A**) *via* homolysis and subsequently releases carbon dioxide under heating. The radical **A** attacks a xanthate **1** to form stable *O*-ethyl *S*-undecyl xanthate **4** and a carbonylmethyl radical **B**, which undergoes a radical addition with allylmethylsulfone (**2a**) followed by a subsequent radical rearrangement to generate a terminal olefin **5** and methylsulfonyl radical. The methylsulfonyl radical further decomposes to sulfur dioxide and a methyl radical. The highly reactive methyl radical attacks xanthate **1** as well to regenerate the radical **B** and another stable *O*-ethyl *S*-methyl xanthate **6**. The radical **B** further undergoes a radical addition with the terminal olefin **5** to produce a secondary radical **C**, which is also a highly reactive radical and reacts with the xanthate **1** to give rise to the stable product xanthate **3** and the radical **B** as well. During the tandem reaction, all *S*-alkyl *O*-ethyl xanthates **3**, **4**, and **6** are inert byproducts or products, while all simple aliphatic radicals (methyl radical, undecyl radical **A** and the radical **C**) are highly reactive and show short half-lives. They are readily captured by the sulfur atom in the xanthate group. The alkyl radicals are nucleophilic radicals and only react with electron-deficient acceptors rather than with electron-rich olefins **2a** and **5**, whilst carbonylmethyl radicals **B** have an electrophilic character and thus are reactive to nucleophilic radical acceptors, such as simple alkenes. They can undergo radical addition with olefins **2a** and **5**. This reactivity difference determines the selectivity of the radical.[25] This is the reason why the radical tandem addition–elimination–addition reaction can be realized successfully.

Conclusion

In summary, we developed a one-pot tandem radical addition–elimination–addition reaction to synthesize symmetric 1,7-dicarbonyl compounds from *S*-carbonylmethyl xanthates with allylmethylsulfone and analogues, including allylalkyl/arylsulfones, allylalkyl/arylsulfoxides, allylalkyl/arylthioethers, and allyl thioacetate. The method shows several advantages, such as mild and efficient protocols, readily available and inexpensive starting materials, and the non-use of toxic transition metals.

Experimental

General method

Melting points were determined with a melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ with TMS as the internal standard. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$. IR spectra were determined directly. HRMS spectra were recorded with an LC/MSD TOF mass spectrometer. TLC analysis was performed on glass plate pre-coated with silica gel (10–40 μm). Spots were visualized with UV light or iodine. Column chromatography was performed on silica gel (200–300 mesh) with a mixture of petroleum ether and ethyl acetate as the eluent. Allylthioethers **2f** and **2g**,[26] and allyl thioacetate (**2h**)[27] were prepared by referring to the previously reported methods.

General procedure for the synthesis of xanthates 1 (except for 1d)

Potassium *O*-ethyl xanthate (841 mg, 5.25 mmol) was added portion-wise to a solution of carbonylmethyl chloride (5 mmol; for the synthesis of **1a–c**, carbonylmethyl bromides were used) in 20 mL of acetone in an ice-water bath while stirring. The resulting solution was further stirred for 2 h at room temperature. After removal of the solvent the residue was purified using silica gel column chromatography (petroleum ether–ethyl acetate = 20/1 to 1/1, v/v) to give xanthate **1**.

***O*-Ethyl *S*-[2-oxo-2-phenylethyl] carbonodithioate (1a).** Pale yellow solid, yield: 1.08 g, 90%, m.p. 32–33 °C, lit.[19] m.p. 31–32 °C.

***O*-Ethyl *S*-[2-(4-methoxyphenyl)-2-oxoethyl] carbonodithioate (1b).** Pale yellow solid, yield: 1.20 g, 89%, m.p. 69–70 °C, lit.[19] m.p. 68–69 °C.

***O*-Ethyl *S*-(2-oxopropyl) carbonodithioate (1c)[17b].** Pale yellow liquid, yield: 0.81 g, 91%.

***S*-(2-Ethoxyl-2-oxoethyl) *O*-ethyl carbonodithioate (1e)[20].** Pale yellow liquid, yield: 0.92 g, 88%.

***O*-Ethyl *S*-(2-oxo-2-phenoxyethyl) carbonodithioate (1f)[21].** Pale yellow liquid, yield: 1.18 g, 92%.

***S*-[2-(4-Chlorophenoxy)-2-oxoethyl] *O*-ethyl carbonodithioate (1g).** R_f = 0.35 (petroleum ether–ethyl acetate = 10/1, v/v). Pale yellow solid, yield: 1.37 g, 95%, m.p. 50–51 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.44 (t, J = 7.1 Hz, 3H, CH_3), 4.13 (s, 2H, CH_2), 4.68 (q, J = 7.1 Hz, 2H, CH_2), 7.07 (d, J = 8.7 Hz, 2H, ArH), 7.35 (d, J = 8.7 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 37.9 (CH_2), 70.9 (CH_2), 122.6 (CH), 129.5 (CH), 131.5 (C), 149.0 (C), 166.4 (C=O), 212.4 (C=S). IR (neat) ν = 3096, 3064, 2981, 2922, 2854, 1758, 1485, 1225, 1045 cm^{-1}. HRMS (ESI) calcd. for $C_{11}H_{12}ClO_3S_2$ $[M+H]^+$ m/z = 290.9916; found 290.9902.

***O*-Ethyl *S*-[2-(4-nitrophenoxy)-2-oxoethyl] carbonodithioate (1h).** R_f = 0.23 (petroleum ether–ethyl acetate = 5/1, v/v). Pale yellow solid, yield: 1.40 g, 93%, m.p. 56–57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.45 (t, J = 7.1 Hz, 3H, CH_3), 4.18 (s, 2H, CH_2), 4.69 (q, J = 7.1 Hz, 2H, CH_2), 7.32 (d, J = 9.0 Hz, 2H, ArH), 8.28 (d, J = 9.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 37.9 (CH_2), 71.1 (CH_2), 122.2 (CH), 125.2 (CH), 145.5 (C), 155.1 (C), 165.8 (C=O), 212.3 (C=S). IR (neat) ν = 3114, 3081, 2981, 2923, 2854, 1770, 1524, 1205, 1045 cm^{-1}. HRMS (ESI) calcd. for $C_{11}H_{11}NNaO_5S_2$ $[M+Na]^+$ m/z = 323.9976; found 323.9959.

***S*-(2-Benzyloxy-2-oxoethyl) *O*-ethyl carbonodithioate (1i).** R_f = 0.31 (petroleum ether–ethyl acetate = 10/1, v/v). Pale yellow liquid, yield: 1.25 g, 93%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.36 (t, J = 7.1 Hz, 3H, CH_3), 3.95 (s, 2H, CH_2), 4.60 (q, J = 7.1 Hz, 2H, CH_2), 5.19 (s, 2H, CH_2), 7.36 (s, 5H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 37.8 (CH_2), 67.5 (CH_2), 70.6 (CH_2), 128.3 (CH), 128.4 (CH), 128.5 (CH), 135.2 (C), 167.7 (C=O), 212.3 (C=S). IR (neat) ν = 3065, 3032, 2980, 2928, 2856, 1741, 1450, 1215, 1048 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{14}NaO_3S_2$ $[M+Na]^+$ m/z = 293.0282; found 293.0275.

***S*-(2-Diphenylamino-2-oxoethyl) *O*-ethyl carbonodithioate (1j).** R_f = 0.20 (petroleum ether–ethyl acetate = 3/1, v/v). Pale yellow solid, yield: 1.52 g, 92%, m.p. 112–113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.38 (t, J = 7.1 Hz, 3H, CH_3), 3.92 (s, 2H, CH_2), 4.60 (q, J = 7.1 Hz, 2H, CH_2), 7.33 (s, 10H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 40.6 (CH_2), 70.4 (CH_2), 125.9 (CH), 128.8 (CH), 129.9 (CH), 142.1 (C), 166.4 (C=O), 213.7 (C=S). IR (neat) ν = 3065, 2980, 2923, 2854, 1681, 1488, 1379, 1296, 1217, 1052 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{17}NNaO_2S_2$ $[M+Na]^+$ m/z = 354.0598; found 354.0591.

***O*-Ethyl *S*-[2-(*N*-methanesulfonyl-*N*-phenylamino)-2-oxoethyl] carbonodithioate (1k).** R_f = 0.24 (petroleum ether–ethyl acetate = 1/1, v/v). Pale yellow solid, yield: 1.58 g, 95%, m.p. 109–110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.41 (t, J = 7.1 Hz, 3H, CH_3), 3.48 (s, 3H, CH_3), 3.75 (s, 2H, CH_2), 4.61 (q, J = 7.1 Hz, 2H, CH_2), 7.42–7.44 (m, 2H, ArH), 7.53–7.55 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 41.3 (CH_2), 42.1 (CH_3), 71.1 (CH_2), 130.0 (CH), 130.2 (CH), 130.6 (CH), 134.8 (C), 167.5 (C=O), 213.0 (C=S). IR (neat) ν = 3035, 2982, 2932, 2854, 1710, 1491, 1355, 1231, 1150, 1048 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{15}NNaO_4S_3$ $[M+Na]^+$ m/z = 356.0061; found 356.0051.

***O*-Ethyl *S*-[2-oxo-2-(oxazolidin-2-on-3-yl)ethyl] carbonodithioate (1l).** Pale yellow solid, yield: 1.11 g, 89%, m.p. 100–101 °C, lit.[22] m.p. 96 °C.

***S*-(Cyanomethyl) *O*-ethyl carbonodithioate (1m)[23].** Pale yellow liquid, yield: 0.71 g, 88%.

Synthesis of *S*-(3-chloro-2-oxopropyl) *O*-ethyl carbonodithioate (1d). 1,3-Dichloro-2-propanone (957 mg, 7.54 mmol) was added to a solution of potassium *O*-ethyl xanthate (1.21 g, 7.54 mmol) in water (10 mL) portion-wise under stirring at 0 °C. The resulting solution was further stirred for 1 h at the same temperature and then filtered. The solid was washed with water and dried in the air to give xanthate **1d** as a white solid, yield: 1.12 g, 70%, m.p. 52–53 °C, lit.[24] 49–50 °C.

Synthesis of sodium ethanesulphinate

Diethyl disulfide (1.83 g, 15 mmol) was added dropwise to a mixture of NCS (16.02 g, 120 mmol), 2 M HCl (7.2 mL) and MeCN (41 mL) in a 10 °C water bath. The mixture was further stirred at room temperature for 30 min. After removal of the MeCN, 100 mL of ether was added. The resulting mixture was washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the pale yellow liquid ethanesulfonyl chloride 3.10 g (80%),[28] which was used directly in the next step.

Ethanesulfonyl chloride (3.10 g, 24 mmol) was added dropwise to a solution of sodium bicarbonate (4.05 g, 48 mmol) and sodium sulfide (6.08 g, 48 mmol) in water (30 mL) at 75–80 °C. The mixture was further stirred at the same temperature for 2 h. After removal of the water, the resulting solid was extracted with absolute ethanol (5 × 30 mL). White solid sodium ethanesulphinate (2.70 g, 96%) was obtained following the subsequent evaporation of ethanol.

Synthesis of allylsulfones 2

A mixture of sodium methanesulphinate (10.21 g, 0.1 mol) [or sodium ethanesulphinate (2.50 g, 21.5 mmol) or sodium benzenesulfinate (16.42 g, 0.1 mol)] and allyl bromide (15.7 g, 0.13 mol) [3.38 g, 28 mmol for sodium ethanesulphinate] was stirred at 60 °C for 4 h in PEG-400 (40 mL). After removal of the excess allyl bromide, the reaction mixture was poured into water (300 mL). The resulting mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent the residue was purified using silica gel column chromatography (petroleum ether–ethyl acetate = 3/1, v/v) to produce allylsulfone **2**.

Allyl methylsulfone (2a)[29]. Colorless liquid, yield: 10.5 g, 87%.

Allyl ethylsulfone (2b)[28b]. Colorless liquid, from sodium ethanesulphinate (2.50 g, 21.5 mmol), yield: 1.75 g, 60%.

Allyl phenylsulfone (2c)[30]. Colorless liquid, yield: 15.6 g, 85%.

Synthesis of allylsulfoxides 2d and 2e

30% H_2O_2 (1.36 g, 20 mmol) was added dropwise to a solution of allyl thioether (10 mmol) and thiourea (38 mg, 0.5 mmol) in dichloromethane (10 mL) under stirring at room temperature. The resulting mixture was further stirred at the same temperature for 24 h. After removal of the solvent the residue was purified using silica gel column chromatography (petroleum ether–ethyl acetate = 3/1, v/v) to produce allylsulfoxide.

Allyl butylsulfoxide (2d). R_f = 0.32 (petroleum ether–ethyl acetate = 3/1, v/v). Colorless liquid, yield: 0.72 g, 49%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 0.96 (t, J = 7.2 Hz, 3H, CH_3), 1.43–1.55 (m, 2H, CH_2), 1.71–1.89 (m, 2H, CH_2), 2.65–2.77 (m, 2H, CH_2), 3.44 (dd, J = 12.8, 7.6 Hz, 1H in CH_2), 3.52 (dd, J = 12.8, 7.6 Hz, 1H in CH_2), 5.39 (d, J = 17.2 Hz, 1H in CH_2), 5.44 (d, J = 10.2 Hz, 1H in CH_2), 5.84–5.95 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.5 (CH_3), 21.9 (CH_2), 24.3 (CH_2), 50.5 (CH_2), 55.5 (CH_2), 123.3 (CH_2), 125.7 (CH). IR (neat) ν = 3439, 3235, 3085, 3013, 2959, 2932, 2873, 1637, 1316, 1132, 1031 cm^{-1}. HRMS (ESI) calcd. for $C_7H_{15}OS$ $[M+H]^+$ m/z = 147.0844; found 147.0838.

Allyl phenylsulfoxide (2e)[31]. Colorless liquid, yield: 0.83 g, 50%.

General procedure for the synthesis of symmetric 1,7-dicarbonyl compounds 3

A solution of allylmethylsulfone or analogs **2** (1 mmol) and xanthate **1** (2.2 mmol) in 1,2-dichloroethane (1.5 mL) was degassed by vacuum, then filled with nitrogen. After the solution was heated to reflux, dilauroyl peroxide (DLP) (44 mg, 0.11 mmol) was added portion-wise. DLP (88 mg, 0.22 mmol) was added portion-wise every 1 h until 0.99 mmol of DLP was added. The reaction mixture was further refluxed for another 3–15 h until the starting material disappeared. After evaporation of the solvent, the residue was purified using silica gel column chromatography (petroleum ether–ethyl acetate = 15/1 to 1/2, v/v) to afford the adduct xanthate **3**.

***S*-(1,7-Dioxo-1,7-diphenylheptan)-4-yl *O*-ethyl carbonodithioate (3a).** R_f = 0.15 (petroleum ether–ethyl acetate = 15/1, v/v). Pale yellow solid, yield: 325 mg, 81%, m.p. 72–73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.36 (t, J = 7.1 Hz, 3H, CH_3), 2.09 (dddd, J = 14.8, 8.9, 7.2, 6.5 Hz, 2H in $2CH_2$), 2.31 (dddd, J = 14.8, 8.5, 6.8, 4.9 Hz, 2H in $2CH_2$), 3.16 (ddd, J = 15.0, 8.5, 6.5 Hz, 2H in $2CH_2$), 3.23 (ddd, J = 15.0, 7.2, 6.8 Hz, 2H in $2CH_2$), 3.96 (tt, J = 8.9, 4.9 Hz, 1H, CH), 4.57 (q, J = 7.1 Hz, 2H, CH_2), 7.46 (dd, J = 7.6, 7.2 Hz, 4H, ArH), 7.56 (t, J = 7.2 Hz, 2H, ArH), 7.95 (d, J = 7.6 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 28.9 (CH_2), 35.7 (CH_2), 50.7 (CH), 70.0 (CH_2), 128.0 (CH), 128.5 (CH), 133.1 (CH), 136.7 (C), 199.1 (C=O), 213.8 (C=S). IR (neat) ν = 3057, 2980, 2926, 2853, 1685, 1448, 1214, 1048 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{24}NaO_3S_2$ $[M+Na]^+$ m/z = 423.1065; Ffound 423.1057.

***S*-[1,7-Dioxo-1,7-di(4-methoxyphenyl)heptan]-4-yl *O*-ethyl carbonodithioate (3b).** R_f = 0.20 (petroleum ether–ethyl acetate = 5/1, v/v). White solid, yield: 360 mg, 78%, m.p. 60–61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.36 (t, J = 7.1 Hz, 3H, CH_3), 2.08 (dddd, J = 14.5, 8.5, 6.3, 6.0 Hz, 2H in $2CH_2$), 2.27 (dddd, J = 14.5, 8.5, 6.7, 5.0 Hz, 2H in $2CH_2$), 3.06–3.20 (m, 4H, $2CH_2$), 3.86 (s, 6H, $2CH_3$), 3.93 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.57 (q, J = 7.1 Hz, 2H, CH_2), 6.92 (d, J = 8.8 Hz, 4H, ArH), 7.94 (d, J = 8.8 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 29.0 (CH_2), 35.3 (CH_2), 50.8 (CH), 55.4 (CH_3), 69.9 (CH_2), 113.6 (CH), 129.8 (CH), 130.2 (C), 163.4 (C), 197.6 (C=O), 213.9 (C=S). IR (neat) ν = 3073, 2930, 2839, 1675, 1599, 1575, 1509, 1456, 1257, 1169, 1048 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{29}O_5S_2$ $[M+H]^+$ m/z = 461.1456; found 461.1450.

***S*-(1,7-Dioxononan)-5-yl *O*-ethyl carbonodithioate (3c).** R_f = 0.18 (petroleum ether–ethyl acetate = 5/1, v/v). Pale yellow liquid, yield: 199 mg, 72%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.43 (t, J = 7.1 Hz, 3H, CH_3), 1.83 (dddd, J = 14.7, 8.5, 7.7, 6.7 Hz, 2H in $2CH_2$), 2.04 (dddd, J = 14.7, 8.5, 7.5, 5.0 Hz, 2H in $2CH_2$), 2.14 (s, 6H, $2CH_3$), 2.59 (ddd, J = 15.0, 7.7, 6.7 Hz, 2H in $2CH_2$), 2.63 (dt, J = 15.0, 7.5 Hz, 2H in $2CH_2$), 3.71 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.64 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 28.2 (CH_2), 30.0 (CH_3), 40.5 (CH_2), 50.5 (CH), 70.1 (CH_2), 207.6 (C=O), 214.1 (C=S). IR (neat) ν = 2982, 2926, 2853, 1718, 1364, 1215, 1047 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{21}O_3S_2$ $[M+H]^+$ m/z = 277.0932; found 277.0924.

***S*-(1,7-Dichloro-1,7-dioxononan)-5-yl *O*-ethyl carbonodithioate (3d).** R_f = 0.21 (petroleum ether–ethyl acetate = 5/1, v/v). White solid, yield: 225 mg, 65%, m.p. 83–84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.43 (t, J = 7.1 Hz, 3H, CH_3), 1.90 (dddd, J = 14.6, 8.5, 7.7, 6.9 Hz, 2H in $2CH_2$), 2.12 (dddd, J = 14.6, 8.5, 7.5, 5.0 Hz, 2H in $2CH_2$), 2.71–2.85 (m, 4H, $2CH_2$), 3.74 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.09 (s, 4H, $2CH_2$), 4.65 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 28.2 (CH_2), 36.8 (CH_2), 48.1 (CH_2), 50.2 (CH), 70.4 (CH_2), 201.6 (C=O), 213.8 (C=S). IR (neat) ν = 2925, 2853, 1732, 1399, 1219, 1046 cm^{-1}. HRMS (ESI) calcd. for $C_{12}H_{19}Cl_2O_3S_2$ $[M+H]^+$ m/z = 345.0153; found 345.0148.

***S*-(1,7-Diethoxyl-1,7-dioxoheptan)-4-yl *O*-ethyl carbonodithioate (3e).** R_f = 0.25 (petroleum ether–ethyl acetate = 10/1, v/v). Pale yellow liquid, yield: 240 mg, 71%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$), 1.42 (t, J = 7.1 Hz, 3H, CH_3), 1.93 (ddt, J = 14.3, 8.9, 6.5 Hz, 2H in $2CH_2$), 2.09 (dddd, J = 14.3, 8.5, 7.2, 5.1 Hz, 2H in $2CH_2$), 2.45 (ddd, J = 15.5, 8.5, 6.5 Hz, 2H in $2CH_2$), 2.49 (ddd, J = 15.5, 7.2, 6.5 Hz, 2H in $2CH_2$), 3.81 (tt, J = 8.9, 5.1 Hz, 1H, CH), 4.13 (q, J = 7.1 Hz, 4H, $2CH_2$), 4.64 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 14.1 (CH_3), 29.5 (CH_2), 31.5 (CH_2), 50.2 (CH), 60.4 (CH_2), 70.0 (CH_2), 172.7 (C=O), 213.7 (C=S). IR (neat) ν = 2981, 2930, 2856, 1735, 1446, 1215, 1050 cm^{-1}. HRMS (ESI) calcd. for $C_{14}H_{25}O_5S_2$ $[M+H]^+$ m/z = 337.1143; found 337.1135.

***S*-(1,7-Dioxo-1,7-diphenoxyheptan)-4-yl *O*-ethyl carbonodithioate (3f).** R_f = 0.25 (petroleum ether–ethyl acetate = 10/1, v/v). Pale yellow oil, yield: 299 mg, 69%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.42 (t, J = 7.1 Hz, 3H, CH_3), 2.09 (ddt, J = 14.8, 8.5, 6.5 Hz, 2H in $2CH_2$), 2.27 (dddd, J = 14.8, 8.5, 7.6, 5.0 Hz, 2H in $2CH_2$), 2.71–2.83 (m, 4H, $2CH_2$), 4.00 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.66 (q, J = 7.1 Hz, 2H, CH_2), 7.08 (d, J = 7.8 Hz, 4H, ArH), 7.22 (t, J = 7.5 Hz, 2H, ArH), 7.36 (dd, J = 7.8, 7.5 Hz, 4H,

ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 29.7 (CH_2), 31.6 (CH_2), 50.4 (CH), 70.3 (CH_2), 121.5 (CH), 125.8 (CH), 129.4 (CH), 150.6 (C), 171.3 (C=O), 213.7 (C=S). IR (neat) ν = 3064, 3042, 2980, 2925, 2855, 1747, 1592, 1492, 1214, 1044 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{24}NaO_5S_2$ $[M+Na]^+$ m/z = 455.0963; found 455.0957.

***S*-[1,7-Di(4-chlorophenoxy)-1,7-dioxoheptan]-4-yl *O*-ethyl carbonodithioate (3g).** R_f = 0.32 (petroleum ether–ethyl acetate = 10/1, v/v). Pale yellow oil, yield: 422 mg, 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.42 (t, J = 7.1 Hz, 3H, CH_3), 2.06 (ddt, J = 14.8, 8.5, 6.5 Hz, 2H in $2CH_2$), 2.25 (dddd, J = 14.8, 8.5, 7.6, 5.1 Hz, 2H in $2CH_2$), 2.70–2.83 (m, 4H, $2CH_2$), 3.99 (tt, J = 8.5, 5.1 Hz, 1H, CH), 4.66 (q, J = 7.1 Hz, 2H, CH_2), 7.03 (d, J = 8.6 Hz, 4H, ArH), 7.33 (d, J = 8.6 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.8 (CH_3), 29.7 (CH_2), 31.5 (CH_2), 50.4 (CH), 70.4 (CH_2), 122.9 (CH), 129.4 (CH), 131.2 (C), 149.0 (C), 171.1 (C=O), 213.7 (C=S). IR (neat) ν = 3097, 3070, 2980, 2925, 2855, 1758, 1486, 1201, 1050 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}Cl_2NaO_5S_2$ $[M+Na]^+$ m/z = 523.0183; found 523.0180.

***S*-[1,7-Di(4-nitrophenoxy)-1,7-dioxoheptan]-4-yl *O*-ethyl carbonodithioate (3h).** R_f = 0.20 (petroleum ether–ethyl acetate = 5/1, v/v). Pale yellow oil, yield: 210 mg, 40%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.44 (t, J = 7.1 Hz, 3H, CH_3), 2.10 (ddt, J = 14.8, 9.0, 7.2 Hz, 2H in $2CH_2$), 2.30 (ddt, J = 14.8, 5.0, 7.2 Hz, 2H in $2CH_2$), 2.84 (t, J = 7.2 Hz, 4H, $2CH_2$), 4.03 (tt, J = 9.0, 5.0 Hz, 1H, CH), 4.68 (q, J = 7.1 Hz, 2H, CH_2), 7.29 (d, J = 8.5 Hz, 4H, ArH), 8.26 (d, J = 8.5 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.8 (CH_3), 29.6 (CH_2), 31.5 (CH_2), 50.4 (CH), 70.6 (CH_2), 122.4 (CH), 125.2 (CH), 145.3 (C), 155.2 (C), 170.4 (C=O), 213.7 (C=S). IR (neat) ν = 3115, 3082, 2980, 2926, 2855, 1762, 1592, 1522, 1346, 1209, 1119, 1050 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}N_2NaO_9S_2$ $[M+Na]^+$ m/z = 545.0664; found 545.0662.

***S*-(1,7-Dibenzyloxy-1,7-dioxoheptan)-4-yl *O*-ethyl carbonodithioate (3i).** R_f = 0.27 (petroleum ether–ethyl acetate = 10/1, v/v). Pale yellow oil, yield: 318 mg, 69%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.37 (t, J = 7.1 Hz, 3H, CH_3), 1.93 (ddt, J = 14.8, 9.0, 6.5 Hz, 2H in $2CH_2$), 2.10 (dddd, J = 14.8, 8.5, 7.2, 5.0 Hz, 2H in $2CH_2$), 2.49 (ddd, J = 15.0, 8.5, 6.5 Hz, 2H in $2CH_2$), 2.54 (ddd, J = 15.0, 7.2, 6.5 Hz, 2H in $2CH_2$), 3.81 (tt, J = 9.0, 5.0 Hz, 1H, CH), 4.59 (q, J = 7.1 Hz, 2H, CH_2), 5.10 (s, 4H, $2CH_2$), 7.31–7.37 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 29.6 (CH_2), 31.5 (CH_2), 50.3 (CH), 66.4 (CH_2), 70.1 (CH_2), 128.2 (CH), 128.5 (CH), 135.8 (C), 172.5 (C=O), 213.6 (C=S). IR (neat) ν = 3065, 3033, 2980, 2928, 2856, 1731, 1455, 1215, 1049 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NaO_5S_2$ $[M+Na]^+$ m/z = 483.1276; found 483.1269.

***S*-{[1,7-Di(diphenylamino)-1,7-dioxo]heptan}-4-yl *O*-ethyl carbonodithioate (3j).** R_f = 0.15 (petroleum ether–ethyl acetate = 3/1, v/v). Pale yellow oil, yield: 205 mg, 35%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.34 (t, J = 7.1 Hz, 3H, CH_3), 1.88 (dddd, J = 14.5, 8.5, 6.8, 6.5 Hz, 2H in $2CH_2$), 2.11 (dddd, J = 14.5, 8.5, 7.8, 5.0 Hz, 2H in $2CH_2$), 2.31–2.43 (m, 4H, $2CH_2$), 3.71 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.55 (q, J = 7.1 Hz, 2H, CH_2), 7.22–7.33 (m, 20H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 30.0 (CH_2), 32.5 (CH_2), 50.5 (CH), 69.7 (CH_2), 126.3 (CH), 127.6 (CH), 129.1 (CH), 142.6 (C), 172.0 (C=O), 213.9 (C=S). IR (neat) ν = 3060, 3032, 2980, 2923, 2854, 1671, 1593, 1491, 1377, 1288, 1216, 1050 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{35}N_2O_3S_2$ $[M+H]^+$ m/z = 583.2089; found 583.2082.

***S*-[1,7-Di(methanesulfonylphenylamino)-1,7-dioxoheptan]-4-yl *O*-ethyl carbonodithioate (3k).** R_f = 0.21 (petroleum ether–ethyl acetate = 1/1, v/v). Pale yellow solid, yield: 407 mg, 69%, m.p. 136–137 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.37 (t, J = 7.1 Hz, 3H, CH_3), 1.76 (dddd, J = 14.3, 8.5, 7.3, 7.0 Hz, 2H in $2CH_2$), 2.01 (dddd, J = 14.3, 8.2, 6.3, 5.0 Hz, 2H in $2CH_2$), 2.19 (ddd, J = 15.0, 8.2, 7.3 Hz, 2H in $2CH_2$), 2.23 (ddd, J = 15.0, 7.5, 6.3 Hz, 2H in $2CH_2$), 3.44 (s, 6H, $2CH_3$), 3.63 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.57 (q, J = 7.1 Hz, 2H, CH_2), 7.23–7.26 (m, 4H, ArH), 7.43–7.47 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.7 (CH_3), 29.1 (CH_2), 33.8 (CH_2), 42.0 (CH_3), 49.9 (CH), 70.2 (CH_2), 129.7 (CH), 129.9 (CH), 130.1 (CH), 135.1 (C), 173.1 (C=O), 213.6 (C=S). IR (neat) ν = 3060, 3032, 2980, 2922, 2847, 1701, 1490, 1352, 1218, 1152, 1047 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{30}N_2NaO_7S_4$ $[M+Na]^+$ m/z = 609.0834; found 609.0832.

***S*-[1,7-Dioxo-1,7-di(2-oxooxazolidin-3-yl)heptan]-4-yl *O*-ethyl carbonodithioate (3l).** R_f = 0.26 (petroleum ether–ethyl acetate = 1/2, v/v). Pale yellow oil, yield: 332 mg, 79%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.43 (t, J = 7.1 Hz, 3H, CH_3), 2.01 (dddd, J = 14.5, 8.5, 7.1, 6.8 Hz, 2H in $2CH_2$), 2.17 (dddd, J = 14.5, 8.5, 7.5, 5.0 Hz, 2H in $2CH_2$), 3.07 (ddd, J = 15.5, 8.5, 7.1 Hz, 2H in $2CH_2$), 3.12 (ddd, J = 15.5, 7.5, 6.8 Hz, 2H in $2CH_2$), 3.80–3.87 (m, 1H, CH), 4.02 (t, J = 8.0 Hz, 4H, $2CH_2$), 4.41 (t, J = 8.0 Hz, 4H, $2CH_2$), 4.63 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 28.8 (CH_2), 32.4 (CH_2), 42.4 (CH_2), 49.8 (CH), 62.0 (CH_2), 70.1 (CH_2), 153.4 (C=O), 172.4 (C=O), 213.9 (C=S). IR (neat) ν = 3532, 3366, 2984, 2922, 2862, 1771, 1696, 1389, 1223, 1113, 1043 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{23}N_2O_7S_2$ $[M+H]^+$ m/z = 419.0947; found 419.0937.

***S*-(1,5-Dicyanopentan-3-yl) *O*-ethyl carbonodithioate (3m).** R_f = 0.13 (petroleum ether–ethyl acetate = 5/1, v/v). Pale brown liquid, yield: 124 mg, 51%. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) 1.46 (t, J = 7.1 Hz, 3H, CH_3), 2.01 (dddd, J = 14.5, 8.5, 7.5, 7.0 Hz, 2H in $2CH_2$), 2.17 (dddd, J = 14.5, 8.5, 6.5, 5.0 Hz, 2H in $2CH_2$), 2.54 (ddd, J = 15.0, 8.5, 7.5 Hz, 2H in $2CH_2$), 2.63 (ddd, J = 15.0, 7.5, 6.5 Hz, 2H in $2CH_2$), 3.94 (tt, J = 8.5, 5.0 Hz, 1H, CH), 4.68 (q, J = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) (δ, ppm) 13.6 (CH_3), 14.9 (CH_2), 30.4 (CH_2), 48.9 (CH), 70.9 (CH_2), 118.5 (CN), 211.3 (C=S). IR (neat) ν = 2982, 2932, 2868, 2247, 1447, 1224, 1045 cm^{-1}. HRMS (ESI) calcd. for $C_{10}H_{14}N_2NaOS_2$ $[M+Na]^+$ m/z = 265.0445; found 265.0442.

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