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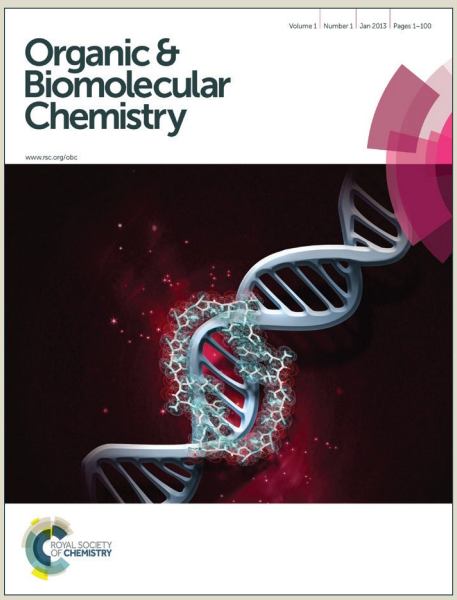

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ARTICLE

Synthesis of Functionalized 5-Substituted Thiazolidine-2-thiones via Adscititious Xanthates-Promoted Radical Cyclization of Allyl(alkyl/aryl)dithiocarbamates

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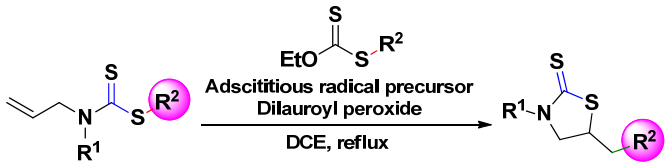

Abstract: Functionalized 5-substituted thiazaolidine-2-thiones were synthesized efficiently from alkyl allyl(alkyl/aryl)-dithiocarbamates via radical cyclization with the corresponding *S*-alkyl *O*-ethyl xanthates as the adscititious radical precursors. The application of the adscititious radical precursors improves not only the yields, but also the efficiency in the radical cyclization reaction significantly. The current adscititious radical precursor method provides a new strategy in achievement and improvement of some radical reactions which are hardly or difficultly realized under the traditionally direct methods.

Introduction

Thiazolidine-2-thiones and their derivatives are important organic intermediates and have been widely-used as synthetic building blocks in pharmaceutical chemistry,[1] especially their structural analogs–Rhodanines are common scaffolds in drug discovery.[2] Beyond that, thiazolidine-2-thione derivatives, especially 4-substituent ones, are well-known chiral auxiliaries in asymmetric synthesis[3] and have been widely applied in the total synthesis.[4] However, most reported studies focused on various 4-subsituted thiazolidine-2-thiones because they could be easily generated from the corresponding readily available vicinal aminoalkyl primary alcohols[5] or thiols,[6] and 2-alkylaziridines[7] with carbon disulfide. Other synthetic methods includes reactions of vicinal haloisothiocyanates and sodium sulfide or bisulfide,[8] or of vicinal halo secondary amines and carbon disulfide.[9] The later has been applied in the preparation of 4,5-disubstituted thiazolidine-2-thiones.[9] Due to the relative lack of vicinal aminoalkyl secondary alcohols or their corresponding halides,[10] studies on the synthesis and further application of 5-substituted thiazolidine-2-thiones are rare and limited.[11] Hence, to develop efficient way for the preparation of 5-substituted thiazolidine-2-thiones, especially functionalized ones, is very important for both methodological and pharmaceutical research.

The radical reactions have become one of the most important strategies in the synthesis of various functionalized heterocycles during recent decades.[12] In these radical reactions, the tandem intermolecular radical additions and subsequently intramolecular cyclizations are an efficient route to construct heterocycles from xanthates[13] and dithiocarbamates.[14] Our recent interest in the radical chemistry arose from the application of dithiocarbamates in heterocyclic synthesis. We have previously described the radical-induced tandem intramolecular cyclization and intermolecular radical coupling reactions in the synthesis of 2-alkylthiothiazoline derivatives from *N*-monosubstituted allyldithiocarbamates,[15] and dimerization in the preparation of the corresponding disulfides.[16] We also synthesized 5-substituted thiazolidin-2-ones from xanthates and *tert*-butyl *N*-allylcarbamate via an intermolecular radical addition and subsequently acid-catalyzed intramolecular cyclization.[17] In continuation of our studies, we herein present the synthesis of various functionalized 5-substituted thiazolidine-2-thiones from alkyl allyl(alkyl/aryl)dithiocarbamates through the corresponding xanthate-promoted radical cyclization.

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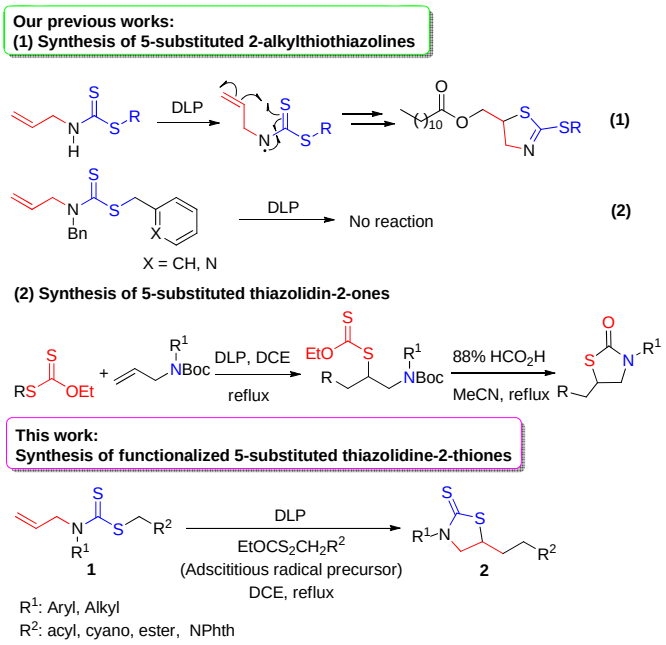
Electronic Supplementary Information (ESI) available: [Copies of ^{1}H and ^{13}C NMR spectra of products **1** and **2**]. See DOI: 10.1039/x0xx00000x



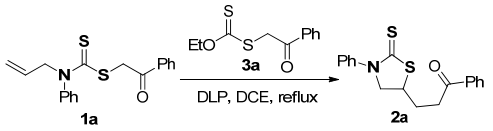
Scheme 1 Application of allyldithiocarbamates in synthesis of heterocyclic compounds via radical cyclizations.

Results and discussion

In our previous studies,[17] 2-alkylthiothiazolines were obtained readily from *N*-monosubstituted dithiocarbamates in the presence of dilauroyl peroxide (DLP) (Scheme 1, eqn 1). However, no reaction occurred while *N*,*N*-disubstituted benzyl allyl(benzyl)dithiocarbamate was used (Scheme 1, eqn 2) even under the equivalent amount of radical initiator (DLP). According to the detailed mechanism in DLP-catalyzed radical reactions,[13] nucleophilic undecyl radical, generated from dilauroyl peroxide (DLP), can abstract the hydrogen in *N*-monosubstituted dithiocarbamates [15] or attack the electron-deficient thiocarbonyl group in *N*,*N*-disubstituted dithiocarbamates to afford the tertiary carbon radical, which further undergoes a β-cleavage to form benzyl ($PhCH_2^{\cdot}$) radical. Apparently, as a moderate nucleophilic radical,[18] the benzyl radical hardly attacks the electron-rich allyl group in the dithiocarbamates, resulting in no reaction occurred. A slightly more electrophilic pyridin-2-ylmethyl radical, yielded from pyridin-2-ylmethyl allyl(benzyl)dithiocarbamate, gave the same result which was also without any cyclized product (Scheme 1, eqn 2).

With the elaborative investigation on the electrophilicity of different alkyl radicals, we rationalize that strongly electron-withdrawing group stabilized substituted methylene ($EWG\text{-}CH_2$) radicals are electrophilic and can undergo their selective addition to the electron-rich *N*-allyl group in dithiocarbamates. We therefore selected (2-oxo-2-phenyl)ethyl allyl(phenyl)dicarbamate (**1a**) as a model substrate to optimize reaction conditions (Table 1). No cyclized product was observed when 2 mol% of DLP was added one-portion as radical initiator and the reaction mixture was refluxed in 1,2-dichloroethane (DCE) for 2 hrs (Table 1, entry 1). When DLP was increased to 16 mol% (2 mol% of DLP was added into the refluxing reaction solution per hour), the desired cyclized product, 5-(3-oxo-3-phenyl)-1-phenylthiazolidine-2-thione (**2a**), was obtained in 5% yield (Table 1, entry 2). The yield was improved apparently to 33% with the increase of DLP amount to 5 mol% per hour (Table 1, entry 3). The portion-wise addition was tedious and time-consuming, so we tried one-portion addition while the yield was increased to 48% just under 1 h refluxing (Table 1, entry 4). The above results reveal that the tandem reaction is very fast and the increase of the initiator may improve the yield. The highest yield was obtained under reflux for 8 h when 50 mol% of DLP was added (Table 1, entry 5). However, further increasing the amount of DLP to 100 and 150 mol% resulted in slightly decrease of the yield and made the reaction system much more complicated (Table 1, entries 6 and 7). Benzoyl peroxide (BPO) was also attempted instead of DLP. However, no desired product was observed (Table 1, entry 8).

Table 1. Optimization for the radical cyclization of 2-oxo-2-phenylethyl allyl(phenyl)dicarbamate (**1a**)

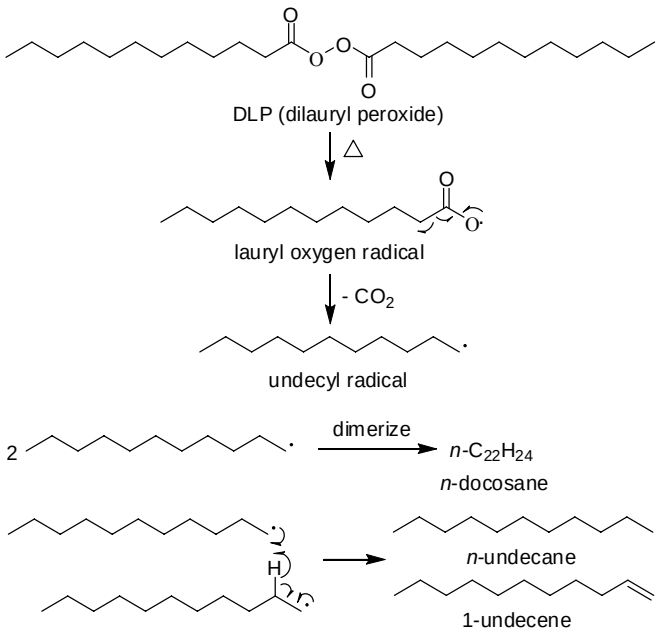


Entry	DLP (mol%)[a]	Transfer agent **3a** (mol%)	Time (h)	Yield (%)[b]
1	2	0	2	0
2	16[c]	0	8	5
3	40[d]	0	8	33
4	40	0	1	48
5	50	0	8	58
6	100	0	8	57
7	150	0	8	56
8	50[e]	0	8	0
9	40	20	1	60
10	40	50	1	76
11	40	100	1	88
12	50	50	1	87
13	50	100	1	91
14	50	100	2	90

[a] DLP was added in one portion unless mentioned. [b] Isolated yield from column chromatography. [c] DLP was added 2 mol% per hour. [d] DLP was added 5 mol% per hour. [e] Using benzoyl peroxide (BPO) instead of DLP.

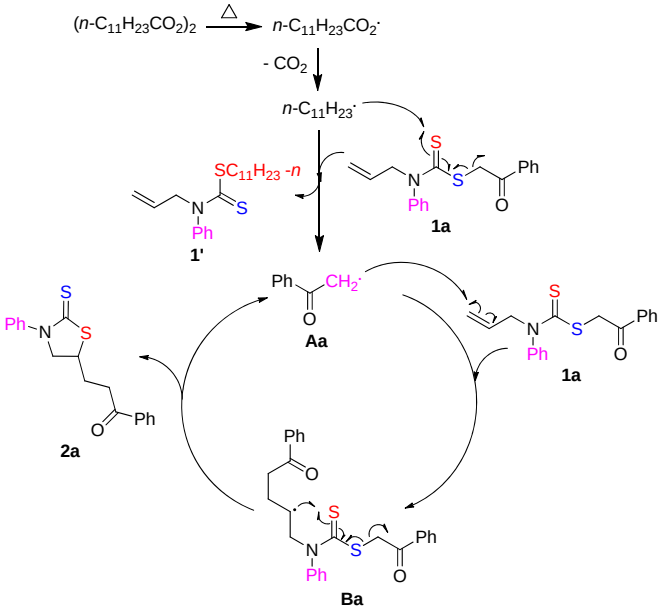
It has been reported that the half-life of DLP is approximately 1 h at the temperature of 85 °C.[19] On the basis of our previous and current results, the undecyl radical generated from DLP was too active and existed only in short time. It could react each other to give rise to *n*-docosane, *n*-undecane, and 1-undecene, having less opportunity to nucleophilically attack on the thiocarbonyl group in the dithiocarbamate due to weak electrophilicity of the thiocarbonyl group (Scheme 2). Only when a high concentration of the undecyl radical was kept by the addition of large amount of DLP, the nucleophilic attack could occur competitively. However, excessive addition of DLP resulted in the increase of formation of *n*-docosane, *n*-undecane, and 1-

undecene, rather than the nucleophilic attack, making reaction more complex.

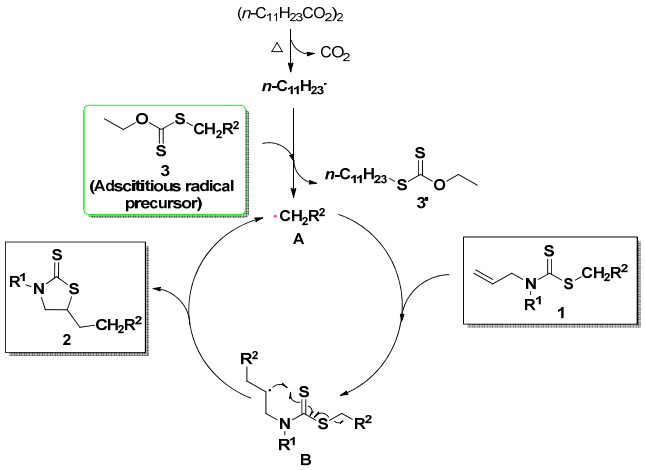


Scheme 2. Radical reactions of DLP under heating conditions.

Further investigation of the mechanism, the nucleophilic undecyl radical can only react with the sulfur atom in the electron-deficient thiocarbonyl group in the dithiocarbamate **1a** to generate electrophilic 2-oxo-2-phenylethyl radical (**Aa**) and undecyl allyl(phenyl)dicarbamate (**1'**) as byproduct. The radical **Aa** reacts with another molecule of dithiocarbamate **1a** through electrophilic radical addition to the *N*-allyl group to yield radical **Ba**, which undergoes a *5-endo-trig* cyclization with



Scheme 3. Proposed cyclization mechanism of (2-oxo-2-phenyl) allyl(phenyl)dithiocarbamate (**1a**) in the presence of DLP.



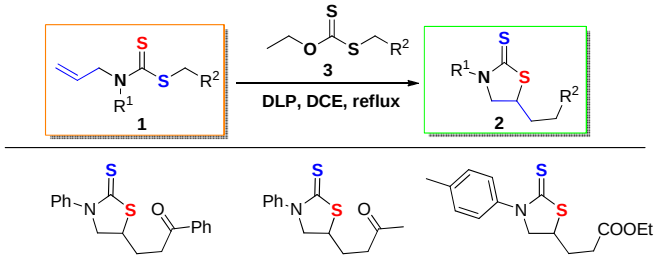
Scheme 4. Proposed mechanism for the xanthate-promoted radical cyclization of alkyl allyl(alkyl/aryl)dithiocarbamates **1**.

the regeneration of the radical **Aa** for the chain propagation and releases the desired product **2a** (Scheme 3). We therefore rationalized that the current strategy would consume some amount of the dithiocarbamate, even more amount of the dithiocarbamate especially at high concentration of DLP, leading to decrease of the product yield, due to the generation of the byproduct undecyl allyl(phenyl)dithicarbamate (**1'a**), which was inactive in the cyclization (Scheme 3). However, the reaction efficiency was very low under low concentration of DLP. Hence, to improve the yield, we had to seek for a new strategy, in which more electrophilic additives would be added to capture the nucleophilic undecyl radical to provide the relatively stable and active $R^2CH_2^{\cdot}$ radical, rather than generation of the R^2CH_2 radical directly from dithiocarbamates **1**. The adscititious additives would serve as the radical precursors of the radicals $R^2CH_2^{\cdot}$. On the other hand, the adscititious radical precursors should be more electrophilic than the corresponding raw material dithiocarbamates **1** for the predominant reaction with the undecyl radical in the competitive reactions (Scheme 4). Because the carbonyl group in esters is more electrophilic than that in amides, we rationalized that the thiocarbonyl group in xanthates should be more electrophilic than that in dithicarbamates. Thus, *O*-ethyl *S*-(2-oxo-2-phenyl)ethyl xanthate (**3a**) was first selected as the adscititious radical precursor in the model reaction. The xanthate **3a** can be simply obtained from widely-used and inexpensive sodium *O*-ethylxanthate and phenylacyl halide. The yield was improved to 60%, 76%, and 88% and the reaction time was shortened obviously to 1 h when 20 mol%, 50 mol%, and 100 mol% of the adscititious radical precursor **3c** were added, respectively, under 40 mol% of DLP conditions (Table 1, entries 9–11). The highest yield was obtained with one equivalent of the adscititious radical precursor under 50 mol% of DLP conditions (Table 1, entry 13). Prolonging the reaction time to 2 h did not improve the yield any more (Table 1, entry 14). The results demonstrate that the adscititious radical precursor improved not only the yield of the desired

product, but also the reaction efficiency. Finally, the optimal conditions were established in the presence of the adscititious radical precursor (1 equiv.) and DLP (0.5 equiv.) under reflux for 1 h in DCE (Table 1, entry 13).

A variety of substituted alkyl allyl(alkyl/aryl)dithiocarbamates **1** were then examined to probe the versatility of the cyclization system for the synthesis of functionalized 5-substituted thiazolidine-2-thiones with the corresponding xanthates **2** as the adscititious radical precursors (Table 2). All of the substrates **1** were easily synthesized from *N*-allyl secondary amines, carbon disulfide, and alkyl halides in moderate to good yields according to our previous report.[15] Compared with allyl(aryl)substrates **1a–1d** which exist only as one isomer in each case, all allyl(alkyl)dithiocarbamates **1e–1q** showed the presence of two different rotamers in ratioes of 1:1 to 1.3:1. Various methylene substituents with strongly electron-withdrawing radical stabilized groups, such as acyl, ester, cyano, and phthalimido groups, linked in the *S*-side participate in the reaction to give the desired cyclized products **2** in good to excellent yields (Table 2).

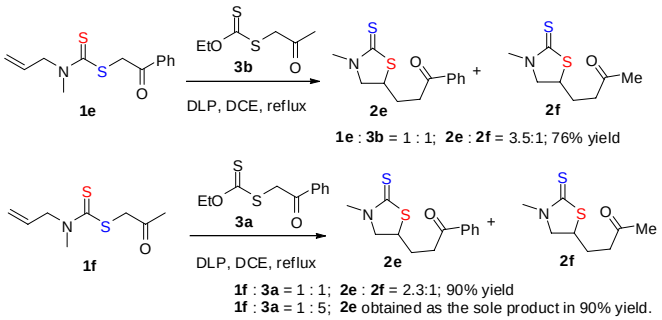
Table 2. The scope for the synthesis of thiazolidine-2-thiones



[a] Isolated yield from column chromatography.

Allyl(phenyl)dithiocarbamates **1a** and **1b** were converted to the corresponding 3-phenylthiazolidine-2-thiones **2a** and **2b** in excellent yields (Table 2, **2a** and **2b**). The yield dropped to 77% and 72% when electron-donating groups (Me and MeO) were introduced into the phenyl ring (Table 2, **2c** and **2d**). The results demonstrate that electron-donating groups in the phenyl decrease the electrophilicity of the thiocarbonyl group in dithiocarbamates **1c** and **1d,** further retarding the intramolecularly nucleophilic attack in intermediates **B** (Scheme 3). To our delight, all of allyl(alkyl)dithiocarbamates **1e–q** with *N*-alkyl substituents, like methyl, benzyl, and isobutyl groups (Table 2, **2e–q**) show good to excellent transfer efficiency in the current system. The yield dropped slightly with the substituents changed from *N*-methyl to *N*-isobutyl due to the increasing steric hindrance (Table 2, **2e**,**f**,**p**,**q**). The results indicate that both electronic and steric effects impact on the radical cyclization of alkyl allyl(alkyl/aryl)dithiocarbamates **1**.

Finally, the adscititious radical precursor-promoted cyclization mechanism was further clarified via the cross over experiments (Scheme 5). When dithiocarbamate **1e**, which provides the phenylacyl radical (**Aa**), reacted with equimolar xanthate **3b**, which provides 2-oxopropyl radical (**Ab**) in the presence of DLP, mixed cyclized products **2e** and **2f** were obtained in 76% yield with a ratio of 3.5:1 (**2e**:**2f**). Conversely, while equimolar dithiocarbamate **1f** and xanthate **3a** were applied, thiazolidine-2-thione **2e** was also obtained as the major product (**2e**:**2f** = 2.3:1). Both results indicate that more electrophilic 2-oxo-2-phenylethyl radical (**Aa**) shows better reactivity than 2-oxopropyl radical (**Ab**) in the adscititious radical precursor-promoted cyclization. Hence, the electrophilic ability of alkyl radical affects the cyclization transfer process obviously.



Scheme 5. Cross over experiments with different alkyl radical precursors between dithiocarbamates **2** and xanthates **3**.

Though the well-known atom transfer radical addition (ATRA), cyclization (ATRC), and polymerization (ATRP) have been widely investigated in the past decades,[20] the group transfer radical additions and cyclizations were still limited.

Conclusions

In conclusion, an adscititious radical precursor-promoted cyclization was designed and translated into an efficient synthesis of functionalized 5-substituted thiazolidine-2-thiones

from alkyl allyl(alkyl/aryl)dithiocarbamates with the corresponding *S*-alkyl *O*-ethyl xanthates as functionalized adscititious radical precursors in the presence of dilauroyl peroxide as radical initiator. Dilauroyl peroxide generated the undecyl radical under heating. The undecyl radical reacted favorably with more electrophilic xanthates, which serviced as functionalized alkyl radical precursors, to give more stable functionalized alkyl radicals, which further electrophilically attacked the allyl group in the dithiocarbamates followed by a *5-endo-trig* cyclization, affording functionalized 5-substituted thiazolidine-2-thiones and regenerating the functionalized alkyl radicals. The application of adscititious radical precursors improves not only the yield, but also the efficiency in the radical cyclization reaction significantly. The current adscititious radical precursor method provides an efficient synthesis of various functionalized *N*-alkyl/aryl 5-substituted thioazolidine-2-thiones and importantly a new strategy in achievement and improvement of some radical reactions which are hardly or difficultly realized under the traditionally direct methods.

Experimental

General: Melting points were determined on a Yanaco MP-500 melting point apparatus and are uncorrected. All ^{1}H (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker 400 NMR spectrometer in $CDCl_3$ with TMS as an internal standard and chemical shifts are reported in ppm. All coupling constants (J) in ^{1}H NMR are absolute values given in hertz (Hz) with peaks labeled as single (s), broad singlet (br), doublet (d), triplet (t), quartet (q), double doublet (dd), double triplet (dt), double quartet (dq), double double doublet (ddd), double double double doublet (dddd), and multiplet (m). IR spectra were carried out on a Nicolet AVATAR 330 FT-IR spectrometer. HRMS spectra were performed on a Bruker LC/MSD TOF mass spectrometer. Commercially available reagents were used directly without purification. Column chromatography with silica gel was carried out (200–300 mesh) with petroleum ether (PE, 60 °C–90 °C) and ethyl acetate (EA) as the eluent. All reactions were followed by thin-layer chromatography (TLC) where practical, using silica gel 60 F254 fluorescent treated silica gel plates, which were visualised under UV light (254 nm).

General procedure for the synthesis of alkyl allyl(alkyl/aryl)di-thiocarbamates[15]

A mixture of *N*-allyl alkyl/arylamine (10 mmol), carbon disulfide (6.1 mL, 100 mmol), and NaOH (400 mg, 10 mmol) in CH_3CN (50 mL) was stirred at room temperature overnight. After removing the extra carbon disulfide and solvent in vacuum, the residue was dissolved in CH_3CN (50 mL) again and then added alkyl chloride (or bromide) (10 mmol). The whole system was stirred for 6 to 20 h with the monitor of TLC. After removal of the solvent in vacuum, the residue was dissolved in CH_2Cl_2 (30 mL). The organic phase was then washed with water (15 mL), brine (15 mL), and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified on a silica gel column with ethyl acetate/petroleum ether (PE) (60–90 °C) (1:20, *v/v*) as eluents to furnish the dithiocarbamates **1**.

2-Oxo-2-phenylethyl allyl(phenyl)dithiocarbamate (1a). Yellowish crystals, 1.50 g, yield, 46%. M.p. 107–109 °C. IR (KBr): 2956, 2921, 2850, l691, 1644, 1594, 1488, 1432, 1384, 1251, 1202, 1093, 988, 953, 745, 688 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm) = 8.07–8.01 (m, 2H, ArH), 7.58 (t, *J* = 7.2 Hz, 1H, ArH), 7.51–7.42 (m, 5H, ArH), 7.27 (dd, *J* = 8.0, 2.0 Hz, 2H, ArH), 5.98 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H, C*H*=), 5.21 (dd, *J* = 10.4, 0.8 Hz, 1H in CH_2=), 5.14 (dd, *J* = 16.8, 0.8 Hz, 1H in CH_2=), 4.89 (d, *J* = 6.4 Hz, 2H, CH_2N), 4.76 (s, 2H, CH_2S). ^{13}C NMR ($CDCl_3$, 101 MHz) (δ, ppm) = 198.2, 193.3, 136.2, 133.4, 130.7, 129.7, 129.3, 128.6, 128.5, 128.0, 119.6, 60.7, 45.5 (with one peak overlapped in aromatic area). HRMS (ESI) calcd. for $C_{18}H_{18}NOS_2^+$ $[M+H]^+$ *m/z* 328.0824; Found 328.0820.

2-Oxopropyl allyl(phenyl)dithiocarbamate (1b). Colorless crystals, 1.22 g, yield, 46%. M.p. 102–104 °C. IR (KBr): 1710, 1644, 1093 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49–7.42 (m, 3H, ArH), 7.27–7.24 (m, 2H, ArH), 5.97 (ddt, *J* = 17.0, 10.2, 6.4 Hz, 1H, CH=), 5.21 (d, *J* = 10.2 Hz, 1H, =CHH_{cis}), 5.14 (d, *J* = 17.0 Hz, 1H, =CH_{trans}H), 4.87 (d, *J* = 6.4 Hz, 2H, CH_2N), 4.07 (s, 2H, CH_2S), 2.30 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 202.2, 198.1, 142.8, 130.6, 129.6, 129.3, 127.9, 119.6, 60.7, 47.4, 29.3. HRMS (ESI) *m/z*, calcd. for $C_{13}H_{16}NOS_2^+$, $[M+1]^+$, 266.0668; found, 266.0671.

Ethyl 2-((allyl(p-tolyl)carbamothioyl)thio)acetate (1c). Yellowish crystals, 681 mg, yield, 22%, m. p. 53–54 °C. R_f = 0.32 (PE/EA = 10:1). IR (KBr): 1732, 1384, 1180, 1027 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.16 (d, *J* = 8.9 Hz, 2H, ArH), 6.94 (d, *J* = 8.9 Hz, 2H, ArH), 5.97 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H, NCH_2CH), 5.18 (d, *J* =10.1, 0.7 Hz, 1H, CH*H*), 5.10 (d, *J* = 17.1 , 0.92 Hz, 1H, C*H*H), 4.83 (d, *J* = 6.2 Hz, 2H, NCH_2), 4.18 (q, *J* = 7.12 Hz, 2H, OCH_2), 4.01 (s, 2H, SCH_2), 2.40 (s, 3H, OCH_3), 1.25 (t, *J* = 7.13 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) = 198.0, 168.6, 143.4, 139.6, 130.6, 130.3, 127.7, 119.5, 61.7, 60.6, 39.8, 21.3, 14.2. HRMS (ESI) *m/z*, calcd. for $C_{15}H_{20}NO_2S_2^+$ $[M+H]^+$, 310.0930; found: 310.0932.

Ethyl 2-((allyl(4-methoxyphenyl)carbamothioyl)thio)acetate (1d). Yellowish crystals, 1.27 g, yield, 39%, m. p. 95–97 °C. R_f = 0.21 (PE/EA = 10:1). IR (KBr): 1738, 1604, 1435, 1027 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.16 (d, *J* = 8.9 Hz, 2H, ArH), 6.94 (d, *J* = 8.9 Hz, 2H, ArH), 5.97 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H, NCH_2CH), 5.20 (m, 2H, CH*H*), 5.13 (m, 1H, C*H*H), 4.85 (d, *J* = 6.4 Hz, 2H, NCH_2), 4.18 (q, *J* = 7.1 Hz, 2H, OCH_2), 4.00 (s, 2H, SCH_2), 3.84 (s, 3H, OCH_3), 1.28 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) = 198.5, 168.7, 160.0, 135.4, 130.9, 129.2, 119.5, 114.7, 61.6, 60.7, 55.5, 39.8, 14.2. HRMS (ESI) *m/z*, calcd. for $C_{15}H_{20}NO_3S_2^+$ $[M+H]^+$, 326.0879; found: 326.0873.

2-Oxo-2-phenylethyl allyl(methyl)dithiocarbamate (1e). Colorless crystals, 2.20 g, yield, 83%, two rotamers (58:42). M.p. 59–61 °C. IR (KBr): 3342, 2922, 1691, 1640, 1448, 1384, 1320, 1219, 747 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.08 (d, *J* = 7.6 Hz, 2H, ArH_{ortho}), 7.60 (t, *J* = 7.4 Hz, 1H, ArH_{para}), 7.50 (dd, *J* = 7.6, 7.4 Hz, 2H, ArH_{meta}), 5.95–5.78 (m, 1H, CH=), 5.36–5.15 (m, 2H, CH_2=), 4.91 (s, 2H, CH_2S), 4.71 (d, *J* = 5.4 Hz, 1.12 H, CH_2N, Rotamer A), 4.46 (d, *J* = 4.5 Hz, 0.82H, CH_2N, Rotamer B), 3.48 (s, 1.35H, CH_3, Rotamer B), 3.38 (s, 1.67H, CH_3, Rotamer A). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 196.33 (Rotamer A), 195.66 (Rotamer B), 193.26, 136.17, 133.53, 130.69 (Rotamer A), 130.18 (Rotamer B), 128.72 (Rotamer A), 128.57 (Rotamer B), 118.86 (Rotamer A), 118.59 (Rotamer B), 59.65

(Rotamer A), 56.99 (Rotamer B), 45.49 (Rotamer A), 45.35 (Rotamer B), 43.65 (Rotamer A), 39.09 (Rotamer B). HRMS (ESI) *m/z*, calcd. for $C_9H_{16}NO_2S_2^+$ $[M+H]^+$, 266.0668; found: 266.0678.

2-Oxopropyl allyl(methyl)dithiocarbamate (1f). Yellow oil, 1.68 g, yield, 83%, two rotamer (59:41). IR (KBr): 3082, 2925, 1721, 1642, 1485, 1386, 986 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.88–5.81 (m, 1H, CH=), 5.32–5.19 (m, 2H, CH_2=), 4.69 (d, *J* = 4.8 Hz, 1.18 H, CH_2N, Rotamer A), 4.43 (d, *J* = 3.6 Hz, 0.83H, CH_2N, Rotamer), 4.22 (s, 2H, CH_2S), 3.48 (s, 1.34H, CH_3, Rotamer B), 3.35 (s, 1.67H, CH_3, Rotamer A), 2.36 (s, 3H, O=CCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 202.1, 196.3 (Rotamer A), 195.6 (Rotamer B), 130.6 (Rotamer A), 130.1 (Rotamer B), 118.8 (Rotamer A), 118.6 (Rotamer B), 59.7 (Rotamer A), 57.0 (Rotamer B), 47.3 (Rotamer A), 47.1 (Rotamer B), 43.7 (Rotamer A), 39.1 (Rotamer B), 29.6 (Rotamer B), 18.4 (Rotamer A). HRMS (ESI) *m/z*, calcd. for $C_8H_{14}NOS_2^+$ $[M+H]^+$, 204.0511; found: 204.0519. HRMS (ESI) *m/z*, calcd. for $C_8H_{14}NOS_2^+$ $[M+H]^+$, 204.0511; found: 204.0500.

Ethyl 2-((allyl(methyl)carbamothioyl)thio)acetate (1g). Yellow oil, 1.98 g, yield, 85%, two Rotamers (56:44). IR (KBr): 3342, 2929, 1736, 1642, 1485, 1416 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.89–5.80 (m, 1H, CH=), 5.27–5.15 (m, 2H, CH_2=), 4.70 (d, *J* = 5.3 Hz, 1.12H, CH_2N, Rotamer B), 4.41 (d, *J* = 4.0 Hz, 0.88 H, CH_2N, Rotamer A), 4.22(q, *J* = 7.1 Hz, 2H, OCH_2), 4.16 (s, 2H, CH_2S), 3.48 (s, 1.33H, CH_3, Rotamer B), 3.34 (s, 1.67H, CH_3, Rotamer A), 1.30 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 196.1 (Rotamer A), 195.2 (Rotamer B), 168.5, 130.6 (Rotamer A), 130.1 (Rotamer B), 118.8 (Rotamer A), 118.5 (Rotamer B), 61.8 (Rotamer A), 59.5 (Rotamer B), 56.8, 43.5, 39.5 (Rotamer A), 39.4 (Rotamer B), 38.9 (Rotamer A), 14.1 (Rotamer B). HRMS (ESI) *m/z*, calcd. for $C_9H_{16}NO_2S_2^+$ $[M+H]^+$, 234.0617; found: 234.0626.

Cyanomethyl allyl(methyl)dithiocarbamate (1h). Colorless crystals, 1.45 g, yield, 78%, two Rotamers (55:45). M.p. 37–39 °C. IR (KBr): 3343, 2295, 2246, 1488, 1388, 1217, 747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.86–5.80 (m, 1H, CH=), 5.34–5.22 (m, 2H, CH_2=), 4.70 (d, *J* = 5.6 Hz, 1.12 H, CH_2N, Rotamer A), 4.36 (d, *J* = 4.4 Hz, 0.82H, CH_2N, Rotamer B), 4.22 (s, 2H, CH_2S), 3.51 (s, 1.37H, CH_3, Rotamer B), 3.31 (s, 1.63H, CH_3, Rotamer A). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 192.8 (Rotamer A), 192.1 (Rotamer B), 130.3 (Rotamer A), 129.7 (Rotamer B), 119.2 (Rotamer A), 116.1 (Rotamer B), 60.1 (Rotamer A), 58.5 (Rotamer B), 44.2 (Rotamer A), 39.0 (Rotamer B), 23.2 (Rotamer A), 18.6 (Rotamer B). HRMS (ESI) *m/z*, calcd. for $C_7H_{11}N_2S_2^+$ $[M+H]^+$, 187.0358; found: 187.0357.

Phthalimidomethyl allyl(methyl)dithiocarbamate (1i). Light yellow crystals, 2.51 g, yield, 82%, two rotamers (57:43). M.p. 106-108 °C. IR (KBr): 2923, 1776, 1721, 1643, 1484, 1407, 1382 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 (d, *J* = 3.2 Hz, 2H, ArH), 7.75 (dd, *J* = 3.2, 2.8 Hz, 2H, ArH), 5.88-5.74 (m, 1H, CH=), 5.63 (d, *J* = 9.6 Hz, 2H, CH_2S), 5.27–5.18 (m, 2H, CH_2=), 4.70 (d, *J* = 5.2 Hz, 1.13 H, CH_2N, Rotamer A), 4.32 (d, *J* = 4.4 Hz, 0.87H, CH_2N, Rotamer B), 3.48 (s, 1.35H, CH_3, Rotamer B), 3.25 (s, 1.64H, CH_3, Rotamer A). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 194.5 (Rotamer A), 193.9 (Rotamer B), 166.7, 134.3 (Rotamer A), 131.8 (Rotamer B), 130.6 (Rotamer A), 130.07 (Rotamer B), 123.6, 118.8 (Rotamer A), 118.7 (Rotamer B), 58.7 (Rotamer A), 56.7 (Rotamer B), 44.1 (Rotamer A), 43.0 (Rotamer B), 38.7. HRMS (ESI) *m/z*, calcd. for $C_{14}H_{15}N_2O_2S_2^+$ $[M+H]^+$, 307.0569; found: 307.0576.

***Tert*-butyl 2-((allyl(methyl)carbamothioyl)thio)acetate (1j).** Yellow crystals, 2.11 g, yield, 81%, two rotamers (57:43). M.p. 46–49 °C. IR (KBr): 2928, 1735, 1642, 1385, 1197, 1143, 989 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.89–5.80 (m, 1H, CH=), 5.30–5.19 (m, 2H, CH_2=), 4.70 (d, *J* = 4.8 Hz, 1.13 H, CH_2N, Rotamer A), 4.41 (d, *J* = 3.2 Hz, 0.86H, CH_2N, Rotamer A), 4.07 (s, 2H, CH_2S), 3.47 (s, 1.30H, CH_3, Rotamer B), 3.33 (s, 1.60H, CH_3, Rotamer A), 1.48 (s, 9H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: (ppm) = 192.5 (Rotamer A), 191.8 (Rotamer B), 130.0 (Rotamer A), 129.4 (Rotamer B), 119.1 (Rotamer A), 116.0 (Rotamer B), 59.8 (Rotamer A), 56.7 (Rotamer B), 44.0 (Rotamer A), 38.8 (Rotamer B), 23.0 (Rotamer A), 18.3 (Rotamer B). HRMS (ESI) *m/z*, calcd. for $C_{11}H_{19}NNaO_2S_2^+$ $[M+Na]^+$, 284.0749; found: 284.0755.

2-Oxo-2-phenylethyl allyl(benzyl)dithiocarbamate (1k). Yellow sticky oil, 2.56 g, yield, 75%, two rotamers (50:50). IR (KBr): 1686, 1640, 1075 cm^{-1}. ^1H NMR of **1k** and its Rotamer (1:1): ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.08 (d, *J* = 7.6 Hz, 4H, ArH in PhCO), 7.60 (t, *J* = 7.6 Hz, 2H, ArH in PhCO), 7.50 (d, *J* = 7.6 Hz, 4H in PhCO), 7.31–7.29 (m, 10H, ArH in Bn), 5.92–5.81 (m, 2H, CH=), 5.33 (s, 2H, CH_2), 5.29–5.16 (m, 4H, CH_2=), 5.04 (s, 2H, CH_2), 4.95 (s, 2H, CH_2), 4.93 (s, 2H, CH_2), 4.64 (s, 2H, CH_2), 4.37 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) = 197.6, 196.9, 193.2, 193.2, 136.2, 133.5, 130.6, 130.1, 128.9, 128.7, 128.7, 128.5, 128.0, 127.8, 127.2, 119.1, 118.8, (seven overlapped peaks in the aromatic area) 57.0, 56.8, 54.7, 53.7, 45.6, 45.5. HRMS (ESI) calcd. for $C_{19}H_{20}NOS_2^+$ $[M+H]^+$ *m/z* 342.0981; Found 342.0975.

Ethyl 2-((allyl(benzyl)carbamothioyl)thio)acetate (1l). Yellow sticky oil, 2.32 g, yield, 75%, two rotamers (50:50). IR (KBr): 1737, 1641, 1225, 1076 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.40–7.23 (m, 10H, ArH), 5.95–5.75 (m, 2H, CH=), 5.32 (s, 2H, CH_2), 5.31–5.13 (m, 4H, CH_2=), 5.00 (s, 2H, CH_2), 4.62 (s, 2H, CH_2), 4.31 (s, 2H, CH_2), 4.27–4.18 (m, 2H, OCH_2), 4.21–4.16 (m, 2H, NCH_2), 1.30 (t, *J* = 7.2 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) = 197.3, 196.6, 168.4 (overlapped peak), 135.4, 134.5, 130.6, 130.0, 128.9, 128.7, 128.0, 127.8, 127.8, 127.2, 127.1, 119.1, 118.8, 61.8 (overlapped peak), 56.9, 56.7, 54.54, 53.50, 53.49, 39.65, 39.54, 14.1 (overlapped peak). HRMS (ESI) *m/z*, calcd. for $C_{15}H_{20}NO_2S_2^+$, $[M+H]^+$, 310.0930; found, 310.0931.

Cyanomethyl allyl(benzyl)dithiocarbamate (1m). Yellow sticky oil, 1.78 g, yield, 68%, two rotamers (50:50). IR (KBr) 2247, 1642, 1078 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.42–7.18 (m, 10H, ArH), 5.95–5.70 (m, 2H, CH=), 5.32 (s, 2H, CH_2), 5.29–5.17 (m, 4H, CH_2=), 4.92 (s, 2H, CH_2), 4.64 (m, 2H, CH_2), 4.30–4.18 (m, 6H, CH_2 and SCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) = 193.7, 192.9, 134.8, 133.8, 130.0, 129.4, 129.1, 128.8, 128.2, 128.0, 127.9, 126.9, 119.5, 115.8, (2 overlapped peaks in aromatic area) 57.5, 57.4, 54.7, 53.5, 23.2 (overlapped peak). HRMS (ESI) *m/z*, calcd. for $C_{13}H_{15}N_2S_2^+$, $[M+H]^+$, 263.0671; found, 263.0666.

2-Oxopropyl allyl(benzyl)dithiocarbamate (1n). Yellow sticky oil, 1.75 g, yield, 63%, two rotamers (50:50). IR (CH_2Cl_2): 1712, 1642, 1077 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.40–7.23 (m, 10H, ArH), 5.95–5.75 (m, 2H, CH=), 5.31 (s, 2H, CH_2), 5.30–5.13 (m, 4H, CH_2=), 5.00 (s, 2H, CH_2), 4.62 (s, 2H, CH_2), 4.30 (s, 2H, CH_2), 4.26 (s, 2H, CH_2), 4.24 (s, 2H, CH_2), 2.36 (s, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) = 201.9 (overlapped peak), 197.4, 196.8, 135.2, 134.4, 130.5, 130.0, 128.9, 128.7, 128.0, 127.8, 127.1, 119.0, 118.8 (1 overlapped peak in aromatic area), 57.1, 56.9, 54.7, 53.6, 47.3,

47.2, 29.4 (overlapped peak). HRMS (ESI) *m/z*, calcd. for $C_{14}H_{18}NOS_2^+$ $[M+H]^+$, 280.0824; found, 280.0828.

Phthalimidomethyl allyl(benzyl)dithiocarbamate (1o). Colorless crystals, 3.02 g, yield, 79%, two rotamers (50:50). M.p. 112-114 °C. IR (KBr): 1777, 1722, 1641, 1078 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.95–7.83 (m, 4H in Phth), 7.77–7.70 (m, 4H in Phth), 7.38–7.18 (m, 10H in Ph), 5.95–5.68 (m, 2H, CH=), 5.67 (s, 2H, CH_2), 5.32 (s, 2H, CH_2), 5.25 (d, *J* = 10.4 Hz, 2H, CH*H*=), 5.18 (d, *J* = 17.2 Hz, 2H, CH_2=), 4.89 (s, 2H, CH_2), 4.62 (d, *J* = 4.8 Hz, 2H, CH_2), 4.21 (d, *J* = 4.0 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 195.7, 166.8, 135.4, 134.3, 131.9, 130.6, 130.0, 128.9, 128.7, 127.97, 127.8, 127.1, 123.6, 119.2, 119.0, 56.1, 54.5, 53.5, 44.4 (nine overlapped peaks). HRMS (ESI, *m/z*), calcd. for $C_{20}H_{19}N_2O_2S_2^+$ $[M+H]^+$, 383.0882; found, 383.8880.

2-Oxo-2-phenylethyl allyl(isobutyl)dithiocarbamate (1p). Yellowish sticky oil, 613 mg (5 mmol), yield, 25%, two rotamers (57:43). IR (KBr): 3080, 2959, 2922, 1692, 1596, 1580, 1448, 1437, 1236, 1204, 990, 747, 688 cm^{-1}. Rotamer A: ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 8.06 (d, *J* = 7.2 Hz, 2H, ArH), 7.59 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 (t, *J* = 7.2 Hz, 4H, ArH), 5.94–5.81 (m, 1H, CH=), 5.29–5.16 (m, 2H, CH_2=), 4.91 (s, 2H, SCH_2CO), 4.88 (d, *J* = 4.8 Hz, 2H, CH_2), 3.61 (d, *J* = 7.2 Hz, 2H, CH_2), 2.42–2.24 (m, 1H, $CH(CH_3)_2$), 0.99 (d, *J* = 6.4 Hz, 3H, CH_3). Rotamer B: ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 8.06 (d, *J* = 7.2 Hz, 2H, ArH), 7.59 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 (t, *J* = 7.2 Hz, 4H, ArH), 5.94–5.81 (m, 1H, CH=), 5.29–5.16 (m, 2H, CH_2=), 4.91 (s, 2H, SCH_2CO), 4.46 (d, *J* = 4.8 Hz, 2H, CH_2), 3.82 (d, *J* = 7.2 Hz, 2H, CH_2), 2.42–2.24 (m, 1H, $CH(CH_3)_2$), 0.94 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR of **1p** and its rotamer: (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.3, 196.2, 193.3, 136.1, 133.4, 130.8, 130.3, 128.6, 128.5, 118.5, 118.1 (4 peaks overlapped in Ar), 62.1, 59.2, 58.1, 55.7, 45.3 (overlapped peak), 29.6, 27.5, 26.7, 20.2 (overlapped peak). HRMS (ESI) *m/z*, calcd. for $C_{16}H_{22}NOS_2^+$, $[M+H]^+$, 308.1137; found, 308.1144.

2-Oxopropyl allyl(isobutyl)dithiocarbamate (1q). Yellowish sticky oil, 1.47 g, yield, 60%, two rotamers (59:41). IR (KBr) 3082, 2960, 2928, 1721, 1642, 1477, 1407, 1353, 1237, 1149, 997, 942 cm^{-1}. Rotamer A: ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 5.92–5.80 (m, 1H, CH=), 5.30–5.16 (m, 2H, CH_2=), 4.68 (d, *J* = 5.2 Hz, 2H, CH_2N), 4.22 (s, 2H, CH_2S), 3.58 (d, *J* = 7.6 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.42–2.24 (m, CH in *i*-Pr), 0.99 (d, *J* = 6.8 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 202.1, 196.2, 130.7, 118.1, 59.2, 58.1, 47.0, 29.3, 27.4, 20.1. Rotamer B: ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 5.92–5.80 (m, 1H, CH=), 5.30–5.16 (m, 2H, CH_2=), 4.43 (d, *J* = 3.2 Hz, 2H, CH_2N), 4.22 (s, 2H, CH_2S), 3.82 (d, *J* = 7.2 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.42–2.24 (m, CH in *i*-Pr), 0.94 (d, *J* = 6.4 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 202.1, 196.2, 130.2, 118.4, 62.1, 55.7, 47.0, 29.3, 26.6, 20.1. HRMS (ESI) *m/z*, calcd. for $C_{11}H_{20}NOS_2^+$, $[M+H]^+$, 246.0981; found, 246.0973.

(Pyridin-2-yl)methyl allyl(benzyl)dithiocarbamate. Orange oil, 2.35 g, yield, 75%, two rotamers (54:46). IR (KBr): 3062, 3029, 2919, 1642, 1591, 1568, 1496.5, 1495, 1352, 1226, 747, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 8.55 (s, 1H, ArH), 7.63–7.17 (m, 8H, ArH), 5.85–5.79 (m, 1H, CH=), 5.35 (s, 1.07H, CH_2N, Rotamer A), 5.26–5.17 (m, 2H, CH_2=), 4.98 (s, 0.93H, CH_2N, Rotamer B), 4.79 (s, 2H, SCH_2, Rotamer A), 4.66 (s, 1H, SCH_2, Rotamer B), 4.31 (s, 1H, CH_2N). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 198.3 (Rotamer A), 197.8 (Rotamer B), 156.6 (Rotamer A), 149.4 (Rotamer B), 136.5 (Rotamer A), 135.5 (Rotamer B), 134.6, 130.7 (Rotamer A), 130.2 (Rotamer B), 128.8 (Rotamer A), 128.7 (Rotamer B), 127.8 (Rotamer A), 127.1 (Rotamer B), 123.8, 122.2, 118.9 (Rotamer A), 118.6 (Rotamer B), 77.2, 56.6 (Rotamer A), 56.4 (Rotamer B), 54.4, 53.4, 44.1 (Rotamer A), 44.0 (Rotamer B). HRMS (ESI) calcd. for $C_{17}H_{19}N_2S_2^+$ $[M+H]^+$ *m/z*: 315.0984; Found 315.0992.

General procedure for the synthesis of functionalized 5-substituted thiazolidiene-2-thiones.

Alkyl allyl(alkyl/aryl)dithiocarbamate **1** (1 mmol), the corresponding *S*-alkyl *O*-ethyl xanthate **3** (1 mmol), and DLP (198 mg, 0.5 mmol) were added into 3 mL of dried 1,2-dichloroethane under the N_2 protection. The whole system was heated to reflux and stirred for 1 hour. After removal of the solvent in vacuum, the product was purified on a silica gel column with ethyl acetate/petroleum ether (PE) (60–90 °C)/ethyl acetate (EA) as eluent or recrystallized from ethanol or a mixture of PE/EA to furnish the 5-subtituted thiazolidine-2-thione **2**.

5-(3-Oxo-3-phenyl)propyl-3-phenylthiazolidine-2-thione (2a). Yel-lowish crystals, yield, 297 mg (91%), m.p. 100–101 °C. R_f = 0.54 (PE/EA = 5:1, *v/v*). IR (KBr) 2954, 2920, 2850, 1680, 1594, 1492, 1408, 1263, 1059, 747, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 8.02-7.35 (m, 10H, ArH), 4.66 (dd, *J* = 11.6, 7.6 Hz, 1H in NCH_2), 4.19 (dd, *J* = 11.6, 4.4 Hz, 1H in NCH_2), 3.93 (dddd, *J* = 9.6, 7.2, 7.2, 4.4 Hz, 1H, CH), 3.23 (ddd, *J* = 14.0, 7.2, 6.4 Hz, 1H, CH_2CO), 3.18 (ddd, *J* = 14.0, 7.2, 7.2 Hz, 1H, CH_2CO), 2.42–2.22 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 198.4, 196.8, 140.4, 136.4, 133.5, 129.3, 128.7, 128.04, 127.97, 125.7, 65.9, 44.1, 35.4, 29.0. HRMS (ESI) calcd. for $C_{18}H_{18}NOS_2^+$ $[M+H]^+$ *m/z* 328.0824; Found 328.0830.

5-(3-Oxobutyl)-3-phenylthiazolidine-2-thione (2b). Yellowlish sticky oil, yield, 244 mg (92%). R_f = 0.15 (PE/EA = 4:1, *v/v*). IR (KBr) 1707, 1141 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.53–7.30 (m, 5H), 4.60 (dd, *J* = 11.3, 7.3 Hz, 1H in CH_2N), 4.10 (dd, *J* = 11.3, 4.4 Hz, 1H in CH_2N), 3.82 (dddd, *J* = 9.5, 7.3, 5.2, 4.4 Hz, 1H), 2.68 (ddd, *J* = 18.2, 7.4, 6.0 Hz, 1H in CH_2CO), 2.62 (ddd, *J* = 18.2, 7.4, 7.4 Hz, 1H in CH_2CO), 2.18 (s, 3H, CH_3), 2.18 (dddd, *J* = 13.7, 7.4, 7.4, 5.2 Hz, 1H in CH_2) 2.08 (dddd, *J* = 13.7, 9.5, 7.4, 6.0 Hz, 1H in CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 196.7, 140.3, 129.3, 128.0, 125.7, 65.8, 43.8, 40.3, 30.1, 28.5. HRMS (ESI) calcd. for $C_{13}H_{16}NOS_2^+$ $[M+H]^+$ *m/z* 266.0668; found 266.0674.

Ethyl [3-(4-methylphenyl)-2-thioxothiazolidin-5-yl]propanoate (2c). Yellowish oil, 238 mg, yield, 77%. R_f = 0.22 (PE/EA = 3:1, *v/v*). IR (KBr) 1728, 1510, 1418, 1052 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.30–7.22 (m, 4H, ArH), 4.59 (dd, *J* = 11.3, 7.4 Hz, 1H, CH*H*N), 4.15 (q, *J* = 7.1 Hz, 2H, OCH_2), 4.09 (dd, *J* = 11.4, 4.4 Hz, 1H, C*H*HN), 3.89–3.77 (m, 1H, CHS), 2.37 (s, 3H, CH_3), 2.57–2.40 (m, 2H, CH_2CO), 2.22–2.13 (m, 2H, CH_2C), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 172.3, 138.2, 137.8, 130.1, 125.6, 65.7, 60.9, 43.7, 31.4, 30.1, 21.2, 14.2. HRMS (ESI) *m/z*, calcd. for $C_{15}H_{20}NO_2S_2^+$ $[M+H]^+$, 310.0930; found: 310.0925.

Ethyl [3-(4-methyloxyphenyl)-2-thioxothiazolidin-5-yl]propanoate (2d). Yellowish oil, 234 mg, yield, 72%. R_f = 0.22 (PE/EA = 3:1, *v/v*). IR (KBr) 1724, 1509, 1292, 1026 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.27 (d, *J* = 8.9, 2H, ArH), 6.93 (d, *J* = 8.9, 2H, ArH), 4.54 (dd, *J* = 11.4, 7.4 Hz, 1H, CH*H*N), 4.12 (q, *J* = 7.2 Hz, 2H, OCH_2), 4.05 (dd, *J* = 11.4, 4.4 Hz, 1H, C*H*HN), 3.83–3.77 (m, 4H, CHS, CH_3), 2.53–2.38 (m, 2H, CH_2CO), 2.20–2.08 (m, 2H, CH_2C), 1.24 (t, *J* = 7.1

Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 172.3, 138.2, 137.8, 130.1, 125.6, 65.7, 60.9, 43.7, 31.4, 30.1, 21.2, 14.2. HRMS (ESI) *m/z*, calcd. for $C_{15}H_{20}NO_3S_2^+$ $[M+H]^+$, 326.0879; found: 326.0878.

3-Methyl-5-(3-oxo-3-pheny)propylthiazolidine-2-thione (2e). Light yellow crystals, 156 mg, yield, 72%. M.p. 119–121 °C. R_f = 0.14 (PE/EA = 3:1, *v*/*v*). IR (KBr): 2922, 1682, 1596, 1504, 1447, 1308, 1112 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.94 (d, *J* = 7.8 Hz, 2H, ArH_{ortho-}), 7.51 (t, *J* = 7.4 Hz, 1H, ArH_{para}), 7.47 (dd, *J* = 7.8, 7.4 Hz, 1H, ArH_{meta}), 4.23 (dd, *J* = 11.0, 7.5 Hz, 1H, CH*H*N), 3.84 (dd, *J* = 11.0, 4.5 Hz, 1H, C*H*HN), 3.81 (dddd, *J* = 9.3, 7.5, 4.8, 4.5 Hz, 1H, CHS), 3.27 (s, 3H, CH_3), 3.14 (ddd, *J* = 17.8, 7.2, 6.0 Hz, 1H, CH*H*CO), 3.08 (ddd, *J* = 17.8, 7.2, 7.2 Hz, 1H, C*H*HCO), 2.26 (dddd, *J* = 14.2, 7.2, 7.2, 4.8 Hz, 1H, CH*H*), 2.14 (dddd, *J* = 14.2, 9.3, 7.2, 6.0 Hz, 1H, CH*H*). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* (ppm) = 198.4, 195.6, 136.3, 133.4, 128.7, 128.0, 64.3, 42.7, 36.7, 35.3, 29.3. HRMS (ESI) *m/z*, calcd. for $C_{13}H_{16}NOS_2^+$ $[M+H]^+$, 266.0668; found: 266.0667.

3-Methyl-5-(3-oxo)butylthiazolidine-2-thione (2f). Light yellow sticky oil, 181 mg, yield, 89%. R_f = 0.05 (PE/EA = 3:1, *v*/*v*). IR (KBr): *v* = 2922, 1708, 1507, 1305, 1109 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 4.20 (dd, *J* = 11.4, 7.7 Hz, 1H, CH*H*N), 3.77 (dd, *J* = 11.4, 4.5 Hz, 1H, C*H*HN), 3.70 (dddd, *J* = 9.2, 7.7, 5.0, 4.5 Hz, 1H, CHS), 3.27 (s, 3H, CH_3), 2.63 (ddd, *J* = 18.2, 7.2, 6.2 Hz, 1H, CH*H*CO), 2.54 (ddd, *J* = 18.2, 7.2, 7.2 Hz, 1H, C*H*HCO), 2.17 (s, 3H, $OCCH_3$), 2.06 (dddd, *J* = 14.2, 7.2, 7.2, 5.0 Hz, 1H, CH*H*), 1.94 (dddd, *J* = 14.2, 9.2, 7.2, 6.2 Hz, 1H, CH*H*). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* (ppm) = 207.02, 195.62, 64.29, 42.57, 40.30, 36.72, 30.10, 28.87. HRMS (ESI) m/z, calcd. for $C_8H_{14}NOS_2^+[M+H]^+$, 204.0511; found: 204.0507.

Ethyl [3-methyl-2-thioxothiazolidin-5-yl]propanoate (2g). Light yellow sticky oil, 212 mg, yield, 91%. R_f = 0.11 (PE/EA = 3:1, *v*/*v*). IR (KBr): 2924, 1728, 1508, 1309, 1123 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 4.20 (dd, *J* = 11.3, 7.5 Hz, 1H, CH*H*N), 4.14 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.78 (dd, *J* = 11.3, 4.6 Hz, 1H, C*H*HN), 3.73 (dddd, *J* = 9.9, 7.6, 5.5, 4.6 Hz, 1H, CHS), 3.28 (s, 3H, CH_3), 2.46 (ddd, *J* = 16.6, 7.5, 6.5 Hz, 1H, CH*H*CO), 2.38 (ddd, *J* = 16.6, 7.5, 7.5 Hz, 1H, C*H*HCO), 2.10 (dddd, *J* = 14.0, 7.5, 7.5, 5.5 Hz, 1H, CH*H*), 2.05 (dddd, *J* = 14.0, 9.9, 7.5, 6.5 Hz, 1H, CH*H*), 1.26 (t, *J* = 7.1 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* (ppm) = 195.76, 172.24, 64.06, 60.83, 42.42, 36.74, 31.43, 30.35, 14.20. HRMS (ESI) m/z, calcd. for $C_9H_{16}NO_2S_2^+[M+H]^+$, 234.0617; found: 234.0617.

[3-Methyl-2-thioxothiazolidin-5-yl]propanenitrile (2h). Light yellow sticky oil, 170 mg, yield, 91%. R_f = 0.05 (PE/EA = 3:1, *v*/*v*). IR (KBr): 2921, 2246, 1710, 1506, 1308, 1110 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 4.30 (dd, *J* = 11.6, 7.7 Hz, 1H, CH*H*N), 3.84 (dd, *J* = 11.6, 3.6 Hz, 1H, C*H*HN), 3.76 (dddd, *J* = 9.7, 7.7, 6.6, 3.6 Hz, 1H, CHS), 3.30 (s, 3H, NCH_3), 2.56 (ddd, *J* = 17.2, 6.6, 6.6 Hz, 1H, CH*H*CN), 2.49 (ddd, *J* = 17.2, 7.4, 7.4 Hz, 1H, C*H*HCN), 2.14–2.09 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* (ppm) = 194.8, 118.3, 63.6, 41.6, 36.8, 31.2, 15.0. HRMS (ESI) m/z, calcd. for $C_7H_{11}N_2S_2^+$ $[M+H]^+$, 187.0358; found: 187.0357.

3-Methyl-5-(2-phthalimidoethyl)thiazolidine-2-thione (2i). Colorless crystals, 212 mg, yield, 70%. M.p. 192–195 °C. R_f = 0.08 (PE/EA = 3:1, *v*/*v*). IR (KBr): 2926, 1708, 1612, 1504, 1433, 1395, 1111 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.75 (dd, *J* = 5.4, 3.0 Hz, 1H, ArH), 4.25 (dd, *J* = 11.5, 7.9 Hz, 1H, CH*H*N), 3.84 (dd, *J* = 11.5, 4.9 Hz, 1H, C*H*HN), 3.83-3.78 (m, 2H, CH_2N), 3.67–3.60 (m, 1H, CHS), 3.29 (s, 3H, CH_3), 2.21–2.08 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* (ppm) = 196.0, 168.3, 134.3, 131.8, 123.5, 63.7, 40.5, 36.8, 35.4, 34.3. HRMS (ESI) m/z, calcd. for $C_{14}H_{15}N_2O_2S_2^+$ $[M+H]^+$, 307.0569; found: 307.0566.

***Tert*-butyl 3-(3-methyl-2-thioxothiazolidin-5-yl)propanoate (2j).** Light yellow sticky oil, 240 mg, yield, 92%. R_f = 0.22 (PE/EA = 3:1, *v*/*v*). IR (KBr): *v* = 2926, 1723, 1503, 1392, 1151 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 4.19 (dd, *J* = 11.2, 7.6 Hz, 1H, C*H*HN), 3.77 (dd, *J* = 11.2, 4.8 Hz, 1H, CH*H*N), 3.72 (dddd, *J* = 8.5, 7.6, 5.5, 4.5 Hz, 1H, CHS), 3.28 (s, 3H, NCH_3), 2.36 (ddd, *J* = 16.4, 7.8, 6.5 Hz, 1H, CH*H*CO), 2.31 (ddd, *J* = 16.4, 7.4, 7.4 Hz, 1H, C*H*HCO), 2.06 (dddd, *J* = 13.9, 7.4, 7.4, 5.5 Hz, 1H, C*H*H), 1.98 (dddd, *J* = 13.9, 8.5, 7.8, 6.5 Hz, 1H, CH*H*). ^{13}C NMR (101 MHz, CDCl3) *δ* (ppm) = 195.86, 171.54, 81.06, 64.07, 42.49, 36.74, 32.65, 30.43, 28.08. HRMS (ESI) m/z, calcd. for $C_{11}H_{20}NO_2S_2^+[M+H]^+$, 262.0930; found: 262.0925.

3-Benzyl-5-(3-oxo-3-phenyl)propylthiazolidine-2-thione (2k). Yellowish crystals, 103 mg, yield, 82%, m.p. 77–79 °C. R_f = 0.43 (PE/EA = 3:1, *v*/*v*). IR (KBr) 2956, 2921, 2850, 1686, 1482, 1448, 1260, 1219, 1040, 832, 772, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 7.91 (d, *J* = 7.2 Hz, 2H, PhCO), 7.58 (t, *J* = 7.2 Hz, 1H, PhCO), 7.46 (t, *J* = 7.6 Hz, 2H, PhCO), 7.40–7.28 (m, 5H, Ph in Bn), 5.07 (d, *J* = 14.8 Hz, 1H in $PhCH_2N$), 4.89 (d, *J* = 14.8 Hz, 1H in $PhCH_2N$), 4.06 (dd, *J* = 11.2, 7.2 Hz, 1H in NCH_2), 3.74 (dddd, *J* = 9.6, 7.2, 5.2, 4.4 Hz, 1H, CH), 3.68 (dd, *J* = 11.2, 4.4 Hz, 1H in NCH_2), 3.04 (t, *J* = 6.8 Hz, 2H, CH_2CO), 2.14 (ddt, *J* = 14.2, 5.2, 6.8 Hz, 1H, C*H*HCH), 2.01 (ddt, *J* = 14.2, 9.6, 6.8 Hz, 1H, CH*H*CH). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 198.3, 196.0, 136.3, 134.9, 133.4, 128.9, 128.7, 128.3, 128.2, 128.0, 61.2, 52.6, 42.7, 35.2, 29.3. HRMS (ESI) calcd. for $C_{19}H_{20}NOS_2^+$ $[M+H]^+$ *m/z* 342.0981; found 342.0990.

Ethyl (3-benzyl-2-thioxothiazolidin-5-yl)propanoate (2l). Colorless crystals, 295 mg, yield, 76%, m.p. 37–38 °C. TLC, R_f = 0.43 (PE/EA = 3:1, *v*/*v*). IR (KBr) 2955, 2921, 2850, 1724, 1656, 1631, 1480, 1376, 1303, 1217, 1027, 735, 670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 7.40–7.29 (m, 5H, ArH), 5.07 (d, *J* = 14.6 Hz, 1H in $PhCH_2N$), 4.89 (d, *J* = 14.6 Hz, 1H in $PhCH_2N$), 4.11 (q, *J* = 7.2 Hz, 2H, OCH_2), 4.02 (dd, *J* = 11.2, 7.2 Hz, 1H in NCH_2), 3.71–3.64 (m, 1H, CH), 3.61 (dd, *J* = 11.2, 4.4 Hz, 1H in NCH_2), 2.35 (ddd, *J* = 16.6, 7.3, 7.3 Hz, 1H in CH_2CO), 2.33 (ddd, *J* = 16.6, 7.3, 7.3 Hz, 1H in CH_2CO), 2.04–1.86 (m, 2H, CH_2CH), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 196.0, 172.1, 134.9, 128.9, 128.2, 128.1, 60.8, 60.7, 52.5, 42.4, 31.2, 30.1, 14.1. HRMS (ESI) calcd. for $C_{15}H_{20}NOS_2^+$ $[M+H]^+$ *m/z* 310.0930; found 310.0936.

3-(3-Benzyl-2-thioxothiazolidin-5-yl)propanenitrile (2m). Yellowish sticky oil, 228 mg, yield, 87%. R_f = 0.13 (PE/EA = 5:1, *v*/*v*). IR (KBr) 2921, 2851, 2238, 1484, 1452, 1306, 1219, 1180, 1035 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 7.40–7.32 (m, 5H, ArH), 5.14 (d, *J* = 14.5 Hz, 1H in CH_2Ph), 4.82 (d, *J* = 14.5 Hz, 1H in CH_2Ph), 4.10 (dd, *J* = 12.5, 8.3 Hz, 1H in CH_2N), 3.72–3.63 (m, 1H, CHS), 3.64 (dd, *J* = 12.5, 3.4 Hz, 1H in CH_2N), 2.42 (t, *J* = 7.1 Hz, 2H, CH_2CN), 1.96 (dt, *J* = 7.1, 7.1 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 194.9, 134.7, 129.0, 128.4, 128.2, 118.1, 60.3, 52.5, 41.6, 30.9, 14.8. HRMS (ESI) calcd. for $C_{13}H_{15}N_2S_2^+$ $[M+H]^+$ *m/z* 263.0671; found 263.0677.

3-Benzyl-5-(3-oxobutyl)thiazolidine-2-thione (2n). Yellowish sticky oil, 215 mg, yield, 77%. R_f = 0.31 (PE/EA = 3:1, *v*/*v*). IR (KBr) 2955, 2923, 1710, 1465, 1377, 1216, 1142, 742, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 7.39–7.31 (m, 5H, ArH), 5.05 (d, *J* = 14.5 Hz, 1H in CH_2Ph), 4.88 (d, *J* = 14.5 Hz, 1H in CH_2Ph), 4.05–4.00 (m, 1H in CH_2N), 3.66–3.58 (m, 2H, CHS & CH*H*N), 2.50 (ddd, *J* = 18.1, 6.8, 6.4 Hz, 1H in CH_2CO), 2.47 (ddd, *J* = 18.1, 7.4, 6.9 Hz, 1H in

CH_2CO), 2.11 (s, 3H, CH_3), 1.94 (dddd, *J* = 14.1, 7.4, 7.4, 4.8 Hz, 1H in CH_2), 1.81 (dddd, *J* = 14.1, 9.0, 6.8, 6.8 Hz, 1H in CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 206.9, 195.9, 134.9, 128.9, 128.3, 128.2, 61.0, 52.5, 42.5, 40.0, 30.0, 28.7. HRMS (ESI) calcd. for $C_{14}H_{18}NOS_2^+$ $[M+H]^+$ *m/z* 280.0824; found 280.0828.

3-Benzyl-5-(2-phthalimidoethyl)thiazolidine-2-thione (2o). Colorless crystals, 237 mg, yield, 62%, m.p. 141–143 °C. R_f = 0.38 (PE/EA = 5:1, *v*/*v*). IR (KBr) 2920, 2850, 1770, 1709, 1632, 1482, 1395, 1077, 1044, 915, 875, 719, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 7.83 (dd, *J* = 5.6, 3.2 Hz, 2H, ArH), 7.73 (dd, *J* = 5.6, 3.2 Hz, 2H, ArH), 7.39–7.29 (m, 5H, ArH), 5.13 (d, *J* = 14.8 Hz, 1H in $PhCH_2N$), 4.83 (d, *J* = 14.8 Hz, 1H in $PhCH_2N$), 4.05 (dd, *J* = 11.6, 7.6 Hz, 1H in NCH_2), 3.76 (ddd, *J* = 14.3, 6.8, 6.4 Hz, 1H in CH_2NPhth), 3.68 (ddd, *J* = 14.3, 6.8, 6.4 Hz, 1H in CH_2NPhth), 3.65 (dd, *J* = 11.6, 4.8 Hz, 1H in NCH_2), 3.54 (dddd, *J* = 7.6, 6.8, 6.4, 4.8 Hz, 1H, CH), 2.04 (dddd, *J* =14.1, 6.8, 6.4, 6.4 Hz, 1H in CH_2), 1.98 (dddd, *J* =14.1, 6.8, 6.4, 6.4 Hz, 1H in CH_2). ^{13}C NMR ($CDCl_3$, 101 MHz) (*δ*, ppm) 196.3, 168.2, 135.0, 134.2, 131.8, 129.0, 128.3, 128.2, 123.4, 60.5, 52.6, 40.7, 35.3, 34.2. HRMS (ESI) calcd. for $C_{20}H_{19}N_2O_2S_2^+$ $[M+H]^+$ *m/z* 383.0882; found 383.0883.

3-(2-Methylpropyl)-5-(3-oxo-3-phenyl)propyl)thiazolidine-2-thione (2p). Yellowish sticky oil, 230 mg, yield, 75%. R_f = 0.35 (PE/EA = 4:1, *v*/*v*). IR (KBr) 1709, 1458, 1139 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.95 (d, *J* = 7.8 Hz, 2H, ArH), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (dd, *J* = 7.8, 7.4 Hz, 2H), 4.19 (dd, *J* = 11.4, 7.5 Hz, 1H, CHN), 3.83 (dd, *J* = 11.4, 4.3 Hz, 1H, CH_2N), 3.77 (dddd, *J* = 9.8, 7.5, 4.8, 4.3 Hz, CHS), 3.67 (dd, *J* = 13.4, 7.7 Hz, 1H, C*H*HN), 3.52 (dd, *J* = 13.4, 7.5 Hz, 1H, CH*H*N), 3.15 (ddd, *J* = 17.9, 7.2, 6.0 Hz, 1H, CH*H*CO), 3.10 (ddd, *J* = 17.9, 7.3, 7.2 Hz, 1H, CH*H*CO), 2.28 (dddd, *J* = 14.2, 7.3, 7.2, 4.8 Hz, 1H, CH*H*C), 2.19–2.07 (m, 1H in ^{i}Pr), 2.09 (dddd, *J* = 14.2, 9.8, 7.2, 6.0 Hz, 1H, C*H*HC), 0.98 (d, *J* = 6.7 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 198.4, 195.7, 136.4, 133.5, 128.7, 128.0, 62.8, 56.3, 43.1, 35.5, 29.4, 27.4, 20.1, 20.1. HRMS (ESI) calcd. for $C_{16}H_{22}NOS_2^+$, $[M+H]^+$, *m/z*, 308.1137; found, 308.1130.

3-(2-Methylpropyl)-5-(3-oxo)butylthiazolidine-2-thione (2q) Yellowlish sticky oil, yield, 172 mg (70%). IR (KBr) 2956, 2923, 1720, 1468, 1381, 1163 cm^{-1}. R_f = 0.38 (PE/EA = 2:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) 4.16 (dd, *J* = 11.6, 7.6 Hz, 1H, CH_2N), 3.77 (dd, *J* = 11.6, 4.6 Hz, 1H, CH_2N), 3.68 (dddd, *J* = 9.9, 7.8, 7.5, 4.9 Hz, 1H, CHS), 3.66 (dd, *J* = 13.4, 7.8 Hz, 1H, CH_2N), 3.54 (dd, *J* = 13.4, 7.5 Hz, 1H, CH_2N), 2.64 (ddd, *J* = 18.2, 7.4, 5.9 Hz, 1H in CH_2CO), 2.55 (ddd, *J* = 18.2, 7.3, 7.3 Hz, 1H in CH_2CO), 2.18 (s, 1H, CH_3), 2.10 (dddd, *J* = 14.0, 7.3, 7.4, 4.9 Hz, 1H in CH_2), 2.21-2.01 (m, 1H, CH in ^{i}Pr), 1.91 (dddd, *J* = 14.0, 9.9, 7.3, 5.9 Hz, 1H in CH_2), 0.98 (d, *J* = 6.7 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) (*δ*, ppm) 207.0, 195.6, 62.7, 56.3, 42.9, 40.4, 30.0, 28.9, 27.3, 20.1, 20.0. HRMS (ESI) *m/z* calcd. for $C_{11}H_{20}NOS_2^+$ $[M+H]^+$ 246.0981; found 246.0983.

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