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Pronounced Catalytic Effect of a Micellar Solution of Sodium Dodecyl Sulfate (SDS) on the Efficient C-S Bond Formation *via* an Odorless Thia-Michael Addition Reaction through the *in situ* Generation of *S*-Alkylisothiouronium Salts

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Abstract: A pronounced catalytic effect of sodium dodecyl sulfate (SDS) was observed on the *in situ* production of *S*-alkylisothiouronium salts *via* the reaction of primary, allyl and benzyl halides with thiourea in SDS droplets .Hydrolysis of the generated *S*-alkylisothiouronium salts in the palisade layer of the droplets produces the corresponding thiol moieties which are immediately added to the electron-deficient olefins that are present in the micellar core to produce the thia-Michael adducts. The entire route is an almost odorless process. The yields of the products are good to excellent and the method is applicable to large-scale operation without any problem.

Keywords: alkyl halides; *S*-alkylisothiouronium salts; sodium dodecyl sulfate; thia-Michael addition; thioureas; water

Introduction

The thia-Michael addition is one of the most versatile and practical reactions for C–S bond formation in organic synthesis.[1] Conversion of α,β-unsaturated carbonyl compounds to the corresponding β-sulfido carbonyl derivatives provides a strategy for the chemoselective protection of C=C bonds. Regeneration of the olefinic double bond is easily achieved by oxidative elimination[2] or induced by Cu^+.[3] In addition, these compounds are starting materials for the generation of β-acylvinyl cations[4] and homoenolate anion equivalents.[5] For these and other reasons, the thia-Michael addition is an important reaction in organic synthesis and plays a crucial role in biosynthesis and the synthesis of bioactive compounds.[6] The reported methods for thia-Micheal addition are mainly focused on the use of acidic and basic catalysts for the direct addition of thiols to Michael acceptors in organic solvents. However, efforts have been made constantly to introduce new methodologies which are efficient and more compatible with the environment. For this goal, the reactions conducted under solvent-free conditions,[7,8] in ionic liquids[9] and using water as the medium[10,11] have been reported. In all the reported methods, the use of highly volatile and foul-smelling thiols leads to serious environmental and safety problems and also limits the use of these methods for large-scale operations. In order to minimize or eliminate the encountered problems, a range of odorless protocols has also been reported. The use of long-chain alkyl thiols or substituted thiophenols with a trimethylsilyl moiety as odorless substrates have been reported for this purpose.[12] The use of 3-[bis(alkylthio)methylene]pentane-2,4-diones,[13] dialkyl disulfides,[14] 4,4-bis(alkylthio)but-3-en-2-ones[15] and *S*-alkylisothiouronium salts[16] as thiol equivalent precursors is also reported. However, these odorless procedures encounter disadvantages, such as that most of the reagents should be prepared from thiols, unavailability and cost of some catalysts, long reaction times and use of strong alkaline media.

Disposing of organic solvents in industry is a major problem and around 80% of the wastes are composed of these solvents.[17,18] The replacement of expensive, toxic, flammable, not recyclable organic solvents with water is thus an important practical achievement. Water is a cheap, abundant, non-toxic, non-flammable and relatively green solvent.[19,20] On the other hand, water with its chemical and physical properties imposes selectivity and reactivity in reactions conducted in aqueous media which cannot be gained using organic solvents.[21–23] However, dissolving many organic compounds in water is difficult and for this reason, reactions cannot proceed easily in aqueous media.[24] One way to improve the solubility of substrates in water is the use of surface-active reagents that can form micelles or vesicular cavities. Due to the applicability and practicability of the surfactant-aided reactions, the use of micellar and vesicle-forming surfactants as catalysts is widespread and has been studied for different synthetic transformation in water.[25–28]

Using water as the reaction media has been one of our interests in recent years. Along this line, we have successfully used water and micellar solutions for Michael and some other synthetic transformations.[11,29–33] Now, herein we report a pronounced catalytic effect of a micellar solution of sodium dodecyl sulfate (SDS) for the *in situ* generation of the thiol moiety to perform an efficient and odorless addition to electron-deficient alkenes *via* the thia-Michael reaction. For this purpose, commercially available and cheap thiourea, alkyl, benzyl and allyl halides and electron-deficient α,β-unsaturated olefins were reacted in a vessel under mild basic ($NaHCO_3$ or Na_2CO_3) conditions.

Results and Discussion

As a part of our interest in C–S bond forming reactions,[7,11] we have initiated an investigation on the use of non-thiolic precursors for C–S bond formation *via* the thia-Michael addition reaction.

In this regard, we have studied the reaction of *n*-butyl acrylate with 1-bromooctane and thiourea as the source for the *in situ* generation of thiol in a micellar solution of sodium dodecyl sulfate in the presence of $NaHCO_3$. We observed that the optimized conditions for completion of the reaction were *n*-butyl acrylate (1 mmol), 1-bromooctane (1.2 mmol), thiourea (1.3 mmol) and $NaHCO_3$ (1.5 mmol) in 0.5 mL of a 0.2 molar (25 CMC, 1 CMC $= 8.1 \times 10^{-3}$ M) solution of SDS in water at 80–90 °C. More studies showed that the presence of SDS in this reaction is crucial, such that the similar reaction in the absence of SDS completely failed and both *n*-butyl acrylate and 1-bromooctane were isolated intact from the reaction mixture after 8 h. This finding shows the pronounced catalytic effect of SDS for the generation of the thiol moiety under applied conditions. Then the above optimized conditions were applied for the preparation of thia-Michael adducts using structurally diverse primary alkyl halides and electron-deficient olefins. The results of this study are summarized in Table 1. As the results show, this method is general and applicable for the preparation of thioethers from both primary alkyl bromides and iodides in the presence of thiourea and Michael acceptors such as α,β-unsaturated ketones, esters and acrylonitrile with good to excellent yields. Secondary and tertiary halides remained unreacted in the reaction mixture under such conditions.

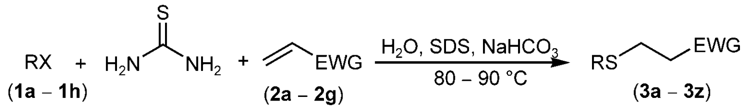
Moreover, we have also found that the reaction of more reactive primary benzylic and allylic halides with thiourea and Michael acceptors was efficiently catalyzed by the SDS micellar solution at room temperature in the presence of Na_2CO_3. The corresponding thia-Michael adducts were obtained in good to excellent yields. These results are presented in Table 2.

In order to show the merit of the SDS micellar solution, the reaction of benzyl chloride, thiourea, and *n*-butyl acrylate was studied in the absence of SDS under similar reaction conditions as mentioned in the preceding paragraph. It was observed that the reaction proceeded very slowly and only 40% (GC analysis) of the desired Michael adduct (**5l**) was produced after 24 h.

Then we applied the above-mentioned optimized conditions to the reaction of acrylamide with different halides. Under such reaction conditions, no Michael adduct were formed at all. Then we decided to perform the reactions in two consecutive steps. For this purpose, in the first step, thiourea (1.3 mmol) was added to the alkyl halides (1.2 mmol) in 0.2 mL aqueous solution of 0.5 molar SDS and the resulting mixture was heated at 80–90 °C for the appropriate times as indicated in Table 3. Then acrylamide (1 mmol), Na_2CO_3 (1.5 mmol) in H_2O (1 mL) were added to the reaction mixture at 80–90 °C with stirring for 1 h. By this protocol, the reactions proceeded to completion and the resulting thia-Michael adducts were isolated in 85–92% yields (Table 3).

The catalytic effect of the micellar solution of SDS may be explained as follows. Alkyl halides are hydrophobic molecules thus they are not soluble in aqueous media, and this could be the reason why no reaction occurs between alkyl halides and thiourea in the absence of SDS. Moreover, in the micellar solution, hydrophobic alkyl halides are pushed by water molecules towards the hydrophobic core of the micelle droplets. In the droplets, efficient collisions between alkyl halides and thiourea take place more effectively to enhance the reaction rates for the formation of *S*-alkylisothiouronium salts. This salt is an amphiphilic molecule containing both an apolar hydrocarbon tail moiety and a polar head group. The apolar hydrocarbon tail moiety of the salt dissolves in the hydrophobic core of the micelle, while the polar head group is located at the hydrophilic micellar core (palisade and Gouy–Chapman layers) in contact with and hydrated by a number of water molecules in the layers. Simultaneous hydrolysis of the salt followed by the generation of the thiol moiety and its addition to the alkene

Table 1. One-pot thia-Michael addition using RX (X=Br, I), thiourea and electron-deficient alkenes catalyzed by SDS micellar solution.



RX: *n*-decyl iodide (**1a**), *n*-octyl iodide (**1b**), *n*-octyl bromide (**1c**), *n*-butyl iodide (**1d**), *n*-butyl bromide (**1e**), *n*-propyl iodide (**1f**), methyl iodide (**1g**), (2-bromoethyl)-benzene (**1h**).

: 2-cyclohexenone (**2a**), methyl vinyl ketone (**2b**), acrylonitrile (**2c**), *n*-butyl acrylate (**2d**), ethyl acrylate (**2e**), ethyl methacrylate (**2f**), ethyl crotonate (**2g**).

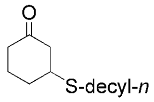
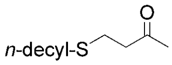
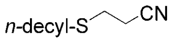
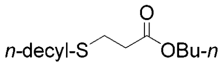
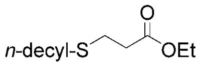
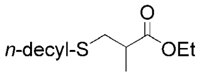
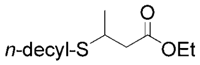
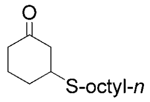
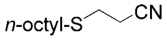
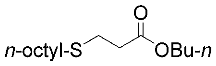
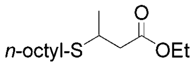
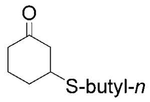
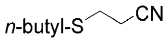
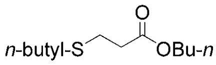
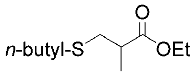
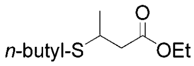
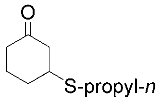
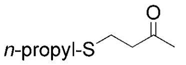
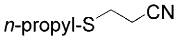
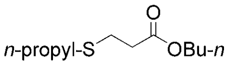
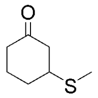
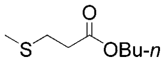
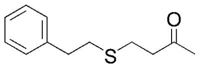
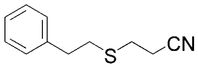
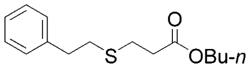
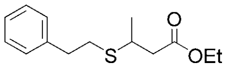
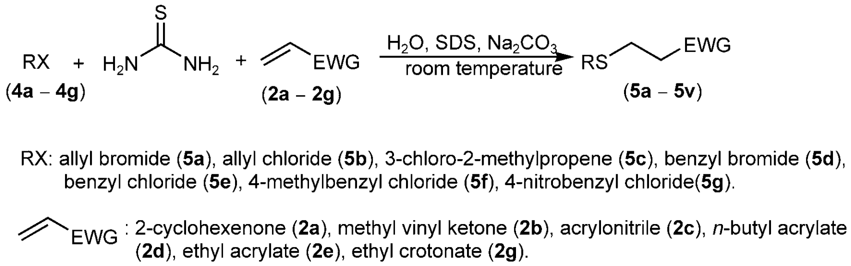
Entry	RX		Product		Time [h]	Isolated Yield [%]	Ref.
1	**1a**	**2a**	**3a**		3.5	73	[34]
2	**1a**	**2b**	**3b**		3.5	70	[35]
3	**1a**	**2c**	**3c**		3.5	84	[36]
4	**1a**	**2d**	**3d**		3.5	87	
5	**1a**	**2e**	**3e**		3.5	83	[37]
6	**1a**	**2f**	**3f**		3.5	83	
7	**1a**	**2g**	**3g**		3.5	80	
8	**1b**	**2a**	**3h**		3	75	[34]
9	**1b**	**2c**	**3i**		3	87	[38]
10	**1b**	**2d**	**3j**		3	87	
11	**1b**	**2g**	**3k**		3	88	
12	**1c**	**2a**	**3h**		8	73	
13	**1c**	**2c**	**3i**		8	85	
14	**1c**	**2d**	**3j**		8	86	
15	**1c**	**2g**	**3k**		8	84	
16	**1d**	**2a**	**3l**		1	80	[14a]
17	**1d**	**2c**	**3m**		1	88	[9a]
18	**1d**	**2d**	**3n**		1	90	[16]
19	**1d**	**2f**	**3o**		1	88	[15c]
20	**1d**	**2g**	**3p**		1	87	[39]
21	**1e**	**2a**	**3l**		5	73	
22	**1e**	**2c**	**3m**		5	87	
23	**1e**	**2d**	**3n**		5	91	

Table 1. (Continued)

Entry	RX	EWG	Product		Time [h]	Isolated Yield [%]	Ref.
24	**1e**	**2f**	**3o**		5	84	
25	**1e**	**2g**	**3p**		5	88	
26	**1f**	**2a**	**3q**		0.75	75	[40]
27	**1f**	**2b**	**3r**		0.75	70	[40]
28	**1f**	**2c**	**3s**		0.75	87	[41]
29	**1f**	**2d**	**3t**		0.75	92	[42]
30	**1g**	**2a**	**3u**		1	81[a]	[16]
31	**1g**	**2d**	**3v**		1	92[a]	[43]
32	**1h**	**2b**	**3w**		6	71	[44]
33	**1h**	**2c**	**3x**		6	88	
34	**1h**	**2d**	**3y**		6	84	
35	**1h**	**2g**	**3z**		6	83	

[a] The reaction was carried out in the sealed tube.

Table 2. One-pot thia-Michael addition using allyl and benzyl halides, thiourea and electron-deficient alkenes catalyzed by SDS micellar solution at room temperature.



RX: allyl bromide (**5a**), allyl chloride (**5b**), 3-chloro-2-methylpropene (**5c**), benzyl bromide (**5d**), benzyl chloride (**5e**), 4-methylbenzyl chloride (**5f**), 4-nitrobenzyl chloride(**5g**).

EWG : 2-cyclohexenone (**2a**), methyl vinyl ketone (**2b**), acrylonitrile (**2c**), *n*-butyl acrylate (**2d**), ethyl acrylate (**2e**), ethyl crotonate (**2g**).

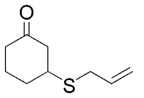
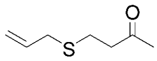
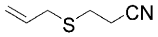
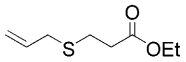
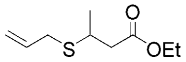
Entry	RX	EWG	Product		Time [h]	Isolated Yield [%]	Ref.
1	**4a**	**2a**	**5a**		2	82	[16]
2	**4a**	**2b**	**5b**		2	75	[16]
3	**4a**	**2c**	**5c**		2	90	[16]
4	**4a**	**2e**	**5d**		2	92	[45]
5	**4a**	**2g**	**5e**		2	92	
6	**4b**	**2a**	**5a**		10	80	

Table 2. (Continued)

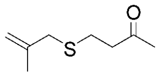
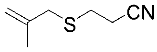
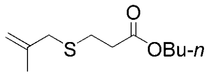
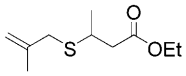
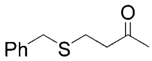
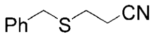
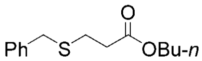
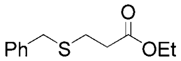
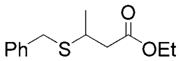
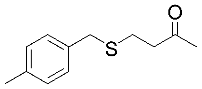
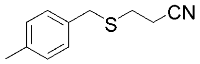
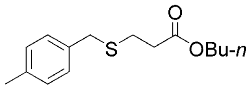
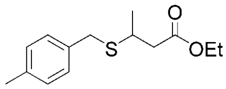
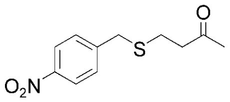
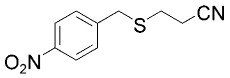
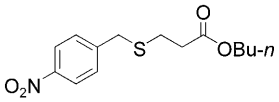
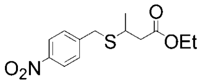
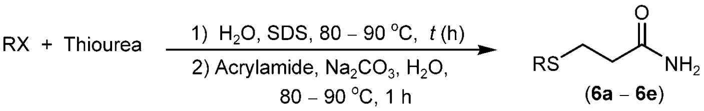
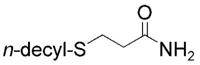
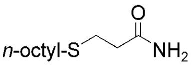
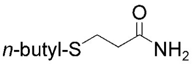
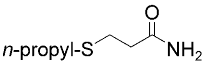
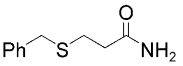
Entry	RX		Product		Time [h]	Isolated Yield [%]	Ref.
7	**4b**	**2b**	**5b**		10	72	
8	**4b**	**2c**	**5c**		10	90	
9	**4b**	**2e**	**5d**		10	90	
10	**4b**	**2g**	**5e**		10	90	
11	**4c**	**2b**	**5f**		10	75	
12	**4c**	**2c**	**5g**		10	90	[46]
13	**4c**	**2d**	**5h**		10	90	
14	**4c**	**2g**	**5i**		10	88	
15	**4d**	**2b**	**5j**		2	76	[16]
16	**4d**	**2c**	**5k**		2	91	[16]
17	**4d**	**2d**	**5l**		2	92	[47]
18	**4d**	**2e**	**5m**		2	91	[12]
19	**4d**	**2g**	**5n**		2	85	[12]
20	**4e**	**2b**	**5j**		4	70	
21	**4e**	**2c**	**5k**		4	90	
22	**4e**	**2d**	**5l**		4	90	
23	**4e**	**2e**	**5m**		4	91	
24	**4e**	**2g**	**5n**		4	85	
25	**4f**	**2b**	**5o**		3	72	[48]
26	**4f**	**2c**	**5p**		3	91	
27	**4f**	**2d**	**5q**		3	89	
28	**4f**	**2g**	**5r**		3	85	
29	**4g**	**2b**	**5s**		48	70	[49]
30	**4g**	**2c**	**5t**		48	89	
31	**4g**	**2d**	**5u**		48	89	
32	**4g**	**2g**	**5v**		48	80	

Table 3. Thia-Michael addition at acrylamide using alkyl halides and thiourea in the presence of Na_2CO_3 in SDS micellar solution.



Entry	RX	Product		t [h]	Isolated Yield [%]	Ref.
1	*n*-decyl iodide	**6a**		2.5	90	
2	*n*-octyl iodide	**6b**		2	87	[50]
3	*n*-octyl bromide	**6b**		5	85	
4	*n*-butyl iodide	**6c**		1	90	
5	*n*-butyl bromide	**6c**		2.5	87	
6	*n*-propyl iodide	**6d**		0.7	92	
7	benzyl bromide	**6e**		0.5	91	[51]
8	benzyl chloride	**6e**		0.5	90	

molecule which is present in the hydrophobic micellar core results in the formation of the Michael adduct. The role of SDS droplets for the formation of *S*-alkylisothiouronium salt and its consecutive reactions for the formation of thia-Michael adducts are schematically presented by Figure 1.

Conclusions

We have introduced a new, one-pot, odorless procedure for C–S bond formation *via* a conjugate addition reaction using alkyl halides, thiourea and electron-deficient olefins in the SDS micellar solution. In this procedure, water is employed as the reaction media, non-thiolic precursors are used for the *in situ* generation of thiol moiety, which makes the reaction an odorless process and, more importantly, makes the synthesis of structurally diverse thia-Michael adducts possible. Because structurally different thiols are not usually commercially available compounds for the previously used protocol, this limitation has been eliminated for the preparation of more versatile thia-Michael products. By this method, we have shown another important catalytic role of the micellar solution of SDS in organic synthesis. The yields of the obtained thia-Michael adducts are high to excellent and the work-up of the reaction mixture is very convenient, which could be applied easily for large-scale operations.

Experimental Section

General Procedure for the Synthesis of Thia-Michael Adducts with Alkyl Halides (1a–1h), Thiourea and Electron-Deficient Alkenes (2a–2g) in a Micellar Solution of SDS at 80–90 °C

To a micellar solution of SDS (0.5 mL, 0.2 M), was added an electron-deficient alkene (**2a–2g**) (1 mmol), alkyl halide (**1a–1h**) (1.2 mmol), thiourea (1.3 mmol) and $NaHCO_3$ (1.5 mmol). The resulting mixture was heated at 80–90 °C with stirring. The progress of the reaction was monitored by TLC or GC until the starting materials were consumed (Table 1, entries 1–35). Then the reaction mixture was extracted with ethyl acetate (5 × 2 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel chromatography using petroleum ether/EtOAc (20/1) as eluent afforded the desired products in 70–92% yields.

General Procedure for the Synthesis of Thia-Michael Adducts with Allylic and Benzylic Halides (4a–4g), Thiourea and Electron-Deficient Alkenes (2a–2g) in a Micellar Solution of SDS at Room Temperature

An allylic or benzylic halide (**4a–4g**) (1.2 mmol) was added to a micellar solution of SDS (1 mL, 0.1 M), electron deficient alkene (**2b–2g**) (1 mmol), thiourea (1.33 mmol), and Na_2CO_3 (1.5 mmol) and the mixture was stirred magnetically at room temperature. Monitoring of the reaction by TLC or GC showed the completion of the reaction within 2–48 h (Table 2). The product was then extracted with ethyl acetate (5 × 2 mL), dried over Na_2SO_4, and concentrated. Silica gel chromatography using petroleum ether/EtOAc (20/1) as eluent afforded the pure product in 70–92% yields.

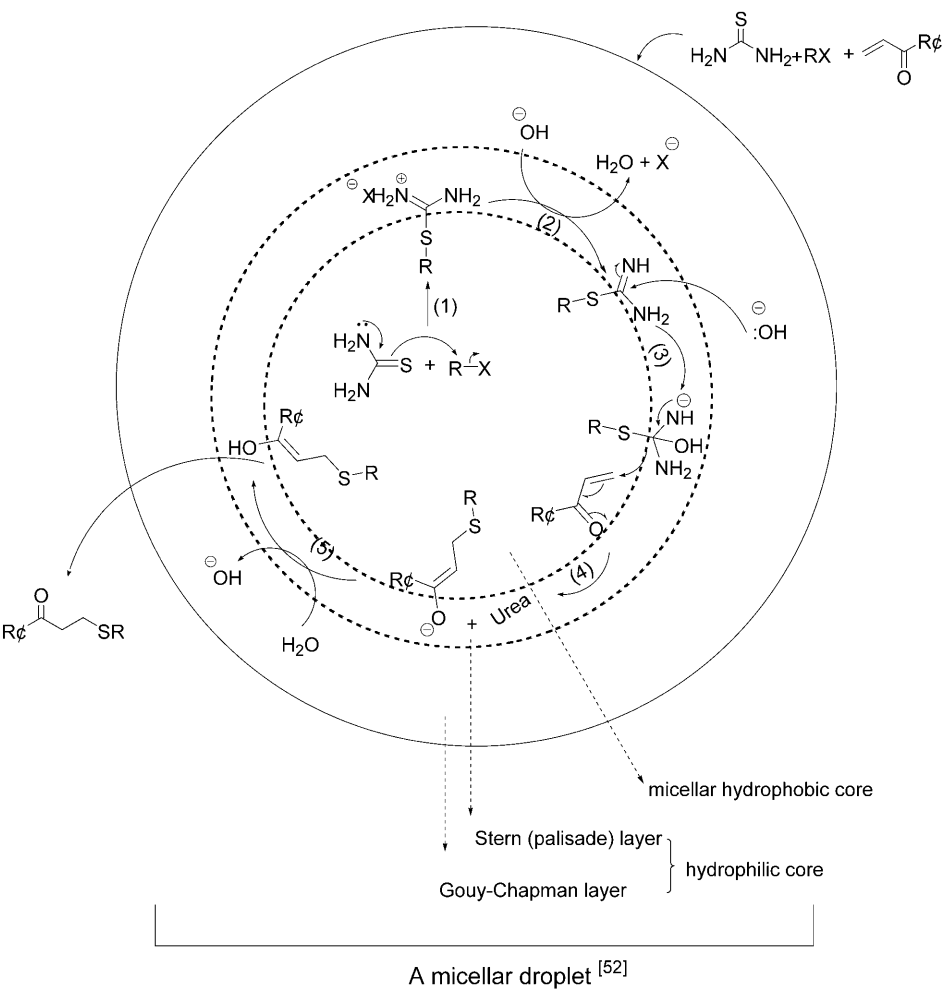


Figure 1. The proposed role of micellar SDS droplets for thia-Michael adduct formation.

General Procedure for Thia-Michael Addition to Acrylamide in a Micellar Solution of SDS using Alkyl Halides, Thiourea and Na_2CO_3 at 90 °C

A micellar solution of SDS (0.2 mL, 0.5 M), alkyl halide (1.2 mmol) and thiourea (1.3 mmol) was stirred at 80–90 °C for the appropriate times as indicated in Table 3. Then a mixture of acrylamide (1 mmol), and Na_2CO_3 (1.5 mmol) in water (1 mL) was added to the reaction mixture while being magnetically stirred at 80–90 °C for 1 h. Then, the mixture was diluted with water (5 mL) and extracted with EtOAc (5 × 10 mL). Organic phase was washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4 and evaporated. Recrystallization of the crude products in ethyl acetate afforded the purified products in excellent yields.

Typical Procedure for Large-Scale Preparation of Thia-Michael Adduct using *n*-Butyl Acrylate, Thiourea, *n*-Butyl Bromide and $NaHCO_3$ in SDS Micellar Solution

To a micellar solution of SDS (10 mL, 0.2 M), was added *n*-butyl acrylate (20 mmol), *n*-butyl bromide (24 mmol), thiourea (26 mmol) and $NaHCO_3$ (30 mmol). The resulting mixture was heated at 80–90 °C with stirring. The progress of the reaction was monitored by GC until the starting *n*-butyl acrylate was consumed. The reaction was completed in 5 h. Then the reaction mixture was extracted with ethyl acetate (5 × 10 mL), dried over Na_2SO_4, and concentrated. Purification by silica gel chromatography using petroleum ether/EtOAc (20/1) as eluent afforded the desired product; yield: 3.8 g (87%).

3-Decylsulfanylcyclohexanone (3a): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.00–2.94$ (m, 1H), 2.64 (dd, $J = 14.2$, 4.4 Hz, 1H), 2.47 (t, $J = 7.3$ Hz, 2H), 2.35–2.24 (m, 3H), 2.13–2.03 (m, 2H), 1.72–1.50 (m, 2H), 1.55–1.44 (m, 2H), 1.28–1.19 (m, 14H), 0.83–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 208.88$, 48.22, 42.72, 40.92, 31.84, 31.63, 30.51, 29.68, 29.50, 29.46, 29.26, 29.17, 28.91, 24.23, 22.63, 14.07; IR (neat): $\nu = 1717$ cm^{-1} (C=O); anal. calcd. for ($C_{16}H_{30}OS$): C 71.05, H 11.18, S 11.86; found: C 71.01, H 11.10, S 11.91.

4-Decylsulfanylbutan-2-one (3b): Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.66$ (s, 4H), 2.44 (t, $J = 7.3$ Hz, 2H), 2.10 (s, 3H), 1.56–1.44 (m, 2H), 1.28–1.19 (m, 14H), 0.81–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 207.01$, 43.72, 32.42, 31.87, 30.07, 29.55, 29.53, 29.51, 29.29, 29.21, 28.86, 25.74, 22.66, 14.10; IR: $\nu = 1717$ cm^{-1} (C=O); anal.

calcd. for ($C_{14}H_{28}OS$): C 68.79, H 11.55, S 13.12; found: C 68.71, H 11.59, S, 13.17.

3-Decylsulfanylpropionitrile (3c): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.79–2.71 (m, 2H), 2.65–2.49 (m, 4H), 1.61–1.47 (m, 2H), 1.30–1.05 (m, 14H), 0.84–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 118.40, 32.25, 31.86, 29.51, 29.47, 29.42, 29.27, 29.16, 28.75, 27.59, 22.65, 18.89, 14.09; IR: ν = 2249 cm^{-1} (CN); anal. calcd. for ($C_{13}H_{25}NS$): C 68.66, H 11.08, N 6.16, S 14.10; found: C 68.60, H 11.06, N 6.19, S 14.15.

3-Decylsulfanylpropionic acid butyl ester (3d): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.03 (t, J = 6.7 Hz, 2H), 2.74–2.68 (m, 2H), 2.59–2.45 (m, 4H), 1.64–1.45 (m, 4H), 1.39–1.19 (m, 16H), 0.89–0.78 (m, 6H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 172.09, 64.51, 34.94, 32.12, 31.86, 30.60, 29.53, 29.50, 29.28, 29.20, 28.85, 26.99, 22.65, 19.10, 14.08, 13.67; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd. for ($C_{17}H_{34}O_2S$): C 67.49, H 11.33, S 10.60; found: C 67.53, H 11.27, S 10.65.

3-Decylsulfanylpropionic acid ethyl ester (3e): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.09 (q, J = 7.1 Hz, 2H), 2.73–2.68 (m, 2H), 2.55–2.43 (m, 4H), 1.54–1.47 (m, 2H), 1.29–1.17 (m, 17H), 0.83–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 170.78, 44.81, 31.75, 30.39, 30.18, 29.10, 29.04, 28.82, 28.79, 22.60, 14.05; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd. for ($C_{15}H_{30}O_2S$): C 65.64, H 11.02, S 11.68; found: C 65.58, H 11.06, S 11.75.

3-Decylsulfanyl-2-methylpropionic acid ethyl ester (3f): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.09 (q, J = 7.1 Hz, 2H), 2.80–2.73 (m, 1H), 2.62–2.44 (m, 4H), 1.56–1.44 (m, 2H), 1.22–1.16 (m, 20H), 0.83–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 175.23, 60.50, 40.23, 35.47, 32.62, 31.86, 29.60, 29.53, 29.50, 29.28, 29.20, 28.83, 22.65, 16.80, 14.18, 14.09; IR (neat): ν = 1736 cm^{-1} (C=O); MS: m/e = 288 [M^{+}]; anal. calcd. for ($C_{16}H_{32}O_2S$): C 66.61, H 11.18, S 11.11; found: C 66.66, H 11.16, S 11.14.

3-Decylsulfanylbutyric acid ethyl ester (3g): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.09 (q, J = 7.1 Hz, 2H), 3.19–3.06 (m, 1H), 2.59–2.31 (m, 4H), 1.56–1.45 (m, 2H), 1.32–1.17 (m, 20H), 0.83–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.54, 60.49, 42.38, 36.20, 31.87, 30.63, 29.68, 29.53, 29.50, 29.28, 29.21, 28.97, 22.65, 21.41, 14.20, 14.08; IR (neat): ν = 1736 cm^{-1} (C=O); MS: m/e = 288 [M^{+}]; anal. calcd. for ($C_{16}H_{32}O_2S$): C 66.61, H 11.18, S 11.11; found: C 66.65, H 11.12, S 11.13.

3-Octylsulfanylcyclohexanone (3h): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.99–2.94 (m, 1H), 2.65 (dd, J = 14.2, 4.5 Hz, 1H), 2.47 (t, J = 7.5 Hz, 2H), 2.35–2.24 (m, 3H), 2.10–2.03 (m, 2H), 1.68–1.59 (m, 2H), 1.53–1.44 (m, 2H), 1.32–1.20 (m, 10H), 0.83–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 208.96, 48.26, 42.75, 40.95, 31.76, 31.67, 30.54, 29.70, 29.14, 28.93, 24.26, 22.61, 14.06; IR (neat): ν = 1717 cm^{-1} (C=O); anal. calcd. for ($C_{14}H_{26}OS$): C 69.36, H 10.81, S 13.23; found: C 69.33, H 10.75, S 13.29.

3-Octylsulfanylpropionitrile (3i): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.66–2.60 (m, 2H), 2.50–2.40 (m, 4H), 1.53–1.38 (m, 2H), 1.25–1.12 (m, 10H), 0.75–0.65 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 118.43, 32.24, 31.76, 29.41, 29.12, 28.75, 27.57, 22.61, 18.90, 14.09; IR (neat): ν = 2249 cm^{-1} (CN); anal. calcd. for ($C_{11}H_{21}NS$): C 66.27, H 10.62, N 7.03, S 16.08: found: C 66.33, H 10.67, N 7.01, S 15.99.

3-Octylsulfanylpropionic acid butyl ester (3j): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.03 (t, J = 6.63 Hz, 2H), 2.74–2.68 (m, 2H), 2.56–2.43 (m, 4H), 1.61–1.45 (m, 4H), 1.39–1.20 (m, 12H), 0.90–0.78 (m, 6H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 172.13, 64.54, 34.96, 32.14, 31.79, 30.61, 29.55, 29.17, 28.86, 27.01, 22.63, 19.11, 14.07, 13.68; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd. for ($C_{15}H_{30}O_2S$): C 65.64, H 11.02, S 11.68; found: C 65.66, H 11.06, S 11.62.

3-Octylsulfanylbutyric acid ethyl ester (3k): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.09 (q, J = 7.1 Hz, 2H), 3.19–3.06 (m, 1H), 2.59–2.31 (m, 4H), 1.56–1.45 (m, 2H), 1.29–1.17 (m, 16H), 0.83–0.78 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.53, 60.49, 42.39, 36.13, 31.78, 30.63, 29.68, 29.16, 28.97, 22.61, 21.40, 14.20, 14.06; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd. for ($C_{14}H_{28}O_2S$): C 64.56, H 10.84, S 12.31; found: C 64.63, H 10.80, S 12.33.

3-Butylsulfanylcyclohexanone (3l): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.15–2.98 (m, 1H), 2.70 (dd, J = 14.1, 4.5 Hz, 1H), 2.54 (t, J = 7.3 Hz, 2H), 2.42–2.30 (m, 3H), 2.17–2.10 (m, 2H), 1.58–1.50 (m, 2H), 1.44–1.35 (m, 2H), 0.91 (t, J = 7.2, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 208.96, 48.27, 42.74, 40.96, 31.76, 31.67, 30.21, 24.28, 22.04, 13.64; IR (neat): ν = 1717 cm^{-1} (C=O); anal. calcd. for ($C_{10}H_{18}OS$): C 64.46, H 9.74, S 17.21; found: C 64.53, H 9.70, S 17.19.

3-Butylsulfanyl-2-methylpropionic acid ethyl ester (3o): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.07 (q, J = 7.1 Hz, 2H), 2.78–2.71 (m, 1H), 2.67–2.40 (m, 4H), 1.53–1.42 (m, 2H), 1.39–1.24 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H), 1.16 (d, J = 6.7 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 175.08, 60.38, 40.16, 35.40, 32.19, 31.60, 21.83, 16.70, 14.10, 13.54; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd. for ($C_{10}H_{20}O_2S$): C 58.78, H 9.87, S 15.69; found: C 58.87, H 9.82, S 15.73.

3-Butylsulfanylbutyric acid ethyl ester (3p): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.04 (q, J = 7.1 Hz, 2H), 3.15–3.01 (m, 1H), 2.55–2.70 (m, 4H), 1.52–1.40 (m, 2H), 1.37–1.28 (m, 2H), 1.22–1.13 (m, 6H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.38, 60.36, 42.29, 36.02, 31.67, 30.17, 21.94, 21.32, 14.11, 13.55; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd. for ($C_{10}H_{20}O_2S$): C 58.78, H 9.87, S 15.69; found: C 58.70, H 9.91, S 15.72.

3-Methylsulfanylcyclohexanone (3u): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.93–2.85 (m, 1H), 2.65 (dd, J = 14.1, 4.2 Hz, 1H), 2.36–2.19 (m, 3H), 2.08–2.05 (m, 5H), 1.73–1.57 (m, 2H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 208.85, 47.57, 44.17, 40.91, 31.00, 24.12, 13.53; IR (neat): ν = 1713 cm^{-1} (C=O); anal. calcd. for ($C_7H_{12}OS$): C 58.29, H 8.39, S 22.23; found: C 58.22, H 8.42, S 22.20.

3-Methylsulfanylpropionic acid butyl ester (3v): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.03 (t, J = 6.6 Hz, 2H), 2.72–2.67 (m, 2H), 2.57–2.51 (m, 2H), 2.05 (s, 3H), 1.61–1.50 (m, 2H), 1.39–1.24 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.90, 64.42, 34.40, 30.55, 29.03, 19.04, 15.34, 13.59; IR (neat): ν = 1736 cm^{-1} (C=O); anal. calcd for ($C_8H_{16}O_2S$): C 54.51, H 9.15, S 18.19; found: C 54.57, H 9.10, S, 18.12.

4-Phenethylsulfanylbutan-2-one (3w): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.33–7.19 (m, 5H), 2.81–2.65 (m, 8H), 2.15 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 206.84, 140.40, 128.49, 126.38, 43.66, 36.22, 33.99, 30.08, 25.90; IR (neat): ν = 1717 (C=O), 1605, 1496 cm^{-1} (aromatic

C=C); anal. calcd. for ($C_{12}H_{16}OS$): C 69.19, H 7.74, S 15.39; found: C 69.14, H 7.80, S 15.34.

3-Phenethylsulfanylpropionitrile (3x): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.34–7.22 (m, 5H), 2.91–2.84 (m, 4H), 2.76–2.70 (m, 2H), 2.58–2.53 (m, 2H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 142.28, 128.61, 126.62, 118.59, 36.13, 33.78, 27.82, 18.89; IR (neat): ν = 2249 (CN), 1601, 1497 cm^{-1} (aromatic C=C); anal. calcd. for ($C_{11}H_{13}NS$): C 69.07, H 6.85, N, 7.32, S 16.76; found: C 69.10, H 6.82, N 7.29, S 16.79.

3-Phenethylsulfanylpropionic acid butyl ester (3y): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.17–7.06 (m, 5H), 3.99 (t, J = 6.6 Hz, 2H), 2.77–2.63 (m, 6H), 2.47 (t, J = 7.2 Hz, 2H), 1.58–1.42 (m, 2H), 1.32–1.15 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.92, 140.42, 128.47, 126.37, 64.50, 36.25, 34.92, 33.66, 30.66, 27.18, 19.15, 13.74; IR (neat): ν = 1736 (C=O), 1605, 1497 cm^{-1} (aromatic C=C); anal. calcd. for ($C_{15}H_{22}O_2S$): C 67.63, H 8.32, S 12.04; found: C 67.59, H 8.33, S 12.06.

3-Phenethylsulfanylbutyric acid ethyl ester (3z): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.13–7.06 (m, 5H), 4.04 (q, J = 7.1 Hz, 2H), 3.22–3.13 (m, 1H), 2.83–2.64 (m, 4H), 2.51 (dd, J = 15.4, 6.3 Hz, 1H), 2.33 (dd, J = .15.4, 8.1 Hz, 1H), 1.23 (d, J = 6.8 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.26, 138.79, 128.47, 128.45, 126.34, 60.44, 42.34, 36.33, 32.17, 21.47, 14.27; IR (neat): ν = 1736 (C=O), 1605, 1497 cm^{-1} (aromatic C=C); anal. calcd for ($C_{14}H_{20}O_2S$): C 66.63, H 7.99, S 12.71; found: C 66.67, H 8.03, S 12.67.

3-Allylsulfanylcyclohexanone (5a): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 5.69–5.53 (m, 1H), 5.00–4.88 (m, 2H), 3.00 (d, J = 7.0 Hz, 2H), 2.87–2.81 (m, 1H), 2.50 (dd, J = 14.3, 4.5 Hz, 1H), 2.24–2.12 (m, 3H), 1.98–1.90 (m, 2H), 1.57–1.43 (m, 2H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 208.75, 134.20, 117.18, 47.88, 41.39, 40.92, 33.54, 31.32, 24.16; IR (neat): ν = 1716 (C=O), 1634 cm^{-1} (C=C); anal. calcd. for ($C_9H_{14}OS$): C 63.48, H 8.29, S 18.83; found: C 63.55, H 8.35, S 18.76.

4-Allylsulfanylbutan-2-one (5b): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 5.77–5.63 (m, 1H), 5.08–5.01 (m, 2H), 3.07 (d, J = 7.1 Hz, 2H), 2.66–2.58 (m, 4H), 2.10 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 206.78, 134.20, 117.16, 43.42, 35.09, 30.04, 24.44; IR (neat): ν = 1716 (C=O), 1634 cm^{-1} (C=C); anal. calcd. for ($C_7H_{12}OS$): C 58.29, H 8.39, S 22.23; found: C 58.35, H 8.33, S 22.27.

3-Allylsulfanylpropionitrile (5c): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 5.82–5.64 (m, 1H), 5.15–5.08 (m, 2H), 3.17 (d, J = 7.2 Hz, 2H), 2.71–2.66 (m, 2H), 2.60–2.54 (m, 2H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 133.60, 118.44, 117.99, 34.69, 25.81, 18.63; IR (neat): ν = 2249 (CN), 1634 cm^{-1} (C=C); anal. calcd. for (C_6H_9NS): C 56.65, H 7.13, N 11.01, S 25.21; found: C 56.59, H 7.09, N 11.07, S 25.25.

3-Allylsulfanylpropionic acid ethyl ester (5d): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 5.86–5.69 (m, 1H), 5.14–5.07 (m, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.14 (d, J = 7.1 Hz, 2H), 2.75–2.69 (m, 2H), 2.59–2.53 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.89, 134.12, 117.20, 60.61, 34.74, 34.58, 25.50, 14.18; IR (neat): ν = 1732 (C=O), 1634 cm^{-1} (C=C); anal. calcd. for ($C_8H_{14}O_2S$): C 55.14, H 8.10, S 18.40; found: C 55.20, H 8.02, S 18.42.

3-Allylsulfanylbutyric acid ethyl ester (5e): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 5.83–5.67 (m, 1H), 5.11–5.00 (m, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.17–3.03 (m, 3H), 2.55 (dd, J = 15.4, 6.1 Hz, 1H), 2.35 (dd, J = 15.4, 8.3 Hz, 1H), 1.25–1.16 (m, 6H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.31, 134.43, 116.93, 60.44, 42.03, 35.13, 33.87, 21.13, 14.17; IR (neat): ν = 1736 (C=O), 1636 cm^{-1} (C=C); anal. calcd. for ($C_9H_{16}O_2S$): C 57.41, H 8.57, S 17.03, found: C 57.44, H 8.50, S 17.06.

4-(2-Methylallylsulfanyl)-butan-2-one (5f): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.69 (s, 2H), 2.96 (s, 2H), 2.59–2.41 (m, 4H), 2.01 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 206.96, 141.12, 113.63, 43.26, 39.65, 30.04, 24.68, 20.56; IR (neat): ν = 1717 (C=O), 1647 cm^{-1} (C=C); anal. calcd. for ($C_8H_{14}OS$): C 60.71, H 8.92, S 20.26; found: C 60.66, H 8.99, S 20.25.

3-(2-Methylallylsulfanyl)-propionitrile (5g): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.75–4.72 (m, 2H), 3.04 (s, 2H), 2.61–2.44 (m, 4H), 1.67 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 140.57, 118.53, 114.35, 39.20, 26.05, 20.34, 18.39; IR (neat): ν = 2249 (CN), 1647 cm^{-1} (C=C); anal. calcd. for ($C_7H_{11}NS$): C 59.53, H 7.85, N, 9.92, S 22.70; found: C 59.55, H 7.81, N 9.86, S 22.78.

3-(2-Methylallylsulfanyl)-propionic acid butyl ester (5h): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.78–4.77 (m, 2H), 4.03 (t, J = 6.6 Hz, 2H), 3.06 (s, 2H), 2.65–2.59 (m, 2H), 2.53–2.46 (m, 2H), 1.75 (s, 3H), 1.60–1.49 (m, 2H), 1.39–1.27 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.99, 141.02, 113.64, 64.46, 39.30, 34.41, 30.59, 25.77, 20.49, 19.08, 13.65; IR (neat): ν = 1736 (C=O), 1647 cm^{-1} (C=C); anal. calcd. for ($C_{11}H_{20}O_2S$): C 61.07, H 9.32, S 14.82; found: C 61.01, H 9.35, S 14.87.

3-(2-Methyl-allylsulfanyl)-butyric acid ethyl ester (5i): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.59–4.55 (m, 2H), 3.88 (q, J = 7.0 Hz, 2H), 2.88 (s, 2H), 2.83–2.74 (m, 1H), 2.32 (dd, J = 15.3, 6.3 Hz, 1H), 2.13 (dd, J = 15.3, 8.2 Hz, 1H), 1.53 (s, 3H), 1.03–0.94 (m, 6H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.21, 141.33, 113.31, 60.29, 41.87, 38.37, 20.96, 20.82, 20.55, 14.12; IR (neat): ν = 1736 (C=O), 1647 cm^{-1} (C=C); anal. calcd. for ($C_{10}H_{18}O_2S$): C 59.37, H 8.97, S 15.85; found: C 59.41, H 8.90, S 15.89.

3-Benzylsulfanylpropionic acid butyl ester (5l): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.16–7.04 (m, 5H), 3.92 (t, J = 6.6 Hz, 2H), 3.53 (s, 2H), 2.53–2.47 (m, 2H), 2.39–2.32 (m, 2H), 1.49–1.38 (m, 2H), 1.28–1.14 (m, 2H), 0.77 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.55, 138.21, 128.81, 128.41, 126.92, 64.24, 36.08, 34.45, 30.63, 26.21, 19.11, 13.69; IR (neat): ν = 1736 (C=O), 1601, 1493 cm^{-1} (aromatic C=C); anal. calcd. for ($C_{14}H_{20}O_2S$): C 66.63, H 7.99, S 12.71; found: C 66.69, H 7.95, S 12.85.

3-Benzylsulfanylpropionic acid ethyl ester (5m): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.18–7.04 (m, 5H), 3.99 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 2.57–2.51 (m, 2H), 2.42–2.36 (m, 2H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 171.80, 138.14, 128.84, 128.18, 127.05, 60.57, 36.24, 34.52, 26.23, 14.22; IR (neat): ν = 1732 (C=O), 1601, 1493 cm^{-1} (aromatic C=C); anal. calcd. for ($C_{12}H_{16}O_2S$): C 64.25, H 7.19, S 14.29; found: C 64.30, H 7.17, S 14.24.

3-Benzylsulfanylbutyric acid ethyl ester (5n): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.28–7.06 (m, 5H), 4.02 (q, J = 7.1 Hz, 2H), 3.65 (s, 2H), 3.08–2.94 (m, 1H), 2.50 (dd, J = 15.3, 6.1 Hz, 1H), 2.31 (dd, J = 15.3, 8.2 Hz, 1H), 1.19 (d, J=6.8 Hz, 3H), 1.13 (t, J=7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=171.27, 138.23, 129.00, 128.82, 126.98, 60.48, 42.10, 36.17, 35.92, 21.20, 14.22; IR (neat): ν=1736 (C=O), 1601, 1493 cm^{-1} (aromatic C=C); anal. calcd. for ($C_{13}H_{18}O_2S$): C 65.51, H 7.61, S 13.45; found: C 65.55, H 7.56, S 13.50.

4-(4-Methylbenzylsulfanyl)-butan-2-one (5o): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.07 (d, J=8.0 Hz, 2H), 6.98 (d, J=8.0 Hz, 2H), 3.53 (s, 2H), 2.48 (s, 4H), 2.17 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$); δ=206.58, 136.52, 135.19, 129.19, 128.89, 43.54, 36.23, 29.90, 25.13, 21.07; IR (neat): ν=1717 (C=O), 1582 cm^{-1} (aromatic C=C); MS: m/e=208 [M$^+$]; anal. calcd. for ($C_{12}H_{16}OS$): C 69.19, H 7.74, S 15.39; found: C 69.25, H 7.80, S 15.32.

3-(4-Methylbenzylsulfanyl)-propionitrile (5p) Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.07 (d, J=8.0 Hz, 2H), 6.99 (d, J=8.0 Hz, 2H), 3.61 (s, 2H), 2.52–2.46 (m, 2H), 2.38–2.31 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=137.00, 134.26, 129.34, 128.73, 118.42, 35.85, 26.50, 20.99, 18.49; IR (neat): ν=2249 (CN), 1512 cm^{-1} (aromatic C=C); MS: m/e=191 [M$^+$]; anal. calcd. for ($C_{11}H_{13}NS$): C 69.07, H 6.85, N 7.32, S 16.76; found: C 69.01, H 6.80, N 7.37, S 16.82.

3-(4-Methylbenzylsulfanyl)-propionic acid butyl ester (5q): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.11 (d, J=8.0 Hz, 2H), 7.03 (d, J=8.0 Hz, 2H), 4 (t, J=6.6 Hz, 2H), 3.61 (s, 2H), 2.62–2.56 (m, 2H), 2.48–2.42 (m, 2H), 2.24 (s, 3H), 1.55–1.46 (m, 2H), 1.33–1.24 (m, 2H), 0.85 (t, J=7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=171.99, 136.67, 134.95, 129.21, 128.72, 64.52, 35.92, 34.53, 30.61, 26.21, 21.07, 19.12, 13.70; IR (neat): ν=1736 (C=O), 1589 cm^{-1} (aromatic C=C); MS: m/e=266 [M$^+$]; anal. calcd. for ($C_{15}H_{22}O_2S$): C 67.63, H 8.32, S 12.04; found: C 67.70, H 8.25, S 12.07.

3-(4-Methylbenzylsulfanyl)-butyric acid ethyl ester (5r): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.13 (d, J=7.9 Hz, 2H), 7.03 (d, J=7.9 Hz, 2H), 4.05 (q, J=7.2 Hz, 2H), 3.65 (s, 2H), 3.10–2.97 (m, 1H), 2.53 (dd, J=15.3, 6.0 Hz, 1H), 2.34 (dd, J=15.3, 8.4 Hz, 1H), 2.24 (s, 3H), 1.23–1.14 (m, 6H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=171.38, 136.59, 135.06, 129.19, 128.71, 60.51, 42.11, 35.85, 35.00, 21.18, 21.09, 14.21; IR (neat): ν=1736 (C=O), 1512 cm^{-1} (aromatic C=C); MS: m/e=252 [M$^+$]; anal. calcd for ($C_{14}H_{20}O_2S$): C 66.63, H 7.99, S 12.71; found: C 66.66, H 7.92, S 12.79.

4-(4-Nitrobenzylsulfanyl)-butan-2-one (5s): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=8.09 (d, J=8.5 Hz, 2H), 7.42 (d, J=8.5 Hz, 2H), 3.72 (s, 2H), 2.86–2.53 (m, 4H), 2.07 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=206.44, 146.94, 146.21, 129.76, 123.75, 43.12, 36.17, 30.02, 25.20; IR (neat): ν=1713(C=O), 1601 (aromatic C=C), 1520, 1346 cm^{-1} (NO$_2$); MS: m/e=239 [M$^+$]; anal. calcd. for ($C_{11}H_{13}NO_3S$): C 55.21, H 5.48, N 5.85, S 13.40; found: C 55.25, H 5.56, N 5.78, S 13.43.

3-(4-Nitrobenzylsulfanyl)-propionitrile (5t): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=8.06 (d, J=8.4 Hz, 2H), 7.46 (d, J=8.4 Hz, 2H), 3.83 (s, 2H), 2.66–2.52 (m, 4H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=147.11, 145.31, 129.32, 123.91, 118.36, 35.65, 26.82, 18.66; IR (neat): ν=2249 (CN), 1601 (aromatic C=C), 1520, 1346 cm^{-1} (NO$_2$); MS: m/e=222 [M$^+$]; anal. calcd. for ($C_{10}H_{10}N_2O_2S$): C 54.04, H 4.53, N 12.60, S 14.43; found: C 53.98, H 4.50, N 12.65, S 14.41.

3-(4-Nitrobenzylsulfanyl)-propionic acid butyl ester (5u): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.96 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 3.89 (t, J=6.7 Hz, 2H), 3.71 (s, 2H), 2.54–2.48 (m, 2H), 2.40–2.34 (m, 2H), 1.46–1.35 (m, 2H), 1.24–1.12 (m, 2H), 0.75–0.69 (m, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=171.63, 146.90, 146.10, 129.64, 124.09, 64.57, 35.68, 34.35, 30.52, 26.91, 19.04, 13.62; IR (neat): ν=1732 (C=O), 1601 (aromatic C=C), 1520, 1346 cm^{-1} (NO$_2$); MS: m/e=297 [M$^+$]; anal. calcd. for ($C_{14}H_{19}NO_4S$): C 56.55, H 6.44, N 4.71, S 10.78; found: C 56.60, H 6.40, N 4.73, S 10.72.

3-(4-Nitrobenzylsulfanyl)-butyric acid ethyl ester (5v): Colorless oil; ^{1}H NMR (250 MHz, CDCl$_3$): δ=8.09 (d, J=8.7 Hz, 2H), 7.44 (d, J=8.7 Hz, 2H), 4.03 (q, J=7.1 Hz, 2H), 3.77 (s, 2H), 3.1–2.96 (m, 1H), 2.53 (dd, J=15.5, 6.5 Hz, 1H), 2.36 (dd, J=15.5, 7.8 Hz, 1H), 1.24–1.13 (m, 6H); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ=171.08, 146.95, 146.18, 129.66, 123.75, 60.66, 42.02, 36.21, 34.75, 21.26, 14.18; IR (neat): ν=1732 (C=O), 1601 (aromatic C=C), 1520, 1346 cm^{-1} (NO$_2$); MS: m/e=283 [M$^+$]; anal. calcd. for ($C_{13}H_{17}NO_4S$): C 55.11, H 6.05, N 4.94, S 11.32; found: C 55.17, H 6.02, N 5.01, S 11.37.

3-Decylsulfanylpropionamide (Table 3, entry 1): white solid; mp 97–98 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ=7.19 (S, b, 1H), 6.67 (s, b, 1H), 2.52–2.46 (m, 2H), 2.35–2.29 (m, 2H), 2.19–2.13 (m, 2H), 1.34–1.29 (m, 2H), 1.09 (s, b,14H), 0.73–0.67 (m, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ=172.64, 35.49, 31.27, 30.97, 30.22, 29.03, 28.96, 28.68, 28.62, 28.22, 26.87, 22.06, 13.84; IR (KBr): ν (cm^{-1})=1659 cm^{-1} (C=O); MS: m/e=245 [M$^+$]; anal. calcd. for ($C_{13}H_{27}NOS$): C 63.62, H 11.09, N 5.71, S 13.07; found: C 63.66, H 11.06, N 5.75, S 13.03.

3-Octylsulfanylpropionamide (Table 3, entries 2, 3): white solid; mp 92–93 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ=7.32 (s, b, 1H), 6.81 (s, b, 1H), 2.64–2.58 (m, 2H), 2.48–2.42 (m, 2H), 2.31–2.25 (m, 2H), 1.47–1.44 (m, 2H), 1.22 (s, b, 10H), 0.84–0.80 (m, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ=172.60, 35.50, 31.19, 30.94, 29.02, 28.59, 28.54, 28.20, 26.86, 22.03, 13.88; IR (KBr): ν=1651 cm^{-1} (C=O); MS: m/e=217 [M$^+$]; anal. calcd. for ($C_{11}H_{23}NOS$): C 60.78, H 10.66, N 6.44, S 14.75; found: C 60.72, H 10.71, N 6.47, S 14.70.

3-Propylsulfanylpropionamide (Table 3, entry 6): white solid; mp 59–61 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ=7.35 (s, b, 1H), 6.83 (s, b, 1H), 2.64–2.58 (m, 2H), 2.47–2.39 (m, 2H), 2.32–2.25 (m, 2H), 1.57–1.42 (m, 2H), 0.92–0.85 (m, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ=172.76, 35.49, 32.99, 26.78, 22.31, 13.16; IR (KBr): ν=1659 cm^{-1} (C=O); anal. calcd. for ($C_6H_{13}NOS$): C 48.94, H 8.90, N 9.51, S 21.78; found: C 48.88, H 8.84, N 9.59, S, 21.83.

3-Benzylsulfanylpropionamide (Table 3, entries 7, 8): white solid; mp 104–105 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ=7.29 (s, b, 1H), 7.19–7.02 (m, 5H), 6.80 (s, b, 1H), 3.60 (s, 2H), 2.45 (t, J=7.2 Hz, 2H), 2.23 (t, J=7.2 Hz, 2H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ=172.59, 138.54, 129.03, 128.29, 126.69, 34.97, 34.88, 26.43; IR (KBr): ν=1659 (C=O), 1495 cm^{-1} (aromatic C=C); MS: m/e=195 [M$^+$]; anal. calcd. for ($C_{10}H_{13}NOS$): C 61.50, H 6.71, N 7.17, S 16.42; found: C 61.42, H 6.74, N 7.21, S 16.36.

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