# Micellar Solution of Sodium Dodecyl Sulfate (SDS) Catalyzes Facile Michael Addition of Amines and Thiols to α,β-Unsaturated Ketones in Water under Neutral Conditions

H. Firouzabadi,* N. Iranpoor,* A. A. Jafari

Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, IranFax: (+98)-711-228-6008, (+98)-711-228-0926, e-mail: firouzabadi@chem.susc.ac.ir, iranpoor@chem.susc.ac.ir

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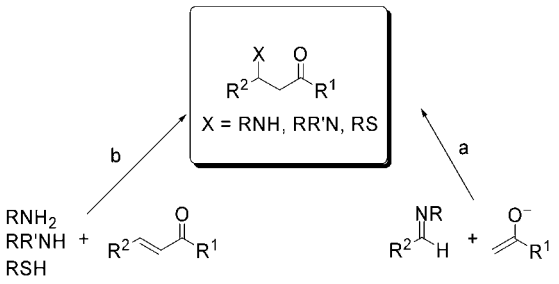
**Abstract:** Sodium dodecyl sulfate (SDS) catalyzes facile Michael additions of amines and thiols to α,β-unsaturated ketones under neutral micellar conditions to afford the corresponding Michael adducts in good to high yields.

**Keywords:** amines; hetero-Michael reaction; micelles; sodium dodecyl sulfate; thiols; α,β-unsaturated ketones

## Introduction

Today's environmental concerns demand clean reaction processes that do not use harmful organic solvents.[1] Moreover, environmental consciousness demands the use of water as a cheap and green solvent for organic processes from both industrial and academic view points.[2,3] Furthermore, water has unique physical and chemical properties, and by utilizing these it would be possible to realize reactivity or selectivity that cannot be attained in organic solvents.[4] However, organic solvents are still used instead of water for mainly two reasons; first, most organic substrates are not soluble in water, and as a result, water cannot function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are sensitive towards water so that they are decomposed or deactivated in aqueous media. A possible new way to improve the solubility of substrates is the use of surface-active reagents that can form micelles[5] or vesicular structures. The use of micellar and vesicle-forming surfactants as catalysts is widespread and has been investigated in detail for different reactions in aqueous solutions.[6,7] However, from the viewpoints of practicability and applicability, the surfactant-aided organic reactions are still at their preliminary stages. Recently we have applied successfully a micellar solution of sodium dodecyl sulfate (SDS) for the ring opening of epoxides with various types of nucleophiles.[8]

β-Aminocarbonyl and β-thiocarbonyl moieties are usually encountered in natural products such as alkaloids and polyketides.[9] β-Aminocarbonyl compounds are also important intermediates for the synthesis of amino alcohols, diamines, and β-amino acid derivatives, many of which serve as powerful antibiotics or other drugs.[10–12] β-Aminocarbonyl compounds can be prepared *via* the reaction of enolates with imines (pathway **a**, Mannich reaction) through carbon-carbon bond formation.[13] Mannich reactions are not usually straightforward reactions which often suffer from harsh reaction conditions, long reaction times and generally need stoichiometric amounts of base to form preactivated enolates.




**Scheme 1.**

For the preparation of β-thiocarbonyl compounds the analogous Mannich reaction **a** does not exist. Alternatively, Michael additions can be used for the generation of carbon-heteroatom bonds by the reaction of α,β-unsaturated carbonyl compounds with amines or thiols[14] to produce β-amino- or β-thiocarbonyl compounds. Hetero-Michael reactions normally require catalytic amounts of a strong base or a Lewis acid[15] to activate either the nucleophile or the acceptor compound which usually results in many side reactions effected by strong acids, e.g., polymerization of vinyl ketones, or bases in the medium. In spite of the vast range of applications of β-amino and β-thio ketones, an easy, clean and high

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yielding method for the preparation of these compounds has still remained a challenging task.

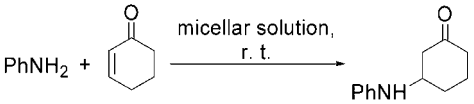
In this article, we report an effective method for the addition of amines and thiols to α,β-unsaturated ketones under mild and neutral conditions to produce β-amino and β-thio ketones in high yields using micellar media.

## Results and Discussion

In order to optimize the reaction conditions, we first studied the reaction of cyclohexenone (1.1 mmol) with aniline (1 mmol) as a model reaction at room temperature in water (5 mL) with stirring (800 rpm). The reaction proceeded sluggishly and after a prolonged reaction time (24 h) the corresponding Michael adduct was produced in 60% yield. We have also studied similar reaction under basic conditions using aqueous $NaHCO_3$ solution (5 mL, 5%). The reaction under such conditions proceeded slowly and the corresponding Michael adduct was isolated in 40–50% yield after 10 h. Then, a similar reaction was performed in micellar media using sodium dodecyl sulfate (SDS) as an anionic micelle, cetyltrimethylammonium bromide (CTAB) as a cationic micelle, and Triton X-100 as a neutral micelle at their critical micelle concentrations (CMC). We observed a drastic rate enhancement when cyclohexenone was reacted with aniline in an aqueous solution of sodium dodecyl sulfate (SDS) at its CMC to produce the desired Michael adduct in 96% yield after 2.5 h. Similar reactions in the presence of cetyltrimethylammonium bromide (CTAB) and Triton X-100 at their critical micellar concentrations (CMC) in water did not proceed to completion even after 24 h and the desired adduct was produced in 83% and 90% yields (GC), respectively, together with unreacted starting materials. Furthermore, we have also studied similar reactions in organic solvents such as acetonitrile and ethanol at room temperature in the presence of SDS. We noticed that SDS cannot efficiently catalyze this reaction in these solvents and the corresponding Michael adduct was produced in 20% yield in acetonitrile and 45% yield in ethanol after 24 h. The results of this study are summarized in Table 1.

In order to show the general applicability of the method, the addition of structurally diverse amines to methyl vinyl ketone and cyclohexenone under similar reaction conditions was studied. By this method, aromatic and aliphatic amines easily reacted with methyl vinyl ketone and cyclohexenone to produce the hetero-Michael adducts within short reaction times in good to excellent yields. The results of this study are tabulated in Table 2. We have also studied the addition of imidazole and pyrimidine as biologically important amines to methyl vinyl ketone and cyclohexenone under similar reaction conditions. Imidazole reacted with methyl vinyl ketone and cyclohexenone cleanly to produce the corresponding Michael adducts in excellent yields. The addition of pyrimidine as a nucleobase to methyl vinyl ketone and cyclohexenone in micellar SDS medium is neither a straightforward nor a smooth reaction. Pyrimidine was added to methyl vinyl ketone to afford the Michael adduct in only 10% plus unreacted starting materials after 24 h. Similarly, addition to cyclohexenone completely failed and the unreacted materials were isolated intact from the reaction mixture after 24 h. In order to solve this problem, we decided to run similar reactions in the presence of $NaHCO_3$ in micellar SDS media. The addition of pyrimidine to methyl vinyl ketone proceeded well under such conditions and the desired Michael adduct was isolated in 94% yield after 1.25 h. However, its addition to cyclohexenone under similar conditions completely failed (Table 2, entries 13–19).

**Table 1.** Results of the reaction of aniline (1 mmol) with cyclohexenone (1.1 mmol) in different media at room temperature.




| Entry | Media | Time [h] | Yields [%] |
|---|---|---|---|
| 1 | Water | 24 | 60 |
| 2 | Micellar SDS solution | 2.5 | 96[a] |
| 3 | Micellar CTAB solution | 24 | 90[b] |
| 4 | Micellar Triton X-100 solution | 24 | 83[c] |
| 5 | $CH_3CN$/SDS | 24 | 25 |
| 6 | EtOH/SDS | 24 | 45 |

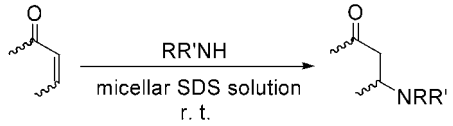
[a] 5 mL of $8.1 \times 10^{-3}$ M (CMC of SDS).
[b] 5 mL of $1.3 \times 10^{-3}$ M (CMC of CTAB).
[c] 5 mL of $3 \times 10^{-4}$ M (CMC of Triton X-100).

In this study, we have also investigated the applicability of the method for the addition of structurally diverse thiols to methyl vinyl ketone and cyclohexenone in the presence of sodium dodecyl sulfate (SDS) at its critical micellar concentration (CMC) in water. The reactions progressed well at room temperature and the desired β-thio ketones were produced rapidly (5–10 min) in high yields except the reaction of benzylideneacetone with thiophenol which was sluggish and, after 24 h, the desired Michael adduct was isolated in only 50% yield (Table 3, entry 4). Through this study, we have also investigated the double Michael addition of dithiols such as 1, 2-ethanedithiol and 1,3-propanedithiol to methyl vinyl ketone and cyclohexenone. The reactions proceeded well and the desired Michael adducts were isolated in 58–80% yields within 0.5–1 h at room temperature (Table 3, entries 11–14). These double Michael adducts are potential precursors for the preparation of macrocyclic or polymeric compounds carrying sulfur atoms.

The catalytic effect of micellar SDS in these reactions can be explained as follows. Thiols, amines and α,β-unsaturated ketones which react to produce β-thio- or β-

**Table 2.** Conjugative addition of various amines to α β-unsaturated ketones in micellar SDS solution at room temperature.



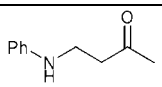
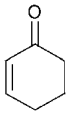
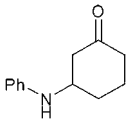
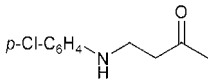
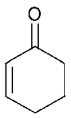
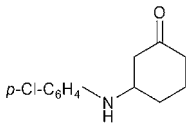
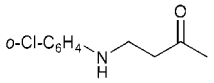
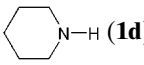
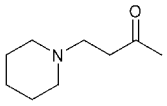
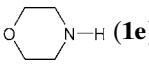
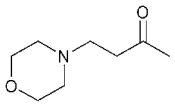
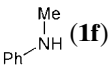
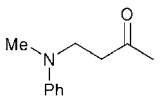
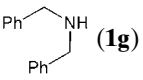
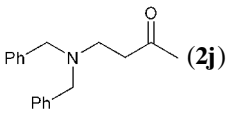
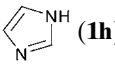
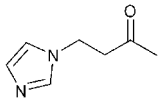
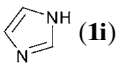
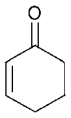
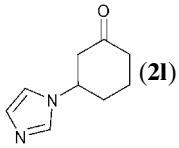
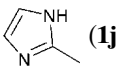
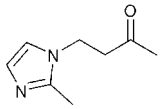
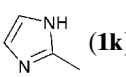
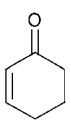
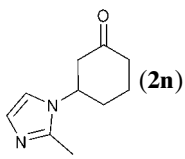
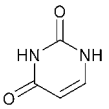
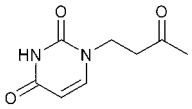

| Entry | Amine | α,β-Unsaturated ketones | Product | Time [h] | Isolated Yield [%] |
|---|---|---|---|---|---|
| 1 | $PhNH_2$ (**1a**) |  |  (**2a**) | 0.25 | 92 |
| 2 | $PhNH_2$ (**1a**) |  |  (**2b**) | 2.5 | 90 |
| 3 | *p*-Cl-$C_6H_4NH_2$ (**1b**) |  |  (**2c**) | 2 | 89 |
| 4 | *p*-Cl-$C_6H_4NH_2$ (**1b**) |  |  (**2d**) | 15 | 83 |
| 5 | *o*-Cl-$C_6H_4NH_2$ (**1c**) |  |  (**2e**) | 2 | 85 |
| 6 |  (**1d**) |  |  (**2g**) | 0.1 | 91 |
| 7 |  (**1e**) |  |  (**2h**) | 0.1 | 93 |
| 8 |  (**1f**) |  |  (**2i**) | 1.5 | 95 |
| 9 |  (**1g**) |  |  (**2j**) | 0.25 | 98 |
| 10 |  (**1h**) |  |  (**2k**) | 0.5 | 87 |
| 11 |  (**1i**) |  |  (**2l**) | 10 | 80 |
| 12 |  (**1j**) |  |  (**2m**) | 0.25 | 72 |
| 13 |  (**1k**) |  |  (**2n**) | 15 | 65 |

**Table 2** (cont.)

| Entry | Amine | α,β-Unsaturated ketones | Product | Time [h] | Isolated Yield [%] |
|---|---|---|---|---|---|
| 14 |  **(1l)** |  |  **(2o)** | 1.25 | 94[a] |

[a] The reaction proceeded in 5 mL of $NaHCO_3$ (5%) solution that contains micellar SDS solution at its CMC ($8.1 \times 10^{-3}$ M) at room temperature.

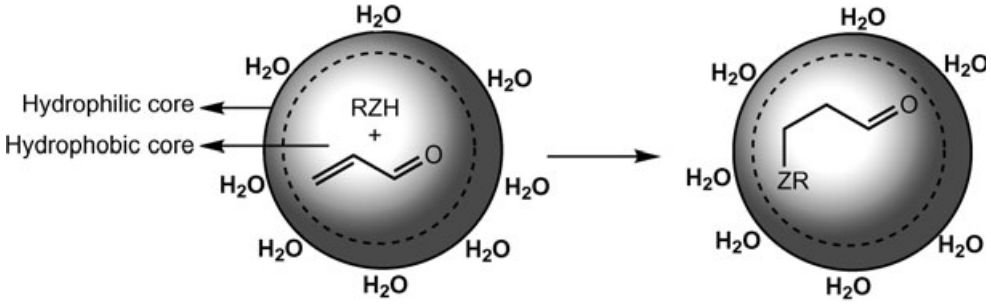



**Figure 1.** The function of micellar SDS droplets is shown for hetero-Michael reactions in aqueous media.

aminocarbonyl compounds are hydrophobic molecules in aqueous media. In the micellar solution of SDS, the hydrophobic moieties escape away from water molecules which encircle the micelle core of SDS. However, they are pushed by water to go inside the hydrophobic core of the micelle droplets, where the reactions take place more easily. This explanation is schematically presented by Figure 1.

## Conclusion

In summary, we have described the use of sodium dodecyl sulfate (SDS) as a powerful catalyst in aqueous media for C–X (X=S and N) bond formation in water *via* Michael addition to produce β-amino and β-thio ketones in high yields at room temperature. We have used SDS at its critical micellar concentration (CMC) in all reactions. The use of water as a cheap and environmentally benign solvent is of great importance from both industrial and academic points of view. Thus, in this protocol water has been used as a media for the formation of selective hetero-Michael adducts.

## Experimental Section

### General Procedure for the Synthesis of Hetero-Michael Adducts

To a micellar solution of SDS (5 mL), at the CMC concentration (CMC of SDS = $8.1 \times 10^{-3}$ M), was added an α,β-unsaturated ketone (1.1 mmol), an amine (1 mmol) or a thiol (1 mmol) at room temperature. The mixture was stirred vigorously (800 rpm) and monitored by TLC or GC until the starting material had been consumed. Then the mixture extracted with ethyl acetate (10 mL), dried over $Na_2SO_4$, and concentrated. Purification by silica gel chromatography afforded the desired products in 58–98% yields.

**4-(Methylphenylamino)-butan-2-one (2i):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 7.24–7.12 (m, 2H), 6.82–6.55 (m, 3H), 3.6 (t, 2H), 2.88 (s, 3H), 2.65 (t, 2H), 2.32.17 (s, 3H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 207.95, 148.63, 129.25, 116.61, 112.44, 47.25, 40.56, 38.42, 30.63; IR: ν = 1710 (C=O) $cm^{-1}$; MS: *m/e* = 177 $[M]^+$; anal. calcd. for $C_{11}H_{15}NO$: C 74.54, H 8.53; found: C 74.51, H 8.53.

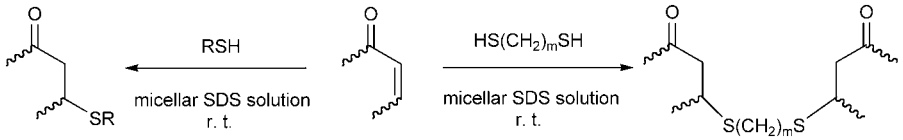
**4-(2-Methylimidazol-1-yl)-butan-2-one (2m):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 6.86 (d, 1H), 6.82 (d, 1H), 4.11 (t, 2H), 2.87 (t, 2H), 2.38 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 205.55, 144.77, 127.68, 119.37, 44.2, 40.43, 30.68, 13.29; IR: ν = 1710 (C=O) $cm^{-1}$; MS: *m/e* = 152 $[M]^+$; anal. calcd. for $C_8H_{12}N_2O$: C 63.13, H 7.95; found: C 63.08, H 7.93.

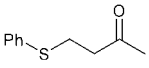
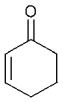
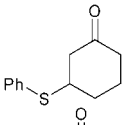
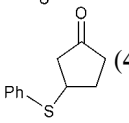
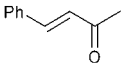
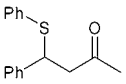
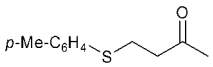
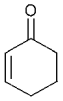
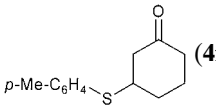
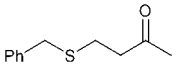
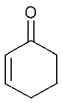
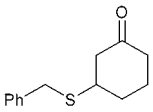
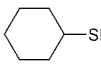
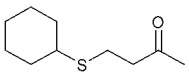
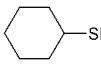
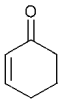
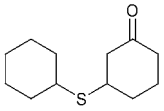
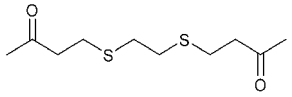
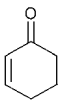
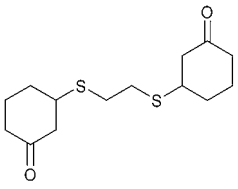
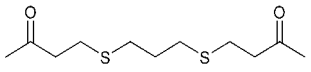
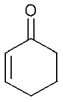
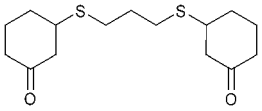
**3-(2-Methylimidazol-1-yl)-cyclohexanone (2n):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 6.94 (dd, 2H), 4.27 (m, 1H), 2.71–2.64 (m, 2H), 2.46–2.35 (m, 5H), 2.2–2.0 (m, 3H), 1.82–1.74 (m, 1H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 207.5, 151.3, 130.1, 115.48, 54.4, 48.9, 40.74, 32.3, 25.96, 22.35, 13.43; IR: ν = 1705 (C=O) $cm^{-1}$; MS: *m/e* = 178 $[M]^+$; anal. calcd. for $C_{10}H_{14}N_2O$: C 67.39, H 7.92; found: C 67.18, H 7.9.

**1-(3-Oxobutyl)-1*H*-pyrimidine-2,4-dione (2o):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 11.11 (s, 1H), 7.53 (d, 1H), 5.52 (d, 1H), 3.88 (t, 2H), 2.92 (t, 2H), 2.12 (s, 3H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 211.6, 169.5, 156.4, 151.3, 106.3, 48.97, 45.73, 35.2; IR: ν = 1700 (C=O) $cm^{-1}$; MS: *m/e* = 182 $[M]^+$; anal. calcd. for $C_8H_{10}N_2O_3$: C 52.73, H 5.53; found: C 52.61, H 5.49.

**4-Phenyl-4-phenylsulfanylbutan-2-one (4d):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 7.5–7.7 (m, 3H), 7.15–7.3 (m, 7H),

**Table 3.** Conjugative addition of thiols (1 mmol) to α,β-unsaturated ketones (1.1 mmol) in 5 mL micellar SDS solution at its CMC ($8.1 \times 10^{-3}$ M)] at room temperature.




| Entry | Thiol | α,β-Unsaturated ketone | Product | Time [min] | Isolated yields [%] |
|---|---|---|---|---|---|
| 1 | PhSH (**3a**) |  |  (**4a**) | 5 | 92 |
| 2 | PhSH (**3a**) |  |  (**4b**) | 5 | 96 |
| 3 | PhSH (**3a**) |  |  (**4c**) | 5 | 90 |
| 4 | PhSH (**3a**) |  |  (**4d**) | 24 [h] | 50 |
| 5 | *p*-$MeC_6H_4SH$ (**3b**) |  |  (**4e**) | 5 | 96 |
| 6 | *p*-$MeC_6H_4SH$ (**3b**) |  |  (**4f**) | 10 | 91 |
| 7 | $PhCH_2SH$ (**3c**) |  |  (**4g**) | 5 | 91 |
| 8 | $PhCH_2SH$ (**3c**) |  |  (**4h**) | 10 | 94 |
| 9 |  (**3d**) |  |  (**4i**) | 5 | 87 |
| 10 |  (**3d**) |  |  (**4j**) | 10 | 90 |
| 11 |  (**3e**) |  |  (**4k**) | 30 | 80[a] |
| 12 |  (**3e**) |  |  (**4l**) | 60 | 61[a] |
| 13 |  (**3f**) |  |  (**4m**) | 30 | 73[a] |
| 14 |  (**3f**) |  |  (**4n**) | 60 | 58[a] |

[a] Isolated yields after column chromatography. The molar ratio of α,β-unsaturated ketones:dithiols is 1:2.2.

4.6 (t, 1H), 2.8–3.1 (dd, 2H), 2.15 (s, 3H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 205.88, 141.51, 137.43, 133.28, 129.44, 129.22, 129.05, 128.18, 128.06, 49.89, 48.45, 30.71; IR: ν = 1710 (C=O) $cm^{-1}$; MS: *m/e* = 256 $[M]^+$; anal. calcd. for $C_{16}H_{16}OS$: C 74.96, H 6.29; found: C 75.2, H 6.28.

**4-Cyclohexylsulfanylbutan-2-one (4i):** $^1$H NMR( $CDCl_3$, 250 MHz): δ = 2.75–2.73 (dd + m, 5H), 2.17–2.18 (m, 2H), 2.00 (m, 2H), 1.77 (m, 2H), 1.63 (m, 1H), 1.30 (m, 6H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 207.25, 44.08, 34.34, 30.74, 26.10, 24.10; IR: ν = 1710 (C=O) $cm^{-1}$; MS: *m/e* = 186 $[M]^+$; anal. calcd. for $C_{10}H_{18}OS$: C 64.47, H 9.74; found: C 64.48, H 9.74.

**3-Cyclohexylsulfanylcyclohexanone (4j):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 3.15 (m, 1H), 2.71–2.64 (m, 2H), 2.41–2.31 (m, 3H), 2.15–2.11 (m, 2H), 1.92 (m, 2H), 1.74–1.63 (m, 5H), 1.35–1.28 (m, 5H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 209.11, 49.00, 42.36, 41.38, 34.51, 33.11, 26.28, 25.61; IR: ν = 1700 (C=O) $cm^{-1}$; MS: *m/e* = 212 $[M]^+$; anal. calcd. for $C_{12}H_{20}OS$: C 67.88, H 9.49; found: C 67.25, H 9.48.

**4-[2-(3-Oxobutylsulfanyl)-ethylsulfanyl]-butan-2-one (4k):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 2.76–2.70 (m, 12H), 2.18 (s, 6H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 207.00, 43.97, 32.63, 30.45, 26.01; IR: ν = 1710 (C=O) $cm^{-1}$; MS: *m/e* = 234 $[M]^+$; anal. calcd. for $C_{10}H_{18}O_2S_2$: C 51.25, H 7.74; found: C 51.19, H 7.72.

**3-[2-(3-Oxocyclohexylsulfanyl)-ethylsulfanyl]-cyclohexane-1-one (4l)** (Table 2, Entry 3): $^1$H NMR ($CDCl_3$, 250 MHz): δ = 3.20–3.10 (m, 2H), 2.76 (m, 4H), 2.7–2.65 (m, 2H), 2.42–2.32 (m, 6H), 2.16–2.13 (m, 4H), 1.74–1.70 (m, 4H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 208.53, 48.27, 42.68, 41.09, 31.74, 30.91, 24.25; IR: ν = 1700 (C=O) $cm^{-1}$; MS: *m/e* = 286 $[M]^+$; anal. calcd for $C_{14}H_{22}O_2S_2$: C 58.70, H 7.74; found: C 58.64, H 7.73.

**4-[3-(3-Oxobutylsulfanyl)-propylsulfanyl]-butan-2-one (4m):** $^1$H NMR ($CDCl_3$, 250 MHz): δ = 2.74 (m, 8H), 2.62 (m, 4H), 2.18 (s, 6H), 2.18 (t, 2H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 207.13, 43.91, 31.33, 30.43, 29.34, 26.00; IR: ν = 1710 (C=O) $cm^{-1}$; MS: *m/e* = 248 $[M]^+$; anal. calcd. for $C_{11}H_{20}O_2S_2$: C 53.19, H 8.12; found: C 53.15, H 8.11.

**3-[3-(3-Oxocyclohexylsulfanyl)-propylsulfanyl]-cyclohexane-1-one (4n)** (Table 2, Entry 4): $^1$H NMR ($CDCl_3$, 250 MHz): δ = 3.01–3.00 (m, 2H), 2.74–2.62 (t + m, 6H), 2.42–2.33 (m, 6H), 2.17–2.12 (m, 4H), 1.87–1.69 (m, 6H); $^{13}$C NMR ($CDCl_3$, 63 MHz): δ = 209.10, 48.47, 43.24, 41.28, 31.93, 29.74, 29.725, 24.51; IR: ν = 1700 (C=O) $cm^{-1}$; MS: *m/e* = 300 $[M]^+$; anal. calcd. for $C_{15}H_{24}O_2S_2$: C 59.96, H 8.05; found: C 59.92, H 8.02.

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