A Clean, Facile, and Stereospecific Synthesis of α-Oxoketene *O*,*S*-Acetals in Water

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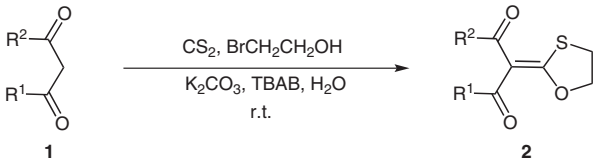
Abstract: A facile and practical method for the stereospecific synthesis of α-oxoketene *O*,*S*-acetals in water has been developed. Catalyzed by tetrabutylammonium bromide at room temperature, the one-pot reaction of various β-dicarbonyl compounds, 2-bromoethanol, and carbon disulfide, in the presence of potassium carbonate, leads to the corresponding α-oxoketene *O*,*S*-acetals stereospecifically in good to excellent yields. The catalyst in the aqueous phase can be recycled after the separation of the organic products.

Key words: α-oxoketene *O*,*S*-acetals, one-pot synthesis, stereospecificity, tetrabutylammonium bromide, water

Over the past decades, the utility of α-oxoketene *S*,*S*-acetals as versatile intermediates[1] and odorless thiol equivalents[2] in organic synthesis has been recognized. In contrast, the chemistry of α-oxoketene *O*,*S*-acetals has remained largely unexplored. Generally, α-oxoketene *O*,*S*-acetals are prepared via alkylation of xanthates[3] or displacement of the alkylsulfanyl group of an α-oxoketene dithioacetal by a alkoxy group.[4] However, these methods require a two-step operation starting from an active methylene compound. Although it has been reported that α-oxoketene *O*,*S*-acetals can be prepared directly from β-dicarbonyl compounds, 2-bromoethanol, and carbon disulfide under basic conditions, the product yields were relatively low (24–58%) because the corresponding α-oxoketene *S*,*S*-acetals were formed as the byproducts (18–26%).[5] In a recent report by Vila and co-workers, some α-EWG ketene *O*,*S*-acetals (EWG = electron-withdrawing group) and analogues were synthesized from the reaction of dithiocarbonates (xanthates) with base and an alkylating agent through extrusion of sulfur.[6] However, inseparable mixtures of geometrical isomers were observed when two different EWGs were present in the starting xanthates. In this paper, we would like to report a facile and practical method for the synthesis of α-oxoketene *O*,*S*-acetals. As a result, α-oxoketene *O*,*S*-acetals **2** were synthesized stereospecifically from the reaction of β-dicarbonyl compounds **1**, carbon disulfide, and 2-bromoethanol under basic conditions in a one-pot procedure with water as the solvent (Scheme 1).



Scheme 1

The use of water as a solvent in organic chemistry was rediscovered in the 1980s in Breslow's work, which showed that a hydrophobic effect can strongly enhance the rates of some organic reactions.[7] Organic reactions in water, without the use of an organic solvent, also benefit from the fact that water is an easily available, inexpensive, safe, and environmentally benign solvent. Later, extensive work revealed that a variety of organic reactions[8] including the aldol,[9a] allylation,[9b] Diels–Alder,[9c] Michael,[9d] Mannich-type,[9e] and even dehydration reactions[9f] can be realized in the presence of various catalysts, such as inverse phase-transfer catalysts and surfactant-type Lewis or Brønsted acids, in water. As part of our research on the chemistry of α-EWG ketene *S*,*S*-acetals[10–13] and encouraged by our recent report on their clean syntheses,[13] herein, the successfully synthesis of α-oxoketene *O*,*S*-acetals in water is realized.

In the initial experiment, we first tested the reaction by mixing *N*-(2-methoxyphenyl)-3-oxobutanamide (**1a**, 1.0 equiv) with carbon disulfide (1.1 equiv), 2-bromoethanol (1.2 equiv), potassium carbonate (4.0 equiv), and tetrabutylammonium bromide (0.1 equiv) in water (10 mL); after 12 hours at room temperature, the desired *N*-(2-methoxyphenyl)-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (**2a**) was obtained in 61% yield together with the corresponding dithioacetal **3a** (Table 1, entry 1) as a byproduct in 11% yield. To optimize the reaction conditions, several reactions were carried out and the results are listed in Table 1. It was found that the feed order of the reagents had a substantial effect on the dispersion of product (Table 1, entries 1–3). For example, following the procedure described in our previous work,[13a] the reaction was performed with **1a** (1.0 equiv) and carbon disulfide (1.1 equiv) in the presence of potassium carbonate (4.0 equiv) and tetrabutylammonium bromide (0.1 equiv) in water (10 mL) at room temperature for one hour and subsequent alkylation with 2-bromoethanol (1.2 equiv) for another 12 hours to afford the desired **2a** in 35% yield and the corresponding dithioacetal **3a** in 60% yield (Table 1, entry 2). When the mixture of **1a** (1.0 equiv), potassium carbonate (4.0 equiv), tetrabutylammonium bromide (0.1 equiv), and water (10 ml) was stirred at room temperature for one

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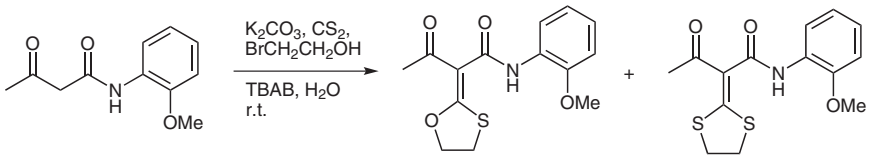
Table 1 Reaction of **1a** with Carbon Disulfide and 2-Bromoethanol in Water under Different Conditions[a]



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

Entry	TBAB (mmol)	K_2CO_3 (mmol)	H_2O (mL)	Time (h)	Yield (%)	
					2a[b]	**3a**
1	0.5	20	10	12	61	11
2	0.5	20	10	13	35	60
3	0.5	20	10	14	81	trace
4	0.5	15	10	18	61[c]	trace
5	0.5	25	10	14	82	trace
6	1.25	20	10	12	80	trace
7	0.25	20	10	16	54[d]	trace
8	0.0	20	10	24	0	trace
9	2nd use[e]	20	0	14	78	0
10	3nd use[f]	20	0	14	77	trace
11	4nd use[g]	20	0	15	70	trace

[a] **1a** (5 mmol), CS_2 (6 mmol), 2-bromoethanol (5.5 mmol) were added in all the reactions.
[b] Isolated yields.
[c] The substrate was recovered in 36% yield.
[d] The substrate was recovered in 29% yield.
[e] Aqueous filtrate from entry 3.
[f] Aqueous filtrate from entry 9.
[g] Aqueous filtrate from entry 10.

hour and subsequent co-addition of carbon disulfide (1.1 equiv) and 2-bromoethanol (1.2 equiv) in one portion and then stirred for 13 hours, product **2a** was obtained in 81% yield with a trace amount of **3a** (entry 3). It was also found that 4.0 equiv of potassium carbonate and 10 mol% of tetrabutylammonium bromide was enough to provide **2a** efficiently (entries 4–8). In addition, the catalyst (TBAB) can be recycled, at least several times, by reuse of the aqueous phase after the separation of organic products (entries 9–11). Surprisingly, **2a** was found to be the only regioisomer (*Z*-configuration) with OCH_2 *cis* to the acetyl group as observed in its X-ray diffraction analysis (Figure 1).[14]

To test the general applicability of this protocol, a series of active methylene compounds **1b**–**p** were selected for investigation. Subjected to the optimized reaction conditions as described in Table 1, entry 3, acetylacetamide compounds **1a**–**j** (Table 2, entries 1–10) were converted into the corresponding *O*,*S*-acetals **2a**–**j** in high yields. In addition, the *O*,*S*-acetals **2k**–**p** (Table 2, entries 11–16) were obtained in moderate to good yields starting from active methylene compounds **1k**–**p**. It is worth noting that products **2k**–**m** were also formed stereospecifically (*Z* or *E* configuration).

Based on the experimental results mentioned above, a possible mechanism for the reaction of **1** with carbon disulfide and 2-bromoethanol is proposed as shown in Scheme 2. The intermediate 1,3-oxathiolane-2-thione **A** is initially generated in the presence of potassium carbonate. Next nucleophilic attack of the deprotonated active methylene compounds **4** on **A** occurs to form intermediate **6**, which could be stabilized by the intramolecular

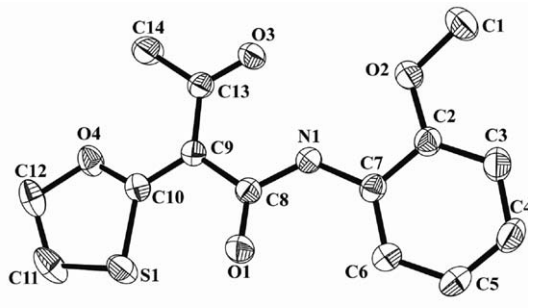
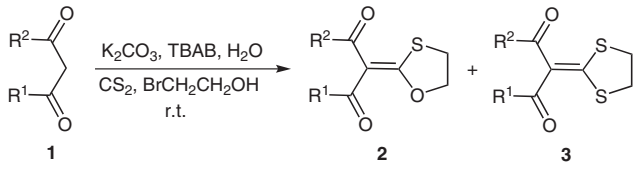


Figure 1 The ORTEP drawing of **2a**

Table 2 Preparation of α-Oxoketene *O*,*S*-Acetals **2** from Active Methylene Compounds **1** in Water



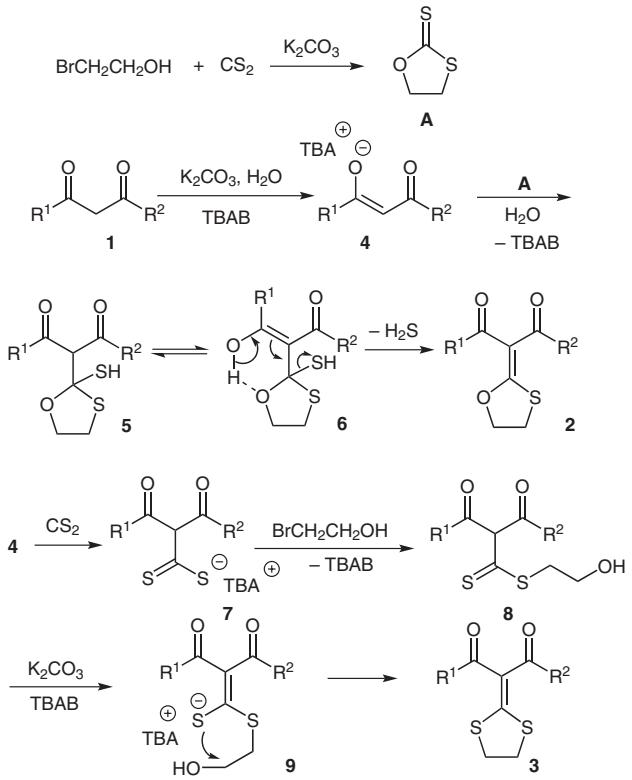
1 2 3

Entry	Product	R^1	R^2	Time (h)	Yield (%) of **2**/**3**[a]
1	**2a**	Me	2-$MeOC_6H_4NH$	14	81/–[b]
2	**2b**	Me	2-ClC_6H_4NH	12	82/–[b]
3	**2c**	Me	2-MeC_6H_4NH	12	86/–[b]
4	**2d**	Me	NHPh	13	80/–[b]
5	**2e**	Me	4-ClC_6H_4NH	15	82/–[b]
6	**2f**	Me	4-MeC_6H_4NH	13	76/–[b]
7	**2g**	Me	4-$MeOC_6H_4NH$	16	81/–[b]
8	**2h**	Me	2,4-$Me_2C_6H_3NH$	14	80/–[b]
9	**2i**	Me	NHMe	12	67/10
10	**2j**	Me	NH_2	13	70/8
11	**2k**	Me	OEt	22	65/12
12	**2l**	Me	Ph	20	70/10
13	**2m**	Ph	OEt	14	63/13
14	**2n**	Me	Me	20	60/12
15	**2o**	OEt	OEt	22	32/18
16	**2p**	Ph	Ph	19	54/16

[a] Isolated yields.
[b] A trace amount of **3** was detected.

O–H···O bond. The subsequent elimination of H_2S affords (*Z*)-*O*,*S*-acetals **2**. Further evidence for the formation of the intermediate **A**[15] in the above proposed mechanism was provided by the reaction of carbon disulfide (1.0 equiv) and 2-bromoethanol (1.0 equiv) in the presence of potassium carbonate (2.2 equiv) and tetrabutylammonium bromide (0.1 equiv) in water. As a result, **A** was obtained in 44% isolated yield. In addition, **2a** was obtained in 28% yield when the reaction of intermediate **A** (1.0 equiv) and **1a** (1.0 equiv) was performed in the presence of potassium carbonate (2.2 equiv) and tetrabutylammonium bromide (0.1 equiv) in water for one hour. On the other hand, the intermediate **4** reacted with carbon disulfide and 2-bromoethanol to provide intermediate **8** and, thus, lead to the formation of *S*,*S*-acetals **3** as byproducts.

In summary, a clean, facile, practical and stereospecific synthesis of α-oxoketene *O*,*S*-acetals has been developed based on the reaction of active methylene compounds with carbon disulfide and 2-bromoethanol catalyzed by tetrabutylammonium bromide in the presence of potassium carbonate in water. The simple procedure, mild conditions, good yields, and, especially, the relation to the current environmental concerns, make this protocol most attractive for academic research and practical applications.



Scheme 2 A proposed mechanism for the reaction of **1** with carbon disulfide and 2-bromoethanol in the presence of tetrabutylammonium bromide and potassium carbonate in water

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel; PE = petroleum ether. ^1H NMR and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively, with TMS as internal standard. IR spectra (KBr) were recorded on a FTIR spectrophotometer in the range of 400–4000 cm^{-1}. Compounds **2k**,**l**,**n**,**o** are known compounds.[5]

(*Z*)-*N*-(2-Methoxyphenyl)-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (2a); Typical Procedure

3-Oxo-*N*-phenylbutanamide **1a** (0.885 g, 5 mmol), K_2CO_3 (2.758 g, 20 mmol), and TBAB (0.161 g, 0.5 mmol) were dissolved in H_2O (10 mL) at r.t. and stirred for 1.0 h. Then the mixture of CS_2 (0.456 g, 6 mmol) and 2-bromoethanol (0.682 g, 5.5 mmol) was added dropwise. The resulting mixture was stirred for another 13.0 h at r.t. The precipitated solid was collected by filtration, washed with H_2O (3 × 10 mL). The crude product was purified by flash column chromatography (PE–Et_2O, 1:2) to afford **2a** (1.186 g, 81%) as a white solid; mp 124–126 °C.

IR (KBr): 2360, 1646, 1362, 1119, 746 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 3.17 (t, *J* = 7.0 Hz, 2 H), 3.94 (s, 3 H), 4.73 (t, *J* = 7.0 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 1 H), 6.94 (d, *J* = 8.0 Hz, 1 H), 7.00 (d, *J* = 8.0 Hz, 1 H), 8.44 (d, *J* = 8.0 Hz, 1 H), 11.68 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.8, 33.0, 55.8, 74.3, 107.9, 110.0, 120.4, 120.7, 123.2, 128.5, 148.9, 164.1, 186.1, 197.2.

MS (EI): *m*/*z* = 294.0 $[M + 1]^+$.

Anal. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.15; N, 4.77. Found: C, 57.20; H, 4.98; N, 4.51.

(*Z*)-*N*-(2-Chlorophenyl)-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (2b)
White solid; mp 144–146 °C.

IR (KBr): 3105, 3002, 1360, 1652, 1452, 1082, 935 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 3.20 (t, *J* = 7.5 Hz, 2 H), 4.77 (t, *J* = 7.5 Hz, 2 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 8.45 (d, *J* = 8.5 Hz, 1 H), 11.89 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9, 33.1, 74.6, 107.4, 122.2, 123.7, 123.9, 127.1, 129.1, 135.8, 164.5, 187.0, 197.2.

MS (EI): *m*/*z* = 298.2 $[M + 1]^+$.

Anal. Calcd for $C_{13}H_{12}ClNO_3S$: C, 52.44; H, 4.06; N, 4.70. Found: C, 52.09; H, 4.27; N, 4.95.

(*Z*)-2-(1,3-Oxathiolan-2-ylidene)-3-oxo-*N*-(2-tolyl)butanamide (2c)
White solid; mp 120–122 °C.

IR (KBr): 3248, 3038, 2917, 1654, 1305, 1074, 753 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.55 (s, 3 H), 3.17 (t, *J* = 7.0 Hz, 2 H), 4.75 (t, *J* = 7.0 Hz, 2 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 7.17 (d, *J* = 7.0 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 1 H), 8.12 (d, *J* = 8.0 Hz, 1 H), 11.33 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.3, 29.9, 33.19, 74.5, 107.5, 121.9, 123.8, 126.3, 128.3, 130.1, 136.8, 164.2, 186.8, 197.5.

MS (EI): *m*/*z* = 278.1 $[M + 1]^+$.

Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.35; H, 5.28; N, 5.21.

(*Z*)-2-(1,3-Oxathiolan-2-ylidene)-3-oxo-*N*-phenylbutanamide (2d)
White solid; mp 110–112 °C.

IR (KBr): 3032, 2919, 1651, 1302, 1078, 754 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 3.18 (t, *J* = 7.5 Hz, 2 H), 4.74 (t, *J* = 7.5 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 7.30 (t, *J* = 7.0 Hz, 2 H), 7.61 (t, *J* = 8.0 Hz, 2 H), 11.41 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.1, 33.4, 74.7, 107.6, 120.7 (2 C), 123.9, 129.0 (2 C), 138.7, 164.5, 186.9, 197.7.

MS (EI): *m*/*z* = 264.0 $[M + 1]^+$.

Anal. Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.32. Found: C, 59.57; H, 4.62; N, 5.14.

(*Z*)-*N*-(4-Chlorophenyl)-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (2e)
White solid; mp 171–173 °C.

IR (KBr): 2359, 1646, 1539, 1302, 1077, 935 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 3.19 (t, *J* = 7.0 Hz, 2 H), 4.76 (t, *J* = 7.0 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 7.57 (d, *J* = 8.5 Hz, 2 H), 11.49 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.2, 33.4, 74.8, 107.5, 121.9 (2 C), 128.7, 128.9 (2 C), 137.4, 164.6, 187.1, 197.7.

MS (EI): *m*/*z* = 298.1 $[M + 1]^+$.

Anal. Calcd for $C_{13}H_{12}ClNO_3S$: C, 52.44; H, 4.06; N, 4.70. Found: C, 52.06; H, 4.24; N, 4.98.

(*Z*)-2-(1,3-Oxathiolan-2-ylidene)-3-oxo-*N*-(4-tolyl)butanamide (2f)
White solid; mp 152–154 °C.

IR (KBr): 1645, 1455, 1310, 1079, 937 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.53 (s, 3 H), 3.15 (t, *J* = 7.5 Hz, 2 H), 4.72 (t, *J* = 7.5 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 11.32 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8, 29.9, 33.1, 74.4, 107.5, 120.5 (2 C), 129.3 (2 C), 133.2, 135.9, 164.1, 186.4, 197.4.

MS (EI): *m*/*z* = 278.2 $[M + 1]^+$.

Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.39; H, 5.20; N, 5.31.

(*Z*)-*N*-(4-Methoxyphenyl)-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (2g)
White solid; mp 136–138 °C.

IR (KBr): 1641, 1452, 1236, 1079, 639 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 3.16 (t, *J* = 7.0 Hz, 2 H), 3.78 (s, 3 H), 4.73 (t, *J* = 7.0 Hz, 2 H), 6.84 (d, *J* = 9.0 Hz, 2 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 11.25 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9, 33.1, 55.4, 74.4, 107.4, 113.9 (2 C), 122.2 (2 C), 131.7, 155.9, 164.0, 186.3, 197.4.

MS (EI): *m*/*z* = 294.3 $[M + 1]^+$.

Anal. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.15; N, 4.77. Found: C, 57.16; H, 4.88; N, 4.81.

(*Z*)-*N*-(2,4-Dimethylphenyl)-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (2h)
White solid; mp 84–86 °C.

IR (KBr): 1653, 1539, 1360, 1073, 938 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 2.31 (s, 3 H), 2.56 (s, 3 H), 3.18 (t, *J* = 7.5 Hz, 2 H), 4.75 (t, *J* = 7.0 Hz, 2 H), 7.00 (d, *J* = 6.0 Hz, 2 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 11.20 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.1, 20.8, 29.9, 33.1, 74.4, 107.6, 122.2, 126.8, 128.5, 130.8, 133.5, 134.3, 154.9, 164.2, 197.5.

MS (EI): *m*/*z* = 292.1 $[M + 1]^+$.

Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.55; H, 5.97; N, 4.63.

(*Z*)-*N*-Methyl-2-(1,3-oxathiolan-2-ylidene)-3-oxobutanamide (2i)
Light yellow solid; mp 136–138 °C.

IR (KBr): 3303, 1647, 1490, 1276, 1176, 1084, 632 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 2.87 (s, 3 H), 3.14 (t, *J* = 7.5 Hz, 2 H), 4.70 (t, *J* = 7.5 Hz, 2 H), 9.13 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.9, 29.8, 33.0, 73.1, 107.2, 166.7, 185.3, 197.1.

MS (EI): *m*/*z* = 202.1 $[M + 1]^+$.

Anal. Calcd for $C_8H_{11}NO_3S$: C, 47.75; H, 5.51; N, 6.96. Found: C, 47.42; H, 5.63; N, 7.09.

(*Z*)-2-(1,3-Oxathiolan-2-ylidene)-3-oxobutanamide (2j)
White solid; mp 178–180 °C.

IR (KBr): 3415, 1613, 1455, 1267, 1081 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.18 (t, *J* = 7.5 Hz, 2 H), 4.75 (t, *J* = 7.0 Hz, 2 H), 5.50 (s, 1 H), 8.94 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9, 33.0, 74.4, 107.0, 168.1, 186.0, 196.5.

MS (EI): *m*/*z* = 188.1 [M + 1]$^+$.

Anal. Calcd for $C_7H_9NO_3S$: C, 44.91; H, 4.85; N, 7.48. Found: C, 45.02; H, 4.97; N, 7.63.

Ethyl 2-(1,3-Oxathiolan-2-ylidene)-3-oxo-3-phenylpropanoate (2m)

White solid; mp 60–62 °C.

IR (KBr): 3060, 2907, 2341, 1595, 1386, 1014, 930 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.5 Hz, 3 H), 3.26 (t, *J* = 7.0 Hz, 2 H), 4.11 (q, *J* = 7.0 Hz, 2 H), 4.48 (t, *J* = 7.0 Hz, 2 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.53 (t, *J* = 7.0 Hz, 1 H), 7.85 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 30.6, 60.5, 73.8, 103.8, 128.3 (2 C), 129.0 (2 C), 132.8, 138.1, 166.5, 175.8, 191.5.

MS (EI): *m*/*z* = 279.0 [M + 1]$^+$.

Anal. Calcd for $C_{14}H_{14}O_4S$: C, 60.42; H, 5.07. Found: C, 60.58; H, 4.92.

2-(1,3-Oxathiolan-2-ylidene)-1,3-diphenylpropane-1,3-dione (2p)

White solid; mp 155–157 °C.

IR (KBr): 1647, 1616, 1595, 1256, 1004, 536 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.27 (t, *J* = 7.0 Hz, 2 H), 4.55 (t, *J* = 7.0 Hz, 2 H), 7.20 (t, *J* = 7.0 Hz, 2 H), 7.27 (t, *J* = 7.0 Hz, 1 H), 7.33 (t, *J* = 7.5 Hz, 2 H), 7.43 (d, *J* = 7.5 Hz, 1 H), 7.48 (d, *J* = 7.5 Hz, 2 H), 7.79 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.4, 74.1, 113.2, 128.2 (2 C), 128.3 (2 C), 128.5 (2 C), 129.5 (2 C), 131.4, 133, 138.9, 139.7, 180.0, 191.6, 193.6.

MS (EI): *m*/*z* = 311.0 [M + 1]$^+$.

Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55. Found: C, 69.95; H, 4.37.

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(14) Crystal data for **3d**: $C_{14}H_{15}NO_4S$, white needle crystals, *M* = 293.33, monoclinic, *C*2/*c*, *a* = 15.640(5) Å, *b* = 8.249(5) Å, *c* = 23.035(5) Å, α = 90.000(5)°, β = 106.460(5)°, γ = 90.000(5)°, *V* = 2850(2) Å^3, *Z* = 8, *T* = 293(2) K, F_{000} = 1232, R_1 = 0.0490, ωR_2 = 0.1237. The CCDC deposition number 661621.

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