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Reactions of 5-Methylene-1,3-thiazolidine-2-thione and 5-Methylene-2-oxazolidinone with Isocyanates Catalyzed by Bases

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ABSTRACT: *5-Methylene-1,3-thiazolidine-2-thione and 5-methylene-2-oxazolidinone can react with isocyanates to give the corresponding condensed urethanes in high yields in the presence of organic or inorganic bases under mild reaction conditions.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:610–616, 2001

INTRODUCTION

We have found that 5-methylene-1,3-thiazolidine-2-thione (**1**) can be prepared in high yield by the reaction of propargylamine with carbon disulfide in the presence of a palladium catalyst (Scheme 1). Also, a mixture of 5-methylene-2-oxazolidinone (**2**) and compound **3** can be obtained by the reaction of propargylamine with carbon dioxide in the presence of a palladium catalyst. We then investigated the reaction of **1** and **2**/**3** with isocyanates in the presence of a catalyst. Organic isocyanates readily react with compounds containing an acidic hydrogen, such as acids, alcohols, and amines, to produce the corresponding carbamate derivatives [1]. Most of these transformations are subject to catalysis by bases, acids, or certain metal compounds [1,2], of which tertiary amines and tin carboxylates have been used on a large scale in the industrial production of polyurethanes from diisocyanates and polyalcohols [2c,f]. However, the reactions of amides or carbamates with an isocyanate are, in general, very difficult to carry out. Only some very special amides or carbamates can react with isocyanates under basic conditions [3]. Recently, Blass reported a KF/Al_2O_3 mediated method for the synthesis of substituted oxazolidinones [4]. Herein, we wish to report the reactions of **1** and **2**/**3** with isocyanates in the presence of very common organic or inorganic bases.

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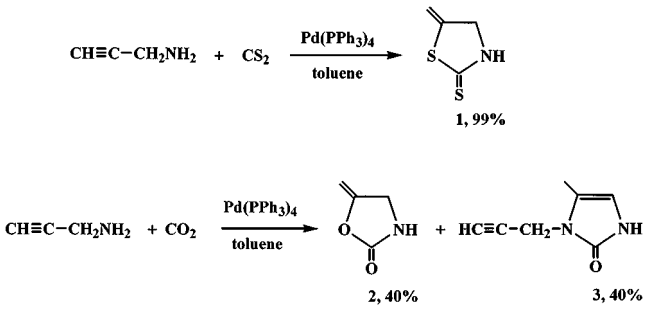
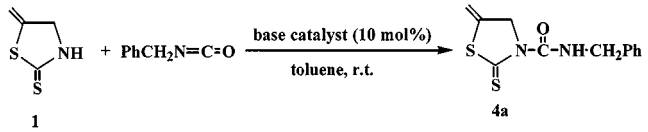
RESULTS AND DISCUSSION

We found that 5-methylene-1,3-thiazolidine-2-thione (**1**) can react with benzyl isocyanate in the presence of triethylamine (Et_3N) or K_2CO_3 (10 mol%) to give the condensed product **4a** in excellent yields under mild reaction conditions (Scheme 2, Table 1, entries 1 and 4). The use of other organic bases, such as 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), diethylamine (Et_2NH), and condensing reagents, such as 1,3-dicyclohexylcarbodiimide (DCC) or 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCL) gave only low or moderate yields of **4a** (Table 1, entries 2–5). No reactions occurred without the base catalysts. Thus, the reactions of **1** with other isocyanates were examined in the presence of Et_3N or K_2CO_3 (10 mol%) (Scheme 3, Table 2). We found that **1** can react with an aliphatic isocyanate to give the condensed product **4b** in high yield at room temperature (Scheme 3, Table 2, entries 1 and 2). However, as can be seen from Table 2,



SCHEME 1

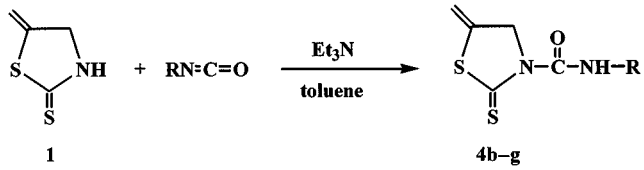


SCHEME 2

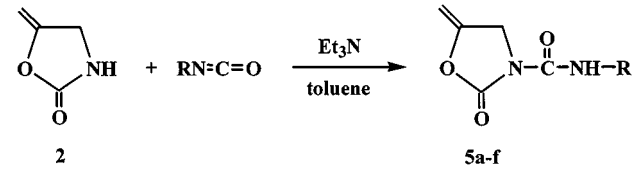
aromatic isocyanates required a higher temperature to affect the reaction, and the condensed products could be obtained in 64–95% yield at 60°C (Scheme 3, Table 2, entries 3–8). Hanefild and coworkers have reported the synthesis of **1** in 88% yield by the direct reaction of propargylamine with carbon disulfide. A subsequent acylation of **1** with an acyl chloride could be carried out under basic conditions [5]. Recently, acylated thioamides (**4**) and related compounds have been shown to be potential antituberculotics [6]. In our reaction system, we have found that, by use of a catalytic amount of a very common tertial amine as a base, compounds **4** can be easily synthesized from the reaction of **1** with isocyanates.

Reactions of 5-methylene-2-oxazolidinones (**2**) with isocyanates in the presence of Et_3N or K_2CO_3 (10 mol%) were also examined (Scheme 4). The aliphatic isocyanates gave the final products **5** in high yields at room temperature and the aromatic isocyanates gave the products in high yields at 60°C. The results are summarized in Table 3.

In reactivity comparisons of **1** and **2** with isocyanates, we found that **2** is more reactive than **1**. Furthermore, we also found that **3** can react with



SCHEME 3



SCHEME 4

benzyl isocyanate in toluene in the presence of Et_3N at 60°C to give the corresponding condensed compound **6** in moderate yield (Scheme 5). It should be emphasized here that only one isomer of **4a–g** and **5a–f** was formed during the earlier reactions, owing to the N—C bond of the carbamate having double bond character. This has been determined to be the endo-form by X-ray analysis. From the crystal structures of **4a** and **5a** (Figs. 1 and 2), it is very clear

TABLE 1 Base Catalyzed Reactions of 5-Methylene-1,3-thiazolidine-2-thione (**1**) with Benzylisocyanate

Entry	*Base*	*Isolated yield [%]*
1	Et_3N	98
2	Et_2NH	10
3	DBU	2
4	K_2CO_3	94
5	DCC	85
6	EDCL	77

TABLE 2 Et_3N Catalyzed Reactions of 5-Methylene-1,3-thiazolidine-2-Thione (**1**) with Isocyanates

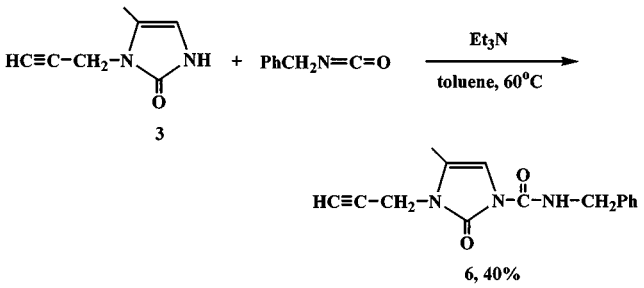
Entry	*Isocyanates RN=C=O*	*Temp. [°C]*	*Product*	*Isolated yield [%]*
1	$CH_3(CH_2)_{17}$	20	**4b**	98
2	$CH_3(CH_2)_{17}$	20	**4b**	98[a]
3	*p*-MeOPh	60	**4c**	87
4	*p*-MeOPh	60	**4c**	87[a]
5	*m*-MeOPh	60	**4d**	75
6	*o*-EtOPh	60	**4e**	95
7	*p*-ClPh	60	**4f**	80
8	2,4-$(Meo)_2$Ph	60	**4g**	68

[a]Using K_2CO_3 (10 mol%) as a catalyst.

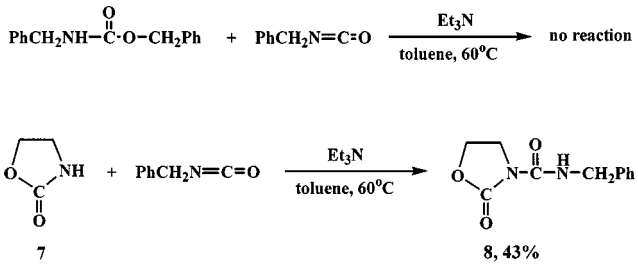
TABLE 3 Et_3N Catalyzed Reactions of 5-Methylene-2-oxazolidinone (**2**) with Isocyanates

Entry	*Isocyanates RN=C=O*	*Temp. [°C]*	*Product*	*Isolated yield [%]*
1	$PHCH_2$	20	**5a**	98
2	$PHCH_2$	20	**5a**	98[a]
3	$CH_3(CH_2)_{17}$	20	**5b**	97
4	*p*-MeOPh	60	**5c**	90
5	*m*-MeOPh	60	**5d**	80
6	*o*-EtOPh	60	**5e**	95
7	*p*-ClPh	60	**5f**	95

[a]The reaction was catalyzed by K_2CO_3.



SCHEME 5



SCHEME 6

that an intramolecular hydrogen bond between the carbonyl oxygen atom or thiocarbonyl sulfur atom and the hydrogen atom of the amide to form a six-membered ring is a driving force to give the endo-form configuration (Fig. 3).

In order to clarify the scope and limitations of these novel base catalyzed reactions of carbamates with isocyanates, we attempted to carry out the reaction of linear amides with isocyanates. However, we found that no reaction could take place under the same reaction conditions (Scheme 6). For the cyclic carbamate **7**, the reaction could take place, but the condensed product **8** was obtained in only 43% yield (Scheme 6).

In conclusion, we have discovered a novel reaction of cyclic carbamates with isocyanates that take place in the presence of base catalysts and under mild reaction conditions.

EXPERIMENTAL SECTION

General

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hertz. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo–Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash Column Chromatography was carried out using 200–300 mesh silica gel.

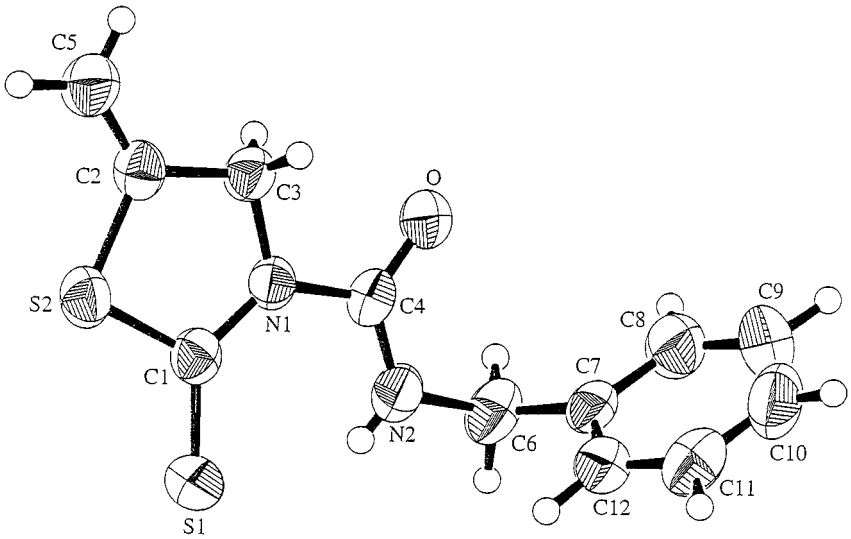


FIGURE 1 The crystal structure of **4a** [7].

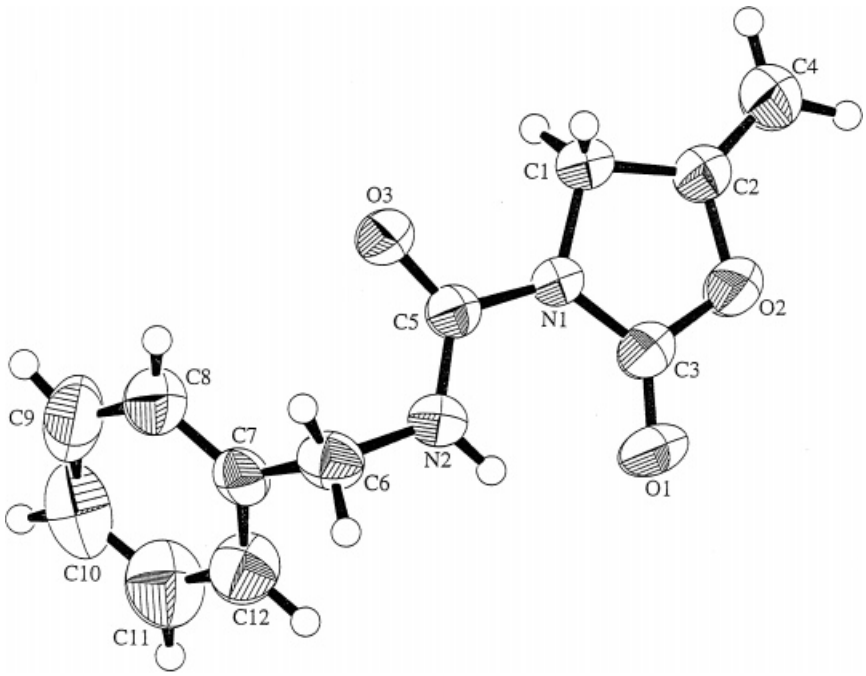


FIGURE 2 The crystal structure of **5a** [8].

FIGURE 3 The intermolecular hydrogen bond of **4a** and **5a**.

A General Procedure for the Formation of Cyclic Enol Carbamate 1[5]

The Formation of 1. To a solution of propargylamine (500 mg, 9.1 mmol) and carbon disulfide (800 mg, 10.5 mmol) in anhydrous toluene (15 ml) was added a catalytic amount of $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and triphenylphosphine (PPh_3) (5.24 mg, 0.02 mmol) and the reaction mixture was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give **1** as a white solid: 1189 mg, 99%; m.p. 120–121°C; IR ($CHCl_3$) ν 1626, 1490, 902 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.67 (2H, t, $J = 2.7$ Hz, CH_2), 5.14 (1H, dd, $J = 5.4$, 2.7 Hz, CH_2), 5.24 (1H, dd, $J = 4.8$, 2.4 Hz, CH_2), 7.96 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 57.05, 105.67, 141.13, 199.11 (C=S); MS (EI) m/z 131 (M^+) [Calc. for $C_4H_6NS_2$ (132.2292): requires M, 131.9942. Found: M^+ 131.9954].

A General Procedure for the Formation of the Cyclic Enol Carbamate 2 and Cyclic Urethane 3

The Formation of 2. To a solution of propargylamine (550 mg, 10 mmol) in anhydrous toluene (20 ml) was added a catalytic amount of $Pd(PPh_3)_4$ (45 mg, 0.05 mmol) and triphenylphosphine (PPh_3) (13 mg, 0.05 mmol), and the reaction mixture was stirred at room temperature under a carbon dioxide atmosphere for 24 h. The solution was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give **2** as a white solid. This solid was further recrystallized from dichloromethane/petroleum ether = 1/4 to afford a crystal: 395 mg, 40%; m.p. 50–52°C; IR ($CHCl_3$) ν 1780 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 4.10–4.30 (2H, dd, $J = 1.8$ 1.0, CH_2), 4.31 (1H, dd, $J = 2.11$ 0.86 Hz, CH_2), 4.78 (1H, dd, $J = 2.9$ 2.2 Hz, CH_2), 5.77 (1H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 44.35, 86.86, 151.34, 157.64 (C=O); MS (EI) m/z 100 (100) $(MH)^+$, 71 (24.71) ($M^+ - 28$), 43 (66.17) ($M^+ - 56$); HRMS (EI) m/z 99.0321, $C_4H_5NO_2$ requires M, 99.0320; Anal. Calc. For $C_4H_5NO_2$: C, 48.48, H, 5.05, N, 14.14. Found: C, 48.39, H, 5.03, N, 14.15.

The Formation of 3. This compound was obtained as a white solid at the same time in the preparation of **2** as that described earlier: 543 mg, 40%; m.p. 122–124°C; IR ($CHCl_3$) ν 1682 cm^{-1} (C=O);

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.14 (3H, s, CH_3), 2.24 (1H, dd, $J = 2.6$, 2.2 Hz, CH), 4.42 (2H, d, $J = 2.6$ Hz, CH_2), 6.02 (1H, s, CH), 9.90 (1H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 10.22, 29.87, 71.87, 78.26, 104.43, 119.44, 154.33 (C=O); MS (EI) m/z 136 (100) (M^+), 97 (63.98) ($M^+ - 39$), 42 (28.98) ($M^+ - 94$); Anal. Calc. For $C_7H_8N_2O$: C, 61.76, H, 5.88, N, 20.59. Found: C, 61.66, H, 6.14, N, 20.67.

A General Procedure for the Base-Catalyzed Reactions of Cyclic Carbamate 1 with Isocyanate

To a 50 ml round bottom flask with a magnetic stir bar containing 5-methylene-1,3-thiazolidine-2-thione (**1**) (52 mg, 0.40 mmol) in toluene (10 ml), benzyl isocyanate (60 mg, 0.44 mmol) and triethylamine (4.0 mg, 0.040 mmol) were added, and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/5) to give **4a** as a white solid: 103 mg, 98%; m.p. 40–42°C; IR ($CHCl_3$) ν 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.53 (2H, d, $J = 5.6$ Hz, CH_2), 5.07 (1H, dd, $J = 5.1$, 2.7 Hz, CH), 5.25 (3H, d, $J = 2.4$ Hz, CH), 7.26–7.36 (5H, m, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 44.53, 62.00, 105.22, 127.49, 127.51, 128.66, 134.03, 137.27, 151.81 (C=O), 197.49 (C=S); MS (EI) m/z 264 (M^+) [Calc. for $C_{12}H_{12}N_2OS_2$ (264.3686): requires M, 264.0391. Found: M^+ 264.0386].

The Formation of Compound **4b**. A white solid, 96 mg, 98%; m.p. 76–78°C; IR ($CHCl_3$) ν 1705 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.88 (3H, t, $J = 6.3$ Hz, CH_3), 1.19–1.31 (30H, m, CH_2), 1.52–1.59 (2H, m, CH_2), 3.32 (2H, q, $J = 6.8$ Hz, CH), 5.07 (1H, dd, $J = 5.1$, 2.6 Hz, CH_2), 5.25 (3H, d, $J = 2.5$ Hz, CH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.11, 22.69, 26.97, 29.10, 29.18, 29.37, 29.49, 29.57, 29.64, 29.70, 31.93, 40.74, 62.10, 105..08, 134.26, 151.76 (C=O), 197.33 (C=S); MS (EI) m/z 426 (M^+) [Calc. for $C_{23}H_{42}N_2OS_2$ (426.7245): requires M, 426.2739. Found: M^+ 426.2713].

The Formation of Compound **4c**. A white solid, 97 mg, 87%; m.p. 104–106°C; IR ($CHCl_3$) ν 1705 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.79 (3H, s, OCH_3), 5.11 (1H, dd, $J = 5.0$, 2.6 Hz, CH), 5.30 (3H, d, $J = 4.3$ Hz, CH), 6.85–6.89 (2H, m, Ar), 7.39–7.42 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 55.51, 62.03, 105.52, 114.37, 122.29, 129.62, 133.61, 149.26, 156.92 (C=O), 197.13 (C=S); MS (EI) m/z 280 (M^+) [Calc. for $C_{12}H_{12}N_2O_2S_2$ (280.3680): requires M, 280.0340. Found: M^+ 280.0351].

The Formation of Compound **4d**. A white solid, 84 mg, 75%; m.p. 106–108°C; IR ($CHCl_3$) ν 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.82 (3H, s, OCH_3), 5.13 (1H, dd, $J = 5.2$, 2.6 Hz, CH), 5.33 (3H, d, $J = 2.6$ Hz, CH), 6.70 (1H, dd, $J = 8.2$, 1.9 Hz, Ar), 7.04 (1H, dd, $J = 6.7$, 1.3 Hz, Ar), 7.20 (1H, dd, $J = 4.4$, 2.2 Hz, Ar), 7.26 (1H, d, $J = 7.8$ Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 55.31, 61.91, 105.58, 106.17, 110.67, 112.72, 129.77, 133.41, 137.82, 146.89, 160.20 (C=O), 197.79 (C=S); MS (EI) m/z 280 (M^+) [Calc. for $C_{12}H_{12}N_2O_2S_2$ (280.3680): requires M, 280.0340. Found: M^+ 280.0338].

The Formation of Compound **4e**. A white solid, 112 mg, 95%; m.p. 117–119°C; IR ($CHCl_3$) ν 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.45 (3H, t, $J = 7.0$ Hz, CH_3), 4.09 (2H, q, $J = 7.0$ Hz, CH_2), 5.10 (1H, dd, $J = 5.0$, 2.6 Hz, CH), 5.29 (1H, dd, $J = 4.8$, 2.4 Hz, CH), 5.33 (2H, dd, $J = 5.0$, 2.4 Hz, CH), 6.89 (1H, td, $J = 8.1$, 1.3 Hz, Ar), 6.95 (1H, td, $J = 7.7$, 1.3 Hz, Ar), 7.08–7.25 (1H, m, Ar), 8.22 (1H, ddd, $J = 8.1$, 6.6, 1.6 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 15.05, 29.72, 62.11, 64.52, 105.24, 111.29, 120.42, 120.78, 125.04, 126.68, 134.15, 148.50 (C=O), 197.22 (C=S); MS (EI) m/z 294 (M^+) [Calc. for $C_{13}H_{14}N_2S_2O_2$ (294.3945): requires M, 294.0497. Found: M^+ 294.0483].

The Formation of Compound **4f**. A white solid, 91 mg, 80%; m.p. 152–154°C; IR ($CHCl_3$) ν 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 5.13 (1H, dd, $J = 5.0$, 2.5 Hz, CH), 5.31 (3H, d, $J = 2.4$ Hz, CH), 7.25–7.32 (2H, m, Ar), 7.42–7.51 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 61.88, 105.80, 121.67, 128.59, 129.19, 132.21, 133.29, 135.32, 148.98 (C=O), 198.03 (C=S); MS (EI) m/z 285 (MH)$^+$ [Calc. for $C_{11}H_9N_2OClS_2$ (284.7867): requires M, 283.9845. Found: M^+ 283.9839].

The Formation of Compound **4g**. A slight yellow solid, 84 mg, 68%; m.p. 116–118°C; IR ($CHCl_3$) ν 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.80 (3H, s, OMe), 3.88 (3H, s, OMe), 5.09 (1H, dd, $J = 5.0$, 2.6 Hz, CH_2), 5.28 (1H, dd, $J = 4.6$, 2.3 Hz, CH), 5.31 (2H, dd, $J = 5.0$, 2.4 Hz, CH_2), 6.49 (2H, dt, $J = 6.7$, 2.2 Hz, Ar), 8.03 (1H, s, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 55.51, 55.84, 62.08, 98.84, 98.90, 103.91, 121.55, 126.68, 134.12, 148.98, 150.65, 157.13 (C=O), 198.83 (C=S); MS (EI) m/z 310 (MH)$^+$ [Calc. for $C_{13}H_{14}N_2O_3S_2$ (310.3939): requires M, 310.0446. Found: M^+ 310.0442].

The Formation of Compound **5a**. A white solid, 92 mg, 98%; m.p. 83–85°C; IR ($CHCl_3$) ν 1780 and 1702 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.49 (2H, d, $J = 5.7$ Hz, CH_2), 4.49 (1H, dd, $J = 4.1$, 2.2 Hz, CH_2), 4.63 (2H, t, $J = 2.4$ Hz, CH_2), 4.88 (1H, dd, $J = 6.3$, 2.7 Hz, CH_2), 7.26–7.38 (5H, m, Ar), 7.98 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 44.19, 46.23, 88.91, 127.63, 127.69, 128.77, 137.63, 147.30, 150.63 (C=O), 153.23 (C=O); MS (EI) m/z 232 (M^+) [Calc. for $C_{12}H_{12}N_2O_3$ (232.2354): C, 62.06; H, 5.21; N, 12.06%; Found: C, 61.90, H, 5.23, N, 11.97%].

The Formation of Compound **5b**. A white solid, 155 mg, 97%; m.p. 80–82°C; IR ($CHCl_3$) ν 1780 and 1704 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.85 (3H, t, $J = 7.0$ Hz, CH_3), 1.16–1.27 (30H, m, CH_2), 1.32–1.60 (2H, m, CH_2), 3.27 (2H, q, $J = 7.0$ Hz, CH_2), 4.32 (1H, dd, $J = 4.3$, 1.6 Hz, CH_2), 4.57 (2H, t, $J = 2.3$ Hz, CH_2), 4.84 (1H, dd, $J = 5.6$, 2.9 Hz, CH_2); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) ν 14.13, 22.71, 26.83, 29.26, 29.38, 29.53, 29.58, 29.60, 29.66, 29.72, 31.95, 40.34, 46.22, 88.67, 147.41, 150.52 (C=O), 153.27 (C=O); MS (EI) m/z 395 (MH^+) [Calc. for $C_{23}H_{42}N_2O_3$ (394.5913): requires M, 394.3195. Found: M^+ 394.3190].

The Formation of Compound **5c**. A white solid, 90 mg, 90%; m.p. 116–118°C; IR ($CHCl_3$) ν 1778 and 1704 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.81 (3H, s, OCH_3), 4.54 (1H, dd, $J = 4.0$, 2.2 Hz, CH_2), 4.69 (2H, t, $J = 2.3$ Hz, CH_2), 4.94 (1H, dd, $J = 6.3$, 2.7 Hz, CH_2), 6.88–6.92 (2H, m, Ar), 7.39–7.42 (2H, m, Ar), 9.48 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 46.17, 55.51, 89.23, 114.34, 122.03, 129.65, 147.05, 148.51, 153.02 (C=O), 156.79 (C=O); MS (EI) m/z 248 (M^+) [Calc. for $C_{12}H_{12}N_2O_4$ (248.2348): requires M, 248.0797. Found: M^+ 248.0796].

The Formation of Compound **5d**. A white solid, 80 mg, 80%; m.p. 116–118°C; IR ($CHCl_3$) ν 1770 and 1713 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.80 (3H, s, OCH_3), 4.52 (1H, dd, $J = 3.9$, 2.2 Hz, CH_2), 4.66 (2H, t, $J = 2.4$ Hz, CH_2), 4.92 (1H, dd, $J = 5.8$, 3.0 Hz, CH_2), 6.68 (1H, dt, $J = 8.1$, 0.8 Hz, Ar), 7.0 (1H, dd, $J = 8.1$, 1.3 Hz, Ar), 7.10–7.30 (2H, m, Ar), 9.62 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 46.07, 55.31, 89.26, 105.61, 110.46, 112.15, 129.80, 137.90, 146.93, 147.77, 153.28 (C=O), 160.24 (C=O); MS (EI) m/z 248 (M^+) [Calc. for $C_{12}H_{12}N_2O_4$ (248.2348): requires M, 248.0797. Found: M^+ 248.0779].

The Formation of Compound **5e**. A white solid, 101 mg, 95%; m.p. 117–119°C; IR ($CHCl_3$) ν 1780 and 1704 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.48 (3H, t, $J = 7.0$ Hz, CH_3), 4.08 (2H, q, $J = 7.0$ Hz, CH_2), 4.49 (1H, dd, $J = 4.1$, 2.3 Hz, CH_2), 4.66 (2H, t, $J = 2.3$ Hz, CH_2), 4.89 (1H, dd, $J = 6.1$, 2.8 Hz, CH_2), 6.90 (1H, dt, $J = 6.5$, 1.3 Hz, Ar), 6.93 (1H, dd, $J = 7.9$, 1.4 Hz, Ar), 7.02 (1H, dt, $J = 6.1$, 1.6 Hz, Ar), 8.15 (1H, dd, $J = 8.0$, 1.6 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.75, 46.14, 64.54, 88.98, 111.35, 119.35, 120.92, 123.99, 127.10, 147.19, 147.73, 147.94 (C=O), 153.01 (C=O); MS (EI) m/z 262 (M^+) [Calc. for $C_{13}H_{14}N_2O_4$: requires C, 59.54%, H, 5.34%, N, 10.68%. Found: C, 59.46%, H, 5.51%, N, 10.73%].

The Formation of Compound **5f**. A white solid, 98 mg, 95%; m.p. 162–164°C; IR ($CHCl_3$) ν 1778 and 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.54 (1H, dd, $J = 4.1$, 2.2 Hz, CH_2), 4.67 (2H, t, $J = 2.4$ Hz, CH_2), 4.94 (1H, dd, $J = 6.3$, 2.8 Hz, CH_2), 7.26–7.32 (2H, m, Ar), 7.42–7.47 (2H, m, Ar), 9.65 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 46.06, 89.49, 121.20, 129.16, 129.69, 135.31, 146.80, 147.82 (C=O), 153.31 (C=O); MS (EI) m/z 252 (M^+) [Calc. for $C_{11}H_9N_2O_3Cl$ (252.6535): requires M, 252.0302. Found: M^+ 252.0299].

The Formation of Compound **6**. A white solid, 43 mg, 40%; m.p. 123–125°C; IR ($CHCl_3$) ν 1713 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.17 (3H, s, CH_3), 2.30 (1H, t, $J = 2.1$ Hz, CH), 4.41 (2H, d, $J = 2.3$ Hz, CH_2), 4.45 (2H, d, $J = 5.8$ Hz, CH_2), 6.74 (1H, s, CH), 6.91–7.37 (5H, m, Ar), 8.92 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 10.0, 30.18, 43.90, 72.61, 104.07, 119.77, 127.43, 127.55, 128.64, 137.88, 150.09 (C=O), 151.60 (C=O); MS (EI) m/z 269 $(MH)^+$ [Calc. for $C_{15}H_{15}N_3O_2$ (269.2986): requires M, 269.1164. Found: M^+ 269.1165].

The Formation of Compound **8**. A white solid, 43 mg, 43%; m.p. 66–68°C; IR ($CHCl_3$) ν 1691 and 1749 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 3.91 (2H, dd, $J = 8.6$, 7.2 Hz, CH_2), 4.25 (2H, dd, $J = 8.6$, 7.2 Hz, CH_2), 4.42 (2H, d, $J = 5.9$ Hz, CH_2), 7.19–7.32 (5H, m, Ar), 8.14 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 42.10, 43.57, 62.09, 127.12, 127.17, 128.31, 137.84, 151.41 (C=O), 155.43 (C=O); MS (EI) m/z 220 (M^+) [Calc. for $C_{11}H_{12}N_2O_3$ (220.2247): requires M, 220.0848. Found: M^+ 220.1165].

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[7] X-Ray Crystallographic Analysis of **4a**: All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a 12 kW rotating anode generator. The data were collected at a temperature of 20°C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1951 observed reflections ($I > 3.00\ \sigma(I)$) and 155 variable parameters and converged with unweighted and weighted agreement factors. The crystal data of **4a**: Empirical formula: $C_{12}H_{12}ON_2S_2$; Formula Weight: 264.36; Crystal Color, Habit: colorless, prismatic; Crystal dimensions: $0.20 \times 0.20 \times 0.30$ mm; Crystal system: triclinic; Lattice type: primitive; Lattice parameters: $a = 10.769(1)$ Å, $b = 12.311(3)$ Å, $c = 4.7820(7)$ Å, $\alpha = 97.06(1)°$, $\beta = 97.17(1)°$, $\gamma = 88.61(1)°$, $V = 624.2(2)$ Å^3; Space group: $P\bar{1}$(#2); $Z_{value} = 2$; $D_{calc.} = 1.406$ g/cm^3; $F_{000} = 276.00$; μ(Mo Kα) = 4.10 cm^{-1}; Temperature of data collection: 20°C; Residuals: R; $R_w = 0.054$; 0.064.

[8] X-Ray Crystallographic Analysis of **5a**: All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a 12 kW rotating anode generator. The data were collected at a temperature of 20°C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1454 observed reflections ($I > 2.00\ \sigma(I)$) and 155 variable parameters and converged with unweighted and weighted agreement factors. The crystal data of **5a**: Empirical formula: $C_{12}H_{12}N_2O_3$; Formula Weight: 232.24; Crystal Color, Habit: colorless, primitive; Crystal dimensions: 0.20 × 0.20 × 0.30 mm; Crystal system: triclinic; Lattice type: primitive; Lattice parameters: $a = 10.621(2)$ Å, $b = 12.393(3)$ Å, $c = 4.4400(9)$ Å, $\alpha = 92.72(2)°$, $\beta = 95.09(2)°$, $\gamma = 96.77(2)°$, $V = 577.1(2)$ Å^3; Space group: $P\bar{1}$(#2); $Z_{value} = 2$; $D_{calc.} = 1.336$ g/cm^3; $F_{000} = 244.00$; μ (Mo Kα) = 0.98 cm^{-1}; Temperature of data collection: 20°C; Residuals: R; $R_w = 0.040$; 0.045.