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Facile *S*-alkyl thiocarbamate synthesis by a novel DBU-assisted carbonylation of amines with carbon monoxide and sulfur

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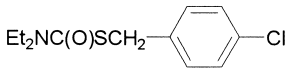
Abstract—A novel DBU-assisted carbonylation of amines with carbon monoxide and sulfur has been developed for the synthesis of *S*-alkyl thiocarbamates. In the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), *S*-alkyl thiocarbamates are synthesized in excellent yields from amines, carbon monoxide, sulfur, and alkyl halides under mild conditions (1 atm, 20°C). In the absence of DBU, however, no formation of *S*-alkyl thiocarbamate is observed. The present DBU-assisted carbonylation can also be applied to new synthetic methods for benthiocarb and orthobencarb (herbicides) and carbamoyl chlorides.

1. Introduction

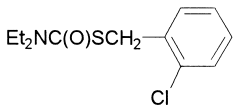
Carbonylation of primary amines with carbon monoxide and sulfur to form urea derivatives was introduced by Franz and Applegath in 1961.[1–3] Furthermore, Grisley and Stephens developed *S*-alkyl thiocarbamate (**1**) synthesis from secondary amines, carbon monoxide, sulfur, and alkyl halides in similar manners.[4,5] However, these reactions require high temperature and pressurized carbon monoxide.

In 1989, our research group has found that selenium exhibits an excellent catalytic activity toward the carbonylation of amines with carbon monoxide and sulfur. This selenium-catalyzed carbonylation of amines (**2**) smoothly proceeds under mild conditions to give thiocarbamate salts (**3**), and the alkylation of which leads to the formation of *S*-alkyl thiocarbamates (**1**) in excellent yields.[7,8]

Owing to the toxicity of elemental selenium, however, use of this preparative method is considerably limited for industrial large-scale production of *S*-alkyl thiocarbamates, some of which are used as herbicides (e.g. benthiocarb (**1d**) and orthobencarb (**1e**)).[9]



Benthiocarb, **1d**



Orthobencarb, **1e**

Therefore, in our strategy, we explored a new and useful route to the *S*-alkyl thiocarbamates under mild conditions.

Recently, we reported the sulfur-assisted carbonylation of alcohols,[12,13] amides,[14] and ketones[15] with carbon monoxide using DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as a base. Herein, we wish to report a facile synthesis of *S*-alkyl thiocarbamates (**1**) from amines, carbon monoxide, sulfur, and alkyl halides under mild conditions (1 atm, 20°C), strongly assisted by DBU.

2. Results and discussion

Our trial employing DBU as a base, which is cheap and commercially available, leads to a successful carbonylation of di-*n*-propylamine (**2a**) with carbon monoxide and sulfur. Di-*n*-propylamine (**2a**) easily reacts with carbon monoxide (1 atm) and sulfur (1.5 equiv.) at 20°C for 18 h in the presence of DBU (1.5 equiv.) in THF. The resulting

Keywords: *S*-alkyl thiocarbamates; DBU; carbon monoxide; sulfur; carbonylation.

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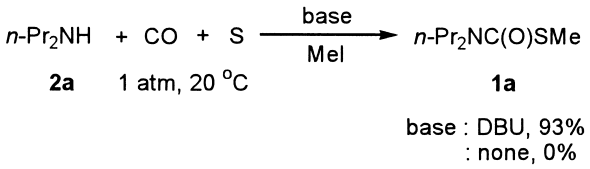
Table 1. Influence of bases (1.5 equiv.) on the synthesis of **1a**

Entry	Base	Yield (%)
1	DBU[a]	93
2	DBU	88[b]
3	DBN[c]	94
4	DBA–DBU[d]	99
5	K_2CO_3	68
6	Dabco[e]	11
7	Et_3N	0
8	*N*-Methylpyrrolidine	0
9	NaOH	39
10	KOH	0
11	Na_2CO_3	0
12	$NaHCO_3$	0
13	None	0[f]

[a] 1,8-Diazabicyclo[5.4.0]undec-7-ene.
[b] 4 h.
[c] 1,5-Diazabicyclo[4.3.0]non-5-ene.
[d] 6-Dibutylamino-1,8-diazabicyclo[5.4.0]undec-7-ene.
[e] 1,4-Diazabicyclo[2.2.2]octane.
[f] Di-*n*-propylamine (**2a**) (2.0 equiv.) was used.

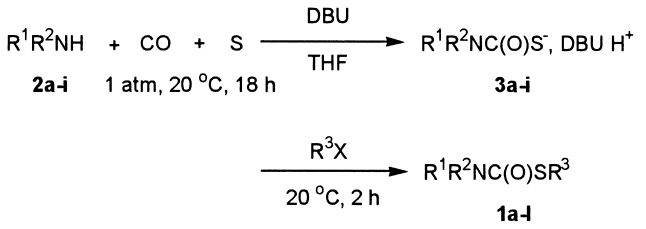
thiocarbamate salt (**3a**) in THF solution is esterified by methyl iodide (1.5 equiv.) under an ambient pressure at 20°C for 2 h. Finally, *S*-methyl *N*,*N*-di-*n*-propylthiocarbamate (**1a**) is obtained in 93% yield. In the absence of DBU, however, **1a** is not obtained at all (Eq. (1)).



(1)

The influence of bases on this carbonylation of di-*n*-propylamine (**2a**) with carbon monoxide and sulfur is examined (Table 1). When strong bases such as DBU, DBN (1,5-diazabicyclo[4.3.0]non-5-ene), and DBA–DBU (6-dibutylamino-1,8-diazabicyclo[5.4.0]undec-7-ene) are employed for this carbonylation, *S*-methyl *N*,*N*-di-*n*-propylthiocarbamate (**1a**) is obtained in excellent yields (93–99%) (entries 1, 3, and 4). Shorter reaction time (4 h) provides the almost same yield (88%) of **1a** (entry 2). K_2CO_3 also affords **1a** in fairly good yields (68%) (entry 5). In contrast, the use of other bases (Dabco (1,4-diazabicyclo-[2.2.2]octane), Et_3N, *N*-methylpyrrolidine, NaOH, KOH, Na_2CO_3, $NaHCO_3$, and none) results in the poor yields (0–39%) of the desired **1a** (entries 6–13).

In the presence of 1.5 equiv. of DBU under 1 atm of carbon monoxide at 20°C for 18 h, *S*-alkyl thiocarbamates (**1a–l**) are synthesized from the corresponding amines (**2a–i**) and alkyl halides (Eq. (2), Table 2).

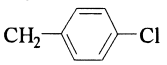
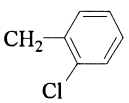


(2)

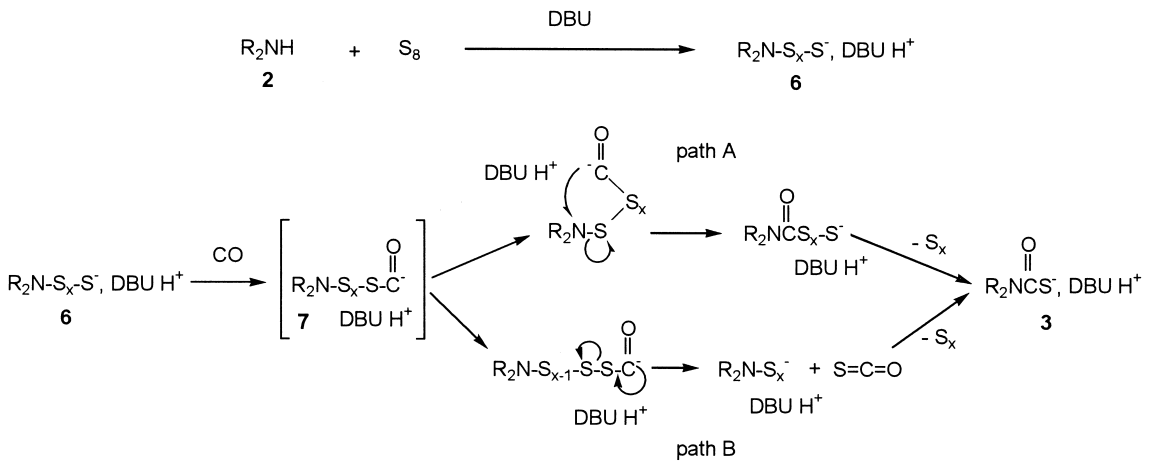
S-Alkyl thiocarbamates (**1a–j**) from secondary amines (**2a–g**) are prepared in excellent yields under mild conditions (1 atm, 20°C) (entries 1–11), even in considerably large scale (entries 2–4). EPTC (**1b**),[8,10] benthiocarb (**1d**),[8,11] and orthobencarb (**1e**)[8] used as herbicides, can also be synthesized in good yields (entries 3, 5, and 6). The yield of *S*-methyl *N*-*n*-butylthiocarbamate (**1k**) from the primary amine (*n*-butylamine, **2h**) is slightly lowered, accompanied with the formation of the corresponding urea derivative (entry 12).[16] Furthermore, in spite of the low basicity of aniline (**2i**), *S*-methyl *N*-phenylthiocarbamate (**1l**) is obtained in good yield (entry 13).

Next, the chlorination of *S*-alkyl thiocarbamate (**1**) by sulfuryl chloride is successfully performed to afford the

Table 2. Synthesis of *S*-alkyl thiocarbamates (**1a–l**)

Entry	R^1	R^2		R^3	X		Yield (%)[a]
1	*n*-Pr	*n*-Pr	**2a**	Me	I	**1a**	93
2	*n*-Pr	*n*-Pr	**2a**	Me	I	**1a**	91[b]
3	*n*-Pr	*n*-Pr	**2a**	Et	I	**1b**[c]	91[b]
4	Et	Et	**2b**	Me	I	**1c**	94[b]
5	Et	Et	**2b**		Cl	**1d**[d]	87
6	Et	Et	**2b**		Cl	**1e**[e]	88
7	*n*-Bu	*n*-Bu	**2c**	Me	I	**1f**	93
8	*i*-Pr	*i*-Pr	**2d**	Me	I	**1g**	83
9	$-(CH_2)_4-$		**2e**	Me	I	**1h**	84
10	$-(CH_2)_5-$		**2f**	Me	I	**1i**	84
11	$-(CH_2)_2O(CH_2)_2-$		**2g**	Me	I	**1j**	95
12	*n*-Bu	H	**2h**	Me	I	**1k**	78 (14)[f]
13	Ph	H	**2i**	Me	I	**1l**	81

[a] Reaction conditions: amine (10 mmol), sulfur (481 mg, 15 mmol), DBU (2.24 mL, 15 mmol), alkyl halide (15 mmol), THF (10 mL).
[b] Amine (50 mmol), sulfur (2.40 g, 75 mmol), DBU (11.2 mL, 75 mmol), alkyl halide (75 mmol), THF (20 mL).
[c] EPTC.
[d] Benthiocarb.
[e] Orthobencarb.
[f] Yield of *N*,*N*′-di-*n*-butylurea.



Scheme 1.

corresponding carbamoyl chloride (**4**) under mild conditions.[18,19,21] The slow addition of sulfuryl chloride to *S*-methyl *N*,*N*-di-*n*-propylthiocarbamate (**1a**) at 0°C followed by vigorous stirring at 20°C for 1 h gave *N*,*N*-di-*n*-propylcarbamoyl chloride (**4a**) in quantitative yield after purification by vacuum distillation (Eq. (3)). *N*,*N*-Di-*n*-propylcarbamoyl chloride (**4a**) from **1b** and *N*,*N*-diethylcarbamoyl chloride (**4b**) from **1c** are also prepared in good yields, by the chlorination using sulfuryl chloride.

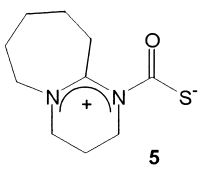
$$\underset{\textbf{1a-c}}{R_2NC(O)SR'} + SO_2Cl_2 \xrightarrow{0\ ^{o}C\text{-}\ 20\ ^{o}C} \underset{\textbf{4a,b}}{R_2NC(O)Cl}$$

4a from **1a**, R = *n*-Pr, R' = Me : 100%
4a from **1b**, R = *n*-Pr, R' = Et : 71%
4b, R = Et, R' = Me : 72%

(3)

In regard to the role of DBU on this carbonylation with carbon monoxide and sulfur, we assumed DBU contributes to the efficiency of the formation of carbonyl sulfide in situ from carbon monoxide and sulfur at an early reaction stage.

We have found that carbonyl sulfide, when is blown into the DMF solution of DBU at room temperature, affords white solid, COS–DBU complex (**5**), which is thermally unstable and regenerates carbonyl sulfide on warming to 45°C.[22,23]



5

However, COS–DBU complex (**5**) was not generated from DBU and sulfur in THF solution under the atmosphere of carbon monoxide at 20°C, although the conditions are similar to those of the present carbonylation. This result shows that no formation of carbonyl sulfide from carbon monoxide and sulfur, even in the presence of DBU, when primary or secondary amines are not present in situ.

Based on our finding on the smooth reaction for salts of thiolates **6** with carbon monoxide to convert into salts of thiocarbamates **3**,[25] we suggest a plausible pathway for this DBU-assisted carbonylation of amines with carbon monoxide and sulfur as follows (Scheme 1). Elemental sulfur is readily subject to S–S bond fission by the reaction with amines strongly assisted by DBU, to form DBU salts of thiolate anions **6**. The reaction of **6** with carbon monoxide gives the carbonylated species **7**. Through an intramolecular rearrangement of **7** (path A) or elimination of carbonyl sulfide from **7** (path B), DBU salts of thiocarbamates **3** are generated.

It seems that main role of DBU on this carbonylation is the acceleration on the formation of thiolates **6**.

3. Conclusion

A useful synthetic method for *S*-alkyl thiocarbamates (**1**) has been developed under mild conditions, in which the carbonylation of amines with carbon monoxide and sulfur is powerfully assisted by DBU, DBN, and DBA–DBU. This carbonylation is employed successfully for the synthesis of benthiocarb (**1d**), orthobencarb (**1e**) (herbicides), and carbamoyl chlorides (**4**).

From the viewpoint of application to actual industrial production of *S*-alkyl thiocarbamates (**1**) as herbicides, the present reaction is very significant, in terms of the use of easily available carbon monoxide, sulfur and DBU, and mild reaction conditions.

4. Experimental

4.1. General

Melting points were determined on a Mettler FP 5 instrument and were uncorrected. FT-IR spectra were recorded on a Nicolet Magna-IR 550 instrument. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 (300 MHz, 75 MHz) instrument. Chemical shifts were reported in ppm relative to tetramethylsilane (δ-units). Mass and exact mass spectra were recorded on a JEOL JMS-600 spectrometer. Amines (**2a**–**i**), alkyl halides, THF, DBU,

other bases, sulfur (99.5%), carbon monoxide (99.9%), and sulfuryl chloride were used as purchased.

4.2. Typical procedure for the synthesis of *S*-methyl *N*,*N*-di-*n*-propyl thiocarbamate (1a) from di-*n*-propylamine (2a), methyl iodide, carbon monoxide and sulfur

A THF (10 mL) solution containing di-*n*-propylamine (**2a**) (1.37 mL, 10 mmol), powdered sulfur (481 mg, 15 mmol) and DBU (2.24 mL, 15 mmol) was vigorously stirred under carbon monoxide (1 atm) at 20°C for 18 h. Into the THF solution of thiocarbamate salt, methyl iodide (0.93 mL, 15 mmol) was added slowly at 0°C under argon atmosphere. The reaction mixture was stirred for additional 2 h at 20°C. The resulting mixture was then poured into 1N HCl (100 mL), and extracted with *t*-butyl methyl ether (100 mL, 50 mL×2). After evaporation of solvents and purification by short-column chromatography (silica gel, toluene/AcOEt=1:1), *S*-methyl *N*,*N*-di-*n*-propylthiocarbamate (**1a**) was afforded in an 93% yield (1.63 g). *S*-Methyl *N*,*N*-di-*n*-propylthiocarbamate (**1a**)[6–8,25]: oil; IR (neat) 2965, 1655, 1405, 1225, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J*=7 Hz, 6H), 1.60 (brs, 4H), 2.32 (s, 3H), 3.28 (brs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 12.8, 21.4, 49.3, 168.2; MS (*m*/*z*, %) 175 (M^+, 100), 128 (89), 86 (79), 75 (65). Exact MS calcd for $C_8H_{17}NOS$: 175.1031. Found: 175.1012.

4.2.1. *S*-Ethyl *N*,*N*-di-*n*-propylthiocarbamate (1b).[6–8] Oil; IR (neat) 2965, 1650, 1405, 1220, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J*=7 Hz, 6H), 1.28 (t, *J*=7 Hz, 3H), 1.59 (brs, 4H), 2.90 (q, *J*=7 Hz, 2H), 3.27 (brs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 15.3, 21.5, 24.6, 47.8, 167.7; MS (*m*/*z*, %) 189 (M^+, 47), 128 (100), 86 (59).

4.2.2. *S*-Methyl *N*,*N*-diethylthiocarbamate (1c).[6–8] Oil; IR (neat) 2975, 1650, 1405, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, *J*=7 Hz, 6H), 2.32 (s, 3H), 3.38 (brs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.6, 13.3, 41.8, 167.4; MS (*m*/*z*, %) 147 (M^+, 53), 100 (100), 72 (72).

4.2.3. *S*-4-Chlorobenzyl *N*,*N*-diethylthiocarbamate (1d).[7,8] Oil; IR (neat) 2975, 1650, 1410, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7 Hz, 6H), 3.37 (brs, 4H), 4.10 (s, 2H), 7.23–7.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 33.7, 42.1, 128.5, 130.2, 132.7, 137.1, 166.2; MS (*m*/*z*, %) 257 (M^+, 34), 125 (21), 100 (100), 72 (35).

4.2.4. *S*-2-Chlorobenzyl *N*,*N*-diethylthiocarbamate (1e).[8] Oil; IR (neat) 2975, 1650, 1410, 1250, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7 Hz, 6H), 3.38 (brs, 4H), 4.28 (s, 2H), 7.16–7.22 (m, 2H), 7.34–7.37 (m, 1H), 7.50–7.53 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 32.3, 42.0, 126.9, 128.5, 129.4, 131.2, 134.1, 136.3, 166.4; MS (*m*/*z*, %) 257 (M^+, 12), 222 (56), 189 (32), 128 (72), 100 (100), 86 (40), 72 (39).

4.2.5. *S*-Methyl *N*,*N*-di-*n*-butylthiocarbamate (1f).[6–8] Oil; IR (neat) 2960, 1655, 1410, 1205, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J*=7 Hz, 6H), 1.26–1.38 (m, 4H), 1.55 (brs, 4H), 2.32 (s, 3H), 3.30 (brs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 13.7, 20.0, 30.1, 47.3, 167.9; MS (*m*/*z*, %) 203 (M^+, 57), 156 (100), 132 (33), 100 (39), 75 (34), 57 (98).

4.2.6. *S*-Methyl *N*,*N*-diisopropylthiocarbamate (1g). Oil; IR (neat) 2970, 1660, 1280 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (brs, 12H), 2.30 (s, 3H), 3.51 (brs, 1H), 4.08 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 20.5, 47.2, 49.0, 166.2; MS (*m*/*z*, %) 175 (M^+, 25), 128 (100), 86 (76), 75 (30). Exact MS calcd for $C_8H_{17}NOS$: 175.1031. Found: 175.1027.

4.2.7. *S*-Methyl pyrrolidinecarbothioate (1h).[8,25] Oil; IR (neat) 2975, 2875, 1660, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86–1.97 (m, 4H), 2.35 (s, 3H), 3.37 (t, *J*=7 Hz, 2H), 3.53 (t, *J*=7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5, 24.5, 25.5, 45.8, 47.0, 166.2; MS (*m*/*z*, %) 145 (M^+, 75), 98 (100), 55 (50).

4.2.8. *S*-Methyl piperidinecarbothioate (1i).[6–8] Oil; IR (neat) 2935, 1650, 1410, 1210 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56–1.64 (m, 6H), 2.33 (s, 3H), 3.49 (brs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.8, 24.5, 25.6, 45.7, 167.2; MS (*m*/*z*, %) 159 (M^+, 55), 112 (100), 69 (51).

4.2.9. *S*-Methyl morpholinecarbothioate (1j).[25,26] Mp 71.8°C (71–73°C[26]); IR (melt) 2930, 2870, 1650, 1405, 1220 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.49 (brs, 4H), 3.61 (t, *J*=5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 44.9, 66.5, 168.2; MS (*m*/*z*, %) 161 (M^+, 63), 114 (100), 70 (56).

4.2.10. *S*-Methyl *N*-butylthiocarbamate (1k).[7,8] Oil; IR (neat) 3320, 2960, 1655, 1520, 1215 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, *J*=7 Hz, 3H), 1.31–1.41 (m, 2H), 1.46–1.53 (m, 2H), 2.35 (s, 3H), 3.30 (d, *J*=5 Hz, 2H), 5.31 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 13.5, 19.7, 31.6, 41.1, 167.5; MS (*m*/*z*, %) 147 (M^+, 77), 100 (99), 75 (31), 57 (100).

4.2.11. *N*,*N*′-Dibutylurea.[2] Mp 68.2°C (67–69°C[2]); IR (KBr) 3330, 2960, 1620, 1580, 1460, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, *J*=7 Hz, 6H), 1.20–1.36 (m, 8H), 2.95 (q, *J*=6 Hz, 4H), 5.68 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 19.5, 32.1, 38.8, 158.0; MS (*m*/*z*, %) 172 (M^+, 100), 130 (17), 101 (15), 74 (14), 57 (14).

4.2.12. *S*-Methyl *N*-phenylthiocarbamate (1k).[7,8,27] Mp 84.6°C (78–78.5°C,[8] 80°C[27]); IR (KBr) 3290, 1660, 1600, 1540, 1445, 1245, 1165, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 7.08 (t, *J*=7 Hz, 1H), 7.34 (t, *J*=8 Hz, 2H), 7.55 (d *J*=8 Hz, 2H), 10.5 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.7, 118.9, 123.2, 128.8, 139.0, 165.2; MS (*m*/*z*, %) 167 (M^+, 80), 119 (100), 92 (27), 77 (25).

4.3. General procedure for the synthesis of *N*,*N*-di-*n*-propylcarbamoyl chloride (4a) by the chlorination of *S*-methyl *N*,*N*-di-*n*-propylthiocarbamate (1a) with sulfuryl chloride

Into neat *S*-methyl *N*,*N*-di-*n*-propylthiocarbamate (**1a**) (3.51 g, 20 mmol), sulfuryl chloride (2.41 mL, 30 mmol) was added slowly at 0°C under argon atmosphere. The reaction mixture was stirred for additional 1 h at 20°C. After

purification by vacuum distillation, *N*,*N*-di-*n*-propyl-carbamoyl chloride (**4a**) was given in 100% yield (3.27 g). *N*,*N*-Di-*n*-propylcarbamoyl chloride (**4a**)[6]: oil; IR (neat) 2965, 1735, 1405, 1220, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90–0.96 (m, 6H), 1.58–1.73 (m, 4H), 3.29–3.39 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.9, 20.6, 21.6, 51.4, 52.7, 148.9; MS (*m*/*z*, %) 165 (9), 163 (M^+, 26), 136 (32), 134 (100), 128 (31), 92 (31). Exact MS calcd for $C_7H_{14}NOCl$: 163.0764. Found: 163.0751.

4.3.1. *N*,*N*-Diethylcarbamoyl chloride (4b).[28] Oil; IR (neat) 2980, 1735, 1405, 1250, 1210, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19–1.26 (m, 6H), 3.38–3.52 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 13.6, 44.4, 45.6, 148.5; MS (*m*/*z*, %) 137 (29), 135 (M^+, 90), 122 (32), 120 (100), 100 (90), 92 (40), 72 (46).

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