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One-Pot Convenient and High Yielding Synthesis of Dithiocarbamates[#]

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Summary. A convenient and high yielding method for the synthesis of diverse dithiocarbamates having various substituents including alkyl, aryl, heteroaryl, and alkylaryl at the thiol chain or at the amine chain or at both thiol and amine chains were developed by the one-pot reaction of mercaptans, amines, and bis(benzotriazolyl)methanethione in presence of amidine base under mild reaction conditions.

Keywords. Amines; Amidine base; Benzotriazole; Catalysis; Dithiocarbamates; Thiols.

Introduction

Organic dithiocarbamates (*DTC*s) have received much attention by synthetic and medicinal chemists due to their interesting chemistry and diverse pharmacological properties including potential anti-mycobacterial [1a–d], fungicidal [1e–g], herbicidal [2a], anthelmintic [2b, c], antifouling [2d], growth depressant [2e], algicidal [2f], antiparkinson [2g], antioxidant [2h], and anti-radiation activities [2i]. Diethyl dithiocarbamic acid sodium salt (*DEDTC*), a well known immunopotentiator has been a safe clinical candidate for the treatment of HIV infections [3]. The *DTC* framework is ubiquitously found in a variety of biologically active molecules [4] and it gained importance as building block, combinatorial scaffold, as well as intermediate in organic synthesis to develop new active chemical entities (NCEs) [5]. In addition, they are used extensively as effective catalyst in photo-polymerization [6a], vulcanization processes [6b, c], as radical precursors [6d–f], linkers in solid phase combinatorial synthesis (SPCS) [6g], as well as intermediates for the protection of amino groups in peptide synthesis [6h], and recently they have got an important role in the synthesis of ionic liquids [6i]. In spite of the growing interest in applications of these compounds, preparative methods available for their synthesis are still limited [7].

Well known routes for their synthesis (depicted in Scheme 1) include the reactions of (i) dithiocarbamic acid salt either with alkyl halides [8a–d], dialkyl phosphates [8e], or electron deficient olefin [8f], (ii) amine, CS_2, electron deficient olefin under one-pot aqueous condition [9a], (iii) amines and CS_2 followed by treatment with formaldehyde and other amines in presence of phosphate buffer [9b], (iv) acylation of amines with chlorodithioformates [9c], (v) dialkylthiocarbamyl chloride with ArS- (generated either from Ar-SH/NaH or from Ar-S-S-Ar/$LiAlH_4$) [9d], (vi) alcohol and a polymer supported diethyl dithiocarbamate anion [9e], (vii) aldehyde, *Bt*H, and thiols for functionalized dithiocarbamates [10a], (viii) thiocarbamoylation of thiols under *Bt* assisted and triethylamine mediated condition [10b], (ix) functionalization of *DTC*s by means of R^3SO_2Na and CH_2O [11a], (x) mercaptans and isothiocyanates using suitable basic catalyst [11b], (xi) tosylates and CS_2 under Triton-B catalysed con-

[#] This work is dedicated to my (*VKT*) Hon'ble teacher (Late) Prof. *Arya K. Mukherjee*, Department of Chemistry, Banaras Hindu University, Varanasi-5, India.

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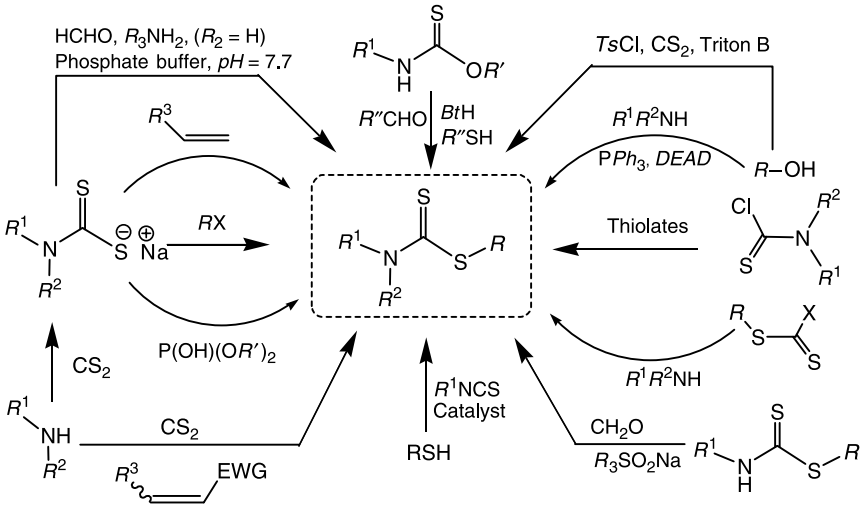


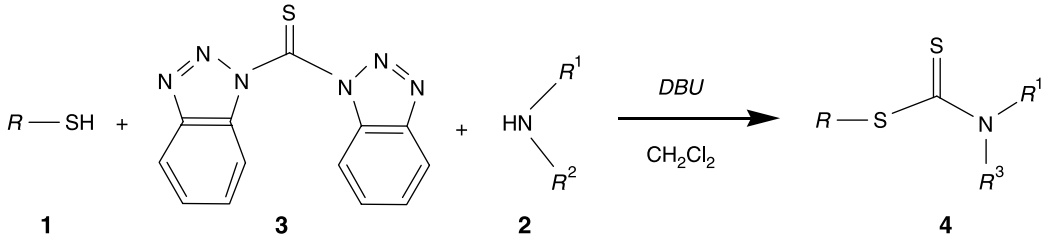
Scheme 1

dition [12a–c], and (xii) alcohols and amines under *Mitsunobu*'s conditions [12d].

However, all these synthetic methods are associated with one or the other limitations, such as low availability of starting material, or employment of harsh reaction conditions, high reaction temperatures, long reaction times, low yields, or two or more steps. Due to the above mentioned facts and reasons, the synthesis of dithiocarbamates with different substitution patterns either at the thiol chain, at the amine chain, or at both chains by a convenient, safe, and high yielding methodology has become a field of increasing interest in synthetic and medicinal organic chemistry during the past few years.

Results and Discussion

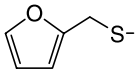
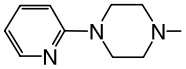
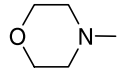
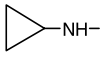
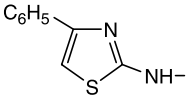
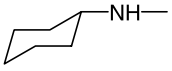
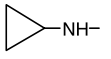
Benzotriazole can easily enter into molecules by a variety of reactions such as benzotriazolyl-alkylation, additions or condensations, and can also easily be cleaved after the reaction as a good leaving group [10]. During the course of our studies for the synthesis of biologically active glycoconjugates, 1,5-diazabicyclo[5.4.0]undec-5-ene (*DBU*) has been found to be an efficient and mild catalyst [13]. The reaction of thioalcohols (*e.g.* $CH_3CH_2CH_2SH$) with isocyanates or isothiocyanates is much slower than the analogous reaction of amines or alcohols and proceeds at a very slow rate even in presence of NEt_3 as catalyst at moderate temperature [11a]. According to our experience mentioned above, we selected *DBU*, which is not only soluble in organic solvents, but also comprising an excellent balance between reactivity and selectivity for this purpose. The reaction is very clean, smooth, and fast, where the desired dithiocarbamate started to form after 30 min [11b, c]. Based on these observations, a benzotriazole mediated and *DBU* catalysed one-pot synthesis of dithiocarbamates with different substitution patterns was developed by the reaction of various thiols with primary or secondary amines including aliphatic, aromatic, and heterocyclic amines using the bis(benzotriazolyl)methanethione (**3**). The methodology is convenient, safe, high yielding, less time consuming, and chemoselective. Thus, various mercaptans **1** (*viz.* furfurylmercaptans, propanethiol,



1 **3** **2** **4**

Scheme 2

Table 1. Dithiocarbamates **4a**–**4o** synthesized *via* Scheme 2

Entry	Product	*R*S–	R^1R^2N–	Base	Time/h	Yield/%
1	**4a**	 **1a**		*DBU*	2	92
2	**4b**	**1a**		*DBU*	2	94
3	**4c**	**1a**	C_6H_5NH–	*DBU*	2	84
4	**4d**	**1a**	$CH_3(CH_2)_6CH_2NH$–	*DBU*	2	84
5	**4e**	**1a**		*DBU*	2	85
6	**4f**	**1a**		*DABCO*	2.5	85
7	**4g**	$CH_3CH_2CH_2S$–	C_6H_5NH	*DBU*	2	84
8	**4h**	$CH_3CH_2CH_2S$–	$C_6H_5CH_2NH$–	*DBU*	2	95
9	**4i**	$CH_3CH_2CH_2S$–	3-Fluoro-C_6H_4NH–	*DBU*	2	80
10	**4j**	$CH_3CH_2CH_2S$–		*DBU*	2	90
11	**4k**	C_6H_5S–	$(CH_3)_2N$–	*DBU*	2	90
12	**4l**	C_6H_5S		*DBU*	2	84
13	**4m**	$C_6H_5CH_2S$	$(CH_3)_2N$–	*DBU*	2	95
14	**4n**	$C_6H_5CH_2S$	$(CH_3CH_2)_2N$–	*DBU*	2	95
15	**4o**	$HOCH_2CH_2CH_2S$	$(CH_3CH_2)_2N$	*DBU*	2	88

thiophenol, benzyl mercaptan, and 3-hydroxypropanethiol) were reacted with amines **2** (*viz.* 1-(2-pyridyl)piperazine, morpholine, 4-phenylthiazol-2-amine, cyclopropylamine, cyclohexylamine, aniline, 3-fluoroaniline, dimethylamine, and diethylamine) using **3** and *DBU* at room temperature for 2–3 h yielding dithiocarbonates (Scheme 2) in good to excellent yields (80–95%) as shown in Table 1.

The progress of the reaction was monitored by TLC on 60 F-254 silica and desired dithiocarbamates were isolated by column chromatography. The synthesized dithiocarbamates were characterized by spectroscopic and analytical techniques including ^{1}H NMR, ^{13}C NMR, FTIR, MS, and microanalysis. We tried several solvents like benzene, acetonitrile, methanol, dichloromethane, and chloroform where we found anhydrous dichloromethane to be the most suited one for this reaction. Thus, *e.g.* stirring a solution of 1-(2′-pyridyl)piperazine, bis(benzotriazolyl)methanethione **3** in presence of *DBU* with furfurylmercaptan in dichloromethane yielded the desired *S*-furfuryl-*N*-4-(2′-pyridyl)piperazine-1-yl dithiocarbamate (**4a**) *via* the benzotriazole-equivalent isothiocyanate intermediate in good yield (92%). The reactions with morpholine, cyclopropylamine, cyclohexylamine, aniline, 3-fluoroaniline, dimethylamine, and diethylamine were found to proceed smoothly. Exceptionally, the reaction with furfurylmercaptan (**1a**), 4-phenyl-thiazol-2-ylamine, and bis(benzotriazolyl)methanethione (**3**) did not yield the desired *DTC* **4f** even after 5 h stirring in anhydrous dichloromethane. However, when *DABCO* was used the reaction proceeded and after 2.5 h the starting materials had disappeared and product was isolated by column chromatography using SiO_2 (20% *Et*O*Ac* in *n*-hexane).

In conclusion, we developed an efficient one-pot chemoselective and high yielding protocol for the synthesis of diverse dithiocarbamates (through benzotriazole methodology) by *DBU*/*DABCO* catalysed addition of mercaptans and amines to bis(benzotriazolyl)methanethione. The synthesized *DTCs* by this method may be useful for the development of pharmacologically active compounds and they can also be used as scaffolds in solid phase combinatorial synthesis (SPCS).

Experimental

Glassware was dried over an open flame before use in connection with an inert atmosphere (N_2) and solvents were evaporated under reduced pressure at temperature <55°C. Thin layer chromatography (TLC) was performed using silica gel 60 F-254 plates with I_2 vapors as detecting agents followed by spraying with *Draggendorff* reagent. Silica gel (230–400 mesh) was used for column chromatography. *TMS* (0.0 ppm) was used as an internal standard in ^{1}H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR. Infrared spectra were recorded as KBr pelletes by a Perkin Elemer RX-1 spectrometer. Melting points were determined on a Büchi 535 melting point apparatus. Elemental analyses were performed on a Perkin-Elmer 2400 C, H, N analyzer and results were found to be within ±0.4% of the calculated values. Unless otherwise stated, all materials were obtained from commercial suppliers, Sigma Aldrich Company, SRL, and Spectrochem Pvt. Ltd., and were used without further purification.

S-Furfuryl-N-4-(2′-pyridyl)piperazine-1-yl dithiocarbamate (**4a**, $C_{15}H_{17}N_3OS_2$)
To the stirred solution of 0.52 g **3** (1.84 mmol) in 10 cm^3 anhydrous CH_2Cl_2 0.30 g 1-(2′-pyridyl)piperazine (1.84 mmol) was added slowly at 0°C and the reaction mixture was stirred for 5 min. Furfurylmercaptan (186 mm^3, 1.84 mmol) and *DBU* (265 mm^3, 1.77 mmol) was added drop-wise to the stirred reaction mixture at 0°C under N_2 atmosphere. After 5 min the reaction was brought to room temperature and stirring was continued for 2 h. Completion of the reaction was monitored by TLC. Then the reaction mixture was washed with 5% Na_2CO_3 solution followed by 10 cm^3 distilled H_2O to keep the reaction mixture free from liberated benzotriazole, extracted with 2×75 cm^3 $CHCl_3$, dried (Na_2SO_4), and finally, the chloroform layer was concentrated under reduced pressure. The crude mass thus obtained was purified over SiO_2 column using 12–15% *EtOAc* in *n*-hexane as eluent to afford **4a** as colorless solid. Yield 92%; mp 70°C, MS: $m/z = 320$ ($M + H^+$); IR (KBr): $\bar{\nu} = 984$, 1357, 1596, and 2832–2922 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.20$ (d, $J =$ 3.30 Hz, 1Pyridyl-*H*), 8.20 (t, $J = 7.2$ Hz, 1Pyridyl-*H*), 7.36 (s, 1Furfuryl-*H*), 6.68 (m, t and d merged, where for d, $J =$ 8.4 Hz, 2Pyridyl-*H*), 6.34–6.32 (m, 2Furfuryl-*H*), 4.68 (s, SCH_2) 4.09 and 3.71 (each m, each 4H, $4 \times$ CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 196.01$ (C=S), 158.48 (Pyridyl-q*C*), 149.21 (Furfuryl-q*C*), 148.03 (Pyridyl-*C*H), 142.43 (Furfuryl-*C*H), 137.73 (Pyridyl-*C*H), 113.95 (Pyridyl-*C*H), 110.63 and 108.87 (Furfuryl-*C*H), 106.88 (Pyridyl-*C*H), 44.27 (N*C*H_2), 34.39 (S*C*H_2), 29.68 (N*C*H_2) ppm.

S-Furfuryl-N-morpholin dithiocarbamate (**4b**, $C_{10}H_{13}NO_2S_2$)
According to the procedure described for **4a**: Yield 94%; mp 43°C, IR (KBr): $\bar{\nu} = 744$, 996, 1110, 1426, 1500, 1593, and 2720–2970 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.36$ (s, 1H), 6.32 (m, 2H), 4.67 (s, SCH_2), 4.24 (m, 4H, $2 \times$ OCH_2), 3.76 (m, 4H, $2 \times$ NCH_2) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 196.02$ (C=S), 149.19 (Furfuryl-q*C*), 142.26, 110.51, and 108.72 (Furfuryl-*C*H), 66.05, 50.73, and 34.12 (*C*H_2) ppm.

S-Furfuryl-N-phenyl dithiocarbamate (**4c**, $C_{12}H_{11}NOS_2$)
According to the procedure described for **4a**: Yield 84%; IR (KBr): $\bar{\nu} = 1085$, 1518, 2820–2900 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.75$ (bs, D_2O exchangeable N*H*), 7.30–7.48 (m, 5*Ph-H* and 1Furfuryl-*H*), 6.38 (m, 2Furfuryl-*H*), 4.56 (s, SCH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 196.72$ (C=S), 149.21 (Furfuryl-q*C*), 142.43 (Furfuryl-*C*H), 137.68 (Ar-q*C*), 129.23, 127.69, and 125.15 (Ar-*C*H), 110.63 and 108.87 (Furfuryl-*C*H) ppm.

S-Furfuryl-N-n-octyl dithiocarbamate (**4d**, $C_{14}H_{23}NOS_2$)
According to the procedure described for **4a**: Yield 83%; IR (KBr): $\bar{\nu} = 1106$, 1490, 2800–2900 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.37$ (m, N*H* and 1Furfuryl-*H*), 6.22 (m, 2Furfuryl-*H*), 4.04 (s, SCH_2), 3.98 (t, $J = 6.3$ Hz, NCH_2), 1.68 (m, NCH_2CH_2), 1.28 (m, $5 \times CH_2$), 0.88 (t, $J = 6.6$ Hz, $-NCH_2(CH_2)_6CH_3$) ppm.

S-Furfuryl-N-cyclopropyl dithiocarbamate (**4e**, $C_9H_{11}NOS_2$)
According to the procedure described for **4a**: Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.38$ (m, N*H*, and 1Furfuryl-*H*), 6.35 (m, 2Furfuryl-*H*), 4.66 (s, SCH_2), 2.00 (m, N*CH*), 0.91–0.69 (m, $2 \times CH_2$) ppm.

S-Furfuryl-N-4-phenylthiazol-2-yl dithiocarbamate (**4f**, $C_{15}H_{12}N_2OS_2$)
According to the procedure described for **4a**, however *DABCO* was used in place of *DBU* for **4f**: Yield 85%; IR (KBr): $\bar{\nu} = 743$, 1355, 1596, 2728, 2819, 2929, and 3432 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.76$ (bs, 1N–*H*), 8.15 (m, 2*Ph-H*), 7.69–7.26 (m, 3Ar-*H*, 1Furfuryl-*H* and 1Thiazole-*H*), 6.42 (m, 2Furfuryl-*H*), 4.68 (s, SCH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 196.72$ (C=S), 147.68 and 147.24 (Furfuryl and Thiazol-q*C*), 142.84 (Furfuryl-*C*H), 142.38 (Ar-q*C*), 131.12, 126.27, 120.69, and 115.51 (Ar-*C*H), 110.76 and 109.63 (Furfuryl-*C*H), 33.04 (S*C*H_2) ppm.

S-n-Propyl-N-phenyl dithiocarbamate (**4g**, $C_{10}H_{13}NS_2$)
According to the procedure described for **4a**: Yield 84%; IR (KBr): $\bar{\nu} = 1102$, 1505, 2800–2900, and 3492 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.30 (m, 6H, 1N*H* and 5Ar-*H*), 3.18 (t, $J = 6.3$ Hz, $SCH_2CH_2CH_3$), 1.60 (m, $SCH_2CH_2CH_3$), 0.99 (t, $J = 6.3$ Hz, $SCH_2CH_2CH_3$) ppm; ^{13}CNMR (75 MHz, $CDCl_3$): $\delta = 198.42$ (C=S), 136.27 (Ar-q*C*), 128.82, 128.49, and 127.84 (Ar-*C*H), 38.16 ($SCH_2CH_2CH_3$), 22.45 ($SCH_2CH_2CH_3$), 13.40 ($SCH_2CH_2CH_3$) ppm.

S-n-Propyl-N-3-fluorophenyl dithiocarbamate (**4h**, $C_{10}H_{12}NS_2F$)
According to the procedure described for 4a: Yield 80%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.27$ and 6.80–6.60 (m, 4Ar-*H*), 5.09 (s, N*H*), 3.02 (t, $J = 6.3$ Hz, $SCH_2CH_2CH_3$), 1.71 (m, $SCH_2CH_2CH_3$), 0.98 (t, $J = 6.3$ Hz, $SCH_2CH_2CH_3$) ppm.

S-n-Propyl-N-benzyl dithiocarbamate (**4i**, $C_{11}H_{15}NS_2$)
According to the procedure described for **4a**: Yield 95%; IR (KBr): $\bar{\nu} = 1098$, 1502, 2800–2900, and 3402 cm^{-1}; ^{1}H NMR

(300 MHz, $CDCl_3$): $\delta = 7.35$ (m, 5Ar-*H*), 7.0 (bs, N*H*), 4.90 (s, NCH_2Ph), 3.10 (t, $J = 6.6$ Hz, $SCH_2CH_2CH_3$), 1.70 (m, $SCH_2CH_2CH_3$), 1.0 (t, $J = 6.6$ Hz, $SCH_2CH_2CH_3$) ppm.

S-n-Propyl-N-cyclohexyl dithiocarbamate (**4j**, $C_{10}H_{19}NS_2$)
According to the procedure described for **4a**: Yield 90%; IR (KBr): $\bar{\nu} = 985$, 1345, 1377, 1502, 1597, 2800–2932, and 3243cm^{-1}; MS: $m/z = 218$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.63$ and 6.85 (bs, N*H*), 4.44 (m, 1H), 3.33 (t, $J =$ 7.2 Hz, $SCH_2CH_2CH_3$), 2.08 (m, 4H), 1.77 (m, $2 \times CH_2$ and $SCH_2CH_2CH_3$), 1.23 (m, $2 \times CH_2$), 1.00 (t, $J = 7.2$ Hz, $SCH_2CH_2CH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 199.08 and 196.30 (C=S), 55.46, 55.38, 37.73, 36.91, 32.19, 31.63, 25.23, 24.90, 24.54, 22.35, 21.98, and 13.22 ppm.

S-Phenyl N,N-dimethyl dithiocarbamate (**4k**, $C_9H_{11}NS_2$)
According to the procedure described for **4a**: Yield 90%; White solid; mp 92°C, IR (KBr): $\bar{\nu} = 1100$, 1475, and 2800–2900 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.45$ (m, 5Ar-*H*), 3.55 and 3.49 (each s, each 3H, $2 \times NCH_3$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 197.62$ (C=S), 136.94 (Ar-q*C*), 131.68, 130.03, and 129.12 (Ar-*C*H), 42.01 and 45.64 ($2 \times NCH_3$) ppm.

S-Phenyl N-cyclopropyl dithiocarbamate (**4l**, $C_{10}H_{11}NS_2$)
According to the procedure described for **4a**: Yield 84%; MS: $m/z = 210$; IR (KBr): $\bar{\nu} = 1009$, 1512, 2884, and 3997 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.30 (m, N*H* and 5Ar-*H*), 2.10 (m, NC*H*), 0.90–0.68 (m, $2 \times CH_2$) ppm.

S-Benzyl-N,N-dimethyl dithiocarbamate (**4m**, $C_{10}H_{13}NS_2$)
According to the procedure described for **4a**: Yield 95%; Colorless Foam, mp Ref. [9d] 39.0–39.8°C; IR (KBr): $\bar{\nu} =$ 1105, 1499, and 2870 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.36$ (d, $J = 7.2$ Hz, 2Ar-*H*), 7.28–7.23 (m, 3Ar-*H*), 4.53 (s, SCH_2Ph), 3.51 and 3.29 (each s, $2 \times NCH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 196.45$ (C=S), 135.92 (Ar-q*C*), 129.14, 128.33, and 127.21 (Ar-*C*H), 45.1, 42.3, and 41.2 ($2 \times NCH_3$ and SCH_2Ph) ppm.

S-Benzyl-N,N-diethyl dithiocarbamate (**4n**, $C_{12}H_{17}NS_2$)
According to the procedure described for **4a**: Yield 95%; IR (KBr): $\bar{\nu} = 1502$ and 2800–2900 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.30 (m, 5Ar-*H*), 4.50 (s, SCH_2Ph), 4.00 (q, $J = 6.6$ Hz, NCH_2), 3.70 (q, $J = 6.9$ Hz, NCH_2), 1.27 (m, $2 \times NCH_2CH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.04$ (C=S), 136.04 (Ar-q*C*), 129.27, 128.68, and 127.59 (Ar-*C*H), 49.41 and 46.66 ($2 \times NCH_2CH_3$), 42.08 (SCH_2Ph), 12.46 and 11.56 ($2 \times NCH_2CH_3$) ppm.

S-3-Hydroxypropyl-N,N-diethyl dithiocarbamate
(**4o**, $C_8H_{17}NOS_2$)
According to the procedure described for **4a**: Yield 88%; IR (KBr): $\bar{\nu} = 1104$, 2800–2920, and 3406 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.05$ (m, CH_2), 3.80–3.68 (m, $2 \times$ CH_2 and OH), 3.49 (t, $J = 6.6$ Hz, SCH_2), 2.37 and 1.98 (m, CH_2), 1.27 (m, $2 \times NCH_2CH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.98$ (C=S), 60.31, 58.99, 49.72, 46.88, 41.83, 35.10, 33.39, and 31.99 (CH_2), 12.41, and 11.59 ($2 \times CH_3$) ppm.

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