

Triton-B Catalyzed Efficient One-Pot Synthesis of Dithiocarbamate Esters⁺

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Received June 30, 2005; accepted August 9, 2005

Published online February 27, 2006 © Springer-Verlag 2006

Summary. A novel process for the one-step chemoselective conversion of alkyl halides into dithiocarbamates as protected amines was developed using benzyltrimethylammonium hydroxide (Triton-B) in presence of carbon disulfide. Thus, dithiocarbamates of different amines were prepared in very good to excellent yields. This protocol is mild, chemoselective, and efficient compared to other methods.

Keywords. Triton-B; Carbon disulfide; Alkyl halides; Amines; Thiocarbamation.

Introduction

The importance of dithiocarbamates in organic chemistry, including agrochemicals [1], pharmaceuticals [2], intermediates in organic synthesis [3], protection of amino groups in peptide synthesis [4], linkers in solid phase organic synthesis [5], radical precursors in free radical chemistry [6], and recent use in the synthesis of ionic liquids [7], necessitates their preparation by a convenient and safe methodology. To satisfy this demand, their synthesis has been changed from the use of harmful and toxic chemicals like dithiophosgene [8] and its derivatives [9] directly or indirectly, to abundantly available, cheap, and safe reagents like CS₂. However, their formation from CS₂ employed harsh reaction conditions, such as strong bases, high reaction temperatures, and long reaction times [10]. Thus, we were prompted to embark on improved procedures. Our group [11] has been engaged for several years in the development of new methodologies for the synthesis of carbamates and dithiocarbamates. Recently, we have reported [12] a chemoselective, highly efficient, one-pot, novel synthesis of carbamates from alkyl halides using the

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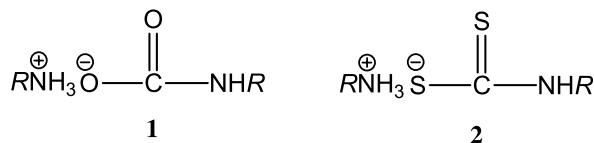
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+ CDRI Communication No.: 6189; this paper is dedicated to Dr. N. Anand, Former Director CDRI, on his 80th birthday

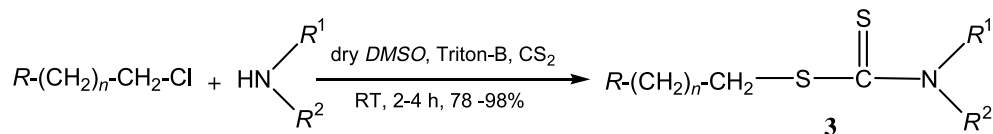
Triton-B/ CO_2 system. In the present communication, we report a chemoselective, highly efficient, one-pot, synthesis of *N*-alkyl/aryl dithiocarbamates of different amines from alkyl halides using the Triton-B/ CS_2 system.

Results and Discussion

We have recently assumed [12] that two equivalents amine reacted with CO_2 to form ionic species **1**, *i.e.* the monoalkylammonium alkyl carbamate ion (Formulae 1). It has been observed that the nucleophilicity of **1** could be enhanced by a basic phase transfer catalyst like Triton-B. This ionic species **1** gets stabilized in the presence of the phase transfer catalyst and would react with alkylating agents to afford carbamates in high yields. By adopting a similar approach, the monoalkyl ammoniumalkyl dithiocarbamate ion **2** should be formed by reacting two molar equivalents of amine with CS_2 . The nucleophilic S of ion **2** would then attack the electrophilic carbon of alkylating agents, *i.e.* the alkyl halides. Moreover, due to the higher reactivity of CS_2 as compared to CO_2 the reaction was tried at room temperature and the proposed product was obtained indeed. It was characterized by spectroscopic and analytical techniques. Thus, the amine was taken in organic solvent and reacted with CS_2 and alkyl halide in the presence of Triton-B at room temperature for 2–4 h to furnish the desired dithiocarbamate ester. We tried *n*-hexane, *n*-heptane, dichloromethane, chloroform, methanol, benzene, toluene, *DMF*, *DMSO*, *HMPA*, acetonitrile, and dry *DMSO* was found to be most suitable to get good to excellent yields. It is important to note that the amine used for this reaction should have at least one available hydrogen atom to help in the formation of ionic species **2**. Furthermore, we have tried quaternary ammonium salts, like Triton-B, tetra-*n*-butylammonium iodide, tetra-*n*-butylammonium bromide, tetra-*n*-butylammonium hydrogensulfate, tetra-*n*-butylammonium hydrogencarbonate, etc., but Triton-B was found to be most suitable to get good to excellent yields of dithiocarbamates of aliphatic, aromatic, and cyclic (primary and secondary) amines. Accordingly, the reaction condition for the synthesis of dithiocarbamates **3** from alkyl halides and amines using Triton-B/ CS_2 system is shown in Scheme 1; the yields of the products are contained in Table 1.



Formulae 1



Scheme 1

Table 1. Conversion of alkyl halides into dithiocarbamates of general formula **3**

Product	R	R ¹	R ²	n	Time/h	Yield/%
1a	2-Naphthyloxy	<i>n</i> -C ₄ H ₉	H	3	2.5	97
1b	2-Naphthyloxy	<i>n</i> -C ₆ H ₁₃	H	2	2.5	96
1c	2-Naphthyloxy	<i>n</i> -C ₈ H ₁₇	H	1	3	94
1d	2-Naphthyloxy	<i>n</i> -C ₁₂ H ₂₅	H	3	2	98
1e	2-Naphthyloxy	Cyclohexyl	H	2	3	89
1f	2-Naphthyloxy	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	2	3	85
1g	2-Naphthyloxy	R ¹ =R ² =Morpholinyl		2	4	82
1h	2-Naphthyloxy	R ¹ =R ² =Pyrrolidinyl		2	4	83
1i	2-Naphthyloxy	C ₆ H ₅ CH ₂	H	1	3.5	87
1j	2-Naphthyloxy	3-Phenylpropyl	H	3	2.5	97
1k	2-Naphthyloxy	4- <i>Me</i> C ₆ H ₄ -	H	2	3.5	92
1l	2-Naphthyloxy	4- <i>MeO</i> C ₆ H ₄ -	H	2	3.5	93
1m	<i>Ph</i>	<i>n</i> -C ₄ H ₉	H	1	3.5	88
1n	<i>Ph</i>	<i>n</i> -C ₆ H ₁₃	H	2	3	92
1o	<i>Ph</i>	<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	1	3.5	81
1p	C ₂ H ₅	<i>n</i> -C ₈ H ₁₇	H	1	3	90
1q	<i>n</i> -C ₃ H ₇	Cyclohexyl	H	2	3	88
1r	<i>n</i> -C ₄ H ₉	3-Methoxybenzyl	H	3	2.5	92
1s	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₆ H ₁₃	H	2	2.5	87
1t	<i>n</i> -C ₅ H ₁₁	4- <i>MeO</i> C ₆ H ₄ -	H	2	3.5	80
1u	<i>Ph</i>	4- <i>Me</i> C ₆ H ₄ -	H	1	3.5	78

In conclusion, we developed a convenient, safe, and efficient protocol for a one-pot, four components coupling of various primary and secondary aliphatic/aromatic and cyclic amines with alkyl halides *via* a Triton-B/CS₂ system. This highly chemoselective reaction generates the corresponding dithiocarbamates in good to excellent yields. Furthermore, this method exhibits substrate versatility, mild reaction conditions, and experimental convenience. This synthetic protocol is believed to offer a more general method of formation of carbon-sulfur bonds, essential to numerous organic syntheses.

Experimental

Chemicals were obtained from Merck, Aldrich, and Fluka chemical companies. IR spectra were obtained on a Bomem MB-104 FTIR spectrometer and ¹H NMR spectra were scanned on a AC-300F NMR (300 MHz) instrument using CDCl₃ as solvent and TMS as internal standard. Elemental analyses were made by Carlo-Erba EA1110 CHNO-S analyzer and agreed favourably with calculated values.

Procedure

A mixture of 6 mmol Triton-B and 6 mmol CS₂ was taken in 40 cm³ dry DMSO and was allowed to stir 20 min at room temperature. Amine (5 mmol) was added and the reaction was continued at rt for 1 h. Now 2 mmol of the corresponding chloro compound were added. The reaction was further continued until completion (*cf.* Table 1). The reaction mixture was poured into 50 cm³ distilled H₂O and extracted with ethyl acetate thrice. The organic layer was separated, dried (Na₂SO₄), and concentrated to get the desired compound.

[4-(2-Naphthyloxy)but-1-yl] n-butyldithiocarbamate (1a, C₁₉H₂₅NOS₂)

Yield 97%; IR (KBr): $\bar{\nu}$ = 670 (C–S), 1114 (C=S), 1474 (Ar), 1510 (Ar), 1609 (Ar), 2874 (CH), 2937 (CH), 3418 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 0.93–0.97 (t, CH_3), 1.30–1.34 (m, CH_2CH_3), 1.53–1.56 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70–1.72 (m, naphthyl-O- CH_2CH_2), 1.95–1.98 (m, S- CH_2CH_2), 2.0 (br, NH), 2.63–2.66 (m, NHCH_2), 2.84–2.88 (t, CH_2 -S-C=S), 4.01–4.04 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 347.

3-(2-Naphthyloxy)prop-1-yl] n-hexyldithiocarbamate (1b, C₂₀H₂₇NOS₂)

Yield 96%; IR (KBr): $\bar{\nu}$ = 664 (C–S), 1116 (C=S), 1474 (Ar), 1512 (Ar), 1601 (Ar), 2874 (CH), 2937 (CH), 3395 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 0.92–0.96 (t, CH_3), 1.27–1.29 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30–1.34 (m, CH_2CH_3), 1.53–1.56 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.2 (br, NH), 2.36–2.40 (m, naphthyl-O- $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.63–2.66 (m, NHCH_2), 2.83–2.87 (t, CH_2 -S-C=S), 4.01–4.04 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 361.

2-(2-Naphthyloxy)eth-1-yl] n-octyldithiocarbamate (1c, C₂₁H₂₉NOS₂)

Yield 94%; IR (KBr): $\bar{\nu}$ = 662 (C–S), 1109 (C=S), 1464 (Ar), 1512 (Ar), 1604 (Ar), 2864 (CH), 2927 (CH), 3391 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 0.93–0.96 (t, CH_3), 1.27–1.29 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30–1.34 (m, CH_2CH_3), 1.53–1.56 (m, $\text{CH}_2\text{CH}_2\text{N}$), 2.1 (br, NH), 2.64–2.66 (m, NHCH_2), 3.27–3.30 (t, CH_2 -S-C=S), 4.70–4.72 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 375.

4-(2-Naphthyloxy)but-1-yl] n-dodecyldithiocarbamate (1d, C₂₇H₄₁NOS₂)

Yield 98%; IR (KBr): $\bar{\nu}$ = 683 (C–S), 1154 (C=S), 1474 (Ar), 1524 (Ar), 1610 (Ar), 2890 (CH), 2937 (CH), 3398 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 0.91–0.94 (t, CH_3), 1.27–1.29 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30–1.34 (m, CH_2CH_3), 1.53–1.56 (m, $\text{CH}_2\text{CH}_2\text{N}$), 1.70–1.72 (m, naphthyl-O- CH_2CH_2), 1.95–1.98 (m, S- CH_2CH_2), 2.2 (br, NH), 2.63–2.66 (m, NHCH_2), 2.84–2.88 (t, CH_2 -S-C=S), 4.01–4.04 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 459.

[3-(2-Naphthyloxy)prop-1-yl] cyclohexyldithiocarbamate (1e, C₂₀H₂₅NOS₂)

Yield 89%; IR (KBr): $\bar{\nu}$ = 670 (C–S), 1105 (C=S), 1465 (Ar), 1510 (Ar), 1609 (Ar), 2864 (CH), 2937 (CH), 3402 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 1.41–1.44 (m, CH_2), 1.62–1.66 (m, CH_2), 2.1 (br, NH), 2.35–2.38 (m, naphthyl-O- $\text{CH}_2\text{CH}_2\text{CH}_2$ -S-C=S), 2.56–2.58 (m, CH), 2.63–2.66 (m, NHCH_2), 2.83–2.87 (t, CH_2 -S-C=S), 4.01–4.04 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 359.

[3-(2-Naphthyloxy)prop-1-yl] diisopropyldithiocarbamate (1f, C₂₀H₂₇NOS₂)

Yield 85%; IR (KBr): $\bar{\nu}$ = 669 (C–S), 1116 (C=S), 1464 (Ar), 1512 (Ar), 1610 (Ar), 2864 (CH), 2927 (CH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 0.92–0.96 (t, CH_3), 1.44–1.46 (m, CHCH_3), 2.36–2.40 (m, naphthyl-O- $\text{CH}_2\text{CH}_2\text{CH}_2$ -S-C=S), 2.54–2.56 (m, CH_2N), 2.83–2.87 (t, CH_2 -S-C=S), 4.01–4.04 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 361.

3-[(2-Naphthyloxy)prop-1-yl] 4-morpholinylthiocarbonylate (1g, C₁₈H₂₁NO₂S₂)

Yield 84%; IR (KBr): $\bar{\nu}$ = 671 (C–S), 1129 (C=S), 1477 (Ar), 1528 (Ar), 1610 (Ar), 2884 (CH), 2937 (CH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 2.34–2.38 (m, naphthyl-O- $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.83–2.87 (t, S- CH_2), 2.89–2.93 (m, NCH_2), 3.65–3.69 (t, - OCH_2 -), 4.05–4.09 (t, CH_2 -O-naphthyl), 6.97–7.64 (m, Ar-H) ppm; MS: m/z = 347.

[3-(2-Naphthyloxy)prop-1-yl] 1-pyrrolidinylthiocarbonylate (1h, C₁₈H₂₁NOS₂)

Yield 83%; IR (KBr): $\bar{\nu}$ = 673 (C–S), 1126 (C=S), 1474 (Ar), 1522 (Ar), 1606 (Ar), 2884 (CH), 2937 (CH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ = 1.58–1.60 (m, CH_2), 2.35–2.38 (m, naphthyl-O-

$\text{CH}_2\text{CH}_2\text{CH}_2\text{-S-C=S}$), 2.8 (t, CH_2N), 2.83–2.87 (t, $\text{CH}_2\text{-S-C=S}$), 4.01–4.04 (t, $\text{CH}_2\text{-O-naphthyl}$), 6.97–7.64 (m, Ar-H) ppm; MS: $m/z = 331$.

2-(2-Naphthyloxy)eth-1-yl] benzylidithiocarbamate (1i, C₂₀H₁₉NOS₂)

Yield 87%; IR (KBr): $\bar{\nu} = 660$ (C-S), 1110 (C=S), 1463 (Ar), 1511 (Ar), 1603 (Ar), 2864 (CH), 2927 (CH), 3384 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 2.0$ (br, NH), 3.28–3.30 (t, $\text{CH}_2\text{-S-C=S}$), 3.90–3.92 (d, benzylic proton), 4.70–4.72 (t, $\text{CH}_2\text{-O-naphthyl}$), 6.97–7.64 (m, Ar-H of naphthyloxy and benzyl) ppm; MS: $m/z = 353$.

[4-(2-Naphthyloxy)but-1-yl] (3-phenylpropyl)dithiocarbamate (1j, C₂₄H₂₇NOS₂)

Yield 97%; IR (KBr): $\bar{\nu} = 693$ (C-S), 1139 (C=S), 1488 (Ar), 1537 (Ar), 1629 (Ar), 2884 (CH), 2949 (CH), 3429 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.70$ – 1.72 (m, naphthyl-O- CH_2CH_2), 1.87–1.89 (m, PhCH_2CH_2 CH_2NH), 1.95–1.98 (m, S- CH_2CH_2), 2.2 (br, NH), 2.55–2.57 (t, PhCH_2), 2.65–2.67 (m, $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{-N}$), 2.85–2.87 (t, $\text{CH}_2\text{-S-C=S}$), 2.98–3.00 (m, CH_2NH), 4.01–4.04 (t, $\text{CH}_2\text{-O-naphthyl}$), 6.97–7.64 (m, Ar-H) ppm; MS: $m/z = 409$.

[3-(2-Naphthyloxy)prop-1-yl] 4-toluedinyldithiocarbamate (1k, C₂₁H₂₁NOS₂)

Yield 92%; IR (KBr): $\bar{\nu} = 660$ (C-S), 1095 (C=S), 1449 (Ar), 1504 (Ar), 1604 (Ar), 2860 (CH), 2927 (CH), 3380 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 2.33$ – 2.35 (s, CH_3), 2.36–2.40 (m, naphthyl-O- $\text{CH}_2\text{CH}_2\text{CH}_2\text{-S-C=S}$), 2.83–2.87 (t, $\text{CH}_2\text{-S-C=S}$), 4.0 (br, NH), 4.01–4.04 (t, $\text{CH}_2\text{-O-naphthyl}$), 6.34–7.64 (m, Ar-H) ppm; MS: $m/z = 367$.

[3-(2-Naphthyloxy)prop-1-yl] 4-anisidinyldithiocarbamate (1l, C₂₁H₂₁NO₂S₂)

Yield 93%; IR (KBr): $\bar{\nu} = 669$ (C-S), 1119 (C=S), 1471 (Ar), 1522 (Ar), 1612 (Ar), 2877 (CH), 2939 (CH), 3398 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 2.36$ – 2.40 (m, naphthyl-O- $\text{CH}_2\text{CH}_2\text{CH}_2\text{-S-C=S}$), 2.83–2.87 (t, $\text{CH}_2\text{-S-C=S}$), 3.73 (s, OCH_3), 4.1 (br, NH), 4.01–4.04 (t, $\text{CH}_2\text{-O-naphthyl}$), 6.35–7.64 (m, Ar-H) ppm; MS: $m/z = 383$.

(2-Phenylethyl) n-butylidithiocarbamate (1m, C₁₃H₁₉NS₂)

Yield 88%; IR (KBr): $\bar{\nu} = 659$ (C-S), 1086 (C=S), 1467 (Ar), 2884 (CH), 2927 (CH), 3398 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.89$ – 0.93 (t, CH_3), 1.28–1.34 (m, CH_2CH_3), 1.54–1.57 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.2 (br, NH), 2.63–2.65 (m, CH_2NH), 3.18–3.20 (t, PhCH_2CH_2), 3.23–3.25 (t, PhCH_2), 7.08–7.21 (m, Ar-H) ppm; MS: $m/z = 253$.

(3-Phenylpropyl) n-hexyldithiocarbamate (1n, C₁₆H₂₅NS₂)

Yield 92%; IR (KBr): $\bar{\nu} = 669$ (C-S), 1116 (C=S), 1512 (Ar), 2864 (CH), 2937 (CH), 3408 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.88$ – 0.92 (t, CH_3), 1.28–1.30 (m, CH_2CH_2), 1.32–1.35 (m, CH_2CH_3), 1.54–1.57 (m, NHCH_2CH_2), 2.2 (br, NH), 2.27–2.29 (m, $\text{PhCH}_2\text{CH}_2\text{CH}_2$), 2.54–2.56 (t, PhCH_2), 2.63–2.66 (t, CH_2NH), 2.84–2.86 (m, S-CS-NH- CH_2), 7.08–7.21 (m, Ar-H) ppm; MS: $m/z = 295$.

(2-Phenylethyl) diisopropyldithiocarbamate (1o, C₁₅H₂₃NS₂)

Yield 81%; IR (KBr): $\bar{\nu} = 659$ (C-S), 1096 (C=S), 1502 (Ar), 2854 (CH), 2927 (CH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.90$ – 0.94 (t, CH_3), 1.43–1.45 (m, CH_2CH_3), 2.53–2.55 (t, NCH_2), 3.17–3.20 (t, PhCH_2CH_2), 3.24–3.26 (t, PhCH_2), 7.08–7.21 (m, Ar-H) ppm; MS: $m/z = 281$.

n-Butyl n-octyldithiocarbamate (1p, C₁₃H₂₇NS₂)

Yield 90%; IR (KBr): $\bar{\nu} = 648$ (C-S), 1086 (C=S), 2864 (CH), 2917 (CH), 3388 (NH) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.89$ – 0.92 (t, CH_3), 1.26–1.30 (m, CH_2), 1.32–1.34 (m, CH_2CH_3), 1.54–1.57 (m, $\text{NH-CH}_2\text{CH}_2$), 1.93–1.96 (m, S- CH_2CH_2), 2.0 (br, NH), 2.63–2.65 (t, CH_2NH), 2.85–2.87 (t, CH_2S) ppm; MS: $m/z = 261$.

n-Hexyl cyclohexyldithiocarbamate (**1q**, C₁₃H₂₅NS₂)

Yield 88%; IR (KBr): $\bar{\nu}$ = 669 (C–S), 1116 (C=S), 2864 (CH), 2927 (CH), 3395 (NH) cm⁻¹; ¹H NMR (CDCl₃): δ = 0.90–0.94 (t, CH₃), 1.26–1.30 (m, CH₂), 1.32–1.34 (m, CH₂CH₃), 1.42–1.44 (m, CH₂), 1.64–1.67 (m, CH₂), 1.94–1.96 (m, S–CH₂CH₂), 2.0 (br, NH), 2.56–2.58 (m, CH), 2.85–2.88 (t, CH₂) ppm; MS: m/z = 259.

n-Octyl (3-methoxybenzyl)dithiocarbamate (**1r**, C₁₇H₂₇NOS₂)

Yield 92%; IR (KBr): $\bar{\nu}$ = 669 (C–S), 1116 (C=S), 1512 (Ar), 2864 (CH), 2927 (CH), 3408 (NH) cm⁻¹; ¹H NMR (CDCl₃): δ = 0.89–0.91 (t, CH₃), 1.26–1.30 (m, CH₂), 1.32–1.34 (m, CH₂CH₃), 1.93–1.96 (m, S–CH₂CH₂), 2.0 (br, NH), 2.85–2.87 (t, CH₂–S), 3.72–3.74 (s, OCH₃), 3.90–3.93 (m, CH₂), 6.57–7.03 (m, Ar–H) ppm; MS: m/z = 325.

n-Decyl *n*-hexyldithiocarbamate (**1s**, C₁₇H₃₅NS₂)

Yield 87%; IR (KBr): $\bar{\nu}$ = 659 (C–S), 1103 (C=S), 2851 (CH), 2917 (CH), 3398 (NH) cm⁻¹; ¹H NMR (CDCl₃): δ = 0.90–0.94 (t, CH₃), 1.26–1.30 (m, CH₂), 1.32–1.34 (m, CH₂CH₃), 1.54–1.56 (m, NHCH₂CH₂), 1.94–1.97 (m, S–CH₂CH₂), 2.2 (br, NH), 2.64–2.66 (m, NHCH₂), 2.87–1.89 (t, CH₂–S–CS–NH) ppm; MS: m/z = 317.

n-Octyl 4-anisidyldithiocarbamate (**1t**, C₁₆H₂₅NOS₂)

Yield 80%; IR (KBr): $\bar{\nu}$ = 668 (C–S), 1115 (C=S), 1510 (Ar), 2860 (CH), 2927 (CH), 3387 (NH) cm⁻¹; ¹H NMR (CDCl₃): δ = 0.89–0.93 (t, CH₃), 1.26–1.30 (m, CH₂), 1.32–1.34 (m, CH₂CH₃), 1.93–1.96 (m, S–CH₂CH₂), 2.85–2.88 (t, S–CH₂), 3.73 (s, OCH₃), 4.1 (br, NH), 6.35–6.52 (m, Ar–H) ppm; MS: m/z = 311.

(2-Phenylethyl) 4-toluedinyldithiocarbamate (**1u**, C₁₆H₁₇NS₂)

Yield 78%; IR (KBr): $\bar{\nu}$ = 673 (C–S), 1126 (C=S), 1522 (Ar), 2874 (CH), 2947 (CH), 3408 (NH) cm⁻¹; ¹H NMR (CDCl₃): δ = 2.34–2.36 (s, CH₃), 3.19–3.22 (t, SCH₂CH₂·Ph), 3.23–3.26 (t, S–CH₂CH₂Ph), 4.0 (br, NH), 6.34–7.21 (m, Ar–H) ppm; MS: m/z = 287.

Acknowledgements

The authors are grateful to SIAF division of CDRI for providing the spectroscopic and analytical data.

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