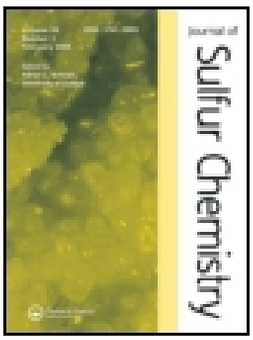

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SHORT COMMUNICATION

Cyclic ammonium salts of dithiocarbamic acid: stable alternative reagents for the synthesis of *S*-alkyl carbodithioates from organyl thiocyanates in water

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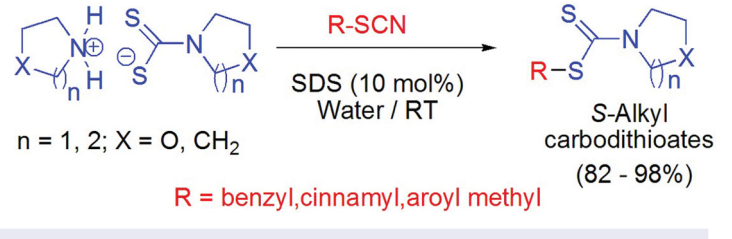
ABSTRACT

Carbodithioate esters are important functional organosulfur compounds widely used in diverse fields such as pharmaceuticals, agrochemicals and material sciences. Common preparative methods include reaction of alkyl halides, carbon disulfide and bases under both metal-free and metal-catalyzed conditions. However, organyl thiocyanates have not been previously explored, possibly because of their conversion to organyl disulfides under basic conditions. Here, we report an efficient and practical method for the preparation of libraries of carbodithioate esters from organyl thiocyanates by reacting with cyclic amine-based dithiocarbamic acid salts in water. The protocol is found to be applicable in general to various thiocyanates such as benzyl/aroyl methyl/cinnamyl and so on. Other notable features include no by-products such as disulfides, metal- and alkali-free, aqueous conditions, and finally easy and near-quantitative formation of cyclic amine-based dithiocarbamic acid salt as a stable alternative reagent.



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Alkyl thiocyanate; aqueous medium; carbodithioate ester; cyclic *sec.* amine; dithiocarbamate salt

1. Introduction

S-alkyl carbodithioate esters, also known as dithiocarbamate esters, are functional organosulfur compounds that were first utilized as fungicides during the Second World War.[1] These are also largely used as important fungicides of crops, vegetables and

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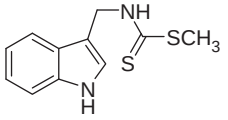
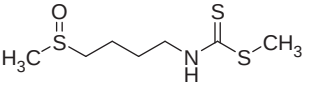
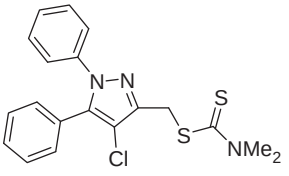


Brassinin,
cancer chemopreventive activity



Sulforamate
cancer chemopreventive agent



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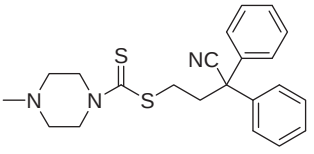
attenuating effects on tumor necrosis factor a (TNFa)-induced apoptosis in murine fibrosarcoma WEHI 164 cells



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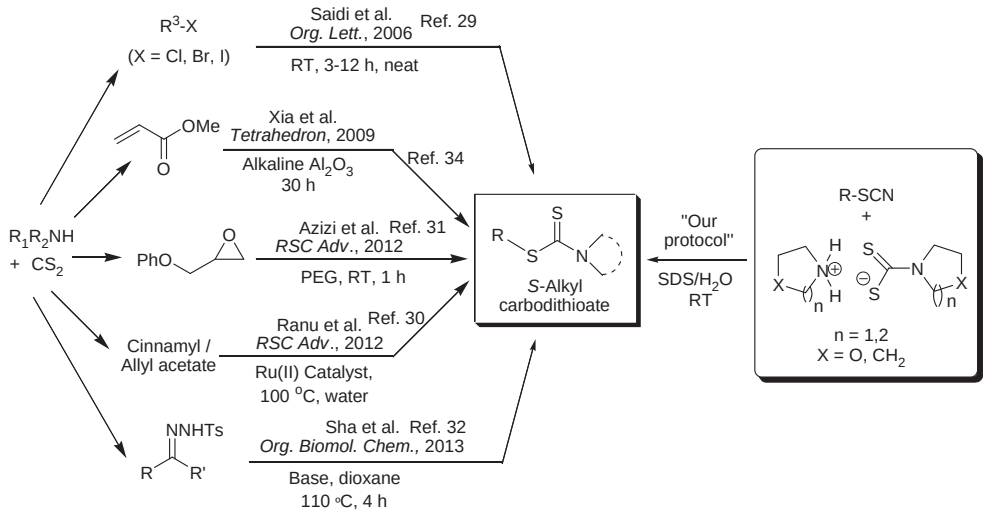
inhibiting the tumor growth of sarcoma 180 (S_{180}), hepatocyte carcinoma 22 (H_{22})

Figure 1. Examples of compounds of potential therapeutic value bearing the *S*-alkyl carbodithioate ester function.

plants.[2–4] Many literature reports demonstrate that the *S*-alkyl carbodithioate esters and its derivatives exhibit antibacterial,[5–7] anthelmintic,[8] anticandidal activity and cytotoxicity,[9] antihistaminic,[10] as well as anticancer properties.[8,11–13] They can also be helpful for the treatment of cardiovascular disorders and inflammatory diseases.[14] They show *in vitro* antitumor activity against human myelogenous leukemia K562 cells,[15] and can be used as HIV-I NCp7 inhibitors,[16] or non-vanilloid TRPV1 antagonists.[17] A few structures of *S*-alkyl carbodithioate esters with potential therapeutic value are shown in Figure 1. Further utility of carbodithioate esters as linkers in solid-phase organic synthesis is also well documented.[18,19] In surface science and nanomaterial chemistry, carbodithioate esters are widely used as suitable ligands for assembly on metal nanoparticles.[20,21] They are familiar in the rubber industry as sulfur vulcanization acceptors,[22] and radical chain transfer agents in the reversible addition fragmentation chain transfer polymerizations.[23–25] They also represent useful synthetic intermediates.[26,27] As a result, several methods for the synthesis of carbodithioate esters have been developed.[28]

Commonly, synthesis of *S*-alkyl/aryl carbodithioate esters is achieved by either nucleophilic substitution reactions under basic medium or transition metal-catalyzed cross-coupling reactions (Scheme 1). The reaction of *sec*. amine with carbon disulfide (CS_2) produces an intermediate nucleophile that reacts with various substrates, such as alkyl halide,[29] allyl acetate,[30] epoxide,[31] tosyl hydrazone [32]and α,β-unsaturated carbonyl compounds,[33–35] in one-pot metal-free or under metal-catalyzed reaction conditions to afford the corresponding carbodithioate esters (Scheme 1). Anilines can also be used for the preparation of carbodithioate esters bearing *sec*. NH group in the presence of DMSO and a strong base such as NaOH.[36] Most of the procedures involve harsh reaction conditions, long reaction time, hazardous organic solvents, metal catalysts and bases. Organyl thiocyanates, often considered as psuedohalides and are easily available, were not



Scheme 1. Methods for the synthesis of *S*-alkyl carbodithioate esters.

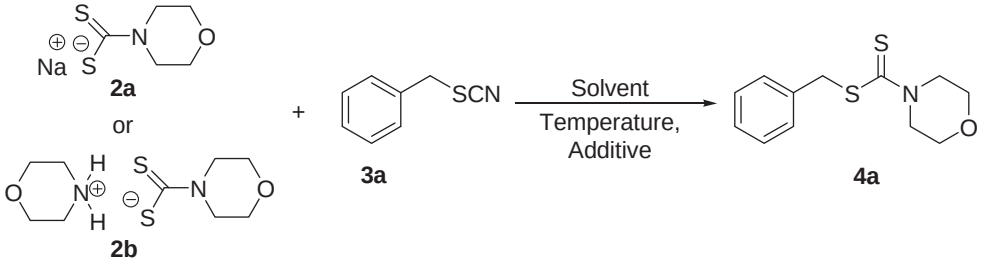
used as the starting materials, presumably because of the fact that the thiocyanate may undergo disulfide (–S–S–) bond formation under basic medium.[37,38]

We found that the reaction of a *sec*. amine with CS_2 produces a stable salt, which can be isolated easily in almost quantitative yield and stored for several weeks in the air. The salt can efficiently react with alkyl/aroyl methyl/cinnamyl thiocyanates in water medium at room temperature to afford corresponding carbodithioate esters in the presence of the anionic phase transfer agent (sodium dodecyl sulfate (SDS)) in excellent yields without formation of other by-products such as organyl disulfide. We report herein an efficient, base- and metal-free protocol for the synthesis of various *S*-substituted carbodithioate esters by using variety of cyclic *sec*. amine-based dithiocarbamate salts from diverse organyl thiocyanates. While organyl thiocyantes have not been used previously as the precursor for preparation of carbodithioate esters, other notable advantages of this protocol are metal- and alkali-free conditions, which possibly lead to the avoidance of disulfide bond formation and clean reactions affording excellent yields, and can be carried out in water medium at room temperature (Scheme 1).

2. Results and discussion

As a part of preliminary study, as presented in Table 1, we have conducted the reaction of a neat mixture of benzyl thiocyanate, CS_2 and morpholine in a one-pot manner, which led to the pure desired benzyl morpholine-4-carbodithioate ester **4a** in 72% isolated yield (Table 1, entry 1). The reaction showed partial formation of dibenzyl disulfide on TLC monitoring of the experiment, although it was not isolated in appreciable quantity after column chromatography. Considering that the intermediate salt derived from the amine and CS_2 could be the actual nucleophile, the sodium salt of morpholinodithioformate **2a** was used to react with benzyl thiocyanate **3a** (Table 1, entry 2). However, we obtained the desired carbodithioate ester **4a** again with the formation of dibenzyl disulfide, presumably attributable to the basic reaction medium that facilitates disulfide formation from benzyl

Table 1. Optimization of the reaction conditions for the conversion of benzyl thiocyanate to *S*-alkyl cabodithioates.



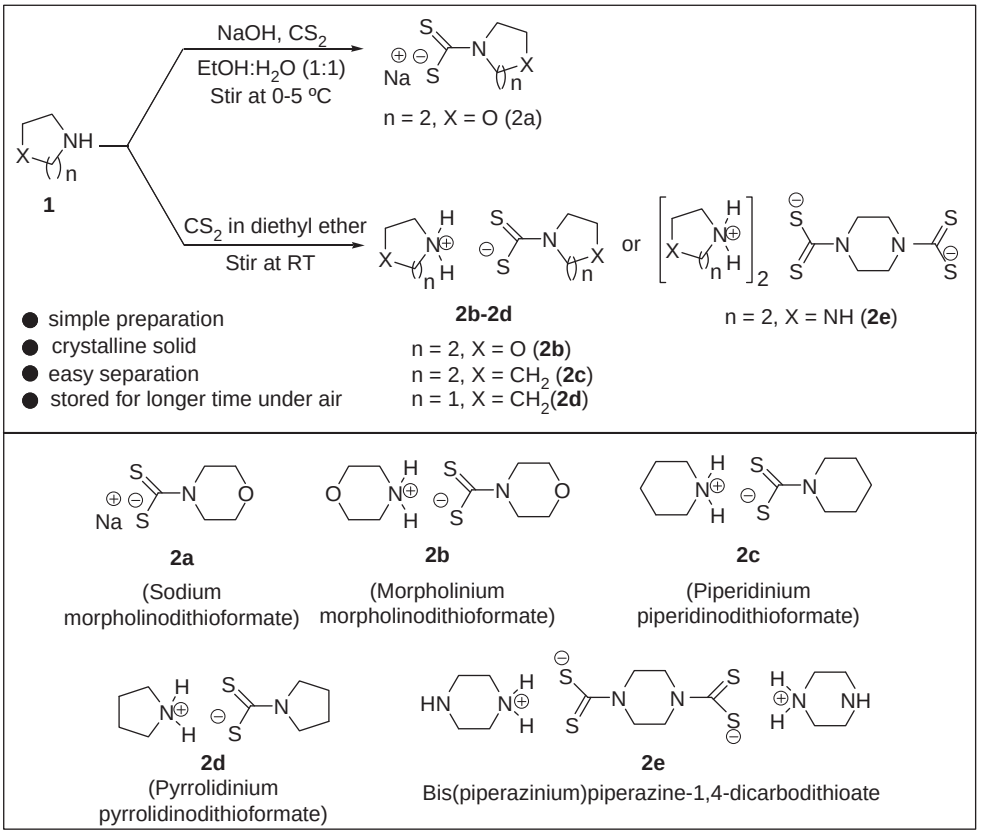
Entry	Solvent	*T* (°C)	Additive	Time (h)	Yield[a] (%)
1[b]	Neat	RT	No	1	72
2[c]	Water	RT	No	1	60[d]
3[e]	Water	RT	No	1	76
4	Water	60	No	1	78
5	EtOH	60	No	1	82
6	Water: EtOH	RT	No	1	80
7[f]	Water	RT	TBAB	1	84
8[g]	Water	RT	SDS	1	96
9[h]	**Water**	**RT**	**SDS**	**1**	**96**

[a]Yield represents pure isolated product after purification by column chromatography.
[b]Mixture of benzyl thiocyanate (1 mmol), morpholine (2 mmol) and CS_2 (1 mmol) in 2 mL solvent was stirred at room temperature.
[c]Salt **2a** was used.
[d]20% dibenzyl disulphide was isolated.
[e]Salt **2b** was used.
[f]Tetrabutyl ammonium bromide (TBAB; stoichiometric) was used.
[g]Sodium dodecyl sulfate (SDS; stoichiometric) was used.
[h]SDS (10 mol%) was used.

thiocyanate **3a**.[37,38] In order to avoid the basic reaction medium, we considered that the dithiocarbamate salt consisting of both organyl cationic and anionic part might be a better alternative and accordingly, we prepared the salt **2b** from a mixture of morpholine and CS_2 in diethyl ether following the reported procedure.[39]

The salt **2b** contains the morpholino-based cationic and anionic part and stirring a mixture of benzyl thiocyanate **3a** and **2b** (in equimolar quantity) in water at room temperature gave rise to a clean reaction without any trace of disulfide formation, producing **4a** in 76% isolated yield (Table 1, entry 3). Heating the reaction mixture of **2b** and **3a** in water or ethanol at 60°C resulted in a better yield of **4a** (78–82%; Table 1, entries 4 and 5). On the other hand, use of water–ethanol (1:1) as the solvent and conducting the reaction at room temperature gave **4a** in 80% yield (Table 1, entry 6).

It is likely that organyl thiocyanates are poorly soluble in water, and we employed two different phase transfer agents, *n*-tetrabutyl ammonium bromide (TBAB) and SDS. While the use of TBAB was found to lead to a marginal increase in the yield of **4a** (Table 1, entry 7), the presence of SDS (either in stoichiometric or in 10 mol%) afforded **4a** in excellent yield (96%) (Table 1, entries 8 and 9). Thus, excellent conversion of benzyl thiocyanate to benzyl morpholine-4-carbodithioate ester **4a** is indeed possible if we use separately prepared amine-based salt, and perform the reaction under conditions as described in entry 9 of Table 1. In aqueous medium reactions, anionic phase transfer agents as additive are usually more effective than cationic agents.[40] Here, we used both TBAB (cationic) and

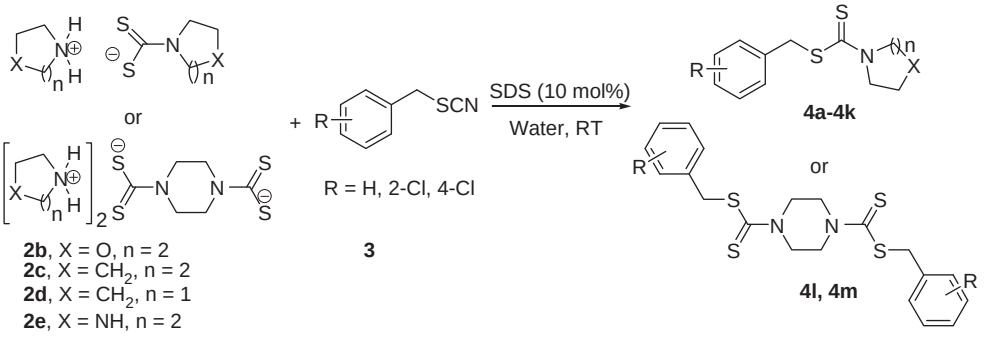


Scheme 2. Synthesis of *sec*. cyclic aliphatic amine-based dithiocarbamate salts (**2b–2e**).

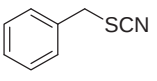
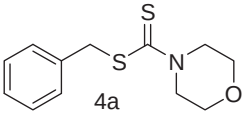
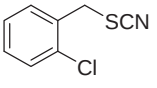
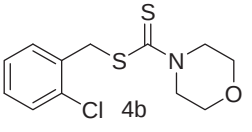
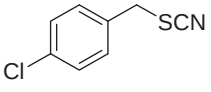
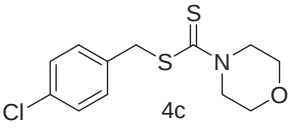
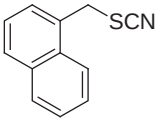
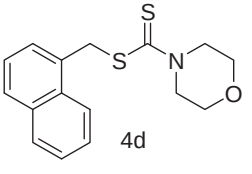
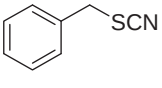
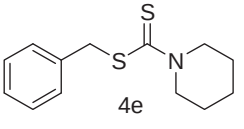
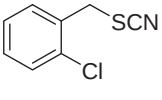
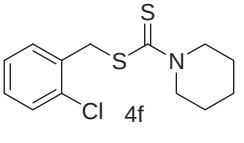
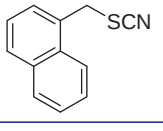
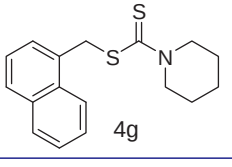
SDS (anionic) additives and the results are in conformity with previous reports. The better functioning of the anionic phase transfer agents such as SDS might be explained in the light of considering the whole system as a microreactor, where organyl thiocyanate having resided in the hydrophobic dodecyl core may come in contact with the reactant (here the dithocarbamate salt) being present in water through the formation of hydrogen bond with anionic sulfate ion.

Encouraged by this observation, we wanted to develop a general and practical procedure for the conversion of organyl thiocyanates into carbodithioate esters. We prepared other dithiocarbamate salts (**2c–2e**) from three different cyclic *sec*. amines such as piperidine, pyrrolidine and piperazine (Scheme 2), and employed our optimized conditions (as in Table 1, entry 9) for reaction with various functionalized organyl thiocyanates. The results are presented in Table 2. It is clearly evident that different chloro-substituted benzyl thiocyanates and naphthyl methyl thiocyanate underwent smooth conversion to the corresponding carbodithioate esters with all types of dithiocarbamate salts (**4a**–**4m** of Table 2). While 2- and 4-chloro benzyl thiocyanates worked equally efficiently without any steric encumbrance, the piperazine-based dithiocarbamate salt **2e** reacted with benzyl or 2-chlorobenzyl thiocyanates to produce bis-carbodithioate esters in 82–83% yields within 3 h (**4l** and **4m**).

Table 2. Synthesis of diverse *S*-alkyl carbodithioates from organyl thiocyanates and dithiocarbamate salts.[a,b]

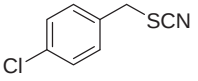
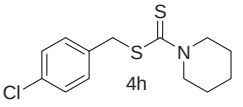
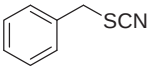
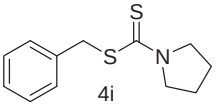
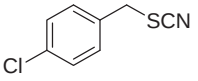
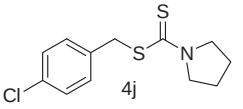
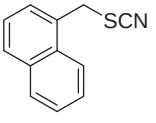
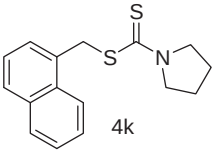
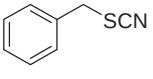
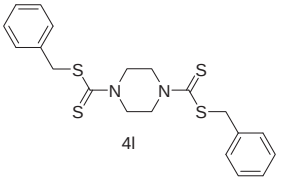
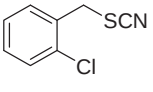
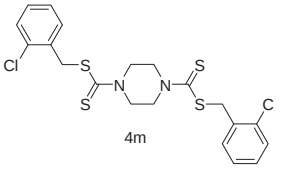


2b, X = O, n = 2
2c, X = CH_2, n = 2
2d, X = CH_2, n = 1
2e, X = NH, n = 2

Entry	R^1—SCN (**3**)	Salt (**2**)	Time (h)	*T* (°C)	Product (**4**)	Yield (%)
1		**2b**	1.0	RT	 4a	96
2		**2b**	1.0	RT	 4b	98
3		**2b**	1.0	RT	 4c	97
4		**2b**	1.5	RT	 4d	87
5		**2c**	1.0	RT	 4e	95
6		**2c**	1.0	RT	 4f	98
7		**2c**	1.5	RT	 4g	89

(*continued*)

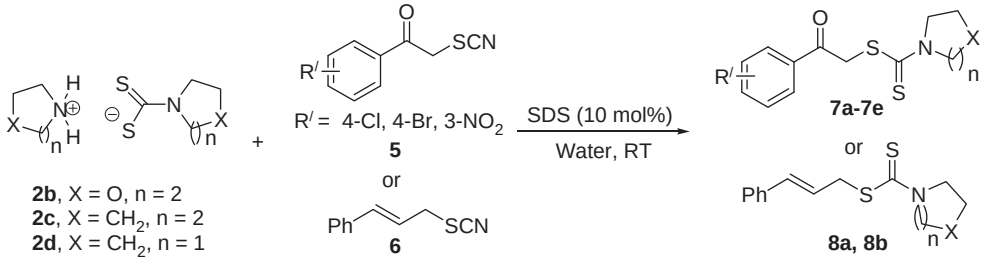
Table 2. Continued.

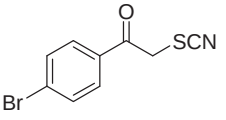
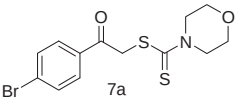
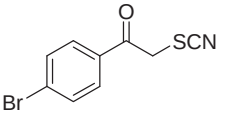
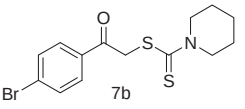
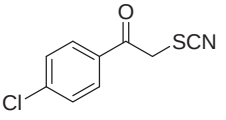
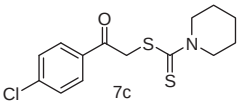
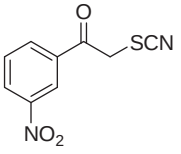
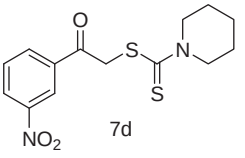
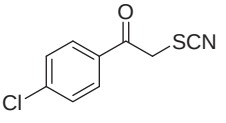
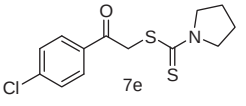
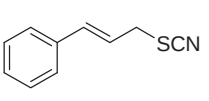
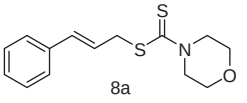
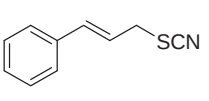
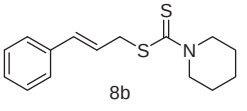
Entry	R^1—SCN (**3**)	Salt (**2**)	Time (h)	*T* (°C)	Product (**4**)	Yield (%)
8		**2c**	1.0	RT	 4h	97
9		**2d**	2.0	RT	 4i	94
10		**2d**	2.5	RT	 4j	96
11		**2d**	2.5	RT	 4k	86
12		**2e**	3.0	RT	 4l	82
13		**2e**	3.0	RT	 4m	83

[a]A mixture of **2** (1.0 mmol), **3** (1.0 mmol), SDS (10 mol%) in water (2 mL) was stirred at RT in open air. For **4l** and **4m**, compound **3** (2 mmol) was used.
[b]Yield represents pure product isolated by column chromatography.

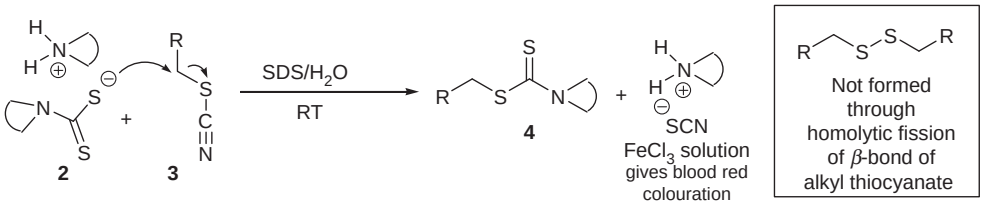
To broaden the scope of the reaction further, alkyl thiocyanates bearing β-carbonyl function (*e.g.* aroyl methyl, **5**) or β-alkenyl function (*e.g.* styrenyl methyl, **6**) were subjected to similar reaction conditions. Corresponding functionalized organic carbodithioate esters bearing carbonyl or styrenyl methyl group could be easily synthesized in aqueous medium at ambient temperature. Three different *sec*. amine-based dithiocarbamate salts (**2b–2d**) were used and corresponding carbodithioates bearing Cl, Br or NO_2 groups attached with the aromatic ring (**7a–7e**, **8a** and **8b**) were obtained in high yields (Table 3). All the compounds were characterized by spectral data and compared with melting points wherever known and reported.

Table 3. Synthesis of functionalized *S*-alkyl carbodithioates.[a,b]



Entry	R^2—SCN (**5** and **6**)	Salt (**2**)	Time (h)	*T* (°C)	Product (**7** and **8**)	Yield (%)
1		**2b**	3.0	RT	 7a	95
2		**2c**	3.0	RT	 7b	94
3		**2c**	4.0	RT	 7c	95
4		**2c**	3.5	RT	 7d	86
5		**2d**	3.0	RT	 7e	96
6		**2b**	1.5	RT	 8a	92
7		**2c**	1.5	RT	 8b	93

[a]A mixture of **2** (1.0 mmol), **5** or **6** (1.0 mmol), SDS (10 mol%) in water (2 mL) was stirred at RT in open air.
[b]Yield represents pure product isolated by column chromatography.



Scheme 3. Proposed reaction mechanism.

3. Mechanism

The reaction presumably occurs via a simple nucleophilic substitution reaction. Organyl thiocyanates are considered as psuedohalides that might not produce the corresponding carbocation easily and hence the reaction is expected to proceed via the S_N2 pathway (Scheme 3). The dithiocarbamate salt consisting of both organyl cationic and anionic system seems to render better results than using an *in situ* mixture of *sec*. amine and CS_2 or the corresponding sodium salt. Use of additives such as SDS likely help the organic reactants become more homogeneous affording excellent conversions. The possibility of the formation of thiyl radical via β-bond cleavage of the alkyl thiocyanate can be excluded since the reaction conditions do not support radical formation nor is the corresponding disulfide formed in the reaction.[41,42] On the other hand, aqueous ferric chloride solution produces blood-red coloration indicating elimination of the thiocyanate anion.

4. Conclusion

In conclusion, we have shown that easily accessible and air-stable cyclic *sec*. amine-based dithiocarbamate salts can serve as efficient reagents for the preparation of a large variety of *S*-substituted carbodithioate esters from rarely used organyl thiocyanates as a common strategy. The use of this type of salt not only shows superior activity to the existing one-pot three-component procedure but also establishes it as alternative reagent, obtained easily in quantitative conversion, for the preparation of carbodithioate esters. The simple procedure can be carried out at room temperature, in water medium and affords excellent yields. Further applications of these easily accessible salts are currently under active pursuit from this laboratory. This method also establishes that the *sec*. amine-based dithiocarbamate salts can serve as a stable more reactive alternative than *in situ* use of volatile CS_2 and *sec*. amine reagent, not only for this reaction, but also for other purposes, which are currently being pursued in this laboratory.

5. Experimental

5.1. General information

Morpholine, piperidine and pyrrolidine were purchased from Lancaster and used after distillation. Piperazine was purchased from Loba Chemie. CS_2 and SDS were purchased from SD Fine-Chem Limited and used directly. Benzyl, naphthyl methyl, cinnamyl and aroyl methyl thiocyanates were prepared from reported procedure and purified by column chromatography before use. Melting point of the solid compounds was determined in a

concentrated H_2SO_4 bath. FT-IR spectra were recorded with a FT-IR-8300 SHIMADZU spectrophotometer using a KBr pellet method for solid compounds and in neat for liquid compounds. NMR spectra were taken in $CDCl_3$ using a Bruker AV-300 spectrometer operating for ^1H at 300 MHz and for ^{13}C at 75 MHz.

5.2. General procedure for the synthesis cyclic ammonium salts of dithiocarbamic acid (2b–2e) [39]

A solution of CS_2 (5 mmol) in diethyl ether (5 mL) was slowly added to a solution of morpholine (10 mmol) or piperidine (10 mmol) or pyrrolidine (10 mmol) in diethyl ether (5 mL). The reaction mixtures were stirred for 30 min at room temperature. Solid salts were precipitated during this time and were filtered off through a Buchner funnel, washed with diethyl ether and dried under vacuum to obtain the desired salts **2b–2d**. In the case of **2e**, a solution of CS_2 (6 mmol) in diethyl ether (5 mL) was slowly added to a solution of piperazine (9 mmol) in diethyl ether (6 mL). The reaction mixture was stirred for 45 min at room temperature. The grey solids were filtered off, washed with diethyl ether and dried under vacuum to obtain the desired salt **2e**.

5.2.1. Morpholinium morpholinodithioformate (salt 2b) [39]

White solid; yield: 1.23 g (98%); Mp: 197–200°C, Lit. Mp 195–197°C.[39] IR (KBr): ν_{max} = 2854, 2711, 2475, 1583, 1420, 1255, 1215, 1112, 978, 876 cm^{-1}.

5.2.2. Piperidinium piperidinodithioformate (salt 2c) [39]

White solid; yield: 1.20 g (98%); Mp: 164–166°C, Lit. Mp 160°C.[39] IR (KBr): ν_{max} = 2936, 2843, 2731, 2497, 1583, 1409, 1215, 1122, 958 cm^{-1}.

5.2.3. Pyrrolidinium pyrrolidinodithioformate (salt 2d)

Off-white solid; yield: 1.05 g (96%); Mp: 149–151°C. IR (KBr): ν_{max} = 2946, 2864, 2516, 2393, 1390, 1318, 1164, 999, 938 cm^{-1}.

5.2.4. Bis(piperazinium)piperazine-1,4-dicarbodithioate (salt 2e)

Grey solid; yield: 1.19 g (97%); Mp: 238–242°C. IR (KBr): ν_{max} = 3162, 2915, 2434, 2331, 1634, 1390, 1225, 1123, 958, 855 cm^{-1}.

5.3. General procedure for the synthesis of S-alkyl carbodithioate esters

A mixture of organyl thiocyanate (1 mmol), dithiocarbamate salt (1 mmol) and SDS (0.1 mmol) in water (2 mL) was stirred vigorously using a magnetic bar at room temperature. The progress of the reaction was monitored by TLC. After the reaction was continued for specified time, as mentioned in Tables 2 and 3, the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and the combined organic extracts were collected over anhydrous Na_2SO_4. Evaporation of the volatiles afforded the crude product, which was further purified by column chromatography over silica gel. Elution with a mixture of ethyl acetate-light petroleum furnished the desired product. Yields of the products are shown in Tables 2 and 3.

All the products were identified and characterized by spectral data (FT-IR, ^{1}H and ^{13}C NMR), by melting point for solid compounds (compared wherever known).

5.3.1. Benzyl morpholine-4-carbodithioate (Table 2, 4a) [32]

Light yellow solid; yield: 0.243 g (96%); Mp: 64–65°C, Lit. Mp 59–60°C.[32] IR (KBr): ν_{max} = 3038, 2976, 2869, 1920, 1635, 1617, 1559, 1489, 1456, 1304, 1271, 1235, 924, 825, 725, 543 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.73 (s, 4H, 2 × OCH_2), 4.01–4.33 (m, 4H, 2 × NCH_2), 4.57 (s, 2H, SCH_2), 7.22–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 42.02 (SCH_2), 50.81 (NCH_2), 66.27 (OCH_2), 127.65, 128.67, 129.42, 135.78, 197.11 (C=S).

5.3.2. 2-Chlorobenzyl morpholine-4-carbodithioate (Table 2, 4b)

White crystalline solid; yield: 0.281 g (98%); Mp: 94–96°C. IR (KBr): ν_{max} = 3053, 2992, 2931, 2855, 1918, 1654, 1635, 1617, 1542, 1444, 1347, 1310, 1271, 1053, 1028, 868, 731, 582 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.77 (s, 4H, 2 × OCH_2), 4.17 (s, br, 4H, 2 × NCH_2), 4.76 (s, 2H, SCH_2), 7.21–7.64 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.48 (SCH_2), 50.91 (NCH_2), 66.25 (OCH_2), 126.98, 129.10, 129.61, 131.56, 134.12, 134.58, 196.91 (C=S).

5.3.3. 4-Chlorobenzyl morpholine-4-carbodithioate (Table 2, 4c)

White solid; yield: 0.278 g (97%); Mp: 79–81°C. IR (KBr): ν_{max} = 3007, 2977, 2916, 2870, 1833, 1656, 1620, 1542, 1423, 1268, 1217, 1034, 998, 837, 643 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.66 (s, 4H, 2 × OCH_2), 3.90 (s, 2H, NCH_2), 4.17 (s, 2H, NCH_2), 4.47 (s, 2H, SCH_2), 7.17–7.25 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.83 (SCH_2), 50.83 (NCH_2), 66.10 (OCH_2), 128.60, 130.57, 133.26, 134.59, 196.50 (C=S).

5.3.4. (Naphthalen-1-yl) methyl morpholine-4-carbodithioate (Table 2, 4d)

Light brown solid; yield: 0.263 g (87%); Mp: 115–117°C. IR (KBr): ν_{max} = 3053, 2976, 2900, 2869, 1699, 1578, 1538, 1420, 1356, 1301, 1271, 1189, 998, 786, 630 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.66 (s, 4H, 2 × OCH_2), 3.91–4.06 (m, 4H, 2 × NCH_2), 4.95 (s, 2H, SCH_2), 7.31–7.52 (m, 4H), 7.71–7.98 (m, 2H), 8.00–8.01 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.34 (SCH_2), 50.47 (NCH_2), 66.23 (OCH_2), 123.93, 125.46, 126.01, 126.50, 128.34, 128.80, 128.83, 131.06, 131.84, 133.90, 197.25 (C=S).

5.3.5. Benzyl piperidine-1-carbodithioate (Table 2, 4e) [43]

Pale yellow viscous liquid; yield: 0.238 g (95%). IR (neat): ν_{max} = 3040, 2974, 2864, 1945, 1620, 1590, 1545, 1495, 1358, 1340, 1291, 1279, 1222, 1016, 980, 840, 742 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.80 (s, br, 2H, NCH_2), 4.21 (s, br, 2H, NCH_2), 4.49 (s, 2H, SCH_2), 7.15–7.33 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.29 ($NCH_2CH_2\underline{CH_2}$), 25.79 ($NCH_2\underline{CH_2}$), 42.25 ($SCH_2$), 52.67 ($NCH_2$), 127.45, 128.56, 129.38, 136.12, 195.31 (C=S).

5.3.6. 2-Chlorobenzyl piperidine-1-carbodithioate (Table 2, 4f)

Yellow viscous liquid; yield: 0.280 g (98%). IR (neat): ν_{max} = 3010, 2970, 2860, 1996, 1580, 1546, 1493, 1357, 1340, 1280, 1224, 1074, 946, 840, 746, 650 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.69 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.87 (s, br, 2H, NCH_2), 4.29 (s, br, 2H, NCH_2), 4.72 (s, 2H, SCH_2), 7.18–7.23 (m, 2H), 7.34–7.38 (m, 1H), 7.54–7.58 (m, 1H). ^{13}C NMR

($CDCl_3$, 75 MHz): δ 24.29 ($NCH_2CH_2\underline{CH_2}$), 25.62 ($NCH_2\underline{CH_2}$), 39.66 ($SCH_2$), 51.42 ($NCH_2$), 53.10 ($NCH_2$), 126.96, 128.95, 129.55, 131.56, 134.45, 134.54, 194.91 (C=S).

5.3.7. (Naphthalen-1-yl) methyl piperidine-1-carbodithioate (Table 2, 4g)

White solid; yield: 0.268 g (89%); Mp: 93–95°C. IR (KBr): ν_{max} = 3038, 2947, 2870, 1620, 1596, 1563, 1542, 1474, 1435, 1399, 1365, 1281, 1235, 1210, 1113, 980, 870, 776, 670, 588 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.63 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.75 (s, br, 2H, NCH_2), 4.27 (s, br, 2H, NCH_2), 4.93 (s, 2H, SCH_2), 7.31–7.58 (m, 4H), 7.71–7.85 (m, 2H), 8.0–8.01 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.29 ($NCH_2CH_2\underline{CH_2}$), 25.90 ($NCH_2\underline{CH_2}$), 40.56 ($SCH_2$), 52.83 ($NCH_2$), 124.11, 125.49, 125.96, 126.43, 128.30, 128.66, 128.78, 131.42, 131.90, 133.88, 195.26 (C=S).

5.3.8. 4-Chlorobenzyl piperidine-1-carbodithioate (Table 2, 4h)

White solid; yield: 0.277 g (97%); Mp: 83–85°C. IR (KBr): ν_{max} = 3007, 1961, 2855, 1632, 1617, 1577, 1542, 1508, 1481, 1429, 1378, 1281, 1225, 1110, 1080, 974, 843, 746, 652 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.79 (s, br, 2H, NCH_2), 4.22 (s, br, 2H, NCH_2), 4.44 (s, 2H, SCH_2), 7.15–7.27 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.27 ($NCH_2CH_2\underline{CH_2}$), 25.54 ($NCH_2\underline{CH_2}$), 41.20 ($SCH_2$), 53.08 ($NCH_2$), 128.67, 130.70, 133.21, 135.04, 194.70 (C=S).

5.3.9. Benzyl pyrrolidine-1-carbodithioate (Table 2, 4i) [43]

Yellow liquid; yield: 0.223 g (94%). IR (neat): ν_{max} = 3048, 2970, 2865, 1903, 1590, 1440, 1365, 1308, 1216, 1070, 1012, 944, 826, 780, 503 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.92−2.10 (m, 4H, $NCH_2(\underline{CH_2})_2$), 3.62 (t, J = 6.3 Hz, 2H, NCH_2), 3.93 (t, J = 6.9 Hz, 2H, NCH_2), 4.58 (s, 2H, SCH_2), 7.22–7.33 (m, 3H), 7.38–7.41 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.29 ($NCH_2\underline{CH_2}$), 26.08 ($NCH_2\underline{CH_2}$), 41.30 (SCH_2), 50.52 (NCH_2), 55.03 (NCH_2), 127.39, 128.56, 129.27, 136.55, 192.46 (C=S).

5.3.10. 4-Chlorobenzyl pyrrolidine-1-carbodithioate (Table 2, 4j)

Pale yellow solid; yield: 0.261 g (96%); Mp: 60–62°C. IR (KBr): ν_{max} = 2966, 2864, 1903, 1595, 1441, 1328, 1092, 1009, 948, 825, 744, 507 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.92−2.10 (m, 4H, $NCH_2(\underline{CH_2})_2$), 3.62 (t, J = 6.3 Hz, 2H, NCH_2), 3.93 (t, J = 6.9 Hz, 2H, NCH_2), 7.24–7.27 (m, 2H), 7.32–7.35 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.25 ($NCH_2\underline{CH_2}$), 26.05($NCH_2\underline{CH_2}$), 40.21 (SCH_2), 50.56 (NCH_2), 55.15 (NCH_2), 128.61, 130.56, 133.10, 135.42, 191.81 (C=S).

5.3.11. (Naphthalen-1-yl) methyl pyrrolidine-1-carbodithioate (Table 2, 4k)

White solid; yield: 0.247 g (86%); Mp: 116–118°C. IR (KBr): ν_{max} = 3040, 2950, 2880, 1542, 1450, 1400, 1364, 1342, 1280, 1210, 1134, 1072, 980, 808, 770, 672, 540 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.87–1.97 (m, 4H, $NCH_2(\underline{CH_2})_2$), 3.51 (t, J = 6.9 Hz, 2H, NCH_2), 3.94 (t, J = 6.6 Hz, 2H, NCH_2), 5.01 (s, 2H, SCH_2), 7.34–7.40 (m, 1H), 7.43–7.54 (m, 2H), 7.58 (d, J = 6.9 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.81–7.84 (m, 1H), 8.08 (d, J = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.29 ($NCH_2\underline{CH_2}$), 26.06 ($NCH_2\underline{CH_2}$), 39.64 (SCH_2), 50.51 (NCH_2), 55.02 (NCH_2), 124.08, 125.50, 125.98, 126.44, 128.17, 128.61, 128.81, 131.77, 131.85, 133.92, 192.33 (C=S).

5.3.12. Dibenzyl piperazine-1,4-dicarbodithioate (Table 2, 4l) [44]

White solid; yield: 0.343 g (82%); Mp: 124–126°C, Lit. Mp 122–123°C. IR (KBr): ν_{max} = 3068, 3038, 2931, 1538, 1505, 1474, 1435, 1413, 1277, 1210, 1159, 1043, 924, 849, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.18 (s, br, 8H, 4 × NCH_2), 4.51 (s, 4H, 2 × SCH_2), 7.19–7.32 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 42.16 (SCH_2), 48.71 (NCH_2), 127.74, 128.69, 129.39, 135.51, 197.53 (C=S).

5.3.13. Bis-(2-chlorobenzyl) piperazine-1,4-dicarbodithioate (Table 2, 4 m)

Grey solid; yield: 0.404 g (83%); Mp: 148–150°C. IR (KBr): ν_{max} = 2916, 1640, 1420, 1276, 1041, 990, 928, 846, 744 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.28 (s, br, 8H, 4 × NCH_2), 4.72 (s, 4H, 2 × SCH_2), 7.18–7.26 (m, 4H), 7.35–7.39 (m, 2H), 7.53–7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.64 (SCH_2), 48.99 (NCH_2), 126.98, 129.21, 129.63, 131.54, 133.81, 134.56, 197.19 (C=S).

5.3.14. 4-Bromo phenacyl morpholine-4-carbodithioate (Table 3, 7a)

White solid; yield: 0.342 g (95%); Mp: 164–166°C. IR (KBr): ν_{max} = 2967, 2906, 2855, 1686, 1583, 1430, 1276, 1125, 1112, 990, 816, 539 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.71 (t, J = 4.8 Hz, 4H, 2 × OCH_2), 3.97 (s, br, 2H, NCH_2), 4.2 (s, br, 2H, NCH_2), 4.77 (s, 2H, SCH_2), 7.54–7.59 (m, 2H), 7.84–7.88 (m, 2H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 44.28 (SCH_2), 51.55 (NCH_2), 66.21 (OCH_2), 128.85, 130.06, 132.08, 134.88, 192.28 (C=O), 195.65 (C=S).

5.3.15. 4-Bromo phenacyl piperidine-1-carbodithioate (Table 3, 7b)

White solid; yield: 0.336 g (94%); Mp: 116–118°C. IR (KBr): ν_{max} = 3007, 2947, 2869, 1687, 1584, 1438, 1362, 1286, 1253, 973, 858, 666 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.65 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.89 (s, br, 2H, NCH_2), 4.18 (s, br, 2H, NCH_2), 4.77 (s, 2H, SCH_2), 7.54–7.57 (m, 2H), 7.86–7.89 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.16 ($NCH_2CH_2\underline{CH_2}$), 25.95 ($NCH_2\underline{CH_2}$), 44.50 ($SCH_2$), 51.76 ($NCH_2$), 53.66 ($NCH_2$), 128.62, 130.09, 131.99, 135.04, 192.71 (C=O), 193.70 (C=S).

5.3.16. 4-Chloro phenacyl piperidine-1-carbodithioate (Table 3, 7c)

Yellowish white solid; yield: 0.298 g (95%); Mp: 110–112°C. IR (KBr): ν_{max} = 3007, 2961, 2855, 1690, 1587, 1438, 1347, 1244, 1113, 971, 858, 682, 548 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.65 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.89 (s, br, 2H, NCH_2), 4.19 (s, br, 2H, NCH_2), 4.77 (s, 2H, SCH_2), 7.54–7.58 (m, 2H), 7.85–7.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.18 ($NCH_2CH_2\underline{CH_2}$), 25.42 ($NCH_2\underline{CH_2}$), 26.09 ($NCH_2\underline{CH_2}$), 44.49 ($SCH_2$), 51.78 ($NCH_2$), 53.72 ($NCH_2$), 128.67, 130.11, 132.01, 135.00, 192.75 (C=O), 193.63 (C=S).

5.3.17. 3-Nitro phenacyl piperidine-1-carbodithioate (Table 3, 7d)

Pale yellow solid; yield: 0.279 g (86%); Mp: 109–111°C. IR (KBr): ν_{max} = 2926, 2854, 1697, 1613, 1532, 1430, 1337, 1204, 1112, 1072, 979, 804, 733, 672 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.73 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.97 (s, br, 2H, NCH_2), 4.25 (s, br, 2H, NCH_2), 4.86 (s, 2H, SCH_2), 7.69–7.74 (m, 1H), 8.40–8.46 (m, 2H), 8.90–8.91 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.16 ($NCH_2CH_2\underline{CH_2}$), 26.02 ($NCH_2\underline{CH_2}$), 44.09 ($SCH_2$), 52.09 ($NCH_2$), 53.79 ($NCH_2$), 123.45, 127.49, 129.95, 134.13, 137.87, 148.58, 191.84 (C=O), 193.39 (C=S).

5.3.18. 4-Chloro phenacyl pyrrolidine-1-carbodithioate (Table 3, 7e)

Pale yellow solid; yield: 0.287 g (96%); Mp: 102–104°C. IR (KBr): ν_{max} = 2957, 2876, 1676, 1583, 1430, 1286, 1184, 1080, 990, 958, 825, 528 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.94–2.03 (m, 2H, $NCH_2\underline{CH_2}$), 2.06–2.14 (m, 2H, $NCH_2\underline{CH_2}$), 3.74 (t, J = 6.9 Hz, 2H, NCH_2), 3.9 (t, J = 6.9 Hz, 2H, NCH_2), 4.85 (s, 2H, SCH_2), 7.44–7.47 (m, 2H), 8.01–8.04 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.33 ($NCH_2\underline{CH_2}$), 26.12 ($NCH_2\underline{CH_2}$), 44.04 (SCH_2), 50.80 ($N\underline{CH_2}$), 55.53 ($N\underline{CH_2}$), 128.99, 130.01, 134.43, 139.88, 190.68 (C=O), 192.43 (C=S).

5.3.19. (E)-Cinnamyl morpholine-4-carbodithioate, (Table 3, 8a) [30]

White crystalline solid, yield: 0.257 g (92%); Mp: 80–82°C (Lit. reported as yellowish viscous liquid). IR (KBr): ν_{max} = 3038, 2961, 2869, 1720, 1620, 1577, 1469, 1304, 1268, 1220, 1113, 992, 755 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.78 (t, J = 4.5 Hz, 4H, 2 × OCH_2), 4.17–4.24 (m, 6H, 2 × NCH_2, SCH_2), 6.28–6.38 (m, 1H, PhCH=C$\underline{H}$$CH_2$), 6.67 (d, J = 15.6 Hz, 1H, PhCH), 7.23–7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.97 (SCH_2), 50.90 (NCH_2), 66.26 (OCH_2), 123.68, 126.45, 127.76, 128.56, 133.95, 136.60, 197.03 (C=S).

5.3.20. (E)-Cinnamyl piperidine-1-carbodithioate (Table 3, 8b) [30]

White crystalline solid; yield: 0.258 g (93%); Mp: 73–75°C (Lit. reported as yellowish viscous liquid). IR (KBr): ν_{max} = 3048, 2947, 2869, 1617, 1566, 1472, 1435, 1265, 1235, 1135, 1116, 1110, 973, 743 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.63 (s, 6H, $NCH_2(\underline{CH_2})_3$), 3.82 (s, br, 2H, NCH_2), 4.01–4.13 (m, 2H, SCH_2), 4.23 (s, br, 2H, NCH_2), 6.20–6.31 (m, 1H, PhCH=C$\underline{H}$$CH_2$), 6.56 (d, J = 15.9 Hz, 1H, PhCH), 7.12–7.31 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): 24.32 ($NCH_2CH_2\underline{CH_2}$), 26.00 ($NCH_2\underline{CH_2}$), 40.23 ($SCH_2$), 51.37 ($NCH_2$), 124.17, 126.44, 127.67, 128.54, 133.59, 136.72, 195.04 (C=S).

Disclosure statement

No potential conflict of interest was reported by the authors.

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