

Synthesis of *N*-Aryl *S*-Alkylthiocarbamates

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ABSTRACT: *Several *N*-aryl *S*-alkylthiocarbamates were synthesized by reactions of isocyanates with LiAlHSH and then with alkyl halides.* © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:374–378, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10163

INTRODUCTION

Thiocarbamates have been used as key intermediates for the synthesis of ureas [1] and isocyanates [2] and are very important moieties in pesticides [3]. However, only a limited number of methods have been reported for the preparation of the thiocarbamates. For example, *S*-allylic thiocarbamates were obtained from *O*-allylic thiocarbamates by 1,3-allyl migration from the oxygen to the sulfur atom [4]. Other routes are the reactions of alkyl thiocyanates with alcohols [5], and of amines with elemental sulfur and carbon monoxide in the presence of selenium [6]. A facile method for the preparation of thiocarbamates would certainly be very useful. Recently, we developed a novel selenating reagent [7], LiAlHSeH which is generated by the stirring selenium powder with LiAlH₄ in THF. This reagent is useful for preparing a variety of selenium containing compounds [8]. However, application of same procedure to the sulfur atom, while reasonable, has not yet been demonstrated. In the present study, we investigated the preparation of various thiocarbamates from the corresponding

isocyanates **1** and alkyl halides **3**, using LiAlHSH **2**. Herein, we report a new method for preparation of *S*-alkyl thiocarbamates **4** and confirm the usefulness of LiAlHSH as a reagent for the introduction of sulfur atom.

RESULTS AND DISCUSSION

The reaction leading to *N*-aryl *S*-alkylthiocarbamates **4** is shown in Scheme 1. Phenyl isocyanate **1a** was added to an anhydrous THF solution of LiAlHSH **2** [9]. The reaction mixture was stirred at room temperature for 1 h under an argon atmosphere. A solution of methyl iodide **3a** in THF was added to the reaction mixture at room temperature. The resulting reaction mixture was stirred for an additional 3 h.

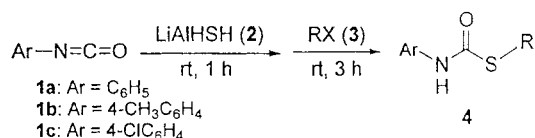
After workup, *S*-methyl *N*-phenylthiocarbamate **4a** was obtained in 84% yield. Reactions of three isocyanates **1** with nine alkyl halides **3** also gave the corresponding *N*-aryl *S*-alkylthiocarbamates **4** (Table 1). The yield using alkyl halides bearing longer carbon chains tended to decrease because of their reduced electrophilicity. These results confirm that LiAlHSH **2** affords a variety of *N*-aryl *S*-alkylthiocarbamates, showing a reactivity similar to LiAlHSeH [8b]. The ¹³C NMR spectra of **4** in CDCl₃ show interesting spectral features at 20°C. There is significant line broadening of the peaks of C1, C2, C4, C6, and C7, while those of C3, C5, and alkyl carbons gave typically sharp peaks (Fig. 1, upper). These spectral features were highly dependent on the conditions of the NMR measurement. For example, the broad signals of **4** became sharper when the spectrum was measured in DMSO-*d*₆ or in CDCl₃ at lower temperatures (0 and –20°C). The ¹³C NMR spectra measured in CDCl₃ at –40°C showed sharp peaks similar to ordinary spectra along with new small satellite peaks (Fig. 1, lower). These interesting observations in the NMR

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SCHEME 1

spectra are predicted based on equilibrium in **4**, between the major *s-trans* and the minor *s-cis* forms (Scheme 2), as was previously observed in the NMR spectra of *Se*-aryl *N*-alkylselenocarbamates [8b].

In conclusion, various *S*-aryl *N*-alkylthiocarbamates have been synthesized by reacting isocyanates **1** with LiAlHSH **2** and then with alkyl halides. It was confirmed that LiAlHSH **2** behaves similar to LiAlHSeH [7], and represents an excellent reagent for the introduction of sulfur.

EXPERIMENTAL

Melting points were determined by use of Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were measured on Perkin-Elmer 1600 spectrometer. ¹H and ¹³C spectra were recorded on a JEOL-JNM-α400 (400 MHz) spectrometer. Mass spectra were obtained on a Shimadzu 9020-DF mass spectrometer. Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use.

***S*-Methyl *N*-phenylthiocarbamate 4a.** Phenyl isocyanate **1a** (0.22 ml, 2.0 mmol) was added to a THF solution (10 ml) of LiAlHSH **2** (1.0 mmol). The reaction mixture was stirred at room temperature for 1 h. Methyl iodide **3a** (0.06 ml, 1.0 mmol) was added to the reaction mixture. The resulting reaction mixture was stirred at room temperature for 3 h. The mixture was extracted with dichloromethane and washed with water. The organic layer was dried

over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane/hexane (1:2) to give **4a** 0.14 g (84%) as white crystals; mp 71.2–72.8°C; IR (KBr) 1661, 3288 cm⁻¹; ¹H NMR (CDCl₃); δ 2.42 (3H, s, CH₃), 7.11 (1H, t, *J* = 7.2 Hz, Ar), 7.12 (1H, br s, NH), 7.31 (2H, t, *J* = 7.2 Hz, Ar), 7.41 (2H, d, *J* = 7.2 Hz, Ar); ¹³C NMR (CDCl₃); δ 12.6, 119.8, 124.4, 129.1, 137.7, (Ar), 162.6; MS (CI): *m/z* = 168 [*M*⁺ + 1].

***S*-Ethyl *N*-phenylthiocarbamate 4b.** White crystals; mp 63.9–65.1°C; IR (KBr) 1651, 3281 cm⁻¹; ¹H NMR (CDCl₃); δ 1.33 (3H, t, *J* = 7.2 Hz, CH₃), 2.98 (2H, q, *J* = 7.2 Hz, CH₂), 7.09 (1H, t, *J* = 7.2 Hz, Ar), 7.21 (1H, br s, NH), 7.30 (2H, t, *J* = 7.2 Hz, Ar), 7.41 (2H, d, *J* = 7.2 Hz, Ar); ¹³C NMR (CDCl₃); δ 15.5, 24.7, 119.7, 124.4, 129.1, 137.6 (Ar), 165.8; MS (CI): *m/z* = 182 [*M*⁺ + 1].

***S*-Propyl *N*-phenylthiocarbamate 4c.** White crystals; mp 73.2–75.6°C; IR (KBr) 1653, 3280 cm⁻¹; ¹H NMR (CDCl₃); δ 1.00 (3H, t, *J* = 7.6 Hz, CH₃), 1.67 (2H, m, CH₂), 2.95 (2H, t, *J* = 7.6 Hz, CH₂), 7.02 (1H, br s, NH), 7.10 (1H, t, *J* = 7.6 Hz, Ar), 7.31 (2H, t, *J* = 7.6 Hz, Ar), 7.41 (2H, d, *J* = 7.6 Hz, Ar); ¹³C NMR (CDCl₃); δ 13.2, 23.6, 32.2, 119.7–137.7 (Ar), 165.9; MS (CI): *m/z* = 196 [*M*⁺ + 1].

***S*-Butyl *N*-phenylthiocarbamate 4d.** White crystals; mp 64.3–65.0°C; IR (KBr) 1652, 3287 cm⁻¹; ¹H NMR (CDCl₃); δ 0.92 (3H, t, *J* = 7.6 Hz, CH₃), 1.42 (2H, m, *J* = 7.6 Hz, CH₂), 1.64 (2H, quint, *J* = 7.6 Hz, CH₂), 2.97 (2H, t, *J* = 7.6 Hz, CH₂), 7.09 (1H, t, *J* = 7.2 Hz, Ar), 7.13 (1H, br s, NH), 7.30 (2H, t, *J* = 7.2 Hz, Ar), 7.40 (2H, d, *J* = 7.2 Hz, Ar); ¹³C NMR (CDCl₃); δ 13.6, 21.8, 29.9, 32.3, 119.6–137.8 (Ar), 166.0; MS (CI): *m/z* = 210 [*M*⁺ + 1].

TABLE 1 Synthesis of *N*-Aryl *S*-Alkylthiocarbamate

RX (3)	Thiocarbamate (4), Yield (%) ^a		
	Ar = C ₆ H ₅ (4a–4i)	Ar = 4-CH ₃ C ₆ H ₄ (4j–4r)	Ar = 4-ClC ₆ H ₄ (4s–4v)
CH ₃ I	84	59	— ^b
C ₂ H ₅ I	71	51	47
CH ₃ (CH ₂) ₂ I	66	50	— ^b
CH ₃ (CH ₂) ₃ I	54	46	— ^b
(CH ₃) ₂ CH(CH ₂) ₂ I	50	52	— ^b
CH ₃ (CH ₂) ₇ Br	25	24	— ^b
C ₆ H ₅ CH ₂ Br	55	36	35
C ₆ H ₅ (CH ₂) ₂ Br	44	32	24
C ₆ H ₅ (CH ₂) ₃ Br	36	44	23

^aIsolated yield.

^bNot tried.

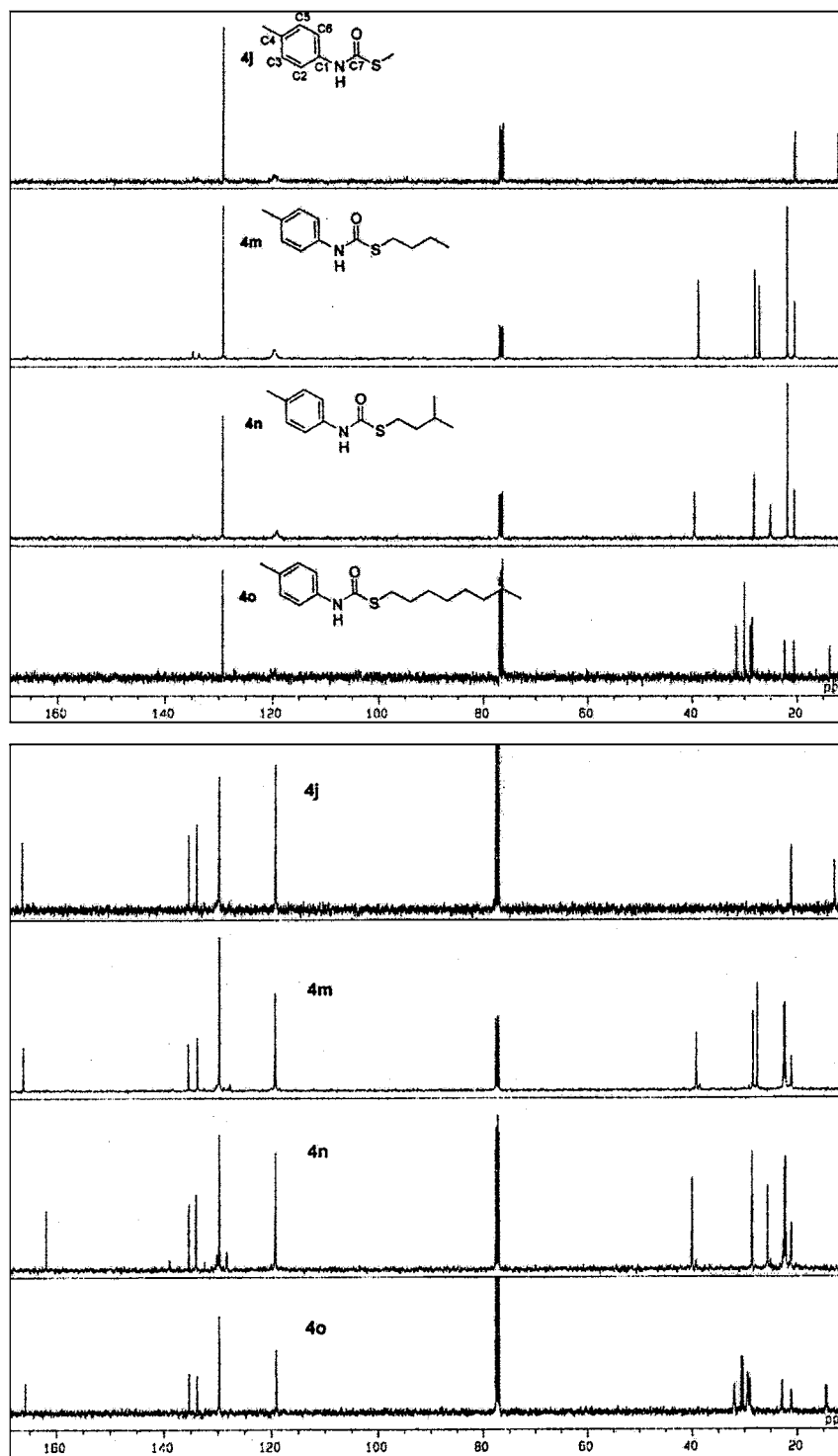
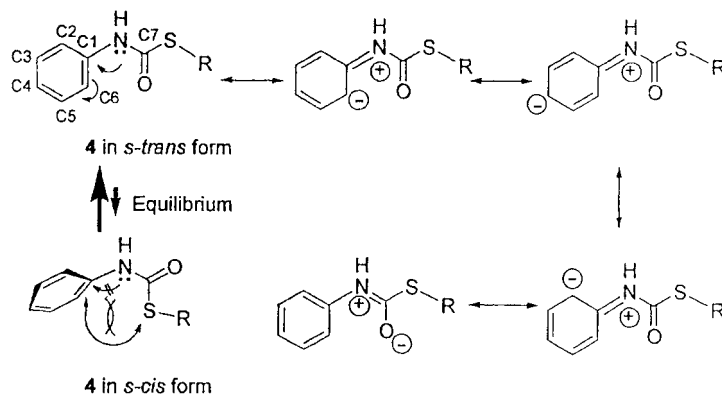


FIGURE 1 ^{13}C NMR spectra of compounds **4** at 20°C (upper) and -40°C (lower).

S-Isopentyl *N*-phenylthiocarbamate **4e**. White crystals; mp 66.1–69.3°C; IR (KBr) 1655, 3290 cm^{-1} ; ^1H NMR (CDCl_3); δ 0.92 (6H, t, $J = 6.8$ Hz, CH_3), 1.54 (2H, q, CH_2), 1.68 (1H, m, CH), 2.97 (2H, t, $J = 8.0$ Hz, CH_2), 7.09 (1H, t, $J = 7.2$ Hz, Ar), 7.19 (1H, br s, NH), 7.30 (2H, t, $J = 7.2$ Hz, Ar), 7.41 (2H, d, $J = 7.2$

Hz, Ar); ^{13}C NMR (CDCl_3); δ 22.1, 27.4, 28.3, 30.8, 39.1, 119.6–137.7 (Ar), 165.9; MS (CI): $m/z = 224$ [$\text{M}^+ + 1$].

S-Octyl *N*-phenylthiocarbamate **4f**. White crystals; mp 56.1–58.9°C; IR (KBr) 1658, 3328 cm^{-1} ; ^1H



SCHEME 2

NMR (CDCl₃); δ 0.86 (3H, t, J = 6.8 Hz, CH₃), 1.33 (10H, d, J = 6.8 Hz, CH₂), 1.65 (2H, m, CH₂), 2.96 (2H, t, J = 6.8 Hz, CH₂), 7.09 (1H, t, J = 7.2 Hz, Ar), 7.10 (1H, br s, NH), 7.30 (2H, t, J = 7.2 Hz, Ar), 7.41 (2H, d, J = 7.2 Hz, Ar); ¹³C NMR (CDCl₃); δ 14.0, 22.6, 28.7, 29.0, 29.1, 30.2, 30.3, 31.7, 119.6–137.7 (Ar), 165.9; MS (CI): m/z = 266 [M^+ + 1].

S-Benzyl *N*-phenylthiocarbamate **4g**. White powder; mp 92.1–94.2°C; IR (KBr) 1653, 3250 cm⁻¹; ¹H NMR (CDCl₃); δ 4.22 (2H, s, CH₂), 7.08–7.40 (10H, m, Ar), 7.10 (1H, br s, NH); ¹³C NMR (CDCl₃); δ 34.4, 119.8–137.8 (Ar), 165.1; MS (CI): m/z = 244 [M^+ + 1].

S-Phenetyl *N*-phenylthiocarbamate **4h**. White crystals; mp 108.1–110.3°C; IR (KBr) 1652, 3382 cm⁻¹; ¹H NMR (CDCl₃); δ 2.96 (2H, t, J = 6.8 Hz, CH₂), 3.21 (2H, t, J = 7.7 Hz, CH₂), 7.08–7.40 (10H, m, Ar), 7.43 (1H, br s, NH); ¹³C NMR (CDCl₃); δ 31.5, 36.6, 119.7–139.9 (Ar), 165.5; MS (CI): m/z = 258 [M^+ + 1].

S-3-Phenyl-propyl *N*-phenylthiocarbamate **4i**. White crystals; mp 78.3–79.8°C; IR (KBr) 1652, 3386 cm⁻¹; ¹H NMR (CDCl₃); δ 1.99 (2H, quint, J = 7.2 Hz, CH₂), 2.73 (2H, t, J = 7.2 Hz, CH₂), 2.99 (2H, t, J = 7.2 Hz, CH₂), 7.08–7.41 (10H, m, Ar), 7.17 (1H, br s, NH); ¹³C NMR (CDCl₃); δ 29.7, 31.8, 34.7, 119.6–141.5 (Ar), 165.7; MS (CI): m/z = 272 [M^+ + 1].

S-Methyl *N*-(4-methylphenyl)thiocarbamate **4j**. Yellow crystals; mp 102.1–103.5°C; IR (KBr) 1654, 3242 cm⁻¹; ¹H NMR (CDCl₃); δ 2.30 (3H, s, CH₃), 2.39 (3H, s, CH₃), 7.10 (1H, d, J = 8.4 Hz, Ar), 7.27 (1H, br s, NH), 7.28 (2H, t, J = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 12.5, 20.7, 119.9–135.0, (Ar), 166.3; MS (CI): m/z = 182 [M^+ + 1].

S-Ethyl *N*-(4-methylphenyl)thiocarbamate **4k**. White crystals; mp 81.0–81.5°C; IR (KBr) 1654, 3260 cm⁻¹; ¹H NMR (CDCl₃); δ 1.33 (3H, t, J = 7.2 Hz, CH₃), 2.30 (3H, s, CH₃), 2.96 (2H, q, J = 7.2 Hz, CH₂), 7.10 (1H, d, J = 8.4 Hz, Ar), 7.21 (1H, br s, NH), 7.28 (2H, t, J = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 15.5, 20.8, 119.8–134.6 (Ar), 165.8; MS (CI): m/z = 196 [M^+ + 1].

S-Propyl *N*-(4-methylphenyl)thiocarbamate **4l**. White crystals; mp 74.2–75.8°C; IR (KBr) 1653, 3294 cm⁻¹; ¹H NMR (CDCl₃); δ 1.00 (3H, t, J = 7.6 Hz, CH₃), 1.68 (2H, m, CH₂), 2.30 (3H, s, CH₃), 2.95 (2H, t, J = 7.6 Hz, CH₂), 7.03 (1H, br s, NH), 7.10 (1H, d, J = 8.4 Hz, Ar), 7.28 (2H, t, J = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 13.2, 20.8, 23.6, 32.1, 119.9–135.2 (Ar), 166.0; MS (CI): m/z = 210 [M^+ + 1].

S-Butyl *N*-(4-methylphenyl)thiocarbamate **4m**. White crystals; mp 73.9–75.1°C; IR (KBr) 1651, 3297 cm⁻¹; ¹H NMR (CDCl₃); δ 0.91 (3H, t, J = 7.6 Hz, CH₃), 1.40 (2H, m, J = 7.6 Hz, CH₂), 1.62 (2H, quint, J = 7.6 Hz, CH₂), 2.29 (3H, s, CH₃), 2.95 (2H, t, J = 7.6 Hz, CH₂), 7.08 (1H, d, J = 8.4 Hz, Ar), 7.23 (1H, br s, NH), 7.28 (2H, t, J = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 13.5, 20.7, 21.8, 29.9, 32.3, 119.9–135.1 (Ar), 166.0; MS (CI): m/z = 224 [M^+ + 1].

S-Isopentyl *N*-(4-methylphenyl)thiocarbamate **4n**. White crystals; mp 33.1–35.6°C; IR (KBr) 1657, 3318 cm⁻¹; ¹H NMR (CDCl₃); δ 0.92 (6H, t, J = 6.8 Hz, CH₃), 1.53 (2H, q, CH₂), 1.67 (1H, m, CH), 2.30 (3H, s, CH₃), 2.96 (2H, t, J = 7.2 Hz, CH₂), 7.06 (1H, br s, NH), 7.10 (1H, d, J = 8.4 Hz, Ar), 7.28 (2H, t, J = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 20.8, 22.1, 27.4, 28.3, 30.8, 39.1, 120.0–135.1 (Ar), 164.2; MS (CI): m/z = 238 [M^+ + 1].

S-Octyl N-(4-methylphenyl)thiocarbamate 4o. Yellow crystals; mp 61.0–62.1°C; IR (KBr) 1650, 3301 cm⁻¹; ¹H NMR (CDCl₃); δ 0.87 (3H, t, *J* = 6.8 Hz, CH₃), 1.31 (10H, d, *J* = 6.8, CH₂), 1.64 (2H, quint, *J* = 6.8 Hz, CH₂), 2.30 (3H, s, CH₃), 2.95 (2H, t, *J* = 6.8 Hz, CH₂), 7.02 (1H, br s, NH), 7.10 (1H, d, *J* = 8.4 Hz, Ar), 7.28 (2H, t, *J* = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 14.0, 20.8, 22.6, 28.7, 29.0, 29.1, 30.2, 30.3, 31.7, 119.8–135.1 (Ar), 165.9; MS (CI): *m/z* = 280 [*M*⁺ + 1].

S-Benzyl N-(4-methylphenyl)thiocarbamate 4p. White powder; mp 109.1–110.3°C; IR (KBr) 1653, 3250 cm⁻¹; ¹H NMR (CDCl₃); δ 2.30 (3H, s, CH₃), 4.21 (2H, s, CH₂), 7.02 (1H, br s, NH), 7.09–7.36 (9H, m, Ar); ¹³C NMR (CDCl₃); δ 20.8, 34.4, 119.9–137.9 (Ar), 166.2; MS (CI): *m/z* = 258 [*M*⁺ + 1].

S-Phenetyl N-(4-methylphenyl)thiocarbamate 4q. White crystals; mp 97.5–98.7°C; IR (KBr) 1651, 3270 cm⁻¹; ¹H NMR (CDCl₃); δ 2.29 (3H, s, CH₃), 2.71 (2H, t, *J* = 7.8 Hz, CH₂), 2.97 (2H, t, *J* = 7.8 Hz, CH₂), 7.08–7.29 (9H, m, Ar), 7.13 (1H, br s, NH); ¹³C NMR (CDCl₃); δ 20.8, 29.6, 31.8, 119.9–141.1 (Ar), 167.7; MS (CI): *m/z* = 272 [*M*⁺ + 1].

S-3-Phenyl-propyl N-(4-methylphenyl)thiocarbamate 4r. White crystals; mp 85.3–86.0°C; IR (KBr) 1653, 3274 cm⁻¹; ¹H NMR (CDCl₃); δ 1.98 (2H, quint, *J* = 7.6 Hz, CH₂), 2.29 (3H, s, CH₃), 2.71 (2H, t, *J* = 7.6 Hz, CH₂), 2.97 (2H, t, *J* = 7.6 Hz, CH₂), 7.08–7.29 (9H, m, Ar), 7.13 (1H, br s, NH); ¹³C NMR (CDCl₃); δ 20.8, 29.6, 31.8, 34.7, 119.9–141.1 (Ar), 167.7; MS (CI): *m/z* = 286 [*M*⁺ + 1].

S-Ethyl N-(4-chlorophenyl)thiocarbamate 4s. White crystals; mp 95.1–96.2°C; IR (KBr) 1651, 3271 cm⁻¹; ¹H NMR (CDCl₃); δ 1.33 (3H, t, *J* = 7.6 Hz, CH₃), 2.98 (2H, q, *J* = 7.6 Hz, CH₂), 7.13 (1H, br s, NH), 7.26 (2H, t, *J* = 8.4 Hz, Ar), 7.36 (2H, t, *J* = 8.4 Hz, Ar); ¹³C NMR (CDCl₃); δ 15.4, 24.7, 120.8–136.2 (Ar), 166.0; MS (CI): *m/z* = 216 [*M*⁺ + 1].

S-Benzyl N-(4-chlorophenyl)thiocarbamate 4t. White powder; mp 115.0–116.3°C; IR (KBr) 1649, 3244 cm⁻¹; ¹H NMR (CDCl₃); δ 4.21 (2H, s, CH₂), 7.07 (1H, br s, NH), 7.11–7.35 (9H, m, Ar); ¹³C NMR (CDCl₃); δ 34.4, 121.0–137.6 (Ar), 165.4; MS (CI): *m/z* = 278 [*M*⁺ + 1].

S-Phenetyl N-(4-chlorophenyl)thiocarbamate 4u. White crystals; mp 120.1–121.9°C; IR (KBr) 1651, 3293 cm⁻¹; ¹H NMR (CDCl₃); δ 2.96 (2H, t, *J* = 7.8 Hz, CH₂), 3.22 (2H, t, *J* = 7.8 Hz, CH₂), 7.03 (1H, br s, NH), 7.23–7.37 (9H, m, Ar); ¹³C NMR (CDCl₃); δ

31.6, 36.5, 120.8–139.8 (Ar), 165.6; MS (CI): *m/z* = 292 [*M*⁺ + 1].

S-3-Phenyl-propyl N-(4-chlorophenyl)thiocarbamate 4v. White crystals; mp 85.3–86.0°C; IR (KBr) 1655, 3328 cm⁻¹; ¹H NMR (CDCl₃); δ 1.99 (2H, quint, *J* = 7.6 Hz, CH₂), 2.73 (2H, t, *J* = 7.6 Hz, CH₂), 2.98 (2H, t, *J* = 7.6 Hz, CH₂), 7.06 (1H, br s, NH), 7.17–7.37 (9H, m, Ar); ¹³C NMR (CDCl₃); δ 29.7, 31.7, 34.7, 120.8–141.0 (Ar), 165.8; MS (CI): *m/z* = 306 [*M*⁺ + 1].

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- [9] Preparation of LiAlHSH 2: To a solution of sulfur powder (0.3 g, 10 mmol) in dry THF (100 ml) was added lithium aluminum hydride (0.38 g, 10.0 mmol) at 0°C under an argon atmosphere. The mixture was stirred for 30 min. The sulfur powder was consumed within 10 min. The reaction mixture became a heterogeneous grayish suspension. The reagent, formed in situ in this way, was used for further reaction.