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Synthesis of Unsymmetrical Ureas and *S*-Thiocarbamates under Catalyst-free Conditions in a [BMIM]BF_4 Ionic Liquid

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ABSTRACT: *Unsymmetrical ureas and S-thiocarbamates were prepared in good to excellent yields by direct condensation of phenylurea with amines and thiols in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) without the addition of any additives. The [BMIM]BF_4 ionic liquid is a mild medium and can be recycled and reused several times.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–8, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21244

INTRODUCTION

The synthesis of substituted ureas and *S*-thiocarbamates is a fundamental task in organic chemistry due to their many applications in the fields of agriculture [1] and medicine [1a], [2]. Conventional methods for the synthesis of these *S*-thiocarbamates and ureas involve highly toxic reagents, such as isocyanates [1a], [3], phosgene [1a], [4], and phosgene derivatives, such as carbamoyl chloride [5]. It is evident that most of these methods utilize hazardous and toxic reagents. In addition, the main group elements such as sulfur [6] and selenium [7] and transition-metal elements such as palladium [8], nickel [9], and copper [10] can serve as catalysts in the synthesis of these compounds. However, these methods suffer from one or more disadvantages, including high temperature and pressure [6], the use of toxic and expensive ligands or catalysts [8–10], and the formation of some by-products [7, 8a, b].

In recent years, ionic liquids have been widely used as novel and green solvents for various transformations in chemistry, because of their unique properties of, for example, tuneable polarity, high thermal stability, immiscibility with a number of organic solvents, negligible vapor pressure, and recyclability [11, 12].

Owing to the importance of imidazolium-based ionic liquids as reaction media, we now report the use of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) (Fig. 1) as an environmentally friendly and recyclable solvent for the synthesis of unsymmetrical ureas **1** and *S*-thiocarbamates **2** via the direct condensation of phenylurea with primary or secondary aliphatic and aromatic amines and thiols (Scheme 1).

Although ureas are very stable compounds and are sometimes prepared as derivatives of amines for characterization purposes, they can be dissociated to the corresponding isocyanates and amines at high temperature (Scheme 2) [13].

The main advantage of this method is in situ formation of phenyl isocynate in the reaction media,

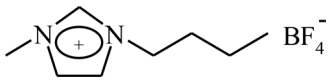

FIGURE 1 1-Butyl-3-Methylimidazolium tetrafluoroborate ([BMIM]BF_4).

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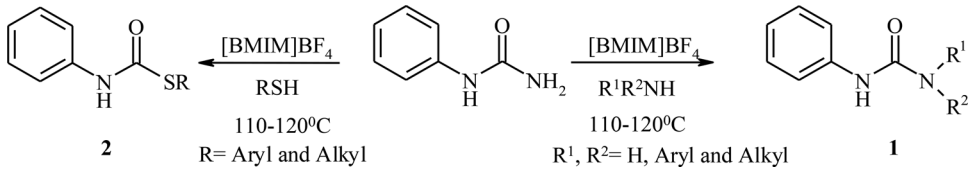
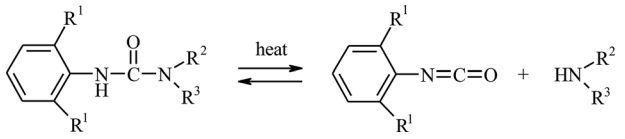


SCHEME 1 Synthesis of unsymmetrical ureas and *S*-thiocarbamates.



SCHEME 2 Thermal dissociation of arylureas into corresponding isocyanates and amines.

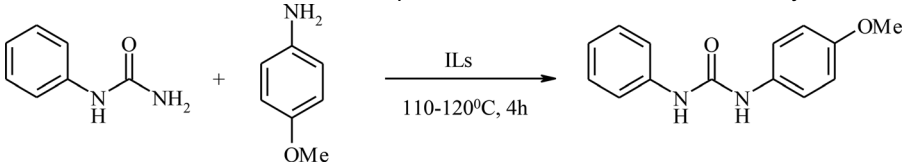
instead of using it as a starting precursor, as we previously reported in the synthesis of unsymmetrical ureas from phenylurea and amines under the refluxing temperature of dioxane [14].

RESULTS AND DISCUSSION

In situ generation of phenyl isocyanate by thermal dissociation of phenylurea and its subsequent reactions with nucleophiles, such as amines and thiols, in [BMIM]BF_4 ionic liquid media as shown in Scheme 1, is an efficient method for the preparation of unsymmetrical ureas **1** and *S*-thiocarbamates **2.** The reaction of phenylurea with *p*-anisidine was selected as the model reaction to optimize the reaction conditions. The effect of different ionic liquids on the rate of the reaction and the yield of product was investigated (Table 1). It can be inferred from Table 1 that among the ionic liquids used, [BMIM]BF_4, [BMIM]Cl, [BMIM][OctylOSO_3], *n*-Bu_4NCl, and [NMP][HSO_4] (Table 1, entries 1–5), the highest yield was obtained in [BMIM]BF_4 (Table 1, entry 1). Among the imidazolium ionic liquids (entries 1–3), [BMIM]BF_4 with the BF_4^- anion showed much higher activity in comparison with similar ionic liquids with other anions (entries 2 and 3). The difference in catalytic activity of the similar ionic liquids in organic transformations is well documented in the literature [15]. When tetrabutylammonium chloride was used as the solvent in the model reaction, only a low yield of the product was obtained (entry 4). The lowest yield was observed when [NMP][HSO_4] was used as the reaction media (entry 5) together with the formation of a significant amount of aniline. This could be probably due to the acidity of the media which can deactivate the amine nucleophile by protonation leading to formation of aniline. However, we have previously reported that, when *p*-nitroaniline was applied as a nucleophile in this reaction, the same results were observed due to the weak nucleophilicity of the amine [14].

To show the generality of this method, a variety of aryl and alkyl amines and thiols were reacted with phenylurea in [BMIM]BF_4 at 110–120°C and the corresponding unsymmetrical ureas **1** and *S*-thiocarbamates **2** were obtained in good to excellent yields (Table 2). Aryl amines and thiols with electron-releasing substituents, such as –OMe (entries 1 and 15) and –Me (entries 2, 3 and 16), in the para- and meta-positions and also aryl amine

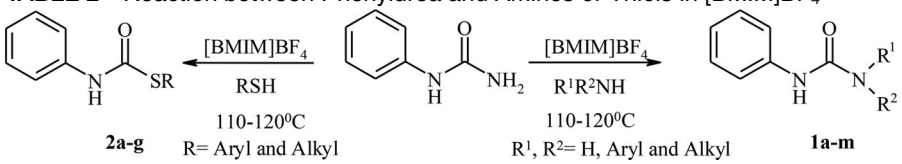
TABLE 1 Effect of Different Ionic Liquids on Direct Condensation of Phenylurea with *p*-Anisidine



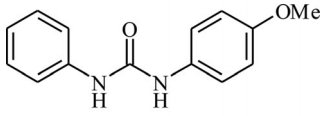
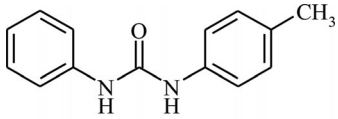
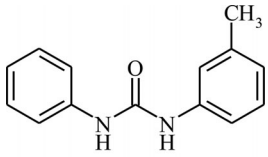
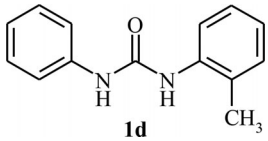
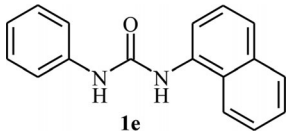
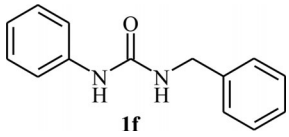
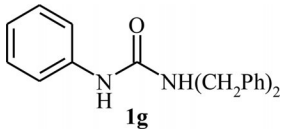
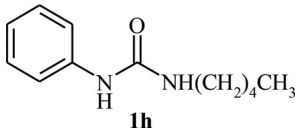
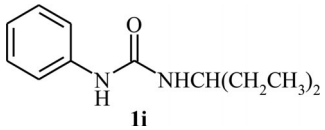
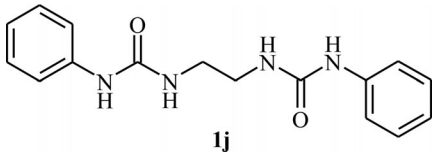
Entry	*Ionic Liquid*	*Product[a] (%)*
1	[BMIM]BF_4	89
2	[BMIM]Cl	46
3	[BMIM][OctylOSO_3]	58
4	*n*-Bu_4NCl	35
5	[NMP]HSO_4	15[b]

[a]Reactions were carried out with 2 mmol of *p*-anisidine, 1 mmol of phenylurea in 2 mL ILs.
[b]Aniline (20%) was also detected.

TABLE 2 Reaction between Phenylurea and Amines or Thiols in $[BMIM]BF_4$

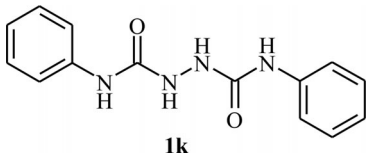
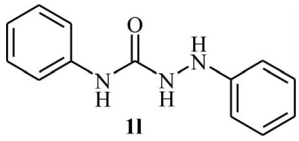
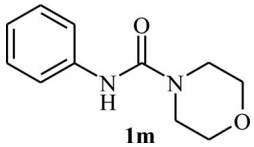
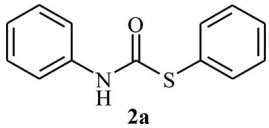
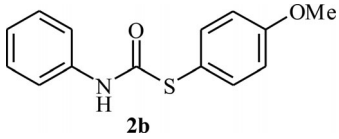
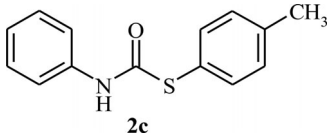
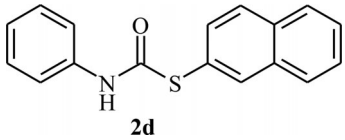
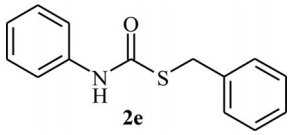
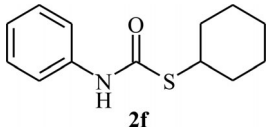
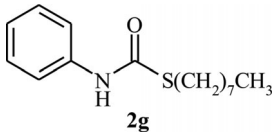


2a-g **1a-m**

Entry	*Substrate*	*Product*	*Time[a] (h)*	*Yield[b] (%)*
1	$4\text{-}CH_3OC_6H_4NH_2$	 **1a**	4	89
2	$4\text{-}CH_3C_6H_4NH_2$	 **1b**	4	85
3	$3\text{-}CH_3C_6H_4NH_2$	 **1c**	4	85
4	$2\text{-}CH_3C_6H_4NH_2$	 **1d**	5	80
5	1-NaphthylNH_2	 **1e**	4	78
6	$C_6H_5CH_2NH_2$	 **1f**	4	98
7	$(C_6H_5CH_2)_2NH$	 **1g**	4	95
8	$CH_3(CH_2)_4NH_2$	 **1h**	6	90
9	$(CH_3CH_2)_2CHNH_2$	 **1i**	6	90
10	$H_2NCH_2CH_2NH_2$	 **1j**	6	88

(*Continued*)

TABLE 2 Continued

Entry	*Substrate*	*Product*	*Time[a] (h)*	*Yield[b] (%)*
11	NH_2NH_2	 **1k**	6	90
12	$C_6H_5NHNH_2$	 **1l**	6	92
13	Morpholine	 **1m**	5	80
14	C_6H_5SH	 **2a**	5	80
15	4-$CH_3OC_6H_4SH$	 **2b**	4	85
16	4-$CH_3C_6H_4SH$	 **2c**	4	80
17	2-NaphthylSH	 **2d**	4	75
18	$C_6H_5CH_2SH$	 **2e**	4	95
19	CyhexSH	 **2f**	6	82
20	$CH_3(CH_2)_7SH$	 **2g**	6	87

[a]Reactions were carried out with 2 mmol of amines or thiols, 1 mmol of phenylurea in $[BMIM]BF_4$; except entries 10 and 11, were carried out with 1 mmol of substrate and 2 mmol of phenylurea
[b]Isolated yields and products were characterized by ^1H NMR and melting point.

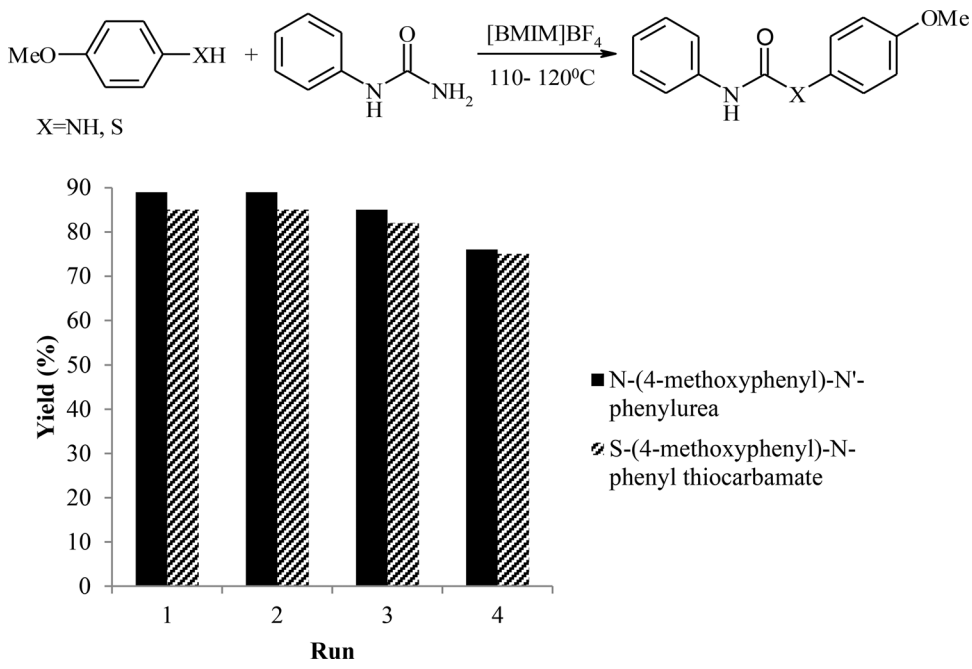


FIGURE 2 Recyclability and Reusability of [BMIM]BF_4 in the synthesis of unsymmetrical ureas and *S*-thiocarbamates.

with substituent in the ortho-position (entry 4) gave good to excellent yields of the corresponding diarylureas and *S*-thiocarbamates. The reaction of bulky naphthyl amine and thiol (entries 5 and 17) with phenylurea gave *N*-(1-naphthyl)-*N′*-phenylurea and *S*-(2-naphtyl)-*N*-phenyl thiocarbamate in good yields. Benzyl amines and thiols (entries 6, 7, and 18) gave excellent yields of expected unsymmetrical ureas and *S*-thiocarbamate. Primary aliphatic amines and thiols (entries 8, 9, 19, and 20), secondary aliphatic amine (entry 13), and ethylenediamine (entry 10) reacted smoothly with phenylurea to achieve high yields of the desired products. Interestingly, the reaction of hydrazine and phenylhydrazine (entries 11 and 12) with phenylurea under reaction conditions afforded 1-phenylcarbamoyl-4-phenyl semicarbazide and 1,4-semicarbazide in excellent yields.

It is noteworthy to mention that, when *para*-nitroaniline or *para*-nitrobenzenethiol reacted with phenylurea in [BMIM]BF_4 ionic liquid at 120°C, the corresponding products were not formed, only *N,N′*-diphenylurea was obtained and the starting amine or thiol remained intact. This could be probably due to the low nucleophilicity of *para*-nitroaniline and *para*-nitrobenzenethiol.

We have also demonstrated the recyclability and reusability of [BMIM]BF_4 in the reaction of *p*-anisidine or *p*-methoxythiophenol with phenylurea under reaction conditions (Fig. 2). As it is clear from Fig. 2, the recovered ionic liquid afforded similar yields to the corresponding urea or *S*-thiocarbamate to those obtained in the first runs. In addition, reasonable yields of the products were obtained even after the fourth run.

To show the limitation or advantages of this method with other reported procedures, in the preparation of substituted ureas and *S*-thiocarbamates, a comparison was made, as shown in Table 3.

In this table, three derivatives of ureas (**1a**, **1f**, **1m**) and *S*-thiocarbamates (**2a**, **2e**, **2f**) have been considered. Although the present protocol gives a high yield of the products in short reaction times comparable with other methods, the merit of the present method is that there is no need for any additive and metal catalysts (Table 3, entries 4, 5, 6, 7, 12, 18, 20, 21, and 22). Furthermore, the process can be productive without the use of hazardous starting materials, such as isocyanates (Table 3, entries 11, 16, 17, 18, 19, and 25) or phosgene derivatives (Table 3, entry 24) and CO gas (Table 3, entries 12, 20, 21, and 22). Rather, in this method ureas and *S*-thiocarbamates are prepared under benign conditions in recyclable ionic liquid media.

CONCLUSIONS

In conclusion, we have developed an efficient, safe, and inexpensive method for the synthesis of unsymmetrical ureas and *S*-thiocarbamates via the direct condensation of phenylurea with primary or

TABLE 3 Comparison of the Present Protocol with Reported Methods

Entry	*Product*	*Catalyst*	*Reaction Condition/Solvent*	*Time (h)*	*Yield (%)*	*Reference*
1	**1a**	–	$[BMIM]BF_4$	4	89	–
2	**1f**	–	$[BMIM]BF_4$	4	98	–
3	**1m**	–	$[BMIM]BF_4$	5	80	–
4	**1a**	CuI	Reflux/THF	4	78	[10a]
5	**1a**	CuI	85°C/DMF	24	90	[10c]
6	**1a**	Cu_2O	MW/120°C /solvent-free	0.33	85	[10d]
7	**1a**	Cu_2O	MW/100°C/NMP	0.33	65	[10e]
8	**1a**	–	120°C/dioxane	7	88	[14]
9	**1a, 1f**	–	0.8 GPa/100°C/THF	72, 30	41, 97	[16]
10	**1f**	–	0°C to 84°C /DCE	16.5	90	[17]
11	**1m**	–	PhNCO/80°C/$[Bmim]BF_4$	2	81	[3c]
12	**1m**	Se	CO (3 MPa)/150°C/toluene	1.5	70	[7a]
13	**2a**	–	$[BMIM]BF_4$	5	80	–
14	**2e**	–	$[BMIM]BF_4$	4	95	–
15	**2f**	–	$[BMIM]BF_4$	6	82	–
16	**2a**	–	PhNCO /45°C/solvent-free	0.58	91	[3d]
17	**2a**	–	PhNCO /45°C/CH_2Cl_2	1	74	[3d]
18	**2a**	Zn/$AlCl_3$	PhNCO/65°C/CH_3CN,H_2O	0.66	90	[3h]
19	**2a, 2f**	–	CH_3NCO /reflux, 60°C /CH_3CN	16, 0.5	89, 86	[3i]
20	**2a, 2e, 2f**	Se	CO (0.8 MPa)/60°C/solvent-free	10	15, 62, 67	[7c]
21	**2a, 2e, 2f**	Se	CO (1 MPa), O_2/r.t/solvent-free	10	35, 86, 72	[7d]
22	**2a, 2e, 2f**	Se	CO (1 atm) /r.t/solvent-free	10	31, 70, 74	[7e]
23	**2a**	–	0–84°C /DCE	16.5	73	[17]
24	**2a, 2e**	–	BTC/ 0°C/CH_2Cl_2	2, 7	88, 70	[18]
25	**2e**	–	PhNCO/r.t/THF	4	55	[3b]

Abbreviations: BTC, bis(trichloromethyl)carbamate; DCE, dichloroethane

secondary amines and thiols in $[BMIM]BF_4$ ionic liquid. The lack of additive requirements, as well as the recyclability and reusability of the ionic liquid and easy workup procedure, makes this method an excellent alternative for the synthesis of ureas and thiocarbamates.

EXPERIMENTAL

General Procedure for the Synthesis of Unsymmetrical Ureas and S-Thiocarbamates

A mixture of amine or thiol (2 mmol) and phenylurea (1 mmol), in $[BMIM]BF_4$ (2 mL) was stirred at a specified temperature for specified periods of time. After completion of the reaction, as indicated by TLC, the reaction mixture was extracted by Et_2O/EtOAc (v/v = 2/3, 3×5 mL) and purified by column chromatography. The remaining ionic liquid was dried at 80°C under reduced pressure to retain its activity in subsequent runs.

*1-Phenylcarbamoyl-4-phenyl semicarbazide (***1k***) [19a].* White solid; mp 255–256°C;^{1}H NMR (400 MHz, DMSO-d_6): δ 8.77 (s, 2H), 7.97 (s, 2H), 7.49 (d, J = 8.0 Hz, 4H), 7.25 (t, J = 7.2 Hz, 4H), 6.95 (t, J = 7.2 Hz, 2H).

*1,4- Diphenyl semicarbazide (***1l***) [19b].* White solid; mp 176–177°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.69 (s, 1H), 8.17 (s, 1H), 7.73 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.24–7.16 (m, 4H), 6.93 (t, J = 7.2 Hz, 1H), 6.79–6.73 (m, 3H).

*N-Phenyl morpholine-N-carboxamide (***1m***) [7a].* White solid; mp 161–163°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.51 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 8.4 Hz, 2H), 6.93 (t, J = 6.8 Hz, 1H), 3.60 (t, J = 4.8 Hz, 4H), 3.41 (t, J = 4.8 Hz, 4H).

*S-Phenyl-N-phenyl thiocarbamate (***2a***) [3j].* White solid; mp 121–122°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (bs, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.38–7.26 (m, 4H), 7.48–7.44 (m, 3H), 7.63–7.60 (m, 2H).

*S-(4-Methoxyphenyl)-N-phenyl thiocarbamate (***2b***) [7d].* White solid; mp 110°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H), 7.48 (dd, J = 1.2 Hz, 8.8 Hz, 2H), 7.45–7.41 (m, 2H), 7.30 (t, J = 8.4 Hz, 2H), 7.07–7.03 (m, 1H), 7.02–6.99 (m, 2H), 3.80 (s, 3H).

*S-(4-Methylphenyl)-N-phenyl thiocarbamate (***2c***) [3j].* White solid; mp 130–132°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.43 (s, 1H), 7.47 (d, J =

8.5 Hz, 2H), 7.39 (d, $J = 6.4$ Hz, 2H), 7.31–7.23 (m, 4H), 7.04 (t, $J = 6.8$ Hz, 1H), 2.33 (s, 3H).

*S-(2-Naphtyl)-N-phenyl thiocarbamate (***2d***).* White solid; mp 170–173°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.60 (s, 1H), 8.17 (d, $J = 1.6$ Hz, 1H), 7.99–7.97 (m, 3H), 7.63–7.56 (m, 3H), 7.52–7.50 (m, 2H), 7.31 (t, $J = 7.4$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6):119.55, 124.10, 125.97, 127.15, 127.69, 128.08, 128.26, 128.81, 129.41, 132.49, 133.17, 133.51, 135.26, 139.26, 163.34. Anal. Calcd. for $C_{17}H_{13}NOS$: (%) C 73.09, H 4.69, N 5.01, S 11.48. Found: C 73.27, H 4.57, N 5.11, S 11.54.

*S-Benzyl-N-phenyl thiocarbamate (***2e***) [3i].* White solid; mp 93°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.32 (s, 1H), 7.49 (d, $J = 7.8$ Hz, 2H), 7.37–7.20 (m, 7H), 7.04 (t, $J = 7.3$ Hz, 2H), 4.14 (s, 2H).

*S-Cyclohexyl-N-phenyl thiocarbamate (***2f***) [3j].* White solid; mp 114–116°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.15 (s, 1H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.27 (t, $J = 7.4$ Hz, 2H), 7.02 (t, $J = 7.1$ Hz, 1H), 3.42–3.34 (m, 1H), 1.86–1.95 (m, 2H), 1.66–1.22 (m, 7H).

*S-Octyl-N-phenyl thiocarbamate (***2g***) [3i].* White solid; mp 56–58°C (lit. 56.1–58.9°C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.22 (s, 1H), 4.49 (d, $J = 8.5$ Hz, 2H), 7.27 (t, $J = 7.4$ Hz, 2H), 7.02 (t, $J = 7.1$ Hz, 1H), 2.85 (t, $J = 7.2$ Hz, 2H), 1.51–1.60 (m, 2H), 1.23–1.35 (m, 10H), 0.83 (t, $J = 6.6$ Hz, 3H).

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