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# Benzotriazole-Assisted Thioacylation

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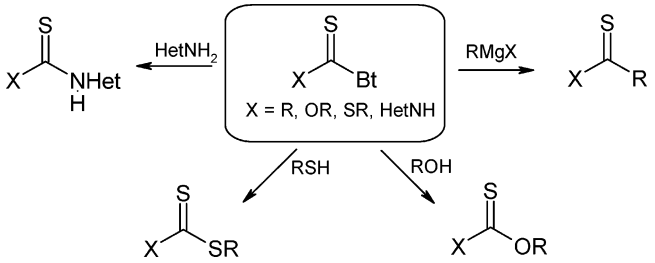


Benzotriazole reagents for thioacylation (RCSBt), thiocarbamoylation (RR′NCSBt), aryl/alkoxythioacylation (ROCSBt), and aryl/alkylthiothioacylation (RSCSBt) are synthesized, and their utility is assessed by syntheses of representative heteroaryl thioureas **3a**−**g**, thioamides **15a**−**s**, thionoesters **16a**−**h**, thiocarbamates **17a**−**e**, dithiocarbamates **18a**−**d**, thiocarbonates **19a**−**c**, and dithiocarbonates **20a**−**c**.

## Introduction

Classical thioacylating agents, including thiophosgene,[1] carbon disulfide,[2] and 1,1′-thiocarbonyldiimidazole,[3] provide access to a number of diversely functionalized thioamides, thioureas, thionoesters, (di)thiocarbamates, and (di)thiocarbonates. Thiocarbonyl,[4−6] thiocarbamoyl,[7−9] and (di)thiocarbonyl[10−12] derivatives of these classical thioacylating agents can also be prepared and reacted further with nucleophiles. Alternatively, thionating agents such as sulfur dihydride,[13] phosphorus pentasulfide,[14,15] and Lawesson's reagent[13] convert carbonyls into thiocarbonyl compounds.

Our group has applied *N*-acylbenzotriazoles to the syntheses of amides,[16] β-keto sulfones,[17] α-substituted β-ketonitriles,[18] oxazolines and thiazolines,[19] and C-acylated pyrroles and indoles.[20] We have recently reported the application of the thioacylating reagent bis(benzotriazolyl)methanethione (BtCSBt, **1**) in the preparation of unsymmetrical di- and trisubstituted thioureas **3** by intermediate 1-(alkyl/arylthiocarbamoyl)benzotriazoles (RNHCSBt, **2**) (Scheme 1).[21]

We have now greatly extended this work by preparing a range of reagents for thioacylation (RCSBt), thiocarbamoylation (RR′NCSBt), aryl/alkoxythioacylation (ROCS-

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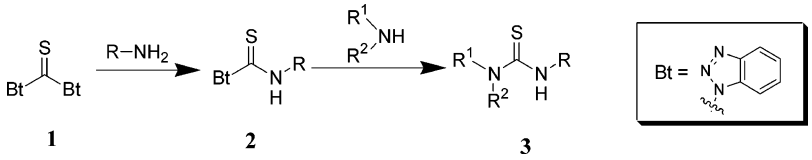
**SCHEME 1**



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

Bt), and aryl/alkylthiothioacylation (RSCSBt). In addition, hitherto unreported reactions of **1**, **2**, and other related compounds were explored, allowing access to thioamides, thionoesters, thio- and dithiocarbonates, and thio- and dithiocarbamates.

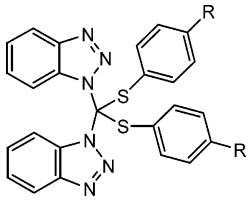
## Results and Discussion

**A. Preparation of Benzotriazolethioacylation Reagents. A.1. Preparation of Thiocarbonylbenzotriazoles (RCSBt).** We found that direct reaction of bis(benzotriazol-1-yl)methanethione (**1**) with Grignard reagents provides low yields (12−34%) of bis(benzotriazol-1-yl)diarylsulfidemethanes **4** (Figure 1) instead of the expected thiocarbonylbenzotriazoles. X-ray crystal structures of the phenyl and 4-methylphenyl dithioketal derivatives **4a** and **4b**, respectively, were determined to definitively ascertain the structures of these unusual products of S-arylation and rearrangement (crystallographic data for **4a** and **4b** are included in the Supporting Information).

Reactions of **1** with organolithium reagents resulted in complex mixtures; neither thiocarbonylbenzotriazoles nor dithioketals were obtained. In light of these findings, alternate routes to thiocarbonylbenzotriazoles were investigated.

In our previously reported syntheses of thioamides in one-pot reactions from Grignard reagents, carbon disulfide and amines mediated by 1-trifluoromethylsulfonylbenzotriazole,[22] the putative intermediates **6** were evidently formed but were not isolated. The instability of the thione group and its tendency to form stable C−S single bonds (i.e., by spontaneous trimerization in the case of 2-thiopropanone) are well documented.[1] Additionally, in situ decomposition of analogous methyl-substituted thioacylimidazoles prepared from ethanethioyl chloride and imidazole has been reported.[5b] We now report that the use of 1-chlorobenzotriazole (instead of 1-trifluoromethylsulfonylbenzotriazole) as the mediating reagent allows isolation of **6** in some cases (Scheme 2).

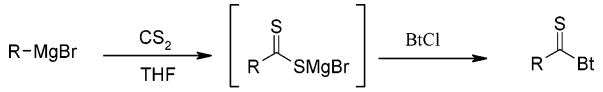
Thiocarbonylbenzotriazoles **6a**−**d** were prepared from carbon disulfide, 1-chlorobenzotriazole, and the respective Grignard or organolithium reagents (Table 1). The benzenoid thiocarbonylbenzotriazoles (42−89%, average 68%)



**4a** R = H
**4b** R = Me

**FIGURE 1.** Structures of bis(benzotriazol-1-yl)diarylsulfidemethanes (**4**).

**SCHEME 2**

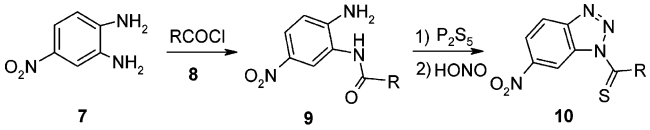


**5** **6**

**TABLE 1. Preparation of Thiocarbonylbenzotriazoles 6a−d**

| 6 | R | % yield |
|---|---|---|
| **a** | *p*-tolyl | 63 |
| **b** | 4-methoxyphenyl | 89 |
| **c** | phenyl | 76 |
| **d** | 4-chlorophenyl | 42 |

**SCHEME 3**



**7** **9** **10**

are all stable, reddish solids. Structural assignment of **6a**−**d** was supported by $^1$H and $^{13}$C NMR spectra and elemental analyses.

One limitation of this method is that it is restricted to Grignard-compatible functionalities. In addition, although benzenoid aryl Grignard reagents react quite smoothly to give thiocarbonylbenzotriazoles **6**, only poor yields are attained for alkyl, alkynyl, and heteroaryl Grignard reagents. In our hands, attempts to obtain *n*-butyl-substituted thiocarbonylbenzotriazole in higher yields by conducting the reactions at 0 °C and at −78 °C failed. Likewise, conversion of *n*-butyllithium to *n*-butylzinc bromide or *n*-butylcuprous bromide for reactions with carbon disulfide and 1-chlorobenzotriazole also failed.

The stability of non-benzenoid thiocarbonylbenzotriazoles thus appears to be poor. Rapoport utilized the route of Scheme 3 to obtain aliphatic thiocarbonyl-1*H*-6-nitrobenzotriazoles in good yields (48−67%).[23] Apparently, the electron-withdrawing nitro group on the benzotriazole moiety improves the stability and allows the isolation of aliphatic thiocarbonylbenzotriazoles **10**. Following this method, we have prepared several novel aliphatic and aromatic thiocarbonyl-1*H*-6-nitrobenzotriazoles **10a**−**h** (Scheme 3, Table 2).

Treatment of 4-nitro-1,2-phenylethylenediamine (**7**) with the respective acid chlorides **8** gave regioselectively amides **9** (83−99%). Resonance and the inductive effect of the nitro group lowered the nucleophilicity of the amino group in the para position, leaving the meta-amino group

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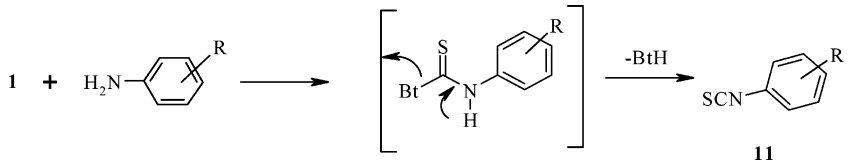
**SCHEME 4**



**11**

**TABLE 2. Aliphatic and Aromatic Thiocarbonyl-1*H*-6-nitrobenzotriazoles 10a−h**

| | acid chloride **8** R | amide **9** % yield | thiocarbonyl-6-nitrobenzotriazole **10** % yield from **9** |
|---|---|---|---|
| **a** | ethyl | 84 | 52 |
| **b** | 4-methylphenyl | 98 | 80 |
| **c** | 2-furanyl | 95 | 80 |
| **d** | 4-nitrophenyl | 83 | 69 |
| **e** | 4-methoxyphenyl | 86 | 66 |
| **f** | 4-bromophenyl | 99 | 45 |
| **g** | pentyl | 81 | 53 |
| **h** | 2-thienyl | 91 | 81 |

**TABLE 3. Thiocarbamoylbenzotriazoles 2**

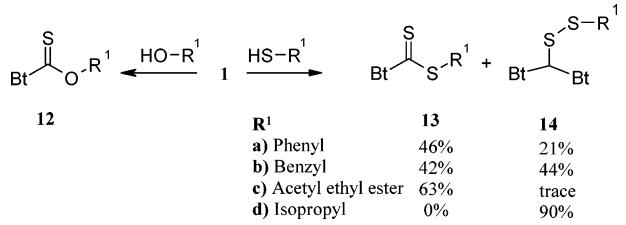
| **2** | $R^1$ | $R^2$ | % yield | mp (°C) |
|---|---|---|---|---|
| **a** | cyclohexyl | H | 85 | 128−130 |
| **b** | furfuryl | H | 94 | 119−120 |
| **c** | (*R*)-methylbenzyl | H | 87 | oil |
| **d** | phenethyl | H | 89 | 112−113 |
| **e** | *tert*-butyl | H | 60 | 61−63 |
| **f** | 1,5-dimethylhexyl | H | 87 | oil |
| **g** | $-CH_2CO_2CH_3$ | H | 76 | 129−130 |
| **h** | 2,3-dihydroindolyl | $=R^1$ | 84 | 123−124 |
| **i** | pyrrolidinyl | $=R^1$ | 76 | 86−87 |
| **j** | phenyl | methyl | 92 | 137−138 |
| **k** | ethyl | ethyl | 98 | oil |
| **l** | *n*-butyl | methyl | 76 | oil |

to attack the carbonyl of acid chloride **8**. Amides **9** were converted to thioamides in crude yields of 59−96% by stirring at room temperature with phosphorus pentasulfide (Scheme 3, Table 2). Thioamides were cyclized by treatment with sodium nitrite and acetic acid to afford thiocarbonyl-1*H*-6-nitrobenzotriazoles **10a**−**h** in 45−81% yields from amides **9**.

Thiocarbonyl-6-nitro-1*H*-benzotriazoles **10a**−**h** are stable crystalline solids. Structural assignment of **10a**−**h** was supported by $^1$H and $^{13}$C NMR spectra and elemental analyses. The thiocarbonyl $^{13}$C NMR signal of thiocarbonyl-6-nitro-1*H*-benzotriazoles **10** is further downfield as compared with that of thiocarbonylbenzotriazoles **6** and is found at 211.6 ppm for **10a**. Although this method is general and alkyl derivatives are obtained in moderate overall yields (44−72%) from 4-nitro-1,2-phenylethylenediamine (**7**) and the respective acid chlorides (**8**), the lengthy 3-step procedure is a drawback. Thus, the Grignard method of Scheme 2 is the preferred means of obtaining arylthiocarbonylbenzotriazoles.

**A.2. Preparation of Thiocarbamoylbenzotriazoles (RR′NCSBt).** Treatment of bis(benzotriazol-1-yl)methanethione (**1**) with primary or secondary (alkyl or heteroaryl) amines at room temperature in $CH_2Cl_2$ affords thiocarbamoylbenzotriazoles **2a**−**l** (60−98%) (Scheme 1, Table 3). Thiocarbamoylbenzotriazoles **2a**−**l** are crystalline solids with the exception of certain alkyl compounds **2c**,**f**,**k**,**l** which are viscous oils. A $^{13}$C NMR signal at ∼170 ppm is characteristic of thiocarbamoylbenzotriazoles **2a**−**l**.

**SCHEME 5**



**12**

| $R^1$ | **13** | **14** |
|---|---|---|
| **a)** Phenyl | 46% | 21% |
| **b)** Benzyl | 42% | 44% |
| **c)** Acetyl ethyl ester | 63% | trace |
| **d)** Isopropyl | 0% | 90% |

**TABLE 4. Synthesis of Aryloxythioacylbenzotriazoles (ROCSBt)**

| **12** | $R^1$ | % yield |
|---|---|---|
| **a** | 2-naphthyl | 87 |
| **b** | 3-pyridinyl | 66 |
| **c** | 1-naphthyl | 81 |
| **d** | phenyl | 83 |
| **e** | 4-*tert*-butylphenyl | 75 |

Reactions of **1** with primary arylamines (such as aniline, 4-nitroaniline, and 4-aminobenzoic acid ethyl ester) did not provide the corresponding thiocarbamoylbenzotriazoles; aryl isothiocyanates (**11**) were isolated instead (Scheme 4).

**A.3. Synthesis of Aryloxythioacylbenzotriazoles (ROCSBt).** Different reactivity is seen in reactions of bis(benzotriazol-1-yl)methanethione (**1**) with alkyl alcohols vs phenols. Reaction of **1** with 1 equiv of sodium ethoxide provided *O*-ethyl benzotriazole-1-carbothioate (**12**, $R^1$ = Et) in only 19% yield. Other conditions, such as refluxing in $CH_2Cl_2$ or treatment with $Et_3N$ or DBU under reflux, did not improve the yield. Likewise, reactions of **1** treated with cyclohexanol or 2-methylcyclohexanol under various conditions (sodium salt in $CH_2Cl_2$ at −78 °C to room temperature over 4 h, treatment with $Na_2CO_3$ in $CH_3CN$ at room temperature during 14 h, or treatment with $Et_3N$ in $CH_2Cl_2$ at room temperature and 0 °C from 4 to 14 h) yielded only complex mixtures.

On the other hand, reactions with phenols occurred quite readily. For example, treatment of bis(benzotriazol-1-yl)methanethione (**1**) with the sodium salt of 2-naphthol afforded novel thioesterification agent *O*-naphth-2-yl benzotriazole-1-carbothioate (**12a**) in 87% yield (Scheme 5).

Aryloxythioacylbenzotriazoles **12a**−**e** were obtained as stable crystalline solids in good yields (66−83%, average 73%) (Table 4) and were characterized by $^1$H and $^{13}$C NMR. The $^{13}$C NMR peak of the thioester thiocarbonyl typically appeared at ∼180 ppm for compounds of type **12**.

**A.4. Preparation of Aryl/Alkylthiothioacylbenzotriazoles (RSCSBt).** Treatment of bis(benzotriazol-1-yl)methanethione (**1**) with thiols in the presence of $Et_3N$ at −78 °C afforded *S*-alkyl and *S*-aryl(benzotriazolyl)-dithiocarbamates **13a**−**c** in 42−63% yields (Scheme 5). These novel aryl/alkylthiothioacylbenzotriazoles (**13**) are

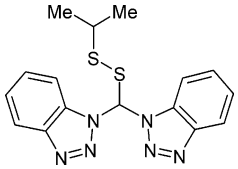


**FIGURE 2.** Structure of isopropyl di(benzotriazol-1-yl)methyl disulfide (**14d**).

all crystalline solids characterized as in **13c** by benzotriazole peaks in the aromatic region of the $^1$H NMR at 7.52 (t, $J$ = 7.8 Hz, 1H), 7.66 (t, $J$ = 8.1 Hz, 1H), 8.12 (d, $J$ = 8.2 Hz, 1H), and 8.67 ppm (d, $J$ = 8.4 Hz, 1H) and of the $^{13}$C NMR at 115.5, 120.9, 126.9, 131.4, 132.3, and 147.4 ppm with a thioester thiocarbonyl peak at 196.4 ppm.

With this method, in most cases, only modest yields of **13** were obtained with significant disulfide byproduct formation even under optimized conditions. Additionally, the reaction of **1** with the sodium salt of isopropylthiol under the same reaction conditions afforded the disulfide **14d** in 90% yield instead of **13d**. The structure of **14d** (Figure 2) was unambiguously determined by single-crystal X-ray structure analysis (Supporting Information).

It is interesting that both Grignard reagents and alkanethiols preferentially attack the sulfur of the thiocarbonyl of bis(benzotriazol-1-yl)methanethione (**1**), whereas oxygen and nitrogen nucleophiles add to the carbon of the thiocarbonyl in the normal manner. Stabilization of the resultant carbanion by the two benzotriazole moieties and the general polarizabilty of thiols and the thiocarbonyl bonds may be factors in the preference for reaction at the sulfur atom.

**B. Applications of Thiocarbonylbenzotriazoles (RCSBt). B.1. Synthesis of Thioamides from Thiocarbonylbenzotriazoles (RCSBt).** Thioamides exhibit broad biological activity as pesticidal,[24,25] fungicidal,[26,27] and anthelmintic[28] agents. N-Substituted *p*-alkoxythiobenzamides possess potent antitubercular activity,[29] and azadecalinthioamides inhibit cholesterol biosynthesis.[30] Thioamides are also used in organic synthesis[31,32] as synthons for the preparation of heterocycles,[33,34] e.g., to give thiazoles via Hantzsch reaction with α-haloketones.[35,36] Addition−cyclization reactions of thioamides

**SCHEME 6**

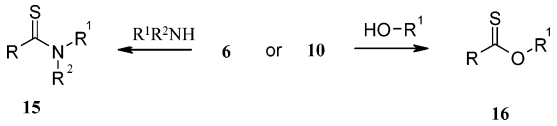


**TABLE 5. Preparation of Thioamides 15a−j**

| **15** | R | $R^1$ | $R^2$ | % yield |
|---|---|---|---|---|
| **a** | 4-$MeC_6H_4$− | $C_6H_5CH_2$− | H | 99 |
| **b** | 4-$MeOC_6H_4$− | −$(CH_2)_5$− | =$R^1$ | 93 |
| **c** | 4-$MeC_6H_4$− | $C_2H_5$− | $C_2H_5$− | 87 |
| **d** | $C_6H_5$− | $C_6H_5CH_2$− | H | 97 |
| **e** | $C_6H_5$− | −$(CH_2)_2O(CH_2)_2$− | =$R^1$ | 78 |
| **f** | 4-$ClC_6H_5$− | $PhCH_2CH_2$- | H | 66 |
| **g** | 4-$BrC_6H_4$− | −$(CH_2)_2O(CH_2)_2$− | =$R^1$ | 91 |
| **h** | 4-$MeC_6H_4$− | −$(CH_2)_4$− | =$R^1$ | 95 |
| **i** | 4-$NO_2C_6H_4$− | *tert*-butyl− | H | 98 |
| **j** | 2-thienyl | $C_6H_5CH_2$− | H | 80 |

with ketone alkylidenes afford pyridine-2-thiones.[37] Pyrroles are synthesized from reactions of *N*-(benzotriazolylmethyl)thioamides with α,β-unsaturated esters, ketones, or nitriles;[38] imidazoles are obtained from reactions with imines.

Synthetically useful N-monosubstituted and N,N-disubstituted thioamides **15a**−**f** were readily prepared by reactions of thiocarbonylbenzotriazoles **6a**−**d** with the appropriate primary and secondary amines, respectively (Scheme 6, Table 5). Simple column isolation (5% ethyl acetate/hexanes) gives thioamides **15a**−**f** in near quantitative yields. Formation of the thioamide is indicated by the loss of benzotriazole signals in $^1$H and $^{13}$C NMR spectra and the shift of the thiocarbonyl peak to ∼200 ppm.

N-Monosubstituted and N,N-disubstituted thioamides **15g**−**j** were likewise obtained in 80−98% yields from reactions of thiocarbonyl-6-nitrobenzotriazoles **10b**,**d**,**f**,**h** with the appropriate primary and secondary amines, respectively, in the presence of $Et_3N$ (Table 5).

Classically, thioamides have been synthesized via six main routes: (i) thionation of an amide by utilization of phosphorus pentasulfide[32] or Lawesson's reagent, which have the drawbacks of variable yields and significant byproduct formation;[13] (ii) use of thiocarbonyl transfer reagents, 1,1′-thiocarbonyldiimidazole (known to be hygroscopic and relatively unstable[39]) or bis(1,2,4-triazole)-methanethione in reactions with aldolnitrones;[4] (iii) reactions of thiuram monosulfides with organolithium reagents (65−81% yields);[40] (iv) treatment of aryl isothiocyanates with Grignard reagents;[41,42] (v) reactions of *N,N*-dimethylthiocarbamoyl chloride and Grignard reagents catalyzed by $NiCl_2$ (dppe);[43] and (vi) reaction of amines

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**TABLE 6. Synthesis of Thionoesters 16 from Thioacylating Agents 6 and 10**

| thionoesters 16 | alcohol $R^1$ | thioacylating agent R | % yield |
|---|---|---|---|
| **a** | 4-methoxyphenyl | 4-methoxyphenyl (**6b**) | 77 |
| **b** | ethyl | 4-chlorophenyl (**6d**) | 60 |
| **c** | 1-naphthyl | 4-methoxyphenyl (**10e**) | 88 |
| **d** | 1-naphthyl | 4-nitrophenyl (**10d**) | 99 |
| **e** | 1-naphthyl | 2-thienyl (**10i**) | 62 |

with aryl thioesters (with arylamines only, 64−99%),[29] thiobenzoyl chlorides (5−92%),[6] or *N*-thiobenzoyl triazoles (0−72% yields).[5] In comparison, preparation of N-monosubstituted and N,N-disubstituted thioamides by reactions of stable and readily accessible thiocarbonylbenzotriazoles or thiocarbonyl-1*H*-6-nitrobenzotriazoles, as reported previously by Rapoport,[23] occurs cleanly and in near quantitative yields.

**B.2. Synthesis of Thionoesters from Thiocarbonylbenzotriazoles (RCSBt).** Successful application of thioacylbenzotriazole reagents to the synthesis of novel thioamides led to the extension of our methodology to thionoesters, which are generally less studied than thioamides or their thiolester counterparts because few reported syntheses for thionoesters provide sufficiently general access to these compounds; i.e., most literature methods are limited to the preparation of *O*-phenyl thionoesters.[1,15]

Despite the lack of efficient methods to provide diverse thionoesters, these compounds are attractive synthetic targets because of their utility when incorporated into macrocycles, such as crown ethers,[44] and also for their application as chemical probes of the enzyme binding sites of cysteine[45] and serine[46] proteases.

Thiocarbonylbenzotriazoles **6b** and **6d** were reacted with alcohols in the presence of $Et_3N$ to give thionoesters **16a** and **16b** in 77 and 60% yields, respectively (Scheme 6, Table 6). Similarly, thiocarbonyl-6-nitrobenzotriazoles **10d**,**e**,**i** were reacted with 1-naphthol, providing thionoesters **16c**−**e** in 62−99% yields. No observable difference in reactivity was noted between thioacylation reagents **6** and **10**.

In an attempt to extend our methodology to dithioesters, it was observed that both reactions of **6** and **10** with phenylthiol or its sodium salt (under reflux conditions and in the presence of $Et_3N$, pyridine, or DMAP) failed. However, refluxing **6c** with benzyl mercaptan in acetonitrile in the presence of triethylamine provided benzyl dithiobenzoate in 14% yield.

Although limited to the preparation of thionoesters, our method compares favorably to classical syntheses (Scheme 7), which have involved treatment of esters with phosphorus pentasulfide[14,15] or Lawesson's reagent, both often requiring a large excess of reagent and long reaction times;[47] reactions of imino esters with hydrogen sulfide, which often results in significant byproduct formation;[13] low-yielding reactions of dithioacids with 2-halo-1-methylpyridinium salts and subsequent treatment with the respective alcohols;[48] and Friedel−Crafts acylations of unstable 1-chlorothioformates with aromatics.[10]

The advantages of our thioacylation methodology are primarily that the use of unstable or hazardous reagents (e.g., $H_2S$) is avoided, the mild conditions employed are tolerable to a wide variety of functional groups, and yields are either higher or comparable to those of known methods.

**B.3. Thiocarbamoylation Using Thiocarbamoylbenzotriazoles (RR′NCSBt).** As will be discussed below, there are important differences in the reactivity of N-monosubstituted and N,N-disubstituted thiocarbamoyls toward nucleophiles. Our results indicate that N-monosubstituted thiocarbamoylbenzotriazoles **2a**−**g** are isothiocyanate synthons, reacting with nucleophiles (amines, alcohols, and organometallic reagents) by an elimination−addition mechanism. N,N-Disubstituted thiocarbamoyls **2h**−**l** appear to react with oxygen, sulfur, and carbon nucleophiles by an addition−elimination mechanism to effect thiocarbamoylation, but **2h**−**l** are unreactive toward amines.

**B.4. Synthesis of Thioamides from Reactions of C-Nucleophiles with Thiocarbamoylbenzotriazoles (RR′NCSBt).** Reactions of both N-monosubstituted thiocarbamoylbenzotriazoles **2a**−**c**,**e**,**f** and N,N-disubstituted thiocarbamoylbenzotriazoles **2i**,**l**,**j** with organolithium or Grignard reagents provided secondary thioamides **15k**−**p** in yields of 35−99% (average 68%) and tertiary thioamides **15q**−**s** in 35−99% yields (average 79%), respectively (Scheme 8, Table 7). As with parallel thioamide formation by thioacylation agents **6** and **10**, confirmation of thioamide synthesis is indicated by the loss of the benzotriazole signals in $^1H$ and $^{13}C$ NMR spectra and by the shift of the thiocarbonyl peak to ∼200 ppm.

Reactions were conducted with excess organometallic reagent. For example, monosubstituted thiocarbamoylbenzotriazoles **2a**−**c**,**e**,**f** were reacted with 2.5 equiv of the organometallic reagent and disubstituted thiocarbamoylbenzotriazoles **2i**,**j**,**l** were reacted with 1.2 equiv. Commercially available Grignard reagents provided higher yields of thioamides in comparison with organolithium reagents prepared by following literature procedures.

Although N-monobenzenoid aryl-substituted thioamides cannot be synthesized because of the incompatibility of primary benzenoid arylamines for the synthesis of thiocarbamoylbenzotriazoles **2**, our method has the advantage of milder conditions and higher yields as compared with classical syntheses.

**B.5. Syntheses of Heteroaryl-Substituted Thioureas from Reactions of N-Nucleophiles with Thiocarbamoylbenzotriazoles (RR′NCSBt).** Heteroaryl-substituted thiocarbamoylbenzotriazoles are readily prepared in moderate yields (57−63%) from reactions of **1** with heteroarylamines, but because conversion to the isothiocyanates occurs quite easily in solution, yields are lower in comparison with other thiocarbamoylbenzotriazoles **2**. To avoid this problem, we now report one-pot syntheses of symmetrical and asymmetrical heteroaryl-substituted thioureas **3a**−**g** from heteroaryl-substituted

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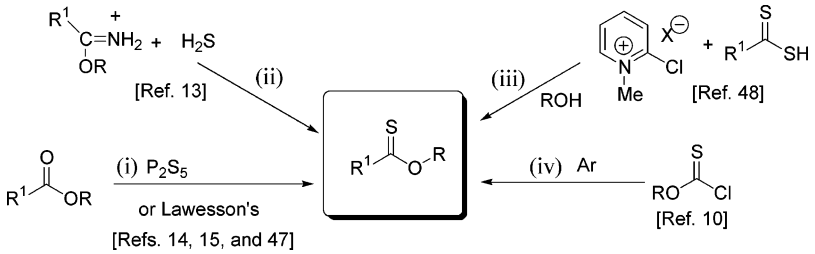
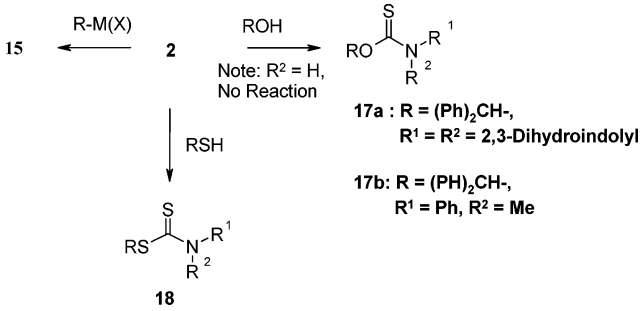
**SCHEME 7**




**SCHEME 8**




thiocarbamoylbenzotriazoles prepared in situ (Scheme 1 (R, $R^1$ = Het, $R^2$ = H), Table 8).

Symmetrical heteroaryl-substituted thioureas **3a**−**d** were prepared in 82−85% yields by refluxing 2 equiv of the appropriate amines with **1** in $CH_2Cl_2$. We have found that $^1$H NMR spectra taken in DMSO-$d_6$ provide the signals expected for symmetric thiourea molecules; however, an inequivalency of protons was observed in spectra of thioureas **3c** and **3d** taken in $CDCl_3$. As Kaminsky et al.[49] have reported, the crystal structure of **3d** reveals that strong intramolecular hydrogen-bonding interactions occur between the pyridine nitrogen and the thiourea N−H (Figure 3); the $CDCl_3$ $^1$H NMR signals for **3d** show corresponding differences in the electronic environment of the methyl groups and the protons of the pyridine rings.

For asymmetric thiourea **3e**, exactly 1 equiv of 2-pyridinylamine was refluxed with **1** in $CH_2Cl_2$ until TLC indicated complete conversion of **1** to the expected thiocarbamoylbenzotriazole intermediate with some isothiocyanate formation. 3-Pyridinylamine was added at this point, and reflux was continued until conversion to product was complete as indicated by TLC. Asymmetric thioureas **3f** and **3g** were similarly prepared in yields of 80 and 83%, respectively.

Our one-pot syntheses of symmetrical and asymmetrical heteroaryl-substituted thioureas provided **3a**−**g** in 78−85% yields, offering a definitive advantage over previously reported syntheses (Table 8). Symmetric thioureas **3b**−**d** were reportedly obtained in poor to moderate yields by reaction of amines with $CS_2$ at room temperature in the presence of $I_2$ in pyridine (**3b**, 23% yield),[50] at 100 °C catalyzed by Zn−Al HT(500) (**3c**, 57% yield),[51] and by heating in methanol (**3d**, 17%).[49]

In addition to providing a route to symmetric thioureas, our method offers access to novel asymmetric thioureas that are traditionally a more difficult problem.[21] The significance of a mild, high-yielding route to symmetric and asymmetric thioureas is emphasized in view of the diverse properties and important applications of thioureas and heteroaryl thioureas. For example, thioureas display diverse biological activity as phenoloxidase enzymatic inhibitors,[52] bacteriocides,[53] rodenticides,[54] and insecticides.[55] Heteroaryl-substituted thioureas are particularly active, and certain pyridinyl thioureas are HIV reverse-transcriptase inhibitors.[8] Thioureas are also important synthons for the preparation of five-[56] and six-membered heterocycles.[57]

**B.6. Thiocarbamates from Reactions of O-Nucleophiles with Thiocarbamoylbenzotriazoles (RR′NCS-Bt).** Thiocarbamates are potent insecticides,[58] herbicides,[59] and nematocides.[60] 3-(1*H*-Imidazol-4-yl)propyl *N*-phenylthiocarbamate is a potent histamine $H_3$-receptor antagonist,[61] and dimethylthiocarbamate is an alcohol-protecting group.[62]

To prepare thiocarbamates **17a** and **17b** (59 and 60% yields, respectively), N,N-disubstituted thiocarbamoylbenzotriazoles **2h** and **2j** were reacted with benzhydrol sodium salts (Scheme 8); N-monosubstituted thiocarbamoylbenzotriazoles failed to react with oxygen nucleophiles, either as free alcohols in the presence of $Et_3N$ or as salts at room temperature or under refluxing conditions.

Classical syntheses of thiocarbamates have utilized either carbon disulfide or thiophosgene in direct reactions with amines and alcohols, particularly 4-substituted 3-hydroxybutylamines (31−73% yields).[1] Also, 1-chlorothioformates, formed by reactions of thiophosgene with alcohols, have been reacted with amines (49−98% yields).[62,63] Reactions of isothiocyanates[64,65] (limited to

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**TABLE 7. Preparation of Secondary Thioamides 15k−s from Thiocarbamoylbenzotriazoles 2**

| R−M | | thiocarbamoylbenzotriazole 2 | | | thioamide | |
|---|---|---|---|---|---|---|
| R | M | | $R^1$ | $R^2$ | 15 | % yield |
| phenyl | MgBr | **2a** | cyclohexyl | H | **15k** | 87 |
| pentyl | MgBr | **2b** | furfuryl | H | **15l** | 99 |
| 2-furanyl | Li | **2e** | *tert*-butyl | H | **15m** | 47 |
| phenyl | MgBr | **2f** | 1,5-dimethylhexyl | H | **15n** | 56 |
| 4-methoxyphenyl | MgBr | **2c** | (*R*)-methylbenzyl | H | **15o** | 85 |
| 2-pyridinyl | Li | **2a** | cyclohexyl | H | **15p** | 35 |
| allyl | MgBr | **2l** | *n*-Butyl | methyl | **15q** | 98 |
| 2-thienyl | Li | **2i** | piperidinyl | $=R^1$ | **15r** | 53 |
| allyl | MgBr | **2j** | phenyl | methyl | **15s** | 78 |

**TABLE 8. Symmetrical and Asymmetrical Heteroaryl-Substituted Thioureas 3a−g**

| thiourea 3 | $het^1$ | $het^2$ | % yield | % lit. yield |
|---|---|---|---|---|
| **a** | 4-pyridinyl | 4-pyridinyl | 85 | |
| **b** | 3-pyridinyl | 3-pyridinyl | 83 | 23[50] |
| **c** | 2-pyridinyl | 2-pyridinyl | 82 | 57[51] |
| **d** | 2-(4,6-dimethyl)pyridinyl | 2-(4,6-dimethyl)pyridinyl | 83 | 17[49] |
| **e** | 2-pyridinyl | 3-pyridinyl | 78 | |
| **f** | 4-pyridinyl | 2-pyridinyl | 80 | |
| **g** | 2-pyridinyl | 2-(4,6-dimethyl)pyridinyl | 83 | |

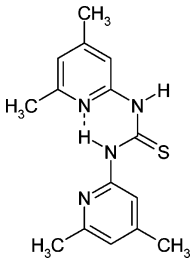

**FIGURE 3.** Intramolecular hydrogen-bonding interactions influencing the conformation of 1,3-bis(4,6-dimethylpyridin-2-yl)thiourea (**3d**).

**TABLE 9. Dithiocarbamates Prepared (18: $RSCSNR^1R^2$)**

| dithiocarbamate 18 | thiol R | reagent 2 | | % yield |
|---|---|---|---|---|
| | | $R^1$ | $R^2$ | |
| **a** | 3-methoxyphenyl | 2,3-dihydroindolyl | $=R^1$ | 99 |
| **b** | 3-methoxyphenyl | furfuryl | H | 83 |
| **c** | benzyl | cyclohexyl | H | 92 |
| **d** | phenyl | phenethyl | H | 60 |

allyl and aryl isothiocyanates) or chlorothiocarbamoyls[7] with alcohols are traditional alternatives. Our method, although limited to reactions of N,N-disubstituted thiocarbamoylbenzotriazoles with sodium salts of alcohols, offers a viable alternative to classical syntheses that avoids the use of hazardous or unstable reagents.

**B.7. Dithiocarbamates from Reactions of S-Nucleophiles with Thiocarbamoylbenzotriazoles (RR′NCSBt).** In reactions with sulfur nucleophiles, dithiocarbamates **18** were prepared from both N-monosubstituted and N,N-disubstituted thiocarbamoylbenzotriazoles (Scheme 8, Table 9). N-Monosubstituted thiocarbamoylbenzotriazoles (**2a**,**b**,**d**) did not require the use of salts because the reactions occurred readily at room temperature in the presence of 1 equiv of $Et_3N$.

Dithiocarbamates have been prepared (Scheme 9) in the following ways: (i) by activation of a dithiocarbamate with a 2-halothiazolium salt and subsequent reaction with a thiol (two examples, 37% and 87% yields),[66] (ii) by reaction of a dithiocarbamate with an alkyl or arylhalide,[67] (iii) by reaction of an organolithium reagent with a thiuram disulfide at −70 °C under $N_2$,[40] and (iv) by zeolite-catalyzed (Zn−Al HT) reaction of carbon disulfide with 2-aminothiophenol.[51]

The main advantage of our benzotriazole-assisted thiocarbamoylation methodology is the use of stable reagents, which provide high yields (60−99%) and clean conversion to dithiocarbamates in short reaction times under mild conditions.

**C. Alkoxythiocarbonylations with Aryloxythioacylbenzotriazoles (ROCSBt). C.1. Synthesis of Thionoesters 16.** Reactions of Grignard reagents with *O*-naphth-2-yl benzotriazole-1-carbothioate (**12a**) provided thionoesters **16f**−**h** in good yields (64−76%) (Scheme 10, Table 10). This general method complements the preparation of thionoesters from thiocarbonylbenzotriazoles **6** or thiocarbonyl-1*H*-6-nitrobenzotriazoles **10**, sharing the advantages of these methods over classical routes.

**C.2. Synthesis of Thiocarbamates 17 from Aryloxythioacylbenzotriazole 12a.** Thiocarbamates **17c**−**e** were prepared by refluxing aryloxythioacylbenzotriazole **12a** with amines in $CH_2Cl_2$ for 2 h (Scheme 10, Table 11). Column chromatography (silica gel, 1:10 ethyl acetate/hexanes) afforded thiocarbamates **17c**−**e** in 70−85% yields.

Reaction of aryloxythioacylbenzotriazoles **12** with amines does not require use of a base and is a mild and efficient means of preparing thiocarbamates **17c**−**e**. Therefore, this synthetic route is preferred in comparison with the alternative preparation of thiocarbamates **17** from N,N-disubstituted thiocarbamoylbenzotriazoles **2**

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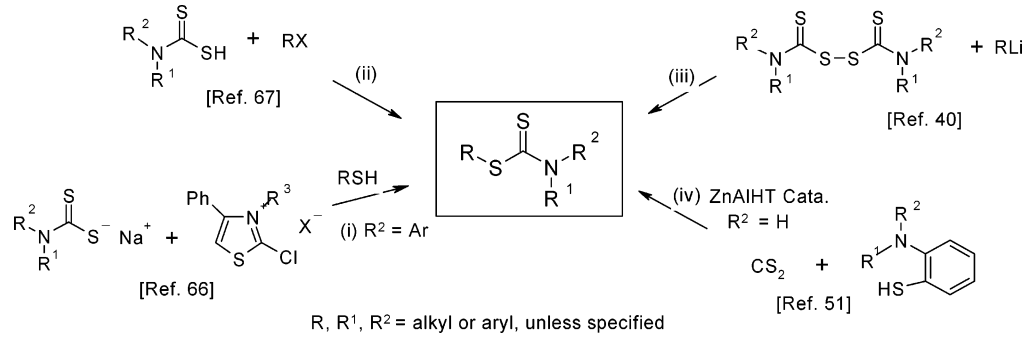
**SCHEME 9**




**SCHEME 10**

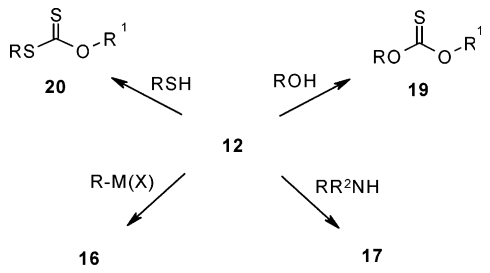



**TABLE 10. Synthesis of Thionoesters 16 from Aryloxythioacylbenzotriazole 12a**

| thionoester **16** | reagent **12a** | organometallic reagent | | |
|---|---|---|---|---|
| | $R^1$ | R | M(X) | % yield |
| **f** | 2-naphthyl | 4-methylphenyl | MgBr | 70 |
| **g** | 2-naphthyl | phenyl | MgBr | 76 |
| **h** | 2-naphthyl | methyl | MgBr | 64 |

**TABLE 11. Synthesis of Thiocarbamates 17 from Aryloxythioacylbenzotriazole 12a**

| thiocarbamate **17** | reagent **12** | amine | | |
|---|---|---|---|---|
| | $R^1$ | R | $R^2$ | % yield |
| **c** | 2-naphthyl | morpholinyl | =R | 70 |
| **d** | 2-naphthyl | benzyl | H | 85 |
| **e** | 2-naphthyl | pyrrolidinyl | =R | 85 |

because reactions of **2** with sodium salts of alcohols require use of excess sodium hydride to obtain good yields (~60%).

**C.3. Preparation of Thiocarbonates 19 from Aryloxythioacylbenzotriazole 12a.** Thiocarbonates have utility as intermediates in olefin synthesis.[11,68−71] Notably, stereospecific Corey−Winter alkene synthesis involves reactions of cyclic thiocarbonates with alkyl phosphites.[72,73]

Reactions of aryloxythioacylbenzotriazole **12a** with alcohols provide a general and efficient route to thiocarbonates **19**. Good yields of thiocarbonates **19a**−**c** (70−72%) were obtained under mild conditions (stirring the sodium salt of the alcohol in $CH_2Cl_2$ at room temperature) (Scheme 10, Table 12).

**TABLE 12. Synthesis of Thiocarbonates 19 from Aryloxythioacylbenzotriazole 12a**

| thiocarbonate **19** | reagent **12** | alcohol | |
|---|---|---|---|
| | $R^1$ | R | % yield |
| **a** | 2-naphthyl | ethyl | 70 |
| **b** | 2-naphthyl | 3-pyridinyl | 72 |
| **c** | 2-naphthyl | 4-methylphenyl | 70 |

**TABLE 13. Synthesis of Dithiocarbonates 20 from Aryloxythioacylbenzotriazole 12a**

| dithiocarbonate **20** | reagent **12** | thiol | |
|---|---|---|---|
| | $R^1$ | R | % yield |
| **a** | 2-naphthyl | 4-methylphenyl | 70 |
| **b** | 2-naphthyl | dodecyl | 70 |
| **c** | 2-naphthyl | *i*-propyl | 60 |

In comparison, thiocarbonates have been previously prepared by reactions of alcohols with 1-chlorothioformates derived from thiophosgene,[74] 1,2-dihydroxy compounds with thiophosgene[75] or 1,1′-thiocarbonyl-2,2′-pyridone (requiring synthesis from di-2-pyridylthionocarbonate),[76] alcohols with 1,1′-thiocarbonyldiimidazole (known to be hygroscopic and relatively unstable),[3,12,39] and alkenes with osmium tetraoxide and subsequent treatment with 1,1′-thiocarbonyldiimidazole.[77] Most significantly, the primary advantage of our methodology is the use of a stable, non-hazardous reagent.

**C.4. Preparation of Dithiocarbonates 20 from Aryloxythioacylbenzotriazole 12a.** Similar to the preparation of thiocarbonates **19**, dithiocarbonates **20a**−**c** were readily provided in 60−70% yields from aryloxythioacylbenzotriazole **12a** (Scheme 10, Table 13). Reactions occur with both alkyl- and aryl-thiols, providing dithiocarbonates in good yields.

Dithiocarbonates have been classically prepared for Barton−McCombie reactions by reacting alkylhalides (usually MeI; lower yields are obtained with other alkylhalides), carbon disulfide, and alcohols.[78−80] Synthesis from 1-chlorodithioformate and sodium thiolates has also been reported.[81] Benzotriazole-assisted aryloxy-

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thioacylation of thiols is a mild and general method, which offers a competitive alternative to traditional syntheses.

## Conclusion

We have developed and applied benzotriazole reagents for thioacylation (RCSBt), thiocarbamoylation (RR′NCSBt), aryl/alkoxythioacylation (ROCSBt), and aryl/alkylthiothioacylation (RSCSBt) to the syntheses of numerous novel thioamides, thionoesters, dithioesters, heteroaryl thioureas, thiocarbamates, dithiocarbamates, thiocarbonates, and dithiocarbonates. Thioamide formation by thiocarbamoylbenzotriazoles and thioacylbenzotriazoles is complementary, with one method being the reverse order of steps in respect to the other. Complementary methods for thionoester synthesis (from thioacylbenzotriazoles or aryloxythioacylbenzotriazoles) and thiocarbamate preparation (from thiocarbamoylbenzotriazoles or aryloxythioacylbenzotriazoles) have also been described. Advantages of benzotriazole methods are primarily that the use of unstable or hazardous reagents is avoided, the mild conditions employed are tolerable of a large variety of functional groups, and yields are comparable and in many cases higher than those in previously reported methods.

## Experimental Section

Melting points were uncorrected. $^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra were recorded on a 300 MHz NMR spectrometer in chloroform-*d* solution unless otherwise stated. Column chromatography was performed on silica gel (230−425 mesh). THF was distilled from sodium−benzophenone ketyl prior to use. Commercially available Grignard reagents were used for the preparation of thioamides. Bis(benzotriazol-1-yl)methanethione (now available from a commercial supplier) was prepared according to a literature procedure.[82] The organometallic reactions were performed under a nitrogen atmosphere and in oven-dried glassware.

**General Procedure for the Preparation of 1-Alkyl/Arylthiocarbamoylbenzotriazoles 2a−l.** Bis(benzotriazol-1-yl)methanethione[82] (**1**) (0.56 g, 2 mmol) was dissolved in $CH_2Cl_2$ at room temperature. The appropriate amine (2 mmol) was added dropwise, and the reaction mixture was stirred for 18 h. Solvent was removed under vacuum, and the residue was redissolved in EtOAc and washed with 5% aqueous sodium carbonate, water, and brine before drying over anhydrous $Na_2SO_4$. Solvent was removed under vacuum, and the 1-alkyl/arylthiocarbamoylbenzotriazole (**2**) was recrystallized from EtOAc/hexanes or by column chromatography as indicated.

Ethyl 4-isothiocyanatobenzoate (**11a**) is provided as a representative example of isocyanates obtained from reactions of primary arylamines with bis(benzotriazolyl)methanethione under the above conditions.

**Benzotriazole-1-carbothioic Acid Cyclohexylamide (2a):** white cubes (from EtOAc/hexanes) (95%); mp 72−73 °C (lit.[21] mp 72−73 °C); $^1$H NMR ($CDCl_3$) $\delta$ 1.25−1.58 (m, 5H), 1.69−1.85 (m, 3H), 2.04−2.23 (m, 2H), 4.45−4.48 (m, 1H), 7.47 (t, $J$ = 7.7 Hz, 1H), 7.63 (t, $J$ = 7.7 Hz, 1H), 8.09 (d, $J$ = 8.4 Hz, 1H), 8.99 (br d, $J$ = 6.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 24.6, 25.4, 31.6, 53.6, 116.1, 120.1, 125.5, 130.1, 132.4, 147.0, 173.0. Anal. Calcd for $C_{13}H_{16}N_4S$: C, 59.97; H, 6.19; N, 21.52. Found: C, 60.07; H, 6.32; N, 21.60.

**Benzotriazole-1-carbothioic Acid (Furan-2-ylmethyl)-amide (2b):** brown and colorless needles (94%); mp 119−120 °C (lit.[21] mp 117−119 °C); $^1$H NMR $\delta$ 5.04 (d, $J$ = 5.1 Hz, 2H), 6.38−6.46 (m, 2H), 7.44−7.52 (m, 2H), 7.62−7.70 (m, 1H), 8.10 (d, $J$ = 8.1 Hz, 1H), 8.91 (d, $J$ = 8.4 Hz, 1H), 9.30 (br s, 1H); $^{13}$C NMR $\delta$ 41.8, 103.4, 109.4, 110.7, 116.0, 120.4, 125.8, 130.5, 143.0, 147.1, 148.5, 174.3. Anal. Calcd for $C_{12}H_{10}N_4OS$: C, 55.80; H, 3.90; N, 21.69. Found: C, 56.10; H, 3.86; N, 21.70.

**Benzotriazole-1-carbothioic Acid ((*R*)-1-Phenylethyl)-amide (2c):** purified by column chromatography with hexanes/EtOAc (90:10) as eluent to afford yellow oil (87%); $^1$H NMR ($CDCl_3$) $\delta$ 1.77 (d, $J$ = 7.2 Hz, 3H), 5.74−5.84 (m, 1H), 7.30−7.50 (m, 6H), 7.61−7.66 (m, 1H), 8.09 (d, $J$ = 8.2 Hz, 1H), 8.90 (d, $J$ = 8.5 Hz, 1H), 9.32 (d, $J$ = 6.3 Hz, 1H); $^{13}$C NMR $\delta$ 21.0, 54.0, 116.0, 120.1, 125.6, 126.4, 127.9, 128.8, 130.2, 132.3, 141.0, 147.0, 173.3. Anal. Calcd for $C_{15}H_{14}N_4S$: C, 63.80; H, 5.00; N, 19.84. Found: C, 63.63; H, 4.95; N, 19.82.

**Benzotriazole-1-carbothioic Acid Phenethylamide (2d):** white needles (89%); mp 112−113 °C; $^1$H NMR $\delta$ 3.12 (t, $J$ = 6.9 Hz, 2H), 4.07−4.14 (m, 2H), 7.22−7.39 (m, 5H), 7.43−7.51 (m, 1H), 7.60−7.68 (m, 1H), 8.09 (d, $J$ = 8.7 Hz, 1H), 8.92 (d, $J$ = 8.7 Hz, 1H), 9.14 (br s, 1H); $^{13}$C NMR $\delta$ 34.1, 46.1, 116.0, 120.2, 125.7, 127.0, 128.7, 128.9, 130.3, 132.4, 137.8, 147.0, 174.4. Anal. Calcd for $C_{15}H_{14}N_4S$: C, 63.80; H, 5.00; N, 19.84. Found: C, 63.81; H, 4.90; N, 19.70.

**Benzotriazole-1-carbothioic Acid *tert*-Butylamide (2e):** yellow needles (60%); mp 61−63 °C; $^1$H NMR $\delta$ 1.71 (s, 9H), 7.45 (t, $J$ = 7.8 Hz, 1H), 7.59−7.64 (m, 1H), 8.07 (d, $J$ = 8.4 Hz, 1H), 8.91 (d, $J$ = 8.7 Hz, 1H), 9.05 (br s, 1H); $^{13}$C NMR $\delta$ 27.9, 55.5, 103.3, 116.4, 120.1, 125.4, 130.0, 132.2, 147.1, 172.6. Anal. Calcd for $C_{11}H_{14}N_4S$: C, 56.38; H, 6.02; N, 23.91. Found: C, 56.31; H, 5.93; N, 24.10.

**Benzotriazole-1-carbothioic Acid (1,5-Dimethylhexyl)-amide (2f):** purified by column chromatography with hexanes/EtOAc (94:6) as eluent to afford yellow oil (87%); $^1$H NMR $\delta$ 0.87 (d, $J$ = 6.3 Hz, 6H), 1.22−1.85 (m, 10H), 4.60−4.75 (m, 1H), 7.42−7.51 (m, 1H) 7.58−7.68 (m, 1H), 8.08 (d, $J$ = 8.1 Hz, 1H), 8.92−8.95 (m, 2H); $^{13}$C NMR $\delta$ 19.5, 22.5, 23.7, 27.8, 36.1, 38.6, 51.0, 116.1, 120.1, 125.5, 130.1, 132.4, 147.0, 173.3. Anal. Calcd for $C_{15}H_{22}N_4S$: C, 62.03; H, 7.64; N, 19.29. Found: C, 62.16; H, 7.96; N, 19.68.

**[(Benzotriazole-1-carbothioyl)amino] Acetic Acid Methyl Ester (2g):** cream flakes (76%); mp 129−130 °C; $^1$H NMR $\delta$ 3.87 (s, 3H), 4.62 (d, $J$ = 3.6 Hz, 2H), 7.50 (t, $J$ = 7.5 Hz, 1H), 7.68 (t, $J$ = 7.5 Hz, 1H), 8.12 (d, $J$ = 8.1 Hz, 1H), 8.86 (d, $J$ = 8.7 Hz, 1H), 9.53 (br s, 1H); $^{13}$C NMR $\delta$ 46.2, 52.8, 115.8, 120.4, 125.8, 130.5, 132.3, 147.0, 168.5, 174.7. Anal. Calcd for $C_{10}H_{10}N_4O_2S$: C, 47.99; H, 4.03; N, 22.39. Found: C, 48.42; H, 4.18; N, 21.92.

**1*H*-1,2,3-Benzotriazol-1-yl(2,3-dihydro-1*H*-indol-1-yl)-methanethione (2h):** purified by column chromatography with hexanes/EtOAc (91:9) as eluent to afford yellow flakes (84%); mp 123−124 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 3.26 (t, $J$ = 7.5 Hz, 2H), 4.53 (t, $J$ = 7.5 Hz, 2H), 7.02 (s, 1H), 7.14 (t, $J$ = 7.5 Hz, 1H), 7.41 (d, $J$ = 7.5 Hz, 1H), 7.53−7.58 (m, 1H), 7.68−7.73 (m, 1H), 7.99 (d, $J$ = 8.4 Hz, 1H), 8.20 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 26.6, 56.7, 112.7, 115.9, 119.5, 125.2, 125.7, 126.0, 126.6, 129.2, 131.4, 135.5, 140.9, 145.1, 168.8. Anal. Calcd for $C_{15}H_{12}N_4S$: C, 64.26; H, 4.31; N, 19.98. Found: C, 64.26; H, 4.21; N, 20.15.

**Benzotriazol-1-yl-piperidin-1-yl-methanethione (2i):** yellow prisms (76%); mp 86−87 °C; $^1$H NMR $\delta$ 1.71−2.03 (m, 6H), 3.60 (s, 2H), 4.33 (s, 2H), 7.41−7.47 (m, 1H), 7.57−7.62 (m, 2H), 8.07 (d, $J$ = 9.0 Hz, 2H); $^{13}$C NMR $\delta$ 24.0, 25.4, 26.8, 52.7, 53.4, 113.7, 119.8, 125.0, 128.8, 133.3, 146.0, 174.1. Anal. Calcd for $C_{12}H_{14}N_4S$: C, 58.51; H, 5.73; N, 22.74. Found: C, 58.88; H, 5.73; N, 22.95.

**Benzotriazole-1-carbothioic Acid *N*-Methyl-*N*-phenylamide (2j):** colorless plates (92%); mp 138 °C; $^1$H NMR $\delta$ 3.96 (s, 3H), 7.01−7.10 (m, 2H), 7.15−7.26 (m, 3H), 7.36−7.42

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(m, 1H), 7.56−7.61 (m, 1H), 7.94 (d, $J$ = 8.4 Hz, 1H), 8.13 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 46.0, 113.0, 119.8, 124.6, 124.8, 127.7, 128.8, 129.4, 133.0, 145.4, 145.5, 175.7. Anal. Calcd for $C_{14}H_{12}N_4S$: C, 62.66; H, 4.51; N, 20.88. Found: C, 63.00; H, 4.49; N, 20.97.

**Benzotriazol-1-yl-(*N*,*N*-diethyl)methanethione (2k):** yellow needles (98%); mp 37−38 °C; $^1$H NMR $\delta$ 1.33 (t, $J$ = 6.9 Hz, 3H), 1.49 (t, $J$ = 6.9 Hz, 3H), 3.51 (q, $J$ = 6.6 Hz, 2H), 4.12 (q, $J$ = 6.6 Hz, 2H), 7.43 (t, $J$ = 6.9 Hz, 1H), 7.60−7.55 (m, 1H), 8.08−8.02 (m, 2H); $^{13}$C NMR $\delta$ 10.1, 14.0, 48.1, 48.2, 113.5, 119.7, 124.9, 128.7, 133.2, 145.8, 174.7. Anal. Calcd for $C_{11}H_{14}N_4S$: C, 56.38; H, 6.02; N, 23.91. Found: C, 55.94; H, 5.81; N, 23.99.

**Benzotriazole-1-carbothioic Acid *N*-Butyl-*N*-methylamide (2l):** purified by column chromatography with hexanes/EtOAc (90:10) as eluent to afford yellow oil (76%); rotamers (50:50 ratio) observed in$^1$H NMR at 25 °C; signals double the expected proton signals; $^1$H NMR $\delta$ 0.76 (t, $J$ = 7.4 Hz, 3H), 1.02 (t, $J$ = 7.5 Hz, 3H), 1.10−1.18 (m, 2H), 1.43−1.55 (m, 2H), 1.64−1.76 (m, 2H), 1.82−1.93 (m, 2H), 3.23 (s, 3H), 3.49−3.59 (m, 5H), 4.09 (t, $J$ = 7.7 Hz, 2H), 7.42 (t, $J$ = 7.7 Hz, 2H), 7.58 (t, $J$ = 7.7 Hz, 2H), 7.99−8.10 (m, 4H); $^{13}$C NMR $\delta$ 13.2, 13.6, 19.4, 19.8, 27.4, 30.0, 41.4, 42.0, 55.6, 55.7, 113.2, 113.6, 119.5, 124.8, 128.6, 128.7, 132.9, 133.1, 145.6, 174.8, 175.3. Anal. Calcd for $C_{12}H_{16}N_4S$: C, 58.04; H, 6.49; N, 22.56. Found: C, 57.81; H, 6.41; N, 22.85.

**Ethyl 4-Isothiocyanatobenzoate (11a):** yellow needles (99%); mp 47−50 °C (lit.[83] mp 50−53 °C); $^1$H NMR $\delta$ 1.44 (t, $J$ = 8.4 Hz, 3H), 4.42 (q, $J$ = 8.0 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.55 (d, $J$ = 8.7 Hz, 1H), 8.09 (t, $J$ = 8.1 Hz, 2H); $^{13}$C NMR $\delta$ 14.2, 61.3, 123.3, 125.6, 128.2, 129.0, 130.9, 131.0, 141.2, 165.4.

**General Procedure for the One-Pot Preparation of Symmetrical Thioureas 3a−d**. To 0.28 g of bis(benzotriazol-1-yl)methanethione (**1**) (1 mmol) in 30 mL of THF was added the appropriate primary amine (2 mmol), and the mixture was refluxed for 5 h. Solvent was evaporated, and the crude product was purified by column chromatography on alumina (30% EtOAc/hexanes). Recrystallization from $CH_2Cl_2$ afforded crystalline thioureas in 82−85% yields.

**1,3-Dipyridin-4-ylthiourea (3a).** Yellow granules (85%), mp 179−180 °C, $^1$H NMR (DMSO-$d_6$) $\delta$ 7.65 (d, $J$ = 5.9 Hz, 4H), 8.46 (d, $J$ = 5.9 Hz, 4H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 179.0, 149.3, 147.8, 115.8. Anal. Calcd for $C_{11}H_{10}N_4S$: C, 57.37; H, 4.38; N, 24.33. Found: C, 57.33; H, 4.27; N, 24.04.

**1,3-Dipyridin-3-ylthiourea (3b):** yellow granules (83%); mp 179−180 °C (lit.[40] mp 178−180 °C); $^1$H NMR (DMSO-$d_6$) $\delta$ 7.45 (dd, $J$ = 8.2, 4.8 Hz, 2H), 8.03 (d, $J$ = 8.2 Hz, 2H), 8.38 (d, $J$ = 4.5 Hz, 2H), 8.70 (d, $J$ = 2.2 Hz, 2H), 10.36 (br s, 2H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 123.6, 132.1, 136.3, 144.7, 144.9, 180.9.

**1,3-Dipyridin-2-ylthiourea (3c):** white powder (82%); mp 163−164 °C (lit.[51] mp 163 °C); $^1$H NMR $\delta$ 7.04 (bs, 3H), 7.70 (bs, 2H), 8.37 (bs, 2H), 8.85 (bs, 1H), 9.99 (bs, 1H), 14.41 (bs, 1H); $^{13}$C NMR $\delta$ 114.5, 119.3, 137.9, 146.9, 152.5, 177.4.

**1,3-Bis-(4,6-dimethylpyridin-2-yl)thiourea (3d):** yellow granules (83%); mp 214−216 °C (lit.[49] mp 218−219 °C); $^1$H NMR $\delta$ 2.11 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.54 (s, 3H), 6.21 (s, 2H), 6.36 (s, 1H), 7.00 (s, 1H); $^{13}$C NMR $\delta$ 19.4, 21.1, 21.3, 21.8, 107.3, 114.1, 115.0, 115.7, 145.6, 148.9, 151.4, 152.5, 155.6, 157.0, 167.2.

**General Procedure for the One-Pot Preparation of Asymmetrical Thioureas 3e−g**. To bis(benzotriazol-1-yl)-methanethione (**1**) (0.28 g, 1 mmol) in THF (30 mL) was added the appropriate primary amine (1 mmol), and the mixture was heated under reflux for 5 h. Then, the second primary amine or a secondary amine (1 mmol) was added, and the mixture was stirred for 48 h. Solvent was evaporated, and the crude product was purified by column chromatography on alumina (30% EtOAc/hexanes).

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**1-(Pyridin-2-yl)-3-(pyrid-3-yl)thiourea (3e):** white microcrystals (78%); mp 180−181 °C; $^1$H NMR $\delta$ 7.01 (dd, $J$ = 6.6, 5.2 Hz, 1H), 7.16 (d, $J$ = 8.4 Hz, 1H), 7.35 (dd, $J$ = 8.2, 4.8 Hz, 1H), 7.69 (t, $J$ = 8.9 Hz, 1H), 8.23 (dd, $J$ = 5.0, 1.1 Hz, 1H), 8.32 (dd, $J$ = 8.2, 3.6 Hz, 1H), 8.46 (dd, $J$ = 4.8, 1.3 Hz, 1H), 8.76 (d, $J$ = 2.3 Hz, 1H), 10.41 (br s, 2H); $^{13}$C NMR $\delta$ 113.0, 118.2, 123.0, 132.0, 135.7, 138.9, 145.2, 145.8, 146.5, 153.4, 179.6. Anal. Calcd for $C_{11}H_{10}N_4S$: C, 57.37; H, 4.38; N, 24.33. Found: C, 57.70; H, 4.43; N, 24.05.

**1-(Pyridin-2-yl)-3-(pyrid-4-yl)thiourea (3f):** white microcrystals (80%); mp 183−184 °C; $^1$H NMR $\delta$ 7.17 (t, $J$ = 6.0 Hz, 1H), 7.29 (d, $J$ = 8.2 Hz, 1H), 7.88 (t, $J$ = 8.2 Hz, 1H), 7.97 (d, $J$ = 5.7 Hz, 2H), 8.39 (d, $J$ = 4.5 Hz, 1H), 8.53 (d, $J$ = 5.6 Hz, 2H), 11.17 (br, 1H); $^{13}$C NMR $\delta$ 113.1, 116.5, 118.6, 139.6, 145.6, 145.8, 150.0, 153.2, 178.1. Anal. Calcd for $C_{11}H_{10}N_4S$: C, 57.37; H, 4.38; N, 24.33. Found: C, 57.49; H, 4.30; N, 24.22.

**1-(4,6-Dimethylpyridin-2-yl)-3-(pyrid-3-yl)thiourea (3g):** white microcrystals (83%); mp 180−181 °C; $^1$H NMR $\delta$ 2.32 (s, 3H), 2.48 (s, 3H), 6.41 (s, 1H), 6.73 (s, 1H), 7.33−7.38 (m, 1H), 8.39 (s, 1H), 8.45 (d, $J$ = 4.8 Hz, 1H), 8.56 (d, $J$ = 8.4 Hz, 1H), 8.69 (d, $J$ = 2.4 Hz, 1H); $^{13}$C NMR $\delta$ 21.4, 23.9, 109.5, 119.6, 123.4, 131.1, 136.1, 145.1, 146.8, 151.4, 152.6, 155.1, 179.3. Anal. Calcd for $C_{13}H_{14}N_4S$: C, 60.44; H, 5.46; N, 21.69. Found: C, 60.62; H, 5.54; N, 21.65.

**General Procedure for the Preparation of Bis(benzotriazol-1-yl)diarylsulfidemethanes 4.** To bis(benzotriazol-1-yl)methanethione (**1**) (0.56 g, 2 mmol) in THF at room temperature was added the appropriate Grignard reagent (2 mmol). After stirring overnight at room temperature, solvent was removed in vacuo. The residue was redissolved in EtOAc (100 mL) and washed with 5% $Na_2CO_3$ solution (3 × 100 mL), 1 M HCl (2 × 100 mL), water, and brine. The collected organic layers were dried with $Na_2SO_4$, and then solvent was removed under vacuum. Recrystallization from EtOAc/hexanes afforded the desired bis(benzotriazol-1-yl)diarylsulfidemethanes (**4**). Compounds **4a** and **4b** are given as representative examples.

**Bis(benzotriazolyl)-bis(phenylthio)methane (4a):** yellow orthorhombic crystals (23%); mp 162−163 °C; $^1$H NMR $\delta$ 6.86 (d, $J$ = 8.4 Hz, 2H), 7.12−7.19 (m, 8H), 7.27 (t, $J$ = 7.2 Hz, 2H), 7.31−7.40 (m, 4H), 8.06 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR $\delta$ 111.6, 120.4, 123.8, 124.9, 128.5, 129.6, 131.4, 136.9, 141.5, 146.7. Anal. Calcd for $C_{25}H_{18}N_6S2$: C, 64.36; H, 3.89; N, 18.01. Found: C, 63.71; H, 3.41; N, 18.01.

**Bis(benzotriazolyl)-bis(4-methylphenylthio)-methane (4b):** yellow monoclinic crystals (34%); mp 189−190 °C; $^1$H NMR $\delta$ 2.27 (s, 6H), 6.81 (d, $J$ = 8.4 Hz, 2H), 6.92 (s, 8H), 7.21 (t, $J$ = 8.1 Hz, 2H), 7.31 (t, $J$ = 8.1 Hz, 2H), 8.02 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR $\delta$ 21.3, 111.7, 120.4, 123.8, 124.9, 128.4, 129.6, 131.4, 136.9, 141.5, 146.7. Anal. Calcd for $C_{27}H_{22}N_6S2$: H, 4.48; N, 16.99. Found: H, 4.29; N, 16.68.

**General Procedure for the Preparation of Thiocarbonylbenzotriazoles 6a−d.** To 4-methylphenylmagnesium bromide (10 mL, 1 M) in THF at room temperature was added carbon disulfide (0.9 mL, 10 mmol). The reaction mixture was heated under reflux for 3 h and then cooled to room temperature, and 1-chlorobenzotriazole (3.06 g, 20 mmol) was added. After stirring overnight at room temperature, solvent was removed in vacuo and the mixture was separated on a silica gel column (2% EtOAc/hexanes). Recrystallization from EtOAc/hexanes provided the desired thiocarbonylbenzotriazoles **6a−d**.

**Benzotriazol-1-yl-4-methylphenyl Methanethione (6a):** red needles (63%); mp 140−142 °C; $^1$H NMR $\delta$ 2.49 (s, 3H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.55 (t, $J$ = 7.5 Hz, 1H), 7.71 (t, $J$ = 7.5 Hz, 1H), 8.14−8.19 (m, 3H), 8.39 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 21.8, 114.8, 120.1, 126.2, 128.6, 129.2, 130.3, 131.9, 144.9, 171.8. Anal. Calcd for $C_{14}H_{11}N_3S$: C, 66.38; H, 4.38; N, 16.59. Found: C, 66.83; H, 4.34; N, 16.66.

**Benzotriazol-1-yl-4-methoxyphenyl Methanethione (6b):** red-orange needles (89%); mp 131−134 °C; $^1$H NMR $\delta$ 3.92 (s, 3H), 6.95 (d, $J$ = 6.9 Hz, 2H), 7.55 (t, $J$ = 8.1 Hz, 1H),

7.69 (t, $J$ = 7.5 Hz, 1H), 7.84 (d, $J$ = 6.9 Hz, 2H), 8.18 (d, $J$ = 8.1 Hz, 1H), 8.52 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 55.7, 113.6, 113.9, 114.8, 115.2, 120.1, 120.4, 126.1, 126.4, 133.7, 134.4, 147.0, 164.1. Anal. Calcd for $C_{14}H_{11}N_3OS$: C, 62.43; H, 4.12; N, 15.60. Found: C, 62.02; H, 4.17; N, 15.43.

**Benzotriazol-1-yl-phenyl Methanethione (6c):** red-pink needles (76%); mp 134−136 °C (lit.[5b] mp 139−141 °C); $^1$H NMR $\delta$ 7.46 (t, $J$ = 7.5 Hz, 2H), 7.64−7.56 (m, 2H), 7.70−7.79 (m, 3H), 8.19 (d, $J$ = 8.4 Hz, 1H), 8.63 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 115.4, 120.5, 126.8, 128.0, 130.6, 130.7, 132.5, 133.2, 142.7, 147.0, 202.1.

**Benzotriazol-1-yl-4-chlorophenyl Methanethione (6d):** red-pink needles (42%); mp 123−124 °C; $^1$H NMR $\delta$ 7.43 (t, $J$ = 8.7 Hz, 2H), 7.59 (t, $J$ = 7.8 Hz, 1H), 7.73 (t, $J$ = 6.9 Hz, 1H), 7.73 (d, $J$ = 8.7 Hz, 1H), 8.19 (d, $J$ = 8.1 Hz, 1H), 8.63 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR $\delta$ 115.4, 120.6, 127.0, 128.3, 130.9, 131.9, 133.1, 139.1, 140.9, 147.0, 200.2. Anal. Calcd for $C_{13}H_8ClN_3S$: H, 2.95; N, 15.35. Found: H, 2.80; N, 15.06.

**General Procedure for the Preparation of 2-Amino-5-nitrophenylamides 9a−h.** $Et_3N$ (3.0 g, 30 mmol) was added to a solution of 4-nitro-1,2-phenylenediamine (3.06 g, 20 mmol) in THF (100 mL) at −40 °C, followed by dropwise addition of the respective acid chloride (20 mmol). The mixture was stirred at −40 °C for 3 h and at room temperature overnight. The precipitate was filtered off, and the filtrate evaporated to dryness in vacuo. The residue was recrystallized from EtOH to afford the desired 2-amino-5-nitrophenylamides **9a**−**h** in 81−99% yields.

***N*-(2-Amino-5-nitrophenyl)propionamide (9a):** yellow microcrystals (84%); mp 189−191 °C (lit.[23] mp 191 °C); $^1$H NMR $\delta$ 1.10 (t, $J$ = 7.6 Hz, 3H), 2.38 (q, $J$ = 7.6 Hz, 2H), 6.49 (br s, 2H), 6.76 (d, $J$ = 9.0 Hz, 1H), 7.84 (dd, $J$ = 9.0, 2.5 Hz, 1H), 8.27 (d, $J$ = 2.5 Hz, 1H), 9.13 (s, 1H); $^{13}$C NMR $\delta$ 9.6, 28.9, 113.6, 121.2, 121.7, 122.6, 135.5, 148.9, 172.6.

***N*-(2-Amino-5-nitrophenyl)-4-methylbenzamide (9b):** yellow needles (98%); mp 197−198 °C; $^1$H NMR $\delta$ 2.39 (s, 3H), 6.59 (s, 2H), 6.82 (d, $J$ = 9.1 Hz, 1H), 7.34 (d, $J$ = 8.1 Hz, 2H), 7.91 (d, $J$ = 9.2 Hz, 1H), 7.93 (d, $J$ = 8.1 Hz, 2H), 8.15 (d, $J$ = 2.6 Hz, 1H), 9.68 (s, 1H); $^{13}$C NMR $\delta$ 21.0, 113.9, 121.4, 123.5, 128.0, 128.8, 131.4, 135.4, 141.6, 150.6, 165.9. Anal. Calcd. For $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 62.35; H, 4.76; N, 15.13.

**Furan-2-yl Carboxylic Acid (2-Amino-5-nitrophenyl)-amide (9c):** yellow needles (95%); mp 176−178 °C. $^1$H NMR $\delta$ 6.61 (s, 2H), 6.71 (dd, $J$ = 3.3, 1.5 Hz, 1H), 6.81 (d, $J$ = 9.0 Hz, 1H), 7.33 (d, $J$ = 3.6 Hz, 1H), 7.91−7.94 (m, 2H), 8.06 (d, $J$ = 2.4 Hz, 1H), 9.69 (s, 1H). $^{13}$C NMR $\delta$ 112.1, 113.9, 114.9, 120.4, 123.8, 135.4, 145.6, 147.4, 150.9, 157.0, 168.0. Anal. Calcd for $C_{11}H_9N_3O_4$: C, 53.44; H, 3.67; N, 17.00. Found: C, 54.65; H, 3.28; N, 13.25.

***N*-(2-Amino-5-nitrophenyl)-4-nitrobenzylamide (9d):** brown needles (83%); mp 303−305 °C; $^1$H NMR $\delta$ 6.58 (s, 2H), 6.84 (d, $J$ = 9 Hz, 1H), 7.93 (dd, $J$ = 9, 2.4 Hz, 1H), 8.25−8.30 (m, 4H), 8.38 (s, 1H); $^{13}$C NMR $\delta$ 113.6, 122.8, 123.1, 123.8, 129.3, 129.6, 129.7, 148.0, 148.4, 150.8, 193.5. Anal. Calcd for $C_{13}H_{10}N_4O_5$: C, 51.66; H, 3.33. Found: C, 52.03; H, 3.39.

***N*-(2-Amino-5-nitrophenyl)-4-methoxybenzylamide (9e):** brown needles (86%); mp 221−224 °C; $^1$H NMR $\delta$ 3.84 (s, 3H), 6.59 (s, 2H), 6.80 (d, $J$ = 9.3 Hz, 1H), 7.08 (d, $J$ = 9.3 Hz, 2H), 7.91 (dd, $J$ = 9.3, 2.7 Hz, 1H), 8.00 (d, $J$ = 2.7 Hz, 1H), 8.11 (d, $J$ = 2.4 Hz, 1H), 9.62 (s, 1H); $^{13}$C NMR $\delta$ 55.6, 113.6, 114.0, 121.7, 123.7, 130.1, 130.8, 135.5, 150.9, 162.1, 165.6, 204.5. Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 58.53; H, 4.56; N, 14.63. Found: C, 58.55; H, 4.57; N, 14.09.

***N*-(2-Amino-5-nitrophenyl)-4-bromobenzylamide (9f):** brown needles (99%); mp 222−223 °C; $^1$H NMR $\delta$ 6.65 (s, 2H), 6.80 (d, $J$ = 9 Hz, 1H), 7.75 (d, $J$ = 8.4 Hz, 2H), 7.91−7.98 (m, 3H), 8.11 (s, 1H), 9.83 (s, 1H); $^{13}$C NMR $\delta$ 114.0, 121.1, 124.0, 125.6, 130.3, 131.4, 133.5, 135.4, 151.0, 161.8, 165.4. Anal. Calcd for $C_{13}H_{10}NBrO_2$: C, 46.45; H, 3.00; N, 12.50. Found: C, 46.34; H, 2.93; N, 11.89.

***N*-(2-Amino-5-nitrophenyl)hexylamide (9g):** brown needles (81%); mp 130−131 °C; $^1$H NMR $\delta$ 0.90 (t, $J$ = 6.6 Hz, 3H), 1.32−1.34 (m, 4H), 1.62 (quintet, $J$ = 6.6 Hz, 2H), 2.37 (t, $J$ = 6.6 Hz, 2H), 6.49 (s, 2H), 6.78 (d, $J$ = 9 Hz, 1H), 7.85 (dd, $J$ = 9.0, 2.4 Hz, 1H), 8.31 (d, $J$ = 2.4 Hz, 1H), 9.16 (s, 1H); $^{13}$C NMR $\delta$ 14.0, 22.1, 24.9, 31.1, 36.0, 113.8, 121.2, 121.9, 122.7, 135.7, 148.8, 172.1. Anal. Calcd for $C_{12}H_{17}N_3O_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.88; H, 7.04; N, 15.97.

**Thien-2-yl Carboxylic Acid (2-Amino-5-nitrophenyl)-amide (9h):** brown needles (91%); mp 192−196 °C; $^1$H NMR $\delta$ 6.65 (s, 2H), 6.81 (d, $J$ = 9 Hz, 1H), 7.22−7.25 (m, 1H), 7.86−7.95 (m, 2H), 8.03−8.09 (m, 2H), 9.81 (s, 1H); $^{13}$C NMR $\delta$ 114.0, 120.8, 124.0, 128.2, 129.9, 131.9, 135.5, 139.5, 151.1, 160.8, 167.6. Anal. Calcd for $C_{11}H_9N_3O_3S$: C, 50.18; H, 3.45; N, 15.96. Found: C, 49.98; H, 3.29; N, 15.43.

**General Procedure for the Preparation of Thiocarbonyl-1*H*-6-nitrobenzotriazoles 10a−h.** Phosphorus pentasulfide (2.22 g, 10 mmol) was mixed with $Na_2CO_3$ (0.54 g, 5 mmol) in dry THF (150 mL). The mixture was stirred at room temperature for 1 h and then cooled to 0 °C. The amide (**9**) (10 mmol) was added in one portion, and the resulting mixture was stirred at 0 °C for 3 h and at room temperature for 10 h. The mixture was filtered, and the filtrate evaporated to dryness. The residue was dissolved in EtOAc (100 mL) and washed with 5% $NaHCO_3$ (2 × 30 mL), and the aqueous layers were back-extracted with EtOAc (100 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, and evaporated to obtain a residue. The residue was placed on a silica gel column and eluted with hexanes/EtOAc (5:1) to give thioamides in crude yields of 59−96%.

Sodium nitrite (0.21 g, 3 mmol) was added to a stirred solution of the obtained thioamide (2 mmol), dissolved by gentle warming in aqueous acetic acid (95%, 25 mL), and then cooled to 0 °C. The resulting mixture was stirred at 0 °C for 45 min, ice-cold water (100 mL) was added, and the precipitated product was filtered and washed with water. Compound **10g** was an exception requiring sonication and extraction with EtOAc, which entailed washing the aqueous solution three times with 50 mL of EtOAc, collecting the organic layers and washing them with water (2 × 30 mL) and brine (40 mL), drying with sodium sulfate, and filtration. The obtained solid was dried in vacuo overnight to afford the desired thiocarbonyl-1*H*-6-nitrobenzotriazoles **10a**−**h** in 45−81% yields from the amide (**9**).

**(6-Nitrobenzotriazol-1-yl)propane-1-thione (10a):** orange microcrystals (52%); mp 107−109 °C (lit.[23] mp 108 °C); $^1$H NMR $\delta$ 1.54 (t, $J$ = 7.1 Hz, 3H), 3.79 (q, $J$ = 7.1 Hz, 2H), 8.31 (d, $J$ = 9.0 Hz, 1H), 8.44 (dd, $J$ = 9.0, 1.8 Hz, 1H), 9.74 (s, 1H); $^{13}$C NMR $\delta$ 13.4, 40.6, 113.1, 121.2, 121.7, 131.7, 149.0, 149.4, 211.6.

**(4-Methylphenyl)(6-nitrobenzotriazol-1-yl)methanethione (10b):** red microcrystals (80%); mp 140−141 °C; $^1$H NMR $\delta$ 2.45 (s, 3H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.0 Hz, 2H), 8.32 (d, $J$ = 9.0 Hz, 1H), 8.44 (dd, $J$ = 9.0, 1.1 Hz, 1H), 9.42 (s, 1H); $^{13}$C NMR $\delta$ 21.8, 112.1, 121.2, 121.5, 129.1, 131.2, 133.1, 139.4, 145.1, 148.8, 148.9, 200.5. Anal. Calcd for $C_{14}H_{10}N_4O_2S$: C, 56.37; H, 3.38; N, 18.78. Found: C, 56.65; H, 3.29; N, 18.69.

**Furan-2-yl-(6-nitrobenzotriazol-1-yl)-methanethione (10c):** orange microcrystals (80%); mp 162 °C; $^1$H NMR $\delta$ 6.79 (dd, $J$ = 3, 1.5 Hz, 1H), 7.66 (d, $J$ = 3.6 Hz, 1H), 8.00 (d, $J$ = 0.9 Hz, 1H), 8.32 (d, $J$ = 9 Hz, 1H), 8.43 (dd, $J$ = 9, 2.1 Hz, 1 H), 9.47 (d, $J$ = 1.8 Hz, 1H); $^{13}$C NMR $\delta$ 112.1, 114.4, 121.2, 121.4, 122.4, 132.9, 148.6, 148.8, 151.8, 154.3, 180.1. Anal. Calcd for $C_{11}H_6N_4O_3S$: C, 48.17; H, 2.21. Found C, 47.83; H, 2.12.

**(4-Nitrophenyl)(6-nitrobenzotriazol-1-yl)methanethione (10d):** orange needles (69%); mp 174 °C; $^1$H NMR $\delta$ 7.46 (d, $J$ = 8.7 Hz, 2H), 7.82 (d, $J$ = 8.7 Hz, 2H), 7.93 (d, $J$ = 8.7 Hz, 1H), 8.02 (d, $J$ = 8.7 Hz, 2H), 9.00 (d, $J$ = 1.8 Hz, 1H); $^{13}$C NMR $\delta$ 114.3, 114.7, 121.1, 123.4, 123.9, 130.9, 131.4, 136.4,

150.2, 166.0, 208.0. Anal. Calcd for $C_{13}H_7N_5O_4S$: C, 47.42; H, 2.14; N, 21.27. Found C, 47.50; H, 2.02; N, 20.93.

**(4-Methoxyphenyl)(6-nitrobenzotriazol-1-yl)methanethione (10e):** orange needles (66%); mp 162 °C; $^1$H NMR $\delta$ 3.93 (s, 3H), 6.98 (d, $J$ = 9.0 Hz, 2H), 7.86 (d, $J$ = 9.0 Hz, 2H), 8.31 (d, $J$ = 9.0 Hz, 1H), 8.42 (dd, $J$ = 9.0, 2.1 Hz, 1H), 9.37 (d, $J$ = 2.1 Hz, 1H); $^{13}$C NMR $\delta$ 55.8, 112.0, 113.9, 112.1, 133.3, 134.0, 134.7, 148.6, 148.9, 164.8, 198.4. Anal. Calcd for $C_{14}H_{10}N_4O_3S$: C, 53.50; H, 3.21; N, 17.82. Found C, 53.61; H, 3.14; N, 17.62.

**(4-Bromophenyl)(6-nitrobenzotriazol-1-yl)methanethione (10f):** orange microcrystals (45%); mp 170 °C; $^1$H NMR $\delta$ 7.67−7.74 (m, 4H), 8.39 (d, $J$ = 9 Hz, 1H), 8.52 (dd, $J$ = 9, 1.8 Hz, 1H), 9.54 (d, $J$ = 2.1 Hz, 1H); $^{13}$C NMR $\delta$ 112.1, 121.4, 121.9, 128.8, 131.6, 132.1, 132.8, 140.6, 149.0, 149.1, 199.6. Anal. Calcd for $C_{13}H_7BrN_4O_2S$: C, 42.99; H, 1.94. Found: C, 42.81; H, 1.79.

**(6-Nitrobenzotriazol-1-yl)-1-hexylthioamide (10g):** yellow microcrystals (53%); mp 94−97 °C; $^1$H NMR $\delta$ 0.94 (t, $J$ = 6.9 Hz, 3H), 1.37−1.52 (m, 4H), 1.95−2.05 (m, 2H), 3.78 (t, $J$ = 7.5 Hz, 2H), 8.30 (d, $J$ = 9.0 Hz, 1H), 8.44 (dd, $J$ = 9.0, 1.8 Hz, 1H), 9.79 (d, $J$ = 2.1 Hz, 1H); $^{13}$C NMR $\delta$ 13.9, 22.3, 29.4, 31.1, 47.6, 113.1, 121.2, 121.8, 131.7, 149.1, 149.4, 210.7. Anal. Calcd for $C_{12}H_{14}N_4O_2S$: C, 51.78; H, 5.07; N, 20.13. Found: C, 52.14; H, 5.12; N, 19.79.

**(6-Nitrobenzotriazol-1-yl)thiophen-2-yl Methanethione (10h):** orange microcrystals (81%); mp 134 °C; $^1$H NMR $\delta$ 7.25 (dd, $J$ = 4.0, 1.2 Hz, 1H), 7.97 (d, $J$ = 4.8 Hz, 1H), 8.10 (d, $J$ = 4.0 Hz, 1H), 8.31 (d, $J$ = 8.7 Hz, 1H), 8.42 (d, $J$ = 8.7 Hz, 1H), 9.45 (s, 1H); $^{13}$C NMR $\delta$ 112.3, 121.2, 121.4, 129.2, 133.0, 136.5, 140.5, 146.6, 148.7, 187.3. Anal. Calcd for $C_{11}H_6N_4O_2S_2$: C, 45.51; H, 2.08; N, 19.30. Found: C, 44.66; H, 1.90; N, 18.45.

**General Procedure for the Preparation of *O*-Aryloxythioacylbenzotriazoles 12a−e.** Bis(benzotriazol-1-yl)methanethione (0.28 g, 1 mmol) was dissolved in 10 mL of $CH_2Cl_2$. In another flask, the aryl alcohol (1 mmol) and NaH (0.18 g, 4.5 mmol) were stirred for 5 min in $CH_2Cl_2$ (10 mL). The solution of the sodium salt was added to the bis(benzotriazol-1-yl)-methanethione solution, and the mixture was stirred for 24 h. The solvent was evaporated and water was added and extracted with EtOAc (2 × 25 mL). The organic layer was washed with water and 10% $Na_2CO_3$ solution (2 × 30 mL), dried over $Mg_2SO_4$, filtered, and concentrated. Recrystallization from hexanes gave **12a−e** in 66−87% yields.

***O*-Naphth-2-yl Benzotriazole-1-carbothioate (12a):** colorless microcrystals (87%); mp 159−160 °C; $^1$H NMR $\delta$ 7.41 (dd, $J$ = 8.8, 2.4 Hz, 1H), 7.53−7.58 (m, 3H), 7.68−7.73 (m, 2H), 7.87−7.94 (m, 2H), 7.98 (d, $J$ = 8.9 Hz, 1H), 8.20 (d, $J$ = 8.2 Hz, 1H), 8.52 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 115.4, 119.7, 121.1, 121.2, 126.6, 126.7, 127.2, 128.1, 128.2, 130.1, 131.0, 132.0, 132.3, 133.9, 146.9, 150.5, 182.4. Anal. Calcd for $C_{17}H_{11}N_3OS$: C, 66.87; H, 3.63; N, 13.76. Found: C, 66.77; H, 3.57; N, 13.46.

***O*-Pyridin-3-yl benzotriazole-1-carbothioate (12b):** granules (66%); mp 139−140 °C; $^1$H NMR $\delta$ 7.52−7.48 (m, 1H), 7.61 (t, $J$ = 7.3 Hz, 1H), 7.68−7.64 (m, 1H), 7.74 (t, $J$ = 8.2 Hz, 1H), 8.21 (d, $J$ = 8.2 Hz, 1H), 8.52 (d, $J$ = 8.4 Hz, 1H), 8.63 (d, $J$ = 2.7 Hz, 1H), 8.66 (dd, $J$ = 4.7, 1.1 Hz, 1H); $^{13}$C NMR $\delta$ 115.1, 121.1, 124.4, 126.7, 130.2, 131.1, 131.9, 144.2, 146.7, 148.5, 149.5, 181.4. Anal. Calcd for $C_{12}H_8N_4OS$: C, 56.24; H, 3.15; N, 21.86. Found: C, 56.27; H, 3.04; N, 21.64.

***O*-Naphth-1-yl Benzotriazole-1-carbothioate (12c):** colorless microcrystals (81%); mp 148−149 °C; $^1$H NMR $\delta$ 7.44 (d, $J$ = 7.4 Hz, 1H), 7.49−7.62 (m, 4H), 7.69−7.74 (m, 1H), 7.89−7.97 (m, 3H), 8.24 (d, $J$ = 8.2 Hz, 1H), 8.55 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 115.4, 119.3, 121.2, 121.3, 125.5, 126.5, 126.6, 127.1, 127.3, 127.7, 128.5, 131.1, 132.1, 135.1, 147.0, 148.9, 182.0. Anal. Calcd for $C_{17}H_{11}N_3OS$: C, 66.87; H, 3.63; N, 13.76. Found: C, 66.76; H, 3.49; N, 13.71.

***O*-Phenyl Benzotriazole-1-carbothioate (12d):** yellow microcrystals (83%); mp 68 °C; $^1$H NMR $\delta$ 7.30−7.36 (m, 2H), 7.42−7.52 (m, 1H), 7.56−7.64 (m, 3H), 7.76 (t, $J$ = 8.0 Hz, 1H), 8.24 (d, $J$ = 8.0 Hz, 1H), 8.55 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 115.2, 120.9, 122.1, 126.4, 122.3, 129.9, 130.8, 131.7, 146.7, 152.7, 182.2. Anal. Calcd for $C_{13}H_9N_3OS$: C, 61.16; H, 3.55. Found: C, 60.79; H, 3.48.

***O*-4-*tert*-Butylphenyl Benzotriazole-1-carbothioate (12e):** yellow microcrystals (75%); mp 122−123 °C; $^1$H NMR $\delta$ 1.38 (s, 9H), 7.21 (d, $J$ = 9.0 Hz, 2H), 7.53 (d, $J$ = 9.0 Hz, 2H), 7.55 (t, $J$ = 8.1 Hz, 1H), 7.69 (t, $J$ = 7.5 Hz, 1H), 8.19 (d, $J$ = 8.4 Hz, 1H), 8.48 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 115.2, 120.9, 122.1, 126.4, 122.3, 129.9, 130.8, 131.7, 146.7, 152.7, 182.2. Anal. Calcd for $C_{17}H_{17}N_3OS$: C, 65.57; H, 5.50; N, 13.49. Found: C, 65.77; H, 5.54; N, 13.50.

**General Procedure for the Preparation of Aryl/Alkylthiothioacylbenzotriazoles 13a−c and Disulfides 14a,b,d.** To bis(benzotriazol-1-yl)methanethione (10 mmol) in $CH_2Cl_2$ at room temperature was added thiol (10 mmol) and a catalytic amount of $Et_3N$. Stirring was continued for 3 h, and then solvent was removed under vacuum, water was added, and the organic layer was extracted with EtOAc (2 × 25 mL). The organic layer was washed with water and 10% $Na_2CO_3$ solution (2 × 30 mL), dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave a mixture, which was further purified by column chromatography (1:10 EtOAc/hexanes).

**Phenyl-1*H*-benzotriazole-1-carbodithioate (13a):** yellow microcrystals (46%); mp 85−87 °C; $^1$H NMR $\delta$ 7.46−7.64 (m, 7H), 8.12 (d, $J$ = 8.1 Hz, 1H), 8.63 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 115.7, 120.8, 126.7, 129.4, 129.9, 131.0, 131.3, 132.4, 136.6, 147.4, 198.1. Anal. Calcd for $C_{13}H_9N_3S_2$: C, 57.54; H, 3.34; N, 15.49. Found: C, 57.93; H, 3.33; N, 15.39.

**Benzyl-1*H*-benzotriazole-1-carbodithioate (13b):** yellow microcrystals (42%); mp 108−109 °C; $^1$H NMR $\delta$ 4.57 (s, 2H), 7.25−7.37 (m, 3H), 7.41−7.51 (m, 3H), 7.62 (t, $J$ = 8.4 Hz, 1H), 8.09 (d, $J$ = 8.2 Hz, 1H), 8.71 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 41.0, 115.7, 120.8, 126.7, 128.1, 128.9, 129.7, 131.2, 132.4, 134.1, 147.3, 197.6. Anal. Calcd for $C_{14}H_{11}N_3S_2$: C, 58.92; H, 3.88; N, 14.72. Found: C, 58.86; H, 3.81; N, 14.66.

**Ethyl-2-[(1*H*-benzotriazol-1-ylcarbothioyl)sulfanyl]-acetate (13c):** yellow microcrystals (63%); mp 67−68 °C; $^1$H NMR $\delta$ 1.33 (t, $J$ = 7.1 Hz, 3H), 4.20 (s, 2H), 4.27 (q, $J$ = 7.1 Hz, 2H), 7.52 (t, $J$ = 7.8 Hz, 1H), 7.66 (t, $J$ = 8.1 Hz, 1H), 8.12 (d, $J$ = 8.2 Hz, 1H), 8.67 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 14.3, 37.9, 62.3, 115.5, 120.9, 126.9, 131.4, 132.3, 147.4, 167.2, 196.4. Anal. Calcd for $C_{11}H_{11}N_3O_2S_2$: C, 46.96; H, 3.94; N, 14.93. Found: C, 47.25; H, 3.92; N, 14.78.

**Phenyl Di(benzotriazol-1-yl)methyl Disulfide (14a):** yellow microcrystals (21%); mp 95−96 °C; $^1$H NMR $\delta$ 6.93−7.02 (m, 3H), 7.18 (d, $J$ = 7.0 Hz, 2H), 7.30 (t, $J$ = 7.7 Hz, 2H), 7.80 (d, $J$ = 8.2 Hz, 2H), 7.94 (d, $J$ = 8.4 Hz, 2H), 8.45 (s, 1H); $^{13}$C NMR $\delta$ 76.2, 110.9, 120.3, 125.0, 128.5, 128.8, 128.9, 130.4, 131.4, 133.3, 146.4. Anal. Calcd for $C_{19}H_{14}N_6S_2$: C, 58.44; H, 3.61; N, 21.52. Found: C, 58.25; H, 3.51; N, 21.46.

**Benzyl Di(benzotriazol-1-yl)methyl Disulfide (14b):** white microcrystals (44%); mp 115−116 °C; $^1$H NMR $\delta$ 3.63 (s, 2H), 7.19−7.25 (m, 2H), 7.30−7.41 (m, 5H), 7.49 (t, $J$ = 7.1 Hz, 2H), 7.64 (s, 1H), 7.78 (d, $J$ = 8.4 Hz, 2H), 8.03 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR $\delta$ 43.0, 75.3, 111.2, 120.4, 125.2, 128.3, 128.8, 129.1, 129.8, 131.5, 135.9, 146.5. Anal. Calcd for $C_{20}H_{16}N_6S_2$: C, 59.38; H, 3.99; N, 20.78. Found: C, 59.25; H, 3.97; N, 20.45.

**Isopropyl Di(benzotriazol-1-yl)methyl Disulfide (14d):** white microcrystals (90%); mp 107−108 °C; $^1$H NMR $\delta$ 1.11 (d, $J$ = 6.7 Hz, 6H), 2.43 (m, 1H), 7.39 (t, $J$ = 7.3 Hz, 2H), 7.52 (t, $J$ = 7.3 Hz, 2H), 7.97 (d, $J$ = 8.4 Hz, 2H), 8.06 (d, $J$ = 8.4 Hz, 2H), 8.47 (s, 1H); $^{13}$C NMR $\delta$ 22.2, 41.0, 76.9, 111.0, 120.4, 125.2, 128.9, 131.5, 146.4. Anal. Calcd for $C_{16}H_{16}N_6S_2$: C, 53.91; H, 4.52; N, 23.58. Found: C, 53.73; H, 4.56; N, 23.25.

**General Procedure for the Preparation of Thioamides 15a−f.** The appropriate amine (0.5 mmol) and $Et_3N$ (0.05 g, 0.5 mmol) were added to the respective thiocarbonylbenzotriazole (**6**) (0.5 mmol) dissolved in $CH_2Cl_2$ (30 mL) at room temperature. Stirring was continued overnight, and then

solvent was removed by rotary evaporation. The residue was redissolved in EtOAc (100 mL) and washed with 5% $Na_2CO_3$ solution (3 × 100 mL), 1 M HCl (2 × 100 mL), water, and brine. The collected organic layers were dried with $Na_2SO_4$, and the solvent was removed under vacuum. Recrystallization from EtOAc/hexanes afforded thioamides **15a**−**f** in 91−99% yields.

**4-Methylthiobenzoic Acid Benzylamide (15a):** colorless needles (99%); mp 78−79 °C (lit.[32] mp 87.5−88.5 °C); $^1$H NMR $\delta$ 2.37 (s, 3H), 5.00 (d, $J$ = 5.1 Hz, 2H), 7.17 (d, $J$ = 8.1 Hz, 2H), 7.39−7.41 (m, 5H), 7.67 (d, $J$ = 8.1 Hz, 3H); $^{13}$C NMR $\delta$ 21.3, 51.0, 126.7, 128.2, 128.4, 129.0, 129.1, 136.3, 138.8, 141.8, 198.9. Anal. Calcd for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80. Found: C, 74.43; H, 6.31; N, 6.38.

**1-(4-Methoxythiobenzoyl)piperidine (15b):** yellow needles (93%); mp 94−97 °C (lit.[84] mp 107−108 °C); $^1$H NMR $\delta$ 1.58−1.59 (m, 2H), 1.75−1.82 (m, 4H), 3.56−3.60 (m, 2H), 3.82 (s, 3H), 4.32−4.36 (m, 2H), 6.86 (d, $J$ = 6.6 Hz, 2H), 7.27 (d, $J$ = 6.6 Hz, 2H); $^{13}$C NMR $\delta$ 24.2, 25.5, 26.9, 51.0, 53.3, 55.3, 113.6, 127.5, 128.8, 135.9, 159.8, 199.8.

***N,N*-Diethyl-4-methylthiobenzamide (15c):** yellow powder (87%); mp 89−90 °C (lit.[85] mp 93−94 °C); $^1$H NMR $\delta$ 1.05 (t, $J$ = 7.2 Hz, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H), 2.26 (s, 3H), 3.36 (q, $J$ = 7.2 Hz, 2H), 4.03 (q, $J$ = 7.2 Hz, 2H), 7.05 (s, 4H); $^{13}$C NMR $\delta$ 11.1, 13.7, 21.0, 45.9, 47.6, 124.8, 127.7, 128.7, 137.7, 140.9, 200.4. Anal. Calcd for $C_{13}H_{19}NS$: C, 69.51; H, 8.26; N, 6.76. Found: C, 69.87; H, 8.47; N, 6.67.

***N*-Benzyl Thiobenzamide (15d):** white needles (97%); mp 86 °C (lit.[86] mp 87−88 °C); $^1$H NMR $\delta$ 4.99 (d, $J$ = 4.8 Hz, 1H), 7.35−7.46 (m, 8H), 7.75 (d, $J$ = 7.5 Hz, 3H); $^{13}$C NMR $\delta$ 51.0, 126.7, 128.2, 128.4, 128.5, 129.0, 131.1, 136.1, 141.6, 199.1.

**1-Thiobenzoyl Morpholine (15e):** clear needles (78%); mp 135−136 °C (lit.[5a] mp 137−138 °C); $^1$H NMR $\delta$ 3.62 (d, $J$ = 5.4 Hz, 4H), 3.89 (t, $J$ = 4.8 Hz, 2H), 4.45 (t, $J$ = 4.8 Hz, 2H), 7.26−7.32 (m, 2H), 7.34−7.38 (m, 3H); $^{13}$C NMR $\delta$ 49.5, 52.5, 66.5, 66.7, 125.9, 128.5, 128.9, 142.5, 201.0.

**4-Chlorothiobenzoic Acid Phenethylamide (15f):** yellow needles (66%); mp 103−105 °C; $^1$H NMR $\delta$ 3.07 (s, 2H), 4.08 (d, $J$ = 5.1 Hz, 2H), 7.27−7.32 (m, 7H), 7.55 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR $\delta$ 33.7, 47.5, 126.9, 127.8, 128.6, 128.7, 128.9, 137.2, 138.1, 140.1, 197.7. Anal. Calcd for $C_{15}H_{14}ClNS$: C, 65.32; H, 5.12; N, 5.08. Found: C, 64.99; H, 5.13; N, 4.99.

**General Procedure for the Preparation of Thioamides 15g**−**j.** The appropriate amine (0.5 mmol) and triethylamine (0.05 g, 0.5 mmol) were added to the respective thiocarbonyl-1*H*-6-nitrobenzotriazole **10** dissolved in $CH_2Cl_2$ (30 mL) at room temperature. Stirring was continued overnight, and then solvent was removed by rotary evaporation. The residue was redissolved in EtOAc (100 mL) and washed with 5% $Na_2CO_3$ solution (3 × 100 mL), 1 M HCl (2 × 100 mL), water, and brine. The collected organic layers were dried with $Na_2SO_4$, and then the solvent was removed under vacuum. Recrystallization from EtOAc/hexanes afforded thioamides **15g**−**j** in 80−98% yields.

**1-(4-Bromothiobenzoyl)morpholine (15g):** yellow granules (91%); mp 135−136 °C (lit.[87] mp 134−135 °C). Broadening of the morpholine-ring signals are observed in $^1$H NMR and $^{13}$C NMR spectra due to restricted rotation and ring flipping. $^1$H NMR $\delta$ 3.62−3.65 (m, 4H), 3.88−3.89 (m, 2H), 4.41−4.42 (m, 2H), 7.18 (d, $J$ = 8.1 Hz, 2H), 7.51 (d, $J$ = 7.5 Hz, 2H); $^{13}$C NMR $\delta$ 49.1, 52.1, 65.9, 66.2, 122.5, 127.2, 131.2, 140.8, 198.8.

**1-(4-Methylthiobenzoyl)pyrrolidine (15h):** yellow powder (95%); mp 150−152 °C; $^1$H NMR $\delta$ 1.85−1.93 (m, 2H), 1.96−2.03 (m, 2H), 2.26 (s, 3H), 3.42 (t, $J$ = 6.6 Hz, 2H), 3.99 (t, $J$ = 6.9 Hz, 2H), 7.06 (d, $J$ = 7.8 Hz, 2H), 7.19 (d, $J$ = 7.8 Hz, 2H); $^{13}$C NMR $\delta$ 21.2, 24.6, 26.4, 53.5, 53.8, 125.7, 128.8, 138.8, 141.1, 197.4. Anal. Calcd for $C_{12}H_{15}NS$: C, 70.20; N, 6.82. Found: C, 70.38; N, 6.74.

***N-tert*-Butyl-4-nitrothiobenzamide (15i):** orange powder (98%); mp 143−147 °C (lit.[88] mp 140−141 °C). $^1$H NMR $\delta$ 1.67 (s, 9H), 7.42 (br s, 1H), 7.74 (d, $J$ = 8.7 Hz, 2H), 8.18 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR $\delta$ 27.5, 56.8, 123.6, 127.3, 148.3, 149.6, 196.1.

**Thiophene-2-carbothioic Acid Benzylamide (15j):** yellow needles (80%); mp 87−88 °C (lit.[89] mp 85−87 °C); $^1$H NMR $\delta$ 4.98 (d, $J$ = 5.4 Hz, 2H), 7.02−7.05 (m, 1H), 7.32−7.42 (m, 5H), 7.41−7.42 (m, 1H), 7.48−7.50 (m, 1H), 7.68 (br s, 1H); $^{13}$C NMR $\delta$ 50.4, 124.4, 127.7, 128.1, 128.2, 128.9, 132.2, 136.0, 146.2, 188.3.

**General Procedure for the Preparation of *N*-Monosubstituted Thioamides 15k**−**p.** The thiocarbamoylbenzotriazole **2** (0.495 mmol) was dissolved in 10 mL of dry THF under a nitrogen atmosphere. The desired Grignard or organolithium reagent (1.24 mmol) was added dropwise at room temperature, and the reaction mixture was stirred for 16 h. Water was added, and the organic layer was extracted with EtOAc (20 mL × 3). The organic layers were combined, washed with water, washed with 10% $Na_2CO_3$ solution (35 mL × 5), washed with brine, dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave the pure product or a mixture, which was further purified either by recrystallization from EtOAc/hexanes or column chromatography.

***N*-Cyclohexylthiobenzamide (15k):** purified by column chromatography with hexanes/EtOAc (91:9) as eluent and obtained as yellow microcrystals (87%); mp 84−86 °C (lit.[90] mp 91−92 °C); $^1$H NMR $\delta$ 1.19−1.60 (m, 5H), 1.62−1.85 (m, 3H), 2.17−2.25 (m, 2H), 4.48−4.61 (m, 1H), 7.33−7.49 (m, 4H), 7.68−7.74 (m, 2H); $^{13}$C NMR $\delta$ 24.6, 25.5, 31.6, 54.8, 126.5, 128.5, 130.9, 142.4, 197.7. Anal. Calcd for $C_{13}H_{17}NS$: C, 71.18; H, 7.81; N, 6.39. Found: C, 70.96; H, 7.94; N, 6.48.

**Hexanethioic Acid (Furan-2-ylmethyl)amide (15l):** brown oil (99%); $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.2 Hz, 3H), 1.25−1.40 (m, 4H), 1.72−1.83 (m, 2H), 2.66 (t, $J$ = 7.8 Hz, 2H), 4.82 (d, $J$ = 4.8 Hz, 2H), 6.33−6.37 (m, 2H), 7.39−7.45 (m, 2H); $^{13}$C NMR $\delta$ 13.9, 22.3, 29.0, 31.0, 42.9, 47.0, 108.9, 110.6, 142.6, 149.1, 205.8. Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.52; H, 8.11; N, 6.63. Found: C, 62.86; H, 8.43; N, 6.63.

**Furan-2-carbothioic Acid *tert*-Butylamide (15m):** purified by column chromatography with hexanes/EtOAc (90:10) as eluent and obtained as brown oil (47%) (lit.[91] mp 45−46 °C); $^1$H NMR $\delta$ 1.65 (s, 9H), 6.45 (dd, $J$ = 3.3, 1.8 Hz, 1H), 7.33 (d, $J$ = 3.6 Hz, 1H), 7.39 (m, 1H), 7.82 (br s, 1H); $^{13}$C NMR $\delta$ 28.0, 55.5, 113.1, 116.8, 143.0, 153.2, 181.3. Anal. Calcd for $C_9H_{13}NOS$: C, 59.82; H, 7.15; N, 7.64. Found: C, 59.22; H, 7.29; N, 7.93.

***N*-(1,5-Dimethylhexyl)thiobenzamide (15n):** purified by column chromatography with hexanes/EtOAc (92:8) as eluent and obtained as yellow oil (56%); $^1$H NMR $\delta$ 0.88 (d, $J$ = 6.6 Hz, 6H), 1.20−1.26 (m, 2H), 1.32 (d, $J$ = 6.6 Hz, 3H), 1.35−1.70 (m, 5H), 4.72−4.77 (m, 1H), 7.34−7.47 (m, 4H), 7.67−7.70 (m, 2H); $^{13}$C NMR $\delta$ 19.4, 22.5, 23.7, 27.8, 36.2, 38.7, 52.0, 126.5, 128.4, 130.8, 142.4, 198.0. Anal. Calcd for $C_{15}H_{23}NS$: C, 72.23; H, 9.29; N, 5.62. Found: C, 72.00; H, 9.50; N, 5.90.

**4-Methoxy-*N*-((*R*)-1-phenylethyl)thiobenzamide (15o):** purified by column chromatography with hexanes/EtOAc (90:10) as eluent and obtained as yellow needles (85%); mp 89−91 °C; $^1$H NMR $\delta$ 1.68 (d, $J$ = 6.6 Hz, 3H), 3.81 (s, 3H), 5.90 (quintet, $J$ = 7.2 Hz, 1H), 6.84 (d, $J$ = 8.7 Hz, 2H), 7.25−7.42 (m, 5H), 7.62−7.74 (m, 3H); $^{13}$C NMR $\delta$ 20.2, 55.0, 55.4, 113.5, 126.5, 127.7, 128.4, 128.8, 134.2, 141.5, 162.1, 196.8. Anal.

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Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.78; H, 6.27; N, 5.11.

**Pyridine-2-carbothioic Acid Cyclohexylamide (15p):** purified by column chromatography with hexanes/EtOAc (95:5) as eluent and obtained as yellow oil (35%); $^1$H NMR $\delta$ 1.25−1.90 (m, 9H), 2.13−2.29 (m, 2H), 4.52−4.68 (m, 1H), 7.46 (dd, $J$ = 7.2, 5.4 Hz, 1H), 7.87 (t, $J$ = 7.8 Hz, 1H), 8.53 (d, $J$ = 4.5 Hz, 1H), 8.76 (d, $J$ = 8.1 Hz, 1H), 10.13 (br s, 1H); $^{13}$C NMR $\delta$ 24.6, 25.6, 31.4, 53.8, 124.9, 125.8, 137.1, 146.8, 151.2, 188.8. Anal. Calcd for $C_{12}H_{16}N_2S$: C, 65.41; H, 7.32; N, 12.71. Found: C, 65.79; H, 7.58; N, 12.57.

**General Procedure for the Preparation of Tertiary Thioamides 15q−s.** The appropriate thiocarbamoylbenzotriazole **2** (0.495 mmol) was dissolved in 10 mL of dry THF under a nitrogen atmosphere. The desired Grignard or organolithium reagent (0.743 mmol) was added dropwise at room temperature, and the reaction mixture was stirred for 16 h. Water was added, and the organic layer was extracted with EtOAc (20 mL × 3). The organic layers were combined, washed with water, washed with 10% $Na_2CO_3$ solution (35 mL × 5), washed with brine, dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave crude product, which was further purified by column chromatography.

**But-3-enethioic Acid *N*-Butyl-*N*-methylamide (15q):** purified by column chromatography with hexanes/EtOAc (95:5) as eluent and obtained as brown oil (98%); rotamers (50:50 ratio) observed in$^1$H NMR at 25 °C; signals are double the expected proton signals; $^1$H NMR $\delta$ 0.96 (t, 6H), 1.30−1.43 (m, 4H), 1.60−1.75 (m, 4H), 3.25 (s, 3H), 3.43 (s, 3H), 3.53−3.67 (m, 6H), 3.99 (t, $J$ = 7.8 Hz, 2H), 5.11−5.22 (m, 4H), 5.90−6.03 (m, 2H); $^{13}$C NMR $\delta$ 13.6, 13.7, 19.8, 19.9, 27.6, 30.1, 39.5, 42.4, 47.8, 48.8, 54.2, 55.7, 116.8, 117.0, 132.7, 133.5, 199.9. Anal. Calcd for $C_9H_{17}NS$: C, 63.10; H, 10.00; N, 8.18. Found: C, 62.89; H, 10.30; N, 8.40.

**Piperidin-1-ylthiophen-2-ylmethanethione (15r):** purified by column chromatography with hexanes/EtOAc (90:10) as eluent and obtained as yellow cubes (53%); mp 85−86 °C (lit.[92] mp 89 °C); broadening of the piperidine-ring signals are observed in $^1$H NMR and $^{13}$C NMR spectra due to restricted rotation and ring flipping; $^1$H NMR (DMSO-$d_6$) $\delta$ 1.67 (br s, 6H), 3.83 (br s, 2H), 4.21 (br s, 2H), 7.02−7.06 (m, 1H), 7.14−7.15 (m, 1H), 7.67−7.69 (m, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 23.8, 25.8, 26.8, 51.9, 52.9, 125.6, 126.8, 129.7, 145.0, 188.7. Anal. Calcd for $C_{10}H_{13}NS_2$: C, 56.83; H, 6.20; N, 6.63. Found: C, 56.96; H, 6.27; N, 6.55.

**But-3-enethioic Acid *N*-Methyl-*N*-phenylamide (15s):** purified by column chromatography with hexanes/EtOAc (85:15) as eluent and obtained as brown oil (78%); $^1$H NMR $\delta$ 3.30 (d, $J$ = 6.6 Hz, 2H), 3.74 (s, 3H), 4.86 (dd, $J$ = 17.1, 1.2 Hz, 1H), 5.03 (d, $J$ = 9.9 Hz, 1H), 5.89−6.02 (m, 1H), 7.17−7.20 (m, 2H), 7.38−7.50 (m, 3H); $^{13}$C NMR $\delta$ 45.8, 48.5, 116.9, 125.7, 128.6, 129.8, 134.3, 145.3, 202.7. Anal. Calcd for $C_{11}H_{13}NS$: C, 69.06; H, 6.85; N, 7.32. Found: C, 69.18; H, 7.14; N, 7.53.

**General Procedure for the Preparation of Thionoesters 16a−e.** The appropriate alcohol (0.5 mmol) and $Et_3N$ (0.05 g, 0.5 mmol) were added to the respective thiocarbonylbenzotriazole **6** or thiocarbonyl-6-nitrobenzotriazole **10** dissolved in $CH_2Cl_2$ (30 mL) at room temperature. Stirring was continued overnight, and then solvent was removed by rotary evaporation. The residue was redissolved in EtOAc (100 mL), washed with 5% $Na_2CO_3$ solution (3 × 100 mL), 1 M HCl (2 × 100 mL), water, and brine. The collected organic layers were dried with $Na_2SO_4$, and the solvent was removed under vacuum. Recrystallization from EtOAc/hexanes afforded thionoesters **16a−e**.

***O*-(4-Methoxyphenyl)-4-methoxythiobenzoate (16a):** yellow powder (77%); mp 105−106 °C; $^1$H NMR $\delta$ 3.83 (s, 3H), 3.89 (s, 3H), 6.92 (d, $J$ = 9.0 Hz, 2H), 6.96 (d, $J$ = 9.0 Hz, 2H), 7.03 (d, $J$ = 9.0 Hz, 2H), 8.34 (d, $J$ = 9.0 Hz, 2H); $^{13}$C NMR $\delta$ 55.6, 113.4, 114.4, 122.9, 131.1, 131.7, 148.3, 157.5, 164.1, 210.5. Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.47; H, 5.14.

***O*-Ethyl 4-Chlorothiobenzoate (16b):** yellow powder (60%); mp 34−35 °C (lit.[93] mp 36 °C); $^1$H NMR $\delta$ 1.53 (t, $J$ = 7.2 Hz, 3H), 4.72 (q, $J$ = 7.2 Hz, 2H), 7.35 (d, $J$ = 8.7 Hz, 2H), 8.12 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR $\delta$ 13.7, 68.7, 128.2, 130.0, 136.6, 139.2, 209.8.

***O*-Naphth-1-yl 4-Methoxythiobenzoate (16c):** yellow needles (88%); mp 93−95 °C; $^1$H NMR $\delta$ 3.91 (s, 3H), 6.98 (d, $J$ = 9.0 Hz, 2H), 7.24−7.27 (m, 1H), 7.44−7.56 (m, 3H), 7.80 (t, $J$ = 6.3 Hz, 2H), 7.90 (d, $J$ = 7.8 Hz, 1H), 8.49 (d, $J$ = 9.0 Hz, 2H); $^{13}$C NMR $\delta$ 55.7, 113.7, 119.0, 121.6, 125.4, 126.4, 126.6, 126.8, 128.2, 131.0, 131.8, 134.8, 151.0, 164.3, 209.6. Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79. Found: C, 72.65; H, 4.89.

***O*-Naphth-1-yl 4-Nitrothiobenzoate (16d):** red needles (99%); mp 139−140 °C; $^1$H NMR $\delta$ 7.28 (d, $J$ = 7.5 Hz, 1H), 7.46−7.59 (m, 3H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.86 (d, $J$ = 8.4 Hz, 1H), 7.94 (d, $J$ = 7.8 Hz, 1H), 8.35 (d, $J$ = 9.0 Hz, 2H), 8.61 (d, $J$ = 9.0 Hz, 2H); $^{13}$C NMR $\delta$ 118.6, 121.0, 123.6, 125.4, 126.1, 126.75, 126.84, 127.0, 128.4, 130.2, 134.8, 141.7, 150.4, 150.5, 207.2; Anal. Calcd for $C_{17}H_{11}NO_3S$: C, 66.01; H, 3.58; N, 4.53. Found: C, 66.07; H, 3.47; N, 4.45.

***O*-Naphth-1-yl 2-Thienylcarbothioate (16e):** yellow needles (62%); mp 97−98 °C; $^1$H NMR $\delta$ 7.08 (dd, $J$ = 4.8, 3.9 Hz, 1H), 7.24 (d, $J$ = 7.5 Hz, 1H), 7.39−7.49 (m, 3H), 7.57 (dd, $J$ = 4.8, 1.2 Hz, 1H), 7.75 (d, $J$ = 8.4 Hz, 1H), 7.81−7.85 (m, 2H), 8.07 (dd, $J$ = 3.9, 1.2 Hz, 1H); $^{13}$C NMR $\delta$ 119.3, 121.6, 125.5, 126.8, 126.9, 128.4, 128.8, 132.9, 134.8, 135.3, 144.8, 150.3, 201.7. Anal. Calcd for $C_{15}H_{10}OS_2$: C, 66.64; H, 3.73. Found: C, 66.23; H, 3.71.

**General Procedure for the Preparation of Thionoesters 16f−h.** *O*-Naphth-2-yl benzotriazole-1-carbothioate (**13a**) (0.3 g, 1 mmol) was dissolved in 10 mL of dry THF under nitrogen atmosphere. The appropriate Grignard reagent (1 mmol) was added dropwise at room temperature, and the reaction mixture was stirred for 12 h. A solution of saturated $NH_4Cl$ (25 mL) was added, and the organic layer was extracted with EtOAc (30 mL × 2). The organic layers were combined, washed with water (10 mL × 2), washed with brine, dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave the crude product, which was further purified by column chromatography (hexanes) and recrystallized from $Et_2O$.

***O*-Naphth-2-yl 4-Methylthiobenzoate (16f):** yellow microcrystals (70%); mp 108−109 °C; $^1$H NMR $\delta$ 2.44 (s, 3H), 7.24−7.30 (m, 3H), 7.47−7.57 (m, 3H), 7.82−7.93 (m, 3H), 8.30 (d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR $\delta$ 21.9, 119.3, 121.9, 126.1, 126.8, 128.0, 128.1, 129.2, 129.6, 131.9, 134.0, 135.8, 144.7, 152.6, 211.2. Anal. Calcd for $C_{18}H_{14}OS$: C, 77.66; H, 5.07. Found: C, 77.35; H, 5.42.

***O*-Naphth-2-yl Thiobenzoate (16g):** yellow microcrystals (76%); mp 52−53 °C; $^1$H NMR $\delta$ 7.23 (d, $J$ = 8.8 Hz, 1H), 7.38−7.46 (m, 4H), 7.52−7.58 (m, 2H), 7.76−7.87 (m, 3H), 8.38 (d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR $\delta$ 119.2, 121.7, 126.1, 126.8, 127.9, 128.1, 128.4, 129.4, 129.6, 131.8, 133.5, 134.0, 138.0, 152.6, 211.2. Anal. Calcd for $C_{17}H_{12}OS$: C, 77.24; H, 4.58. Found: C, 77.17; H, 4.56.

***O*-Naphth-2-yl Ethanecarbothioate (16h):** yellow microcrystals (64%); mp 94−95 °C (lit.[94] mp 95−96 °C); $^1$H NMR $\delta$ 2.87 (s, 3H), 7.19 (dd, $J$ = 9.0, 1.8 Hz, 2H), 7.48−7.51 (m, 3H), 7.80−7.86 (m, 3H), 7.89 (d, $J$ = 9.0 Hz, 1H); $^{13}$C NMR $\delta$ 34.7, 119.0, 121.5, 126.2, 126.9, 128.0, 128.1, 129.7, 131.9, 133.9,-152.4, 220.0.

**General Procedure for the Preparation of Tertiary Thiocarbamates 17a,b from Thiocarbamoylbenzotriazoles.** The desired thiocarbamoylbenzotriazole (**2**) (0.36 mmol) was dissolved in $CH_2Cl_2$ (7 mL). In another flask, the desired alcohol (0.36 mmol) and NaH (0.17 g, 4.32 mmol) were stirred

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for 10 min in $CH_2Cl_2$ (7 mL). The sodium salt solution was added to the thiocarbamoylbenzotriazole solution, and the mixture was stirred for 18 h. The solvent was removed under vacuum; water was added and extracted with EtOAc (2 × 25 mL). The organic layer was washed with water and 10% $Na_2CO_3$ solution (2 × 30 mL), dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave the crude product, which was further purified by recrystallization.

**2,3-Dihydroindole-1-carbothioic Acid *O*-Benzhydrol Ester (17a):** colorless prisms (from EtOAc hexanes) (59%); mp 150−154 °C; $^1$H NMR $\delta$ 3.12 (t, $J$ = 8.4 Hz, 2H), 4.40 (t, $J$ = 8.4 Hz, 2H), 6.99−7.42 (m, 12H), 7.76−7.87 (m, 2H); $^{13}$C NMR $\delta$ 26.6, 54.2, 83.9, 117.7, 124.3, 125.5, 127.6, 127.7, 128.0, 128.5, 133.6, 139.6, 141.3, 184.0. Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.49; H, 5.54; N, 4.05. Found: C, 76.62; H, 5.55; N, 4.04.

***N*-Methyl-*N*-phenylthiocarbamic Acid Benzhydrol Ester (17b):** colorless plates (from EtOAc) (60%); mp 102−103 °C; $^1$H NMR $\delta$ 3.62 (s, 3H), 7.09−7.49 (m, 16H); $^{13}$C NMR $\delta$ 44.0, 83.3, 126.1, 126.8, 127.6, 128.3, 129.2, 130.0, 140.3, 143.5, 187.3. Anal. Calcd for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.65; H, 5.91; N, 4.17.

**General Procedure for the Preparation of Thiocarbamates 17c−e from Aryloxythioacylbenzotriazole 12a.** To *O*-naphth-2-yl benzotriazole-1-carbothioate **(12a)** (1 mmol)-in 20 mL of $CH_2Cl_2$ at room temperature was added 1 mmol of amine, and the reaction mixture was refluxed for 2 h. Solvent was evaporated, and the crude product was purified by recrystallization from EtOH.

**Morpholine-1-carbothioic Acid *O*-Naphthalen-2-yl Ester (17c):** colorless microcrystals (70%); mp 145−146 °C (lit.[95] mp 145−146 °C); $^1$H NMR $\delta$ 3.79 (t, $J$ = 5.1 Hz, 2H), 3.84 (t, $J$ = 5.1 Hz, 2H), 4.02 (t, $J$ = 4.7 Hz, 2H), 4.18 (t, $J$ = 4.7 Hz, 2H), 7.24 (d, $J$ = 9.0 Hz, 1H), 7.45−7.49 (m, 3H), 7.79−7.87 (m, 3H); $^{13}$C NMR $\delta$ 47.0, 50.4, 66.4, 66.6, 119.7, 122.5, 126.0, 126.7, 127.9, 128.1, 129.2, 131.8, 133.9, 151.6, 187.6.

**Benzyl-1-carbothioic Acid *O*-Naphthalen-2-yl Ester (17d):** colorless microcrystals (80%), mp 47−48 °C; 70:30 ratio of rotamers was observed in $^1$H NMR at 25 °C; $^1$H NMR signals are reported for the major rotamer; $^1$H NMR $\delta$ 4.91 (d, $J$ = 5.3 Hz, 2H), 7.05 (br, 1H), 7.61−7.29 (m, 9H), 7.94−7.87 (m, 3H); $^{13}$C NMR $\delta$ 50.2, 119.8, 122.4, 126.1, 126.8, 128.0, 128.4, 129.2, 129.3, 131.8, 133.8, 136.5, 150.9, 189.9. Anal. Calcd for $C_{18}H_{15}NOS$: H, 5.15; N, 4.77. Found: H, 5.31; N, 4.46.

**Pyrrolidine-1-carbothioic Acid *O*-Naphthalen-2-yl Ester (17e):** colorless oil (85%); $^1$H NMR $\delta$ 1.79−2.00 (m, 4H), 3.71−3.79 (m, 4H), 7.27 (d, $J$ = 8.8 Hz, 1H), 7.42−7.51 (m, 3H), 7.77−7.85 (m, 3H); $^{13}$C NMR $\delta$ 24.6, 25.8, 48.8, 52.5, 119.5, 122.6, 125.6, 126.4, 127.7, 127.8, 128.9, 131.4, 133.6, 151.3, 184.4. Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44. Found: C, 69.89; H, 6.00; N, 5.37.

**General Procedure for the Preparation of Tertiary Dithiocarbamate 18a.** The desired thiocarbamoylbenzotriazole **2** (0.32 mmol) was dissolved in $CH_2Cl_2$ (7 mL). In another flask, the desired mercapto reagent (0.36 mmol) and NaH (0.02 g, 0.49 mmol) were stirred for 10 min in $CH_2Cl_2$ (7 mL). The sodium salt solution was added to the thiocarbamoylbenzotriazole solution, and the mixture was stirred for 18 h. The solvent was removed under vacuum; water was added and extracted with EtOAc (2 × 25 mL). The organic layer was washed with water and 10% $Na_2CO_3$ solution (2 × 30 mL), dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave a residue, which was further purified by column chromatography.

**2,3-Dihydroindole-1-Carbodithioic Acid 3-Methoxyphenyl Ester (18a):** purified by column chromatography with hexanes/EtOAc (92:8) as eluent and obtained as orange powder (99%); mp 104−105 °C; $^1$H NMR (DMSO-$d_6$ at 70 °C) $\delta$ 3.23 (t, $J$ = 8.1 Hz, 2H), 3.79 (s, 3H), 4.56 (t, $J$ = 7.5 Hz, 2H), 7.04−7.43 (m, 5H), 7.34−7.43 (m, 2H), 8.93 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$ at 70 °C) $\delta$ 26.7, 54.8, 55.1, 115.8, 117.7, 121.7, 125.0, 125.1, 126.0, 128.5, 129.6, 131.0, 135.0, 143.2, 159.3, 190.5. Anal. Calcd for $C_{16}H_{15}NOS_2$: C, 63.75; H, 5.02; N, 4.65. Found: C, 63.38; H, 5.03; N, 4.28.

**General Procedure for the Preparation of Secondary Dithiocarbamates 18b−d.** The secondary thiocarbamoylbenzotriazole **2** (0.36 mmol) was dissolved in $CH_2Cl_2$ (7 mL). The mercapto reagent (0.36 mmol) was added dropwise followed by exactly 1 equiv of $Et_3N$ (0.36 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum, water was added, and the organic layer was extracted with EtOAc (2 × 25 mL). The organic layer was washed with water, dried over $Na_2SO_4$, and filtered. Concentration under reduced pressure gave a crude product that was further purified by column chromatography.

**Furan-2-ylmethyldithiocarbamic Acid 3-Methoxyphenyl Ester (18b):** purified by column chromatography with hexanes/EtOAc (95:5) as eluent and obtained as white prisms (83%); mp 73−75 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 1.05−1.35 (m, 5H), 1.55−1.62 (m, 1H), 1.67−1.76 (m, 2H), 1.84−1.95 (m, 2H), 4.25 (s, 1H), 4.49 (s, 2H), 7.20−7.42 (m, 5H), 9.86 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 24.7, 25.1, 31.0, 38.0, 56.0, 127.1, 128.5, 129.0, 137.5, 194.1. Anal. Calcd for $C_{13}H_{13}NO_2S_2$: C, 55.89; H, 4.69; N, 5.01. Found: C, 55.90; H, 4.71; N, 5.01.

**Cyclohexyldithiocarbamic Acid Benzyl Ester (18c):** purified by column chromatography with hexanes/EtOAc (95:5) as eluent and obtained as colorless crystals (92%); mp 70−71 °C (lit.[96] mp 66−67 °C); $^1$H NMR (DMSO-$d_6$) $\delta$ 1.05−1.35 (m, 5H), 1.55−1.62 (m, 1H), 1.67−1.76 (m, 2H), 1.84−1.95 (m, 2H), 4.25 (s, 1H), 4.49 (s, 2H), 7.20−7.42 (m, 5H), 9.86 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 24.7, 25.1, 31.0, 38.0, 56.0, 127.1, 128.5, 129.0, 137.5, 194.1. Anal. Calcd for $C_{14}H_{19}NS_2$: C, 63.35; H, 7.21; N, 5.28. Found: C, 63.42; H, 7.38; N, 5.22.

**Phenethyldithiocarbamic Acid Phenyl Ester (18d):** purified by column chromatography with hexanes/EtOAc (95:5) as eluent and obtained as colorless crystals (60%); mp 70−71 °C (lit.[97] mp 73−74 °C); $^1$H NMR $\delta$ 2.82 (t, $J$ = 6.6 Hz, 2H), 3.87 (q, $J$ = 6.3 Hz, 2H), 6.55 (s, 1H), 6.94−6.97 (m, 2H), 7.20−7.22 (m, 3H), 7.37−7.39 (m, 4H), 7.42−7.50 (m, 1H); $^{13}$C NMR $\delta$ 33.6, 46.9, 126.6, 128.0, 128.4, 128.8, 130.3, 131.0, 135.4, 137.5, 194.8. Anal. Calcd for $C_{15}H_{15}NS_2$: C, 65.89; H, 5.53. Found: C, 65.00; H, 5.58.

**General Procedure for the Preparation of Thiocarbamates 19a−c**. To the appropriate alcohol (1 mmol) was added NaH (0.18 g, 4.5 mmol) dissolved in $CH_2Cl_2$ (10 mL) at room temperature. In another flask, aryloxythioacylbenzotriazole **12a** (0.30 g, 1 mmol) was dissolved in $CH_2Cl_2$ (10 mL). The prepared salt solution was added to the solution of **12a**, and the mixture was allowed to stir at room temperature for 24 h. The solvent was evaporated to give a crude residue, to which water (25 mL) was added and the organic phase was extracted with EtOAc (2 × 30 mL). The combined organic fractions were washed with water (2 × 10 mL) and 10% $Na_2CO_3$ solution (2 × 30 mL), dried over $MgSO_4$, and filtered. Solvent was removed in vacuo and the product was purified by recrystallization from EtOAc/hexanes to afford thiocarbamates **19a−c** in 70−72% yields.

**Thiocarbonic Acid Ethyl Ester Naphthalen-2-yl Ester (19a):** white microcrystals (70%); mp 33−34 °C (lit.[98] mp 33−34 °C); $^1$H NMR $\delta$ 1.45 (t, $J$ = 7.1 Hz, 3H), 4.60 (q, $J$ = 7.1 Hz, 2H), 7.26 (dd, $J$ = 8.8, 2.2 Hz, 1H), 7.45−7.54 (m, 3H), 7.78−7.87 (m, 3H); $^{13}$C NMR $\delta$ 13.9, 70.6, 119.1, 121.5, 126.2, 126.8, 128.0 (2C), 129.6, 131.9, 133.8, 151.0, 195.4.

**Thiocarbonic Acid Pyridin-3-yl Ester Naphthalen-2-yl Ester (19b):** white microcrystals (72%); mp 91−92 °C; $^1$H NMR $\delta$ 7.34−7.40 (m, 2H), 7.46−7.54 (m, 2H), 7.56−7.60 (m, 1H), 7.66 (d, $J$ = 2.2 Hz, 1H), 7.82−7.92 (m, 3H), 8.56 (dd, $J$

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= 4.7, 1.1 Hz, 2H), 8.60 (d, $J$ = 2.6 Hz, 1H); $^{13}$C NMR $\delta$ 119.0, 120.8, 124.2, 126.5, 127.1, 128.0, 128.1, 129.8, 130.0, 132.0, 133.7, 144.0, 148.0, 150.3, 151.1, 194.5. Anal. Calcd for $C_{16}H_{11}NO_2S$: C, 68.31; H, 3.94; N, 4.98. Found: C, 68.13; H, 3.77; N, 4.94.

**Thiocarbonic Acid 4-Methoxyphenyl Ester Naphthalen-2-yl Ester (19c):** white microcrystals (70%); mp 163−164 °C; $^1$H NMR $\delta$ 3.82 (s, 3H), 6.96 (d, $J$ = 9.0 Hz, 2H), 7.15−7.18 (m, 2H), 7.36 (dd, $J$ = 9.0, 2.1 Hz, 2H), 7.47−7.54 (m, 2H), 7.66 (s, 1H), 7.93−7.84 (m, 3H); $^{13}$C NMR $\delta$ 55.8, 114.8, 119.1, 121.3, 122.8, 126.4, 127.0, 128.1 (2C), 129.9, 132.0, 133.9, 147.4, 151.3, 158.1, 195.7. Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55. Found: C, 69.26; H, 4.42.

**General Procedure for the Preparation of Dithiocarbamates 20a−c**. The appropriate thiol (1 mmol) was dissolved in an aqueous solution (10 mL) of NaOH (0.08 g, 2 mmol) at room temperature. A solution of the aryloxythioacylbenzotriazole **12a** (0.3 g, 1 mmol) in THF (10 mL) was added dropwise to the aqueous mixture, which was then allowed to stir at room temperature for 12 h. The mixture was diluted with water (25 mL) and extracted with EtOAc (2 × 30 mL). The combined organic fractions were washed with water (2 × 10 mL), dried over $MgSO_4$, and filtered. Solvent was removed in vacuo, and the crude product was purified by column chromatography (silica gel, hexanes/EtOAc, 3:1 as eluent) to afford dithiocarbamates **20a−c** in 60−70% yields.

**Dithiocarbonic Acid *O*-Naphthalen-2-yl Ester *S*-(4-Methylphenyl)ester (20a):** yellow microcrystals (70%); mp 88−89 °C; $^1$H NMR $\delta$ 2.22 (s, 3H), 7.09−7.13 (m, 3H), 7.28−7.35 (m, 2H), 7.38−7.40 (m, 3H), 7.61−7.70 (m, 3H); $^{13}$C NMR $\delta$ 21.6, 119.2, 121.3, 126.2, 126.8, 127.0, 127.9, 128.0, 129.6, 130.4, 131.8, 133.7, 135.2, 140.9, 152.2, 214.0. Anal. Calcd for $C_{18}H_{14}OS_2$: C, 69.64; H, 4.55. Found: C, 69.51; H, 4.62.

**Dithiocarbonic Acid *O*-Naphthalen-2-yl Ester *S*-(Dodecyl)ester (20b):** yellow oil (70%); $^1$H NMR $\delta$ 0.98 (t, $J$ = 6.3 Hz, 3H), 1.36 (m, 18H), 1.87 (quintet, $J$ = 7.5 Hz, 2H), 3.33 (t, $J$ = 7.4 Hz, 2H), 7.37 (dd, $J$ = 8.7, 2.1 Hz, 1H), 7.56−7.64 (m, 3H), 7.88−7.97 (m, 3H); $^{13}$C NMR $\delta$ 14.3, 22.9, 28.2, 29.1, 29.3, 29.5, 29.6, 29.8 (2C), 32.1, 37.4, 119.3, 121.6, 126.2, 126.8, 128.0 (2C), 129.6, 131.9, 133.9, 152.3, 215.3. Anal. Calcd for $C_{23}H_{32}OS_2$: C, 71.08; H, 8.30. Found: C, 70.82; H, 8.97.

**Dithiocarbonic Acid *O*-Naphthalen-2-yl Ester *S*-Isopropyl Ester (20c):** yellow oil (60%); $^1$H NMR $\delta$ 1.46 (d, $J$ = 6.9 Hz, 6H), 3.89 (septet, $J$ = 7.0 Hz, 1H), 7.23 (dd, $J$ = 8.9, 2.2 Hz, 1H), 7.45−7.53 (m, 3H), 7.77−7.86 (m, 3H); $^{13}$C NMR $\delta$ 22.3, 42.5, 119.4, 121.6, 126.2, 126.8, 127.9, 128.0, 129.6, 131.9, 133.8, 152.0, 214.5. Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 64.08; H, 5.38. Found: C, 64.20; H, 5.58.

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**Supporting Information Available:** Crystallographic data (CIF and PDF formats) for bis(benzotriazol-1-yl)diarylsulfidemethanes (**4a** and **4b**) (Figure 1) and isopropyl di(benzotriazol-1-yl)methyl disulfide (**14d**) (Figure 2). This information is available free of charge via the Internet at http://pubs.acs.org.

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