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Synthesis of 2-*N*/*S*/*C*-Substituted Benzothiazoles via Intramolecular Cyclative Cleavage of Benzotriazole Ring

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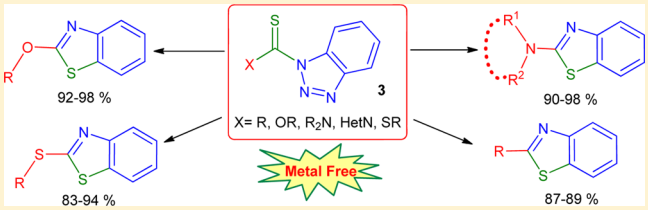
Supporting Information

ABSTRACT: The synthesis of numerous 2-*N*/*S*/*C*-substituted benzothiazoles was achieved from substituted thiocarbonylbenzotriazoles via free-radical intramolecular cyclative cleavage of the benzotriazole ring in the presence of $(TMS)_3SiH$ and AIBN under mild conditions. The developed methodology demonstrates significant compatibility under microwave conditions and is important as it avoids the use of toxic metals for radical cyclization.



INTRODUCTION

Benzothiazoles are sulfur- and nitrogen-containing heterocycles that have emerged in their usage as a core structure for diversified therapeutic applications, including antimicrobial and antifungal,[1,2] cytotoxic,[3] and antidiabetic[4] uses. In recent years, an increasing number of 2-substituted benzothiazoles have been designed and synthesized for biological evaluations. These heterocycles include the immunosuppressive drug frentizole (**I**), the antiparasitic tioxidazole (**II**), a cathepsin-D inhibitior (**III**), a PPARγ receptor activator (**IV**), a heat shock protein-90 inhibitor (**V**), a human CCR1 and CCR3 receptor antagonist (**VI**), an antiproliferative (**VII**), and the calcium channel blocker fostedil (**VIII**) (Figure 1).[5] These moieties are also found in fluorescent pH indicators,[6] an iminocoumarin-based zinc sensor,[7] a bioluminogenic substrate,[8] cleavage agents for soluble oligomers of amyloid β-peptides,[9] and ligands for catalytic reactions.[10,11]

Earlier, several methods for the synthesis of benzothiazole derivatives have been reported, including condensation of 2-aminothiophenol with carbonyl compounds such as aldehydes,[12−14] carboxylic acids,[15−17] acid chlorides,[18] and esters;[19] conversion of 2-haloamides into the corresponding thioamides using P_4S_{10} or Lawesson's reagent, which is generally not feasible for substrates containing ketone, ester, and amide moieties;[20] cyclization of thioformanilides with the aid of transition-metal catalysts[21] under SNAr[22] or radical conditions;[23] and cyclization of an arylthioamide using potassium ferricyanide (Jacobson's method).[24] These methods suffer from disadvantages such as harsh reaction conditions, use of toxic metal catalysts and reagents, air-sensitive and toxic substances, cumbersome workup procedures, generation of acidic and metallic wastes. etc. Recently, Katritzky and co-workers reported a metal-free environmentally benign synthesis of 2-substituted benzothiazoles in water under microwave (*MW*) irradiation.[25] However, this methodology utilizes substrates that are soluble in water only, which poses significant challenges.

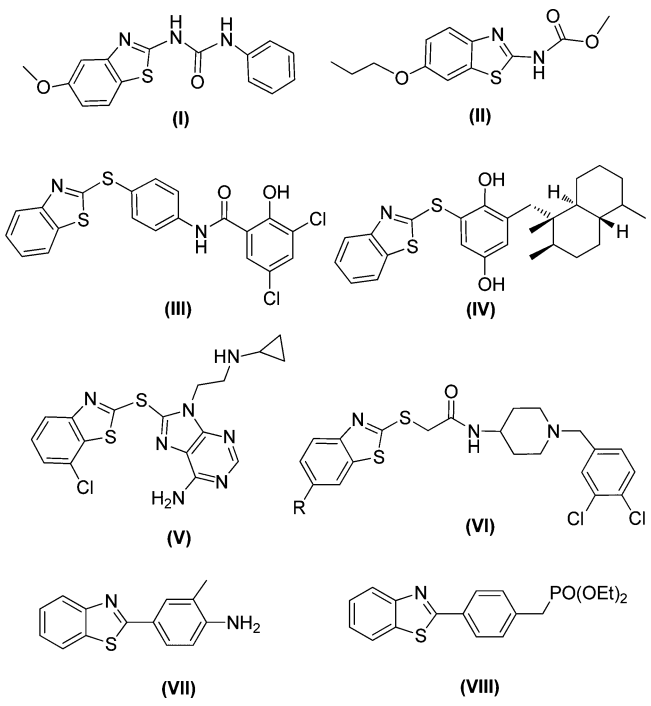


Figure 1. Structures of bioactive 2-*N*/*S*/*C*-substituted benzothiazoles.

In last few decades, the ring-opening reactions of benzotriazole derivatives emerged as an attractive way to generate a wide variety of benzoheterocycles such as indoles, benzoazines, quinazolines, 3,4-dihydroquinazolines, quinazoline-4-thiones, etc.[26,27] We envisioned exploring the feasibility of utilizing the benzotriazole ring-opening approach for the preparation of a library of 2-*N*/*S*/*C*-substituted benzothiazoles. Thus, as part of our ongoing work on the development of benzotriazole

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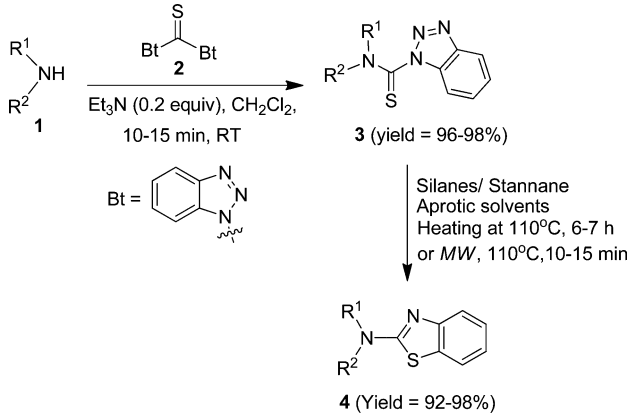
methodologies for the synthesis of novel heterocyclic scaffolds of multifaceted biological profiles,[27,28] we herein report our efforts toward the synthesis of 2-(*N*,*N*-dialkylamino)-benzothiazoles **4**, 2-(aryl)benzothiazoles **9**, and 2-(aryl/alkylthio)-benzothiazoles **13** via disruption of the benzotriazole ring.

RESULTS AND DISCUSSION

In a recent communication, our group reported that 2-*O*-substituted benzothiazoles could be readily prepared from sugar-based benzotriazolemethanethiones via cyclative cleavage catalyzed by tributyltin hydride (*n*-Bu_3SnH).[27] We speculated that a similar transformation would occur to provide 2-(*N*,*N*-dialkylamino)benzothiazoles **4** and 2-(aryl/alkylthio)-benzothiazoles **13** if the nucleophiles were replaced with amines and thiols, respectively. We undertook an investigation to explore this possibility and synthesized *N*,*N*-dialkylthiocarbamoylbenzotriazoles (R^1R^2NCSBt, **3**) by thiocarbamoylation of secondary amines **1** with bis(benzotriazole)methanethione **2** in a very short time span of 10−15 min (Scheme 1).

Scheme 1. Synthesis of 2-(*N*,*N*-Dialkylamino)-benzothiazoles 4



At first sight indeed, *N*,*N*-dialkylthiocarbamoylbenzotriazoles **3** have several important features. First is their preparation from **2**, which in turn can be prepared easily from readily available benzotriazole. Second, these compounds should incorporate a relatively weak N−N bond β to the thiocarbonyl moiety, similar to Barton−McCombie deoxygenation,[29] in which a C−O single bond β to a thiocarbonyl moiety is reduced to C−H. Thus, treatment of 1-(2-fluorophenyl)piperazine (**1a**) with compound **2** in the presence of Et_3N (0.2 equiv) in anhydrous CH_2Cl_2 at room temperature furnished (1*H*-benzo[*d*][1,2,3]-triazol-1-yl)(4-(2-fluorophenyl)piperazin-1-yl)methanethione (**3a**) quantitatively in a very short reaction time. The high stability of the resulting adduct **3a** prevented it from being further attacked by another amine molecule, and indeed, no disubstituted product was observed during the synthesis of benzotriazolemethanethiones **3a**−**o** (Table 1). The structures of compounds **3a**−**o** were elucidated using NMR spectroscopy. Single-crystal X-ray analysis unambiguously evidenced the structure of compound **3a** (see Figure S1 and Table S1 in the Supporting Information).

Treatment of compound **3a** with reagents capable of inducing a free-radical reaction in dry toluene afforded 2-(4-(2-fluorophenyl)piperazin-1-yl)benzo[*d*]thiazole (**4a**) in good to excellent yields. In a reaction optimization study, we briefly investigated the effect of a diverse range of silanes in terms of yield and reaction time, and the results are summarized in Table 2. The cyclizations carried out in the presence of triethylsilane (Et_3SiH) and tris(isopropyl)silane (Pr^i_3SiH) resulted in poor yields (entries 3−6). Silanes with two or more hydrogens [e.g., phenylsilane ($PhSiH_3$) and diphenylsilane (Ph_2SiH_2); entries 1, 2, 7, and 8] furnished poor yields of **4a**. In cyclizations carried out with alkyl-, phenyl-, and trimethylsilyl-substituted silanes and disilanes, the yield of **4a** increased persistently with substitution of phenyl or trimethylsilyl groups (entries 9−24). Among disilanes, 1,1,2,2-tetraphenyldisilane ($Ph_4Si_2H_2$) performed better than 1,1,2,2-tetraanisyldisilane [$(p\text{-MeOPh})_4Si_2H_2$] and 1,2-dimethyl-1,2-diphenydiailane [$(Ph(CH_3)SiH)_2$]. The reaction accomplished in the presence of pentamethyldisilane (Me_5Si_2H) required a longer reaction time.[30] Cyclizations with tris(trimethylsilyl)silane [$(TMS)_3SiH$], $Ph_4Si_2H_2$ and *n*-butylgermanium hydride (*n*-Bu_3GeH) were quantitative (entries 21−26), but a higher yield of **4a** was noticed with *n*-Bu_3SnH (entries 27 and 28).

The high cost of $Ph_4Si_2H_2$ limited its further exploration in our free-radical cyclization, while the use of Bu_3SnH was ruled out on the basis of toxicity and complication in removal of the tin byproducts.[31,32] Moreover, it appeared inappropriate to utilize toxic Bu_3SnH as a radical reducing agent for the synthesis of compounds having value to medicine and agriculture.

Chatgilialogu and co-workers described the use of $(TMS)_3SiH$ as a substitute for Bu_3SnH under moderate conditions.[33] In comparison to *n*-$Bu_3Sn^{\bullet}$ and *n*-$Bu_3Ge^{\bullet}$ radicals, trialkylsilyl radicals are more reactive in additions to multiple bonds[34] and abstraction of halogen.[35] However, they are rather poor H-atom donors toward alkyl radicals and therefore tend to support chain reactions only at elevated temperatures. Also, the greater strength of the Si−H bond in $(TMS)_3SiH$ (78 kcal mol^{-1}) compared with the Sn−H bond in *n*-Bu_3SnH (74 kcal mol^{-1}) causes cyclization with silanes to be relatively slow, requiring considerably high temperatures or an added initiator.[36] In the optimization study, a gradual increase in the yield of **4a** was observed upon substitution of silanes with phenyl or trimethylsilyl groups, indicating that the Si−H bond weakening effect was operative here. The factors that moderate Si−H bond dissociation enthalpies are not yet completely understood, but the available thermochemical data on Si−H bond dissociation energies[37] and the rate constants for the reactions of some radicals with a variety of silicon hydrides strongly suggest that the bond-weakening effects operative upon trimethylsilyl or phenyl substitution are due to radical stabilization by π-conjugation of the phenyl group(s) and d-orbital participation of the trimethylsilyl group(s).

Furthermore, significant reductions in the reaction time were observed when the reactions were executed in the presence of 5 mol % AIBN as a radical initiator (Table 2). The reagent $(TMS)_3SiH$ proved to be the best among an array of silanes tested, and addition of AIBN was found to be crucial for the aforementioned conversion (Table 2, entry 21). In the reaction optimization study executed by varying the ratio of $(TMS)_3SiH$ under refluxing conditions, an increase in the total yield of **4a** was observed as the amount of reagent was increased quantitatively. The optimum yield of **4a** was realized using 2.2 equiv of $(TMS)_3SiH$ in the presence of AIBN (5 mol %) under refluxing conditions. Additionally, we explored the reactions under microwave (*MW*) conditions, where the reaction times were significantly reduced (ranging from 5 to 30 min; Table 2).

Next, under the optimized reaction conditions, the developed benzotriazolemethanethiones **3a**−**o** were cyclized to their

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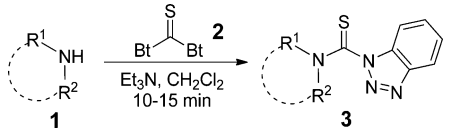
Table 1. Synthesis of Thiocarbamoylbenzotriazoles (R^1R^2NCSBt)



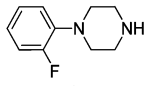
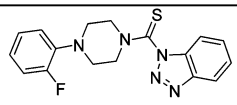
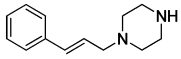
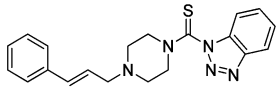
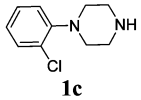
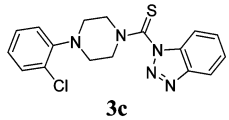
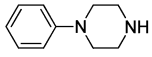
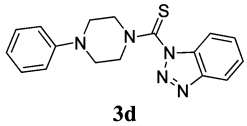
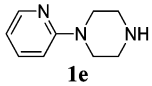
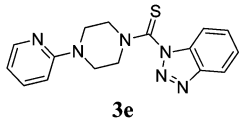
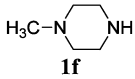
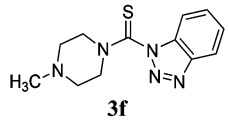
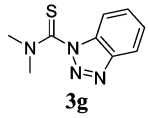
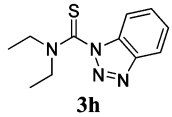
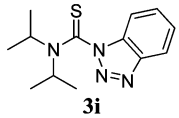
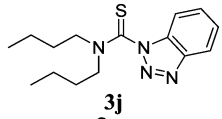
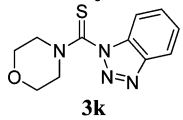
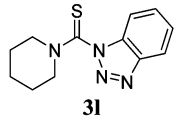
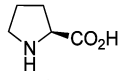
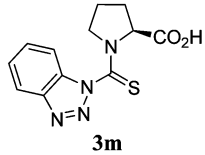
entry[a]	substrate	product[b]	time[c]	yield (%)[d]
1	 **1a**	 **3a**	10	95
2	 **1b**	 **3b**	6	96
3	 **1c**	 **3c**	6	94
4	 **1d**	 **3d**	7	95
5	 **1e**	 **3e**	6	96
6	 **1f**	 **3f**	5	95
7	$(Me)_2NH$ **1g**	 **3g**	12	79
8	$(Et)_2NH$ **1h**	 **3h**	10	87
9	$(^{i}Pr)_2NH$ **1i**	 **3i**	15	84
10	$(^{n}Bu)_2NH$ **1j**	 **3j**	15	88
11	 **1k**	 **3k**	6	98
12	 **1l**	 **3l**	5	97
13	 **1m**	 **3m**	15	92

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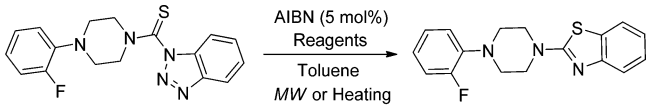
Table 2. Optimization[a] of Radical Conversion of 3a to 4a Using 2.2 molar equiv of Reagents



3a **4a**

entry	reagent[b]	mol % initiator[c]	T (°C)[d]	yield % by heating (t)[e]	yield % by microwave (t)[f]
1	$PhSiH_3$	5	110	7 (12)	12 (30)
2	$PhSiH_3$	0	150	trace (12)	trace (30)
3	Et_3SiH	5	110	9 (12)	16 (30)
4	Et_3SiH	0	150	trace (12)	trace (30)
5	Pr^i_3SiH	5	110	12 (12)	17 (30)
6	Pr^i_3SiH	0	150	trace (12)	trace (30)
7	Ph_2SiH_2	5	110	15 (12)	14 (30)
8	Ph_2SiH_2	0	150	trace (12)	trace (30)
9	$(CH_3)_5Si_2H$	5	110	23 (12)	20 (30)
10	$(CH_3)_5Si_2H$	0	150	8 (12)	11 (30)
11	$MePh_2SiH$	5	110	73 (12)	79 (30)
12	$MePh_2SiH$	0	150	65 (12)	43 (30)
13	Bu^tPh_2SiH	5	110	71 (12)	75 (30)
14	Bu^tPh_2SiH	0	150	55 (12)	47 (30)
15	$(Ph(CH_3)SiH)_2$	5	110	89 (4)	92 (20)
16	$(Ph(CH_3)SiH)_2$	0	150	83 (12)	64 (30)
17	$(p\text{-MeOPh})_4Si_2H_2$	5	110	90 (3)	93 (15)
18	$(p\text{-MeOPh})_4Si_2H_2$	0	150	87 (12)	74 (30)
19	Ph_3SiH	5	110	92 (3)	94 (15)
20	Ph_3SiH	0	150	93 (10)	77 (30)
21	**$(TMS)_3SiH$**	**5**	**110**	**94 (3)**	**95 (14)**
22	**$(TMS)_3SiH$**	**0**	**150**	**94 (10)**	**78 (30)**
23	**$(Ph)_4Si_2H_2$**	**5**	**110**	**92 (3)**	**97 (12)**
24	**$(Ph)_4Si_2H_2$**	**0**	**150**	**95 (10)**	**81 (30)**
25	$^nBu_3GeH$	5	80	93 (3)	95 (10)
26	$^nBu_3GeH$	0	80	91 (7)	92 (30)
27	**Bu_3SnH**	**5**	**80**	**96 (2)**	**98 (9)**
28	**Bu_3SnH**	**0**	**80**	**92 (7)**	**92 (30)**

[a]All reactions in the microwave were accomplished at 110 °C. [b]Reagents are arranged in order of increasing product yield. [c]AIBN was used as the radical initiator. [d]Reaction temperatures were in the range 80−150 °C. [e]Reaction times in hours. [f]Reaction times in minutes.

respective benzothiazoles **4a−o** in excellent yields ranging from 85 to 94% (Table 3). Among these, most of the substituted benzothiazoles were obtained in the crystalline state, while a few were formed as viscous liquids.

The structures of compounds **4a−o** were assigned by comparison with NMR spectra of their respective benzotriazolemethanethiones **3a−o**. For example, relative to the benzotriazolyl C−H protons resonating at δ 8.08 (t, J = 7.8 Hz, 2H), 7.59 (dd, J = 7.8, 7.5 Hz, 1H), and 7.43 (dd, J = 7.8, 7.5 Hz, 1H) in the ^{1}H NMR spectrum of compound **3k**, the four benzothiazolyl C−H protons of **4k** were observed downfield. In the ^{13}C NMR spectrum of **3k**, the signal corresponding to the thiocarbonyl carbon resonated at δ 174.5, while this signal was shifted upfield to δ 168.8 for compound **4k**. In addition, the mass spectrum of **4k** exhibited the $[M + H]^+$ peak at m/z 221, which is 28 units less than the $[M + H]^+$ molecular ion peak of **3k** observed at m/z 249. The structures of compounds **4b**, **4c**, and **4e** were also confirmed by single-crystal X-ray analysis (see Figures S2−S4 and Tables S2−S4 in the Supporting Information).

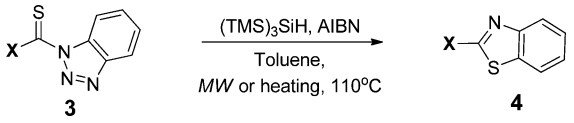
The synthesis of 2-*N*-substituted benzothiazoles **4** through this optimized procedure has several features that make it attractive from the perspective of scale-up and environmental considerations. It is relatively insensitive to the rate of addition of reagents, uses a silicon-based reagent rather than the more toxic tin-based reagent, and reaches completion rapidly after a brief induction period. The workup is simple, and the reaction is conveniently carried out by microwave irradiation. However, in the presence of functionalities bearing acidic hydrogen (i.e., **3m** and **3n** having −COOH and −OH groups, respectively), the cyclizations were unsuccessful, and no products could be observed under the optimized conditions. Likewise, mono-*N*-alkylthiocarbamoylbenzotriazole **3o** having an NH moiety furnished isothiocyanate derivative **5** when treated with $(TMS)_3SiH$ and AIBN in refluxing toluene.

Furthermore, the efficacy of the developed methodology was demonstrated by treatment of compound **2** with $(TMS)_3SiH$ (2 equiv) and AIBN (5 mol %) in dry toluene under refluxing conditions to afford 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzo[*d*]thiazole (**6**) in 97% yield in 3 h (Scheme 2). The structure of compound **6** was assigned by NMR spectroscopy, and single-crystal X-ray analysis unambiguously evidenced the structure (see Figure S5 and Table S5 in the Supporting Information).

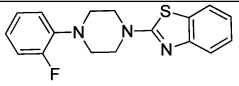
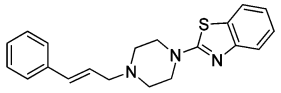
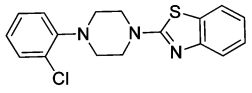
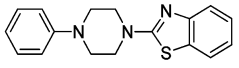
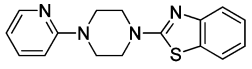
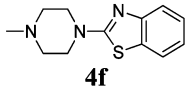
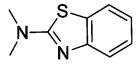
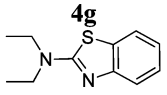
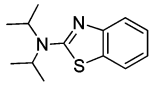
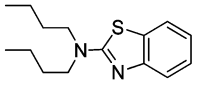
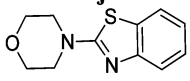
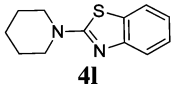
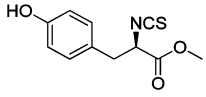
The methodology was also successfully used for the preparation of a library of *N*-alkyl-*N*-(ferrocenylmethyl)benzothiazol-2-amines **4p−t** from the respective *N*-(ferrocenylmethyl)-*N*-alkylthiocarbamoylbenzotriazoles **3p−t** (Table 4), which were readily prepared by the reaction of ferrocene-based secondary amines with compound **2**. The structures of compounds **3p−t**

dx.doi.org/10.1021/jo4024107 | J. Org. Chem. 2014, 79, 251−266

Table 3. Synthesis of Diverse 2-(*N*,*N*′-Dialkyl)benzothiazoles 4



3 4

entry[a]	3	product	yield % by heating (t)[b]	yield % by microwave (t)[c]
1	3a	 4a	94(3)	95(14)
2	3b	 4b	89(3.5)	91(14)
3	3c	 4c	90(3.5)	94(14)
4	3d	 4d	93(3)	96(13)
5	3e	 4e	91(3)	95(14)
6	3f	 4f	88(3)	93(14)
7	3g	 4g	86(3)	92(14)
8	3h	 4h	89(3)	93(14)
9	3i	 4i	86(3)	90(14)
10	3j	 4j	85(3)	91(14)
11	3k	 4k	92(3)	93(12)
12	3l	 4l	94(3)	96(12)
13	3m	Not observed	---	---
14	3n	Not observed	---	---
15	3o	 5	---	---

[a]Molar ratios: **3** (1.0 equiv), $(TMS)_3SiH$ (2.2 equiv), and AIBN (5 mol %). [b]Reaction times in hours. [c]Reaction times in minutes.

and **4p**−**t** were deduced from extensive spectral studies (IR, NMR, and MS). Single-crystal X-ray analyses unambiguously evidenced the structures of compounds **3p** and **4p** (see Figures S6 and S7 and Tables S6 and S7 in the Supporting Information).

Earlier, Katritzky et al. reported the synthesis of compounds **3k**, **3l**, and **3h** for the development of unsymmetrical di- and trisubstituted thioureas, thioamides, thiocarbamates, and dithiocarbamates.[38,39] Toward this end, we investigated the

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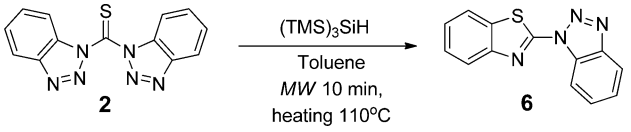
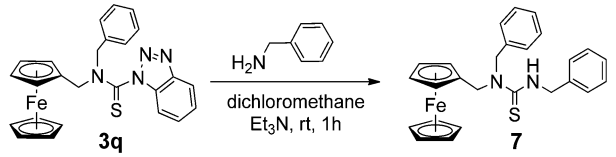
Scheme 2. Synthesis of 2-(1*H*-Benzo[*d*]triazol-1-yl)benzo[*d*]thiazole (6) from 2



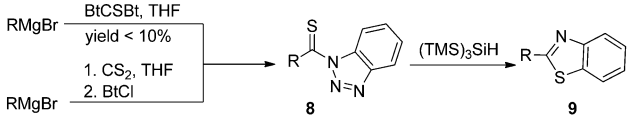
Scheme 3. Synthesis of 1,3-Dibenzyl-1-(ferrocenylmethyl)thiourea (7)



scope of compounds **3p–t** in the synthesis of novel ferrocene-containing unsymmetrical trisubstituted thiourea derivatives. Treatment of compound **3q** with benzylamine in the presence of Et_3N in anhydrous CH_2Cl_2 at rt afforded 1,3-dibenzyl-1-(ferrocenylmethyl)thiourea (7) in 87% yield (Scheme 3). The structure of compound **7** was elucidated by NMR spectroscopy and also confirmed by single-crystal X-ray analysis (see Figure S8 and Table S8 in the Supporting Information).

The methodology was further successfully extended to the synthesis of 2-aryl/alkyl-substituted benzothiazoles **9** from their respective aryl/alkylthiocarbonylbenzotriazoles **8**, which were readily prepared by the previously reported method.[39] The

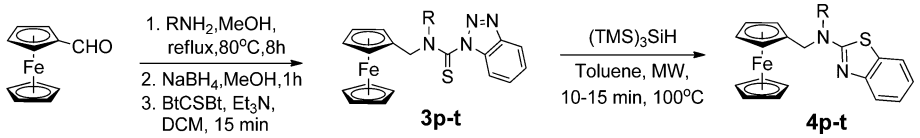
Scheme 4. Synthesis of 2-(Aryl)benzothiazoles from Thioacylbenzotriazoles

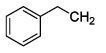
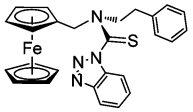
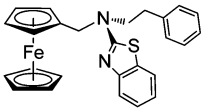
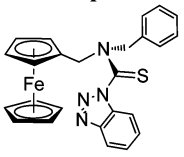
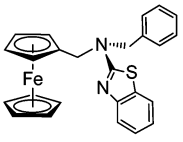
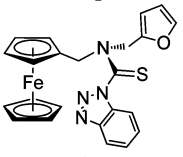
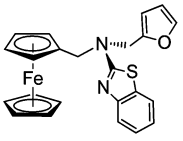
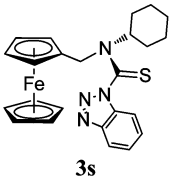
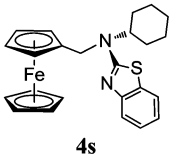
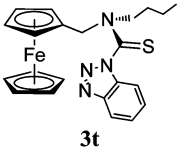
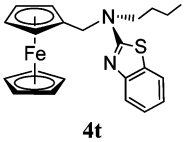


8	R	yield %
8a	*p*-(MeO)-phenyl	47
8b	*p*-tolyl	53

9	R	yield % by heating (t)	yield % by microwave (t)
9a	*p*-(MeO)-phenyl	83 (3 h)	89 (14 min)
9b	*p*-tolyl	77 (3 h)	87 (15 min)

Table 4. Synthesis of *N*-(Ferrocenylmethyl)-*N*-alkylthiocarbamoylbenzotriazoles (3p–t) and the Corresponding *N*-Alkyl-*N*-(ferrocenylmethyl)benzothiazol-2-amines (4p–t)



entry[a]	R	RR'NCSBt[b] (3)	product[c] (4)	yield[d] % by heating (t)[e]	yield[d] % by microwave (t)[f]
1		 3p	 4p	92(3)	94(13)
2		 3q	 4q	89(3)	95(14)
3		 3r	 4r	84(3)	90(15)
4		 3s	 4s	93(3)	94(13)
5		 3t	 4t	91(3)	93(13)

[a]Molar ratios: bis(benzotriazole)methanethione (1.01 equiv), $(TMS)_3SiH$ (2.2 equiv), and AIBN (5 mol %). [b]Ferrocene-based benzotriazolemethanethiones. [c]Ferrocene-containing benzothiazoles. [d]Yields of final step only, reported after purification by column chromatography. [e]Reaction times in hours. [f]Reaction times in minutes.

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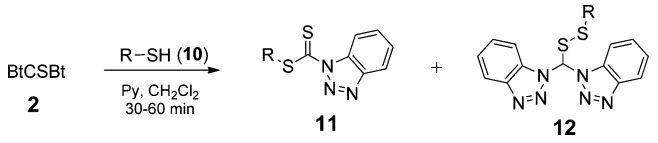
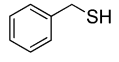
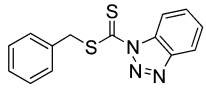
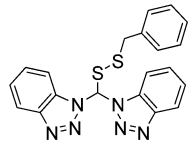
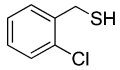
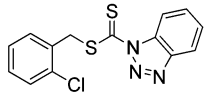
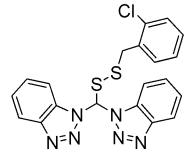
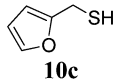
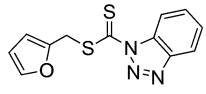
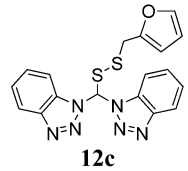
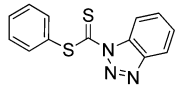
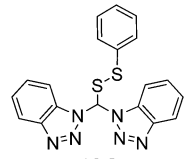
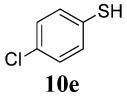
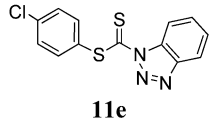
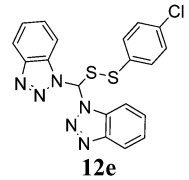
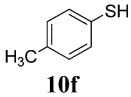
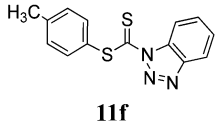
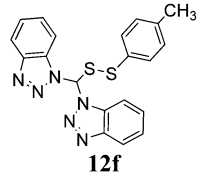
Table 5. Synthesis[a] of (Alkyl/arylthio)thioacylbenzotriazoles 11



entry[b]	10[c]	11[d]	yield (%)[e]	12[f]	yield (%)[g]
1	 **10a**	 **11a**	56	 **12a**	38
2	 **10b**	 **11b**	53	 **12b**	35
3	 **10c**	 **11c**	49	 **12c**	41
4	 **10d**	 **11d**	68	 **12d**	19
5	 **10e**	 **11e**	62	 **12e**	17
6	 **10f**	 **11f**	64	 **12f**	20

[a]All of the reactions were complete within 1 h. [b]Molar ratios: alkyl/arylthiol (1.0 equiv), pyridine (0.3 equiv), bis(benzotriazole)methanethione (1.01 equiv). [c]Alkyl/arylthiols. [d]*S*-Alkyl/aryl(benzotriazolyl)dithiocarbamates. [e]Yields of compounds **11** after purification. [f]Disulfide byproducts. [g]Yields of compounds **12** after purification.

reactions of compounds **8a** and **8b** with a mixture of $(TMS)_3SiH$ (2.2 equiv) and AIBN (5 mol %) in dry toluene under refluxing or *MW* conditions were accomplished smoothly (Scheme 4). However, because of the low-yielding initial thioacylation step, this does not appear to be a good way to access 2-(aryl/alkylbenzothiazoles **9** under the optimized conditions. The structures of compounds **9a** and **9b** were assigned from their NMR spectra.

Furthermore, in order to access the scope of the developed methodology in the synthesis of a library of (alkyl/arylthio)-benzothiazoles **13**, a diverse range of thiols **10a−f** were reacted with compound **2** in the presence of pyridine at rt to afford *S*-alkyl/aryl(benzotriazolyl) dithiocarbamates **11a−f** in 49−68% yield along with the observed disulfide byproducts **12a−f** (Table 5).

We briefly investigated the reaction and found that the yields of compounds **11** could be improved by slow addition of the thiol in the presence of a suitable weak organic base. Further cyclization of **11a−f** under the optimized conditions furnished the corresponding 2-(alkyl/arylthio)benzothiazoles **13a−f** in excellent yields ranging from 83 to 95% in 5−6 h (Table 6).

Mechanistic Considerations. The thiocarbonyl derivatives of primary and secondary alcohols can be reduced easily by *n*-Bu_3SnH using AIBN as a radical initiator.[40] In such reactions, the 2-cyanoprop-2-yl radical generated from AIBN initiates the process by rapidly reacting with tin hydride to produce a tin radical, which attacks the thione function of thiocarbonyl and propagates the reaction. A similar mechanism of radical cyclization can also be argued with $(TMS)_3SiH$, which upon

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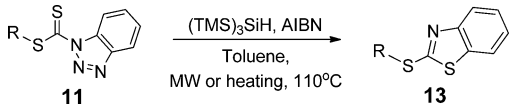
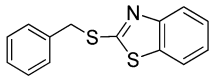
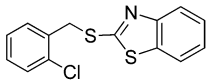
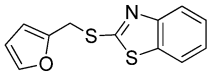
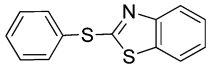
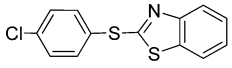
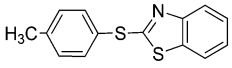
Table 6. Synthesis of 2-(Alkyl/arylthio)benzothiazoles 13



11 13

entry[a]	11[b]	13[c]	yield % by heating (t)[d]	yield % by microwave (t)[e]
1	**11a**	 **13a**	95(4)	96(20)
2	**11b**	 **13b**	92(4)	94(25)
3	**11c**	 **13c**	83(4)	86(30)
4	**11d**	 **13d**	90(3)	95(15)
5	**11e**	 **13e**	87(3)	92(20)
6	**11f**	 **13f**	91(3)	93(20)

[a]Molar ratios: **11a–f** (1 equiv), $(TMS)_3SiH$ (2.2 equiv), and AIBN (5 mol %). [b]*S*-Alkyl/aryl(benzotriazolyl)dithiocarbamates **11a–f**. [c]2-(Alkyl/arylthio)benzothiazoles **13a–f**. [d]Reaction times in hours; [e]Reaction times in minutes.

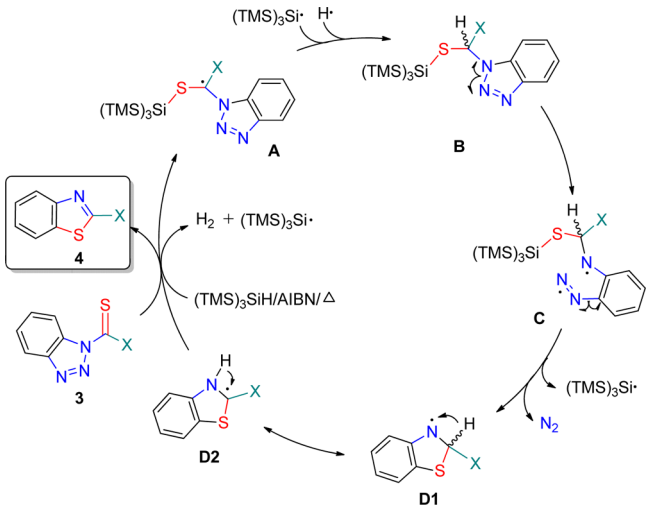


Figure 2. Proposed mechanism of radical cyclization.

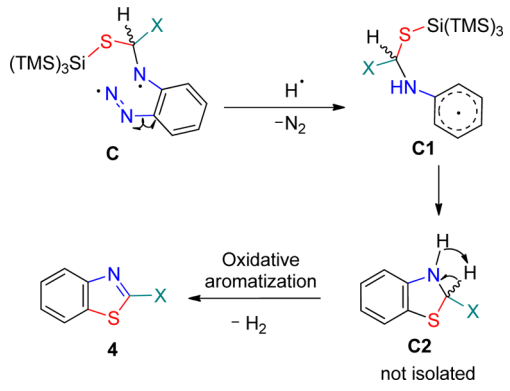


Figure 3. Another mechanistic pathway.

reaction with 2-cyanoprop-2-yl radical generates a silyl radical that attacks the thiocarbonyl derivative and propagates a chain reaction. The generated intermediate **A** is further reduced by H· radical followed by subsequent attack of a silyl radical to produce radical intermediate **B**, which decomposes to give resonance-stabilized nitrogen-centered biradical **C** via N–N bond cleavage. The stabilization of **C** through delocalization of the electron density over the aryl ring results in the elimination of a nitrogen molecule followed by a consequent intramolecular attack of sulfur, producing resonance-stabilized nitrogen-centered radical **D**, which furnishes benzothiazole **4** via a thermodynamically favored and thermally induced oxidation process leading to aromatization at the cost of two σ bonds to form a π bond (Figure 2).

Several mechanisms could be operative. For example, radical intermediate **C** could eliminate molecular nitrogen and simultaneously get reduced to a resonance-stabilized radical intermediate **C1** that could transform into dihydro product **C2** (Figure 3). However, this species could not be isolated.

All of the reactions were carried out typically under an inert atmosphere, and the benzothiazoles **4** were isolated as sole aromatic cyclized products with no dihydro derivatives observed

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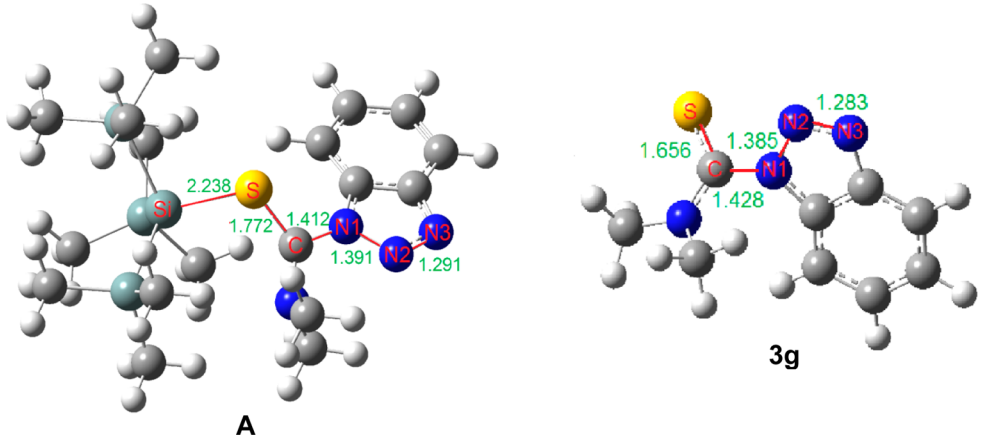

Figure 4. Optimized geometries of radical intermediate **A** [$(TMS)_3Si{-}SC(Bt)(N(Me)_2$] and molecule **3g** at the B3LYP/6-31G(d,p) level of theory in the gas phase. The bond between $(TMS)_3Si\cdot$ radical and the thiocarbonyl sulfur of **3g** along with elongated bond distances (in Å) are shown.

even when oxygen was rigorously excluded. We exploited here the addition of silyl radical onto the thiocarbonyl moiety and investigated the reductive cyclization reported with *n*-Bu_3SnH[41] and subsequent oxidation of the dihydro product. The reductive cyclization using $(TMS)_3SiH$ possibly includes "oxidation" by either autooxidation or a process in which $(TMS)_3SiH$ acts as a base and abstracts the acidic proton from the cyclized dihydro intermediate.[42] The oxidation process may be photochemical or thermal, as both are thermodynamically favorable and lead to aromatization at the cost of two σ bonds to form a π bond in the final product. However, the problem is explaining how the hydrogen is lost. Moreover, it was difficult to observe N_2 and H_2 in the stream of nitrogen and under refluxing conditions. Additionally, the possibility of auto or air oxidation of the dihydro product was ruled out because the reaction was carried out under inert conditions. However, this could be effectively explained by considering $(TMS)_3SiH$ as a base, which abstracts hydrogen from the radical intermediate **C2** or **D2** and affords the benzothiazole **4** as product. Hence, the silane is not only catalytic and reductive but also acts as a base.

The mechanism of the reaction was also supported by density functional theory (DFT), where the geometries of intermediate **A** and compound *N*,*N*-dimethyl-1*H*-benzo[*d*][1,2,3]-triazole-1-carbothioamide (**3g**) were optimized at the B3LYP/6-31G(d,p) level in the gas phase using the Gaussian 03 package.[43] Gaussview 3.09 was used to visualize the optimized molecular geometries, bond lengths, and bond angles. The calculations at this level provided evidence for a strong interaction between silicon and the sulfur of the thiocarbonyl group in intermediate **A** (Figure 4). In addition, close observation of the IR frequencies of the optimized molecule **3g** and intermediate **A** calculated by DFT predict an enhancement in the intensity of the N1−N2 stretching frequency, while the interaction of **3g** with $(TMS)_3Si\cdot$ radical suggests the cleavage of benzotriazole ring (for details, see Figures S9−S12 and Tables S9−S12 in the Supporting Information).

CONCLUSION

We have developed a concise and efficacious benzotriazole-mediated, two-step, novel and toxic-metal-free approach that provides easy access to a diverse range of 2-*N*/*S*/*C*-substituted benzothiazoles under mild conditions. The developed methodology also demonstrates significant compatibility under microwave conditions and is important as it avoids the use of toxic *n*-Bu_3SnH for radical cyclization. The synthesis of 2-(*N*,*N*-dialkylamino)benzothiazoles, 2-(aryl/alkyl)benzothiazoles, and 2-(aryl/alkylthio)benzothiazoles via benzotriazole ring cleavage using $(TMS)_3SiH$ as radical reducing agent had not been realized previously, and thus, this approach should be of further interest to synthetic and medicinal chemists. The short reaction period, simple workup, high yield, and mild conditions of this methodology express significant tolerance toward a number of functional groups such benzyl ethers, acetals, thioethers, esters, aryl halides (Ar−F and Ar−Cl), and alkenes. In addition to the generality with respect to the substrate scope, the facile access to the starting materials is also highly appealing. The developed methodology performs well in both small and gram-scale syntheses of 2-*N*/*S*/*C*-substituted benzothiazoles and thus may have industrial significance.

EXPERIMENTAL SECTION

General Remarks. All of the reactions were executed in anhydrous solvents under an argon atmosphere in glassware oven-dried for 1 h at 110 °C. All of the reagents and solvents were of pure analytical grade. Thin-layer chromatography (TLC) was performed on TLC silica gel 60 F_{254} precoated on aluminum plates and revealed with a UV lamp and/or with iodine vapors. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shifts (δ) are given in parts per million downfield from internal TMS; coupling constant (J) values are given in hertz. Mass spectra were recorded using electrospray ionization mass spectrometry (ESI-MS). Infrared spectra were recorded as Nujol mulls in KBr plates. Elemental analysis was performed using a C, H, N analyzer, and the results were found to be within ±0.4% of the calculated values. Reactions under microwave irradiation were carried out in a single-mode microwave reactor. Single-crystal X-ray data were collected on a CCD diffractometer.

Procedure for the Synthesis of *N*,*N*-Dialkylthiocarbamoyl-benzotriazoles (R^1R^2NCSBt, 3a−o). To a stirring solution of bis-(benzotriazole)methanethione (**2**) (0.567 g, 2.02 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise a solution of amine **1a−o** (2.0 mmol) in dry CH_2Cl_2 (5 mL) in the presence of Et_3N under an inert atmosphere at room temperature. After completion of the reaction (10−15 min as monitored by TLC), the reaction mixture was concentrated in vacuo. After extraction with CH_2Cl_2 and washing with 10% Na_2CO_3, water, and saturated brine solution followed by drying over anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure. Further purification with flash column chromatography using gradient mixtures of ethyl acetate and *n*-hexane afforded pure benzotriazolemethanethione **3a−o**.

*(1H-Benzo[d][1,2,3]triazol-1-yl)(4-(2-fluorophenyl)piperazin-1-yl)-methanethione (**3a**).* Yellow crystals, 0.635 g, yield 93%, mp 106−107 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^1H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.48 (dd, J = 7.2, 6.6 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 6.98−6.81 (m, 4H), 4.41

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(m, 2H), 3.76 (m, 2H), 3.26 (m, 2H), 3.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.6, 155.52 (d, J = 244.1 Hz), 146.0, 138.59 (d, J = 7.8 Hz), 133.3, 128.9, 125.0, 124.51 (d, J = 3.7 Hz), 123.38 (d, J = 7.3 Hz), 119.7, 119.2 (d, J = 2.4 Hz), 116.19 (d, J = 20.4 Hz), 113.7, 52.1, 51.1, 50.5, 49.7. IR (KBr) ν_{max}: 3059, 2923, 2846, 1612, 1585, 1505, 1447, 1269, 1158, 1041, 1010, 737, 424 cm^{-1}. MS: m/z 342 [M + H]$^+$. Anal. Calcd for $C_{17}H_{16}FN_5S$: C, 59.65; H, 4.95; N, 20.51. Found: C, 59.81; H, 4.72; N, 20.12.

(E)-(1H-Benzo[d][1,2,3]triazol-1-yl)(4-cinnamylpiperazin-1-yl)-methanethione (**3b**). White crystals, 0.662 g, yield 91%, mp 92−94 °C. R_f = 0.7 (50% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (t, J = 8.4 Hz, 2H), 7.56 (dd, J = 7.8, 7.2 Hz, 1H), 7.43−7.18 (m, 6H), 6.53 (d, J = 15.9 Hz, 1H), 6.22 (ddd, J = 15.9, 6.7, 6.6 Hz, IH), 4.38 (m, 2H), 3.707 (m, 2H), 3.20 (d, J = 6.6 Hz, 2H), 2.77 (m, 2H), 2.62 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.2, 145.9, 136.3, 133.5, 133.2, 128.8, 128.4 (2C), 127.5, 126.1 (2C), 125.2, 124.9, 119.6, 113.6, 60.1, 53.3, 52.9, 51.9, 51.0. IR (KBr) ν_{max}: 3029, 2925, 2810, 2766, 1608, 1509, 1441, 1022, 1047, 780, 748, 695 cm^{-1}. MS: m/z 364 [M + H]$^+$. Anal. Calcd for $C_{20}H_{21}N_5S$: C, 66.09; H, 5.82; N, 19.27. Found: C, 66.48; H, 6.06; N, 19.08.

(1H-Benzo[d][1,2,3]triazol-1-yl)(4-(2-chlorophenyl)piperazin-1-yl)methanethione (**3c**). Yellow crystals, 0.644 g, yield 90%, mp 144−145 °C. R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J = 9.3 Hz, 1H), 8.07 (d, J = 9.6 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.44 (dd, J = 7.8, 7.5 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.24 (dd, J = 7.5, 7.2 Hz, 1H), 7.03 (dd, J = 11.7, 7.8 Hz, 2H), 4.54 (m, 2H), 3.88 (m, 2H), 3.34 (m, 2H), 3.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.7, 147.6, 146.0, 133.3, 130.6, 128.9, 128.7, 127.6, 125.0, 124.5, 120.5, 119.7, 113.7, 52.4, 51.2 (2C), 50.3. IR (KBr) ν_{max}: 1597, 1536, 1067, 1007, 959, 891, 728, 692, 650 cm^{-1}. MS: m/z 358 [M + H]$^+$. Anal. Calcd for $C_{17}H_{16}ClN_5S$: C, 57.13; H, 4.52; N, 19.61. Found: C, 57.32; H, 4.18; N, 19.77.

(1H-Benzo[d][1,2,3]triazol-1-yl)(4-phenylpiperazin-1-yl)-methanethione (**3d**). Yellow crystals, 0.588 g, yield 91%, mp 107−108 °C. R_f = 0.5 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 7.8, 7.2 Hz, 1H), 7.42 (dd, J = 7.8, 7.2 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 8.1 Hz, 1H), 6.91 (d, J = 7.2 Hz, 3H), 4.47 (m, 2H), 3.86 (m, 2H), 3.46 (m, 2H), 3.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 149.9, 146.0, 133.3, 129.1 (2C), 128.9, 125.1, 120.5, 119.7, 116.3 (2C), 113.8, 51.8, 50.8, 49.3, 48.4. IR (KBr) ν_{max}: 3060, 2909, 2828, 1602, 1581, 1505, 1448, 1280, 1230, 1167, 1049, 1016, 741, 517, 429 cm^{-1}. MS: m/z 324 [M + H]$^+$. Anal. Calcd for $C_{17}H_{17}N_5S$: C, 63.13; H, 5.30; N, 21.65. Found: C, 63.0; H, 5.57; N, 21.29.

(1H-Benzo[d][1,2,3]triazol-1-yl)(4-(pyridin-2-yl)piperazin-1-yl)-methanethione (**3e**). Yellow crystals, 0.596 g, yield 92%, mp 112−113 °C. R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, J = 3.9 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.60 (dd, J = 8.1, 7.2 Hz, 1H), 7.52 (ddd, J = 7.2, 6.9, 1.5 Hz, 1H), 7.45 (dd, J = 7.8, 7.5 Hz, 1H), 6.69 (dd, J = 6.6, 6.9 Hz, 1H), 6.65 (d, J = 8.7 Hz, 1H), 4.46 (m, 2H), 3.89 (m, 4H), 3.74 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.7, 158.3, 147.9, 146.1, 137.7, 133.7, 129.0, 125.1, 119.8, 114.1, 113.9, 106.9, 51.6, 50.8, 45.2, 44.0. IR (KBr) ν_{max}: 3026, 2924, 2810, 1612, 1579, 1443, 1044, 1020, 746, 685, 497 cm^{-1}. MS: m/z 325 [M + H]$^+$. Anal. Calcd for $C_{16}H_{16}N_6S$: C, 59.24; H, 4.98; N, 25.92. Found: C, 58.91; H, 5.20; N, 26.19.

(1H-Benzo[d][1,2,3]triazol-1-yl)(4-methylpiperazin-1-yl)-methanethione (**3f**). Yellow crystals, 0.496 g, yield 95%, mp 103−104 °C. R_f = 0.6 (80% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, J = 6.0 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.8, 7.5 Hz, 1H), 4.39 (m, 2H), 3.72 (m, 2H), 2.71 (m, 2H), 2.56 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 146.1, 133.4, 128.9, 125.1, 119.7, 113.7, 54.9, 53.0, 52.0, 51.0, 45.4. MS: m/z 262 [M + H]$^+$. Anal. Calcd for $C_{12}H_{15}N_5S$: C, 55.15; H, 5.79; N, 26.80. Found: C, 54.78; H, 5.94; N, 26.50.

N,N-Dimethyl-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3g**). Yellow crystals, 0.326 g, yield 79%, mp 111−112 °C. R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.1 Hz, 2H), 7.58 (dd, J = 7.5, 7.2 Hz, IH), 7.43 (dd, J = 7.5, 7.2 Hz, 1H), 3.65 (s, 3H), 3.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.5, 145.8, 133.1, 128.8, 125.0, 119.7, 113.8, 44.1, 43.7. IR (KBr) ν_{max}: 3082, 2927, 1605, 1590, 1532, 1449, 1390, 1258, 1148, 1025, 784, 749 cm^{-1}. MS: m/z 207 [M + H]$^+$. Anal. Calcd for $C_9H_{10}N_4S$: C, 52.41; H, 4.89; N, 27.18. Found: C, 52.02; H, 4.56; N, 26.97.

N,N-Diethyl-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3h**). Yellow oil, 0.408 g, yield 87%. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (m, 2H), 7.56 (dd, J = 8.1, 7.2 Hz, 1H), 7.41 (dd, J = 7.8, 7.5 Hz, 1H), 4.11 (d, J = 6.6 Hz, 2H), 3.49 (d, J = 6.9 Hz, 2H), 1.47 (t, J = 6.9 Hz, 3H), 1.31 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 145.6, 133.1, 128.6, 124.8, 119.5, 113.3, 48.1, 48.0, 13.8, 10.7. IR (KBr) ν_{max}: 3060, 2984, 2937, 2875, 1611, 1592, 1519, 1448, 1279, 1031, 746 cm^{-1}. MS: m/z 335 [M + H]$^+$. Anal. Calcd for $C_{11}H_{14}N_4S$: C, 56.39; H, 6.03; N, 23.93. Found: C, 56.72; H, 6.42; N, 23.70.

N,N-Diisopropyl-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3i**). Yellow oil, 0.441 g, yield 84%. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11−8.08 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 7.5, 7.8 Hz, 1H), 3.89−3.80 (m, 2H), 1.34 (s, 3H), 1.32 (s, 3H), 1.24 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 146.8, 130.4, 126.8, 120.8, 113.7, 47.4, 47.2, 22.4 (2C), 20.6 (2C). IR (KBr) ν_{max}: 3038, 2944, 2927, 2845, 1610, 1589, 1532, 1444, 1282, 1021, 738, 585, 487 cm^{-1}. MS: m/z 263 [M + H]$^+$. Anal. Calcd for $C_{13}H_{18}N_4S$: C, 59.51; H, 6.92; N, 21.37. Found: C, 59.25; H, 7.09; N, 21.13.

N,N-Dibutyl-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3j**). Yellow oil, 0.511 g, yield 88%. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 7.8, 7.2 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 4.05 (d, J = 7.8, 7.5 Hz, 2H), 3.46 (dd, J = 7.8, 7.2 Hz, 2H), 1.91 (m, 2H), 1.61 (m, 2H), 1.47 (m, 2H), 1.11 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H), 0.72 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.6, 145.4, 132.9, 128.4, 124.5, 119.3, 113.0, 53.4, 53.3, 30.1, 27.4, 19.8, 19.4, 13.5, 13.1. IR (KBr) ν_{max}: 3077, 2929, 2861, 1611, 1590, 1530, 1438, 1226, 1042, 1021, 757, 595 cm^{-1}. MS: m/z 291 [M + H]$^+$. Anal. Calcd for $C_{15}H_{22}N_4S$: C, 62.04; H, 7.64; N, 19.30. Found: C, 62.21; H, 7.88; N, 19.63.

(1H-Benzo[d][1,2,3]triazol-1-yl)(morpholino)methanethione (**3k**). Yellow crystals, 0.528 g, yield 93%, mp 112−113 °C. R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (t, J = 7.8 Hz, 2H), 7.59 (dd, J = 7.8, 7.5 Hz, 1H), 7.43 (dd, J = 7.8, 7.5 Hz, 1H), 4.36 (m, 2H), 3.95−3.75 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 145.9, 133.2, 128.9, 125.0, 119.7, 113.7, 66.5, 66.0, 52.6, 51.3. IR (KBr) ν_{max}: 2927, 1860, 1610, 1589, 1497, 1447, 1237, 1115, 1051, 1024, 738, 524 cm^{-1}. MS: m/z 249 [M + H]$^+$. Anal. Calcd for $C_{11}H_{12}N_4OS$: C, 53.21; H, 4.88; N, 22.58. Found: C, 52.90; H, 5.07; N, 22.21.

(1H-Benzo[d][1,2,3]triazol-1-yl)(piperidin-1-yl)methanethione (**3l**). Yellow crystals, 0.453 g, yield 92%, mp 105−106 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, J = 8.7 Hz, 2H), 7.57 (dd, J = 7.8, 7.2 Hz, 1H), 7.41 (dd, J = 7.8, 7.2 Hz, 1H), 4.30 (m, 2H), 3.56 (m, 2H), 1.90 (m, 2H), 1.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 145.8, 133.1, 128.6, 124.8, 119.6, 113.4, 53.2, 52.5, 26.6, 25.2, 23.8. IR (KBr) ν_{max}: 3086, 2942, 1859, 1612, 1589, 1513, 1446, 1257, 1049, 1021, 727, 534 cm^{-1}. MS: m/z 247 [M + H]$^+$. Anal. Calcd for $C_{12}H_{14}N_4S$: C, 58.51; H, 5.73; N, 22.76. Found: C, 58.24; H, 5.54; N, 22.55.

(S)-1-(1H-Benzo[d][1,2,3]triazole-1-carbonothioyl)pyrrolidine-2-carboxylic Acid (**3m**). White crystals, 0.508 g, yield 92%, mp 152−154 °C. R_f = 0.5 (10% methanol/chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.08 (bs, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.60 (dd, J = 7.2, 7.5 Hz, 1H), 7.45 (dd, J = 7.8, 6.9 Hz, 1H), 5.13−5.10 (m, 1H), 4.21−4.18 (m, 1H), 4.02−4.00 (m, 1H), 2.52−2.42 (m, 1H), 2.31−2.06 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 173.7, 145.7, 133.1, 129.1, 125.3, 119.8, 114.5, 65.9, 54.6, 29.3, 25.0. MS: m/z 277 [M + H]$^+$. Anal. Calcd for $C_{12}H_{12}N_4O_2S$: C, 52.16; H, 4.38; N, 20.28. Found: C, 51.89; H, 4.20; N, 20.05.

(1H-Benzo[d][1,2,3]triazol-1-yl)(4-hydroxypiperidin-1-yl)-methanethione (**3n**). White crystals, 0.372 g, yield 71%, mp 110−111 °C. R_f = 0.7 (40% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz,

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$CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 7.5, 7.8 Hz, 1H), 4.64 (s, 1H), 4.23−4.21 (m, 3H), 3.78 (m, 2H), 2.24 (m, 2H), 2.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 146.2, 133.4, 129.2, 125.3, 120.0, 113.9, 52.3, 48.5, 47.8, 32.7, 31.6. MS: m/z 263 $[M + H]^+$. Anal. Calcd for $C_{12}H_{14}N_4OS$: C, 54.94; H, 5.38; N, 21.36. Found: C, 55.25.; H, 5.12; N, 21.58.

*Methyl 2-(1H-Benzo[d][1,2,3]triazole-1-carbothioamido)-3-(4-hydroxyphenyl)propanoate (**3o**).* Viscous liquid, 0.484 g, yield 68%. R_f = 0.6 (40% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.37 (d, J = 6.9 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.65 (dd, J = 8.1, 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 5.46−5.39 (m, 1H), 5.10 (bs, 1H), 3.78 (s, 3H), 3.40 (dd, J = 13.2, 5.7 Hz, 1H), 3.28 (dd, J = 13.2, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 171.0, 155.9, 147.2, 132.7, 130.7 (3C), 126.8, 126.3, 120.5, 116.3 (3C), 58.9, 53.1, 36.6. IR (KBr) ν_{max}: 3521, 3328, 2978, 2941, 1738, 1545, 1438, 1228, 1009, 747, 546 cm^{-1}. MS: m/z 357 $[M + H]^+$. Anal. Calcd for $C_{17}H_{16}N_4O_3S$: C, 57.29; H, 4.52; N, 15.72. Found: C, 57.13; H, 4.75; N, 15.51.

Procedure for the Synthesis of 2-(*N*,*N*-Dialkylamino)-benzothiazoles (4a−l). To a stirring solution of benzotriazolemethanethione **3a−l** (1 mmol) in dry toluene were added tris(trimethylsilyl)silane (2.2 equiv) and AIBN (5 mol %) under an inert atmosphere. The reaction mixture was stirred under heating at 110 °C or exposed to single-mode microwave reactor with a new sealed pressure regulation 10 mL pressurized vial with "snap-on" cap and Teflon-coated magnetic stir bar. The standard temperature control system consisted of a noncontact calibrated infrared sensor that monitored and controlled the temperature conditions of the reaction vessel located in the instrument cavity. For each reaction, the reaction temperature was kept at 110 °C. After completion of the reaction (as monitored by TLC), the reaction mixture was concentrated in vacuo, extracted with CH_2Cl_2, and washed with 10% LiOH, water, and brine solutions. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification using flash column chromatography afforded benzothiazole **4a−l**.

*2-(4-(2-Fluorophenyl)piperazin-1-yl)benzo[d]thiazole (**4a**).* White crystals, 0.297 g, yield 95%, mp 121−122 °C. R_f = 0.5 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.32−7.24 (m, 1H), 7.10−6.93 (m, 5H), 3.82−3.79 (m, 4H), 3.23−3.19 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 155.75 (d, J = 244.2 Hz), 152.6, 139.57 (d, J = 8.6 Hz), 130.7, 126.0, 124.5, 123.18 (d, J = 8.1 Hz), 121.5, 120.7, 119.1 (2C), 116.24 (d, J = 20.4 Hz), 50.0 (2C), 48.5 (2C). IR (KBr) ν_{max}: 3059, 2955, 2929, 1588, 1538, 1453, 1280, 744, 697, 567 cm^{-1}. MS: m/z 314 $[M + H]^+$. Anal. Calcd for $C_{17}H_{16}FN_3S$: C, 65.15; H, 5.15; N, 13.41. Found: C, 65.52; H, 5.45; N, 13.62.

*(E)-2-(4-Cinnamylpiperazin-1-yl)benzo[d]thiazole (**4b**).* White crystals, 0.305 g, yield 91%, mp 122−123 °C. R_f = 0.7 (50% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.40−7.21 (m, 6H), 7.07 (dd, J = 7.8, 7.5 Hz, 1H), 6.55 (d, J = 15.6 Hz, 1H), 6.32−6.24 (m, 1H), 3.67 (dd, J = 5.1, 4.8 Hz, 4H), 3.22 (d, J = 6.9 Hz, 2H), 2.64 (dd, J = 5.1, 4.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8, 152.5, 136.5, 133.6, 130.6, 128.5, 127.6, 126.3, 126.0, 125.7, 125.5, 121.4, 120.6, 118.9, 114.9, 60.9, 52.2 (2C), 48.3 (2C). IR (KBr) ν_{max}: 3051, 3025, 2923, 1594, 1543, 1446, 1291, 752, 693 cm^{-1}. MS: m/z 336 $[M + H]^+$. Anal. Calcd for $C_{20}H_{21}N_3S$: C, 71.61; H, 6.31; N, 12.53. Found: C, 71.33; H, 6.64; N, 12.16.

*2-(4-(2-Chlorophenyl)piperazin-1-yl)benzo[d]thiazole (**4c**).* White crystals, 0.310 g, yield 94%, mp 132−133 °C. R_f = 0.5 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.30 (dd, J = 8.1, 7.2 Hz, 1H), 7.24 (dd, J = 11.4, 8.1 Hz, 1H), 7.11−6.98 (m, 3H), 3.82 (m, 4H), 3.18 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8, 152.6, 148.6, 130.7 (2C), 128.9, 127.6, 126.0, 124.2, 121.4, 120.7, 120.5, 119.1, 50.7 (2C), 48.6 (2C). IR (KBr) ν_{max}: 3072, 2946, 2923, 1592, 1540, 1445, 1265, 758, 677 cm^{-1}. MS: m/z 330 $[M + H]^+$. Anal. Calcd for $C_{17}H_{16}ClN_3S$: C, 61.99; H, 4.90; N, 12.77. Found: C, 62.3; H, 4.73; N, 12.64.

*2-(4-Phenylpiperazin-1-yl)benzo[d]thiazole (**4d**).* White crystals, 0.283 g, yield 96%, mp 181−182 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J = 8.9 Hz, 1H), 7.57 (d, J = 9.0 Hz, 1H), 7.31−7.24 (m, 3H), 7.08 (t, J = 7.2 Hz, 1H), 6.98 (m, 3H), 3.80−3.77 (m, 4H), 3.32−3.29 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 152.6, 150.9, 130.7, 129.2 (2C), 126.0, 121.5, 120.7 (2C), 119.2, 116.8 (2C), 49.1 (2C), 48.3 (2C). IR (KBr) ν_{max}: 2926, 2841, 1594, 1539, 1444, 1230, 755, 687, 518 cm^{-1}. MS: m/z 296 $[M + H]^+$. Anal. Calcd for $C_{17}H_{17}N_3S$: C, 69.12; H, 5.80; N, 14.22. Found: 69.33; H, 5.61; N, 14.06.

*2-(4-(Pyridin-2-yl)piperazin-1-yl)benzo[d]thiazole (**4e**).* White crystals, 0.281 g, yield 95%, mp 192−193 °C. R_f = 0.5 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, J = 4.2 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.51 (dd, J = 7.2, 8.4 Hz, 1H), 7.30 (dd, J = 7.5, 7.8 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.70−6.65 (m, 2H), 3.74−3.73 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 159.0, 152.5, 148.0, 137.6, 130.6, 126.0, 121.5, 120.7, 119.1, 113.9, 107.3, 48.0 (2C), 44.7 (2C). IR (KBr) ν_{max}: 3028, 2929, 2821, 1564, 1540, 1449, 1298, 1230, 738, 623, 516, 496 cm^{-1}. MS: m/z 297 $[M + H]^+$. Anal. Calcd for $C_{16}H_{16}N_4S$: C, 64.84; H, 5.45; N, 18.92. Found: C, 65.07; H, 5.16; N, 19.25.

*2-(4-Methylpiperazin-1-yl)benzo[d]thiazole (**4f**).* White crystals, 0.217 g, yield 93%, mp 94−95 °C. R_f = 0.7 (80% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (t, J = 9.0 Hz, 2H), 7.28 (dd, J = 7.2, 7.5 Hz, 1H), 7.06 (dd, J = 7.5, 7.2 Hz, 1H), 3.66−3.63 (m, 4H), 2.54−2.51 (m, 4H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 152.6, 130.6, 125.9, 121.3, 120.5, 119.0, 54.1 (2C), 48.1 (2C), 46.0. MS: m/z 234 $[M + H]^+$. Anal. Calcd for $C_{12}H_{15}N_3S$: C, 61.77; H, 6.48; N, 18.01. Found: C, 61.49; H, 6.79; N, 17.64.

*N,N-Dimethylbenzo[d]thiazol-2-amine (**4g**).* White crystals, 0.164 g, yield 92%, mp 84−85 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (t, J = 6.3 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.03 (dd, J = 7.2, 7.5 Hz, 1H), 3.17 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 153.1, 131.0, 125.8, 120.8, 120.5, 118.7, 40.1, 40.0. IR (KBr) ν_{max}: 3054, 2919, 1598, 1567, 1548, 1452, 1418, 1294, 751, 724 cm^{-1}. MS: m/z 179 $[M + H]^+$. Anal. Calcd for $C_9H_{10}N_2S$: C, 60.65; H, 5.66; N, 15.73. Found: C, 60.40; H, 5.95; N, 15.57.

*N,N-Diethylbenzo[d]thiazol-2-amine (**4h**).* Colorless oil, 0.192 g, yield 93%. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (t, J = 8.4 Hz, 2H), 7.25 (dd, J = 7.8, 7.2 Hz, 1H), 7.01 (dd, J = 7.5, 7.2 Hz, 1H), 3.59−3.52 (m, 4H), 1.29−1.25 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 153.2, 130.5, 125.6, 120.5, 120.4, 118.4, 45.5 (2C), 12.7 (2C). IR (KBr) ν_{max}: 3067, 2966, 2871, 1597, 1536, 1256, 1067, 1007, 728, 692, 550 cm^{-1}. MS: m/z 207 $[M + H]^+$. Anal. Calcd for $C_{11}H_{14}N_2S$: C, 64.05; H, 6.85; N, 13.59. Found: C, 63.86; H, 7.06; N, 13.78.

*N,N-Diisopropylbenzo[d]thiazol-2-amine (**4i**).* Colorless oil, 0.220 g, yield 94%. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 7.2, 7.5 Hz, 1H), 7.22 (dd, J = 8.4, 7.2 Hz, 1H), 3.71−3.62 (m, 2H), 1.29 (s, 3H), 1.24 (s, 6H), 1.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 152.4, 130.5, 125.5, 121.3, 120.5, 119.0, 46.0 (2C), 20.7 (2C), 19.6 (2C). IR (KBr) ν_{max}: 3089, 2944, 2856, 1562, 1540, 1258, 729, 692, 545 cm^{-1}. MS: m/z 235 $[M + H]^+$. Anal. Calcd for $C_{13}H_{18}N_2S$: C, 66.63; H, 7.75; N, 11.96. Found: C, 66.93; H, 7.91; N, 11.78.

*N,N-Dibutylbenzo[d]thiazol-2-amine (**4j**).* Colorless oil, 0.239 g, yield 91%. R_f = 0.8 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (dd, J = 9.3, 8.4 Hz, 2H), 7.24 (ddd, J = 8.1, 7.3, 1.2 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 3.48 (t, J = 7.5 Hz, 4H), 1.66 (quintet, J = 7.2 Hz, 4H), 1.37 (sextuplet, J = 7.5 Hz, 4H), 0.95 (t, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 153.2, 130.6, 125.6, 120.5, 120.3, 118.4, 50.9 (2C), 29.5 (2C), 20.0 (2C), 13.8 (2C). IR (KBr) ν_{max}: 3077, 2931, 2841, 1550, 1533, 1262, 1223, 736, 545 cm^{-1}. MS: m/z 263 $[M + H]^+$. Anal. Calcd for $C_{15}H_{22}N_2S$: C, 68.66; H, 8.46; N, 10.68. Found: C, 68.82; H, 8.16; N, 10.55.

*4-(Benzo[d]thiazol-2-yl)morpholine (**4k**).* White crystals, 0.204 g, yield 93%, mp 123−124 °C. R_f = 0.5 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (dd, J = 8.7, 8.4 Hz, 2H), 7.29

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(dd, J = 7.8, 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 3.80 (t, J = 4.8 Hz, 4H), 3.59 (t, J = 4.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8, 152.3, 130.4, 125.9, 121.5, 120.6, 119.2, 66.1 (2C), 48.3 (2C). IR (KBr) ν_{max}: 2960, 2855, 1594, 1563, 1540, 1442, 1290, 1229, 1113, 1032, 1017, 757 cm^{-1}. MS: m/z 221 [M + H]$^+$. Anal. Calcd for $C_{11}H_{12}N_2OS$: C, 59.98; H, 5.50; N, 12.73. Found: C, 60.11; H, 5.84; N, 12.40.

*2-(Piperidin-1-yl)benzo[d]thiazole (**4l**).* White crystals, 0.209 g, yield 96%, mp 82−83 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 3.56 (m, 4H), 1.65 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 152.8, 130.5, 125.7, 120.8, 120.4, 118.6, 49.4 (2C), 25.1 (2C), 24.1. IR (KBr) ν_{max}: 3028, 2953, 2845, 1544, 1531, 1436, 1224, 1028, 737 cm^{-1}. MS: m/z 219 [M + H]$^+$. Anal. Calcd for $C_{12}H_{14}N_2S$: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.33; H, 6.16; N, 13.13.

*Methyl 3-(4-Hydroxyphenyl)-2-isothiocyanatopropanoate (**5**).* Viscous liquid, 0.175 g, yield 74%. R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.10 (bs, 1H), 4.45 (dt, J = 4.5, 3.0 Hz, 1H), 3.77 (s, 3H), 3.19−3.02 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 155.1, 137.5, 130.5 (2C), 126.6, 115.6 (2C), 60.9, 53.1, 38.8. IR (KBr) ν_{max}: 3540, 2947, 1742, 1537, 1431, 1228, 1178, 1019, 767, 546 cm^{-1}. MS: m/z 238 [M + H]$^+$. Anal. Calcd for $C_{11}H_{11}NO_3S$: C, 55.68; H, 4.67; N, 5.90. Found: C, 56.05; H, 4.97; N, 6.13.

*2-(1H-Benzo[d][1,2,3]triazol-1-yl)benzo[d]thiazole (**6**).* White crystals, 0.244 g, yield 97%, mp 175−176 °C. R_f = 0.6 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.69 (dd, J = 7.8, 7.5 Hz, 1H), 7.50 (dd, J = 7.8, 7.5 Hz, 2H), 7.40 (dd, J = 7.8, 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 150.6, 146.6, 132.2, 131.0, 129.8, 126.6, 125.8, 125.4, 122.9, 121.4, 120.1, 113.7. IR (KBr) ν_{max}: 3098, 2967, 1610, 1595, 1578, 1528, 1487, 1440, 1288, 1157, 989, 891, 735, 665 cm^{-1}. MS: m/z 253 [M + H]$^+$. Anal. Calcd for $C_{13}H_8N_4S$: C, 61.89; H, 3.20; N, 22.22. Found: C, 62.10; H, 3.07; N, 21.91.

Procedure for the Synthesis of *N*-(Ferrocenylmethyl)-*N*-alkylthiocarbamoylbenzotriazoles (3p−t). The ferrocene-containing secondary amines **1p−t** were prepared from readily available ferrocenecarboxaldehyde and various primary amines using a standard protocol reported in literature.[44] Thus, to a stirring solution of bis(benzotriazole)methanethione (**2**) (0.567 g, 2.02 mmol) in dry CH_2Cl_2 (5 mL) was added a solution of amine **1p−t** (2.0 mmol) in dry CH_2Cl_2 (5 mL) in the presence of Et_3N under an inert atmosphere at room temperature. After completion of the reaction (10−15 min, as monitored by TLC), the reaction mixture was concentrated in vacuo. After extraction with CH_2Cl_2 and washing twice with 10% Na_2CO_3, water, and saturated brine solution, the organic layer was dried over anhydrous Na_2SO_4. Further concentration under reduced pressure followed by purification with flash column chromatography using gradient mixtures of ethyl acetate and *n*-hexane afforded pure benzotriazolemethanethione **3p−t**.

*N-(Ferrocenylmethyl)-N-phenethyl-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3p**).* Red crystals, 0.826 g, yield 86%, mp 144−145 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.60 (dd, J = 7.2, 7.5 Hz, 1H), 7.48 (dd, J = 8.1, 7.8 Hz, 1H), 7.33−7.28 (m, 3H), 7.14−7.09 (m, 2H), 5.15 (s, 2H), 4.47 (s, 2H), 4.24−4.10 (m, 7H), 3.69 (t, J = 7.2 Hz, 2H), 2.86 (t, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 145.9, 138.1, 133.4, 128.8 (2C), 128.6 (3C), 126.7, 124.9, 119.8, 113.5, 80.7, 70.0 (2C), 69.4 (2C), 68.8 (5C), 54.7, 53.4, 31.7. IR (KBr) ν_{max}: 2941, 1605, 1589, 1509, 1232, 1167, 1032, 1009, 749, 489 cm^{-1}. MS: m/z 481 [M + H]$^+$. Anal. Calcd for $C_{26}H_{24}N_4FeS$: C, 64.99; H, 5.04; N, 11.67. Found: C, 64.60; H, 5.30; N, 11.36.

*N-Benzyl-N-(ferrocenylmethyl)-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3q**).* Red crystals, 0.783 g, yield 84%, mp 124−125 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.59 (dd, J = 7.8, 7.5 Hz, 1H), 7.46−7.31 (m, 6H), 5.12 (s, 2H), 4.72 (s, 2H), 4.48 (s, 2H), 4.20−4.14 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 146.6, 134.6, 128.9 (2C), 128.5 (2C), 127.9, 127.0, 124.7, 119.6, 113.2, 80.5, 70.0 (2C), 69.1 (2C), 68.7 (5C), 55.2, 51.9. IR (KBr) ν_{max}: 3029, 2947, 1609, 1590, 1530, 1228, 1170, 1023, 1012, 751, 469 cm^{-1}. MS: m/z 467 [M + H]$^+$. Anal. Calcd for $C_{25}H_{22}N_4FeS$: C, 64.37; H, 4.76; N, 12.02. Found: C, 64.10; H, 4.43; N, 11.77.

*N-(Furan-2-ylmethyl)-N-(ferrocenylmethyl)-1H-benzo[d][1,2,3]-triazole-1-carbothioamide (**3r**).* Red crystals, 0.739 g, yield 81%, mp 104−105 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 8.1 Hz, 2H), 7.49−7.41 (m, 2H), 7.34 (d, J = 3.6 Hz, 1H), 6.52 (s, 1H), 6.36 (s, 1H), 5.05 (s, 2H), 4.55 (s, 2H), 4.43 (s, 2H), 4.15−4.06 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 147.9, 145.8, 142.6, 133.4, 128.8, 124.9, 119.6, 113.5, 110.6, 109.5, 80.1, 70.0 (2C), 69.3 (2C), 68.6 (5C), 52.3, 48.3. IR (KBr) ν_{max}: 2962, 2921, 1596, 1531, 1444, 1105, 1018, 816, 473 cm^{-1}. MS: m/z 457 [M + H]$^+$. Anal. Calcd for $C_{23}H_{20}FeN_4OS$: C, 60.52; H, 4.42; N, 12.28. Found: C, 60.71; H, 4.18; N, 12.67.

*N-Cyclohexyl-N-(ferrocenylmethyl)-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3s**).* Red crystals, 0.761 g, yield 83%, mp 106−107 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (m, 2H), 7.43−7.32 (m, 2H), 4.88 (s, 2H), 4.35 (s, 2H), 4.19−4.11 (m, 7H), 3.33−3.26 (m, 1H), 2.15 (m, 2H), 1.92 (m, 2H), 1.80−1.36 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.5, 145.7, 133.2, 128.4, 124.6, 119.2, 113.3, 82.1, 69.6, 69.5, 68.8 (2C), 68.6 (3C), 68.1, 67.7, 64.0, 47.2, 32.8, 30.1, 25.5 (3C). IR (KBr) ν_{max}: 2935, 2855, 1660, 1909, 1470, 1449, 1036, 747, 482 cm^{-1}. MS: m/z 459 [M + H]$^+$. Anal. Calcd for $C_{24}H_{26}N_4FeS$: C, 62.87; H, 5.72; N, 12.23. Found: C, 62.64; H, 5.87; N, 12.49.

*N-Butyl-N-(ferrocenylmethyl)-1H-benzo[d][1,2,3]triazole-1-carbothioamide (**3t**).* Red crystals, 0.735 g, yield 85%, mp 92−93 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.56−7.52 (m, 2H), 5.14 (s, 2H), 4.50 (s, 2H), 4.22 (m, 7H), 3.40 (m, 2H), 1.80 (m, 2H), 1.53 (m, 2H), 0.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.3, 145.6, 133.2, 128.6, 124.8, 119.6, 113.3, 80.4, 69.8, 69.1, 68.9 (2C), 68.6 (3C), 68.4 (2C), 52.9, 51.7, 27.5, 20.0, 13.2. IR (KBr) ν_{max}: 1597, 1536, 1067, 1007, 959, 891, 728, 692, 650 cm^{-1}. MS: m/z 433 [M + H]$^+$. Anal. Calcd for $C_{22}H_{24}FeN_4S$: C, 61.10; H, 5.60; N, 12.96. Found: C, 61.33; H, 5.31; N, 13.15.

Procedure for the Synthesis of *N*-Alkyl-*N*-(ferrocenylmethyl)benzothiazol-2-amines (4p−t). Compounds **4p−t** were obtained by the same procedure as for the synthesis of 2-(*N*,*N*-dialkylamino)benzothiazoles **4a−l**.

*N-(Ferrocenylmethyl)-N-phenethylbenzo[d]thiazol-2-amine (**4p**).* Red crystals, 0.425 g, yield 94%, mp 158−159 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 8.1 Hz, 1H), 7.31−7.26 (m, 3H), 7.23−7.15 (m, 3H), 7.04 (dd, J = 7.5, 7.8 Hz, 1H), 4.45 (s, 1H), 4.27 (s, 1H), 4.17 (s, 5H), 4.13 (s, 2H), 3.58 (dd, J = 7.5, 7.8 Hz, 2H), 2.88 (dd, J = 8.1, 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 153.1, 138.8, 130.7, 128.8 (2C), 128.5 (2C), 126.4, 125.8, 120.8, 120.5, 118.7, 82.5, 69.5, 69.4, 68.7, 68.6 (2C), 68.4 (3C), 68.3, 52.0, 50.4, 33.5. IR (KBr) ν_{max}: 3020, 2927, 1597, 1542, 1384, 1229, 1148, 753, 481 cm^{-1}. MS: m/z 453 [M + H]$^+$. Anal. Calcd for $C_{26}H_{24}N_2FeS$: C, 69.01; H, 5.35; N, 6.19. Found: C, 68.62; H, 5.52; N, 6.43.

*N-Benzyl-N-(ferrocenylmethyl)benzo[d]thiazol-2-amine (**4q**).* Red crystals, 0.416 g, yield 95%, mp 151−152 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.35−7.24 (m, 6H), 7.07−7.02 (m, 1H), 4.66 (s, 2H), 4.49 (s, 2H), 4.24−4.23 (m, 2H), 4.14−4.10 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 153.0, 136.5, 130.8, 128.6, 127.5 (2C), 125.8, 121.0, 120.8, 120.5, 118.8, 82.1, 69.7, 69.5, 68.6 (5C), 68.2, 52.8, 49.3. IR (KBr) ν_{max}: 3027, 2921, 1593, 1562, 1536, 1441, 1297, 750, 728, 472 cm^{-1}. MS: m/z 439 [M + H]$^+$. Anal. Calcd for $C_{25}H_{22}N_2FeS$: C, 68.48; H, 5.06; N, 6.39. Found: C, 68.69; H, 5.26; N, 6.70.

*N-(Furan-2-ylmethyl)-N-(ferrocenylmethyl)benzo[d]thiazol-2-amine (**4r**).* Red crystals, 0.771 g, yield 90%, mp 99−100 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 1.2 Hz, 1H), 7.28 (dd, J = 8.4, 6.9 Hz,

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1H), 7.08−7.05 (m, 1H), 6.34−6.32 (m, 1H), 6.28 (d, J = 2.4 Hz, 1H), 4.62 (s, 2H), 4.50 (s, 2H), 4.29 (d, J = 1.8 Hz, 2H), 6.91 (s, 5H), 4.13 (t, J = 1.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 152.8, 150.2, 142.3, 130.8, 125.8, 121.1, 120.5, 118.9, 110.2, 108.7, 81.9, 69.7, 69.5, 68.7 (2C), 68.5 (3C), 68.4, 68.2, 49.4, 45.4. IR (KBr) ν_{max}: 3031, 2947, 1581, 1548, 1518, 1443, 1257, 755, 723, 492 cm^{-1}. MS: m/z 429 $[M + H]^+$. Anal. Calcd for $C_{23}H_{20}N_2OFeS$: C, 64.48; H, 4.71; N, 6.54. Found: C, 64.29; H, 4.34; N, 6.21.

*N-Cyclohexyl-N-(ferrocenylmethyl)benzo[d]thiazol-2-amine (**4s**).* Red crystals, 0.404 g, yield 94%, mp 134−135 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56−7.53 (m, 2H), 7.26 (dd, J = 8.4, 6.9 Hz, 1H), 7.01 (dd, J = 7.5, 7.2 Hz, 1H), 4.51 (s, 2H), 4.40 (s, 2H), 4.21−4.19 (m, 5H), 4.06 (s, 2H), 3.77−3.73 (m, 1H), 1.80−1.65 (m, 3H), 1.53−1.29 (m, 4H), 1.18−1.10 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 153.0, 130.4, 125.6, 120.5, 120.3, 118.6, 84.9, 69.9, 69.7, 68.7, 68.67 (2C), 68.60 (2C), 67.8, 67.6, 61.1, 45.9, 31.0 (2C), 26.0 (2C), 25.5. IR (KBr) ν_{max}: 2934, 2850, 1595, 1561, 1525, 1443, 1282, 748, 483 cm^{-1}. MS: m/z 431 $[M + H]^+$. Anal. Calcd for $C_{24}H_{26}FeN_2S$: C, 66.96; H, 6.09; N, 6.51. Found: C, 66.66; H, 6.48; N, 6.27.

*N-Butyl-N-(ferrocenylmethyl)benzo[d]thiazol-2-amine (**4t**).* Red oil, 0.375 g, yield 93%. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, J = 6.9 Hz, 2H), 7.26 (dd, J = 7.8, 7.5 Hz, 1H), 7.01 (dd, J = 7.5, 7.2 Hz, 1H), 4.52 (s, 2H), 4.28 (s, 2H), 4.18−4.10 (m, 7H), 3.36 (t, J = 6.9 Hz, 2H), 1.65−1.53 (m, 2H), 1.38−1.26 (m, 2H), 0.92 (t, J = 6.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 153.1, 130.6, 125.7, 120.6, 120.4, 118.5, 82.6, 69.4, 69.3, 68.6 (4C), 68.5, 68.2 (2C), 50.0, 49.5, 29.1, 20.0, 13.8. IR (KBr) ν_{max}: 3088, 2976, 2857, 1580, 1540, 1528, 1445, 1244, 761, 728, 488 cm^{-1}. MS: m/z 405 $[M + H]^+$. Anal. Calcd for $C_{22}H_{24}FeN_2S$: C, 65.35; H, 5.98; N, 6.93. Found: C, 65.62; H, 6.26; N, 6.59.

1,3-Dibenzyl-1-(ferrocenylmethyl)thiourea (7). Compound 7 was obtained using a known procedure reported by Katritzky et al.[38] To a stirring solution of *N*-benzyl-*N*-(ferrocenylmethyl)-1*H*-benzo[*d*][1,2,3]triazole-1-carbothioamide (**3q**) (0.454 g, 1.01 mmol) in dry CH_2Cl_2 (5 mL) was added a solution of benzylamine (1.0 mmol) in dry CH_2Cl_2 (5 mL) in the presence of Et_3N under an inert atmosphere at room temperature. After completion of the reaction (10−15 min, as monitored by TLC), the reaction mixture was concentrated in vacuo. After extraction with CH_2Cl_2 and washing twice with 10% Na_2CO_3, water, and saturated brine solution, the organic layer was dried over anhydrous Na_2SO_4. In vacuo concentration followed by purification with flash column chromatography using gradient mixtures of ethyl acetate and *n*-hexane afforded pure benzotriazolemethanethione 7. Red crystals, 0.399 g, yield 87%, mp 116−117 °C. R_f = 0.6 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29−7.18 (m, 8H), 7.05 (m, 2H), 5.69 (bs, 1H), 4.84 (s, 2H), 4.80−4.76 (m, 4H), 4.22 (s, 2H), 4.10 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.1, 137.7, 135.9, 128.9 (2C), 128.5 (2C), 127.7, 127.6 (2C), 127.4, 126.8 (2C), 82.5, 69.2 (2C), 68.7 (5C), 68.3 (2C), 53.3, 50.8, 50.5. IR (KBr) ν_{max}: 3337, 3057, 2909, 1603, 1536, 1339, 1182, 1020, 732, 697, 497, 480, 453 cm^{-1}. MS: m/z 455 $[M + H]^+$. Anal. Calcd for $C_{26}H_{26}FeN_2S$: C, 68.72; H, 5.77; N, 6.16. Found: C, 68.48; H, 6.13; N, 5.85.

Procedure for the Synthesis of Arylthiocarbonylbenzotriazoles (8a and 8b). To a solution of *p*-methoxy/*p*-methylphenylmagnesium bromide (5 mL, 1 M, 5.0 mmol) in THF at 0 °C was added carbon disulfide (450 μL, 5 mmol). The reaction mixture was heated for 3 h and then cooled to room temperature, and 1-chlorobenzotriazole (1.55 g, 10 mmol) was added. After stirring overnight at room temperature, the reaction mixture was concentrated in vacuo and purified by flash silica gel column chromatography.[38]

*(1H-Benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methanethione (**8a**).* Orange crystals, 0.632 g, yield 47%, mp 130−131 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.55 (dd, J = 7.2, 8.4 Hz, 1H), 7.19 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.6, 158.2, 146.6, 146.1, 131.7, 130.7, 126.2, 122.8 (2C), 120.8, 115.2, 114.7 (2C), 55.5. IR (KBr) ν_{max}: 3242, 2926, 1596, 1502, 1448, 1381, 1194, 1028, 1013, 833, 769, 752, 574 cm^{-1}. MS: m/z 270 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}N_3OS$: C, 62.44; H, 4.12; N, 15.60. Found: C, 62.44; H, 4.12; N, 15.60.

*(1H-Benzo[d][1,2,3]triazol-1-yl)(p-tolyl)methanethione (**8b**).* Orange crystals, 0.6671 g, yield 53%, mp 140−142 °C. R_f = 0.7 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 7.5, 7.8 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.4, 150.5, 146.6, 137.1, 131.7, 130.7, 130.4 (2C), 126.2, 121.6 (2C), 120.8, 115.1, 21.0. IR (KBr) ν_{max} 3244, 2923, 1584, 1535, 1452, 1367, 1176, 1023, 1011, 842, 758, 577 cm^{-1}. MS: m/z 254 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}N_3S$: C, 66.38; H, 4.38; N, 16.59. Found: C, 66.72; H, 4.65; N, 16.93.

Procedure for the Synthesis of 2-(Aryl)benzothiazoles (9a and 9b). Compounds **9a** and **9b** were obtained by the same procedure as for the synthesis of 2-(*N*,*N*-dialkylamino)benzothiazoles (**4a**−**l**).

*2-(4-Methoxyphenyl)benzo[d]thiazole (**9a**).* White solid, 0.214 g, yield 89%, mp 130−132 °C. R_f = 0.8 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.28−7.25 (m, 3H), 6.95 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 157.7, 149.2, 148.3, 132.2, 126.2, 123.8, 121.8 (2C), 121.6, 121.2, 114.8 (2C), 55.5. IR (KBr) ν_{max}: 3242, 2925, 1597, 1531, 1501, 1441, 1227, 1034, 828, 755 cm^{-1}. MS: m/z 242 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.51; H, 4.80; N, 5.64.

*2-(p-Tolyl)benzo[d]thiazole (**9b**).* White solid, 0.196 g, yield 87%, mp 85−86 °C. R_f = 0.8 (20% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.28−7.20 (m, 4H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 153.8, 139.8, 136.4 (2C), 131.1 (3C), 127.8, 126.4, 124,3, 121.3, 120.2, 22.7. IR (KBr) ν_{max}: 3254, 2931, 1579, 1540, 159, 1445, 1225, 1040, 845, 747 cm^{-1}. MS: m/z 226 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}NS$: C, 74.96; H, 4.92; N, 6.22. Found: C, 74.63; H, 5.09; N, 6.09.

Procedure for the Synthesis of (Alkyl/arylthio)thioacylbenzotriazoles (RSCSBt, 11a−f) and Disulfide Byproducts (12a−f). To a stirring solution of bis(benzotriazole)methanethione (**2**) (0.842 g, 3.0 mmol) in dry CH_2Cl_2 at 0 °C was slowly added a chilled solution (0 °C) of mercaptan **10a**−**f** (3.0 mmol) in dry CH_2Cl_2 in the presence of pyridine under an inert atmosphere. After completion of the reaction (as monitored by TLC), the reaction mixture was concentrated in vacuo, extracted with CH_2Cl_2, washed twice with 10% Na_2CO_3, water, and saturated brine solution, and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure. Further purification using flash column chromatography with gradient mixtures of ethyl acetate and *n*-hexane afforded pure (alkyl/arylthio)thioacylbenzotriazole **11a**−**f** along with byproduct **12a**−**f**.

*Benzyl 1H-Benzo[d][1,2,3]triazole-1-carbodithioate (**11a**).* Yellow crystals, 0.479 g, yield 56%, mp 108−110 °C. R_f = 0.7 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 8.1, 7.5 Hz, 1H), 7.49 (dd, J = 8.1, 7.5 Hz, 1H), 7.45−7.42 (m, 2H), 7.36−7.29 (m, 3H), 4.59 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 147.1, 133.9, 132.1, 131.0, 129.5 (2C), 128.7 (2C), 127.9, 126.5, 120.6, 115.5, 40.7. IR (KBr) ν_{max}: 3123, 2934, 1609, 1596, 1541, 1438, 1357, 1259, 1147, 1078, 1019, 845, 753, 559 cm^{-1}. MS: m/z 286 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}N_3S_2$: C, 58.92; H, 3.89; N, 14.72. Found: C, 59.11; H, 3.65; N, 14.53.

*2-Chlorobenzyl 1H-Benzo[d][1,2,3]triazole-1-carbodithioate (**11b**).* Yellow crystals, 0.508 g, yield 53%, mp 99−100 °C. R_f = 0.7 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 7.5, 7.8 Hz, 1H), 7.55−7.52 (m, 1H), 7.48 (dd, J = 8.4, 7.5 Hz, 1H), 7.41−7.38 (m, 1H), 7.27−7.20 (m, 2H), 4.71 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 147.1, 134.7, 132.2, 132.1, 131.4, 131.0, 129.7, 129.4, 126.9, 126.4, 120.5, 115.5, 38.4. IR (KBr) ν_{max}: 3111, 2937, 1610, 1596, 1540, 1444, 1351, 1259, 1170, 1021, 828, 755, 640 cm^{-1}. MS: m/z 320 $[M + H]^+$. Anal. Calcd for $C_{14}H_{10}ClN_3S_2$: C, 52.66; H, 3.16; N, 13.17. Found: C, 52.49; H, 3.39; N, 12.81.

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*Furan-2-ylmethyl 1H-Benzo[d][1,2,3]triazole-1-carbodithioate (**11c**).* Yellow crystals, 0.405 g, yield 49%, mp 124−125 °C. R_f = 0.7 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 7.2, 8.1 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.38 (s, 1H), 6.40 (s, 1H), 6.34 (s, 1H), 4.66 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 147.6, 147.2, 142.8, 132.2, 131.1, 126.5, 120.6, 115.4, 110.6, 109.5, 33.0. IR (KBr) ν_{max}: 3126, 2927, 1593, 1540, 1446, 1361, 1289, 1163, 1098, 1009, 830, 747, 638, 601, 556, 427 cm^{-1}. MS: *m*/*z* 276 $[M + H]^+$. Anal. Calcd for $C_{12}H_9N_3OS_2$: C, 52.36; H, 3.30; N, 15.28. Found: C, 52.64; H, 3.08; N, 15.65.

*Phenyl 1H-Benzo[d][1,2,3]triazole-1-carbodithioate (**11d**).* Yellow crystals, 0.553 g, yield 68%, mp 86−88 °C. R_f = 0.7 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 7.8, 8.1 Hz, 1H), 7.56−7.46 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.0, 147.2, 136.3 (2C), 132.3, 131.1, 130.8, 129.6 (2C), 129.2, 126.5, 120.6, 115.5. IR (KBr) ν_{max}: 3060, 2924, 1591, 1447, 1370, 1289, 1164, 1098, 1082, 827, 750, 689, 517, 424 cm^{-1}. MS: *m*/*z* 272 $[M + H]^+$. Anal. Calcd for $C_{13}H_9N_3S_2$: C, 57.56; H, 3.35; N, 15.50. Found: C, 57.31; H, 3.64; N, 15.31.

*4-Chlorophenyl 1H-Benzo[d][1,2,3]triazole-1-carbodithioate (**11e**).* Yellow crystals, 0.568 g, yield 62%, mp 128−129 °C. R_f = 0.7 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.67 (dd, *J* = 7.2, 8.1 Hz, 1H), 7.56 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 147.3, 137.7 (2C), 137.5, 132.3, 131.3, 130.1 (2C), 127.7, 126.7, 120.7, 115.6. IR (KBr) ν_{max}: 3071, 2944, 1608, 1597, 1443, 1389, 1232, 1134, 1087, 1062, 835, 758, 690, 554 cm^{-1}. MS: *m*/*z* 306 $[M + H]^+$. Anal. Calcd for $C_{13}H_8ClN_3S_2$: C, 51.15; H, 2.64; N, 13.77. Found: C, 51.32; H, 2.88; N, 14.15.

*p-Tolyl 1H-Benzo[d][1,2,3]triazole-1-carbodithioate (**11f**).* Yellow crystals, 0.547 g, yield 64%, mp 88−89 °C. R_f = 0.7 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.62 (dd, *J* = 7.5, 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.44 (d. *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.6, 147.2, 141.3, 136.1 (2C), 132.3, 131.0, 130.5 (2C), 126.5, 125.7, 120.5, 115.6, 21.4. IR (KBr) ν_{max}: 3073, 2928, 1603, 1589, 1450, 1378, 1289, 1176, 1024, 817, 778, 661, 534 cm^{-1}. MS: *m*/*z* 286 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}N_3S_2$: C, 58.94; H, 3.89; N, 14.74. Found: C, 59.25; H, 4.18; N, 15.06.

*1,1′-((Benzyldisulfanyl)methylene)bis(1H-benzo[d][1,2,3]triazole) (**12a**).* White crystals, 0.461 g, yield 38%, mp 114−116 °C. R_f = 0.6 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.68 (s, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.31−7.30 (m, 3H), 7.19 (d, *J* = 3.6 Hz, 2H), 3.61 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2, 135.6, 131.2, 129.4 (3C), 128.8 (2C), 128.5 (2C), 128.0, 124.9 (2C), 120.1, 120.0, 110.9, 75.1, 75.0, 42.7. IR (KBr) ν_{max}: 2944, 1611, 1449, 1079, 1038, 745, 703 cm^{-1}. MS: *m*/*z* 405 $[M + H]^+$. Anal. Calcd for $C_{20}H_{16}N_6S_2$: C, 59.39; H, 3.99; N, 20.79. Found: C, 59.03; H, 4.25; N, 21.0.

*1,1′-(((2-Chlorobenzyl)disulfanyl)methylene)bis(1H-benzo[d][1,2,3]triazole) (**12b**).* White crystals, 0.461 g, yield 35%, mp 113−114 °C. R_f = 0.7 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.89 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.51 (dd, *J* = 7.5, 8.1 Hz, 2H), 7.43−7.35 (m, 3H), 7.28−7.23 (m, 1H), 7.13 (d, *J* = 4.5 Hz, 2H), 3.74 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3 (2C), 134.4, 133.5, 131.3, 131.2 (2C), 130.1, 129.5, 128.7 (2C), 126.8, 125.0 (2C), 120.2 (2C), 110.8 (2C), 75.6, 40.7. IR (KBr) ν_{max}: 2940, 2931, 1611, 1594, 1489, 1447, 1277, 1231, 1088, 1063, 1021, 765, 538, 487 cm^{-1}. MS: *m*/*z* 439 $[M + H]^+$. Anal. Calcd for $C_{20}H_{15}ClN_6S_2$: C, 54.79; H, 3.45; N, 19.18. Found: C, 55.06; H, 3.24; N, 19.01.

*1,1′-(((Furan-2-ylmethyl)disulfanyl)methylene)bis(1H-benzo[d][1,2,3]triazole) (**12c**).* White crystals, 0.485 g, yield 41%, mp 124−125 °C. R_f = 0.7 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.88 (s, 1H), 7.52−7.47 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 6.32 (s, 1H), 6.14 (d, *J* = 3.0 Hz, 1H), 3.68 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6, 146.2 (2C), 143.1, 131.3 (2C), 128.6 (2C), 124.9 (2C), 120.2 (2C), 111.0, 110.8 (2C), 109.8, 75.4, 35.3. IR (KBr) ν_{max}: 2956, 2919, 1610, 1591, 1491, 1450, 1287, 1226, 1058, 1053, 1011, 788, 748, 597, 529, 437 cm^{-1}. MS: *m*/*z* 395 $[M + H]^+$. Anal. Calcd for $C_{18}H_{14}N_6OS_2$: C, 54.81; H, 3.58; N, 21.32. Found: C, 55.12; H, 3.41; N, 21.19.

*1,1′-((Phenyldisulfanyl)methylene)bis(1H-benzo[d][1,2,3]triazole) (**12d**).* Yellow crystals, 0.222 g, yield 19%, mp 94−96 °C. R_f = 0.7 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.39 (dd, *J* = 7.5, 8.1 Hz, 2H), 7.28 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.99−6.95 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1 (2C), 133.0, 131.1 (2C), 130.1 (2C), 128.6 (2C), 128.4 (2C), 128.2, 124.7 (2C), 110.7 (2C), 75.9. IR (KBr) ν_{max}: 3060, 2924, 1611, 1591, 1490, 1449, 1219, 1048, 786, 742, 687, 572, 528, 482, 429 cm^{-1}. MS: *m*/*z* 391 $[M + H]^+$. Anal. Calcd for $C_{19}H_{14}N_6S_2$: C, 58.45; H, 3.62; N, 21.54. Found: C, 58.71; H, 3.29; N, 21.17.

*1,1′-((((4-Chlorophenyl)disulfanyl)methylene)bis(1H-benzo[d][1,2,3]triazole) (**12e**).* Yellow crystals, 0.216 g, yield 17%, mp 106−107 °C. R_f = 0.7 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 7.2, 7.8 Hz, 2H), 7.34 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2 (2C), 134.6, 131.6, 131.5 (2C), 131.2 (2C), 128.7 (4C), 125.0 (2C), 120.2 (2C), 110.7 (2C), 76.2. IR (KBr) ν_{max}: 2950, 2933, 1610, 1593, 1495, 1444, 1265, 1227, 1078, 1061, 1017, 766, 587, 559, 474 cm^{-1}. MS: *m*/*z* 225 $[M + H]^+$. Anal. Calcd for $C_{19}H_{13}ClN_6S_2$: C, 53.77; H, 3.09; N, 19.81. Found: C, 53.94; H, 3.30; N, 20.20.

*1,1′-((p-Tolyldisulfanyl)methylene)bis(1H-benzo[d][1,2,3]triazole) (**12f**).* Yellow solid, 0.243 g, yield 20%, mp = 97−98 °C. R_f = 0.7 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.37 (dd, *J* = 6.9, 7.8 Hz, 2H), 7.29 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7 (2C), 139.9, 138.1, 133.9 (2C), 130.4, 130.1 (2C), 129.3, 127.1 (2C), 124.0 (2C), 119.9, 119.8, 112.3, 112.2, 73.1, 21.1. IR (KBr) ν_{max}: 3078, 2954, 2920, 1612, 1595, 1480, 1446, 1240, 1223, 1032, 1008, 777, 767, 576 cm^{-1}. MS: *m*/*z* 405 $[M + H]^+$. Anal. Calcd for $C_{20}H_{16}N_6S_2$: C, 59.39; H, 3.99; N, 20.79. Found: C, 59.11; H, 4.33; N, 20.42.

Procedure for the Synthesis of 2-(Alkyl/arylthio)-benzothiazoles (13a−f). Compounds **13a−f** were obtained by the same procedure as for the synthesis of 2-(*N*,*N*-dialkylamino)-benzothiazoles **4a−l**.

*2-(Benzylthio)benzo[d]thiazole (**13a**).* Colorless oil, 0.247 g, yield 96%. R_f = 0.8 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.31−7.22 (m, 3H), 7.18−7.08 (m, 4H), 4.44 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 152.9, 136.0, 135.1, 128.9 (2C), 128.5 (2C), 127.6, 125.9, 124.1, 121.3, 120.8, 37.5. IR (KBr) ν_{max}: 2917, 1588, 1451, 1409, 1223, 1010, 987, 565 cm^{-1}. MS: *m*/*z* 258 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}NS_2$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.55; H, 4.57; N, 5.64.

*2-(2-Chlorobenzylthio)benzo[d]thiazole (**13b**).* Colorless oil, 0.274 g, yield 94%. R_f = 0.8 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.42−7.35 (m, 2H), 7.26 (dd, *J* = 7.8, 8.1 Hz, 1H), 7.22−7.16 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 153.0, 135.3, 134.2, 131.2, 129.6, 129.1, 128.8, 126.9, 126.6, 125.9, 124.2, 121.4, 35.1. IR (KBr) ν_{max}: 3065, 2943, 2922, 1597, 1536, 1067, 1007, 959, 891, 728, 692, 650 cm^{-1}. MS: *m*/*z* 292 $[M + H]^+$. Anal. Calcd for $C_{14}H_{10}ClNS_2$: C, 57.73; H, 3.46; N, 4.81. Found: C, 58.01; H, 3.23; N, 5.19.

*2-(Furan-2-ylmethylthio)benzo[d]thiazole (**13c**).* Colorless oil, 0.212 g, yield 86%. R_f = 0.8 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, IH), 7.74 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 6.9, 8.1 Hz, 1H), 7.35 (s, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 6.29 (s, 1H), 4.63 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.5, 153.0, 149.4, 142.5, 135.3, 128.6, 126.0, 124.3, 121.5, 120.9, 110.6, 108.9, 29.9. IR (KBr) ν_{max}: 2924, 1602, 1457, 1427, 1240, 1074, 995, 597 cm^{-1}. MS: *m*/*z* 248 $[M + H]^+$. Anal. Calcd for $C_{12}H_9NOS_2$: C, 58.30; H, 3.67; N, 5.67. Found: C, 58.03; H, 3.48; N, 5.43.

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*2-(Phenylthio)benzo[d]thiazole (**13d**).* Colorless oil, 0.231 g, yield 95%. R_f = 0.8 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 5.7 Hz, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.47−7.42 (m, 3H), 7.38 (dd, J = 7.5, 7.8 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 153.8, 135.4, 135.2 (2C), 130.3, 129.8 (3C), 126.0, 124.2, 121.8, 120.6. IR (KBr) ν_{max}: 3059, 2955, 2923, 1581, 1457, 1425, 1020, 1007, 753, 726, 497, 430 cm^{-1}. MS: m/z 244 $[M + H]^+$. Anal. Calcd for $C_{13}H_9NS_2$: C, 64.19; H, 3.73; N, 5.76. Found: C, 64.49; H, 3.92; N, 5.62.

*2-(4-Chlorophenylthio)benzo[d]thiazole (**13e**).* Colorless oil, 0.255 g, yield 92%. R_f = 0.8 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 7.8 Hz, 1H), 7.66−7.62 (m, 3H), 7.43−7.37 (m, 3H), 7.26 (dd, J = 7.8, 6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 153.7, 136.8, 136.3 (2C), 135.4, 130.0 (2C), 128.2, 126.2, 124.4, 121.9, 120.7. IR (KBr) ν_{max}: 3056, 2950, 2931, 1578, 1455, 1431, 1019, 757, 497 cm^{-1}. MS: m/z 278 $[M + H]^+$. Anal. Calcd for $C_{13}H_8ClNS_2$: C, 56.32; H, 2.91; N, 5.06. Found: C, 56.50; H, 2.60; N, 4.91.

*2-(p-Tolylthio)benzo[d]thiazole (**13f**).* Colorless oil, 0.239 g, yield 93%. R_f = 0.8 (5% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.5 Hz, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.27−7.20 (m, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 153.9, 141.0, 135.4 (3C), 130.6 (2C), 126.2, 126.0, 124.1, 121.7, 120.6, 21.3. IR (KBr) ν_{max}: 3061, 2945, 2920, 1588, 1540, 1097, 1011, 995, 867, 735, 665, 587 cm^{-1}. MS: m/z 258 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}NS_2$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.75; H, 4.65; N, 5.72.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all of the new compounds; X-ray crystallographic data for **3a**, **4b**, **4c**, **4e**, **3p**, **4p**, **6**, and **7** (CIF); and computational data and images related to the optimized geometry of intermediate **A** and molecule **3g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

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