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Diastereo- and Regioselective Addition of Thioamide Dianions to Imines and Aziridines: Synthesis of *N*-Thioacyl-1,2-diamines and *N*-Thioacyl-1,3-diamines

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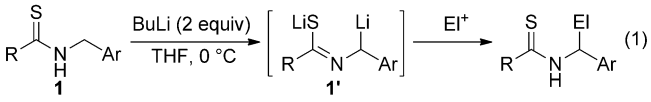
Abstract: Addition reactions of thioamide dianions that were derived from *N*-arylmethyl thioamides to imines and aziridines were carried out. The reactions of imines gave the addition products of *N*-thioacyl-1,2-diamines in a highly diastereoselective manner in good-to-excellent yields. The diastereomeric purity of these *N*-thioacyl-1,2-diamines could be enriched by simple recrystallization. The reduction of *N*-thioacyl-1,2-diamines with $LiAlH_4$ gave their corresponding 1,2-diamines in moderate-to-good yields with retention of their stereochemistry. The oxidative-desulfurization/cyclization of an *N*-thioacyl-1,2-diamine in $CuCl_2/O_2$ and I_2/pyridine systems gave the cyclized product in moderate yield and the *trans* isomer was obtained as the sole product. On the other hand, a similar cyclization reaction with antiformin (aq. NaClO) as an oxidant gave the *cis* isomer as the major product. The reactions of *N*-tosylaziridines gave the addition products of *N*-thioacyl-1,3-diamines with low diastereoselectivity but high regioselectivity and in good-to-excellent yields. The use of $AlMe_3$ as an additive improved the efficiency and regioselectivity of the reaction. The stereochemistry of the obtained products was determined by X-ray diffraction.

Keywords: addition reactions · carbanions · diamines · diastereoselectivity · regioselectivity

Introduction

Vicinal (1,2-) and 1,3-diamines are important structural motifs in natural products, pharmaceuticals, and ligands for catalysts and supramolecules.[1] Many methods for the preparation of these motifs have been reported.[2] Among them, the addition of carbanions that are α to the nitrogen atom to imines or aziridines is one of the most efficient approaches for obtaining diverse diamines, owing to the ready availability of these electrophiles. However, probably owing to the selectivity of these processes for the generation of carbanions from primary and secondary amine derivatives, as well as the lability of the carbanions,[3] the previous reports on addition reactions to imines have been limited to those of carbanions from tertiary amides and carbamates.[2c,d] Furthermore, to the best of our knowledge, the addition of such carbanions to aziridines has never been reported.[4] Recently, we described the synthetic applications of α-nitrogen carbanions, *N*-arylmethyl thioamide dianions (**1′**), which were generated by the treatment of 2 equivalents of BuLi with their corresponding secondary *N*-arylmethyl thioamides (**1**, [Eq. (1)]).[5] Thioamide dianions have previously been shown to lead to *N*-thioacyl amino alcohols, amines, and α-silylmethylamines by treatment with their corresponding electrophiles, such as aldehydes, oxiranes, alkyl halides, and silyl chlorides. Herein, we describe the diastereo- and regioselective addition of thioamide dianions to imines or aziridines, thereby leading to *N*-thioacyl-1,2- or 1,3-diamines, and the synthetic application of the resulting products, thereby leading to their corresponding diamines and heterocycles.



(1)

Results and Discussion

Initial investigation of the reaction between a thioamide dianion and an imine: Initially, the reaction of thioamide dianion **1a′** with 1 equivalent of imine **2a** at 0 °C in THF was carried out (Scheme 1). The reaction proceeded smoothly to give the corresponding *N*-thioacyl-1,2-diamine (**3aa**) in quantitative yield. In this case, no diastereoselectivity was observed (d.r. = 1:1). The reaction even proceeded at −78 or −95 °C and showed significantly improved d.r. values of 4:1 and 9:1, respectively. Further enrichment of the major diastereomer of compound **3aa** was observed after recrystallization of the crude mixture. For example, diastereomerically

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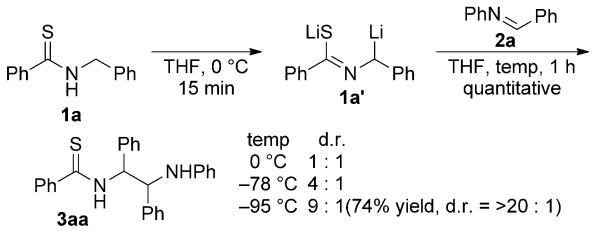
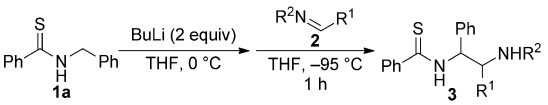


Scheme 1. Initial investigation of the reaction between thioamide dianion **1a′** and imine **2a**.

and analytically pure compound **3aa** (d.r. > 20:1) was obtained in 74% yield from the crude mixture of the reaction at −95 °C after a single recrystallization process. The stereochemistry of the major isomer was determined to be (*S**,*S**) by single-crystal X-ray analysis (Figure 1).

Scope of the substrates in the coupling reactions of thioamide dianions with imines: Next, the coupling reactions between thioamide **1a** and several imines (**2**) were examined at −95 °C (Table 1). The reaction of compound **1a′** with an imine that contained a trifluoromethylphenyl group on the imino carbon atom (**2b**) gave the corresponding product (**3ab**) in good yield with high diastereoselectivity (Table 1, entry 2). Again, diastereomerically pure product (*S**,*S**)-**3ab** was obtained in 74% yield after a single recrystallization process. Although these reactions also furnished adducts **3ac** and **3ad** in good yields, the use of electron-rich imines **2c** and **2d**, which were derived from *p*-methoxy- and *p*-methylbenzaldehydes, respectively, slightly decreased the d.r. values of both the crude mixtures and the isolated products (Table 1, entries 3 and 4). Meanwhile, the reaction between compound **1a** and an imine that contained an *o*-methoxyphenyl group on the imino carbon atom (**2e**) gave the corresponding product (**3ae**) in 63% yield, similar to the reaction of compound **2c** but with higher diastereoselectivity (Table 1, entry 5). The reactions between compound **1a′** and aliphatic imines **2f** and **2g** also afforded adducts **3af** and **3ag** in good yields, although 2 equivalents of the imines were required to achieve good conversions of compound **1a′** (Table 1, entries 6 and 7); in this case, the reaction of a *tert*-butyl-substituted imine (**2g**) with compound **1a′** showed complete diastereoselectivity. The substituents on the nitrogen atoms of the imine groups significantly affected the reactivity and selectivity of the reaction, compared to those on the imino carbon atoms. The reaction with *N*-*p*-methoxyphenyl (PMP) imine **2h** still furnished the product with a high d.r. under the standard conditions (Table 1, entry 8); in contrast, almost no diastereoselectivity was observed in the reaction of 4-trifluoromethylphenyl-substituted imine **2i** with compound **1a′** (Table 1, entry 9). The reaction of 4-bromophenyl-substituted imine **2j** with compound **1a′** also showed poor diastereoselectivity, but, notably, the bromine atom on the substrate remained intact under the reaction conditions to result in the formation of compound **3aj** in good yield. The reaction of compound **1a′** with *N*-*o*-methoxyphenyl imine **2k** showed the complete absence of diastereoselectivity (Table 1, entry 11). The reaction of *N*-*tert*-butyl imine **2l** did not afford any product at all (Table 1, entry 12).

Table 1. Reactions between thioamide **1a** and imines **2**.[a,b]



Entry	Imine			Conversion [%][c]	Yield [%][d]	
1	R^1 = Ph	R^2 = Ph	**2a**	quant. (9:1)	74 (>20:1)	**3aa**
2	R^1 = 4-$F_3CC_6H_4$	R^2 = Ph	**2b**	89 (9:1)	74 (>20:1)	**3ab**
3	R^1 = PMP	R^2 = Ph	**2c**	quant. (4:1)	78 (9:1)	**3ac**
4	R^1 = 4-MeC_6H_4	R^2 = Ph	**2d**	90 (9:1)	71 (20:1)	**3ad**
5	R^1 = *o*-$MeOC_6H_4$	R^2 = Ph	**2e**	quant. (9:1)	63 (>20:1)	**3ae**
6[e]	R^1 = *i*Pr	R^2 = Ph	**2f**	94 (1:1)	67 (1:1)[f]	**3af**
7[e]	R^1 = *t*Bu	R^2 = Ph	**2g**	86 (>20:1)	91 (>20:1)[f]	**3ag**
8	R^1 = Ph	R^2 = PMP	**2h**	quant. (9:1)	78 (9:1)	**3ah**
9	R^1 = Ph	R^2 = 4-$CF_3C_6H_4$	**2i**	90 (2:3)	76 (2:3)	**3ai**
10[e]	R^1 = Ph	R^2 = 4-BrC_6H_4	**2j**	quant. (1:1)	80 (3:1)[f]	**3aj**
11	R^1 = Ph	R^2 = *o*-$MeOC_6H_4$	**2k**	quant. (1:1)	83 (1:1)	**3ak**
12	R^1 = Ph	R^2 = *t*Bu	**2l**	no reaction		

[a] The reactions were carried out with 1.1 equiv of imines **2**. [b] The generation of thioamide dianion **1a′** was carried out in a 0.5 M solution. [c] Determined by ^{1}H NMR spectroscopy with reference to unconsumed starting thioamides in the crude mixture and 1,1,2,2-tetrachloroethane as an internal standard. The d.r. values of the isolated products are given in parentheses. [d] Yield of the isolated product after recrystallization; the d.r. values of the products are given in parentheses. [e] To complete the reaction, 2 equiv of imine were used. [f] Isolated by column chromatography on silica gel.

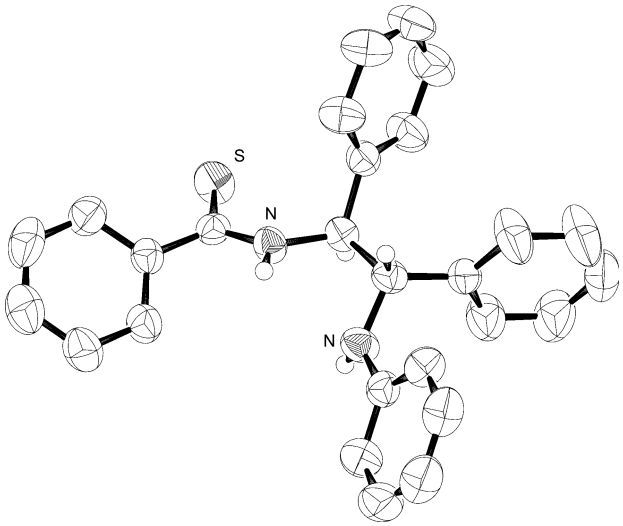
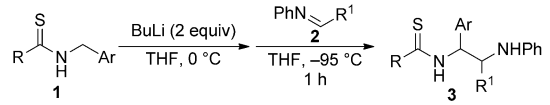


Figure 1. ORTEP of compound **3aa**;[6] thermal ellipsoids are set at 50% probability.

Next, we turned our attention to the scope of the thioamides (**1**; Table 2). The substituents on thioamides **1** affected

Table 2. Reactions of thioamides **1** with imines **2**.[a,b]



1b: R = PMP, Ar = Ph
1c: R = Ph, Ar = PMP
1d: R = *t*Bu, Ar = Ph

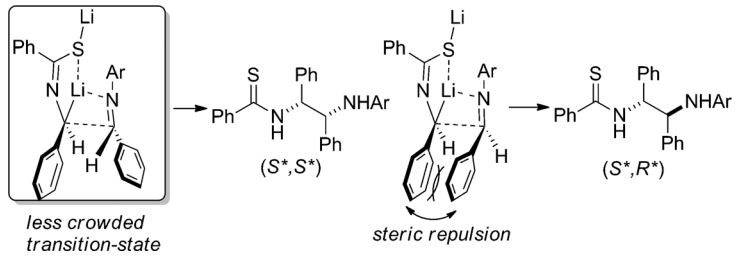
2a: R^1 = Ph
2b: R^1 = 4-$F_3CC_6H_4$
2c: R^1 = PMP

Entry	Thioamide	Imine	d.r.[c]	Yield[%][d]	
1[e]	**1b**	**2a**	9:1	66 (>20:1)	**3ba**
2		**2b**	4:1[f]	68 (19:1)	**3bb**
3		**2c**	4:1	81 (4:1)[g]	**3bc**
4	**1c**	**2a**	4:1	84 (13:1)	**3ca**
5		**2b**	3:1	78 (3:1)[g]	**3cb**
6[e]		**2c**	4:1	74 (4:1)[g]	**3cc**
7	**1d**	**2a**	1:2[h]	62 (2:3)	**3da**

[a] The reactions were carried out with 1.1 equiv of imines **2**. Unless otherwise noted, the reactions were performed under the conditions given in the running text. [b] The generation of thioamide dianion **1a′** was carried out in a 0.5 M solution. [c] The diastereomeric ratios of the crude products were determined by ^{1}H NMR spectroscopy. [d] Yield of the isolated product after recrystallization; the d.r. values of the products are given in parentheses. [e] Owing to the solubility of dianion **1′**, the reaction was carried out in 0.125 M solution. [f] 94% Conversion. [g] Isolated mixture.

the crystal formation in the products. For example, product **3bc** barely crystallized and was obtained as a sticky oil, even after purification by column chromatography on silica gel, and thus recrystallization did not increase its d.r. (Table 2, entry 3). In contrast, the d.r. values of compounds **3ba** and **3bb** improved after recrystallization (Table 2, entries 1 and 2). A similar tendency for crystallization was observed for the products that were obtained from the reactions of compound **1c** with imines **2a**–**2c** (Table 2, entries 4-6). In addition, the reaction between alkyl-substituted thioamide **1d** and compound **2a** showed low diastereoselectivity (Table 2, entry 7).

Consideration of stereocontrol in the coupling of thioamide dianions with imines: The high diastereoselectivity in the formation of compound **3** can be explained if the reaction passes through a chelation transition state during the addition step of thioamide dianion **1′** to imines **2** (Scheme 2). The conformation of the thioamide dianions (**1′**) may be fixed by intramolecular chelation of the benzylic lithium moiety to a sulfur atom. The ligation of the imino nitrogen atom to the benzylic lithium moiety of the dianion, followed by the addition reaction, should favor the formation of a less-crowded transition-state structure, thereby resulting in the (*S**,*S**)-isomer (Scheme 2, left). A similar mechanism for stereoselection in the reaction between imines and α-nitrogen carbanions of tertiary carbamates was proposed by Kise, Yoshida, and co-workers.[2c]



Scheme 2. Proposed stereocontrol pathway through chelation control.

Synthetic applications of *N*-thioacyl-1,2-diamines (3): The products (**3**) can be transformed into their corresponding 1,2-diamine derivatives. For example, the reduction of compounds **3** with $LiAlH_4$ gave 1,2-diamines **4** in moderate-to-good yields with the retention of stereochemistry ([Eq. (2)]).[7] Unsymmetrical 1,2-diamines that were similar to compounds **4** were synthesized by aldimine cross-coupling or by the reduction of 1,2-diimine, but their diastereoselectivities depended on the substituents. Therefore, this method can be used as a complementary process for the synthesis of stereochemically defined unsymmetrical 1,2-diamines (**4**).[8] Oxidative-desulfurization/cyclization[9] of compound **3aa** allowed us to access imidazoline *trans*-**5** in moderate yields ([Eq. (3)]). The configuration of *trans*-**5** was determined by X-ray analysis (Figure 2). In contrast, a similar cyclization

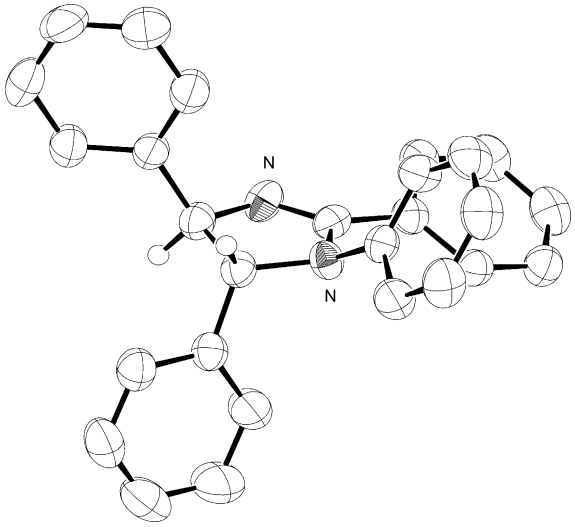
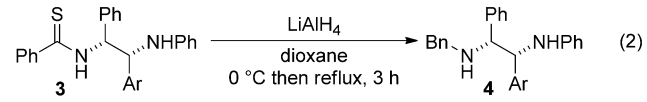
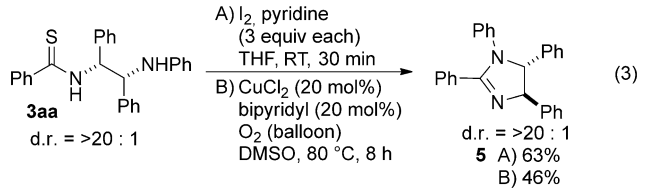


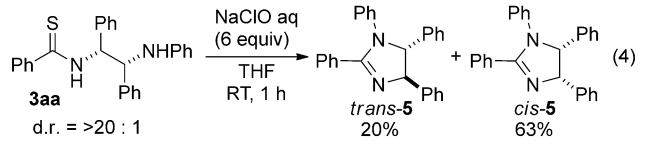
Figure 2. ORTEP of compound *trans*-**5**;[6] thermal ellipsoids are set at 50% probability.

reaction of compound **3aa** with antiformin (aq. NaClO) as the oxidant gave *cis*-**5** as the major product ([Eq. (4)]). Although all of the stereochemistry was lost, the aromatization of compound **5** by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) led to the corresponding tetraphenylated imidazole (**6**; [Eq. (5)]).

Reactions between thioamide dianion 1a′ and aziridines 7: The reactions between dianion **1a′** and N-protected 2-methylaziridines **7** instead of imines were investigated under the standard conditions described in Table 3. Initial investigation







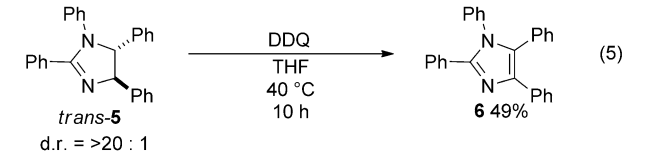
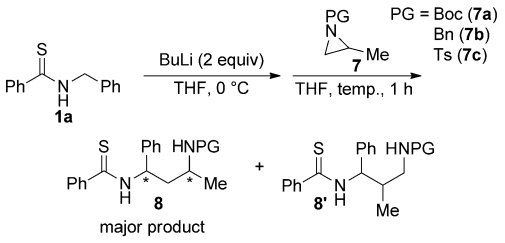


Table 3. Reactions between thioamide **1a** and N-protected 2-methylaziridines **7**.[a]



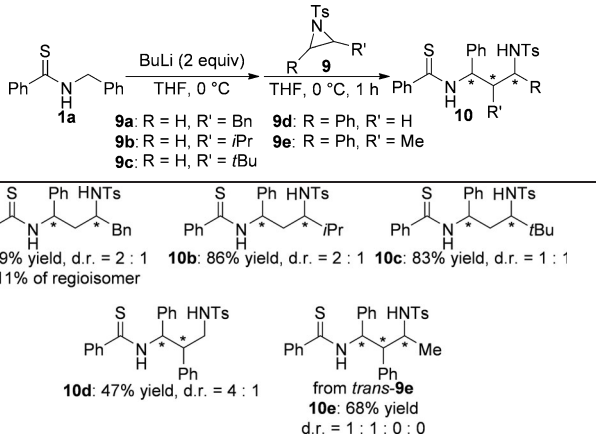
Entry	**7**	*T* [°C]	Additive	Conversion [%][b]	Yield [%][c]	**8**:**8′**
1	**7a**	−95	–	complex mixture		
2	**7b**	−95	–	no reaction		
3	**7c**	−95	–	85	56[d]	5:1
4	**7c**	0	–	quant.	66	5:1
5	**7c**	−95	BF_3•OEt_2	complex mixture		
6	**7c**	−95	$Cu(OTf)_2$	complex mixture		
7	**7c**	−95	$AlMe_3$	96	79	13:1
8	**7c**	0	$AlMe_3$	quant.	99	5:1

[a] The reactions were carried out with 1.1 equiv of aziridines **7**. Unless otherwise noted, the reactions gave a 1:1 diastereomeric mixture. [b] Determined by ^{1}H NMR spectroscopy, with reference to unconsumed starting thioamides in the crude mixture and 1,1,2,2-tetrachloroethane as an internal standard. [c] Yield of isolated product. [d] d.r. = 2:1.

of the protecting groups on the nitrogen atom of aziridines **7** (Table 3, entries 1–3) showed that *N*-tosyl aziridine **7c** was an appropriate electrophile and gave its corresponding *N*-thioacyl-1,3-diamine (**8c**) in 56% yield with good regioselectivity (Table 3, entry 3). In this case, the reaction preferred to proceed at the less-crowded 3-position of compound **7c**.[10] Unfortunately, the efficiency of the reaction did not improve when the reaction was carried out at 0°C (Table 3, entry 4). To improve the yield and diastereoselectivity of this reaction, several Lewis acids, such as BF_3•OEt_2, $Cu(TfO)_2$, and $AlMe_3$, were tested as additives (Table 3, entries 5–7). However, only $AlMe_3$ showed a positive effect as an additive in the reaction, thereby affording compound **8c** in an improved yield of 79% and better regioselectivity, but the d.r. did not improve at all (Table 3, entry 7). The reaction still showed good regioselectivity and the yield of adduct **8c** was improved to 99% at 0°C (Table 3, entry 8). Presumably, $AlMe_3$ not only activated the reaction but also avoided side-reactions. In fact, when the reaction was run in the absence of $AlMe_3$ at 0°C, the crude mixture was found to be contaminated by a small amount of unidentified byproducts, as well as by trace amounts of the regioisomer (Table 3, entry 4).

Scope of the substrates in the reactions between thioamide dianion 1a′ and aziridines 9 in the presence of $AlMe_3$ as an additive: Benzyl (**9a**)-, isopropyl (**9b**)-, and *tert*-butyl-substituted aziridines (**9c**) were also used as electrophiles in the reactions with dianion **1′** to give compounds **10a**–**10c**, respectively, in moderate-to-high yields (Table 4). In these

Table 4. Reactions between compound **1a** and aziridines **9**.[a,b]



[a] The reactions were carried out with 1.1 equiv of aziridines **9**. [b] Yield of isolated product after column chromatography on silica gel.

cases, relatively sterically hindered aziridines **9b** and **9c** afforded the products (**10b** and **10c**) with exclusive regioselectivity, whereas the reaction of compound **9a** gave compound **10a** together with a small amount of the regioisomer, similar to the reaction of compound **7c**. On the other hand, the reaction of compound **1a′** with styrene-derived aziridine **9d** gave the other regioisomer (**10d**) as the major product, as confirmed by X-ray analysis (Figure 3). Similar regioselectivity was observed in the reaction between β-methylstyrene-derived *trans*-**9e** and dianion **1a′**.[11] That is, the reac-

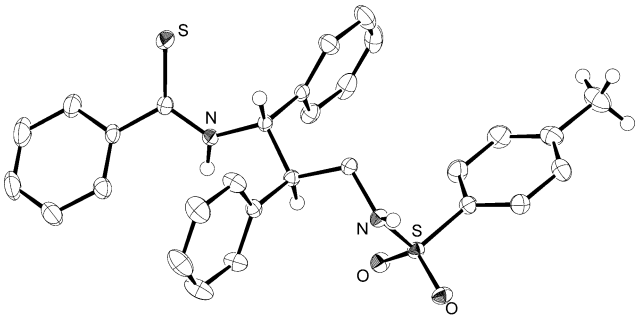


Figure 3. ORTEP of compound **10d**;[6] thermal ellipsoids are set at 50% probability.

tions of styrene-derived aziridines proceeded at the position α to the phenyl group, probably owing to the electrophilicity of the benzylic position.[12,13] In addition, the diastereomers of products **10d** and **10e** could be easily separated by conventional flash column chromatography on silica gel or by preparative HPLC.

Conclusion

In conclusion, the addition of thioamide dianions to imines and aziridines has been achieved. These reactions gave a variety of *N*-thioacyl-1,2- and 1,3-diamines in moderate-to-high yields. Coupling between the thioamide dianions and imines proceeded in a diastereoselective manner and, notably, the d.r. values were readily improved by simple recrystallization. On the other hand, the reactions between thioamide dianions and aziridines showed poor diastereoselectivity but they proceeded in a regioselective manner. These reactions may lead to highly substituted sterically defined 1,2- and 1,3-diamine derivatives from readily available starting materials. Their use in enantioselective addition reactions and in further synthetic applications, such as the stereodefined construction of heavily substituted nitrogen-containing heterocycles, are underway in our laboratory.

Experimental Section

General remarks: IR spectra were obtained on a JASCO FTIR 410 spectrometer. ^{1}H NMR spectra were recorded on a JEOL α-400 (400 MHz) in $CDCl_3$; the chemical shifts (δ) were referenced to tetramethylsilane as an internal standard. ^{13}C NMR spectra were measured on a JEOL α-400 (100 MHz) in $CDCl_3$. ^{19}F NMR spectra were measured on a JEOL α-400 (376 MHz) in $CDCl_3$ and with CF_3COOH as an external standard. MS and HRMS were performed on a JMS-700 mass spectrometer. Elemental analysis was carried out by the Elemental Analysis Center of Kyoto University. Melting points were determined by using a Yanaco seisakusho MP-S2 micro melting point apparatus and are uncorrected. HPLC was performed on a Japan Analytical Industry LC-908 recycling preparative HPLC that was coupled to an RI indicator and a UV detector (256 nm) with a Mightysil Si 60 column (250 mm × 20 mm). Preparative recycling gel-permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 recycling preparative HPLC that was equipped with JAIGEL-1H and JAIGEL-2H columns and LC9201R/U recycling preparative HPLC ($CHCl_3$).

Materials: Unless otherwise noted, the reagents were commercially available and were used without further purification. THF (dehydrated) was purchased from Kanto Chemical Co. and used without further purification. DMSO was distilled over calcium hydride under reduced pressure. The imines were prepared according to standard procedures. *N*-*tert*-butoxycarbonyl-2-methylaziridine (**7a**),[14] *N*-benzyl-2-methylaziridine (**7b**),[15] 2-methyl-*N*-tosylaziridine (**7c**),[16] 2-benzyl-*N*-tosylaziridine (**9a**),[17] 2-isopropyl-*N*-tosylaziridine (**9b**),[18] 2-*tert*-butyl-*N*-tosylaziridine (**9c**),[19] 2-phenyl-*N*-tosylaziridine (**9d**),[20] and *trans*-2-methyl-3-phenyl-*N*-tosylaziridine (**9e**)[21] were prepared according to literature procedures. Column chromatography was performed on silica gel 60 N (Spherical, Neutral, 100–210 μm or 40–50 μm) from Kanto Chemical Co., Inc.

General procedure for the reaction between thioamide dianion 1′ and imines 2: To a 0.25 M solution of thioamide **1** in THF was added *n*BuLi (1.6 M in *n*-hexane, 2 equiv) at 0 °C and the mixture was stirred at 0 °C for 5 min. A 0.2 M solution of aldimine **2** (1 equiv) in THF was added to the reaction mixture at −95 °C and the solution was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by recrystallization or by column chromatography on silica gel to give the *N*-thioacyl-1,2-diamines.

***N*-(1,2-Diphenyl-2-phenylaminoethyl)benzenecarbothioamide (3aa)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 74% yield; d.r. > 20:1; R_f = 0.43 (*n*-hexane/EtOAc, 5:1); m.p. 194.8–195.5 °C; ^{1}H NMR ($CDCl_3$): δ = 4.77 (br s, 1H; PhN*H*), 5.00 (d, *J* = 8.1 Hz, 1H; PhNHC*H*), 6.14 (t, *J* = 8.1 Hz, 1H; C(=S)NHC*H*), 6.57 (d, *J* = 7.6 Hz, 2H; Ar), 6.67 (t, *J* = 7.3 Hz, 1H; Ar), 7.08 (dd, *J* = 8.6, 7.3 Hz, 2H; Ar), 7.14 (dd, *J* = 6.8, 3.5 Hz, 2H; Ar), 7.18–7.31 (m, 8H; Ar), 7.35 (dd, *J* = 7.8, 7.3 Hz, 2H; Ar), 7.45 (t, *J* = 7.8 Hz, 1H; Ar), 7.63 (d, *J* = 7.1 Hz, 2H; Ar), 8.10 ppm (d, *J* = 8.1 Hz, 1H; NH); ^{13}C NMR ($CDCl_3$): δ = 62.8, 64.7 (CH), 113.9, 118.2, 126.6, 127.6, 127.7, 127.8, 128.3, 128.5, 128.6, 128.8, 129.2, 131.2, 137.0, 139.3, 142.0, 146.7 (Ar) 199.7 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3333, 3282, 3029, 2925, 1761, 1604, 1506, 1496, 1484, 1454, 1389, 1342, 1314, 1274, 1252, 1219, 1189, 1156, 1117, 1065, 1029, 954, 926, 873, 849, 619, 593, 518, 469 cm^{-1}; MS (EI): *m*/*z*: 408 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{27}H_{24}N_2S$: 408.1660 [*M*]$^+$; found: 408.1642.

***N*-[1-Phenyl-2-phenylamino-2-(4-trifluoromethylphenyl)ethyl]benzenecarbothioamide (3ab)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 74% yield; d.r. > 20:1; R_f = 0.45 (*n*-hexane/EtOAc, 5:1); m.p. 187.8–188.1 °C; ^{1}H NMR (CD_3CN): δ = 5.20 (dd, *J* = 9.8, 8.8 Hz, 1H; PhNHC*H*), 5.57 (d, *J* = 8.8 Hz, 1H; PhN*H*), 5.97 (dd, *J* = 9.8, 7.8 Hz, 1H; C(=S)NHC*H*), 6.61 (t, *J* = 7.3 Hz, 1H; Ar), 6.65 (d, *J* = 7.8 Hz, 2H; Ar), 7.06 (dd, *J* = 8.3, 7.3 Hz, 2H; Ar), 7.22–7.24 (m, 5H; Ar), 7.39–7.43 (m, 4H; Ar), 7.48–7.50 (m, 3H; Ar), 7.76 (d, *J* = 8.1 Hz, 2H; Ar); 9.46 ppm (d, *J* = 7.8 Hz, 1H; C(=S)NH); ^{13}C NMR ($CDCl_3$): δ = 62.9, 64.6 (CH), 113.7, 118.4 (Ar), 124.0 (q, *J* = 272.1 Hz; CF_3), 125.4 (q, *J* = 4.1 Hz; *C*CCF$_3$), 126.7, 127.7, 128.0, 128.68, 128.71, 129.1, 129.3, 130.0 (q, *J* = 32.3 Hz; *C*CF$_3$), 131.5, 136.6, 141.8, 143.8, 146.3 (Ar), 200.4 ppm (C=S); ^{19}F NMR (CD_3CN): δ = −63.3 ppm; IR (KBr): $\tilde{\nu}$ = 3352, 2360, 1601, 1508, 1446, 1327, 1256, 1167, 1119, 1067, 1017, 840, 758, 695 cm^{-1}; MS (EI): *m*/*z*: 476 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{28}H_{23}F_3N_2S$: 476.1534 [*M*]$^+$; found: 476.1561.

***N*-[2-(4-Methoxyphenyl)-1-phenyl-2-phenylaminoethyl]benzenecarbothioamide (3ac)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 78% yield; d.r. = 9:1; R_f = 0.33 (*n*-hexane/EtOAc, 5:1); m.p. 166.1–166.9 °C; ^{1}H NMR ($CDCl_3$, major isomer): δ = 3.78 (s, 3H; OCH_3), 4.78 (br s, 1H; PhN*H*), 4.99 (d, *J* = 7.8 Hz, 1H; PhNHC*H*), 6.09 (t, *J* = 7.8 Hz, 1H; C(=S)NHC*H*), 6.57 (d, *J* = 8.3 Hz, 2H; Ar), 6.66 (t, *J* = 7.3 Hz, 1H; Ar), 6.82 (d, *J* = 8.3 Hz, 2H; Ar), 7.04–7.10 (m, 4H; Ar), 7.20–7.25 (m, 5H; Ar), 7.35 (dd, *J* = 8.3, 7.3 Hz, 2H; Ar), 7.42 (t, *J* = 8.1 Hz, 1H; Ar), 7.62 (d, *J* = 8.3 Hz, 2H; Ar), 8.02 ppm (d, *J* = 7.8 Hz, 1H; C(=S)NH); ^{13}C NMR ($CDCl_3$, major isomer): δ = 55.2 (CH_3), 62.5, 64.1 (CH), 113.9, 114.2, 116.4, 118.1, 126.6, 127.6, 127.7, 128.5, 128.6, 128.9, 129.2, 131.2, 139.3, 142.0, 146.7, 159.4 (Ar), 199.5 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3327, 3292, 1714, 1602, 1507, 1387, 1251, 829, 760,

697, 524 cm^{-1}; MS (FAB): *m/z*: 439 $[M+H]^+$; HRMS (FAB): *m/z* calcd for $C_{28}H_{27}N_2OS$: 439.1844 $[M+H]^+$; found: 439.1860.

***N*-[2-(4-Methylphenyl)-1-phenyl-2-phenylaminoethyl]benzenecarbothioamide (3ad)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 71% yield; d.r. = 20:1; R_f = 0.43 (*n*-hexane/EtOAc, 5:1); m.p. 194.0–194.4 °C; ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 3H; CH_3), 4.68 (brs, 1H; PhN*H*), 4.97 (d, *J* = 7.8 Hz, 1H; PhNHC*H*), 6.11 (dd, *J* = 8.3, 7.8 Hz, 1H; C(=S)NHC*H*), 6.57 (d, *J* = 7.8 Hz, 2H; Ar), 6.67 (t, *J* = 7.3 Hz, 1H; Ar), 7.03–7.10 (m, 5H; Ar), 7.14–7.15 (m, 3H; Ar), 7.24–7.30 (m, 3H; Ar), 7.35 (dd, *J* = 7.8, 7.3 Hz, 2H; Ar), 7.44 (t, *J* = 7.3 Hz, 1H; Ar), 7.63 (d, *J* = 7.3 Hz, 2H; Ar), 8.10 ppm (d, *J* = 8.3 Hz, 1H; C(=S)NH); ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_3), 62.2, 64.5 (CH), 113.9, 118.1, 126.6, 127.4, 127.7, 128.2, 128.5, 128.7, 129.16, 129.18, 131.2, 136.0, 137.0, 137.4, 141.9, 146.7 (Ar), 199.5 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3332, 3279, 3027, 2924, 1603, 1498, 1484, 1446, 1388, 1317, 1258, 1066, 1028, 955, 818, 754, 720, 694, 651, 576, 514 cm^{-1}; MS (EI): *m/z*: 422 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{28}H_{26}N_2S$: 422.1817 $[M]^+$; found: 422.1817.

***N*-[2-(2-Methoxyphenyl)-1-phenyl-2-phenylaminoethyl]benzenecarbothioamide (3ae)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 63% yield; d.r. > 20:1; R_f = 0.33 (*n*-hexane/EtOAc, 5:1); m.p. 175.5–176.3 °C; ^{1}H NMR ($CDCl_3$): δ = 3.75 (s, 3H; OCH_3), 4.75 (brs, 1H; PhN*H*), 5.30 (d, *J* = 7.3 Hz, 1H; PhNHC*H*), 6.13 (t, *J* = 7.3 Hz, 1H; C(=S)NHC*H*), 6.60 (d, *J* = 8.8 Hz, 2H; Ar), 6.67 (t, *J* = 7.3 Hz, 1H; Ar), 6.81 (t, *J* = 7.8 Hz, 2H; Ar), 7.07–7.11 (m, 3H; Ar), 7.14–7.26 (m, 6H; Ar), 7.33 (t, *J* = 7.3 Hz, 2H; Ar), 7.42 (dd, *J* = 7.8, 7.3 Hz, 1H; Ar), 7.63 (d, *J* = 7.8 Hz, 2H; Ar), 8.44 ppm (d, *J* = 7.3 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 55.4 (CH_3), 57.6, 63.7 (CH), 110.8, 114.0, 118.3, 120.8, 126.7, 126.9, 127.5, 127.7, 128.3, 128.5, 128.7, 128.9, 129.2, 131.1, 137.6, 142.1, 146.9, 156.9 (Ar), 199.4 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3334, 3292, 2929, 2854, 1505, 1484, 1455, 1379, 1292, 1233, 1033, 818, 775, 725, 699 cm^{-1}; MS (FAB): *m/z*: 439 $[M+H]^+$; HRMS (FAB): *m/z* calcd for $C_{28}H_{27}N_2OS$: 439.1844 $[M+H]^+$; found: 439.1859.

***N*-[3-Methyl-1-phenyl-2-(phenylamino)butyl]benzenecarbothioamide (mixture of diastereomers) (3af)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 10:1; R_f = 0.18). Yellow solid; 67% yield; d.r. = 1:1; ^{1}H NMR ($CDCl_3$): δ = 0.89 (d, *J* = 6.8 Hz, 3H; CH_3), 1.05 (d, *J* = 6.8 Hz, 3H; CH_3), 1.11 (d, *J* = 6.8 Hz, 3H; CH_3), 1.29 (d, *J* = 6.8 Hz, 3H; CH_3), 1.50 (dsept, *J* = 6.8, 2.4 Hz, 1H; CH_3CH), 1.82 (dsept, *J* = 6.8, 2.9 Hz, 1H; CH_3CH), 3.45 (d, *J* = 9.3 Hz, 1H; PhNHC*H*), 3.88–3.95 (m, 2H; PhNHC*H*, PhN*H*), 4.05 (brs, 1H; PHN*H*), 6.16–6.20 (m, 2H; C(=S)NHC*H*), 6.67 (d, *J* = 7.8 Hz, 2H; Ar), 6.72–6.78 (m, 4H; Ar), 7.14–7.51 (m, 22H; Ar), 7.60 (d, *J* = 7.8 Hz, 2H; Ar), 7.88 (d, *J* = 8.3 Hz, 1H; C(=S)N*H*), 8.40 ppm (d, *J* = 7.3 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 15.9, 19.9, 20.5, 20.8 (CH_3), 29.6, 32.1 (CH_3CH), 61.2, 62.3, 63.0, 64.9 (NHCH), 112.9, 113.3, 117.9, 118.1, 126.5, 126.6, 127.5, 128.21, 128.24, 128.25, 128.27, 128.4, 128.8, 129.2, 129.6, 129.8, 130.7, 131.0, 136.7, 139.2, 141.7, 142.1, 149.8, 149.5 (Ar), 197.6, 199.6 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3389, 3362, 3059, 3030, 2959, 2930, 1598, 1507, 1448, 1377, 1310, 1278, 1248, 1183, 1151, 1068, 1029, 944, 922, 870, 769, 750, 695, 652, 565 cm^{-1}; MS (EI): *m/z*: 374 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{24}H_{26}N_2S$: 374.1817 $[M]^+$; found: 374.1814.

***N*-[3,3-Dimethyl-1-phenyl-2-(phenylamino)butyl]benzenecarbothioamide (3ag)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 10:1; R_f = 0.33). Yellow solid; 91% yield; d.r. > 20:1; m.p. 134.9–135.8 °C; ^{1}H NMR ($CDCl_3$): δ = 1.09 (s, 9H; CH_3), 3.53 (brs, 1H; PhNHC*H*), 3.79 (brs, 1H; PhN*H*), 6.20 (dd, *J* = 8.8, 2.1 Hz, 1H; C(=S)NHC*H*), 6.25 (d, *J* = 7.8 Hz, 2H; Ar), 6.68 (t, *J* = 7.3 Hz, 1H; Ar), 7.00 (dd, *J* = 8.3, 7.6 Hz, 2H; Ar), 7.28–7.34 (m, 7H; Ar), 7.44 (dd, *J* = 7.6, 7.1 Hz, 1H; Ar), 7.66 (d, *J* = 8.3 Hz, 2H; Ar), 8.55 ppm (d, *J* = 8.8 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 27.0 (CH_3), 36.9 ((CH_3)$_3C$), 58.2, 70.7 (CH), 114.1, 118.8, 126.5, 126.6, 127.6, 128.6, 129.1, 129.3, 131.0, 141.7, 142.2, 149.0 (Ar), 197.9 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3337, 2958, 1601, 1496, 1478, 1370, 1333, 1312, 1300, 1247, 1233, 1071, 1031, 981, 917, 744, 693 cm^{-1}; MS (FAB): *m/z*: 389 $[M+H]^+$; HRMS (FAB): *m/z* calcd for $C_{25}H_{29}N_2S$: 389.2051 $[M+H]^+$; found: 389.2051.

***N*-[2-(4-Methoxyphenylamino)-1,2-diphenylethyl]benzenecarbothioamide (3ah)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 78% yield; d.r. = 9:1; R_f = 0.25 (*n*-hexane/EtOAc, 5:1); m.p. 180.5–181.3 °C; ^{1}H NMR ($CDCl_3$, major isomer): δ = 3.68 (s, 3H; OCH_3), 4.35 (brs, 1H; ArN*H*), 4.92 (d, *J* = 7.3 Hz, 1H; ArNHC*H*), 6.08 (dd, *J* = 7.8, 7.3 Hz, 1H; C(=S)NHC*H*), 6.52 (d, *J* = 8.8 Hz, 2H; Ar), 6.67 (d, *J* = 8.8 Hz, 2H; Ar), 7.14–7.48 (m, 13H; Ar), 7.66 (d, *J* = 6.8 Hz, 2H; Ar), 8.20 ppm (d, *J* = 7.8 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$, major isomer): δ = 55.6 (CH_3), 63.3, 64.7 (CH), 114.7, 115.5, 126.6, 127.45, 125.47, 127.8, 128.1, 128.50, 128.52, 128.8, 131.2, 137.1, 139.3, 140.5, 141.9, 152.6 (Ar), 199.4 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3394, 3290, 3028, 2838, 2358, 1602, 1507, 1496, 1448, 1385, 1316, 1244, 1230, 955, 752, 694 cm^{-1}; MS (FAB): *m/z*: 439 $[M+H]^+$; HRMS (FAB): *m/z* calcd for $C_{28}H_{27}N_2OS$: 439.1844 $[M+H]^+$; found: 439.1840.

***N*-[2-(4-Trifluoromethylphenylamino)-1,2-diphenylethyl]benzenecarbothioamide (mixture of diastereomers) (3ai)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f = 0.35). Yellow solid; 76% yield; d.r. = 2:3; ^{1}H NMR ($CDCl_3$): δ = 5.01–5.06 (m, 1H; ArNHC*H*), 5.02 (d, *J* = 7.3 Hz, 1.5H; ArN*H*), 5.23 (dd, *J* = 7.3, 3.4 Hz, 1.5H; ArNHC*H*), 5.57 (d, *J* = 6.3 Hz, 1H; ArN*H*), 6.22 (dd, *J* = 8.8, 8.3 Hz, 1H; C(=S)NHC*H*), 6.40 (dd, *J* = 8.3, 3.4 Hz, 1.5H; C(=S)NHC*H*), 6.55–6.59 (m, 5H; Ar), 6.98–7.00 (m, 3H; Ar), 7.09–7.14 (m, 7H; Ar), 7.18–7.20 (m, 4H; Ar), 7.26–7.45 (m, 23.5H; Ar), 7.61 (d, *J* = 8.3 Hz, 2H; Ar), 7.68 (d, *J* = 8.3 Hz, 3H; Ar), 8.17–8.22 (brs, 1H; C(=S)N*H*), 8.17–8.22 ppm (brs, 1.5H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 61.3, 62.7, 63.6, 64.5 (CH), 112.7, 113.3 (Ar), 119.1 (q, *J* = 33.1 Hz; *C*CF_3), 119.9 (q, *J* = 33.1 Hz; *C*CF_3), 124.7 (q, *J* = 271.3 Hz; CF_3), 124.8 (q, *J* = 270.5 Hz; CF_3), 126.48 (q, *J* = 4.1 Hz; *C*CCF_3), 126.53 (q, *J* = 4.1 Hz; *C*CCF_3), 126.65, 126.68, 127.2, 127.3, 127.5, 127.8, 128.0, 128.2, 128.39, 128.49, 128.51, 128.55, 128.63, 128.67, 128.70, 128.9, 131.4, 131.5, 135.3, 136.5, 137.1, 138.5, 141.5, 141.7, 149.1, 149.3 (Ar), 199.5, 200.3 ppm (C=S); ^{19}F NMR ($CDCl_3$): δ = −61.6, −61.5 ppm; IR (KBr): $\tilde{\nu}$ = 3374, 3060, 3030, 1703, 1616, 1530, 1484, 1450, 1367, 1322, 1278, 1109, 1064, 825, 768, 698 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{23}F_3N_2S$: C 70.57, H 4.86, N 5.88; found: C 70.74, H 4.85, N 5.86.

***N*-[2-(4-Bromophenylamino)-1,2-diphenylethyl]benzenecarbothioamide (mixture of diastereomers) (3aj)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 80% yield; d.r. = 3:1; R_f = 0.34 (*n*-hexane/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$, major isomer): δ = 4.95 (d, *J* = 8.3 Hz, 1H; ArNHC*H*), 4.96 (brs, 1H; ArN*H*), 6.15 (t, *J* = 8.3 Hz, 1H; C(=S)NHC*H*), 6.43 (d, *J* = 8.8 Hz, 2H; Ar), 7.09–7.14 (m, 6H; Ar), 7.19–7.22 (m, 3H; Ar), 7.27–7.29 (m, 3H; Ar), 7.35 (dd, *J* = 8.3, 6.8 Hz, 2H; Ar), 7.45 (t, *J* = 7.3 Hz, 1H; Ar), 7.62 (d, *J* = 7.8 Hz, 2H; Ar), 8.00 ppm (d, *J* = 8.3 Hz, 1H; C(=S)NH); ^{13}C NMR ($CDCl_3$, major isomer): δ = 62.8, 64.5 (CH), 109.7, 115.3, 126.6, 127.5, 127.7, 128.0, 128.48, 128.52, 128.6, 128.9, 131.4, 131.9, 136.6, 138.7, 141.8, 145.6 (Ar), 199.9 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3354, 3286, 2925, 1593, 1478, 1453, 1380, 1311, 1251, 1065, 955, 816, 769, 697, 643, 585, 512 cm^{-1}; MS (FAB): *m/z*: 487 (51) $[M(^{79}Br)+H]^+$, 489 (49) $[M(^{81}Br)+H]^+$; HRMS (EI): *m/z* calcd for $C_{27}H_{23}BrN_2S$: 486.0765 $[M]^+$; found: 486.0762.

***N*-[2-(2-Methoxyphenylamino)-1,2-diphenylethyl]benzenecarbothioamide (mixture of diastereomers) (3ak)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f = 0.45). Yellow solid; 83% yield; d.r. = 1:1; ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3H; OCH_3), 3.88 (s, 3H; OCH_3), 4.97–5.03 (m, 2H; ArN*H*, PhC*H*), 5.15 (brs, 1H; ArN*H*), 5.28 (dd, *J* = 9.3, 2.9 Hz, 1H; PhC*H*), 6.06 (dd, *J* = 7.8, 7.1 Hz, 1H; C(=S)NHC*H*), 6.25 (dd, *J* = 7.8, 3.7 Hz, 1H; C(=S)NHC*H*), 6.47 (dd, *J* = 7.4, 1.8 Hz, 1H; Ar), 6.51 (dd, *J* = 7.2, 2.1 Hz, 1H; Ar), 6.67–6.81 (m, 6H; Ar), 6.97–7.51 (m, 26H; Ar), 7.71 (d, *J* = 7.3 Hz, 2H; Ar), 7.78 (d, *J* = 7.3 Hz, 2H; Ar), 8.29 (d, *J* = 7.1 Hz, 1H; C(=S)N*H*), 8.62 ppm (d, *J* = 7.8 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 55.5, 55.6 (CH_3), 60.5, 62.4, 64.2, 64.7 (CH), 109.7, 109.7, 111.9, 112.3, 117.8, 118.1, 121.1, 121.2, 126.8, 126.8, 127.1, 127.55, 127.69, 127.73, 127.77, 127.9, 128.1, 128.35, 128.48, 128.52, 128.58, 128.62-(3C), 131.18, 131.24, 135.3, 136.2, 136.6, 137.3, 138.2, 139.3, 141.9, 142.1, 147.4, 147.5 (Ar), 198.7, 199.4 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3338, 3288, 2931, 2831, 1601, 1509, 1480, 1456, 1430, 1375, 1327, 1250, 1225, 1177, 1126, 1065, 1050, 1028, 957, 853, 772, 749, 736, 699, 645, 591 cm^{-1}; MS (FAB): *m/z*: 439 $[M+H]^+$; HRMS (FAB): *m/z* calcd for $C_{28}H_{27}N_2OS$: 439.1844 $[M+H]^+$; found: 439.1859.

***N*-(1,2-Diphenyl-2-phenylaminoethyl)-4-methoxybenzenecarbothioamide (3ba)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-

hexane. Yellow solid; 66% yield; d.r. > 20:1; R_f = 0.28 (*n*-hexane/EtOAc, 5:1); m.p. 169.5–170.1 °C; ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3H; OC*H*$_3$), 4.81 (brs, 1H; PhN*H*) *J* = 4.98 (d, *J* = 8.3 Hz, 1H; PhNHC*H*), 6.14 (dd, *J* = 8.3, 7.8 Hz, 1H; C(=S)NHC*H*), 6.56 (d, *J* = 8.8 Hz, 2H; Ar), 6.66 (t, *J* = 7.3 Hz, 1H; Ar), 6.84 (d, *J* = 8.8 Hz, 2H; Ar), 7.08 (dd, *J* = 8.3, 7.8 Hz, 2H; Ar), 7.13 (dd, *J* = 7.3, 2.9 Hz, 2H; Ar), 7.19–7.29 (m, 6H; Ar), 7.39 (d, *J* = 4.4 Hz, 2H; Ar), 7.66 (d, *J* = 8.8 Hz, 2H; Ar), 8.02 ppm (d, *J* = 7.8 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 55.5 (CH_3), 62.8, 64.6 (CH), 113.7, 113.8, 118.1, 127.5, 127.6, 127.7, 128.2, 128.4, 128.5, 128.7, 129.2, 134.1, 137.2, 139.3, 146.7, 162.3 (Ar), 198.5 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3356, 2360, 1714, 1604, 1503, 1455, 1372, 1310, 1260, 1179, 1029, 943, 833, 748, 698, 525 cm^{-1}; MS (FAB): *m*/*z*: 439 [*M*+H]$^+$; HRMS (FAB): *m*/*z* calcd for $C_{28}H_{27}N_2OS$: 439.1844 [*M*+H]$^+$; found: 439.1828.

***N*-[1-Phenyl-2-phenylamino-2-(4-trifluoromethylphenyl)ethyl]-4-methoxybenzenecarbothioamide (3bb)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 68% yield; d.r. = 19:1; R_f = 0.23 (*n*-hexane/EtOAc, 5:1); ^{1}H NMR (CD_3CN): δ = 3.81 (s, 3H; OCH_3), 5.16 (dd, *J* = 9.6, 8.6 Hz, 1H; PhNHC*H*), 5.55 (d, *J* = 8.6 Hz, 1H; PhN*H*), 5.94 (dd, *J* = 9.6, 7.3 Hz, 1H; C(=S)NHC*H*), 6.57–6.62 (m, 3H; Ar), 6.92 (d, *J* = 8.8 Hz, 2H; Ar), 7.04 (dd, *J* = 8.8, 7.3 Hz, 2H; Ar), 7.21 (s, 5H; Ar), 7.38 (d, *J* = 8.3 Hz, 2H; Ar), 7.47 (d, *J* = 8.3 Hz, 2H; Ar), 7.76 (d, *J* = 9.3 Hz, 2H; Ar), 9.28 ppm (d, *J* = 7.3 Hz, 1H; C(=S)NH); ^{13}C NMR ($CDCl_3$): δ = 55.4 (CH_3), 63.0, 64.6 (CH), 113.6, 113.8, 118.3 (Ar), 124.4 (q, *J* = 272.1 Hz; CF_3), 125.3 (q, *J* = 4.1 Hz; *C*CF_3), 127.7, 128.0, 128.6 (2C), 129.1, 129.3, 129.9 (q, *J* = 32.3 Hz; *C*CF_3), 133.9, 136.8, 144.0, 146.4, 162.6 (Ar), 199.0 ppm (C=S); ^{19}F NMR ($CDCl_3$): δ = −63.3 ppm; IR (KBr): $\tilde{\nu}$ = 3369, 3029, 1603, 1497, 1420, 1326, 1252, 1176, 1125, 1068, 1019, 957, 842, 751, 700, 417, 407 cm^{-1}; MS (EI): *m*/*z*: 472 [*M*−H_2S]$^+$; elemental analysis calcd (%) for $C_{29}H_{25}F_3N_2OS$: C 68.76, H 4.97, N 5.53; found: C 68.98, H 5.27, N 5.39.

***N*-[2-(4-Methoxyphenyl)-1-phenyl-2-phenylaminoethyl]-4-methoxybenzenecarbothioamide (mixture of diastereomers) (3bc)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane . Yellow solid; 81% yield; d.r. = 4:1; R_f = 0.18 (*n*-hexane/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$, major isomer): δ = 3.74 (s, 3H; OCH_3), 3.82 (s, 3H; OCH_3), 4.76 (brs, 1H; PhN*H*), 4.94 (d, *J* = 7.8 Hz, 1H; PhNHC*H*), 6.10 (dd, *J* = 8.3, 7.8 Hz, 1H; C(=S)NHC*H*), 6.57 (d, *J* = 7.8 Hz, 2H; Ar), 6.66 (t, *J* = 7.3 Hz, 1H; Ar), 6.76 (d, *J* = 8.8 Hz, 2H; Ar), 6.85 (d, *J* = 8.8 Hz, 2H; Ar), 6.96- 6.99 (m, 1H; Ar), 7.06–7.14 (m, 5H; Ar), 7.25–7.29 (m, 3H; Ar), 7.66 (d, *J* = 8.8 Hz, 2H; Ar), 8.01 ppm (d, *J* = 7.8 Hz, 1H; NH); ^{13}C NMR ($CDCl_3$, major isomer): δ = 55.1, 55.5 (CH_3), 62.8, 64.6 (CH), 113.7, 113.80, 113.82, 118.0, 127.7, 128.1, 128.5, 128.6, 128.7, 129.2, 131.2, 134.1, 137.3, 146.7, 159.0, 162.3 (Ar), 198.3 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3361, 2834, 1603, 1492, 1378, 1305, 1252, 1177, 1029, 834, 752, 696, 425 cm^{-1}; MS (EI): *m*/*z*: 434 [*M*−H_2S]$^+$; elemental analysis calcd (%) for $C_{29}H_{28}N_2O_2S$: C 74.33, H 6.02, N 5.98; found: C 74.28, H 6.09, N 5.92.

***N*-[1-(4-Methoxyphenyl)-2-phenyl-2-phenylaminoethyl]benzenecarbothioamide (3ca)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane. Yellow solid; 84% yield; d.r. = 13:1; R_f = 0.33 (*n*-hexane/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$, major isomer): δ = 3.77 (s, 3H; OCH_3), 4.88 (brs>, 1H; PhN*H*), 4.96 (d, *J* = 7.8 Hz, 1H; PhNHC*H*), 6.08 (dd, *J* = 8.6, 7.8 Hz, 1H; C(=S)NHC*H*), 6.56 (d, *J* = 8.3 Hz, 2H; Ar), 6.66 (t, *J* = 7.3 Hz, 1H; Ar), 6.81 (d, *J* = 8.8 Hz, 2H; Ar), 7.04–7.10 (m, 4H; Ar), 7.18–7.26 (m, 5H; Ar), 7.34 (dd, *J* = 7.8, 7.3 Hz, 2H; Ar), 7.44 (t, *J* = 7.3 Hz, 1H; Ar), 7.62 (d, *J* = 7.3 Hz, 2H; Ar), 8.03 ppm (d, *J* = 8.6 Hz, 1H; NH); ^{13}C NMR ($CDCl_3$, major isomer): δ = 55.2 (OCH_3), 62.0, 64.7 (CH), 113.86, 113.88, 118.1, 126.6, 127.7, 128.2, 128.55, 128.60, 128.8, 129.2, 131.1, 131.2, 137.1, 141.9, 146.7, 159.0 (Ar) 199.5 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3329, 3291, 2925, 2359, 1602, 1507, 697, 460 cm^{-1}; MS (EI): *m*/*z*: 438 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{28}H_{26}N_2OS$: 438.1766 [*M*]$^+$; found: 438.1736.

***N*-[1-(4-Methoxyphenyl)-2-phenylamino-2-(4-trifluoromethylphenyl)ethyl]benzene-carbothioamide (mixture of diastereomers) (3cb)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 3:1; R_f = 0.48). Yellow solid; 78% yield; d.r. = 3:1; ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 9H; OCH_3), 3.79 (s, 3H; OCH_3), 4.42 (brs, 1H; PhN*H*), 5.07 (d, *J* = 8.8 Hz, 3H; PhNHC*H*), 5.09 (brs, 3H; PhN*H*), 5.32 (brs, 1H; PhNHC*H*), 6.10 (dd, *J* = 8.8, 8.3 Hz, 3H; C(=S)NHC*H*), 6.24 (dd, *J* = 8.3, 2.9 Hz, 1H; C(=S)NHC*H*), 6.55 (d, *J* = 8.3 Hz, 6H; Ar), 6.60 (d, *J* = 8.3 Hz, 2H; Ar), 6.68 (t, *J* = 7.3 Hz, 3H; Ar), 6.82–6.90 (m, 10H; Ar), 7.05–7.14 (m, 14H; Ar), 7.27–7.40 (m, 17H; Ar), 7.43–7.49 (m, 10H; Ar), 7.54 (d, *J* = 7.8 Hz, 2H; Ar), 7.63 (d, *J* = 7.8 Hz, 6H; Ar), 7.71 (d, *J* = 7.3 Hz, 2H; Ar), 8.07 (d, *J* = 8.3 Hz, 3H; C(=S)N*H*), 8.38 ppm (d, *J* = 8.3 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ = 55.1 (2C; OCH_3), 60.3, 62.6, 63.3, 64.1 (CH), 113.6, 114.1, 114.3, 114.4, 118.2 119.0 (Ar), 124.0 (q, *J* = 272.9 Hz; CF_3), 125.3 (q, *J* = 4.1 Hz; *C*CF_3), 125.4 (q, *J* = 4.1 Hz; *C*CF_3), 128.3 (q, *J* = 272.1 Hz; CF_3), 126.7 (2C), 127.6, 128.0, 128.49, 128.54, 128.58, 128.62, 128.9, 129.3, 129.4 (Ar), 129.8 (q, *J* = 32.3 Hz; *C*CF_3), 130.0 (q, *J* = 32.3 Hz; *C*CF_3), 131.4 (2C), 141.6, 141.7, 142.8, 144.0, 146.0, 146.3, 159.55, 159.57 (Ar), 198.9, 200.0 ppm (C=S); ^{19}F NMR ($CDCl_3$): δ = −62.80, −62.77 ppm; IR (KBr): $\tilde{\nu}$ = 3351, 2360, 1602, 1512, 1325, 1250, 1164, 1126, 1068, 1026, 842, 756, 723, 698, 419 cm^{-1}; MS (EI): *m*/*z*: 506 [*M*]$^+$; HRMS (FAB): *m*/*z* calcd for $C_{29}H_{24}F_3N_2OS$: 507.1718 [*M*+H]$^+$; found: 507.1735.

***N*-[1,2-Bis(4-methoxyphenyl)-2-(phenylamino)ethyl]benzenecarbothioamide (mixture of diastereomers) (3cc)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f = 0.38). Yellow solid; 74% yield; d.r. = 4:1; ^{1}H NMR ($CDCl_3$, major isomer): δ = 3.74 (s, 3H; OCH_3), 3.77 (s, 3H; OCH_3), 4.71 (brs, 1H; PhN*H*), 4.94 (d, *J* = 7.8 Hz, 1H; PhNHC*H*), 6.03 (dd, *J* = 7.8, 7.3 Hz, 1H; C(=S)NHC*H*), 6.56–6.60 (m, 2H; Ar), 6.65 (t, *J* = 7.3 Hz, 1H; Ar), 6.76 (d, *J* = 8.3 Hz, 2H; Ar), 6.81 (d, *J* = 8.8 Hz, 2H; Ar), 7.04 (d, *J* = 8.8 Hz, 2H; Ar), 7.07–7.09 (m, 4H; Ar), 7.33 (dd, *J* = 7.8, 7.3 Hz, 2H; Ar), 7.43 (t, *J* = 7.3 Hz, 1H; Ar), 7.62 (d, *J* = 8.3 Hz, 2H; Ar), 8.01 ppm (d, *J* = 7.3 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$, major isomer): δ = 55.06, 55.14 (CH_3), 61.6, 64.1 (CH), 113.8, 113.9, 114.1, 114.4, 117.9, 126.7, 128.5, 128.7, 128.9, 129.0, 129.2, 131.2, 141.9, 146.7, 159.0, 159.3 (Ar), 199.4 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3350, 3277, 3001, 2955, 2930, 2894, 2835, 1604, 1587, 1513, 1481, 1461, 1448, 1377, 1305, 1278, 1249, 1179, 1034, 955, 911, 830, 770, 753, 727, 694, 647 cm^{-1}; elemental analysis calcd (%)for $C_{29}H_{28}N_2O_2S$: C 74.33, H 6.02, N 5.98; found: C 74.16, H 6.05, N 5.96.

***N*-(1,2-Diphenyl-2-phenylaminoethyl)-2,2-dimethylpropanethioamide (mixture of diastereomers) (3da)**: Purified by recrystallization from a solution in CH_2Cl_2 and *n*-hexane . Yellow solid; 62% yield; d.r. = 2:3; R_f = 0.55 (*n*-hexane/EtOAc, 5:1); ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 9H; CH_3), 1.34 (s, 13.5H; CH_3), 4.48 (brs, 1.5H; PhN*H*), 4.68 (brs, 1H; PhN*H*), 4.89 (d, *J* = 7.3 Hz, 1H; PhNHC*H*), 5.07 (brs, 1.5H; PhNHC*H*), 6.09 (dd, *J* = 7.8, 7.3 Hz, 1H; C(=S)NHC*H*), 6.26 (dd, *J* = 8.3, 3.4 Hz, 1.5H; C(=S)NHC*H*), 6.53 (d, *J* = 8.8 Hz, 2H; Ar), 6.56 (d, *J* = 8.3 Hz, 3H; Ar), 6.67 (t, *J* = 7.3 Hz, 1H; Ar), 6.70 (t, *J* = 7.3 Hz, 1.5H; Ar), 6.87–6.89 (m, 3H; Ar), 7.06–7.28 (m, 27H; Ar), 7.91 (d, *J* = 6.8 Hz, 1H; C(=S)NH), 8.15 ppm (d, *J* = 7.3 Hz, 1.5H; C(=S)NH); ^{13}C NMR ($CDCl_3$): δ = 29.8, 29.9 (C(*C*H$_3$)$_3$), 44.7, 44.8 (*C*(CH$_3$)$_3$), 61.7, 62.5, 62.9, 63.6 (CH), 113.8, 114.3 118.1, 118.6, 127.1, 127.3, 127.5, 127.7, 127.8, 128.0 128.1, 128.36, 128.38, 128.4, 128.7, 128.8, 129.1, 129.2, 135.8, 136.9, 137.8, 139.2, 146.5, 146.7 (Ar), 213.4, 213.9 ppm (C=S); IR (KBr): $\tilde{\nu}$ = 3347, 3024, 2966, 1601, 1510, 1454, 1380, 1359, 1318, 1261, 1074, 1027, 1003, 822, 747, 699 cm^{-1}; MS (EI): *m*/*z*: 389 [*M*+H]$^+$; HRMS (EI): *m*/*z* calcd for $C_{25}H_{29}N_2S$: 389.2051 [*M*+H]$^+$; found: 389.2043.

General procedure for the reaction between $LiAlH_4$ and diamines 3: To a solution of *N*-thioacyl-1,2-diamine **3** (0.50 mmol) in 1,4-dioxane (7 mL) was slowly added $LiAlH_4$ (0.076 g, 2.0 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred at reflux for 6 h. The reaction mixture was quenched with 15% NaOH (aq., 1 mL) and water (5 mL), filtered through a pad of Celite and then the pad was rinsed with CH_2Cl_2. The resulting mixture was extracted with CH_2Cl_2 (3×3 mL). The organic layer was washed with water (3×3 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting solid was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 10:1) to give 1,2-diamine **4** as a yellow oil.

***N*-Benzyl-1,2-*N*′-triphenylethane-1,2-diamine (4aa)**:[22] ^{1}H NMR ($CDCl_3$): δ = 1.83 (brs, 1H; CH_2N*H*), 3.45 (d, *J* = 13.4 Hz, 1H; PhC*H*H), 3.68 (d, *J* = 13.4 Hz, 1H; PhC*H*H), 3.86 (d, *J* = 6.1 Hz, 1H; CH), 4.37 (d, *J* = 6.1 Hz, 1H; CH), 5.23 (brs, 1H; PhN*H*), 6.46 (d, *J* = 7.8 Hz, 2H; Ar), 6.59 (t, *J* = 7.3 Hz, 1H; Ar), 7.02 (dd, *J* = 7.8, 7.3 Hz, 2H; Ar), 7.13–7.28 ppm (m, 15H; Ar).

***N*-benzyl-2-(4-trifluoromethylphenyl)-1-*N*′-diphenylethane-1,2-diamine (4ab)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 10:1; R_f=0.30). Yellow oil; 77% yield; ^{1}H NMR ($CDCl_3$): δ= 1.81 (br s, 1H; CH_2NH), 3.46 (d, J=13.2 Hz, 1H; PhC*H*H), 3.69 (d, J= 13.2 Hz, 1H; PhCH*H*), 3.78 (d, J=6.8 Hz, 1H; CH), 4.38 (d, J=6.8 Hz, 1H; CH), 5.35 (br s, 1H; PhN*H*), 6.44 (d, J=7.8 Hz, 2H; Ar), 6.63 (t, J= 7.3 Hz, 1H; Ar), 7.04 (t, J=7.3 Hz, 2H; Ar), 7.12–7.31 (m, 12H; Ar), 7.41 ppm (d, J=8.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=51.2 (CH_2), 63.7, 67.6 (CH), 113.8, 117.8 (Ar), 124.1 (q, J=271.8 Hz; CF_3), 125.2 (q, J=3.9 Hz; *C*CCF_3), 127.1, 127.5, 127.70, 127.73, 128.0, 128.4, 128.5, 129.0 (Ar), 129.3 (q, J=32.3 Hz; *C*CF_3), 139.7, 139.9, 145.7, 147.3 ppm (Ar); ^{19}F NMR ($CDCl_3$): δ=−62.6 ppm; IR (neat): $\tilde{\nu}$=3333, 3027, 2922, 2850, 1602, 1504, 1455, 1428, 1325, 1164, 1121, 1066, 1017, 846, 751, 698, 610 cm^{-1}; MS (FAB): *m*/*z*: 447 [*M*+H]$^+$; HRMS (EI): *m*/*z* calcd for $C_{28}H_{26}F_3N_2$: 447.2048 [*M*+H]$^+$; found: 447.2068.

***N*-Benzyl-2-(4-methoxyphenyl)-1-*N*′-diphenylthane-1,2-diamine (4ac)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 10:1; R_f=0.20). Yellow oil; 79% yield; ^{1}H NMR ($CDCl_3$): δ=1.83 (br s, 1H; CH_2NH), 3.45 (d, J=13.5 Hz, 1H; PhC*H*H), 3.68 (d, J=13.5 Hz, 1H; PhCH*H*), 3.72 (s, 3H; OCH_3), 3.82 (d, J=6.6 Hz, 1H; CH), 4.33 (d, J= 6.6 Hz, 1H; CH), 5.19 (br s, 1H; PhN*H*), 6.46 (d, J=8.8 Hz, 2H; Ar), 6.59 (t, J=7.3 Hz, 1H; Ar), 6.72 (d, J=8.8 Hz, 2H; Ar), 7.00–7.07 (m, 4H; Ar), 7.15–7.30 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ=51.1 (CH), 55.0 (CH_3), 63.7, 67.6 (CH), 113.6, 113.7, 117.1, 126.9, 127.3, 127.8, 127.9, 128.0, 128.2, 128.3, 128.9, 133.0, 140.0, 140.5, 147.7, 158.5 ppm (Ar); IR (neat): $\tilde{\nu}$=3334, 3027, 2930, 2834, 1602, 1508, 1457, 1245, 1172, 1113, 1034, 747, 693 cm^{-1}; MS (EI): *m*/*z*: 408 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{28}H_{28}N_2O$: 408.2202 [*M*]$^+$; found: 408.2204.

Oxidative-desulfurization/cyclization of compound 3aa [Eq. (3)]: *Method A*. To a solution of *N*-(1,2-diphenyl-2-phenylaminoethyl)benzenecarbothioamide (**3aa**; 0.20 g, 0.50 mmol) in THF (3 mL) was added I_2 (0.38 g, 1.5 mmol) and pyridine (0.12 mL, 1.5 mmol) at RT. The mixture was stirred at RT for 30 min. The reaction mixture was poured onto $Na_2S_2O_3$ (aq.) and extracted with CH_2Cl_2 (3×3 mL). The organic layer was washed with saturated $NaHCO_3$ (aq., 3 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 3:1, with 1% of triethylamine v/v; R_f=0.40) to give (4*R**,5*R**)-1,2,4,5-tetraphenyl-4,5-dihydro-1*H*-imidazole (*trans*-**5**; 0.12 g, 63%) as a colorless solid.

Method B. A solution of copper(II) chloride (0.013 g, 20 mol%), 2,2′-bipyridyl (0.016 g, 20 mol%), and *N*-(1,2-diphenyl-2-phenylaminoethyl)-benzenecarbothioamide (**3aa**; 0.20 g, 0.50 mmol) in DMSO (2 mL) was stirred at 80°C for 8 h under an O_2 atmosphere. The mixture was quenched with aqueous ammonia (28%) and the aqueous layer was extracted with CH_2Cl_2 (3×3 mL). The combined organic layer was washed with aqueous ammonia (28%, 3×3 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 3:1; R_f=0.41) to give (4*R**,5*R**)-1,2,4,5-tetraphenyl-4,5-dihydro-1*H*-imidazole (*trans*-**5**; 0.087 g, 46%) as a colorless solid. M.p. 165.2–165.5°C; ^{1}H NMR ($CDCl_3$): δ=4.77 (d, J= 5.9 Hz, 1H; CH), 5.11 (d, J=5.9 Hz, 1H; CH), 6.74 (d, J=7.8 Hz, 2H; Ar), 6.94 (t, J=7.3 Hz, 1H; Ar), 7.04 (dd, J=7.8, 7.3 Hz, 2H; Ar), 7.25–7.42 (m, 13H; Ar), 7.76 ppm (d, J=7.3 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=78.2, 78.3 (CH), 123.7, 124.5, 126.5, 126.6, 127.5, 127.9, 128.3, 128.80, 128.82, 129.18, 129.21, 130.4, 130.9, 143.3, 143.4, 143.7 (Ar), 163.1 ppm (C=N); MS (EI): *m*/*z*: 374 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{27}H_{24}N_2S$: 374.1783 [*M*]$^+$; found: 374.1776.

Method C [Eq. (4)]. To a solution of *N*-(1,2-diphenyl-2-phenylaminoethyl)benzenecarbothioamide (**3aa**; 0.20 g, 0.50 mmol) in DMSO (3 mL) was added aqueous NaClO (12%, 1.86 g, 3 mmol). The mixture was stirred at RT for 30 min. The reaction mixture was extracted with CH_2Cl_2 (3 mL×3). The organic layer was washed with water (3 mL×2) and brine (3 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 10:1) to give (4*R**,5*S**)-1,2,4,5-tetraphenyl-4,5-dihydro-1*H*-imidazole (*cis*-**5**; 0.12 g, 63%, R_f=0.63) and (4*R**,5*R**)-1,2,4,5-tetraphenyl-4,5-dihydro-1*H*-imidazole (*trans*-**5**; 0.037 g, 20%, R_f=0.13) as a brown oil and a colorless solid, respectively. Major isomer (*cis*-**5**): ^{1}H NMR ($CDCl_3$): δ=4.84 (d, J=6.3 Hz, 1H; CH), 5.39 (d, J=6.3 Hz, 1H; CH), 6.81 (t, J=7.3 Hz, 1H; Ar), 6.97 (d, J=7.8 Hz, 2H; Ar), 7.09 (dd, J=8.3, 7.3 Hz, 2H; Ar), 7.17–7.23 (m, 10H; Ar), 7.40–7.46 (m, 3H; Ar), 8.02 ppm (d, J=6.8 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=66.3, 67.2 (CH), 118.8, 121.4, 126.8, 127.2, 127.8, 127.9, 128.1, 128.3, 128.5, 128.76, 128.84, 131.5, 136.1, 139.6, 140.9, 149.5 (Ar), 165.7 ppm (C=N); IR (KBr): $\tilde{\nu}$=3060, 3030, 2925, 1593, 1492, 1449, 1248, 1030, 941, 908, 751, 691 cm^{-1}; MS (EI): *m*/*z*: 374 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{27}H_{24}N_2S$: 374.1783 [*M*]$^+$; found: 374.1772.

General procedure for the reaction between thioamide dianion 1a′ and aziridines 7 and 9: To a solution of *N*-benzylbenzenecarbothioamide (**1a**; 0.11 g 0.50 mmol) in THF (1 mL) was added *n*BuLi (1.6 M solution in *n*-hexane, 0.63 mL, 1.0 mmol) at 0°C. The mixture was stirred at 0°C for 5 min. A solution of aziridine **7** or **9** (0.55 mmol) in THF (1 mL) and trimethylaluminum (2.0 M solution in toluene, 0.28 mL, 0.55 mmol) was stirred at RT for 5 min before being added to the reaction mixture at 0°C and the solution was stirred at that temperature for 1 h. The reaction mixture was poured onto water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting solid was purified by column chromatography on silica gel to give a diastereomeric mixture of *N*-thioacyl-1,3-diamine **8** or **10** as a yellow solid.

***N*-[3-(4-Methylphenylsulfonylamino)-1-phenylbutyl]benzenecarbothioamide (mixture of diastereomers) (8ac)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f=0.18). Yellow solid; 99% yield; d.r.=3:2; ^{1}H NMR ($CDCl_3$): δ=1.07 (d, J=6.3 Hz, 4.5H; $CHCH_3$), 1.17 (d, J=6.3 Hz, 3H; $CHCH_3$), 1.95–2.05 (m, 1.5H; CH_3CH), 2.18–2.30 (m, 1H; CH_3CHCHH), 2.18–2.30 (m, 1.5H; CH_3CHCHH), 2.37–2.46 (m, 1H; CH_3CH), 2.37 (s, 4.5H; $C_6H_4CH_3$), 2.41 (s, 3H; $C_6H_4CH_3$), 3.21 (m, 1H; CH_3CHCHH), 3.26 (dt, 1.5H; CH_3CHCHH), 5.07 (d, J=6.8 Hz, 1.5H; SNH), 5.45 (q, J=7.3 Hz, 1H; C(=S)NHC*H*), 5.57 (d, J=6.3 Hz, 1H; SNH), 5.84 (q, J=7.3 Hz, 1.5H; C(=S)NHC*H*), 7.04 (d, J=6.3 Hz, 2H; Ar), 7.19–7.23 (m, 5.5H; Ar), 7.26–7.37 (m, 15.5H; Ar), 7.39–7.46 (m, 2.5H; Ar), 7.60 (d, J=7.8 Hz, 3H; Ar), 7.68–7.76 (m, 6.5H; Ar), 8.02 (d, J=6.8 Hz, 1H; C(=S)N*H*), 8.38 ppm (d, J= 6.8 Hz, 1.5H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ=20.6, 20.9, 21.4, 22.4 (CH_3), 41.4, 42.4 (CH_2), 47.3, 47.5, 57.1, 57.2, (CH), 126.8, 126.9, 127.09, 127.13, 127.2, 128.0, 128.3, 128.4, 128.5, 129.00, 129.02, 129.7, 129.8 (2C), 131.1, 131.3, 137.1, 137.5, 139.2, 139.4, 141.4, 141.5, 143.3, 143.5 (Ar), 198.1, 198.3 ppm (C=S); IR (KBr): $\tilde{\nu}$=3280, 3060, 3029, 2972, 2971, 1598, 1519, 1488, 1449, 1377, 1325, 1157, 1092, 815, 769, 721, 697, 665, 581, 551 cm^{-1}; MS (EI): *m*/*z*: 438 [*M*]$^+$; HRMS (EI): *m*/*z* calcd for $C_{24}H_{26}N_2O_2S_2$: 438.1436 [*M*]$^+$; found: 438.1434.

***N*-[3-(4-Methylphenylsulfonylamino)-1,4-diphenylbutyl]benzenecarbothioamide (mixture of diastereomers) (10a)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f=0.18). Yellow solid; 69% yield; d.r.=2:1. The d.r. improved slightly to 5:2 by separating by preparative HPLC that was equipped with mightysil (*n*-hexane/EtOAc, 3:1). ^{1}H NMR ($CDCl_3$): δ=2.03–2.10 (m, 1H; SNHC*H*), 2.22–2.26 (m, 2.5H; SNHC*H*), 2.28 (s, 7.5H; CH_3), 2.30 (s, 3H; CH_3), 2.33–2.40 (m, 2.5H; BnCHC*H*H), 2.33–2.40 (m, 1H; BnCHC*H*H), 2.58 (dd, J=13.9, 7.6 Hz, 2.5H; PhC*H*H), 2.74–2.80 (m, 2.5H; PhCH*H*), 2.74–2.80 (m, 1H; PhC*H*H), 2.89 (dd, J=13.7, 6.8 Hz, 1H; PhCH*H*), 3.15–3.28 (m, 1H; BnCHCH*H*), 3.15–3.28 (m, 2.5H; BnCHCH*H*), 4.77 (d, J=6.8 Hz, 2.5H; SNH), 5.29 (d, J=6.3 Hz, 1H; SNH), 5.49 (q, J=7.3 Hz, 1H; C(=S)NHC*H*), 5.90 (q, J=7.3 Hz, 2.5H; C(=S)NHC*H*), 6.73 (d, J=7.8 Hz, 5H; Ar), 6.83 (d, J=7.3 Hz, 2H; Ar), 6.93 (d, J=6.6 Hz, 2H; Ar), 6.97–7.10 (m, 17.5H; Ar), 7.13–7.19 (m, 4H; Ar), 7.23–7.32 (m, 24H; Ar), 7.34–7.41 (m, 5H; Ar), 7.67 (d, J=6.8 Hz, 2H; Ar), 7.70 (d, J=7.3 Hz, 5H; Ar), 7.88 (d, J=7.3 Hz, 1H; C(=S)N*H*), 8.31 ppm (d, J=7.3 Hz, 2.5H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ=21.4 (2C; CH_3), 39.1, 39.3, 40.0, 42.0 (CH_2), 52.4, 52.9, 56.8, 57.0 (CH), 126.7, 126.80, 126.88, 126.94, 127.07, 127.09, 128.1, 128.4, 128.56, 128.63, 128.8, 129.0, 129.08, 129.11, 129.3, 129.7, 131.3, 131.5, 136.0, 136.4, 136.5, 137.0, 138.6, 139.4, 141.3, 141.6, 143.2, 143.5 (Ar), 198.2, 198.3 ppm (C=S) (some of the aromatic peaks are overlapped); IR (KBr): $\tilde{\nu}$=3296, 3027, 2920, 1598, 1517, 1495, 1449, 1325, 1154, 1090, 1030, 953, 813, 770, 747, 721, 698, 665, 581, 549 cm^{-1}; MS (FAB): *m*/*z*: 515 [*M*+H]$^+$; HRMS (FAB): *m*/*z* calcd for $C_{30}H_{31}N_2O_2S_2$: 515.1827 [*M*+H]$^+$; found: 515.1815.

***N*-(4-Methyl-3-(4-methylphenylsulfonylamino)-1-phenylpentyl)benzenecarbothioamide (mixture of diastereomers) (10b)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f=0.15). Yellow solid; 86% yield; d.r.=7:3. The d.r. improved slightly to 5:2 by separating by preparative HPLC that was equipped with mightysil (*n*-hexane/EtOAc, 3:1). ^{1}H NMR ($CDCl_3$): δ=0.55 (d, J=6.8 Hz, 6H; CH(CH_3)$_2$), 0.71 (d, J=6.8 Hz, 15H; CH(CH_3)$_2$), 1.69–1.77 (m, 2.5H; (CH_3)$_2$C*H*), 1.93–2.01 (m, 1H; (CH_3)$_2$C*H*), 2.02–2.10 (m, 1H; SNHCHC*H*H), 2.02–2.10 (m, 2.5H; SNHCHC*H*H), 2.15–2.24 (m, 1H; SNHC*H*), 2.31 (s, 7.5H; $C_6H_4CH_3$), 2.33 (s, 3H; $C_6H_4CH_3$), 2.33–2.38 (m, 2.5H; SNHC*H*), 2.82–2.96 (m, 1H; SNHCHCH*H*), 2.82–2.96 (m, 2.5H; SNHCHCH*H*), 4.68 (d, J=7.8 Hz, 2.5H; SNH), 5.26 (q, J=7.3 Hz, 1H; C(=S)NHC*H*), 5.38 (d, J=6.3 Hz, 1H; SNH), 5.75 (q, J=7.3 Hz, 2.5H; C(=S)NHC*H*), 6.92–6.95 (m, 2H; Ar), 7.11–7.14 (m, 6H; Ar), 7.21–7.41 (m, 27H; Ar), 7.49 (d, J=8.3 Hz, 5H; Ar), 7.58 (d, J=8.3 Hz, 2H; Ar), 7.67–7.69 (m, 7H; Ar), 7.92 (d, J=7.3 Hz, 1H; C(=S)N*H*), 8.12 ppm (d, J=7.3 Hz, 2.5H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ=16.9, 17.7, 18.6, 21.4 (CH_3), 29.6, 31.7 (CH_2), 35.9, 36.6, 56.0, 56.3, 57.2, 57.6 (CH), 126.8, 126.9, 127.15 (2C), 127.21, 127.4, 128.1, 128.35, 128.44, 128.5, 129.0, 129.1, 129.6, 129.7, 131.2, 131.4, 137.0, 137.1, 139.0, 139.2, 141.3, 141.6, 143.3, 143.5 (Ar), 198.1, 198.2 ppm (C=S); IR (KBr): $\tilde{\nu}$=3289, 2932, 1598, 1518, 1487, 1449, 1323, 1157, 1092, 1029, 947, 815, 770, 697, 666, 590, 550 cm^{-1}; MS (FAB): m/z: 467 [M+H]$^+$; HRMS (FAB): m/z calcd for $C_{26}H_{31}N_2O_2S_2$: 467.1827 [M+H]$^+$; found: 467.1836.

***N*-[4,4-Dimethyl-3-(4-methylphenylsulfonylamino)-1-phenylpentyl]benzenecarbothioamide (mixture of diastereomers) (10c)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1; R_f=0.15). Yellow solid; 83% yield; d.r.=1:1; ^{1}H NMR ($CDCl_3$): δ=0.70 (s, 9H; C(CH_3)$_3$), 0.81 (s, 9H; C(CH_3)$_3$), 2.10 (ddd, J=15.1,7.1, 4.2 Hz, 1H; C*H*H), 2.30 (dt, J=15.1, 6.4 Hz, 1H; CH*H*), 2.36 (s, 3H; $C_6H_4CH_3$), 2.37 (s, 3H; $C_6H_4CH_3$), 2.43 (dt, J=15.1, 4.2 Hz, 1H; CH*H*), 2.51 (ddd, J=15.1,7.8, 4.1 Hz, 1H; C*H*H), 2.84 (ddd, J=8.1, 6.4, 4.1 Hz, 1H; SNHC*H*), 3.16 (ddd, J=9.0,7.1, 4.2 Hz, 1H; SNHC*H*), 4.87 (d, J=9.0 Hz, 1H; SNH), 5.09 (d, J=8.1 Hz, 1H; SNH), 5.62 (ddd, J=7.8, 7.1, 6.4 Hz, 1H; C(=S)NHC*H*), 5.96 (dt, J=7.8, 4.2 Hz, 1H; C(=S)NHC*H*), 7.08 (d, J=8.3 Hz, 2H; Ar), 7.20 (d, J=8.3 Hz, 2H; Ar), 7.27–7.50 (m, 18H; Ar), 7.61 (d, J=8.3 Hz, 2H; Ar), 7.84 (d, J=8.3 Hz, 2H; Ar), 7.89 (d, J=8.3 Hz, 2H; Ar), 8.73 (d, J=7.8 Hz, 1H; C(=S)N*H*), 8.83 ppm (d, J=7.1 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ=21.37, 21.39, 26.2, 26.5 (CH_3), 35.1, 35.3 (CH_2), 37.8, 38.9 (CH_3C), 57.8, 59.1, 59.3, 59.4 (CH), 126.9 (2C), 127.4, 127.1, 127.2, 127.3, 127.5, 128.0, 128.35, 128.44, 128.7, 128.9, 129.5, 129.6, 131.0, 131.3, 136.5, 137.5, 140.0, 140.2, 141.5, 141.8, 143.4, 143.5 (Ar), 198.47, 198.50 ppm (C=S); IR (KBr): $\tilde{\nu}$=3295, 2962, 1598, 1479, 1449, 1324, 1154, 1093, 1025, 957, 814, 768, 698, 665, 549 cm^{-1}; MS (FAB): m/z: 481 [M+H]$^+$; HRMS (FAB): m/z calcd for $C_{27}H_{33}N_2O_2S_2$: 481.1983 [M+H]$^+$; found: 481.1996.

***N*-[3-(4-Methylphenylsulfonylamino)-1,2-diphenylpropyl]benzenecarbothioamide (10d)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1). Yellow solid; 36% yield; d.r.>20:1. Other diastereomers of compound **10d** were obtained as a diastereomeric mixture after the major isomer had eluted (0.028 g, 11% yield, d.r.=3:2, R_f=0.23). Major isomer of **10d**: M.p. 221.5–223.2°C; ^{1}H NMR ($CDCl_3$): δ=2.36 (s, 3H; CH_3), 3.08 (dt, J=13.7, 6.8 Hz, 1H; C*H*H), 3.19 (dt, J=13.7, 6.8 Hz, 1H; CH*H*), 3.39 (dt, J=7.3, 6.8 Hz, 1H; CH_2CH), 4.82 (t, J=6.8 Hz, 1H; SNH), 6.04 (dd, J=8.8, 7.3 Hz, 1H; C(=S)NHC*H*), 6.96 (d, J=6.8 Hz, 2H; Ar), 7.09 (d, J=6.8 Hz, 2H; Ar), 7.18–7.34 (m, 13H; Ar), 7.51 (d, J=8.3 Hz, 2H; Ar), 7.58 ppm (d, J=8.8 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ=21.5 (CH_3), 45.1 (CH), 51.7 (CH_2), 60.3 (CH), 126.5, 127.1, 127.4, 128.2, 128.3, 128.5, 128.6, 128.9, 129.2, 129.8, 131.2, 136.8, 136.9, 138.4, 141.8, 143.6 (Ar), 199.0 ppm (C=S); IR (KBr): $\tilde{\nu}$=3312, 3264, 2924, 2853, 1595, 1533, 1495, 1449, 1385, 1316, 1287, 1253, 1155, 1090, 945, 836, 811, 759, 727, 697, 660 cm^{-1}; MS (FAB): m/z: 501 [M+H]$^+$; HRMS (FAB): m/z calcd for $C_{29}H_{28}N_2O_2S_2$: 501.1670 [M+H]$^+$; found: 501.1667.

***N*-[3-(4-Methylphenylsulfonylamino)-1,2-diphenylbutyl]benzenecarbothioamide (10e)**: Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 5:1). Diastereomers of *N*-[3-(4-methylphenylsulfonylamino)-1,2-diphenylbutyl]benzenecarbothioamide (**10e**) were isolated as yellow solids in 31% (0.080 g; R_f=0.35) and 37% yield (0.095 g; R_f=0.23), respectively. Minor isomer: M.p. 191.3–192.1°C; ^{1}H NMR ($CDCl_3$): δ=0.89 (d, J=6.3 Hz, 3H; CHCH_3), 2.29 (s, 3H; $C_6H_4CH_3$), 3.55 (dd, J=7.3, 2.9 Hz, 1H; CH_3CHC*H*), 3.68 (dq, J=6.3, 2.9 Hz, 1H; CH_3CH), 4.38 (brs, 1H; SN*H*), 6.33 (dd, J=8.3, 7.3 Hz, 1H; C(=S)NHC*H*), 7.05–7.43 (m, 15H; Ar), 7.55 (d, J=8.3 Hz, 2H; Ar), 7.85 (d, J=7.3 Hz, 2H; Ar), 9.03 ppm (d, J=8.3 Hz, 1H; C(=S)N*H*); ^{13}C NMR ($CDCl_3$): δ=19.2, 21.4 (CH_3), 50.1, 54.5, 60.9 (CH), 127.1, 127.2, 127.5, 127.6, 127.8, 128.5(2C), 128.6, 129.6, 129.9, 131.2, 136.5, 137.2, 139.2, 141.4, 144.0 (Ar), 197.9 ppm (C=S); IR (KBr): $\tilde{\nu}$=3303, 3060, 3029, 2922, 1598, 1520, 1494, 1450, 1374, 1325, 1158, 1091, 946, 909, 815, 761, 698, 670, 563, 550 cm^{-1}; MS (FAB): m/z: 515 [M+H]$^+$; HRMS (FAB): m/z calcd for $C_{30}H_{31}N_2O_2S_2$: 515.1827 [M+H]$^+$; found: 515.1822. Major isomer: M.p. 115.8–117.0°C; ^{1}H NMR ($CDCl_3$): δ=0.90 (d, J=6.8 Hz, 3H; CHCH_3), 2.38 (s, 3H; $C_6H_4CH_3$), 3.27 (dd, J=11.2, 2.9 Hz, 1H; CH_3CHC*H*), 3.37–3.46 (m, 1H; CH_3CH), 3.81 (d, J=10.3 Hz, 1H; SN*H*), 6.13 (dd, J=11.2, 8.8 Hz, 1H; C(=S)NHC*H*), 6.91 (d, J=8.3 Hz, 2H; Ar), 7.03 (dd, J=7.8, 7.3 Hz, 2H; Ar), 7.14–7.32 (m, 13H; Ar), 7.43 (d, J=8.8 Hz, 1H; C(=S)N*H*), 7.61 ppm (d, J=7.8 Hz, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ=21.3, 21.5 (CH_3), 49.1, 56.7, 58.7 (CH), 126.3, 127.4, 128.18, 128.21, 128.24, 128.3, 128.8, 129.1, 129.8, 129.9, 130.7, 135.3, 137.7, 139.0, 142.3, 143.7 (Ar), 198.0 ppm (C=S); IR (KBr): $\tilde{\nu}$=3294, 2924, 1599, 1496, 1449, 1337, 1158, 1092, 948, 814, 755, 702, 670, 550 cm^{-1}; MS (FAB): m/z: 515 [M+H]$^+$; HRMS (FAB): m/z calcd for $C_{30}H_{31}N_2O_2S_2$: 515.1827 [M+H]$^+$; found: 515.1837.

X-ray structure analysis: X-ray diffraction of compounds **3aa**, *trans*-**5**, and **10d** was performed on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ=0.71069 Å). Reflection data were collected at 133–293 K with a Rigaku XR-TCS-2–050 temperature controller. X-ray absorptions were corrected by using numerical methods based on the crystal shape.[23] Single crystals that were suitable for X-ray diffraction were obtained by the slow diffusion of *n*-hexane into a solution of the compounds in CH_2Cl_2 at RT in air. The single crystals were cut from the grown crystals and mounted on a MicroMount (MiTeGen, LLC). The structures were solved and refined by using direct methods with SHELX-97[24] and the Yadokari-XG crystallographic software package from the Molecular Structure Corporation.[25] Hydrogen atoms on carbon atoms were placed at idealized positions and treated as riding atoms with C–H distances in the range 95–100 pm. Crystal data and measurement description are summarized in the Supporting Information, Table S1.

CCDC-903304 (**3aa**), CCDC-903305 (*trans*-**5**), and CCDC-903306 (**10d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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