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Decarboxylation of isatoic anhydrides with disulfides: an efficient and general synthesis of *S*-aryl 2-aminobenzothioate derivatives

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ABSTRACT

The decarboxylation of isatoic anhydrides with disulfides was realized in the presence of sodium dithionite, leading to *S*-aryl 2-aminobenzothioate derivatives in moderate to excellent yields. Furthermore, the decarboxylation of diphenyldiselenide with isatoic anhydrides was also examined. It was noted that unexpected 2-(dimethylamino)-4*H*-benzo[*d*][1,3]thiazin-4-one was obtained using tetramethylthiuram disulfide as sulfur source.

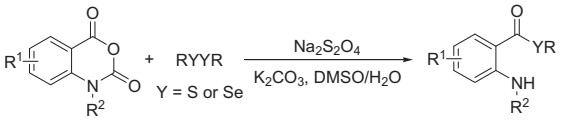
1. Introduction

In synthetic organic chemistry, the impact of organo-sulfur chemistry has led to a resurgence of interest in this field since sulfur-containing compounds can serve as important auxiliary functions in synthetic sequences. Thioesters, an important class of sulfur-containing compounds, are widely presented in a great number of biologically active compounds and natural products.[1] In recent years, there are a large amount of reports on the synthesis of bioactive proteins thioesters by native chemical ligation (NCL).[2] In addition, these compounds have been used as acylation agents in synthetic chemistry.[3] Therefore, considerable efforts have been made in the development of efficient strategies for the construction of thioesters.[4] However, the preparation of *S*-aryl 2-aminobenzothioate derivatives has been scarcely explored.[5] Recently, Temperini and co-workers developed synthesis of *S*-aryl 2-aminobenzothioate derivatives by the acylation of the odorous, unstable and highly toxic thiols.[6] However, this method usually suffer from one or more limitations, such as very limited substrate scope[7] and long reaction times (10–24 h). Moreover, the use of highly volatile and unpleasant smelling free thiols leads to serious environmental, safety problems and also limits the use of these methods, especially in large-scale preparations. Besides the drawback of these methodologies are associated with undesirable side reactions owing to the oxidation of thiols and certain thiols are difficult to prepare. In this vein, developing an efficient and general method for the synthesis of *S*-aryl 2-aminobenzothioates still remain in great demand.

As part of the continuing efforts in our laboratory towards the development of new methodologies using disulfides as sulfur sources[8] or isatoic anhydrides as reaction partners,[9] we herein report a new strategy for the preparation of *S*-aryl 2-aminobenzothioates by the decarboxylation of isatoic anhydrides with disulfides[10] under mild conditions (Scheme 1). The present protocol could be a synthetically alternative route, that is, environmentally friendly, avoiding the use of odorous thiols.

2. Results and discussion

The reaction between isatoic anhydride (**1a**) and diphenyl disulfide (**2a**) was chosen as a model reaction to screen the optimal



Scheme 1.

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reaction conditions and the results were listed in Table 1. Our investigation began with an attempted the model reaction in the absence of reductant, but no target product was detected (Table 1, entry 1). The yield of the target product *S*-phenyl 2-aminobenzothioate (**3aa**) was enhanced to some extent when the reaction was conducted in the presence of reductant (e.g., $NaHSO_3$, Na_2SO_3, $Na_2S_2O_3\cdot 5H_2O$, $Na_2S_2O_5$, $Na_2S_2O_4$ and Rongalite[11]). Among these reductants used, the reaction afforded **3aa** in the highest yield using $Na_2S_2O_4$ (65% yield, Table 1, entry 4). It is noteworthy that the model reaction gave **3aa** in 46% yield accompanied by the formation of 1,2-dihydrobenzo[*d*][1,3]thiazin-4-one (**4**)[12] in the presence of Rongalite (Fig. 1).

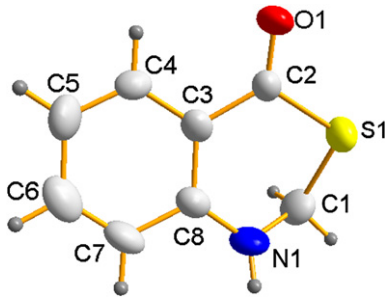
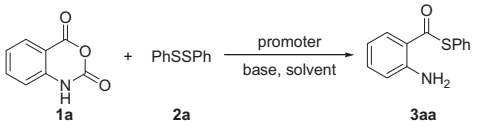


Fig. 1. X-ray analysis of compound **4**.

Table 1
Screening for optimal reaction conditions[a]



Entry	Reductant (equiv)	Solvent	Base	Yield[b] (%)
1	—	DMF	K_2CO_3	0
2	Na_2SO_3 (3)	DMF	K_2CO_3	Trace
3	$NaHSO_3$ (3)	DMF	K_2CO_3	Trace
4	$Na_2S_2O_4$ (3)	DMF	K_2CO_3	65
5	$Na_2S_2O_5$ (3)	DMF	K_2CO_3	47
6	$Na_2S_2O_3\cdot 5H_2O$ (3)	DMF	K_2CO_3	21
7	Rongalite (3)	DMF	K_2CO_3	46
8	$Na_2S_2O_4$ (1.5)	DMF	K_2CO_3	36
9	$Na_2S_2O_4$ (2.5)	DMF	K_2CO_3	47
10	$Na_2S_2O_4$ (3.5)	DMF	K_2CO_3	70
11	$Na_2S_2O_4$ (4.5)	DMF	K_2CO_3	76
12	$Na_2S_2O_4$ (5.5)	DMF	K_2CO_3	73
13	$Na_2S_2O_4$ (4.5)	CH_3CN	K_2CO_3	26
14	$Na_2S_2O_4$ (4.5)	CH_2Cl_2	K_2CO_3	0
15	$Na_2S_2O_4$ (4.5)	NMP[c]	K_2CO_3	76
16	$Na_2S_2O_4$ (4.5)	THF	K_2CO_3	0
17	$Na_2S_2O_4$ (4.5)	HMPA[d]	K_2CO_3	32
18	$Na_2S_2O_4$ (4.5)	DMSO	K_2CO_3	81
19	$Na_2S_2O_4$ (4.5)	DMSO	NaOH	75
20	$Na_2S_2O_4$ (4.5)	DMSO	$NaHCO_3$	53
21	$Na_2S_2O_4$ (4.5)	DMSO	Et_3N	45
22	$Na_2S_2O_4$ (4.5)	DMSO	K_3PO_4	51
23	$Na_2S_2O_4$ (4.5)	DMSO	Cs_2CO_3	64
24	$Na_2S_2O_4$ (4.5)	DMSO	—	0
25	$Na_2S_2O_4$ (4.5)	DMSO	K_2CO_3	86,[e] 80,[f] 65[g]

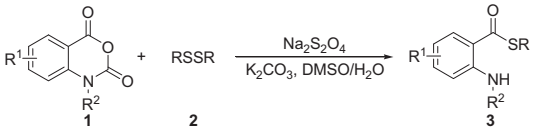
[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), base (0.6 mmol), reductant loading based on **2a**, undried solvent (2 mL) 50 °C, 30 min.
[b] Isolated yield.
[c] NMP=*N*-methyl-2-pyrrolidone.
[d] HMPA=hexamethyl phosphoryl triamide.
[e] At 60 °C.
[f] At 70 °C.
[g] At 80 °C.

Increasing the amount of $Na_2S_2O_4$ to 4.5 equiv resulted in 76% yield (Table 1, entries 8–12). Subsequently, we studied the solvent effect and found that DMSO was superior to other solvents including DMF, CH_3CN, CH_2Cl_2, NMP, THF and HMPA (Table 1, entries 13–17). Screening revealed that the use of K_2CO_3 as base achieved the best result (Table 1, entries 18–23).

No target product was detected in the absence of base (Table 1, entry 24). After a series of trial experiments, we were delighted to find that the yield could be improved to 81% when the combination of K_2CO_3 and DMSO was employed (Table 1, entry 18). Finally, the reaction temperature was also examined. The results showed that reaction at 60 °C was most efficient (86% yield, Table 1, entry 25).

Having the optimized reaction conditions in hand, we next explored the scope and generality of decarboxylation of isatoic anhydrides with disulfides. As shown in Table 2, a series of aromatic

Table 2
Decarboxylation of isatoic anhydrides with diaryl disulfides[a]



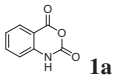
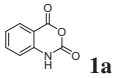
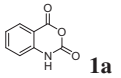
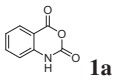
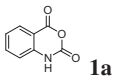
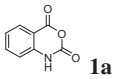
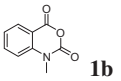
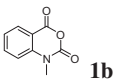
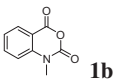
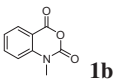
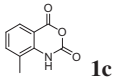
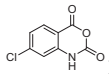
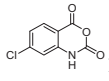
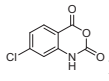
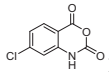
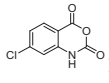
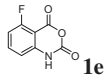
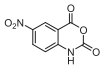
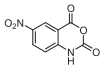
Entry	Isatoic anhydride	Disulfide	Time (min)	Product	Yield[b] (%)
1	 **1a**	Ph **2a**	30	**3aa**	86
2	 **1a**	*p*-(Me)C_6H_4 **2b**	30	**3ab**	87
3	 **1a**	*p*-(OMe)C_6H_4 **2c**	30	**3ac**	91
4	 **1a**	*p*-(F)C_6H_4 **2d**	45	**3ad**	80
5	 **1a**	*p*-(Cl)C_6H_4 **2e**	45	**3ae**	85
6	 **1a**	*p*-(Br)C_6H_4 **2f**	45	**3af**	82
7	 **1b**	Ph **2a**	30	**3ba**	87
8	 **1b**	*p*-(Me)C_6H_4 **2b**	30	**3bb**	87
9	 **1b**	*p*-(OMe)C_6H_4 **2c**	30	**3bc**	89
10	 **1b**	*p*-(Cl)C_6H_4 **2e**	45	**3be**	75
11	 **1c**	Ph **2a**	45	**3ca**	81

Table 2 (*continued*)

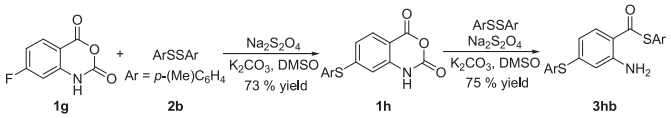
Entry	Isatoic anhydride	Disulfide	Time (min)	Product	Yield[b] (%)
12	 **1c**	*p*-(Me)C_6H_4 **2b**	45	**3cb**	83
13	 **1c**	*p*-(OMe)C_6H_4 **2c**	45	**3cc**	84
14	 **1d**	Ph **2a**	75	**3da**	76
15	 **1d**	*p*-(Me)C_6H_4 **2b**	75	**3db**	79
16	 **1d**	*p*-(OMe)C_6H_4 (**2c**)	75	**3dc**	81
17	 **1d**	*p*-(Cl)C_6H_4 **2e**	90	**3de**	71
18	 **1d**	*p*-(Br)C_6H_4 **2f**	90	**3df**	68
19	 **1e**	*p*-(Me)C_6H_4 **2b**	45	**3eb**	63
20	 **1f**	Ph **2a**	45	**3fa**	54
21	 **1f**	*p*-(Me)C_6H_4 **2b**	45	**3fb**	57

[a] Reaction conditions: **1** (0.6 mmol), **2** (0.2 mmol), K_2CO_3 (0.6 mmol), $Na_2S_2O_4$ (0.9 mmol) and DMSO (2 mL) 60 °C.
[b] Isolated yield.

disulfides bearing either electron-donating or electron-withdrawing groups on the aromatic ring were examined (Table 2, entries 1–6). The electronic properties of the groups on the phenyl ring of aromatic disulfides affected the yields of the reaction to some extent. Generally, the aromatic disulfides bearing electron-donating groups (Table 2, entries 2 and 3) produced the corresponding products in slightly higher yields than those analogues bearing electron-withdrawing groups (Table 2, entries 4–6). On the other hand, *N*-substituted isatoic anhydrides, such as *N*-methyl-isatoic anhydride (**1b**), delivered the corresponding **3ba**, **3bb**, **3bc** and **3be** in 87%, 87%, 89% and 75% yields, respectively (Table 2, entries 7–10).

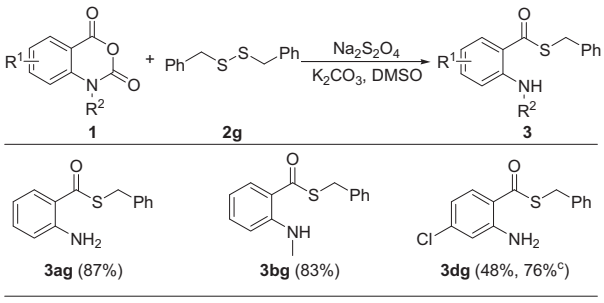
Next, the decarboxylative reactions of aromatic disulfides with several benzo-substituted isatoic anhydrides were investigated. As expected, the groups on the phenyl ring of isatoic anhydrides, such as methyl, chloro, nitro and fluoro, were compatible under the optimized reaction conditions. Benzo-substituted isatoic anhydrides possessing electron-donating (Table 2, entries 11–13) and electron-withdrawing (Table 2, entries 14–19) groups on the phenyl ring provided the corresponding *S*-aryl 2-aminobenzothioates in moderate to good yields (Table 2, entries 11–19). However, benzo-substituted isatoic anhydride containing a strong electron-withdrawing group ($-NO_2$) on the benzene ring, such as 5-nitroisatoic anhydride (**1f**), achieved the corresponding desired products **3fa** and **3fb** in slightly lower yields (Table 2, entries 20–21).

Unexpectedly, treatment of 4-fluoroisatoic anhydride (**1g**) with 1,2-di*p*-tolyldisulfane (**2b**) under the optimized conditions afforded substitution product 4-(*p*-tolylthio)isatoic anhydride (**1h**) in 73% yield, accompanied by a trace amount of *S*-*p*-tolyl 2-amino-4-(*p*-tolylthio)benzothioate (**3hb**). As expected, **3hb** was isolated in 75% yield when **1h** was used as substrate under the optimized conditions (Scheme 2).



Scheme 2. Reaction of **1g** with **2b**.

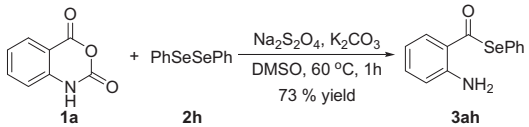
Moreover, it is worth noting that aliphatic disulfides, such as dibenzyl disulfide (**2g**) was still good partner for this transformation, affording the corresponding products **3ag**, **3bg** and **3dg** in 87%, 83% and 76% yields, respectively (Scheme 3).



[a] Reaction conditions: **1** (0.6 mmol), **2g** (0.2 mmol), $Na_2S_2O_4$ (0.9 mmol) and DMSO (2 mL), 60 °C, 30 min.
[b] Isolated yields were given in parenthesis.
[c] For 75 min.

Scheme 3. Reaction of isatoic anhydrides with dibenzyl disulfide.

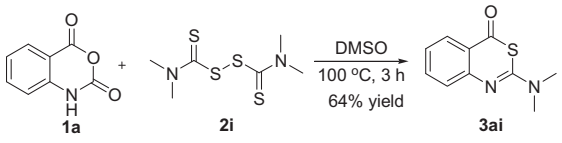
To extend the scope of this reaction, decarboxylation of isatoic anhydride (**1a**) with diphenyldiselenide (**2h**) as a representative example is shown in Scheme 4. Under the standard conditions, the corresponding *Se*-phenyl 2-aminobenzoselenoate (**3ah**) was obtained in 73% yield.



Scheme 4. Decarboxylation of **1a** with diphenyldiselenide.

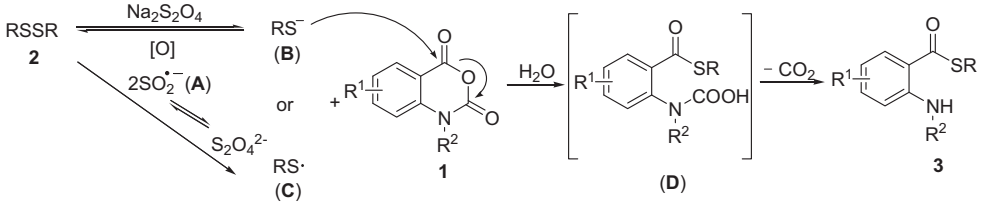
Interestingly, trace yield of 2-(dimethylamino)-4*H*-benzo[*d*][1,3]thiazin-4-one (**3ai**) was detected by GC/MS analysis when tetramethylthiuram disulfide (**2i**) was used under the standard conditions. However, we further adjusted reaction parameters and found that the yield of **3ai** was improved to 64% at 100 °C in DMSO in the absence of reductant and base (Scheme 5).

According to the above observations, a tentative mechanism for the formation of *S*-aryl 2-aminobenzothioates was proposed based on the previous proposed mechanism in Scheme 6. $Na_2S_2O_4$ can be



Scheme 5. Reaction of **1a** with tetramethylthiuram disulfide.

readily decomposed into radical anion intermediates **A**. The sulfur–sulfur bond in disulfides **2** is cleaved by the generated from $Na_2S_2O_4$, to generate intermediate anion **B** or radical **C**. Thus, intermediate anion **B** or radical **C** could be converted to intermediate **D** by nucleophilic attack of the sulfur to carbonyl group in isatoic anhydride **1**. Finally, unstable intermediate **D** would result in the liberation of carbon dioxide and the formation of the corresponding *S*-aryl 2-aminobenzothioates **3**.



Scheme 6. A tentative mechanism for the formation of *S*-aryl 2-aminobenzothioates **3**.

3. Conclusion

In summary, we have developed an efficient and general method for the synthesis of *S*-aryl 2-aminobenzothioates by decarboxylation of isatoic anhydrides with disulfides. The decarboxylation of diphenyldiselenide with isatoic anhydrides was also conducted smoothly to afford *Se*-phenyl 2-aminobenzoselenoate under the standard conditions. It is worth noting that unexpected 2-(dimethylamino)-4*H*-benzo[*d*][1,3]thiazin-4-one was obtained when tetramethylthiuram disulfide was used as sulfur source. Further efforts to expand the scope of the chemistry are currently underway in our laboratories.

4. Experimental section

4.1. General

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. IR spectra were recorded on an AVATAR 370 FI-Infrared Spectrophotometer. NMR spectroscopy was performed on both a Bruck spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GC/MS-QP2010). Elemental analysis was determined on a Carlo-Erba 1108 instrument. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

4.2. General procedure for the synthesis of *S*-aryl 2-aminobenzothioates

A mixture of isatoic anhydride **1** (0.6 mmol), disulfide **2** (0.2 mmol), and $Na_2S_2O_4$ (0.9 mmol) in undried DMSO (2 mL) was stirred at 60 °C for respective time in Table 2 and Scheme 2. After the completion of the reaction, as monitored by TLC and GC–MS analysis, the reaction mixture washed with brine and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (300–400 mesh) with petroleum ether–EtOAc as eluent to provide the desired product.

*4.2.1. S-4-Methoxyphenyl 2-aminobenzothioate (**3ac**).* Solid; mp 75–76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ=3.84 (s, 3H), 5.81 (s, 2H), 6.63–8.00 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=55.3, 114.8, 116.3, 117.0, 117.4, 118.3, 130.1, 134.6, 137.1, 148.4, 160.7, 192.3. IR (KBr): 3007 (NH), 1716 (C=O) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=259 (M$^+$, 9), 120 (100), 92 (23), 65 (16). Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05. Found: C, 64.81; H, 5.06.

*4.2.2. S-4-Fluorophenyl 2-aminobenzothioate (**3ad**).* Solid; mp 103–104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.81 (s, 2H), 6.65–6.73 (m, 2H), 7.14–7.99 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=116.3, 116.5 (d, $^2J_{CF}$=22.3 Hz, 1C), 117.1, 117.2, 123.1, 130.1, 134.8, 137.6 (d, $^3J_{CF}$=8.0 Hz, 1C), 148.5, 163.5 (d, $^1J_{CF}$=246.6 Hz, 1C), 191.2. IR (KBr): 3004 (NH), 1716 (C=O) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=247 (M$^+$, 7), 120 (100), 92 (66), 65 (17), 108 (17), 58 (16). Anal. Calcd for $C_{13}H_{10}FNOS$: C, 63.14; H, 4.08. Found: C, 63.17; H, 4.11.

*4.2.3. S-p-Tolyl 2-(methylamino)benzothioate (**3bb**).* Solid; mp 114–115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.33 (s, 2H), 2.76 (d, *J*=5.1 Hz, 2H), 6.56–6.61 (m, 2H), 7.18–7.31 (m, 5H), 7.79 (s, 1H), 7.96 (dd, *J*=8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.3, 30.8, 111.2, 114.4, 116.8, 124.5, 129.9, 130.7, 135.2, 135.6, 139.6, 150.2, 192.0. IR (KBr): 2923 (NH), 1635 (C=O) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=257 (M$^+$,16), 134 (100), 116 (13), 91 (10), 77 (20). Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87. Found: C, 70.04; H, 5.82.

*4.2.4. S-4-Methoxyphenyl 2-(methylamino)benzothioate (**3bc**).* Solid; mp 86–87 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.84 (s, 3H), 3.84 (s, 3H), 6.64–7.41 (m, 7H), 7.88 (s, 1H), 8.03 (d, *J*=7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=29.3, 55.3, 111.2, 114.4, 114.8, 116.7, 118.6, 130.6, 135.2, 137.2, 150.1, 160.6, 192.5. IR (KBr): 3010 (NH), 1716 (C=O) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=273 (M$^+$, 16), 134 (100), 116 (13), 77 (17). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53. Found: C, 65.95; H, 5.56.

*4.2.5. S-4-Chlorophenyl 2-(methylamino)benzothioate (**3be**).* Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.04 (s, 3H), 6.66–6.70 (m, 2H), 7.41–7.44 (m, 5H), 7.82 (s, 1H), 7.99 (d, *J*=8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.0, 111.3, 114.6, 116.4, 126.6, 129.3, 130.6, 135.5, 136.9, 150.3, 171.1, 190.8. IR (KBr): 3360 (NH), 1635 (C=O) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)= 277 ([M+2]$^+$, 7), 277 (M$^+$, 21), 134 (100), 116 (17), 77 (23). Anal. Calcd for $C_{14}H_{12}ClNOS$: C, 60.54; H, 4.35. Found: C, 60.59; H, 4.38.

*4.2.6. S-Phenyl 2-amino-3-methylbenzothioate (**3ca**).* Solid; mp 102–103 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.17 (s, 3H), 5.92 (s, 2H), 6.65–7.52 (m, 7H), 7.93 (d, *J*=8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=22.6, 115.7, 123.4, 128.2, 129.1, 129.4, 135.3, 135.6, 147.0, 191.8. IR

(KBr): 3360 (NH), 1615 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=243 (M^+, 12), 134 (100), 106 (21), 77 (16). Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.11; H, 5.39. Found: C, 69.15; H, 5.42.

*4.2.7. S-p-Tolyl 2-amino-3-methylbenzothioate (**3cb**).* Solid; mp 111–112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ=2.16 (s, 3H), 2.41 (s, 3H), 5.92 (s, 2H), 6.41–7.40 (m, 6H), 7.93 (d, *J*=8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.3, 22.6, 115.7, 117.0, 123.4, 124.5, 128.2, 130.0, 135.3, 135.6, 139.7, 147.0, 192.3. IR (KBr): 3001 (NH), 1706 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=257 (M^+, 7), 134 (100), 106 (18), 77 (14). Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87. Found: C, 70.06; H, 5.93.

*4.2.8. S-4-Methoxyphenyl 2-amino-3-methylbenzothioate (**3cc**).* Oil. ^1H NMR (500 MHz, $CDCl_3$): δ=1.97 (s, 3H), 3.72 (s, 3H), 4.04 (s, 2H), 6.72–7.33 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.1, 55.5, 114.6, 114.7, 119.8, 128.4, 132.4, 132.6, 146.1, 158.3, 159.9, 171.1, 192.4. IR (KBr): 2959 (NH), 1741 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=273 (M^+, 21), 134 (100), 126 (27), 77 (19). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53. Found: C, 65.97; H, 5.58.

*4.2.9. S-Phenyl 2-amino-4-chlorobenzothioate (**3da**).* Solid; mp 127.2–127.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ=5.81 (s, 2H), 6.61 (d, *J*=8.8 Hz, 1H), 7.23–7.50 (m, 6H), 7.97 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=118.1, 118.5, 120.7, 127.3, 129.2, 129.6, 130.2, 134.6, 135.5, 147.0, 190.7. IR (KBr): 3010 (NH), 1716 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=263 ($[M+2]^+$, 4), 263(M^+, 13), 154 (100), 156 (31), 126 (31), 90 (16). Anal. Calcd for $C_{13}H_{10}ClNOS$: C, 59.20; H, 3.82. Found: C, 59.23; H, 3.86.

*4.2.10. S-p-Tolyl 2-amino-4-chlorobenzothioate (**3db**).* Solid; mp 134–135 °C. ^1H NMR (500 MHz, $CDCl_3$): δ=2.42 (s, 3H), 5.81 (s, 2H), 6.61–7.98 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.3, 118.2, 118.5, 120.7, 123.7, 129.2, 130.1, 134.6, 135.5, 140.0, 146.9, 191.2. IR (KBr): 3362 (NH), 1651 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=277 ($[M+2]^+$, 6), 277 (M^+, 19), 154 (100), 156 (32), 126 (27), 90 (14), 99 (13). Anal. Calcd for $C_{14}H_{12}ClNOS$: C, 60.54; H, 4.35. Found: C, 60.57; H, 4.38.

*4.2.11. S-4-Methoxyphenyl 2-amino-4-chlorobenzothioate (**3dc**).* Solid; mp 91–92 °C. ^1H NMR (500 MHz, $CDCl_3$): δ=2.04 (s, 3H), 6.81–6.85 (m, 5H), 7.38 (s, 2H), 7.39–7.41 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=55.3, 114.6, 114.9, 115.8, 128.4, 128.8, 132.6, 134.1, 137.0, 159.9, 171.1, 192.6. IR (KBr): 3345 (NH), 1640 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=295 ($[M+2]^+$, 6), 293 (M^+, 17), 154 (100), 156 (28), 126 (27), 90 (12), 77 (9). Anal. Calcd for $C_{14}H_{12}ClNO_2S$: C, 57.24; H, 4.12. Found: C, 57.27; H, 4.17.

*4.2.12. S-4-Chlorophenyl 2-amino-4-chlorobenzothioate (**3de**).* Solid; mp 107–108 °C. ^1H NMR (500 MHz, $CDCl_3$): δ=5.82 (s, 2H), 6.66–7.43 (m, 6H), 7.97 (dd, *J*=8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=116.3, 117.1, 126.3, 129.3, 130.1, 134.8, 135.8, 136.8, 148.6, 171.1, 190.6. IR (KBr): 3330 (NH), 1630 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=299 ($[M+2]^+$, 9), 297 (M^+, 24), 154 (100), 156 (32), 126 (30), 99 (17), 90 (15). Anal. Calcd for $C_{13}H_9C_{l2}NOS$: C, 52.36; H, 3.04. Found: C, 52.41; H, 3.08.

*4.2.13. S-4-Bromophenyl 2-amino-4-chlorobenzothioate (**3df**).* Oil. ^1H NMR (500 MHz, $CDCl_3$): δ=5.83 (s, 2H), 6.23 (d, *J*=9 Hz, 1H), 7.24–7.93 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=116.2, 117.1, 123.9, 126.9, 130.1, 130.7, 132.2, 135.0, 136.8, 148.6, 190.6. IR (KBr): 3230 (NH), 1646 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=345 ($[M+2]^+$, 18), 343 (M^+, 19), 154 (100), 156 (27), 77 (18). Anal. Calcd for $C_{13}H_9BrClNOS$: C, 45.57; H, 2.65. Found: C, 45.59; H, 2.63.

*4.2.14. S-Benzyl 2-amino-4-chlorobenzothioate (**3dg**).* Oil. ^1H NMR (500 MHz, $CDCl_3$): δ=4.26 (s, 2H), 5.86 (s, 2H), 6.59 (d, *J*=8.5 Hz, 1H), 7.18–7.83 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=33.0, 111.1, 114.4, 116.4, 117.3, 127.0, 128.5, 128.8, 130.6, 135.0, 137.9, 149.9, 192.3. IR (KBr): 3360 (NH), 1615 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=279 ($[M+2]^+$, 8), 277 (M^+, 24), 154 (100), 156 (36), 126 (23), 91 (26). Anal. Calcd for $C_{14}H_{12}ClNOS$: C, 60.54; H, 4.35. Found: C, 60.61; H, 4.37.

*4.2.15. Se-Phenyl 2-aminobenzoselenoate (**3ah**).* Oil. ^1H NMR (500 MHz, $CDCl_3$): δ=6.47 (s, 2H), 6.74–6.75 (m, 2H), 7.28–8.23 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=116.7, 116.7, 126.2, 127.7, 128.6, 129.7, 133.6, 136.4, 146.7, 149.6, 159.2. IR (KBr): 2998 (NH), 1716 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%)=276 (M^+,7), 120 (100), 199 (23), 108 (10), 65 (17). Anal. Calcd for $C_{13}H_{11}NOSe$: C, 56.53; H, 4.01. Found: C, 56.56; H, 4.05.

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Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2013.01.024.

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