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Synthesis of Phenyl Dithiocarbamates Starting from Sodium Dialkyldithiocarbamates and Aryl Boronic Acids: a Copper Catalyzed *S*-Arylation

Ming-Yuan Gao,[a][‡] Wan Xu,[a][‡] Shi-Bo Zhang,[a] Yue-Sheng Li,[c] and Zhi-Bing Dong*[a][b]

Abstract: A convenient and efficient protocol for the *S*-arylation of sodium dialkyldithiocarbamates was developed. With the catalysis of copper(I) bromide, sodium dialkyldithiocarbamates coupled with aryl boronic acids giving the C-S coupling products smoothly in good to excellent yields. This protocol features easily available starting materials, easy performance, short reaction time, broad substrate scope and nice yields, showing its potential synthetic value for the convenient preparation of some potentially biologically active compounds.

Introduction

Sodium dialkyldithiocarbamates are a class of cheap and common compounds as industrial products, which are used in a wide range of fields such as medicine,[1] pesticide[2] and vulcanization accelerators.[3] They can also be ideal reagents for the development of completely new synthetic transformations.[4] On the other hand, organic dithiocarbamates (especially phenyl dithiocarbamates) play very important roles in biologically active compounds,[5] agriculture[6] and versatile synthetic intermediates in organic synthesis.[7] This fragment is also very useful in the pharmaceutical field[8] as anti-infective agents (**a, b**) and nervous system agents (**c**) (Figure 1). Moreover, they can be used as protecting groups in peptide synthesis,[9] and have recently been used in the synthesis of ionic liquids.[10]

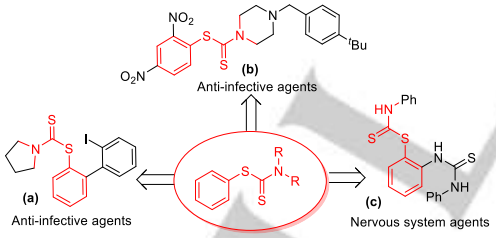


Figure 1. Representative drugs containing phenyl dithiocarbamates skeletons.

On the basis of their important natures, phenyl dithiocarbamates have been paid extensive attention by the synthetic and medicinal chemists. The most commonly used method is the reaction of amines with thiophosgene and its substituted derivatives,[11] which is not attractive for environmental concerns. Besides, a couple of procedures involving the reactions of sodium dithiocarbamates with diazonium chlorides,[12] diaryl diazonium salts in the presence of hypervalent iodines,[13] as well as the cross-coupling by using organometallic reagents with tetramethyllithium disulfides[14] have also been achieved. Although effective, these methods still suffer from environmental issues, difficulty in preparing the reagents, high reaction temperatures, or multiple reaction steps which limit their applications (Figure 2).

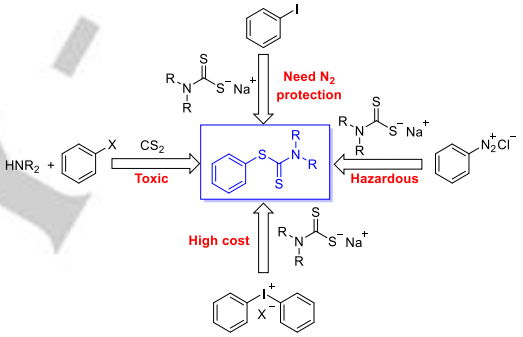
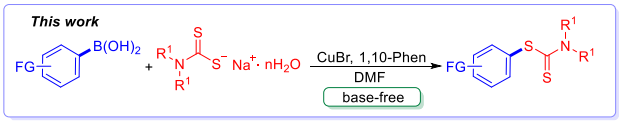


Figure 2. Previously reported synthetic methods of phenyl dithiocarbamates.

Recently, our group has reported alternative methods for the synthesis of these important compounds starting from tetraalkylthiuram disulfides with aryliodides[15] or aryl boronic acids,[16] while most of these protocols involve the use of base. As part of our longstanding interests in organosulfur chemistry[17] and to further extend our work, we would like to report herein an efficacious, mild and base-free method for the synthesis of *S*-aryl dithiocarbamates through C-S coupling starting from sodium dialkyldithiocarbamates and aryl boronic acids (Scheme 1), which could be attractive and alternative approach for the construction of these important compounds.



Scheme 1. Synthesis of *S*-aryl dithiocarbamates (this work).

Results and Discussion

We began our investigation using phenyl boronic acid (**1a**) and sodium dimethyldithiocarbamates (**2a**) to optimize the reaction conditions (Table 1). In the initial investigations, a series of copper catalysts were screened (Table 1, entries 1-6), only trace (or none) of the product was obtained. To our delight, the desired product **3a** could be obtained in moderate yield (55%,

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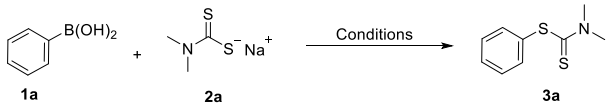
59%) by using CuI or CuBr (10 mol%) as catalyst (Table 1, entries 7-8). Encouraged by this result, various ligands were screened (Table 1, entries 8-15) and 1,10-phenanthroline (Table 1, entry 8) was chosen as the best one. Subsequently, the loading of the catalyst and ligand were examined (entries 8, 16-18), and the optimal loading is 10 mol% of CuBr and 10 mol% of 1,10-phenanthroline. The examination of reaction temperature (Table 1, entries 19-23) and solvents (Table 1, entries 22, 24-27) showed that *N, N*-dimethylformamide (DMF) was the best solvent, and 80°C was the optimal reaction temperature. In the end, the substrate ratio of **1a** to **2a** was screened (Table 1, entries 28-33), and it turned out that the equivalent ratio (**1a** : **2a**) is 2:1 (entry 32). The optimal reaction conditions are summarized in entry 32, Table 1.

Table 1. Optimization of the reaction conditions [a]



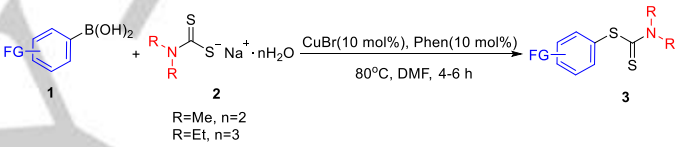
1a **2a** **3a**

Entry	Catalyst (mol%)	Ligand (mol%)	Solvent	T (°C)	Yield (%)[b]
1	$Cu(OAc)_2$	1,10-Phen	DMF	100	<5
2	CuO	1,10-Phen	DMF	100	<5
3	$Cu(OTf)_2$	1,10-Phen	DMF	100	N.R.
4	$CuSO_4$	1,10-Phen	DMF	100	<5
5	$NiBr_2$	1,10-Phen	DMF	100	N.R.
6	$NiCl_2$	1,10-Phen	DMF	100	N.R.
7	CuI	1,10-Phen	DMF	100	55
8	CuBr	1,10-Phen	DMF	100	59
9	CuBr	PPh_3	DMF	100	43
10	CuBr	Py	DMF	100	N.R.
11	CuBr	bipy	DMF	100	<5
12	CuBr	glycine	DMF	100	<5
13	CuBr	L-proline	DMF	100	<5
14	CuBr	DEMDA	DMF	100	N.R.
15	CuBr	TEMDA	DMF	100	N.R.
16	CuBr (5%)	1,10-Phen (5%)	DMF	100	34
17	CuBr (15%)	1,10-Phen (15%)	DMF	100	60
18	CuBr (20%)	1,10-Phen (20%)	DMF	100	60
19	CuBr	1,10-Phen	DMF	r.t.	N.R.
20	CuBr	1,10-Phen	DMF	40	35
21	CuBr	1,10-Phen	DMF	60	51
22	CuBr	1,10-Phen	DMF	80	61
23	CuBr	1,10-Phen	DMF	120	54
24	CuBr	1,10-Phen	DMSO	80	51
25	CuBr	1,10-Phen	DMAc	80	43
26	CuBr	1,10-Phen	THF	80	31
27	CuBr	1,10-Phen	PhMe	80	54
28[c]	CuBr	1,10-Phen	DMF	80	54
29[d]	CuBr	1,10-Phen	DMF	80	72
30[e]	CuBr	1,10-Phen	DMF	80	70
31[f]	CuBr	1,10-Phen	DMF	80	77
32[g]	**CuBr**	**1,10-Phen**	**DMF**	**80**	**86**
33[h]	CuBr	1,10-Phen	DMF	80	71
34	-	-	DMF	80	N.R.

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), CuBr (10 mol%), solvent (3 mL), stirred for 4 hours. [b] Isolated yield. [c] **1a** (1 mmol), **2a** (1 mmol). [d] **1a** (1 mmol), **2a** (1.5 mmol). [e] **1a** (1 mmol), **2a** (2 mmol). [f] **1a** (1.5 mmol), **2a** (1 mmol). [g] **1a** (2 mmol), **2a** (1 mmol). [h] **1a** (2.5 mmol), **2a** (1 mmol).

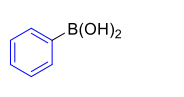
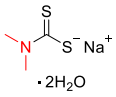
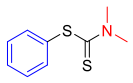
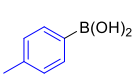
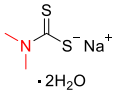
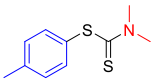
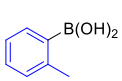
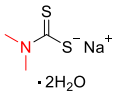
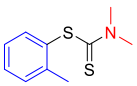
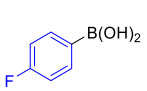
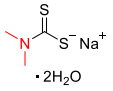
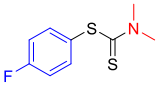
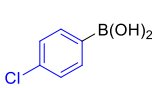
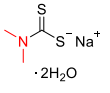
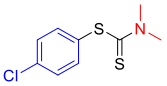
With the optimal reaction conditions in hand, the scope of the reaction was examined by checking the diverse substituted aryl boronic acids and sodium dialkyldithiocarbamates. The results are summarized in Table 2. In general, the substituted aryl boronic acids reacted well with sodium dialkyldithio-carbamates, furnishing the C-S coupling products (aryl dithio-carbamates) in good to excellent yields. Aryl boronic acids bearing electron-donating groups, such as Me- and MeO- (**1b**, **1i**) promoted the reaction slightly, and weak electron-withdrawing groups, such as F, Cl and Br (**1d**, **1e**, **1f**) deactivated the aryl boronic acids, providing the desired products in slightly lower yields (entries 4, 5 and 6). However, aryl boronic acid bearing a strong electron-withdrawing group such as CN (**1h**) gave the product in a moderate yield (entry 8). *Ortho* steric hindrance also influenced the reaction and slightly decreased the yields (entries 3, 7 and 10). In addition, general good yields were achieved when naphthalen-2-yl boronic acid was surveyed (entries 11 and 12), and sodium diethyldithiocarbamates reacted with phenyl boronic acids giving the desired products in also good yields (entries 13-15).

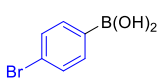
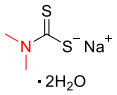
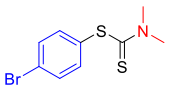
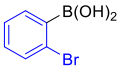
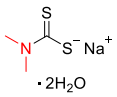
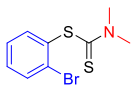
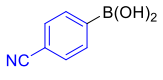
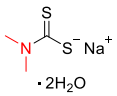
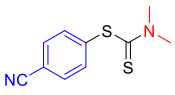
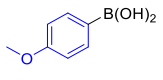
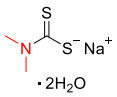
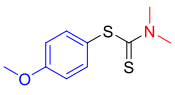
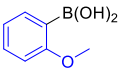
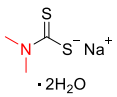
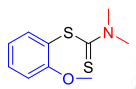
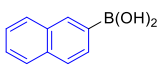
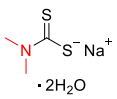
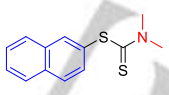
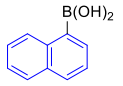
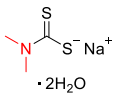
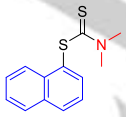
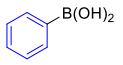
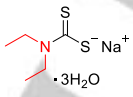
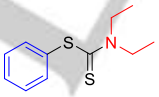
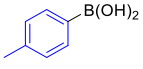
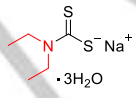
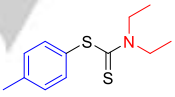
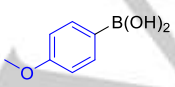
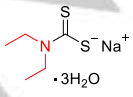
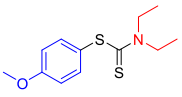
Table 2. Synthesis of phenyl dithiocarbamates [a]



1 **2** **3**

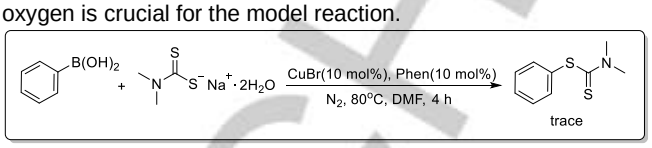
R=Me, n=2
R=Et, n=3

Entry	Substrate **1**	Substrate **2**	Product **3** Yield[b]
1	 **1a**	 **2a**	 **3a**: 86%
2	 **1b**	 **2a**	 **3b**: 91%
3	 **1c**	 **2a**	 **3c**: 73%
4	 **1d**	 **2a**	 **3d**: 72%
5	 **1e**	 **2a**	 **3e**: 80%

6		**1f**		**2a**		**3f**: 84%
7		**1g**		**2a**		**3g**: 77%
8		**1h**		**2a**		**3h**: 66%
9		**1i**		**2a**		**3i**: 94%
10		**1j**		**2a**		**3j**: 84%
11		**1k**		**2a**		**3k**: 82%
12		**1l**		**2a**		**3l**: 83%
13		**1a**		**2b**		**3m**: 83%
14		**1b**		**2b**		**3n**: 86%
15		**1i**		**2b**		**3o**: 89%

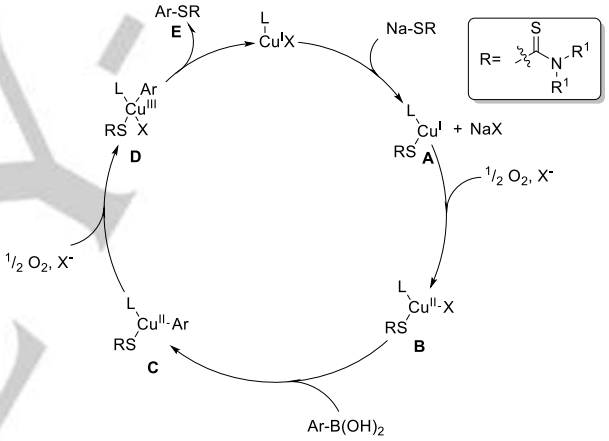
[a] Reaction conditions: **1** (2.0 mmol), **2** (1.0 mmol), CuBr (10 mol%), 1,10-Phenantroline (10 mol%), DMF (3 mL), stirred at 80 °C for 4-6 h. [b] Isolated yields based on **2**.

A control experiment in the nitrogen atmosphere was conducted and trace of the product was obtained (Scheme 2), indicating the oxygen is crucial for the model reaction.



Scheme 2. Control experiment under nitrogen atmosphere.

Based on the reaction results and the control experiment, the mechanism of this reaction is proposed (Scheme 3). Firstly, Cu^{I} catalyst reacts with sodium dialkyldithiocarbamate to generate intermediate **A**. Secondly, **A** is oxidized by oxygen in the air to give intermediate **B** which is ready for the transmetallation with aryl boronic acid, furnishing intermediate **C**, and **C** is oxidized again to produce the Cu(III) intermediate **D**. Finally, **D** undergoes reductive elimination easily, giving the desired product **E** along with recyclable Cu^{I} catalyst.



Scheme 3. Proposed reaction mechanism.

Conclusions

In summary, we have developed a copper-catalyzed efficient and useful method for the synthesis of various substituted *S*-aryl dithiocarbamates. In the presence of CuBr/1,10-Phenantroline, aryl boronic acids reacts with sodium dialkyldithiocarbamates which are a class of common and stable industrial products, furnishing a series of 15 desired phenyl dithiocarbamates in good to excellent yields. This protocol features easily available starting materials, easy operations, short reaction time, broad substrate scope and nice yields, illustrating its potential synthetic value for the convenient preparation for some potentially bioactive compounds.

Experimental Section

General remarks: All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. Yields refer to isolated compounds estimated to be >95% pure as determined by ^{1}H NMR and capillary GC analysis. NMR spectra were recorded on a Bruker AM400 NMR instrument in $CDCl_3$ using TMS as an internal standard. Chemical shifts are given in ppm and coupling constants (*J*) are given in Hz. All melting points were determined on a RY-1G melting point instrument without correction. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 95Q or Finnigan 90 mass instrument (ESI). TLC was performed using aluminum plates coated with SiO_2 (Merck 60, F-254) and visualized with UV light at 254 nm. Column chromatography was performed on silica gel (200-300 mesh) with PE-EtOAc as eluent.

Typical procedure (TP): To a dried tube equipped with a magnetic stirrer and a septum were added phenyl boronic acid (2.0 mmol) and sodium dialkyldithiocarbamates (1.0 mmol) dissolved in DMF (3.0 mL). The mixture was stirred for 5 min, and then 1,10-Phenantroline (10 mol%) and CuBr (10 mol%) were added. The reaction mixture was heated at 80 °C and monitored by TLC until the starting material was finished. The mixture was cooled down to room temperature, and the reaction was quenched with sat. NH_4Cl solution (10 mL), after the mixture was extracted with ethyl acetate, dried with anhydrous Na_2SO_4, and then concentrated under vacuum. The residue was purified by flash column chromatography to afford the desired product.

Phenyl dimethylcarbamodithioate (3a): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3a** 169 mg (yield: 86 %), a white solid. M.p.: 90-92 °C, ^{1}H NMR (400 MHz, CDCl3): δ = 7.49-7.45(m, 5 H), 3.56 (s, 3 H), 3.50 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ = 197.6, 137.0, 131.7, 130.0, 129.1, 45.7, 42.0 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_9H_{12}NS_2$ (198.0406), found 198.0411.

4-Methylphenyl dimethylcarbamodithioate (3b): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to give the target compound **3b** 192 mg (yield: 91 %), a white solid. M.p.: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, *J* = 6.0 Hz, 2 H), 7.26 (t, *J* = 6.0 Hz, 2 H), 3.56 (s, 3 H), 3.49 (s, 3 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 140.4, 136.8, 130.0, 128.3, 45.7, 41.9, 21.5 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{14}NS_2$ (212.0562), found 212.0559.

2-Methylphenyl dimethylcarbamodithioate (3c): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to give the target compound **3c** 154 mg (yield: 73 %), a white solid. M.p.: 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.32 (m, 3 H), 7.27–7.23 (m, 2 H), 3.54 (s, 3 H), 3.50 (s, 3 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 143.8, 137.7, 131.1, 130.7, 130.7, 126.7, 45.7, 42.0 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{14}NS_2$ (212.0562), found 212.0569.

4-Fluorophenyl dimethylcarbamodithioate (3d): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3d** 154 mg (yield: 72 %), a white solid. M.p.: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.39 (m, 2 H), 7.14–7.09 (m, 2 H), 3.53 (s, 3 H), 3.48 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 165.2, 162.7, 139.1 (d, J_{C-F} = 8 Hz), 127.15 (d, J_{C-F} = 3 Hz), 116.36 (d, J_{C-F} = 22 Hz), 45.8, 41.9 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_9H_{11}FNS_2$ (216.0312), found 216.0308.

4-Chlorophenyl dimethylcarbamodithioate (3e): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3e** 184 mg (yield: 80 %), a white solid. M.p.: 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.37 (m, 4 H), 3.54 (s, 3 H), 3.48 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 138.2, 136.6, 130.1, 129.4, 45.7, 42.0, 43.0 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_9H_{11}ClNS_2$ (232.0007), found 232.0010.

4-Bromophenyl dimethylcarbamodithioate (3f): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3f** 231 mg (yield: 84 %), a white solid. M.p.: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (s, 1 H), 7.55 (s, 1 H), 7.33 (s, 1 H), 7.31 (s, 1 H), 3.54 (s, 3 H), 3.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 138.4, 132.4, 130.8, 125.0, 45.8, 42.0 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_9H_{11}BrNS_2$ (275.9511), found 275.9503.

2-Bromophenyl dimethylcarbamodithioate (3g): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3g** 210 mg (yield: 77 %), a white solid. M.p.: 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J*=8.0 Hz, 1H), 7.55 (d, *J*=8.0 Hz, 1H), 7.31-7.22 (m, 2H), 3.52 (s, 3H), 3.48 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 139.7, 133.5, 133.1, 131.8, 131.6, 128.1, 45.5, 42.1 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_9H_{11}BrNS_2$ (275.9511), found 275.9514.

4-Cyanophenyl dimethylcarbamodithioate (3h): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3h** 146 mg (yield: 66 %), a white solid. M.p.: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.68 (m, 2H), 7.60-7.57 (m, 2H), 3.55 (s, 3H), 3.51 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 137.5, 137.4, 132.4, 118.2, 113.6, 45.6, 42.1 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{11}N_2S_2$ (223.0358), found 223.0360.

4-Methoxyphenyl dimethylcarbamodithioate (3i): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3i** 213 mg (yield: 94 %), a white solid. M.p.: 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 4.0 HZ, 2 H), 6.96 (d, *J* = 4.0 Hz, 2 H), 3.83 (s, 3 H), 3.54 (s, 3H), 3.48 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 161.1, 138.4, 122.6, 114.7, 55.3, 45.8, 41.9 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{14}NOS_2$ (228.0512), found 228.0509.

2-Methoxyphenyl dimethylcarbamodithioate (3j): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3j** 190 mg (yield:

84 %), a white solid. M.p.: 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.40 (m, 2H), 7.05-6.99 m, 2H), 3,86 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 160.5, 138.8, 132.5, 121.2, 119.9, 111.9, 66.2, 45.7, 42.1 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{14}NOS_2$ (228.0512), found 228.0512.

Naphthalene-2-yl dimethylcarbamodithioate (3k): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3k** 202 mg (yield: 82 %), a colorless oil. ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.52 (q, 3 H), 3.54 (s, 3 H), 3.51 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 137.0, 135.1, 134.2, 131.5, 129.0, 128.6, 127.2, 126.3, 125.7, 45.6, 42.1 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{14}NS_2$ (248.0562), found 248.0566.

Naphthalene-1-yl dimethylcarbamodithioate (3l): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3l** 205 mg (yield: 83%), a yellow solid. M.p.: 150.8-152.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (m, 1H), 7.99 (d, J = 8Hz, 1H), 7.88 (m, 1H), 7.74 (m, 1H), 8.24 (m, 1H), 7.56-7.49 (m, 3H), 3.61 (s, 3H), 3.55 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 137.0, 135.0, 134.1, 131.4, 128.9, 128.6, 127.1, 126.2, 125.7, 125.7, 45.5, 42.1 ppm; HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{14}NS_2$ (248.0562), found 248.0570.

Phenyl diethylcarbamodithioate (3m): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **3m** 186 mg (yield: 83 %), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 12.0 Hz, 5 H), 4.02 (d, *J* = 4.0 Hz, 2 H), 3.84 (d, *J* = 8.0 Hz, 2 H), 1.39 (t, *J* = 4.0 Hz, 3 H), 1.29 (d, *J* = 4.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 137.2, 131.6, 130.0, 129.0, 49.9, 47.3, 12.8, 11.6 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{11}H_{16}NS_2$ (226.0677), found 226.0673.

4-Methylphenyl diethylcarbamodithioate (3n): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to give the target compound **3n** 203 mg (yield: 85 %), a white solid, M.p.: 75-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 4.0 Hz, 2 H), 3.94 (d, *J* = 8.0 Hz, 2 H), 3.76 (d, *J* = 4.0 Hz, 2 H), 2.32 (s, 3 H), 1.31 (t, *J* = 4.0 Hz, 3 H), 1.20 (t, *J* = 4.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 140.2, 137.0, 129.9, 128.1, 49.9, 47.2, 21.5, 12.7, 11.6 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{18}NS_2$ (240.0875), found 240.0877.

4-Methoxyphenyl diethylcarbamodithioate (3o): According to **TP**, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to give the target compound **3o** 226 mg (yield: 89%), a white solid. M.p.: 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 8.0 Hz, 2 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 3.87 (d, *J* = 8.0 Hz, 2 H), 3.68 (s, 5 H), 1.24 (t, *J* = 6.4 Hz, 3 H), 1.13 (t, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 161.0, 138.6, 122.4, 114.6, 55.3, 50.0, 47.1, 12.7, 11.6 ppm. HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{18}NOS_2$ (256.0825), found 256.0830.

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Keywords: Dialkyldithiocarbamates • Boronic acid • Arylation • C-S Coupling • Synthesis

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*Ming-Yuan Gao, Wan Xu, Shi-Bo Zhang, Yue-Sheng Li, and Zhi-Bing Dong**

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Synthesis of Phenyl Dithiocarbamates Starting from Sodium Dialkyldithiocarbamates and Aryl Boronic Acids: a Copper Catalyzed S-Arylation

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A convenient and efficient protocol for *S*-arylation of sodium dialkyldithiocarbamates was developed. The desired aryl dithiocarbamates were synthesized in good to excellent yields in the presence of CuBr as catalyst and 1,10-phenantroline as ligand, a variety of functional groups on aryl boronic acids could be tolerated. The method features easily available starting materials, easy performance, short reaction time, broad substrate scope and nice yields, illustrating its potential synthetic value for the convenient preparation of some potentially biologically active compounds.