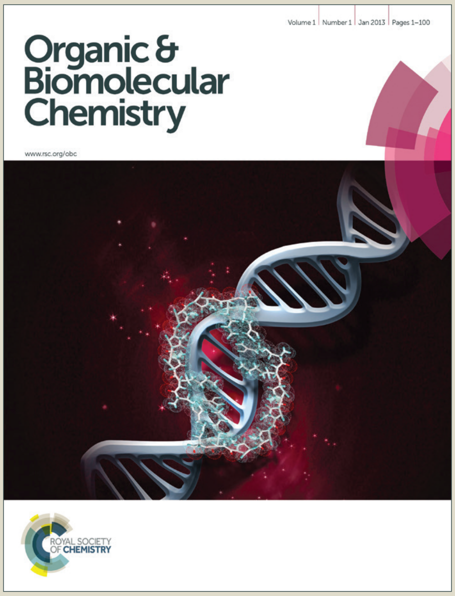
Organic & Biomolecular Chemistry

Accepted Manuscript



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A Mild Copper-catalyzed Aerobic Oxidative Thiocyanation of Arylboronic Acids with TMSNCS

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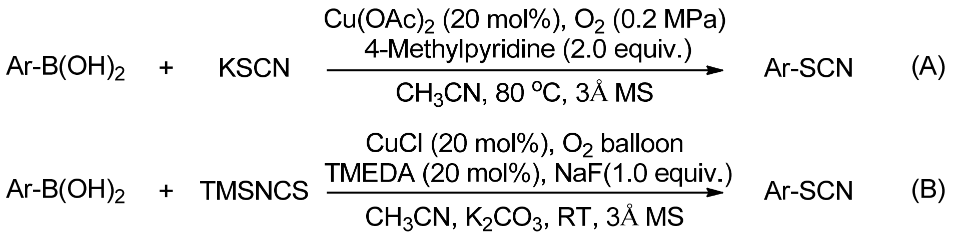
Received Date (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT: A facile and efficient transformation of arylboronic acids to their corresponding arylthiocyanates has been successfully developed. Based on the CuCl-catalyzed oxidative cross-coupling reaction between arylboronic acids and trimethylsilylisothiocyanate (TMSNCS) under oxygen atmosphere, the transformation could be readily conducted at ambient temperature. The newly developed protocol provided a competitive synthetic approach to aryl thiocyanates, which can tolerate a broad range of reactive functional groups and/or strong electron-withdrawing groups.

Introduction

As an important family member in the sulfur chemistry, organic thiocyanate compounds can be commonly found in natural products and many of them exhibit biological activities to some extent.[1] More important, organic thiocyanates are usually served as the synthetic precursors, which could be conveniently converted into various sulfur-containing derivatives, including sulfur heterocycles,[2] thioethers,[3] disulfides,[4] thiols,[5] thiocarbamates,[6] and so on.[7] Because of the importance, a number of methods have been reported to synthesize organic thiocyanates in the past decades.[8] However, very limited methods are efficient and practical in the synthesis of aryl thiocyanates. In fact, aryl thiocyanates could be prepared via two classic routes. One is the direct electrophilic thiocyanation of arenes by thiocyanogen or its equivalents,[9] and the other is the nucleophilic substitution of aryl diazonium salts by thiocyanate salts (Sandmeyer-type reaction).[10] Unfortunately, both approaches could not avoid some inherent drawbacks, such as the use of high toxic reagents, low regio- and chemo-selectivity, as well as narrow substrate scope. Although great efforts have been devoted to the improvement of these classic processes during the past years, they are largely relied on the use of some special reagents and thus far from the potential application.[11] In view of all the above reasons, some approaches have also been investigated for the synthesis of aryl thiocyanates, which include the copper-promoted nucleophilic replacement of aryl iodides with thiocyanate salts,[12] thiocyanation of aryl organometallic compounds (aryllithium, arylthallium and arylzinc compounds)[13] and cyanation of organosulfur compounds.[14] However, these methods have also been encountered some difficulties, such as, the limited availability of starting materials, the poor functional group compatibility, harsh reaction conditions and/or low yields.

Over the past decades, great interests have been attracted on the transition-metal-mediated aryl carbon-heteroatom bond (C-X) formations, which are becoming powerful tools for the access of heteroatom-functionalized aromatic compounds.[15] In particular, the aryl C-X bond formation by the copper-mediated oxidative cross-coupling of arylboronic acids or their derivatives with heteroatom nucleophiles, *i.e.* Cham-Lam reaction, has received considerable attentions, because of the readily availablility of arylboronic acids, the lower cost of copper source and the relatively mild reaction conditions.[16] Since its initial report in 1998, significant progress has been achieved on Cham-Lam reaction and a wide range of heteroatom-functionalized aromatic compounds, such as arylamines,[17] arylesters,[18] arylthioesters,[19] and others,[20] have been successful synthesized form arylboronic acids (and/or their derivatives) and the corresponding heteroatom-containing nucleophiles by this strategy. Previously, we have described a novel method for the synthesis of aryl thiocyanates from arylboronic acids and KSCN by $Cu(OAc)_2$-catalyzed aerobic oxidative aryl C-S bond formation (Scheme 1, A).[21] It is a straightforward approach that can access a number of aryl thiocyanates in good to excellent yields. However, the reaction was not well favorable for the electrophilic substituents (such as ester, ketone and aldehyde groups) in arylboronic acids, because of strong nucleophilic character of KSCN. Moreover the reaction was inert in the transformation of those arylboronic acids bearing with strong electron-withdrawing groups (such as, CN and NO_2), together with the autoclave operation (0.2 Mpa of O_2 as terminal oxidant) and the elevated reaction temperature (80 °C). And thus, we are greatly interesting in developing a more general and facile procedure to overcome these problems. In this work, we proposed a new method for the preparation of aryl thiocyanates from arylboronic acids by using trimethylsilylisothiocyanate (TMSNCS) as thiocyantion reagent (Scheme 1, B). In the presence of NaF, thiocyanation reaction of arylboronic acids with TMSNCS could proceed at room temperature with a catalytic amount of CuCl and under balloon oxygen. Under the newly developed procedure, a broad range of functionalized aryl thiocyanates could be obtained in moderate to good yields. Noteworthy, TMSNCS was commercially available, and has already been used as reliable NCS^- nucleophile source in the ring-opening of oxiranes[22] and nucleophilic substitution of alkyl halides[23] under the promotion of n-Bu_4NF (TBAF), while its application in the metal-catalyzed aromatic thiocyanation reaction has never been reported.

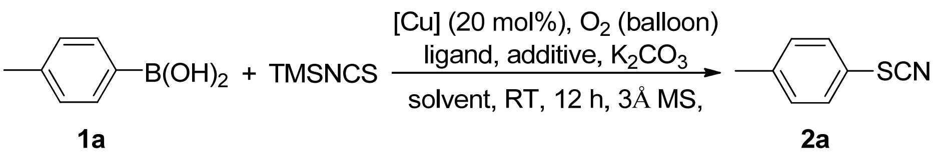


Scheme 1 Copper-catalyzed aerobic oxidative thiocyanation of arylboronic acids

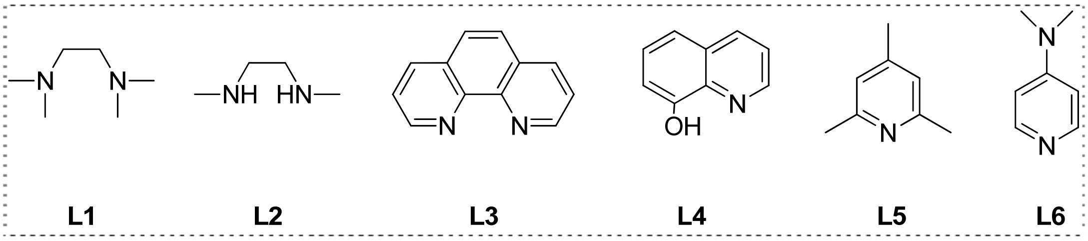
Results and discussion

We initiated our investigation by choosing the cross-coupling of 4-methylphenylboronic acid (**1a**) and TMSNCS to form 4-methylphenyl thiocyanate (**2a**) as model reaction and the results were summarized in Table 1. At first, the reaction was carried out in acetonitrile by employing 20 mol% $Cu(OAc)_2$ as catalyst, O_2 as terminal oxidant, 20 mol% tetramethylethylenediamine (TMEDA, **L1**) as ligand, 4 equiv. of K_2CO_3 as base and 3Å molecular sieves as desiccant. After stirred at room temperature for 12 h under a balloon of O_2 atmosphere, only a trace of thiocyanation product **2a** was observed according to GC-MS detection, and the residual was mainly the starting material, 4-methylphenylboronic acid (Entry 1, Table 1). Pleasantly, when 1 equiv. of TBAF was added into the reaction system, the thiocyanation reaction occurred quite smoothly, and the desired product **2a** was obtained in 58% yield (Entry 2, Table 1). It is obvious that the additive TBAF promoted the cleavage of N-Si bond in TMSNCS to free the active NCS^- nucleophile. With this preliminary result in hand, we then further investigated the other effective factors on this thiocyanation reaction, including catalysts, ligands, additives and solvents. Screening experiments of catalysts revealed that quite a lot of copper compounds, either Cu(II) salts ($CuSO_4$, $CuBr_2$ and $CuCl_2$) or Cu(I) salts (CuCl and CuI), were able to catalyze this oxidative cross-coupling reaction, and the thiocyanation product **2a** could be obtained ranging from 50 to 61% yields (Entries 3-7, Table 1). Considering that CuCl provided a relative better result on this transformation, it was selected as catalyst for our further research. More experiments showed that the reaction efficiency was significantly depended on the ligand property. For example, replacing ligand **L1** with dimethylethylenediamine (**L2**), the yield of **2a** was dramatically decreased to 43% (Entry 8, Table 1). Ligands phenanthroline (**L3**), 8-hydroxyquinoline (**L4**) and 2,4,6-collidine (**L5**) were even found to retrain the reaction (Entries 9-11, Table 1). Ligand 4-(*N*,*N*-dimethylamino)pyridine (DMAP, **L6**) could be almost comparable to **L1**, and the reaction with **L6** afforded **2a** in 58% yield (Entry 12, Table 1). To our delight, when we switched additive TBAF to inorganic F^- source, NaF, the yield of **2a** was greatly improved to 93% (Entry 13, Table 1). Other inorganic F^--containing salts, KF and NH_4F, also can achieve higher yields of **2a** with 83% and 81%, respectively (Entries 14 and 15, Table 1). We reckoned that these inorganic F^--containing salts have lower solubility than TBAF in reaction solvent (CH_3CN), and thus the concentrate of active NCS^- nucleophile was kept in a low level by in situ generating in a slower rate, which favored the reaction selectivity. In addition, it was found that reaction solvent and/or moisture could be also crucial to the reaction efficiency. When the reaction was carried out in DMF, the yield of **2a** was dropped to 24%, whilst trace product was resulted in DCE, THF and MeOH (Entries 16-19, Table 1). On other hand, 3Å MS played a marginal role in the reaction (87% yield without 3 Å MS, Entry 20, Table 1). Further optimized experiments indicated that 2 equiv. of phenylboronic acid (comparison to TMSNCS) was essential to achieve high yield (Entry 21, Table 1). Cutting down the loading of catalyst (CuCl) led to extremely longer reaction time while maintaining the reaction selectivity (Entry 22, Table 1). It is noteworthy to point that O_2 was necessary for this transformation. When the reaction was set up under N_2 atmosphere, only a little amount of **2a** was observed (Entry 23, Table 1). With the above experimental results, the optimal condition was concluded that the reaction was carried out with 20 mol% of CuCl, 20 mol% of **L1,** 1 equiv. of NaF and 4 equiv. of K_2CO_3 in CH_3CN at room temperature for 12 h and under oxygen balloon, together with 3Å molecular sieves.

Table 1 Optimization studies for the copper-catalyzed cross-coupling of 4-methoxylphenylboronic acid and TMSNCS [a]



Ligand:



Entry	[Cu]	Ligand (equiv.)	Additive (equiv.)[b]	Solvent	Yield (%)[c]
1	$Cu(OAc)_2$	L1(0.2)	-	CH_3CN	Trace
2	$Cu(OAc)_2$	L1(0.2)	TBAF(1.0)	CH_3CN	58
3	$CuSO_4$	L1(0.2)	TBAF(1.0)	CH_3CN	50

4	$CuCl_2$	L1(0.2)	TBAF(1.0)	CH_3CN	55
5	$CuBr_2$	L1(0.2)	TBAF(1.0)	CH_3CN	60
6	CuCl	L1(0.2)	TBAF(1.0)	CH_3CN	61
7	CuI	L1(0.2)	TBAF(1.0)	CH_3CN	51
8	CuCl	L2(0.2)	TBAF(1.0)	CH_3CN	43
9	CuCl	L3(0.2)	TBAF(1.0)	CH_3CN	8
10	CuCl	L4(0.2)	TBAF(1.0)	CH_3CN	5
11	CuCl	L5(0.4)	TBAF(1.0)	CH_3CN	Trace
12	CuCl	L6(0.4)	TBAF(1.0)	CH_3CN	56
13	CuCl	L1(0.2)	NaF(1.0)	CH_3CN	93(89)[d]
14	CuCl	L1(0.2)	KF(1.0)	CH_3CN	83
15	CuCl	L1(0.2)	NH_4F(1.0)	CH_3CN	81
16	CuCl	L1(0.2)	NaF(1.0)	DMF	24
17	CuCl	L1(0.2)	NaF(1.0)	DCM	Trace
18	CuCl	L1 (0.2)	NaF(1.0)	THF	Trace
19	CuCl	L1(0.2)	NaF(1.0)	MeOH	Trace
20[e]	CuCl	L1(0.2)	NaF(1.0)	CH_3CN	87
21[f]	CuCl	L1(0.2)	NaF(1.0)	CH_3CN	66
22[g]	CuCl(0.1)	L1(0.1)	NaF(1.0)	CH_3CN	69(12 h) 89(30 h)
23[h]	CuCl	L1(0.2)	NaF(1.0)	CH_3CN	13

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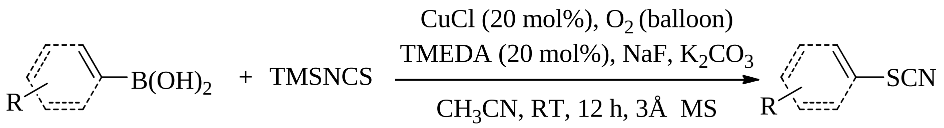
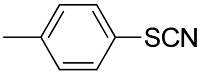
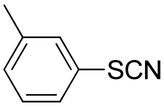
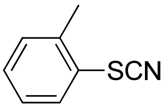
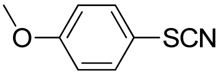
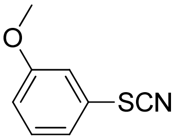
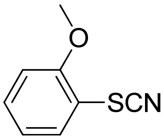
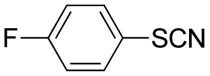
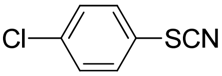
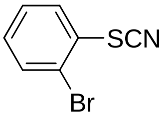
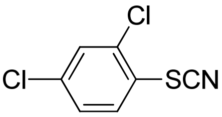
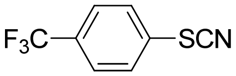
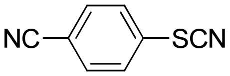
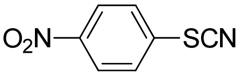
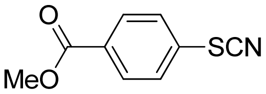
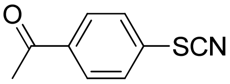
[a] Reaction condition: 4-methoxyl phenylboronic acid **1a** (2.0 mmol), TMSNCS (1.0 mmol), [Cu] (20 mol%), K_2CO_3 (4.0 mmol), O_2 balloon, 2.5 g 3Å MS, solvent (5 ml), room temperature, 12h; [b] GC yield by internal standard method with biphenyl as internal standard, and the yield in parentheses was isolated yield. [c] TBAF was used as a 1 mol/L solution in THF, and NaF, KF and NH_4F were AR grade. [d] 4-Methylphenyl thiocyanate **2a** was somewhat volatile. [e] Without 3Å MS. [f] 1.5 mmol of 4-methoxylphenylboronic acid were used. [g] 10 mol% of CuCl were used. [h] Under a N_2 balloon.

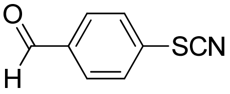
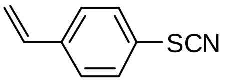
With the optimal conditions in hand, we then investigated the substrate scope of this transformation. As listed in Table 2, not only arylboronic acids bearing with electron-donating groups (**1a-1f**) could afford the desired products in good yields (Entries 1-6, Table 2), but those arylboronic acids with electron-withdrawing groups (**1g-1m**) also worked well under the standard procedure and their corresponding aryl thiocyanates were obtained in moderate to good yields (Entries 7-13, Table 2). It is specially noted that the substrates with strong electron-withdrawing groups (CN and NO_2) could smoothly convert to the desired 4-cyanophenyl thiocyanate **2l** (62%) and 4-nitrophenyl thiocyanate **2m** (45%) (Entries 12 and 13, Table 2), while these two substrates were almost inert in our previously report.[21] Generally, the yield of *ortho*-substituted thiocyanates was a slightly lower than its *para*- and *meta*-substituted analogs, which was ascribed to its steric hindrance (Entries 1-3 and 4-6, Table 2). Halogen-substituted arylboronic acids were good reaction substrates, and their corresponding thiocyanates **2g-2j** were obtained in good yields (74-84%), which could be potentially used for further transformations. To our delight, the novel reaction system was also favorable for the synthesis of aryl thiocyanates containing electrophilic ester, ketone and aldehyde groups and these thiocyanates (**2n**-**2p**) could be obtained in moderate to good yields (57-73%), which was attributed to non-nucleophilic property of TMSNCS (Entries 14-16, Table 2). Moreover, reactive vinyl group could be survived well under the present procedure, leading to **2q** in 72% yields. Unfortunately, as the same results in our previous report, we found that this reaction system is still not suitable in the synthesis of both vinyl thiocyanates and aliphatic thiocyanates. In addition, the protocol was also inefficient in the transformation of heteroaryl boronic acids to their thiocyanates. When the current developed procedure was applied to the cross-coupling between pyridin-4-ylboronic acid and TMSNCS, only a little amount of 4-thiocyanatopyridine was resulted (less than 10% yield according to GC-MS) and no pure product was finally isolated.

Table 2 CuCl-catalyzed aerobic oxidative thiocyanation of arylboronic acids at room temperature [a]



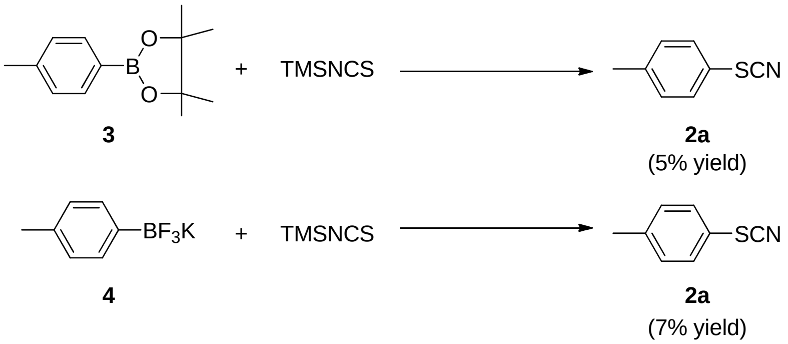
1 **2**

Entry	**1**(R)	Product	**2**	Yield (%)^b
1	**1a** (4-CH_3)		**2a**	89
2	**1b** (3-CH_3)		**2b**	88
3	**1c** (2-CH_3)		**2c**	82
4	**1d** (4-OMe)		**2d**	76
5	**1e** (3-OMe)		**2e**	74
6	**1f** (2-OMe)		**2f**	72
7	**1g** (4-F)		**2g**	84
8	**1h** (4-Cl)		**2h**	81
9	**1i** (2-Br)		**2i**	78
10	**1j** (2,4-diCl)		**2j**	74
11	**1k** (4-CF_3)		**2k**	79
12	**1l** (4-CN)		**2l**	62
13	**1m** (4-NO_2)		**2m**	45
14	**1n** (4-COOMe)		**2n**	73
15	**1o** (4-COMe)		**2o**	68

16	**1p** (4-CHO)		**2p**	57
17	**1q** (4-CH=CH_2)		**2q**	72

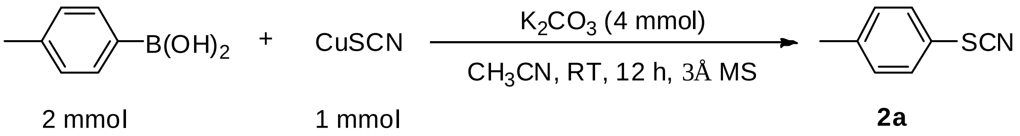
[a] Reaction conditions: arylboronic acid (2.0 mmol), TMSNCS (1.0 mmol), CuCl (20 mol%), TMEDA (20 mol%), NaF(1.0 mmol), K_2CO_3 (4.0 mmol), O_2 balloon, 2.5 g 3Å MS, CH_3CN (5 ml), room temperature, 12 h. [b] Isolated yields.

In order to further investigate the scope of this reaction, we also tested the reaction of various phenylboronic acid derivatives, pinacol 4-methylphenylboronate **3** and potassium 4-methylphenyltrifluoroborate **4,** with TMSNCS under our proposed reaction system (Scheme 2). Unfortunately, both of them afforded the desired product **2a** in less than 10% yield with recovering a large amount of starting materials. Prolonging the reaction time or elevating the reaction temperature to 60 °C was also not facilitated the transformation.



Scheme 2 CuCl-catalyzed thiocyanation of 4-methylphenylboronic acid derivatives with TMSNCS under standard reaction conditions

For the purpose of investigation of the reaction mechanism, CuSCN was considered as an intermediate and its reactivity on this transformation was examined (Scheme 3). When 0.5 equiv. of CuSCN was reacted with 4-methylphenylboronic acid **1a** under the standard procedure, the corresponding thiocyanate **2a** was obtained in 46% yield. Particularly, both the ligand TMEDA and O_2 were essential for this transformation. Without TMEDA or O_2, only trace **2a** was observed.



O_2	TMEDA	**2a** (%)
balloon	1 mmol	46%
balloon	-	trace
N_2	1mmol	trace

Scheme 3 Reaction of 4-methylphenylboronic acid with CuSCN

From these results, a plausible reaction mechanism is proposed in Figure 1.[24] It was assumed that LCu(I)Cl **A** was first exchanged with the in situ generated NCS^- anion to form reactive LCu(I)SCN **B**, which could be oxidized by O_2 to yield bis(μ-oxo)-dicopper (III) complex **C.** In this step, the existence of the diamine ligand TMEDA (L) was essential. It would increase electron density on the copper center by coordination. Once **C** was resulted, it combined with two molecules of arylboronic acid by O-B coordinate bond interaction, followed by transferring aryl group to copper atom to afford intermediate **D**. The **D** was unstable and decomposed to two monomeric copper (III) complex **E**. Finally, the resulted **E** underwent facile reductive elimination to the desired product aryl thiocyanates and the LCu(I)-$OB(OH)_2$ **F**. The formed **F** further exchanged with the NCS^- anion to form LCu(I)SCN **B** to complete the catalytic cycle.

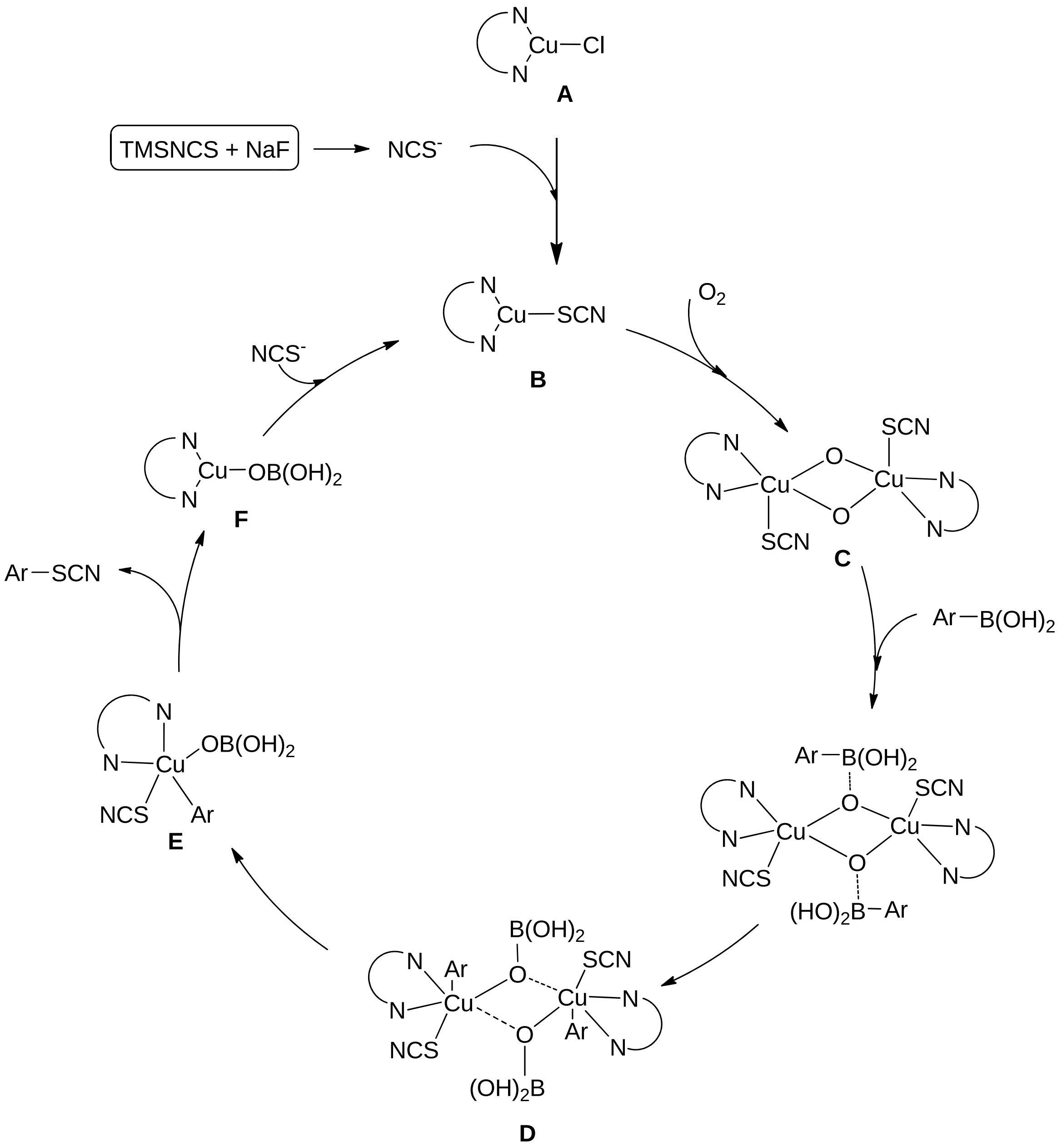


Figure 1 Plausible reaction pathway for thiocyanation of arylboronic acids with TMSNCS

Conclusion

In conclusion, we have developed a novel protocol for the copper-catalyzed aerobic oxidative thiocyanation of arylboronic acids. By using TMSNCS as NCS^- nucleophile precursor and in presence of NaF, this cross coupling reaction could proceed smoothly at room temperature with the promotion of catalytic amount of CuCl and under an O_2 atmosphere. The proposed reaction system was suitable in the synthesis of a broad range of aryl thiocyanates, especially which contained reactive functional groups, such as halo, ester, ketone, aldehyde and vinyl groups, as well as strong electron-withdrawing groups, such as cyano and nitro groups. We believe that the milder and more efficient reaction conditions described herein will be widely used for aromatic oxidative thiocyanation.

Acknowledgements

This work was supported by the National Natural Science Foundations of China (21376224). We also thank the support from "Zhejiang Key Course of Chemical Engineering and Technology" and "Zhejiang Key Laboratory of Green Pesticides and Cleaner Production Technology of Zhejiang Province" of Zhejiang University of Technology.

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