EurJOC
European Journal of Organic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

Title: Three-Component Synthesis of 2-Subsituted Thiobenzoazoles using Tetramethyl Thiuram Monosulfide (TMTM) as Thiocarbonyl Surrogate

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202001214

Link to VoR: https://doi.org/10.1002/ejoc.202001214

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A Chemoselective and Desulfurative Chan-Lam Coupling: C-N Bond Formation between Benzimidazoline-2-Thiones and Arylboronic Acids

Jin-Quan Chen,[a] Xing Liu,[a] Jia Guo,[b],[c] and Zhi-Bing Dong* [a],[b],[c],[d]

Abstract: An efficient method for the chemoselective and desulfurative Chan-Lam cross-coupling based on benzimidazoline-2-thiones was developed. By modulating the amount of the catalyst $Cu(OAc)_2 \cdot H_2O$, alkali, temperature and solvent, the desulfurizational C-N bond formation product (N-arylbenzimidazoles) could be selectively furnished smoothly. The features of this protocol are an inexpensive and readily available catalyst, ligand-free conditions, wide substrate scope, easy performance, and moderate to excellent yields. It shows potential synthetic value for the preparation of a diversity of arylbenzoheterocyclic compounds, which are potentially active in pharmaceuticals and agrochemicals.

Introduction

Imidazole-based compounds are a class of very important and versatile nitrogen-containing heterocyclic compounds due to their numerous applications, such as drugs, pharmaceutical intermediates, agrochemicals, antimicrobial agents, functional materials, and biomimetic catalysts.[1] Among these, the N-arylbenzimidazoles have attracted much attention since they are key building blocks in a large number of pharmaceutical molecules (**Figure 1**).[2] Besides, the N-arylbenzimidazoles also have many comprehensive applications in other respects. For instance, they can be applied in the synthesis of natural products, and they are also fundamental materials for ionic liquids, ligands for transition-metal catalysis, and versatile N-heterocyclic carbene precursors.[3] Thus, the development of simple and efficient approaches for the synthesis of N-arylbenzimidazoles has attracted considerable attention in the past decades.

Several strategies have been developed for the synthesis of N-arylbenzimidazoles (**Scheme 1**). Synthetic protocols that afford N-arylbenzimidazoles generally involve transition-metal-catalyzed Ullmann-type cross-couplings between benzimidazoles and aryl halides (**Scheme 1**, a),[4] intramolecular cross coupling of aromatic o-diamines with CO_2 (**Scheme 1**, b),[5] or cyclization of aromatic o-diamines with CO_2 and H_2 (**Scheme 1**, c).[6] In addition, N-arylation of azole compounds using reactive and selective TMP-iodonium(III) salts (**Scheme 1**, d),[7] and copper-catalyzed couplings of N-H substrates with $NaBPh_4$ (**Scheme 1**, e) are also optional pathways.[8] However, these synthetic processes suffer from harsh reaction conditions such as high reaction temperature, requirement of stoichiometric amount of copper catalyst, or usage of toxic solvents and non-commercially available ligands. Though N-arylations *via* cross-coupling reactions between benzimidazoles and arylboronic acids have been reported (**Scheme 1**, f),[9-10] the expanded research based on classic Chan-Lam coupling is still desirable.

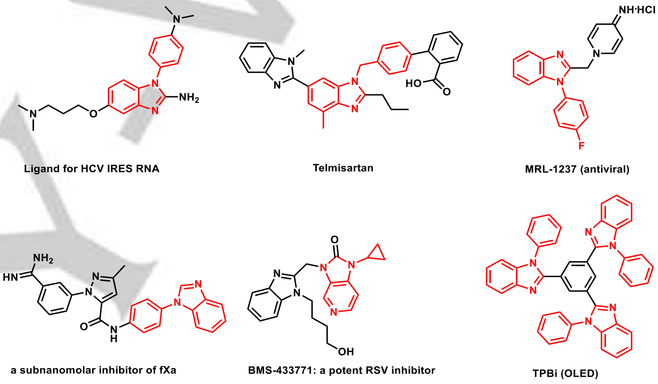
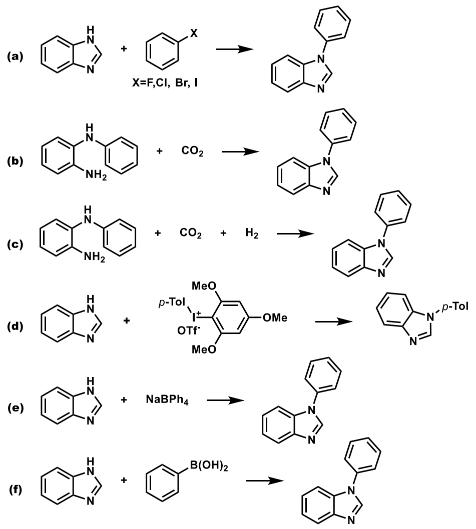


Figure 1. Some biologically active N-arylbenzimidazoles.



Scheme 1. Existing Synthetic Strategies towards N-arylbenzimidazoles.

Recently, we disclosed an efficient chemoselective Chan–Lam coupling reactions between benzimidazoline-2-thiones and arylboronic acids,[11] and the coupling reactions could be selectively directed to two different products (**Scheme 2**, S-arylbenzimidazoles or N,S-diarylbenzimidazoles). On the other

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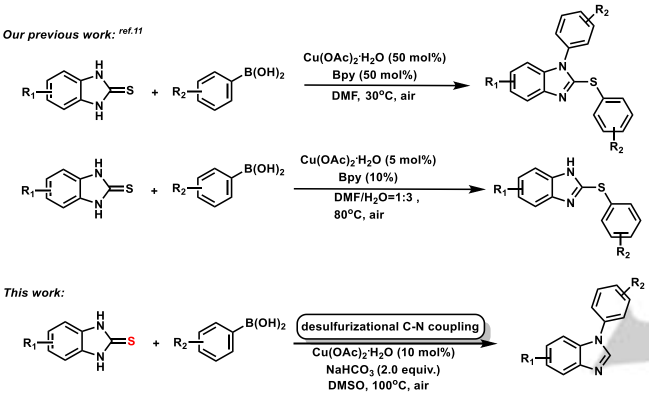
10.1002/ejoc.202001214

hand, it is known that desulfurative couplings, such as the Liebeskind reaction[12] or the Suzuki-Miyaura reaction,[13] are generally performed under harsh reaction conditions, which usually involve the use of expensive transition metal catalysts and ligands, high temperature, as well as the use of inert atmosphere for the construction of C-C bonds.[14] As part of our longstanding interest in heterocyclic chemistry[12] and organosulfur chemistry in the development of Chan-Lam couplings,[13] we herein disclose a chemoselective and desulfurative Chan–Lam coupling which affords C-N formation products (N-arylbenzimidazoles, **Scheme 2**) starting from benzimidazoline-2-thiones and arylboronic acids. The selectivity can be controlled by modulating the amount of $Cu(OAc)_2•H_2O$, base, temperature and solvent, which could provides attractive and alternative approach to access these important compounds.

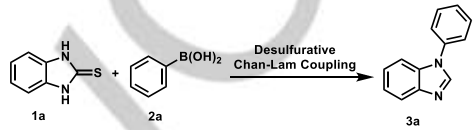


Scheme 2. Chan-Lam-type Coupling Reactions: (i) Previous Work: Chemoselective C-S and C-N Bond Formations. (ii)This Work: Desulfurizational C-N Coupling.

Results and Discussion

Thus, the reaction condition survey for the chemoselective and desulfurative Chan–Lam coupling reaction of benzimidazoline-2-thione (**1a**) with phenylboronic acid (**2a**) are summarized in Table 1. Initially, the reaction of benzimidazoline-2-thione (**1a**) and phenylboronic acid (**2a**) was examined in DMSO at 100 °C in the presence of $Cu(OAc)_2•H_2O$ (0.2 eq.) and 2,2'-bipyridine (Bpy; 0.2 equiv). A mixture of S-arylbenzimidazole and N,S-diarylbenzimidazole were detected simultaneously (entry 1) without the addition of base. To our delight, the N-arylation product **3a** was obtained with 62% yield as the single product when KOH (2.0 eq.) was added (entry 2), which demonstrated that base was crucial to afford the desulfurative N-arylation product. Encouraged by this result, various bases were screened (entry 2-9), revealing that $NaHCO_3$ was superior to other bases, providing the desired product **3a** in 88% yield (entry 7). Next, the amount of $NaHCO_3$ was surveyed (entry 10-11), and it was found that 2 equiv. of $NaHCO_3$ was the optimal. The control experiment for copper catalyst $Cu(OAc)_2•H_2O$ and ligand Bpy revealed that copper catalyst was crucial for the reaction while ligand was not necessary (entry 12). Based on these results, several copper catalysts were screened (entry 13-19) and it showed that $Cu(OAc)_2•H_2O$ was the most effective catalyst (entry 13). In addition, the screenings also showed that the yields obtained from Cu(II) salts were slightly higher than the ones obtained from Cu(I) salts. The catalyst loading (entries 20-22) indicated that 0.1 equiv. of $Cu(OAc)_2•H_2O$ was optimal (entry 21). To further optimize the reaction conditions, we screened the substrate ratio, the temperature, and the solvent (entry 23-33), while the yield of **3a** could not be improved. Thus, the optimal reaction conditions for desired product **3a** were as follows: **1a**:**2a** = 1:1.5, $Cu(OAc)_2•H_2O$ (10 mol%), $NaHCO_3$ (2.0 equiv), DMSO (3 mL), 100 °C, 8h (entry 21).

Table 1. Optimization of Desulfurizational Chan–Lam Coupling for the Synthesis of **3a**.[a]



Entry	Base	Catalyst [Cu]	Ligand	Solvent	Yield 3a (%)[b]
1	--	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy[c]	DMSO	0
2	KOH(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	62
3	NaOH(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	71
4	K_2CO_3(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	64
5	Na_2CO_3(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	65
6	Cs_2CO_3(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	47
7	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	88
8	pyridine(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	N.R.[d]
9	EtN_3(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	trace
10	$NaHCO_3$(1eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	58
11	$NaHCO_3$(3eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	BPy	DMSO	80
12	$NaHCO_3$(2eq.)	--	BPy	DMSO	N.R.
13	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.2eq.)	--	DMSO	[illegible]
14	$NaHCO_3$(2eq.)	$CuSO_4$(0.2eq.)	--	DMSO	72
15	$NaHCO_3$(2eq.)	$CuCl_2·2H_2O$(0.2eq.)	--	DMSO	[illegible]
16	$NaHCO_3$(2eq.)	$CuBr_2$(0.2eq.)	--	DMSO	75
17	$NaHCO_3$(2eq.)	CuI(0.2eq.)	--	DMSO	77
18	$NaHCO_3$(2eq.)	CuCl(0.2eq.)	--	DMSO	81
19	$NaHCO_3$(2eq.)	$Cu(OTf)_2$(0.2eq.)	--	DMSO	63
20	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.05eq.)	--	DMSO	82
21	**$NaHCO_3$(2eq.)**	**$Cu(OAc)_2·H_2O$(0.1eq.)**	**--**	**DMSO**	**92**
22	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(1.0eq.)	--	DMSO	79
23[e]	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMSO	[illegible]
24[f]	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMSO	92
25[g]	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMSO	N.R.
26[h]	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMSO	N.R.
27[i]	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMSO	44
28[j]	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMSO	74
29	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMF	75
30	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	DMAc	65
31	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	H_2O	N.R.
32	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	$PhCH_3$	N.R.
33	$NaHCO_3$(2eq.)	$Cu(OAc)_2·H_2O$(0.1eq.)	--	1,4-dioxane	N.R.

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), base (2.0 equiv.), solvent (3 mL), temperature : 100 °C, stirred for 6-8 h. [b] Isolated yield based on **1a**. [c] Bpy = 2,2'-bipyridine (0.2 equiv.). [d] No Reaction. [e] **1a** : **2a** = 1:1. [f] **1a** : **2a** = 1:2. [g] temperature: 25 °C. [h] temperature: 60 °C. [i] temperature: 80 °C. [j] temperature: 120 °C.

With the optimal conditions established, we next explored the scope of this desulfurative Chan–Lam coupling by employing structurally diverse arylboronic acids and benzimidazoline-2-thiones, and the results are summarized in Table 2. It was

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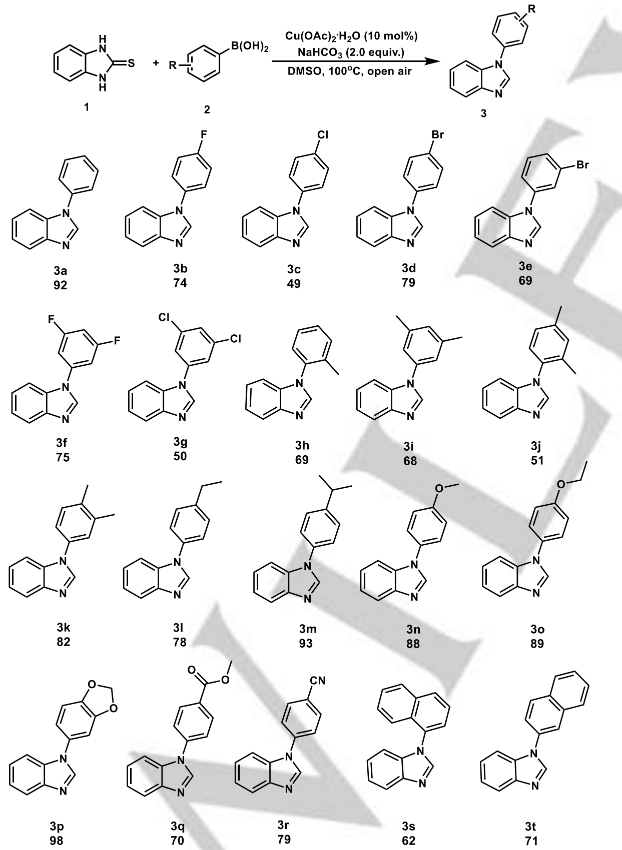
satisfying that a serious of substituted phenylboronic acids could couple with benzimidazoline-2-thione in moderate to excellent yields. Phenylboronic acids bearing electron-withdrawing groups (F, Cl, Br, CN) successfully coupled with benzimidazoline-2-thione, providing the desired products (**3b-3g, 3r**) in moderate to good yields (49%-79%), and electron-donating groups on the phenylboronic acids gave the corresponding products (**3h-3p**) with moderate to excellent yields (51%-98%). The investigation results indicated that the electronic nature of the substituent somehow effected the reaction. The electron donating arylboronic acids were more reactive than the electron withdrawing ones. The steric effect on this transformation was also studied. Thus, disubstituted arylboronic acids (with *ortho-, meta-* and *para-* groups) were employed, giving the corresponding products N-arylbenzimidazoles (**3i-3k**) with 51%-82% yields, which showed a certain steric effect. To our delight, 4-(methoxycabonyl)phenylboronic acid was also suitable for this transformation, giving the intended product **3q** in 70% yield. Furthermore, 1-naphthylboronic acid and 2-naphthylboronic acid successfully coupled with benzimidazoline-2-thione, giving the target products **3s** and **3t** in good yields (62% and 71%), respectively.

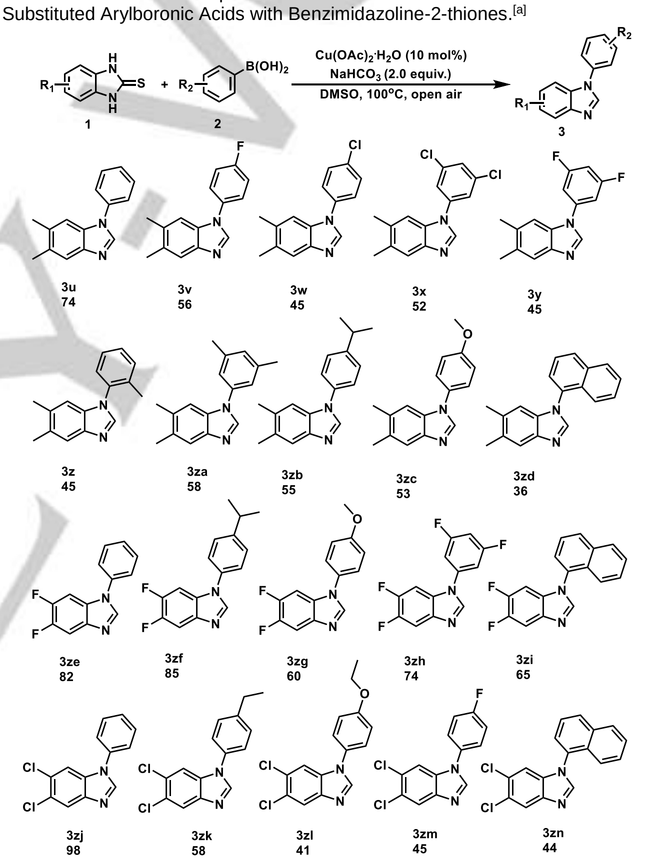
Table 2. Substrate Scope for the Desulfurizational Chan-Lam Reaction of Substituted Arylboronic Acids with Benzimidazoline-2-thione.[a]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), $Cu(OAc)_2$•H_2O (10 mol%), $NaHCO_3$ (2.0 equiv.), DMSO (3 mL), 100 ºC, open air for 8-24 h; Isolated yield based on **1**.

Subsquently, we continued to explore the substrate scope either for benzimidazoline-2-thiones or for arylboronic acids, and the results are listed in Table 3. It was gratifying to find that whether the electron-donating or the electron-withdrawing groups attaching to the substituted benzimidazoline-2-thiones reacted with a variety of substituted arylboronic acids in moderate to good yields, showing good substrate compatibility of this protocol. The substrates surveyed also revealed that benzimidazoline-2-thiones bearing electron-withdrawing substituents were more reactive than the electron-donating ones (**3ze** *vs* **3u, 3zf** *vs* **3z**b), and arylboronic acids bearing electron donating groups showed higher yields than the ones with electron withdrawing groups (**3zb** *vs* **3v, 3zf** *vs* **3zh, 3zk** *vs* **3zm**).

Table 3. Substrate Scope for the Desulfurative Chan-Lam Reaction of Substituted Arylboronic Acids with Benzimidazoline-2-thiones.[a]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), $Cu(OAc)_2$•H_2O (10 mol%), $NaHCO_3$ (2.0 equiv.), DMSO (3 mL), 100 ºC, open air for 8-24 h; Isolated yield based on **1**.

To further explore the mechanism of this desulfurative C-N coupling, the following control experiments were performed (**Scheme 3**). Firstly, benzimidazoline-2-thione was treated with $NaHCO_3$ in DMSO at 100 ºC for 20 h. In the reaction, the starting material benzimidazoline-2-thione was remained a lot and the desulfurative product benzimidazole was detected (isolation yield: 30%). The yield of benzimidazole could not be improved when the reaction time was prolonged to 48 h. Sequently, arylboronic acid (1.5 equiv.) and $Cu(OAc)_2$•H_2O (10 mol%) were added to the hybrid system, and the mixture

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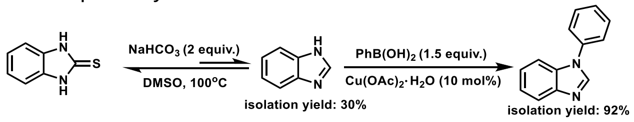
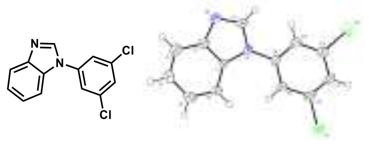
(benzimidazoline-2-thione and benzimidazole) were transformed to N-arylbenzimidazole smoothly (isolation yield: 92%), which might be due to the driving force of Chan-Lam C-N coupling. To further confirm the fact of this desulfurative Chan-Lam coupling, product **3g** was characterized by X-ray crystallography (Figure 2, CCDC 1953877), and it was identified with our speculated reaction pathway.



Scheme 3. Control Experiments

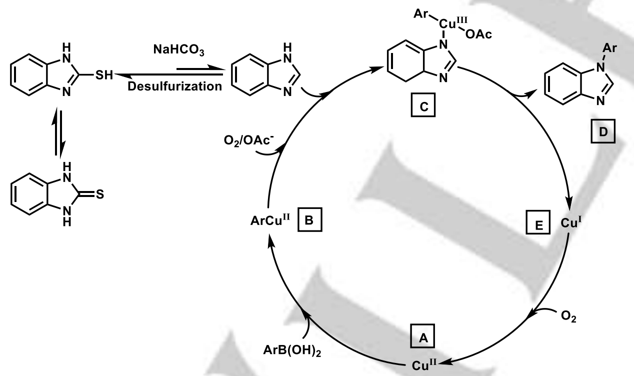


3g X-Ray crystal of 3g

Figure 2. X-ray Crystallography of Product **3g** from the Desulfurizational Chan-Lam Coupling.

According to the above experimental results and previous literature reports,[17] we proposed a possible mechanism for this reaction (**Scheme 4**). Firstly, the benzimidazoline-2-thione was transformed to 2-mercaptobenzimidazole *via* isomerization (it is a dynamic equilibrium), followed by desulfuration under the action of base ($NaHCO_3$), giving benzimidazole (a dynamic equilibrium as well). Secondly, the arylboronic acid reacted with the copper catalyst (**A**) to form complex **B**, which could be oxidized by O_2 to give Cu(III) species, and the subsequent transmetalation with readily available desulfurative intermediate (benzimidazole) gave intermediate **C**. Intermediate **C** easily provided the desired C-N coupling product **D** along with Cu(I) species (**E**) by reductive elimination. **E** was then oxidized by oxygen to regenerate Cu(II) catalyst **A**.

Scheme 4. Proposed Reaction Mechanism.



Conclusions

In summary, we reported herein a chemoselective, desulfurative Chan-Lam coupling by using inexpensive and commercially available arylboronic acids and benzimidazoline-2-thiones. This expanded research together with our previous work[11] affords a useful protocol for the chemoselective formation of N-arylbenzimidazoles, S-arylbenzimidazoles, as well as N,S-diarylbenzimidazoles starting from benzimidazoline-2-thiones and arylboronic acids, by modulating the amount of $Cu(OAc)_2•H_2O$, base, temperature, and solvent. The protocol features good selectivity, broad functional group tolerance, easy performance and moderate to excellent yields. This protocol showed potential application value for the preparation of a diversity of N-aryl benzoheterocyclic compounds, which are potentially active in pharmaceuticals and agrochemicals.

Experimental Section

Flash column chromatography was operated on silica gel with petroleum ether-EtOAc (PE-EA) as the eluent. Thin layer Chromatography was adopted and visualized under UV light. The RY-1G instrument was adopted to determine melting points of target compounds. The HRMS (high-resolution mass spectra) was recorded from a Finnigan MAT 95Q mass instrument (ESI). A Bruker AM400 NMR instrument was operated in $CDCl_3$ to record NMR spectra.

Typical procedure for the synthesis of N-arylbenzimidazoles 3a (TP).

Benzimidazoline-2-thione **1a** (0.5 mmol) and phenylboronic acid **2a** (0.75 mmol), $Cu(OAc)_2•H_2O$ (0.05 mmol), $NaHCO_3$ (1.0 mmol) were added to a dried tube (open to air) equipped with a magnetic stirring bar, DMSO (3.0 mL) was then added. The mixture was stirred at 100 ºC and checked by TLC. The reaction was quenched with sat. NH_4Cl solution and then extracted with ethyl acetate. The preliminary solution was dried over Na_2SO_4 and evaporated. The crude material was further purified by column chromatography to get the intended product **3a**.

Analytical data of the products

1-phenyl-1*H*-benzo[*d*]imidazole (3a) [5]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3a** as a colorless oil (90 mg, yield = 92%). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.76-7.78 (m, 1H), 7.30-7.45 (m, 6H), 7.18-7.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.8, 141.2, 135.2, 132.6, 128.9, 126.9, 122.9, 122.6, 121.7, 119.4, 109.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_{11}N_2$ (195.0917), found: 195.0915.

1-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (3b) [9e]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3b** as a white soild (78 mg, yield = 74%). mp: 112-116 ºC. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.98 (s, 1H), 7.78-7.81 (m, 1H), 7.36-7.41 (m, 3H), 7.24-7.28 (m, 2H), 7.16-7.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 160.9 (d, J = 247.0 Hz), 142.8, 141.2, 132.8, 131.3 (d, J = 3.0 Hz), 125.0 (d, J = 8.0 Hz), 122.8, 121.8, 119.6, 116.0 (d, J = 23.0 Hz), 109.1. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_{10}FN_2$ (213.0823), found: 213.0826.

1-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (3c) [9a]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3c** as a white soild (56 mg, yield = 49%). mp: 108-110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.79-7.81 (m, 1H), 7.46-7.48 (m, 2H), 7.36-7.42 (m, 3H), 7.24-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.9, 141.0, 133.8, 132.8, 132.5, 129.2, 124.2, 122.9, 122.0, 119.7, 109.1. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_{10}ClN_2$ (229.0527), found: 229.0521.

1-(4-bromophenyl)-1*H*-benzo[*d*]imidazole (3d) [9a]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3d** as a white soild (99 mg, yield = 79%). mp: 100-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.98 (s, 1H), 7.77-7.81 (m, 1H), 7.58-7.62 (m, 2H), 7.38-7.41 (m, 1H), 7.22-7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.9, 140.9, 134.3, 132.3, 132.2, 124.4, 122.9, 122.0, 120.5, 119.7, 109.1. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_{10}BrN_2$ (273.0022), found: 273.0027.

1-(3-bromophenyl)-1*H*-benzo[*d*]imidazole (3e) [18a]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3e** as a white soild (94 mg, yield = 69%). mp: 98-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.76-7.81 (m, 1H), 7.59-7.60 (m, 1H), 7.48-7.51 (m, 1H), 7.41-7.45 (m, 1H), 7.32-7.38 (m, 2H), 7.23-7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.9, 140.9, 136.4, 132.2, 130.3, 130.0, 125.9, 123.0, 122.4, 122.0, 121.4, 119.7, 109.2. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_{10}BrN_2$ (273.0022), found: 273.0025.

1-(3,5-difluorophenyl)-1*H*-benzo[*d*]imidazole (3f)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3f** as a white soild (86 mg, yield = 75%). mp: 84-86 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.01 (s, 1H), 7.77-7.81 (m, 1H), 7.47-7.51 (m, 1H), 7.26-7.30 (m, 2H), 6.98-7.05 (m, 2H), 6.80-6.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 162.7 (dd, J = 250.0 Hz, J = 14.0 Hz), 143.1, 140.6, 137.4 (t, J = 12.0 Hz), 131.9, 123.3, 122.4, 119.9, 109.2, 106.1 (d, J = 28.0 Hz), 102.4 (t, J = 25.0 Hz). HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_9F_2N_2$ (271.0728), found: 231.0729.

1-(3,5-dichlorophenyl)-1*H*-benzo[*d*]imidazole (3g)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3g** as a white soild (65 mg, yield = 50%). mp: 162-164 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.99 (s, 1H), 7.78-7.80 (m, 1H), 7.43-7.46 (m, 1H), 7.36-7.37 (m, 3H), 7.25-7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 143.0, 140.6, 137.0, 135.4, 131.9, 127.0, 123.2, 122.3, 119.9, 109.1. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_9Cl_2N_2$ (263.0173), found: 263.0177.

1-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (3h) [9e]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3h** as a yellow oil (72 mg, yield = 69%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.88 (s, 1H), 7.79-7.81 (m, 1H), 7.32-7.37 (m, 2H), 7.17-7.29 (m, 4H), 7.03-7.06 (m, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.2, 141.9, 134.3, 133.7, 133.6, 130.4, 128.3, 126.6, 126.1, 122.4, 121.4, 119.3, 109.4, 16.5. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{14}H_{13}N_2$ (209.1073), found: 209.1074.

1-(3,5-dimethylphenyl)-1*H*-benzo[*d*]imidazole (3i) [18c]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3i** as a yellow oil (75 mg, yield = 68%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.77-7.79 (m, 1H), 7.43-7.46 (m, 1H), 7.21-7.25 (m, 2H), 7.02 (d, J=12 Hz, 3H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.9, 141.3, 138.9, 135.1, 132.7, 128.6, 122.4, 121.6, 120.6, 119.4, 109.6, 20.2. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{15}N_2$ (223.1230), found: 223.1235.

1-(2,4-dimethylphenyl)-1*H*-benzo[*d*]imidazole (3j)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3j** as a yellow oil (57 mg, yield = 51%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.86 (s, 1H), 7.79-7.86 (m, 1H), 7.04-7.26 (m, 6H), 2,35 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.2, 142.1, 138.3, 134.0, 133.8, 131.0, 126.7, 126.4, 122.4, 121.3, 119.2, 109.5, 20.1, 16.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{15}N_2$ (223.1230), found: 223.1236.

1-(3,4-dimethylphenyl)-1*H*-benzo[*d*]imidazole (3k) [18b]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3k** as a yellow oil (91 mg, yield = 82%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.99 (s, 1H), 7.76-7.80 (m, 1H), 7.41-7.45 (m, 1H), 7.71-7.26 (m, 5H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.8, 141.3, 137.5, 135.7, 132.9, 132.8, 129.9, 124.1, 122.4, 120.3, 119.4, 109.5, 18.8, 18.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{15}N_2$ (223.1230), found: 223.1234.

1-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole (3l) [18e]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3l** as a yellow oil (87 mg, yield = 78%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.76-7.80 (m, 1H), 7.40-7.43 (m, 1H), 7.27-7.32 (m, 4H), 7.20-7.25 (m, 2H), 2.62-2.68 (m, 2H), 1.21 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 143.3, 142.8, 141.3, 132.8, 132.8, 128.3, 123.0, 122.5, 121.6, 119.4, 27.4, 14.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{15}N_2$ (223.1230), found: 223.1236.

1-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3m)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3m** as a yellow oil (110 mg, yield = 93%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.98 (s, 1H), 7.76-7.79 (m, 1H), 7.42-7.43 (m, 1H), 7.30 (s, 4H), 7.19-7.22 (m, 2H), 2.87-2.96 (m, 1H), 1.21 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 147.8, 142.8, 141.3, 132.8, 132.7, 126.9, 122.9, 122.4, 121.5, 119.4, 109.4, 32.7, 22.9. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{16}H_{16}N_2$ (236.1313), found: 236.1311.

1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (3n) [9e]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3n** as a yellow oil (98 mg, yield = 88%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.05 (s, 1H), 7.86-7.88 (m, 1H), 7.39-7.46 (m, 3H), 7.28-7.35 (m, 2H), 7.05-7.08 (m, 2H) 3.88 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ

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(ppm) 159.3, 143.8, 142.5, 134.2, 129.1, 125.7, 123.5, 122.6, 120.4, 115.1, 110.3, 55.6. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{14}H_{13}N_2O$ (225.1022), found: 225.1027.

1-(4-ethoxyphenyl)-1*H*-benzo[*d*]imidazole (3o)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3o** as a yellow oil (106 mg, yield = 89%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.04 (s, 1H), 7.84-7.89 (m, 1H), 7.43-7.46 (m, 1H), 7.37-7.39 (m, 2H), 7.29-7.32 (m, 2H), 7.03-7.07 (m, 2H), 4.07-4.12 (m, 2H) 1.46 (t, *J* =8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 158.7, 143.8, 142.5, 134.2, 128.9, 125.7, 123.5, 122.5, 120.4, 115.6, 110.3, 63.9, 14.7. HRMS (ESI) m/z [M+H]$^+$ Calcd for C15H15N2O (239.1179), found: 239.1172.

1-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-benzo[*d*]imidazole (3p)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3p** as a yellow oil (117 mg, yield = 98%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.03 (s, 1H), 7.85-7.87 (m, 1H), 7.45-7.47 (m, 1H), 7.29-7.34 (m, 2H), 6.93-6.96 (m, 3H), 6.07 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 148.7, 147.5, 143.7, 142.4, 143.0, 130.1, 123.6, 122.7, 120.5, 117.8, 110.3, 108.8, 105.7, 102.0. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{14}H_{11}N_2O_2$ (239.0815), found: 239.0818.

methyl 4-(1*H*-benzo[*d*]imidazol-1-yl)benzoate (3q) [18d]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3q** as a white soild (89 mg, yield = 70%). mp: 100-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.26 (d, *J* = 8.0 Hz, 2H), 8.17 (s, 1H), 7.88-7.90 (m, 1H), 7.58-7.63 (m, 3H), 7.35-7.38 (m, 2H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 166.0, 144.2, 141.9, 140.1, 133.1, 131.6, 129.4, 124.1, 123.2, 123.2, 120.8, 110.4, 52.4. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{15}H_{13}N_2O_2$ (253.0972), found: 253.0978.

4-(1*H*-benzo[*d*]imidazol-1-yl)benzonitrile (3r) [10a]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3r** as a white soild (87 mg, yield = 79%). mp: 112-114 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.18 (s, 1H), 7.89-7.91 (m, 3H), 7.68-7.70 (m, 2H), 7.57-7.60 (m, 1H), 7.38-7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 144.3, 141.6, 140.1, 134.2, 133.0, 132.8, 129.1, 124.5, 123.9, 123.6, 121.0, 117.8, 111.5, 110.2. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{14}H_{10}N_3$ (220.0869), found: 220.0866.

1-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (3s) [9e]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3s** as a colorless oil (76 mg, yield = 62%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.12 (s, 1H), 7.94-8.04 (m, 3H), 7.53-7.62 (m, 3H), 7.40-7.46 (m, 2H), 7.33-7.37 (m, 1H), 7.22-7.26 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 143.7, 143.3, 134.4, 129.6, 128.4, 127.5, 120.7, 125.4, 124.9, 123.6, 122.7, 122.5, 120.4, 110.8. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{17}H_{13}N_2$ (245.1073), found: 245.1079.

1-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole (3t) [9n]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3t** as a yellow oil (87 mg, yield = 71%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.20 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.89-7.94 (m, 4H), 7.55-7.62 (m, 4H), 7.32-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 144.1, 142.4, 133.9, 133.7, 133.6, 132.4, 130.2, 127.9, 127.9, 127.3, 126.8, 123.7, 122.9, 122.2, 122.1, 120.6, 110.5. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{17}H_{13}N_2$ (245.1073), found: 245.1075.

5,6-dimethyl-1-phenyl-1*H*-benzo[*d*]imidazole (3u) [18d]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3u** as a yellow oil (82 mg, yield = 74%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.01 (s, 1H), 7.63 (s, 1H), 7.53-7.57 (m, 2H), 7.41-7.50 (m, 3H), 7.30-7.38 (s, 1H), 2.36 (t, *J* = 12.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.5, 141.5, 136.6, 132.9, 132.1, 131.7, 129.9, 127.7, 123.8, 120.4, 110.5, 20.5, 20.2. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{15}H_{15}N_2$ (223.1230), found: 223.1233.

1-(4-fluorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3v)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3v** as a yellow oil (67 mg, yield = 56%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.95 (s, 1H), 7.62 (s, 1H), 7.44-7.47 (m, 2H), 7.22-7.27 (m, 3H), 2.38 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 161.8 (d, *J* = 247.0 Hz）, 142.4, 141.4, 133.1, 132.7 (d, *J* = 3.0 Hz), 132.4, 131.8, 125.8 (d , *J* = 9.0 Hz), 120.5, 116.9 (d, *J* = 23.0 Hz), 110.2, 20.5, 20.2. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{15}H_{14}FN_2$ (241.1136), found: 241.1138.

1-(4-chlorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3w) [18d]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3w** as a yellow solid (58 mg, yield = 45%). mp: 116-118 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.79 (s, 1H), 7.63 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 1H), 2.39 (d, *J* = 12.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.6, 141.2, 135.2, 133.5, 133.2, 132.0, 132.0, 130.2, 125.1, 120.6, 110.3, 20.6, 20.2. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{15}H_{14}ClN_2$ (257.0840), found: 257.0846.

1-(3,5-dichlorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3x)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3x** as a yellow solid (76 mg, yield = 52%). mp: 99-102 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.91 (s, 1H), 7.53 (s, 1H), 7.36 (s, 3H), 7.21 (t, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 206.1, 141.3, 139.8, 137.3, 135.3, 132.7, 131.5, 126.7, 121.0, 119.6, 109.2, 19.6, 19.2. HRMS (ESI) m/z [M+H]$^+$ Calcd for $C_{15}H_{12}Cl_2N_2$ (290.0378), found: 259.0377.

1-(3,5-difluorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3y)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3y** as a yellow solid (58 mg, yield = 45%). mp: 110-114 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.91 (s, 1H), 7.54 (s,1H), 7.26 (s, 1H), 7.01 (d, *J* = 12.0 Hz, 2H), 6.79-6.84 (m, 1H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 162.6 (dd, *J* = 249.0 Hz, *J* = 14.0 Hz), 141.6, 139.8, 137.7 (t, *J* = 12.0 Hz), 132.6, 131.4, 130.3, 119.8, 109.3, 105.8 (d,

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J = 28.0 Hz), 102.0 (t, *J* = 26.0 Hz), 19.6, 19.2. HRMS (ESI) m/z [M+H]+ Calcd for $C_{15}H_{13}F_2N_2$ (259.1041), found: 259.1042.

5,6-dimethyl-1-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (3z)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3z** as a yellow oil (53 mg, yield = 45%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.78 (s, 1H), 7.56 (s, 1H), 7.33-7.35 (m, 2H), 7.26-7.30 (m, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 141.1, 140.8, 134.3, 134.0, 132.2, 131.7, 130.4, 130.4, 128.1, 126.4, 126.0, 119.2, 109.5, 19.4, 19.2, 16.6. HRMS (ESI) m/z [M+H]+ Calcd for $C_{16}H_{17}N_2$ (237.1386), found: 237.1385.

1-(3,5-dimethylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3za)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3za** as a yellow oil (73 mg, yield = 58%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.90 (s, 1H), 7.53 (s, 1H), 7.21 (s, 1H), 7.00(d, *J* = 12.0 Hz, 3H), 2.31 (t, *J* = 8.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 141.4, 140.6, 138.8, 135.4, 131.6, 130.5, 128.3, 120.5, 119.3, 109.6, 20.3, 19.5, 19.2. HRMS (ESI) m/z [M+H]+ Calcd for $C_{17}H_{19}N_2$ (251.1543), found: 251.1545.

1-(4-isopropylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3zb)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zb** as a yellow oil (73 mg, yield = 55%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.89 (s, 1H), 7.54 (s, 1H), 7.32 (s, 4H), 7.22 (s, 1H), 2.89-2.95 (m, 1H), 2.30 (d, *J* = 12.0 Hz, 6H), 1.23 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 147.6, 141.5, 140.5, 133.2, 131.7, 131.3, 130.5, 126.8, 122.8, 119.3, 109.6, 32.8, 22.9, 19.5, 19.2. HRMS (ESI) m/z [M+H]+ Calcd for $C_{18}H_{21}N_2$ (265.1699), found: 265.1696.

1-(4-methoxyphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3zc)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zc** as a yellow oil (66 mg, yield = 53%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.86 (s. 1H), 7.53 (s, 1H), 7.31 (d, *J* = 12.0 Hz, 2H), 7.14 (s, 1H), 6.98 (d, *J* = 12.0 Hz, 2H), 3.80 (s, 3H), 2.29 (d, *J* = 16.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 158.1, 141.3, 140.7, 131.7, 131.7, 130.4, 128.4, 124.5, 119.3, 114.0, 109.4, 54.6, 19.5, 19.2. HRMS (ESI) m/z [M+H]+ Calcd for $C_{16}H_{17}N_2O$ (253.1335), found: 253.1335.

5,6-dimethyl-1-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (3zd)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zd** as a yellow oil (50 mg, yield = 36%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7,89-7.94 (m, 3H), 7.61 (s, 1H), 7.43-7.54 (m, 3H), 7.36 (d, *J* = 4.0 Hz, 2H), 6.79 (s, 1H), 2.32 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 142.0, 140.8, 133.7, 133.3, 131.8, 131.6, 130.6, 128.8, 128.4, 127.3, 126.4, 125.9, 124.4, 123.8, 121.6, 119.3,, 109.8, 19.4, 19.2. HRMS (ESI) m/z [M+H]+ Calcd for $C_{19}H_{17}N_2$ (273.1386), found: 273.1389.

5,6-difluoro-1-phenyl-1*H*-benzo[*d*]imidazole (3ze)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3ze** as a yellow solid (94 mg, yield = 82%). mp: 78-80 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.03 (s, 1H), 7.48-7.55 (m, 3H), 7.36-7.43 (m, 3H), 7.18-7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 156.1, 147.8 (dd, *J* = 243.0 Hz, *J* = 16.0 Hz), 147.1 (dd, *J* = 240.0 Hz, *J* = 16.0 Hz), 142.5 (d, *J* = 2.0 Hz), 138.0 (d. *J* = 12.0 Hz), 134.6, 129.2, 127.6, 122.8, 118.6, 114.6, 106.7 (d, *J* = 20.0 Hz), 97.5 (d, *J* = 23.0 Hz). HRMS (ESI) m/z [M+H]+ Calcd for $C_{13}H_9F_2N_2$ (231.0728), found: 231.0723.

5,6-difluoro-1-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3zf)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zf** as a white solid (94 mg, yield = 85%). mp: 136-138 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.51-7.55 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19-7.23 (m, 1H), 2.90-2.97 (m, 1H), 1.24 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 148.6, 147.7 (dd, *J* = 243.0Hz, *J* = 15.0 Hz), 147.1 (dd, *J* = 241.0Hz, *J* = 15.0 Hz),142.6, 138.0 (d, *J* = 10.0 Hz), 132.3, 128.3 (d, *J* = 10.0 Hz), 127.1, 122.9, 106.6(d, *J* = 20.0 Hz), 97.5 (d, *J* = 24.0 Hz), 32.8, 22.8. HRMS (ESI) m/z [M+H]+ Calcd for $C_{16}H_{15}F_2N_2$ (273.1198), found: 273.1193.

5,6-difluoro-1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (3zg)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zg** as a white solid (78 mg, yield = 60%). mp: 130-132 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.96 (s, 1H), 7.50-7.55 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10-7.15 (m, 1H), 7.00 (d, *J* = 12.0 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 158.6, 147.7 (dd, *J* = 243.0 Hz, *J* = 16.0 Hz), 147.0 (dd, *J* = 240.0 Hz, *J* = 15.0 Hz), 142.8, 137.8 (d, *J* = 10.0 Hz), 128.6 (d, *J* = 11.0 Hz), 127.4, 124.6, 114.2, 106.6 (d, *J* = 19.0 Hz), 97.3 (d, *J* = 23.0 Hz), 54.6. HRMS (ESI) m/z [M+H]+ Calcd for $C_{14}H_{11}F_2N_2O$ (261.0834), found: 261.0838.

1-(3,5-difluorophenyl)-5,6-difluoro-1*H*-benzo[*d*]imidazole (3zh)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zh** as a white solid (98 mg, yield = 74%). mp: 156-158 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.04 (s, 1H), 7.54-7.58 (m, 1H), 7.26-7.30 (m, 1H), 6.98-7.01 (m, 2H), 6.86-6.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 168.2 (dd, *J* = 250.0 Hz, *J* = 15.0 Hz), 148.1 (dd, *J* = 245.0 Hz, *J* = 14.0 Hz), 147.4 (dd, *J* = 242.0 Hz, *J* = 15.0 Hz), 141.9 (d, *J* = 3.0 Hz), 138.3 (d, *J* = 10.0 Hz), 136.7 (t, *J* = 13.0 Hz), 127.3 (d, *J* = 11.0 Hz), 107.3 (d, *J* = 19.0 Hz), 106.2 (d, *J* = 29.0 Hz), 103.1 (t, *J* = 25.0 Hz), 97.5 (d, *J* = 24.0 Hz). HRMS (ESI) m/z [M+H]+ Calcd for $C_{13}H_7F_4N_2$ (267.0540), found: 267.0541.

5,6-difluoro-1-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (3zi)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zi** as a yellow solid (91 mg, yield = 65%). mp: 144-146 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.10 (s, 1H), 7.95 (d, *J* = 12.0 Hz, 1H), 7.79-7.86 (m, 3H), 7.43-7.57 (m, 4H), 7.23-7.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 147.8 (dd, *J* = 243.0 Hz, *J* = 16.0 Hz), 147.1 (dd, *J* = 241.0 Hz, *J* = 15.0 Hz), 142.7, 138.2 (d, *J* = 11.0 Hz), 132.5, 132.0, 131.6, 129.4, 128.2 (d, *J* = 10.0 Hz), 126.9 (d, *J* = 10.0 Hz), 126.5, 126.1, 121.1, 120.7, 106.8 (d, *J* = 19.0 Hz), 97.7, 97.4. HRMS (ESI) m/z [M+H]+ Calcd for $C_{17}H_{11}F_2N_2$ (281.0885), found: 281.0883.

5,6-dichloro-1-phenyl-1*H*-benzo[*d*]imidazole (3zj)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zj** as a white solid (130 mg, yield = 98%). mp: 120-124 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.03 (s, 1H), 7.85 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 3H), 7.37-7.43 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 134.4, 129.2, 127.6, 126.8, 125.9, 122.9, 120.6, 110.9. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_9Cl_2N_2$ (263.0173), found: 263.0175.

5,6-dichloro-1-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole (3zk) [18e]

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zk** as a white solid (84 mg, yield = 58%). mp: 120-122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.01 (s, 1H), 7.86 (s, 1H), 7.52 (s, 1H), 7.28-7.34 (m, 4H), 2.65-2.71 (m, 2H), 1.23 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 144.1, 143.1, 142.1, 132.1, 132.0, 128.6, 126.7, 125.8, 123.0, 120.6, 110.9, 27.5, 14.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{13}Cl_2N_2$ (291.0540), found: 291.0545.

5,6-dichloro-1-(4-ethoxyphenyl)-1*H*-benzo[*d*]imidazole (3zl)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zl** as a white solid (63 mg, yield = 41%). mp: 138-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.97 (s, 1H), 7.85 (s, 1H), 7.45 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.98-7.00 (m, 2H), 4.01-4.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 158.1, 143.3, 141.9, 132.5, 126.9, 126.7, 125.7, 124.6, 120.5, 114.8, 110.8, 62.9, 13.7. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{13}Cl_2N_2O$ (307.0399), found: 307.0396.

5,6-dichloro-1-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (3zm)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zm** as a white solid (63 mg, yield = 45%). mp: 210-214 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.00 (s, 1H), 7.88 (s, 1H), 7.47 (s, 1H), 7.37-7.41 (m, 2H), 7.19-7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 161.3 (d, *J* = 249.0 Hz), 142.9, 142.0, 132.1, 130.4, 127.1, 126.1, 125.1 (d, *J* = 8.0 Hz), 120.8, 116.3 (d, *J* = 23.0 Hz), 110.6. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_8Cl_2FN_2$ (281.0043), found: 281.0048.

5,6-dichloro-1-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (3zn)

Based on **THE ABOVE MENTIONED PROCEDURE**, the crude material was isolated by column (PE/EA = 2:1) to give the intended compound **3zn** as a colorless oil (69 mg, yield = 44%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.05 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7,94 (d, *J* = 4.0 Hz, 2H), 7.51-7.57 (m, 2H), 7.39-7.47 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) 144.4, 141.6, 133.7, 133.4, 130.3, 129.2, 128.4, 127.6, 126.9, 126.9, 126.2, 126.0, 124.4, 123.9, 120.9, 120.6, 111.1. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{17}H_{11}Cl_2N_2$ (313.0294), found: 313.0298.

Acknowledgments

The financial support from Hubei Key Laboratory of Radiation Chemistry and Functional Materials, Hubei University of Science & Technology (2019-20KZ01), Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University (KLSAOFM1810), Science and Technology Department of Hubei Province (2019CFB596), Key Laboratory of Hubei Province for Coal Conversion and New Carbon Materials (WKDM202003) are all greatly appreciated. J.-Q. C. thanks the support of Postgraduate Innovation Foundation from Wuhan Institute of Technology (CX2019170).

Keywords: Chemoselective • Desulfurative • Chan-Lam Coupling • C-N Bond

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Key Topic*

*Author(s), Corresponding Author(s)**

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Title

*one or two words that highlight the emphasis of the paper or the field of the study

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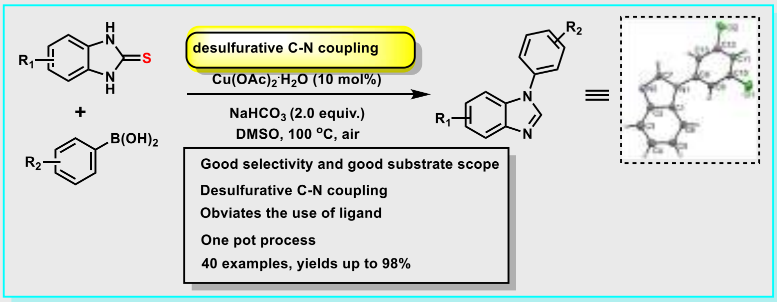

Key Topic*: Chan-Lam Coupling

*Jin-Quan Chen, Xing Liu, Jia Guo, and Zhi-Bing Dong **

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A Chemoselective and Desulfurative Chan-Lam Coupling: C-N Bond Formation between Benzimidazoline-2-Thiones and Arylboronic Acids

*one or two words that highlight the emphasis of the paper or the field of the study

An efficient method for the chemoselective and desulfurative Chan-Lam cross-coupling was developed. By modulating the amount of the catalyst $Cu(OAc)_2$•H_2O, alkali, temperature and solvent, the desulfurative C-N bond formation product (N-arylbenzimidazoles) could be selectively furnished smoothly. The features of this protocol are the use of inexpensive and readily available catalyst, ligand-free condition, wide substrate scope, easy performance, giving the C-N cross-coupling products in moderate to excellent yields. It shows potential synthetic value for the preparation of a diversity of arylbenzoheterocyclic compounds which are potentially active in pharmaceuticals and agrochemicals.