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Graphical Abstract

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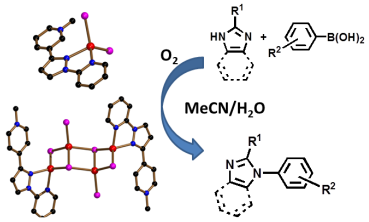
Jiang-Yan Xue[a], Jun-Chi Li[a], Hong-Xi Li[a]*, Hai-Yan Li[a], Jian-Ping Lang[a,b]*
[a]*State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 210032, P. R. China*



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Chan-Lam cross-coupling reactions promoted by anionic copper(I)/iodide species with cationic methyl-((pyridinyl)-pyrazolyl)pyridin-1-ium

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[a] *State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 210032, P. R. China*

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ABSTRACT

Four anionic ligands including 1-methyl-3(or 4)-(1-(pyridin-2-yl)-1H-pyrazol-3-yl)pyridin-1-ium iodide ([3,2'-pypzpym]I, [4,2'-pypzpym]I) and 1-methyl-3(or 4)-(3-(pyridin-2-yl)-1H-pyrazol-1-yl)pyridin-1-ium iodide ([2,3'-pypzpym]I, [2,4'-pypzpym]I) are prepared. Reaction of CuI with [3,2'-pypzpym]I affords a mononuclear complex $[CuI_2(3,2'\text{-pypzpym})]$ (**1**) and a one-dimensional coordination polymer $[(Cu_4I_6)(3,2'\text{-pypzpym})_2]_n$ (**2**). Analogous reactions of CuI with [4,2'-pypzpym]I, [2,3'-pypzpym]I or [2,4'-pypzpym]I yield $[Cu_4I_6(4,2'\text{-pypzpym})_2]$ (**3**), $[CuI_2(2,3'\text{-pypzpym})]$ (**4**) and $[CuI_2(2,4'\text{-pypzpym})]$ (**5**), respectively. Relative to that of CuI, complexes **1**-**5** exhibits enhanced catalytic activities towards the Chan-Lam cross-coupling reactions of imidazole and arylboronic acids in a H_2O-MeCN (v/v = 2:1). This catalytic system is involved in the C-N cross-coupling reaction and works for a variety of imidazole derivatives as well as arylboronic acids with different electronic properties.

1. Introduction

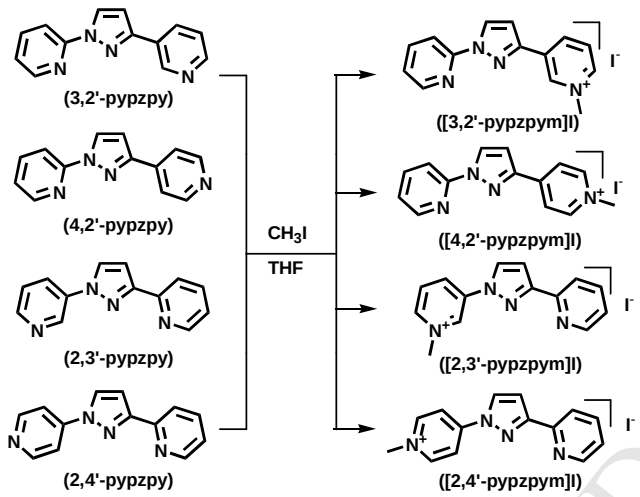
N-aryl heterocycles have attracted increasing attention due to their wide applicability in biochemical, biological, medicinal and material sciences.[1] The most straightforward routes for synthesis of N-arylazole derivatives involve copper-mediated Ullmann-type coupling[2] and Pd-catalyzed Buchwald-Hartwig reaction of nitrogen-containing heterocycles with aryl halides.[3] These reactions require expensive catalysts, or hard reaction conditions (such as high reaction temperature) and produce large amount of harmful wastes. Since 1998, the Chan-Lam coupling reaction[4] has emerged as a highly efficient and valuable alternative to traditional methods for the construction of C-N bond due to the wide variety of commercially available boronic acids and the mildness of the reaction conditions.[5] These reactions are often carried out in organic solvents[6] or ionic liquids.[7] It would be a greener and more economic approach if the Chan-Lam coupling reaction could be conducted in water or aqueous solvents. Recently, a number of green water-soluble catalysts have been used to promote C−C cross-coupling reactions in water.[8] So far, the homogeneous copper-catalyzed Chan-Lam cross-coupling systems in water or in aqueous solvents have less explored.[9] Collman et al. reported that $[Cu(OH)\cdot TMEDA]_2Cl_2$ could catalyze coupling reactions of imidazole with arylboronic acids in water with relatively low yields (up to 63%). It is noted that water-soluble catalysts could be obtained by incorporating hydrophilic moieties such as sulfonate, carboxylate, imidazolium salts, ammonium groups into the hydrophobic organic ligands. As our continuous effort on the syntheses of water-soluble metal coordination complexes[10] and the formation of C-N bond,[11] we have designed and prepared a set of N,N-bidentate coordination ligands attached 1-methyl-pyridinium group (1-methyl-((pyridinyl)pyrazolyl)pyridin-1-ium iodide ([pypzpym]I)) (Scheme 1). Reactions of CuI with these ligands afforded five anionic $[Cu_xI_y]$-based coordination complexes $[CuI_2(3,2'\text{-pypzpym})]$ (**1**), $[Cu_4I_6]_n[(3,2'\text{-pypzpym})_{2n}]$ (**2**), $[Cu_4I_6(4,2'\text{-pypzpym})_2]$ (**3**), $[CuI_2(2,3'\text{-pypzpym})]$ (**4**) and $[(CuI_2)(2,4'\text{-pypzpym})]$ (**5**). Compared with that of CuI, complexes **1**-**5** displayed greatly enhanced catalytic activities toward the coupling of imidazole with arylboronic acid in H_2O/MeCN (v/v = 2:1). Described below are their syntheses, crystal structures and catalytic properties.

2. Results and discussion

According to the literature,[12] reactions of 3-/4-(1H-pyrazol-3-yl)-pyridine with 2-iodopyridine or 2-(1H-pyrazol-3-yl)pyridine with 3-iodopyridine or 4-iodopyridine produced 2-(3-(pyridin-3-

* Corresponding author. Tel.: +86-512-6588-3569; e-mail: lihx@suda.edu.cn
* Corresponding author. Tel.: +86-512-6588-2865; fax: +86-512-6588-0328; e-mail: jplang@suda.edu.cn

yl)-1H-pyrazol-1-yl)pyridine (3,2'-pypzpy), 2-(3-(pyridin-4-yl)-1H-pyrazol-1-yl)pyridine (4,2'-pypzpy), 2-(1-(pyridin-3-yl)-1H-pyrazol-3-yl)pyridine (2,3'-pypzpy) and 2-(1-(pyridin-4-yl)-1H-pyrazol-3-yl)pyridine (2,4'-pypzpy), respectively. As shown Scheme 1, reactions of 3,2'-pypzpy, 4,2'-pypzpy, 2,3'-pypzpy or 2,4'-pypzpy with excess MeI in refluxing THF for 12 h produced 1-methyl-3(or 4)-(1-(pyridin-2-yl)-1H-pyrazol-3-yl)pyridin-1-ium iodide ([3,2'-pypzpym]I, [4,2'-pypzpym]I) and 1-methyl-3(or 4)-(3-(pyridin-2-yl)-1H-pyrazol-1-yl)pyridin-1-ium iodide ([2,3'-pypzpym]I, [2,4'-pypzpym]I) in high yields. These four organic ligands were fully characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. Their high-resolution positive-ion mass spectra reveal that there exists one peak at m/z = 237.1142 ([3,2'-pypzpym]I, [4,2'-pypzpym]I), 237.1140 ([2,3'-pypzpym]I) and 237.1146 ([2,4'-pypzpym]I), which can be assigned to the corresponding $[pypzpym]^+$ cation. These cationic ligands are stable toward air and moisture, and freely soluble in H_2O, MeOH, DMSO, slightly soluble in CH_2Cl_2 and $CHCl_3$, but insoluble in toluene and Et_2O.



Scheme 1 Synthesis of [pypzpym]I ligands.

Diffusion of Et_2O into the MeCN solution containing CuI and [3,2'-pypzpym]I afforded red crystals of mononuclear complex $[CuI_2(3,2'\text{-pypzpym})]$ (**1**) and yellow crystals of 1D polymer $[(Cu_4I_6)(3,2'\text{-pypzpym})_2]_n$ (**2**) in 23 % and 35 % yields, respectively. The similar reaction in refluxing MeCN only produced **1** in a higher yield (88%). Refluxing of the MeCN solution of **2** could also produce complex **1**. Reactions of CuI with [4,2'-pypzpym]I, or [2,3'-pypzpym]I or [2,4'-pypzpym]I in MeCN at room temperature resulted in the formation of one tetranuclear Cu(I) cluster $[Cu_4I_6(4,2'\text{-pypzpym})_2]$ (**3**) and two mononuclear complexes $[CuI_2(2,3'\text{-pypzpym})]$ (**4**) and $[(CuI_2)(2,4'\text{-pypzpym})]$ (**5**), respectively. Compounds **1**–**5** are also relatively air and moisture-stable. They are soluble in common organic solvents such as CH_2Cl_2, MeOH, EtOH and MeCN, DMF, DMSO and H_2O, but insoluble in Et_2O and n-hexane. The elemental analyses are consistent with their chemical formula. Their identities of **1**-**4** are finally confirmed by single-crystal X-ray crystallography. Numerous attempts to grow crystals of **5** always failed. As described below in this article, the sites of pyridinium group in pypzpym ligands have a significant influence on the anionic $[Cu_xX_y]^{(y-x)-}$ structural motifs such as monomeric unit $[CuI_2]^-$ in **1** and **4**, chair-like unit $[Cu_4I_6]^{2-}$ in **3** and ribbon chain $[Cu_4I_6]_n^{2n-}$ in **2**. For the pypzpym ligands in **1**-**4**, the cationic part on one end of its backbone is used to balance the anionic charges for anionic $[CuI_2]^-$, $[Cu_4I_6]^{2-}$ and $[Cu_4I_6]_n^{2n-}$ aggregates. On the other end, the pyridyl and pyrazol groups in **1**, **3** and **4** work together to chelate one Cu center in a N,N'-bidentate coordination fashion.

Being crystallized in the monoclinic space group $P2_1/n$, the asymmetric unit of **1** or **4** contains the discrete molecule $[CuI_2(3,2'\text{-pypzpym})]$ or $[CuI_2(2,3'\text{-pypzpym})]$. Their cell parameters are essentially identical, and so are their molecular structures (Fig. 1 and Fig. S1). Therefore only the molecular structure of **1** is described below. Each Cu(I) in **1** is tetrahedrally coordinated by two I and two N atoms from 3,2'-pypzpym ligand. Compound **2** crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit contains $[Cu_2I_3]^-$ anion and one 3,2'-pypzpym cation. As shown in Fig. 2, I(1) atom bridges four Cu(I) atoms. The two adjacent Cu(I) atoms are further connected by μ-I^- ion, forming a pyramid-shaped structure. Such $[Cu_4I_5]$ unit shares two "$[Cu_2I_2]$" rhomboids with two adjacent ones to form an infinite 1D anionic ribbon $[Cu_4(\mu_4\text{-}I)_2(\mu\text{-}I)_4]_n^{2n-}$ running parallel to the *a* axis. Compound **3** crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit has half a discrete molecule $[Cu_4I_6(4,2'\text{-pypzpym})_2]$. It may be viewed as having a chairlike $[\{Cu(CuI)\}(\mu\text{-}I)(\mu_3\text{-}I)]_2$ core structure (Fig. 3). All Cu(I) centers in **3** are tetrahedrally coordinated by one μ-I, one μ_3-I and two N atoms of 4,2'-pypzpym and (Cu1 or Cu1A), or by one I, one μ-I and two μ_3-I atoms (Cu2 or Cu2A).

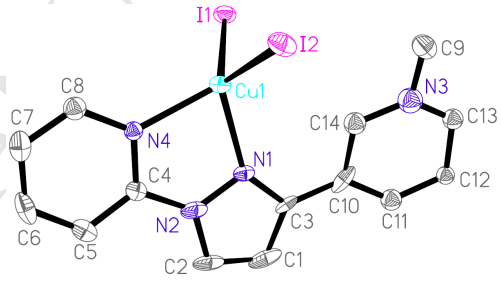


Fig. 1 View of the molecular structure of **1** with a labeling scheme and 50% thermal ellipsoids. All H atoms are omitted for clarity.

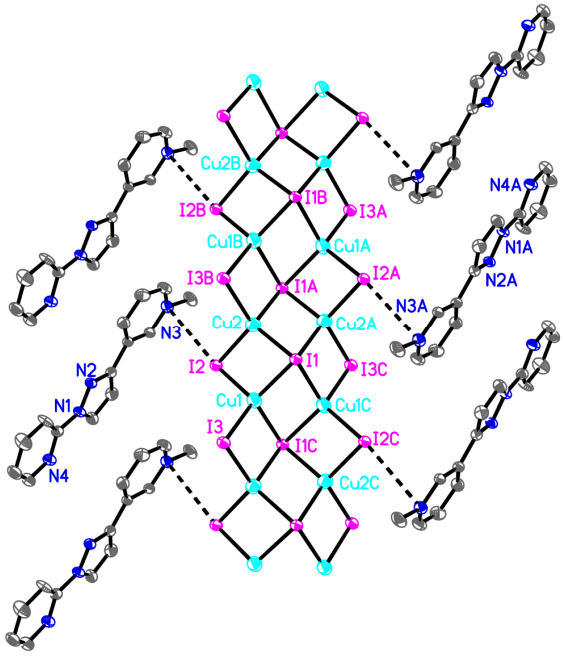


Fig. 2 View of the 1D $[Cu_4(\mu_4\text{-}I)_2(\mu\text{-}I)_4]_n^{2n-}$ chain in **2** with a labeling scheme and 50% thermal ellipsoids. All H atoms are omitted for clarity.

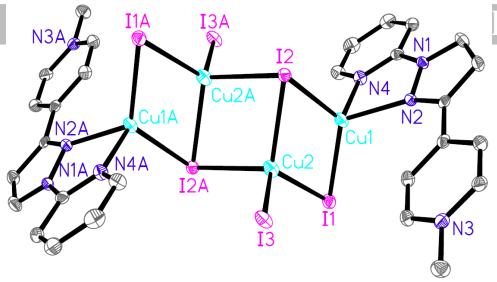
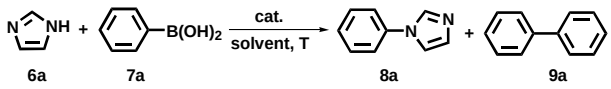


Fig. 3 View of the molecular structure of **3** with a labeling scheme and 50% thermal ellipsoids. All H atoms are omitted for clarity.

Since complexes **1-5** can dissolve in water, they may show high catalytic activity towards some reactions in H_2O. To this end, we examined the catalytic activity of the as-synthesized Cu(I) complexes for the Chan–Lam coupling reaction. The initial experiment was performed by stirring a mixture of imidazole (**6a**, 1 mmol), phenylboronic acid (**7a**, 2 mmol) and **1** (0.02 mmol) in H_2O at 60 ºC. After 24 hours, the desired product 1-phenyl-1H-imidazole (**8a**) could be isolated in 65% yield (Table 1, entry 1). This preliminary result suggested that **1** could initialize the N-arylation of imidazole. The relatively low yield showed that H_2O may not be the optimal solvent. When the reaction was carried out in MeCN, only the coupling product 1,1'-biphenyl (**9a**) was isolated in 58% (entry 2). Considering the structure of arylboronic acid containing the hydrophilic boronic acid and the hydropholic aryl group, the aqueous organic solvent mixtures may be more suitable for such a cross-coupling reaction. When the reaction was carried out in a H_2O-MeCN (v/v = 1:1) mixture, the isolated yield of **8a** was increased dramatically (89%, entry 3). However, this catalyst showed slightly lower activity in aqueous DMF, DMSO, MeOH, EtOH (entries 4-7). The reaction temperature also exerted great impact on this reaction. At lower temperature (40 ºC) or higher temperature (80 ºC), the reaction gave the product in lower yields (entries 8 and 9). As shown in Table 1, the optimal ratio of H_2O and MeCN was finally determined to be 2 : 1 (entries 10-12). A blank experiment confirmed that no arylated product was observed in the absence of the catalyst (entry 13). Notably, the catalyst loading for this reaction could be increased from 2 to 5 mol% without affecting the product yields (entry 15). When the catalyst loading was reduced to 1 mol%, it gave the product in lower yields (entry 14). Based on these results, the optimized reaction conditions were fixed to be 2 mol% of **1**, at 60 ºC in H_2O-MeCN (v/v = 2:1) for 24 h. Under these optimized conditions, the catalytic performances of **2**-**5** and CuI/[3,2'-pypzpym]I were also investigated. They also exhibited good catalytic activity towards the cross-coupling reaction of 1H-Imidazole with phenylboronic acid to 1-phenyl-1H-imidazole (85-90%, entries 16-20). As discussed above, **2** could be transformed into "(3,2'-pypzpym)Cu" active catalytic species in the catalytic process. Comparative run with CuI (67 %) catalytic system under the same reaction conditions indicated that **1-5** exhibited better catalytic performance (entry 20).

Table 1. Optimizing the reaction conditions for the cross-coupling reaction of 1H-Imidazole with phenylboronic acid.

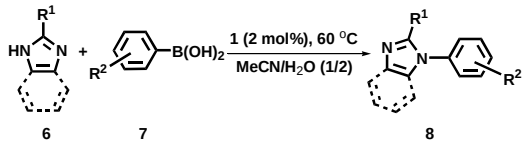


Entry[a]	Cat.	[Cu] Loading (mol%)	Solvent	Temp (ºC)	Yield of **8a** (%)[b]	Yield of **9a** (%)[b]
1	**1**	2	H_2O	60	65	-
2	**1**	2	MeCN	60	trace	58
3	**1**	2	H_2O/MeCN (1:1)	60	89	-
4	**1**	2	H_2O/MeOH (1:1)	60	84	trace
5	**1**	2	H_2O/EtOH (1:1)	60	79	trace
6	**1**	2	H_2O/DMF (1:1)	60	83	trace
7	**1**	2	H_2O/DMSO (1:1)	60	81	-
8	**1**	2	H_2O/MeCN (1:1)	40	43	-
9	**1**	2	H_2O/MeCN (1:1)	80	78	-
10	**1**	2	H_2O/MeCN (2:1)	60	91	-
11	**1**	2	H_2O/MeCN (3:1)	60	87	-
12	**1**	2	H_2O/MeCN (4:1)	60	82	-
13	-	-	H_2O/MeCN (2:1)	60	-	-
14	**1**	1	H_2O/MeCN (2:1)	60	82	-
15	**1**	5	H_2O/MeCN (2:1)	60	90	-
16	**2**	2	H_2O/MeCN (2:1)	60	90	-
17	**3**	2	H_2O/MeCN (2:1)	60	90	-
18	**4**	2	H_2O/MeCN (2:1)	60	85	-
19	**5**	2	H_2O/MeCN (2:1)	60	87	-
20	CuI/[3,2'-pypzpym]I	2	H_2O/MeCN (2:1)	60	88	-
21	CuI	2	H_2O/MeCN (2:1)	60	67	-

[a] Reaction conditions: phenylboronic acid (2.0 mmol), imidazole (1.0 mmol), solvent (4.0 ml) in O_2 for 24h.

[b] Isolated yield.

Table 2. Reaction of 1H-imidazole with various arylboronic acids.



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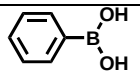
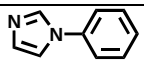
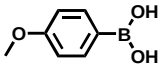
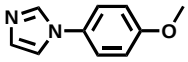
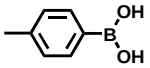
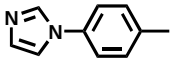
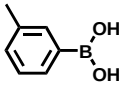
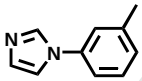
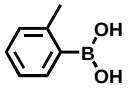
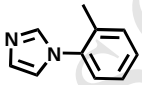
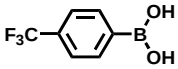
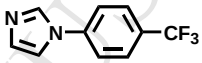
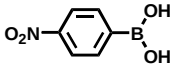
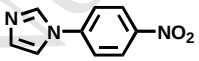
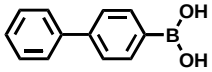
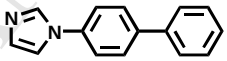
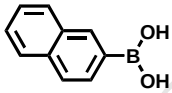
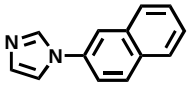
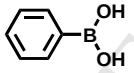
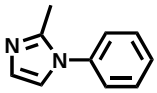
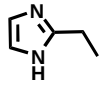
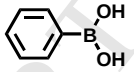
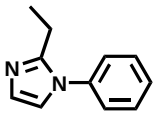
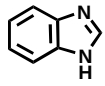
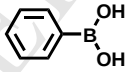
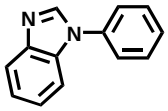
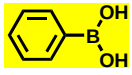
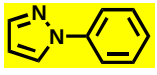
Entry[a]	nitroarene		alcohol		product		Yield (%)[b]
1		**6a**		**7a**		**8a**	91
2		**6a**		**7b**		**8b**	95
3		**6a**		**7c**		**8c**	92
4		**6a**		**7d**		**8d**	87
5		**6a**		**7e**		**8e**	81
6		**6a**		**7f**		**8f**	74
7		**6a**		**7g**		**8g**	63
8		**6a**		**7h**		**8h**	87
9		**6a**		**7i**		**8i**	85
10		**6b**		**7a**		**8j**	83
11		**6c**		**7a**		**8k**	85
12		**6d**		**7a**		**8l**	86
13		**6e**		**7a**		**8m**	90
14		**6f**		**7a**		**8n**	55
15		**6g**		**7a**		**8o**	15

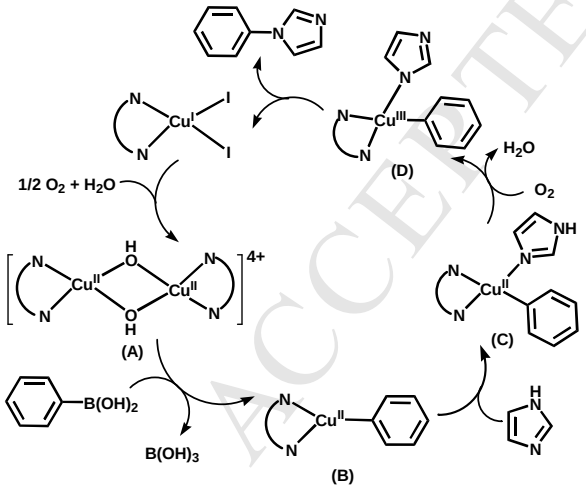
[a] Reaction conditions: imidazole (1.0 mmol), arylboronic acid (2.0 mmol), H_2O/MeCN (2/1) (4.0 ml), 1 atm O_2 and 2 mol% **1** at 60 °C for 24 h.

[b] Isolated yield.

With the optimized reaction conditions in hand, a variety of arylboronic acids were chosen as the substrates in this cross-coupling reaction. As demonstrated in Table 2, the cross-coupling reactions of 1H-imidazole with arylboronic acids were performed well for all the substrates examined, and the desired products were isolated in moderate to excellent yields (entries 1-9). The electronic nature of substituents on phenylboronic acid had some effects on such a cross-coupling reaction. As shown in Table 2, electron-donating *p*-substituted arylboronic acids were found to proceed in higher yields than those with electron-

deficient substituent groups. For example, the *p*-methyl, *p*-methoxyphenylboronic acids were converted smoothly into 1-(*p*-tolyl)-1H-imidazole and 1-(4-methoxyphenyl)-1H-imidazole in 92% and 95% yields, respectively (entries 2 and 3). Phenylboronic acids ((4-(trifluoromethyl)phenyl)boronic acid, 1-nitro-4-(trifluoromethyl)benzene) with electron-withdrawing substituents like $-CF_3$ and $-NO_2$ could proceed conveniently, in 74% and 63% yields (entries 6 and 7). It seemed that 3-substituent on phenyl ring of phenylboronic acid did not hamper the N-arylation reaction (87%, entry 4). *o*-Tolylboronic acid with higher steric hindrance was also converted into its corresponding 1-*o*-tolyl-1H-imidazole in good yield (81%, entry 5). We also examined the scope of the substrate imidazole derivatives. As shown in Table 2, the coupling reactions of 2-methyl-1H-imidazole, 2-ethyl-1H-imidazole or 1H-benzo[d]imidazole with phenylboronic acid were also performed well, and the corresponding desired products were isolated in good yields (entries 10-12). Encouraged by the high efficiency for the reaction of imidazole derivatives described above, we also examined 1H-pyrazole, aniline and benzamide. As shown in Table 2, the coupling reaction of 1H-pyrazole and phenylboronic acid was performed well, and the desired product was isolated in an excellent yield (entry 13). Reaction of aniline with **7a** gave diphenylamine in 55% yield (entry 14), while that of benzamide with **7a** gave the expected coupling product only in 15% yield (entry 15).

The catalytic reaction mechanism[1e,9b] for the above cross-coupling reactions is proposed as follows (Scheme 2). Firstly, reaction of complex **1** with O_2 and H_2O may lead to the formation of a hydroxo copper(II) intermediate A. Secondly, phenylboronic acid may undergo transmetalation with the intermediate A to give boric acid and the intermediate B. Thirdly, reaction of the intermediate B with imidazole may give the intermediate C, which might be oxidized into a Cu(III) intermediate D by O_2. Finally, the intermediate D may undergo reductive elimination to yield complex **1** and the product, thus furnishing the catalytic cycle.



Scheme 2. Proposed catalytic mechanism.

3. Conclusions

In summary, the assemblies of copper(I) iodide with four pypzpymI ligands give rise to five anionic-$[Cu_xI_y]$-based coordination complexes **1**-**5**. The structures of **1**-**4** are structurally confirmed. In **2**, 3,2'-pypzpym ligand is only used as counter ion. The 3,2'-pypzpym, 4,2'-pypzpym and 2,3'-pypzpym anions in **1**, **3** and **4** are used as both counter ion and chelating ligand. It seems that the structure of pypzpym ligands has exerted a significant influence on the $[Cu_xI_y]^{(y-x)-}$ motifs such as monnuclear $[CuI_2]^-$ unit in **1** and **4**, chair-like unit $[Cu_4I_6]^{2-}$ in **3** and 1D ribboned chain $[Cu_4I_6]_n^{2n-}$ in **2**. In comparison with that of CuI, complexes **1-5** display highly improved catalytic activity toward the Chan-Lam cross-coupling of 1H-imidazole with various arylboronic acids in aqueous MeCN to produce the corresponding N-arylimidazoles with high yields. It is anticipated that the new cationic/anionic N-coordinating ligands may be applied in other $[Cu_xI_y]$-based coordination complexes with better catalytic properties. Studies in this respect are underway in our laboratory.

4. Experimental

4.1. General

The 3,2'-pypzpy, 4,2'-pypzpy, 2,3'-pypzpy and 2,4'-pypzpy ligands were synthesized according to the literature method.[11b] All other commercial reagents were used without further purification. Column chromatography was performed on silica gel. Electrospray ion mass spectra (ESI-MS) were performed on an Agilent 1200/6200 mass spectrometer. High-resolution mass spectra were obtained by using a Microma GCT-TOF instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. ^{1}H chemical shifts were referenced to Me_4Si (δ 0.0 ppm) and residual protons in $CDCl_3$ (δ 7.26 ppm), DMSO-d_6 (δ 2.50 ppm). ^{13}C NMR spectra were reported relative to $CDCl_3$ (δ 77.16 ppm), DMSO-d_6 (δ 39.5 ppm). The uncorrected melting points were determined on a Mel-Temo II apparatus.

4.2. Synthesis of [3,2'-pypzpym]I.

To a 100 mL round-bottomed flask fitted with reflux condenser was added 2-(3-(pyridin-3-yl)-1H-pyrazol-1-yl)pyridine (2.22 g, 10 mmol), MeI (5.68 g, 40 mmol) and THF (20 mL). The mixture was refluxed for 6 h under N_2 atmosphere. During this time, a yellow solid was precipitated in the flask. The suspension was cooled to room temperature, and the supernatant was decanted off. The resulting solid was washed with anhydrous Et_2O for three times to afford the yellow solid of [3,2'-pypzpym]I. Yield: 3.3 g, 92%. m.p. 405-406 ºC. Anal. Calcd for $C_{14}H_{13}N_4I$: C, 46.17; H, 3.60; N, 15.38 %; Found: C, 46.02; H, 3.95; N, 15.69 %. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.65 (s, 1H), 9.09-9.02 (m, 2H), 8.85 (d, J = 4.0 Hz, 1H), 8.56 (d, J = 4.0 Hz, 1H), 8.26 (t, J = 4.0 Hz, 1H), 8.13 (d, J = 4.0 Hz, 2H), 7.50-8.46 (m, 1H), 7.40 (d, J = 4.0 Hz, 1H), 4.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 150.6, 149.0, 147.3, 144.9, 142.9, 140.8, 140.2, 132.3, 130.2, 128.5, 123.3, 113.0, 107.6, 48.8. HRMS (EI) Calcd for $C_{14}H_{13}N_4^+$ 237.1140, found 237.1142. IR (KBr pellet, ν/cm^{-1}): 1636 (w), 1616 (w), 1594 (m), 1579 (m), 1505 (w), 1471 (w), 1458 (s), 1444 (m), 1371 (m), 1325 (w), 1296 (w), 1282 (m), 1205 (w), 1179 (w), 1146 (w), 1124 (w), 1065 (m), 992 (w), 958 (w), 825 (w), 797 (s), 785 (s), 717 (w), 676 (m), 621 (m), 511 (w).

4.3. Synthesis of [4,2'-pypzpym]I.

Yellow solid of [4,2'-pypzpym]I was obtained by the similar approach to that used for the isolation of [3,2'-pypzpym]I, using 2-(3-(pyridin-4-yl)-1H-pyrazol-1-yl)pyridine and MeI as starting materials. Yield: 85 %. m.p. > 430 ºC. Anal. Calcd for $C_{14}H_{13}N_4I$: C, 46.17; H, 3.60; N, 15.38 %; Found: C, 46.36; H, 3.78; N, 15.87 %. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.04 (d, J = 8.0 Hz, 2H), 8.90 (s, 1H), 8.63-8.57 (m, 3H), 8.16-8.11 (m, 2H), 7.58 (s, 1H), 7.51(t, J = 4.0 Hz, 1H), 4.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 150.6, 149.0, 148.1, 146.9, 146.4, 140.4, 130.7, 123.8, 123.2, 113.1, 109.3, 47.8. HRMS (EI) Calcd

for $C_{14}H_{13}N_4^+$ 237.1140, found 237.1142. IR (KBr pellet, ν/cm^{-1}): 1638 (s), 1593 (m), 1575 (w), 1546 (w), 1507 (w), 1469 (s), 1451 (s), 1375 (s), 1326 (w), 1275 (m), 1241 (w), 1218 (m), 1190 (m), 1120 (w), 1058 (w), 992 (w), 962 (w), 948 (w), 850 (w), 781 (m), 718 (w), 508 (w).

4.4. Synthesis of [2,3'-pypzpym]I.

Yellow solid of [2,3'-pypzpym]I was obtained by the similar method to that used for the isolation of [3,2'-pypzpym]I, using 2-(1-(pyridin-3-yl)-1H-pyrazol-3-yl)pyridine and MeI as starting materials. Yield: 89 %. m.p. > 430 ºC. Anal. Calcd for $C_{14}H_{13}N_4I$: C, 46.17; H, 3.60; N, 15.38 %; Found: C, 45.94; H, 3.83; N, 15.44 %. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.78 (s, 1H), 9.13 (d, J = 8.0 Hz, 1H), 9.00 (d, J = 8.0 Hz, 1H), 8.90 (d, J = 4.0 Hz, 1H), 8.73 (d, J = 4.0 Hz, 1H), 8.35 (t, J = 4.0 Hz, 1H), 8.22(d, J = 4.0 Hz, 1H), 8.01 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 4.0 Hz, 1H), 7.34 (d, J = 4.0 Hz, 1H), 4.53 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ 154.6, 150.0, 149.6, 142.5, 138.2, 137.1, 136.2, 132.7, 131.1, 128.2, 123.9, 120.3, 108.3, 48.5. HRMS (EI) Calcd for $C_{14}H_{13}N_4^+$ 237.1140, found 237.1148. IR (KBr pellet, ν/cm^{-1}): 1591(s), 1539 (s), 1484 (m), 1457 (m), 1382 (s), 1371 (m), 1281 (m), 1171 (m), 1094 (w), 963 (w), 812 (w), 778 (m), 747 (w), 687 (w), 664 (w).

4.5. Synthesis of [2,4'-pypzpym]I.

Yellow solid of [2,3'-pypzpym]I was obtained by the similar route to that used for the isolation of [3,2'-pypzpym]I, using 2-(1-(pyridin-4-yl)-1H-pyrazol-3-yl)pyridine and MeI as starting materials. Yield: 94 %. m.p. 400-402 ºC. Anal. Calcd for $C_{14}H_{13}N_4I$: C, 46.17; H, 3.60; N, 15.38 %; Found: C, 46.59; H, 3.86; N, 15.13 %. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.09 (t, J = 8.0 Hz, 3H), 8.75 (d, J = 4.0 Hz, 1H), 8.61 (d, J = 8.0 Hz, 2H), 8.24 (d, J = 8.0 Hz, 1H), 8.02 (t, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 4.0 Hz, 1H), 4.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 156.4, 149.7, 149.5, 149.4, 147.0, 137.3, 132.3, 124.4, 120.6, 114.5, 110.1, 46.8. HRMS (EI) Calcd for $C_{14}H_{13}N_4^+$ 237.1140, found 237.1146. IR (KBr pellet, ν/cm^{-1}): 1683(s), 1591(w), 1544 (s), 1525 (s), 1482 (m), 1425 (w), 1372 (s), 1316 (w), 1288 (w), 1213 (w), 1191 (m), 1148 (w), 1045 (m), 991 (w), 952 (m), 935 (m), 801 (w), 742 (w), 721 (w)

4.6. Synthesis of [CuI_2(3,2'-pypzpym)] (1) and [(Cu_4I_6)(3,2'-pypzpym)$_2$]$_n$ (2).

To a MeCN (3 mL) solution of [3,2'-pypzpym]I (18.2 mg, 0.05 mmol) was added a solution of CuI (9.6 mg, 0.05 mmol) in MeCN (3 mL). The mixture was stirred at room temperature for 2 h and then filtered. The filtrate was layered with Et_2O (30 ml) to produce dark red crystals of **1** and yellow crystals of **2** in several days. They were separated mechanically under microscope. Complex **1**: Yield: 6.4 mg (23 % based on Cu). Anal. Calcd for $C_{14}H_{13}CuI_2N_4$: C, 30.32; H, 2.36; N, 10.10 %; Found: C, 30.57; H, 2.47; N, 10.77 %. IR (KBr pellet, ν/cm^{-1}): 1630 (w), 1598(m), 1509 (m), 1474 (s), 1438 (s), 1373 (s), 1317 (s), 1297 (w), 1183 (w), 1159 (w), 1064 (w), 952 (w), 825 (w), 778 (m), 718 (w), 692 (w).

Complex **2**: Yield: 6.5 mg (35 % based on Cu). Anal. Calcd for $C_{28}H_{26}Cu_4I_6N_8$: C, 22.57; H, 1.76; N, 7.52 %; Found: C, 22.72; H, 2.04; N, 8.26 %. IR (KBr pellet, ν/cm^{-1}): 1635 (w), 1594 (m), 1575 (m), 1504 (w), 1478 (s), 1455 (s), 1440 (s), 1370 (s), 1325 (w), 1271 (m), 1208 (w), 1174 (w), 1121 (w), 1054 (m), 1038 (w), 957 (w), 777 (m), 717 (m), 669 (w).

4.7. Synthesis of [Cu_4I_6(4,2'-pypzpym)$_2$] (3).

Compound **3** was prepared as orange crystals in a similar manner to that described for **1**, using [4,2'-pypzpym]I (18.2 mg, 0.05 mmol) and CuI (9.6 mg, 0.05 mmol) as starting materials in MeCN. Yield: 14.2 mg (76% based on Cu). Anal. Calcd (%) for $C_{28}H_{26}Cu_4I_6N_8$: C, 22.57; H, 1.76; N, 7.52 %. Found: C, 22.46; H, 1.81; N, 7.54 %. IR (KBr pellet, ν/cm^{-1}): 1630 (s), 1599 (w), 1570 (w), 1503 (w), 1477 (s), 1448 (s), 1371 (s), 1320 (s), 1277 (w), 1190 (m), 1167 (w), 1066 (w), 963 (w), 845 (w), 787 (m) ,775 (m), 716 (w).

4.8. Synthesis of [CuI_2(2,3'-pypzpym)] (4).

Compound **4** was prepared as orange crystals in a similar way to that described for **1**, using [2,3'-pypzpym]I (18.2 mg, 0.05 mmol) and CuI (9.6 mg, 0.05 mmol) as starting materials in MeCN. Yield: 16.1 mg (58% based on Cu). Anal. Calcd (%) for $C_{14}H_{13}CuI_2N_4$: C, 30.32; H, 2.36; N, 10.10 %. Found: C, 30.47; H, 2.36; N, 10.28 %. IR (KBr pellet, ν/cm^{-1}): 1629 (m), 1586 (m), 1531 (m), 1511 (s), 1478 (w), 1459 (m), 1396 (m), 1370 (s), 1296 (m), 1241 (w), 1181 (w), 1156 (w), 1098 (w), 1059 (m), 970 (m), 818 (w), 797 (w), 770 (m), 713 (w).

4.9. Synthesis of [(CuI_2)(2,4'-pypzpym)] (5).

Compound **5** was prepared as orange crystals in a similar manner to that described for **1**, using [2,4'-pypzpym]I (18.2 mg, 0.05 mmol) and CuI (9.6 mg, 0.05 mmol) as starting materials in MeCN. Yield: 23.5 mg (81% based on Cu). Anal. Calcd (%) for $C_{14}H_{13}CuI_2N_4$: C, 30.32; H, 2.36; N, 10.10 %. Found: C, 30.89; H, 2.59; N, 10.44 %. IR (KBr pellet, ν/cm^{-1}): 1637 (s), 1618 (s), 1538 (m), 1525 (w), 1410 (m), 1384 (m), 1375 (w), 1191 (m), 1138 (w), 1047 (w), 950 (w), 843 (w), 754 (w).

4.10. General catalytic procedure for the N-arylation of 1H-imidazole with arylboronic acids.

To a solution of **1** (0.02 mmol) in H_2O/MeCN (V/V = 2/1, 4 mL) was added 1H-imidazole (1.0 mmol) and arylboronic acid (2 mmol) under O_2 atmosphere. The mixture was stirred at 60 ºC for 24 h. After cooling to ambient temperature, the mixture was partitioned between water and CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel.

1-phenyl-1H-imidazole (8a).[9b] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.16 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.02 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 137.3, 135.9, 130.3, 130.2, 127.2, 120.7, 118.4. HRMS *m/z* calcd for $C_9H_9N_2$ $[M + H]^+$ 145.0766, found 145.0763.

1-(4-methoxyphenyl)-1H-imidazole (8b).[9b] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.15 (s, 1H), 7.65 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 158.3, 135.8, 130.5, 129.9, 122.4, 118.7, 115.2, 55.8. HRMS *m/z* calcd for $C_{10}H_{11}N_2O$ $[M + H]^+$ 175.0871, found 175.0870.

1-(p-tolyl)-1H-imidazole (8c).[9b] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.20 (s, 1H), 7.69 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.09 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 136.6, 135.8, 135.0, 130.6, 130.1, 120.6, 118.4, 20.84. HRMS *m/z* calcd for $C_{10}H_{11}N_2$ $[M + H]^+$ 159.0922, found 159.0919.

1-(m-tolyl)-1H-imidazole (8d).[13] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.23 (s, 1H), 7.72 (s, 1H), 7.48 (s, 1H), 7.44-7.36 (m, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.10 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 139.9, 137.2, 135.8, 130.2,

130.0, 128.0, 121.2, 118.3, 117.8, 21.35. HRMS *m/z* calcd for $C_{10}H_{11}N_2$ [M + H]$^+$ 159.0922, found 159.0924.

1-(o-tolyl)-1H-imidazole (8e).[9b] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.82 (s, 1H), 7.40 (t, J = 8.0 Hz, 3H), 7.36-7.28 (m, 2H), 7.09 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 137.6, 136.5, 133.1, 131.1, 128.6, 128.4, 126.9, 126.2, 120.8, 17.3. HRMS *m/z* calcd for $C_{10}H_{11}N_2$ [M + H]$^+$ 159.0922, found 159.0925.

1-(4-(trifluoromethyl)phenyl)-1H-imidazole (8f).[6d] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.47 (s, 1H), 7.96-7,90 (m, 5H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 140.3, 130.9, 127.4, 127.2, 125.3, 123.5, 121.7, 120.9. HRMS *m/z* calcd for $C_{10}H_8F_3N_2$ [M + H]$^+$ 213.0640, found 213.0636.

1-(4-nitrophenyl)-1H-imidazole (8g).[14] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.51 (s, 1H), 8.36 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 12.0 Hz, 3H), 7.19 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 145.7, 142.1, 136.5, 131.3, 125.9, 120.8, 118.3. HRMS *m/z* calcd for $C_9H_8N_3O_2$ [M + H]$^+$ 190.0617, found 190.0618.

1-([1,1'-biphenyl]-4-yl)-1H-imidazole (8h).[14] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.33 (s, 1H), 7.80 (d, J = 4.0 Hz, 3H), 7.76-7.70 (m, 4H), 7.48 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.14 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 139.4, 138.9, 136.6, 135.9, 130.4, 129.4, 128.4, 128.1, 126.9, 121.1, 118.3. HRMS *m/z* calcd for $C_{15}H_{13}N_2$ [M + H]$^+$ 221.1079, found 221.1080.

1-(naphthalen-2-yl)-1H-imidazole (8i).[15] ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.41 (s, 1H), 8.20 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.97 (t, J = 8.0 Hz, 2H), 7.87 (t, J = 12.0 Hz, 2H), 7.61-7.52 (m, 2H), 7.17 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 136.2, 134.8, 133.7, 131.8, 130.4, 130.2, 128.2, 128.1, 127.6, 126.5, 120.0, 118.5, 117.8. HRMS *m/z* calcd for $C_{13}H_{11}N_2$ [M + H]$^+$ 195.0922, found 195.0924.

2-methyl-1-phenyl-1H-imidazole (8j).[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 6.5 Hz, 2H), 7.33 (d, *J* = 6.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 11.1 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.6, 138.0, 129.4, 128.1, 127.6, 125.5, 120.6, 13.7. HRMS *m/z* calcd for $C_{10}H_{11}N_2$ [M + H]$^+$ 159.0922, found 159.0921.

2-ethyl-1-phenyl-1H-imidazole (8k).[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, *J* = 7.2 Hz, 2H), 7.45-7.39 (m, 1H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 31.3 Hz, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.6, 138.0, 129.5, 128.3, 127.6, 125.9, 120.7, 20.6, 12.4. HRMS *m/z* calcd for $C_{11}H_{13}N_2$ [M + H]$^+$ 173.1079, found 173.1081.

1-phenyl-1H-benzo[d]imidazole (8l).[9b] ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.56 (s, 1H), 7.81-7.76 (m, 1H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.65-7.60 (m, 3H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.32 (p, *J* = 7.9 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 143.8, 143.3, 135.0, 133.1, 130.1, 127.7, 123.7, 123.5, 122.4, 119.9, 110.6. HRMS *m/z* calcd for $C_{13}H_{11}N_2$ [M + H]$^+$ 195.0922, found 195.0924.

1-Phenyl-1H-pyrazole (8m).[17] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.75 (s, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 6.54 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.7, 139.7, 129.2, 127.7, 126.3, 118.2, 107.7. HRMS *m/z* calcd for $C_9H_9N_2$ [M + H]$^+$ 145.0766, found 145.0763.

Diphenylamine (8n).[18] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.14 (s, 1H), 7.22 (t, *J* = 7.7 Hz, 4H), 7.07 (d, *J* = 7.9 Hz, 4H), 6.81 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 143.4, 129.3, 119.6, 116.8. HRMS *m/z* calcd for $C_{12}H_{12}N$ [M + H]$^+$ 170.0970, found 170.0972.

N-Phenylbenzamide (8o).[18] ^{1}H NMR (400 Hz, DMSO-d_6, ppm): *δ* 10.27 (s, 1H), 7.98 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): *δ* 165.6, 139.2, 135.0, 128.7, 128.5, 128.2, 127.7, 127.6, 120.2. HRMS *m/z* calcd for $C_{13}H_{12}NO$ [M + H]$^+$ 198.0919, found 198.0916.

4.11. A X-ray crystallography.

Single crystals of **1-4** were obtained directly from the above preparations. X-ray diffraction data collection was performed on a Xcalibur, Atlas, Gemini (**1** and **2**) or a Bruker APEX-II CCD (**3** and **4**) X-ray diffractometer by using graphite monochromated Mo K_α (λ = 0.71073 Å). Single crystals of **1-4** were mounted with grease at the top of a glass fiber. **1**, **2** and **3** were cooled to 223 K in a liquid-nitrogen stream while **4** was kept at 153 K. The collected data were reduced by using the program *Bruker APEX2* or *CrysAlisPro, Agilent Technologies* (CrysAlis171 .NET, Version 1.171.36.28) and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The reflection data were also corrected for Lorentz and polarization effects. The structures of **1-4** were solved by direct method applying SHELXS-97 program and refined by full matrix least-squares on F^2.[19] All the non-H atoms were refined on F^2 anisotropically by full-matrix least squares method. All hydrogen atoms were introduced at the calculated positions and included in the structure-factor calculations. A summary of the important crystallographic information for **1-4** are summarized in Table S1. The selected bond distances and angles of **1-4** are listed in Table S2.

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Supplementary data

Crystal data and refinement parameters for **1-4** (CCDC No. 1485367-1485370). The ^{1}H and ^{13}C NMR spectra for the isolated products for this article can be found in online version at doi:

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