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CuI/8-Hydroxyquinalidine Promoted *N*-Arylation of Indole and Azoles†

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An efficient catalytic system of CuI/8-hydroxyquinalidine was developed for the coupling of aryl iodides and indole as well as some azoles. The reaction could be carried out at 90 ℃ under the condition of relatively low catalyst loading, affording various *N*-arylindoles and *N*-aryl azoles in good yields. The functionalized and hindered aryl iodides were suitable substrates for this transformation.

Keywords copper, Ullmann reaction, 8-hydroxyquinalidine, cross-coupling, indole, azoles

Introduction

N-Arylindoles as well as *N*-aryl azoles are very important core skeletons in numerous natural products and pharmaceutical compounds.[1] They could be used as antipsychotic agents,[2] cyclooxygenase (COX)-1 inhibitors,[3] COX-2 inhibitors,[4] 5-HT_6 receptor antagonists,[5] anti-HIV-1 agents[6] and herbicides.[7]

Ullmann coupling reaction is a classical method for the formation of C—N bond although the high reaction temperature is required.[8] In past decade, great progress in ligand-promoted Ullmann-type coupling reactions makes the coupling of aryl halides with conjugated nitrogen-containing heterocycles carry out under mild reaction conditions.[9] For example, amino acids,[10] 1,10-phenanthroline,[11] diamines,[12] BINOL,[13] Salox,[14] *N*-hydroxyimides,[15] 8-hydroxyquinoline[16] and so on are very efficient for this transformation. However, in most cases a relatively high loading of the catalytic system, at least 5 mol% of copper salt and 10 mol% of ligand for *N*-arylation of indole, was essential for getting the satisfied yields. In addition, the coupling of indole with hindered 2-substituted aryl iodides required higher reaction temperature (120 ℃).[17] Recently, Teo and coworkers developed a ligand-free Cu_2O-catalyzed strategy for the N-arylation of indole and azoles under the promotion of phase transfer catalyst in water.[18] While 10 mol% of Cu_2O and high reaction temperature (130 ℃) were necessary. As an extension of our research work,[9d] we found that CuI/8-hydroxyquinalidine as a powerful catalytic system could promote the coupling reaction of aryl iodides with indole and azoles efficiently at 90 ℃ under relatively low loading (2 mol% of CuI and 4 mol% of 8-hydroxyquinalidine). Herein, we wish to detail the results.

Results and Discussion

Initially, we used the coupling of 4-iodoanisole and indole as the model and screened a series of ligands under the conditions of 2 mol% CuI, 4 mol% ligand, K_2CO_3 as the base and DMSO as the solvent at 90 ℃ for 24 h. It was found that some reported efficient ligands such as *L*-proline (**L1**),[10] 8-hydroquinoline (**L2**),[16] 1,10-phen (**L4**),[11] *N*,*N*-dimethylethylenediamine (**L5**)[12] and pyrrole 2-carboxylic acid (**L7**)[19] only afforded low yields under the condition of low catalyst loading (Table 1, Entries 1, 2, 4, 5, 7). 8-Hydroxyquinalidine (**L3**) afforded the best result (Entry 3) while 2-picolinic acid (**L6**)[20] also got the *N*-aryl indole in 90% yield (Entry 6). It seemed that the ligand is crucial for this transformation, as an evidence that only 20% yield was obtained in the absence of the ligand (Entry 8). The combination of K_2CO_3 and DMSO was found as a more suitable system by screening the bases and the solvents (Entry 3 vs. Entries 9—16). When the catalyst loading was further reduced to 1 mol%, the yield also decreased slightly (Entry 17). In addition, decreasing the reaction temperature to 70 ℃ got poor result (Entry 18). However, the reaction was carried out well at 40 ℃ when 10 mol% of CuI and 20 mol% of 8-hydroxyquinalidine were used (Entry 19). It indicated that the

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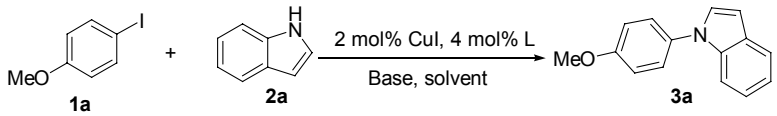
† Dedicated to Professor Weiyuan Huang on the occasion of his 90th birthday.

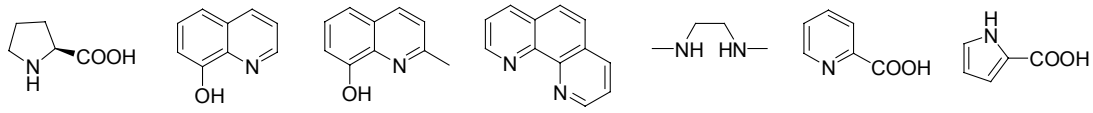
reaction temperature was very important for this coupling under the condition of low catalyst loading. For less active 4-bromoanisole, even increasing the amount of catalyst and reaction temperature only got low yield (Entry 20).

Then various aryl iodides and indoles were investigated for this transformation. As summarized in Table 2, both electron-withdrawing and electron-donating aryl iodides could be converted into the corresponding *N*-arylindoles **3b**—**3j** in excellent yields (Entries 1, 2—10). For 3-nitro-iodobenzene and 4-iodo-phenylamine, shortening the reaction time could get good results possibly because the products were unstable at high temperature (Entries 7 and 8). It is notable that the coupling of steric hindered 2-substituted aryl iodides with indole worked well, affording the *N*-arylindoles **3k**—**3o** in moderate to good yields (Entries 11—17). Increasing the amount of catalysts got better results (Entries 11, 13 vs. 12, 14). For 2-methyl indole, slightly low yield was obtained (Entry 18). In addition, 1*H*-pyrrolo[2,3-*b*]pyridine as well as 2-iodothiophene, 2-iodopyridine and 3-iodopyridine were available substrates for this transformation and the *N*-arylation products **3q**—**3t** were isolated in excellent yields (Entries 19—22). Regretfully, under our reaction conditions, aryl bromides were less active for this coupling, only affording *N*-aryl indoles in low yields (Entries 2 and 23).

The catalytic system was also suitable for *N*-arylation of some other azoles such as imidazole, pyrazole, triazole, pyrrole, benzimidazole and carbazole (Table 3). When pyrrole and carbazole were used as the nucleophiles, 5 mol% of CuI and 10 mol% of 8-hydroxyquinalidine were required (Entries 4 and 6).

Table 1 Screening the reaction condtions for the coupling of 4-iodoanisole and indole[a]





L1 L2 L3 L4 L5 L6 L7

Entry	Ligand (mol%)	Copper source (mol%)	Base	Solvent	Temp./℃	Yield[b]/%
1	**L1** (2)	CuI (4)	K_2CO_3	DMSO	90	50
2	**L2** (2)	CuI (4)	K_2CO_3	DMSO	90	23
3	**L3** (2)	CuI (4)	K_2CO_3	DMSO	90	97
4	**L4** (2)	CuI (4)	K_2CO_3	DMSO	90	42
5	**L5** (2)	CuI (4)	K_2CO_3	DMSO	90	37
6	**L6** (2)	CuI (4)	K_2CO_3	DMSO	90	90
7	**L7** (2)	CuI (4)	K_2CO_3	DMSO	90	47
8	—	CuI (4)	K_2CO_3	DMSO	90	20
9	**L3** (2)	CuI (4)	K_2CO_3	DMF	90	84
10	**L3** (2)	CuI (4)	K_2CO_3	NMP	90	52
11	**L3** (2)	CuI (4)	K_2CO_3	Dioxane	90	—
12	**L3** (2)	CuI (4)	Cs_2CO_3	DMSO	90	50
13	**L3** (2)	CuI (4)	K_3PO_4	DMSO	90	82
14	**L3** (2)	CuI (4)	Na_2CO_3	DMSO	90	—
15	**L3** (2)	CuBr (4)	K_2CO_3	DMSO	90	50
16	**L3** (2)	CuCl (4)	K_2CO_3	DMSO	90	80
17	**L3** (1)	CuI (2)	K_2CO_3	DMSO	90	82
18	**L3** (2)	CuI (4)	K_2CO_3	DMSO	70	64
19	**L3** (10)	CuI (20)	K_2CO_3	DMSO	40	85
20[c]	**L3** (5)	CuI (10)	K_2CO_3	DMSO	110	40

[a] Reaction conditions: 4-iodoanisole (1 mmol), indole (1.2 mmol), CuI (0.02 mmol), ligand (0.04 mmol), and K_2CO_3 (2.5 mmol) in DMSO (2 mL) under Ar atmosphere, 90 ℃, 24 h. [b] Isolated yield. [c] 4-Bromoanisole was used, 36 h.

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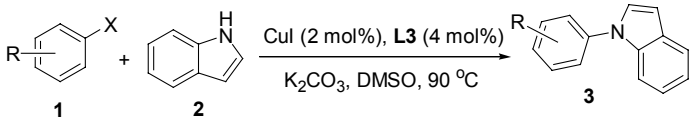
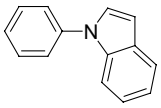
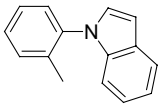
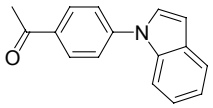
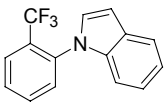
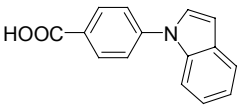
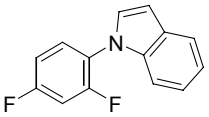
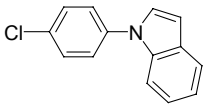
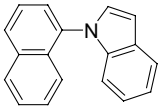
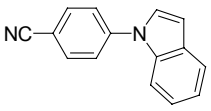
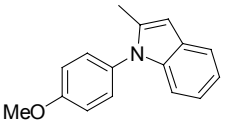
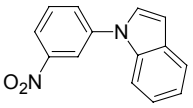
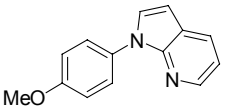
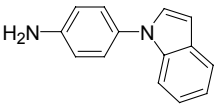
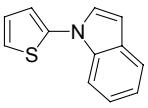
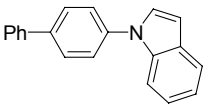
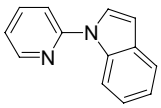
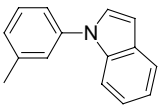
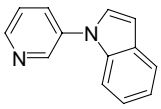
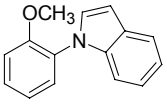
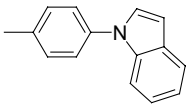
Table 2 CuI/8-Hydroxyquinalidine-catalyzed coupling of aryl halides and indole[a]



1 X = I, Br **2** **3**

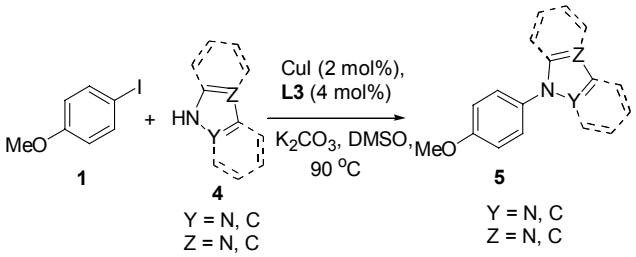
Entry	Product	Yield[b]/%	Entry	Product	Yield[b]/%
1		92	13		76
2		30[c,d]	14		87[f]
	3b			**3l**	
3		98	15		52[d]
	3c			**3m**	
4		93	16		89
	3d			**3n**	
5		94	17		78
	3e			**3o**	
6		94	18		45[d]
	3f			**3p**	
7		92[e]	19		97
	3g			**3q**	
8		78[e]	20		93
	3h			**3r**	
9		85	21		98
	3i			**3s**	
10		91	22		98
	3j			**3t**	

Continued

Entry	Product	Yield[b]/%	Entry	Product	Yield[b]/%
11		75	**23**		**31**[c,d]
12		82[f]			
	3k			**3u**	

[a] Reaction conditions: aryl iodide (1 mmol), Indole (1.2 mmol), CuI (0.02 mmol), **L3** (0.04 mmol), and K_2CO_3 (2.5 mmol) in DMSO (2 mL) under Ar atmosphere, 90 ℃, 24 h. [b] Isolated yield. [c] Ary bromide was used, 110 ℃, 36 h. [d] 0.05 mmol of CuI and 0.1 mmol of **L3** were used. [e] 16 h. [f] 0.1 mmol of CuI and 0.2 mmol of **L3** were used and the reaction was stirred at 40 ℃ for 48 h.

Table 3 CuI/8-hydroxyquinalidine-catalyzed coupling of 4-iodoanisole and azoles[a]



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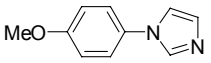
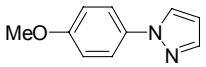
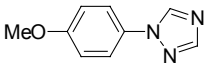
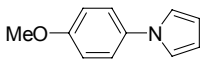
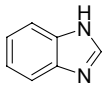
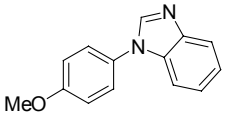
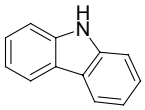
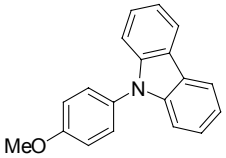
1			98
	4a	**5a**	
2			95
	4b	**5b**	
3			90
	4c	**5c**	
4			85[c]
	4d	**5d**	
5			95
	4e	**5e**	
6			91[c]
	4f	**5f**	

[a] Reaction conditions: 4-iodoanisole (1 mmol), azole (1.2 mmol), CuI (0.02 mmol), **L3** (0.04 mmol), and K_2CO_3 (2.5 mmol) in DMSO (2 mL) under Ar atmosphere, 90 ℃, 24 h. [b] Isolated yield. [c] 0.05 mmol of CuI and 0.1 mmol of **L3** were used.

Conclusions

As a conclusion, we developed an efficient catalytic system of CuI/8-hydroxyquinalidine for the coupling of aryl iodides and indole as well as some azoles. The reaction could be carried out at 90 ℃ under the condition of relatively low catalyst loading, affording various *N*-arylindoles and *N*-aryl azoles in good yields. The functionalized and hindered aryl iodides were suitable substrates for this transformation. This method would be applicable in the synthesis of some pharmaceutical compounds.

Experimental

General procedure for CuI/8-hydroxyquinalidine-catalyzed coupling reaction of aryl iodides with indole and azoles

A Schlenk tube was charged with aryl iodide (1.0 mmol), indole or azole (1.2 mmol), CuI (0.02 mmol), 8-hydroxyquinalidine (0.04 mmol), K_2CO_3 (2.5 mmol), and 2 mL of DMSO, evacuated and backfilled with argon. The reaction mixture was stirred at 90 ℃ for 24 h. The cooled reaction mixture was partitioned between ethyl acetate and water. The organic layer was washed with water, brine, and dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to provide the desired product.

1-(4-Methoxyphenyl)-1*H*-indole (3a)[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.68 (d, J=8.1 Hz, 1H), 7.45 (d, J=8.1 Hz, 1H), 7.41 (d, J=9.0 Hz, 2H), 7.27 (d, J=3.3 Hz, 1H), 7.22—7.12 (m, 2H), 7.03 (m, J=9.3 Hz, 2H), 6.65 (d, J=3.0 Hz, 1H), 3.88 (s, 3H); ESI-MS *m/z*: 224.0 $(M+H)^+$.

1-Phenyl-1-indole (3b)[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.68 (d, J=7.5 Hz, 1H), 7.57 (d, J=8.0 Hz, 1H), 7.50—7.51 (m, 4H), 7.32—7.37 (m, 2H), 7.15—7.24 (m, 2H), 6.68 (d, J=3.1 Hz, 1H); ESI-MS *m/z*: 194.1 $(M+H)^+$.

1-[4-(1*H*-Indol-1-yl)phenyl]ethanone (3c)[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13 (d, J=8.4 Hz, 2H), 7.68—7.60 (m, 4H), 7.38 (d, J=3.3 Hz, 1H), 7.30—7.18 (m, 2H), 6.74 (d, J=3.6 Hz, 1H), 2.66 (s, 3H); ESI-MS *m/z*: 236.2 $(M+H)^+$.

4-(1*H*-Indol-1-yl)benzoic acid (3d) ^{1}H NMR (300

MHz, DMSO-d_6) δ: 13.08 (brs, 1H), 8.13 (d, J=7.8 Hz, 2H), 7.76—7.67 (m, 5H), 7.28—7.14 (m, 2H), 6.76 (d, J=3.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 167.0, 143.0, 134.9, 131.3 (2C), 129.7, 128.3, 128.2, 123.2 (2C), 123.0, 121.4, 121.0, 110.8, 104.9; ESI-MS *m/z*: 235.9 $(M-H)^-$; HRMS (ESI) calcd for $C_{15}H_{10}NO_2$ $(M-H)^-$ 236.07115, found 236.07170

1-(4-Chlorophenyl)-1*H*-indole (3e)[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69 (dd, J=1.2 Hz, 6.9 Hz, 1H), 7.52—7.41 (m, 5H), 7.29 (d, J=3.3 Hz, 1H), 7.26—7.15 (m, 2H), 6.69 (d, J=2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.5, 135.9, 132.1, 129.9 (2C), 129.5, 127.8, 125.6 (2C), 122.7, 121.4, 120.7, 110.4, 104.2; ESI-MS *m/z*: 228.1 $(M+H)^+$.

1-(4-Cyanophenyl)-1*H*-benzimidazole (3f)[22] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (d, J=8.4 Hz, 2H), 7.71—7.60 (m, 4H), 7.35 (d, J=3.3 Hz, 1H), 7.30—7.19 (m, 2H), 6.76 (d, J=3.3 Hz, 1H); ESI-MS *m/z*: 219.1 $(M+H)^+$.

1-(3-Nitrophenyl)-1*H*-indole (3g)[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.40 (s, 1H), 8.20 (d, J=8.1 Hz, 1H), 7.89—7.86 (m, 1H), 7.74—7.71 (m, 2H), 7.59 (d, J=8.1 Hz, 1H), 7.38 (d, J=3.3 Hz, 1H), 7.32—7.20 (m, 2H), 6.76 (d, J=3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 140.8, 135.4, 130.5, 129.7, 129.4, 127.3, 123.2, 121.5, 121.2, 120.7, 118.5, 110.0, 105.3. ESI-MS *m/z*: 239.1 $(M+H)^+$.

4-(1*H*-Indol-1-yl)benzenamine (3h) ^{1}H NMR (300 MHz, CD_3OD) δ: 7.59 (d, J=7.8 Hz, 1H), 7.36 (d, J=7.8 Hz, 1H), 7.27 (d, J=3.0 Hz, 1H),7.2 (d, J=8.7 Hz, 2H), 7.13—7.02 (m, 2H), 6.85 (d, J=8.7 Hz, 2H), 6.56 (d, J=3.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ: 147.9, 137.9, 131.7, 130.4, 129.5, 126.9 (2C), 122.9, 121.8, 120.8, 117.0 (2C), 111.4, 103.3; ESI-MS *m/z*: 209.0 $(M+H)^+$; HRMS (ESI) calcd for $C_{14}H_{13}N_2$ $(M+H)^+$ 209.10787, found 209.10732.

***N*-(4-Biphenyl)indole (3i)**[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.74—7.56 (m, 8H), 7.50—7.45 (m, 2H), 7.40—7.35 (m, 2H), 7.27—7.16 (m, 2H), 6.71 (d, J=3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 139.4, 139.1, 135.9, 129.5, 129.0 (2C), 128.4 (2C), 128.0, 127.6, 127.2 (2C), 124.6 (2C), 122.6, 121.3, 120.6, 110.7, 103.9; ESI-MS *m/z*: 270.2 $(M+H)^+$.

1-*m*-Tolyl-1*H*-indole (3j)[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69 (d, J=7.5 Hz, 1H), 7.58 (d, J=8.1 Hz, 1H), 7.42—7.30 (m, 4H), 7.25—7.14 (m, 3H), 6.68 (d, J=3.3 Hz, 1H); ESI-MS *m/z*: 208.1 $(M+H)^+$.

1-(2-Methoxyphenyl)-1*H*-indole (3k)[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.68 (d, J=8.4 Hz, 1H), 7.39—7.37 (m, 2H), 7.27 (d, J=3.0 Hz, 1H), 7.20—7.06 (m, 5H), 6.66 (d, J=3.3 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5, 136.9, 129.4, 128.6, 128.5, 128.2, 128.1, 121.9, 120.9, 120.8, 120.0, 112.5, 110.9, 102.6, 55.7; ESI-MS *m/z*: 224.1 $(M+H)^+$.

1-*o*-Tolyl-1*H*-indole (3l)[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.67—7.70 (m, 1H), 7.35—7.28 (m, 4H), 7.16—7.13 (m, 3H), 7.04—7.01 (m, 1H), 6.66 (d, J=3.3 Hz, 1H), 2.05 (s, 3H); ESI-MS *m/z*: 208.1 $(M+H)^+$.

1-(2-(Trifluoromethyl)phenyl)-1*H*-indole (3m)[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.90 (d, J=7.5 Hz, 1H), 7.71—7.64 (m, 2 H), 7.61 (t, J=7.5 Hz, 1H), 7.47 (d, J=7.8 Hz, 1H), 7.23—7.17 (m, 3H), 7.06—7.00 (m, 1H), 6.71 (d, J=3.3 Hz, 1H); ESI-MS *m/z*: 262.2 $(M+H)^+$.

1-(2,4-Difluorophenyl)-1*H*-indole (3n) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69 (d, J=7.2 Hz, 1H), 7.51—7.44 (m, 1H), 7.25—7.15 (m, 4H), 7.10—7.00 (m, 2H), 6.71 (d, J=2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5 (dd, J=10.9, 248.1 Hz), 157.2 (dd, J=12.4, 252.1 Hz), 136.7, 128.9 (dd, J=2.0, 10.4 Hz), 128.8, 128.6 (d, J=1.4 Hz), 123.8 (dd, J=4.1, 12.9 Hz), 122.6, 121.2, 120.7, 111.9 (dd, J=3.8, 22.3 Hz), 110.3 (d, J=1.1 Hz), 105.4 (dd, J=23.4, 49.4 Hz), 104.0; ESI-MS *m/z*: 230.1 $(M+H)^+$; HRMS (ESI) calcd for $C_{14}H_{10}F_2N$ $(M+H)^+$ 230.07813, found 230.07758.

1-Naphthylindole (3o)[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.96 (d, J=7.8 Hz, 2H), 7.74 (d, J=7.8 Hz, 1H), 7.60—7.40 (m, 5H), 7.34 (d, J=3.0 Hz, 1H), 7.20—7.02 (m, 3H), 6.76 (d, J=3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.1, 136.2, 134.6, 130.7, 129.9, 128.6 (2C), 128.4, 127.1, 126.8, 125.6, 125.2, 123.5, 122.3, 121.0, 120.2, 111.0, 103.0; ESI-MS *m/z*: 244.1 $(M+H)^+$.

1-(4-Methoxylphenyl)-2-methyl-1*H*-indole (3p)[12d] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57—7.54 (m, 1H), 7.26—7.23 (m, 2H), 7.10—7.01 (m, 5H), 6.37 (s, 1H), 3.86 (s, 3H), 2.26 (s, 3H); ESI-MS *m/z*: 238.1 $(M+H)^+$.

1-(4-Methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (3q)[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.38—8.36 (m, 1H), 7.99—7.96 (m, 1H), 7.59—7.63 (m, 2H), 7.46 (d, J=3.6 Hz, 1H), 7.12 (dd, J=4.5, 7.5 Hz, 1H), 7.07—7.03 (m, 2H), 6.61 (d, J=3.3 Hz, 1H), 3.87 (s, 3H); ESI-MS *m/z*: 225.1 $(M+H)^+$.

1-Thiophen-2-yl-1*H*-indole (3r)[11f] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66 (d, J=6.3 Hz, 1H), 7.59 (d, J=8.1 Hz, 1H), 7.29—7.16 (m, 4H), 7.09—7.03 (m, 2H), 6.66 (d, J=3.3 Hz, 1H); ESI-MS *m/z*: 200.0 $(M+H)^+$.

1-Pyridin-2-yl-1*H*-indole (3s)[28] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.58 (d, J=3.6 Hz, 1H), 8.21 (d, J=8.4 Hz, 1H), 7.86—7.80 (m, 1H), 7.73 (d, J=3.6 Hz, 1H), 7.68 (d, J=8.1 Hz, 1H), 7.51 (d, J=8.4 Hz, 1 H), 7.33—7.16 (m, 3H), 6.71 (d, J=3.3 Hz, 1H); ESI-MS *m/z*: 195.1 $(M+H)^+$.

1-(Pyridin-3-yl)-1*H*-indole (3t)[29] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (d, J=2.4 Hz, 1H), 8.61 (dd, J=1.6, 4.8 Hz, 1H), 7.84 (ddd, J=1.6, 2.4, 8.0 Hz, 1H), 7.69—7.72 (m, 1H), 7.52—7.54 (m, 1H), 7.45—7.49 (m, 1H), 7.33 (d, J=3.2 Hz, 1H), 7.18—7.28 (m, 2H), 6.74 (dd, J=0.8, 3.2 Hz, 1H); EI-MS *m/z*: 194 (M^+).

1-*p*-Tolyl-1*H*-indole (3u)[30] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67—7.68 (m, 1H), 7.51—7.53 (m, 1H), 7.37—7.39 (m, 2H), 7.29—7.31 (m, 3H), 7.13—7.24 (m, 2 H), 6.66 (dd, J=0.8, 3.2 Hz, 1H), 2.43 (s, 3H); ESI-MS *m/z*: 208.1 $(M+H)^+$.

1-(4-Methoxyphenyl)-1*H*-imidazole (5a)[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76 (s, 1H), 7.29 (d, J=

8.7 Hz, 2H), 7.19 (d, J=6.6 Hz, 2H), 6.98 (d, J=9.0 Hz, 2H), 3.85 (s, 3H); ESI-MS *m/z*: 175.0 $(M+H)^+$.

1-(4-Methoxyphenyl)-1*H*-pyrazole (5b)[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.83 (d, J=2.1 Hz, 1H), 7.70 (d, J=1.8 Hz, 1H), 7.57—7.60 (m, 2H), 6.92—6.96 (m, 2H), 6.43—6.44 (m, 1H), 3.84 (s, 3H); ESI-MS *m/z*: 175.0 $(M+H)^+$.

1-(4-Methoxyphenyl)-1*H*-1,2,4-triazole (5c)[31] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.45 (s, 1H), 8.08 (s, 1H), 7.57 (dd, J=2.1, 6.9 Hz, 2H), 7.02 (dd, J=2.1, 6.9 Hz, 2H), 3.86 (s, 3H); ESI-MS *m/z*: 176.0 $(M+H)^+$.

1-(4-Methoxyphenyl)-1*H*-pyrrole (5d)[32] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32 (d, J=8.4 Hz, 2H), 7.02 (d, J=2.1 Hz, 2H), 6.95 (d, J=9.0 Hz, 2H), 6.33 (d, J=1.8 Hz, 2H), 3.85 (s, 3H); ESI-MS *m/z*: 174.0 $(M+H)^+$.

1-(4-Methoxyphenyl)-1*H*-benzoimidazole (5e)[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.89—7.86 (m, 1H) 7.48—7.40 (m, 3H), 7.34—7.31 (m, 2H), 7.10—7.06 (m, 2H), 3.90 (s, 3H); ESI-MS *m/z*: 225.1 $(M+H)^+$.

***N*-[(*p*-Methoxy)phenyl]carbazole (5f)**[33] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.15—8.13 (m, 2H), 7.46—7.24 (m, 8H), 7.12—7.09 (m, 2H), 3.91 (s, 3H); ESI-MS *m/z*: 274.2 $(M+H)^+$.

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