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Copper Iodide as a Recyclable Catalyst for Buchwald *N*-Arylation

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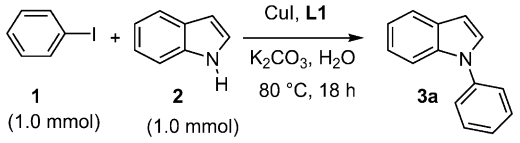
An experimentally simple, efficient, and inexpensive catalyst system was developed for the *N*-arylation of indole, substituted indoles, pyrazole, imidazole, benzamide, morpholine, benzimidazole, thiobenzamide, aniline, benzylaniline, octylaniline, heptylaniline, and cyclohexylaniline with aryl iodides and bromides by using CuI as catalyst, *trans*-1,2-diaminocyclohexane (**L1**) as ligand, K_2CO_3 as base, and water as solvent at 80 °C. The yields were excellent, and the catalytic system was recyclable up to four times without loss of catalytic activity.

Introduction

N-Arylazoles are important building blocks in organic synthesis as well as in pharmaceutical, agrochemical, and material sciences.[1] Over the past decades, versatile catalytic procedures for cabon–nitrogen bond formation, for instance, amination of aryl halides,[2] amidation,[3] and hydroamination,[4] have been reported. Nevertheless, further improvements are still possible. Moreover, these nitrogen-containing heterocycles are of interest as antiallergic,[5] antipsychotic,[6] herbicidal agents,[7] COX-2 inhibitors,[8] and melatonin receptor MT_1 agonists,[9] and are also used as synthetic intermediates in the synthesis of many biologically active compounds.[10] This has led to the development of various synthetic strategies for this important heterocyclic system. Traditional synthesis of *N*-arylated indoles consists of copper-mediated Ullmann-type[11] reactions of these heterocycles with aryl halides, but it has various limitations, such as high-temperature reaction conditions,[12] moderate yields,[13] use of well-designed but expensive ligands,[14] and stoichiometric amounts of the catalyst.[15] Hence, efforts have been directed towards the development of new, inexpensive and efficient recyclable catalytic systems for the amination of aryl halides with various nitrogen nucleophiles.[16]

The most appropriate methods for the synthesis of *N*-arylazoles are based upon transition-metal-mediated coupling of azoles with aryl halides. *N*-Arylation of azoles with aryl halides in the presence of palladium[17] has extensively been used to synthesize the corresponding *N*-arylazoles. Nevertheless, the use of expensive palladium limits the attractiveness of these methods for industrial applications. A general and efficient method for the synthesis of *N*-arylated compounds involves copper-catalyzed *N*-arylation by aryl halides to yield a wide range of target products under mild conditions (room temperature).[18] However, although the reaction can be carried out at room temperature, it suffers from the requirement to use more than stoichiometric amounts of copper salts. Recently, a number of transition metals, such as Fe,[19] Fe/Cu,[20] Ni,[21] and Cd,[22] have been employed in combination with various ligands for C–N cross-coupling reactions (Scheme 1). In this respect, copper is an interesting option, and the economic viability of this metal has led to a resurgence of interest in Ullmann-type reactions.



Scheme 1. Copper-catalyzed C–N cross-coupling.

Ma and co-workers[23] reported that by using L-proline as additive, the cross-coupling reactions of aryl halides with N-heterocycles under mild conditions gave *N*-arylazoles in good to excellent yields. Venkataraman and co-workers[24] showed that the coupling of aryl halides with various nucleophiles could be successfully performed in good yields at 110 °C with catalysts derived from copper(I) bromide and 1,10-phenanthroline as ligand. Ma and Jiang[25] reported a mild and efficient copper-catalyzed system for *N*-arylation of N–H heterocycles with aryl halides by using an *N*-hydroxy imide as ligand.

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Buchwald and co-workers[26] discovered the copper-catalyzed *N*-arylation of aryl halides with N–H heterocycles in the presence of diamine ligands.[27] However, this method also suffers from certain limitations, such as the use of organic solvents and lack of catalyst recovery and recyclability. In view of these drawbacks, the reaction could be further explored and refined to overcome some of these shortcomings by using an environmentally benign solvent with recyclable catalyst under mild reaction conditions. Currently, organic reactions in aqueous medium have become the focus of organic syntheses, because they avoid the harmful effects of organic solvents and are environmentally friendly. Water[28] is clearly a cheap, non-toxic and readily available reaction medium, which makes it an ideal solvent for green chemistry protocols. Very recently, Chua and coworkers reported cobalt-[29] and manganese-catalyzed[30] C–N cross-coupling of aryl iodides and N-heterocycles by using a diamine as ligand and water as medium at 120 °C.

Results and Discussion

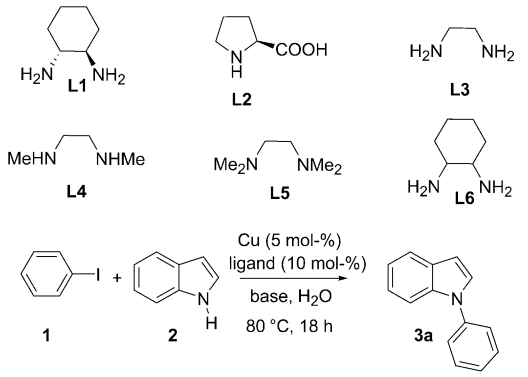
Here, we report a highly efficient, reusable-copper-catalyzed *N*-arylation of nitrogen heterocycles with aryl halides in water as a reaction medium in combination with commercially available copper(I) iodide and a diamine. The reaction of iodobenzene and indole was selected as a preliminary model reaction for C–N cross-coupling. The reaction conditions were optimized by taking into consideration parameters such as ligands, copper sources, and base. No product formation was seen in the presence of ligand alone (Table 1, Entry 1), even after prolonged stirring, and only a trace amount of the expected product was formed with a copper source in the absence of ligand or base at 80 °C in water after 18 h (Table 1, Entries 2–3). Among several ligands tested (**L1**–**6**), the inexpensive ligand **L1** provided the best result. We have also carried out the reaction with different copper sources, such as CuBr, CuCl, $Cu(OAc)_2$, Cu_2O, CuI, and CuO. Amongst them, CuI and CuO were found to be efficient for the *N*-arylation of indoles in water, and CuI was found to be superior among these copper sources. We then examined the effect of different bases, such as K_2CO_3, K_3PO_4, Cs_2CO_3, and NaOMe. Of the bases tested, K_2CO_3 provided the arylated compound in highest yield. The optimization results are summarized in Table 1 for the reaction of iodobenzene and indole (Scheme 1).

With optimized reaction conditions for the reaction of iodobenzene and indole in hand, we expanded the scope of the coupling reaction to various aryl iodides/bromides with indoles in the presence of 5 mol-% CuI, 10 mol-% **L1** and 2 equiv. of K_2CO_3 in water under air at 80 °C; the results are summarized in Table 2. In general, aryl iodides were more reactive than aryl bromides, and gave the corresponding *N*-arylated products in higher yields (up to 98%).

Various aromatic iodides were subjected to this protocol, and it was found that the reactions worked well in all cases, yielding the expected products in good yields, although *ortho* substitution hampered the reaction and gave lower yields (Table 2, Entry 4). We then extended the optimized reaction conditions to the coupling of aryl halides with other substituted indoles and found that in all the cases satisfactory yields were obtained (Table 2). Here, less reactive aryl bromides required higher reaction temperatures than aryl iodides to ensure completion of the reaction. In the case of aryl iodides, the reaction proceeded at 80 °C to give the coupling products in good to excellent yields, whereas aryl bromides gave the coupling products in good yields at 95–100 °C (Table 2, Entries 11–16). After performing the reactions with other aryl halides, such as *para*-bromo/iodo-nitrobenzene, *para*-bromo/iodo-acetophenone, methyl *para*-bromo/iodo-benzoate, and ethyl *para*-bromo/iodo-benzoate, with indole, the corresponding products were obtained in good to moderate yields (Table 2, Entries 17–20).

In the case of the reaction of *para*-formylaryl halides with indole, the biologically active bis(indole) product was

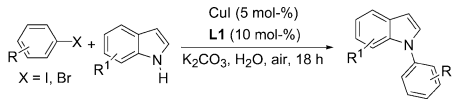
Table 1. Optimization studies on copper-catalyzed *N*-arylation of indoles in water.

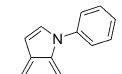
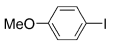
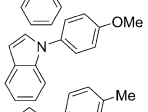
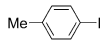
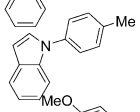
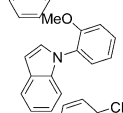
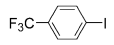
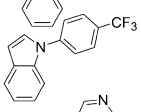
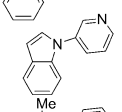
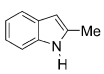
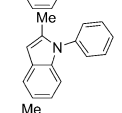
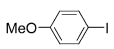
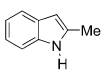
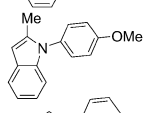
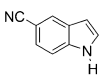
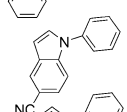
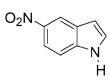
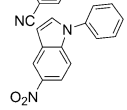


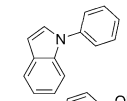
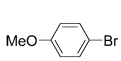
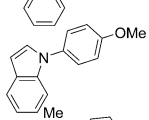
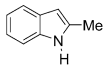
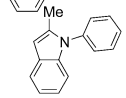
Entry	Copper source	Ligand	Base [equiv.]	Yield[a] [%]
1	–	**L1**	–	–
2	CuI	–	K_2CO_3	trace
3	CuI	**L1**	–	50
4	CuI	**L1**	K_2CO_3	98
5	CuI	**L2**	K_2CO_3	11
6	CuI	**L3**	K_2CO_3	10
7	CuI	**L4**	K_2CO_3	90
8	CuI	**L5**	K_2CO_3	11
9	CuI	**L6**	K_2CO_3	26
10	CuBr	**L1**	K_2CO_3	18
11	CuCl	**L1**	K_2CO_3	15
12	$Cu(OAc)_2$	**L1**	K_2CO_3	10
13	Cu_2O	**L1**	K_2CO_3	85
14	CuO	**L1**	K_2CO_3	90
15	CuI	**L1**	K_3PO_4	79
16	CuI	**L1**	Cs_2CO_3	50
17	CuI	**L1**	NaOMe	65

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), Cu (5 mol-%), ligand (10 mol-%), base (2.0 equiv.), air, 80 °C, 18 h.

Table 2. Reaction of indoles with aryl halides by using CuI as a recyclable catalyst.



Entry	ArX	NuH	Product		Yield[a] [%]
1				**3a**	98
2				**3b**	92
3				**3c**	92
4				**3d**	78
5				**3e**	89
6				**3f**	90
7				**3g**	89
8				**3h**	90
9				**3i**	91
10				**3j**	91

Entry	ArX	NuH	Product		Yield[a] [%]
11				**3a**	85
12				**3b**	84
13				**3g**	89
14				**3h**	87
15				**3j**	85
16				**3e**	86
17				**3k**	68 60
18				**3l**	70 65
19				**3m**	65 50
20				**3n**	67 60

[a] Reaction conditions: CuI (5 mol-%), **L1** (10 mol-%), K_2CO_3 (2 equiv.), **2** (1 mmol), **1** (1 mmol), air, 80 °C (with aryl iodides) or 100 °C (with aryl bromides).

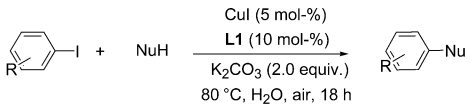
observed (confirmed by mass spectrometry), rather than the arylated product.

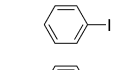
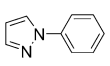
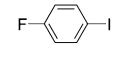
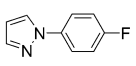
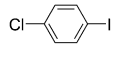
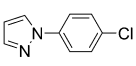
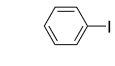
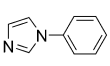
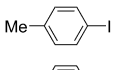
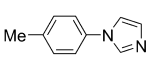
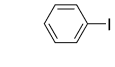
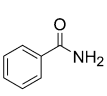
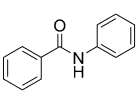
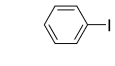
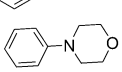
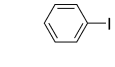
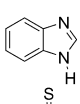
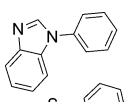
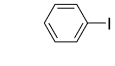
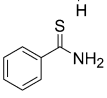
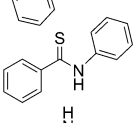
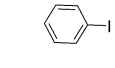
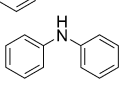
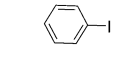
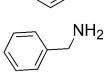
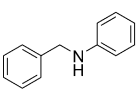
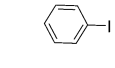
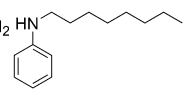
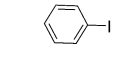
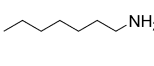
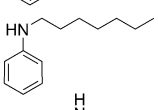
Finally, the scope of the copper-catalyzed cross-coupling reaction was tested with other nitrogen-containing compounds (Table 3). Pyrazole, imidazole, benzamide, morpholine, benzimidazole, thiobenzamide, aniline, benzylamine, octylamine, heptylamine, and cyclohexylamine were all found to be effective nucleophilic partners in the coupling reaction, which afforded the corresponding products with good to excellent yields under the conditions given in Table 1. The results obtained in our studies support the oxidative addition/reductive elimination type of reaction mechanism (Scheme 2). Thus, CuI and **L1**, when heated under reflux in the presence of a base, lead to the formation of complex **A**, to which ArX oxidatively adds to form complex **B**. Replacement of X with a nucleophile, followed by reductive elimination affords the *N*-arylated product, and the CuI and **L1** are released to complete the catalytic cycle.

We then checked the reusability of the aqueous copper catalyst system[31] after extraction of the organic compounds with ethyl acetate. The recovered violet aqueous layer was placed in a 25 mL round-bottomed flask and used again to accomplish the respective transformation up to four times with iodobenzene and indole as substrates (Table 4). Normally, in the case of nanoparticle-catalyzed cross-coupling reactions or other heterogeneous systems, the metal complex has to be recycled and reused; in our case, both the metal complex and the aqueous medium itself could be recycled.

IR spectral studies revealed that in this copper catalytic system, the copper remained in the same state even after the fourth cycle. From the FTIR spectrum, the absorption bands at 570 and 510 cm^{-1} indicate the presence of Cu–I,[36] and the band at 494 cm^{-1} corresponding to Cu–O[37] is absent in the catalytic system. On the basis of this evidence (Figure S1),[38] we conclude that the copper is not converted into any form of oxide.

Table 3. Reaction of aryl iodides with various amines by using CuI as a recyclable catalyst.



Entry	ArI	Nucleophile	Product		Yield[a] [%]
1				**4a**	82
2				**4b**	81
3				**4c**	81
4				**5a**	65
5				**5b**	68
6				**6a**	51
7				**7a**	52
8				**8a**	70
9				**9a**	58
10				**10a**	80
11				**11a**	80
12				12a	60
13				**13a**	60
14				**14a**	60

[a] Reaction conditions: CuI (5 mol-%), **L1** (10 mol-%), K_2CO_3 (2 equiv.), ArI (1 mmol), NuH (1 mmol), H_2O, air, 80 °C.

Scheme 2. Plausible mechanism for the *N*-arylation.

Table 4. Reusability study of the catalyst.

Cycle	1	2	3	4
Yield [%]	98	94[a]	93[a]	91[a]

[a] Catalyst recovered and reused.

Conclusions

We have developed an experimentally simple and recyclable copper(I) iodide catalyzed *N*-arylation of indoles with a variety of aryl iodides and bromides by using water as an environmentally benign, safe, and nontoxic reaction medium. This methodology will be a valuable addition to the development of green chemistry protocols.

Experimental Section

General: Iodobenzene (99%), indole (98%) and other nucleophiles and aryl halides were purchased from Sigma–Aldrich and used without purification. All experiments were carried out under air. Column chromatography was carried out with 60–120 mesh silica gel by using hexane as eluent. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV irradiation. ^1H and ^{13}C NMR (Bruker Avance 300, Innova 400 MHz and Bruker Gemini 200 MHz) spectra were recorded in $CDCl_3$ by using TMS as internal standard. Chemical shifts (δ) are reported in ppm, and spin–spin coupling constants (J) are given in Hz. Melting points were determined with a Fischer–Johns melting point apparatus. IR spectra and MS data were recorded with a Thermo Nicolet Nexus 670 FTIR spectrometer and with a Finnigan MAT 1020 mass spectrometer operating at 70 eV, respectively.

Representative Procedure for the Cross-Coupling Reactions of Indole with Iodobenzene: Indole (117 mg, 1 mmol), CuI (10 mg, 5 mol-%), **L1** (10 μL, 10 mol-%), K_2CO_3 (2.0 equiv.), and iodobenzene (0.1 mL, 1 mmol) were charged in a 25 mL round-bottomed flask with a condenser, under air, followed by the addition of water (4 mL). The reaction mixture was heated in an oil bath at 80 °C and stirred at this temperature for 18 h. After completion of the reaction (monitored by TLC), the homogeneous mixture was then cooled to room temp. and treated with ethyl acetate (2 mL). The aqueous layer was separated and extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the product, which was purified by column chromatography using silica gel (ethyl acetate/hexane, 1:9) to obtain the pure product **3a** (189 mg, 98%) as a pale-yellow oil. All the products were characterized by ^1H and ^{13}C NMR, and MS analyses and compared with literature values.

Representative Procedure for Recycling: After extraction of the organic compounds with ethyl acetate, the recovered violet aqueous layer was placed in a 25 mL round-bottomed flask with a condenser. Indole (117 mg, 1 mmol), **L1** (5 μL, 5 mol-%), K_2CO_3 (1.0 equiv.), and iodobenzene (0.1 mL, 1 mmol) were added under air, followed by addition of water (4 mL). The reaction mixture was heated in an oil bath at 80 °C and stirred at this temperature for 18 h. After completion of the reaction (monitored by TLC), the homogeneous mixture was then cooled to room temp. and treated with ethyl acetate (2 mL). The aqueous layer was separated and extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the product, which was purified by column

chromatography using silica gel (ethyl acetate/hexane, 1:9) to obtain the pure product **3a** (181 mg, 94%) as a pale-yellow oil. All the products were characterized by ^{1}H and ^{13}C NMR, and MS analyses and compared with literature values. The same procedure was extended for further cycles.

1-Phenyl-1*H*-indole (3a):[13] Table 2, Entry 1. Yield: 189 mg (98%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.60 (d, J = 7.96 Hz, 1 H), 7.51–7.44 (m, 5 H), 7.33–7.27 (m, 2 H), 7.20–7.04 (m, 2 H), 6.62–6.61 (d, J = 2.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8, 135.8, 129.5, 129.2, 127.9, 126.4, 124.3, 122.3, 121.0, 120.3, 110.4, 103.5 ppm. IR: $\tilde{\nu}_{max}$ = 2923, 1596, 1503, 1137, 745, 689 cm^{-1}. ESI-MS: m/z = 194.5 [M + H].

1-(4-Methoxyphenyl)-1*H*-indole (3b):[18g] Table 2, Entry 2. Yield: 205 mg (92%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.59 (d, J = 7.32 Hz, 1 H), 7.39–7.36 (m, 3 H), 7.23–7.20 (m, 1 H), 7.15–7.06 (m, 2 H), 6.99–6.96 (m, 2 H), 6.58–6.57 (d, J = 2.93 Hz, 1 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 136.2, 132.7, 128.8, 128.2, 125.8, 122.0, 120.9, 120.0, 114.6, 110.2, 102.8, 55.4 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 1586, 1248, 1118, 1014, 821, 787 cm^{-1}. ESI-MS: m/z = 224 [M + H].

1-*p*-Tolyl-1*H*-indole (3c):[25] Table 2, Entry 3. Yield: 190 mg (92%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.58 (d, J = 7.55 Hz, 1 H), 7.46–7.44 (d, J = 7.55 Hz, 1 H), 7.36–7.33 (d, J = 8.30 Hz, 2 H), 7.25–7.22 (m, 3 H), 7.19–7.05 (m, 2 H), 6.59–6.58 (d, J = 3.77 Hz, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 136.2, 135.9, 130.1, 129.1, 128.0, 124.2, 122.1, 121.0, 120.1, 110.4, 103.1, 21.0 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 1587, 1518, 1014, 821, 787 cm^{-1}. ESI-MS: m/z = 208 [M + H].

1-(2-Methoxyphenyl)-1*H*-indole (3d):[23e] Table 2, Entry 4. Yield: 173 mg (78%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.61 (m, 1 H), 7.45–7.33 (m, 2 H), 7.25–7.05 (m, 6 H), 6.62–6.61 (d, J = 3.39 Hz, 1 H), 3.79 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 133.9, 133.7, 129.2, 128.9, 128.1, 127.5, 126.8, 125.0, 123.5, 122.0, 121.6, 55.6 ppm. IR: $\tilde{\nu}_{max}$ = 2926, 1577, 1248, 1112, 1011, 821, 788 cm^{-1}. ESI-MS: m/z = 224 [M + H].

1-[4-(Trifluoromethyl)phenyl]-1*H*-indole (3e):[12b] Table 2, Entry 5. Yield: 232 mg (89%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.58 (m, 3 H), 7.49–7.43 (m, 1 H), 7.41–7.36 (m, 2 H), 7.26–7.23 (m, 2 H), 7.20–7.08 (m, 1 H), 6.64–6.61 (d, J = 3.02 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 135.4, 129.6, 127.3, 126.8, 125.7, 123.8, 122.9, 121.4, 120.9, 110.3, 104.8 ppm. IR: $\tilde{\nu}_{max}$ = 1585, 1346, 1416, 1350, 1020, 1013, 810, 776 cm^{-1}. ESI-MS: m/z = 262 [M + H].

1-(Pyridin-3-yl)-1*H*-indole (3f):[27g] Table 2, Entry 6. Yield: 174 mg (90%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.58 (d, J = 8.12 Hz, 1 H), 7.51–7.48 (d, J = 8.49 Hz, 1 H), 7.41–7.37 (m, 1 H), 7.27–7.05 (m, 6 H), 6.58–6.57 (d, J = 3.21 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 136.0, 128.9, 127.8, 126.0, 123.6, 122.4, 121.0, 120.5, 114.7, 110.5, 103.3, 96.1 ppm. IR: $\tilde{\nu}_{max}$ = 2898, 2100, 1585, 1521, 1456, 1134, 1014, 876, 756 cm^{-1}. ESI-MS: m/z = 195.2 [M + H].

2-Methyl-1-phenyl-1*H*-indole (3g):[32] Table 2, Entry 7. Yield: 184 mg (89%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.23 (m, 6 H), 7.06–6.98 (m, 3 H), 6.32 (s, 1 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1, 137.9, 136.9, 129.3, 128.1, 127.9, 127.6, 120.9, 119.9, 119.4, 109.9, 101.2, 13.3 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 2167, 1739, 1587, 1558, 1064, 857, 767 cm^{-1}. ESI-MS: m/z = 208 [M + H].

1-(4-Methoxylphenyl)-2-methyl-1*H*-indole (3h):[23e] Table 2, Entry 8. Yield: 213 mg (90%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.45 (d, J = 7.88 Hz, 1 H), 7.23–7.20 (m, 2 H), 7.03–6.95 (m, 5 H), 6.28 (s, 1 H), 3.86 (s, 3 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 138.5, 137.0, 130.7, 129.1, 128.0, 120.9, 119.8, 119.5, 114.5, 109.9, 100.9, 55.4, 13.3 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 1585, 1518, 1456, 1134, 1014, 876, 756 cm^{-1}. ESI-MS: m/z = 238 [M + H].

1-Phenyl-1*H*-indole-5-carbonitrile (3i):[27g] Table 2, Entry 9. Yield: 198 mg (91%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.35 (m, 7 H), 7.32–7.30 (m, 1 H), 7.15–7.11 (m, 1 H), 6.65–6.64 (d, J = 3.39 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 134.6, 130.9, 129.6, 129.0, 128.0, 126.8, 125.1, 124.2, 123.5, 113.6, 111.9, 102.9 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 2250, 1567, 1538, 1074, 956, 845, 723 cm^{-1}. ESI-MS: m/z = 219.5 [M + H].

5-Nitro-1-phenyl-1*H*-indole (3j):[27g] Table 2, Entry 10 Yield: 216 mg (91%); yellow solid; m.p. 83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65–8.60 (d, J = 1.7 Hz, 1 H), 8.12–8.06 (d, J = 9.0 Hz, 1 H), 7.58–7.40 (m, 7 H), 6.83–6.82 (d, J = 3.02 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 138.5, 131.2, 129.9, 128.4, 127.7, 124.7, 118.2, 117.8, 110.3, 105.6, 96.1 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 1587, 1518, 1014, 821, 787 cm^{-1}. ESI-MS: m/z = 239 [M + H].

1-(4-Nitrophenyl)-1*H*-indole (3k):[27a] (Table 2, Entry 17. Yield: 162 mg (68%); yellow solid; m.p.[35] 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42–8.37 (m, 2 H), 7.71–7.64 (m, 4 H), 7.39–7.37 (m, 1 H), 7.32–7.21 (m, 2 H), 6.78–6.77 (d, J = 3.77 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 145.4, 144.2, 131, 125.5, 122.7, 120.1, 118, 111.4, 104.2 ppm. IR: $\tilde{\nu}_{max}$ = 1599, 1553, 1459, 1388, 1324, 1277, 1224, 774, 746, 708 cm^{-1}. ESI-MS: m/z = 239 [M + H].

1-[4-(1*H*-Indol-1-yl)phenyl]ethanone (3l):[23e] Table 2, Entry 18. Yield: 164 mg (70%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.64 (d, J = 1.9 Hz, 1 H), 7.39–7.51 (m, 4 H), 7.09–7.33 (m, 4 H), 6.52–6.53 (d, J = 3.12 Hz, 1 H), 2.52 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.2, 144.1, 133.3, 130.1, 129.2, 125.6, 121, 120, 118.3, 110.2, 104.1, 29.2 ppm. IR: $\tilde{\nu}_{max}$ = 3200, 1657, 1519, 1568, 1456, 1314, 1213, 845, 745 cm^{-1}. ESI-MS: m/z = 236 [M + H].

Methyl 4-(1*H*-Indol-1-yl)benzoate (3m):[17a] Table 2, Entry 19. Yield: 163 mg (65%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25–8.18 (d, J = 8.03 Hz, 1 H), 7.70–7.52 (m, 3 H), 7.39–7.34 (m, 2 H), 7.29–7.10 (m, 3 H), 6.73–6.72 (d, J = 3.77 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 143.8, 135, 131.3, 129.8, 127.6, 127.5, 123.3, 122.0, 121.6, 121.0, 110.7, 104, 52.0 ppm. IR: $\tilde{\nu}_{max}$ = 3045, 2945, 1705, 1538, 1456, 1213, 1052, 777, 745, 686 cm^{-1}. ESI-MS: m/z = 252 [M + H].

Ethyl 4-(1*H*-Indol-1-yl)benzoate (3n):[27g] Table 2, Entry 20. Yield: 177 mg (67%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21–8.23 (m, 2 H), 7.51–7.78 (m, 4 H), 7.10–7.28 (m, 3 H), 6.71–6.72 (t, J = 3.75 Hz, 1 H), 3.99–4.04 (br. s, 2 H), 1.33 (t, J = 8.02 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.1, 146.3, 130.5, 126.1, 125.4, 122.3, 121.1, 120.5, 118.5, 111.4, 104.1, 61.2, 14.9 ppm. IR: $\tilde{\nu}_{max}$ = 3046, 3100, 2948, 1978, 1705, 1538, 1503, 1213, 1345, 1052, 777, 748, 694 cm^{-1}. ESI-MS: m/z = 266 [M + H].

1-Phenyl-1*H*-pyrazole (4a):[13] Table 3, Entry 1. Yield: 118 mg (82%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.88 (m, 1 H), 7.69–7.65 (m, 3 H), 7.45–7.39 (m, 2 H), 7.27–7.20 (m, 1 H), 6.42 (t, J = 2.26 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9, 140.1, 129.4, 126.8, 126.5, 119.2, 107.5 ppm. IR: $\tilde{\nu}_{max}$ = 1601, 1592, 1464, 1157, 837, 750, 749 cm^{-1}. ESI-MS: m/z = 145 [M + H].

1-(4-Fluorophenyl)-1*H*-pyrazole (4b):[13] Table 3, Entry 2. Yield: 131 mg (81%); white solid; m.p. 62 °C. ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 7.86 (d, J = 2.26 Hz, 1 H), 7.74 (d, J = 9.0 Hz, 2 H), 7.65 (d, J = 1.5 Hz, 1 H), 7.46 (d, J = 9.0 Hz, 2 H) ppm. 6.42 (t, 1 H, J = 2.25 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 141.4, 138.4, 126.5, 120.8, 114.4, 108.0 ppm. IR: $\tilde{\nu}_{max}$ = 1531, 1546, 1394, 1168, 1068, 844, 756 cm^{-1}. ESI-MS: m/z = 163.77 [M + H].

1-(4-Chlorophenyl)-1*H*-pyrazole (4c):[13] Table 3, Entry 3. Yield: 144 mg (81%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.84 (m, 1 H), 7.73–7.71 (m, 1 H), 7.65–7.53 (m, 2 H), 7.43–7.36 (m, 2 H), 6.43–6.42 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9, 140.3, 137.6, 129.6, 127.1, 120.6, 108.0 ppm. IR: $\tilde{\nu}_{max}$ = 1716, 1597, 1520, 1436, 1122, 883, 748 cm^{-1}. ESI-MS: m/z = 179.7 [M + H].

1-Phenyl-1*H*-imidazole (5a):[11b] Table 3, Entry 4. Yield: 94 mg (65%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.49–7.45 (m, 2 H), 7.40–7.34 (s, 3 H), 7.25–7.19 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 135.5, 130.2, 129.8, 127.4, 121.4, 118.2 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 1674, 1599, 1304, 1249, 1113, 1059, 817, 760 cm^{-1}. ESI-MS: m/z = 145 [M + H].

1-*p*-Tolyl-1*H*-imidazole (5b):[11b] Table 3, Entry 5. Yield: 108 mg (68%); white-crystalline solid; m.p. 63–65 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.39–7.19 (m, 6 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9, 137.4, 135.3, 129.5, 128.1, 121.2, 118.4, 29.5 ppm. IR: $\tilde{\nu}_{max}$ = 2852, 1903, 1678, 1506, 1055, 892, 758 cm^{-1}. ESI-MS: m/z = 159 [M + H].

***N*-Phenylbenzamide (6a):**[13] Table 3, Entry 6. Yield: 100 mg (51%); brown solid; m.p. 162–165 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–6.78 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 137.8, 134.9, 131.8, 130.0, 129.0, 128.7, 127.0, 124.5, 120.1 ppm. IR: $\tilde{\nu}_{max}$ = 2928, 1651, 1604, 1531, 1440, 858, 764, 690 cm^{-1}. ESI-MS: m/z = 198 [M + H].

4-Phenylmorpholine (7a):[34] Table 3, Entry 7. Yield: 85 mg (52%); brown solid; m.p. 54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.19 (m, 2 H), 6.86–6.80 (m, 3 H), 3.82 (t, J = 4.5 Hz, 4 H), 3.12 (t, J = 4.5 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.2, 129.1, 120.0, 115.6, 66.9, 49.3 ppm. IR: $\tilde{\nu}_{max}$ = 2854, 1599, 1496, 1377, 1232, 758, 692 cm^{-1}. ESI-MS: m/z = 164 [M + H].

1-Phenyl-1*H*-benzo[*d*]imidazole (8a):[11b] Table 3, Entry 8. Yield: 135 mg (70%); brown solid; m.p. 96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.59–7.51 (m, 4 H), 748–7.35 (m, 1 H), 7.15–6.95 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 134.2, 130.4, 129.6, 127.9, 126.2, 122.4, 121.6, 110.1, 108.9 ppm. IR: $\tilde{\nu}_{max}$ = 2914, 1593, 1502, 1294, 1045, 859, 753, 609 cm^{-1}. ESI-MS: m/z = 195.3 [M + H].

***N*-Phenylbenzothioamide (9a):**[33] Table 3, Entry 9. Yield: 123 mg (58%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.16 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.2, 140.5, 135.7, 131.0, 129.1, 128.7, 127.5, 127.0 ppm. IR: $\tilde{\nu}_{max}$ = 1690, 1600, 1531, 1500, 1395, 691 cm^{-1}. ESI-MS: m/z = 214 [M + H].

Diphenylamine (10a):[11b] Table 3, Entry 10. Yield: 135.2 mg (80%); white solid; m.p. 48 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.18 (m, 4 H), 7.02–6.99 (m, 4 H), 6.89–6.84 (m, 2 H), 5.56 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8, 129.3, 121.1, 117.8 ppm. IR: $\tilde{\nu}_{max}$ = 3030, 3045, 1650, 1550, 670, 780 cm^{-1}. ESI-MS: m/z = 170 [M + H].

***N*-Benzylaniline (11a):**[11b] Table 3, Entry 11. Yield: 135 mg (80%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.14 (m, 7 H), 6.73–6.61 (m, 3 H), 4.31 (s, 2 H), 4.0 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 139.3, 129.2, 128.5, 127.4, 127.1, 117.5, 112.8, 48.2 ppm. IR: $\tilde{\nu}_{max}$ = 3031, 3030, 2900, 1600, 1450, 610, 720 cm^{-1}. ESI-MS: m/z = 184 [M + H].

***N*-Octylaniline (12a):**[11b] Table 3, Entry 12. Yield: 123 mg (60%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.14 (m, 2 H), 6.70–6.59 (m, 3 H), 3.4 (br. s, 1 H), 3.12–3.07 (m, 2 H), 1.63–1.56 (m, 2 H), 1.28–1.25 (m, 10 H), 0.895 (t, J = 6.98 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 129.1, 117.0, 112.6, 44.0, 31.8, 30.9, 29.5, 29.2, 27.1, 22.6, 14.0 ppm. IR: $\tilde{\nu}_{max}$ = 3350, 3000, 2950, 2800, 1459, 1389, 700 cm^{-1}. ESI-MS: m/z = 206 [M + H].

***N*-Heptylaniline (13a):**[11b] Table 3, Entry 13. Yield: 114 mg (60%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08 (t, J = 6.79 Hz, 2 H), 6.60 (t, J = 6.04 Hz, 1 H), 6.51–6.49 (m, 2 H), 3.40 (br. s, 1 H), 3.06 (t, J = 6.79 Hz, 2 H), 1.63–1.54 (m, 2 H), 1.40–1.22 (m, 8 H), 0.91–0.87 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 129.1, 116.9, 112.5, 43.9, 31.7, 29.5, 29.0, 27.0, 22.5, 14.0 ppm. IR: $\tilde{\nu}_{max}$ = 3400, 3010, 2850, 1678, 1450, 650, 780 cm^{-1}. ESI-MS: m/z = 192 [M + H].

***N*-Cyclohexylaniline (14a):**[11b] Table 3, Entry 14. Yield: 105 mg (60%); yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.12 (m, 2 H), 6.66–6.63 (m, 1 H), 6.59–6.57 (m, 2 H), 3.27–3.21 (m, 1 H), 2.15–2.03 (m, 2 H), 1.77–1.73 (m, 2 H), 1.66–1.62 (m, 1 H), 1.41–1.10 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3, 129.1, 116.8, 113.1, 51.6, 33.4, 25.8, 24.9 ppm. IR: $\tilde{\nu}_{max}$ = 3400, 3010, 2850, 2910, 1450, 1350, 750 cm^{-1}. ESI-MS: m/z = 176 [M + H].

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectroscopic data of all the compounds.

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