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# Direct Arylation of Arene and *N*-Heteroarenes with Diaryliodonium Salts without the Use of Transition Metal Catalyst

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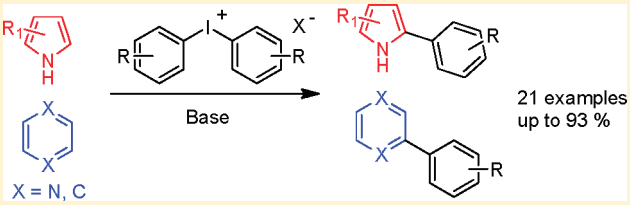
Supporting Information

**ABSTRACT:** A novel and simple transition metal-free direct arylation of arene and *N*-heteroarenes with diaryliodonium salts has been developed. This cross-coupling reaction is promoted only by base and gives the desired products in moderate to good yields.




Direct arylation of unreactive C−H bonds has received considerable attention in the field of cross-coupling reactions in recent years.[1] Transition metal complexes, especially Pd, Rh, and Ru complexes, played a key role in most of these reactions. Recently, some cheap and environmentally benign metal catalysts such as iron[2] and cobalt[3] have also been developed. However, to avoid the drawbacks of metal usage such as toxicity and heavy transition metal impurities in final products, the development of transition-metal-free cross-coupling reactions is of special importance. Very recently, significant progresses have been made in direct arylation of C−H bonds in the absence of transition metal catalyst.[4] Hayashi,[4a] Shi,[4b] and Lei's groups[4c] respectively reported the base-mediated arylation of benzene with aryl halides in the presence of 1,10-phenanthroline or *N*,*N*′-dimethyl-ethylene diamine. These findings provided a new strategy for direct C−H cross-coupling reactions in the absence of transition metal catalyst.

Diaryliodonium salts were used widely in organic synthesis because of their low toxicity, stability, high reactivity, and availability. They have been utilized in direct electrophilic arylation of various nucleophiles and transition-metal-mediated cross-coupling reactions.[5] In recent years, significant progresses have been made in transition-metal-catalyzed direct arylation of C−H bonds with diaryliodonium salts.[6] However, seeking relative arylation in the absence of transition metal still remains a challenge. In 2010, Kita and co-workers reported direct arylation of electron-rich aromatic compounds with diaryliodonium salts in the absence of transition metal catalyst.[7] More recently, Ackermann and co-workers found that indoles could be directly arylated with diaryliodonium salts under metal-free conditions.[8] Nevertheless, in these reports, only some special substrates such as methoxybenzenes and indole derivatives can provide the cross-coupling products in good yields. Herein, we wish to report a novel transition metal-free direct arylation of arene and *N*-heteroarenes with diaryliodonium salts.

Diaryliodonium salts could be simply prepared by oxidation of arenes and aryl iodides.[9] To optimize the reaction conditions, we first studied the cross-coupling reaction between diphenyliodonium salt and pyrrole, and the results were summarized in Table 1. Without the use of inorganic base as additive, only poor yield was obtained (32%, entry 1, Table 1). Therefore, a range of bases including $K_3PO_4$, $Na_2CO_3$, $K_2CO_3$, $NaHCO_3$, NaOH, and KOH were screened (entries 2−7, Table 1), and NaOH was found to be the most suitable one to give the desired product **3a** in 78% yield. The use of organic bases such as tetramethylethylenediamine (TMEDA) and triethylamine led to much decreased yields, and only trace and 47% yields were obtained, respectively (entries 9 and 10, Table 1). Investigation of reaction temperature revealed that 80 °C was the most efficient temperature (entries 6, 11, and 12, Table 1). The counteranions on diphenyliodonium salts seemed to have little effect on the reactions, in which almost same yields were found (entries 6, 13, and 14, Table 1). It was noteworthy that this reaction has excellent regioselectivity on the active 2-position of pyrrole. No C-3 arylated or poly-substitution product, which was commonly found in the literature,[6i,8] was detected. To rule out the effect of the trace amount of palladium metal contaminants in NaOH, the quantitative elemental analysis of NaOH was conducted by ICP-AES to give the Pd concentration of 0.0366 ppm. Under this concentration of Pd, palladium dichloride was used to catalyze this reaction without any base, and the yield of 34% was found, which was almost identical with the yield in entry 1 (Table 1). This result implicates that the present reaction is not likely to be catalyzed by trace palladium contaminants. Unfortunately, the attempt to reduce the amount of pyrrole only led to a harshly decreased yield (28%, entry 15, Table 1).

The substrate scope was subsequently investigated under the optimized conditions. First, various substituted diaryliodonium salts were prepared and used for the direct coupling toward pyrrole. The results listed in Table 2 indicate that diaryliodonium salts with electron-withdrawing substituents can give

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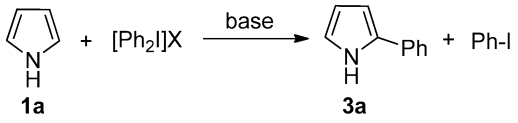
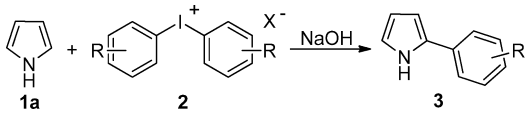
**Table 1. C-2 Arylation of Pyrrole with Diphenyliodonium Salt**[a]




| entry | base | X | temp (°C) | yield of **3a**[b] (%) |
|---|---|---|---|---|
| 1 | | OTf | 80 | 32 |
| 2 | $K_3PO_4$ | OTf | 80 | 61 |
| 3 | $Na_2CO_3$ | OTf | 80 | 75 |
| 4 | $K_2CO_3$ | OTf | 80 | 71 |
| 5 | $NaHCO_3$ | OTf | 80 | 60 |
| 6 | NaOH | OTf | 80 | 78 |
| 7 | KOH | OTf | 80 | 63 |
| 8 | t-BuOK | OTf | 80 | 68 |
| 9 | TMEDA | OTf | 80 | trace |
| 10 | $Et_3N$ | OTf | 80 | 47 |
| 11 | NaOH | OTf | 60 | 55 |
| 12 | NaOH | OTf | 100 | 68 |
| 13 | NaOH | $BF_4$ | 80 | 78 |
| 14 | NaOH | Br | 80 | 77 |
| 15[c] | NaOH | OTf | 80 | 28 |

[a]Reaction conditions: $[Ph_2I]X$ (0.2 mmol), **1a** (1 mL), base (1.5 equiv), 10 h, under air. [b]Isolated yields. [c]**1a** (5 equiv).

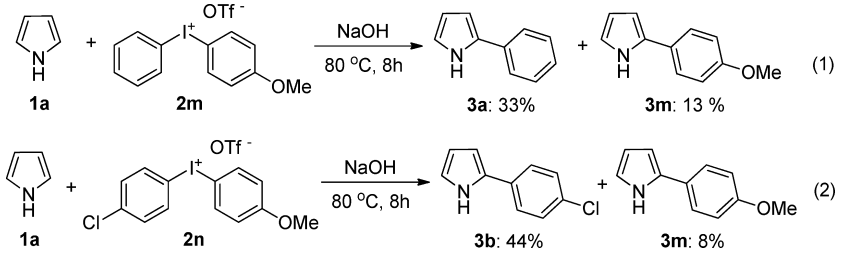
**Table 2. Base-Mediated Arylation of Pyrrole with Diaryliodonium Salts**[a]




| entry | R | X | product | yield[b] (%) |
|---|---|---|---|---|
| 1 | H (**2a**) | OTf | **3a** | 78 |
| 2 | 4-Cl (**2b**) | Br | **3b** | 91 |
| 3 | 4-Br (**2c**) | Br | **3c** | 65 |
| 4 | 4-F (**2d**) | Br | **3d** | 93 |
| 5 | 4-Me (**2e**) | OTf | **3e** | 71 |
| 6 | 4-$CH(CH_3)_2$ (**2f**) | Br | **3f** | 50 |
| 7 | 3-$NO_2$ (**2g**) | Br | **3g** | 84 |
| 8 | 3-COOEt (**2h**) | Br | **3h** | 76 |
| 9 | 2-Me-5-$NO_2$ (**2i**) | Br | **3i** | 83 |
| 10 | 3,4-diMe (**2j**) | OTf | **3j** | 73 |
| 11 | 2,4-diMe (**2k**) | OTf | **3k** | 73 |
| 12 | 2,4,6-triMe (**2l**) | OTf | **3l** | 12 |

[a]Reaction conditions: **2** (0.2 mmol), **1a** (1 mL), NaOH (1.5 equiv), 80 °C, 10 h, under air. [b]Isolated yields.

**Scheme 1. Intramolecular Competition Experiment**




relative products with better yields. Excellent yields of 91 and 93% were achieved for the reactions involving chloro- and fluoro-groups, respectively (entries 2 and 4, Table 2). The electron-withdrawing nitro-group also benefits the reaction (84% yield, entry 7, Table 2), and even the *ortho*-methyl group with steric hindrance would not affect the result (entry 9, Table 2). Some alkyl-substitued diaryliodonium salts also gave good results, and only 2,4,6-trimethyl diphenyliodonium triflate **2l** gave a dramatically decreased yield (entry 12, Table 2). In addition, intramolecular competition experiments with iodonium salts bearing two different aryl substituents (**2m** and **2n**) were carried out. As shown in Scheme 1, the cross-coupling products **3a** and **3m** were obtained in 33 and 13% yields, respectively (eq 1, Scheme 1). Moreover, the more electron-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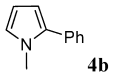
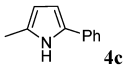
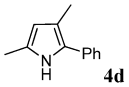
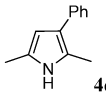
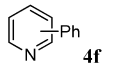
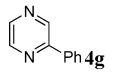
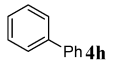
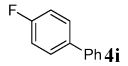
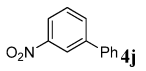
withdrawing chloro-group showed higher selectivity (eq 2, Scheme 1). These results suggest that the less electron-rich group is favored as arylating agent.

Different arenes, including substituted pyrroles, pyridine, pyrazine, and benzene, were then applied to the coupling reaction. As shown in Table 3, substituted pyrroles could be 2-

**Table 3. Base-Mediated Arylation of Arene Derivatives with Diaryliodonium Salts**[a]

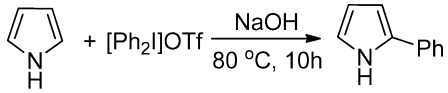
| entry | heteroarenes or arene **1** | diaryliodonium salts **2** | product | yield (%)[b] |
|---|---|---|---|---|
| 1 |  **1b** | **2a** |  **4b** | 69 |
| 2[c] |  **1c** | **2a** |  **4c** | 67 |
| 3[c] |  **1d** | **2a** |  **4d** | 53 |
| 4[c] |  **1e** | **2a** |  **4e** | trace |
| 5[d] |  **1f** | **2a** |  **4f** | 58 (o : m : p= 5 : 3.7 : 1) |
| 6[d] |  **1g** | **2a** |  **4g** | 71 |
| 7[e] |  **1h** | **2a** |  **4h** | 31 |
| 8[e] |  **1h** | **2d** |  **4i** | 21 |
| 9[e] |  **1h** | **2g** |  **4j** | 50 |

[a]Reaction conditions: **2** (0.2 mmol), **1** (1 mL), NaOH (1.5 equiv), 80 °C, 10 h, under air. [b]Isolated yields. [c]Reaction under 130 °C. [d]*t*-BuONa (1.5 equiv) instead of NaOH, 110 °C. [e]$NaHCO_3$ (1.5 equiv) instead of NaOH, with TMEDA (3 equiv).

arylated smoothly with high regioselectivity (entries 1−3, Table 3). When one of the α-positions of pyrrole was occupied, a higher reaction temperature was needed. However, if both α,α-occupied pyrrole were employed, only trace 3-phenyl product was detected (entry 4, Table 3), indicating that the coupling has excellent regioselectivity toward the active 2-position of pyrrole. For pyridine, after preliminary optimization of reaction conditions, we used *t*-BuONa instead of NaOH as a base, and the mixed ortho, meta, and para coupling products were obtained in a total yield of 58% with the amount ratio of 5:3.7:1 (entry 5, Table 3). Meanwhile, pyrazine could also give phenyl product with good yield (entry 6, Table 3). Benzene seemed to be unreactive for this coupling, and diphenyl ether was found as main byproduct. After optimization of reaction conditions, it was found that the formation of diphenyl ether could be inhibited by addition of TMEDA (entries 7−9, Table 3). In the presence of $NaHCO_3$ instead of NaOH, the coupling between benzene and di-*m*-nitrophenyliodonium bromide **2g** gave the desired product with moderate yield of 50% (entry 9, Table 3). Although a higher efficiency of this reaction would be desirable, this might be a promising method for the coupling of unactivated arenes.

Diaryliodonium salts are known to be able to transform into aryl radicals via decomposition.[10] To get further insight into our reaction, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the base-mediated reaction between pyrrole and diphenyliodonium triflate as a radical scavenger (Scheme 2).

**Scheme 2. Radical Trapping Experiments**




**1a** **2a** **3a**

| | |
|---|---|
| No Scavenger | 78 % |
| TEMPO | <3 % |
| 1,1-diphenylethylene | 19 % |

Only trace product was found in the reaction using 1 equiv of TEMPO, and a considerable amount of byproduct 2,2,6,6-tetramethyl-1-phenylpiperidine was detected. These results indicate that radical intermediates were involved in such reaction. Kita et al have proposed a cationic radical species via single-electron-transfer (SET) pathway for the TMSOTf-promoted direct arylation of electron-rich aromatic compounds with diaryliodonium salts.[7] However, in our reaction system, no homocoupling product of pyrrole was detected, while biphenyl was observed as byproduct. Besides, as shown in Scheme 2, an efficient phenyl radical trapping agent 1,1-diphenylethylene was also added to a reaction (Scheme 2), and the product was obtained in only 19% yield. This result was consistent with the aryl radical mechanism.[4b]

In conclusion, we report here a novel and simple cross-coupling between an inert aromatic C−H and diaryliodonium salts in the absence of any added transition metal catalyst. This direct arylation was promoted only by inorganic base. Some *N*-heteroarenes were arylated smoothly to provide target products in moderate to good yields. Benzene was also found to be suitable for the coupling. Mechanistic studies suggest that this reaction is possibly a phenyl radical pathway by decomposition of the diaryliodonium salts.

## EXPERIMENTAL SECTION

**General Information.** All reagents were purchased from commercial suppliers and used without further purification. Diaryliodonium salts were prepared according to the literature procedure.[9] $^1H$ NMR and $^{13}C$ NMR spectra were measured on a NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. Mass spectroscopy data of the products were collected on GCMS-EI or ESI mass spectrometers; ICP-AES data of the NaOH was collected on an ICP-AES.

**General Procedure for the Arylation of Pyrrole.** A reflux tube equipped with a magnetic stir bar charged with diaryliodonium salts 0.2 mmol (**2**, 1.0 equiv), NaOH (1.5 equiv), pyrrole (1 mL), and the reaction vessel was placed in an 80 °C oil bath. After stirring at this temperature for 10 h, the mixture was distilled in vacuo to recover the redundant pyrrole. The residue was cooled to room temperature, diluted with 20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mL of ethyl acetate, and washed with brine (15 mL) and water (15 mL), and then the organic layer was dried over $Na_2SO_4$. After being concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by $^1$H NMR, $^{13}$C NMR, and GC-MS.

**General Procedure for the Arylation of Pyridine and Pyrazine.** A reflux tube equipped with a magnetic stir bar charged with diaryliodonium salts 0.2 mmol (**2**, 1.0 equiv), *t*-BuONa (1.5 equiv), pyridine or pyrazine (1 mL), and the reaction vessel was placed in a 110 °C oil bath. After stirring at this temperature for 10 h, the mixture was distilled in vacuo to recover the redundant pyridine or pyrazine. The residue was cooled to room temperature, diluted with 20 mL of ethyl acetate, and washed with brine (15 mL) and water (15 mL), and then the organic layer was dried over $Na_2SO_4$. After being concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by $^1$H NMR, $^{13}$C NMR, and GC-MS.

**General Procedure for the Arylation of Benzene.** A reflux tube equipped with a magnetic stir bar charged with diaryliodonium salts 0.2 mmol (**2**, 1.0 equiv), $NaHCO_3$ (1.5 equiv), TMEDA (3 equiv), benzene (1 mL), and the reaction vessel was placed in an 80 °C oil bath. After stirring at this temperature for 10 h, the mixture was distilled in vacuo to recover the redundant benzene. The residue was cooled to room temperature, diluted with 20 mL of ethyl acetate, and washed with brine (15 mL) and water (15 mL), and then the organic layer was dried over $Na_2SO_4$. After being concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by $^1$H NMR, $^{13}$C NMR, and GC-MS.

**Investigation of Radical Scavenger Effect.** Following the general procedure using diphenyliodonium salt (0.2 mmol), 2,2,6,6-tetramethyl-1-piperridinyloxy (free radical, TEMPO, 50 mol % and 100 mol %, respectively), NaOH (1.5 equiv), and pyrrole (1 mL) at 80 °C for 10 h, decreased yields of 17 and less than 3% were obtained, respectively.

Following the general procedure using diphenyliodonium salt (0.2 mmol), 1,1-diphenylethylene (1 equiv), NaOH (1.5 equiv), and pyrrole (1 mL) at 80 °C for 10 h, the product was detected in 19% yield.

**2-Phenyl-1*H*-pyrrole** (**3a**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 78%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.43 (s, 1H), 7.45−7.47 (m, 2H), 7.34−7.39 (m, 2H), 7.18−7.23 (m, 1H), 6.85−6.88 (d, 1H, $J$ = 8 Hz), 6.51−6.54 (m, 1H), 6.29−6.32 (d, 1H, $J$ = 8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 132.8, 132.1, 128.9, 126.2,123.9, 118.9, 110.1, 105.9; MS (EI) $m/z$ (%) 143 ($M^+$, 100), 115 (45).

**2-(4-Chlorophenyl)-1*H*-pyrrole** (**3b**, unknown compound) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 91%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.28 (s, 1H), 7.29−7.26 (d, 2H, $J$ = 8.4 Hz), 7.24−7.21 (d, 2H, $J$ = 8.4 Hz), 6.75 (s, 1H), 6.42 (s, 1H), 6.22−6.20 (d, 1H, $J$ = 2.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 131.7, 131.3, 131.0, 129.1, 125.0, 119.3, 110.3, 106.4; MS (EI) $m/z$ (%) 179 ($M^+$, 35), 177 (100), 142 (9), 115 (43). HRMS (ESI) Calcd for: C10H9ClN, 178.0424. Found: 178.0421.

**2-(4-Bromophenyl)-1*H*-pyrrole** (**3c**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 65%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.44 (s, 1H), 7.49−7.52 (d, 2H, $J$ = 8.4 Hz), 7.34−7.37 (d, 2H, $J$ = 8.4 Hz), 6.85 (s, 1H), 6.51 (s, 1H), 6.30−6.28 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.3, 149.8, 138.3, 136.9, 131.9, 128.5, 123.4, 122.4, 120.3; MS (EI) $m/z$ (%) 223 ($M^+$, 98), 221 (100), 142 (12), 115 (46).

**2-(4-Fluorophenyl)-1*H*-pyrrole** (**3d**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 93%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.35 (s, 1H), 7.40−7.38 (m, 2H), 7.06−7.20 (t, 2H, $J$ = 8.8 Hz), 6.82 (s, 1H), 6.45 (s, 1H), 6.29−6.28 (d, 1H, $J$ = 2.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.7, 160.3, 131.3, 129.2, 129.1, 125.6, 125.5, 118.9, 115.9, 115.7, 110.2, 105.9; MS (EI) $m/z$ (%) 161 ($M^+$, 100), 133 (54).

**2-(*p*-Tolyl)-1*H*-pyrrole** (**3e**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 71%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.43 (s, 1H), 7.39−7.42 (d, 2H, $J$ = 8 Hz), 7.19−7.22 (d, 2H, $J$ = 8 Hz), 6.86−6.87 (d, 1H, $J$ = 1.2 Hz), 6.50−6.52 (m, 1H), 6.31−6.34 (m, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 135.9, 132.3, 130.1, 129.6, 123.9, 118.5, 110.0, 105.4, 21.2; MS (EI) $m/z$ (%) 157 ($M^+$, 100), 128 (11).

**2-(4-Isopropylphenyl)-1*H*-pyrrole** (**3f**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 50%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.30 (s, 1H), 7.31−7.34 (d, 2H, $J$ = 8 Hz), 7.14−7.17 (d, 2H, $J$ = 8.4 Hz), 6.75−6.76 (d, 1H, $J$ = 1.6 Hz), 6.39−6.41 (m, 1H), 6.20−6.22 (d, 1H, $J$ = 3.2 Hz), 2.79−2.87 (m, 1H), 1.17−1.20 (d, 6H, $J$ = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.0, 132.3, 130.5, 127.0, 124.0, 118.4, 110.0, 105.5, 33.8, 24.0; MS (EI) $m/z$ (%) 185 ($M^+$, 66), 170 (100).

**2-(3-Nitrophenyl)-1*H*-pyrrole** (**3g**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a yellow solid (yield 84%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.71 (s, 1H), 8.28 (s, 1H), 8.01−7.99 (m, 1H), 7.78−7.76 (m, 1H), 7.52−7.48 (m, 1H), 6.94 (s, 1H), 6.65 (s, 1H), 6.34−6.33 (d, 1H, $J$ = 2.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.8, 134.4, 129.8, 129.6, 129.5, 120.6, 120.4, 118.0, 110.7, 108.0; MS (EI) $m/z$ (%) 188 ($M^+$, 100), 142 (44), 115 (48).

**Ethyl 3-(1*H*-pyrrol-2-yl)benzoate** (**3h**, unknown compound) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a colorless oil (yield 76%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.72 (s, 1H), 8.13 (s, 1H), 7.87−7.84 (d, 1H, $J$ = 7.6 Hz), 7.68−7.66 (d, 1H, $J$ = 8 Hz), 7.43−7.38 (m, 1H), 6.88 (s, 1H), 6.59 (s, 1H), 6.31−6.30 (d, 1H, $J$ = 2.4 Hz), 4.42−4.36 (q, 2H), 1.42−1.38 (t, 3H, $J$ = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.7, 133.0, 131.1, 131.0, 128.9, 128.2, 127.0, 124.5, 119.5, 110.3, 106.7, 61.2, 14.4. HRMS (ESI) Calcd for: C13H12NO2, 214.0868. Found: 214.0884.

**2-(2-Methyl-5-nitrophenyl)-1*H*-pyrrole** (**3i**, unknown compound) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a yellow solid (yield 83%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (s, 1H), 8.19−8.18 (d, 2H, $J$ = 2 Hz), 7.99−7.96 (m, 1H), 7.39−7.37 (d, 1H, $J$ = 8.4 Hz), 6.95 (s, 1H), 6.45, (s, 1H), 6.37−6.35 (m, 1H), 2.56 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 146.4, 142.6, 134.0, 132.0, 128.8, 122.2, 121.0, 119.5,


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110.5, 109.9, 21.7. HRMS (ESI) Calcd for: C11H9N2O2, 201.0664. Found: 201.0675.

**2-(3,4-Dimethylphenyl)-1*H*-pyrrole** (**3j**, unknown compound) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a pale pink solid (yield 73%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.36 (s, 1H), 7.23−7.18 (m, 2H), 7.12−7.10 (d, 1H, $J$ = 8 Hz), 6.81 (s, 1H), 6.46, (s, 1H), 6.28−6.27 (d, 1H, $J$ = 2.8 Hz), 2.28 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 137.0, 134.6, 132.4, 130.5, 130.1, 125.4, 121.4, 118.3, 109.9, 105.3, 19.9, 19.4; MS (EI) $m/z$ (%) 171 ($M^+$, 100), 156 (29), 143 (17), 128 (24). HRMS (ESI) Calcd for: C12H14N, 172.1126. Found: 172.1129.

**2-(2,4-Dimethylphenyl)-1*H*-pyrrole** (**3k**, known compound, see ref 11) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a colorless oil (yield 73%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 (s, 1H), 7.24−7.22 (d, 1H, $J$ = 7.6 Hz), 7.07 (s, 1H), 7.04−7.01 (d, 1H, $J$ = 7.6 Hz), 6.84−6.83 (d, 1H, $J$ = 2 Hz), 6.30−6.29 (d, 2H, $J$ = 2 Hz), 2.41 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 136.5, 135.0, 131.8, 131.4, 130.1, 128.0, 126.7, 117.6, 109.1, 108.4, 21.1, 21.0; MS (EI) $m/z$ (%) 171 ($M^+$, 100), 156 (27), 143 (17), 128 (22).

**1-Methyl-2-phenyl-1*H*-pyrrole** (**4b**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 10:1), as a colorless oil (yield 69%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 (m, 4H), 7.29−7.31 (m, 1H), 6.70−6.72 (m, 1H), 6.20−6.23 (m, 2H), 3.66 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 134.6, 133.4, 128.7, 128.4, 126.7, 123.6, 108.7, 107.8, 35.1; MS (EI) $m/z$ (%) 157 ($M^+$, 100), 115 (19).

**2-Methyl-5-phenyl-1*H*-pyrrole** (**4c**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a white solid (yield 67%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (s, 1H), 7.40−7.43 (d, 2H, $J$ = 7.6 Hz), 7.30−7.35 (m, 2H), 7.13−7.17 (m, 1H), 6.38−6.41 (m, 1H), 5.94 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 133.0, 130.8, 129.1, 128.8, 125.7, 123.4, 108.0, 106.2, 13.2; MS (EI) $m/z$ (%) 157 ($M^+$, 100), 128 (6).

**3,5-Dimethyl-2-phenyl-1*H*-pyrrole** (**4d**, known compound, see ref 2b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a red solid (yield 53%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (s, 1H), 7.36−7.39 (m, 4H), 7.19−7.21 (m, 1H), 5.82 (s, 1H), 2.29 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 133.9, 128.6, 127.5, 126.7, 125.9, 125.5, 116.5, 110.3, 13.0, 12.5; MS (EI) $m/z$ (%) 170 ($M^+$, 100), 156 (10), 128 (7).

**2-Phenylpyridine** (**4f**, known compound, see ref 12) and **3-phenylpyridine** (**4f′**, known compound, see ref 12) were obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 10:1), both as white solids (yield 52%). **4f**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.70−8.68 (m, 1H), 7.97−8.02 (m, 2H), 7.70−7.77 (m, 2H), 7.39−7.50 (m, 3H), 7.20−7.25 (m, 1H); MS (EI) $m/z$ (%) 155 ($M^+$, 100), 127 (10), 77 (8). **4f′**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.86−8.85 (d, 1H, $J$ = 1.6 Hz), 8.60−8.59 (d, 1H, $J$ = 4.4 Hz), 7.89−7.87 (m, 1H), 7.60−7.58 (d, 2H, $J$ = 7.6 Hz), 7.51−7.46 (m, 2H), 7.43−7.35 (m, 2H); MS (EI) $m/z$ (%)155 ($M^+$, 100), 127 (13).

**2-Phenylpyrazine** (**4g**, known compound, see ref 2c) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane/EtOAc 4:1), as a yellow solid (yield 71%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.03 (s, 1H), 8.63 (s, 1H), 8.50 (s, 1H), 8.03−8.01 (d, 2H, $J$ = 7.6 Hz), 7.54−7.45 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.9, 144.2, 142.9, 142.2, 136.4, 129.9, 129.1, 127.0; MS (EI) $m/z$ (%) 156 ($M^+$, 100), 129 (11), 103 (59), 76 (12).

**1,1′-Biphenyl** (**4h**, known compound, see ref 4b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane), as a white solid (yield 31%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.58−7.61 (d, 4H, $J$ = 8 Hz), 7.41−7.46 (m, 4H), 7.32−7.36 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 128.8, 127.3, 127.2; MS (EI) $m/z$ (%) 154 ($M^+$, 100), 76 (10).

**4-Fluoro-1,1′-biphenyl** (**4i**, known compound, see ref 4b) was obtained following the general procedure, after purification by flash chromatography (*n*-hexane), as a white solid (yield 21%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.56−7.52 (m, 4H), 7.45−7.41 (m, 2H), 7.36−7.32 (m, 1H), 7.14−7.12 (d, 2H, $J$ = 8.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.3, 140.3, 133.1, 128.8, 128.7, 128.6, 127.2, 127.0, 115.7, 115.5; MS (EI) $m/z$ (%) 171 ($M^+$, 100).

**3-Nitro-1,1′-biphenyl** (**4j**, known compound, see ref 2a) was obtained following the general procedure, after purification by flash chromatography *n*-hexane/EtOAc 10:1), as a yellow solid (yield 50%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.45−8.47 (m, 1H), 8.23−8.26 (d, 1H, $J$ = 8.4 Hz), 7,91−7.93 (d, 1H, $J$ = 8 Hz), 7.61−7.65 (m, 3H), 7.41−7.51 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 149.0, 143.0, 138.8, 133.2, 129.8, 128.7, 127.3, 122.2, 122.1; MS (EI) $m/z$ (%) 199 ($M^+$, 100), 152 (89), 76 (9).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Optimization of reaction conditions, reaction mechanism, $^1$H and $^{13}$C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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