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Synthesis and Direct C2 Functionalization of Imidazolium and 1,2,4-Triazolium *N*-Imides

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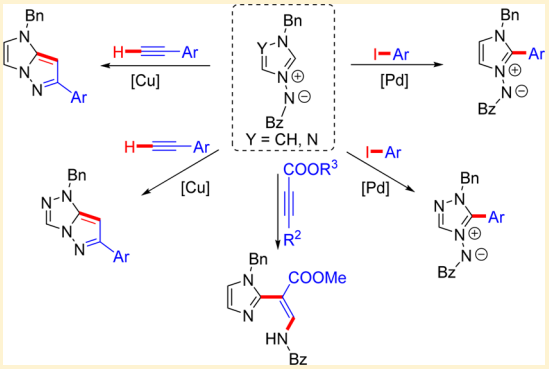
Supporting Information

ABSTRACT: Pd-catalyzed direct C2 arylation and Cu-catalyzed direct one-pot alkynylation/intramolecular cyclization of azolium *N*-imides are reported. Various acetylenes, aryl iodides, and 1-alkyl substituents were examined. The mild protocol allows direct C2 arylation of azolium *N*-imides without the use of specialized reagents together with novel one-pot regioselective preparations of imidazole-pyrazolo and pyrazolo-1,2,4-triazole ring systems. The electronic properties of selected examples were examined by fluorescence spectroscopy.



Imidazole and 1,2,4-triazole moieties occur in many natural products,[1−4] and their derivatives show antifungal,[5] anti-inflammatory,[6] antitubercular,[7] antidepressant,[8] anticancer,[9] antiviral,[10] and neuron-protective activity.[11] Thus, the development of novel synthetic routes to substituted imidazoles and 1,2,4-triazoles are of considerable interest.

Reports of metal-catalyzed carbon−carbon and carbon−heteroatom bond forming reactions have increased substantially in recent years.[12−17] The pharmaceutical industry utilizes various transition-metal-catalyzed cross-coupling reactions among which Suzuki coupling is the most widely employed.[18−20] Such reactions require specialized reagents such as expensive boron derivatives, and the desired products are difficult to isolate.[21,22] Topical interest in cross-coupling reactions motivated the development of several nontraditional methods, such as cross-coupling of organotrifluoroborates[23] or aryltrifluorosilanes[24] with halides or direct C−H functionalization of aromatic[25−34] and heteroaromatic systems.[22,35−37]

Direct C−H functionalization techniques have emerged as viable alternatives to traditional cross-coupling methods because they avoid the use of specialized reagents, reduce the number of synthetic steps, and achieve products in high yield and purity.[14,38−42] Recent reports on direct C2 functionalization of azines and azoles demonstrated their potential in cross-coupling reactions with aromatic halides.[43−47]

Our interest in *N*-substituted heterocycles[48−52] prompted a study that resulted in the discovery of a highly selective C2 functionalization of imidazolium and triazolium *N*-imides. In previous work, we reported a regioselective one-pot synthesis of pyrazolo-1,2,4-triazoles from 1,2,4-triazolium *N*-imides.[49] We now report Pd-catalyzed direct C2 arylation and Cu-catalyzed one-pot C2 alkynylation/intramolecular cyclization of imidazolium and triazolium *N*-imides. This methodology affords high atom economy and provides a novel route to C2-functionalized azolium *N*-imides as well as bicyclic systems such as imidazo-pyrazoles and pyrazolo-1,2,4-triazoles without the use of specialized precursors. Electronic properties of the imidazo-pyrazoles and pyrazolo-1,2,4-triazoles products are also reported.

Imidazolium *N*-imide **2** was prepared from commercially available *N*-benzyl imidazole via a two-step procedure, and 1,2,4-triazolium *N*-imides **4a−c** were prepared by the reaction of 4-amino-1,2,4-triazolium salts **3a−c** with benzoyl chloride (Scheme 1).

Phenyl iodide reacted with imidazolium *N*-imide **2** in the presence of Pd(II) acetate (5 mol %), tricoordinate phosphorus

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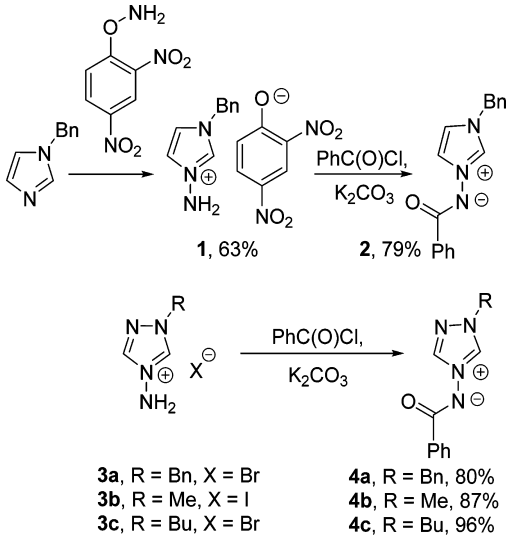
Scheme 1. Synthesis of Imidazolium and 1,2,4-Triazolium *N*-Imides 2, 4a−c



ligand **L1** (15 mol %), and Cs_2CO_3 (2 equiv) at 70 °C to give cross-coupled product **5a** as a single regioisomer with no detectable formation of **5a′** or **5a″**. The use of $Pd(OAc)_2$ as catalyst with ligand **L1** and Cs_2CO_3 in acetonitrile at 70 °C was found to be optimal (Table 1). Reactions in toluene gave no detectable products, and ligands **L2** and **L3** with $Pd(OAc)_2$ in CH_3CN also failed. Under optimum conditions, however, electron donating or withdrawing groups in the aryl iodides gave similar yields of **5a−g** (Table 2).

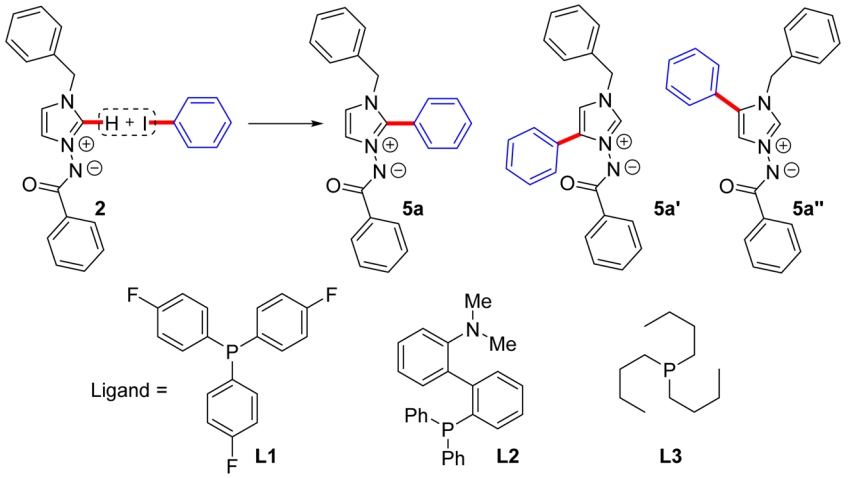
Analogous reactions were achieved with imidazolium or 1,2,4-triazolium *N*-imides to generate cross-coupling products **5a−g**, and the structures of **5a** and **5c** were confirmed by X-ray crystallography (see the Supporting Information).

Reaction of *N*-imides **2** and **4a** with aryl acetylenes in the presence of copper(I) bromide led to a one-pot C2 alkynylation/intramolecular cyclization, affording the corresponding imidazolo-pyrazoles **6a−f** and pyrazolo-1,2,4-triazoles **6g−i** in 60−83 and 63−75% yields, respectively (Table 3). The reaction tolerates a range of aryl acetylenes and is a novel, regioselective pathway for the synthesis of imidazo/triazolo-pyrazole bicyclic systems (Table 3).

Attempts to use methyl propiolate for the synthesis of imidazo-pyrazoles resulted in the formation of ring-opened products **7** both in the presence and absence of Cu catalyst, possibly by a [3 + 2] dipolar cycloaddition−elimination tandem sequence[46] (Scheme 2). The structure of **7** was also confirmed by X-ray crystallography (see the Supporting Information).

The electronic nature of imidazolo-pyrazoles **6a−f** and pyrazolo-1,2,4-triazoles **6g−i** together with previously prepared pyrazolo-1,2,4-triazole systems **6j−o**[49] (see the Supporting

Table 1. Optimization of Reaction Conditions



entry	catalyst/ligand	*t* °C/time (h)	solvent	**5a**/**5a′**/**5a″** (%)
1[a]	$Pd(OAc)_2$/**L1**	70/24	CH_3CN	70/0/0
2[b]	$Pd(OAc)_2$/**L1**	70/24	CH_3CN	40/0/0
3	$Pd(OAc)_2$/**L1**	23/24	CH_3CN	<5/0/0
4	$Pd(OAc)_2$/**L1**	70/12	CH_3CN	28/0/0
5	$Pd(OAc)_2$/-	70/24	CH_3CN	<5/0/0
6	$Pd(OAc)_2$/**L3**	70/24	CH_3CN	0/0/0
7[b]	$Pd(OAc)_2$/**L3**	70/24	CH_3CN	0/0/0
8	$Pd(OAc)_2$/**L2**	70/24	CH_3CN	0/0/0
9	$Pd(PPh_3)_4$/**L1**	70/24	CH_3CN	15/0/0
10	$Pd(PPh_3)_4$/**L2**	70/24	CH_3CN	0/0/0
11	$Pd(PPh_3)_4$/**L3**	70/24	CH_3CN	0/0/0
12	$Pd(PPh_3)_2Cl_2$/**L1**	70/24	CH_3CN	10/0/0
13	$Pd(OAc)_2$/**L1**	120/24	toluene	0/0/0
14	$Pd(OAc)_2$/**L2**	120/24	toluene	0/0/0
15	$Pd(OAc)_2$/**L3**	120/24	toluene	0/0/0

[a]Optimized conditions. [b]K_2CO_3 (2 equiv) as base.

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Table 2. Direct C2 Arylation of Azolium *N*-Imides 2 and 4a

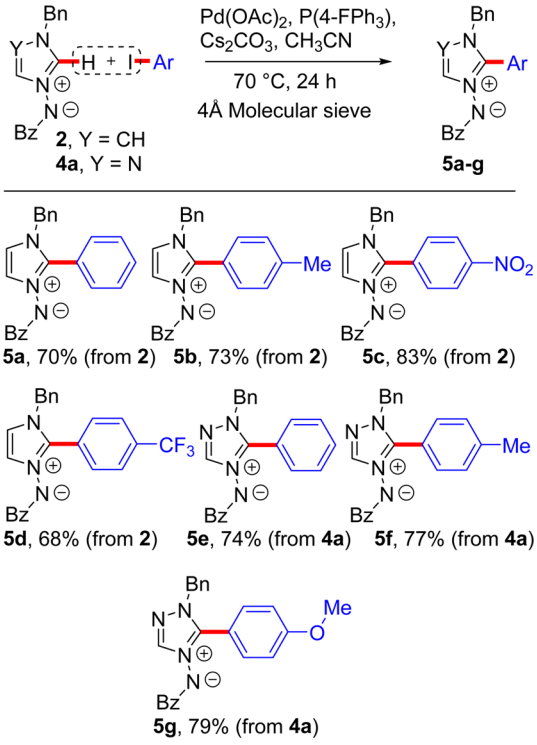
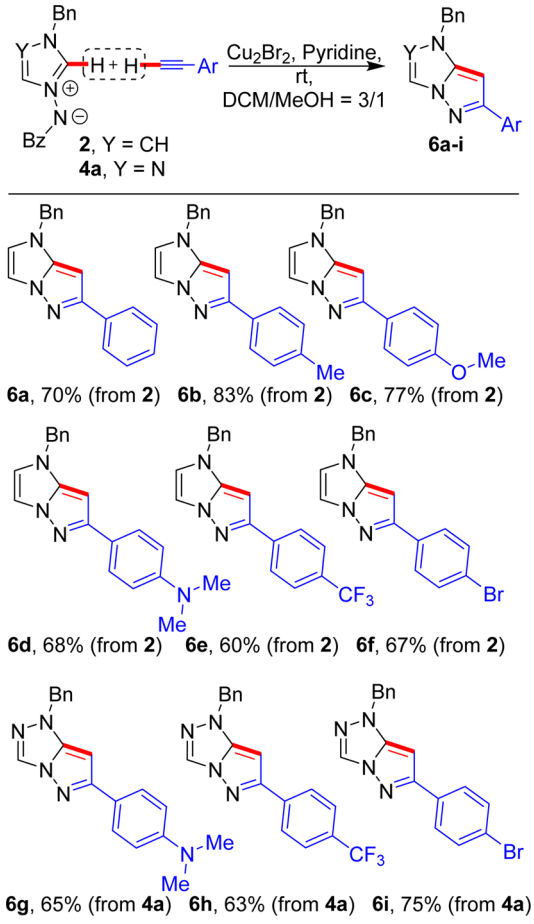
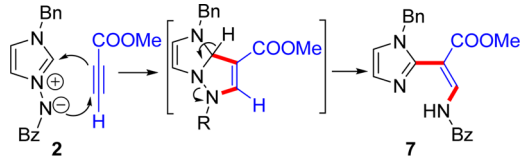


Table 3. Cu(I)-Catalyzed One-Pot Regioselective C2 Alkynylation/Intramolecular Cyclization of 2 and 4a



Scheme 2. Reaction of Imidazolium *N*-Imides 2 with Methyl Propiolate



Information for details) was examined by fluorescence spectroscopy. Absorption and emission spectra were recorded in dichloromethane, and quantum yields were calculated with respect to 2-aminopyridine in a 0.1 N aqueous H_2SO_4. Both the imidazolo-pyrazole and the pyrazolo-1,2,4-triazole series were found to be active with **6a** and **6j** showing the highest quantum yields of 0.68 and 0.58, respectively (see the Supporting Information for details).

In conclusion, we have developed an efficient protocol for the Pd-catalyzed direct C2 arylation and Cu-catalyzed one-pot C2 alkynylation/intramolecular cyclization of imidazolium and 1,2,4-triazolium *N*-imides as a mild alternative to traditional cross-coupling reactions.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were carried out in single-neck round-bottom flasks under a positive pressure of nitrogen unless otherwise noted. Reaction progress was monitored by thin-layer chromatography (TLC) and visualized by UV light. Solvents were freshly distilled. Melting points were determined on a capillary point apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with TMS for ^{1}H (300 MHz) and ^{13}C (75 MHz) as an internal reference. Elemental analysis was performed on a CarloErba-1106 instrument.

3-Amino-1-benzyl-1*H*-imidazol-3-ium 2,4-Dinitrophenolate (1). A mixture of *N*-benzyl imidazole (3 g, 18.96 mmol) and *O*-(2,4-dinitrophenyl)hydroxylamine (5.66 g, 28.44 mmol) in EtOH/CH_2Cl_2 (3:1, 200 mL) was heated under reflux for 24 h. The reaction mixture was concentrated under vacuum to dryness and treated with an EtOH/Et_2O mixture to give 3-amino-1-benzyl-1*H*-imidazol-3-ium 2,4-dinitrophenolate **1** as yellow microcrystals in 63% yield: mp 119−120 °C. ^{1}H NMR (DMSO-d_6) δ 9.32 (s, 1H), 8.61 (d, J = 3.0 Hz, 1H), 7.81 (dd, J = 9.8, 3.2 Hz, 1H), 7.75 (t, J = 2 0.1, 1.8 Hz, 1H), 7.66 (t, J = 2.1, 1.8 Hz, 1H), 7.43−7.34 (m, 5H), 6.90 (s, 2H), 6.37 (d, J = 9.6 Hz, 1H), 5.38 (s, 2H); ^{13} C NMR (DMSO-d_6) δ 169.6, 136.0, 135.3, 134.9, 128.9, 128.6, 128.1, 127.5, 126.1, 124.8, 124.1, 120.9, 52.0; HRMS (+ESI-TOF) m/z for $C_{10}H_{12}N_3$ $[M]^+$ calcd. 174.1026, found 174.1025.

Benzoyl(3-benzyl-1*H*-imidazol-3-ium-1-yl)amide (2). A solution of **2** (6.0 g, 16.79 mmol) in PhC(O)Cl (40 mL) was heated at 90 °C for 12 h. The reaction mixture was concentrated under vacuum at 60 °C, and the crude residue was triturated with a mixture of anhydrous Et_2O/Hexane (1:1, 20 mL) and dried under vacuum. The residue was treated with K_2CO_3 (2.4 equiv) in CH_2Cl_2 (40 mL) for 45 min at room temperature, and the solid was removed by filtration. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography (CH_2Cl_2/CH_3OH 94:6) to give pure benzoyl(1-benzyl-1*H*-imidazol-3-ium-3-yl)amide **2** (3.7 g, 13.3 mmol) in 79% yield as an off-white solid, mp 167−168 °C. ^{1}H NMR (DMSO-d_6) δ 9.98 (s, 1H), 7.99 (d, J = 5.7, 3.3 Hz, 2H), 7.68 (s, 1H), 7.62 (s, 1H), 7.53−7.23 (m, 8H), 5.37 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 167.2, 138.7, 135.7, 132.4, 128.8, 128.3, 127.9, 127.3, 127.2, 121.9, 118.2, 51.5. HRMS (+ESI-TOF) m/z for $C_{17}H_{16}N_3O$ $[M + H]^+$ calcd. 278.1288, found 278.1289.

General Method for the Synthesis of 1,2,4-Triazolium Salts 3a−c. Compounds **3a−c** were prepared previously by our group.[46]

General Method for the Synthesis of 1,2,4-Triazolium *N*-Imides 4a−c. A mixture of 1,2,4-triazolium halide **3a−c** (5.87 mmol)

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in PhC(O)Cl (7 mL) was heated at 90 °C for 12 h. The mixture was concentrated under vacuum at 60 °C, and the residue was triturated with anhydrous Et_2O and filtered. A solution of the solid in CH_2Cl_2 (7 mL) was treated with K_2CO_3 (2.7 equiv), and the mixture was stirred at room temperature for 30 min. The solid was removed by filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by flash silica gel column chromatography (DCM/MeOH, 96:4) to give ylids **4a–c**.

*Benzoyl(1-benzyl-4H-1,2,4-triazol-1-ium-4-yl)amide (**4a**).* White microcrystals (80%), mp 169–170 °C. ^{1}H NMR (DMSO-d_6) δ 10.98 (d, J = 2.7 Hz, 1H), 9.70 (s, 1H), 8.06 (dd, J = 8.4, 1.2 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.8, 7.5 Hz, 1H), 7.64–7.30 (m, 6H), 5.79 (s, 2H) ^{13} C NMR (DMSO-d_6) δ 165.8, 145.7, 143.9, 133.6, 132.8, 129.7, 129.2, 129.1, 128.2, 55.6; Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.74; H, 4.90; N, 20.17.

*Benzoyl(1-methyl-1H-1,2,4-triazol-4-ium-4-yl)amide (**4b**).* White microcrystals (87%), mp 196–197 °C (lit.[53] mp 192.0–194.0 °C). ^{1}H NMR (DMSO-d_6) δ 10.53 (s, 1H), 9.17 (s, 1H), 8.03–7.94 (m, 2H), 7.43–7.30 (m, 3H), 4.02 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 168.6, 143.1, 140.3, 138.2, 129.9, 128.0, 127.8, 38.8.

*Benzoyl(1-butyl-1H-1,2,4-triazol-4-ium-4-yl)amide (**4c**).* White microcrystals (96%), mp 143–144 °C. ^{1}H NMR (DMSO-d_6) δ 10.90 (s, 1H), 9.68 (s, 1H), 8.13 (d, J = 7.0 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.5 Hz, 2H), 4.50 (t, J = 2H), 1.95–1.84 (m, 2H), 1.38–1.24 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (DMSO-d_6) δ 165.7, 145.3, 143.6, 133.4, 129.7, 128.8, 128.2, 52.1, 29.7, 18.6, 13.1; HRMS (+ESI-TOF) m/z for $C_{13}H_{17}N_4O$ $[M + H]^+$ calcd. 245.1397 found 245.1401.

General Procedure for Direct C2 Arylation of Imidazolium and 1,2,4-Triazolium *N*-Imide. Imidazolium or triazolium *N*-imides **2**, **4a** (1 mmol), Cs_2CO_3 (2 mmol), $Pd(OAc)_2$ (0.05 mmol), P(4-F-C_6H_5)$_3$ (0.15 mmol), and 4 Å molecular sieve were placed in an oven-dried Schlenk flask. The aryl iodide (1 mmol) and freshly distilled MeCN (to produce a reaction concentration of 0.3 M in aryl iodide) were added, and the flask was backfilled three times with argon. The reaction mixture was then stirred at 70 °C until the reaction was complete, after which it was dissolved in 10% MeOH/DCM and filtered on a pad of Celite. The reaction mixture was concentrated under reduced pressure, and the residue was purified via silica gel column chromatography using EtOAc/hexanes (1:5) as eluent to afford pure cross-coupling products **5a–g**.

*Benzoyl(1-benzyl-2-phenyl-1H-imidazol-3-ium-3-yl)amide (**5a**).* White microcrystals (247 mg, 70%), mp 214–215 °C. ^{1}H NMR ($CDCl_3$) δ 8.00 (dd, J = 7.4, 2.0 Hz, 2H), 7.75 (d, J = 1.8 Hz, 1H), 7.63–7.60 (m, 2H), 7.52–7.28 (m, 9H), 7.15–7.08 (m, 2H), 7.04 (d, J = 2.1 Hz, 1H), 5.17 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 172.3, 141.3, 137.9, 133.8, 131.4, 130.3, 129.4, 129.0, 128.8, 127.9, 127.5, 127.2, 124.4, 122.4, 117.9, 51.9.

*Benzoyl(1-benzyl-2-(p-tolyl)-1H-imidazol-3-ium-3-yl)amide (**5b**).* White microcrystal (268 mg, 73%), mp 178–179 °C. ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 7.1 Hz, 2H), 7.70 (s, 1H), 7.50 (d, J = 7.8 Hz, 2H), 7.40–7.22 (m, 8H), 7.14–7.11 (m, 2H), 7.01 (s, 1H), 5.16 (s, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 172.2, 141.9, 141.5, 138.1, 134.1, 130.2, 129.6, 129.4, 129.0, 128.0, 127.6, 127.2, 124.3, 119.5, 118.0, 51.9, 21.7. HRMS (+ESI-TOF) m/z for $C_{24}H_{22}N_3O$ $[M + H]^+$ calcd. 368.1757, found 368.1775.

*Benzoyl(1-benzyl-2-(4-nitrophenyl)-1H-imidazol-3-ium-3-yl)-amide (**5c**).* Yellow microcrystal (330 mg, 83%), mp 197–198 °C. ^{1}H NMR ($CDCl_3$) δ 8.31 (dd, J = 8.7, 1.8 Hz, 2H), 7.96 (dd, J = 8.1, 1.8 Hz, 1H), 7.89–7.80 (m, 3H), 7.44–7.24 (m, 6H), 7.16 (d, J = 2.1 Hz, 1H), 7.14–7.05 (m, 2H), 5.21 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 171.9, 149.1, 138.9, 137.2, 133.1, 131.7, 129.8, 129.5, 129.3, 128.6, 127.7, 127.0, 124.7, 123.8, 119.3, 52.4; Anal. Calcd For $C_{23}H_{18}N_4O_3$: C, 69.34; H, 4.55; N, 14.06. Found: C, 69.12; H, 4.46; N, 14.25.

*Benzoyl(1-benzyl-2-(4-(trifluoromethyl)phenyl)-1H-imidazol-3-ium-3-yl)amide (**5d**).* White microcrystals (286 mg, 68%), mp 170–171 °C. ^{1}H NMR ($CDCl_3$) δ 7.99 (dd, J = 7.8, 1.8 Hz, 2H), 7.81 (d, J = 2.1 Hz, 1H), 7.79–7.70 (m, 4H), 7.43–7.28 (m, 6H), 7.14–7.07 (m, 3H), 5.18 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 172.3, 139.8, 137.7, 133.5, 133.1, 131.1, 129.8, 129.7, 129.4, 128.0, 127.8, 127.2, 126.2, 126.0, 125.9, 125.3, 124.8, 121.7, 118.9, 52.3; Anal. Calcd For $C_{24}H_{18}F_3N_3O$: C, 68.40; H, 4.31; N, 9.97. Found: C, 68.09; H, 3.97; N, 9.83.

*Benzoyl(1-benzyl-5-phenyl-1H-1,2,4-triazol-4-ium-4-yl)amide (**5e**).* White microcrystals (262 mg, 74%), mp 158–159 °C. ^{1}H NMR ($CDCl_3$) δ 9.28, 8.01 (d, J = 6.8 Hz, 2H), 7.65–7.48 (m, 4H), 7.39–7.27 (m, 5H), 7.19–7.12 (m, 2H), 5.38 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 171.5, 147.2, 144.6, 137.4, 133.3, 132.6, 130.2, 129.8, 129.3, 129.2, 128.0, 127.7, 127.5, 120.4, 54.7; HRMS (+ESI-TOF) m/z for $C_{22}H_{19}N_4O$ $[M + H]^+$ calcd. 355.1553, found 355.1569.

*Benzoyl(1-benzyl-5-(p-tolyl)-1H-1,2,4-triazol-4-ium-4-yl)amide (**5f**).* White microcrystal (283 mg, 77%), mp 185–186 °C. ^{1}H NMR ($CDCl_3$) δ 9.21 (s, 1H), 8.02 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.39–7.15 (m, 10H), 5.42 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.6, 147.6, 144.6, 143.5, 137.5, 133.5, 130.1, 130.0, 130.0, 129.4, 129.2, 128.0, 127.8, 127.5, 117.4, 54.7, 21.9; HRMS (+ESI-TOF) m/z for $C_{23}H_{21}N_4O$ $[M + H]^+$ calcd. 369.1710, found 369.1707.

*Benzoyl(1-benzyl-5-(4-methoxyphenyl)-1H-1,2,4-triazol-4-ium-4-yl)amide (**5g**).* White microcrystals (303 mg, 79%), mp 184–185 °C. ^{1}H NMR ($CDCl_3$) δ 9.20 (s, 1H), 8.04 (d, J = 6.0 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.45–7.25 (m, 6H), 7.23–7.13 (m, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.39 (s, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.5, 162.8, 147.3, 144.5, 137.5, 133.5, 132.0, 129.8, 129.3, 129.1, 128.0, 127.7, 127.4, 114.7, 112.0, 55.6, 54.6; Anal. Calcd For $C_{23}H_{20}N_4O_2$: C, 71.86; H, 5.24; N,14.57. Found: C, 71.77; H, 5.14; N, 14.79.

General Procedure for the Preparation of Imidazolo-pyrazoles 6a–f and Pyrazolo-1,2,4-triazoles 6g-i. Copper(I) bromide (5 mol %) was added to a mixture of the corresponding *N*-imide **2** or **4a** (1 mmol), aryl acetylene (1 mmol), and pyridine (2 mmol) in dichloromethane (3 mL), and the mixture was stirred at rt under an air atmosphere until completion. Solvent was removed under reduced pressure, and the residue was purified by silica-gel column chromatography using DCM/EtOAc (95:5) as eluent to afford the corresponding imidazole-pyrazoles **6a–f** and pyrazolo-1,2,4-triazoles **6g–i**.

*1-Benzyl-6-phenyl-1H-imidazo[1,2-b]pyrazole (**6a**).* White microcrystals (191 mg, 70%), mp 70–71 °C. ^{1}H NMR ($CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 2H), 7.41–7.32 (m, 6H), 7.31–2.24 (m, 4H), 6.72 (d, J = 2.4 Hz, 1H), 5.84 (s, 1H), 5.06 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 155.1, 143.1, 135.4, 134.6, 128.9, 128.5, 128.3, 127.5, 127.4, 125.6, 119.3, 108.1, 76.3, 51.8; HRMS (+ESI-TOF) m/z for $C_{18}H_{16}N_3$ $[M + H]^+$ calcd. 274.1339, found 274.1345.

*1-Benzyl-6-(p-tolyl)-1H-imidazo[1,2-b]pyrazole (**6b**).* White microcrystal (238 mg, 83%), mp 186–187 °C. ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H), 7.39–7.16 (m, 9H), 6.69 (s, 1H), 5.81 (s, 1H), 5.05 (s, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 155.4, 143.4, 137.3, 135.6, 133.0, 132.0, 129.4, 129.1, 128.5, 127.7, 125.7, 119.3, 108.3, 76.3, 51.9, 21.5; Anal. Calcd For $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.40; H, 6.07; N, 14.60.

*1-Benzyl-6-(4-methoxyphenyl)-1H-imidazo[1,2-b]pyrazole (**6c**).* White microcrystal (233 mg, 77%), mp 141.0–142.0 °C. ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 8.7 Hz, 2H), 7.41–7.22 (m, 6H), 6.91 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 2.1 Hz, 1H), 5.75 (s, 1H), 5.03 (s, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.3, 155.1, 143.4, 135.6, 129.1, 128.5, 127.7, 127.0, 119.2, 114.0, 108.2, 75.9, 55.4, 51.9; HRMS (+ESI-TOF) m/z for $C_{19}H_{18}N_3O$ $[M + H]^+$ calcd. 304.1444, found 304.1441.

*4-(1-Benzyl-1H-imidazo[1,2-b]pyrazol-6-yl)-N,N-dimethylaniline (**6d**).* Gray microcrystal (215 mg, 68%), mp 175.0–176.0 °C. ^{1}H NMR ($CDCl_3$) δ 7.69 (d, J = 9.0 Hz, 2H), 7.39–7.29 (m, 5H), 6.75 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 2.4 Hz, 1H), 5.74 (s, 1H), 5.04 (s, 2H), 2.97 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 155.8, 150.3, 135.8, 129.1, 128.5, 127.7, 126.8, 123.4, 118.9, 112.7, 108.4, 75.5, 51.9, 40.8; Anal. Calcd For $C_{20}H_{20}N_4$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.26; H, 6.07; N, 17.32.

*1-Benzyl-6-(4-(trifluoromethyl)phenyl)-1H-imidazo[1,2-b]-pyrazole (**6e**).* White microcrystal (204 mg, 60%), mp 83–84 °C. ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.45–7.31 (m, 5H), 7.28–7.3 (m, 2H), 7.72 (d, J = 1.5 Hz, 1H), 7.75 (s, 1H), 5.03 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 152.8, 142.6, 135.5, 134.4, 132.6, 131.5, 129.1, 128.6, 128.1, 127.9, 127.8, 126.3, 126.2, 122.6,

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119.4, 108.2, 80.6, 51.9; Anal. Calcd For $C_{19}H_{14}F_3N_3$: C, 66.86; H, 4.13; N, 12.31. Found: C, 66.64; H, 3.96; N, 11.99.

*1-Benzyl-6-(4-bromophenyl)-1H-imidazo[1,2-b]pyrazole (**6f**).* White microcrystals (235 mg, 67%), mp 181−182 °C. ^{1}H NMR ($CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.39−7.32 (m, 4H), 7.27−7.22 (m, 2H), 6.72 (d, J = 1.5 Hz, 1H), 5.80 (s, 1H), 5.04 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 154.0, 143.3, 135.4, 133.8, 131.7, 129.2, 128.6, 127.7, 127.4, 121.5, 119.8, 108.3, 76.6, 52.0; Anal. Calcd For $C_{18}H_{14}BrN_3$: C, 61.38; H, 4.01; N, 11.93. Found: C, 61.04; H, 3.76; N, 11.73.

*4-(1-Benzyl-1H-pyrazolo[5,1-c][1,2,4]triazol-6-yl)-N,N-dimethylaniline (**6g**).* White microcrystal (216 mg, 68%), mp 180−181 °C. ^{1}H NMR ($CDCl_3$) δ 8.21 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.40−7.30 (m, 5H), 7.73 (d, J = 8.4 Hz, 2H), 5.61 (s, 1H), 5.26 (s, 2H), 2.98 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.7, 134.6, 128.9, 128.5, 128.1, 127.9, 127.0, 121.6, 112.1, 74.1, 54.4, 40.4; HRMS (+ESI-TOF) m/z for $C_{19}H_{20}N_5$ $[M + H]^+$ calcd. 318.1713, found 318.1723.

*1-Benzyl-6-(4-(trifluoromethyl)phenyl)-1H-pyrazolo[5,1-c][1,2,4]-triazole (**6h**).* White microcrystal (233 mg, 63%), mp 86.0−87.0 °C. ^{1}H NMR ($CDCl_3$) δ 8.27 (s, Hz, 2H), 7.74 (d, J = 7.5 Hz, 1H), 6.64 (d, J = 7.2 Hz, 1H), 5.56 (t, J = 7.5 and 6.9 Hz, 1H), 7.47 (t, J = 7.8 and 7.5 Hz, 1H), 7.39−7.34 (s, 5H), 5.89 (s, 1H), 5.29 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 158.2, 146.7, 134.6, 133.4, 132.5, 131.7, 129.1, 128.8, 128.6, 128.0, 126.4, 126.3, 126.0, 122.4, 79.4, 54.8; Anal. Calcd For $C_{18}H_{13}F_3N_4$: C, 63.15; H, 3.83; N, 16.37. Found: C, 62.79; H, 3.58; N, 16.54.

*1-Benzyl-6-(4-bromophenyl)-1H-pyrazolo[5,1-c][1,2,4]triazole (**6i**).* White microcrystal (264 mg, 75%), mp 152−153 °C. ^{1}H NMR ($CDCl_3$) δ ^{1}H NMR ($CDCl_3$) δ 8.24 (s, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.45−7.28 (m, 5H), 5.66 (s, 1H), 5.29 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 158.9, 147.2, 134.3, 132.7, 131.7, 129.0, 128.7, 128.2, 127.9, 127.6, 122.5, 75.1, 54.5; HRMS (+ESI-TOF) m/z for $C_{17}H_{14}N_4Br$ $[M + H]^+$ calcd. 353.0396, found 353.0403.

*(E)-Methyl 3-Benzamido-2-(1-benzyl-1H-imidazol-2-yl)acrylate (**7**).* Methyl propiolate (0.17 g, 2.00 mmol) was added dropwise to a solution of imidazolium *N*-imide **3a** (0.55 g, 2.00 mmol) in DCM (5 mL), and the mixture was stirred for 24 h under reflux. The reaction mixture was concentrated under reduced pressure to afford pure (*E*)-methyl 3-benzamido-2-(1-benzyl-1*H*-imidazol-2-yl)acrylate **7** as white microcrystals (0.67g, 93%), mp 135−136 °C. ^{1}H NMR ($CDCl_3$) δ 79 (d, J = 11.0 Hz, 1H), 8.53 (d, J = 11.1 Hz, 1H), 7.97−7.92 (m, 2H), 7.62−7.46 (m, 3H), 7.32−7.25 (m, 3H), 7.22 (d, J = 1.2 Hz, 1H), 7.12−7.07 (m, 2H), 6.90 (d, J = 1.2 Hz, 1H), 5.13 (s, 2H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.5, 164.8, 142.5, 139.0, 136.4, 133.1, 132.4, 129.1, 129.0, 128.3, 128.1, 127.7, 121.6, 103.2, 52.1, 51.7.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C spectra for **1**, **2**, **4a−c**, **5a−g**, **6a−i**, and **7**. X-ray structures of **5a**, **5c** and **7** and emission spectra and quantum yields for **6a−6o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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