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Copper-Catalyzed Direct Aryl Quaternization of *N*-Substituted Imidazoles to Form Imidazolium Salts

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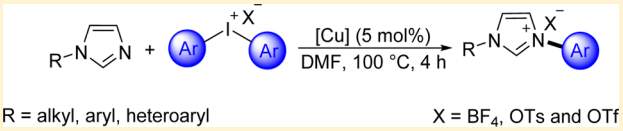
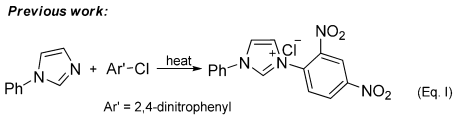
Supporting Information

ABSTRACT: Diaryliodonium salts are employed to directly quaternize *N*-substituted imidazoles by using a copper catalyst to construct aryl imidazolium salts in moderate to excellent yields. This transformation is tolerant to a broad range of functional groups and provides a straightforward, efficient, and versatile route to synthesize aryl imidazolium as well as triazolium salts, especially the unsymmetric version.

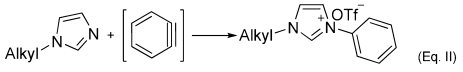


In the presence of a base, primary and secondary amines are readily arylated by aryl halides using a palladium or copper catalyst.[1] However, *N*-heteroarenes with no N−H such as *N*-substituted imidazoles and triazoles etc. are generally hard to be directly arylated, i.e., quaternized to furnish imidazolium and triazolium salts by using aryl halides, except strongly electron-deficient ones such as 2,4-dinitrochlorobenzene (Eq. I).[2] These

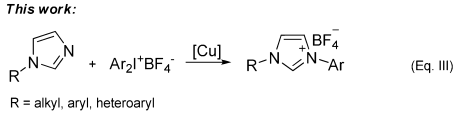


compounds now are prevalently synthesized using multistep ring closing methods.[3] A general methodology of direct aryl quaternization is still absent and even considered as "mission impossible" with aryl halides.[4] Nevertheless, these aryl onium salts are important precursors of *N*-heterocyclic carbenes[5] (NHCs) and cationic functional materials.[6] Particularly attractive is the recent spurt of interesting asymmetric catalyzes by the chiral NHCs derived from unsymmetric arylated imidazolium and triazolium salts.[7,8] These prominent applications make us reconsider the possibility of direct aryl quaternization strategy by using other arylating reagents.

In 2002, Yoshida and Kunai et al. succeeded in the direct aryl quaternization of *N*-alkylimidzoles in moderate yields using arynes but *N*-arylimidazoles were not applicable (Eq. II).[9] We



envisaged that a more electrophilic reagent instead of aryl halides might overcome the weak nucleophilicity of *N*-substituted imidazoles and eventually lead to the formation of arylated imidazolium salts. Diaryliodonium salts, known for its "hyperleaving group ability"[10] of the aryliodanyl group (ArI), are prominent reagents for arylations. Chen's group[11a] and Kang's groups[11b] have previously reported that diaryliodonium salts could arylate imidazole to form *N*-arylimidazoles by using $Co(OAc)_2$ and $Cu(acac)_2$ as the catalysts in the presence of potassium carbonate (K_2CO_3) under mild conditions, respectively. Herein, we wish to report that diaryliodonium salts could further aryl-quaternize *N*-substituted imidazoles by using a copper catalyst (Eq. III).



We started with the quaternization of *N*-phenylimidazole **1a** with diphenyliodonium tetrafluoroborate salt (Ph_2IBF_4, **2a**) by screening a range of metal salts as the catalyst in DMF at 100 °C (Table 1). To our delight, all copper salts catalyzed the aryl quaternization of **1a** efficiently, while other metal salts showed no activity (Table 1, entries 1−8). Considering the cost of the catalyst and the ease of handling, $Cu(OAc)_2{\cdot}H_2O$ was chosen as the catalyst. Without the copper catalyst, the quaternization did not occur (Table 1, entry 9). The reactions in DMSO, toluene, or dioxane resulted in lower yields than in DMF (Table 1, entries 5 and 10−12). The counteranion effect investigation showed that the reaction did not take place when using **2a** associated with halide anions such as chloride and bromide, whereas high yields were obtained when using **2a** with the non-nucleophilic anions (Table 1, entries 13−16). Using 1.0 equiv of **2a** resulted in a diminished yield of 57% due to the thermolysis of **2a** (Table 1, entry 17). Finally, the best conditions were to use 1.5 equiv of $\mathbf{2a}{\cdot}BF_4$ in the presence of 5 mol % $Cu(OAc)_2{\cdot}H_2O$ as the catalyst in DMF at 100 °C for 4 h, under which diphenylimidazolium salt **3a** was obtained in 97% isolated yield (Table 1, entry 5).

With the optimized conditions in hand, we tried to use **2a** to quaternize various *N*-substituted imidazoles to synthesize a range of unsymmetric *N*,*N*′-diaylated imidazolium compounds

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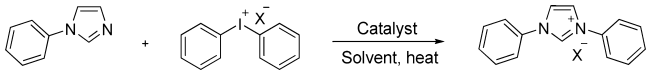
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

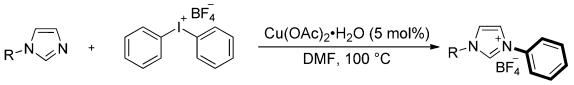
entry	2a	catalyst	solvent	yield (%)[b]
1	Ph_2IBF_4	$CuBr_2$	DMF	86
2	Ph_2IBF_4	$CuCl_2·2H_2O$	DMF	94
3	Ph_2IBF_4	$Cu(OTf)_2$	DMF	96
4	Ph_2IBF_4	CuCl	DMF	97
5	Ph_2IBF_4	$Cu(OAc)_2·H_2O$	DMF	97
6	Ph_2IBF_4	$Pd(OAc)_2$	DMF	0
7	Ph_2IBF_4	$Ni(OAc)_2$	DMF	0
8	Ph_2IBF_4	$Co(OAc)_2$	DMF	0
9	Ph_2IBF_4		DMF	0
10	Ph_2IBF_4	$Cu(OAc)_2·H_2O$	DMSO	91
11	Ph_2IBF_4	$Cu(OAc)_2·H_2O$	toluene	91
12	Ph_2IBF_4	$Cu(OAc)_2·H_2O$	dioxane	83
13	Ph_2ICl	$Cu(OAc)_2·H_2O$	DMF	0
14	Ph_2IBr	$Cu(OAc)_2·H_2O$	DMF	0
15	Ph_2IOTs	$Cu(OAc)_2·H_2O$	DMF	92
16	Ph_2IOTf	$Cu(OAc)_2·H_2O$	DMF	68
17	Ph_2IBF_4	$Cu(OAc)_2·H_2O$	DMF	57[c]

[a]General conditions: **1a** (0.25 mmol), **2a** (0.375 mmol), and $Cu(OAc)_2·H_2O$ (5 mol %) were stirred in a solvent (1 mL) at 100 °C for 4 h. [b]Isolated yields. [c]**2a** (0.25 mmol).

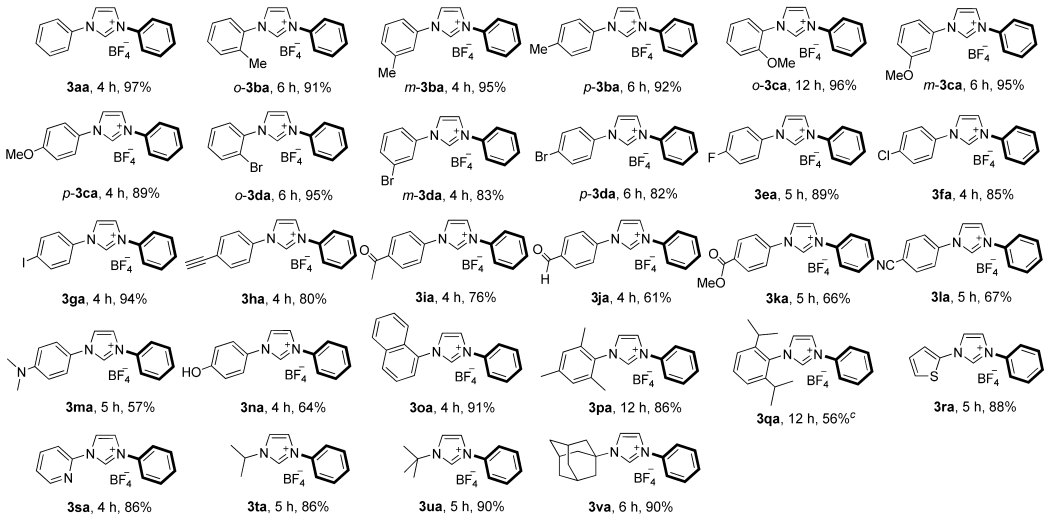
3, and the results are summarized in Table 2. *N*-Phenylimidazoles bearing common substituents on the phenyl ring such as methyl, methoxy, and bromide at the *ortho*-, *meta*-, and *para*-positions all gave very good yields (Table 2, *o*-**3ba**−*p*-**3da**). There was no significant difference in the reactions of the *N*-phenylimidazoles bearing different halide substitutents (Table 2, *p*-**3da**−**3ga**). Other functional groups such as alkynyl, acetyl, formyl, ester, cyano, *N*,*N*-dimethylamino, and hydroxyl groups were all intact under the reaction conditions and the corresponding imidazolium salts were obtained in moderate to high yields (Table 2, **3ha**−**3na**). The bulky 1-naphthylimidazole was quaternized smoothly in 4 h to give the corresponding imidazolium salt **3oa** in 91% yield. The more bulky meistylimidazole could also give rise to a good yield of 86%, but longer reaction time was required. Further increasing the steric hindrance of the phenylimidazole by introducing two isopropyl groups at the C2 and C6 positions on the phenyl ring resulted in a decreased yield of 56% (Table 2, **3pa** and **3qa**). These results indicated that this reaction is sensitive to the steric hindrance effect. Notably, *N*-heteroarylimidazoles were exclusively quaternized to afford the corresponding imidazolium salts. For example, *N*-(2-thienyl)-imidazole was successfully converted to the corresponding imidazolium salt **3ra** in 88% yield and the C/S-arylation of the thienyl ring was not observed.[12] **2a** selectively quaternized the imidazole ring of *N*-(2-pyridyl)-imidazole rather than the pyridine ring to afford the corresponding imidazolium salt **3sa** in 86% yield. Finally, **2a** was used to furnish a few *N*-*sec*- and -*tert*-alkylphenylimidazolium salts, which are difficult to synthesize through quaternization of phenylimidazole with *sec*- and -*tert*-alkyl halides.[4,9] Isopropyl, *t*-butyl, and 1-adamantanyl substituted imidazoles all gave the corresponding alkylphenylimidazolium salts in good yields (Table 2, **3ta**−**3va**). To the best of our knowledge, this is the first direct aryl quaternization method for both *N*-aryl and *N*-alkyl imidazoles.

By using substituted diaryliodonium salts **2**, a variety of symmetric diarylimidazolium compounds **3** were obtained, as shown in Table 3. The di-*o*-, -*m*-, and -*p*-methoxyphenylimidzolium salts were directly synthesized by the quaternization of *o*-, *m*-, and *p*-methoxyphenylimidzoles with the corresponding diaryliodonium salts for 4−5 h in good yields (Table 3, *o*-**3cc**−*p*-**3cc**). The quaternization of di-*m*- and -*p*-bromophenylimidzoles, however, needed much longer reaction time (48 h) and

Table 2. Substrate Scope of the Synthesis of Unsymmetric Diarylimidazolium Salts[a,b]



1a-v 2a 3



[a]General conditions: **1** (0.25 mmol), **2a** (0.375 mmol), and $Cu(OAc)_2·H_2O$ (5 mol %) were stirred in DMF (1 mL) at 100 °C for the indicated time. [b]Isolated yields. [c]**2a** (3.0 equiv, 0.75 mmol).

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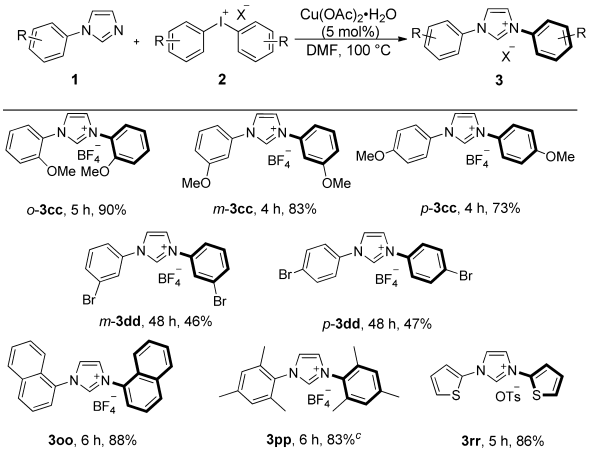
Table 3. Synthesis of Symmetric Diarylimidazolium Salts[a,b]



[a]General conditions: **1** (0.25 mmol), **2** (0.375 mmol), and $Cu(OAc)_2·H_2O$ (5 mol %) were stirred in DMF (1 mL) at 100 °C for the indicated time. [b]Isolated yields. [c]**2** (3.0 equiv, 0.75 mmol).

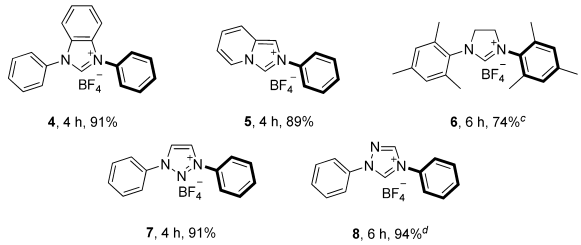
yet afforded lowered yields (Table 3, *m*-**3dd** and *p*-**3dd**). These results suggested that electron-rich diaryliodonium salts are more reactive to quaternize imidazoles than electron-deficient diaryliodonium salts. Bulky diarylimidazolium salts were also accessible directly. For example, di-1-naphthylimidazolium salt **3oo** was obtained in 88% yield after 6 h; a 83% yield was achieved for the classic dimeistylimidazolium salt **3pp**[13] after 6 h, but 3 equiv of $[mesityl]_2IBF_4$ was needed to consume all the imidazole **1p**. It was delightful that diheteroarylimidazolium salts could be prepared under our standard conditions. We obtained di(2-thienyl)imidazolium OTs salt **3rr** in 86% yield by the quaternization of *N*-(2-thienyl)-imidazole with $[2\text{-thienyl}]_2IOTs$ in 5 h.

Obviously, unsymmetric diarylimidazolium salts bearing an electron-deficient aryl and an electron-rich aryl could be synthesized in two directions. Namely, an electron-deficient arylimidazole reacts with an electron-rich diaryliodonium salt or vice versa. In view of the higher reactivity of the electron-rich diaryliodonium salts, the former strategy should be the prime consideration. For instance, *N*-(4-bromophenyl)-*N*′-(4-methoxyphenyl)-imidazolium salt (*p*-**3cd** or *p*-**3dc**) was obtained in 93% yield by using $[p\text{-MeOPh}]_2IBF_4$ *p*-**2cc** to quaternize *p*-**1d** for 5 h, whereas only 76% yield was given by using $[p\text{-BrPh}]_2IBF_4$ *p*-**2dd** to quaternize *p*-**1c** even for 48 h (Supporting Information, Section II).

The selectivity of this reaction toward unsymmetric diaryliodonium salts was also investigated. [*p*-MeOPh-I-(*p*-BrPh)]-OTf **2cd** reacted with *N*-phenylimidazole **1a** for 4 h to afford **3ac** and **3ad** in a 1:1 ratio, which exhibited no chemoselectivity of the electron-rich phenyl ring over the electron-deficient phenyl ring (Supporting Information, Section III, eq 1). However, when [Ph-I-thienyl]OTf **2ar** was used instead, the more electron-rich thienyl ring was preferentially transferred to afford a 3.8:1 mixture of **3ar** in 74% yield and **3aa** in 17% yield (Supporting Information, Section III, eq 2). In addition, [Ph-I-mesityl]OTf **2ap** quaternized **1a** to exclusively afford **3aa** in 94% yield (Supporting Information, Section III, eq 3), suggesting that the bulky mesityl group could serve as a "dummy ligand" in circumstances that starting materials are expensive or symmetric iodonium salts are difficult to make.[10c,14]

The generality of the present methodology was further investigated by the quaternization of *N*-heteroarenes other than imidazoles (Table 4). *N*-Phenylbenzimidazole was smoothly

Table 4. Quaternization of Other *N*-Heteroarenes[a,b]



[a]General conditions: heteroarene (0.25 mmol), **2** (0.375 mmol), and $Cu(OAc)_2·H_2O$ (5 mol %) were stirred in DMF (1 mL) at 100 °C for the indicated time. [b]Isolated yields. [c]**2p** (3.0 equiv, 0.75 mmol). [d]**2a** (2.0 equiv, 0.50 mmol).

quaternized by **2a** to afford diphenylbenzimidazolium salt **4** in 91% yield. Imidazo[1,5-*a*]pyridine was converted to the desired onium salt **5** in 89% yield. The partially hydrogenated imidazole, imidazoline compound could also be directly quaternized. We obtained dimeistylimidazolinium salt **6**[13] in 74% yield by using $[mesityl]_2IBF_4$ to quaternize *N*-mesitylimidazoline. *N*-Phenyl 1,2,3- and 1,2,4-triazoles were directly quaternized at the 3 and 4 positions to afford the corresponding triazolium salts **7** and **8** in excellent yields, respectively.

Although Canty et al. suggested that the reaction of diaryliodonium salts with neutral nucleophiles may proceed through a radical pathway,[15] the preliminary mechanism study ruled out the possibility. When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as the radical scavenger into the reaction of **1a** and **2a**, both the reactions gave the desired imidazolium salt **3a** after 4 h in 94% and 91% yields, respectively. The process possibly involved a typical mechanism for Cu-catalyzed C−H arylation by diaryliodonium salts through Cu^{III} species (Supporting Information, Section IV).[16] Because of the weak nucleophilicity of *N*-substituted imidazoles, only the counteranions with even weaker nucleophilicity could be displaced at the Cu^{III} center. This explained the counteranion effect we observed in this reaction.

In conclusion, we disclose herein to use diaryliodonium salts for the direct aryl quaternization of *N*-substituted imidazoles in the presence of a copper catalyst. This methodology solves a long-standing problem in imidazolium salt synthesis and has the following advantages: (1) it is straightforward, efficient and versatile to quaternize a variety of imidazoles, as well as imidazoline, triazoles, and imidazo[1,5-*a*]pyridine, etc.; (2) it is particularly convenient to synthesize unsymmetric imidazolium salts; (3) it is tolerant to sensitive functional groups such as acetyl, formyl, ester, and hydroxyl groups, etc.; (4) the reaction conditions are mild with no need for a strong base or acid and inert atmosphere; and (5) the procedure is simple and easy to scale up for mass production. It would provide a new possibility to construct complicated and diverse azolium salts, especially unsymmetric ones, for novel *N*-heterocyclic carbenes and functional materials.

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EXPERIMENTAL SECTION

Synthesis of 1-(2-Bromophenyl)-1*H*-imidazole (*o*-1d). 1,2-Dibromobenzene (1.18 g, 5.0 mmol), imidazole (0.48 g, 7.0 mmol), CuI (0.19 g, 1 mmol), Cs_2CO_3 (3.26 g, 10.0 mmol), and freshly distilled DMF (10 mL) were added to a flame-dried Schlenk tube with a magnetic stir bar under N_2. The reaction was stirred at 120 °C for 40 h. After cooled down to room temperature, the reaction mixture was diluted with 10−15 mL of ethyl acetate, filtered, and the solid was washed with 50−100 mL of ethyl acetate. The combined extracts were then concentrated under reduced pressure and the residue was passed through a silica gel column (petroleum/ethyl acetate = 1:1 v/v) to afford the desired product (0.51 g, 46% yield); mp 52−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.45−7.41 (m, 1H), 7.34−7.30 (m, 2H), 7.21 (s, 1H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 136.7, 134.0, 130.2, 129.3, 128.5, 128.2, 120.6, 120.0. HRMS (ESI) $[M + Na]^+$ calcd for $C_9H_7BrN_2Na$, 244.9690; found, 244.9689.

Synthesis of Bis(3-methoxyphenyl)iodonium Tetrafluoroborate (*m*-2cc). This compound was synthesized by a modified procedure of similar compounds previously reported:[17] $BF_3{\cdot}Et_2O$ was added to a dichloromethane (25 mL) solution of 3-methoxyphenylboronic acid (0.76 g, 5.0 mmol) at room temperature. After stirring at room temperature for 15 min, a solution of 3-methoxyphenyliodine diacetate (1.94 g, 5.5 mmol) in dichloromethane (25 mL) was added. The reaction was stirred at reflux for 60 min and quenched by adding a saturated aqueous solution of sodium tetrafluoroborate (30 mL). The organic phase was separated and the aqueous phase was extracted with dichloromethane twice. The combined organic phases were dried over Na_2SO_4. After removal of the volatile solvents, the residue was purified by column chromatography (dichloromethane/methanol = 30:1 v/v) to afford the desired product (0.64 g, 30% yield); mp 170−172 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.93 (s, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.47−7.43 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 132.5, 127.1, 120.7, 117.8, 116.5, 55.9. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{14}H_{14}IO_2$, 341.0038; found, 341.0033.

General Procedure for Quaternization of *N*-Heteroarenes by Diaryliodonium Salts. A *N*-heteroarene (0.25 mmol), a diaryiodonium salt (0.375 mmol), $Cu(OAc)_2{\cdot}H_2O$ (2.5 mg, 5 mol %), and DMF (1 mL) were added to an schlenck tube with a magnetic stir bar. The reaction was stirred at 100 °C for an indicated time in an oil bath. After cooled down to room temperature, the solvent was removed under reduced pressure, and the residue was passed through a silica gel column (dichloromethane/acetone = 5:1−2:1 v/v) to afford the desired onium salt.

1,3-Diphenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3aa).[18] Reacted for 4 h. A gray solid (75 mg, 97% yield); mp 143−145 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 10.10 (s, 1H), 8.43 (s, 2H), 7.96 (d, J = 8.0 Hz, 4H), 7.73−7.64 (m, 6H).

3-Phenyl-1-*o*-tolyl-1*H*-imidazol-3-ium Tetrafluoroborate (*o*-3ba). Reacted for 6 h. A gray solid (73 mg, 91% yield); mp 133−135 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.12 (s, 1H), 8.59 (s, 1H), 8.35 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.74−7.50 (m, 7H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.2, 134.7, 134.2, 133.5, 131.7, 130.8, 130.1, 130.0, 127.3, 126.7, 124.6, 122.1, 121.4, 17.1. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{16}H_{15}N_2$, 235.1230; found, 235.1228.

3-Phenyl-1-*m*-tolyl-1*H*-imidazol-3-ium Tetrafluoroborate (*m*-3ba). Reacted for 4 h. A gray solid (77 mg, 95% yield); mp 128−130 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.33 (s, 1H), 8.58 (s, 2H), 7.92 (d, J = 7.6 Hz, 2H), 7.78 (s, 1H), 7.72−7.70 (m, 3H), 7.65−7.58 (m, 2H), 7.45 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.1, 134.73, 134.66, 134.4, 130.6, 130.2, 130.1, 130.0, 122.4, 122.1, 122.0, 121.9, 119.1, 20.9. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{16}H_{15}N_2$, 235.1230; found, 235.1230.

3-Phenyl-1-*p*-tolyl-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3ba).[19] Reacted for 6 h. A gray solid (74 mg, 92% yield); mp 146−148 °C (literature,[19] 135 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.30 (s, 1H), 8.56 (s, 1H), 8.55 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.73−7.70 (m, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H).

1-(2-Methoxyphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (*o*-3ca). Reacted for 12 h. A gray solid (82 mg, 96% yield); mp 113−115 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.15 (s, 1H), 8.53 (s, 1H), 8.33 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.76−7.62 (m, 5H), 7.42 (d, J = 8.4 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.3, 136.2, 134.6, 132.1, 130.2, 130.1, 126.5, 124.8, 123.3, 122.2, 121.1, 113.3, 56.4. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{16}H_{15}N_2O$, 251.1179; found, 251.1178.

1-(3-Methoxyphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (*m*-3ca). Reacted for 6 h. A gray solid (81 mg, 95% yield); mp 144−146 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.34 (s, 1H), 8.60 (s, 1H), 8.58 (s, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.72 (t, J = 7.6 Hz, 2H), 7.66−7.60 (m, 2H), 7.54 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 135.7, 134.7, 134.6, 131.2, 130.2, 130.1, 122.1, 121.9, 115.6, 113.8, 108.0, 55.9. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{16}H_{15}N_2O$, 251.1179; found, 251.1182.

1-(4-Methoxyphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3ca). Reacted for 4 h. A gray solid (76 mg, 89% yield); mp 151−153 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.24 (s, 1H), 8.54 (s, 1H), 8.49 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.73−7.70 (m, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.3, 134.8, 134.2, 130.2, 130.0, 127.8, 123.7, 122.2, 122.0, 121.7, 115.2, 55.8. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{16}H_{15}N_2O$, 251.1179; found, 251.1173.

1-(2-Bromophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (*o*-3da). Reacted for 6 h. A gray solid (92 mg, 95% yield); mp 118−120 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.29 (s, 1H), 8.64 (s, 1H), 8.42 (s, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.92−7.90 (m, 3H), 7.76−7.63 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.7, 134.5, 133.9, 133.0, 130.4, 130.3, 129.4, 129.0, 125.2, 122.1, 121.4, 119.1. HRMS (ESI) $[M - BF_4^-]^+$ calcd for $C_{15}H_{12}BrN_2$, 299.0178; found, 299.0184.

1-(3-Bromophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (*m*-3da). Reacted for 4 h. A gray solid (80 mg, 83% yield); mp 110−113 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H), 8.61 (s, 1H), 8.60 (s, 1H), 8.27 (s, 1H), 7.97−7.91 (m, 3H), 7.85 (d, J = 8.0 Hz, 1H), 7.75−7.63 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.9, 134.9, 134.6, 132.8, 132.0, 130.23, 130.15, 125.0, 122.6, 122.1, 122.0,

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121.9, 121.2. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{12}BrN_2$, 299.0178; found, 299.0178.

1-(4-Bromophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3da). Reacted for 6 h. A gray solid (79 mg, 82% yield); mp 246−248 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.37 (s, 1H), 8.58 (s, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.92−7.88 (m, 4H), 7.74−7.70 (m, 2H), 7.64 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.8, 134.7, 134.0, 133.1, 130.23, 130.15, 124.2, 123.1, 122.1, 122.0, 121.9. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{12}BrN_2$, 299.0178; found, 299.0187.

1-(4-Fluorophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ea). Reacted for 5 h. A gray solid (68 mg, 89% yield); mp 202−204 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.32 (s, 1H), 8.58 (s, 1H), 8.55 (s, 1H), 8.00−7.96 (m, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.72 (t, J = 7.6 Hz, 2H), 7.66−7.59 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.5 (d, J = 246 Hz), 134.8, 134.7, 131.2 (d, J = 3 Hz), 130.2, 130.1, 124.8 (d, J = 9 Hz), 122.3, 122.1, 121.9, 117.1 (d, J = 23 Hz). HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{12}FN_2$, 239.0979; found, 239.0975.

1-(4-Chlorophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3fa). Reacted for 4 h. A gray solid (73 mg, 85% yield); mp 230−232 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.36 (s, 1H), 8.58 (s, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.74−7.70 (m, 2H), 7.64 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.8, 134.7, 134.6, 133.6, 130.2, 130.2, 124.0, 122.1, 122.0. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{12}ClN_2$, 255.0684; found, 255.0683.

1-(4-Iodophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ga). Reacted for 4 h. A gray solid (102 mg, 94% yield); mp 248−250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.36 (s, 1H), 8.58 (s, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.74−7.70 (m, 4H), 7.64 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 138.9, 134.6, 134.5, 130.2, 130.1, 124.0, 122.1, 122.0, 121.8, 96.3. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{12}IN_2$, 347.0040; found, 347.0038.

1-(4-Ethynylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ha). Reacted for 4 h. A gray solid (66 mg, 80% yield); mp 206−208 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 1H), 8.61 (s, 1H), 8.59 (s, 1H), 7.97−7.91 (m, 4H), 7.84 (d, J = 8.4 Hz, 2H), 7.74−7.70 (m, 2H), 7.64 (t, J = 7.2 Hz, 1H), 4.47 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.8, 134.7, 133.5, 130.24, 130.16, 123.4, 122.3, 122.10, 122.07, 121.8, 83.2, 82.1. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{13}N_2$, 245.1073; found, 245.1074.

1-(4-Acetylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ia). Reacted for 4 h. A gray solid (66 mg, 76% yield); mp 208−210 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H), 8.69 (s, 1H), 8.62 (s, 1H), 8.27 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H), 7.73 (m, 2H), 7.65 (t, J = 7.2 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.1, 137.8, 137.5, 135.0, 134.6, 130.2, 130.1, 122.21, 122.15, 122.0, 121.7, 27.0. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{15}N_2O$, 263.1179; found, 263.1177.

1-(4-Formylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ja). Reacted for 4 h. A gray solid (51 mg, 61% yield); mp 148−150 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.48 (s, 1H), 10.13 (s, 1H), 8.68 (s, 1H), 8.62 (s, 1H), 8.24 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.73 (m, 2H), 7.65 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.2, 138.6, 136.6, 135.1, 134.6, 131.2, 130.2, 122.6, 122.2, 122.1, 121.7. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{16}H_{13}N_2O$, 249.1022; found, 249.1021.

1-(4-(Methoxycarbonyl)phenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ka). Reacted for 5 h. A gray solid (61 mg, 66% yield); mp 196−198 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H), 8.68 (s, 1H), 8.62 (s, 1H), 8.27 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H), 7.73 (m, 2H), 7.65 (t, J = 7.2 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.2, 138.1, 135.1, 134.6, 131.1, 130.8, 130.2, 122.3, 122.2, 122.1, 121.8, 52.6. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{15}N_2O_2$, 279.1128; found, 279.1125.

1-(4-Cyanophenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3la). Reacted for 5 h. A gray solid (55 mg, 67% yield); mp 222−224 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.48 (s, 1H), 8.67 (s, 1H), 8.62 (s, 1H), 8.27 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.73 (m, 2H), 7.65 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 138.0, 135.3, 134.6, 134.5, 130.3, 122.9, 122.3, 122.1, 121.7, 117.8, 112.6. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{16}H_{12}N_3$, 246.1026; found, 246.1022.

1-[4-(Dimethylamino)phenyl]-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ma). Reacted for 5 h. A gray solid (50 mg, 57% yield); mp 162−164 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1H), 8.52 (s, 1H), 8.45 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.72−7.67 (m, 4H), 7.62 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.00 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.0, 134.8, 133.4, 130.2, 129.9, 123.4, 122.8, 122.02, 121.99, 121.6, 112.3, 40.0. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{18}N_3$, 264.1495; found, 264.1498.

1-(4-Hydroxylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3na). Reacted for 4 h. A gray solid (52 mg, 64% yield); mp 188−190 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.20 (s, 1H), 10.18 (s, 1H), 8.52 (s, 1H), 8.43 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.72−7.69 (m, 4H), 7.62 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.8, 134.8, 134.1, 130.2, 130.0, 126.4, 123.8, 122.3, 122.0, 121.7, 116.3. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{13}N_2O$, 237.1022; found, 237.1025.

1-(Naphthalen-1-yl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3oa). Reacted for 4 h. A gray solid (81 mg, 91% yield); mp 112−114 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.31 (s, 1H), 8.69 (s, 1H), 8.49 (s, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.2 Hz, 1H), 7.99−7.94 (m, 3H), 7.86−7.72 (m, 6H), 7.65 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.9, 134.8, 133.6, 131.2, 131.1, 130.1, 130.0, 128.5, 128.4, 127.62, 127.57, 125.5, 125.4, 125.1, 122.2, 121.8, 121.6. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{19}H_{15}N_2$, 271.1230; found, 271.1231.

1-Mesityl-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3pa). Reacted for 12 h. A gray solid (75 mg, 86% yield); mp 166−168 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.05 (s, 1H), 8.66 (s, 1H), 8.21 (s, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.71 (m, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.19 (s, 2H), 2.36 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.6, 136.3, 134.7, 134.5, 131.2, 130.2, 130.1, 129.4, 124.9, 122.1, 121.9, 20.7, 17.1. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{18}H_{19}N_2$, 263.1543; found, 263.1546.

1-(2,6-Diisopropylphenyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3qa). Ph_2IBF_4 (276.0 mg, 0.75 mmol, 3.0 equiv) was used to react for 12 h. A gray solid (55 mg, 56% yield); mp 210−212 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.24 (s, 1H), 8.71 (s, 1H), 8.37 (s, 1H), 7.91 (d,

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J = 7.6 Hz, 2H), 7.74−7.63 (m, 4H), 7.51 (d, J = 7.6 Hz, 2H), 2.47−2.43 (m, 2H), 1.19 (d, J = 8.0 Hz, 6H), 1.17 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.3, 136.3, 134.6, 131.7, 130.5, 130.2, 130.1, 126.0, 124.5, 122.1, 122.0, 28.0, 24.1, 23.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{21}H_{25}N_2$, 305.2012; found, 305.2017.

3-Phenyl-1-(thiophen-2-yl)-1*H*-imidazol-3-ium Tetrafluoroborate (3ra). Reacted for 5 h. A gray solid (69 mg, 88% yield); mp 124−126 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.31 (s, 1H), 8.56 (s, 1H), 8.49 (s, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.74−7.62 (m, 5H), 7.23 (t, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.7, 135.1, 134.5, 130.2, 126.8, 126.2, 123.7, 123.3, 122.2, 122.0. HRMS (ESI) [M-BF_4^-]$^+$ calcd for $C_{13}H_{11}N_2S$, 227.0637; found, 227.0641.

3-Phenyl-1-(pyridin-2-yl)-1*H*-imidazol-3-ium Tetrafluoroborate (3sa). Reacted for 4 h. A gray solid (66 mg, 86% yield); mp 162−164 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.60 (s, 1H), 8.75 (s, 1H), 8.71 (d, J = 4.4 Hz, 1H), 8.58 (s, 1H), 8.30−8.26 (m, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.74−7.69 (m, 3H), 7.65 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.3, 146.3, 140.7, 134.7, 134.3, 130.2, 130.1, 125.5, 122.3, 120.0, 114.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{14}H_{12}N_3$, 222.1026; found, 222.1030.

1-Isopropyl-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ta). Reacted for 5 h. A semisolid (59 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 7.69 (s, 1H), 7.64 (s, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.50−7.43 (m, 3H), 4.83 (septet, J = 6.4 Hz, 1H), 1.58 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 133.1, 130.6, 130.4, 122.1, 121.8, 121.3, 54.1, 22.7. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{12}H_{15}N_2$, 187.1230; found, 187.1232.

1-*tert*-Butyl-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3ua). Reacted for 5 h. A gray solid (67 mg, 90% yield); mp 146−148 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.69 (s, 1H), 8.38 (s, 1H), 8.28 (s, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.69−7.65 (m, 2H), 7.59 (t, J = 7.2 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.0, 133.7, 130.0, 129.7, 122.2, 121.5, 121.2, 60.3, 29.0. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{13}H_{17}N_2$, 201.1386; found, 201.1386.

1-(1-Adamantyl)-3-phenyl-1*H*-imidazol-3-ium Tetrafluoroborate (3va). Reacted for 6 h. A gray solid (86 mg, 90% yield); mp 163−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 7.67−7.66 (m, 4H), 7.55−7.46 (m, 3H), 2.29 (s, 3H), 2.33 (s, 6H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 131.7, 130.5, 130.3, 122.3, 121.7, 120.3, 61.5, 42.3, 35.3, 29.6. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{19}H_{23}N_2$, 279.1856; found, 279.1857.

1,3-Bis(2-methoxyphenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*o*-3cc). Reacted for 5 h. A gray solid (83 mg, 90% yield); mp 178−180 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 8.25 (s, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.66−7.62 (m, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.25−7.21 (m, 2H), 3.93 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.3, 138.1, 132.0, 126.4, 123.7, 123.3, 121.1, 113.3, 56.4. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{17}N_2O_2$, 281.1285; found, 281.1284.

1,3-Bis(3-methoxyphenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*m*-3cc). Reacted for 4 h. A gray solid (76 mg, 83% yield); mp 117−119 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.32 (s, 1H), 8.59 (s, 2H), 7.62 (t, J = 8.0 Hz, 2H), 7.54 (s, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 3.89 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 135.7, 134.6, 131.2, 121.9, 115.7, 113.9, 108.1, 55.9. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{17}N_2O_2$, 281.1285; found, 281.1283.

1,3-Bis(4-methoxyphenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3cc). Reacted for 4 h. A gray solid (67 mg, 73% yield); mp 232−234 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.12 (s, 1H), 8.43 (s, 2H), 7.82 (d, J = 8.8 Hz, 4H), 7.23 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.2, 134.0, 127.9, 123.7, 122.0, 115.2, 55.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{17}H_{17}N_2O_2$, 281.1285; found, 281.1277.

1,3-Bis(3-bromophenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*m*-3dd). Reacted for 48 h. A gray solid (54 mg, 46% yield); mp 162−164 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H), 8.61 (s, 2H), 8.26 (s, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.7, 135.3, 132.9, 132.1, 124.9, 122.6, 121.9, 121.1. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{11}Br_2N_2$, 376.9283; found, 376.9275.

1,3-Bis(4-bromophenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3dd). Reacted for 48 h. A gray solid (55 mg, 47% yield); mp > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 2H), 8.58 (s, 2H), 7.97 (d, J = 8.4 Hz, 4H), 7.88 (d, J = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.0, 133.9, 133.1, 124.1, 123.1, 121.9. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{15}H_{11}Br_2N_2$, 376.9283; found, 376.9283.

1,3-Di(naphthalen-1-yl)-1*H*-imidazol-3-ium Tetrafluoroborate (3oo). Reacted for 6 h. A gray solid (89 mg, 88% yield); mp 146−148 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.23 (s, 1H), 8.60 (s, 2H), 8.32 (d, J = 8.4 Hz, 2H), 8.22 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.84−7.76 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.2, 133.7, 131.3, 131.2, 128.6, 127.7, 127.6, 125.5, 125.4, 125.3, 121.9. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{23}H_{17}N_2$, 321.1386; found, 321.1386.

1,3-Dimesityl-1*H*-imidazol-3-ium Tetrafluoroborate (3pp).[20] [Mesityl]$_2$IBF_4 (339.0 mg, 0.75 mmol, 3.0 equiv) was used to react for 6 h. A gray solid (81 mg, 83% yield); mp 206−208 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.64 (s, 1H), 8.28 (s, 2H), 7.21 (s, 4H), 2.36 (s, 6H), 2.12 (s, 12H).

1,3-Di(thiophen-2-yl)-1*H*-imidazol-3-ium 4-Methylbenzenesulfonate (3rr). Reacted for 5 h. A gray solid (87 mg, 86% yield); mp 154−156 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.28 (s, 1H), 8.46 (s, 2H), 7.73 (d, J = 5.2 Hz, 2H), 7.64 (d, J = 2.8 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.22−7.20 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.6, 137.7, 136.7, 134.9, 128.1, 126.8, 126.3, 125.5, 123.7, 123.4, 20.8. HRMS (ESI) [M − OTs^-]$^+$ calcd for $C_{11}H_9N_2S_2$, 233.0202; found, 233.0202.

1,3-Diphenyl-1*H*-benzo[*d*]imidazol-3-ium Tetrafluoroborate (4). Reacted for 4 h. A gray solid (81 mg, 91% yield); mp > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.58 (s, 1H), 7.98−7.93 (m, 6H), 7.83−7.74 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.8, 133.0, 131.2, 130.8, 130.5, 127.8, 125.4, 113.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{19}H_{15}N_2$, 271.1230; found, 271.1234.

2-Phenylimidazo[1,5-*a*]pyridin-2-ium Tetrafluoroborate (5). Reacted for 4 h. A gray solid (63 mg, 89% yield); mp 154−156 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.30 (s, 1H), 8.75 (s, 1H), 8.58 (d, J = 6.8 Hz, 1H), 7.94−7.90 (m, 3H), 7.76−7.66 (m, 3H), 7.38−7.34 (m, 1H), 7.29−7.26 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.1, 130.6, 130.4, 129.8, 125.9, 125.3, 124.3, 122.9, 118.4, 118.3, 112.3. HRMS

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(ESI) [M − BF_4^-]$^+$ calcd for $C_{13}H_{11}N_2$, 195.0917; found, 195.0916.

1,3-Dimesityl-4,5-dihydro-1*H*-imidazol-3-ium Tetrafluoroborate (6).[21] [Mesityl]$_2$IBF_4 (339.0 mg, 0.75 mmol, 3.0 equiv) was used to react for 6 h. A gray solid (72 mg, 74% yield); mp > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.99 (s, 1H), 7.10 (s, 4H), 4.45 (s, 4H), 2.36 (s, 12H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.3, 139.7, 135.5, 130.9, 129.5, 50.9, 20.6, 17.2. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{21}H_{27}N_2$, 307.2169; found, 307.2166.

1,3-Diphenyl-1*H*-1,2,3-triazol-3-ium Tetrafluoroborate (7). Reacted for 4 h. A gray solid (71 mg, 91% yield); mp 158−160 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.83 (s, 2H), 8.16 (d, J = 6.4 Hz, 4H), 7.82−7.76 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.9, 132.1, 130.5, 129.9, 121.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{14}H_{12}N_3$, 222.1026; found, 222.1026.

1,4-Diphenyl-1*H*-1,2,4-triazol-4-ium Tetrafluoroborate (8). Ph_2IBF_4 (184.0 mg, 0.50 mmol, 2.0 equiv) was used to react for 6 h. A gray solid (74 mg, 94% yield); mp 166−168 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.43 (s, 1H), 10.02 (s, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.94 (d, J = 7.6 Hz, 2H), 7.79−7.75 (m, 4H), 7.71−7.67 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.3, 140.5, 135.0, 132.1, 130.8, 130.4, 122.6, 120.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{14}H_{12}N_3$, 222.1026; found, 222.1024.

1-(4-bromophenyl)-3-(4-methoxyphenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3dc). Reacted for 5 h. A gray solid (97 mg, 93% yield); mp 179−181 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.24 (s, 1H), 8.52 (s, 1H), 8.47 (s, 1H), 7.94 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.3, 134.4, 134.1, 133.1, 127.7, 124.2, 123.7, 123.0, 122.3, 121.7, 115.2, 55.8. HRMS (ESI) [M − BF_4^-]$^+$ calcd for $C_{16}H_{14}BrN_2O$, 329.0284; found, 329.0287.

3-(4-bromophenyl)-1-(4-methoxyphenyl)-1*H*-imidazol-3-ium Tetrafluoroborate (*p*-3cd). Reacted for 48 h. A gray solid (79 mg, 76% yield). *p*-**3cd** and *p*-**3dc** are the same compound.

■ ASSOCIATED CONTENT

Supporting Information

Data and copies of NMR for compounds. 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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