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Exploiting the Narrow Gap of Rearrangement between the Substituents in the Vicinal Disubsitution Reactions of Diaryliodonium Salts with Pyridine N-sulfonamidates

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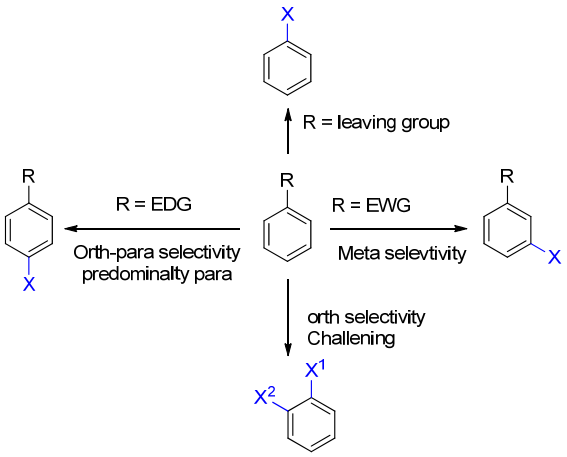
The vicinal disubstitution reaction of diaryliodonium salts with pyridine N-sulfonamidates were fully examined to afford o-pyridinium anilines. A pathway of N-arylation occurred at the amidate group followed by a radical rearrangement was proposed for the reaction. The scope and more important, the electronic effect of substituents of this radical rearrangement were investigated.

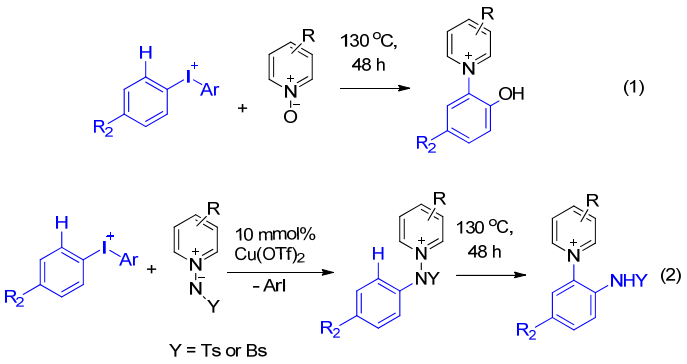
Introduction

Polysubstituted benzene derivatives are highly important compounds in organic chemistry, natural product chemistry, pharmaceutical chemistry and materials science.[1] Consequently, there exists vast and long-termed demand for the regioselective synthesis of benzene derivatives with multiple substituents in organic synthesis. Besides asembly of benzene ring with acyclic small molecules (e.g. Reepe type reactions)[2], traditionally, more practical and efficient approaches towards polysubstituted benzene derivatives are based on aromatic substitution on C-H bond, which introduces a substituent on the given arene complying various substitution effect. A majority of these synthetic methodologies are based on electrophilic substitution[3], but the additional substituent is normally introduced on meta-position (when R is EWG) or para-position (when R is EDG) (Scheme 1). Regio-selectively introducing substituent on the orth position of benzene ring is not so common and challenging. The utilization of directing group is mainly approach to introduce substituent on the orth C-H bond (via orth-metallation[4] or C-H activation catalyzed by transition metal[5]), but the scope of this reaction is highly restricted by its nature. Additionally, Fries rearrangement is an efficient and regio-selective way to synthesize orth-substituted benzene derivatives.[6]



Scheme 1 Various types of introducing X groups on a given benzene ring via electrophilic substitution.

As part of our ongoing interest in the efficient synthesis of poly-substituted benzene derivatives, lately we reported a vicinal disubstitution reaction of diaryliodonium salts[7] with pyridine N-oxides (eq 1).[8] The reaction provided a selective manner to introduce two substituents at orth- and ipso-position of benzene ring simultaneously (eq 2). Interestingly, this vicinal disubsitution is also applicable to pyridine N-sulfonamidate,[9] where o-pyridinium aniline was isolated instead. In the primary communication, a pathway of N-arylation occurred at the amidate group followed by a radical rearrangement was proposed for the reaction. In this account, we would like to report the scope and more important, the effect of substituents of this radical rearrangement.



Results and discussion

I) Arylation of pyridinium sulfonamidates with diaryliodonium salts

Firstly, the arylation products of pyridinium sulfonamidates with diaryliodonium salts were prepared for the investigation of rearrangement. However, the arylation product **3aa** was unable to isolate by treatment of the reaction mixture of **1a** and **2a** with heating at 130 °C, while rearrangement reaction occurred to produce o-pyridinium aniline. Gladly, we found out when 10 mmol% of $Cu(OTf)_2$ was added, the arylation product **3aa** could be obtained in 57% yield at 75 °C (see detailed condition screening in SI). By this manner, a series of arylation products **3** of **2** with substituted iodonium salts **1** (scheme 2) were isolated in good to excellent yields (scheme 3). As shown in scheme 3, the iodonium salts bearing *o*-, *m*-, or *p*-methyl and 2,4-dimethyl groups all worked well to give products **3a**-**3e**. Other iodonium salts with functional groups including fluoro, chloro, bromo and trifluoromethyloxyl groups on phenyl ring (**1f**-**1n**) were also tolerated in the Cu-catalyzed N-arylation reactions. When unsymmetric iodonium salts (**1g**, **1l** and **1m**) were used, the amination took place on the less hindered phenyl ring. Finally, several substituted pyridinium sulfonamidates were chosen for the arylation reaction and the corresponding products were isolated also in good yield. Apparently, normal substituents on the pyridine ring didn't affect the arylation of sulfonamidate group. All new compounds were characterized by ^{1}H, ^{13}C NMR, ESI and HRMS. Furthermore, the structure of product **3kb** was confirmed by XRD analysis of its single crystal (figure 1).[10]

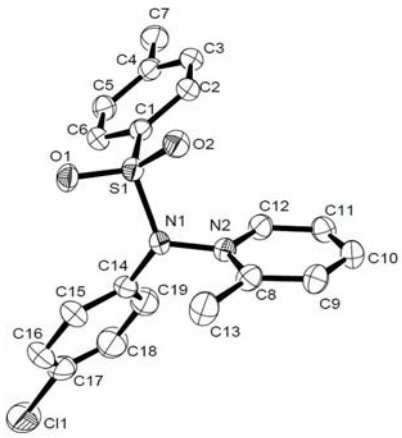
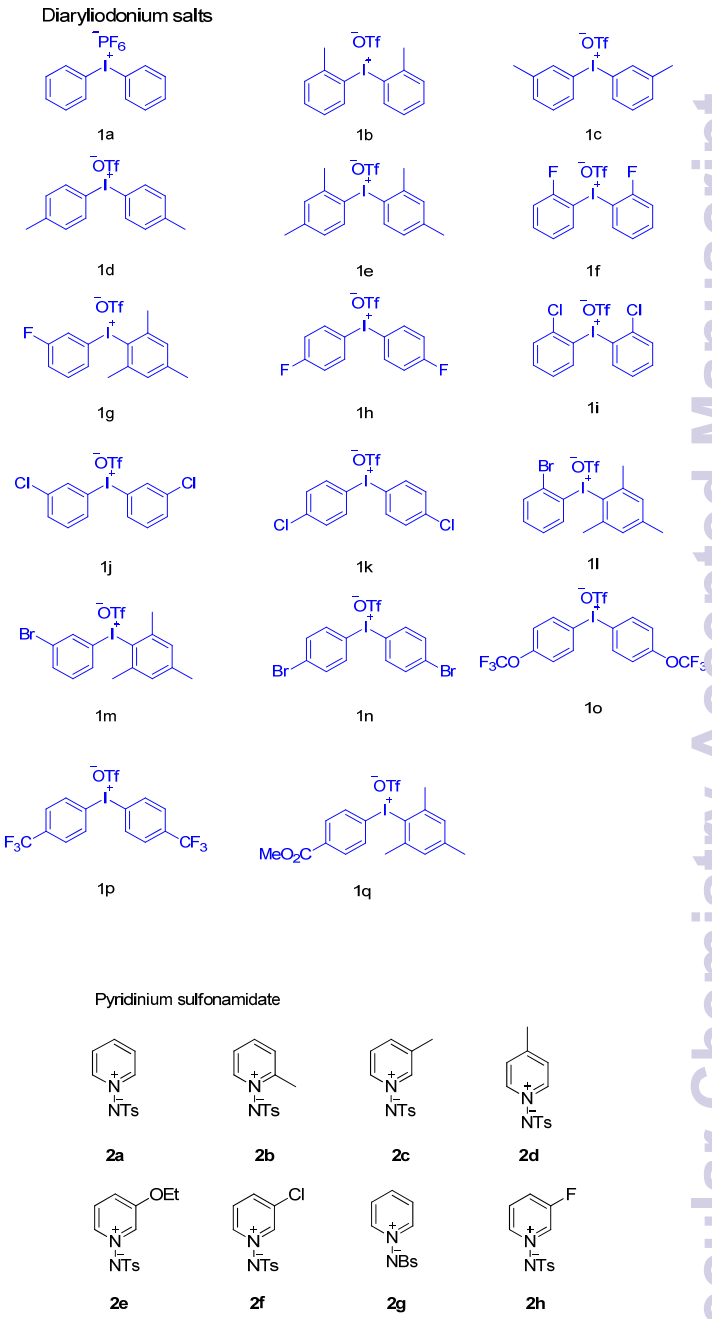
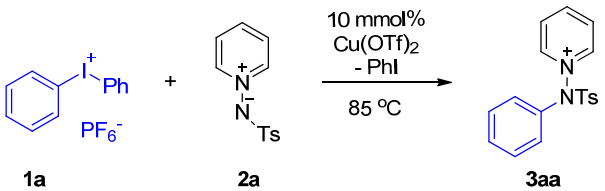
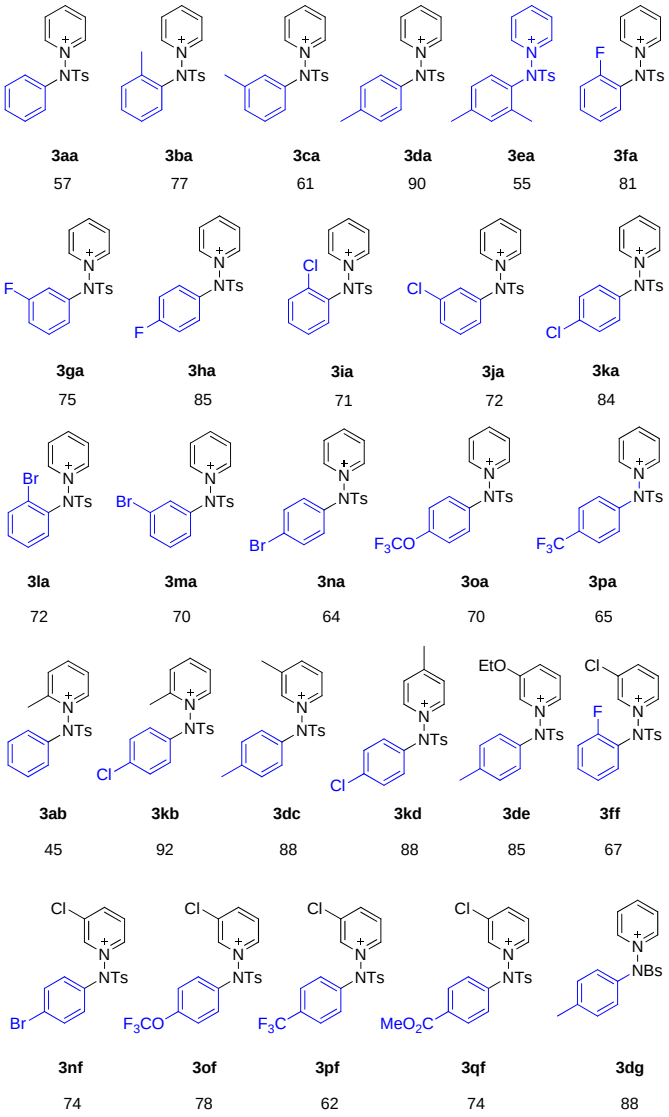


Figure 1 Crystal structure of **3kb**. Counteranion of triflate and Hydrogen atoms were omitted for clarity.



Scheme 2 Diaryiodonium salts **1** and pyridinium sulfonamidates **2** used in the reaction for the preparation of products **3**.

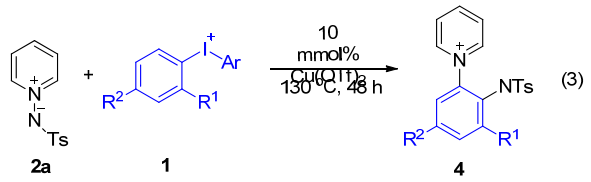


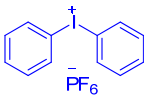
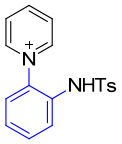
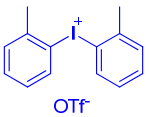
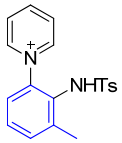
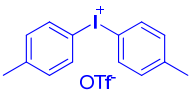
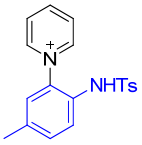
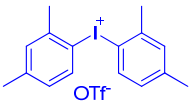
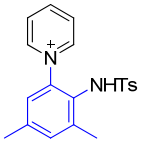
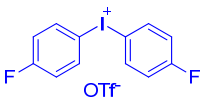
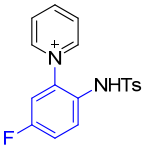
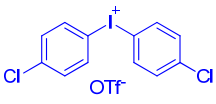
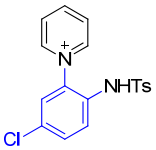
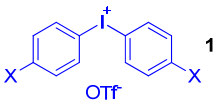
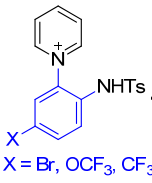


Scheme 3 Isolated yields of products **3**.

II) Rearrangement of arylated pyridinium sulfonamidates

Next, we investigated the formation of rearrangement products by reacting pyridinium salts with diaryliodonium salts. First, N-pyridine tosylamidate **2a** was reacted with a range of diaryliodonium salts with various substituents on the aromatic ring **1a-1k** at 130 °C (eq 3, for the results see scheme 4). When the subsituent R^1 or R^2 was electro-donating group such as H, methy, dimethyl group, the reaction worked well to give rearrangement product. The structure of **4da** was further demonstrated by XRD analysis of its single crystal (figure 2).[11] In its crystal structure, it's clearly shown N-N bond was cleaved and inserted by a phenylene group. Moreover, the ipso-position of iodonium salt was substituted by tosylamide group and orth-position was substituted by pyridinium moiety. When the para-subsitutent R^2 was fluoro- or chloro- atom, the reaction proceeded smoothly to give expected product. However, when the para-substituent R^2 was alternated to bromo-, trifluoromethyoxyl or trifluoromethy group (**1n-1p**), the reaction couldn't afford rearrangement product. *These results suggest electro-donating substituent on the phenyl ring of the diaryliodonium salts is prior for the rearrangement but electro-withdrawing one inhibits the rearrangement.*



Diaryliodonium salt		Product		Isolated yield (%)
	**1a**		**4aa**	45
	**1b**		**4ba**	58
	**1d**		**4da**	77
	**1e**		**4ea**	48
	**1h**		**4ha**	74
	**1k**		**4ka**	63
	**1n-1p**		**4na-4pa**	0

Scheme 4. Diaryiodonium trilates **1** (hexafluorophosphate for **1a**) and pyridinium sulfonamidates **2a** used in the reaction for the preparation of products **4**.

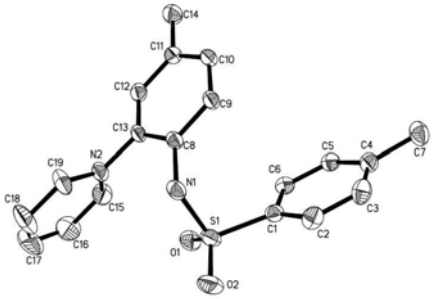
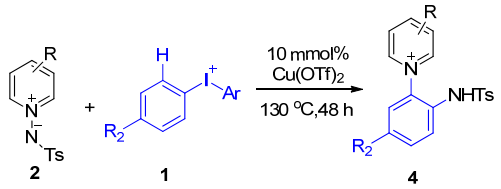


Figure 2. Crystal structure of **4da**. Counteranion and Hydrogen atoms were omitted for clarity.



Pyridinium amidate	Diaryliodonium salt	Produc	Isolated yield (%)
2b	**1d**	**4db**	78
2c	**1d**	**4dc**	76
2d	**1d**	**4dd**	80
2e	**1d**	**4de**	73
2c	**1h, 1k, 1n-1p**	**4hc, 4kc, 4nc-4pc** X = F, Cl Br, OCF_3, CF_3,	0

Scheme 5. Diaryiodonium trilates **1** and pyridinium N-sulfonamidates with electron-donating groups **2** used in the reaction for the preparation of products **4**.

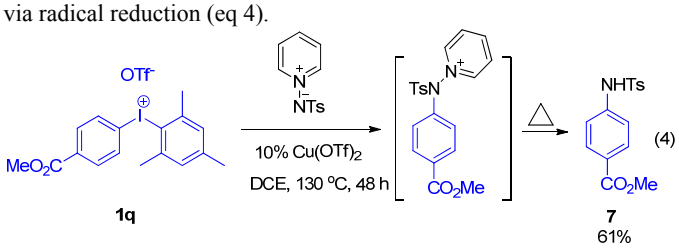
Encouraged by the above results, we attempted to investigate the influence of substitution of pyridinium sulfonamidate on the rearrangement. For this goal, a series of substituted pyridinium sulfonamidates were reacted with diaryliodonium salts to generate the rearrangement products (scheme 5). Interestingly, pyridinium sulfonamidates with electro-donating groups (**2b-2e**) could react with electron-riched iodonium salts to give rearrangement products **4db-4de**, The reaction of **2c** with electron-deficient iodonium salts (**1h, 1k, 1n-1p**) didn't afford any rearrangement product.

Pyridinium amidate	Diaryliodonium salt	Product	Isolated yield (%)
2h	**1a**	**4ah**	79
	1h	**4hh**	85
2f	**1a**	**4af**	76
	1f	**4ff**	42
	1h	**4hf**	75
	1k	**4kf**	75
	1n	**4nf**	68
	1o	**4of**	65

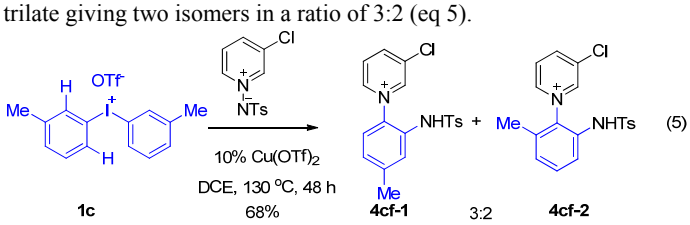
Scheme 6. Diaryiodonium trilates **1** (hexafluorophosphate for **1a**) and halogen-substituted pyridinium sulfonamidates **2** used in the reactions for the preparation of products **4**.

Halogen-substituted pyridinium sulfonamidates showed more reactive to give reaarangement products (scheme 6). As proved, 3-chloropyridinium sulfonamidates could react with diaryliodonium salts with bromo-, chloro- and trifluoromethyoxyl groups to generate the rearrangement products.

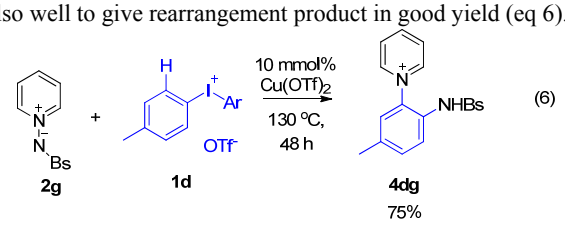
The reaction of diaryliodonium trilate **1q** and pyridinium sulfonamidate **2a** could give the arylated production, which didn't undergo the rearrangement reaction. Overlong heating of the arylated product would afford decomposition product **7** presumably via radical reduction (eq 4).



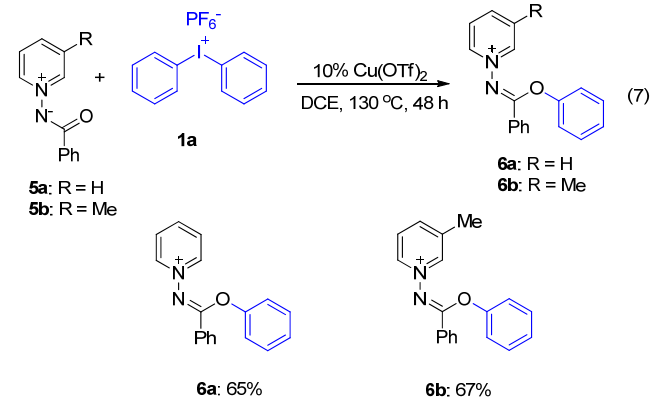
The reaction of pyridinium sulfonamidate with meta-substituted diaryliodonium trilate produced regio-isomer. For example, 3-chloro-pyridinium sulfonamidate reacted with di(*m*-tolyl) iodonium trilate giving two isomers in a ratio of 3:2 (eq 5).



Finally, the effect of protecting group on the amide moiety was investigated. Similarly as tosylate group, pyridinium benzenesulfonamidate amide **2g** worked with ditolyliodonium trilate **1d** also well to give rearrangement product in good yield (eq 6).



When protecting group on the amide moiety was changed to benzoate group, O-arylated product was obtained insteadly (eq 7). The structure of product **6a** was confirmed by XRD analysis of its single crystal (figure 3).[12]



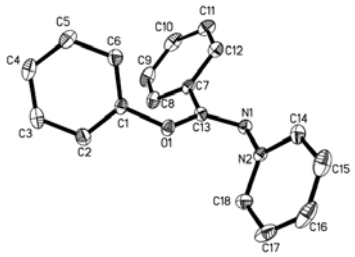


Figure 3. Crystal structure of **6a**. Counteranion and Hydrogen atoms were omitted for clarity.

Conclusions

In this account, we have described a regio-selective way to synthesize benzene derivatives with vincinal disubstitution by the reaction of diaryiodonium salts with pyridinium N-sulfonamidates. The reaction proceeds via the arylation of pyridinium N-sulfonamidates and then key rearrangement of the arylated products **3** (Figure 4). Previous study and this work have proven that rearrangement is generally initiated by a homo-cleveage to give a radical pair: tosylate aniline radical A[13] and pyridinium radical B[14]. The recombination of the radical pair would afford the final product **4** and this process was sensitively influenced by the substituents on the pyridinium ring and the phenyl ring, as shown in scheme 6. This result has shown us the nature of radical rearrangement resembling the electrophilic substitution on the phenyl ring (scheme 7).[15]

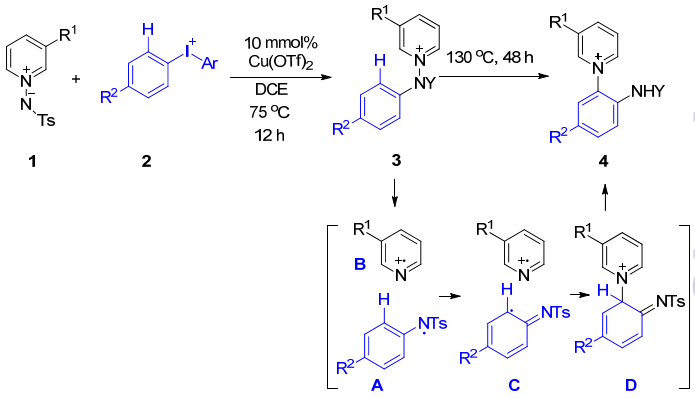
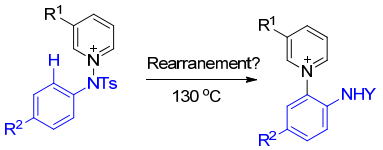


Figure 4. Plausible reaction mechanism.



R1 \ R2	Me	H	F	Cl	Br	OCF_3	CF_3	CO_2Et
Me	√	√	-	-	-	-	-	-
H	√	√	√	√	-	-	-	-
Cl	√	√	√	√	√	√	-	-

Scheme 7. Influence of the substituents on the pyridinium ring and the phenyl ring on the rearrangement.

Experimental section

All the reactions were carried out in pre-dried a screwcapped tube with a Teflon-lined septum under N_2 atmosphere. Ph_2IPF_6 was purchased from Alfa-aesar. Other diaryliodonium salts are Ar_2IOTf, because the activity of Ar_2IOTf is almost same to Ar_2IPF_6 (just a slight decrease) and Ar_2IOTf are easier to synthesized according to literature. All of the solvents were fresh distilled. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL AL-300MHz or AL-400MHz spectrometer at ambient temperature with $CDCl_3$, CD_3OD and DMSO-D_6 as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), CD_3OD (3.31) and DMSO-D_6 (2.50) to the carbon resonance of $CDCl_3$ (77.16), CD_3OD (49.00) and DMSO-D_6 (39.52). Coupling constants (J) were given in Hertz (Hz). The term m, dq, q, t, d, s referred to multiplet, doublet quartet, quartet, triplet, doublet, singlet. Mass spectra were obtained using Bruker Esquire ion trap mass spectrometer in positive mode.

Preparation of starting materials: Diaryliodonium salts were synthesized according to the literature procedures.[7] N-pyridine tosylamidates **2a-2f**, **2h**, N-pyridinium benzenesulfonated amide **2g** and N-pyridinium benzoated amides **5a-5b** were all synthesized according to the literature procedures.[16]

General procedure for the preparation of desired compound 3: $Cu(OTf)_2$ (0.05 mmol) was added to a mixture of appropriate N-tosylpyridinium imides or N-pyridine tosylamidates (or N-pyridinium benzenesulfonated amide) **2** (0.5 mmol) and appropriate diaryliodonium salt **1** (0.5 mmol) in a sealed tube. Then the tube was evacuated and recharged with N_2 for 3 times. After 2 mL of dichloroethane was added, the tube was sealed and the mixture was allowed to stir at 75 ℃ for 12 h until completion of the reaction checked by TLC. At last the desired compound **3** was purified by silica gel column chromatography (dichloromethane/petroleum ether/methanol = 5:5:1) as a yellow solid.

General procedure for the preparation of desired compound 4: $Cu(OTf)_2$ (0.05 mmol) was added to a mixture of appropriate N-pyridine tosylamidates (or N-pyridinium benzenesulfonated amide) **2** (0.5 mmol) and appropriate diaryliodonium salt **1** (0.5 mmol) in a sealed tube. Then the tube was evacuated and recharged with N_2 for 3 times. After 2 mL of dichloroethane was added, the tube was sealed and the mixture was allowed to stir at 130 ℃ for 48 h until completion of the reaction checked by TLC. At last the desired compound **4** was purified by silica gel column chromatography (dichloromethane/petroleum ether/methanol = 5:3:1) as a yellow solid.

1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium hexafluorophosphate(V) (3aa). yellow solid (134 mg, 0.28 mmol, 57%). ^1H NMR (301 MHz, METHANOL-D3): δ 9.47 (d, *J* = 5.8 Hz, 2H), 8.88 (t, *J* = 7.8 Hz, 1H), 8.31 (t, *J* = 7.2 Hz, 2H), 7.81 - 7.70 (m, 4H), 7.60 - 7.49 (m, 5H), 2.52 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 149.69, 148.07 (2×CH), 147.92, 137.53, 131.59, 131.41, 130.73 (2×CH), 130.40 (2×CH), 129.97 (2×CH), 129.03 (2×CH), 128.57 (2×CH), 20.54; ESI-MS: m/z calcd for $C_{18}H_{17}N_2O_2S$ $[M\text{-}PF_6^-]^+$: 325.1; found: 325.0; ESI-HRMS: m/z calcd for $C_{18}H_{17}N_2O_2S$ $[M\text{-}PF_6^-]^+$: 325.1005; found: 325.1005.

1-(4-methyl-N-(o-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ba). yellow solid (188 mg, 0.39 mmol, 77%). ^1H NMR (400 MHz, METHANOL-D3) δ 9.40 (d, *J* = 5.9 Hz, 2H), 8.82 (t, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.53 - 7.44 (m, 3H), 7.38 (t, *J* = 7.0 Hz, 2H), 2.50 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 149.40, 148.04, 147.73 (2×CH), 140.34, 135.78, 132.34, 132.01, 131.23, 130.73 (2×CH), 129.76 (2×CH), 129.24, 129.16 (2×CH), 127.70, 120.47 (q, *J* = 318.5 Hz), 20.51, 17.45; ESI-MS: m/z calcd for $C_{19}H_{19}N_2O_2S$ $[M\text{-}TfO^-]^+$: 339.1; found: 339.0; ESI-HRMS: m/z calcd for $C_{19}H_{19}N_2O_2S$ $[M\text{-}TfO^-]^+$: 339.1162; found: 339.1166.

1-(4-methyl-N-(m-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ca). yellow solid (149 mg, 0.31 mmol, 61%). ^1H NMR (400 MHz, METHANOL-D3) δ 9.40 (d, *J* = 5.7 Hz, 2H), 8.83 (t, *J* = 7.8 Hz, 1H), 8.25 (dd, *J* = 7.6, 6.9 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 13.3, 5.3 Hz, 4H), 7.41 - 7.33 (m, 2H), 2.49 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 149.59, 148.01 (2×CH), 147.82, 141.12, 137.44, 132.04, 131.64, 130.67 (2×CH), 130.02, 129.89 (2×CH), 129.01 (2×CH, 1×C), 125.46, 120.46 (q, *J* = 318.7 Hz), 20.48, 19.82; ESI-MS: m/z calcd for $C_{19}H_{19}N_2O_2S$ $[M\text{-}TfO^-]^+$: 339.1; found: 339.0; ESI-HRMS: m/z calcd for $C_{19}H_{19}N_2O_2S$ $[M\text{-}TfO^-]^+$: 339.1162; found: 339.1163.

1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3da). yellow solid (220 mg, 0.45 mmol, 90%). ^1H NMR (301 MHz, METHANOL-D3): δ 9.46 (d, *J* = 6.5 Hz, 2H), 8.88 (t, *J* = 7.8 Hz, 1H), 8.30 (t, *J* = 6.8 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 2.53 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 149.54, 147.93 (2×CH), 147.79, 142.48, 134.87, 131.65, 130.84 (2×CH), 130.66 (2×CH), 129.89 (2×CH), 129.02 (2×CH), 128.63 (2×CH), 120.50 (q, *J* = 316.5 Hz), 20.49, 19.92; ESI-MS: m/z calcd for $C_{19}H_{19}N_2O_2S$ $[M\text{-}TfO^-]^+$: 339.1; found: 339.0; ESI-HRMS: m/z calcd for $C_{19}H_{19}N_2O_2S$ $[M\text{-}TfO^-]^+$: 339.1162; found: 339.1161.

1-(N-(2,4-dimethylphenyl)-4-methylphenylsulfonamido)-pyridine-1-ium trifluoromethanesulfonate (3ea). yellow solid (138 mg, 0.28 mmol, 55%). ^1H NMR (301 MHz, METHANOL-D3): δ 9.03 (d, *J* = 5.8 Hz, 2H), 8.71 (t, *J* = 7.8 Hz, 1H), 8.19 (t, *J* = 6.9 Hz, 1H), 7.47 - 7.38 (m, 3H), 7.27 (dd, *J* = 14.5, 8.2 Hz, 4H), 2.42 (s, 6H), 1.74 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 146.75 (2×CH), 146.61, 144.46, 139.96, 139.46, 137.19, 134.52, 129.68 (2×CH), 128.64, 127.24 (2×CH), 126.76 (2×CH), 125.67, 125.24, 120.44 (q, *J* = 318.8 Hz), 20.19, 19.55, 16.31; ESI-MS: m/z calcd for $C_{20}H_{21}N_2O_2S$ $[M\text{-}TfO^-]^+$: 353.13; found: 353.2; ESI-HRMS: m/z calcd for $C_{20}H_{21}N_2O_2S$ $[M\text{-}TfO^-]^+$: 353.1318; found: 353.1317.

1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3fa). yellow solid (199 mg, 0.41 mmol, 81%). ^1H NMR (301 MHz, DMSO-D6) δ 9.43 (d, *J* = 6.0 Hz, 2H), 8.87 (t, *J* = 7.7 Hz, 1H), 8.32 (t, *J* = 7.1 Hz, 2H), 8.00 (dd, *J* = 11.2, 4.3 Hz, 1H), 7.73 - 7.61 (m, 3H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.49 - 7.35 (m, 2H), 2.46 (d, *J* = 9.8 Hz, 3H); ^{13}C NMR (76 MHz, DMSO-D6) δ 159.56 (d, J^1 = 253.8 Hz), 150.81, 148.83 (2×CH), 147.81, 135.11 (d, J^3 = 8.6 Hz), 132.43, 131.93, 131.48 (2×CH), 130.91 (2×CH), 129.20 (2×CH), 126.50 (d, J^3 = 3.1 Hz), 124.36 (d, J^2 = 12.8 Hz) 121.23 (q, *J* = 322.1 Hz), 118.01 (d, J^2 = 19.7 Hz), 21.79; ESI-MS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ $[M\text{-}TfO^-]^+$: 343.1; found: 343.0.; ESI-HRMS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ $[M\text{-}TfO^-]^+$: 343.0911; found: 343.0912.

1-(N-(3-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ga). yellow solid (185 mg, 0.38 mmol, 75%). ^1H NMR (400 MHz, METHANOL-D3) δ 9.40 (d, *J* = 5.9 Hz, 2H), 8.86 (t, *J* = 7.8 Hz, 1H), 8.28 (t, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.58 - 7.48 (m, 5H), 7.36 - 7.27 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 162.91 (d, J^1 = 249.3 Hz), 149.91, 148.14 (3×CH), 138.42 (d, J^2 = 9.8 Hz), 131.79 (d, J^3 = 8.8 Hz), 131.25, 130.81 (2×CH), 130.03 (2×CH), 129.03 (2×CH), 124.26 (d, J^3 = 3.3 Hz), 120.48 (q, *J* = 318.8 Hz), 118.30 (d, J^2 =

21.1 Hz), 115.84 (d, *J* = 24.3 Hz), 20.50; ESI-MS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO$^-$]$^+$: 343.1; found: 343.0.; ESI-HRMS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO$^-$]$^+$: 343.0911; found: 343.0912.

1-(N-(4-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ha). yellow solid (209 mg, 0.43 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-D6) δ 9.65 (d, *J* = 6.4 Hz, 2H), 8.89 (t, *J* = 7.3 Hz, 1H), 8.36 (t, *J* = 7.1 Hz, 2H), 7.93 - 7.84 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.41 (dd, *J* = 12.1, 5.1 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 163.86 (d, J^1 = 250.3 Hz), 150.57, 148.64 (2×CH), 147.64, 133.55, 132.71 (d, J^3 = 9.6 Hz), 131.82, 131.43 (2×CH), 130.78 (2×CH), 129.37 (2×CH), 121.21 (q, *J* = 322.4 Hz), 117.86 (d, J^2 = 23.2 Hz), 21.79; ESI-MS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO$^-$]$^+$: 343.1; found: 343.0.; ESI-HRMS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO$^-$]$^+$: 343.0911; found: 343.0912.

1-(N-(2-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ia). yellow solid (181 mg, 0.36 mmol, 71%). ^{1}H NMR (301 MHz, METHANOL-D3) δ 9.41 (d, *J* = 6.0 Hz, 2H), 8.84 (t, *J* = 7.7 Hz, 1H), 8.26 (t, *J* = 7.0 Hz, 1H), 8.06 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.61 - 7.48 (m, 5H), 2.49 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3) δ 149.89, 148.25, 148.16 (2×CH), 135.57, 133.79, 133.55, 131.64, 131.43, 131.20, 130.80 (2×CH), 129.82 (2×CH), 129.09 (2×CH), 128.90, 120.46 (q, *J* = 318.5 Hz), 20.55; ESI-MS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO$^-$]$^+$: 359.1; found: 359.0; ESI-HRMS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO$^-$]$^+$: 359.0616; found: 359.0616.

1-(N-(3-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ja). yellow solid (183 mg, 0.36 mmol, 72%).^{1}H NMR (400 MHz, METHANOL-D3) δ 9.40 (dd, *J* = 4.2, 2.5 Hz, 2H), 8.85 (t, *J* = 7.8 Hz, 1H), 8.27 (t, *J* = 7.5 Hz, 1H), 7.81 (t, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.59 - 7.55 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 149.92, 148.20, 148.11 (2×CH), 138.29, 135.49, 131.51, 131.49, 131.22, 130.84 (2×CH), 130.04 (2×CH), 129.02 (2×CH), 128.78, 126.87, 120.46 (q, *J* = 318.5 Hz), 20.53; ESI-MS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO$^-$]$^+$: 359.1; found: 359.0.; ESI-HRMS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO$^-$]$^+$: 359.0616; found: 359.0616.

1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ka). yellow solid (214 mg, 0.36 mmol, 84%).^{1}H NMR (400 MHz, METHANOL-D3) δ 9.40 (dd, *J* = 4.2, 2.5 Hz, 2H), 8.85 (t, *J* = 7.8 Hz, 1H), 8.27 (t, *J* = 7.5 Hz, 1H), 7.81 (t, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.59 - 7.55 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 149.92, 148.20, 148.11 (2×CH), 138.29, 135.49, 131.51, 131.49, 131.22, 130.84 (2×CH), 130.04 (2×CH), 129.02 (2×CH), 128.78, 126.87, 120.46 (q, *J* = 318.5 Hz), 20.53; ESI-MS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO$^-$]$^+$: 359.1; found: 359.0.; ESI-HRMS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO$^-$]$^+$: 359.0616; found: 359.0616.

1-(N-(2-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3la). yellow solid (199 mg, 0.36 mmol, 72%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.40 (d, *J* = 6.1 Hz, 2H), 8.81 (t, *J* = 7.7 Hz, 1H), 8.23 (t, *J* = 7.1 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 8.6 Hz, 3H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 8.3 Hz, 3H), 2.45 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3) δ 149.87, 148.36, 148.05 (2×CH), 135.25, 134.80, 133.67, 131.75, 130.88, 130.82 (2×CH), 129.75 (2×CH), 129.55, 129.22 (2×CH), 125.87, 120.45 (q, *J* = 318.5 Hz), 20.58; ESI-MS: m/z calcd for C18H16BrN2O2S [M-TfO-]+: 403.0; found: 403.0; ESI-HRMS: m/z calcd for C18H16BrN2O2S [M-TfO-]+: 403.0110; found: 403.0115.

1-(N-(3-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ma). yellow solid (193 mg, 0.35 mmol, 70%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.43 (d, *J* = 5.6 Hz, 2H), 8.86 (t, *J* = 7.8 Hz, 1H), 8.27 (t, *J* = 7.5 Hz, 1H), 7.95 (t, *J* = 2.0 Hz, 1H), 7.77 - 7.67 (m, 4H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 8.1 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 149.88, 148.15 (2×CH, 1×C), 138.38, 134.47, 131.67 (2×CH), 131.35, 130.80 (2×CH), 130.00 (2×CH), 129.02 (2×CH), 127.28, 123.04, 120.48 (q, *J* = 318.4 Hz), 20.49; ESI-MS: m/z calcd for $C_{18}H_{16}BrN_2O_2S$ [M-TfO$^-$]$^+$: 403.0; found: 403.0; ESI-HRMS: m/z calcd for $C_{18}H_{16}BrN_2O_2S$ [M-TfO$^-$]$^+$: 403.0110; found: 403.0111.

1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3na). yellow solid (177 mg, 0.32 mmol, 64%). ^{1}H NMR (301 MHz, DMSO-D6) δ 9.61 (d, *J* = 5.8 Hz, 2H), 8.90 (t, *J* = 7.8 Hz, 1H), 8.35 (t, *J* = 7.3 Hz, 1H), 7.80 - 7.70 (m, 6H), 7.54 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (76 MHz, DMSO-D6) δ 150.68, 148.72 (2×CH), 147.78, 136.66, 133.86 (2×CH), 131.68, 131.47 (2×CH), 131.43 (2×CH), 130.80 (2×CH), 129.41 (2×CH), 125.47, 121.22 (q, *J* = 322.2 Hz), 21.81; ESI-MS: m/z calcd for $C_{18}H_{16}BrN_2O_2S$ [M-TfO$^-$]$^+$: 403.0; found: 413.0.; ESI-HRMS: m/z calcd for $C_{18}H_{16}BrN_2O_2S$ [M-TfO$^-$]$^+$: 403.0110; found: 403.0113.

1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3oa). yellow solid (195 mg, 0.32 mmol, 70%).^{1}H NMR (400 MHz, METHANOL-D3) δ 9.39 (d, *J* = 5.7 Hz, 2H), 8.85 (t, *J* = 7.8 Hz, 1H), 8.27 (t, *J* = 7.3 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 150.80, 149.86, 148.16, 148.07 (2×CH), 135.76, 131.23, 130.90 (2×CH), 130.84 (2×CH), 130.04 (2×CH), 129.00, 122.38, 120.42 (q, *J* = 318.5 Hz), 120.31 (q, *J* = 257.4 Hz), 20.51; ESI-MS: m/z calcd for $C_{19}H_{16}F_3N_2O_3S$ [M-TfO$^-$]$^+$: 409.1; found: 409.0; ESI-HRMS: m/z calcd for $C_{19}H_{16}F_3N_2O_3S$ [M-TfO$^-$]$^+$: 409.0828; found: 409.0829.

1-(4-methyl-N-(4-(trifluoromethyl)phenyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3pa). yellow solid (177 mg, 0.32 mmol, 65%).^{1}H NMR (301 MHz, DMSO-D6) δ 9.63 (d, *J* = 5.9 Hz, 2H), 8.93 (t, *J* = 7.6 Hz, 1H), 8.38 (t, *J* = 7.0 Hz, 2H), 7.94 (s, 4H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (76 MHz, DMSO-D6) δ 150.93, 149.07 (2×CH), 147.97, 140.94, 131.66, 131.57 (2×CH), 131.03 (q, *J* = 31.7 Hz), 130.92, 129.48 (2×CH), 128.78 (2×CH), 127.96 (q, *J* = 3.2 Hz), 124.01 (q, *J* = 272.7 Hz), 121.22 (q, *J* = 322.1 Hz), 21.83; ESI-MS: m/z calcd for $C_{19}H_{16}F_3N_2O_2S$ [M-TfO$^-$]$^+$: 393.1; found: 393.0; ESI-HRMS: m/z calcd for $C_{19}H_{16}F_3N_2O_2S$ [M-TfO$^-$]$^+$: 393.0879; found: 393.0882.

2-methyl-1-(4-methyl-N-phenylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ab). yellow solid (108 mg, 0.23 mmol, 45%). ^{1}H NMR (400 MHz, METHANOL-D3): δ 9.19 (d, *J* = 6.3 Hz, 1H), 8.75 (t, *J* = 7.7 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.16 (t, *J* = 6.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.64 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.60 - 7.50 (m, 5H), 3.05 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3): δ 161.02, 148.96, 148.05, 147.37, 136.86, 131.87, 131.59, 130.82 (2×CH), 130.47, 130.35 (2×CH), 128.93 (2×CH), 127.48, 126.86 (2×CH), 120.51 (q, *J* = 318.4 Hz), 20.53, 19.33; ESI-MS: m/z calcd for $C_{19}H_{19}N_2O_2S$ [M-TfO$^-$]$^+$: 339.1; found: 339.0; ESI-HRMS: m/z calcd for $C_{19}H_{19}N_2O_2S$ [M-TfO$^-$]$^+$: 339.1162; found: 339.1162.

1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-2-methylpyridin-1-ium trifluoromethanesulfonate (3kb). yellow solid (240 mg, 0.46 mmol, 92%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 9.16 (dd, *J* = 6.6, 1.1 Hz, 1H), 8.75 (td, *J* = 7.9, 1.2 Hz, 1H), 8.29 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.14 (td, *J* = 7.7, 1.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.67 - 7.59 (m, 2H), 7.57 (t, *J* = 2.4 Hz, 2H), 7.55 (d, *J* = 2.7 Hz, 2H), 3.03 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 161.15, 149.05, 148.24, 147.26, 136.44,

135.35, 131.67, 131.61, 130.87 (2×CH), 130.35 (2×CH), 128.97 (2×CH), 128.54 (2×CH), 127.49, 124.86 (q, J = 346.1 Hz), 20.48, 19.25; ESI-MS: m/z calcd for $C_{19}H_{18}ClN_2O_2S$ [M-TfO$^-$]$^+$: 373.0; found: 372.9; ESI-HRMS: m/z calcd for $C_{19}H_{18}ClN_2O_2S$ [M-TfO$^-$]$^+$: 373.0772; found: 373.0770.

X-ray crystal structure analysis of compound 3kb. Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH_3OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1008472. Formula: C20H18ClF3N2O5S2, M = 522.95, colourless crystal, 0.20 x 0.14 x 0.13 mm, a = 8.6089(17), b = 8.8898(18), c = 15.632(3) Å, α = 98.35(3), β = 96.13(3), γ = 104.16(3), V = 1135.0(4) Å^3, ρ_{calc} = 1.530 gcm^{-3}, μ = 0.412 mm^{-1}, Z = 2, Triclinic, space group *P-1*, λ = 0.71073 Å, T = 173(2) K. Data completeness = 0.987, Theta (max) = 27.46, R (reflections) = 0.0884, wR2 (reflections) = 0.2084 (5129).

3-methyl-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3dc). yellow solid (221 mg, 0.44 mmol, 88%). ^{1}H NMR (301 MHz, METHANOL-D3) δ 9.28 (s, 1H), 9.19 (d, J = 6.1 Hz, 1H), 8.64 (d, J = 7.9 Hz, 1H), 8.11 (dd, J = 7.8, 6.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.59 (s, 3H), 2.48 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3) δ 150.04, 147.67, 147.20, 144.88, 142.41, 142.32, 134.92, 131.79, 130.78 (2×CH), 130.61 (2×CH), 129.03 (2×CH), 128.83, 128.66 (2×CH), 120.52 (q, J = 318.4 Hz), 20.50, 19.93, 17.08; ESI-MS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO$^-$]$^+$: 353.1318; found: 353.1; ESI-HRMS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO$^-$]$^+$: 353.1318; found: 353.1319.

1-(N-(4-chlorophenyl)-4-methylphenylsulfonamido)-4-methylpyridin-1-ium trifluoromethanesulfonate (3kd). yellow solid (230 mg, 0.44 mmol, 88%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 8.87 (d, J = 6.8 Hz, 2H), 8.06 (d, J = 6.6 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 2.77 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 161.75, 145.37 (2×CH), 143.89, 141.22, 141.04, 129.96 (2×CH), 129.59 (2×CH), 129.12, 128.67, 125.66 (2×CH), 120.36 (q, J = 318.4 Hz), 117.09 (2×CH), 21.04, 20.03; ESI-HRMS: m/z calcd for $C_{19}H_{18}ClN_2O_2S$ [M-TfO$^-$]$^+$: 373.0772; found: 373.0772.

***3-ethoxy-1-(4-methyl-N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3de)*[8].** yellow solid (226 mg, 0.44 mmol, 85%). ^{1}H NMR (400 MHz, METHANOL-D4) δ 9.07 - 9.05 (m, 1H), 8.94- 8.90 (m, 1H), 8.38 - 8.32 (m, 1H), 8.09 (dd, J = 8.9, 6.3 Hz, 1H), 7.74 - 7.69 (m, 2H), 7.63 - 7.59 (m, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 4.30 (dq, J = 13.9, 7.0 Hz, 2H), 2.46 (s, 3H), 2.32 (s, 3H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, METHANOL-D4) δ 160.6, 148.9, 143.5, 140.5, 137.1, 136.1, 135.5, 132.8, 132.0, 131.9, 130.7, 130.5, 130.3, 130.0, 129.8, 129.1, 128.2, 68.4, 21.8, 21.2, 14.4.

3-chloro-1-(N-(2-fluorophenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3ff). yellow solid (177 mg, 0.34 mmol, 67%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.35 (s, 1H), 8.93 (d, J = 6.1 Hz, 1H), 8.59 (d, J = 8.3 Hz, 1H), 7.93 (t, J = 7.3 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 6.2 Hz, 2H), 7.34 - 7.25 (m, 1H), 7.19 (d, J = 6.0 Hz, 2H), 7.09 - 6.94 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 159.27 (d, J^1 = 254.0 Hz), 149.61, 147.80, 147.27, 146.75 (d, J^4 = 1.1 Hz), 137.07, 134.23 (d, J^3 = 8.4 Hz), 131.34, 131.20, 130.52 (2×CH), 129.83, 128.56 (2×CH), 125.50 (d, J^3 = 2.6 Hz), 123.71 (d, J^2 = 12.7 Hz), 120.34 (q, J = 318.3 Hz), 116.98 (d, J^2 = 20.0 Hz), 20.23; ESI-MS: m/z calcd for $C_{18}H_{15}ClFN_2O_2S$ [M-TfO$^-$]$^+$: 377.1; found: 376.9; ESI-HRMS: m/z calcd for $C_{18}H_{15}ClFN_2O_2S$ [M-TfO$^-$]$^+$: 377.0521; found: 377.0518.

1-(N-(4-bromophenyl)-4-methylphenylsulfonamido)-3-chloropyridin-1-ium trifluoromethanesulfonate (3nf). yellow solid (217 mg, 0.37 mmol, 74%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.81 (s, 1H), 9.38 (d, J = 8.2 Hz, 1H), 8.98 (d, J = 7.3 Hz, 1H), 8.27 (dd, J = 8.5, 6.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.69 - 7.62 (m, 4H), 7.52 (d, J = 8.3 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 149.71, 148.23, 147.68, 146.62, 137.44, 136.12, 133.48 (2×CH), 131.09, 130.86 (2×CH), 130.67 (2×CH), 130.12, 129.14 (2×CH), 125.75, 120.49 (q, J = 318.6 Hz), 20.57; ESI-MS: m/z calcd for $C_{18}H_{15}BrClN_2O_2S$ [M-TfO$^-$]$^+$: 437.0; found: 437.1; ESI-HRMS: m/z calcd for $C_{18}H_{15}BrClN_2O_2S$ [M-TfO$^-$]$^+$: 436.9721; found: 436.9719.

3-chloro-1-(4-methyl-N-(4-(trifluoromethoxy)phenyl)-phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3of). yellow solid (221 mg, 0.39 mmol, 78%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.72 (s, 1H), 9.27 (d, J = 6.0 Hz, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.13 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 150.38, 150.29, 148.22, 147.70, 147.58, 136.85, 135.75, 132.36 (2×CH), 131.71, 131.39 (2×CH), 130.88, 129.41 (2×CH), 123.00 (2×CH), 121.13 (d, J = 322.6 Hz), 120.30 (q, J = 257.9 Hz), 21.74; ESI-MS: m/z calcd for $C_{19}H_{15}ClF_3N_2O_3S$ [M-TfO$^-$]$^+$: 443.0; found: 443.0; ESI-HRMS: m/z calcd for $C_{19}H_{15}ClF_3N_2O_3S$ [M-TfO$^-$]$^+$: 443.0439; found: 443.0438.

3-chloro-1-(4-methyl-N-(4-(trifluoromethyl)phenyl)-phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3pf). yellow solid (179 mg, 0.31 mmol, 62%). ^{1}H NMR (400 MHz, DMSO-D6) δ 10.09 (s, 1H), 9.56 (d, J = 5.9 Hz, 1H), 9.03 (d, J = 8.2 Hz, 1H), 8.35 (t, J = 7.2 Hz, 1H), 7.90 (dd, J = 20.1, 8.5 Hz, 4H), 7.75 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 150.55, 148.46, 147.93, 147.85, 140.60, 136.98, 131.65, 131.48, 131.24 (q, J = 32.6 Hz), 130.98, 129.53 (4×CH), 127.78 (q, J = 3.1 Hz), 123.99 (q, J = 272.7 Hz), 121.18 (q, J = 322.2 Hz), 21.79; ESI-MS: m/z calcd for $C_{19}H_{15}ClF_3N_2O_2S$ [M-TfO$^-$]$^+$: 427.0; found: 427.0.; ESI-HRMS: m/z calcd for $C_{19}H_{15}ClF_3N_2O_2S$ [M-TfO$^-$]$^+$: 427.0489; found: 427.0487.

3-chloro-1-(N-(4-(methoxycarbonyl)phenyl)-4-methylphenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3qf). yellow solid (210 mg, 0.37 mmol, 74%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.77 (s, 1H), 9.32 (d, J = 6.1 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H), 8.23 (t, J = 7.3 Hz, 1H), 8.02 (d, J = 8.5 Hz, 2H), 7.72 (dd, J = 8.3, 1.2 Hz, 4H), 7.46 (d, J = 8.1 Hz, 2H), 3.83 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 165.49, 149.93, 148.31, 147.92, 146.92, 140.84, 137.51, 132.06, 131.11 (2×CH), 130.88 (2×CH), 130.17, 129.13 (2×CH), 127.60 (2×CH), 120.37 (q, J = 318.2 Hz), 51.79, 20.52; ESI-MS: m/z calcd for $C_{20}H_{18}ClN_2O_4S$ [M-TfO$^-$]$^+$: 417.1; found: 417.1; ESI-HRMS: m/z calcd for $C_{20}H_{18}ClN_2O_4S$ [M-TfO$^-$]$^+$: 417.0670; found: 417.0670.

***1-(N-(p-tolyl)phenylsulfonamido)pyridin-1-ium trifluoromethanesulfonate (3dg)*[8].** yellow solid (209 mg, 0.44 mmol, 88%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.44 (dd, J = 5.3, 1.4 Hz, 2H), 8.84 (td, J = 7.8, 1.2 Hz, 1H), 8.27 (t, J = 7.5 Hz, 1H), 7.90 - 7.83 (m, 1H), 7.73 - 7.65 (m, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ: 149.64, 147.96 (2×CH), 142.59, 135.79, 134.84, 134.70, 130.86 (2×CH), 130.13 (2×CH), 129.95 (2×CH), 128.95 (2×CH), 128.77 (2×CH), 120.48 (q, J = 318.6 Hz), 19.93; ESI-MS: m/z calcd for $C_{18}H_{17}N_2O_2S$ [M-TfO$^-$]$^+$: 325.1; found: 325.1; ESI-HRMS: m/z calcd for $C_{18}H_{17}N_2O_2S$ [M-TfO$^-$]$^+$: 325.1005; found: 325.1006.

***1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium hexafluorophosphate(V) (4aa)*[8].** yellow solid (106 mg, 0.23 mmol,

45%). ^{1}H NMR (301 MHz, DMSO-D6) δ 8.99 (dd, *J* = 6.6, 1.2 Hz, 2H), 8.68 (tt, *J* = 8.0, 1.3 Hz, 1H), 8.20 (dd, *J* = 7.7, 6.7 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.25 - 7.11 (m, 4H), 6.71 (t, *J* = 6.9 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR: (76 MHz, DMSO-D6): δ 147.22 (2×CH), 146.14, 144.18, 143.71, 139.95, 134.81, 131.43, 129.25 (2×CH), 127.70 (2×CH), 126.59 (2×CH), 125.95, 121.33, 116.73, 21.37; ESI-MS: m/z calcd for $C_{18}H_{17}N_2O_2S$ [M-PF_6^-]$^+$: 325.1; found: 325.1; ESI-HRMS: m/z calcd for $C_{18}H_{17}N_2O_2S$ [M-PF_6^-]$^+$: 325.1005; found: 325.1004.

1-(3-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ba). yellow solid (142 mg, 0.29 mmol, 58%). ^{1}H NMR (400 MHz, METHANOL-D3): δ 9.04 (d, *J* = 5.8 Hz, 2H), 8.70 (t, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 6.9 Hz, 1H), 7.58 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.53 - 7.44 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.39 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 146.83 (2×CH), 146.77, 144.67, 141.96, 139.85, 137.07, 134.14, 129.75 (2×CH), 129.04, 128.61, 127.33 (2×CH), 126.76 (2×CH), 124.87, 120.44 (q, *J* = 318.2 Hz), 20.21, 16.35; ESI-MS: m/z calcd for $C_{19}H_{19}N_2O_2S$ [M-TfO^-]$^+$: 339.1; found: 339.0; ESI-HRMS: m/z calcd for $C_{19}H_{19}N_2O_2S$ [M-TfO^-]$^+$: 339.1162; found: 339.1159.

1-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4da). yellow solid (188 mg, 0.39 mmol, 77%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 9.00 (d, *J* = 6.3 Hz, 2H), 8.77 (t, *J* = 7.8 Hz, 1H), 8.24 (t, *J* = 6.7 Hz, 2H), 7.58 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 3H), 6.83 (d, *J* = 8.2 Hz, 1H), 3.39 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3) δ 146.74, 146.57 (2×CH), 144.31, 139.77, 139.60, 135.85, 132.67, 129.55 (2×CH), 128.73, 128.65, 127.48 (2×CH), 127.34, 127.07 (2×CH), 120.37 (q, *J* = 318.3 Hz), 20.23, 19.54; ESI-MS: m/z calcd for $C_{19}H_{19}N_2O_2S$ [M-TfO^-]$^+$: 339.1; found: 339.0; ESI-HRMS: m/z calcd for $C_{19}H_{19}N_2O_2S$ [M-TfO^-]$^+$: 339.1162; found: 339.1162.

X-ray crystal structure analysis of compound 4da. Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH_3OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1008474. Formula: C19H19F6N2O2PS, *M* = 484.40, colourless crystal, 0.48 x 0.43 x 0.26 mm, *a* = 15.338(3), *b* = 10.040(2), *c* = 14.189(3) Å, *α* = 90, *β* = 94.34(3), *γ* = 90, *V* = 2178.7(8) Å^3, ρ_{calc} = 1.477 gcm^{-3}, μ = 0.291 mm^{-1}, *Z* = 4, Monoclinic, space group *P2(1)c*, *λ* = 0.71073 Å, *T* = 173(2) K. Data completeness = 0.997, Theta (max) = 27.48, R (reflections) = 0.0811, wR2 (reflections) = 0.2007 (4971).

1-(3,5-dimethyl-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4ea). yellow solid (121 mg, 0.24 mmol, 48%). ^{1}H NMR (400 MHz, METHANOL-D3): δ 9.06 (d, *J* = 5.9 Hz, 2H), 8.75 (t, *J* = 7.8 Hz, 1H), 8.22 (t, *J* = 7.2 Hz, 2H), 7.53 - 7.41 (m, 3H), 7.34 (d, *J* = 8.3 Hz, 3H), 2.45 (s, 6H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3): δ 146.76 (2×CH), 146.64, 144.55, 141.69, 140.06, 139.41, 137.11, 134.58, 129.72 (2×CH), 127.26 (2×CH), 126.78 (2×CH), 125.80, 125.30, 120.48 (q, *J* = 318.7 Hz), 20.20, 19.58, 16.28; ESI-MS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1; found: 353.1; ESI-HRMS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1312; found: 353.1312.

1-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ha). yellow solid (182 mg, 0.37 mmol, 74%). ^{1}H NMR (301 MHz, METHANOL-D3) δ 9.03 (d, *J* = 5.7 Hz, 2H), 8.75 (t, *J* = 7.9 Hz, 1H), 8.21 (dd, *J* = 7.5, 6.8 Hz, 2H), 7.67 (dd, *J* = 8.1, 2.9 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.34 - 7.23 (m, 3H), 6.86 (dd, *J* = 8.9, 5.2 Hz, 1H), 2.35 (d, *J* = 17.5 Hz, 3H); ^{13}C NMR (76 MHz, METHANOL-D3) δ 162.50 (d, J^1 = 251.1 Hz), 148.67, 147.98 (2×CH), 145.95, 142.16 (d, J^3 = 10.6 Hz), 136.53, 132.33, 132.21, 130.91 (2×CH), 128.85 (2×CH), 128.45 (2×CH), 121.69 (q, *J* = 318.3 Hz), 120.39 (d, J^2 = 22.3 Hz), 116.37 (d, J^2 = 27.6 Hz), 21.47; ESI-MS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO^-]$^+$: 343.1; found: 343.1; ESI-HRMS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO^-]$^+$: 343.0911; found: 343.0907.

1-(5-chloro-2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ka). yellow solid (160 mg, 0.32 mmol, 63%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 8.92 (d, *J* = 5.8 Hz, 2H), 8.75 (t, *J* = 7.9 Hz, 1H), 8.21 (t, *J* = 6.8 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 146.76, 146.49 (2×CH), 143.21, 141.00, 138.11, 131.78, 129.41 (2×CH), 129.13, 128.68 (2×CH), 127.53 (2×CH), 126.58, 126.44, 125.67, 120.37 (q, *J* = 318.2 Hz), 20.16; ESI-MS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO^-]$^+$: 359.1; found: 359.0; ESI-HRMS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO^-]$^+$: 359.0616; found: 359.0614.

2-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4db). yellow solid (196 mg, 0.39 mmol, 78%). ^{1}H NMR (400 MHz, METHANOL-D3): δ 8.80 (d, *J* = 6.0 Hz, 1H), 8.64 (t, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 6.8 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 3H), 7.39 (d, *J* = 8.1 Hz, 3H), 6.78 (d, *J* = 8.2 Hz, 1H), 2.62 (s, 3H), 2.44 (dd, *J* = 13.6, 2.1 Hz, 6H); ^{13}C NMR (101 MHz, METHANOL-D3): δ 157.08, 147.57, 146.84, 144.65, 140.61, 135.72, 132.89, 129.66 (2×CH), 129.28, 128.98, 128.43, 127.85, 127.23 (2×CH), 126.42, 124.68, 120.48 (q, *J* = 318.6 Hz), 20.25, 20.11, 19.58; ESI-MS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1; found: 353.1; ESI-HRMS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1318; found: 353.1315.

3-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4dc). yellow solid (191 mg, 0.38 mmol, 76%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 8.82 (s, 1H), 8.74 (d, *J* = 3.5 Hz, 1H), 8.53 (d, *J* = 7.9 Hz, 1H), 8.04 (dd, *J* = 7.1, 4.3 Hz, 1H), 7.52 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 3H), 6.78 (s, 1H), 2.61 (s, 3H), 2.41 (s, 6H); ^{13}C NMR (76 MHz, METHANOL-D3) δ 147.03 (2×CH), 146.19, 144.01, 143.78, 139.57, 139.19, 138.86, 136.65, 132.40, 129.41 (2×CH), 128.45, 127.02 (2×CH), 126.66 (2×CH), 120.49 (q, *J* = 318.7 Hz), 20.16, 19.39, 17.18; ESI-MS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.13; found: 353.1; ESI-HRMS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1318; found: 353.1319.

4-methyl-1-(5-methyl-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4dd). yellow solid (201 mg, 0.4 mmol, 80%). ^{1}H NMR (400 MHz, METHANOL-D3): δ 8.81 (d, *J* = 6.8 Hz, 2H), 8.04 (d, *J* = 6.4 Hz, 2H), 7.55 (d, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 6.0, 5.4 Hz, 3H), 6.78 (d, *J* = 8.2 Hz, 1H), 2.79 (s, 3H), 2.44 (s, 6H); ^{13}C NMR (101 MHz, METHANOL-D3): δ 145.40 (2×CH), 144.40, 140.00, 139.72, 135.78, 132.48, 129.51 (3×CH), 128.84, 128.40, 128.36, 127.87, 127.43, 127.14 (2×CH), 120.49 (q, *J* = 318.5 Hz), 20.21, 20.06, 19.53; ESI-MS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1; found: 353.1; ESI-HRMS: m/z calcd for $C_{20}H_{21}N_2O_2S$ [M-TfO^-]$^+$: 353.1318; found: 353.1319.

3-ethoxy-1-(5-methyl-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium hexafluorophosphate(V) (4de)[8]. yellow solid (193 mg, 0.37 mmol, 73%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 8.68 (s, 1H), 8.50 (d, *J* = 5.8 Hz, 1H), 8.27 (dt, *J* = 16.8, 8.4 Hz, 1H), 8.07 (dd, *J* = 8.8, 5.8 Hz, 1H), 7.59 - 7.44 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 3H), 6.89 (d, *J* = 8.1 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 2.41 (d, *J* = 16.8 Hz, 6H), 1.54 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 157.79, 143.89, 139.53, 138.71, 138.59, 136.84, 134.40, 132.49, 131.88, 129.75, 129.46 (2×CH), 128.24, 127.66, 127.13, 126.93 (2×CH), 66.37, 20.19, 19.45, 13.32; ESI-MS: m/z calcd for $C_{21}H_{23}N_2O_3S$ [M-PF_6^-]$^+$: 383.1; found: 383.1; ESI-

HRMS: m/z calcd for $C_{21}H_{23}N_2O_3S$ [M-PF_6^-]$^+$: 383.1424; found: 383.1420.

3-fluoro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4ah). yellow solid (194 mg, 0.4 mmol, 79%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 9.04 (d, *J* = 6.1 Hz, 1H), 8.76 (dd, *J* = 16.7, 8.5 Hz, 1H), 8.35 (dt, *J* = 8.9, 5.7 Hz, 1H), 7.81 (dd, *J* = 8.8, 3.8 Hz, 1H), 7.67 - 7.42 (m, 5H), 7.37 (t, *J* = 8.6 Hz, 2H), 7.04 - 6.94 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 160.34 (d, J^1 = 255.4 Hz), 144.62, 144.06 (d, J^4 = 3.4 Hz), 139.40, 135.37, 134.35 (d, J^2 = 18.6 Hz), 132.58, 131.11, 129.81, 129.58 (2×CH), 128.93 (d, J^2 = 8.1 Hz), 128.77 (d, J^3 = 7.4 Hz), 127.77, 127.16 (2×CH), 127.08, 120.44 (q, *J* = 318.5 Hz), 20.20; ESI-MS: m/z calcd for $C_{18}H_{16}FN_2O_2S$ [M-TfO^-]$^+$:343.1; found:343.0; ESI-HRMS: m/z calcd for $C_{18}H_{16}FN_2O_2S$[M-TfO^-]$^+$: 343.0911; found: 343.0911.

3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4hh). yellow solid (217 mg, 0.4 mmol, 85%). ^{1}H NMR (600 MHz, METHANOL-D3) δ 9.54 (s, 1H), 9.13 (d, *J* = 5.6 Hz, 1H), 8.82 (t, *J* = 7.9 Hz, 1H), 8.42 (dt, *J* = 8.9, 5.4 Hz, 1H), 7.84 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 8.2 Hz, 3H), 6.97 (dd, *J* = 8.6, 5.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (151 MHz, METHANOL-D3): δ 162.66 (d, J^1 = 251.8 Hz), 161.64 (d, J^1 = 256.2 Hz), 146.21, 145.43 (d, J^4 = 2.3 Hz), 141.68 (d, J^3 = 9.0 Hz), 138.47 (d, J^2 = 38.6 Hz), 136.24, 136.14 (d, J^3 = 3.0 Hz), 132.57 (d, J^2 = 8.4 Hz), 130.96 (2×CH), 130.35 (d, J^3 = 7.4 Hz), 128.53 (2×CH), 128.25 (d, J^4 = 2.0 Hz), 121.70 (q, *J* = 318.2 Hz), 120.81 (d, J^2 = 22.2 Hz), 116.45 (d, J^2 = 28.0 Hz), 21.47; ESI-MS: m/z calcd for $C_{18}H_{15}F_2N_2O_2S$ [M-TfO^-]$^+$: 361.1; found: 361.0; ESI-HRMS: m/z calcd for $C_{18}H_{15}F_2N_2O_2S$ [M-TfO^-]$^+$: 361.0817; found: 361.0807.

***3-chloro-1-(2-(4-methylphenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4af)*[8].** yellow solid (193 mg, 0.38 mmol, 76%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 9.41 (s, 1H), 9.07 (d, *J* = 6.0 Hz, 1H), 8.86 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 7.1 Hz, 1H), 7.9 - 7.7 (m, 1H), 7.53 (d, *J* = 7.4 Hz, 4H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.05 (d, *J* = 25.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 147.97, 147.53, 146.81, 145.98, 140.73, 136.46, 136.34, 133.82, 132.08, 130.84 (2×CH), 130.26, 129.81, 129.38, 128.44 (2×CH), 126.90, 121.72 (q, *J* = 318.5 Hz), 21.49; ESI-MS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO^-]$^+$: 359.1; found: 359.1; ESI-HRMS: m/z calcd for $C_{18}H_{16}ClN_2O_2S$ [M-TfO^-]$^+$: 359.0616; found: 359.0613.

3-chloro-1-(3-fluoro-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4ff). yellow solid (110 mg, 0.21 mmol, 42%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.58 (s, 1H), 9.18 (d, *J* = 6.0 Hz, 1H), 8.92 - 8.86 (m, 1H), 8.28 (dd, *J* = 8.5, 6.1 Hz, 1H), 7.66 (ddd, *J* = 13.2, 9.6, 6.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 - 7.40 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, METHANOL-D3) δ 158.63 (d, J^1 = 254.9 Hz), 147.04, 146.36, 145.60, 144.62, 136.03, 135.21, 130.10 (d, J^3 = 9.2 Hz), 129.54, 129.40 (2×CH, 1×C), 128.07, 126.97 (2×CH), 122.84 (d, J^4 = 2.3 Hz), 120.43 (q, *J* = 318.2 Hz), 119.62 (d, J^2 = 21.0 Hz), 20.19; ESI-MS: m/z calcd for $C_{18}H_{15}ClFN_2O_2S$ [M-TfO^-]$^+$: 377.1; found: 377.0; ESI-HRMS: m/z calcd for $C_{18}H_{15}ClFN_2O_2S$ [M-TfO^-]$^+$: 377.0521; found: 377.0523.

3-chloro-1-(5-fluoro-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4hf). yellow solid (197 mg, 0.38 mmol, 75%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 9.53 (s, 1H), 9.15 (d, *J* = 5.3 Hz, 1H), 8.92 (d, *J* = 8.4 Hz, 1H), 8.31 (dd, *J* = 7.9, 5.7 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 12.1 Hz, 3H), 6.93 (dd, *J* = 8.0, 4.9 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3) δ161.35 (d, J^1 = 251.6 Hz), 147.18, 146.35, 145.57, 144.89, 140.35 (d, J^3 = 13.7 Hz), 135.26, 135.14, 134.85, 131.17 (d, J^3 = 8.8 Hz), 129.67 (2×CH), 128.16, 127.25 (2×CH), 120.44 (q, *J* = 318.6 Hz), 119.48 (d, J^2 = 22.4 Hz), 115.16 (d, J^2 = 27.7 Hz), 20.25; ESI-MS: m/z calcd for $C_{18}H_{15}ClFN_2O_2S$ [M-TfO^-]$^+$: 377.1; found: 377.0; ESI-HRMS: m/z calcd for $C_{18}H_{15}ClFN_2O_2S$ [M-TfO^-]$^+$: 377.0521; found: 377.0514.

3-fluoro-1-(5-fluoro-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4kf). yellow solid (147 mg, 0.38 mmol, 75%). ^{1}H NMR (301 MHz, METHANOL-D3): δ 9.23 (s, 1H), 8.91 (d, *J* = 5.8 Hz, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 8.16 (dd, *J* = 8.2, 6.2 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (76 MHz, METHANOL-D3): δ 147.63, 147.37, 146.71, 144.24, 139.89, 138.69, 137.44, 136.34, 133.30, 130.62 (2×CH), 129.55, 129.28, 128.21, 127.79 (2×CH), 127.51, 121.75 (q, *J* = 319.2 Hz), 21.43; ESI-MS: m/z calcd for $C_{18}H_{15}Cl_2N_2O_2S$ [M-TfO^-]$^+$: 393.0; found: 393.1; ESI-HRMS: m/z calcd for $C_{18}H_{15}Cl_2N_2O_2S$ [M-TfO^-]$^+$: 393.0226; found: 393.0224.

1-(5-bromo-2-(4-methylphenylsulfonamido)phenyl)-3-chloropyridin-1-ium trifluoromethanesulfonate (4nf). yellow solid (199 mg, 0.34 mmol, 68%). ^{1}H NMR (400 MHz, DMSO-D6) δ 9.49 (s, 1H), 9.06 (d, *J* = 5.1 Hz, 1H), 8.91 (d, *J* = 8.2 Hz, 1H), 8.27 (t, *J* = 6.3 Hz, 1H), 7.89 (s, 1H), 7.52 (t, *J* = 8.7 Hz, 3H), 7.26 (d, *J* = 7.1 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 146.67, 146.32, 146.02, 145.98, 142.29, 139.90, 136.33, 134.97, 134.29, 134.16, 129.84 (2×CH), 129.48, 128.54, 126.77 (2×CH), 125.57, 120.99 (q, *J* = 321.7 Hz), 21.39; ESI-MS: m/z calcd for $C_{18}H_{15}BrClN_2O_2S$ [M-TfO^-]$^+$: 437.0; found: 437.2; ESI-HRMS: m/z calcd for $C_{18}H_{15}BrClN_2O_2S$ [M-TfO^-]$^+$: 436.9721; found: 436.9722.

3-chloro-1-(2-(4-methylphenylsulfonamido)-5-(trifluoromethoxy)phenyl)pyridin-1-ium trifluoromethanesulfonate (4of). yellow solid (193 mg, 0.33 mmol, 65%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.46 (s, 1H), 9.08 (d, *J* = 5.3 Hz, 1H), 8.86 (d, *J* = 8.2 Hz, 1H), 8.24 (t, *J* = 6.2 Hz, 1H), 7.88 (s, 1H), 7.58 - 7.46 (s, 3H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.06 (d, *J* = 7.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 147.37, 146.96, 146.26, 145.09, 144.06, 137.45, 136.85, 134.43, 130.23 (2×CH), 128.84, 127.87, 127.27 (2×CH), 126.31 (q, *J* = 63.0 Hz), 125.39, 122.76, 121.15 (q, *J* = 322.2 Hz), 120.40 (q, *J* = 258.0 Hz), 21.51; ESI-MS: m/z calcd for $C_{19}H_{15}ClF_3N_2O_3S$ [M-TfO^-]$^+$: 443.0; found: 443.1; ESI-HRMS: m/z calcd for $C_{19}H_{15}ClF_3N_2O_3S$ [M-TfO^-]$^+$: 443.0439; found: 443.0436.

Synthesis of methyl 4-(4-methylphenylsulfonamido)benzoate (7). $Cu(OTf)_2$ (18.1 mg, 0.05 mmol) was added to a mixture of mesityl(4-(methoxycarbonyl)phenyl)iodonium trifluoromethanesulfonate **1q** (265.2mg, 0.5mmol) and (3-chloropyridin-1-ium-1-yl)(tosyl)amide **2f** (141.4mg, 0.5mmol) in a sealed tube. Then the tube was evacuated and recharged with N_2 for 3 times. After 2 mL of dichloroethane was added, the tube was sealed and the mixture was allowed to stir at 130 ℃ for 48 h until completion of the reaction checked by TLC. At last the desired compound **7** was purified by silica gel column chromatography petroleum ether/ethyl acetate = 10:1) as a yellow solid (93 mg, 0.3 mmol, 61%). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.26 (s, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 166.50, 14 4.52, 141.07, 135.79, 131.18 (2×CH), 129.96 (2×CH), 127.35 (2×CH), 126.22, 119.06 (2×CH), 52.22, 21.67; ESI-MS: m/z calcd for $C_{15}H_{16}NO_4S$ [M+H]$^+$: 306.1; found: 306.6; ESI-HRMS: m/z calcd for $C_{15}H_{16}NO_4S$ [M+H]$^+$: 306.0800; found: 306.0801.

3-chloro-1-(4-methyl-2-(4-methylphenylsulfonamido)-phenyl)pyridin-1-ium trifluoromethanesulfonate (4cf-1), 3-chloro-1-(2-methyl-6-(4-methylphenylsul-

fonamido)phenyl)pyridin-1-ium trifluorometh-anesulfonate (4cf-2). yellow solid (178 mg, 0.34 mmol, 68% (3: 2)). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.38 (s, 2H), 9.02 (d, *J* = 6.0 Hz, 1H), 8.97 (d, *J* = 6.1 Hz, 1H), 8.89 (dd, *J* = 8.7, 0.9 Hz, 1H), 8.81 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.27 (dd, *J* = 8.5, 6.1 Hz, 1H), 8.22 (dd, *J* = 8.5, 6.2 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.44 - 7.37 (m, 2H), 7.37 - 7.31 (m, 4H), 6.75 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.69 (s, 1H), 2.42 (s, 5H), 2.26 (s, 3H), 2.18 (s, 2H); ^{13}C NMR (101 MHz, METHANOL-D3) δ 147.19, 146.91, 146.40, 146.23 (1×CH, 1×C), 145.59, 144.52, 144.48, 143.73, 139.00, 136.94, 135.75, 135.50, 135.44, 135.10, 134.83, 132.10, 131.89, 130.92, 130.42, 129.58 (2×CH), 129.50 (2×CH), 129.07, 129.00, 128.39, 128.05, 127.21 (2×CH), 127.15 (2×CH), 126.66, 126.28, 125.20, 122.03, 118.86, 115.69, 20.24, 20.23, 19.77, 16.28; ESI-MS: m/z calcd for $C_{19}H_{18}ClN_2O_2S$ [M-TfO$^-$]$^+$: 373.1; found: 373.1; ESI-HRMS: m/z calcd for $C_{19}H_{18}ClN_2O_2S$ [M-TfO$^-$]$^+$: 373.0772; found: 373.0774.

***1-(5-methyl-2-(phenylsulfonamido)phenyl)pyridin-1-ium trifluoromethanesulfonate (4dg)*[8].** yellow solid (178 mg, 0.38 mmol, 75%). ^{1}H NMR (400 MHz, METHANOL-D3) δ 9.06 (d, *J* = 5.5 Hz, 2H), 8.77 (t, *J* = 7.9 Hz, 1H), 8.24 (t, *J* = 6.8 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.63 - 7.56 (m, 3H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, METHANOL-D3) δ: 146.92, 146.70 (2×CH), 140.60, 140.15, 138.14, 133.34, 132.72, 129.06 (2×CH), 128.90, 127.63, 127.57, 127.51 (2×CH), 127.17 (2×CH), 120.45 (q, *J* = 318.5 Hz), 19.56; ESI-MS: m/z calcd for $C_{18}H_{17}N_2O_2S$ [M-TfO$^-$]$^+$: 325.1; found: 325.2; ESI-HRMS: m/z calcd for $C_{18}H_{17}N_2O_2S$ [M-TfO$^-$]$^+$: 325.1005; found: 325.1004.

(Z)-1-((phenoxy(phenyl)methylene)amino)pyridin-1-ium hexafluorophosphate(V) (6a). $Cu(OTf)_2$ (18.1 mg, 0.05 mmol) was added to a mixture of diphenyliodonium hexafluorophosphate(V) **1a** (213 mg, 0.5mmol) and benzoyl(pyridin-1-ium-1-yl)amide **5a** (99.1 mg, 0.5mmol) in a sealed tube. Then the tube was evacuated and recharged with N_2 for 3 times. After 2 mL of dichloroethane was added, the tube was sealed and the mixture was allowed to stir at 130 ℃ for 48 h until completion of the reaction checked by TLC. At last the desired compound **6a** was purified by silica gel column chromatography (dichloromethane/petroleum ether/methanol = 5:3:1) as a yellow solid (137 mg, 0.33 mmol, 65%). ^{1}H NMR (301 MHz, DMSO-D6): δ 9.24 (d, *J* = 5.9 Hz, 2H), 8.52 (t, *J* = 8.3 Hz, 1H), 8.19 (t, *J* = 7.1 Hz, 2H), 7.77 - 7.69 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.26 - 7.17 (m, 2H), 7.09 (dd, *J* = 17.5, 7.4 Hz, 3H); ^{13}C NMR (76 MHz, DMSO-D6) δ 166.95, 153.26, 144.50, 141.60, 141.31, 133.32, 130.11 (4×CH), 128.88 (2×CH), 128.67 (2×CH), 126.76, 126.16, 119.86 (2×CH); ESI-MS: m/z calcd for $C_{18}H_{15}N_2O$ [M-PF_6^-]$^+$: 275.1; found: 275.2.; ESI-HRMS: m/z calcd for $C_{18}H_{15}N_2O$ [M-PF_6^-]$^+$: 275.1179; found: 275.1178.

X-ray crystal structure analysis of compound 6a. Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in CH_3OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1008473. Formula: C18H15F6N2OP, *M* = 420.29, colourless crystal, 0.28 x 0.25 x 0.19 mm, *a* = 13.927(3), *b* = 10.771(2), *c* = 24.361(5) Å, *α* = 90, *β* = 93.49(3), *γ* = 90, *V* = 3647.6(13) Å^3, ρ_{calc} = 1.531 gcm^{-3}, *μ* = 0.221 mm^{-1}, *Z* = 8, Monoclinic, space group *C2/c*, *λ* = 0.71073 Å, *T* = 173(2) K. Data completeness = 0.997, Theta (max) = 27.47, R (reflections) = 0.0567, wR2 (reflections) = 0.1107 (4173).

Synthesis of (Z)-3-methyl-1-((phenoxy(phenyl)methylene)amino)-pyridin-1-ium hexafluorophosphate(V) (6b). $Cu(OTf)_2$ (18.1 mg, 0.05 mmol) was added to a mixture of diphenyliodonium hexafluorophosphate(V) **1a** (213 mg, 0.5mmol) and (2-methylpyridin-1-ium-1-yl)(tosyl)amide **5b** (131.2 mg, 0.5mmol) in a sealed tube. Then the tube was evacuated and recharged with N_2 for 3 times. After 2 mL of dichloroethane was added, the tube was sealed and the mixture was allowed to stir at 130 ℃ for 48 h until completion of the reaction checked by TLC. At last the desired compound **6b** was purified by silica gel column chromatography (dichloromethane/petroleum ether/methanol = 5:3:1) as a yellow solid (145 mg, 0.34 mmol, 67%). ^{1}H NMR (301 MHz, DMSO-D6) δ 9.23 (s, 1H), 9.17 (d, *J* = 6.1 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.17 (t, *J* = 7.1 Hz, 1H), 7.85 - 7.75 (m, 2H), 7.62 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.52 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.30 (dd, *J* = 11.2, 4.5 Hz, 2H), 7.24 - 7.10 (m, 3H), 2.53 (s, 3H); ^{13}C NMR (76 MHz, DMSO-D6): δ 167.34, 153.75, 145.31, 141.19, 140.23, 139.12, 133.84, 130.62 (2×CH), 130.52 (2×CH), 129.44 (2×CH), 128.33, 127.35, 126.66, 120.40 (2×CH), 18.47; ESI-MS: m/z calcd for $C_{19}H_{17}N_2O$ [M-PF_6^-]$^+$: 289.1; found: 289.1; ESI-HRMS: m/z calcd for $C_{19}H_{17}N_2O$ [M-PF_6^-]$^+$: 289.1334; found: 289.1333.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Spectra of synthesized compounds (**3, 4, 6a, 6b** and **7**). See DOI:DOI: 10.1039/b000000x/

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