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Exploiting the narrow gap of rearrangement between the substituents in the vicinal disubstitution reactions of diaryliodonium salts with pyridine *N*-sulfonamidates†

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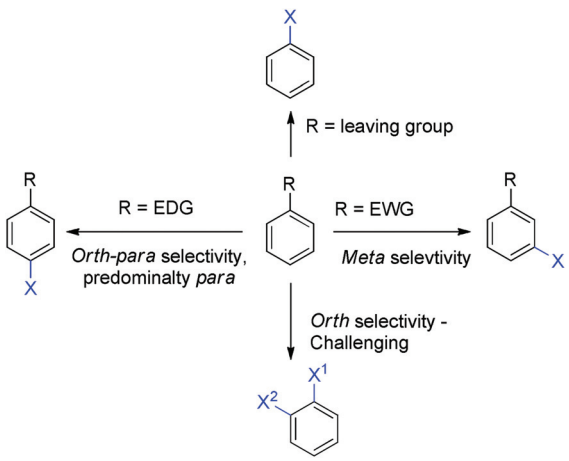
The vicinal disubstitution reactions of diaryliodonium salts with pyridine *N*-sulfonamidates to give *o*-pyridinium anilines were fully examined. A reaction pathway of N-arylation occurring at the amidate group followed by a radical rearrangement is proposed. The electronic effects of various substituents in this radical rearrangement were investigated.

Introduction

Polysubstituted benzene derivatives are very important compounds in organic chemistry, natural product chemistry, pharmaceutical chemistry and materials science.[1] Consequently, there is a vast and long-term demand for the regio-selective organic synthesis of benzene derivatives with multiple substituents. In addition to the assembly of benzene rings using small acyclic molecules (*e.g.*, Reepe-type reactions),[2] more practical and efficient approaches towards polysubstituted benzene derivatives are traditionally based on aromatic substitution on the C–H bond, which introduces a substituent on the given arene with various substitution effects. A majority of these synthetic methodologies are based on electrophilic substitution,[3] but the additional substituent is usually introduced at the *meta* position [when R is an electron withdrawing group (EWG)] or the *para* position [when R is an electron donating group (EDG)] (Scheme 1). Regio-selectively introducing a substituent on the *ortho* position of the benzene ring is less common and more challenging. The use of a directing group is the main approach to introducing a substituent at the *ortho* C–H bond (*via* ortho-metallation[4] or C–H activation catalyzed by transition metals[5]), but the scope of this reaction is highly restricted in nature. The Fries rearrangement is also an efficient and regio-selective way of synthesizing *ortho*-substituted benzene derivatives.[6]



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

As part of our ongoing interest in the efficient synthesis of polysubstituted benzene derivatives, we have previously reported a vicinal disubstitution reaction of diaryliodonium salts with pyridine *N*-oxides (reaction 1).[8] The reaction provided a selective technique to introduce two substituents at the *ortho*- and *ipso*-positions of the benzene ring simultaneously (reaction 2). Interestingly, this vicinal disubstitution reaction is also applicable to pyridine *N*-sulfonamidate,[9] where *o*-pyridinium aniline is isolated instead. In our previously published work,[7] a pathway of N-arylation at the amidate group followed by a radical rearrangement was proposed for the reaction. In this paper the effect of substituents on this radical rearrangement is reported.

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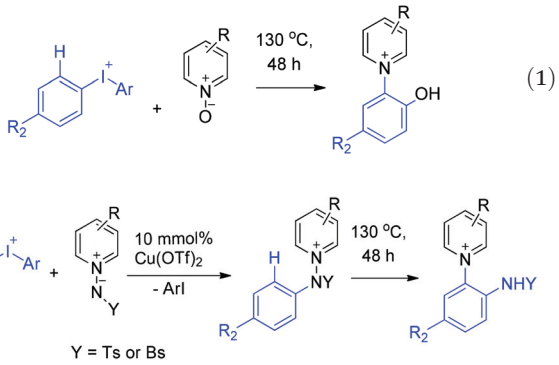
†Electronic supplementary information (ESI) available: Spectra of synthesized compounds (**3**, **4**, **6a**, **6b** and **7**). CCDC 1008472–1008474. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob01744g



(1)

(2)

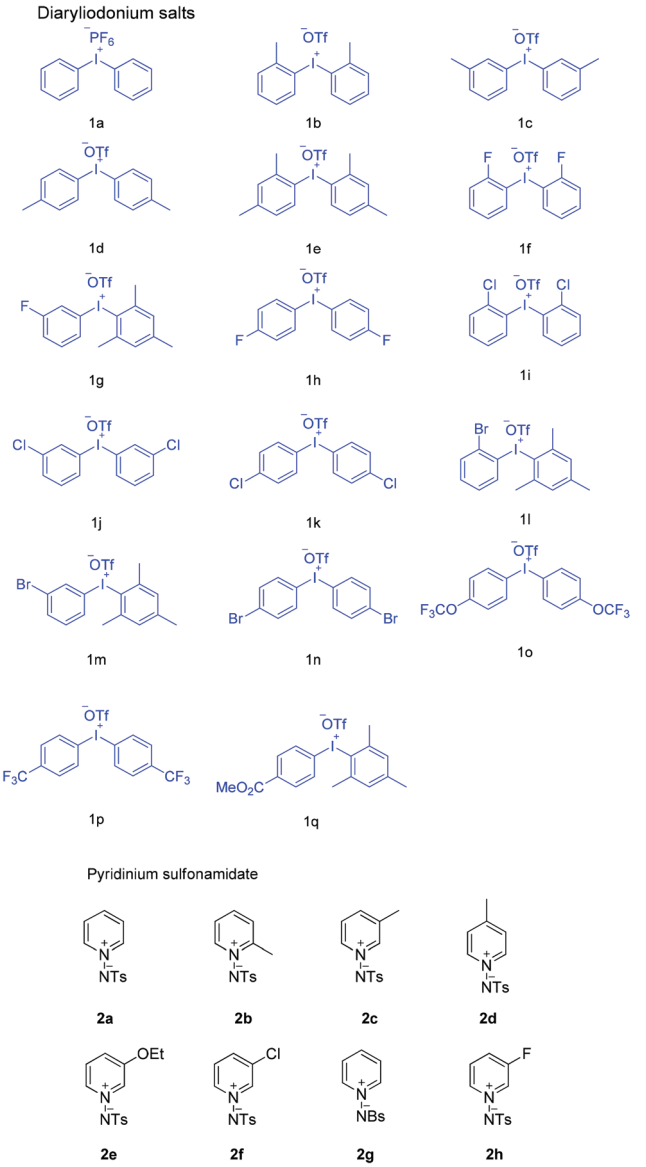
Results and discussion

Arylation of pyridinium sulfonamidates with diaryliodonium salts

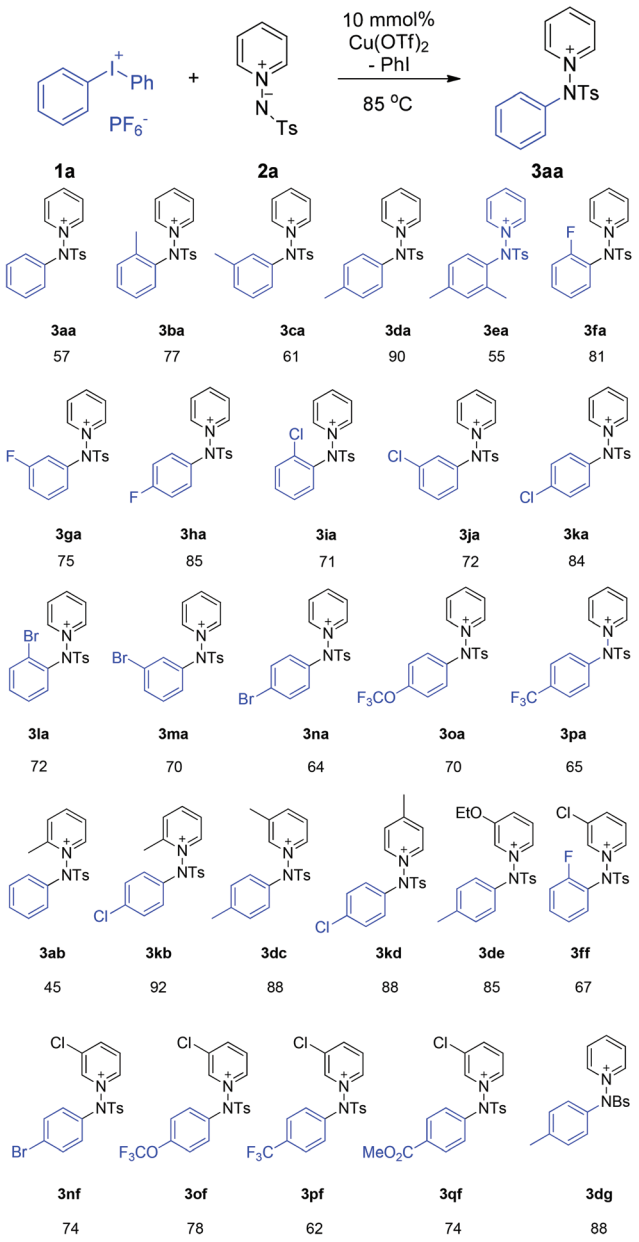
The arylation products of pyridinium sulfonamidates with diaryliodonium salts were prepared to investigate the proposed rearrangement. It was not possible to isolate the arylation product **3aa** by heating the reaction mixture of **1a** and **2a** at 130 °C, although a rearrangement reaction producing *o*-pyridinium aniline occurred. However, when 10 mmol% copper(II) triflate ($Cu(OTf)_2$) was added, a 57% yield of the arylation product **3aa** was obtained at 75 °C (see ESI† for details). In this manner, a series of arylation products (**3**) of **2** with substituted iodonium salts **1** (Scheme 2) were isolated at 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 the products **3a–3e**. Other iodonium salts with functional groups including fluoro-, chloro-, bromo- and trifluoro-methyloxyl-groups on a phenyl ring (**1f–1n**) were also tolerated in the Cu-catalyzed N-arylation reactions. When unsymmetrical 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 also isolated in good yield. Normal substituents on the pyridine ring did not affect the arylation of the sulfonamidate group. All the new compounds were characterized by proton nuclear magnetic resonance (^{1}H-NMR), carbon-13 nuclear magnetic resonance (^{13}C-NMR), electrospray ionisation-mass spectrometry (ESI-MS) and high-resolution mass spectrometry (HRMS). The structure of product **3kb** was confirmed by single-crystal X-ray diffraction (XRD) analysis (Fig. 1).[10]

Rearrangement of arylated pyridinium sulfonamidates

Next the formation of the rearrangement products was investigated 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 (reaction 3; for results, see Scheme 4). When the substituent R^1 or R^2 was an electron-donating group such as H or a methyl or dimethyl group, the reaction worked well to give the rearranged product. The structure of **4da** was further demonstrated by single-crystal XRD analysis (Fig. 2).[11] The crystal structure clearly shows that the N–N bond was cleaved and inserted by a phenylene group. In addition, the *ipso* position of the iodonium salt was substituted by a tosylamide group and the *ortho* position was substituted by a pyridinium moiety. When the *para* substituted R^2 was a fluoro- or chloro-atom, the reaction proceeded smoothly to give the expected product. However, when the *para* substituted R^2 was replaced by a bromo-, trifluoromethyloxyl or trifluoromethyl group (**1n–1p**), the reaction could not give the rearrangement product. These results suggest that an electro-donating substituent on the phenyl ring of the diaryliodonium salts is required for the rearrangement, but an electron withdrawing substituent inhibits the rearrangement.



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



Scheme 3 Isolated yields of the series of products (**3**).

Encouraged by these results, we attempted to investigate the influence of the substitution of pyridinium sulfonamidate on the rearrangement. To achieve this, a series of substituted pyridinium sulfonamidates was reacted with diaryliodonium salts to generate the rearrangement products (Scheme 5). Interestingly, the pyridinium sulfonamidates with electron-donating groups (**2b–2e**) could react with electron-enriched iodonium salts to give the rearrangement products **4db–4de**, The reaction of **2c** with electron-deficient iodonium salts (**1h**, **1k**, **1n–1p**) did not give any rearrangement products.

Halogen-substituted pyridinium sulfonamidates were more reactive and gave rearrangement products (Scheme 6). 3-Chloropyridinium sulfonamidates reacted with diaryliodonium salts

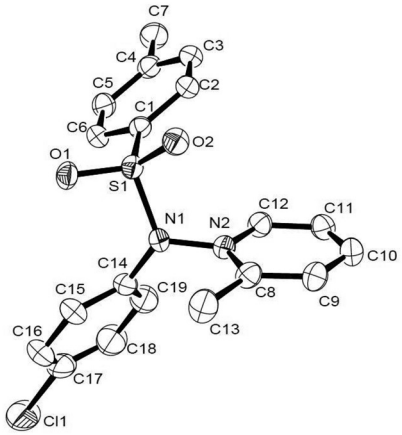
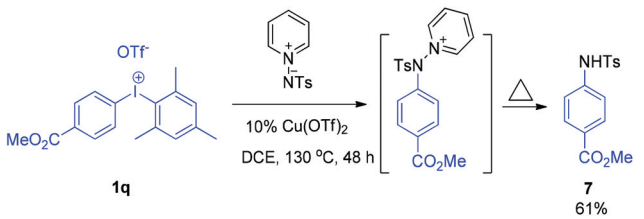


Fig. 1 Crystal structure of compound **3kb**. The counter anion of triflate and hydrogen atoms are omitted for clarity.

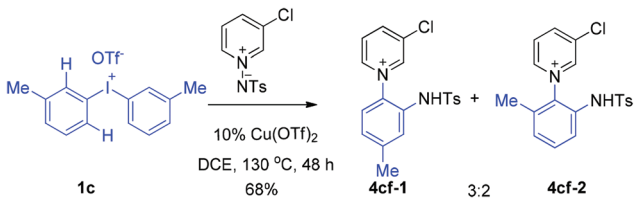
with bromo-, chloro- and trifluoromethyloxyl groups to generate the rearrangement products.

The reaction of diaryliodonium triflate (**1q**) and pyridinium sulfonamidate (**2a**) gave the arylated product, which did not undergo the rearrangement reaction. Over-long heating of the arylated product gave the decomposition product 7, presumably *via* radical reduction (reaction 4):



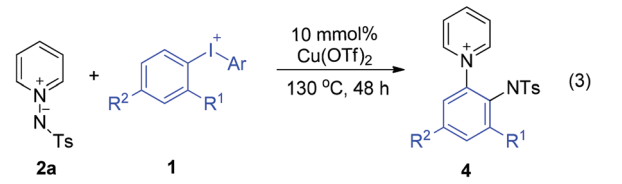
(4)

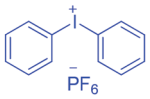
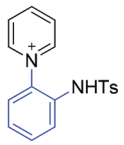
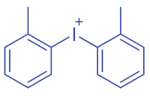
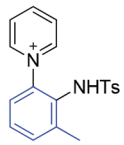
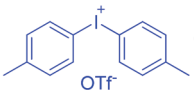
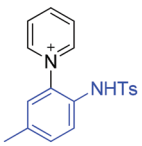
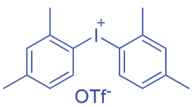
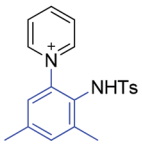
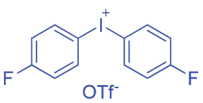
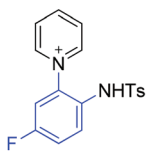
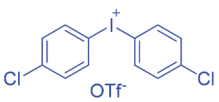
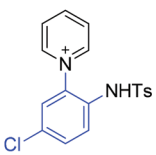
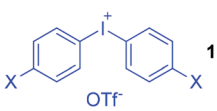
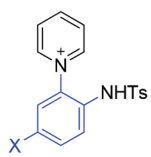
The reaction of pyridinium sulfonamidate with *meta*-substituted diaryliodonium triflate produced the regio-isomer. For example, 3-chloropyridinium sulfonamidate reacted with di-(*m*-tolyl) iodonium triflate to give two isomers in a ratio of 3 : 2 (reaction 5):



(5)

Finally, the effect of a protecting group on the amide moiety was investigated. In a similar manner to the tosylate group, pyridinium benzenesulfonamidate amide (**2g**) also worked with ditolyliodonium triflate (**1d**) to give the rearrangement product in good yield (reaction 6):



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	 X = Br, OCF_3, CF_3	4na-4pa	0

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

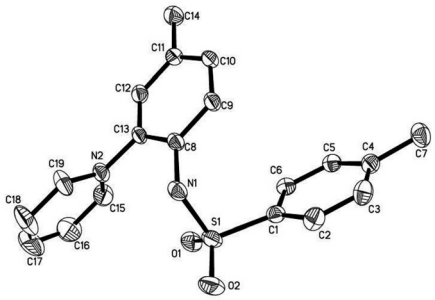
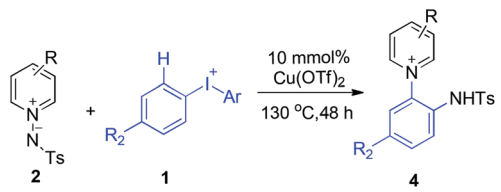
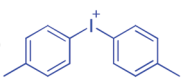
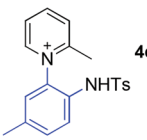
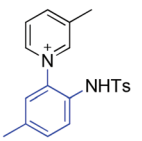
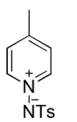
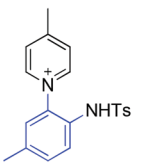
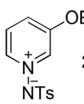
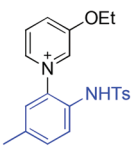
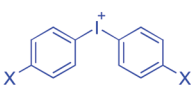
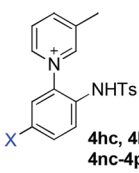
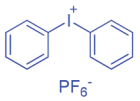
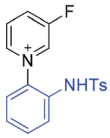
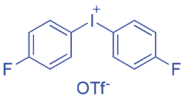
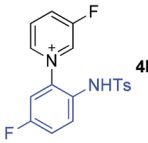
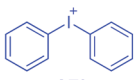
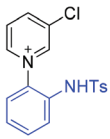
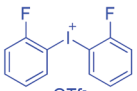
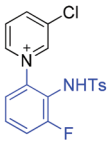
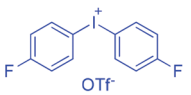
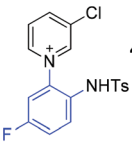
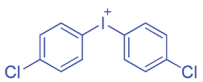
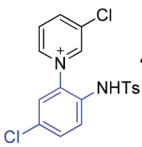
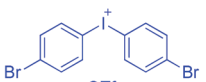
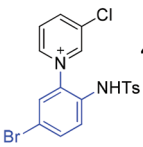
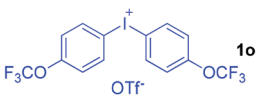
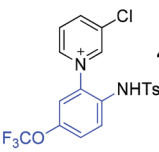


Fig. 2 Crystal structure of **4da**. Counter anions and hydrogen atoms are omitted for clarity.

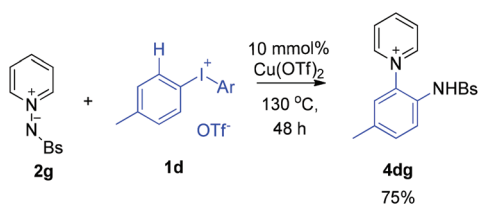


Pyridinium amidate		Diaryliodonium salt		Product		Isolated yield (%)
	2b		1d		4db	78
	2c		1d		4dc	76
	2d		1d		4dd	80
	2e		1d		4de	73
	2c		1h, 1k, 1n-1p	 X = F, Cl Br, OCF_3, CF_3,	4hc, 4kc, 4nc-4pc	0

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

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

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



(6)

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

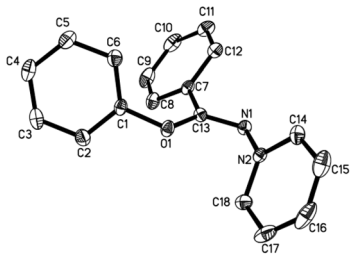
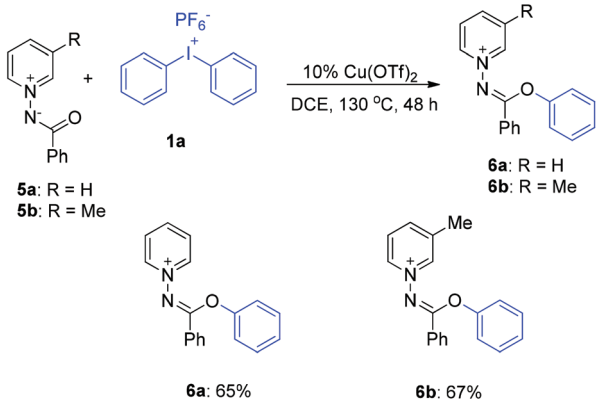


Fig. 3 Crystal structure of **6a**. The counter anion and hydrogen atoms are omitted for clarity.



(7)

Conclusions

We have reported here a regio-selective method of synthesizing benzene derivatives with vicinal disubstitution by the reaction of diaryliodonium salts with pyridinium *N*-sulfonamidates. The reaction proceeds *via* the arylation of pyridinium *N*-sulfonamidates followed by the key rearrangement of the arylated products **3** (Fig. 4). Previously reported studies and this work have proved that the rearrangement is generally initiated by a homo-cleavage to give a radical pair: the tosylate aniline

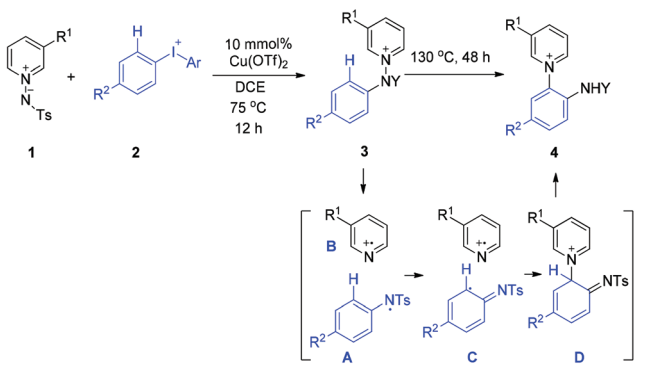
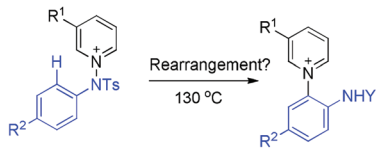


Fig. 4 Likely reaction mechanism for the synthesis of benzene derivatives with vicinal disubstitution by the reaction of diaryliodonium salts with pyridinium *N*-sulfonamidates.



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 reactions.

radical A[13] and the pyridinium radical B.[14] The recombination of the radical pair gives the final product **4** and this process is sensitively influenced by the substituents on the pyridinium and phenyl rings (Scheme 6). This result shows that the nature of the radical rearrangement depends on the electrophilic substitution on the phenyl ring (Scheme 7).[15]

Experimental section

All the reactions were carried out in a pre-dried screw-capped tube with a Teflon-lined septum under an N_2 atmosphere. Diphenyliodonium hexafluorophosphate (Ph_2IPF_6) was purchased from Alfa Aesar. The other diaryliodonium salt used was diaryl iodonium triflate (Ar_2IOTf) because its activity is almost the same as that of diaryliodonium hexafluorophosphate (Ar_2IPF_6) (only a slight decrease) and Ar_2IOTf is easier to synthesize. All the solvents were freshly distilled. Column chromatography was carried out using a silica gel column (particle size 10–40 μm, Ocean Chemical Factory of Qingdao, China). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Jeol AL-300 MHz or AL-400 MHz spectrometer at ambient temperature with deuterated chloroform ($CDCl_3$), deuterated methanol (CD_3OD) or deuterated dimethylsulfoxide (DMSO-D_6) as the solvent. Chemical shifts (δ) are given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), CD_3OD (3.31) and DMSO-D_6 (2.50) and to the carbon resonance of $CDCl_3$ (77.16), CD_3OD (49.00) and DMSO-D_6 (39.52). Coupling constants (J) are given in Hertz (Hz). The terms m, dq, q, t, d and s refer to multiplet, doublet quartet, quartet, triplet, doublet and singlet peaks. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in the positive mode.

Preparation of starting materials

The diaryliodonium salts were synthesized according to previously published procedures.[7] The *N*-pyridine tosylamidates (**2a–2f**, **2h**), the *N*-pyridinium benzene sulfonated amide (**2g**) and the *N*-pyridinium benzoated amides (**5a–5b**) were all also synthesized according to previously published procedures.[16]

General procedure for the preparation of the desired compound 3

$Cu(OTf)_2$ (0.05 mmol) was added to a mixture of the appropriate *N*-tosylpyridinium imides or *N*-pyridine tosylamidates (or *N*-pyridinium benzene sulfonated amide) (**2**) (0.5 mmol) and the appropriate diaryliodonium salt (**1**) (0.5 mmol) in a sealed tube. The tube was then evacuated and recharged three times with N_2. After 2 mL of dichloroethane (DCE) had been added, the tube was sealed and the mixture was stirred at 75 °C for 12 h until the reaction was complete [confirmed using thin layer chromatography (TLC)]. Finally, the desired compound **3** was purified using silica gel column chromatography (dichloromethane–petroleum ether–methanol = 5 : 5 : 1) and was obtained 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 the appropriate *N*-pyridine tosylamidates (or *N*-pyridinium benzene sulfonated amide) (**2**) (0.5 mmol) and the appropriate diaryliodonium salt (**1**) (0.5 mmol) in a sealed tube. The tube was then evacuated and recharged three times with N_2. After 2 mL of DCE had been added, the tube was sealed and the mixture was stirred at 130 °C for 48 h until completion of the reaction (confirmed using TLC). Finally, the desired compound **4** was purified using a silica gel column chromatography (dichloromethane–petroleum ether–methanol = 5 : 3 : 1) and was obtained as a yellow solid.

1-(4-Methyl-*N*-phenylphenylsulfonamido)pyridin-1-ium hexafluorophosphate(v) (3aa). Yellow solid (134 mg, 0.28 mmol, 57%). ^{1}H-NMR (301 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{17}N_2O_2S$ $[M - PF_6^-]^+$ 325.1; found 325.0. ESI-HRMS: m/z calculated for $C_{18}H_{17}N_2O_2S$ $[M - PF_6^-]^+$ 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%). ^{1}H-NMR (400 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{19}N_2O_2S$ $[M - TfO^-]^+$ 339.1; found 339.0. ESI-HRMS: m/z calculated for $C_{19}H_{19}N_2O_2S$ $[M - TfO^-]^+$ 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%). ^{1}H-NMR (400 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{19}N_2O_2S$ [M − TfO^-]$^+$ 339.1; found 339.0. ESI-HRMS: m/z calculated for $C_{19}H_{19}N_2O_2S$ [M − 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%). ^{1}H-NMR (301 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{19}N_2O_2S$ [M − TfO^-]$^+$ 339.1; found 339.0. ESI-HRMS: m/z calculated for $C_{19}H_{19}N_2O_2S$ [M − 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%). ^{1}H-NMR (301 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{21}N_2O_2S$ [M − TfO^-]$^+$ 353.13; found 353.2. ESI-HRMS: m/z calculated for $C_{20}H_{21}N_2O_2S$ [M − 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%). ^{1}H-NMR (301 MHz, DMSO-D_6): 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-D_6): 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 calculated for $C_{18}H_{16}FN_2O_2S$ [M − TfO^-]$^+$ 343.1; found 343.0. ESI-HRMS: m/z calculated for $C_{18}H_{16}FN_2O_2S$ [M − 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%). ^{1}H-NMR (400 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}FN_2O_2S$ [M − TfO^-]$^+$ 343.1; found 343.0. ESI-HRMS: m/z calculated 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-D_6): 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-D_6): 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 calculated for $C_{18}H_{16}FN_2O_2S$ [M − TfO^-]$^+$ 343.1; found 343.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}ClN_2O_2S$ [M − TfO^-]$^+$ 359.1; found 359.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}ClN_2O_2S$ [M − TfO^-]$^+$ 359.1; found 359.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}ClN_2O_2S$ [M − TfO^-]$^+$ 359.1; found 359.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}BrN_2O_2S$ $[M - TfO^-]^+$ 403.0; found 403.0. ESI-HRMS: m/z calculated for $C_{18}H_{16}BrN_2O_2S$ $[M - TfO^-]^+$ 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}BrN_2O_2S$ $[M - TfO^-]^+$ 403.0; found 403.0. ESI-HRMS: m/z calculated 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-D_6): 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-D_6): 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 calculated for $C_{18}H_{16}BrN_2O_2S$ $[M - TfO^-]^+$ 403.0; found 413.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{16}F_3N_2O_3S$ $[M - TfO^-]^+$ 409.1; found 409.0. ESI-HRMS: m/z calculated 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-D_6): 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-D_6): 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 calculated for $C_{19}H_{16}F_3N_2O_2S$ $[M - TfO^-]^+$ 393.1; found 393.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{19}N_2O_2S$ $[M - TfO^-]^+$ 339.1; found 339.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{18}ClN_2O_2S$ $[M - TfO^-]^+$ 373.0; found 372.9. ESI-HRMS: m/z calculated 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 the solution of compound **3kb** in CH_3OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 1008472. Formula: $C_{20}H_{18}ClF_3N_2O_5S_2$, M = 522.95, colorless crystals, 0.20 × 0.14 × 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 g cm^{-3}, μ = 0.412 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$, λ = 0.71073 Å, T = 173(2) K. Data completeness = 0.987, theta (max) = 27.46, R (reflections) = 0.0884, wR_2 (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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{21}N_2O_2S$ $[M - TfO^-]^+$ 353.1318; found 353.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated 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, CD_3OD): 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, CD_3OD): 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-methylphenylsulfon-amido)-pyridin-1-ium trifluoromethanesulfonate (3ff). Yellow solid (177 mg, 0.34 mmol, 67%). ^{1}H-NMR (400 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{15}ClFN_2O_2S$ $[M - TfO^-]^+$ 377.1; found 376.9. ESI-HRMS: m/z calculated for $C_{18}H_{15}ClFN_2O_2S$ $[M - TfO^-]^+$ 377.0521; found 377.0518.

1-(*N*-(4-Bromophenyl)-4-methylphenylsulfonamido)-3-chloro-pyridin-1-ium trifluoromethanesulfonate (3nf). Yellow solid (217 mg, 0.37 mmol, 74%). ^{1}H-NMR (400 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{15}BrClN_2O_2S$ $[M - TfO^-]^+$ 437.0; found 437.1; ESI-HRMS: m/z calculated 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, CD_3OD): 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-D_6): 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 calculated for $C_{19}H_{15}ClF_3N_2O_3S$ $[M - TfO^-]^+$ 443.0; found 443.0. ESI-HRMS: m/z calculated 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-D_6): 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-D_6) 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 calculated for $C_{19}H_{15}ClF_3N_2O_2S$ $[M - TfO^-]^+$ 427.0; found 427.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{18}ClN_2O_4S$ $[M - TfO^-]^+$ 417.1; found 417.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{17}N_2O_2S$ $[M - TfO^-]^+$ 325.1; found 325.1. ESI-HRMS: m/z calculated 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-D_6): 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-D_6): 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 calculated for $C_{18}H_{17}N_2O_2S$ $[M - PF_6^-]^+$ 325.1; found 325.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{19}N_2O_2S$ [M − TfO$^-$]$^+$ 339.1; found 339.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{19}N_2O_2S$ [M − TfO$^-$]$^+$ 339.1; found 339.0. ESI-HRMS: m/z calculated 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 a solution of compound **4da** in CH_3OH. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1008474. Formula: $C_{19}H_{19}F_6N_2O_2PS$, M = 484.40, colorless crystals, 0.48 × 0.43 × 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 g cm^{-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, wR_2 (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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{21}N_2O_2S$ [M − TfO$^-$]$^+$ 353.1; found 353.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}FN_2O_2S$ [M − TfO$^-$]$^+$ 343.1; found 343.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}ClN_2O_2S$ [M − TfO$^-$]$^+$ 359.1; found 359.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{21}N_2O_2S$ [M − TfO$^-$]$^+$ 353.1; found 353.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{21}N_2O_2S$ [M − TfO$^-$]$^+$ 353.13; found 353.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{20}H_{21}N_2O_2S$ [M − TfO$^-$]$^+$ 353.1; found 353.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{21}H_{23}N_2O_3S$ $[M - PF_6^-]^+$ 383.1; found 383.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}FN_2O_2S$ $[M - TfO^-]^+$ 343.1; found 343.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{15}F_2N_2O_2S$ $[M - TfO^-]^+$ 361.1; found 361.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{16}ClN_2O_2S$ $[M - TfO^-]^+$ 359.1; found 359.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{15}ClFN_2O_2S$ $[M - TfO^-]^+$ 377.1; found 377.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): δ 161.35 (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 calculated for $C_{18}H_{15}ClFN_2O_2S$ $[M - TfO^-]^+$ 377.1; found 377.0. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{15}Cl_2N_2O_2S$ $[M - TfO^-]^+$ 393.0; found 393.1. ESI-HRMS: m/z calculated for $C_{18}H_{15}Cl_2N_2O_2S$ $[M - TfO^-]^+$ 393.0226; found 393.0224.

1-(5-Bromo-2-(4-methylphenylsulfonamido)phenyl)-3-chloro-pyridin-1-ium trifluoromethanesulfonate (4nf). Yellow solid (199 mg, 0.34 mmol, 68%). ^{1}H-NMR (400 MHz, DMSO-D_6): 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-D_6): 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 calculated for $C_{18}H_{15}BrClN_2O_2S$ $[M - TfO^-]^+$ 437.0; found 437.2. ESI-HRMS: m/z calculated for $C_{18}H_{15}BrClN_2O_2S$ $[M - TfO^-]^+$ 436.9721; found 436.9722.

3-Chloro-1-(2-(4-methylphenylsulfonamido)-5-(trifluoro-methoxy)phenyl)pyridin-1-ium trifluoromethanesulfonate (4of). Yellow solid (193 mg, 0.33 mmol, 65%). ^{1}H-NMR (400 MHz, CD_3OD): 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-D_6): 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 calculated for $C_{19}H_{15}ClF_3N_2O_3S$ $[M - TfO^-]^+$ 443.0; found 443.1. ESI-HRMS: m/z calculated 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** (265.2 mg, 0.5 mmol) and (3-chloropyridin-1-ium-1-yl)(tosyl)amide **2f** (141.4 mg, 0.5 mmol) in a sealed tube. The tube was evacuated, recharged three times with N_2 and then 2 mL of DCE were added. The tube was then sealed and the mixture was stirred at 130 °C for 48 h until the reaction was complete (confirmed using TLC). Finally, the desired compound **7** was purified using silica gel column chromatography with petroleum ether–ethyl acetate (10 : 1) and was obtained as a yellow solid (93 mg, 0.3 mmol, 61%). ^{1}H-NMR (400 MHz, $CDCl_3$): 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, $CDCl_3$): δ 166.50, 144.52, 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 calculated for $C_{15}H_{16}NO_4S$ $[M + H]^+$ 306.1; found 306.6. ESI-HRMS: m/z calculated 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 trifluoromethanesulfonate (4cf-2). Yellow solid [178 mg, 0.34 mmol, 68% (3 : 2)]. ^{1}H-NMR (400 MHz, CD_3OD): 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, CD_3OD): 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 calculated for $C_{19}H_{18}ClN_2O_2S$ $[M - TfO^-]^+$ 373.1; found 373.1. ESI-HRMS: m/z calculated 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, CD_3OD): 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, CD_3OD): 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 calculated for $C_{18}H_{17}N_2O_2S$ $[M - TfO^-]^+$ 325.1; found 325.2. ESI-HRMS: m/z calculated 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, 0.5 mmol) and benzoyl(pyridin-1-ium-1-yl)amide (**5a**) (99.1 mg, 0.5 mmol) in a sealed tube. The tube was then evacuated and recharged three times with N_2. After 2 mL of DCE had been added, the tube was sealed and the mixture was stirred at 130 °C for 48 h until the reaction was complete (confirmed using TLC). Finally, the desired compound **6a** was purified using silica gel column chromatography (dichloromethane–petroleum ether–methanol = 5 : 3 : 1) and was obtained as a yellow solid (137 mg, 0.33 mmol, 65%). ^{1}H-NMR (301 MHz, DMSO-D_6): 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-D_6): 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 calculated for $C_{18}H_{15}N_2O$ $[M - PF_6^-]^+$ 275.1; found 275.2. ESI-HRMS: m/z calculated 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 a solution of compound **6a** in CH_3OH. The crystal structure was deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1008473. Formula: $C_{18}H_{15}F_6N_2OP$, M = 420.29, colorless crystal, 0.28 × 0.25 × 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 g cm^{-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, wR_2 (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, 0.5 mmol) and (2-methylpyridin-1-ium-1-yl)(tosyl)amide (**5b**) (131.2 mg, 0.5 mmol) in a sealed tube. The tube was evacuated and recharged three times with N_2. After 2 mL of DCE had been added, the tube was sealed and the mixture was stirred at 130 °C for 48 h until the reaction was complete (confirmed using TLC). Finally, the desired compound **6b** was purified by silica gel column chromatography (dichloromethane–petroleum ether–methanol = 5 : 3 : 1) and was obtained as a yellow solid (145 mg, 0.34 mmol, 67%). ^{1}H-NMR (301 MHz, DMSO-D_6): 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-D_6): 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 calculated for $C_{19}H_{17}N_2O$ $[M - PF_6^-]^+$ 289.1; found 289.1. ESI-HRMS: m/z calculated for $C_{19}H_{17}N_2O$ $[M - PF_6^-]^+$ 289.1334; found 289.1333.

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