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Aryldiazonium bis(trifluoromethyl)imides

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ABSTRACT

Aryldiazonium bis(trifluoromethyl)imides, $[ArN_2][N(CF_3)_2]$, are the first examples of diazonium salts with this type of anion. Their syntheses and properties will be presented and compared to aryldiazonium bis(trifluoromethylsulfonyl)imides. $[ArN_2][N(CF_3)_2]$ are less stable diazonium salts in comparison to $[ArN_2][N(SO_2CF_3)_2]$ due to the higher nucleophilicity of the $[N(CF_3)_2]^-$ anion.

1. Introduction

First aryldiazonium salts were synthesised by Peter Griess [1] in 1858 through the reaction of 2-amino-4,6-dinitrophenol with nitrous acid. Now, this class of compounds is well investigated and has broad applications in the syntheses of various chemicals, for example via Balz–Schiemann reaction, Sandmeyer reaction, Meerwein arylation, Gomberg–Bachmann reaction, Japp–Klingemann reaction, azo coupling, reduction to hydrazine, solvolysis, or palladium catalysed cross coupling reaction [2]. With exception of the Japp–Klingemann reaction, the reduction to hydrazine and the azo coupling, most reactions of aryl diazonium salts are based on dediazoniation processes. The stability of aryldiazonium salts depends on the substituents in the aromatic ring and the nature of the counter anion. Aryldiazonium salts with nucleophilic and easily oxidisable anions tend to be less stable.

Here, we report the synthesis of the previously unknown aryldiazonium bis(trifluoromethyl)imides, $[ArN_2][N(CF_3)_2]$, which are convenient reagents for introduction of the $N(CF_3)_2$ group in aromatic compounds. The properties of these new aryldiazonium salts are compared to the related aryldiazonium bis(trifluoromethylsulfonyl)imides, $[ArN_2][N(SO_2CF_3)_2]$ [3,4].

2. Results and discussion

2.1. Syntheses of aryldiazonium bis(trifluoromethyl)imides, $[ArN_2][N(CF_3)_2]$

The common source for the $[N(CF_3)_2]^-$ anion is the addition of CsF to perfluoroazopropene, $CF_3–N{=}CF_2$ [5]. However, this reaction is not convenient for practical application because it yields also to the dimer of $CF_3–N{=}CF_2$ (Scheme 1) and in addition $CF_3–N{=}CF_2$ is highly toxic and not commercial available.

Much more suitable is the precursor *N,N*-bis(trifluoromethyl)-trifluoromethylsulfonyl amide, $CF_3SO_2N(CF_3)_2$, synthesised by electrochemical fluorination (Simons process) of $CF_3SO_2N(CH_3)_2$ (Scheme 2) [6].

The $[N(CF_3)_2]^-$ anion is generated in situ by the reaction of $CF_3SO_2N(CF_3)_2$ with RbF (Scheme 3) [7] and used for the preparation of aryldiazonium bis(trifluoromethyl)imides without isolation.

The reaction of $Rb[N(CF_3)_2]$ with aryldiazonium tetrafluoroborates results in a fast metathesis to the hitherto unknown aryldiazonium bis(trifluoromethyl)imides in good yields (79 to 98%) (Scheme 4).

A similar procedure was used to prepare 2-(methoxycarbonyl)thiophene-3-diazonium bis(trifluoromethyl)imide (Scheme 5).

Parallel to the synthesis of aryldiazonium bis(trifluoromethyl) imides a series of aryldiazonium bis(trifluoromethylsulfonyl) imides, $[ArN_2][N(SO_2CF_3)_2]$, have been prepared for comparison purposes. $[ArN_2][N(SO_2CF_3)_2]$ salts are well known [3,4] and synthesised by metathesis of aryldiazonium chlorides with

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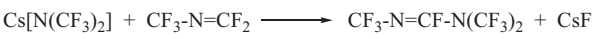
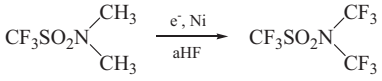


Scheme 1.



Scheme 2.

N,*N*-bis(trifluoromethylsulfonyl)imide, $(CF_3SO_2)_2NH$ or its sodium salt.

We have modified this method by using the more stable aryldiazonium tetrafluoroborates as starting compounds and commercially available $Li[N(SO_2CF_3)_2]$ as a source of the bis(trifluoromethylsulfonyl)imide anion. Besides known $[4\text{-}FC_6H_4N_2][N(SO_2CF_3)_2]$, the new substances $[X\text{-}C_6H_4N_2][N(SO_2CF_3)_2]$ (*X* = 2-Br, 3-Br, 4-Br, 4-I) have been prepared and characterised (Table 1).

2.2. Properties of aryldiazonium bis(trifluoromethyl)imides in comparison to aryldiazonium bis(trifluoromethylsulfonyl)imides

The diazonium salts $[2\text{-}CF_3C_6H_4N_2][N(CF_3)_2]$ and $[4\text{-}IC_6H_4N_2][N(CF_3)_2]$ are solids which are intrinsically unstable at room temperature. They decompose at room temperature within hours into several compounds. Other aryldiazonium bis(trifluoromethyl)imides were isolated at 0 °C as oily substances which undergo decomposition at room temperature, in some cases explosively. All diazonium salts with the $[N(CF_3)_2]^-$ anion are moisture sensitive and react vigorously with water. In contrast to the aryldiazonium bis(trifluoromethyl)imides, solid aryldiazonium bis(trifluoromethylsulfonyl)imides are much more stable (can be stored over months at room temperature) and are not moisture sensitive.

Aryldiazonium bis(trifluoromethylsulfonyl)imides melt above 50 °C (DSC measurements, T_{Onset}) and the melt decomposes into a mixture of phenyl-N and phenyl-O compounds. At higher temperature (135 °C) the reaction follows Scheme 6 as described in literature [3,4].

The products can be considered as aryl esters of triflic acid in which one oxygen atom is replaced by a $=NSO_2CF_3$ group.

The diazonium salts with $[N(CF_3)_2]^-$ and $[N(SO_2CF_3)_2]^-$ anions have lower melting points than their analogues with the $[BF_4]^-$ anion. The thermal stability of aryldiazonium salts are decreasing in the following order $[BF_4]^- > [N(SO_2CF_3)_2]^- > [N(CF_3)_2]^-$ which reflects the increase in the coordination ability (nucleophilicity) of these anions.

In the ^{19}F NMR spectra, the resonance of the bis(trifluoromethyl)imide anion in $[4\text{-}FC_6H_4N_2][N(CF_3)_2]$ or in $[4\text{-}BrC_6H_4N_2][N(CF_3)_2]$ ($\delta_F = -37$ ppm; solvent: CH_3CN) appears deshielded in comparison to the signal of the covalently bonded *N*,*N*-bis(trifluoromethyl)amino group in $4\text{-}FC_6H_4N(CF_3)_2$ or in $4\text{-}BrC_6H_4N(CF_3)_2$ ($\delta_F = -56$ ppm; solvent: CCl_3F) [8]. In the case of the bis(trifluoromethylsulfonyl)imide salt, $[4\text{-}FC_6H_4N_2][N(SO_2CF_3)_2]$ ($\delta_F = -80$ ppm; CH_3CN) and the covalently bonded compound $4\text{-}FC_6H_4N(SO_2CF_3)_2$ ($\delta_F = -80$ ppm; CCl_3F) [4] the chemical shift of the *N*,*N*-bis(trifluoromethylsulfonyl)amino moiety is almost the same.

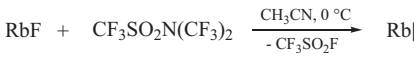
In the ^{13}C NMR spectra the signal of the $N(CF_3)_2$ group is displayed at about 125 ppm as quartet of quartets: $^1J_{C,F} \approx 243$ Hz and $^3J_{C,F} \approx 11$ Hz. However, the $N(SO_2CF_3)_2$ group shows in the ^{13}C NMR spectra only one quartet ($^1J_{C,F} \approx 321$ Hz) at 121 ppm. The coupling constant $^3J_{C,F}$ is too small to be observed.

The coordination ability of both types of anions also influences the N≡N stretching vibrations (Table 1). In the Raman spectra of $[4\text{-}BrC_6H_4N_2][N(CF_3)_2]$ and $[4\text{-}FC_6H_4N_2][N(CF_3)_2]$ the ν(N≡N) values are slightly shifted to higher wavenumbers (2283 cm^{-1} and 2288 cm^{-1}) in comparison to the corresponding bis(trifluoromethylsulfonyl)imides (2279 cm^{-1} and 2281 cm^{-1}).

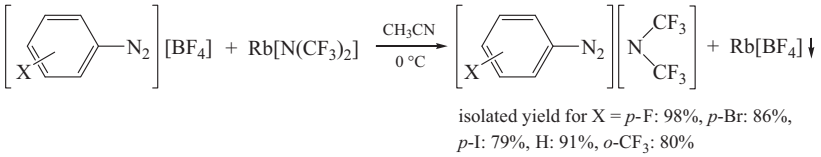
3. Experimental part

All moisture sensitive compounds were handled under an atmosphere of dry argon. Reactions were carried out in glass vessels or in traps made from FEP tubes (o.d. = 4.1 mm, i.d. = 3.5 mm or o.d. = 9.0 mm, i.d = 8.0 mm). CH_3CN (supplier: KMF) was purified by reflux and distillation in sequence over $KMnO_4$ and P_4O_{10}.

NMR spectra were recorded on a Bruker NMR spectrometer AVANCE 300 (^{13}C at 75.47 MHz, ^{19}F at 282.40 MHz, and ^1H at 300.13 MHz) and a Bruker spectrometer AVANCE 400 (^{13}C at 100.61 MHz, ^{19}F at 376.50 MHz, and ^1H at 400.13 MHz) with external Deuterium lock (CD_3CN) if non-deuterated solvents were used for the NMR-measurements. The chemical shifts were referenced to TMS (^{13}C, ^1H), CCl_3F (^{19}F) (C_6F_6 as a secondary reference, $\delta = -162.9$ ppm). The ratio of ^{19}F and ^1H nuclei in products was determined by NMR spectroscopy after addition of 1,3,5-trifluorobenzene or benzotrifluoride. Raman spectra were recorded on a Bruker FT-Raman spectrometer FRA 106/S using the 1064 nm line of a Nd/YAG laser. The backscattered (180°) radiation was sampled and analysed (Stoke range: 50–4000 cm^{-1}). The samples were placed in glass capillaries or FEP tubes.

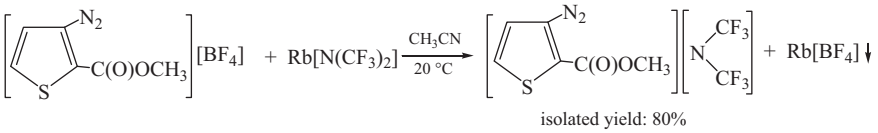


Scheme 3.



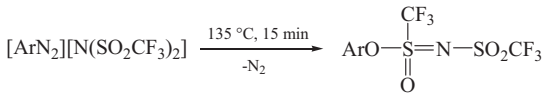
isolated yield for X = *p*-F: 98%, *p*-Br: 86%, *p*-I: 79%, H: 91%, *o*-CF_3: 80%

Scheme 4.



isolated yield: 80%

Scheme 5.



Scheme 6.

3.1. Chemicals

Diazonium tetrafluoroborates were prepared according to the methods described in the literature [9]: [4-$FC_6H_4N_2$][BF_4] (yield 92%, m.p. 157 °C, ν(N≡N) 2297 cm^{-1}), [4-$BrC_6H_4N_2$][BF_4] (yield 77%, m.p. 139 °C, ν(N≡N) 2288 cm^{-1}), [4-$IC_6H_4N_2$][BF_4] (yield 91%, m.p. 130 °C, ν(N≡N) 2285 cm^{-1}), [3-$BrC_6H_4N_2$][BF_4] (yield 80%, m.p. 143 °C, ν(N≡N) 2309 cm^{-1}), [2-$BrC_6H_4N_2$][BF_4] (yield 69%, m.p. 155 °C, ν(N≡N) 2294 cm^{-1}), [2-$CF_3C_6H_4N_2$][BF_4] (yield 65%, m.p. 140 °C, ν(N≡N) 2299 cm^{-1}), [$C_6H_5N_2$][BF_4] (yield 76%, m.p. 105 °C, ν(N≡N) 2297 cm^{-1}).

2-(Methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate was prepared by the method presented in [10] which has been optimised to improve the yield and to characterise the isolated product (see description below).

N,*N*-dimethylmethanesulfonamide was obtained by reaction of dimethyl amine and trifluoromethanesulfonic acid anhydride in diethyl ether.

3.2. Syntheses of aryldiazonium bis(trifluoromethyl)imides

3.2.1. Synthesis of [4-$FC_6H_4N_2$][$N(CF_3)_2$]

$CF_3SO_2N(CF_3)_2$ (0.98 g, 3.41 mmol) was added to a cold suspension (0 °C) of RbF (0.354 g, 3.385 mmol) in CH_3CN (4 mL). After 35 min the RbF was consumed and the suspension turned to a solution which subsequently was added to a cold solution (0 °C) of [4-$FC_6H_4N_2$][BF_4] (0.646 g, 3.077 mmol) in CH_3CN (2.5 mL). The reaction mixture was stirred for 15 min and the pale orange supernatant was separated from the precipitate. The solvent was removed in vacuum and the residue was dried in vacuum (0.05 hPa, −42 °C, 2 h; −42 °C to −20 °C, 2 h; −15 °C, 2 h). Orange oil was obtained in 98% yield (0.833 g, 3.028 mmol).

^{19}F NMR (CH_3CN, −30 °C) δ, ppm: −36.9 (s, 6F, N(CF_3)$_2$), −84.2 (tt, $^3J_{F,H}$ = 8 Hz, $^4J_{F,H}$ = 4 Hz, 1F, 4-FC_6H_4). ^1H NMR (CH_3CN, −30 °C) δ, ppm: 8.70 (m, 2H, $H^{2,6}$), 7.66 (m, 2H, $H^{3,5}$). ^{13}C NMR (CH_3CN, −30 °C) δ, ppm: 169.5 (dtt, $^1J_{C,F}$ = 270 Hz, $^2J_{C,H}$ = 10 Hz, $^3J_{C,H}$ = 5 Hz, C^4), 136.6 (ddd, $^1J_{C,H}$ = 181 Hz, $^3J_{C,F}$ = 13 Hz, $^2J_{C,H}$ = 5 Hz, $C^{2,6}$), 125.0 (qq, $^1J_{C,F}$ = 243 Hz, $^3J_{C,F}$ = 11 Hz, N(CF_3)$_2$), 119.7 (ddd, $^1J_{C,H}$ = 176 Hz, $^2J_{C,F}$ = 25 Hz, $^2J_{C,H}$ = 4 Hz, $C^{3,5}$), 110.0 (td, $^2J_{C,H}$ = 12 Hz, $^4J_{C,F}$ = 3 Hz, C^1).

The other aryldiazonium bis(trifluoromethyl)imides, [X-$C_6H_4N_2$][$N(CF_3)_2$], were prepared using similar procedures.

[4-$BrC_6H_4N_2$][$N(CF_3)_2$]: Yield 86% (0.365 g, 1.086 mmol). ^{19}F NMR (CH_3CN, −30 °C) δ, ppm: −36.8 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_3CN, −30 °C) δ, ppm: 8.42 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, $H^{2,6}$), 8.04 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, $H^{3,5}$). ^{13}C NMR (CH_3CN, −30 °C) δ, ppm: 138.4 (tt, $^2J_{C,H}$ = 10 Hz, $^3J_{C,H}$ = 2 Hz), 135.0 (dd, $^1J_{C,H}$ = 177 Hz, $J_{C,H}$ = 5 Hz), 133.4 (dd, $^1J_{C,H}$ = 181 Hz, $J_{C,H}$ = 4 Hz), 125.0 (qq, $^1J_{C,F}$ = 243 Hz, $^3J_{C,F}$ = 12 Hz, N(CF_3)$_2$), 113.5 (tt, $^2J_{C,H}$ = 12 Hz, $^3J_{C,H}$ = 3 Hz).

[4-$IC_6H_4N_2$][$N(CF_3)_2$]: Yield 79% (0.473 g, 1.234 mmol). ^{19}F NMR (CH_3CN, −30 °C) δ, ppm: −36.8 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_3CN, −30 °C) δ, ppm: 8.26 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, $H^{2,6}$), 8.17 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, $H^{3,5}$). $^{13}C\{^1H\}$ NMR (CH_3CN, −30 °C) δ, ppm: 141.1 (s), 132.4 (s), 124.9 (qq, $^1J_{C,F}$ = 244 Hz, $^3J_{C,F}$ = 11 Hz, N(CF_3)$_2$), 114.7 (s), 113.8 (s).

[2-$CF_3C_6H_4N_2$][$N(CF_3)_2$]: Yield 81% (0.50 g, 1.54 mmol). ^{19}F NMR (CH_3CN, −30 °C) δ, ppm: −37.4 (s, 6F, N(CF_3)$_2$), −60.1 (s, 3F, CF_3). ^1H NMR (CH_3CN, −30 °C) δ, ppm: 8.96 (m, 1H), 8.42 (m, 1H), 8.30 (m, 1H), 8.20 (m, 1H). ^{13}C NMR (CH_3CN, −30 °C) δ, ppm: 142.3 (dd, $^1J_{C,H}$ = 173 Hz, $J_{C,H}$ = 7 Hz), 135.5 (ddd, $^1J_{C,H}$ = 181 Hz, $J_{C,H}$ = 8 Hz, $J_{C,H}$ = 2 Hz), 135.2 (dd, $^1J_{C,H}$ = 176 Hz, $J_{C,H}$ = 8 Hz), 131.7 (m), 129.6 (qm, $J_{C,F}$ = 36 Hz), 124.8 (qq, $^1J_{C,F}$ = 243 Hz, $^3J_{C,F}$ = 11 Hz, N(CF_3)$_2$), 120.5 (qd, $^1J_{C,F}$ = 274 Hz, $J_{C,H}$ = 5 Hz, CF_3), 111.9 (t, $J_{C,H}$ = 12 Hz).

[$C_6H_5N_2$][$N(CF_3)_2$]: Yield 91% (0.61 g, 2.37 mmol). ^{19}F NMR (CH_3CN, −30 °C) δ, ppm: −38.3 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_3CN, −30 °C) δ, ppm: 8.49 (m, 2H), 8.19 (m, 1H), 7.87 (m, 2H). $^{13}C\{^1H\}$ NMR (CH_3CN, −30 °C) δ, ppm: 142.0 (s), 132.5 (s), 131.8 (s), 124.8 (qq, $^1J_{C,F}$ = 244 Hz, $^3J_{C,F}$ = 11 Hz, N(CF_3)$_2$), 114.8 (s).

3.3. Syntheses of 2-(methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate and bis(trifluoromethyl)imide [$C_6H_5N_2O_2S$][BF_4]

To the stirred suspension of methyl-3-aminothiophene-2-carboxylate (4.2 g, 26.8 mmol) in HBF_4 (50%, 8 mL, 128 mmol) an aqueous solution of $NaNO_2$ (2.0 g, 29.0 mmol) was added at 0 °C. The reaction mixture was left stirring for 5 min at 0 °C and for 20 min at 20 °C. The precipitant was filtered off and washed first with the mixture of acetone/diethyl ether (10 mL/15 mL) and than with 20 mL of diethyl ether. The residue was dried in vacuum (1.6 hPa, 20 °C, 2 h). 2-(Methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate was obtained as white solid material in 88% yield (6.01 g, 23.48 mmol).

M.p. 143.9 °C (DSC: endothermic; $T_{Onset;}$ lit.: 142–143 °C [10]). ^{19}F NMR (CD_3CN, 27 °C) δ, ppm: −151.5 (s, 4F, BF_4). ^1H NMR (CD_3CN, 27 °C) δ, ppm: 8.14 (s, 2H, $H^{3,4}$), 4.04 (s, 3H, CH_3). ^{11}B NMR (CD_3CN, 27 °C) δ, ppm: −1.21 (s, BF_4). $^{13}C\{^1H\}$ NMR (CD_3CN, 27 °C) δ, ppm: 158.0 (s), 149.9 (s), 136.0 (s), 129.9 (s), 108.5 (s), 55.0 (s). Raman spectrum: ν(N≡N): 2285 cm^{-1}.

[$C_6H_5N_2O_2S$][$N(CF_3)_2$]: $CF_3SO_2N(CF_3)_2$ (0.50 g, 1.75 mmol) was added to a cold suspension (−10 °C) of RbF (0.15 g, 1.44 mmol) in CH_3CN (1.1 mL). After 20 min the RbF was consumed and the suspension turned to a solution which subsequently was added to a suspension (20 °C) of 2-(methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate (0.35 g, 1.37 mmol) in CH_3CN (2 mL). The reaction mixture was stirred for 15 min and the pale yellow

Table 1
Synthesis and some properties of aryldiazonium bis(trifluoromethyl)imides and aryldiazonium bis(trifluoromethylsulfonyl)imides.

Compound	Method of synthesis (solvent)	Yield (%)	M.p. (°C)	ν(N≡N) (cm^{-1})
[4-$FC_6H_4N_2$][$N(CF_3)_2$]	A	98	–	2288
[4-$FC_6H_4N_2$][$N(SO_2CF_3)_2$]	B (acetone)	59	81	2281
	B (CH_3CN)	88	–	–
[4-$BrC_6H_4N_2$][$N(CF_3)_2$]	A	82	–	2283
[4-$BrC_6H_4N_2$][$N(SO_2CF_3)_2$]	B (acetone)	66	69	2279
[4-$IC_6H_4N_2$][$N(CF_3)_2$]	A	79	–	–
[4-$IC_6H_4N_2$][$N(SO_2CF_3)_2$]	B (acetone)	56	88	2281
[3-$BrC_6H_4N_2$][$N(SO_2CF_3)_2$]	B (acetone/CH_3CN)	58	89	2294
[2-$BrC_6H_4N_2$][$N(SO_2CF_3)_2$]	B (H_2O)	64	57	2276
[2-$CF_3C_6H_4N_2$][$N(CF_3)_2$]	A	81	–	–
[$C_6H_5N_2$][$N(CF_3)_2$]	A	91	–	–

(A) metathesis with Rb[$N(CF_3)_2$] in CH_3CN, (B) metathesis with Li[$N(SO_2CF_3)_2$].

supernatant was separated from the precipitate. The solvent was removed in vacuum and the residue was dried in vacuum (2 hPa, 20 °C, 3 h). 0.35 g (1.09 mmol) of pale-orange solid 2-(methoxycarbonyl)thiophene-3-diazonium bis(trifluoromethyl)imide was obtained in 80% yield.

^{19}F NMR (CD_3CN + 1,3,5-$F_3C_6H_3$, 27 °C) δ, ppm: −41.3 (s, 6F, $N(CF_3)_2$). ^{1}H NMR (CD_3CN + 1,3,5-$F_3C_6H_3$, 27 °C) δ, ppm: 8.14 (s, 2H), 4.05 (s, 3H, CH_3).

3.4. Syntheses of aryldiazonium bis(trifluoromethylsulfonyl)imides

3.4.1. Synthesis of [4-$FC_6H_4N_2$][$N(SO_2CF_3)_2$]

CH_3CN (10 mL) was added to the mixture of solid [4-$FC_6H_4N_2$][BF_4] (2.33 g, 11.0 mmol) and Li[$N(SO_2CF_3)_2$] (4.2 g, 14.6 mmol). After 30 min of stirring the solution was concentrated in vacuum (0.05 hPa, 20 °C, 2 h). The residue was washed three times with H_2O (3 × 30 mL) and with Et_2O (3 × 10 mL). The white solid product was dried in vacuum (0.05 hPa, 20 °C, 2 h). Yield of [4-$FC_6H_4N_2$][$N(SO_2CF_3)_2$] was 88% (3.96 g, 9.82 mmol).

^{19}F NMR (CD_3CN, 20 °C) δ, ppm: −80.5 (s, 6F, $N(SO_2CF_3)_2$), −84.8 (tt, $^3J_{F,H3,5}$ = 8 Hz, $^4J_{F,H2,6}$ = 4 Hz, 1F, 4-FC_6H_4). ^{1}H NMR (CD_3CN, 20 °C) δ, ppm: 8.60 (m, 2H, $H^{2,6}$), 7.67 (m, 2H, $H^{3,5}$). ^{13}C{^{1}H} NMR (CD_3CN, 20 °C) δ, ppm: 170.7 (d, $^1J_{C,F}$ = 271 Hz, C^4), 137.4 (d, $^3J_{C,F}$ = 12 Hz, $C^{2,6}$), 120.8 (d, $^2J_{C,F}$ = 25 Hz, $C^{3,5}$), 120.6 (q, $^1J_{C,F}$ = 320 Hz, $N(SO_2CF_3)_2$), 110.6 (d, $^4J_{C,F}$ = 3 Hz, C^1).

The other aryldiazonium bis(trifluoromethylsulfonyl)imides, [X-$C_6H_4N_2$][$N(SO_2CF_3)_2$], were prepared in a similar manner.

[4-$BrC_6H_4N_2$][$N(SO_2CF_3)_2$]: Yield 66% (3.42 g, 7.34 mmol). ^{19}F NMR (CD_3CN, 20 °C) δ, ppm: −80.4 (s, 6F, $N(SO_2CF_3)_2$). ^{1}H NMR (CD_3CN, 20 °C) δ, ppm: 8.35 (m, 2H, $H^{2,6}$), 8.10 (m, 2H, $H^{3,5}$). ^{13}C{^{1}H} NMR (CD_3CN, 20 °C) δ, ppm: 139.7 (s), 136.1 (s), 134.1 (s), 120.6 (q, $^1J_{C,F}$ = 321 Hz, $N(SO_2CF_3)_2$), 113.9 (s).

[4-$IC_6H_4N_2$][$N(SO_2CF_3)_2$]: Yield 56% (2.69 g, 5.26 mmol). ^{19}F NMR (CD_3CN, 20 °C) δ, ppm: −80.4 (s, 6F, $N(SO_2CF_3)_2$). ^{1}H NMR (CD_3CN, 20 °C) δ, ppm: 8.34 (m, 2H, $H^{2,6}$), 8.13 (m, 2H, $H^{3,5}$). ^{13}C{^{1}H} NMR (CD_3CN, 20 °C) δ, ppm: 142.1 (s), 132.9 (s), 120.6 (q, $^1J_{C,F}$ = 321 Hz, $N(SO_2CF_3)_2$), 114.4 (s), 114.2 (s).

[3-$BrC_6H_4N_2$][$N(SO_2CF_3)_2$]: Yield 58% (3.01 g, 6.48 mmol). ^{19}F NMR (CD_3CN, 20 °C) δ, ppm: −80.4 (s, 6F, $N(SO_2CF_3)_2$). ^{1}H NMR (CD_3CN, 20 °C) δ, ppm: 8.61 (m, 1H), 8.49 (m, 1H), 8.39 (m, 1H), 7.84 (m, 1H). ^{13}C{^{1}H} NMR (CD_3CN, 20 °C) δ, ppm: 146.0 (s), 134.6 (s), 133.8 (s), 132.3 (s), 124.3 (s), 120.6 (q, $^1J_{C,F}$ = 321 Hz, $N(SO_2CF_3)_2$), 116.7 (s).

[2-$BrC_6H_4N_2$][$N(SO_2CF_3)_2$]: Yield 64% (7.94 g, 17.11 mmol). ^{19}F NMR (CD_3CN, 20 °C) δ, ppm: −80.5 (s, 6F, $N(SO_2CF_3)_2$). ^{1}H NMR (CD_3CN, 20 °C) δ, ppm: 8.57 (m, 1H), 8.15 (m, 2H), 7.92 (m, 1H). ^{13}C{^{1}H} NMR (CD_3CN, 20 °C) δ, ppm: 143.9 (s), 136.8 (s), 135.9 (s), 131.6 (s), 125.9 (s), 120.7 (q, $^1J_{C,F}$ = 321 Hz, $N(SO_2CF_3)_2$), 117.7 (s).

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