Supplementary Information

The nature of $[N\text{-}Cl\text{-}N]^+$ and $[N\text{-}F\text{-}N]^+$ halogen bonds in solution

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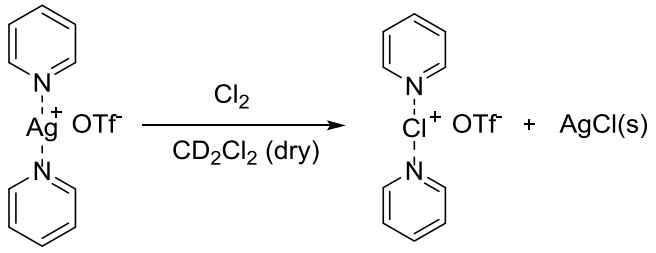
1. Experimental details – Synthesis and NMR

General information. CH_2Cl_2 was freshly distilled from CaH_2, and *n*-hexane was distilled from sodium metal/benzophenone ketyl in presence of tetraethylene glycol dimethyl ether prior to use. Reactions were carried out in capped Biotage microwave process vials. All glassware used in the syntheses of $[N\cdots X\cdots N]^+$ complexes was dried in an oven at 150 °C for several hours prior to use. The halogenation reactions were all performed under dry conditions with dry solvents, and in a nitrogen or argon atmosphere. Centrifugations were carried out with a Heraeus Christ Labofuge A centrifuge. *N*-fluoropyridinium tetrafluoroborate and pyridine *N*-fluoropyridinium heptafluoro-diborate were purchased from Sigma Aldrich. Pyridine was distilled from CaH_2 prior to use.



Scheme S1 Synthesis of bis(pyridine)chloronium triflate **3**

Bis(pyridine)chloronium triflate (3). Into an oven dried 0.5-2 mL microwave vial equipped with a stir bar, bis(pyridine)silver(I) triflate (115 mg, 0.267 mmol), prepared as described earlier,[1] was weighed in. The vial was immediately sealed, and dried thoroughly under vacuum for 3 to 4 hours. Then dry CD_2Cl_2 (4 mL) was added, and the mixture was sonicated while being kept in a dry ice/acetone bath at -78°C for 30 minutes to ensure that the sample reached the desired temperature. Subsequently, Cl_2 (g) was transferred into a balloon and introduced into the microwave vial containing the bis(pyridine)silver(I) complex via a connector and needle (Fig. S1). Immediately upon introduction of the gas, the solution turned yellow, AgCl was precipitated, and the bis(pyridine)chloronium complex **3** was formed. The balloon was left inside the vial for 20 minutes until no further precipitation was observed. This vial was then centrifuged at 2500 rpm for 5 minutes at -78°C under an Ar(g) atmosphere. After 5 minutes, the vial was removed and the supernatant was transferred at -78°C via a cannula (pre-dried in a 150°C oven and purged with Ar(g)) wrapped in a dry ice jacket into a dried NMR tube, which was immersed in a dry ice/acetone bath. Immediately following the transfer, the NMR tube was inserted into the spectrometer for measurements at -80°C.

Figure S1.
Bis(pyridine)chloronium triflate **3** was synthesized by bubbling Cl_2 gas into a carefully dried solution of bis(pyridine) silver(I) triflate kept at -80°C and mixed by ultrasonication for 30 minutes.

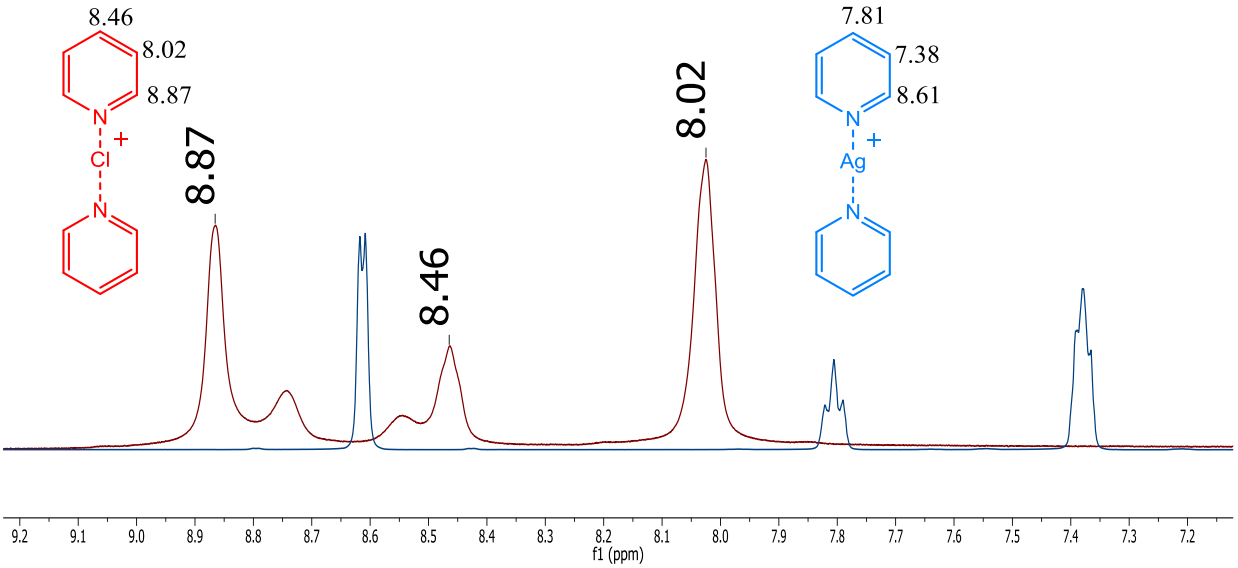


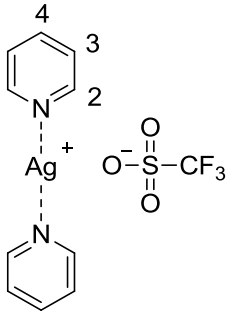
Figure S2 Superimposed ^{1}H NMR spectra of bis(pyridine)silver(I) triflate (blue) and bis(pyridine)-chloronium triflate **3** (red) in CD_2Cl_2 solution, obtained at -80°C.

A considerable shift change is observed when chlorine gas is introduced into a bis(pyridine)silver(I) triflate solution. In Figure S2, the ^{1}H NMR spectrum of bis(pyridine)- silver(I) triflate is shown in blue. The signals of **3** are shown in red, marked with the corresponding chemical shifts. Due to the high reactivity of the $[N\text{-}Cl\text{-}N]^{+}$ complex **3**, upon contact with humidity it decomposes to the corresponding $[N\text{-}H\text{-}N]^{+}$ complex, bis(pyridinium) triflate. The signals of bis(pyridinium) triflate are shown as broad peaks in the spectrum of **3**, in red.

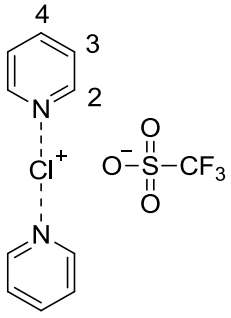
NMR. Spectra were recorded on a four-channel Varian VNMR-S 500 spectrometer equipped with a ^{1}H-$^{19}F/^{15}N$-^{31}P 5 mm pulse-field gradient dual broadband probe and an extended-duration liquids variable temperature accessory using liquid N_2 for cooling. Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard for ^{1}H (CD_2Cl_2 δ_H 5.32, CD_3CN δ_H 1.94) and ^{13}C NMR (CD_2Cl_2 δ_C 54.0, CD_3CN δ_C 1.32) , whereas for the ^{19}F and ^{15}N NMR spectra a sealed capillary filled with hexafluorobenzene (δ_F -164.4) or nitromethane (δ_N 0) was used as an internal standard.

2. NMR data

2.1 Bis(pyridine)silver(I) triflate, Bis(pyridine)chloronium triflate 3



Bis(pyridine)silver(I) triflate.[1] ^{1}H NMR (499.89 MHz, CD_2Cl_2, 25 °C) δ 8.61 (m, 4H, H-2), 7.81 (m, 2H, H-4), 7.38 (m, 4H, H-3). ^{1}H NMR (499.89 MHz, CD_2Cl_2, -80 °C) δ 8.67 (m, 4H, H-2), 7.96 (m, 2H, H-4), 7.56 (m, 4H, H-3). ^{13}C NMR (125.61 MHz, CD_2Cl_2, -80 °C) δ 151.2 (C-2), 139.0 (C-4), 125.3 (C-3). ^{19}F NMR (470.3 MHz, CD_2Cl_2, 25 °C) δ 155 (CF_3).



Bis(pyridine)chloronium triflate (**3**). ^{1}H NMR (499.89 MHz, CD_2Cl_2, -80 °C) δ 8.87 (br s, 4H, H-2), 8.46 (br s, 2H, H-4), 8.02 (br s, 4H, H-3).^{13}C NMR (125.61 MHz, CD_2Cl_2, -80 °C) δ 145.7 (C-2), δ 144.8 (C-4), δ 129.4 (C-3).

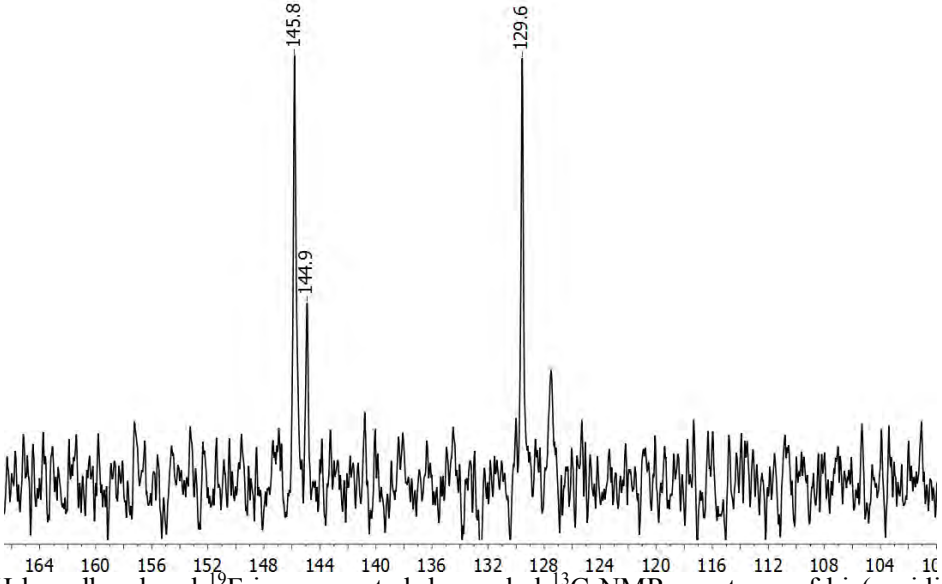
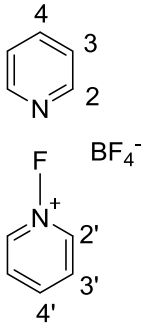


Fig. S3 The ^{1}H broadband and ^{19}F inverse gated decoupled ^{13}C NMR spectrum of bis(pyridine)chloronium triflate **3**, acquired at -80 °C in CD_2Cl_2 at 125.71 MHz.

2.2 Pyridine *N*-fluoropyridinium tetrafluoroborate 4



Pyridine *N*-fluoropyridinium tetrafluoroborate (**4**). ^{1}H NMR (499.89 MHz, CD_3CN, -35 °C) δ 9.22 (m, 2H, H-2'), 8.65 (m, 1H, H-4'), 8.55 (m, 2H, H-2), 8.23 (m, 2H, H-3'), 7.75 (m, 1H, H-4), 7.34 (m, 2H, H-3). ^{13}C NMR (125.61 MHz, CD_3CN, -35 °C) δ 150.2 (C-2), 147.7 (C-4'), 137.1 (C-4), 131.3 (C-3'), 136.9 (C-2'), 130.8 (C-3'), 124.7 (C-3). ^{19}F NMR (470.3 MHz, CD_3CN, -35 °C) δ 45.9 (N-F), -150.9 ($B_2F_7^-$). ^{15}N NMR (50.67 MHz, CD_3CN, -35 °C) δ-70.6 (N-1), -127.9 (N-1').

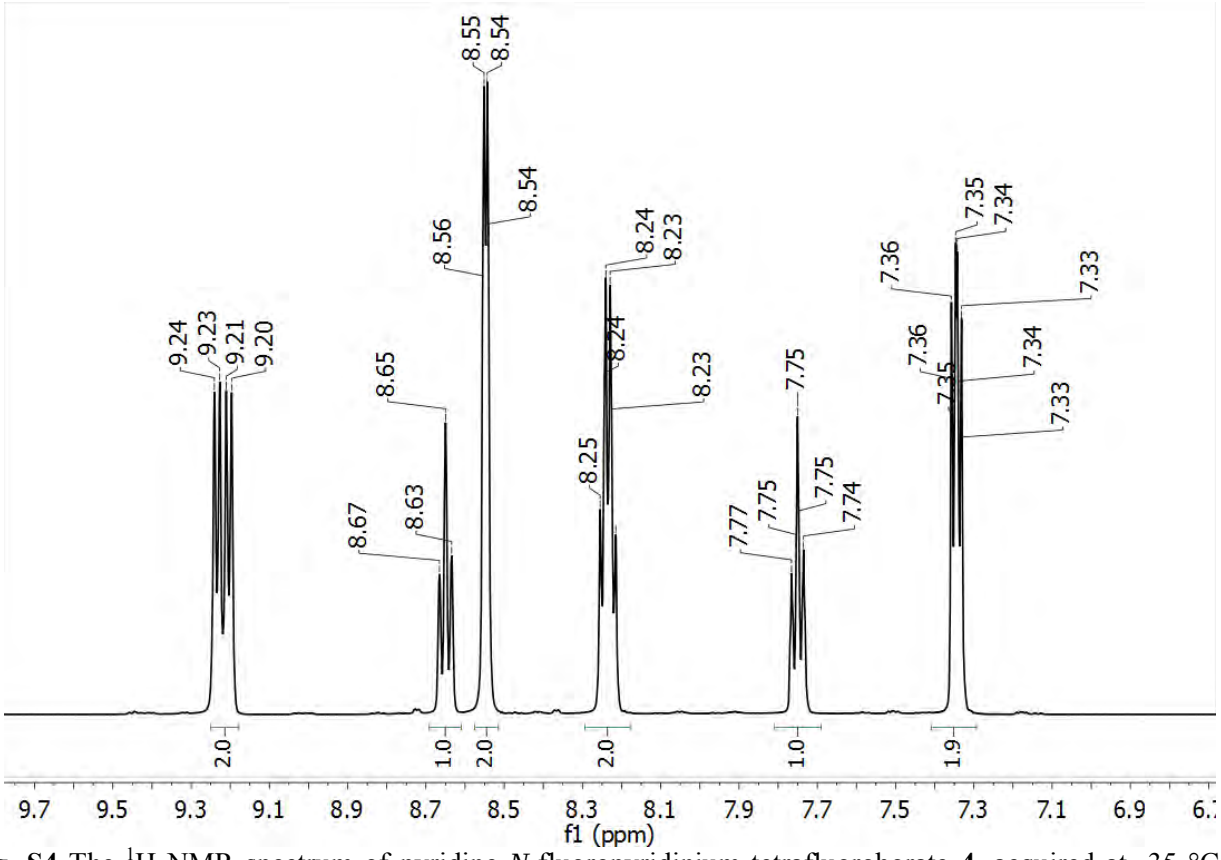


Fig. S4 The ^{1}H NMR spectrum of pyridine *N*-fluoropyridinium tetrafluoroborate **4**, acquired at -35 °C in CD_3CN at 499.89 MHz.

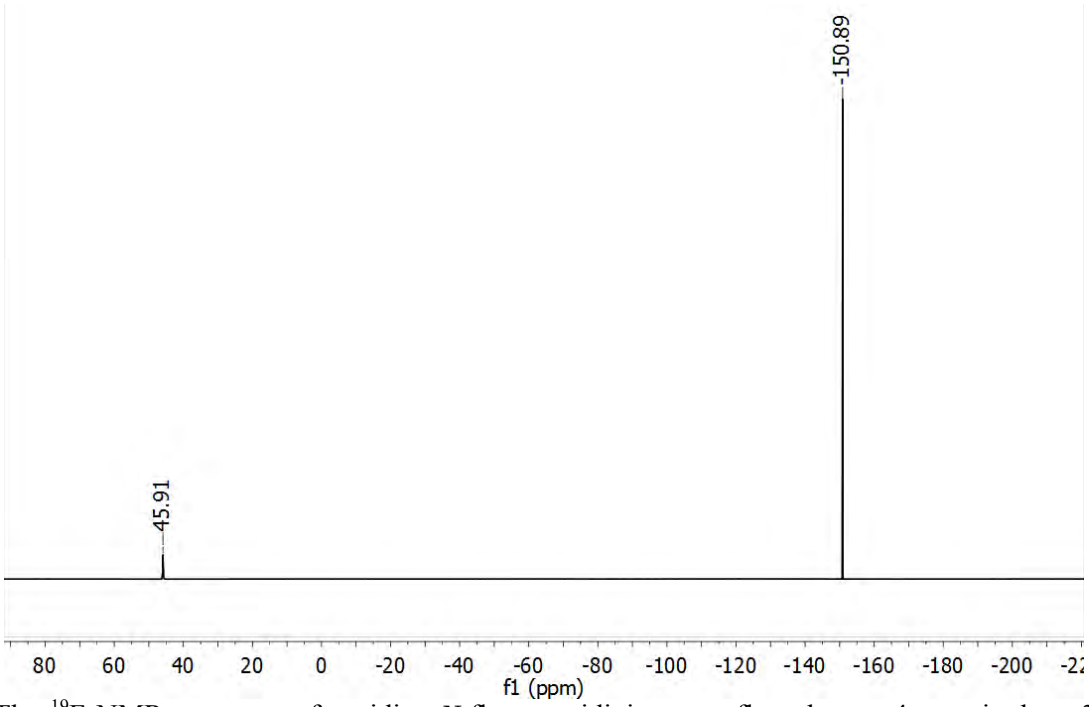


Fig.S5 The ^{19}F NMR spectrum of pyridine *N*-fluoropyridinium tetrafluoroborate **4**, acquired at -35 °C in CD_3CN at 470.3 MHz. The signal at 45.91 ppm of the nitrogen bound fluorine (N-F) is broadened by J_{HF} couplings and possibly by the quadrupolar relaxation of the quaternalized nitrogen it binds to.

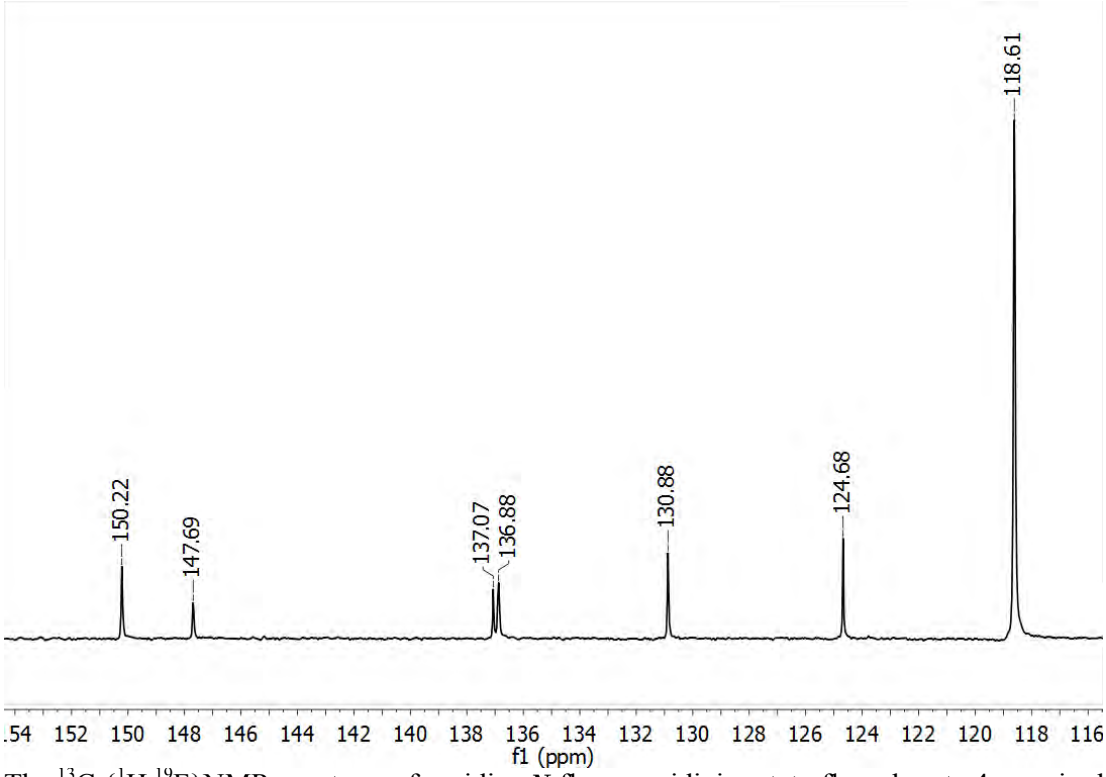


Fig. S6 The ^{13}C {^{1}H,^{19}F}NMR spectrum of pyridine *N*-fluoropyridinium tetrafluoroborate **4**, acquired at -35 °C in CD_3CN at 125.71 MHz.

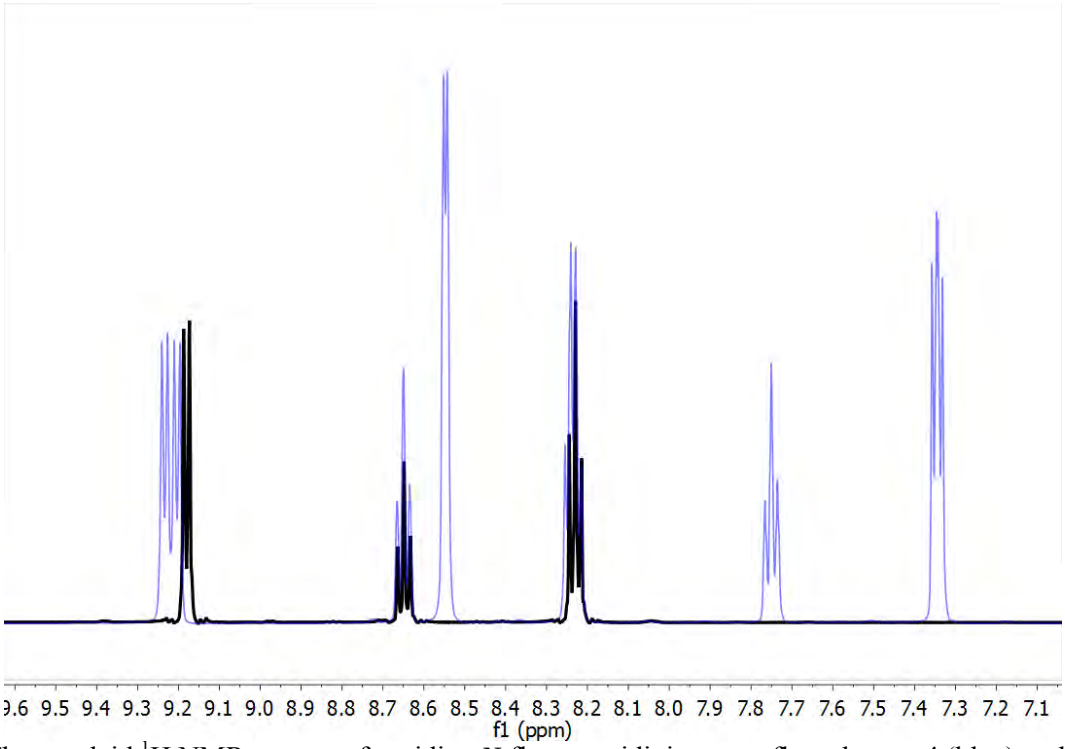


Fig. S7 The overlaid ^{1}H NMR spectra of pyridine *N*-fluoropyridinium tetrafluoroborate **4** (blue) and *N*-fluoropyridinium tetrafluoroborate **8** (black), acquired at -35 °C in CD_3CN at 499.89 MHz.

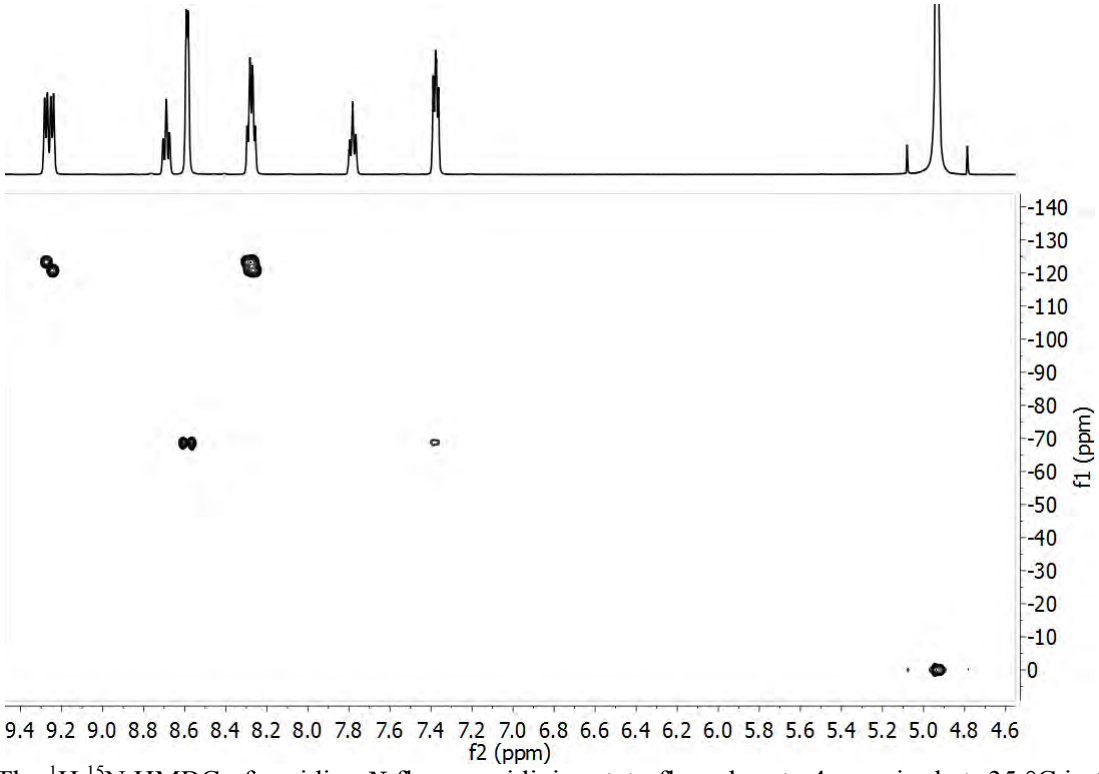


Fig S8 The ^{1}H,^{15}N HMBC of pyridine *N*-fluoropyridinium tetrafluoroborate **4**, acquired at -35 °C in CD_3CN. The *N*-fluorinated pyridine, with ^{19}F-^{1}H couplings observed in the ^{1}H spectrum, gives correlation to a nitrogen at -127.9 ppm with a $^{1}J_{F,N}$=133 Hz. The second set of pyridine protons gives correlation to a nitrogen at -70.6 ppm.

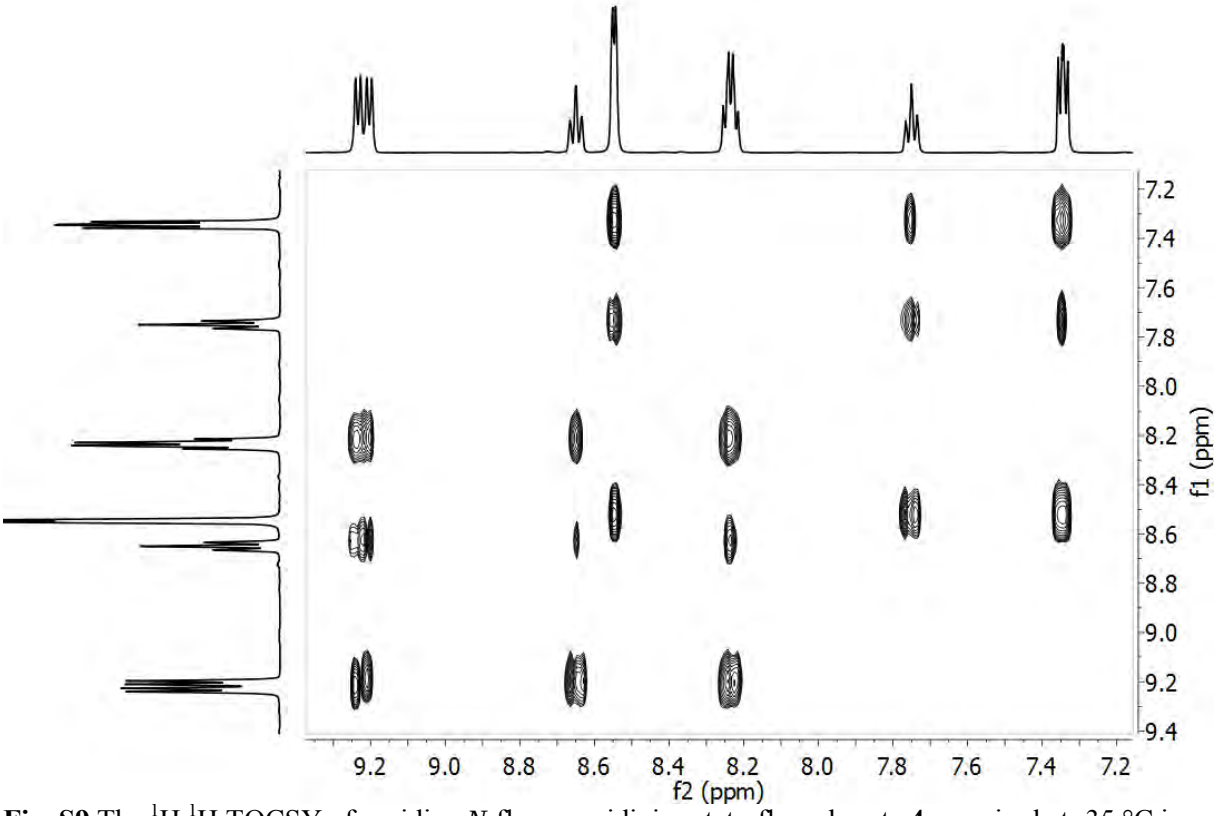
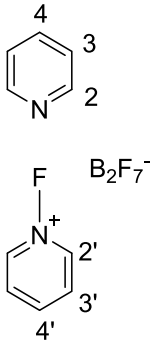


Fig. S9 The $^{1}H,^{1}H$ TOCSY of pyridine *N*-fluoropyridinium tetrafluoroborate **4**, acquired at -35 °C in CD_3CN, confirms the assignation of the involved pyridine rings.

2.3 Pyridine *N*-fluoropyridinium heptafluorodiborate 10



Pyridine *N*-fluoropyridinium heptafluorodiborate (**10**). ^{1}H NMR (499.95 MHz, CD_3CN, 25 °C) δ 13.06 (br s, 2H, H_2O), 9.19 (m, 2H, H-2'), 8.74 (br m, 2H, H 2), 8.69 (m, 1H, H-4'), 8.63 (br m, 1H, H-4), 8.27 (m, 2H, H-3'), 8.08 (br m, 2H, H-3). ^{13}C NMR (125.61 MHz, CD_3CN, 25 °C) δ 148.9 (C-2), 148.1 (C-2'), 142.6 (C-4), 137.2 (C-4'), 131.3 (C-3'), 128.8 (C-3). ^{19}F NMR (470.3 MHz, CD_3CN, 25 °C) δ 45.8 (N-F), -150.7 ($B_2F_7^-$). ^{11}B NMR (128.3 MHz, CD_3CN, 25 °C) δ -1.12 ($B_2F_7^-$). ^{15}N NMR (50.67 MHz, CD_3CN, -35 °C) δ 123.6 (N-1'), -185.3 (N-1).

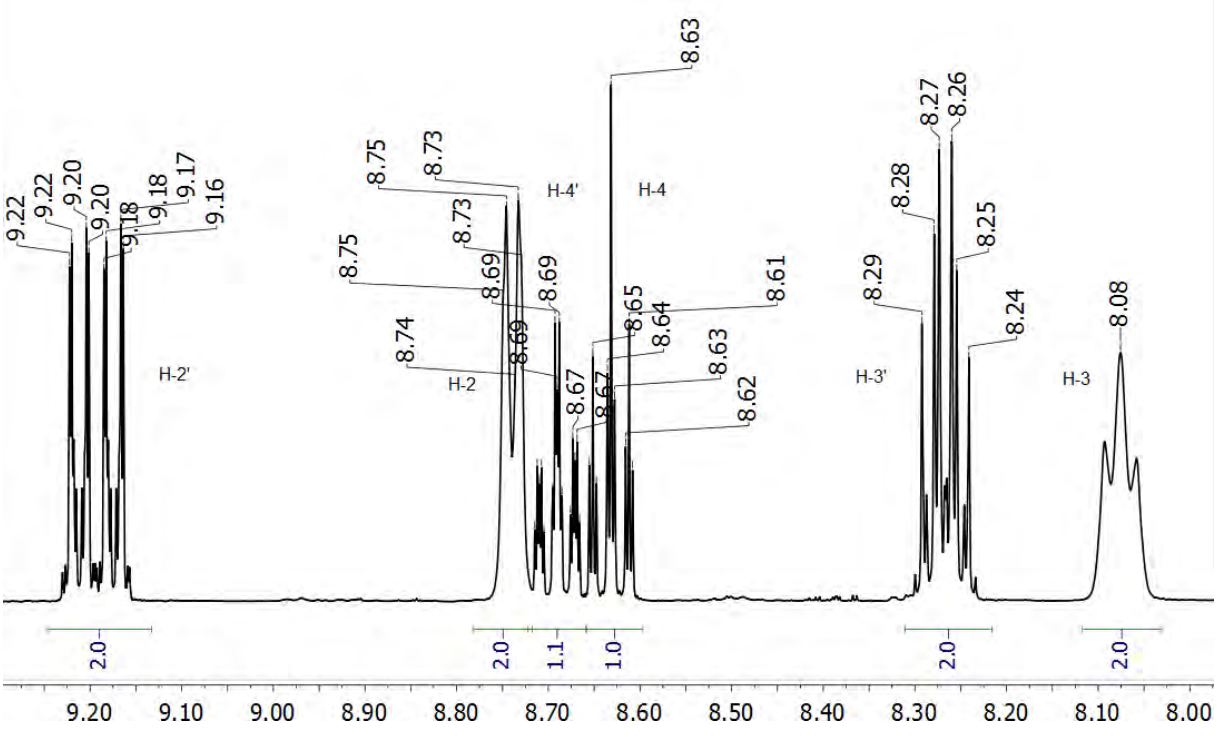


Fig. S10 The ^{1}H NMR spectrum of pyridine *N*-fluoropyridinium heptafluorodiborate **10**, acquired at 25 °C in CD_3CN at 499.89 MHz.

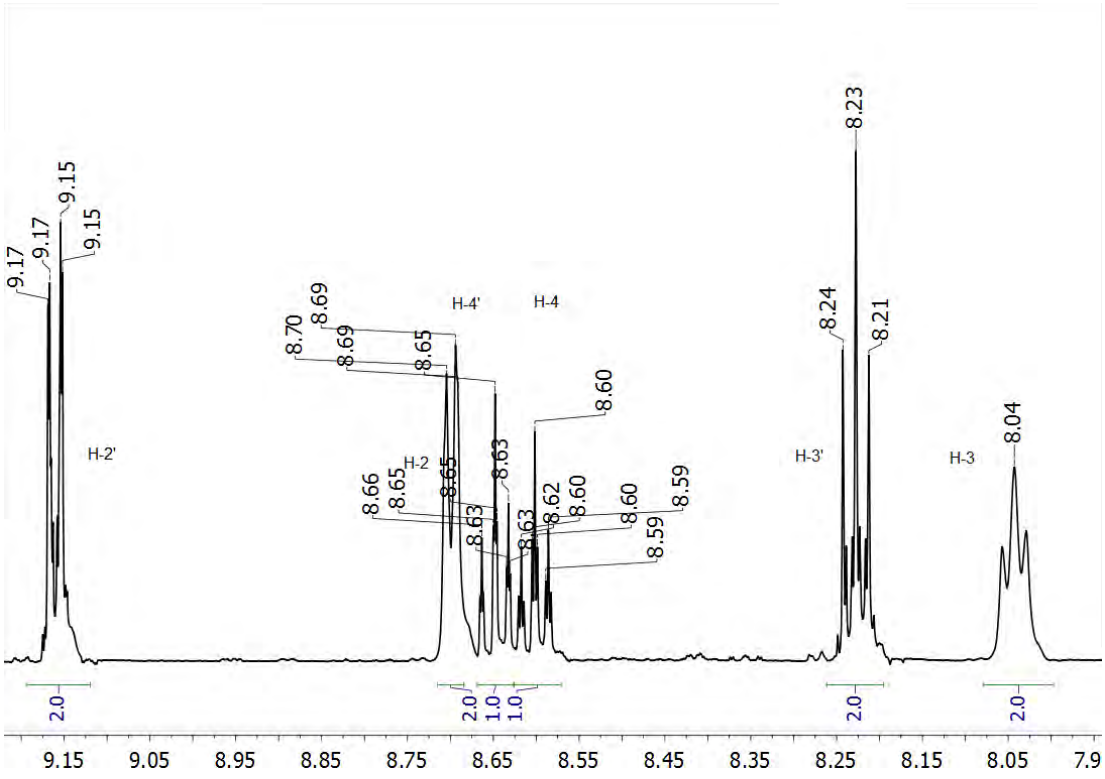


Fig. S11 The ^{19}F-decoupled ^{1}H NMR spectrum of pyridine *N*-fluoropyridinium heptafluorodibo-rate **10**, acquired at 25 °C in CD_3CN at 499.89 MHz.

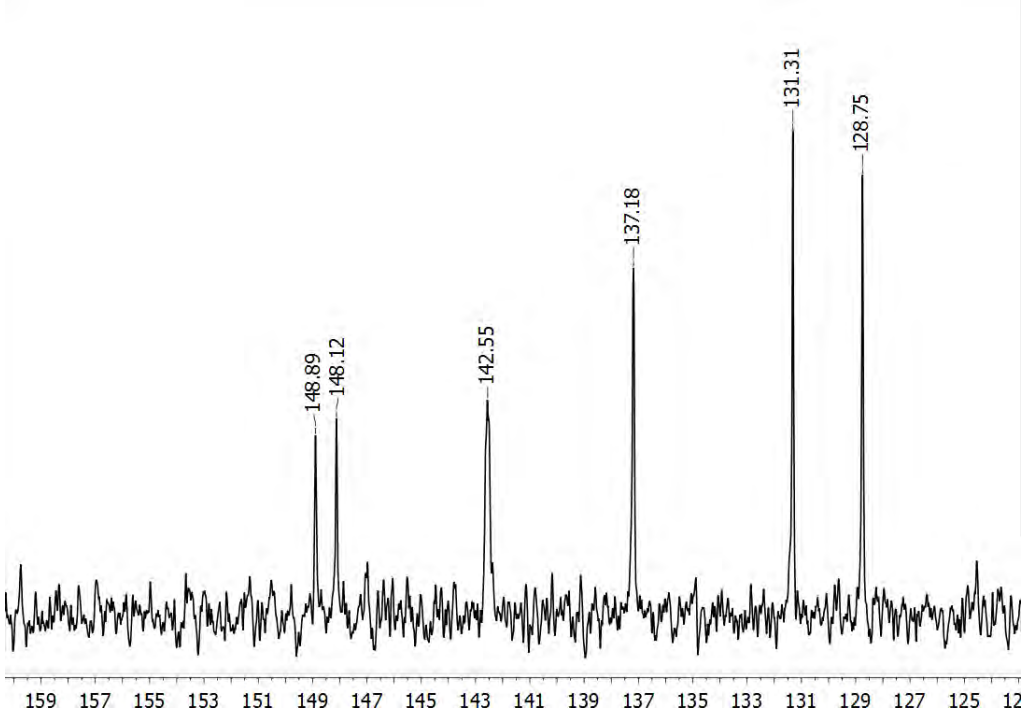


Fig. S12 The ^{1}H broadband and ^{19}F inverse gated decoupled ^{13}C NMR spectrum of pyridine *N*-fluoropyridinium heptafluorodiborate **10**, acquired at 25 °C in CD_3CN at 125.71 MHz.

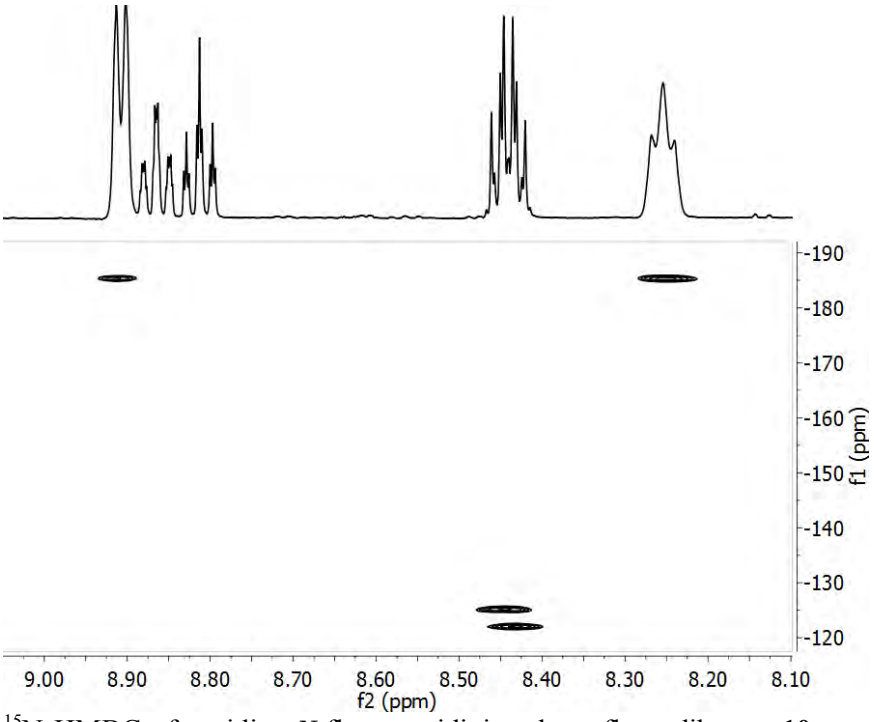


Fig. S13 The $^{1}H,^{15}N$ HMBC of pyridine *N*-fluoropyridinium heptafluorodiborate **10**, acquired at 25 °C in CD_3CN. The pyridine ring with broadened ^{1}H NMR signals gives correlations to a nitrogen at -185.5 ppm, whereas the other pyridine ring with sharper signals and distinct J_{HF} couplings to gives correlation to a nitrogen at -123.6 ppm. This signal, in turn, is splitted by a $^{1}J_{NF}$=128 Hz coupling.

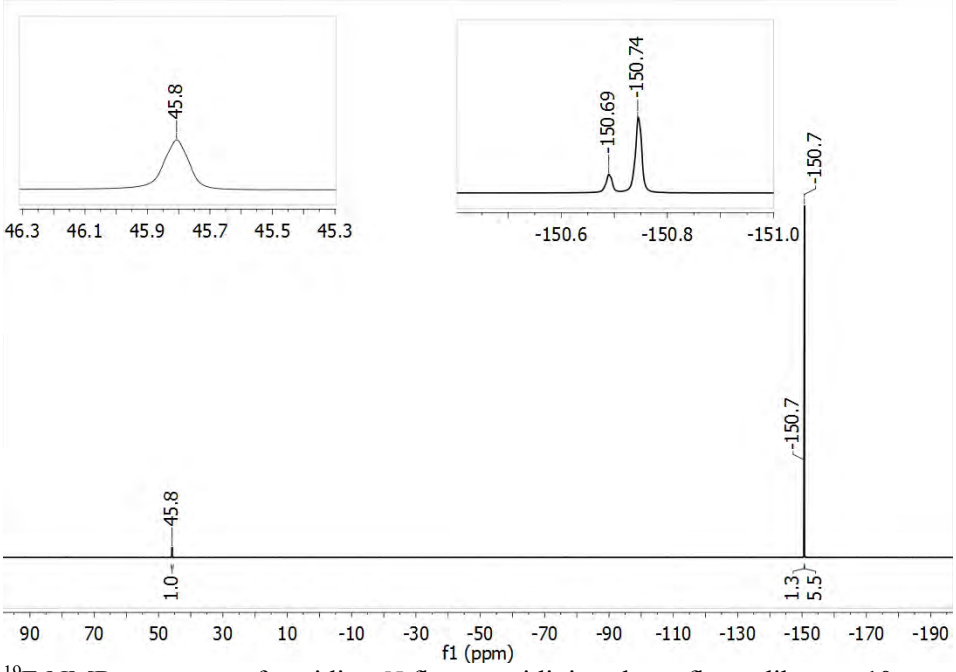


Fig. S14 The ^{19}F NMR spectrum of pyridine *N*-fluoropyridinium heptafluorodiborate **10**, acquired at 25 °C in CD_3CN at 470.3 Hz. The signal at 45.8 ppm of the nitrogen bound fluorine (N-F) is broadened by J_{HF} couplings and possibly by the quadrupolar relaxation of the quaternalized nitrogen it binds to. The signal at 150.7 ppm of the $B_2F_7^-$ counter ion is splitted by the isotope effect of boron, reflecting the 1 to 4 distribution of ^{10}B and ^{11}B.

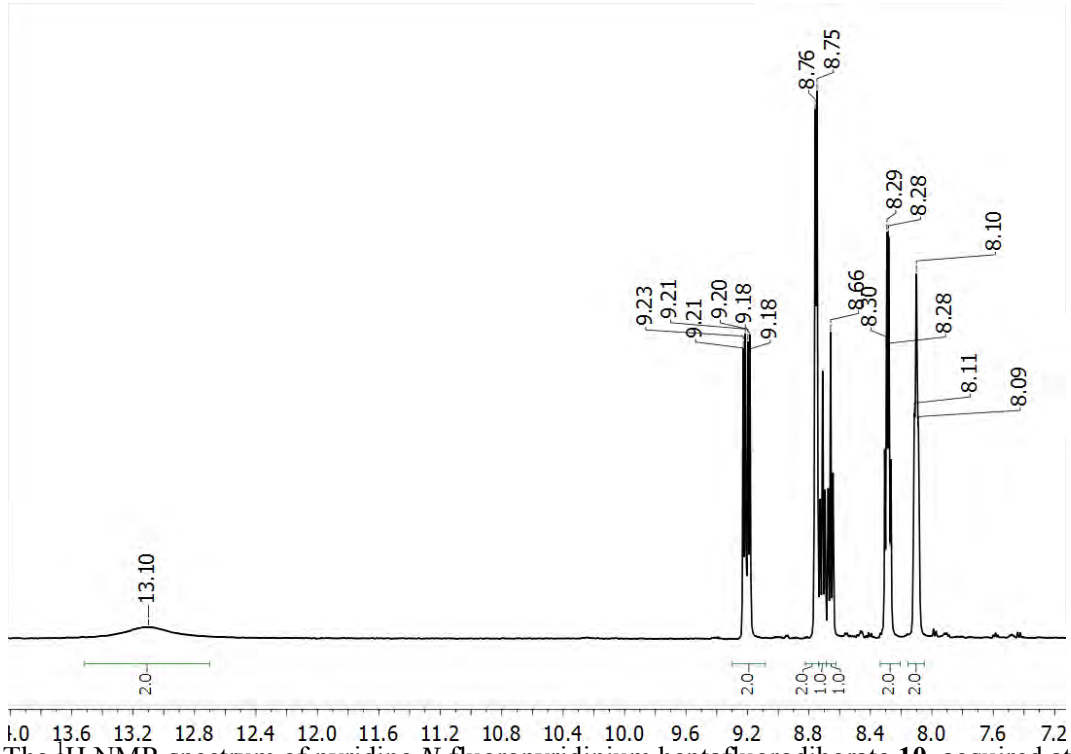


Fig. S15 The ^{1}H NMR spectrum of pyridine *N*-fluoropyridinium heptafluorodiborate **10**, acquired at 25 °C in CD_3CN at 399.95 MHz, indicating the broad OH peak at 13.1 ppm.

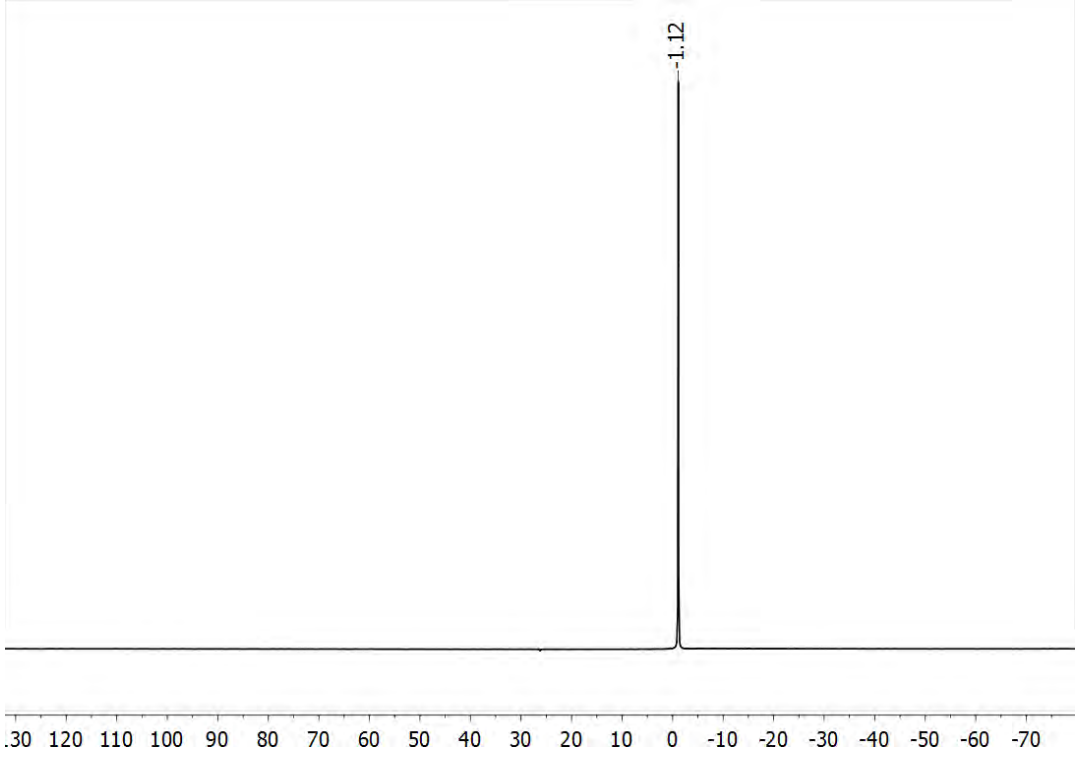
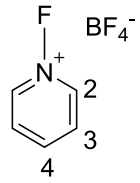


Fig. S16 The ^{11}B NMR spectrum of *N*-fluoropyridinium heptafluorodiborate **10** acquired at 25 °C in CD_3CN at 128.32 MHz.

2.4 Pyridine *N*-fluoropyridinium tetrafluoroborate 8



***N*-Fluoropyridinium tetrafluoroborate** (**8**). ^{1}H NMR (399.95 MHz, CD_3CN, 25 °C) δ 9.19 (m, 2H, H-2), 8.69 (m, 1H, H-4), 8.27 (m, 2H, H-3). ^{13}C NMR (125.61 MHz, CD_3CN, 25 °C) δ 148.9 (C-2), 148.1 (C-2'), 142.6 (C-4), 137.2 (C-4'), 131.3 (C-3'), 128.8 (C-3). ^{19}F NMR (470.3 MHz, CD_2Cl_2, 25 °C) δ 45.8 (N-F), -150.7 ($B_2F_7^-$). ^{11}B NMR (128.3 MHz, CD_3CN, 25 °C) δ -1.12 ($B_2F_7^-$). ^{15}N NMR (50.67 MHz, CD_3CN, -35 °C) δ -120.5 (N-1).

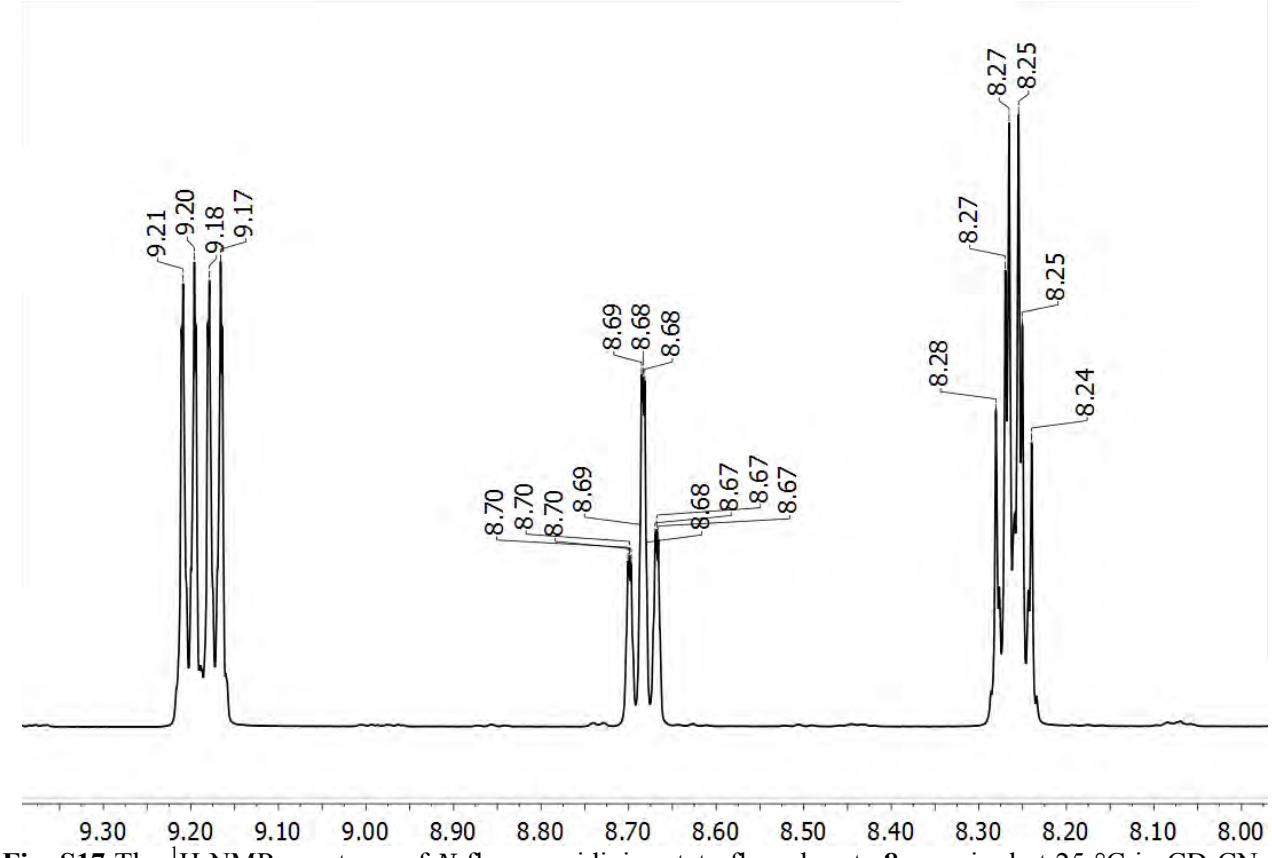


Fig. S17 The ^{1}H NMR spectrum of *N*-fluoropyridinium tetrafluoroborate **8**, acquired at 25 °C in CD_3CN at 499.89 MHz.

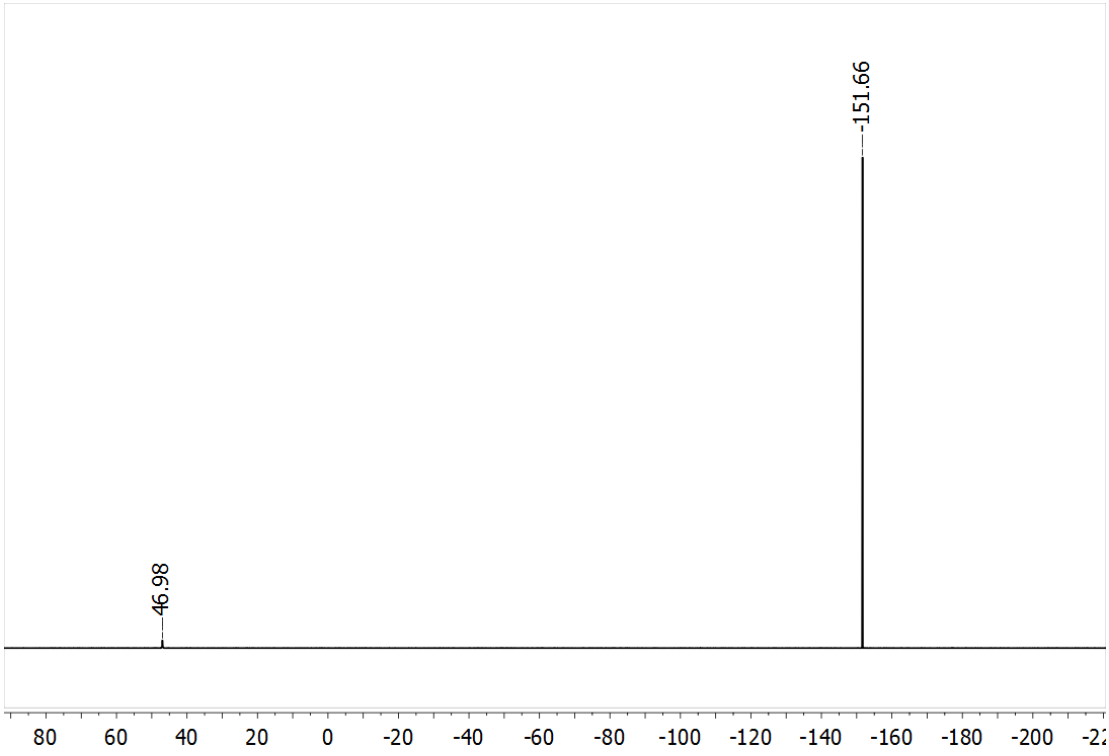


Fig. S18 The ^{19}F NMR spectrum of *N*-fluoropyridinium tetrafluoroborate **8** acquired at 25 °C in CD_3CN at 470.3 MHz.

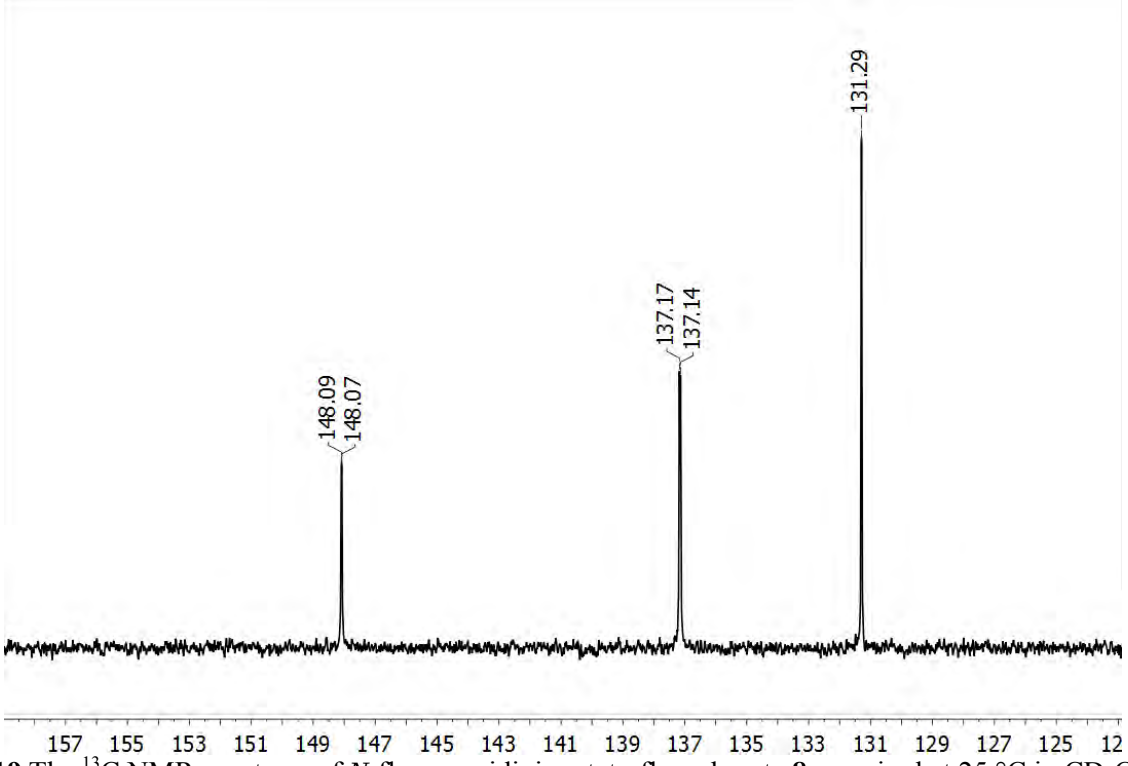


Fig. S19 The ^{13}C NMR spectrum of *N*-fluoropyridinium tetrafluoroborate **8**, acquired at 25 °C in CD_3CN at 125.61 MHz.

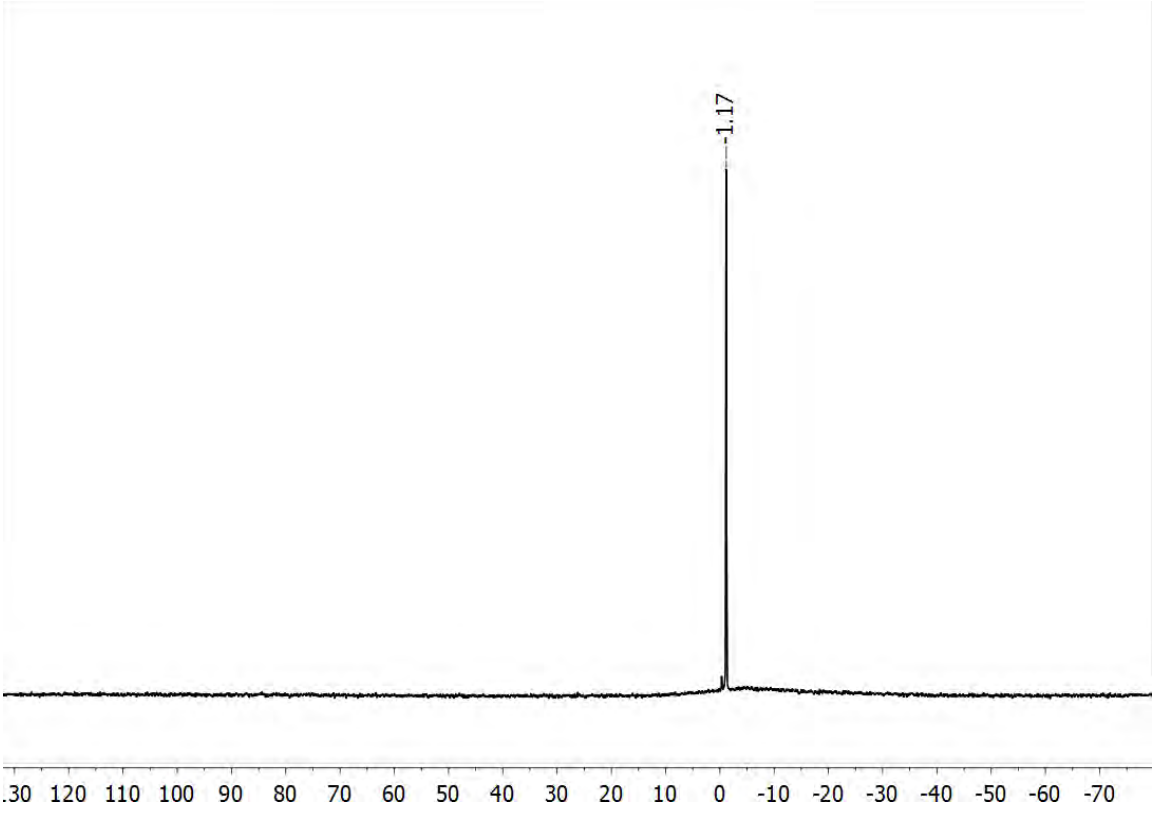


Fig. S20 The ^{11}B NMR spectrum of *N*-fluoropyridinium tetrafluoroborate **8**, acquired at 25 °C in CD_3CN at 128.32 MHz

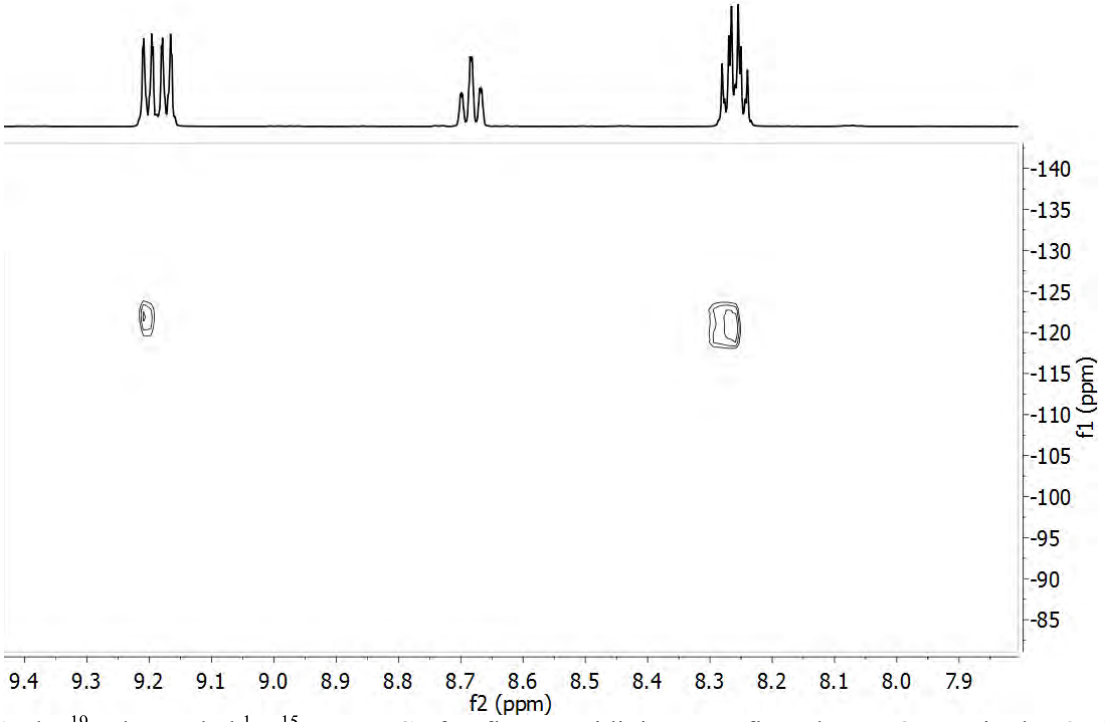


Fig. S21 The ^{19}F-decoupled ^{1}H,^{15}N HMBC of *N*-fluoropyridinium tetrafluoroborate **8**, acquired at 25 °C in CD_3CN.

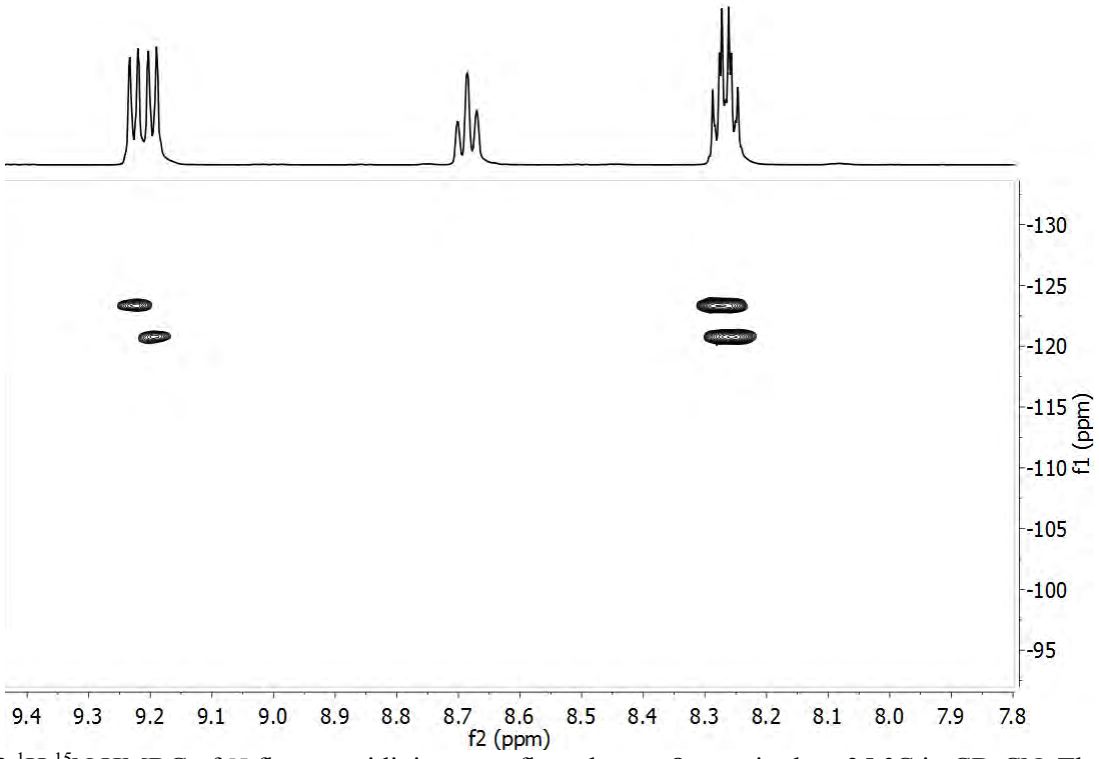


Fig. S22 $^{1}H,^{15}N$ HMBC of *N*-fluoropyridinium tetrafluoroborate **8**, acquired at -35 °C in CD_3CN. The signal is splitted by a $^{1}J_{NF}$=129 Hz coupling.

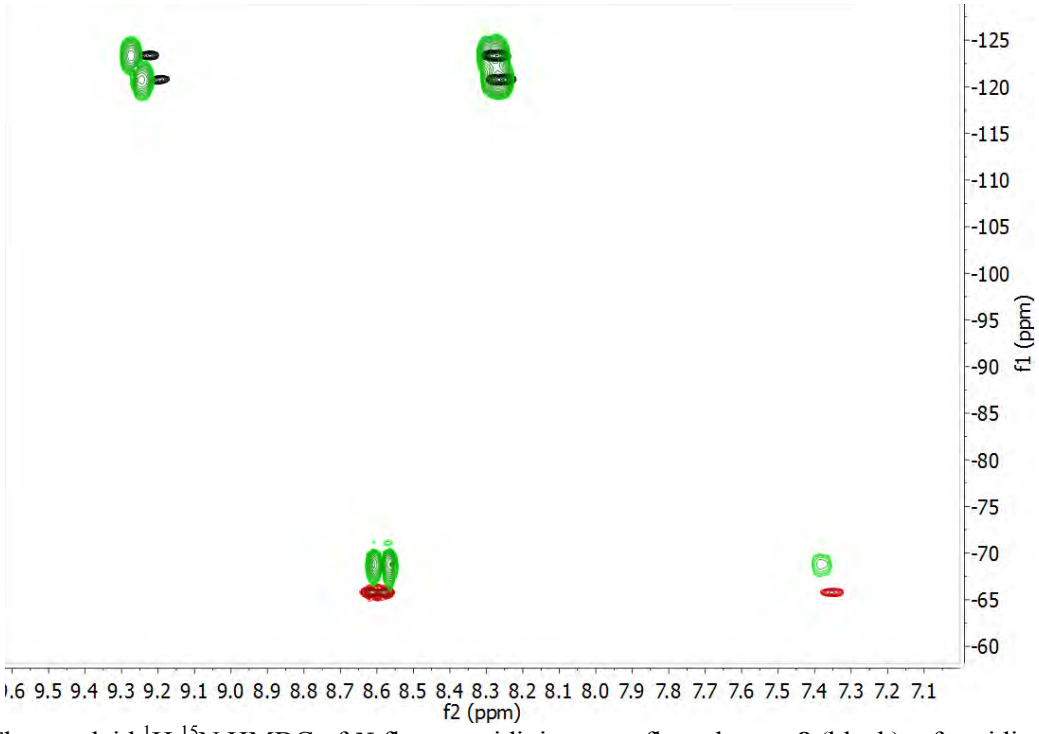


Fig. S23 The overlaid $^{1}H,^{15}N$ HMBC of *N*-fluoropyridinium tetrafluoroborate **8** (black), of pyridine **9** (red), and of **4** (green, a mixture of *N*-fluoropyridinium tetrafluoroborate **8** and pyridine **9**) acquired at -35 °C in CD_3CN. Significant ^{15}N chemical shift change is observed for one of the pyridines of **4** as compared to **9**. Upon mixing **8** and **9**, some signal broadenings is seen (**4**).

2.5 Addition of water to *N*-fluoropyridinium tetrafluoroborate

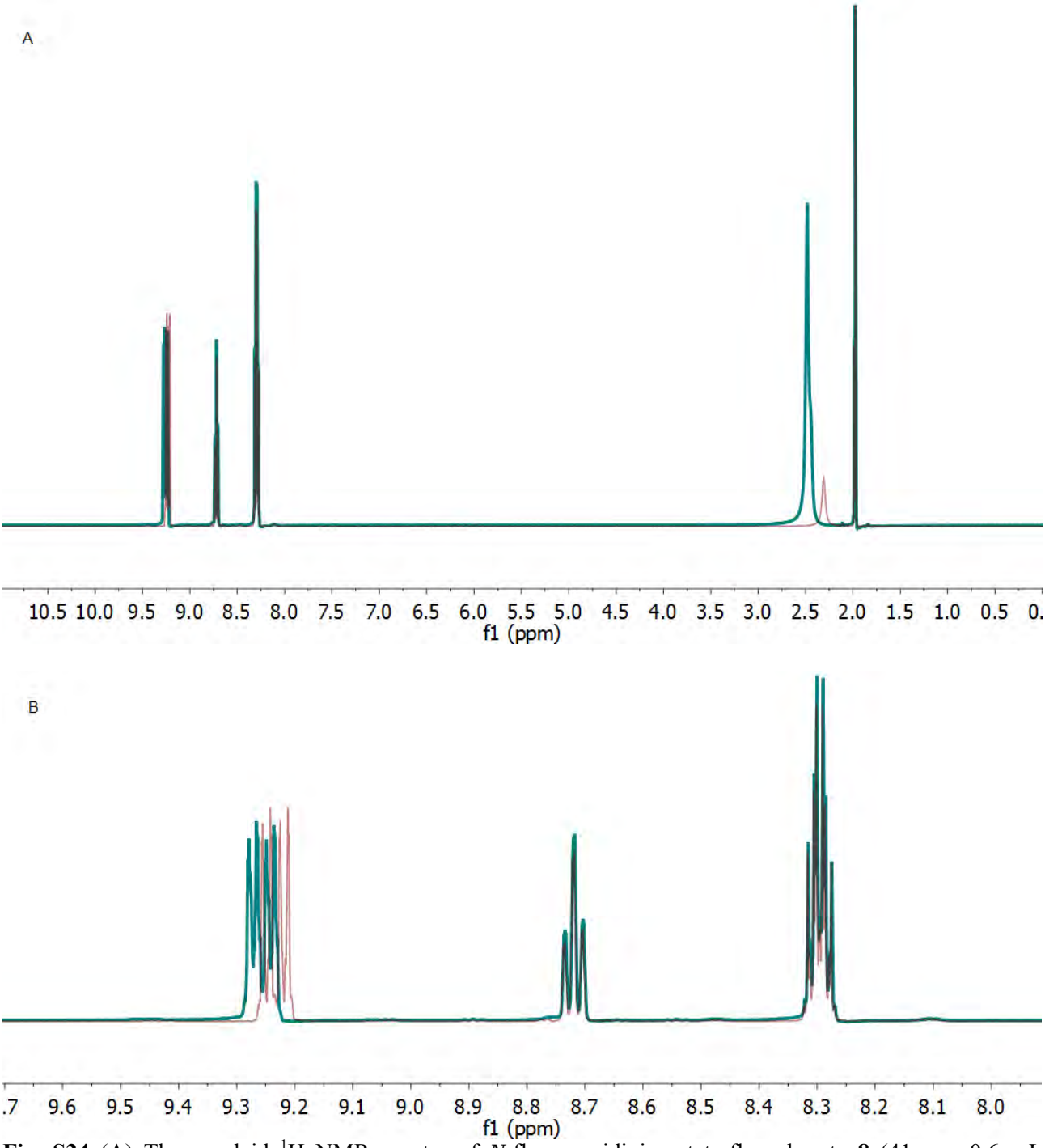
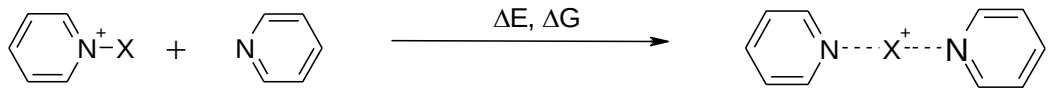


Fig. S24 (A) The overlaid ^{1}H NMR spectra of *N*-fluoropyridinium tetrafluoroborate **8** (41 mg, 0.6 mL CD_3CN, 25 °C) before (red), and after (blue) addition of 1 equivalent water (7 µl). (B) The enlarged aromatic region of the spectrum shown in (A). Upon addition of water a small chemical shift change of the H-2 pyridine proton (9.23 to 9.26 ppm) is observed. However, no sign of hydrolysis was observed. Hence the commercially available "pyridine *N*-fluoropyridinium heptafluorodiborate" **10** (*N*-fluoropyridinium pyridinium tetrafluoroborate trifluorohydroxyborate) is unlikely to form upon hydrolysis of pyridine *N*-fluoropyridinium heptafluorodiborate **4**.

3. Computational Details: Geometry Optimization and Thermochemistry

3.1 Equilibrium geometries and thermochemistry

Table S1 Equilibrium geometries and relative stabilities of **1** – **4**. Δ*E*: electronic energy, Δ*G*: Gibbs free energy. Calculations done with the basis set described in Section 2 and for CH_2Cl_2 solution.

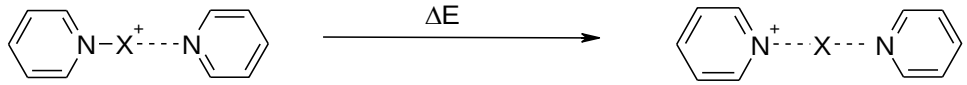


X	**Method**	**N_1-X** (Å)	**N_2-X** (Å)	**ΔE** (kJ/mol)	**ΔG** (kJ/mol)
I	B3LYP	2.303	2.303	-109.23	-58.61
Br	B3LYP	2.140	2.140	-92.89	-42.70
Cl	B3LYP	2.025	2.025	-57.47	-9.46
	B3LYP-D3	2.025	2.025	-65.72	-18.97
	MP2	1.994	1.994	-58.79	-10.54
	M06-2X	1.982	1.982	-46.63	-0.70
F	B3LYP	1.360	3.792	-2.73	21.30

Table S2 The energy-cost of stretching an N-X bond from the optimized covalent length of **5** - **8** to the bond length of symmetric $[N\cdots X\cdots N]^+$ complexes **1** – **4.** This N-F bond length corresponds to the lowest energy of the symmetric geometry identified in the PES-scan (saddle point), which is described in the main text. Calculations were done at the B3LYP level of theory with the basis set described in Section 2, and for CH_2Cl_2 solution.

X	**N-X** (Å)	**N-X** (Å)	**ΔE** (kJ/mol)
I	2.093	2.303	22.31
Br	1.893	2.140	35.63
Cl	1.726	2.027	57.94
F	1.360	1.800[(a)]	140.69

Table S3 The energy gain upon forming the symmetric $[N^{\cdots}X^{\cdots}N]^{+}$ geometry of **1** – **3**, from the corresponding asymmetric $[N\text{-}X^{\cdots}N]^{+}$ complexes.[a]



X	**N_1-X** (Å)	**N_2-X** (Å)	**N-X** (Å)	**ΔE** (kJ/mol)
I	2.093	2.403	2.303	15.94
Br	1.893	2.315	2.140	20.09
Cl	1.726	2.371	2.027	16.31
F	1.360	3.781	1.360, 3.792	0.00074

[a]Calculations done at the B3LYP level of theory with the basis set described in Section 2 and for CH_2Cl_2 solution. For **4** the unrestrained asymmetric geometry is the global energy minimum. In the asymmetric starting geometries one bond was fixed to the covalent N-X distance, corresponding to that in **5**-**8**, whereas the second pyridine nitrogen was allowed to interact with the sigma hole of X in a geometry optimization. The symmetric **1**-**3** and asymmetric **4** geometries correspond to the global energy minimum of each complex.

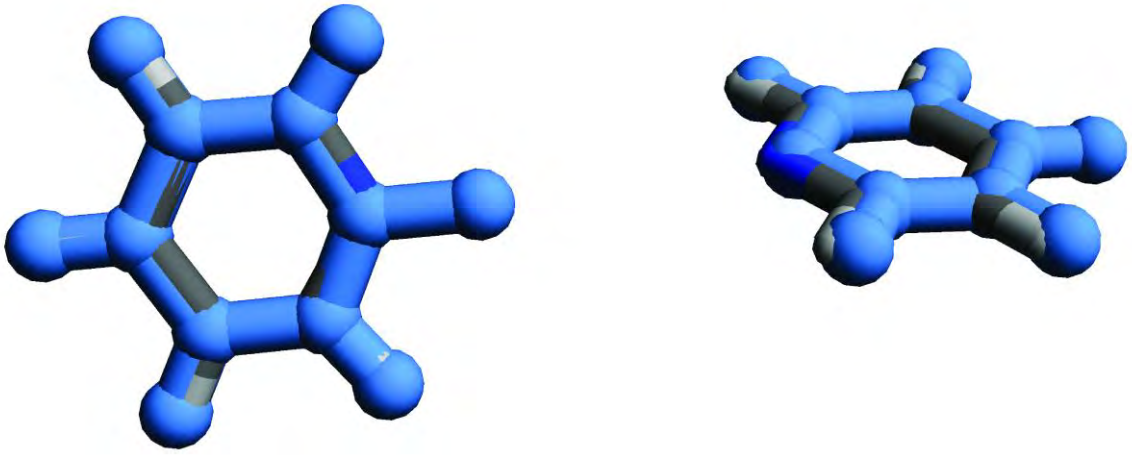


Fig. S25 The superimposed structure of pyridine *N*-fluoropyridinium tetrafluoroborate **4**, geometry optimized using dichloromethane (gray) and acetonitrile (blue) solvent models. Cartesian coordinates are given below in section 3.3.The comparable structure of 4 in the two solvents is in line with previous studies of **1** and **2**.[2]

3.2 Natural bond orbital (NBO) analyses

Table S4 Natural polulation analysis (NPA) charges for the halogen and nitrogen atoms in the equilibrium geometries of complexes **1**-**4**. **X**, denotes the halogen, whereas **ΔQ(NPA)** the change of the NPA charge upon the reaction of pyridine-$\mathbf{X}^+$ to of pyridine-$\mathbf{X}^+$–pyridine. Calculations were done at the B3LYP level of theory with the basis set described in Section 2, and for CH_2Cl_2 solution.

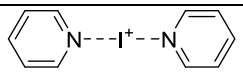
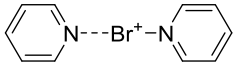
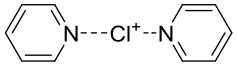
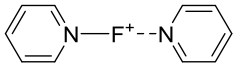
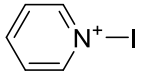
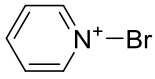
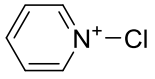
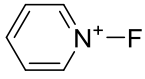
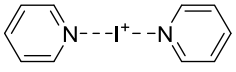
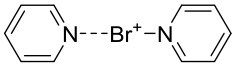
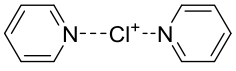
Structure	Compound	N1	N2	X	ΔQ(NPA)
	**1**	-0.52306	-0.52306	+0.41109	-0.09846
	**2**	-0.47079	-0.47079	+0.27835	-0.11412
	**3**	-0.41031	-0.41039	+0.15503	-0.12131
	**4**	+0.08956	-0.50874	-0.15437	+0.00405
	**5**	-0.51726	n.a.	0.50955	
	**6**	-0.44625	n.a.	0.39247	
	**7**	-0.35104	n.a.	0.27634	
	**8**	0.09074	n.a.	-0.15842	
		-0.50705	n.a.	n.a.	

Table S5 Second-order perturbation theory analysis of the Fock matrix for the delocalization from the N lone-pair NBO into the N–X virtual bond NBO in compounds **1**–**3**. [a]

Structure	Compound	ε(N lp)[b]	ε(N–X bd*)[c]	Δε[d]	F [e]	ΔE_{PT2} [f]
	**1**	-0.4573	-0.2066	0.2508	0.159	454
	**2**	-0.4519	-0.2366	0.2154	0.177	628
	**3**	–0.4570	-0.2764	0.1806	0.188	808

[a]Calculations done at the B3LYP level of theory with the basis set described in Section 2, and for CH_2Cl_2 solution. [b]Orbital energy for the N lone-pair NBO. [c]Orbital energy for the N–X virtual bond NBO. [d]Orbital energy difference. [e]Fock matrix element between the two mentioned NBOs. [f]Energy contribution (in second-order perturbation theory) arising from the from the mentioned delocalization.

3.3 Cartesian coordinates, energies and selected vibrational frequencies

Energies are given in Hartree units unless otherwise stated, coordinates in Ångström, and vibrational frequencies in cm^{-1}. E(e) denotes the electronic energy (without ZPE), E(298), H(298) and G(298) the energy (including vibrational corrections), enthalpy and Gibbs free energy at 298.15k and 1 atm.

Pyridine, CH_2Cl_2, B3LYP

Charge = 0 Multiplicity = 1

C	1.197085	-0.671415	0.000000
C	1.144194	0.720604	-0.000001
C	0.000001	-1.382075	0.000000
C	-1.197084	-0.671416	0.000000
C	-1.144195	0.720603	0.000000
N	-0.000001	1.417441	0.000000
H	2.061237	1.304206	0.000002
H	2.154382	-1.180558	0.000002
H	0.000001	-2.467179	0.000000
H	-2.154381	-1.180561	-0.000001
H	-2.061238	1.304204	-0.000001

E(e)	=	-248.3548683	
ZPE	=	0.088293	
	=	231.8133	kJ/mol
E(298)	=	-248.262296	
H(298)	=	-248.261352	
G(298)	=	-248.293976	

Pyr-F^+, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	0.000000	0.000000	-2.910571
C	0.000000	0.000000	-1.825977
C	0.000000	1.208579	-1.130017
C	0.000000	1.198961	0.252370
N	0.000000	0.000000	0.852972
C	0.000000	-1.198961	0.252370
C	0.000000	-1.208579	-1.130017
H	0.000000	2.163151	-1.642588
H	0.000000	2.070205	0.898038
F	0.000000	0.000000	2.212944
H	0.000000	-2.070205	0.898038
H	0.000000	-2.163151	-1.642588

E(e)	=	-347.965659271
ZPE	=	0.092084

	=	241.7666	kJ/mol
E(298)	=	-347.868394	
H(298)	=	-347.867450	
G(298)	=	-347.901778	

Frequencies:

Stretch (N-F) 534.04

Pyr-F$^+$ (N-F frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	0.000000	0.000000	-3.121566
C	0.000000	0.000000	-2.036061
C	0.000000	1.211273	-1.347128
C	0.000000	1.207714	0.048907
N	0.000000	0.000000	0.571255
C	0.000000	-1.207714	0.048907
C	0.000000	-1.211273	-1.347128
H	0.000000	2.173611	-1.849377
H	0.000000	2.079426	0.697574
F	0.000000	0.000000	2.371255
H	0.000000	-2.079426	0.697574
H	0.000000	-2.173611	-1.849377

E(e) = -347.912074592

Pyr-Cl$^+$, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	3.335371	0.000000	0.000104
C	2.250770	0.000000	0.000135
C	1.549713	-1.204110	0.000004
C	0.169279	-1.191041	-0.000087
N	-0.472969	-0.000001	-0.000109
C	0.169279	1.191043	-0.000087
C	1.549711	1.204111	0.000004
H	2.058521	-2.160906	0.000035
H	-0.447657	-2.081392	-0.000248
Cl	-2.198755	0.000000	0.000075
H	-0.447660	2.081391	-0.000246
H	2.058522	2.160906	0.000035

E(e)	=	-708.352318819	
ZPE	=	0.091035	
	=	239.0124	kJ/mol

E(298) = -708.255757
H(298) = -708.254813
G(298) = -708.291109
Frequencies:
Stretch (N-Cl) 424.68

Pyr-Cl$^+$ (N-Cl frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	3.479310	0.000001	0.000059
C	2.394472	0.000000	0.000025
C	1.697891	-1.206534	-0.000017
C	0.310996	-1.196022	-0.000070
N	-0.285956	0.000000	-0.000095
C	0.310996	1.196022	-0.000069
C	1.697890	1.206534	-0.000017
H	2.205588	-2.164691	-0.000007
H	-0.311812	-2.082546	-0.000104
Cl	-2.312956	0.000000	-0.000141
H	-0.311813	2.082546	-0.000103
H	2.205588	2.164692	-0.000006

E(e) = -708.330251506

Pyr-Br$^+$, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	3.929906	0.000066	0.000010
C	2.845304	0.000023	0.000098
C	2.143319	-1.203172	0.000029
C	0.762287	-1.187879	-0.000081
N	0.113773	-0.000025	-0.000144
C	0.762236	1.187857	-0.000078
C	2.143277	1.203197	0.000029
H	2.651105	-2.160561	0.000140
H	0.152753	-2.083028	-0.000264
Br	-1.779213	0.000000	0.000036
H	0.152675	2.082985	-0.000261
H	2.651055	2.160588	0.000127

E(e) = -261.309526253
ZPE = 0.090505

	=	237.6209	kJ/mol
E(298)	=	-261.213253	
H(298)	=	-261.212308	
G(298)	=	-261.250000	

Frequencies:

Stretch (N-Br)		317.48

Pyr-Br$^+$ (N-Br frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	4.048475	0.000039	0.000081
C	2.963732	0.000023	0.000036
C	2.265205	-1.205037	-0.000005
C	0.879475	-1.190806	-0.000071
N	0.262792	-0.000015	-0.000100
C	0.879442	1.190794	-0.000073
C	2.265171	1.205064	-0.000007
H	2.772991	-2.162880	0.000016
H	0.265299	-2.082821	-0.000106
Br	-1.877208	-0.000039	-0.000152
H	0.265242	2.082792	-0.000108
H	2.772932	2.162920	0.000013

E(e)	=	-261.295955390

Pyr-I$^+$, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	4.386623	-0.000113	0.000077
C	3.302018	-0.000087	0.000259
C	2.598546	-1.201905	0.000052
C	1.216979	-1.183013	-0.000161
N	0.558009	0.000087	-0.000293
C	1.217111	1.183112	-0.000159
C	2.598667	1.201823	0.000045
H	3.105337	-2.159800	0.000110
H	0.616712	-2.084272	-0.000416
I	-1.534663	-0.000001	0.000044
H	0.616892	2.084408	-0.000379
H	3.105605	2.159639	0.000087

E(e)	=	-259.537455058	
ZPE	=	0.090266	
	=	236.9776	kJ/mol
E(298)	=	-259.441310	
H(298)	=	-259.440366	
G(298)	=	-259.479050	

Frequencies:

Stretch (N-I)	260.40

Pyr-I^+ (N-I frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	4.487639	-0.000113	0.000135
C	3.402970	-0.000069	0.000081
C	2.702180	-1.203435	-0.000016
C	1.317218	-1.184696	-0.000125
N	0.680980	0.000049	-0.000172
C	1.317320	1.184739	-0.000123
C	2.702281	1.203358	-0.000015
H	3.209811	-2.161142	-0.000008
H	0.712464	-2.082748	-0.000207
I	-1.621020	0.000122	-0.000246
H	0.712637	2.082840	-0.000202
H	3.209997	2.161020	-0.000005

E(e) = -259.528958428

Pyr-F^+-Pyr, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

C	-4.681931000	-0.937006000	-0.586024000
C	-3.302663000	-0.907931000	-0.779008000
C	-5.260677000	0.035423000	0.224792000
C	-4.436267000	0.994273000	0.806963000
C	-3.067950000	0.938134000	0.552510000
N	-2.497035000	0.008204000	-0.225048000
H	-2.821750000	-1.653358000	-1.407149000
H	-5.282383000	-1.704337000	-1.061807000
H	-6.331555000	0.045923000	0.399089000
H	-4.840146000	1.771808000	1.445749000
H	-2.398791000	1.672950000	0.992765000

F	0.999449000	-0.068332000	-0.132544000
N	2.356799000	-0.038060000	-0.053041000
C	2.972764000	0.982435000	-0.667958000
C	4.352519000	1.022879000	-0.590745000
C	2.941946000	-1.031008000	0.632966000
C	4.321485000	-1.007574000	0.720229000
C	5.031564000	0.023947000	0.106473000
H	2.339403000	1.698918000	-1.179239000
H	4.876301000	1.836641000	-1.078061000
H	6.113933000	0.049207000	0.171169000
H	2.286213000	-1.777430000	1.067456000
H	4.820650000	-1.797771000	1.268354000

E(e)	=	-596.3215555	
ZPE	=	0.180828	
	=	474.5303	kJ/mol
E(298)	=	-596.128815	
H(298)	=	-596.127871	
G(298)	=	-596.185821	

Frequencies:

Twist	39.76
Stretch (N-F-N symm)	32.19

Pyr-F$^+$---Pyr (N-F frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	0.042125	0.132479	-3.611909
C	0.030250	0.083155	-2.528501
C	0.095396	1.256616	-1.777649
C	0.079523	1.184081	-0.397227
N	0.000994	-0.038681	0.148527
C	-0.064434	-1.206713	-0.507578
C	-0.050056	-1.153575	-1.888938
H	0.158259	2.231835	-2.245674
H	0.124203	2.023339	0.288031
F	-0.014034	-0.100651	1.507003
H	-0.123384	-2.104623	0.097629
H	-0.101701	-2.082217	-2.444817
C	1.012679	0.007395	7.330248
C	0.965385	-0.104380	5.942639
C	-0.137092	-0.281170	8.060131
C	-1.283501	-0.668618	7.371890
C	-1.229689	-0.750383	5.982390
N	-0.130549	-0.475643	5.267084

H	1.846883	0.113779	5.345262
H	1.929911	0.312975	7.821183
H	-0.139650	-0.205890	9.142542
H	-2.202990	-0.903880	7.896184
H	-2.108218	-1.050124	5.416857

E(e) = -596.321568802

Pyr-Cl$^+$-Pyr, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	0.000000
N	0.000000	0.000000	2.024485
C	-0.521116	1.047300	2.675480
C	0.521116	-1.047300	2.675480
C	0.000000	0.000000	4.764823
C	-0.535475	1.077195	4.062462
C	0.535475	-1.077195	4.062462
H	-0.921850	1.850654	2.067362
H	0.921850	-1.850654	2.067362
H	0.000000	0.000000	5.849401
H	-0.960881	1.932464	4.573813
H	0.960881	-1.932464	4.573813
N	0.000000	0.000000	-2.024485
C	0.521116	1.047300	-2.675480
C	-0.521116	-1.047300	-2.675480
C	0.000000	0.000000	-4.764823
C	0.535475	1.077195	-4.062462
C	-0.535475	-1.077195	-4.062462
H	0.921850	1.850654	-2.067362
H	-0.921850	-1.850654	-2.067362
H	0.000000	0.000000	-5.849401
H	0.960881	1.932464	-4.573813
H	-0.960881	-1.932464	-4.573813

E(e) = -956.7290220980
ZPE = 0.180712
= 474.4597 kJ/mol
E(298) = -956.536653
H(298) = -956.535709
G(298) = -956.587703

Frequencies:

Stretch (N-Cl-N, asym)	123.02
Twist	19.99
Stretch (N-Cl-N, sym)	174.98

Pyr-Cl$^+$-Pyr (N-Cl frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	-5.826173	-0.000049	0.000595
C	-4.741742	-0.000083	0.000447
C	-4.038523	-1.076366	0.536608
C	-2.656892	-1.056782	0.527411
N	-2.000796	-0.000165	0.000060
C	-2.656966	1.056485	-0.527110
C	-4.038599	1.076149	-0.535915
H	-4.547353	-1.932389	0.963318
H	-2.043201	-1.855317	0.926578
Cl	-0.275016	-0.000235	-0.000193
H	-2.043335	1.854981	-0.926453
H	-4.547492	1.932205	-0.962483
C	4.162399	1.067587	0.549161
C	2.772484	1.026958	0.527925
C	4.869405	0.000411	0.001011
C	4.163219	-1.066937	-0.547857
C	2.773271	-1.026668	-0.528003
N	2.096166	0.000055	-0.000372
H	2.178861	1.835551	0.944170
H	4.672833	1.917799	0.986540
H	5.954212	0.000547	0.001552
H	4.674307	-1.917009	-0.984744
H	2.180272	-1.835398	-0.944872

E(e) = -956.722864325

Pyr-Br^{+}-Pyr, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	3.873254	0.047569	-0.023682
C	2.789144	0.016321	-0.029979
C	2.121122	-1.196090	-0.183285
C	0.734411	-1.202637	-0.187347
N	0.040748	-0.062887	-0.045930
C	0.665922	1.114864	0.103172
C	2.050666	1.188183	0.115205
H	2.659288	-2.129275	-0.299179
H	0.157555	-2.113200	-0.303226
Br	-2.098399	-0.124241	-0.058801
H	0.036258	1.990638	0.212104
H	2.532802	2.150773	0.237065
C	-6.304299	0.694593	-0.838048

C	-4.917940	0.707022	-0.808536
C	-6.986062	-0.260993	-0.088533
C	-6.261309	-1.177208	0.669731
C	-4.876148	-1.112172	0.657350
N	-4.237624	-0.184171	-0.071547
H	-4.330757	1.424791	-1.370093
H	-6.831565	1.424379	-1.440783
H	-8.070197	-0.291283	-0.095240
H	-6.754379	-1.935483	1.266210
H	-4.256793	-1.796153	1.226463

E(e) = -509.699774924
ZPE = 0.180595
= 474.1522 kJ/mol
E(298) = -509.507424
H(298) = -509.506479
G(298) = -509.560239

Frequencies:

Stretch (N-Br-N, asym)	165.15
Twist	22.03
Stretch (N-Br-N, sym)	172.95

Pyr-Br^{+}-Pyr (N-Br frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	3.837040	0.065302	-0.023366
C	2.753016	0.034984	-0.026147
C	2.082242	-1.174525	-0.189590
C	0.699468	-1.186481	-0.189785
N	-0.000615	-0.041997	-0.033309
C	0.633612	1.139793	0.126558
C	2.014867	1.205112	0.133551
H	2.617046	-2.108011	-0.317253
H	0.119277	-2.093156	-0.313343
Br	-1.892849	-0.094862	-0.038311
H	0.003022	2.012615	0.246912
H	2.496010	2.167009	0.263809
C	-6.291298	0.709503	-0.809188
C	-4.902656	0.716024	-0.781488
C	-6.971727	-0.236744	-0.047002
C	-6.241795	-1.143944	0.716877
C	-4.854855	-1.073442	0.692664

N	-4.207417	-0.160061	-0.043539
H	-4.324834	1.431799	-1.357280
H	-6.821401	1.432919	-1.417379
H	-8.056012	-0.266775	-0.048360
H	-6.732458	-1.895714	1.323774
H	-4.239683	-1.756154	1.269916

E(e) = -509.692122679

Pyr-I^{+}-Pyr, CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	4.276318	0.014009	-0.046183
C	3.192130	-0.014975	-0.052120
C	2.520168	-1.226637	-0.190723
C	1.133816	-1.229353	-0.194589
N	0.433759	-0.088713	-0.067237
C	1.070439	1.087658	0.067443
C	2.454916	1.159015	0.078761
H	3.055247	-2.162934	-0.295418
H	0.561281	-2.143939	-0.299937
I	-1.868882	-0.150326	-0.079981
H	0.448740	1.970319	0.166250
H	2.938027	2.122532	0.189034
C	-6.246365	0.674834	-0.848966
C	-4.860338	0.684755	-0.819911
C	-6.929904	-0.285799	-0.108145
C	-6.204264	-1.208702	0.640555
C	-4.819451	-1.144430	0.627005
N	-4.171524	-0.211941	-0.092711
H	-4.279063	1.409928	-1.378121
H	-6.772223	1.411087	-1.445064
H	-8.014089	-0.314834	-0.114218
H	-6.696599	-1.972222	1.230953
H	-4.206477	-1.837629	1.191897

E(e)	=	-507.933925174	
ZPE	=	0.180414	
	=	473.6770	kJ/mol
E(298)	=	-507.741606	
H(298)	=	-507.740662	
G(298)	=	-507.795349	

Frequencies:

Stretch (N-I-N, asym) 167.00

Twist	20.80
Stretch (N-I-N, sym)	166.26

Pyr-I^+-Pyr (N-I frozen), CH_2Cl_2, B3LYP

Charge = 1 Multiplicity = 1

H	4.218993	0.064656	-0.008045
C	3.134913	0.035198	-0.013266
C	2.462259	-1.175893	-0.152953
C	1.078851	-1.183300	-0.156503
N	0.370153	-0.039935	-0.026595
C	1.014428	1.140199	0.109841
C	2.396165	1.207934	0.119622
H	2.995978	-2.112696	-0.259307
H	0.506485	-2.097455	-0.262720
I	-1.721724	-0.096744	-0.036766
H	0.392264	2.021891	0.210308
H	2.877170	2.172313	0.230870
C	-6.206518	0.721546	-0.805205
C	-4.819061	0.728425	-0.774190
C	-6.890047	-0.236973	-0.061684
C	-6.162710	-1.157246	0.688582
C	-4.776691	-1.088937	0.670841
N	-4.124236	-0.161983	-0.048454
H	-4.241095	1.454286	-1.336330
H	-6.733474	1.455872	-1.402842
H	-7.974292	-0.266399	-0.066846
H	-6.654843	-1.919186	1.281321
H	-4.165613	-1.782553	1.238644

E(e) = - 507.927854856

Pyridine, CH_3CN, B3LYP

Charge = 0 Multiplicity = 1

C	1.197236000	0.671386000	-0.000001000
C	1.144765000	-0.720618000	-0.000002000
C	-0.000001000	1.382086000	0.000000000
C	-1.197238000	0.671383000	0.000001000
C	-1.144763000	-0.720621000	0.000001000
N	0.000001000	-1.417456000	0.000000000
H	2.062252000	-1.303729000	0.000000000
H	2.154830000	1.180333000	-0.000001000
H	-0.000003000	2.467302000	0.000000000
H	-2.154832000	1.180330000	0.000001000
H	-2.062249000	-1.303733000	0.000001000

E(e)	=	-248.355810472	
ZPE	=	0.088256	
	=	231.7161	kJ/mol
E(298)	=	-248.263275	
H(298)	=	-248.262331	
G(298)	=	-248.294956	

Pyr-F^{+}-Pyr, CH_3CN, B3LYP

Charge = 1 Multiplicity = 1

H	6.257701000	0.073888000	0.172291000
C	5.175397000	0.039353000	0.106690000
C	4.473419000	-0.995309000	0.724360000
C	3.094287000	-1.030895000	0.635846000
N	2.502320000	-0.045585000	-0.055084000
C	3.109646000	0.977670000	-0.673752000
C	4.488855000	1.029713000	-0.595262000
H	4.978453000	-1.779253000	1.276577000
H	2.444429000	-1.781474000	1.073006000
F	1.144703000	-0.088134000	-0.136224000
H	2.470966000	1.687401000	-1.188681000
H	5.006142000	1.846159000	-1.085587000
C	-4.864905000	-0.930629000	-0.584745000
C	-3.485117000	-0.914242000	-0.775454000
C	-5.436401000	0.048064000	0.223943000
C	-4.604662000	1.000479000	0.806505000
C	-3.236321000	0.932372000	0.554760000
N	-2.672741000	-0.003930000	-0.221015000
H	-3.009384000	-1.664911000	-1.401456000
H	-5.471294000	-1.693504000	-1.060515000
H	-6.507611000	0.068108000	0.396474000
H	-5.002772000	1.782307000	1.443927000
H	-2.561195000	1.661638000	0.995319000

E(e)	=	-596.329156606	
ZPE	=	0.180606	
	=	474.1819	kJ/mol
E(298)	=	-596.136575	
H(298)	=	-596.135630	
G(298)	=	-596.194739	

Frequencies:

Twist	38.29

Stretch (N-F-N symm) 27.94

Pyr-F$^+$---Pyr (N-F frozen), CH_3CN, B3LYP

Charge = 1 Multiplicity = 1

C	-4.870060000	-0.927639000	-0.578635000
C	-3.492212000	-0.913222000	-0.783042000
C	-5.431828000	0.050603000	0.237376000
C	-4.592741000	1.000661000	0.813245000
C	-3.227106000	0.930731000	0.547690000
N	-2.672847000	-0.005198000	-0.235195000
H	-3.024019000	-1.663639000	-1.415002000
H	-5.482442000	-1.688676000	-1.049637000
H	-6.501229000	0.072125000	0.420609000
H	-4.983196000	1.782033000	1.455934000
H	-2.546401000	1.658162000	0.982678000
F	1.143616000	-0.086013000	-0.141930000
N	2.500317000	-0.045026000	-0.057070000
C	3.110688000	0.977490000	-0.674068000
C	4.489739000	1.027801000	-0.592022000
C	3.089425000	-1.031126000	0.635276000
C	4.468353000	-0.997288000	0.727373000
C	5.173239000	0.036527000	0.111606000
H	2.474239000	1.688023000	-1.190634000
H	5.009328000	1.843617000	-1.080945000
H	6.255409000	0.069673000	0.179979000
H	2.437510000	-1.780949000	1.070649000
H	4.970982000	-1.781915000	1.280802000

E(e) = -596.329156434

Pyr-F$^+$, CH_3CN, B3LYP

Charge = 1 Multiplicity = 1

H	0.000000000	0.000000000	-2.910571000
C	0.000000000	0.000000000	-1.825977000
C	0.000000000	1.208579000	-1.130017000
C	0.000000000	1.198961000	0.252370000
N	0.000000000	0.000000000	0.852972000
C	0.000000000	-1.198961000	0.252370000
C	0.000000000	-1.208579000	-1.130017000
H	0.000000000	2.163151000	-1.642588000
H	0.000000000	2.070205000	0.898038000
F	0.000000000	0.000000000	2.212944000

H	0.000000000	-2.070205000	0.898038000
H	0.000000000	-2.163151000	-1.642588000

E(e)	=	-347.972879887	
ZPE	=	0.091995	
	=	241.5329	kJ/mol
E(298)	=	-347.875700	
H(298)	=	-347.874756	
G(298)	=	-347.909090	

Frequencies:
Stretch (N-F) 535.11

Pyr-F$^+$ (N-F frozen), CH_3CN, B3LYP

Charge = 1 Multiplicity = 1

H	0.000000000	0.000000000	-2.967086000
C	0.000000000	0.000000000	-1.881291000
C	0.000000000	1.211077000	-1.192412000
C	0.000000000	1.207762000	0.203749000
N	0.000000000	0.000000000	0.725208000
C	0.000000000	-1.207762000	0.203749000
C	0.000000000	-1.211077000	-1.192412000
H	0.000000000	2.174139000	-1.694020000
H	0.000000000	2.080615000	0.851748000
F	0.000000000	0.000000000	2.525208000
H	0.000000000	-2.080615000	0.851748000
H	0.000000000	-2.174139000	-1.694020000

E(e)	=	-347.919801365

Pyridine, CH_2Cl_2, B3LYP-D3

Charge = 0 Multiplicity = 1

N	0.000000	0.000000	1.419319
C	0.000000	1.144430	0.721473
C	0.000000	-1.144430	0.721473
C	0.000000	0.000000	-1.383966
C	0.000000	1.197810	-0.672182
C	0.000000	-1.197810	-0.672182
H	0.000000	2.062492	1.303683
H	0.000000	-2.062492	1.303683
H	0.000000	0.000000	-2.469219
H	0.000000	2.155790	-1.180541
H	0.000000	-2.155790	-1.180541

E(e) = -248.360690361
ZPE = 0.087964
= 230.9491 kJ/mol
E(298) = -248.268439
H(298) = -248.267495
G(298) = -248.299477

Frequencies:
A2 385.5131
A1 618.0185

Pyr-Cl$^+$, CH_2Cl_2, B3LYP-D3

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	2.199385
N	0.000000	0.000000	0.473633
C	0.000000	1.192209	-0.169234
C	0.000000	-1.192209	-0.169234
C	0.000000	0.000000	-2.251703
C	0.000000	1.204984	-1.550203
C	0.000000	-1.204984	-1.550203
H	0.000000	2.083970	0.446360
H	0.000000	-2.083970	0.446360
H	0.000000	0.000000	-3.336421
H	0.000000	2.161931	-2.058902
H	0.000000	-2.161931	-2.058902

E(e) = -708.360313058
ZPE = 0.090795
= 238.3825 kJ/mol
E(298) = -708.263988
H(298) = -708.263044
G(298) = -708.298688

Frequencies:
Stretch (N-Cl) 715.28

Pyr-Cl$^+$-Pyr, CH_2Cl_2, B3LYP-D3

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	0.000000
N	0.000000	0.000000	2.024539
C	-0.514463	1.051398	2.675990
C	0.514463	-1.051398	2.675990
C	0.000000	0.000000	4.766558
C	-0.528744	1.081543	4.063813
C	0.528744	-1.081543	4.063813

H	-0.909471	1.856711	2.066441
H	0.909471	-1.856711	2.066441
H	0.000000	0.000000	5.851250
H	-0.948589	1.939760	4.575056
H	0.948589	-1.939760	4.575056
N	0.000000	0.000000	-2.024539
C	0.514463	1.051398	-2.675990
C	-0.514463	-1.051398	-2.675990
C	0.000000	0.000000	-4.766558
C	0.528744	1.081543	-4.063813
C	-0.528744	-1.081543	-4.063813
H	0.909471	1.856711	-2.066441
H	-0.909471	-1.856711	-2.066441
H	0.000000	0.000000	-5.851250
H	0.948589	1.939760	-4.575056
H	-0.948589	-1.939760	-4.575056

E(e) = -956.746036003
ZPE = 0.180122
= 472.9091 kJ/mol
E(298) = -956.554234
H(298) = -956.553289
G(298) = -956.605390

Frequencies:

Stretch (N-Cl-N, asym)	121.23
Twist	18.87
Stretch (N-Cl-N, sym)	173.48

Pyr, CH_2Cl_2, MP2

Charge = 0 Multiplicity = 1

N	0.000000	0.000000	1.427792
C	0.000000	1.147189	0.722826
C	0.000000	-1.147189	0.722826
C	0.000000	0.000000	-1.390449
C	0.000000	1.199455	-0.674567
C	0.000000	-1.199455	-0.674567
H	0.000000	2.066213	1.306238
H	0.000000	-2.066213	1.306238
H	0.000000	0.000000	-2.477585
H	0.000000	2.159649	-1.182920
H	0.000000	-2.159649	-1.182920

E(e) = -247.6101728473
ZPE = 0.088248
= 231.6950 kJ/mol

E(298) = -247.517524
H(298) = -247.516580
G(298) = -247.548748

Pyr-Cl$^+$, CH_2Cl_2, MP2

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	2.189138
N	0.000000	0.000000	0.477574
C	0.000000	1.193697	-0.159383
C	0.000000	-1.193697	-0.159383
C	0.000000	0.000000	-2.255243
C	0.000000	1.204592	-1.548823
C	0.000000	-1.204592	-1.548823
H	0.000000	2.083355	0.463299
H	0.000000	-2.083355	0.463299
H	0.000000	0.000000	-3.341896
H	0.000000	2.164802	-2.056571
H	0.000000	-2.164802	-2.056571

E(e) = -707.0383674677
ZPE = 0.091142
= 239.2928 kJ/mol
E(298) = -706.941584
H(298) = -706.940640
G(298) = -706.976446

Frequencies:
Stretch (N-Cl) 719.65

Pyr-Cl$^+$-Pyr, CH_2Cl_2, MP2

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	0.000000
N	0.000000	0.000000	-1.993590
C	-0.788563	0.872994	-2.643398
C	0.788563	-0.872994	-2.643398
C	0.000000	0.000000	-4.743771
C	-0.808523	0.894570	-4.036561
C	0.808523	-0.894570	-4.036561
H	-1.389596	1.538460	-2.028869
H	1.389596	-1.538460	-2.028869
H	0.000000	0.000000	-5.830454
H	-1.450331	1.604938	-4.549384
H	1.450331	-1.604938	-4.549384
N	0.000000	0.000000	1.993590
C	-0.788563	-0.872994	2.643398
C	0.788563	0.872994	2.643398

C	0.000000	0.000000	4.743771
C	-0.808523	-0.894570	4.036561
C	0.808523	0.894570	4.036561
H	-1.389596	-1.538460	2.028869
H	1.389596	1.538460	2.028869
H	0.000000	0.000000	5.830454
H	-1.450331	-1.604938	4.549384
H	1.450331	1.604938	4.549384

E(e) = -954.6709322532
ZPE = 0.180598
= 474.1596 kJ/mol
E(298) = -954.478591
H(298) = -954.477647
G(298) = -954.529208

Frequencies:

Stretch (N-Cl-N, asym)	212.91
Twist	24.71
Stretch (N-Cl-N, sym)	185.66

Pyr, CH_2Cl_2, M06-2X

Charge = 0 Multiplicity = 1

N	0.000000	0.000000	1.413888
C	0.000000	1.140280	0.719511
C	0.000000	-1.140280	0.719511
C	0.000000	0.000000	-1.379508
C	0.000000	1.194606	-0.670137
C	0.000000	-1.194606	-0.670137
H	0.000000	2.056708	1.303021
H	0.000000	-2.056708	1.303021
H	0.000000	0.000000	-2.464140
H	0.000000	2.152181	-1.177278
H	0.000000	-2.152181	-1.177278

E(e) = -248.2420247410
ZPE = 0.089170
= 234.1152 kJ/mol
E(298) = -248.148603
H(298) = -248.147658
G(298) = -248.179587

Pyr-Cl^+, CH_2Cl_2, M06-2X

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	2.181799
N	0.000000	0.000000	0.475634
C	0.000000	1.187256	-0.164136
C	0.000000	-1.187256	-0.164136
C	0.000000	0.000000	-2.239805
C	0.000000	1.202749	-1.541876
C	0.000000	-1.202749	-1.541876
H	0.000000	2.075403	0.457777
H	0.000000	-2.075403	0.457777
H	0.000000	0.000000	-3.324570
H	0.000000	2.159684	-2.050015
H	0.000000	-2.159684	-2.050015

E(e) = -708.2104945990
ZPE = 0.092036
= 241.6399 kJ/mol
E(298) = -708.113008
H(298) = -708.112064
G(298) = -708.147557

Frequencies:
Stretch (N-Cl) 732.94

Pyr-Cl^{+}-Pyr, CH_2Cl_2, M06-2X

Charge = 1 Multiplicity = 1

Cl	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.982259
C	-0.466492	1.069129	2.630575
C	0.466492	-1.069129	2.630575
C	0.000000	0.000000	4.714390
C	-0.480552	1.101251	4.014909
C	0.480552	-1.101251	4.014909
H	-0.824357	1.890100	2.017411
H	0.824357	-1.890100	2.017411
H	0.000000	0.000000	5.798854
H	-0.862684	1.976309	4.526102
H	0.862684	-1.976309	4.526102
N	0.000000	0.000000	-1.982259
C	0.466492	1.069129	-2.630575
C	-0.466492	-1.069129	-2.630575
C	0.000000	0.000000	-4.714390
C	0.480552	1.101251	-4.014909
C	-0.480552	-1.101251	-4.014909
H	0.824357	1.890100	-2.017411
H	-0.824357	-1.890100	-2.017411
H	0.000000	0.000000	-5.798854
H	0.862684	1.976309	-4.526102

H -0.862684 -1.976309 -4.526102

E(e) = -956.4702781280
ZPE = 0.182101
= 478.1051 kJ/mol
E(298) = -956.276616
H(298) = -956.275672
G(298) = -956.327410

Frequencies:

Stretch (N-Cl-N, asym)	90.15
Twist	19.80
Stretch (N-Cl-N, sym)	190.91

4. References

1. R. Kleinmaier, S. Arenz, A. Karim, A.-C. C. Carlsson and M. Erdelyi, *Magn. Reson. Chem.,* 2013, **51**, 46.
2. A.-C. C. Carlsson, M. Uhrbom, A. Karim, U. Brath, J. Gräfenstein and M. Erdelyi, *CrystEngComm*, 2013, **15**, 3087.