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Synthesis and characterization of a novel N–F reagent derived from the ethano-Tröger's base: $^1J_{FN}$ coupling constants as a signature for the N–F bond†

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Methylation of 2,8-dimethyl-6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*][1,5]-diazocine (ethano-Tröger's base) with methyl iodide followed by ion metathesis and fluorination with *N*-fluoro-2,3,4,5,6-pentachloro-pyridinium triflate affords a new electrophilic N–F reagent, that is more reactive than Selectfluor. 2D ^{19}F–^{15}N HMQC experiments provide $^1J_{NF}$ coupling constants which are diagnostic for the N–F functional group.

The progress made in recent years in the field of modern organofluorine chemistry indicates that the nature of the fluorine source is critical for a particular fluorination process to succeed.[1] This observation stands true for nucleophilic and electrophilic fluorination, and this is independent of the activation manifold applied to induce C–F bond formation. Much research has therefore focused on the development of new reagents for late stage fluorination.[2] The appearance of safe and easy to handle N–F reagents[2d,3] has revolutionized the field of electrophilic fluorination by providing alternatives to F_2, XeF_2,[4] perchloryl fluoride[5] or O–F reagents, such as trifluoromethyl hypofluorite,[6] acyl[2b,c,7] and perfluoroacyl hypofluorites.[8] The preparation, properties and reactivity of *N*-fluoro electrophilic fluorinating agents have been discussed in authoritative reviews.[9] In this category, Selectfluor bis(tetrafluoroborate) and its analogues constitute a series of doubly quaternized *N*-fluoro-1,4-bicyclo[2.2.2]octane reagents of remarkable stability and relatively low toxicity. Our own work has concentrated on the development of chiral Selectfluor bis(triflate)[10] featuring the stereogenicity elements on the DABCO core, and more recently as a corollary to this, the development of new chiral N–F reagents derived from alternative scaffolds amenable to double *N*-quaternization. The Tröger's base **1** (TB)[11] and its analogues are attractive candidates for transformation into N–F reagents, due to their C_2 symmetry, and concave Λ-shape (Fig. 1). In our hands, the methylene-bridged TB proved to be unstable towards F^+ electrophiles,[12] so we focused our efforts on the synthesis and characterization of the N–F reagent **2** derived from the ethylene-bridged Tröger's base **3**[13] (ETB = 2,8-dimethyl-6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*][1,5]-diazocine). ETB is readily available by reacting TB with dibromoethane and Li_2CO_3 in DMF. In this report, we disclose the synthesis and characterization of **2** along with a preliminary study on reactivity. For the first time, 2D ^{19}F–^{15}N Heteronuclear Multiple-Quantum Correlation (HMQC) experiments were performed on **2** and known N–F reagents. The resulting $^1J_{NF}$ coupling constants constitute a new signature for the N–F functional group.

The synthesis of **2** was investigated with a study of a racemic series. Modifying a literature procedure, the treatment of (±)-ETB with a large excess of methyl iodide in a mixture of $MeOH/CH_2Cl_2$ afforded the desired monoquaternized iodide salt,[14] which was then subjected to ion metathesis with AgOTf to afford **4** isolated in 70% yield over two steps (Scheme 1).

The validation and optimization of the critical fluorination step was carried out with **4**. The reaction was monitored by

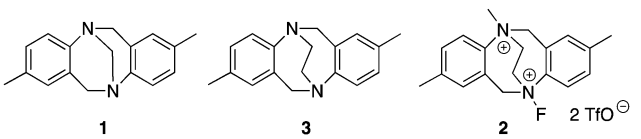
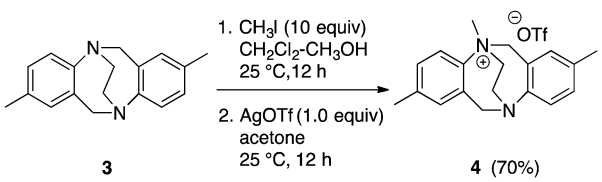


Fig. 1 Structures of the methylene- and ethylene-bridged Tröger's bases **1** and **3**, and of the N–F reagent **2**.



Scheme 1 Synthesis of the monoquaternized salt **4**.

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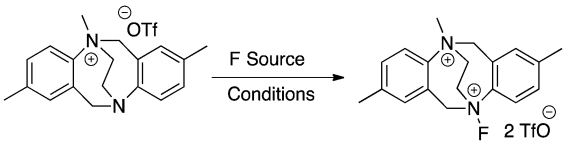
Table 1 Optimization for the fluorination of **4**[a]



4 **2**

No.	F source	Equiv.	Temp. [°C]	Conversion[b] [%]
1	XeF_2	1	40	0
2	XeF_2	1	80	0[c]
3	F_2[d,e]	2	−35	0
4	F_2[d,f]	2	−35	0
5	F_2[d,g]	2	−35	0[c]
6	F_2[d,e]	2	−10	0
7	F_2[d,e]	2	0	0[c]
8	**5**[h]	1	25	0
9	**6**[i]	1	25	0
10	**7**[j]	1	25	55
11	**7**[j]	1	−35	>95

[a] Conditions: **4** (0.1 mol, 1 equiv.), fluorine donor (1 equiv.), CH_3CN (0.05 M). [b] Conversion measured by ^{19}F NMR with respect to triflate as the internal standard. [c] Degradation of the *in situ* formed N–F reagent. [d] F_2 (10% in N_2). [e] Reaction with NaOTf (1 equiv.). [f] Reaction with HOTf (1 equiv.). [g] Reaction with $NaBF_4$ (1 equiv.). [h] **5**: 1-chloromethyl-4-fluoro-1,4-diazonia-bicyclo[2.2.2]octane bis(tetrafluoroborate) [Selectfluor bis-(tetrafluoroborate)]. [i] **6**: *N*-fluoro-2,6-dichloropyridinium triflate. [j] **7**: *N*-fluoro-2,3,4,5,6-pentachloropyridinium triflate.

^{19}F NMR spectroscopy (Table 1). XeF_2, F_2 and a series of commercially available N–F reagents were tested for their ability to transfer fluorine onto **4**; these experiments also gave information on relative reactivity. XeF_2 and F_2 are atom economical reagents, and have the advantage to facilitate post-fluorination purification since no organic co-product is produced upon fluorine transfer. Regrettably, we found that these reagents were not suitable for the synthesis of **2**. XeF_2 did not react at 40 °C or led to decomposition at 80 °C. Similarly, F_2 (10% in N_2) led to decomposition at 0 °C, or returned the unreacted starting material at −10 °C or −35 °C. No fluorine transfer took place upon treatment of **4** with one equivalent of Selectfluor bis(tetrafluoroborate) (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]octane bis(tetra-fluoroborate)) **5** or *N*-fluoro-2,6-dichloropyridinium triflate **6** in acetonitrile at room temperature, suggesting that these known N–F reagents would be less reactive than **2**. Pleasingly, the more reactive *N*-fluoro-2,3,4,5,6-pentachloropyridinium triflate **7** gave 55% of **2** when the reaction was performed at ambient temperature. A significant improvement was observed when the reaction temperature was lowered to −35 °C. Under these conditions, the pyridinium salt fully transferred F^+ on to **4**. Stability studies indicate that decomposition was taking place when a solution of **2** in acetonitrile was left at room temperature for eight hours or more. As a result, the reagent is best prepared immediately before use. Therefore, the optimized procedure for the synthesis of **2** consists of treating a solution of **4** (43 mg, 0.1 mmol, 1 equiv.) in dry CH_3CN (1 mL) with a slurry of *N*-fluoro-2,3,4,5,6-pentachloropyridinium triflate **7** (1 equiv.) in dry CH_3CN (1 mL) at −35 °C. The resulting solution is composed of the novel N–F reagent **2** and an equimolar amount of 2,3,4,5,6-pentachloropyridine.

The relative instability and the difficulties encountered upon isolation and purification of **2** did not allow for the analysis of a single crystal by X-ray crystallography. The theoretical and experimentally measured HR-ESI spectra of **2** are in excellent agreement showing a parent peak at *m*/*z* 149.0917 and *m*/*z* 149.0918, respectively. To help characterize the N–F bond in particular, we performed 1D ^{19}F NMR and 2D ^{19}F–^{15}N heteronuclear correlation experiments with **2** (Fig. 2). From this, we observe a $^{14}N/^{15}N$ one-bond isotope shift[15] $\Delta\delta$ equal to 0.27 ppm. Similar experiments were performed with Selectfluor bis(tetrafluoroborate) **5** and the two chiral analogues **8** and **9**; for completeness, we also performed these measurements on the *N*-fluoropyridiniums **6**, **7**, **10** and **11**. All of the N–F reagents in this NMR study, as expected, exhibit the characteristic one-bond isotope shift (see ESI† for further details). Table 2 assembles the ^{19}F and ^{15}N chemical shifts for these compounds. Nitrogen chemical shifts clearly reflect the differing hybridization states of the nitrogen in the $[NF]^{2+}$ and $[NF]^+$ compound groups, but otherwise exhibit little variation within each series. The ^{19}F chemical shifts show a more pronounced difference for compound **2** specifically, which exhibited a very high shift of +103 ppm for the N–F group. This is well above the corresponding signals recorded for Selectfluor bis(triflate) and its derivatives, and the $[NF]^+$ reagents that typically range from 30 ppm to 50 ppm,[2d,10] as considered further below.

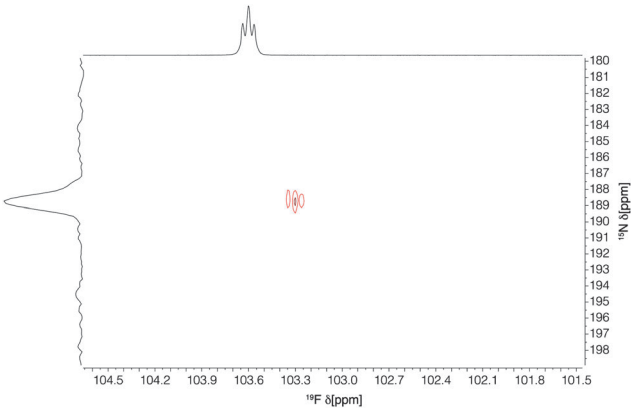
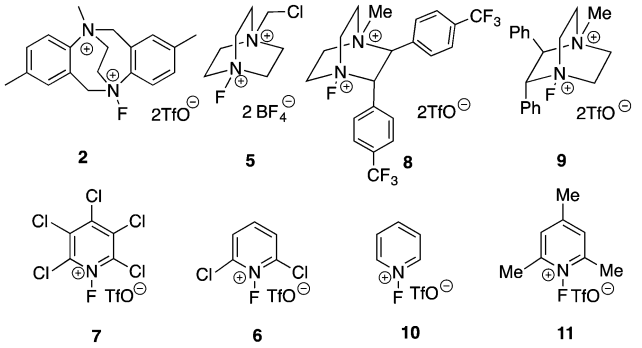


Fig. 2 2D ^{19}F–^{15}N HMQC of **2** (0.1 mM) in CD_3CN at 298 K. ^{15}N (60.8 MHz) & ^{19}F (565.2 MHz). ^{19}F $^1\Delta\delta(^{14}N–^{15}N)$ = 0.27 ppm.

We also measured $^1J_{FN}$ coupling constants to further characterise the N–F bond (Table 2). In the literature, experimental measurements of two-bond ^{19}F–^{15}N spin–spin coupling constants across N–H···F hydrogen bonds ($^{2h}J_{FN}$) are available, due primarily to the work of Limbach and co-workers.[16] These have also been reported for complexes with F–H···N and N–H^+···F hydrogen bonds.[17] The directly recorded $^1J_{FN}$ coupling constant of **5** is in agreement with a literature precedent.[18] To the best of our knowledge, the values of the other reagents reported here are the first measurements of $^1J_{FN}$ coupling constants of electrophilic N–F reagents. These magnitudes principally reflect the nitrogen hybridization state in the two compound classes, increasing with greater s-character. We note that compound **2** shows the smallest $^1J_{FN}$ value, although the limited data set makes meaningful comparisons difficult.

With regard to the notably greater fluorine chemical shift of **2**, previous studies[19] have suggested that ^{19}F NMR shifts of N–F

Table 2 ^{19}F and ^{15}N chemical shifts, and $^{1}J_{FN}$ coupling constants for **2**, **5–11**. ^{15}N NMR (60.8 MHz, CD_3CN, 298 K) and ^{19}F NMR (565.2 MHz, CD_3CN, 298 K)



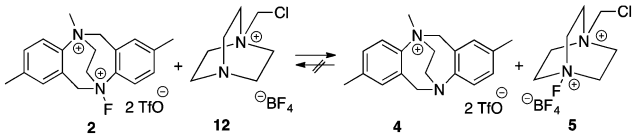
$[NF]^{2+}$ Reagent	**2**	**5**	**8**	**9**
^{19}F NMR (ppm)	+103.6	+48.1	+36.7	+36.0
^{15}N NMR (ppm)	+188	+177	+182	+183
$^{1}J_{FN}$ (Hz)[a]	70	85	90	91

$[NF]^{+}$ Reagent	**7**	**6**	**10**	**11**
^{19}F NMR (ppm)	+46.2	+30.2	+46.9	+15.9
^{15}N NMR (ppm)	+253	+256	+260	+259
$^{1}J_{FN}$ (Hz)[a]	140	145	130	125

[a] Although not determined, the sign of these coupling constants are expected to be negative due to the negative magnetogyric ratio of ^{15}N. The chemical shifts are relative to external NH_3 (^{15}N) and $CFCl_3$ (^{19}F) at 0.0 ppm.

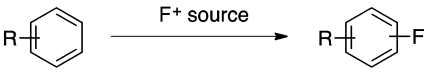
reagents correlate with reactivity for a series of structurally related reagents; for the dicationic $[NF]^{2+}$ type reagents, this trend would suggest that **2** is more reactive than Selectfluor and could therefore serve as a reagent to prepare Selectfluor from its monoquaternized precursor. Experimentally, we found that fluorine transfer from **2** to **12** was complete after 5 minutes at room temperature in acetonitrile (Scheme 2).

We probed next the ability of **2** to transfer F^+ onto substrates other than the Selectfluor precursor **12**. Scheme 3 presents selected fluorination processes, and compare the reaction conditions and yields with data obtained from the literature for Selectfluor bis(tetrafluoroborate) **5**,[20] and when available for *N*-fluoro-2,3,4,5,6-pentachloropyridinium triflate **7**.[3c] The fluorination reactions of benzene, fluorobenzene and anisole were successful and overall required shorter reaction times with **2** compared to **5**. The ortho-para ratios of the fluorinated products of anisole and fluorobenzene by **2** and **5** are similar suggesting a similar mode of reactivity. The reactivity profile of N–F reagents **7** and **2** is more similar. Styrene derivatives underwent fluorination in the presence of **2** and acetic acid giving the products of fluoroacetoxylation in good yields. Additional experiments



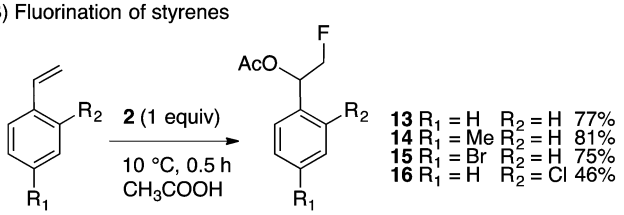
Scheme 2 Fluorine transfer from **2** to **12**.

A) Fluorination of aromatics



R	F^+ source	Temp [°C]	Time [h]	Yield [%][e]	*o* [%][e]	*p* [%][e]
H	**2**[a]	40	6	85	–	–
	7[b]	Reflux	2	48		
	5[c]	Reflux	20	83		
OMe	**2**[a]	0	1	85	65	35
	7[d]	25	0.25	91	36	38
	5[c]	Reflux	12	99	45	55
F	**2**[a]	40	1	89	33	67
	5[c]	Reflux	12	99	31	69

B) Fluorination of styrenes



Scheme 3 (A) Fluorination of arenes: [a] arene (4 equiv.), **2** (1.5 equiv.), CH_3CN. [b] Data from ref. 3c; substrate (excess), **7** (1.0 equiv.) in CH_2Cl_2. [c] Data from ref. 20; arene (2.8 equiv.), **5** (1.4 equiv.), TfOH (3 mL) in refluxing CH_2Cl_2. [d] Data from ref. 3c; substrate (co-solvent), **7** (1.0 equiv.), CH_2Cl_2. [e] Yields determined by ^{19}F NMR spectroscopy using 1-fluoro-4-nitrobenzene as the internal standard. (B) Fluorination of styrenes: styrene (1 mmol, 1 equiv.), **2** (1 equiv.), CH_3COOH (0.04 M), 10 °C, 30 min. Yields refer to the product isolated after silica gel chromatography.

demonstrate that the ethylene-bridged Tröger based reagent **2** does not react with less activated alkenes, for example cyclohexene. This result defines the limitation of the novel N–F reagent **2** in terms of reactivity.

In summary, we have prepared and characterized the novel N–F reagent **2** derived from the ethylene-bridged Tröger base. This reagent was found to be a competent F^+ source, more reactive than Selectfluor, and of similar reactivity to pentachloropyridinium triflate. Moreover, we present the first $^{1}J_{(F-N)}$ coupling constants for eight N–F reagents inclusive of **2**, a set of data serving as a new signature for the N–F bond. This study opens the door towards asymmetric fluorination since the ethylene-bridged Tröger's base is a chiral molecule.

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