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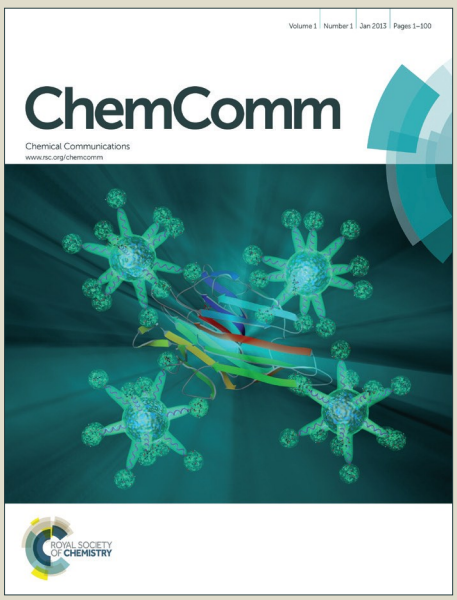





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# Synthesis and Characterization of a Novel N-F Reagent derived from the Ethano-Tröger's Base: $^1J_{FN}$ Coupling Constant as Signature for the N-F Bond

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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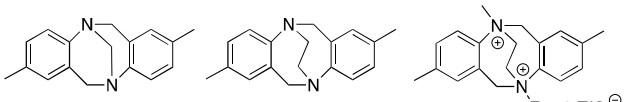
**Methylation of 2,8-dimethyl-6*H*,12*H*-5,11-ethanodibenzo[b,*f*][1,5]-diazocine (Ethano-Tröger's base) with methyl iodide followed by ion metathesis and fluorination with *N*-fluoro-2,3,4,5,6-pentachloropyridinium triflate affords a new electrophilic N–F reagent, that is more reactive than Selectfluor.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

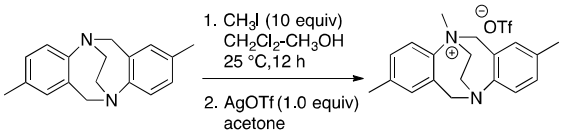
The progress made in recent years in the field of modern organofluorine chemistry indicates that the nature of the fluorine source is critical for a particular fluorination process to succeed.[1] This observation stands true for nucleophilic and electrophilic fluorination, and this independently of the 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 an alternative to $F_2$, $XeF_2$,[4] perchloryl fluoride[5] or O–F reagents, such as trifluoromethyl hypofluorite,[6] acyl[2b, 2c, 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. In our hands, the methylene-bridged TB proved 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.




1 3 2

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

The synthesis of **2** was investigated with a study in 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).




3 4 (70%)

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

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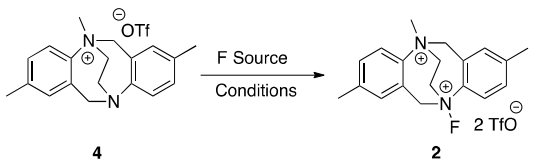
Electronic Supplementary Information (ESI) available: Experimental details and NMR spectra.
See DOI: 10.1039/x0xx00000x

**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 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.

The validation and optimization of the critical fluorination step was carried out with **4**. The reaction was monitored by $^{19}F$ 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 room temperature or led to decomposition at 40 °C or 80 °C. Similarly, $F_2$ (10 % in $N_2$) led to decomposition at 0 °C, or returned 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-chloro-methyl-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. Significant improvement was observed when the reaction temperature was lowered to -35 °C. Under these conditions, the pyridinium salt fully transferred $F^+$ on to **2**. 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 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** (Figure 2). From this, we observe a $^{14}N/^{15}N$ one-bond isotope shift[15] Δδ equal to 0.27ppm. 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, do 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.

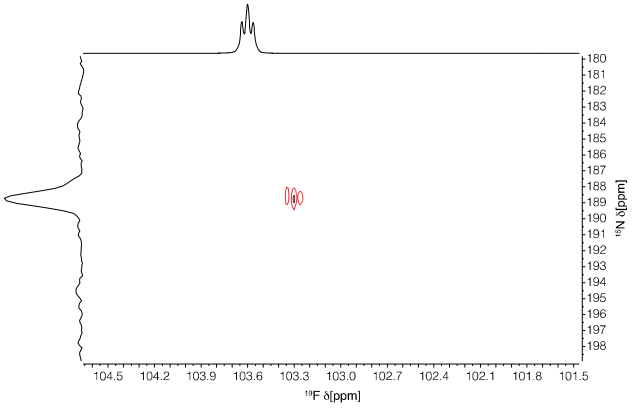
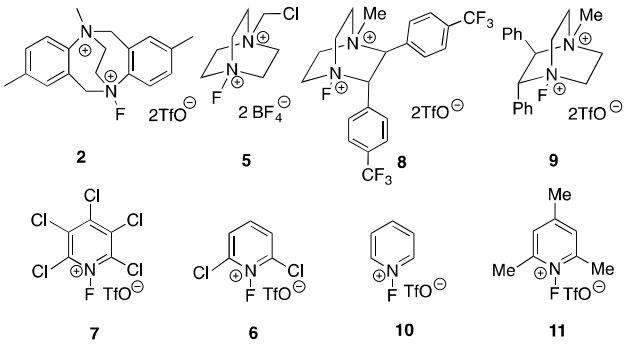



**Figure 2**. 2D $^{19}F$-$^{15}N$ HMQC of **2** (0.1 mM) in $CD_3CN$ at 298K. $^{15}N$ (60.8 MHz) &$^{19}F$ (565.2 MHz). $^{19}F$ $^{1}\Delta\delta(^{14}N$-$^{15}N)$ = 0.27 ppm.

**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, $CD_3CN$, 298K) and $^{19}F$ NMR (565.2 MHz, $CD_3CN$, 298K).



**2** **5** **8** **9**



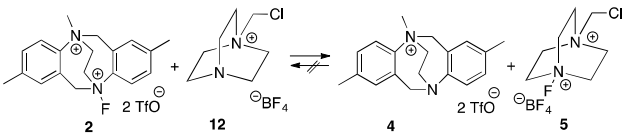
**7** **6** **10** **11**

| **$[NF]^{2+}$ 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.

We also measured $^{1}J_{FN}$ couplings 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 $^{1}J_{FN}$ 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 $^{1}J_{FN}$ 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 compound **2** shows the smallest $^{1}J_{FN}$ value, although the limited data set makes meaningful comparisons difficult.

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

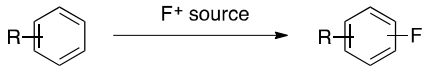


**2** **12** **4** **5**

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

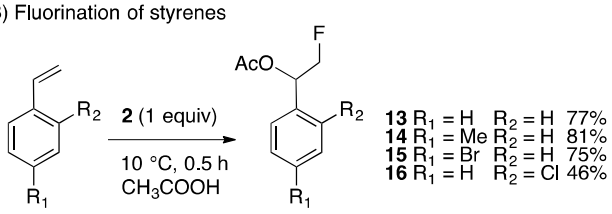
We probed next the ability of **2** to transfer $F^+$ onto substrates other than the Selectfluor precursor **12**. Scheme 3 presents selected fluorination processes, and compare the reaction conditions and yields with data obtained from the literature for Selectfluor *bis*(tetrafluoroborate) **5**,[20] 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 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 term of reactivity.

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

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 $^1J_{(F\text{-}N)}$ 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.

The financial support from the Swiss National Science Foundation (Doc.Mobility project P1EZP2_155528), AstraZeneca (J.W.) and the EPSRC (J.W.) is gratefully acknowledged. R.P. thanks the ETH for a PhD finishing scholarship. VG holds a Royal Society Wolfson Merit Award (2013-2018).

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