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Synthesis of diazafluorene- and diazafluorenone-*N*,*N*′-dioxides using HOF·CH_3CN

Tal Harel, Neta Shefer, Youlia Hagooly, Shlomo Rozen *

School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel

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ABSTRACT

A variety of diazafluorenes and diazafluorenones were oxidized using the HOF·CH_3CN complex to form the corresponding *N*,*N*′-dioxide derivatives under mild conditions. The products exhibit red-shift absorptions in the UV/visible spectrum relative to the parent compounds. Many such oxidations could not be achieved with any other oxygen-transfer agent.

1. Introduction

Recently, diazafluorene derivatives are receiving extensive attention as high performance electron transporting compounds, hole-blocking materials, good candidates for flat panel displays and more.[1,2] In order to succeed in these fields it is necessary, among other requirements, to introduce electron-withdrawing groups into the π-conjugated systems[3] and add electron deficient units such as oxadiazole.[4,5] Previous works showed that oxidation of the heteroatom in the relevant heterocycles narrowed the HOMO–LUMO gap significantly thus increasing their electron delocalization and affinity. Promising results were demonstrated when thiazoles were transferred to the respective *N*-oxides[6] and oligothiophenes to their *S*,*S*′-dioxides.[7,8] These results prompted us to explore the oxidation of the diazafluorene and diazafluorenone systems, by construction their respective *N*,*N*′-dioxide derivatives, which in many cases could not be achieved because of lack of suitable and powerful enough oxygen-transfer agents. We present here a novel route for the preparation of these bis-oxidized heterocycles by using the acetonitrile complex of the hypofluorous acid – HOF·CH_3CN. Indeed, the electron affinity of the aforementioned *N*,*N*′-dioxides was improved, as expected, and the HOMO–LUMO gap reduced.

The HOF·CH_3CN complex, easily prepared from diluted fluorine[9] and aqueous acetonitrile, was developed some years ago.[10] It has established itself as one of the best oxygen-transfer agents chemistry has in its arsenal. Earlier processes developed with the aid of this reagent are summarized in two reviews describing many first or difficult to achieve transformations.[11,12] Other unique reactions of this reagent involve synthesis of episulfones[13] and quinoxaline *N*,*N*′-dioxides,[14] transforming aldehydes to nitriles,[15] amino acids to α-alkyl ones[16] and oxidizing thiols and disulfides to either sulfonic or sulfinic acids at will.[17]

2. Results and discussion

Because of its potential importance, attempts to fully oxidize 4,5-diazafluoren-9-one (**1a**) have been made in the past including the use of concentrated H_2O_2/Na_2WO_4 system, but only partial oxidation was achieved and 4,5-diazafluoren-9-on-4-oxide (**1c**) was isolated in 7% yield only.[18] No traces of the target 4,5-diazafluoren-9-on-4,5-dioxide (**1b**) were found. In order to check if other oxygen-transfer agents are up to the challenge, we reacted **1a** with large excess of both dimethyl dioxirane (DMDO) and MCPBA, but even after prolonged reaction times only minute traces of the desired **1b** were formed. We turned our attention to HOF·CH_3CN, and when using stochiometric amount or small excess of this reagent only the starting material was recovered. However, using a large excess (10 mol equiv) changed the picture completely and the previously unknown **1b** was formed in almost quantitative yield in less then a minute (Scheme 1).

Another interesting substrate was 1,8-diazafluoren-9-one (DFO) (**2a**). This compound is used extensively for fingerprint visualization especially on paper. It seems that this compound is easier to oxidize than **1a**, and indeed it has been described once in the literature where it was reported that 1,8-diazafluoren-9-on-1,8-dioxide (**2b**) was formed in 47% yield after about 20 h heating with very large excess of hydrogen peroxide.[18] The facile formation of **2b**

* Corresponding author. Tel.: +972 3 640 8378; fax: +972 3 640 9293; e-mail address: rozens@post.tau.ac.il.

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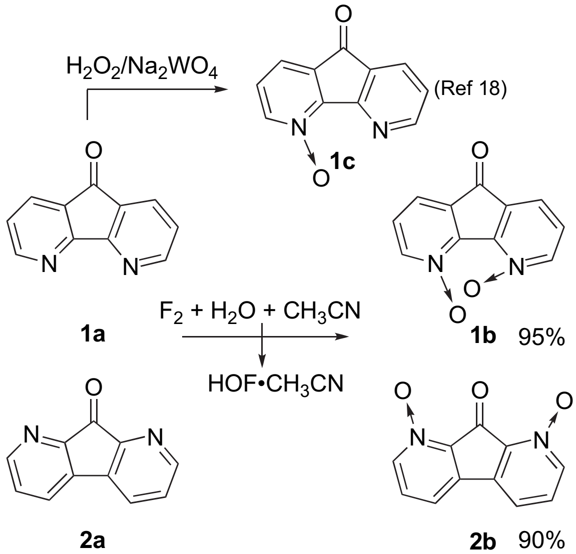
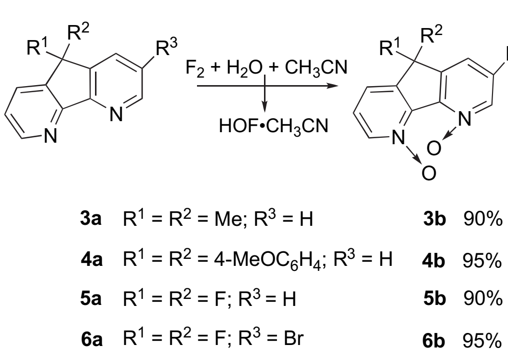


Scheme 1. Oxygenation of diazafluoren-9-ones.

relative to **1b** is also evident from its reaction with HOF·CH_3CN where only 3 mol equiv were needed to produce it practically instantaneously and in 90% yield (Scheme 1).

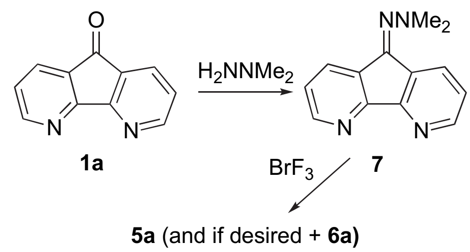
It is worth noting that, when **1b** was qualitatively compared to **2a** in regard to their affinity toward amino acids, in particular alanine (i.e., a preliminary test for the efficiency of fingerprint detection), no substantial differences were noticed.[19] This indicates that further studies on **1b** should be conducted in order to evaluate its possible role in this field.

Very few 4,5-diazafluorene *N*,*N*-dioxide derivatives such as 9,9-dimethyl-4,5-diazafluoren-4,5-dioxide (**3b**) were synthesized in the past with orthodox oxygen-transfer agents.[20] They were used as precursors for building oligomeric diazafluorenes and published mainly as patents. However, a prerequisite for a success in the oxidation of diazafluorenes is the presence of electron donating groups at C-9. Obviously, HOF·CH_3CN could transfer oxygen to the nucleophilic sites of such compounds as well, as seen, for example, when 9,9-dimethyl-4,5-diazafluorene (**3a**) was converted to the appropriate *N*,*N*′-dioxide (**3b**) in a few seconds and in 90% yield. Similarly, 9,9-bis(4-methoxyphenyl)-4,5-diazafluorene (**4a**)[1] was oxidized to provide the new 9,9-bis(4-methoxyphenyl)-4,5-diazafluoren-4,5-dioxide (**4b**) using 3 equiv of HOF·CH_3CN in 95% yield. The situation, however, was radically different when electron-withdrawing groups are located at the 9-position. We have chosen to demonstrate this point by using the previously unknown 9,9-difluoro-4,5-diazafluorene (**5a**) (Scheme 2).



Scheme 2. Oxygenation of 4,5 diazafluorenes.

The preparation of **5a** seemed to be a worthy challenge since, in addition to the fluorine's electron withdrawing ability, in many cases it also contributes to the molecular stability, an important issue in organic electronic devices.[21] In several cases we have used bromine trifluoride (BrF_3) as an efficient tool for converting carbonyls to the CF_2 group.[22] Thus, we have prepared the corresponding 9-dimethyl-hydrazone-4,5-diazafluorene (**7**)[23] from **1a** and reacted it with 2.5 mol equiv of BrF_3. In a few seconds the difluoro derivative **5a** was obtained in higher than 95% yield and 60% conversion. If an excess of BrF_3 (3.5 mol equiv) was applied, a full conversion was achieved and the yield of **5a** reached 70%, but was also accompanied by 30% of the unknown 2-bromo-9,9-difluoro-4,5-diazafluorene (**6a**), a typical result of aromatic brominations with BrF_3 (Scheme 3).[24]



Scheme 3. Preparation of 9,9-difluoro diazafluorenes.

Indeed, the HOF·CH_3CN complex demonstrated its unique oxygen transfer abilities when reacted with both electron deficient **5a** and **6a**. Applying 5 mol equiv of the reagent at room temperature on **5a** gave the unknown 9,9-difluoro-4,5-diazaflouren-4,5-dioxide (**5b**) in 90% yield in a few seconds. The same procedure was repeated with **6a** and the new 2-bromo-9,9-difluoro-4,5-diazafluoren-4,5-dioxide (**6b**) was formed quantitatively in 10 s (Scheme 2). For comparison, we have reacted both **5a** and **6a** with large excess of either DMDO or MCPBA for several hours, but this gave mostly the starting materials with less then 5% of the desired products.

The spectral UV/vis properties of these easily obtained diazafluorenes and diazafluorenones *N*,*N*′-dioxides are summarized in Table 1. One can clearly see that a substantial narrowing of the HOMO–LUMO energy gap, relative to the starting materials (ΔE_g), did take place.

Table 1
Absorption (λ_{max}, nm) and HOMO–LUMO energy gap (ΔE_g, eV) from UV/vis, HOMO–LUMO energy gap change ($\Delta\Delta E_g$, eV) from UV/vis

Compd	λ_{max} [nm]	ΔE_g[eV]	$\Delta\Delta E_g$[eV]
1a	303	4.10	0.27
1b	324	3.83	
2a	380	3.27	0.38
2b	430	2.89	
3a	309	4.02	0.26
3b	330	3.76	
4a	310	4.00	0.12
4b	320	3.88	
5a	309	4.02	0.37
5b	340	3.65	
6a	309	4.02	0.13
6b	319	3.89	

ΔE_g(HOMO–LUMO gap)$=h\nu/\lambda$.
$\Delta\Delta E_g=\Delta E_g$(starting material)$-\Delta E_g$(product).

3. Conclusion

All the above-mentioned results show initial promising characteristics suitable for compounds serving as electron transporting, hole blocking and electroluminescent devices, and in all cases better than the parent compounds. The oxygen transfer accomplished by the HOF·CH_3CN complex is conducted under very mild conditions and in very good yields. Considering the commercial availability of premixed gases of fluorine/nitrogen, this method of transferring oxygen may become a method of choice for many cases were the alternatives are not potent enough.

4. Experimental section

4.1. General procedures

^{1}H NMR spectra were recorded using 400 and 200 MHz spectrometers. The proton broadband decoupled ^{13}C NMR spectra were recorded at 100.5 MHz. MeOH-d_4, DMSO-d_6, D_2O, and $CDCl_3$ (Me_4Si as an internal standard) served as solvents. IR spectra were recorded in KBr or $CHCl_3$ on an FTIR spectrometer. MS were measured under FAB, MALDI-TOF, DCI-CH4 or ESI-QqTOF conditions. UV spectra were recorded in CH_2Cl_2 or MeOH.

4.2. General procedure for working with fluorine

Fluorine is a strong oxidant and a corrosive material. It should be used with an appropriate vacuum line.[25] For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, thereby simplifying the process. Unreacted fluorine should be captured by a simple trap containing a solid base such as sodalime located at the outlet of the glass reactor. If elementary precautions are taken, work with fluorine is relatively simple and we have never experienced any difficulties or unpleasant situations.

4.3. General procedure for producing HOF·CH_3CN

A mixture of 10–20% F_2 in nitrogen was used throughout this work. The gas mixture was prepared in a secondary container prior to the reaction and passed at a rate of about 400 mL per minute through a cold (−15 °C) mixture of 100 mL CH_3CN and 10 mL H_2O in a regular glass reactor. The development of the oxidizing power was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. The typical concentrations of the oxidizing reagent were around 0.4–0.6 M.

4.4. General procedure for working with HOF·CH_3CN

The diazafluorene or diazafluorenone derivative was dissolved in CH_2Cl_2, and the mixture was either cooled to 0 °C or left in rt. The oxidizing agent was then added in one portion to the reaction vessel. The reaction was stopped after a few seconds and the excess of HOF·CH_3CN and the solvents evaporated. The crude product was usually purified either by vacuum flash chromatography using silica gel aminopropyl (Merck) with increasing portion of MeOH in EtOAc or by recrystallization.

4.5. Preparing and handling of BrF_3

Although commercially available, we prepare BrF_3 simply by passing 0.6 mol commercial fluorine (ca. 95%) through 0.2 mol of bromine placed in a copper reactor and held at temperatures between 4 and +10 °C. Under these conditions, the higher oxidation state of bromine, BrF_5, does not form in any appreciable amount.[26] Since practically all fluorine is consumed during the reaction as evident from the very small amount of F_2 found at the outlet of the reactor (could be determined by any iodometric method) it could be concluded that the reaction is complete. The reagent can be stored in Teflon® containers indefinitely. BrF_3 tends to react very exothermically with water and oxygenated organic solvents such as acetone or THF. Alkanes, like petroleum ether cannot serve as solvents either since they too react fast with BrF_3. Solvents such as $CHCl_3$, CH_2Cl_2, $CFCl_3$ or, if solubility is not an issue, any perfluoroalkane or perfluoroether may be used. Any use of BrF_3 should be conducted in a well-ventilated area, and caution and common sense should be exercised.

At this point we would like to clarify that when dealing with BrF_3 all mol-equivalent numbers stated in this work are of approximate values since the reagent usually contains some bromine. What is more, no matter what the solvent is, it will slowly react with the reagent, effectively reducing the amount of bromine trifluoride reaching the substrate.

4.6. General procedure for the preparation of the 9,9-difluorodiazafluorene derivatives with BrF_3[22c]

9-Dimethylhydrazone-4,5-diazafluorene (**7**) (0.5 g, 2.2 mmol) was dissolved in $CHCl_3$ (20 mL) in a glass flask and cooled to 0 °C. The best results were achieved when the reagent (3.5 mol equiv) BrF_3 was dissolved in a few milliliter of $CFCl_3$, cooled to 0 °C, and added drop wise at the same temperature using a glass dropping funnel. The reaction mixture was then washed with aqueous Na_2SO_3 till colorless. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography yielded the desired fluorinated compounds.

4.7. Experimental procedures and characterization data

*4.7.1. 4,5-Diazafluoren-9-on-4,5-dioxide (**1b**).* Compound **1b** was prepared from commercially available **1a** (0.5 g, 2.75 mmol) as described above, using 10 equiv of the oxidizing agent and recrystallized from acetonitrile. A crystalline yellow solid (0.56 g, 95% yield) was obtained; mp=277–279 °C decomp.; λ_{max}(MeOH) 324 nm; IR(KBr) 1226, 1741 cm^{-1}; ^{1}H NMR(DMSO-d_6) δ 9.10 (2H, d, J=6.6 Hz), 8.52 (2H, d, J=7.6 Hz), 8.16 ppm (2H, t, J=7.0 Hz); ^{13}C NMR δ 182.31, 145.95, 143.77, 132.87, 132.37, 131.88 ppm; HRMS (ESI-QqTOF) (m/z): calcd for $C_{11}H_6N_2O_3$ 237.0270 $(MNa)^+$, found 237.0280 (3.95 ppm error).

*4.7.2. 1,8-Diazafluoren-9-on-1,8-dioxide (**2b**)[18].* Compound **2b** was prepared from commercially available **2a** (0.5 g, 2.75 mmol) as described above, using 3 equiv of the oxidizing agent and recrystallized from methanol. A crystalline yellow solid (0.53 g, 90% yield) was obtained; mp=274 °C decomp.; λ_{max}(MeOH) 430 nm; IR 1270, 1713 cm^{-1}; ^{1}H NMR (DMSO-d_6+D_2O) δ 8.23 (2H, d, J=6.6 Hz), 7.99 (2H, d, J=7.7 Hz), 7.72 ppm (2H, t, J=7.2 Hz); ^{13}C NMR (DMSO-d_6+D_2O) δ 188.89, 144.18, 139.78, 133.79, 130.33, 124.98 ppm; HRMS (ESI-QqTOF) (m/z) calcd for $C_{11}H_6N_2O_3$ 237.0270 $(MNa)^+$, found 237.0262 (3.64 ppm error).

*4.7.3. 9,9-Dimethyl-4,5-diazafluoren-4,5-dioxide (**3b**)[20].* Compound **3b** was prepared from **3a**[20] (0.5 g, 2.5 mmol) as described above, using 3 equiv of the oxidizing agent and chromatographed on aminopropyl silica gel using ethyl acetate: methanol 70:30 as eluent. A crystalline cream solid (0.52 g, 90% yield) was obtained; mp=85–86 °C; λ_{max}(MeOH) 330 nm; IR 1293 cm^{-1}; ^{1}H NMR(200 MHz) δ 8.35 (2H, dd, ^1J=6.4 Hz, ^2J=0.8 Hz), 7.76 (2H, dd, ^1J=7.6 Hz, ^2J=0.8 Hz), 7.58 (2H, dt, ^1J=7.6 Hz, ^1J=6.4 Hz), 1.61 (6H, s); ^{13}C NMR δ 155.12, 143.16, 128.80 (two carbons), 124.13, 46.90, 26.96 ppm; MS (FAB) (m/z) calcd for $C_{13}H_{12}N_2O_2$ 228.25, found 229 $(MH)^+$ and 251 $(MNa)^+$.

*4.7.4. 9,9-Bis(4-methoxyphenyl)-4,5-diazafluoren-4,5-dioxide (**4b**) was prepared from **4a**[27].* Compound **4b** (0.5 g, 1.3 mmol) as described above, using 3 equiv of the oxidizing agent and chromatographed on aminopropyl silica gel using acetonitrile/ethyl acetate 30:70 as eluent. A crystalline cream solid (0.51 g, 95% yield) was obtained; mp=236.5–238 °C decomp.; λ_{max}(MeOH) 320 nm; IR 1254, 2835 cm^{-1}; ^{1}H NMR(MeOH-d_4) δ 8.35 (2H, dd, ^{1}J=6.5 Hz, ^{2}J=0.9 Hz), 7.49–7.57 (4H, m), 7.17 (4H, d, J=8.8 Hz) 6.9 (4H, d, J=8.8 Hz), 3.79 (6H, s); ^{13}C NMR δ 161.95, 153.56, 143.94, 143.09, 135.38, 131.15, 130.92, 128.82, 128.38, 127.13, 116.26, 63.98, 56.67 ppm; HRMS (ESI-QqTOF) (*m/z):* calcd for $C_{25}H_{20}N_2O_4$ 413.1484 (MH)$^+$, found 413.1495 (2.86 ppm error). Anal. Calcd for $C_{25}H_{20}N_2O_4/H_2O$: C, 69.76; H, 5.15; N, 6.51. Found: C, 70.16; H, 5.21; N, 6.35.

*4.7.5. 9-Dimethylhydrazone-4,5-diazafluorene (**7**)*[23]. Compound **7** was prepared from **1a** (1 g, 5.5 mmol), but not analytically purified. Dimethyl hydrazine, **1a** and acetic acid (1:1:1) in 50 mL of MeOH were refluxed for 4 h resulting in the formation of **1c**, which was chromatographed on silica gel using ethyl acetate/petroleum ether 50:50 as eluent (1.1 g, 90% yield). ^{1}H NMR ($CDCl_3$) δ 8.70–8.73 (2H, m), 8.32 (1H, dd, ^{1}J=7.8 Hz, ^{2}J=1.5 Hz), 8.13 (1H, dd, ^{1}J=7.8 Hz, ^{2}J=1.5 Hz) 7.37 (1H, m), 7.30 (1H, m), 2.99 (6H, s); ^{13}C NMR δ 151.10, 151.02, 134.54, 129.00, 123.75, 123.65, 48.85 ppm.

*4.7.6. 9,9-Difluoro-4,5-diazafluorene (**5a**).* Compound **5a** was prepared from **7** (0.5 g, 2.2 mmol) as described above using 3.5 equiv of BrF_3 and was chromatographed on silica gel using ethyl acetate/petroleum ether 20:80 as eluent. A crystalline cream-brown solid (0.32 g, 70% yield) was obtained; λ_{max}(MeOH) 309 nm. ^{1}H NMR (200 MHz) δ 8.62–8.69 (2H, m), 7.67–7.91 (2H, m), 7.17–7.24 (2H, m); ^{13}C NMR δ 157.76, 153.74, 133.31, 131.38, 124.287, 119.89 (t, ^{1}J=245.1 Hz) ppm; ^{19}F NMR δ −115.43 ppm. HRMS (MALDI-TOF) (*m/z*) calcd for $C_{11}H_6N_2F_2$ 227.0397 (MNa)$^+$, found 227.0391 (2.53 ppm error).

*4.7.7. 2-Bromo-9,9-difluoro-4,5-diazafluorene (**6a**).* Compound **6a** was prepared from **7** (0.5 g, 2.2 mmol) as described above using 3.5 equiv of BrF_3 and was chromatographed on silica gel using ethyl acetate/petroleum ether 20:80 as eluent. A crystalline cream-brown solid (0.19 g, 30% yield) was obtained; λ_{max}(MeOH) 309 nm. ^{1}H NMR δ 8.78 (1H, d, ^{2}J=2 Hz), 8.74 (1H, dd, ^{1}J=4.8, ^{2}J=1.2 Hz), 8.048–8.052 (1H, m), 7.92 (1H, dd, ^{1}J=7.6 Hz, ^{2}J=1.2 Hz), 7.33 (1H, dd, ^{1}J=7.6 Hz, ^{1}J=4.8 Hz); ^{13}C NMR δ 156.79, 156.100, 154.78, 154.33,134.40, 133.04 (^{2}J=25.5 Hz), 131.48, 124.432, 121.47, 116.57(^{1}J=246.3 Hz) ppm; ^{19}F NMR δ −115.03 ppm. HRMS (CI) (*m/z*) calcd for $C_{11}H_5N_2F_2Br$ 282.9682 (MH)$^+$, found 282.9690 (2.8 ppm error).

*4.7.8. 9,9-Difluoro-4,5-diazafluoren-4,5-dioxide (**5b**).* Compound **5b** was prepared from **5a** (0.5 g, 2.4 mmol) as described above, using 5 equiv of the oxidizing agent and chromatographed on aminopropyl silica gel using acetonitrile/ethyl acetate 50:50 as eluent. A crystalline cream solid (0.52 g, 90% yield) was obtained; mp=186–187 °C decomp.; λ_{max} ($CHCl_3$) 340 nm; IR 1222 cm^{-1}; ^{1}H NMR δ 8.28 (2H,d, J=6.8 Hz), 7.46 (2H, d, J=6.8 Hz), 7.33 ppm (2H, t, J=6.8 Hz); ^{13}C NMR δ 146.19, 142.3, 136.72 (t, ^{2}J=27.16 Hz), 126.70, 119.46, 117.09 (^{1}J=244.7 Hz) ppm; ^{19}F NMR δ −109.08 ppm. HRMS (DCI+CH_4) (*m/z*) calcd for $C_{11}H_6F_2N_2O_2$ 237.0521 (MH)$^+$, found 237.0516 (2.2 ppm error). Anal. Calcd for $C_{11}H_6F_2N_2O_2$: C, 55.94; H, 2.56. Found: C, 56.00; H, 3.01.

*4.7.9. 2-Bromo-9,9-difluoro-4,5-diazafluoren-4,5-dioxide (**6b**).* Compound **6b** was prepared from **6a** (0.5 g, 1.8 mmol) as described above, using 5 equiv of the oxidizing agent and chromatographed on aminopropyl silica gel using acetonitrile/ethyl acetate 50:50 as eluent. A crystalline cream solid (0.53 g, 95% yield) was obtained; mp=180–182 °C; λ_{max}($CHCl_3$) 319 nm; IR 1208 cm^{-1}; ^{1}H NMR δ 8.43 (1H, s), 8.27 (1H, d, J=6.7 Hz), 7.59 (1H, d, ^{3}J=1.3 Hz), 7.45 (1H, d, J=7.4 Hz), 7.34 (1H, d, J=7.1 Hz) ppm; ^{13}C NMR δ 146.98, 146.31, 141.71, 141.41, 136.56 (^{2}J=27 Hz), 136.21 (^{2}J=26.3 Hz), 126.85, 123.15. 121.96, 119.55, 116.78 (t, ^{1}J=247 Hz) ppm; ^{19}F NMR δ −108.62 ppm; HRMS (DCI+CH_4) (*m/z*) calcd for $C_{11}H_5BrF_2N_2O_2$ 316.9590 (MH)$^+$, found. 316.9600 (3.3 ppm error). Anal. Calcd for $C_{11}H_5BrF_2N_2O_2$: C, 41.93; H, 1.60; N, 8.89; Br, 25.36; F, 12.06. Found: C, 41.68; H, 1.62; N, 8.42; Br, 25.43; F, 11.58.

Acknowledgements

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Supplementary data

Complete ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and IR data for all new compounds. This material is available free of charge via the Internet at http://www.Sciencedirect.com. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.03.011.

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