Reactivity of perfluoro-(*cis*-2,3-dialkyloxaziridines) with heteroaromatic nitrogen compounds

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Pyridine *N*-oxides 3 are exclusively formed under particularly mild conditions when perfluorinated dialkyloxaziridines 1 are reacted with pyridine derivatives 2 bearing a substituent at the 2-position. Starting from pyridines substituted at the 3- and 4-positions, the previously unreported *N*-perfluoroacylpyridiniumaminides 4 are also produced and isolated as solid, stable compounds. Bis(pyridinium-*N*-aminides) 9, which have been prepared starting from bis-pyridine substrates and pyridazine and quinoxaline starting materials, also show the same reactivity. This behaviour reveals how oxaziridines 1 can work as both aminating and oxygenating agents.

The chemistry of perfluorinated oxaziridines has recently been developed to include new and useful applications of these compounds in organic synthesis.[1] Pioneering papers on perfluoro(2-methyloxaziridine) revealed the unusual reactivity of this heterocyclic system[2] which undergoes cycloadditions with fluorinated olefins but performs the oxidation of hydrocarbon olefins. Interestingly, reaction with a variety of nucleophiles (*e.g.* fluoride ion, alcohols and alcoholates), leads to the opening of the three-membered ring of this oxaziridine *via* attack at the nitrogen atom. More recent studies on perfluoro-(*cis*-2,3-dialkyloxaziridines) **1**† have shown the unique properties of these compounds. Compounds **1a,b** proved to be versatile oxidizing agents,[3] being powerful enough to give a clean oxyfunctionalization of unactivated hydrocarbon sites,[4] but also mild enough to allow the selective and high yielding oxidation of sulfides to sulfoxides to be performed.[5]

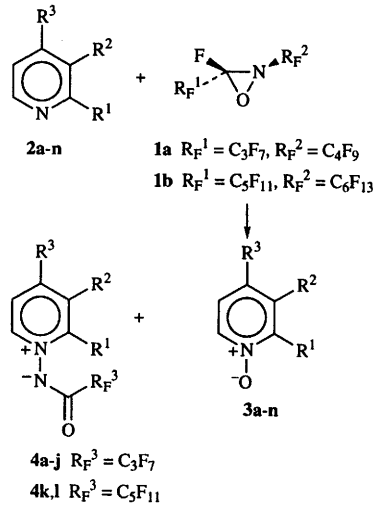
After studying the reactivity of oxaziridines **1a,b** with carbon, silicon and sulfur substrates, we have examined their behaviour with nitrogen functionalities and here we describe the results obtained using heteroaromatic nitrogen derivatives. Oxygenation of the heteroatom site of substrates **2** to give *N*-oxides **3** has been observed for all tested substrates and in some cases amination of the same site also occurred to give variable amounts of *N*-aminides **4**.

Results and discussion

When pyridine **2a** was reacted with the perfluoro(2-butyl-3-propyloxaziridine) **1a** the corresponding *N*-oxide **3a** and *N*-(perfluorobutanoyl)pyridinium-1-aminide **4a** were isolated in 77% yield (43:57 ratio). Similar yields and product ratios were obtained starting from various pyridine derivatives bearing electron-releasing or electron-withdrawing residues at the 4-position (**2b–d** and **2e–g**, respectively). The same behaviour was observed with pyridines substituted at the 3-position (3-alkylpyridines **2h,i** and 3-alkoxycarbonylpyridine **2j**) while compounds **2k–n** with a substituent at the 2-position gave exclusively the corresponding *N*-oxides **3k–n** (Scheme 1). The perfluoro(2-hexyl-3-pentyloxaziridine) **1b** showed the same reactivity, *N*-(perfluorohexanoyl)pyridinium-1-aminides **4k,l** being formed along with *N*-oxides **3a,h** starting from pyridine **2a** and its 3-methyl derivative **2h**.

To further prove the ability of oxaziridines **1** to give *N*-perfluoroacylpyridiniumaminides, we have studied the reaction of **1a** with pyridazine **5a** and quinoxaline **5b** and for these substrates too, both *N*-oxides **6a,b** and *N*-aminides **7a,b** were obtained (Scheme 2).

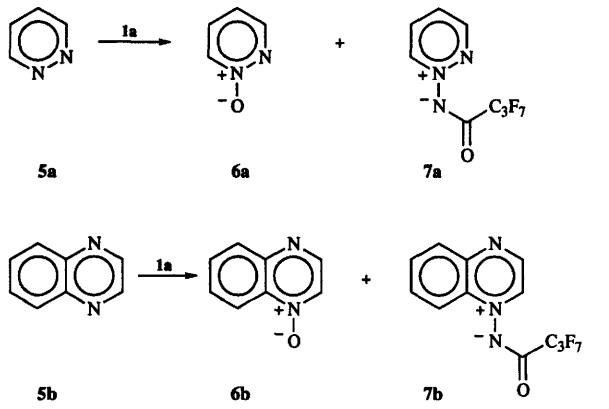
1,1′-Disubstituted-4,4′-bipyridinium derivatives are particularly interesting compounds. For instance, the so called viologens[6] are oxidation–reduction indicators and have been used as herbicides since the mid-thirties. More recently some bis(bipyridinium) compounds[7] or branched tris(bipyridinium)



2a, 3a, 4a, k	$R^1 = R^2 = R^3 = H$
2b, 3b, 4b	$R^1 = R^2 = H$; $R^3 = CH_3$
2c, 3c, 4c	$R^1 = R^2 = H$; $R^3 = (CH_3)_2CH$
2d, 3d, 4d	$R^1 = R^2 = H$; $R^3 = CH_2CH_2$-4-pyridyl
2e, 3e, 4e	$R^1 = R^2 = H$; $R^3 = (E)$-CH=CH-4-pyridyl
2f, 3f, 4f	$R^1 = R^2 = H$; R^3 = 4-pyridyl
2g, 3g, 4g	$R^1 = R^2 = H$; $R^3 = CN$
2h, 3h, 4h, l	$R^1 = R^3 = H$; $R^2 = CH_3$
2i, 3i, 4i	$R^1 = R^3 = H$; $R^2 = (S)$-1-methyl-2-oxopyrrolidin-3-yl
2j, 3j, 4j	$R^1 = R^3 = H$; $R^2 = COOC_6H_{13}$
2k, 3k	$R^1 = CH_3$; $R^2 = R^3 = H$
2l, 3l	$R^1 = (CH_2)_2CH_3$; $R^2 = R^3 = H$
2m, 3m	R^1 = 2-pyridyl; $R^2 = R^3 = H$
2n, 3n	R^1 = 2-pyridylcarbonyl; $R^2 = R^3 = H$

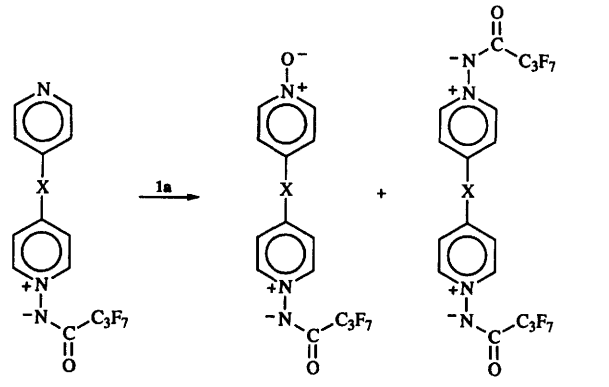
Scheme 1

† In compounds **1a** and **b**, the *cis* prefix describes the relative positions of the two ring substituents which rank higher following the Cahn–Ingdd–Prelog sequence rules (*i.e.* F for C-2 and R_F^2 for N).



Scheme 2

derivatives[8] have been used as components of catenanes and dendritic-type rotaxanes. For this reason, *N*-aminides **4d,f**, monoamination products of dipyridylethane, and bipyridyl, **2d,f** respectively, were further reacted with the oxaziridine **1a** under standard reaction conditions (Scheme 3). Both oxidation



Scheme 3

and amination of the non-derivatized pyridine nitrogen of these substrates occurred to give the corresponding *N*-aminide *N'*-oxides **8a,b** and *N,N'*-diaminides **9a,b**.

N-Aminides **4**, **7** and **9** have been routinely isolated in pure form through chromatography on silica gel and are stable crystalline compounds. In Schemes 1–3 we have shown these *N*-aminides as the mesomeric forms bearing the negative charge localized on the imine nitrogen. It is known that pyridinium-1-aminides can be isolated only when the group attached on the imine nitrogen can delocalize the negative charge and this implies that for our substrates the alternative mesomeric form, with a carbon–nitrogen double bond and the negative charge localized on the oxygen atom, also contributes to the real structure of these compounds.[9]

N-Aminides **4**, **7** and **9** could be easily identified through their physical and spectral properties. On silica gel TLC they had as a rule a definitively higher R_f than the corresponding *N*-oxides **3**, **6** and **8**. In their IR spectra they showed characteristic absorption bands at 1635–1650 cm^{-1} due to CO stretching.[10] While the ^1H NMR signals of the pyridine ring protons are shifted upfield in *N*-oxides compared to the parent heterocycle, a downfield shift was observed in *N*-aminides. The effect is particularly relevant for the protons at the 3-position ($\Delta\delta \geqslant 0.4$ ppm), it becomes smaller for protons in the 4-position ($\Delta\delta \geqslant 0.3$ ppm) but it can usually be observed also on the protons at the 2-position. This effect has already been reported for other pyridinium-*N*-aminides[10a,11] and it might be indicative of a decrease of electron density in the pyridine ring on *N*-aminide formation. A clear indication of the presence of an ylide-type structure comes from the UV spectra as a strong blue shift was observed on increasing the polarity of the solvent.[12] For instance, *N*-aminide **4g** showed a maximum at 265 nm in water and at 352 nm in THF. Intermediate wavelengths were obtained with solvents of intermediate polarity and a good linear correlation ($R^2 = 0.92$) was found between absorption maximum and polarity (measured with Dimroth's parameters).[13]

It is interesting to observe that the reactions occurred under particularly mild conditions (less than 30 min at −60 °C). Reagents commonly employed for the synthesis of heteroaromatic *N*-oxides either require more drastic conditions[14] or have a limited shelf life.[15] *N*-Sulfonyloxaziridines can be considered as prototypes for oxaziridines with good oxidizing abilities and while they readily transform tertiary amines into the corresponding *N*-oxides,[16] no similar reaction was observed with pyridine.[16,17] The stronger oxidizing properties of perfluorinated oxaziridines **1**, already observed for other types of substrates,[1] is therefore further confirmed by the results reported here.

N-Acylaminides have been typically prepared through acylation of 1-aminopyridines,[10,18] but the condensation of hydrazides with pyrylium salts,[19] and the reaction between pyridines and nitrenes[20] have also been described. To the best of our knowledge this is the first time that an oxaziridine has been used to perform the formal delivery of the acylnitrene group to a pyridine. Furthermore, *N*-perfluoroacylaminides have not been previously described, only one partially fluorinated analogue, namely *N*-(2,3,3,3-tetrafluoropropionyl)pyridiniumaminide, being reported as a minor product (0.2% yield) of the reaction of pyridinium-*N*-aminide with perfluoropropene.[21]

The formation of the products obtained can be rationalized by considering that pyridine derivatives **2** behave as nucleophiles with the oxaziridines **1a,b** and attack either the oxygen or the nitrogen atom of the three-membered ring giving *N*-oxides or *N*-aminides, respectively. (*Z*)-Perfluoro-5-azanon-5-ene was formed as a 'co-product' in oxidation reactions of various substrates with **1a**. The ^{19}F NMR spectra of crude reaction mixtures revealed that this compound was also formed on reaction with pyridine substrates **2**. It has been reported that fluoride ion and perfluorinated alcoholates[22] attack perfluorodialkyloxaziridine **1a,b** at nitrogen, but this site selectivity has not been previously observed with hydrogenated nucleophiles.

In general, it is well known that both the oxygen[23] and the nitrogen[24] atom of the oxaziridine ring can act as electrophilic sites in the reaction with a large variety of nucleophiles[25] meaning that the three-membered ring can act as both an oxygenating and aminating reagent. The structure of the oxaziridine and the nature of the nucleophile both influence the site of attack of the nucleophile.

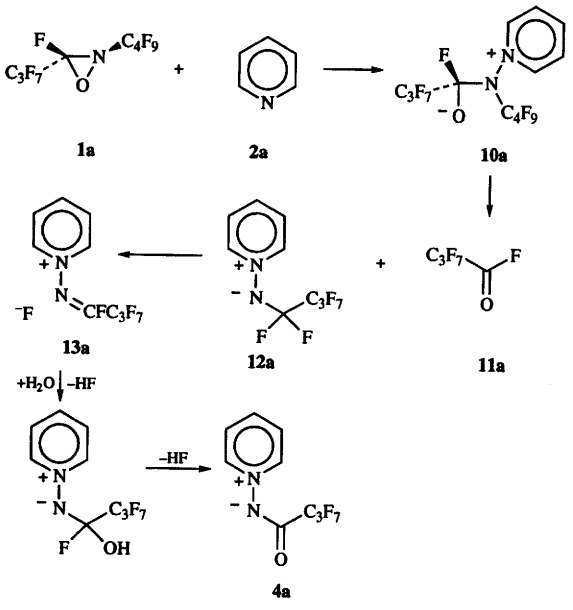
N-Unsubstituted oxaziridines transfer cleanly the NH group to sulfur[24] and nitrogen[24,26] functionalitites as well as to carbon–carbon[27] and carbon–nitrogen[28] double bonds. Some *N*-alkyl substituted oxaziridines can work as both oxygenating and aminating agents[29] and *N*-acyl analogues are very efficient acylamino transfer reagents[30] and have been employed for the synthesis of α-hydrazino acids and peptides. On the other hand, *N*-sulfonyloxaziridines have emerged as effective and versatile oxygen transfer agents and oxidative properties have been shown also by *N*-phosphinoyloxaziridines[31] and oxaziridinium salts.[32]

Less data are available in the literature on the behaviour of nucleophiles with perfluorinated oxaziridines. The fluoride ion attacks the nitrogen of the ring and isolated products depend on the substitution pattern of the oxaziridine and the employed

reaction conditions.[2b,e,22] Alcohols are aminated by perfluoro(2-methyloxaziridine),[2f] but are oxidized by **1a,b**.[3c]

The literature data discussed above would suggest that in general nitrogen is the preferential site of attack of nucleophiles on the oxaziridine ring. The presence of sterically demanding substituents on the ring and particularly on the nitrogen atom can change this preference dramatically, diverting the attack on the oxygen centre, and when either the oxaziridine or the nucleophile is too hindered no attack occurs at all.[33] These general trends are in agreement with the observation here described that for pyridine nucleophiles **2** the site selectivity of the attack is controlled by the position of the substituent on the ring. Pyridine substrates **2** give a mixture of oxygenation and amination products **3** and **4** when they bear a substituent at the 3- and 4-positions, but *N*-oxides **3** are formed exclusively when starting from the more hindered compounds substituted in the 2-position.

No specific studies have been performed to elucidate the mechanistic details of the formation of *N*-aminides, but the pathway reported in Scheme 4 starting from pyridine **2a** seems



Scheme 4

quite reasonable. The oxy anion **10a** is formed through the attack of pyridine on the nitrogen atom of the oxaziridine ring and evolves through fragmentation to give perfluorobutyryl fluoride **11a** and aza anion **12a**. This latter intermediate eliminates a fluoride anion to afford the imine derivative **13a** which gives pyridinium-*N*-aminide **4a** *via* addition of water (during the aqueous work-up or from the humidity of the air) and final elimination of HF. The initial cleavage of the nitrogen–oxygen bond to give compounds similar to **10a** and the successive fragmentation through cleavage of the carbon–nitrogen bond to afford perfluoroacyl fluorides and aza anions have already been suggested to rationalize the products formed when compounds **1a,b** are reacted with fluoride anion and perfluorinated alkoxides.[22] The same holds for the evolution of aza anions of type **12a** through fluoride ion elimination. The ^{19}F NMR spectra of the crude reaction mixture of **1a** and **2a** showed the presence of typical signals of perfluoroacyl fluorides. Finally, the proposed reaction pathway is in agreement with the observation that a number of nucleophiles attack the nitrogen atom of unsubstituted oxaziridines to give carbonyl compounds and ylide intermediates which rearrange to different final products depending on the nature of the nucleophile.[29]

In conclusion, *N*-oxides **3** are exclusively formed under particularly mild conditions on reaction of perfluorinated oxaziridines **1** with pyridine derivatives **2** bearing a substituent at the 2-position. Starting from 3- and 4-substituted pyridines, the previously unreported *N*-perfluoroacylpyridiniumaminides **4** are also produced. Following the same procedure *N*-aminides **7** of other diazines and *N,N'*-aminides **9** have also been prepared.

Experimental

NMR Spectra were recorded on a Bruker AC 250 spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F. *J* values are in Hz and chemical shifts are reported in ppm. Mass spectra were registered with a VG-70EQ apparatus and UV spectra with a Jasco Uvidec-510. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR and frequencies are reported in cm^{-1}. Optical rotations were measured with a Jasco DIP-181 and are given in units of 10^{-1} deg cm^2 g^{-1}. Flash chromatography was performed with silica gel 60 (60–200 μm, Merck). Microanalyses were performed by Redox Snc, Cologno Monzese, Milano, Italy. Melting points were measured in open capillary tubes and are uncorrected.

General procedure for the preparation of pyridine *N*-oxides and pyridinium-1-aminides with perfluoro(*cis*-2-butyl-3-propyloxaziridine) 1a

To a solution of pyridine (100 mg, 1.26 mmol) in $CHCl_3$ (0.6 ml) was added a solution of the oxaziridine **1a** (682 mg, 1.52 mmol) in $CFCl_3$ (0.6 ml) at −60 °C. After stirring for 30 min at the same temperature, the reaction was quenched by the addition of perfluorotributylamine. The mixture was stirred, then allowed to warm to room temperature. The perfluorinated layer was extracted with $CHCl_3$ and combined organics were evaporated under reduced pressure. The residue was flash chromatographed (AcOEt–MeOH, 9:1) to give pyridine *N*-oxide **3a** (53 mg, 44%) and *N*-(perfluorobutanoyl)pyridinium-1-aminide **4a** (121 mg, 33%). **4a**: (Found: C, 37.3; H, 1.7; N, 9.5. Calc. for $C_9H_5F_7N_2O$: C, 37.2; H, 1.8; N, 9.7%); ν_{max}(neat)/cm^{-1} 1217, 1642; δ_H($CDCl_3$) 7.79 (2 H, tt, *J* 7.5, 2.0, H-3), 8.08 (1 H, tt, *J* 7.5, 1.5, H-4), 8.73 (2 H, dd, *J* 7.5, 1.5, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 10, CF_3), −120.0 (2 F, q, *J* 10, CF_2), −128.0 (2 F, br s, CF_2); *m/z* (CI, CH_4) 291 (M + 1).

A similar procedure was employed when perfluoro(*cis*-2-hexyl-3-pentyloxaziridine) **1b** was used, giving *N*-oxide **3a** and *N*-(perfluorohexanoyl)pyridinium-1-aminide **4k**, isolated in 49% and 30% yield, respectively.

***N*-(Perfluorohexanoyl)pyridinium-1-aminide 4k.** (30%), mp 45 °C (from $CHCl_3$) (Found: C, 33.9; H, 1.2; N, 7.3. Calc. for $C_{11}H_5F_{11}N_2O$: C, 33.9; H, 1.3; N, 7.2%); ν_{max}(KBr)/cm^{-1} 1230, 1641; δ_H($CDCl_3$ and CD_3OD) 7.86 (2 H, t, *J* 7, H-3), 8.17 (1 H, t, *J* 7, H-4), 8.65 (2 H, d, *J* 7, H-2); δ_F($CDCl_3$ and CD_3OD) −82.3 (3 F, m, CF_3), −119.5 (2 F, m, CF_2), −124.0 (4 F, m, CF_2CF_2), −127.6 (2 F, m, CF_2); *m/z* (CI, CH_4) 391 (M + 1).

4-Methyl-*N*-(perfluorobutanoyl)pyridinium-1-aminide 4b. (35%) (Found: C, 39.3; H, 2.2; N, 9.4. Calc. for $C_{10}H_7F_7N_2O$: C, 39.5; H, 2.3; N, 9.2%); ν_{max}(neat)/cm^{-1} 1219, 1645, 1726; δ_H($CDCl_3$) 2.6 (3 H, s, CH_3), 7.54 (2 H, d, *J* 6.7, H-3), 8.52 (2 H, td, *J* 6.7, 2.0, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −128.1 (2 F, br s, CF_2); *m/z* (CI, CH_4) 305 (M + 1).

4-Isopropyl-*N*-(perfluorobutanoyl)pyridinium-1-aminide 4c. (24%), mp 70 °C (from $CHCl_3$) (Found: C, 43.5; H, 3.3; N, 8.3. Calc. for $C_{12}H_{11}F_7N_2O$: C, 43.4; H, 3.3; N, 8.4%); ν_{max}(KBr)/cm^{-1} 1228, 1645; δ_H($CDCl_3$) 1.35 (6 H, d, *J* 7.2, CH_3), 3.12 (1 H, septet, *J* 7.2, CH), 7.58 (2 H, td, *J* 7.0, 2.0, H-3), 8.55 (2 H, td, *J* 7.0, 2.0, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 8, CF_3), −120.0 (2 F, q, *J* 8, CF_2), −128.1 (2 F, br s, CF_2); *m/z* (EI) 332 (M).

4-[2-(4-Pyridyl)ethyl]pyridine *N*-oxide 3d. (35%), mp 155 °C (from $CHCl_3$) (Found: C, 72.0; H, 6.0; N, 13.9. Calc. for

$C_{12}H_{12}N_3O$: C, 72.0; H, 6.0; N, 14.0%); ν_{max}(KBr)/cm^{-1} 1228; δ_H($CDCl_3$) 2.96 (4 H, s, CH_2CH_2), 7.02 and 7.04 (4 H, d each, *J* 6.0, 6.8, H-3 and H-3′), 8.12 (2 H, d, *J* 6.8, H-2), 8.52 (2 H, d, *J* 6.0, H-2′); *m*/*z* (EI) 200 (M).

***N*-(Perfluorobutanoyl)-4-[2-(4-pyridyl)ethyl]pyridinium-1-aminide 4d.** (40%) (Found: C, 48.5; H, 3.2; N, 11.0. Calc. for $C_{16}H_{12}F_7N_3O$: C, 48.6; H, 3.1; N, 10.6%); ν_{max}(KBr)/cm^{-1} 1218, 1645; δ_H($CDCl_3$) 3.05 and 3.17 (4 H, A_2B_2 system, CH_2CH_2), 7.08 (2 H, d, *J* 6.2, H-3′), 7.5 (2 H, d, *J* 7.2, H-3), 8.55 (2 H, d, *J* 6.2, H-2′), 8.58 (2 H, d, *J* 7.2, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 10, CF_3), −120.0 (2 F, q, *J* 10, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (EI) 395 (M).

4-[2-(1-Oxidopyridin-1-ium-4-yl)ethyl]-*N*-(perfluorobutanoyl)pyridinium-1-aminide 8a. (27%) (Found: C, 46.8; H, 2.9; N, 10.2. Calc. for $C_{16}H_{12}F_7N_3O_2$: C, 46.7; H, 2.9; N, 10.2%); ν_{max}(KBr)/cm^{-1} 1227, 1646; δ_H($CDCl_3$) 3.07 and 3.17 (4 H, A_2B_2 system, CH_2CH_2), 7.23 (2 H, d, *J* 7.0, H-3′), 7.63 (2 H, d, *J* 7.0, H-3), 8.19 (2 H, d, *J* 7.0, H-2′), 8.54 (2 H, d, *J* 7.0, H-2); δ_F($CDCl_3$) −82.1 (3 F, t, *J* 9, CF_3), −120.3 (2 F, q, *J* 9, CF_2), −128.3 (2 F, br s, CF_2); *m*/*z* (CI, CH_4) 412 (M + 1).

***N*,*N*′-Bis(perfluorobutanoyl)-4,4′-ethylenedipyridinium-1-aminide 9a.** (34%) (Found: C, 39.5; H, 1.8; N, 9.4. Calc. for $C_{20}H_{12}F_{14}N_4O_2$: C, 39.6; H, 2.0; N, 9.2%); ν_{max}(KBr)/cm^{-1} 1220, 1644; δ_H($CDCl_3$) 3.27 (4 H, s, CH_2CH_2), 7.70 (4 H, d, *J* 7.0, H-3), 8.54 (4 H, d, *J* 7.0, H-2); δ_F($CDCl_3$) −82.1 (6 F, t, *J* 9, 2 × CF_3), −120.4 (4 F, q, *J* 8, 2 × CF_2), −128.3 (4 F, br s, 2 × CF_2); *m*/*z* (CI, CH_4) 607 (M + 1).

4-[2-(*E*)-(4-Pyridyl)ethenyl]pyridine *N*-oxide 3e. (30%), mp 125 °C (from $CHCl_3$) (Found: C, 72.6; H, 5.2; N, 14.2. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%); ν_{max}(KBr)/cm^{-1} 1230; δ_H($CDCl_3$) 7.12 (2 H, d, *J* 11.3, CH=), 7.37 (2 H, d, *J* 6.2, H-3′), 7.41 (2 H, d, *J* 7.2, H-3), 8.20 (2 H, d, *J* 7.2, H-2), 8.63 (2 H, d, *J* 6.2, H-2′); *m*/*z* (CI, CH_4) 198 (M).

***N*-(Perfluorobutanoyl)-4-[2-(*E*)-(4-pyridyl)ethenyl]pyridinium-1-aminide 4e.** (25%), mp 145 °C ($CHCl_3$) (Found: C, 48.7; H, 2.5; N, 10.8. Calc. for $C_{16}H_{10}F_7N_3O$: C, 48.9; H, 2.6; N, 10.7%); ν_{max}(KBr)/cm^{-1} 1229, 1638; δ_H($CDCl_3$) 7.3 (2 H, d, *J* 15.6, CH=), 7.45 (2 H, br s, H-3′), 7.79 (2 H, d, *J* 7.3, H-3), 8.73 (4 H, d, *J* 7.3, H-2 and H-2′); δ_F($CDCl_3$) −81.8 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (CI, CH_4) 394 (M + 1).

***N*-(Perfluorobutanoyl)-4,4′-bipyridin-1-ium-1-aminide 4f.** (25%), mp 148 °C (from $CHCl_3$) (Found: C, 45.6; H, 2.2; N, 11.6. Calc. for $C_{14}H_8F_7N_3O$: C, 45.8; H, 2.2; N, 11.4%); ν_{max}(KBr)/cm^{-1} 1229, 1643; δ_H($CDCl_3$) 7.60 (2 H, d, *J* 6.6, H-3′), 7.99 (2 H, d, *J* 6.6, H-3), 8.85–8.90 (4 H, m, H-2 and H-2′); δ_F($CDCl_3$) −81.8 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (EI) 367 (M).

4-(1-Oxidopyridin-1-ium-4-yl)-*N*-(perfluorobutanoyl)-pyridinium-1-aminide 8b. (35%), mp 200 °C (from $CHCl_3$) (Found: C, 44.0; H, 2.1; N, 11.0. Calc. for $C_{14}H_8F_7N_3O_2$: C, 43.9; H, 2.1; N, 11.0%); ν_{max}(KBr)/cm^{-1} 1277, 1652; δ_H($CDCl_3$) 7.65 (2 H, d, *J* 7.5, H-3′), 7.91 (2 H, d, *J* 7.2, H-3), 8.35 (2 H, d, *J* 7.5, H-2′), 8.87 (2 H, d, *J* 7.2, H-2); δ_F($CDCl_3$) −81.8 (3 F, t, *J* 8, CF_3), −120.0 (2 F, q, *J* 8, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (EI) 383 (M).

***N*,*N*′-Bis(perfluorobutanoyl)-4,4′-bipyridine-1,1′-diium-1,1′-diaminide 9b.** (30%), mp 263 °C (from $CHCl_3$) (Found: C, 37.3; H, 1.4; N, 9.7. Calc. for $C_{18}H_8F_{14}N_4O_2$: C, 37.4; H, 1.4; N, 9.7%); ν_{max}(KBr)/cm^{-1} 1226, 1637; δ_H($CDCl_3$) 8.05 (4 H, d, *J* 7.2, H-3), 9.10 (4 H, d, *J* 7.2, H-2); δ_F($CDCl_3$) −81.8 (6 F, t, *J* 9, 2 × CF_3), −120.0 (4 F, q, *J* 9, 2 × CF_2), −127.9 (4 F, br s, 2 × CF_2); *m*/*z* (CI, CH_4) 579 (M + 1).

4-Cyano-*N*-(perfluorobutanoyl)pyridinium-1-aminide 4g. (35%), mp 104 °C (from $CHCl_3$) (Found: C, 38.2; H, 1.3; F, 42.0; N, 13.2; O, 5.1. Calc. for $C_{10}H_4F_7N_3O$: C, 38.1; H, 1.3; F, 42.2; N, 13.3; O, 5.1%); ν_{max}(KBr)/cm^{-1} 1640; δ_H($CDCl_3$) 8.02 (2 H, d, *J* 7.5, H-3), 9.16 (2 H, d, *J* 7.5, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (CI, CH_4) 316 (M + 1).

3-Methyl-*N*-(perfluorobutanoyl)pyridinium-1-aminide 4h. (20%), mp 70 °C (from $CHCl_3$) (Found: C, 39.6; H, 2.2; N, 9.2. Calc. for $C_{10}H_7F_7N_2O$: C, 39.5; H, 2.3; N, 9.2%); ν_{max}(KBr)/cm^{-1} 1212, 1642; λ_{max}/nm (THF) 352, (AcOEt) 350, ($CHCl_3$) 356, (CH_3COCH_3) 345, (DMF) 345, (DMSO) 340, (CH_3CN) 342, (MeOH) 275, (ethylene glycol) 272, (H_2O) 265; δ_H($CDCl_3$) 2.55 (3 H, s, CH_3), 7.65 (1 H, t, *J* 7.5, H-5), 7.86 (1 H, d, *J* 7.5, H-4), 8.50 (1 H, d, *J* 7.5, H-6), 8.53 (1 H, s, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (EI) 304 (M).

3-Methyl-*N*-(perfluorohexanoyl)pyridinium-1-aminide 4l. This compound and **3h** were obtained in 35% and 50% yield, respectively, when 3-methylpyridine (3-picoline) **2h** was reacted with the oxaziridine **1b** under standard reaction conditions. **4l**: (35%), mp 45 °C (from $CHCl_3$) (Found: C, 35.5; H, 1.7; N, 7.1. Calc. for $C_{12}H_7F_{11}N_2O$: C, 35.7; H, 1.7; N, 6.9%); ν_{max}(KBr)/cm^{-1} 1202, 1641; δ_H($CDCl_3$ and CD_3OD), 2.55 (3 H, s, CH_3), 7.74 (1 H, dd, *J* 8.1, 7.0, H-5), 7.97 (1 H, d, *J* 8.1, H-4), 8.44 (1 H, s, H-2), 8.46 (1 H, d, *J* 7.0, H-6); δ_F($CDCl_3$ and CD_3OD) −82.3 (3 F, m, CF_3), −119.3 (2 F, m, CF_2), −124.0 (4 F, m, CF_2CF_2), −127.7 (2 F, m, CF_2); *m*/*z* (CI, CH_4) 405 (M + 1).

3-[(*S*)-1-Methyl-2-oxo-pyrrolidin-3-yl]-*N*-(perfluorobutanoyl)pyridinium-1-aminide 4i. (45%) (Found: C, 43.5; H, 3.2; N, 10.7. Calc. for $C_{14}H_{12}F_7N_3O_2$: C, 43.4; H, 3.1; N, 10.8%); $[\alpha]_D^{20}$ −24.5 (*c* 1.0 in $CHCl_3$); ν_{max}(neat)/cm^{-1} 1228, 1652, 1684; δ_H($CDCl_3$) 1.90–2.00 (2 H, m, CH_2), 2.45–2.68 (2 H, m, CH_2), 2.76 (3 H, s, CH_3), 4.72 (1 H, t, *J* 6.5, CH), 7.80–7.93 (2 H, m, H-4 and H-5), 8.71 (1 H, d, *J* 1.5, H-2), 8.74 (1 H, td, *J* 6.0, 1.5, H-6); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (EI) 387 (M).

3-Hexyloxycarbonylpyridine *N*-oxide 3j. (25%) (Found: C, 64.4; H, 7.6; N, 6.4. Calc. for $C_{12}H_{17}NO_3$: C, 64.6; H, 7.7; N, 6.3%); ν_{max}(neat)/cm^{-1} 1226, 1732; δ_H($CDCl_3$) 0.9 (3 H, t, *J* 7.0, CH_3), 1.30–1.40 [6 H, m, $(CH_2)_3$], 1.72 (2 H, m, CH_2), 4.32 (2 H, t, *J* 6.4, CH_2O), 7.34 (1 H, br s, H-5), 7.90 (1 H, d, *J* 6.4, H-4), 8.37 (1 H, br s, H-6), 8.77 (1 H, s, H-2); *m*/*z* (CI, CH_4) 224 (M + 1).

3-Hexyloxycarbonyl-*N*-(perfluorobutanoyl)pyridinium-1-aminide 4j. (45%) (Found: C, 45.8; H, 4.2; N, 6.8. Calc. for $C_{16}H_{17}F_7N_2O_3$: C, 45.9; H, 4.1; N, 6.7%); ν_{max}(neat)/cm^{-1} 1229, 1646, 1727; δ_H($CDCl_3$) 0.9 (3 H, t, *J* 7.0, CH_3), 1.26–1.51 [6 H, m, $(CH_2)_3$], 1.71–1.87 (2 H, m, CH_2), 4.44 (2 H, t, *J* 6.8, CH_2O), 7.90 (1 H, dd, *J* 7.9, 6.4, H-5), 8.63 (1 H, td, *J* 7.9, 1.5, H-4), 8.97 (1 H, td, *J* 6.4, 1.5, H-6), 9.26 (1 H, br s, H-2); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 8, CF_3), −120.0 (2 F, q, *J* 8, CF_2), −128.0 (2 F, br s, CF_2); *m*/*z* (EI) 418 (M).

2,2′-Bipyridine *N*-oxide 3m. (20%) (Found: C, 69.9; H, 4.7; N, 16.2. Calc. for $C_{10}H_8N_2O$: C, 69.8; H, 4.7; N, 16.3%); ν_{max}(neat)/cm^{-1} 1227; δ_H($CDCl_3$) 7.25–7.43 (3 H, m, H-4, H-5 and H-5′), 7.84 (1 H, dt, *J* 8.3, 1.5, H-4′), 8.18 (1 H, dd, *J* 7.9, 2.2, H-3), 8.33 (1 H, dd, *J* 8.3, 1.5, H-3′), 8.71–8.75 (1 H, m, H-6), 8.88 (1 H, td, *J* 8.2, 1.5, H-6′); *m*/*z* (EI) 172 (M).

2-(2-Pyridylcarbonyl)pyridine *N*-oxide 3n. (59%), mp 156 °C (from $CHCl_3$) (Found: C, 65.5; H, 5.0; N, 13.7. Calc. for $C_{11}H_{10}N_2O_2$: C, 65.3; H, 5.0; N, 13.8%); ν_{max}(KBr)/cm^{-1} 1257, 1690; δ_H($CDCl_3$) 7.38–7.52 (4 H, m, H-3, H-4, H-5, H-5′), 7.90 (1 H, dt, *J* 7.7, 1.9, H-4′), 8.11 (1 H, d, *J* 7.7, H-3′), 8.15–8.20 (1 H, m, H-6), 8.60 (1 H, d, *J* 4.6, H-6′); *m*/*z* (CI, isobutane) 201 (M + 1).

***N*-(Perfluorobutanoyl)pyridazinium-1-aminide 7a.** (20%), mp 70 °C (from $CHCl_3$) (Found: C, 33.2; H, 1.4; N, 14.3. Calc. for $C_8H_4F_7N_3O$: C, 33.0; H, 1.4; N, 14.4%); ν_{max}(KBr)/cm^{-1} 1202, 1640; δ_H($CDCl_3$) 7.86–7.90 and 8.20–8.26 (2 H, m each, H-4 and H-5), 9.15 (1 H, d, *J* 5.7, H-3), 9.90 (1 H, d, *J* 6.6, H-6); δ_F($CDCl_3$) −81.9 (3 F, t, *J* 9, CF_3), −120.0 (2 F, q, *J* 9, CF_2), −127.9 (2 F, br s, CF_2); *m*/*z* (CI, isobutane) 292 (M + 1).

***N*-(Perfluorobutanoyl)quinoxalinium-1-aminide 7b.** (45%), mp 86 °C (from $CHCl_3$) (Found: C, 42.2; H, 1.7; F, 38.6; N, 12.2. Calc. for $C_{12}H_6F_7N_3O$: C, 42.2; H, 1.8; F, 39.0; N, 12.3%); ν_{max}(KBr)/cm^{-1} 1217, 1639; δ_H($CDCl_3$) 8.02–8.10 (2 H,

m, H-6 and H-7), 8.33–8.38 (1 H, m, H-5), 8.82–8.89 (1 H, m, H-8), 9.22 (1 H, d, J 3.3, H-3), 9.88 (1 H, d, J 3.3, H-2); $\delta_F(CDCl_3)$ −81.8 (3 F, t, J 9, CF_3), −119.5 (2 F, q, J 9, CF_2), −127.7 (2 F, br s, CF_2); m/z (CI, isobutane) 342 (M + 1).

Pyridine *N*-oxide **3a** (40%), 4-methylpyridine *N*-oxide **3b** (35%), 4-cyanopyridine *N*-oxide **3g** (50%), 2-methylpyridine *N*-oxide **3k** (70%), were identified through comparison with authentic samples (purchased from Aldrich).

4-Isopropylpyridine *N*-oxide **3c** (40%),[34] 4,4′-bipyridine *N*-oxide **3f** (30%),[35] 3-methylpyridine *N*-oxide **3h** (52%),[36] 3-[(*S*)-*N*-methyl-2-oxo-pyrrolidin-3-yl]pyridine *N*-oxide [(−)-cotinine *N*-oxide] **3i** (30%),[37] 2-propylpyridine *N*-oxide **3l** (68%),[38] pyridazine *N*-oxide **6a** (70%),[39] and quinozaline *N*-oxide **6b** (30%)[40] were identified through comparison of their spectral and physical data with those reported in the literature.

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