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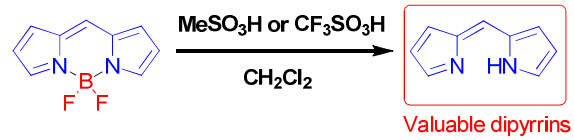
Graphical Abstract



Soft conditions
Straighforward
Compatible with hihgly reactive functionalities
Workable with strongly electron-poor starting products

Journal Name

ARTICLE

Preparation of dipyrrins from *F*-BODIPYs by treatment with methanesulfonic acids†

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

DOI: 10.1039/x0xx00000x

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An alternative metal-free soft procedure for the preparation of dipyrrins from *F*-BODIPYs is reported. The new method makes possible to obtain certain dipyrrin derivatives that were unaccessible from *F*-BODIPYs to date. To demonstrate the ability of the new procedure, dipyrrins having highly reactive groups, such as chloro, cyano or acetoxyl, have been easily obtained from the corresponding *F*-BODIPY, which shows the synthetic utility of the reported methodology.

Introduction

Difluoroboron-dipyrromethene (*F*-BODIPY) complexes (see **1** in Figure 1) are widely known as valuable organic dyes for the development of useful photonic tools, such as fluorescent chemical sensors and probes, fluorescent security labels, dye-lasing systems, dyes for bioimaging, light harvesting materials, energy-converting antenna systems, or photodynamic therapy agents, among other interesting photonic applications.[1]

Beyond photonics, *F*-BODIPYs can be also employed as synthetic precursors in the preparation of dipyrrins (see **2** in Figure 1),[2] which are important molecules in medicinal chemistry and materials science (*e.g.*, as synthetic intermediates for biologically active porphyrinoids, or for the design of specific cation- or anion-binding supramolecular systems).[3] The importance of this synthetic use of *F*-BODIPYs is due to their higher chemical stability when compared to the corresponding dipyrrins, making possible chemical transformations on the BODIPY core which are impracticable on the dipyrrin.[2a,b] In other words, the *F*-BODIPY difluoroboron (BF_2) group is a very convenient protecting/activating group to take into account when projecting the synthesis of a functionalized dipyrrin. Moreover, the so-obtained dipyrrins can be also used for preparing other BODIPYs (*e.g.*, certain *C*-BODIPYs which cannot be synthesized directly from the corresponding parent *F*-BODIPYs by simple fluorine substitution).[4] However, the known stability of *F*-BODIPYs, joined to the also known high instability of dipyrrins,[3a] makes the decomplexation of *F*-BODIPYs a non-trivial process, especially when highly reactive dipyrrins are required.

Up to now, two main procedures are available for decomplexing *F*-BODIPYs (see Figure 1): The useful "basic" method developed by Thompson and co-workers,[2a,b] which involves strong basic conditions (*e.g.*, potassium hydroxide or *tert*-butoxide in *tert*-BuOH under microwave, MW, irradiation), and the "Lewis-acid" method, developed first by Ravinkanth and co-workers (*e.g.*, $ZrCl_4$ or $TiCl_4$ in refluxing MeCN/MeOH),[2e] further improved by the Thompson group under softer conditions (*e.g.*, BF_3 or BCl_3 in CH_2Cl_2 at room temperature, r.t.).[2f]

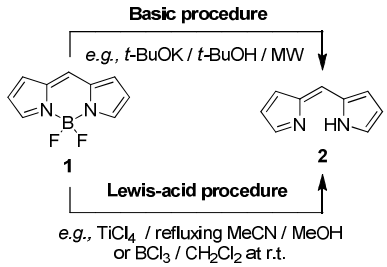

Figure 1. Dipyrrins by BF_2 removal in BODIPYs. Established procedures.

However, the scope of these procedures is not general: the Ravinkanth method seems to be efficient only for 8-aryl-*F*-BODIPYs;[2e] the basic Thompson procedure cannot be applied to *F*-BODIPYs having functional groups labile under the required strong basic conditions (*e.g.*, halogen at the C3/5 BODIPY positions,[2d] or easily enolizable functionalities[2b]); the softer (r.t.) Lewis-acid Thompson procedure requires electron-rich enough *F*-BODIPYs (*e.g.*, polyalkylated *F*-BODIPYs).[2f] Moreover, metal cations are involved in all these procedures, and this can be a limitation when obtaining highly chelating dipyrrins. These drawbacks make necessary the establishment of an alternative wide-scope method for the preparation of dipyrrins from *F*-BODIPYs, taking place under soft enough reaction conditions and free of metal cations, as well. Herein, we report such a method, in which methanesulfonic acid or trifluoromethanesulfonic acid in methylene dichloride promotes the desired *F*-BODIPY decomplexation.

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† Electronic Supplementary Information (ESI) available: ^1H, ^{13}C and ^{19}F NMR spectra. See DOI: 10.1039/x0xx00000x

Results and discussion

Within the frame of our research work in the chemistry of BODIPYs,[5] we found that methanesulfonic acid was able to remove the BF_2 group in electron-poor *F*-BODIPYs under very soft conditions (methylene dichloride at r.t.), despite the known stability of this kind of BODIPYs (electron poor) toward strong acids (*e.g.*, trichloroacetic or trifluoroacetic acid) reported before.[6] Oppositely to this statement, the electron-rich polyalkylated 1,3,5,7,8-pentamethyl-2,6-diethyl-*F*-BODIPY has been demonstrated to be unstable in the presence of di- or trichloroacetic acid.[7] Related to the latter result, Yu *et al.* have recently reported BF_2 removal in certain 1,3,5,7-tetramethyl-8-aryl-*F*-BODIPYs by using trifluoroacetic acid or HCl in aqueous organic solvents,[8] as it was also observed by Liras *et al.* in *F*-BODIPYs substituted with amino or amido groups.[9] However, these procedures are expected to fail for *F*-BODIPYs with higher electron-poor character (*F*-BODIPY protonation must be involved in the decomplexation activation, see later), and they have been shown incompatible with certain hydrolyzable functionalities (*e.g.*, acetamide).[9]

To prove the ability of methanesulfonic acids to activate the BF_2 removal in *F*-BODIPYs under soft conditions, we came interested in testing a difficult case: the decomplexation of dichlorinated 8-aryl-*F*-BODIPY **3**[10] (Figure 2). Although the corresponding dichlorinated dipyrrin can be easily obtained by well-established methods from pyrrole derivatives,[10] we chose the study of this case for three main reasons: (1) the high electron-poor character of **3**, that should make it highly inert toward standard Lewis acid conditions; (2) the known S_NAr reactivity of **3** toward nucleophiles (chlorine substitution), due to the said electron-poor character; (3) the known instability of the corresponding dichlorinated dipyrrin.

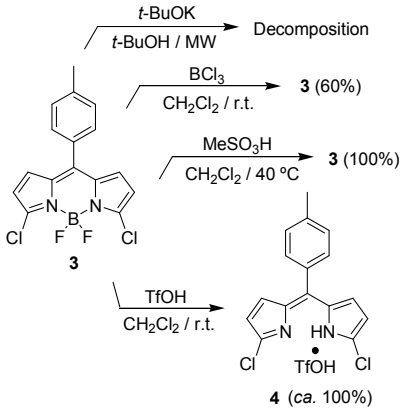


Figure 2. BF_2 removal in **3** (final water treatment was conducted in all cases).

Indeed, trying to remove the BF_2 group in **3** by the basic Thompson procedure affords decomposition (Figure 2). This result was expected, due to the presence of chlorine atoms at the C3/5 positions of the starting *F*-BODIPY. These chlorine atoms must easily undergo S_NAr under the used strong basic reaction conditions.[2d,10] Besides, said chlorines would make the final dipyrrin highly reactive and therefore, unstable under the severe conditions employed for the removal.

On the other hand, **3** was recovered in 60% yield (isolated yield after chromatographic purification) when performing the softer Lewis-acid (BCl_3) Thompson procedure (Figure 2). It must be noted here that the desired final dipyrrin was not detected by ^{1}H-NMR analysis of the crude mixture prior purification. The observed result is explained on the basis of the electron-poor character of **3** (note the strong electron-withdrawing inductive effect (-I) exerted by the chlorine atoms), which should diminish the Lewis basicity of its nitrogen centers.[2f]

Trying to remove the BF_2 group of **3** by treatment with methanesulfonic acid was also unsuccessful. Thus, **3** does not react with this acid in CH_2Cl_2 solution, even under refluxing conditions (40 ºC for 24 h; see Figure 2). However, using the stronger trifluoromethanesulfonic acid, TfOH, at r.t. gave fairly place to the desired dichlorinated dipyrrin as the corresponding salt **4** in *ca.* quantitative yield (see Figure 2).

The latter result clearly shows that the BF_2 removal is activated by the protonation of the *F*-BODIPY core (**1**), which requires a strong enough Brönsted acid due to its weak-base character (Figure 3). After final hydrolysis (nucleophilic water attack to the electrophylic boron in the formed intermediate), the so-obtained free dipyrrin (**2)** would be protonated by a second mol equiv. of the strong acid present in the reaction medium, to generate the corresponding dipyrrin salt (isolated final product), whereas the formed BF_2OH would react with additional water molecules to generate $B(OH)_3$.[11]

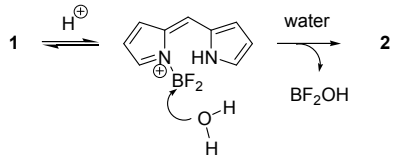


Figure 3. Activation of *F*-BODIPY decomplexation by protonation.

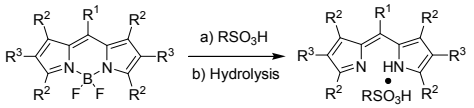
Encouraged by the result obtained by **3**, we decided to carry out a screening of BF_2 removal from a set of differently substituted *F*-BODIPYs using methanesulfonic and trifluoromethanesulfonic acids (Table 1). We observed that, in agreement with the proposed way of activation (*i.e.*, involving an initial protonation), the use of a softer acid (methanesulfonic) led to the corresponding dipyrrin salt starting from alkyl *F*-BODIPYs **5a-d**–(see Table 1), due to the expected higher basic character of the involved *F*-BODIPY core when compared to **3**. (Note the expected different effect of the electron-withdrawing chlorines *vs.* the electron-donor alkyls on the basicity of the *F*-BODIPY core). The dipyrrins were obtained as the corresponding stable methanesulfonic acid salt.

To check the expected presence of a single unit of organic acid in the structure of the obtained dipyrrin salts, the amount of fluorine in salt **6b** (involving strong-acid and -base partners) was determined by ^{19}F-NMR (*p*-trifluoromethylacetophenone

was used as internal standard; see ESI†), showing a single unit of TfOH in its structure.

Also in agreement with the mechanism shown in Figure 3, it was possible to remove the BF_2 group in the presence of water. Thus, **5b** was converted to the corresponding dipyrrin salt by treatment with TfOH in aqueous CH_2Cl_2 (Method C) instead of dry CH_2Cl_2 (Method B). However, using water as the only solvent (Method D) noticeably reduces the effectiveness of the process, probably due to the insolubility of both the starting BODIPY and the final dipyrrin salt in water (see Table 1).

Table 1. BF_2 removal in selected *F*-BODIPYs promoted by methanesulfonic acids.



5a-g **6a-g**

BODIPY	R^1	R^2	R^3	R	Met.[a]	Dipyrrin salt (yield)
5a	Me	Me	H	Me	A	**6a** (92%)
5b	Me	Me	Et	Me	A	**6b** (99%)
				CF_3	B	**6b'** (98%)
				CF_3	C	**6b'** (98%)
				CF_3	D	**6b'** (trace)
5c	Nonyl	Me	*t*Bu	Me	A	**6c** (97%)
5d	Me	Me	Bu	Me	A	**6d** (100%)
5e	CH_2OAc	Me	Et	Me	A	No reaction
				CF_3	B	**6e/7**[b] (99%)
				CF_3	C	Complex mixt.
5f	CN	Me	Et	Me	A	No reaction
				CF_3	B	**6f** (98%)
5g	Mesityl	H	H	CF_3	B	**6g** (98%)

[a] Method A: Methanesulfonic acid in refluxing CH_2Cl_2 overnight; Method B: TfOH in CH_2Cl_2 at r.t. overnight; Method C: TfOH in aqueous CH_2Cl_2 at r.t. overnight; Method D: TfOH in water at r.t. overnight. [b] **7** is the corresponding hydroxylated dipyrrin salt coming from the ester hydrolysis (**6e**/**7** = 5/6 determined by ^{1}H NMR).

Noticeably, the essayed decomplexations of *meso*-alkyl-*F*-BODIPYs took place without detecting dypyrrin tautomerization to the corresponding 1,1-di-1*H*-pyrrol-2-ylethene derivative (Figure 4), despite the known tautomerizable character of the involved *meso* alkyl groups.[12] In regard to this, it is known that the decomplexation of **5b** under basic conditions affords the corresponding 1,1-dipyrrolylethene instead of the dipyrrin.[2b]

Interestingly, the sulfonic acid-promoted decomplexation took place without tautomerization even for acetoxylated **5e** (see Table 1), despite the higher reactivity towards tautomerization expected for its *meso* methylene group. However, TfOH instead of methanesulfonic acid was required to remove the BF_2 group in this case, probably due to the electron-withdrawing effect exerted by the acetoxyl group, which lowers the key BODIPY basicity. For the same reasons, the decomplexation of electronically deactivated (electron-poor) **5f** required the use of TfOH, as well (see Table 1).

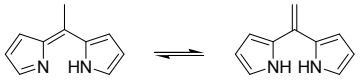


Figure 4. Dipyrrin - 1,1-di-1*H*-pyrrol-2-ylethene tautomerization in *meso*-methyldipyrrins.

It is worth to mention that, despite the highly hydrolyzable character of the acetoxyl group of **5e**, *ca.* 45% mol equiv. of this functional group remained unaltered (final product **6e**) when using Method B for the removal process (see Table 1). However, when the aqueous-solvent procedure (Method C) is applied instead, a complex mixture of reaction products is obtained, being **6e** and **7** minor products (see Table 1) as shown by the ^{1}H NMR analysis of the said mixture (see ESI†). This result clearly shows the interest of Methods A or B for straightforwardly decomplexing *F*-BODIPYs having easily hydrolyzable functions.

Significantly, it was also possible to remove the BF_2 group in electronically deactivated **5g** (*meso*-aryl group as the only *F*-BODIPY substituent), in the absence of metals and under soft reaction conditions (Method B; see Table 1). It must be noted that, up to date, this kind of *F*-BODIPYs could only be decomplexed by using the Ravinkanth method,[2e] but not under soft (r.t.) Lewis-acid conditions.[2f]

Conclusions

In summary, methanesulfonic acids are able to remove BF_2 in *F*-BODIPYs under soft reaction conditions (r.t. or refluxing CH_2Cl_2), which constitutes a valuable alternative to obtain dipyrrins from *F*-BODIPYs.

The new procedure is efficient for both *meso*-alkyl and *meso*-aryl *F*-BODIPYs, and its main goals are: (1) possibility of undergoing BF_2 removal in electron-poor *F*-BODIPYs under metal-free soft acid conditions, (2) compatibility with labile functional groups (*e.g.*, easily hydrolyzable functionalities), and (3) possibility of synthesizing highly reactive dipyrrins. We are convinced that the herein reported new procedure to obtain dipyrrins from *F*-BODIPYs has a great potential for the future development of new porphyrinoids and ion binding systems through dipyrrins having reactive groups which can only be straightforwardly introduced by using a *F*-BODIPY intermediate (*e.g.*, by regiocontrolled S_NAr reactions in halo-*F*-BODIPYs).

Experimental

General methods

Common solvents were dried and distilled by standard procedures. All starting materials and reagents were obtained commercially and used without further purifications. NMR spectra were recorded at 20 ºC and the residual solvent peaks

were used as internal standards. High resolution mass spectrometry (HRMS) was performed using electrospray ionization. Fourier transform infrared (FTIR) spectra were recorded without solving the sample, by using the attenuated total reflection (ATR) technique.

General synthetic procedures

Method A. Methanesulfonic acid (480 mg, 1.00 mmol) was added to the corresponding *F*-BODIPY (0.05 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred at 40 ºC for 24 h. Then, the reaction mixture was allowed to cool to room temperature and them H_2O was added (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to obtain the corresponding pure dipyrrin, as pyrrolium methanesulfonate salt (the known chemical instability of the free dipyrrins usually makes necessary their isolation as acid salts[2a,b]). If further purification is necessary, it can be achieved by washing the salt with a proper solvent (*e.g.*, cold pentane).

Method B. Analogous to Method A, but using TfOH (150 mg, 1.00 mmol) instead of methanesulfonic acid, and conducting the reaction at room temperature.

Method C. Analogous to Method B, but using aqueous CH_2Cl_2/water (40:1 in volume) instead of CH_2Cl_2.

Method D. Analogous to Method B, but using water instead of CH_2Cl_2.

(2*Z*)-5-Chloro-2-[(5-chloro-1*H*-pyrrol-2-yl)(4-methylphenyl)methylene]-2*H*-pyrrolium trifluoromethanesulfonate (4). Prepared according to Method B. Bright orange solid. 20.8 mg (92%). M.p.: 194-199 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.57 (d, *J* = 4.3 Hz, 2H), 6.26 (d, *J* = 4.3 Hz, 2H), 2.44 (s, 3H, CH_3), ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.5, 139.6, 138.3, 132.5, 130.9, 130.2, 128.6, 116.8, 21.4 (Me) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz) δ -78.53 (s, 3F) ppm. ATR-FTIR ν 3233, 2924, 1578, 1443, 1424, 1366, 1343, 1316, 1252. 1038 cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{16}H_{13}Cl_2N_2$ 330.0452 found 330.0444.

(2*Z*)-2-[1-(3,5-Dimethyl-1*H*-pyrrol-2-yl)ethylidene]-3,5-dimethyl-2*H*-pyrrolium methanesulfonate (6a). Prepared according to Method A. Bright orange solid. 14.3 mg (92%). M.p.: 160-163 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.62 (br s, 2H), 6.18 (s, 2H), 2.77 (s, 3H), 2.76 (s, 3H), 2.47 (s, 6H), 2.13 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.2, 149.3, 141.3, 132.3, 119.3, 39.5, 22.6, 14.4, 13.9 ppm. ATR-FTIR ν 3186, 2925, 1546, 1449, 1294, 1179, 1040, 973 cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{14}H_{19}N_2$ 215.1541 found 215.1533.

(2*Z*)-4-Ethyl-2-[1-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)ethylidene]-3,5-dimethyl-2*H*-pyrrolium methanesulfonate (6b). Prepared according to Method A. Bright red solid. 18.1 mg (99%). M.p.: 154-157 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.87 (br s, 2H), 2.82 (s, 3H), 2.79 (s, 3H), 2.46 (s, 6H), 2.39 (q, *J* = 7.5 Hz, 4H), 1.99 (s, 6H), 1.04 (t, *J* = 7.5 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.8, 146.9, 137.0, 132.0, 131.6, 39.7, 23.2, 17.5, 14.4, 12.2, 11.7 ppm. ATR-FTIR ν 3169, 2927, 1570, 1514, 1304, 1226, 1178, 1062, 1041, 958 cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{27}N_2$ 271.2169 found 271.2163.

(2*Z*)-4-Ethyl-2-[1-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)ethylidene]-3,5-dimethyl-2*H*-pyrrolium trifluoromethanenesulfonate (6b'). Prepared according to Method B. Bright red solid. 20.6 mg (98%). M.p.: 139-143 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.97 (br s, 2H), 2.75 (s, 3H), 2.48-2.37 (m, 10H), 2.03 (s, 6H), 1.07 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.1, 146.2, 137.6, 132.1, 131.8, 22.5, 17.5, 14.4, 12.1, 11.8 ppm. ^{19}F NMR ($CDCl_3$, 282 MHz) δ -78.73 (s, 3F) ppm. ATR-FTIR ν 3229, 2966, 2928, 1569, 1514, 1290, 1224, 1161, 1031, 958 cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{18}H_{27}N_2$ 271.2169 found 271.2158.

(2*Z*)-4-*tert*-Butyl-2-[1-(4-*tert*-butyl-3,5-dimethyl-1*H*-pyrrol-2-yl)decylidene]-3,5-dimethyl-2*H*-pyrrolium methanesulfonate (6c). Prepared according to Method A. Bright red solid. 25.9 mg (97%). M.p.: 161-165 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.91 (br s, 2H), 3.28 (t. *J* = 7.1 Hz, 2H), 2.77 (s, 3H), 2.68 (s, 6H), 2.09 (s, 6H), 1.40 (s, 18 H), 1.45-1.10 (m, 14H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.1, 148.7, 136.9, 136.8, 132.2, 36.3, 33.3, 31.9, 31.6, 31.4, 29.7, 29.4, 29.3, 29.2, 22.6, 17.0, 14.9, 14.1 ppm. ATR-FTIR ν 3181, 2925, 1557, 1464, 1291. 1172, 1042, 970 cm^{-1}. HRMS-ESI (*m/z*): $[M+H]^+$ calcd. for $C_{30}H_{51}N_2$ 439.4049 found 439.4037.

(2*Z*)-4-Butyl-2-[1-(4-butyl-3,5-dimethyl-1*H*-pyrrol-2-yl)ethylidene]-3,5-dimethyl-2*H*-pyrrolium methanesulfonate (6d). Prepared according to Method A. Bright orange solid. 21.1 mg (*ca.* quantitative). M.p.: 159-162 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.00 (br s, 2H), 2.84 (s, 3H), 2.80 (s, 3H), 2.47 (s, 6H), 2.36 (t, *J* = 7.3 Hz, 4H), 1.98 (s, 6H), 1.45-1.22 (m, 8H), 0.92 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.0, 146.9, 137.2, 132.0, 130.2, 39.8, 32.1, 24.0, 23.5, 22.5, 13.9, 12.3, 11.9 ppm. ATR-FTIR ν 3163, 2956, 2929, 1570, 1546, 1513, 1442, 1419, 1307, 1177, 1041, 924cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{22}H_{35}N_2$ 327.2795 found 327.2787.

(2*E*)-2-[2-(Acetyloxy)-1-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)ethylidene]-4-ethyl-3,5-dimethyl-2*H*-pyrrolium trifluoromethanesulfonate (6e) and (2*E*)-4-ethyl-2-(1-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)-2-hydroxyethylidene)-3,5-dimethyl-2*H*-pyrrolium trifluoromethanesulfonate (7). Prepared according to Method B. 22.5 mg, mixture of **6e** (44%) and **7** (55%). ^{1}H NMR (mixture, $CDCl_3$, 300 MHz) δ 11.03 (br s, 2H), 10.97 (br s, 2.4), 5.38 (s, 2H), 4.98 (s, 2.4H), 2.47 (s, 6H), 2.49-2.39 (m, 8.8H), 2.37 (s, 7.2H), 2.07 (s, 3H), 2.04 (s, 6H), 2.02 (s, 7.2H), 1.10 (t, *J* = 7.5 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 7.2H) ppm. ^{13}C NMR (mixture, $CDCl_3$, 75 MHz) δ 170.0, 151.6, 150.0, 145.8, 139.1, 138.8, 133.8, 132.9, 130.5, 130.1, 120.2 (q, *J* = 319.0 Hz), 62.5, 61.6, 20.7, 17.6, 17.5, 14.3, 14.2, 12.6, 12.2, 11.7, 11.6 ppm. ^{19}F NMR ($CDCl_3$, 282 MHz) δ -78.69 (s, 3F) ppm.

(2*E*)-2-[Cyano(3,4,5-trimethyl-1*H*-pyrrol-2-yl)methylene]-3,4,5-trimethyl-2*H*-pyrrolium trifluoromethanesulfonate (6f). Prepared according to Method B. Bright purple solid. 19.8 mg (98%). M.p.: 177-179 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.10 (br s, 2H), 2.59 (s, 6H), 2.49 (s, 6H), 2.04 (s, 6H) ppm.^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.0, 142.1, 129.2, 129.0, 120.1 (q, *J* = 319.4 Hz), 114.5, 105.2, 13.4, 12.8, 9.2 ppm. ^{19}F NMR ($CDCl_3$, 282 MHz) δ -78.67 (s, 3F) ppm. ATR-FTIR ν 3210, 2925, 2197, 1613, 1565, 1287, 1242, 1157, 1029, 940 cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{16}H_{28}N_3$ 254.1650 found 254.1642.

(2*Z*)-2-[(Mesityl)(1*H*-pyrrol-2-yl)methylene]-2*H*-pyrrolium trifluoromethanesulfonate (6g). The title compound was prepared according to Method B. Bright green solid. 20.2 mg (98%). M.p.: 174-176 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.22 (br s, 2H), 8.08 (s, 2H), 6.98 (s, 2H), 6.77 (m, 2H), 6.61 (m, 2H), 2.38 (s, 3H), 2.03 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.9, 144.7, 139.9, 136.7, 135.5, 132.4, 131.6, 128.4, 118.1, 21.1, 19.7 ppm. ^{19}F NMR ($CDCl_3$, 282 MHz) δ -78.47 (s, 3F) ppm. ATR-FTIR ν 3194, 2927, 1565, 1449, 1331, 1284, 1250, 1038 cm^{-1}. HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{18}H_{19}N_2$ 263.1543 found 263.1533.

Acknowledgements

Financial support from the MINECO (grant MAT2014-51937-C3-2-P) and UCM (grants GR3/14-910107 and -910150) is gratefully acknowledged.

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