Helical chirality of pyrrolo[1,2-a][4,5]diazafluoren-5-one derivatives

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Abstract

The treatment of the *N*-phenacyl-4,5-diazafluorenium-9-one bromides **4a,b** and the diesters of acetylenedicarboxylic acid with Et_3N in methylene chloride at room temperature gave *trans*-9,10-dihydro-pyrrolo[1,2-a][4,5]diazafluoren-5-one derivatives **7** along with the corresponding aromatized compounds **8**. The non-planarity of the diethyl (**8c,e**) and diisopropyl (**8d,f**) pyrrolodiazafluorenone esters was deduced by H-NMR spectroscopy. The 1,3-dipolar cycloaddition between diazafluorenonium *N*-ylides, generated from **4**, and an activated olefinic dipolarophile (acrylonitrile) is reported for the first time. The optical properties of pyrrolodiazafluorenone **8** were also investigated.

Keywords: 1,3-Dipolar cycloaddition, *N*-ylides, pyrrolo[1,2-a][4,5]diazafluoren-5-ones, helical chirality

Introduction

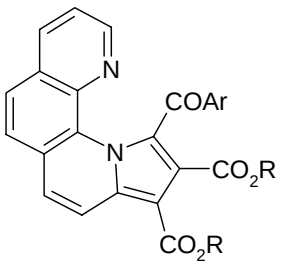
Diazahelicenes are of interest owing to their properties and practical applications in photo- and optoelectronics as well as their ability to act as proton sponges, with the degree of helicity correlated with the base strength.[1,2] Since the discovery of "classical" helicenes, the concept of helical chirality or helicity has been extended to non-fully aromatized systems. Therefore, helicity can be induced by intramolecular sterical strain. This in turn may be caused by five or more ortho condensed rings or by overcrowding the bay region with bulky substituents.[3-14] The latter class of azahelicenes has received considerable attention lately, due to the possibility of producing three- or four-membered helicenes.[15-19]

The helical chirality of pyrrolophenanthroline derivatives **1** was deduced from NMR experiments performed in solution on ethyl and isopropyl esters containing diastereotopic protons as probe groups. The activation free energy for ring flipping at coalescence temperature

was found to be approximately 16 kcal mol^{-1} at T_c = 60 ºC in both diethylesters and diisopropyl esters. The helical structure of tetracyclic derivatives **1**[18,19] was confirmed by X-ray studies and contrasts with the planarity of condensed heterocyclic compound **2**.[2]

Recently, the pyrrolo[1,2-a][4,5]diazafluoren-5-one derivatives **3** were synthesized by 1,3-dipolar cycloaddition reaction between 4,5-diazofluorenonium-9-one ylides and dimethyl acetylenedicarboxylate (DMAD).[20]

In order to check the helicity of this heterocyclic system by H-NMR spectroscopy, the new compounds **8c-f** containing as enantiotopic groups ethyl and isopropyl were prepared. Also, the 1,3-dipolar cycloaddition between diazafluorenonium N-ylides, generated from **4**, and an activated olefinic dipolarophile (acrylonitrile) is reported for the first time. The optical properties of pyrrolodiazafluorenone **8** were also investigated.



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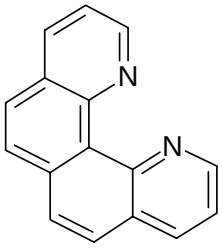

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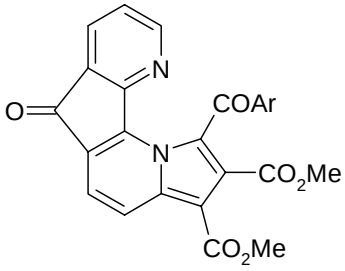

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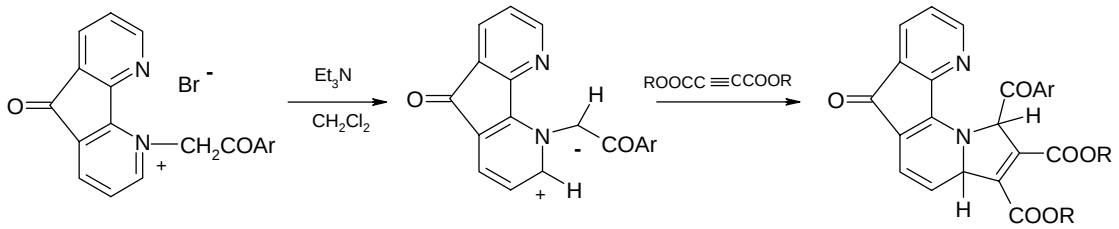
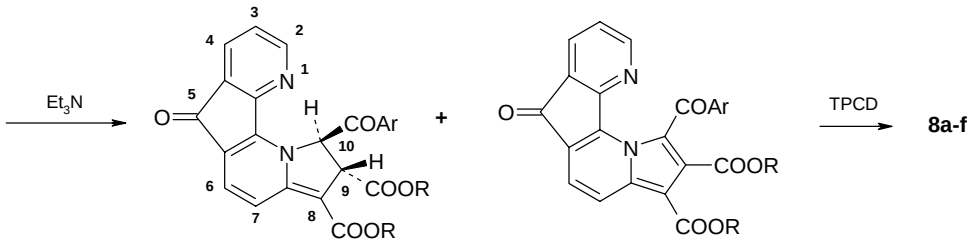
Results and Discussion

The synthesis of pyrrolo[1,2-*a*][4,5]diazafluoren-5-one **8** (Scheme 1) used as key intermediates the cycloimmonium bromides **4a,b** which were prepared by reaction between 4,5-diazafluoren-9-one and corresponding phenacyl bromides similarly to previous literature procedure.[20] The heteroaromatic N-ylides **5** were generated *in situ*, by action of triethylamine on bromides **4**. 1,3-Dipolar cycloaddition reaction of N-ylides **5** with dimethyl, diethyl or diisopropyl acetylenedicarboxylate in dichloromethane at room temperature gave a mixture consisting of dihydroderivatives **7** along with variable amounts of aromatized pyrrolodiazafluoren-5-ones **8**. In order to establish the structure of the dihydroderivatives, compound **7a** was isolated and characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The positions for the two protons of the pyrrolinic moiety came from their multiplicity, two doublets with J = 3.4 Hz, as well as the high chemical shifts of 6.88 ppm which were attributed to H-10. The low value of the vicinal coupling constant between H-9 and H-10 indicates a *trans* configuration. In the aromatic region of compound **7a**, the diazafluoren-9-one moiety appears as an ABC system due to the protons H-2, H-3 and H-4 of the pyridine ring and an AB doublet due to the protons of the pyridine ring condensed with the pyrrole ring.

The position of the double bond in the pyrroline moiety could be deduced from the chemical shifts of the three carbonyl groups. Thus, the large difference between the two carbonyl ester group shifts (δ = 164.7 ppm and 174.0 ppm) shows that they are attached to a Csp^2 (δ = 164.7 ppm) and a Csp^3 (δ = 174.0 ppm), respectively. The deshielding of the carbonyl group of the 4-bromobenzoyl moiety (δ = 184.4 ppm) by 6 ppm relative to those of the corresponding aromatic compounds **8a** is good evidence that the group is attached to a Csp^3.



4a,b **5a,b** **6a-f**



7a-f **8a-f**

a,b: R = Me; **c,d**: R = Et; **e,f**: R = *i*Pr; **a,c,e**: Ar = 4-BrC_6H_4; **b,d,f**: Ar = 4-$O_2NC_6H_4$

Scheme 1

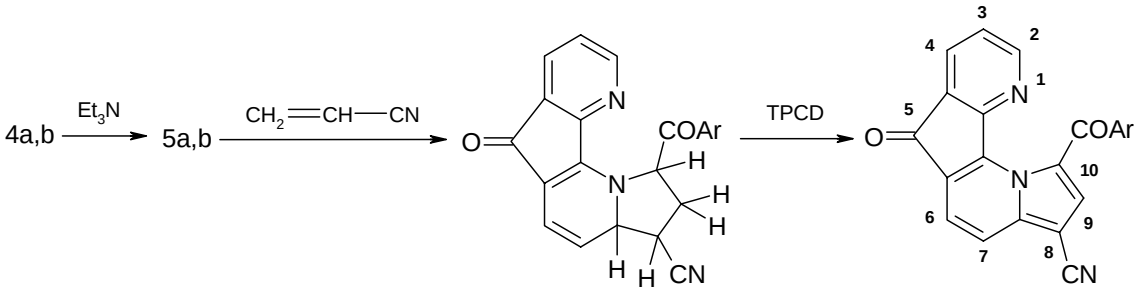
The formation of dihydroderivatives **7** may be explained by the regio- and stereoselective prototropic rearrangement of the primary cycloadducts **6** in the presence of an excess of triethylamine. The aromatization of the dihydroderivative to pyrrolodiazafluoren-5-ones **8** was performed by the action of tetrakis-pyridino Co(II) dichromate (TPCD). This reagent was used for aromatization of cycloadducts obtained by reaction between heteroaromatic N-ylides and activated olefines.[21-24] The pyrrolodiazafluoren-5-one derivatives **8** were also obtained from bromides **4**, esters of acetylenedicarboxylic acid, triethylamine and TPCD, in DMF at 90 °C, as well as by the procedure described in literature for compounds **3**.[20]

As previously reported,[15,16] in the ^{1}H-NMR spectra of diethyl esters of pyrrolophenanthroline **1** (R=Et), recorded in $CDCl_3$ at room temperature, the methylenic protons in both ester groups appear as two distinct ABX_3 patterns. Under the same conditions, in the ^{1}H-NMR spectra of pyrrolodiazafluoren-5-ones **8c,d** the methylenic protons of the ester group in the 8 position appear as a quartet, whereas the methylenic protons of the other ester group show as a broad singlet. A similar observation was made for the isopropyl esters. Thus, in the series of isopropyl

esters **1** the methyl groups in each isopropyl group were found to be non-equivalent in ^{1}H-NMR spectra, each appearing as a doublet with the integral curve corresponding to three protons. In the case of pyrrolodiazafluoren-5-ones **8e,f**, the methyl groups from the isopropyl moieties appear as a doublet with the integral curve corresponding to six protons and as a broad doublet, also with an integral curve of six protons.

From these ^{1}H-NMR data one can conclude that compounds **8c-f** possess a certain amount of helical distortion in solution, caused by intramolecular strain. Furthermore, this helical distortion is smaller than that present in pyrrolophenanthrolines **1**, as the enantiotopic groups are near coalescence temperature. This assumption is supported by previously reported X-ray data.[18,19,30] The 1,3-dipolar cycloaddition reactions between heteroaromatic N-ylides and non-symmetrical olefines gave rise to interesting problems of regio- and stereochemistry.[16,25-29]

In order to study the regioselectivity of the 1,3-dipolar cycloaddition, the corresponding ylides **5a,b** were treated with acrylonitrile as a non-symmetrical dipolarophile, affording tetrahydro derivatives **9a,b**. However, as these were too unstable to characterize, by the action of TPCD in DMF at 90 ºC, the crude products **9a,b** were aromatized to the pyrrolodiazafluorenones **10a,b** (Scheme 2). The overall synthesis of compounds **10a,b** was therefore performed as a "one pot" reaction between the bromides **4a,b**, acrylonitrile and Et_3N in DMF, followed by heating and the addition of TPCD.



Scheme 2

The NMR data for compounds **8** and **10** are in good agreement with the assigned structures. In ^{1}H-NMR spectra of compounds **8b-f**, recorded in $CDCl_3$, the signal of H-7 (δ~8.50 ppm) is deshielded in comparison with the protons of the diazafluorenone moiety due to the presence of the carboalkoxy group in position 8 of the pyrrole ring. The deshielding effect of the cyano group (compounds **10a,b**) on H-7 is smaller by comparison (δ = 7.92 ppm). Also, the proton H-2 is deshielded due to the fact that it is linked to a C=N double bond.

Due to the low solubility of compound **10b**, the H-NMR spectrum was recorded in a $CDCl_3$+TFA mixture. We found the coupling constant between H-2 and H-3 in $CDCl_3$ to be 5.2 Hz (compounds **8** and **10a**), whereas in the $CDCl_3$+TFA mixture the respective constant was found to be 5.8 Hz. The same coupling constant was observed when ^{1}H-NMR spectra of pyrrolodiazafluorenones were recorded in $CDCl_3$+TFA. The difference in the values of the

coupling constant between H-2 and H-3 may be explained by the protonation at the nitrogen N1 by TFA.

Electronic absorption spectra of pyrrolo[1,2-*a*][4,5]diazafluoren-5-ones

Pyrroloazines are known to possess high fluorescence and luminescence, making them useful in NLO, as organic luminophores and optoelectronic devices.[31-39] In order to explain the effects of the molecular structure and solvent-solute interactions on absorption spectroscopic properties, the compounds were investigated in different solvents.

Representative solvents have been selected for this investigation. A comparison of the effect of substitution on the photochemical properties of compounds **8e** and **8f** in different solvents is presented.

The UV-VIS absorption spectra of the compounds in the spectral range 240-600 nm exhibit two electronic bands (Figures 1 and 2).

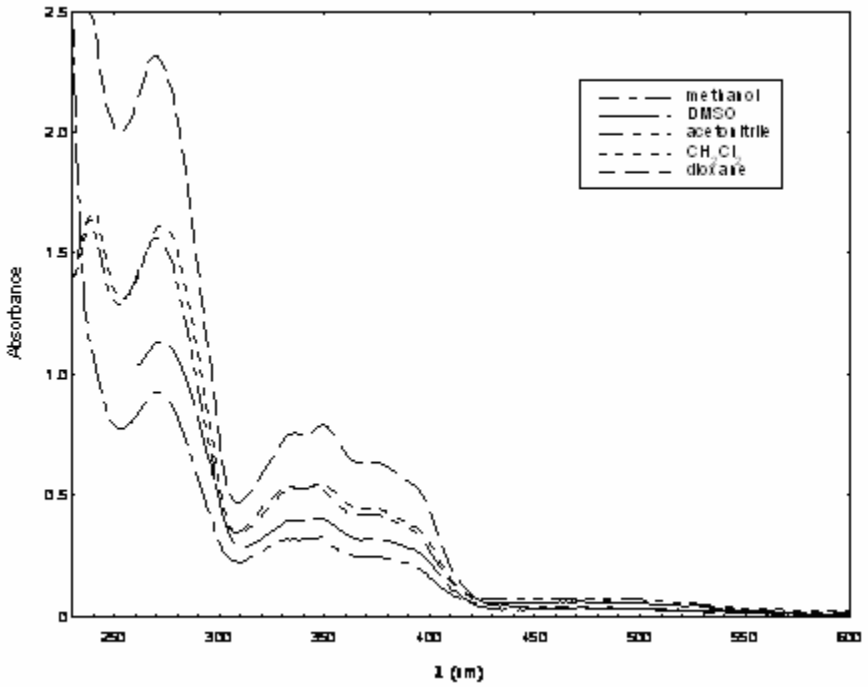


Figure 1. The absorption spectra of the compound **8e** ($c=5x10^{-5}$ M) in different solvents.

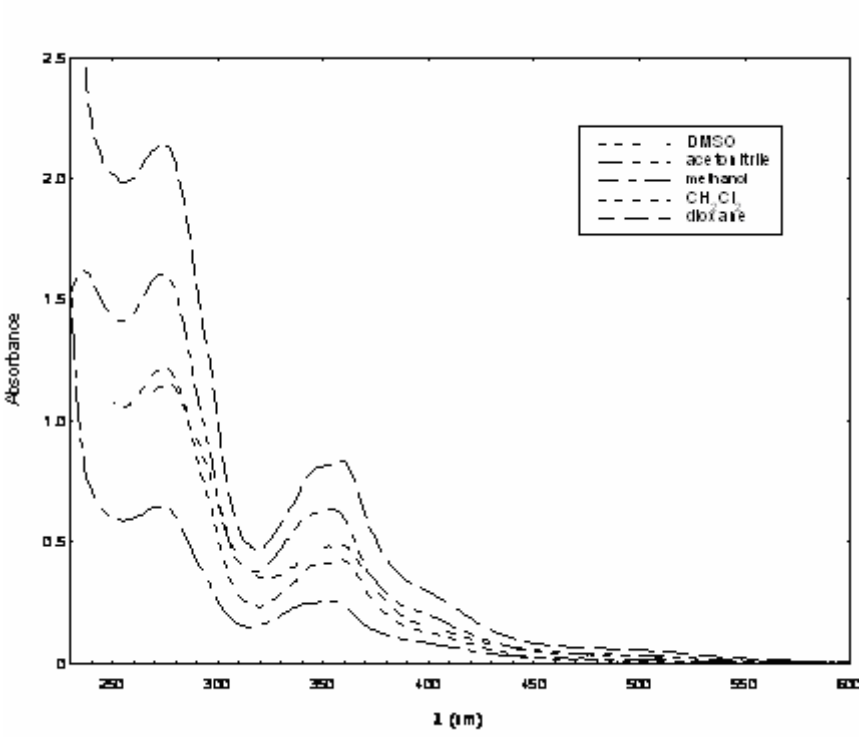


Figure 2. The absorption spectra of the compound **8f** ($c=5x10^{-5}$ M) in different solvents.

Tables 1 and 2 show the absorption band maxima wavelengths in the 240-650 nm range and the corresponding absorbances for **8e** in methanol, acetonitrile, dimethylsulfoxide (DMSO), dioxane and dichloromethane (CH_2Cl_2).

Table 1. Wavelengths, λ_{max}, and molar extinction coefficients, lgε , for the main absorption bands of **8e** in various solvents

Solvent	λ_{max} [lgε], (nm) (L mol^{-1} cm^{-1})				
dioxane		269.5 [4.667]	335.2 (sh)	349.6 [4.201]	374.6 [4.106]
CH_2Cl_2	240.1 [4.525]	272.9 [4.504]	335.2 [4.022]	348.4 [4.041]	372.7 (sh)
methanol		270.5 [4.267]	333.2 (sh)	345.3 [3.813]	373.4 (sh)
acetonitrile	238.7 [4.514]	270.5 [4.496]	332.4 [4.029]	345.7 [4.024]	371.5 [3.929]
DMSO		272.4 [4.356]	335.2 (sh)	348.0 [3.908]	374.2 (sh)

Table 2. Wavelengths, λ_{max}, and molar extinction coefficients, lgε , for the main absorption bands of **8f** in various solvents

Solvent	λ_{max} [lgε], (nm) (L mol^{-1} cm^{-1})		
dioxane	273.8 [4.633]	348.6 (sh)	357.8[4.224]
CH_2Cl_2	273.8 [4.388]	346.1 (sh)	358.8 [2.930]
methanol	272.9 [4.118]	343.4 (sh)	352.5 [3.713]
acetonitrile 236.3 [4.517]	274.3 [4.508]	342.9 (sh)	354.9 [4.103]
DMSO	276.7 [4.363]		358.6 [3.989]

The positions of the absorption bands and the values of the molar extinction coefficient values evidence the influence of the substituent and the nature of the solvent. By substitution of the 4-bromobenzoyl group (in **8e**) with the 4-nitrobenzoyl group (in **8f**) a bathochromic shift of the spectra is observed. The position of the substituent is reflected by the shape modification of absorption spectra of the compounds **8e** and **8f**.

In comparison with other pyrroloazines, the pyrrolodiazafluorenones **8** and **10** did not present fluorescence either in solution or in the solid state.

Conclusions

Six new pyrrolodiazafluorenones were synthesized by the "one pot" reaction between diazafluorenonium salts, dipolarophiles, Et_3N and TPCD as oxidant in DMF. The regioselectivity of the reaction was evidenced by the novel use of acrylonitrile as dipolarophile. All the compounds were characterized by NMR spectroscopy, complemented by IR spectroscopy in the case of the novel cyano-bearing compounds.

The non-planarity of these diazafluorenones substituted at the 10 position by a phenacyl group was put in evidence by NMR spectroscopy.

The optical properties of some representative compounds were also investigated.

Experimental Section

General Procedures. Melting points were determined on a Boëtius hot plate and are uncorrected. The NMR spectra were recorded on a Varian Gemini 300 BB instrument, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Supplementary evidence was given by HETCOR and COSY experiments.

Preparation of solutions. Solvents (spectroscopic grade) from Merck have been used without further purification. Because of the high solubility of the compounds in CH_2Cl_2, a fresh stock

CH_2Cl_2 solution (ca. 1mM) was prepared for each derivative. Appropriate amounts of stock solutions were transferred into a volumetric flask and the solvent evaporated under a stream of nitrogen; the different solvents were then added. The concentrations of the solutions were in the 10^{-5} M – 5×10^{-5} M range. The UV-VIS absorption and fluorescence measurements have been performed both in protic solvent, methanol and in a series of aprotic solvents including dioxane, acetonitrile, DMSO, and CH_2Cl_2.

Methods. Absorption spectra were recorded with a Shimadzu UV-VIS 2501 PC spectrophotometer, at 23 °C, with a 0.2 nm increment.

General procedure for synthesis of compounds 8

Method A. 2Mmol 4,5-diazafluorenium-9-one bromide **4** were suspended in dichloro- methane (20 mL) and dimethyl (diethyl or diisopropyl) acetylenedicarboxylate (2.2 mmol) were then added. Under vigorous stirring, triethylamine (0.35 mL, 2.5 mmol, dissolved in 3 mL of methylene chloride) was added dropwise. After 20 min the reaction mixture was washed with water and the solvent evaporated. The residue consisting of a mixture of dihydroderivative **7** and aromatized **8** was dissolved in DMF (15 mL) and was stirred with TPCD (3 mmol) at 80-90 ºC for 4 h. It was then cooled to room temperature and a 5% aqueous HCl solution (40 mL) was added. The precipitate was filtered and purified by recrystallization from nitromethane or by column chromatography on neutral Al_2O_3 (Aluminium oxide 70-230 mesh) using methylene chloride or chloroform as eluents.

Method B. A solution of salt **4** (2.5 mmol), alkyne (3 mmol), triethylamine (3 mmol) and TPCD (3 mmol) in DMF (20 mL) was stirred at 80-90 ºC for 6 h. It was then cooled to room temperature and a 5% aqueous HCl solution (40 mL) was added. The precipitate was filtered and purified as above.

***trans*-Dimethyl 10-(4-bromobenzoyl)-9,10-dihydro-pyrrolo[1,2-*a*][4,5]diaza-fluoren-5-one-8,9-dicarboxylate** (**7a**). The compound was isolated as black-green crystals by column chromatography on neutral Al_2O_3 using CH_2Cl_2 as eluent from the residue obtained by method A. The purity was ascertained by H-NMR spectroscopy and was found to be ca. 92 %. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.71, 3.83 (6H, 2s, 2MeO); 4.15 (1H, d, *J* = 3.4 Hz, H-9); 6.88 (1H, d, *J* = 3.4 Hz, H-10); 7.12 (1H, dd, *J* = 7.4, 5.3 Hz, H-3); 7.32, 7.36 (2H, 2d, *J* = 9.6 Hz, H-6, H-7); 7.72 (2H, d, *J* = 8.8 Hz, H-3', H-5'); 7.75 (1H, dd, *J* = 7.4, 1.5 Hz, H-4); 7.98 (1H, d, *J* = 8.8 Hz, H-2', H-6'); 8.18 (1H, dd, *J* = 5.3, 1.5, H-2). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 50.1 (C-9); 50.9, 53.2 (2MeO); 68.7 (C-10); 92.6 (C-8); 114.3, 128.2, 129.8, 131.3 (C-4a, C-5a, C-4'); 116.5 (C-3); 125.0, 129.5 (C-6, C-7); 130.6 (C-2', C-6'); 132.4 (C-3', C-5'); 139.8 (C-1'); 151.1 (C-2); 152.3; 156.0; 156.0 (C-7a, C-11a, C-11b); 165.0 (8-COO); 172.3 (9-COO); 184.4 (5-CO); 190.4 (COAr).

Diethyl 10-(4-bromobenzoyl)-pyrrolo[1,2-*a*][4,5]diazafluoren-5-one-8,9-dicarboxylate (8c). The product was recrystallized from nitromethane and red crystals with mp 257-9 °C were obtained; yield 81%. Anal. Calcd. $C_{27}H_{19}BrN_2O_6$: C 59.25; H 3.50; Br 14.60; N 5.12. Found: C

59.50; H 4.88; Br 15.02; N 5.27. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.03 (t, 3H, *J* = 7.1 Hz, 9-Me); 1.38 (t, 3H, *J* = 7.1 Hz, 8-Me); 3.90 (bs, 2H, 9-OCH_2); 4.39 (q, 2H, *J* = 7.1 Hz, 8-OCH_2); 7.12 (dd, 1H, *J* = 7.4, 5.2 Hz, H-3); 7.65 (d, 2H, *J* = 8.6 Hz, H-3', H-5'); 7.67 (d, 1H, *J* = 9.1 Hz, H-6); 7.82 (dd, 1H, *J* = 7.4, 1.5 Hz, H-4); 7.86 (d, 2H, *J* = 8.6 Hz, H-2', H-6'); 8.17 (d, 1H, *J* = 5.2, 1.5 Hz, H-2); 8.50 (d, 1H, *J* = 9.1 Hz, H-7). ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 1.06 (t, 3H, *J* = 7.1 Hz, 9-Me); 1.30 (t, 3H, *J* = 7.1 Hz, 8-Me); 3.96 (q, 2H, *J* = 7.1 Hz, 9-OCH_2); 4.32 (q, 2H, *J* = 7.1 Hz, 8-OCH_2); 7.28 (dd, 1H, *J* = 7.4, 5.2 Hz, H-3); 7.71 (s, 4H, H-2', H-3', H-5', H-6'); 7.80 (d, 1H, *J* = 9.1 Hz, H-6); 7.95 (dd, 1H, *J* = 7.4, 1.5 Hz, H-4); 8.21 (d, 1H, *J* = 5.2, 1.5 Hz, H-2); 8.42 (d, 1H, *J* = 9.1 Hz, H-7). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.6 (9-Me); 14.2 (8-Me); 60.9 (9-CH_2O); 62.0 (8-CH_2O); 106.1 (C-8); 119.2 (C-6); 121.5 (C-7); 123.6 (C-3); 123.8, 124.0, 124.9, 128.1, 130.9 (C-4, C-4a, C-5a, C-9, C-10, C-4'); 130.2 (C-4); 131.1 (C-2', C-6'); 131.6 (C-3', C-5'); 136.6 (C-1'); 139.8 (C-7a); 145.6 (C-11a); 151.4 (C-2); 158.8 (C-11b); 162.5 (8-COO); 164.1 (9-COO); 184.4 (COAr); 187.6 (5-CO).

Diethyl 10-(4-nitrobenzoyl)-pyrrolo[1,2-*a*][4,5]diazafluoren-5-one-8,9-dicarboxylate (**8d**). The product was recrystallized from nitromethane and red crystals with mp 257-9 °C were obtained; yield 63%. Anal. Calcd. $C_{27}H_{19}N_3O_8$: C 63.16; H 3.73; N 8.18. Found: C 63.55; H 4.04; N 8.37. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.11 (t, 3H, *J* = 7.1 Hz, 9-Me); 1.38 (t, 3H, *J* = 7.1 Hz, 8-Me); 3.93 (bs, 2H, 9-OCH_2); 4.40 (q, 2H, *J* = 7.1 Hz, 8-OCH_2); 7.13 (dd, 1H, *J* = 7.4, 5.2 Hz, H-3); 7.71 (d, 1H, *J* = 9.1 Hz, H-6); 7.83 (dd, 1H, 7 *J* =.4, 1.5 Hz, H-4); 8.13-8.16 (m, 3H, H-2, H-2', H-6'); 8.26 (d, 2H, *J* = 8.9 Hz, H-3', H-5'); 8.53 (d, 1H, *J* = 9.1 Hz, H-7). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.7 (9-CH_3); 14.2 (8-CH_3); 60.9 (9-OCH_2); 62.0 (8-OCH_2); 106.2 (C-8); 119.6 (C-6); 121.6 (C-7); 123.5 (C-3', C-5'); 123.8 (C-3); 124.1; 124.3, 128.1; 131.5 (C-4a, C-5a, C-9, C-10); 130.5 (C-2', C-6', C-4); 140.2 (C-7a); 142.6 (C-1'); 145.5 (C-11a); 150.2 (C-4'); 151.3 (C-2); 158.5 (C-11b); 162.4 (8-COO); 164.1 (9-COO); 183.4 (COAr); 187.6 (5-CO).

Diisopropyl 10-(4-bromobenzoyl)-pyrrolo[1,2-*a*][4,5]diazafluoren-5-one-8,9-dicarboxylate(**8e**) The product was recrystallized from nitromethane and red crystals with mp 269-271 °C were obtained; yield 63%. Anal. Calcd. $C_{29}H_{23}BrN_2O_6$: C 60.53; H 4.03; Br 13.89; N 4.87. Found: C 60.77; H 4.29; Br 14.07; N 5.06. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.03 (bd, 6H, *J* = 6.2 Hz, 9-**Me$_2$**CH); 1.38 (d, 6H, *J* = 6.3 Hz, 8-**Me$_2$**CH); 4.85 (sep, 1H, *J* = 6.2 Hz, 9-OCH); 5.29 (sep, 1H, *J* = 6.3 Hz, 8-OCH); 7.09 (dd, 1H, *J* = 7.4, 5.2 Hz, H-3); 7.64 (d, 2H, 8.6, H-3', H-5'); 7.66 (d, 1H, *J* = 9.1 Hz, H-6); 7.79 (dd, 1H, *J* = 7.4, 1.5 Hz, H-4); 7.88 (d, 1H, 8.6, H-2', H-6'); 8.13 (dd, 1H, *J* = 5.2, 1.5 Hz, H-2); 8.49 (d, 1H, *J* = 9.1 Hz, H-7). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 21.03, 21.97 (9-Me_2); 22.0 (8-Me_2); 68.4 (9-OCH); 72.2 (8-OCH); 106.1 (C-8); 118.9 (C-6); 121.5 (C-7); 123.5 (C-3); 123.8 (C-4'); 124.5, 128.1, 128.2, 131.0 (C-4a, C-5a, C-9, C-10); 130.2 (C-4); 131.1 (C-2', C-6'); 131.6 (C-3', C-5'); 136.6 (C-1'); 139.8 (C-7a); 145.5 (C-11a); 151.7 (C-2); 158.7 (C-11b); 162.1 (8-COO); 163.9 (9-COO); 184.4 (COAr); 187.9 (5-CO).

Diisopropyl 10-(4-nitrobenzoyl)-pyrrolo[1,2-*a*][4,5]diazafluoren-5-one-8,9-dicarboxylate (**8f**). The product was recrystallized from nitromethane and red crystals with mp 265-7 °C were obtained; yield 58 %. Anal. Calcd. $C_{29}H_{23}N_3O_8$: C 64.32; H 4.28; N 7.76. Found: C 64.60; H 4.55; N 8.07. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.98 (bd, 6H, *J* = 6.3 Hz, 9-Me_2CH); 1.32 (d, 6H,

J =6.3 Hz, 8-Me_2CH); 4.78 (sep, 1H, *J* =6.3 Hz, 9-OCH); 5.24 (sep, 1H, *J* = 6.3 Hz, 8-OCH); 7.05 (dd, 1H, 7 *J* =.4, 5.2 Hz, H-3); 7.63 (d, 1H, *J* = 9.1 Hz, H-6); 7.75 (dd, 1H, *J* = 7.4, 1.5 Hz, H-4); 8.04 (dd, 1H, *J* = 5.2, 1.5 Hz, H-2); 8.09 (d, 2H, *J* = 9.0 Hz, H-2', H-6'); 8.26 (d, 2H, *J* = 9.0 Hz, H-3', H-5'); 8.45 (d, 1H, *J* = 9.1 Hz, H-7). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 21.2, 21.3 (9-Me_2); 22.0 (8-Me_2); 60.7 (9-OCH); 70.3 (8-OCH); 106.6 (C-8); 119.2 (C-6); 121.8 (C-7); 123.5 (C-3', C-5'); 123.8 (C-3); 124.1, 124.8; 128.2, 131.5 (C-4a, C-5a, C-9, C-10); 130.4 (C-4); 130.6 (C-2', C-6'); 139.9 (C-7a); 142.7 (C-1'); 145.3 (C-11a); 150.3 (C-4'); 151.1 (C-2); 158.5 (C-11b); 161.9 (8-COO); 163.6 (9-COO); 183.4 (COAr); 187.5 (5-CO).

8-Cyano-10-(4-bromobenzoyl)-pyrrolo[1,2-*a*][4,5]diazafluoren-5-one (10a). The product was recrystallized from nitromethane and red crystals with mp 239-241 °C were obtained; yield 38 %. Anal. Calcd. $C_{22}H_{10}BrN_3O_2$: C 61.70; H 2.35; Br 18.66; N 9.81. Found: C 61.98; H 2.71; Br 19.02; N 10.05. IR (ATR, cm^{-1}): 1725, 2222 (CN), 3059, 3092. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.20 (1H, dd, *J* = 7.4, 5.2 Hz; H-3); 7.58 (1H, s, H-9); 7.74 (2H, d, *J* = 8.6 Hz, H-3', H-5'); 7.75 (1H, d, *J* = 8.9 Hz, H-6); 7.88 (1H, dd, *J* = 7.4, 1.6 Hz; H-4); 7.92 (1H, d, *J* = 8.9 Hz, H-7); 7.98 (2H, d, *J* = 8.6 Hz, H-2', H-6'); 8.35 (1H, dd, *J* = 5.2, 1.6 Hz; H-2). ^{1}H-NMR ($CDCl_3$+TFA, 300 MHz) δ: 7.75, 7.84 (4H, 2d, *J* = 8.7 Hz, H-2', H-3', H-5', H-6'); 7.90 (1H, dd, *J* = 7.5, 6.0 Hz, H-3); 8.07 (1H, s, H-9); 8.09 (1H, d, *J* = 8.7 Hz, H-6); 8.32 (1H, d, *J* = 8.7 Hz, H-7); 8.58 (1H, dd, *J* = 7.5, 1.4 Hz; H-4); 8.76 (1H, dd, *J* = 6.0, 1.4 Hz; H-2). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 87.1 (C-8); 114.3 (CN); 118.8, 119.6, 123.8, 127.7, 130.4 (C-3, C-4, C-6, C-7, C-9); 131.3, 132.1 (C-2', C-3', C-5', C-6'); 135.3 (C-1'); 143.5, 146.6, 158.9 (C-7a, C-11b, C-11b); 152.1 (C-2); 182.4 (COAr); 187.6 (5-CO). ^{13}C-NMR ($CDCl_3$+TFA, 75 MHz) δ: 90.6 (C-8); 112.1 (CN); 121.7, 123.5, 126.9, 134.3, 137.3 (C-3, C-4, C-6, C-7, C-9); 128.4, 128.7, 129.7, 130.3, 133.8 (C-4a, C-5a, C-10, C-1', C-4'); 131.1, 132.7 (C-2', C-3', C-5', C-6'); 141.4, 145.7, 154.5 (C-7a, C-11b, C-11b); 144.6 (C-2); 183.5, 183.9 (5-CO, COAr).

8-Cyano-10-(4-nitrobenzoyl)-pyrrolo[1,2-*a*][4,5]diazafluoren-5-one (10b). The product was recrystallized from chloroform and red crystals with mp 266-8 °C were obtained; yield 36 %. Anal. Calcd. $C_{22}H_{10}N_4O_4$: C 67.01; H 2.56; N 14.21. Found: C 67.33; H 2.81; N 14.37. IR (ATR, cm^{-1}): 1714, 2221 (CN), 2952, 3052. ^{1}H-NMR ($CDCl_3$+TFA, 300 MHz) δ: 7.78 (1H, dd, *J* = 7.5, 5.8 Hz; H-3); 7.99 (1H, s, H-9); 8.08 (1H, d, *J* = 8.7 Hz, H-6); 8.21 (2H, d, *J* = 8,9 Hz, H-3', H-5'); 8.28 (1H, d, *J* = 8.7 Hz, H-7); 8.44-8.48 (3H, m, H-4, H-2', H-6'); 8.75 (1H, dd, *J* = 5.8, 1.4 Hz; H-2). ^{13}C-NMR ($CDCl_3$+TFA, 75 MHz) δ: 90.6 (C-8) 113.0 (CN); 122.3, 123.6, 127.1, 134.3, 137.5 (C-3, C-4, C-6, C-7, C-9); 124.2, 130.7 (C-2', C-3', C-5', C-6'); 128.6, 128.7, 129.7, (C-4a, C-5a, C-10); 140.5 (C-1'); 141.4, 146.0, 154.4 (C-7a, C-11b, C-11b); 144.6 (C-2); 150.7 (C-4'); 182.3, 183.3 (5-CO, COAr).

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