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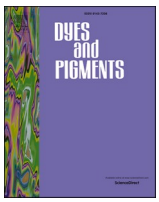

Core-fluorinated dipyrromethanes and BODIPYs. Synthesis and study of photophysical properties

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ABSTRACT

An efficient synthetic protocol for the preparation of novel 1,7-difluorinated BODIPYs was elaborated. A set of novel dipyrromethanes, which are key intermediates for the target dyes, was prepared by acid-catalyzed condensation of ethyl 3-aryl-4-fluoro-1*H*-pyrrole-2-carboxylates with aldehydes in up to quantitative yield. Subsequent oxidation and boron difluoride complexation under microwave irradiation afforded a family of novel core-fluorinated BODIPYs in up to 92 % yield. Their photophysical properties were studied by UV–visible and fluorescence spectroscopy. In addition, DFT calculations were performed to estimate 2,6-substituents effect. This revealed that the values of the absorption and emission maxima perfectly correlated with the energy gap between the frontier orbitals.

1. Introduction

Dipyrromethanes [1] are convenient substrates for the synthesis of porphyrins [2,3], π-extended porphyrins[4], calixpyrroles[5], chlorins [6], corroles [7], and other porphyrinoids. Another important area of application of dipyrromethanes is the creation of various dipyrrines and their complexes [8], including borondipyrromethenes, better known as BODIPYs.

Over the past five decades BODIPYs have gained immense popularity in the scientific community [9]. BODIPYs have found wide application in different areas due to the capability to tune their chemical and photophysical properties by introducing various substituents into the structure [10]. Indeed, BODIPYs have been employed as fluorescent sensors [11], fluorescent markers for bioimaging [12], in materials for drug delivery [13], optoelectronic devices [14], electrochemiluminescence [15], as triplet photosensitizers for solar energy conversion, photoredox catalysis and photodynamic therapy [16] and many others.

On the other hand, fluorination of organic molecules can lead to improved stability of compounds due to the replacement of potentially oxidizable C–H bonds with stronger C–F bonds [17]. It is also known that the incorporation of fluorine or fluorine-containing groups into fluorophores can positively affect the quality and efficiency of many applications of these compounds [18]. For example, fluorination of fluorescein has led to the so-called Oregon green dyes, which have exhibited increased photostability [19]. An enhanced resistance to photobleaching has been observed for fluorinated derivatives of Rhodamine dyes [20]. Even non-selective electrophilic fluorination of classical laser dyes has improved power output and significantly enhanced their photostability [21].

In this context, the preparation of BODIPY derivatives containing C–F bonds is of great importance. Numerous research works have been devoted to the preparation of such structures. The most common examples of BODIPYs have fluorine or fluorine-containing group in various substituents attached to the BODIPY core [22]. The preparation of diverse structural types of BODIPYs contained CF_3-group at *meso*--position has been also described [23]. Moreover, nucleophilic mono- and di-trifluoromethylation at 2 and 6-positions [24] and electrophilic 3-trifluoromethylation of BODIPYs [25] have been recently reported.

However, the preparation of BODIPYs with fluorine atoms directly bonded to the dipyrromethene core is not a trivial task. Indeed, to our best knowledge only three examples of core-fluorinated BODIPY are currently known [24]. Their preparation is based on the late-stage fluorination of BODIPYs with the Selectfluor™ and allows the incorporation of only one fluorine atom in very low yield (Scheme 1a). Nevertheless, considerable increase in photostability was observed after monofluorination at the 2-position [24].

Meanwhile, the use of fluorinated building blocks capable to

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participate in assembling of the dipyrromethene core could be considered as the most effective way to obtain core-fluorinated BODIPYs. Indeed, this very convenient constructive approach can allow fluorine to be properly installed at the desired position of the pyrrole fragments. The use of fluorinated building blocks is in many cases an indispensable alternative to the late-stage fluorination [26]. However, to the best of our knowledge, no example of such transformations has been known to date.

Recently we have reported the preparation of 3-aryl-4-fluoro-1*H*-pyrrole-2-carboxylates **1** from β-fluoro-β-nitrostyrenes [27] by the Barton-Zard reaction with ethyl 2-isocyanoacetate [28]. These novel fluorine-containing pyrroles have demonstrated appealing synthetic utility. In particular, they can be transformed into novel fluorinated dipyrromethanes. The latter in turn are the key intermediates to related dipyrrines and their boron complexes. This work is devoted to the preparation of novel core-fluorinated BODIPYs and study of their photophysical properties (Scheme 1b).

2. Results and discussions

2.1. Synthesis

First, we studied acid-catalyzed condensation of a model pyrrole **1a** with 4-chlorobenzaldehyde to obtain the corresponding dipyrromethane **2a** (Scheme 2). We performed the optimization of reaction conditions. The reactions were carried out in dichloromethane (DCM) with various acids as a catalyst (Table 1). It was found that the reaction did not proceed at all in the presence of TFA even at 60 °C (Table 1, entry 1). The reaction conducted at 60 °C in presence of catalytic amounts of hydrochloric acid (HCl) achieved 40 % conversion of **1a** in 36 h (Table 1, entry 2). The use of $BF_3{\cdot}Et_2O$ under the same reaction conditions led to 94 % conversion of **1a**. However, the isolated yield of product **2a** was 67 % (Table 1, entry 3). The reaction proceeds more efficiently in the presence of *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$) (Table 1, entries 4–7). In this case, the reaction can be run at room temperature (Table 1, entry 4). However, it took 4 days to achieve 92 % conversion of **1a**. The TsOH-catalized reaction proceeded much faster when heated with 20 % molar excess of aldehyde resulting in 84–90 % yield of **2a** (Table, entries 6–7).

The use of methanesulfonic acid allowed to complete the reaction at room temperature in 4 h (Table 1, entry 8). However, triflic acid demonstrated the best catalytic activity in this reaction. The complete conversion of **1a** and quantitative yield of **2a** were achieved within just 1 h at room temperature (Table 1, entry 9).

Having the optimal reaction conditions in hand, we studied a scope of pyrroles **1** in this transformation (Scheme 3). The reaction proceeded smoothly for pyrroles containing both electron-donating and electron-withdrawing substituents in the aryl fragment. As a result, a set of novel fluorinated dipyrromethanes **2** with different aryl-substituents at 2,8-positions was prepared in high yields (83–99 %).

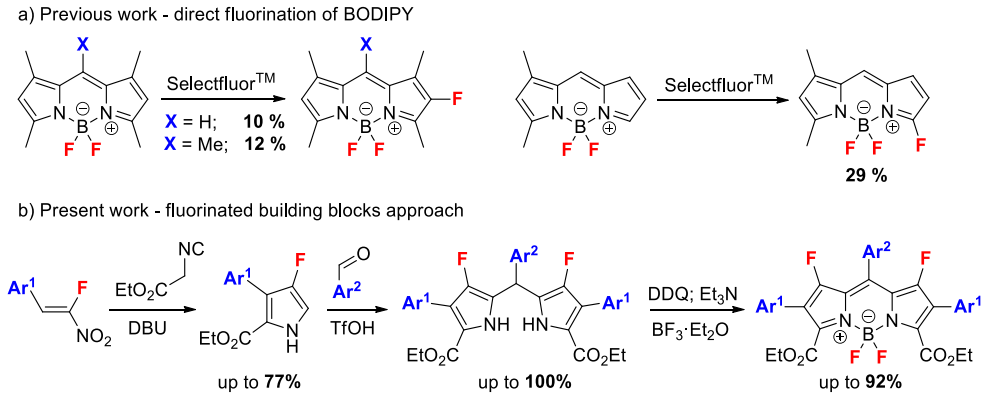
In spite of the use of very strong triflic acid we observed a high stability of pyrroles **1** under the reaction conditions. The presence of a strong electron-withdrawing carboxyethyl group reduces nucleophilicity and acidophobicity of these pyrrole derivatives. As a result all the target dipyrromethanes **2** were prepared in high yield. The reaction was found scalable up to gram scale. For example, 1.2 g (>99 %) of dipyrromethane **2m** was prepared in one batch from 1.0 g (3.6 mmol) of pyrrole **1m**.

Next, we studied a scope of aromatic aldehydes to vary substituents at 5-position of dipyrromethane (Scheme 4). It was found that the reaction takes place efficiently with a large number of aldehydes having both donor and acceptor substituents on the phenyl ring (Scheme 4). Thiophene-2-carbaldehyde also gave the corresponding dipyrromethane **2aa** in 81 % yield. The reaction with aromatic aldehydes of higher steric demand also proceeded smoothly; the corresponding products **2ab**, **2ac**, **2ad** were obtained in 72–99 % yields.

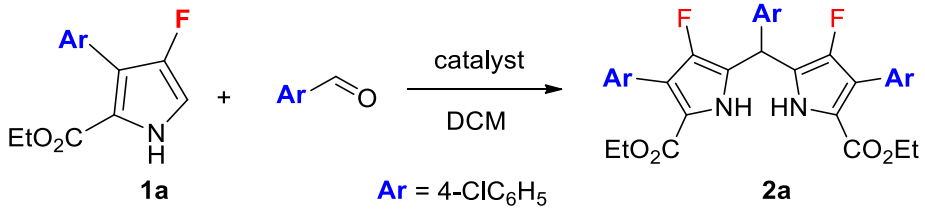
To expand the range of core-fluorinated dipyrromethanes, we carried out the condensation pyrroles **1** with aliphatic aldehydes or their synthetic equivalents. Condensation with acetaldehyde diethyl acetal led to the formation of 5-methyl-substituted dipyrromethanes **2ae** in quantitative yields (Scheme 5). In turn, the use of trifluoroacetic aldehyde methyl hemiacetal resulted in 5-trifluoromethyl-substituted dipyrromethane **2af** in 71 % yield. 5-Chloromethyl-substituted dipyrromethane **2ag** was obtained in 74 % yield from chloroacetaldehyde under the same conditions. On the other hand, the use of triflic acid as catalyst in the reaction of pyrrole **1a** with trioxane did not lead to the formation of the corresponding dipyrromethane. Intense decomposition of trioxane was observed under these conditions. However, the use of weaker methanesulfonic acid (MsOH) instead of TfOH afforded the target product **2ah** in 90 % yield (Scheme 5).

Having developed the route to dipyrromethanes **2**, we searched for conditions to convert them into core-fluorinated BODIPYs **4**. We studied the oxidation of the model dipyrromethane **2a** into dipyrromethene **3a** and the subsequent complexation with boron trifluoride (Scheme 6).

We found that *p*-chloranil widely used for the oxidation of dypyrromethanes did not oxidize at all these dipyrromethanes **2** bearing EWG carboxyethyl groups even at heating. However, another common oxidizing agent, DDQ, proved to be an efficient one. The oxidation of **2a** with DDQ proceeded even at room temperature; however, the reaction rate was very low. A 71 % conversion of **2a** was only achieved in 20 h (Table 2, entry 1). To intensify the oxidation, we carried out the reactions under microwave irradiation at constant temperature (Table 2, entries 2–8). A raise of temperature to 80 °C significantly increased the reaction rate without lowering the product yield (Table 2, entries 6–8). The complete conversion of **2a** was achieved within 1.5 h to afford **3a** in 81 % yield. To assess the effectiveness of microwave irradiation in this process, the reaction was also conducted on a hot plate at 80 °C for 0.5–1 h. A significant decrease of the yield of **3a** down to 49 % was



Scheme 1. Strategies toward core-fluorinated BODIPYs.



Scheme 2. Model reaction of pyrrole **1a** with 4-chlorobenzaldehyde to form dipyrromethane **2a**.

Table 1
Optimization of the reaction of pyrrole **1a** with 4-chlorobenzaldehyde.[a].

Entry	T, °C	Time, h	Catalyst	Molar ratio Aldehyde: 1a	Conversion[b], %	Yield of 2a[b], %
1	60	36	TFA	1 : 2	0	0
2	60	36	$HCl_{(conc)}$	1 : 2	40	40
3	60	36	$BF_3{\cdot}Et_2O$	1 : 2	94	80 (67)
4	rt	96	$TsOH{\cdot}H_2O$	1 : 2	92	(83)
5	60	36	$TsOH{\cdot}H_2O$	1 : 2	98	88 (86)
6	60	36	$TsOH{\cdot}H_2O$	1.2 : 2	100	(84)
7	80	18	$TsOH{\cdot}H_2O$	1.2 : 2	100	(90)
8	rt	4	MsOH	1.2 : 2	100	93
9	**rt**	**1**	**TfOH**	**1.2 : 2**	**100**	**100 (91)**

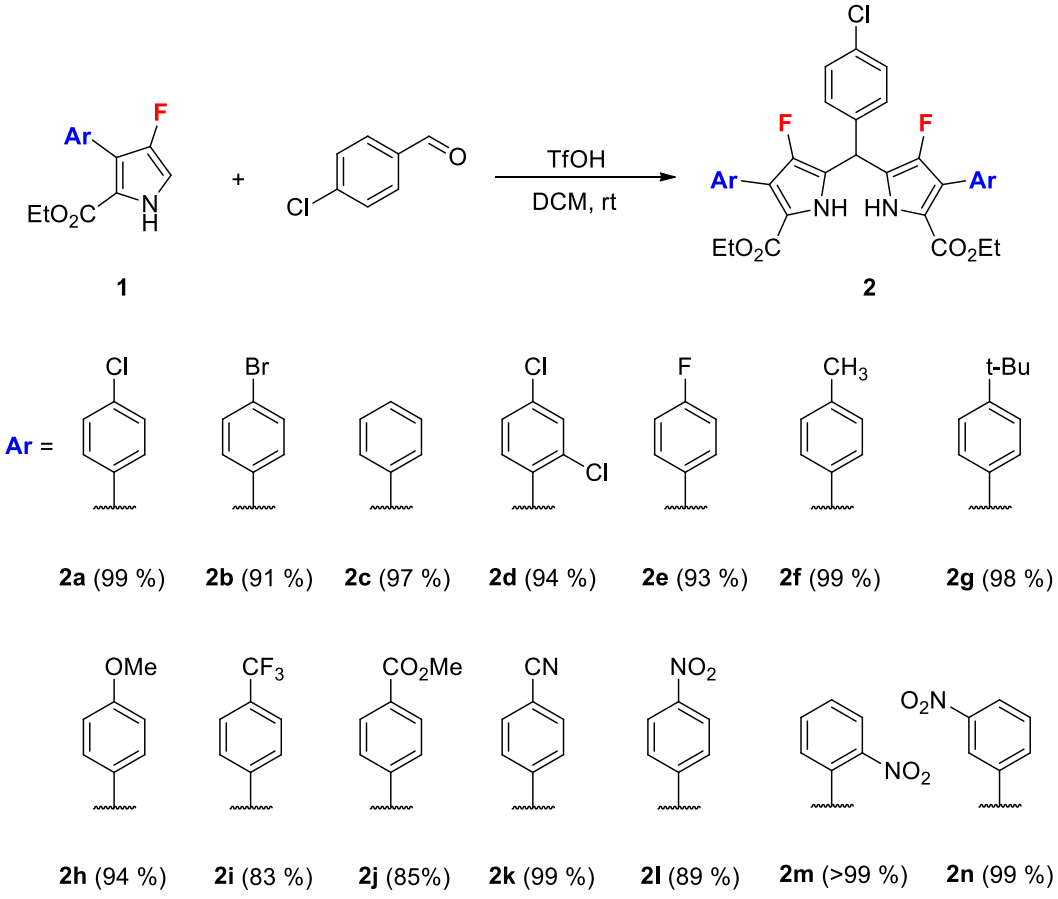
[a] – reaction conditions: pyrrole **1a** (0.2 mmol); 4-chlorobenzaldehyde (0.12 mmol); acid catalyst (0.03 mmol); DCM (1 mL).

[b] the yields that are not in parentheses are calculated by ^{19}F NMR spectra using α,α,α-trifluorotoluene as a standard; the isolated yields obtained by column chromatography are given in parentheses.

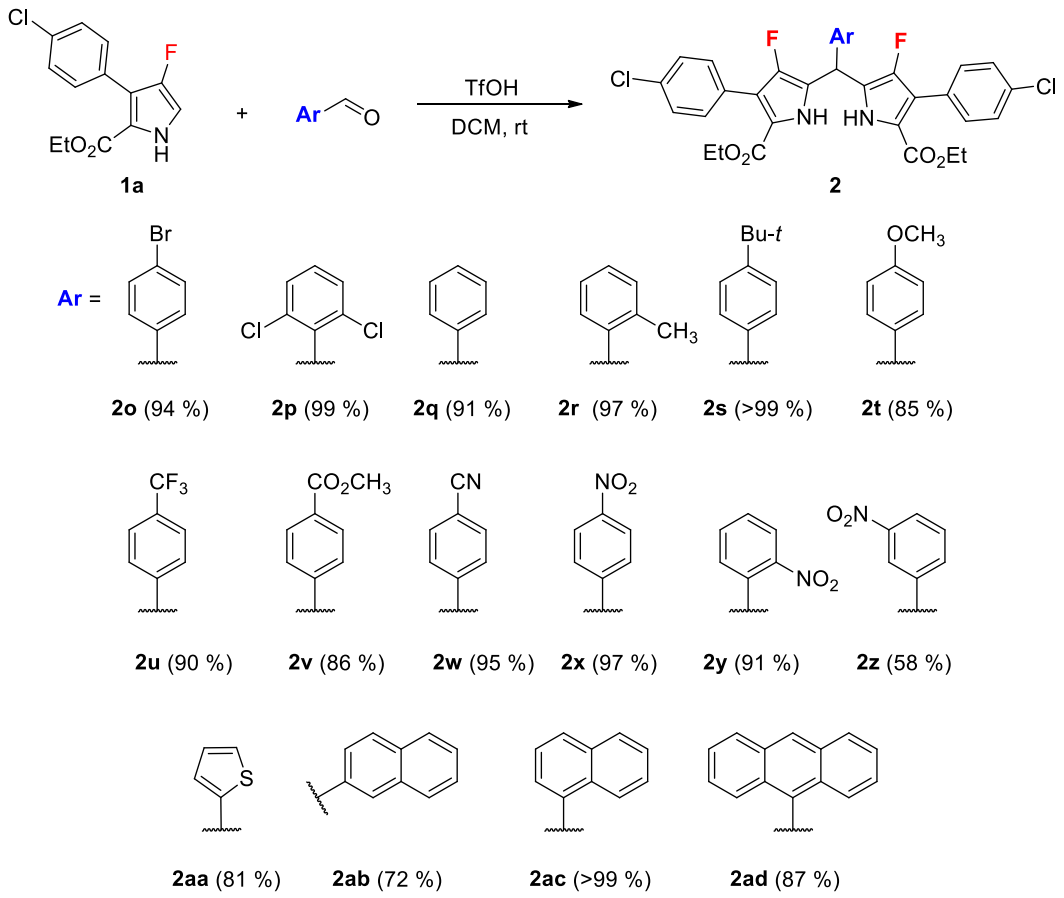
observed. This indicated the intensification of decomposition process under these conditions (Table 2, entries 9–10).

The subsequent complexation was conducted without isolation of unstable dipyrromethene **3a**. Trimethylamine as a base and boron trifluoride etherate ($BF_3{\bullet}Et_2O$) were added to the resulting dipyrromethene **3a**. The formation of boron complex can proceed even at room temperature; however, it took 4 days to complete the reaction (Table 3, entry 1). The use of microwave irradiation shortened the reaction time to 15 h at 60 °C and to 1.5 h at 80 °C to give BODIPY **4a** in 75 % yield (Table 3, entries 2–3). Under thermal activation the complexation proceeded less efficiently to form **4a** in somewhat lower product yield (Table 3, entry 4). As a result, the one-pot procedure for the preparation of novel core-fluorinated BODIPYs **4** under microwave irradiation at 80 °C was developed.

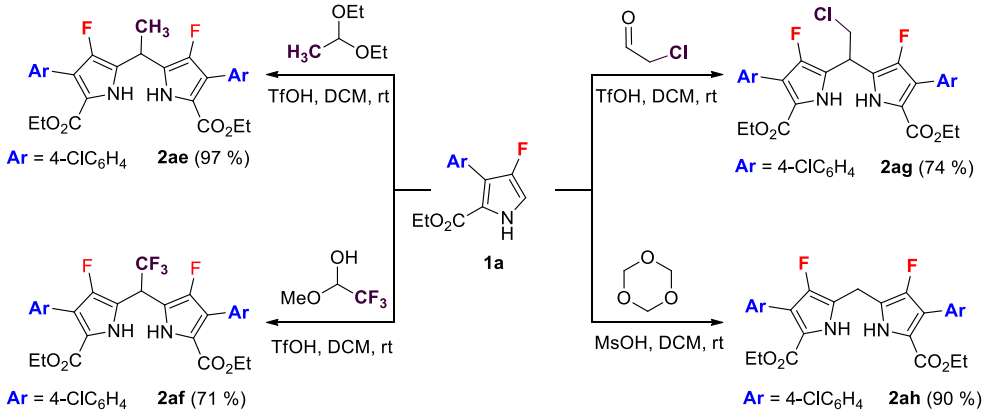
Having in hand the optimal reaction conditions, we carried out this transformation for a series of dipyrromethanes **2** (Scheme 7). To our delight, the reaction has a broad scope. Various dipyrromethanes can participate in this transformation. We obtained a wide range of novel core-fluorinated BODIPYs **4** with different aryl substituents in both the pyrrole fragments and at meso-position in up to 92 % yields. We also



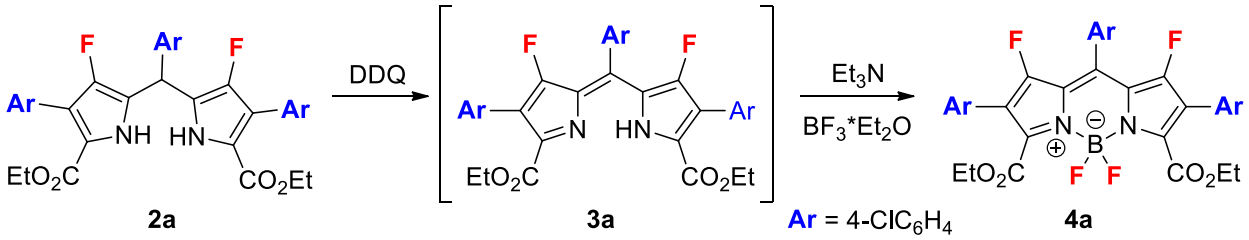
Scheme 3. Scope of pyrroles **1** in condensation with 4-chlorobenzaldehyde.



Scheme 4. Scope of aromatic aldehydes in the condensation with pyrrole **1a**.



Scheme 5. Scope of aliphatic aldehydes or their synthetic equivalents in the condensation with pyrrole **1a**.



Scheme 6. Preparation of core-fluorinated BODIPY **4a**.

Table 2
Optimization of oxidation of the model dipyrromethane **2a** with DDQ.[a].

Entry	Activation	T, °C	Time, h	Conversion of 2a, %[b]	Yield of 3a, %[b]
1	–	rt	20	71	54
2	μW	40	10	96	67
3	μW	60	1	91	80
4	μW	60	2	97	80
5	μW	60	3	100	83
6	μW	80	0.5	86	84
7	μW	80	1	97	88
8	μW	80	1.5	100	81
9	thermal	80	0.5	87	64
10	thermal	80	1	98	49

[a] Molar ratio **2a**: DDQ = 1:3, DCM, C_{2a} = 0.2 mol/L.
[b] Calculated *via* ^{19}F NMR spectra using α,α,α-trifluorotoluene as a standard.

Table 3
Optimization of complexation of **3a** into BODIPY **4a**.[a]

Entry	Activation	T, °C	Time, h	Yield of BODIPY 4a,[b] %
1	–	rt	92	75
2	μW	60	15	74
3	μW	80	1.5	73 (75)
4	thermal	80	3	67

[a] 1st step (oxidation): molar ratio **2a**: DDQ = 1:3, DCM, C_{2a} = 0.2 mol/L, μW, T = 80 °C, 1.5 h; 2nd step (complexation): molar ratio **2a**: Et_3N: $BF_3{\cdot}Et_2O$ = 1:10:15.
[b] the yields that are not in parentheses are calculated by ^{19}F NMR spectra using α,α,α-trifluorotoluene as a standard; the isolated yield obtained by column chromatography is given in parentheses.

synthesized meso-unsubstituted BODIPY **4i** in 30 % yield. All structures were confirmed by combination of ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR analysis, high resolution mass-spectrometry (HRMS) and X-Ray analysis of a single crystal of **4a** (Fig. 1).

Both aryl groups at meso- and β-positions are non-coplanar to the central moiety with the corresponding torsion angles equal to 59 and 37°, respectively. Assuming that the above torsion angles in crystal and gas phase are close to each other, we can propose that these values are inherent characteristic of **4a** rather than consequence of crystal packing effects. Analysis of crystal packing revealed that in addition to the expected C–H···O and C–H···Cl interactions ester groups also are involved in rather rare C═O ….C═O intermolecular interactions with parallel arrangement of C–O groups and shortened C···O distance equal to 3.033 (2)Å (See Supplementary Data, Fig. S1). Although a shortened C···C contact (3.41 Å) between carbon atoms at β-position of pyrrole moiety and aryl cycles is noted (See Supplementary Data, Fig. S2), the angle

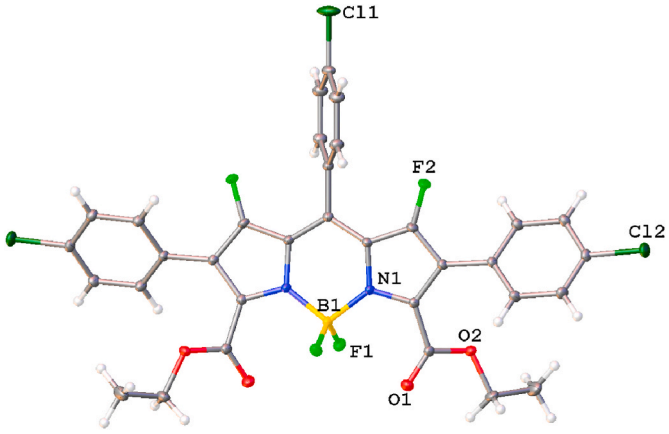
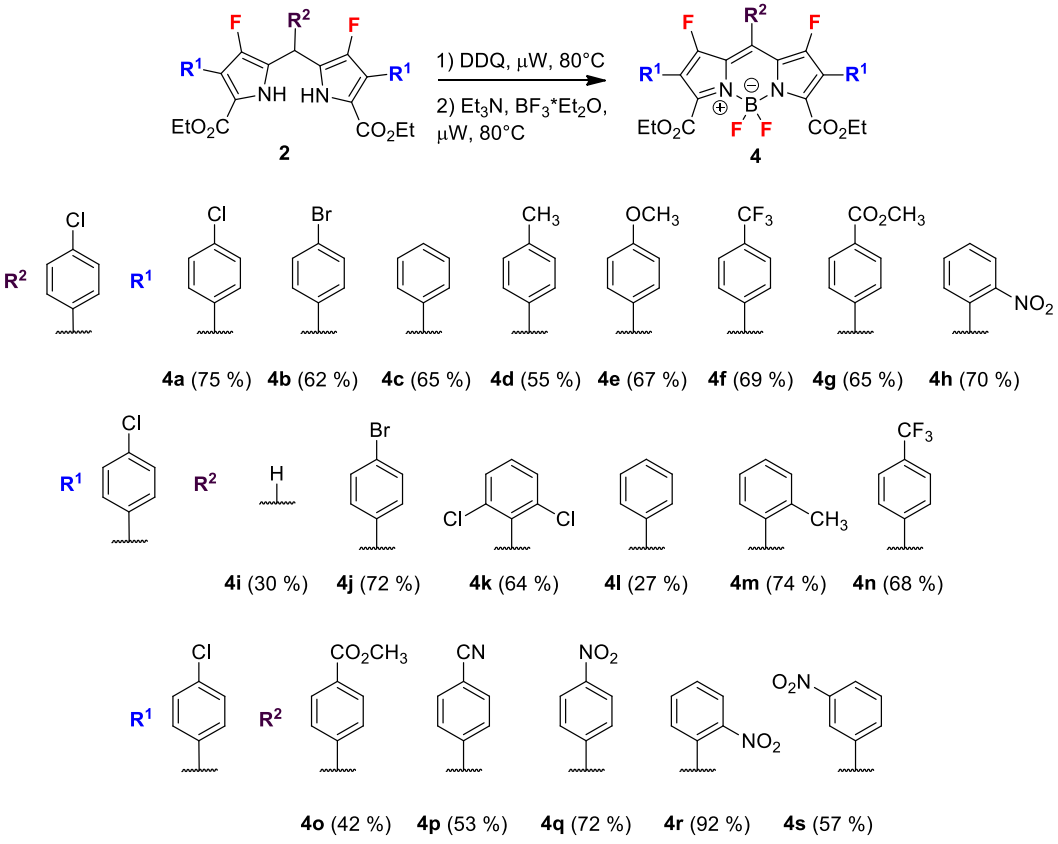


Fig. 1. The general view of **4a** in representation of atoms by atomic displacement parameters (p = 50 %).



Scheme 7. Scope of BODIPYs **4** obtained from dipyrromethanes **2**.

between their planes (38°) is clearly unfavorable for stacking interaction. Assuming the directionality of C═O···O═C interaction, we can propose that it exclude the formation of stacking interactions in a crystal.

2.2. Photophysical properties

Afterwards, we studied influence of structural changes on UV–vis absorption and IR spectral properties in a series of transformations from pyrrole **1a** to BODIPY **4a** (Figs. 2–3). For these experiments, after oxidation of **2a** dipyrromethene **3a** was isolated in pure form in 35 % yield using column chromatography. As expected, dipyrromethane **2a** showed a significant increase in a molar absorption coefficient by more than 2 times, while slight bathochromic shifts of both absorption maxima in the UV region were observed compared to pyrrole **1a** (Fig. 2). The oxidation of **2a** to dipyrromethene **3a** leads to formation of the chromophore system, absorbing in visible region (λ_{abs} (max) = 463 nm). The absorption maximum represents a very wide band probably as a result of two maximums overlapping. However, when ligand **3a** is coordinated with boron difluoride, the formation of two clear absorption maxima at 400 and 530 nm are observed. Thus, the main absorption maximum (530 nm) is *ca* 70 nm red-shifted in comparison with that of the ligand **3a**.

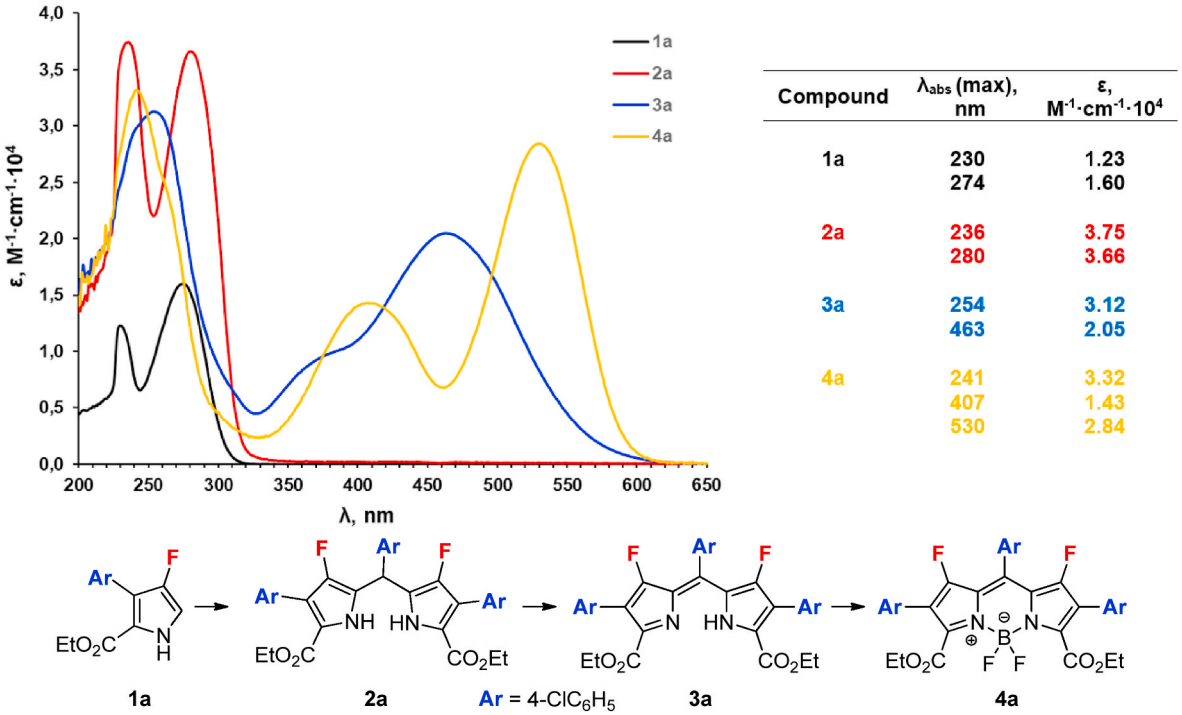
The IR spectrum of compound **1a** (Fig. 3) shows a single intense band of stretching vibrations of N–H bonds (3284 cm^{-1}) and a band of stretching vibrations of C═O in the ester group (1668 cm^{-1}). The low-frequency shift of the latter indicates the formation of the previously discovered intermolecular hydrogen bond between sp^2-hybridized oxygen of the ester group of one pyrrole molecule and pyrrolic hydrogen of the other pyrrole molecule [28]. The IR spectrum of dipyrromethane **2a** is more complicated, apparently due to the formation of additional intermolecular hydrogen bonds (and rotational isomerism) in the crystal cell. The wavenumber of stretching vibrations N–H decreases by 50 cm^{-1}, and the band of stretching vibrations C = O, without changing its position, slightly splits (1668, 1661 cm^{-1}). In the IR spectrum of ligand **3a**, the C═O stretching vibration band shifts to the high-frequency region up to 1716 cm^{-1} with a noticeable splitting, and the N–H band practically disappears. Finally, in the IR spectrum of BODIPY **4a**, the position of the carbonyl group band acquires a typical for an ester value (1742 cm^{-1}), which confirms that this fragment is not involved in coordination. The low-intensity N–H band most likely belongs to the residual ligand **3a**.

Next, the UV–vis absorption and fluorescence spectra of novel core-fluorinated BODIPYs **4a-s** were measured in chloroform (Fig. 4). Their spectroscopic and photophysical data are summarized in Table 4. BODIPYs **4a-s** have maximum of absorption for the main intense band in range 516–557 nm and maximum of emission in range 549–618 nm. The molar absorption coefficients of the main band are high that is typical for other structurally related BODIPY. We found that the resulting structural type of BODPY exhibited low quantum yields of fluorescence (Φ_f) were in most cases below 1 %.

It is known that a phenyl ring at *meso*-position can be an effective fluoresce quencher because of its free rotation [29]. However, even in case of BODIPYs **4k**, **4m** and **4r** having hard-to-rotate *ortho*-substituted phenyl ring at *meso*-position, we did not observe any enhancement of the Φ_f values. Therefore, we believe that the ethoxycarbonyl groups have the most significant impact in fluorescence quenching probably due to their strong electron withdrawing nature as well as their free rotation.

We found that the presence of electron-donating substituents on the benzene ring attached to BODIPY core at 2,6-position caused a bathochromic shift by up to 27 nm for the absorption and fluorescence spectra for dyes **4d-e** compared to 2,6-diphenyl substituted BODIPY **4c** (Table 4, cf. entries 3 and 4–5). On the contrary, the presence of strong electron-withdrawing groups on the benzene ring led to a hypsochromic shift by up to 14 nm for the absorption and up to 45 nm for the fluorescence spectra for dyes **4f-h** (Table 4, cf. entries 3 and 6–8).

Influence of substituent at the *meso*-position on spectroscopic properties was also studied. Introduction of aryl substituent at *meso*-position have negligible impact. For example, the absorption and emission maxima of *meso*-unsubstituted BODIPY **4i** are almost the same as those for *meso*-aryl substituted BODIPYs **4j**, **4n**, **4o** (Table 4, cf. entries 9, 10, 14 and 15). However, slight bathochromic shift of absorption and emission maxima in range of 4–19 nm was observed for aryls at *meso*-position bearing electron-withdrawing substituents compared to *meso*-



Compound	λ_{abs} (max), nm	ε, $M^{-1}\cdot cm^{-1}\cdot 10^4$
1a	230	1.23
	274	1.60
2a	236	3.75
	280	3.66
3a	254	3.12
	463	2.05
4a	241	3.32
	407	1.43
	530	2.84

Fig. 2. UV–vis absorption spectra of compounds **1a**-**4a**

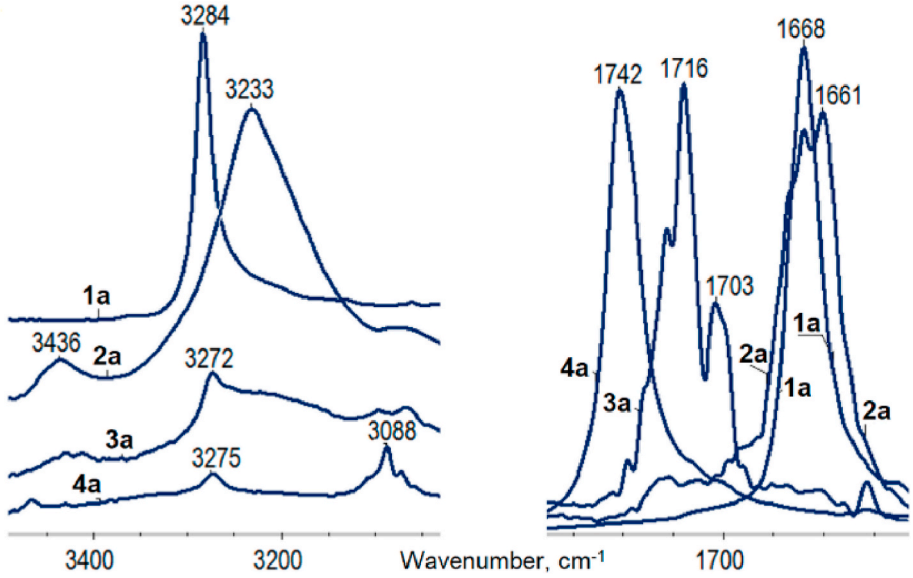


Fig. 3. IR spectra of **1a**-**4a** in the region of N–H and C═O stretching vibrations.

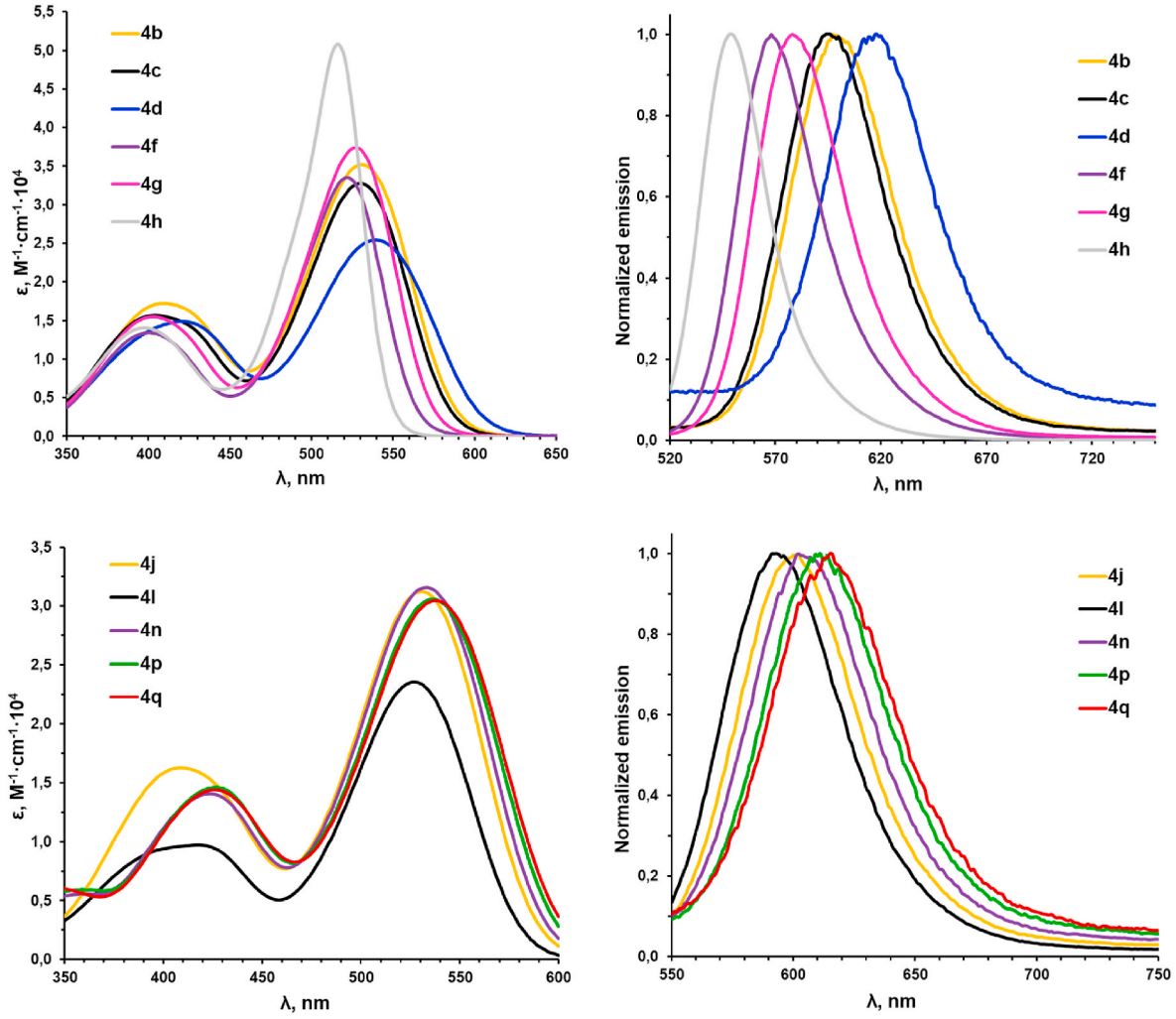


Fig. 4. UV–vis absorption and emission spectra of selected examples of BODIPYs **4**.

Table 4
Photophysical properties of BODIPYs **4a-r** in $CHCl_3$.

Entry	BODIPY	R^1	R^2	ε, $M^{-1}\cdot cm^{-1}\cdot 10^4$	λ_{abs} (max), nm	λ_{em} (max), nm	$\Delta\nu_{St}$, cm^{-1}	Φ_f^a
1	**4a**	4-ClC_6H_4	4-ClC_6H_4	3.11	530	601	2229	<0.01
2	**4b**	4-BrC_6H_4	4-ClC_6H_4	3.52	531	597	2082	<0.01
3	**4c**	C_6H_5	4-ClC_6H_4	3.28	530	594	2032	<0.01
4	**4d**	4-MeC_6H_4	4-ClC_6H_4	2.54	540	618	2337	<0.01
5	**4e**	4-$MeOC_6H_4$	4-ClC_6H_4	2.16	557	–	–	–
6	**4f**	4-$CF_3C_6H_4$	4-ClC_6H_4	3.35	522	568	1551	0.02
7	**4g**	4-$MeO_2CC_6H_4$	4-ClC_6H_4	3.74	527	578	1674	0.02
8	**4h**	2-$NO_2C_6H_4$	4-ClC_6H_4	5.08	516	549	1165	0.05
9	**4i**	4-ClC_6H_4	H	2.87	533	602	2150	<0.01
10	**4j**	4-ClC_6H_4	4-BrC_6H_4	3.13	531	602	2221	<0.01
11	**4k**	4-ClC_6H_4	2,6-$Cl_2C_6H_3$	2.44	542	612	2110	<0.01
12	**4l**	4-ClC_6H_4	C_6H_5	2.36	527	593	2112	<0.01
13	**4m**	4-ClC_6H_4	2-MeC_6H_4	3.07	527	593	2112	0.02
14	**4n**	4-ClC_6H_4	4-$CF_3C_6H_4$	3.16	534	602	2115	<0.01
15	**4o**	4-ClC_6H_4	4-$MeO_2CC_6H_4$	2.33	532	605	2268	<0.01
16	**4p**	4-ClC_6H_4	4-CNC_6H_4	3.06	536	611	2290	<0.01
17	**4q**	4-ClC_6H_4	4-$NO_2C_6H_4$	3.04	537	615	2362	<0.01
18	**4r**	4-ClC_6H_4	2-$NO_2C_6H_4$	3.15	535	609	2271	<0.01
19	**4s**	4-ClC_6H_4	3-$NO_2C_6H_4$	2.55	536	612	2317	<0.01

a – measured related to Rhodamin 6G in EtOH.

phenyl substituted BODIPY **4l** (Table 4, cf. entries 10–11, 14–19 and 12).

Next, we studied influence of a solvent for BODIPY **4h** on its photophysical properties (See Supplementary Data, Table S1). Solutions of **4h** in both polar and nonpolar solvents demonstrated the similar values of absorption and emission maxima with difference within 1–7 nm. However, the molar absorption coefficient measured in THF is considerably lower than those measured in other solvents.

2.3. DFT calculations

It should be noted that the obtained spectroscopic data are in good agreement with DFT calculations. The geometry of the ground electronic state of compounds **4a-h** was optimized by the DFT PBE/L1 method in PRIRODA program. The frontier orbitals localization is depicted in Fig. 5. The calculated energies of the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO) and energy gap between them (E_{gap}) are depicted in Fig. 6. We found that the frontier orbitals are almost not localized on a phenyl ring at the *meso*-position (Fig. 5). Indeed, the optimized geometry as well as X-ray analysis (Fig. 1) showed that the aryl at the *meso*-position is not coplanar to BODIPY core and practically does not conjugate with the chromophore π-system. On the contrary, HOMO in significant extent is localized on the phenyl rings at 2,6-positions. Therefore, electronic effect of substituents introduced into the aryls attached at 2,6-positions considerably influences on HOMO energy and consequently on E_{gap} (Fig. 6).

Moreover, we found that the experimental values of the absorption and emission maxima give linear correlations with the E_{gap} values (Fig. 7; Eqs. (1) and (2)):

$$\lambda_{abs}(max) = -72.7E_{gap} + 651.6 \ (R = 0.962) \quad \text{(Eq. 1)}$$

$$\lambda_{em}(max) = -209.6E_{gap} + 942.4 \ (R = 0.938) \quad \text{(Eq. 2)}$$

Noteworthy, such the relationships can be used for predicting the wavelength of absorption and emission maxima depending on the electronic nature of the substituents of BODIPY [30].

Finally, we compared the core-fluorinated BODIPYs **4** with other non-fluorinated 3,5-diesters analogs known in the literature. We found only six examples of 1,7-dimethylated BODIPYs related to the similar structural type (Table 5) [31]. They were prepared from the corresponding dimethylated dipyrromethanes under conditions milder than ours. However, in contrast to our data negligible yields were obtained for 1,7-dimethylated BODIPYs having strong EWG and EDG in aryl fragments attached to 2,6-position compared to those of 1,7-difluorinated BODIPYs (Table 5, entries 2,4). Most probably, the presence of fluorines in the core leads to considerable increase of chemical stability of intermediates and products providing good yields in all cases. Next, we compared photophysical properties for the structures with the most similar aryl fragments. For 1,7-dimethylated BODIPYs only data of absorption and emission maxima are available.

We found that the spectral properties are very similar. The replacement of methyl by fluorine have low impact on absorption maxima. However, somewhat higher impact was observed on the emission maxima. For example, 1,7-difluorinated BODIPYs demonstrated higher values of Stockes shifts ($\Delta\nu_{St}$) that those of 1,7-dimethylated BODIPYs (Table 5, entries 1, 3, 4). Only 1,7-dimethylated BODIPYs having methoxy-groups demonstrated higher value of $\Delta\nu_{St}$, whereas for 1,7-difluorinated analog

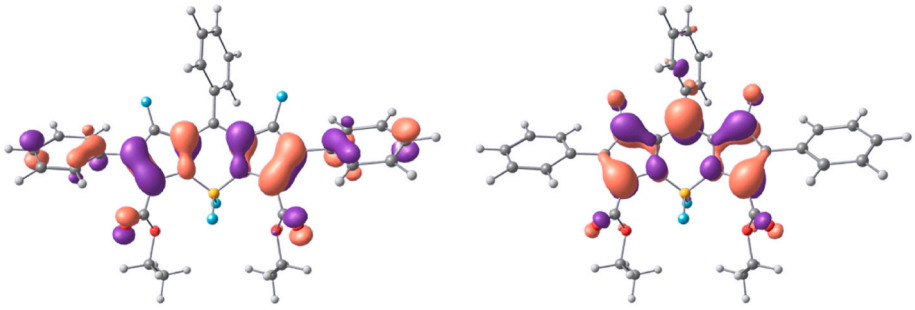


Fig. 5. Frontier orbitals localization for a model 2,6,8-triphenyl substituted BODIPY.

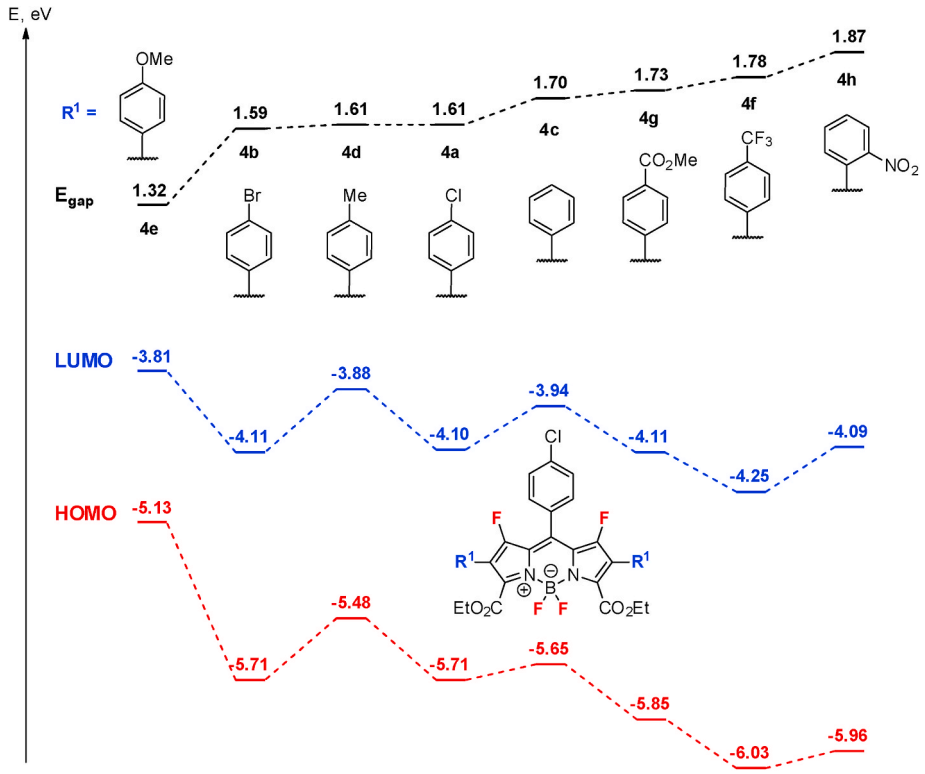


Fig. 6. Frontier orbitals and energy gap calculated for dyes **4a**-**h**.

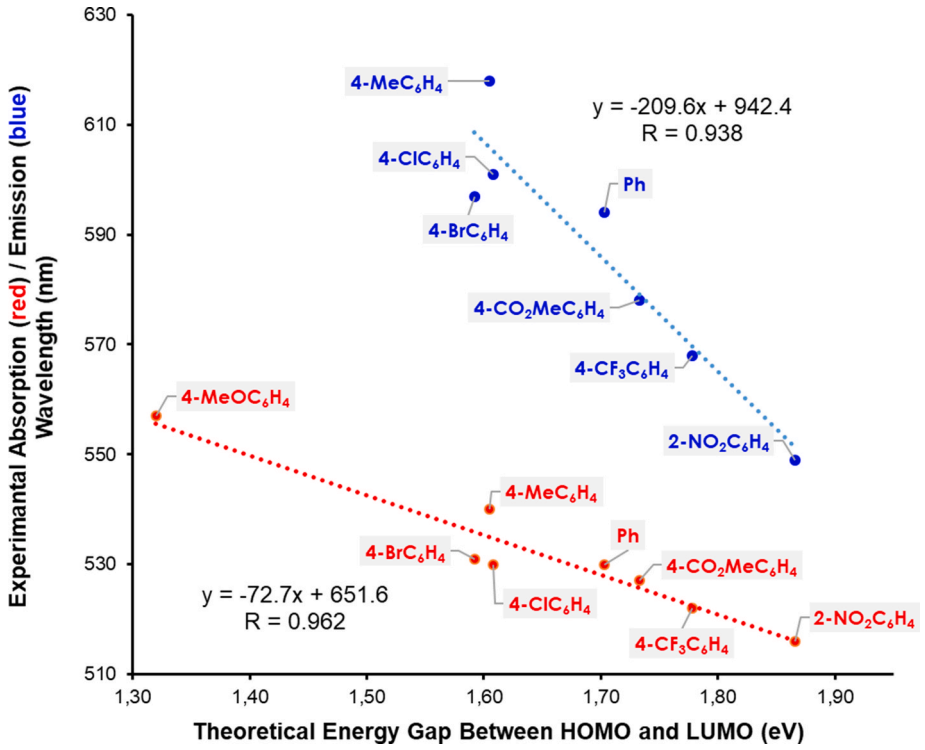


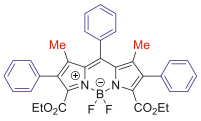
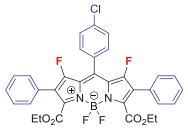
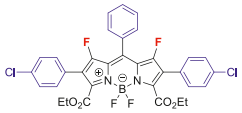
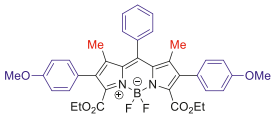
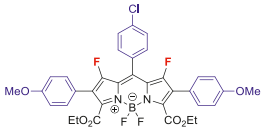
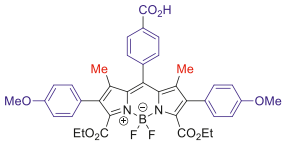
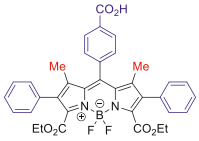
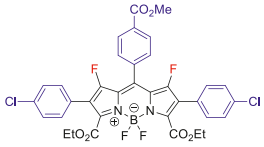
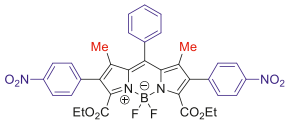
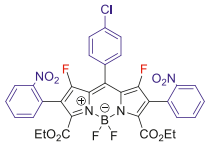
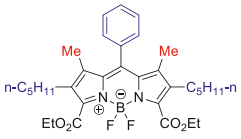
Fig. 7. Plot of λ_{em} *versus* E_{gap} and λ_{abs} *versus* E_{gap} (aryl fragments at 2,6-positions are shown).

fluorescence was not observed at all (Table 5, entry 2).

3. Conclusions

In summary, an efficient route to novel core-fluorinated BODIPYs **4** was developed using the corresponding fluorinated pyrroles **1** as staring building blocks. Pyrroles **1**, in turn, are the product of the Barton-Zard reaction of β-fluoro-β-nitrostyrenes with 2-ethyl isocyanoacetate. Broad scope of this approach was demonstrated. The key intermediates, dipyrromethanes **2**, were prepared by the condensation of pyrroles **1** and aldehydes. Highly efficient triflic acid catalyzed reaction was elaborated for this aim. The subsequent oxidation and boron difluoride complexation of

Table 5
Comparison of 1,7-dimethylated and 1,7-difluorinated BODIPY-3,5-diesters.[a].

#	Known 1,7-dimethylated BODIPYs	Yield, %	λ_{abs} (max), nm	λ_{em} (max), nm	$\Delta\nu_{St}$, cm^{-1}	BODIPYs obtained in present work	Yield, %	λ_{abs} (max), nm	λ_{em} (max), nm	$\Delta\nu_{St}$, cm^{-1}
1		80 %	535	576	1330		65 %	530	594	2032
							27 %	527	593	2112
2		4 %	541	620	2355		67 %	557	–	–
		4 %	547	628	2358					
3		58 %	538	586	1523		65 %	532	605	1674
4		2 %	530	558	947		70 %	516	549	1165
5		30 %	537	557	669	–	–	–	–	–

a –data from the reference [31].

the resulting dipyrromethanes **2** under microwave irradiation led to a family of novel core-fluorinated BODIPYs **4**. It was found that they have absorption maxima and emission maxima in range of 516–557 nm and 549–618 nm correspondingly. In addition, it was found that the photophysical properties of the dyes obtained are in perfect agreement with the DFT calculations. Finally, the BODIPYs obtained were compared with known 1,7-dimethylated analogs. We found that both fluorinated and methylated BODIPYs show the similar photophysycal properties. The replacement of methyl by fluorine have low impact on absorption maxima and somewhat higher impact on emission maxima.

4. Experimental section

4.1. Materials and equipments

Starting pyrroles **1** were prepared according to the described procedures and are all known compounds [28]. All the other reagents were purchased from commercial sources and used without any further purification. Solvents were dried before use by the standard procedures [32] Melting points (mp) were measured with a Büchi B-545 melting point apparatus. Microwave-assisted reactions were performed in a microwave reactor Monowave 200 (Anton Paar) in sealed vessels at constant temperature.

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra were obtained with Bruker Avance-400 and Agilent 400-MR spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectroscopic data were referenced to the residual

solvent resonance. Chemical shifts for ^{19}F NMR spectroscopic data were referenced to $PhCF_3$ ($\delta = -63.72$ ppm) or C_6F_6 ($\delta = -164.9$ ppm) added as a reference standard. Data are reported as follows: chemical shift, integration multiplicity (s = *singlet*, d = *doublet*, t = *triplet*, q = *quadruplet*, br = *broad*, m = *multiplet*, dd = *doublet of doublets*, ddd = *doublet of doublet of doublets,* td = *triplet of doublets*, tt = *triplet of triplets,* dm = *doublet of multiplets*) and coupling constants (Hz). IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer (Thermo Scientific) at a resolution of 4 cm^{-1}, the number of scans was 20. Electronic absorption spectra were recorded on Genesys 50 (Thermo Scientific) and Agilent Cary 60 UV–visible spectrophotometers with pulsed xenon lamps as radiation source in quartz cuvettes with an optical path length of 0.1 and 1.0 cm. Concentrations of the analyzed solutions were in a range of $2.6{\cdot}10^{-4}$ – $3.2{\cdot}10^{-4}$ mol/l.

Emission spectra were recorded on a Hitachi F-2700 fluorescence spectrophotometer with xenon lamp as excitation source in 1 cm quartz cuvette. Concentrations of the analyzed solutions were in a range of $1.6{\cdot}10^{-5}$ – $5.8{\cdot}10^{-5}$ mol/l. Fluorescence quantum yields for BODIPY **4** solutions were calculated using Rhodamine 6G ($\Phi_F = 0.94$ in EtOH) as a standard [33]. Excitation wavelength was 490 nm.

4.2. Experimental procedures and characterization of products

General procedure for preparation of dipyrromethanes 2. In typical experiment a solution of a selected pyrrole **1** (0.2 mmol, 1 mol. eq.) and a corresponding aldehyde or its synthetic equivalent (0.12 mmol, 0.6 mol equiv.) in DCM (1 mL) was loaded into a vial (4 mL). Then triflic acid (0.03 mmol, 0.15 mol equiv.) was added to the resulting mixture. The reaction mixture was stirred at room temperature for 1 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the pure product was isolated by column chromatography on silica gel using appropriate elution mixtures.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2a). Eluent: Hex/DCM 1:1, Hex/DCM 1:2, DCM. Yield: 0.368 g (99 %) from 0.302 g (1.13 mmol) of **1a**, 0.095 g (0.68 mmol) of 4-chlorobenzaldehyde and 0.015 mL (0.17 mmol) of triflic acid. Analysis of the sample matched previously reported data [28].

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(3-(4-bromophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2b). Eluent: Hex/DCM 1:1, Hex/DCM 1:2, DCM. Yield: 0.099 g (91 %). Pale pink solid; mp 266–268 °C (with decomposition). ^1H NMR (400 MHz, DMSO-d_6): δ 11.97 (br s, 2H), 7.61–7.50 (m, 4H), 7.46–7.41 (m, 2H), 7.38 (d, $J = 8.4$ Hz, 4H), 7.19 (d, $J = 8.5$ Hz, 2H), 5.83 (s, 1H), 4.15 (q, $J = 7.1$ Hz, 4H), 1.14 (t, $J = 7.1$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 160.1, 146.1 (d, $^1J_{CF} = 243.7$ Hz), 138.2, 132.3, 131.8, 130.7, 129.9, 129.7, 128.5, 120.5, 118.8 (d, $^2J_{CF} = 20.9$ Hz), 115.6 (d, $^2J_{CF} = 10.3$ Hz), 113.9, 60.1, 36.0, 14.1.^{19}F NMR (376 MHz, DMSO-d_6): δ −169.56 (s). HRMS (ESI) *m/z*: $[M - H]^-$ calcd. for $C_{33}H_{24}^{79}Br^{81}Br^{35}ClF_2N_2O_4$ 742.9765; found 742.9765.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-phenyl-1*H*-pyrrole-2-carboxylate) (2c). Eluent: Hex/DCM (2:1); Hex/DCM (1:7). Yield: 0.090 g (97 %). Cream-colored solid; mp 221–223 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 11.32 (br s, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.35–7.26 (m, 8H), 7.23–7.17 (m, 4H), 5.76 (s, 1H), 4.03 (q, $J = 7.1$ Hz, 4H), 0.99 (t, $J = 7.1$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.5 (d, $^4J_{CF} = 2.9$ Hz), 147.1 (d, $^1J_{CF} = 245.4$ Hz), 137.7, 133.4, 130.6, 130.3 (d, $^3J_{CF} = 2.3$ Hz), 129.9, 129.0, 127.6, 127.4, 120.1 (d, $^2J_{CF} = 19.8$ Hz), 118.6 (d, $^2J_{CF} = 10.4$ Hz), 113.8 (d, $^3J_{CF} = 3.8$ Hz), 61.4, 38.8, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.49 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{28}^{35}ClF_2N_2O_4$ 589.1700; found 589.1706.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(3-(2,4-dichlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2d). Eluent: Hex/DCM 1:1, Hex/DCM 1:2, DCM. Yield: 0.119 g (94 %). Pale yellow solid; mp 129–131 °C. NMR spectra of the sample show the presence of several stable rotamers and are complex due to overlap of the similar signals. Groups of peaks related to the similar protons are described as multiplets. ^1H NMR (400 MHz, $CDCl_3$): δ 10.36–10.12 (m, 2H), 7.55–7.43 (m, 2H), 7.38–7.21 (m, 6H), 7.21–7.11 (m, 2H), 5.96–5.88 (m, 1H), 4.08–3.82 (m, 4H), 1.04–0.93 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.6 (d, $^4J_{CF} = 2.8$ Hz), 161.6 (d, $^4J_{CF} = 2.5$ Hz), 161.5 (d, $^4J_{CF} = 2.4$ Hz), 147.0 (d, $^1J_{CF} = 245.8$ Hz), 146.9 (d, $^1J_{CF} = 245.8$ Hz), 146.8 (d, $^1J_{CF} = 245.9$ Hz), 137.2, 137.1, 137.0, 135.33 (d, $^3J_{CF} = 2.5$ Hz), 135.27 (d, $^3J_{CF} = 3.7$ Hz), 134.5, 133.8, 133.7, 133.7, 133.5, 133.4, 129.2, 129.2, 129.1, 129.1, 128.8, 128.8, 126.6, 126.5, 118.78 (d, $^2J_{CF} = 19.9$ Hz), 118.68 (d, $^2J_{CF} = 23.3$ Hz), 118.59 (d, $^2J_{CF} = 23.7$ Hz), 118.57 (d, $^2J_{CF} = 19.4$ Hz), 115.91 (d, $^2J_{CF} = 9.7$ Hz), 115.86 (d, $^2J_{CF} = 10.8$ Hz), 115.81 (d, $^2J_{CF} = 9.7$ Hz), 114.60 (d, $^3J_{CF} = 2.5$ Hz), 114.48 (d, $^3J_{CF} = 2.8$ Hz), 114.45 (d, $^3J_{CF} = 2.7$ Hz), 114.35 (d, $^3J_{CF} = 3.2$ Hz), 114.32 (d, $^3J_{CF} = 2.6$ Hz), 61.2, 61.2, 36.5, 36.2, 35.6, 13.8. ^{19}F NMR (376 MHz, CDCl3) δ −163.09 (s), −163.13 (s), −163.52 (s), −163.57 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{24}^{35}Cl_5F_2N_2O_4$ 725.0141; found 725.0146.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(4-fluorophenyl)-1*H*-pyrrole-2-carboxylate) (2e). Eluent: Hex/DCM (2:1), Hex/DCM (1:7), DCM. Yield: 0.100 g (93 %). Pink solid; mp 242–244 °C (with decomposition). ^1H NMR (400 MHz, $CDCl_3$): δ 11.26 (br s, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.26 (dd, $J = 8.7$, 5.3 Hz, 4H), 6.91 (t, $J = 8.7$, 8.7 Hz, 4H), 5.72 (s, 1H), 4.13–3.86 (m, 4H), 1.02 (t, $J = 7.1$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^4J_{CF} = 2.9$ Hz), 162.3 (d, $^1J_{CF} = 247.2$ Hz), 147.0 (d, $^1J_{CF} = 245.5$ Hz), 137.3, 133.6, 132.3 (d, $^3J_{CF} = 8.0$ Hz), 129.8, 129.0, 126.2 (pseudo-t, $^3J_{CF} = 2.7$, $^4J_{CF} = 2.7$ Hz), 120.1 (d, $^2J_{CF} = 19.6$ Hz), 117.5 (d, $^2J_{CF} = 10.5$ Hz), 114.6 (d, $^2J_{CF} = 21.4$ Hz), 113.8 (d, $^3J_{CF} = 3.8$ Hz), 61.5, 38.7, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.13 (tt, $^3J_{HF} = 8.7$, $^4J_{HF} = 5.3$ Hz, 2 F), −165.58 (s, 2 F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{26}^{35}ClF_4N_2O_4$ 625.1512; found 625.1516.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(*p*-tolyl)-1*H*-pyrrole-2-carboxylate) (2f). Eluent: Hex/DCM (1:2), Hex/DCM (1:3), Hex/DCM (1:5). Yield: 0.095 g (99 %). Pale pink solid; mp 242–243 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 11.08 (s, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 4H), 7.02 (d, $J = 7.8$ Hz, 4H), 5.75 (s, 1H), 4.02 (q, $J = 7.0$ Hz, 4H), 2.39 (s, 6H), 1.03 (t, $J = 7.0$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.4 (d, $^4J_{CF} = 2.9$ Hz), 147.1 (d, $^1J_{CF} = 245.0$ Hz), 137.7, 137.0, 133.4, 130.5, 129.8, 128.9, 128.3, 127.3 (d, $^3J_{CF} = 2.2$ Hz), 119.8 (d, $^2J_{CF} = 20.2$ Hz), 118.6 (d, $^2J_{CF} = 10.3$ Hz), 113.8 (d, $^3J_{CF} = 3.9$ Hz), 61.3, 38.5, 21.4, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -165.69$ (s, 2 F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{35}H_{32}^{35}ClF_2N_2O_4$ 617.2013; found 617.2006.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(3-(4-(*tert*-butyl)phenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2g). Eluent: Hex/DCM (1:1); Hex/DCM (1:3); Hex/DCM (1:7). Yield: 0.109 g (98 %). Pink solid; mp 140–143 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 11.12 (s, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.35–7.29 (m, 6H), 7.29–7.23 (m, 4H), 5.78 (s, 1H), 4.10–3.96 (m, 4H), 1.36 (s, 18H), 0.99 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, $^4J_{CF} = 2.6$ Hz), 150.4, 147.2 (d, $^1J_{CF} = 245.0$ Hz), 137.7, 133.4, 130.3, 129.8, 128.9, 127.4 (d, $^3J_{CF} = 2.2$ Hz), 124.4, 119.8 (d, $^2J_{CF} = 20.2$ Hz), 118.7 (d, $^2J_{CF} = 10.5$ Hz), 113.8 (d, $^3J_{CF} = 3.9$ Hz), 61.2, 34.7, 38.5, 31.5, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.55 (s, 2 F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{41}H_{44}^{35}ClF_2N_2O_4$ 701.2952; found 701.2964.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate) (2h). Eluent: Hex/DCM (1:1), Hex/DCM (1:3), DCM, DCM/EtOAc (10:1). Yield: 0.080 g (94 %). Pale pink solid; mp 234–236 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 11.11 (s, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 6.9$ Hz, 4H), 6.74 (d, $J = 8.8$ Hz, 4H), 5.71 (s, 1H), 4.08–3.95 (m, 4H), 3.82 (s, 6H), 1.02 (t, $J = 7.1$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.42 (d, $^4J_{CF} = 2.9$ Hz), 159.0, 147.1 (d, $^1J_{CF} = 244.7$ Hz), 137.7, 133.4, 131.9, 129.9, 129.0, 122.6 (d, $^3J_{CF} = 2.3$ Hz), 119.9 (d, $^2J_{CF} = 20.0$ Hz), 118.3 (d, $^2J_{CF} = 10.4$ Hz), 113.7 (d, $^3J_{CF} = 4.0$ Hz), 113.0, 61.3, 55.3, 38.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.80 (s, 2 F).

HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{35}H_{32}^{35}ClF_2N_2O_6$ 649.1911; found 649.1920.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2-carboxylate) (**2i**). Eluent: Hex/DCM (2:1), Hex/DCM (1:7). Yield: 0.098 g (83 %). Cream-colored solid; mp 223–226 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.29 (s, 2H), 7.55 (d, J = 7.9 Hz, 2H), 7.47–7.37 (m, 8H), 7.33 (d, J = 7.9 Hz, 2H), 5.75 (s, 1H), 4.05 (q, J = 6.8 Hz, 4H), 1.02 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^4J_{CF}$ = 2.6 Hz), 147.1 (d, $^1J_{CF}$ = 247.0 Hz), 136.9, 133.9, 133.9, 130.9, 129.8 (q, $^2J_{CF}$ = 32.5 Hz), 129.8, 129.2, 124.5 (d, $^3J_{CF}$ = 3.5 Hz), 124.2 (q, $^1J_{CF}$ = 272.0 Hz), 120.2 (d, $^2J_{CF}$ = 19.3 Hz), 117.0 (d, $^2J_{CF}$ = 10.2 Hz), 114.1 (d, $^3J_{CF}$ = 3.4 Hz), 61.8, 38.7, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.83 (s, 6 F), −164.79 (s, 2 F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{35}H_{26}^{35}ClF_8N_2O_4$ 725.1448; found 725.1456.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(4-(methoxycarbonyl)phenyl)-1*H*-pyrrole-2-carboxylate) (**2j**). Eluent: Hex/DCM (1:2), Hex/DCM (1:7), DCM/EtOAc (20:1). Yield: 0.178 g (85 %). Peach solid; mp 232–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.34 (s, 2H), 7.83 (d, J = 8.2 Hz, 4H), 7.54 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.2 Hz, 4H), 7.31 (d, J = 8.5 Hz, 2H), 5.75 (s, 1H), 4.08–3.99 (m, 4H), 3.95 (s, 6H), 1.01 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.9, 162.2 (d, $^4J_{CF}$ = 2.9 Hz), 147.0 (d, $^1J_{CF}$ = 247.0 Hz), 137.0, 134.9 (d, $^3J_{CF}$ = 2.2 Hz), 133.6, 130.5, 129.7, 129.0, 129.0, 128.8, 120.1 (d, $^2J_{CF}$ = 19.5 Hz), 117.3 (d, $^2J_{CF}$ = 10.1 Hz), 114.1 (d, $^3J_{CF}$ = 3.8 Hz), 61.7, 52.2, 38.5, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −164.71 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{37}H_{32}^{35}ClF_2N_2O_8$ 705.1810; found 705.1820.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(3-(4-cyanophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (**2k**). Eluent: Hex/DCM (1:2), DCM, DCM/EtOAc (10:1). Yield: 0.100 g (99 %). Pink solid; mp 202–204 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.66 (s, 2H), 7.57 (d, J = 8.4 Hz, 4H), 7.50 (d, J = 8.2 Hz, 4H), 7.33 (s, 4H), 5.83 (s, 1H), 4.10–3.98 (m, 4H), 1.06 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.6 (d, $^4J_{CF}$ = 2.8 Hz), 146.8 (d, $^1J_{CF}$ = 247.3 Hz), 136.5, 135.1 (d, $^3J_{CF}$ = 2.5 Hz), 133.9, 131.4, 131.1, 129.4, 129.2, 119.5 (d, $^2J_{CF}$ = 21.1 Hz), 118.8, 116.5 (d, $^2J_{CF}$ = 10.4 Hz), 114.6 (d, $^3J_{CF}$ = 3.5 Hz), 111.2, 61.6, 37.1, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.38 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{35}H_{26}^{35}ClF_2N_4O_4$ 639.1605; found 639.1597.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(4-nitrophenyl)-1*H*-pyrrole-2-carboxylate) (**2l**). Eluent: Hex/DCM (1:2), DCM, DCM/EtOAc (20:1). Yield: 0.085 g (89 %). Orange waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.62 (s, 2H), 8.17–8.11 (m, 4H), 7.58 (d, J = 8.3 Hz, 4H), 7.34 (s, 4H), 5.85 (s, 1H), 4.14–4.00 (m, 4H), 1.09 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.6 (d, $^4J_{CF}$ = 2.8 Hz), 147.1, 146.9 (d, $^1J_{CF}$ = 247.5 Hz), 137.1 (d, $^3J_{CF}$ = 2.6 Hz), 136.4, 134.1, 131.3, 129.4, 129.3, 122.9, 119.5 (d, $^2J_{CF}$ = 21.1 Hz), 116.2 (d, $^2J_{CF}$ = 10.3 Hz), 114.9 (d, $^3J_{CF}$ = 3.3 Hz), 61.8, 37.1, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.14 (s). HRMS (ESI) *m/z*: $[M - H]^-$ calcd. for $C_{33}H_{24}^{35}ClF_2N_4O_8$ 677.1256; found 677.1251.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate) (**2m**). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.098 g (95 %) from 0.085 g (0.30 mmol) of ethyl 4-fluoro-3-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate, 0.026 g (0.18 mmol) of 4-chlorobenzaldehyde and 0.004 mL (0.05 mmol) of triflic acid; 1.222 g (>99 %) from 1.012 g (3.64 mmol) of ethyl 4-fluoro-3-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate, 0.307 g (2.18 mmol) of 4-chlorobenzaldehyde and 0.048 mL (0.55 mmol) of triflic acid. Peach solid; mp 118–119 °C (with decomposition). NMR spectra of the sample show the presence of several stable rotamers and are complex due to overlap of the similar signals. Groups of peaks related to the similar protons and carbons are described as multiplets. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45–9.75 (m, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.65–7.57 (m, 2H), 7.56–7.45 (m, 4H), 7.32 (d, J = 8.4 Hz, 2H), 7.15 (br s, 2H), 6.00–5.78 (m, 1H), 4.00–3.72 (m, 4H), 0.92 (br s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5–160.9 (m), 149.4, 146.9 (dm, $^1J_{CF}$ = 244.8 Hz), 137.1–136.7 (m), 133.7, 133.6, 132.5, 129.2, 128.9, 126.1, 124.5, 118.8 (dm, $^2J_{CF}$ = 21.8 Hz), 115.4–115.1 (m), 115.1–114.8 (m), 114.5–113.6 (m), 61.23 (s), 36.2–35.1 (m), 13.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −164.69 (s), −164.90 (s), −165.77 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{26}^{35}ClF_2N_4O_8$ 679.1402; found 679.1408.

Diethyl 5,5'-((4-chlorophenyl)methylene)bis(4-fluoro-3-(3-nitrophenyl)-1*H*-pyrrole-2-carboxylate) (**2n**). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.086 g (99 %). Peach waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.95 (s, 2H), 8.22 (s, 2H), 8.13 (ddd, J = 8.3, 2.2, 0.9 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.43–7.27 (m, 6H), 5.79 (s, 1H), 4.16 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^4J_{CF}$ = 2.9 Hz), 147.8, 146.9 (d, $^1J_{CF}$ = 247.2 Hz), 136.6, 136.3, 134.0, 131.8 (d, $^3J_{CF}$ = 2.5 Hz), 129.6, 129.2, 128.5, 125.4, 122.5, 119.8 (d, $^2J_{CF}$ = 20.2 Hz), 115.9 (d, $^2J_{CF}$ = 10.3 Hz), 114.7 (d, $^3J_{CF}$ = 3.5 Hz), 62.0, 37.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.48 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{26}^{35}ClF_2N_4O_8$ 679.1402; found 679.1400.

Diethyl 5,5'-((4-bromophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (**2o**). Eluent: Hex/DCM (1:1), Hex/DCM (1:2), DCM. Yield: 0.065 g (94 %). Peach solid; mp 250–252 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.17 (s, 2H), 7.46 (s, 4H), 7.25–7.13 (m, 8H), 5.69 (s, 1H), 4.02 (q, J = 6.9 Hz, 4H), 1.04 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^4J_{CF}$ = 2.9 Hz), 146.9 (d, $^1J_{CF}$ = 246.1 Hz), 137.7, 133.6, 132.0, 131.8, 130.1, 128.6 (d, $^3J_{CF}$ = 2.5 Hz), 127.8, 121.8, 120.0 (d, $^2J_{CF}$ = 19.8 Hz), 117.3 (d, $^2J_{CF}$ = 10.2 Hz), 113.9 (d, $^3J_{CF}$ = 3.8 Hz), 61.6, 38.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.21 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{26}^{79}Br^{35}Cl_2F_2N_2O_4$ 701.0416; found 701.0406.

Diethyl 5,5'-((2,6-dichlorophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (**2p**). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.070 g (99 %) from 0.055 g (0.20 mmol) of ethyl 3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate, 0.022 g (0.12 mmol) of 2,6-dichlorobenzaldehyde and 0.003 mL (0.03 mmol) of triflic acid; 0.192 g (92 %) from 0.161 g (0.60 mmol) of ethyl 3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate, 0.063 g (0.36 mmol) of 2,6-dichlorobenzaldehyde and 0.008 mL (0.09 mmol) of triflic acid. Pink solid; mp 234–237 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.01 (br s, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.26–7.14 (m, 9H), 6.71 (s, 1H), 4.16–3.94 (m, 4H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (d, $^4J_{CF}$ = 2.3 Hz), 146.5 (d, $^1J_{CF}$ = 246.0 Hz), 136.0, 132.9, 132.0, 131.5, 129.3, 128.8, 128.5 (d, $^3J_{CF}$ = 2.3 Hz), 127.3, 117.0, 116.2 (d, $^2J_{CF}$ = 10.4 Hz), 113.6 (d, $^3J_{CF}$ = 3.7 Hz), 60.9, 35.5, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −166.16 (s). HRMS (ESI) *m/z*: $[M - H]^-$ calcd. for $C_{33}H_{23}^{35}Cl_4F_2N_2O_4$ 689.0385; found 689.0381.

Diethyl 5,5'-(phenylmethylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (**2q**). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (10:1). Yield: 0.053 g (91 %). Pale pink solid; mp 216–218 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.92 (br s, 2H), 7.48–7.40 (m, 8H), 7.40–7.33 (m, 2H), 7.33–7.26 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 5.83 (s, 1H), 4.15 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 160.2, 146.2 (d, $^1J_{CF}$ = 243.3 Hz), 139.2, 132.0, 131.9, 129.6, 128.6, 127.7, 127.7, 127.1, 119.5 (d, $^2J_{CF}$ = 19.6 Hz), 115.4 (d, $^2J_{CF}$ = 10.1 Hz), 113.9 (d, $^3J_{CF}$ = 2.6 Hz), 60.0, 36.2, 14.1. ^{19}F NMR (376 MHz, DMSO-d_6): δ −169.99 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{27}^{35}Cl_2F_2N_2O_4$ 623.1310; found 623.1306.

Diethyl 5,5'-(*o*-tolylmethylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (**2r**). Eluent: Hex/DCM (1:1), DCM. Yield: 0.069 g (97 %). Peach solid; mp 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.95 (br s, 2H), 7.66–7.58 (m, 1H), 7.27–7.15 (m, 11H), 5.99 (s, 1H), 4.13–3.99 (m, 4H), 2.50 (s, 3H), 1.05 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.1 (d, $^4J_{CF}$ = 2.9 Hz), 146.8 (d, $^1J_{CF}$ = 245.7 Hz), 136.7, 135.9, 133.5, 131.9, 130.8, 128.8 ($^3J_{CF}$ = 2.6 Hz), 128.7, 127.8, 127.8, 126.6, 120.3 (d, $^2J_{CF}$ = 20.0 Hz), 117.2 (d, $^2J_{CF}$ = 10.3 Hz), 113.7 ($^3J_{CF}$ = 3.7 Hz), 61.5, 35.0, 19.8, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.97 (s, 2 F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{34}H_{29}^{35}Cl_2F_2N_2O_4$

637.1467; found 637.1473.

Diethyl 5,5'-((4-(*tert*-butyl)phenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2s). Eluent: Hex/DCM (1:2), DCM. Yield: 0.067 g (>99 %). Peach solid; mp 204–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.43 (s, 2H), 7.40–7.30 (m, 8H), 7.27 (d, J = 8.4 Hz, 4H), 5.78 (s, 1H), 4.05 (q, J = 7.1 Hz, 4H), 1.31 (s, 9H), 1.08 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.8 (d, $^{4}J_{CF}$ = 3.1 Hz), 150.8, 146.8 (d, $^{1}J_{CF}$ = 245.3 Hz), 135.2, 133.5, 131.9, 129.0 (d, $^{3}J_{CF}$ = 2.3 Hz), 127.9, 127.8, 125.9, 120.0 (d, $^{2}J_{CF}$ = 21.3 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.8 Hz), 114.1 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.2, 37.6, 34.6, 31.4, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −166.24 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{37}H^{35}_{35}Cl_2F_2N_2O_4$ 679.1936; found 679.1944.

Diethyl 5,5'-((4-methoxyphenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2t). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.103 g (85 %) from 0.099 g (0.37 mmol) of ethyl 3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate, 0.030 g (0.22 mmol) of 4-methoxybenzaldehyde and 0.005 mL (0.06 mmol) of triflic acid; 0.209 g (86 %) from 0.199 g of ethyl 3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate, 0.061 g (0.45 mmol) of 4-methoxybenzaldehyde and 0.010 mL (0.11 mmol) of triflic acid. Pale pink solid; mp 199–201 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.90 (br s, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 4H), 7.22 (d, J = 8.6 Hz, 4H), 6.87 (d, J = 8.7 Hz, 2H), 5.73 (s, 1H), 4.06 (q, J = 7.1 Hz, 4H), 3.79 (s, 3H), 1.06 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.1 (d, $^{4}J_{CF}$ = 2.8 Hz), 159.1, 146.8 (d, $^{1}J_{CF}$ = 245.6 Hz), 133.5, 131.9, 130.5, 129.4, 128.8 (d, $^{3}J_{CF}$ = 2.2 Hz), 127.8, 120.6 (d, $^{2}J_{CF}$ = 20.0 Hz), 117.2 (d, $^{2}J_{CF}$ = 10.4 Hz), 114.2, 113.8 (d, $^{3}J_{CF}$ = 3.9 Hz), 61.4, 55.3, 38.0, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.94 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{34}H^{35}_{29}Cl_2F_2N_2O_5$ 653.1416; found 653.1396.

Diethyl 5,5'-((4-(trifluoromethyl)phenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2u). Eluent: Hex/DCM (1:2), DCM. Yield: 0.061 g (90 %). Pale pink solid; mp 242–245 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.25 (s, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.23–7.13 (m, 8H), 5.79 (s, 1H), 4.03 (q, J = 7.1 Hz, 4H), 1.04 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^{4}J_{CF}$ = 2.8 Hz), 147.0 (d, $^{1}J_{CF}$ = 246.2 Hz), 142.5, 133.7, 131.8, 130.1 (q, $^{2}J_{CF}$ = 32.3 Hz), 128.8, 128.5 (d, $^{3}J_{CF}$ = 2.3 Hz), 127.9, 125.9 (q, $^{3}J_{CF}$ = 3.6 Hz), 124.1 (q, $^{1}J_{CF}$ = 272.2 Hz), 119.7 (d, $^{2}J_{CF}$ = 19.8 Hz), 117.4 (d, $^{2}J_{CF}$ = 10.3 Hz), 114.1 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.7, 39.1, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.49 (s, F), −165.00 (s, 2 F). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{34}H^{35}_{26}Cl_2F_5N_2O_4$ 691.1184; found 691.1188.

Diethyl 5,5'-((4-(methoxycarbonyl)phenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2v). Eluent: Hex/DCM (1:5), DCM, DCM/EtOAc (10:1). Yield: 0.058 g (86 %). Pale peach solid; mp 192–195 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.22 (s, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.23–7.13 (m, 8H), 5.78 (s, 1H), 4.04 (q, J = 6.8 Hz, 4H), 3.90 (s, 3H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.8, 162.2 (d, $^{4}J_{CF}$ = 2.8 Hz), 147.0 (d, $^{1}J_{CF}$ = 246.3 Hz), 143.6, 133.6, 131.8, 130.3, 129.6, 128.5 (d, $^{3}J_{CF}$ = 2.6 Hz), 128.5, 127.8, 119.7 (d, $^{2}J_{CF}$ = 20.0 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.2 Hz), 114.0 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.6, 52.3, 39.2, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −165.10 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{35}H^{35}_{29}Cl_2F_2N_2O_6$ 681.1365; found 681.1375.

Diethyl 5,5'-((4-cyanophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2w). Eluent: Hex/DCM (1:5), DCM, DCM/EtOAc (20:1). Yield: 0.063 g (95 %). Pink solid; mp 248–250 °C (with decomposition). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.04 (br s, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.46–7.40 (m, 8H), 7.37 (d, J = 8.3 Hz, 2H), 5.93 (s, 1H), 4.15 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 160.1, 146.3 (d, $^{1}J_{CF}$ = 244.1 Hz), 144.8, 132.6, 132.1, 132.0, 129.4, 129.0, 127.8, 118.8, 117.9 (d, $^{2}J_{CF}$ = 19.8 Hz), 115.6 (d, $^{2}J_{CF}$ = 10.2 Hz), 114.1 (d, $^{3}J_{CF}$ = 2.0 Hz), 110.0, 60.2, 36.8, 14.1. ^{19}F NMR (376 MHz, DMSO-d_6): δ = −169.26 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{34}H^{35}_{26}Cl_2F_2N_3O_4$ 648.1263; found 648.1259.

Diethyl 5,5'-((4-nitrophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2x). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.242 g (97 %). Pink solid; mp 228–230 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.32 (s, 2H), 8.20 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 7.16 (s, 8H), 5.81 (s, 1H), 4.04 (q, J = 7.0 Hz, 4H), 1.05 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^{4}J_{CF}$ = 2.7 Hz), 147.5, 147.1 (d, $^{1}J_{CF}$ = 246.5 Hz), 145.7, 133.9, 131.8, 129.4, 128.2 (d, $^{3}J_{CF}$ = 2.4 Hz), 127.9, 124.3, 119.1 (d, $^{2}J_{CF}$ = 19.5 Hz), 117.4 (d, $^{2}J_{CF}$ = 10.3 Hz), 114.2 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.8, 39.3, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −164.64 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{33}H^{35}_{26}Cl_2F_2N_3O_6$ 668.1161; found 668.1164.

Diethyl 5,5'-((2-nitrophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2y). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.060 g (91 %). Pale pink solid; mp 107–110 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.35 (s, 2H), 7.99 (dd, J = 8.2, 1.1 Hz, 1H), 7.88–7.81 (m, 1H), 7.59–7.40 (m, 2H), 7.20–7.11 (m, 8H), 6.54 (s, 1H), 4.00 (q, J = 7.1 Hz, 4H), 1.02 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^{4}J_{CF}$ = 2.9 Hz), 148.8, 147.2 (d, $^{1}J_{CF}$ = 246.7 Hz), 133.7, 133.4, 133.3, 131.8, 131.5, 128.8, 128.4 (d, $^{3}J_{CF}$ = 2.1 Hz), 127.8, 125.0, 119.1 (d, $^{2}J_{CF}$ = 19.4 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.2 Hz), 114.1 (d, $^{3}J_{CF}$ = 3.6 Hz), 61.7, 34.1, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.28 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{33}H^{35}_{26}Cl_2F_2N_3O_6$ 668.1161; found 668.1149.

Diethyl 5,5'-((3-nitrophenyl)methylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2z). Eluent: Hex/DCM (1:2), DCM. Yield: 0.040 g (58 %). Peach solid; mp 218–220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.46 (s, 2H), 8.52 (s, 1H), 8.16 (dd, J = 8.2, 1.2 Hz, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.15 (s, 8H), 5.83 (s, 1H), 4.08 (q, J = 7.1 Hz, 4H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^{4}J_{CF}$ = 2.8 Hz), 148.9, 147.1 (d, $^{1}J_{CF}$ = 246.2 Hz), 140.6, 134.7, 133.8, 131.8, 129.9, 128.4 (d, $^{3}J_{CF}$ = 2.3 Hz), 127.9, 123.5, 123.0, 119.2 (d, $^{2}J_{CF}$ = 19.3 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.2 Hz), 114.3 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.9, 39.4, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −166.94 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{33}H^{35}_{26}Cl_2F_2N_3O_6$ 668.1161; found 668.1173.

Diethyl 5,5'-(thiophen-2-ylmethylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2aa). Eluent: Hex/DCM (1:1), Hex/DCM (1:4), Hex/DCM (1:5). Yield: 0.097 g (81 %). Pale peach solid; mp 208–210 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.53 (s, 2H), 7.39 (d, J = 8.4 Hz, 4H), 7.31 (d, J = 8.4 Hz, 4H), 7.25 (dd, J = 5.3, 1.5 Hz, 1H), 7.00 (d, J = 3.5 Hz, 1H), 6.96 (dd, J = 5.3, 3.5 Hz, 1H), 6.09 (s, 1H), 4.22–3.92 (m, 4H), 1.09 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.9 (d, $^{4}J_{CF}$ = 2.8 Hz), 146.5 (d, $^{1}J_{CF}$ = 245.7 Hz), 141.6, 133.6, 131.9, 128.8 (d, $^{3}J_{CF}$ = 2.5 Hz), 127.9, 127.1, 126.3, 125.6, 119.3 (d, $^{2}J_{CF}$ = 21.6 Hz), 117.2 (d, $^{2}J_{CF}$ = 10.6 Hz), 114.5 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.3, 32.8, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −166.29 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{31}H^{35}_{25}Cl_2F_2N_2O_4S$ 629.0875; found 629.0875.

Diethyl 5,5'-(naphthalen-2-ylmethylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2 ab). Eluent: Hex/DCM (2:1), Hex/DCM (1:2), Hex/DCM (1:4). Yield: 0.089 g (72 %). Red-orange solid; mp 213–215 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.10 (s, 2H), 7.94 (s, 1H), 7.88–7.79 (m, 3H), 7.73 (dd, J = 8.6, 1.4 Hz, 1H), 7.57–7.41 (m, 2H), 7.26 (d, J = 8.5 Hz, 4H), 7.20 (d, J = 8.5 Hz, 4H), 5.97 (s, 1H), 4.15–3.95 (m, 4H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^{4}J_{CF}$ = 2.9 Hz), 147.0 (d, $^{1}J_{CF}$ = 246.0 Hz), 135.9, 133.6, 133.5, 132.8, 131.9, 128.8, 128.8, 128.0, 127.8, 127.8, 127.1, 126.6, 126.4, 126.2, 120.3 (d, $^{2}J_{CF}$ = 20.2 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.4 Hz), 114.0 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.5, 38.9, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.60 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{37}H^{35}_{29}Cl_2F_2N_2O_4$ 673.1467; found 673.1464.

Diethyl 5,5'-(naphthalen-1-ylmethylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2ac). Eluent: Hex/DCM (1:2), DCM. Yield: 0.250 g (>99 %). Red-orange solid; mp 200–202 °C (with

decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.75 (br s, 2H), 8.24 (d, J = 8.3 Hz, 1H), 7.96–7.90 (m, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 7.1 Hz, 1H), 7.61–7.50 (m, 2H), 7.50–7.45 (m, 1H), 7.34 (d, J = 8.4 Hz, 4H), 7.28–7.24 (m, 4H), 6.64 (s, 1H), 4.07 (q, J = 7.1 Hz, 4H), 1.06 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^{4}J_{CF}$ = 3.0 Hz), 146.8 (d, $^{1}J_{CF}$ = 245.9 Hz), 134.0, 133.9, 133.4, 131.8, 131.3, 129.2, 128.8 (d, $^{3}J_{CF}$ = 2.5 Hz), 128.8, 127.8, 126.9, 126.5, 126.0, 125.5, 122.8, 119.9 (d, $^{2}J_{CF}$ = 20.2 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.5 Hz), 114.1 (d, $^{3}J_{CF}$ = 3.6 Hz), 61.3, 34.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −165.65 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{37}H^{35}_{29}Cl_2F_2N_2O_4$ 673.1467; found 673.1459.

Diethyl 5,5'-(anthracen-9-ylmethylene)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2ad). Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (20:1). Yield: 0.063 g (87 %). Brown solid; mp 266–268 °C (with decomposition). NMR spectra of the sample show the presence of two stable rotamers and are complex due to overlap of the similar signals. Some groups of peaks related to the similar protons are described as multiplets. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (br s, 1H), 8.40 (br s, 1H), 8.37 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.69–7.59 (m, 4H), 7.58–7.51 (m, 2H), 7.47–7.40 (m, 4H), 7.39–7.34 (m, 2H), 5.05 (s, 2H), 4.06–3.93 (m, 4H), 1.12 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.1 (d, $^{4}J_{CF}$ = 2.9 Hz), 160.8 (d, $^{4}J_{CF}$ = 3.1 Hz), 148.3 (d, $^{1}J_{CF}$ = 246.6 Hz), 146.1 (d, $^{1}J_{CF}$ = 243.0 Hz), 133.6, 133.5, 132.0, 132.0, 131.8, 130.6, 130.1, 129.1 (d, $^{3}J_{CF}$ = 2.4 Hz), 129.1 (d, $^{3}J_{CF}$ = 2.8 Hz), 128.1, 128.0, 127.2, 127.1, 126.7, 124.0, 123.5, 123.5, 119.0 (d, $^{2}J_{CF}$ = 24.6 Hz), 117.3 (d, $^{2}J_{CF}$ = 10.2 Hz), 117.2 (d, $^{2}J_{CF}$ = 10.3 Hz), 116.8 (d, $^{2}J_{CF}$ = 25.0 Hz), 115.7 (d, $^{3}J_{CF}$ = 3.3 Hz), 113.8 (d, $^{3}J_{CF}$ = 3.7 Hz), 60.9, 60.6, 23.0, 23.0, 14.1, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −163.59 (s), −168.53 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{41}H^{35}_{31}Cl_2F_2N_2O_4$ 723.1623; found 723.1608.

Diethyl 5,5'-(ethane-1,1-diyl)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2ae). Eluent: Hex/DCM (1:5), DCM, DCM/EtOAc (50:1). Yield: 0.098 g (97 %). Pale yellow solid; mp 261–263 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.75 (s, 2H), 7.27 (d, J = 8.3 Hz, 4H), 7.22 (d, J = 8.6 Hz, 4H), 4.58 (q, J = 7.0 Hz, 1H), 4.07 (q, J = 7.1 Hz, 4H), 1.80 (d, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.1 (d, $^{4}J_{CF}$ = 3.2 Hz), 146.6 (d, $^{1}J_{CF}$ = 243.9 Hz), 133.5, 131.9, 129.0 (d, $^{3}J_{CF}$ = 2.5 Hz), 127.8, 122.1 (d, $^{2}J_{CF}$ = 21.3 Hz), 117.16 (d, $^{2}J_{CF}$ = 10.9 Hz), 113.4 (d, $^{3}J_{CF}$ = 3.8 Hz), 61.3, 27.8, 19.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −167.31 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{28}H^{35}_{25}Cl_2F_2N_2O_4$ 561.1154; found 561.1153.

Diethyl 5,5'-(2,2,2-trifluoroethane-1,1-diyl)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2af). Eluent: Hex/DCM (1:2), Hex/DCM (1:5), Hex/DCM (1:10). Yield: 0.041 g (71 %). Colorless solid; mp 214–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 2H), 7.44 (d, J = 8.3 Hz, 4H), 7.40–7.34 (m, 4H), 5.33 (q, J = 9.2 Hz, 1H), 4.27 (q, J = 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.6 (d, $^{4}J_{CF}$ = 2.9 Hz), 147.9 (d, $^{1}J_{CF}$ = 246.5 Hz), 133.9, 131.8, 128.4 (d, $^{3}J_{CF}$ = 2.3 Hz), 128.1, 124.2 (q, $^{1}J_{CF}$ = 281.4 Hz), 117.2 (d, $^{2}J_{CF}$ = 11.5 Hz), 116.2 (d, $^{3}J_{CF}$ = 3.6 Hz), 110.7 (d, $^{2}J_{CF}$ = 23.0 Hz), 61.6, 37.4 (q, $^{2}J_{CF}$ = 32.3 Hz), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −69.32 to −69.53 (m, 3 F), −165.51 (s, 2 F). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{28}H^{35}_{22}Cl_2F_5N_2O_4$ 615.0871; found 615.0871.

Diethyl 5,5'-(2-chloroethane-1,1-diyl)bis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2 ag). Eluent: Hex/DCM (1:1), Hex/DCM (1:3), Hex/DCM (1:5). Yield: 0.079 g (74 %). Pale yellow solid; mp 214–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.70 (s, 2H), 7.34–7.21 (m, 8H), 4.86 (t, J = 6.8 Hz, 1H), 4.22 (d, J = 6.9 Hz, 2H), 4.08 (q, J = 7.1 Hz, 4H), 1.07 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^{4}J_{CF}$ = 2.8 Hz), 147.5 (d, $^{1}J_{CF}$ = 244.9 Hz), 133.7, 131.9, 128.6 (d, $^{3}J_{CF}$ = 2.4 Hz), 127.9, 117.4 (d, $^{2}J_{CF}$ = 21.9 Hz), 117.1 (d, $^{2}J_{CF}$ = 11.0 Hz), 114.5 (d, $^{3}J_{CF}$ = 3.6 Hz), 61.5, 44.3, 36.1, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −165.69 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{28}H^{35}_{24}Cl_3F_2N_2O_4$ 595.0764; found 595.0772.

Diethyl 5,5′-methylenebis(3-(4-chlorophenyl)-4-fluoro-1*H*-pyrrole-2-carboxylate) (2ah). Eluent: DCM, DCM/EtOAc (50:1). Yield: 0.045 g (90 %). Pale yellow solid; mp 189–191 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.75 (s, 2H), 7.28–7.19 (m, 8H), 4.13 (s, 2H), 4.09 (q, J = 7.1 Hz, 4H), 1.08 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^{4}J_{CF}$ = 3.0 Hz), 147.2 (d, $^{1}J_{CF}$ = 243.4 Hz), 133.5, 131.9, 128.9 (d, $^{3}J_{CF}$ = 2.3 Hz), 127.8, 117.0 (d, $^{2}J_{CF}$ = 13.1 Hz), 116.9, 113.7 (d, $^{3}J_{CF}$ = 3.7 Hz), 61.4, 19.1, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −169.21 (s). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{27}H^{35}_{23}Cl_2F_2N_2O_4$ 547.0997; found 547.0982.

Preparation of dipyrromethene 3a. A solution of dipyrromethane **2a** (0.064 g, 0.10 mmol, 1 mol. equiv.) and DDQ (0.066 g, 0.29 mmol, 3 mol. equiv.) in DCM (6 mL) were placed in a vial G10 for the microwave reactor Monowave 200 (Anton-Paar). The vial was sealed with a septum and the reaction mixture was heated at 80 °C with stirring under microwave irradiation for 1.5 h. After completion of the reaction (^{19}F NMR spectroscopy control) the reaction mixture was concentrated under vacuum. The pure product **3a** was isolated by column chromatography on silica gel.

(Z)-**Ethyl 3-(4-chlorophenyl)-5-((4-chlorophenyl)(4-(4-chlorophenyl)-5-(ethoxycarbonyl)-3-fluoro-2*H*-pyrrol-2-ylidene)methyl)-4-fluoro-1*H*-pyrrole-2-carboxylate (3a)**. Eluent: Hex/DCM (1:3), DCM, DCM/EtOAc (10:1). Yield: 0.017 g (35 %). Dark red waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.78 (br s, 1H), 7.50–7.36 (m, 4H), 7.33 (s, 8H), 4.37 (q, J = 7.1 Hz, 4H), 1.35 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.1 (d, $^{4}J_{CF}$ = 1.5 Hz), 158.0 (d, $^{1}J_{CF}$ = 281.8 Hz), 142.2 (d, $^{4}J_{CF}$ = 1.8 Hz), 140.8 (d, $^{3}J_{CF}$ = 6.0 Hz), 136.6, 134.1, 131.0 (d, $^{4}J_{CF}$ = 1.0 Hz), 130.9, 130.4, 128.7, 128.3, 127.7 (d, $^{2}J_{CF}$ = 10.1 Hz), 127.5 (d, $^{3}J_{CF}$ = 3.4 Hz), 118.6 (d, $^{2}J_{CF}$ = 12.1 Hz), 61.9, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −133.35 (s). IR (KBr): ν 3273, 2987, 2956, 2926 (N–H), 2852, 1716 (C═O), 1643, 1592, 1571, 1558, 1517, 1492, 1480, 1467, 1419, 1411, 1399, 1379, 1330, 1296 (C–*O*–C), 1269, 1239, 1221, 1186, 1221, 1186, 1143, 1121, 1093, 1026, 1017, 975, 936, 870, 853, 832, 819, 791, 778, 750, 692, 687. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{33}H^{35}_{24}Cl_3F_2N_2O_4$ 655.0764; found 657.0730.

General procedure for preparation of BODIPYs 4. In a typical experiment a solution of a selected dipyrromethane **2** (0.1 mmol, 1 mol. equiv.) and DDQ (0.3 mmol, 3 mol. equiv.) in DCM (5 mL) were placed in a vial G10 for the microwave reactor Monowave 200 (Anton-Paar). The vial was sealed with a septum and the reaction mixture was heated at 80 °C with stirring under microwave irradiation for 1–3 h. After completion of the oxidation (^{19}F NMR spectroscopy control) the reaction mixture was cooled to room temperature. Next, triethylamine (0.141 mL, 1 mmol, 10 mol. equiv.) was added and the resulting mixture was stirred for 15 min. Afterwards, $BF_3{\cdot}Et_2O$ (0.185 mL, 1.5 mmol, 15 mol. equiv.) was added and the vial was purged with argon. The resulting mixture was heated at 80 °C with stirring under microwave irradiation for 1.5–3 h. After completion of the reaction (^{19}F NMR spectroscopy control), the reaction mixture was concentrated under vacuum with adding toluene to distill off the residual $BF_3{\cdot}Et_2O$. The pure product was isolated by column chromatography on silica gel using appropriate eluents.

2,8,10-Tris(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (4a). Eluent: Hex/DCM (1:5). Yield: 0.041 g (75 %). Brick red solid; mp 230–232 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 8.5 Hz, 4H), 4.40 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8, 159.1 (d, $^{1}J_{CF}$ = 284.5 Hz), 146.4, 144.7, 137.8, 134.8, 130.0, 130.0, 129.1, 129.0, 128.1 (d, $^{3}J_{CF}$ = 1.2 Hz), 126.2 (d, $^{3}J_{CF}$ = 1.2 Hz), 121.3 (d, $^{2}J_{CF}$ = 12.1 Hz), 117.6 (d, $^{2}J_{CF}$ = 10.2 Hz), 63.2, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.04 (s, 2 F), −141.72 (dd, J = 53.1, 25.5 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.27 (t, J = 26.5 Hz). IR (KBr): ν 3088, 3073, 2986, 2959, 2926, 2871, 2852, 1742 (C═O), 1595, 1570, 1558, 1534, 1491, 1476, 1446, 1413, 1389, 1385, 1323, 1274, 1255, 1206, 1193, 1160, 1113, 1096, 1051, 1012, 999, 970,

869, 845, 838, 783, 762, 756, 603. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{33}H_{22}^{11}B^{35}Cl_3F_4N_2NaO_4$ 725.0567; found 725.0577.

2,8-Bis(4-bromophenyl)-10-(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4b**). Eluent: Hex/DCM (2:1), Hex/DCM (1:2). Yield: 0.041 g (62 %). Red solid with a golden sheen; mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 6H), 7.43 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.3 Hz, 4H), 4.40 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8, 159.1 (d, $^1J_{CF}$ = 287.3 Hz), 146.4, 144.6, 137.8, 132.0, 130.2, 129.9, 129.1, 128.1, 126.6 (d, $^3J_{CF}$ = 1.8 Hz), 123.0, 121.3 (d, $^2J_{CF}$ = 12.2 Hz), 117.6 (d, $^2J_{CF}$ = 9.8 Hz), 63.2, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.93 (s, 2 F), −141.64 (dd, J = 52.8, 24.5 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ −2.26 (t, J = 26.8 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{33}H_{22}^{11}B^{79}Br_2^{35}ClF_4N_2NaO_4$ 812.9556; found 812.9551.

10-(4-Chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-2,8-diphenyl-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4c**). Eluent: Hex/DCM (1:1), Hex/DCM (1:2). Yield: 0.062 g (65 %). Burgundy solid with a golden sheen; mp 237–239 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.42–7.29 (m, 10H), 4.40 (q, J = 7.1 Hz, 4H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.0, 159.1 (d, $^1J_{CF}$ = 283.4 Hz), 146.0, 144.8, 137.6, 130.0, 129.0, 128.7, 128.6, 128.6, 128.3, 127.7 (d, $^3J_{CF}$ = 1.8 Hz), 121.3 (d, $^2J_{CF}$ = 11.3 Hz), 118.6 (d, $^2J_{CF}$ = 10.1 Hz), 63.0, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.50 (s, 2 F), −141.82 (dd, J = 53.6, 26.2 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ −2.22 (t, J = 27.0 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{33}H_{24}^{11}B^{35}ClF_4N_2NaO_4$ 657.1346; found 657.1335.

10-(4-Chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-2,8-di-*p*-tolyl-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4d**). Eluent: DCM. Yield: 0.049 g (55 %). Red solid with a golden sheen; mp 238–240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.47 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.1 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 4.40 (q, J = 7.1 Hz, 4H), 2.35 (s, 6H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.2, 159.0 (d, $^1J_{CF}$ = 282.4 Hz), 145.7, 144.8, 138.6, 137.5, 130.0, 129.4, 129.0, 128.4, 128.4, 124.7 (d, $^3J_{CF}$ = 2.0 Hz), 121.3 (d, $^2J_{CF}$ = 10.7 Hz), 118.6 (d, $^2J_{CF}$ = 10.7 Hz), 63.0, 21.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.88 (s, 2 F), −141.98 (dd, J = 53.8, 25.5 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ −4.53 (t, J = 27.1 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{35}H_{28}^{11}B^{35}ClF_4N_2NaO_4$ 685.1659; found 685.1648.

10-(4-Chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-2,8-bis(4-methoxyphenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4e**). Eluent: Hex/DCM (1:5), DCM. Yield: 0.098 g (67 %). Merlot solid; mp 216–218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.46 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.31–7.26 (m, 4H), 6.95–6.84 (m, 4H), 4.41 (q, J = 7.1 Hz, 4H), 3.80 (s, 6H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.2, 159.8, 158.8 (d, $^1J_{CF}$ = 283.0 Hz), 145.4, 144.7, 137.4, 130.0, 129.9, 128.9, 128.4, 121.2 (d, $^2J_{CF}$ = 12.5 Hz), 119.9 (d, $^3J_{CF}$ = 1.8 Hz), 118.3 (d, $^2J_{CF}$ = 10.6 Hz), 114.2, 62.9, 55.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −130.45 (s, 2 F), −142.07 (dd, J = 53.6, 25.2 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.25 (t, J = 27.1 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{35}H_{28}^{11}B^{35}ClF_4N_2NaO_6$ 717.1557; found 717.1566.

10-(4-Chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-2,8-bis(4-(trifluoromethyl)phenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4f**). Eluent: Hex/DCM (1:1), Hex/DCM (1:3). Yield: 0.064 g (69 %). Red solid; mp 245–247 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.2 Hz, 4H), 7.53 (d, J = 8.5 Hz, 2H), 7.50–7.42 (m, 6H), 4.42 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 159.4 (d, $^1J_{CF}$ = 285.2 Hz), 147.0, 144.8, 138.0, 131.4, 130.7 (q, $^2J_{CF}$ = 32.8 Hz), 129.9, 129.2, 129.0, 127.9, 125.7 (q, $^3J_{CF}$ = 3.4 Hz), 124.0 (q, $^1J_{CF}$ = 272.3 Hz), 121.4 (d, $^2J_{CF}$ = 12.0 Hz), 117.5 (d, $^2J_{CF}$ = 9.9 Hz), 63.3, 13.82. ^{19}F NMR (376 MHz, $CDCl_3$): δ −65.97 (s, 6 F), −130.47 (s, 2 F), −143.59 (dd, J = 52.0, 24.5 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.29 (t, J = 26.5 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{35}H_{22}^{11}B^{35}ClF_{10}N_2NaO_4$ 793.1094; found 793.1083.

10-(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-2,8-bis(4-(methoxycarbonyl)phenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4g**). Eluent: DCM, DCM/EtOAc (50:1), DCM/EtOAc (10:1). Yield: 0.062 g (65 %). Raspberry solid; mp 251–253 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 4H), 7.52 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.4 Hz, 4H), 4.40 (q, J = 7.1 Hz, 4H), 3.91 (s, 6H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.6, 160.7, 159.3 (d, $^1J_{CF}$ = 286.1 Hz), 146.7, 144.8, 137.9, 132.3 (d, J = 1.5 Hz), 130.1, 129.9, 129.9, 129.1, 128.5, 128.0, 121.4 (d, $^3J_{CF}$ = 11.2 Hz), 117.7 (d, $^2J_{CF}$ = 10.2 Hz), 63.2, 52.4, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.16 (s, 2 F), −141.47 (dd, J = 52.4, 22.4 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.23 (t, J = 26.0 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{37}H_{28}^{11}B^{35}ClF_4N_2NaO_8$ 773.1456; found 773.1476.

10-(4-Chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-2,8-bis(2-nitrophenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4h**). Eluent: DCM. Yield: 0.067 g (70 %). Red solid; mp 210–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, J = 8.1, 1.1 Hz, 2H), 7.65 (td, J = 7.5, 1.3 Hz, 2H), 7.57 (td, J = 8.0, 1.4 Hz, 2H), 7.53–7.44 (m, 4H), 7.37 (dd, J = 7.6, 1.2 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 1.15 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.3 (d, $^1J_{CF}$ = 284.7 Hz), 159.3, 148.5, 147.5, 143.7, 137.9, 133.3, 132.7, 130.1, 129.1, 128.0, 125.1, 123.6 (d, $^3J_{CF}$ = 0.9 Hz), 122.2 (d, $^2J_{CF}$ = 11.5 Hz), 117.0 (d, $^2J_{CF}$ = 11.6 Hz), 114.2, 62.7, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.03 (s, 2 F), −139.04 (br s, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.46 (t, J = 23.9 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{33}H_{22}^{11}B^{35}ClF_4N_4NaO_8$ 747.1048; found 747.1043.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-5H-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4i**). Eluent: DCM. Yield: 0.011 g (30 %). Carmine solid; mp 209–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.44–7.38 (m, 4H), 7.38–7.32 (m, 4H), 4.39 (q, J = 7.1 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5, 159.3 (d, $^1J_{CF}$ = 283.9 Hz), 145.6 (d, $^3J_{CF}$ = 4.2 Hz), 135.0, 130.1, 129.1, 126.1 (d, $^3J_{CF}$ = 1.5 Hz), 125.6, 123.1 (d, $^2J_{CF}$ = 21.7 Hz), 117.3 (d, $^2J_{CF}$ = 8.9 Hz), 63.2, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −138.16 (s, 2 F), −141.36 (dd, J = 51.1, 23.2 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.33 (t, J = 26.7 Hz). HRMS (ESI) *m/z*: $[M + NH_4]^+$ calcd. for $C_{27}H_{23}^{11}B^{35}Cl_2F_4N_3O_4$ 610.1089; found 610.1078.

10-(4-Bromophenyl)-2,8-bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4j**). Eluent: Hex/DCM (1:10). Yield: 0.036 g (72 %); Burgundy solid with a golden sheen; mp 234–235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.64 (m, 2H), 7.39–7.32 (m, 6H), 7.31–7.27 (m, 4H), 4.40 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8, 159.1 (d, $^1J_{CF}$ = 286.1 Hz), 146.4, 144.7, 134.8, 132.1, 130.1, 130.0, 129.0, 128.6, 126.14 (d, $^3J_{CF}$ = 1.4 Hz), 126.1, 121.2 (d, $^2J_{CF}$ = 12.3 Hz), 117.62 (d, $^2J_{CF}$ = 10.3 Hz), 63.2, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.97 (s, 2 F), −141.67 (dd, J = 53.2, 24.7 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ −4.54 (t, J = 26.7 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{33}H_{22}^{11}B^{79}Br^{35}Cl_2F_4N_2NaO_4$ 769.0061; found 769.0052.

2,8-Bis(4-chlorophenyl)-10-(2,6-dichlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-4-ium-5-uide (**4k**). Eluent: Hex/DCM (1:10), DCM. Yield: 0.040 g (64 %). Burgundy solid with a golden sheen; mp 286–288 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.39 (m, 3H), 7.35 (d, J = 8.6 Hz, 4H), 7.31 (d, J = 8.6 Hz, 4H), 4.43 (q, J = 7.1 Hz, 4H), 1.33 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.7, 159.0 (d, $^1J_{CF}$ = 284.5 Hz), 145.3 (d, $^3J_{CF}$ = 4.1 Hz), 140.3, 134.9, 133.8, 132.1, 130.0, 129.0, 128.5, 128.3, 126.0, 121.7 (d, $^2J_{CF}$ = 11.2 Hz), 117.5 (d, $^2J_{CF}$ = 9.1 Hz), 63.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −133.05 (s, 2 F), −141.95 (dd, J = 52.1, 23.4 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.28 (t, J = 26.2 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for

$C_{33}H_{21}^{11}B^{35}Cl_4F_4N_2NaO_4$ 759.0177; found 759.0193.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-phenyl-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4l**). Eluent: DCM. Yield: 0.009 g (27 %). Brick red solid; mp 232–234 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.46 (m, 5H), 7.36–7.27 (m, 8H), 4.40 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.9, 159.2 (d, $^1J_{CF}$ = 286.7 Hz), 148.1, 144.4, 134.7, 131.3, 130.0, 129.0, 128.7, 128.4, 128.3, 126.3 (d, $^3J_{CF}$ = 1.4 Hz), 121.5 (d, $^2J_{CF}$ = 10.7 Hz), 117.5 (d, $^2J_{CF}$ = 10.6 Hz), 63.1, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.95 (s, 2 F), −141.71 (dd, J = 53.7, 25.4 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ −4.50 (t, J = 26.9 Hz). HRMS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{33}H_{23}^{11}B^{35}Cl_2F_4N_2NaO_4$ 691.0956; found 691.0947.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-(*o*-tolyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4m**). Eluent: DCM. Yield: 0.048 g (74 %). Merlot solid with a golden sheen; mp 233–235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, J = 7.0 Hz, 1H), 7.37–7.26 (m, 11H), 4.42 (q, J = 7.1 Hz, 4H), 2.33 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 159.3 (d, $^1J_{CF}$ = 284.6 Hz), 147.6, 144.4, 135.4, 134.7, 130.7, 130.5, 130.0, 129.7, 129.0, 127.7, 126.2, 121.8 (d, $^2J_{CF}$ = 12.1 Hz), 117.4 (d, $^2J_{CF}$ = 9.7 Hz), 63.2, 19.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −130.92 (s, 2 F), −141.29 (ddd, J = 77.3, 52.6, 25.1 Hz, 1 F), −142.55 (ddd, J = 82.1, 54.2, 26.5 Hz, 1 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.29 (t, J = 26.8 Hz). HRMS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{34}H_{25}^{11}B^{35}Cl_2F_4N_2NaO_4$ 705.1113; found 705.1124.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-(4-(trifluoromethyl)phenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4n**). Eluent: Hex/DCM (1:2), Hex/DCM (1:10). Yield: 0.044 g (68 %). Raspberry solid with a golden sheen; mp 245–247 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.5 Hz, 4H), 4.41 (q, J = 7.1 Hz, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.7, 159.2 (d, $^1J_{CF}$ = 286.4 Hz), 145.4, 145.2, 134.9, 133.4, 133.0 (q, $^2J_{CF}$ = 33.2 Hz), 129.9, 129.1, 128.9, 126.0 (d, $^3J_{CF}$ = 1.7 Hz), 125.8 (q, $^3J_{CF}$ = 3.6 Hz), 123.7 (d, $^1J_{CF}$ = 272.7 Hz), 121.4 (d, $^2J_{CF}$ = 12.3 Hz), 117.7 (d, $^2J_{CF}$ = 9.8 Hz), 63.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.90 (s, 3 F), −128.98 (s, 2 F), −141.64 (dd, J = 51.9, 24.6 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.25 (t, J = 26.7 Hz). HRMS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{34}H_{22}^{11}B^{35}Cl_2F_7N_2NaO_4$ 759.0830; found 759.0825.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-(4-(methoxycarbonyl)phenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4o**). Eluent: DCM. Yield: 0.023 g (42 %). Brick red solid; mp 204–206 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.6 Hz, 4H), 7.27 (d, J = 9.5 Hz, 4H), 4.41 (q, J = 7.1 Hz, 4H), 3.96 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.2, 160.8, 159.2 (d, $^1J_{CF}$ = 286.8 Hz), 146.2, 145.0, 134.9, 134.2, 132.6, 130.0, 129.9, 129.0, 128.5, 126.1 (d, $^3J_{CF}$ = 1.7 Hz), 121.3 (d, $^2J_{CF}$ = 11.5 Hz), 117.7 (d, $^2J_{CF}$ = 10.7 Hz), 63.2, 52.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.98 (s, 2 F), −141.68 (dd, J = 52.1, 24.8 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.23 (t, J = 26.2 Hz). HRMS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{35}H_{25}^{11}B^{35}Cl_2F_4N_2NaO_6$ 749.1011; found 749.0997.

2,8-Bis(4-chlorophenyl)-10-(4-cyanophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4p**). Eluent: Hex/DCM (1:3), DCM. Yield: 0.024 g (53 %). Burgundy solid; mp 286–288 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 8.3 Hz, 4H), 4.41 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 159.1 (d, $^1J_{CF}$ = 286.4 Hz), 145.6, 144.3, 135.0, 132.5, 129.9, 129.2, 129.1, 128.4, 125.9, 121.1 (d, $^2J_{CF}$ = 11.5 Hz), 117.8 (d, $^2J_{CF}$ = 10.1 Hz), 117.7, 115.0, 63.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −128.23 (s, 2 F), −140.65 (dd, J = 52.4, 23.1 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ −2.25 (t, J = 26.1 Hz). HRMS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{34}H_{22}^{11}B^{35}Cl_2F_4N_3NaO_4$ 716.0909; found 716.0897.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-(4-nitrophenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4q**). Eluent: DCM. Yield: 0.039 g (72 %). Carmine solid; mp 285–286 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.37–7.32 (m, 4H), 7.27 (d, J = 8.5 Hz, 4H), 4.41 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 159.1 (d, $^1J_{CF}$ = 284.4 Hz), 149.4, 145.6, 143.9, 136.1, 135.0, 129.9, 129.7, 129.1, 125.8 (d, $^3J_{CF}$ = 1.5 Hz), 124.0, 121.2 (d, $^2J_{CF}$ = 13.8 Hz), 117.8 (d, $^2J_{CF}$ = 10.4 Hz), 63.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.27 (s, 2 F), −141.64 (dd, J = 51.7, 24.2 Hz, 2 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.22 (t, J = 26.1 Hz). HRMS (ESI) *m/z*: [M + NH_4]$^+$ calcd. for $C_{33}H_{26}^{11}B^{35}Cl_2F_4N_4O_6$ 731.1253; found 731.1274.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-(2-nitrophenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4r**). Eluent: Hex/DCM (1:10), DCM. Yield: 0.063 g (92 %). Burgundy solid with a golden sheen; mp 236–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 8.2, 1.0 Hz, 1H), 7.85 (td, J = 7.5, 1.2 Hz, 1H), 7.78 (td, J = 8.0, 1.4 Hz, 1H), 7.56 (dd, J = 7.6, 1.3 Hz, 1H), 7.36–7.31 (m, 4H), 7.29–7.23 (m, 4H), 4.41 (q, J = 7.1 Hz, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 158.8 (d, $^1J_{CF}$ = 282.7 Hz), 146.9, 144.8, 143.5, 134.8, 134.5, 131.8, 130.4, 130.0, 129.0, 126.0, 126.0, 125.6, 121.0 (d, $^2J_{CF}$ = 14.2 Hz), 117.5 (d, $^2J_{CF}$ = 9.6 Hz), 63.2, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −132.89 (s, 2 F), −140.25 to −140.97 (m, 1 F), −142.47 to −143.17 (m, 1 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.29 (t, J = 26.0 Hz). HRMS (ESI) *m/z*: [M + NH_4]$^+$ calcd. for $C_{33}H_{26}^{11}B^{35}Cl_2F_4N_4O_6$ 731.1253; found 731.1241.

2,8-Bis(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-1,5,5,9-tetrafluoro-10-(3-nitrophenyl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*] [1,3,2] diazaborinin-4-ium-5-uide (**4s**). Eluent: Hex/DCM (1:10), DCM. Yield: 0.016 g (57 %). Red-brown solid; mp 267–269 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 8.2 Hz, 1H), 8.40 (s, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.35 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H), 4.41 (q, J = 7.1 Hz, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 159.1 (d, $^1J_{CF}$ = 286.4 Hz), 148.3, 145.7, 143.5, 135.1, 134.3, 131.3, 130.1, 130.0, 129.1, 125.9 (d, $^3J_{CF}$ = 1.9 Hz), 125.8, 123.7, 121.4 (d, $^2J_{CF}$ = 11.7 Hz), 117.9 (d, $^2J_{CF}$ = 10.6 Hz), 63.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.55 (s, 2 F), −140.93 to −141.48 (m, 1 F), −141.75 to −142.48 (m, 1 F). ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.23 (t, J = 26.1 Hz). HRMS (ESI) *m/z*: [M+Na]$^+$ calcd. for $C_{33}H_{22}^{11}B^{35}Cl_2F_4N_3NaO_6$ 736.0807; found 736.0796.

CRediT authorship contribution statement

Roman V. Larkovich: Methodology, Investigation, Visualization, Formal analysis. **Victoria E. Shambalova:** Methodology, Investigation, Visualization, Formal analysis. **Savva A. Ponomarev:** Methodology, Investigation. **Alexander S. Aldoshin:** Conceptualization, Supervision, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Boris N. Tarasevich:** Investigation, Formal analysis, Validation, Writing – original draft. **Konstantin A. Lyssenko:** Investigation, Formal analysis, Validation, Writing – original draft. **Valentine G. Nenajdenko:** Conceptualization, Supervision, Project administration, Writing – original draft, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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