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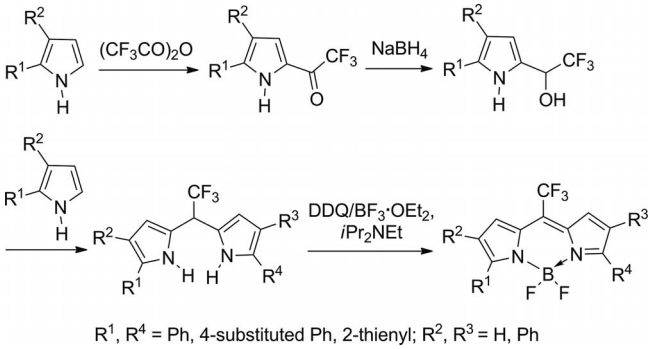
Synthetic Dyes

Keywords: Synthetic methods / Dyes/pigments / Nitrogen heterocycles / Fluorescence



R^1, R^4 = Ph, 4-substituted Ph, 2-thienyl; R^2, R^3 = H, Ph

A new strategy for the synthesis of highly efficient symmetric and asymmetric BODIPY fluorophores that combine trifluoromethyl and 3,5-aryl substituents has been developed. The key step is the P_2O_5-promoted condensation of 2,2,2-trifluoro-1-(5-arylpyrrol-2-yl)-1-ethanols with diverse 2-arylpyrroles.

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Synthesis and Optical Properties of Difluorobora-*s*-diazaindacene Dyes with Trifluoromethyl *meso*-Substituents

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A series of *meso*-CF_3-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes with aryl and hetaryl substituents at the C-3 and C-5 positions, both symmetric and asymmetric, have been synthesized in 36–90 % yields by a new strategy involving as the key step the condensation of 2,2,2-trifluoro-1-(5-arylpyrrol-2-yl)-1-ethanols with diverse 2-arylpyrroles. The starting 2,2,2-trifluoro-1-(5-arylpyrrol-2-yl)-1-ethanols are easily prepared by reduction of the available 2-trifluoroacetyl-5-arylpyrroles. The synthesized dyes fluoresce in a longer wavelength region (626–698 nm) with high quantum yield (0.84–0.99).

Introduction

BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) possess many distinctive and desirable properties such as high molar absorption coefficient, fluorescence quantum yields and long wavelength emission.[1] They have found numerous applications as optical chemosensors,[2] fluorescent biolabels,[3] light-harvesting molecules,[4] emitters in organic light-emitting diodes,[5] and light absorbers for solar cells.[6]

Biochemical applications of BODIPYs include conjugation with a variety of biomolecules such as lipids,[7] proteins,[8] DNA,[9] carbohydrates[10] and cholesterol.[11]

BODIPYs that absorb and emit in the near-infrared (NIR) region are efficiently used to visualize and investigate in vivo molecular targets.[12] Therefore, it is of applied interest to shift the absorption or fluorescence maximum of BODIPYs into the red or NIR region as far as possible and increasing simultaneously the quantum yield.

An efficient way to red-shift the absorption and emission maxima is to extend the conjugated π-system of the BODIPY molecule by introducing aromatic substituents in the 5- and/or 3-positions at the indacene core.[13] This approach allows both absorption and emission to be shifted by 100–200 nm towards red. Very important shifts towards the NIR end of the visible spectra have been recently achieved by introducing a strong electron acceptor such as pentafluorobenzene[14] or CF_3[15,16] at the *meso*-position of the BODIPY core, though the asymmetrical representatives with a *meso*-CF_3 moiety can only be synthesized by using a specific methodology.[16]

We have concisely reported that the presence of a CF_3 group in the *meso*-position of the BODIPY core does cause a deep bathochromic shift relative to congeners with other substituents in this position.[16] Despite this progress, synthesis of new *meso*-CF_3-BODIPY derivatives with aryl groups remains challenging because the fluorescence maxima of BODIPY strongly depend on the nature of the aryl substituent.[17]

Results and Discussion

The key step in the *meso*-CF_3-BODIPYs synthesis has been briefly outlined.[16] The step represents the P_2O_5-promoted condensation of available 2,2,2-trifluoro-1-(pyrrol-2-yl)-1-ethanols with pyrroles. It should be noted that this methodology makes it possible to synthesize both symmetrical and asymmetrical BODIPYs as opposed to other methods[14,15] affording exclusively symmetrical BODIPYs.

Inspired by this success, we have undertaken the synthesis of BODIPY derivatives combining aryl groups and a *meso*-CF_3 substituent.

We disclose herein the further development of the above-mentioned synthesis and describe the preparation of a variety of new *meso*-trifluoromethylated BODIPY dyes with aryl and heteroaryl substituents at the C-3 and C-5 positions. The synthesis starts from easily available 2-phenylpyrroles **1a**–**1g**, which have different substituents at the *p*-position of the benzene ring.

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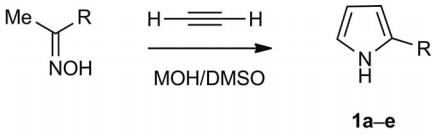
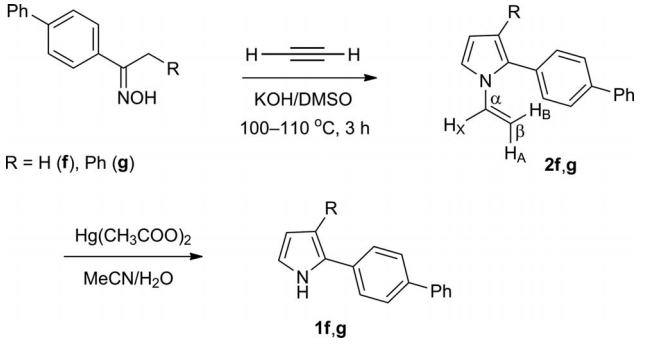
Pyrroles **1a**–**1e** are readily obtained from alkylarylketoximes and acetylene through the Trofimov reaction[18] in a one-pot procedure (Scheme 1).



Scheme 1. Synthesis of pyrroles **1a**–**1e**.

Previously unknown 2-[(1,1-biphenyl)-4-yl]pyrrole (**1f**) and 2-[(1,1-biphenyl)-4-yl]-3-phenylpyrrole (**1g**) have been synthesized by devinylation[19] of the corresponding *N*-vinyl derivatives **2f** and **2g**, which are the major products of the Trofimov reaction owing to rapid vinylation of the intermediate *NH*-pyrroles (Scheme 2).



Scheme 2. Synthesis of pyrroles **1f** and **1g**.

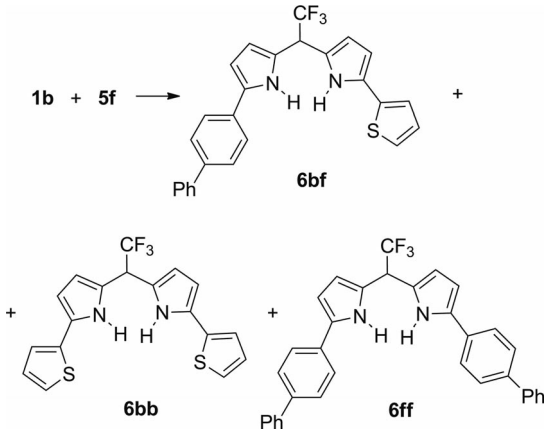
Scheme 3 shows the synthetic route to BODIPY dyes **3** from pyrroles **1a**–**1g**. The reaction sequence includes trifluoroacetylation of pyrroles **1c**–**1g** to afford 2-trifluoroacetylpyrroles **4c**–**4g**. The reduction products of pyrroles **4c**–**4g** with $NaBH_4$, 2,2,2-trifluoro-1-(pyrrol-2-yl)-1-ethanols **5c**–**5g**, reacted with pyrroles **1a**–**1g** in the presence of P_2O_5 (equimolar ratio) to give dipyrromethanes **6**. The latter are easily isolated and can be used as intermediates in syntheses of other compounds, in particular, porphyrins.[20]

Oxidation of dipyrromethanes **6** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and subsequent complexation of the resulting dipyrromethenes with BF_3 is realized as a one-pot procedure to furnish target BODIPY dyes **3** in 36–90% yields (Scheme 3, Table 1).

This general strategy allows, depending on the structure of pyrroles **1a**–**1g** and ethanols **5c**–**5g**, both symmetric and asymmetric BODIPY dyes **3** to be easily assembled.

Thus, the synthesis of asymmetric BODIPY dyes, which was a long-standing challenge, has been incidentally an elegantly overcome.

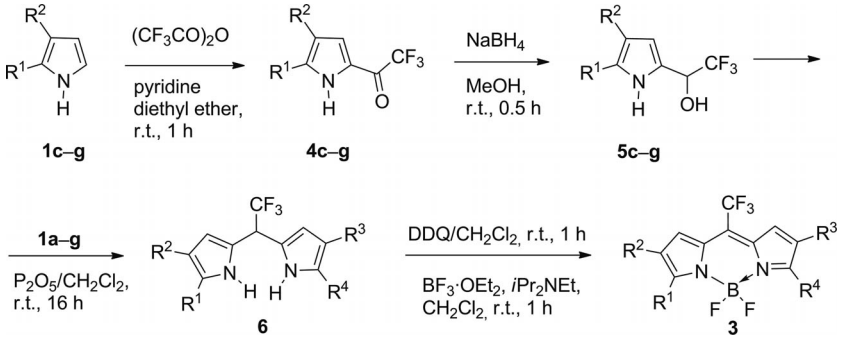
In some cases the synthesis of asymmetric dipyrromethanes is accompanied by the formation of insignificant quantities (2–3%) of two symmetric ones. For instance, dipyrromethanes **6bb** and **6ff** have been identified (^{19}F NMR spectroscopy) in the synthesis of the asymmetric dipyrromethane **6bf** (Scheme 4).



Scheme 4. The formation of dipyrromethanes **6bf**, **6bb** and **6ff**.

The formation of symmetric dipyrromethanes as minor products may be rationalized as follows: under the acidic conditions of the synthesis, the asymmetric dipyrromethanes (for instance **6bf**) disproportionate partially into pyrrole carbocations (**7b** and **7f**) and pyrroles (**1b** and **1f**; Scheme 5). Cation **7b** may attack pyrrole **1b** to afford symmetric dipyrromethane **6bb**. Analogously, attack of pyrrole **1f** at cation **7f** gives dipyrromethane **6ff**.

Another plausible pathway to symmetric dipyrromethanes, and hence to symmetric BODIPYs, may be the dissociation of starting pyrrolylethanols **5c**–**5g** to the free pyrrole and trifluoroacetaldehyde, the latter able to react with the two same pyrrole molecules (Scheme 6).



Scheme 3. Synthesis of BODIPY dyes **3**.

Table 1. Preparation of BODIPY dyes **3** from ethanols **5c**–**5g** and pyrroles **1a**–**1g** through Scheme 3.

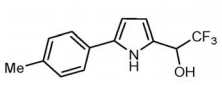
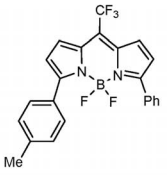
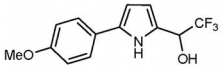
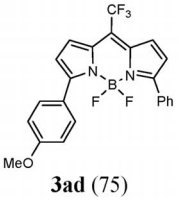
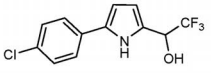
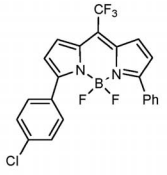
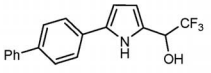
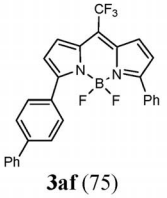
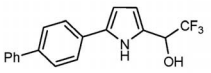
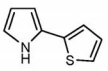
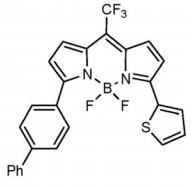
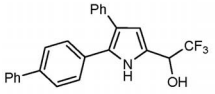
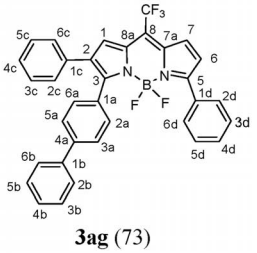
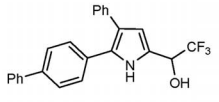
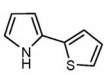
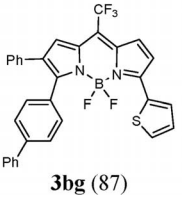
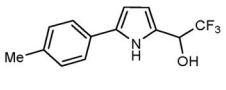
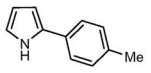
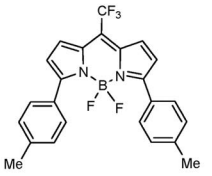
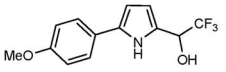
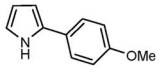
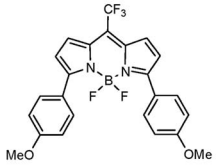
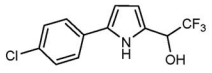
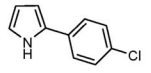
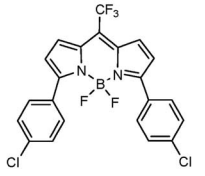
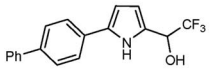
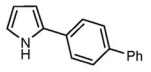
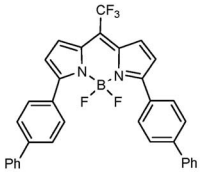
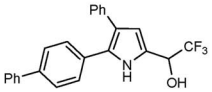
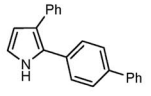
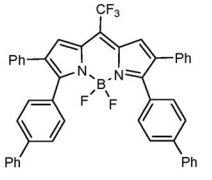
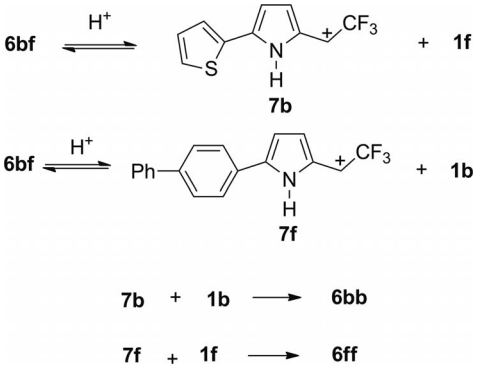
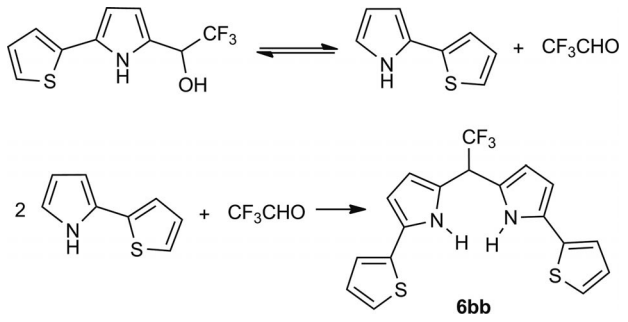
Ethanols **5c–g**	Pyrroles **1a–g**	BODIPYs **3** (yield, %)
 **5c**	 **1a**	 **3ac** (55)
 **5d**	 **1a**	 **3ad** (75)
 **5e**	 **1a**	 **3ae** (83)
 **5f**	 **1a**	 **3af** (75)
 **5f**	 **1b**	 **3bf** (79)
 **5g**	 **1a**	 **3ag** (73)
 **5g**	 **1b**	 **3bg** (87)

Table 1. (*Continued*).

Ethanols **5c–g**	Pyrroles **1a–g**	BODIPYs **3** (yield, %)
 **5c**	 **1c**	 **3cc** (89)
 **5d**	 **1d**	 **3dd** (57)
 **5e**	 **1e**	 **3ee** (88)
 **5f**	 **1f**	 **3ff** (36)
 **5g**	 **1g**	 **3gg** (90)



Scheme 5. Proposed symmetrisation of dipyrromethanes **6bb** and **6ff**.



Scheme 6. Alternative pathway to symmetric dipyrromethane **6bb** (dipyrromethane **6ff** is formed analogously).

Figure 1 depicts the absorption and fluorescence spectra of synthesized dyes **3cc**, **3ff** and **3bf**. The spectra show intense long-wave absorption bands and almost symmetrical corresponding fluorescence bands. Detailed spectroscopic and photophysical characteristics of BODIPY dyes **3** including lifetime (τ_f), fluorescence rate constant (k_f, $k_f = 1/\tau_f$) as well as rate constants of radiative (k_r) and non-radiative (k_{nr}) deactivation are given in Table 2. The same data for 4,4-difluoro-3,5-diphenyl-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (**3aa**) synthesized earlier[16] are also given in Table 2 and Figure 1.

Simple, "transparent", substituents (-Cl, -CH_3, -OCH_3) in the *p*-position of the benzene ring do not change the general character of absorption and fluorescence spectra. Nevertheless, the bands maxima are progressively shifted towards the red region according to the electron-donating ability of the substituents (Cl < CH_3 < OCH_3) and their number (Table 2). Relative to known *meso*-4′-iodophenyl-BODIPYs[13a] bearing the same substituents in the C-3 and C-5 positions, dyes **3** absorb and emit in longer-wave regions and have much higher Φ_f values. For example, 4,4-difluoro-8-(4′-iodophenyl)-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene has $\lambda_{max,abs}$ = 558 nm, $\lambda_{max,fl}$ = 592 nm and Φ_f = 0.15,[13a] whereas BODIPY dye **3aa** has $\lambda_{max,abs}$ = 586 nm, $\lambda_{max,fl}$ = 626 nm and Φ_f = 0.74 and 4,4-difluoro-8-(4′-iodophenyl)-3,5-bis(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene has $\lambda_{max,abs}$ = 585 nm, $\lambda_{max,fl}$ = 629 nm, Φ_f = 0.33,[13a] and **3dd** has $\lambda_{max,abs}$ = 616 nm, $\lambda_{max,fl}$ = 665.5 nm, Φ_f = 0.98. On average, replacing a 4′-iodophenyl substituent by a CF_3 group in the *meso*-position leads to a shift in the most long-wave absorption band and fluorescence band by ca. 900 cm^{-1}. Replacement of the *meso*-aryl with a trifluoromethyl moiety reduces the non-radiative decay through rotation, and leads to fluorophores with higher quantum yields.[15b]

The extension of the π-system owing to the increase in number of phenyl substituents in the BODIPY molecules also favors the red shift of the absorption and fluorescence bands (BODIPY **3ff**, **3ag**, **3bg**, **3gg**; Table 2). At the same time, asymmetric BODIPYs have decreased red-shift values.

Relative to BODIPY **3af** and **3ag**, their thienyl analogs **3bf** and **3bg** absorb and fluoresce at longer wave lengths, their absorption and fluorescent bands are narrower and they have lower $\Delta\nu_{St}$ values. The aforementioned changes in

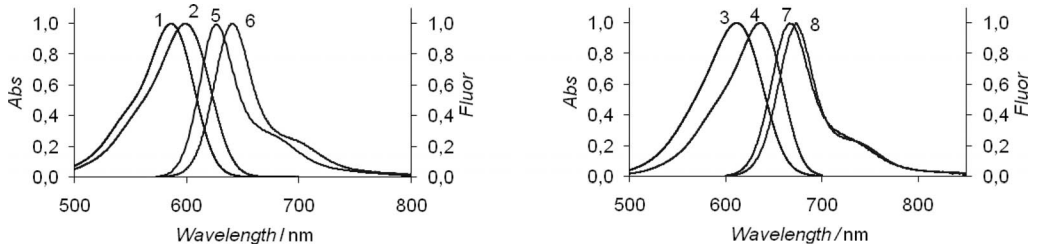


Figure 1. Normalized absorption (1–4) and fluorescence spectra (5–8) of BODIPYs **3aa** (1, 5), **3cc** (2, 6), **3ff** (3,7) and **3bf** (4, 8) in MeCN.

Table 2. Spectroscopic and photophysical data of BODIPYs **3** recorded in MeCN at 22 °C.

BODIPY	$\lambda_{max,abs}$ [nm]	Absorption coefficient (ε [$M^{-1}cm^{-1}$])	$\lambda_{max,fl}$ [nm]	$\lambda_{max,ex}$ [nm]	Stokes shift ($\Delta\nu_{St}$ [cm^{-1}])	τ_f [ns]	Fluorescence quantum yield (Φ_f)[a]	$k_f \times 10^9$ [s^{-1}]	$k_r \times 10^9$ [s^{-1}][b]	$k_{nr} \times 10^9$ [s^{-1}][c]
3aa[16]	586	46000	626.0	586	1090	6.4	0.74	0.16	0.12	0.04
3ac	593	57800	632.5	592	1050	6.2	0.92	0.16	0.15	0.01
3cc	599	56400	640.5	598	1080	6.2	0.88	0.16	0.14	0.02
3ad	606	55700	650.5	606	1130	5.7	0.89	0.18	0.16	0.02
3dd	616	57200	665.5	617	1180	5.7	0.98	0.18	0.17	0.01
3ae	589	55700	629.0	588	1080	6.3	0.89	0.16	0.14	0.02
3ee	592	56800	634.0	592	1120	6.3	0.89	0.16	0.14	0.02
3af	599	54500	646.5	598	1200	5.9	0.88	0.17	0.15	0.02
3bf	636	57600	674.0	635	890	5.6	0.84	0.18	0.15	0.03
3ff	612	55800	667.0	611	1350	5.7	0.91	0.18	0.16	0.02
3ag	613	53000	673.0	614	1450	0.6	0.05	1.67	0.08	1.59
3bg	644	52300	688.5	643	1000	1.2	0.13	0.83	0.11	0.72
3gg	637	52000	698.0	638	1370	1.0	0.07	1.00	0.07	0.93

[a] Nile blue as standard [Φ_f = 0.27, 0.5% (v/v) 0.1 M HCl in ethanol]. [b] $k_r = \Phi_f/\tau_f$. [c] $k_{nr} = \tau_f^{-1} - k_r$.

spectroscopic characteristics indicate a more planar structure for the thienyl-containing BODIPY, likely owing to lower steric hindrance from the five-membered thienyl ring.[16,21]

Of special interest is the dependence of value rate constants k_r and k_{nr} on the presence or absence of the phenyl substituents conjugated with the BODIPY core in the 2 and/or 6 positions. The BODIPYs containing no such substituents have $k_r >> k_{nr}$, and their $\Phi_f = (k_r/k_r + k_{nr})$ values are close to 1. However compounds **3ag**, **3bg** and **3gg** bearing substituents possess approximately two-times lower k_r values and 40-times higher k_{nr} constants. For these BODIPYs, radiative transitions are much less probable than non-radiative deactivation and they have low Φ_f values (Table 2).

Apparently, the main cause for the drop of k_r value and increase of k_{nr} value is the decrease of **3ag**, **3bg** and **3gg** planarity in the S_0 and S_1 states from steric strain between bulky phenyl substituents. This is supported by high $\Delta\nu_{St}$ and half-width absorption band values as well as by quantum-chemical calculations of similar systems.[16] The drop of k_r values with the decrease of planarity is a natural consequence of weakening of the π-orbitals interaction, and growth of k_{nr} values results from non-radiative losses owing to significant changes of torsion angles in the S_1 state.

These inferences are in accordance with quantum-chemical calculations of BODIPY **3af** and **3ag**, which have been selected as molecules containing or not containing phenyl substituents at the 2 position. Geometries for the molecules in the S_0 state were optimized by using the RI-DFT/BP86/def2-TZVP method. Energies of $S_0 \rightarrow S_i$ (i = 1–3) transitions were determined by using a time-dependent DFT (TDDFT) method RI-TD-BP86/def2-TZVP based on the optimized geometries of the S_0 state. To decrease the calculation time the resolution identity (RI) was applied.

Optimized structures **3af** and **3ag** and calculated values of excitation energy are given in Figure 2 and Table 3, respectively. Both molecules have an almost planar structure for the BODIPY core with a tetragonal boron atom, two fluorine atoms perpendicular to the BODIPY plane and phenyl substituents deviated from the BODIPY skeleton. In compound **3af**, the torsion angle between the BODIPY plane and biphenyl fragment is ca. 30°. The introduction of another phenyl substituent in the 2 position (compound **3ag**) increases this angle up to ca. 50°, whereas the torsion angle between the phenyl moieties in the biphenyl fragments remains the same (ca. 36°; Figure 2). Thus, based on the phenyl substituent size it can be concluded the biphenyl fragment of BODIPY **3ag** is significantly twisted from the molecule plane relative to compound **3af**. The phenyl substituent itself in the 2 position deviates from the BODIPY core by ca. 40°.

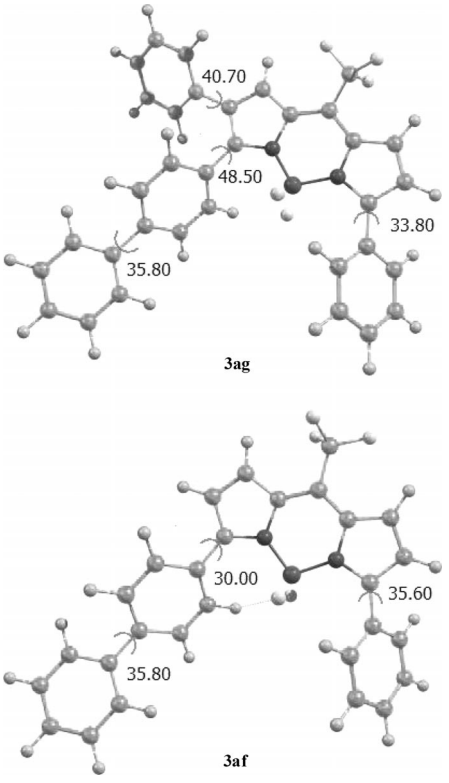


Figure 2. Optimized structures of BODIPY **3af** and **3ag** in state S_0 according to RI-BP86/def2-TZVP.

The increase in torsion angle between the BODIPY core and biphenyl moiety should lead to a hypsochromic shift of the absorption band of compound **3ag** relative to **3af** owing to the partial loss of conjugation. However, experimentally (Table 2) a bathochromic shift is observed. Probably, any hypsochromic shift is compensated for by the bathochromic shift exerted by the phenyl substituent in the 2 position.

The calculated (on the basis of optimized geometries) energy values of vertical $S_0 \rightarrow S_1$ transitions for compounds **3af** and **3ag** are 614.1 and 642.6 nm, respectively (Table 3) and are in good agreement with experimental data: 599 (**3af**) and 614 nm (**3ag**) (Table 2). Theoretical values of excitation energies and oscillator strength allow one to evaluate the radiation rate constants for emission of **3af** and **3ag** by using the Einstein transition probabilities[22] (au): $k_r = 2E^2 f/c^3$, in which c is the velocity of light, E is the transition

Table 3. Excitation energies and oscillator strength of BODIPY **3af** and **3ag** in the gas phase (RI-TD-BP86/def2-TZVP).

BODIPY	Transition	Energy [eV]	λ [nm]	f	Main configuration	Coefficient [%]
3af	$S_0 \rightarrow S_1$	2.02	614.1	0.48	HOMO–LUMO	75.8
	$S_0 \rightarrow S_2$	2.48	500.6	0.23	HOMO–1–LUMO	72.8
	$S_0 \rightarrow S_3$	2.59	479.0	0.0001	HOMO–2–LOMO	96.6
3ag	$S_0 \rightarrow S_1$	1.93	642.6	0.35	HOMO–LUMO	68.2
	$S_0 \rightarrow S_2$	2.16	573.7	0.09	HOMO–1–LUMO	64.6
	$S_0 \rightarrow S_3$	2.49	498.7	0.12	HOMO–3–LUMO	53.6

energy, and *f* is the oscillator strength. The theoretical value of k_r (**3af**)/k_r (**3ag**), is 1.5, which correlates well with the experimental value (1.9).

It should be noted that attempts to evaluate the excitation-induced changes in geometries of BODIPY **3af** and **3ag** have not met with success at this stage. Geometry optimization (TDDFT) of both molecules in the excited S_1 state give a structure with an orthogonal location for the biphenyl fragment and an almost forbidden $S_1 \rightarrow S_0$ transition ($f \approx 0.001$) and unreal low fluorescence energy values (ca. 1000 nm) that contradict the experimental data.

Conclusions

In conclusion, an expedient strategy for the synthesis of highly efficient BODIPY fluorophores that combine trifluoromethyl and 3,5-aryl or heteroaryl substituents fluorescing in the 626–698 nm region with quantum yields close to unity has been developed. The key step of the strategy is the P_2O_5-promoted condensation of readily accessible 2,2,2-trifluoro-1-(5-arylpyrrol-2-yl)-1-ethanols with diverse 2-arylpyrroles. Additionally, the strategy proved to be an easy and general route to previously inaccessible asymmetric BODIPY fluorophores.

Experimental Section

General: IR spectra were obtained with a Bruker IFS-25 spectrometer (400–4000 cm^{-1}, KBr pellets). ^1H (400.1 MHz), ^{13}C (100.6 MHz), ^{19}F (376.5 MHz) and ^{15}N (40.5 MHz) NMR spectra were recorded with a Bruker Avance 400 instrument in $CDCl_3$ and [D_6]DMSO. The assignment of signals in the ^1H NMR spectra was made by using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^1H–^{13}C HSQC and ^1H–^{13}C HMBC experiments. Chemical shifts for ^{15}N NMR spectra were measured through 2D ^1H–^{15}N HMBC experiments. The ^1H and ^{13}C chemical shifts were referenced to hexamethyldisilazane, ^{19}F to $CFCl_3$, and ^{15}N to CH_3NO_2. UV/Vis absorption spectra were measured with a Lambda-35 (Perkin–Elmer) spectrophotometer. The absorption coefficients have been determined with an accuracy of $\pm 500\ M^{-1}\ cm^{-1}$. Excitation and emission spectra were measured with a FLSP-920 combined steady-state and time-resolved fluorescence spectrometers (Edinburgh Instrument). All fluorescence and excitation spectra were corrected. Fluorescence decay curves were obtained with a time-correlated single-photon-counting method. The experimental errors in the determination of τ_f values were estimated to be 1%. For samples, a right-angle configuration was used and to avoid re-absorption, the maximum absorbance was kept below 0.1. The solvent used was CH_3CN (spectroscopic grade) from Sigma–Aldrich. The fluorescence quantum yields (Φ_f) of the BODIPY systems were calculated by using the following relationship [Equation (1)].

$$\Phi_f = \Phi_{ref}\, F_{sampl}\, A_{ref}\, n^2_{sampl} / F_{ref}\, A_{sampl}\, n^2_{ref} \quad (1)$$

F denotes the integral of the corrected fluorescence spectrum, *A* is the absorbance at the excitation wavelength, and *n* is the refractive index of the medium, and ref and sampl denote parameters from the reference and unknown experimental samples, respectively. The reference system used is Nile blue [Φ_f = 0.27, 0.5% (v/v) 0.1 M HCl in ethanol].

Quantum-chemical calculations were performed by using Turbomole v.6.1 software.[23]

General Procedure for the Preparation of 2-(1,1-biphenyl-4-yl)pyrroles 1f and 1g: 1,1-Biphenyl-4-yl-methylketoxime or 1,1-biphenyl-4-yl-benzylketoxime (25 mmol), KOH·0.5H_2O (1.63 g, 25 mmol) and dimethyl sulfoxide (DMSO; 120 mL) were placed into a 0.25 L steel rotating autoclave and acetylene was fed from a cylinder at room temperature (initial pressure 14 atm). The autoclave was heated (100 °C) for 3 h. The reaction mixture, after cooling to room temperature, was diluted with a threefold volume excess of water and extracted with diethyl ether (5 × 30 mL). Ether extracts were washed with water (5 × 30 mL) to remove DMSO and dried with Na_2SO_4. The residue after removing diethyl ether was fractionated by column chromatography (Al_2O_3, *n*-hexane) to afford 1-vinyl-2-(1,1-biphenyl-4-yl)pyrrole (**2f**) or 1-vinyl-2-(1,1-biphenyl-4-yl)-3-phenylpyrrole (**2g**).

A suspension of pyrrole **2f** or **2g** (5 mmol) and mercury acetate (1.59 g, 5 mmol) in aqueous acetonitrile (200 mL, 1:2) was stirred for 2 h at room temperature and then heated at 55–60 °C for 15 min. The reaction mixture was diluted with water (100 mL) and the solid formed was filtered off and dried. The solid was purified by flash-chromatography (Al_2O_3, hexane/diethyl ether, 1:1) to afford pyrrole **1f** or **1g**.

2-(1,1-Biphenyl-4-yl)pyrrole (1f): Yield 0.48 g (44%) as grayish crystals, m.p. 213-215 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3433, 3395, 1488, 1426, 836, 800, 763, 719, 691 cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 11.40 (br. s, 1 H, NH), 7.72 (m, 2 H, Ph-2a,6a), 7.68 (m, 2 H, Ph-2b,6b), 7.65 (m, 2 H, Ph-3a,5a), 7.45 (m, 2 H, Ph-3b,5b), 7.33 (m, 1 H, Ph-4b), 6.86 (m, 1 H, 2-H), 6.56 (m, 1 H, 4-H), 6.13 (m, 1 H, 3-H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 139.9 (C-1b), 136.9 (C-4a), 132.2 (C-1a), 130.8 (C-5), 129.0 (C-3b,5b), 127.3 (C-4b), 127.0 (C-3a,5a), 126.3 (C-2b,6b), 123.9 (C-2a,6a), 119.7 (C-2), 109.3 (C-3), 106.0 (C-4) ppm. ^{15}N NMR ([D_6]DMSO): δ = –228.4 ppm. $C_{16}H_{13}N$ (219.29): calcd. C 87.64, H 5.98, N 6.39; found C 87.38, H 5.85, N 6.23.

2-(1,1-Biphenyl-4-yl)-1-vinylpyrrole (2f): Yield 3.25 g (53%) as white crystals, m.p. 126–127 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3145, 1640, 1465, 1316, 1290, 971, 960, 875, 841, 766, 713, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.73 (m, 4 H, Ph-2a,6a,2b,6b), 7.55 (m, 4 H, Ph-3a,5a,3b,5b), 7.45 (m, 1 H, Ph-4b), 7.24 (m, 1 H, 5-H), 7.07 (dd, *J* = 15.6, 8.8 Hz, 1 H, H_X), 6.42 (m, 2 H, 3-H,4), 5.30 (d, *J* = 15.6 Hz, 1 H, H_B), 4.82 (d, *J* = 8.8 Hz, 1 H, H_A) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.7 (C-1b), 140.0 (C-4a), 134.0 (C-1a), 132.1 (C_α), 131.5 (C-2), 129.6 (C-3b,5b), 128.9 (C-2a,6a), 127.5 (C-4b), 127.2 (C-3a,5a), 127.1 (C-2b,6b), 118.6 (C-5), 110.2 (C-3,4), 99.0 (C_β) ppm. $C_{18}H_{15}N$ (245.32): calcd. C 88.13, H 6.16, N 5.71; found C 88.12, H 6.38, N 5.54.

2-(1,1-Biphenyl-4-yl)-3-phenylpyrrole (1g): Yield 0.92 g (62%) as beige crystals, m.p. 184–185 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3409, 1604, 1501, 1488, 1095, 895, 838, 764, 722, 699, 689 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.27 (br. s, 1 H, NH), 7.59 (m, 2 H, Ph-2b,6b), 7.53 (m, 2 H, Ph-3a,5a), 7.41 (m, 6 H, Ph-2a,6a,3b,5b,2c,6c), 7.33 (m, 1 H, Ph-4b), 7.27 (m, 2 H, Ph-3c,5c), 7.20 (m, 1 H, Ph-4c), 6.89 (dd, *J* = 2.5, 2.8 Hz, 1 H, 2-H), 6.43 (dd, *J* = 2.5, 2.8 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.6 (C-1b), 139.4 (C-4a), 136.7 (C-1c), 132.4 (C-1a), 128.9 (C-2a,6a), 128.6 (C-2c,6c), 128.4 (C-3c,5c), 128.0 (C-5), 127.8 (C-3b,5b), 127.4 (C-4b), 127.3 (C-3a,5a), 126.9 (C-2b,6b), 125.8 (C-4c), 122.4 (C-4), 118.3 (C-2), 111.3 (C-3) ppm. $C_{22}H_{17}N$ (295.38): calcd. C 89.46, H 5.80, N 4.74; found C 89.12, H 5.39, N 4.51.

2-(1,1-Biphenyl-4-yl)-3-phenyl-1-vinylpyrrole (2g): Yield 3.21 g (40%) as white crystals, m.p. 113–114 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3449, 1636, 1599, 1494, 1472, 1446, 1423, 1382, 1316, 1297, 1281, 1253, 1075, 958, 929, 910, 855, 841, 768, 736, 723, 693 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.61 (m, 2 H, Ph-2b,6b), 7.58 (m, 2 H, Ph-3a,5a), 7.42 (m, 2 H, Ph-3b,5b), 7.32 (m, 3 H, Ph-2a,6a,4b), 7.20 (m, 2 H, Ph-2c,6c), 7.17 (d, J = 3.2 Hz, 1 H, 2-H), 7.16 (m, 2 H, Ph-3c,5c), 7.08 (m, 1 H, Ph-4c), 6.76 (dd, J = 15.9, 9.1 Hz, 1 H, H_X), 6.51 (d, J = 3.2 Hz, 1 H, 3-H), 5.15 (d, J = 15.9 Hz, 1 H, H_B), 4.63 (d, J = 9.1 Hz, 1 H, H_A) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.5 (C-1b), 140.4 (C-4a), 136.0 (C-1c), 131.9 (C-2a,6a), 131.7 (C_α), 130.8 (C-1a), 129.6 (C-5), 128.9 (C-3b,5b), 128.3 (C-3c,5c), 128.0 (C-2c,6c), 127.6 (C-4b), 127.2 (C-3a,5a), 127.1 (C-2b,6b), 125.6 (C-4c), 124.2 (C-4), 117.3 (C-2), 110.8 (C-3), 98.4 (C_β) ppm. ^{15}N NMR ($CDCl_3$): δ = –207.6 ppm. $C_{24}H_{19}N$ (321.42): calcd. C 89.68, H 5.96, N 4.36; found C 89.41, H 5.78, N 4.38.

Preparation of 2,2,2-trifluoro-1-(5-aryl-1*H*-pyrrol-2-yl)-1-ethanones 4f and 4g: A solution of trifluoroacetic anhydride (6.30 g, 30 mmol) in dry diethyl ether (10 mL) was added dropwise to a mixture of 2-(1,1-biphenyl)-4-ylpyrroles **1f** or **1g** (20 mmol) and pyridine (2.37 g, 30 mmol) in dry diethyl ether (50 mL) and stirred for 30 min. Then the reaction mixture was stirred for 2 h and diluted with a saturated solution of Na_2CO_3. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined extracts were washed with water (3 × 10 mL) and dried with $MgSO_4$. After removing the solvent the residue was washed with cold ethanol to give compound **4f** and **4g**.

The 2,2,2-trifluoro-1-(5-aryl-1*H*-pyrrol-2-yl)-1-ethanones **4c**–**4e** were obtained analogously. Their spectroscopic data are described in ref.[24]

1-[5-(1,1-Biphenyl)-4-yl]-1*H*-pyrrol-2-yl-2,2,2-trifluoro-1-ethanone (4f): Yield 5.61 g (89%) as light-violet crystals, m.p. 238–239 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3308, 1644, 1479, 1266, 1201, 1138, 1076, 882, 840, 796, 764, 756 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 12.92 (br. s, 1 H, NH), 8.06 (m, 2 H, Ph-2a,6a), 7.74 (m, 4 H, Ph-3a,5a,2b,6b), 7.47 (m, 2 H, Ph-3b,5b), 7.39 (m, 1 H, Ph-4b), 7.29 (dd, J = 4.0, 2.0 Hz, 1 H, 3-H), 6.96 (dd, J = 4.2, 2.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 167.6 (q, J = 34.7 Hz, CO), 143.4 (C-5), 140.6 (C-1b), 139.2 (C-4a), 129.1 (C-3b,5b), 128.9 (C-1a), 128.0 (C-3), 127.2 (C-3a,5a), 127.0 (C-2b,6b), 126.7 (C-2a,6a), 126.1 (C-4b), 123.6 (C-2), 117.3 (q, J = 290.3 Hz, CF_3), 111.1 (C-4) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –70.9 ppm. $C_{18}H_{12}F_3NO$ (315.29): calcd. C 68.57, H 3.84, F 18.08, N 4.44; found C 68.12, H 3.69, F 17.82, N 4.54.

1-{5-[(1,1-Biphenyl)-4-yl]-4-phenyl-1*H*-pyrrol-2-yl}-2,2,2-trifluoro-1-ethanone (4g): Yield 5.64 g (72%) as light yellow crystals, m.p. 202–203 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3300, 1660, 1642, 1478, 1453, 1263, 1220, 1194, 1177, 1141, 896, 846, 765, 758, 735, 701 cm^{-1}. ^1H NMR ([D$_6$]-DMSO): δ = 13.03 (br. s, 1 H, NH), 7.69 (m, 4 H, Ph-2a,6a,2b,6b), 7.53 (m, 2 H, Ph-3a,5a), 7.51 (m, 2 H, Ph-3b,5b), 7.46 (m, 7 H, 3-H, Ph-4b,2c-6c) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 168.1 (q, J = 34.8 Hz, CO), 141.0 (C-1b), 140.7 (C-4a), 139.6 (C-1c), 134.7 (C-1a), 130.0 (C-3b,5b), 129.6 (C-5), 129.5 (C-3c,5c), 129.1 (C-2c,6c), 129.0 (C-2a,6a), 128.4 (C-4b), 127.5 (C-2), 127.2 (C-2b,6b), 127.1 (C-3a,5a), 126.5 (C-4), 125.4 (C-4c), 122.8 (C-3), 117.6 (q, J = 290.2 Hz, CF_3) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –70.8 ppm. $C_{24}H_{16}F_3NO$ (391.39): calcd. C 73.65, H 4.12, F 14.56, N 3.58; found C 73.46, H 4.08, F 14.71, N 3.52.

General Procedure for the Preparation of 2,2,2-Trifluoro-1-(5-aryl-pyrrol-2-yl)-1-ethanols 5c–5g: To an rigorously stirred mixture of 2,2,2-trifluoro-1-(5-arylpyrrol-2-yl)-1-ethanones **4c**–**4g** (5 mmol) and $NaHCO_3$ (2.1 equiv., 0.882 g, 10.5 mmol) in MeOH (15 mL), $NaBH_4$ (2 equiv., 0.378 g, 10 mmol) was added in portions over 10 min and the reaction mixture was stirred for 30 min. The residue after removal of MeOH was diluted with water (30 mL), extracted with diethyl ether (4 × 10 mL) and dried with Na_2SO_4. The diethyl ether was removed and the resulting residue was purified by flash chromatography (Al_2O_3, diethyl ether) to give products **5c**–**g**.

1-[5-(4-Methylphenyl)-1*H*-pyrrol-2-yl]-2,2,2-trifluoro-1-ethanol (5c): Yield 1.23 g (96%) as beige crystals, m.p. 156–157 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3487, 3404, 3308, 1525, 1381, 1269, 1254, 1171, 1124, 1075, 1049, 995, 853, 824, 792, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.60 (br. s, 1 H, NH), 7.36 (m, 2 H, Ph-2,6), 7.17 (m, 2 H, Ph-3,5), 6.40 (m, 1 H, 4-H), 6.32 (m, 1 H, 3-H), 5.10 (q, J = 6.6 Hz, 1 H, $CHCF_3$), 2.34 (s, 3 H, Me), 2.61 (br. s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 136.8 (C-4, Ph), 134.1 (C-5), 129.7 (C-3,5, Ph), 129.4 (C-1, Ph), 124.2 (C-2,6, Ph), 124.0 (C-2), 124.0 (q, J_{CF} = 280.9 Hz, CF_3), 110.9 (C-3), 105.8 (C-4), 67.7 (q, J_{CF} = 33.6 Hz, C-OH), 21.2 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ = –78.2 (d, J = 6.6 Hz) ppm. $C_{13}H_{12}F_3NO$ (255.24): calcd. C 61.17, H 4.74, F 22.33, N 5.49; found C 61.01, H 4.92, F 22.67, N 5.36.

1-[5-(4-Methoxyphenyl)-1*H*-pyrrol-2-yl]-2,2,2-trifluoro-1-ethanol (5d): Yield 1.06 g (78%) as beige crystals, m.p. 120–121 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3355, 3322 (NH, OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.60 (br. s, 1 H, NH), 7.42 (m, 2 H, Ph-2,6), 6.93 (m, 2 H, Ph-3,5), 6.37 (m, 1 H, 4-H), 6.35 (m, 1 H, 3-H), 5.12 (q, J = 6.7 Hz, 1 H, $CHCF_3$), 3.84 (s, 3 H, MeO), 2.81 (br. s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.8 (C-4, Ph), 134.0 (C-5), 125.6 (C-2,6, Ph), 125.2 (C-1, Ph), 124.0 (q, J_{CF} = 281.8 Hz, CF_3), 123.8 (C-2), 114.5 (C-3,5, Ph), 110.9 (C-3), 105.3 (C-4), 67.7 (q, J_{CF} = 33.6 Hz, C-OH), 55.4 (MeO) ppm. ^{19}F NMR ($CDCl_3$): δ = –78.2 (d, J = 6.7 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –240.7 ppm. $C_{13}H_{12}F_3NO_2$ (271.24): calcd. C 57.57, H 4.46, F 21.01, N 5.16; found C 57.23, H 4.23, F 20.87, N 5.16.

1-[5-(4-Chlorophenyl)-1*H*-pyrrol-2-yl]-2,2,2-trifluoro-1-ethanol (5e): Yield 1.32 g (96%) as beige crystals, m.p. 112–113 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3504, 3413, 3297 (NH, OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.61 (br. s, 1 H, NH), 7.38 (m, 2 H, Ph-2,6), 7.32 (m, 2 H, Ph-3,5), 6.44 (m, 1 H, 4-H), 6.33 (m, 1 H, 3-H), 5.12 (q, J = 6.5 Hz, 1 H, $CHCF_3$), 2.61 (br. s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 132.6 (C-4, Ph), 132.5 (C-5), 130.5 (C-1, Ph), 129.1 (C-3,5, Ph), 125.3 (C-2,6, Ph), 124.7 (C-2), 123.8 (q, J_{CF} = 281.8 Hz, CF_3), 111.0 (C-3), 107.0 (C-4), 67.6 (q, J_{CF} = 33.6 Hz, C-OH) ppm. ^{19}F NMR ($CDCl_3$): δ = –78.4 (d, J = 6.7 Hz) ppm. $C_{12}H_9ClF_3NO$ (275.66): calcd. C 52.29, H 3.29, Cl 12.86, F 20.68, N 5.08; found C 52.29, H 2.94, Cl 12.73, F 20.28, N 4.77.

1-(5-[1,1-Biphenyl]-4-yl-1*H*-pyrrol-2-yl)-2,2,2-trifluoro-1-ethanol (5f): Yield 1.43 g (90%) as beige crystals, m.p. 171–172 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3430, 1608, 1596, 1272, 1215, 1174, 1123, 1046, 837, 787, 764, 702, 695 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 11.55 (br. s, 1 H, NH), 7.76 (m, 2 H, Ph-2a,6a), 7.68 (m, 2 H, Ph-2b,6b), 7.66 (m, 2 H, Ph-3a,5a), 7.45 (m, 2 H, Ph-3b,5b), 7.33 (m, 1 H, Ph-4b), 6.77 (d, J = 6.1 Hz, 1 H, OH), 6.56 (m, 1 H, 4-H), 6.24 (m, 1 H, 3-H), 5.14 (q, J = 6.5 Hz, 1 H, $CHCF_3$) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 139.8 (C-1b), 137.4 (C-4a), 131.7 (C-1a), 131.4 (C-5), 129.0 (C-3b,5b), 127.8 (C-2), 127.3 (C-4b), 127.0 (C-3a,5a), 126.4 (C-2b,6b), 124.9 (q, J_{CF} = 281.1 Hz, CF_3), 124.2 (C-2a,6a), 109.0 (C-3), 106.4 (C-4), 65.9 (q, J_{CF} = 31.7 Hz, C-OH) ppm. ^{19}F NMR ([D$_6$]-DMSO): δ = –76.6 (d, J = 7.2 Hz) ppm. $C_{18}H_{14}F_3NO$ (317.31): calcd. C 68.13, H 4.45, F 17.96, N 4.41; found C 68.29, H 4.24, F 18.28, N 4.65.

1-(5-[1,1-Biphenyl]-4-yl-4-phenyl-1*H*-pyrrol-2-yl)-2,2,2-trifluoro-1-ethanol (5g): Yield 1.79 g (91%) as white crystals, m.p. 129 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3449, 3330, 3290, 1265, 1207, 1183, 1165, 1130, 1045,

1001, 845, 805, 766, 699 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 11.46 (br. s, 1 H, NH), 7.66 (m, 2 H, Ph-2b,6b), 7.60 (m, 2 H, Ph-3a,5a), 7.43 (m, 2 H, Ph-3b,5b), 7.42 (m, 2 H, Ph-2a,6a), 7.32 (m, 1 H, Ph-4b), 7.27 (m, 2 H, Ph-2c,6c), 7.25 (m, 2 H, Ph-3c,5c), 7.18 (m, 1 H, Ph-4c), 6.83 (d, J = 6.1 Hz, 1 H, OH), 6.38 (d, J = 2.2 Hz, 1 H, 3-H), 5.16 (m, 1 H, CHCF$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 139.6 (C-1b), 138.3 (C-4a), 136.8 (C-1c), 132.1 (C-1a), 129.1 (C-3b,5b), 128.6 (C-3c,5c), 128.2 (C-2c,6c), 128.1 (C-2a,6a), 127.7 (C-4b), 127.6 (C-5), 127.1 (C-2), 126.7 (C-3a,5a), 126.5 (C-2b,6b), 126.0 (C-4c), 125.0 (q, J_{CF} = 282.5 Hz, CF$_3$), 122.0 (C-4), 109.9 (C-3), 66.0 (q, J_{CF} = 32.3 Hz, C-OH) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –76.6 (d, J = 7.2 Hz) ppm. ^{15}N NMR ([D$_6$]DMSO): δ = –222.3 ppm. $C_{24}H_{18}F_3NO$ (393.41): calcd. C 73.27, H 4.61, F 14.49, N 3.56; found C 73.00, H 4.38, F 14.28, N 3.69.

Preparation of Dipyrromethanes 6: A mixture of 2,2,2-trifluoro-1-(5-arylpyrrol-2-yl)-1-ethanol **5c**–**5g** and pyrrole **1a**–**1g** (molar ratio **1a**–**1g**:**5c**–**5g** 1:1) in dry CH_2Cl_2 was added to P_2O_5 (1 equiv.) under argon and stirred at room temperature for 16 h. Then $NaHCO_3$ (1.5 equiv.) was added and the mixture was stirred at room temperature for 1 h. The precipitate was filtered off and washed with CH_2Cl_2 (5 times). Compounds **6** were isolated by column chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 3:1 or 2:1).

2-(4-Methylphenyl)-5-[2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)-ethyl]-1*H*-pyrrole (6ac): Yield 0.314 g (55%) as dark cherry crystals, m.p. 70–72 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3438, 3026, 2956, 2924, 1607, 1523, 1512, 1474, 1454, 1256, 1210, 1190, 1162, 1109, 1072, 1046, 819, 777, 757, 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.29 (br. s, 1 H, NH′), 8.25 (br. s, 1 H, NH), 7.40 (m, 2 H, Ph-2b,6b), 7.32 (m, 4 H, Ph-2a,6a,3b,5b), 7.19 (m, 1 H, Ph-4b), 7.14 (m, 2 H, Ph-3a,5a), 6.47 (m, 1 H, 4′-H), 6.43 (m, 1 H, 3-H), 6.30 (m, 2 H, 3′,4-H), 4.88 (q, J_{HF} = 8.8 Hz, 1 H, CH), 2.32 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 136.6 (C-4a), 133.5 (C-2), 133.3 (C-5′), 132.2 (C-1b), 129.7 (C-3a,5a), 129.5 (C-1a), 129.0 (C-3b,5b), 126.8 (C-4b), 125.2 (q, J_{CF} = 280.1 Hz, CF$_3$), 124.0 (C-2a,6a,2b,6b), 123.8 (C-2′), 123.3 (C-5), 111.1 (C-3′), 111.0 (C-4), 106.6 (C-4′), 106.0 (C-3), 43.7 (q, J_{CF} = 30.2 Hz, CH), 21.2 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.3 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.9 ppm. $C_{23}H_{19}F_3N_2$ (380.41): calcd. C 72.62, H 5.03, F 14.98, N 7.36; found C 72.29, H 4.94, F 14.58, N 7.65.

2-(4-Methoxyphenyl)-5-[2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)-ethyl]-1*H*-pyrrole (6ad): Yield 0.285 g (72%) as red needles, m.p. 132–135 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3459, 3431 1522, 1263, 1251, 1245, 1166, 1103, 1020, 780, 772, 760, 707, 691, 529 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.31 (br. s, 1 H, NH′), 8.20 (br. s, 1 H, NH), 7.40 (m, 2 H, Ph-2b,6b), 7.34 (m, 2 H, Ph-2a,6a), 7.33 (m, 2 H, Ph-3b,5b), 7.19 (m, 1 H, Ph-4b), 6.88 (m, 2 H, Ph-3a,5a), 6.48 (m, 1 H, 4′-H), 6.36 (m, 1 H, 3-H), 6.32 (m, 1 H, 3′-H), 6.29 (m, 1 H, 4-H), 4.88 (q, J_{HF} = 8.8 Hz, 1 H, CH), 3.79 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.7 (C-4a), 133.4 (C-2), 133.2 (C-5′), 132.2 (C-1b), 129.0 (C-3b,5b), 126.7 (C-4b), 125.5 (C-2a,6a), 125.3 (q, J_{CF} = 280.7 Hz, CF$_3$), 125.3 (C-1a), 124.0 (C-2b,6b), 123.9 (C-2′), 123.0 (C-5), 114.5 (C-3a,5a), 111.0 (C-3′, C-4), 106.6 (C-4′), 105.5 (C-3), 55.4 (Me), 43.7 (q, J_{CF} = 30.1 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.3 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –237.0 (N,N′) ppm. $C_{23}H_{19}F_3N_2O$ (396.41): calcd. C 69.69, H 4.83, F 14.38, N 7.07; found C 69.90, H 4.97, F 14.20, N 7.00.

2-(4-Chlorophenyl)-5-[2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)-ethyl]-1*H*-pyrrole (6ae): Yield 0.263 g (66%) as violet solid, m.p. 118–120 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3452 1507, 1260, 1212, 1182, 1162, 1101, 827, 781, 772, 758, 705, 690, 514 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.27 (br. s, 1 H, NH′), 8.22 (br. s, 1 H, NH), 7.39 (m, 2 H, Ph-2b,6b), 7.32 (m, 2 H, Ph-3b,5b), 7.30 (m, 2 H, Ph-3a,5a), 7.27 (m, 2 H, Ph-2a,6a), 7.19 (m, 1 H, Ph-4b), 6.47 (m, 1 H, 4′-H), 6.44 (m, 1 H, 3-H), 6.31 (m, 2 H, 3′,4-H), 4.85 (q, J_{HF} = 8.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 133.4 (C-5′), 132.3 (C-4a), 132.2 (C-1b), 132.1 (C-2), 130.7 (C-1a), 129.2 (C-3a,5a), 129.0 (C-3b,5b), 126.8 (C-4b), 125.2 (C-2a,6a), 125.2 (q, J_{CF} = 280.1 Hz, CF$_3$), 124.2 (C-5), 124.0 (C-2b,6b), 123.6 (C-2′), 111.3 (C-4), 111.2 (C-3′), 107.1 (C-3), 106.6 (C-4′), 43.7 (q, J_{CF} = 30.2 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.2 (d, J = 8.9 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.9 (N,N′) ppm. $C_{22}H_{16}ClF_3N_2$ (400.83): calcd. C 65.92, H 4.02, Cl 8.85, F 14.22, N 6.99; found C 65.60, H 4.07, Cl 8.47, F 14.38, N 6.71.

2-[1,1-Biphenyl]-4-yl-5-[2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)-ethyl]-1*H*-pyrrole (6af): Yield 0.201 g (96%) as light violet solid, m.p. 108–110 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3457, 3422, 1607, 1495, 1473, 1424, 1257, 1210, 1167, 1102, 1072, 1051, 836, 804, 781, 764, 754, 705, 692 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.35 (br. s, 1 H, NH), 8.33 (br. s, 1 H, NH′), 7.57 (m, 4 H, Ph-3a,5a,2b,6b), 7.47 (m, 2 H, Ph-2a,6a), 7.42 (m, 4 H, Ph-3b,5b,2c,6c), 7.34 (m, 3 H, Ph-4b,3c,5c), 7.20 (m, 1 H, Ph-4c), 6.52 (m, 1 H, 4-H), 6.49 (m, 1 H, 3′-H), 6.34 (m, 2 H, 3,4′-H), 4.86 (q, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.6 (C-1b), 139.4 (C-4a), 133.3 (C-5′), 132.9 (C-2), 132.2 (C-1c), 131.1 (C-1a), 129.0 (C-3b,5b), 128.9 (C-3c,5c), 127.6 (C-3a,5a), 127.4 (C-4b), 126.9 (C-2b,6b), 126.8 (C-4c), 125.3 (q, J_{CF} = 280.3 Hz, CF$_3$), 124.3 (C-2a,6a), 124.0 (C-2c,6c), 123.9 (C-5), 123.8 (C-2′), 111.2 (C-4), 111.1 (C-3′), 106.8 (C-3), 106.6 (C-4′), 43.7 (q, J_{CF} = 30.2 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.2 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.9 (N,N′) ppm. $C_{28}H_{21}F_3N_2$ (442.48): calcd. C 76.00, H 4.78, F 12.88, N 6.33; found C 75.96, H 4.67, F 12.92, N 6.31.

2-[1,1-Biphenyl]-4-yl-3-phenyl-5-[2,2,2-trifluoro-1-(5-phenyl-1*H*-pyrrol-2-yl)ethyl]-1*H*-pyrrole (6ag): Yield 0.060 g (45%) as a violet solid, m.p. 72–74 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3429, 1604, 1511, 1492, 1472, 1446, 1254, 1199, 1160, 1108, 1073, 843, 760, 697 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.38 (br. s, 1 H, NH′), 8.15 (br. s, 1 H, NH), 7.54 (m, 2 H, Ph-2b,6b), 7.48 (m, 2 H, Ph-3a,5a), 7.40 (m, 4 H, Ph-3b,5b,2c,6c), 7.29–7.37 (m, 7 H, Ph-2a,6a,4b,2d,6d,3d,5d), 7.26 (m, 2 H, Ph-3c,5c), 7.18 (m, 2 H, Ph-4c,4d), 6.48 (m, 1 H, 3′-H), 6.44 (m, 1 H, 4-H), 6.35 (m, 1 H, 4′-H), 4.92 (q, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.5 (C-1b), 139.9 (C-4a), 136.1 (C-1c), 133.5 (C-5′), 132.2 (C-1d), 131.7 (C-1a), 129.1 (C-3d,5d), 128.9 (C-3b,5b, C-2), 128.5 (C-2c,6c), 128.4 (C-3c,5c), 127.9 (C-2a,6a), 127.5 (C-4b), 127.4 (C-3a,5a), 127.0 (C-2b,6b), 126.8 (C-4d), 126.2 (C-4c), 125.2 (q, J_{CF} = 280.1 Hz, CF$_3$), 124.1 (C-2d,6d), 123.5 (C-2′), 123.4 (C-5), 122.8 (C-3), 111.9 (C-4), 111.3 (C-3′), 106.6 (C-4′), 43.7 (q, J_{CF} = 30.2 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.1 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –237.6 (N′), –231.5 (N) ppm. $C_{34}H_{25}F_3N_2$ (518.58): calcd. C 78.75, H 4.86, F 10.99, N 5.40; found C 78.55, H 4.90, F 11.09, N 5.36.

2-[1,1-Biphenyl]-4-yl-5-{2,2,2-trifluoro-1-[5-(2-thienyl)-1*H*-pyrrol-2-yl]ethyl}-1*H*-pyrrole (6bf): Yield 0.168 g (79%) as a violet solid, m.p. 138–140 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3451, 3422, 2919, 1607, 1596, 1528, 1495, 1426, 1259, 1169, 1102, 1052, 1040, 836, 781, 764, 705, 691 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.32 (br. s, 1 H, NH), 8.18 (br. s, 1 H, NH′), 7.57 (m, 4 H, Ph-2b,6b,3a,5a), 7.47 (m, 2 H, Ph-2a,6a), 7.41 (m, 2 H, Ph-3b,5b), 7.31 (m, 1 H, Ph-4b), 7.12 (m, 1 H, 5-H of thiophene), 7.00 (m, 1 H, 3-H of thiophene), 6.96 (m, 1 H, 4-H of thiophene), 6.51 (m, 1 H, 3-H), 6.37 (m, 1 H, 4′-H), 6.33 (m, 1 H, 4-H), 6.29 (m, 1 H, 3′-H), 4.88 (q, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.6 (C-1b), 139.5 (C-4a), 135.5 (C-2 of thiophene), 133.0 (C-2), 131.1 (C-1a), 128.9 (C-3b,5b), 127.8 (C-3a,5a), 127.7 (C-4 of thiophene, C-5′), 127.4 (C-4b), 126.9 (C-2b,6b), 125.2 (q, J_{CF} = 280.2 Hz, CF$_3$), 124.4 (C-,a), 123.8 (C-5 of

thiophene, C-5), 123.7 (C-2′), 121.6 (C-3 of thiophene), 111.3 (C-4), 111.0 (C-3′), 107.4 (C-4′), 106.8 (C-3), 43.7 (q, J_{CF} = 30.2 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.2 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.8 (N), –235.6 (N′) ppm. $C_{26}H_{19}F_3N_2S$ (448.50): calcd. C 69.63, H 4.27, F 12.71, N 6.25, S 7.15; found C 69.57, H 4.52, F 12.49, N 6.07, S 7.27.

2-[1,1-Biphenyl]-4-yl-3-phenyl-5-{2,2,2-trifluoro-1-[5-(2-thienyl)-1*H*-pyrrol-2-yl]ethyl}-1*H*-pyrrole (6bg): Yield 0.144 g (68%) as a dark blue solid, m.p. 76–78 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3420, 1601, 1527, 1510, 1492, 1473, 1253, 1184, 1160, 1107, 843, 764, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.25 (br. s, 1 H, NH′), 8.15 (br. s, 1 H, NH), 7.56 (m, 2 H, Ph-2b,6b), 7.50 (m, 2 H, Ph-3a,5a), 7.40 (m, 2 H, Ph-3b,5b), 7.36 (m, 4 H, Ph-2a,6a,2c,6c), 7.32 (m, 1 H, Ph-4b), 7.27 (m, 2 H, Ph-3c,5c), 7.19 (m, 1 H, Ph-4c), 7.14 (m, 1 H, 5-H of thiophene), 7.01 (m, 1 H, 3-H of thiophene), 6.98 (m, 1 H, 4-H of thiophene), 6.44 (m, 1 H, 4-H), 6.38 (m, 1 H, 4′-H), 6.23 (m, 1 H, 3′-H), 4.88 (dd, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.5 (C-1b), 140.0 (C-4a), 136.0 (C-1c), 135.5 (C-2 of thiophene), 131.7 (C-1a), 129.0 (C-2), 128.9 (C-3b,5b), 128.5 (C-2c,6c), 128.4 (C-3c,5c), 127.8 (C-2a,6a), 127.7 (C-4 of thiophene, C-5′), 127.5 (C-4b), 127.4 (C-3a,5a), 126.9 (C-2b,6b), 126.2 (C-4c), 125.2 (q, J_{CF} = 278.6 Hz, CF_3), 123.4 (C-2′), 123.3 (C-5), 123.2 (C-5 of thiophene), 122.9 (C-3), 121.6 (C-3 of thiophene), 112.0 (C-4), 111.2 (C-3′), 107.4 (C-4′), 43.6 (q, J_{CF} = 30.5 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.1 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.8 (N′), –231.9 (N) ppm. $C_{32}H_{23}F_3N_2S$ (524.60): calcd. C 73.26, H 4.42, F 10.86, N 5.34, S 6.11; found C 72.98, H 4.35, F 10.90, N 5.45, S 6.21.

2-(4-Methylphenyl)-5-{2,2,2-trifluoro-1-[5-(4-methylphenyl)-1*H*-pyrrol-2-yl]ethyl}-1*H*-pyrrole (6cc): Yield 0.167 g (28%) as a dark violet solid, m.p. 85–86 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3437, 3023, 2989, 2953, 2921, 2864, 1637, 1616, 1523, 1480, 1451, 1433, 1384, 1336, 1299, 1256, 1190, 1161, 1109, 1069, 1044, 865, 818, 802, 774, 709, 518 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.25 (br. s, 2 H, NH), 7.30 (m, 4 H, Ph-2a,6a), 7.14 (m, 4 H, Ph -3a,5a), 6.43 (m, 2 H, 3,4′-H), 6.30 (m, 2 H, 3′,4-H), 4.88 (q, J_{HF} = 8.8 Hz, 1 H, CH), 2.32 (s, 6 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 136.5 (C-4a,4a′), 133.4 (C-2,5′), 129.7 (C-3a,5a, 3a′,5a′), 129.5 (C-1a,1a′), 125.3 (q, J_{CF} = 280.4 Hz, CF_3), 123.4 (C-2′,5), 124.0 (C-2a,6a,2a′,6a′), 111.0 (C-3′,4), 106.0 (C-3,4′), 43.7 (q, J_{CF} = 30.2 Hz, CH), 21.2 (Me, Me′) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.3 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.8 (N,N′) ppm. $C_{24}H_{21}F_3N_2$ (394.44): calcd. C 73.08, H 5.37, F 14.45, N 7.10; found C 72.89, H 5.44, F 14.28, N 7.29.

2-(4-Methoxyphenyl)-5-{2,2,2-trifluoro-1-[5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl]ethyl}-1*H*-pyrrole (6dd): Yield 0.095 g (64%) as a violet solid, m.p. 156–157 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3465, 3399, 1613, 1589, 1522, 1480, 1469, 1439, 1255, 1244, 1180, 1159, 1101, 1028, 1019, 828, 772, 706, 611, 537 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.23 (br. s, 2 H, NH), 7.31 (m, 4 H, Ph-2a,6a), 6.85 (m, 4 H, Ph-3a,5a), 6.34 (m, 2 H, 3,4′-H), 6.28 (m, 2 H, 3′,4-H), 4.82 (q, J_{HF} = 8.8 Hz, 1 H, CH), 3.76 (s, 6 H, OMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.6 (C-4a,4a′), 133.2 (C-2,5′), 125.3 (q, J_{CF} = 280.3 Hz, CF_3), 125.3 (C-1a,1a′), 125.4 (C-2a,6a,2a′,6a′), 123.2 (C-2′,5), 114.5 (C-3a,5a,3a′,5a′), 110.8 (C-3′,4), 105.5 (C-3,4′), 55.4 (OMe, OMe′), 43.6 (q, J_{CF} = 30.2 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.3 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.8 (N,N′) ppm. $C_{24}H_{21}F_3N_2O_2$ (426.44): calcd. C 67.60, H 4.96, F 13.37, N 6.57; found C 67.79, H 4.98, F 13.42, N 6.37.

2-(4-Chlorophenyl)-5-{2,2,2-trifluoro-1-[5-(4-chlorophenyl)-1*H*-pyrrol-2-yl]ethyl}-1*H*-pyrrole (6ee): Yield 0.292 g (67%) as a violet solid, m.p. 110–111 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3462, 3433, 1631, 1507, 1268, 1259, 1212, 1192, 1159, 1104, 826, 772, 705, 516 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.25 (br. s, 2 H, NH), 7.32 (m, 4 H, Ph-3a,5a), 7.29 (m, 4 H, Ph-2a,6a), 6.46 (m, 2 H, 3,4′-H), 6.32 (m, 2 H, 3′,4-H), 4.88 (q, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 132.4 (C-2,5′), 132.3 (C-4a,4a′), 130.6 (C-1a,1a′), 129.2 (C-3a,5a,3a′,5a′), 125.2 (C-2a,6a,2a′,6a′), 125.1 (q, J_{CF} = 280.1 Hz, CF_3), 124.0 (C-2′,5), 111.3 (C-4,3′), 107.1 (C-3,4′), 43.7 (q, J_{CF} = 29.8 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.2 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –236.9 (N,N′) ppm. $C_{22}H_{15}Cl_2F_3N_2$ (435.27): calcd. C 60.71, H 3.47, Cl 16.29, F 13.09, N 6.44; found C 60.61, H 3.38, Cl 16.19, F 13.18, N 6.30.

2-[1,1-Biphenyl]-4-yl-5-{1-[5-(1,1-biphenyl)-4-yl-1*H*-pyrrol-2-yl]-2,2,2-trifluoroethyl}-1*H*-pyrrole (6ff): Yield 0.186 g (91%) as a light pink solid, m.p. 184–185 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3472, 3454, 3412, 1610, 1598, 1528, 1494, 1253, 1241, 1210, 1169, 1150, 1105, 847, 837, 781, 765, 705, 694, 519 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.37 (br. s, 2 H, NH), 7.58 (m, 8 H, Ph-3a,5a,2b,6b), 7.48 (m, 4 H, Ph-2a,6a), 7.42 (m, 4 H, Ph-3b,5b), 7.32 (m, 2 H, Ph-4b), 6.54 (m, 2 H, 3,4′-H), 6.36 (m, 2 H, 3′,4-H), 4.92 (q, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.6 (C-1b,1b′), 139.5 (C-4a,4a′), 133.0 (C-2,5′), 131.2 (C-1a,1a′), 128.9 (C-3b,5b,3b′,5b′), 127.7 (C-3a,5a,3a′,5a′), 127.4 (C-4b,4b′), 126.9 (C-2b,6b,2b′,6b′), 125.3 (q, J_{CF} = 280.0 Hz, CF_3), 124.4 (C-2a,6a,2a′,6a′), 123.9 (C-2′,5), 111.3 (C-3′,4), 106.8 (C-3,4′), 43.8 (q, J_{CF} = 30.1 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –68.2 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –237.4 (N,N′) ppm. $C_{34}H_{25}F_3N_2$ (518.58): calcd. C 78.75, H 4.86, F 10.99, N 5.40; found C 78.96, H 4.67, F 11.12, N 5.25.

2-[1,1-Biphenyl]-4-yl-5-{1-[5-(1,1-biphenyl)-4-yl-4-phenyl-1*H*-pyrrol-2-yl]-2,2,2-trifluoroethyl}-3-phenyl-1*H*-pyrrole (6gg): Yield 0.120 g (70%) as a dark blue solid, m.p. 112–114 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3427, 3056, 3027, 1602, 1510, 1492, 1443, 1253, 1160, 1108, 909, 843, 764, 731, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.25 (br. s, 2 H, NH), 7.57 (m, 4 H, Ph-2b,6b), 7.53 (m, 4 H, Ph-3a,5a), 7.41 (m, 4 H, Ph-3b,5b), 7.38 (m, 8 H, Ph-2a,6a,2c,6c), 7.32 (m, 2 H, Ph-4b), 7.28 (m, 4 H, Ph-3c,5c), 7.20 (m, 2 H, Ph-4c), 6.50 (d, J = 2.7 Hz, 2 H, 4,3′-H), 4.94 (q, J_{HF} = 8.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.5 (C-1b,1b′), 140.0 (C-4a,4a′), 136.0 (C-1c,1c′), 131.7 (C-1a,1a′), 129.1 (C-2,5′), 128.9 (C-3b,5b,3b′,5b′), 128.6 (C-2c,6c,2c′,6c′), 128.5 (C-3c,5c,3c′,5c′), 127.9 (C-2a,6a,2a′,6a′), 127.5 (C-4b,4b′), 127.4 (C-3a,5a,3a′,5a′), 127.0 (C-2b,6b,2b′,6b′), 126.2 (C-4c,4c′), 125.2 (q, J_{CF} = 280.1 Hz, CF_3), 123.2 (C-2′,5), 122.8 (C-3,4′), 112.1 (C-3′,4), 43.6 (q, J_{CF} = 29.7 Hz, CH) ppm. ^{19}F NMR ($CDCl_3$): δ = –67.9 (d, J = 8.8 Hz) ppm. ^{15}N NMR ($CDCl_3$): δ = –231.9 (N,N′) ppm. $C_{46}H_{33}F_3N_2$ (670.77): calcd. C 82.37, H 4.96, F 8.50, N 4.18; found C 82.55, H 4.86, F 8.39, N 4.16.

General Procedure for the Synthesis of BODIPY 3: A mixture of dipyrromethanes **6** and DDQ (molar ratio 1:1) in dry CH_2Cl_2 was stirred at room temperature for 1 h. Then *i*Pr_2NEt (10 equiv.) was added and the solution was stirred for 10 min, before BF_3·OEt_2 (15 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 1 h, then approximately two thirds of the solvent was removed under reduced pressure and residue obtained was purified by column chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 2:1or 3:1) to yield BODIPY **3**.

4,4-Difluoro-3-(4-methylphenyl)-5-phenyl-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3ac): Yield 0.129 g (55%) as a dark blue solid with metallic luster, m.p. 90–92 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2924, 2853, 1739, 1708, 1566, 1477, 1454, 1300, 1277, 1228, 1178, 1142, 1087, 1054, 970, 949, 750 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.88 (m, 2 H, Ph-2b,6b), 7.82 (m, 2 H, Ph-2a,6a), 7.45 (m, 1 H, 1-H), 7.44 (m, 3 H, Ph-3b,4b,5b), 7.43 (m, 1 H, 7-H), 7.25 (m, 2 H, Ph-3a,5a),

6.70 (d, J = 4.5 Hz, 1 H, 6-H), 6.74 (d, J = 4.5 Hz, 1 H, 2-H), 2.40 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 162.4 (C-3), 161.1 (C-5), 141.2 (C-4a), 133.8 (C-8a), 133.1 (C-7a), 132.0 (C-1b), 130.5 (C-1), 130.2 (C-4b), 129.8 (C-7), 129.7 (t, J = 4.2 Hz, C-2a,6a), 129.6 (t, J = 3.8 Hz, C-2b,6b), 129.3 (C-3a,5a), 129.1 (C-1a), 128.3 (C-3b,5b), 126.2 (q, J = 33.6 Hz, C-8), 123.1 (C-2), 122.7 (q, J = 275.9 Hz, CF_3), 122.6 (C-6), 21.6 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.4 (m, J_{BF} = 31.1 Hz, BF_2), –54.5 (t, J_{HF} = 2.3 Hz, CF_3) ppm. ^{15}N NMR ($CDCl_3$): δ = –193.4 ppm. $C_{23}H_{16}BF_5N_2$ (426.19): calcd. C 64.82, H 3.78, B 2.54, F 22.29, N 6.57; found C 65.10, H 3.68, F 22.16, N 6.36.

4,4-Difluoro-3-(4-methoxyphenyl)-5-phenyl-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3ad): Yield 0.110 g (75%) as dark blue needles with metallic luster, m.p. 136–138 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1604, 1562, 1474, 1452, 1434, 1398, 1299, 1272, 1222, 1188, 1171, 1134, 1086, 1070, 1052, 838, 795, 750, 735, 730 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.89 (m, 2 H, Ph-2a,6a), 7.83 (m, 2 H, Ph-2b,6b), 7.43 (m, 1 H, 7-H), 7.42 (m, 3 H, Ph-3b,4b,5b), 7.37 (m, 1 H, 1-H), 6.94 (m, 2 H, Ph-3a,5a), 6.75 (d, J = 4.5 Hz, 1 H, 6-H), 6.67 (d, J = 4.4 Hz, 1 H, 2-H), 3.83 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 162.5 (C-5), 161.9 (C-4a), 160.2 (C-3), 134.1 (C-7a), 132.8 (C-8a), 132.3 (C-1b), 131.8 (t, J = 4.0 Hz, C-2a,6a), 130.7 (C-1), 130.5 (C-4b), 129.6 (t, J = 4.2 Hz, C-2b,6b), 129.2 (C-7), 128.4 (C-3b,5b), 126.0 (q, J = 32.8 Hz, C-8), 124.1 (C-1a), 123.3 (C-6), 122.8 (q, J = 276.7 Hz, CF_3), 122.2 (C-2), 114.2 (C-3a,5a), 55.4 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.8 (m, J_{BF} = 30.1 Hz, BF_2), –54.5 (CF_3) ppm. $C_{23}H_{16}F_5N_2O$ (431.38): calcd. C 62.47, H 3.65, B 2.44, F 21.48, N 6.34; found C 62.67, H 3.30, F 21.73, N 6.17.

4,4-Difluoro-3-(4-chlorophenyl)-5-phenyl-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3ae): Yield 0.155 g (83%) as a dark blue solid with metallic luster, m.p. 136–137 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1595, 1562, 1509, 1478, 1452, 1432, 1299, 1275, 1224, 1173, 1139, 1086, 1070, 1053, 970, 947, 763, 748, 731, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.84 (m, 2 H, Ph-2b,6b), 7.77 (m, 2 H, Ph-2a,6a), 7.46 (m, 1 H, 7-H), 7.45 (m, 1 H, Ph-4b), 7.44 (m, 2 H, Ph-3b,5b), 7.42 (m, 1 H, 1-H), 7.38 (m, 2 H, Ph-3a,5a), 6.73 (d, J = 4.5 Hz, 1 H, 6-H), 6.67 (d, J = 4.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 162.7 (C-5), 159.9 (C-3), 136.7 (C-4a), 133.8 (C-7a), 133.4 (C-8a), 131.5 (C-1b), 131.0 (C-2a,6a), 130.9 (C-4b), 130.8 (C-7), 130.4 (C-1a), 130.2 (C-1), 129.7 (t, J = 4.2 Hz, C-2b,6b), 128.8 (C-3a,5a), 128.6 (C-3b,5b), 126.7 (q, J = 33.5 Hz, C-8), 122.5 (q, J = 276.0 Hz, CF_3), 123.3 (C-6), 122.4 (C-2) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.4 (m, J_{BF} = 30.5 Hz, BF_2), –54.6 (CF_3) ppm. $C_{22}H_{13}BClF_5N_2$ (446.61): calcd. C 59.16, H 2.93, B 2.42, Cl 7.94, F 21.27, N 6.27; found C 59.42, H 2.80, Cl 7.89, F 21.12, N 6.04.

4,4-Difluoro-3-[(1,1-biphenyl)-4-yl]-5-phenyl-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3af): Yield 0.084 g (75%) as a dark blue solid with metallic luster, m.p. 204–206 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1603, 1570, 1522, 1471, 1448, 1410, 1372, 1329, 1292, 1272, 1236, 1205, 1154, 1122, 1082, 1043, 970, 907, 839, 819, 796, 763, 724, 683 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.95 (m, 2 H, Ph-2a,6a), 7.85 (m, 2 H, Ph-2c,6c), 7.64 (m, 2 H, Ph-3a,5a), 7.60 (m, 2 H, Ph-2b,6b), 7.45 (m, 1 H, 1-H), 7.43 (m, 2 H, Ph-3b,5b), 7.41 (m, 2 H, Ph-3c,5c), 7.40 (m, 2 H, 7-H, Ph-4c), 7.35 (m, 1 H, Ph-4b), 6.78 (d, J = 4.6 Hz, 1 H, 2-H), 6.70 (d, J = 4.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.7 (C-5), 161.5 (C-3), 143.3 (C-4a), 140.3 (C-1b), 139.8 (C-8a), 133.5 (C-7a), 132.0 (C-1c), 130.7 (C-7), 130.4 (C-1,4c), 130.2 (C-1a,2a,6a), 129.6 (t, J = 4.2 Hz, C-2c,6c), 128.4 (C-3c,5c), 128.9 (C-3b,5b), 128.0 (C-4b), 127.3 (C-2b,6b), 127.2 (C-3a,5a), 126.5 (q, J = 33.3 Hz, C-8), 123.1 (C-6), 122.8 (q, J = 275.7 Hz, CF_3), 122.9 (C-2) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.4 (m, J_{BF} = 31.3 Hz, BF_2), –54.5 (CF_3) ppm. ^{15}N NMR ($CDCl_3$): δ = –192.8 ppm. $C_{28}H_{18}BF_5N_2$ (488.26): calcd. C 68.88, H 3.72, B 2.21, F 19.46, N 5.74; found C 69.25, H 3.42, F 19.41, N 5.40.

4,4-Difluoro-3-[(1,1-biphenyl)-4-yl]-2,5-diphenyl-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3ag): Yield 0.047 g (73%) as a dark blue solid with metallic luster, m.p. 212–214 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1602, 1562, 1520, 1479, 1471, 1451, 1410, 1398, 1251, 1224, 1208, 1138, 1126, 1087, 1073, 1064, 1006, 998, 881, 844, 772, 753, 744, 738, 699, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.83 (m, 2 H, Ph-2d,6d), 7.60 (m, 2 H, Ph-2b,6b), 7.56 (m, 4 H, Ph-2a,6a,3a,5a), 7.53 (m, 1 H, 1-H), 7.47 (m, 1 H, 7-H), 7.40 (m, 5 H, Ph-3d,5d,4d,3b,5b), 7.33 (m, 1 H, Ph-4b), 7.22 (m, 3 H, Ph-3c,4c,5c), 7.09 (m, 2 H, Ph-2c,6c), 6.73 (d, J = 4.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 162.3 (C-5), 159.4 (C-3), 142.3 (C-4a), 140.3 (C-1b), 136.8 (C-1c), 133.9 (C-7a), 133.2 (C-2), 131.9 (C-8a), 131.8 (C-1d), 130.9 (C-2a,6a), 130.6 (C-4d), 130.5 (C-7), 130.1 (C-1a), 129.7 (t, J = 4.2 Hz, C-2d,6d), 128.9 (C-3b,5b), 128.6 (C-2c,6c), 128.5 (C-3c,5c,3d,5d), 127.9 (C-4b), 127.8 (C-1), 127.7 (C-4c), 127.2 (C-2b,6b), 126.6 (C-3a,5a), 126.4 (q, J = 33.3 Hz, C-8), 123.1 (C-6), 122.7 (q, J = 276.2 Hz, CF_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.3 (m, J_{BF} = 30.5 Hz, BF_2), –54.6 (CF_3) ppm. $C_{34}H_{22}BF_5N_2$ (564.36): calcd. C 72.36, H 3.93, B 1.92, F 16.83, N 4.96; found C 72.18, H 3.59, F 17.20, N 4.69.

4,4-Difluoro-3-[(1,1-biphenyl)-4-yl]-5-(2-thienyl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3bf): Yield 0.133 g (79%) as dark green needles with metallic luster, m.p. 214–216 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1566, 1527, 1473, 1296, 1275, 1138, 1119, 1102, 1088, 1045, 1036, 852, 841, 790, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.24 (dd, J = 3.9, 1.0 Hz, 1 H, 3-H of thiophene), 8.07 (m, 2 H, Ph-2a,6a), 7.74 (m, 2 H, Ph-3a,5a), 7.70 (m, 2 H, Ph-2b,6b), 7.60 (dd, J = 4.9, 1.0 Hz, 1 H, 5-H of thiophene), 7.50 (m, 2 H, Ph-3b,5b), 7.43 (m, 1 H, 7-H), 7.42 (m, 1 H, 1-H), 7.40 (m, 1 H, Ph-4b), 7.20 (dd, J = 3.9, 4.9 Hz, 1 H, 4-H of thiophene), 6.96 (d, J = 4.5 Hz, 1 H, 6-H), 6.82 (d, J = 4.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 159.9 (C-3), 153.6 (C-5), 153.6 (C-2 of thiophene), 142.9 (C-4a), 140.3 (C-1b), 134.3 (C-7a), 133.9 (C-2 of thiophene), 133.8 (C-3 of thiophene), 133.6 (C-8a), 131.8 (C-5 of thiophene), 131.0 (C-1a), 130.2 (C-2a,6a), 130.1 (C-7), 129.7 (C-4 of thiophene), 129.2 (C-1), 128.9 (C-3b,5b), 127.9 (C-4b), 127.3 (C-2b,6b), 127.2 (C-3a,5a), 124.5 (q, J = 33.2 Hz, C-8), 123.2 (C-6), 122.6 (C-2), 122.8 (q, J = 275.8 Hz, CF_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –135.9 (m, J_{BF} = 32.0 Hz, BF_2), –54.5 (CF_3) ppm. $C_{26}H_{16}BF_5N_2S$ (494.29): calcd. C 63.18, H 3.26, B 2.19, F 19.22, N 5.67, S 6.49; found C 63.38, H 3.22, F 19.09, N 5.70, S 6.31.

4,4-Difluoro-3-[(1,1-biphenyl)-4-yl]-2-phenyl-5-(2-thienyl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3bg): Yield 0.066 g (87%) as a dark green solid with metallic luster, m.p. 214–215 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1563, 1526, 1482, 1470, 1451, 1426, 1415, 1283, 1252, 1236, 1167, 1142, 1117, 1052, 1029, 915, 850, 755, 719, 696, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.14 (dd, J = 3.9, 1.0 Hz, 1 H, 3-H of thiophene), 7.65 (m, 2 H, Ph-2b,6b), 7.62 (m, 2 H, Ph-2a,6a), 7.59 (m, 2 H, Ph-3a,5a), 7.54 (dd, J = 4.9, 1.0 Hz, 1 H, 5-H of thiophene), 7.53 (m, 1 H, 1-H), 7.43 (m, 3 H, Ph-3b,5b, 7-H), 7.35 (m, 1 H, Ph-4b), 7.22 (m, 3 H, Ph-3c,4c,5c), 7.20 (dd, J = 3.9, 4.9 Hz, 1 H, 4-H of thiophene), 7.12 (m, 2 H, Ph-2c,6c), 6.94 (d, J = 4.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.5 (C-3), 154.2 (C-5), 142.1 (C-4a), 140.4 (C-1b), 136.2 (C-1c), 136.1 (C-7a), 134.7 (C-8a), 133.9 (C-3 of thiophene), 133.8 (C-2 of thiophene), 133.4 (C-2), 132.0 (C-5 of thiophene), 131.2 (C-2a,6a), 130.5 (C-7), 129.9 (C-1a), 129.7 (C-4 of thiophene), 128.9 (C-3b,5b), 128.6 (C-2c,6c), 128.5 (C-3c,5c), 127.8 (C-4b), 127.5 (C-4c), 127.2 (C-2b,6b), 126.7 (C-1), 126.5 (C-3a,5a), 125.9 (q, J = 33.2 Hz, C-8), 123.3 (C-6), 122.9 (q, J = 275.3 Hz, CF_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –136.4

(m, J_{BF} = 31.3 Hz, BF_2), –54.5 (CF_3) ppm. $C_{32}H_{20}BF_5N_2S$ (570.38): calcd. C 67.38, H 3.53, B 1.90, F 16.65, N 4.91, S 5.62; found C 67.77, H 3.25, F 16.93, N 4.71, S 5.49.

4,4-Difluoro-3,5-bis(4-methylphenyl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3cc): Yield 0.114 g (89%) as a dark blue solid with metallic luster, m.p. 118–120 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1565, 1474, 1426, 1392, 1301, 1275, 1226, 1170, 1139, 1085, 1052, 968, 946, 888, 822, 788, 750, 729 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.81 (m, 4 H, Ph-2a,6a), 7.44 (m, 2 H, 1,7-H), 7.26 (m, 4 H, Ph-3a,5a), 6.72 (d, J = 4.6 Hz, 2 H, 2,6-H), 2.40 (s, 6 H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.7 (C-3,5), 140.9 (C-4a,4a′), 133.4 (C-8a,7a), 130.0 (C-1,7), 129.6 (t, J = 4.0 Hz, C-2a,6a,2a′,6a′), 129.2 (C-3a,5a,3a′,5a′), 129.1 (C-1a,1a′), 125.8 (q, J = 33.2 Hz, C-8), 122.8 (q, J = 276.1 Hz, CF_3) 122.7 (C-2,6), 21.6 (Me,Me′) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.5 (m, J_{BF} = 31.1 Hz, BF_2), –54.5 (t, J_{HF} = 2.3 Hz, CF_3) ppm. ^{15}N NMR ($CDCl_3$): δ = –193.5 ppm. $C_{24}H_{18}BF_5N_2$ (440.22): calcd. C 65.48, H 4.12, B 2.46, F 21.58, N 6.36; found C 65.21, H 4.02, F 21.92, N 6.12.

4,4-Difluoro-3,5-bis(4-methoxyphenyl)-8-trifluoro-methyl-4-bora-3a,4a-diaza-*s*-indacene (3dd): Yield 0.113 g (57%) as a dark blue solid with metallic luster, m.p. 180–182 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1604, 1564, 1474, 1429, 1395, 1297, 1265, 1221, 1179, 1137, 1083, 1045, 833, 791, 742, 620 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.87 (m, 4 H, Ph-2a,6a), 7.38 (m, 2 H, 1,7-H), 6.94 (m, 4 H, Ph-3a,5a), 6.70 (d, J = 4.6 Hz, 2 H, 2,6-H), 3.84 (s, 6 H, OMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.7 (C-4a,4a), 160.9 (C-3,5), 133.4 (C-8a,7a), 131.5 (t, J = 4.0 Hz, C-2a,6a,2a′,6a′), 129.2 (C-1,7), 126.3 (q, J = 33.2 Hz, C-8), 124.3 (C-1a,1a′), 122.6 (q, J = 276.0 Hz, CF_3), 122.5 (C-2,6), 114.1 (C-3a,5a,3a′,5a′), 55.4 (OMe,OMe′) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.9 (m, J_{BF} = 31.2 Hz, BF_2), –54.5 (t, J_{HF} = 2.3 Hz, CF_3) ppm. $C_{24}H_{18}BF_5N_2O_2$ (472.22): calcd. C 61.04, H 3.84, B 2.29, F 20.12, N 5.93; found C 60.73, H 3.59, F 20.47, N 5.58.

4,4-Difluoro-3,5-bis(4-chlorophenyl)-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3ee): Yield 0.088 g (88%) as a lustrous bronze solid, m.p. 176–178 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1593, 1569, 1559, 1471, 1429, 1313, 1299, 1277, 1224, 1145, 1112, 1081, 1053, 1012, 969, 888, 838, 791, 751, 728 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.77 (m, 4 H, Ph-2a,6a), 7.44 (m, 2 H, 1,7-H), 7.39 (m, 4 H, Ph-3a,5a), 6.69 (d, J = 4.6 Hz, 2 H, 2,6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 160.7 (C-3,5), 137.0 (C-4a,4a′), 133.7 (C-8a,7a), 130.9 (t, J = 4.2 Hz, C-2a,6a,2a′,6a′), 130.7 (C-1,7), 130.1 (C-1a,1a′), 128.9 (C-3a,5a,3a′,5a′), 127.0 (q, J = 33.4 Hz, C-8), 122.9 (C-2,6), 122.6 (q, J = 276.2 Hz, CF_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.3 (m, J_{BF} = 31.3 Hz, BF_2), –54.6 (t, J_{HF} = 2.1 Hz, CF_3) ppm. $C_{22}H_{12}BCl_2F_5N_2$ (481.06): calcd. C 54.93, H 2.51, B 2.25, Cl 14.74, F 19.75, N 5.82; found C 54.55, H 2.48, Cl 14.49, F 20.10, N 5.71.

4,4-Difluoro-3,5-bis[(1,1-biphenyl)-4-yl]-8-trifluoromethyl-4-bora-3a,4a-diaza-*s*-indacene (3ff): Yield 0.102 g (36%) as dark blue needles with metallic luster, m.p. 234–236 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1604, 1573, 1544, 1525, 1487, 1470, 1411, 1384, 1374, 1330, 1292, 1275, 1245, 1205, 1156, 1122, 1082, 1046, 972, 908, 837, 819, 800, 764, 733, 725, 694 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.98 (m, 4 H, Ph-2a,6a), 7.66 (m, 4 H, Ph-3a,5a), 7.61 (m, 4 H, Ph-2b,6b), 7.46 (m, 2 H, 1,7-H), 7.45 (m, 4 H, Ph-3b,5b), 7.35 (m, 2 H, Ph-4b), 6.80 (d, J = 4.6 Hz, 2 H, 2,6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.1 (C-3,5), 143.1 (C-4a,4a′), 140.1 (C-1b,1b′), 133.8 (C-8a,7a), 130.0 (C-1,7), 129.9 (C-2a,6a,2a′,6a′), 130.5 (C-1a,1a′), 127.1 (C-2b,6b,2b′,6b′), 128.6 (C-3b,5b,3b′,5b′), 127.8 (C-4b,4b′), 126.9 (C-3a,5a,3a′,5a′), 126.1 (q, J = 33.4 Hz, C-8), 122.9 (C-2,6), 122.7 (q, J = 276.2 Hz, CF_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –132.4 (m, J_{BF} = 31.3 Hz, BF_2), –54.5 (t, J_{HF} = 2.1 Hz, CF_3) ppm. ^{15}N NMR ($CDCl_3$): δ = –192.8 ppm. $C_{34}H_{22}BF_5N_2$ (564.36): calcd. C 72.36, H 3.93, B 1.92, F 16.83, N 4.96; found C 71.98, H 3.90, F 17.18, N 4.65.

4,4-Difluoro-3,5-bis[(1,1-biphenyl)-4-yl]-2,6-diphenyl-8-trifluoro-methyl-4-bora-3a,4a-diaza-*s*-indacene (3gg): Yield 0.071 g (90%) as dark green needles with metallic luster, m.p. 296–298 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1570, 1406, 1275, 1245, 1226, 1141, 1082, 1002, 966, 919, 842, 748, 629 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.57 (m, 4 H, Ph-2b,6b), 7.53 (m, 8 H, Ph-3a,5a,2a,6a), 7.52 (m, 2 H, 1,7-H), 7.39 (m, 4 H, Ph-3b,5b), 7.31 (m, 2 H, Ph-4b), 7.22 (m, 6 H, Ph-3c,5c,4c), 7.10 (m, 4 H, Ph-2c,6c) ppm. ^{13}C NMR ($CDCl_3$): δ = 159.7 (C-3,5), 142.4 (C-4a,4a′), 140.3 (C-1b,1b′), 136.9 (C-1c,1c′), 133.2 (C-2,6), 132.1 (C-8a,7a), 131.0 (C-2a,6a,2a′,6a′), 130.0 (C-1a,1a′), 128.9 (C-3b,5b,3b′,5b′), 128.7 (C-2c,6c,2c′,6c′), 128.5 (C-3c,5c,3c′,5c′), 127.8 (C-4b,4b′), 127.9 (C-1,7), 127.8 (C-4c,4c′), 127.2 (C-2b,6b,2b′,6b′), 126.6 (C-3a,5a,3a′,5a′), 126.3 (q, J = 33.4 Hz, C-8), 125.5 (q, J = 276.4 Hz, CF_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –131.7 (m, J_{BF} = 29.8 Hz, BF_2), –54.6 (t, J_{HF} = 2.0 Hz, CF_3) ppm. $C_{46}H_{30}BF_5N_2$ (716.56): calcd. C 77.10, H 4.22, B 1.51, F 13.26, N 3.91; found C 77.02, H 3.98, F 13.62, N 3.52.

Supporting Information (see footnote on the first page of this article): Analytical data for compounds 6 and analytical data and absorption and fluorescence spectra of compounds 3 are reported.

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