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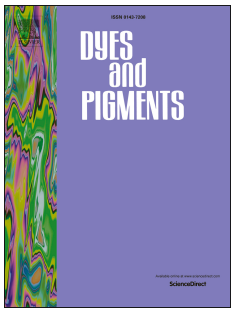

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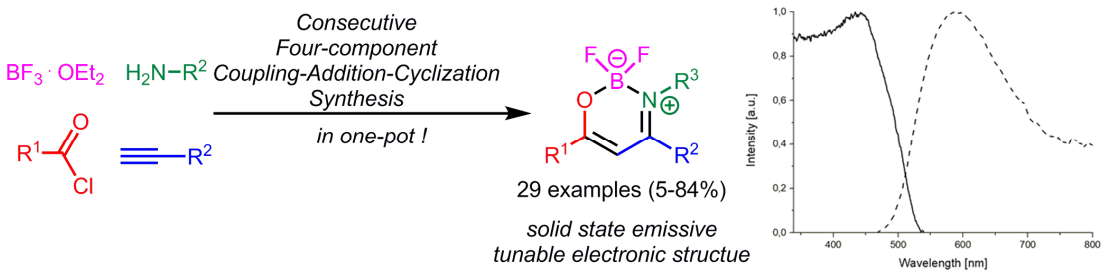

Diversity-oriented Four-component Synthesis of Solid State Luminescent Difluoro Oxazaborinines

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ABSTRACT

(Hetero)aroyl chlorides, alkynes, anilines, and BF_3 diethyl etherate are reacted in an alkynylation-amination-cyclization one-pot process to give trisubstituted difluoro oxazaborinines in moderate to very good yield in the sense of a consecutive four-component synthesis. The obtained title compounds are intensely fluorescent with bluish to yellow color, however, only in the solid state. Photophysical measurements, physical organic correlation studies, and DFT and TD DFT calculations are employed to rationalize the substituent effects on the dominant chromophores, which is oriented along the dipole axis spanning from the (hetero)aroyl substituent to the aniline moiety.

1. Introduction

Difluoro oxazaborinines **A**, i.e. BF_2-ketoimino complexes, can formally be considered as borondifluoride-enaminone complexes, which are in a line with BF_2-diketo (**B**) and BF_2-diimino complexes (**C**), the alternate complexes of 1,3-dicarbonyl synthetic equivalents (Figure 1) [1].

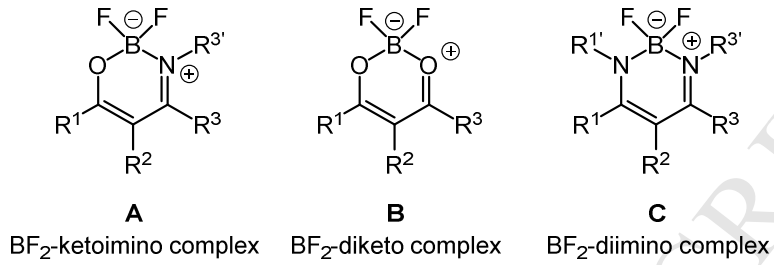


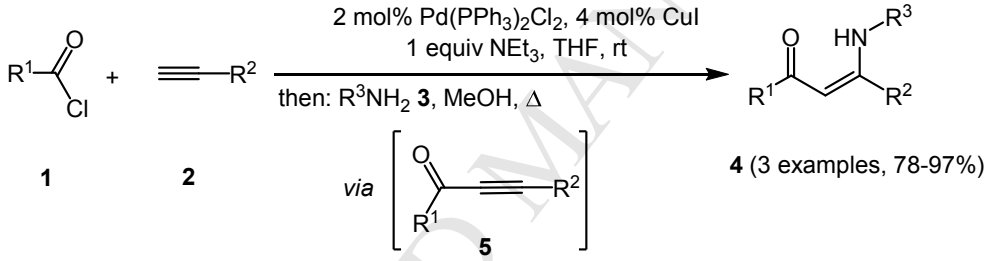
Figure 1. Structurally related BF_2-ketoimino (**A**), BF_2-diketo (**B**), and BF_2-diimino (**C**) complexes.

Although already structurally characterized some decades ago [2,3] and employed in [2+2] photodimerizations [4], difluoro oxazaborinines **A** as polar heterocyclic π-systems have gained considerable interest as a consequence of their electronic ground and excited state properties [1]. According to cyclic voltammetry the chelating enaminone can be regarded as a weak electron acceptor. Its LUMO can be stabilized by extending the π-conjugation with suitable aromatic substituents, and thereby the reduction is facilitated. More recently, the observation of pronounced solid state fluorescence has led to closer inspection of the induction of luminescence by aggregation induced emission (AIE) [5] of the difluoro oxazaborinines with extended π-conjugation [6], displaying mechanoluminescence and even heat-resistant mechanoluminescent chromism of oligomeric silsesquioxane boron ketoiminate hybrids [7]. In comparison to the diketo analogue **B** the B-N bond in the heterocycle **A** is considerably longer than the B-O bonds in structure **B** and therefore essential for the occurrence of AIE.

Classical syntheses of difluoro oxazaborinines **A** are stepwise, starting from 1,3-dicarbonyl compounds and require isolation of the enaminone or the BF_2-diketo complexes **B** [6]. A major drawback of this approach clearly is the inherent lack of control of the enaminone's regioselectivity. Alternative routes to enaminones are either long linear stepwise processes [8] or only deliver very specific substitution patterns [9]. For overcoming this shortcoming we reasoned that a diversity-oriented synthesis [10] obtained by the same reaction principle through variation of suitable starting

materials could be favorable. In particular, multicomponent reactions (MCR) [11] most beneficially combine economic and ecological aspects for reaching this challenging goal. In the sense of a chromophore concept, a chromogenic application of the MCR concept, functional chromophores have become accessible more easily and more generally [12], an approach that has now been systematically extended to a powerful tool in fluorophore design [13].

In the course of our program to devise multicomponent syntheses of heterocycles initiated by transition metal catalyzed alkynylation [14], we also disclosed a straightforward, highly stereoselective consecutive three-component synthesis of *Z*-configured enaminones **4** with perfect regiospecificity from acid chlorides **1**, alkynes **2**, and primary amines **3** via the intermediacy of alkynones **5** (Scheme 1) [15], which was later on expanded to four-component syntheses of tetrahydro-β-carbolines [16], pyridones [17], and pyrroles [18].



Scheme 1. Consecutive three-component synthesis of enaminones ***Z*-4**.

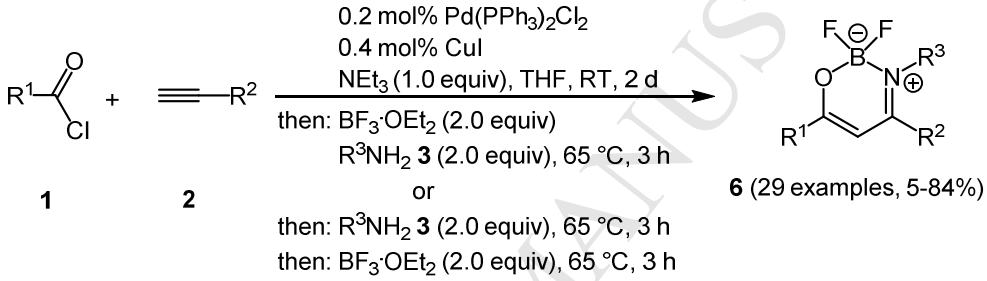
Herein, inspired by the interesting solid state luminescence of difluoro oxazaborinines **A** with extended π-conjugation [6,7] we report a novel consecutive four-component synthesis of difluoro oxazaborinines with perfect regioselectivity and their photophysical properties.

2. Results and discussion

2.1. Synthesis and structure

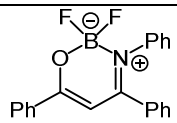
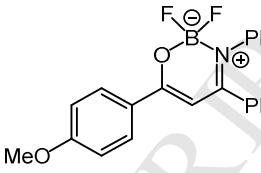
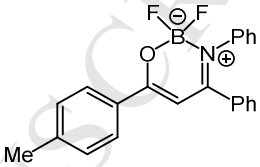
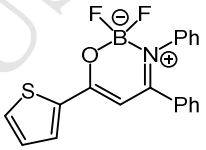
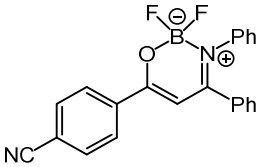
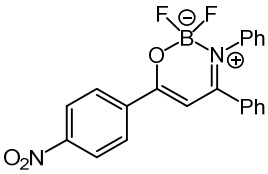
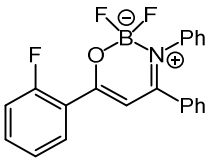
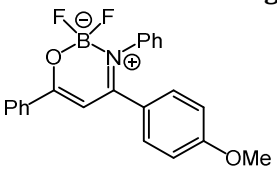
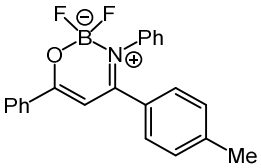
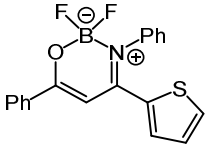
Initiated by our catalytic synthesis of alkynones **5** [14a,b,15] and a detailed optimization of the amine addition in the presence of boron trifluoride as an activating Lewis acid and the remaining fourth component (for details see Supp Inf) we identified optimal conditions for a diversity-oriented one-pot approach to difluoro oxazaborinines **6**. Upon subsequently reacting of acid chloride **1**, alkyne **2**, boron trifluoride, and amine **3** in the sense of a consecutive four-component process the title compounds **6** were obtained in modest to good yield as yellow solids in most cases (Scheme 2, Table 1), which are

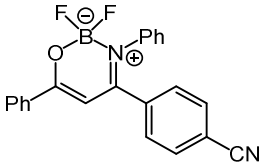
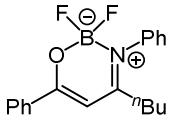
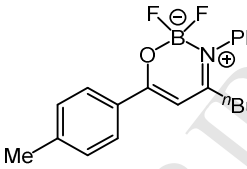
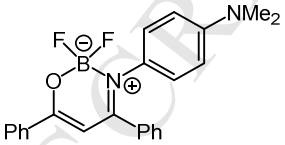
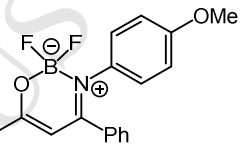
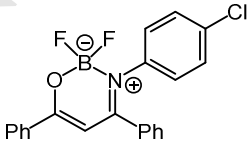
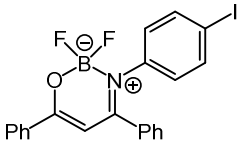
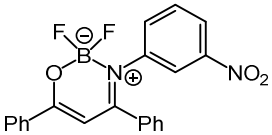
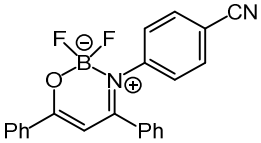
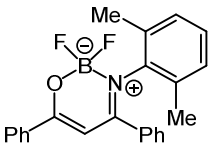
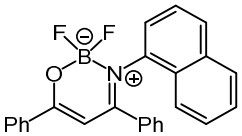
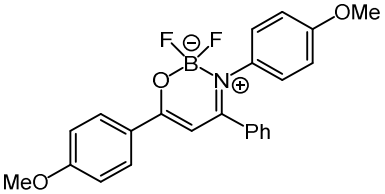
nonemissive in solution but display pronounced solid state emission under UV light. A practical aspect is the isolation of the products **6**, which can often be obtained analytically pure by simple precipitation into cold methanol. Thereby, a facile scale-up to 10 mmol was readily achieved (Table 1, entries 2, 5, 8-11, 14, and 16-29). Although the substrate scope is broad with respect to the alkynylation substitution pattern, a special attention has to be paid to electron rich amines in the latter part of the sequence. The domino formation of the difluoro oxazaborinines is considerably hampered in these cases by formation of Lewis acid-base adducts between boron trifluoride and the amine nucleophiles. To some extent this problem could be circumvented by first performing the enaminone generation after the alkynylation, i. e. prior to the addition of the boron trifluoride as a cyclizing component.

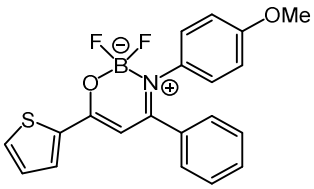
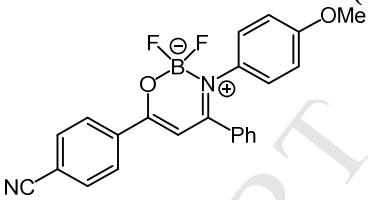
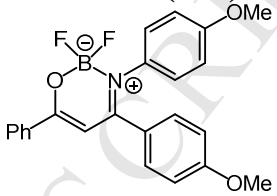
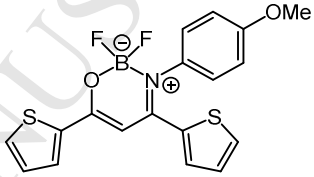
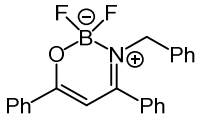
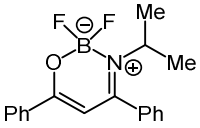
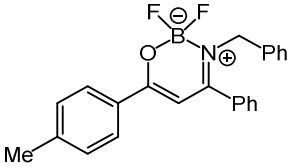


Scheme 2. Consecutive four-component synthesis of 2,2-difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines **6**.

Table 1. Experimental details of the four-component synthesis of 2,2-difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines **6**.

entry	acid chloride 1	alkyne 2	primary amine 3	2,2-difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines 6 (yield)
1	R^1 = Ph (**1a**)	R^2 = Ph (**2a**)	R^3 = Ph (**3a**)	 **6a** (73%)
2[a]	R^1 = *p*-$MeOC_6H_4$ (**1b**)	**2a**	**3a**	 **6b** (64%)
3	R^1 = *p*-MeC_6H_4 (**1c**)	**2a**	**3a**	 **6c** (62%)
4	R^1 = 2-thienyl (**1d**)	**2a**	**3a**	 **6d** (74%)
5[a]	R^1 = *p*-NCC_6H_4 (**1e**)	**2a**	**3a**	 **6e** (26%)
6	R^1 = *p*-$O_2NC_6H_4$ (**1f**)	**2a**	**3a**	 **6f** (52%)
7	R^1 = *o*-FC_6H_4 (**1g**)	**2a**	**3a**	 **6g** (74%)
8[a]	**1a**	R^2 = *p*-$MeOC_6H_4$ (**2b**)	**3a**	 **6h** (46%)
9[a]	**1a**	R^2 = *p*-MeC_6H_4 (**2c**)	**3a**	 **6i** (50%)
10[a]	**1a**	R^2 = 2-thienyl (**2d**)	**3a**	 **6j** (56%)

11[a]	**1a**	R^2 = *p*-NCC_6H_4 (**2e**)	**3a**	 **6k** (48%)
12	**1a**	R^2 = *n*-Bu (**2f**)	**3a**	 **6l** (40%)
13	**1c**	**2f**	**3a**	 **6m** (44%)
14[a]	**1a**	**2a**	R^3 = *p*-$Me_2NC_6H_4$ (**3b**)	 **6n** (5%)
15	**1a**	**2a**	R^3 = *p*-$MeOC_6H_4$ (**3c**)	 **6o** (61%)
16[a]	**1a**	**2a**	R^3 = *p*-ClC_6H_4 (**3d**)	 **6p** (71%)
17[a]	**1a**	**2a**	R^3 = *p*-IC_6H_4 (**3e**)	 **6q** (73%)
18[a]	**1a**	**2a**	R^3 = *m*-$O_2NC_6H_4$ (**3f**)	 **6r** (27%)
19[a]	**1a**	**2a**	R^3 = *p*-NCC_6H_4 (**3g**)	 **6s** (36%)
20[a]	**1a**	**2a**	R^3 = 2,6-$Me_2C_6H_3$ (**3h**)	 **6t** (51%)
21[a]	**1a**	**2a**	R^3 = 1-naphthyl (**3i**)	 **6u** (73%)
22[a]	**1b**	**2a**	**3c**	 **6v** (69%)

23[a]	**1d**	**2a**	**3c**	 **6w** (47%)
24[a]	**1e**	**2a**	**3c**	 **6x** (46%)
25[a]	**1a**	**2b**	**3c**	 **6y** (84%)
26[a]	**1d**	**2d**	**3c**	 **6z** (66%)
27[b]	**1a**	**2a**	$R^3 = CH_2Ph$ (**3j**)	 **6aa** (73%)
28[b]	**1a**	**2a**	$R^3 = i$-Pr (**3k**)	 **6ab** (36%)
29[b]	**1c**	**2a**	**3j**	 **6ac** (74%)

[a]Performed on 10 mmol scale with the alkynylation step at room temp for 2 d and the amination-cyclization step at 65 °C for 3 h. [b]Performed on 10 mmol scale with the alkynylation step at room temp for 2 d, the amination step at 65 °C for 3 h and the cyclization step at 65 °C for 3 h.

The structures of the difluoro oxazaborinines **6** were unambiguously assigned by comprehensive ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Most characteristically the proton resonances for the central CH appear between δ 6.0 and 7.0, depending of on shielding or deshielding by anisotropy cone of the neighboring (hetero)aryl substituents. The corresponding methine carbon nuclei resonate in range from δ 93.7 to 101.9, but mostly in a very narrow window between δ 95 to 98. In addition, heteronuclear NMR spectra were recorded. The BF_2-unit gives rise to coupling between the boron and the fluorine nuclei that can be found in the ^{11}B (δ 0.86-1.56; t, $^{1}J_{B\text{-}F}$ = 14.1.-17.1 Hz) and ^{19}F (δ -132.3 to -138.7; q, $^{1}J_{F\text{-}B}$ = 13.7-19.7 Hz) NMR spectra. Due to the steric hindrance of the 1-naphthyl

substitution compound **6u** displays atropisomerism, which can be detected at room temp in both the ^{11}B and the ^{19}F NMR spectra by the occurrence of diastereotopic fluorine nuclei (Figure 2). While in the ^{11}B NMR spectrum the signal at δ 1.5 splits into a doublet of doublets with direct coupling constants of ^{1}J of 12.4 and 17.1 Hz, the two diastereotopic fluorine nuclei give two doublets of quartets at δ-133.09 (dq, $^{2}J_{F\text{-}F}$ = 89.3 Hz, $^{1}J_{F\text{-}B}$ = 16.6 Hz) and -138.43 (dq, $^{2}J_{F\text{-}F}$ = 91.4 Hz, $^{1}J_{F\text{-}B}$ = 11.5 Hz), with direct coupling constants at $^{1}J_{F\text{-}B}$ = 11.5 and 16.6 Hz, respectively, and large geminal coupling constants at $^{2}J_{F\text{-}F}$ = 89.3 and 91.4 Hz. This sterically hindered rotation of the R^3 substituent can be additionally supported by inspection of the variable temperature (VT) ^{19}F NMR spectra of compound **6r** (Figure 3), where the broad signal at δ-133.37 for a coalescence temperature T_c = 258 K can be used to estimate the rotational barrier $\Delta G^{\neq}$ = 11.35 ± 0.23 kcal/mol ($\Delta G^{\neq} = 4.575 \cdot 10^{-3} \cdot T_c [9.972 + \log_{10}(T_c/\Delta\nu)]$. But it has to be mentioned that in the measuring range the signals are broad and do not resolve to quartets by coupling to the boron nucleus.

In all EI mass spectra of the compounds **6**, with exception of difluoro oxazaborinine **6k**, the molecular peak can be detected, which undergoes extrusion of BF_2 to give the corresponding enaminoyl radical cations. This intermediate fragments into three dominant units, i.e. the fragments R^{1+}, R^1CO^+, and $R^2CN^+R^3$, which appear in most cases and can be rationalized by α-cleavages.

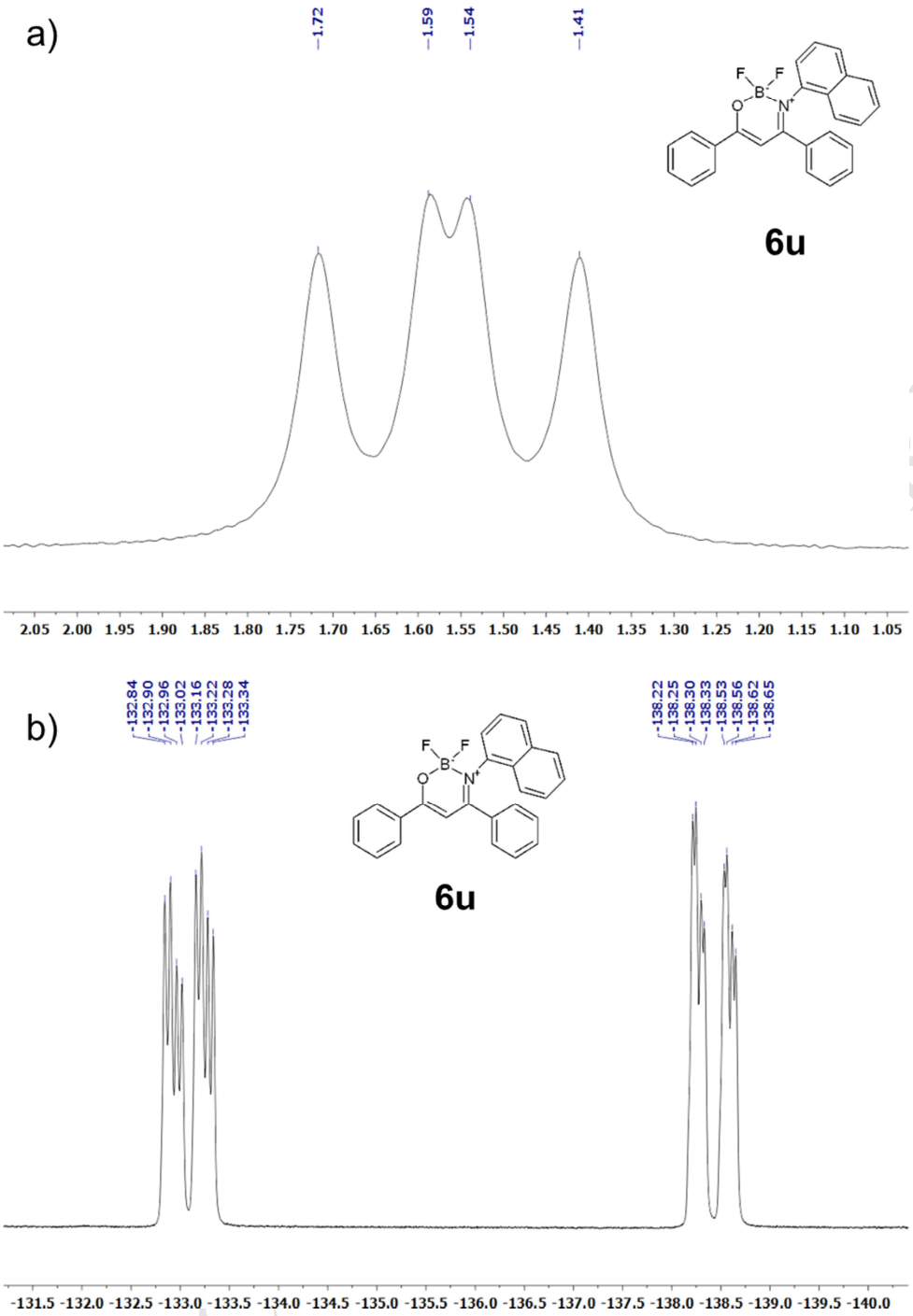


Figure 2. a) ^{11}B NMR spectrum of compound **6u** (recorded in $CDCl_3$, 96 MHz, T = 298 K). b) ^{19}F NMR spectrum of compound **6u** (recorded in $CDCl_3$, 282 MHz, T = 298 K).

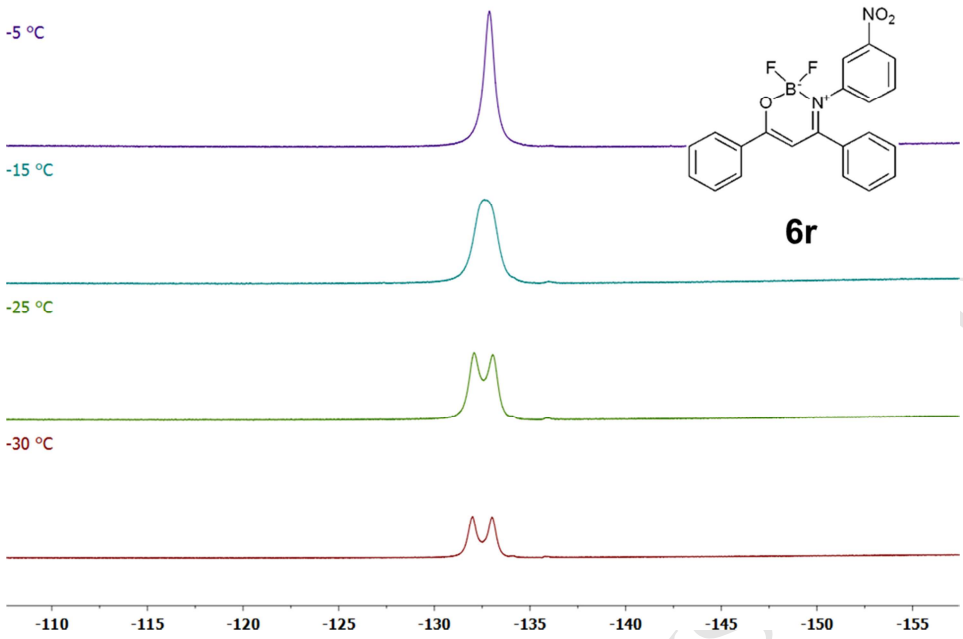


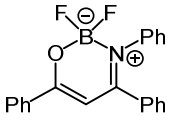
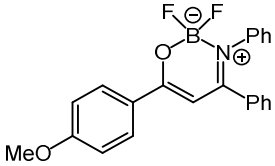
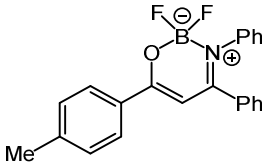
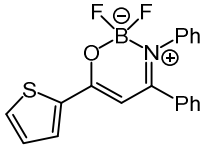
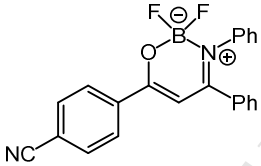
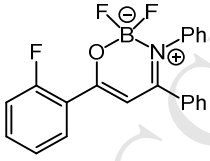
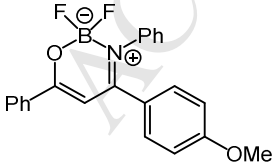
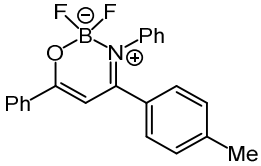
Figure 3. VT ^{19}F NMR spectra of compound **6r** (recorded in $CDCl_3$, 565 MHz, T = 268, 258, 248, and 243 K).

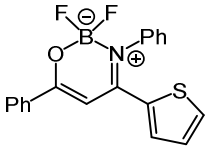
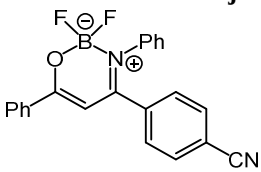
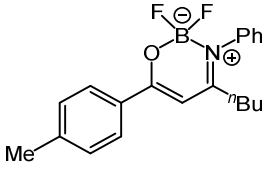
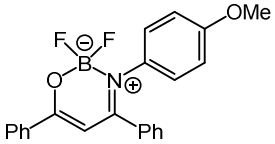
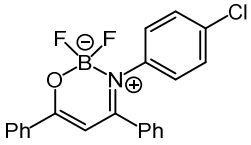
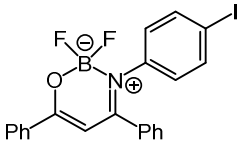
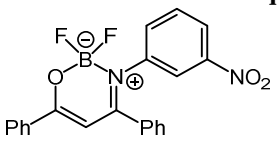
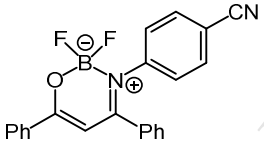
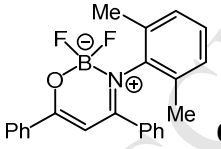
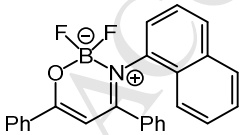
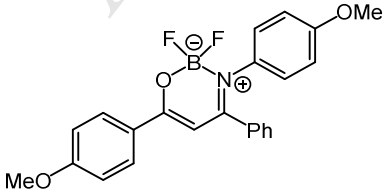
2.2. Photophysical properties

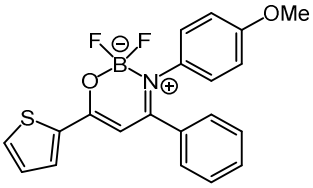
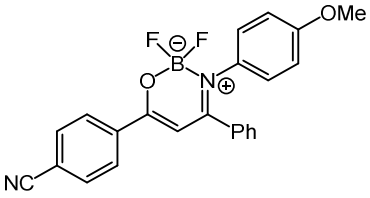
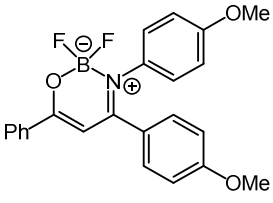
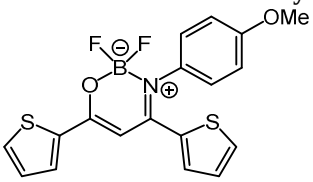
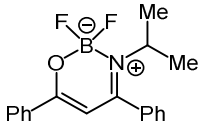
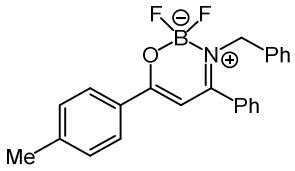
Most remarkably difluoro oxazaborinines **6** are nonluminescent in solution, but the vast majority distinctly fluoresces in the solid state upon excitation of the solid materials with a handheld UV lamp and aroused our interest to study their photophysical properties by solid state absorption and emission spectroscopy (Table 3). Only exemplarily, three representative difluoro oxazaborinines (**6a**, **6c**, and **6o**) were characterized by the solution absorption spectra (Table 1, entries 1, 3, and 12) showing broad longest wave length absorption bands at 360 to 367 nm with decadic molar extinction coefficients ε between 23000 and 34500 $L \cdot mol^{-1} \cdot cm^{-1}$. In the solid state the excitation maxima of the *N*-aryl substituted difluoro oxazaborinines **6a-z**, which correspond to the longest absorption bands are considerably red shifted and appear between 389 and 448 nm. The *N*-alkyl substituted derivatives **6ab** and **6ac** absorb in the solid state with a maxima at 384 and 360 nm, respectively. This already indicates that that the nature of *N*-substituent R^3 is of prominent importance for the absorption behavior as a consequence of extending the π-conjugation for *N*-aryl substituents. With exception of compounds **6f**, **6l**, **6n**, and **6aa**, which did not fluoresce in the solid state, all other compounds were studied in the emission behavior with an integrated sphere (Ulbricht sphere). Thereby, the emission

maxima $\lambda_{max,em}$, the fluorescence quantum yields Φ_f, the excitation maxima $\lambda_{max,abs}$ (determined from the fluorescence excitation spectra) (Figure 3), and the huge Stokes shifts $\Delta\tilde{\nu}$ in a range from 2400 to 6500 cm^{-1} were determined.

Table 3. Selected photophysical data (solid state absorption and emission, Stokes shifts) of difluoro oxazaborinines **6** (recorded at T = 293 K).

entry	compound	solution absorption	solid state absorption	emission	
		$\lambda_{max,abs}$ [nm] (ε [L·mol^{-1}·cm^{-1}])[a]	λ_{exc} [nm]	$\lambda_{max,em}$ [nm] (Φ_f [%])	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}][b]
1	 **6a**	253 (6100) 360 (23200)	425	523 (18)	4400
2	 **6b**	-	444	497 (34)	2400
3	 **6c**	367 (34500)	430	500 (39)	3300
4	 **6d**	-	448	525 (16)	4900
5	 **6e**	-	423	563 (2)	5900
6	 **6g**	-	406	512 (13)	5100
7	 **6h**	-	443	533 (12)	3800
8	 **6i**	-	422	526 (10)	4700

9	 **6j**	-	446	539 (4)	3900
10	 **6k**	-	429	549 (12)	5100
11	 **6m**	-	389	520 (6)	6500
12	 **6o**	255 (10000) 345 (23000) 363 (24000)	435	551 (12)	4800
13	 **6p**	-	420	533 (9)	5000
14	 **6q**	-	414	526 (6)	5100
15	 **6r**	-	423	488 (3)	3100
16	 **6s**	-	422	497 (14)	3600
17	 **6t**	-	441	503 (1)	2800
18	 **6u**	-	429	563 (3)	5500
19	 **6v**	-	441	524 (26)	3600

20	 **6w**	-	448	573 (6)	4900
21	 **6x**	-	446	588 (2)	5400
22	 **6y**	-	443	582 (3)	5400
23	 **6z**	-	448	578 (3)	5000
24	 **6ab**	-	384	477 (5)	5100
25	 **6ac**	-	360	455 (14)	5800

[a]Recorded in CH_2Cl_2, c(**6**) = 10^{-5} M at T = 293 K. [b]$\Delta\tilde{\nu} = 1/\lambda_{exc} - 1/\lambda_{max,em}$ [cm^{-1}].

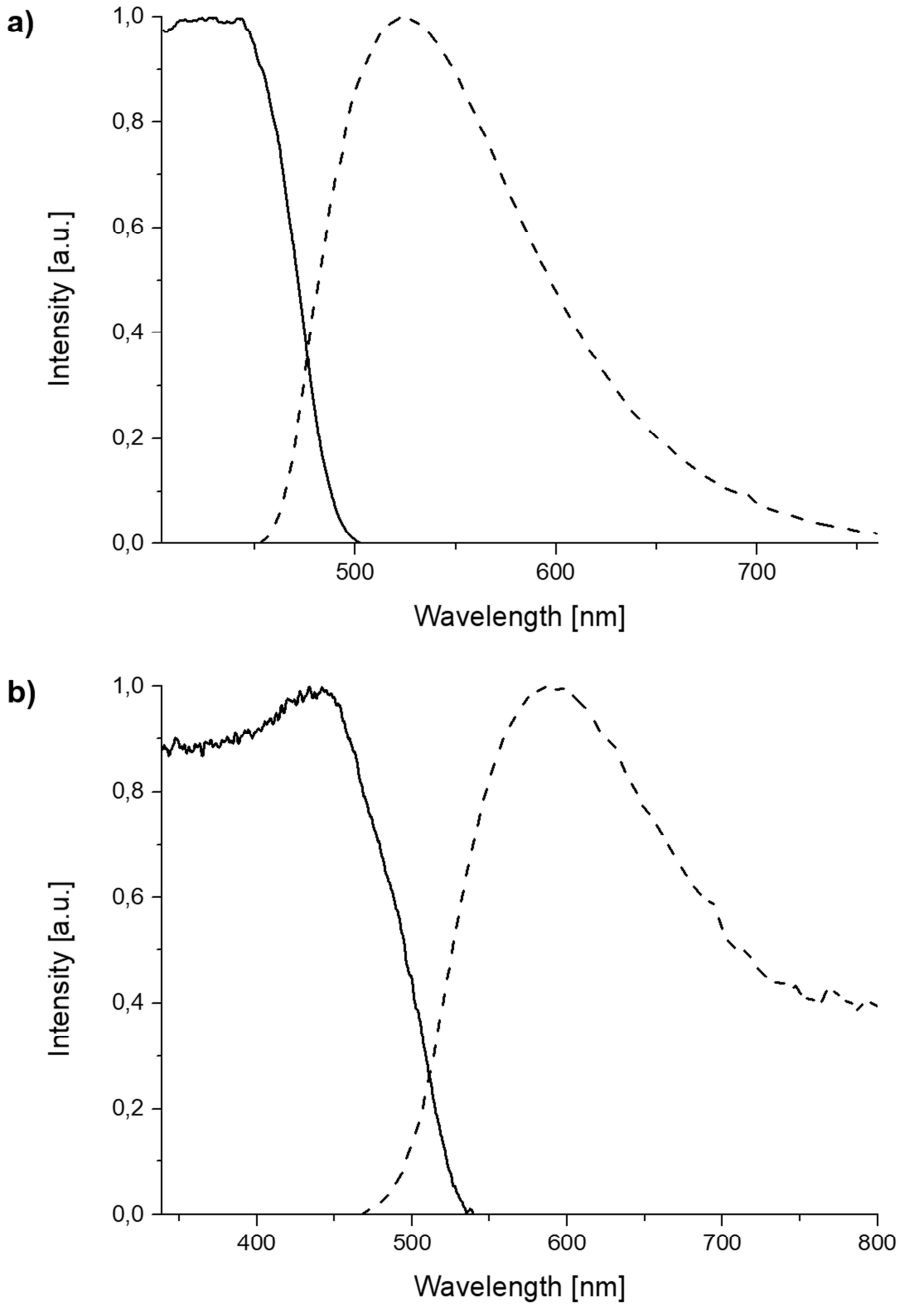


Figure 3. a) Normalized solid state excitation (solid line) and fluorescence spectra (dashed line) of compound **6v** (recorded at T = 293 K). b) Normalized solid state excitation (solid line) and fluorescence spectra (dashed line) of compound **6x** (recorded at T = 293 K).

The physical organic treatment of the substituent effects on difluoro oxazaborinines **6** was performed by screening for possible linear structure-property relationships based upon Hammett-Taft correlations for the three points of diversity represented by the *para*-phenyl substituents R^1, R^2, and R^3. The photophysical data λ_{exc} (excitation maximum), $\lambda_{max,em}$ (emission maximum), Φ_f (fluorescence quantum

yield), and $\Delta\tilde{\nu}$ (Stokes shift) of three consanguineous series, where one substituent was varied while the other two substituents were held constant (as phenyl substituents), were plotted against the Hammett-Taft parameters [19] σ_p, σ_I, σ_R, σ_{p+}, and σ_{p-} (for details, see Supp Inf).

The excitation spectra which were determined from the emission maxima did not reveal any correlation in either substituent position. While substituent R^1, introduced by the acid chloride **1**, is not affected by steric interactions with the neighboring substituents as for R^2 and R^3 stemming from the alkyne **2** and the aniline **3**, respectively, the electronic ground state properties, represented by the excitation maxima λ_{exc}, are obviously affected by the presence of different conformers, which are in a thermodynamic equilibrium. Also the fluorescence quantum yields Φ_f do not give systematic linear free energy relationships. This is partly reflected by the fact that fluorescence quantum yield are far from unity in all cases and, therefore, nonradiative deactivation dominates all excited stated processes in all three series. Most interestingly, best correlations are found for the emission maxima $\lambda_{max,em}$, and for the Stokes shifts $\Delta\tilde{\nu}$ in the series of the variation of substituent R^1.

The series of R^1 consists of compounds **6a-e**, where the variation proceeds from electron releasing (**6b**) over electro neutral (**6a**) to electron deficient (**6e**). The emission maxima $\lambda_{max,em}$ give a good linear correlation with the substituent parameter σ_p ($\lambda_{max,em} = -2558.5 \cdot \sigma_p + 19348$ [cm^{-1}]; $r^2 = 0.9593$) indicating that the substituent effect is transmitted both by resonance and inductive pathways in the excited state. The negative reaction parameter accounts for a lowering of the energy of the emission by electron withdrawing substituents. Most remarkably the Stokes shifts $\Delta\tilde{\nu}$ of this first series correlates excellently with the substituent parameter ($\Delta\tilde{\nu} = 2459.6 \cdot \sigma_{p+} + 4266.9$ [cm^{-1}]; $r^2 = 0.9876$), which accounts for a significant charge transfer character in the vibrationally relaxed excited singlet state from an electron releasing substituent capable of stabilizing positive charge to the nitrogen atom of the difluoro oxazaborinine.

The second series of R^2 consists of compounds **6a,h-k**, where the variation proceeds from electron releasing (**6h**) over electro neutral (**6a**) to electron deficient (**6k**). The only good linear correlation that could be established occurs with the inductive parameter σ_I ($\lambda_{max,em} = -1710.5 \cdot \sigma_I + 19003$ [cm^{-1}], r^2 =

0.9335). This indicates that in the vibrationally relaxed excited singlet state the aromatic substituent is distorted considerably out of coplanarity with the major chromophore.

The last series of R^3 encompasses the compounds **6a,o-q,s**, where the variation proceeds from electron releasing (**6o**) over electro neutral (**6a**) to electron deficient (**6s**). The best linear correlation can be established with the resonance parameter σ_R ($\lambda_{max,em}$ = 3091.6 · σ_R + 19360 [cm^{-1}], r^2 = 0.9393), indicating that delocalization with substituents in the *para*-position stabilize the formally electron deficient difluoro oxazaborinine nitrogen. This is further supported by the positive slope of the reaction parameter.

This physical organic analysis of the difluoro oxazaborinine fluorophore suggests R^1 adopts the function as an acceptor moiety, whereas R^3 acts as the donor counterpart (Figure 4). Substituent R^2 is obviously distorted out of coplanarity in the excited state and only can operate by its inductive effect.

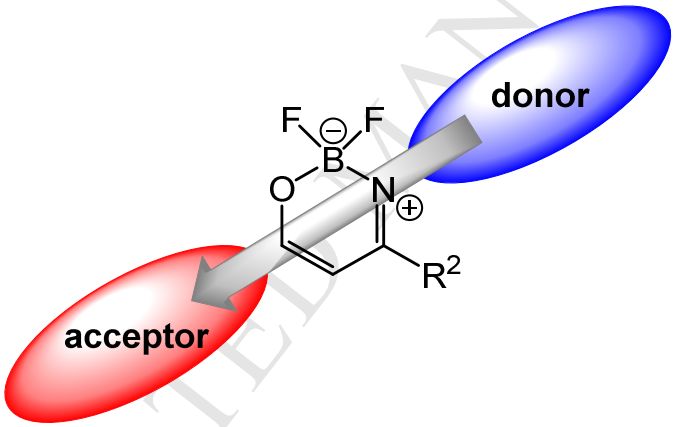


Figure 4. Electronic substituent design of difluoro oxazaborinine fluorophores.

The interaction between substituents can be nicely demonstrated for variation of substituents R^1 and R^3 compared to the mother system **6a** (R^1 = R^2 = R^3 = Ph). Donor (*p*-anisyl) and acceptor substituents (*p*-cyanophenyl) were placed at positions R^1 and R^3 and for the compounds **6a** (R^1 = Ph, R^3 = Ph), **6b** (R^1 = *p*-anisyl, R^3 = Ph), **6e** (R^1 = *p*-NCC_6H_4, R^3 = Ph), **6o** (R^1 = Ph, R^3 = *p*-anisyl), **6s** (R^1 = Ph, R^3 = *p*-NCC_6H_4), **6v** (R^1 = *p*-anisyl, R^3 = *p*-anisyl), and **6x** (R^1 = *p*-NCC_6H_4, R^3 = *p*-anisyl) the Stokes shifts $\Delta\tilde{\nu}$ and the fluorescence quantum yields Φ_f, were compared (Figure 5). While the placement of *p*-anisyl donors at the positions R^1 and/or R^3 in tendency leads to smaller Stokes shifts, the placement of *p*-cyanophenyl acceptors leads to an increase in the Stokes shifts compared to the all phenyl-substituted reference chromophore **6a** (Figure 5a). Interestingly the fluorescence quantum yields Φ_f are

consistently higher for the donor systems in comparison to the acceptor chromophores, while the electroneutral reference chromophore **6a** adopts the intermediate position (Figure 5b).

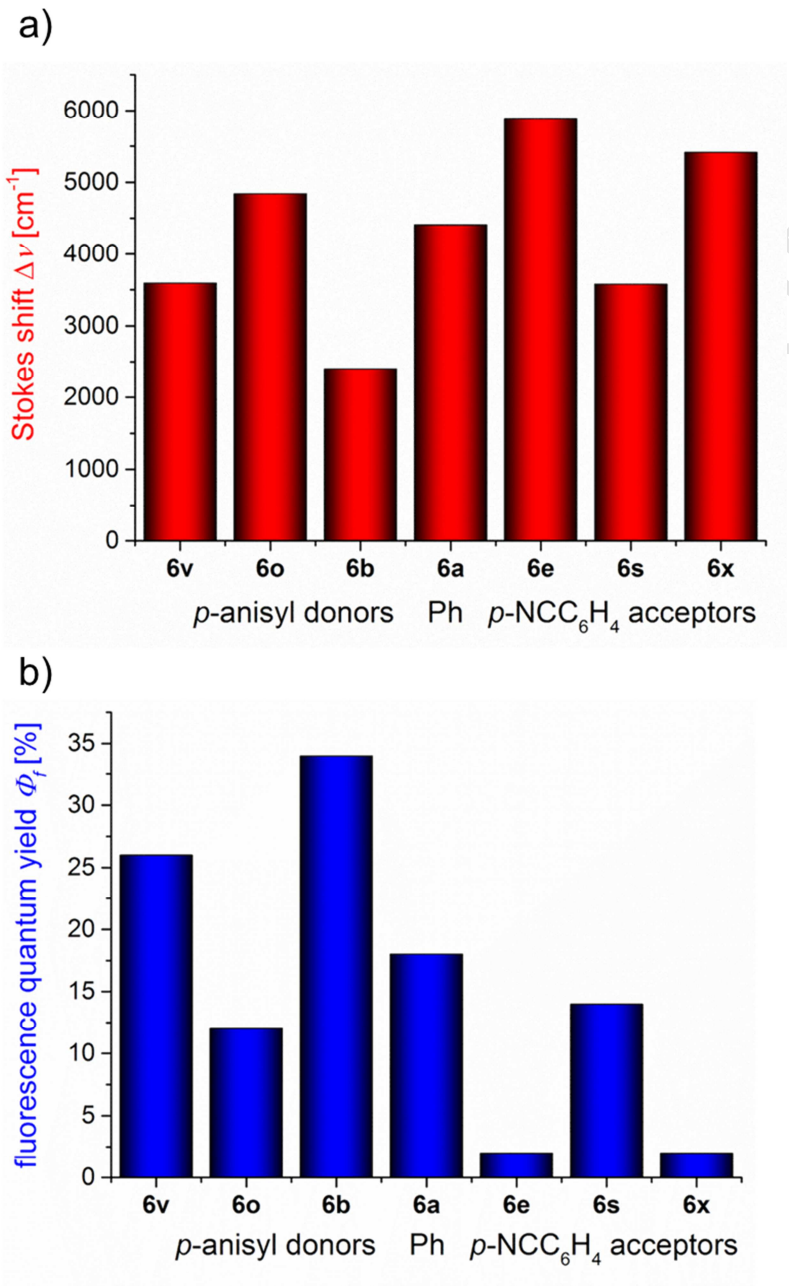


Figure 5. Qualitative comparison of a) Stokes shifts $\Delta\tilde{\nu}$ and b) fluorescence quantum yields Φ_f of compounds **6a** (R^1 = Ph, R^3 = Ph), **6b** (R^1 = *p*-anisyl, R^3 = Ph), **6e** (R^1 = *p*-NCC_6H_4, R^3 = Ph), **6o** (R^1 = Ph, R^3 = *p*-anisyl), **6s** (R^1 = Ph, R^3 = *p*-NCC_6H_4), **6v** (R^1 = *p*-anisyl, R^3 = *p*-anisyl), and **6x** (R^1 = *p*-NCC_6H_4, R^3 = *p*-anisyl) with donor (*p*-anisyl) and/or acceptor substituents (*p*-cyanophenyl) (the data were taken from Table 3).

Therefore, it was reasoned that the fluorescence quantum yield Φ_f might correlate with the Stokes shift $\Delta\tilde{\nu}$. Indeed, a good linear correlation was found (Φ_f = -0.0092 · $\Delta\tilde{\nu}$* + 54.858 [%]; R^2 = 0.84311; *$\tilde{\nu}$ is normalized to a dimensionless value), indicating that increased changes in the electronic structure, reflected by the considerable charge transfer in the vibrationally relaxed excited singlet state with increased polarity by enhanced donor-acceptor substitution, causes a decrease in the fluorescence quantum yield (Figure 6). This finding is in agreement with the energy gap law [20], i. e. the nonradiative decay of the excited state with increasing redshift of the emission bands.

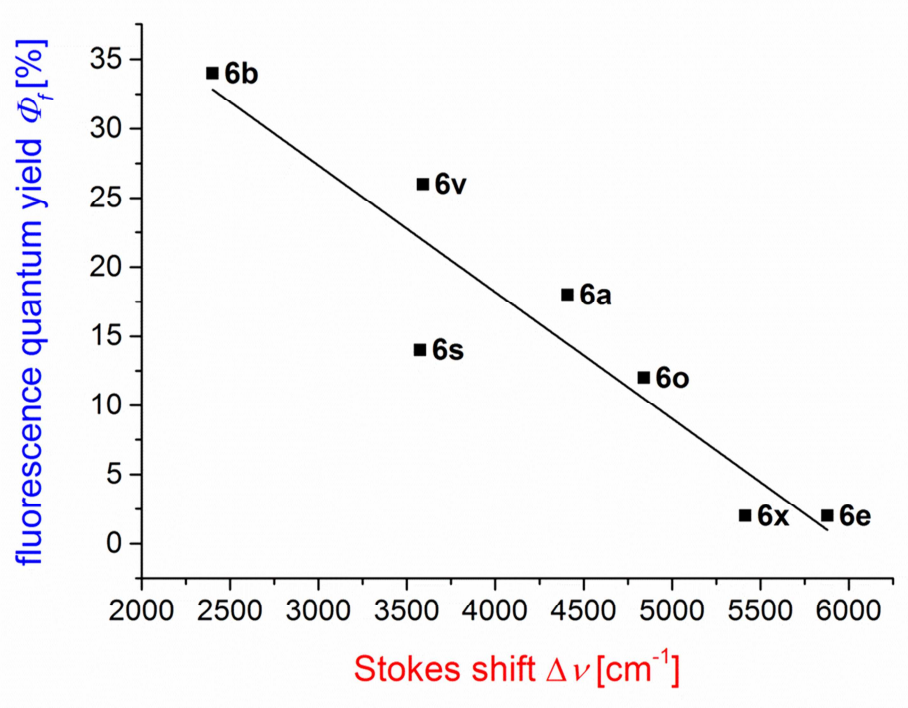


Figure 6. Linear correlation plot of the fluorescence quantum yields Φ_f against the Stokes shifts $\Delta\tilde{\nu}$ (normalized) of compounds **6a** (R^1 = Ph, R^3 = Ph), **6b** (R^1 = *p*-anisyl, R^3 = Ph), **6e** (R^1 = *p*-NCC_6H_4, R^3 = Ph), **6o** (R^1 = Ph, R^3 = *p*-anisyl), **6s** (R^1 = Ph, R^3 = *p*-NCC_6H_4), **6v** (R^1 = *p*-anisyl, R^3 = *p*-anisyl), and **6x** (R^1 = *p*-NCC_6H_4, R^3 = *p*-anisyl).

2.3. Calculated electronic structure

Since computations of solid state absorption properties are particularly difficult due to the combination of intermolecular interaction, crystal packing and ultimately aggregation, a qualitative understanding of the photophysical behavior of difluoro oxazaborinines in solution was sought in elucidating the electronic structure by calculating UV/vis absorption spectra at the TD DFT level of theory employing

Gaussian09 [21] (B3LYP functional [22] and Pople 6-311+G(d,p) basis set [23]). The computations were performed on the DFT optimized structures of compounds **6a** ($R^1 = R^2 = R^3 = Ph$), **6c** ($R^1 = p$-tolyl, $R^2 = R^3 = Ph$), and **6o** ($R^1 = R^2 = Ph$, $R^3 = p$-anisyl,) where experimental absorption spectra were recorded, in the electronic ground state applying the PCM model [24] with dichloromethane as a dielectric to model the solvent influence (Table 4).

Table 4. Experimental and TD-DFT calculated (B3LYP/6-311+G(d,p)) UV/Vis absorption maxima of the structures **6a**, **6c**, and **6o**, applying PCM with dichloromethane as a solvent.

	$\lambda_{max,abs}$ [nm] (ε [L mol^{-1} cm^{-1}])[a]	$\lambda_{max,calcd}$ [nm]	Most dominant contributions	Oscillator strength
6a	253			
	360	368	HOMO → LUMO (97 %)	0.6336
6c	367	371	HOMO → LUMO (98 %)	0.8009
6o	255 (10000)			
	345 (23000)	336	HOMO-1 → LUMO (96 %)	0.6219
	363 (24000)	413	HOMO → LUMO (99 %)	0.3723

[a] Recorded in dichloromethane, T = 293 K, c(**6**) = 10^{-5} M.

The calculated spectra qualitatively reproduce the experimental data and as can be seen the longest wavelength absorption maxima are represented by HOMO-LUMO transitions, with the exception of structure **6o**, where the experimentally determined longest wavelength band consists of a HOMO-1 to LUMO transition. The calculated longest wavelength maximum is found at 413 as a HOMO-LUMO transition. A closer inspection of the frontier molecular orbitals of structure **6a** reveals that the coefficient density in the HOMO is aligned the heuristically assigned chromophore axis (vide supra), i.e. including on the R^1 and R^3 substituents (Figure 7). Interestingly, the substituent R^2 does not bear coefficient density in the HOMO, but in the LUMO. Therefore, a Franck-Condon transition can be assumed that leads to the S_1 state after relaxation the HOMO-LUMO transition in this mother system accounts for a partial charge transfer proceeding into this appending substituent.

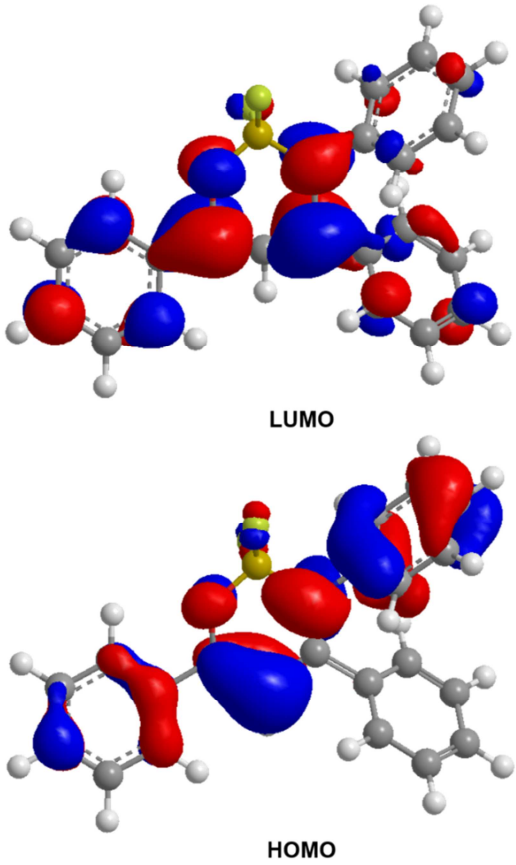


Figure 7. DFT calculated HOMO (bottom) and LUMO (top) of structure **6a**.

The qualitative substituent effect on the FMO energies of the selected difluoro oxazaborinines **6** was determined computationally by considering the HOMO-LUMO gap $\Delta E_{HOMO\text{-}LUMO}$ and the differences of the HOMO ΔE_{HOMO}(**6a** – **6**) and LUMO energies ΔE_{LUMO}(**6a** – **6**) to the mother chromophore **6a**. In detail the FMO energies of the *p*-anisyl donors **6b** (R^1 = *p*-anisyl, R^2 = R^3 = Ph), **6h** (R^1 = R^3 = Ph, R^2 = *p*-anisyl) and **6o** (R^1 = R^2 = Ph, R^3 = *p*-anisyl), of the reference **6a** (R^1 = R^2 = R^3 = Ph), of the *p*-cyanophenyl acceptors **6e** (R^1 = *p*-NCC_6H_4, R^2 = R^3 = Ph), **6k** (R^1 = R^3 = Ph, R^2 = *p*-NCC_6H_4), and **6s** (R^1 = R^2 = Ph, R^3 = *p*-NCC_6H_4), as well as the donor-acceptor chromophore **6x** (R^1 = *p*-NCC_6H_4, R^2 = Ph, R^3 = *p*-anisyl) were calculated (Table 5, Supp Inf Figure S1).

As can be seen by comparing the FMOs of the three *p*-anisyl donor chromophores **6b** (R^1 = *p*-anisyl), **6h** (R^2 = *p*-anisyl) and **6o** (R^3 = *p*-anisyl) with the mother system **6a** the donor rises the HOMO most when positioned at R^3, followed by R^1 and only to a minor extend when positioned at R^2 (Table 5, entries 1-3). The LUMO is risen most when the donor is positioned at R^1 and only slightly at the two other positions.

Table 5. DFT calculated HOMO and LUMO energies, HOMO-LUMO gap $\Delta E_{HOMO-LUMO}$ and differences of the HOMO ΔE_{HOMO}(**6a** – **6**) and LUMO energies ΔE_{LUMO}(**6a** – **6**) of the difluoro oxazaborinines **6b**, **6h**, **6o**, **6a**, **6e**, **6k**, **6s**, and **6x**.

entry	structure	E_{HOMO} [eV]	E_{LUMO} [eV]	$\Delta E_{HOMO-LUMO}$ [eV]	ΔE_{HOMO}(**6a** – **6**) [eV]	ΔE_{LUMO}(**6a** – **6**) [eV]
1	**6b** (R^1 = *p*-anisyl)	-6.067	-2.328	3.739	+ 0.265	+ 0.164
2	**6h** (R^2 = *p*-anisyl)	-6.249	-2.394	3.855	+ 0.083	+ 0.098
3	**6o** (R^3 = *p*-anisyl)	-5.909	-2.415	3.494	+ 0.423	+ 0.077
4	**6a** (R^1 = R^2 = R^3 = Ph)	-6.332	-2.492	3.840	0	0
5	**6e** (R^1 = *p*-NCC_6H_4),	-6.653	-3.002	3.651	- 0.321	- 0.510
6	**6k** (R^2 = *p*-NCC_6H_4)	-6.591	-2.892	3.699	- 0.259	- 0.400
7	**6s** (R^3 = *p*-NCC_6H_4)	-6.667	-2.856	4.081	- 0.335	- 0.364
8	**6x** (R^1 = *p*-NCC_6H_4, R^3 = *p*-anisyl)	-6.144	-2.933	3.211	+ 0.188	- 0.441

The HOMO-LUMO gap $\Delta E_{HOMO-LUMO}$ largely affected by the positioning of the HOMO, and, therefore, in this consanguineous series the donor placed at R^3 in structure **6o** gives with 3.494 eV the smallest HOMO-LUMO gap. For the *p*-cyano phenyl acceptor the chromophores **6e** (R^1 = *p*-NCC_6H_4), **6k** (R^1 = R^3 = Ph, R^2 = *p*-NCC_6H_4), and **6s** (R^3 = *p*-NCC_6H_4) the HOMO is lowered by 0.26 and 0.34 eV, i.e. in a narrow range (Table 5, entries 5-7). However, the effect on the LUMO spans a range from -0.36 to -0.51 eV upon variation the substituent position from R^1 over R^2 to R^3. In this consanguineous series the LUMO energy determines the $\Delta E_{HOMO-LUMO}$ and here positioning at R^1 in structure **6e** causes the most redshifted gap. Hence, the positioning of the donor at R^3 and the acceptor at R^1 in structure **6x** consequently leads to the lowest $\Delta E_{HOMO-LUMO}$ with 3.211eV (Table 5, entry 8). The considerable charge transfer character along the chromophore main axis of this computationally modelled HOMO-LUMO transition is additionally underlined by the electronic structure, where the coefficient density in the HOMO is localized in the central difluoro oxazaborinine core and the *p*-anisyl substituent at R^3. In contrast, the LUMO bears the coefficient density in the central difluoro oxazaborinine core and the *p*-cyanophenyl moiety at R^1 (Figure 8). In essence the increase in polarity upon HOMO-LUMO excitation, representing the S_1 state, is also supported by the solid state emission spectrum, where compound **6x** displays the most redshifted emission maximum of all synthesized compounds **6**. Therefore, this semiempirical computational approach allows qualitatively predicting the photonic properties of trisubstituted difluoro oxazaborinines **6**.

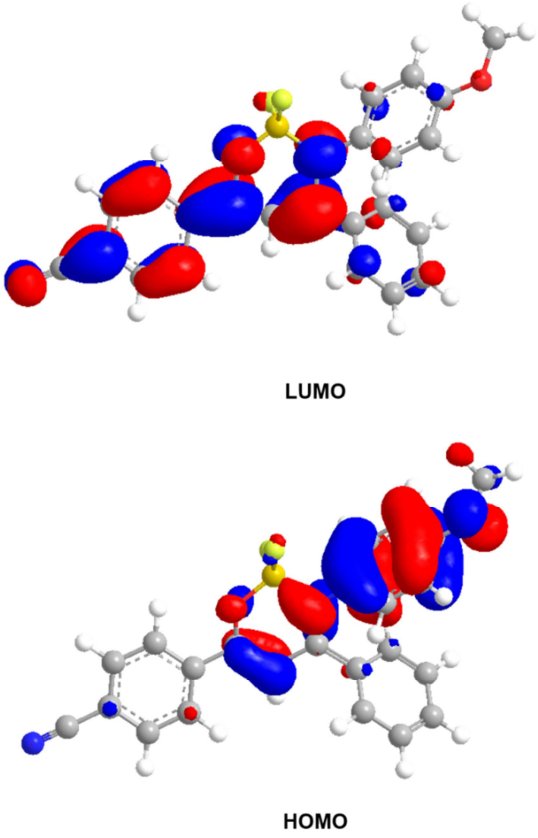
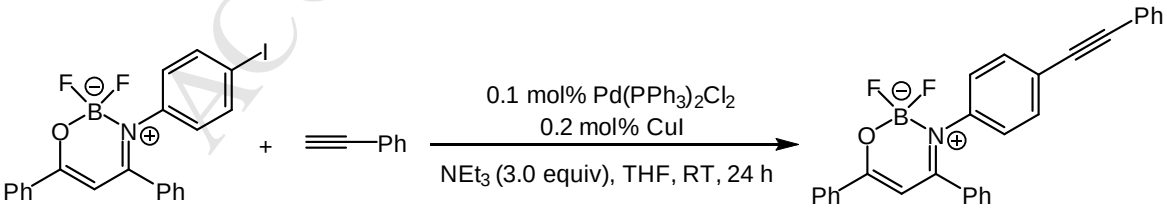


Figure 8. DFT calculated HOMO (bottom) and LUMO (top) of structure **6x**.

Indeed, expanding the π-conjugation of the difluoro oxazaborinine can be easily accomplished by Sonogashira coupling of the iodide **6q** with phenylacetylene (**2a**) to give π-expanded difluoro oxazaborinine **6ad** in 92% yield (Scheme 3). The solid state fluorescence spectrum of compound **6ad** shows a maximum 595 nm with a solid state fluorescence quantum yield Φ_f of 3% with an excitation maximum of 433 nm. This allows now for redshifting the emission maximum even to orange and red solid state luminescence without further decreasing the solid state fluorescence quantum yield.



6q **2a** **6ad** (92%)

Scheme 3. Sonogashira coupling of 2,2-difluoro-3-(4-iodophenyl)-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (**6q**) with phenylacetylene (**2a**) furnishing the π-expanded difluoro oxazaborinine **6ad**.

3. Conclusion

In summary we have developed a novel diversity-oriented one-pot approach to trisubstituted difluoro oxazaborinines in the sense of a consecutive four-component synthesis starting from (hetero)aroylchlorides, terminal alkynes, anilines, and boron trifluoride etherate. In contrast to 1,3-dicarbonyl based syntheses of difluoro oxazaborinines this alkynylation-amination-cyclization is completely regioselective and allows the preparation of unsymmetrically decorated difluoro oxazaborinines. All representatives show only luminescence in the solid state, but not in solution. Therefore, photophysical and physical organic investigations were elaborated to give a general rationale of relevant transitions in the absorption spectra and the polar nature of the difluoro oxazaborinine core was correlated with the substitution pattern. In addition first DFT and TD DFT calculations guide the way to lower the HOMO-LUMO gap and thereby also the emission characteristics. Further studies to redshift the solid state emissions of these unusual solid state emitters by expanding the methodology are currently underway.

4. Experimental

4.1. General considerations

Reagents, catalysts, and solvents were purchased in reagent grade and used without further purification. Anhydrous 1,4-dioxane was obtained from a drying system (*MBraun system MB*-SPS-800). The reaction progress and the purification process were observed qualitatively by using TLC silica gel 60 F_{254} sheets obtained by *Merck* KGaA. The spots were detected with UV light at 254 and 365 nm and with aqueous potassium permanganate solution. Chemical shifts δ in the ^{1}H NMR and ^{13}C NMR spectra are reported relative to $CDCl_3$ or d_6-DMSO. The assignments of quaternary C, CH, CH_2, and CH_3 signals were made by using DEPT-135 spectra. IR spectra were recorded with neat compounds under attenuated total reflection (ATR) and the intensities were characterized as strong (s), middle (m), and weak (w).

4.2. General procedure (GP) for the Four-component Synthesis of 2,2-Difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines 6.

$PdCl_2$ (2.0 mg, 10 μmol) were placed in an oven-dried Schlenk tube with a magnetic stir bar under nitrogen, and 1,4-dioxane (2mL), acid chloride **1** (1.00 mmol), terminal alkyne **2** (1.00 mmol) and triethylamine (0.14 mL, 1.00 mmol) were successively added (for experimental details, see Table 6). The reaction mixture was stirred at room temp under nitrogen until complete conversion (monitored by TLC). Then, $BF_3 \cdot OEt_2$ (0.26 mL, 2.00 mmol) and primary amine **3** (2.00 mmol) was added to the reaction mixture, which was then stirred under nitrogen at 100 °C for 3 h. After cooling to room temp the mixture was poured into cold methanol (150 mL, cooled by an external NaCl/ice bath) and stirred for 15 min. If no precipitate was formed ice water was added to the solution until no further precipitate formed. The solid was collected by filtration and dried in vacuo overnight to give analytical pure 2,2-difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines **6** as yellow to brown solids.

Table 6. Experimental details of the four-component synthesis of 2,2-difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines **6**.

entry	acid chloride 1	alkyne 2	primary amine 3	2,2-difluoro-2*H*-1,3λ^4,2λ^4-oxazaborinines 5 (yield)
1	115 μL (1.00 mmol) of benzoyl chloride (**1a**)	112 μL (1.00 mmol) of phenylacetylene (**2a**)	183 μL (2.00 mmol) of aniline (**3a**)	253 mg (73%) of **6a**
2[a]	1.35 mL (10.0 mmol) of *p*-methoxybenzoyl chloride (**1b**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	1.83 mL (20.0 mmol) of aniline (**3a**)	2.42 g (64%) of **6b**
3	132 μL (1.00 mmol) of *p*-toluoyl chloride (**1c**)	112 μL (1.00 mmol) of phenylacetylene (**2a**)	183 μL (2.00 mmol) of aniline (**3a**)	224 mg (62%) of **6c**
4	110 μL (1.00 mmol) of 2-thienoyl chloride (**1d**)	112 μL (1.00 mmol) of phenylacetylene (**2a**)	183 μL (2.00 mmol) of aniline (**3a**)	261 mg (74%) of **6d**
5[a]	1.66 g (10.0 mmol) of *p*-cyanobenzoyl chloride (**1e**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	1.83 mL (20.0 mmol) of aniline (**3a**)	0.98 g (26%) of **6e**
6	186 mg (1.00 mmol) of *p*-nitrobenzoyl chloride (**1f**)	112 μL (1.00 mmol) of phenylacetylene (**2a**)	183 μL (2.00 mmol) of aniline (**3a**)	204 mg (52%) of **6f**
7	119 μL (1.00 mmol) of *o*-fluorobenzoyl chloride (**1g**)	112 μL (1.00 mmol) of phenylacetylene (**2a**)	183 μL (2.00 mmol) of aniline (**3a**)	270 mg (74%) of **6g**
8[a]	1.15 mL (10.0 mmol) of benzoyl chloride	1.32 g (10.0 mmol) of *p*-methoxy-	1.83 mL (20.0 mmol) of aniline (**3a**)	1.75 g (46%) of **6h**

	(**1a**)	phenylacetylene (**2b**)		
9[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.27 mL (10.0 mmol) of *p*-tolylacetylene (**2c**)	1.83 mL (20.0 mmol) of aniline (**3a**)	1.82 g (50%) of **6i**
10[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	0.95 mL (10.0 mmol) of 2-thiophenyl-acetylene (**2d**)	1.83 mL (20.0 mmol) of aniline (**3a**)	1.98 g (56%) of **6j**
11[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.27 g (10.0 mmol) of *p*-cyano-phenylacetylene (**2e**)	1.83 mL (20.0 mmol) of aniline (**3a**)	1.80 g (48%) of **6k**
12	115 µL (1.00 mmol) of benzoyl chloride (**1a**)	115 µL (1.00 mmol) of hex-1-yne (**2f**)	183 µL (2.00 mmol) of aniline (**3a**)	131 mg (40%) of **6l**
13	132 µL (1.00 mmol) of *p*-toluoyl chloride (**1c**)	115 µL (1.00 mmol) of hex-1-yne (**2f**)	183 µL (2.00 mmol) of aniline (**3a**)	150 mg (44%) of **6m**
14[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.72 g (20.0 mmol) of *p*-*N*,*N*-dimethyl phenylene diamine (**3b**)	195 mg (5%) of **6n**
15	115 µL (1.00 mmol) of benzoyl chloride (**1a**)	112 µL (1.00 mmol) of phenylacetylene (**2a**)	246 mg (2.00 mmol) of *p*-methoxyaniline (**3c**)	230 mg (61%) of **6o**
16[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.55 g (20.0 mmol) of *p*-chloroaniline (**3d**)	2.71 g (71%) of **6p**
17[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	4.38 g (20.0 mmol) of *p*-iodoaniline (**3e**)	3.47 g (73%) of **6q**
18[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.76 g (20.0 mmol) of *m*-nitroaniline (**3f**)	1.07 g (27%) of **6r**
19[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.36 g (20.0 mmol) of *p*-cyanoaniline (**3g**)	1.35 g (36%) of **6s**
20[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.46 mL (20.0 mmol) of 2,6-dimethylaniline (**3h**)	1.92 g (51%) of **6t**
21[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.86 g (20.0 mmol) of 1-naphthylamine (**3i**)	2.88 g (73%) of **6u**
22[a]	1.35 mL (10.0 mmol) of *p*-methoxybenzoyl chloride (**1b**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.46 g (20.0 mmol) of *p*-methoxyaniline (**3c**)	2.82 g (69%) of **6v**
23[a]	1.10 mL (10.0 mmol) of 2-thienoyl chloride (**1d**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.46 g (20.0 mmol) of *p*-methoxyaniline (**3c**)	1.80 g (47%) of **6w**
24[a]	1.66 g (10.0 mmol) of *p*-cyanobenzoyl chloride (**1e**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.46 g (20.0 mmol) of *p*-methoxyaniline (**3c**)	1.85 g (46%) of **6x**
25[a]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.32 g (10.0 mmol) of *p*-methoxy-phenylacetylene (**2b**)	2.46 g (20.0 mmol) of *p*-methoxyaniline (**3c**)	3.41 g (84%) of **6y**

26[a]	1.10 mL (10.0 mmol) of 2-thienoyl chloride (**1d**)	0.95 mL (10.0 mmol) of 2-thio-phenylacetylene (**2d**)	2.46 g (20.0 mmol) of *p*-methoxyaniline (**3c**)	2.39 g (66%) of **6z**
27[b]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.18 mL (20.0 mmol) of benzylamine (**3j**)	2.65 g (73%) of **6aa**
28[b]	1.15 mL (10.0 mmol) of benzoyl chloride (**1a**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	1.64 mL (20.0 mmol) of *i*-propylamine (**3k**)	1.12 g (36%) of **6ab**
29[b]	1.32 mL (10.0 mmol) of *p*-toluoyl chloride (**1c**)	1.12 mL (10.0 mmol) of phenylacetylene (**2a**)	2.18 mL (20.0 mmol) of benzylamine (**3j**)	2.79 g (74%) of **6ac**

[a]Performed on 10 mmol scale with $Pd(PPh_3)_2Cl_2$ (14 mg, 20 μmol), CuI (7.0 mg, 40 μmol), THF (7 mL), triethylamine (1.40 mL, 10.0 mmol) (alkynylation step: room temp, 2 d); $BF_3 \cdot OEt_2$ (2.56 mL, 20.0 mmol) (amination-cyclization step: 65 °C, 3 h). [b]Performed on 10 mmol scale with $Pd(PPh_3)_2Cl_2$ (14 mg, 20 μmol), CuI (7.0 mg, 40 μmol), THF (7 mL), triethylamine (1.40 mL, 10.0 mmol) (alkynylation step: room temp, 2 d); amination step: 65 °C, 3 h; $BF_3 \cdot OEt_2$ (2.56 mL, 20.0 mmol) (cyclization step: 65 °C, 3 h).

4.2.1. 2,2-Difluoro-3,4,6-triphenyl-2*H*-1,3λ⁴,2λ⁴-oxazaborinine (6a)

According to the GP compound **6a** (253 mg, 73%) was obtained as a yellow solid, Mp 195 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.39 (s, 1 H), 7.11-7.22 (m, 5 H), 7.22-7.36 (m, 5 H), 7.43-7.60 (m, 3 H), 8.01-8.06 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 96.8 (CH), 126.9 (CH), 127.3 (CH), 127.7 (CH), 128.4 (CH), 128.6 (CH), 128.7, (CH), 128.7 (CH), 130.4 (CH), 132.8 (CH), 133.1 (C_{quat}), 134.9 (C_{quat}), 140.5 (C_{quat}), 170.6 (C_{quat}), 172.2 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.15 (q, $^1J_{F\text{-}B}$ = 14.2 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.46 (t, $^1J_{B\text{-}F}$ = 15.1 Hz). EI MS (*m/z* (%)): 347 ($(M)^+$, 44), 180 ($(C_{13}H_{10}N)^+$, 5), 105 ($(C_7H_5O)^+$, 21), 77 ($(C_6H_5)^+$, 28), 51 ($(C_3H_2N)^+$, 8). IR: $\tilde{\nu}$ [cm^{-1}] = 1595 (w), 1568 (m), 1558 (m), 1476 (s), 1454 (m), 1443 (m), 1402 (m), 1358 (m),1312 (w), 1287 (w), 1233 (w), 1153 (w), 1109 (s), 1076 (w), 1057 (m), 1022 (s), 997 (s), 976 (m), 930 (w), 912 (w), 868 (w), 839 (w), 806 (w), 779 (s), 762 (s), 727 (w), 691 (s), 658 (w), 631 (m), 619 (w). Anal. calcd. for $C_{21}H_{16}BF_2NO$ (347.2): C 72.65, H 4.65, N 4.03; Found: C 72.68, H 4.76, N 3.90.

4.2.2. 2,2-Difluoro-6-(4-methoxyphenyl)-3,4-diphenyl-2*H*-1,3λ⁴,2λ⁴-oxazaborinine (6b)

According to the GP compound **6b** (2.42 g, 64%) was obtained as a yellow solid, Mp 191 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.89 (s, 3 H), 6.31 (s, 1 H), 6.94-7.00 (m, 2 H), 7.11-7.22 (m, 5 H), 7.22-7.37 (m, 5 H), 7.99-8.06 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.2 (CH_3), 95.8 (CH), 114.1 (CH), 125.4 (C_{quat}), 127.0 (CH), 127.1 (CH), 128.4 (CH), 128.6 (CH), 128.6 (CH), 129.9 (CH), 130.2 (CH), 135.2 (C_{quat}), 140.7 (C_{quat}), 163.6 (C_{quat}), 170.1 (C_{quat}), 172.0 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -

134.66 (q, $^{1}J_{F\text{-}B}$ = 15.2 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.43 (t, $^{1}J_{B\text{-}F}$ = 15.4 Hz). EI MS (*m/z* (%)): 377 ($(M)^+$, 51), 362 ($(M\text{-}CH_3)^+$, 6), 333 (6), 312 ($(M\text{-}BF_2O)^+$, 5), 135 ($(C_8H_7O_2)^+$, 28), 107 ($(C_7H_7O)^+$, 5), 77 ($(C_6H_5)^+$, 16). IR: $\tilde{\nu}$ [cm^{-1}] = 2995 (w), 2961 (w), 2945 (w), 2914 (w), 2849 (w), 1603 (m), 1393 (s), 1362 (m), 1308 (m), 1265 (s), 1234 (s), 1175 (s), 1152 (m), 1136 (m), 1117 (s), 1101 (s), 1072 (m), 1051 (m), 1018 (s), 997 (s), 974 (m), 947 (m), 928 (m), 912 (w), 858 (s), 841 (m), 822 (m), 798 (s), 764 (s), 723 (m), 721 (m), 692 (s), 675 (m), 637 (m), 617 (m). Anal. calcd. $C_{22}H_{18}BF_2NO_2$ (377.2): C 70.05, H 4.81, N 3.71; Found: C 69.96, H 4.84, N 3.64.

4.2.3. 2,2-Difluoro-3,4-diphenyl-6-(*p*-tolyl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6c)

According to the GP compound **6c** (224 mg, 62%) was obtained as a yellow solid, Mp 214 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.42 (s, 3 H), 6.36 (s, 1 H), 7.12-7.18 (m, 3 H), 7.18-7.21 (m, 2 H), 7.21-7.23 (m, 1 H), 7.24 (m, 2 H), 7.25-7.29 (m, 3 H), 7.30-7.33 (m, 1 H), 7.92-7.95 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.8 (CH_3), 96.6 (CH), 127.1 (CH), 127.3 (CH), 127.9 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.7 (CH), 130.5 (CH), 130.5 (C_{quat}), 135.2 (C_{quat}), 140.8 (C_{quat}), 143.9 (C_{quat}), 170.6 (C_{quat}), 172.5 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -134.26 (q, $^{1}J_{F\text{-}B}$ = 14.7 Hz). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.46 (t, $^{1}J_{B\text{-}F}$ = 15.2 Hz). EI MS (*m/z* (%)): 361 ($(M)^+$, 55), 119 ($(C_8H_7O)^+$, 10), 91 ($(C_7H_7)^+$, 5), 77 ($(C_6H_5)^+$, 5), 40 ($(C_3H_4)^+$, 5). IR: $\tilde{\nu}$ [cm^{-1}] = 1603 (w), 1589 (w), 1491 (s), 1452 (m), 1425 (m), 1391 (m), 1364 (m), 1315 (w), 1296 (w), 1248 (w), 1231 (w), 1215 (w), 1192 (m), 1152 (w), 1099 (m), 1074 (w), 1057 (m), 1018 (s), 970 (m), 957 (w), 916 (w), 887 (w), 862 (w), 835 (m), 795 (s), 764 (s), 731 (w), 694 (s), 665 (w). Calcd. for $C_{22}H_{18}BF_2NO$ (361.2): C 73.16, H 5.02, N 3.88; Found: C 72.98, H 5.01, N 3.73.

4.2.4. 2,2-Difluoro-3,4-diphenyl-6-(thiophen-2-yl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6d)

According to the GP and after recrystallization compound **6d** (261 mg, 74%) was obtained as a yellow solid, Mp 268 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.23 (s, 1 H), 7.09-7.13 (m, 1 H), 7.14 (s, 1 H), 7.15-7.18 (m, 1 H), 7.18-7.20 (m, 1 H), 7.20-7.36 (m, 7 H), 7.64 (dd, *J* = 5.0 Hz, *J* = 1.2 Hz, 1 H), 7.86 (dd, *J* = 3.8 Hz, *J* = 1.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 96.2 (CH), 127.0 (CH), 127.2 (CH), 128.4 (CH), 128.6 (CH), 128.6 (CH), 128.7 (CH), 130.4 (CH), 131.4 (CH), 132.8 (CH), 137.9 (C_{quat}), 140.6 (C_{quat}), 154.6 (C_{quat}), 166.9 (C_{quat}), 170.2 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.96 (q, $^{1}J_{F\text{-}B}$

= 15.2 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.23 (t, $^{1}J_{B\text{-}F}$ = 15.1 Hz). EI MS (*m/z* (%)): 353 ($(M)^+$, 47), 288 ($(M\text{-}BF_2O)^+$, 100), 180 ($(C_{13}H_{10}N)^+$, 6), 111 ($(C_5H_3OS)^+$, 46), 97 (12), 83 ($(C_4H_3S)^+$, 11), 77 ($(C_6H_5)^+$, 23), 71 ($(C_3H_3S)^+$, 10), 57 (13), 55 (8). IR: $\tilde{\nu}$ [cm^{-1}] = 3109 (w), 3096 (w), 2990 (w), 2963 (w), 2901 (w), 1601 (w), 1543 (w), 1526 (m), 1491 (s), 1477 (m), 1443 (m), 1412 (m), 1377 (m), 1329 (m), 1314 (m), 1285 (m), 1261 (w), 1229 (m), 1153 (m), 1136 (m), 1121 (m), 1074 (s), 1055 (s), 1015 (s), 998 (s), 978 (m), 916 (m), 903 (w), 880 (w), 862 (m), 851 (m), 841 (m), 797 (s), 785 (m), 762 (s), 748 (m), 726 (s), 696 (s), 681 (m), 654 (m), 619 (w). Anal. calcd. for $C_{19}H_{14}BF_2NOS$ (353.2): C 64.61, H 4.00, N 3.97, S 9.08; Found: C 64.32, H 4.08, N 3.86, S 8.92.

4.2.5. 4-(2,2-Difluoro-3,4-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinin-6-yl)benzonitrile (6e)

According to the GP and after recrystallization compound **6e** (1.06 g, 34%) was obtained as a yellow solid, Mp 244 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.44 (s, 1 H), 7.06-7.44 (m, 10 H), 7.72-7.84 (m, 2 H), 8.07-8.20 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 98.2 (CH), 115.7 (C_{quat}), 118.0 (C_{quat}), 126.7 (CH), 127.7 (CH), 127.9 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 130.9 (CH), 132.4 (CH), 134.3 (C_{quat}), 137.2 (C_{quat}), 140.1 (C_{quat}), 169.0 (C_{quat}), 171.1 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -133.71 (q, $^{1}J_{F\text{-}B}$ = 13.9 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.37 (t, $^{1}J_{B\text{-}F}$ = 14.4 Hz). EI MS (*m/z* (%)): 372 ($(M)^+$, 50), 130 ($(C_8H_4NO)^+$, 22), 77 ($(C_6H_5)^+$, 14). IR: $\tilde{\nu}$ [cm^{-1}] = 3127 (w), 3065 (w), 2230 (m), 1601 (m), 1578 (m), 1558 (m), 1487 (s), 1476 (s), 1435 (m), 1393 (m), 1373 (w), 1352 (m), 1323 (m), 1308 (w), 1290 (w), 1236 (m), 1221 (w), 1179 (m), 1140 (m), 1101 (m), 1063 (m), 1026 (s), 1015 (m), 997 (m), 972 (m), 957 (w), 937 (w), 918 (w), 907 (w), 868 (w), 853 (m), 810 (s), 768 (s), 756 (s), 741 (m), 723 (m), 696 (s), 667 (m), 646 (m), 615 (m). Anal. calcd. for $C_{22}H_{15}BF_2N_2O$ (372.2): C 71.00, H 4.06, N 7.53; Found: C 71.18, H 4.03, N 7.54.

4.2.6. 2,2-Difluoro-6-(4-nitrophenyl)-3,4-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6f)

According to the GP and after recrystallization compound **6f** (204 mg, 52%) was obtained as a brown solid, Mp 247 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.47 (s, 1 H), 7.15 (dd, *J* = 7.7 Hz, *J* = 2.1 Hz, 2 H), 7.19-7.28 (m, 6 H), 7.28-7.33 (m, 1 H), 7.33-7.40 (m, 1 H), 8.15-8.23 (m, 2 H), 8.29-8.36 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 98.6 (CH), 123.9 (CH), 126.7 (CH), 127.8 (CH), 128.5 (CH), 128.5 (CH), 128.7 (CH), 128.9 (CH), 130.9 (CH), 134.3 (C_{quat}), 138.9 (C_{quat}), 140.1 (C_{quat}), 150.0 (C_{quat}),

168.6 (C_{quat}), 171.2 (C_{quat}).^{19}F NMR ($CDCl_3$, 282 MHz): δ -133.63 (q, $^{1}J_{F-B}$ = 13.7 Hz).^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.39 (t, $^{1}J_{B-F}$ = 14.4 Hz). EI MS (*m/z* (%)): 392 ($(M)^+$, 68), 375 (8), 346 ($(M-NO_2)^+$, 16), 180 ($(C_{13}H_{10}N)^+$, 12), 150 ($(C_7H_4NO_3)^+$, 21), 104 ($(C_7H_4O)^+$, 16), 77 ($(C_6H_5)^+$, 29). IR: $\tilde{\nu}$ [cm^{-1}] = 2918 (w), 2857 (w), 1587 (m), 1574 (m), 1558 (m), 1522 (s), 1501 (s), 1481 (s), 1466 (s), 1456 (m), 1437 (m), 1420 (w), 1391 (w), 1341 (s), 1321 (m), 1298 (w), 1240 (w), 1229 (w), 1144 (m), 1128 (m), 1099 (m), 1076 (w), 1061 (m), 1024 (s), 997 (m), 972 (m), 962 (w), 937 (w), 920 (w), 908 (w), 849 (m), 812 (m), 802 (m), 758 (s), 733 (m), 714 (m), 698 (s), 669 (w), 658 (w), 635 (w). Anal. calcd. for $C_{21}H_{15}BF_2N_2O_3$ (392.2): C 64.32, H 3.86, N 7.14; Found: C 64.24, H 3.92, N 7.10.

4.2.7. 2,2-Difluoro-6-(2-fluorophenyl)-3,4-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6g)

According to the GP compound **6g** (270 mg, 74%) was obtained as a yellow solid, Mp 177 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.64 (s,1H), 7.11-7.24 (m, 6 H), 7.24-7.28 (m, 4 H), 7.28-7.37 (m, 2 H), 7.51 (m, 1 H), 8.21 (td, *J* = 7.9 Hz, *J* = 1.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 101.9 (d, $^{4}J_{C-F}$ = 17.6 Hz, CH), 116.5 (d, $^{2}J_{C-F}$ = 23.4 Hz, CH), 121.8 (d, $^{2}J_{C-F}$ = 10.3 Hz, C_{quat}), 124.8 (d, $^{4}J_{C-F}$ = 3.5 Hz, CH), 126.9 (CH), 127.5 (CH), 128.5 (CH), 128.8 (CH), 128.8 (CH), 128.8 (CH), 130.7 (d, $^{3}J_{C-F}$ = 32.7 Hz, CH), 134.0 (d, $^{3}J_{C-F}$ = 9.4 Hz, CH), 134.7 (C_{quat}), 140.4 (C_{quat}), 161.7 (d, $^{1}J_{C-F}$ = 256.2 Hz, C_{quat}), 166.8 (d, $^{5}J_{C-F}$ = 3.5 Hz, C_{quat}), 171.1 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -134.27 (q, $^{1}J_{F-B}$ = 14.6 Hz), -108.77 (s). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.33 (t, $^{1}J_{B-F}$ = 14.7 Hz). EI MS (*m/z* (%)): 365 ($(M)^+$, 64), 346 ($(C_{21}H_{15}BF_2NO)^+$, 100), 297 (15), 269 ($(C_6H_4F)^+$, 17), 180 ($(C_{12}H_{10}N)^+$, 11), 172 ($(C_6H_4BF_3O)^+$, 11), 139 (19), 123 ($(C_7H_4FO)^+$, 75), 77 ($(C_6H_5)^+$, 32), 51 ($(C_3HN)^+$, 19). IR: $\tilde{\nu}$ [cm^{-1}] = 1597 (m), 1572 (m), 1555 (w), 1516 (s), 1506 (s), 1489 (s), 1443 (w), 1435 (w), 1412 (m), 1387 (w), 1352 (m), 1318 (w), 1302 (w), 1267 (w), 1229 (w), 1217 (w), 1163 (w), 1099 (s), 1069 (m), 1045 (m), 1032 (m), 989 (w), 976 (m), 953 (w), 920 (w), 872 (w), 824 (w), 814 (w), 766 (s), 746 (m), 723 (w), 692 (s), 667 (m), 650 (w), 633 (w). Anal. calcd. for $C_{21}H_{15}BF_3NO$ (365.2): C 69.07, H 4.14, N 3.84; Found: C 68.89, H 3.96, N 3.72.

4.2.8. 2,2-Difluoro-4-(4-methoxyphenyl)-3,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6h)

According to the GP compound **6h** (1.75 g, 46%) was obtained as a yellow solid, Mp 150 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.77 (s, 3 H), 6.39 (s, 1 H), 6.70-6.83 (m, 2 H), 7.10-7.30 (m, 8 H), 7.42-

7.60 (m, 2 H), 7.97-8.10 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3 (CH_3), 96.9 (CH), 113.9 (CH), 126.9 (CH), 126.9 (C_{quat}), 127.1 (CH), 127.6 (CH), 128.7 (CH), 128.8 (CH), 130.8 (CH), 132.6 (CH), 133.3 (C_{quat}), 140.9 (C_{quat}), 161.3 (C_{quat}), 169.9 (C_{quat}), 171.6 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.73 (q, $^{1}J_{F\text{-}B}$ = 15.2 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.47 (t, $^{1}J_{B\text{-}F}$ = 15.2 Hz). EI MS (*m/z* (%)): 378 ($(M+H)^+$, 10), 377 ($(M)^+$, 54), 105 ($(C_7H_5O)^+$, 16), 77 ($(C_6H_5)^+$, 16). IR: $\tilde{\nu}$ [cm^{-1}] = 1597 (m), 1558 (m), 1501 (m), 1483 (s), 1460 (m), 1418 (m), 1400 (m), 1391 (m), 1358 (m), 1304 (m), 1261 (m), 1240 (m), 1231 (m), 1177 (m), 1138 (m), 1117 (s), 1101 (m), 1078 (m), 1001 (m), 976 (m), 957 (w), 928 (m), 864 (w), 839 (m), 802 (m), 775 (s), 754 (m), 721 (m), 689 (s), 669 (m), 640 (m). Anal. calcd. for $C_{22}H_{18}BF_2NO_2$ (377.2): C 70.05, H 4.81, N 3.71; Found: C 70.07, H 4.89, N 3.60.

4.2.9. 2,2-Difluoro-3,6-diphenyl-4-(*p*-tolyl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6i)

According to the GP compound **6i** (1.82 g, 50%) was obtained as a yellow solid, Mp 212 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.32 (s, 3 H), 6.41 (s, 1 H), 7.01-7.12 (m, 2 H), 7.11-7.33 (m, 7 H), 7.41-7.63 (m, 3 H), 7.96-8.12 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4 (CH_3), 96.9 (CH), 126.9 (CH), 127.2 (CH), 127.6 (CH), 128.7 (CH), 128.7 (CH), 128.7 (CH), 129.1 (CH), 132.0 (C_{quat}), 132.6 (CH), 133.2 (C_{quat}), 140.7 (C_{quat}), 141.1 (C_{quat}), 170.6 (C_{quat}), 171.8 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.43 (q, $^{1}J_{F\text{-}B}$ = 15.2 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.46 (t, $^{1}J_{B\text{-}F}$ = 15.2 Hz). EI MS (*m/z* (%)): 361 ($(M)^+$, 50), 360 ($(M\text{-}H)^+$, 100), 313 (15), 298 (15), 236 (17), 208 ($(C_{10}H_9BF_2NO)^+$, 41), 193 ($(C_9H_6BF_2NO)^+$, 9), 105 ($(C_7H_5O)^+$, 26), 77($(C_6H_5)^+$, 26). IR: $\tilde{\nu}$ [cm^{-1}] = 1593 (m), 1566 (m), 1485 (s), 1470 (m), 1452 (m), 1404 (m), 1358 (m), 1309 (w), 1138 (m), 1117 (m), 1105 (m), 1053 (m), 1022 (s), 1001 (m), 974 (m), 775 (s), 756 (s), 691 (s). Anal. calcd. for $C_{22}H_{18}BF_2NO$ (361.2): C 73.16, H 5.02, N 3.88; Found: C 73.27, H 5.19, N 3.93.

4.2.10. 2,2-Difluoro-3,6-diphenyl-4-(thiophen-2-yl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6j)

According to the GP compound **6j** (1.98 g, 56%) was obtained as a brown solid, Mp 192 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.63 (s, 1 H), 6.97 (dd, *J* = 5.0 Hz, *J* = 3.9 Hz, 1 H), 7.20-7.60 (m, 10 H), 8.00-8.08 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 95.3 (CH), 127.3 (CH), 127.5 (CH), 127.5 (CH), 128.4 (CH), 128.7 (CH), 129.4 (CH), 132.6 (CH), 133.4 (CH), 133.4 (C_{quat}), 134.1 (CH), 135.1 (C_{quat}), 140.4 (C_{quat}), 161.9 (C_{quat}), 171.4 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -135.80 (q, $^{1}J_{F\text{-}B}$ = 14.4 Hz). ^{11}B

NMR ($CDCl_3$, 96 MHz): δ 1.33 (t, $^1J_{B\text{-}F}$ = 14.6 Hz). EI MS (*m/z* (%)): 354 ($(M+H)^+$, 14), 353 ($(M)^+$, 57), 105 ($(C_7H_5)^+$, 19), 77 ($(C_6H_5)^+$, 24). IR: $\tilde{\nu}$ [cm^{-1}] = 1605 (w), 1593 (w), 1570 (w), 1518 (m), 1489 (m), 1449 (w), 1400 (w), 1373 (w), 1352 (w), 1340 (w), 1309 (w), 1292 (w), 1244 (w), 1204 (w), 1178 (w), 1157 (w), 1096 (m), 1080 (m), 1072 (m), 1059 (m), 1018 (m), 1001 (m), 972 (w), 910 (w), 895 (w), 885 (w), 858 (w), 797 (w), 779 (w), 762 (m), 731 (m), 694 (s), 658 (w), 642 (w). Anal. calcd. for $C_{19}H_{14}BF_2NOS$ (353.2): C 64.61, H 4.00, N 3.97, S 9.08; Found: C 64.39, H 3.99, N 3.83, S 9.08.

4.2.11. 4-(2,2-Difluoro-3,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinin-4-yl)benzonitrile (6k)

According to the GP compound **6k** (1.80 g, 48%) was obtained as a yellow solid, Mp 242 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.35 (s, 1 H), 7.13 (dd, *J* = 7.7 Hz, *J* = 2.1 Hz, 2 H), 7.20-7.29 (m, 3 H), 7.35-7.42 (m, 2 H), 7.47-7.55 (m, 2 H), 7.56-7.64 (m, 3 H), 8.00-8.08 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 96.2 (CH), 114.1 (C_{quat}), 117.5 (C_{quat}), 126.8 (CH), 127.9 (CH), 127.9 (CH), 128.9 (CH), 129.0 (CH), 129.2 (CH), 132.2 (CH), 132.6 (C_{quat}), 133.4 (CH), 139.2 (C_{quat}), 139.8 (C_{quat}), 168.6 (C_{quat}), 173.6(C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -133.57 (q, $^1J_{F\text{-}B}$ = 13.7 Hz).^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.36 (t, $^1J_{B\text{-}F}$ = 14.4 Hz). MALDI (*m/z* (%)): 353 ($(M\text{-}F)^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 3132 (w), 3102 (w), 3071 (w), 2228 (m), 1614 (m), 1601 (m), 1574 (m), 1558 (m), 1508 (s), 1487 (m), 1476 (m), 1456 (m), 1404 (m), 1358 (m), 1344 (m), 1314 (m), 1294 (m), 1281 (m), 1252 (m), 1234 (m), 1188 (m), 1157 (m), 1098 (s), 1063 (m), 1026 (s), 997 (m), 978 (m), 961 (m), 924 (m), 908 (w), 835 (m), 822 (m), 808 (m), 768 (s), 721 (m), 706 (m), 691 (s), 673 (m), 635 (m), 621 (m). Anal. calcd. for $C_{22}H_{15}BF_2N_2O$ (372.2): C 71.00, H 4.06, N 7.53; Found: C 70.87, H 3.90, N 7.40.

4.2.12. 4-Butyl-2,2-difluoro-3,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6l)

According to the GP compound **6l** (131 mg, 40%) was obtained as a beige solid, Mp 127 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.81 (t, *J* = 7.3 Hz, 3 H), 1.19-1.33 (m, 2 H), 1.47-1.62 (m, 2 H), 2.21-2.42 (m, 2 H), 6.23 (s, 1 H), 7.23-7.33 (m, 2 H), 7.36-7.58 (m, 6 H), 7.94-8.06 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.5 (CH_3), 22.4 (CH_2), 29.9 (CH_2), 33.7 (CH_2), 94.2 (CH), 126.4 (CH), 127.4 (CH), 128.1 (CH), 128.6 (CH), 129.2 (CH), 132.3 (CH), 133.3 (C_{quat}), 139.4 (C_{quat}), 170.9 (C_{quat}), 175.4 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.91 (q, $^1J_{F\text{-}B}$ = 14.8 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.08 (t, $^1J_{B\text{-}F}$ = 15.0 Hz). EI MS (*m/z* (%)): 327 ($(M)^+$, 23), 284 ($(M\text{-}C_3H_7)^+$, 100), 262 (9), 220 (8), 105 ($(C_7H_5O)^+$,

57), 77 ($(C_6H_5)^+$, 22). IR: $\tilde{\nu}$ [cm^{-1}] = 2963 (w), 2934 (w), 2866 (w), 1607 (w), 1574 (w), 1514 (s), 1487 (s), 1456 (m), 1410 (m), 1350 (w), 1312 (w), 1287 (w), 1260 (w), 1221 (w), 1184 (w), 1121 (m), 1069 (m), 1045 (m), 1026 (m), 999 (m), 978 (m), 966 (w), 932 (w), 907 (w), 897 (w), 876 (w), 860 (w), 851 (w), 833 (w), 808 (w), 773 (m), 764 (m), 708 (m), 696 (s), 667 (w), 640 (w). Anal. calcd. for $C_{19}H_{20}BF_2NO$ (327.2): C 69.75, H 6.16, N 4.28; Found: C 69.79, H 6.24, N 4.27.

4.2.13. 4-*n*-Butyl-2,2-difluoro-3-phenyl-6-(*p*-tolyl)-2*H*-1,3λ⁴,2λ⁴-oxazaborinine (6m)

According to the GP compound **6m** (150 mg, 44%) was obtained as a colorless solid, Mp 135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80 (t, *J* = 7.3 Hz, 3 H), 1.26 (dt, *J* = 14.8 Hz, *J* = 7.4 Hz, 2 H), 1.45-1.68 (m, 2 H), 2.22-2.38 (m, 2 H), 2.42 (s, 3 H), 6.20 (s, 1 H), 7.20-7.34 (m, 4 H), 7.33-7.56 (m, 3 H), 7.85-7.97 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.5 (CH_3), 21.6 (CH_3), 22.4 (CH_2), 30.0 (CH_2), 33.7 (CH_2), 93.7 (CH), 126.5 (CH), 127.4 (CH), 128.1 (CH), 129.1 (CH), 129.4 (CH), 130.5 (C_{quat}), 139.5 (C_{quat}), 143.1 (C_{quat}), 171.1 (C_{quat}), 175.1 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -135.04 (q, $^1J_{F\text{-}B}$ = 14.6 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.08 (t, $^1J_{B\text{-}F}$ = 15.2 Hz). EI MS (*m/z* (%)): 341 ($(M)^+$, 24), 298 ($(M\text{-}C_3H_7)^+$, 100), 284 ($(M\text{-}C_4H_9)^+$, 20), 119 ($(C_8H_7O)^+$, 68), 91 ($(C_6H_5N)^+$, 29), 77 ($(C_6H_5)^+$, 14). IR: $\tilde{\nu}$ [cm^{-1}] = 2955 (w), 2930 (w), 2874 (w), 2864 (w), 1609 (m), 1570 (w), 1494 (s), 1491 (s), 1466 (m), 1542 (m), 1431 (m), 1395 (m), 1354 (m), 1315 (w), 1283 (w), 1261 (w), 1227 (m), 1200 (m), 1190 (m), 1117 (s), 1070 (s), 1028 (s), 1020 (s), 982 (s), 958 (m), 924 (m), 910 (m), 902 (m), 881 (m), 839 (m), 816 (s), 764 (m), 748 (m), 735 (m), 694 (s), 669 (m). Anal. calcd. for $C_{20}H_{22}BF_2NO$ (341.2): C 70.40, H 6.50, N 4.11; Found: C 70.20, H 6.61, N 4.03.

4.2.14. 4-(2,2-Difluoro-4,6-diphenyl-2*H*-1,3λ⁴,2λ⁴-oxazaborinin-3-yl)-*N*,*N*-dimethylaniline (6n)

According to the GP and after three recrystallizations and hot filtration compound **6n** (195 mg, 5%) was obtained as an orange solid, Mp 260 °C (dec.). ^{1}H NMR ($(CD_3)_2SO$, 600 MHz, 353 K): δ 2.86 (s, 6 H), 6.52-6.61 (m, 2 H), 6.63 (s, 1 H), 6.89-6.98 (m, 2 H), 7.30-7.43 (m, 5 H), 7.56 (q, *J* = 7.8 Hz, *J* = 6.4 Hz, 2 H), 7.59-7.66 (m, 1 H), 8.05-8.14 (m, 2 H). ^{13}C NMR ($(CD_3)_2SO$, 151 MHz, 353 K): δ 96.8 (CH), 111.3 (CH_3), 126.5 (CH), 126.8 (CH), 126.9 (CH), 127.9 (CH), 128.2 (CH), 128.5 (CH), 128.8 (C_{quat}), 129.8 (CH), 132.2 (CH), 132.6 (C_{quat}), 134.6 (C_{quat}), 148.8 (C_{quat}), 169.4 (C_{quat}), 169.8 (C_{quat}). ^{19}F NMR ($(CD_3)_2SO$, 565 MHz): δ -132.27 (q, $^1J_{F\text{-}B}$ = 17.7 Hz). ^{11}B NMR ($(CD_3)_2SO$, 193 MHz): δ

1.27 (t, $^{1}J_{B\text{-}F}$ = 15.0 Hz). EI MS (*m/z* (%)): 390 ((M^+), 100), 342 (19), 105 (($C_7H_5O)^+$, 35), 77 (($C_6H_5)^+$, 16). IR: $\tilde{\nu}$ [cm^{-1}] = 3003 (w), 2889 (w), 2806 (w), 1697 (w), 1608 (m), 1574 (m), 1508 (m), 1479 (m), 1445 (m), 1410 (m), 1398 (m), 1344 (m), 1312 (m), 1288 (m), 1236 (m), 1225 (m), 1192 (m), 1163 (m), 1101 (s), 1074 (m), 1045 (s), 1013 (m), 999 (m), 976 (m), 926 (m), 912 (m), 851 (m), 822 (m), 808 (m), 795 (m), 773 (s), 756 (m), 735 (m), 719 (m), 694 (s), 681 (m), 667 (m), 627 (m). Anal. calcd. for $C_{23}H_{21}BF_2N_2O$ (390.2): C 70.79, H 5.42, N 7.18; Found: C 71.08, H 5.59, N 7.28.

4.2.15. 2,2-Difluoro-3-(4-methoxyphenyl)-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6o)

According to the GP compound **6o** (230 mg, 61%) was obtained as a yellow solid, Mp 258 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.73 (s, 3 H), 6.37 (s, 1 H), 6.68-6.76 (m, 2 H), 7.02-7.11 (m, 2 H), 7.21-7.37 (m, 5 H), 7.40-7.60 (m, 3 H), 7.99-8.08 (m, 2 H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 55.3 (CH_3), 96.8 (CH), 114.0 (CH), 127.6 (CH), 127.9 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 130.3 (CH), 132.7 (CH), 133.2 (C_{quat}), 133.4 (C_{quat}), 135.1 (C_{quat}), 158.5 (C_{quat}), 170.4 (C_{quat}), 171.8 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.55 (q, $^{1}J_{F\text{-}B}$ = 14.8 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.42 (t, $^{1}J_{B\text{-}F}$ = 15.0 Hz). EI MS (*m/z* (%)): 377 (($M)^+$, 66), 105 (($C_7H_5O^+$, 31), 77 (($C_6H_5)^+$, 13). IR: $\tilde{\nu}$ [cm^{-1}] = 3013 (w), 2970 (w), 2936 (w), 2841 (w), 1609 (m), 1574 (m), 1560 (s), 1512 (s), 1506 (s), 1483 (s), 1460 (m), 1447 (m), 1410 (m), 1352 (m), 1314 (m), 1294 (m), 1248 (s), 1229 (m), 1159 (m), 1140 (m), 1107 (s), 1101 (s), 1065 (s), 1026 (s), 1015 (m), 1001 (m), 976 (m), 918 (m), 868 (m), 837 (m), 818 (m), 793 (m), 783 (m), 768 (s), 721 (m), 689 (s), 629 (m), 617 (m). Anal. calcd. for $C_{22}H_{18}BF_2NO_2$ (377.2): C 70.05, H 4.81, N 3.71; Found: C 69.78, H 4.80, N 3.58.

4.2.16. 3-(4-Chlorophenyl)-2,2-difluoro-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6p)

According to the GP compound **6p** (2.71 g, 71%) was obtained as a beige solid, Mp 257 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.42 (s, 1 H), 7.06-7.14 (m, 2 H), 7.17-7.42 (m, 7 H), 7.45-7.54 (m, 2 H), 7.54-7.62 (m, 1 H), 8.02-8.10 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 97.0 (CH), 127.8 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 130.7 (CH), 132.9 (C_{quat}), 133.0 (CH), 133.2 (C_{quat}), 134.6 (C_{quat}), 139.1 (C_{quat}), 170.8 (C_{quat}), 172.7 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -133.99 (q, $^{1}J_{F\text{-}B}$ = 14.8 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.39 (t, $^{1}J_{B\text{-}F}$ = 15.1 Hz). EI MS (*m/z* (%)): 381 ((^{37}Cl-M)$^+$, 58), 379 ((^{35}Cl-M)$^+$, 23) 105 (($C_7H_5O)^+$, 27), 77 (($C_6H_5)^+$, 13). IR: $\tilde{\nu}$ [cm^{-1}] = 3130 (w), 1608 (m), 1572

(m), 1510 (s), 1489 (s), 1458 (m), 1447 (m), 1416 (w), 1402 (w), 1354 (m), 1314 (w), 1296 (w), 1234 (w), 1186 (w), 1186 (w), 1109 (m), 1090 (m), 1067 (m), 1038 (m), 1018 (m), 1001 (m), 978 (m), 970 (w), 951 (w), 914 (w), 837 (m), 795 (w), 781 (m), 768 (s), 745 (w), 714 (m), 692 (s), 664 (m), 615 (m). Anal. calcd. for $C_{21}H_{15}BClF_2NO$ (381.6): C 66.09, H 3.96, N 3.67; Found: C 65.90, H 4.21, N 3.52.

4.2.17. 2,2-Difluoro-3-(4-iodophenyl)-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6q)

According to the GP compound **6q** (3.47 g, 73%) was obtained as a green solid, Mp 230 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.43 (s, 1 H), 6.87-6.97 (m, 2 H), 7.21-7.45 (m, 5 H), 7.45-7.63 (m, 5 H), 8.01-8.12 (m, 2 H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 92.7 (C_{quat}), 97.1 (CH), 97.1 (CH), 127.8 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 130.8 (CH), 132.9 (C_{quat}), 133.0 (CH), 134.6 (C_{quat}), 137.9 (CH), 140.4 (C_{quat}), 170.6 (C_{quat}), 172.8 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -134.00 (q, $^1J_{F-B}$ = 14.8 Hz). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.36 (t, $^1J_{B-F}$ = 15.0 Hz). EI MS (*m/z* (%)): 473 ($(M)^+$, 64), 345 ($(C_{21}H_{16}BF_2NO)^+$, 17), 105 ($(C_7H_5O)^+$,17). IR: $\tilde{\nu}$ [cm^{-1}] = 3067 (w), 2990 (w), 2972 (w), 2901 (w), 2884 (w), 1614 (w), 1601 (w), 1574 (w), 1558 (w), 1508 (m), 1487 (m), 1450 (m), 1406 (m), 1395 (m), 1358 (m), 1342 (w), 1314 (w), 1294 (w), 1280 (w), 1250 (w), 1236 (m), 1188 (w), 1157 (w), 1098 (s), 1067 (s), 1034 (s), 1028 (s), 997 (m), 978 (m), 961 (w), 934 (w), 924 (w), 908 (w), 860 (w), 835 (m), 808 (m), 768 (m), 706 (m), 691 (s), 669 (w), 635 (w), 621 (m). Anal. calcd. for $C_{21}H_{15}BF_2INO$ (473.1): C 53.32, H 3.20, N 2.96 Found: C 53.37, H 3.14, N 2.85.

4.2.18. 2,2-Difluoro-3-(3-nitrophenyl)-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6r)

According to the GP compound **6r** (1.07 g, 27%) was obtained as a yellow solid, Mp 164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.48 (s, 1 H), 7.20-7.63 (m, 10 H), 7.98 (t, *J* = 2.1 Hz, 1 H), 8.01-8.12 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 97.2 (CH), 122.1 (CH), 122.3 (CH), 128.0 (CH), 128.6 (CH), 128.9 (CH), 128.9 (CH), 129.6 (CH), 131.1 (CH), 132.6 (C_{quat}), 133.1 (CH), 133.4 (CH), 134.0 (C_{quat}), 141.8 (C_{quat}), 148.1 (C_{quat}), 171.4 (C_{quat}), 173.9 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz, 243 K): δ -132.50 (d, $^1J_{F-B}$ = 579.1 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.40 (t, $^1J_{B-F}$ = 15.1 Hz). EI MS (*m/z* (%)): 406 (10), 392 ($(M)^+$, 44), 391 ($(M+H)^+$, 100), 344 ($(C_{21}H_{16}N_2O_3)^+$, 10), 155 (14), 105 ($(C_7H_5O)^+$, 27), 77 ($(C_6H_5)^+$, 14). IR: $\tilde{\nu}$ [cm^{-1}] = 3084 (w), 2988 (w), 2860 (w), 1593 (m), 1570 (m), 1555 (w), 1526 (m), 1503 (s),

1481 (s), 1456 (m), 1443 (m), 1395 (m), 1346 (s), 1314 (m), 1236 (w), 1186 (w), 1101 (m), 1069 (m), 1038 (m), 1026 (m), 997 (m), 970 (w), 918 (w), 903 (w), 885 (w), 843 (w), 814 (w), 799 (w), 785 (m), 770 (s), 752 (m), 733 (m), 721 (m), 687 (s), 671 (m), 654 (w). Anal. calcd. for $C_{21}H_{15}BF_2N_2O_3$ (392.2): C 64.32, H 3.86, N 7.14; Found: C 64.31, H 3.82, N 7.02.

4.2.19. 4-(2,2-Difluoro-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinin-3-yl)benzonitrile (6s)

According to the GP compound **6s** (1.12 g, 36%) was obtained as a yellow solid, Mp 249 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.46 (s, 1 H), 7.20-7.26 (m, 3 H), 7.27-7.35 (m, 3 H), 7.36-7.44 (m, 1 H), 7.45-7.56 (m, 4 H), 7.56-7.65 (m, 1 H), 8.06 (dd, J = 8.4 Hz, J = 1.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 97.2 (CH), 111.0 (C_{quat}), 118.0 (C_{quat}), 127.9 (CH), 127.9 (CH), 128.6 (CH), 128.9 (CH), 128.9 (CH), 131.1 (CH), 132.6 (CH), 132.6 (C_{quat}), 133.4 (CH), 134.2 (C_{quat}), 144.8 (C_{quat}), 170.9 (C_{quat}), 173.9 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -133.51 (q, $^1J_{F\text{-}B}$ = 19.4 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.37 (t, $^1J_{B\text{-}F}$ = 15.2 Hz). EI MS (*m/z* (%)): 372 ($(M)^+$, 48), 205 ($(C_{14}H_9N_2)^+$, 4), 118 (10), 105 ($(C_7H_5O)^+$, 16), 77 ($(C_6H_5)^+$, 13). IR: $\tilde{\nu}$ [cm^{-1}] = 3096 (w), 3078 (w), 3038 (w), 2228 (w), 1591 (m), 1568 (m), 1501 (s), 1479 (s), 1456 (m), 1443 (m), 1396 (m), 1358 (m), 1315 (w), 1302 (w), 1279 (w), 1238 (w), 1182 (w), 1125 (s), 1103 (s), 1063 (m), 1034 (s), 1026 (s), 1001 (m), 976 (m), 962 (w), 930 (w), 914 (w), 868 (w), 851 (m), 841 (w), 814 (w), 800 (w), 779 (m), 764 (s), 721 (m), 689 (s), 667 (w), 652 (w), 631 (m). Anal. calcd. for $C_{22}H_{15}BF_2N_2O$ (372.2): C 71.00, H 4.06, N 7.53; Found: C 71.04, H 4.24, N 7.32.

4.2.20. 3-(2,6-Dimethylphenyl)-2,2-difluoro-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6t)

According to the GP compound **6t** (1.92 g, 51%) was obtained as a beige solid, Mp 178 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.24 (s, 6 H), 6.44 (s, 1 H), 6.90-7.06 (m, 3 H), 7.22-7.29 (m, 4 H), 7.29-7.39 (m, 1 H), 7.43-7.59 (m, 3 H), 8.02-8.10 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.8 (CH_3), 96.8 (CH), 127.4 (CH), 127.6 (CH), 127.7 (CH), 128.2 (CH), 128.3 (CH), 128.7 (CH), 130.8 (CH), 132.7 (CH), 133.2 (C_{quat}), 134.6 (C_{quat}), 134.7 (C_{quat}), 138.5 (C_{quat}), 171.6 (C_{quat}), 172.1 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -138.73 (q, $^1J_{F\text{-}B}$ = 19.3 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.29 (t, $^1J_{B\text{-}F}$ = 15.1 Hz). EI MS (*m/z* (%)): 375 ($(M)^+$, 48), 355 (17), 278 (46), 208 ($(C_{15}H_{14}N)^+$, 18), 105 ($(C_7H_5O)^+$, 34), 77 ($(C_6H_5)^+$, 21). IR: $\tilde{\nu}$ [cm^{-1}] = 3063 (w), 2963 (w), 2914 (w), 1589 (w), 1570 (m), 1508 (s), 1481 (s),

1452 (m), 1439 (m), 1408 (w), 1377 (w), 1354 (m), 1315 (w), 1288 (w), 1269 (w), 1233 (w), 1215 (w), 1196 (w), 1146 (m), 1125 (w), 1098 (m), 1057 (m), 1022 (s), 999 (m), 970 (m), 926 (w), 901 (w), 862 (w), 841 (w), 816 (w), 770 (s), 727 (m), 692 (s), 667 (w), 627 (w), 617 (w). Anal. calcd. for $C_{23}H_{20}BF_2NO$ (375.2): C 73.62, H 5.37, N 3.73; Found: C 73.41, H 5.39, N 3.58.

4.2.21. 2,2-Difluoro-3-(naphthalen-1-yl)-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6u)

According to the GP compound **6u** (2.88 g, 73%) was obtained as a yellow solid, Mp 202 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.41 (s, 1 H), 6.91-7.01 (m, 2 H), 7.00-7.08 (m, 1 H), 7.08-7.19 (m, 2 H), 7.24-7.34 (m, 2 H), 7.35-7.46 (m, 4 H), 7.46-7.54 (m, 1 H), 7.63 (ddt, *J* = 1.2 Hz, 6.5 Hz, 8.2 Hz, 2 H), 7.76-7.83 (m, 1 H), 7.98-8.05 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 96.6 (CH), 123.4 (CH), 123.4 (CH), 124.8 (CH), 125.5 (CH), 126.2 (CH), 126.7 (CH), 127.5 (CH), 127.8 (CH), 128.0 (CH), 128.0 (CH), 128.3 (CH), 128.8 (CH), 129.6 (C_{quat}), 130.4 (CH), 132.9 (CH), 133.1 (C_{quat}), 133.8 (C_{quat}), 134.9 (C_{quat}), 136.9 (C_{quat}), 172.6 (C_{quat}), 172.6 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -133.09 (dq, $^2J_{F-F}$ = 89.3 Hz, $^1J_{F-B}$ = 16.6 Hz), -138.42 (dq, $^2J_{F-F}$ = 91.4 Hz, $^1J_{F-B}$ = 11.5 Hz, 1F).^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.56 (dd, $^1J_{B-F}$ = 14.1 Hz, $^1J_{B-F}$ = 12.2 Hz). MALDI (*m/z* (%)): 398 ($(M+H)^+$), 378 ($(M - F)^+$), 350 ($(M - BF_2)^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 3130 (w), 3065 (w), 3003 (w), 2968 (w), 2874 (w), 1605 (m), 1593 (w), 1572 (m), 1558 (w), 1504 (s), 1489 (s), 1479 (m), 1447 (m), 1410 (w), 1394 (m), 1358 (m), 1342 (w), 1312 (w), 1296 (w), 1265 (w), 1250 (w), 1236 (w), 1223 (w), 1182 (w), 1159 (w), 1109 (m), 1090 (m), 1072 (m), 1057 (m), 1042 (s), 1018 (m), 991 (w), 953 (w), 808 (m), 795 (m), 775 (s), 764 (s), 750 (w), 725 (m), 685 (m), 667 (w), 650 (w). Anal. calcd. for $C_{25}H_{18}BF_2NO$ [397.2]: C 75.59, H 4.57, N 3.53; Found: C 75.34, H 4.41, N 3.45.

4.2.22. 2,2-Difluoro-3,6-bis(4-methoxyphenyl)-4-phenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6v)

According to the GP compound **6v** (2.82 g, 69%) was obtained as a yellow solid, Mp 207 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.73 (s, 3 H), 3.88 (s, 3 H), 6.29 (s, 1 H), 6.68-6.77 (m, 2 H), 6.93-7.00 (m, 2 H), 7.02-7.09 (m, 2 H), 7.21-7.38 (m, 5 H), 8.01 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3 (CH_3), 55.5 (CH_3), 95.7 (CH), 113.9 (CH), 114.1 (CH), 125.5 (C_{quat}), 127.9 (CH), 128.4 (CH), 128.5 (CH), 129.8 (CH), 130.1 (CH), 133.5 (C_{quat}), 135.3 (C_{quat}), 158.3 (C_{quat}), 163.4 (C_{quat}), 169.9 (C_{quat}), 171.6 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.95 (q, $^1J_{F-B}$ = 19.7 Hz). ^{11}B NMR ($CDCl_3$, 193

MHz): δ 1.42 (t, $^{1}J_{B\text{-}F}$ = 15.3 Hz). EI MS (*m/z* (%)): 407 ($(M)^+$, 83), 230 (18), 210 ($(C_{14}H_{12}NO)^+$, 3), 135 ($(C_8H_7O_2)^+$ 48), 77 ($(C_6H_5)^+$, 8). IR: $\tilde{\nu}$ [cm^{-1}] = 3117 (w), 2976 (w), 2934 (w), 2835 (w), 1603 (m), 1591 (m), 1458 (s), 1437 (s), 1420 (m), 1391 (s), 1364 (m), 1339 (w), 1308 (m), 1292 (m), 1269 (m), 1250 (s), 1238 (s), 1229 (m), 1171 (s), 1132 (m), 1117 (m), 1103 (m), 1063 (m), 1013 (s), 997 (m), 972 (m), 957 (m), 930 (m), 912 (w), 891 (w), 868 (w), 845 (m), 824 (m), 808 (m), 795 (m), 768 (m), 753 (m), 731 (m), 719 (m), 702 (m), 669 (m). Anal. calcd. for $C_{23}H_{20}BF_2NO_3$ (407.2): C 67.84, H 4.95, N 3.44; Found: C 68.10, H 5.06, N 3.34.

4.2.23. 2,2-Difluoro-3-(4-methoxyphenyl)-4-phenyl-6-(thiophen-2-yl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6w)

According to the GP compound **6w** (1.80 g, 47%) was obtained as a yellow solid, Mp 235 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.71 (s, 3 H), 6.19 (s, 1 H), 6.66-6.74 (m, 2 H), 6.98-7.07 (m, 2 H), 7.14 (dd, *J* = 5.0 Hz, *J* = 3.8 Hz, 1 H), 7.20-7.24 (m, 2 H), 7.26 (ddd, *J* = 8.3 Hz, *J* = 6.9 Hz, *J* = 1.3 Hz, 2 H), 7.29-7.33 (m, 1 H), 7.60 (dd, *J* = 5.0 Hz, *J* = 1.2 Hz, 1 H), 7.82 (dd, *J* = 3.8 Hz, *J* = 1.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 55.3 (CH_3), 96.2 (CH), 113.9 (CH), 127.9 (CH), 128.5 (CH), 128.5 (CH), 128.6 (CH), 130.3 (CH), 131.2 (CH), 132.6 (CH), 133.4 (C_{quat}), 134.9 (C_{quat}), 138.0 (C_{quat}), 158.4 (C_{quat}), 166.5 (C_{quat}), 170.0 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -135.25 (q, $^{1}J_{F\text{-}B}$ = 19.7 Hz). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.20 (t, $^{1}J_{B\text{-}F}$ = 15.2 Hz). EI MS (*m/z* (%)): 383 ($(M)^+$, 86), 318 ($(M\text{-}BF_2O)^+$, 100), 210 ($(C_{14}H_{12}NO)^+$, 4), 111 ($(C_5H_3OS)^+$, 52), 77 ($(C_6H_5)^+$, 6). IR: $\tilde{\nu}$ [cm^{-1}] = 3107 (w), 3065 (w), 3019 (w), 2970 (w), 2934 (w), 2901 (w), 2841 (w), 1605 (m), 1593 (m), 1574 (m), 1497 (s), 1487 (s), 1460 (s), 1445 (s), 1416 (m), 1368 (m), 1327 (m), 1312 (m), 1296 (m), 1246 (s), 1227 (m), 1182 (m), 1171 (m), 1138 (m), 1107 (s), 1072 (s), 1055 (s), 1013 (s), 1001 (s), 976 (m), 935 (w), 920 (w), 912 (w), 864 (w), 847 (w), 831 (m), 806 (m), 795 (w), 766 (s), 746 (s), 727 (s), 689 (s), 664 (w), 650 (w), 608 (w). Anal. calcd. for $C_{20}H_{16}BF_2NO_2S$ (383.2): C 62.68, H 4.21, N 3.66, S 8.37; Found: C 62.86, H 4.32, N 3.62, S 8.28.

4.2.24. 4-(2,2-Difluoro-3-(4-methoxyphenyl)-4-phenyl-2*H*-1,3λ^4,2λ^4-oxazaborinin-6-yl)benzonitrile (6x)

According to the GP compound **6x** (1.85 g, 46%) was obtained as a yellow solid, Mp 226 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.73 (s, 3 H), 6.40 (s, 1 H), 6.69-6.77 (m, 2 H), 7.00-7.07 (m, 2 H), 7.20-7.40 (m, 5 H), 7.70-7.79 (m, 2 H), 8.06-8.15 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4 (CH_3), 98.2 (CH), 114.1 (CH), 115.6 (C_{quat}), 118.0 (C_{quat}), 127.7 (CH), 127.9 (CH), 128.5 (CH), 128.7 (CH), 130.8 (CH), 132.4 (CH), 133.0 (C_{quat}), 134.5 (C_{quat}), 137.3 (C_{quat}), 158.8 (C_{quat}), 168.6 (C_{quat}), 170.8 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -134.18 (q, $^1J_{F-B}$ = 13.4 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.34 (t, $^1J_{B-F}$ = 14.5 Hz). EI MS (*m/z* (%)): 402 ($(M)^+$, 60), 338 (10), 130 ($(C_8H_4NO)^+$, 44), 102 ($(C_7H_4N)^+$, 16). IR: $\tilde{\nu}$ [cm^{-1}] = 3107 (w), 3061 (w), 3011 (w), 2961 (w), 2930 (w), 2907 (w), 2891 (w), 2837 (w), 2228 (w), 1603 (m), 1578 (w), 1558 (w), 1508 (s), 1491 (s), 1460 (m), 1439 (m), 1420 (w), 1395 (w), 1348 (m), 1396 (m), 1246 (s), 1231 (m), 1202 (w), 1173 (m), 1101 (m), 1069 (m), 1036 (s), 1015 (m), 1001 (m), 976 (m), 943 (w), 853 (m), 837 (m), 822 (m), 806 (w), 795 (w), 772 (s), 754 (w), 743 (w), 719 (m), 692 (m), 667 (w), 642 (w). Anal. calcd. for $C_{23}H_{17}BF_2N_2O_2$ (402.2): C 68.68, H 4.26, N 6.97; Found: C 68.71, H 4.23, N 6.82.

4.2.25. 2,2-Difluoro-3,4-bis(4-methoxyphenyl)-6-phenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6y)

According to the GP compound **6y** (3.41 g, 84%) was obtained as a yellow solid, Mp 213 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.87 (s, 3 H), 3.90 (s, 3 H), 6.48 (s, 1 H), 6.82-6.93 (m, 4 H), 7.16-7.21 (m, 2 H), 7.31-7.35 (m, 2 H), 7.58 (dd, *J* = 8.4 Hz, 7.0 Hz, 2 H), 7.62-7.68 (m, 1 H), 8.12-8.17 (m, 2 H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 55.3 (CH_3), 55.3 (CH_3), 96.8 (CH), 113.9 (CH), 114.0 (CH), 127.0 (C_{quat}), 127.5 (CH), 127.8 (CH), 128.7 (CH), 130.8 (CH), 132.5 (CH), 133.4 (C_{quat}), 133.8 (C_{quat}), 158.4 (C_{quat}), 161.2 (C_{quat}), 169.7 (C_{quat}), 171.2 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -135.00 (q, $^1J_{F-B}$ = 15.0 Hz). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.42 (t, $^1J_{B-F}$ = 15.2 Hz). EI MS (*m/z* (%)): 407 ($(M)^+$, 61), 298 ($(C_{15}H_{14}BF_2NO_2)^+$, 14), 105($(C_7H_5O)^+$, 40), 77 ($(C_6H_5)^+$, 18). IR: $\tilde{\nu}$ [cm^{-1}] = 3005 (w), 2972 (w), 2901 (w), 2839 (w), 1605 (m), 1574 (m), 1504 (s), 1487 (m), 1456 (m), 1441 (m), 1408 (m), 1358 (m), 1296 (m), 1248 (m), 1238 (m), 1171 (m), 1159 (m), 1144 (m), 1101 (s), 1065 (m), 1022 (s), 1001 (m), 978 (m), 959 (m), 916 (w), 866 (w), 833 (m), 810 (m), 795 (m), 775 (s), 758 (w), 743 (w), 696 (s), 679

(m), 671 (w), 646 (w). Anal. calcd. for $C_{23}H_{20}BF_2NO_3$ (407.2): C 67.84, H 4.95, N 3.44 Found: C 67.58, H 5.10, N 3.26.

4.2.26. 2,2-Difluoro-3-(4-methoxyphenyl)-4,6-di(thiophen-2-yl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6z)

According to the GP compound **6z** (2.39 g, 66%) was obtained as a brown solid, Mp 255 °C. ^{1}H NMR ($(CD_3)_2SO$, 600 MHz) δ 3.80 (s, 3 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 7.07 (s, 1 H), 7.15-7.22 (m, 3 H), 7.33 (dd, *J* = 5.0 Hz, *J* = 3.8 Hz, 1 H), 8.00 (dd, *J* = 5.0 Hz, *J* = 1.2 Hz, 1 H), 8.03 (dd, *J* = 5.0 Hz, *J* = 1.1 Hz, 1 H), 8.14 (dd, *J* = 4.0 Hz, *J* = 1.3 Hz, 1 H), 8.28 (dd, *J* = 3.8 Hz, *J* = 1.2 Hz, 1 H). ^{13}C NMR ($(CD_3)_2SO$, 151 MHz): δ 55.4 (CH_3), 93.4 (CH), 114.7 (CH), 127.3 (CH), 128.7 (CH), 129.2 (CH), 131.7 (CH), 132.4 (C_{quat}), 133.7 (C_{quat}), 133.7 (CH), 137.0 (CH), 137.2 (CH), 137.8 (C_{quat}), 159.4 (C_{quat}), 161.6 (C_{quat}), 164.2 (C_{quat}). ^{19}F NMR ($(CD_3)_2SO$, 565 MHz) δ -134.40 (q, $^1J_{F-B}$ = 13.7 Hz). ^{11}B NMR ($(CD_3)_2SO$, 193 MHz) δ 0.86 (t, $^1J_{B-F}$ = 14.4 Hz). EI MS (*m/z* (%)): 389 ($(M)^+$, 56), 324 (100), 110 ($(C_5H_3OS)^+$, 51). IR: $\tilde{\nu}$ [cm^{-1}] = 3098 (w), 2839 (w), 1582 (m), 1506 (s), 1489 (m), 1472 (m), 1456 (w), 1406 (m), 1387 (w), 1373 (w), 1346 (w), 1325 (w), 1298 (w), 1242 (s), 1233 (m), 1184 (w), 1171 (m), 1134 (m), 1096 (m), 1070 (m), 1051 (s), 1028 (m), 1003 (m), 974 (m), 934 (w), 908 (m), 829 (m), 808 (m), 789 (m), 719 (s), 712 (m), 667 (m), 658 (w), 636 (w). Anal. calcd. for $C_{18}H_{14}BF_2NO_2S_2$ (389.2): C 55.54, H 3.63, N 3.60, S 16.47; Found: C 55.79, H 3.83, N 3.57, S 16.28.

4.2.27. 3-Benzyl-2,2-difluoro-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6aa)

According to the GP compound **6aa** (2.65 g, 73%) was obtained as a yellow solid, Mp 131 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.75-4.86 (m, 2 H), 6.18 (s, 1 H), 7.01-7.08 (m, 2 H), 7.17 (d, *J* = 1.6 Hz, 1 H), 7.18-7.24 (m, 4 H), 7.36-7.41 (m, 1 H), 7.43 (t, *J* = 1.0 Hz, 1 H), 7.44-7.52 (m, 3 H), 7.52-7.59 (m, 1 H), 7.98-8.00 (m, 1 H), 8.01 (dd, *J* = 1.9 Hz, *J* = 0.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 50.6 (CH_2), 96.8 (CH), 126.5 (CH), 127.1 (CH), 127.5 (CH), 127.6 (CH), 128.2 (CH), 128.7 (CH), 128.7 (CH), 130.2 (CH), 132.0 (CH), 133.1 (C_{quat}), 134.6 (C_{quat}), 137.5 (C_{quat}), 170.6 (C_{quat}), 173.3 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -136.97 (q, $^1J_{F-B}$ = 17.0 Hz). ^{11}B NMR ($CDCl_3$, 96 MHz): δ 1.50 (t, $^1J_{B-F}$ = 16.9 Hz). EI MS (*m/z* (%)): 361 ($(M)^+$, 90), 341 (21), 349 (73), 297 (14), 296 (57), 270 ($(C_{15}H_{11}BF_2NO)^+$, 23), 193 ($(C_9H_7BF_2NO)^+$, 36), 192 ($(C_{15}H_{12})^+$, 11), 191 ($(C_{15}H_{11})^+$, 8), 165 ($(C_8H_8BF_2O)^+$, 11), 105 ($(C_7H_5O)^+$, 31), 91 ($(C_7H_7)^+$, 100), 77 ($(C_6H_5)^+$, 25), 65 (13). IR: $\tilde{\nu}$ [cm^{-1}] =

3570 (w), 3067 (w), 2926 (w), 2839 (w), 1601 (m), 1593 (w), 1574 (m), 1508 (s), 1483 (m), 1460 (m), 1450 (m), 1439 (m), 1408 (m), 1400 (w), 1348 (m), 1333 (w), 1309 (w), 1279 (w), 1236 (w), 1213 (w), 1155 (w), 1126 (m), 1112 (m), 1092 (m), 1058 (m), 1024 (s), 999 (m), 981 (m), 928 (w), 893 (w), 843 (w), 808 (w), 756 (m), 731 (s), 719 (m), 688 (s), 657 (w), 650 (w), 615 (m). Anal. calcd. for $C_{22}H_{18}BF_2NO$ (361.2): C 73.16, H 5.02, N 3.88; Found: C 72.90, H 5.06, N 3.77.

4.2.28. 2,2-Difluoro-3-isopropyl-4,6-diphenyl-2*H*-1,3λ^4,2λ^4-oxazaborinine (6ab)

According to the GP and after work up with deionized water until no further precipitation was formed, after filtration and drying overnight compound **6ab** (1.12 g, 36%) was obtained as a yellow solid, Mp 125 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.45 (dt, J = 6.9 Hz, J = 1.3 Hz, 6 H), 4.10 (hd, J = 6.7 Hz, J = 2.9 Hz, 1 H), 6.08 (s, 1 H), 7.38 (ddd, J = 6.2 Hz, J = 3.0 Hz, J = 1.6 Hz, 2 H), 7.46 (dd, J = 8.4 Hz, J = 7.0 Hz, 2 H), 7.50-7.59 (m, 4 H), 7.95-8.00 (m, 2 H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 22.1 (t, J = 2.8 Hz, CH_3), 52.9 (CH), 95.8-97.6 (d, J = 2.8 Hz, CH), 126.1 (CH), 127.3 (CH), 128.6 (CH), 129.1 (CH), 129.9 (CH), 132.1 (CH), 133.1 (d, J = 3.5 Hz, C_{quat}), 135.6 (C_{quat}), 169.2 (C_{quat}), 171.1 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -134.90 (q, $^1J_{F\text{-}B}$ = 19.5 Hz). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.21-1.64 (m). EI MS (*m/z* (%)): 313 ($[M]^+$, 26), 298 ($(C_{17}H_{15}BF_2NO)^+$, 100), 277 ($(C_{18}H_{20}BNO)^+$, 14), 105 ($(C_7H_5O)^+$, 39), 77 ($(C_6H_5)^+$, 20). IR: $\tilde{\nu}$ [cm^{-1}] = 2970 (w), 2943 (w), 2922 (w), 2891 (w), 2864 (w), 2826 (w), 1666 (w), 1599 (w), 1574 (w), 1551 (w), 1510 (m), 1485 (s), 1460 (m), 1445 (w), 1422 (m), 1389 (w), 1368 (w), 1341 (m), 1310 (w), 1300(w), 1281 (w), 1248 (m), 1221 (m), 1182 (w), 1163 (w), 1132 (m), 1109 (w), 1092 (m), 1063 (m), 1045 (s), 997 (s), 927 (w), 912 (w), 883 (w), 858 (w), 849 (w), 799 (w), 762 (s), 743 (m), 679 (m), 660 (w), 642 (w), 625 (m). Anal. calcd. for $C_{22}H_{18}BF_2NO_2$ (377.2): C 70.05, H 4.81, N 3.71; Found: C 70.07, H 4.89, N 3.60.

4.2.29. 3-Benzyl-2,2-difluoro-4-phenyl-6-(*p*-tolyl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6ac)

According to the GP compound **6ac** (2.79 g, 74%) was obtained as a colorless solid, Mp 153 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3 H), 4.66 (s, 2 H), 6.01 (s, 1 H), 6.87-6.95 (m, 2 H), 7.00-7.10 (m, 5 H), 7.10-7.18 (m, 2 H), 7.21-7.38 (m, 3 H), 7.74-7.80 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6 (CH_3), 50.5 (CH_2), 96.3 (CH), 126.5 (CH), 127.1 (CH), 127.5 (CH), 127.6 (CH), 128.2 (CH), 128.7 (CH), 129.4 (CH), 130.1 (CH), 130.3 (C_{quat}), 134.7 (C_{quat}), 137.6 (C_{quat}), 143.3 (C_{quat}), 170.7 (C_{quat}), 173.1 (C_{quat}). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -137.07 (q, $^1J_{F\text{-}B}$ = 17.2 Hz). ^{11}B NMR ($CDCl_3$,

96 MHz): δ 1.51 (t, $^{1}J_{B\text{-}F}$ = 17.1 Hz). ESI (*m/z* (%)): 376 ($(M+H)^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 1609 (m), 1599 (w), 1574 (w), 1522 (s), 1497 (s), 1456 (m), 1443 (m), 1433 (m), 1396 (w), 1362 (m), 1346 (m), 1335 (w), 1310 (w), 1292 (w), 1242 (w), 1215 (w), 1204 (w), 1190 (w), 1151 (w), 1105 (m), 1018 (m), 1057 (m), 1028 (m), 1016 (m), 1001 (m), 989 (w), 955 (m), 910 (w), 893 (w), 845 (w), 827 (w), 802 (m), 779 (m), 756 (s), 736 (w), 719 (m), 696 (m), 671 (w), 650 (w). Anal. calcd. for $C_{23}H_{20}BF_2NO$ (375.2): C 73.62, H 5.37, N 3.73; Found: C 73.34, H 5.21, N 3.67.

4.2.30. 2,2-Difluoro-4,6-diphenyl-3-(4-(phenylethynyl)phenyl)-2*H*-1,3λ^4,2λ^4-oxazaborinine (6ad)

$Pd(PPh_3)_2Cl_2$, (7 mg, 10 μmol), CuI (4 mg, 20 μmol), and 2,2-difluoro-3-(4-iodophenyl)-4,6-diphenyl-2H-1,3λ^4,2λ^4-oxazaborinine (**6q**) (4.73 g, 10.0 mmol) were placed in a dry Schlenk vessel with a magnetic stir bar under nitrogen. Then, THF (15 mL), phenylacetylen (**2a**) (3.3 mL, 30.0 mmol) and triethylamine (4.20 mL, 30.0 mmol) were added under nitrogen. The reaction mixture was stirred at room temp for 24 h. Then the mixture was poured into cold (with an NaCl/ice bath) methanol (150 mL) and stirred for 15 min. The precipitate was filtered and the solid was dried for 14 h to give compound **6ad** (4.11 g, 92%) as a yellow solid, Mp 153 °C.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.43 (s, 1 H), 7.11-7.19 (m, 2 H), 7.22-7.44 (m, 10 H), 7.50 (ddd, *J* = 7.4 Hz, *J* = 5.7 Hz, *J* = 2.0 Hz, 4 H), 7.54-7.62 (m, 1 H), 8.04-8.09 (m, 2 H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 88.6 (C_{quat}), 90.4 (C_{quat}), 97.1 (CH), 122.4 (C_{quat}), 122.9 (C_{quat}), 127.0 (CH), 127.8 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 130.7 (CH), 131.6 (CH), 132.0 (CH), 133.0 (CH), 133.0 (C_{quat}), 134.8 (C_{quat}), 140.4 (C_{quat}), 170.6 (C_{quat}), 172.7 (C_{quat}). ^{19}F NMR ($CDCl_3$, 565 MHz): δ -134.2 (q, $^{1}J_{F\text{-}B}$ = 14.8 Hz). ^{11}B NMR ($CDCl_3$, 193 MHz): δ 1.45 (t, $^{1}J_{B\text{-}F}$ = 15.2 Hz). EI (*m/z* (%)): 447 ($(M)^+$, 66), 223 (11), 176 ($(C_{14}H_8)^+$, 14), 105 ($(C_7H_5O)^+$, 20), 77 ($(C_6H_5)^+$, 11). IR: $\tilde{\nu}$ [cm^{-1}] = 3117 (w), 3088 (w), 3061 (w), 3042 (w), 3015 (w), 2220 (w), 1503 (m), 1483 (m), 1456 (m), 1441 (m), 1396 (m), 1354 (m), 1310 (w), 1292 (w), 1233 (w), 1200 (w), 1184 (w), 1128 (m), 1101 (m), 1063 (w), 1018 (m), 997 (m), 978 (m), 957 (w), 912 (w), 860 (w), 835 (w), 814 (w), 785 (m), 758 (s), 713 (w), 668 (s), 667 (w), 650 (w). Anal. calcd. for $C_{29}H_{20}BF_2NO$ (447.3): C 77.87, H 4.51 , N 3.13; Found: C 78.06, H 4.40, N 3.12.

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