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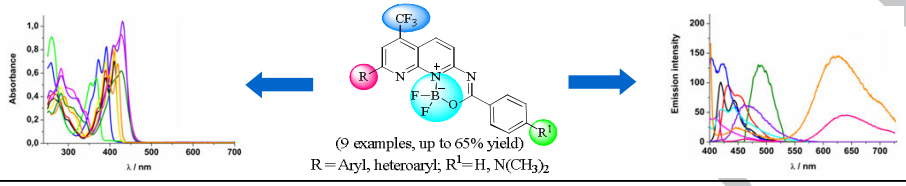

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ABSTRACT

A new series of nine examples of 9-aryl-3-(aryl/heteroaryl)-1,1-difluoro-7-(trifluoromethyl)-1*H*-[1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridin-11-ium-1-uides, which contained 1,8-naphthyridine-based boron complexes with variable ligand structures, were synthesized at yields of 50 – 65 % from the reaction of unpublished 2-benzoylamino-7-aryl(heteroaryl)-5-trifluoromethyl-1,8-naphthyridines — in which aryl(heteroaryl) = phenyl, 4-MeC_6H_4, 4-FC_6H_4, 4-BrC_6H_4, 4-OMeC_6H_4, 4-$NO_2C_6H_4$, and 2-thienyl — with BF_3•Et_2O and fully characterized by ^{1}H-, ^{13}C-, ^{19}F- and ^{11}B-NMR spectroscopy and X-ray diffractometry. The optical and electrochemical properties of the new complexes were investigated, and the results for quantum yield calculations, Stokes shift, UV-vis, fluorescence, and redox potential data analysis indicated an important relationship with the aryl(heteroaryl) substituents attached to the 3- and 9-position of the naphthyridine boron complexes.

Introduction

Organoboron complexes are some of the most important fluorescent dyes.[1] These compounds exhibit properties such as fluorescence, high quantum yields, excellent photochemical and chemical stability, long excited-state lifetimes, good solubility, and narrow emission spectra with high color purity.[2] Moreover, these complexes are widely used as chemosensors,[3] laser dyes,[4] sensitizers in solar cells,[5,6] probes in detecting molecular rotor viscosity,[7] and as agents in photodynamic therapy.[8,9] The photophysical properties of well-known borondipyrromethenes (BODIPYs) and derivatives can be fine-tuned by changing the substituents of different electron densities, manipulating the conjugation length, or via chemical modification at various positions.[10] In this area of research, 1,8-naphthyridines are also highlighted, due to their important biological potential[11] and wide range of applications as fluorescent probes.[12] Their biocompatibility, good fluorescence properties,[13] and proven interactions with the nitrogenous bases of DNA through hydrogen bonding, have identified this heterocyclic system for potential applications in the areas of medicine and biology.[1]

Recent reports[15] have provided the synthesis of novel fluorescent 1,8-naphthyridine-BF_2 complexes. They are synthesized by introducing a BF_2 core into 1,8-naphthyridine derivatives through NNO and/or NCO functional groups, and have been utilized as visible colorimetric probes for highly selective sensing of phosphoric ion.[16] Moreover, it has been recognized that the attachment of a trifluoromethyl group to heterocycles can be used to modulate the physical, chemical, and biological properties.[17]

In view of this, in 2012, Wu et al.[18] elaborated the synthesis and a photophysical study of some 1,8-naphthyridine-BF_2 complexes; however, the work was only able to present identical substituents (CH_3 or CF_3) at the 5- and 7-position in the respective boron complexes, probably due to the well-known low regioselectivity when the reaction of 2,6-diaminopyridine is performed with non-symmetrical 1,3-diketones to obtain 2-amino-1,8-naphthyridines (mixture of 5- and 7-regioisomers).[19]

At this point, it is important to mention that our research group has also reported the synthesis of trifluoromethylated 1,8-naphthyridines. These diazaheterocycles were obtained by us from the reaction of 2,6-diaminopyridine (2,6-DAP) with 4-

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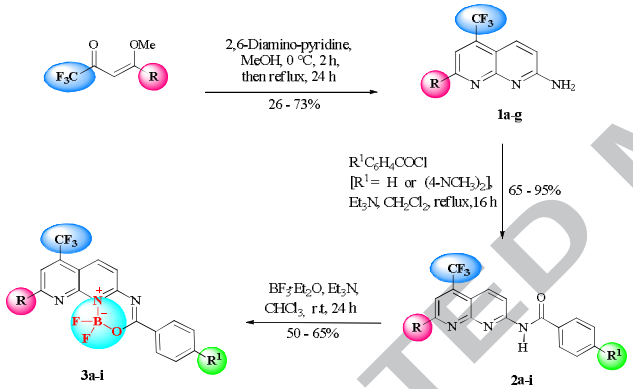
methoxy-4-aryl(heteroaryl)-1,1,1-trifluoroalk-3-en-2-ones.[20] Our method allowed: easier regioselective introduction of the CF_3 group at the 5-position, a wider scope for both electron-donating and electron-withdrawing substituents at the 7-position, and cycloalkanes to be fused to the C6-C7 bond of the 1,8-naphthyridine rings.

Given that the introduction of a BF_2 core into a π-conjugated 1,8-naphthyridine is expected to furnish new functional organic dyes with rigid structures and high fluorescence quantum yields,[18,21] and that our development of the regioselective synthesis of 5,7-substituted 2-amino-1,8-naphthyridines was successful,[20] we decided to synthesize new organoboron complexes from 1,8-naphthyridines that have the CF_3 group at the 5-position and aryl(heteroaryl)substituents with an electron-donating or electron-withdrawing effect at the 7-position. Thus, it is possible to conduct photophysical studies in order to evaluate the influence of the substituents on these new complexes, as well as boron and fluorine NMR studies, which are very rare in the literature.

Results and discussion

The synthetic route and the structures of the synthesized fluorescent boron complexes are depicted in Scheme 1. Specific details of the experimental procedures and complete data for structural characterization are described in the Supporting Information.



1 - 3	a	b	c	d	e
R	C_6H_5	4-$CH_3C_6H_4$	4-FC_6H_4	4-BrC_6H_4	4-$OMeC_6H_4$
R^1	H	H	H	H	H
Yields **3** (%)	58	50	54	51	65

1 - 3	f	g	h	i
R	4-$NO_2C_6H_4$	2-Thienyl	4-$OMeC_6H_4$	4-$NO_2C_6H_4$
R^1	H	H	NMe_2	NMe_2
Yields **3** (%)	50	61	60	51

Scheme 1. Synthetic route for 1,8-naphthyridine-BF_2 complexes (**3a–i**).

Given that 7-aryl(heteroaryl)-2-amino-5-trifluoromethyl-1,8-naphthyridines (**1**) can be obtained regioselectively from the cyclocondensation reaction of 2,6-DAP with 4-methoxy-4-aryl(heteroaryl)-1,1,1-trifluoroalk-3-en-2-ones,[20] we started our work by resynthesizing the series of seven examples of 4-methoxy-4-aryl(heteroaryl)-1,1,1-trifluoroalk-3-en-2-ones, which were converted at good yields to 7-aryl(heteroaryl)-2-amino-5-trifluoromethyl-1,8-naphthyridines (**1a–g**) when added dropwise to 2,6-diaminopyridine (2,6-DAP) at a molar ratio of 1:1, respectively, in methanol as solvent, at 0 °C for 2 h, and then heated under reflux for 24 h, in accordance with the method described in the literature.[20]

The amines **1a–g** were converted to the corresponding unpublished 2-benzoylamide derivatives **2a–i** at yields of 65–95 % by the reaction of compounds **1** with acyl chloride, using

After purification and full characterization, amides **2** were employed in the synthesis of the respective BF_2 complexes (**3a–i**). Subsequently, amides **2a–i** were subjected to reaction with BF_3•Et_2O in anhydrous chloroform at room temperature for 24 h, also employing trimethylamine as base, and this furnished the desired fluorine-boron complexes **3a–i** at good yields (50–65 %).[23]

The new organoboron complexes **3a–g** were obtained as yellow solids, while the complexes **3h–i** were obtained as red solids. The compounds showed fluorescent properties when in dichloromethane solution (**3a–g** were yellow-green in color and **3h–i** were red).

It can be seen that the best yields for the series of **3** are obtained for complexes containing a substituent with an electron-donating effect at the 7-position of the naphthyridine ring — i.e., **3e** (R = 4-$OMeC_6H_4$ and R^1 = H) at 65 % yield — while the lowest yield is observed for the complex that contains the electron-withdrawing group — i.e., **3f** (R = 4-$NO_2C_6H_4$ and R^1 = H) at 50 % yield.

In order to determine the real molecular structure of compound **3g**, an X-ray monocrystal diffraction measurement was also performed (Figure 1).

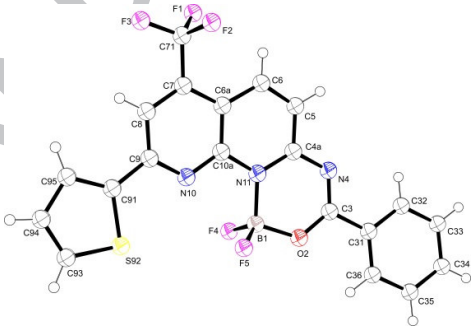


Figure 1. ORTEP of complex **3g** (CCDC 1497181).[24] Displacement ellipsoids are drawn at the 50% probability level.

The new structures were confirmed and characterized by ^{1}H-, ^{13}C-, ^{11}B-, and ^{19}F-NMR, and their purity was evaluated from CHN elemental analysis. The structural assignments for amides **2a–i** are consistent with the ^{1}H- and ^{13}C-NMR spectra described in the literature for similar compounds.[18,20] For amides **2**, the ^{1}H NMR chemical shifts in DMSO-d_6 show, among other typical signals, the proton of the NH group bonded to C-2 as a singlet in the range of 11.60–11.09 ppm.

The ^{13}C NMR spectra of amides **2** showed chemical shifts on average for C-5 at 135.3 ppm, as a quartet with $^2J_{CF}$ ~ 31 Hz; for the CF_3 group, it was at 123.6 ppm, as a quartet with $^1J_{CF}$ ~ 275 Hz; and for the C-6 at 115.6 ppm it was also as a quartet, with $^3J_{CF}$ ~ 5.0 Hz. Finally, a singlet was registered for the carbonyl carbon (amide function) at an average of 167.8 ppm. It is notable that the strong IR absorption peaks at ~ 1700 cm-1, which are related to the C=O stretch vibration of the amide precursors **2a–i**, vanished after coordination with the boron atom.

Upon comparing the ^{1}H NMR and ^{13}C NMR data for the amide precursor and the new complex, no significant differences were seen in the chemical shift values. Thus, in order to demonstrate the formation of the BF_2 complexes, ^{19}F-NMR and ^{11}B-NMR data analysis was also performed.

The ^{19}F NMR in the $CDCl_3$ spectra for compounds **3a–i** show: a singlet on average at -60.81 ppm in relation to the CF_3 group, and a distorted quartet with a broad base in the range of -132.05 to -130.18 ppm. The quartet is due to the coupling between the nuclei of the ^{19}F and the ^{11}B (spin = 3/2, natural abundance =

signals, with those originating from the ^{19}F nuclei coupling with ^{10}B nuclei (spin = 3, natural abundance = 19.9 %).

A small difference in the isotopic shifts caused by ^{10}B and ^{11}B (the heavier isotope is less deshielding) results in distortion of the quartet's intensity.[25] In the ^{11}B-NMR spectra, the series of compounds showed a singlet in the range of 1.02–1.21 ppm, which corresponds to the boron atom (BF_2 moiety).

For derivatives **3a–g**, the absorption UV-vis spectra[26,27] were recorded in dichloromethane solutions, and they are reported in Figure 2.

The wavelength maxima and molar absorption coefficients of all the compounds are listed in Table 1. The absorption in the derivatives shows two major bands: one at around 250–300 nm (log ε = 3.60–4.30), which can be assigned to the intraligand π-π* transition band; and the other at around 350–460 nm, which can be assigned to the n → π transition (S0→ S1, log ε = 3.50–4.50). It can be seen that the band shifts occur due to the electronic properties of the substituents present in the molecules. For compounds with substituent R^1 = H (e.g., **3d**), a blue shift (R = 4-BrC_6H_4) is seen, contrary to what is observed for derivatives **3g** (R = 2-thienyl) and **3i** (R = 4-$NO_2C_6H_4$), for which there is a red shift into the spectrum (Figure 2).

These facts can be attributed to: the withdrawing effect of the bromine atom, the π-electronic conjugation in the thiophene ring, and the internal resonance of the nitro group.

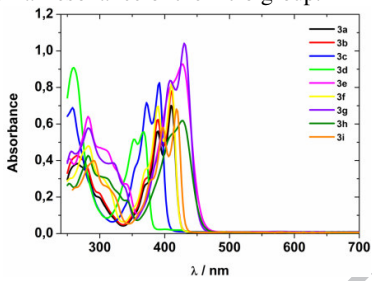


Figure 2. Electronic UV-vis absorption spectra of compounds **3a–i**.

All of the 1,8-naphthyridine-BF_2 complexes **3a–i** showed fluorescence with moderate to good quantum yields (Φ_f) in dichloromethane solution. Emission band shifts can be seen in derivatives **3a** (R = C_6H_5 and R^1= H), **3e** (R = 4-$OMeC_6H_4$ and R^1 = H), and **3f** (R = 4-$NO_2C_6H_4$ and R^1 = H), when comparing compounds containing donor or acceptor groups. Compound **3e** had the greatest shift towards the red region, due to the presence of the methoxyl group (Figure 3). When the BF_2 derivatives contained the R^1 = NMe_2 substituent group in the aromatic structure (**3h** and **3i**), we saw a large Stokes shift and red emission within the 600–650 nm range (Figure 3).

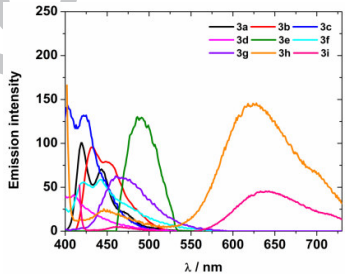


Figure 3. Emission spectra (λexc = 390 nm) for compds. **3a–i**.

The fluorescence quantum yield values for these compounds also show differences; for example, compound **3e** is almost five times greater than the derivative **3a**, which explains the influence of the donor group in the molecule (Table 1).

Shorter Stokes shifts are observed in compounds **3a** (R = C_6H_5 and R^1 = H), **3c** (R = 4-FC_6H_4 and R^1 = H), and **3f** (R = 4-$NO_2C_6H_4$ and R^1= H), in accordance with the electronic properties of the groups in the molecule.

Satisfactory Stokes shifts were exhibited by compounds **3e** (R = 4-$OMeC_6H_4$ and R^1 = H) and **3g** (R = 2-thienyl and R^1 = H), which is attributed to the presence of groups with a strong donor effect. Large Stokes shifts were observed in: the compounds with R^1 = NMe_2, compound **3h** (R = 4-$OMeC_6H_4$), and compound **3i** (R = 4-$NO_2C_6H_4$), and this can be attributed to the ICT state and the strong push-pull that exists in these structures.

When the emission spectra were performed for compound **3i** in more polar solvents as methanol and dimethyl sulfoxide, it was observed that the lower Φ_f and emission band shifted within the 421–437 nm range (see Supporting Information).

Table 1. UV-vis and fluorescence analysis data of compounds **3a-i**.

Compd.	λ / nm (log ε)[a]	Emission / nm[b]	Φ_f[c]	Stoke shifts[d]	$E_{0\text{-}0}$ / eV[e]
3a	266 (3.86), 369(sh), 389 (4.04) and 410 (4.13)	419. 443	0.183	7 nm	2.982
3b	265 (4.05), 300 (sh), 369 (sh), 389 (4.21) and 410 (4.31)	432. 451	0.495	19.5nm	2.945
3c	258 (4.12), 354(sh), 372 (4.14) and 391 (4.20)	403. 423	0.421	10 nm	3.128
3d	259 (4.20), 352 (3.95) and 367 (3.99)	392. 410	0.277	23 nm	3.263
3e	282 (4.09), 311 (sh), 342 (sh), 408 (sh) and 427 (4.26)	489	0.519	76 nm	2.907
3f	283 (3.67), 313 (sh), 369 (sh), 389 (3.83) and 410 (3.90)	422. 442	0.302	8 nm	2.952
3g	283 (4.09), 321 (sh), 339 (sh), 408 (4.25) and 430 (4.35)	465	0.256	53 nm	2.906
3h	281 (4.07), 312 (sh), 341 (sh) and 427 (4.22)	624	0.620	197 nm	2.666
3i	290 (3.65), 315 (sh), 396 (3.80) and 417 (3.87)	637	0.542	220 nm	2.857

[a] sh: shoulder; [b] λ_{exc} = 390 nm; [c] 9,10-diphenylanthracene (DPA) as a standard quencher in $CHCl_3$ (ϕ_{fl} = 0.65); [d] Stokes shifts: $\Delta\lambda = \lambda_{em} - \lambda_{abs}$; [e] $E_{0\text{-}0}$ (eV) = 1240 / λ;

Cyclic voltammetry (CV) of BF_2-naphthyridines **3a–i** were recorded in 0.1 M $TBAPF_6$ DMF solution with a glassy carbon electrode, using a platinum wire with a pseudo-reference electrode in dichloromethane (DCM), within a range of -2.0 to +2.0 V (Table 2). The CV shown in Figure 4 is referenced to the internal standard Fc/Fc+ (0.500 V in DCM). In general, the electrochemical behavior of compounds **3a–i** shows that the compound is anodically and cathodically stable in DCM until -2.0 V, after which the BF_2 derivative values decrease within the cathodic current range from -2.0 to -1.5 V, which can be attributed to the reduction in the naphthyridine moiety (Figure 4). In almost all cases, the reoxidation of derivatives is not observed, except for compounds **3h** (R = 4-$OCH_3C_6H_4$ and R^1 = NMe_2) and **3i** (R= 4-$NO_2C_6H_4$ and R^1 = NMe_2), which indicates the decomposition of the naphthyridine unit upon reduction.[28]

In the anodic region, oxidation peaks were observed in compounds **3h** and **3i** within the 0.8 to 0.9 V potential range, and this can be attributed to the reoxidation of the naphthyridine's heterocyclic skeleton, coordinated to the BF_2 moiety.

Table 2. Redox potential data for compounds **3a–i**.

Compd.	R	R^1	E_1 (V)	E_2 (V)	E_3 (V)
3a	C_6H_5	H	-1.533[a]	-----	------
3b	4-$CH_3C_6H_4$	H	-1.673[a]	-----	------
3c	4-FC_6H_4	H	-1.948[a]	-----	------
3d	4-BrC_6H_4	H	-1.681[a]	-----	-----
3e	4- $OCH_3C_6H_4$	H	-1.869[a]	-----	-----
3f	4- $NO_2C_6H_4$	H	-1.872[a]	-1.528[a]	-----
3g	2- Thienyl	H	-1.580[a]	+0.831[b]	-----
3h	4- $OCH_3C_6H_4$	NMe_2	-1.818[a]	-1.584[a]	+0.827[b]
3i	4- $NO_2C_6H_4$	NMe_2	-1.690[a]	+0.815[b]	-----

[a]Cathodic peak, [b]Anodic peak, *Fc^+/Fc redox couple pair in DCM -$E_{1/2}$ = 0.5 V.

In conclusion, we presented a highly regioselective synthesis, ^{11}B- and ^{19}F-NMR spectroscopy, and the optical and electrochemical properties of a series of nine new fluorescent trifluoromethylated organoboron derivatives, which were synthesized and easily purified at good yields. The 1,8-naphthyridine-BF_2 complexes **3a–i** showed moderate quantum yields, and the best Stokes shifts were found in the compounds that contain electron-donating substituents (**3e** and **3g**) and those with a strong push-pull system (**3h** and **3i**). This is an initial study of the potential of these new complexes which have possible application in materials science. The electronic effect of some other substituents and other physical-chemical properties will be studied in the near future.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at……

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23. General procedure for the preparation of complex 1,8-naphthyridine-BF_2 **3a-i**: Solutions of the respective amides **2a-i** (3 mmol), BF_3•Et_2O (6.0 mL) and anhydrous triethylamine (4.5 mL) in anhydrous chloroform (60 mL) were magnetic stirring for 24 h at room temperature. After the end of the reactions (TLC), the mixtures were extracted with dichoromethane (3 x 20 mL) and water (3 x 20 mL). The organic phase of each reaction was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude products **3a-i** were purified by column chromatography on silica gel using dichloromethane as the eluent. Data for 1,1-difluoro-3,9-diphenyl-7-(trifluoromethyl)-1*H*-[1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridin-11-ium-1-uide (**3a**): yellow solid, yield 58 %, mp 225 – 227 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.57 (d, *J* = 9 Hz, 1H, H-5), 8.46 (d, *J* = 8 Hz, 2H, H-6 and Ph), 8.41 (d, *J* = 8 Hz, 2H, Ph), 8.30 (s, 1H, H-8), 7.65 (t, *J* = 7 Hz, 1H, Ph), 7.59 -7.56 (m, 4H, Ph), 7.53 (t, *J* = 8 Hz, 2H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 169.3 (C-3), 160.3 (C-10a), 159.3 (C-9), 149.4 (C-6a), 138.5 (C-4a), 136.2 (q, ^2J = 32 Hz, C-7), 136.1 (C-Ph), 134.3 (C-6), 131.9 (C-Ph), 131.7 (C-Ph), 130.4 (C-Ph), 129.4 (C-Ph), 128.6 (C-Ph), 128.2 (C-Ph), 124.5 (Ph), 122.6 (q, ^1J = 275 Hz, CF_3), 115.7 (q, ^3J = 5 Hz,C-8), 114.9 (C-5).^{19}F NMR (564 MHz, $CDCl_3$): δ (ppm): -60.56 (CF_3), -130.18 , -130.20 (BF_2). ^{11}B NMR (192 MHz, $CDCl_3$): δ (ppm): 1.21. Anal. Calcd. For $C_{22}H_{13}BF_5N_3O$: C, 59.90; H, 2.97; N, 9.52. Found : C, 60.06 ; H, 2.98; N, 9.38.
24. The crystallographic data for the structure of **3g** have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 1497181. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:+44 1223336033 or deposit@ccdc.com.ac.uk).
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26. UV-vis absorption spectra of derivatives **3a-i** in DCM were measured with a Shimadzu UV2600 spectrophotometer (data interval, 1.0 nm). Fluorescence spectra of samples in DCM solutions were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer (excitation and emission; slit 2.0 mm) and were corrected according to the manufacturer's instructions. Fluorescence quantum yields (Φ_f) of the compounds **3a-i** in solutions were determined by comparing the corrected fluorescence spectra with that of 9,10-diphenylanthracene (DPA) in chloroform (Φ_f = 0.650, λ_{ex} = 366 nm) as the standard as the fluorescence yield.
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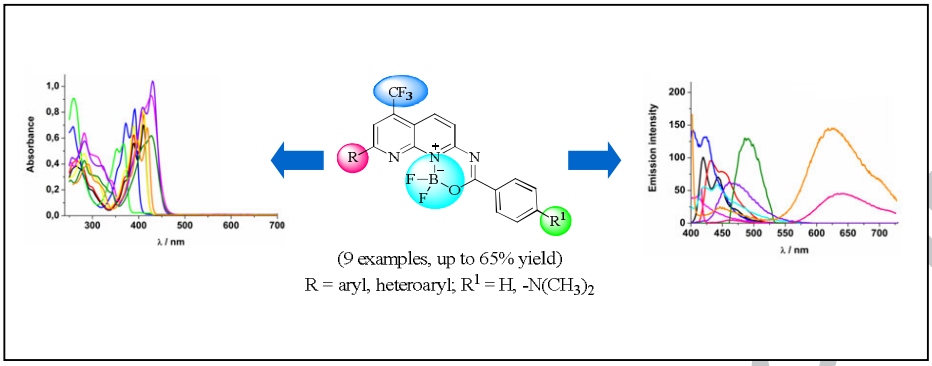
Graphical Abstract Picture



HIGHLIGHTS

- Regioselective synthesis of a new series of 1,8-naphthyridine-based boron complexes.
- ^{1}H-, ^{13}C-, ^{19}F- and ^{11}B-NMR spectroscopy and X-ray diffractometry data presented.
- Organoboron complexes displayed fluorescence and excellent photochemical proprieties.
- Quantum yield, Stokes shift, UV-vis, fluorescence, and redox potential discussed.
- Aryl(heteroaryl) substituents influence the optical and electrochemical properties.