JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

Organolithium-Mediated Postfunctionalization of Thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine Fluorescent Dyes

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Cite This: *J. Org. Chem.* 2020, 85, 6060–6072 Read Online

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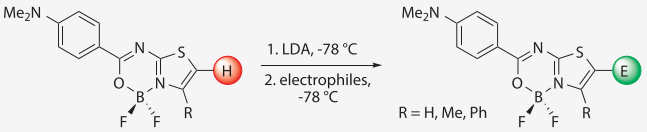
ABSTRACT: An effective method for transition-metal-free postfunctionalization of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine dyes via direct lithiation of the 1,3-thiazole ring was developed. The reaction allows valuable regioselective C−H modification of these N,O-chelated organoboron chromophores incorporating different groups, including C-, Hal-, Si-, S-, Se-, and Sn-substituents. As a result, a library of novel fluorescent 1,3-thiazole-based organoboron complexes has been synthesized and characterized. The influence of the donor/acceptor strength of the substituent E on the photophysical properties has been established. The compound with a bulky lipophilic substituent ($SnBu_3$) exhibits a relatively high solid-state photoluminescence quantum yield of 44%.



INTRODUCTION

N,O-coordinating organoboron dyes are currently intensively investigated because of their light-emissive properties.[1−4] They have been successfully used as emitters in organic light-emitting diodes[1] and organic solid-state lasers.[2] Other N,O-coordinating organoboron dyes exhibit aggregation-induced emission[3] properties and have found applications in biological imaging.[4] Classical synthesis of organoboron complexes is based on the preparation of the corresponding ligands and following complexation with boron-containing agents, such as $BF_3{\cdot}OEt_2$, $BAlk_3$, BAr_3, Ar_2BOH, Ar_2BOAlk, Ar_2BCl, etc.[5] Another way is postfuctionalization of compounds based on the organoboron core. The modification methods of N,N-coordinating organoboron dyes are developed well, including nucleophilic substitution,[6] aldol addition,[7] Knoevenagel condensation,[6a,b,8] 1,3-dipolar cycloaddition,[9] photocatalytic transformations,[10] and transition metal catalytic reactions[11] (such as Suzuki,[6c,12] Stille,[6c] Negishi,[12c,13] Sonogashira,[14] C−H arylation,[15] C−H alkylation,[16] and oxidative aromatic coupling[17]). Meanwhile, the postfunctionalization of N,O-coordinating organoboron complexes is still scarcely described, mainly represented by nitro group reduction and *N*-acylation/alkylation,[18] as well as some examples of Pd-catalytic coupling reactions.[4a,19] Moreover, the most problematic point of the postfunctionalization of such compounds is their poor stability in hard reaction conditions.[20] The development of effective various C−C and C−heteroatom bond formation reactions can open the way to a large library of new practically important N,O-coordinating organoboron fluorophores. Consequently, research of such stable synthetically modified complexes is an actual scientific challenge.

One of the least studied classes of the N,O-coordinating organoboron dyes is based on the oxadiazaborinine ring.[5] Usually, the oxadiazaborinine dyes have been synthesized by complexation of boron trifluoride with amide of electron-poor 2-amino-*N*-heterocycles such as pyridine,[21] pyrazine,[21c,22] pyridazine,[21c] 1,8-naphthyridine,[23] or 1,3,4-thiadiazole.[24] Our conception is based on the incorporation of an electron-rich heterocyclic building block into the oxadiazaborinine structure to increase the chemical stability of these complexes. Recently, we have described a simple synthetic route to highly fluorescent oxadiazaborinine dyes **1** based on electron-rich 1,3-thiazole building blocks (Figure 1a),[25] as well as to their benzo[*d*]thiazole analogues.[19b,26]

Herein, we report a simple method for postfunctionalization of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **1** based on direct lithiation and following reaction with electrophiles (Figure 1b). This transition-metal-free synthetic method enables the incorporation of substituents ranging from electron-donating (E = Me and $SiMe_3$) to highly electron-withdrawing (E = CN, SO_2Ph, and CHO) groups in the thiazolo[3,2-*c*][1,3,5,2]-oxadiazaborinine core, yielding a large library of novel fluorescent dyes. The influence of the substituent E on the photophysical properties of the obtained complexes both in solution and in the solid state was established.

RESULTS AND DISCUSSION

Synthesis and Characterization. The regioselectivity of organolithium-mediated electrophilic functionalization of 4,5-

Received: March 2, 2020
Published: April 9, 2020

https://dx.doi.org/10.1021/acs.joc.0c00552
J. Org. Chem. 2020, 85, 6060–6072

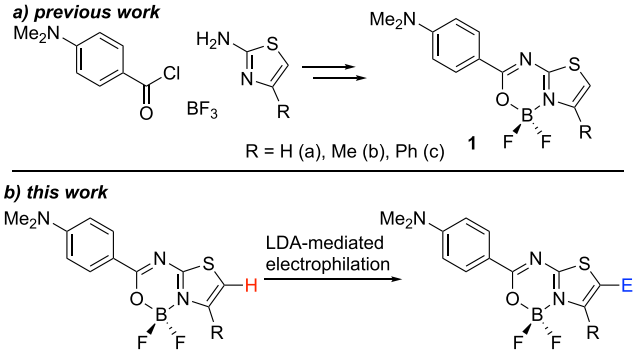
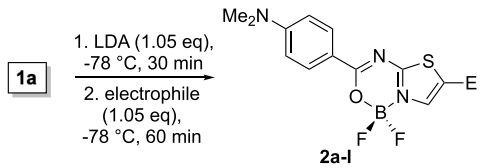


Figure 1. (a) Synthesis of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine dyes and (b) modification of thiazolo[3,2-*c*][1,3,5,2]-oxadiazaborinines via LDA-mediated electrophilation reaction.

unsubstituted 1,3-thiazoles depends on the acidity of thiazole protons (H-5 > H-4) and occurs preferentially at position 5 of the thiazole ring.[27] The substitution at position 4 could be realized for halogenation reaction in the presence of excess of organolithium reagent caused by halogen-dance reaction.[28] Therefore, first of all, our attention was concerned on the organolithium-mediated halogenation reaction of compound **1a** with the 4,5-unsubstituted 1,3-thiazole unit. As an effective base, we selected lithium diisopropylamide (LDA), which is a well-known mediator of the thiazole ring modification.[28c,29] Carbon tetrachloride, carbon tetrabromide, bromine, and iodine were tested as the halogenating electrophilic agents. In all cases, 5-substituted thiazole derivatives (**2a**–**c**) were isolated. The highest yields of the products (60–67%, Table 1, entries 1–4) were achieved when the molar ratio of the thiazole substrate/LDA/electrophile was 1.00:1.05:1.05.

Next, these reaction conditions were expanded for several C-electrophiles. In the case of methylation (Table 1, entry 5), the

Table 1. Scope for the LDA-Mediated Electrophilic Postfunctionalization of Complex 1a

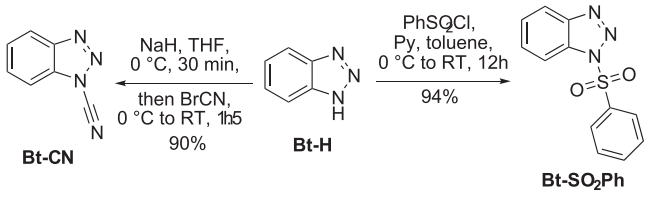


entry	electrophile	E	product	yield, %
1	CCl_4	Cl	**2a**	67
2	CBr_4	Br	**2b**	64
3	Br_2	Br	**2b**	60
4	I_2	I	**2c**	60
5	MeI[a]	Me	**2d**	71
6	$ClCO_2Me$	CO_2Me	**2e**	76
7	Br-CN	Br	**2b**	71
8	Bt-CN[a,b]	CN	**2f**	70
9	DMF	CHO	**2g**	76
10	Me_3SiCl	$SiMe_3$	**2h**	85
11	$(PhS)_2$	SPh	**2i**	73
12	$PhSO_2Cl$	Cl	**2a**	65
13	Bt-SO_2Ph[a,b]	SO_2Ph	**2j**	80
14	$(PhSe)_2$	SePh	**2k**	73
15	Bu_3SnCl	$SnBu_3$	**2l**	64

[a]With HMPA addition. [b]Bt—benzotriazole.

cation-complexing agent (hexamethylphosphoramide, HMPA)[30] was necessary for the reaction course; product **2d** was synthesized with 71% yield. The use of methyl chloroformate and dimethylformamide (DMF) (Table 1, entries 6 and 9) gave ester **2e** and aldehyde **2g** in 76% yield in both cases. Interestingly, using cyanogen bromide as the electrophile, the obtained product had a halogenide substituent (**2b**, entry 7 in Table 1). Meanwhile, to synthesize compound **2f** with the cyano group, benzotriazole-carbonitrile (**Bt-CN**) was selected as an effective electrophilic cyanation reagent,[31] which was synthesized in the reaction of benzothriazole (**Bt-H**) with cyanogen bromide under basic conditions with good yield (90%, Scheme 1). **Bt-CN** was successfully used in the presence of HMPA, giving expected product **2f** with 70% yield (entry 8 in Table 1).

Scheme 1. Synthesis of Benzotriazole-Based Electrophiles



Furthermore, starting from compound **1a** and using Si-, S-, Se-, and Sn-electrophiles, we obtained regioselective organoboron complexes **2h**–**l** in good yields ranging from 64 to 85% (Table 1, entries 10, 11, and 13–15). Notably, analogically to cyanation, sulfonation reaction did not occur with electrophilic halogenide (phenylsulfonyl chloride, entry 12 in Table 1); chloro-substituted product **2a** in 65% yield was isolated in this case. Compound **2j** with sulfone group was successfully obtained in 80% yield using phenylsulfonyl-benzotriazole (**Bt-SO_2Ph**)[32] as the electrophile. The synthesis of **Bt-SO_2Ph** was efficiently realized by sulfonation of unsubstituted benzotriazole with phenylsulfonyl chloride in basic conditions (Scheme 1).

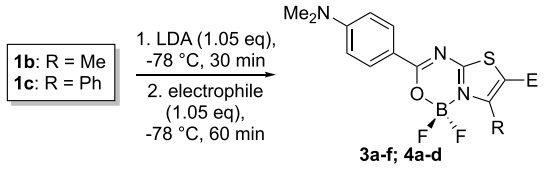
Having in hand the elaborated conditions for the effective LDA-mediated electrophilation of complex **1a**, we examined this reaction for complexes **1b,c** (Table 2). Using methylating, silylating, halogenating, sulfenylating, and ethoxycarboxylating reagents, we synthesized products **3a**–**f** and **4a**–**d** with the 4,5-disubstituted thiazole unit in very good yields (67–88%).

The structures of the synthesized products were confirmed by NMR (^{1}H, ^{13}C, ^{19}F, and, if possible, ^{77}Se or ^{119}Sn) spectroscopy, high-resolution mass spectrometry (HRMS), as well as, for compounds **2c,d,j**, **3a**, and **3f**, single-crystal X-ray analysis. Thus, all ^{1}H NMR spectra of compounds **2a**–**l** displayed the presence of a characteristic singlet signal for the H-4 atom in the range from 7.14 ppm for complex **2a** to 8.06 ppm for aldehyde **2g**. *Nota bene*: compound **2d** (Me-group at position 5 of the thiazole ring) is a regioisomer of analogue **1b** (Me-group at position 4 of thiazole ring), which exhibits the characteristic singlet for the H-5 atom at 6.05 ppm.[25]

X-ray Analysis. The X-ray crystallographic structures of complexes **2c,d,j**, and **3a,f** (Figures S1–S5 and Tables S1–S6 in the Supporting Information) unambiguously confirm not only the position of the substituent E but also the invariability of the tetrahedral coordination of boron atom, as well as the coplanarity of the donor (dimethylaminophenyl) and acceptor (thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine) units in the solid

https://dx.doi.org/10.1021/acs.joc.0c00552
J. Org. Chem. 2020, 85, 6060–6072

Table 2. Scope for the LDA-Mediated Electrophilic Postfunctionalization of Complexes 1b,c



3a-f; 4a-d

entry	R	electrophile	E	product	yield, %
1	Me	MeI[a]	Me	**3a**	80
2	Me	Me_3SiCl	$SiMe_3$	**3b**	88
3	Me	CCl_4	Cl	**3c**	86
4	Me	CBr_4	Br	**3d**	85
5	Me	$(PhS)_2$	SPh	**3e**	82
6	Me	$ClCO_2Et$	CO_2Et	**3f**	67
7	Ph	Me_3SiCl	$SiMe_3$	**4a**	88
8	Ph	CBr_4	Br	**4b**	81
9	Ph	$(PhS)_2$	SPh	**4c**	68
10	Ph	$ClCO_2Et$	CO_2Et	**4d**	72

[a]With HMPA addition.

state. The sulfur atom from the phenylsulfone group of compound **2j** has a near-to-tetrahedral coordination by two carbon and two oxygen atoms: the C−S−C bond angle is 104.6°, the O−S−C bond angles are in the range 105.9−108.6°, while the O−S−O bond angle is much higher (121.3°) (Table S6 in the Supporting Information), and slightly differs from the typical value (118.8°).[33]

Photophysical Properties of the Solutions. Having obtained a large library of thiazolo[3,2-*c*][1,3,5,2]-oxadiazaborinines **2a−l**, **3a−f**, and **4a−d**, we investigated their photophysical properties. The absorption and emission spectroscopic data of the dilute solution of these compounds in toluene are summarized in Table 3. The corresponding normalized spectra of the selected dyes are shown in Figure 2. Additionally, the normalized absorption and emission spectra and the spectroscopic data of the solutions of oxadiazaborinines **2a−l**, **3a−f**, and **4a−d** in five organic solvents with different polarities [toluene, dichloromethane (DCM), tetrahydrofuran (THF), acetone, and acetonitrile] are given in the Supporting Information (Figures S6−S27 and Table S7).

The solutions of the synthesized thiazolo[3,2-*c*][1,3,5,2]-oxadiazaborinines generally exhibited a strong absorption band and intense emission in the blue-green region. The absorption spectra of the complexes had high-energy shoulders, which were more clearly observed for the solutions of the compounds **2d**, **2h**, **2l**, **3a**, **3b**, and **4a** with donor substituents (Me, $SiMe_3$, and $SnBu_3$) at the thiazole ring in nonpolar media (i.e., toluene) and were induced by vibrational transition. The wavelengths of absorption (λ_{abs}) and emission (λ_{em}) maxima were found to be dependent on the donor/acceptor strength of the substituent E. The maxima were bathochromically shifted with increasing acceptor strength. Thus, the incorporation of halogen substituents in the thiazole unit (compounds **2a−c**, **3c,d**, and **4b**) slightly increased the wavelengths of absorption and emission maxima, comparative to the corresponding parameters of complexes **1a−c**: λ_{abs} = 416−421 nm and λ_{em} = 447−451 nm for products **2a−c**, **3c,d**, and **4b**, while λ_{abs} = 405−409 nm and λ_{em} = 439−444 nm for substrates **1a−c**.

Much stronger changes were observed in the case of compounds with different C-substituents (−Me, $-CO_2Me$, −CN, and −CHO). In particular, the incorporation of methyl

Table 3. Photophysical Properties of the Dilute Solutions of Complexes 1a−c, 2a−l, 3a−f, and 4a−d in Toluene

comp.	λ_{abs} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	λ_{em} (nm)	$\Delta\nu$ (cm^{-1})	Φ	τ, ns	B ($M^{-1}\cdot cm^{-1}$)[a]
1a	405	56,600	439	1912	>0.99	2.22	56,600
1b	407	59,300	437	1687	0.99	2.24	58,707
1c	409	56,600	444	1927	0.94	2.06	53,204
2a	416	62,000	449	1767	0.83	2.01	51,500
2b	416	58,300	449	1767	0.77	1.80	44,900
2c	418	57,500	451	1750	0.21	0.63	12,100
2d	406	57,900	437	1747	0.83	1.54	48,000
2e	425	36,300	464	1978	0.79	1.84	28,700
2f	430	32,700	470	1979	0.66	1.68	21,600
2g	437	43,100	481	2093	0.79	2.64	34,100
2h	407	59,700	440	1843	0.85	1.82	50,700
2i	420	62,500	457	1927	0.84	1.90	52,500
2j	429	68,700	471	2079	0.83	2.47	57,000
2k	417	76,100	454	1954	0.70	1.51	53,300
2l	406	56,100	438	1799	0.84	1.71	47,100
3a	395	58,000	439	2537	0.79	1.71	45,800
3b	407	48,000	439	1791	0.82	1.74	39,400
3c	419	51,200	449	1595	0.76	2.00	38,900
3d	419	59,300	449	1595	0.79	1.81	46,800
3e	420	68,500	457	1928	0.80	1.85	54,800
3f	424	63,700	458	1751	0.82	2.15	52,300
4a	409	51,700	441	1774	0.84	1.68	43,500
4b	418	62,500	447	1552	0.63	1.37	39,400
4c	421	64,200	462	2108	0.70	1.66	44,900
4d	423	87,500	458	1807	0.85	1.64	74,400

[a]$B = \varepsilon \times \Phi$.

https://dx.doi.org/10.1021/acs.joc.0c00552
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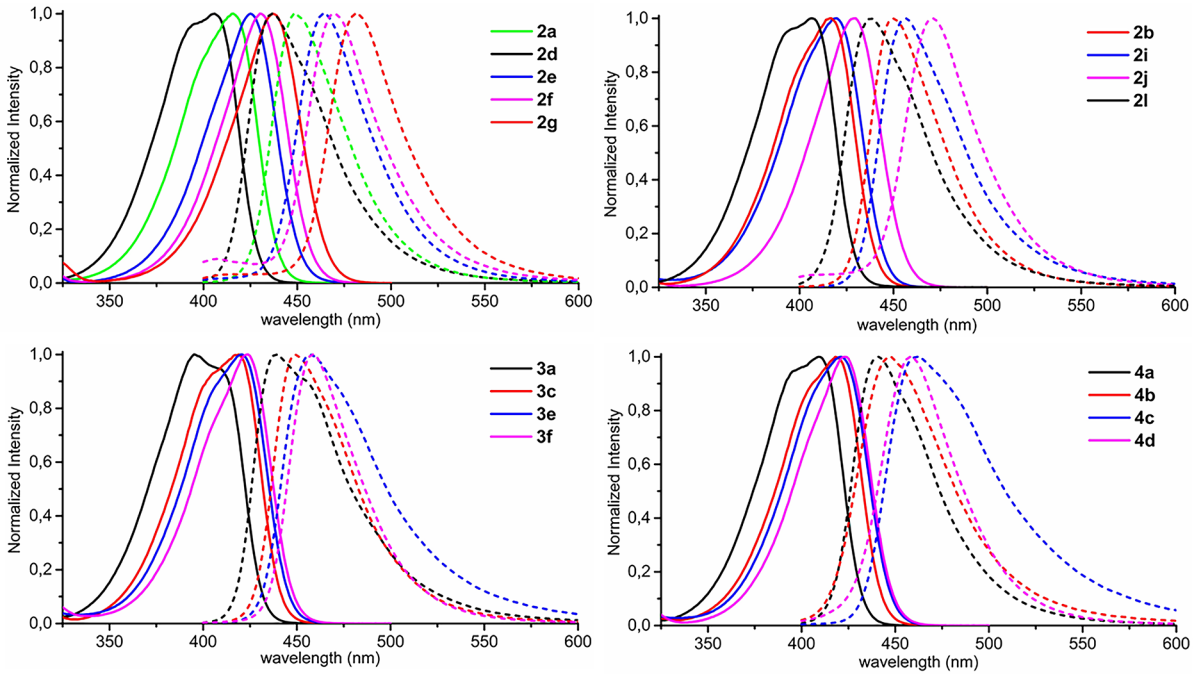

Figure 2. Normalized absorption (solid lines) and emission (dashed lines) spectra of the solutions of the selected complexes in toluene.

group (compounds **2d** and **3a**) provided almost no changes in the absorption and emission properties comparatively to those of the thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **1a,b** (Table 3), except the increasing intensity of high-energy absorption shoulder (Figure 2). However, electron-withdrawing ester, nitryl, and aldehyde groups exhibited more considerable influence on the photophysical parameters of the corresponding compounds: λ_{abs} = 405, 425, 430, 437 nm and λ_{em} = 439, 464, 470, 481 nm for dyes **1a**, **2e**, **2f**, and **2g**, respectively. The result of this dependency is also a growth of the Stokes shifts ($\Delta\nu$) from 1747 cm^{-1} for compound **2d** to 2093 cm^{-1} for aldehyde **2g**. It should be noted that the influence of the substituents at position 5 of the thiazole ring on the location of absorption and emission maxima of the thiazolo[3,2-*c*]-[1,3,5,2]oxadiazaborinines is definitely much higher than the corresponding influence of the substituents at position 4.[25]

The absorption maxima demonstrated almost no changes with the variation of solvent polarity. Meanwhile, the emission spectra clearly demonstrated the positive solvatofluorochromism of all investigated organoboron complexes (Figures S6–S27 and Table S7 in the Supporting Information), which is presumably due to an intramolecular charge transfer (ICT) process in the excited state.

The solutions of the complexes in nonpolar solvents exhibited high fluorescence quantum yields (Φ = 0.63–0.85 in toluene, Table 3). The exception was observed for iodo derivative **2c**: this compound due to "heavy atom effect" demonstrated a significant decrease of fluorescence efficiency (Φ = 0.21 in toluene). The value of fluorescence quantum yield of all investigated difluoroboron fluorophores decreased with the increase of the solvent polarity (Table S7, the Supporting Information). The excited-state lifetimes (τ) of the solutions in toluene vary from 0.63 to 2.64 ns, which was comparative with the corresponding values for substrates **1a–c** (τ = 2.06–2.24 ns, Table 3).

All investigated thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines are characterized by high value of the molecular fluorescence brightness (*B*, the product of the molar absorption coefficient and the fluorescence quantum yield) in the range from 12,100 to 74,400 $M^{-1}\cdot cm^{-1}$ for toluene solutions (Table 3), which indicated evident perspectives of their practical applications.

Electrochemical Properties. To investigate the redox behavior of the synthesized difluoroboron complexes, cyclic voltammograms (Figures S28–S49 in the Supporting Information) of the corresponding solutions in deoxygenated DCM were recorded using a voltage scan rate of 100 mV/s, 0.1 M Bu_4NPF_6 as the supporting electrolyte, and ferrocene as the internal standard. Obtained from cyclic voltammograms, the values of onset oxidation potentials (E_{ox}^{onset}) and onset reduction potentials (E_{red}^{onset}) were converted into the corresponding values of ionization potentials (IPs) and electron affinities (EAs) using equations IP = E_{ox}^{onset} + 4.4 and EA = E_{red}^{onset} + 4.4 (Table 4). The IPs of the investigated oxadiazaborinines were assessed in the range of 5.01–5.21 eV. Compounds with strong electron-accepting substituents exhibited slightly higher IPs: 5.13 (for **2g**), 5.14 (**2e,2j**), and 5.21 (**2f**) eV. The EAs ranged from 2.22 eV for complex **3b** to 2.73 eV for aldehyde **2g** (Table 4).

Quantum Chemical Calculations. In order to gain more insight into the electronic structures and the photophysical properties of the obtained thiazolo[3,2-*c*][1,3,5,2]-oxadiazaborinines, density functional theory (DFT), as well as time-dependent DFT (TD-DFT), calculations have been performed by Gaussian 09 software[34] with the inclusion of DCM solvent effect through the integral equation formalism polarizable continuum model. The ground-state geometries of most of the complexes have been optimized at the B3LYP functional and the 6-31g(d) basis set. However, to perform the calculations for iodo- and tin-derivatives **2c** and **2l**, the mixed LANL2DZ/6-31g(d) basic set was necessary to use, where the LANL2DZ basic set was used for I and Sn atoms, while the 6-31g(d) basic set was used for all other atoms.

The optimized geometries of the complexes (Figures 3 and S50 in the Supporting Information) are in good agreement

https://dx.doi.org/10.1021/acs.joc.0c00552
J. Org. Chem. 2020, 85, 6060–6072

Table 4. Onset Oxidation and Onset Reduction Potentials, IPs, and EAs of Compounds 2a−l, 3a−f, and 4a−d

compound	E_{ox}^{onset}, V	E_{red}^{onset}, V	IP, eV	EA, eV	E_g, eV[a]
2a	0.70	−1.92	5.10	2.48	2.62
2b	0.69	−1.82	5.09	2.58	2.51
2c	0.67	−2.03	5.07	2.37	2.70
2d	0.67	−2.17	5.07	2.23	2.84
2e	0.74	−1.84	5.14	2.56	2.58
2f	0.81	−1.76	5.21	2.64	2.57
2g	0.73	−1.67	5.13	2.73	2.40
2h	0.66	−2.10	5.06	2.30	2.76
2i	0.68	−1.99	5.08	2.41	2.67
2j	0.74	−1.78	5.14	2.62	2.52
2k	0.66	−2.02	5.06	2.38	2.68
2l	0.63	−2.01	5.03	2.39	2.64
3a	0.61	−2.17	5.01	2.23	2.78
3b	0.63	−2.18	5.03	2.22	2.81
3c	0.68	−1.96	5.08	2.44	2.64
3d	0.66	−1.88	5.06	2.52	2.54
3e	0.68	−2.00	5.08	2.40	2.68
3f	0.70	−1.93	5.10	2.47	2.63
4a	0.61	−2.10	5.01	2.30	2.71
4b	0.68	−1.85	5.08	2.55	2.53
4c	0.67	−2.00	5.07	2.40	2.67
4d	0.63	−1.91	5.03	2.49	2.54

[a] E_g = IP − EA.

with the X-ray crystal structures (Figures S1−S5 in the Supporting Information): 3-(4-dimethylaminophenyl)-thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine core is planar, except the tetrahedral coordinating boron unit. The phenylsulfone group in complex **2j** is twisted with respect to the rest of the molecule and has a near-to-tetrahedral geometry. Analogical geometry is observed for molecules **2i**, **2k**, **3e**, and **4c** with phenylthiolyl and phenylselanyl substituents.

Similarly to unsubstituted complex **1a**, the calculated highest occupied molecular orbitals (HOMOs) of compounds **2a−l** are mainly localized on the (*N*,*N*-dimethylamino)phenyl donor group, while the lowest unoccupied molecular orbitals (LUMOs) are delocalized along the whole planar π-conjugated dye scaffold (Figure 3). In the cases of compounds **2e−g,j**, the LUMOs are much shifted to the strong electron-withdrawing groups (CO_2Me, CN, CHO, and SO_2Ph), which causes the increase of ICT character of emission of these dyes.

The frontier molecular orbital densities of compounds **3a−f** and **4a−d** (Figures 3 and S50 in the Supporting Information) are analogical to its dyes **2a−l**; the methyl and phenyl substituents at position 4 of the thiazole ring do not make significant influence on the HOMO and LUMO distributions. The HOMO and LUMO energy levels correlate with the corresponding values of the IPs and the EAs determined from cyclic voltammograms (Table 4). The incorporation of an electron-withdrawing group into position 5 of the thiazole ring causes the increase of the absolute value of the HOMO and LUMO energy, as well as the decrease of $\Delta E_{HOMO-LUMO}$.

TD-DFT results (Figures S51−S75 and Table S8 in the Supporting Information) indicate that the lowest-energy absorption bands of all investigated complexes calculated in the range 392−442 nm correspond to the $S_0 \rightarrow S_1$ transition, which is characterized by high values of oscillator strength (f = 0.94−1.30). This transition is mainly contributed by the HOMO → LUMO excitation.

Taken together, the computational results are in good agreement with the experimentally obtained data and confirm the influence of the substituent E on the absorption properties of the corresponding compounds.

Solid-State Fluorescence Properties. The solid films of compounds **2a−l**, **3a−f**, and **4a−d** demonstrated single broad emission peaks (Figure 4). The exception was the emission spectrum of complex **2i**, in which an additional hypsochromic shoulder was observed. The solid-state emission maxima of the investigated dyes (Table S9 in the Supporting Information) were bathochromically shifted, relative to those of the corresponding dilute solutions.

In the solid state, because of aggregation-caused quenching (ACQ), most of the complexes exhibited weak emissions ($\Phi \leq$ 20%). However, compound **2l** exhibited an increased solid-state fluorescence quantum yield of 44%. Because of the presence of bulky lipophilic $SnBu_3$ substituent, this difluoroboron fluorophore possesses an extended intermolecular distance, which could reduce the intermolecular $\pi-\pi$ stacking in the solid state and eventually restrain the ACQ effect.

CONCLUSIONS

Conjugated with the donor 4-dimethylaminophenyl group thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine can be easily modified by direct regioselective lithiation of the thiazole unit. This simple transition-metal-free synthetic method provides a large library of novel fluorescent thiazole-based organoboron complexes with varied substituents at position 5 of the thiazole ring, including electron-donating or electron-withdrawing groups. The photophysical and electrochemical properties of these difluoroboron fluorophores can be effectively tuned by manipulation of donor/acceptor strength of the incorporated substituents. The incorporation of bulky lipophilic substituent ($SnBu_3$) in the thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine scaffold causes an increase of solid-state photoluminescence quantum yield up to 44%.

EXPERIMENTAL SECTION

General. All reagent-grade chemicals (including *n*-butyllithium, diisopropylamine, HMPA, and electrophilic reagents) and solvents were received from commercial suppliers (TCI, Aldrich, or Acros Organics). Column chromatography was performed on silica gel (Merck, 230−400 mesh). Melting points of all synthesized compounds were measured on an Automatic Melting Point System (OptiMelt, Stanford Research Systems). The NMR spectra were recorded with Bruker Avance II 400 MHz (at 400, 100, and 375 MHz for ^{1}H, ^{13}C, and ^{19}F NMR spectra, respectively) or Varian VNMRS 500 MHz (at 500, 125, 470, 95, and 186 MHz for ^{1}H, ^{13}C, ^{19}F, ^{77}Se, and ^{119}Sn NMR spectra, respectively) spectrometers for solutions in $CDCl_3$ and tetramethylsilane as the internal standard.

Mass spectra were measured using a Synapt G2-S HDMS (Waters Inc.) mass spectrometer equipped with an electrospray ion source and a quadrupole time-of-flight type mass analyzer or using a magnetic sector mass spectrometer AutoSpec Premier (Waters, USA) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass analyzer. Both instruments were controlled, and recorded data were processed using MassLynx 4.1 software package (Waters, USA).

UV−vis absorption spectra were recorded using a PerkinElmer Lambda 35 spectrometer for ca. 10^{-5} M solutions of dyes. Emission spectra were recorded using a Edinburgh Instruments' FLS980 fluorescence spectrometer (λ_{ex} = 374 nm) for both ca. 10^{-5} M solutions and thin solid films of the investigated dyes. Thin-film samples were fabricated on the precleaned quartz plates by using a spin-coating technique utilizing an SPS-Europe Spin150 Spin

https://dx.doi.org/10.1021/acs.joc.0c00552
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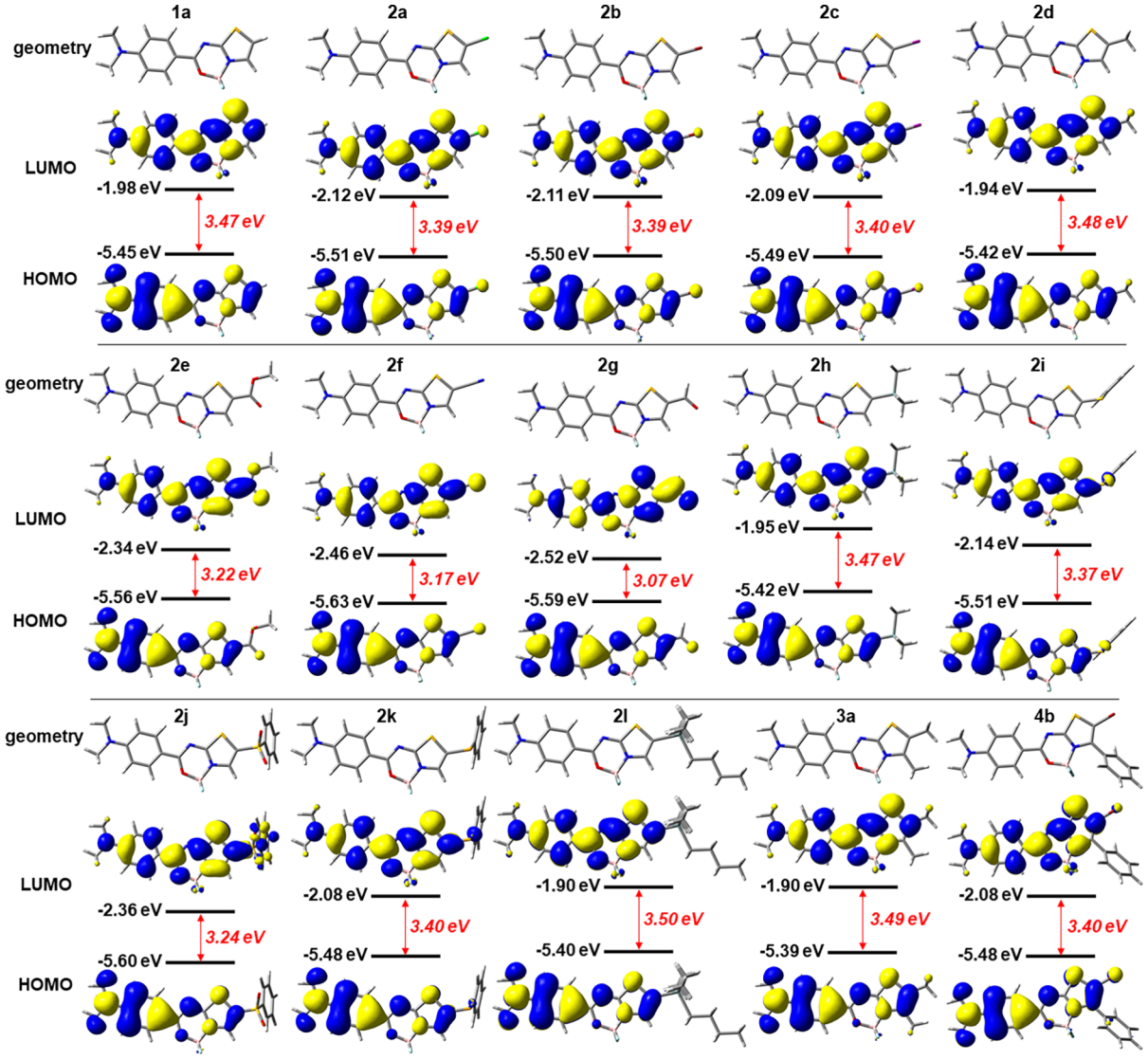

Figure 3. Optimized geometries and frontier molecular orbitals of compounds **1a**, **2a**–**l**, **3a**, and **4b**.

processor using 2.5 mg/mL of solutions of the complexes in DCM. Fluorescence quantum yields of the samples were obtained with a calibrated integrating sphere in a FLS980 spectrometer. Fluorescence decays of the solutions and of the solid-state samples were recorded with the PicoQuant PDL 820 ps pulsed diode laser as an excitation source (λ_{ex} = 374 nm) using a time-correlated single-photon counting technique. Electrochemical experiments were performed using the mAUTOLAB Type III apparatus and glassy carbon, platinum coil, and silver wire as the working, auxiliary, and reference electrodes, respectively.

Single crystals of organoboron complexes **2c**, **2d**, **2j**, **3a**, and **3f** were grown by the slow evaporation of their solution in hexanes/DCM (1:1). The X-ray measurements were made on a SuperNova Agilent diffractometer using Cu Kα (λ = 1.54184 Å) radiation at 100 K. Data reduction was done with CrysAlisPro (Agilent Technologies, Version 1.171.35.21b). The obtained structures were determined by direct methods and refined using SHELXL Software Package.[35] Crystallographic data of compounds **2c**, **2d**, **2j**, **3a**, and **3f** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and can be obtained, free of charge, from CCDC via https://www.ccdc.cam.ac.uk/structures/.

Synthesis. *1H-Benzo[d][1,2,3]triazole-1-carbonitrile (**Bt-CN**).* This compound was obtained in 90% yield (1.09 g) using a literature procedure[31] from benzotriazole (1.00 g, 8.39 mmol), sodium hydride (60% in mineral oil, 0.37 g, 9.23 mmol), and cyanogen bromide (0.98 g, 9.23 mmol).

*1-(Phenylsulfonyl)-1H-benzo[d][1,2,3]triazole (**Bt-SO$_2$Ph**).* This compound was obtained using a modified literature procedure.[32] A solution of benzotriazole (1.00 g, 8.39 mmol) and pyridine (1.5 equiv, 1.01 mL, 12.59 mmol) in dry toluene (12 mL) was cooled to 0 °C. Then, a solution of phenylsulfonyl chloride (1.2 equiv, 1.29 mL, 10.07 mmol) in toluene (3 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature. Then, water (10 mL) and ethyl acetate (15 mL) were added. The organic layer was separated, washed with water (15 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The obtained solid was recrystallized from toluene to afford **Bt-SO$_2$Ph** in 94% (2.06 g) yield. mp 122.9–124.1 °C, colorless needles. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.15 (4H, m, Ar-H), 7.61–7.69 (2H, m, Ar-H), 7.44–7.56 (3H, m, Ar-H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 145.4, 137.1, 135.2, 131.6, 130.3, 129.7 (2C), 127.9 (2C), 125.9, 120.6, 112.0 ppm.

General Procedure A: For Organolithium-Mediated Postfunctionalization of Thiazolo[3,2-c][1,3,5,2]oxadiazaborinines without an Additive. This reaction was conducted under an argon atmosphere. A solution of LDA (1.05 equiv, 0.15–0.18 mmol) in THF (1 mL) [previously obtained by sequential additions of 2.5 M solution (61–75 μL) of *n*-butyllithium (1.1 equiv, 0.15–0.19 mmol) in hexanes and diisopropylamine (1.05 equiv, 0.15–0.18 mmol, 20–

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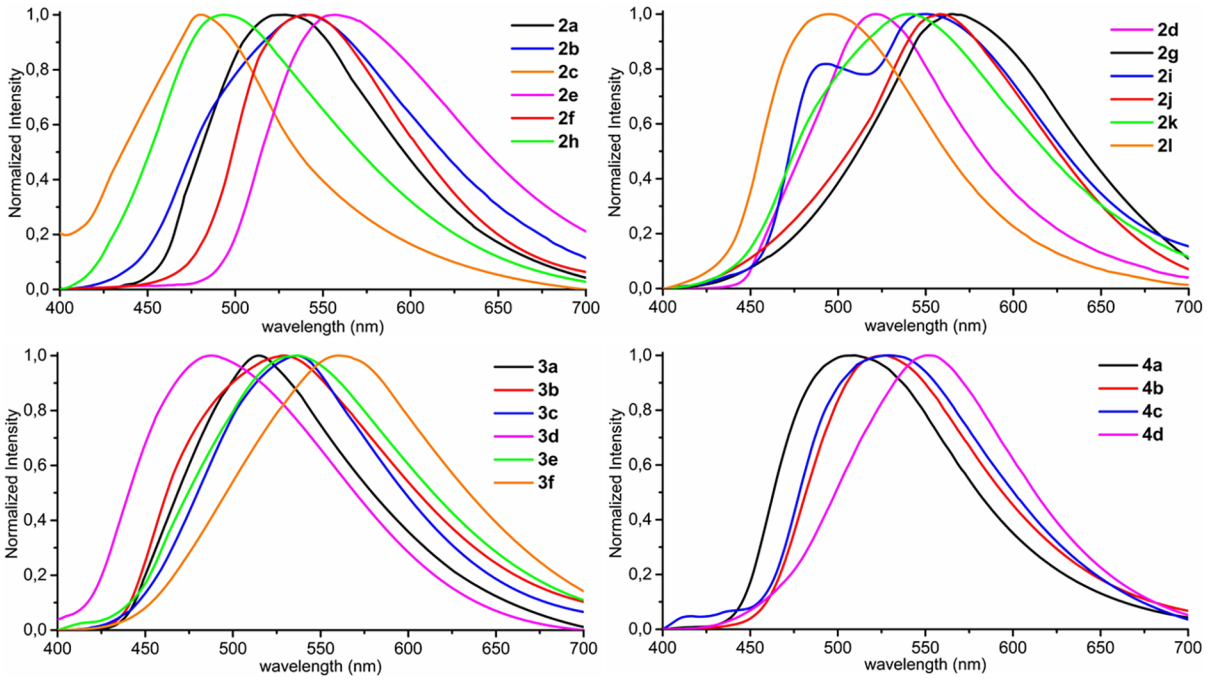
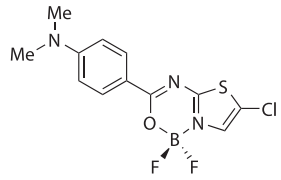


Figure 4. Normalized solid-state emission spectra of complexes **2a**–**l**, **3a**–**f**, and **4a**–**d** (λ_{ex} = 374 nm).

25 μL) to cooled THF (1 mL) at 0 °C and stirring for 15 min] was added to a solution of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine (**1a**–**c**, 1.0 equiv, 0.14–0.17 mmol) in dry THF (4 mL) at −78 °C. The mixture was stirred for 30 min at −78 °C. Then, a solution of electrophilic reagent (1.05 equiv, 0.15–0.18 mmol) in THF (1 mL) was slowly added, and the stirring was continued for 60 min at −78 °C. Next, a saturated aqueous solution (10 mL) of NH_4Cl was added to quench the rest of LDA at −78 °C. The reaction mixture was then brought to room temperature and extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel.

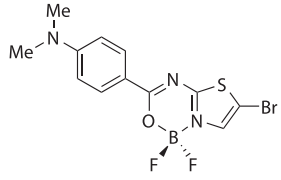
General Procedure B: For Organolithium-Mediated Postfunctionalization of Thiazolo[3,2-c][1,3,5,2]oxadiazaborinines in the Presence of HMPA. This reaction was conducted under an argon atmosphere. HMPA (5 equiv, 0.75–0.85 mmol, 130–148 μL) was added to a solution of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine (**1a**–**b**, 1.0 equiv, 0.15–0.17 mmol) and in dry THF (4 mL), and the mixture was cooled to −78 °C. Then, a solution of LDA (1.05 equiv, 0.16–0.18 mmol) in THF (1 mL) [previously obtained by sequential additions of 2.5 M solution (66–75 μL) of *n*-butyllithium (1.1 equiv, 0.17–0.19 mmol) in hexanes and diisopropylamine (1.05 equiv, 0.16–0.18 mmol, 22–25 μL) to cooled THF (1 mL) at 0 °C and stirring for 15 min] was added. The mixture was stirred for 30 min at −78 °C. Then, a solution of electrophilic reagent (1.05 equiv, 0.16–0.18 mmol) in THF (1 mL) was slowly added, and the stirring was continued for 60 min at −78 °C. Next, a saturated aqueous solution (10 mL) of NH_4Cl was added to quench the rest of LDA at −78 °C. The reaction mixture was then brought to room temperature and extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel.

*4-(6-Chloro-1,1-difluoro-1H-1λ⁴,8λ⁴-thiazolo[3,2-c][1,3,5,2]-oxadiazaborinin-3-yl)-N,N-dimethylaniline (**2a**).* Product **2a** was obtained in 67% yield (33 mg) using general procedure A from compound **1a** (44 mg, 0.15 mmol) and tetrachloromethane (15 μL, 0.16 mmol) and in 65% yield (32 mg) using general procedure B from compound **1a** (44 mg, 0.15 mmol) and benzenesulfonyl chloride (20 μL, 0.16 mmol). Column chromatography purification in both cases was performed with hexanes and DCM mixtures (3:1 to 1:1, v/v) as eluent.



mp 228.5–230.5 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (2H, d, *J* = 9.2 Hz, Ar-H), 7.30 (1H, s, thiazole-H), 6.69 (2H, d, *J* = 9.2 Hz, Ar-H), 3.11 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 172.4, 167.5, 154.4, 132.6 (2C), 127.0, 119.8, 117.2, 111.1 (2C), 40.2 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.54 (2F, m, BF_2) ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{12}BN_3OF_2SCl$, 330.0451; found, 330.0439.

*4-(6-Bromo-1,1-difluoro-1H-1λ⁴,8λ⁴-thiazolo[3,2-c][1,3,5,2]-oxadiazaborinin-3-yl)-N,N-dimethylaniline (**2b**).* Product **2b** was obtained in 60% (32 mg), 64% (34 mg), and 71% (38 mg) yields from compound **1a** (42 mg, 0.14 mmol) and bromine (26 mg, 0.16 mmol), tetrabromomethane (50 mg, 0.15 mmol), or cyanogen bromide (16 mg, 0.15 mmol), respectively, using general procedure A. Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1.5:1, v/v) as an eluent.



mp 231.2–233.0 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (2H, d, *J* = 9.1 Hz, Ar-H), 7.40 (1H, s, thiazole-H), 6.69 (2H, d, *J* = 9.1 Hz, Ar-H), 3.11 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 174.3, 167.3, 154.3, 132.6 (2C), 130.1, 117.2, 111.2 (2C), 101.7, 40.2 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.42 (2F, m, BF_2) ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{12}H_{11}BN_3OF_2SBrNa$, 395.9765; found, 395.9761.

*4-(1,1-Difluoro-6-iodo-1H-1λ⁴,8λ⁴-thiazolo[3,2-c][1,3,5,2]-oxadiazaborinin-3-yl)-N,N-dimethylaniline (**2c**).* Product **2c** was obtained in 60% yield (41 mg) using general procedure A from compound **1a** (48 mg, 0.16 mmol) and iodine (43 mg, 0.17 mmol).

https://dx.doi.org/10.1021/acs.joc.0c00552
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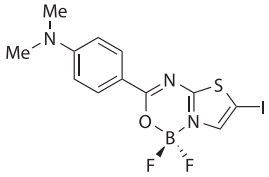
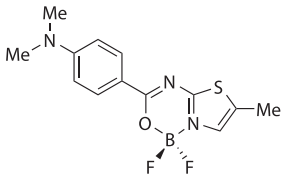
Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.



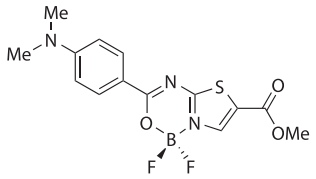
mp 197.8−200.5 °C, yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 9.2 Hz, Ar-H), 7.50 (1H, s, thiazole-H), 6.67 (2H, d, J = 9.2 Hz, Ar-H), 3.09 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 177.2, 167.2, 154.4, 136.1, 132.6 (2C), 117.1, 111.1 (2C), 61.3, 40.1 (2C) ppm; ^{19}F NMR (375 MHz, $CDCl_3$): δ −136.31 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{12}BN_3OF_2SI$, 421.9807; found, 421.9793.

*4-(1,1-Difluoro-6-methyl-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]-oxadiazaborinin-3-yl)-N,N-dimethylaniline (**2d**).* Product **2d** was obtained in 71% yield (38 mg) using general procedure B from compound **1a** (51 mg, 0.17 mmol) and methyl iodide (11 μL, 0.18 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1:3, v/v) as an eluent.



mp 258.9−260.5 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.1 Hz, Ar-H), 7.14 (1H, d, J = 1.4 Hz, thiazole-H), 6.71 (2H, d, J = 9.1 Hz, Ar-H), 3.09 (6H, s, NMe_2), 2.42 (3H, d, J = 1.4 Hz, CH_3) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 172.7, 166.4, 153.8, 132.2 (2C), 125.9, 118.0, 112.4, 111.2 (2C), 40.3 (2C), 12.6 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.94 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}BN_3OF_2S$, 310.0997; found, 310.0988.

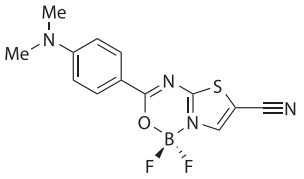
*Methyl 3-[4-(Dimethylamino)phenyl]-1,1-difluoro-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinine-6-carboxylate (**2e**).* Product **2e** was obtained in 76% yield (40 mg) using general procedure A from compound **1a** (44 mg, 0.15 mmol) and methyl chloroformate (12 μL, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1:2, v/v) as an eluent.



mp 236.4−238.1 °C, yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 9.1 Hz, Ar-H), 8.04 (1H, s, thiazole-H), 6.68 (2H, d, J = 9.1 Hz, Ar-H), 3.94 (3H, s, OMe), 3.12 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 175.4, 168.3, 160.4, 154.8, 135.4, 133.1 (2C), 120.7, 116.8, 111.0 (2C), 53.0, 40.1 (2C) ppm; ^{19}F NMR (375 MHz, $CDCl_3$): δ −136.77 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}BN_3O_3F_2SNa$, 376.0715; found, 376.0707.

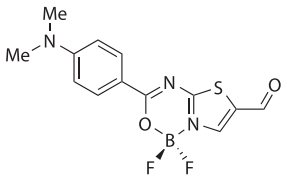
*3-[4-(Dimethylamino)phenyl]-1,1-difluoro-1H-1λ^4,8λ^4-thiazolo-[3,2-c][1,3,5,2]oxadiazaborinine-6-carbonitrile (**2f**).* Product **2f** was obtained in 70% yield (38 mg) using general procedure B from compound **1a** (50 mg, 0.17 mmol) and **Bt-CN** (26 mg, 0.18 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1:2, v/v) as an eluent.

mp 245.1−247.3 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 9.3 Hz, Ar-H), 7.89 (1H, s, thiazole-H), 6.69 (2H,



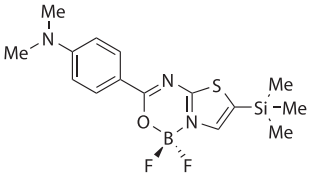
d, J = 9.3 Hz, Ar-H), 3.94 (3H, s, OMe), 3.14 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 175.7, 169.0, 155.2, 139.3, 133.6 (2C), 116.0, 111.2 (2C), 110.5, 110.0, 40.1 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.15 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{11}BN_4OF_2SNa$, 343.0612; found, 343.0602.

*3-[4-(Dimethylamino)phenyl]-1,1-difluoro-1H-1λ^4,8λ^4-thiazolo-[3,2-c][1,3,5,2]oxadiazaborinine-6-carbaldehyde (**2g**).* Product **2g** was obtained in 76% yield (40 mg) using general procedure A from compound **1a** (48 mg, 0.16 mmol) and DMF (13 μL, 0.17 mmol). This compound was also synthesized in a larger scale in 73% yield (308 mg), starting from substrate **1a** (385 mg, 1.30 mmol), DMF (106 μL, 1.37 mmol), LDA (1.37 mmol) in THF (8 mL) [previously obtained from cooled THF (8 mL) at 0 °C, 2.5 M solution (575 μL) of *n*-butyllithium (1.43 mmol) in hexanes, and diisopropylamine (1.37 mmol, 193 μL)], and THF (30 mL) using the same reaction conditions. Column chromatography purification in both cases was performed with hexanes and DCM mixtures (2:1 to 1:2, v/v) as an eluent.



mp 238.0−240.2 °C, orange powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (1H, s, CHO), 8.23 (2H, d, J = 9.1 Hz, Ar-H), 8.06 (1H, s, thiazole-H), 6.72 (2H, d, J = 9.1 Hz, Ar-H), 3.14 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 180.6, 175.9, 168.8, 154.9, 138.7, 133.5 (2C), 130.4, 116.8, 111.4 (2C), 40.3 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.69 (2F, m, BF_2) ppm. HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{12}BN_3O_2F_2S$, 323.0711; found, 323.0717.

*4-{1,1-Difluoro-6-(trimethylsilyl)-1H-1λ^4,8λ^4-thiazolo[3,2-c]-[1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**2h**).* Product **2h** was obtained in 85% yield (50 mg) using general procedure A from compound **1a** (47 mg, 0.16 mmol) and trimethylsilyl chloride (21 μL, 0.17 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.



mp 186.4−188.0 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 9.1 Hz, Ar-H), 7.42 (1H, s, thiazole-H), 6.68 (2H, d, J = 9.1 Hz, Ar-H), 3.08 (6H, s, NMe_2), 0.36 (9H, s, $SiMe_3$) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 176.6, 166.4, 154.1, 134.1, 132.3 (2C), 126.6, 117.5, 110.9 (2C), 40.0 (2C), −0.8 (3C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.59 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{21}BN_3OF_2SSi$, 368.1236; found, 368.1234.

*4-{1,1-Difluoro-6-(phenylthio)-1H-1λ^4,8λ^4-thiazolo[3,2-c]-[1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**2i**).* Product **2i** was obtained in 73% yield (42 mg) using general procedure A from compound **1a** (42 mg, 0.14 mmol) and diphenyl disulfide (33 mg, 0.15 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.

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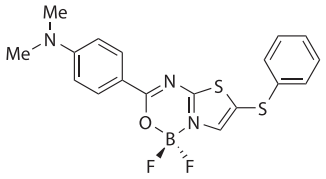
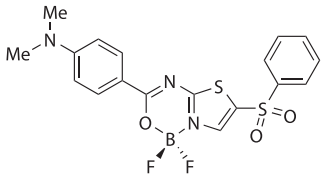


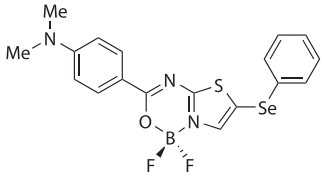
mp 218.2−219.5 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.2 Hz, Ar-H), 7.56 (1H, s, thiazole-H), 7.32−7.39 (4H, m, Ar-H), 7.29 (1H, m, Ar-H), 6.67 (2H, d, J = 9.2 Hz, Ar-H), 3.10 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 175.6, 167.3, 154.4, 134.4, 134.4, 132.6 (2C), 129.6 (2C), 129.3 (2C), 127.9, 122.5, 117.1, 111.0 (2C), 40.1 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.61 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}BN_3OF_2S_2$, 404.0874; found, 404.0866.

*4-{1,1-Difluoro-6-(phenylsulfonyl)-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**2j**).* Product **2j** was obtained in 80% yield (52 mg) using general procedure B from compound **1a** (44 mg, 0.15 mmol) and **Bt-SO$_2$Ph** (40 mg, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (1:1 to 1:3, v/v) as an eluent.



mp 225.5−227.3 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (2H, d, J = 9.2 Hz, Ar-H), 7.99 (2H, d, J = 7.2 Hz, Ar-H), 7.91 (1H, s, thiazole-H), 7.69 (1H, t, J = 7.4 Hz, Ar-H), 7.60 (2H, dd, J = 7.4 Hz, J = 7.2 Hz, Ar-H), 6.67 (2H, d, J = 9.2 Hz, Ar-H), 3.12 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 176.3, 168.6, 154.9, 140.1, 134.7, 134.5, 133.4 (2C), 130.6, 129.9 (2C), 127.6 (2C), 116.5, 111.2 (2C), 40.2 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.22 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{16}BN_3O_3F_2S_2Na$, 458.0592; found, 458.0589.

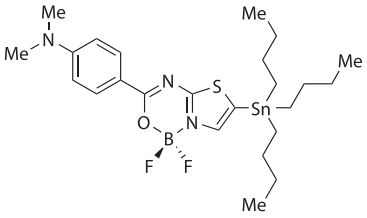
*4-{1,1-Difluoro-6-(phenylselanyl)-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**2k**).* Product **2k** was obtained in 73% yield (50 mg) using general procedure A from compound **1a** (45 mg, 0.15 mmol) and diphenyl diselenide (50 mg, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.



mp 209.4−211.5 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.2 Hz, Ar-H), 7.58 (1H, s, thiazole-H), 7.48−7.52 (2H, m, Ar-H), 7.30−7.34 (3H, m, Ar-H), 6.70 (2H, d, J = 9.2 Hz, Ar-H), 3.10 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 176.6, 167.0, 154.2, 135.2, 132.6 (2C), 132.0 (2C), 129.8 (2C), 129.7, 128.4, 117.6, 113.6, 111.3 (2C), 40.2 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.49 (2F, m, BF_2) ppm; ^{77}Se NMR (95 MHz, $CDCl_3$): δ 314.68 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}BN_3OF_2SSe$, 452.0319; found, 452.0303.

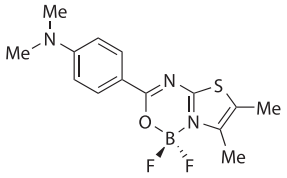
*4-{1,1-Difluoro-6-(tributylstannyl)-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**2l**).* Product **2l** was obtained in 64% yield (56 mg) using general procedure A from compound **1a** (44 mg, 0.15 mmol) and tributyltin chloride (42 μL, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.

mp 94.0−96.1 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 9.1 Hz, Ar-H), 7.33 (1H, s, thiazole-H), 6.69 (2H, d, J = 9.1 Hz, Ar-H), 3.08 (6H, s, NMe_2), 1.56 (6H, m, 3 × CH_2), 1.34



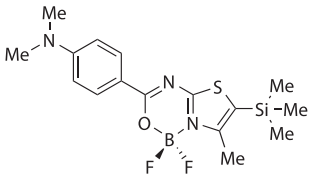
(6H, m, 3 × CH_2), 1.17 (6H, m, 3 × CH_2), 0.91 (9H, t, J = 7.3 Hz, 3 × CH_3) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 177.3, 165.7, 154.0, 134.7, 132.1 (2C), 123.2, 117.8, 110.9 (2C), 40.0 (2C), 28.8 (3C), 27.2 (3C), 13.6 (3C), 11.1 (3C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.61 (2F, m, BF_2) ppm; ^{119}Sn NMR (186 MHz, $CDCl_3$): δ −29.54 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{39}BN_3OF_2SSn$, 586.1897; found, 586.1876.

*4-{1,1-Difluoro-6,7-dimethyl-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]-oxadiazaborinin-3-yl}-N,N-dimethylaniline (**3a**).* Product **3a** was obtained in 80% yield (42 mg) using general procedure B from compound **1b** (50 mg, 0.16 mmol) and methyl iodide (11 μL, 0.18 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (1:1 to 1:2, v/v) as an eluent.



mp 227.6−229.0 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.1 Hz, Ar-H), 6.69 (2H, d, J = 9.1 Hz, Ar-H), 3.08 (6H, s, NMe_2), 2.38 (3H, s, CH_3), 2.31 (3H, s, CH_3) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 170.7, 165.6, 153.8, 136.4, 132.0 (2C), 119.3, 118.0, 111.1 (2C), 40.2 (2C), 12.0, 11.2 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −133.88 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}BN_3OF_2S$, 324.1153; found, 324.1150.

*4-{1,1-Difluoro-7-methyl-6-(trimethylsilyl)-1H-1λ^4,8λ^4-thiazolo-[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**3b**).* Product **3b** was obtained in 88% yield (48 mg) using general procedure A from compound **1b** (44 mg, 0.14 mmol) and trimethylsilyl chloride (19 μL, 0.15 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1:1, v/v) as an eluent.



mp 149.8−151.0 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 9.1 Hz, Ar-H), 6.68 (2H, d, J = 9.1 Hz, Ar-H), 3.08 (6H, s, NMe_2), 2.53 (3H, s, CH_3-thiazole), 0.38 (9H, s, $SiMe_3$) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 175.2, 165.5, 153.9, 146.6, 132.1 (2C), 119.0, 117.7, 111.0 (2C), 40.1 (2C), 15.5, −0.3 (3C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −133.70 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{23}BN_3OF_2SSi$, 382.1392; found, 382.1380.

*4-(6-Chloro-1,1-difluoro-7-methyl-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl)-N,N-dimethylaniline (**3c**).* Product **3c** was obtained in 86% yield (48 mg) using general procedure A from compound **1b** (50 mg, 0.16 mmol) and tetrachloromethane (16 μL, 0.17 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.

mp 237.1−239.7 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 8.9 Hz, Ar-H), 6.68 (2H, d, J = 8.9 Hz, Ar-H), 3.10 (6H, s, NMe_2), 2.44 (3H, s, CH_3-thiazole) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 170.7, 166.7, 154.3, 138.1, 132.4 (2C), 117.2, 113.7,

https://dx.doi.org/10.1021/acs.joc.0c00552
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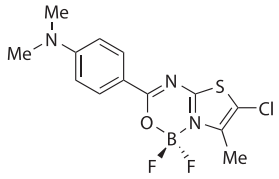
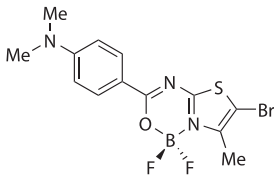


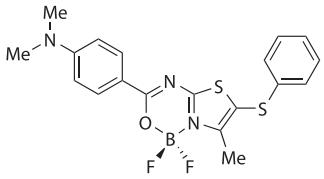
111.0 (2C), 40.1 (2C), 12.0 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −133.81 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}BN_3OF_2SCl$, 344.0607; found, 344.0606.

4-(6-Bromo-1,1-difluoro-7-methyl-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl)-N,N-dimethylaniline (**3d**). Product **3d** was obtained in 85% yield (50 mg) using general procedure A from compound **1b** (47 mg, 0.15 mmol) and tetrabromomethane (50 mg, 0.15 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1.5:1, v/v) as an eluent.



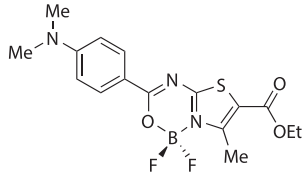
mp 224.1−226.6 °C, yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 9.1 Hz, Ar-H), 6.68 (2H, d, J = 9.1 Hz, Ar-H), 3.09 (6H, s, NMe_2), 2.54 (3H, s, CH_3-thiazole) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 172.8, 166.6, 154.3, 140.5, 132.4 (2C), 117.2, 111.1 (2C), 97.6, 40.1 (2C), 13.4 ppm; ^{19}F NMR (375 MHz, $CDCl_3$): δ −133.82 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}BN_3OF_2SBr$, 388.0102; found, 388.0086.

4-{1,1-Difluoro-7-methyl-6-(phenylthio)-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**3e**). Product **3e** was obtained in 82% yield (52 mg) using general procedure A from compound **1b** (47 mg, 0.15 mmol) and diphenyl disulfide (35 mg, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1.5:1, v/v) as an eluent.



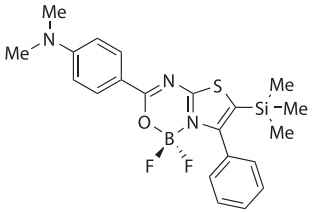
mp 231.6−233.5 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 9.1 Hz, Ar-H), 7.30−7.34 (2H, m, Ar-H), 7.22−7.26 (3H, m, Ar-H), 6.69 (2H, d, J = 9.1 Hz, Ar-H), 3.10 (6H, s, NMe_2), 2.59 (3H, s, CH_3-thiazole) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 173.9, 166.5, 154.2, 147.6, 135.2, 132.5 (2C), 129.5 (2C), 127.9 (2C), 127.2, 117.4, 114.7, 111.1 (2C), 40.2 (2C), 13.1 (t, J_{C-F} = 2.6 Hz) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −133.98 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}BN_3OF_2S_2Na$, 440.0850; found, 440.0849.

Ethyl 3-[4-(Dimethylamino)phenyl]-1,1-difluoro-7-methyl-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinine-6-carboxylate (**3f**). Product **3f** was obtained in 67% yield (44 mg) using general procedure A from compound **1b** (53 mg, 0.17 mmol) and ethyl chloroformate (21 μL, 0.18 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (1:1 to 1:2, v/v) as and eluent.



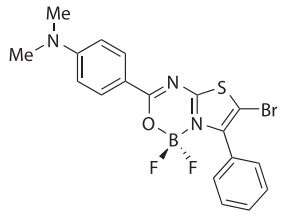
mp 231.0−233.6 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 9.2 Hz, Ar-H), 6.68 (2H, d, J = 9.2 Hz, Ar-H), 4.37 (2H, q, J = 7.2 Hz, OCH_2), 3.11 (6H, s, NMe_2), 2.82 (3H, s, thiazole-CH_3), 1.39 (3H, t, J = 7.2 Hz, CH_2CH_3) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 173.2, 167.5, 160.9, 154.5, 149.9, 132.8 (2C), 116.9, 114.2, 111.0 (2C), 61.9, 40.1 (2C), 14.3, 14.0 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −133.55 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}BN_3O_3F_2S$, 382.1208; found, 382.1204.

4-{1,1-Difluoro-7-phenyl-6-(trimethylsilyl)-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**4a**). Product **4a** was obtained in 88% yield (59 mg) using general procedure A from compound **1c** (56 mg, 0.15 mmol) and trimethylsilyl chloride (20 μL, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 1.5:1, v/v) as an eluent.



mp 195.1−197.8 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (2H, d, J = 9.1 Hz, Ar-H), 7.42−7.49 (5H, m, Ar-H), 6.69 (2H, d, J = 9.1 Hz, Ar-H), 3.08 (6H, s, NMe_2), 0.08 (9H, s, $SiMe_3$) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 175.1, 165.9, 153.9, 149.9, 132.2 (2C), 132.0, 130.6 (2C), 129.6, 127.8 (2C), 122.7, 118.0, 111.1 (2C), 40.2 (2C), −0.2 (3C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −131.43 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{24}BN_3OF_2SSiNa$, 466.1368; found, 466.1370.

4-(6-Bromo-1,1-difluoro-7-phenyl-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl)-N,N-dimethylaniline (**4b**). Product **4b** was obtained in 81% yield (55 mg) using general procedure A from compound **1c** (56 mg, 0.15 mmol) and tetrabromomethane (53 mg, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (3:1 to 2:1, v/v) as an eluent.



mp 200.5−202.8 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.2 Hz, Ar-H), 7.53−7.58 (2H, m, Ar-H), 7.47−7.53 (3H, m, Ar-H), 6.68 (2H, d, J = 9.2 Hz, Ar-H), 3.10 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 173.1, 166.8, 154.3, 143.5, 132.6 (2C), 130.3 (2C), 130.0, 128.8, 128.3 (2C), 117.1, 111.0 (2C), 99.4, 40.1 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −131.27 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{15}BN_3OF_2SBrNa$, 472.0078; found, 472.0076.

4-{1,1-Difluoro-7-phenyl-6-(phenylthio)-1H-1λ^4,8λ^4-thiazolo[3,2-c][1,3,5,2]oxadiazaborinin-3-yl}-N,N-dimethylaniline (**4c**). Product **4c** was obtained in 68% yield (49 mg) using general procedure A from compound **1c** (56 mg, 0.15 mmol) and diphenyl disulfide (35 mg, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1:1, v/v) as an eluent.

mp 240.8−242.8 °C, yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (2H, d, J = 9.0 Hz, Ar-H), 7.53 (2H, d, J = 7.7 Hz, Ar-H), 7.44−7.50 (3H, m, Ar-H), 7.31 (2H, dd, J = 7.6 Hz, J = 7.1 Hz, Ar-H), 7.23−7.28 (3H, m, Ar-H), 6.66 (2H, d, J = 9.0 Hz, Ar-H), 3.10 (6H, s, NMe_2) ppm; ^{13}C{H} NMR (125 MHz, $CDCl_3$): δ 173.9, 166.7, 154.3, 148.7, 135.2, 132.6 (2C), 130.3 (2C), 129.9, 129.4 (2C), 129.1, 129.0 (2C), 128.0 (2C), 127.6, 118.3, 117.3, 111.1 (2C), 40.1 (2C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −131.25 (2F, m,

https://dx.doi.org/10.1021/acs.joc.0c00552
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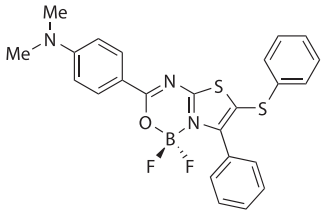
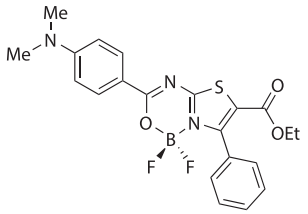


BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{20}BN_3OF_2S_2Na$, 502.1007; found, 502.0984.

*Ethyl 3-[4-(Dimethylamino)phenyl]-1,1-difluoro-7-phenyl-1H-1λ⁴,8λ⁴-thiazolo[3,2-c][1,3,5,2]oxadiazaborinine-6-carboxylate (**4d**).* Product **4d** was obtained in 72% yield (48 mg) using general procedure A from compound **1c** (56 mg, 0.15 mmol) and ethyl chloroformate (15 μL, 0.16 mmol). Column chromatography purification was performed with hexanes and DCM mixtures (2:1 to 1:1, v/v) as an eluent.



mp 208.6−210.3 °C, yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 9.2 Hz, Ar-H), 7.44−7.53 (5H, m, Ar-H), 6.69 (2H, d, J = 9.2 Hz, Ar-H), 4.16 (2H, q, J = 7.2 Hz, OCH_2), 3.10 (6H, s, NMe_2), 1.11 (3H, t, J = 7.2 Hz, CH_2CH_3) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 173.3, 167.7, 160.0, 154.5, 150.3, 132.9 (2C), 129.9, 129.8 (2C), 129.4, 127.7 (2C), 117.2, 116.7, 111.2 (2C), 61.9, 40.2 (2C), 13.8 ppm; ^{19}F NMR (375 MHz, $CDCl_3$): δ −130.99 (2F, m, BF_2) ppm. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}BN_3O_3F_2SNa$, 466.1184; found, 466.1175.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c00552.

ORTEP diagrams for the X-ray structures and crystal data of complexes; additional photophysical data in solutions, cyclic voltammograms; photophysical properties of complexes in the solid state; fluorescence decays of dyes; and NMR spectra of all synthesized compounds (PDF)

Crystal data of **2c**, **2d**, **2j**, **3a**, and **3f** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to acknowledge Poland's National Science Centre (UMO-2019/03/X/ST4/00037) for financial support. The calculation research was supported in part by PLGrid Infrastructure. D.V. and I.H. also acknowledge the Research Council of Lithuania ("PolyTADFer", No. P-LLT-19-14).

■ DEDICATION

This paper is dedicated to Professor Mykola D. Obushak on his 65th birthday.

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https://dx.doi.org/10.1021/acs.joc.0c00552
J. Org. Chem. 2020, 85, 6060−6072