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Carbonyl Derivatives of Boradiazaindacene via Catalytic CO Insertion

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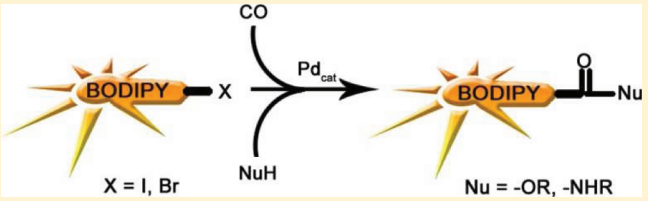
Supporting Information

ABSTRACT: A methodological study is presented dealing with carbopalladation reactions on BODIPY dyes bearing aryl−halogen functions. Using this technique, several ester and amide groups were efficiently introduced on the dyes. These changes do not affect the optical properties of the dyes and thus allow the construction of new BODIPY-based functional dyes with carboxylic anchoring groups or peptide links.



INTRODUCTION

The development of sophisticated fluorescent molecules able to satisfy the needs of biologists and material scientists is a topic of intense current research. Derivatives of boradiazaindacene (BODIPY) have been the subject of particular interest due to their bright emission characteristics and the recent progress in their chemistry.[1] Contributions from many research groups have led to the development of synthetic procedures which enable modification of the indacene core on most of the substitution positions in order to tune the color and the solubility or to introduce additional functions.[1] Our introduction of chemistry based on the use of organometallic reagents to displace the fluoride groups of the basic difluoroboradiazaindacene,[2] for example, opened the way to the design of various sophisticated molecular architectures[3] and water-soluble derivatives.[4] Unfortunately, the incompatibility of the organometallic reagents with carbonyl derivatives prevented the use of this procedure for applications requiring carbonyl derivatives such as carboxylic acid groups for biolabeling or grafting on solid surfaces (i.e., semi-conducting TiO_2). To introduce such substituents, preferably at the end of a multistep synthesis, the use of a protected acid in the form of an oxazolidine was envisaged,[5] but the deprotection techniques necessary to recover the free acid were thought to be too harsh. Thus, we opted for carbon monoxide insertion on an aryl halogenide in the presence of palladium catalyst.[6] This reaction was first described by Heck et al. for the formation of esters[7] and amides.[8] By using these mild reaction conditions, we have been able to introduce substituents on the boron center, via organometallic reagents, before the creation of the carbonyl group. We have thereby opened up the possibility of using *C*-BODIPY (diaryl or dialkyl boron) or *E*-BODIPY (diethynylboron)[2] in biolabeling experiments or in optoelectronic devices where carboxylic groups are necessary. To illustrate the potential of this approach, we present here a detailed study of carbopalladation reactions involving several nucleophiles at various positions on the BODIPY nucleus.

RESULTS AND DISCUSSION

To confirm the versatility of the carbopalladation reaction applied to boradiazaindacene dyes, we reacted a BODIPY bearing an iodoaryl group with a palladium catalyst under a stream of carbon monoxide and in the presence of various nucleophiles:[6] primary or secondary alcohols to obtain ester groups[7] or amines to get amide derivatives.[8] Amines were considered to be key connecting groups as they are often used in biolabeling (e.g., through the reaction of a diamine and a protected aminoacid).[9] The known precursor dyes shown in Scheme 1 possess a common iodophenyl substituent in the 8-position and various substituents on the diazaindacene core and on the boron (fluoride, arylethynyl, and alkylethynyl groups). These different iodophenyl derivatives were reacted at 70−80 °C in benzene or toluene with 20 mol % of $Pd(PPh_3)_2Cl_2$ under a slow stream of carbon monoxide in the presence of a tertiary amine to trap the nascent HI. The reactions proceeded in good yields with primary, secondary, and benzylic alcohols (over 57%) and primary amines except in the case of ethyl glycine ester. Here, the poor solubility of the glycine ester hydrochloride and double insertion of CO (vide infra) are likely the reasons for slow reaction and poor reaction yields.

Following this successful introduction of carboxylate derivatives onto the pseudomeso position of various BODIPY dyes, we decided to check the versatility of this technique with a dye bearing a halogen group directly on the boradiazaindacene core. We opted for a simple dye bearing iodine on the 2-position.[13] Following the same synthetic procedure, we were again able to insert the carboxyl derivatives in fair yields with both alcohols and amines as nucleophiles (Scheme 2).

To complete the study, we extended the use of the same procedure with dipyrromethene borate or diisoindolemethene-borate[5] (Scheme 3) species bearing iodophenyl groups on the boron center via an ethynyl tether. This procedure allowed us

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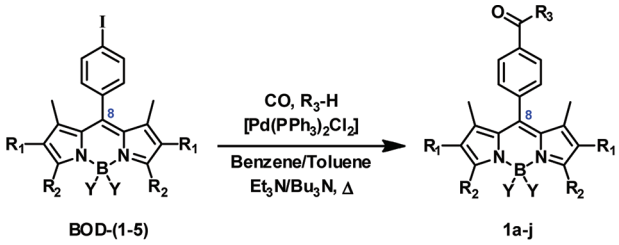
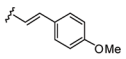
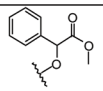
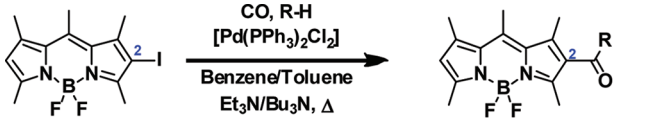
Scheme 1. Synthesis of *meso*-Phenylcarbonyl BODIPY Derivatives



BOD-(1-5) 1a-j

Cmpds	Entry	R_1	R_2	Y	R_3	Yield %
1a	BOD-1[10]	Et	Me	F	-O*i*Pr	83
1b	BOD-2[11]	H	Me		-OEt	97
1c	BOD-3	H			-OEt	76
1d	BOD-4[12]	Et	Me		-OEt	93
1e	BOD-5	H	Me		-OEt	85
1f	BOD-1	Et	Me	F		57
1g	BOD-1	Et	Me	F	-NH$(CH_2)_2NH_2$	90
1h	BOD-2	H	Me		-NH$(CH_2)_2NH_2$	90
1i	BOD-1	Et	Me	F	-NHCH_2COOEt	25
1j	BOD-2	H	Me		-NHCH_2COOEt	43

Scheme 2. Synthesis of 2-Carbonyl BODIPY Derivatives



BOD-6

2a: R = -OEt 93%
2b: R = -OiPr 55%
2c: R = -NHC_3H_7 84%
2d: R = -$NHCH_2COOEt$ 30%

to introduce a carbonyl function after the functionalization of the boron center by ethynyl-Grignard reagents.[3b] The carbopalladation proceeded efficiently with primary alcohols with no degradation of the dye, giving easy access to ester functions on the boron side of the BODIPY dyes. Amines could also be used to obtain the corresponding amides in similar yields, just as for the 8-(iodophenyl) derivatives.

We then used this efficient procedure to introduce two different carbonyl derivatives successively on the dye core. Thus, after carboalkoxylation of the corresponding 8-(iodophenyl) compound to give **1b**, the compound was smoothly iodinated with ICl,[13] enabling subsequent formation of the glycine derivative **6** following the standard protocol (Scheme 4).

Another example of the utility of Pd catalysis was provided by reaction of the distyryl-BODIPY derivative **7** bearing three halogen groups (Scheme 5). It has been previously demonstrated that a relatively selective Sonogashira cross-coupling reaction is effective on the phenyl iodo residue.[14] It was tempting at this stage to use the same reaction mixture to perform two orthogonal reactions (Sonogashira and carboalkoxylation) using different substrates with the same palladium precursor. After some experimentation, we succeeded in coupling in one pot: (i) first 2-methyl-3-butyn-2-ol at the 8-phenyl substitution position and then (ii) replacing both bromo groups by two ethyl ester units via a carbopalladation in the presence of ethanol and carbon monoxide. The target derivative **8** was easily purified by column chromatography due to the presence of the polar hydroxyl function with a 58% yield. The intermediate monosubstituted derivative can be detected by thin-layer chromatography but does not required purification to undergo the second in situ carbopalladation reaction. This is an interesting reaction saving the use of a second batch of the palladium precursor and avoiding chromatographic purification of the intermediate.

During this survey, we observed some secondary products, and we were able to isolate and characterize one of these. It has previously been reported that the use of phosphine-ligated

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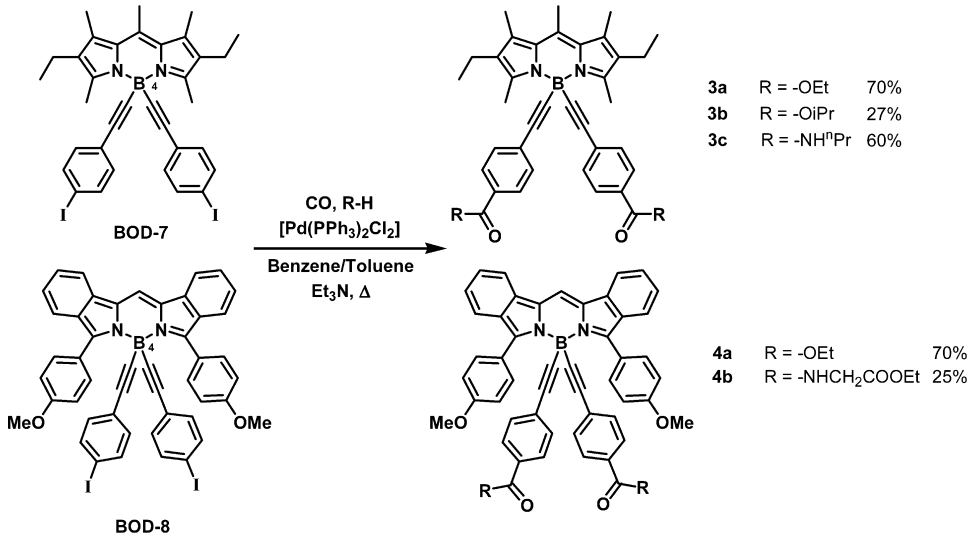
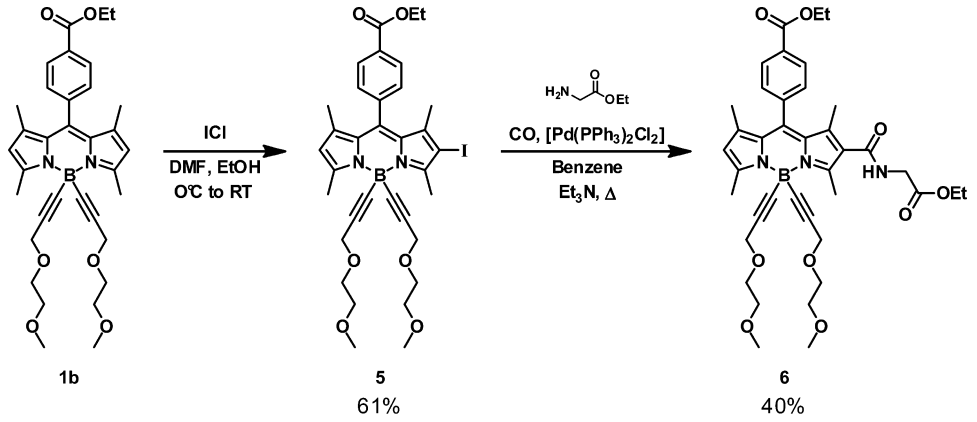
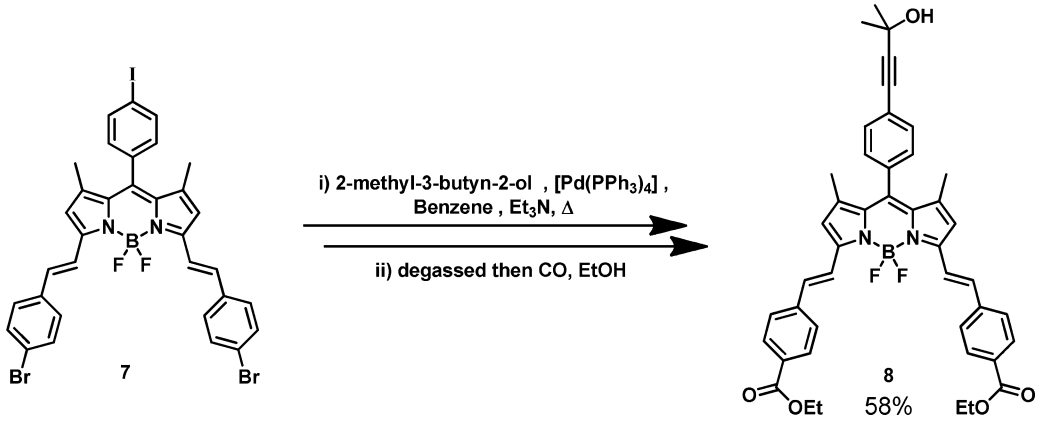
Scheme 3. Synthesis of Boron-Substituted BODIPY Derivatives



Scheme 4. Synthesis of Boron-Substituted BODIPY Derivatives



Scheme 5. One-Pot Synthesis of a Trifunctional BODIPY Dye



palladium complexes, a trialkylamine as base, and a moderate pressure of CO favors the formation of α-keto amide derivatives.[15] In our case, we observed this double CO insertion even at atmospheric pressure, as depicted in Scheme 6, affording compound **9** in 23% yield.

To illustrate the utility of our methodology for the attachment of a luminescent tag, we first saponified compound **1b** by a standard procedure under basic conditions. The corresponding benzoic acid **10** was obtained in good yields without any side reaction. This acid was used in a peptidic coupling with ethylglycine ester in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and dimethylaminopyridine (DMAP) in dichloromethane to give compound **1j** in fair yield, demonstrating the insensitivity of the synthesis to strongly basic conditions. A supplementary, efficient saponification step affording the glycine acid **11** confirmed the high

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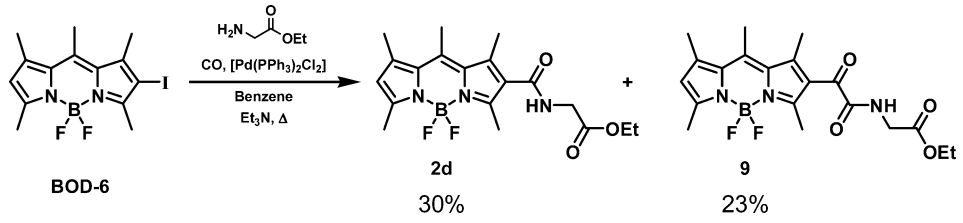
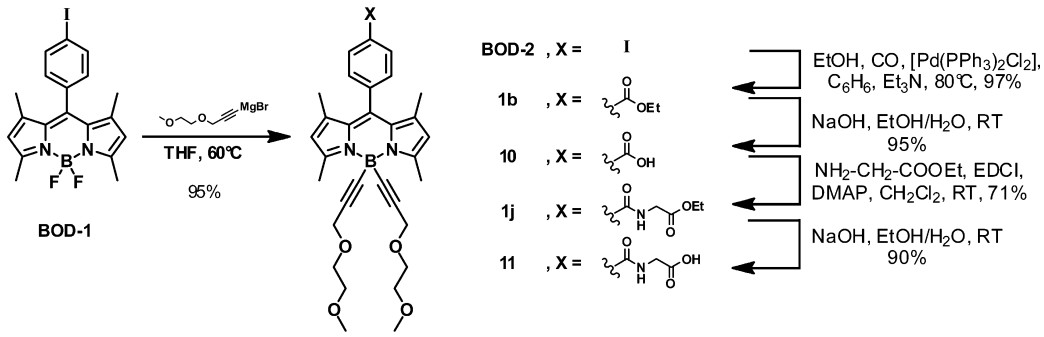
Scheme 6. Synthesis of 2-Substituted BODIPY Derivatives



Scheme 7. Synthesis of Boron-Substituted Dyes and Use in the Schotten–Bauman Reaction



chemical stability. Such improved stability has been previously observed during deprotection of TMS groups of *E*-BODIPY.[3a]

X-RAY STRUCTURE DETERMINATIONS

Single-crystal X-ray diffraction measurements provided the molecular structures of compound **1f** and **2d**, confirming the identity expected on the basis of their synthesis.

Compound **1f** crystallizes in the centrosymmetric triclinic space group, *P*-1, whereas crystals of **2d** belong to the monoclinic space group, *C*2/*c*. Both molecules display an overall approximate planar shape with a meso extension of the BODIPY core for **1f** and a β asymmetric elongation for **2d**. In **1f**, the BODIPY core with C atom substituents in meso, α, and β positions is quasiplanar with a maximum deviation from planarity of 0.121(8) Å observed for the boron atom compared to the mean deviation of 0.029 Å from the mean plane of the other 19 atoms (Figure 1). For **2d**, the boron atom lies within the mean plane of the 12 atoms of the BODIPY core (mean deviation 0.042 Å), whereas the methyl substituents are significantly displaced from this mean plane, with a maximum displacement of 0.186(8) Å for C12 (Figure 2). In both **1f** and **2d**, the boron atom adopts a distorted tetrahedral environment and bond lengths and angles around it are typical of *F*-BODIPY analogues. F1–B1, F2–B1, N1–B1, and N2–B1 are, respectively, 1.349(10), 1.379(9), 1.541(11), and 1.567(10) Å and F1 B1 F2, F1 B1 N1, F1 B1 N2, F2 B1 N1, and N1 B1 N2 are 110.2(7), 112.3(6), 110.4(6), 109.3(6), 108.5(6), and 106.0(6)°, respectively, for **1f**, and 1.392(6), 1.391(6), 1.528(6), and 1.536(6) Å and 108.1(4), 109.9(4), 110.7(4), 110.6(4), 110.2(4) and 107.4(4)° for **2d**. The pronounced double bond character known for F-BODIPY analogues is conserved for N1–C1 and N2–C5 (1.356(10) and 1.333(10) Å for **1f** and 1.357(6) and 1.350(6) Å for **2d**, respectively) in contrast with N1–C4 and N2–C8 bond values (1.383(9) and 1.402(9) Å for **1f**, and 1.403(6) and 1.396(6) Å for **2d**, respectively). For **1f**, the ethyl groups in the β position adopt an anti conformation. The *meso*-phenyl group, constrained by the methyl β substituents on both sides, stands almost orthogonal to the diisoindolemethene fragment with a dihedral

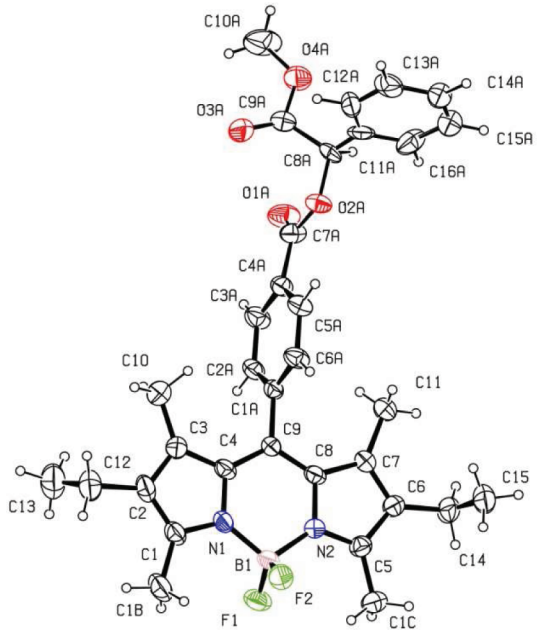


Figure 1. ORTEP view of compound **1f**. Displacement ellipsoids are drawn at the 30% probability level. For clarity the major conformer of the acetoxyphenylacetate moiety is shown.

angle of 78.6°. At the extremity of the meso substituent, the phenylacetate group is approximately orthogonal to both previous rings with dihedral angles of 87.6° and of 69.2°, respectively. Inside the crystal, the meso-extended molecules are organized around centers of inversion between boron centers in molecular tapes parallel to (3 1 8) and running in the [3−1−1] direction (Figure 3). The interplanar distance is ca. 3.9 Å, indicative of edge-to-face interactions with an adjacent molecule in the *a* direction (e.g., between C3A (phenyl)−H3A and one pyrrole ring of the BODIPY core (H···*Cg* (π-ring) of 2.81 Å and angle of 152°) and between a C10-methyl hydrogen atom and the phenyl acetate ring (H···*Cg* (π-ring) of 2.95 Å and angle of 113°)) rather than π–π interactions between

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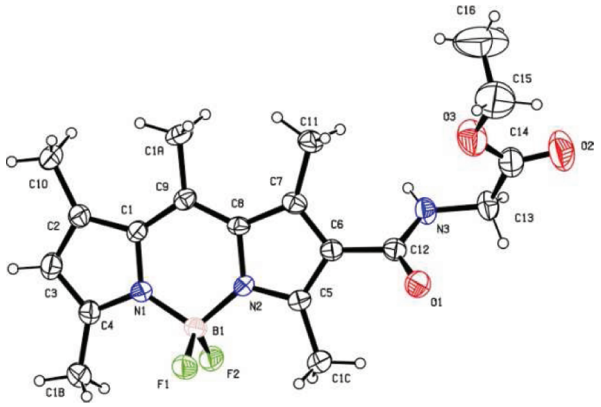

Figure 2. ORTEP view of compound **2d**. Displacement ellipsoids are drawn at the 30% probability level. For clarity the disordered methyl H atoms are not shown.

offset inversion related BODIPY cores. B1−F1···Cg (π-pyrrole) interactions between these two cores (distance of 3.168(6) Å and angle of 132.8(5)°) appear to be more significant. Regarding the molecular arrangement of **2d** within the crystal, the amide atom N3 in the molecule at (x, y, z) acts as hydrogen-bond donor to the carbonyl atom O1 in the molecule at (x, 1 − y, 1/2 + z), so forming a C(4) chain[16] running parallel to the [001] direction and containing molecules related by the c-glide plane at a = 1/4 (Figure 4). The molecules are all lying in planes parallel to (2 0 1) with average interplanar distance of 3.88 Å but with nonoptimized overlap of BODIPY cores in infinite stacks along the aforementioned direction.

OPTICAL PROPERTIES

In order to determine the influence of such functionalization, we carried out a full study of both the electronic absorption and emission spectra.

All compounds exhibited the absorptions typical of BODIPY dyes: from 350 to 400 nm, a broad weak absorption band attributed to the S_0-S_2 transition, and an intense low energy band in the 495−650 nm region attributed to the S_0-S_1 excitation. All extinction coefficients lie in the range 40000 to 134000 $M^{-1}\cdot cm^{-1}$ (depending on the chemical structure) for the S_0-S_1 transition.

To show the influence of the displacement of the halogeno group by an ester or amide function, we present the absorption spectra of three families of dyes in Figure 5. In the series with substituents at the 8-position, no significant modification of absorption properties is observed (Figure 5a). The same observation applies for compounds with carboxyl groups nonconjugated to the dye core (Figure 5c). Substitution of the iodine on the 2-position (BOD-6), does induce a hypsochromic shift (Figure 5b), due to the removal of the heavy atom. The values observed for **2a−d** and **6**, are close to those of 1,3,5,7-tetramethyl-BODIPY-based dyes (i.e., **1b**, **1j**), which confirms the weak influence of ester or amide groups on the absorption properties.

In the case of compounds **1c−e** (Figure 7 and Supporting Information),[2b] in the UV region, the well-defined vibronic structure, unambiguously assigned to $\pi-\pi^*$ transitions in the pyrene subunit, was not affected by the carbonylation.

All compounds showed the usual BODIPY S_1-S_0 transition in emission, as can be observed in Figure 6 and Table 1, and the carbonylation had negligible effects on the emission wavelengths and quantum yields. The quantum yields were in the range 70−95% for all compounds except those bearing an amino moiety (**1g** and **1h** 38−40%) or an iodo substituent (**5**: 4%) which are known for generating photoinduced charge transfer or facilitating intersystem crossing, respectively.[13,18] The introduction of a carbonyl group has negligible influence on the efficiency of the fluorescence. The mirror image symmetry observed between the lowest energy absorption band and the emission and the short lifetimes (range 4.3−13.8 ns) are in agreement with a singlet excited state. In the case of compounds **1c−e**, an excitation in the pyrene subunit absorption band at 380 nm led to exclusive emission from the BODIPY subunit (Figure 7), demonstrating an almost quantitative energy transfer, as previously described for similar cassette systems.[2b] Confirmation of the electronic energy transfer (EET) was obtained by running an excitation spectrum. The good match between the absorption and the excitation spectra are in favor of this very efficient EET process.

CONCLUSION

We have succeeded in introducing carboxyl derivatives such as ester or amide groups by way of a carbopalladation on various substitution positions of BODIPY dyes. These insertions proceed smoothly using carbon monoxide at atmospheric pressure. By this methodology we are now able to functionalize BODIPY dyes with carboxylic functions, potentially allowing grafting to biomolecules via Schotten−Bauman coupling with the pendent amines of proteins. Furthermore, *E*-BODIPY dyes formed by fluorine substitution using Grignard reagents can now be functionalized easily by carboxyl groups, opening the way to new functional BODIPY dyes bearing water solubilizing groups or high energy antenna on the boron center. The absence of noticeable side reactions (except for double CO insertion in the glycine ester case) and the modest perturbation

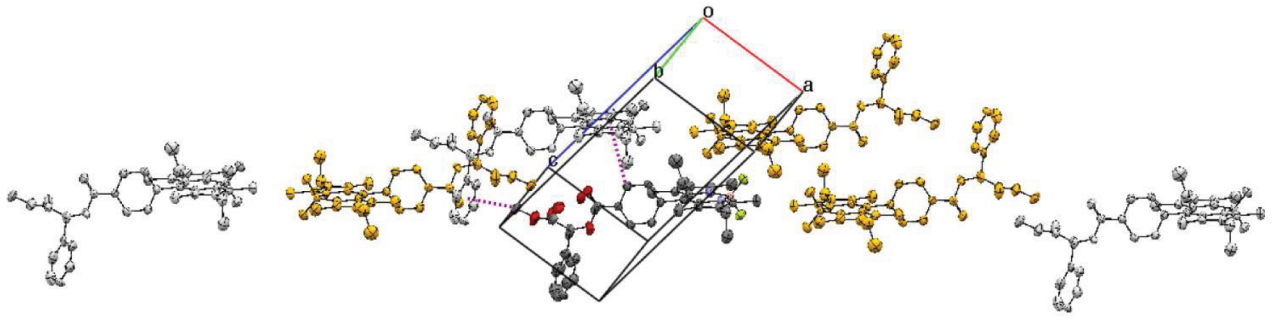

Figure 3. View of molecular packing for **1f**. In gold, molecules related by a center of inversion. Magenta dotted lines indicate X−H···Cg(π-ring).

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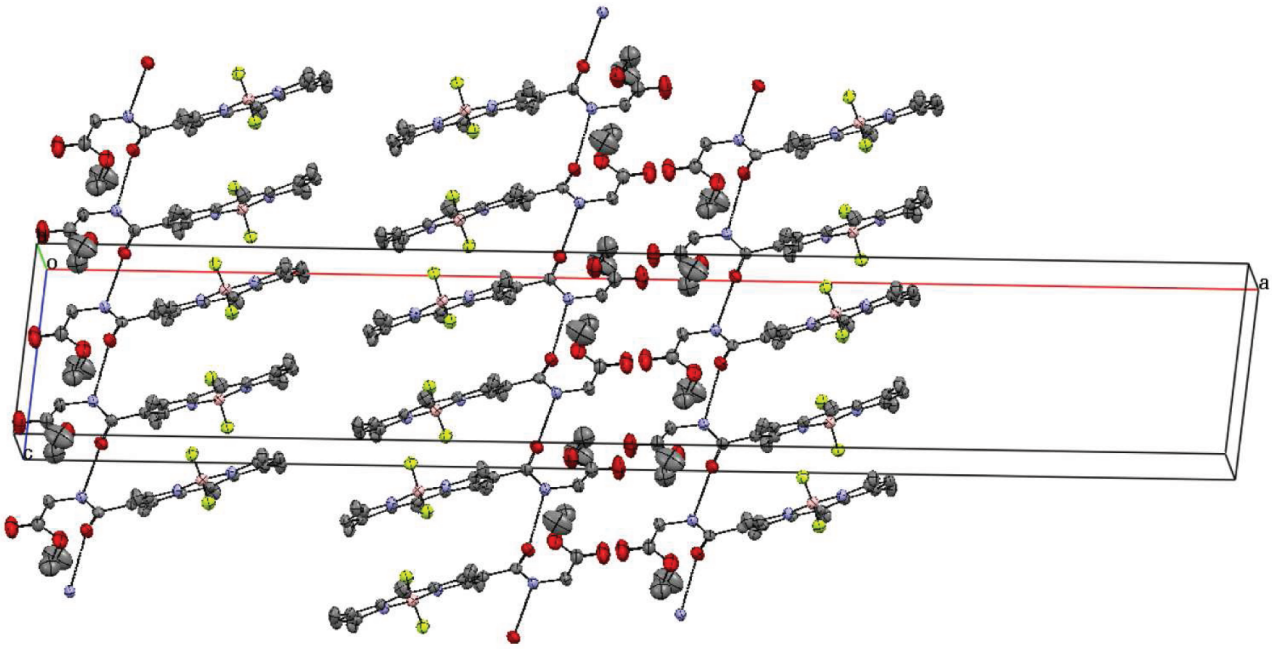

Figure 4. View of molecular packing for **2d** down the *b* axis. Black dotted lines indicate the hydrogen bond chain between N3 and O1.

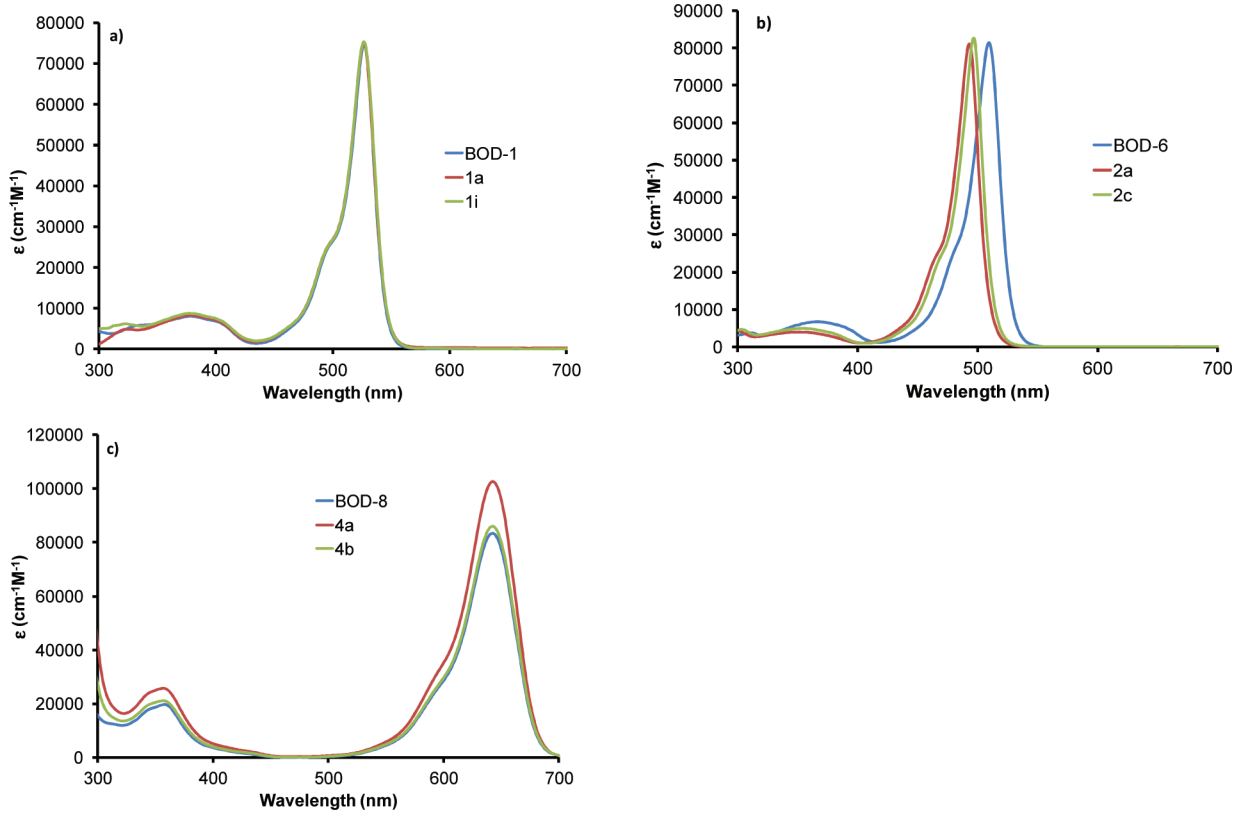

Figure 5. (a) Absorption spectra of **BOD-1**, **1a**, and **1i** in CH_2Cl_2, at rt. (b) Absorption spectra of **BOD-6**, **2a**, and **2b** in CH_2Cl_2, at rt. (c) Absorption spectra of **BOD-8**, **4a**, and **4b** in CH_2Cl_2, at rt.

of the spectroscopic properties make this methodology useful for many applications in the optoelectronic and biomedical domains.

EXPERIMENTAL SECTION

General Methods. ^1H and ^{13}C spectra were recorded at room temperature on 200, 300, or 400 MHz spectrometers using perdeuterated solvents as internal standards. Chemical shifts of ^1H and ^{13}C spectra are given in ppm relative to residual protiated solvent or relative to the solvent, respectively. ^{11}B spectra were recorded at room temperature at 400 MHz spectrometer using $BF_3{\cdot}Et_2O$ chemical shift as reference. FT-IR spectra were recorded on thin solid layers using an apparatus equipped with ATR "diamond" apparatus. Steady-state emission and excitation spectra were recorded on a

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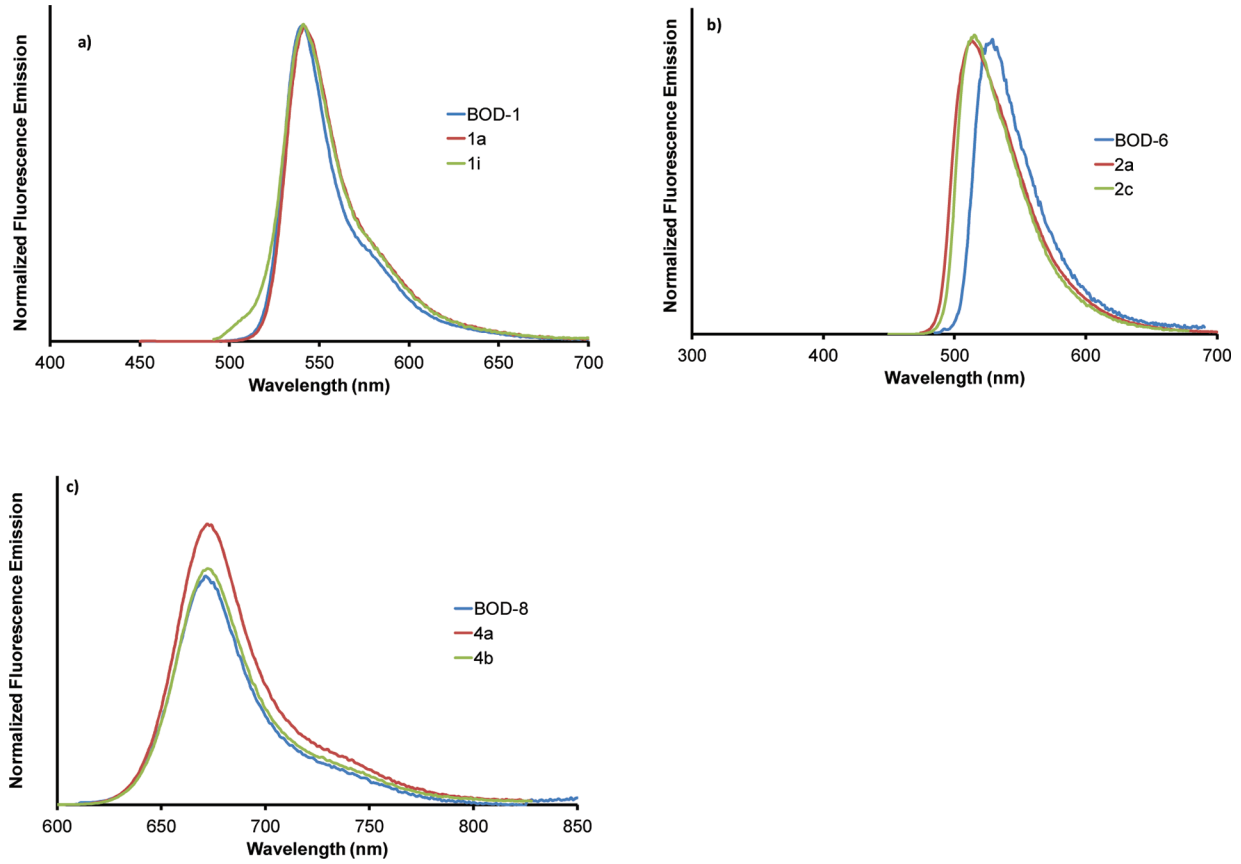

Figure 6. (a) Emission spectra of **BOD-1**, **1a**, and **1j** in CH_2Cl_2, at rt. (b) Emission spectra of **BOD-6**, **2a**, and **2b** in CH_2Cl_2, at rt. (c) Emission spectra of **BOD-8**, **4a**, and **4b** in CH_2Cl_2, at rt.

spectrofluorimeter. All fluorescence spectra were corrected. The fluorescence quantum yield (Φ_{cmp}) was calculated from eq 1:

$$\Phi_{cmp} = \Phi_{ref}\frac{I}{I_{ref}}\frac{OD_{ref}}{OD}\frac{n^2}{n_{ref}^2} \quad (1)$$

Here, I denotes the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength, and η is the refractive index of the medium. The reference system used were rhodamine 6G (Φ_{em} = 0.78 in H_2O) and cresyl violet (Φ_{em} = 0.53 in CH_3OH).[18] Luminescence lifetimes were measured on a spectrofluorimeter equipped with a R928 photomultiplier and a pulsed diode connected to a delay generator. No filter was used for the excitation. Emission wavelengths were selected by a monochromator. Lifetimes were deconvoluted with adequate software using a light-scattering solution (LUDOX) for instrument response.

Reagents. Chromatographic purification was conducted using standard silica gel 60 (0.063−0.200 mm) or deactivated aluminum oxide (Act. III). Thin-layer chromatography (TLC) was performed on silica gel plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio. Anhydrous solvents were obtained by distillation: anhydrous CH_2Cl_2 over P_2O_5, anhydrous THF over sodium benzophenone, anhydrous toluene over sodium, and DMF under reduced pressure over aluminum oxide. Benzene, Et_3N, $MgSO_4$, KOH, methanol, ethanol, 1-propanol, THF, diisopropylamine, tributylamine, ethyl acetate, NaCl, petroleum ether, cyclohexane, ICl, NaOH, propargyl alcohol, K_2CO_3, Na_2SO_4, $NaHCO_3$, ethyl magnesiumbromide, ethylenediamine, glycine ethyl ester hydrochloride, 2-propanol, methyl-D,L-mandelate, EDCI. and propylamine were purchased from commercial sources and used without further purification. $[Pd(PPh_3)_2Cl_2]$,[19] 1-ethynyl-4-iodobenzene,[3b] 1-ethynylpyrene,[20] 3-(2-methoxyethoxy)prop-1-yne,[21] 2,6-diethyl-4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene,[22] 4,4-difluoro-3,5-di(4-methoxystyryl)-1,7-dimethyl-8-(*p*-iodophenyl)-4-bora-3a,4a-diaza-*s*-indacene,[23] 4,4-difluoro-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene,[10] 2,6-diethyl-4,4-difluoro-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (**BOD-1**),[10] 2,6-diethyl-4,4-di(1-pyrenylethynyl)-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (**BOD-4**),[12] 4,4-difluoro-2-iodo-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene (**BOD-6**),[13] **BOD-8**,[12] and compound **7**[24] were obtained according to the respective references.

General Procedure for Carboalkoxylation/Amidation. In a 25 mL two-neck flask equipped with a reflux condenser, a gas bubbler, and a magnetic stirring bar $[Pd(PPh_3)_2Cl_2]$ (20 mol %) was added to a solution of the two derivatives in a mixture of benzene/triethylamine (3/1). The reaction mixture was degassed under a continuous flow of CO at atmospheric pressure and stirred along with heating. After being cooled to room temperature, the mixture was extracted with CH_2Cl_2 and washed with water three times. The organic phase was dried over $MgSO_4$ or Celite, and the solvent was evaporated under reduced pressure. The resulting crude residue was purified by column chromatography.

4,4-Bis(3-(2-methoxyethoxy)prop-1-ynyl)-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (BOD-2). In a Schlenk flask, ethylmagnesium bromide (3.10 mL, 3.10 mmol) was added to a stirred solution of 3-(2-methoxyethoxy)prop-1-yne (426 μL, 3.56 mmol) in anhydrous THF (5 mL). The mixture was stirred at 60 °C for 2 h. The resulting anion solution was added via cannula to a solution of 4,4-difluoro-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (400 mg, 0.89 mmol) in anhydrous THF. The solution was stirred at 60 °C overnight. Water was added, and the solution was extracted with AcOEt. The organic phase was washed with water (2×) and dried over $MgSO_4$. After evaporation, the residue was dissolved in AcOEt/petroleum ether (40:60) and the desired compound precipitated. The solid was washed with petroleum ether and pentane to give the titled compound (540 mg, 95%) as a shiny

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Table 1. Selected Optical Data[a]

compd	λ_{abs} (nm)	$\varepsilon_{\lambda max}$ ($M^{-1}\cdot cm^{-1}$)	λ_{em} (nm)	τ (ns)	Φ_F[c]	k_R ($10^7 s^{-1}$)[d]	k_{NR} ($10^7 s^{-1}$)[d]
1a	527	74900	542	5.7	0.57	9.93	7.49
1f	528	71900	544	6.3	0.58	9.21	6.67
1g	527	41800	542	5.1	0.39	7.68	12.01
1i	527	75400	542	6.6	0.7	10.6	4.55
1b	500	89900	510	6.7	0.6	8.97	5.98
1h	500	60000	513	5.9	0.35	5.97	11.09
1j	501	84200	511	5.9	0.7	11.93	5.11
10	501	78500	512	4.8	0.5	10.53	10.53
10[a]	494	74000	207	3.5	0.55	15.7	12.9
11	501	71500	511	5.7	0.60	10.5	7.0
11[a]	495	62000	507	4.4	0.55	12.5	10.2
1c[b]	653	134000	665	5.8	0.90	14.71	2.60
	370	129700	665		0.90		
1d	523	90500	537	7.1	0.95	13.4	0.7
	370	116500	537		0.95		
1e	502	77700	514	5.1	0.53	7.78	11.67
	370	95300	513		0.52		
2a	493	81100	510	7.9	0.95	12.03	0.63
2b	494	76600	513	5.9	0.87	14.85	2.22
2c	498	82600	515	6.6	0.85	12.96	2.29
2d	496	85500	513	5.4	0.95	17.6	0.92
5	514	89300	527	0.2	0.04	17.39	417.39
6	502	69800	514	4.5	0.65	14.38	7.74
BOD-7	516	83300	532	10.0	0.95	9.44	0.50
3a	516	87200	533	9.9	0.9	9.12	1.01
3b	516	78800	533	10.5	0.86	8.16	1.33
3c	516	76200	534	8.6	0.8	9.27	2.32
4a	642	102500	672	13.8	0.86	6.23	1.01
4b	642	86000	672	7.9	0.82	10.33	2.27
8	636	111300	645	4.3	0.73	17.10	6.32
9	640	122100	651	4.8	0.7	14.55	6.24

[a]Data measured in CH_2Cl_2 at rt except: (a) PBS buffer (pH 7.2); (b) toluene; (c) quantum yield determined in dilute solution (1×10^{-6} M) using rhodamine 6G (Φ_F = 0.78 in water, λ_{exc} = 488 nm), or cresyl violet as reference (Φ_F = 0.51 in EtOH, λ_{exc} = 578 nm).[17] All ϕ_F are corrected for changes in refractive index. k_r and k_{nr} were calculated using the following equations: $k_r = \Phi_F/\tau$, $k_{nr} = (1 - \Phi_F)/\tau$.

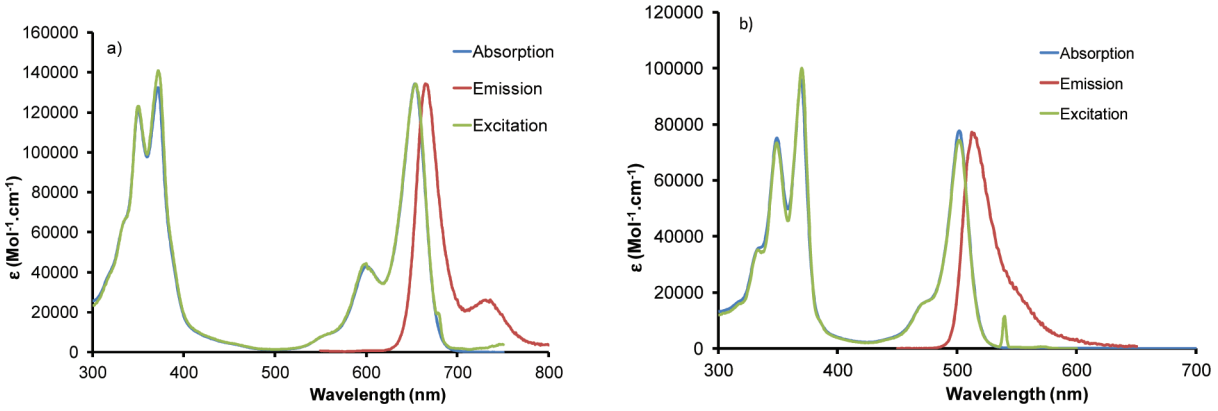

Figure 7. (a) Absorption, emission, and excitation spectra of **1c** in CH_2Cl_2, at rt. (b) Absorption, emission, and excitation spectra of **1e** in CH_2Cl_2, at rt.

orange powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.94 (t, 3H, ^3J = 7.55 Hz), 1.26 (s, 6H), 2.29 (q, 4H, ^3J = 7.55 Hz), 2.65 (s, 6H), 3.31 (s, 6H), 3.50 (m, 4H), 3.61 (m, 4H), 4.15 (s, 4H), 7.40 (AB sys, 4H, J_{AB} = 8.55 Hz, $\nu_o\delta$ = 226.46 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 12.2, 14.1, 14.8, 17.4, 59.1, 59.8, 68.6, 71.9, 90.7, 94.4, 128.8, 130.7, 133.1, 136.1, 136.1, 138.2, 138.5, 154.0; UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 500 (90600), 470 (sh, 19300), 370 (4900), 326 (5000); EI-MS m/z 638.2 (100). Anal. Calcd for $C_{31}H_{36}BIN_2O_4$: C, 58.33; H, 5.68; N, 4.39. Found: C, 58.12; H, 5.41; N, 4.19.

3,5-Bis(4-methoxystyryl)-1,7-dimethyl-4,4-di(1-pyreneethynyl-)-8-(*p*-iodophenyl)-4-bora-3a,4a-diaza-*s*-indacene (BOD-3). In a Schlenk flask, ethylmagnesium bromide (386 μL, 0.386 mmol) was added to a stirred solution of 1-ethynylpyrene (98 mg, 0.43 mmol) in anhydrous THF. The mixture was stirred at 60 °C for 2 h. The resulting anion solution was added via cannula to a solution of 4,4-difluoro-3,5-di(4-methoxystyryl)-1,7-dimethyl-8-(*p*-iodophenyl)-4-bora-3a,4a-diaza-*s*-indacene (100 mg, 0.15 mmol) in anhydrous THF. The solution was stirred at 60 °C overnight. Water was added, and the

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solution was extracted with AcOEt and washed with water (2 × 20 mL). After evaporation, the organic layer was purified by column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (50:50) to give the pure titled compound (93 mg, 57% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.58 (s, 6H), 3.59 (s, 6H), 6.86 (s, 2H), 7.19 (AB sys, 8H, J_{AB} = 8.8 Hz, $\nu_o\delta$ = 308.0 Hz), 7.30 (AB sys, 4H, J_{AB} = 8.9 Hz, $\nu_o\delta$ = 44.5 Hz), 7.44 (d, 2H, ^3J = 16.2 Hz), 7.87−8.10 (m, 16H), 8.72 (d, 2H, ^3J = 9.1 Hz), 8.86 (d, 2H, ^3J = 16.2 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 15.4, 55.3, 94.7, 96.1, 114.5, 118.5, 119.6, 120.4, 124.4, 124.5, 124.5, 125.0, 125.1, 125.9, 126.5, 127.4, 127.5, 127.9, 129.2, 129.8, 130.2, 131.0, 131.3, 131.4, 131.8, 132.0, 134.8, 135.6, 137.1, 138.3, 140.4, 152.8, 160.4; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −8.51 (s); EI-MS m/z 1098.2 (100). Anal. Calcd for $C_{71}H_{48}BIN_2O_2$: C, 77.60; H, 4.40; N, 2.55. Found: C, 77.19; H, 4.52; N, 2.17.

4,4-Bis(1-pyrene-ethynyl)-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (BOD-5). In a Schlenk flask, ethylmagnesium bromide (1.96 mL, 1.96 mmol) was added to a stirred solution of 1-ethynylpyrene (480 mg, 2.12 mmol) in anhydrous THF (8 mL). The mixture was stirred at 60 °C for 2 h. The resulting anion solution was then added via cannula to a solution of **4,4-difluoro-8-(*p*-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene** (350 mg, 0.79 mmol) in anhydrous THF (10 mL). The solution was stirred at 60 °C for 1 h. Water was added, and the solution was extracted with CH_2Cl_2. After evaporation, the organic layer was purified by column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (gradient from 10:90 to 100:0). Recrystallization by evaporation from CH_2Cl_2/cyclohexane gave 600 mg of **BOD-5** (89% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.52 (s, 6H), 3.17 (s, 6H), 6.20 (s, 2H), 7.54 (AB sys, 4H, J_{AB} = 8.2 Hz, $\nu_o\delta$ = 135.8 Hz), 7.99−8.18 (m, 16H), 8.79 (d, 2H, ^3J = 9.1 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 15.2, 16.8, 82.7, 94.7, 120.4, 122.1, 124.5, 124.5, 124.6, 124.7, 125.3, 125.4, 125.8, 125.9, 126.2, 126.3, 126.4, 127.3, 127.5, 127.7, 128.1, 128.5, 128.7, 129.8, 130.3, 130.5, 130.6, 131.3, 131.5, 132.2, 135.4, 138.4, 141.3, 156.1; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −8.89 (s); EI-MS m/z 862.1 (100), 456.7 (25). Anal. Calcd for $C_{55}H_{36}BIN_2$: C, 76.58; H, 4.21; N, 3.25. Found: C, 76.49; H, 3.90; N, 2.92.

2,6-Diethyl-4,4-di(4-iodophenyl-1-ethynyl-)-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene (BOD-7). In a Schlenk flask, ethylmagnesium bromide (2.55 mL, 2.55 mmol) was added to a stirred solution of 1-ethynyl-4-iodobenzene (645 mg, 2.83 mmol) in anhydrous THF (10 mL). The mixture was stirred at 60 °C for 2 h. The resulting anion solution was added via cannula to a solution of 2,6-diethyl-4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene (300 mg, 0.94 mmol) in anhydrous THF. The solution was stirred at 60 °C overnight. Water was added, and the solution was extracted with Et_2O. The organic phase was washed with water (2×) and dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (gradient from 0:100 to 10:90). Recrystallization from CH_2Cl_2/cyclohexane gave 570 mg of the titled compound (82% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.08 (t, 6H, ^3J = 7.5 Hz), 2.37 (s, 6H), 2.46 (q, 4H, ^3J = 7.5 Hz), 2.64 (s, 3H), 2.78 (s, 6H), 7.31 (AB sys, 8H, J_{AB} = 8.6 Hz, $\nu_o\delta$ = 137.1 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.0, 14.8, 15.2, 17.4, 17.6, 92.5, 125.1, 130.3, 132.8, 133.3, 134.8, 137.2, 139.9, 152.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −9.82 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 516 (83300), 488 (sh, 22600), 370 (6600), 265 (62100). IR (ATR, cm^{-1}) 3043, 2962, 2926, 2868, 2721, 2172, 2032, 1896, 1552, 1478, 1386, 1359, 1322, 1262, 1221, 1182, 1122, 1091, 1030, 1003, 975, 935, 817, 758, 715; EI-MS m/z 734.1 (100). Anal. Calcd for $C_{34}H_{33}BI_2N_2$: C, 55.62; H, 4.53; N, 3.82. Found: C, 55.49; H, 4.31; N, 3.69.

Compound 1a. Prepared according to the general procedure from **BOD-1** (30 mg, 0.06 mmol), 2-propanol (1 mL), [Pd(PPh$_3$)$_2$Cl$_2$] (12 mg, 0.017 mmol), toluene (6 mL), and tributylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (40:60) gave **1a** (23 mg, 83%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.98 (t, 6H, ^3J = 7.5 Hz), 1.27 (s, 6H), 1.42 (d, 6H, ^3J = 6.2 Hz), 2.30 (q, 4H, ^3J = 7.5 Hz) 2.53 (s, 6H), 5.30 (sep, 1H, ^3J = 6.3 Hz), 7.77 (AB sys, 4H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 230.5 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 12.0, 12.7, 14.7, 17.2, 22.1, 69.1, 128.7, 130.3, 130.5, 131.5, 133.2, 138.3, 139.0, 140.6, 154.4, 165.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.87 (t, J_{B-F} = 32.7 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 527 (74900), 500 (sh, 26800), 379 (8300); IR (ATR, cm^{-1}) 2964, 2930, 2871, 2730, 1713, 1609, 1538, 1472, 1363, 1319, 1274, 1187, 1105, 1075, 974, 854, 736; EI-MS m/z 466.1 (100), 447.1 (30). Anal. Calcd for $C_{27}H_{33}BF_2N_2O_2$: C, 69.53; H, 7.13; N, 6.01. Found: C, 69.28; H, 6.97; N, 5.91.

Compound 1b. Prepared according to the general procedure from **BOD-2** (235 mg, 0.37 mmol), ethanol (1 mL), [Pd(PPh$_3$)$_2$Cl$_2$] (44 mg, 0.07 mmol), benzene (15 mL) and triethylamine (5 mL); stirred overnight; column chromatography on silica gel eluting with AcOEt/petroleum ether (40:60) gave **1b** (210 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.33 (s, 6H), 1.42 (t, 3H, ^3J = 7.0 Hz), 2.71 (s, 6H), 3.35 (s, 6H), 3.53 (m, 4H), 3.64 (m, 4H), 4.19 (s, 4H), 4.40 (q, 2H, ^3J = 7.0 Hz), 6.00 (s, 2H), 7.78 (AB sys, 4H, J_{AB} = 8.5 Hz, $\nu_o\delta$ = 300.4 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.4, 14.8, 16.1, 59.0, 59.7, 61.4, 68.4, 68.6, 71.8, 90.9, 121.8, 128.6, 129.1, 130.3, 131.0, 140.3, 140.3, 140.9, 155.6, 166.1; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −10.2 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 500 (90000), 479 (sh, 20600), 366 (4900), 308 (7700); IR (ATR, cm^{-1}) 3060, 2979, 2881, 2839, 2158, 1717, 1608, 1544, 1503, 1467, 1404, 1347, 1305, 1271, 1178, 1149, 1076, 977, 856, 734, 692; EI-MS m/z 585.2 (100), 539.3 (45). Anal. Calcd for $C_{34}H_{41}BN_2O_6$: C, 69.86; H, 7.07; N, 4.79. Found: C, 69.77; H, 7.04; N, 4.59.

Compound 1c. Prepared according to the general procedure from **BOD-3** (50 mg, 0.045 mmol), ethanol (1 mL), [Pd(PPh$_3$)$_2$Cl$_2$] (6 mg, 0.01 mmol), benzene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (60:40) gave **1c** (36 mg, 76%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.46 (t, 3H, ^3J = 7.2 Hz), 1.54 (s, 6H), 3.60 (s, 6H), 4.46 (q, 2H, ^3J = 7.2 Hz), 6.86 (s, 2H), 7.19 (AB sys, 8H, J_{AB} = 8.9 Hz, $\nu_o\delta$ = 307.0 Hz), 7.37 (d, 2H, ^3J = 9.0 Hz), 7.45 (d, 2H, ^3J = 16.2 Hz), 7.92 (AB sys, 4H, J_{AB} = 8.4 Hz, $\nu_o\delta$ = 193.5 Hz), 7.90−8.11 (m, 14H), 8.72 (d, 2H, ^3J = 9.0 Hz), 8.86 (d, 2H, ^3J = 16.2 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.5, 15.3, 55.3, 61.5, 114.5, 118.5, 119.6, 120.4, 124.4, 124.5, 124.6, 126.0, 126.5, 127.4, 127.5, 127.6, 127.9, 128.3, 129.3, 129.4, 129.8, 130.3, 130.4, 130.5, 131.1, 131.3, 131.4, 131.6, 132.1, 134.8, 137.3, 140.4, 140.8, 152.9, 160.4, 166.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −8.44 (s); UV−vis (toluene) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 654 (134200), 602 (sh, 42700), 372 (132500), 351 (120600), 285 (103200); IR (ATR, cm^{-1}) 3047, 2994, 2959, 2921, 2847, 2115, 1710, 1595, 1538, 1509, 1480, 1367, 1271, 1256, 1194, 1156, 1081, 986, 957, 846, 821, 737, 719, 682; EI-MS m/z 1044.3 (100), 983.2 (10). Anal. Calcd for $C_{74}H_{53}BN_2O_4$: C, 85.05; H, 5.11; N, 2.68. Found: C, 84.72; H, 4.88; N, 2.52.

Compound 1d. Prepared according to the general procedure from **BOD-4** (100 mg, 0.11 mmol), ethanol (1 mL), [Pd(PPh$_3$)$_2$Cl$_2$] (17 mg, 0.02 mmol), benzene (9 mL), and triethylamine (3 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (35:65) gave **1d** (88 mg, 93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.11 (t, 6H, ^3J = 7.7 Hz), 1.39 (s, 6H), 1.47 (t, 3H, ^3J = 7.1 Hz), 2.46 (q, 4H, ^3J = 7.5 Hz), 3.16 (s, 6H), 4.46 (q, 2H, ^3J = 7.0 Hz), 7.90 (AB sys, 4H, J_{AB} = 8.5 Hz, $\nu_o\delta$ = 195.6 Hz), 7.96−8.18 (m, 16H), 8.79 (d, 2H, ^3J = 9.0 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 12.3, 14.5, 14.7, 15.0, 17.6, 61.5, 94.9, 120.6, 124.6, 124.7, 124.7, 125.3, 126.2, 126.4, 127.5, 127.6, 128.0, 129.1, 129.2, 129.8, 130.3, 130.6, 131.0, 131.4, 131.5, 132.3, 133.6, 136.5, 139.2, 141.5, 154.5, 166.4; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −8.93 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 523 (90500), 495 (sh, 24700), 370 (116500), 349 (91300), 285 (106100); IR (ATR, cm^{-1}) 3038, 2961, 2927, 2870, 2163, 2039, 1723, 1542, 1473, 1400, 1368, 1311, 1272, 1170, 1149, 1110, 1063, 1020, 973, 836, 730, 678; EI-MS m/z 865.1 (100), 000 (30). Anal. Calcd for $C_{62}H_{49}BN_2O_2$: C, 86.10; H, 5.71; N, 3.24. Found: C, 85.79; H, 5.52; N, 3.07.

Compound 1e. Prepared according to the general procedure from **BOD-5** (100 mg, 0.11 mmol), ethanol (1 mL), [Pd(PPh$_3$)$_2$Cl$_2$] (17 mg, 0.02 mmol), benzene (9 mL), and triethylamine (3 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/

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petroleum ether (40:60) gave **1e** (80 mg, 85%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.48 (t, 3H, ^3J = 7.0 Hz), 1.50 (s, 6H), 3.20 (s, 6H), 4.47 (q, 2H, ^3J = 7.2 Hz), 6.23 (s, 2H), 7.92 (AB sys, 4H, J_{AB} = 8.1 Hz, $\nu_o\delta$ = 198.9 Hz), 7.99−8.20 (m, 16H), 8.83 (d, 2H, ^3J = 9.2 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.5, 15.0, 16.8, 61.5, 120.4, 122.2, 124.6, 124.6, 124.7, 125.3, 126.2, 126.3, 127.5, 127.7, 128.1, 128.8, 129.6, 129.8, 130.4, 130.6, 131.2, 131.4, 131.5, 132.3, 140.6, 140.7, 141.3, 156.2, 166.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −8.85 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 502 (77700), 479 (sh, 18000), 369 (96000), 350 (74600), 285 (82200); IR (ATR, cm^{-1}) 3040, 2979, 2933, 1716, 1545, 1508, 1466, 1401, 1361, 1305, 1278, 1180, 1152, 1100, 1021, 977, 838, 747, 729, 679; EI-MS m/z 808.1 (100). Anal. Calcd for $C_{58}H_{41}BN_2O_2$: C, 86.13; H, 5.11; N, 3.46. Found: C, 86.04; H, 5.07; N, 3.29.

Compound 1f. Prepared according to the general procedure from **BOD-1** (50 mg, 0.10 mmol), methyl DL-mandelate (49.3 mg, 0.296 mmol), [$Pd(PPh_3)_2Cl_2$] (14 mg, 0.020 mmol), benzene (5 mL), and triethylamine (1 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (50:50) gave **1f** (30 mg, 57%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.98 (t, 6H, ^3J = 7.5 Hz), 1.26 (s, 6H), 2.30 (q, 4H, ^3J = 7.5 Hz), 2.53 (s, 6H), 3.79 (s, 3H), 6.20 (s, 1H), 7.41−7.46 (m, 5H), 7.59−7.62 (m, 2H), 8.25 (d, 2H, ^3J = 8.5 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 529 (71800), 504 (sh, 24300), 383 (7300), 284 (13100). IR (ATR, cm^{-1}) 2964, 2929, 2870, 1762, 1719, 1607, 1547, 1475, 1404, 1322, 1275, 1255, 1197, 1083, 1038, 973, 735, 694; EI-MS m/z 572.1 (100), 553.1 (15). Anal. Calcd for $C_{33}H_{35}BF_2N_2O_4$: C, 69.24; H, 6.16; N, 4.89. Found: C, 68.99; H, 5.91; N, 4.72.

Compound 1g. Prepared according to the general procedure from **BOD-1** (53 mg, 0.104 mmol), [$Pd(PPh_3)_2Cl_2$] (15 mg, 0.021 mmol), benzene (6 mL), and ethylenediamine (2 mL); NEt_3 was replaced by ethylenediamine; stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/MeOH (90:10) gave **1g** as a red powder (25 mg, 51%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.97 (t, 6H, ^3J = 7.5 Hz), 1.25 (s, 6H), 2.28 (q, 4H, ^3J = 7.5 Hz), 2.53 (s, 6H), 3.07 (br s, 2H), 3.60 (br s, 4H), 7.19 (br s, 1H), 7.67 (AB sys, 4H, J_{AB} = 8.0 Hz, $\nu_o\delta$ = 177.5 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 12.0, 12.7, 14.7, 17.2, 27.1, 128.0, 128.9, 130.6, 133.2, 134.8, 138.2, 139.5, 154.4, 167.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.83 (t, J_{B-F} = 31.9 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 527 (41800), 501 (sh, 16000), 382 (4900); IR (ATR, cm^{-1}) 3291, 2963, 2927, 2869, 1635, 1540, 1474, 1386, 1313, 1274, 1180, 1158, 1058, 970, 854, 732, 701; EI-MS m/z 467.2 (100). Anal. Calcd for $C_{26}H_{33}BF_2N_4O$: C, 66.96; H, 7.13; N, 12.01. Found: C, 66.77; H, 6.89; N, 11.82.

Compound 1h. Prepared according to the general procedure from **BOD-2** (200 mg, 0.31 mmol), ethylenediamine (1 mL), [Pd-(PPh_3)$_2$$Cl_2$] (65 mg, 0.010 mmol), benzene (6 mL), and triethylamine (1 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/ethanol (gradient from 100:0 to 75:25) gave **1h** (160 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.34 (s, 6H), 2.72 (s, 6H), 3.01 (t, 2H, ^3J = 5.7 Hz), 3.36 (s, 6H), 3.55 (m, 6H), 3.64 (m, 4H), 4.20 (s, 4H), 6.01 (s, 2H), 6.98 (t, 1H, ^3J = 5.5 Hz), 7.69 (AB sys, 4H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 162.7 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 15.0, 16.2, 41.3, 42.2, 59.1, 59.8, 68.7, 71.9, 90.6, 121.9, 127.9, 128.8, 129.4, 134.9, 139.1, 140.4, 141.0, 155.7, 167.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −10.3 (s); EI-MS m/z 599.2 (100), 511.2 (35). Anal. Calcd for $C_{34}H_{43}BN_4O_5$: C, 68.23; H, 7.24; N, 9.36. Found: C, 67.84; H, 7.07; N, 9.22.

Compound 1i. Prepared according to the general procedure from **BOD-1** (30 mg, 0.06 mmol), glycine ethyl ester hydrochloride (25 mg, 0.18 mmol), [$Pd(PPh_3)_2Cl_2$] (12 mg, 0.017 mmol), benzene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with AcOEt/petroleum ether (30:70) gave**1i** (8 mg, 25%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.98 (t, 6H, ^3J = 7.7 Hz), 1.26 (s, 6H), 1.34 (t, 3H, ^3J = 7.2 Hz), 2.30 (q, 4H, ^3J = 7.5 Hz), 2.53 (s, 6H), 4.28 (d, 2H, ^3J = 4.9 Hz), 4.29 (q, 2H, ^3J = 7.2 Hz), 6.75 (t, 1H, ^3J = 4.7 Hz), 7.68 (AB sys, 4H, J_{AB} = 8.1 Hz, $\nu_o\delta$ = 163.4 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 12.0, 12.7, 14.3, 14.7, 17.2, 42.2, 62.0, 128.0, 129.0, 130.6, 133.2, 134.2, 138.3, 138.8, 139.8, 154.4, 166.7, 170.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.83 (t, J_{B-F} = 32.8 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 527 (75400), 503 (sh, 28300), 381 (8800), 323 (6200); IR (ATR, cm^{-1}) 3275, 2958, 2925, 2868, 2159, 1759, 1634, 1540, 1474, 1373, 1314, 1268, 1179, 1157, 1055, 969, 854, 740, 700; EI-MS m/z 509.2 (100). Anal. Calcd for $C_{28}H_{34}BF_2N_3O_3$: C, 66.02; H, 6.73; N, 8.25. Found: C, 65.89; H, 6.53; N, 7.97.

Compound 1j. Prepared according to the general procedure from **BOD-2** (100 mg, 0.16 mmol), glycine ethyl ester hydrochloride (80 mg, 0.57 mmol), [$Pd(PPh_3)_2Cl_2$] (22 mg, 0.03 mmol), benzene (9 mL), and triethylamine (3 mL); stirred overnight; column chromatography on silica gel eluting with AcOEt/petroleum ether (50:50) gave **1j** (43 mg, 43%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.33 (t, 3H, ^3J = 7.2 Hz), 1.34 (s, 6H), 2.72 (s, 6H), 3.36 (s, 6H), 3.55 (m, 4H), 3.66 (m, 4H), 4.20 (s, 4H), 4.27 (d, 2H, ^3J = 4.5 Hz), 4.29 (q, 2H, ^3J = 7.1 Hz), 6.01 (s, 2H), 6.77 (t, 1H, ^3J = 4.9 Hz), 7.69 (AB sys, 4H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 156.4 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.3, 14.9, 16.2, 42.1, 59.1, 59.8, 61.9, 68.7, 71.9, 91.0, 121.9, 127.9, 129.0, 129.3, 134.2, 139.5, 140.2, 141.0, 155.8, 166.7, 170.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −10.3 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 501 (84200), 476 (sh, 17600), 368 (4100), 309 (6500); IR (ATR, cm^{-1}) 3357, 3274, 2981, 2924, 2850, 2159, 1749, 1662, 1632, 1543, 1509, 1467, 1404, 1352, 1305, 1180, 1152, 1076, 980, 852, 834, 734, 694; EI-MS m/z 641.2 (100), 596.1 (20). Anal. Calcd for $C_{36}H_{44}BN_3O_7$: C, 67.40; H, 6.91; N, 6.55. Found: C, 67.23; H, 6.64; N, 6.18.

Compound 2a. Prepared according to the general procedure from **BOD-6** (30 mg, 0.07 mmol), ethanol (1 mL), [$Pd(PPh_3)_2Cl_2$] (11 mg, 0.015 mmol), benzene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (50:50) gave **2a** (24 mg, 93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.38 (t, 3H, ^3J = 7.1 Hz), 2.45 (s, 3H), 2.55 (s, 3H), 2.66 (s, 3H), 2.69 (s, 3H), 2.75 (s, 3H), 4.32 (q, 2H, ^3J = 7.1 Hz), 6.17 (s, 1H); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.5, 14.7, 14.9, 15.5, 17.5, 17.9, 60.1, 123.5, 131.1, 133.4, 134.0, 141.9, 143.4, 144.1, 154.5, 157.9, 165.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.63 (t, J_{B-F} = 32.4 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 493 (81100), 468 (sh, 25700), 355 (3900); IR (ATR, cm^{-1}) 3108, 2981, 1699, 1562, 1509, 1436, 1409, 1361, 1316, 1255, 1200, 1140, 1098, 1064, 1024, 981, 881, 834, 820, 730; EI-MS m/z 334.1 (100), 315.2 (20). Anal. Calcd for $C_{17}H_{21}BF_2N_2O_2$: C, 61.10; H, 3.33; N, 8.38. Found: C, 61.02; H, 3.26; N, 8.22.

Compound 2b. Prepared according to the general procedure from **BOD-6** (40 mg, 0.1 mmol), 2-propanol (1 mL), [$Pd(PPh_3)_2Cl_2$] (14 mg, 0.02 mmol), and benzene (6 mL); triethylamine was substituted by 25 mg of K_2CO_3 (0.18 mmol); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (gradient from 30:70 to 70:30) gave **2b** (20 mg, 55%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.36 (d, 6H, ^3J = 6.2 Hz), 2.44 (s, 3H), 2.55 (s, 3H), 2.65 (s, 3H), 2.65 (s, 3H), 2.74 (s, 3H), 5.22 (sep, 1H, ^3J = 6.2 Hz), 6.16 (s, 1H); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.7, 14.9, 15.4, 17.5, 17.9, 22.2, 67.6, 123.4, 128.9, 131.1, 134.0, 141.8, 143.4, 144.0, 154.5, 157.7, 164.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.62 (t, J_{B-F} = 32.4 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 494 (76600), 470 (sh, 25000), 355 (3900), 272 (5800); IR (ATR, cm^{-1}) 2977, 2934, 1697, 1556, 1505, 1434, 1407, 1313, 1257, 1201, 1139, 1099, 1059, 981, 923, 803, 726; EI-MS m/z 348.1 (100), 329.2 (30). Anal. Calcd for $C_{18}H_{23}BF_2N_2O_2$: C, 62.09; H, 6.66; N, 8.05. Found: C, 61.78; H, 6.40; N, 7.78.

Compound 2c. Prepared according to the general procedure from **BOD-6** (40 mg, 0.1 mmol), propylamine (1 mL), [$Pd(PPh_3)_2Cl_2$] (14 mg, 0.02 mmol), and benzene (3 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/AcOEt (gradient from 100:0 to 90:10) gave **2c** (30 mg, 84%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.99 (t, 3H, ^3J = 7.5 Hz), 1.62 (m, 2H), 2.41 (s, 3H), 2.48 (s, 3H), 2.53 (s, 3H), 2.56 (s, 3H), 2.60 (s, 3H), 3.39 (dt, 2H, ^3J = 6.7 Hz, ^3J = 6.7 Hz), 5.73 (br s, 1H), 6.12 (s, 1H); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 11.7, 13.4, 14.8, 15.3, 16.9, 17.7, 23.2, 41.6, 122.9, 127.9, 131.0, 133.6, 137.5, 143.0, 143.5, 149.9, 156.9, 165.6; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.65 (t, J_{B-F} = 32.4 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 498 (82600), 472 (sh, 24600), 358 (5000), 305

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(4700); IR (ATR, cm^{-1}) 3291, 2967, 2933, 2877, 2160, 2030, 1624, 1539, 1469, 1407, 1359, 1316, 1204, 1165, 1069, 991, 915, 805, 726, 679; EI-MS *m/z* 347.2 (100), 328.1 (20). Anal. Calcd for $C_{18}H_{24}BF_2N_3O$: C, 62.27; H, 6.97; N, 12.10. Found: C, 62.12; H, 6.88; N, 12.07.

Compound 2d. Prepared according to the general procedure from **BOD-6** (30 mg, 0.07 mmol), glycine ethyl ester hydrochloride (32 mg, 0.21 mmol), $[Pd(PPh_3)_2Cl_2]$ (11 mg, 0.015 mmol), benzene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2 gave **2d** (10 mg, 30%): ^1H NMR (200 MHz, $CDCl_3$) δ = 1.31 (t, 3H, ^3J = 7 Hz), 2.43 (s, 3H), 2.53 (s, 6H), 2.61 (s, 3H), 2.65 (s, 3H), 4.21 (d, 2H, ^3J = 5.1 Hz), 4.25 (q, 2H, ^3J = 7.0 Hz), 6.14 (s, 1H); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 13.4, 14.3, 14.8, 15.3, 17.1, 17.8, 41.7, 61.8, 123.1, 131.1, 137.8, 143.1, 143.9, 150.1, 157.5, 165.6, 170.1; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = 3.60 (t, J_{B-F} = 32.0 Hz); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 497 (85000), 473 (sh, 28500), 369 (5200); IR (ATR, cm^{-1}) 3249, 2982, 2890, 1739, 1630, 1548, 1513, 1472, 1406, 1316, 1294, 1210, 1161, 1066, 1026, 1010, 979, 854, 792, 749, 725, 683; EI-MS *m/z* 391.1 (100), 372.2 (20). Anal. Calcd for $C_{19}H_{24}BF_2N_3O_3.H_2O$: C, 55.76; H, 6.40; N, 10.27. Found: C, 55.49; H, 6.32; N, 10.04.

Compound 3a. Prepared according to the general procedure from **BOD-7** (60 mg, 0.08 mmol), ethanol (1 mL), $[Pd(PPh_3)_2Cl_2]$ (10 mg, 0.016 mmol), benzene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (50:50) gave **3a** (35 mg, 70%): ^1H NMR (300 MHz, $CDCl_3$) δ = 1.10 (t, 6H, ^3J = 7.5 Hz), 1.37 (t, 6H, ^3J = 7.2 Hz), 2.38 (s, 6H), 2.48 (q, 4H, ^3J = 7.5 Hz), 2.66 (s, 3H), 2.82 (s, 6H), 4.35 (q, 4H, ^3J = 7.2 Hz), 7.66 (AB sys, 8H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 146.6 Hz); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 14.1, 14.5, 14.8, 15.2, 17.4, 17.6, 61.0, 121.8, 129.3, 130.3, 131.5, 132.8, 134.9, 140.0, 152.0, 166.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −9.8 (s); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 516 (87200), 491 (sh, 25700), 372 (7000), 290 (56800), 277 (56400); IR (ATR, cm^{-1}) 3043, 2967, 2928, 2869, 1713, 1603, 1550, 1475, 1402, 1361, 1321, 1306, 1268, 1172, 1108, 1019, 960, 935, 855, 768, 715, 694; EI-MS *m/z* 626.2 (80). Anal. Calcd for $C_{40}H_{43}BN_2O_4$: C, 76.67; H, 6.92; N, 4.47. Found: C, 76.55; H, 6.89; N, 4.38.

Compound 3b. Prepared according to the general procedure from **BOD-7** (50 mg, 0.07 mmol), 2-propanol (1 mL), $[Pd(PPh_3)_2Cl_2]$ (10 mg, 0.016 mmol), benzene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (gradient from 50:50 to 70:30) gave **3b** (25 mg, 45%): ^1H NMR (300 MHz, $CDCl_3$) δ = 1.10 (t, 6H, ^3J = 7.7 Hz), 1.35 (d, 12H, ^3J = 6.2 Hz), 2.38 (s, 6H), 2.48 (q, 4H, ^3J = 7.6 Hz), 2.66 (s, 3H), 2.82 (s, 6H), 5.22 (sep, 2H, ^3J = 6.2 Hz), 7.64 (AB sys, 8H, J_{AB} = 8.6 Hz, $\nu_o\delta$ = 145.2 Hz); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 14.1, 14.8, 15.2, 17.4, 17.6, 22.0, 68.5, 129.2, 129.2, 130.2, 130.3, 131.5, 132.8, 134.9, 140.0, 152.0, 166.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −9.8 (s); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 516 (78900), 490 (sh, 23000), 372 (6700), 289 (52900), 277 (52400); IR (ATR, cm^{-1}) 2964, 2931, 2870, 1712, 1603, 1549, 1479, 1402, 1360, 1322, 1266, 1172, 1092, 960, 934, 854, 765, 715, 693; EI-MS *m/z* 654.2 (100), 611.2 (35). Anal. Calcd for $C_{42}H_{47}BN_2O_4$: C, 77.06; H, 7.24; N, 4.28. Found: C, 76.84; H, 7.02; N, 3.98.

Compound 3c. Prepared according to the general procedure; from **BOD-7** (59 mg, 0.117 mmol), propylamine (1.5 mL), $[Pd(PPh_3)_2Cl_2]$ (10 mg, 0.014 mmol), and benzene (5 mL); stirred overnight (the solvent partially evaporated because there was no water in the cooling apparatus); column chromatography on silica gel eluting with CH_2Cl_2/AcOEt (gradient from 100:0 to 80:20) gave **3c** (30 mg, 57%): ^1H NMR (300 MHz, $CDCl_3$) δ = 0.97 (t, 6H, ^3J = 7.4 Hz), 1.09 (t, 6H, ^3J = 7.5 Hz), 1.62 (sext, 4H, ^3J = 7.4 Hz), 2.38 (s, 6H), 2.47 (q, 4H, ^3J = 7.5 Hz), 2.66 (s, 3H), 2.81 (s, 6H), 3.40 (dt, 4H, ^3J = 7.4 Hz, ^3J = 5.6 Hz), 6.057 (t, 2H, ^3J = 5.6 Hz), 7.51 (AB sys, 8H, J_{AB} = 8.4 Hz, $\nu_o\delta$ = 63.3 Hz); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 11.6, 14.2, 14.9, 15.2, 17.4, 17.6, 23.1, 41.9, 99.8, 126.6, 128.4, 128.8, 129.2, 130.3, 131.8, 132.8, 133.0, 134.9, 152.0, 167.2; UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 516 (76900), 489 (sh, 21600), 373 (6200); IR (ATR, cm^{-1}) 3603, 3253, 3078, 2959, 2931, 2871, 1629, 1605, 1549, 1479, 1400, 1360, 1324, 1239, 1186, 1123, 1019, 979, 938, 846, 767, 715, 693; EI-MS *m/z* 652.3 (100). Anal. Calcd for $C_{42}H_{49}BN_4O_2$: C, 77.29; H, 7.57; N, 8.58. Found: C, 77.02; H, 7.38; N, 8.34.

Compound 4a. Prepared according to the general procedure from **BOD-8** (40 mg, 0.04 mmol), ethanol (1 mL), $[Pd(PPh_3)_2Cl_2]$ (6 mg, 0.009 mmol), toluene (6 mL) and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (80:20) gave **4a** (25 mg, 70%): ^1H NMR (300 MHz, $CDCl_3$) δ = 1.37 (t, 6H, ^3J = 7.2 Hz), 3.80 (s, 6H), 4.34 (q, 4H, ^3J = 7.2 Hz), 7.24 (t, 2H, ^3J = 7.2 Hz), 7.39 (AB sys, 8H, J_{AB} = 8.7 Hz, $\nu_o\delta$ = 246.3 Hz), 7.46 (t, 2H, ^3J = 7.2 Hz), 7.54 (AB sys, 8H, J_{AB} = 9.0 Hz, $\nu_o\delta$ = 314.9 Hz), 7.61 (d, 2H, ^3J = 8.1 Hz), 7.93 (s, 1H), 7.94 (d, 2H, ^3J = 8.1 Hz); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 14.5, 55.5, 61.1, 98.4, 113.6, 115.2, 118.5, 123.3, 124.9, 126.1, 128.4, 128.9, 129.0, 129.6, 131.4, 132.6, 133.9, 151.3, 160.5, 166.4; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −7.24 (s); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 644 (102300), 357 (25900), 288 (77300); IR (ATR, cm^{-1}) 3049, 2977, 2933, 2836, 1710, 1618, 1594, 1552, 1516, 1460, 1383, 1307, 1269, 1242, 1174, 1146, 1095, 1028, 960, 857, 789, 769, 747, 696; EI-MS *m/z* 812.1 (100), 767.2 (10). Anal. Calcd for $C_{53}H_{41}BN_2O_6$: C, 78.33; H, 5.08; N, 3.45. Found: C, 78.55; H, 5.22; N, 3.44.

Compound 4b. Prepared according to the general procedure from **BOD-8** (40 mg, 0.04 mmol), glycine ethyl ester hydrochloride (18 mg, 0.12 mmol), $[Pd(PPh_3)_2Cl_2]$ (6 mg, 0.009 mmol), toluene (6 mL), and triethylamine (2 mL); stirred overnight; column chromatography on silica gel eluting with CH_2Cl_2/MeOH (99:1) gave **4b** (10 mg, 25%): ^1H NMR (300 MHz, $CDCl_3$) δ = 1.30 (t, 6H, ^3J = 7.1 Hz), 3.80 (s, 6H), 4.20 (d, 4H, ^3J = 4.9 Hz), 4.25 (q, 4H, ^3J = 7.1 Hz), 6.56 (t, 2H, ^3J = 5.1 Hz), 7.24 (t, 2H, ^3J = 7.1 Hz), 7.29 (AB sys, 8H, J_{AB} = 8.5 Hz, $\nu_o\delta$ = 176.2 Hz), 7.46 (t, 2H, ^3J = 7.1 Hz), 7.54 (AB sys, 8H, J_{AB} = 8.9 Hz, $\nu_o\delta$ = 314.5 Hz), 7.61 (d, 2H, ^3J = 8.5 Hz), 7.93 (s, 1H), 7.94 (d, 2H, ^3J = 7.7 Hz); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 14.3, 42.0, 55.5, 61.8, 98.1, 113.6, 115.2, 118.5, 123.4, 124.8, 126.1, 126.6, 128.4, 128.6, 131.4, 131.7, 132.0, 132.6, 133.9, 151.3, 160.5, 167.0, 170.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −7.39 (s). UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 644 (85800), 361 (20700), 283 (62200), 262 (85900); IR (ATR, cm^{-1}) 3285, 2975, 2931, 2837, 1741, 1640, 1614, 1592, 1552, 1458, 1383, 1309, 1236, 1211, 1174, 1145, 1094, 1027, 965, 853, 752, 710; EI-MS *m/z* 927.1 (100), 824.2 (20). Anal. Calcd for $C_{57}H_{47}BN_4O_8\cdot H_2O$: C, 72.46; H, 5.23; N, 5.93. Found: C, 72.24; H, 5.04; N, 5.64.

Compound 5. A solution of **1b** (100 mg, 0.17 mmol) in DMF/EtOH (10/10 mL) was degassed with argon for 20 min and cooled to 0 °C. Then a cold solution (<15 °C) of ICl (28 mg, 0.17 mmol) in ethanol (5–10 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min and then at rt for 2 h. Saturated aqueous $NaHCO_3$ solution was added. The organic phase was washed with water 3 times, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel eluting with AcOEt/petroleum ether (40:60) to give **5** as an orange powder (34 mg, 61%): ^1H NMR (300 MHz, $CDCl_3$) δ = 1.34 (s, 3H), 1.36 (s, 3H), 1.44 (t, 3H, ^3J = 7.1 Hz), 2.74 (s, 3H), 2.82 (s, 3H), 3.37 (s, 6H), 3.55 (m, 4H), 3.65 (m, 4H), 4.19 (s, 4H), 4.43 (q, 2H, ^3J = 7.1 Hz), 6.08 (s, 1H), 7.80 (AB sys, 4H, J_{AB} = 8.1 Hz, $\nu_o\delta$ = 234.3 Hz); ^{13}C NMR {^1H} (75.4 MHz, $CDCl_3$) δ = 14.5, 15.1, 16.5, 17.2, 17.6, 59.1, 59.7, 61.6, 68.8, 71.9, 84.9, 123.0, 128.6, 129.7, 130.5, 131.3, 140.2, 141.3, 142.8, 154.7, 157.9, 166.1; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −9.96 (s); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 514 (89300), 488 (sh, 25300), 378 (6300), 316 (6100); IR (ATR, cm^{-1}) 3061, 2981, 2909, 2879, 2840, 2818, 2160, 1717, 1608, 1539, 1512, 1401, 1347, 1304, 1272, 1153, 1077, 1025, 983, 854, 733, 693; EI-MS *m/z* 710.1 (100), 666.0 (35). Anal. Calcd for $C_{34}H_{40}BIN_2O_6$: C, 57.48; H, 5.68; N, 3.94. Found: C, 57.18; H, 5.40; N, 3.72.

Compound 6. Prepared according to the general procedure from **5** (65 mg, 0.06 mmol), glycine ethyl ester hydrochloride (80 mg, 0.60 mmol), $[Pd(PPh_3)_2Cl_2]$ (12 mg, 0.02 mmol), benzene (9 mL), and triethylamine (3 mL); stirred overnight; column chromatography on silica gel eluting with AcOEt/petroleum ether (gradient from 50:50 to 80:20) gave **6** (16 mg, 40%): ^1H NMR (300 MHz, $CDCl_3$) δ = 1.28 (t, 3H, ^3J = 7.1 Hz), 1.36 (s, 3H), 1.44 (t, 3H, ^3J = 7.1 Hz), 1.48 (s,

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3H), 2.76 (s, 3H), 2.89 (s, 3H), 3.36 (s, 6H), 3.55 (m, 4H), 3.65 (m, 4H), 4.15 (d, 2H, ^3J = 5.5 Hz), 4.19 (s, 4H), 4.21 (q, 2H, ^3J = 7.1 Hz), 4.43 (q, 2H, ^3J = 7.1 Hz), 6.08 (m, 2H), 7.80 (AB sys, 4H, J_{AB} = 8.4 Hz, $\nu_o\delta$ = 232.3 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 13.1, 14.3, 14.5, 15.1, 15.2, 16.6, 41.6, 59.1, 59.7, 61.6, 61.7, 68.8, 71.9, 123.6, 127.0, 128.6, 130.6, 131.0, 131.4, 137.6, 139.9, 141.6, 143.4, 152.5, 159.5, 159.3, 165.7, 166.1, 170.1; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −10.2 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}.cm^{-1}$) 502 (69800), 476 (sh, 17600), 370 (3200); EI-MS m/z 713.2 (100), 668.2 (25). Anal. Calcd for $C_{39}H_{48}BN_3O_9$: C, 65.64; H, 6.78; N, 5.89. Found: C, 65.47; H, 6.64; N, 5.72.

Compound 8. Prepared in two in situ steps: (i) from **7** (100 mg, 0.127 mmol), HC≡CC$(CH_3)_2$OH (10.7 mg, 0.127 mmol), benzene (10 mL), and triethylamine (1 mL), [Pd$(PPh_3)_4$] (10 mg, 0.009 mmol), 80 °C, one night; (ii) then ethanol (1 mL) and triethylamine (1 mL) under CO (99.2% purity), 70 °C, one day; column chromatography on silica gel eluting with CH_2Cl_2/methanol from 0 to 2%, v/v, to give **8** (54 mg, 58%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.42 (t, 6H, ^3J = 7.5 Hz), 1.48 (s, 6H), 1.66 (s, 6H), 4.40 (q, 4H, ^3J = 7.1 Hz), 6.68 (s, 2H), 7.27 (d, 2H, ^3J = 16.2 Hz), 7.44 (AB sys, 4H, J_{AB} = 8.1 Hz, $\nu_o\delta$ = 85.7 Hz), 7.82 (d, 2H, ^3J = 16.2 Hz), 7.87 (AB sys, 8H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 118.4 Hz); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 14.5, 15.0, 31.6, 61.2, 65.8, 81.6, 95.5, 118.5, 121.4, 124.0, 127.5, 128.6, 130.2, 130.6, 132.6, 133.8, 134.9, 135.4, 139.1, 140.8, 142.6, 152.6, 166.4; UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 640 (122100), 590 (sh, 41000), 363 (100200); IR (ATR, cm^{-1}) 3504, 3068, 2979, 2928, 2160, 1709, 1694, 1615, 1535, 1511, 1489, 1412, 1366, 1282, 1201, 1161, 1103, 1015, 989, 952, 870, 838, 811, 770, 716, 701; EI-MS m/z 726.2 (100), 654.2 (35). Anal. Calcd for $C_{44}H_{41}BF_2N_2O_5$: C, 72.73; H, 5.69; N, 3.86. Found: C, 72.54; H, 5.52; N, 3.64.

Compound 9. Prepared according to the general procedure from **BOD-6** (40 mg, 0.10 mmol), glycine ethyl ester hydrochloride (43 mg, 0.30 mmol), [Pd$(PPh_3)_2Cl_2$] (15 mg, 0.02 mmol), toluene (6 mL), and $NaHCO_3$ (52 mg, 0.60 mmol) instead of triethylamine; stirred 24 h at 70 °C; the reaction mixture was filtered through Celite and evaporated; column chromatography on silica gel eluting with CH_2Cl_2/AcOEt (90:10) gave the single-carbonylation product **2d** (12 mg, 30%) and the α-ketoamide derivative **10** (10 mg, 23%): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.28 (t, 3H, ^3J = 7.2 Hz), 2.43 (s, 3H), 2.44 (s, 3H), 2.54 (s, 6H), 2.63 (s, 3H), 4.23 (q, 2H, ^3J = 7.8 Hz), 4.23 (s, 2H), 6.17 (s, 1H); ^{13}C NMR {^{1}H} (75.4 MHz, $CDCl_3$) δ = 13.5, 14.9, 15.5, 17.1, 17.9, 39.9, 48.3, 62.4, 123.5, 130.9, 134.2, 138.5, 143.3, 144.4, 151.6, 151.9, 158.3, 163.1, 166.4, 167.3; EI-MS m/z 419.1 (100), 332.1 (15). Anal. Calcd for $C_{20}H_{24}BF_2N_3O_4$: C, 57.30; H, 5.77; N, 10.02. Found: C, 57.04; H, 5.59; N, 9.78.

Compound 10. To a solution of **1b** (210 mg, 0.36 mmol) in EtOH (15 mL) and CH_2Cl_2 (1 mL) was added a solution of NaOH (215 mg, 5.4 mmol) in water (5 mL). After being stirred for 3 h at room temperature, the reaction mixture was extracted with AcOEt. The aqueous phase was washed with AcOEt one more time and then acidified with a solution of 1 M HCl. The precipitate was extracted with CH_2Cl_2, dried over Celite, and evaporated. The residue was washed with pentane to give **10** (190 mg, 95%) as an orange powder. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.35 (s, 6H), 2.73 (s, 6H), 3.37 (s, 6H), 3.55 (m, 4H), 3.66 (m, 4H), 4.21 (s, 4H), 6.02 (s, 2H), 7.85 (AB sys, 4H, J_{AB} = 8.2 Hz, $\nu_o\delta$ = 155.2 Hz); ^{13}C NMR {^{1}H} (50.1 MHz, $CDCl_3$) δ = 14.8, 16.1, 59.0, 59.6, 68.5, 71.7, 90.9, 121.8, 129.1, 130.3, 130.8, 140.1, 140.8, 141.0, 155.7, 170.6; UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 501 (72800), 366 (4000), 307 (6400); UV−vis (PBS buffer) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 494 (71500), 364 (3900), 307 (4900); EI-MS m/z 578.2 (20, M + Na), 512.1 (100, M − CO_2). Anal. Calcd for $C_{32}H_{37}BN_2O_6.H_2O$: C, 66.90; H, 6.84; N, 4.88. Found: C, 66.66; H, 6.60; N, 4.61.

Alternative synthesis for **1j** from **10**: To a solution of **10** (2.15 g, 3.88 mmol) in anhydrous dichloromethane (150 mL) were added EDC (1.12 g, 5.82 mmol) and DMAP (0.71 g, 5.82 mmol). The solution was stirred at rt for 30 min, and then glycine ethyl ester (0.815 g, 5.82 mmol) was added and the mixture stirred during 12 h. The organic layer was washed with brine and water and then dried over magnesium sulfate. After evaporation of the solvent the residue was purified by chromatography (SiO2, DCM/EtOAc, gradient from 9:1 to 8:2) to give compound **1j** (1.76 g, 71%)

Compound 11. To a solution of **1j** (40 mg, 0.006 mmol) in EtOH (10 mL) was added a solution of NaOH (60 mg, 1.2 mmol) in water (2 mL). After being stirred for 2 h at room temperature, the reaction mixture was extracted with AcOEt. The aqueous phase was washed with AcOEt one more time and then acidified with a solution of 1 M HCl. The precipitate was extracted with CH_2Cl_2, dried over Na_2SO_4, and evaporated. The residue was washed with pentane to give **12** (35 mg, 90%) as an orange powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.32 (s, 6H), 2.72 (s, 6H), 3.36 (s, 6H), 3.55 (m, 4H), 3.66 (m, 4H), 4.19 (s, ·H), 4.27 (d, 2H, ^3J = 3.4 Hz), 4.87 (br s, 1H), 6.01 (s, 2H), 7.04 (t, 1H, ^3J = 3.8 Hz), 7.69 (AB sys, 4H, J_{AB} = 6.0 Hz, $\nu_o\delta$ = 160.2 Hz); ^{13}C NMR {^{1}H} (100.8 MHz, $CDCl_3$) δ = 14.9, 16.2, 42.0, 59.0, 59.7, 68.6, 71.8, 90.9, 121.9, 128.0, 129.0, 129.3, 133.8, 139.6, 140.2, 140.9, 155.8, 167.3, 172.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ = −10.2 (s); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 501 (65000), 366 (3800), 309 (5900); UV−vis (PBS buffer) λ nm (ε, $M^{-1}\cdot cm^{-1}$) 496 (59600), 367 (4100), 308 (6100); EI-MS m/z 635.2 (100, M + Na), 554.2 (15). Anal. Calcd for $C_{34}H_{40}BN_3O_7.H_2O$: C, 64.66; H, 6.70; N, 6.65. Found: C, 64.44; H, 6.42; N, 6.49.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystal structure determination parameters for **2d** and **1f** as well as proton and carbon NMR traces for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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