Synthesis of a β-isoiindigo-linked 1H-3-benzazepine-modified aza-boron dipyrromethene dimer

Linpeng Zhu and Dennis K. P. Ng*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China
Email: dkpn@cuhk.edu.hk

Dedicated to Prof. Tien-Yau Luh on the occasion of his 76th birthday

Received mm-dd-yyyy
Dates to be inserted by editorial office

Accepted Manuscript mm-dd-yyyy
Published on line mm-dd-yyyy

Abstract

A 1H-3-benzazepine-modified aza-boron dipyrromethene dimer was synthesized by condensation of 2-amino-1H-3-benzazepine with a diamino β-isoiindigo, followed by complexation with BF₃·OEt₂. It possesses an axial chirality with a C₁ symmetry as shown by heteronuclear NMR spectroscopy. Treatment of this compound with tritylium tetrafluoroborate or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone led to the unexpected mono deborylation instead of yielding the desired fully conjugated benzazepine-modified analogue. Upon mono deborylation, the electronic absorption band at 605 nm became significantly weakened and split, which could be attributed to the lowering of the molecular symmetry.

Keywords: Azepine, axial chirality, boron dipyrromethenes, condensation, β-isoiindigo
Introduction

Boron dipyrromethenes (BODIPYs), which comprise two pyrrole units tethered by a methine bridge and a BF$_2$ group, represent a versatile class of functional dyes.\(^1\) Owing to their strong and tunable electronic absorption and fluorescence emission, high thermal and photo-stability, as well as ease of chemical modification, these compounds have been extensively studied for a wide range of applications. In particular, they can serve as multifunctional theranostic agents for fluorescence bioimaging, photoacoustic imaging, photodynamic therapy, and photothermal therapy.\(^2\) They can also be used as photocatalysts in organic synthesis,\(^3\) building blocks of polymeric materials,\(^4\) photo-active materials for solar cells and photonic devices,\(^5\) and chemosensors for various analytes.\(^6\) With a view to revealing the structure-property relationship and optimizing the properties for various applications, numerous BODIPY derivatives have been designed and synthesized.\(^7\) As an important class of BODIPY derivatives, aza-BODIPYs are of particular interest.\(^8\) By replacing the methine bridge with an aza group at the meso position, the longest-wavelength absorption band of these derivatives is significantly red-shifted (to ca. 650 nm) compared with that of BODIPYs, making them particularly suitable for biomedical applications.\(^9\) Further modification, for example, by introducing fused rings to and restricting the conformation of the aza-BODIPY skeleton could further shift the absorption to the red and significantly alter their photophysical properties.\(^10\)

As another interesting series of BODIPY analogues, one of the pyrrole units has been replaced with a pyridine or quinoline group.\(^11,12\) To maintain a π-conjugated system, these compounds usually contain an exocyclic double bond at the pyrrole ring as shown in Figure 1. With such modification, they exhibit a strong electron-accepting ability with a low LUMO level and can emit strong fluorescence even in the solid state. To expand the π skeleton further, a seven-membered azepine ring can be used to give a fully conjugated system (Figure 1). However, to the best of our knowledge, these analogues have not reported so far, though BODIPYs fused with a seven-membered ring are known in the literature.\(^13\) We report herein our attempts to prepare these interesting BODIPY derivatives using a β-isoindigo core\(^14,15\) to form a dimeric species. In recent years, different forms of BODIPY dimers have been reported which exhibit superior electronic and optical properties,\(^16-19\) including the intriguing circularly polarized luminescence.\(^20,21\)

![Figure 1. Ring expanded BODIPY analogues.](image)

Results and Discussion

To prepare the β-isoindigo skeleton, 4,5-dichlorophthalonitrile (1) underwent Suzuki coupling with 3,5-bis(trifluoromethyl)phenylboronic acid (2) in the presence of \([1,1'-\text{bis(diphenylphosphino)ferrocene}]\text{dichloropalladium(II)}\) [Pd(dppf)Cl$_2$], Cs$_2$CO$_3$, and CsF in a mixture of toluene,
dioxane, and water to give the disubstituted product 3 in 77% yield (Scheme 1). The two bulky 3,5-bis(trifluoromethyl)phenyl groups were introduced to prevent molecular stacking of the resulting dimer, thereby enhancing its solubility in common organic solvents. With a large hydrophobic core, the dimer was expected to exhibit strong π-π aggregation that would lower its solubility. According to the procedure reported by Kobayashi et al. for the preparation of β-isoiindigos, treatment of 3 with Na in 1-dodecanethiol resulted in the formation of unreported β-isoiindigo 4, which was isolated as bright orange microcrystals after purification by silica-gel column chromatography followed by recrystallization from a mixture of tetrahydrofuran (THF) and hexane.

To construct the seven-membered ring, 2-amino-1H-3-benzazepine (5) was prepared separately through a two-step procedure reported previously. As shown in Scheme 1, treatment of o-phenylenediacetonitrile (6) with HBr in acetic acid followed by alkaline work up led to the formation of benzazepine 7, which underwent hydrogenolysis to remove the bromo group to afford 5. This compound was then condensed with β-isoiindigo 4 in 1-chloronaphthalene at 180 °C to give the proposed intermediate 8. Without purification and characterization, it was then treated in situ with BF₃·Et₂O and N,N-diisopropylethylamine (DIPEA) to give the dimeric product 9 in 91% overall yield. This compound could be isolated readily by column chromatography and was obtained as a dark blue solid.

**Scheme 1.** Preparation of 1H-3-benzazepine-modified dimeric aza-BODIPY analogue 9.

All the compounds were characterized with various spectroscopic methods (see the spectra given in the Supplementary Material). The dimeric nature of β-isoiindigo 4 was confirmed by its ¹H, ¹³C{¹H}, and ¹⁹F{¹H}
NMR spectra, which showed that the molecule has a C$_2$ symmetry and there is free rotation along the aryl–3,5-bis(trifluoromethyl)phenyl bond. For the known 1H-3-benzazepines 5 and 7, their low-field (60 MHz) NMR spectra were reported previously. In this study, their molecular structures were unambiguously confirmed by high-field $^1$H (400 MHz) and $^{13}$C($^1$H) (100.6 MHz) NMR spectroscopy. For the dimeric aza-BODIPY analogue 9, its $^{19}$F($^1$H) NMR spectrum showed two singlets at $\delta$-63.17 and -63.22, assignable to the two sets of CF$_3$ groups, and two broad signals at $\delta$ -127.25 and -139.91, assignable to the two fluorine atoms attached to each of the boron centers, for which the coupling due to $^{19}$F-$^{19}$F and $^{19}$F-$^{11}$B could not be resolved (Figure 2a). The $^{11}$B($^1$H) NMR spectrum showed a doublet of doublet for the two equivalent boron centers (Figure 2b). The coupling constants (ca. 24 Hz) were comparable to the values of $^1$$J_{B,F}$ for BODIPYs (28-29 Hz). Its $^1$H NMR spectrum showed two doublets at $\delta$ 3.96 and 3.77 both with a coupling constant of 12.0 Hz for the two geminal methylene protons at the seven-membered ring (Figure 2c). All these spectral data strongly suggested that the molecule is not planar and has an axial chirality with a C$_i$ symmetry probably due to the steric constraint induced by the two BF$_2$ units. The compound was also characterized with high-resolution electrospray ionization (ESI) mass spectrometry, which showed the molecular ion signal ($m/z = 1486.2432$) as the base peak. Its isotopic pattern was also in good agreement with the simulated pattern.

Figure 2. Partial (a) $^{19}$F($^1$H), (b) $^{11}$B($^1$H), and (c) $^1$H NMR spectra of 9 and 11 in CDCl$_3$.

Attempts were made to convert 9 into the fully conjugated benzazepine-modified analogue, which contains two benzazepine-modified aza-BODIPY units (compound 10, Scheme 2). We first treated 9 with an excess amount of tritylium tetrafluoroborate (TrBF$_4$) in refluxing dioxane in order to remove a hydride from the seven-membered ring. Surprisingly, mono deborylation occurred to afford 11 as a red-purple solid in 83% yield (Scheme 2). Oxidation of 9 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) also gave 11 (in 33% yield), but the desired product 10 could not be obtained. It is worth mentioning that treatment of the intermediate 8 generated in situ with a less amount of BF$_3$·Et$_2$O (1.5 equiv. with respect to 4) could not give 11, but a significant amount of 8 was recovered. The unsymmetrical structure of this compound was inferred
from its $^{19}$F-$^1$H NMR spectrum, which exhibited four instead of two singlets (at $\delta$ -63.24, -63.25, -63.62, and -63.70) for the CF$_3$ groups (Figure 2a). In addition, a distorted quartet at $\delta$ -131.47 was also observed for the two equivalent fluorine atoms, which were coupled with the boron center with a $^1J_{F,B}$ of 27.6 Hz. The presence of only one BF$_2$ group was also supported by the triplet at $\delta$ 1.41 ($^1J_{B,F} = 27.6$ Hz) in the $^{11}$B-$^1$H NMR spectrum (Figure 2b). Furthermore, the four methylene protons now resonated as two singlets at $\delta$ 3.91 and 3.87 in the $^1$H NMR spectrum (Figure 2c), showing that the axial chirality was lost in this compound. A very downfield signal at $\delta$ 13.68 was also observed, which could be assigned to the NH proton at the seven-membered ring. Compound 11 was further characterized by high-resolution ESI mass spectrometry. Both the accurate mass and the isotopic pattern of the molecular ion signal were in good agreement with the theoretical values, providing strong evidence to support the identity of this compound.

**Scheme 2.** Attempted synthesis of the fully conjugated benzazepine-modified aza-BODIPY dimer 10.

The electronic absorption spectra of compounds 9 and 11 were recorded in CHCl$_3$ (Figure 3). It can be seen that while the dimeric aza-BODIPY analogue 9 exhibited a broad band at 605 nm, the mono-deborylated analogue 11 displayed a much weaker and split signal at around 570 nm, which might be due to the loss of symmetry caused by the removal of one of the BF$_2$ units. Upon excitation at the respective $\lambda_{max}$ both compounds showed negligible fluorescence. It is worth noting that while the absorption of 9 was slightly red shifted compared with that of general BODIPYs due to the extended conjugation, the non-fluorescent property of 9 was in contrast with the highly emissive nature of BODIPYs.
Figure 3. Electronic absorption spectra of 9 and 11 in CHCl₃ (18 μM).

Conclusions

In summary, we have successfully synthesized a novel β-isoidinggo-linked 1H-3-benzazepine-modified aza-BODIPY dimer (compound 9) in 91% yield through a one-pot condensation of β-isoidinggo 4 with 2-amino-1H-3-benzazepine (5) followed by borylation with BF₃-OEt₂. To the best of our knowledge, it is the first example of BODIPY analogue in which one of the five-membered pyrrole rings is replaced with a seven-membered azepine ring. Unfortunately, attempts to convert this compound to the fully conjugated benzazepine-modified aza-BODIPY dimer were unsuccessful. As shown by heteronuclear NMR spectroscopy, the axial chirality of 9 was lost upon mono deborylation, which also resulted in weakening and splitting of the electronic absorption band at 605 nm.

Experimental Section

General. Toluene was dried using an INERT solvent drying system prior to use. All other solvents and reagents were of reagent grade and used without further purification. All the reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC; Merck pre-coated silica gel 60F254 plates). For reactions that required heating, oil bath was used as the heating source. Chromatographic purification was performed on silica gel (Macherey-Nagel, 230–400 mesh) column with the indicated eluent. ¹H, ¹³C{¹H}, ¹⁹F{¹H}, and ¹¹B{¹H} NMR spectra were recorded on a Bruker Avance III 400 spectrometer (¹H, 400 MHz; ¹³C, 100.6 MHz; ¹¹B, 128.4 MHz) or a Bruker Avance III 500 spectrometer (¹H, 500 MHz; ¹³C, 125.8 MHz; ¹⁹F, 470.4 MHz) in a deuterated solvent. The ¹H and ¹³C{¹H} NMR spectra were referenced internally using the residual solvent [¹H: δ = 7.26 (for CDCl₃), δ = 2.5 (for DMSO-d₆)] or solvent [¹³C: δ = 77.2 (for CDCl₃), δ = 39.7 (for DMSO-d₆)] resonance relative to tetramethylsilane. For ¹⁹F{¹H} and ¹¹B{¹H} NMR spectra, trifluoromethylbenzene (δ = -64 ppm) and BF₃-OEt₂ (δ = 0 ppm) were used as the external reference, respectively. High-resolution ESI mass spectra were recorded on a Q Exactive Focus Orbitrap mass
spectrometer. UV-Vis spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer. Melting points were measured on a Büchi melting point apparatus (model B-545).

4,5-Bis(3',5'-bis(trifluoromethyl)phenyl)phthalonitrile (3). A mixture of 4,5-dichlorophthalonitrile (1) (1.03 g, 5.2 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (2) (2.80 g, 10.9 mmol), Pd(dpdpf)Cl₂ (430 mg, 10 mol%), Cs₂CO₃ (2.56 g, 7.8 mmol), and CsF (1.18 g, 7.8 mmol) in toluene (30 mL), dioxane (30 mL), and water (20 mL) was stirred at 90 °C until compound 1 was fully consumed as indicated by TLC. After cooling to room temperature, the mixture was mixed with ethyl acetate (100 mL) and water (100 mL). The organic phase was washed with water and brine sequentially, and then it was dried over anhydrous Na₂SO₄. The solvent was then evaporated under vacuum, and the crude product was purified by silica gel column chromatography using n-hexane/EtOAc (19:1 v/v) as the eluent to give the product as a white solid (2.23 g, 77%). mp 168-169 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.01 (s, 2 H, ArH), 7.89 (s, 2 H, ArH), 7.51 (s, 4 H, ArH). ¹³C¹H NMR (CDCl₃, 100.6 MHz): δ 163.3, 143.6, 143.0, 141.5, 141.1, 138.2, 136.4, 133.3, 131.1, 130.4 (quartet, ¹JCF = 33.2 Hz, CCF₃), 130.2 (quartet, ²JCF = 32.7 Hz, CCF₃), 126.7, 126.6, 124.4, 122.2, 120.9, 120.7, 120.1 (the two CF₃ quartets could not be identified). ¹⁹F¹H NMR (CDCl₃, 470.4 MHz): δ -63.36 (s, CF₃). HRMS (ESI): m/z calcd for C₂₄H₁₇F₁₂N₂ [M⁺]⁺ 552.0501, found 552.0504.

Diamino β-isoidingo 4. Sodium metal (32 mg, 1.4 mmol) was dissolved in dodecanethiol (2.5 mL) at 100 °C. After the sodium was completely dissolved, phthalonitrile 3 (770 mg, 1.4 mmol) was added, and the mixture was stirred at this temperature for 1 h. The reaction temperature was then elevated to 180 °C, and the mixture was kept stirring for 1 h. The reaction was then quenched with an excess of n-hexane. The precipitate that was collected by filtration was purified by silica gel column chromatography using CHCl₃ as eluent, followed by recrystallization from THF/hexane to give the product as bright yellow microcrystals (324 mg, 42%). mp >310 °C. ¹H NMR (DMSO-d₆, 500 MHz): δ 8.85 (s, 2 H, ArH), 8.18 (s, 2 H, ArH), 8.06 (s, 2 H, ArH), 7.93 (s, 4 H, ArH), 7.85 (s, 4 H, ArH), 7.67 (s, 2 H, NH₂). ¹³C¹H NMR (DMSO-d₆, 125.8 MHz): δ 163.3, 143.6, 143.0, 141.5, 141.1, 138.2, 136.4, 133.3, 131.1, 130.4 (quartet, ¹JCF = 33.2 Hz, CCF₃), 130.2 (quartet, ²JCF = 32.7 Hz, CCF₃), 126.7, 126.6, 124.4, 122.2, 120.9, 120.7, 120.1 (the two CF₃ quartets could not be identified). ¹⁹F¹H NMR (DMSO-d₆, 470.4 MHz): δ -61.55 (s, CF₃), -61.67 (s, CF₃). HRMS (ESI): m/z calcd for C₄₈H₂₀F₂₄N₄ [M+H]⁺ 1109.1378, found 1109.1377.

2-Amino-4-bromo-1H-3-benzazepine (7). According to the reported procedure, 22 a 30% solution of HBr in acetic acid (11 mL) was added dropwise into a solution of o-phenylenediacetonitrile (6) (3.61 g, 23 mmol) in acetic acid (6 mL) with stirring. After 2 h, the precipitate formed was collected by filtration and washed with acetic acid and diethyl ether. The solid was then redissolved in N,N-dimethylformamide (DMF) (20 mL), and the solution was added dropwise into a saturated NaHCO₃ solution (100 mL). After vigorous stirring for 30 min, the precipitate was collected by filtration, washed thoroughly with water, and dried. The crude product was purified by recrystallization from acetone as colorless crystals (4.23 g, 77%). mp 195 °C (decomp.). ¹H NMR (CDCl₃, 400 MHz): δ 7.23-7.35 (m, 3 H, ArH), 7.13 (d, J = 7.2 Hz, 1 H, ArH), 6.78 (s, 1 H, C=CH), 3.30 (s, 2 H, CH₂). ¹³C¹H NMR (CDCl₃, 100.6 MHz): δ 153.6, 153.5, 131.5, 129.1, 128.2, 127.7, 127.1, 117.0, 40.0. HRMS (ESI): m/z calcd for C₁₀H₉BrN₂ [M+H]⁺ 237.0022, found 237.0023.

2-Amino-1H-3-benzazepine (5). According to the reported procedure, 22 a mixture of 7 (1.20 g, 5.1 mmol), KHCO₃ (1.02 g, 10.2 mmol), and 10% Pd/C (150 mg) in ethanol (150 mL) was stirred under an atmosphere of hydrogen at normal pressure. After 2 h, the mixture was filtered through Celite and the filtrate was evaporated in vacuo with temperature lower than 40 °C. The crude product was purified by recrystallization from CH₂Cl₂ to afford colorless crystals (0.55 g, 69%). mp 154 °C (decomp.). ¹H NMR (CDCl₃, 400 MHz): δ 7.28-7.34 (m, 3 H, ArH), 7.15 (d, J = 7.6 Hz, 1 H, ArH), 6.90 (d, J = 8.8 Hz, 1 H, C=CH), 6.37 (d, J = 8.8 Hz, 1 H, C=CH),
3.23 (s, 2 H, CH$_2$). $^{13}$C($^1$H) NMR (CDCl$_3$, 100.6 MHz): $\delta$ 152.7, 137.9, 135.6, 130.6, 127.7, 127.5, 127.3, 126.7, 115.3, 40.0. HRMS (ESI): $m/z$ calcd for C$_{10}$H$_{10}$N$_2$ [M+H]$^+$ 159.0917, found 159.0917.

1H-3-Benzazepine-modified aza-BODIPY dimer 9. A mixture of $\beta$-isoidindo 4 (57 mg, 0.05 mmol) and 2-amino-1H-3-benzazepine (5) (40 mg, 0.25 mmol) in 1-chloronaphthalene (2.5 mL) was stirred at 180 °C for 1 h. The mixture turned to deep red purple gradually. It was expected that the intermediate 8 was formed, which was not purified and characterized. After cooling to room temperature, DIPEA (55 µL) and toluene (10 mL) were added, followed by the dropwise addition of BF$_3$-Et$_2$O (80 µL, 0.65 mmol). The mixture was stirred at room temperature for 30 min. It was then evaporated in vacuo, and the residue was loaded onto a silica gel column and eluted with hexane/CH$_2$Cl$_2$ (1:3 v/v) to give the product as a dark blue solid (70 mg, 91%). mp >310 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.54 (s, 2 H, ArH), 8.18 (s, 2 H, ArH), 7.81 (s, 2 H, ArH), 7.78 (s, 2 H, ArH), 7.58 (s, 4 H, ArH), 7.56 (s, 4 H, ArH), 7.43-7.49 (m, 4 H, ArH), 7.34-7.39 (m, 4 H, ArH), 7.05 (d, $J$ = 9.6 Hz, 2 H, C=CH), 6.97 (d, $J$ = 9.6 Hz, 2 H, C=CH), 3.96 (d, $J$ = 12.0 Hz, 2 H, CH), 3.77 (d, $J$ = 12.0 Hz, 2 H, CH). $^{13}$C($^1$H) NMR (CDCl$_3$, 100.6 MHz): $\delta$ 165.6, 161.9, 141.4, 141.3, 139.0, 137.4, 134.3, 133.7, 132.5, 132.2, 132.0 (quartet, $^{2}$J$_{CF}$ = 33.7 Hz, CCF$_3$), 131.9 (quartet, $^{2}$J$_{CF}$ = 33.7 Hz, CCF$_3$), 130.5, 130.2, 129.9, 129.6, 129.5, 128.5, 127.9, 127.7, 126.9, 126.7, 125.0, 124.6, 124.2, 121.5, 118.8, 42.6 (the two CF$_3$ quartets could not be identified). $^{19}$F($^1$H) NMR (CDCl$_3$, 470.4 MHz): $\delta$ -63.17 (s, CF$_3$), -63.22 (s, CF$_3$), -127.25 (br s, BF), -139.91 (br s, BF). $^{11}$B($^1$H) NMR (CDCl$_3$, 128.4 MHz): $\delta$ 1.20 (virtual t, $^{3}$J$_{BF}$ = 24.1 Hz). HRMS (ESI): $m/z$ calcd for C$_{68}$H$_{32}$B$_2$F$_{28}$N$_6$ [M]$^-$ 1486.2453, found 1486.2432. UV-Vis (CDCl$_3$) $\lambda_{max}$/nm (log $\epsilon$): 344 (4.47), 605 (4.56).

Mono deborylated aza-BODIPY dimer 11. A mixture of 9 (15 mg, 0.01 mmol) and TrBF$_4$ (3.4 mg, 0.01 mmol) in dioxane (1 mL) was stirred under reflux for 1 h. The solvent was removed in vacuo and the residue was subject to column chromatography using hexane/CH$_2$Cl$_2$ (1:4 v/v) as eluent to give the product as a red-purple solid (12 mg, 83%). mp >310 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 13.68 (s, 1 H, NH), 8.53 (s, 1 H, ArH), 8.37 (s, 1 H, ArH), 8.33 (s, 1 H, ArH), 8.12 (s, 1 H, ArH), 7.79 (s, 1 H, ArH), 7.78 (s, 1 H, ArH), 7.73 (s, 1 H, ArH), 7.70 (s, 1 H, ArH), 7.53 (s, 2 H, ArH), 7.51 (s, 2 H, ArH), 7.37-7.49 (m, 8 H, ArH), 7.35 (s, 2 H, ArH), 7.32 (s, 2 H, ArH), 7.19 (d, $J$ = 7.6 Hz, 1 H, C=CH), 7.03 (d, $J$ = 8.4 Hz, 1 H, C=CH), 6.89 (dd, $J$ = 3.2, 7.6 Hz, 1 H, C=CH), 6.73 (d, $J$ = 7.6 Hz, 1 H, C=CH), 3.91 (s, 2 H, CH$_2$), 3.87 (s, 2 H, CH$_2$). $^{13}$C($^1$H) NMR (CDCl$_3$, 100.6 MHz): $\delta$ 169.8, 162.2, 162.1, 161.2, 144.5, 141.7, 141.64, 141.60, 141.3, 141.2, 141.1, 139.3, 138.8, 138.7, 138.4, 136.2, 134.6, 133.9, 133.5, 132.8, 132.7, 132.5, 132.4, 132.3, 132.2, 132.1, 131.9, 131.8, 131.7, 131.5, 130.1, 129.9, 129.5, 129.1, 128.7, 127.8, 127.7, 127.6, 126.0, 125.5, 125.3, 125.2, 124.6, 124.5, 124.2, 124.1, 124.0, 123.8, 121.6, 121.4, 121.1, 120.6, 43.2, 29.7 (the CF$_3$ and CCF$_3$ quartets could not be identified). $^{19}$F($^1$H) NMR (CDCl$_3$, 470.4 MHz): $\delta$ -63.24 (s, CF$_3$), -63.25 (s, CF$_3$), -63.62 (s, CF$_3$), -63.70 (s, CF$_3$), -131.47 (quartet, $^{3}$J$_{BF}$ = 27.6 Hz, BF$_2$). $^{11}$B($^1$H) NMR (CDCl$_3$, 128.4 MHz): $\delta$ 1.41 (t, $^{3}$J$_{BF}$ = 27.6 Hz, BF$_2$). HRMS (ESI): $m/z$ calcd for C$_{68}$H$_{33}$BF$_{26}$N$_6$ [M-H]$^-$ 1437.2384, found 1437.2371. UV-Vis (CDCl$_3$) $\lambda_{max}$/nm (log $\epsilon$): 567 (4.07).

Supplementary Material

NMR and ESI mass spectra of all the compounds are available on the supplementary material file associated with this paper.

References


©AUTHOR(S)
https://doi.org/10.1002/adma.202207546

https://doi.org/10.1002/ejoc.202001446

https://doi.org/10.1039/d0py01513j

https://doi.org/10.3390/molecules26010153

https://doi.org/10.3390/chemosensors8030051

https://doi.org/10.1016/j.ccr.2022.214684

https://doi.org/10.1039/c6cs00200e

https://doi.org/10.1039/d0cs00234h

https://doi.org/10.1016/j.ccr.2022.214709

https://doi.org/10.1021/jo702265x

https://doi.org/10.1039/c3cc48316a

https://doi.org/10.1021/acs.jmedchem.2c00859

https://doi.org/10.1021/jacs.5b09853

https://doi.org/10.1002/anie.202100888

https://doi.org/10.1002/anie.200604763

https://doi.org/10.1021/ja207545t

https://doi.org/10.1021/ja502477a

https://doi.org/10.1002/anie.202207459
https://doi.org/10.1002/anie.202204358

https://doi.org/10.1002/anie.202218023

https://doi.org/10.1002/het.5570020106

https://doi.org/10.1039/d0nj02576c

This paper is an open access article distributed under the terms of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/)