Synthesis of 4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene Dyes Bearing New Aryl Substituents at C3- and C5-Positions†

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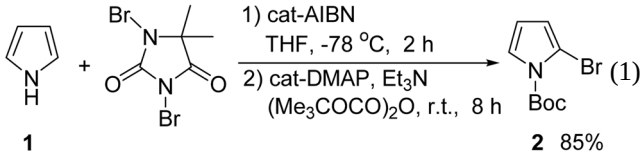
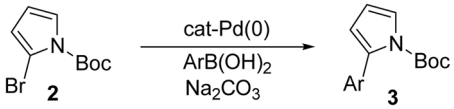
Dipyrrometheneboron difluoride (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) known as the trademark BODIPY shows many intriguing chemical and physical properties such as high absorption coefficient and fluorescence quantum yield, long wavelength emission, photochemical stability and insensitivity toward changes of the polarity, acidity and oxygen content of the medium.[1] BODIPY has been conjugated to a variety of biomolecules such as proteins,[1] DNA,[2] carbohydrates[3] and cholesterol.[4] BODIPY derivatives have been used in fluorescent switches,[5] probes for protons,[6] mercuric ion[7] and nitric oxide,[8] biological labeling and syntheses of molecular devices.[9] Therefore, synthesis of diverse BODIPY derivatives and their application to biomolecules are of current interest. Recently, efficient synthetic methods of BODIPY derivatives were reported.[10] Boenes *et al.* synthesized new BODIPY dyes with phenolic or naphtholic subunits as fluorescent pH probes[10f] and Burgess *et al.* reported BODIPY dyes having aryl group[10a,10c] and 2-ketopyrrole-BF_2 complexes.[10d] Despite this recent progress synthesis of BODIPY derivatives having alkyl- and aryl-groups have been remained an important objective because fluorescence maxima of BODIPY depend on change of substituents on aryl group. We describe herein synthesis of a variety of tunable and new BODIPY dyes by introducing new aryl substituents at C-3 and C-5 positions (Scheme 1).

First, *N*-Boc-2-bromopyrrole was prepared by the treatment of pyrrole (**1**) with 1,3-dibromo-5,5-dimethylhydantoin in the presence of AIBN followed by amine protection with di-*tert*-butyl dicarbonate and a catalytic amount of DMAP in 85% yield (eq. 1).[11]



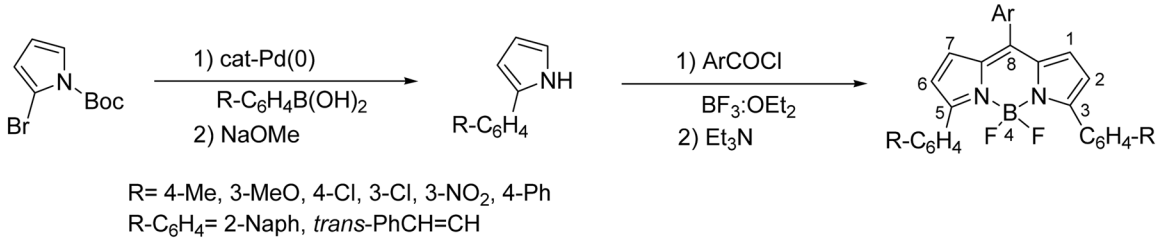
N-Boc-2-arylpyrroles were prepared from the reactions of *N*-Boc-2-bromopyrrole (**2**) with a variety of arylboronic acids under the conditions of Miyaura-Suzuki cross-coupling reactions and the results are summarized in Table 1. Reaction of **2** with 4-methyl- and 4-phenylphenylboronic acid in the presence of 2 mol% of $(Ph_3P)_4Pd$ and Na_2CO_3 (2 equiv.) gave *N*-Boc-2-(4-methylphenyl)pyrrole and *N*-Boc-2-(4-phenylphenyl)pyrrole in 73% and 90% yields, respectively (entries 1 and 6). Phenylboronic acids having 3-

Table 1. Preparation of *N*-Boc-2-arylpyrrole[a]



Entry	$ArB(OH)_2$		Yield (%)[b]
1	4-Me-C_6H_4-$B(OH)_2$	**a**	73
2	3-MeO-C_6H_4-$B(OH)_2$	**b**	92
3	4-Cl-C_6H_4-$B(OH)_2$	**c**	90
4	3-Cl-C_6H_4-$B(OH)_2$	**d**	77
5	3-NO_2-C_6H_4-$B(OH)_2$	**e**	72
6	4-Ph-C_6H_4-$B(OH)_2$	**f**	90
7	2-Naph-$B(OH)_2$	**g**	83
8	*trans*-PhCH=CH-$B(OH)_2$	**h**	84

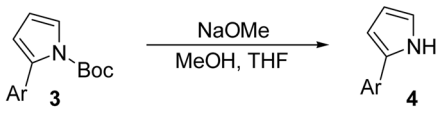
[a]Reactions were carried out with **2** (1 equiv.), $ArB(OH)_2$ (1 equiv.) and Na_2CO_3 (2 equiv.) in the presence of $(Ph_3P)_4Pd$ (2 mol%) in MePh/MeOH (2.6 mL, 5:1) at 80 °C for 14 h. [b]Isolated yield.



Scheme 1. Preparation of BODIPY derivatives.

†This paper is dedicated to Professor Yong Kwang Park on his 60th birthday.

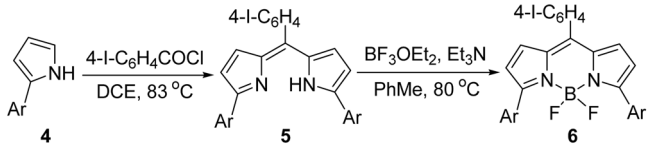
Table 2. Preparation of 2-arylpyrrole[a]



Entry	Ar-		Yield (%)[b]
1	4-Me-C_6H_4-	**a**	84
2	3-MeO-C_6H_4-	**b**	70
3	4-Cl-C_6H_4-	**c**	73
4	3-Cl-C_6H_4-	**d**	95
5	3-NO_2-C_6H_4-	**e**	75
6	4-Ph-C_6H_4-	**f**	93
7	2-Naph-	**g**	82
8	*trans*-PhCH=CH-	**h**	45

[a]Reactions were carried out in **3** (1 equiv.), and NaOMe (3.1 equiv.) in MeOH and THF at 25 °C for 3 h. [b]Isolated yield.

Table 3. Preparation of BODIPY dyes



Entry	Ar-		Yield (%)[a]	
			5	**6**
1	4-Me-C_6H_4-	**a**	34	34
2	3-MeO-C_6H_4-	**b**	52	48
3	4-Cl-C_6H_4-	**c**	30	29
4	3-Cl-C_6H_4-	**d**	–	23
5	4-Ph-C_6H_4-	**f**	–	29
6	2-Naph-	**g**	–	31

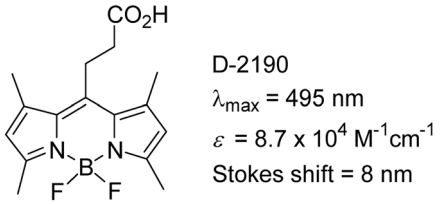
[a]Isolated yield.

methoxy and 3-nitro group proceeded smoothly to produce the desired products under the optimum conditions (entries 2 and 5). In the case of 4- and 3-chlorophenylboronic acid, *N*-Boc-2-arylpyrrole derivatives were obtained in good yields (entries 3 and 4). Under the optimum conditions, 2-naphthylboronic acid provided the coupling product in 83% yield (entry 7). Subjecting compound **2** to *trans*-β-strylboronic acid afforded **3h** in 84% yield (entry 8).

Deprotection of *N*-Boc group in compound **3** was carried out with sodium methoxide in methanol and THF, producing 2-arylpyrroles in more than 70% yields except **3h** and the results are summarized in Table 2.

Next, we carried out the reaction of 4-arylpyrrole with 4-iodobenzoyl chloride to obtain bispyrromethane **5** and the results are summarized in Table 3. 4-Iodobenzoyl chloride was used for further functionalizations such as cross-coupling reactions. Treatment of 4-(4-methylphenyl)pyrrole (**4a**) with 4-iodobenzoyl chloride in dichloroethane at 83 °C gave the condensation product **5a** in 34% yield (entry 1). Exposure of 4-(3-methoxyphenyl)pyrrole (**4b**) and 4-(4-chlorophenyl)pyrrole (**4c**) to 4-iodobenzoyl chloride resulted in **5b** and **5c** in 52% and 30% yields, respectively (entries 2 and 3). The product **5a** was treated with boron trifluoride etherate in the presence of triethylamine (3.16 equiv.) in toluene at 80 °C to produce BODIPY **6a** in 34% yield. Subjecting compound **5b** and **5c** to boron trifluoride etherate afforded the BODIPY **6b** and **6c** in 48% and 29% yields, respectively. Because total yields of product **6** through compound **5** were low, condensation reactions followed by treatment of boron trifluoride etherate were carried out in one-pot procedure without separation of **5**. Yield of **6** in one-pot procedure is better than one in two-pot procedure. Reaction of 2-(3-chlorophenyl)pyrrole (**4d**) with 4-iodobenzoyl chloride followed by reaction of boron trifluoride etherate in the presence of triethylamine (2.94 equiv.) produced BODIPY **6d** in 23% yield in toluene at 80 °C (entry 4). 2-(4-Phenylphenyl)pyrrole (**4f**) and 2-(2-naphthyl)pyrrole (**4g**) gave **6f** and **6g** in 29% and 31% yields, respectively, under the same reaction conditions (entries 5 and 6).

The spectroscopic data for six BODIPY compounds **6a-6d**, **6f** and **6g** in chloroform was listed in Table 4. Four methyl substituted BODIPY system D-2190[12] shows λ_{max} (absorption) = 495 nm and $\varepsilon = 8.7 \times 10^4$ M^{-1} cm^{-1}, while the wavelength for the absorption of aryl substituted BODIPY is 558-581 nm (red-shifted) and their extinction coefficients (ε) obtained are smaller.



In addition, these 3,5-diaryl BODIPY dyes exhibited larger Stokes shifts (32-44 nm) than the methyl substituted system (8 nm for D-2190). The fluorescence intensities of BODIPY **6a-6d**, **6f** and **6g** are lower than those of methyl substituted BODIPY due to nonradiative decay of twisted biaryl conformations in the excited state.[13]

In conclusion, Miyaura-Suzuki cross-coupling reactions of arylboronic acids with *N*-BOC protected 2-bromopyrrole followed by deprotection of *N*-Boc group with sodium methoxide in methanol afforded 2-arylpyrroles in good to excellent yields. These compounds reacted with 4-iodobenzoyl chloride to give bispyrromethane in good yields through elimination of hydrogen chloride and water. Treat-

Table 4. Spectroscopic data for BODIPY dyes

Entry	BODIPY	Absorption (nm)	Emission (nm)	ε (M^{-1} cm^{-1})	Stokes Shift (nm)[a]
1	**6a**	569	608	4.1×10^4	39
2	**6b**	565	602	6.5×10^3	37
3	**6c**	564	598	2.8×10^4	34
4	**6d**	558	590	5.3×10^4	32
5	**6f**	581	623	3.6×10^4	42
6	**6g**	580	624	4.7×10^4	44

[a]Stokes shift = emission − absorption.

ment of bispyrromethanes with boron trifluoride diethyl etherate in toluene produced the novel 3,5-diaryl BODIPY dyes whose emission wavelength are shifted to red compared with alkyl substituted BODIPY dyes.

Experimental Section

***N-tert*-Butoxycarbonyl-2-(4'-methylphenyl)pyrrole (3a):** To a suspension of $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and 4-methylphenylboronic acid (68.0 mg, 0.5 mmol) was added **2** (123.0 mg, 0.5 mmol) dissolved in toluene (2.6 mL) and methanol (0.3 mL) under nitrogen atmosphere. After 2.0 M Na_2CO_3 (aq.) (106.0 mg, 1.0 mmol) was added to reaction mixture, it was refluxed for 14 h at 80 °C. The mixture was concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (elution solvent: ethyl acetate/hexane = 1/30) to give the desired compound **3a** (94.0 mg, 73%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32 (q, J = 1.69 Hz, 1H), 7.23 (d, J = 7.75 Hz, 2H), 7.15 (d, J = 8.15 Hz, 2H), 6.20 (t, J = 3.25 Hz, 1H), 6.15 (q, J = 1.63 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.4, 136.9, 135.2, 131.4, 129.1, 128.3, 122.3, 114.1, 110.5, 83.4, 27.6, 21.2.

***N-tert*-Butoxycarbonyl-2-(3'-methoxyphenyl)pyrrole (3b):** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34 (q, J = 1.68 Hz, 1H), 7.25 (t, J = 7.90 Hz, 1H), 6.93 (dd, J = 7.64 Hz, 0.82 Hz, 1H), 6.89 (t, J = 1.89 Hz, 1H), 6.87-6.84 (m, 1H), 6.22 (t, J = 3.28 Hz, 1H), 6.20 (q, J = 1.72 Hz, 1H), 3.82 (s, 3H), 1.36 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.3, 149.8, 136.1, 135.2, 128.9, 123.0, 122.2, 115.2, 114.8, 113.2, 110.9, 84.0, 55.6, 28.0.

***N-tert*-Butoxycarbonyl-2-(4'-chlorophenyl)pyrrole (3c):** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.34 (m, 1H), 7.32-7.25 (m, 4H), 6.22 (t, J = 3.26 Hz, 1H), 6.18-6.17 (m, 1H), 1.39 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.6, 133.1, 132.5, 132.2, 129.8, 127.1, 122.2, 114.2, 110.0, 83.2, 27.1.

***N-tert*-Butoxycarbonyl-2-(3'-chlorophenyl)-pyrrole (3d):** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36 (q, J = 1.65 Hz, 1H), 7.33 (d, J = 1.12 Hz, 1H), 7.28-7.26 (m, 2H), 7.25-7.21 (m, 1H), 6.23-6.19 (m, 2H), 1.37 (s, 9H).

***N-tert*-Butoxycarbonyl-2-(3'-nitrophenyl)pyrrole (3e):** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (t, J = 1.92 1H), 8.17-8.14 (m, 1H), 7.70-7.68 (m, 1H), 7.51 (t, J = 7.94 Hz, 1H), 7.40 (q, J = 1.68 Hz, 1H), 6.30-6.29 (m, 1H), 6.26 (t, J = 3.32 Hz, 1H), 1.40 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.4, 148.1, 136.2, 135.4, 132.7, 128.8, 124.6, 124.1, 122.3, 116.3, 111.3, 85.0, 28.1.

***N-tert*-Butoxycarbonyl-2-(4'-biphenyl)pyrrole (3f):** ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.66-7.57 (m, 4H), 7.49-7.35 (m, 6H), 6.25 (d, J = 2.75 Hz, 2H), 1.39 (s, 9H).

***N-tert*-Butoxycarbonyl-2-(2'-naphthyl)pyrrole (3g):** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 4H), 7.49-7.44 (m, 3H), 7.40 (t, J = 2.47 Hz, 1H), 6.29-6.26 (m, 2H), 1.31 (s, 9H).

***N-tert*-Butoxycarbonyl-2-styrenylpyrrole (3h):** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 16.32 Hz, 1H), 7.47 (d, J = 7.47 Hz, 2H), 7.35-7.30 (m, 1H), 7.27 (q, J = 1.64 Hz, 1H), 7.24-7.19 (m, 2H), 6.88 (d, J = 16.30 Hz, 1H), 6.55 (d, J = 2.82 Hz, 1H), 6.18 (t, J = 6.83 Hz, 1H), 1.62 (s, 1H).

2-(4'-Methylphenyl)pyrrole (4a): To a solution of **3a** (207.0 mg, 0.81 mmol) in THF was added 3.0 M NaOMe (dissolved in methanol) (136.0 mg, 2.5 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 3 h. The mixture was washed with H_2O and brine. The aqueous layer was extracted with Et_2O, dried with $MaSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography on basic alumina (elution solvent: ethyl acetate/hexane = 1/10) to give the desired compound **4a** (107.0 mg, 84%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.40 (d, J = 7.94 Hz, 2H), 7.20 (d, J = 7.63 Hz, 2H), 6.87-6.85 (m, 1H), 6.50-6.49 (m, 1H), 6.32-6.30 (m, 1H), 2.37 (s, 3H).

2-(3'-Methoxyphenyl)pyrrole (4b): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.34 (d, J = 7.94 Hz, 1H), 7.12-7.04 (m, 2H), 6.89-6.88 (m, 1H), 6.80 (dd, J = 8.09 Hz, 2.60 Hz, 1H), 6.58-6.54 (m, 1H), 6.33 (q, J = 2.85 Hz, 1H), 3.88 (s, 3H).

2-(4'-Chlorophenyl)pyrrole (4c): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.39 (d, J = 8.15 Hz, 2H), 7.32 (d, J = 8.58 Hz, 2H), 6.87 (d, J = 0.99 Hz, 1H), 6.51 (s, 1H), 6.30 (q, J = 2.86 Hz, 1H).

2-(3'-Chlorophenyl)pyrrole (4d): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.44 (t, J = 1.81 Hz, 1H), 7.34 (dt, J = 7.85 Hz, 1.40 Hz, 1H), 7.28 (t, J = 7.79 Hz, 1H), 7.18-7.15 (m, 1H), 6.89-6.87 (m, 1H), 6.55-6.53 (m, 1H), 6.30 (q, J = 2.94 Hz, 1H).

2-(3'-Nitrophenyl)pyrrole (4e): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.29 (t, J = 1.92, 1H), 8.04-8.01 (m, 1H), 7.78 (d, J = 7.88 Hz, 1H), 7.52 (t, J = 8.00 Hz, 1H), 6.96-6.94 (m, 1H), 6.67-6.66 (m, 1H), 6.35 (q, J = 2.91 Hz, 1H).

2-(4'-Biphenyl)pyrrole (4f): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.62-7.59 (m, 4H), 7.56-7.54 (m, 2H), 7.46-7.42 (m, 2H), 7.36-7.32 (m, 1H), 6.90-6.88 (m, 1H), 6.58-6.56 (m, 1H), 6.32 (q, J = 2.85 Hz, 1H).

2-(2'-Naphthyl)pyrrole (4g): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.84-7.79 (m, 4H), 7.65 (dd, J = 8.54 Hz, 1.79 Hz, 2H), 7.48-7.39 (m, 2H), 6.91 (dd, J = 3.90 Hz, 2.50 Hz, 2H), 6.66-6.64 (m, 2H), 6.36-6.34 (m, 2H).

2-Styrenylpyrrole (4h): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.41 (d, J = 7.47 Hz, 2H), 7.31 (t, J = 7.64 Hz, 2H), 7.22-7.18 (m, 1H), 6.95 (d, J = 16.48 Hz, 1H), 6.79-6.77 (m, 1H), 6.64 (d, J = 16.46 Hz, 1H), 6.35 (s, 1H), 6.24 (q, J = 2.78 Hz, 1H).

6-(4''-Iodophenyl)-5,5'-bis(4'-methylphenyl)pyrromethene (5a): The mixture of **4a** (107.0 mg, 0.68 mmol) and 4-iodobenzoyl chloride (426.0 mg, 1.6 mmol) in 1,2-dichloroethane (3.5 mL) was refluxed for 18 h at 83 °C under nitrogen atmosphere. The mixture was washed with H_2O and brine. The aqueous layer was extracted with CH_2Cl_2, dried with $MaSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography on basic alumina (elution solvent: ethyl acetate/hexane = 1/5) to give the desired compound **5a** (59.0 mg, 34%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.99-7.93 (m, 6H), 7.47-7.40 (m, 7H), 6.96 (d, J = 4.27 Hz, 2H), 6.80 (d, J = 4.27 Hz, 2H), 2.58 (s, 6H).

6-(4''-Iodophenyl)-5,5'-bis(3'-methoxyphenyl)pyrro-

methene (5b): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 13.64 (s, 1H), 7.81 (d, *J* = 8.16 Hz, 2H), 7.48 (m, 4H), 7.36 (t, *J* = 7.84 Hz, 2H), 7.28 (d, *J* = 8.17 Hz, 2H), 6.94 (dd, *J* = 2.27 Hz, 1.98 Hz, 2H), 6.83 (d, *J* = 4.33 Hz, 2H), 6.66 (d, *J* = 4.32 Hz, 2H), 3.90 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.1, 154.4, 141.6, 138.1, 137.0, 136.7, 134.4, 132.6, 129.9, 129.6, 118.9, 116.2, 115.0, 111.0, 95.0, 55.3.

6-(4''-Iodophenyl)-5,5'-bis(4'-chlorophenyl) pyrromethene (5c): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 6H), 7.49 (d, *J* = 8.53 Hz, 4H), 7.28 (d, *J* = 8.32 Hz, 4H), 6.81 (d, *J* = 4.36, 2H), 6.68 (d, *J* = 4.32 Hz, 2H).

4,4-Difluoro-8-(4'-iodophenyl)-3,5-bis(4'-methylphenyl)-4-bora-3a,4a-diaza-*s*-indancene (6a): After stirred mixture of **5a** (20.0 mg, 0.038 mmol) and Et_3N (12.0 mg, 0.12 mmol) in toluene (1.1 mL) for 10 min under nitrogen atmosphere, BF_3OEt_2 (28.0 mg, 0.2 mmol) was added to reaction mixture and then, refluxed for 30 min at 80 °C. The reaction mixture was cooled to room temperature and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (elution solvent: ethyl acetate/hexane = 1/5) and basic alumina (elution solvent: methylene chloride/hexane = 1/1) to give the desired compound **6a** (20.5 mg, 34%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.19 Hz, 1.44 Hz, 2H) 7.71 (d, *J* = 8.18 Hz, 4H), 7.24 (dd, *J* = 8.22 Hz, 1.40 Hz, 2H), 7.18-7.15 (m, 4H), 6.75 (d, *J* = 4.27 Hz, 2H), 6.54 (d, *J* = 4.24 Hz, 2H), 2.31 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.6, 142.1, 140.3, 137.9, 136.4, 134.4, 132.5, 130.7, 130.1, 129.8, 129.5, 121.4, 96.8, 21.9.

4,4-Difluoro-8-(4'-iodophenyl)-3,5-bis(3'-chloroyphenyl)-4-bora-3a,4a-diaza-*s*-indancene (6d): The mixture of **4d** (128.0 mg, 0.72 mmol) and 4-iodobenzoyl chloride (88.7 mg, 0.36 mmol) in 1,2-dichloroethane (4.9 mL) was refluxed for 48 h at 83 °C under nitrogen atmosphere. The mixture was cooled to room temperature and then, Et_3N (214.0 mg, 2.12 mmol) was added to reaction mixture. After stirred for 5 min, BF_3OEt_2 (499.0 mg, 3.52 mmol) was added and then, the reaction mixture was refluxed at 80 °C for 30 min. After concentration under reduced pressure, the residue was purified by column chromatography on silica gel (elution solvent: methylene chloride/hexane = 1/1) followed by column chromatography on neutral alumina (elution solvent: methylene chloride/hexane = 1/1) to give the desired compound **6d** (51.0 mg, 23%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.81 (dt, *J* = 6.52 Hz, 1.91 Hz, 2H), 7.77 (d, *J* = 1.79 Hz, 2H), 7.38-7.37 (m, 4H), 7.33-7.31 (m, 2H), 6.89 (d, *J* = 4.18 Hz, 2H), 6.63 (d, *J* = 4.17 Hz, 2H).

4,4-Difluoro-8-(4'-iodophenyl)-3,5-bis(3'-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indancene (6b): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.43 Hz, 2H), 7.52 (t, *J* = 1.88 Hz, 2H), 7.42 (d, *J* = 7.68 Hz, 2H), 7.33-7.29 (m, 4H), 6.96 (dd, *J* = 2.28 Hz, 2.32 Hz, 2H), 6.84 (d, *J* = 4.27Hz, 2H), 6.64 (d, *J* = 4.21 Hz, 2H), 3.84 (s, 6H).

4,4-Difluoro-8-(4'-iodophenyl)-3,5-bis(4'-chloroyphenyl)-4-bora-3a,4a-diaza-*s*-indan-cene (6c): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.30, 2H), 7.80 (dd, *J* = 2.28 Hz, 1.77 Hz, 4H), 7.41 (d, *J* = 10.92 Hz, 4H), 7.32 (d, *J* = 8.20 Hz, 2H), 6.88 (d, *J* = 4.24 Hz, 2H), 6.63 (d, *J* = 4.25 Hz, 2H).

4,4-Difluoro-8-(4'-iodophenyl)-3,5-bis(4'-biphenyl)-4-bora-3a,4a-diaza-*s*-indancene (6f): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.39 Hz, 4H), 7.90 (d, *J* = 8.25 Hz, 2H), 7.68-7.62 (m, 8H), 7.44 (t, *J* = 7.56 Hz, 4H), 7.35 (t, *J* = 8.00 Hz, 4H), 6.88 (d, *J* = 4.30 Hz, 2H), 6.71 (d, *J* = 4.27, 2H).

4,4-Difluoro-8-(4'-iodophenyl)-3,5-bis(2'-naphthyl)-4-bora-3a,4a-diaza-*s*-indancene (6g): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 2H), 8.00 (dd, *J* = 8.59 Hz, 1.67 Hz, 2H), 7.92-7.81 (m, 8H), 7.49-7.46 (m, 4H), 7.36 (d, *J* = 8.24 Hz, 2H), 6.91 (d, *J* = 4.28 Hz, 2H), 6.77 (d, *J* = 4.24 Hz, 2H).

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