Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Copper(II)-Promoted Oxidative C−H/C−H Cross-Coupling for A Rapid Access to Aza-BODIPY-indole Derivatives with Broad Optical Absorption

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I. General remarks

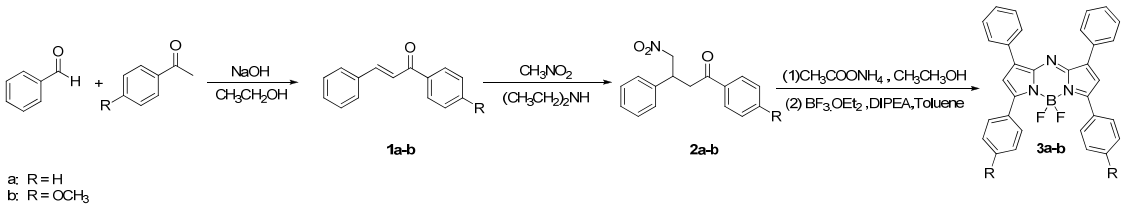
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Agilent 400-MR DD2 spectrometer. The ^{1}H NMR chemical shifts were measured relative to $CDCl_3$, CD_3CN or TMS as internal reference ($CDCl_3$: δ = 7.26 ppm; CD_3CN: δ = 1.94 ppm; TMS: δ = 0.00 ppm). The ^{13}C NMR chemical shifts were given using $CDCl_3$ as internal standard ($CDCl_3$: δ = 77.16 ppm). High-resolution mass spectra (HRMS) were obtained with Waters-Q-TOF-Premier (ESI). Melting points were measured with SGW®X-4/4A/4B and uncorrected. Absorption spectra were detected on HITACHI U-2910 absorption spectrophotometer. Cyclic voltammetries (CV) were performed on LK2005A at a scan rate of 50 $mV \cdot s^{-1}$ in dry CH_3CN solution of compounds containing 0.10 M of *tetra*-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. Ag/Ag^{+} (0.01 M of $AgNO_3$ in CH_3CN) was employed as a reference electrode. A platinum wire was used as a counter electrode and a platinum plate as a working electrode. Energy levels were calculated with respect to a standard ferrocene/ferrocenium (Fc/Fc^{+}) redox couple as an external reference.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Anhydrous solvents were freshly distilled from CaH_2 (dimethylsulfoxide (DMSO), dimethylformimide (DMF), acetonitrile (CH_3CN), dichloroethane(DCE)) or sodium/benzophenone (toluene, tetrahydrofuran (THF)) before using. $TBAPF_6$ was recrystallized from ethanol and further dried under vacuum for 48 h. All syntheses and manipulations were carried out under an N_2 atmosphere.

TBAF: tetrabutylammonium fluoride; TBAC: tetrabutylammonium chloride; TBAB: tetrabutylammonium bromide; TBAI: tetrabutylammonium iodide.

II. Synthesis and characterization

i) Synthesis of aza-BODIPYs



Scheme S1 Synthetic routes toward aza-BODIPYs. Intermediates **1** and **2** were prepared according to the literatures[S1].

Compound 3a: 2a (13.46 g, 50 mmol), ammonium acetate (96.31 g, 1.25 mol) and ethanol (250 mL) were heated under reflux for 24 h. During the reaction, the intermediate product precipitated as a blue-black solid. The reaction was allowed to cool to room temperature and solid was filtered and washed with ethanol. After the intermediate product was dried by vacuum oven at 40 ^{o}C, it was dissolved in toluene (150 mL). Diisopropylethylamine (DIPEA, 19.83 mL, 120 mmol) and boron trifluoride diethyl etherate (BF_3·OEt_2, 19.75 mL, 160 mmol) were added and then the mixture was refluxed for 3 h. The mixture was washed with water and the organic layer was collected, dried over Na_2SO_4 and evaporated under vacuum. The residue was washed by hot ethanol twice to give the product as a metallic brown solid. Yield: 7.96 g (32%). M.p.: 231.7-232.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02-8.08(m, 8H), 7.40-7.55(m, 12H), 7.04(s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ= 119.3, 128.75, 128.78, 129.5, 129.66, 129.7, 129.8, 131.1, 131.7, 132.4, 144.3, 159.7 ppm. HRMS (ESI^+): calcd for $C_{32}H_{22}BF_2N_3Na$ $[M+Na]^+$ 520.1773, found 520.1771.

Compound 3b: The synthetic procedure was the same as **3a**. **2b**（14.96 g, 50 mmol）was used instead of **2a**. **3b** was given as a metallic red solid. Yield: 9.50 g (34 %). M.p.: 201.1-201.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.89 (s, 6H), 6.01-7.04 (m, 6H), 7.44-7.46 (m, 6H), 8.06-8.10 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ= 55.6, 114.4, 118.8, 124.3, 128.7, 129.35, 129.41, 131.8, 132.6, 143.3, 145.5, 158.3, 162.0 ppm. HRMS (ESI^+): calcd for $C_{32}H_{27}BF_2N_3O_2$ $[M+H]^+$ 580.1984, found

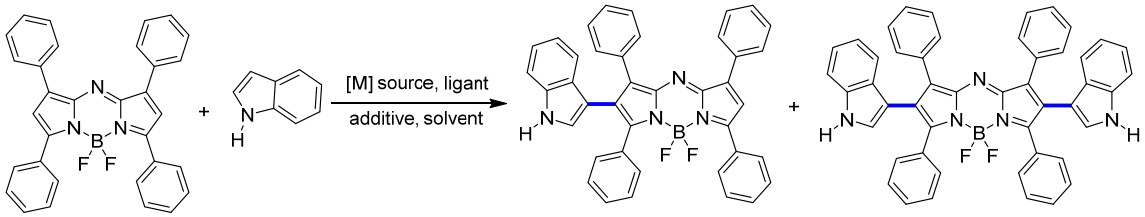
580.1976.

ii) Synthesis of aza-BODIPYs derivatives

1) Optimization of Copper(II)-Promoted Oxidative C−H/C−H Cross-Coupling

A 25 mL Schlenk tube with a magnetic stir bar was charged with **3a** (0.20 mmol), indole (0.60 mmol, 3.0 equiv.), metal source (20 mol%), ligand (50 mol%) and additive/oxidant (2.0 equiv.). The system was evacuated twice and back filled with N_2. Next, the solvent was added via a syringe and the rubber septum was replaced with a glass stopper under N_2. Then the reaction mixture was stirred at the indicated temperature for 2-24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was filtered through a celite pad, and then washed with CH_2Cl_2 (20-30 mL). The combined filtrate was concentrated and purified via column chromatography on silica gel (200-300 mesh) to provide the desired products.

Table S1. Optimization of the direct C–H/C–H arylation of aza-BODIPY 3a with indole[a]



3a **4** **5a** **5b**

Entry	[M] source	Ligand	Additive /Oxidant	Solvent	time (h)	Isolated yield (5a + 5b) /%[b]
1	$Pd(OAc)_2$	2,2'-bipyridine	Ag_2CO_3	toluene	12	15 (15+ trace)
2	$Pd(OAc)_2$	PPh_3	$Cu(OAc)_2$	toluene	12	14 (9+5)
3	$Pd(CF_3COO)_2$	2,2'-bipyridine	Ag_2CO_3	toluene	12	30 (20+10)
4	$CuBr_2$	2,2'-bipyridine	Ag_2CO_3	toluene	12	28 (13+15)
5	CuO	2,2'-bipyridine	Ag_2CO_3	toluene	12	28 (21+17)
6	CuI	2,2'-bipyridine	Ag_2CO_3	toluene	12	39 (25+14)
7	$Cu(OAc)_2$	2,2'-bipyridine	Ag_2CO_3	dioxane	12	ND[c]

8	$Cu_2(OH)_2CO_3$	2,2'-bipyridine	$Cu(OAc)_2$	CH_3CN/toluene (1:1)	12	43(20+23)
9[d]	$Cu(OAc)_2$	2,2'-bipyridine	/	CH_3CN/dioxane (1:1)	12	17 (7+10)
10[d]	$Cu(OAc)_2$	2,2'-bipyridine	/	CH_3CN/DCE (1:1)	12	ND[c]
11[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAB	CH_3CN/DCE (1:1)	12	52 (32+20)
12[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAC	CH_3CN/DCE (1:1)	12	ND[c]
13[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAI	CH_3CN/DCE (1:1)	12	36 (17+19)
14[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	12	68 (30+38)
15[d]	$Cu(OAc)_2$	PPh_3	TBAF	CH_3CN/DCE (1:1)	12	25 (14+10)
16[d]	$Cu(OAc)_2$	Pcy_3•HBF_4	TBAF	CH_3CN/DCE (1:1)	12	28 (15+13)
17[d]	$Cu(OAc)_2$	P^tBu_3•HBF_4	TBAF	CH_3CN/DCE (1:1)	12	trace
18[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	24	66 (34+32)
19[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	6	77 (35+42)
20[d]	**$Cu(OAc)_2$**	2,2'-bipyridine	**TBAF**	**CH_3CN/DCE (1:1)**	**2**	**83 (34+49)**
21[d]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	0.5	68 (45+23)
22[d,e]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	2	60 (23+37)
23[d,f]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	2	36 (11+25)
24[d,g]	$Cu(OAc)_2$	2,2'-bipyridine	TBAF	CH_3CN/DCE (1:1)	2	28 (7+21)

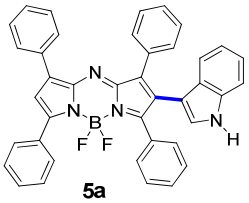
[a]Reaction conditions: **3a** (0.20 mmol), indole (0.60 mmol), palladium source (20 mol%) or copper source (20 mol%) ligand (50 mol%), additive (0.40 mmol) and solvent (1.0 mL) at 120 °C and reaction time under N_2 atmosphere, unless otherwise noted. [b]Total yield with **5a** and **5b** inside parenthesis. [c]not detected. [d]$Cu(OAc)_2$ (0.60 mmol). [e]100 °C. [f]80 °C. [g]60 °C.

$PCy_3 \cdot HBF_4$ = tricyclohexylphosphonium, P^tBu_3•HBF_4 = tri-tert-butyphosphine tetrafluoroborate.

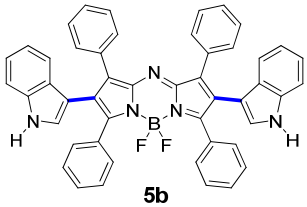
2) General procedure for direct C–H/C–H arylation of aza-BODIPYs with indoles

A 25 mL Schlenk tube with a magnetic stirbar was charged with **3a** or **3b** (0.20 mmol), indoles (3.0 equiv.), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.). The system was evacuated twice and back filled with N_2. Then, DCE (0.5 mL) and CH_3CN (0.5 mL) was added via a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at 120 ºC for 2 h in an oil bath. After the reaction mixture

was cooled to ambient temperature, the solvent was removed under reduced pressure. The solvent was filtered through a Celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified via column chromatography on silica gel (200-300 mesh) to provide the desired products.



5a



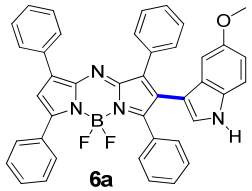
5b

Following the general procedure, the mixture of **aza-BODIPY 3a** (99.4 mg, 0.20 mmol), indole (70.24 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/4/1, v/v) afforded the monoarylated product **5a** (41.6 mg) in 34% yield and the diarylated product **5b** (71.3 mg) in 49% yield.

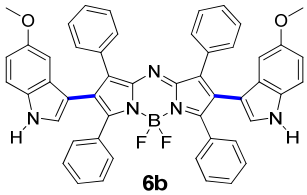
5a: A brown solid with metallic lustre. M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.70 (s, 1H), 6.85 (t, *J*= 8.0 Hz, 1H), 6.93 (d, *J*= 8.0 Hz, 1H), 7.04 (s, 1H), 7.10 (t, *J*= 8.0 Hz, 1H), 7.24-7.26 (m, 5H), 7.30 (d, *J*= 8.0 Hz, 2H), 7.41-7.44 (m, 6H), 7.53 (d, *J*= 8.0 Hz, 2H), 7.61 (d, *J*= 8.0 Hz, 2H), 8.00-8.01 (m, 2H), 8.11-8.12 (m, 3H) ppm. HRMS (ESI$^+$): calcd for $C_{40}H_{28}BF_2N_4$ $[M+H]^+$ 613.2375, found 613.2372.

5b: A wine-red solid. M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.70 (s, 2H), 6.85 (t, *J*= 8.0 Hz, 2H), 6.96 (d, 8.0 Hz, 2H), 7.10 (t, *J*= 8.0 Hz, 2H), 7.18-7.21 (m, 12H), 7.30 (d, *J*= 8.0 Hz, 2H), 7.49 (d, *J*= 8.0 Hz, 4H), 7.63 (d, *J*= 8.0 Hz, 4H), 8.09 (s, 2H) ppm. HRMS (ESI$^+$): calcd for $C_{48}H_{33}BF_2N_5$ $[M+H]^+$ 728.2797, found

728.2792.



6a

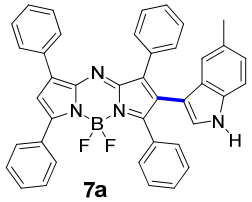


6b

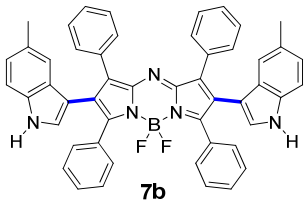
Following the general procedure, the mixture of **aza-BODIPY 3a** (99.4 mg, 0.20 mmol), 5-methoxyindole (88.3 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/4/1, v/v) afforded the monoarylated product **6a** (56.5 mg) in 44% yield and the diarylated product **6b** (75.6 mg) in 48% yield.

6a: A brown solid with a metallic lustre. M.p.: 202.2-202.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.42 (s, 3H), 6.29 (s, 1H), 6.61 (s, 1H), 6.73 (d, *J*= 8.0 Hz, 1H), 7.03 (s, 1H), 7.16 (d, *J*= 8.0 Hz, 1H), 7.26-7.29 (m, 5H), 7.34 (d, *J*= 4.0 Hz, 1H), 7.41-7.44(m, 6H), 7.55 (d, *J*= 8.0 Hz, 2H), 7.63 (d, *J*= 8.0 Hz, 2H), 7.99-8.01 (m, 3H), 8.12 (d, *J*= 8.0 Hz, 2H) ppm. HRMS (ESI^+): calcd for $C_{41}H_{30}BF_2N_4O$ $[M+H]^+$ 643.2481, found 643.2493.

6b: A wine-red solid. M.p.: >250 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.43 (s, 6H), 6.31 (s, 2H), 6.62 (s, 2H), 6.73 (d, *J*= 8.0 Hz, 2H), 7.16-7.24 (m, 12H), 7.26-7.31 (m, 2H), 7.51 (d, *J*= 8.0 Hz, 4H), 7.64 (d, *J*= 8.0 Hz, 4H), 7.98 (s, 2H) ppm. HRMS (ESI^+): calcd for $C_{50}H_{37}BF_2N_5O_2$ $[M+H]^+$ 788.3008, found 788.3001.



7a

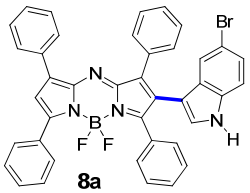


7b

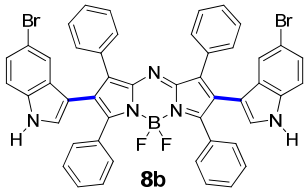
Following the general procedure, the mixture of **aza-BODIPY 3a** (99.4 mg, 0.20 mmol), 5-methylindole (78.7 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/4/1, v/v) afforded the monoarylated product **7a** (75.2 mg) in 60% yield and the diarylated product **7b** (51.4 mg) in 34% yield.

7a: A brown solid with a metallic lustre. M.p.: 224.7-225.4 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.17 (s, 3H), 6.62 (s, 1H), 6.68 (s, 1H), 6.91 (d, *J*= 8.0 Hz, 1H), 7.03(s, 1H), 7.15 (d, *J*= 8.0 Hz, 1H), 7.24-7.26 (m, 4H), 7.29-7.31 (m, 2H), 7.42-7.44 (m, 6H), 7.55 (d, *J*= 8.0 Hz, 2H), 7.63(d, *J*= 8.0 Hz, 2H), 7.97-8.01 (m, 3H), 8.13 (d, *J*= 8.0 Hz, 2H) ppm. HRMS (ESI^+): calcd for $C_{41}H_{29}BF_2N_4Na$ $[M+Na]^+$ 649.2351, found 649.2353.

7b: A wine-red solid. M.p.: >250 °C.^{1}H NMR (400 MHz, CDCl3): δ= 2.17 (s, 6H), 6.65 (s, 2H), 6.70 (s, 2H), 6.91 (d, *J*= 8.0 Hz, 2H), 7.17-7.21 (m, 14H), 7.50 (d, *J*= 8.0 Hz, 4H), 7.63 (d, *J*= 8.0 Hz, 4H), 7.98 (s, 2H) ppm. HRMS (ESI^+): calcd for $C_{50}H_{36}BF_2N_5Na$ $[M+Na]^+$ 778.2930, found 778.2938.



8a

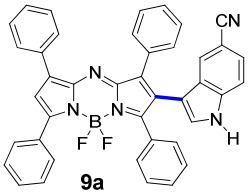


8b

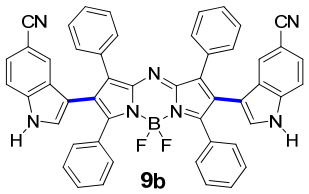
Following the general procedure, the mixture of **aza-BODIPY 3a** (99.4 mg, 0.20 mmol), 5-bromoindole (117.6 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/2/1, v/v) afforded the monoarylated product **8a** (60.73 mg) in 44% yield and the diarylated product **8b** (86.5 mg) in 49% yield.

8a: A brown solid. M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.72 (s, 1H), 7.06 (s, 1H), 7.06 (s, 1H), 7.17 (s, 2H), 7.26-7.35 (m, 6H), 7.42-7.45 (m, 6H), 7.52 (d, *J*= 8.0 Hz, 2H), 7.58 (d, *J*= 8.0 Hz, 2H), 8.01 (bs, 2H), 8.11-8.13 (m, 3H) ppm. HRMS (ESI^-): calcd for $C_{42}H_{26}BBrF_2N_4Na$ $[M+Na]^+$ 713.1300, found 713.1304.

8b: A brown solid. M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.71 (s, 2H), 7.03 (s, 2H), 7.17 (bs, 4H), 7.20-7.23 (m, 8H), 7.26 (bs, 4H), 7.48 (d, *J*= 8.0 Hz, 4H), 7.59 (d, *J*= 8.0 Hz, 4H), 8.11 (s, 2H) ppm. HRMS (ESI^+): calcd for $C_{48}H_{30}BBr_2F_2N_5Na$ $[M+Na]^+$ 908.0806, found 908.0804.



9a

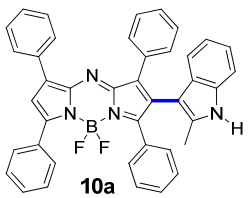


9b

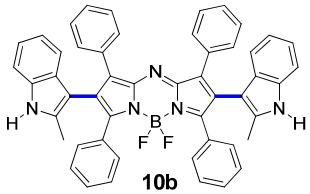
Following the general procedure, the mixture of **aza-BODIPY 3a** (99.4 mg, 0.20 mmol), 5-cyanoindole (78.7 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/2/1, v/v) afforded the monoarylated product **9a** (35.7 mg) in 28% yield and the diarylated product **9b** (15.5 mg) in 10% yield.

9a: A black solid. M.p.: >250 °C.^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.82 (s, 1H), 7.08 (s, 1H), 7.22-7.26 (m, 5H), 7.28-7.32 (m, 4H), 7.43-7.46 (m, 6H), 7.49 (d, *J*= 8.0 Hz, 2H), 7.54(d, *J*= 8.0 Hz, 2H), 8.02 (bs, 2H), 8.11-8.13 (m, 2H), 8.38 (s, 1H) ppm. HRMS (ESI$^-$): calcd for $C_{41}H_{25}BF_2N_5$ $[M-H]^-$ 636.2171, found 636.2173.

9b: A black solid. M.p.: >250 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.11 (d, *J* = 4.0 Hz, 2H), 7.24-7.35 (m, 14H), 7.37 (s, 2H), 7.45-7.49 (t, *J* = 8.0 Hz, 6H), 7.56 (d, *J* = 1.6 Hz, 2H), 7.57 (d, *J* = 1.6 Hz, 2H), 9.75 (s, 2H) ppm. HRMS (ESI$^+$): calcd for $C_{50}H_{30}BF_2N_7Na$ $[M+Na]^+$ 800.2522, found 800.2523.



10a

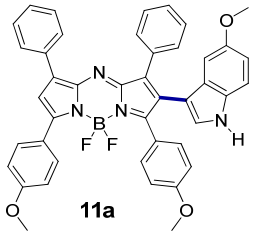


10b

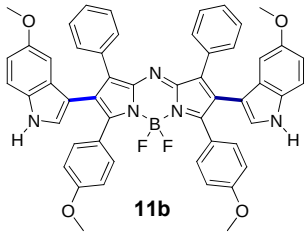
Following the general procedure, the mixture of **aza-BODIPY 3a** (99.4 mg, 0.20 mmol), 2-methylindole (78.7 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/4/1, v/v) afforded the monoarylated product **10a** (68.9 mg) in 55% yield and the diarylated product **10b** (58.9 mg) in 39% yield.

10a: A bronw solid with a gold metalliclustre. M.p.: 203.7-204.5 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.81 (s, 3H), 6.85 (t, *J*= 8.0 Hz, 1H), 6.97 (d, *J*= 8.0 Hz, 1H), 7.03-7.05 (m, 2H), 7.19-7.26 (m, 7H), 7.43-7.45(m, 6H), 7.53 (d, *J*= 8.0 Hz, 2H), 7.60 (d, *J*= 8.0 Hz, 2H), 7.84 (s, 1H), 8.02 (s, 2H), 8.14 (d, *J*= 4.0 Hz, 2H) ppm. HRMS (ESI^+): calcd for $C_{41}H_{29}BF_2N_4Na$ $[M+Na]^+$ 649.2351, found 649.2346.

10b: A wine-red solid. M.p.: >250 °C.^{1}H NMR (400 MHz, CDCl3): δ = 1.81 (s, 6H), 6.86-6.88 (m, 2H), 6.97 (bs, 2H), 7.04 (t, *J* = 8.0 Hz, 2H), 7.15-7.21 (m, 14H), 7.49 (d, *J* = 8.0 Hz, 4H), 7.63 (d, *J* = 4.0 Hz, 4H), 7.83 (s, 2H) ppm. HRMS (ESI^+): calcd for $C_{50}H_{36}BF_2N_5$ $[M+Na]^+$ 778.2930, found 778.2925.



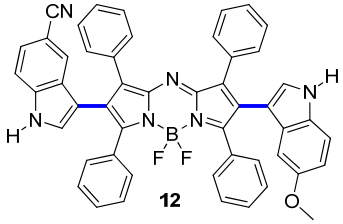
11a



Following the general procedure, the mixture of **aza-BODIPY 3b** (111.5 mg, 0.20 mmol), 5-methoxyindole (88.3 mg, 0.60 mmol), $Cu(OAc)_2$ (109.0 mg, 3.0 equiv.), 2,2'-bipyridine (15.6 mg, 50 mol%), TBAF (104.6 mg, 2.0 equiv.), DCE (0.5 mL) and CH_3CN (0.5 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/2/1, v/v) afforded the monoarylated product **11a** (60.4 mg) in 43% yield and the diarylated product **11b** (67.8 mg) in 40% yield.

11a: A black solid. M.p.: >250 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.44 (s, 3H), 3.79 (s, 3H), 3.87 (s, 3H), 6.33 (s, 1H), 6.67 (s, 1H), 6.75 (d, J = 12 Hz, 1H), 6.79 (d, J = 18 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 7.05 (s, 1H), 7.18-7.26 (m, 4H), 7.40-7.42 (m, 3H), 7.53 (d, J= 8.0 Hz, 2H), 7.61 (d, J = 4.0 Hz, 2H), 8.00 (s, 1H), 8.05 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H) ppm. HRMS (ESI$^-$): calcd for $C_{43}H_{33}BF_2N_4O_3Na$ $[M+Na]^+$ 725.2511, found 725.2511.

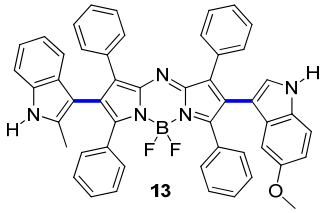
11b: A black solid. M.p.: 212.3-212.9 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.45 (s, 6H), 3.77 (s, 6H), 6.34 (s, 2H), 6.67 (s, 2H), 6.75 (d, J = 8 Hz, 6H), 7.19-7.20 (m, 8H), 7.50 (d, J= 8.0 Hz, 4H), 7.62 (d, J= 4.0 Hz, 4H), 8.00 (s, 2H) ppm. HRMS (ESI$^+$): calcd for $C_{52}H_{40}BF_2N_5O_4Na$ $[M+Na]^+$ 870.3039, found 870.3043.



Following the general procedure, the mixture of mono-arylated **aza-BODIPY 6a** (64.2 mg, 0.10 mmol), 5-cyanoindole (42.7 mg, 0.30 mmol), $Cu(OAc)_2$ (54.5 mg, 3.0

equiv.), 2,2'-bipyridine (7.8 mg, 50 mol%), TBAF (52.3 mg, 2.0 equiv.), DCE (0.25 mL) and CH_3CN (0.25 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/2/1, v/v) afforded the monoarylated product **12** (10.2 mg) in 13% yield.

12: A black solid. M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.43 (s, 3H), 6.28 (s, 1H), 6.60 (s, 1H), 6.74 (d, *J*= 8.0 Hz, 1H), 6.80 (s, 1H), 7.16-7.23 (m, 12H), 7.26-7.31(m, 4H), 7.45 (d, *J*= 8.0 Hz, 2H), 7.50-7.54 (m, 4H), 7.64 (d, *J*= 4.0 Hz, 2H), 8.02 (s, 1H), 8.38 (s, 1H) ppm. HRMS (ESI$^-$): calcd for $C_{50}H_{32}BF_2N_6O$ $[M-H]^-$ 781.2699, found 781.2636.



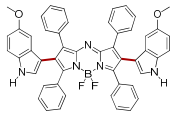
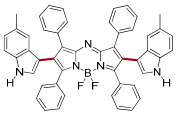
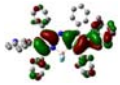
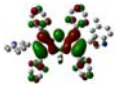
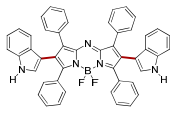
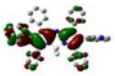
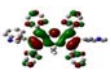
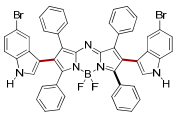
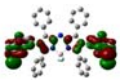
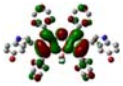
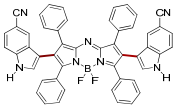
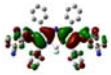
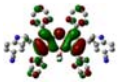
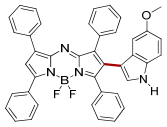
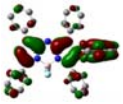
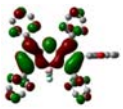
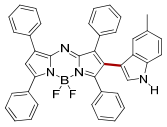
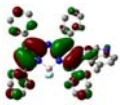
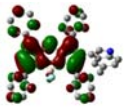
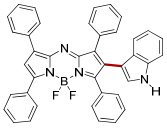
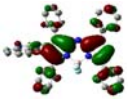
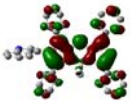
13

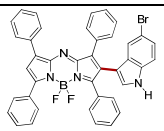
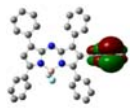
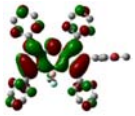
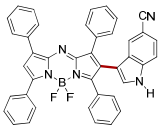
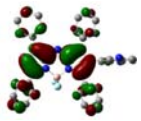
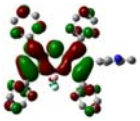
Following the general procedure, the mixture of mono-arylated **aza-BODIPY 6a** (64.2 mg, 0.10 mmol), 2-methylindole (39.4 mg, 0.30 mmol), $Cu(OAc)_2$ (54.5 mg, 3.0 equiv.), 2,2'-bipyridine (7.8 mg, 50 mol%), TBAF (52.3 mg, 2.0 equiv.), DCE (0.25 mL) and CH_3CN (0.25 mL) was stirred at 120 °C for 2 h. Purification via column chromatography on silica gel (Ethyl acetate/petroleum ether/dichloromethane = 1/10/1 to 1/2/1, v/v) afforded the monoarylated product **13** (57.1 mg) in 74% yield.

13: A black solid. M.p.: 222.3-222.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.81 (s, 3H), 3.44 (s, 3H), 6.31 (s, 1H), 6.63 (s, 1H), 6.74 (d, *J*= 8 Hz, 1H), 6.83-6.87 (m, 1H), 6.97 (d, *J* = 8 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 7.14-7.23 (m, 12H), 7.29-7.30 (m, 2H), 7.47-7.53 (m, 4H), 7.63 (t, *J* = 8.0 Hz, 4H), 7.83 (s, 1H), 7.97 (s, 1H) ppm. HRMS (ESI^+): calcd for $C_{50}H_{36}BF_2N_5ONa$ $[M+Na]^+$ 794.2879, found 794.2875.

III. UV-*vis*-NIR absorption spectra

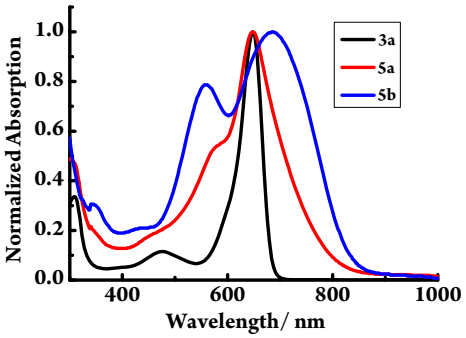
Table S2 Photoelectrical properties and calculated front orbital distributions of D-A-D and D-A compounds

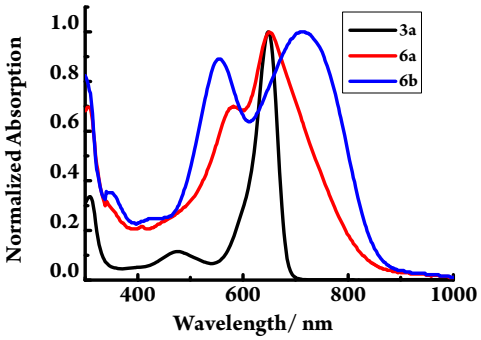
Compound	λ^{long}, λ^{short}/nm ($lg\varepsilon^{long}$, $lg\varepsilon^{short}$)	$\lambda_{cut\text{-}off}$/nm (E_g^{opt}/eV)[a]	HOMO[cal]/eV[b]	LUMO[cal]/eV[b]
 **6b**	713, 554 (4.3, 4.3)	429-900 1.38	 -5.00	 -2.89
 **7b**	685, 559 (4.4, 4.4)	435-890 1.39	 -5.06	 -2.92
 **5b**	685, 559 (4.5, 4.4)	443-859 1.44	 -5.10	 -2.94
 **8b**	678, 555 (4.6, 4.4)	433-839 1.48	 -5.25	 -3.07
 **9b**	667, 555 (4.3, 4.1)	336-832 1.49	 -5.44	 -3.12
 **6a**	650, 580 (4.5, 4.3)	410-825 1.50	 -5.29	 -3.02
 **7a**	647, 580 (4.5, 4.3)	443-788 1.57	 -5.26	 -3.04
 **5a**	648, 574 (4.6, 4.3)	417-770 1.61	 -5.27	 -3.05

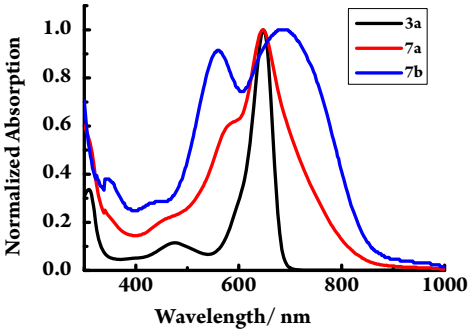
 **8a**	648, 562 (4.7, 4.3)	400-755 1.64	 -5.35	 -3.11
 **9a**	6487, 521 (4.7, 4.2)	418-749 1.66	 -5.44	 -3.19

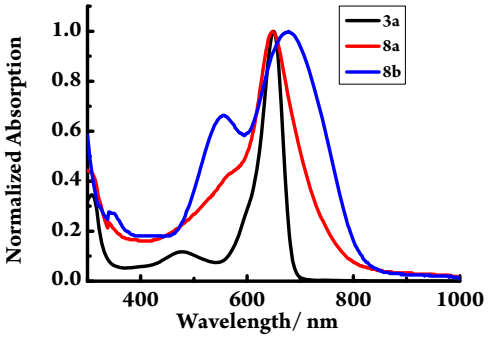
[a]Estimated from the edge of both ends of the absorption band in DCM, $E_g^{opt} = 1240/\lambda_{onset}$ [eV].

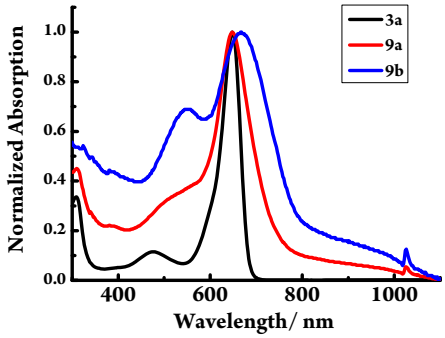
[b]From DFT calculation. For details, see the following part.

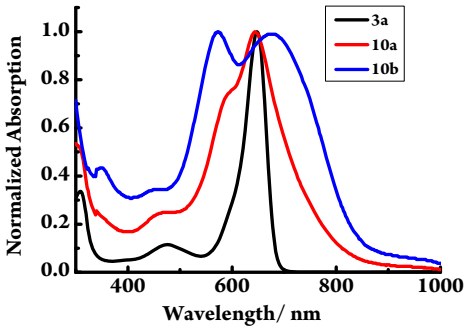












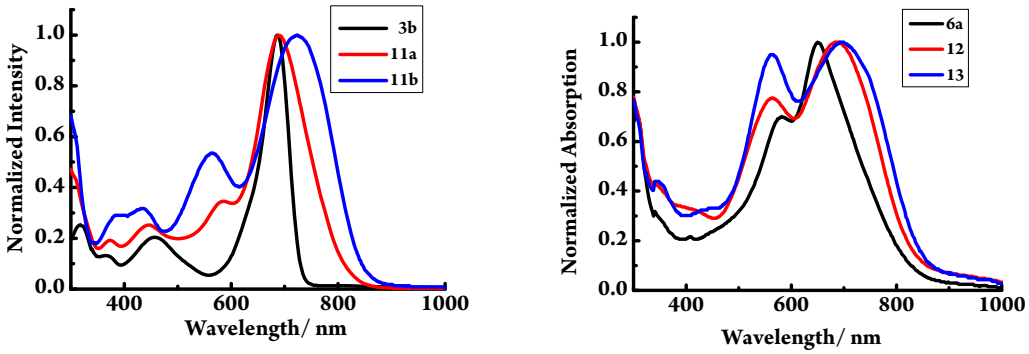


Figure S1 Normalized UV-*vis*-NIR absorption spectra of D-A and D-A-D compounds in CH_2Cl_2 ($c = 2.0 \times 10^{-5}$).

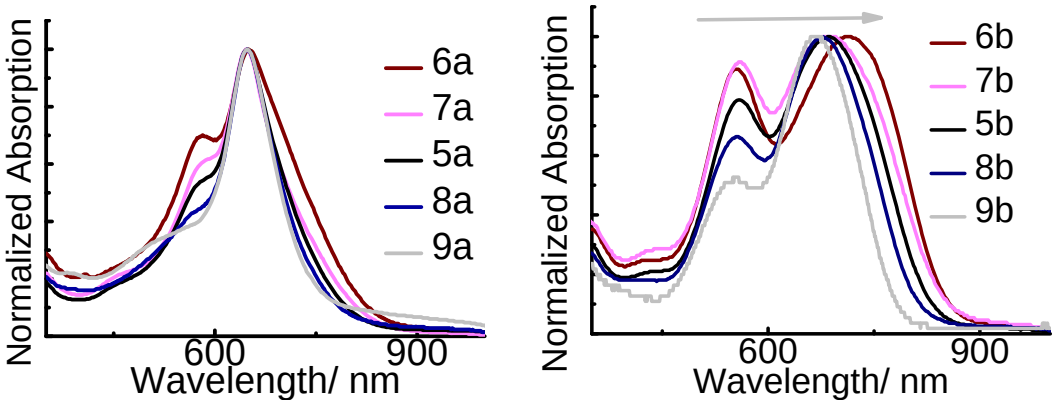
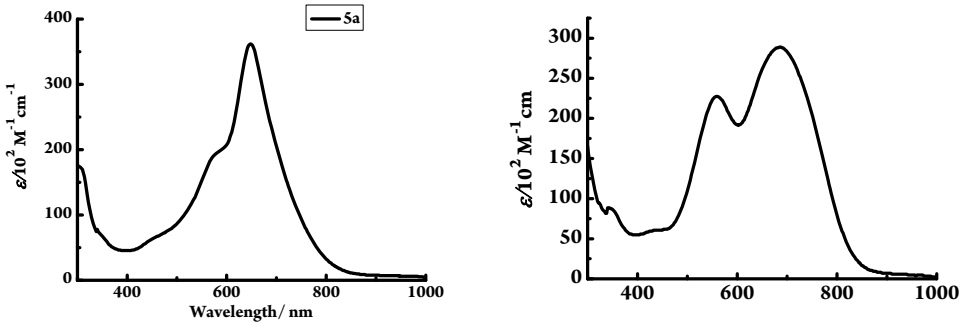
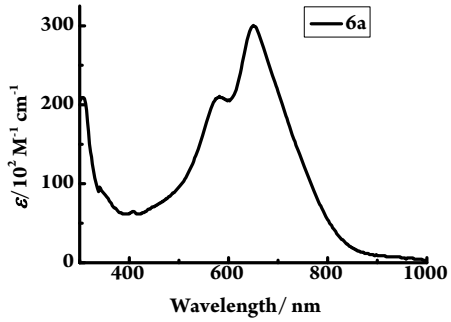
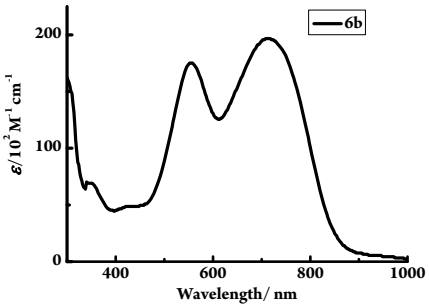
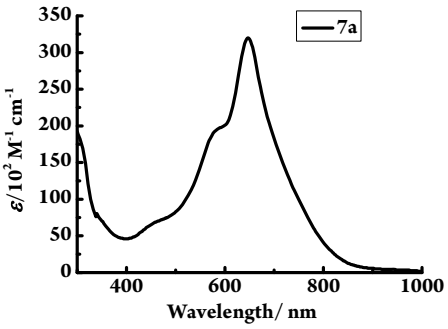


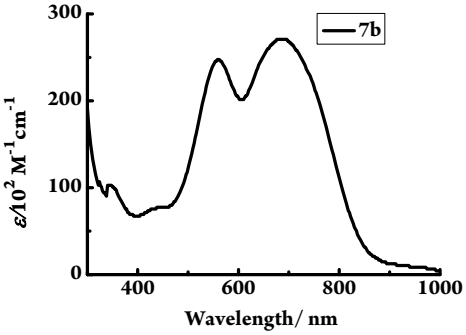
Figure S2 Normalized UV-*vis*-NIR absorption spectra of D-A and D-A-D compounds in CH_2Cl_2 ($c = 2.0 \times 10^{-5}$).

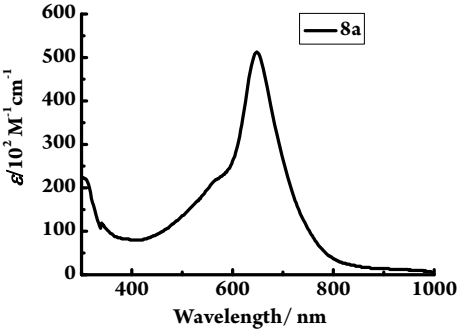


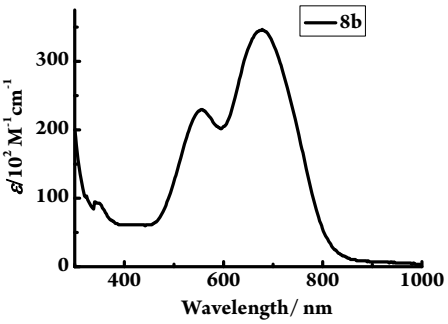

6a
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm

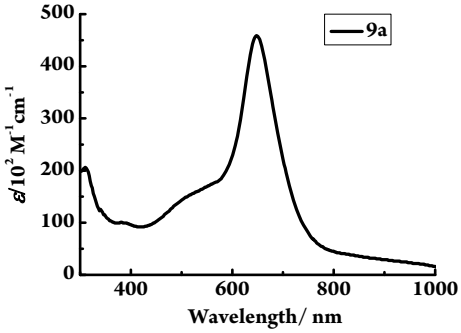

6b
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm

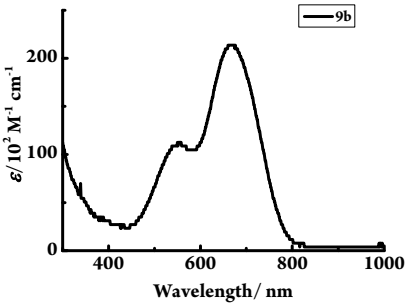

7a
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm


7b
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm


8a
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm


8b
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm


9a
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm


9b
ε/10² M⁻¹ cm⁻¹
Wavelength/ nm

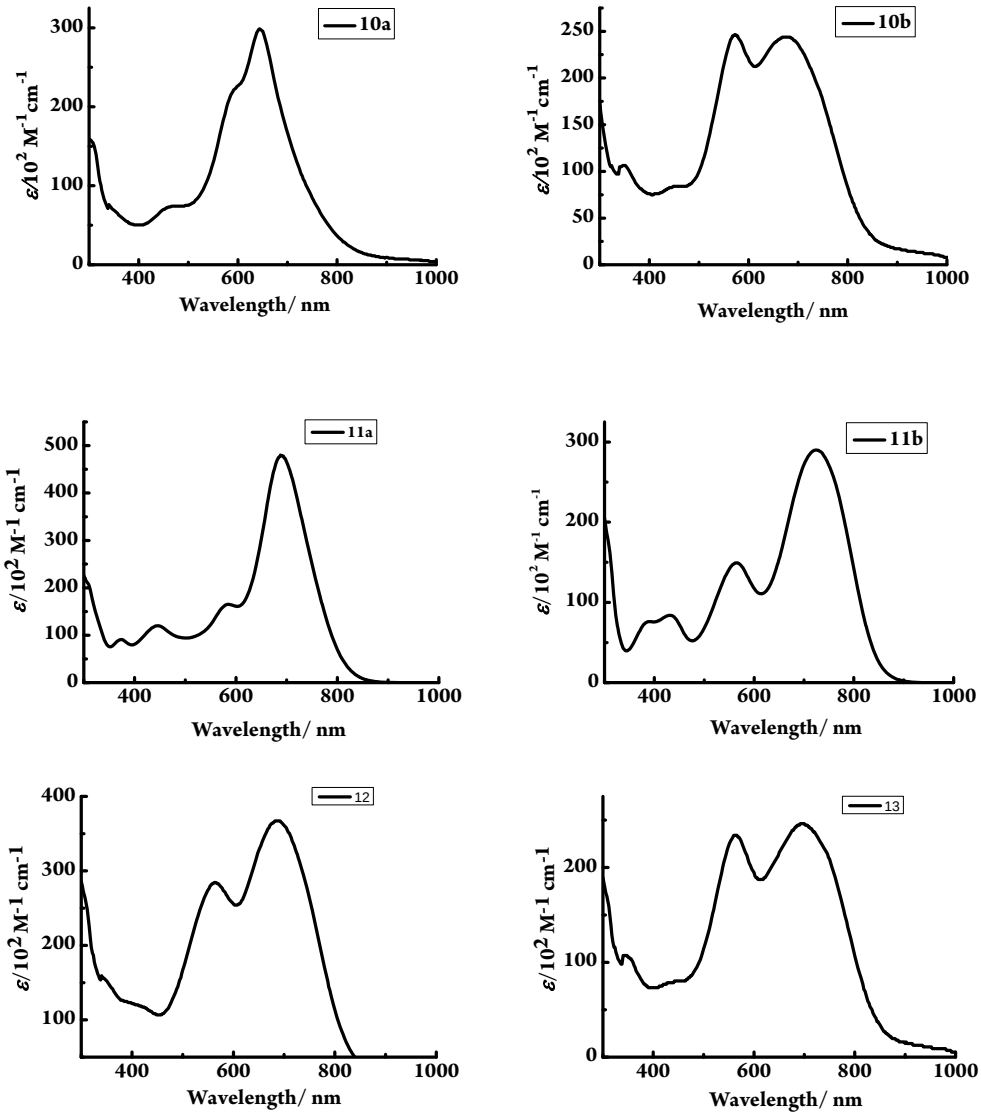
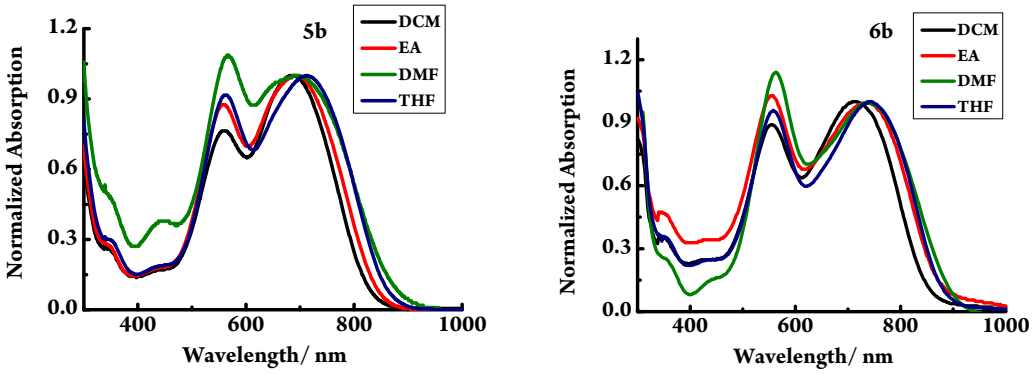


Figure S3 UV-*vis*-NIR Absorption spectra of D-A and D-A-D compounds in CH_2Cl_2 ($c = 2.0 \times 10^{-5}$).



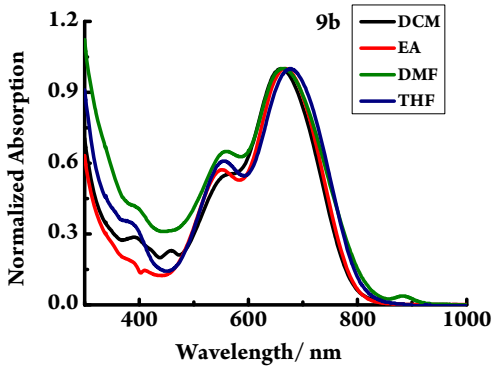
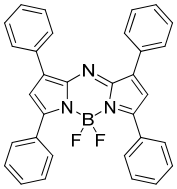
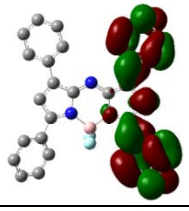


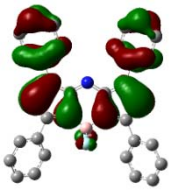
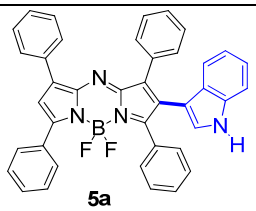
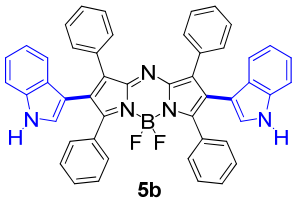
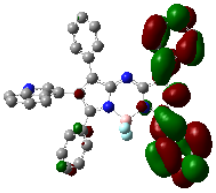
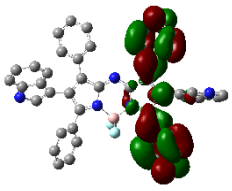
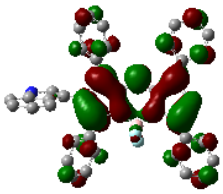
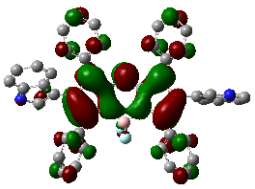
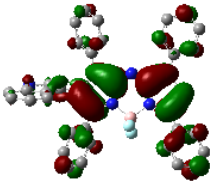
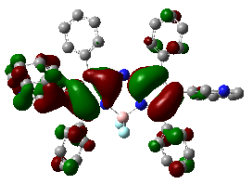
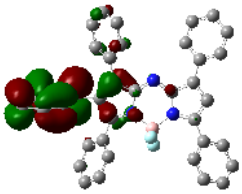
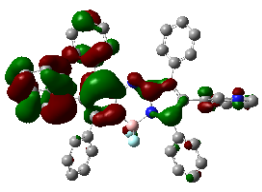
Figure S4 Normalized UV-*vis*-NIR absorption spectra of **5b**, **6b** and **9b** in different solvents ($c = 2.0 \times 10^{-5}$).

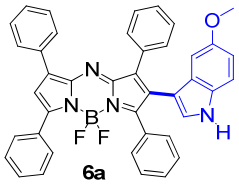
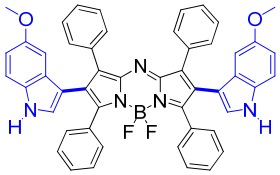
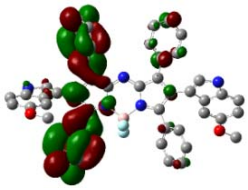
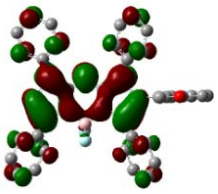
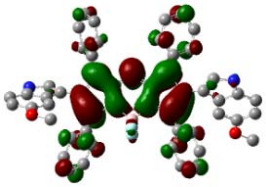
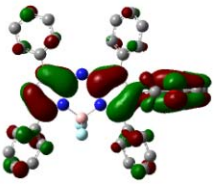
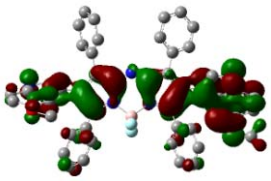
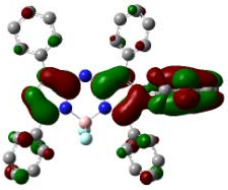
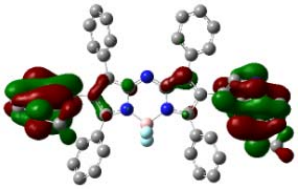
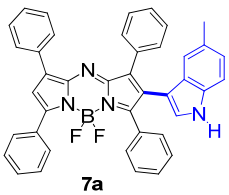
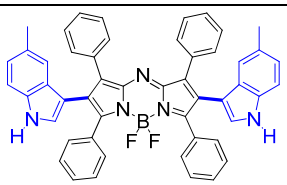
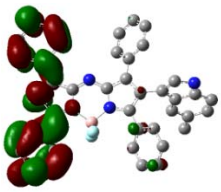
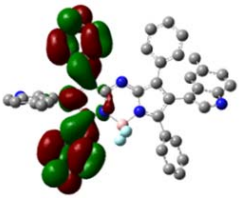
IV. DFT Computational detail

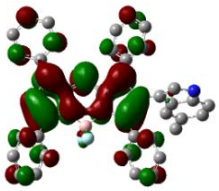
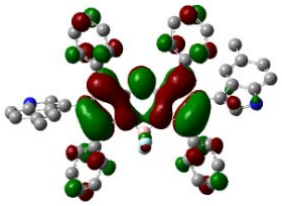
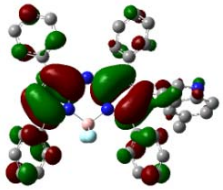
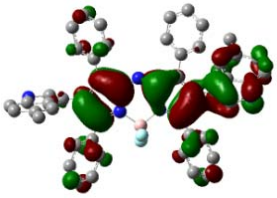
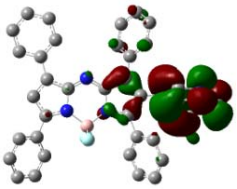
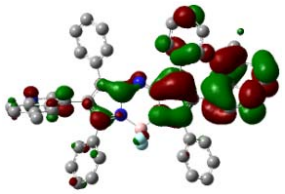
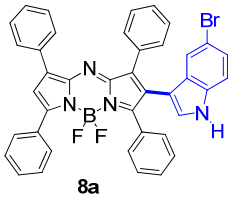
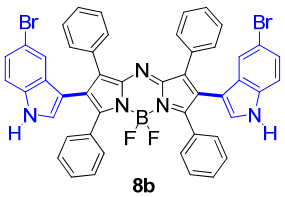
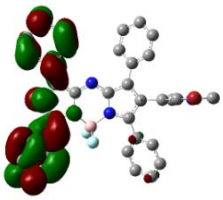
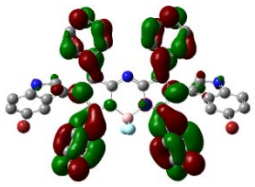
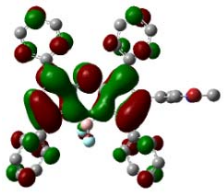
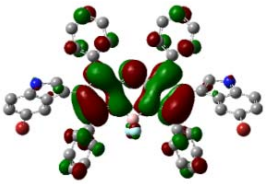
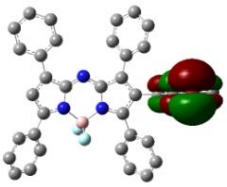
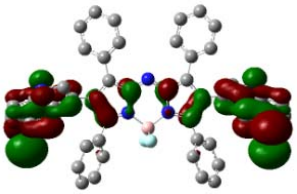
The calculations were performed at TDDFT/B3LYP/6–31G(d,p) level using Gaussian 03 package[S2]. Ground state geometries of aza-BODIPYs were fully optimized in gas phase at DFT/B3LYP/6–31G(d,p) level using the default convergence criteria without any constraints and confirmed by frequency calculations. Front orbital levels and distributions of the optimized structure are shown in **Table S3**.

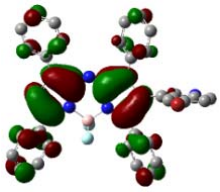
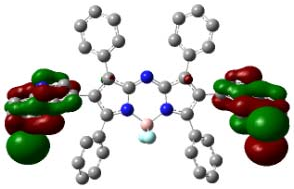
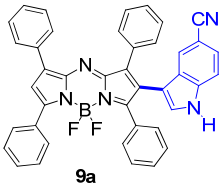
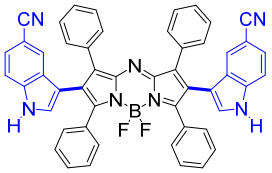
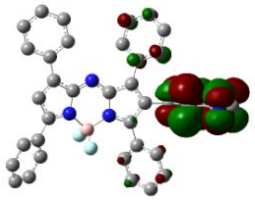
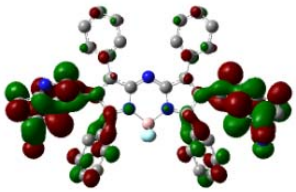
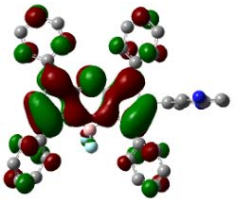
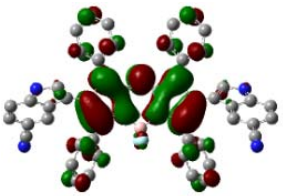
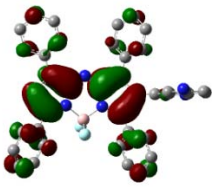
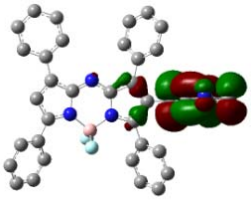
Table S3. Front orbital levels and distributions of the optimized structures

Molecule	
LUMO+1	
LUMO	

HOMO		
HOMO-1		
LUMO+1	-0.06 eV	
LUMO	-3.17 eV	
HOMO	-5.37 eV	
HOMO-1	-6.25 eV	
Band gap	2.20 eV	
Molecule	 5a	 5b
Dihedral	83.05 °	53.9 °
LUMO+1		
LUMO		
HOMO		
HOMO-1		
LUMO+1	-0.54 eV	-0.41 eV
LUMO	-3.05 eV	-2.94 eV
HOMO	-5.27 eV	-5.10 eV

HOMO-1	-5.55 eV	-5.45 eV
Band gap	2.22 eV	2.16 eV
Molecule	 6a	 6b
Dihedral	89.35 °	60.45 °
LUMO+1		
LUMO		
HOMO		
HOMO-1		
LUMO+1	-0.54 eV	-0.40 eV
LUMO	-3.06 eV	-2.89 eV
HOMO	-5.29 eV	-5.00 eV
HOMO-1	-5.46 eV	-5.19 eV
Band gap	2.23 eV	2.11 eV
Molecule	 7a	 7b
Dihedral	70.01 °	55.30 °
LUMO+1		

LUMO		
HOMO		
HOMO-1		
LUMO+1	-0.53 eV	-0.38 eV
LUMO	-3.04 eV	-2.92 eV
HOMO	-5.26 eV	-5.06 eV
HOMO-1	-5.50 eV	-5.40 eV
Band gap	2.22 eV	2.14 eV
Molecule	 8a	 8b
Dihedral	83.09 °	59.77 °
LUMO+1		
LUMO		
HOMO		

HOMO-1		
LUMO+1	-0.73 eV	-0.63 eV
LUMO	-3.11 eV	-3.07eV
HOMO	-5.35 eV	-5.25 eV
HOMO-1	-5.85 eV	-5.59 eV
Band gap	2.24 eV	2.18 eV
Molecule	 9a	 9b
Dihedral	88.91 °	58.14 °
LUMO+1		
LUMO		
HOMO		
HOMO-1		
LUMO+1	-1.15 eV	-1.04 eV
LUMO	-3.19 eV	-3.22 eV
HOMO	-5.44 eV	-5.44 eV
HOMO-1	-6.14 eV	-5.86 eV
Band gap	2.25 eV	2.22 eV

V. Electrochemical Properties

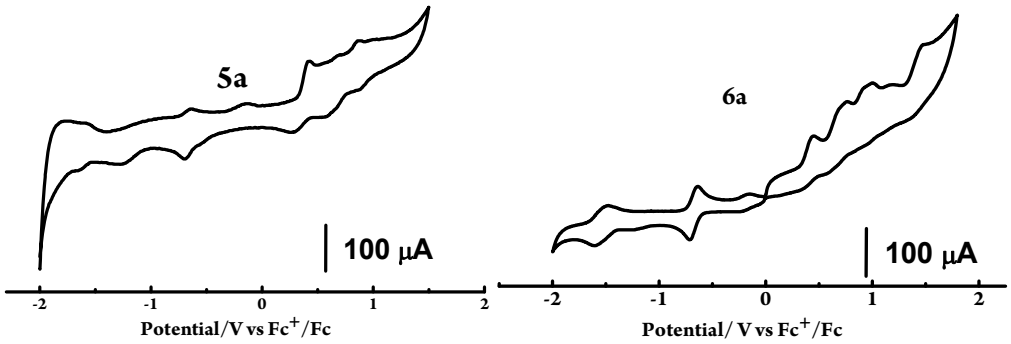


Fig. S5. Cyclic voltammogram of **5a** and **6a.**

Table S4. Energy levels**.**

Dye	E_{on}^{ox} [V][a]	HOMO [eV][b]	E_{on}^{red} [V][a]	LUMO [eV][c]	E_g^{cv} [eV][d]	E_g^{opt} [eV][e]	$E_g^{cal.}$ [eV][d]
3a	0.32	-5.46	-0.62	-4.02	1.44	1.78	2.20
5a	0.34	-5.14	-0.67	-4.13	1.01	1.61	2.22
5b	0.55	-5.35	-0.74	-4.06	1.29	1.44	2.16
6a	0.33	-5.13	-0.68	-4.12	1.01	1.50	2.23
6b	0.53	-5.33	-0.74	-4.06	1.27	1.38	2.11

[a] E_{on}^{ox} = Initiative reduction potential, E_{on}^{red} = Initiative reduction potential. [b] HOMO = - (4.80 + E_{on}^{ox}) (eV); [c] LUMO = - (4.80 + E_{on}^{red}) (eV); [d] $E_g^{cv} = E_{on}^{ox} - E_{on}^{red}$; [e] $E_g^{opt} = 1240/\lambda_{onset}$ (eV).

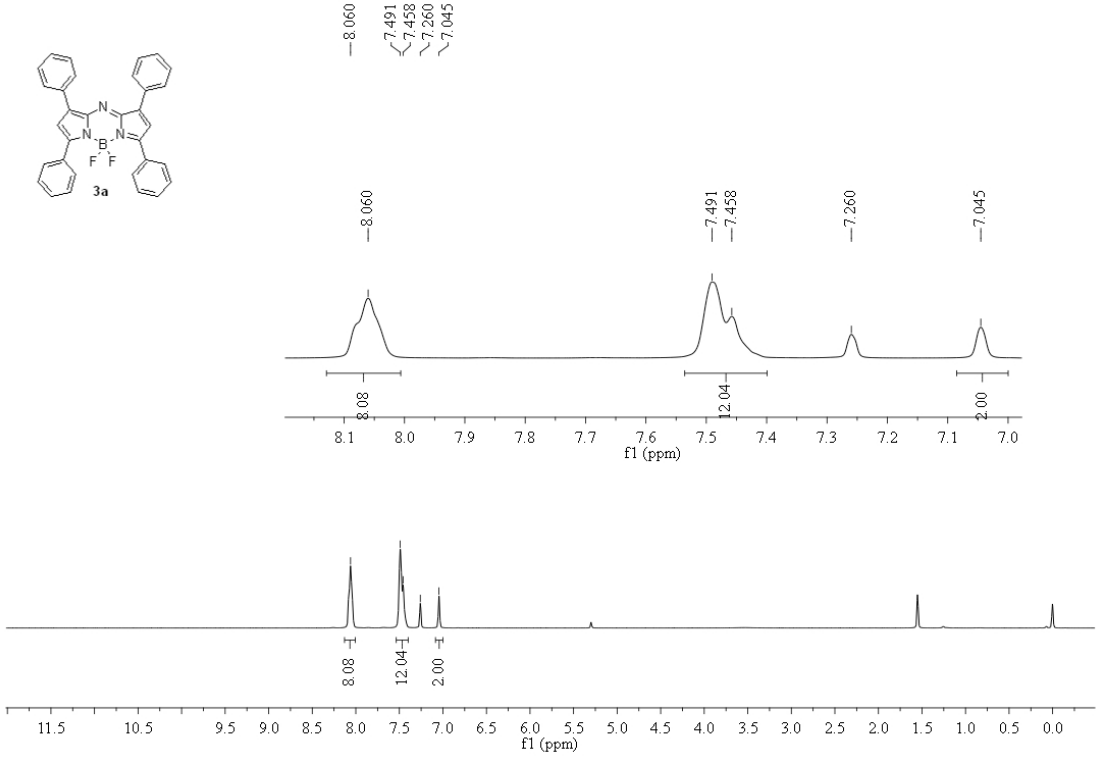
VI. Reference

S1. (a) R. Gresser, H. Hartmann, M. Wrackmeyer, K. Leo and M. Riede, *Tetrahedron*, **2011**, 67, 7148; (b) A. N. Amin, M. E. El-Khouly, N. K. Subbaiyan, M. E. Zandler, S. Fukuzumi and F. D'Souza, *Chem. Commun.,* **2012**, *48*, 206; (c) M.-Y. Chang, Y.-C. Chen and C.-K. Chan, *Tetrahedron*, **2014**, *70*, 2257; (d) R. Umeda, T. Mashino and Y. Nishiyama, *Tetrahedron*, **2014**, *70*, 4395.

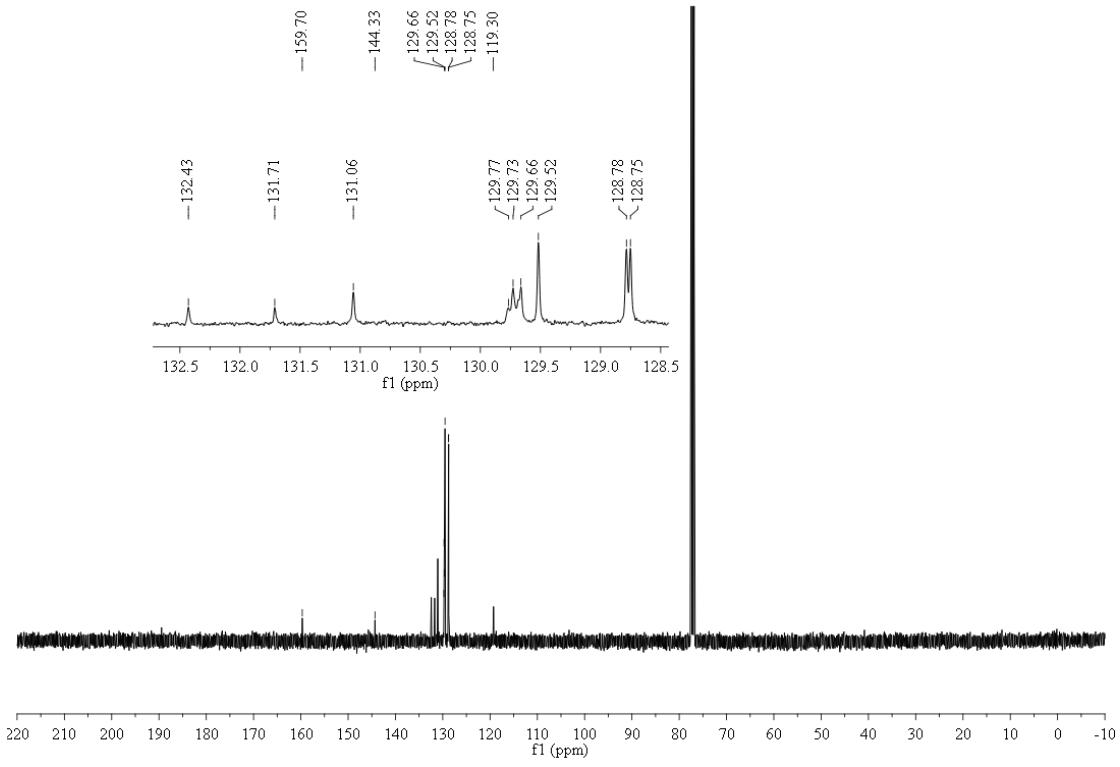
S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S.Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A.Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L.Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 03, revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2005.

VII. Copies of NMR spectra

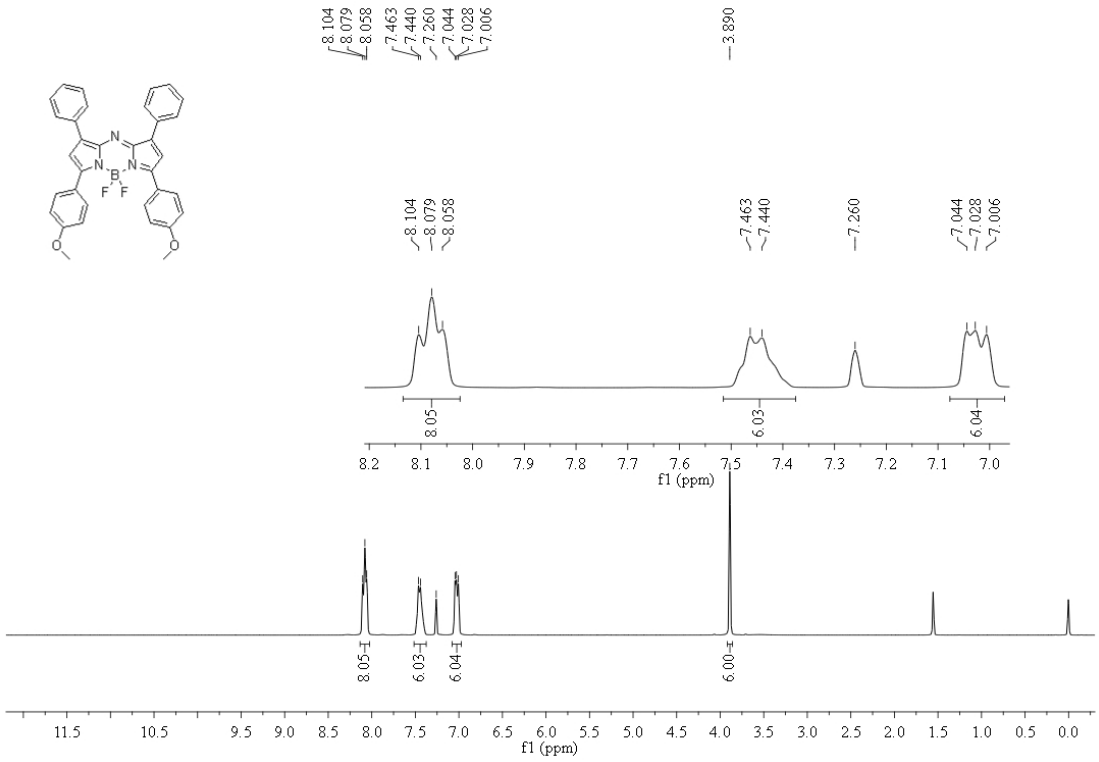
^{1}H NMR spectrum of **3a** in $CDCl_3$



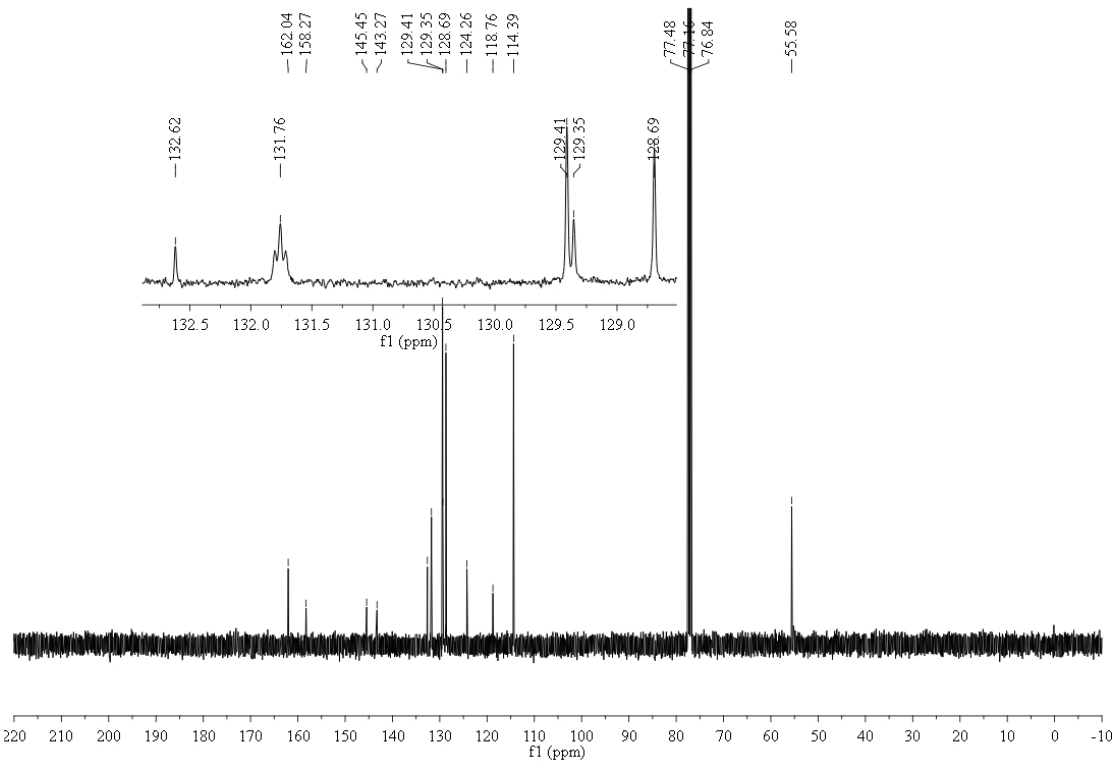
^{13}C NMR spectrum of **3a** in $CDCl_3$



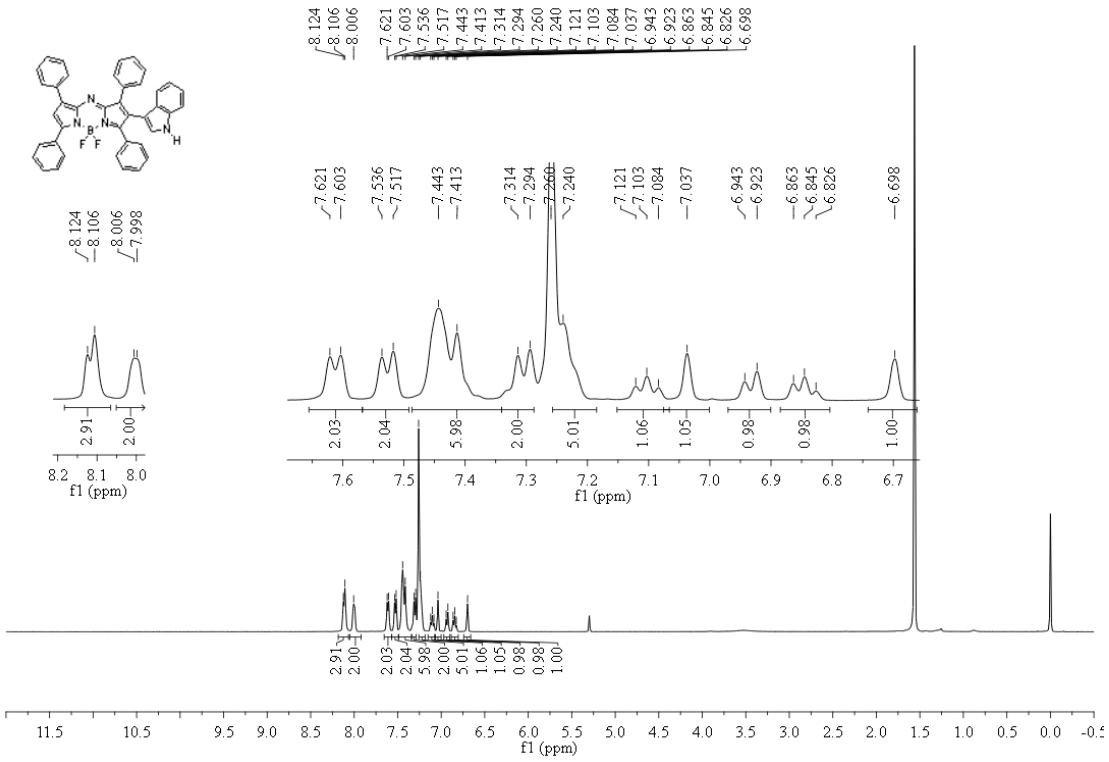
^{1}H NMR spectrum of **3b** in $CDCl_3$



^{13}C NMR spectrum of **3b** in $CDCl_3$



^{1}H NMR spectrum of **5a** in $CDCl_3$



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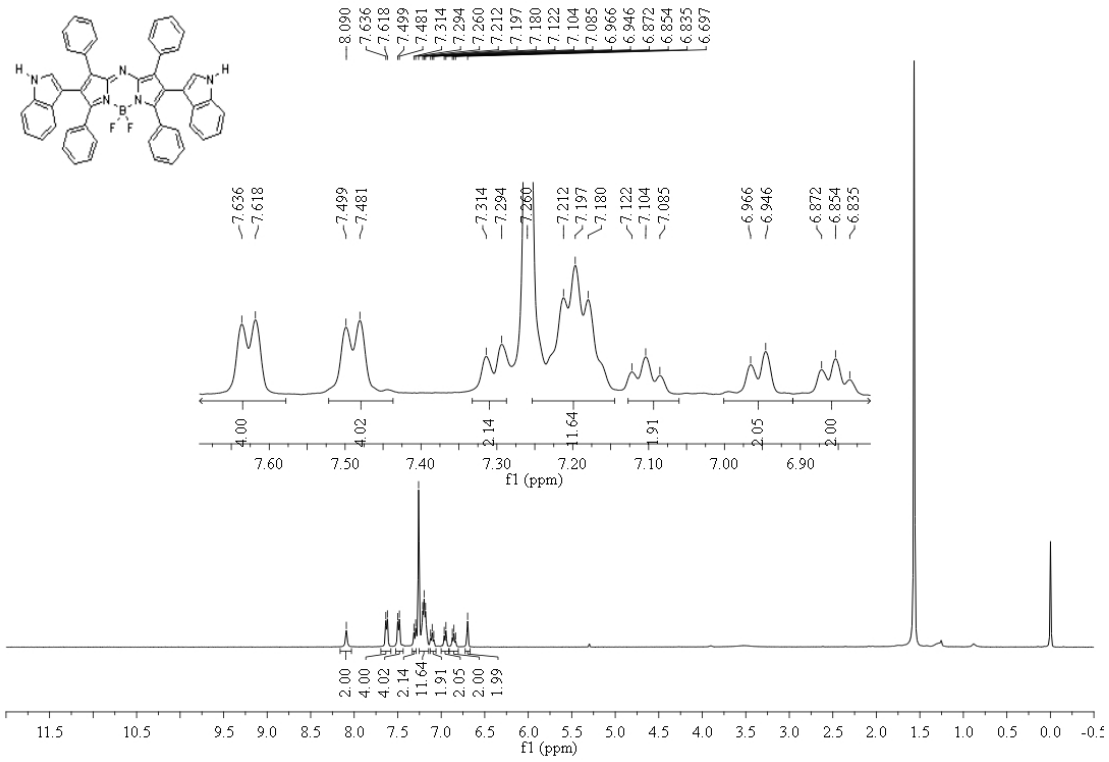
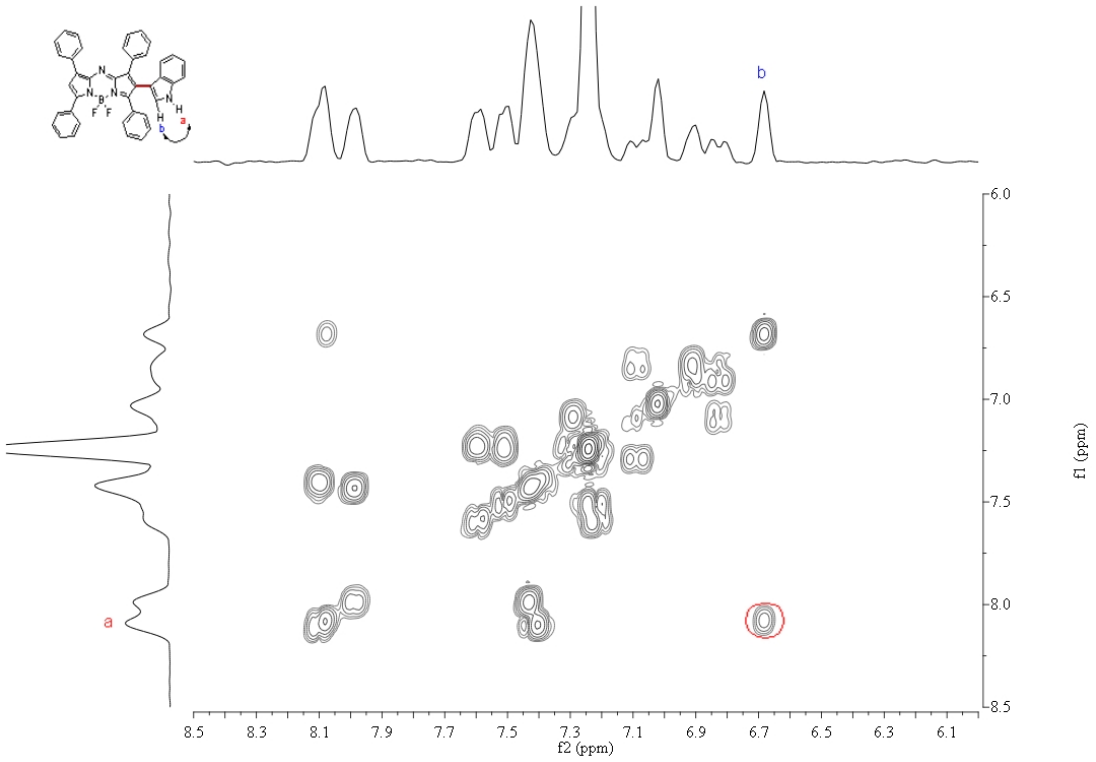


^{1}H-^{1}H COSY spectrum of **5a** in $CDCl_3$



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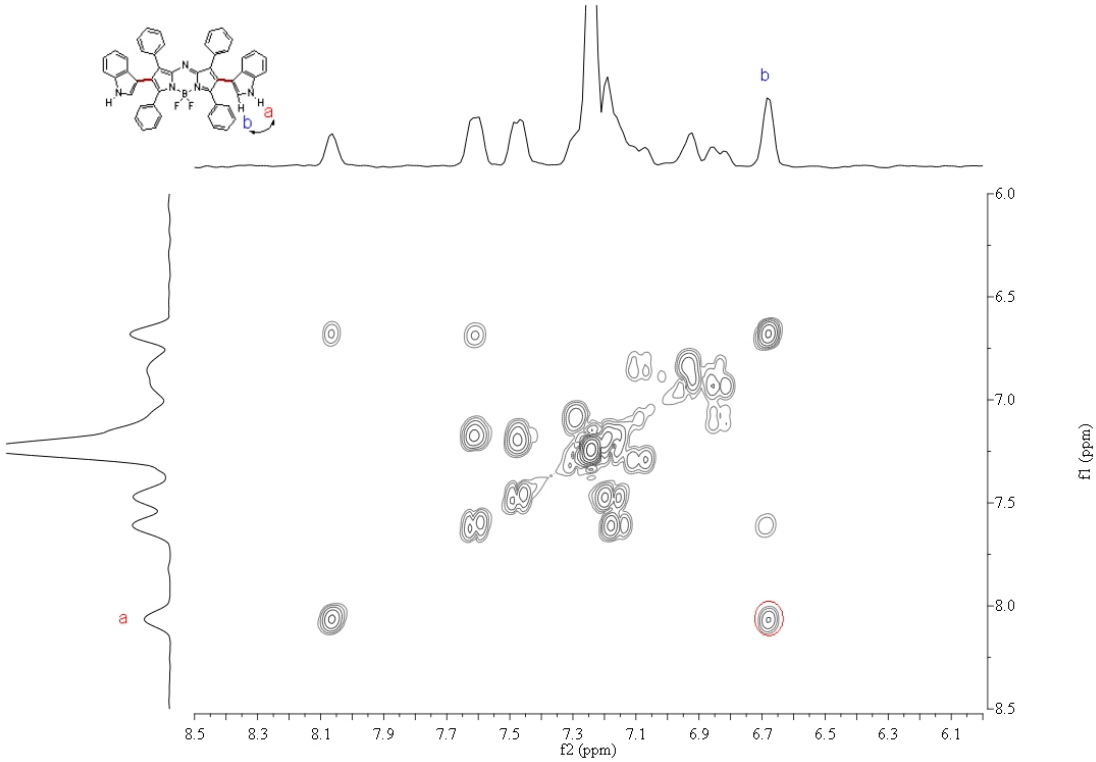
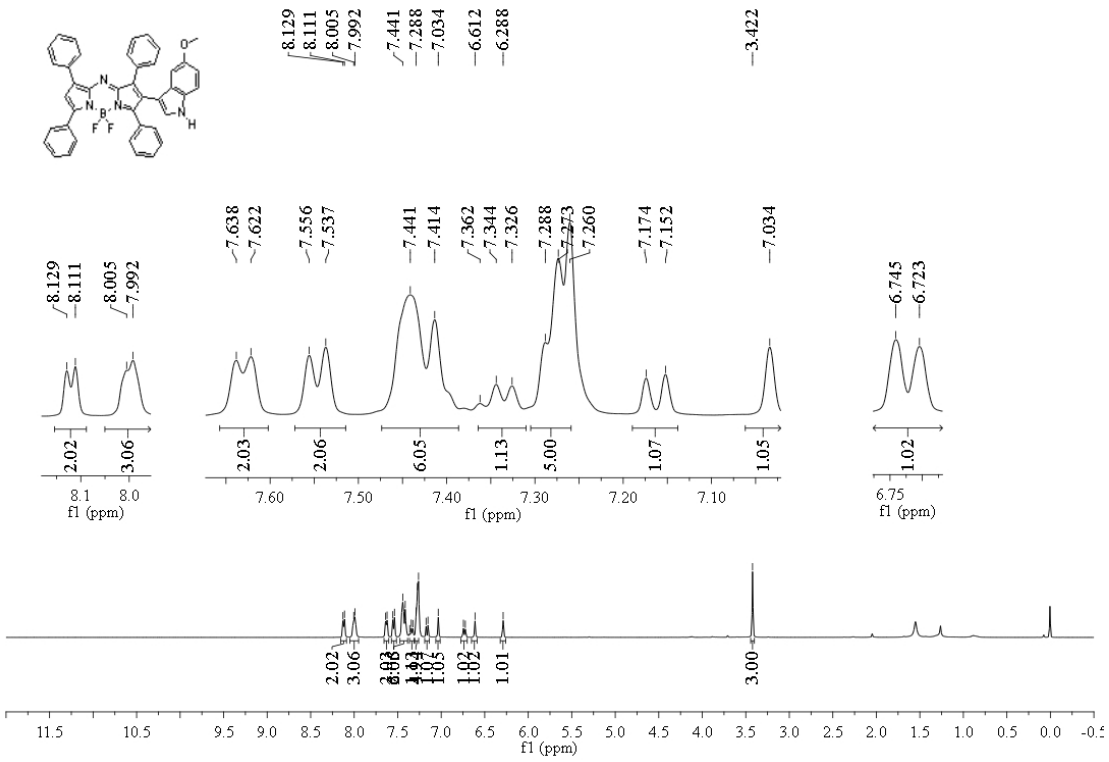
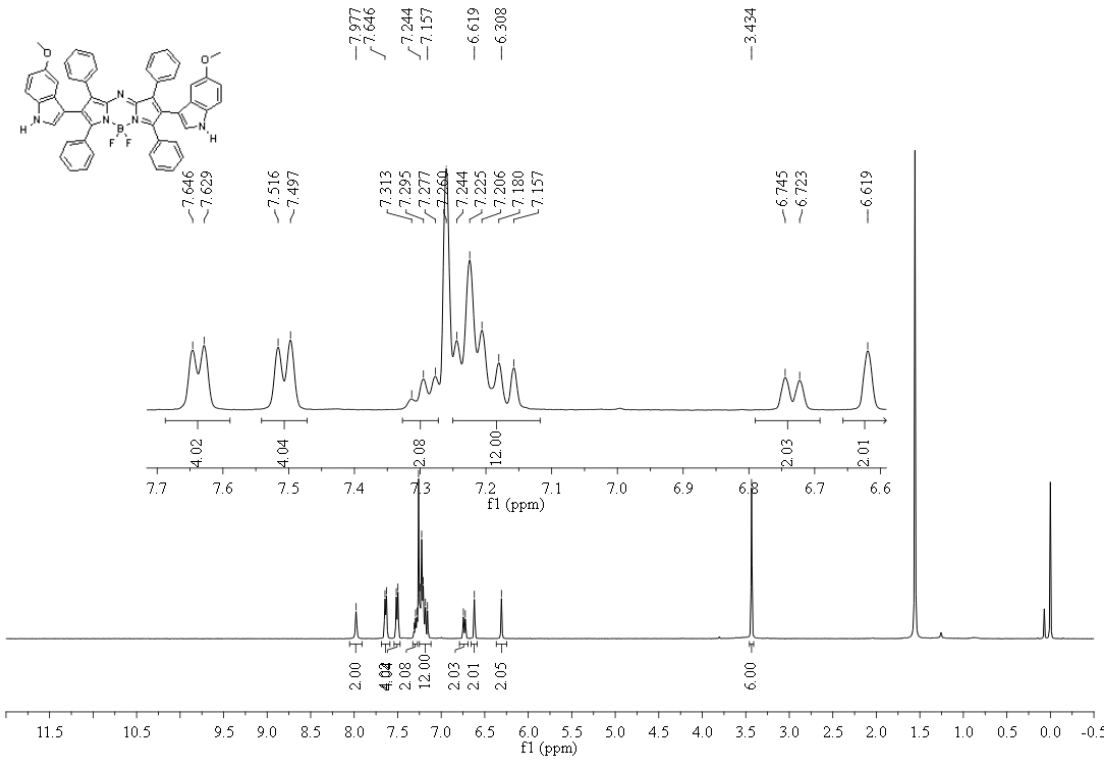


^{1}H NMR spectrum of **6a** in $CDCl_3$



^{1}H NMR spectrum of **6b** in $CDCl_3$



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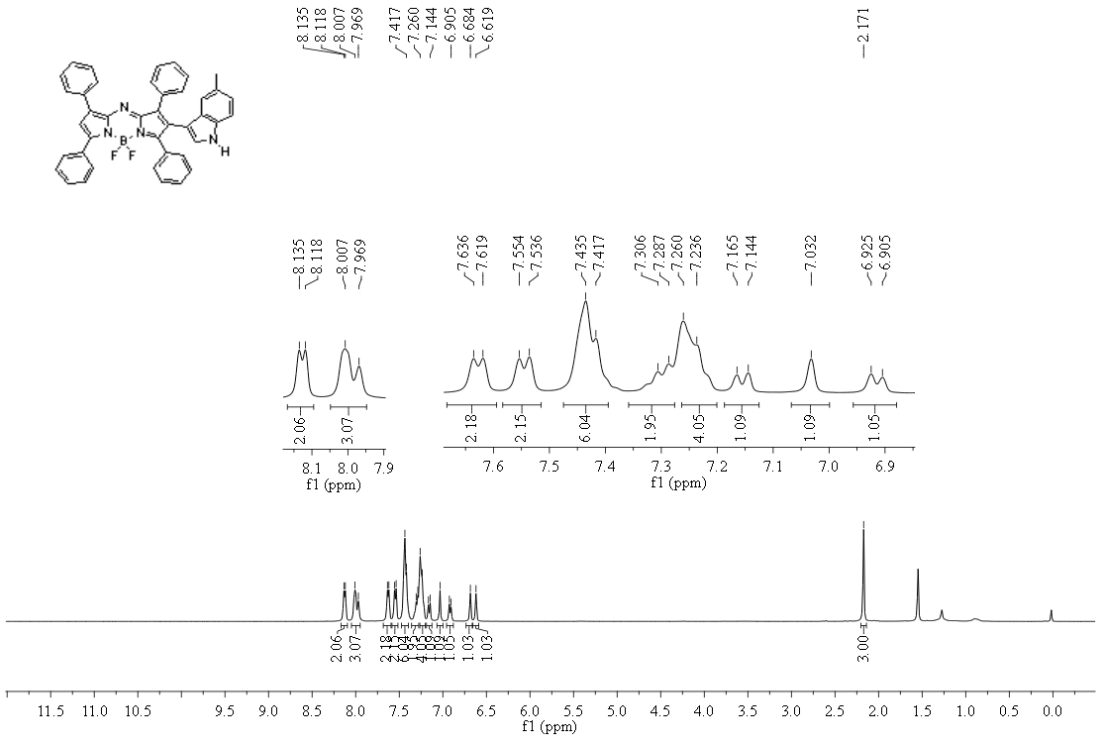

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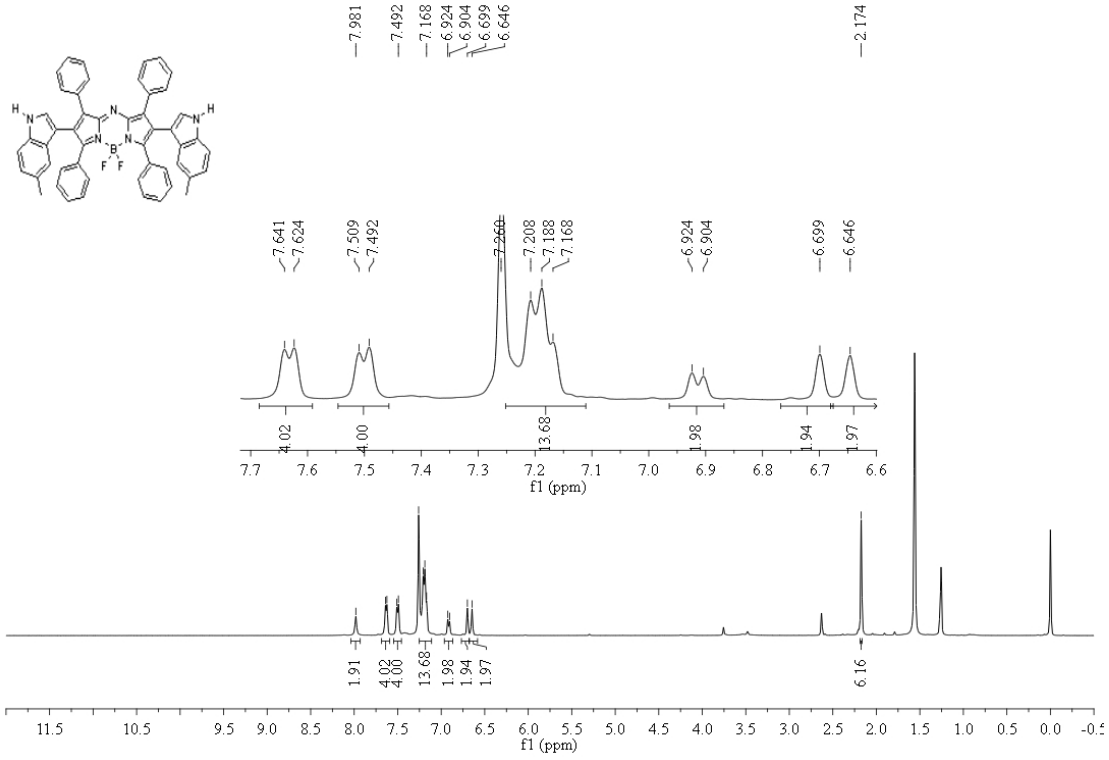
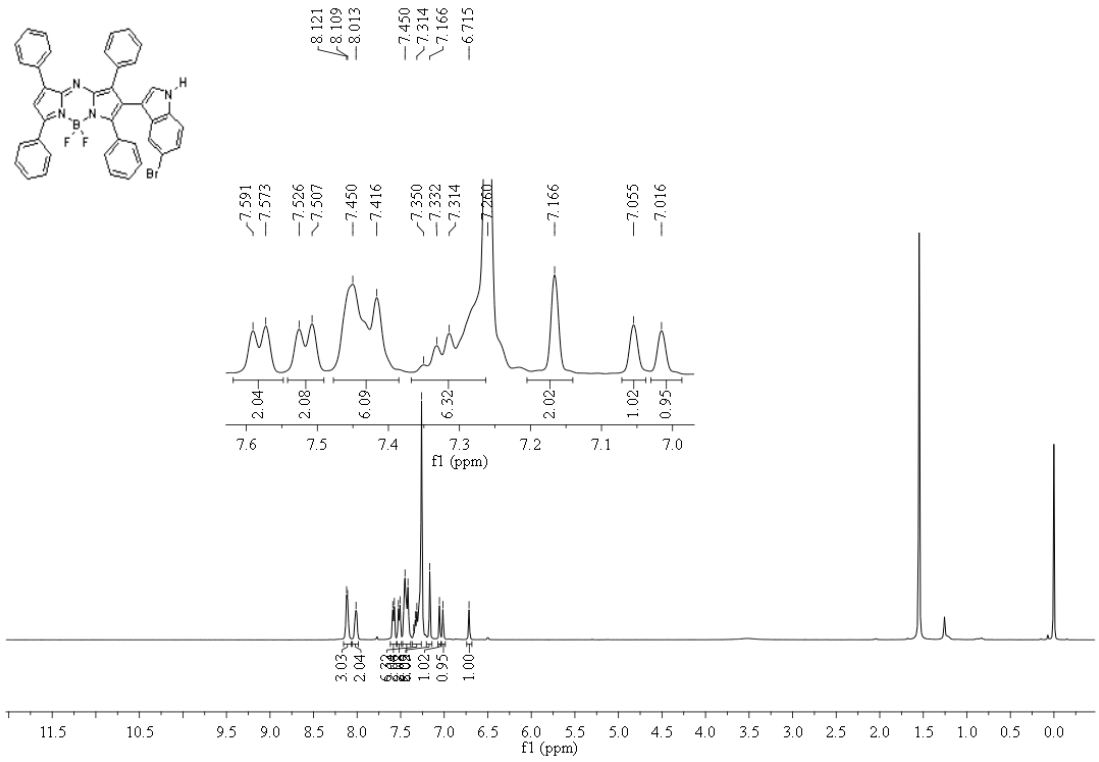
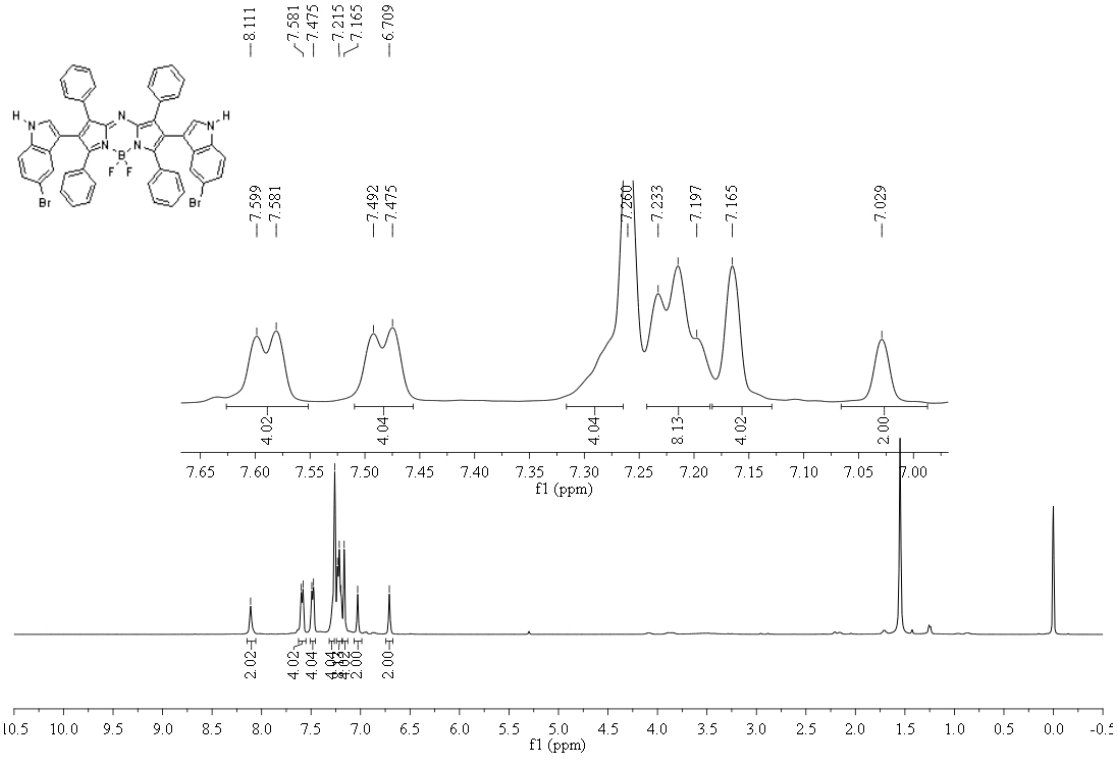


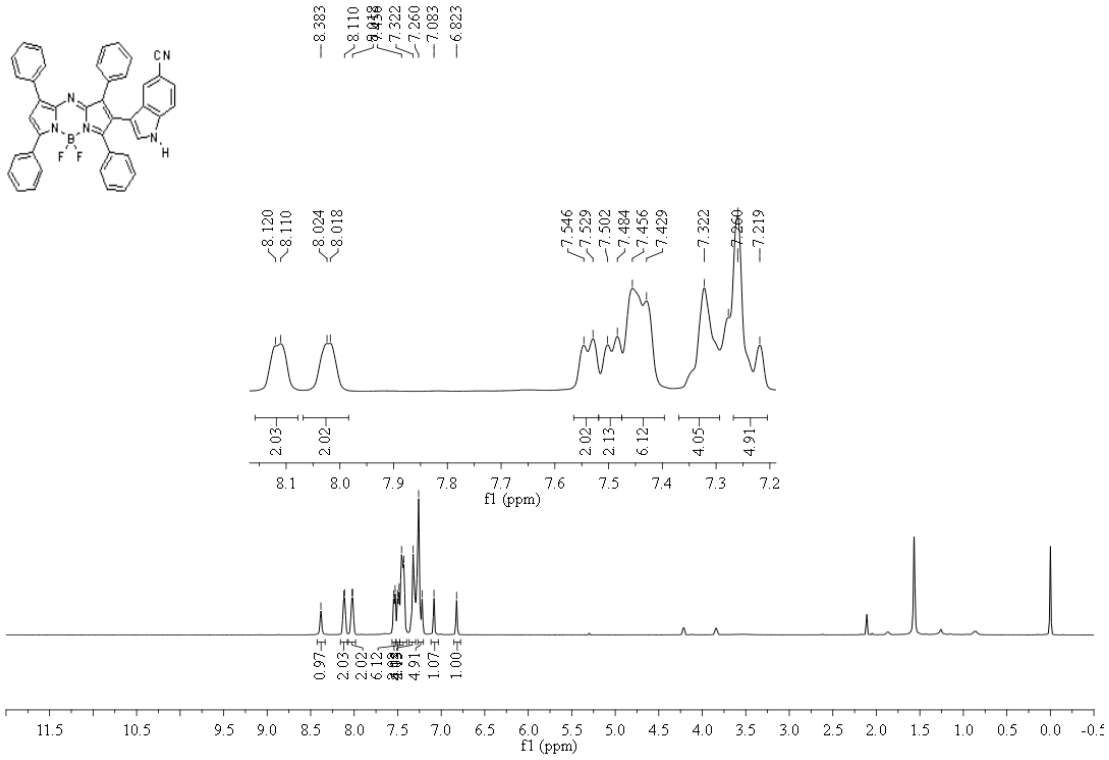
^{1}H NMR spectrum of **8a** in $CDCl_3$



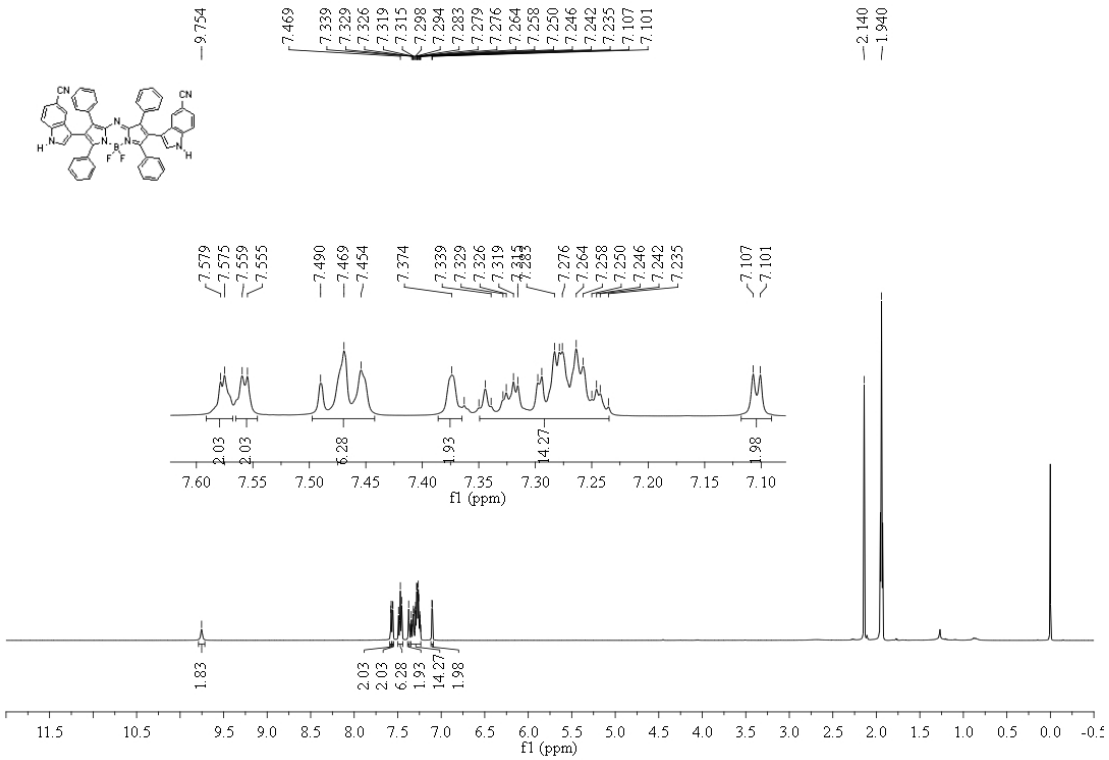
^{1}H NMR spectrum of **8b** in $CDCl_3$



^{1}H NMR spectrum of **9a** in $CDCl_3$



^{1}H NMR spectrum of **9b** in CD_3CN



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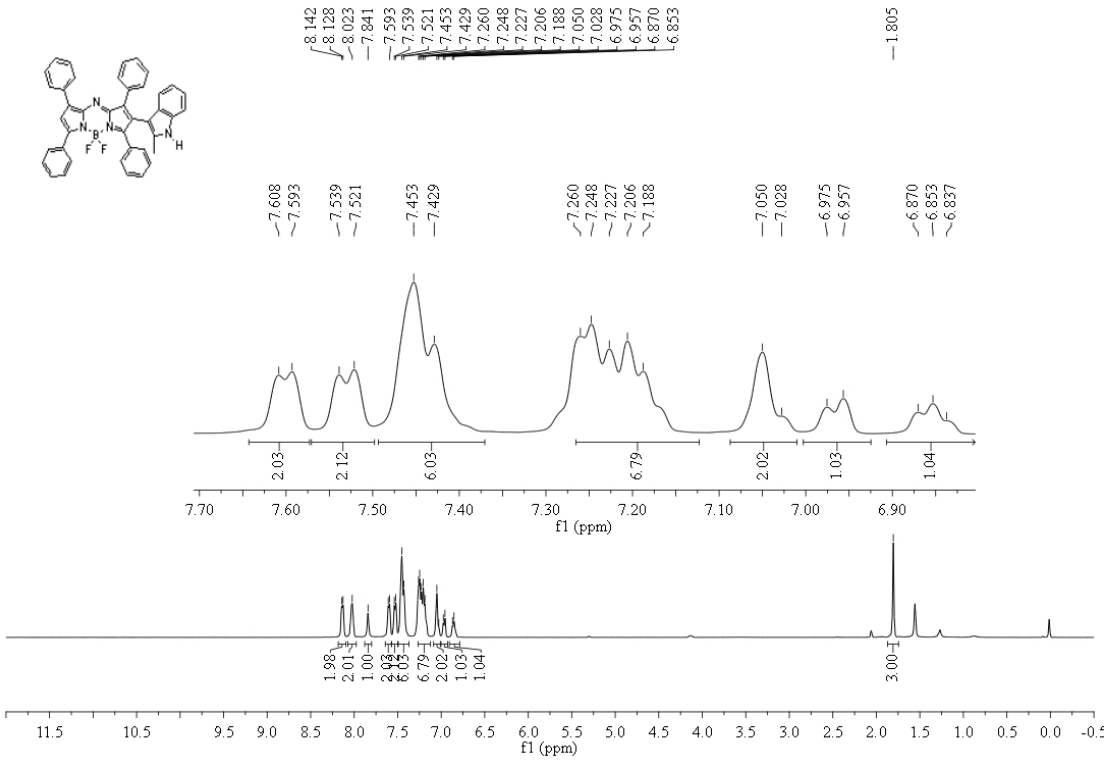

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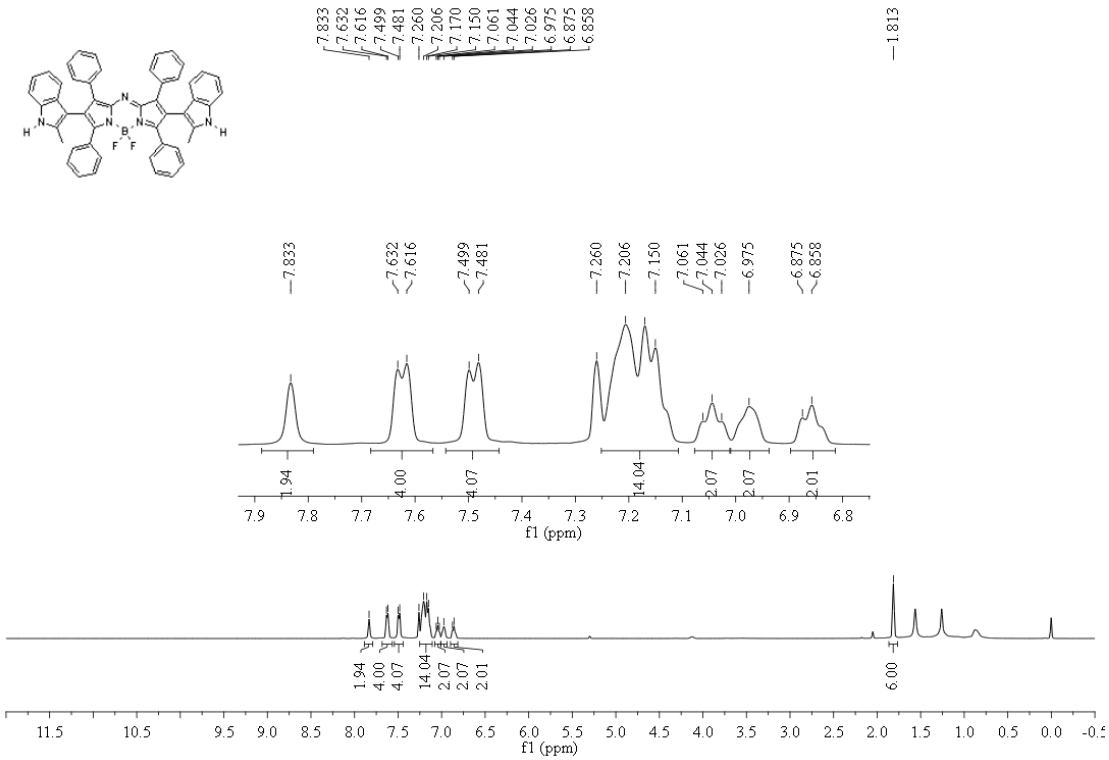
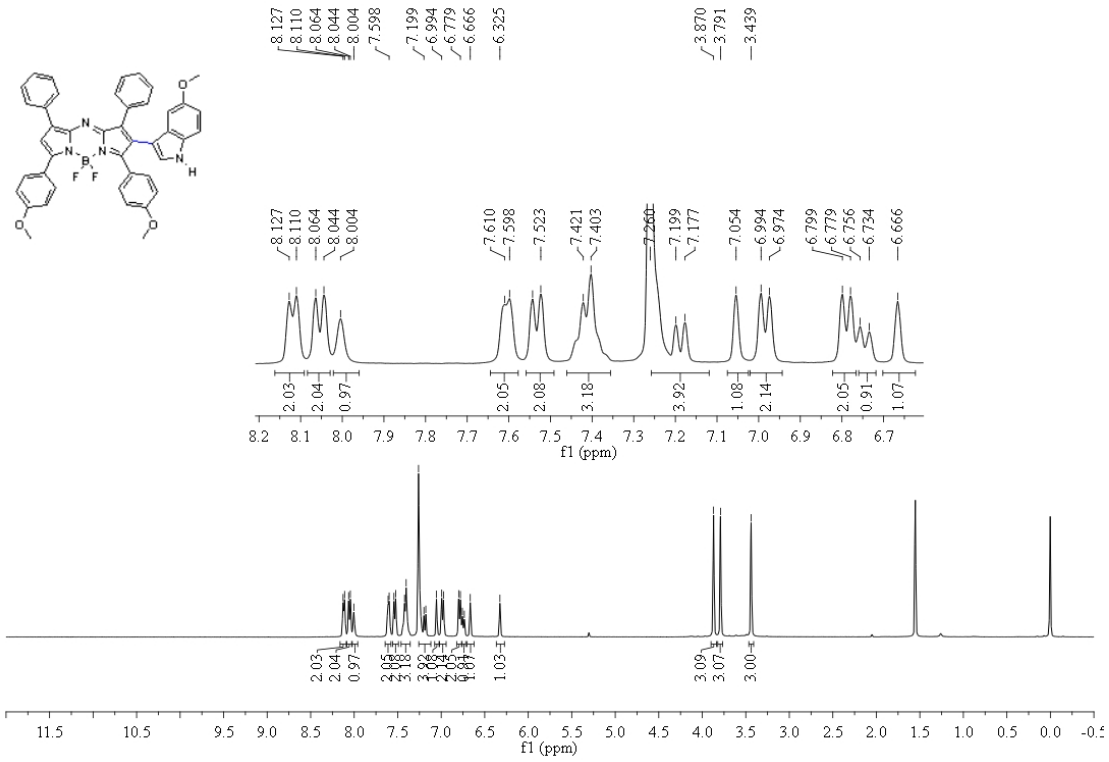


^{1}H NMR spectrum of **11a** in $CDCl_3$



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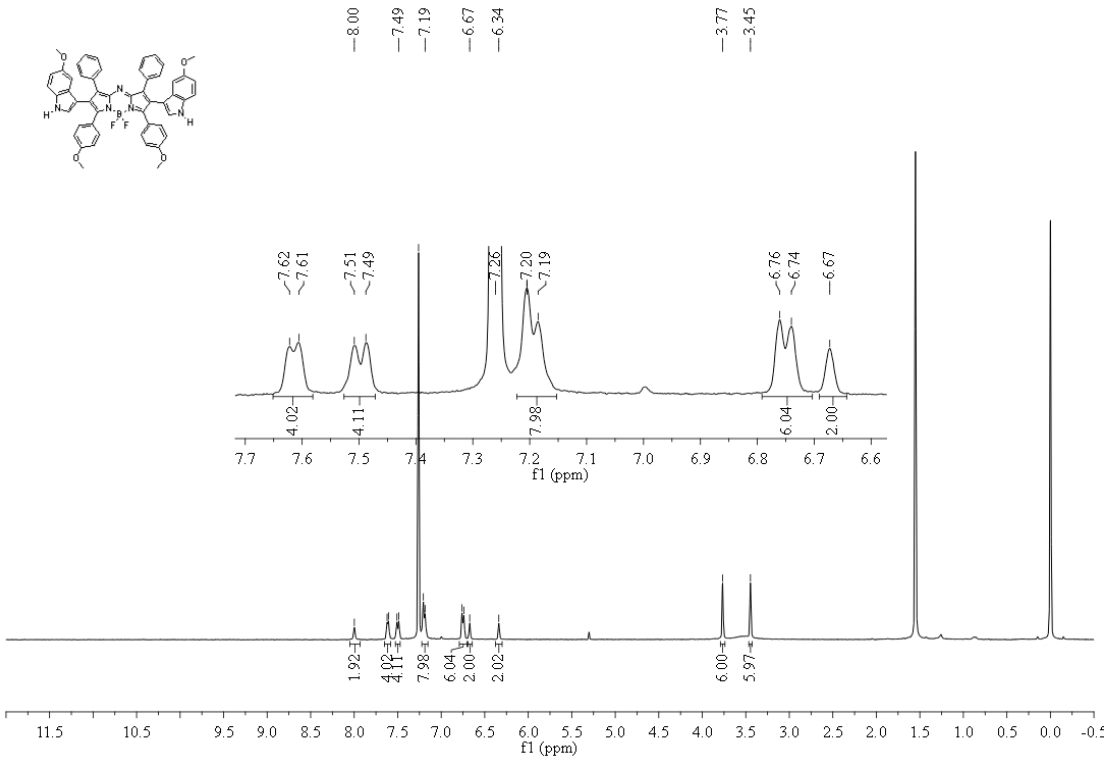

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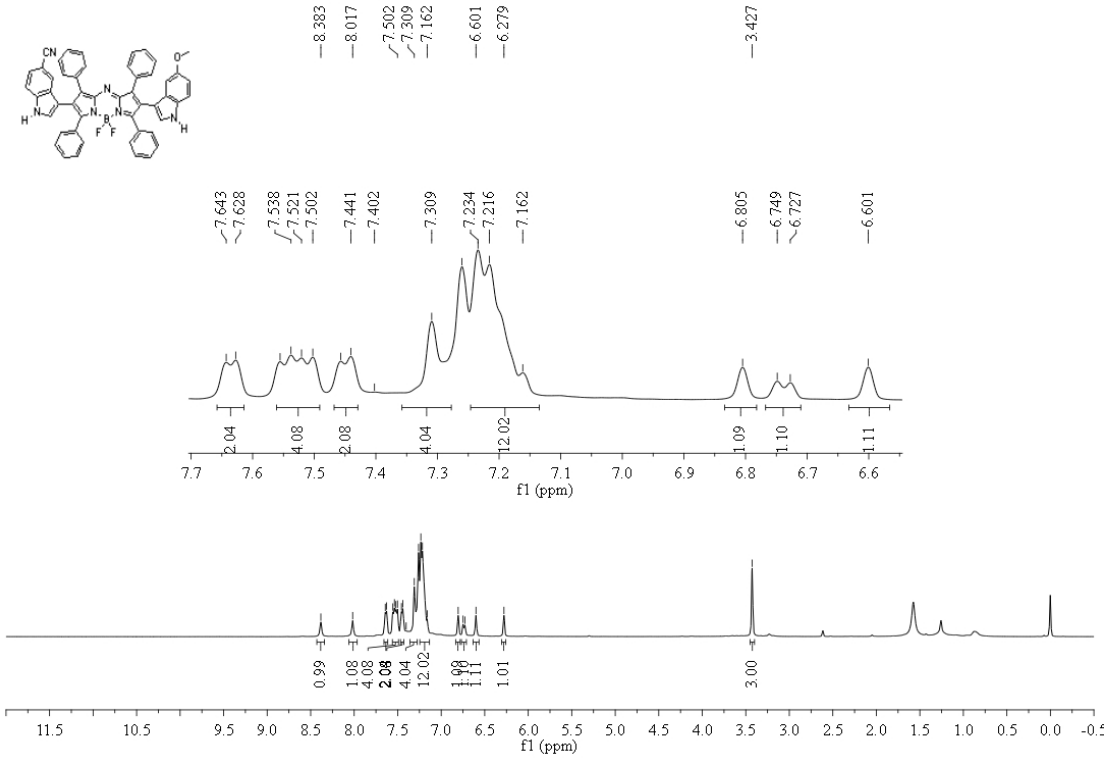

^{1}H NMR spectrum of **13** in $CDCl_3$