Supporting Information

for

Si-Bridged Annulated BODIPYs: Synthesis, Unique Structure and Photophysical Properties

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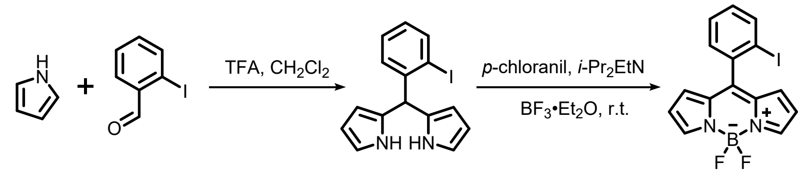
Contents

1. Materials and instrumentations

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under argon atmosphere in oven-dried glassware. Glassware was dried in an oven at 120 °C and cooled under a stream of inert gas before use. Dichloromethane and N,N-diisopropylethylamine were distilled over calcium hydride. Toluene and THF were refluxed with sodium and distilled out immediately before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of deuterated solvents ($CDCl_3$: 7.26 ppm; CD_2Cl_2: 5.32 ppm; acetone-d_6: 2.05 ppm). HR-MS were recorded on a Bruker Daltonics microTOF-Q II spectrometer. All the solvents employed for the spectroscopic measurements were of UV spectroscopic grade (Aldrich).

2. Synthesis and characterization

- **Synthesis of 1**



dipyrrole intermediate, 62%

1, 38%

2-Iodobenzaldehyde (1.0 g, 4.3 mmol) was dissolved in dry pyrrole (11.0 g, 38 eq) under N_2. Trifluoroacetic acid (TFA) (0.1 mL) was added dropwise and the mixture was stirred for 30 minutes at room temperature. The reaction mixture was concentrated under reduced pressure to remove excess pyrrole, the residue was dissolved in CH_2Cl_2 (10 mL), washed with water (30 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluting with 20% DCM in PE) yielding dipyrrole intermediate as a white powder (930 mg, 62%).

To a solution of dipyrrole intermediate (930 mg, 2.7 mmol) in dried CH_2Cl_2 (100 mL), *p*-chloranil (780 mg, 3.2 mmol) was added. The mixture was stirred overnight. *N*,*N*-Diisopropylethylamine (DIPEA, 3.3 mL, 18 mmol) was added, and the mixture was stirred at room temperature for 20 mins. BF_3•OEt_2 (3.3 mL, 26.7 mmol) was added dropwise, and stirring was continued for 1 h. The reaction was quenched by saturated $NaHCO_3$ (30 mL), extracted with CH_2Cl_2 (3 x 30 mL), and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography (5% EA in PE) to give **1a** as orange solid (645 mg, 38% yield).

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.17 – 8.01 (m, 3H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 1.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 3.8 Hz, 2H), 6.64 (d, *J* = 3.9 Hz, 2H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 148.72, 146.12, 140.50, 139.28, 136.02, 132.20, 131.84, 131.29, 128.94, 119.96.

HR-MS: Calcd. for $C_{15}H_{10}BFIN_2$ $[M-F]^+$ 374.9963, Found 374.9953.

- **Optimization of reaction conditions**

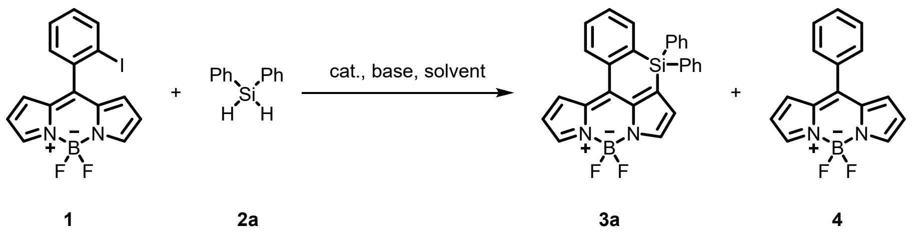
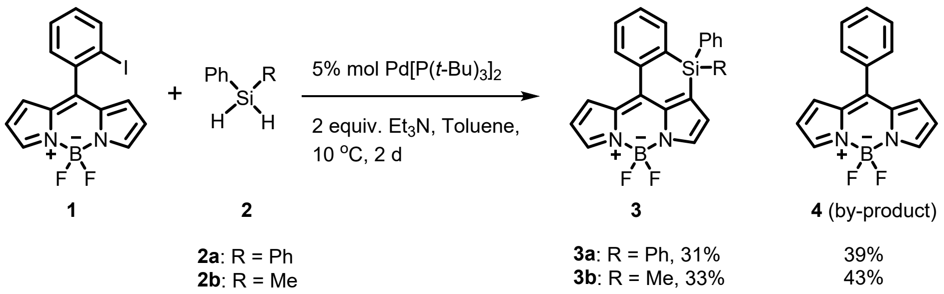


Table S1 Optimization of reaction conditions for the synthesis of **3a**.

Entry [a]	Catalyst	Base	Solvent	Yield(%) [b]	
				3a	4
1	$Pd_2(dba)_3$	Et_3N	Toluene	-[c]	-
2	$Pd(PPh_3)_4$	Et_3N	Toluene	-	-
3	$Pd(PPh_3)_2Cl_2$	Et_3N	Toluene	-	-
4	$[Rh(cod)_2]BF_4$	Et_3N	Toluene	-	-
5	$Pd(P(t\text{-}Bu)_3)_2$	Et_3N	Toluene	31	40
6	$Pd(P(t\text{-}Bu)_3)_2$	Et_3N	THF	7	45
7	$Pd(P(t\text{-}Bu)_3)_2$	Et_3N	CH_2Cl_2	<2	60
8	$Pd(P(t\text{-}Bu)_3)_2$	Et_3N	Mesitylene	15	43
9	$Pd(P(t\text{-}Bu)_3)_2$	Et_3N	CH_3CN	5	56
10	$Pd(P(t\text{-}Bu)_3)_2$	Et_3N	NMP	-	-
11	$Pd(P(t\text{-}Bu)_3)_2$	None	Toluene	-	-
12	$Pd(P(t\text{-}Bu)_3)_2$	K_3PO_4	Toluene	-	-
13	$Pd(P(t\text{-}Bu)_3)_2$	$NaCO_3$	Toluene	-	-
14	$Pd(P(t\text{-}Bu)_3)_2$	*i*-Pr_2NH	Toluene	13	61
15	$Pd(P(t\text{-}Bu)_3)_2$	*i*-Pr_2EtN	Toluene	10	59

[a] Reaction condition: **1** (0.2 mmol, 1.0 eq), dihydrosilane **2a** (0.3 mmol, 1.5 eq), base (0.6 mmol, 3.0 eq), catalyst (0.01 mmol, 5 %), dry solvent (3.0 mL) with stirring under an argon atmosphere at 10 ^{o}C until the starting material was not observable in TLC. [b] Isolated yield. [c] No desirable product was detected.

- **Synthesis of 3a and 3b**



An ovendried Schlenk flask was charged with **1** (100 mg, 0.25 mmol) and $Pd(P(t\text{-}Bu)_3)_2$ (6.50 mg, 0.0125 mmol, 0.05 eq) under argon. Dry toluene (3 mL) was added, after the mixture was stirred for 30 minutes, diphenylsilane (71 µL, 0.38 mmol, 1.5 eq) and Et_3N (106 μL, 0.76 mmol, 3.0 eq) were then successively added by a syringe, and the reaction mixture was stirred at 10 °C for 48 h. The reaction was quenched with water when the starting material was not observable on TLC plate. The reaction was quenched by adding 2 mL water. The aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified through column chromatography on silica gel (eluent: PE:EA=9:1, v:v), then recrystallization from *n*-hexane/DCM to afforded **3a** (34 mg, 0.078 mmol) as purple solid, yield 31%; **4** (26 mg, 0.1 mmol) as orange solid, yield 39%.

3b was synthesized following the above procedure using methylphenylsilane as starting material. The isolated yield of **3b** is 33%, with 43% of **4** as byproduct.

3a: ^1H NMR (500 MHz, CD_2Cl_2) δ 8.26 (d, J = 7.7 Hz, 1H), 7.98 (s, 1H), 7.90 (s, 1H), 7.84 (d, J = 5.6 Hz, 1H), 7.65 – 7.56 (m, 6H), 7.50 (d, J = 4.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.34 (m, 4H), 6.87 (d, J = 1.6 Hz, 1H), 6.65 (d, J = 2.6 Hz, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.17, 145.16, 145.11, 141.63, 141.58, 140.25, 138.82, 137.92, 137.89, 137.78, 136.03, 135.60, 135.58, 135.51, 134.48, 133.01, 132.78, 131.76, 130.81, 130.39, 128.66, 123.58, 123.53, 119.03, 119.00, 118.98, 118.95.

HR-MS: Calcd. for $C_{27}H_{20}BF_2N_2Si$ $[M+H]^+$ 449.1456, Found 449.1460.

3b: ^1H NMR (500 MHz, CD_2Cl_2) δ 8.25 – 8.22 (m, 1H), 7.97 (s, 1H), 7.88 (s, 1H), 7.81 – 7.78 (m, 1H), 7.61 – 7.57 (m, 2H), 7.52 (d, *J* = 1.4 Hz, 1H), 7.50 (d, *J* = 1.4 Hz, 1H), 7.49 (d, *J* = 4.4 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.31 (m, 2H), 6.79 (d, *J* = 1.5 Hz, 1H), 6.66 (dd, *J* = 4.2, 1.5 Hz, 1H), 0.78 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.36, 144.57, 144.52, 141.76, 141.72, 140.06, 139.92, 138.35, 136.68, 135.35, 135.33, 135.04, 134.83, 134.79, 134.12, 131.79, 130.48, 130.11, 128.58, 123.15, 118.72, -3.25.

HR-MS: Calcd. for $C_{22}H_{17}BF_2N_2NaSi$ $[M+Na]^+$ 409.1119, Found 409.1098.

4: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2 H), 7.60 – 7.51(m, 5 H), 6.94 (d, *J* = 4.1 Hz, 2 H), 6.55 (d, *J* = 3.6 Hz, 2H).

3. Spectroscopic properties

UV-visible absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. Fluorescence spectra and the fluorescence lifetimes of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter. The goodness of the fit of the single exponential decays was judged using the chi-squared (X_R^2) and the autocorrelation function C(*j*) values. Low residuals ($X_R^2 < 1.2$) were consistently observed. Absorption and emission measurements were carried out in 1×1 cm quartz cuvettes. For all measurements, the temperature was kept constant at (298±2) K. Dilute solutions with the absorbance of less than 0.05 at the excitation wavelength were used for the measurement of fluorescence quantum yields. Fluorescein and rhodamine B were used as the standard ($\Phi_F = 0.90$ in 0.1mol/L NaOH and $\Phi_F = 0.49$ in EtOH). The quantum yield, Φ, was calculated using the equation

$$\Phi_{sample} = \Phi_{std}\left[\frac{I_{sample}}{I_{std}}\right]\left[\frac{A_{std}}{A_{sample}}\right]\left[\frac{n_{sample}}{n_{std}}\right]^2$$

where the sample and *std* subscripts denote the sample and standard, respectively, *I* is the integrated emission intensity, A stands for the absorbance, and n is refractive index.

When the fluorescence decays were monoexponential, the rate constants of radiative (k_r) and nonradiative (k_{nr}) deactivation were calculated from the measured fluorescence quantum yield (Φ_F) and fluorescence lifetime (τ) according to equations (1) and (2):

$$k_r = \Phi_F/\tau \qquad (1)$$

$$k_r = (1-\Phi_F)/\tau \qquad (2)$$

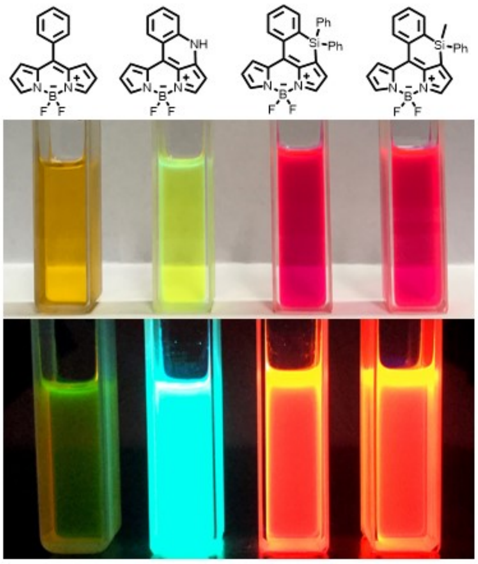


Figure S1 Photographs of color of BODIPYs in dicloromethane under daylight (top) and 365 nm UV irradiation (bottom).

Table S2 Photophysical properties of **4** in various solvents at 298K

	Solvent	λ_{abs}[a] [nm]	ε_{abs} $M^{-1}cm^{-1}$	λ_{em}[b] [nm]	$\Delta\nu_{em\text{-}abs}$[c] [$cm^{-1}$]	Φ_F[d]	τ_f[e] [ns]	k_r[f] [$10^8 s^{-1}$]	k_{nr}[g] [$10^8 s^{-1}$]
4	Hexane	500	33800	515	583	0.02	0.21	0.94	46.01
	Toluene	504	29700	519	573	0.05	0.35	1.42	27.07
	CH_2Cl_2	500	32000	516	620	0.03	0.26	1.15	37.16
	THF	500	37600	519	732	0.02	0.16	1.24	60.87
	MeCN	497	41100	514	665	0.02	0.11	1.90	93.33

[a] Absorption maximum. [b] Fluorescence maximum. [c] Stokes-shift. [d] Relative fluorescence quantum yields of **4** was calculated using fluorescein ($\Phi = 0.90$ in 0.1 M NaOH solution) as the standard. The standard errors are less than 10%. [e] Half-life period. [f] Radiation rate constant. [g] Non-radiation rate constant.

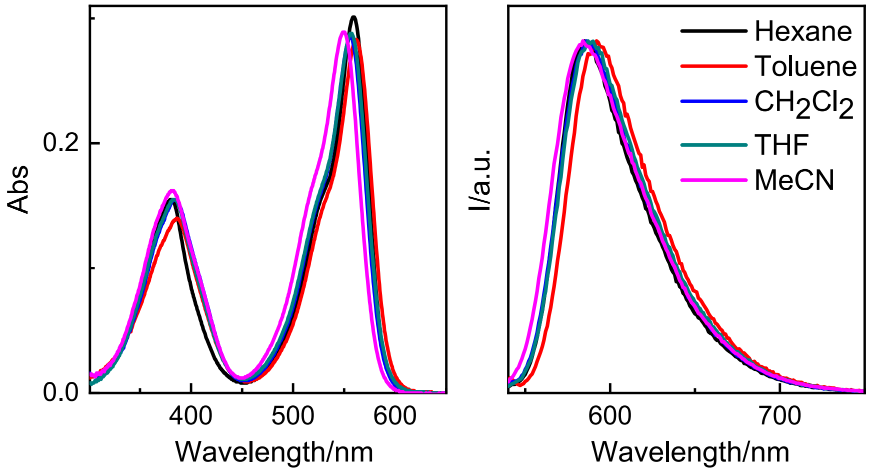


Figure S2 Absorption (left) and fluorescence emission (right) spectra of **3a** recorded in different solvents. Excited at 540 nm.

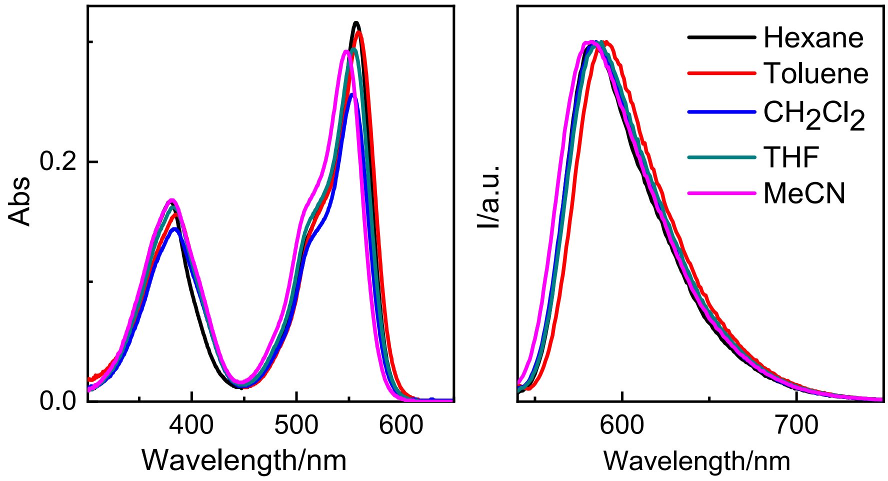


Figure S3 Absorption (left) and fluorescence emission (right) spectra of **3b** recorded in different solvents. Excited at 540 nm.

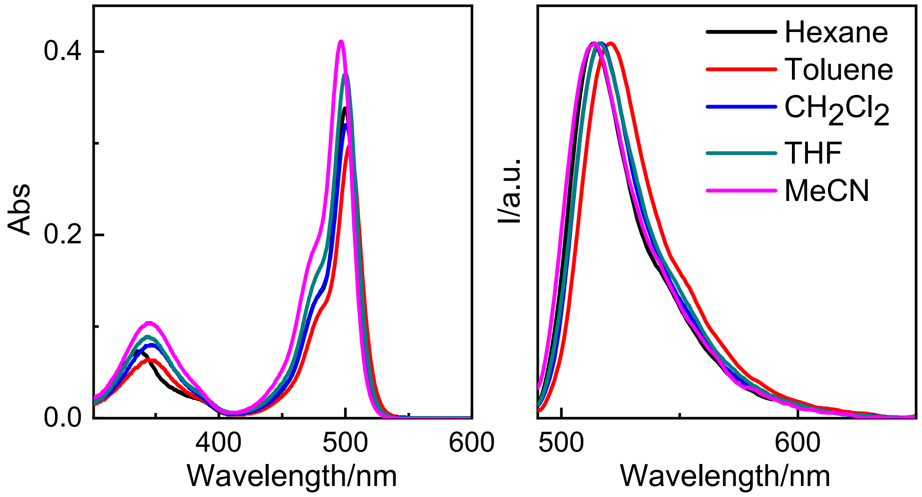


Figure S4 Absorption (left) and fluorescence emission (right) spectra of **4** recorded in different solvents. Excited at 480 nm.

4. Crystallographic structures

Diffraction data were collected on a Bruker Smart Apex II CCD diffractometer or Bruker AXS Apex II diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å). An empirical (multi-scan) or numerical absorption correction was applied with the program SADABS. The structures were solved by the direct method and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXTL). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions or found in the F_{map}. A summary of the crystallographic data and selected experimental information are given in Table S2. CCDC numbers of **1** and **3a** are 1943550 and 2102207, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Table S2 Crystallographic data for **1** and **3a**.

Identification code	**1**	**3a**
Empirical formula	$C_{15}H_{10}BF_2IN_2$	$C_{27}H_{19}BF_2N_2Si$
Formula weight	393.96	448.34
Temperature/K	296.15	296.15
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a/Å	7.7660(8)	9.515(3)
b/Å	15.9828(16)	10.803(4)
c/Å	12.3621(12)	11.632(4)
α/°	90	103.385(6)
β/°	105.335(2)	102.110(6)
γ/°	90	95.597(6)
Volume/Å^3	1479.8(3)	1123.8(7)
Z	4	2
ρ_{calc} g/cm^3	1.768	1.325
μ/mm^{-1}	2.178	0.139

F(000)	760.0	464
Crystal size/mm^3	0.18 × 0.18 × 0.1	0.18 × 0.18 × 0.12
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)
2θ range for data collection/°	4.262 to 60.922	3.708 to 56.94
h/k/l	-10, 11/ -19, 22/ -16, 16	-12, 12/ -14, 14/ -15, 13
Reflections collected	11036	10934
Independent reflections	3842 [R_{int}=0.0286, R_{sigma}=0.0325]	5416 [R_{int}=0.0243, R_{sigma}=0.0379]
Data/restraints/parameters	3842/0/190	5416/0/298
Goodness-of-fit on F^2	1.037	1.013
Final R indexes [I>=2σ (I)]	R_1=0.0371, wR_2=0.0857	R_1=0.0439, wR_2=0.1027
Final R indexes [all data]	R_1=0.0530, wR_2=0.0939	R_1=0.0684, wR_2=0.1156
Largest diff. peak/hole / e Å^{-3}	1.17/-1.03	0.26/-0.20

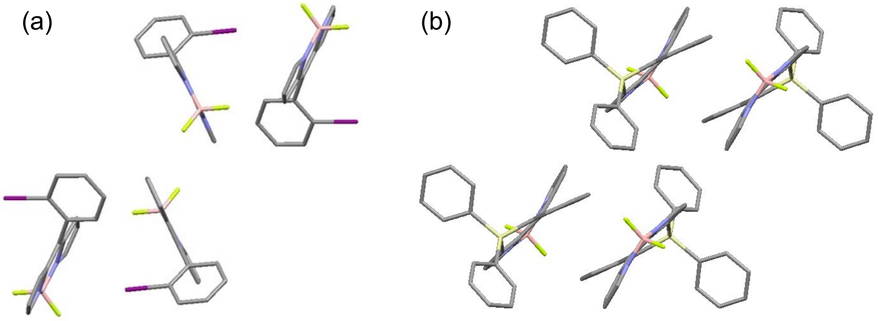
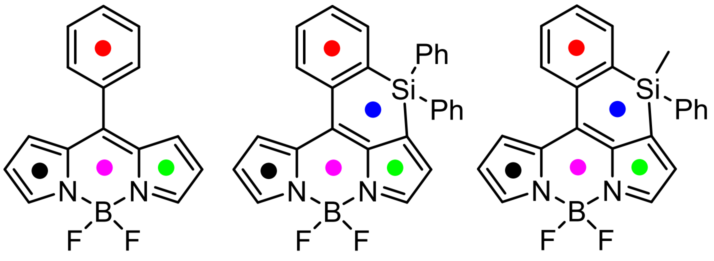


Figure S5 Crystal-packing patterns of (a) BODIPY **1** and (b) **3a**. C, gray; N, blue; B, pink; F, green; I, purple ; Si, yellow. H atoms are omitted for clarity.

5. TD-DFT calculations

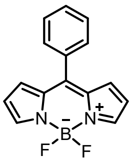
The G09W software package was used to carry out a DFT geometry optimization using the B3LYP functional with 6-31G(d) basis sets. UV-visible were calculated by using the time-dependent density functional theory (TD-DFT) approach with the B3LYP functional and 6-31G(d) basis sets.



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

	4	3a	3b
🔴	-9.05	-7.33	-7.54
🔵	/	3.71	3.41
⚫	-7.43	-7.11	-7.07
🟣	3.18	3.52	3.57
🟢	-7.37	-6.15	-6.32

Figure S6 NICS(0) values of rings in BODIPY **4**, **3a** and **3b**.



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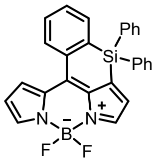
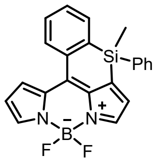
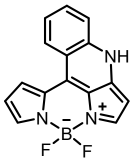


3a



3b



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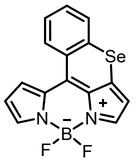

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Table S3 Selected transition energies and wave functions of **4**-**6** calculated using the DT-DFT method with the B3LYP functional and 6-31G(d) basis set.

	State[a]	Energy[a] [eV]	λ [nm]	*f*[b]	Orbitals (coefficient)[c]
4	S1	3.09	401	0.31	H-1 → L (16%), H → L (85%)
3a	S1	2.72	455	0.26	H → L (94%)
3b	S1	2.74	453	0.26	H → L (93%)
5	S1	2.97	417	0.32	H → L (95%)
6	S1	2.76	450	0.20	H-1 → L (36%), H → L (63%)

[a] Excited state. [b] Oscillator strength. [c] MOs involved in the transitions. H and L denote HOMO and LUMO, respectively.

6. Electrochemical Properties

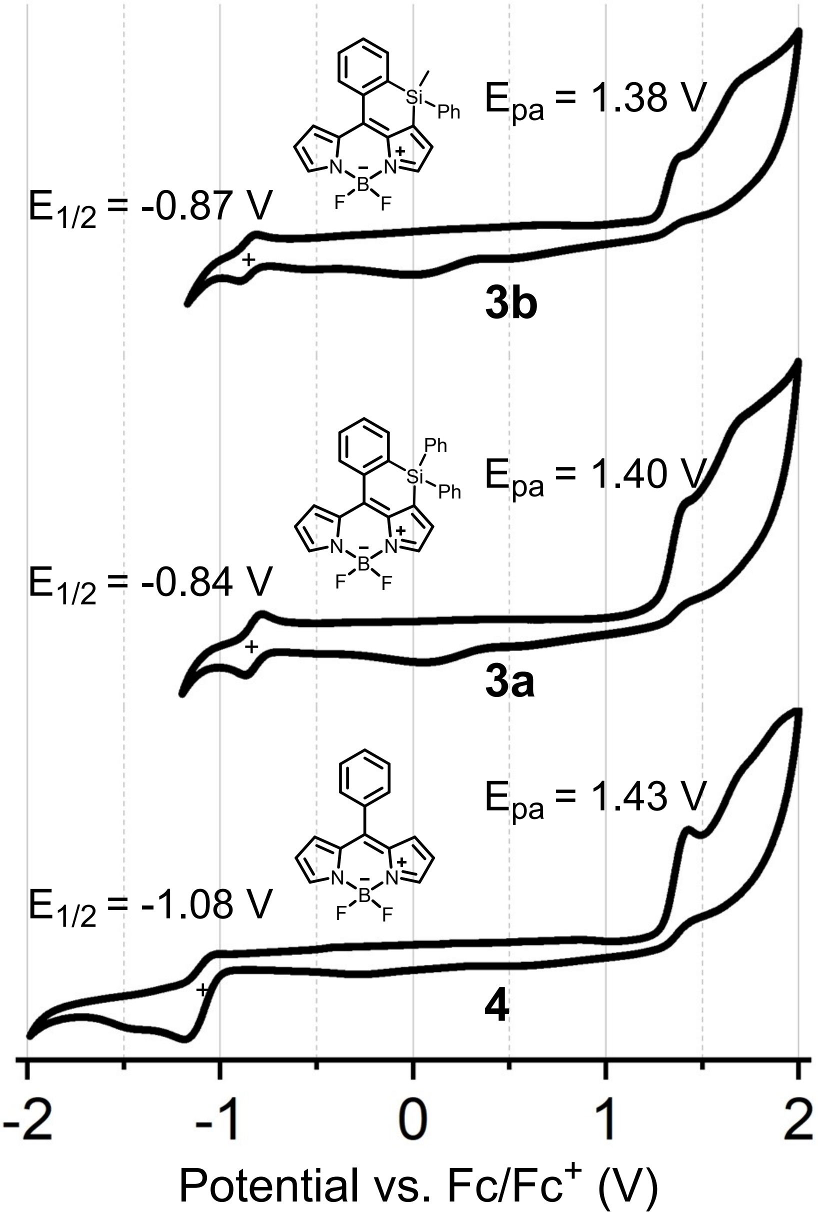
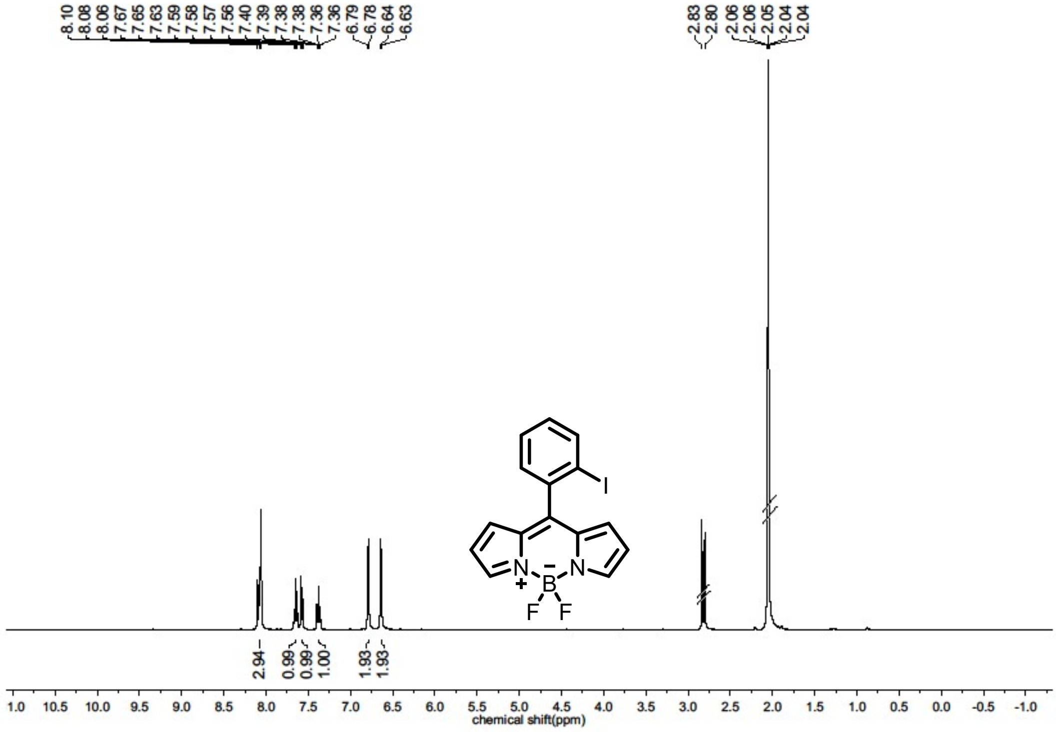


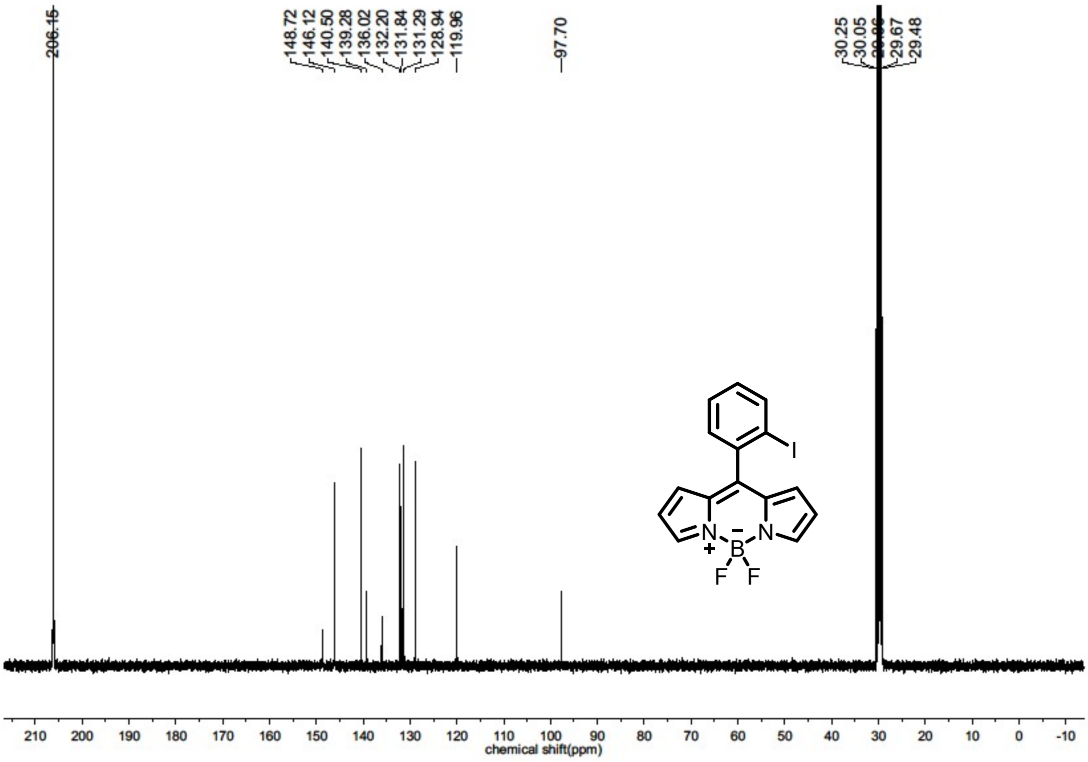
Figure S7 Cyclic voltammograms of 2 mM 4, 3a, and 3b measured in dichloromethane solution containing 0.1 M TBAPF$_6$ as the supporting electrolyte at room temperature.

Glassy carbon electrode as a working electrode, and the scan rate at 100 mV s^{-1}.

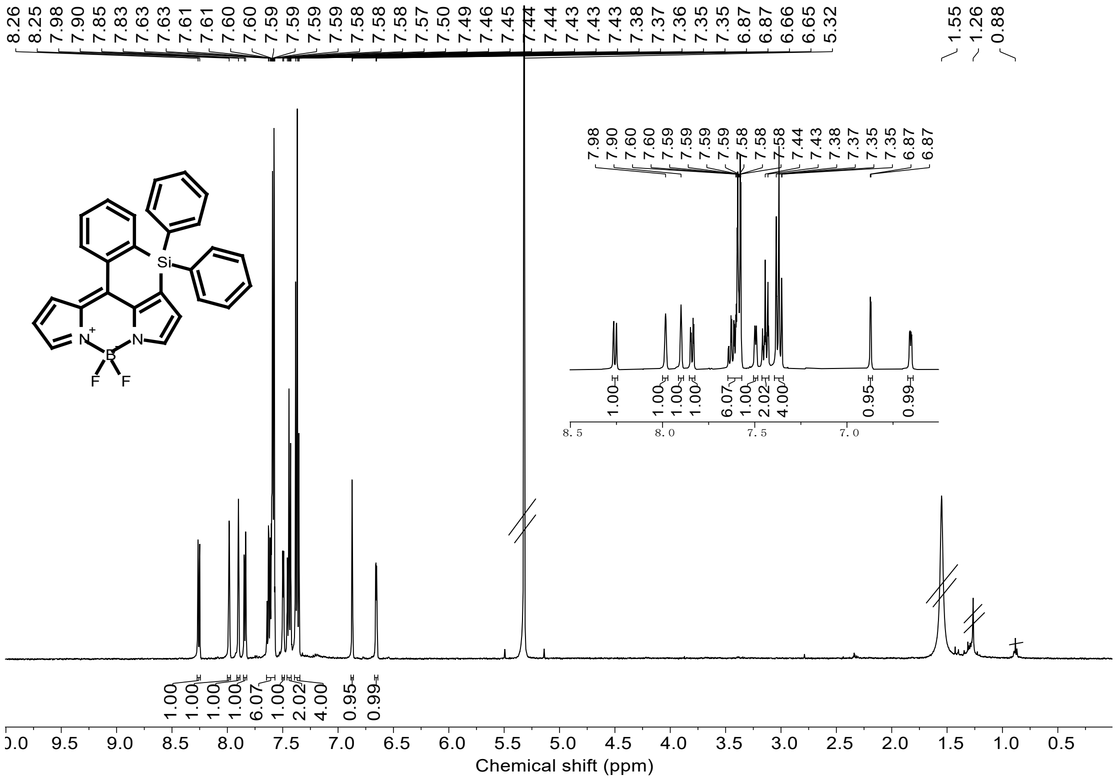
7. ^{1}H NMR, ^{13}C NMR and HR-MS Spectra



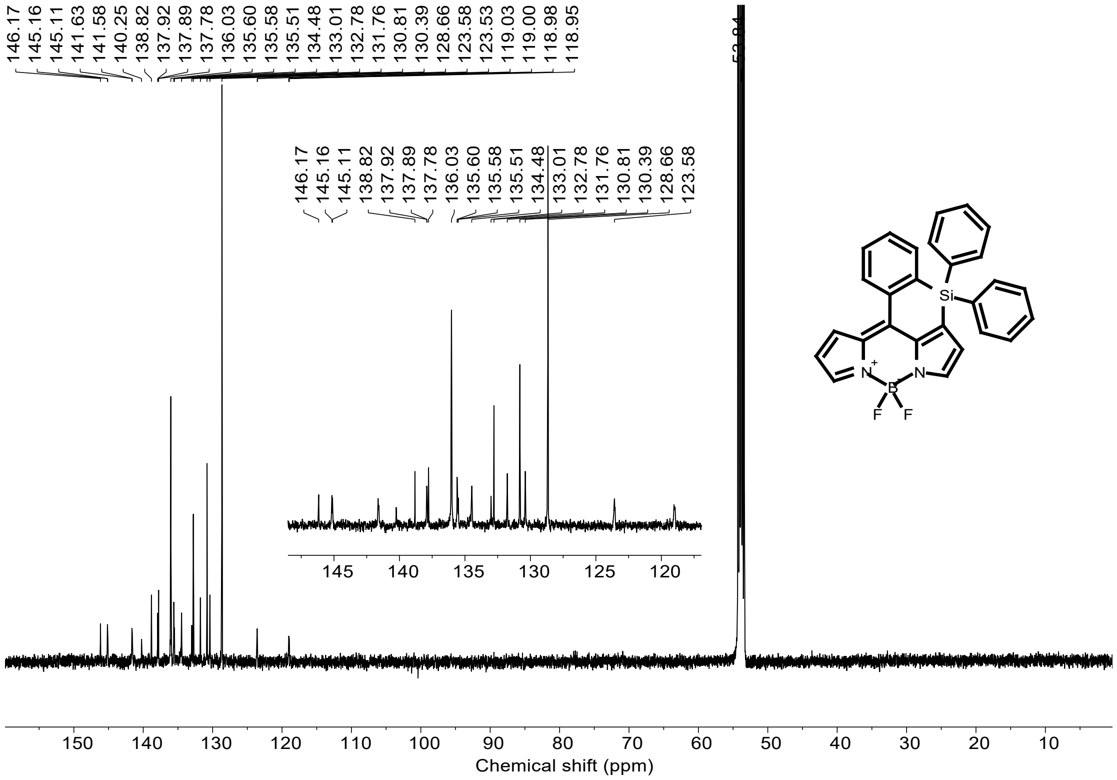
The ^{1}H NMR spectrum of **1** in Acetone-d_6



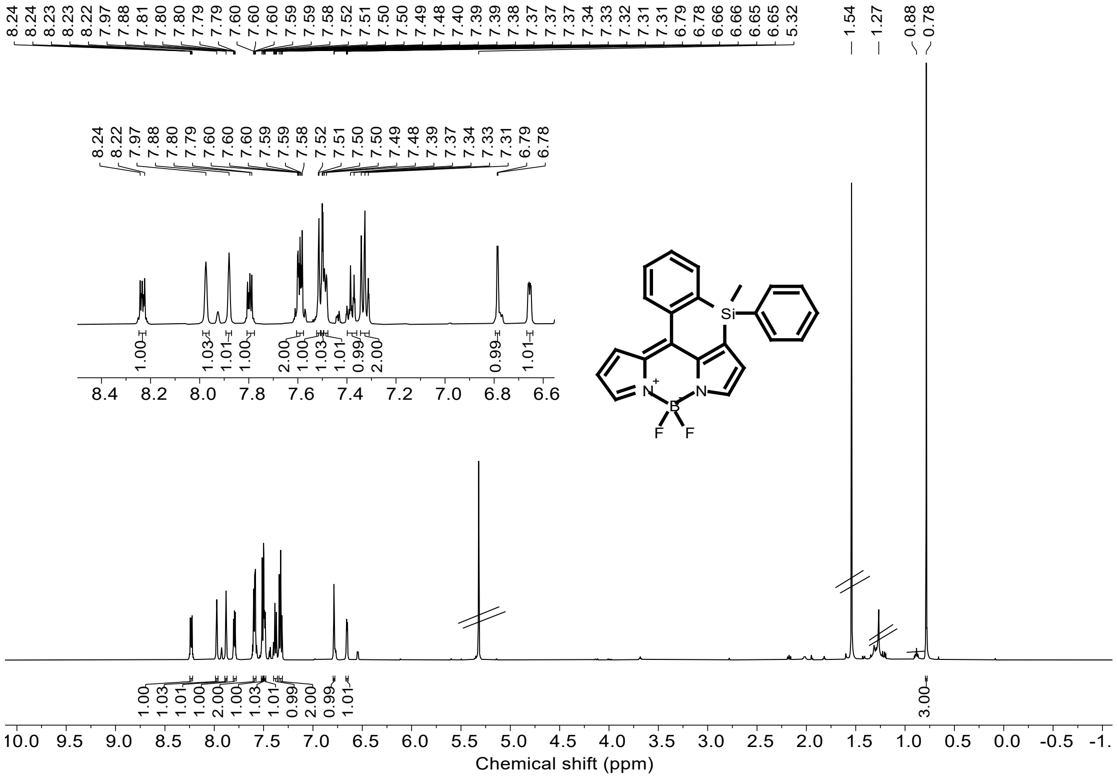
The ^{13}C NMR spectrum of **1** in Acetone-d_6



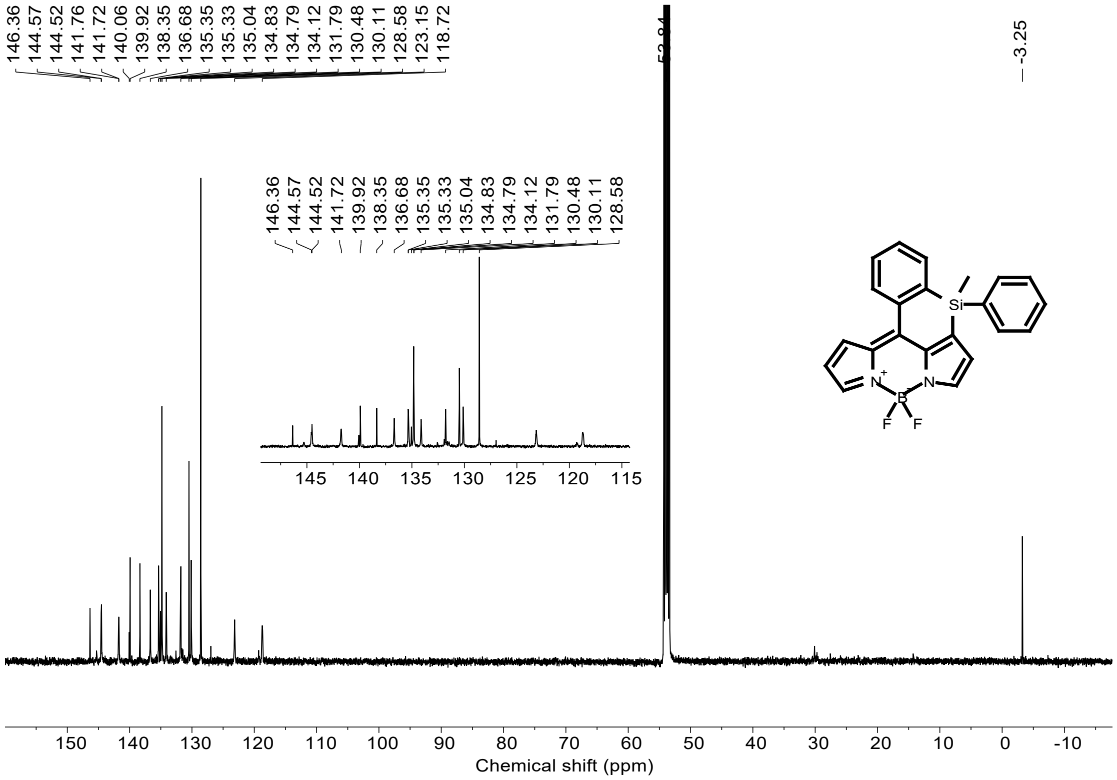
The ^{1}H NMR spectrum of 3**a** in CD_2Cl_2



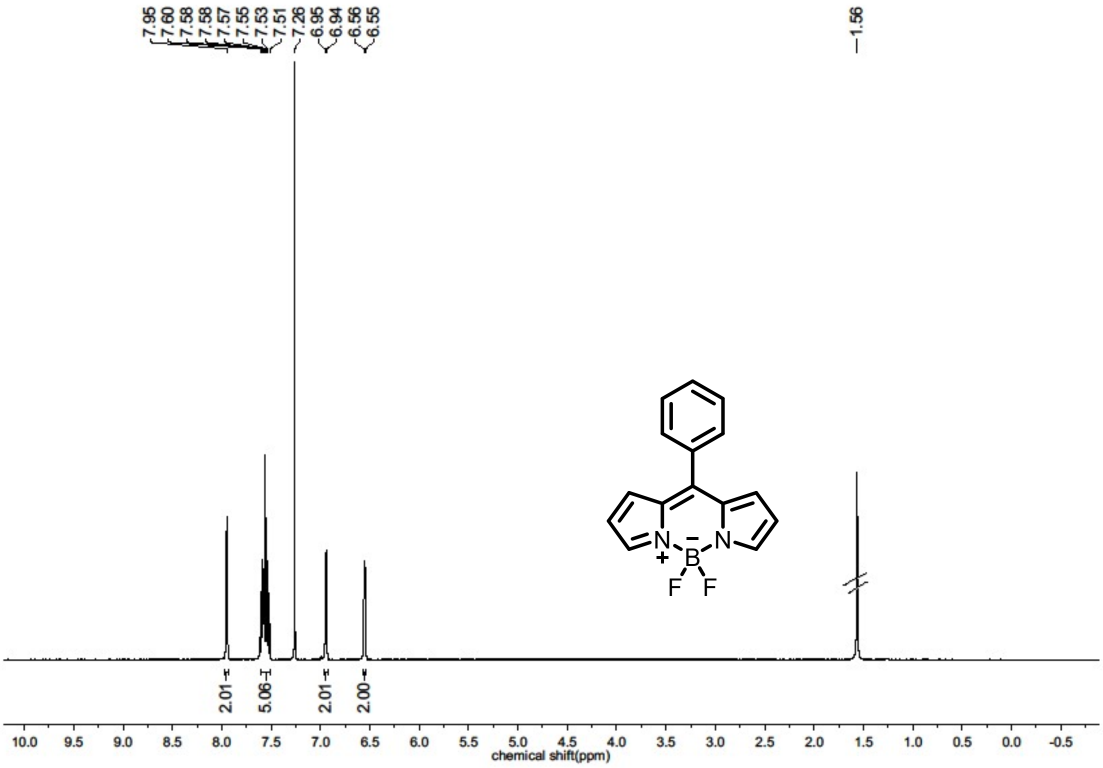
The ^{13}C NMR spectrum of 3**a** in CD_2Cl_2



The ^{1}H NMR spectrum of 3**b** in CD_2Cl_2

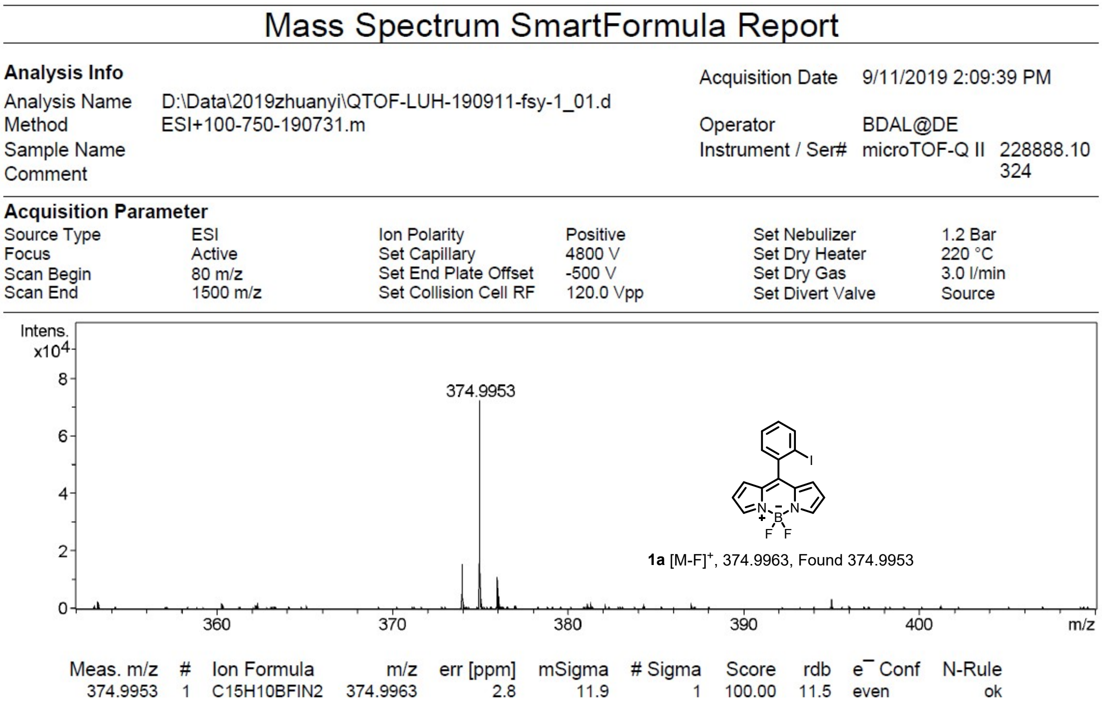


The ^{13}C NMR spectrum of 3**b** in CD_2Cl_2



The ^{1}H NMR spectrum of **4** in $CDCl_3$

HR-MS for **1**



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name
Comment

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Instrument / Ser# microTOF-Q II 228888.10324

Acquisition Parameter

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Scan Begin	80 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min		
Scan End	1500 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source		

1a [M-F]$^+$, 374.9963, Found 374.9953

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
374.9953	1	C15H10BFIN2	374.9963	2.8	11.9	1	100.00	11.5	even	ok

HR-MS for 3**a**

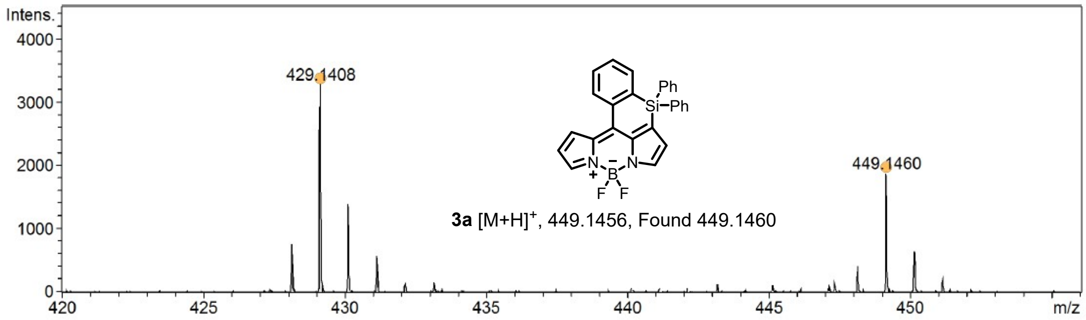
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Q-TOF-LH-190531-fsy-2_01.d	Acquisition Date	5/31/2019 9:16:10 AM
Method	APCI_50-600-180510_pos.m	Operator	BDAL@DE
Sample Name	wangll-1	Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.5 l/min
Scan End	800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



3a [M+H]$^+$, 449.1456, Found 449.1460

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
429.1408	1	C27H19BFN2Si	429.1394	3.2	53.1	1	100.00	20.5	even	ok
449.1460	1	C27H20BF2N2Si	449.1456	-0.9	15.1	1	100.00	19.5	even	ok

HR-MS for 3**b**

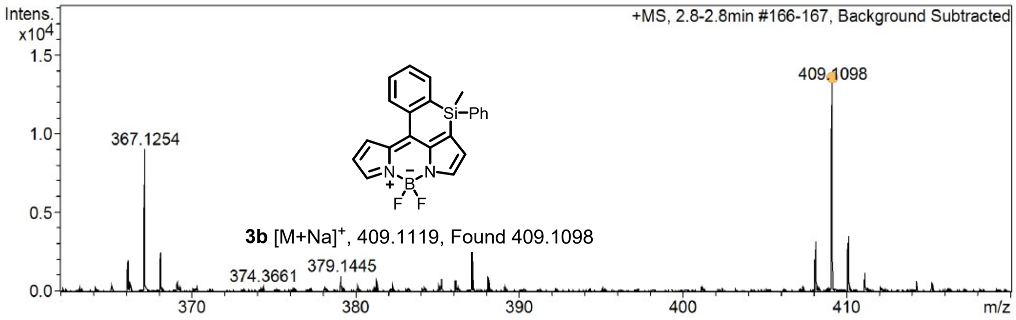
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\ESI-LUH-190724- fsy-386_01.d	Acquisition Date	7/24/2019 2:24:33 PM
Method	tune-100-1000-pos-20181023.m	Operator	BDAL@DE
Sample Name	wangll-1	Instrument / Ser#	microTOF-Q II 228888.10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.5 l/min
Scan End	800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



3b [M+Na]$^+$, 409.1119, Found 409.1098

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
409.1098	1	C22H17BF2N2NaSi	409.1119	5.0	16.3	1	100.00	15.5	even	ok